Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Material for

Diaminophosphinoboranes: effective reagents for phosphinoboration of CO_2

*Natalia Szynkiewicz, Anna Ordyszewska, Jarosław Chojnacki and Rafał Grubba**

*Department of Inorganic Chemistry, Faculty of Chemistry,

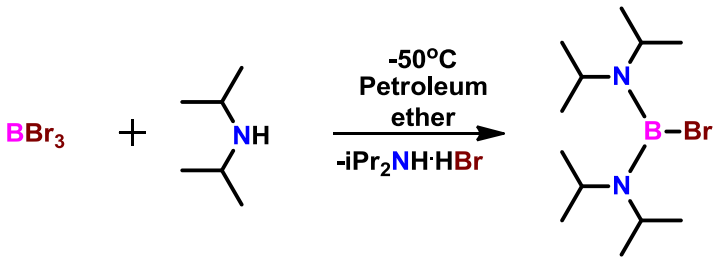
Gdańsk University of Technology, G. Narutowicza St. 11/12. PL-80-233, Gdansk, Poland.

CONTENTS:

Experimental section

All manipulations were carried out under a dry argon atmosphere by using of flame-dried Schlenk-type glassware on a vacuum line or in a glove-box. Solvents were dried by standard procedures over Na(K)/K/Na /benzophenone and distilled under argon. 1D (^{31}P, ^{13}C, ^{11}B and ^{1}H) and 2D NMR spectra in C_6D_6 solution were recorded on a Bruker AV400 MHz spectrometer (external standard TMS for ^{1}H and ^{13}C; 85% H_3PO_4 for ^{31}P) at ambient temperature. Reaction progress was monitored by ^{31}P{^{1}H} and ^{11}B NMR spectra of reaction mixtures. The FTIR spectra of crystalline products were recorded using a Nicolet iS50 FT-IR spectrometer equipped with the Specac Quest single-reflection diamond attenuated total reflectance (ATR) accessory. Spectral analysis was carried out by using the OMNIC software package.

Preparation of $(i\mathrm{Pr_2N)_2BBr}$



A solution of 0.4 mol (56.06 ml, 40.48 g) of iPr_2NH in 150 ml of petroleum ether was added dropwise over 3 h via the dropping funnel to an ice cold solution of 0.1 mol (9.45 ml, 25.05 g) BBr3 dissolved in 500 ml petroleum ether. The solution was allowed to warm up to room temperature and stirred for 48 hours. The resulting precipitate of $iPr_2NH{\cdot}HBr$ was removed by filtration and the solid residue was washed eight times with 20-40 ml of petroleum ether and the solvent was removed from the filtrate. The resulting yellow oil was kept under reduced pressure for 2 h to remove volatile reaction byproducts and the purity of crude residue was checked by means of NMR spectroscopy. Vacuum distillation was not necessary, as the obtained product (23.63g, yield 81.2%) turned out to be very pure.

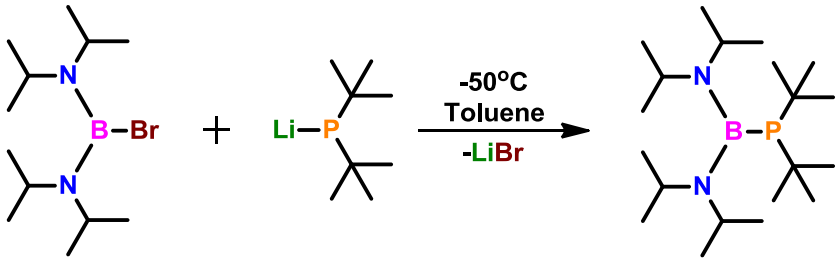
NMR:

^{11}B NMR (C_6D_6): δ 29.4 (s).

^{1}H NMR (C_6D_6): δ 3.49 (sept, $^{3}J_{HH}$ = 7.0 Hz, 4H, C*H*), 1.19 (d, $^{3}J_{HH}$ = 6.8 Hz, 24H, CHC*H*$_3$).

^{13}C{^{1}H} NMR (C_6D_6): δ 47.5 (s, *C*H), 22.8 (s, *C*H$_3$).

Preparation of 1



1

To a solution of *t*Bu$_2$PLi (0.600 g, 3.944 mmol) in 15 cm^3 of toluene cooled to -50°C, (*i*Pr$_2$N)$_2$BBr (1.148 g, 3.944 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 3 hours. The solvent was evaporated and the residue was dried under vacuum (0.01 Torr) for 30 minutes at 40°C to remove all volatiles. The crude product was dissolved in 10 cm^3 of petroleum ether and filtered. Removal of the solvent under vacuum afforded 1.234 g (3.463 mmol) of **1** as a white solid in 88% yield.

NMR :

^{31}P{^{1}H} NMR (C$_6$D$_6$): δ -8.0 (s).

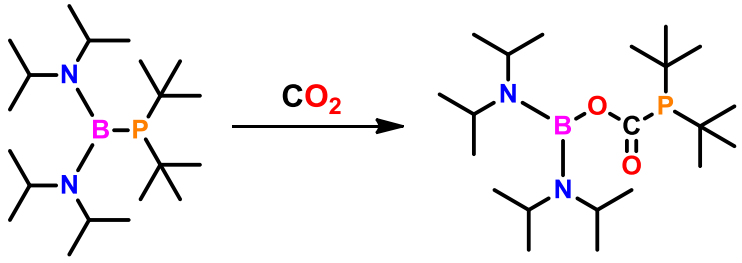
^{11}B NMR (C$_6$D$_6$): δ 39.5 (s).

^{1}H NMR (C$_6$D$_6$): δ 3.92 (dsept, $^3J_{HH}$ = 7.0 Hz, $^4J_{PH}$ = 2.3 Hz, 4H, C*H*), 1.25 (d, $^3J_{PH}$ = 11.5 Hz, 18H, CC*H*$_3$), 1.11 (d, $^3J_{HH}$ = 7.0 Hz, 24H, CHC*H*$_3$).

^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 49.4 (d, $^3J_{PC}$ = 7.3 Hz, *C*HCH$_3$), 33.4 (d, $^2J_{PC}$ = 13.2 Hz, C(*CH*$_3$)$_3$), 31.8 (d, $^1J_{PC}$ = 22.7 Hz, *C*(CH$_3$)$_3$), 25.4 (d, $^4J_{PC}$ = 2.7 Hz, CH*CH*$_3$).

Elemental analysis: calcd. for C$_{20}$H$_{46}$BN$_2$P: C, 67.40; H, 13.01; N, 7.86. Found: C, 67.30; H, 12.87; N, 7.81.

Preparation of 1a



1 **1a**

A solution of **1** (178 mg, 0.5 mmol) in toluene (4 mL) was slowly frozen in a liquid nitrogen bath, evacuated to 0.01 Torr and backfilled with CO_2 (1 atm). The solution was allowed to warm to room temperature and stirred for 3 hours. ^{31}P{^{1}H} of the colourless reaction mixture revealed complete conversion of **1** into **1a**. The solvent was evaporated and the residue was dried under vacuum (0.01 Torr) giving **1a** as a white solid . Yield 87% (175 mg, 0.437 mmol). The solid was

dissolved in 1 cm^3 of petroleum ether and left at -80°C to afford colorless, X-ray quality crystals of **1a** which were dried in vacuum. Yield 78% (157 mg, 0.392 mmol).

NMR:

$^{31}P\{^1H\}$ NMR (C_6D_6): δ 52.4 (s).

^{11}B NMR (C_6D_6): δ 27.4 (s).

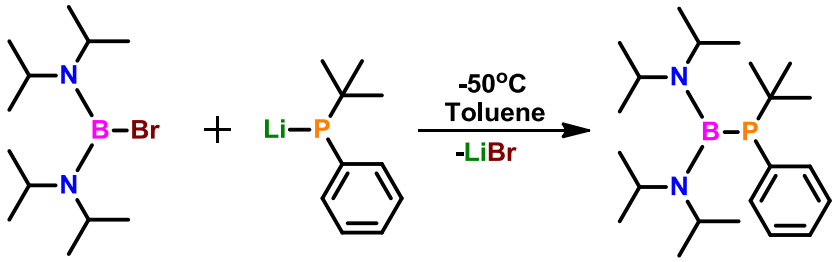
^1H NMR (C_6D_6): δ 3.28 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*), 1.26 (d, $^3J_{PH}$ = 11.5 Hz, 18H, CC*H*$_3$), 1.05 (d, $^3J_{HH}$ = 6.8 Hz, 24H, CHC*H*$_3$).

$^{13}C\{^1H\}$ NMR (C_6D_6): δ 180.2 (d, $^1J_{PC}$ = 30.9 Hz, *C*=O), 46.2 (s, *C*HCH$_3$), 33.6 (d, $^1J_{PC}$ = 22.7 Hz, *C*(CH$_3$)$_3$), 30.6 (d, $^2J_{PC}$ = 12.7 Hz, C(*CH*$_3$)$_3$), 23.8 (s, CH*CH*$_3$).

Elemental analysis: calcd. for $C_{21}H_{46}BN_2O_2P$: C, 63.00; H, 11.58; N, 7.00. Found: C, 62.58; H, 11.42; N, 6.82.

IR (solid): $\tilde{\upsilon}$ = 2998, 2961, 2927, 2866, **1644 (C=O)**, 1474, 1411, 1364, 1329, 1185 1170, 1118, 1087, 1015, 963, 812 cm^{-1}

Preparation of 2



2

To a solution of *t*BuPhPLi (0.516 g, 2.996 mmol) in 15 cm^3 of toluene cooled to -50°C, (*i*Pr$_2$N)$_2$BBr (0.872 g, 2.996 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 3 hours. The solvent was evaporated and the residue was dried under vacuum (0.01 Torr) for 30 minutes at 40°C to remove all volatiles. The crude product was dissolved in 10 cm^3 of petroleum ether and filtered. Removal of the solvent under vacuum afforded 0.934 g (2.482 mmol) of **2** as a yellowish oil in 83% yield. To obtain X-ray quality crystals of **2** the oil was dissolved in 5 cm^3 of petroleum ether and left at -20°C to afford colorless crystals of **2** which were dried in vacuum. Yield 63% (0.710 g, 1.886 mmol).

NMR :

$^{31}P\{^1H\}$ NMR (C_6D_6): δ -26.2 (s).

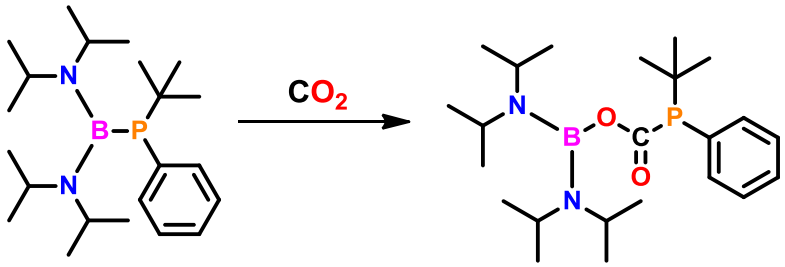
^{11}B NMR (C_6D_6): δ 40.4 (s).

^1H NMR (C_6D_6): δ 7.57 (m, 2H, o-C*H*), 7.12 (m, 2H, m-C*H*), 6.99 (m, 1H, p-C*H*), 4.07 (dsept, $^3J_{HH}$ =7.1 Hz, $^3J_{PH}$ =2.5 Hz, 4H, C*H*), 1.55 (d, $^3J_{PH}$ = 12.1, 9H, C(C*H*$_3$)$_3$), 1.14 (d, $^3J_{HH}$ =7.1 Hz, 24H, CHC*H*$_3$).

$^{13}C\{^1H\}$ NMR (C_6D_6): δ 141.5 (d, $^1J_{PC}$ = 18.2 Hz, *ipso*-C), 132.8 (d, $^2J_{PC}$ = 18.2 Hz, *ortho*-CH*)*, 127.3 (d, $^3J_{PC}$ = 6.4 Hz, *meta*-CH*)*, 124.8 (s, *para*-CH*)*, 49.7 (d, $^3J_{PC}$ = 7.3 Hz, *C*HCH$_3$), 32.0 (d, $^2J_{PC}$ = 11.8 Hz, C*(CH$_3$)$_3$*), 30.8 (d, $^1J_{PC}$ = 13.6 Hz, *C*(CH$_3$)$_3$), 25.1 (s, CH*CH$_3$*).

Elemental analysis: calcd. for $C_{22}H_{42}BN_2P$: C, 70.21; H, 11.25; N, 7.44. Found: C, 69.96; H, 11.15; N, 7.34.

Preparation of 2a



2 **2a**

A solution of **2** (188 mg, 0.5 mmol) in toluene (4 mL) was slowly frozen in a liquid nitrogen bath, evacuated to 0.01 Torr and backfilled with CO_2 (1 atm). The solution was allowed to warm to room temperature and stirred for 3 hours. $^{31}P\{^1H\}$ of the colorless reaction mixture revealed complete conversion of **2** into **2a**. The solvent was evaporated and the residue was dried under vacuum (0.01 Torr) giving **2a** as a colorless oil that slowly crystallize at -20°C giving X-ray quality crystals. Yield 95% (200 mg, 0.476 mmol).

NMR:

$^{31}P\{^1H\}$ NMR (C_6D_6): δ 23.5 (s).

^{11}B NMR (C_6D_6): δ 26.8 (s).

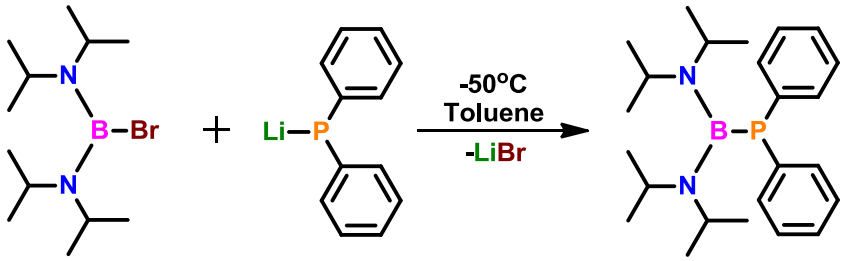
^1H NMR (C_6D_6): δ 7.77 (m, 2H, *o*-C*H*), 7.11 (m, 1H, *p*-C*H*), 7.10 (m, 2H, *m*-C*H*), 3.37 (sept, $^3J_{HH}$ =6.9 Hz, 4H, C*H*), 1.32 (d, $^3J_{PH}$ = 13.2, 9H, CC*H$_3$*), 1.16 (d, $^3J_{HH}$ =6.9Hz, 12H, CHC*H$_3$*), 1.14 (d, $^3J_{HH}$ =6.9Hz, 12H, CHC*H$_3$*).

$^{13}C\{^1H\}$ NMR (C_6D_6): δ 179.1 (d, $^1J_{PC}$ = 14.5 Hz, C=O), 137.2 (d, $^2J_{PC}$ = 20.9 Hz, *ortho*-CH), 131.9 (d, $^1J_{PC}$ = 13.6 Hz, *ipso*-C), 129.5 (s, *para*-CH), 127.8 (d, $^3J_{PC}$ = 8.2 Hz, *meta*-CH), 46.0 (s, *C*HCH$_3$), 31.3 (d, $^1J_{PC}$ = 10.9 Hz, *C*(CH$_3$)$_3$), 27.7 (d, $^2J_{PC}$ = 13.6 Hz, C*(CH$_3$)$_3$*), 23.6 (s, CH*CH$_3$*), 23.2 (s, CH*CH$_3$*).

Elemental analysis: calcd. for $C_{23}H_{42}BN_2O_2P$: C, 65.71; H, 10.07; N, 6.66. Found: C, 65.51; H, 10.00; N, 6.59.

IR (solid): $\tilde{\upsilon}$ = 2958, 2930, 2866, **1664 (C=O),** 1474, 1448, 1414, 1361, 1327, 1186, 1172, 1118, 1085, 1016, 966, 744, 699, 498 cm^{-1}

Preparation of 3



3

To a solution of Ph_2PLi (0.789 g, 4.105 mmol) in 15 cm^3 of toluene cooled to -50°C, $(iPr_2N)_2BBr$ (1.195 g, 4.105 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 3 hours. The solvent was evaporated and the residue was dried under vacuum (0.01 Torr) for 30 minutes at 40°C to remove all volatiles. The crude product was dissolved in 10 cm^3 of petroleum ether and filtered. Keeping the solution at -20°C overnight afforded 1.286 g (3.245 mmol) of **3** as colorless crystals in 79% yield.

NMR :

$^{31}P\{^1H\}$ NMR (C_6D_6): δ -36.1 (s).

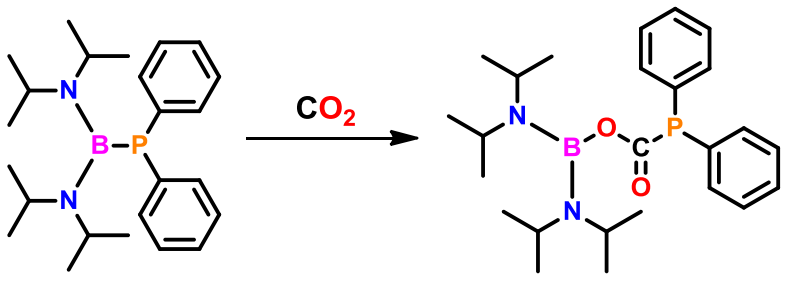
^{11}B NMR (C_6D_6): δ 38.8 (s).

^1H NMR (C_6D_6): δ 7.54 (m, 4H, *o*-C*H*), 7.13 (m, 4H, *m*-C*H*), 7.03 (m, 2H, *p*-C*H*), 3.70 (sept, $^3J_{HH}$ =7.0, 4H, C*H*), 1.14 (d, $^3J_{HH}$ =7.0, 24H, CH_3).

$^{13}C\{^1H\}$ NMR (C_6D_6): δ 139.5 (d, $^1J_{PC}$ = 10.0 Hz, *ipso*-C), 133.9 (d, $^2J_{PC}$ = 16.3 Hz, *ortho*-CH), 127.9 (d, $^3J_{PC}$ = 6.3 Hz, *meta*-CH), 126.3 (s, *para*-CH), 48.8 (d, $^3J_{PC}$ = 3.6 Hz, *C*HCH_3), 24.7 (d, $^4J_{PC}$ = 4.5 Hz, CH*C*H_3).

Elemental analysis: calcd. for $C_{24}H_{38}BN_2P$: C, 72.73; H, 9.66; N, 7.07. Found: C, 72.73; H, 9.68; N, 7.02.

Preparation of 3a



3 **3a**

A solution of **3** (198 mg, 0.5 mmol) in toluene (4 mL) was slowly frozen in a liquid nitrogen bath, evacuated to 0.01 Torr and backfilled with CO_2 (1 atm). The solution was allowed to warm to room temperature and stirred for 65 days. $^{31}P\{^1H\}$ of the colorless reaction mixture revealed

complete conversion of **3** into **3a**. The solvent was evaporated and the residue was dried under vacuum (0.01 Torr) giving **3a** as a colorless oil . Yield 94% (208 mg, 0.472 mmol).

NMR:

$^{31}P\{^{1}H\}$ NMR (C_6D_6): δ -1.0 (s).

^{11}B NMR (C_6D_6): δ 27.0 (s).

^{1}H NMR (C_6D_6): δ 7.78 (m, 4H, *o*-C*H*), 7.09 (m, 4H, *m*-C*H*), 7.07 (m, 2H, *p*-C*H*), 3.29 (sept, $^{3}J_{HH}$ =6.7 Hz, 4H, C*H*), 1.09 (d, $^{3}J_{HH}$ =6.7 Hz, 24H, CHC*H*$_3$).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 177.9 (d, $^{1}J_{PC}$ = 7.3 Hz, C=O), 134.8 (d, $^{2}J_{PC}$ = 20.0 Hz, *ortho*-CH), 132.9 (d, $^{1}J_{PC}$ = 6.4 Hz, *ipso*-C), 129.1 (s, *para*-CH), 128.3 (d, $^{3}J_{PC}$ = 7.3 Hz, *meta*-CH), 45.8 (s, *C*HCH$_3$), 23.3 (s, CH*C*H$_3$).

X-ray structures analysis

Diffraction data of **1a**, **2**, **2a** and **3** were collected on a STOE diffractometer (STOE & Cie GmbH, Darmstadt, Germany) equipped with an image plate detector system IPDS 2T using Mo-Kα (λ = 0.71073 Å) radiation and a graphite monochromator. Good quality single-crystal specimens of **1a**, **2**, **2a** and **3** were manually selected for the X-ray diffraction experiments. The investigated crystal was thermostated in nitrogen stream at 120 K using CryoStream-800 device (Oxford CryoSystem, UK) during the entire experiment. The structures of **1a**, **2**, **2a** and **3** were solved with the Shelxl or Shelxt[1] structure solution programs run under Olex2[2] using Direct Methods or Intrinsic Phasing and refined with the ShelXL[3] refinement package. Non-hydrogen atoms were refined with anisotropic displacement parameters. Positions of the C-H hydrogen atoms were calculated geometrically and taken into account with isotropic temperature factors and refined as constrained, using standard riding model.

Crystallographic data for all structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1906500 (**1a**), 1906496 (**2**), 1906498 (**2a**) and 1906499 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; E mail: deposit@ccdc.cam.ac.uk).

