SUPPORTING INFORMATION

Bicyclic (Alkyl)(Amino)Carbene (BICAAC) Supported Phosphinidenes

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Materials and Methods:

All manipulations and storage of air-sensitive compounds were performed under an inert atmosphere either in dinitrogen filled Jacomex glove box or using dry dinitrogen standard Schenk line techniques. Dry oxygen and water free solvents were used. THF, Toluene and hexane were dried over sodium- potassium alloy and vacuum distilled over molecular sieves (4 Å) and stored overnight prior to use. BICAAC was prepared as reported in literature[S1] for the synthesis of compound **1-3**. NMR Spectra were recorded on Bruker 500MHz and Jeol 400MHz spectrometers and teramethylsilane (TMS) was used as an internal standard. Deuterated NMR solvent C_6D_6 were dried over Na-K alloy and vacuum distilled. Melting points were recorded in sealed glass tube using Fischer-Scientific melting point apparatus. Bruker MicrO-TOF-QII model high-resolution mass spectrometer (HRMS) was used for characterization. Elemental analysis was performed using a UNICUBE Elementar GmBH analyser. Single crystal X-ray diffraction data for compounds **1-4** were collected using a Bruker SMART APEX diffractometer equipped with a 3-axis goniometer. [S2] The crystals were covered with Paratone-N and mounted on a glass capillary. The data were collected at 302 K for compound **1-3** and at 100 K for compound **3** using Mo Kα radiation (λ = 0.71073 Å). The integration of data was performed using the SAINT. Empirical absorption correction was applied using SADABS.[S3] Structural solutions were accomplished by direct methods and refined by fullmatrix least-squares on F2 using either ShelXT[S4] or ShelXL[S5] incorporated in Olex2[S6]. All the non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were fixed according to a riding model and were refined isotropically. Cyclic voltammograms were recorded at room temperature with a BioLogic SP-300 potentiostat. The working electrode was a glassy carbon disk (area = 0.02 cm^2), the reference electrode was Ag/AgCl (saturated), and the counter electrode was a platinum wire. Important crystallographic data are given in Table S1-6. [S7]

Experimental Details:

1. Synthesis of (BICAAC)PCl (**1**): PCl_3 (220 mg, 1.6 mmol) was added dropwise to a solution of free BICAAC (1 g, 3.2 mmol) in THF at 0 ℃ to obtain a yellow solution with little precipitate. The solution was brought to room temperature slowly and stirred overnight to obtain a yellow suspension. The solvent was removed under vacuum and the remaining solid was extracted with n-hexane (2* 40 ml). After filtration, the solvent was evaporated to obtain yellow crystalline solid in 25% yield. Crystals suitable for single crystal X-ray diffraction studies were obtained by keeping concentrated n-hexane solution at -20 ℃. Melting point: 116℃. HRMS (FAB) m/z calculated for [$C_{22}H_{33}ClNP$ $(M+H)^+$] 378.2117, found 378.2119. ^{1}H NMR (500 MHz, C_6D_6) δ(ppm): 7.20-7.16 (m, 1H), 7.02-7.00 (m, 2H), 3.33-3.27 (m, 1H), 3.15 – 3.07 (m, 1H), 1.87 – 1.78 (m, 1H), 1.76 – 1.68 (m, 1H), 1.56 – 1.48 (m, 8H), 1.26 – 1.15 (m, 12H), 1.05 (d, 3H), 0.57 (s, 3H). ^{13}C NMR (126 MHz, C_6D_6) δ(ppm): 189.36 (d, J_{C-P} = 130.5 Hz), 148.60, 148.25, 137.26, 123.96, 58.85, 44.30, 37.19, 36.51, 34.08, 29.28, 28.76, 25.13, 24.73, 23.80, 21.68, 18.26. ^{31}P NMR (203 MHz, C_6D_6) δ(ppm): 115.34 (s). ^{31}P {^{1}H} NMR (203 MHz, C_6D_6) δ(ppm): 115.35 (s). Elemental analysis (%): calcd for $C_{23}H_{35}ClNP$; C 70.48, H 9.00, N 3.57; found: C 69.12, H 9.376, N 3.14.
2. Synthesis of (BICAAC)PBr (**2**): PBr_3 (434 mg, 1.6 mmol) was added dropwise to a solution of free BICAAC (1g, 3.2mmol) in THF at 0 ℃ to obtain a yellow solution with little precipitate. The solution was brought to room temperature slowly and stirred overnight to obtain a yellow suspension. The solvent was removed under vacuum and the remaining solid was extracted with n-hexane (2* 40

ml). After filtration, the solvent was evaporated to obtain yellow solid in 17% yield. Crystals suitable for single crystal X-ray diffraction studies were obtained by keeping concentrated toluene solution at -20 °C. Melting point: 142-145°C. HRMS (FAB) m/z calculated for [$C_{22}H_{33}BrNP$ $(M+H)^+$] 422.1612, found 422.1619. ^{1}H NMR (500 MHz, $CDCl_3$) δ(ppm): 10.34 (s, 1H), 7.49-7.53 (m, 2H), 7.38 – 7.29 (m, 4H), 3.60-3.61 (m, 1H), 3.42-3.47 (m, 3H), 2.71 – 2.66 (m, 2H), 2.39-2.44 (m, 2H), 1.87 – 1.82 (m, 8H), 1.64-1.70(m, 8H)1.39 – 1.34 (m, 12H), 1.29-1.32 (dd, 12H), 0.85-0.88 (m, 3H), 0.81 (s, 3H), 0.11 (s, 3H), 0.07 (s, 3H). ^{31}P NMR (162 MHz) δ (ppm): 103.12. Elemental analysis (%): calcd for $C_{23}H_{35}ClNP$; C 63.30, H 8.08, N 3.21; found: C 64.03, H 8.438, N 3.40.

3. Synthesis of (BICAAC)PI (**3**): PI_3 (660 mg, 1.6 mmol) was added dropwise to a solution of free BICAAC (1g, 3.2mmol) in THF at 0 °C to obtain a yellow solution with little precipitate. The solution was brought to room temperature slowly and stirred overnight to obtain a yellow suspension. The solvent was removed under vacuum and the remaining solid was extracted with n-hexane (2* 40 ml). After filtration, the solvent was evaporated to obtain yellow crystalline solid in 15% yield. Crystals suitable for single crystal X-ray diffraction studies were obtained by keeping concentrated n-hexane solution at -20 °C. Melting point: 156-158 °C. HRMS (FAB) m/z calculated for [$C_{22}H_{33}INP$ $(M+H)^+$] 470.1474, found 470.1475. ^{1}H NMR (500 MHz, C_6D_6) δ(ppm): 7.25 – 7.22 (m, 1H), 7.06 – 7.03 (m, 1H), 3.22-3.17 (m, 1H), 3.01-2.96 (m, 1H), 1.84 – 1.79 (m, 1H), 1.73-1.69 (m, 1H), 1.62-1.59 (m, 6H), 1.48 (s, 2H), 1.32-1.28 (m, 6H), 1.20 – 1.14 (m, 6H), 1.05 (d, 3H), 0.58 (s, 3H). ^{13}C NMR (126 MHz, C_6D_6) δ(ppm): 149.12, 148.82, 136.27, 124.62, 58.94, 47.07, 44.15, 36.39, 33.94, 28.96, 25.64, 25.09, 24.81, 24.31, 23.78, 18.23. ^{31}P NMR (203 MHz, C_6D_6) δ(ppm): 56.13. ^{31}P {^{1}H} NMR (203 MHz, C_6D_6) δ(ppm): 56.13. Elemental analysis (%): calcd for $C_{23}H_{35}ClNP$; C 57.15, H 7.30, N 2.90; found: C 54.14, H 7.45, N 2.80.
4. Synthesis of (BICAAC)P-P(BICAAC) (**4**): KC_8 (144 mg, 1.065 mmol) was added to a solution of (BICAAC)PBr (450 mg, 1.065 mmol) in THF at rt to obtain a blue solution. Within 5 minutes, the colour of solution changed to yellow which was stirred for additional 3 hours. The solvent was removed under vacuum and the remaining solid was extracted with toluene (2* 20 ml). After filtration, the solvent was removed to obtain a yellow solid in 66% yield. Crystals suitable for single crystal X-ray diffraction studies were obtained by keeping concentrated toluene solution at -20 °C. Melting point: 209-211 °C. HRMS (FAB) m/z calculated for [$C_{44}H_{66}N_2P_2$ $(M+H)^+$] 685.4779, found 685.4797. ^{1}H NMR (500 MHz, C_6D_6, ppm) δ: 7.27-7.24 (m, 2H), 7.15 – 7.12 (m, 4H), 3.31-3.27 (m, 2H), 3.10-3.05 (m, 2H), 1.91-1.85 (m, 2H), 1.70 – 1.53 (m, 18H), 1.37 – 1.18 (m, 18H), 1.08-1.03 (m, 12H), 0.63 (s, 6H). ^{13}C NMR (126 MHz, C_6D_6) δ (ppm): 186.39 (d, J_{C-P} = 84.2 Hz), 149.37, 149.03, 140.90, 124.66, 58.19, 46.80, 45.23, 37.36, 34.68, 28.73, 28.32, 26.54, 25.91, 25.21, 24.54, 18.71. ^{31}P NMR (162 MHz) δ (ppm): 66.00. ^{31}P {^{1}H} NMR (162 MHz) δ (ppm): 66.00.

Crystallographic Data:

Table S1: Crystallogaphic details and Refinement parameters for compound 1-4

Compound	**1**	**2**	**3**	**4**
CCDC Number	2264850	2264851	2264852	22648533
Empirical Formula	$C_{22}H_{33}ClNP$	$C_{22}H_{33}BrNP$	$C_{22}H_{33}INP$	$C_{44}H_{66}N_2P_2$

Formula weight	377.91	422.37	469.36	684.92
Temperature	273.15	302	298.00	109.00
Wavelength	0.71073	0.71073	0.71073	0.71073
Crystal system, Space group	Orthorhombic, Pbca	Orthorhombic, Pbca	Orthorhombic, Pbca	Orthorhombic, Pbca
Unit cell dimensions [Å]	a= 8.8488(4) b= 16.8077(9) c= 29.5760(16)	a= 9.2049(8) b=16.6408 (13) c= 29.176(3)	a= 15.5985(9) b=19.4320(13) c= 29.7451(16)	a= 24.690(3) b=35.674(4) c= 18.131(2)
α [°]	90	90	90	90
β [°]	90	90	90	90
γ [°]	90	90	90	90
Volume [$Å^3$]	4398.8(4)	4469.1(7)	9016.0(9)	15970(3)
Z	8	8	16	16
Absorption coefficient [mm^{-1}]	0.251	1.916	1.497	0.141
F (000)	1632.0	1776.0	3840.0	5984.0
Crystal size [mm]	0.2 × 0.1 × 0.08	0.22 × 0.13 × 0.08	0.23 × 0.15 × 0.1	0.2 × 0.08 × 0.08
Theta range for data collection [°]	4.848 to 56.58	4.896 to 52.876	3.784 to 52.738	4.012 to 52.742
Reflection collected/ unique	117468, 5461	120954, 4589	81806, 9211	39142, 7829
Data completeness	99.9	99.6	99.9	99.9
Data/restraints/parameters	5461/0/233	4589/1/243	9211/2/485	7829/3/498
Goodness-of-fit on F^2	1.053	1.063	1.009	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0625, wR_2 = 0.1566	R1 = 0.0393, wR2 = 0.0962	R_1 = 0.0456, wR_2 = 0.1029	R_1 = 0.0703, wR_2 = 0.1684
Final R indexes [all data]	R_1 = 0.0877, wR_2 = 0.1711	R1 = 0.0587, wR2 = 0.1067	R_1 = 0.0873, wR_2 = 0.1255	R_1 = 0.1000, wR_2 = 0.1942
Largest diff. peak/hole [e $Å^{-3}$]	0.36/-0.49	0.38/-0.25	0.63/-0.54	0.87/-0.42

Table S2: Bond length [Å] and Bond angle [°] for compound 1.

Cl1	P1	2.0787(10)	C12	C20	1.515(4)
P1	C1	1.708(2)	C5	C6	1.524(3)
N1	C11	1.444(2)	C5	C9	1.520(3)
N1	C5	1.509(2)	C5	C4	1.528(3)
N1	C1	1.361(2)	C6	C7	1.518(3)
C17	C16	1.514(4)	C7	C2	1.543(3)
C17	C19	1.519(5)	C2	C1	1.533(3)

C17	C18	1.537(5)	C2	C3	1.544(3)
C11	C16	1.397(3)	C2	C8	1.540(3)
C11	C12	1.408(3)	C20	C21	1.530(4)
C16	C15	1.395(3)	C20	C22	1.532(4)
C15	C14	1.379(4)	C4	C3	1.529(3)
C14	C13	1.367(4)	C3	C10	1.520(4)
C13	C12	1.394(3)			

C1	P1	Cl1	109.37(8)	C6	C5	C4	107.55(19)
C11	N1	C5	120.91(15)	C9	C5	C6	111.54(19)
C1	N1	C11	123.13(17)	C9	C5	C4	111.4(2)
C1	N1	C5	115.83(16)	C7	C6	C5	109.74(18)
C16	C17	C19	113.2(2)	C6	C7	C2	110.87(19)
C16	C17	C18	111.0(3)	C7	C2	C3	108.4(2)
C19	C17	C18	110.1(3)	C1	C2	C7	106.31(17)
C16	C11	N1	119.17(19)	C1	C2	C3	108.14(17)
C16	C11	C12	122.0(2)	C1	C2	C8	115.1(2)
C12	C11	N1	118.79(19)	C8	C2	C7	108.07(19)
C11	C16	C17	123.0(2)	C8	C2	C3	110.52(19)
C15	C16	C17	119.2(2)	N1	C1	P1	135.50(16)
C15	C16	C11	117.8(2)	N1	C1	C2	111.58(17)
C14	C15	C16	120.7(3)	C2	C1	P1	112.91(14)
C13	C14	C15	120.7(3)	C12	C20	C21	111.7(2)
C14	C13	C12	121.2(3)	C12	C20	C22	112.1(3)
C11	C12	C20	123.6(2)	C21	C20	C22	109.0(2)
C13	C12	C11	117.4(2)	C5	C4	C3	111.36(19)
C13	C12	C20	118.9(2)	C4	C3	C2	108.77(17)
N1	C5	C6	107.51(18)	C10	C3	C2	113.5(2)
N1	C5	C9	111.51(18)	C10	C3	C4	112.0(2)
N1	C5	C4	107.06(17)				

Table S3: Bond length [Å] and Bond angle [^{o}] for compound 2.

Br2	P1	2.196(3)	C16	C20	1.514(4)
P1	C1	1.710(2)	C5	C6	1.524(3)
P1	Br1	2.322(6)	C5	C4	1.525(3)
N1	C11	1.446(3)	C6	C7	1.512(3)
N1	C5	1.507(3)	C7	C2	1.534(4)
N1	C1	1.357(3)	C2	C3	1.543(4)
C10	C5	1.515(3)	C2	C1	1.540(3)
C11	C12	1.407(3)	C2	C8	1.540(3)
C11	C16	1.395(3)	C3	C4	1.527(4)
C12	C13	1.389(4)	C3	C9	1.515(4)
C12	C17	1.515(4)	C17	C18	1.525(4)
C13	C14	1.362(5)	C17	C19	1.534(4)
C14	C15	1.373(5)	C20	C21	1.519(5)
C15	C16	1.394(4)	C20	C22	1.533(5)

C1	P1	Br2	112.97(11)	C6	C5	C4	107.7(2)
C1	P1	Br1	108.69(18)	C7	C6	C5	109.5(2)
C11	N1	C5	121.21(16)	C6	C7	C2	111.0(2)
C1	N1	C11	122.46(18)	C7	C2	C3	108.5(2)
C1	N1	C5	116.14(17)	C7	C2	C1	106.92(19)
C12	C11	N1	118.9(2)	C7	C2	C8	108.0(2)
C16	C11	N1	118.9(2)	C1	C2	C3	107.81(19)
C16	C11	C12	122.2(2)	C8	C2	C3	110.8(2)
C11	C12	C17	123.4(2)	C8	C2	C1	114.7(2)
C13	C12	C11	117.0(3)	C4	C3	C2	108.89(19)
C13	C12	C17	119.5(2)	C9	C3	C2	113.6(2)
C14	C13	C12	121.7(3)	C9	C3	C4	112.2(2)
C13	C14	C15	120.7(3)	C5	C4	C3	110.9(2)
C14	C15	C16	120.8(3)	C12	C17	C18	111.7(2)
C11	C16	C20	123.3(2)	C12	C17	C19	111.9(3)
C15	C16	C11	117.7(3)	C18	C17	C19	109.7(2)
C15	C16	C20	119.1(3)	C16	C20	C21	113.2(2)
N1	C5	C10	111.61(19)	C16	C20	C22	111.0(3)
N1	C5	C6	107.71(18)	C21	C20	C22	109.8(3)
N1	C5	C4	107.14(18)	N1	C1	P1	136.34(17)
C10	C5	C6	111.2(2)	N1	C1	C2	110.91(18)
C10	C5	C4	111.3(2)	C2	C1	P1	112.74(15)

Table S4: Bond length [Å] and Bond angle [^{o}] for compound 3.

I2	P2	2.510(7)	C40	C42	1.532(7)
I1	P1	2.405(7)	C14	C15	1.371(7)
P2	C23	1.720(4)	C15	C16	1.393(6)
P2	I2A	2.379(10)	C38	C37	1.368(7)
P1	C1	1.715(5)	C5	C6	1.526(7)
P1	I1A	2.505(6)	C5	C4	1.525(8)
N1	C11	1.456(5)	C5	C8	1.520(7)
N1	C1	1.362(5)	C43	C45	1.533(7)
N1	C5	1.502(5)	C43	C44	1.545(7)
N2	C34	1.452(5)	C23	C24	1.539(7)
N2	C27	1.509(5)	C37	C36	1.369(7)
N2	C23	1.363(5)	C20	C22	1.527(7)
C39	C34	1.399(6)	C20	C21	1.502(7)
C39	C40	1.510(6)	C17	C16	1.503(7)
C39	C38	1.393(6)	C17	C18	1.526(7)
C11	C12	1.392(6)	C17	C19	1.528(7)
C11	C16	1.410(6)	C2	C7	1.509(7)
C34	C35	1.396(6)	C2	C3	1.534(9)
C12	C13	1.400(6)	C2	C9	1.543(9)
C12	C20	1.523(6)	C6	C7	1.559(8)
C35	C43	1.503(6)	C33	C25	1.539(8)
C35	C36	1.393(6)	C28	C29	1.545(8)

C1	C2	1.547(6)	C24	C25	1.529(9)
C27	C30	1.526(6)	C24	C29	1.534(9)
C27	C33	1.522(6)	C24	C32	1.563(7)
C27	C28	1.522(7)	C7	C10	1.482(9)
C13	C14	1.362(7)	C4	C3	1.524(10)
C40	C41	1.531(7)	C25	C31	1.473(10)

C23	P2	I2	113.52(18)	C4	C5	C6	107.0(4)
C23	P2	I2A	114.9(2)	C8	C5	C6	112.7(5)
C1	P1	I1	114.5(2)	C8	C5	C4	111.5(5)
C1	P1	I1A	114.57(18)	C35	C43	C45	112.5(4)
C11	N1	C5	121.2(3)	C35	C43	C44	112.3(5)
C1	N1	C11	121.5(3)	C45	C43	C44	108.8(5)
C1	N1	C5	117.3(3)	N2	C23	P2	136.4(3)
C34	N2	C27	121.4(3)	N2	C23	C24	110.7(4)
C23	N2	C34	122.4(3)	C24	C23	P2	112.9(3)
C23	N2	C27	116.2(3)	C38	C37	C36	119.5(4)
C34	C39	C40	123.8(4)	C37	C36	C35	121.9(5)
C38	C39	C34	117.2(4)	C12	C20	C22	111.1(4)
C38	C39	C40	119.0(4)	C21	C20	C12	113.3(5)
C12	C11	N1	119.4(4)	C21	C20	C22	110.5(5)
C12	C11	C16	122.3(4)	C16	C17	C18	111.9(4)
C16	C11	N1	118.3(4)	C16	C17	C19	112.6(5)
C39	C34	N2	118.8(4)	C18	C17	C19	109.7(5)
C35	C34	N2	119.1(4)	C7	C2	C1	107.9(4)
C35	C34	C39	122.1(4)	C7	C2	C3	109.5(5)
C11	C12	C13	117.5(4)	C7	C2	C9	109.8(5)
C11	C12	C20	124.1(4)	C3	C2	C1	106.5(5)
C13	C12	C20	118.3(4)	C3	C2	C9	108.7(6)
C34	C35	C43	123.9(4)	C9	C2	C1	114.4(5)
C36	C35	C34	117.4(4)	C5	C6	C7	109.2(4)
C36	C35	C43	118.8(4)	C27	C33	C25	109.3(4)
N1	C1	P1	137.4(3)	C27	C28	C29	110.7(5)
N1	C1	C2	110.3(4)	C23	C24	C32	114.5(5)
C2	C1	P1	112.3(3)	C25	C24	C23	107.9(5)
N2	C27	C30	111.1(3)	C25	C24	C29	109.8(6)
N2	C27	C33	107.1(4)	C25	C24	C32	110.6(5)
N2	C27	C28	108.2(4)	C29	C24	C23	106.8(5)
C33	C27	C30	111.8(4)	C29	C24	C32	107.1(6)
C33	C27	C28	107.4(4)	C2	C7	C6	110.4(4)
C28	C27	C30	111.0(4)	C10	C7	C2	115.0(6)
C14	C13	C12	121.1(5)	C10	C7	C6	111.5(6)
C39	C40	C41	111.9(4)	C3	C4	C5	111.2(5)
C39	C40	C42	112.3(4)	C11	C16	C17	123.3(4)
C41	C40	C42	108.3(4)	C15	C16	C11	117.0(4)
C13	C14	C15	120.8(4)	C15	C16	C17	119.7(4)
C14	C15	C16	121.3(4)	C4	C3	C2	109.2(5)
C37	C38	C39	122.0(5)	C24	C25	C33	110.3(4)

N1	C5	C6	106.1(4)	C31	C25	C33	113.7(7)
N1	C5	C4	107.9(4)	C31	C25	C24	112.9(6)
N1	C5	C8	111.3(4)	C24	C29	C28	108.4(5)

Table S5: Bond length [Å] and Bond angle [^{o}] for compound 4.

