Addition and N=N bond cleavage of diazo-compounds by phosphino-phosphenium cations

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Supporting Information

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1   General Information

All preparative procedures were performed in a MB Unilab glovebox produced by MBraun or using standard Schlenk techniques under an inert atmosphere of dry, deoxygenated N_2.

- *Drying of glassware, molecular sieves, and other items:* All glassware were oven-dried at temperatures greater than 150 °C for at least 4 hours before use and cooled under vacuum before use. 4 Å molecular sieves were purchased from Sigma-Aldrich, and were activated prior to usage by iteratively heating with 1050 W Haier microwave for 5 minutes and cooling under vacuum. Items such as plastic syringes, glass microsyringes, needles, and septa were shipped into the glovebox after drying in the antechamber overnight.

- *Drying solvents:* Anhydrous pentane, hexane, diethyl ether, dichloromethane (DCM), and toluene solvents were dried using a Grubbs-type Innovative Techonologies solvent purification system. Tetrahydrofuran (THF) was dried over Na/benzophenone. Benzene, and 1,2-difluorobenzene (*o*-DFB) were dried over CaH_2. They were then distilled to an oven-dried Strauss flask under static vacuum, after which it was shipped into the glovebox. All anhydrous solvents in the glovebox were stored over 4 Å molecular sieves for at least 24 hours prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories or Sigma-Aldrich. They were degassed through 3 freeze-pump-thaw cycles, shipped into the glovebox, and stored over 4 Å molecular sieves for at least 24 hours prior to use.
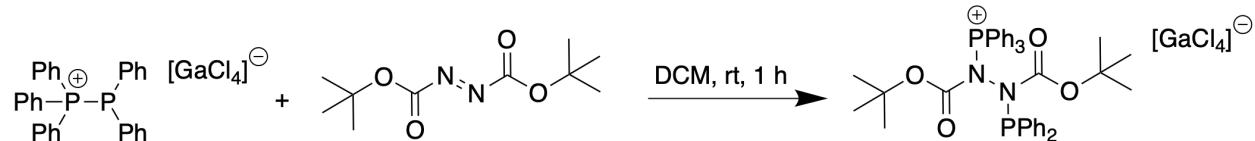
- *Data collection:* NMR spectra were obtained on a Bruker Avance III 400 MHz spectrometer. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts (δ/ppm) are referenced to the residual solvent resonance of the deuterated solvent. ^{31}P NMR spectra were externally referenced to 85% H_3PO_4 (0 ppm). Chemical shifts (δ) are reported in ppm and the absolute values of the coupling constants (J) are in Hz. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br = broad. High resolution mass spectroscopy (HRMS) studies were performed on an Agilent 6538 UHD. For positive polarity, the mobile phase is 50:50 MeOH : 0.1% HCOOH (aq) (v:v). For negative polarity, the mobile phase is 50:50 MeOH : 10 mM NH_4OAc (aq) (v:v). Elemental analyses were carried out by staff at ANALEST at the University of Toronto on a Flash 2000 CHN Analyzer.

- *Syntheses or purchase of known compounds:* Phosphino-phosphenium salts were prepared according to literature procedures.[1] All other reagents were purchased from commercial sources, and used as received. Liquid substrates were stored over 4 Å sieves for 24 hours before use.

- *Photolyzer:* Solderless SemiLEDs UVA LED (365-370 nm) were purchased from RapidLED (https://rapidled.com). A photo of the experimental set-up is shown in Section 2.2 (Figure S9).

2   Experimental Procedures and Spectroscopic Data

2.1   Synthesis of 1

Scheme S1: Synthesis of **1**

In the glovebox, a DCM solution (1.0 mL) of di-tert-butyl azodicarboxylate (0.021 g, 0.089 mmol, 1.0 eq) was added to [Ph$_3$PPPh$_2$][GaCl$_4$] (0.059 g, 0.089 mmol, 1.0 eq) in a 2 dram vial. The solution was stirred at room temperature for 1 hour, during which the colour of the solution turned from bright yellow to colourless. Solvent was removed under vacuum, and the solids were washed with benzene (1 mL). Benzene was decanted, and the product was dried under vacuum. The product was obtained as a white powder (0.078 g, 0.088 mmol, 99% yield).

- ^{1}H NMR (chloroform-d, 400 MHz): δ 7.88–7.84 (m, 4H, ArH), 7.77–7.58 (m, 12H, ArH), 7.55-7.50 (m, 3H, ArH), 7.41–7.25 (m, 6H, ArH), 1.16 (s, -C(CH_3)$_3$), 0.96 (s, -C(CH_3)$_3$).
- ^{13}C{^{1}H} NMR (chloroform-d, 101 MHz): δ 136.10 (d, J = 2.9 Hz), 134.49 (d, J = 11.4 Hz), 131.89 (br s), 130.18 (d, J = 13.9 Hz), 129.21 (d, J = 9.9 Hz), 128.49 (d, J = 4.8 Hz), 118.05 (d, J = 102.0 Hz), 89.62 (s), 85.66 (s), 27.63 (s, -C(CH$_3$)$_3$), 27.60 (s, -C(CH$_3$)$_3$).
- ^{31}P{^{1}H} NMR (chloroform-d, 162 MHz): δ 83.9 (s), 52.1 (s).
- MS (ESI) [M]$^+$ C$_{40}$H$_{43}$N$_2$O$_4$P$_2$$^+$ calc. 677.2698 m/z, found 677.2685 m/z.
- Elem. Anal. Found (Calc'd) for C$_{40}$H$_{43}$N$_2$O$_4$P$_2$GaCl$_4$: C 56.19 (54.03), H 4.79 (4.87), N 2.86 (3.15)
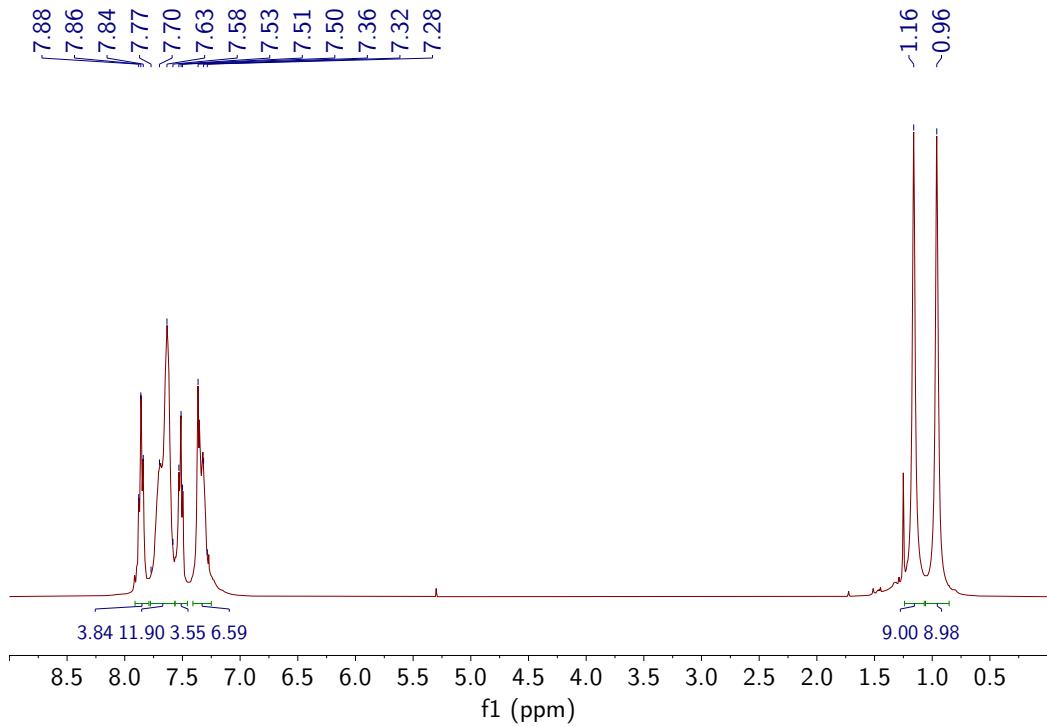
**Figure S1:** ^{1}H NMR spectrum of **1**. (chloroform-*d*, 400 MHz)
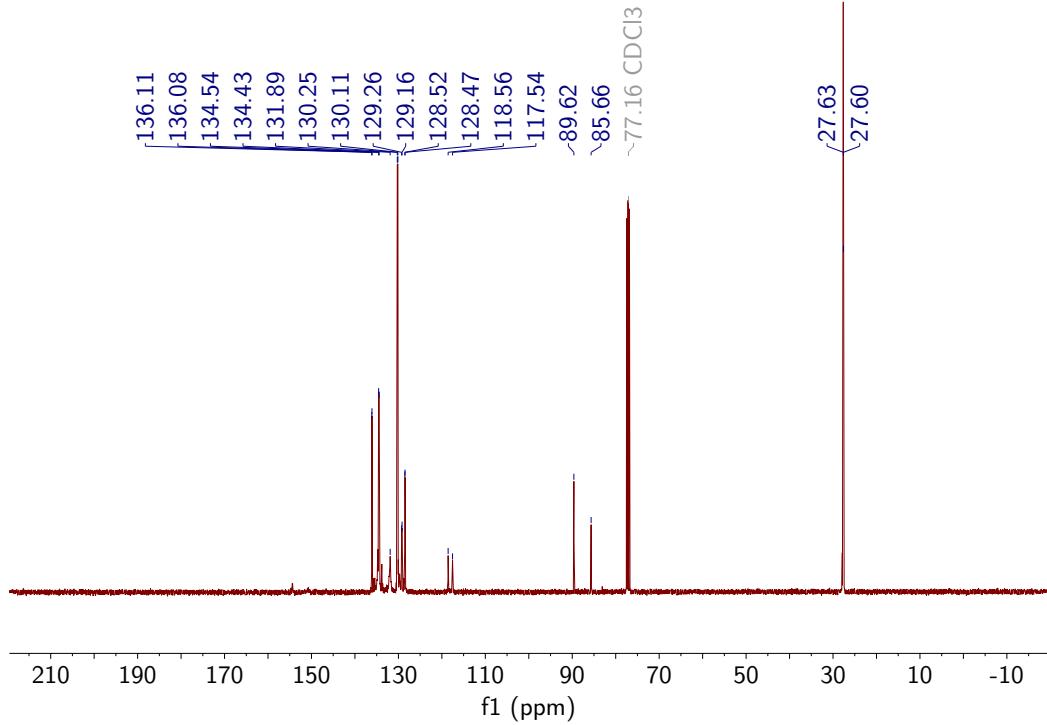
**Figure S2:** ^{13}C{^{1}H} NMR spectrum of **1**. (chloroform-*d*, 101 MHz)

S4
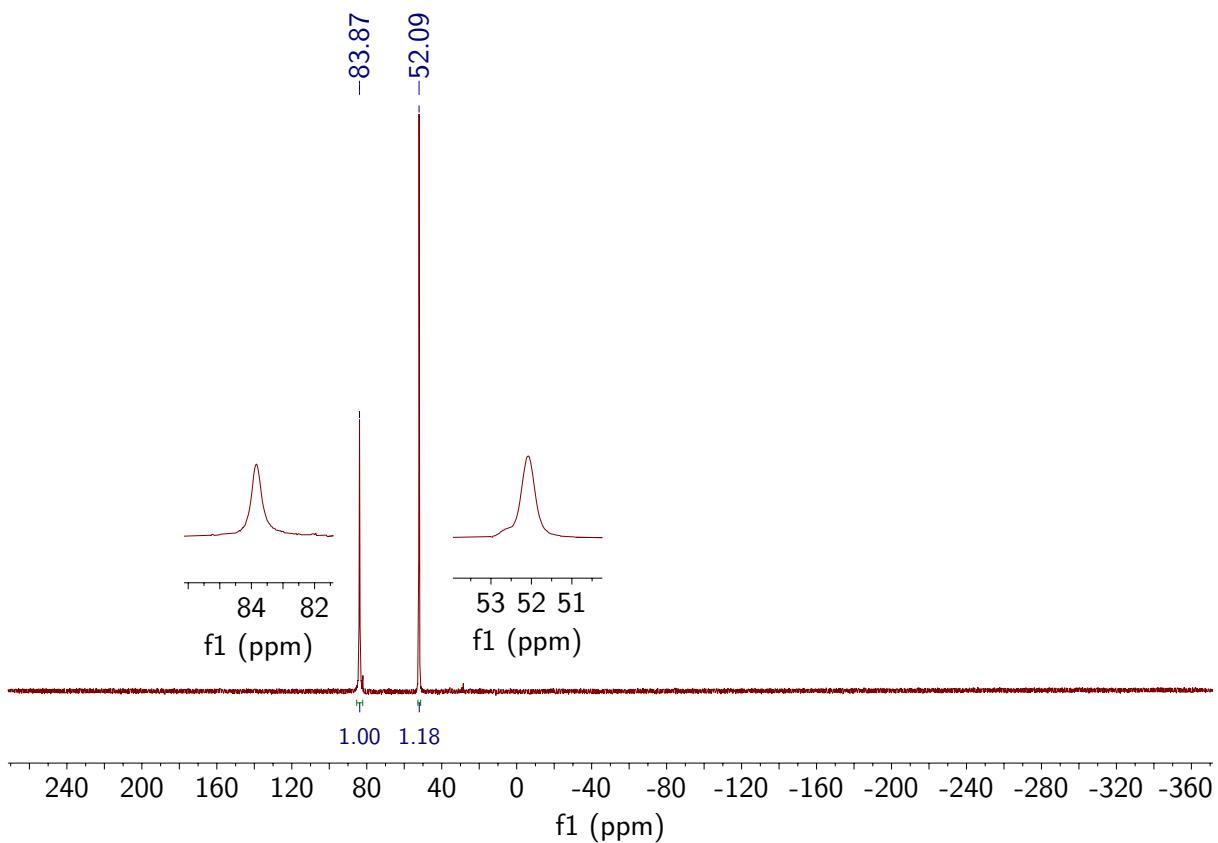
Figure S3: $^{31}P\{^1H\}$ NMR spectrum of **1** with insets showing peak in the ^{31}P NMR. (chloroform-d, 162 MHz)
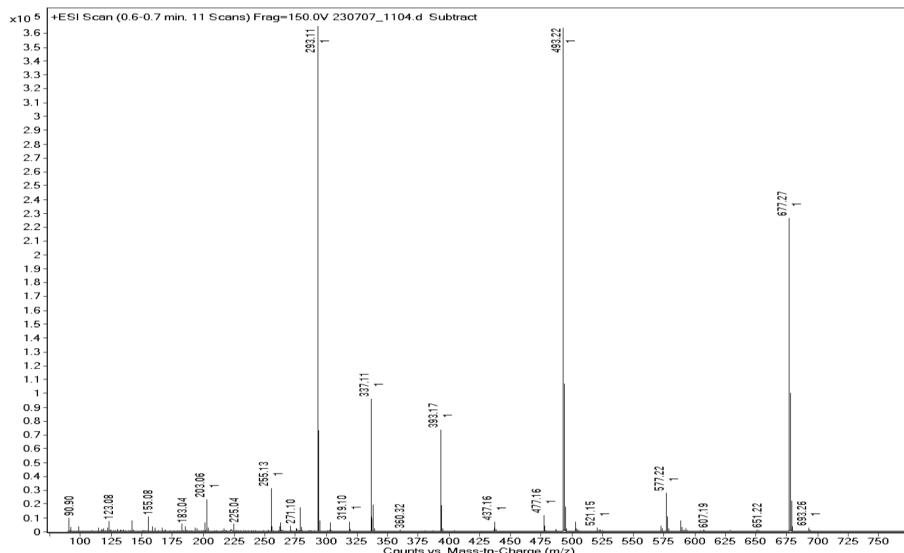
AIMS
MASS SPECTROMETRY LABORATORY