TABLE S1. CRYSTAL DATA AND STRUCTURE REFINEMENT FOR **1A** AND **2**

	1a	**2**
CCDC	1906500	1906496
Empirical formula	$C_{21}H_{46}BN_2O_2P$	$C_{22}H_{42}BN_2P$
M_r [g mol^{-1}]	400.38	376.35
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a [Å]	8.0693 (3)	9.8205 (7)
b [Å]	9.6703 (3)	10.1704 (9)
c [Å]	18.1095 (6)	24.3671 (19)
α [°]	99.245 (3)	91.834 (7)
β [°]	93.689 (3)	92.224 (6)
γ [°]	113.906 (3)	97.271 (6)
V [Å^3]	1261.93 (8)	2410.7 (3)
Z	2	4
Calculated density [Mg m^{-3}]	1.054	1.037
T [K]	120	120
μ [mm^{-1}]	0.13	0.12
Crystal size/mm^3	0.32 × 0.27 × 0.06	0.26 × 0.15 × 0.09
λ [Å]	0.71073 (MoKα)	0.71073 (MoKα)
F(000)	444	832
S	1.03	1.01
R_{int}	0.032	0.075
No. of measured, independent, observed [I > 2σ(I)] reflections	17431, 6782, 5753	29277, 12971, 8086
Final R indices [I>2σ(I)]	R_1 = 0.042	R_1 = 0.061
	wR_2 = 0.110	wR_2 = 0.150
R indices (all data)	R_1 = 0.051	R_1 = 0.103
	wR_2 = 0.116	wR_2 = 0.169
Largest diff. peak/hole / e Å^{-3}	0.53/-0.42	0.42/-0.50

TABLE S2. CRYSTAL DATA AND STRUCTURE REFINEMENT FOR **2A** AND **3**

	2a	**3**
CCDC	1906498	1906499
Empirical formula	$C_{23}H_{42}BN_2O_2P$	$C_{24}H_{38}BN_2P$
M_r [g mol^{-1}]	420.37	396.34
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
a [Å]	9.6850 (12)	10.285 (1)
b [Å]	39.588 (4)	10.3928 (10)
c [Å]	13.4734 (14)	11.6466 (15)
α [°]	90	103.370 (9)
β [°]	91.441 (9)	96.366 (9)
γ [°]	90	91.470 (8)
V [Å^3]	5164.2 (10)	1202.0 (2)
Z	8	2
Calculated density [Mg m^{-3}]	1.081	1.095
T [K]	120	120
μ [mm^{-1}]	0.13	0.13
Crystal size/mm^3	0.4 × 0.28 × 0.06	0.29 × 0.18 × 0.11
λ [Å]	0.71073 (MoKα)	0.71073 (MoKα)
F(000)	1840	432
S	1.05	1.02
R_{int}	0.078	0.016
No. of measured, independent, observed [I > 2σ(I)] reflections	32809, 9362, 5862	16084, 6461, 5629
Final R indices [I>2σ(I)]	R_1 = 0.098	R_1 = 0.034
	wR_2 = 0.271	wR_2 = 0.086
R indices (all data)	R_1 = 0.146	R_1 = 0.041
	wR_2 = 0.319	wR_2 = 0.090
Largest diff. peak/hole / e Å^{-3}	0.69/-0.55	0.32/-0.21

Single crystal X-ray structure analysis of 1a

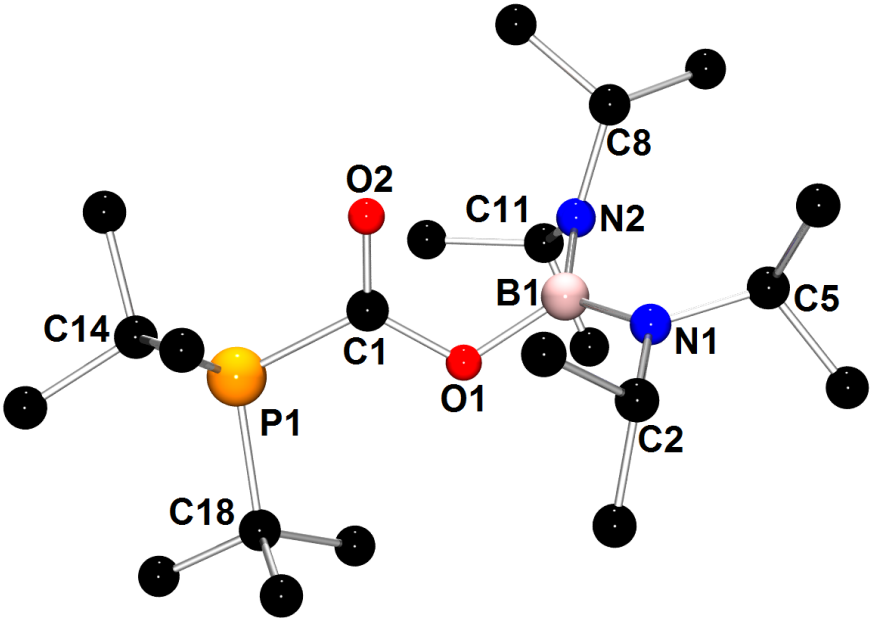


FIG. S1. MOLECULAR STRUCTURE OF **1A**

TABLE S3. SELECTED STRUCTURAL PARAMETERS OF **1A**

Bond lengths [Å]		**Bond angles [°]**		**Dihedrals [°]**	
B1-N1	1.408(1)	C1-P1-C14	99.46(5)	P1-C1-O1-B1	160.17(8)
B1-N2	1.438(2)	C1-P1-C18	108.12(6)	O2-C1-O1-B1	-13.9(2)
B1-O1	1.459(2)	C14-P1-C18	111.53(6)		
C1-O1	1.345(2)	P1-C1-O2	120.31(9)		
C1-O2	1.215(2)	O1-C1-O2	121.3(1)		
P1-C1	1.863(1)	C1-O1-B1	117.42(9)		
P1-C14	1.894(1)	O1-B1-N1	116.6(1)		
P1-C18	1.890(2)	O1-B1-N2	118.2(1)		
N1-C2	1.485(1)	N1-B1-N2	125.0(1)		
N1-C5	1.479(2)				
N2-C8	1.472(2)				
N2-C11	1.472(1)				

Single crystal X-ray structure analysis of 2

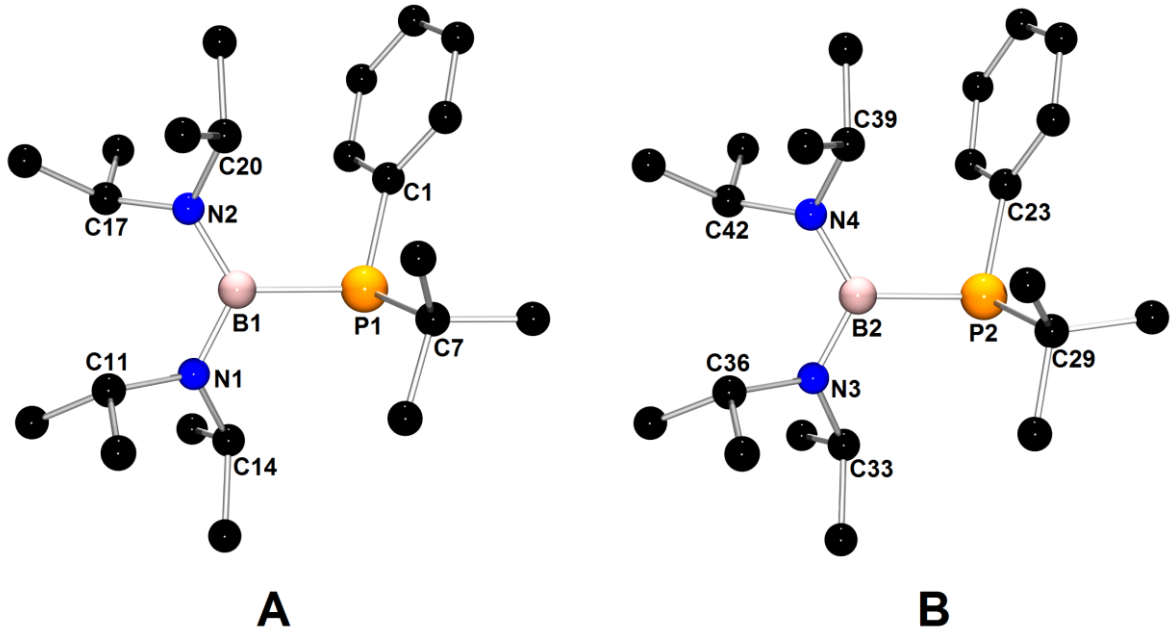


FIG. S2. MOLECULAR STRUCTURE OF **2**

TABLE S4. SELECTED STRUCTURAL PARAMETERS OF **2** (A)

Bond lengths [Å]		**Bond angles [°]**		**Dihedrals [°]**	
P1-B1	1.983(2)	B1-P1-C1	105.50(9)	N1-B1-P1-C7	-83.5(2)
P1-C1	1.827(2)	B1-P1-C7	108.81(9)	N2-B1-P1-C1	-15.2(2)
P1-C7	1.882(2)	C1-P1-C7	109.51(9)		
B1-N1	1.442(3)	P1-B1-N1	116.4(1)		
B1-N2	1.436(2)	P1-B1-N2	121.4(1)		
N1-C11	1.486(2)	N1-B1-N2	121.9(2)		
N1-C14	1.482(3)				
N2-C17	1.478(2)				
N2-C20	1.473(2)				

TABLE S5. SELECTED STRUCTURAL PARAMETERS OF **2** (B)

Bond lengths [Å]		**Bond angles [°]**		**Dihedrals [°]**	
P2-B2	1.983(2)	B2-P2-C23	103.47(8)	N3-B2-P2-C29	-82.7(1)
P2-C23	1.833(2)	B2-P2-C29	107.68(8)	N4-B2-P2-C23	-14.4(2)
P2-C29	1.891(2)	C23-P2-C29	110.77(9)		
B2-N3	1.435(3)	P2-B2-N3	116.7(1)		
B2-N4	1.434(2)	P2-B2-N4	121.5(1)		
N3-C33	1.481(2)	N3-B2-N4	121.6(2)		
N3-C36	1.490(2)				
N4-C39	1.473(2)				
N4-C42	1.482(2)				

Single crystal X-ray structure analysis of 2a

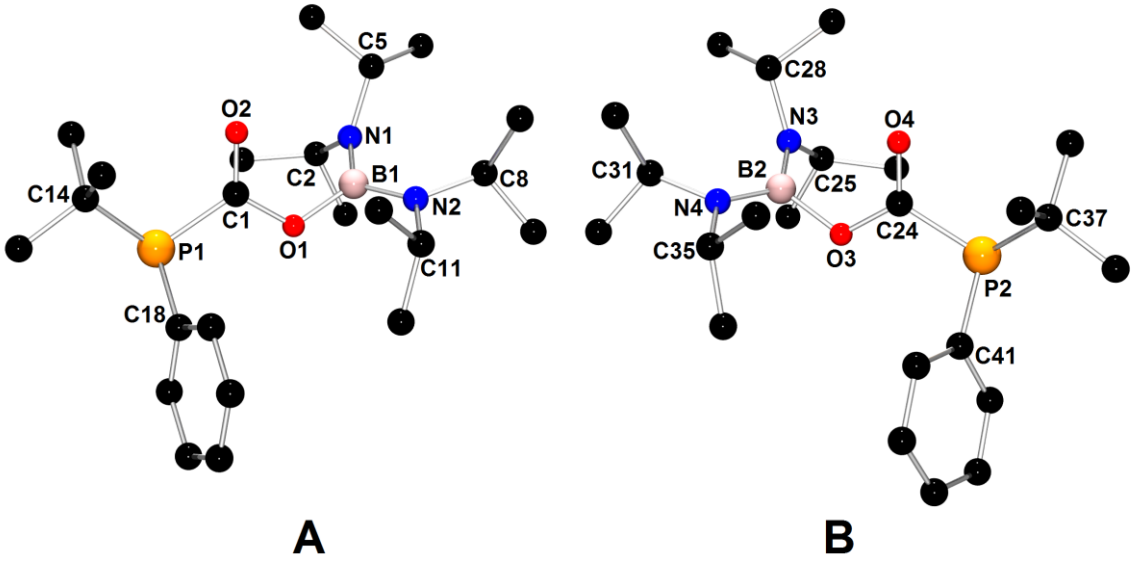


FIG. S3. MOLECULAR STRUCTURE OF **2A**

TABLE S6. SELECTED STRUCTURAL PARAMETERS OF **2A**(A)

Bond lengths [Å]		**Bond angles [°]**		**Dihedrals [°]**	
P1-C1	1.851(5)	C1-P1-C14	103.0(2)	P1-C1-O1-B1	163.8(3)
C1-O1	1.351(5)	C1-P1-C18	100.5(2)	B1-O1-C1-O2	-10.8(6)
C1-O2	1.218(6)	C14-P1-C18	106.4(2)		
B1-O1	1.452(6)	P1-C1-O2	125.6(4)		
B1-N1	1.424(7)	O1-C1-O2	121.5(4)		
B1-N2	1.410(7)	O1-B1-N1	118.8(4)		
P1-C14	1.872(6)	O1-B1-N2	116.1(4)		
P1-C18	1.827(6)	N1-B1-N2	124.9(5)		
N1-C2	1.490(6)	B1-O1-C1	118.3(4)		
N1-C5	1.478(6)				
N2-C8	1.481(6)				
N2-C11	1.489(6)				

TABLE S7. SELECTED STRUCTURAL PARAMETERS OF **2A**(B)

Bond lengths [Å]		**Bond angles [°]**		**Dihedrals [°]**	
P2-C24	1.851(5)	C24-P2-C37	103.4(2)	P2-C24-O3-B2	-160.2(3)
P2-C37	1.870(6)	C24-P2-C41	104.1(2)	B2-O3-C24-O4	13.1(6)
P2-C41	1.822(6)	C37-P2-C41	105.3(2)		
C24-O3	1.348(5)	O4-C24-P2	123.6(4)		
C24-O4	1.207(5)	O3-C24-O4	121.8(4)		
B2-O3	1.471(6)	B2-O3-C24	116.9(3)		
B2-N3	1.430(6)	O3-B2-N3	118.5(4)		
B2-N4	1.411(7)	O3-B2-N4	115.9(4)		
N3-C25	1.472(6)	N3-B2-N4	125.5(4)		
N3-C28	1.481(6)				
N4-C31	1.480(6)				
N4-C35	1.494(6)				

Single crystal X-ray structure analysis of 3

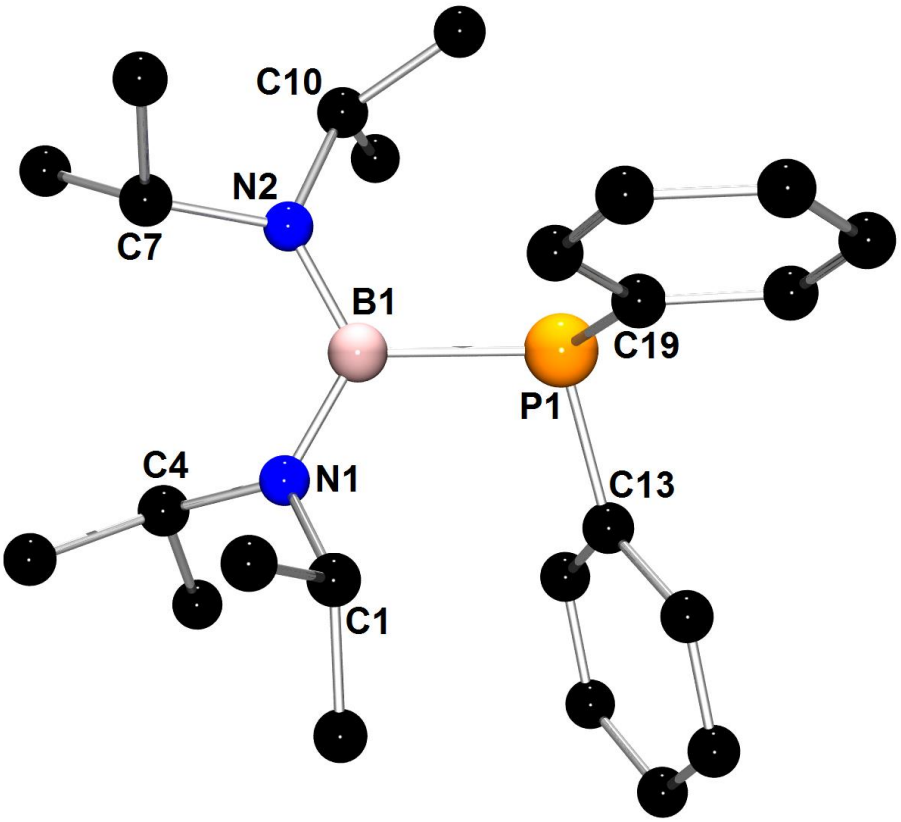


FIG. S4. MOLECULAR STRUCTURE OF **3**

TABLE S8. SELECTED STRUCTURAL PARAMETERS OF **3**

Bond lengths [Å]		**Bond angles [°]**		**Dihedrals [°]**	
P1-B1	1.984(1)	B1-P1-C13	105.09(4)	N1-B1-P1-C13	16.12(9)
P1-C13	1.827(1)	B1-P1-C19	106.24(4)	N2-B1-P1-C19	88.16(8)
P1-C19	1.830(1)	C13-P1-C19	105.62(5)		
B1-N1	1.442(1)	P1-B1-N1	120.55(7)		
B1-N2	1.425(1)	P1-B1-N2	116.94(7)		
N1-C1	1.475(1)	N1-B1-N2	122.40(9)		
N1-C4	1.480(1)				
N2-C7	1.485(1)				
N2-C10	1.487(1)				

