

**(Imido)Titanium Complexes as Hydroamination Catalysts: Substantially Enhanced
Reactivity from an Unexpected Cyclopentadienide/Amide Ligand Exchange**

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I. Synthetic Procedures for preparation of imines from allene and amines

Hydroamination of allene catalyzed by Cp_2TiMe_2 . General Procedure. A vial was charged with 0.2 mmol of amine and *ca.* 0.03 mmol of 1,3,5-trimethoxybenzene. These materials were dissolved in 0.5 mL of a 0.04 M C_6D_6 solution of CpTiMe_2 and the resulting orange solution was transferred to an NMR tube and fitted with a Cajon ultratorr adapter. The solution was degassed with three freeze-pump-thaw cycles and allene (67 torr x 66 mL) was condensed onto the frozen (77 K) solution. The tube was flame-sealed under dynamic vacuum and a single pulse ^1H NMR spectrum was obtained. The tube was heated to 90 °C until the amine was consumed (as judged by ^1H NMR spectroscopy). The yield was measured by comparison of the integration of the aryl resonances of 1,3,5-trimethoxybenzene and a well-resolved signal for the product imine.

II. Synthetic Procedures, and IR and combustion analysis data for **6•py**, **6•OPMe₃**, **15**, **16**, **17**

$\text{Cp}(\text{py})(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NH})\text{Ti}=\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ (6•py**).** An orange solution of 101 mg (0.49 mmol) of dimethyltitanocene, 120 mg (0.99 mmol) of 2,6-dimethylaniline, and 69 mg (0.87 mmol) of pyridine in 5 mL of toluene was heated in a thick-walled glass vessel with Teflon stopcock at 85 °C for 24 h. The resulting brown solution was concentrated *in vacuo* to a brown oil that was vigorously triturated with three 2 mL portions of pentane. The residual oil was subjected to dynamic vacuum to afford 108 mg of a brown foam. The pentane washes were concentrated *in vacuo* to a brown oil that was triturated with three 2 mL portions of pentane. Subjection of the resulting oil to dynamic vacuum afforded another 12 mg of a brown foam. Combined yield = 120 mg. ^1H NMR analysis revealed the ratio of **6•py**:2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{NH}_2$ = 3.5:1 (12.5:1 w/w). IR (KBr) 3463, 3381, 3036, 2966, 2918, 2852, 1625, 1476, 1439, 1274, 1090, 1017 cm^{-1} . In our hands it was not possible to completely remove the amine from **6•py** and repeated attempts to obtain satisfactory combustion analysis for **6•py**·2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{NH}_2$ were unsuccessful.

In a separate experiment, a solution of 64 mg (0.31 mmol) of dimethyltitanocene, 74 mg (0.62 mmol) of 2,6-dimethylaniline, and 16.4 mg (0.098 mmol) of 1,3,5-trimethoxybenzene in 4 mL of toluene was heated at 75 °C for 24 h. The resulting brown solution was cooled to 25 °C, treated with 37 mg (0.47 mmol) of pyridine, and heated at 75 °C for 3 h. An aliquot was taken, concentrated *in vacuo*, and analyzed by ^1H NMR. Integration versus the internal standard revealed the yield of imido complex **6•py** was 62%.

Conversion of $\text{Cp}(\text{py})(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NH})\text{Ti}=\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ (6•py**) into $\text{Cp}(\text{Me}_3\text{PO})(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NH})\text{Ti}=\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ (**6•OPMe₃**).** A mixture of 5.9 mg (0.065 mmol) of trimethylphosphine oxide, 6.3 mg (0.038 mmol) of 1,3,5-trimethoxybenzene, and 30.2 mg (0.065 mmol) of **6•py** containing 20 mol% 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{NH}_2$ was stirred in 3 mL of toluene for 1 h, then concentrated *in vacuo* to a brown oil. The residue was redissolved in 3 mL of toluene, stirred an additional hour, and concentrated *in vacuo*. The residue was analyzed by ^1H NMR spectroscopy; no **6•py** remained. The yield of **6•OPMe₃** versus the internal standard was 90%. The identity of **6•OPMe₃** was corroborated by independent synthesis (*vide infra*).

$\text{Cp}(\text{Me}_3\text{PO})(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NH})\text{Ti}=\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ (6•OPMe₃**).** To a mixture of cyclopentadienyl titanium trichloride (57 mg, 0.26 mmol) and trimethylphosphine oxide (24 mg, 0.26 mmol) in 12 mL of THF at -35 °C was added a pre-cooled (-35 °C) solution of $\text{LiNH}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ (99 mg, 0.78 mmol) in 2 mL of THF. The solution rapidly darkened from orange to greenish-brown, lightening at

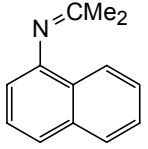
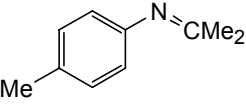
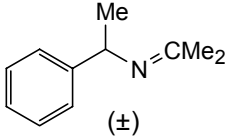
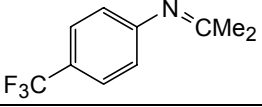
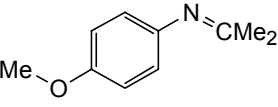
the end of the addition. Over 2 h the trimethylphosphine oxide dissolved, again darkening the solution. After a reaction time of 2 h the mixture was concentrated *in vacuo* and the resulting residue was extracted with 10 mL of 1:1 toluene/pentane. The mixture was filtered and concentrated *in vacuo* to a brown oil. Unpurified yield = 145 mg (*ca.* quantitative for **6-OPMe₃** plus 2,6-Me₂C₆H₃NH₂). ¹H NMR analysis of the unpurified reaction mixture showed only the desired product and 2,6-dimethylaniline. The residue was triturated with three 1 mL portions of cold pentane and concentrated *in vacuo* to a brown foam. Orange crystals suitable for X-ray diffraction were obtained from a saturated toluene solution layered with pentane (-35 °C). Yield = 42 mg (36%). IR (Nujol mull) 1622, 1587, 1461, 1406, 1307, 1258, 1231, 1105, 1014, 946, 858 cm⁻¹; Anal. Calcd for C₂₄H₃₃N₂OPTi: C, 64.86; H, 7.48; N, 6.30. Found C, 64.93; H, 7.60; N, 6.09.

(2,6-Dimethylphenyl)-(1-methyl-2-phenylethylidene)amine (15). A solution of 55 mg (0.45 mmol) of 2,6-dimethylaniline, 58 mg (0.50 mmol) of 1-phenyl-1,2-propadiene, and 13.5 mg (0.031 mmol) of (imido)titanium complex **6•py** in 3 mL of toluene was heated in a thick-walled glass vessel with Teflon stopcock at 90 °C for 24 h. The brown solution was cooled to 25 °C, diluted with 10 mL of hexanes, and treated with two drops of water to yield a flocculent precipitate. The solution was dried (MgSO₄), filtered, and concentrated *in vacuo* to a brown oil that was purified by flash chromatography on silica gel (10-20% Et₂O/petroleum ether) to afford 106 mg (0.43 mmol, 96%) of the title compound as a pale yellow oil: IR (CHCl₃) 3011, 2953, 1660, 1593, 1469, 1366, 1245, 1217 cm⁻¹; TLC (10% Et₂O/hexanes) R_f 0.19; Anal. Calcd for C₁₇H₁₉N: C, 86.03; H, 8.07; N, 5.90. Found C, 85.98; H, 8.18; N, 5.88.

