Supporting Information

Title: Diverse Modes of Reactivity of Dialkyl azodicarboxylates with P(III) Compounds: Synthesis, Structure and Reactivity of Products Other than the Morrison-Brunn-Huisgen Intermediate in a Mitsunobu-Type Reaction

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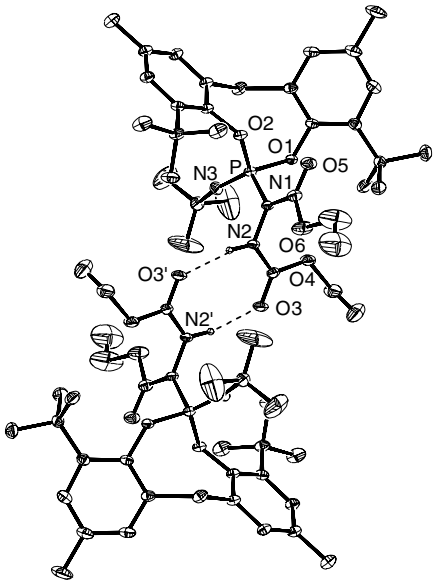


Figure S1. A plot showing the molecular structure of the hydrogen-bonded dimer of **16**; only selected atoms labeled with the hydrogen atoms not shown. The second set in the asymmetric unit is not shown. Selected bond parameters: P-O(1) 1.586(3), P-O(2) 1.593(3), P-N(1) 1.718(4), P-N(3) 1.464(4) Å. P…S 3.237 (2) Å. Hydrogen bonded D-H, H..A, D…A and D-H…A parameters: N(2)-H(N2)…O(3') [dimer] 0.84(4), 2.01(4), 2.833(5)Å, 166(4)°.

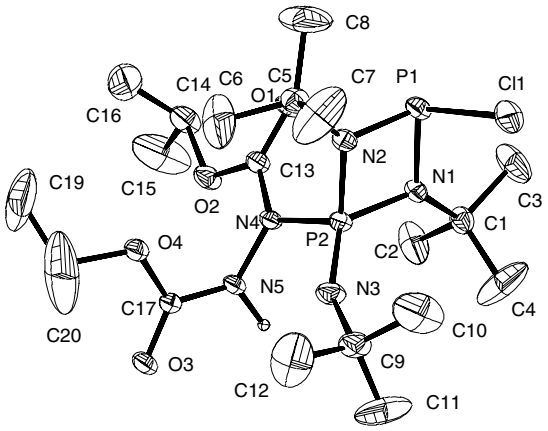


Figure S2. A plot showing the molecular structure of **19**; only selected atoms labeled with the hydrogen atoms [except on N(5)] not shown. The second molecule in the asymmetric unit is not shown. Selected bond parameters: P(1)-N(1) 1.680(3), P(1)-N(2) 1.695(3), P(1)-Cl(1) 2.1425(16), P(2)-N(1) 1.681(3), P(2)-N(2) 1.674(3), P(2)-N(3) 1.488(3), P(2)-N(4) 1.723(3) Å. Hydrogen bonded D-H, H..A, D…A and D-H…A parameters: N(5)-H(N5)…O(3') [dimer] 0.93(4), 1.96(4), 2.892(4)Å, 175(3)°.