Spectroscopic data

NMR spectra of isolated compounds

NMR spectra of $(i\text{Pr}_2\text{N})_2\text{BBr}$

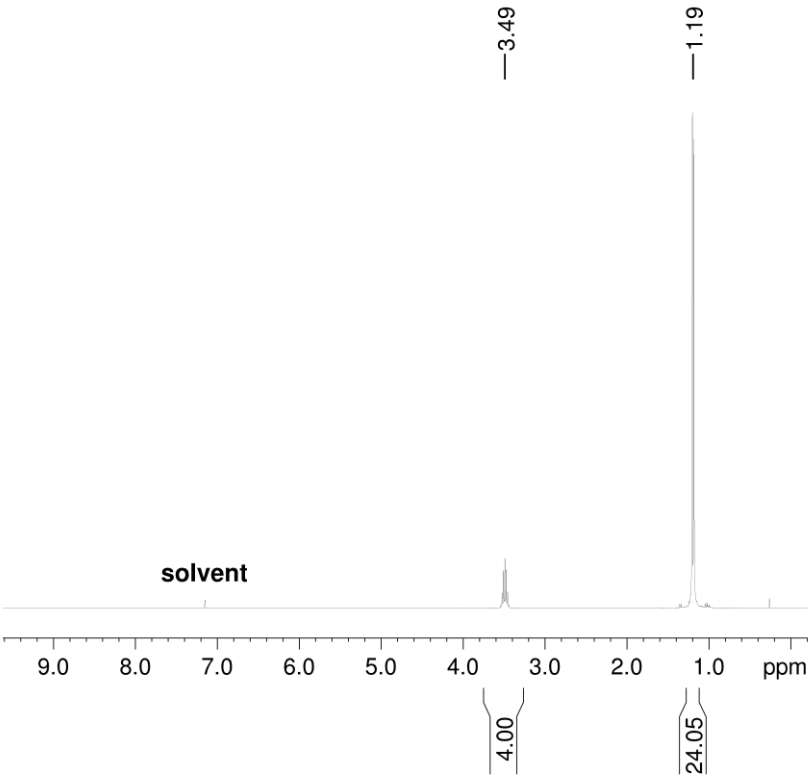


FIG. S5. ^{1}H NMR (C_6D_6) SPECTRUM OF $(i\text{Pr}_2\text{N})_2\text{BBr}$

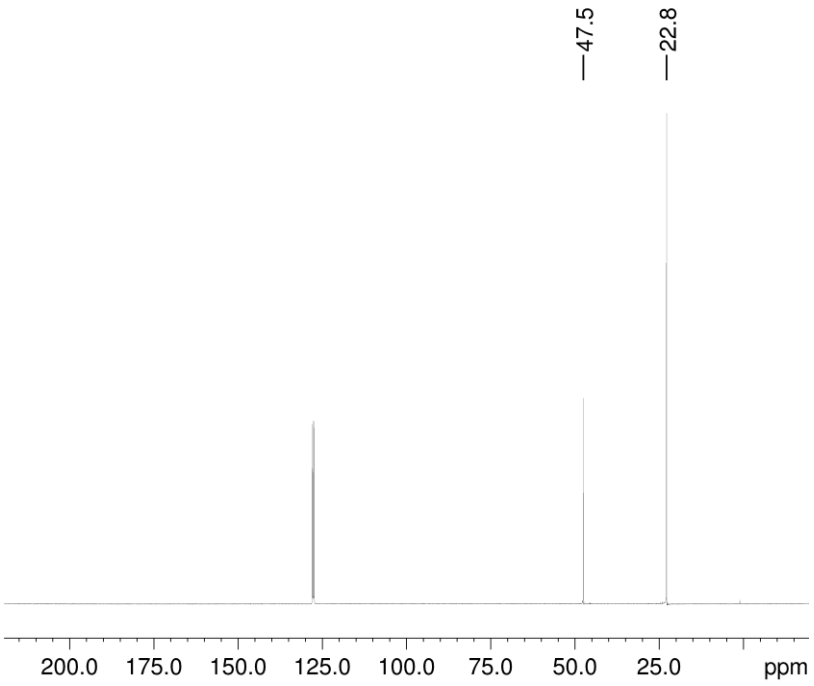


FIG. S6. $^{13}C\{^{1}H\}$ NMR (C_6D_6) SPECTRUM OF **(*i*Pr$_2$N)$_2$BBr**

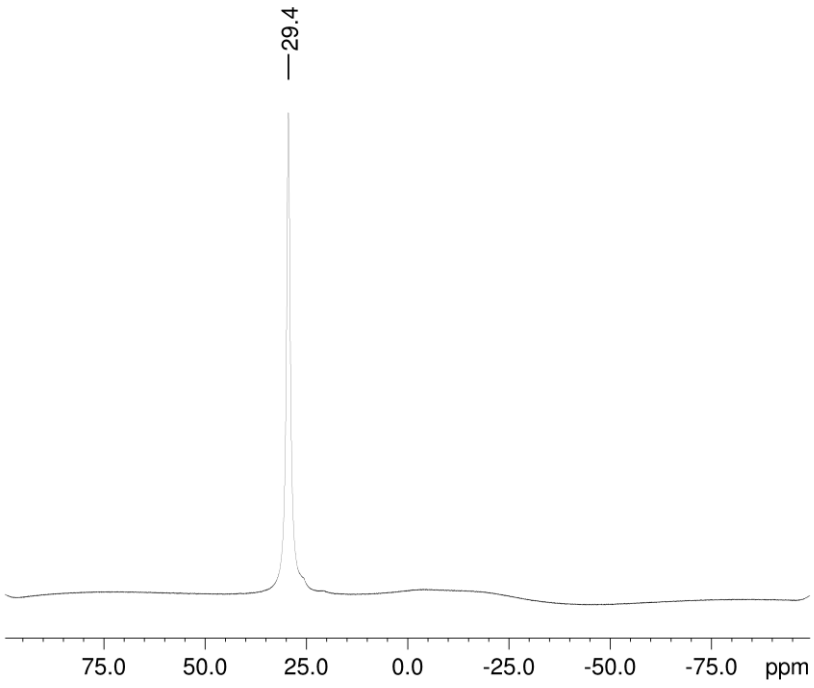


FIG. S7. ^{11}B NMR (C_6D_6) SPECTRUM OF **(*i*Pr$_2$N)$_2$BBr**

NMR spectra of 1

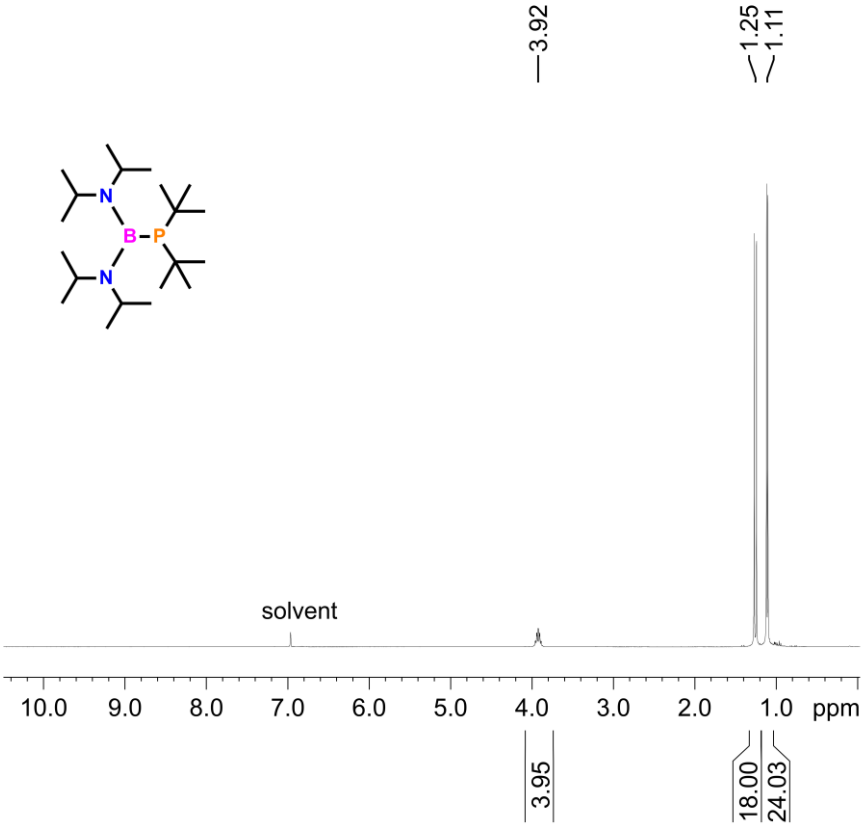


FIG. S8. ^{1}H NMR (C_6D_6) SPECTRUM OF **1**

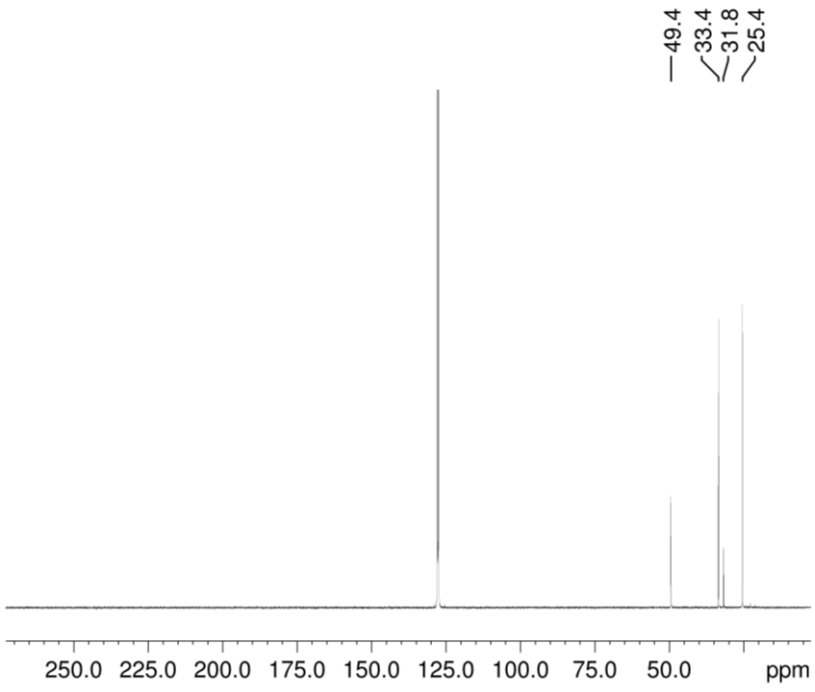


FIG. S9. $^{13}C\{^{1}H\}$ NMR (C_6D_6) SPECTRUM OF **1**

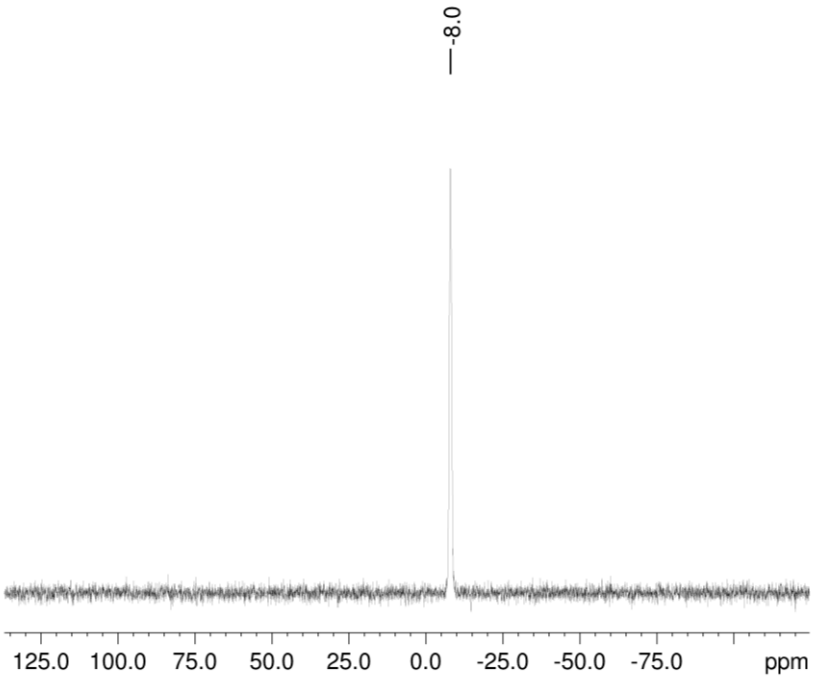


FIG. S10. ^{31}P NMR (C_6D_6) SPECTRUM OF **1**

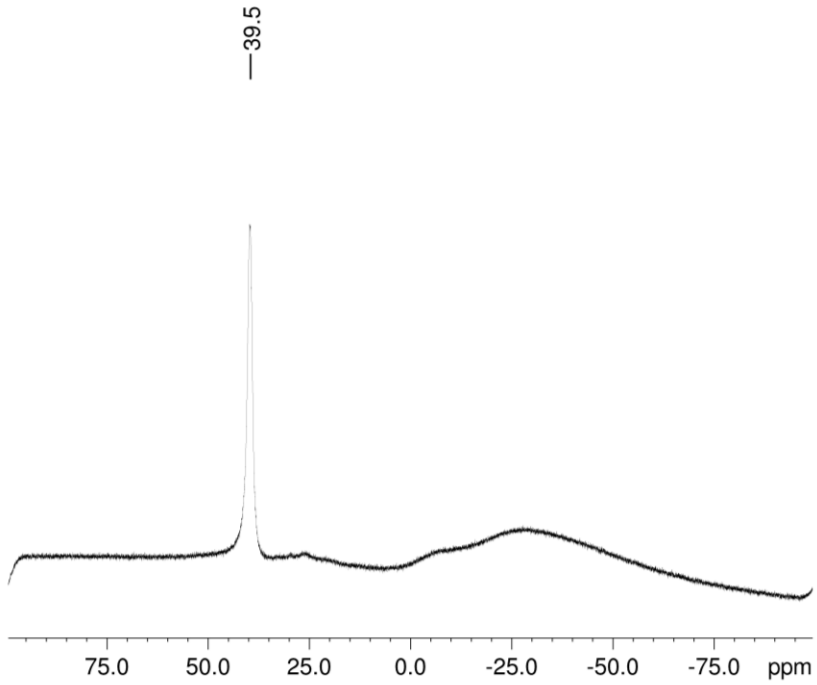


FIG. S11. ^{11}B NMR (C_6D_6) SPECTRUM OF **1**

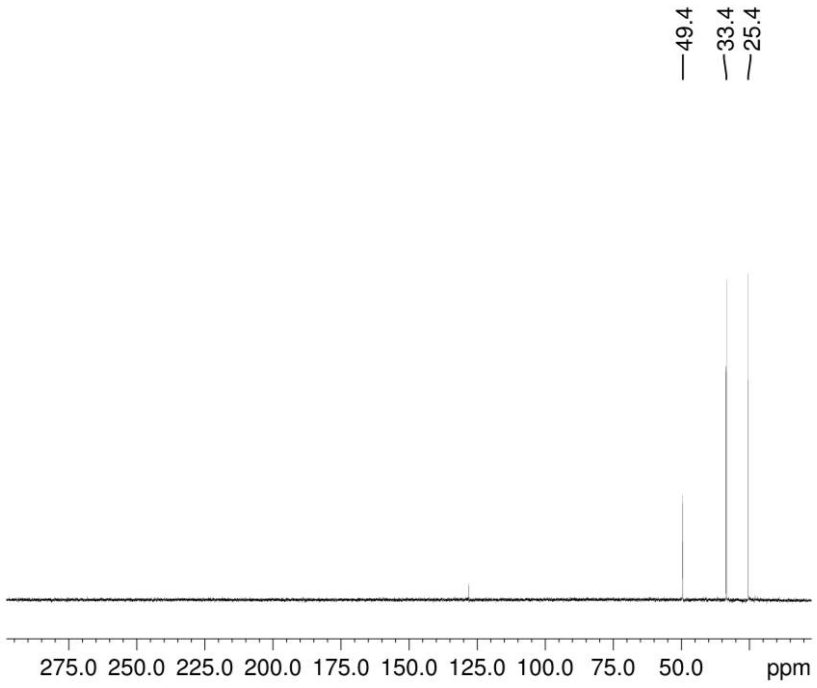


FIG. S12. ^{135}DEPT NMR (C_6D_6) SPECTRUM OF **1**

NMR spectra of 1a

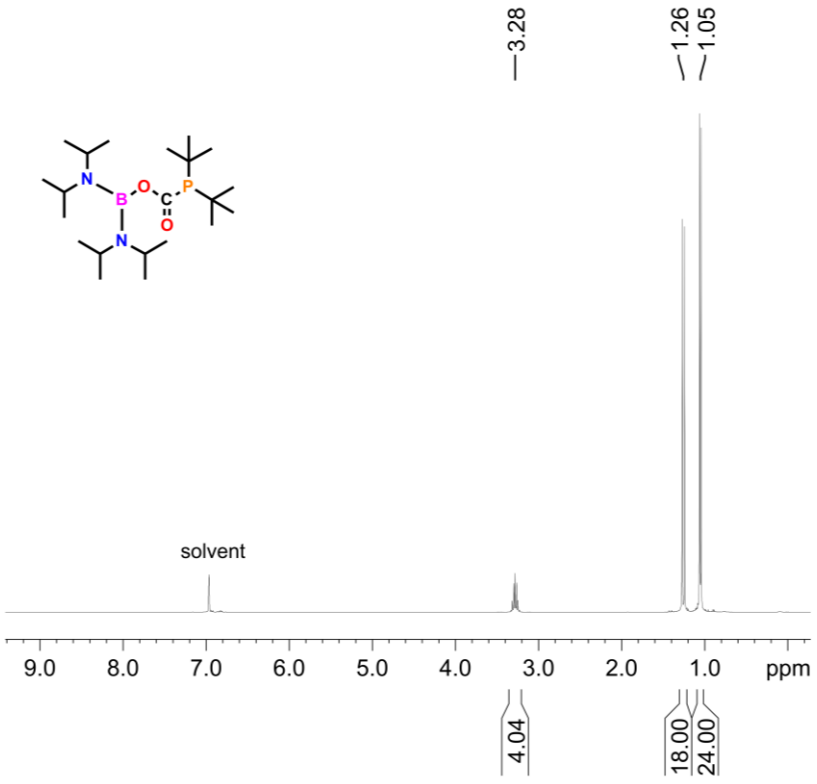


FIG. S13. ^{1}H NMR (C_6D_6) SPECTRUM OF **1A**

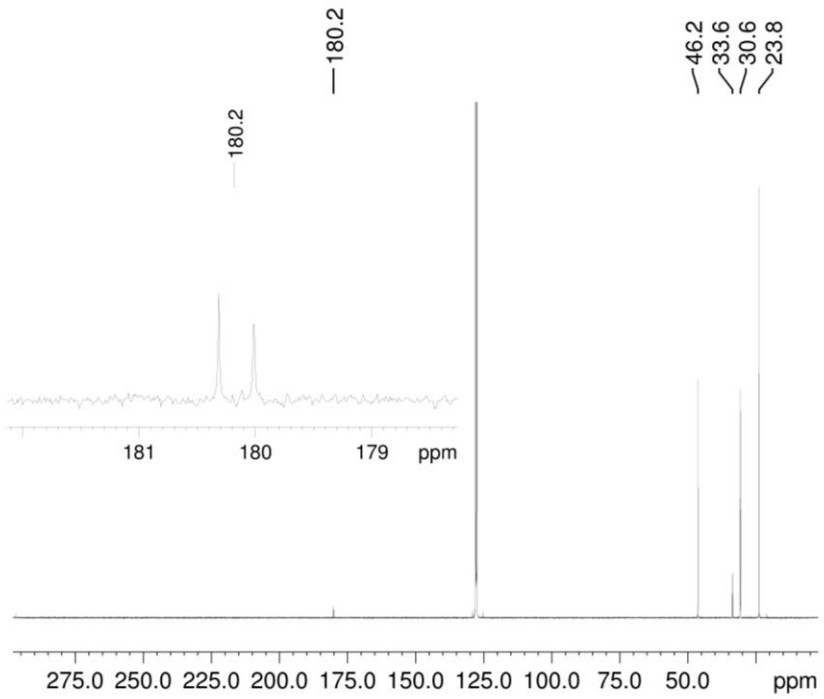


FIG. S14. $^{13}C\{^{1}H\}$ NMR (C_6D_6) SPECTRUM OF **1A**

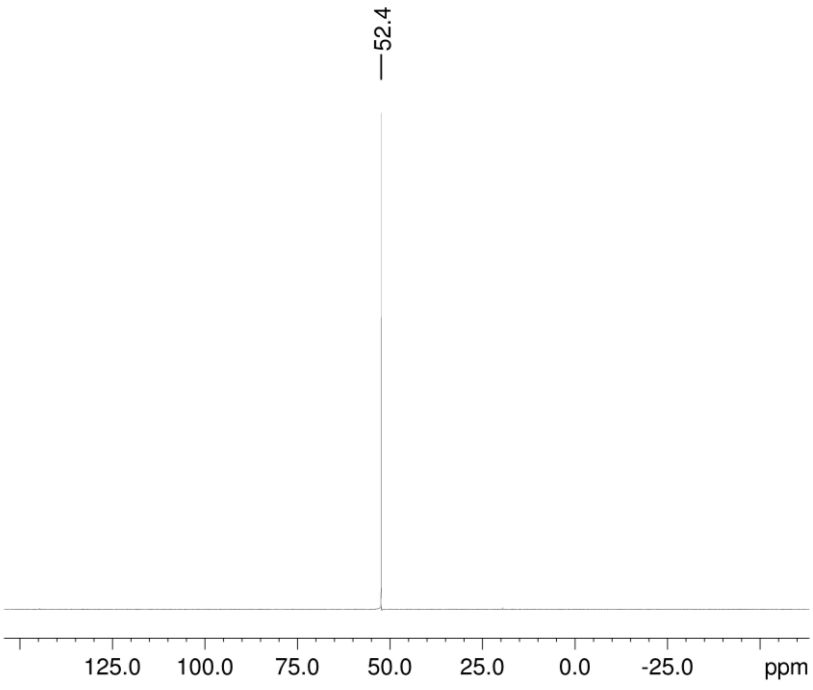


FIG. S15. ^{31}P NMR (C_6D_6) SPECTRUM OF **1A**

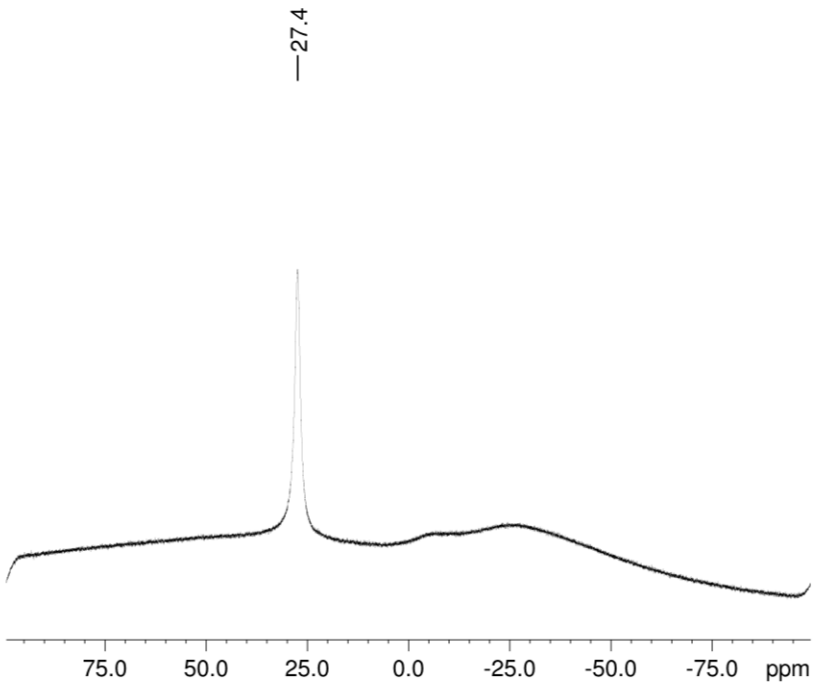


FIG. S16. ^{11}B NMR (C_6D_6) SPECTRUM OF **1A**

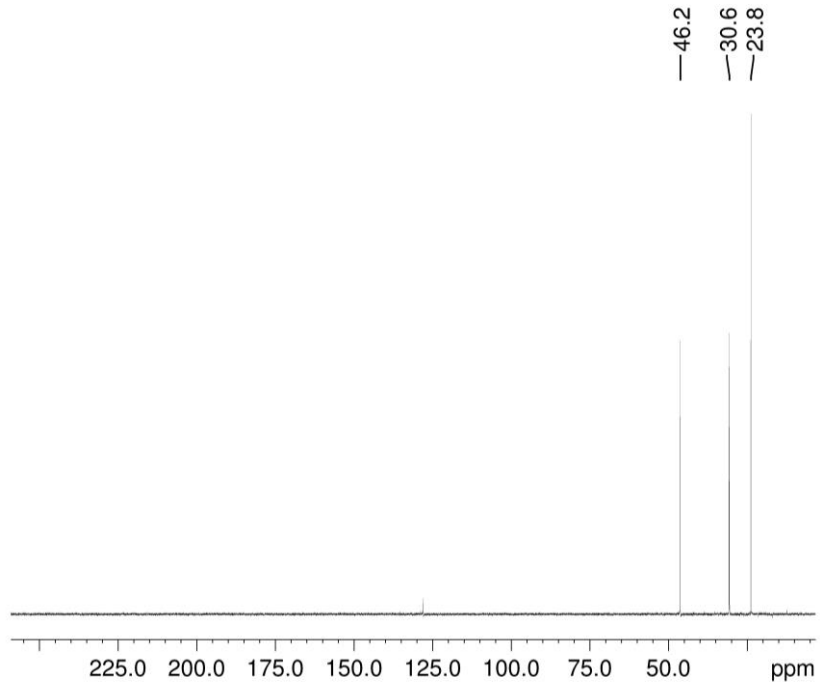


FIG. S17. ^{135}DEPT NMR (C_6D_6) SPECTRUM OF **1A**

NMR spectra of 2

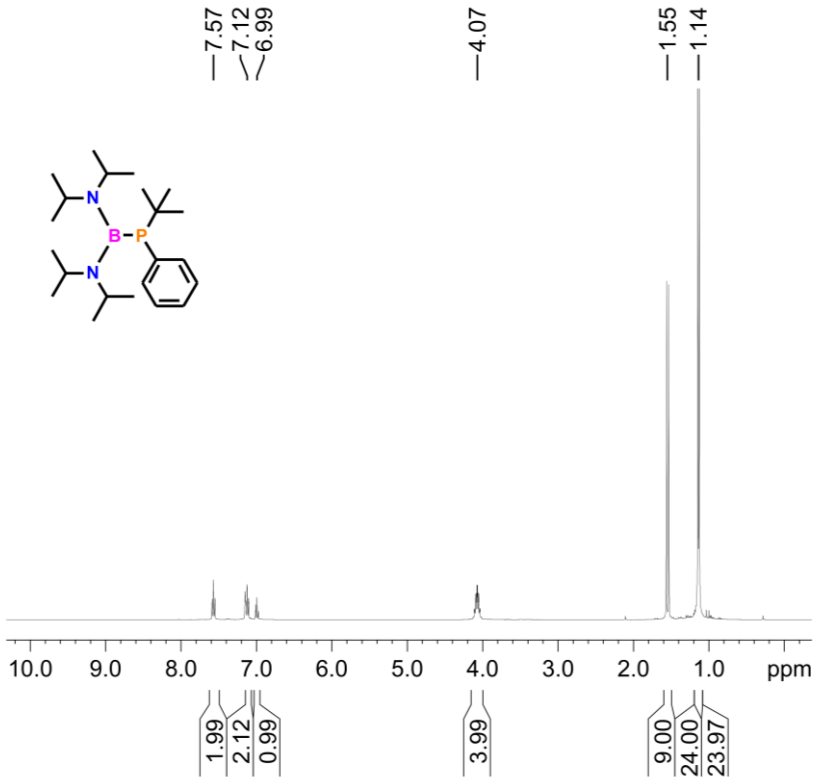


FIG. S18. ^{1}H NMR (C_6D_6) SPECTRUM OF **2**

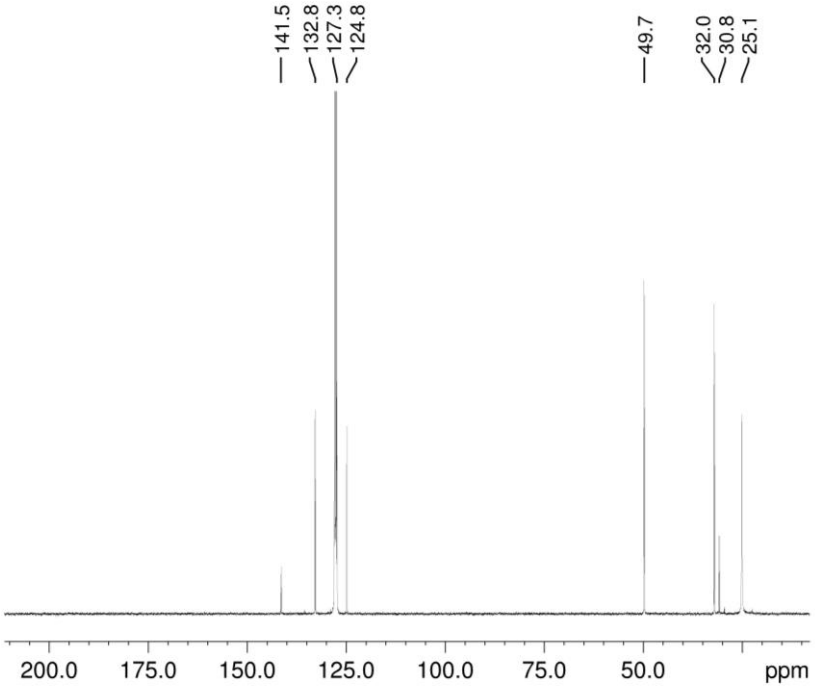


FIG. S19. ^{13}C{^{1}H} NMR (C_6D_6) SPECTRUM OF **2**

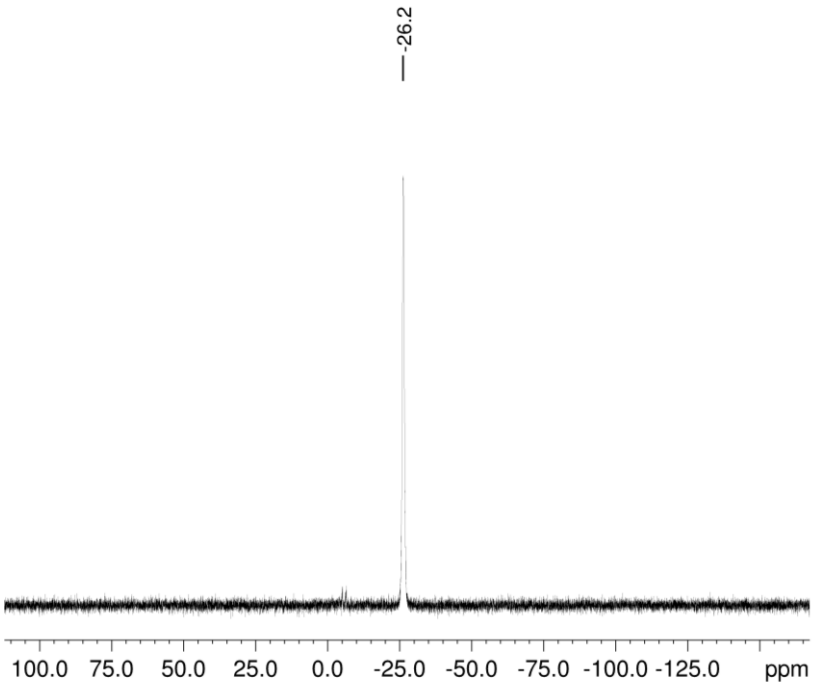


FIG. S20. ^{31}P NMR (C_6D_6) SPECTRUM OF **2**

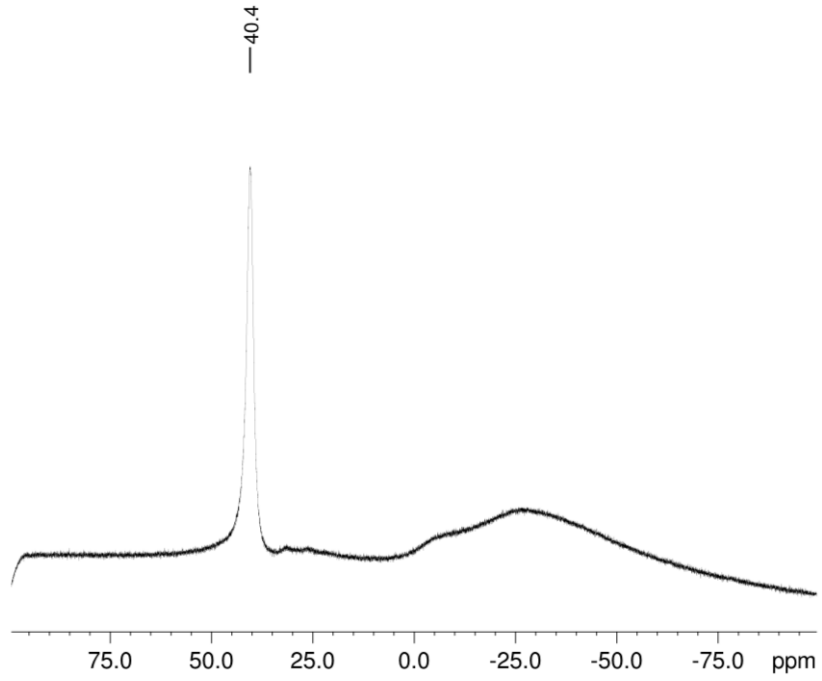


FIG. S21. ^{11}B NMR (C_6D_6) SPECTRUM OF **2**

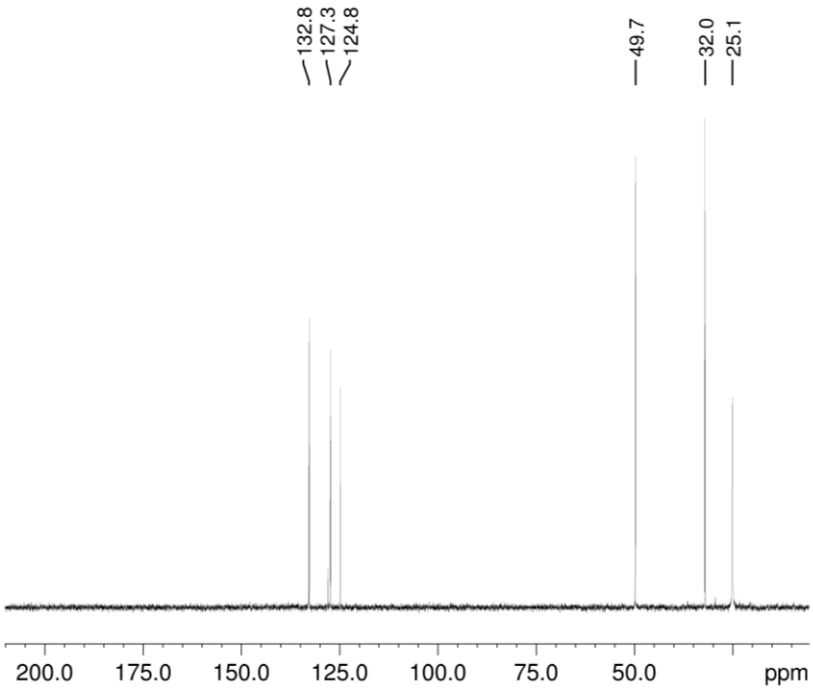


FIG. S22. ^{135}DEPT NMR (C_6D_6) SPECTRUM OF **2**

NMR spectra of 2a

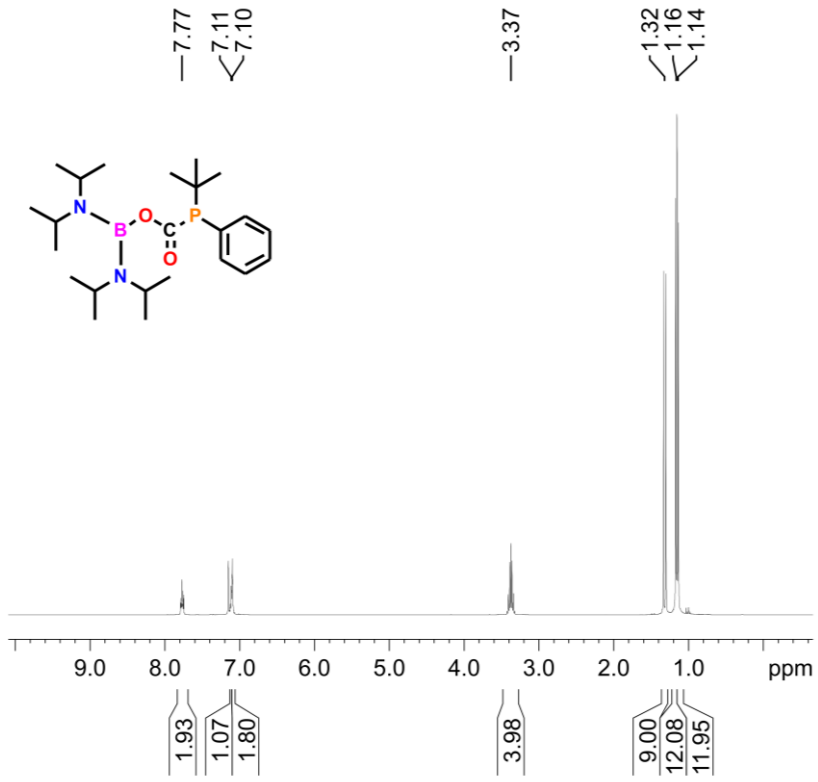


FIG. S23. ^{1}H NMR (C_6D_6) SPECTRUM OF **2A**

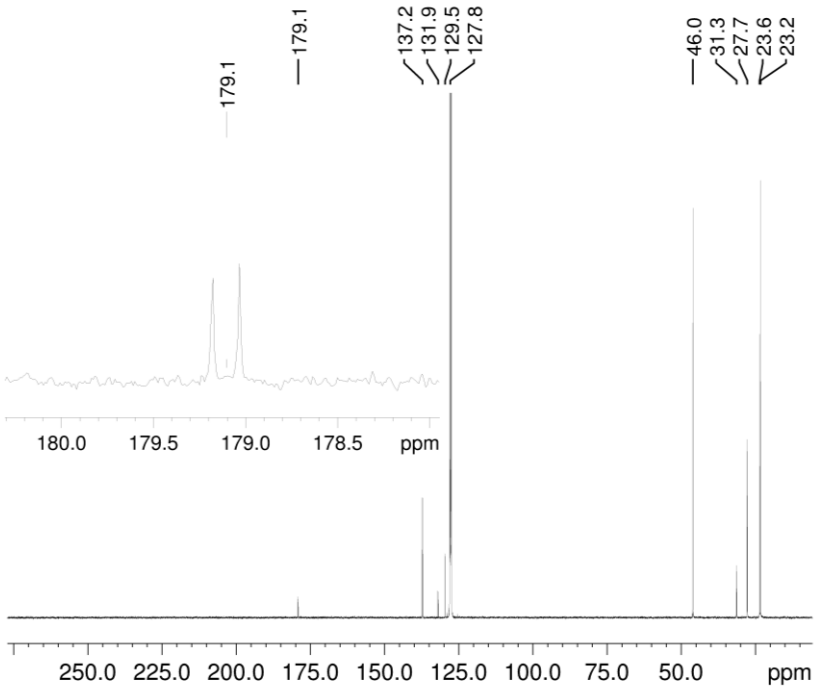


FIG. S24. $^{13}C\{^{1}H\}$ NMR (C_6D_6) SPECTRUM OF **2A**

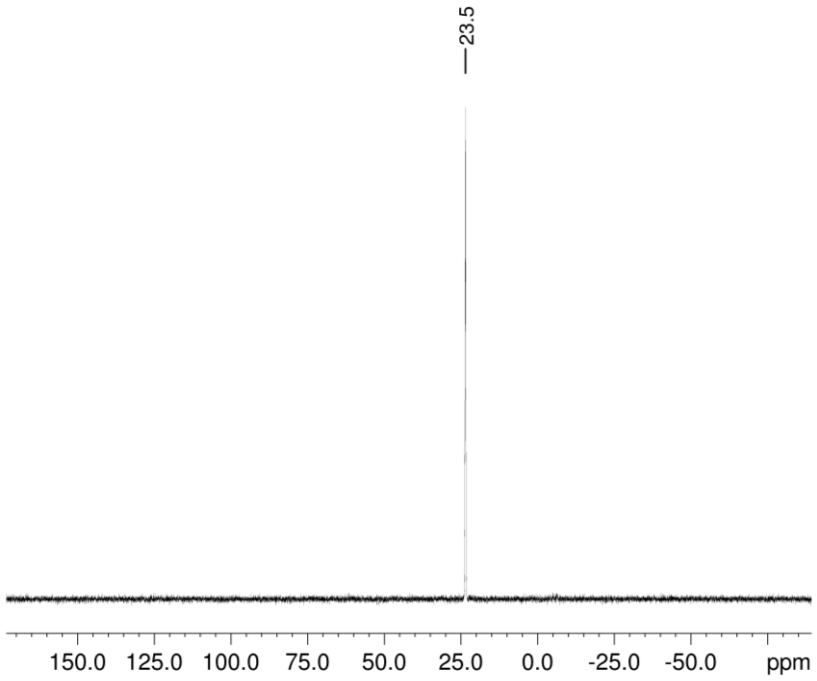


FIG. S25. ^{31}P NMR (C_6D_6) SPECTRUM OF **2A**

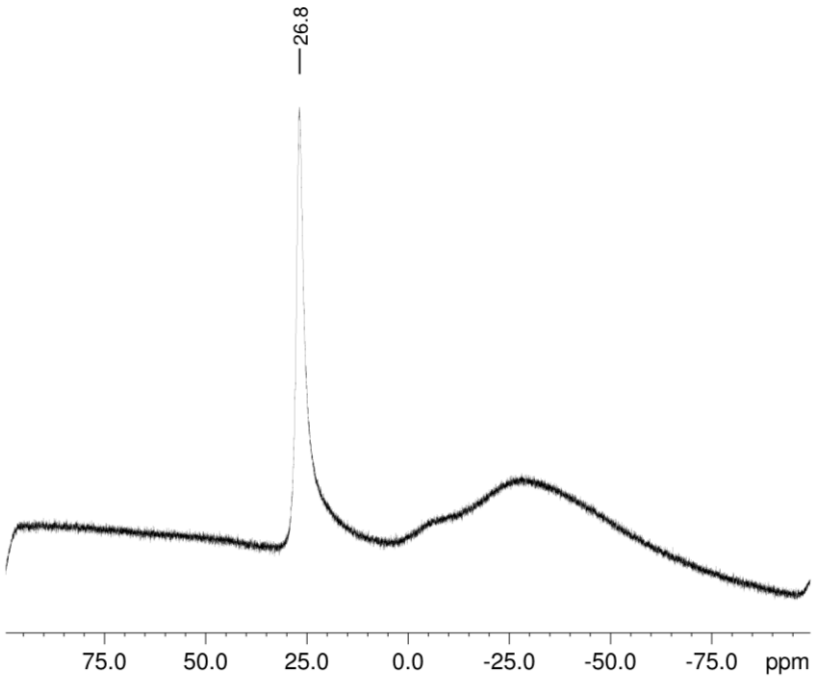


FIG. S26. ^{11}B NMR (C_6D_6) SPECTRUM OF **2A**

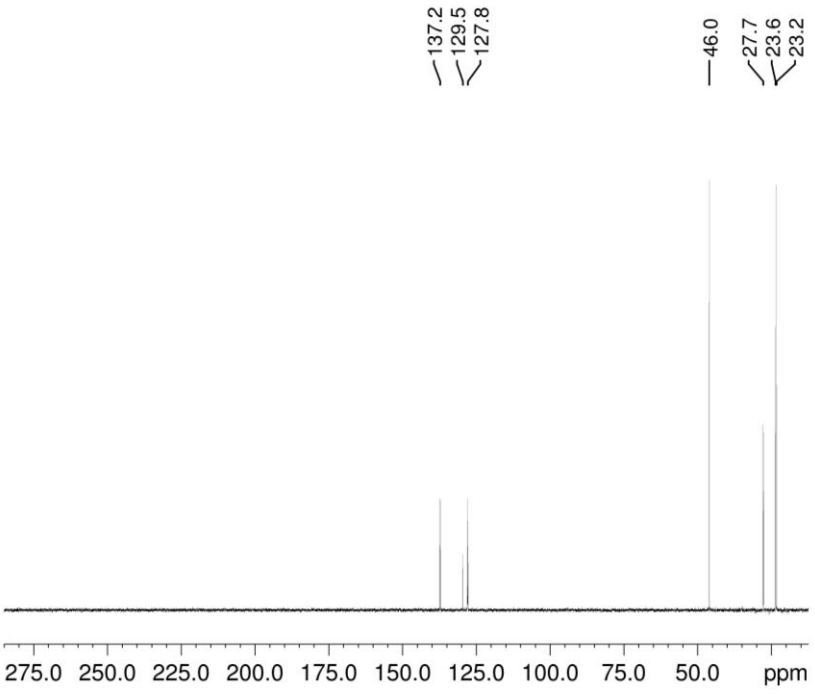


FIG. S27. ^{135}DEPT NMR (C_6D_6) SPECTRUM OF **2A**

NMR spectra of 3

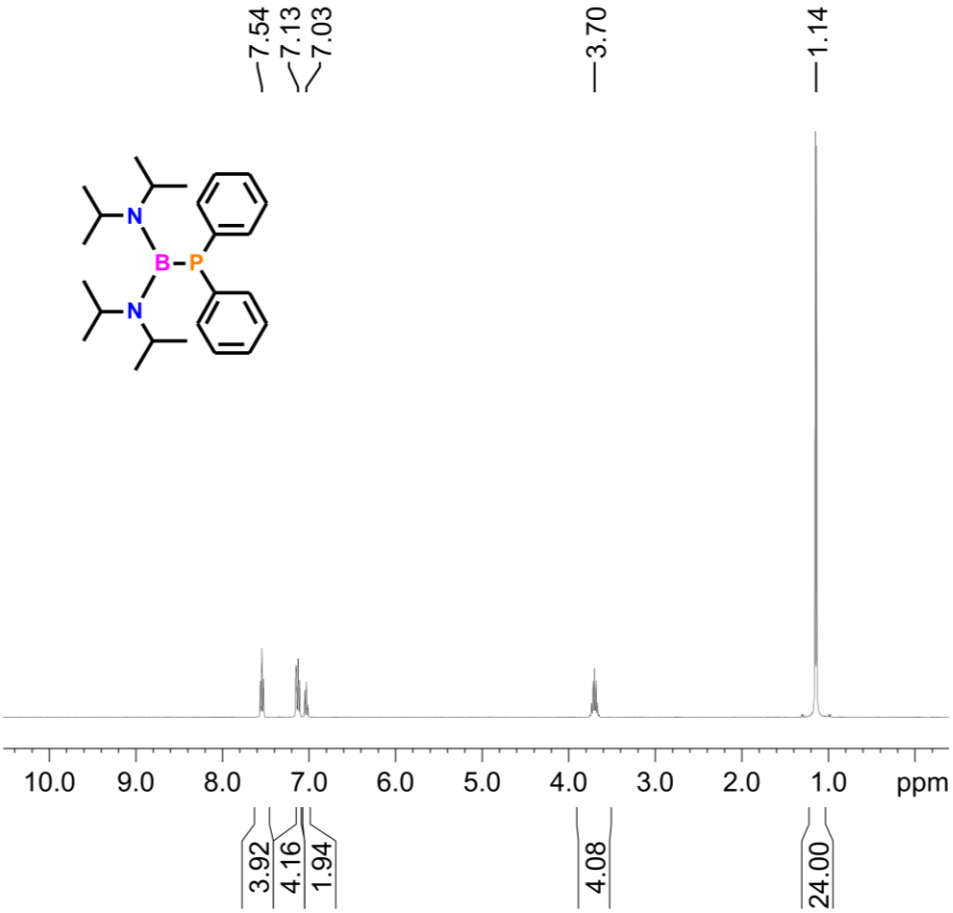


FIG. S28. ^{1}H NMR (C_6D_6) SPECTRUM OF **3**

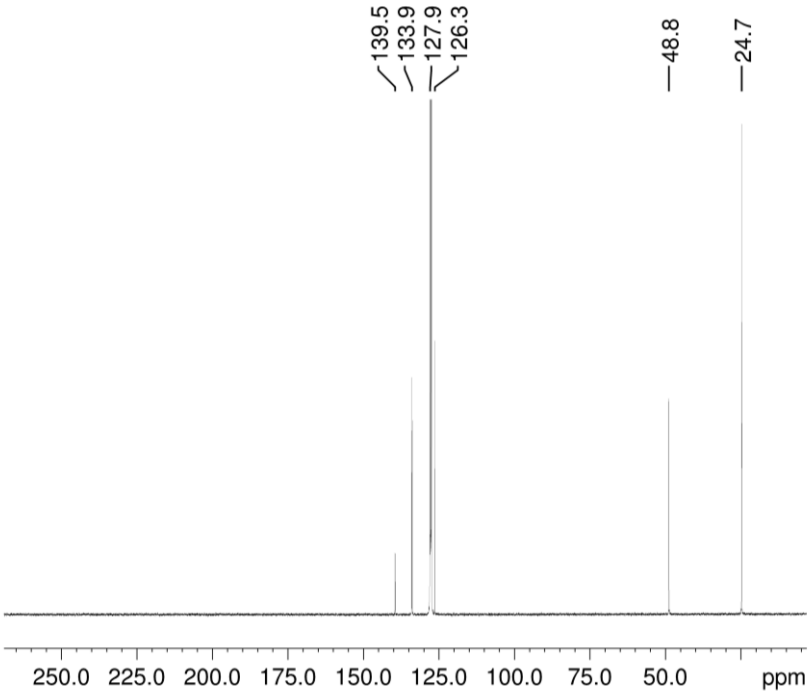


FIG. S29. $^{13}C\{^{1}H\}$ NMR (C_6D_6) SPECTRUM OF **3**

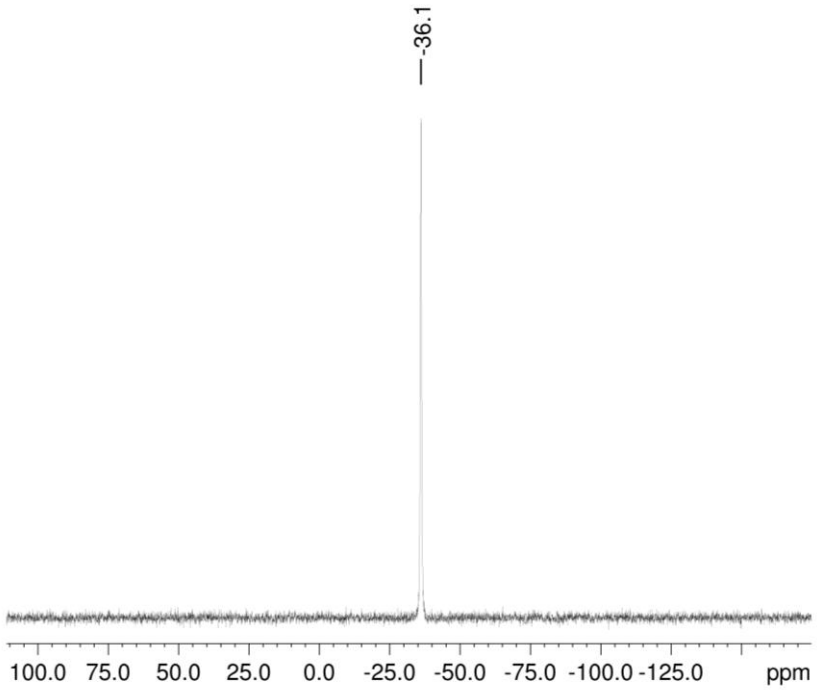


FIG. S30. ^{31}P NMR (C_6D_6) SPECTRUM OF **3**

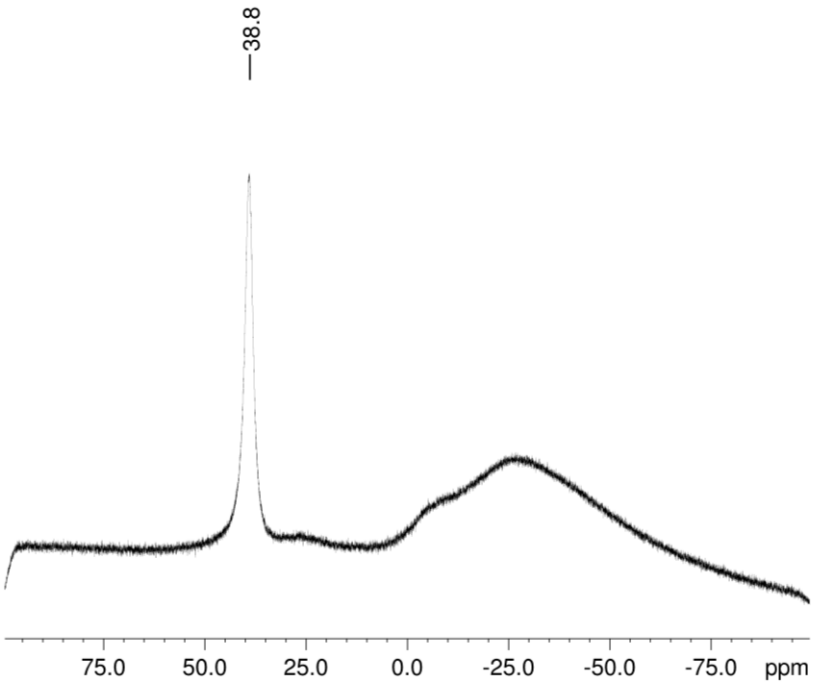


FIG. S31. ^{11}B NMR (C_6D_6) SPECTRUM OF **3**