C1	C7_2	1.516(7)	C5_1	C8_1	1.508(7)
C2	C5	1.514(16)	C5_1	C4_1	1.532(9)
C2	C6	1.680(18)	C6_1	C7_1	1.537(12)
C2	C7_2	1.520(13)	C7_1	C2_1	1.551(13)
C3	C4	1.506(15)	C7_1	C9_1	1.372(13)
C3	C8	1.753(15)	C2_1	C1_1	1.540(7)
C3	C7_2	1.546(12)	C2_1	C3_1	1.546(13)
C7	C10A	1.546(16)	C2_1	C10_1	1.576(11)
C7A	C10_2	1.521(19)	C20_1	C22_1	1.523(9)
C4	C10_2	1.55(3)	C20_1	C21_1	1.538(9)
C5	C10A	1.50(2)	C17_1	C19_1	1.536(9)
C8	C9	1.517(19)	C17_1	C18_1	1.548(8)
C8	C10A	1.57(2)	C4_1	C3_1	1.517(11)
C6	C10	1.53(2)	P1_2	P1_21	2.182(3)
C6	C10_2	1.50(3)	P1_2	C11_2	1.735(6)
C10A	C11_2	1.579(13)	N1_2	C1_2	1.441(7)
C20A	C2_1	1.574(16)	N1_2	C7_2	1.498(7)
P1_1	P1_11	2.193(3)	N1_2	C11_2	1.378(7)
P1_1	C1_1	1.721(5)	C1_2	C2_2	1.401(9)
N1_1	C11_1	1.433(6)	C1_2	C6_2	1.413(10)
N1_1	C5_1	1.508(6)	C2_2	C3_2	1.376(9)
N1_1	C1_1	1.376(6)	C2_2	C12_2	1.527(11)
C11_1	C12_1	1.396(9)	C3_2	C4_2	1.380(11)
C11_1	C16_1	1.414(8)	C4_2	C5_2	1.378(10)
C12_1	C13_1	1.397(8)	C5_2	C6_2	1.396(9)
C12_1	C20_1	1.519(9)	C6_2	C14_2	1.487(10)
C13_1	C14_1	1.370(10)	C10_2	C11_2	1.590(15)
C14_1	C15_1	1.385(10)	C12_2	C13_2	1.539(12)
C15_1	C16_1	1.378(8)	C12_2	C20_2	1.523(11)
C16_1	C17_1	1.515(9)	C14_2	C15_2	1.542(12)
C5_1	C6_1	1.518(9)	C14_2	C21_2	1.533(10)

C5	C2	C7_2	119.6(8)	C3_1	C2_1	C10_1	99.2(8)
C7_2	C2	C6	97.6(8)	N1_1	C1_1	P1_1	134.6(4)
C4	C3	C7_2	119.6(8)	N1_1	C1_1	C2_1	109.9(4)
C7_2	C3	C8	96.9(8)	C2_1	C1_1	P1_1	115.5(4)
C3	C4	C10_2	100.8(12)	C12_1	C20_1	C22_1	112.3(6)
C10A	C5	C2	102.8(12)	C12_1	C20_1	C21_1	111.2(5)
C9	C8	C3	101.5(11)	C22_1	C20_1	C21_1	108.9(6)

C9	C8	C10A	116.2(12)
C10A	C8	C3	115.1(9)
C10	C6	C2	100.5(14)
C10_2	C6	C2	117.2(10)
C10_2	C6	C10	113.0(15)
C7	C10A	C8	107.3(12)
C7	C10A	C11_2	115.8(10)
C5	C10A	C7	110.3(12)
C5	C10A	C8	107.7(12)
C5	C10A	C11_2	114.8(11)
C8	C10A	C11_2	99.8(10)
C1_1	P1_1	P1_1[1]	107.55(18)
C11_1	N1_1	C5_1	119.1(4)
C1_1	N1_1	C11_1	123.8(4)
C1_1	N1_1	C5_1	117.1(4)
C12_1	C11_1	N1_1	119.5(5)
C12_1	C11_1	C16_1	121.5(4)
C16_1	C11_1	N1_1	119.0(5)
C11_1	C12_1	C13_1	117.9(6)
C11_1	C12_1	C20_1	123.5(5)
C13_1	C12_1	C20_1	118.6(5)
C14_1	C13_1	C12_1	121.2(6)
C13_1	C14_1	C15_1	120.0(5)
C16_1	C15_1	C14_1	121.4(6)
C11_1	C16_1	C17_1	122.6(5)
C15_1	C16_1	C11_1	117.8(5)
C15_1	C16_1	C17_1	119.6(5)
N1_1	C5_1	C6_1	106.8(5)
N1_1	C5_1	C4_1	106.5(5)
C6_1	C5_1	C4_1	108.4(5)
C8_1	C5_1	N1_1	112.3(4)
C8_1	C5_1	C6_1	111.4(6)
C8_1	C5_1	C4_1	111.2(5)
C5_1	C6_1	C7_1	109.7(6)
C6_1	C7_1	C2_1	110.3(6)
C9_1	C7_1	C6_1	121.6(11)
C9_1	C7_1	C2_1	112.2(7)
C7_1	C2_1	C20A	92.2(12)
C7_1	C2_1	C10_1	118.5(7)
C1_1	C2_1	C20A	111.9(8)
C1_1	C2_1	C7_1	108.3(7)
C1_1	C2_1	C3_1	108.0(6)
C1_1	C2_1	C10_1	114.6(6)
C16_1	C17_1	C19_1	111.9(5)
C16_1	C17_1	C18_1	111.0(5)
C19_1	C17_1	C18_1	108.8(5)
C3_1	C4_1	C5_1	111.8(6)
C4_1	C3_1	C2_1	109.0(7)
C11_2	P1_2	P1_2[1]	107.6(2)
C1_2	N1_2	C7_2	121.0(4)
C11_2	N1_2	C1_2	122.4(4)
C11_2	N1_2	C7_2	116.6(5)
C2_2	C1_2	N1_2	120.6(6)
C2_2	C1_2	C6_2	121.3(5)
C6_2	C1_2	N1_2	118.1(6)
C1_2	C2_2	C12_2	123.3(6)
C3_2	C2_2	C1_2	118.6(7)
C3_2	C2_2	C12_2	118.1(6)
C2_2	C3_2	C4_2	121.6(7)
C5_2	C4_2	C3_2	119.4(6)
C4_2	C5_2	C6_2	121.9(7)
C1_2	C6_2	C14_2	124.6(6)
C5_2	C6_2	C1_2	117.1(6)
C5_2	C6_2	C14_2	118.2(7)
C1	C7_2	C2	111.2(7)
C1	C7_2	C3	109.6(7)
C2	C7_2	C3	108.8(6)
N1_2	C7_2	C1	111.9(5)
N1_2	C7_2	C2	108.4(6)
N1_2	C7_2	C3	106.8(6)
C7A	C10_2	C4	105.7(14)
C7A	C10_2	C11_2	114.7(12)
C4	C10_2	C11_2	113.4(13)
C6	C10_2	C7A	112.8(14)
C6	C10_2	C4	108.1(13)
C6	C10_2	C11_2	102.2(14)
C10A	C11_2	P1_2	112.8(6)
N1_2	C11_2	C10A	110.3(7)
N1_2	C11_2	P1_2	135.2(5)
N1_2	C11_2	C10_2	108.7(7)
C10_2	C11_2	P1_2	114.5(7)
C2_2	C12_2	C13_2	111.1(6)
C20_2	C12_2	C2_2	111.7(7)
C20_2	C12_2	C13_2	110.7(7)
C6_2	C14_2	C15_2	111.6(6)
C6_2	C14_2	C21_2	112.0(6)

C3_1	C2_1	C20A	126.8(10)	C21_2	C14_2	C15_2	108.3(7)
C3_1	C2_1	C7_1	107.3(6)				

Solid State structure of compound 3

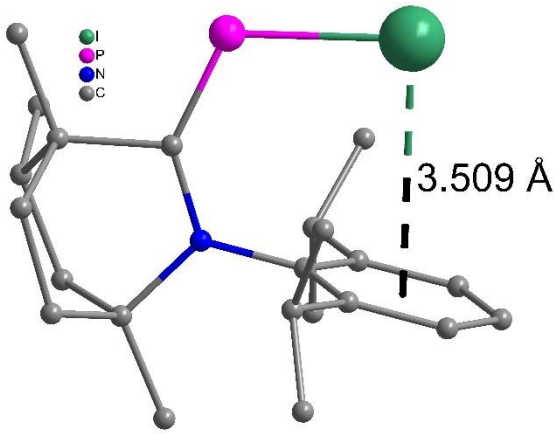


Fig S1: Representation of π interaction of X (X= I) with π electron cloud of Dipp group.

NMR Data:

