Electronic Supplementary Material (ESI) for Dalton Transactions.

Experimental and theoretical investigation of the reactivity of [(BDI*)Ti(Cl){η^2-P(SiMe$_3$)-P*i*Pr$_2$}] towards selected ketones

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PART A. Crystallographic Data

The ORTEP molecular structure of **3e** and crystallographic data for **2a**, **2b**, **3a**, **3e**, **4a**, and **5** (Table S1) are provided in the Electronic Supporting Information.

The X-ray intensity data for **2a**, **2b**, **3a**, **3e**, **4a**, and **5** were measured with an IPDS2T diffractometer equipped with an IPDS2T STOE image plate detector system and microfocus X-ray sources providing *K*α radiation by high-grade multilayer X-ray mirror optics for Mo (λ = 0.71073 Å, **2a**, **2b**, **3a**, **4a**, **5**) and Cu (λ = 0.71073 Å, **3e**) wavelengths. Data for **4d** were collected with a STOE STADIVARI equipped with an EIGER4M detector microfocus source providing Kα radiation by high-grade multilayer X-ray mirror optics for Ga (λ = 1.34143 Å) wavelength. The measurements for **2a**, **2b**, **3a**, **3e**, **4a** and **5** were carried out at 120 K, and only **4d** was measured at 180 K. The structures of the compounds were solved by direct methods and refined against F^2 with the Shelxs-2008 and Shelxl-2008 programs[1] run under WinGX.[2] Non-hydrogen atoms were refined with anisotropic displacement parameters. The isotropic displacement parameters of all hydrogens were fixed to 1.2 U_{eq} for CH and CH_2 (1.5 times for methyl groups).

The crystallographic data for the structures of **2a**, **2b**, **3a**, **3e**, **4a**, **4d**, and **5** reported in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 2024962-2024968. Copies of the data can be obtained free of charge upon application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; E mail: deposit@ccdc.cam.ac.uk).

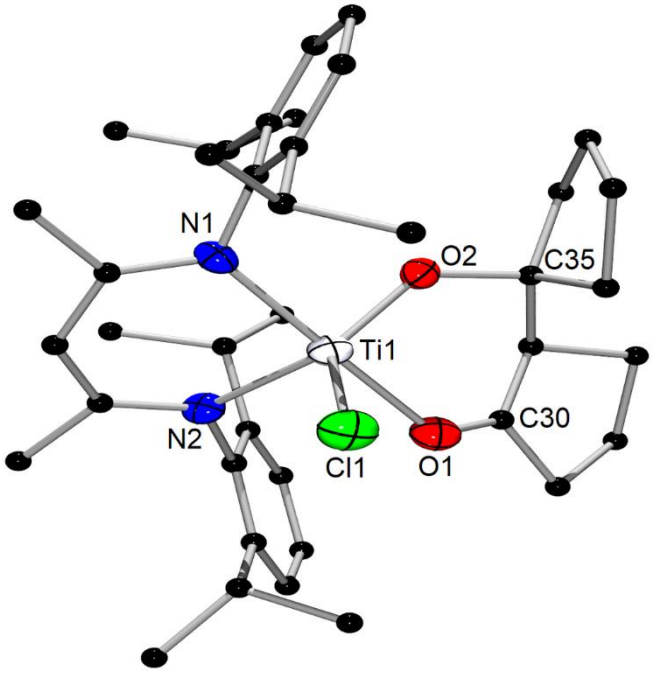

Figure S1. Molecular structure of [(BDI*)Ti(Cl){OC$(CH_2)_3$}CH(C=O)$(CH_2)_5$] (**3e**) (thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity). Important bond lengths (Å) and bond angles (°): Ti1-Cl1 2.326(4). Ti-N1 2.102(10), Ti1-N2 2.093(9), Ti1-O1 2.047(16), Ti1-O2 1.812(12)(12), O1-C30 1.210(2), O2-C35 1.450(3); O1-Ti1-N1 173.3(5), O1-Ti1-O2 86.9(6), N1-Ti1-O2 89.7(5), O1-Ti1-N2 89.5(5), N1-Ti1-N2 88.0(3), O2-Ti1-N2 128.0(5), O1-Ti1-Cl1 84.4(5), N1-Ti1-Cl1 102.2(3), O2-Ti1-Cl1 128.4(4), N2-Ti1-Cl1 102.7(3).

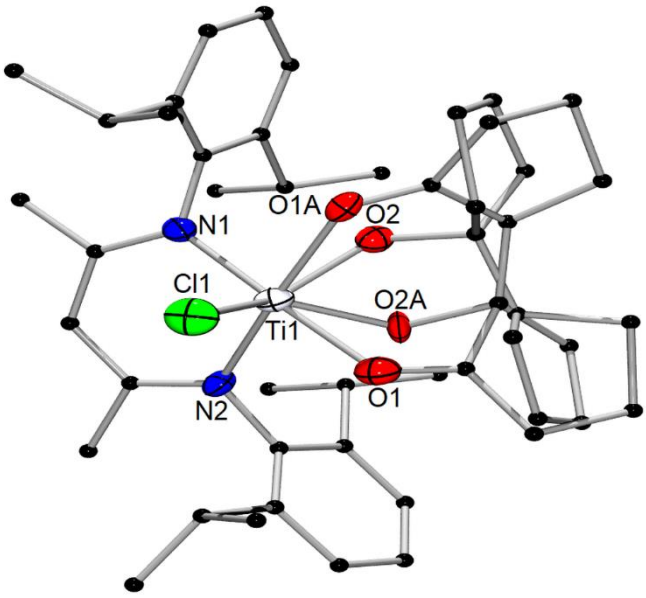

Figure S2. Molecular structure of [(BDI*)Ti(Cl){OC(CH_2)$_3$}CH(C=O)(CH_2)$_5$] (**3e**) with presentation of disorder model of aldol condensation product as ligand (thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity).

Table S1. Crystallographic data for **2a, 2b, 3a.**

	2a	**2b**	**3a**
Empirical formula	$C_{44.5}H_{74}ClN_2OP_2SiTi$	$C_{48}H_{78}ClN_2OP_2SiTi$	$C_{43}H_{72}ClN_2OP_2SiTi$
Formula weight	826.43	872.5	806.4
Radiation source	Mo-*K*α	Mo-*K*α	Mo-*K*α
Crystallographic System	*triclinic*	*triclinic*	*monoclinic*
Space group	*P*-1	*P*-1	$P2_1/n$
***a* [Å]**	9.5032(4)	10.3204(5)	21.3211(7)
***b* [Å]**	11.8444(5)	11.6903(7)	16.2782(4)
***c* [Å]**	22.1430(10)	21.9979(11)	25.8200(8)
***α* [°]**	100.092(3)	101.880(4)	90
***β* [°]**	90.957(3)	90.201(4)	94.309(3)
***γ* [°]**	106.801(3)	108.956(4)	90
***V* [Å^3]**	2343.10(18)	2449.2(2)	8936.0(5)
Z	2	2	8
Calculated Density [g·cm^{-1}]	1.171	1.183	1.199
***T* [K]**	120(2)	120(2)	120(2)
***μ* [mm^{-1}]**	0.367	0.354	0.383
Final R indices	R_1 = 0.0716	R_1 = 0.0824	R_1 = 0.0586
[*I*>2σ(I)]	wR_2 = 0.1818	wR_2 = 0.2127	wR_2 = 0.1383
R indices (all data)	R_1 = 0.0716	R_1 = 0.1236	R_1 = 0.1197
[*I*>2σ(I)] (all data)	wR_2 = 0.2082	wR_2 = 0.2477	wR_2 = 0.1711
CCDC	2024963	2024964	2024966

Table S2. Crystallographic data for **3e.**

	3e
Empirical formula	$C_{39}H_{56}ClN_2O_2Ti$
Formula weight	668.2
Radiation source	Cu-*K*α
Crystallographic System	*triclinic*
Space group	*P*-1
***a* [Å]**	9.0471(8)
***b* [Å]**	12.2788(10)
***c* [Å]**	17.1830(15)
***α* [°]**	74.518(7)
***β* [°]**	78.729(7)
***γ* [°]**	85.262(7)
***V* [Å^3]**	1803.1(3)
Z	2
Calculated Density [g·cm^{-1}]	1.231
***T* [K]**	120(2)
***μ* [mm^{-1}]**	2.954
Final R indices	R_1 = 0.1472
[*I*>2σ(I)]	wR_2 = 0.3678
R indices (all data)	R_1 = 0.2559
[*I*>2σ(I)] (all data)	wR_2 = 0.4349
CCDC	2024968

Table S3. Crystallographic data for **4a, 4d, 5.**

	4a	**4d**	**5**
Empirical formula	$C_{44}H_{74}ClN_2OP_2SiTi$	$C_{57}H_{92}ClN_2O_2P_2SiTi$	$C_{40}H_{63}ClN_2OP_2Ti$
Formula weight	820.43	1010.7	733.21
Radiation source	Mo-*K*α	Ga-*K*α	Mo-*K*α
Crystallographic System	*triclinic*	*triclinic*	*triclinic*
Space group	*P*-1	*P*-1	*P*-1
***a* [Å]**	11.9781(4)	9.9965(8)	8.9870(7)
***b* [Å]**	16.4161(7)	10.3489(8)	12.3952(10)
***c* [Å]**	23.1523(7)	28.541(3)	18.1785(14)
***α* [°]**	90.431(3)	100.401(7)	90.890(6)
***β* [°]**	91.187(3)	93.628(10)	99.601(6)
***γ* [°]**	92.522(3)	96.455(4)	93.077(6)
***V* [Å^3]**	4547.0(3)	2874.1(14)	1993.1(3)
Z	4	2	2
Calculated Density [g·cm^{-1}]	1.198	1.168	1.222
***T* [K]**	120(2)	180(2)	120(2)
***μ* [mm^{-1}]**	0.378	1.754	0.394
Final R indices	R_1 = 0.0985	R_1 = 0.0702	0.1022
[*I*>2σ(I)]	wR_2 = 0.2791	wR_2 = 0.1526	0.2384
R indices (all data)	R_1 = 0.1788	R_1 = 0.1573	0.2487
[*I*>2σ(I)] (all data)	wR_2 = 0.3278	wR_2 = 0.1735	0.3134
CCDC	2024965	2024962	2024967

PART B. NMR Data

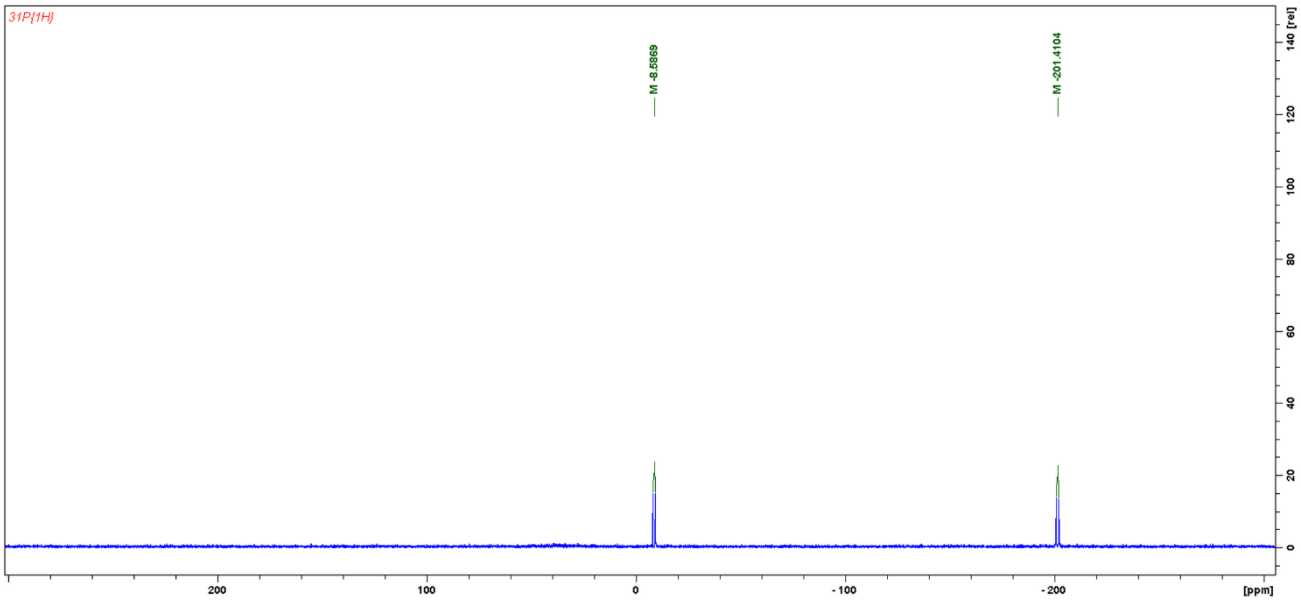

Figure S3. $^{31}P\{^{1}H\}$-NMR spectrum of reaction mixture after isolation of crystals **2a** and **2b**.

- -8.59 ppm, d, J_{PP} = 188.9 Hz, *i*Pr_2**P**P($SiMe_3$)H;
- -201.41 ppm, d, J_{PP} = 188.9 Hz, *i*Pr_2P**P**($SiMe_3$)H;

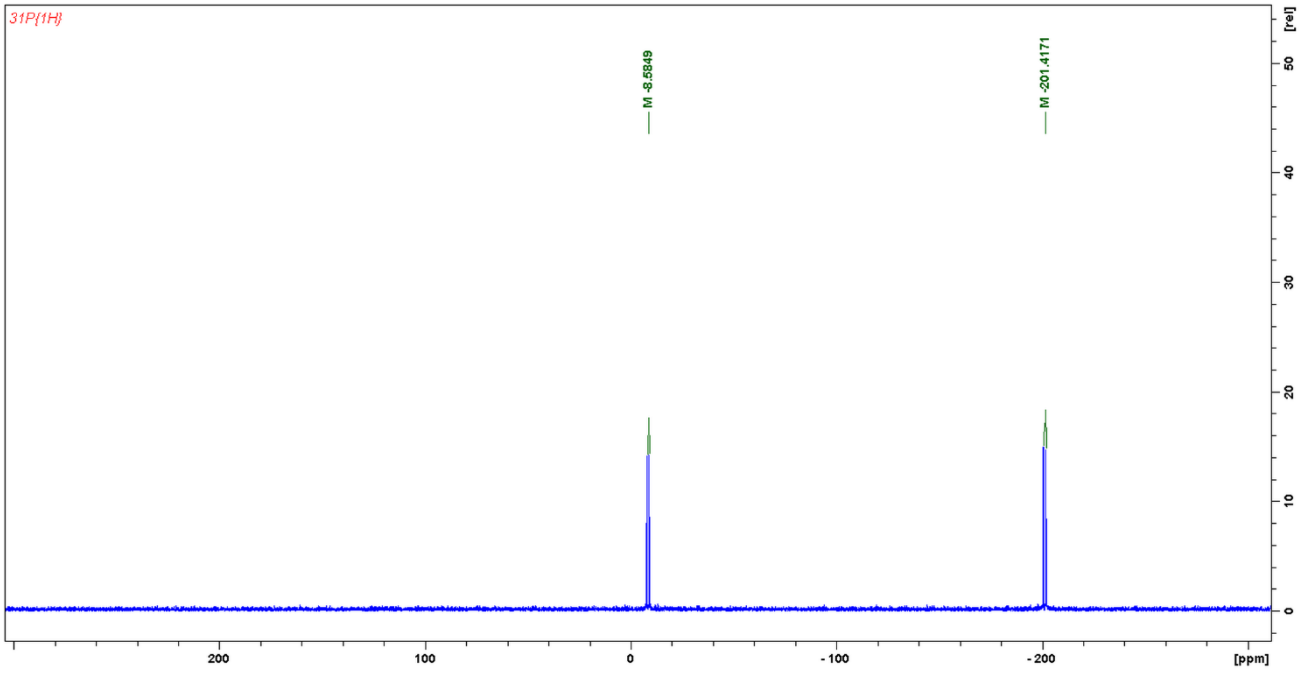

Figure S4. $^{31}P\{^{1}H\}$-NMR spectrum of reaction mixture after isolation of crystal **3a**.

- -8.58 ppm, d, J_{PP} = 188.9 Hz, *i*Pr_2**P**P($SiMe_3$)H;
- -201.41 ppm, d, J_{PP} = 188.9 Hz, *i*Pr_2P**P**($SiMe_3$)H;

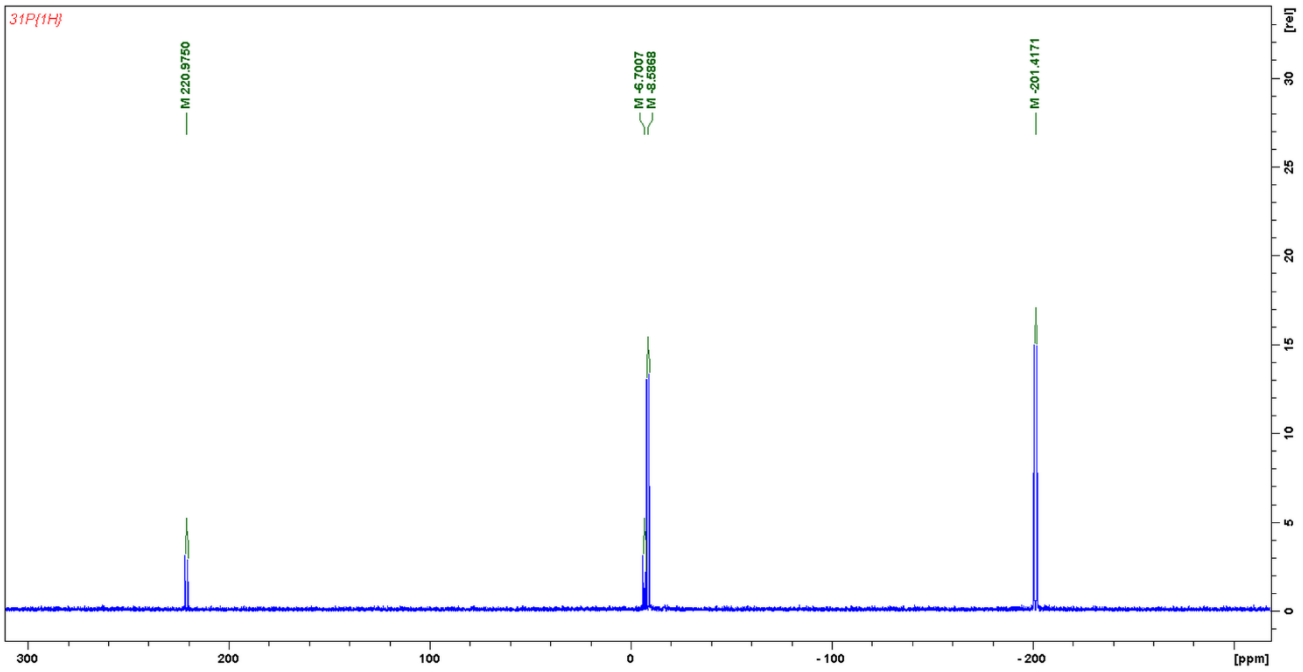

Figure S5. $^{31}P\{^{1}H\}$-NMR spectrum of reaction mixture after isolation of **4d** crystals.

- 220.98 ppm, d, J_{PP} = 217.9 Hz, *i*Pr_2P**P**=C$(CH_2)_5$;
- -6.70 ppm, d, J_{PP} = 217.9 Hz, *i*Pr_2**P**P=C$(CH_2)_5$;
- -8.59 ppm, d, JPP = 188.8 Hz, *i*Pr_2**P**P(SiMe_3)H;
- -201.41 ppm, d, J_{PP} = 188.9 Hz, *i*Pr_2P**P**(SiMe_3)H;

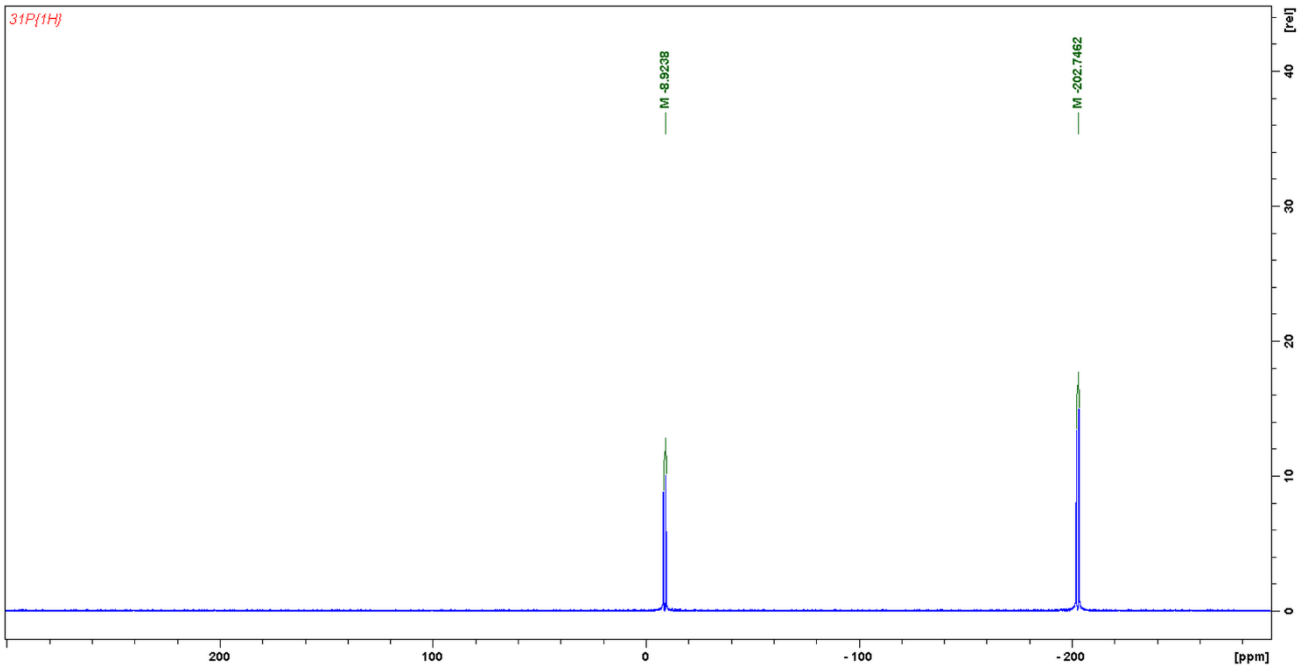

Figure S6. $^{31}P\{^{1}H\}$-NMR spectrum of crystals of **2a** dissolved in THF-d_8.

- -8.92 ppm, d, J_{PP} = 188.2 Hz, *i*Pr_2**P**P(SiMe_3)H;
- -202.75 ppm, d, J_{PP} = 188.2 Hz, *i*Pr_2P**P**(SiMe_3)H;

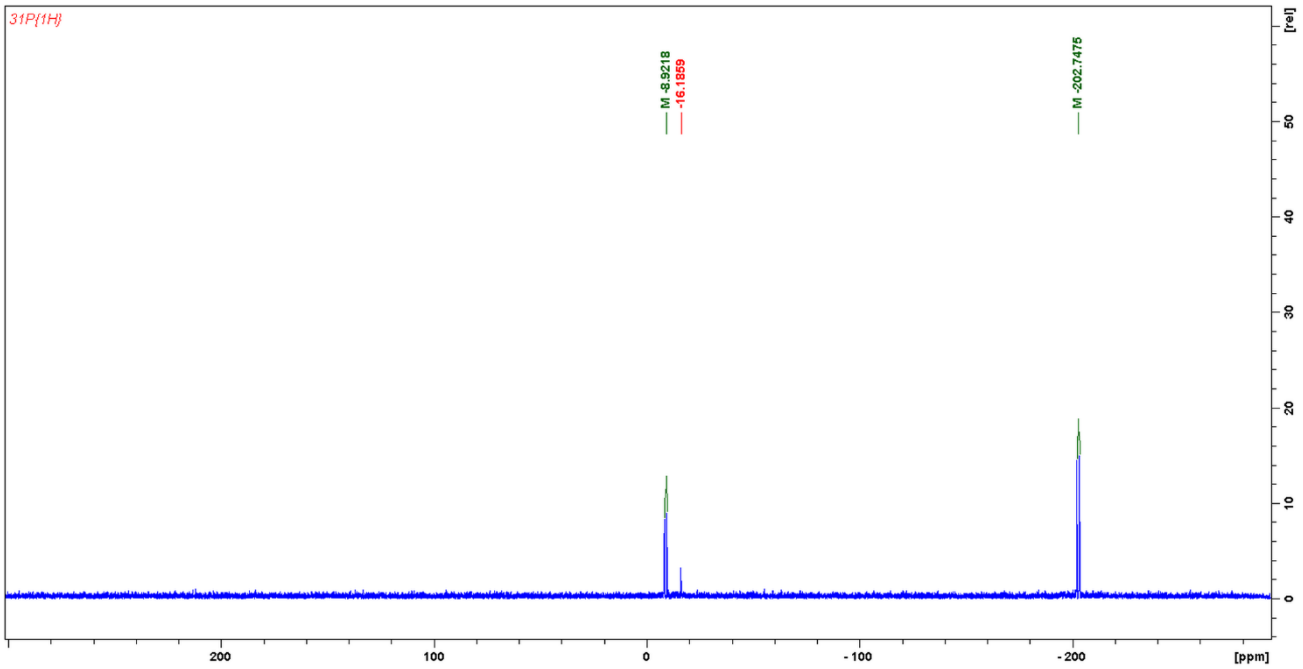

Figure S7. $^{31}P\{^{1}H\}$-NMR spectrum of crystals of **2b** dissolved in THF-d_8.

- -8.92 ppm, d, J_{PP} = 187.8 Hz, *i*Pr_2**P**P(SiMe$_3$)H;
- -202.75 ppm, d, J_{PP} = 187.8 Hz, *i*Pr_2P**P**(SiMe$_3$)H;
- -16.19 ppm, *i*Pr_2PH;

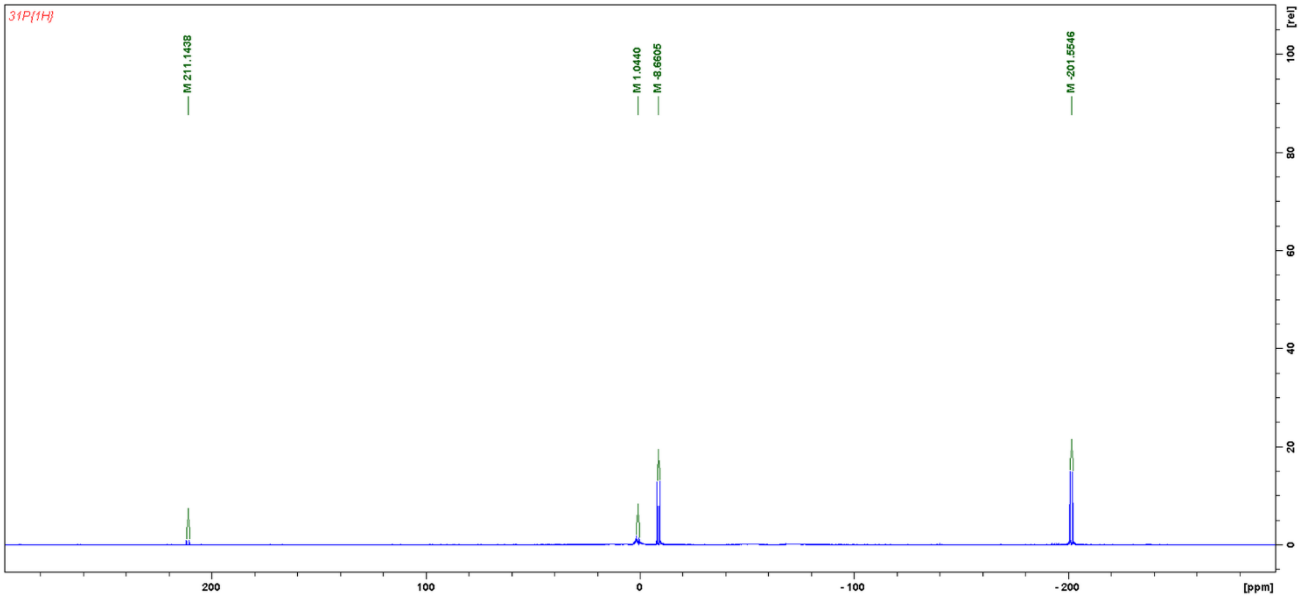

Figure S8. $^{31}P\{^{1}H\}$-NMR spectrum of crystals of **3a** dissolved in THF-d_8.

- 211.14 ppm, d, J_{PP} = 214.3 Hz, *i*Pr_2P**P**=C(CH$_2$)$_4$;
- 1.04 ppm, d, J_{PP} = 214.3 Hz, *i*Pr_2**P**P=C(CH$_2$)$_4$;
- -8.66 ppm, d, J_{PP} = 188.5 Hz, *i*Pr_2**P**P(SiMe$_3$)H;
- -201.55 ppm, d, J_{PP} = 188.5 Hz, *i*Pr_2P**P**(SiMe$_3$)H;

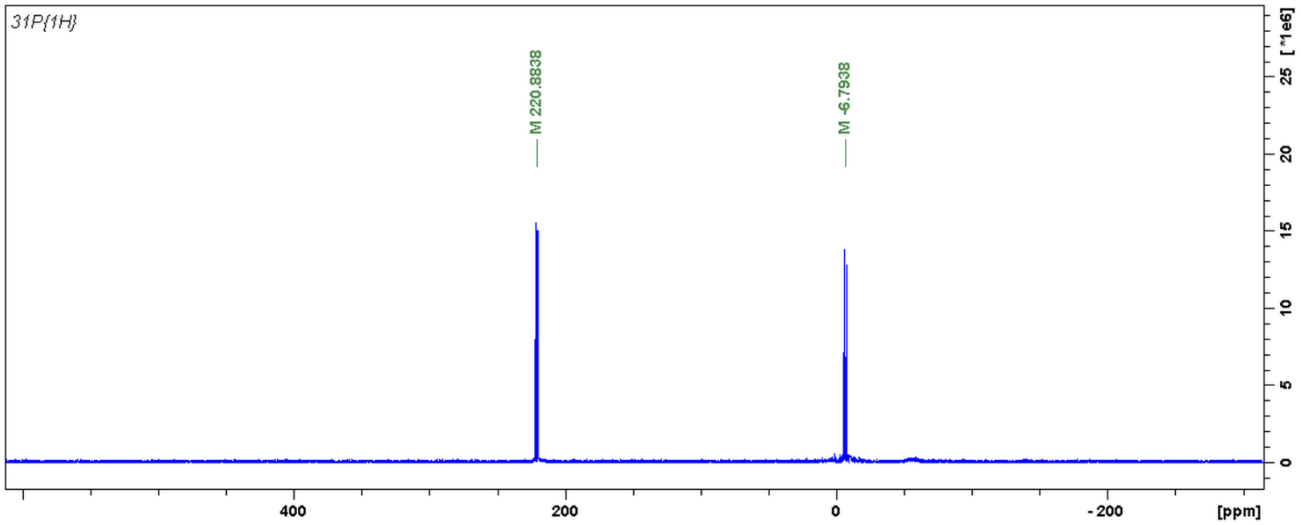

Figure S9. $^{31}P\{^{1}H\}$-NMR spectrum of **4d** crystals dissolved in THF-d_8.