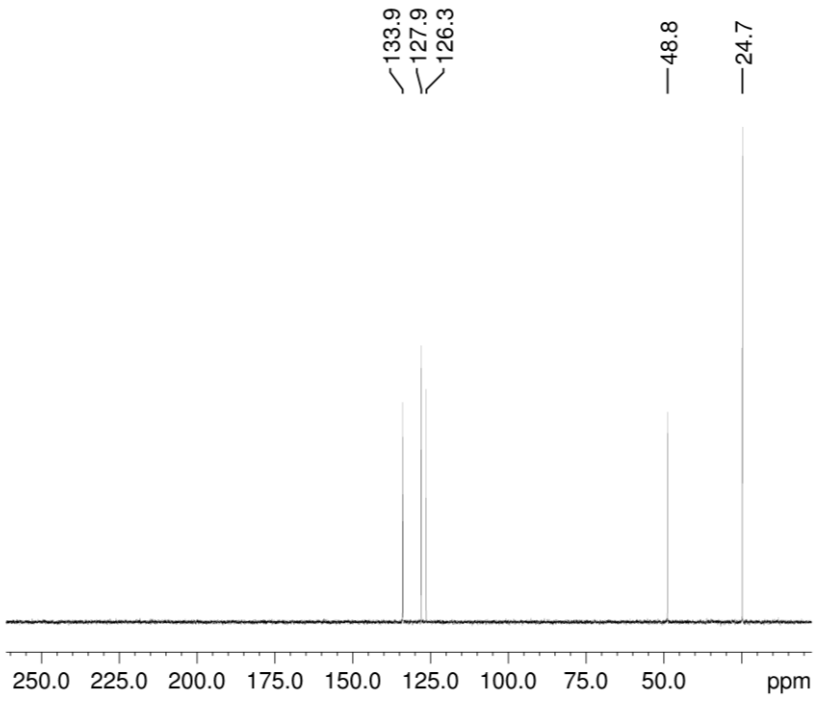


FIG. S32. ^{135}DEPT NMR (C_6D_6) SPECTRUM OF **3**

NMR spectra of 3a

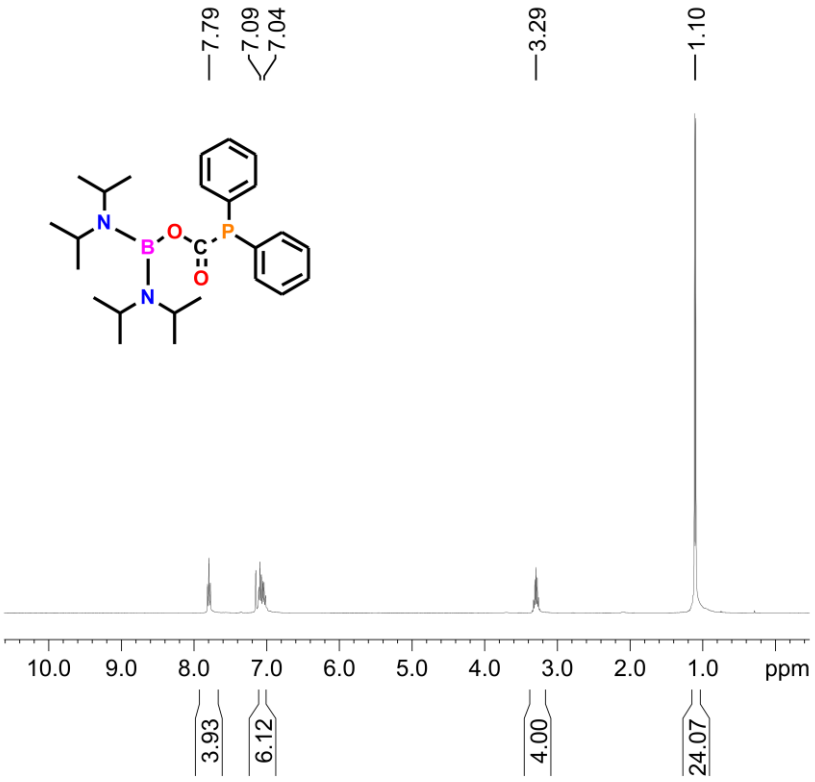


FIG. S33. ^{1}H NMR (C_6D_6) SPECTRUM OF **3A**

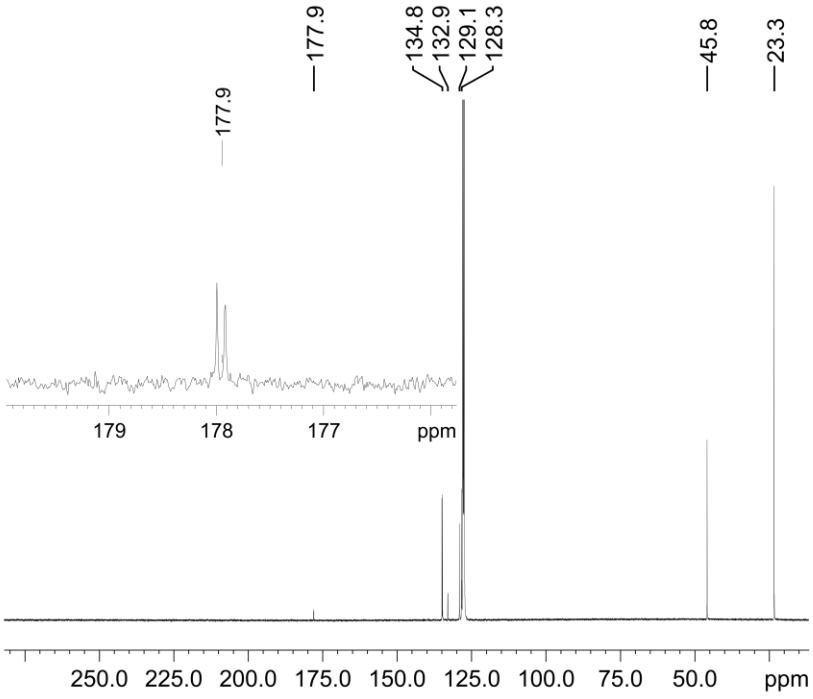


FIG. S34. $^{13}C\{^{1}H\}$ NMR (C_6D_6) SPECTRUM OF **3A**

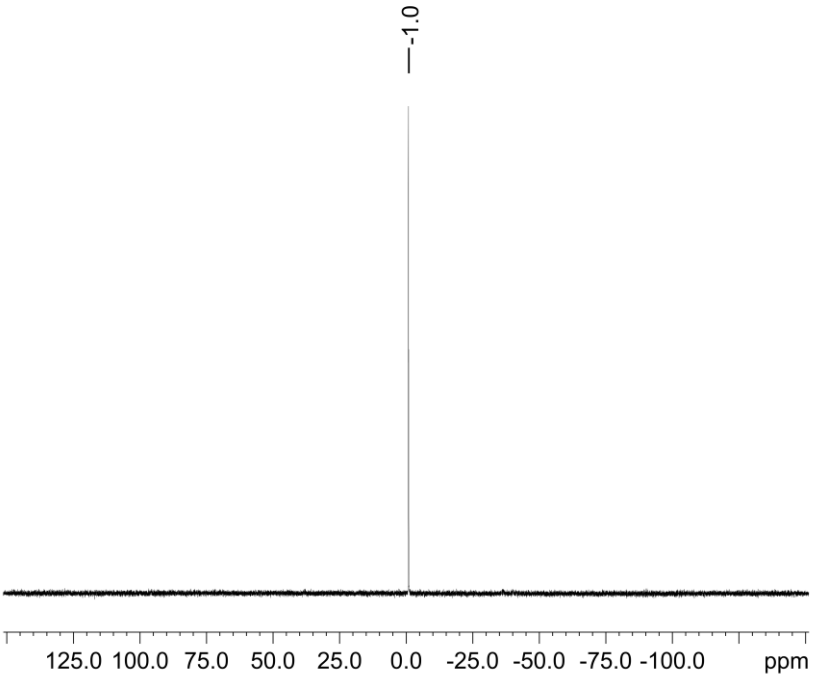


FIG. S35. ^{31}P NMR (C_6D_6) SPECTRUM OF **3A**

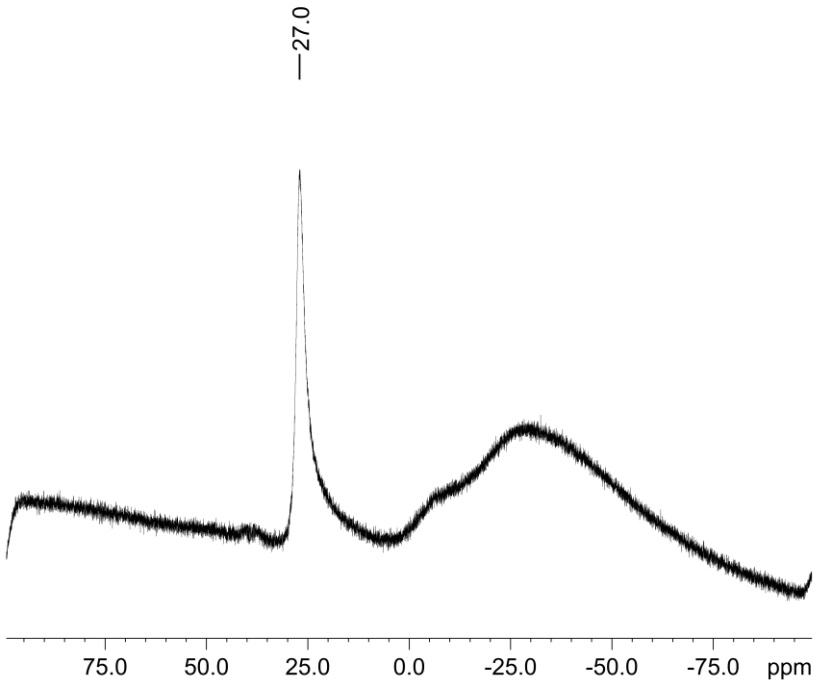


FIG. S36. ^{11}B NMR (C_6D_6) SPECTRUM OF **3A**

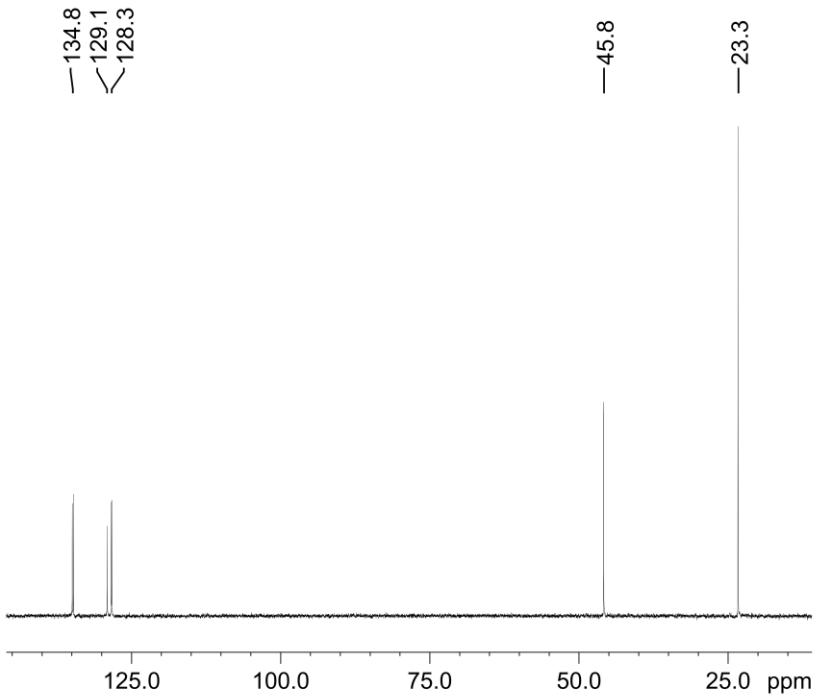


FIG. S37. ^{13}5DEPT NMR (C_6D_6) SPECTRUM OF **3A**

IR spectra of isolated compounds

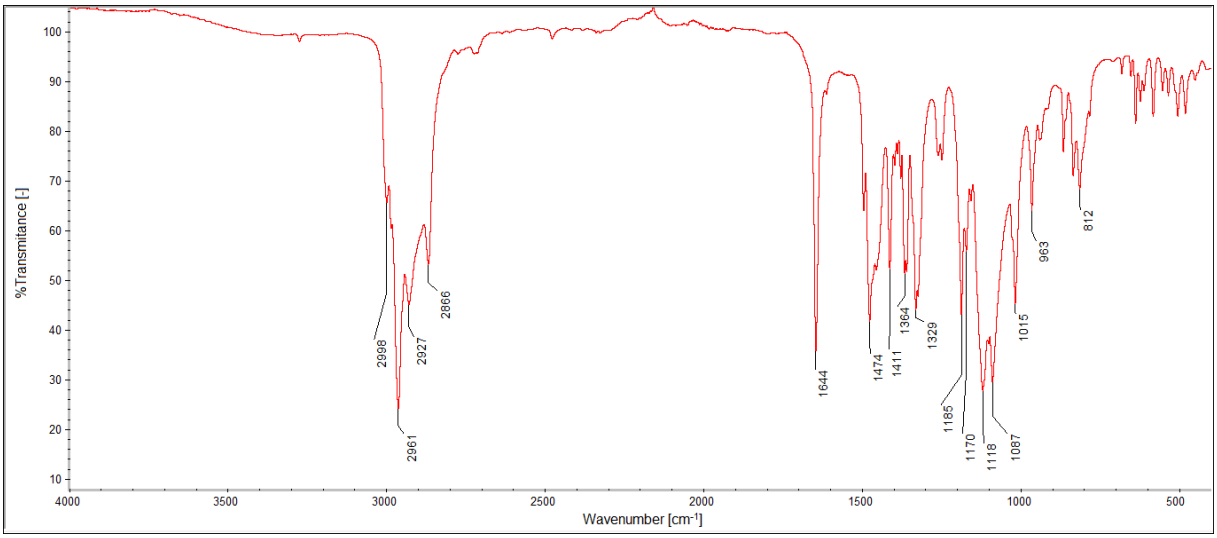


FIG. S38. IR SPECTRUM OF SOLID **1A**

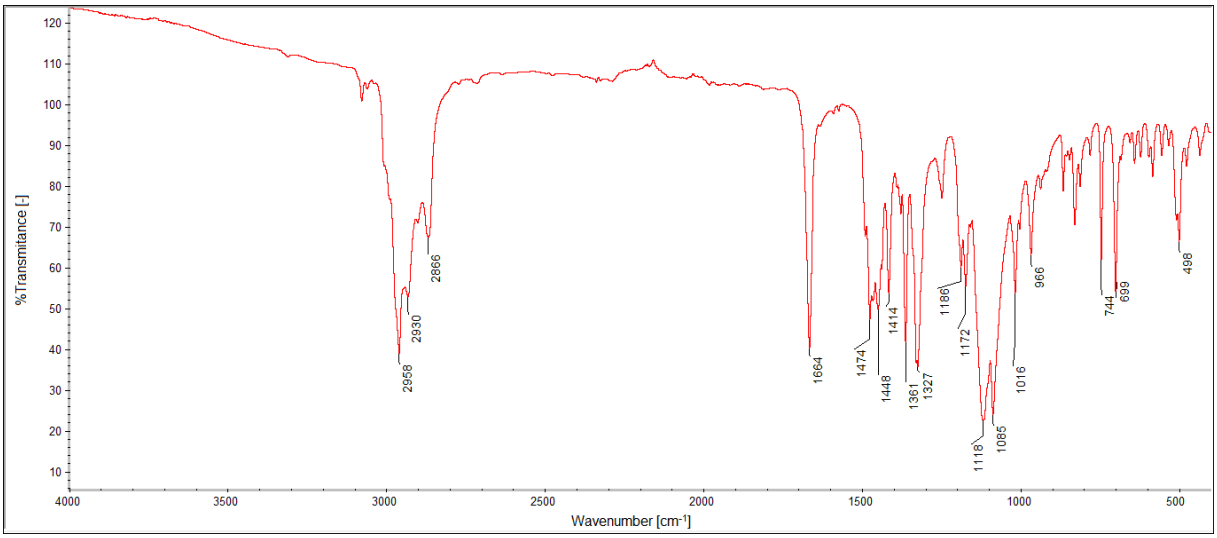


FIG. S39. IR SPECTRUM OF SOLID **2A**

DFT calculations

General methods

All calculations presented in the paper were performed using the Gaussian 09[4] program package. Molecular geometries of all compounds were optimized using density functional theory at the ωB97XD functional by Head-Gordon[5,6] with 6-31+G(d,p) basis set. The ωB97XD exchange-correlation functional has been chosen, as it has good overall performance for the description of main-group element compounds, and it also accounts well for long-range and dispersion interactions. Molecular geometries were energy optimized and the most stable (the lowest energy) conformer was identified during the potential energy surface scanning. Nature of the final gas phase geometries as a local minima (no imaginary frequencies) or transition states (one imaginary frequency) on the potential energy surface was then validated by harmonic frequency calculations at the same level of theory. Values of calculated energies, enthalpies and Gibbs free-energies derived from thermochemical calculations were corrected for the zero-point energy (ZPE). Scans of potential energy surface along the RR'**P-C**O_2 and $(RR'N)_2$**B-O**CO bonds were performed to establish local minima corresponding to transition products and confirm proposed mechanism of the reaction. Local maxima related to transition states were also established and used to determine energy barriers between respective transformations. Values of energy barriers $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ of reactions **1a-3a** were determined as the difference between energy of rate-determining transition state and rate-determining intermediate as described in [7].

Condensed Fukui functions[8] and dual descriptors[8,9] were determined using optimized structures to single point calculations on phosphinoboranes **1-3** and related transitions states, intermediates and products for *N*, *N-1* and *N+1* electron states at ωB97XD/6-31G+(d,p) level of theory. Condensed to atom parameters were calculated using partial charges derived *via* Hirshfeld population analysis.