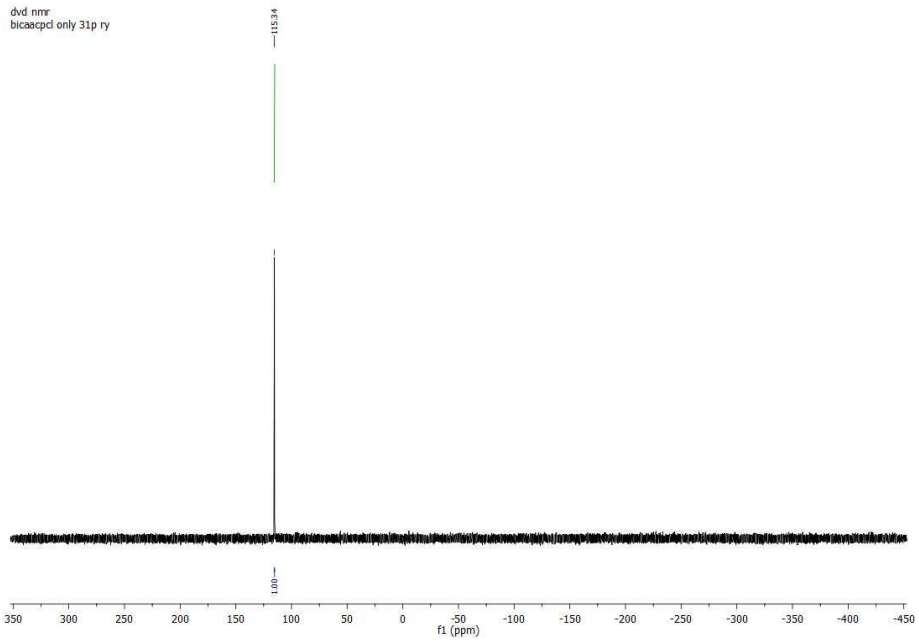


Fig S2: ^{31}P NMR of compound **1**

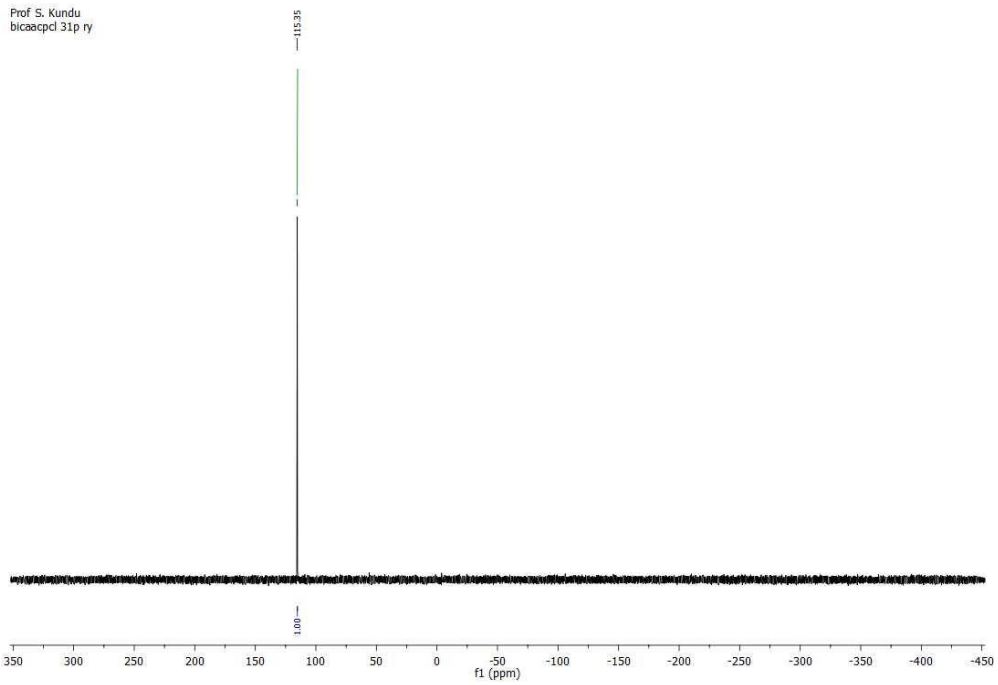


Fig S3: $^{31}P\{^{1}H\}$ NMR of compound **1**

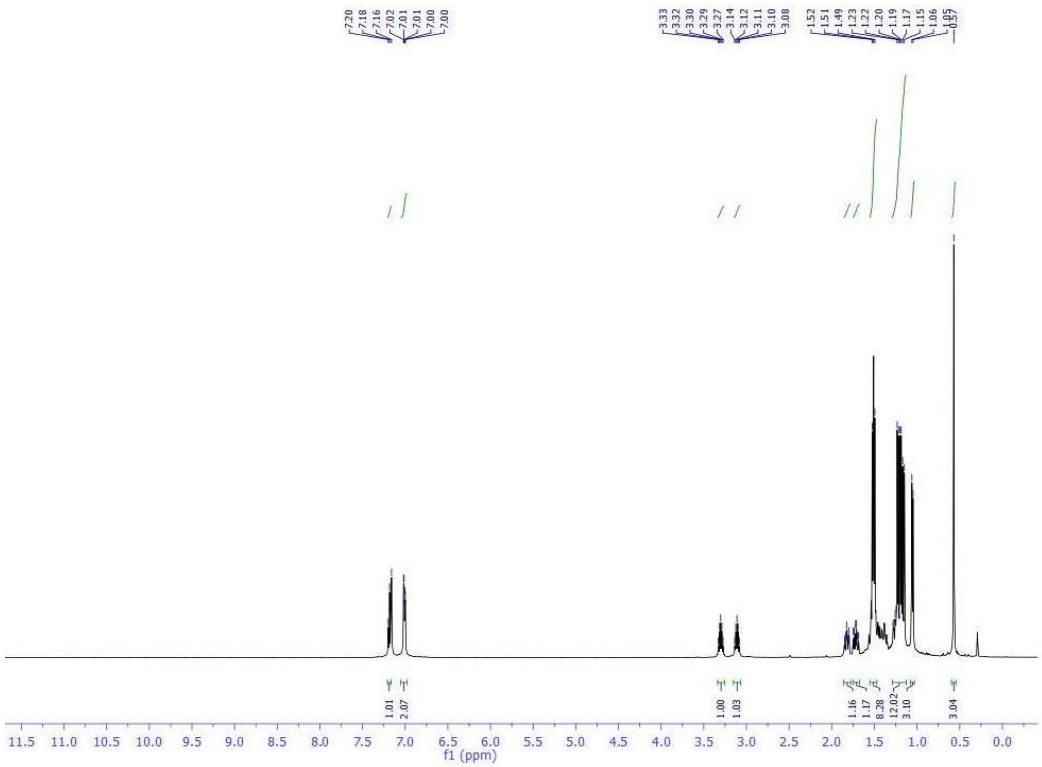


Fig S4: ^{1}H NMR of compound **1**

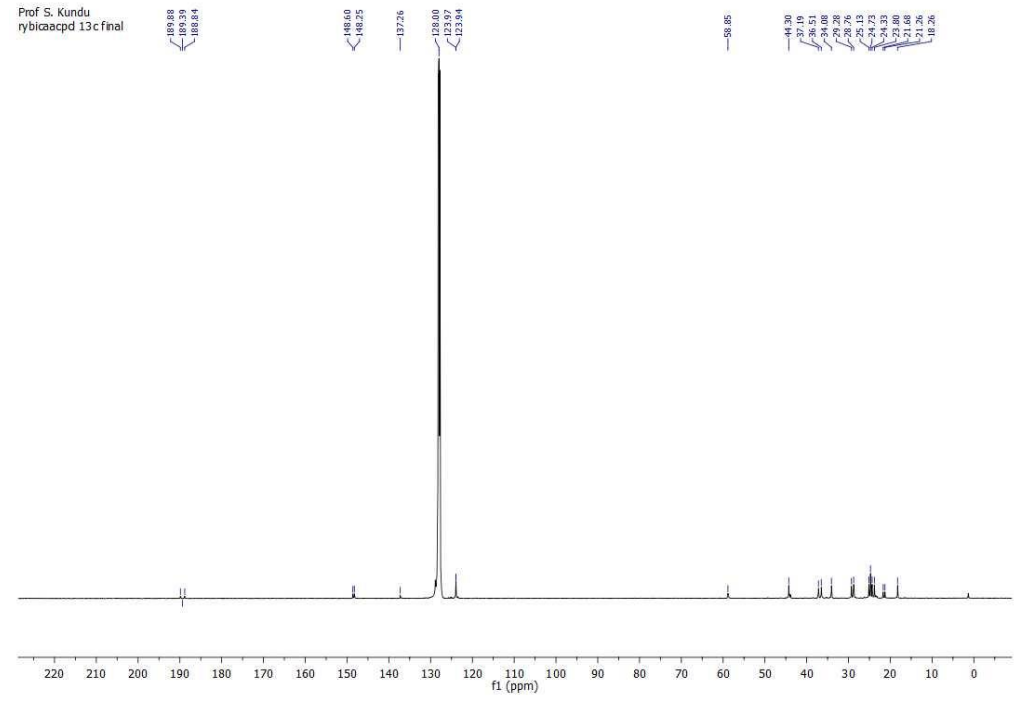


Fig S5: ^{13}C NMR of compound **1**

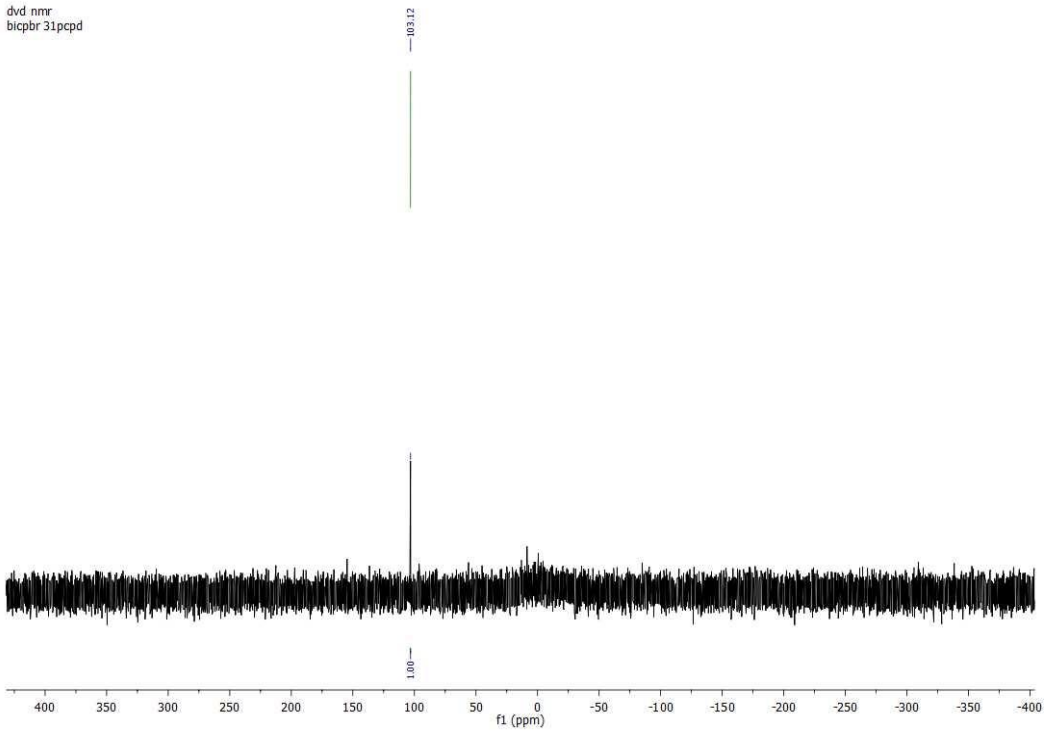


Fig S6: $^{31}P\{^{1}H\}$ NMR of compound **2**

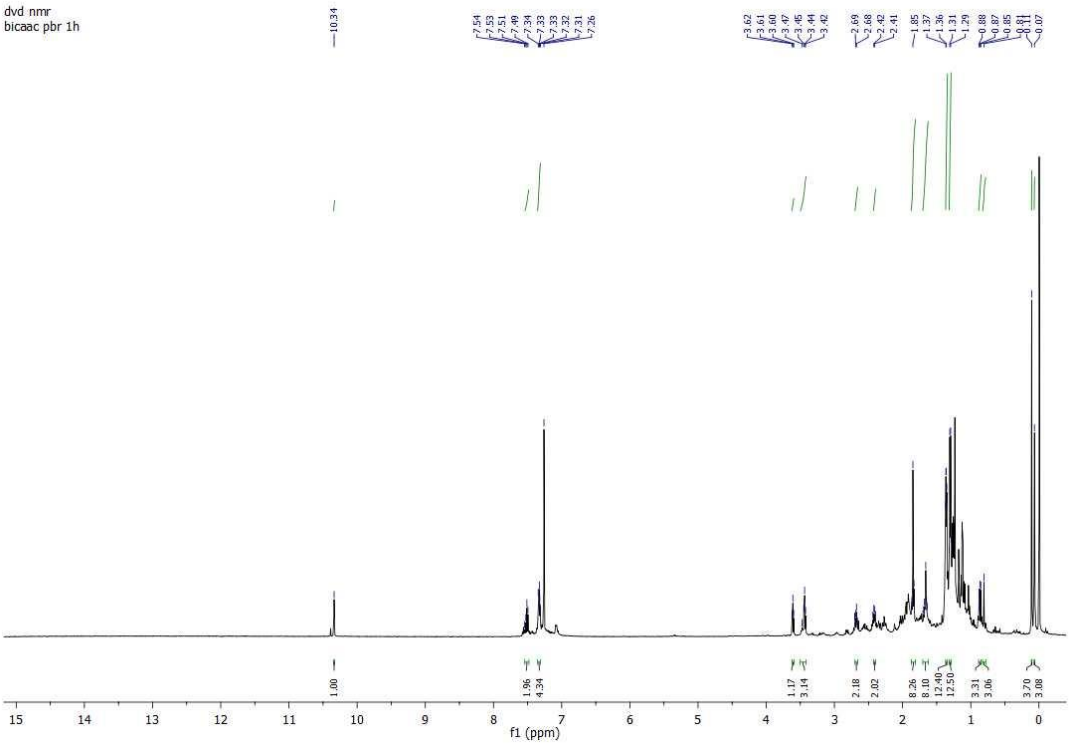


Fig S7: ^{1}H NMR of compound **2**

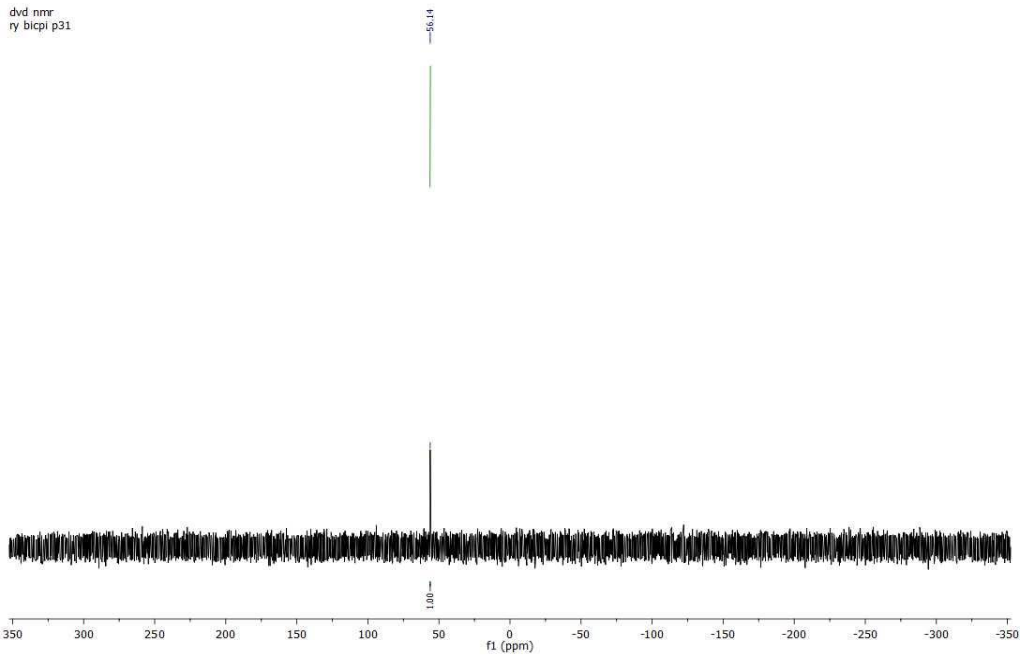


Fig S8: ^{31}P NMR of compound **3**

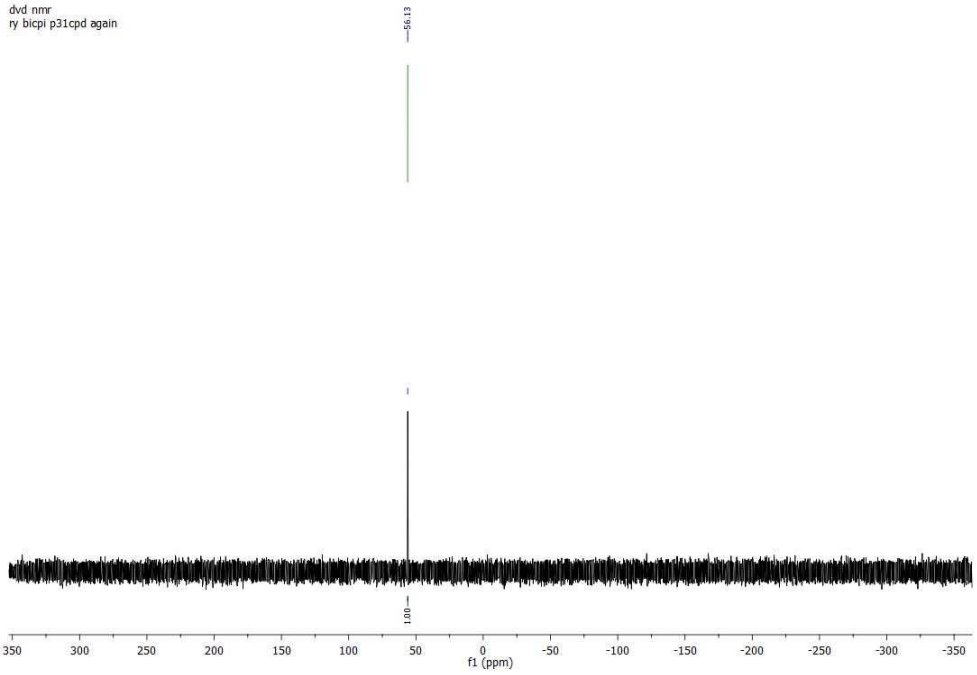


Fig S9: $^{31}P\{^{1}H\}$ NMR of compound **3**

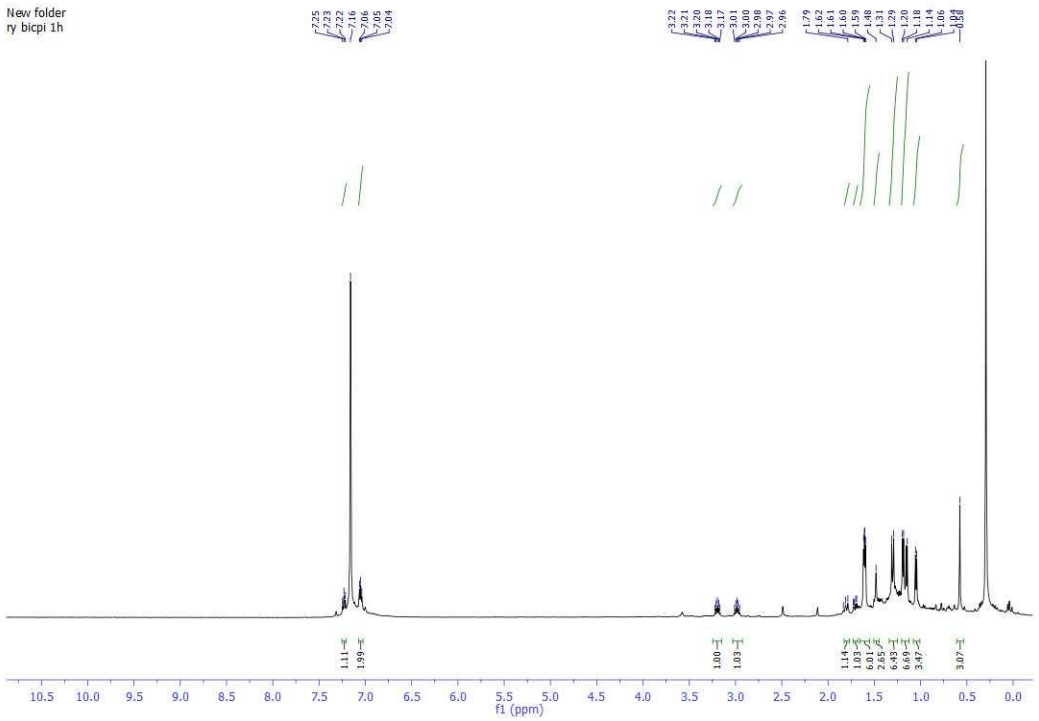


Fig S10: ^{1}H NMR of compound **3**

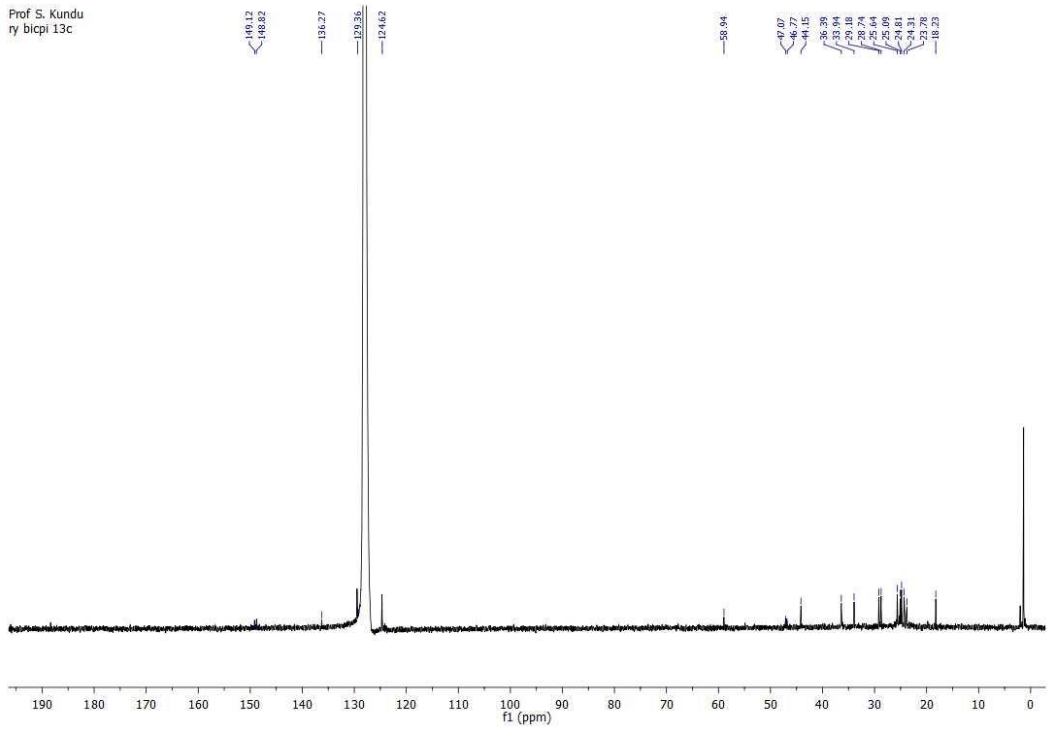


Fig S11: ^{13}C NMR of compound **3**

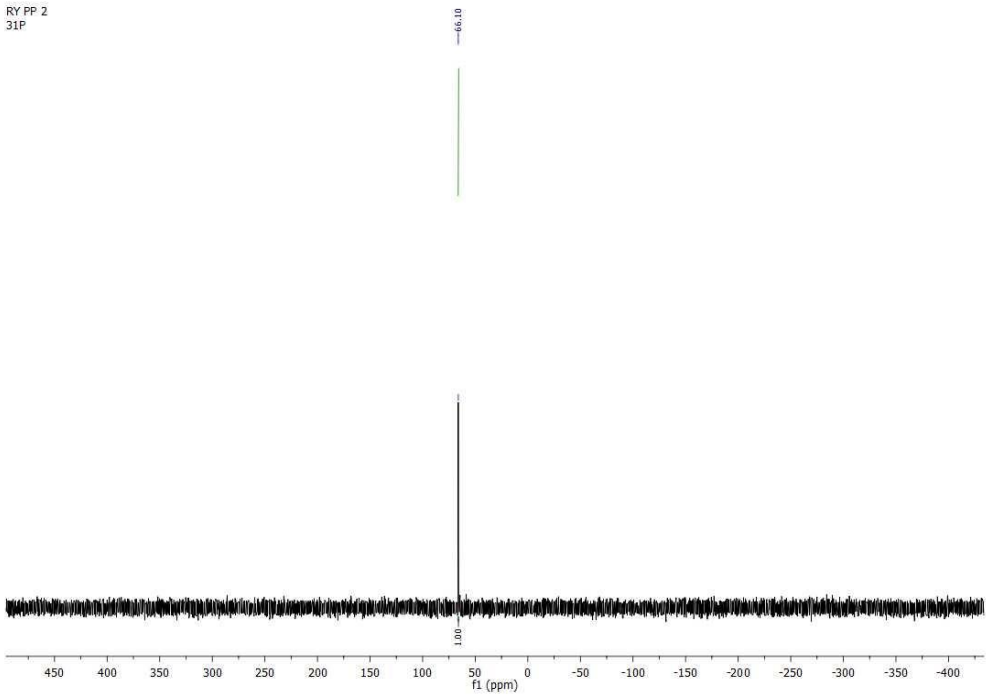


Fig S12: ^{31}P NMR of compound **4**

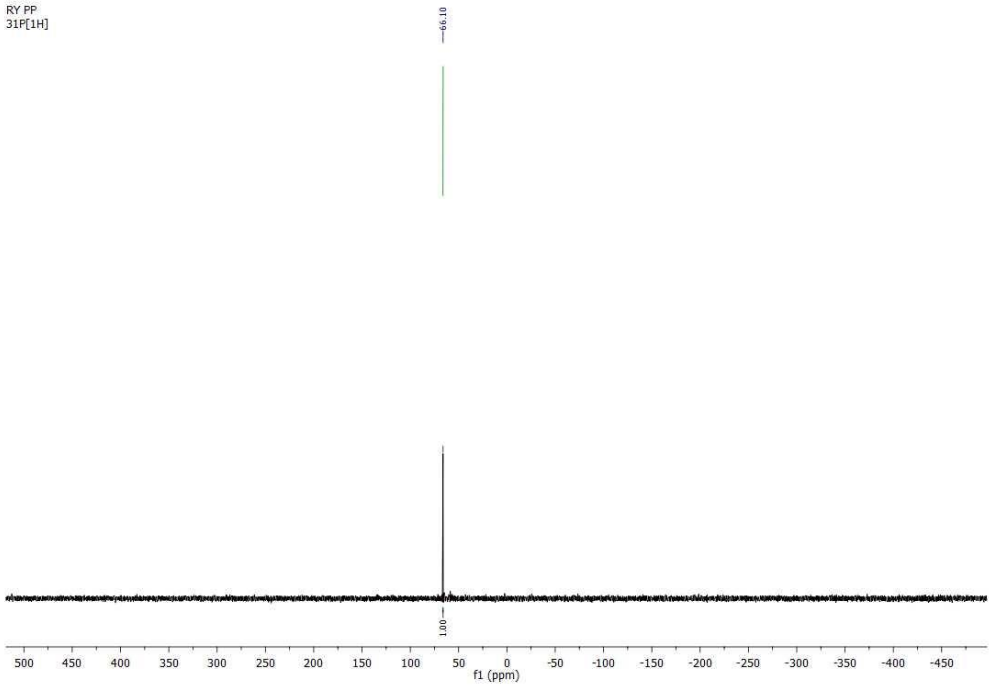


Fig S13: $^{31}P\{^{1}H\}$ NMR of compound **4**

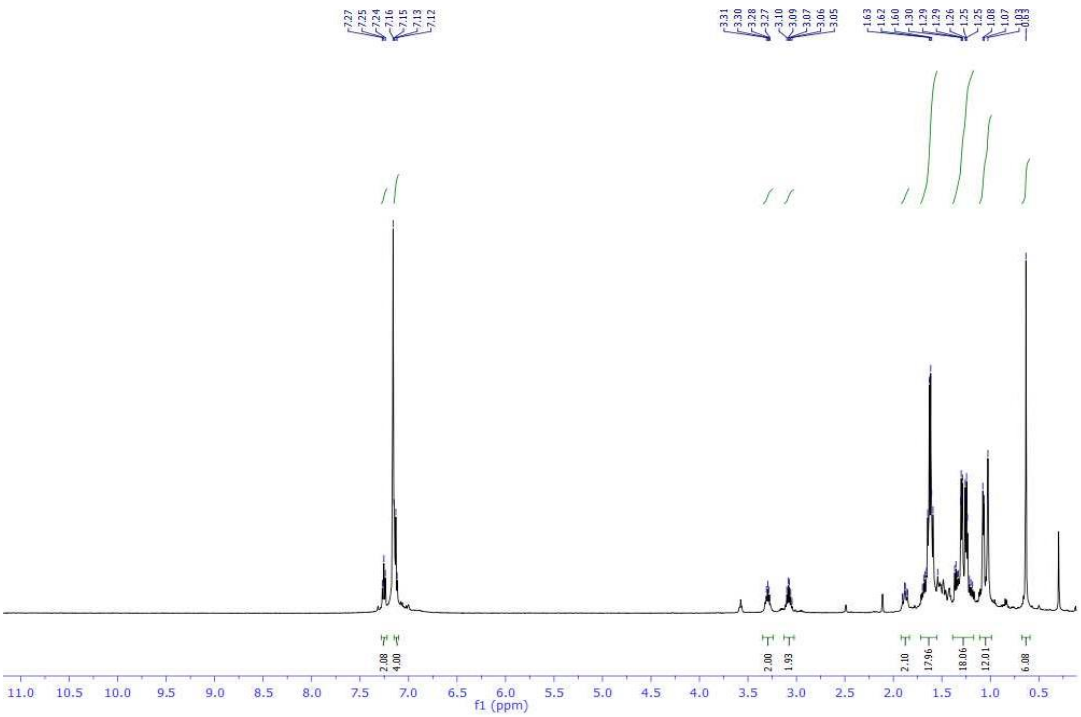


Fig S14: ^{1}H NMR of compound **4**

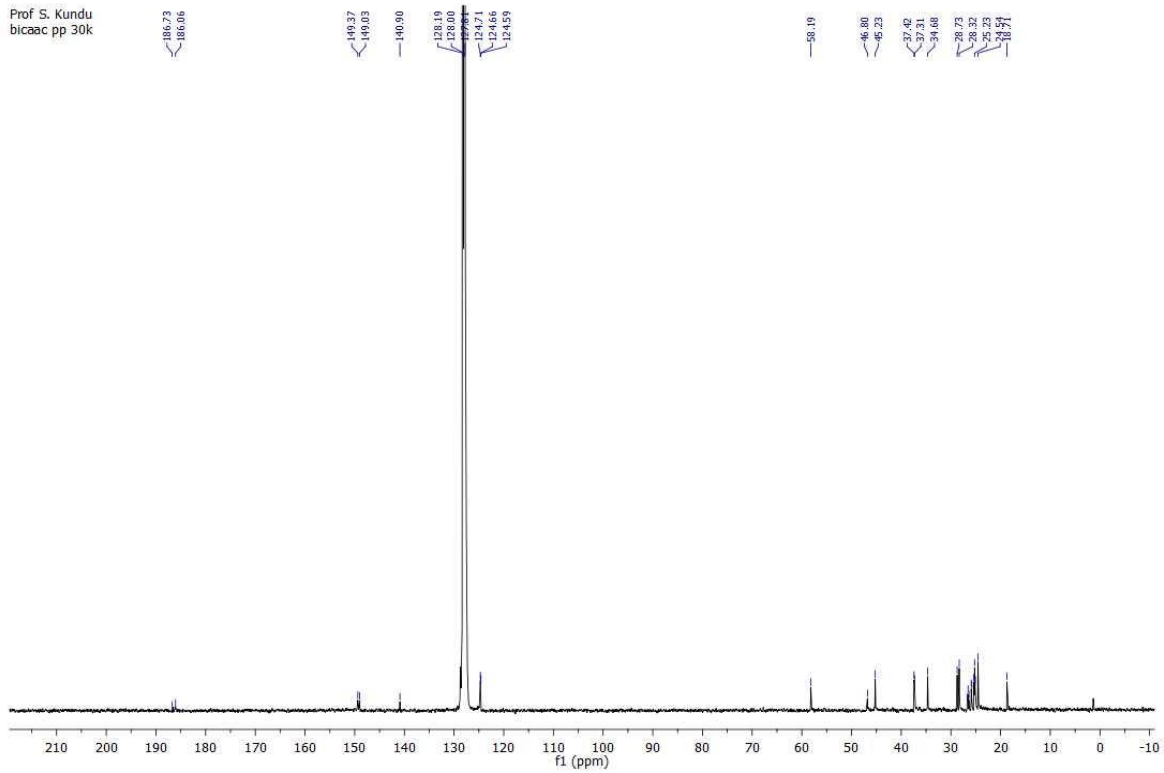
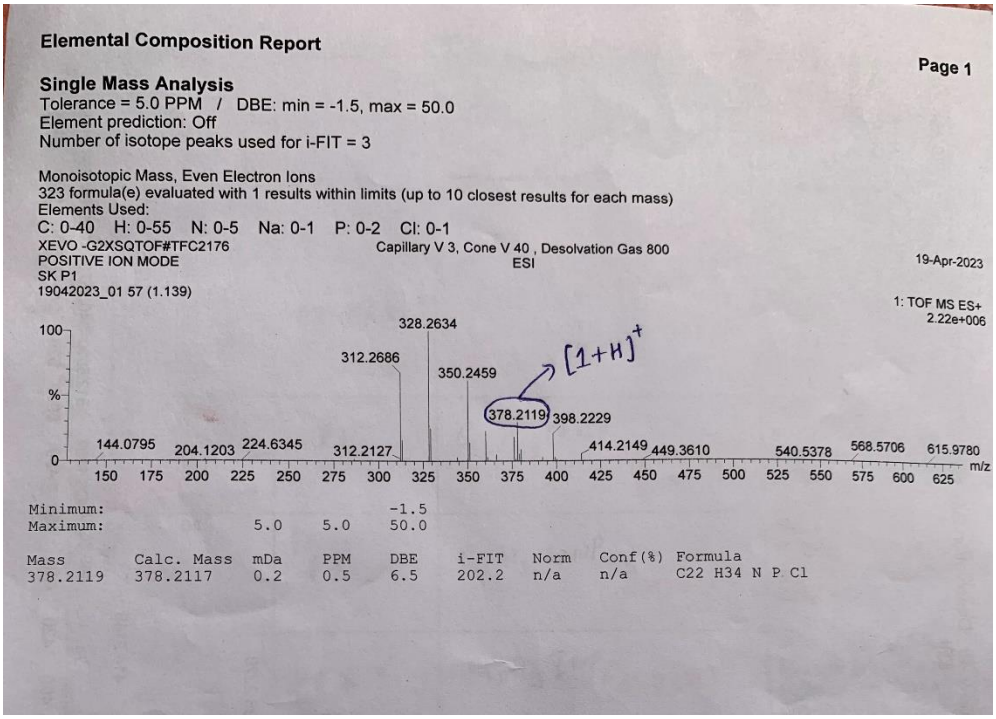


Fig S15: ^{13}C NMR of compound **4**

HRMS Data:



Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

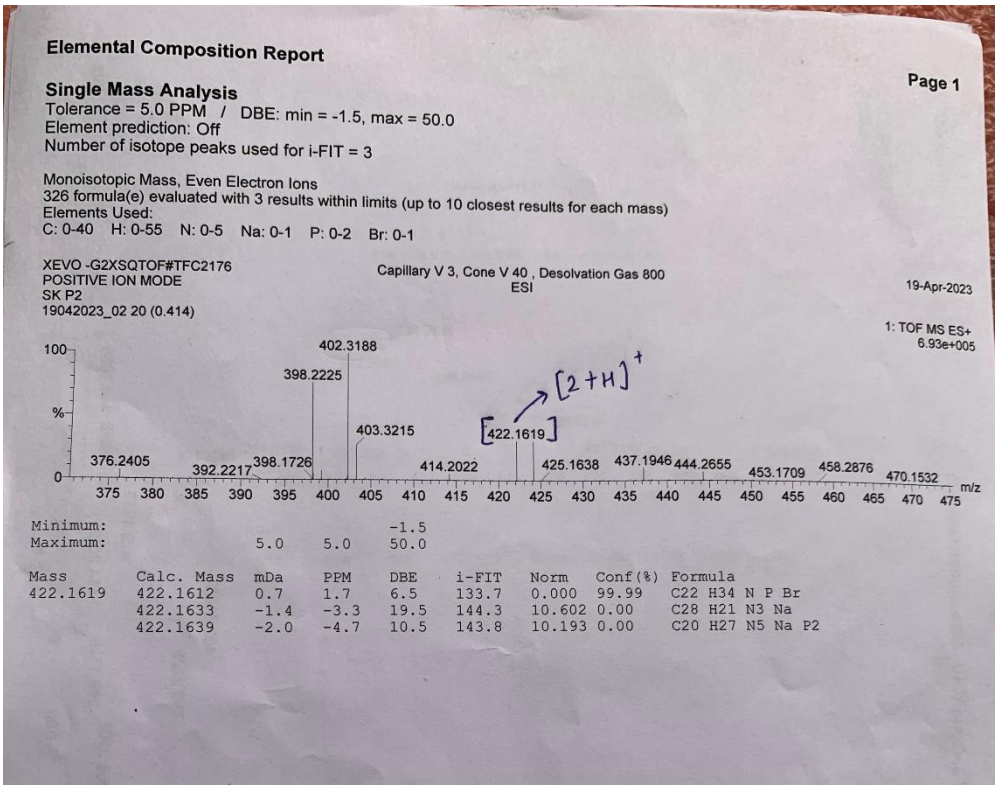
Monoisotopic Mass, Even Electron Ions
323 formula(e) evaluated with 1 results within limits (up to 10 closest results for each mass)
Elements Used:
C: 0-40 H: 0-55 N: 0-5 Na: 0-1 P: 0-2 Cl: 0-1

XEVO -G2XSQTOF#TFC2176 Capillary V 3, Cone V 40 , Desolvation Gas 800
POSITIVE ION MODE ESI
SK P1
19042023_01 57 (1.139)

19-Apr-2023
1: TOF MS ES+
2.22e+006

Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
378.2119	378.2117	0.2	0.5	6.5	202.2	n/a	n/a	C22 H34 N P Cl

Fig S16: HRMS of compound **1**



Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
326 formula(e) evaluated with 3 results within limits (up to 10 closest results for each mass)
Elements Used:
C: 0-40 H: 0-55 N: 0-5 Na: 0-1 P: 0-2 Br: 0-1

XEVO -G2XSQTOF#TFC2176 Capillary V 3, Cone V 40 , Desolvation Gas 800
POSITIVE ION MODE ESI
SK P2
19042023_02 20 (0.414)

19-Apr-2023
1: TOF MS ES+
6.93e+005

Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
422.1619	422.1612	0.7	1.7	6.5	133.7	0.000	99.99	C22 H34 N P Br
	422.1633	-1.4	-3.3	19.5	144.3	10.602	0.00	C28 H21 N3 Na
	422.1639	-2.0	-4.7	10.5	143.8	10.193	0.00	C20 H27 N5 Na P2

Fig S17: HRMS of compound **2**.

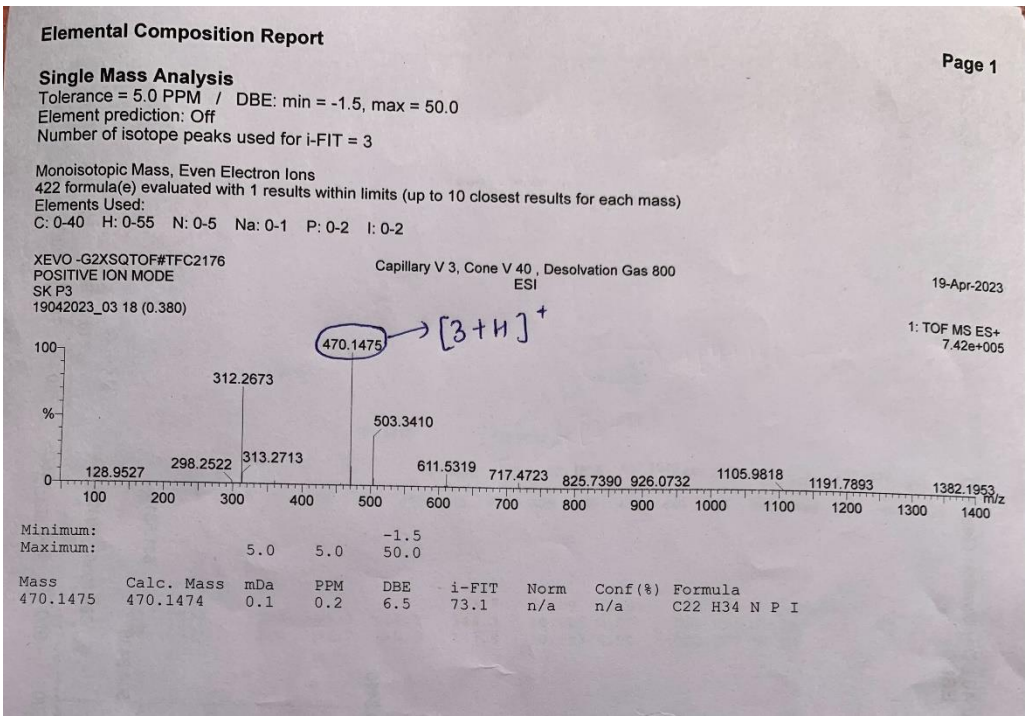


Fig S18: HRMS of compound **3**.

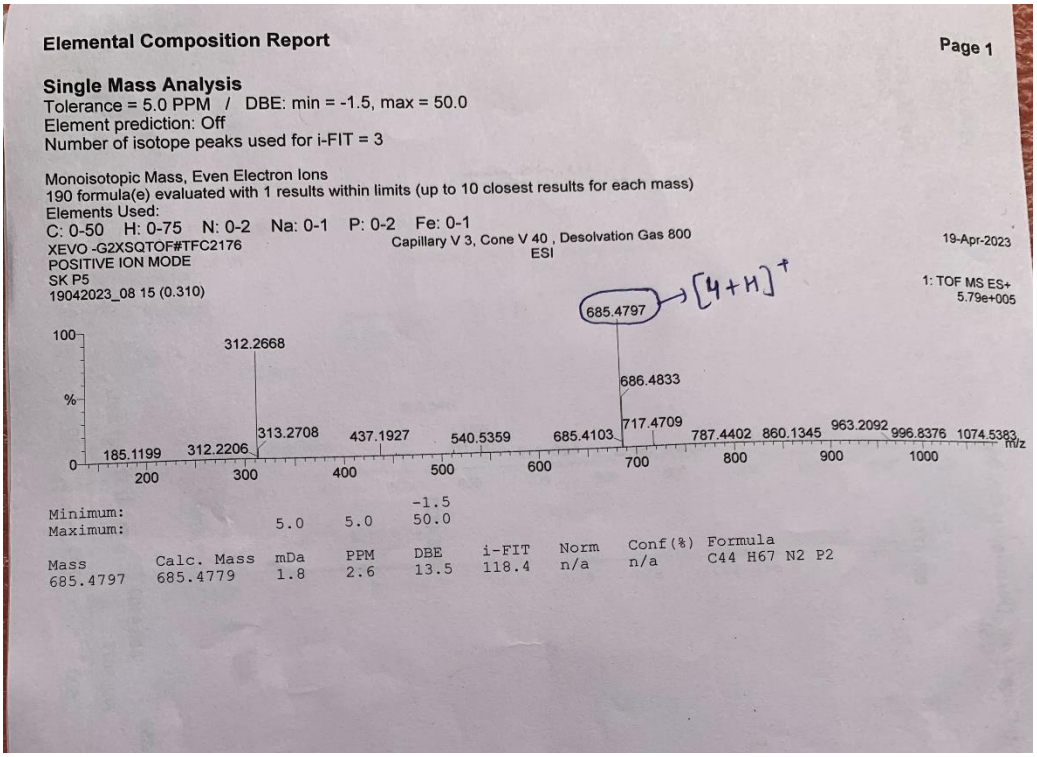


Fig S19: HRMS of compound **4**.

Cyclic Voltammetry:

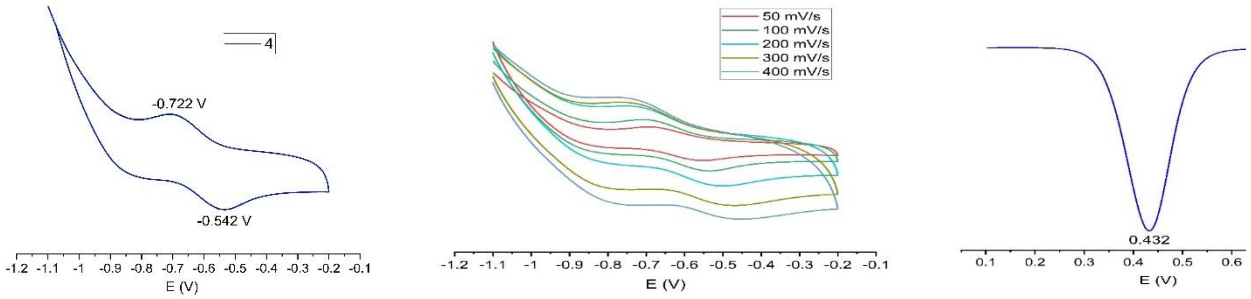


Fig S20: Cyclic Voltagramm (left) at scan rate = 0.1 V/s, Multiple oxidative scan (middle) of THF solution of compound **4** showing $E_{1/2}$ at –0.20 V versus Fc^{+}/Fc and Differential pulse voltammetry (DPV) of ferrocene (mM) (right) against the Bu_4NPF_6 (0.1 M) as the supporting electrolyte (scan rate = 0.1 V/s).

Theoretical Studies

1. Roby-Gould Bond Indices (RGBI) analysis

Roby-Gould method gives two independent covalent and ionic bond indices utilizing the expectation values of quantum mechanical operators and are based on well-known ideas of bonding and antibonding orbitals. This method depends upon the partitioning of either real space or Hilbert space (in case of RGBI), which is non-unique.

For RGBI analysis, geometry was optimized for **1,2** and **4** by using the *Gaussian09* program[S8] at B3LYP/6-311G(d,p) followed by single point energy calculation on optimized geometry of **1,2,4** and crystal geometry of **3** at B3LYP/def2-TZVP. The Roby-Gould Bond Indices (RGBI) of all the molecules were calculated at B3LYP/def2-TZVP level with *TONTO* program.[S16]