CHEMISTRY
UNIVERSITY OF TORONTO

Sample Name	WK-06-125	Data File	230707_1104.d	Acq Method	HRMS.m
DA Method	AIMS_Accurate_Mass.m	Instrument	Agilent 6538 UHD	Acq Date, Time	07/07/2023 3:30:40 PM
Comment	ESI+				

x10 5 +ESI Scan (0.6-0.7 min, 11 Scans) Frag=150.0V 230707_1104.d Subtract

(mass spectrum plot with peaks labeled: 90.90, 123.08, 155.08, 183.04, 203.06, 225.04, 255.13, 271.10, 293.11, 319.10, 337.11, 360.32, 393.17, 437.16, 477.16, 493.22, 521.15, 577.22, 607.19, 651.22, 677.27, 693.26)

Counts vs. Mass-to-Charge (m/z)

AIMS
MASS SPECTROMETRY LABORATORY

ESI-MS Report
Molecular Formula Generation (MFG)

CHEMISTRY
UNIVERSITY OF TORONTO

Sample Name	WK-06-125	Data File	230707_1104.d
Acq Method	HRMS.m	DA Method	AIMS_Accurate_Mass.m
Instrument	Agilent 6538 UHD	Acq Date, Time	07/07/2023 3:30:40 PM
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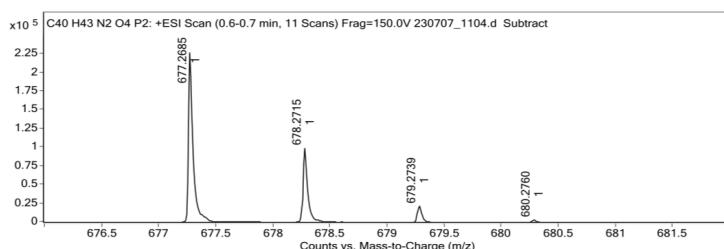
Target Ion Species

Ion Species	m/z	Ionic Formula
M+	677.2685	C40 H43 N2 O4 P2

MFG Calculator Results

Target m/z	Ionic Formula	Calc m/z	+/- (mDa)	+/- (ppm)	DBE	MFG Score
677.2685	C25 H49 N3 O14 P2	677.2684	0.1	0.1	4.0	99.86
677.2685	C24 H43 N10 O9 P2	677.2684	0.1	0.1	9.5	99.76
677.2685	C38 H41 N5 O3 P2	677.2679	0.6	0.9	22.0	99.34
677.2685	C40 H43 N2 O4 P2	677.2693	−0.8	−1.2	21.5	97.76
677.2685	C26 H45 N7 O10 P2	677.2698	−1.3	−1.9	9.0	96.05
677.2685	C27 H51 O15 P2	677.2698	−1.3	−1.9	3.5	94.74
677.2685	C23 H47 N6 O13 P2	677.2671	1.4	2.1	4.5	94.59
677.2685	C37 H45 N O7 P2	677.2666	1.9	2.8	17.0	92.31
677.2685	C36 H39 N8 O2 P2	677.2666	1.9	2.8	22.5	91.07
677.2685	C41 H39 N6 P2	677.2706	−2.1	−3.1	26.5	88.43

x10 5 C40 H43 N2 O4 P2: +ESI Scan (0.6-0.7 min, 11 Scans) Frag=150.0V 230707_1104.d Subtract

(isotope pattern plot with peaks: 677.2685, 678.2715, 679.2739, 680.2760)

Counts vs. Mass-to-Charge (m/z)
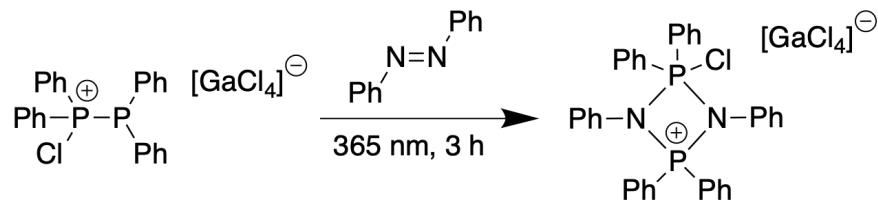
Predicted Isotope Match Table

Isotope	m/z	Calc m/z	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	677.2685	677.2693	−0.8	100.0	100.0	0.0
2	678.2715	678.2725	−1.0	43.8	44.6	0.8
3	679.2739	679.2756	−1.7	9.6	10.6	1.0
4	680.2760	680.2786	−2.6	1.6	1.7	0.1

Figure S4: ESI-MS(+) of $C_{40}H_{43}N_2O_4P_2^+$ with zoomed in portion of the molecular ion, and the predicted isotope pattern.

2.2 Synthesis of 2

Scheme S2: Synthesis of **2**

In the glovebox, an *o*-DFB solution (1.0 mL) of azobenzene (0.023 g, 0.124 mmol, 1.0 eq) was added to [Ph$_2$PClPPh$_2$][GaCl$_4$] (0.076 g, 0.124 mmol, 1.0 eq) in a 2 dram vial. The solution was transferred to a 5 mm NMR tube and was irradiated at 365 nm for 3 hours. Solvent was removed under vacuum, and the product was obtained as a crystalline white powder by recrystallizing twice from a mixture of DCM (0.3 mL) and diethyl ether (0.3 mL) at room temperature (0.042 g, 0.053 mmol, 42% yield).

- ^{1}H NMR (dichloromethane-d_2, 400 MHz): δ 7.97 (t, J = 7.6 Hz, 2H, Ar*H*), 7.86 (d, J = 7.7 Hz, 2H, Ar*H*), 7.81 (d, J = 7.8 Hz, 2H, Ar*H*), 7.78–7.55 (m, 14H, Ar*H*), 7.54–6.86 (m, 8H, Ar*H*), 6.05 (br s, 2H, Ar*H*).

- ^{13}C{^{1}H} NMR (dichloromethane-d_2, 101 MHz): δ 137.76 (s), 137.73 (s), 136.27 (s), 134.38 (d, J = 12.1 Hz), 133.07 (d, J = 4.0 Hz), 130.95 (d, J = 13.9 Hz), 130.57 (s), 129.48 (d, J = 18.3 Hz), 128.94 (d, J = 13.2 Hz), 120.88 (d, J = 104.5 Hz).

- ^{31}P{^{1}H} NMR (dichloromethane-d_2, 162 MHz): δ 37.4 (d, ^{2}J$_{PP}$ = 32.3 Hz), -33.9 (d, ^{2}J$_{PP}$ = 32.3 Hz).

- The molecular ion peak was not observed for this molecule. Rather, only the hydrolyzed compound C$_{36}$H$_{30}$N$_2$P$_2$OH$^+$ was observed: MS (ESI) [M]$^+$ of C$_{36}$H$_{30}$N$_2$P$_2$OH$^+$ calc. 569.1912 *m/z*, found 569.1906 *m/z*.

- Elem. Anal. Found (Calc'd) for C$_{40}$H$_{43}$N$_2$O$_4$P$_2$GaCl$_4$: C 54.08 (51.08), H 3.77 (3.78), N 2.90 (3.50)
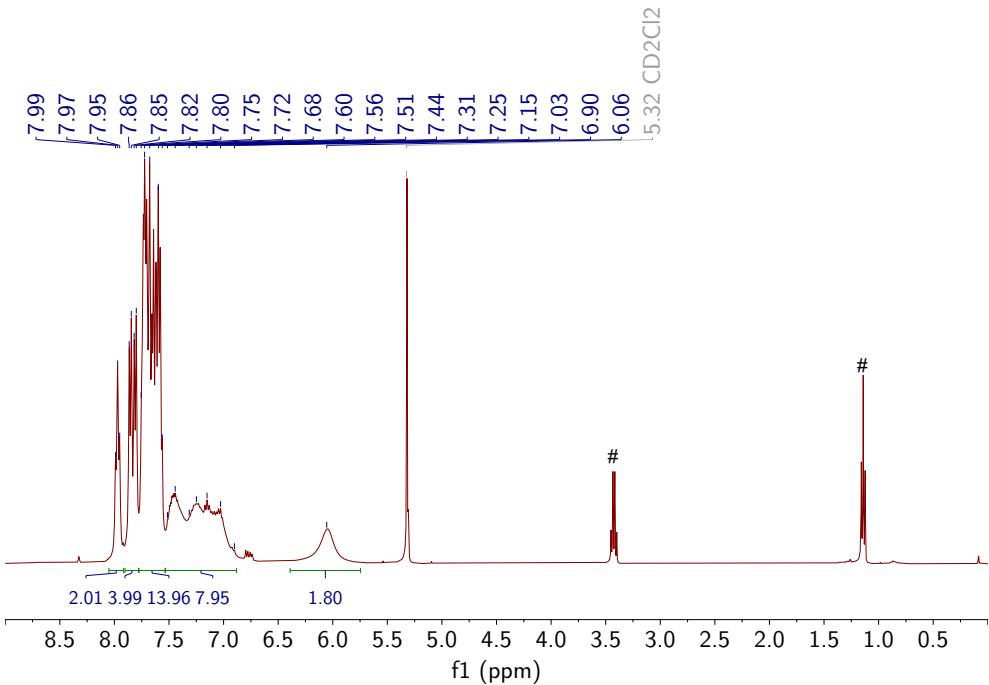
Figure S5: ^{1}H NMR spectrum of **2**. # denotes residual diethyl ether. (dichloromethane-d_2, 400 MHz)
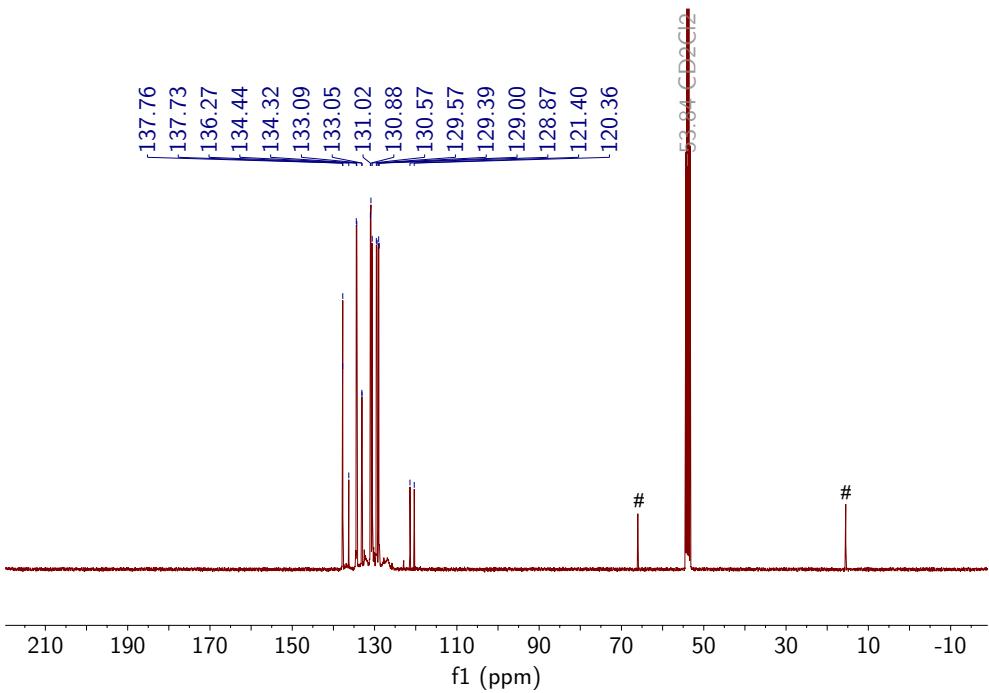
Figure S6: ^{13}C{^{1}H} NMR spectrum of **2**. # denotes residual diethyl ether. (dichloromethane-d_2, 101 MHz)
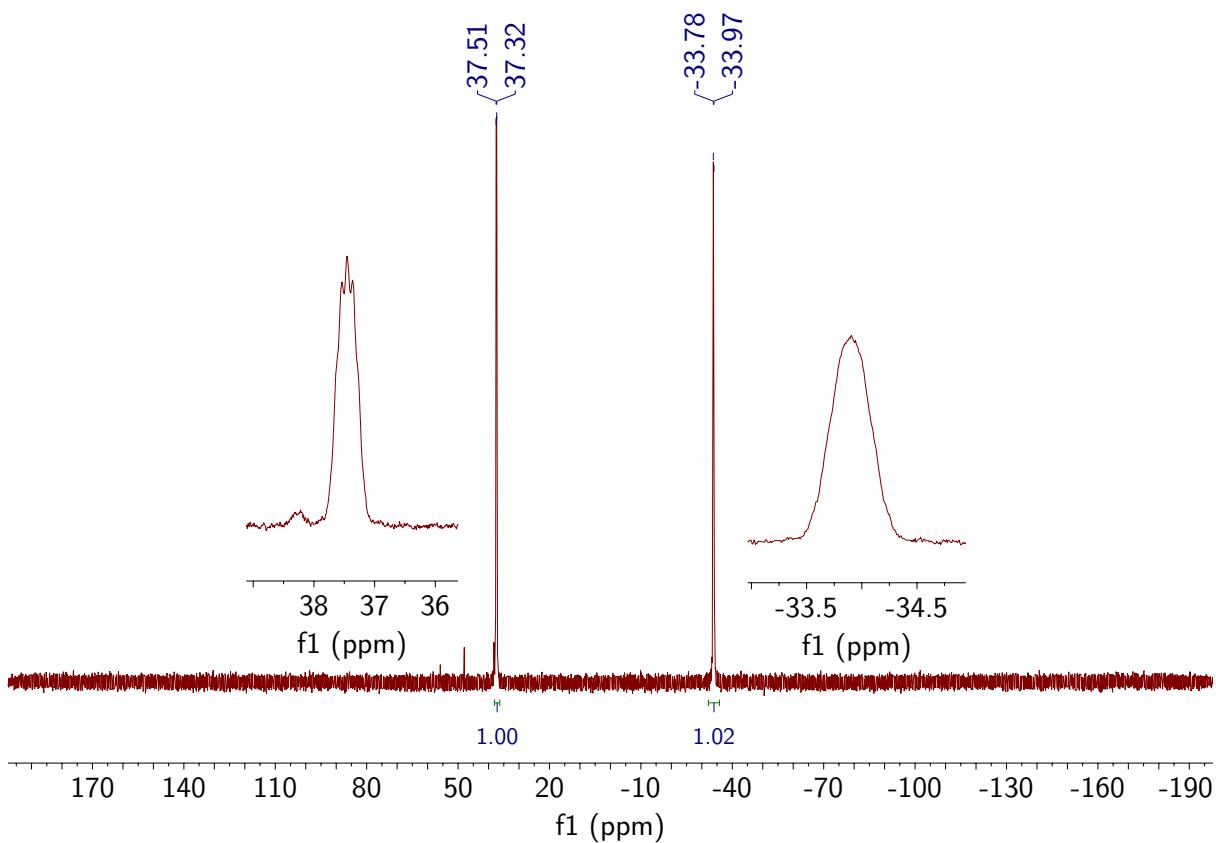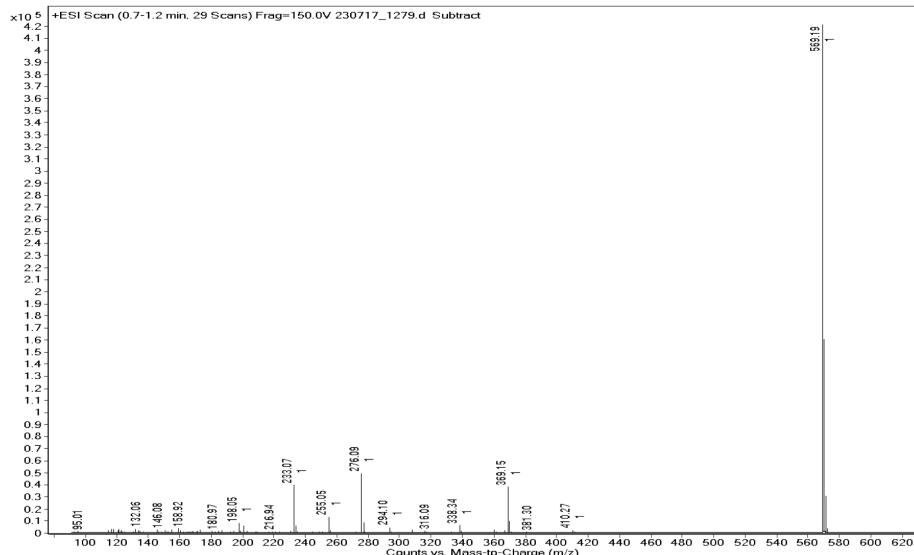
**Figure S7:** ^{31}P{^{1}H} NMR spectrum of **2** with insets showing peaks in the ^{31}P NMR. (dichloromethane-d_2, 162 MHz)
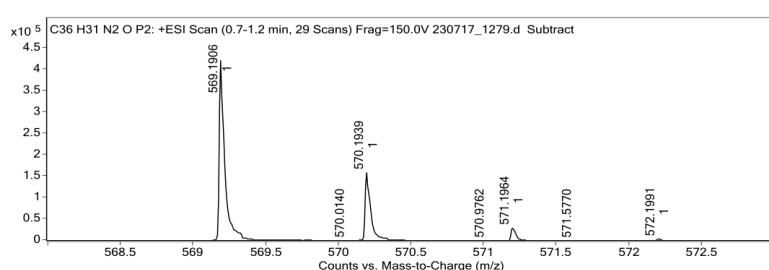
ESI-MS Report
Molecular Formula Generation (MFG)