TABLE S9. SELECTED COMPUTATIONAL PARAMETERS OBTAINED FOR CONSIDERED SYSTEMS (IN ATOMIC UNITS A.U.): $\mathbf{E_0}$ - ELECTRONIC ENERGY; $\mathbf{E_{0+\dots}}$ - SUM OF ELECTRONIC AND: $\mathbf{E_{ZPE}}$ - ZERO-POINT ENERGIES, $\mathbf{E_{THERM}}$ - THERMAL ENERGIES, **H –** THERMAL ENTHALPIES, **G -** THERMAL FREE ENERGIES CALCULATED AT ωB97XD//6-31+G(d,p) LEVEL OF THEORY

Compound	E_{electr} [A.U.]	$\varepsilon_0 + E_{ZPE}$ [A.U.]	$\varepsilon_0 + E_{therm}$ [A.U.]	ε_0 + H [A.U.]	ε_0 + G [A.U.]
1	-1265.421684	-1264.770261	-1264.738632	-1264.737688	-1264.826519
1a_TS1	-1453.930023	-1453.262996	-1453.229211	-1453.228267	-1453.322109
1a_I	-1453.938638	-1453.271539	-1453.237285	-1453.236341	-1453.331035
1a_TS2	-1453.926505	-1453.260703	-1453.226874	-1453.225930	-1453.319777
1a	-1453.998066	-1453.331921	-1453.297286	-1453.296342	-1453.393721
2	-1339.196473	-1338.576818	-1338.545726	-1338.544782	-1338.635094
2a_TS1	-1527.719674	-1527.085847	-1527.052110	-1527.051166	-1527.146761
2a_I	-1527.719935	-1527.085607	-1527.051364	-1527.050420	-1527.147242
2a_TS2	-1527.703133	-1527.069240	-1527.036152	-1527.035208	-1527.129748
2a	-1527.765823	-1527.133361	-1527.098571	-1527.097627	-1527.198674
3	-1412.964844	-1412.376867	-1412.346358	-1412.345414	-1412.436355
3_TS	-1601.463792	-1600.862445	-1600.829717	-1600.828772	-1600.925022
3a	-1601.526839	-1600.924449	-1600.891014	-1600.890070	-1600.989146
CO_2	-188.526945	-188.515158	-188.515158	-188.511588	-188.535860

Nucleophicility of phosphorus and boron centers

TABLE S10. VALUES OF NUCLEOPHILIC (f_N), ELECTROPHILIC (f_E) FUKUI FUNCTIONS AND DUAL DESCRIPTOR (Δf) CALCULATED USING PARTIAL CHARGES DERIVED VIA HIRSHFELD POPULATION ANALYSIS

Compound	P			B		
	f_N	f_E	Δf	f_N	f_E	Δf
1	0.277	0.004	-0.273	0.027	0.001	-0.026
1a_TS1	0.043	0.049	0.006	0.010	0.149	0.139
1a_I	0.022	0.057	0.034	0.007	0.152	0.145
1a_TS2	0.039	-0.005	-0.045	0.004	0.000	-0.005
1a	0.017	0.040	0.023	0.022	0.005	-0.016
2	0.198	0.048	-0.150	0.023	0.028	0.005
2a_TS1	0.069	0.021	-0.047	0.015	0.009	-0.007
2a_I	0.045	0.026	-0.019	0.014	0.010	-0.004
2a_TS2	0.039	0.031	-0.008	0.006	0.014	0.009
2a	0.018	0.072	0.054	0.025	-0.003	-0.028
3	0.175	0.057	-0.118	0.024	0.005	-0.019
3_TS	0.039	0.029	-0.010	0.008	0.015	0.007
3a	0.021	0.090	0.069	0.027	-0.002	-0.028

A Gibbs free-energy profiles of CO_2 adducts formation

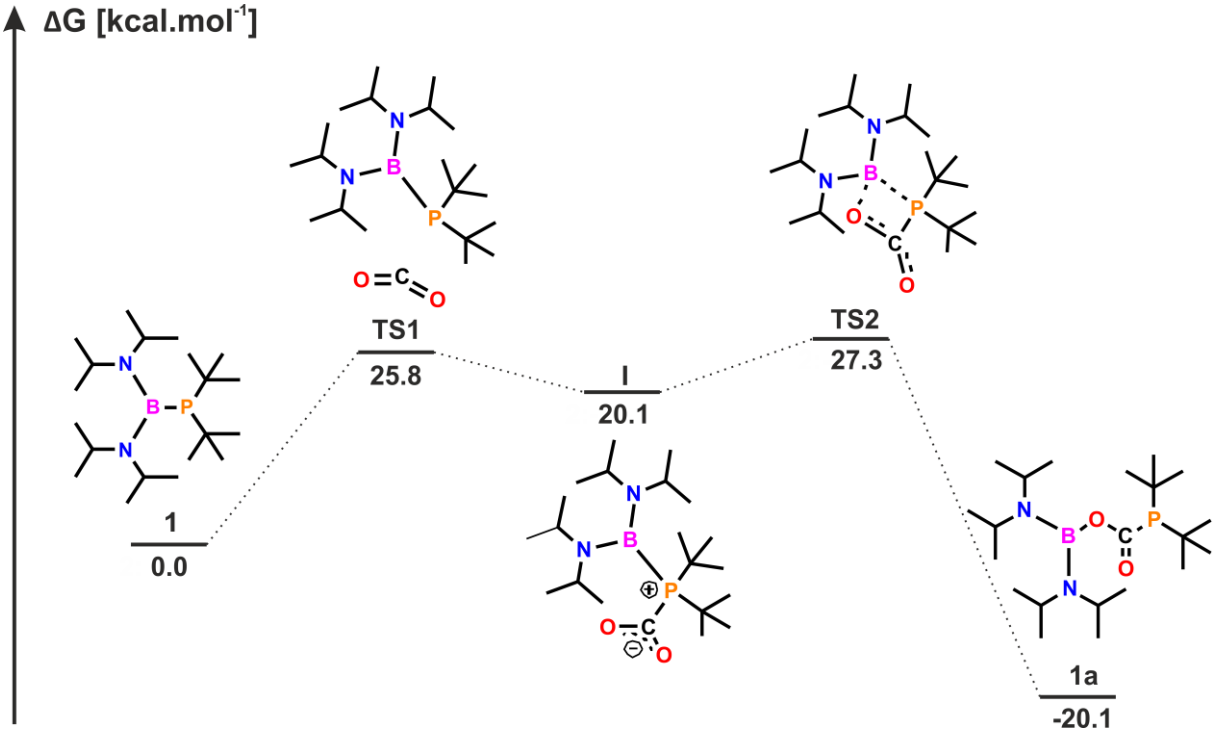


FIG. S40. A GIBBS FREE-ENERGY PROFILE OF REACTION **1A**

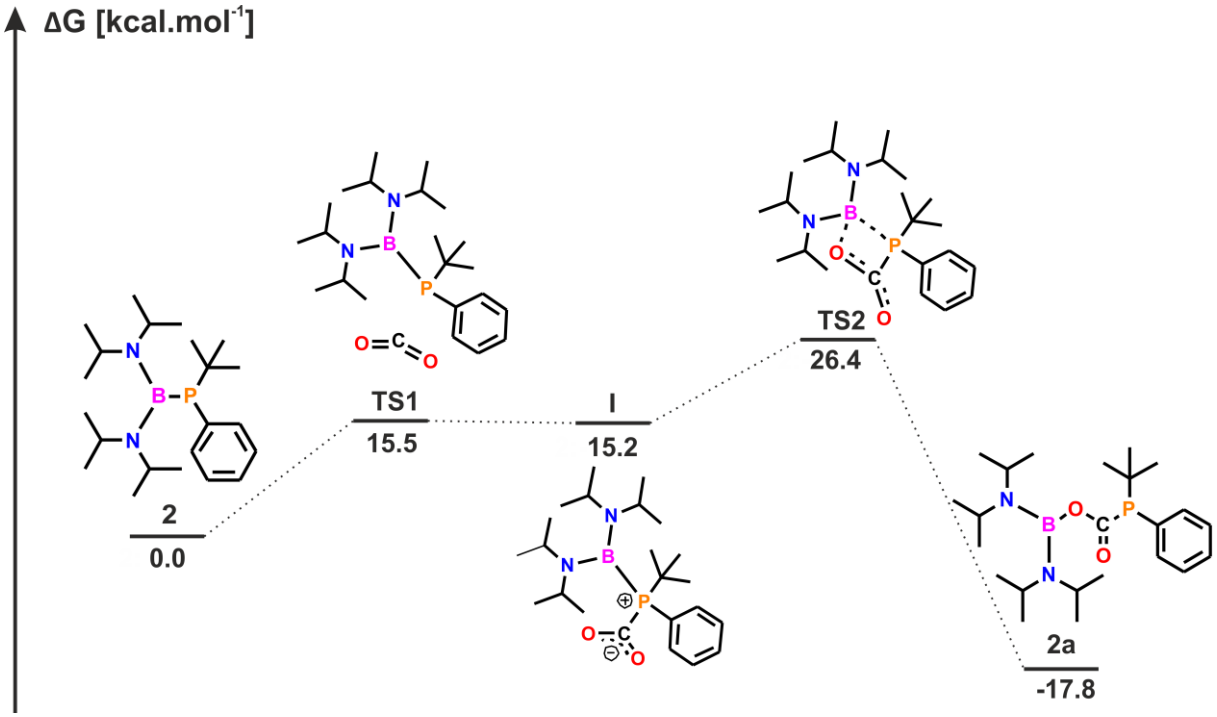


FIG. S41. A GIBBS FREE-ENERGY PROFILE OF REACTION **2A**

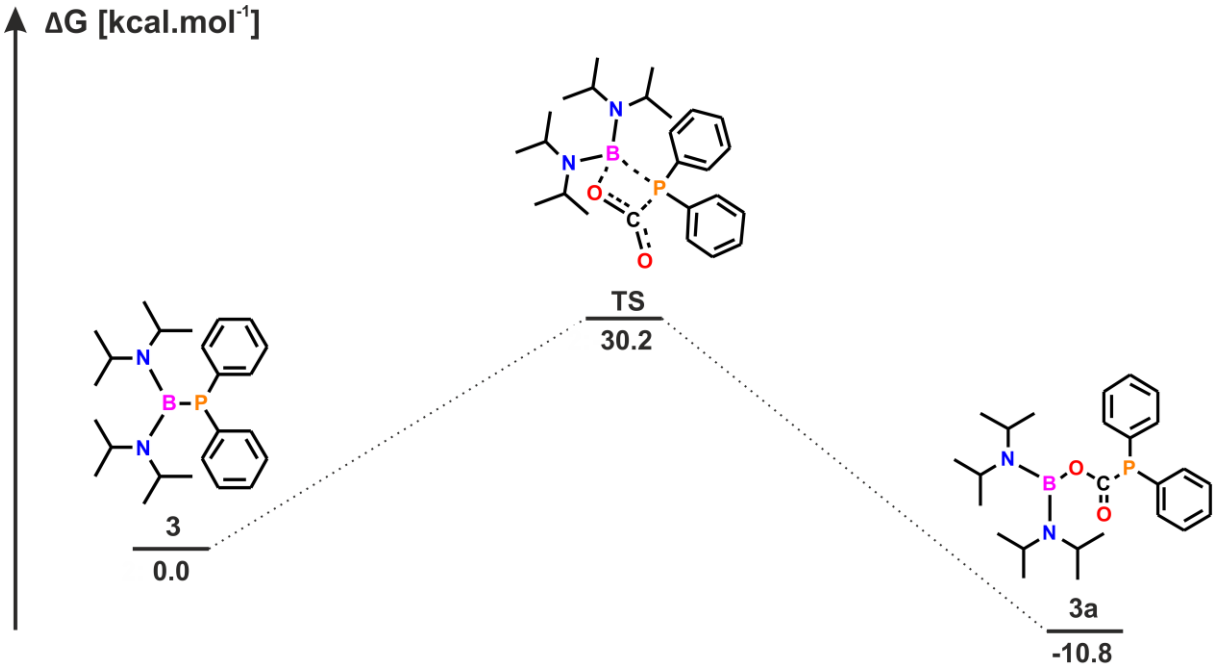


FIG. S42. A GIBBS FREE-ENERGY PROFILE OF REACTION **3A**

TABLE S11. FREE ENERGY OF TRANSFORMATONS ALONG THE REACTION PATH **1A-3A**. $\Delta G^{\ddagger}$ IS AN OVERALL ENERGY BARRIER CALCULATED AS DESCRIBED IN [4]