The covalent bond index (*c*), ionic bond index (*i*), total bond order (*τ*), and percentage covalency for different bonds in **1**-**4** compounds are reported.

Table S6. Roby-Gould bond indices for different bonds in $(BICAAC)_2PCl$ **(1).**

Atoms A-B	d_{AB} (Å)	*c*	*i*	*τ*	% Covalency
Cl--P	2.15	0.86	0.74	1.13	57.61
P--C12	1.73	1.61	-0.17	1.62	98.9
N--C2	1.45	1.07	0.29	1.11	93.17
N--C8	1.51	0.97	0.27	1	92.91
N--C12	1.37	1.42	0.33	1.46	95
C1--C3	1.53	1.07	0.1	1.07	99.11
C1--C13	1.54	1.04	-0.09	1.04	99.24
C1--C21	1.54	1.03	-0.09	1.03	99.25
C2--C3	1.41	1.5	-0.02	1.5	99.98

C2--C7	1.41	1.51	-0.02	1.51	99.98
C3--C4	1.4	1.54	-0.05	1.55	99.88
C4--C5	1.39	1.59	0.01	1.59	100
C5--C6	1.39	1.57	0	1.57	100
C6--C7	1.4	1.54	0.05	1.54	99.88
C7--C14	1.53	1.05	-0.1	1.06	99.1
C8--C9	1.54	1.01	-0.15	1.02	97.84
C8--C16	1.53	1.05	-0.21	1.07	96.22
C8--C17	1.54	1.02	-0.15	1.03	98.02
C9--C10	1.54	1.01	0.01	1.01	100
C10--C11	1.56	1.01	0.09	1.02	99.14
C11--C12	1.55	1.08	0.09	1.08	99.25
C11--C18	1.57	1	-0.04	1	99.8
C11--C20	1.54	1.04	-0.17	1.06	97.56
C14--C15	1.54	1.04	-0.1	1.04	99.1
C14--C22	1.54	1.03	-0.09	1.04	99.29
C17--C18	1.55	1	0.05	1	99.74
C18--C19	1.53	1.05	-0.12	1.06	98.73
C1--H1	1.09	0.87	0.15	0.88	97.1
C4--H2	1.08	0.9	0.16	0.92	97.02
C5--H3	1.08	0.91	0.17	0.92	96.66
C6--H4	1.08	0.9	0.16	0.92	97.03
C9--H5	1.09	0.9	0.16	0.91	96.98
C9--H6	1.09	0.91	0.16	0.92	96.86
C10--H7	1.09	0.91	0.16	0.92	96.83
C10--H8	1.09	0.91	0.17	0.92	96.68
C13--H9	1.09	0.92	0.16	0.94	97.04
C13--H10	1.09	0.91	0.17	0.92	96.58
C13--H11	1.09	0.92	0.15	0.93	97.26
C14--H12	1.09	0.87	0.15	0.89	97.03
C15--H13	1.09	0.92	0.16	0.93	96.96
C15--H14	1.09	0.91	0.15	0.92	97.39
C15--H15	1.09	0.92	0.16	0.93	97.06
C16--H16	1.09	0.92	0.17	0.93	96.86
C16--H17	1.09	0.91	0.16	0.92	97.01
C16--H18	1.09	0.91	0.16	0.92	97
C17--H19	1.09	0.89	0.15	0.91	97.1
C17--H20	1.09	0.91	0.16	0.92	96.89
C18--H21	1.1	0.89	0.16	0.91	96.76
C19--H22	1.09	0.92	0.16	0.94	96.95
C19--H23	1.09	0.92	0.16	0.93	96.96
C19--H24	1.09	0.91	0.16	0.93	96.99
C20--H25	1.09	0.91	0.16	0.93	96.88

C20--H26	1.09	0.92	0.16	0.93	96.94
C20--H27	1.09	0.92	0.17	0.93	96.74
C21--H28	1.09	0.92	0.16	0.94	96.95
C21--H29	1.09	0.92	0.16	0.93	97.1
C21--H30	1.09	0.91	0.15	0.93	97.33
C22--H31	1.09	0.92	0.16	0.93	97.08
C22--H32	1.09	0.92	0.15	0.93	97.24
C22--H33	1.09	0.91	0.17	0.93	96.55

Table S7. Roby-Gould bond indices for different bonds in $(BICAAC)_2PBr$ **(2).**

Atoms A-B	d_{AB}(Å)	*c*	*i*	*τ*	% Covalency
Br--P	2.31	0.87	0.72	1.13	58.85
P--C18	1.73	1.62	-0.14	1.62	99.3
N--C2	1.45	1.07	0.29	1.11	93.37
N--C8	1.51	0.97	0.27	1.01	92.66
N--C18	1.37	1.43	0.34	1.46	94.75
C1--C8	1.53	1.05	0.21	1.07	96.08
C2--C3	1.41	1.51	-0.02	1.51	99.99
C2--C7	1.41	1.51	-0.02	1.51	99.99
C3--C4	1.4	1.55	-0.06	1.55	99.87
C3--C14	1.53	1.07	-0.1	1.07	99.17
C4--C5	1.39	1.59	0.01	1.59	100
C5--C6	1.39	1.58	0	1.58	100
C6--C7	1.4	1.55	0.05	1.55	99.88
C7--C16	1.53	1.06	-0.09	1.06	99.23
C8--C9	1.54	1.02	-0.15	1.03	97.81
C8--C13	1.54	1.02	-0.14	1.03	98.05
C9--C10	1.54	1.01	0.01	1.01	100
C10--C11	1.55	1	0.1	1.01	99.04
C11--C12	1.57	1	-0.04	1	99.81
C11--C18	1.55	1.08	0.1	1.08	99.21
C11--C19	1.54	1.04	-0.17	1.05	97.47
C12--C13	1.55	1	-0.05	1	99.72
C12--C20	1.53	1.04	-0.12	1.05	98.75
C14--C15	1.54	1.03	-0.09	1.03	99.25
C14--C21	1.54	1.03	-0.09	1.04	99.28
C16--C17	1.54	1.03	-0.1	1.04	99.06
C16--C22	1.54	1.03	-0.09	1.04	99.26
C1--H1	1.09	0.92	0.16	0.93	96.88
C1--H2	1.09	0.91	0.16	0.92	96.98
C1--H3	1.09	0.9	0.16	0.92	97.07
C4--H4	1.08	0.9	0.16	0.91	97.01