Target Ion Species

Ion Species	m/z	Ionic Formula
M+	569.1906	C36 H31 N2 O P2

MFG Calculator Results

Target m/z	Ionic Formula	Calc m/z	+/- (mDa)	+/- (ppm)	DBE	MFG Score
569.1906	C36 H31 N2 O P2	569.1906	0.0	0.0	23.5	99.33
569.1906	C23 H39 O12 P2	569.1911	-0.5	-0.9	5.5	83.63
569.1906	C24 H35 N4 O8 P2	569.1925	-1.9	-3.3	10.5	83.19
569.1906	C20 H31 N10 O6 P2	569.1898	0.8	1.4	11.5	82.05
569.1906	C25 H31 N8 O4 P2	569.1938	-3.2	-5.6	15.5	78.72
569.1906	C31 H31 N4 O3 P2	569.1866	4.0	7.0	19.5	77.25
569.1906	C19 H35 N6 O10 P2	569.1884	2.2	3.9	6.5	71.73
569.1906	C18 H39 N2 O14 P2	569.1871	3.5	6.1	1.5	59.36

Predicted Isotope Match Table

Isotope	m/z	Calc m/z	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	569.1906	569.1906	0.0	100.0	100.0	0.0
2	570.1939	570.1939	0.0	38.0	40.1	2.1
3	571.1964	571.1971	-0.7	7.3	8.0	0.7

Figure S8: ESI-MS(+) of $C_{36}H_{30}N_2P_2OH^+$ with zoomed in portion of the molecular ion, and the predicted isotope pattern.
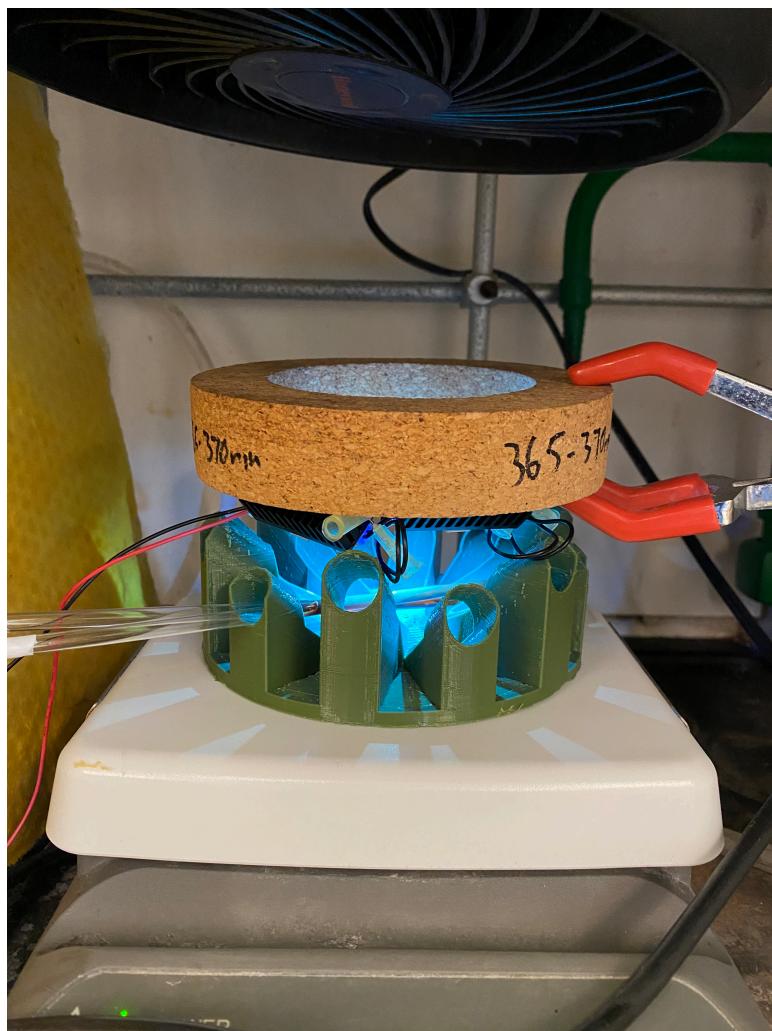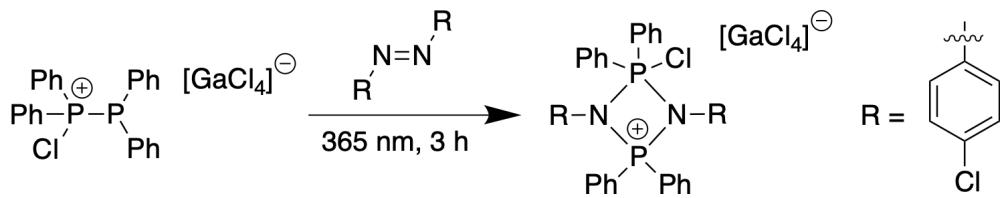
Figure S9: Photo of the photolyzer set-up showing the NMR tubes containing the reaction mixture, the 365-370 nm LEDs, and the cooling fan above.

2.3 Synthesis of 3

Scheme S3: Synthesis of **3**

In the glovebox, an *o*-DFB solution (1.0 mL) of chloroazobenzene (0.042 g, 0.167 mmol, 1.2 eq) was added to [Ph$_2$PClPPh$_2$][GaCl$_4$] (0.086 g, 0.139 mmol, 1.0 eq) in a 2 dram vial. The solution was transferred to a 5 mm NMR tube and was irradiated at 365 nm for 3 hours. Solvent was removed under vacuum, and the product was obtained as a white powder by recrystallizing twice from a mixture of DCM (0.3 mL) and diethyl ether (0.3 mL) at room temperature (0.040 g, 0.046 mmol, 33% yield).

- ^{1}H NMR (dichloromethane-d_2, 400 MHz): δ 8.00 (t, J = 7.6 Hz, 2H, Ar*H*), 7.90–7.69 (m, 10H, Ar*H*), 7.69–7.56 (m, 8H, Ar*H*), 7.23 (br m, 6H, Ar*H*), 6.02 (br s, 2H, Ar*H*).
- ^{13}C{^{1}H} NMR (dichloromethane-d_2, 101 MHz): δ 138.06 (d, J = 2.9 Hz), 137.28 (s), 135.82 (s), 134.31 (d, J = 12.5 Hz), 133.38 (d, J = 4.0 Hz), 131.22 (d, J = 14.3 Hz), 130.84 (s), 129.71 (d, J = 18.3 Hz), 128.91 (d, J = 13.6 Hz), 120.39 (d, J = 104.2 Hz).
- ^{31}P{^{1}H} NMR (dichloromethane-d_2, 162 MHz): δ 37.9 (d, ^{2}J$_{PP}$ = 31.3 Hz), -32.8 (d, ^{2}J$_{PP}$ = 31.3 Hz).
- The molecular ion peak was not observed for this molecule. Rather, only the hydrolyzed compound C$_{36}$H$_{28}$Cl$_2$N$_2$P$_2$OH$^+$ was observed: MS (ESI) [M]$^+$ of C$_{36}$H$_{28}$Cl$_2$N$_2$P$_2$OH$^+$ calc. 637.1132 *m/z*, found 637.1125 *m/z*.
- Elem. Anal. Found (Calc'd) for C$_{36}$H$_{28}$Cl$_3$N$_2$P$_2$GaCl$_4$: C 49.40 (49.79), H 2.77 (3.25), N 2.99 (3.23)
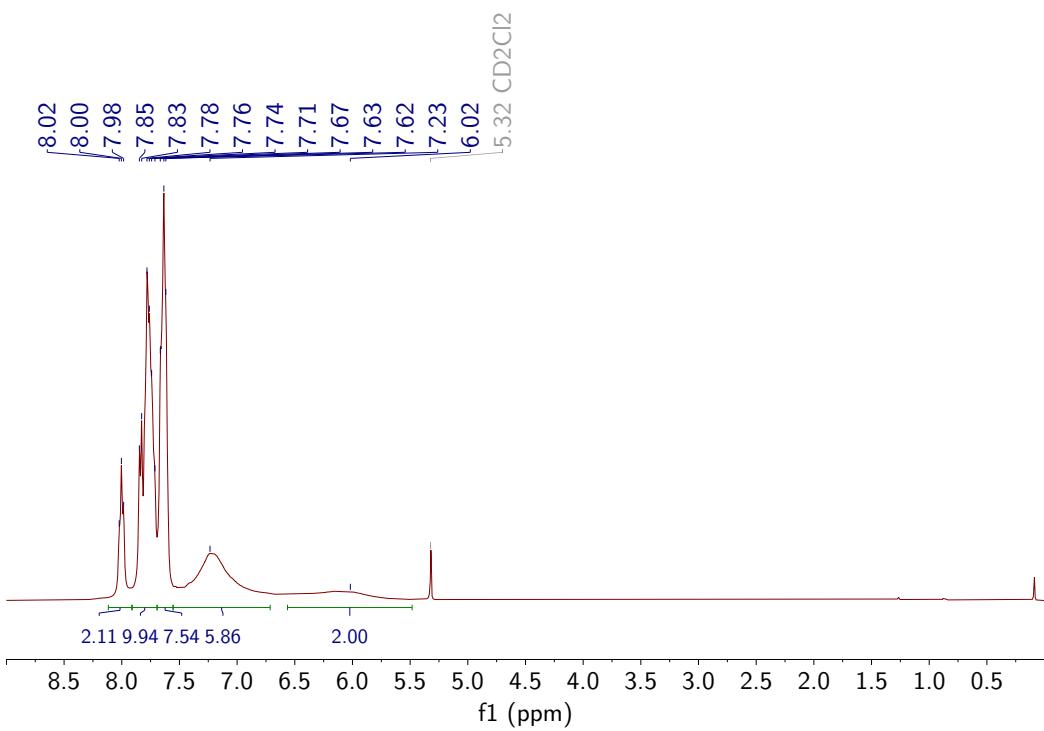
Figure S10: ^{1}H NMR spectrum of **3**. (dichloromethane-d_2, 400 MHz)
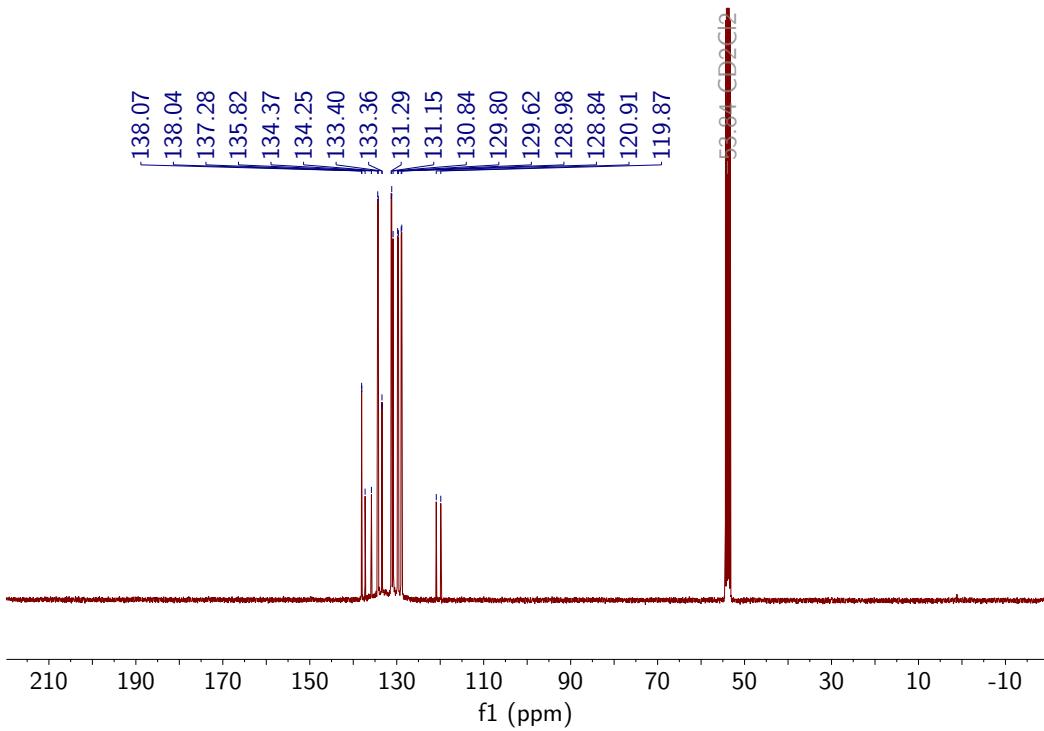
**Figure S11:** ^{13}C{^{1}H} NMR spectrum of **3**. (dichloromethane-d_2, 101 MHz)
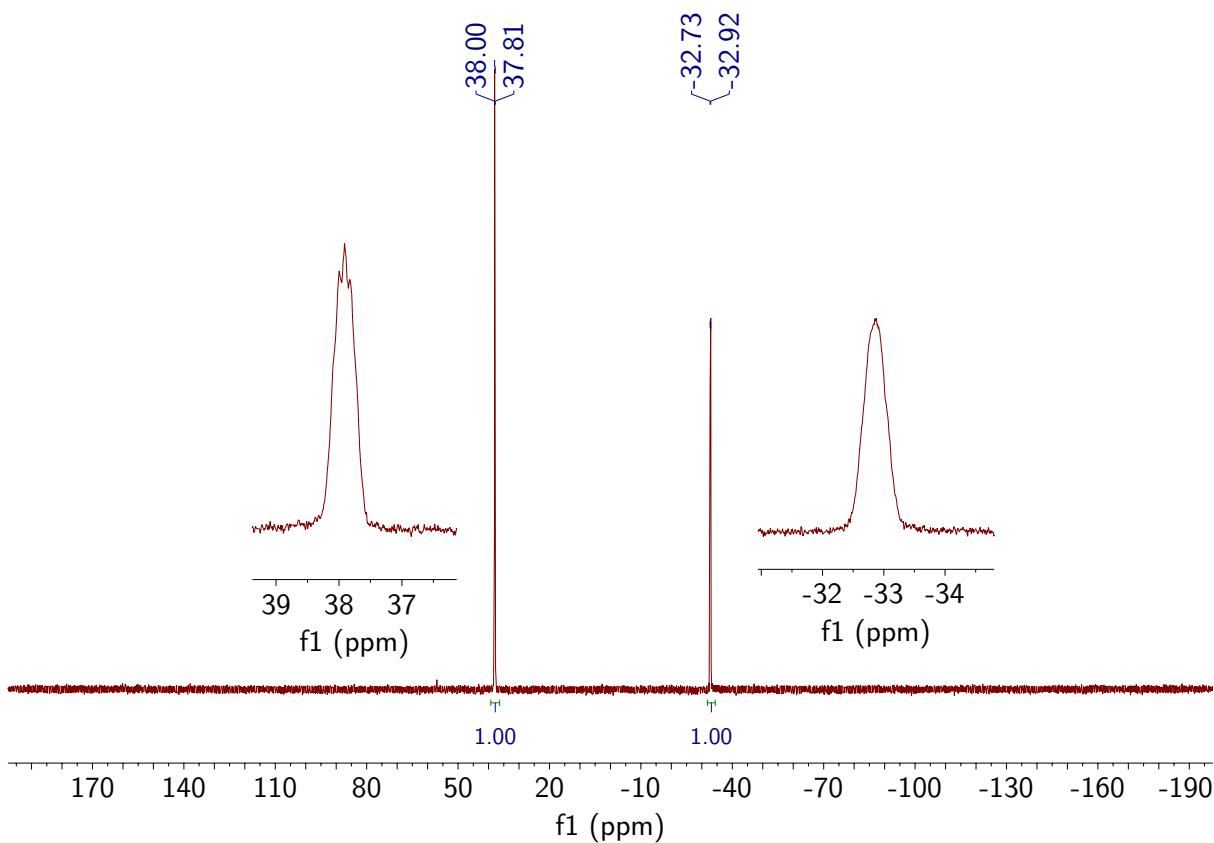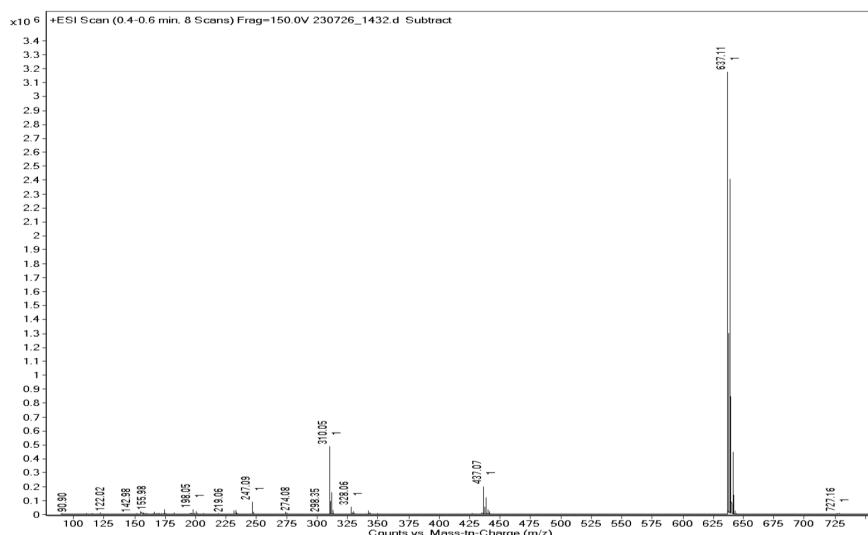
Figure S12: ^{31}P{^{1}H} NMR spectrum of **3** with insets showing peaks in the ^{31}P NMR. (dichloromethane-d_2, 162 MHz)