(2,6-Dimethylphenyl)-(1-methyloctylidene)amine (16). A solution of 42 mg (0.35 mmol) of 2,6-dimethylaniline, 52 mg (0.42 mmol) of 1,2-nonadiene, and 15 mg (0.035 mmol) of (imido)titanium complex **6•py** in 3 mL of toluene was heated in a thick-walled glass vessel with Teflon stopcock at 90 °C for 48 h. The brown solution was cooled to 25 °C, diluted with 10 mL of hexanes, and treated with two drops of water to yield a flocculent precipitate. The mixture was dried (MgSO₄), filtered, and concentrated *in vacuo* to a brown oil that was purified by flash chromatography on silica gel (5-8% Et₂O/petroleum ether) to afford 73 mg (0.30 mmol, 85%) of the title compound as a clear oil: IR (CHCl₃) 3011, 2956, 1661, 1467 cm⁻¹; TLC (10% Et₂O/hexanes) R_f 0.40; Anal. Calcd for C₁₇H₂₇N: C, 83.20; H, 11.09; N, 5.71. Found C, 83.33; H, 10.94; N, 6.09.

Cyclononylidene-(2,6-dimethylphenyl)amine (17). A solution of 62 mg (0.51 mmol) of 2,6-dimethylaniline, 75 mg (0.61 mmol) of cyclononadiene, and 22 mg (0.05 mmol) of (imido)titanium complex **6•py** in 3 mL of toluene was heated in a thick-walled glass vessel with Teflon stopcock at 85 °C for 40 h. The brown solution was cooled to 25 °C, diluted with 10 mL of hexanes, and treated with two drops of water to yield a flocculent precipitate. The mixture was dried (MgSO₄), filtered, and concentrated *in vacuo* to an orange oil that was purified by flash chromatography on silica gel (5-10% Et₂O/petroleum ether) to afford 87 mg (0.36 mmol, 70%) of the title compound as a clear oil: IR (CHCl₃) 3019, 2926, 1642, 1470, 1445, 1214, 781 cm⁻¹; Anal. Calcd for C₁₇H₂₅N: C, 83.89; H, 10.35; N, 5.75. Found C, 84.29; H, 10.21; N, 5.83.

Table S1. ¹H Spectroscopic Data (C₆D₆)

Compound	δ (ppm)	Multiplicity	J (Hz)	Area
Isopropylidene-naphthalen-1-yl-amine 	7.96 7.68 7.45 7.30-7.25 6.65 1.96 1.30	dd dd d m d s s	6.5, 3.3 6.5, 3.3 8.2 - 7.2 - -	1 1 1 3 1 3 3
<i>N'</i> -Isopropylidene- <i>N,N</i> -dimethylhydrazine Me ₂ C=NNMe ₂	2.39 1.73 1.70	s s s	- - -	6 3 3
Isopropylidene- <i>p</i> -tolyl-amine 	6.99 6.67 2.14 1.88 1.42	d d s s s	8.0 8.0 - - -	2 2 3 3 3
<i>tert</i> -Butyl-isopropylidene-amine Me ₂ C=NCMe ₃	1.83 1.52 1.26	s s s	- - -	3 3 9
Isopropylidene-(1-phenylethyl)-amine 	7.47 7.21 7.09 4.42 1.82 1.44 1.36	d t t q s d s	7.6 7.6 7.6 6.4 - 6.4 -	2 2 1 1 3 3 3
Isopropylidene-(4-trifluoromethylphenyl)amine 	7.33 6.46 1.79 1.20	d d s s	8.0 8.0 - -	2 2 3 3
Isopropylidene-(4-methoxyphenyl)amine 	6.78 6.66 3.34 1.90 1.44	dt dt s s s	8.8, 2.4 8.8, 2.4 - - -	2 2 3 3 3
(2,6-Dimethylphenyl)-(1-methyl-2-phenylethylidene)amine (15)	7.23 (<i>E</i>) 7.15 (<i>E</i>) 7.07 (<i>E</i>) 6.99 (<i>E</i>) 6.90 (<i>E</i>)	d t t d dd	7.2 7.2 7.2 7.6 8.0, 6.8	2 2 1 2 1