Reaction	**ΔG [kcal.mol^{-1}]**					**ΔG‡ [kcal.mol^{-1}]**
	Substrates	**TS1**	**I1**	**TS2**	**Product**	
1a	0.0	25.8	20.1	27.3	-20.1	27.3
2a	0.0	15.5	15.2	26.4	-17.8	26.4
Reaction	**ΔG [kcal.mol^{-1}]**					**ΔG‡ [kcal.mol^{-1}]**
	Substrates		**TS**		**Product**	
3a	0.0		30.2		-10.8	30.2

TABLE S12. ENTALPHY OF TRANSFORMATONS ALONG THE REACTION PATH **1A-3A**. $\Delta H^{\ddagger}$ IS AN OVERALL ENERGY BARRIER CALCULATED AS DESCRIBED IN [4]

Reaction	**ΔH [kcal.mol^{-1}]**					**ΔH‡ [kcal.mol^{-1}]**
	Substrates	**TS1**	**I1**	**TS2**	**Product**	
1a	0.0	13.5	8.3	14.9	-30.1	14.9
2a	0.0	3.3	3.8	13.6	-26.4	13.6
Reaction	**ΔH [kcal.mol^{-1}]**					**ΔH‡ [kcal.mol^{-1}]**
	Substrates		**TS**		**Product**	
3a	0.0		18.1		-21.2	18.1

Optimized structures, Hirshfeld atomic charges and Cartesian coordinates

Hirshfeld atomic charges for all optimized structures of substrates, intermediates, transition states and products were presented in Figures S43-S55. Hydrogen atoms are omitted for clarity.

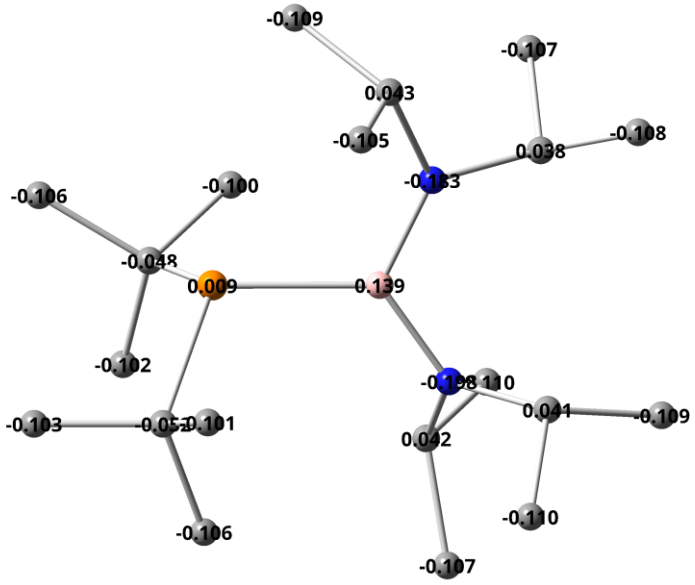


FIG. S43. OPTIMIZED STRUCTURE **1**

C	1.08827900	-2.51289300	-1.04050600
H	2.06352100	-3.00688800	-1.06759200
C	0.73087400	-2.22553000	-2.50039800
H	0.75559200	-3.15313700	-3.08237200
H	-0.27168700	-1.80058800	-2.58277100
H	1.44818600	-1.52328300	-2.93730700
C	0.12956700	-3.53307300	-0.41348400
H	0.21189300	-4.48337700	-0.95352500
H	0.38067800	-3.72095300	0.63394700
H	-0.90427200	-3.18838600	-0.47289200
C	2.60311500	-1.25307800	0.44515400
H	2.64120700	-0.29145300	0.95285300
C	2.65589200	-2.32477700	1.54082400
H	3.57190600	-2.20874600	2.12942900
H	1.79770700	-2.23258700	2.21308000
H	2.65911700	-3.33710100	1.12310000
C	3.84407200	-1.35110600	-0.45451900
H	4.73974700	-1.12675000	0.13420500
H	3.97806200	-2.35358600	-0.87349700
H	3.80292100	-0.64206200	-1.28447900
C	0.48573500	1.96460500	1.24135400
H	-0.54263400	1.62065700	1.38265700
C	1.24809400	1.62569600	2.53684800
H	0.71948400	2.02940400	3.40771600

H	1.34253600	0.54423300	2.67008000
H	2.25558300	2.05262100	2.53183700
C	0.41956700	3.48946200	1.09258400
H	-0.07652100	3.90204000	1.97698800
H	1.41174100	3.94535100	1.03969800
H	-0.14950100	3.80493800	0.21824600
C	2.10123500	1.65219200	-0.72910000
H	2.37309000	0.77686400	-1.32338700
C	1.69683000	2.72783600	-1.75265500
H	2.49066400	2.84305500	-2.49914800
H	0.78038200	2.44005400	-2.27371100
H	1.53602900	3.70508400	-1.29139200
C	3.36933500	2.10060400	0.01411700
H	4.17289400	2.25579200	-0.71358600
H	3.22417300	3.04756300	0.54089500
H	3.71628500	1.36017200	0.73753400
N	0.97058900	1.19100900	0.09379700
B	0.42247000	-0.14274300	-0.13099700
N	1.31011600	-1.26662100	-0.26929500
P	-1.51533000	-0.57815100	-0.33590700
C	-2.37815800	0.79411800	-1.31700000
C	-2.20663000	2.23538900	-0.83046000
C	-1.76063300	0.69351000	-2.72539000
C	-3.87440400	0.46098500	-1.43600100
H	-2.54139400	2.38022900	0.19917200
H	-1.15807800	2.52382400	-0.89630800
H	-2.78546800	2.91679600	-1.46871200
H	-1.97242400	-0.27528400	-3.18798100
H	-2.17622500	1.47761100	-3.37140200
H	-0.67308400	0.82511000	-2.70132300
H	-4.34336500	1.13516800	-2.16445400
H	-4.02955400	-0.56812700	-1.77613800
H	-4.40372300	0.58886900	-0.48760400
C	-2.30197200	-0.78457900	1.39741200
C	-1.22429700	-1.34774800	2.33741000
C	-2.91458100	0.45977700	2.05580600
C	-3.41160000	-1.84469800	1.25236000
H	-0.73114900	-2.22506400	1.91065400
H	-0.45586400	-0.60205300	2.55984800
H	-1.68404100	-1.64881500	3.28750600
H	-3.72375900	0.89023600	1.46124500
H	-3.34117100	0.17778700	3.02754200
H	-2.17645800	1.24334600	2.24365500
H	-3.87087700	-2.04663000	2.22937100
H	-4.20209100	-1.51304200	0.57324600
H	-3.00931300	-2.78376700	0.86102200

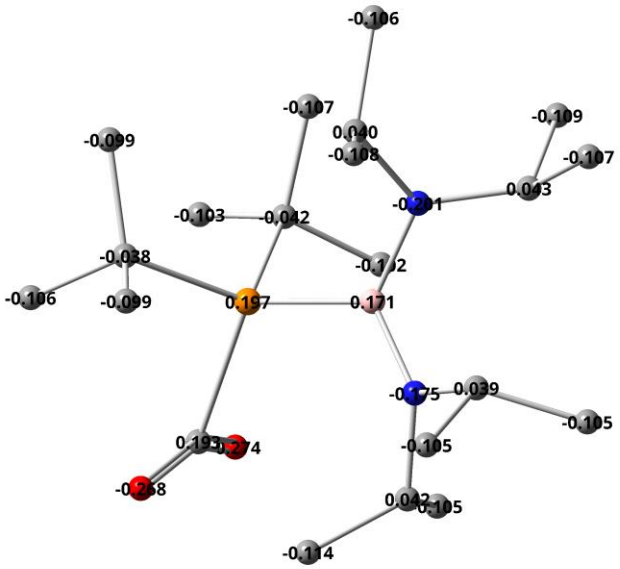


FIG. S44. OPTIMIZED STRUCTURE **1A_TS1**

C	-0.66714500	2.81700300	-0.43937200
H	-1.52946500	3.47969600	-0.54698700
C	-0.04407100	2.76666000	-1.83331800
H	0.23540100	3.77675400	-2.14816700
H	0.85479100	2.15560100	-1.88919000
H	-0.77333700	2.37376500	-2.54977900
C	0.20672200	3.45875400	0.63859900
H	0.63147100	4.39358400	0.25904300
H	-0.38384800	3.69215900	1.52741200
H	1.04109000	2.83065200	0.93649300
C	-2.64546900	1.64288100	0.41586700
H	-2.95955700	0.64008500	0.67869200
C	-2.76234300	2.47345300	1.69807000
H	-3.77590900	2.37324500	2.10016200
H	-2.05489600	2.12329200	2.45528600
H	-2.58248500	3.53854700	1.52394000
C	-3.61160400	2.17252300	-0.65297700
H	-4.64187700	1.99059100	-0.33068900
H	-3.50990000	3.25054000	-0.80978900
H	-3.46776400	1.67846200	-1.61660700
C	-1.45930000	-1.88711400	1.07590300
H	-0.43622300	-1.80404600	1.43911500
C	-2.34333600	-1.42371700	2.24893000
H	-2.11890700	-2.01763500	3.14159600
H	-2.15425000	-0.37386200	2.49196700
H	-3.40879300	-1.53890200	2.03213900
C	-1.69758000	-3.37835300	0.81207400
H	-1.50294800	-3.92750400	1.73887000
H	-2.72943900	-3.59263900	0.52434800
H	-1.03455400	-3.78054800	0.04565900
C	-2.56206600	-1.08601800	-1.10514700
H	-2.53908400	-0.12469400	-1.62410700

C	-2.26681000	-2.14218200	-2.18418200
H	-3.03500200	-2.08783400	-2.96267000
H	-1.29965500	-1.97141400	-2.65881500
H	-2.27682500	-3.15784600	-1.78118600
C	-4.00280600	-1.29425700	-0.60493900
H	-4.68543600	-1.20638600	-1.45579700
H	-4.14775100	-2.28977300	-0.17826400
H	-4.31600500	-0.56081600	0.13890000
N	-1.50105400	-0.98051100	-0.07875100
B	-0.65295600	0.21224100	-0.03838900
N	-1.23961000	1.50684300	-0.04072800
P	1.42946300	-0.05968800	-0.01933000
C	1.81250700	-1.30176000	-1.39764500
C	1.13226700	-2.66518100	-1.22757100
C	1.28474700	-0.65388300	-2.69422300
C	3.32787700	-1.53394200	-1.52147400
H	1.54874000	-3.24318700	-0.40210100
H	0.06371300	-2.55087700	-1.07495800
H	1.28472200	-3.24733800	-2.14479100
H	1.82825800	0.26123300	-2.93124700
H	1.41377300	-1.36176300	-3.52175800
H	0.21675100	-0.41844800	-2.62578700
H	3.50880400	-2.17743000	-2.39108300
H	3.87800000	-0.60403800	-1.66912800
H	3.72691500	-2.05539800	-0.64637900
C	2.07312100	-0.67567800	1.68090000
C	1.26174900	0.08095900	2.74788400
C	1.99970600	-2.19594500	1.92119000
C	3.56363300	-0.30884400	1.86328600
H	1.31161500	1.16172400	2.58537800
H	0.20893000	-0.21739500	2.76813800
H	1.68681900	-0.12621300	3.73710900
H	2.75406800	-2.72191500	1.33020100
H	2.23042800	-2.38068600	2.97709100
H	1.03521500	-2.65765200	1.71653300
H	3.92048500	-0.79306000	2.78002100
H	4.18283200	-0.67119900	1.03818200
H	3.71403600	0.76406900	1.95533800
C	2.78145500	1.60162600	-0.45494900
O	2.99934400	2.23761100	0.55357500
O	3.10153500	1.57793600	-1.62426600

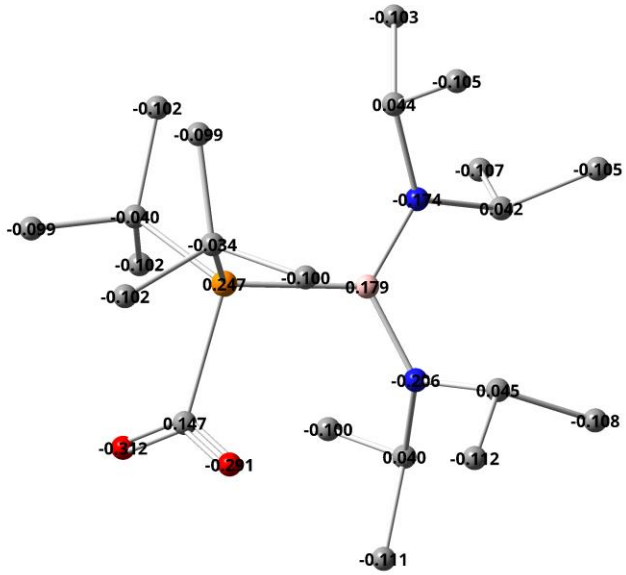


FIG. S45. OPTIMIZED STRUCTURE **1A_I**

C	1.56649200	-2.18072300	-1.21864800
H	2.64185500	-2.14986600	-1.46182300
C	0.84051500	-1.69451000	-2.46887000
H	1.16050100	-2.28847900	-3.32942500
H	-0.24061100	-1.81171500	-2.37731900
H	1.07881400	-0.64691600	-2.68646200
C	1.20830600	-3.64214100	-0.92905500
H	1.30997700	-4.22695700	-1.84911700
H	1.87566500	-4.08417700	-0.18588200
H	0.18326600	-3.72957800	-0.56235200
C	2.19846200	-1.49053500	1.11961100
H	2.17206900	-0.53997700	1.66629700
C	1.60436100	-2.56471100	2.05630600
H	1.78050100	-2.29670700	3.10379400
H	0.53275700	-2.67286600	1.88395600
H	2.06501300	-3.54322600	1.89092000
C	3.67673200	-1.80539600	0.84957200
H	4.20480100	-1.85179800	1.80729700
H	3.79969300	-2.77973100	0.36719400
H	4.17102500	-1.05258500	0.23028500
C	0.82063000	2.45624300	0.52837500
H	-0.25397200	2.28096000	0.56740500
C	1.28351300	2.63577000	1.98473500
H	0.59587000	3.30774300	2.50948400
H	1.29745000	1.68343400	2.51864100
H	2.28141700	3.07423900	2.05082400
C	1.02714300	3.76521900	-0.23748400
H	0.38551500	4.53297800	0.20616100
H	2.05784200	4.12334400	-0.16772400
H	0.76561400	3.67772900	-1.29303600
C	2.73035000	1.24726600	-0.66516800
H	2.93286500	0.19586700	-0.85909400
C	2.81811300	1.93992000	-2.03359500

H	3.72581700	1.60120700	-2.54343700
H	1.96071800	1.67106900	-2.65785000
H	2.86980600	3.02841500	-1.96441200
C	3.82354600	1.74237600	0.28265500
H	4.80097000	1.52144700	-0.15796700
H	3.77924900	2.82302000	0.44455400
H	3.76935600	1.24069500	1.25236300
N	1.35815200	1.24183600	-0.10120900
B	0.66576000	0.00016400	-0.10430000
N	1.37571900	-1.25872800	-0.08876300
P	-1.40171300	-0.07332700	-0.02829200
C	-2.30476900	0.95786500	-1.34128900
C	-2.03164700	2.46694000	-1.27363600
C	-1.82051000	0.47876900	-2.72229500
C	-3.81829500	0.70561000	-1.23523200
H	-2.26651700	2.92070700	-0.30964400
H	-0.99273800	2.68601500	-1.52116400
H	-2.65577100	2.96043300	-2.02802500
H	-2.03856000	-0.57778800	-2.87953300
H	-2.34352000	1.06254800	-3.48921600
H	-0.74845800	0.65325400	-2.85334400
H	-4.30698600	1.16489400	-2.10256700
H	-4.04810700	-0.36239900	-1.24556600
H	-4.24923700	1.16386200	-0.34111100
C	-2.09877300	0.23970900	1.72630700
C	-1.05520100	-0.27720000	2.72885400
C	-2.41381600	1.71221900	2.03152700
C	-3.39817800	-0.56576000	1.93636600
H	-0.89562200	-1.34668500	2.59544300
H	-0.09543200	0.23636700	2.62883400
H	-1.42287800	-0.10282800	3.74687800
H	-3.21266000	2.10436300	1.39814000
H	-2.76615300	1.77304500	3.06767300
H	-1.54691500	2.37089600	1.95305900
H	-3.74976800	-0.38040700	2.95821700
H	-4.19493600	-0.26278400	1.25470000
H	-3.22833400	-1.63661300	1.82528700
C	-1.85154800	-1.98796300	-0.30790100
O	-1.48681700	-2.65184100	0.66298400
O	-2.41493500	-2.23952300	-1.36954200

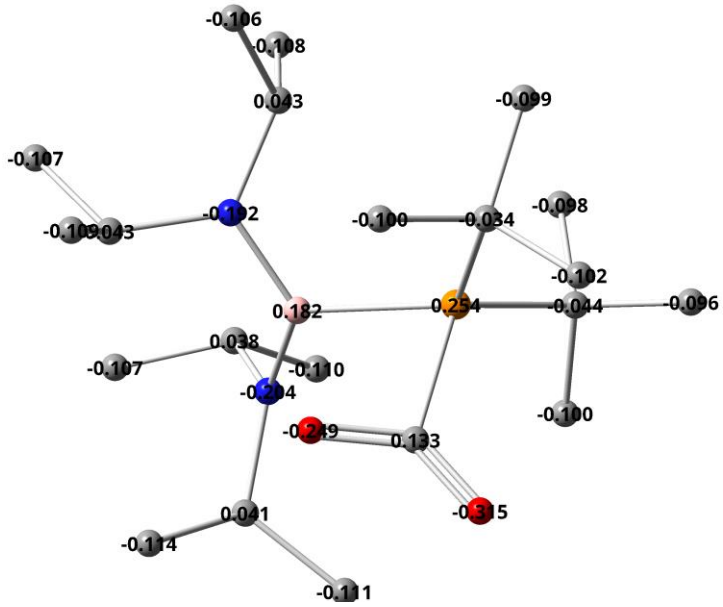


FIG. S46. OPTIMIZED STRUCTURE **1A_TS2**

C	1.83786500	-2.31954600	-0.84263500
H	2.65105900	-2.82575400	-0.31636000
C	2.42911900	-1.87861600	-2.18724500
H	2.79968200	-2.75531600	-2.72982100
H	1.67833000	-1.37895500	-2.79981100
H	3.27672100	-1.20237300	-2.03699800
C	0.78587900	-3.41692600	-1.02467400
H	1.24289600	-4.23473200	-1.59249700
H	0.47523200	-3.82817600	-0.06139800
H	-0.09776800	-3.09944200	-1.57540700
C	2.41383900	-1.06705700	1.19936800
H	2.22069500	-0.09424600	1.65195700
C	2.11796200	-2.13186600	2.26343500
H	2.83838900	-2.06134200	3.08545100
H	1.11514900	-2.01029700	2.68093100
H	2.18991300	-3.14146400	1.84384800
C	3.91548700	-1.08877800	0.85768100
H	4.48374300	-0.75115200	1.73090500
H	4.27545500	-2.09209600	0.61025900
H	4.15948400	-0.42744800	0.02485600
C	0.50216800	2.28634800	0.92730700
H	-0.51614100	1.91734200	1.06799300
C	1.11821300	2.27854100	2.33776400
H	0.50903900	2.89862400	3.00464800
H	1.14087100	1.26867600	2.75592500
H	2.13507300	2.67765600	2.34959600
C	0.38944500	3.73178800	0.42825000
H	-0.20758400	4.30817900	1.14282300
H	1.36369900	4.22077400	0.35740900
H	-0.09927700	3.80195500	-0.54388300
C	2.33878700	1.63448200	-0.74582000
H	2.71081700	0.65931800	-1.06339400

C	2.04086300	2.39916100	-2.04232300
H	2.93895400	2.42452900	-2.66914500
H	1.25082600	1.88813300	-2.59938300
H	1.73587800	3.43303800	-1.85986200
C	3.46520600	2.29303300	0.05562200
H	4.37180200	2.31387200	-0.55794500
H	3.23993500	3.32658000	0.33235300
H	3.69323000	1.73358700	0.96626200
N	1.11004700	1.31960600	0.00937200
B	0.61223500	-0.02030000	-0.12835700
N	1.49418000	-1.17280200	0.03888600
P	-1.46054700	-0.20246800	-0.03100800
C	-2.61717000	1.21824900	-0.57010300
C	-2.99260700	2.19469400	0.55736100
C	-1.90704800	1.97116800	-1.71223900
C	-3.92895600	0.64037600	-1.14784400
H	-3.42357800	1.68786300	1.42445400
H	-2.15804200	2.80955400	0.89586700
H	-3.75675800	2.87923400	0.17138700
H	-1.90876100	1.38460200	-2.63346300
H	-2.44427200	2.90802200	-1.90004600
H	-0.86750500	2.20100200	-1.48349200
H	-4.42934900	1.44768500	-1.69578400
H	-3.75498500	-0.18280900	-1.84382100
H	-4.61679900	0.30207300	-0.37245500
C	-2.13645700	-1.15560900	1.43474700
C	-1.53536600	-2.56577900	1.34417600
C	-1.63009300	-0.46021700	2.71040100
C	-3.66348200	-1.28584800	1.47019700
H	-1.89990300	-3.09360100	0.45862200
H	-0.44744000	-2.52955900	1.29669700
H	-1.82392300	-3.13664700	2.23502600
H	-2.02826300	0.55354700	2.81924800
H	-1.94363300	-1.03777700	3.58808900
H	-0.53751500	-0.39719500	2.72535800
H	-3.93344500	-1.94264700	2.30564600
H	-4.16537100	-0.32929600	1.63270000
H	-4.04832100	-1.73765500	0.55234000
C	-1.29961600	-1.08962300	-1.69134400
O	-2.09769400	-1.89194300	-2.15195700
O	-0.23168400	-0.57965900	-2.14042700