- 220.88 ppm, d, J_{PP} = 217.9 Hz, *i*Pr_2P**P**=C$(CH_2)_5$;
- -6.79 ppm, d, J_{PP} = 217.9 Hz, *i*Pr_2**P**P=C$(CH_2)_5$;

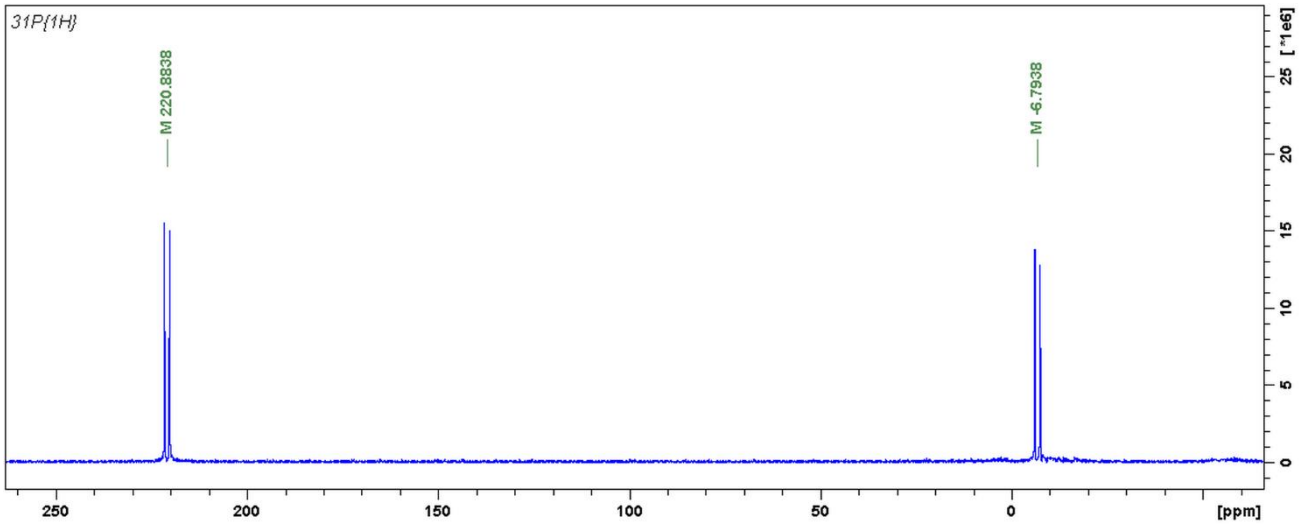

Figure S10. $^{31}P\{^{1}H\}$-NMR spectrum of **4d** crystals dissolved in THF-d_8 in narrow range.

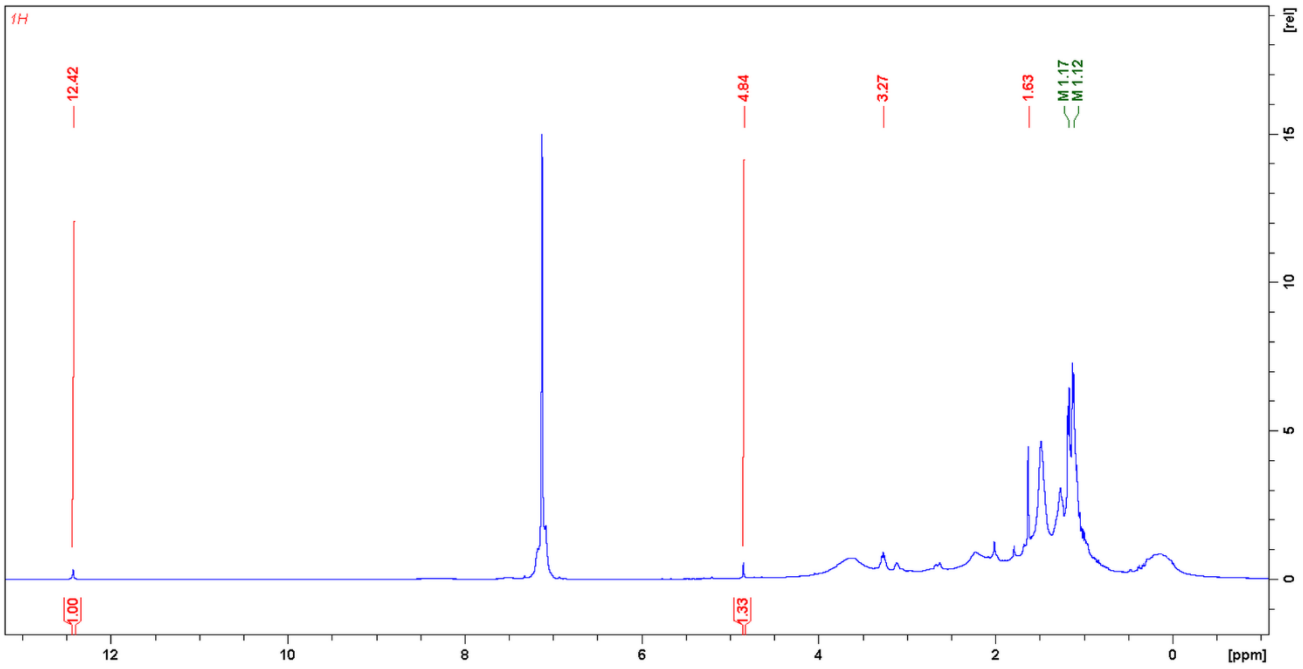

Figure S11. ^{1}H-NMR spectrum of **4d** crystals dissolved in THF-d_8.

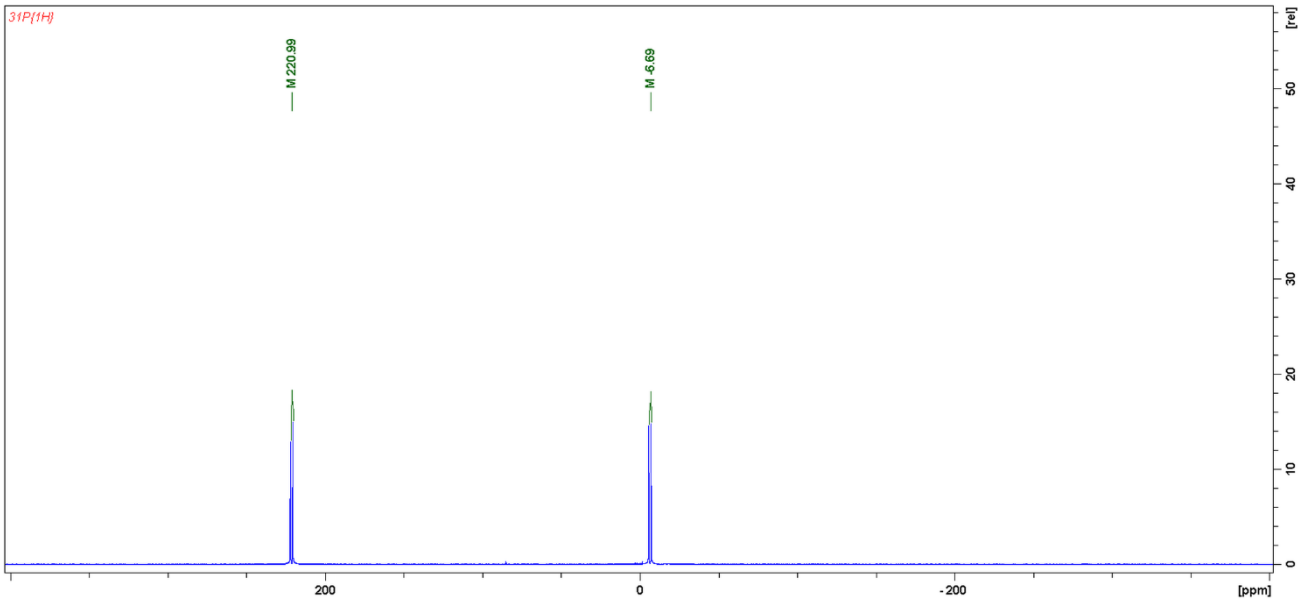

Figure S12. ^{31}P{^{1}H}-NMR spectrum of isolated yellow oil of *i*Pr_2PP=C$(CH_2)_5$ (**4w**).

- 220.99 ppm, d, J_{PP} = 217.9 Hz, *i*Pr_2P**P**=C$(CH_2)_5$;
- -6.69 ppm, d, J_{PP} = 217.9 Hz, *i*Pr_2**P**P=C$(CH_2)_5$;

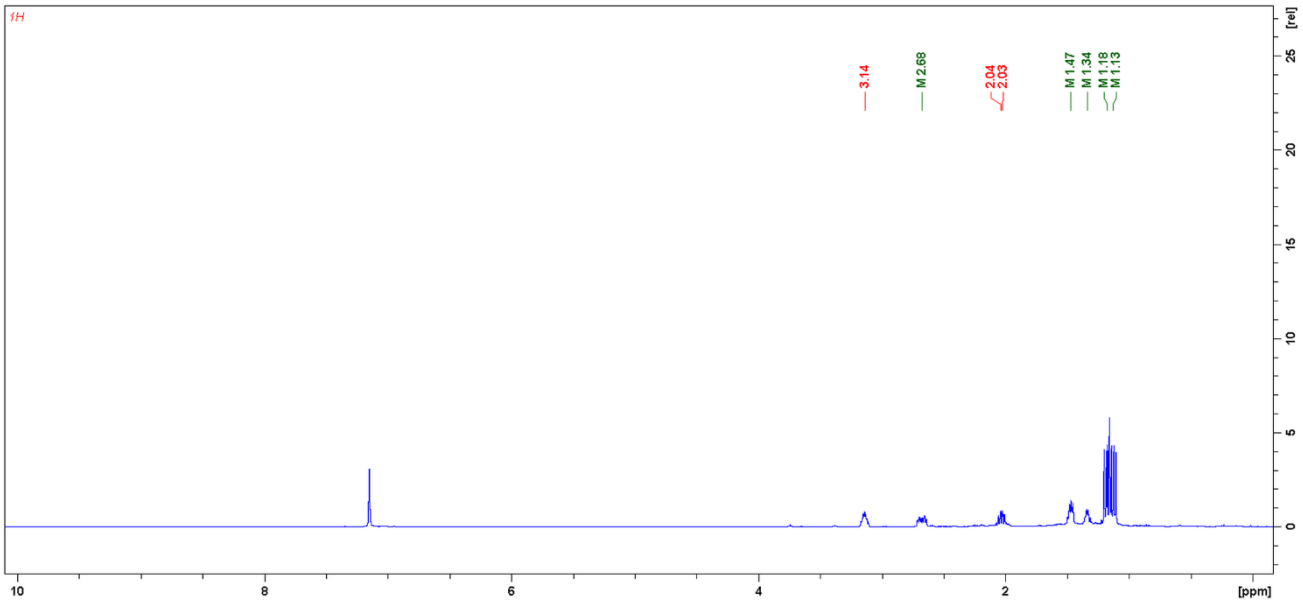

Figure S13. ^{1}H-NMR spectrum of isolated yellow oil of *i*$Pr_2PP{=}C(CH_2)_5$ (**4w**).

- 3.14 ppm, broad m, 2H, *i*$Pr_2PP{=}C(C\mathbf{H}_2)_5$;
- 2.68 ppm, doublet of broad multiplets, 2H, *i*$Pr_2PP{=}C(C\mathbf{H}_2)_5$;
- 2.04 ppm, sept, 1H, $\{(Me)_2C\mathbf{H}\}PP{=}C(CH_2)_5$;
- 2.03 ppm, sept, 1H, $\{(Me)_2C\mathbf{H}\}PP{=}C(CH_2)_5$;
- 1.47 ppm, broad m, 4H, *i*$Pr_2PP{=}C(C\mathbf{H}_2)_5$;
- 1.34 ppm, broad m, 2H, *i*$Pr_2PP{=}C(C\mathbf{H}_2)_5$;
- 1.18 ppm, dd, J_{PH} = 10.8 Hz, J_{HH} = 6.9 ppm, $\{(\mathbf{Me})_2CH\}PP{=}C(CH_2)_5$;
- 1.13 ppm, dd, J_{PH} = 14.3 Hz, J_{HH} = 6.8 ppm, $\{(\mathbf{Me})_2CH\}PP{=}C(CH_2)_5$;

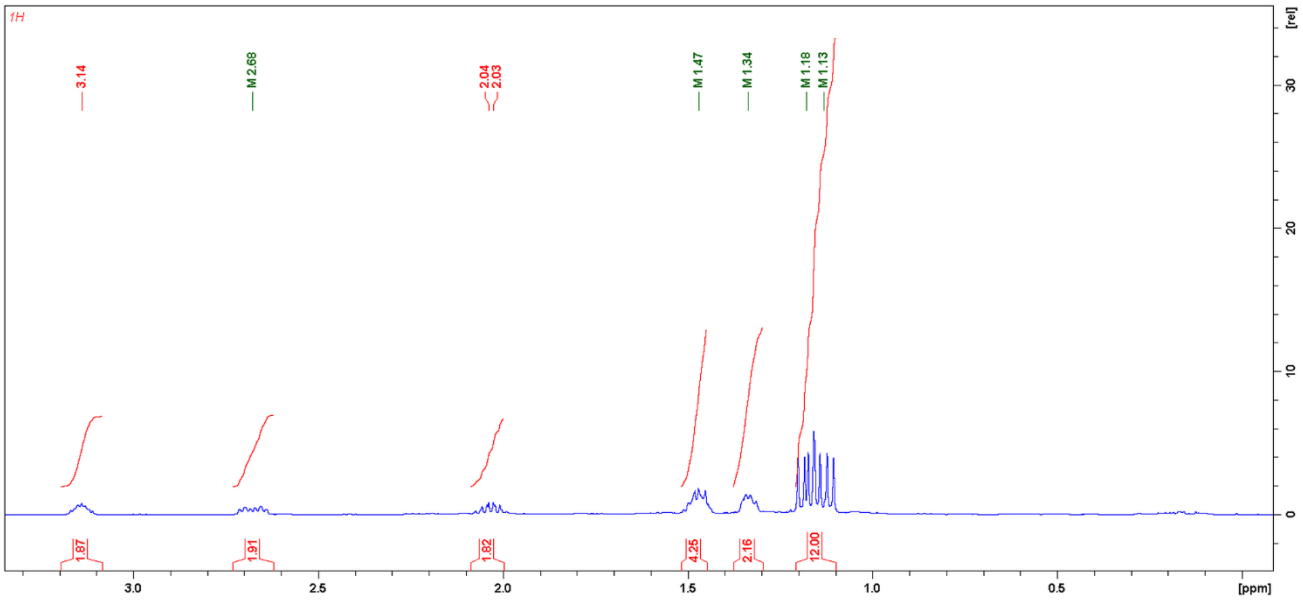

Figure S14. ^{1}H-NMR spectrum of isolated yellow oil of *i*$Pr_2PP{=}C(CH_2)_5$ (**4w**) with integration.

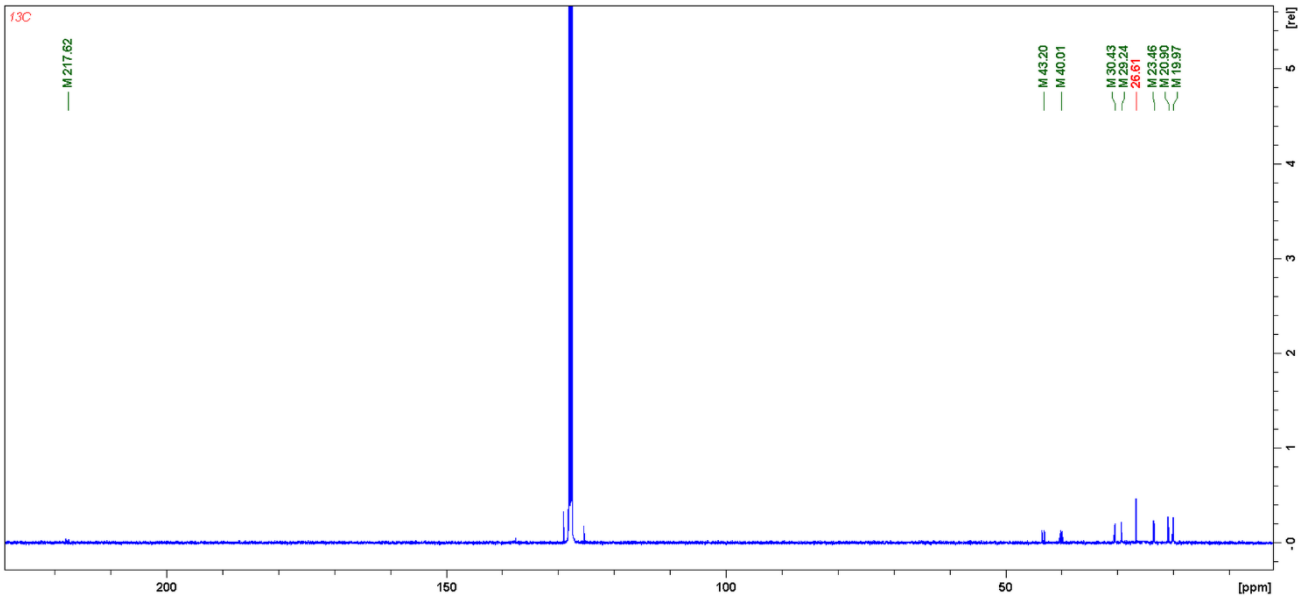

Figure S15. $^{13}C\{^{1}H\}$-NMR spectrum of isolated yellow oil of iPr$_2$PP=C(CH$_2$)$_5$ (**4w**).

- 217.62 ppm, dd, J_{PC} = 55.4 Hz, J_{PC} = 11.8 Hz, iPr$_2$PP=**C**(CH$_2$)$_5$;
- 43.20 ppm, dd, J_{PC} = 39.1 Hz, J_{PC} = 4.5 Hz, iPr$_2$PP=C(**C**H$_2$)$_5$;
- 40.01 ppm, dd, J_{PC} = 28.1 Hz, J_{PC} = 16.3 Hz, iPr$_2$PP=C(**C**H$_2$)$_5$;
- 30.43 ppm, d, J_{PC} = 9.9 Hz, {(Me)$_2$CH}PP=C(**C**H$_2$)$_5$;
- 29.24 ppm, d, J_{PC} = 5.4 Hz, {(Me)$_2$CH}PP=C(**C**H$_2$)$_5$;
- 26.63 ppm, s, {(Me)$_2$CH}PP=C(**C**H$_2$)$_5$;
- 23.46 ppm, broad dd, J_{PC} = 17.2 Hz, J_{PC} = 7.3 Hz, {(Me)$_2$**C**H}PP=C(CH$_2$)$_5$;
- 20.90 ppm, dd, J_{PC} = 17.3 Hz, J_{PC} = 3.6 Hz, {(Me)$_2$CH}PP=C(CH$_2$)$_5$;
- 19.97 ppm, dd, J_{PC} = 9.06 Hz, J_{PC} = 7.3 Hz, {(Me)$_2$CH}PP=C(CH$_2$)$_5$;

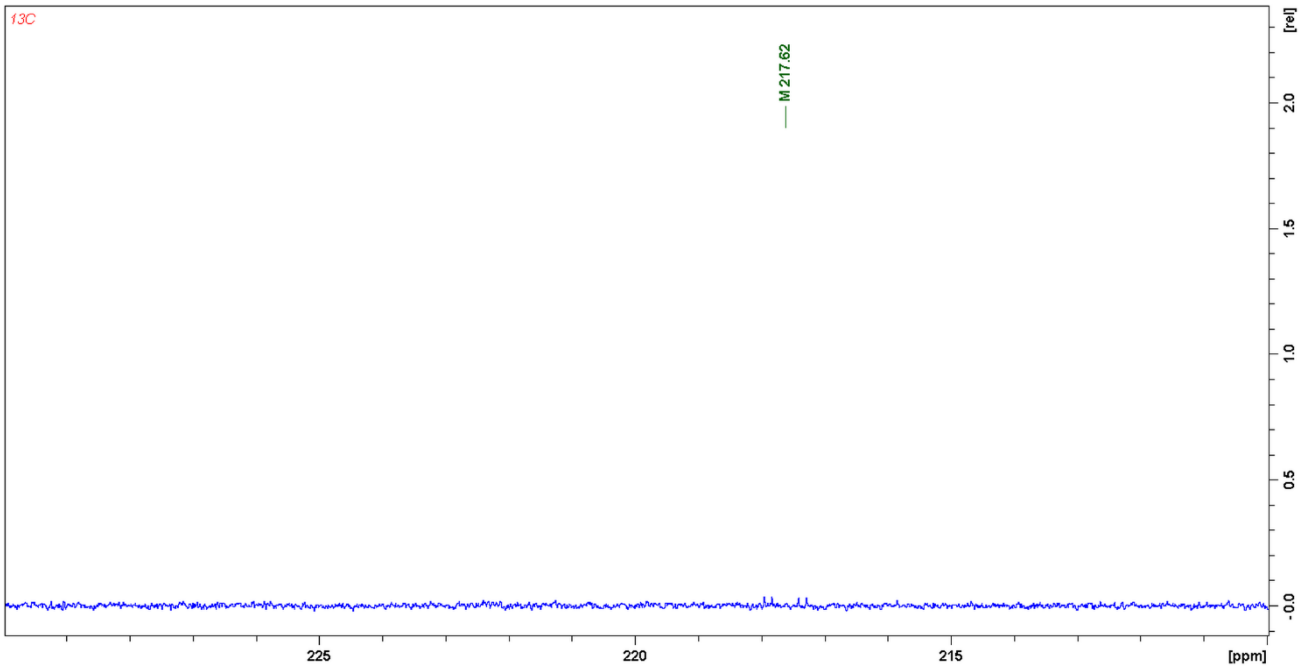

Figure S16. $^{13}C\{^{1}H\}$-NMR spectrum of isolated yellow oil of iPr$_2$PP=C(CH$_2$)$_5$ (**4w**) in the range from 230 ppm to 210 ppm.

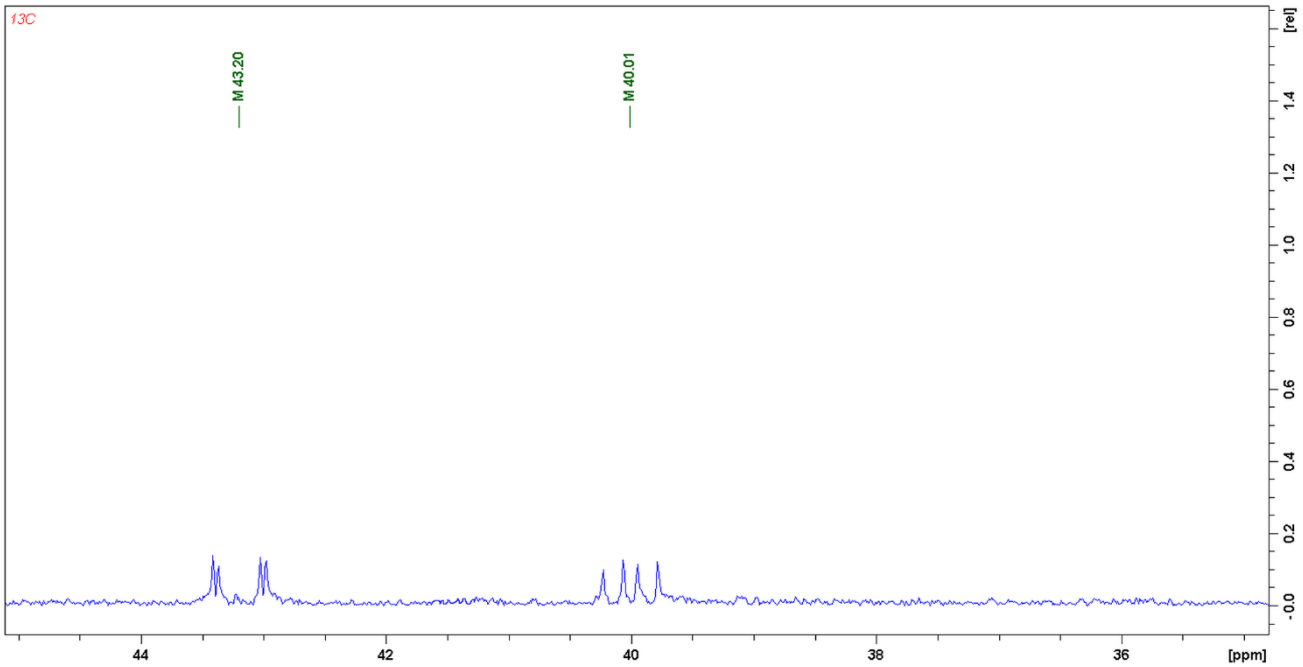

Figure S17. $^{13}C\{^{1}H\}$-NMR spectrum of isolated yellow oil of *i*$Pr_2PP=C(CH_2)_5$ (**4w**) in the range from 45 ppm to 35 ppm.

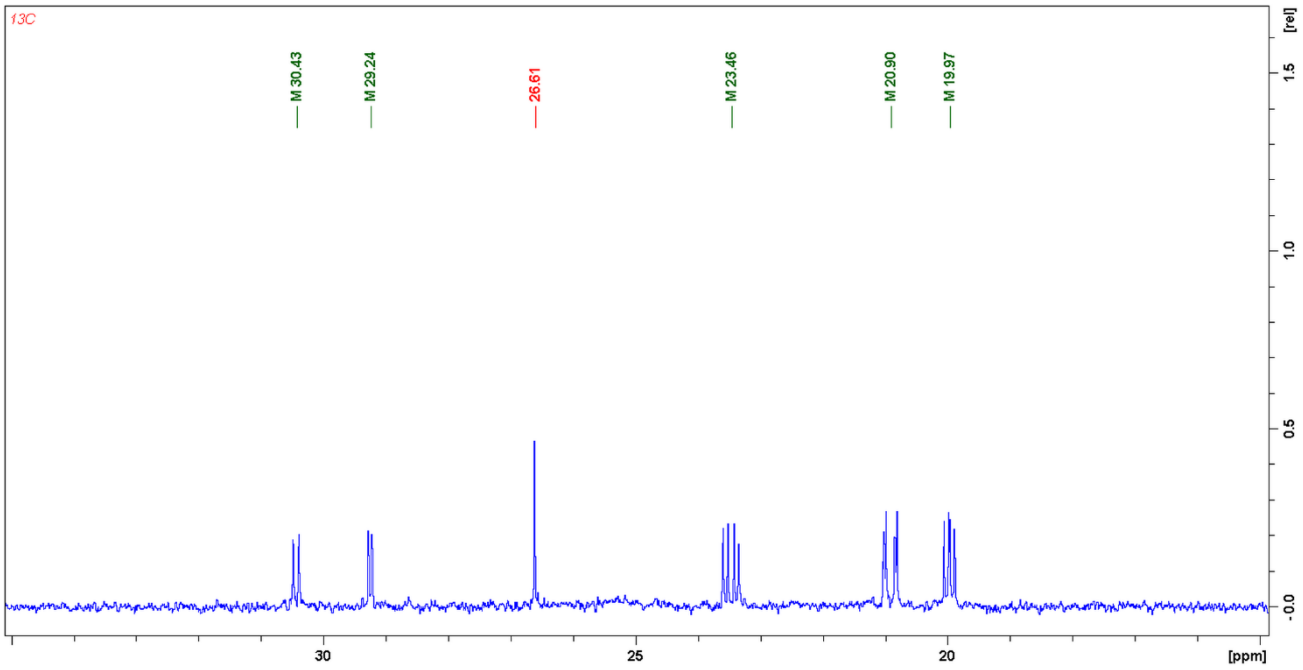

Figure S18. $^{13}C\{^{1}H\}$-NMR spectrum of isolated yellow oil of *i*$Pr_2PP=C(CH_2)_5$ (**4w**) in the range from 35 ppm to 0 ppm.

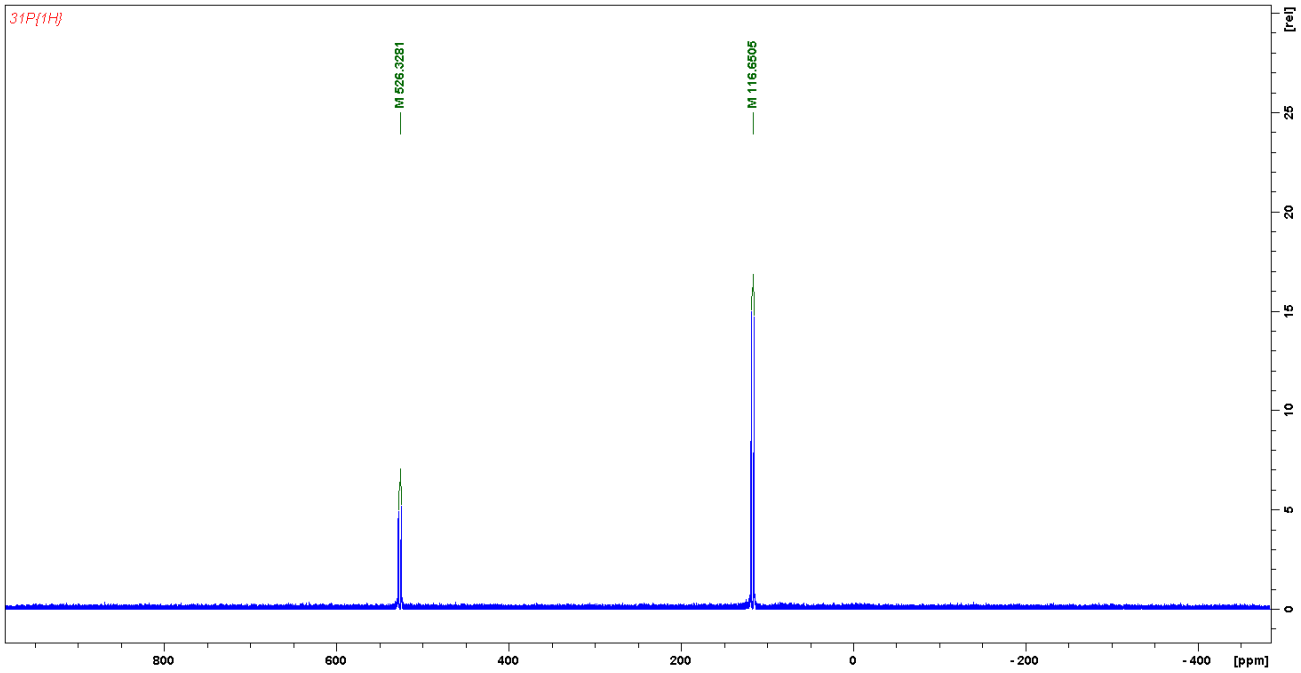

Figure S19. $^{31}P\{^{1}H\}$-NMR spectrum of isolated crystals of **5**.