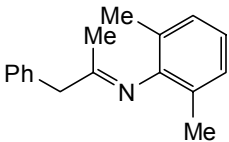
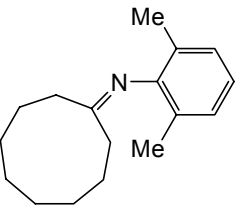
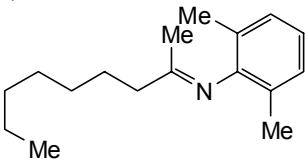
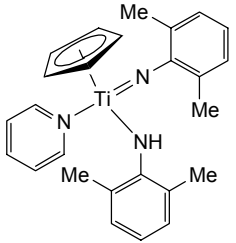
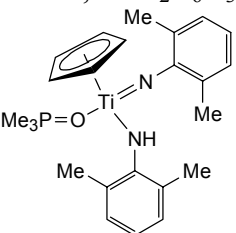
<p>15, cont.</p> 	<p>(<i>Z</i>) aromatic protons not well-resolved</p> <p>3.55 (<i>E</i>)</p> <p>3.04 (<i>Z</i>)</p> <p>2.05 (<i>Z</i>)</p> <p>2.00 (<i>E</i>)</p> <p>1.96 (<i>Z</i>)</p> <p>1.25 (<i>E</i>)</p>	<p>s</p> <p>s</p> <p>s</p> <p>s</p> <p>s</p> <p>s</p>	<p>-</p> <p>-</p> <p>-</p> <p>-</p> <p>-</p> <p>-</p>	<p>2</p> <p>2</p> <p>6</p> <p>6</p> <p>3</p> <p>3</p>
<p>Cyclononylidene-(2,6-dimethylphenyl)amine (17)</p> 	<p>6.99</p> <p>6.86</p> <p>2.62</p> <p>2.11</p> <p>2.07</p> <p>1.97</p> <p>1.68</p> <p>1.68-1.48</p>	<p>d</p> <p>t</p> <p>m</p> <p>m</p> <p>s</p> <p>m</p> <p>m</p> <p>m</p>	<p>7.6</p> <p>7.2</p> <p>-</p> <p>-</p> <p>-</p> <p>-</p> <p>-</p> <p>-</p>	<p>2</p> <p>1</p> <p>2</p> <p>2</p> <p>6</p> <p>2</p> <p>2</p> <p>8</p>
<p>(2,6-Dimethylphenyl)-(1-methyloctylidene)amine (16)</p> 	<p>7.02 (<i>E</i>)</p> <p>6.91 (<i>E</i>)</p> <p>2.23 (<i>E</i>)</p> <p>2.00 (<i>E</i>)</p> <p>1.67 (<i>E</i>)</p> <p>1.30 (<i>E</i>)</p> <p>1.35-0.82 (<i>E</i>)</p>	<p>d</p> <p>t</p> <p>t</p> <p>s</p> <p>quintet</p> <p>s</p> <p>m</p>	<p>7.2</p> <p>7.2</p> <p>7.5</p> <p>-</p> <p>7.4</p> <p>-</p> <p>-</p>	<p>2</p> <p>1</p> <p>2</p> <p>6</p> <p>2</p> <p>3</p> <p>13</p>
<p>Cp(py)(ArNH)Ti=NAr (6•py) (Ar = 2,6-Me₂C₆H₃)</p> 	<p>9.00</p> <p>8.73</p> <p>7.12</p> <p>7.02</p> <p>6.87</p> <p>6.73</p> <p>6.69</p> <p>6.32</p> <p>6.01</p> <p>2.30</p> <p>2.19</p>	<p>br s</p> <p>d</p> <p>d</p> <p>d</p> <p>t</p> <p>t</p> <p>t</p> <p>t</p> <p>s</p> <p>s</p> <p>s</p>	<p>-</p> <p>4.8</p> <p>7.2</p> <p>7.6</p> <p>7.6</p> <p>7.2</p> <p>7.6</p> <p>7.6</p> <p>-</p> <p>-</p> <p>-</p>	<p>1</p> <p>2</p> <p>2</p> <p>2</p> <p>1</p> <p>1</p> <p>1</p> <p>2</p> <p>5</p> <p>6</p> <p>6</p>
<p>Cp(Me₃PO)(ArNH)Ti=NAr (6•OPMe₃) (Ar = 2,6-Me₂C₆H₃)</p> 	<p>8.30</p> <p>7.22</p> <p>7.09</p> <p>6.91</p> <p>6.75</p> <p>6.07</p> <p>2.62</p> <p>2.35</p> <p>0.76</p>	<p>s</p> <p>d</p> <p>d</p> <p>t</p> <p>t</p> <p>s</p> <p>s</p> <p>s</p> <p>d</p>	<p>-</p> <p>7.2</p> <p>7.2</p> <p>7.2</p> <p>7.2</p> <p>-</p> <p>-</p> <p>-</p> <p>13.2</p>	<p>1</p> <p>2</p> <p>2</p> <p>1</p> <p>1</p> <p>5</p> <p>6</p> <p>6</p> <p>9</p>

Table S2. $^{13}\text{C}\{^1\text{H}\}$ Spectroscopic Data (C_6D_6)

Compound	δ (ppm)	assignment
Isopropylidene-naphthalen-1-yl-amine	168.7	C
	148.8	C
	134.8	C
	128.3	CH
	126.7	C
	126.3	CH
	126.2	CH
	125.5	CH
	124.0	CH
	123.2	CH
	113.8	CH
	28.1	CH_3
	20.3	CH_3
<i>N'</i> -Isopropylidene- <i>N,N</i> -dimethylhydrazine	163.0	DEPT not done
	47.1	done
	24.8	
	17.5	
Isopropylidene- <i>p</i> -tolyl-amine	167.1	C
	150.0	C
	132.0	C
	129.7	CH
	119.8	CH
	28.3	CH_3
	20.8	CH_3
	19.8	CH_3
<i>tert</i> -Butyl-isopropylidene-amine	161.8	DEPT not done
	54.5	done
	31.2	
	30.7	
	21.3	
Isopropylidene-(1-phenylethyl)-amine	163.5	C
	147.0	C
	128.5	CH
	127.1	CH
	126.7	CH
	59.8	CH
	29.3	CH_3
	25.6	CH_3
	17.6	CH_3
(2,6-Dimethylphenyl)-(1-methyl-2-phenylethylidene)amine (15)	169.2 (<i>E</i>)	C
	167.8 (<i>Z</i>)	C
	149.4 (<i>E</i>)	C
	149.1 (<i>Z</i>)	C
	137.8 (<i>E</i>)	C

Cp(py)(ArNH)Ti=NAr (6•py) (Ar = 2,6-Me ₂ C ₆ H ₃)	159.6	C
	156.7	C
	151.8 (br)	CH
	138.5 (br)	CH
	131.0	C
	127.6	CH
	126.5	C
	123.9 (br)	CH
	119.7	CH
	119.3	CH
	111.4	CH
	110.5	CH
	20.5	CH ₃
20.0	CH ₃	
Cp(Me ₃ PO)(ArNH)Ti=NAr (6•OPMe₃) (Ar = 2,6-Me ₂ C ₆ H ₃)	159.5	C
	158.1	C
	131.8	C
	128.6	CH
	127.9	CH
	126.2	C
	118.8	CH
	118.7	CH
	110.4	CH
	20.7 (d, <i>J</i> = 2 Hz)	CH ₃
	15.6	CH ₃
	14.8	CH ₃

V. Kinetic Studies of Allene Hydroamination Catalyzed by **6•py**.

A. Preparation of stock solutions. Stock solution #1 was prepared by dissolution of 1.45 g (12.0 mmol) of 2,6-dimethylaniline, 38.8 mg (0.09 mmol) of (imido)Ti complex **6•py**, and 47.6 mg (0.28 mmol) of 1,3,5-trimethoxybenzene in C₆D₆ in a 5.0 ± 0.05 mL volumetric flask ([ArNH₂] = 2.75 M, [1,3,5-C₆H₃(OMe)₃] = 0.056 M).

Stock solution #2 was prepared by dissolution of 395 mg (4.99 mmol) of pyridine in 5.0 mL of C₆D₆ in a 5.0 mL volumetric flask ([py] = 0.999 M).

Stock solution #3 was prepared by condensation of 238 torr x 138 mL of allene onto a frozen (77 K) solution of 31 mg of dimethylzirconocene in *ca.* 2 mL of C₆D₆. The allene concentration of this solution was determined in the following manner: to a solution of 6.4 mg (0.038 mmol) of 1,3,5-trimethoxybenzene in *ca.* 0.4 mL of C₆D₆ was added via syringe 100 μL of stock solution #3. A single-pulse ¹H NMR spectrum was acquired and the Ar-*H* (δ 6.24) and H₂C=C=CH₂ (δ 4.49) resonances were integrated, giving the ratio of C₃H₄:1,3,5-C₆H₃(OMe)₃ = 0.69; thus, [C₃H₄] = (0.038 mmol)(0.69)/0.100 mL = 0.26 M. Reactions conducted in the absence of Cp₂ZrMe₂ as an internal desiccant were plagued by irreproducible concentrations of **6•py**, presumably due to decomposition induced by traces of moisture and/or oxygen. The stock solutions were stored at -35 °C.

Stock solution #4 was prepared by dissolution of 49.0 mg of imidotitanium complex **6•py** in C₆D₆ in a 1.00 ± 0.01 mL volumetric flask.