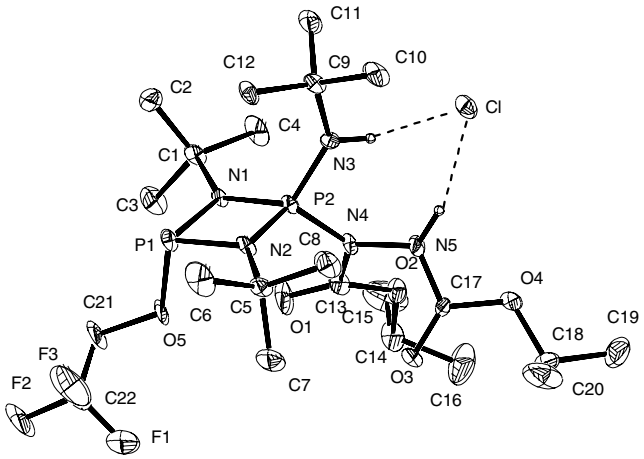


Figure S3 A plot showing the molecular structure of compound **21**. Selected bond parameters: P(1)-N(1) 1.707(7), P(1)-N(2) 1.701(7), P(1) – O(5) 1.605(7), P(2)-N(3) 1.585(7), P(2)-N(1) 1.619(6), P(2)-N(2) 1.630 (7), P(2)-N(4) 1.683(8), N(4)-N(5) 1.436(8), P(1)…P(2) 2.496(3) Å. D-H, H..A, D…A and D-H...A parameters: N(3)-H(3)…Cl 0.86, 2.37, 3.207(8)Å, 163.4°; N(5)-H(5)…Cl 0.86, 2.34, 3.071(9), 142.4°.

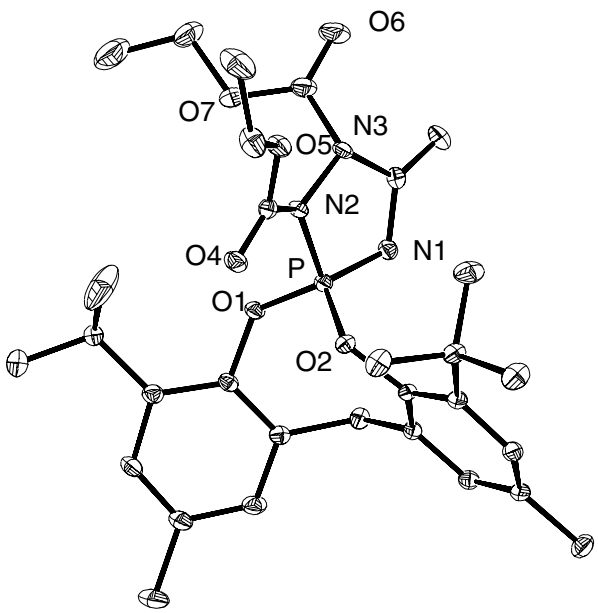


Figure S4. A plot showing the molecular structure of **22**.CH_2Cl_2; only selected atoms labeled with the solvent and hydrogen atoms not shown. Selected bond parameters: P-O(1) 1.556(3), P-O(2) 1.547(3), P-N(1) 1.564(4), P– N(2) 1.656(3) Å.

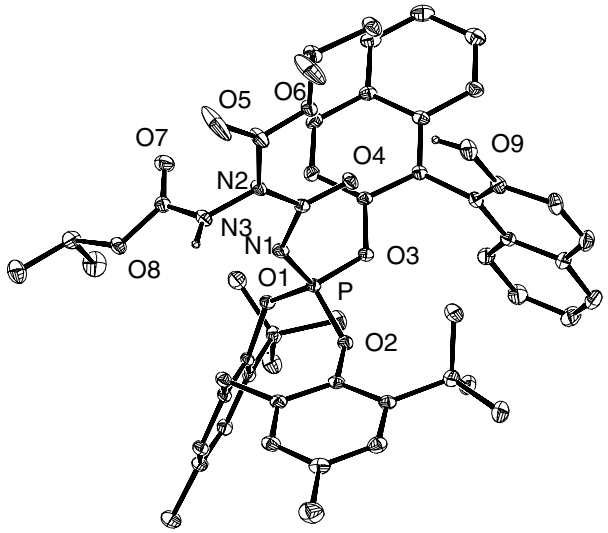


Figure S5 A plot showing the molecular structure of compound **25**.3/2$C_6H_5CH_3$; only selected atoms labeled with the solvent and hydrogen atoms not shown. Selected bond parameters: P-O(1) 1.565(2), P-O(2) 1.545(2), P– O(3) 1.553(3), P-N(1) 1.546(3) Å. D-H, H..A, D…A and D-H…A parameters: N(3)-H(3)…O(8') [dimeric] 0.87, 2.24, 3.062(4)Å, 156.8°; O(9)-H(9)…O(9') [intramolecular] 0.83, 2.31, 2.778(4) Å, 116.1°.