- 526.32 ppm, d, J_{PP} = 518.8 Hz, [(BDI*)Ti(Cl){η^2-**P**-P(*i*Pr)$_2$-{C(CH$_3$)$_2$}O}];
- 116.65 ppm, d, J_{PP} = 518.8 Hz, [(BDI*)Ti(Cl){η^2-P-**P**(*i*Pr)$_2$-{C(CH$_3$)$_2$}O}];

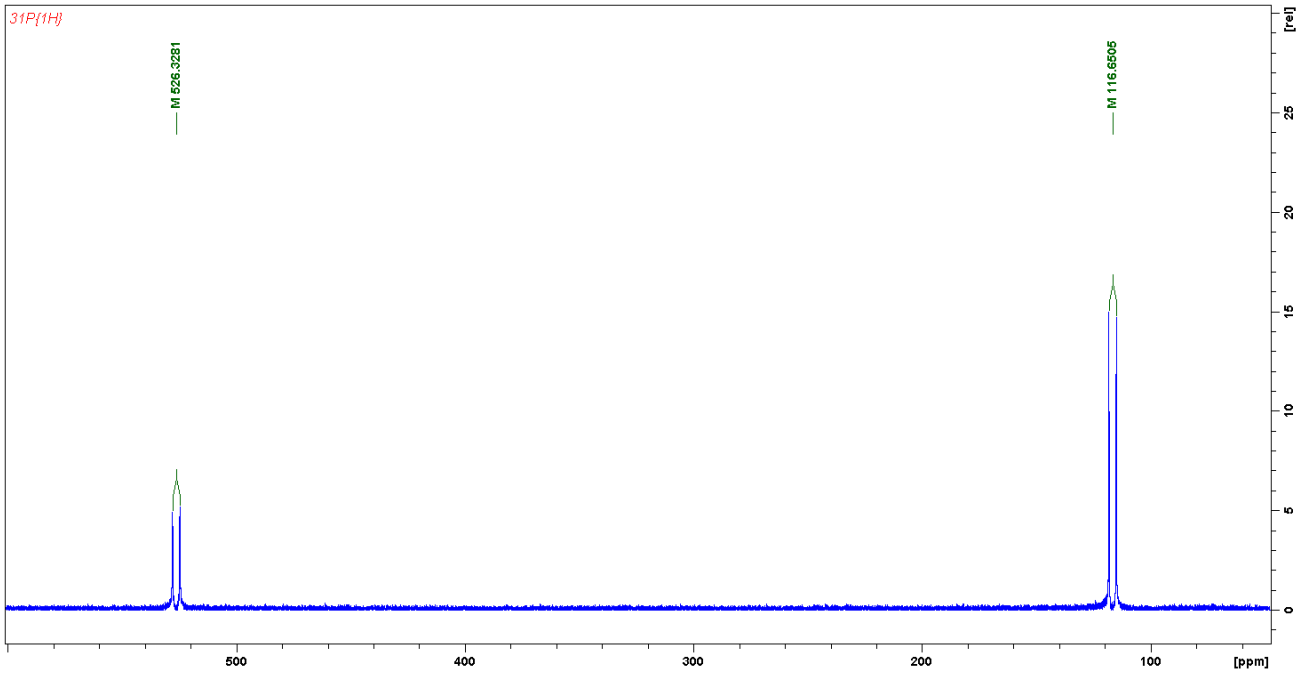

Figure S20. $^{31}P\{^{1}H\}$-NMR spectrum of isolated crystals of **5** in the range of 600 ppm to 50 ppm.

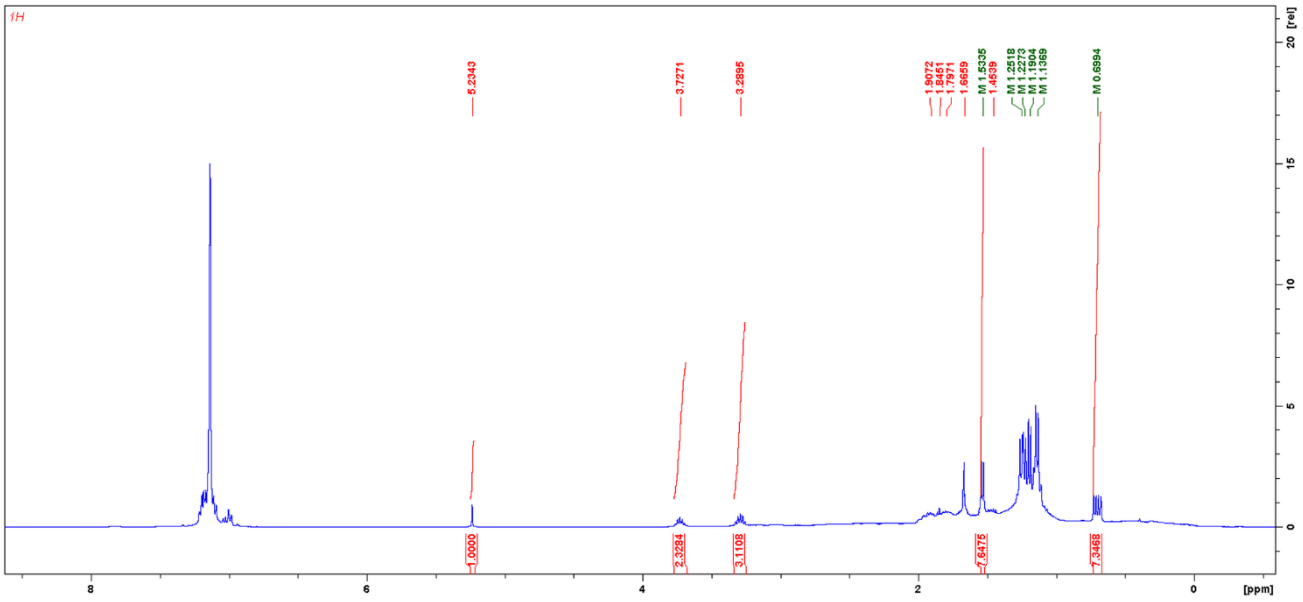

Figure S21. ^{1}H-NMR spectrum of isolated crystals of **5**.

- 7.23 – 6.96 ppm, Ar-**H**;
- 5.23 ppm, s, 1H, (C(Me)C**H**C(Me));
- 3.73 ppm, sept, 2H, J_{HH} = 6.7 Hz, C**H**$(Me)_2$ from β-diketiminate ligand;
- 3.59 ppm, broad m, 2H from cyclopentane ring;
- 3.29 ppm, sept, 2H, J_{HH} = 6.7 Hz, C**H**$(Me)_2$ from β-diketiminate ligand;
- 2.05 ppm, broad m, 2H from cyclopentane ring;
- 1.91 ppm, broad m, 2H from cyclopentane ring;
- 1.84 ppm, broad m, 1H, P{C**H**$(Me_2)\}_2$;
- 1.80 ppm, broad m, 2H from cyclopentane ring;
- 1.67 ppm, s, 6H, (C(**Me**)CHC(**Me**));
- 1.53 ppm, d, 6H, J_{HH} = 6.7 Hz, 6H, CH(**Me**)$_2$ from β-diketiminate ligand;
- 1.45 ppm, broad m, 1H, P{C**H**$(Me_2)\}_2$;
- 1.25 ppm, d, 6H, J_{HH} = 6.8 Hz, 6H, CH(**Me**)$_2$ from β-diketiminate ligand;
- 1.23 ppm, J_{HH} = 6.9 Hz, 6H, CH(**Me**)$_2$ from β-diketiminate ligand;
- 1.19 ppm, J_{HH} = 6.9 Hz, 6H, CH(**Me**)$_2$ from β-diketiminate ligand;
- 1.14 ppm, dd, 6H, J_{PH} = 14.1 Hz, J_{HH} = 7.1 Hz, P{CH(**Me**$_2)\}_2$;
- 0.70 ppm, dd, 6H, J_{PH} = 12.5 Hz, J_{HH} = 5.6 Hz, P{CH(**Me**$_2)\}_2$;

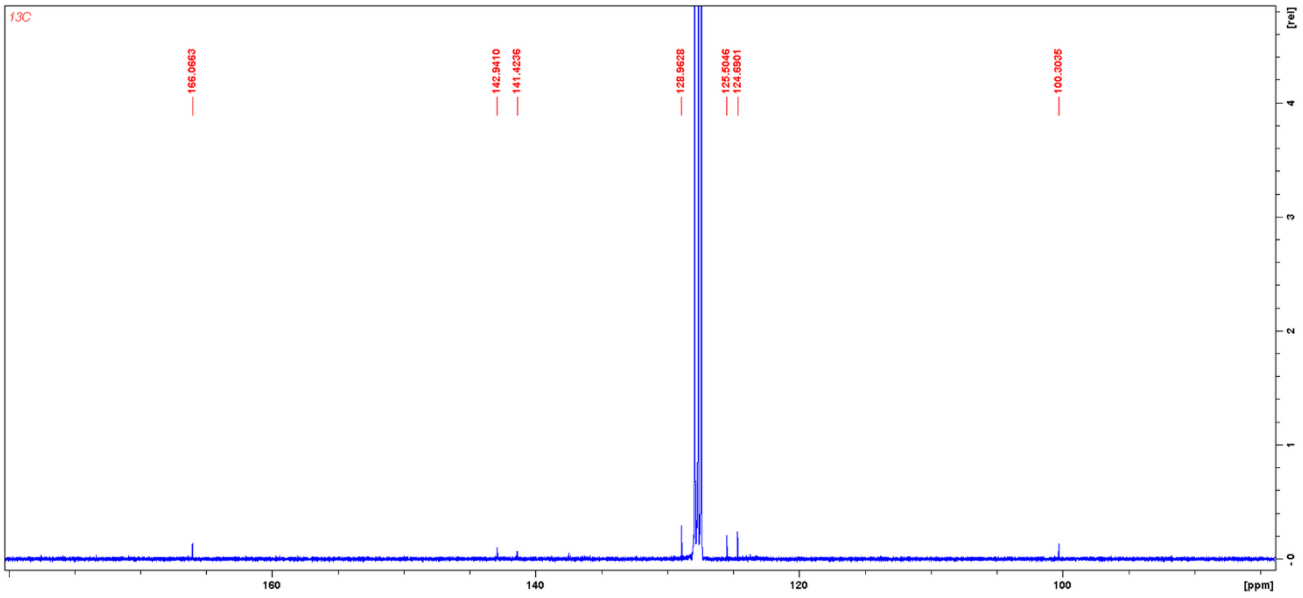

Figure S22. $^{13}C\{^{1}H\}$-NMR spectrum of isolated crystals of **5** in the range from 170 ppm to 90 ppm.

- 166.07 ppm, s, (**C**(Me)CH**C**(Me));
- 142.94 ppm, s, *i*-C_6H_3;
- 141.42 ppm, s, *o*-C_6H_3;
- 128.96 ppm, s, *p*-C_6H_3;
- 125.50 ppm, s, *m*-C_6H_3;
- 124.69 ppm, s, *m*-C_6H_3;
- 100.30 ppm, s, (C(Me)**C**HC(Me));

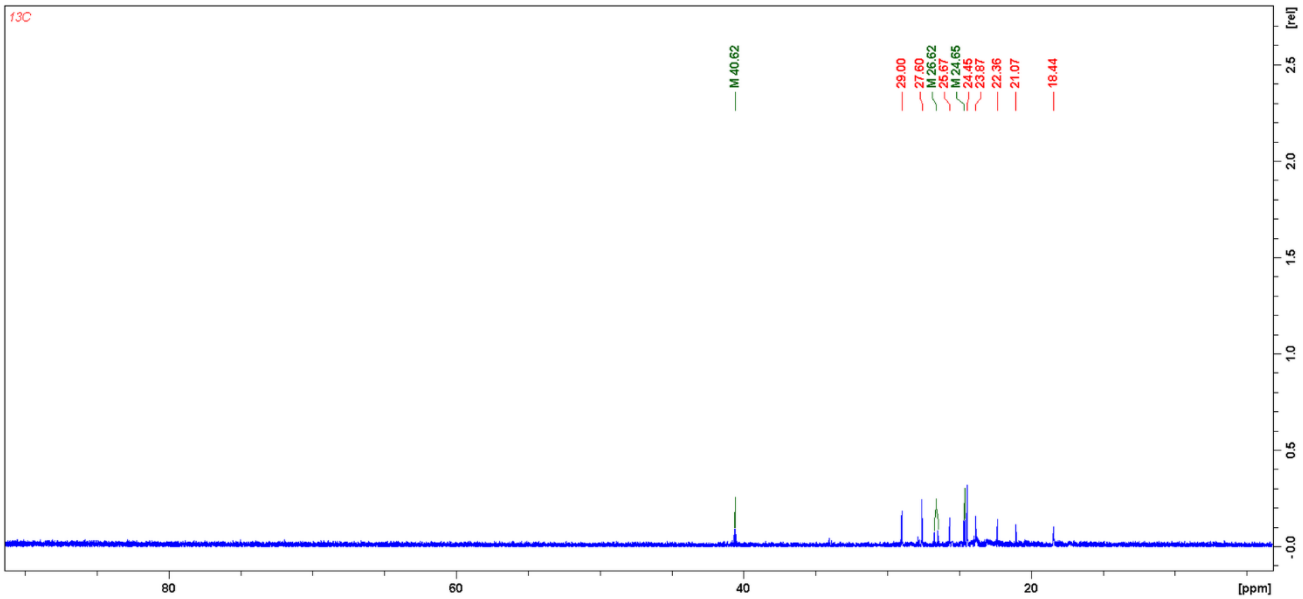

Figure S23. $^{13}C\{^{1}H\}$-NMR spectrum of isolated crystals of **5** in the range from 90 ppm to 0 ppm.

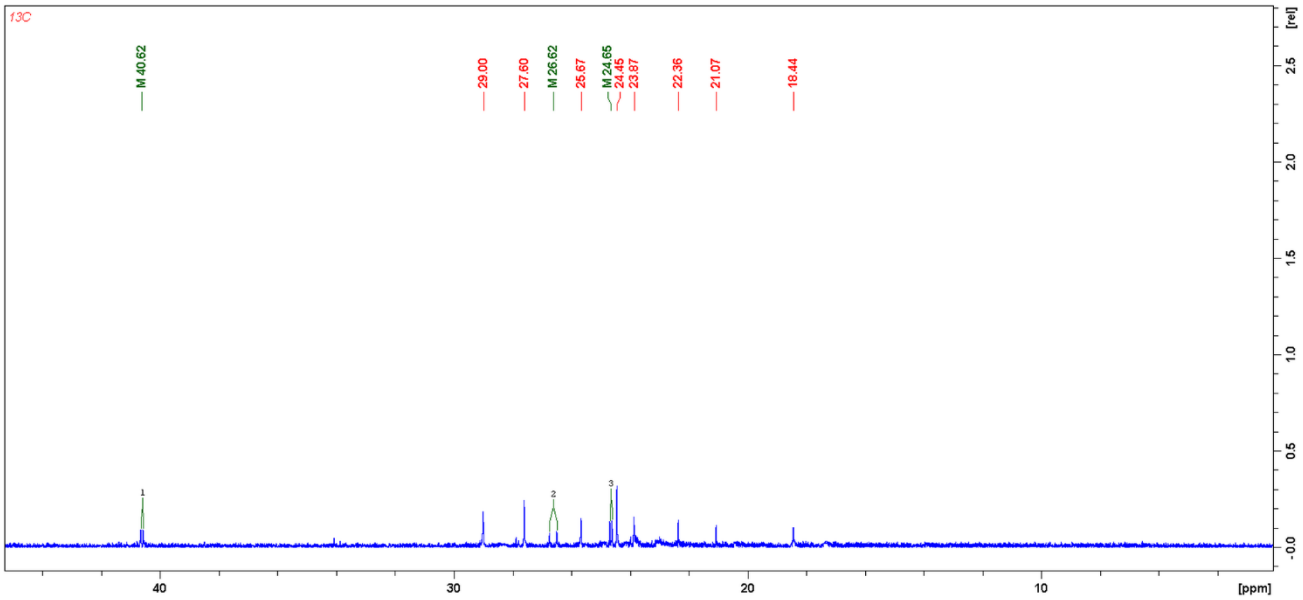

Figure S24. $^{13}C\{^{1}H\}$-NMR spectrum of isolated crystals of **5** in the range from 45 ppm to 0 ppm.

- 40.61 ppm, d, J_{PC} = 7.3 Hz, C(**C**H_2)$_4$
- 29.00 ppm, s, **C**H(Me_2) from the β-diketiminate ligand;
- 27.60 ppm, s, **C**H(Me_2) from the β-diketiminate ligand;
- 26.62 ppm, d, J_{PC} = 24.8 Hz, P{**C**H(Me_2)}$_2$;
- 25.67 ppm, s, CH(**Me**$_2$) from the β-diketiminate ligand;
- 24.65 ppm, d, J_{PC} = 6.8 Hz, P{**C**H(Me_2)}$_2$;
- 24.44 ppm, s, (C(**Me**)CHC(**Me**));
- 23.86 ppm, s, CH(**Me**$_2$) from the β-diketiminate ligand;
- 22.36 ppm, s, C(**C**H_2)$_4$
- 21.07 ppm, s, P{CH(**Me**$_2$)}$_2$;
- 18.44 ppm, s, P{CH(**Me**$_2$)}$_2$;

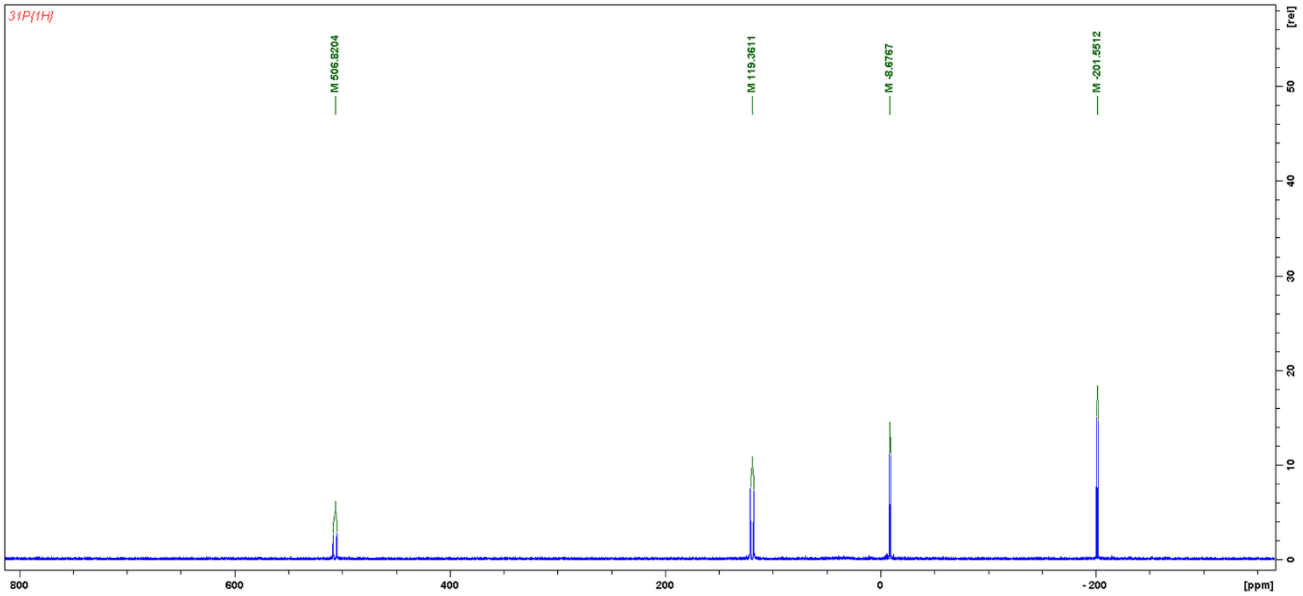

Figure S25. $^{31}P\{^{1}H\}$-NMR of reaction mixture after reaction of **2a** with AgCl in toluene.

- 506.82 ppm, d, J_{PP} = 530.4 Hz, [(BDI*)Ti(Cl){η^2-**P**-P(iPr)$_2$-{C(CH_3)$_2$}O}];
- 119.36 ppm, d, J_{PP} = 530.4 Hz, [(BDI*)Ti(Cl){η^2-P-**P**(iPr)$_2$-{C(CH_3)$_2$}O}];
- -8.68 ppm, d, J_{PP} = 188.9 Hz, iPr$_2$**P**P($SiMe_3$)H;
- -201.55 ppm, d, J_{PP} = 188.9 Hz, iPr$_2$P**P**($SiMe_3$)H;

PART C. DFT Calculations

All calculations presented in this work were performed using the Gaussian 09[3] program package. The molecular geometries of all compounds were optimized using density functional theory with the ωB97XD functional of Head-Gordon[4, 5] and the cc-pVDZ basis set. The ωB97XD exchange-correlation functional was chosen because it has good overall performance for the description of main-group element compounds, and it accounts well for long-range and dispersion interactions. The molecular geometries were energy-optimized, and the nature of the final gas-phase geometries as local minima (no imaginary frequencies) on the potential energy surface was then validated by harmonic frequency calculations at the same level of theory. The calculated energies, enthalpies and Gibbs free energies obtained from thermochemical calculations were corrected for the zero-point energy (ZPE).

The molecular geometries of compounds **3w** and **4w** were optimized using density functional theory with the ωB97XD functional[4, 5] and the 6-31+G(d,p) basis set. The molecular geometries were energy-optimized, and the most stable (the lowest energy) conformer was identified during the potential energy surface scanning of the C-P-P-C dihedral. The nature of the final gas-phase geometries as local minima (no imaginary frequencies) on the potential energy surface was then validated by harmonic frequency calculations at the same level of theory. Theoretical ^{31}P NMR shifts were determined by calculating NMR shielding tensors using the Gauge-Independent Atomic Orbital (GIAO)[6] method at the MN12SX/cc-pvdz level of theory, including the presence of a solvent (benzene), using the CPCM polarizable conductor calculation model.[7]

The NBO (Natural Bond Orbitals) analysis including Wiberg bond orders and second-order perturbative estimates of donor-acceptor (bonding-antibonding) interactions in the NBO basis calculations discussed in this paper were performed on non-optimized X-ray structures of **2a**, **2b** and **5** using density functional theory at the MN12SX[8] level of theory with the Def2TZVP[9, 10] basis set as implemented in the Gaussian09[3] package version of the NBO 3.1 program.[11]

Condensed Fukui functions and dual descriptors[12-14] were determined using optimized structures for single-point calculations on acetone, cyclohexane and cyclopentanone for the *N*, *N-1* and *N+1* electronic states at the ωB97XD//6-31+G(d,p) level of theory. Condensed atom parameters were calculated using the partial charges derived via Hirshfeld population analysis. The more positive value of condensed nucleophilic (f_N) or electrophilic (f_E) Fukui function is, the more nucleophilic or electrophilic considered atom is.

Table S4. Selected computational parameters obtained for considered systems (in atomic units [A.U.]): ε_0 - electronic energy; $\varepsilon_{0+\dots}$ - sum of electronic and: E_{zpe} - zero-point energies, E_{therm} - thermal energies, H – thermal enthalpies, G - thermal free energies calculated at ωB97XD//cc-pVDZ level of theory *(ωB97XD//6-31+G(d,p) for **3w** and **4w**).

Compound	**E_{electr} [A.U.]**	**$\varepsilon_0 + E_{ZPE}$ [A.U.]**	**$\varepsilon_0 + E_{therm}$ [A.U.]**	**$\varepsilon_0 + H$ [A.U.]**	**$\varepsilon_0 + G$ [A.U.]**
1	-3086.468901	-3085.517821	-3085.461570	-3085.460625	-3085.603180
2a	-3279.611516	-3278.571001	-3278.510243	-3278.509299	-3278.660478
2b	-3279.618428	-3278.578099	-3278.517568	-3278.516624	-3278.666401
2c	-3472.727093	-3471.599542	-3471.532697	-3471.531752	-3471.699065
2d	-3472.740357	-3471.614415	-3471.547197	-3471.546253	-3471.715637
3a	-3357.019549	-3355.941116	-3355.879858	-3355.878913	-3356.030000
3b	-3357.019728	-3355.942663	-3355.880917	-3355.879973	-3356.033022
3c	-3627.539888	-3626.336640	-3626.268489	-3626.267544	-3626.437526
3d	-3627.557222	-3626.353870	-3626.285717	-3626.284773	-3626.455655
4a	-3396.333388	-3395.225018	-3395.163096	-3395.162152	-3395.314187
4b	-3396.331989	-3395.223059	-3395.161327	-3395.160382	-3395.311987
4c	-3706.169361	-3704.906644	-3704.836681	-3704.835737	-3705.009051
4d	-3706.190363	-3704.928504	-3704.858485	-3704.857540	-3705.031501
3w*	-1114.995529	-1114.681999	-1114.665441	-1114.664496	-1114.725849
4w*	-1154.309489	-1153.966087	-1153.948696	-1153.947752	-1154.010574
[Ti(III)$SiMe_3PPtBu_2$]	-3165.064402	-3164.056397	-3163.998040	-3163.997096	-3164.142370
a	-3358.206114	-3357.198109	-3357.139752	-3357.044356	-3357.197123
b	-3358.216146	-3357.119264	-3357.056474	-3357.055530	-3357.208497
c	-3551.329112	-3550.145157	-3550.076241	-3550.075297	-3550.245348
d	-3551.348310	-3550.166797	-3550.096985	-3550.096041	-3550.269153
Cy(=O)	-309.816329	-309.664595	-309.658189	-309.657244	-309.694878
$(CH_3)_2CO$	-193.102943	-193.018979	-193.013724	-193.012779	-193.046678
Cp(=O)	-270.505940	-270.384328	-270.378767	-270.377823	-270.413460

Theoretical ^{31}P NMR shifts of phospha-Wittig products

Table S5. Calculated and experimental values of ^{31}P (C_6D_6) chemical shifts for compounds **3w** and **4w.**

Compound	δP_{exp} (C_6D_6)		δP_{calc} (C_6D_6)	
	P1 [ppm]	**P2 [ppm]**	**P1 [ppm]**	**P2 [ppm]**
3w	211.14	1.04	211.8	2.6
4w	220.88	-6.79	218.3	-5.4

NBO analysis of intramolecular interactions in compounds 2a and 2b

Table S6. Second order perturbation analysis of the Fock matrix in NBO basis for selected donors, and acceptors in complexes **2a** and **2b**. E(2) is the stabilization energy associated with electron delocalization between the donor and acceptor [**P1**: $P(SiMe_3)$; **P2**: $PiPr_2$]

No.	P-Ti Wiberg bond index	Donor	Occupancy	Acceptor	Occupancy	E(2) (kcal mol^{-1})
2a	0.642	LP1 (P1)	1.756	LP1* (Ti)	0.342	123.8
		LP2 (P1)	1.637			124.4
				LP2* (Ti)	0.208	23.5
2b	0.430	LP1 (P2)	1.715	LP1* (Ti)	0.316	129.8

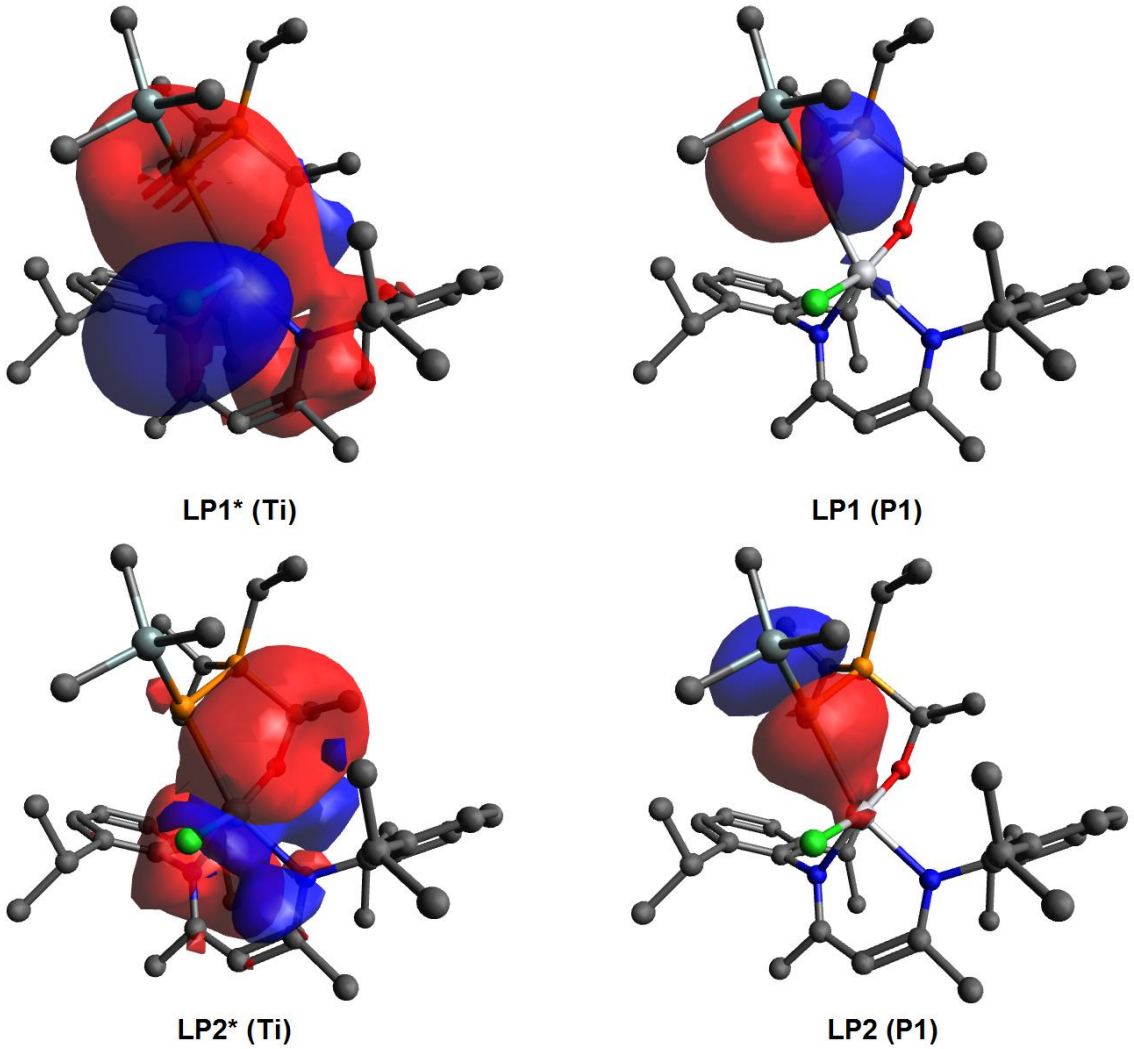

Figure S26. Interacting NBO orbitals of **2a**: antibonding d* orbitals: LP1*(Ti) and LP2*(Ti) lone pairs orbital LP1(P1) and LP2(P1).