C5--H5	1.08	0.91	0.17	0.93	96.6
C6--H6	1.08	0.9	0.16	0.92	97
C9--H7	1.09	0.91	0.16	0.92	96.85
C9--H8	1.09	0.9	0.16	0.91	96.93
C10--H9	1.09	0.9	0.17	0.92	96.75
C10--H10	1.09	0.91	0.17	0.92	96.78
C12--H11	1.1	0.9	0.16	0.91	96.75
C13--H12	1.09	0.91	0.16	0.92	96.89
C13--H13	1.09	0.89	0.15	0.91	97.18
C14--H14	1.09	0.87	0.15	0.89	97.02
C15--H15	1.09	0.92	0.16	0.94	96.96
C15--H16	1.09	0.92	0.16	0.93	97.09
C15--H17	1.09	0.91	0.15	0.93	97.34
C16--H18	1.09	0.87	0.15	0.88	97.08
C17--H19	1.09	0.92	0.16	0.93	96.95
C17--H20	1.09	0.91	0.15	0.92	97.43
C17--H21	1.09	0.92	0.16	0.93	97.06
C19--H22	1.09	0.91	0.16	0.93	96.86
C19--H23	1.09	0.91	0.17	0.93	96.78
C19--H24	1.09	0.92	0.16	0.93	96.91
C20--H25	1.09	0.92	0.16	0.93	97.01
C20--H26	1.09	0.91	0.16	0.93	96.96
C20--H27	1.09	0.91	0.16	0.93	97.04
C21--H28	1.09	0.92	0.16	0.94	97.06
C21--H29	1.09	0.91	0.17	0.92	96.6
C21--H30	1.09	0.92	0.15	0.93	97.26
C22--H31	1.09	0.92	0.16	0.93	97.07
C22--H32	1.09	0.92	0.16	0.93	97.21
C22--H33	1.09	0.91	0.17	0.92	96.57

Table S8. Roby-Gould bond indices for different bonds in $(BICAAC)_2PI$ **(3)**

Atoms A-B	d_{AB}(Å)	*c*	*i*	*τ*	% Covalency
P--C9	1.72	1.64	-0.11	1.64	99.51
N--C2	1.45	1.06	0.3	1.1	92.73
N--C4	1.51	0.97	0.28	1.01	92.51
N--C9	1.36	1.43	0.32	1.47	95.25
C1--C2	1.4	1.5	0.02	1.5	99.99
C1--C5	1.51	1.06	-0.13	1.07	98.6
C1--C7	1.39	1.52	-0.08	1.53	99.7
C2--C3	1.39	1.51	-0.02	1.51	99.98
C3--C8	1.5	1.06	-0.12	1.07	98.72

C3--C11	1.39	1.52	-0.08	1.52	99.74
C4--C6	1.53	1	-0.28	1.04	92.61
C4--C12	1.52	1	-0.19	1.02	96.45
C4--C13	1.52	1	-0.19	1.02	96.4
C5--C14	1.53	0.96	-0.15	0.97	97.59
C5--C16	1.53	0.97	-0.15	0.98	97.73
C7--C10	1.37	1.55	0	1.55	100
C8--C17	1.53	0.97	-0.16	0.98	97.47
C8--C20	1.54	0.97	-0.15	0.98	97.79
C9--C15	1.54	1.08	-0.08	1.08	99.5
C10--C11	1.37	1.54	0	1.54	100
C12--C18	1.54	0.95	0.06	0.95	99.63
C13--C19	1.55	0.95	0.01	0.95	100
C15--C18	1.53	1	-0.09	1	99.25
C15--C19	1.54	1	-0.14	1	98.09
C15--C21	1.56	0.97	-0.23	1	94.66
C18--C22	1.47	1	-0.16	1.02	97.52
C5--H1	0.98	0.88	0.16	0.89	96.69
C6--H2	0.96	0.91	0.17	0.92	96.41
C6--H3	0.96	0.92	0.18	0.94	96.15
C6--H4	0.96	0.91	0.18	0.93	96.31
C7--H5	0.93	0.9	0.17	0.91	96.38
C8--H6	0.98	0.87	0.16	0.89	96.76
C10--H7	0.93	0.9	0.18	0.92	96
C11--H8	0.93	0.9	0.17	0.91	96.37
C12--H9	0.97	0.89	0.17	0.91	96.63
C12--H10	0.97	0.91	0.18	0.93	96.28
C13--H11	0.97	0.91	0.18	0.93	96.27
C13--H12	0.97	0.9	0.17	0.91	96.43
C14--H13	0.96	0.92	0.18	0.93	96.43
C14--H14	0.96	0.92	0.18	0.94	96.28
C14--H15	0.96	0.91	0.17	0.93	96.47
C16--H16	0.96	0.9	0.18	0.92	96.12
C16--H17	0.96	0.92	0.18	0.93	96.34
C16--H18	0.96	0.92	0.18	0.94	96.45
C17--H19	0.96	0.92	0.18	0.93	96.46
C17--H20	0.96	0.92	0.18	0.94	96.26
C17--H21	0.96	0.92	0.18	0.93	96.41
C18--H22	0.98	0.89	0.18	0.91	96.07
C19--H23	0.97	0.91	0.18	0.92	96.04
C19--H24	0.97	0.91	0.18	0.93	96.18
C20--H25	0.96	0.92	0.17	0.94	96.52

C20--H26	0.96	0.92	0.18	0.94	96.33
C20--H27	0.96	0.91	0.18	0.92	96.09
C21--H28	0.96	0.91	0.17	0.92	96.44
C21--H29	0.96	0.91	0.18	0.93	96.29
C21--H30	0.96	0.92	0.19	0.93	96.07
C22--H31	0.96	0.91	0.18	0.93	96.25
C22--H32	0.96	0.91	0.18	0.92	96.38
C22--H33	0.96	0.91	0.18	0.93	96.35

Table S9. Roby-Gould bond indices for different bonds in $(BICAAC)_2P_2$ **(4)**

Atoms A-B	d_{AB}(Å)	*c*	*i*	*τ*	% Covalency
P1--P2	2.23	1.07	0	1.07	100
P1--C6	1.75	1.59	0.03	1.59	99.97
P2--C28	1.75	1.6	0.04	1.6	99.95
N1--C3	1.45	1.08	0.29	1.12	93.45
N1--C6	1.39	1.4	0.35	1.45	94.06
N1--C11	1.52	0.97	0.27	1.01	92.77
N2--C25	1.45	1.08	0.29	1.12	93.37
N2--C28	1.39	1.4	0.36	1.44	93.76
N2--C33	1.52	0.97	0.27	1.01	92.63
C1--C2	1.4	1.55	0.05	1.55	99.89
C1--C5	1.39	1.58	0	1.58	100
C2--C3	1.42	1.51	0.02	1.51	99.97
C2--C12	1.53	1.06	-0.09	1.06	99.23
C3--C4	1.42	1.5	-0.02	1.5	99.98
C4--C7	1.53	1.06	-0.1	1.07	99.15
C4--C9	1.4	1.55	-0.06	1.55	99.86
C5--C9	1.39	1.58	0	1.58	100
C6--C13	1.6	1.06	-0.11	1.06	98.99
C7--C15	1.54	1.03	-0.09	1.04	99.23
C7--C17	1.54	1.03	-0.09	1.04	99.27
C8--C11	1.53	1.03	0.16	1.04	97.68
C8--C19	1.52	1.03	0.05	1.03	99.72
C10--C11	1.54	1.03	0.2	1.05	96.27
C11--C16	1.55	1.02	-0.2	1.04	96.12
C12--C14	1.54	1.03	-0.09	1.04	99.18
C12--C18	1.54	1.03	-0.09	1.04	99.17
C13--C19	1.56	0.99	-0.07	0.99	99.53
C13--C20	1.55	1.03	-0.16	1.04	97.72
C13--C22	1.55	1.02	-0.16	1.04	97.64

C19--C21	1.54	1.04	-0.11	1.05	98.93
C23--C24	1.4	1.55	0.05	1.55	99.87
C23--C27	1.39	1.59	0	1.59	100
C24--C25	1.42	1.51	0.02	1.51	99.97
C24--C34	1.53	1.06	-0.09	1.07	99.23
C25--C26	1.42	1.51	-0.02	1.51	99.98
C26--C29	1.53	1.06	-0.1	1.07	99.18
C26--C31	1.4	1.55	-0.06	1.55	99.87
C27--C31	1.39	1.58	0	1.58	100
C28--C35	1.6	1.05	-0.11	1.06	98.89
C29--C37	1.54	1.04	-0.1	1.04	99.13
C29--C39	1.54	1.03	-0.09	1.04	99.18
C30--C33	1.53	1.02	0.15	1.03	97.79
C30--C41	1.52	1.03	0.05	1.03	99.76
C32--C33	1.54	1.04	0.21	1.06	96.16
C33--C38	1.55	1.02	-0.21	1.04	95.88
C34--C36	1.54	1.03	-0.09	1.03	99.23
C34--C40	1.54	1.03	-0.09	1.03	99.18
C35--C41	1.56	0.99	-0.06	0.99	99.6
C35--C42	1.55	1.04	-0.16	1.05	97.7
C35--C44	1.55	1.03	-0.16	1.04	97.63
C41--C43	1.54	1.04	-0.1	1.05	99
C1--H1	1.08	0.9	0.16	0.92	97.1
C5--H2	1.08	0.91	0.17	0.93	96.73
C7--H3	1.09	0.87	0.15	0.88	97.09
C8--H4	1.1	0.89	0.15	0.9	97.29
C8--H5	1.1	0.9	0.16	0.92	97.06
C9--H6	1.08	0.9	0.15	0.91	97.12
C10--H7	1.09	0.92	0.16	0.93	96.97
C10--H8	1.09	0.9	0.15	0.91	97.28
C10--H9	1.09	0.91	0.16	0.92	97.04
C12--H10	1.09	0.87	0.16	0.89	96.85
C14--H12	1.09	0.89	0.16	0.91	96.96
C14--H13	1.09	0.92	0.16	0.93	97.16
C14--H14	1.09	0.92	0.15	0.93	97.36
C15--H15	1.09	0.92	0.16	0.93	97.14
C15--H16	1.09	0.91	0.15	0.93	97.27
C15--H17	1.09	0.92	0.16	0.93	97.02
C16--H18	1.09	0.9	0.15	0.91	97.26
C16--H19	1.09	0.91	0.16	0.93	97.14
C16--H20	1.09	0.92	0.16	0.93	97.12
C17--H21	1.09	0.92	0.16	0.93	97.15

C17--H22	1.09	0.9	0.16	0.92	96.9
C17--H23	1.09	0.92	0.15	0.93	97.24
C18--H24	1.09	0.92	0.16	0.93	97.1
C18--H25	1.09	0.92	0.16	0.93	96.99
C18--H26	1.09	0.91	0.15	0.92	97.37
C19--H27	1.09	0.88	0.15	0.89	97.15
C20--H11	1.09	0.92	0.16	0.93	97.23
C20--H28	1.09	0.9	0.16	0.91	96.92
C20--H29	1.09	0.91	0.15	0.92	97.4
C21--H30	1.09	0.92	0.16	0.93	96.96
C21--H31	1.09	0.91	0.16	0.93	97.18
C21--H32	1.09	0.92	0.16	0.93	97.12
C22--H33	1.09	0.91	0.15	0.92	97.23
C22--H34	1.09	0.9	0.16	0.92	96.84
C22--H35	1.09	0.91	0.14	0.92	97.57
C23--H36	1.08	0.9	0.15	0.91	97.15
C27--H37	1.08	0.91	0.17	0.93	96.71
C29--H38	1.09	0.87	0.15	0.88	97.18
C30--H39	1.1	0.89	0.15	0.91	97.18
C30--H40	1.1	0.9	0.16	0.92	97.06
C31--H41	1.08	0.9	0.16	0.92	97.06
C32--H42	1.09	0.92	0.16	0.93	96.97
C32--H43	1.09	0.91	0.15	0.92	97.16
C32--H44	1.09	0.9	0.16	0.92	97.1
C34--H45	1.09	0.88	0.16	0.89	96.74
C36--H47	1.09	0.89	0.16	0.91	97.01
C36--H48	1.09	0.92	0.16	0.93	97.19
C36--H49	1.09	0.92	0.15	0.93	97.32
C37--H50	1.09	0.92	0.16	0.93	97.2
C37--H51	1.09	0.91	0.15	0.93	97.28
C37--H52	1.09	0.92	0.16	0.93	96.98
C38--H53	1.09	0.89	0.15	0.91	97.31
C38--H54	1.09	0.91	0.15	0.93	97.2
C38--H55	1.09	0.92	0.16	0.94	97.06
C39--H56	1.09	0.92	0.16	0.93	97.1
C39--H57	1.09	0.9	0.16	0.92	96.85
C39--H58	1.09	0.92	0.15	0.93	97.27
C40--H59	1.09	0.92	0.16	0.93	97.05
C40--H60	1.09	0.92	0.16	0.93	97
C40--H61	1.09	0.91	0.15	0.92	97.35
C41--H62	1.09	0.88	0.16	0.9	96.98
C42--H46	1.09	0.92	0.16	0.93	97.15

C42--H63	1.09	0.9	0.16	0.91	96.86
C42--H64	1.09	0.91	0.15	0.92	97.45
C43--H65	1.09	0.92	0.16	0.93	96.96
C43--H66	1.09	0.91	0.16	0.93	97.17
C43--H67	1.09	0.92	0.16	0.93	97.04
C44--H68	1.09	0.91	0.15	0.92	97.31
C44--H69	1.09	0.91	0.17	0.92	96.76
C44--H70	1.09	0.91	0.14	0.92	97.58

2. Electron localization function (ELF) and Local orbital locator (LOL) plots

The molecular wavefunctions for optimized geometry of **1,2,4** and crystal geometry of **3** were calculated at B3LYP/def2-TZVP(6d,10f) level. These wavefunctions were used to analyze electron density distribution and bonding features. Electron localization function (ELF)[S9] represents the regions where the electron is localized. Local Orbital Locator (LOL)[S10] represents the location of localized electronic groups which makes it easy to interpret the location of electron pairs and shells. ELF and LOL plots were made with the help of molecular wavefunctions by using *Multiwfn*.[S11]

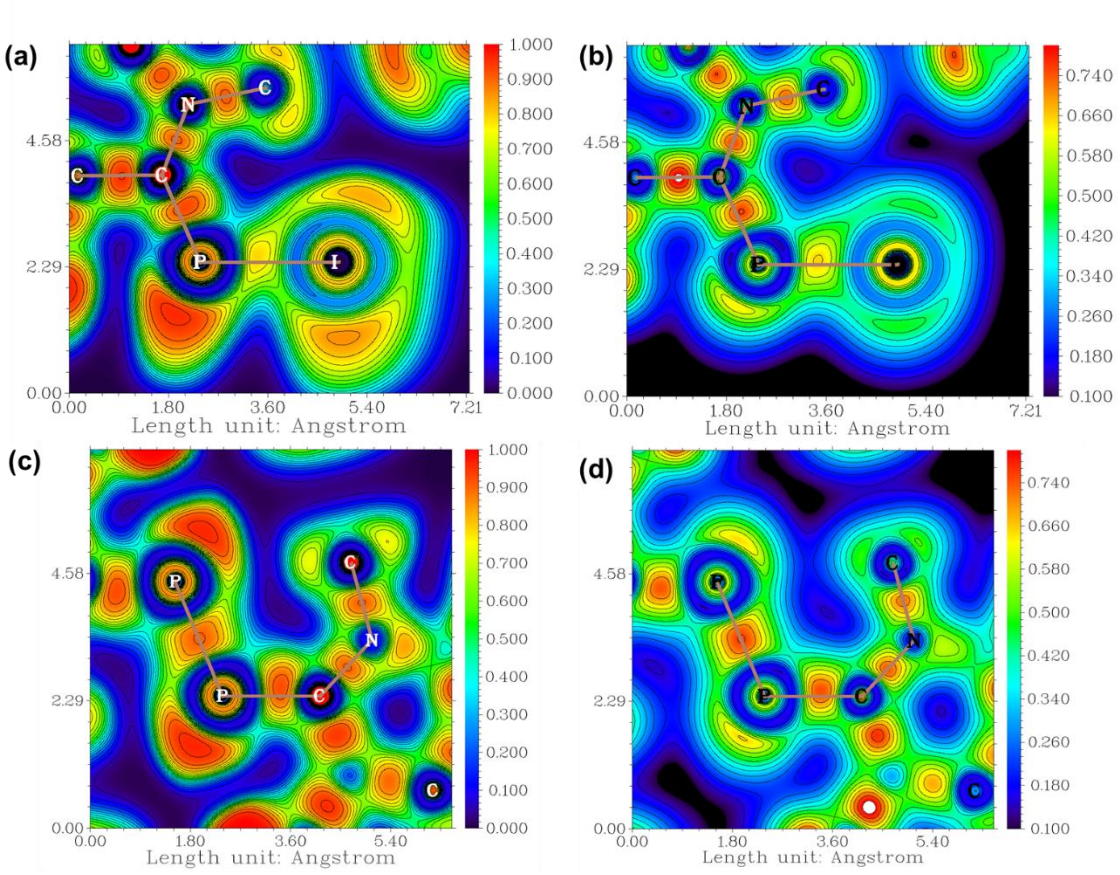


Figure S21: (a) ELF (b) LOL plots of **3** along C-P-I plane, (c) ELF (d) LOL plots of **4** along C-P-P plane.

3. QTAIM analysis

Electron density topological analysis was carried out using the *AIMALL* program[S12] to investigate the topological parameters such as the electronic charge density (ρ), laplacian of electronic charge density ($\nabla^2\rho$), ellipticity (ε), bond path length (R_{ij}), kinetic energy density (V) and potential energy density (G) for **1**-**4**. The molecular wavefunctions for optimized geometry of **1**,**2**,**4** and crystal geometry of **3** were calculated at B3LYP/def2-TZVP level.

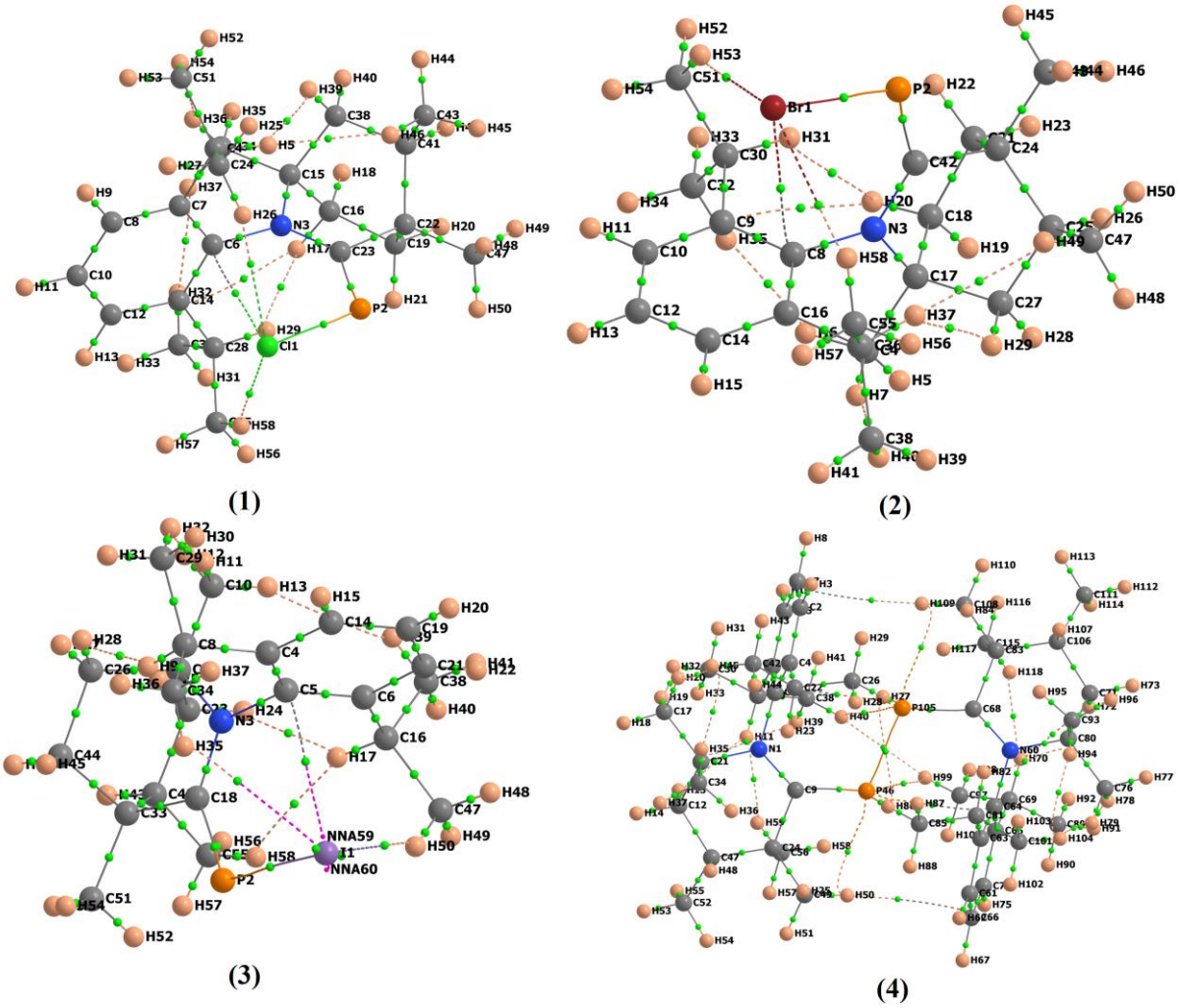


Figure S22: Molecular graphs of **1**-**4** obtained from electron density topology studies from QTAIM approach.