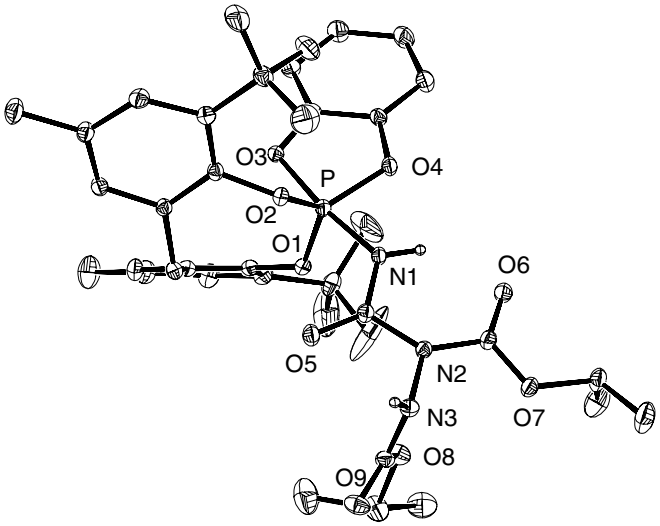


Figure S6 A plot showing the molecular structure of compound **27**.3/2$C_6H_5CH_3$; only selected atoms labeled with the solvent and hydrogen atoms not shown. Selected bond parameters: P-O(1) 1.596(2), P-O(2) 1.587(3), P– O(3) 1.717(2), P-O(4) 1.648(2), P-N(1) 1.738(3) Å, O(3)-P-N(1) 173.16(16)°. D-H, H..A, D…A and D-H…A parameters: N(1)-H(N1)…O(6) [intramolecular] 0.86(3), 1.87(3), 2.613(4)Å, 144(3)°; N(3)-H(N3)…O(9') [dimeric] 0.99(4), 1.99(4), 2.955(5), 166(4)°.

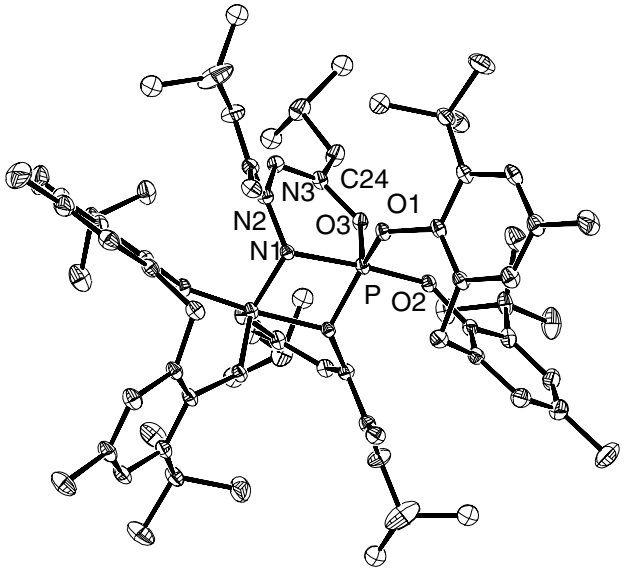


Figure S7. A plot showing the molecular structure of **28**; the asymmetric unit contains only one half of the molecule. The disorder at isopropyl methyl carbons not shown; only selected atoms labeled with the hydrogen atoms not shown. Selected bond parameters: P-O(1) 1.603(3), P-O(2) 1.624(3), P– O(3) 1.622(3), P-N(1) 1.790(3), P-N(1') 1.682(3) Å, O(2)-P-N(1) 174.82(14)°.

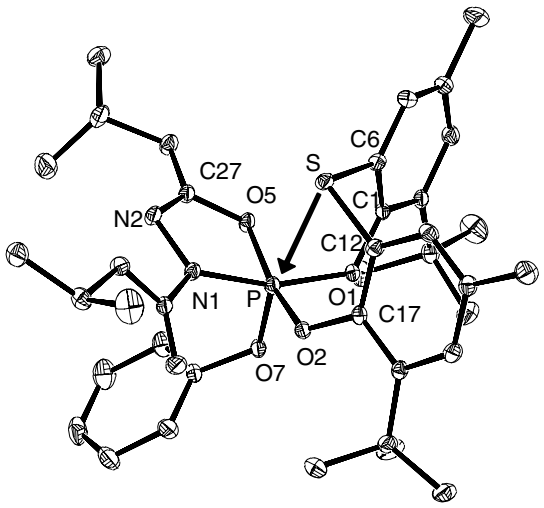


Figure S8 A plot showing the molecular structure of compound **30**; only selected atoms labeled with the solvent and hydrogen atoms not shown. Selected bond parameters: P-O(1) 1.6605(15), P-O(2) 1.6331(17), P– O(5) 1.6894(17), P-O(7) 1.5949(18), P-N(1) 1.7479(19), S→P 2.7942(10) Å, O(1)-P-N(1) 160.76(10), O(2)-P-O(5) 164.67(9), O(7)-P-S 168.66(7)°.