ESI Mass Spectrum

ESI-MS Report
Molecular Formula Generation (MFG)
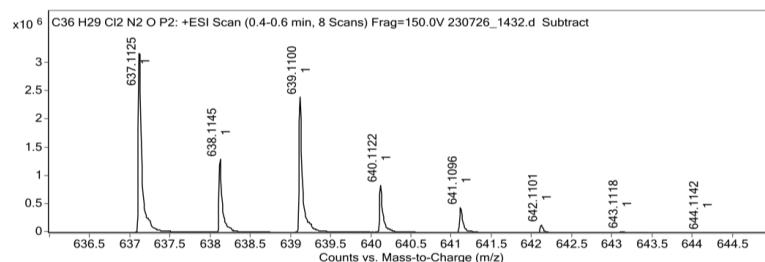
Target Ion Species

Ion Species	m/z	Ionic Formula
M+	637.1125	C36 H29 Cl2 N2 O P2

MFG Calculator Results

Target m/z	Ionic Formula	Calc m/z	+/- (mDa)	+/- (ppm)	DBE	MFG Score
637.1125	C36 H29 Cl2 N2 O P2	637.1127	−0.2	−0.3	23.5	95.93
637.1125	C20 H29 Cl2 N10 O6 P2	637.1118	0.7	1.1	11.5	87.56
637.1125	C23 H37 Cl2 O12 P2	637.1132	−0.7	−1.1	5.5	84.73
637.1125	C24 H33 Cl2 N4 O8 P2	637.1145	−2.0	−3.1	10.5	82.84
637.1125	C31 H29 Cl2 N4 O3 P2	637.1086	3.9	6.1	19.5	80.91
637.1125	C25 H29 Cl2 N8 O4 P2	637.1159	−3.4	−5.3	15.5	77.69
637.1125	C30 H33 Cl2 O7 P2	637.1073	5.2	8.2	14.5	69.96
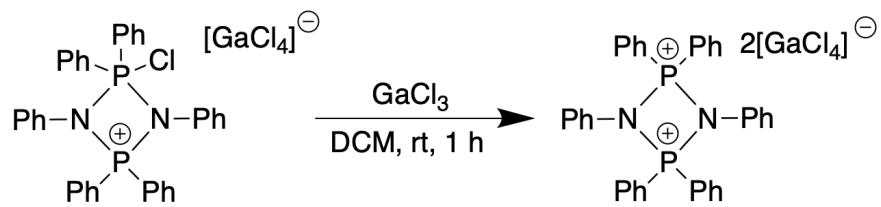
Predicted Isotope Match Table

Isotope	m/z	Calc m/z	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	637.1125	637.1127	−0.2	100.0	100.0	0.0
2	638.1145	638.1159	−1.4	39.5	40.0	0.5
3	639.1100	639.1108	−0.8	72.1	72.0	−0.1
4	640.1122	640.1134	−1.2	25.3	26.7	1.4
5	641.1096	641.1100	−0.4	13.6	15.5	1.9

Figure S13: ESI-MS(+) of $C_{36}H_{28}Cl_2N_2P_2OH^+$ with zoomed in portion of the molecular ion, and the predicted isotope pattern.

2.4 Synthesis of 4

Scheme S4: Synthesis of **4**

In the glovebox, compound **2** was synthesized from azobenzene (0.026 g, 0.141 mmol, 1.0 eq), and $[Ph_2PClPPh_2][GaCl_4]$ (0.087 g, 0.141 mmol, 1.0 eq) as outlined in Section 2.2. DCM was added to the isolated compound **2**, and $GaCl_3$ (0.025 g, 0.141 mmol, 1.0 eq) was added at once. The reaction was stirred at room temperature for 1 hour, during which white precipitate formed. Solvent was removed under vacuum, and the product was washed with a minimal amount of DCM. The product was obtained as a white powder (0.057 g, 0.059 mmol, 41% yield).

- ^{1}H NMR (dichloromethane-d_2, 400 MHz): δ 8.37–8.33 (m, 4H, p-CH of -P(C_6H_5)$_2$), 8.16–8.05 (m, 16H, o- and m-CH of -P(C_6H_5)$_2$), 7.50–7.44 (m, 6H, o- and p-CH of -N(C_6H_5)), 6.90 (m, 4H, m-CH of -N(C_6H_5)).
- ^{13}C{^{1}H} NMR (dichloromethane-d_2, 101 MHz): δ 142.33 (s), 136.38 (m), 133.32 (m), 132.84 (s), 130.53 (s), 129.59 (s), 122.44 (t, J = 5.0 Hz), 114.44 (d, J = 102.7 Hz).
- ^{31}P{^{1}H} NMR (dichloromethane-d_2, 162 MHz): δ 66.3 (s).
- The molecular ion peak was not observed for this molecule. Rather, only the hydrolyzed compound $C_{36}H_{30}N_2P_2OH^+$ was observed: MS (ESI) [M]$^+$ of $C_{36}H_{30}N_2P_2OH^+$ calc. 569.1912 m/z, found 569.1906 m/z.
- Elem. Anal. Found (Calc'd) for $C_{36}H_{30}N_2P_2Ga_2Cl_8$: C 43.92 (44.32), H 3.05 (3.10), N 2.77 (2.87)
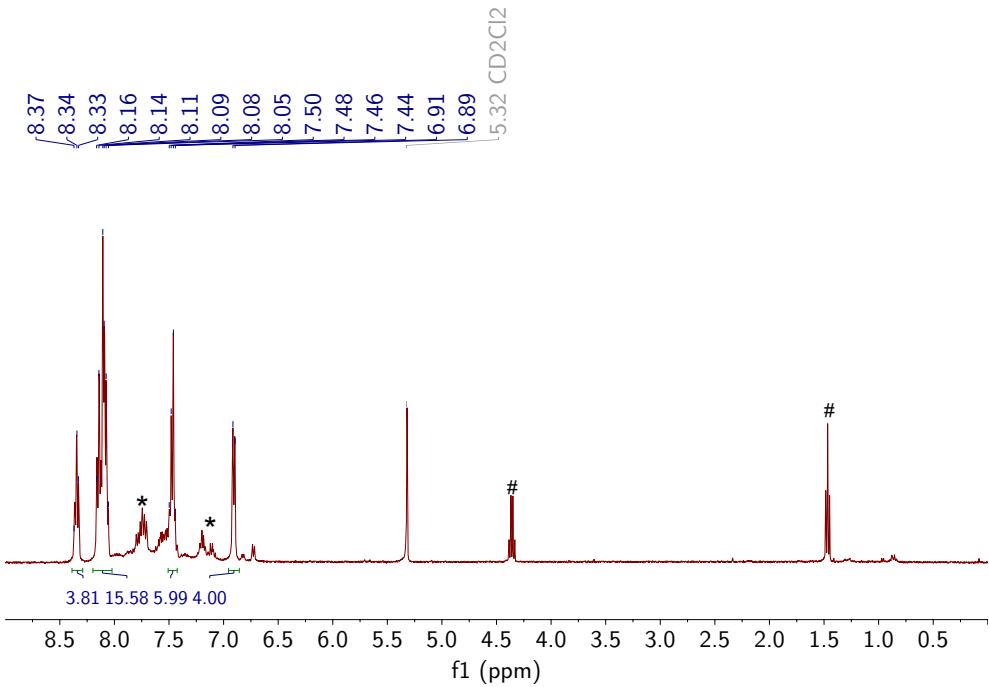
Figure S14: ^{1}H NMR spectrum of **4**. # and ∗ denote residual diethyl ether and minor unidentified impurities, respectively. (dichloromethane-d_2, 400 MHz)
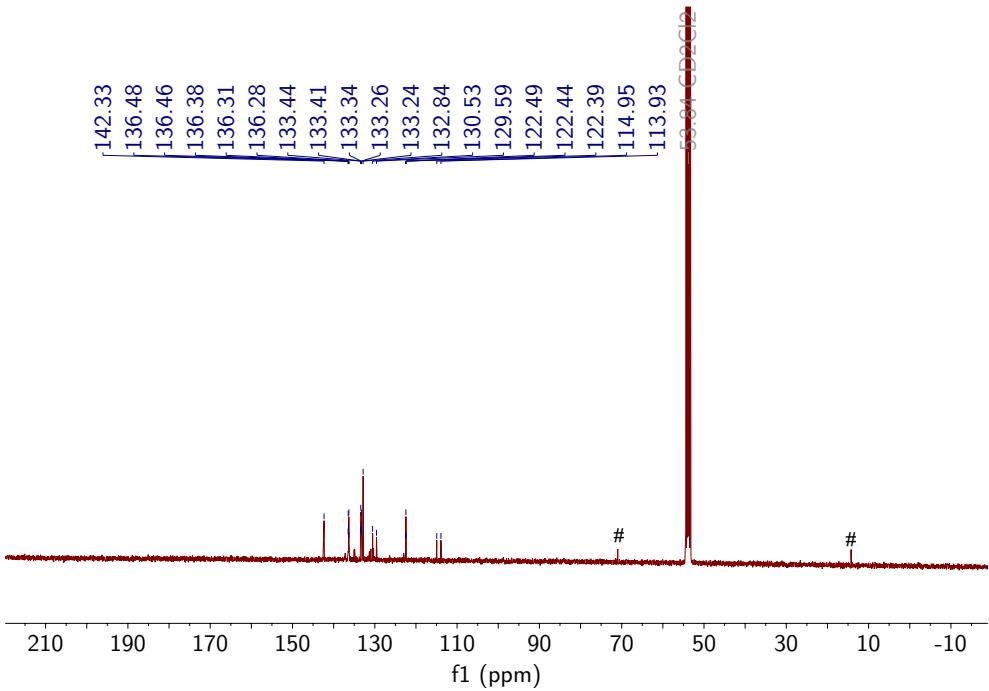
Figure S15: ^{13}C{^{1}H} NMR spectrum of **4**. # denotes residual diethyl ether. (dichloromethane-d_2, 101 MHz)
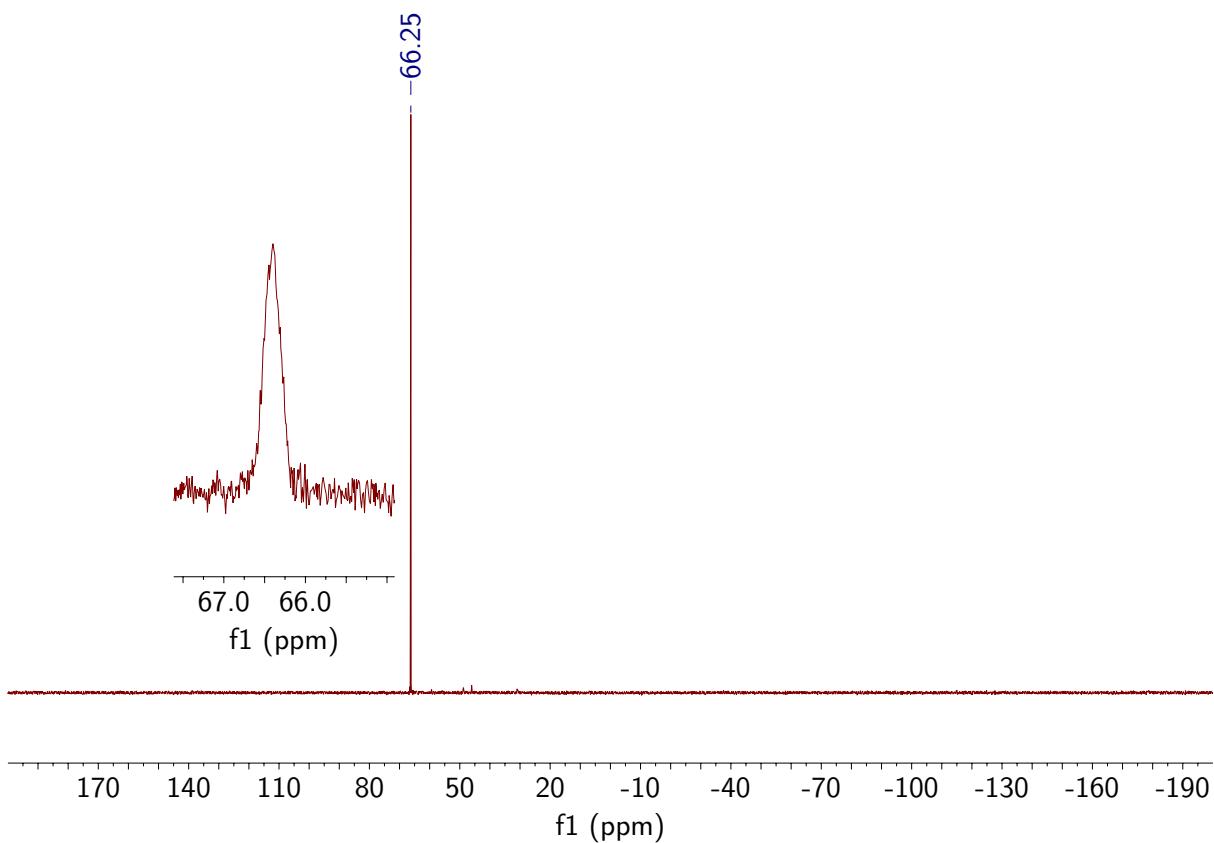
Figure S16: ^{31}P{^{1}H} NMR spectrum of **4** with insets showing the peak in the ^{31}P NMR. (dichloromethane-d_2, 162 MHz)
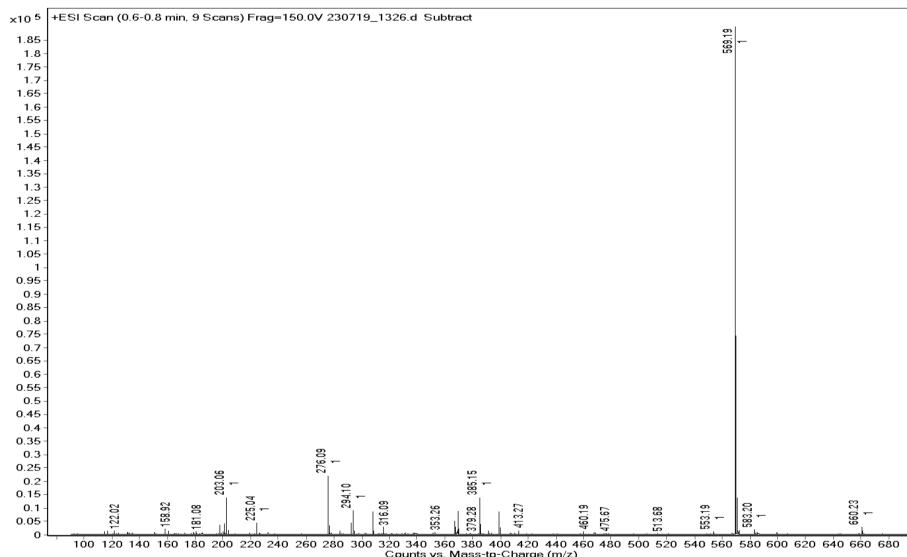
Sample Name WK-06-138a   **Data File** 230719_1326.d   **Acq Method** HRMS.m
DA Method AIMS_Accurate_Mass.m   **Instrument** Agilent 6538 UHD   **Acq Date, Time** 19/07/2023 11:04:20 AM
Comment ESI+