Table S10. Electron density topological descriptors for different bonding interactions in (BICAAC)PCl **(1)**

Atoms	R_{ij}(Å)	ρ(eÅ^{-3})	$\nabla^2\rho$(eÅ^{-5})	ε	|V|/G
C10 - C12	1.387	2.18	-23.48	0.198	4.279
C10 - H11	1.069	1.94	-24.79	0.016	8.752
C12 - C14	1.397	2.14	-22.51	0.199	4.229
C12 - H13	1.069	1.93	-24.64	0.019	8.459
C14 - C28	1.526	1.69	-15.51	0.020	4.705

C15 - C16	1.543	1.66	-14.81	0.024	4.674
C15 - C34	1.526	1.70	-15.64	0.014	4.758
C15 - C38	1.541	1.67	-15.00	0.023	4.696
C16 - C19	1.539	1.64	-14.48	0.001	4.655
C16 - H17	1.076	1.91	-23.73	0.007	7.784
C16 - H18	1.080	1.89	-23.20	0.008	7.582
C19 - C22	1.555	1.60	-13.63	0.008	4.482
C19 - H20	1.080	1.89	-23.24	0.009	7.646
C19 - H21	1.078	1.90	-23.58	0.009	7.846
C22 - C23	1.548	1.62	-13.96	0.034	4.420
C22 - C41	1.566	1.57	-13.16	0.009	4.473
C22 - C47	1.537	1.65	-14.72	0.004	4.653
C24 - H25	1.080	1.87	-22.79	0.011	7.510
C24 - H26	1.076	1.90	-23.68	0.010	8.087
C24 - H27	1.080	1.87	-22.81	0.011	7.481
C28 - C30	1.540	1.63	-14.28	0.015	4.617
C28 - C55	1.541	1.62	-14.21	0.013	4.606
C28 - H29	1.076	1.93	-24.19	0.005	7.840
C30 - H31	1.080	1.87	-22.86	0.009	7.583
C30 - H32	1.079	1.88	-22.97	0.010	7.537
C30 - H33	1.080	1.87	-22.91	0.008	7.578
C34 - H35	1.079	1.88	-22.93	0.008	7.544
C34 - H36	1.075	1.90	-23.48	0.010	7.777
C34 - H37	1.075	1.90	-23.45	0.010	7.790
C38 - C41	1.550	1.62	-14.06	0.006	4.629
C38 - H39	1.077	1.90	-23.58	0.007	7.711
C38 - H40	1.080	1.89	-23.17	0.007	7.578
C4 - C24	1.542	1.62	-14.18	0.013	4.602
C4 - C51	1.540	1.63	-14.28	0.015	4.615
C4 - C7	1.526	1.69	-15.50	0.019	4.702
C4 - H5	1.075	1.94	-24.26	0.004	7.834
C41 - C43	1.532	1.66	-14.87	0.009	4.671
C41 - H42	1.083	1.90	-23.33	0.004	7.586
C43 - H44	1.080	1.87	-22.78	0.009	7.485
C43 - H45	1.077	1.89	-23.19	0.011	7.654
C43 - H46	1.079	1.88	-23.05	0.009	7.707
C47 - H48	1.075	1.90	-23.50	0.012	7.816
C47 - H49	1.081	1.87	-22.70	0.010	7.439
C47 - H50	1.077	1.89	-23.27	0.011	7.779
C51 - H52	1.080	1.87	-22.88	0.009	7.584
C51 - H53	1.079	1.87	-22.92	0.008	7.573

C51 - H54	1.078	1.88	-23.00	0.011	7.534
C55 - H56	1.080	1.87	-22.80	0.011	7.516
C55 - H57	1.080	1.87	-22.82	0.011	7.485
C55 - H58	1.076	1.90	-23.65	0.010	8.083
C6 - C14	1.411	2.09	-21.43	0.253	4.199
C6 - C7	1.412	2.09	-21.41	0.253	4.200
C7 - C8	1.397	2.14	-22.53	0.199	4.230
C8 - C10	1.387	2.18	-23.47	0.198	4.279
C8 - H9	1.069	1.94	-24.64	0.019	8.460
Cl1 - C6	3.199	0.07	0.81	0.453	0.824
Cl1 - H26	2.891	0.05	0.53	0.046	0.766
Cl1 - H58	2.924	0.05	0.50	0.040	0.763
Cl1 - P2	2.147	0.73	-2.70	0.182	2.595
H17 - H29	2.293	0.06	0.68	0.276	0.825
H17 - H32	2.720	0.03	0.44	3.848	0.767
H32 - H37	2.311	0.04	0.44	0.066	0.817
H36 - H54	2.193	0.05	0.53	0.066	0.822
H5 - H39	2.188	0.06	0.69	0.146	0.838
H5 - H46	2.437	0.03	0.37	0.156	0.820
N3 - C15	1.514	1.60	-12.64	0.072	3.319
N3 - C23	1.365	2.16	-23.51	0.126	3.074
N3 - C6	1.451	1.81	-17.62	0.004	3.399
P2 - C23	1.733	1.17	4.72	0.714	1.757

Table S11. Electron density topological descriptors for different bonding interactions in (BICAAC)PBr **(2)**

Atoms	**R_{ij}(Å)**	**ρ(eÅ^{-3})**	**∇^2ρ(eÅ^{-5})**	**ε**	**|V|/G**
Br1 - C8	3.347	0.07	0.70	0.547	0.853
Br1 - H53	3.018	0.05	0.47	0.031	0.806
Br1 - H58	2.975	0.05	0.51	0.033	0.813
Br1 - P2	2.315	0.64	-1.51	0.119	2.509
C10 - C12	1.387	2.18	-23.48	0.197	4.281
C10 - H11	1.069	1.94	-24.66	0.019	8.467
C12 - C14	1.387	2.18	-23.49	0.198	4.280
C12 - H13	1.069	1.94	-24.80	0.016	8.762
C14 - C16	1.397	2.14	-22.52	0.199	4.231
C14 - H15	1.069	1.94	-24.66	0.019	8.469
C16 - C36	1.527	1.69	-15.48	0.020	4.701
C17 - C18	1.544	1.66	-14.78	0.024	4.672
C17 - C27	1.541	1.67	-15.00	0.023	4.696

C18 - C21	1.539	1.64	-14.51	0.001	4.656
C18 - H19	1.080	1.89	-23.21	0.008	7.582
C18 - H20	1.076	1.91	-23.75	0.007	7.790
C21 - C24	1.555	1.60	-13.63	0.009	4.480
C21 - H22	1.079	1.90	-23.58	0.009	7.846
C21 - H23	1.080	1.89	-23.25	0.009	7.649
C24 - C25	1.566	1.57	-13.16	0.009	4.472
C24 - C42	1.550	1.61	-13.81	0.034	4.406
C24 - C43	1.536	1.65	-14.75	0.004	4.655
C25 - C27	1.549	1.62	-14.12	0.007	4.632
C25 - C47	1.532	1.66	-14.86	0.009	4.671
C25 - H26	1.083	1.90	-23.33	0.004	7.586
C27 - H28	1.080	1.89	-23.17	0.007	7.579
C27 - H29	1.078	1.90	-23.56	0.008	7.710
C30 - C32	1.541	1.63	-14.26	0.015	4.614
C30 - C51	1.541	1.62	-14.23	0.013	4.607
C30 - H31	1.076	1.93	-24.20	0.005	7.835
C32 - H33	1.080	1.87	-22.86	0.009	7.582
C32 - H34	1.079	1.88	-22.92	0.008	7.582
C32 - H35	1.079	1.88	-22.99	0.011	7.536
C36 - C38	1.541	1.63	-14.26	0.015	4.614
C36 - C55	1.541	1.62	-14.21	0.013	4.602
C36 - H37	1.075	1.94	-24.25	0.005	7.826
C38 - H39	1.080	1.87	-22.87	0.009	7.585
C38 - H40	1.078	1.88	-23.00	0.011	7.531
C38 - H41	1.080	1.87	-22.91	0.009	7.575
C4 - C17	1.526	1.70	-15.65	0.014	4.757
C4 - H5	1.079	1.88	-22.93	0.008	7.546
C4 - H6	1.075	1.90	-23.47	0.010	7.789
C4 - H7	1.075	1.90	-23.50	0.010	7.778
C43 - H44	1.075	1.90	-23.52	0.011	7.827
C43 - H45	1.077	1.89	-23.29	0.011	7.788
C43 - H46	1.081	1.87	-22.70	0.010	7.437
C47 - H48	1.080	1.87	-22.78	0.009	7.488
C47 - H49	1.079	1.88	-23.05	0.009	7.709
C47 - H50	1.077	1.89	-23.19	0.011	7.658
C51 - H52	1.080	1.87	-22.80	0.011	7.511
C51 - H53	1.075	1.90	-23.68	0.010	8.086
C51 - H54	1.080	1.87	-22.81	0.011	7.484
C55 - H56	1.080	1.87	-22.79	0.011	7.506
C55 - H57	1.080	1.87	-22.81	0.011	7.484

C55 - H58	1.075	1.90	-23.69	0.010	8.088
C8 - C16	1.412	2.09	-21.37	0.253	4.197
C8 - C9	1.412	2.09	-21.37	0.253	4.197
C9 - C10	1.397	2.14	-22.53	0.199	4.230
C9 - C30	1.527	1.69	-15.47	0.020	4.703
H20 - H31	2.285	0.06	0.69	0.279	0.826
H20 - H35	2.708	0.04	0.45	3.109	0.771
H29 - H37	2.169	0.07	0.70	0.136	0.839
H37 - H49	2.467	0.03	0.35	0.196	0.813
H6 - H35	2.275	0.05	0.47	0.059	0.819
H7 - H40	2.169	0.05	0.56	0.066	0.822
N3 - C17	1.514	1.60	-12.57	0.072	3.315
N3 - C42	1.366	2.16	-23.55	0.128	3.079
N3 - C8	1.451	1.82	-17.68	0.003	3.396
P2 - C42	1.736	1.16	4.65	0.690	1.757

Table S12. Electron density topological descriptors for different bonding interactions in (BICAAC)PI **(3)**

Atoms	**R_{ij}(Å)**	**ρ(eÅ^{-3})**	**$\nabla^2\rho$(eÅ^{-5})**	**ε**	**|V|/G**
C10 - H11	0.942	2.50	-38.94	0.018	6.377
C10 - H12	0.943	2.48	-38.48	0.019	6.253
C10 - H13	0.943	2.49	-38.79	0.017	6.408
C14 - C19	1.368	2.26	-25.06	0.184	4.293
C14 - H15	0.911	2.70	-46.49	0.011	6.719
C16 - C38	1.532	1.63	-14.21	0.019	4.484
C16 - C47	1.544	1.60	-13.57	0.016	4.447
C16 - H17	0.964	2.45	-37.59	0.005	7.088
C18 - C33	1.538	1.66	-14.52	0.032	4.419
C19 - C21	1.369	2.25	-24.98	0.184	4.291
C19 - H20	0.911	2.71	-46.84	0.004	6.934
C21 - H22	0.911	2.71	-46.61	0.011	6.723
C23 - C42	1.539	1.64	-14.26	0.013	4.540
C23 - H24	0.953	2.46	-38.07	0.012	6.590
C23 - H25	0.954	2.45	-37.72	0.012	6.515
C26 - C44	1.545	1.60	-13.69	0.008	4.491
C26 - H27	0.954	2.45	-37.74	0.015	6.525
C26 - H28	0.953	2.46	-38.09	0.014	6.610
C29 - H30	0.943	2.48	-38.52	0.016	6.224
C29 - H31	0.942	2.48	-38.65	0.017	6.203
C29 - H32	0.943	2.48	-38.62	0.017	6.200

C33 - C42	1.528	1.69	-15.17	0.015	4.545
C33 - C44	1.535	1.66	-14.55	0.008	4.497
C33 - C51	1.562	1.56	-12.98	0.008	4.452
C34 - H35	0.942	2.51	-39.32	0.018	6.595
C34 - H36	0.943	2.48	-38.46	0.020	6.152
C34 - H37	0.942	2.48	-38.68	0.020	6.197
C38 - H39	0.943	2.48	-38.68	0.018	6.194
C38 - H40	0.943	2.48	-38.62	0.017	6.220
C38 - H41	0.944	2.48	-38.44	0.016	6.236
C4 - C14	1.393	2.16	-22.84	0.189	4.236
C4 - C5	1.398	2.15	-22.60	0.248	4.222
C4 - C8	1.510	1.74	-16.36	0.018	4.675
C42 - C55	1.472	1.85	-18.02	0.015	4.615
C42 - H43	0.963	2.43	-37.12	0.006	6.652
C44 - H45	0.953	2.47	-38.46	0.014	6.820
C44 - H46	0.953	2.46	-37.97	0.014	6.629
C47 - H48	0.944	2.48	-38.45	0.020	6.194
C47 - H49	0.943	2.48	-38.44	0.021	6.188
C47 - H50	0.942	2.51	-39.32	0.018	6.611
C5 - C6	1.395	2.16	-22.86	0.249	4.219
C51 - H52	0.942	2.50	-39.15	0.019	6.473
C51 - H53	0.943	2.47	-38.35	0.023	6.179
C51 - H54	0.943	2.49	-38.83	0.020	6.467
C55 - H56	0.943	2.47	-38.28	0.014	6.057
C55 - H57	0.944	2.48	-38.41	0.014	6.194
C55 - H58	0.943	2.49	-38.68	0.012	6.249
C6 - C16	1.503	1.77	-16.78	0.015	4.688
C6 - C21	1.392	2.16	-22.91	0.188	4.244
C7 - C10	1.526	1.68	-15.17	0.016	4.597
C7 - C23	1.522	1.73	-15.89	0.023	4.670
C7 - C26	1.521	1.73	-15.98	0.024	4.687
C8 - C29	1.531	1.64	-14.33	0.018	4.492
C8 - C34	1.533	1.63	-14.13	0.014	4.466
C8 - H9	0.962	2.45	-37.78	0.006	7.064
H11 - H32	2.355	0.04	0.43	0.195	0.787
H13 - H39	2.486	0.03	0.34	0.227	0.768
H17 - H24	2.220	0.06	0.68	0.201	0.821
H17 - H58	2.415	0.03	0.40	0.117	0.804
H9 - H28	2.183	0.06	0.74	0.197	0.818
I1 - H50	2.973	0.04	0.40	0.040	0.806
I1 - P2	2.212	0.55	-0.72	0.092	2.312

N3 - C18	1.362	2.18	-23.74	0.122	3.061
N3 - C5	1.453	1.81	-17.51	0.009	3.383
N3 - C7	1.509	1.61	-12.91	0.070	3.293
P2 - C18	1.723	1.18	5.54	0.626	1.726

Table S13. Electron density topological descriptors for different bonding interactions in $(BICAAC)_2P_2$ **(4)**

Atoms	**R_{ij}(Å)**	**ρ(eÅ^{-3})**	**∇^2ρ(eÅ^{-5})**	**ε**	**|V|/G**
C10 - C30	1.541	1.63	-14.28	0.015	4.620
C10 - C38	1.540	1.63	-14.25	0.014	4.598
C10 - H11	1.074	1.94	-24.40	0.005	7.859
C101 - H102	1.080	1.87	-22.88	0.008	7.539
C101 - H103	1.080	1.87	-22.82	0.009	7.562
C101 - H104	1.078	1.88	-23.08	0.011	7.548
C106 - C111	1.538	1.64	-14.43	0.007	4.617
C106 - H107	1.080	1.91	-23.60	0.004	7.522
C108 - H109	1.073	1.92	-23.96	0.009	8.054
C108 - H110	1.080	1.87	-22.73	0.011	7.363
C111 - H112	1.080	1.87	-22.76	0.008	7.461
C111 - H113	1.078	1.88	-23.09	0.010	7.574
C111 - H114	1.079	1.88	-23.03	0.009	7.586
C115 - H116	1.079	1.88	-23.02	0.012	7.508
C115 - H117	1.074	1.92	-23.88	0.009	7.997
C115 - H118	1.079	1.87	-22.89	0.013	7.441
C12 - C21	1.531	1.70	-15.63	0.021	4.766
C12 - C47	1.518	1.72	-15.80	0.014	4.664
C12 - H13	1.081	1.88	-23.05	0.006	7.548
C12 - H14	1.082	1.88	-22.98	0.004	7.484
C15 - H16	1.069	1.93	-24.60	0.019	8.414
C17 - C21	1.535	1.67	-15.13	0.017	4.741
C17 - H18	1.079	1.87	-22.87	0.008	7.499
C17 - H19	1.075	1.90	-23.41	0.010	7.709
C17 - H20	1.075	1.90	-23.59	0.009	7.809
C2 - C4	1.398	2.14	-22.47	0.198	4.234
C2 - C7	1.385	2.19	-23.60	0.200	4.276
C2 - H3	1.069	1.94	-24.63	0.019	8.397
C21 - C34	1.548	1.63	-14.42	0.032	4.712
C22 - C26	1.541	1.63	-14.23	0.012	4.602
C22 - C42	1.543	1.62	-14.15	0.016	4.602
C22 - H23	1.075	1.94	-24.39	0.005	7.969

C24 - C47	1.564	1.59	-13.52	0.015	4.592
C24 - C49	1.548	1.62	-14.14	0.008	4.623
C24 - C56	1.554	1.59	-13.65	0.009	4.554
C26 - H27	1.075	1.91	-23.72	0.009	8.065
C26 - H28	1.080	1.87	-22.75	0.010	7.454
C26 - H29	1.080	1.87	-22.76	0.011	7.422
C30 - H31	1.079	1.87	-22.90	0.009	7.533
C30 - H32	1.078	1.88	-23.02	0.010	7.565
C30 - H33	1.080	1.87	-22.83	0.009	7.549
C34 - H35	1.073	1.91	-23.71	0.010	7.681
C34 - H36	1.076	1.89	-23.32	0.010	7.663
C34 - H37	1.080	1.87	-22.72	0.009	7.439
C38 - H39	1.080	1.87	-22.76	0.010	7.493
C38 - H40	1.075	1.90	-23.66	0.009	8.037
C38 - H41	1.080	1.87	-22.77	0.010	7.478
C4 - C22	1.527	1.69	-15.48	0.020	4.708
C4 - C5	1.416	2.07	-21.05	0.251	4.193
C42 - H43	1.080	1.87	-22.88	0.008	7.539
C42 - H44	1.080	1.87	-22.82	0.009	7.562
C42 - H45	1.078	1.88	-23.08	0.011	7.548
C47 - C52	1.538	1.64	-14.43	0.007	4.617
C47 - H48	1.080	1.91	-23.60	0.004	7.522
C49 - H50	1.073	1.92	-23.96	0.009	8.054
C49 - H51	1.080	1.87	-22.73	0.011	7.363
C5 - C6	1.416	2.07	-21.04	0.251	4.198
C5 - P105	3.230	0.08	0.78	1.040	0.880
C52 - H53	1.080	1.87	-22.76	0.008	7.461
C52 - H54	1.078	1.88	-23.09	0.010	7.574
C52 - H55	1.079	1.88	-23.03	0.009	7.586
C56 - H57	1.079	1.88	-23.02	0.012	7.508
C56 - H58	1.074	1.92	-23.88	0.009	7.997
C56 - H59	1.079	1.87	-22.89	0.013	7.441
C6 - C10	1.526	1.69	-15.51	0.019	4.706
C6 - C15	1.396	2.14	-22.58	0.199	4.233
C61 - C63	1.398	2.14	-22.47	0.198	4.234
C61 - C66	1.385	2.19	-23.60	0.200	4.276
C61 - H62	1.069	1.94	-24.63	0.019	8.397
C63 - C64	1.416	2.07	-21.04	0.251	4.193
C63 - C81	1.527	1.69	-15.48	0.020	4.708
C64 - C65	1.416	2.07	-21.04	0.251	4.198
C65 - C69	1.526	1.69	-15.51	0.019	4.706