Stock solution #5 was prepared by adding 100 μL of stock solution #2 to a 1.00 ± 0.01 mL volumetric flask containing 34.5 mg (0.205 mmol) of 1,3,5-trimethoxybenzene. C₆D₆ was added to bring the final volume to 1.00 mL.

B. Determination of order in [6•py] (Table S3). In a typical run a 1.00 ± 0.01 mL volumetric flask was charged with 167 mg (1.38 mmol) of 2,6-dimethylaniline, 346 μL of stock solution #3, 91 μL of stock solution #5, and a volume of stock solution #4 that provided the desired concentration of **6•py** (Table S3). C₆D₆ was added to bring the total volume to 1.00 mL and the solution was transferred to an NMR tube, fitted with a Cajon ultratorr adapter, frozen, and flame-sealed under dynamic vacuum. The tube was inserted into a Bruker AMX 300 MHz NMR spectrometer whose probe temperature had been calibrated immediately beforehand employing a neat ethylene glycol standard. Single-pulse ¹H NMR spectra were acquired at regular time intervals (typically 60-240 s) through at least five half-lives; the disappearance of allene with time was monitored. Absolute reactant, product, and catalyst concentrations were obtained by integration comparison with the internal standard. Within experimental error, [6•py] was constant throughout each run.

C. Determination of order in [ArNH₂] (a) Conditions of excess [ArNH₂] (Table S4). In a typical run a 1.00 ± 0.01 mL volumetric flask was charged with a quantity of 2,6-dimethylaniline that varied with the run (run 5: 109.0 mg; run 6: 135.2 mg; run 7: 189.7 mg), 335 μL of stock solution #3, 91 μL of stock solution #5, and 79 μL of stock solution #4. C₆D₆ was added to bring the final volume to 1.00 mL. At this point, the sample was prepared and the kinetic run was performed as described in section B.

D. Determination of order in [ArNH₂] (b) Confirmation by method of initial rates (Table S5). A 1.00 ± 0.01 mL volumetric flask was charged with a quantity of 2,6-dimethylaniline that varied with the run (run 8: 5.8 mg; run 9: 19.4 mg), 335 μL of stock solution #3, 91 μL of stock solution #5, and 90 μL of stock solution #4. C₆D₆ was added to bring the final volume to 1.00 mL and the sample was

prepared as described in section B. Absolute reactant, product, and catalyst concentrations were obtained by integration comparison with the internal standard. Reaction progress (growth of imine product) was followed to 15% conversion versus the limiting reagent. A plot of $[\text{ArN}=\text{CMe}_2]$ versus time was linear in this region; the slope provided the initial rate constant k_{obs} .

E. Determination of order in [py] (Table S6). In a typical run a 1.00 ± 0.01 mL volumetric flask was charged with 500 μL of stock solution #1, 346 μL of stock solution #3, and a volume of stock solution #2 that provided the desired concentration of pyridine (Table S6). C_6D_6 was added to bring the final volume to 1.00 mL and the solution was transferred to an NMR tube, fitted with a Cajon ultratorr adapter, frozen, and flame-sealed under dynamic vacuum. The kinetic run was performed as described in section B.

Table S3. Dependence of k_{obs} on [6•py]

Run (65.0 ± 0.2 °C)	[6•py] $\times 10^3$ (M)	[2,6-Me ₂ C ₆ H ₃ NH ₂] ₀ (M)	[H ₂ C=C=CH ₂] ₀ (M)	[py] (M)	$k_{\text{obs}} \times 10^4$ (M ⁻¹ s ⁻¹)
1	3.97	1.38	0.072	0.009	8.4 ± 0.2
2	4.48	1.38	0.09	0.009	10.1 ± 0.2
3	8.49	1.38	0.09	0.009	19.8 ± 0.2
4	11.50	1.38	0.09	0.009	25.2 ± 0.3

$$\text{rate} = -d[\text{H}_2\text{C}=\text{C}=\text{CH}_2]/dt = k_{\text{obs}}[\text{H}_2\text{C}=\text{C}=\text{CH}_2] \quad (1)$$

$$k = k_{\text{obs}}[\text{py}][\text{6•py}]^{-1} \quad (2)$$

$$k (65.0 \pm 0.2 \text{ °C}) = (2.00 \pm 0.09) \times 10^{-3} \text{ M}^{-1}\text{s}^{-1} \quad (3)$$

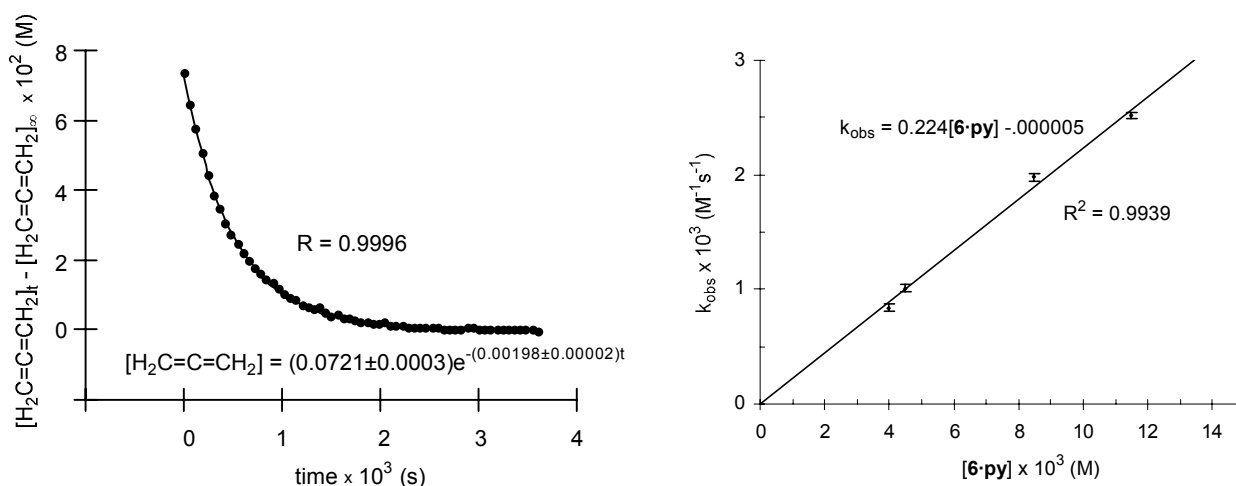


Figure S1. Representative exponential decay plot, run #3 (left); plot of [6•py] versus k_{obs} (right).