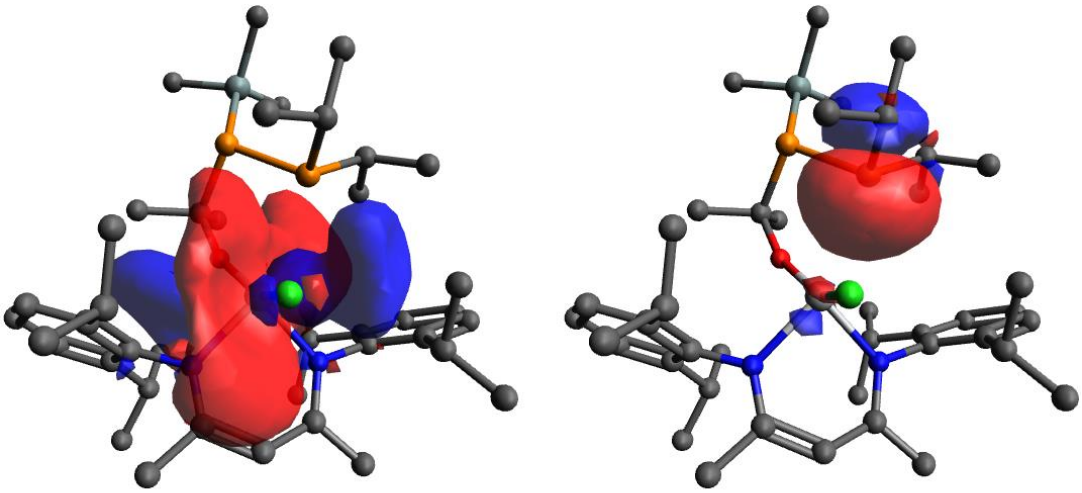

Figure S27. Interacting NBO orbitals of **2b**: antibonding d* orbital LP1*(Ti) and lone pair orbital LP1(P2).

NBO analysis of 5

Tabel S7. Results of NBO analysis and second order perturbation analysis of the Fock matrix in NBO basis for selected donors and acceptors in complexe **5** along with Meyer bond order. E(2) is the stabilization energy associated with electron delocalization between the donor and acceptor.

P1-Ti Meyer bond order	**Bonds**				
	Orbital			**Occupancy**	
1.462	BD1 (P1-Ti)			1.884	
	BD2 (P1-Ti)			1.834	
	Interactions				
	Donor	**Occupancy**	**Acceptor**	**Occupancy**	**E(2) (kcal mol^{-1})**
	LP (P1)	1.853	LP* (Ti)	0.214	13.55

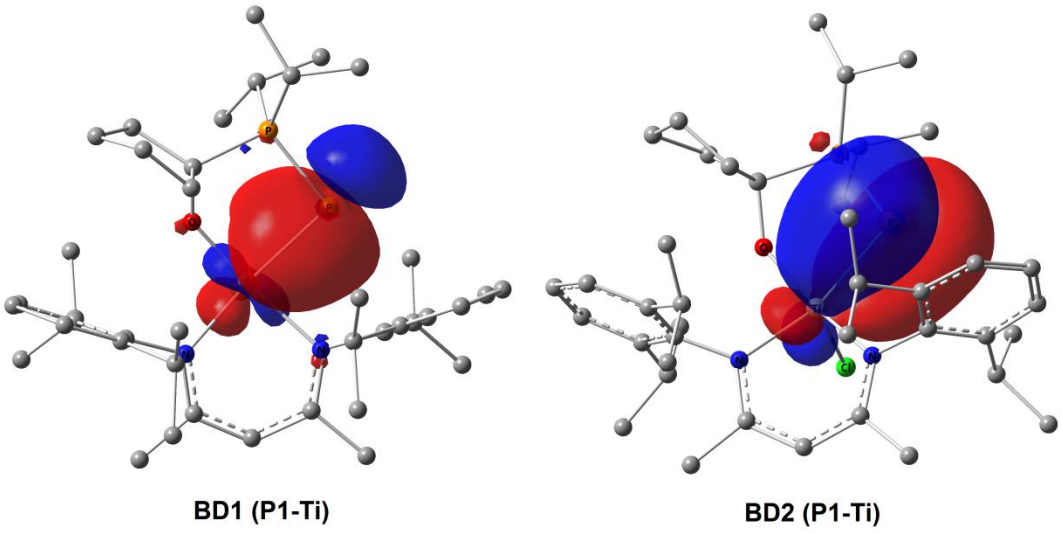

Figure S28. Bonding P1-Ti NBO orbitals of **5:** BD1 and BD2.

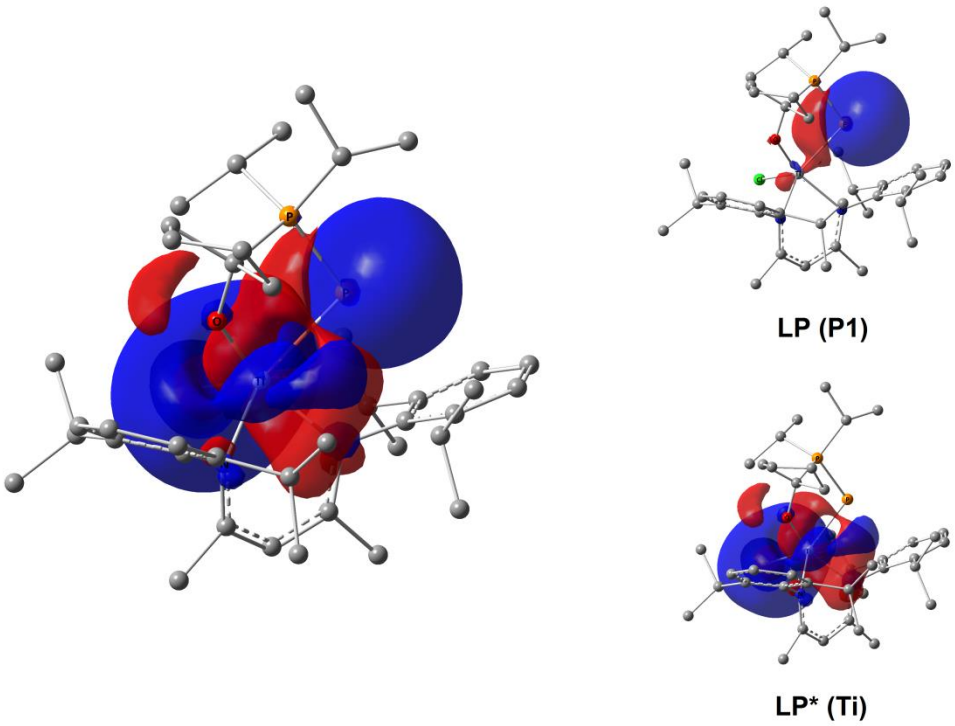

Figure S29. Interacting NBO orbitals of **5**: antibonding d* orbital LP *(Ti) and lone pair orbital LP(P2).

Optimized structures and Cartesian coordinates

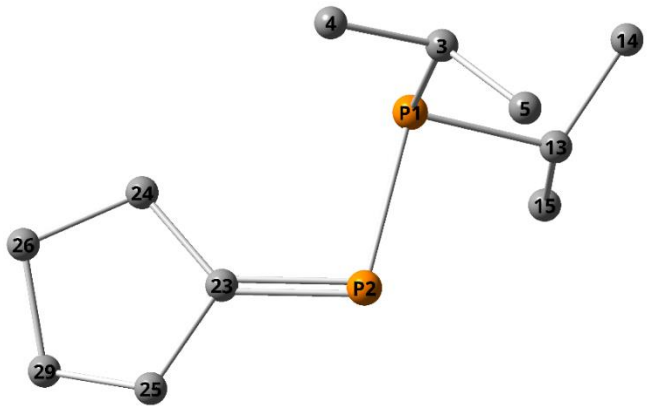

Figure S30. Optimized structure of **3w**.

Below are presented xyz coordinates for optimized geometry for **3w**:

P	1.05459600	-0.07661700	-0.58880900
P	-0.35852800	-0.41563100	1.10893000
C	1.68894000	1.65389000	-0.18943800
C	0.60521900	2.67131300	-0.53159300
C	2.22404400	1.87191900	1.21957600
H	2.52104800	1.79387100	-0.91123400
H	0.97843300	3.70205400	-0.39467400
H	0.26611500	2.57253700	-1.57750000
H	-0.27558100	2.54966800	0.12702200
H	1.42791100	1.74578400	1.97535500
H	3.04402400	1.18039700	1.47614100
H	2.61783200	2.89974200	1.32599700
C	2.44100300	-1.16605900	0.06219700
C	3.75488100	-0.83884700	-0.63878200
C	2.05924300	-2.62690500	-0.15713900
H	2.55928000	-0.99527800	1.15216700
H	4.11532800	0.17888400	-0.41234200
H	4.54612300	-1.54452900	-0.32700200
H	3.65076500	-0.92199900	-1.73660600
H	1.11246200	-2.88872100	0.34725100
H	1.93528600	-2.84540300	-1.23356100
H	2.84344000	-3.29906600	0.23491500
C	-1.85740700	-0.16892200	0.36522600
C	-2.21256200	0.14948200	-1.07345000
C	-3.15572100	-0.32193700	1.12643900
C	-3.74440000	0.19872100	-1.11684000
H	-1.81348900	-0.65261800	-1.72506400
H	-1.73507300	1.07924900	-1.42834900
C	-4.16957000	-0.69333400	0.04571000
H	-3.43361200	0.66507300	1.55309300
H	-3.08732900	-1.02562700	1.97258100
H	-4.09389600	1.23219900	-0.93312500
H	-4.15572700	-0.11492000	-2.09018900
H	-5.21574600	-0.54437900	0.35997400
H	-4.05063700	-1.75912700	-0.22810000

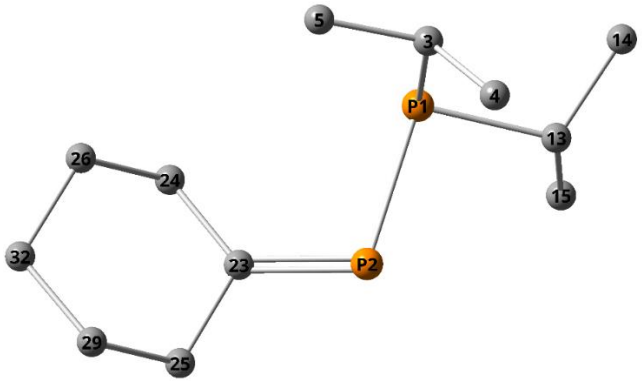

Figure S31. Optimized structure of **4w.**

Below are presented xyz coordinates for optimized geometry for **4w**.

P	1.36845900	-0.00093400	-0.59705400
P	-0.05598600	-0.84937400	0.88668500
C	1.56736000	1.76227700	0.04039700
C	1.96927200	1.92280700	1.50851500
C	0.29620400	2.56025100	-0.26887300
H	2.37204100	2.16713700	-0.58782000
H	2.10038600	2.98455300	1.74871700
H	1.19762200	1.52413600	2.17581000
H	2.90942300	1.41420700	1.74057500
H	0.00593500	2.47220300	-1.32089000
H	-0.54145800	2.20952800	0.34469000
H	0.44892500	3.62193500	-0.04566100
C	2.92099100	-0.84742700	0.03677500
C	4.17066000	-0.16400900	-0.52833500
C	2.88814300	-2.32714600	-0.36169600
H	2.95119200	-0.78653600	1.13211900
H	4.27308200	0.86878600	-0.18177300
H	5.07000000	-0.70691400	-0.21621900
H	4.15072800	-0.15318400	-1.62431900
H	2.01942000	-2.84516500	0.05737500
H	2.85441600	-2.43799000	-1.45137200
H	3.78694300	-2.83708600	0.00303500
C	-1.54560900	-0.82894400	0.09728500
C	-1.90453800	-0.32838200	-1.27765400
C	-2.74835900	-1.33464600	0.86370300
C	-2.99588000	0.75508500	-1.20308400
H	-2.30176600	-1.18119100	-1.84921300
H	-1.02788600	0.03995600	-1.81425000
C	-3.83513500	-0.24916400	0.95544400
H	-3.16083100	-2.20059200	0.32409600
H	-2.46411700	-1.67918500	1.86282500
C	-4.22347600	0.26618800	-0.43156400
H	-3.27503800	1.05644500	-2.21852200
H	-2.58302600	1.64331000	-0.70900800
H	-4.71133700	-0.65135700	1.47545700
H	-3.45318100	0.58136400	1.56329700
H	-4.95963600	1.07267400	-0.34335500
H	-4.70673100	-0.54376200	-0.99552800

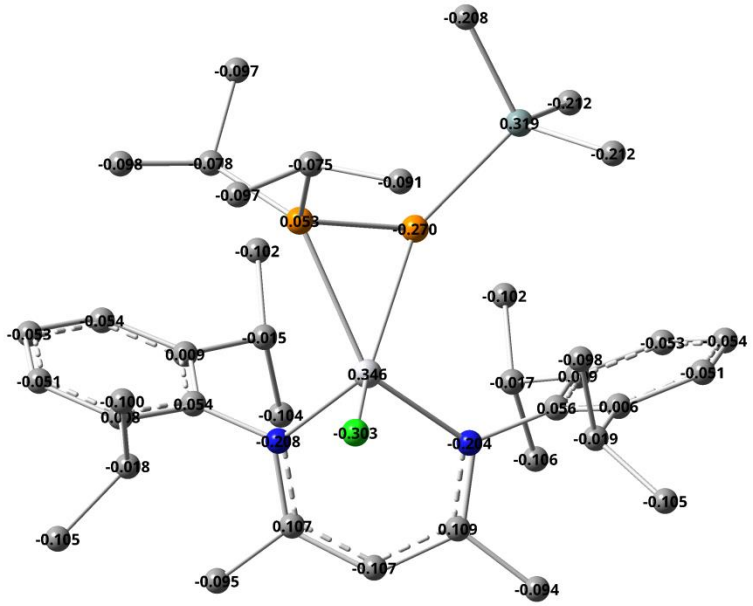

Figure S32. Optimized structure of **1.**

Below are presented xyz coordinates for optimized geometry for **1**.

Ti	0.15602	-0.24607	-0.87345
Cl	0.43906	-0.21753	-3.14259
P	-0.72840	1.36791	0.78478
P	1.03015	2.07522	-0.24206
N	1.54972	-1.56339	-0.15458
N	-1.33006	-1.65865	-0.50918
C	2.78657	-1.10368	0.41934
C	2.83780	-0.88266	1.81375
C	4.05102	-0.47761	2.37671
H	4.11578	-0.30798	3.45178
C	5.17968	-0.27485	1.59012
H	6.11728	0.04369	2.04926
C	5.10327	-0.46723	0.21764
H	5.98694	-0.28733	-0.39797
C	3.91687	-0.88369	-0.39371
C	1.60648	-1.07450	2.68988
H	0.73554	-0.77436	2.08854
C	1.41766	-2.54398	3.08998
H	0.57166	-2.64377	3.78780
H	2.31780	-2.93410	3.59257
H	1.20111	-3.18315	2.22219
C	1.60709	-0.18183	3.93350
H	0.62496	-0.23249	4.42454
H	1.79657	0.87197	3.67903
H	2.35931	-0.49868	4.67398
C	3.88413	-1.04848	-1.90662
H	2.92923	-1.51773	-2.18119
C	5.01722	-1.93815	-2.43289
H	4.88049	-2.12362	-3.50917
H	5.05501	-2.91202	-1.92161
H	6.00226	-1.46157	-2.30507
C	3.92217	0.32350	-2.58761
H	3.81563	0.21947	-3.67823

H	4.87329	0.84237	-2.38014
H	3.09744	0.95340	-2.23083
C	-2.68450	-1.32330	-0.17105
C	-3.60446	-0.93756	-1.16246
C	-4.91432	-0.64271	-0.77238
H	-5.64193	-0.33976	-1.52798
C	-5.30589	-0.72274	0.55875
H	-6.33396	-0.49080	0.84273
C	-4.38188	-1.10394	1.52612
H	-4.69840	-1.17830	2.56867
C	-3.06232	-1.41136	1.18583
C	-3.19883	-0.80613	-2.62142
H	-2.21583	-1.28110	-2.74504
C	-3.03127	0.67217	-2.98926
H	-2.61610	0.77884	-4.00306
H	-2.34748	1.17261	-2.28798
H	-3.99814	1.20036	-2.94624
C	-4.17050	-1.50401	-3.57800
H	-3.77691	-1.46841	-4.60535
H	-5.15891	-1.01770	-3.58862
H	-4.32211	-2.56030	-3.30672
C	-2.08942	-1.89972	2.25194
H	-1.08306	-1.86529	1.81408
C	-2.38078	-3.35846	2.62998
H	-2.31292	-4.02812	1.76042
H	-3.39075	-3.46309	3.05968
H	-1.65570	-3.71321	3.37933
C	-2.07547	-1.01241	3.49838
H	-1.36961	-1.41818	4.23985
H	-3.06137	-0.95996	3.98710
H	-1.75548	0.00916	3.24913
C	2.60138	-3.79904	-0.15249
H	3.07877	-3.60776	0.81835
H	3.36533	-3.62219	-0.92260
H	2.29449	-4.85035	-0.20091
C	1.42101	-2.88239	-0.36754
C	0.22764	-3.48739	-0.78156
C	-1.06942	-2.93952	-0.77763
C	-2.20388	-3.89093	-1.08029
H	-3.00637	-3.81851	-0.33506
H	-1.84952	-4.92713	-1.13111
H	-2.64921	-3.62566	-2.05173
C	0.83510	3.51436	-1.43424
H	0.86983	4.43202	-0.82207
C	-0.48838	3.45493	-2.19259
H	-1.35893	3.48276	-1.52825
H	-0.54614	2.53446	-2.79384
H	-0.55781	4.31118	-2.88261
C	1.98682	3.53258	-2.44784
H	2.97885	3.53439	-1.98056
H	1.91031	4.43528	-3.07572
H	1.92165	2.65527	-3.10977
C	2.29109	2.56420	1.05223

H	2.38751	1.62040	1.60933
C	3.66831	2.90417	0.48002
H	4.00363	2.16153	-0.25725
H	4.40937	2.91778	1.29503
H	3.67697	3.90121	0.01156
C	1.79606	3.64370	2.01165
H	0.86471	3.33340	2.50745
H	1.61321	4.59959	1.49359
H	2.55353	3.83022	2.79090
Si	-2.40912	2.86605	1.07458
C	-3.22002	2.42905	2.72252
H	-3.69651	1.43811	2.67109
H	-4.00096	3.17262	2.95443
H	-2.48963	2.42334	3.54594
C	-3.76750	2.82562	-0.23107
H	-4.18735	1.81247	-0.31199
H	-3.42644	3.13772	-1.22810
H	-4.57343	3.50957	0.08558
H	0.29009	-4.54986	-1.00825
C	-1.69957	4.61357	1.20003
H	-1.21044	4.93569	0.26886
H	-0.96952	4.69213	2.01871
H	-2.52421	5.31595	1.40849

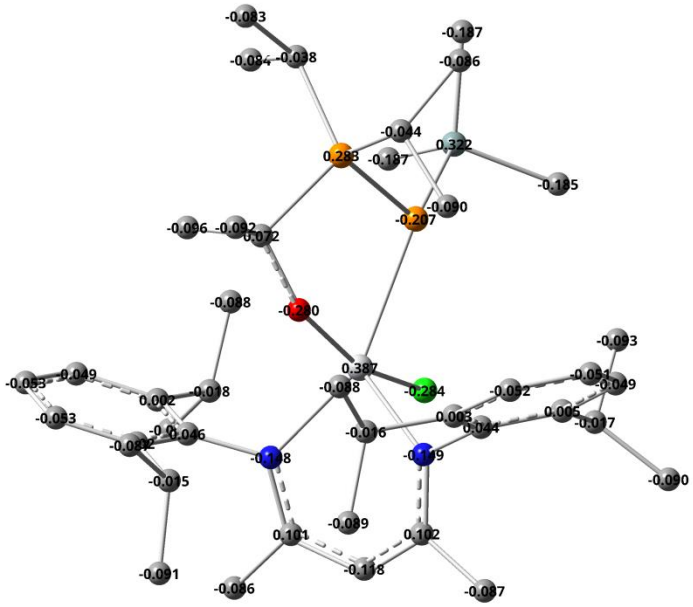

Figure S33. Optimized structure of **2a**.

Below are presented xyz coordinates for optimized geometry for **2a**.

C	2.57642	-1.97098	-0.33131
C	2.14177	-3.15979	-0.94281
C	2.41102	-4.37655	-0.30505
H	2.06844	-5.30641	-0.76418
C	3.11463	-4.42462	0.88978
H	3.32105	-5.38377	1.36846
C	3.55948	-3.24122	1.47374
H	4.11476	-3.28706	2.41185
C	3.29381	-2.00265	0.88800
C	1.40112	-3.16280	-2.26953
H	1.41920	-2.14285	-2.67578
C	2.07308	-4.08211	-3.29636
H	1.59601	-3.96023	-4.28106
H	3.14418	-3.85162	-3.40393
H	1.98738	-5.14494	-3.01756
C	-0.07153	-3.53823	-2.08091
H	-0.58208	-3.58495	-3.05418
H	-0.17701	-4.52085	-1.59031
H	-0.60159	-2.78705	-1.47400
C	3.77321	-0.71635	1.54435
H	3.06413	0.06721	1.24521
C	5.16595	-0.30505	1.04564
H	5.51113	0.59544	1.57749
H	5.89853	-1.10895	1.22696
H	5.17079	-0.07222	-0.02704
C	3.78509	-0.79058	3.07282
H	2.83782	-1.18120	3.47046
H	4.59819	-1.43238	3.44887
H	3.94642	0.21168	3.49814
C	0.54283	3.04879	-0.04729
C	0.81342	3.30923	1.31714
C	0.15508	4.37408	1.93576
H	0.35553	4.59774	2.98387

C	-0.76962	5.15038	1.24538
H	-1.27865	5.97463	1.74897
C	-1.04128	4.86948	-0.08513
H	-1.77031	5.47863	-0.62361
C	-0.39038	3.83035	-0.75950
C	1.79891	2.45323	2.10338
H	1.63670	1.41328	1.78345
C	3.25565	2.83169	1.79961
H	3.93989	2.26944	2.45429
H	3.53712	2.60351	0.76288
H	3.42489	3.90582	1.97957
C	1.56946	2.49674	3.61728
H	0.51186	2.34396	3.88010
H	2.15550	1.70291	4.10444
H	1.88966	3.45504	4.05789
C	-0.71756	3.59959	-2.22774
H	-0.05869	2.80781	-2.60902
C	-0.49817	4.86204	-3.07287
H	0.50275	5.29533	-2.92790
H	-0.61862	4.62743	-4.14173
H	-1.23220	5.64550	-2.82429
C	-2.15648	3.10219	-2.39247
H	-2.32652	2.19288	-1.80119
H	-2.88203	3.86581	-2.06433
H	-2.36208	2.86896	-3.44847
C	4.23911	-0.94456	-2.34547
H	5.04399	-0.31448	-2.74353
H	4.66327	-1.68431	-1.65457
H	3.78985	-1.50165	-3.18377
C	3.15635	-0.11378	-1.69793
C	3.13634	1.25802	-1.99791
H	3.92391	1.61837	-2.65755
C	2.31743	2.23783	-1.41836
C	2.71943	3.67224	-1.67004
H	3.77609	3.73508	-1.95728
H	2.11572	4.08210	-2.49302
H	2.54566	4.30502	-0.79046
C	-3.43938	-2.59298	-2.67253
H	-3.18530	-3.45430	-2.03697
H	-4.26835	-2.88824	-3.33773
H	-2.56272	-2.35529	-3.29418
C	-4.25862	0.30569	-2.96883
H	-3.33229	0.53949	-3.51594
H	-5.01392	-0.03908	-3.69476
H	-4.62185	1.22903	-2.49296
C	-5.52474	-1.39359	-0.74177
H	-5.47406	-2.32659	-0.16072
H	-5.78900	-0.56647	-0.06505
H	-6.34481	-1.50683	-1.47071
C	-3.48981	-2.26210	2.04996
H	-4.47249	-1.83449	1.79503
C	-3.29513	-3.51313	1.18909
H	-3.08818	-3.26434	0.14008

H	-2.46773	-4.13461	1.55562
H	-4.21009	-4.12505	1.22267
C	-3.48651	-2.59679	3.54446
H	-3.71435	-1.72577	4.17564
H	-4.25203	-3.36171	3.74794
H	-2.51804	-3.01044	3.86490
C	-2.93631	0.56874	2.69172
H	-2.71087	0.27527	3.73039
C	-4.44115	0.80078	2.54101
H	-5.04935	-0.03116	2.92590
H	-4.72928	1.70690	3.09570
H	-4.69592	0.96425	1.48113
C	-2.16066	1.84372	2.34858
H	-1.07491	1.68997	2.34024
H	-2.43513	2.21277	1.34894
H	-2.39288	2.62881	3.08450
C	-0.51287	-1.17843	2.03221
C	-0.19425	-0.81876	3.48375
H	-0.80912	-1.39817	4.18935
H	0.86166	-1.05696	3.67285
H	-0.33339	0.24997	3.68205
C	-0.18537	-2.65002	1.77679
H	-0.66795	-3.31365	2.50928
H	-0.47460	-2.95333	0.76162
H	0.90379	-2.77273	1.86393
Cl	-0.19117	0.01262	-2.96314
N	2.26990	-0.68912	-0.88902
N	1.23113	1.96050	-0.68836
O	0.20602	-0.37533	1.15899
P	-2.27489	-0.21630	-0.41306
P	-2.35969	-0.84438	1.61577
Si	-3.92774	-1.04994	-1.70244
Ti	0.33388	0.09287	-0.66257

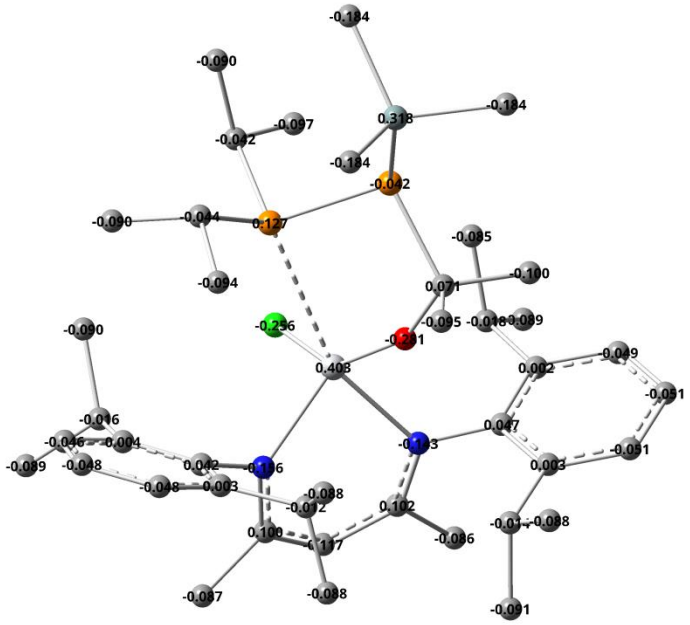

Figure S34. Optimized structure of **2b.**

Below are presented xyz coordinates for optimized geometry for **2b**.