C65 - C74	1.396	2.14	-22.58	0.199	4.233
C66 - C74	1.386	2.18	-23.57	0.198	4.283
C66 - H67	1.070	1.93	-24.69	0.017	8.666
C68 - C83	1.600	1.47	-11.50	0.034	4.364
C68 - P105	1.757	1.11	4.06	0.490	1.771
C69 - C89	1.541	1.63	-14.28	0.015	4.620
C69 - C97	1.540	1.63	-14.25	0.014	4.598
C69 - H70	1.074	1.94	-24.40	0.005	7.859
C7 - C15	1.386	2.18	-23.57	0.198	4.283
C7 - H109	3.304	0.02	0.26	0.524	0.739
C7 - H8	1.070	1.93	-24.69	0.017	8.666
C71 - C106	1.518	1.72	-15.80	0.014	4.664
C71 - C80	1.531	1.70	-15.63	0.021	4.766
C71 - H72	1.081	1.88	-23.05	0.006	7.548
C71 - H73	1.082	1.88	-22.98	0.004	7.484
C74 - H75	1.069	1.93	-24.60	0.019	8.414
C76 - C80	1.535	1.67	-15.13	0.017	4.741
C76 - H77	1.079	1.87	-22.87	0.008	7.499
C76 - H78	1.075	1.90	-23.41	0.010	7.709
C76 - H79	1.075	1.90	-23.59	0.009	7.809
C80 - C93	1.548	1.63	-14.42	0.032	4.712
C81 - C101	1.543	1.62	-14.15	0.016	4.602
C81 - C85	1.541	1.63	-14.23	0.012	4.602
C81 - H82	1.075	1.94	-24.39	0.005	7.969
C83 - C106	1.564	1.59	-13.52	0.015	4.592
C83 - C108	1.548	1.62	-14.14	0.008	4.623
C83 - C115	1.554	1.59	-13.65	0.009	4.553
C85 - H86	1.075	1.91	-23.72	0.009	8.065
C85 - H87	1.080	1.87	-22.75	0.010	7.454
C85 - H88	1.080	1.87	-22.76	0.011	7.422
C89 - H90	1.079	1.87	-22.90	0.009	7.533
C89 - H91	1.078	1.88	-23.02	0.010	7.565
C89 - H92	1.080	1.87	-22.83	0.009	7.549
C9 - C24	1.600	1.47	-11.50	0.034	4.364
C9 - P46	1.757	1.11	4.06	0.490	1.771
C93 - H94	1.073	1.91	-23.71	0.010	7.681
C93 - H95	1.076	1.89	-23.32	0.010	7.663
C93 - H96	1.080	1.87	-22.72	0.009	7.440
C97 - H100	1.080	1.87	-22.77	0.010	7.478
C97 - H98	1.080	1.87	-22.76	0.010	7.493
C97 - H99	1.075	1.90	-23.66	0.009	8.037

H11 - H13	2.340	0.05	0.49	0.385	0.837
H11 - H59	2.223	0.05	0.54	0.039	0.840
H19 - H32	2.174	0.05	0.56	0.092	0.820
H20 - H45	2.385	0.04	0.42	0.049	0.802
H23 - H35	2.350	0.08	0.91	0.735	0.829
H25 - C49	1.079	1.88	-22.97	0.012	7.562
H27 - H86	2.852	0.02	0.30	0.408	0.693
H27 - P105	2.852	0.07	0.54	0.018	0.871
H35 - H45	2.271	0.07	0.79	0.426	0.807
H40 - H99	2.573	0.02	0.24	0.291	0.774
H40 - P105	3.132	0.04	0.37	0.412	0.804
H50 - C66	3.305	0.02	0.26	0.524	0.739
H70 - H118	2.223	0.05	0.54	0.039	0.840
H70 - H72	2.340	0.05	0.49	0.384	0.836
H78 - H91	2.174	0.05	0.56	0.092	0.820
H79 - H104	2.385	0.04	0.42	0.050	0.801
H82 - H94	2.349	0.08	0.91	0.735	0.829
H84 - C108	1.079	1.88	-22.97	0.012	7.562
H94 - H104	2.272	0.07	0.79	0.427	0.807
N1 - C21	1.517	1.59	-12.43	0.060	3.351
N1 - C5	1.453	1.83	-17.64	0.031	3.484
N1 - C9	1.387	2.06	-21.86	0.144	3.160
N60 - C64	1.453	1.83	-17.64	0.031	3.484
N60 - C68	1.387	2.06	-21.86	0.144	3.159
N60 - C80	1.517	1.59	-12.43	0.060	3.351
P105 - H109	2.833	0.11	1.21	1.509	0.908
P46 - C64	3.230	0.08	0.78	1.040	0.880
P46 - H50	2.832	0.11	1.21	1.509	0.908
P46 - H86	2.853	0.07	0.54	0.018	0.871
P46 - H99	3.132	0.04	0.37	0.411	0.804
P46 - P105	2.228	0.77	-3.32	0.187	3.395

4. **Hyperconjugative Interactions using second-order perturbation energetics:** The hyperconjugative interactions in complexes **1**-**4** were studied using second-order perturbation theory. The NBO analyses were performed on the optimized geometry of **1**,**2**,**4** and crystal geometry of **3** at B3LYP/def2-TZVP level using *Gaussian09*. [S8]
   The hyperconjugative stabilization interaction energies (kcal/mol) for selected hyperconjugative interactions involving P atom are mentioned.

   Table S14. Selected second-order perturbation analysis of the hyperconjugative interactions in **1-4**

Compound	Donor orbital	Acceptor orbital	Energy (kcal/mol)
1	LP (1) P	BD*(1)Cl 1 - P 2	1.33
	LP (1) P	BD*(1) N 3 - C 23	17.2
	LP (1) P	BD*(1) C 22 - C 47	0.57
	LP (1) P	BD*(1) C 47 - H 49	1.21
2	LP (1) P	BD*(1)Br 1 - P 2	1.17
	LP (1) P	BD*(1) N 3 - C 42	17.62
	LP (1) P	BD*(1) C 24 - C 42	0.52
	LP (1) P	BD*(1) C 24 - C 43	0.56
	LP (1) P	BD*(1) C 43 - H 46	1.2
3	LP (1) P	BD*(1) I 1 - P 2	0.85
	LP (1) P	BD*(1) N 3 - C 18	18.8
	LP (1) P	BD*(1) C 18 - C 33	0.56
	LP (1) P	BD*(1) C 51 - H 53	0.92
4	LP (1) P	BD*(2) C 9 - P 46	0.9
	LP (1) P	BD*(1) N 60 - C 68	18.91
	LP (1) P	BD*(1) C 108 - H 109	0.5
	LP (1) P	BD*(1) C 108 - H 110	0.57

DFT Calculations

The DFT calculations were carried out using Gaussian 16: ES64L-G16RevA.03.[13] Input coordinates of compound **1** was obtained from the experimental X-ray crystal structure. The optimization of all the stationary points in the gas phase was done using the M06-2X [14] density functional with def2svp3 basis set for all atoms. The vibrational frequencies of the normal modes were calculated to confirm the nature of the stationary points. All intermediates were at minima with no imaginary frequencies. The single point energy correction was done with def2-TZVP[15] for all atoms.

Coordinates of Stationary Points

Compound **1**

Single Point Energy= -1714.464091

Zero-point correction= 0.511261 (Hartree/Particle)

Thermal correction to Energy= 0.537301

Thermal correction to Enthalpy= 0.538245

Thermal correction to Gibbs Free Energy= 0.458391

Sum of electronic and zero-point Energies= -1712.682146

Sum of electronic and thermal Energies= -1712.656106

Sum of electronic and thermal Enthalpies= -1712.655162

Sum of electronic and thermal Free Energies= -1712.735017

Table S15: Coordinates of optimized structure of **1**

Cl	-1.29122400	-0.14753300	2.64299800
P	0.74377600	-0.62437800	2.32111000
N	0.39012400	0.00393100	-0.43787500
C	-0.72554400	2.67480900	-0.19634400
H	0.28033200	2.40012200	-0.53728800
C	-1.04068600	0.14624700	-0.40359100
C	-1.59677800	1.43672200	-0.31978500
C	-2.98682300	1.55790000	-0.27530400
H	-3.43724600	2.54869100	-0.19482400
C	-3.80576200	0.43394000	-0.31762200
H	-4.89042300	0.54626900	-0.27998400
C	-3.23907800	-0.83184700	-0.39716200
H	-3.88552400	-1.71183000	-0.41479100
C	-1.85179100	-1.00253700	-0.43468000
C	1.12176400	0.05397300	-1.74055500
C	1.71108800	-1.34313800	-1.99644100
H	0.89580700	-2.05693400	-2.17483900
H	2.30939400	-1.30295300	-2.91864700
C	2.56781300	-1.74786700	-0.78588400

H	3.61163900	-1.93640300	-1.08069400
H	2.19364700	-2.67372600	-0.32338600
C	2.57457900	-0.63997400	0.29623700
C	1.10692200	-0.36921500	0.65577400
C	-1.21278600	3.83529200	-1.06632200
H	-1.35657300	3.52812800	-2.11306000
H	-0.48219100	4.65715200	-1.04481900
H	-2.16793100	4.24100200	-0.70101800
C	-1.28788400	-2.41376200	-0.46667800
H	-0.19542200	-2.34472900	-0.38143400
C	-1.62508700	-3.11394300	-1.78772100
H	-2.71269300	-3.24981000	-1.88964500
H	-1.15669700	-4.10893300	-1.83014800
H	-1.28244600	-2.53385900	-2.65761600
C	0.21174700	0.48535900	-2.87913600
H	-0.62744600	-0.21048200	-3.01280800
H	0.80081300	0.50662400	-3.80677900
H	-0.20165200	1.48877900	-2.70767000
C	2.30831800	1.01792200	-1.59013300
H	1.94361400	2.05360800	-1.53132400
H	2.91437100	0.95227300	-2.50613500
C	3.14237100	0.66321900	-0.34021800
H	4.17053900	0.41383400	-0.65120100
C	3.20537900	1.83558800	0.63563500
H	2.20189300	2.07849100	1.01965900
H	3.60161400	2.72661300	0.12692700
H	3.85535000	1.62653200	1.49601200
C	3.46375900	-1.10335200	1.44968100
H	3.13513100	-2.07771200	1.83750000
H	3.47650100	-0.39468500	2.28734400

H	4.49291100	-1.21298700	1.07537600
C	-0.59974400	3.10399600	1.27039000
H	-1.58745500	3.36194000	1.68318800
H	0.05268900	3.98641900	1.35712600
H	-0.18549100	2.29513400	1.88803300
C	-1.77546200	-3.24234500	0.72705500
H	-1.56393300	-2.72875500	1.67442400
H	-1.27738200	-4.22323600	0.73652000
H	-2.86034200	-3.42030100	0.67032700

Compound **1'**

Single Point Energy= -1714.456947

Zero-point correction= 0.510976 (Hartree/Particle)

Thermal correction to Energy= 0.537208

Thermal correction to Enthalpy= 0.538152

Thermal correction to Gibbs Free Energy= 0.457489

Sum of electronic and zero-point Energies= -1712.673981

Sum of electronic and thermal Energies= -1712.647749

Sum of electronic and thermal Enthalpies= -1712.646805

Sum of electronic and thermal Free Energies= -1712.727468

Table S16: Coordinates of optimized structure of **1'**

Cl	-2.47824300	-0.65864100	-3.01168000
P	-0.69100100	-0.28667600	-1.95411900
N	0.00057100	-0.06143400	0.56651800
C	0.76020100	2.66064700	-0.23950800
H	-0.22635800	2.27343100	0.04682800
C	1.30739600	0.16360600	0.01892200
C	1.70723000	1.47450500	-0.31535700
C	3.01434900	1.67197900	-0.76958900

H	3.34563300	2.68242300	-1.01859600
C	3.89260700	0.60408500	-0.91818100
H	4.91126100	0.77873800	-1.26795500
C	3.46229800	-0.68975900	-0.64460900
H	4.14498300	-1.52890300	-0.79459600
C	2.16465600	-0.93728000	-0.18793300
C	-0.23593500	-0.04215300	2.03228800
C	-0.78402500	-1.41985400	2.43668100
H	0.02234000	-2.16533000	2.38572300
H	-1.10732100	-1.36762100	3.48733200
C	-1.94923000	-1.77984700	1.50480200
H	-2.84860600	-2.04956300	2.07831300
H	-1.70397400	-2.64618200	0.87187800
C	-2.32279200	-0.59753100	0.57136500
C	-1.06783600	-0.31615200	-0.25760900
C	1.19882500	3.68866600	0.80835400
H	1.27109300	3.25168000	1.81443900
H	0.48021400	4.52076200	0.85093800
H	2.18414100	4.10979900	0.55599400
C	1.71748900	-2.37274800	0.03561800
H	0.65250300	-2.35096200	0.30555400
C	2.49319500	-3.04282500	1.17456000
H	3.56443300	-3.11170300	0.93070900
H	2.12212600	-4.06485600	1.34305600
H	2.40284600	-2.48707800	2.11911500
C	1.03016100	0.29212300	2.80307800
H	1.82398000	-0.44202900	2.61311700
H	0.79803200	0.28577500	3.87726800
H	1.41766700	1.28312700	2.53473000
C	-1.33580700	0.99621100	2.28781600

H	-0.95055700	1.99072400	2.01519300
H	-1.55915700	1.02364400	3.36516700
C	-2.59671300	0.65243600	1.46493800
H	-3.39529700	0.33657000	2.15714700
C	-3.10283000	1.85378400	0.66911600
H	-2.42562000	2.07718500	-0.17183900
H	-3.15594400	2.74394500	1.31299000
H	-4.10470000	1.68131800	0.25484000
C	-3.58928800	-0.98426000	-0.18276500
H	-3.44621200	-1.90974300	-0.75477400
H	-3.92059100	-0.21230700	-0.88291300
H	-4.38576100	-1.15154500	0.55926500
C	0.60650400	3.32842100	-1.61074600
H	1.54728500	3.80213000	-1.93093100
H	-0.16343200	4.11312800	-1.56561500
H	0.30961300	2.59374700	-2.37152500
C	1.84132200	-3.19118500	-1.25447500
H	1.29247100	-2.70874400	-2.07474500
H	1.42932000	-4.20023800	-1.10543700
H	2.89406400	-3.30145100	-1.55656400

Compound **5**

Single Point Energy= -1286.877864

Zero-point correction= 0.288118 (Hartree/Particle)

Thermal correction to Energy= 0.303013

Thermal correction to Enthalpy= 0.303957

Thermal correction to Gibbs Free Energy= 0.247204

Sum of electronic and zero-point Energies= -1285.782284

Sum of electronic and thermal Energies= -1285.767389

Sum of electronic and thermal Enthalpies= -1285.766444

Sum of electronic and thermal Free Energies= -1285.823197

Table S17: Coordinates of optimized structure of **5**

P	-2.02717000	-1.03197900	-0.08782200
N	-0.04963700	0.94783000	0.15044100
C	1.34694900	1.25031800	-0.23922700
C	1.52545200	0.73959800	-1.67924900
H	0.79384400	1.25765000	-2.31591800
H	2.52902700	1.01674400	-2.03282200
C	1.31457800	-0.78002400	-1.71812800
H	2.26409100	-1.31599300	-1.87707800
H	0.63558700	-1.06515700	-2.53390700
C	0.71511000	-1.26219100	-0.37847900
C	-0.45922900	-0.32973500	-0.07662500
C	1.64041100	2.74385400	-0.18976000
H	0.91608500	3.30457700	-0.79793000
H	2.64336700	2.92044600	-0.60241700
H	1.62918400	3.14556400	0.83138900
C	2.26724800	0.43888800	0.68427900
H	2.24523200	0.87943600	1.69413600
H	3.30439400	0.51975600	0.32287600
C	1.78657900	-1.03258800	0.73125900
H	2.62959400	-1.69488200	0.47497300
C	1.28792000	-1.40629300	2.12496400
H	0.41710300	-0.79283600	2.40584300
H	2.07875700	-1.23355400	2.86931800
H	0.99261100	-2.46223000	2.19104900
C	0.34723800	-2.73908600	-0.49424100
H	-0.34249400	-2.90916300	-1.33297600
H	-0.12888000	-3.12562500	0.41705900

H	1.26117100	-3.32282400	-0.68171400
C	-0.74336700	1.83088000	1.07303600
H	-1.28777100	2.64252200	0.56934700
H	-1.46575600	1.24803700	1.65360700
H	-0.01572300	2.26570600	1.77298500
Cl	-3.32457400	0.63794000	-0.10532600

Compound **6**

Single Point Energy= -1254.833554

Zero-point correction= 0.517944 (Hartree/Particle)

Thermal correction to Energy= 0.542853

Thermal correction to Enthalpy= 0.543798

Thermal correction to Gibbs Free Energy= 0.466374

Sum of electronic and zero-point Energies= -1253.201298

Sum of electronic and thermal Energies= -1253.176389

Sum of electronic and thermal Enthalpies= -1253.175445

Sum of electronic and thermal Free Energies= -1253.252868

Table S18: Coordinates of optimized structure of **6**

P	-0.71042500	-0.23692200	-2.50665500
N	-0.24228600	-0.15169100	0.24235800
C	0.46168100	2.67663100	-0.03357100
H	-0.52713000	2.20571600	0.03478300
C	1.13374800	0.20489600	0.06804800
C	1.49600000	1.56423600	-0.00605400
C	2.85254900	1.88586200	-0.11115500
H	3.15030500	2.93569100	-0.16116600
C	3.82405400	0.89205300	-0.16547300

H	4.87871100	1.16109400	-0.24196600
C	3.44498700	-0.44610400	-0.14744200
H	4.20766300	-1.22432200	-0.22454600
C	2.10003200	-0.81399900	-0.04474400
C	-0.82679000	-0.33482900	1.59889800
C	-1.34010700	-1.78203200	1.70376900
H	-0.48621700	-2.47192000	1.76559200
H	-1.89774600	-1.87913100	2.64756000
C	-2.23098000	-2.08706900	0.48818900
H	-3.21492800	-2.47031600	0.79900300
H	-1.77532500	-2.85418100	-0.15643200
C	-2.45190900	-0.81612300	-0.36791300
C	-1.06604900	-0.36855100	-0.82379700
C	0.61593800	3.64265900	1.14478000
H	0.55296600	3.12358600	2.11220600
H	-0.17283900	4.40920200	1.11755500
H	1.58632000	4.16110200	1.10698200
C	1.72361100	-2.28516500	-0.10691400
H	0.62816800	-2.35042000	-0.06255000
C	2.30266800	-3.07440700	1.07124900
H	3.40323300	-3.06632300	1.04808700
H	1.97534800	-4.12407700	1.03002300
H	1.98757300	-2.65580600	2.03841600
C	0.18211600	-0.02922800	2.69342600
H	1.05985300	-0.68584900	2.62701100
H	-0.29811800	-0.18453300	3.66976000
H	0.53353100	1.00951200	2.63743800
C	-2.04687500	0.59314100	1.69400100
H	-1.70357900	1.63774800	1.64058300
H	-2.51381800	0.46247500	2.68203700

C	-3.04933400	0.28555800	0.55826000
H	-3.95719300	-0.16177100	0.99741100
C	-3.45835300	1.54856400	-0.19579200
H	-2.61858000	1.93256500	-0.79758100
H	-3.76451700	2.33338900	0.51156400
H	-4.30095900	1.36530500	-0.87603600
C	-3.40181900	-1.14353400	-1.51398500
H	-3.03698700	-2.00878800	-2.08513100
H	-3.50608100	-0.30483700	-2.21460900
H	-4.39544400	-1.38671200	-1.10657500
C	0.50912400	3.43295800	-1.36595900
H	1.47268500	3.94954400	-1.49636000
H	-0.28723200	4.19153700	-1.40165600
H	0.36621500	2.74423300	-2.21005500
C	2.15417100	-2.90200100	-1.44228100
H	1.70953400	-2.35311500	-2.28397300
H	1.82483600	-3.95004000	-1.50184900
H	3.24917900	-2.88652400	-1.55460800
H	0.65217400	0.15053600	-2.36083300

Table S19: Theoretically calculated Bond length [Å] and Bond angle [^{o}] for optimized structure of compound 1.