Table S4. Dependence of k_{obs} on $[\text{ArNH}_2]$ (conditions of excess $[\text{ArNH}_2]$)

Run (65.0 ± 0.2 °C)	$[\text{ArNH}_2]_0$ (M)	$[\text{H}_2\text{C}=\text{C}=\text{CH}_2]_0$ (M)	$[\text{py}]$ (M)	$[\mathbf{6}\cdot\text{py}] \times 10^3$ (M)	$k_{\text{obs}} \times 10^4$ ($\text{M}^{-1}\text{s}^{-1}$)
5	0.90	0.09	0.009	4.8	6.90 ± 0.16
6	1.13	0.09	0.009	4.8	7.14 ± 0.13
7	1.57	0.09	0.009	4.4	7.47 ± 0.22

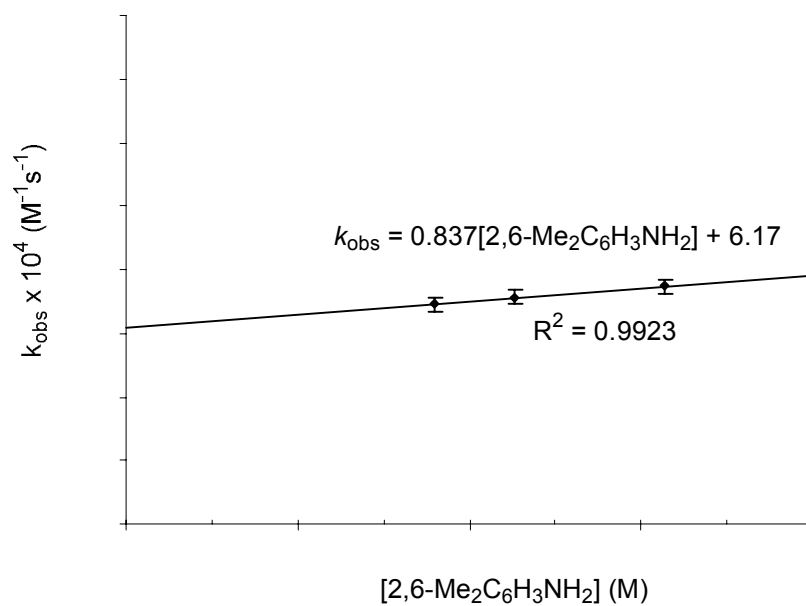
**Figure S2.** Plot of $[2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NH}_2]$ versus k_{obs} .

Table S5. Dependence of k_{obs} on $[\text{ArNH}_2]$ (method of initial rates)

Run (51.0 ± 0.2 °C)	$[\text{ArNH}_2]_0$ (M)	$[\text{H}_2\text{C}=\text{C}=\text{CH}_2]_0$ (M)	$[\text{py}]$ (M)	$[\mathbf{6\cdot py}] \times 10^3$ (M)	$k_{\text{obs}} \times 10^5$ ($\text{M}^{-1}\text{s}^{-1}$)
8	0.069	0.113	0.009	5.7	1.84 ± 0.02
9	0.178	0.110	0.009	5.6	1.96 ± 0.02

$$[\text{ArNH}_2]_0 (\text{run 9}) / [\text{ArNH}_2]_0 (\text{run 8}) = 2.58 \quad (\text{S4})$$

$$k_{\text{obs}} (\text{run 9}) / k_{\text{obs}} (\text{run 8}) = 1.07 \pm 0.03 \quad (\text{S5})$$

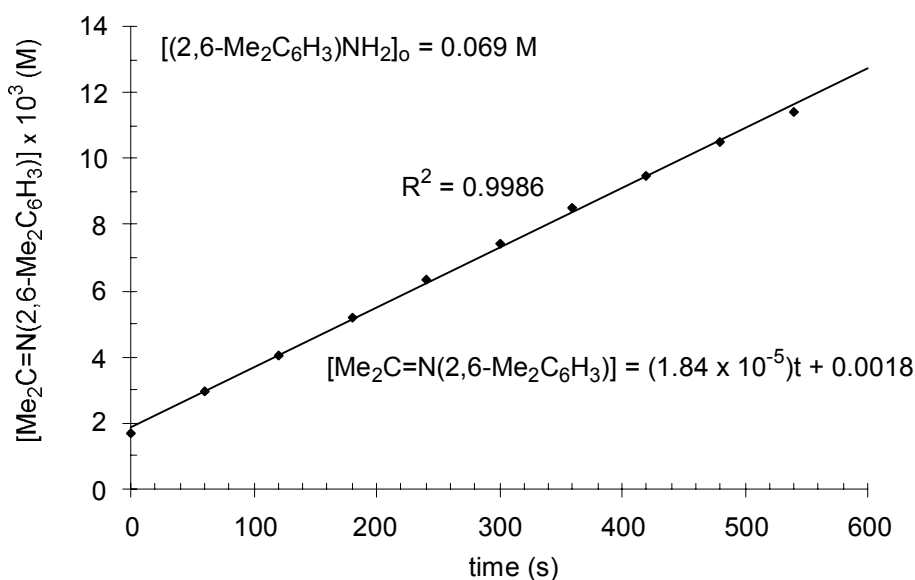
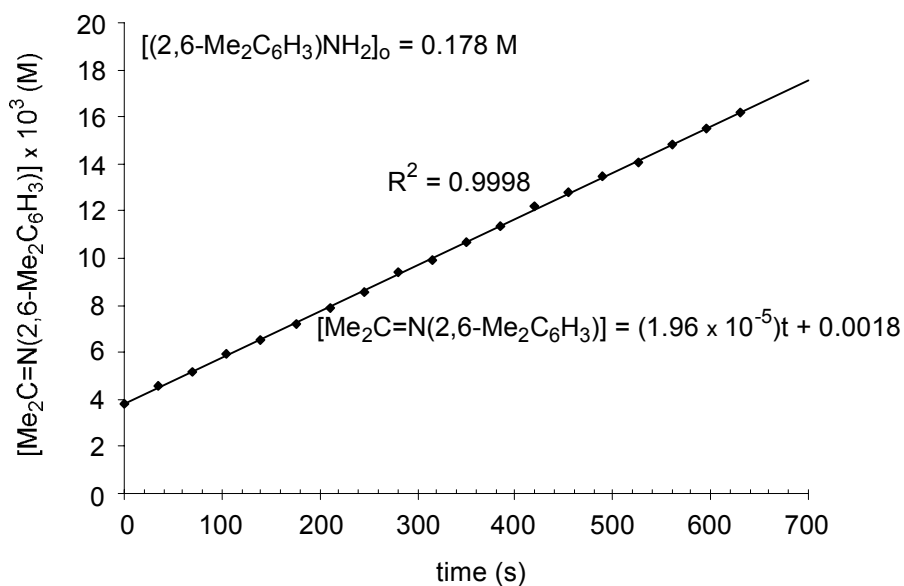
**Figure S3.** Initial rates study (to 15% conversion), Run #8; plot of $[\text{Me}_2\text{C}=\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)]$ vs time.**Figure S4.** Initial rates study (to 15% conversion), Run #9; plot of $[\text{Me}_2\text{C}=\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)]$ vs time.