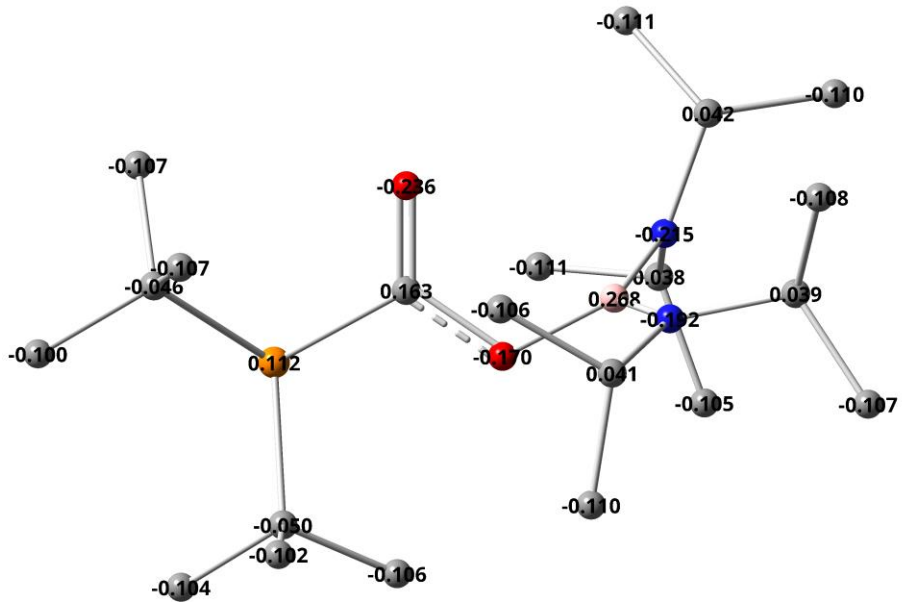


FIG. S47. OPTIMIZED STRUCTURE **1A**

P	-2.56061000	-0.71053300	0.28553900
O	0.03721300	0.18828000	0.38265600
O	-0.49680600	-0.99662400	-1.43076600
N	2.11410200	1.25025800	-0.30355500
N	2.09422200	-1.19852500	0.34612100
C	1.42921100	2.49332300	-0.70828800
H	2.21051600	3.15369800	-1.09729800
C	0.78709100	3.21866700	0.47948100
H	0.03427900	2.58747000	0.95384000
H	0.30254900	4.14253100	0.14508000
H	1.53577000	3.47772500	1.23224900
C	0.43996900	2.29494900	-1.85883900
H	0.88287600	1.68399700	-2.64994100
H	0.16425400	3.26712900	-2.28041800
H	-0.47859700	1.80591200	-1.53209800
C	3.58059100	1.34007800	-0.24499200
H	3.91315900	0.38151300	0.14897800
C	4.06923600	2.40133000	0.74699200
H	3.83047000	3.41946700	0.42130200
H	5.15732900	2.33701600	0.84851100
H	3.62181600	2.23943400	1.73201700
C	4.21981300	1.53224400	-1.62442400
H	3.85492900	0.78474600	-2.33431600
H	5.30756800	1.43384200	-1.54991100
H	4.00868300	2.52288600	-2.04128600
C	2.94728800	-1.81419300	-0.67967900
H	3.07593700	-1.05127400	-1.45336300
C	2.27183900	-3.01454200	-1.35477600
H	2.15954300	-3.84847100	-0.65277700
H	2.88147200	-3.36928900	-2.19285600
H	1.28429800	-2.73325500	-1.72772600
C	4.34525200	-2.20650000	-0.17789300

H	4.83636700	-1.38377900	0.34961400
H	4.97580500	-2.49326200	-1.02563600
H	4.30947800	-3.06513900	0.50067200
C	1.77370000	-2.01220000	1.52686700
H	2.55289100	-2.77957000	1.58164800
C	0.42679500	-2.75027000	1.49438300
H	-0.40464600	-2.07877700	1.72227100
H	0.42072200	-3.54189600	2.25164600
H	0.23735400	-3.20460800	0.51989700
C	1.88844200	-1.16808400	2.79964000
H	2.87857400	-0.70802100	2.87199900
H	1.72033000	-1.78242800	3.69023900
H	1.13605800	-0.37104100	2.80240900
C	-0.83173100	-0.47745500	-0.38246800
C	-2.90847700	0.74766100	1.45298000
C	-2.90734300	2.13457300	0.80024900
H	-1.98381100	2.32409900	0.24816600
H	-2.99907100	2.90793500	1.57367600
H	-3.74845100	2.25808700	0.11236500
C	-4.27662200	0.49164800	2.11899200
H	-5.11212500	0.55711300	1.42171300
H	-4.43794200	1.25025000	2.89457500
H	-4.30854000	-0.49115800	2.60015400
C	-1.86433100	0.69920200	2.58720800
H	-1.80036600	-0.30068300	3.03097500
H	-2.17242400	1.39556900	3.37638500
H	-0.86962800	0.98196300	2.24741100
C	-3.55231300	-0.55200900	-1.33586000
C	-3.43079300	-1.92913400	-2.01975400
H	-2.39110000	-2.16689500	-2.25251000
H	-3.99947300	-1.91474900	-2.95822700
H	-3.83876900	-2.72340900	-1.38630700
C	-3.07483800	0.53583000	-2.31061900
H	-3.10072300	1.53310900	-1.86462700
H	-3.73939100	0.54748600	-3.18403000
H	-2.06266100	0.33785600	-2.66765500
C	-5.03662400	-0.31590600	-1.01614700
H	-5.41786300	-1.02205900	-0.27105700
H	-5.61731400	-0.45839800	-1.93524300
H	-5.22772200	0.70241300	-0.66741800
B	1.45365800	0.06444800	0.09848500

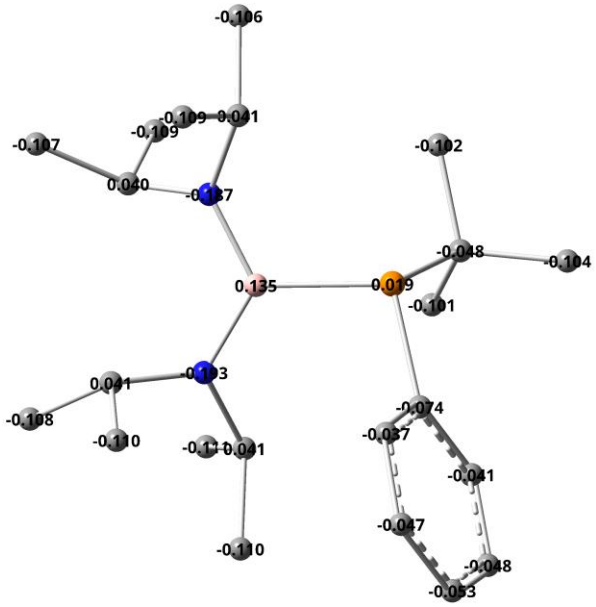


FIG. S48. OPTIMIZED STRUCTURE **2**

P	-0.58040200	1.40466300	-0.64960400
N	2.03658300	0.13010200	-0.34754100
N	0.12677000	-1.32992000	0.38863400
C	-0.61201100	2.16162400	2.16232200
H	-1.57699900	1.68742200	2.35748600
H	-0.49967100	2.98245800	2.88285200
H	0.16884500	1.42377200	2.37350000
C	-2.25928100	0.65463300	-0.69755600
C	-0.48550500	2.70279600	0.73070200
C	-3.73157500	-0.78977800	-2.00110000
H	-3.88687200	-1.41478300	-2.87550600
C	0.66429100	-2.57978300	-0.17722500
H	1.56131200	-2.27421400	-0.71987400
C	-0.89452900	-1.33764000	1.44243300
H	-1.30811300	-0.32860900	1.42929500
C	2.50334700	0.93792800	-1.49163900
H	1.67333100	1.60843300	-1.72496000
C	1.10183900	-3.64322800	0.83629600
H	1.79302000	-3.23927800	1.58124000
H	1.61286700	-4.45501900	0.30832900
H	0.25119500	-4.08380800	1.36380700
C	-2.08109700	-2.27931200	1.22981500
H	-2.53894800	-2.12328800	0.25075900
H	-2.83998200	-2.06726600	1.98982700
H	-1.80533000	-3.33333100	1.33183100
C	4.08941300	-1.38186300	-0.14626800
H	3.66949500	-2.09959200	-0.85609700
H	4.63982100	-1.94627900	0.61359000
H	4.81438900	-0.76178600	-0.67971500
C	-0.28968900	-1.51847400	2.84519400
H	0.01248300	-2.55080400	3.04044100
H	-1.02622600	-1.23841100	3.60653600

H	0.58828700	-0.87647800	2.96953300
C	2.99728800	-0.55452200	0.54087400
H	2.38792700	-1.25629300	1.11049300
C	3.60068000	0.38570600	1.59740500
H	4.32745000	1.08796100	1.18417400
H	4.11232000	-0.20690600	2.36390800
H	2.80816600	0.95948900	2.08748100
C	3.71464000	1.84059800	-1.24490600
H	3.55534500	2.51027600	-0.39710400
H	3.86756900	2.46116400	-2.13342600
H	4.64049100	1.28373100	-1.07832700
C	-1.53616500	3.79489000	0.47208900
H	-1.41281800	4.22751600	-0.52565700
H	-1.41770500	4.59949400	1.20910000
H	-2.56072300	3.42329100	0.54888400
C	-0.25863700	-3.19328200	-1.24281600
H	-1.14470400	-3.66485600	-0.81303800
H	0.28734300	-3.95906800	-1.80543800
H	-0.59167400	-2.42254800	-1.94286300
C	-3.30393600	0.82230500	0.22021400
H	-3.16543900	1.42894900	1.10732000
C	-2.50876500	-0.15180300	-1.81909600
H	-1.72935500	-0.27234700	-2.56772900
C	-4.75687600	-0.61365100	-1.07375100
H	-5.71633800	-1.10097800	-1.21559500
C	0.90895800	3.33905100	0.59432000
H	1.69728200	2.60599500	0.78465700
H	1.01605500	4.14720700	1.32869500
H	1.06478000	3.76305600	-0.40296300
B	0.62905000	-0.07510700	-0.11148000
C	2.70424800	0.07548500	-2.74708300
H	3.55689700	-0.60283400	-2.65607600
H	2.87570400	0.71431000	-3.62023000
H	1.80799800	-0.52398700	-2.93628800
C	-4.53761000	0.20190800	0.03256300
H	-5.32633700	0.35102400	0.76423100

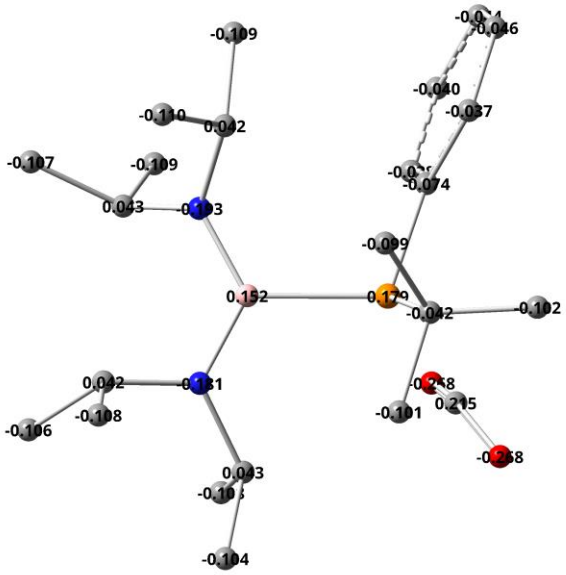


FIG. S49. OPTIMIZED STRUCTURE **2A_TS1**

P	0.63140300	-1.17619400	0.03395200
N	-2.08494700	-0.01643300	-0.11808100
N	-0.22819500	1.67105100	0.14514100
C	0.66049400	-1.17032200	2.89740500
H	1.61906700	-0.65113300	2.96835500
H	0.54497100	-1.76812400	3.80971000
H	-0.13214600	-0.41518500	2.89452300
C	2.27667100	-0.41693200	-0.23998500
C	0.55138300	-2.09612800	1.67547600
C	3.70826200	0.72215600	-1.83952100
H	3.85484300	1.12473200	-2.83695500
C	-0.75812300	2.68215400	-0.79050900
H	-1.61703800	2.19873900	-1.26159400
C	0.72236500	2.01810000	1.20929700
H	1.16839700	1.06636300	1.50527100
C	-2.50260300	-1.20745300	-0.88756300
H	-1.67120400	-1.90682500	-0.80979900
C	-1.27204800	3.98020800	-0.15717900
H	-1.99986700	3.79195900	0.63666500
H	-1.76442700	4.58203900	-0.92743000
H	-0.46166100	4.58485700	0.25922900
C	1.89214500	2.91613400	0.80518400
H	2.41197900	2.51660100	-0.06726000
H	2.60800600	2.95635300	1.63200200
H	1.57982800	3.94298400	0.59399400
C	-4.14751300	1.42347800	-0.54578000
H	-3.69274500	1.83438700	-1.45078300
H	-4.72366500	2.22174800	-0.06671900
H	-4.85404000	0.64539600	-0.84507200
C	0.02071200	2.55080800	2.46965200
H	-0.36122900	3.56604200	2.33570100
H	0.72510900	2.56730900	3.30855000

H	-0.82026100	1.90524600	2.74421800
C	-3.09055100	0.91393500	0.43882900
H	-2.50942700	1.78069600	0.75026100
C	-3.73656600	0.39212900	1.73182200
H	-4.48612300	-0.38172700	1.55824700
H	-4.23335600	1.22296800	2.24458600
H	-2.97176200	-0.01042300	2.40315500
C	-3.71181400	-1.97745600	-0.35355700
H	-3.58828600	-2.25444400	0.69527800
H	-3.80319200	-2.90261800	-0.92998400
H	-4.65232900	-1.43165400	-0.46407200
C	1.62772500	-3.19351500	1.71265100
H	1.49647400	-3.89436600	0.88464200
H	1.53275300	-3.75114700	2.65220400
H	2.64328700	-2.79364600	1.66501900
C	0.21132500	2.99067600	-1.94159100
H	1.07656200	3.57255000	-1.61753400
H	-0.30979100	3.56680300	-2.71402900
H	0.57383200	2.06404700	-2.39220600
C	3.30767800	-0.32444600	0.70259900
H	3.17863900	-0.71567100	1.70380400
C	2.50027200	0.10961800	-1.52004300
H	1.73162800	0.01493800	-2.27881100
C	4.72263800	0.81382000	-0.89019100
H	5.66557400	1.29077500	-1.13819400
C	-0.83517200	-2.76511500	1.72510900
H	-1.63312900	-2.01721200	1.73219900
H	-0.91200000	-3.34424300	2.65285100
H	-0.98661300	-3.44634100	0.88446400
B	-0.70646200	0.32048100	0.03605000
C	-2.66302400	-0.89196300	-2.37993600
H	-3.53925000	-0.26730400	-2.57410100
H	-2.77632200	-1.82217500	-2.94518100
H	-1.77372900	-0.38157800	-2.75934100
C	4.51865000	0.28255800	0.38045700
H	5.30140900	0.34219700	1.13030500
C	0.42906300	-2.62411100	-1.69477400
O	0.59697500	-1.97888400	-2.69560600
O	0.18086100	-3.71058100	-1.24092200

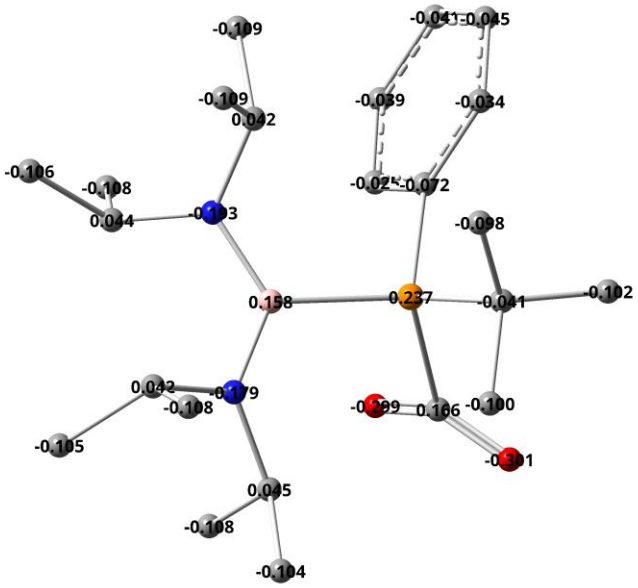


FIG. S50. OPTIMIZED STRUCTURE **2A_I**

P	0.64742400	-1.17167800	-0.00456000
N	-2.09703600	-0.03410700	-0.10510600
N	-0.23784300	1.64953400	0.16806300
C	0.66083400	-1.30272400	2.83844700
H	1.60936800	-0.77185400	2.94607600
H	0.54236200	-1.94131700	3.72176500
H	-0.14472900	-0.56099000	2.85607200
C	2.29611300	-0.41091900	-0.26448800
C	0.58392400	-2.18163500	1.57911500
C	3.76023700	0.75301300	-1.81161100
H	3.92885900	1.16985900	-2.79950900
C	-0.76567800	2.67594900	-0.75322900
H	-1.62647200	2.20140300	-1.23032300
C	0.70754000	1.97403900	1.24343500
H	1.15516600	1.01670800	1.52185400
C	-2.53652900	-1.20802000	-0.89122600
H	-1.70463500	-1.90995500	-0.85754700
C	-1.27580900	3.96598300	-0.10144200
H	-2.01066900	3.76888000	0.68373300
H	-1.75959800	4.58292700	-0.86497800
H	-0.46545400	4.55952600	0.33042200
C	1.87660800	2.88283400	0.86271400
H	2.40228900	2.50058100	-0.01395100
H	2.58764100	2.91127900	1.69408400
H	1.56161000	3.91166000	0.66690500
C	-4.16343600	1.41882900	-0.47100700
H	-3.72356900	1.84174500	-1.37776200
H	-4.72701300	2.21169300	0.03149300
H	-4.87829200	0.64802500	-0.76881000
C	-0.00201300	2.47463900	2.51222700
H	-0.40234500	3.48446900	2.39243400
H	0.70226800	2.49139700	3.35110600

H	-0.83082100	1.80945900	2.77680100
C	-3.09087300	0.89072300	0.48573100
H	-2.50238200	1.75082900	0.80119600
C	-3.71312000	0.34704300	1.78120400
H	-4.47116100	-0.41847200	1.60802100
H	-4.19356100	1.17064800	2.32039600
H	-2.93714000	-0.07419500	2.42792300
C	-3.73019800	-1.98781700	-0.33607600
H	-3.58242800	-2.27992100	0.70557400
H	-3.83532200	-2.90411100	-0.92395500
H	-4.67327800	-1.44096100	-0.41586700
C	1.68775400	-3.25136600	1.56746200
H	1.59081500	-3.89182300	0.68752200
H	1.58341100	-3.87487200	2.46334900
H	2.69312600	-2.82444100	1.57545400
C	0.20630400	2.99243600	-1.89933500
H	1.07961900	3.55632000	-1.56513500
H	-0.30746000	3.58938900	-2.66063800
H	0.55357800	2.06821200	-2.36656500
C	3.30295800	-0.32922000	0.70469400
H	3.15308400	-0.73589000	1.69636700
C	2.54450400	0.13603600	-1.53101400
H	1.79133700	0.05031400	-2.30595200
C	4.75197300	0.83234600	-0.83810400
H	5.69991000	1.31332300	-1.05761800
C	-0.78700600	-2.88440400	1.58958100
H	-1.60200700	-2.15680500	1.63886800
H	-0.84719600	-3.51433500	2.48460100
H	-0.91944800	-3.52163400	0.71235400
B	-0.72119700	0.30508500	0.03238900
C	-2.74473900	-0.86066400	-2.37003500
H	-3.63375400	-0.24326900	-2.52380700
H	-2.86482400	-1.78165700	-2.94831700
H	-1.86926500	-0.34059900	-2.76595100
C	4.51983300	0.28386700	0.42030000
H	5.28512700	0.33295600	1.18847900
C	0.41894800	-2.38674400	-1.66800200
O	0.42088100	-1.68361000	-2.66612900
O	0.30202600	-3.56115100	-1.36717800

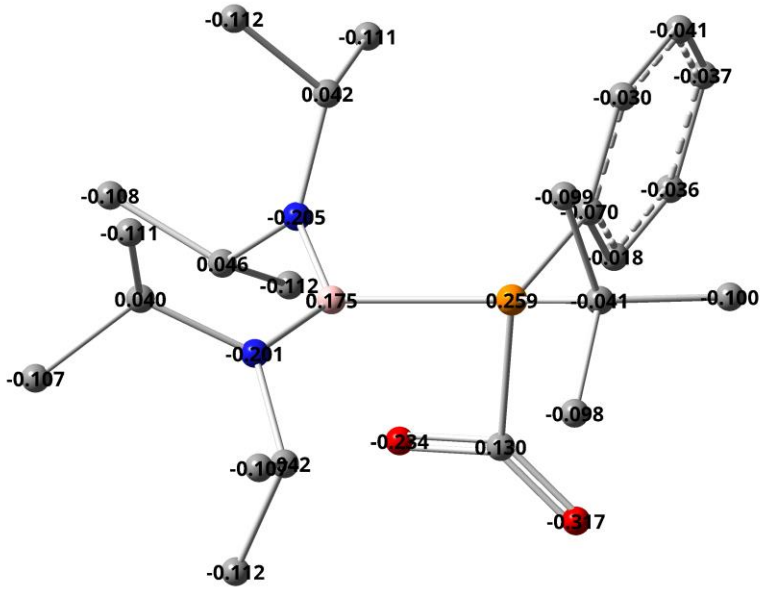


FIG. S51. OPTIMIZED STRUCTURE **2A_TS2**

P	-0.76572600	-1.10196700	0.03492400
N	2.18039500	-0.19313100	-0.05323600
N	0.39552200	1.62248100	-0.06108900
C	-0.73153400	-2.51230600	-2.38096000
H	-1.49255200	-1.87127300	-2.83442300
H	-0.76957100	-3.47842100	-2.89759200
H	0.25055400	-2.06585000	-2.56931000
C	-2.39404200	-0.26566700	0.04630500
C	-0.96425300	-2.73434300	-0.87798800
C	-4.16132600	0.84902000	1.27287500
H	-4.56794800	1.18986300	2.21944600
C	0.87605100	2.55838600	0.97335100
H	1.65372900	1.99899300	1.50558700
C	-0.39261700	2.03674700	-1.21988800
H	-0.83805800	1.11052300	-1.60255500
C	2.64585300	-1.44563800	0.55912400
H	1.74058200	-2.02284400	0.75474900
C	1.54107700	3.83647500	0.44802800
H	2.35514500	3.61934000	-0.24902500
H	1.96254700	4.39055000	1.29268700
H	0.82800700	4.49854500	-0.05175100
C	-1.55717900	2.98041700	-0.90655500
H	-2.17440600	2.59286000	-0.09354300
H	-2.18910200	3.08309400	-1.79441500
H	-1.20972400	3.98148300	-0.63470800
C	4.38030500	1.07155900	0.02558300
H	4.13179900	1.41704400	1.03266900
H	4.89788100	1.88379400	-0.49629100
H	5.08431000	0.23817400	0.10799100
C	0.44665200	2.58252600	-2.38912200
H	0.92845400	3.53236200	-2.14478500
H	-0.19740000	2.75081900	-3.25958100