Number	Atom1	Atom2	Length
1	Cl1	P2	2.1148
2	P2	C23	1.7234
3	N3	C6	1.4383
4	N3	C15	1.4950
5	N3	C23	1.3598
6	C4	H5	1.0970

7	C4	C7	1.5190
8	C4	C24	1.5301
9	C4	C51	1.5334
10	C6	C7	1.4077
11	C6	C14	1.4065
12	C7	C8	1.3960
13	C8	H9	1.0913
14	C8	C10	1.3914
15	C10	H11	1.0911
16	C10	C12	1.3891
17	C12	H13	1.0920
18	C12	C14	1.3983
19	C14	C28	1.5201
20	C15	C16	1.5377
21	C15	C34	1.5201
22	C15	C38	1.5361
23	C16	H17	1.0982
24	C16	H18	1.1000
25	C16	C19	1.5372
26	C19	H20	1.1009
27	C19	H21	1.1005
28	C19	C22	1.5487
29	C22	C23	1.5352
30	C22	C41	1.5575
31	C22	C47	1.5284
32	C24	H25	1.1004
33	C24	H26	1.0999
34	C24	H27	1.1001
35	C28	H29	1.0980
36	C28	C30	1.5326

37	C28	C55	1.5328
38	C30	H31	1.1008
39	C30	H32	1.1006
40	C30	H33	1.1003
41	C34	H35	1.0983
42	C34	H36	1.0991
43	C34	H37	1.0987
44	C38	H39	1.0996
45	C38	H40	1.1003
46	C38	C41	1.5440
47	C41	H42	1.1027
48	C41	C43	1.5267
49	C43	H44	1.1016
50	C43	H45	1.0998
51	C43	H46	1.0984
52	C47	H48	1.0990
53	C47	H49	1.0973
54	C47	H50	1.1005
55	C51	H52	1.1012
56	C51	H53	1.1008
57	C51	H54	1.0988
58	C55	H56	1.0981
59	C55	H57	1.1002
60	C55	H58	1.1008

Number	Atom1	Atom2	Atom3	Angle
1	Cl1	P2	C23	108.45
2	C6	N3	C15	120.29
3	C6	N3	C23	122.16
4	C15	N3	C23	116.87
5	H5	C4	C7	107.25

6	H5	C4	C24	107.77
7	H5	C4	C51	106.99
8	C7	C4	C24	112.91
9	C7	C4	C51	110.67
10	C24	C4	C51	110.96
11	N3	C6	C7	119.02
12	N3	C6	C14	119.49
13	C7	C6	C14	121.48
14	C4	C7	C6	121.70
15	C4	C7	C8	119.85
16	C6	C7	C8	118.35
17	C7	C8	H9	119.48
18	C7	C8	C10	121.00
19	H9	C8	C10	119.52
20	C8	C10	H11	120.06
21	C8	C10	C12	119.85
22	H11	C10	C12	120.09
23	C10	C12	H13	119.58
24	C10	C12	C14	121.17
25	H13	C12	C14	119.24
26	C6	C14	C12	118.15
27	C6	C14	C28	123.01
28	C12	C14	C28	118.81
29	N3	C15	C16	107.58
30	N3	C15	C34	111.66
31	N3	C15	C38	108.28
32	C16	C15	C34	111.27
33	C16	C15	C38	106.88
34	C34	C15	C38	110.96
35	C15	C16	H17	109.45

36	C15	C16	H18	108.35
37	C15	C16	C19	108.77
38	H17	C16	H18	106.94
39	H17	C16	C19	111.75
40	H18	C16	C19	111.51
41	C16	C19	H20	111.26
42	C16	C19	H21	111.28
43	C16	C19	C22	111.36
44	H20	C19	H21	106.91
45	H20	C19	C22	107.78
46	H21	C19	C22	108.04
47	C19	C22	C23	106.60
48	C19	C22	C41	108.34
49	C19	C22	C47	108.24
50	C23	C22	C41	107.26
51	C23	C22	C47	115.65
52	C41	C22	C47	110.49
53	P2	C23	N3	134.97
54	P2	C23	C22	113.68
55	N3	C23	C22	111.34
56	C4	C24	H25	111.76
57	C4	C24	H26	110.13
58	C4	C24	H27	111.56
59	H25	C24	H26	108.30
60	H25	C24	H27	107.78
61	H26	C24	H27	107.14
62	C14	C28	H29	108.00
63	C14	C28	C30	111.14
64	C14	C28	C55	111.56
65	H29	C28	C30	108.34

66	H29	C28	C55	106.86
67	C30	C28	C55	110.76
68	C28	C30	H31	110.71
69	C28	C30	H32	110.64
70	C28	C30	H33	111.85
71	H31	C30	H32	107.78
72	H31	C30	H33	107.44
73	H32	C30	H33	108.27
74	C15	C34	H35	111.64
75	C15	C34	H36	108.47
76	C15	C34	H37	111.57
77	H35	C34	H36	108.60
78	H35	C34	H37	108.07
79	H36	C34	H37	108.40
80	C15	C38	H39	109.88
81	C15	C38	H40	107.85
82	C15	C38	C41	110.64
83	H39	C38	H40	106.46
84	H39	C38	C41	110.63
85	H40	C38	C41	111.26
86	C22	C41	C38	109.03
87	C22	C41	H42	105.42
88	C22	C41	C43	113.36
89	C38	C41	H42	109.11
90	C38	C41	C43	111.30
91	H42	C41	C43	108.39
92	C41	C43	H44	110.77
93	C41	C43	H45	109.96
94	C41	C43	H46	112.27
95	H44	C43	H45	108.11

96	H44	C43	H46	107.93
97	H45	C43	H46	107.66
98	C22	C47	H48	111.17
99	C22	C47	H49	112.77
100	C22	C47	H50	108.51
101	H48	C47	H49	107.86
102	H48	C47	H50	108.14
103	H49	C47	H50	108.25
104	C4	C51	H52	110.52
105	C4	C51	H53	110.39
106	C4	C51	H54	111.25
107	H52	C51	H53	108.32
108	H52	C51	H54	107.45
109	H53	C51	H54	108.81
110	C28	C55	H56	110.97
111	C28	C55	H57	110.15
112	C28	C55	H58	111.14
113	H56	C55	H57	108.80
114	H56	C55	H58	108.06
115	H57	C55	H58	107.60

Table S20: Theoretically calculated Bond length [Å] and Bond angle [^{o}] for optimized structure of compound 1'.

Number	Atom1	Atom2	Length
1	Cl1	P2	2.1097
2	P2	C23	1.7381
3	N3	C6	1.4346
4	N3	C15	1.4849
5	N3	C23	1.3732
6	C4	H5	1.0978

7	C4	C7	1.5197
8	C4	C24	1.5321
9	C4	C51	1.5329
10	C6	C7	1.4107
11	C6	C14	1.4106
12	C7	C8	1.3978
13	C8	H9	1.0921
14	C8	C10	1.3906
15	C10	H11	1.0911
16	C10	C12	1.3908
17	C12	H13	1.0921
18	C12	C14	1.3977
19	C14	C28	1.5200
20	C15	C16	1.5369
21	C15	C34	1.5195
22	C15	C38	1.5341
23	C16	H17	1.0992
24	C16	H18	1.1005
25	C16	C19	1.5348
26	C19	H20	1.1003
27	C19	H21	1.1006
28	C19	C22	1.5520
29	C22	C23	1.5302
30	C22	C41	1.5606
31	C22	C47	1.5240
32	C24	H25	1.0992
33	C24	H26	1.1003
34	C24	H27	1.1008
35	C28	H29	1.0989
36	C28	C30	1.5323

37	C28	C55	1.5328
38	C30	H31	1.1008
39	C30	H32	1.1004
40	C30	H33	1.0996
41	C34	H35	1.0978
42	C34	H36	1.0990
43	C34	H37	1.0974
44	C38	H39	1.1008
45	C38	H40	1.1007
46	C38	C41	1.5444
47	C41	H42	1.1030
48	C41	C43	1.5273
49	C43	H44	1.1026
50	C43	H45	1.0999
51	C43	H46	1.0978
52	C47	H48	1.0973
53	C47	H49	1.0936
54	C47	H50	1.1014
55	C51	H52	1.1009
56	C51	H53	1.1002
57	C51	H54	1.0985
58	C55	H56	1.0985
59	C55	H57	1.1000
60	C55	H58	1.1008

Number	Atom1	Atom2	Atom3	Angle
1	Cl1	P2	C23	107.62
2	C6	N3	C15	121.32
3	C6	N3	C23	120.58
4	C15	N3	C23	118.09
5	H5	C4	C7	107.32

6	H5	C4	C24	108.39
7	H5	C4	C51	107.27
8	C7	C4	C24	112.30
9	C7	C4	C51	110.97
10	C24	C4	C51	110.38
11	N3	C6	C7	119.63
12	N3	C6	C14	119.15
13	C7	C6	C14	121.22
14	C4	C7	C6	122.47
15	C4	C7	C8	119.25
16	C6	C7	C8	118.25
17	C7	C8	H9	119.24
18	C7	C8	C10	121.12
19	H9	C8	C10	119.64
20	C8	C10	H11	120.07
21	C8	C10	C12	119.87
22	H11	C10	C12	120.05
23	C10	C12	H13	119.63
24	C10	C12	C14	121.08
25	H13	C12	C14	119.29
26	C6	C14	C12	118.29
27	C6	C14	C28	122.46
28	C12	C14	C28	119.24
29	N3	C15	C16	107.76
30	N3	C15	C34	111.77
31	N3	C15	C38	106.70
32	C16	C15	C34	111.16
33	C16	C15	C38	107.89
34	C34	C15	C38	111.35
35	C15	C16	H17	109.52

36	C15	C16	H18	108.26
37	C15	C16	C19	108.73
38	H17	C16	H18	106.98
39	H17	C16	C19	111.70
40	H18	C16	C19	111.58
41	C16	C19	H20	111.20
42	C16	C19	H21	111.38
43	C16	C19	C22	111.67
44	H20	C19	H21	106.79
45	H20	C19	C22	107.67
46	H21	C19	C22	107.91
47	C19	C22	C23	105.57
48	C19	C22	C41	107.94
49	C19	C22	C47	107.72
50	C23	C22	C41	107.87
51	C23	C22	C47	117.40
52	C41	C22	C47	109.92
53	P2	C23	N3	114.45
54	P2	C23	C22	135.21
55	N3	C23	C22	110.31
56	C4	C24	H25	112.21
57	C4	C24	H26	110.30
58	C4	C24	H27	110.86
59	H25	C24	H26	107.96
60	H25	C24	H27	107.64
61	H26	C24	H27	107.71
62	C14	C28	H29	107.61
63	C14	C28	C30	111.92
64	C14	C28	C55	110.90
65	H29	C28	C30	108.46

66	H29	C28	C55	107.19
67	C30	C28	C55	110.56
68	C28	C30	H31	110.81
69	C28	C30	H32	110.44
70	C28	C30	H33	112.08
71	H31	C30	H32	107.70
72	H31	C30	H33	107.58
73	H32	C30	H33	108.07
74	C15	C34	H35	111.57
75	C15	C34	H36	108.57
76	C15	C34	H37	111.64
77	H35	C34	H36	108.55
78	H35	C34	H37	107.83
79	H36	C34	H37	108.59
80	C15	C38	H39	108.63
81	C15	C38	H40	108.99
82	C15	C38	C41	110.24
83	H39	C38	H40	106.91
84	H39	C38	C41	110.78
85	H40	C38	C41	111.19
86	C22	C41	C38	109.88
87	C22	C41	H42	104.90
88	C22	C41	C43	112.94
89	C38	C41	H42	108.69
90	C38	C41	C43	111.90
91	H42	C41	C43	108.20
92	C41	C43	H44	110.69
93	C41	C43	H45	110.34
94	C41	C43	H46	112.05
95	H44	C43	H45	108.19

96	H44	C43	H46	107.73
97	H45	C43	H46	107.70
98	C22	C47	H48	111.32
99	C22	C47	H49	112.92
100	C22	C47	H50	107.82
101	H48	C47	H49	107.53
102	H48	C47	H50	108.51
103	H49	C47	H50	108.63
104	C4	C51	H52	111.22
105	C4	C51	H53	110.13
106	C4	C51	H54	110.81
107	H52	C51	H53	107.64
108	H52	C51	H54	108.50
109	H53	C51	H54	108.44
110	C28	C55	H56	110.70
111	C28	C55	H57	110.21
112	C28	C55	H58	111.21
113	H56	C55	H57	108.48
114	H56	C55	H58	108.48
115	H57	C55	H58	107.67

Table S21: Theoretically calculated Bond length [Å] and Bond angle [^{o}] for optimized structure of compound 5.

Number	Atom1	Atom2	Length
1	P1	C11	1.7181
2	P1	Cl33	2.1147
3	N2	C3	1.4810
4	N2	C11	1.3606
5	N2	C29	1.4534
6	C3	C4	1.5383

7	C3	C12	1.5230
8	C3	C16	1.5356
9	C4	H5	1.0996
10	C4	H6	1.0995
11	C4	C7	1.5347
12	C7	H8	1.1019
13	C7	H9	1.0990
14	C7	C10	1.5448
15	C10	C11	1.5296
16	C10	C19	1.5596
17	C10	C25	1.5264
18	C12	H13	1.0994
19	C12	H14	1.0988
20	C12	H15	1.0974
21	C16	H17	1.1019
22	C16	H18	1.1013
23	C16	C19	1.5487
24	C19	H20	1.1023
25	C19	C21	1.5267
26	C21	H22	1.1016
27	C21	H23	1.0997
28	C21	H24	1.0984
29	C25	H26	1.0992
30	C25	H27	1.0984
31	C25	H28	1.1006
32	C29	H30	1.0994
33	C29	H31	1.0949
34	C29	H32	1.0994

Number	Atom1	Atom2	Atom3	Angle
1	C11	P1	Cl33	103.72

2	C3	N2	C11	115.58
3	C3	N2	C29	119.54
4	C11	N2	C29	122.19
5	N2	C3	C4	106.73
6	N2	C3	C12	111.93
7	N2	C3	C16	107.40
8	C4	C3	C12	109.49
9	C4	C3	C16	108.54
10	C12	C3	C16	112.53
11	C3	C4	H5	107.96
12	C3	C4	H6	108.87
13	C3	C4	C7	109.66
14	H5	C4	H6	107.60
15	H5	C4	C7	111.12
16	H6	C4	C7	111.52
17	C4	C7	H8	111.53
18	C4	C7	H9	111.14
19	C4	C7	C10	109.90
20	H8	C7	H9	107.40
21	H8	C7	C10	107.92
22	H9	C7	C10	108.84
23	C7	C10	C11	106.19
24	C7	C10	C19	107.73
25	C7	C10	C25	109.26
26	C11	C10	C19	107.29
27	C11	C10	C25	114.82
28	C19	C10	C25	111.22
29	P1	C11	N2	131.27
30	P1	C11	C10	116.75
31	N2	C11	C10	111.98

32	C3	C12	H13	110.81
33	C3	C12	H14	108.74
34	C3	C12	H15	112.78
35	H13	C12	H14	108.16
36	H13	C12	H15	108.74
37	H14	C12	H15	107.45
38	C3	C16	H17	109.14
39	C3	C16	H18	109.16
40	C3	C16	C19	109.53
41	H17	C16	H18	106.87
42	H17	C16	C19	110.23
43	H18	C16	C19	111.84
44	C10	C19	C16	109.36
45	C10	C19	H20	105.75
46	C10	C19	C21	112.90
47	C16	C19	H20	109.06
48	C16	C19	C21	111.20
49	H20	C19	C21	108.36
50	C19	C21	H22	110.77
51	C19	C21	H23	110.15
52	C19	C21	H24	112.21
53	H22	C21	H23	107.97
54	H22	C21	H24	107.91
55	H23	C21	H24	107.68
56	C10	C25	H26	111.03
57	C10	C25	H27	112.46
58	C10	C25	H28	109.02
59	H26	C25	H27	107.86
60	H26	C25	H28	108.00
61	H27	C25	H28	108.34

62	N2	C29	H30	113.21
63	N2	C29	H31	109.15
64	N2	C29	H32	109.18
65	H30	C29	H31	108.01
66	H30	C29	H32	109.12
67	H31	C29	H32	108.04

Table S22: Theoretically calculated Bond length [Å] and Bond angle [^{o}] for optimized structure of compound 6.

Number	Atom1	Atom2	Length
1	P1	C22	1.7251
2	P1	H58	1.4241
3	N2	C5	1.4321
4	N2	C14	1.4884
5	N2	C22	1.3647
6	C3	H4	1.0973
7	C3	C6	1.5192
8	C3	C23	1.5316
9	C3	C50	1.5329
10	C5	C6	1.4087
11	C5	C13	1.4088
12	C6	C7	1.3981
13	C7	H8	1.0924
14	C7	C9	1.3909
15	C9	H10	1.0911
16	C9	C11	1.3910
17	C11	H12	1.0924
18	C11	C13	1.3982
19	C13	C27	1.5199
20	C14	C15	1.5391
21	C14	C33	1.5196

22	C14	C37	1.5358
23	C15	H16	1.0995
24	C15	H17	1.1005
25	C15	C18	1.5377
26	C18	H19	1.1007
27	C18	H20	1.1007
28	C18	C21	1.5483
29	C21	C22	1.5260
30	C21	C40	1.5584
31	C21	C46	1.5242
32	C23	H24	1.0997
33	C23	H25	1.1001
34	C23	H26	1.1008
35	C27	H28	1.0982
36	C27	C29	1.5317
37	C27	C54	1.5327
38	C29	H30	1.1008
39	C29	H31	1.1003
40	C29	H32	1.1000
41	C33	H34	1.0982
42	C33	H35	1.0991
43	C33	H36	1.0980
44	C37	H38	1.1009
45	C37	H39	1.1005
46	C37	C40	1.5457
47	C40	H41	1.1033
48	C40	C42	1.5268
49	C42	H43	1.1022
50	C42	H44	1.1000
51	C42	H45	1.0983

52	C46	H47	1.0991
53	C46	H48	1.0978
54	C46	H49	1.1011
55	C50	H51	1.1010
56	C50	H52	1.1003
57	C50	H53	1.0988
58	C54	H55	1.0989
59	C54	H56	1.1002
60	C54	H57	1.1009

Number	Atom1	Atom2	Atom3	Angle
1	C22	P1	H58	96.78
2	C5	N2	C14	121.26
3	C5	N2	C22	121.63
4	C14	N2	C22	117.10
5	H4	C3	C6	107.35
6	H4	C3	C23	108.27
7	H4	C3	C50	107.09
8	C6	C3	C23	112.30
9	C6	C3	C50	110.85
10	C23	C3	C50	110.76
11	N2	C5	C6	119.59
12	N2	C5	C13	119.25
13	C6	C5	C13	121.15
14	C3	C6	C5	122.17
15	C3	C6	C7	119.39
16	C5	C6	C7	118.39
17	C6	C7	H8	119.28
18	C6	C7	C9	121.08
19	H8	C7	C9	119.63
20	C7	C9	H10	120.12

21	C7	C9	C11	119.77
22	H10	C9	C11	120.10
23	C9	C11	H12	119.61
24	C9	C11	C13	121.08
25	H12	C11	C13	119.30
26	C5	C13	C11	118.39
27	C5	C13	C27	122.24
28	C11	C13	C27	119.34
29	N2	C14	C15	107.98
30	N2	C14	C33	111.78
31	N2	C14	C37	107.10
32	C15	C14	C33	111.19
33	C15	C14	C37	107.39
34	C33	C14	C37	111.18
35	C14	C15	H16	109.56
36	C14	C15	H17	108.08
37	C14	C15	C18	109.02
38	H16	C15	H17	106.85
39	H16	C15	C18	111.71
40	H17	C15	C18	111.53
41	C15	C18	H19	111.33
42	C15	C18	H20	111.18
43	C15	C18	C21	110.91
44	H19	C18	H20	107.03
45	H19	C18	C21	108.32
46	H20	C18	C21	107.90
47	C18	C21	C22	106.04
48	C18	C21	C40	107.84
49	C18	C21	C46	109.17
50	C22	C21	C40	108.57

51	C22	C21	C46	113.85
52	C40	C21	C46	111.09
53	P1	C22	N2	128.73
54	P1	C22	C21	120.07
55	N2	C22	C21	111.18
56	C3	C23	H24	111.92
57	C3	C23	H25	110.38
58	C3	C23	H26	111.06
59	H24	C23	H25	108.04
60	H24	C23	H26	107.63
61	H25	C23	H26	107.64
62	C13	C27	H28	107.63
63	C13	C27	C29	111.94
64	C13	C27	C54	110.83
65	H28	C27	C29	108.39
66	H28	C27	C54	106.95
67	C29	C27	C54	110.89
68	C27	C29	H30	110.98
69	C27	C29	H31	110.50
70	C27	C29	H32	111.83
71	H30	C29	H31	107.68
72	H30	C29	H32	107.58
73	H31	C29	H32	108.10
74	C14	C33	H34	111.52
75	C14	C33	H35	108.74
76	C14	C33	H36	111.47
77	H34	C33	H35	108.57
78	H34	C33	H36	107.86
79	H35	C33	H36	108.59
80	C14	C37	H38	108.82

81	C14	C37	H39	108.72
82	C14	C37	C40	110.46
83	H38	C37	H39	106.77
84	H38	C37	C40	110.82
85	H39	C37	C40	111.15
86	C21	C40	C37	109.19
87	C21	C40	H41	105.39
88	C21	C40	C42	113.20
89	C37	C40	H41	108.78
90	C37	C40	C42	111.84
91	H41	C40	C42	108.15
92	C40	C42	H43	110.71
93	C40	C42	H44	110.31
94	C40	C42	H45	111.92
95	H43	C42	H44	108.34
96	H43	C42	H45	107.73
97	H44	C42	H45	107.69
98	C21	C46	H47	110.67
99	C21	C46	H48	112.02
100	C21	C46	H49	109.37
101	H47	C46	H48	107.54
102	H47	C46	H49	108.53
103	H48	C46	H49	108.61
104	C3	C50	H51	111.19
105	C3	C50	H52	110.24
106	C3	C50	H53	110.76
107	H51	C50	H52	107.83
108	H51	C50	H53	108.48
109	H52	C50	H53	108.25
110	C27	C54	H55	110.65

111	C27	C54	H56	110.26
112	C27	C54	H57	111.26
113	H55	C54	H56	108.25
114	H55	C54	H57	108.50
115	H56	C54	H57	107.80

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7. CCDC 2264850-2264853 (**1-4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/.
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