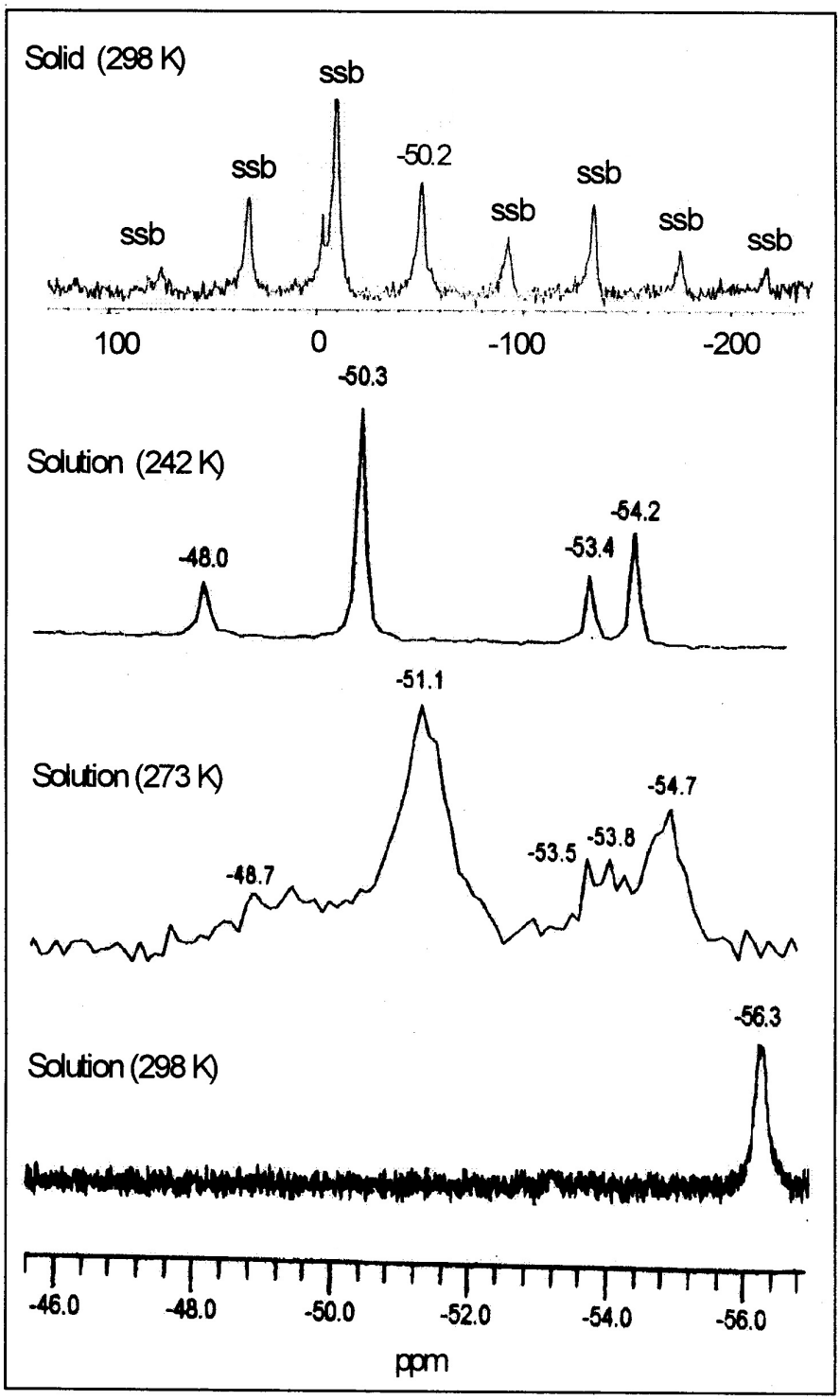


Figure S9 Solution (VT) and solid-state (spinning at 5 kHz) ^{31}P NMR spectra of CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(N-*t*-Bu){N(CO_2Et)NH(CO_2OEt)} (**17**). The spinning side bands were determined by recording the spectrum using a spinning rate of 7 kHz.