C	-3.06826	-1.47272	-0.17782
C	-3.13592	-2.44854	-1.18613
C	-3.57458	-3.73211	-0.84358
H	-3.62774	-4.50260	-1.61527
C	-3.95110	-4.04116	0.45624
H	-4.30470	-5.04426	0.70187
C	-3.86403	-3.06818	1.44738
H	-4.14376	-3.32366	2.47083
C	-3.40546	-1.78182	1.15845
C	-2.70906	-2.15121	-2.61321
H	-2.61267	-1.06280	-2.72019
C	-1.32611	-2.75562	-2.88295
H	-0.97555	-2.49793	-3.89405
H	-0.57665	-2.38247	-2.16691
H	-1.35002	-3.85444	-2.79098
C	-3.72890	-2.62547	-3.65282
H	-3.42752	-2.28925	-4.65678
H	-3.81059	-3.72383	-3.68516
H	-4.73226	-2.22197	-3.44571
C	-3.26191	-0.74682	2.26600
H	-2.47284	-0.05247	1.94438
C	-2.83283	-1.36663	3.59997
H	-2.50166	-0.57945	4.29510
H	-3.66329	-1.89939	4.09120
H	-2.00686	-2.08128	3.47371
C	-4.54889	0.06490	2.46979
H	-4.79530	0.67727	1.59194
H	-5.40118	-0.60345	2.67617
H	-4.44017	0.74940	3.32574
C	0.02130	3.00271	0.57974
C	0.31613	2.88084	1.95683
C	1.30402	3.70504	2.50076
H	1.53681	3.63843	3.56373

C	2.02065	4.59186	1.70440
H	2.79846	5.21806	2.14506
C	1.74900	4.66904	0.34521
H	2.32386	5.35813	-0.27706
C	0.74261	3.89502	-0.24316
C	-0.42389	1.87507	2.83053
H	-0.58068	0.97062	2.22148
C	0.37237	1.44862	4.06691
H	-0.11422	0.58269	4.54102
H	1.40334	1.15925	3.81309
H	0.42058	2.24872	4.82320
C	-1.80290	2.39688	3.25743
H	-2.27114	1.69751	3.96744
H	-1.71074	3.37447	3.75806
H	-2.48754	2.50351	2.40497
C	0.45411	4.06449	-1.73121
H	-0.46705	3.51409	-1.96552
C	1.56154	3.45627	-2.59776
H	1.29961	3.54235	-3.66330
H	2.52244	3.97270	-2.43744
H	1.69279	2.38915	-2.37663
C	0.24850	5.53619	-2.11783
H	-0.11704	5.60669	-3.15365
H	-0.47590	6.04534	-1.46472
H	1.19160	6.10334	-2.06418
C	-4.97840	0.30865	-1.09742
H	-5.66855	1.15708	-1.17740
H	-4.93423	-0.20356	-2.07135
H	-5.37879	-0.41592	-0.37571
C	-3.58792	0.76428	-0.72066
C	-3.36700	2.15217	-0.63466
H	-4.22892	2.78593	-0.83474
C	-2.22707	2.80118	-0.14991
C	-2.39118	4.26743	0.17893
H	-3.45304	4.53791	0.21432
H	-1.92666	4.51264	1.14347
H	-1.90055	4.89027	-0.58119
C	0.58235	-2.05342	1.02321
C	0.91884	-1.75047	2.48030
H	1.49849	-2.56143	2.94518
H	1.47425	-0.81025	2.57165
H	-0.02151	-1.63632	3.04027
C	-0.21025	-3.35924	0.92296
H	0.39996	-4.21355	1.25510
H	-1.10971	-3.29909	1.55377
H	-0.53266	-3.54211	-0.11066
C	4.55672	-2.03209	2.53542
H	3.78486	-1.76842	3.27235
H	5.30580	-2.66434	3.04172
H	5.06001	-1.10867	2.21334
C	5.32126	-3.30953	-0.11190
H	5.01573	-3.89565	-0.99216
H	5.76673	-2.36539	-0.46021

H	6.10524	-3.87391	0.42008
C	3.28811	-4.69594	1.71182
H	2.50177	-4.59765	2.47601
H	2.89568	-5.31897	0.89340
H	4.13706	-5.22779	2.17275
C	2.98043	-0.45652	-2.65896
H	2.92437	0.55986	-3.08772
C	4.42594	-0.94843	-2.73156
H	5.13250	-0.31974	-2.17095
H	4.50295	-1.97736	-2.34986
H	4.75968	-0.96265	-3.78187
C	2.07594	-1.36357	-3.49495
H	1.03868	-1.00884	-3.50060
H	2.43648	-1.37647	-4.53623
H	2.09368	-2.39626	-3.11423
C	3.72508	0.66289	-0.03236
H	4.56699	-0.04993	-0.02842
C	3.33402	0.98714	1.40469
H	3.07500	0.08680	1.97275
H	4.17028	1.48222	1.92507
H	2.47556	1.67152	1.42446
C	4.16074	1.94363	-0.74722
H	4.39563	1.79322	-1.81034
H	3.37606	2.70883	-0.67195
H	5.06299	2.34629	-0.25896
Cl	-0.67780	0.80343	-2.94432
N	-2.64364	-0.13250	-0.46294
N	-1.03861	2.20252	0.03616
O	-0.17907	-0.99863	0.52634
P	2.10939	-2.25832	-0.15847
P	2.30091	-0.19696	-0.91898
Si	3.87949	-3.01655	1.07094
Ti	-0.60203	0.31099	-0.67632

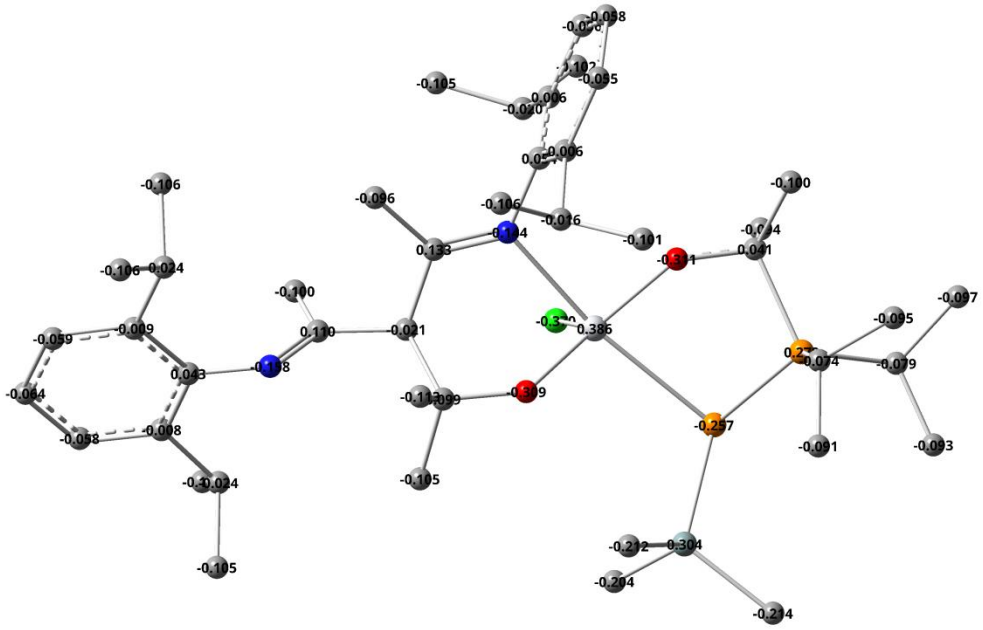

Figure S35. Optimized structure of **2c.**

Below are presented xyz coordinates for optimized geometry for **2c**.

C	0.32445	2.80802	-0.01421
C	0.47449	3.63569	-1.14115
C	1.06103	4.88956	-0.95784
H	1.17985	5.55692	-1.81284
C	1.50164	5.30180	0.29671
H	1.95471	6.28712	0.42131
C	1.37720	4.44858	1.38668
H	1.74506	4.76763	2.36456
C	0.80069	3.18274	1.25156
C	-0.00460	3.17147	-2.50742
H	0.03739	2.07232	-2.51426
C	-1.46277	3.58459	-2.74694
H	-1.82543	3.18827	-3.70848
H	-2.12797	3.21022	-1.95528
H	-1.56365	4.68250	-2.76793
C	0.88013	3.65849	-3.65683
H	0.59128	3.15062	-4.58899
H	0.78257	4.74303	-3.82847
H	1.94129	3.43795	-3.46879
C	0.73328	2.24308	2.44496
H	0.37566	1.26945	2.08368
C	-0.24635	2.74219	3.51304
H	-0.32013	2.01738	4.33911
H	0.08554	3.70402	3.93650
H	-1.25519	2.89078	3.10115
C	2.12328	2.00179	3.03962
H	2.08073	1.22472	3.81907
H	2.80204	1.66919	2.24340
H	2.54116	2.91370	3.49578
C	-2.44145	2.28652	0.57564
H	-2.82511	1.91657	1.53947

H	-1.97874	3.26989	0.71291
H	-3.31581	2.38541	-0.08245
C	-1.48111	1.27432	0.02585
C	-1.97694	-0.14261	-0.22040
H	-1.52326	-0.43758	-1.18179
C	-3.47633	-0.19964	-0.46126
C	-3.88660	0.21710	-1.85263
H	-3.33310	1.11563	-2.16652
H	-3.60373	-0.57826	-2.56189
H	-4.96643	0.39390	-1.93325
C	-5.65336	-0.76768	0.21786
C	-6.14201	-1.86915	-0.51620
C	-7.52652	-2.02387	-0.63053
H	-7.92257	-2.87552	-1.18768
C	-8.41031	-1.12036	-0.05232
H	-9.48704	-1.25860	-0.16294
C	-7.91121	-0.04295	0.67188
H	-8.60553	0.66796	1.12446
C	-6.53746	0.14494	0.82807
C	-5.21586	-2.91194	-1.12637
H	-4.18852	-2.52935	-1.08069
C	-5.24537	-4.20381	-0.30001
H	-4.51843	-4.93406	-0.68971
H	-5.00023	-4.00299	0.75403
H	-6.24458	-4.66801	-0.32847
C	-5.52526	-3.18443	-2.60208
H	-4.77379	-3.86605	-3.02978
H	-6.51111	-3.65757	-2.73555
H	-5.51817	-2.25371	-3.18967
C	-5.99420	1.34044	1.59203
H	-4.93820	1.12251	1.80977
C	-6.69802	1.57023	2.93197
H	-6.67134	0.66340	3.55429
H	-6.20481	2.38363	3.48696
H	-7.75270	1.85935	2.79935
C	-6.04619	2.59929	0.71629
H	-5.55854	3.45312	1.21384
H	-5.54929	2.43294	-0.25242
H	-7.09036	2.88023	0.50225
C	-1.35034	-1.14244	0.81822
C	-1.69541	-0.80322	2.26825
H	-2.78029	-0.85892	2.42785
H	-1.18891	-1.51649	2.93550
H	-1.34650	0.20516	2.53413
C	-1.77366	-2.57441	0.48307
H	-2.83167	-2.74765	0.71635
H	-1.59575	-2.78533	-0.58299
H	-1.16074	-3.26881	1.07526
C	3.91444	1.06412	-0.70051
C	3.97325	1.10402	-2.23215
H	4.99974	1.20383	-2.61565
H	3.50149	0.21610	-2.67748
H	3.39492	1.98306	-2.55546

C	4.55065	2.32269	-0.10888
H	5.60219	2.45285	-0.40431
H	3.96983	3.18127	-0.48130
H	4.47618	2.33793	0.98631
Ti	1.18945	-0.23245	-0.53882
Cl	0.48005	-0.53255	-2.76911
N	-0.23908	1.50536	-0.21226
N	-4.26509	-0.61366	0.44980
O	0.04879	-1.06733	0.64835
O	2.60263	0.99549	-0.26289
P	4.68361	-0.59267	-0.08480
P	3.16364	-1.96939	-0.79391
C	6.25232	-0.99486	-1.01460
C	6.86317	-2.30505	-0.50926
C	7.30413	0.11090	-1.13442
H	5.83439	-1.18432	-2.01766
H	6.10832	-3.10086	-0.43082
H	7.64157	-2.64570	-1.20943
H	7.34013	-2.17335	0.47480
H	6.88364	1.05398	-1.50864
H	7.80783	0.31415	-0.18019
H	8.07623	-0.21042	-1.85122
C	5.02287	-0.38201	1.73824
C	6.30018	0.40010	2.06390
C	5.00506	-1.69695	2.51399
H	4.14644	0.20814	2.05185
H	6.40722	1.32836	1.49055
H	6.29142	0.66636	3.13257
H	7.19371	-0.21850	1.89070
H	4.05955	-2.22981	2.38031
H	5.82755	-2.36228	2.21215
H	5.12295	-1.48766	3.58880
Si	2.66589	-3.74801	0.51815
C	4.14137	-4.89953	0.80016
H	4.62112	-5.15527	-0.15754
H	4.90103	-4.45658	1.46178
H	3.79358	-5.83521	1.26926
C	1.44046	-4.60508	-0.63859
H	1.02788	-5.50502	-0.15313
H	0.60499	-3.93180	-0.88508
H	1.92456	-4.90598	-1.58022
C	1.76815	-3.44136	2.15571
H	2.43222	-3.20651	3.00041
H	1.04820	-2.61941	2.02346
H	1.21374	-4.35850	2.41931

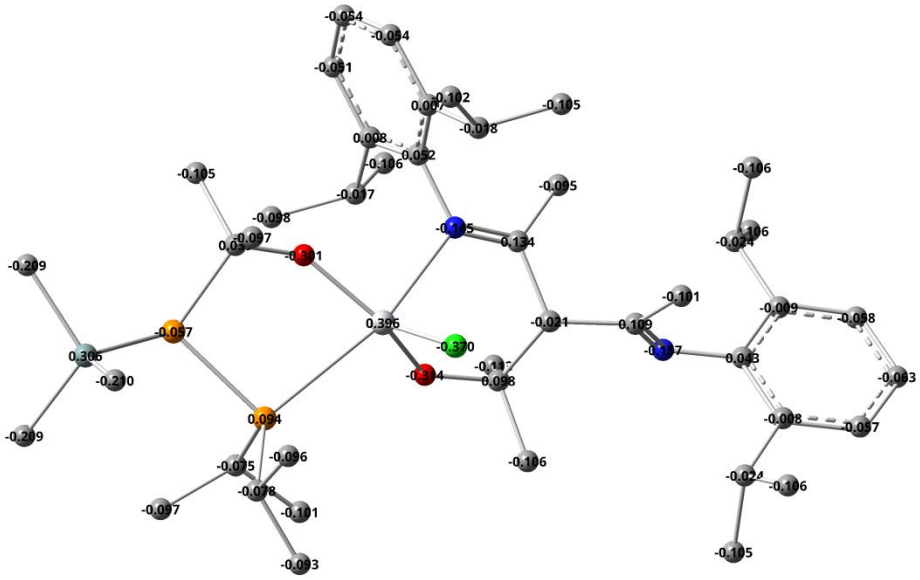

Figure S36. Optimized structure of **2d.**

Below are presented xyz coordinates for optimized geometry for **2d**.

C	-0.15153	2.76443	0.07924
C	-0.38565	3.48361	1.26407
C	-0.97396	4.74461	1.15474
H	-1.16201	5.32999	2.05593
C	-1.33673	5.26261	-0.08589
H	-1.79677	6.25018	-0.15237
C	-1.13156	4.51194	-1.23714
H	-1.44370	4.91323	-2.20387
C	-0.54741	3.24368	-1.17850
C	0.00406	2.89088	2.60934
H	-0.05916	1.79602	2.51324
C	1.45417	3.24651	2.96434
H	1.75474	2.75731	3.90418
H	2.15625	2.93121	2.17871
H	1.57184	4.33531	3.09147
C	-0.93521	3.29632	3.74635
H	-0.69622	2.71752	4.65108
H	-0.83906	4.36346	4.00466
H	-1.98607	3.09965	3.48824
C	-0.38345	2.41689	-2.44467
H	0.04866	1.44845	-2.16133
C	0.58083	3.08229	-3.43389
H	0.75146	2.42968	-4.30445
H	0.17692	4.03766	-3.80637
H	1.55603	3.29191	-2.96897
C	-1.73253	2.10870	-3.10355
H	-1.58277	1.49467	-4.00554
H	-2.38390	1.55577	-2.41194
H	-2.25659	3.02907	-3.40832
C	2.64011	2.25570	-0.41760
H	3.05886	1.96453	-1.39360

H	2.18909	3.25128	-0.49145
H	3.48717	2.29006	0.28143
C	1.64833	1.21470	0.00417
C	2.10462	-0.22819	0.14592
H	1.58095	-0.60594	1.04055
C	3.58337	-0.33505	0.48061
C	3.90540	-0.04175	1.92567
H	3.34402	0.83771	2.27726
H	3.56932	-0.88885	2.54646
H	4.97978	0.10998	2.08910
C	5.79465	-0.88187	-0.10288
C	6.22246	-2.05011	0.56234
C	7.59553	-2.24055	0.74288
H	7.94564	-3.14293	1.24873
C	8.52462	-1.30875	0.29592
H	9.59098	-1.47666	0.45528
C	8.08495	-0.16260	-0.35811
H	8.81497	0.57127	-0.70540
C	6.72585	0.06455	-0.57675
C	5.24758	-3.11835	1.03752
H	4.22969	-2.71583	0.95797
C	5.31034	-4.35085	0.12684
H	4.55989	-5.09800	0.42967
H	5.11979	-4.07729	-0.92202
H	6.30344	-4.82636	0.17403
C	5.46662	-3.49771	2.50599
H	4.68619	-4.19823	2.84112
H	6.43941	-3.99093	2.66070
H	5.43456	-2.61098	3.15746
C	6.24464	1.33467	-1.25743
H	5.20220	1.15604	-1.55949
C	7.03452	1.67921	-2.52249
H	7.03117	0.83999	-3.23360
H	6.59031	2.55439	-3.02184
H	8.08376	1.92968	-2.29884
C	6.25565	2.50458	-0.26443
H	5.80659	3.40837	-0.70678
H	5.70051	2.25536	0.65370
H	7.28766	2.74882	0.03608
C	1.53312	-1.11020	-1.02676
C	2.00815	-0.66573	-2.41017
H	3.09827	-0.76410	-2.49456
H	1.52056	-1.29159	-3.17227
H	1.72870	0.37849	-2.61279
C	1.88982	-2.57806	-0.77888
H	2.96433	-2.75812	-0.91017
H	1.58680	-2.87764	0.23644
H	1.33939	-3.20273	-1.49687
C	-3.03620	-2.39413	-2.23487
C	-4.30081	-3.08446	-2.74294
H	-4.49297	-4.03048	-2.21162
H	-5.18543	-2.44052	-2.63142
H	-4.19461	-3.32491	-3.81309

C	-1.76506	-3.19491	-2.53391
H	-1.78874	-4.19933	-2.08792
H	-1.66620	-3.32375	-3.62433
H	-0.87705	-2.66538	-2.16321
C	-3.79523	-3.21730	0.59597
C	-3.74471	-2.80671	2.06845
H	-2.70373	-2.67889	2.40008
H	-4.26821	-1.86027	2.25273
H	-4.22128	-3.58091	2.69148
C	-2.98360	-4.49829	0.38231
H	-1.90659	-4.31475	0.52667
H	-3.29411	-5.25389	1.12155
H	-3.13209	-4.93126	-0.61608
C	-7.47940	-1.98614	-1.00071
H	-7.47931	-1.61175	-2.03601
H	-6.94555	-2.94922	-0.98383
H	-8.52417	-2.17552	-0.70381
C	-7.66021	0.89347	0.08724
H	-7.30608	1.61334	0.84187
H	-7.56776	1.36115	-0.90508
H	-8.72894	0.70405	0.28109
C	-6.87358	-1.40954	1.93694
H	-6.34898	-0.79532	2.68313
H	-7.94721	-1.41062	2.19128
H	-6.50687	-2.44264	2.01946
C	-3.81597	1.16793	0.35674
C	-4.08799	1.10338	1.85803
H	-5.15774	1.22966	2.08554
H	-3.72960	0.15753	2.28725
H	-3.53348	1.92042	2.34742
C	-4.25004	2.52452	-0.20332
H	-5.32257	2.70506	-0.03268
H	-3.67011	3.31518	0.30015
H	-4.05199	2.58838	-1.28154
Ti	-1.07340	-0.22381	0.21740
Cl	-0.60309	-0.94133	2.41006
N	0.39949	1.44607	0.20390
N	4.42602	-0.68554	-0.40793
O	0.12778	-1.00068	-0.96654
O	-2.45151	1.00041	0.13200
P	-4.66511	-0.21165	-0.70045
P	-3.14610	-1.80465	-0.45312
Si	-6.70249	-0.73428	0.18169
H	-4.84090	-3.40471	0.29697
H	-2.94127	-1.42593	-2.75658

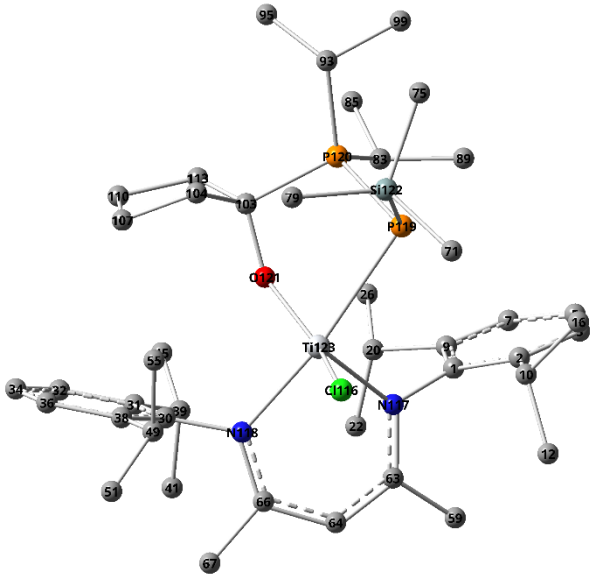

Figure S37. Optimized structure of **3a.**

Below are presented xyz coordinates for optimized geometry for **3a**.

C	1.27221	2.71848	-0.09896
C	2.38855	2.87397	-0.95119
C	3.51463	3.52574	-0.43963
H	4.38318	3.67675	-1.08139
C	3.55120	3.99024	0.86986
H	4.43531	4.51168	1.24136
C	2.47665	3.75008	1.71692
H	2.53755	4.07502	2.75637
C	1.32919	3.09431	1.26044
C	2.39342	2.35711	-2.38761
H	1.72446	1.48658	-2.42137
C	1.85181	3.36417	-3.41247
H	2.36446	4.33739	-3.33073
H	0.77169	3.52548	-3.30428
H	2.01730	2.97789	-4.42995
C	3.78094	1.87608	-2.82466
H	4.21009	1.17579	-2.09220
H	3.69822	1.35467	-3.78982
H	4.48514	2.71178	-2.96912
C	0.18266	2.79104	2.22303
H	-0.23802	1.81652	1.92340
C	-0.94852	3.82657	2.15512
H	-1.51284	3.76659	1.21556
H	-1.66418	3.65909	2.97461
H	-0.54691	4.84707	2.26624
C	0.64438	2.66393	3.68032
H	-0.15497	2.20986	4.28524
H	1.54399	2.04051	3.78400
H	0.86791	3.64711	4.12482
C	-3.38268	-0.23951	-0.14302
C	-3.76376	-0.04058	1.20324
C	-4.69214	-0.91322	1.77311
H	-5.00227	-0.76682	2.80945
C	-5.24008	-1.96150	1.04046
H	-5.96295	-2.63642	1.50246

C	-4.86541	-2.13789	-0.28430
H	-5.29869	-2.95914	-0.85886
C	-3.93960	-1.28774	-0.89998
C	-3.24855	1.15400	1.99133
H	-2.31598	1.47536	1.51015
C	-4.24901	2.31575	1.90840
H	-4.39130	2.65791	0.87379
H	-5.23208	2.01228	2.30450
H	-3.89701	3.17690	2.49715
C	-2.93144	0.83318	3.45200
H	-2.47868	1.71078	3.93889
H	-3.83309	0.57652	4.03101
H	-2.22339	-0.00210	3.52938
C	-3.55330	-1.53811	-2.34748
H	-2.93227	-0.69780	-2.68371
C	-4.77111	-1.62794	-3.27363
H	-4.44392	-1.70046	-4.32228
H	-5.38652	-2.51649	-3.05892
H	-5.42043	-0.74439	-3.17796
C	-2.69248	-2.80082	-2.45371
H	-2.33776	-2.94750	-3.48538
H	-1.80768	-2.72051	-1.80695
H	-3.25591	-3.69766	-2.14619
C	-0.37258	4.60431	-1.21117
H	-0.56067	5.07671	-0.23543
H	0.69121	4.74185	-1.42671
H	-0.96616	5.13764	-1.96433
C	-0.79098	3.14837	-1.14949
C	-2.08867	2.88127	-1.59672
H	-2.59916	3.70729	-2.08848
C	-2.88443	1.75364	-1.30870
C	-4.33398	1.84054	-1.73133
H	-4.62715	2.87876	-1.92903
H	-4.46007	1.26586	-2.66267
H	-5.01456	1.40714	-0.98805
C	2.88912	-1.60857	-3.80608
H	3.83318	-1.04491	-3.75105
H	2.98080	-2.35488	-4.61298
H	2.07436	-0.91637	-4.06152
C	4.13989	-3.49796	-1.82080
H	5.00157	-2.83731	-1.63848
H	4.05227	-4.19805	-0.97641
H	4.36235	-4.09807	-2.71984
C	1.15887	-3.73952	-2.40013
H	0.99919	-4.36017	-1.50481
H	0.22023	-3.22190	-2.64667
H	1.40925	-4.41477	-3.23566
C	2.49731	-0.24344	2.43825
H	1.61363	0.41222	2.36562
C	2.66459	-0.69043	3.89387
H	1.80511	-1.24795	4.28414
H	3.56918	-1.30388	4.02302
H	2.79118	0.20202	4.52656

C	3.71907	0.55822	1.98365
H	3.58591	0.98040	0.97984
H	3.87225	1.39346	2.68399
H	4.63226	-0.05605	1.98496
C	2.95730	-3.16334	1.56086
H	2.70160	-3.75974	0.66931
C	2.55682	-3.97634	2.79589
H	1.50401	-4.28808	2.77359
H	3.16864	-4.89171	2.82794
H	2.73481	-3.42916	3.73165
C	4.46539	-2.89055	1.53947
H	4.75605	-2.26259	0.68658
H	4.79008	-2.39089	2.46476
H	5.01205	-3.84324	1.46505
C	0.14816	-1.82315	1.49277
C	-0.37527	-3.08794	0.79430
H	-0.35046	-2.97679	-0.29702
H	0.24693	-3.96116	1.05483
C	-1.78410	-3.23897	1.37113
H	-2.46482	-2.56927	0.83434
H	-2.17336	-4.26077	1.26192
C	-1.66589	-2.79268	2.84291
H	-1.63871	-3.65651	3.52436
H	-2.53247	-2.18348	3.13256
C	-0.34188	-1.99743	2.94344
H	0.38766	-2.56853	3.53222
H	-0.44867	-1.01176	3.41626
Cl	-0.35551	-0.20117	-3.03699
N	0.03164	2.22148	-0.62660
N	-2.42173	0.66978	-0.69759
P	2.24818	-0.77606	-0.72589
P	2.00920	-1.59101	1.24442
O	-0.40537	-0.67355	0.92709
Si	2.56448	-2.49794	-2.17366
Ti	-0.33665	0.18958	-0.74078

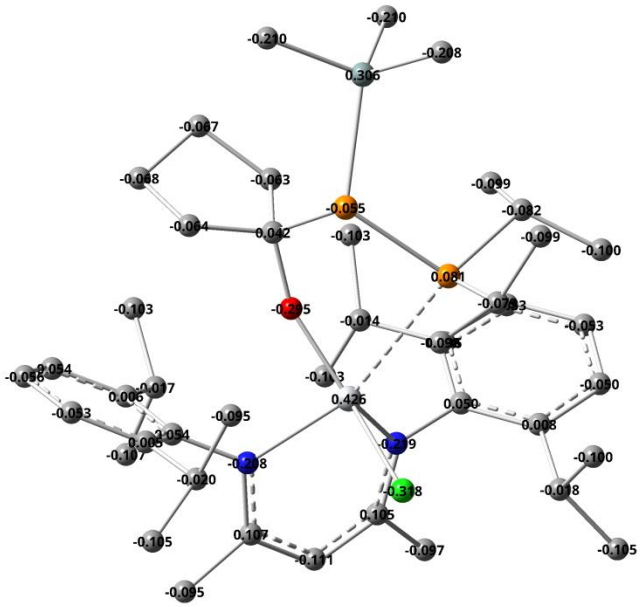

Figure S38. Optimized structure of **3b.**

Below are presented xyz coordinates for optimized geometry for **3b**.