ESI-MS Report
Molecular Formula Generation (MFG)
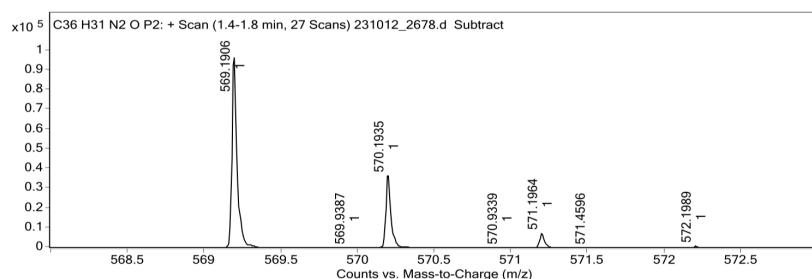
Sample Name WK-07-29   **Data File** 231012_2678.d
Acq Method HRMS.m   **DA Method** AIMS_Accurate_Mass.m
Instrument Agilent 6538 UHD   **Acq Date, Time** 12/10/2023 3:57:51 PM
Comment ESI+

Target Ion Species

Ion Species	m/z	Ionic Formula
M+	569.1906	C36 H31 N2 O P2

MFG Calculator Results

Target m/z	Ionic Formula	Calc m/z	+/- (mDa)	+/- (ppm)	DBE	MFG Score
569.1906	C36 H31 N2 O P2	569.1906	0.0	0.0	23.5	99.52
569.1906	C23 H39 O12 P2	569.1911	−0.5	−0.9	5.5	81.27
569.1906	C20 H31 N10 O6 P2	569.1898	0.8	1.4	11.5	80.65
569.1906	C24 H35 N4 O8 P2	569.1925	−1.9	−3.3	10.5	80.42
569.1906	C31 H31 N4 O3 P2	569.1866	4.0	7.0	19.5	76.96
569.1906	C25 H31 N8 O4 P2	569.1938	−3.2	−5.6	15.5	75.96
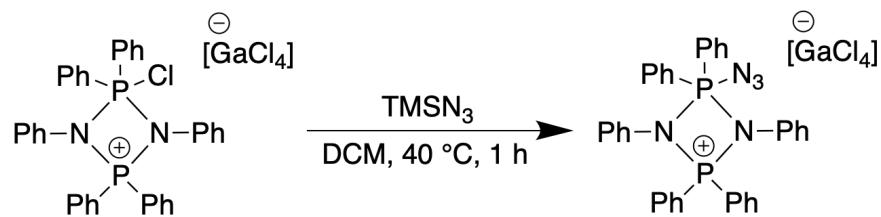
Predicted Isotope Match Table

Isotope	m/z	Calc m/z	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	569.1906	569.1906	0.0	100.0	100.0	0.0
2	570.1935	570.1939	−0.4	39.4	40.1	0.7
3	571.1964	571.1971	−0.7	7.8	8.0	0.2

Figure S17: ESI-MS(+) of $C_{36}H_{30}N_2P_2OH^+$ with zoomed in portion of the molecular ion, and the predicted isotope pattern.

2.5 Synthesis of 5

Scheme S5: Synthesis of **5**

In the glovebox, compound **2** (0.046 g, 0.057 mmol, 1.0 eq) was dissolved in DCM (0.7 mL), and Me_3SiN_3 (11 μL, 0.086 mmol, 1.5 eq) was added directly. The solution was heated at 40 °C for 1 hour, then solvent was removed under vacuum. The product was obtained as a beige powder (0.041 g, 0.051 mmol, 90% yield).

- ^{1}H NMR (dichloromethane-d_2, 400 MHz): δ 7.95–7.53 (m, 21H, ArH), 7.33–7.11 (br m, 6H, ArH), 6.63 (br s, 3H, ArH).
- ^{13}C{^{1}H} NMR (dichloromethane-d_2, 101 MHz): δ 137.18 (d, J = 2.9 Hz), 134.17 (d, J = 12.5 Hz), 133.72 (d, J = 3.7 Hz), 130.77 (d, J = 13.9 Hz), 130.60 (s), 130.00 (d, J = 17.2 Hz), 129.65 (d, J = 12.5 Hz), 128.48 (br s), 121.72 (d, J = 103.8 Hz).
- ^{31}P{^{1}H} NMR (dichloromethane-d_2, 162 MHz): δ 34.2 (d, J = 32.3 Hz), -35.0 (br d).
- The molecular ion peak was not observed for this molecule. Rather, only the hydrolyzed compound $C_{36}H_{30}N_2P_2OH^+$ was observed: MS (ESI) $[M]^+$ of $C_{36}H_{30}N_2P_2OH^+$ calc. 569.1912 m/z, found 569.1911 m/z.
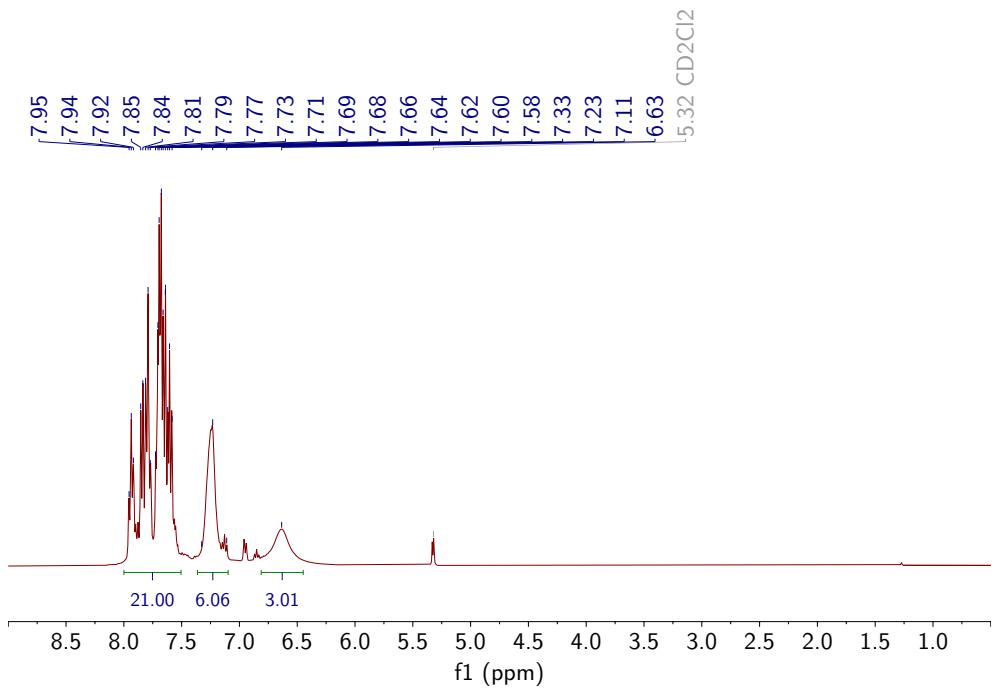
Figure S18: ^{1}H NMR spectrum of **5**. (dichloromethane-d_2, 400 MHz)
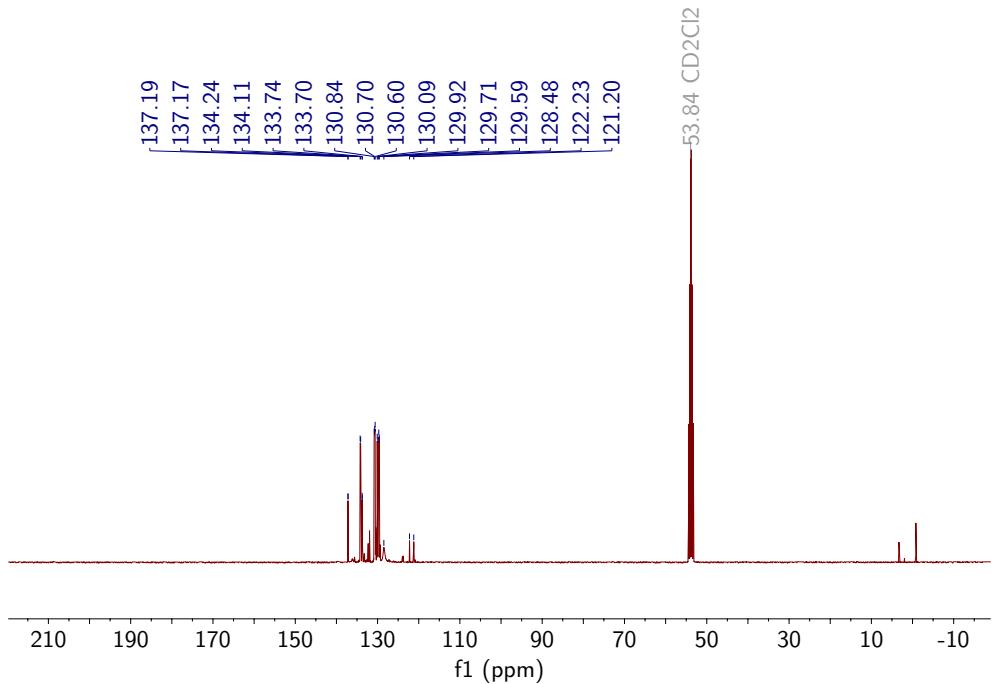
Figure S19: ^{13}C{^{1}H} NMR spectrum of **5**. (dichloromethane-d_2, 101 MHz)
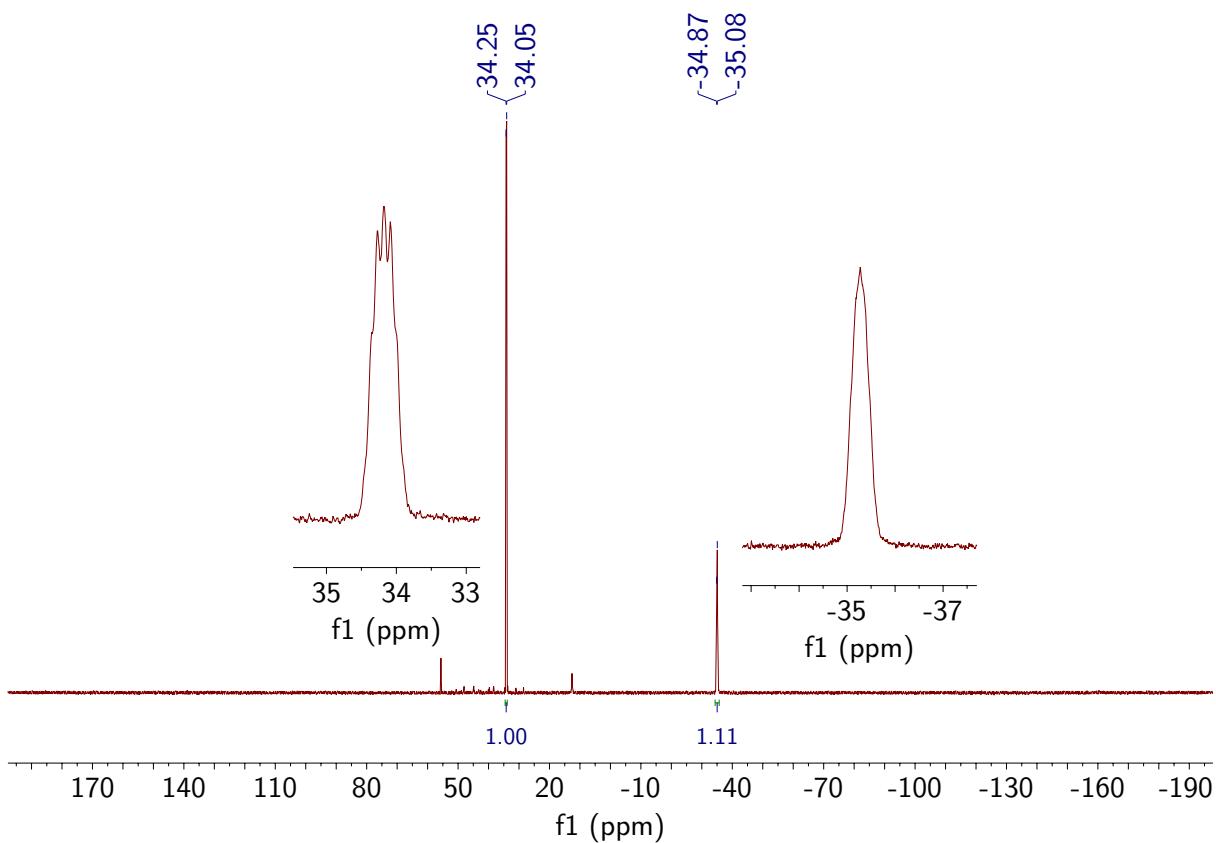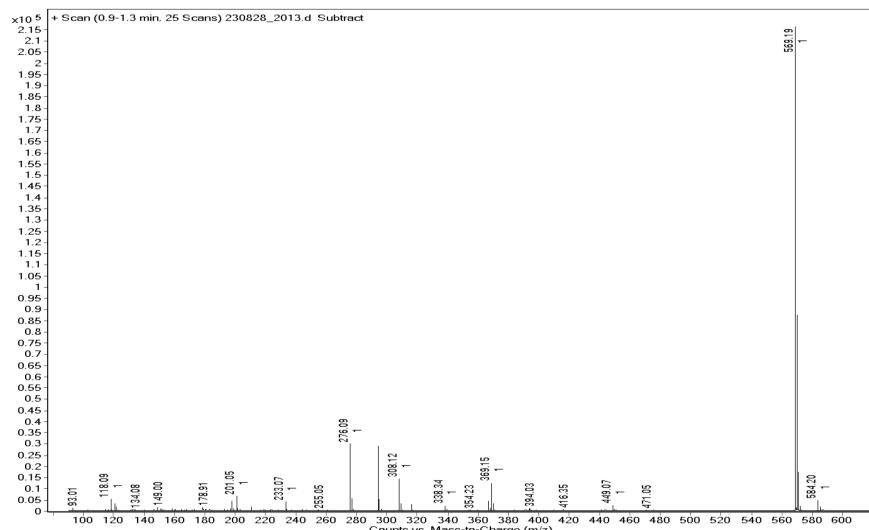
Figure S20: ^{31}P{^{1}H} NMR spectrum of **5** with insets showing peaks in the ^{31}P NMR. (dichloromethane-d_2, 162 MHz)