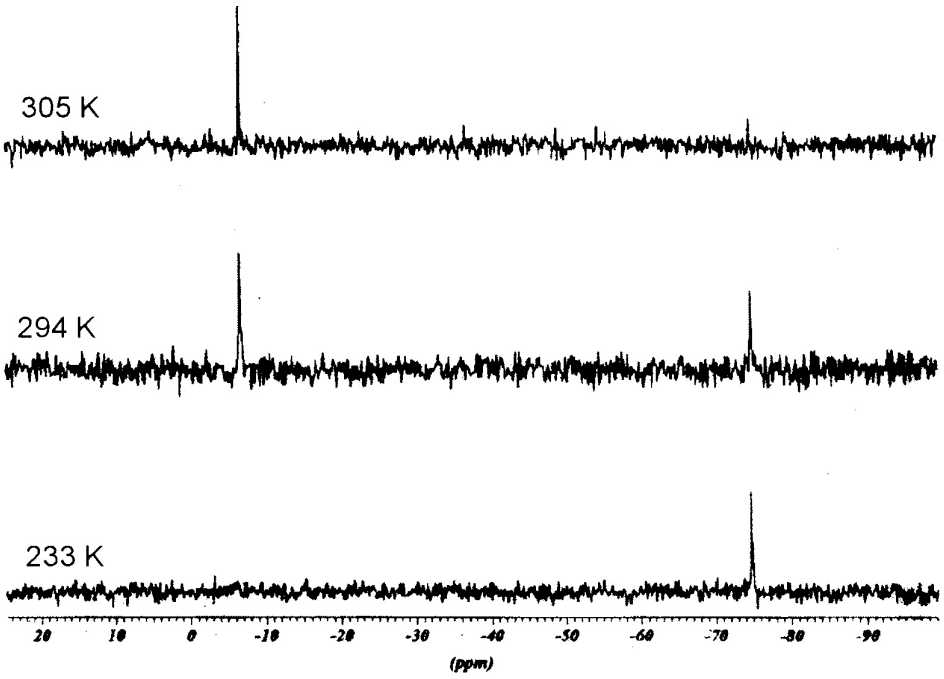


Figure S10 Variable temperature ^{31}P NMR spectra for compound **28**.

Experimental (General Remarks):

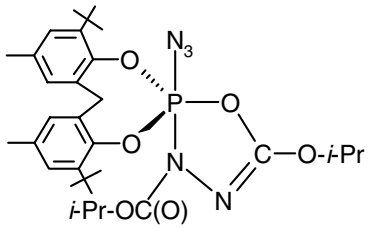
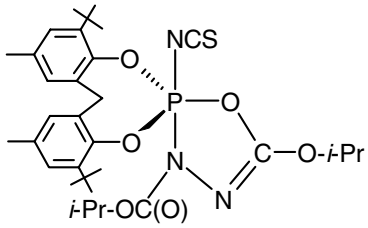
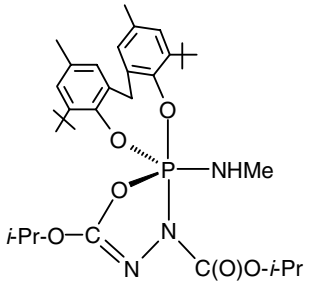
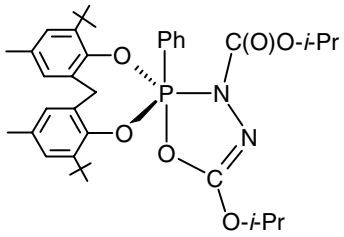
Chemicals and solvents used in this study were purified according to standard procedures.[24] All reactions, unless stated otherwise, were performed in a dry nitrogen atmosphere. ^{1}H, ^{13}C and $^{31}P\{H\}$ NMR spectra were recorded using a 200 MHz spectrometer in $CDCl_3$ or $C_6D_5CD_3$ solutions (unless stated otherwise), with shifts referenced to $SiMe_4$ ($\delta = 0$) or 85 % H_3PO_4 ($\delta = 0$). Variable temperature ^{1}H and ^{31}P NMR spectra were recorded in $C_6D_5CD_3$.