Table S6. Dependence of k_{obs} on $[\text{py}]^{-1}$

Run (65 ± 0.2 °C)	$[\text{ArNH}_2]_0$ (M)	$[\text{H}_2\text{C}=\text{C}=\text{CH}_2]_0$ (M)	$[\text{py}]$ (M)	$[\mathbf{6}\cdot\text{py}] \times 10^3$ (M)	$k_{\text{obs}} \times 10^4$ ($\text{M}^{-1}\text{s}^{-1}$)
10	1.38	0.09	0.009	5.0	11.17 ± 0.33
11	1.38	0.09	0.018	5.0	5.25 ± 0.09
12	1.38	0.09	0.027	5.0	3.52 ± 0.05
13	1.38	0.09	0.036	5.0	2.81 ± 0.05

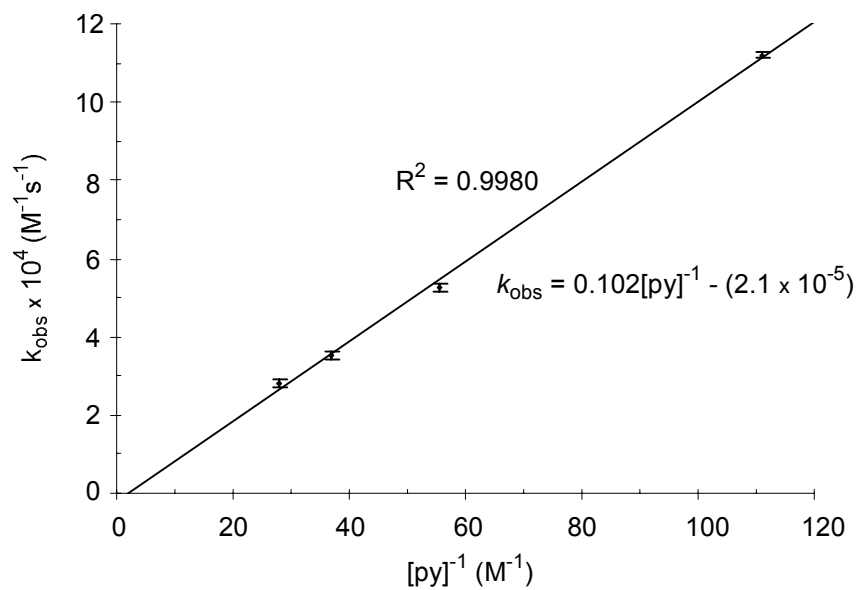
**Figure S5.** Plot of k_{obs} versus $[\text{py}]^{-1}$.

Table S7. Crystal Data for $6 \cdot \text{OPMe}_3 \cdot (\text{C}_5\text{H}_{12})_{0.25}$.

A. Crystal Data

Empirical Formula	TiPON ₂ C _{25.25} H ₃₈
Formula Weight	464.46
Crystal Color, Habit	Yellow, prism
Crystal Dimensions	0.28 x 0.22 x 0.06 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 27.715(2) Å b = 13.2652(9) Å c = 14.5729(9) Å
Space Group	Pbcn (#60)
Z value	8
D _{calc}	1.144 g/cm ³
F ₀₀₀	1988.00
μ (MoKα)	3.94 cm ⁻¹

B. Intensity Measurements

Diffractometer	SMART CCD
Radiation	MoKα (λ = 0.71069 Å)
Detector Position	60.00 mm
Exposure Time	10.0 seconds per frame
Scan Type	ω (0.3 degrees per frame)
2θ _{max}	46.5°
No. of Reflections Measured	Total: 20747 Unique: 4305 (R _{int} = 0.091)
Corrections	Lorentz-polarization Absorption (Tmax = 0.98 Tmin = 0.87)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma \omega (F_o - F_c)^2$
Least Squares Weights	$\omega = 1/\sigma^2(F_o) = [\sigma_c^2(F_o) + (p^2/4) F_o^2]^{-1}$
p-factor	0.0300
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I > 3.00σ(I))	1756
No. Variables	141
Reflection/Parameter Ratio	12.45
Residuals: R; R _w ; R _{all}	0.064; 0.086; 0.133
Goodness of Fit Indicator	2.69
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.55 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.29 e ⁻ /Å ³

Table S8. Atomic coordinates and B_{iso}/B_{eq} and occupancy

atom	x	y	z	B	occ
Ti(1)	0.60281(7)	0.3513(1)	0.1350(1)	2.28(5)	
P(1)	0.6257(1)	0.3299(2)	0.3515(2)	2.82(8)	
O(1)	0.5973(2)	0.3048(4)	0.2654(4)	2.4257	
N(1)	0.6290(3)	0.4708(6)	0.1470(5)	2.0485	
N(2)	0.6579(3)	0.2735(6)	0.0868(6)	2.6244	
C(1)	0.5225(4)	0.2737(8)	0.1240(8)	3.3(3)	
C(2)	0.5179(4)	0.3762(8)	0.1215(7)	3.3(3)	
C(3)	0.5409(4)	0.4112(8)	0.0407(8)	3.3(3)	
C(4)	0.5587(4)	0.3269(8)	0.0043(7)	2.9(3)	
C(5)	0.5478(4)	0.2424(8)	0.0484(8)	3.0(3)	
C(6)	0.6210(4)	0.4584(8)	0.3828(7)	4.1(3)	
C(7)	0.6032(4)	0.2566(8)	0.4424(8)	3.7(3)	
C(8)	0.6882(5)	0.3053(9)	0.3385(8)	5.0(3)	
C(9)	0.6445(4)	0.5693(7)	0.1495(6)	1.9(2)	
C(10)	0.6146(4)	0.6481(8)	0.1792(6)	2.2(2)	
C(11)	0.6313(4)	0.7461(8)	0.1824(7)	2.7(2)	
C(12)	0.6785(4)	0.7679(8)	0.1552(7)	3.3(3)	
C(13)	0.7078(4)	0.6911(8)	0.1255(7)	3.1(3)	
C(14)	0.6916(4)	0.5905(8)	0.1224(7)	2.4(2)	
C(15)	0.5635(4)	0.6301(8)	0.2057(7)	3.6(3)	
C(16)	0.7236(4)	0.5090(9)	0.0902(8)	4.1(3)	
C(17)	0.6621(4)	0.1872(8)	0.0328(7)	2.2(2)	
C(18)	0.6803(4)	0.1916(8)	0.0579(7)	2.6(2)	
C(19)	0.6824(4)	0.1046(8)	0.1100(7)	3.3(3)	
C(20)	0.6678(4)	0.0149(8)	0.0758(8)	3.6(3)	
C(21)	0.6500(4)	0.0081(8)	0.0130(7)	3.1(3)	
C(22)	0.6479(4)	0.0940(8)	0.0680(7)	2.5(2)	
C(23)	0.6955(4)	0.2912(8)	0.0953(7)	3.4(3)	
C(24)	0.6333(4)	0.0837(8)	0.1662(7)	3.6(3)	
C(25)	0.5000	0.088(3)	0.2500	5(1)	1/4
C(26)	0.516(2)	0.008(4)	0.208(3)	4(1)	1/4
C(27)	0.530(1)	0.019(2)	0.128(2)	7.9(9)	1/2
C(28)	0.494(2)	0.074(3)	0.167(3)	4(1)	1/4
C(100)	0.5375	0.3261	0.0661	0.2000	0.000
H(1)	0.677(3)	0.315(6)	0.070(6)	3.4473	
H(2)	0.5098	0.2377	0.1712	4.6154	
H(3)	0.5028	0.4215	-0.1686	3.7059	
H(4)	0.5413	0.4817	-0.0217	3.7313	
H(5)	0.5772	0.3333	0.0613	3.4273	
H(6)	0.5572	0.1753	-0.0314	3.8543	
H(7)	0.6305	0.5003	-0.3382	4.6386	
H(8)	0.6379	0.4690	-0.4391	4.6386	
H(9)	0.5864	0.4713	-0.3978	4.6386	
H(10)	0.5697	0.2710	-0.4570	4.0817	
H(11)	0.6206	0.2710	-0.5008	4.0817	
H(12)	0.6061	0.1859	-0.4338	4.0817	
H(13)	0.6935	0.2319	-0.3250	5.9001	
H(14)	0.7064	0.3177	-0.3925	5.9001	
H(15)	0.7025	0.3403	-0.2890	5.9001	
H(16)	0.6093	0.8023	-0.2025	3.6790	
H(17)	0.6909	0.8390	-0.1580	3.9526	
H(18)	0.7414	0.7081	-0.1069	3.4991	
H(19)	0.5415	0.6255	-0.1512	3.8644	
H(20)	0.5486	0.6808	-0.2434	3.8644	