Sample Name	WK-06-167	**Data File**	230828_2013.d	**Acq Method**	HRMS.m
DA Method	AIMS_Accurate_Mass.m	**Instrument**	Agilent 6538 UHD	**Acq Date, Time**	28/08/2023 1:59:54 PM
Comment	ESI+				

Sample Name	WK-06-167	**Data File**	230921_2353.d	
Acq Method	HRMS.m	**DA Method**	AIMS_Accurate_Mass.m	
Instrument	Agilent 6538 UHD	**Acq Date, Time**	21/09/2023 12:27:46 PM	
Comment	ESI+			
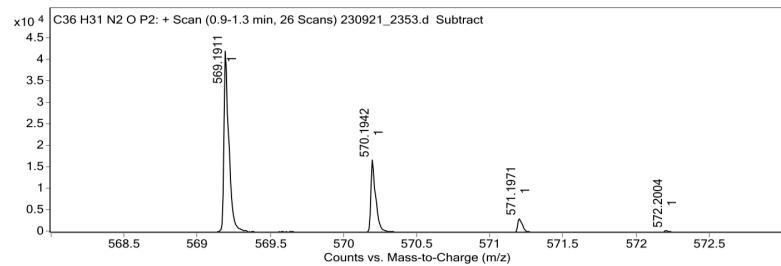
Target Ion Species

Ion Species	m/z	Ionic Formula
M+	569.1911	C36 H31 N2 O P2

MFG Calculator Results

Target m/z	Ionic Formula	Calc m/z	+/- (mDa)	+/- (ppm)	DBE	MFG Score
569.1911	C36 H31 N2 O P2	569.1906	0.5	0.9	23.5	99.37
569.1911	C24 H35 N4 O8 P2	569.1925	-1.4	-2.5	10.5	83.23
569.1911	C23 H39 O12 P2	569.1911	0.0	0.0	5.5	82.02
569.1911	C25 H31 N8 O4 P2	569.1938	-2.7	-4.7	15.5	79.97
569.1911	C20 H31 N10 O6 P2	569.1898	1.3	2.3	11.5	78.10
569.1911	C31 H31 N4 O3 P2	569.1866	4.5	7.9	19.5	72.64
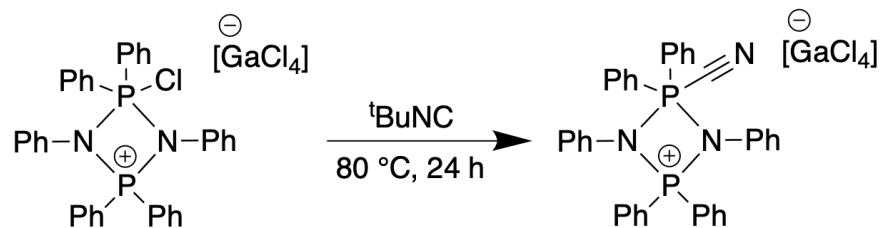
Predicted Isotope Match Table

Isotope	m/z	Calc m/z	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	569.1911	569.1906	0.5	100.0	100.0	0.0
2	570.1942	570.1939	0.3	39.4	40.1	0.7
3	571.1971	571.1971	0.0	7.6	8.0	0.4

Figure S21: ESI-MS(+) of $C_{36}H_{30}N_2P_2OH^+$ with zoomed in portion of the molecular ion, and the predicted isotope pattern.

2.6 Synthesis of 6

Scheme S6: Synthesis of **6**

In the glovebox, compound **2** (0.081 g, 0.10 mmol, 1.0 eq) was dissolved in *o*-DFB (0.7 mL), and *t*BuNC (0.11 mL, 1.0 mmol, 10.0 eq) was added. The solution was heated at 80 °C overnight, during which the colour of the solution turned from pale yellow to dark red. Solvent was removed under vacuum. The product was obtained as a beige powder after twice dissolving the crude product in DCM (0.3 mL) and triturating with diethyl ether (2.0 mL) (0.061 g, 0.077 mmol, 76% yield).

- ^{1}H NMR (dichloromethane-d_2, 400 MHz): δ 8.00–7.61 (m, 22H, ArH), 7.50 (br m, 2H, ArH), 7.27 (br m, 2H, ArH), 7.05 (br m, 2H, ArH), 6.15 (br s, 2H, ArH).
- ^{13}C{^{1}H} NMR (dichloromethane-d_2, 101 MHz): δ 137.79 (d, J = 2.9 Hz), 134.96–133.53 (m), 131.89 (s), 131.74 (br s), 131.13 (d, J = 14.3 Hz), 130.50 (s), 130.38 (s), 130.21 (s), 127.45 (br s), 126.05 (br s), 125.10 (d, J = 10.3 Hz), 120.17 (d, J = 104.9 Hz).
- ^{31}P{^{1}H} NMR (dichloromethane-d_2, 162 MHz): δ 32.0 (d, ^{2}J$_{PP}$ = 38.1 Hz), -62.8 (d, ^{2}J$_{PP}$ = 38.1 Hz).
- The molecular ion peak was not observed for this molecule. Rather, only the hydrolyzed compound $C_{36}H_{30}N_2P_2OH^+$ was observed: MS (ESI) [M]$^+$ of $C_{36}H_{30}N_2P_2OH^+$ calc. 569.1912 *m/z*, found 569.1918 *m/z*.
- Elem. Anal. Found (Calc'd) for $C_{37}H_{30}N_3P_2GaCl_4$: C 55.04 (56.24), H 3.67 (3.83), N 5.54 (5.32)
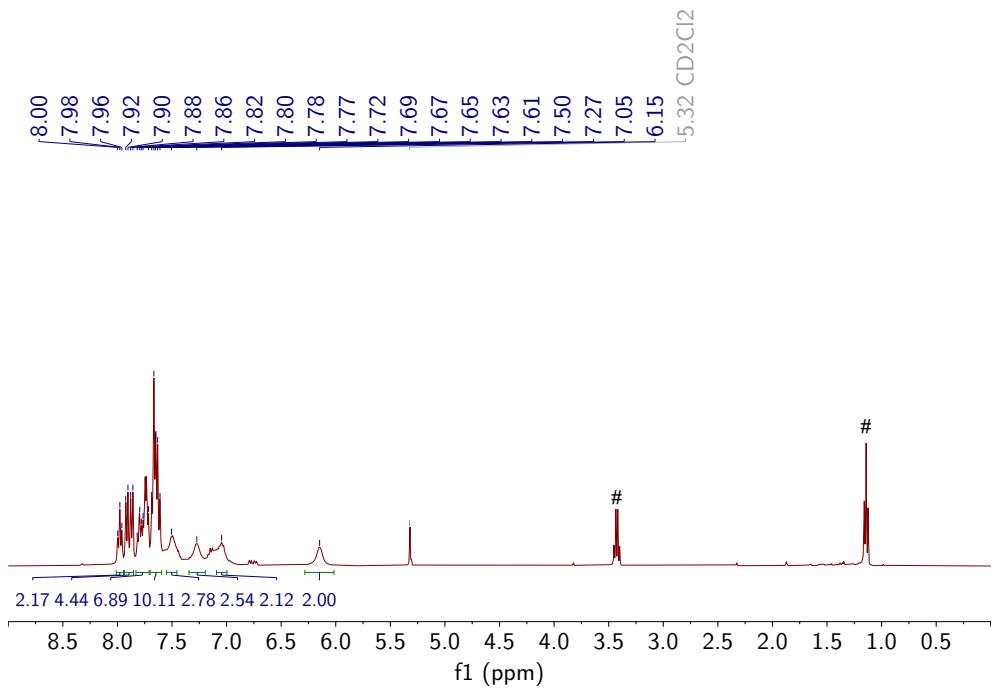
Figure S22: ^{1}H NMR spectrum of **6**. # denotes residual diethyl ether. (dichloromethane-d_2, 400 MHz)
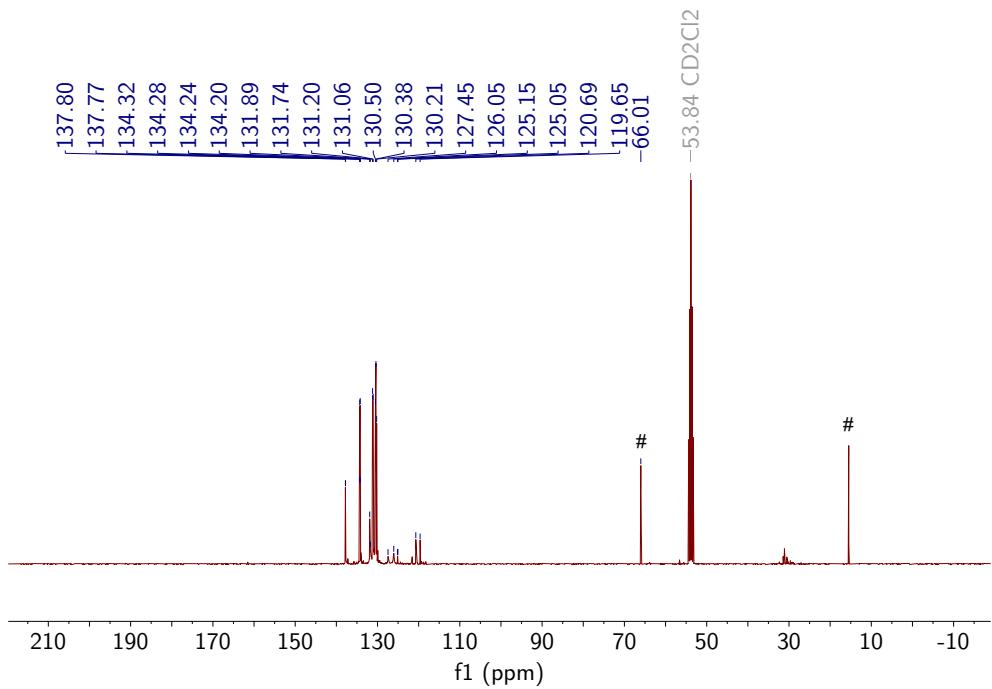
Figure S23: ^{13}C{^{1}H} NMR spectrum of **6**. # denotes residual diethyl ether. (dichloromethane-d_2, 101 MHz)
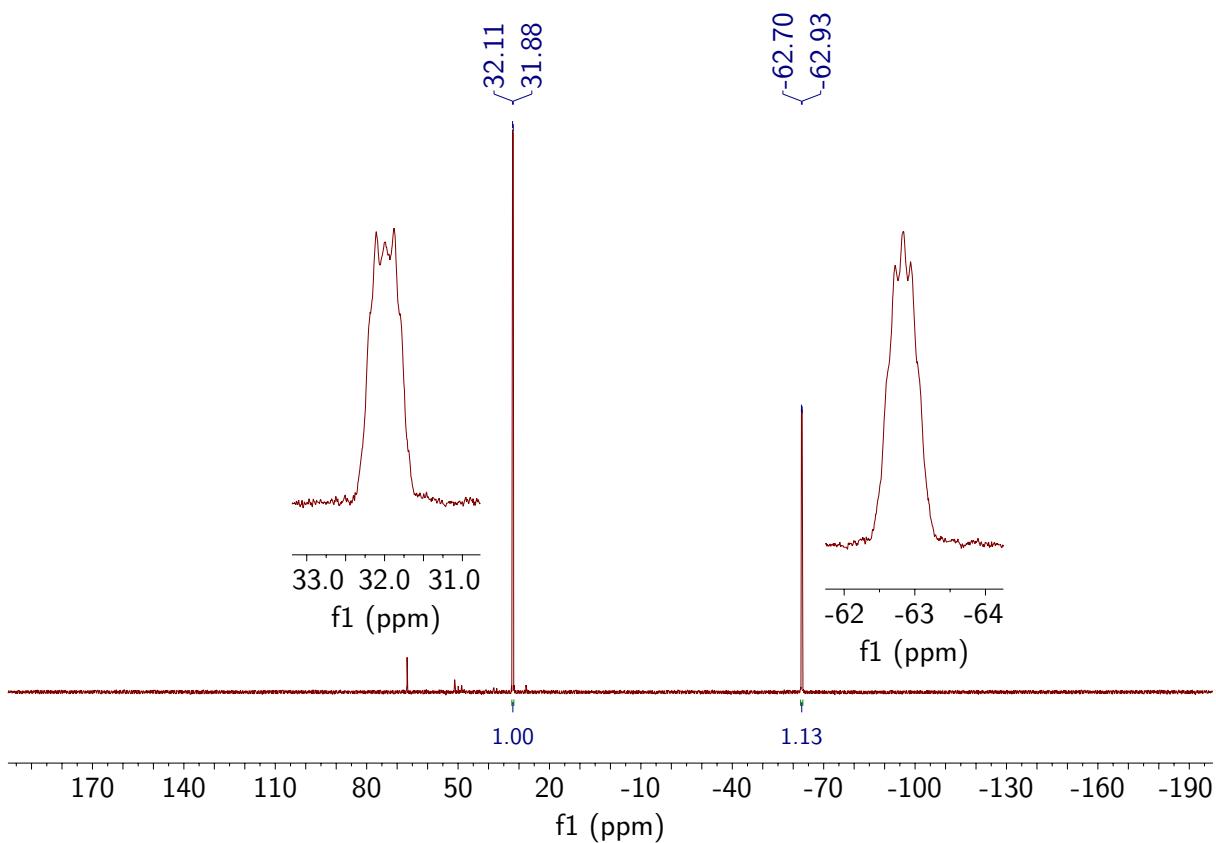
Figure S24: $^{31}P\{^1H\}$ NMR spectrum of **6** with insets showing peak in the ^{31}P NMR. (dichloromethane-d_2, 162 MHz)
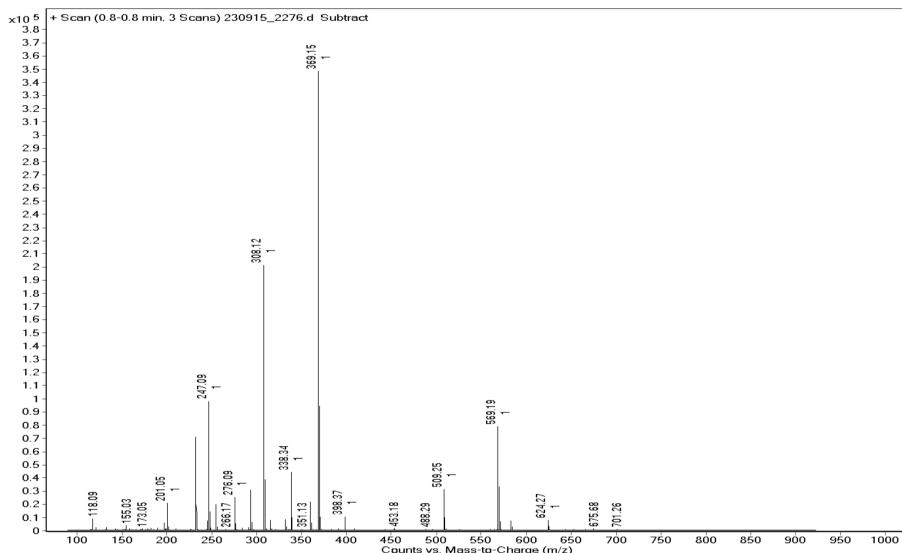
ESI Mass Spectrum