C	-2.77648	-1.82649	-0.44592
C	-2.62729	-2.72688	-1.51423
C	-2.81674	-4.09057	-1.26654
H	-2.70087	-4.80458	-2.08455
C	-3.14773	-4.55290	0.00068
H	-3.29849	-5.61985	0.17445
C	-3.27970	-3.64887	1.05079
H	-3.53292	-4.02185	2.04487
C	-3.08502	-2.28064	0.85573
C	-2.22586	-2.25521	-2.90071
H	-2.32557	-1.16204	-2.92781
C	-0.75098	-2.58177	-3.16637
H	-0.42979	-2.17169	-4.13624
H	-0.09487	-2.15742	-2.39019
H	-0.58233	-3.67165	-3.17624
C	-3.12417	-2.82389	-4.00340
H	-2.87396	-2.36126	-4.97038
H	-3.00021	-3.91276	-4.11849
H	-4.18792	-2.62867	-3.79659
C	-3.23612	-1.30077	2.01342
H	-2.67178	-0.39803	1.74059
C	-2.66540	-1.82864	3.33241
H	-2.72373	-1.04854	4.10667
H	-3.22675	-2.69669	3.71286
H	-1.61238	-2.12292	3.23039
C	-4.70082	-0.88712	2.21315
H	-5.11180	-0.38698	1.32602
H	-5.32911	-1.76639	2.43195
H	-4.79011	-0.18573	3.05782
C	-0.55537	3.01278	0.79067
C	-0.27901	2.79680	2.15924
C	0.54695	3.70515	2.82485
H	0.76471	3.56111	3.88352

C	1.11214	4.78554	2.15617
H	1.76115	5.48129	2.69087
C	0.85021	4.97176	0.80532
H	1.30205	5.81922	0.28556
C	0.01303	4.10294	0.09678
C	-0.89741	1.61935	2.90104
H	-0.95081	0.78096	2.18860
C	-0.06534	1.14596	4.09490
H	-0.47531	0.20006	4.48094
H	0.98445	0.97076	3.81668
H	-0.08533	1.86952	4.92555
C	-2.32938	1.94459	3.34934
H	-2.73637	1.12731	3.96387
H	-2.34531	2.86423	3.95663
H	-3.00727	2.08193	2.49558
C	-0.26311	4.37713	-1.37752
H	-1.06501	3.70251	-1.70675
C	0.95810	4.05863	-2.24608
H	0.71984	4.21148	-3.30971
H	1.81255	4.70553	-1.98698
H	1.25851	3.01036	-2.12279
C	-0.71551	5.82280	-1.62465
H	-1.06023	5.93810	-2.66360
H	-1.53579	6.12360	-0.95588
H	0.10880	6.53800	-1.47295
C	-4.93970	-0.33187	-1.36844
H	-5.78160	0.37085	-1.35850
H	-4.77409	-0.66520	-2.40560
H	-5.20391	-1.22437	-0.78625
C	-3.67248	0.32005	-0.86718
C	-3.70157	1.71130	-0.65855
H	-4.65320	2.20424	-0.84933
C	-2.71016	2.50018	-0.06537
C	-3.14507	3.88351	0.36531
H	-4.23449	3.92330	0.48458
H	-2.66913	4.18564	1.30684
H	-2.85874	4.62275	-0.39625
C	4.73179	-1.70455	2.37016
H	3.92608	-1.89468	3.09353
H	5.63553	-2.22547	2.72947
H	4.94812	-0.62596	2.36442
C	5.84792	-1.94698	-0.44282
H	5.73939	-2.36100	-1.45680
H	6.03439	-0.86606	-0.52484
H	6.73718	-2.40880	0.01797
C	4.20207	-4.23655	0.68990
H	3.33925	-4.58358	1.27692
H	4.10022	-4.64006	-0.32970
H	5.11264	-4.66534	1.14037
C	3.01491	0.59267	-2.64296
H	2.73014	1.61888	-2.93443
C	4.53372	0.45537	-2.74667
H	5.08765	1.13099	-2.07952

H	4.84321	-0.57614	-2.52608
H	4.85170	0.67820	-3.77817
C	2.34059	-0.37404	-3.61903
H	1.24791	-0.29469	-3.58441
H	2.66440	-0.13804	-4.64562
H	2.62277	-1.41534	-3.40166
C	3.50755	1.42058	0.15643
H	4.47565	0.89826	0.07641
C	3.05522	1.41745	1.61252
H	2.98598	0.40262	2.02042
H	3.76806	1.98303	2.23461
H	2.07178	1.89707	1.71280
C	3.67136	2.86125	-0.33143
H	3.94690	2.93447	-1.39305
H	2.73894	3.42169	-0.17875
H	4.45913	3.36144	0.25506
Cl	-0.79208	1.08405	-2.94569
N	-2.59482	-0.41735	-0.62829
N	-1.44144	2.10136	0.12552
O	-0.02505	-1.01448	0.25721
P	2.45435	-1.69524	-0.46306
P	2.28951	0.45687	-0.90574
Si	4.35126	-2.35080	0.63492
Ti	-0.65631	0.38248	-0.73692
C	0.92914	-1.92696	0.70068
C	1.11709	-1.75117	2.22790
C	0.46646	-3.40760	0.53284
C	1.18959	-3.15306	2.82949
H	0.20411	-1.24718	2.57716
H	1.96018	-1.10885	2.50221
C	0.24131	-3.96740	1.94229
H	1.24637	-3.98790	0.01491
H	-0.43260	-3.44554	-0.09488
H	2.21469	-3.55388	2.76774
H	0.90668	-3.16650	3.89317
H	0.42145	-5.05099	2.00025
H	-0.80038	-3.79680	2.24938

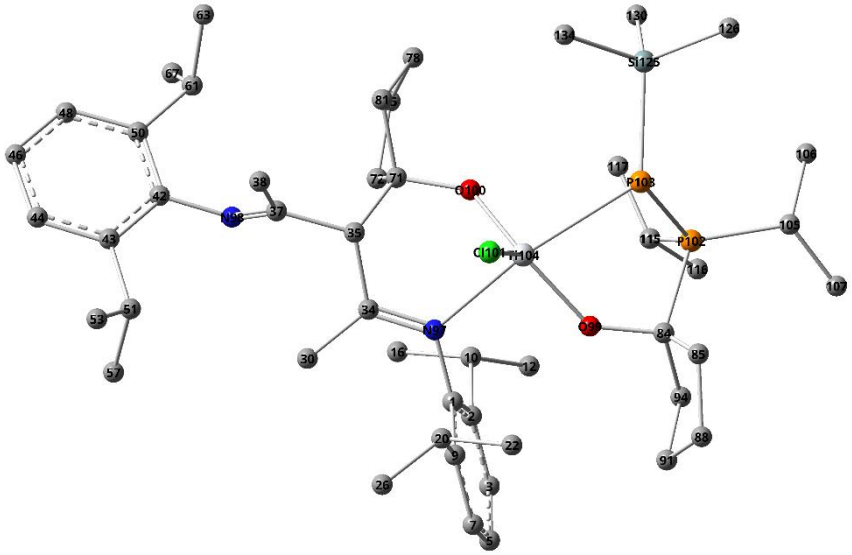

Figure S39. Optimized structure of **3c**.

Below are presented xyz coordinates for optimized geometry for **3c**.

C	0.20041	2.72382	0.57136
C	0.61000	2.77056	1.91725
C	1.09066	3.98325	2.41485
H	1.40481	4.05121	3.45753
C	1.17756	5.11132	1.60441
H	1.55395	6.05059	2.01350
C	0.80648	5.02864	0.26879
H	0.90513	5.90653	-0.37318
C	0.32340	3.83499	-0.27675
C	0.50843	1.54719	2.81610
H	0.58317	0.66099	2.16492
C	1.63316	1.45695	3.85139
H	1.61727	0.46767	4.33500
H	2.62372	1.60000	3.39751
H	1.51885	2.20801	4.64896
C	-0.84719	1.49604	3.53500
H	-1.68647	1.41842	2.83243
H	-0.89798	0.62626	4.20901
H	-0.99379	2.40593	4.13894
C	0.00904	3.74951	-1.76062
H	-0.41158	2.75721	-1.97005
C	1.30610	3.84598	-2.57290
H	2.01095	3.06383	-2.25529
H	1.10305	3.69923	-3.64425
H	1.79005	4.82830	-2.43884
C	-1.01864	4.79604	-2.20147
H	-1.95104	4.71300	-1.62110
H	-0.63785	5.82276	-2.07687
H	-1.26430	4.66094	-3.26597
C	-2.58411	2.21105	0.52599
H	-3.33226	1.70106	1.14436
H	-2.13345	3.05513	1.05800
H	-3.11867	2.60352	-0.35503
C	-1.55530	1.23423	0.04308
C	-1.98015	-0.09982	-0.55593

H	-1.53031	-0.10495	-1.56244
C	-3.47326	-0.32057	-0.75287
C	-3.87783	-0.64712	-2.16693
H	-3.24222	-1.45352	-2.56227
H	-4.93385	-0.93325	-2.24411
H	-3.69280	0.23218	-2.80633
C	-5.65505	-0.49318	0.12234
C	-6.52180	0.48889	-0.40350
C	-7.89465	0.22892	-0.40572
H	-8.57984	0.98144	-0.80088
C	-8.40858	-0.96796	0.08041
H	-9.48402	-1.15177	0.06123
C	-7.54083	-1.92604	0.59135
H	-7.94245	-2.86846	0.97092
C	-6.16301	-1.70572	0.63085
C	-6.00232	1.82762	-0.90668
H	-4.92692	1.72005	-1.09692
C	-6.63987	2.26259	-2.22947
H	-6.54231	1.47901	-2.99616
H	-7.71092	2.49230	-2.11601
H	-6.15044	3.17396	-2.60637
C	-6.16779	2.90423	0.17340
H	-5.67685	2.60332	1.11104
H	-5.73053	3.86144	-0.15368
H	-7.23430	3.07364	0.39333
C	-5.23251	-2.76962	1.18942
H	-4.22601	-2.33520	1.21617
C	-5.18206	-3.99797	0.27360
H	-4.43688	-4.72456	0.63567
H	-6.15930	-4.50580	0.23277
H	-4.91274	-3.71682	-0.75665
C	-5.59150	-3.15769	2.62686
H	-4.85650	-3.87559	3.02514
H	-5.59973	-2.27499	3.28374
H	-6.58312	-3.63427	2.68805
C	-1.28704	-1.31200	0.16966
C	-1.60307	-1.46083	1.67176
H	-0.87794	-0.87592	2.24834
H	-2.60546	-1.06752	1.89270
C	-1.50401	-2.97750	1.96952
H	-2.45694	-3.35022	2.37715
H	-0.73204	-3.20183	2.71928
C	-1.19609	-3.65795	0.61884
H	-0.11024	-3.77369	0.48816
H	-1.65512	-4.65278	0.52578
C	-1.71633	-2.66600	-0.41911
H	-2.81333	-2.73329	-0.47703
H	-1.30405	-2.80652	-1.42867
C	3.97419	1.10710	-0.13082
C	4.62198	1.60994	-1.44417
H	5.57544	1.09490	-1.64140
H	3.95370	1.37288	-2.28194
C	4.84644	3.12861	-1.23778

H	4.36439	3.72633	-2.02356
H	5.92305	3.35930	-1.27345
C	4.27843	3.44591	0.15554
H	4.78257	4.29008	0.64732
H	3.20713	3.68175	0.08785
C	4.43857	2.13004	0.91984
H	3.82191	2.08474	1.82611
H	5.49360	1.97072	1.19475
N	-0.29164	1.48786	0.03261
N	-4.26361	-0.25070	0.24688
O	2.58455	1.13885	-0.19542
O	0.10262	-1.20692	0.01007
Cl	0.50466	0.33736	-3.06133
P	4.31365	-0.72184	0.21829
P	3.22013	-1.49815	-1.45861
Ti	1.19305	0.02075	-0.83242
C	6.10955	-1.21488	0.14244
C	6.29623	-2.64722	0.65456
C	7.11448	-0.23967	0.75884
H	6.26850	-1.22681	-0.94863
H	5.58978	-3.34531	0.18301
H	7.31416	-2.99520	0.42012
H	6.16552	-2.71532	1.74487
H	7.05603	0.75355	0.29203
H	6.97737	-0.12204	1.84275
H	8.13397	-0.62260	0.59337
C	3.58621	-0.91483	1.93376
C	4.55381	-0.59294	3.07459
C	2.85801	-2.23607	2.15273
H	2.82050	-0.12293	1.89561
H	5.03769	0.38604	2.95638
H	3.99449	-0.56968	4.02280
H	5.33804	-1.35741	3.17902
H	2.10572	-2.40243	1.36943
H	3.55145	-3.08986	2.17431
H	2.33644	-2.20409	3.12299
Si	3.04835	-3.74729	-1.56455
C	4.54182	-4.41467	-2.51780
H	5.48240	-4.28150	-1.95974
H	4.41880	-5.49189	-2.72066
H	4.64630	-3.88937	-3.47972
C	2.86090	-4.81469	-0.01356
H	2.73375	-5.85867	-0.34761
H	3.74543	-4.78164	0.64039
H	1.97762	-4.53917	0.57983
C	1.49340	-3.94954	-2.61296
H	0.61038	-3.67264	-2.01710
H	1.51848	-3.29420	-3.49756
H	1.38075	-4.99322	-2.94924

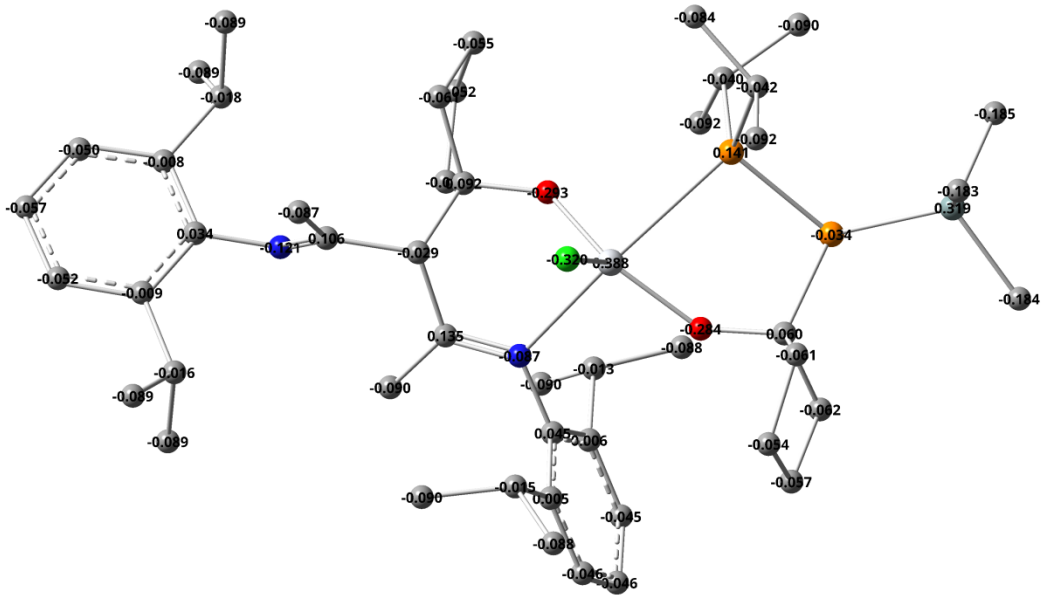

Figure S40. Optimized structure of **3d**.

Below are presented xyz coordinates for optimized geometry for **3d**.

C	-0.00248	2.58912	0.87537
C	0.41943	2.50944	2.21204
C	0.88923	3.67787	2.81772
H	1.21599	3.64602	3.85945
C	0.94423	4.87674	2.11765
H	1.30902	5.78081	2.60827
C	0.55836	4.91894	0.78038
H	0.63560	5.85952	0.23397
C	0.09434	3.77593	0.12542
C	0.35813	1.20977	3.00129
H	0.02117	0.41889	2.31747
C	1.73204	0.77899	3.52402
H	1.64374	-0.16678	4.08118
H	2.43279	0.62137	2.69298
H	2.16275	1.52935	4.20677
C	-0.66136	1.29928	4.14398
H	-1.65729	1.58929	3.77890
H	-0.75562	0.32724	4.65351
H	-0.35049	2.04263	4.89569
C	-0.29424	3.80000	-1.34797
H	-0.03717	2.81296	-1.76594
C	0.46708	4.85567	-2.15483
H	1.55095	4.80300	-1.97943
H	0.29030	4.69788	-3.22917
H	0.13156	5.87801	-1.91539
C	-1.80442	4.00617	-1.53774
H	-2.39513	3.19286	-1.09590
H	-2.13183	4.95077	-1.07299
H	-2.05081	4.04917	-2.61024
C	-2.73232	1.80586	1.12762
H	-3.14057	1.11925	1.88304
H	-2.29769	2.68937	1.60641
H	-3.58854	2.10559	0.51133

C	-1.72498	1.06809	0.30160
C	-2.10626	-0.19631	-0.44839
H	-1.55970	-0.14307	-1.40214
C	-3.57336	-0.37585	-0.79995
C	-3.84138	-0.59052	-2.26698
H	-3.18491	-1.38454	-2.65417
H	-4.88988	-0.84294	-2.46679
H	-3.57782	0.32658	-2.81992
C	-5.83131	-0.54192	-0.16167
C	-6.61099	0.51598	-0.67607
C	-7.98256	0.30654	-0.84130
H	-8.60356	1.11582	-1.22993
C	-8.57471	-0.91158	-0.52687
H	-9.64657	-1.05478	-0.67251
C	-7.79049	-1.94465	-0.02644
H	-8.25374	-2.90406	0.21386
C	-6.41895	-1.77838	0.17236
C	-6.00612	1.87672	-0.99212
H	-4.91916	1.74955	-1.09451
C	-6.49859	2.46044	-2.31960
H	-6.34842	1.74989	-3.14649
H	-7.56874	2.71833	-2.28596
H	-5.94835	3.38442	-2.55562
C	-6.24743	2.84836	0.17041
H	-5.86542	2.43376	1.11589
H	-5.74949	3.81437	-0.01139
H	-7.32495	3.03711	0.30182
C	-5.57034	-2.92420	0.69899
H	-4.58026	-2.51018	0.92970
C	-5.38169	-4.00219	-0.37541
H	-4.68721	-4.78399	-0.02789
H	-6.34058	-4.48440	-0.62537
H	-4.97525	-3.57200	-1.30421
C	-6.12356	-3.52046	1.99620
H	-5.43679	-4.28837	2.38656
H	-6.24568	-2.74533	2.76743
H	-7.10215	-4.00314	1.84295
C	-1.48178	-1.44523	0.27557
C	-1.97002	-1.67945	1.72105
H	-1.34325	-1.11022	2.41986
H	-3.00315	-1.32127	1.83138
C	-1.88030	-3.20796	1.95053
H	-2.86731	-3.60893	2.22953
H	-1.19147	-3.46395	2.76784
C	-1.41410	-3.81304	0.60947
H	-0.32015	-3.92456	0.60477
H	-1.85397	-4.80155	0.41302
C	-1.81744	-2.76843	-0.43062
H	-2.89943	-2.83650	-0.62294
H	-1.28302	-2.85297	-1.38795
C	2.68781	-3.26190	0.79535
H	1.87638	-3.82459	0.30305
C	2.14433	-2.72355	2.12073

H	1.24139	-2.11864	1.95913
H	1.88127	-3.56738	2.77971
H	2.89925	-2.11200	2.63883
C	3.88273	-4.18714	1.01713
H	4.27340	-4.60911	0.07856
H	4.70203	-3.64680	1.51761
H	3.59576	-5.03006	1.66661
C	3.62676	-2.72573	-1.96614
H	4.60313	-3.18833	-1.74087
C	3.78794	-1.70385	-3.09146
H	4.45506	-0.88116	-2.80716
H	4.21611	-2.19022	-3.98285
H	2.81467	-1.26813	-3.36202
C	2.63364	-3.81711	-2.38115
H	2.58165	-4.64480	-1.65926
H	1.62229	-3.39489	-2.50139
H	2.93540	-4.24109	-3.35195
C	7.22809	-2.65171	0.46120
H	6.67928	-3.48938	0.00323
H	8.29983	-2.79370	0.24472
H	7.08724	-2.70421	1.55167
C	7.68738	0.39989	0.53536
H	7.46037	1.37151	0.06893
H	7.51222	0.48753	1.61856
H	8.75872	0.19478	0.37462
C	7.00211	-0.99870	-2.08971
H	6.64154	-0.09163	-2.59621
H	8.09584	-1.05031	-2.22578
H	6.56067	-1.87359	-2.58825
C	3.89421	1.05374	0.06706
C	4.28625	1.60083	-1.31182
H	5.37810	1.52423	-1.44558
H	3.79113	1.05114	-2.12406
C	3.85012	3.06905	-1.22929
H	2.78870	3.13618	-1.50487
H	4.41443	3.70951	-1.92243
C	4.03789	3.47215	0.25645
H	4.83280	4.22230	0.38251
H	3.11184	3.90823	0.65366
C	4.38138	2.16846	1.00706
H	3.89960	2.09436	1.99039
H	5.46846	2.07194	1.15669
N	-0.48512	1.41235	0.21062
N	-4.45564	-0.35829	0.12103
O	2.49994	0.96762	0.14419
O	-0.08963	-1.29948	0.26922
Cl	0.67191	0.24535	-2.75674
Si	6.66056	-0.98922	-0.23232
P	4.55873	-0.66395	0.59588
P	3.01525	-1.87057	-0.41652
Ti	1.07328	-0.03475	-0.45425

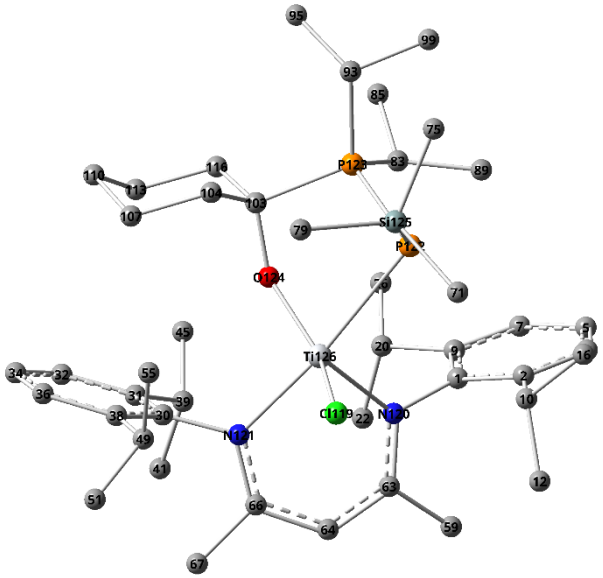

Figure S41. Optimized structure of **4a**.

Below are presented xyz coordinates for optimized geometry for **4a**.

C	-1.44475	2.70426	-0.11177
C	-2.61500	2.85331	0.66689
C	-3.73494	3.42536	0.05572
H	-4.64730	3.57071	0.63440
C	-3.71348	3.81879	-1.27760
H	-4.59549	4.27979	-1.72603
C	-2.58175	3.58437	-2.04745
H	-2.59429	3.85089	-3.10514
C	-1.43695	3.00681	-1.49006
C	-2.68383	2.40701	2.12591
H	-2.00801	1.54728	2.22919
C	-2.20043	3.46117	3.13199
H	-2.71574	4.42562	2.98673
H	-1.11709	3.62573	3.07102
H	-2.41302	3.11526	4.15523
C	-4.08561	1.92952	2.51742
H	-4.46909	1.18638	1.80183
H	-4.04640	1.45998	3.51104
H	-4.80593	2.76141	2.58266
C	-0.22102	2.71482	-2.36681
H	0.25366	1.80369	-1.96564
C	0.82369	3.83986	-2.32716
H	1.33457	3.89921	-1.35723
H	1.59672	3.67070	-3.09236
H	0.35196	4.81347	-2.53848
C	-0.59721	2.43762	-3.82786
H	0.26268	2.00285	-4.35815
H	-1.44173	1.73881	-3.91709
H	-0.87330	3.36197	-4.36010
C	3.34467	0.04249	0.31213
C	3.79681	0.21648	-1.01437
C	4.78722	-0.63900	-1.50105
H	5.15258	-0.51099	-2.52265
C	5.32435	-1.64617	-0.70591

H	6.09344	-2.31054	-1.10427
C	4.88726	-1.78798	0.60451
H	5.31967	-2.56993	1.23235
C	3.90395	-0.94898	1.14026
C	3.29512	1.36673	-1.87742
H	2.43109	1.80609	-1.36398
C	4.37114	2.45520	-1.99058
H	4.68054	2.82026	-1.00027
H	5.26917	2.07483	-2.50449
H	3.99166	3.31691	-2.56197
C	2.81969	0.92754	-3.26451
H	2.58137	1.81008	-3.87799
H	3.58274	0.34951	-3.80929
H	1.91178	0.31493	-3.18598
C	3.47646	-1.13293	2.58729
H	2.81138	-0.30107	2.85305
C	4.67056	-1.10803	3.54871
H	4.31700	-1.12841	4.59113
H	5.33163	-1.97815	3.40711
H	5.28113	-0.20252	3.41182
C	2.66723	-2.42186	2.76039
H	2.31969	-2.52531	3.79976
H	1.77785	-2.41447	2.11485
H	3.26703	-3.31088	2.50294
C	0.01715	4.73852	0.96763
H	0.15305	5.14556	-0.04521
H	-1.04937	4.82389	1.19643
H	0.58734	5.36546	1.66428
C	0.52732	3.31136	1.01096
C	1.81587	3.15319	1.52803
H	2.25560	4.03614	1.98760
C	2.68793	2.06227	1.33698
C	4.11670	2.26511	1.78799
H	4.33055	3.32617	1.96374
H	4.26670	1.72224	2.73483
H	4.84152	1.86328	1.06893
C	-3.06319	-1.35508	3.81028
H	-4.03608	-0.86697	3.64706
H	-3.15283	-2.01772	4.68731
H	-2.30947	-0.58579	4.03137
C	-4.07707	-3.50675	1.95766
H	-4.96634	-2.92173	1.67658
H	-3.90089	-4.26764	1.18239
H	-4.31048	-4.04288	2.89352
C	-1.14337	-3.51512	2.76459
H	-0.91927	-4.26114	1.98646
H	-0.23694	-2.92695	2.96927
H	-1.41095	-4.06173	3.68466
C	-2.38181	-0.50429	-2.49027
H	-1.51153	0.17336	-2.46217
C	-2.52378	-1.07992	-3.90370
H	-1.67459	-1.69650	-4.22047
H	-3.44181	-1.67955	-3.99562

H	-2.61211	-0.24746	-4.61955
C	-3.62584	0.31214	-2.13087
H	-3.52484	0.81808	-1.16328
H	-3.77695	1.08254	-2.90274
H	-4.52797	-0.31761	-2.10008
C	-2.80558	-3.35303	-1.40226
H	-2.55945	-3.87745	-0.46453
C	-2.35990	-4.24582	-2.56461
H	-1.30239	-4.53335	-2.49408
H	-2.95353	-5.17340	-2.54367
H	-2.52405	-3.77215	-3.54189
C	-4.31970	-3.11489	-1.43279
H	-4.64138	-2.42515	-0.64101
H	-4.63640	-2.70093	-2.40216
H	-4.84664	-4.07096	-1.29055
C	-0.00088	-1.93795	-1.31640
C	0.41294	-3.13852	-0.44757
H	0.15020	-2.91142	0.59481
H	-0.16901	-4.02990	-0.74018
C	1.90005	-3.46262	-0.56752
H	2.48670	-2.61651	-0.18472
H	2.13540	-4.32972	0.06923
C	2.29647	-3.71467	-2.01830
H	3.37338	-3.93339	-2.08496
H	1.76213	-4.60003	-2.41201
C	1.96374	-2.48206	-2.85234
H	2.23601	-2.62979	-3.90956
H	2.56340	-1.64364	-2.47552
C	0.48042	-2.11721	-2.76553
H	-0.10737	-2.91241	-3.25124
H	0.28961	-1.18483	-3.31772
Cl	0.18579	0.09527	3.08037
N	-0.21285	2.30437	0.51033
N	2.31201	0.91748	0.78141
P	-2.26264	-0.78886	0.71375
P	-1.90013	-1.73846	-1.17533
O	0.48681	-0.74156	-0.78921
Si	-2.58481	-2.38445	2.30232
Ti	0.26077	0.30243	0.76197

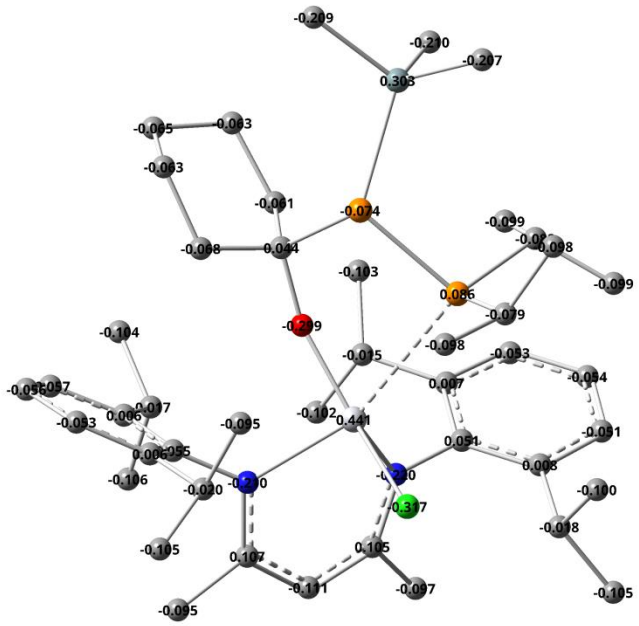

Figure S42. Optimized structure of **4b**.

Below are presented xyz coordinates for optimized geometry for **4b**.