H(21)	0.5587	0.5661	-0.2362	3.8644
H(22)	0.7122	0.4746	-0.0356	5.2984
H(23)	0.7300	0.4582	-0.1347	5.2984
H(24)	0.7566	0.5338	-0.0716	5.2984
H(25)	0.6944	0.1119	0.1729	3.7954
H(26)	0.6683	-0.0452	0.1148	3.7540
H(27)	0.6419	-0.0572	-0.0371	4.0995
H(28)	0.7215	0.3174	0.0597	3.8264
H(29)	0.7078	0.2830	0.1574	3.8264
H(30)	0.6699	0.3369	0.0967	3.8264
H(31)	0.6605	0.0977	-0.2085	3.6158
H(32)	0.6088	0.1341	-0.1850	3.6158
H(33)	0.6209	0.0200	-0.1830	3.6158

Table S9. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ti(1)	0.023(1)	0.036(1)	0.027(1)	0.003(1)	0.001(1)	-0.004(1)
P(1)	0.032(2)	0.042(2)	0.033(2)	0.001(2)	0.004(2)	0.002(2)
O(1)	0.0307	0.0307	0.0307	0.0000	0.0000	0.0000
N(1)	0.0259	0.0259	0.0259	0.0000	0.0000	0.0000
N(2)	0.0332	0.0332	0.0332	0.0000	0.0000	0.0000

Table S10. Bond Lengths (Å)

atom	atom	distance	atom	atom	distance
TI1	O1	2.017(6)	TI1	N1	1.752(8)
TI1	N2	1.975(9)	TI1	C1	2.46(1)
TI1	C2	2.38(1)	TI1	C3	2.34(1)
TI1	C4	2.40(1)	TI1	C5	2.46(1)
TI1	C100	2.099(2)	P1	O1	1.524(7)
P1	C6	1.77(1)	P1	C7	1.76(1)
P1	C8	1.77(1)	N1	C9	1.38(1)
N2	C17	1.40(1)	C1	C2	1.37(1)
C1	C5	1.38(1)	C1	C100	1.17(1)
C2	C3	1.42(1)	C2	C100	1.18(1)
C3	C4	1.39(1)	C3	C100	1.19(1)
C4	C5	1.40(1)	C4	C100	1.19(1)
C5	C100	1.17(1)	C9	C10	1.40(1)
C9	C14	1.39(1)	C10	C11	1.38(1)
C10	C15	1.49(1)	C11	C12	1.40(1)
C12	C13	1.37(1)	C13	C14	1.41(1)
C14	C16	1.48(1)	C17	C18	1.42(1)
C17	C22	1.40(1)	C18	C19	1.39(1)
C18	C23	1.49(1)	C19	C20	1.35(1)
C20	C21	1.40(1)	C21	C22	1.40(1)
C22	C24	1.50(1)	C25	C26	1.30(5)
C25	C26	1.30(5)	C25	C28	1.24(5)
C25	C28	1.24(5)	C26	C26	1.5(1)
C26	C27	1.23(5)	C26	C28	1.22(6)
C27	C28	1.35(5)			
N2	H1	0.81(8)	C1	H2	0.91
C2	H3	1.01	C3	H4	0.98
C4	H5	0.98	C5	H6	0.96
C6	H7	0.90	C6	H8	0.96
C6	H9	1.00	C7	H10	0.97
C7	H11	1.00	C7	H12	0.95

C8	H13	1.00	C8	H14	0.95
C8	H15	0.95	C11	H16	1.01
C12	H17	1.00	C13	H18	1.00
C15	H19	1.01	C15	H20	0.96
C15	H21	0.97	C16	H22	0.97
C16	H23	0.96	C16	H24	1.01
C19	H25	0.98	C20	H26	0.98
C21	H27	0.96	C23	H28	0.95
C23	H29	0.98	C23	H30	0.93
C24	H31	0.99	C24	H32	0.99
C24	H33	0.94			

Table S11. Bond Angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
O1	TI1	N1	102.3 (3)	O1	TI1	N2	103.8 (3)
O1	TI1	C1	82.3 (3)	O1	TI1	C2	92.7 (3)
O1	TI1	C3	127.5 (4)	O1	TI1	C4	136.7 (3)
O1	TI1	C5	105.3 (3)	O1	TI1	C100	110.1 (2)
N1	TI1	N2	100.9 (4)	N1	TI1	C1	139.5 (4)
N1	TI1	C2	107.0 (4)	N1	TI1	C3	93.2 (4)
N1	TI1	C4	114.7 (4)	N1	TI1	C5	147.3 (4)
N1	TI1	C100	123.3 (3)	N2	TI1	C100	114.2 (3)
O1	P1	C6	112.8 (4)	O1	P1	C7	108.9 (5)
O1	P1	C8	112.0 (5)	C6	P1	C7	108.0 (5)
C6	P1	C8	106.0 (6)	C7	P1	C8	109.0 (6)
TI1	O1	P1	132.9 (4)	TI1	N1	C9	172.4 (7)
TI1	N2	C17	134.1 (7)	C2	C1	C5	109 (1)
C1	C2	C3	108 (1)	C2	C3	C4	107 (1)
C3	C4	C5	108 (1)	C1	C5	C4	108 (1)
N1	C9	C10	122.0 (9)	N1	C9	C14	118.4 (9)
C10	C9	C14	119.5 (9)	C9	C10	C11	121 (1)
C9	C10	C15	122 (1)	C11	C10	C15	117.5 (9)
C10	C11	C12	120 (1)	C11	C12	C13	119 (1)
C12	C13	C14	122 (1)	C9	C14	C13	119 (1)
C9	C14	C16	120 (1)	C13	C14	C16	121 (1)
N2	C17	C18	122 (1)	N2	C17	C22	119.5 (9)
C18	C17	C22	119 (1)	C17	C18	C19	120 (1)
C17	C18	C23	119 (1)	C19	C18	C23	121 (1)
C18	C19	C20	121 (1)	C19	C20	C21	121 (1)
C20	C21	C22	120 (1)	C17	C22	C21	120 (1)
C17	C22	C24	121 (1)	C21	C22	C24	119 (1)
C26	C25	C26	72 (5)	C26	C25	C28	57 (3)
C26	C25	C28	108 (5)	C26	C25	C28	108 (5)
C26	C25	C28	57 (3)	C28	C25	C28	163 (6)
C25	C26	C26	54 (2)	C25	C26	C27	118 (4)
C25	C26	C28	59 (3)	C26	C26	C27	161 (7)
C26	C26	C28	96 (5)	C27	C26	C28	67 (3)
C26	C27	C28	56 (3)	C25	C28	C26	64 (3)
C25	C28	C27	114 (4)	C26	C28	C27	57 (3)
TI1	C100	C1	93.0 (5)	TI1	C100	C2	88.6 (5)
TI1	C100	C3	86.1 (5)	TI1	C100	C4	89.6 (5)
TI1	C100	C5	92.8 (5)				
TI1	N2	H1	105 (7)	C17	N2	H1	109 (7)
TI1	C1	H2	121.2	C2	C1	H2	120.4
C5	C1	H2	130.6	C100	C1	H2	175.3
TI1	C2	H3	115.9	C1	C2	H3	127.9