X-ray Crystallography: Single crystal X-ray data were collected on an Enraf-Nonius MACH3 (compounds **16**, **19**, **21**, **22**) or on a Bruker AXS-SMART (**25**, **27**, **28**, **30**) diffractometer, using Mo-K_α ($\lambda = 0.71073$ Å) radiation. The structures were solved by direct methods and refined by full-matrix least squares method using SHELX-97.[25] Structure solution and refinement: Absorption corrections were performed using SADABS program (Sheldrick 96), where applicable. The quality of data for **21** was only good enough to know the structure. In many cases, the terminal ethyl/ isopropyl/ *t*-butyl groups showed disorder as shown by higher thermals. For this reason a few disordered carbon atoms were refined isotropically in **28**; no significant residuals were found in this compound to account for any solvent.

(24) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, Pergamon, Oxford, UK, 1986.

(25) Sheldrick, G. M., *SHELX-97*, *A package for structure solution and refinement*, University of Göttingen, Göttingen, Germany, 1997.

Table S1 ^{31}P NMR chemical shifts of the compounds mentioned in the text

Compound No.	Structure	δ(P) (ppm)
3		-61.0, -69.7 (1:1)
4		-67.3
5		-61.0, -61.7 (1:3)
6		-51.7

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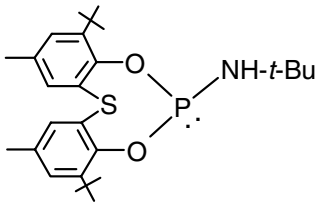
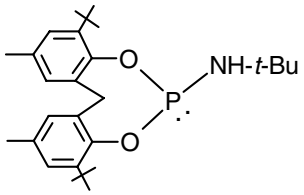
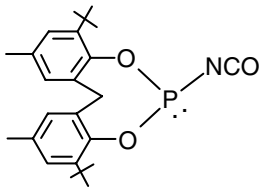
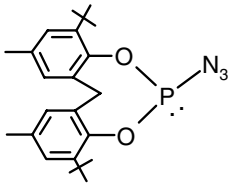
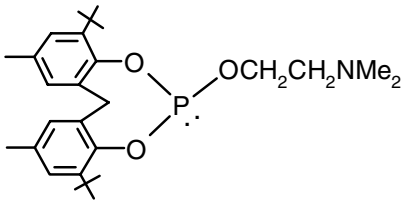
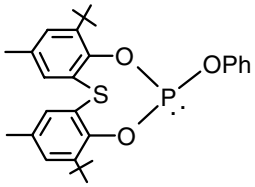
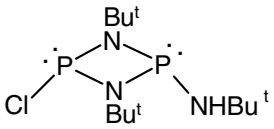
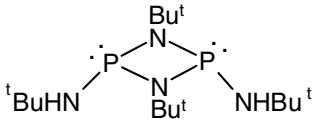
Compound No	Structure	δ(P) ppm
8		138.2
9		141.9
10		121.2
11		136.5
12		129.0
13		136.1
14		135.4, 200.3
15		89.4