|							
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DA Method	AIMS_Accurate_Mass.m	**Instrument**	Agilent 6538 UHD	**Acq Date, Time**	15/09/2023 10:46:32 AM		
Comment	ESI+						

ESI-MS Report
Molecular Formula Generation (MFG)

Sample Name	WK-06-176	**Data File**	230915_2276.d
Acq Method	HRMS.m	**DA Method**	AIMS_Accurate_Mass.m
Instrument	Agilent 6538 UHD	**Acq Date, Time**	15/09/2023 10:46:32 AM
Comment	ESI+		
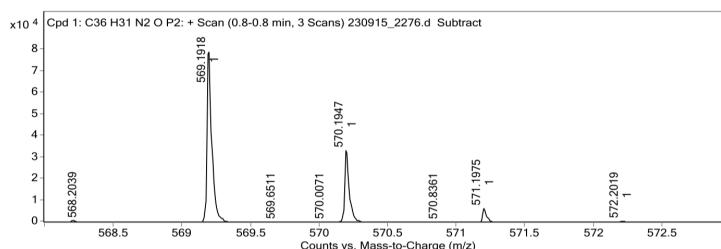
Target Ion Species

Ion Species	m/z	Ionic Formula
M+	569.1918	C36 H31 N2 O P2

MFG Calculator Results

Target m/z	Ionic Formula	Calc m/z	+/- (mDa)	+/- (ppm)	DBE	MFG Score
569.1918	C36 H31 N2 O P2	569.1906	1.2	2.1	23.5	96.35
569.1918	C32 H29 N2 O8	569.1918	0.0	0.0	19.5	93.49
569.1918	C33 H25 N6 O4	569.1932	-1.4	-2.5	24.5	93.47
569.1918	C44 H25 O	569.1900	1.8	3.2	32.5	92.16
569.1918	C27 H26 N10 O3 P	569.1921	-0.3	-0.5	20.5	90.19
569.1918	C34 H21 N10	569.1945	-2.7	-4.7	29.5	87.90
569.1918	C38 H26 N4 P	569.1890	2.8	4.9	28.5	87.63
569.1918	C26 H30 N6 O7 P	569.1908	1.0	1.8	15.5	84.40
569.1918	C30 H34 O9 P	569.1935	-1.7	-3.0	14.5	83.70
569.1918	C24 H35 N4 O8 P2	569.1925	-0.7	-1.2	10.5	80.74
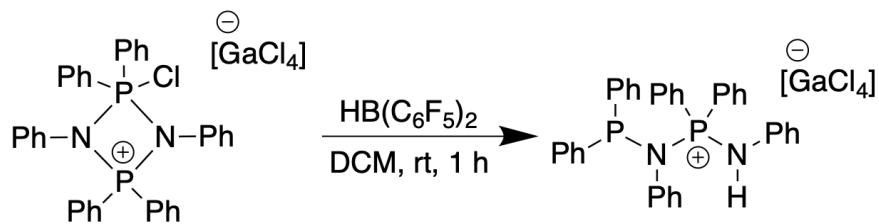
Predicted Isotope Match Table

Isotope	m/z	Calc m/z	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	569.1918	569.1906	1.2	100.0	100.0	0.0
2	570.1947	570.1939	0.8	42.9	40.1	-2.8
3	571.1975	571.1971	0.4	8.0	8.0	0.0

Figure S25: ESI-MS(+) of $C_{36}H_{30}N_2P_2OH^+$ with zoomed in portion of the molecular ion, and the predicted isotope pattern.

2.7 Synthesis of 7

Scheme S7: Synthesis of **7**

In the glovebox, compound **2** (0.040 g, 0.050 mmol, 1.0 eq) was dissolved in DCM (1.0 mL), and HB(C$_6$F$_5$)$_2$ (0.017 g, 0.050 mmol, 1.0 eq) was added directly. The solution was stirred at room temperature for 1 hour, then solvent was removed under vacuum. The crude product was washed with benzene, and the supernatant was decanted. After drying, the product was obtained as a beige powder (0.014 g, 0.019 mmol, 38% yield).

- ^{1}H NMR (dichloromethane-d_2, 400 MHz): δ 7.85–7.74 (m, 6H, ArH), 7.64-7.59 (m, 4H, ArH), 7.46-7.43 (m, 2H, ArH), 7.34–7.30 (m, 6H, ArH), 7.23–7.00 (m, 10H, ArH), 6.49 (d, J = 8.3 Hz, 2H, ArH), 6.04 (d, ^{2}J$_{PH}$ = 9.6 Hz, 1H, -NHPh).

- ^{13}C{^{1}H} NMR (dichloromethane-d_2, 101 MHz): δ 136.45 (dd, J = 7.0, 2.6 Hz), 136.30 (d, J = 2.9 Hz), 135.96 (m), 134.36 (s), 134.20 (d, J = 2.9 Hz), 134.13 (s), 134.09 (d, J = 2.9 Hz), 132.87 (d, J = 11.7 Hz), 131.70 (s), 131.66 (s), 130.99 (d, J = 14.3 Hz), 130.55 (s), 130.53 (s), 130.40 (s), 129.96 (d, J = 2.2 Hz), 129.19 (d, J = 7.3 Hz), 126.24 (d, J = 26.8 Hz), 122.70 (dd, J = 5.5, 2.9 Hz), 122.44 (d, J = 6.2 Hz), 121.24 (dd, J = 125.36, 1.8 Hz), 120.80 (d, J = 127.3 Hz).

- ^{31}P{^{1}H} NMR (dichloromethane-d_2, 162 MHz): δ 67.0 (d, J = 91.9 Hz), 42.9 (d, J = 91.9 Hz).

- The molecular ion peak was not observed for this molecule. Rather, only the decomposition product C$_{24}$H$_{22}$N$_2$P$^+$ was observed: MS (ESI) [M]$^+$ of C$_{24}$H$_{22}$N$_2$P$^+$ calc. 369.1521 m/z, found 369.1517 m/z.

- Elem. Anal. Found (Calc'd) for C$_{36}$H$_{31}$N$_2$P$_2$GaCl$_4$: C 53.53 (56.51), H 4.31 (4.08), N 2.80 (3.66)
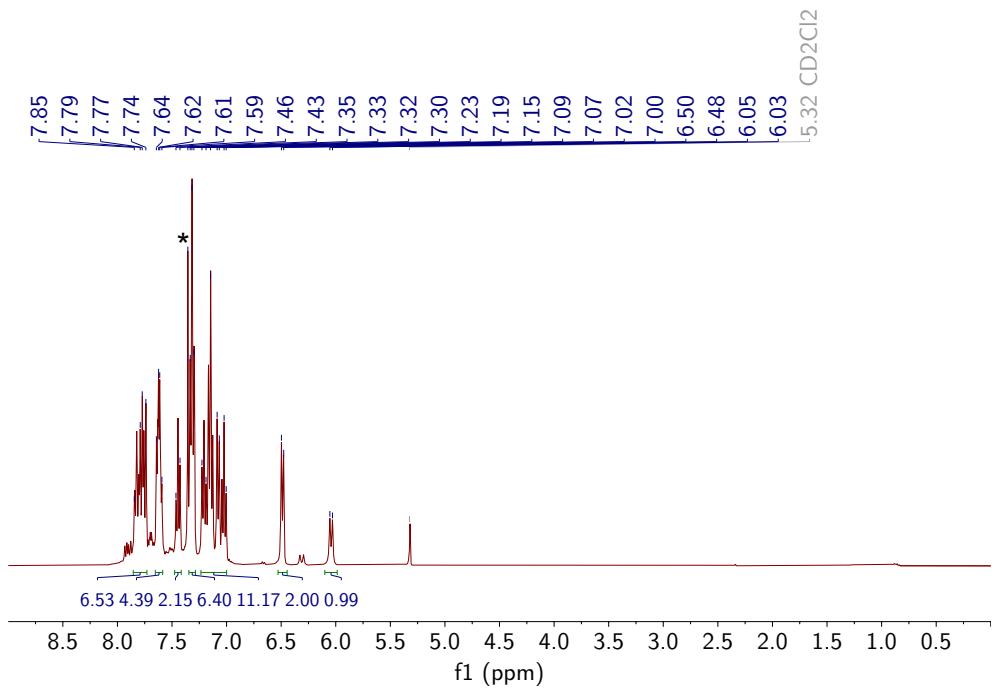
Figure S26: ^{1}H NMR spectrum of **7**. * denotes residual benzene. (dichloromethane-d_2, 400 MHz)
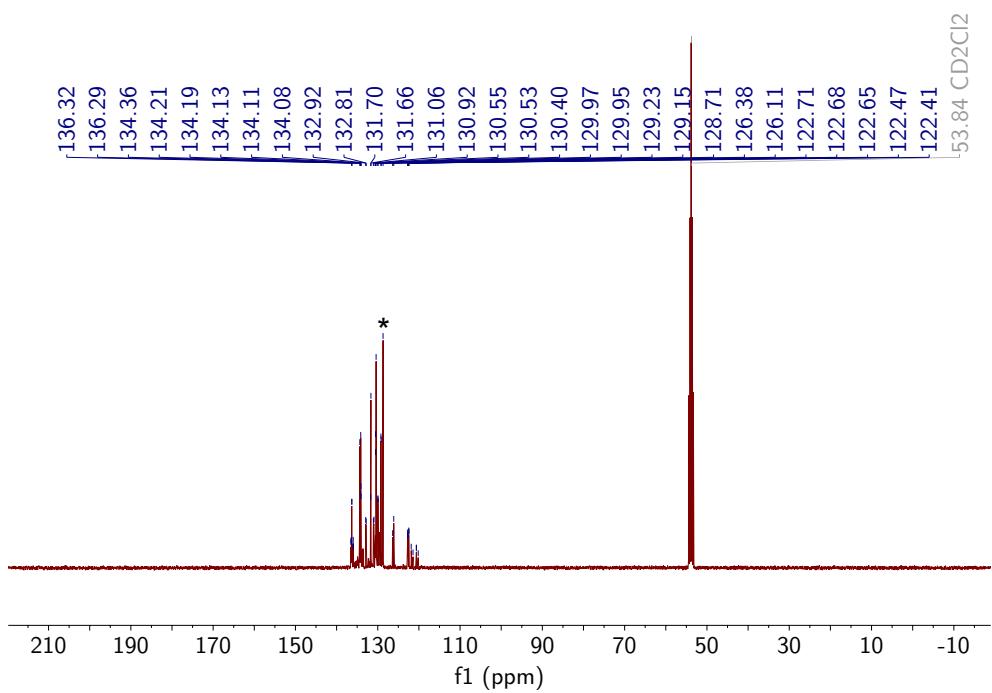
**Figure S27:** ^{13}C{^{1}H} NMR spectrum of **7**. * denotes residual benzene. (dichloromethane-d_2, 101 MHz)
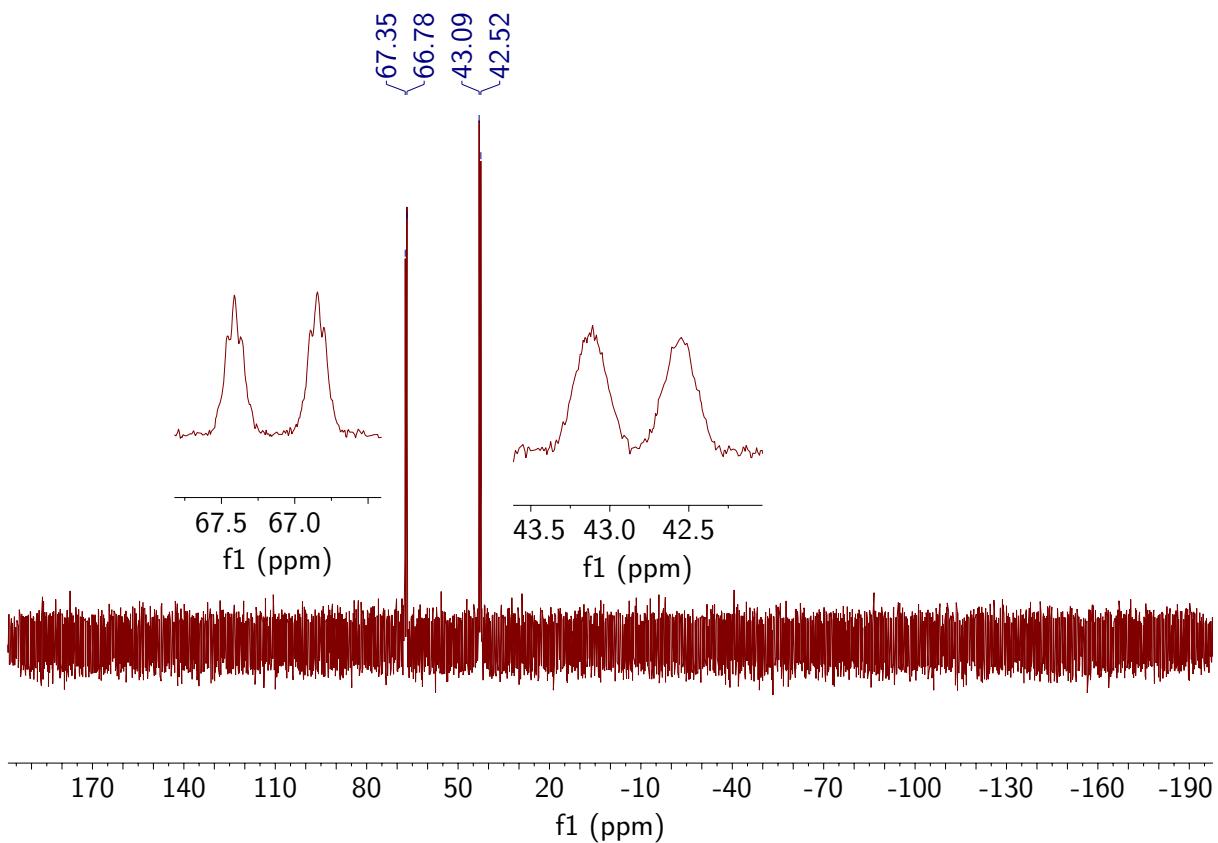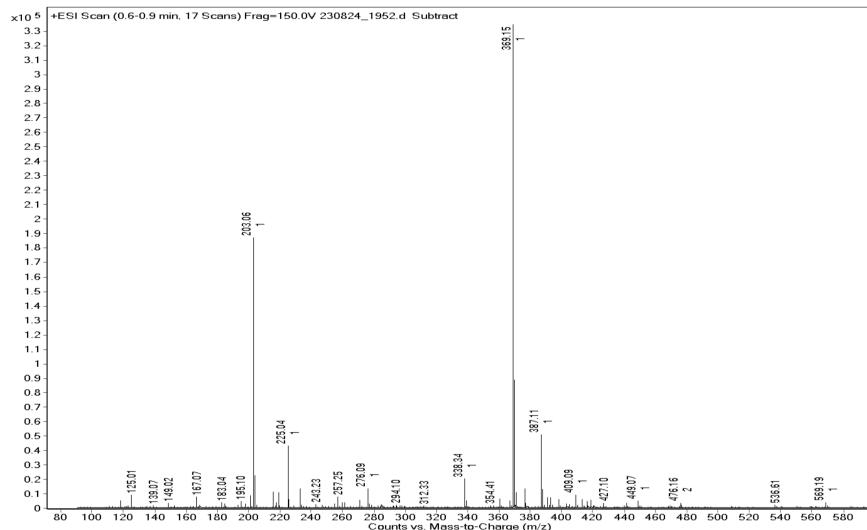
Figure S28: $^{31}P\{^1H\}$ NMR spectrum of **7** with insets showing peaks in the ^{31}P NMR. (dichloromethane-d_2, 162 MHz)