C3	C2	H3	124.2	C100	C2	H3	176.8
TI1	C3	H4	119.1	C2	C3	H4	123.7
C4	C3	H4	129.2	C100	C3	H4	175.8
TI1	C4	H5	116.4	C3	C4	H5	121.3
C5	C4	H5	130.7	C100	C4	H5	175.2
TI1	C5	H6	120.6	C1	C5	H6	128.9
C4	C5	H6	122.8	C100	C5	H6	176.9
P1	C6	H7	112.7	P1	C6	H8	109.1
P1	C6	H9	107.0	H7	C6	H8	113.2
H7	C6	H9	109.7	H8	C6	H9	104.7
P1	C7	H10	113.3	P1	C7	H11	111.8
P1	C7	H12	114.5	H10	C7	H11	103.6
H10	C7	H12	107.5	H11	C7	H12	105.2
P1	C8	H13	110.1	P1	C8	H14	113.4
P1	C8	H15	113.7	H13	C8	H14	104.7
H13	C8	H15	105.1	H14	C8	H15	109.2
C10	C11	H16	120.2	C12	C11	H16	119.9
C11	C12	H17	120.1	C13	C12	H17	120.5
C12	C13	H18	118.1	C14	C13	H18	120.3
C10	C15	H19	112.3	C10	C15	H20	116.4
C10	C15	H21	113.0	H19	C15	H20	103.8
H19	C15	H21	103.5	H20	C15	H21	106.7
C14	C16	H22	114.3	C14	C16	H23	114.2
C14	C16	H24	113.1	H22	C16	H23	107.0
H22	C16	H24	102.9	H23	C16	H24	104.2
C18	C19	H25	116.7	C20	C19	H25	122.3
C19	C20	H26	119.5	C21	C20	H26	119.8
C20	C21	H27	118.9	C22	C21	H27	120.8
C18	C23	H28	109.5	C18	C23	H29	110.0
C18	C23	H30	111.6	H28	C23	H29	106.8
H28	C23	H30	110.4	H29	C23	H30	108.4
C22	C24	H31	112.3	C22	C24	H32	112.9
C22	C24	H33	115.5	H31	C24	H32	102.6
H31	C24	H33	106.2	H32	C24	H33	106.3

Table S12. Torsion Angles (°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
TI1	O1	P1	C6	-62.9(7)	TI1	O1	P1	C7	177.2(5)
TI1	O1	P1	C8	56.6(7)	TI1	N1	C9	C10	-54(6)
TI1	N1	C9	C14	127(5)	TI1	N2	C17	C18	-111(1)
TI1	N2	C17	C22	68(1)	TI1	C100	C1	C2	-87.5(6)
TI1	C100	C1	C5	92.0(6)	TI1	C100	C2	C1	93.6(6)
TI1	C100	C2	C3	-86.3(6)	TI1	C100	C3	C2	89.7(6)
TI1	C100	C3	C4	-90.9(6)	TI1	C100	C4	C3	86.0(6)
TI1	C100	C4	C5	-93.1(6)	TI1	C100	C5	C1	-92.2(6)
TI1	C100	C5	C4	88.7(6)	P1	O1	TI1	N1	26.7(6)
P1	O1	TI1	N2	-77.9(6)	P1	O1	TI1	C100	159.5(5)
O1	TI1	N1	C9	127(5)	O1	TI1	N2	C17	-101(1)
O1	TI1	C100	C1	13.4(6)	O1	TI1	C100	C2	-57.3(6)
O1	TI1	C100	C3	-131.1(6)	O1	TI1	C100	C4	157.6(6)
O1	TI1	C100	C5	85.2(6)	N1	TI1	N2	C17	154(1)
N1	TI1	C100	C1	134.2(6)	N1	TI1	C100	C2	63.5(6)
N1	TI1	C100	C3	-10.2(6)	N1	TI1	C100	C4	-81.6(6)
N1	TI1	C100	C5	-154.0(6)	N1	C9	C10	C11	-179.1(9)
N1	C9	C10	C15	3(2)	N1	C9	C14	C13	179.6(9)
N1	C9	C14	C16	-1(2)	N2	TI1	N1	C9	-127(5)

N2	TI1	C100	C1	-102.9(6)	N2	TI1	C100	C2	-173.6(6)
N2	TI1	C100	C3	112.7(6)	N2	TI1	C100	C4	41.3(6)
N2	TI1	C100	C5	-31.1(6)	N2	C17	C18	C19	178(1)
N2	C17	C18	C23	0(2)	N2	C17	C22	C21	-177(1)
N2	C17	C22	C24	7(2)	C1	C2	C3	C4	0(1)
C1	C5	C4	C3	-1(1)	C2	C1	C5	C4	1(1)
C2	C3	C4	C5	1(1)	C3	C2	C1	C5	0(1)
C9	N1	TI1	C100	2(6)	C9	C10	C11	C12	0(2)
C9	C14	C13	C12	-1(2)	C10	C9	C14	C13	0(2)
C10	C9	C14	C16	179.4(9)	C10	C11	C12	C13	0(2)
C11	C10	C9	C14	0(2)	C11	C12	C13	C14	1(2)
C12	C11	C10	C15	178(1)	C12	C13	C14	C16	-180(1)
C14	C9	C10	C15	-177.7(9)	C17	N2	TI1	C100	19(1)
C17	C18	C19	C20	1(2)	C17	C22	C21	C20	-2(2)
C18	C17	C22	C21	3(2)	C18	C17	C22	C24	-174(1)
C18	C19	C20	C21	0(2)	C19	C18	C17	C22	-2(2)
C19	C20	C21	C22	1(2)	C20	C19	C18	C23	179(1)
C20	C21	C22	C24	174(1)	C22	C17	C18	C23	179.9(9)