H	1.22226900	1.86878400	-2.67901000
C	3.11763900	0.70017100	-0.75641000
H	2.55889600	1.62630700	-0.87949200
C	3.46498000	0.24185700	-2.18285000
H	4.21264300	-0.55397700	-2.20818700
H	3.86861100	1.08862800	-2.74931500
H	2.56744000	-0.11564800	-2.69734800
C	3.51441600	-2.31993100	-0.34858500
H	3.05650500	-2.46220700	-1.33230200
H	3.64203000	-3.30243100	0.11724700
H	4.51300400	-1.89774500	-0.49269400
C	-2.36285600	-3.30933400	-0.60529900
H	-2.53226600	-3.43482700	0.46846500
H	-2.43793200	-4.29430500	-1.08028600
H	-3.15961300	-2.68021600	-1.00784600
C	-0.19389200	2.89435100	2.02234000
H	-0.95062800	3.58145800	1.63462400
H	0.27646200	3.37083100	2.88953400
H	-0.67977900	1.97762400	2.36015800
C	-3.10015600	-0.02651000	-1.13959500
H	-2.69412000	-0.34475500	-2.09408400
C	-2.94115600	0.17579300	1.25481100
H	-2.42377800	-0.00216400	2.19134400
C	-4.85474500	1.07947500	0.08926600
H	-5.80558400	1.60245800	0.10616300
C	0.08236400	-3.73136600	-0.35250000
H	1.09878200	-3.43710800	-0.62073500
H	-0.10588000	-4.70518900	-0.81853300
H	0.01698200	-3.85524700	0.73199600
B	0.82868000	0.25917400	0.10397300
C	3.30330300	-1.26058500	1.93490500
H	4.30688200	-0.83550400	1.86141600
H	3.39033700	-2.23462900	2.42843200
H	2.68216100	-0.61800500	2.56121200
C	-4.32202100	0.63491200	-1.11935900
H	-4.85171300	0.81159600	-2.05005200
C	-0.35907400	-1.27724600	1.87769900
O	0.37761400	-0.25894900	2.06826400
O	-0.76281700	-2.15694800	2.61669300

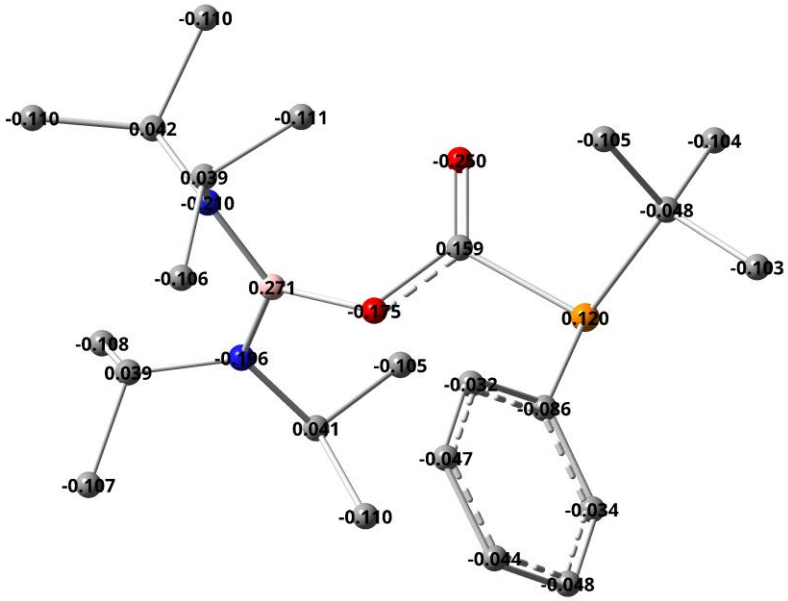


FIG. S52. OPTIMIZED STRUCTURE **2A**

P	-2.30600800	-0.07631100	-1.17213200
O	0.14917500	0.14574100	-0.14844100
O	-0.18095800	-1.75546200	-1.31458200
N	2.30660100	1.07736300	-0.68205600
N	2.16054100	-0.97537700	0.79493200
C	1.74663800	1.93653700	-1.74535300
H	2.56687500	2.58814800	-2.06193600
C	0.62635800	2.86730500	-1.26567200
H	-0.29015300	2.32053300	-1.03941900
H	0.40254000	3.60611900	-2.04285800
H	0.93121900	3.40173400	-0.36159400
C	1.34718300	1.13383100	-2.98517900
H	2.18433700	0.51750300	-3.32580700
H	1.06134800	1.81258000	-3.79539000
H	0.49807300	0.47363600	-2.79536100
C	3.66142300	1.43842400	-0.24126800
H	3.90390000	0.74501000	0.56277500
C	3.70992900	2.84266000	0.37271600
H	3.50339500	3.62398200	-0.36624200
H	4.70455500	3.03508100	0.78783500
H	2.97541200	2.93058200	1.17859600
C	4.71996100	1.27318200	-1.33762700
H	4.66399400	0.28107400	-1.79433400
H	5.72086200	1.40139100	-0.91314400
H	4.60556600	2.01643700	-2.13397500
C	3.33414200	-1.72378700	0.32367000
H	3.66484100	-1.21181200	-0.58348200
C	2.97818200	-3.15717400	-0.09143200
H	2.70515200	-3.76600300	0.77780200
H	3.83996100	-3.63580300	-0.56897300
H	2.13939900	-3.15213300	-0.79236100
C	4.51235200	-1.72992300	1.30850100
H	4.73958100	-0.72600700	1.67827900
H	5.40601600	-2.12350800	0.81388200
H	4.31772000	-2.37044600	2.17505600
C	1.52695100	-1.44663100	2.03350600
H	2.28977800	-2.03091800	2.55877400
C	0.31677600	-2.37384300	1.85450400

H	-0.57052700	-1.81740900	1.54932200
H	0.08478900	-2.86859700	2.80410500
H	0.49934900	-3.13641900	1.09603600
C	1.17845000	-0.26117700	2.93918000
H	2.07437400	0.32552000	3.16352200
H	0.74416400	-0.61003700	3.88220500
H	0.44896600	0.39921400	2.45794100
C	-0.59964200	-0.72882700	-0.81888200
C	-3.40574200	-1.60743400	-1.03090100
C	-3.09760700	-2.51075000	0.16781400
H	-2.08906800	-2.92717200	0.10501100
H	-3.80533900	-3.34930600	0.18009200
H	-3.20712900	-1.97908000	1.11799800
C	-4.85125700	-1.09404200	-0.93174400
H	-5.02973000	-0.56683200	0.01056500
H	-5.54062300	-1.94536100	-0.97831700
H	-5.10110800	-0.41663000	-1.75602700
C	-3.22993200	-2.40048900	-2.33662000
H	-3.48408600	-1.79137500	-3.21040700
H	-3.89780900	-3.27085300	-2.32485500
H	-2.20286300	-2.75713300	-2.44968600
B	1.58376600	0.04756900	-0.02680100
C	-2.70572600	0.94578200	0.30083100
C	-3.39890900	2.13736100	0.05689000
C	-2.38252100	0.62405000	1.62489900
C	-3.77038300	2.97884400	1.10401400
H	-3.64247300	2.41141300	-0.96607000
C	-2.74433300	1.46471400	2.67213900
H	-1.82940400	-0.28155700	1.84387100
C	-3.44261700	2.64385000	2.41438800
H	-4.30593800	3.89935500	0.89345600
H	-2.47804100	1.20052900	3.69113400
H	-3.72436400	3.30045000	3.23178800

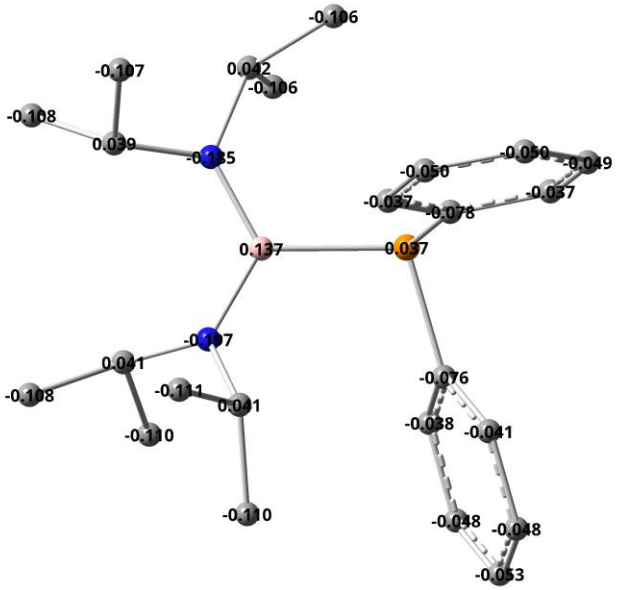


FIG. S53. OPTIMIZED STRUCTURE **3**

P	0.73282500	0.64487900	-1.15507800
N	-0.72684200	-1.35372600	0.53360400

N	-2.13081400	0.40985100	-0.56995700
C	2.10879300	-1.68469700	-1.75849200
H	1.31484900	-1.81228000	-2.49055800
C	2.17934300	2.93732800	-0.48102600
H	2.65600100	2.77855600	-1.44476600
C	1.13574700	-2.62372500	1.71435800
H	0.56508400	-3.48849000	2.06659100
H	1.93734000	-2.44551200	2.43823600
H	1.59859100	-2.86961000	0.75697600
C	1.93341100	4.25135000	1.52939500
H	2.21882000	5.10455000	2.13710400
C	-2.28812700	0.55513700	-3.05335400
H	-1.22905700	0.36472900	-3.24687000
H	-2.67657000	1.16981100	-3.87235300
H	-2.82271500	-0.39986500	-3.05309800
C	0.27601300	-1.36339200	1.60621400
H	0.96189500	-0.55108600	1.35319700
C	2.10726800	-0.55530700	-0.92941700
B	-0.85579300	-0.17756200	-0.29489000
C	3.11424600	-2.64285400	-1.66541800
H	3.08862600	-3.51501400	-2.31206400
C	1.19415400	2.03962700	-0.04628600
C	3.16540700	-0.39423800	-0.02784500
H	3.19251100	0.47497200	0.62318400
C	0.58227300	2.27978600	1.18941900
H	-0.18699800	1.60431200	1.55087700
C	-2.48225600	1.27449500	-1.71646200
H	-3.55645700	1.45611500	-1.62427500
C	4.18005600	-1.34478900	0.05778700
H	4.98802700	-1.20313600	0.76963600
C	4.15566800	-2.47664700	-0.75405800
H	4.94368400	-3.21980900	-0.68272600
C	-2.31729700	-3.08158000	1.52833600
H	-1.61549600	-3.59831700	2.18902000
H	-3.06244800	-3.81634700	1.20675600
H	-2.83230600	-2.31310000	2.11113400
C	-0.31967700	-0.98818300	2.97535700
H	-0.98701800	-0.12463800	2.88411100
H	0.48386600	-0.72387800	3.67146500
H	-0.88875800	-1.80787800	3.42184800
C	-0.95611800	-3.61050900	-0.52950600
H	-0.45567700	-3.18458800	-1.40283300
H	-1.71618400	-4.31912700	-0.87758900
H	-0.21575000	-4.17148200	0.04470700
C	2.55474800	4.02535000	0.30188700
H	3.32436400	4.70473500	-0.05187600
C	-1.82308500	2.65999000	-1.70742900
H	-1.85615000	3.10612900	-0.71006600
H	-2.35724500	3.32106200	-2.39880800
H	-0.77990600	2.61711700	-2.02900600
C	-3.54160600	1.58597200	1.10745600
H	-2.64089300	2.01634400	1.55525900

H	-4.28192300	1.42860900	1.89876000
H	-3.95549000	2.32042400	0.40833700
C	-3.21861500	0.25548600	0.41643400
H	-2.82406900	-0.40859600	1.18529100
C	0.94202500	3.37794900	1.96854600
H	0.45090000	3.54446900	2.92271300
C	-4.49288100	-0.38901500	-0.14541600
H	-5.04370100	0.28581300	-0.80861400
H	-5.16535000	-0.65225000	0.67749200
H	-4.27004100	-1.30192200	-0.70427100
C	-1.62341300	-2.49603800	0.29325900
H	-2.41064700	-2.09805800	-0.35026900

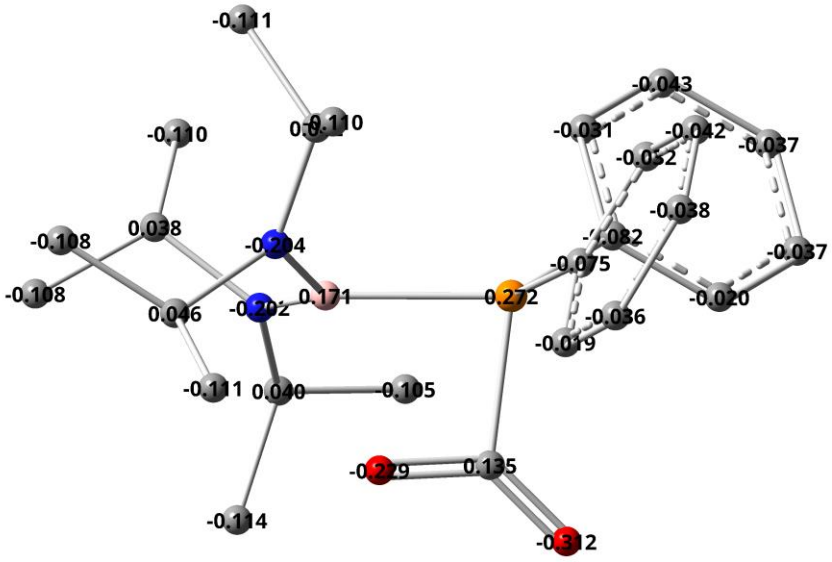


FIG. S54. OPTIMIZED STRUCTURE **3A_TS**

P	0.98899500	-0.15953800	0.37824700
N	-1.52851100	1.12189300	-0.33300400
N	-1.83124000	-1.36578200	0.07058400
C	1.59200900	2.42843900	1.25040500
H	0.93116500	2.21745000	2.08492500
C	3.25010900	-1.77358100	0.45556500
H	3.39093500	-1.37665900	1.45701200
C	-0.70016300	3.27233100	-1.38207800
H	-1.64000900	3.83162200	-1.40390400
H	-0.09467000	3.61469600	-2.22719200
H	-0.16689900	3.51857900	-0.46256900
C	3.93967900	-3.22200700	-1.34942100
H	4.63720900	-3.94875100	-1.75406800
C	-2.34873400	-2.45104200	2.27863900
H	-1.72975800	-1.81895900	2.91634500
H	-2.44600700	-3.43823200	2.74460500
H	-3.34298700	-2.00025000	2.22338000
C	-0.92505200	1.76266700	-1.50314900

H	0.07191200	1.31466100	-1.59237100
C	1.82755100	1.45650600	0.27358900
B	-1.06167200	-0.15426900	0.15286900
C	2.20250700	3.67601100	1.15405200
H	2.01632700	4.42249400	1.91940100
C	2.15166200	-1.36278700	-0.30611200
C	2.68344300	1.74555800	-0.79423100
H	2.88577400	0.99266600	-1.55095800
C	1.94501800	-1.88785900	-1.58455600
H	1.07710600	-1.58167000	-2.16334400
C	-1.74317600	-2.60011900	0.87678700
H	-2.36580400	-3.32960100	0.35027600
C	3.28521800	2.99597300	-0.89014600
H	3.94748900	3.21205100	-1.72248300
C	3.04482100	3.96404500	0.08350000
H	3.51806600	4.93796800	0.00933000
C	-3.87116200	2.09925100	-0.52071600
H	-3.62635200	2.97972700	-1.12217000
H	-4.72478600	2.36530300	0.11087200
H	-4.19037000	1.29960100	-1.19452800
C	-1.62259400	1.42875800	-2.83479500
H	-1.69121100	0.34702300	-2.98310500
H	-1.04423800	1.84428400	-3.66743800
H	-2.63092100	1.84674100	-2.89113600
C	-2.33989700	2.77187000	1.37408200
H	-1.52526700	2.43287000	2.01713700
H	-3.20445500	2.99499000	2.00912200
H	-2.04345500	3.69882300	0.87673900
C	4.14114200	-2.70392900	-0.07036600
H	4.99155000	-3.02867700	0.52045700
C	-0.35618000	-3.24239100	0.93563000
H	0.07294700	-3.35209600	-0.06384600
H	-0.44595600	-4.23976300	1.37831000
H	0.34554100	-2.69075600	1.56582500
C	-2.56026900	-2.39630800	-2.07894400
H	-1.58483400	-2.15700300	-2.51495500
H	-3.31504400	-2.34023800	-2.87044500
H	-2.52588400	-3.43349000	-1.72885000
C	-2.89473100	-1.41073700	-0.95258900
H	-2.91453800	-0.42004600	-1.40182800
C	2.84263900	-2.81575800	-2.10676300
H	2.68222200	-3.22581800	-3.09873900
C	-4.29655800	-1.65681700	-0.38449400
H	-4.40436400	-2.65353000	0.05544100
H	-5.03846300	-1.56997700	-1.18537700
H	-4.53844500	-0.91710500	0.38372400
C	-2.70373900	1.66582700	0.37322700
H	-3.06707800	0.82710600	0.97719100
C	0.55634900	-0.32072400	2.21327300
O	-0.66355100	0.04168200	2.17875700
O	1.30428800	-0.64711500	3.11321400

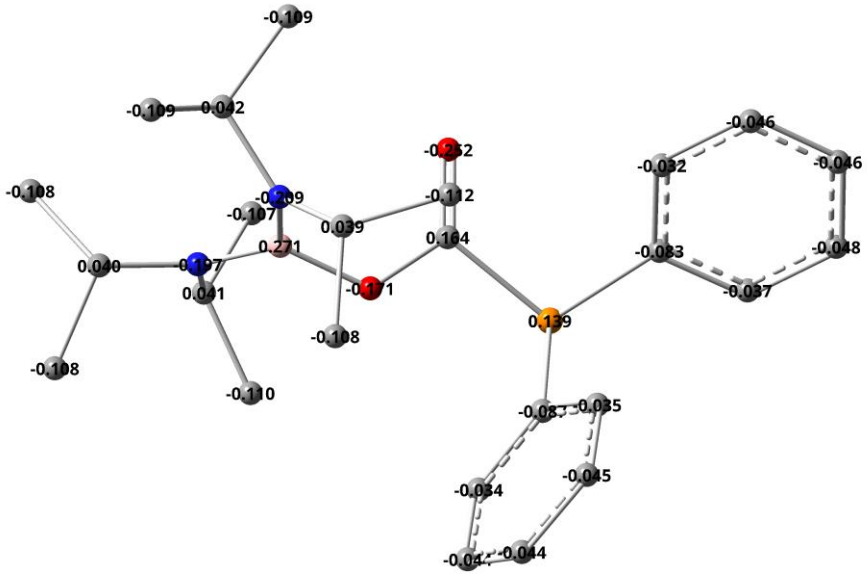


FIG. S55. OPTIMIZED STRUCTURE **3A**

P	-2.00687700	0.58645400	-1.32302200
O	0.49515600	0.32287600	-0.51434700
O	-0.36315800	-1.60801600	-1.28871200
N	2.88350600	0.29741300	-0.89024100
N	1.87735100	-0.97538400	1.06269700
C	2.75200800	0.83578800	-2.25865500
H	3.76976100	1.06925400	-2.58535500
C	1.96571400	2.15024300	-2.33808800
H	0.89772300	1.98648900	-2.18434800
H	2.10310700	2.60548700	-3.32481800
H	2.31604800	2.85733900	-1.58067500
C	2.21981000	-0.21107500	-3.23879900
H	2.83658900	-1.11394800	-3.20480700
H	2.23840400	0.18518700	-4.25951900
H	1.19169800	-0.50101000	-3.01016200
C	4.22878200	0.39679700	-0.30665700
H	4.14352500	-0.00465600	0.70242800
C	4.67941700	1.85477200	-0.15476000
H	4.80949000	2.34852400	-1.12363800
H	5.64061400	1.89791100	0.36762700
H	3.94507100	2.42241700	0.42423900
C	5.27708500	-0.43402800	-1.05544200
H	4.94320000	-1.46746800	-1.18432500
H	6.21841000	-0.44353700	-0.49679200
H	5.49121900	-0.02451600	-2.04834000
C	2.78693800	-2.12888300	1.10205100
H	3.37406300	-2.07279300	0.18217200
C	2.03042600	-3.46237600	1.05241000
H	1.47153900	-3.63652100	1.97857000
H	2.73644700	-4.29122100	0.93366600
H	1.32935700	-3.47051500	0.21358000
C	3.76765000	-2.11373400	2.28338500
H	4.26460000	-1.14485600	2.38649100
H	4.53628100	-2.87943400	2.13692900

H	3.26913900	-2.33669100	3.23234900
C	0.97848600	-0.80178300	2.21617300
H	1.44663100	-1.34988200	3.04047200
C	-0.43559500	-1.37840300	2.05195000
H	-1.06604100	-0.71669000	1.45491100
H	-0.91311000	-1.47252700	3.03348200
H	-0.41933700	-2.36088700	1.57708700
C	0.91243000	0.66758900	2.64224200
H	1.91699200	1.05994000	2.82836000
H	0.32025400	0.77441500	3.55670800
H	0.43522300	1.28025800	1.87064600
C	-0.48534700	-0.44222800	-0.97967900
B	1.78952800	-0.16930500	-0.11598300
C	-2.03758100	1.66189000	0.17482900
C	-2.76967300	1.36113500	1.32733800
C	-1.28321200	2.84045300	0.14078700
C	-2.73013600	2.21070300	2.43055100
H	-3.37026400	0.45737000	1.36856900
C	-1.23640500	3.68447700	1.24635700
H	-0.71910100	3.09332400	-0.75236000
C	-1.95993100	3.37031500	2.39535200
H	-3.29955700	1.96143300	3.32081300
H	-0.64003900	4.59086600	1.20772100
H	-1.92825900	4.03070500	3.25649000
C	-3.39634000	-0.57113100	-1.01681200
C	-4.65802900	-0.11580000	-1.42180000
C	-3.29733400	-1.82015300	-0.39411000
C	-5.80007900	-0.87544000	-1.18497400
H	-4.74996500	0.84541100	-1.92135900
C	-4.43995400	-2.58547900	-0.17065400
H	-2.32932800	-2.20644000	-0.09894500
C	-5.69239800	-2.11463700	-0.55774400
H	-6.77004600	-0.50280300	-1.49921500
H	-4.34695700	-3.55450800	0.30993100
H	-6.58024000	-2.71287200	-0.37756600

References

(1) Sheldrick, G. M. SHELXT – Integrated Space-Group and Crystal-Structure Determination. *Acta Cryst. A* **2015**, *71* (1), 3–8 DOI: 10.1107/S2053273314026370.

(2) Dolomanov, O. V; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341 DOI: 10.1107/S0021889808042726.

(3) Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Cryst. C* **2015**, *71*, 3–8 DOI: 10.1107/S2053229614024218.

(4) M. J. Frisch; G. W. Trucks; H. B. Schlegel; G. E. Scuseria; M. A. Robb; J. R. Cheeseman; G. Scalmani; V. Barone; G. A. Petersson; H. Nakatsuji; X. Li; M. Caricato; A. Marenich; J. Bloino; B. G. Janesko; R. Gomperts; B. Mennucci; H. P. Hratchian; J. V. Ortritz; Izmaylov, A. F.; J. L. Sonnenberg; D. Williams-Young, F. Ding, F. L.; F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throsse, J. B. F.; Fox, D. J. Gaussian09 Revision D.01. Gaussian, Inc.: Wallingford CT 2016.

(5) Chai, J.-D.; Head-Gordon, M. Long-Range Corrected Hybrid Density Functionals with Damped Atom–Atom Dispersion Corrections. *Phys. Chem. Chem. Phys.* **2008**, *10* (44), 6615 DOI: 10.1039/b810189b.

(6) Grimme, S. Density Functional Theory with London Dispersion Corrections. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2011**, *1* (2), 211–228 DOI: 10.1002/wcms.30.

(7) Kozuch, S.; Shaik, S. How to Conceptualize Catalytic Cycles? The Energetic Span Model. *Acc. Chem. Res.* **2011**, *44* (2), 101–110 DOI: 10.1021/ar1000956.

(8) Parr, R. G.; Yang, W. Density Functional Approach to the Frontier-Electron Theory of Chemical Reactivity. *J. Am. Chem. Soc.* **1984**, *106* (14), 4049–4050 DOI: 10.1021/ja00326a036.

(9) Morell, C.; Grand, A.; Toro-Labbé, A. New Dual Descriptor for Chemical Reactivity. *J. Phys. Chem. A* **2005**, *109* (1), 205–212 DOI: 10.1021/jp046577a.