C	2.63230	-2.09658	0.41441
C	2.48832	-2.89561	1.56145
C	2.51733	-4.28654	1.41386
H	2.39659	-4.91973	2.29521
C	2.70765	-4.87573	0.17184
H	2.74335	-5.96266	0.07762
C	2.84171	-4.07227	-0.95682
H	2.97246	-4.54404	-1.93186
C	2.78485	-2.68026	-0.86386
C	2.27499	-2.28897	2.93780
H	2.47721	-1.21212	2.86927
C	0.81234	-2.44721	3.36784
H	0.63534	-1.95621	4.33696
H	0.12703	-1.99488	2.63423
H	0.53936	-3.51160	3.46268
C	3.22207	-2.86841	3.99349
H	3.09962	-2.33079	4.94621
H	3.02230	-3.93418	4.18927
H	4.27513	-2.77859	3.68493
C	2.85658	-1.82304	-2.12127
H	2.28755	-0.90655	-1.90729
C	2.21839	-2.50313	-3.33764
H	2.07047	-1.76882	-4.14494
H	2.85924	-3.30221	-3.74388
H	1.24150	-2.94657	-3.09730
C	4.29547	-1.41232	-2.46619
H	4.72141	-0.73014	-1.71862
H	4.94617	-2.29931	-2.54004
H	4.32284	-0.89159	-3.43620
C	0.91081	2.95088	-0.93478
C	0.48937	2.72987	-2.26530
C	-0.23765	3.73400	-2.90885
H	-0.56162	3.59057	-3.94006

C	-0.58237	4.90770	-2.24706
H	-1.16046	5.67687	-2.76240
C	-0.19658	5.09230	-0.92608
H	-0.48009	6.01173	-0.40953
C	0.56352	4.13389	-0.24668
C	0.82025	1.42560	-2.98012
H	0.76023	0.62427	-2.22645
C	-0.17305	1.07205	-4.08980
H	0.00338	0.04020	-4.43011
H	-1.21501	1.14022	-3.74353
H	-0.06153	1.72800	-4.96826
C	2.24805	1.43277	-3.54264
H	2.43452	0.51354	-4.11939
H	2.39564	2.29084	-4.21839
H	3.00622	1.47928	-2.74902
C	0.99999	4.41591	1.18771
H	1.73495	3.65358	1.47876
C	-0.16755	4.29345	2.17234
H	0.18993	4.44055	3.20285
H	-0.94489	5.04769	1.96577
H	-0.62113	3.29545	2.12057
C	1.65486	5.79673	1.33511
H	2.10107	5.89794	2.33622
H	2.44604	5.96774	0.58967
H	0.91802	6.60811	1.22194
C	5.01902	-0.84634	0.99897
H	5.91753	-0.21770	0.98692
H	4.87743	-1.24316	2.01580
H	5.17622	-1.71166	0.34105
C	3.79384	-0.05758	0.59854
C	3.97661	1.30745	0.30983
H	4.99610	1.68026	0.38841
C	3.04248	2.18736	-0.24522
C	3.60537	3.47130	-0.81293
H	4.69215	3.39308	-0.93430
H	3.15270	3.70855	-1.78490
H	3.39313	4.31643	-0.14421
C	-5.02863	-0.63158	-2.05352
H	-4.23106	-0.77199	-2.79647
H	-5.95670	-1.06038	-2.46806
H	-5.18834	0.44875	-1.92157
C	-5.98546	-0.78303	0.81431
H	-5.94571	-1.29243	1.78891
H	-5.90181	0.29952	0.98184
H	-6.97754	-0.97760	0.37260
C	-5.11584	-3.31226	-0.51416
H	-4.57860	-3.84964	-1.30752
H	-4.91603	-3.81937	0.44272
H	-6.19548	-3.39815	-0.72311
C	-2.62862	1.00070	2.87539
H	-2.17577	1.97565	3.12910
C	-4.13422	1.07217	3.11983
H	-4.65015	1.81121	2.49047

H	-4.59678	0.09000	2.94792
H	-4.32360	1.34452	4.17087
C	-2.00212	-0.05357	3.78926
H	-0.91282	-0.09208	3.67582
H	-2.22290	0.19519	4.83991
H	-2.41571	-1.05203	3.57976
C	-3.21151	1.91943	0.11208
H	-4.23489	1.53106	0.23942
C	-2.83099	1.87255	-1.36336
H	-2.85236	0.85150	-1.76251
H	-3.52674	2.48377	-1.96120
H	-1.82188	2.27866	-1.50866
C	-3.16673	3.36492	0.60997
H	-3.36912	3.46460	1.68582
H	-2.18603	3.81232	0.40066
H	-3.92182	3.95955	0.07047
Cl	1.18812	1.14460	2.86819
N	2.61707	-0.66459	0.49783
N	1.72094	1.95029	-0.30164
O	-0.09628	-0.89526	-0.22367
P	-2.62768	-1.31797	0.60998
P	-2.07751	0.77725	1.08756
Si	-4.69691	-1.46902	-0.38737
Ti	0.79956	0.38893	0.70773
C	-1.11875	-1.77647	-0.55732
C	-1.34073	-1.67394	-2.07296
C	-0.67105	-3.19994	-0.18728
C	-2.15870	-2.80469	-2.69634
H	-0.32690	-1.68342	-2.50590
H	-1.76689	-0.69316	-2.32403
C	-1.58064	-4.28996	-0.74052
H	-0.56758	-3.28207	0.90321
H	0.33520	-3.32621	-0.61364
C	-1.67452	-4.18919	-2.26291
H	-2.12077	-2.70860	-3.79349
H	-3.21890	-2.69931	-2.42587
H	-1.18612	-5.27459	-0.44566
H	-2.58518	-4.21122	-0.29150
H	-0.67571	-4.38127	-2.69441
H	-2.34568	-4.96494	-2.66549

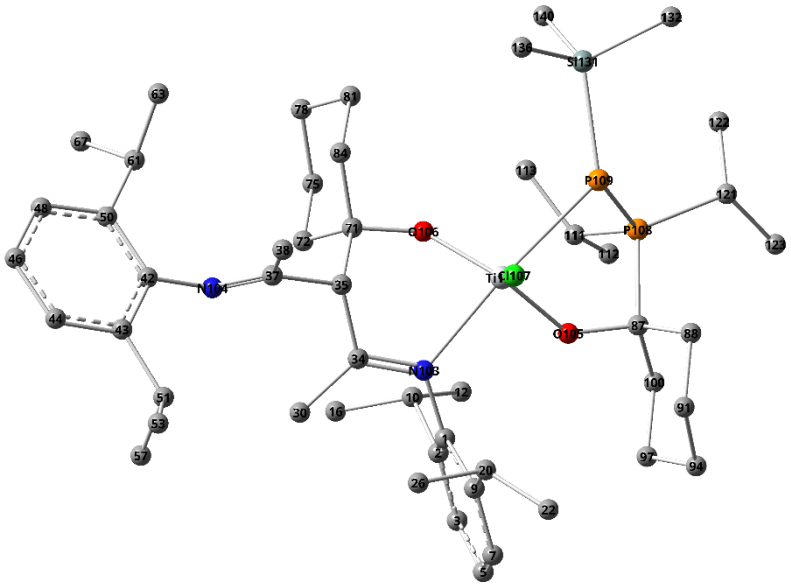

Figure S43. Optimized structure of **4c**.

Below are presented xyz coordinates for optimized geometry for **4c**.

C	0.16342	2.83004	0.59749
C	0.54395	2.89456	1.94959
C	0.97625	4.12582	2.45115
H	1.25874	4.20632	3.50268
C	1.06295	5.24570	1.63369
H	1.40303	6.19824	2.04385
C	0.74741	5.13977	0.28303
H	0.85434	6.01422	-0.35971
C	0.30137	3.93448	-0.26555
C	0.50752	1.67587	2.86104
H	0.39437	0.78584	2.22444
C	1.81554	1.50943	3.64101
H	1.83810	0.52886	4.14255
H	2.67943	1.57883	2.96820
H	1.93194	2.27972	4.41987
C	-0.67440	1.72441	3.83780
H	-1.63945	1.79671	3.31939
H	-0.69527	0.81786	4.46359
H	-0.59063	2.59579	4.50727
C	-0.02758	3.81612	-1.74726
H	0.21152	2.78635	-2.05389
C	0.79711	4.76105	-2.62541
H	1.87071	4.70150	-2.39586
H	0.66245	4.49221	-3.68362
H	0.48169	5.81129	-2.51239
C	-1.52214	4.03430	-2.02067
H	-2.14621	3.28458	-1.51683
H	-1.84515	5.03107	-1.67692
H	-1.72466	3.95939	-3.10020
C	-2.59402	2.15246	0.86121
H	-3.14886	1.55020	1.59320
H	-2.14520	3.03449	1.32897
H	-3.34071	2.48293	0.12618
C	-1.57820	1.29161	0.17638

C	-1.99317	-0.04228	-0.42164
H	-1.49600	-0.07683	-1.40296
C	-3.47694	-0.24340	-0.70405
C	-3.79461	-0.50696	-2.15343
H	-3.19424	-1.35648	-2.51389
H	-4.85922	-0.70971	-2.32057
H	-3.48679	0.36305	-2.75686
C	-5.70992	-0.43526	0.00840
C	-6.53665	0.59630	-0.48902
C	-7.90346	0.34447	-0.62509
H	-8.55748	1.13113	-1.00458
C	-8.45109	-0.88994	-0.29215
H	-9.52080	-1.06682	-0.41486
C	-7.62461	-1.89363	0.19698
H	-8.05287	-2.86507	0.45343
C	-6.25361	-1.68571	0.36315
C	-5.97442	1.97372	-0.80788
H	-4.91054	1.85096	-1.05670
C	-6.62763	2.64160	-2.02006
H	-6.60517	1.98236	-2.90105
H	-7.67684	2.91533	-1.82742
H	-6.09248	3.56993	-2.27234
C	-6.06110	2.87159	0.43373
H	-5.57131	2.39912	1.29809
H	-5.58161	3.84734	0.25313
H	-7.11433	3.05172	0.70264
C	-5.36674	-2.80755	0.87785
H	-4.38319	-2.36880	1.08943
C	-5.17259	-3.88562	-0.19570
H	-4.45456	-4.65056	0.14178
H	-6.12499	-4.38979	-0.42590
H	-4.79246	-3.45053	-1.13324
C	-5.87915	-3.41207	2.18799
H	-5.16334	-4.15784	2.56926
H	-6.00912	-2.63644	2.95747
H	-6.84620	-3.92301	2.05509
C	-1.33002	-1.23007	0.38157
C	-1.75258	-1.24857	1.85714
H	-1.44189	-0.30760	2.33098
H	-2.85056	-1.28143	1.91833
C	-1.13739	-2.43436	2.59920
H	-1.48555	-2.43928	3.64437
H	-0.04200	-2.31014	2.62089
C	-1.48147	-3.75839	1.91513
H	-2.57286	-3.92771	1.97591
H	-1.00234	-4.59901	2.44204
C	-1.05249	-3.74017	0.44728
H	0.04375	-3.64195	0.38870
H	-1.32194	-4.68546	-0.05015
C	-1.67931	-2.56383	-0.29783
H	-2.77146	-2.69366	-0.33081
H	-1.31594	-2.52493	-1.33773
C	3.98380	0.99326	-0.18874

C	4.46785	1.40401	-1.59105
H	5.56787	1.30820	-1.64185
H	4.03971	0.72590	-2.34211
C	4.05062	2.84550	-1.88492
H	2.95000	2.88312	-1.89498
H	4.39183	3.12889	-2.89260
C	4.58727	3.81729	-0.83486
H	4.21734	4.83637	-1.03229
H	5.69043	3.86176	-0.90616
C	4.18094	3.38076	0.57202
H	4.62306	4.04771	1.32903
H	3.08803	3.45150	0.67657
C	4.60154	1.93560	0.85780
H	4.26925	1.65284	1.86483
H	5.70026	1.85227	0.83863
N	-0.33181	1.59853	0.05201
N	-4.32924	-0.20907	0.24591
O	2.59637	1.06380	-0.09606
O	0.06406	-1.07575	0.30868
Cl	0.47936	0.33575	-2.96104
P	4.30977	-0.86982	0.12583
P	3.01645	-1.62016	-1.41240
Ti	1.13369	0.02969	-0.71459
C	3.74150	-1.09633	1.89499
C	4.81248	-0.86216	2.96366
C	2.99428	-2.40725	2.12257
H	2.99910	-0.28482	1.95673
H	5.35001	0.08630	2.83271
H	4.32888	-0.83182	3.95280
H	5.55213	-1.67610	2.98784
H	2.16815	-2.51491	1.40623
H	3.65929	-3.27972	2.03640
H	2.56813	-2.40959	3.13875
C	6.07290	-1.41759	-0.13445
C	6.26462	-2.86383	0.33542
C	7.16415	-0.49355	0.41013
H	6.12916	-1.40762	-1.23574
H	5.47744	-3.53027	-0.04302
H	7.22951	-3.24805	-0.03060
H	6.27347	-2.93808	1.43293
H	7.11554	0.50762	-0.03911
H	7.11609	-0.38608	1.50276
H	8.14986	-0.91838	0.16267
Si	2.87371	-3.85926	-1.61330
C	4.31920	-4.45749	-2.67976
H	4.34326	-3.90007	-3.62890
H	5.29211	-4.31703	-2.18314
H	4.20777	-5.53087	-2.90825
C	1.27774	-4.04026	-2.60551
H	0.40197	-3.88140	-1.95953
H	1.23536	-3.30062	-3.42030
H	1.20951	-5.04968	-3.04334
C	2.78988	-4.98951	-0.09796

H	2.62130	-6.01853	-0.45893
H	3.72735	-4.99114	0.47915
H	1.96520	-4.72775	0.57985

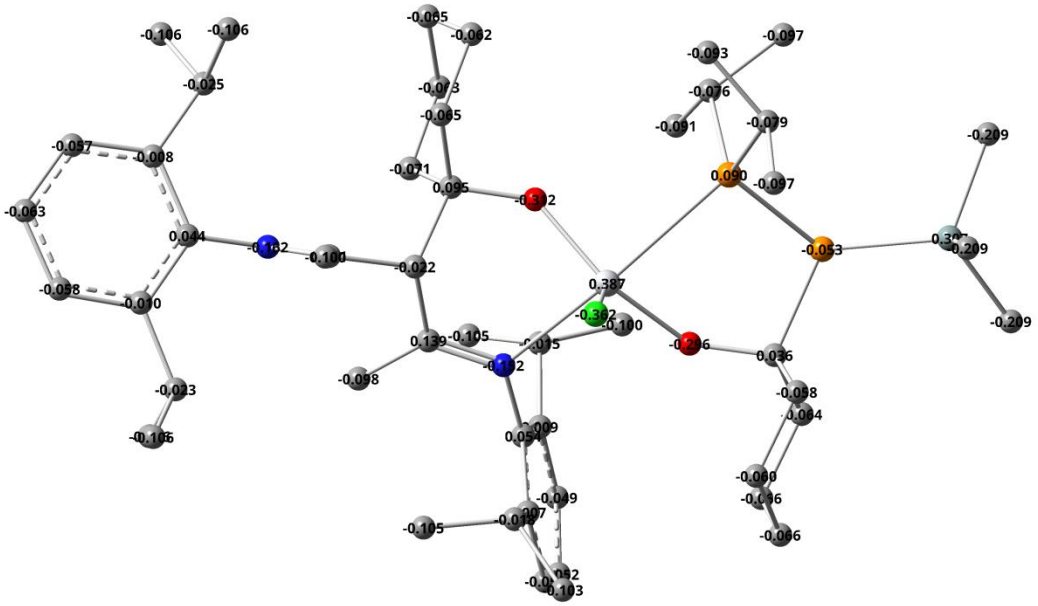

Figure S44. Optimized structure of **4d**.

Below are presented xyz coordinates for optimized geometry for **4d**.

C	-0.00254	2.62203	0.94988
C	0.39424	2.56786	2.29510
C	0.81605	3.75628	2.89785
H	1.11784	3.74620	3.94741
C	0.86330	4.94624	2.18216
H	1.19437	5.86476	2.66965
C	0.51834	4.96029	0.83363
H	0.59321	5.89402	0.27521
C	0.08952	3.79995	0.18441
C	0.37124	1.27138	3.09166
H	0.09448	0.45691	2.40694
C	1.75472	0.92690	3.65175
H	1.71507	-0.02605	4.20202
H	2.48173	0.82351	2.83448
H	2.11735	1.69974	4.34830
C	-0.68547	1.31146	4.20229
H	-1.68648	1.52922	3.80144
H	-0.73262	0.34236	4.72353
H	-0.44853	2.08523	4.95019
C	-0.26760	3.80096	-1.29761
H	-0.01041	2.80540	-1.69387
C	0.51991	4.83746	-2.10445
H	1.59825	4.78015	-1.90207
H	0.36797	4.66096	-3.17972
H	0.18488	5.86585	-1.89209
C	-1.77113	4.01496	-1.52736
H	-2.37764	3.20539	-1.10092
H	-2.10684	4.96218	-1.07407
H	-1.98798	4.05652	-2.60621
C	-2.74143	1.87521	1.14758
H	-3.23397	1.18734	1.84898
H	-2.29828	2.72251	1.68069
H	-3.53738	2.24168	0.48791

C	-1.72150	1.11306	0.35886
C	-2.10647	-0.14346	-0.39808
H	-1.52283	-0.10360	-1.32957
C	-3.56378	-0.26199	-0.81923
C	-3.77172	-0.37322	-2.30778
H	-3.14729	-1.18472	-2.71114
H	-4.82193	-0.54724	-2.57099
H	-3.42249	0.55396	-2.79184
C	-5.85292	-0.40508	-0.29644
C	-6.58341	0.69942	-0.78590
C	-7.94992	0.53496	-1.02693
H	-8.53291	1.38022	-1.39705
C	-8.58437	-0.68328	-0.81131
H	-9.65141	-0.79049	-1.01278
C	-7.84860	-1.76273	-0.33655
H	-8.34406	-2.72244	-0.17410
C	-6.48459	-1.64350	-0.06478
C	-5.93297	2.05969	-0.99321
H	-4.84797	1.90654	-1.07833
C	-6.36927	2.75211	-2.28757
H	-6.22372	2.09633	-3.15926
H	-7.42899	3.05087	-2.26170
H	-5.77839	3.66778	-2.44420
C	-6.17855	2.95473	0.22849
H	-5.82814	2.46778	1.15115
H	-5.65544	3.91902	0.12398
H	-7.25443	3.15958	0.34839
C	-5.69179	-2.84205	0.43032
H	-4.70614	-2.47158	0.74046
C	-5.46855	-3.85399	-0.70020
H	-4.81147	-4.67424	-0.36840
H	-6.42269	-4.29471	-1.03188
H	-5.00256	-3.37627	-1.57630
C	-6.32511	-3.50558	1.65624
H	-5.67030	-4.30548	2.03711
H	-6.47966	-2.77499	2.46420
H	-7.29952	-3.96308	1.42174
C	-1.53689	-1.41986	0.34123
C	-2.08460	-1.55872	1.76992
H	-1.73689	-0.70152	2.36728
H	-3.18309	-1.49726	1.74053
C	-1.63888	-2.86307	2.43174
H	-2.09883	-2.94539	3.42920
H	-0.54787	-2.83628	2.58164
C	-1.99541	-4.08046	1.57788
H	-3.09523	-4.16721	1.50047
H	-1.63950	-5.00380	2.06172
C	-1.40090	-3.95025	0.17557
H	-0.30095	-3.93513	0.24377
H	-1.67538	-4.81768	-0.44567
C	-1.87163	-2.66450	-0.49914
H	-2.96030	-2.72365	-0.65499
H	-1.39797	-2.54613	-1.48737

C	2.64704	-3.20013	1.07374
H	1.75900	-3.75669	0.73112
C	2.27375	-2.48270	2.37204
H	1.42101	-1.80618	2.21911
H	1.98858	-3.22385	3.13642
H	3.12176	-1.89956	2.76209
C	3.80720	-4.17161	1.28412
H	4.06447	-4.72735	0.36942
H	4.70730	-3.63286	1.62132
H	3.54980	-4.90975	2.06083
C	3.33811	-2.99812	-1.80632
H	4.31842	-3.47806	-1.64391
C	3.39622	-2.10597	-3.04608
H	4.09502	-1.26966	-2.91989
H	3.72714	-2.69269	-3.91837
H	2.40690	-1.67737	-3.26193
C	2.26629	-4.08000	-1.98488
H	2.28288	-4.83496	-1.18604
H	1.26080	-3.62821	-2.01321
H	2.42427	-4.60253	-2.94154
C	7.14650	-2.86894	0.03181
H	6.46223	-3.66998	-0.28928
H	8.14760	-3.10030	-0.36787
H	7.20069	-2.88636	1.13120
C	7.74149	0.16581	0.03560
H	7.50148	1.14366	-0.41097
H	7.68656	0.26446	1.13057
H	8.78099	-0.08070	-0.23735
C	6.69123	-1.19919	-2.48768
H	6.24508	-0.30534	-2.94749
H	7.76035	-1.22386	-2.75946
H	6.21382	-2.08930	-2.92199
C	3.92063	0.96329	0.03319
C	4.18014	1.42104	-1.41070
H	5.26951	1.44075	-1.59125
H	3.73321	0.70129	-2.11308
C	3.59363	2.81301	-1.65247
H	2.50005	2.74649	-1.54033
H	3.78919	3.12351	-2.69107
C	4.15376	3.83497	-0.66255
H	3.67787	4.81766	-0.81549
H	5.23415	3.97664	-0.85422
C	3.94578	3.37362	0.78013
H	4.39485	4.09060	1.48573
H	2.86801	3.33750	0.99760
C	4.53079	1.98008	1.01264
H	4.34665	1.64954	2.04553
H	5.62570	1.99859	0.87030
N	-0.47295	1.43316	0.29961
N	-4.48749	-0.27491	0.06077
O	2.53966	0.88511	0.25578
O	-0.14092	-1.29984	0.39382
Cl	0.68069	0.25486	-2.62777

Si	6.58024	-1.18209	-0.60282
P	4.61569	-0.77879	0.47448
P	2.92918	-1.96140	-0.30250
Ti	1.06200	-0.06449	-0.32289

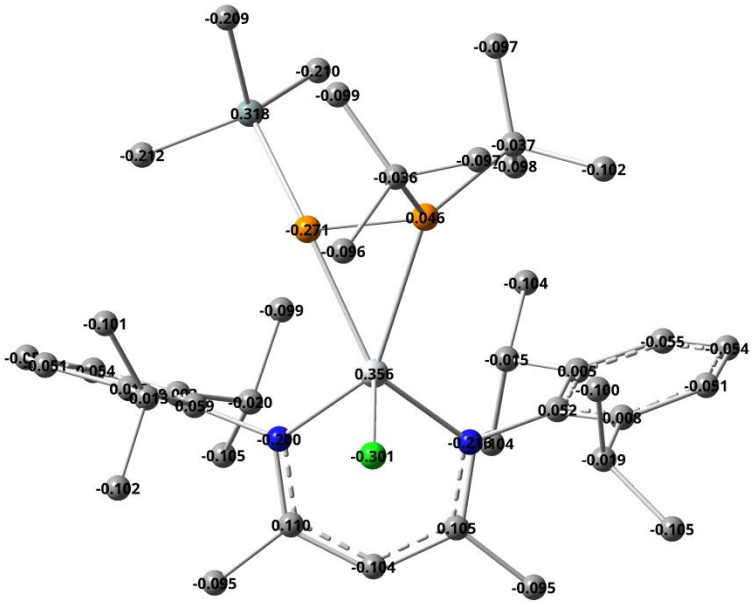

Figure S45. Optimized structure of **[(BDI*)Ti(Cl){η^2-P(SiMe$_3$)P*t*Bu$_2$}]**.

Below are presented xyz coordinates for optimized geometry for **[(BDI*)Ti(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}]**.

Ti	-0.16938	-0.19839	-0.92380
Cl	-0.62288	-0.18944	-3.17290
P	0.98070	1.55527	0.31586
P	-1.01551	2.19396	-0.15645
Si	2.15479	2.49380	2.01188
N	-1.41185	-1.74637	-0.38551
N	1.44797	-1.52163	-0.86236
C	2.80973	-1.19927	-0.52814
C	3.58076	-0.37170	-1.36874
C	4.93803	-0.21309	-1.07314
H	5.55743	0.40424	-1.72598
C	5.51843	-0.83059	0.02791
H	6.58226	-0.69915	0.23301
C	4.72919	-1.59166	0.88118
H	5.17888	-2.04205	1.76822
C	3.36863	-1.78139	0.62790
C	2.99199	0.30230	-2.59783
H	1.90573	0.35437	-2.46329
C	3.23873	-0.52080	-3.86647
H	2.80599	-0.01313	-4.74203
H	2.76556	-1.51114	-3.79696
H	4.31743	-0.66340	-4.04544
C	3.47103	1.74620	-2.76416
H	2.92048	2.22768	-3.58719
H	4.54345	1.81131	-3.00825
H	3.28543	2.32359	-1.84536
C	2.51651	-2.54884	1.62920
H	1.55873	-2.79454	1.15057
C	2.20183	-1.64189	2.82475
H	1.58451	-2.17416	3.56426
H	1.65622	-0.74381	2.49610
H	3.12655	-1.31709	3.32934
C	3.15191	-3.86269	2.09261

H	2.44463	-4.42526	2.72157
H	4.05892	-3.69277	2.69422
H	3.43133	-4.50369	1.24249
C	-2.64341	-1.56295	0.33327
C	-2.63597	-1.77707	1.73130
C	-3.83729	-1.63671	2.42945
H	-3.85746	-1.79833	3.50723
C	-5.01129	-1.27259	1.77902
H	-5.93837	-1.15964	2.34384
C	-4.99734	-1.04833	0.40987
H	-5.92063	-0.75681	-0.09455
C	-3.82638	-1.19766	-0.34115
C	-1.34738	-2.12490	2.47170
H	-0.53601	-1.56852	1.97460
C	-1.37051	-1.70135	3.94355
H	-0.36859	-1.81326	4.38227
H	-2.05102	-2.33060	4.53951
H	-1.67596	-0.65306	4.06846
C	-1.00199	-3.61806	2.37596
H	-0.10537	-3.83875	2.97707
H	-0.78793	-3.93223	1.34586
H	-1.82822	-4.23593	2.76384
C	-3.88057	-0.96350	-1.84508
H	-2.93786	-1.31688	-2.28271
C	-3.98505	0.53166	-2.16707
H	-3.98139	0.69030	-3.25640
H	-3.13092	1.07927	-1.74561
H	-4.91242	0.96391	-1.75493
C	-5.02467	-1.73302	-2.51771
H	-4.93844	-1.64889	-3.61179
H	-6.01123	-1.33226	-2.23531
H	-5.01537	-2.80234	-2.25586
C	2.44086	-3.59406	-1.78357
H	3.25841	-2.99794	-2.20579
H	2.12415	-4.34985	-2.51313
H	2.84494	-4.11788	-0.90390
C	1.26098	-2.74031	-1.37358
C	0.00094	-3.35849	-1.49757
H	0.00483	-4.33870	-1.97017
C	-1.21258	-2.95754	-0.93563
C	-2.33365	-3.96942	-0.96204
H	-2.79592	-4.08261	0.02793
H	-1.96948	-4.94610	-1.30161
H	-3.12465	-3.63420	-1.64793
C	3.87192	1.74549	1.85327
H	3.85023	0.65413	1.97687
H	4.53538	2.17101	2.62461
H	4.30623	1.95524	0.86411
C	1.49289	2.15621	3.75125
H	0.57798	2.72898	3.96503
H	2.26204	2.46941	4.47730
H	1.28211	1.08915	3.91769
C	2.30668	4.36514	1.80966

H	1.33964	4.88450	1.87192
H	2.77766	4.62540	0.84981
H	2.95028	4.74728	2.62019
C	-2.10220	2.57372	1.36390
C	-1.81336	1.48350	2.39600
H	-0.77981	1.51179	2.75729
H	-2.00130	0.49119	1.97158
H	-2.49199	1.61187	3.25634
C	-3.58642	2.45630	0.97856
H	-3.89535	3.18199	0.21595
H	-4.20296	2.63525	1.87598
H	-3.81962	1.44650	0.61296
C	-1.81765	3.94343	1.98795
H	-0.75190	4.06268	2.23334
H	-2.39059	4.04098	2.92575
H	-2.11637	4.77461	1.33432
C	-0.93446	3.70479	-1.33378
C	-0.35563	3.20087	-2.66193
H	-1.01165	2.46416	-3.14255
H	0.63109	2.73423	-2.52229
H	-0.23142	4.05785	-3.34528
C	-0.01463	4.80768	-0.80156
H	-0.35856	5.23297	0.15036
H	0.03151	5.62882	-1.53712
H	1.00530	4.42266	-0.66259
C	-2.33749	4.26644	-1.60043
H	-2.77229	4.75484	-0.71708
H	-3.03305	3.48778	-1.94868
H	-2.27033	5.02938	-2.39398

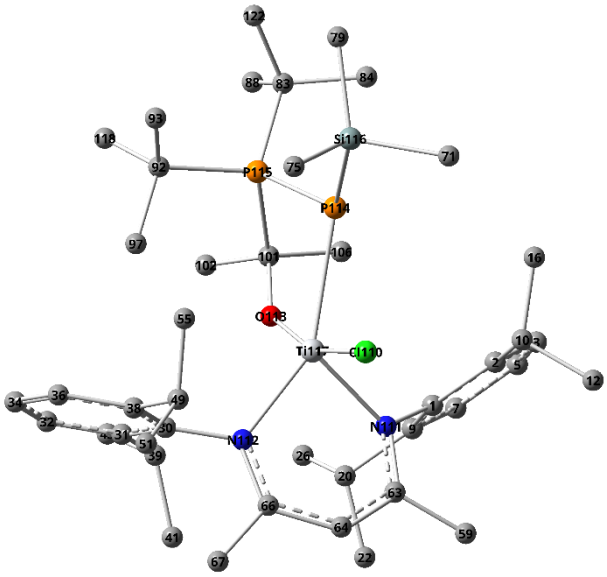

Figure S46. Optimized structure of **a**.

Below are presented xyz coordinates for optimized geometry for **a**.

C	2.03900	-2.57500	-0.12000
C	1.33000	-3.65800	-0.67500
C	1.26900	-4.85400	0.05000
H	0.72600	-5.70200	-0.37000
C	1.90300	-4.99400	1.27600
H	1.85000	-5.94100	1.81800
C	2.61600	-3.92300	1.80500
H	3.11800	-4.03900	2.76700
C	2.68700	-2.70200	1.13200
C	0.69000	-3.60500	-2.05300
H	0.74400	-2.57000	-2.41800
C	1.45500	-4.49700	-3.04200
H	1.04700	-4.37700	-4.05700
H	2.52700	-4.25600	-3.07300
H	1.36400	-5.56100	-2.76600
C	-0.78500	-4.01500	-2.02200
H	-1.22500	-3.90600	-3.02500
H	-0.90900	-5.06800	-1.72200
H	-1.36200	-3.38200	-1.33100
C	3.46600	-1.54300	1.73700
H	3.06800	-0.62400	1.28700
C	4.95800	-1.62900	1.39100
H	5.50800	-0.79200	1.85000
H	5.39300	-2.57000	1.76700
H	5.13000	-1.58300	0.30800
C	3.29300	-1.43500	3.25500
H	2.23200	-1.42300	3.54300
H	3.78000	-2.26600	3.78900
H	3.75600	-0.50600	3.62100
C	1.51400	2.83100	-0.12700
C	1.80200	3.09200	1.23500
C	1.43100	4.32800	1.76900
H	1.64900	4.55200	2.81300
C	0.77800	5.28400	0.99800
H	0.49400	6.24200	1.43800

C	0.49200	5.01100	-0.33000
H	-0.02500	5.76000	-0.93300
C	0.85800	3.79500	-0.91900
C	2.50900	2.06100	2.10600
H	2.06400	1.08600	1.85700
C	4.01500	2.00200	1.81400
H	4.51700	1.33200	2.53000
H	4.23100	1.61900	0.80800
H	4.47200	3.00000	1.91400
C	2.29700	2.29200	3.60500
H	1.23600	2.44400	3.85500
H	2.65300	1.41800	4.17100
H	2.85900	3.16600	3.97100
C	0.51400	3.56400	-2.38200
H	0.99200	2.63200	-2.71200
C	1.01100	4.69900	-3.28500
H	2.08100	4.90700	-3.13200
H	0.86200	4.43300	-4.34300
H	0.46400	5.63900	-3.10400
C	-0.99500	3.36700	-2.55200
H	-1.33900	2.47500	-2.00900
H	-1.55800	4.24000	-2.18300
H	-1.24600	3.21700	-3.61200
C	4.07500	-2.12500	-2.03000
H	5.10600	-1.77500	-2.17300
H	4.07800	-3.00700	-1.37900
H	3.68500	-2.43200	-3.01300
C	3.18800	-1.01800	-1.50900
C	3.56000	0.28600	-1.86400
H	4.45100	0.37800	-2.48300
C	3.02000	1.48700	-1.37800
C	3.80800	2.74000	-1.68600
H	4.84200	2.49300	-1.95800
H	3.34600	3.26400	-2.53700
H	3.81500	3.43700	-0.83900
C	-3.28800	-1.82200	-3.46300
H	-3.44700	-2.81300	-3.01200
H	-3.94300	-1.72700	-4.34500
H	-2.24100	-1.75300	-3.79700
C	-3.57100	1.18200	-3.19600
H	-2.58300	1.26300	-3.67200
H	-4.34000	1.16700	-3.98600
H	-3.73400	2.07800	-2.57900
C	-5.45100	-0.65100	-1.64500
H	-5.60600	-1.59000	-1.09200
H	-5.78900	0.19300	-1.02600
H	-6.09600	-0.68000	-2.54000
C	-3.88800	-1.24500	2.22400
C	-3.85700	-2.65700	1.61400
H	-4.09600	-2.63400	0.54200
H	-2.88600	-3.15300	1.72300
H	-4.61300	-3.27200	2.12900
C	-3.66400	-1.33500	3.74300

H	-3.63100	-0.34900	4.22500
H	-4.50800	-1.88900	4.18600
H	-2.74700	-1.87800	4.00400
C	-2.92300	1.68700	1.59900
C	-4.05500	2.10200	0.64600
H	-5.01700	1.62800	0.87300
H	-4.19400	3.19200	0.72900
H	-3.78900	1.88300	-0.39700
C	-1.68000	2.48400	1.17800
H	-0.79400	2.28600	1.78900
H	-1.41600	2.27600	0.13300
H	-1.90800	3.55900	1.25100
C	-0.77600	-0.57900	2.09000
C	-0.51600	0.07500	3.44700
H	-1.21200	-0.27200	4.22200
H	0.50600	-0.19300	3.75400
H	-0.55700	1.16800	3.38900
C	-0.58000	-2.09500	2.19900
H	-1.20600	-2.55600	2.97300
H	-0.75200	-2.59100	1.23500
H	0.47100	-2.26400	2.46700
Cl	0.14100	0.01000	-3.03000
N	2.11200	-1.30000	-0.77400
N	1.88300	1.55800	-0.68300
O	0.12100	-0.08100	1.15900
P	-2.07800	-0.73900	-0.65100
P	-2.54400	-0.17500	1.36400
Si	-3.66600	-0.43900	-2.23800
Ti	0.47800	-0.00500	-0.68300
C	-3.30600	2.05800	3.04100
H	-3.42100	3.15200	3.09800
H	-4.26200	1.61700	3.35300
H	-2.54000	1.77200	3.77200
C	-5.29500	-0.67900	1.98400
H	-6.02700	-1.40100	2.38000
H	-5.46800	0.27300	2.50100
H	-5.51200	-0.54700	0.91800

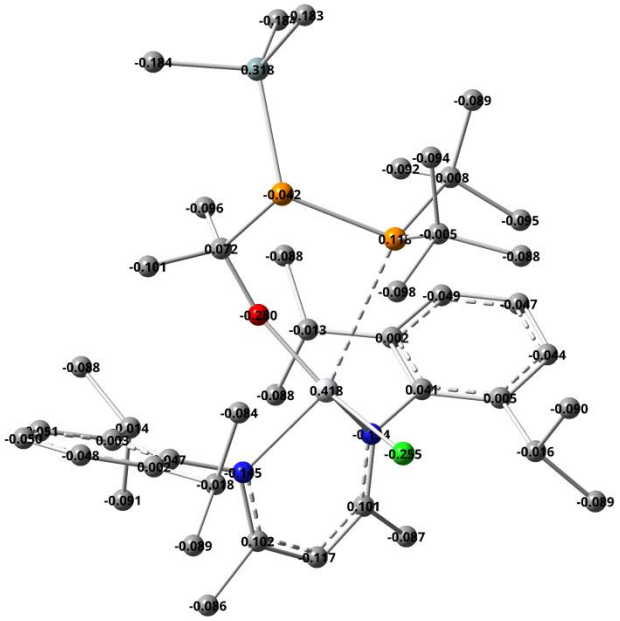

Figure S47. Optimized structure of **b**.