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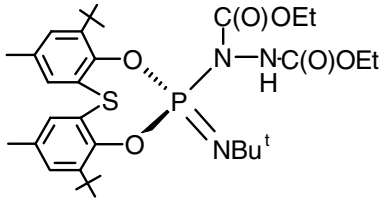
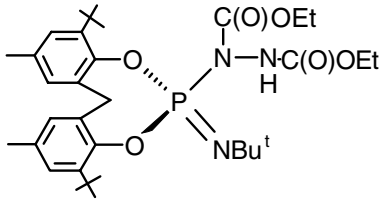
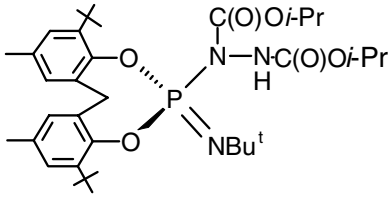
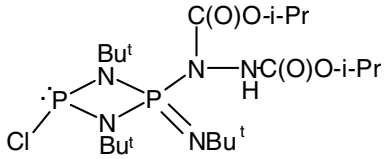
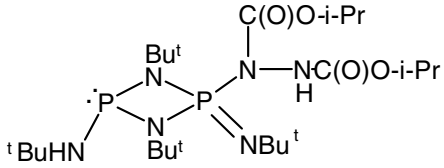
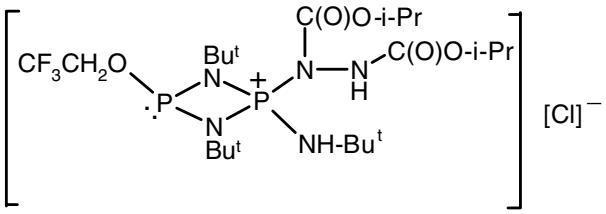
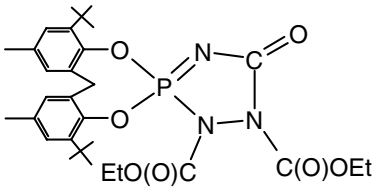
Compound No	Structure	δ(P) ppm
16		-56.2 (br).
17		-56.3 (br)
18		**-**57.6 (br)
19		-38.0, 11.8, 133.6, 140.1
20		-28.9, 68.9
21		11.7, 114.4
22		26.6

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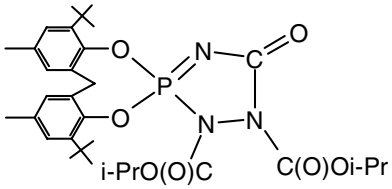
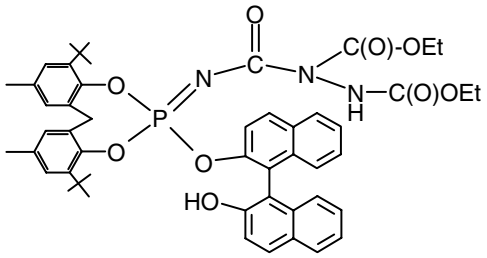
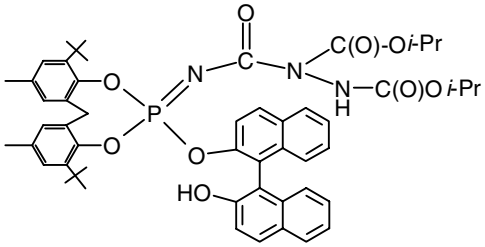
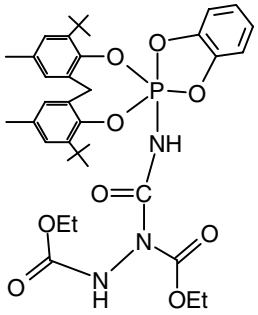
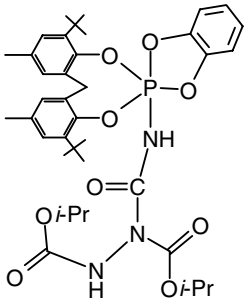
23		27.0
24		-7.4
25		-7.6
26		-59.2
27		-59.3

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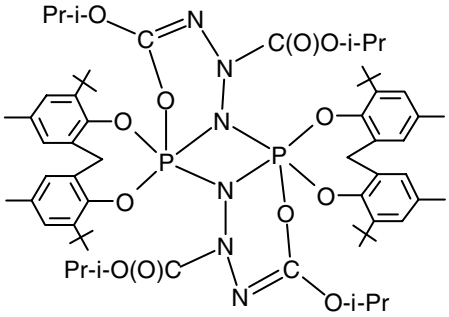
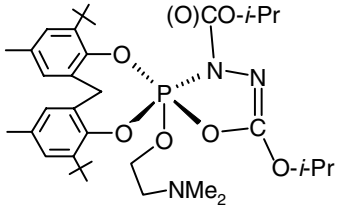
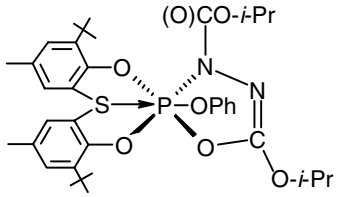
28		15.8 (~ 95%), -6.7 (~ 5%)
29		-59.6, -66.7 (1:5)
30		–67.0