Below are presented xyz coordinates for optimized geometry for **b**.

C	-2.84300	-2.02600	-0.27800
C	-2.71100	-2.94800	-1.33000
C	-2.91200	-4.30500	-1.05800
H	-2.80700	-5.03400	-1.86300
C	-3.25500	-4.73900	0.21500
H	-3.42400	-5.80100	0.40600
C	-3.37100	-3.81600	1.25000
H	-3.62000	-4.16900	2.25200
C	-3.14700	-2.45500	1.03300
C	-2.32300	-2.50400	-2.73000
H	-2.45400	-1.41500	-2.78900
C	-0.83900	-2.79300	-2.98000
H	-0.52300	-2.40700	-3.96100
H	-0.20400	-2.31400	-2.21800
H	-0.63500	-3.87600	-2.94500
C	-3.19600	-3.13000	-3.82200
H	-2.95900	-2.67900	-4.79700
H	-3.03200	-4.21600	-3.91400
H	-4.26700	-2.97000	-3.62400
C	-3.20900	-1.46800	2.19200
H	-2.53100	-0.64200	1.93300
C	-2.72700	-2.07700	3.51300
H	-2.56800	-1.28300	4.25900
H	-3.46800	-2.77300	3.93900
H	-1.78200	-2.62700	3.39400
C	-4.61500	-0.88100	2.38600
H	-4.92500	-0.25900	1.53600
H	-5.35800	-1.68500	2.51800
H	-4.64100	-0.24500	3.28400
C	-0.75500	2.97600	0.70700
C	-0.36700	2.83300	2.06000
C	0.44300	3.81900	2.62700
H	0.75500	3.73000	3.66800

C	0.85800	4.92300	1.89000
H	1.48700	5.68500	2.35400
C	0.47500	5.04700	0.56200
H	0.81600	5.90900	-0.01400
C	-0.32700	4.08400	-0.05900
C	-0.85500	1.65300	2.89500
H	-0.80300	0.75400	2.25900
C	0.00000	1.38100	4.13400
H	-0.30000	0.42400	4.58600
H	1.07300	1.31800	3.89700
H	-0.13300	2.15900	4.90300
C	-2.31900	1.84000	3.32100
H	-2.62300	1.02900	4.00100
H	-2.44800	2.79500	3.85600
H	-3.00800	1.82500	2.46600
C	-0.68400	4.27000	-1.53000
H	-1.44900	3.52800	-1.79900
C	0.52800	3.99600	-2.42800
H	0.25400	4.11900	-3.48700
H	1.35400	4.69100	-2.20100
H	0.88800	2.96900	-2.29600
C	-1.24100	5.66900	-1.82500
H	-1.64700	5.70600	-2.84700
H	-2.04200	5.95900	-1.12800
H	-0.45700	6.44000	-1.75800
C	-5.04700	-0.64300	-1.17800
H	-5.88000	0.06000	-1.30100
H	-4.86800	-1.15100	-2.13800
H	-5.33500	-1.42000	-0.45700
C	-3.78900	0.07600	-0.75000
C	-3.86900	1.47000	-0.59500
H	-4.84500	1.91600	-0.77800
C	-2.90300	2.31700	-0.04100
C	-3.40200	3.68000	0.38500
H	-4.48800	3.65700	0.53300
H	-2.92000	4.01700	1.31100
H	-3.18100	4.42900	-0.38800
C	0.81300	-1.90900	1.04200
C	1.02400	-1.61500	2.52500
H	1.65500	-2.37800	3.00400
H	1.47600	-0.63100	2.67800
H	0.04400	-1.62000	3.02500
C	0.22300	-3.31000	0.86100
H	0.93600	-4.08000	1.18900
H	-0.69900	-3.40600	1.45200
H	-0.02700	-3.49400	-0.19200
C	4.67400	-1.55600	2.80300
H	3.82500	-1.34700	3.47000
H	5.39800	-2.17200	3.36300
H	5.16500	-0.60400	2.55700
C	5.69900	-2.75800	0.18300
H	5.48800	-3.42300	-0.66900
H	6.09900	-1.81300	-0.21000

H	6.48600	-3.22900	0.79500
C	3.66000	-4.26700	1.84300
H	2.84900	-4.24900	2.58600
H	3.33900	-4.89300	0.99600
H	4.53300	-4.75000	2.31400
C	3.17800	-0.12000	-2.58900
C	4.51600	-0.86600	-2.54000
H	5.29500	-0.32400	-1.99200
H	4.39500	-1.86100	-2.08800
H	4.88100	-1.01600	-3.57100
C	2.19600	-0.97500	-3.40500
H	1.21900	-0.48600	-3.50900
H	2.61600	-1.13100	-4.41300
H	2.05000	-1.96400	-2.94600
C	3.40300	1.40800	0.14400
C	2.89200	1.29600	1.58300
H	3.16400	0.33800	2.04000
H	3.32900	2.10400	2.19300
H	1.79900	1.41000	1.62400
C	3.08100	2.83200	-0.33000
H	3.37300	3.02100	-1.37000
H	2.01000	3.04100	-0.22800
H	3.62100	3.55300	0.30600
Cl	-0.89000	0.82200	-2.88400
N	-2.68200	-0.61800	-0.49700
N	-1.61500	1.98200	0.13000
O	-0.06800	-0.95800	0.53000
P	2.41600	-1.87300	-0.05500
P	2.35600	0.17800	-0.88000
Si	4.16700	-2.53600	1.26500
Ti	-0.77500	0.24100	-0.64400
C	3.36100	1.22400	-3.30700
H	2.43100	1.81100	-3.32100
H	4.15900	1.83200	-2.85700
H	3.64900	1.03300	-4.35400
C	4.91600	1.18500	0.11200
H	5.39500	1.83500	0.86600
H	5.19100	0.14700	0.34400
H	5.34900	1.44700	-0.86300

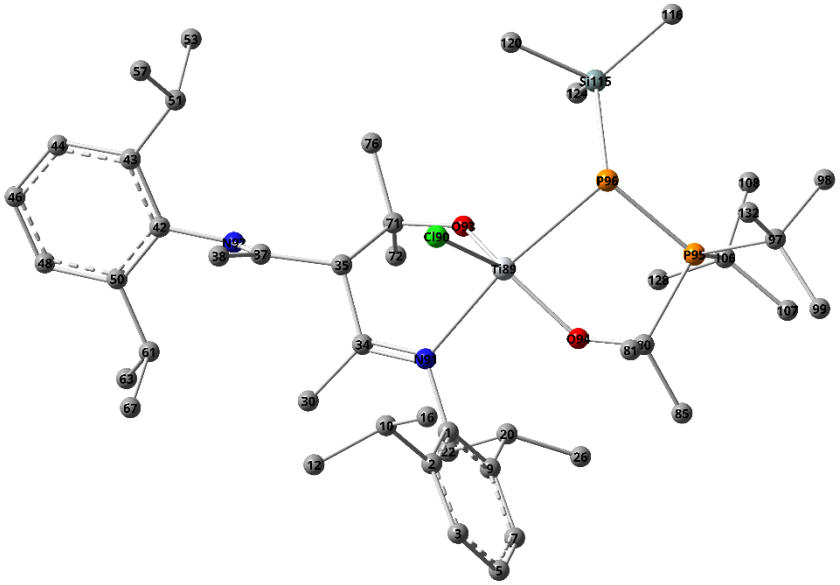

Figure S48. Optimized structure of **c**.

Below are presented xyz coordinates for optimized geometry for **c**.

C	-0.08600	2.88400	0.19100
C	-0.12400	3.60000	1.40000
C	-0.68600	4.88100	1.38700
H	-0.72300	5.45500	2.31500
C	-1.19200	5.43500	0.21900
H	-1.62700	6.43600	0.22800
C	-1.14500	4.70600	-0.96600
H	-1.54700	5.14700	-1.87900
C	-0.60300	3.42000	-1.00400
C	0.43600	3.04000	2.70000
H	0.75400	2.00500	2.52100
C	1.65900	3.84400	3.16100
H	2.10400	3.38600	4.05800
H	2.43200	3.88800	2.37900
H	1.38800	4.88200	3.41400
C	-0.63000	2.97100	3.79700
H	-0.20500	2.52900	4.71000
H	-1.02300	3.96900	4.05200
H	-1.46700	2.33100	3.48200
C	-0.54800	2.64400	-2.31100
H	-0.58400	1.57200	-2.05700
C	0.76400	2.92000	-3.06100
H	0.79800	2.35500	-4.00500
H	0.84900	3.99200	-3.30000
H	1.64700	2.64000	-2.47300
C	-1.72500	2.94300	-3.24300
H	-1.75400	2.20800	-4.06200
H	-2.68400	2.90400	-2.71100
H	-1.63600	3.94000	-3.70500
C	2.70500	2.33100	-0.12900
H	3.32600	2.05000	-0.99100
H	2.27000	3.32400	-0.28300
H	3.37900	2.37200	0.73900
C	1.65800	1.28100	0.09400

C	2.09400	-0.17500	0.22000
H	1.62600	-0.51900	1.15900
C	3.59100	-0.31700	0.45700
C	4.00800	-0.12200	1.89500
H	3.46700	0.72300	2.34700
H	3.71500	-1.01400	2.47500
H	5.09000	0.02500	1.99900
C	5.75300	-0.86000	-0.31000
C	6.21000	-2.04400	0.30600
C	7.59000	-2.26400	0.37500
H	7.96000	-3.17900	0.84300
C	8.50000	-1.34700	-0.13500
H	9.57200	-1.53700	-0.06000
C	8.03300	-0.18900	-0.74800
H	8.74800	0.53100	-1.15100
C	6.66600	0.06700	-0.85700
C	5.26200	-3.10800	0.84100
H	4.24300	-2.70300	0.82600
C	5.26100	-4.34000	-0.07300
H	4.52400	-5.08200	0.27300
H	5.01000	-4.06300	-1.10900
H	6.25100	-4.82400	-0.08700
C	5.57100	-3.49200	2.29200
H	4.80900	-4.18900	2.67400
H	6.54900	-3.99100	2.38500
H	5.58400	-2.60700	2.94700
C	6.15900	1.34700	-1.49700
H	5.10800	1.16300	-1.77200
C	6.90600	1.72600	-2.77800
H	6.90000	0.89800	-3.50200
H	6.43100	2.59900	-3.25100
H	7.95600	1.99500	-2.57900
C	6.19400	2.49400	-0.47900
H	5.72700	3.40600	-0.88600
H	5.66700	2.22100	0.44800
H	7.23400	2.73600	-0.20800
C	1.43700	-1.08700	-0.87900
C	1.74100	-0.62100	-2.30100
H	2.82400	-0.62000	-2.48300
H	1.25000	-1.29700	-3.01600
H	1.34300	0.38900	-2.46800
C	1.87300	-2.54000	-0.68000
H	2.91600	-2.69200	-0.98100
H	1.74900	-2.84200	0.37200
H	1.23100	-3.18600	-1.29500
C	-3.80000	1.19800	0.37400
C	-3.95100	1.45500	1.87900
H	-4.98800	1.65000	2.18400
H	-3.53700	0.62700	2.47200
H	-3.35500	2.35600	2.09400
C	-4.38400	2.37900	-0.40200
H	-5.46200	2.51300	-0.23500
H	-3.85700	3.28300	-0.06100

H	-4.19600	2.28400	-1.47700
Ti	-1.08100	-0.14500	0.48800
Cl	-0.36000	-0.49100	2.71900
N	0.40300	1.53600	0.21000
N	4.37100	-0.62100	-0.50500
O	0.04100	-1.03500	-0.67100
O	-2.45900	1.08200	0.07100
P	-4.55700	-0.54700	-0.10700
P	-3.09400	-1.78300	0.91200
C	-6.29500	-0.78800	0.65800
C	-7.00500	-1.98000	-0.00300
C	-7.16500	0.47000	0.50800
H	-6.36700	-2.87600	-0.02500
H	-7.90000	-2.22600	0.59100
H	-7.34400	-1.75600	-1.02300
H	-6.78900	1.30400	1.11500
H	-7.25300	0.81300	-0.53100
H	-8.18200	0.24000	0.86800
C	-4.63100	-0.68900	-2.01500
C	-5.70600	0.20000	-2.65900
C	-4.91100	-2.14000	-2.44300
H	-5.59700	1.26400	-2.42100
H	-5.62500	0.09600	-3.75400
H	-6.72200	-0.11600	-2.38200
H	-4.31500	-2.86200	-1.87900
H	-5.96700	-2.41600	-2.34700
H	-4.63900	-2.24700	-3.50500
Si	-2.51100	-3.72800	-0.08400
C	-3.91900	-4.99700	-0.08300
H	-4.36200	-5.07200	0.92300
H	-4.72100	-4.74600	-0.79400
H	-3.52600	-5.98900	-0.36000
C	-1.19000	-4.28300	1.14800
H	-0.70900	-5.21100	0.79800
H	-0.41800	-3.50600	1.25900
H	-1.62700	-4.46700	2.14200
C	-1.71000	-3.66700	-1.79700
H	-2.42700	-3.54400	-2.62100
H	-0.98400	-2.84000	-1.82800
H	-1.17100	-4.61600	-1.96200
C	-3.23700	-0.30600	-2.54500
H	-2.95400	0.72000	-2.29100
H	-2.46000	-0.97200	-2.14400
H	-3.24200	-0.41000	-3.64200
C	-6.15200	-1.12200	2.15300
H	-5.63200	-2.07700	2.30300
H	-5.60700	-0.35600	2.71600
H	-7.16500	-1.20100	2.58300

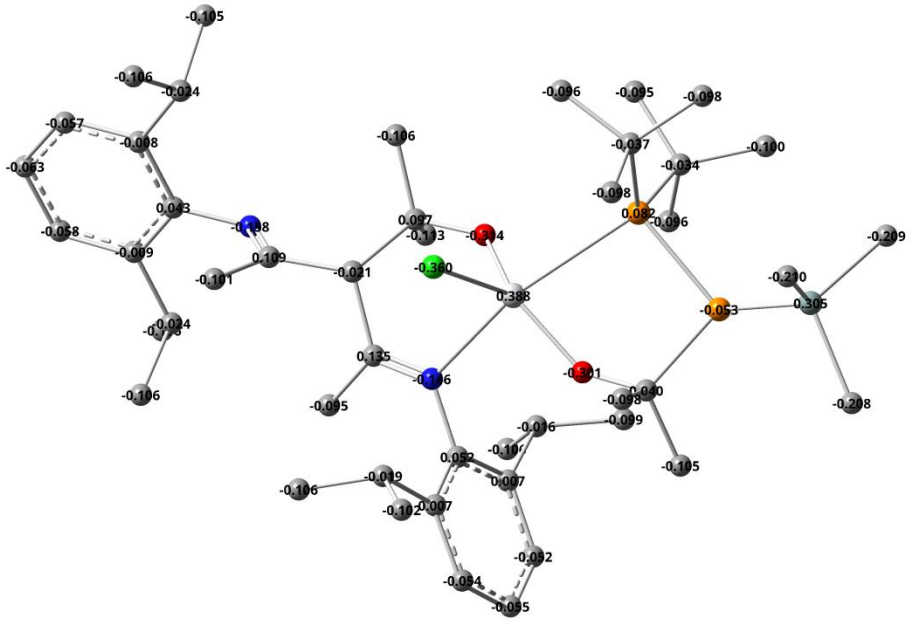

Figure S49. Optimized structure of **d**.

Below are presented xyz coordinates for optimized geometry for **d**.

C	-0.04900	2.86800	-0.12300
C	0.14000	3.58300	-1.31800
C	0.68200	4.86600	-1.23000
H	0.83400	5.44800	-2.14000
C	1.04200	5.41100	-0.00100
H	1.46400	6.41700	0.04900
C	0.88200	4.66600	1.16100
H	1.19000	5.09000	2.11900
C	0.34700	3.37500	1.12400
C	-0.24800	2.96600	-2.65300
H	-0.17600	1.87400	-2.54000
C	-1.70100	3.30600	-3.01000
H	-1.99900	2.80400	-3.94400
H	-2.40000	2.99400	-2.21900
H	-1.82900	4.39300	-3.14900
C	0.69000	3.35800	-3.79600
H	0.44900	2.76800	-4.69300
H	0.59500	4.42200	-4.06700
H	1.74000	3.16200	-3.53400
C	0.23900	2.55400	2.39900
H	-0.11100	1.55000	2.12400
C	-0.78200	3.15200	3.37400
H	-0.89600	2.50600	4.25900
H	-0.46100	4.14700	3.72500
H	-1.77100	3.26900	2.90700
C	1.60400	2.36900	3.06800
H	1.50900	1.72600	3.95700
H	2.30600	1.89200	2.37100
H	2.03500	3.32900	3.39300
C	-2.82300	2.27300	0.38200
H	-3.24100	1.97400	1.35500
H	-2.40300	3.28300	0.45300
H	-3.66500	2.27900	-0.32400

C	-1.79700	1.26000	-0.02600
C	-2.21100	-0.19700	-0.15900
H	-1.68500	-0.56300	-1.05700
C	-3.68900	-0.34800	-0.47900
C	-4.03200	-0.07200	-1.92300
H	-3.49200	0.81500	-2.28800
H	-3.68500	-0.91800	-2.54100
H	-5.11100	0.05600	-2.07700
C	-5.87900	-0.95100	0.12800
C	-6.28200	-2.13300	-0.52800
C	-7.65100	-2.36000	-0.69700
H	-7.98100	-3.27400	-1.19700
C	-8.60000	-1.45000	-0.24800
H	-9.66300	-1.64600	-0.39900
C	-8.18500	-0.29000	0.39800
H	-8.93100	0.42600	0.74800
C	-6.83100	-0.02700	0.60500
C	-5.28400	-3.17900	-1.00600
H	-4.27500	-2.75300	-0.93000
C	-5.31500	-4.41200	-0.09500
H	-4.55100	-5.14300	-0.40100
H	-5.12500	-4.13400	0.95300
H	-6.29800	-4.90800	-0.13600
C	-5.49900	-3.56400	-2.47400
H	-4.70600	-4.24900	-2.81100
H	-6.46300	-4.07700	-2.62500
H	-5.48700	-2.67800	-3.12600
C	-6.37800	1.25800	1.27700
H	-5.32900	1.10800	1.57000
C	-7.16500	1.58600	2.54900
H	-7.13500	0.74900	3.26200
H	-6.73800	2.47300	3.04200
H	-8.22200	1.81000	2.33400
C	-6.43000	2.42300	0.28100
H	-5.99800	3.34000	0.71400
H	-5.88000	2.18500	-0.64300
H	-7.47100	2.64100	-0.00800
C	-1.60400	-1.05800	1.01100
C	-2.06300	-0.60400	2.39600
H	-3.15100	-0.71800	2.49900
H	-1.55400	-1.21300	3.15800
H	-1.79700	0.44700	2.58100
C	-1.93700	-2.53500	0.79000
H	-3.00500	-2.73600	0.94400
H	-1.64700	-2.84500	-0.22600
H	-1.36000	-3.13600	1.50800
C	2.93900	-2.34600	2.14400
C	4.30100	-2.74200	2.72600
H	4.77600	-3.56600	2.17800
H	4.99300	-1.88600	2.73600
H	4.16600	-3.07200	3.77000
C	1.96800	-3.53200	2.20700
H	2.39100	-4.44000	1.75500

H	1.75600	-3.76200	3.26500
H	1.01400	-3.29100	1.71500
C	2.35600	-1.20400	2.99400
H	1.34100	-0.93800	2.66400
H	2.29900	-1.53900	4.04400
H	2.99400	-0.30900	2.96200
C	3.42800	-3.06900	-0.89300
C	3.74600	-2.37600	-2.22500
H	2.87700	-1.81200	-2.59200
H	4.60000	-1.69600	-2.14500
H	3.99200	-3.14400	-2.97700
C	4.58800	-3.98100	-0.48400
H	4.34400	-4.58800	0.40000
H	4.81200	-4.67900	-1.30800
H	5.50500	-3.41200	-0.27100
C	2.14900	-3.90000	-1.10800
H	1.30000	-3.25700	-1.38100
H	2.32300	-4.59800	-1.94400
H	1.87400	-4.49800	-0.23100
C	7.48200	-1.62700	1.13700
H	7.40800	-1.18400	2.14200
H	7.01500	-2.62200	1.17000
H	8.55000	-1.76200	0.89800
C	7.51300	1.20500	-0.03800
H	7.16700	1.88100	-0.83500
H	7.32400	1.68900	0.93300
H	8.60300	1.08100	-0.15500
C	7.05100	-1.17500	-1.87300
H	6.54800	-0.59800	-2.66500
H	8.13900	-1.09800	-2.03800
H	6.76800	-2.23200	-1.98200
C	3.71100	1.30500	-0.43300
C	3.97800	1.27800	-1.93600
H	5.05200	1.37100	-2.16100
H	3.59000	0.35800	-2.39100
H	3.45400	2.12900	-2.40100
C	4.14900	2.64800	0.15700
H	5.21100	2.85100	-0.04300
H	3.54100	3.44400	-0.30300
H	3.98700	2.67700	1.24300
Ti	0.97000	-0.08900	-0.25300
Cl	0.46600	-0.76900	-2.46500
N	-0.55600	1.53000	-0.22500
N	-4.51300	-0.71600	0.41900
O	-0.20300	-0.92700	0.92300
O	2.34700	1.13800	-0.20100
P	4.56400	-0.10300	0.58600
P	3.03600	-1.68600	0.35400
Si	6.68700	-0.49300	-0.14900

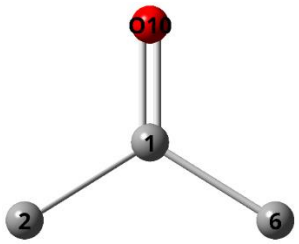

Figure S50. Optimized structure of **$CH_3C(O)CH_3$**.

Below are presented xyz coordinates for optimized geometry for **$CH_3C(O)CH_3$**.

C	-0.00000100	0.18658400	0.00000000
C	-1.28640100	-0.61326800	-0.00262600
H	-1.27290900	-1.37446500	-0.79799200
H	-1.38692400	-1.14952800	0.95503300
H	-2.14357100	0.05794500	-0.13459800
C	1.28640100	-0.61327000	0.00262600
H	2.14356700	0.05794600	0.13461100
H	1.27290600	-1.37447700	0.79798200
H	1.38693100	-1.14951500	-0.95504100
O	0.00000100	1.39647700	0.00000000

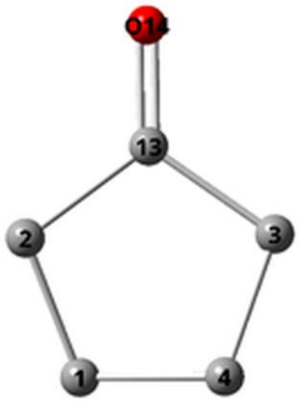

Figure S51. Optimized structure of **Cp (=O)**.

Below are presented xyz coordinates for optimized geometry for **Cp (=O)**.

C	1.37481900	-0.73424000	-0.23192700
C	-0.02833100	-1.23224900	0.12411100
C	-0.02832500	1.23224100	-0.12410400
C	1.37482900	0.73424000	0.23192300
H	2.17738500	-1.32597500	0.22945100
H	1.52163100	-0.77779000	-1.32418500
H	-0.07890900	-1.55806900	1.17826800
H	-0.40997000	-2.06024000	-0.48828200
H	-0.07892000	1.55805800	-1.17826100
H	-0.40995600	2.06023700	0.48828700
H	2.17739100	1.32596400	-0.22947800
H	1.52165100	0.77780800	1.32417800
C	-0.92394300	0.00000200	0.00000800
O	-2.12932500	0.00000700	-0.00000500

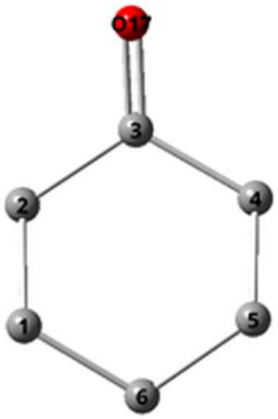

Figure S52. Optimized structure of **Cy(=O)**.

Below are presented xyz coordinates for optimized geometry for **Cy(=O)**.

C	-1.00939800	-1.26020000	-0.28428500
C	0.38919700	-1.28056300	0.35051900
C	1.15556200	0.00000000	0.06705100
C	0.38919700	1.28056400	0.35051800
C	-1.00940000	1.26020000	-0.28428400
C	-1.78349600	-0.00000100	0.10465400
H	0.28472100	-1.36148500	1.44827600
H	0.99178800	-2.13189200	0.00634800
H	-0.90662000	-1.29923900	-1.38295400
H	-1.56358600	-2.16446000	0.01069200
H	0.28472300	1.36148700	1.44827500
H	0.99178600	2.13189200	0.00634400
H	-1.56358900	2.16445800	0.01069700
H	-0.90662400	1.29924100	-1.38295300
H	-1.96122600	-0.00000200	1.19553700
H	-2.77371700	-0.00000100	-0.37648000
O	2.29154700	0.00000000	-0.35110200

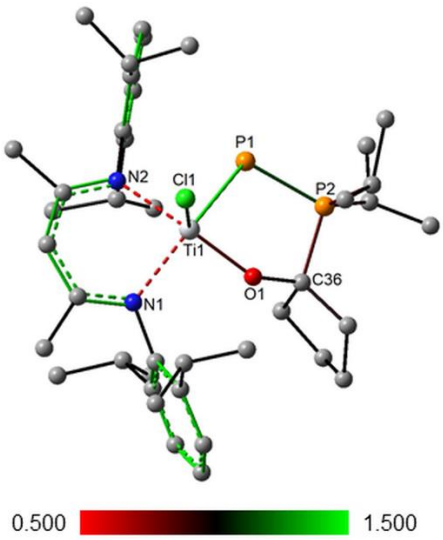

Figure S53. The DFT Mayer bond order (MBO) calculation conducted for **5**.

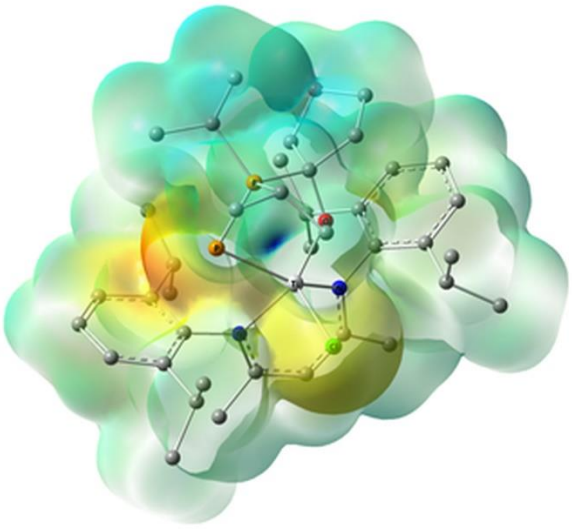

Figure S54. Electron density surface (Isovalue = 0.004 e/Å^3) mapped with electrostatic potential for compound **5**. The red areas correspond to the negative electrostatic potential and the blue areas to the positive one.

PART D. References

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