Figure S29: ESI-MS(+) of $C_{24}H_{22}N_2P^+$ with zoomed in portion of the molecular ion, and the predicted isotope pattern.

3   X-ray Diffraction Studies

Crystals were coated in Paratone-N oil in an N_2 filled glovebox, brought out of the glovebox, mounted on a MiTegen Micromount, and placed under a cold N_2 stream to maintain a dry, O_2-free environment for each crystal during data collection.

*For crystals of compounds **1**, **2**, **6**, **7***: Data were collected on a Bruker Kappa Apex II diffractometer using a graphite monochromator with Mo $\kappa\alpha$ radiation ($\lambda = 0.7103$ Å). Data were collected at 150 K for all crystals. A semi-empirical absorption correction was applied to the diffraction data using SADABS.[2] We used olex2 with an implementation of SHEL-XS added in. This provides both SHEL-XS and Olex2 solutions. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHEL-XL.[3,4] All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors. Descriptions of the refinement anomalies, where present, are given below. Further details can be found in the form of .cif files available from the CCDC.

*For crystals of compound **5** collected by Dr. Alan J. Lough*: Data were collected on a Bruker Kappa APEX-DUO diffractometer equipped with a PHOTON II CMOS detector and were measured using a combination of ϕ scans and ω scans. The data were processed using APEX3 and SAINT. Absorption corrections were carried out using SADABS.[2] The structures were solved with SHELXT[5] and refined using SHELXL-2019[4] for full-matrix least-squares refinement that was based on F^2. H atoms were included in calculated positions and allowed to refine in riding-motion approximation with U_{iso} tied to the carrier atom.

• Crystals of **1** were grown by layering pentane to a concentrated DCM solution of product and placing the vial in a -20 °C freezer overnight.

• Crystals of **2** were grown from a saturated $CHCl_3$ solution at room temperature.

• Crystals of **5** were grown by layering diethyl ether to a concentrated DCM solution of product at room temperature overnight.

• Crystals of **6** were grown by layering hexanes to a concentrated *o*-DFB solution of product at room temperature overnight.

• Crystals of **7** were grown by layering diethyl ether to a concentrated DCM solution of product and placing the vial in a -20 °C freezer overnight.

4 Experimental References

[1] N. Burford, P. J. Ragogna, R. McDonald and M. J. Ferguson, *J. Am. Chem. Soc.,* 2003, **134**, 13978–13981.

[2] G. M. Sheldrick, SADABS. 1996.

[3] G. M. Sheldrick and T. R. Schneider, SHELXL: High-resolution refinement; 1997, pp 319–343.

[4] G. M. Sheldrick, *Acta Crystallogr. C.*, 2015, **71**, 3–8.

[5] G. M. Sheldrick, *Acta Crystallogr. A.*, 2015, **71**, 3–8.

5 Computational Details, Data and References

The quantum chemical DFT calculations have been performed with the TURBOMOLE 7.4 suite of programs.[1] The structures are fully optimized at the TPSS-D3/def2-TZVP + COSMO(CH_2Cl_2) level of theory, which combines the TPSS meta-GGA density functional[2] with the BJ-damped DFT-D3 dispersion correction[3] and the def2-TZVP basis set,[4] using the Conductor-like Screening Model (COSMO) continuum solvation model[5] for CH_2Cl_2 solvent (dielectric constant $\epsilon = 8.93$ and solvent radius $R_{solv} = 2.94$ Å). The density-fitting RI-J approach[4a,6] is used to accelerate the geometry optimization and numerical harmonic frequency calculations[7] in solution. The optimized structures are characterized by frequency analysis to identify the nature of located stationary points (no imaginary frequency for true minima and only one imaginary frequency for transition state) and to provide thermal corrections (at 298.15 K and 1 atm) according to the modified ideal gas-rigid rotor-harmonic oscillator model.[8] This choice of dispersion-corrected meta-GGA functional makes the efficient exploration of all potential reaction paths possible.

The final solvation free energies in CH_2Cl_2 are computed with the COSMO-RS solvation model[9] (parameter file: `BP_TZVP_C30_1601.ctd`) using the COSMOtherm program package[10] on the above TPSS-D3 optimized structures, and corrected by +1.89 kcal·mol⁻¹ to account for higher reference solute concentration of 1 mol·L⁻¹ usually used in solution. To check the effects of the chosen DFT functional on the reaction energies and barriers, single-point calculations at the meta-GGA TPSS-D3[2] and hybrid-meta-GGA PW6B95-D3[11] levels are performed using a larger def2-QZVP basis set.[4b,12] The final reaction Gibbs free energies (ΔG) are determined from the electronic single-point energies plus TPSS-D3 thermal corrections and COSMO-RS solvation free energies. In our discussion, the higher-level PW6B95-D3 Gibbs free energies (in kcal/mol, at 298.15 K and 1 mol/L standard state concentration) will be used in our discussion unless specified otherwise, since meta-GGA functionals usually underestimate reaction barriers that could be improved by using hybrid meta-GGA functionals.

Table S1. TPSS-D3/def2-TZVP + COSMO computed lowest imaginary frequency (ImF), zero-point energies (ZPE), gas-phase enthalpic (Hc) and Gibbs free-energy (Gc) corrections; the COSMO-RS computed solvation enthalpic (Hsol) and Gibbs free-energy (Gsol) corrections in CH_2Cl_2 solution; TPSS-D3/def2-QZVP and PW6B95-D3/def2-QZVP single-point energies (TPSS-D3 and PW6B95-D3); the relative electronic energies (ΔE_T and ΔE_P) and Gibbs free-energies (ΔG_T and ΔG_P) at the TPSS-D3 and PW6B95-D3 levels. Each structure is labeled either by its molecular formula or a specific name in bold. Transition structures (with only one imaginary frequency) are indicated by the "**TS**" suffix while radicals, positive and negative charges are indicated by ·, + and - signs, respectively. See Figure S1 as well for labellings.

Table S2. The TPSS-D3/def2-TZVP + COSMO optimized atomic Cartesian coordi-

nates (in Å) in CH$_2$Cl$_2$ solution. Each structure is labeled by the specific name (see **Table S1**), followed by the number of atoms, the total energy, and the detailed atomic coordinates (in double-column text list).

References

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Table S1. TPSS-D3/def2-TZVP + COSMO computed lowest imaginary frequency (ImF), zero-point energies (ZPE), gas-phase enthalpic (Hc) and Gibbs free-energy (Gc) corrections; the COSMO-RS computed solvation enthalpic (Hsol) and Gibbs free-energy (Gsol) corrections in CH_2Cl_2 solution; TPSS-D3/def2-QZVP and PW6B95-D3/def2-QZVP single-point energies (TPSS-D3 and PW6B95-D3); the relative electronic energies (ΔE_T and ΔE_P) and Gibbs free-energies (ΔG_T and ΔG_P) at the TPSS-D3 and PW6B95-D3 levels. Each structure is labeled either by its molecular formula or a specific name in bold. Transition structures (with only one imaginary frequency) are indicated by the "**TS**" suffix while positive charges are indicated by + sign. See also main-text Figure 3 for labellings.

Reactions	ImF cm⁻¹	Zpe kcal/mol	Hc kcal/mol	Gc kcal/mol	Hsol kcal/mol	Gsol kcal/mol	TPSS Eh	PW6B95 Eh	GP	ET kcal/mol	EP kcal/mol	GT kcal/mol	GP kcal/mol
$Ph_2ClPPPh_2^+$ + *trans*-PhNNPh	0	346.84	370.02	292.60	-71.44	-58.74	-2643.25725	-2645.76092	-2645.38220	0.00	0.00	*0.00*	0.00
$Ph_2ClPPPh_2^+$ + *cis*-PhNNPh	0	345.97	369.34	291.66	-73.89	-59.95	-2643.23917	-2645.74094	-2645.36566	11.35	12.54	*10.38*	9.19
TSA	28i	345.99	369.77	305.78	-60.64	-50.61	-2643.26689	-2645.76001	-2645.35036	-6.05	0.57	*19.98*	13.36
A + Ph_2ClP	0	345.72	369.01	290.87	-74.07	-60.98	-2643.23151	-2645.73413	-2645.36176	16.15	16.81	*12.83*	12.17
TSB + Ph_2ClP	30i	344.90	367.98	290.17	-74.35	-61.13	-2643.21565	-2645.71590	-2645.34488	26.11	28.25	*23.42*	21.28
B + Ph_2ClP	0	346.09	369.32	291.50	-73.20	-60.12	-2643.24874	-2645.74124	-2645.36647	5.34	12.35	*9.87*	2.86
C	0	347.96	371.39	309.12	-63.70	-53.28	-2643.34576	-2645.85054	-2645.43983	-55.54	-56.24	*-36.16*	-35.46
TSC	84i	347.32	370.55	308.12	-62.30	-52.16	-2643.34571	-2645.84966	-2645.43874	-55.51	-55.68	*-35.48*	-35.31
2	0	348.36	371.68	309.74	-62.28	-52.16	-2643.36018	-2645.86543	-2645.45193	-64.59	-65.58	*-43.76*	-42.76

Table S2. The TPSS-D3/def2-TZVP + COSMO optimized atomic Cartesian coordinates (in Å) in CH₂Cl₂ solution. Each structure is labeled by the specific name (See also **Figure S1** and **Table S1**), followed by the number of atoms, the total energy, and the detailed atomic coordinates (in double-column text list).

2 : product
71
Energy = -2643.290179973

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C	-2.3325072	0.4008315	2.4268467
H	-2.1563559	-0.6557521	2.5988560
C	-1.6981778	0.7025195	-2.8647502
H	-0.7667607	0.4218361	-3.3471423
C	2.1901989	4.7260552	-1.0247513
H	2.4624483	5.7180637	-1.3715233
C	3.3989217	-0.0784759	1.5474560
H	3.8358530	0.1991288	0.5928685
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H	-2.2927246	2.0306891	-4.4434286
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H	2.0551076	0.4592296	-2.9391187
C	4.1699540	-2.2052457	-2.7600006
H	5.0396818	-2.6259040	-3.2554378
C	1.3060785	3.9458315	-1.7790698
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H	-2.9742377	-4.9309484	2.6213987
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C   0.8721975   1.9118552   2.1045943
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C   -1.3996552   -1.2216604   -1.0179701
H   0.0050741   0.3724662   -1.3793146
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H   3.7681469   -2.1867216   -2.7444890
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C   4.1132498   -3.1421860   0.4224076
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C   5.9578709   -1.5831837   0.7546979
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H   -2.7606490   2.5641955   -0.9621427

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C	1.7665863	-3.3529693	-2.7017256
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C	-1.0198448	-1.9910028	1.6172661
H	-0.7121991	-2.2420114	0.6076741
C	-5.2685193	-0.3075778	-0.2189000
H	-5.9716726	-1.1067339	-0.0082378
C	-1.3522412	-0.6710439	1.9525151
C	2.3488257	3.5718042	-2.0558987
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H	-1.4659803	-3.4178181	4.6687520
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C	-1.5025782	0.6948903	-4.2669123
H	-1.4025898	1.4418615	-5.0480705

Ph₂ClPPPh₂⁺ :
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H	-4.5530682	-4.4192980	-1.6177510
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C	-2.4915872	3.7017579	-1.5232651
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C	1.3052786	-2.9287931	0.1821796
C	4.0284173	-2.5170538	0.6371916
H	3.7874774	-0.6719160	-0.4396809
C	2.0443146	-3.8719586	0.8925855
H	0.2491658	-3.1087826	0.0023736
C	3.4065580	-3.6682217	1.1227264
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H	1.5548696	-4.7665572	1.2653224
H	3.9807814	-4.4052952	1.6756292
C	1.6603529	1.0758081	-0.9118029
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C	1.9823938	3.3607132	-1.6498728
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C	2.5291240	2.7308595	0.6242333
H	2.1932787	0.6711467	1.1462425
C	2.4490996	3.7009072	-0.3796013
H	1.9254846	4.1122280	-2.4311378
H	2.8933208	2.9971414	1.6117857
H	2.7556082	4.7213399	-0.1702156
Cl	-0.6229177	-0.3779066	1.7908150

Ph₂ClP :
24
Energy = -1265.246217912

P	-0.5200858	-0.9557257	-0.8782696
Cl	0.0084699	-2.1759606	-2.5263567
C	-1.4590455	-2.1519668	0.1353452
C	-1.8565135	0.4541818	-2.9521189
H	-1.0683127	0.1135861	-3.6166363
C	-1.6337387	-3.3287648	2.2501551
H	-1.2477712	-3.5375216	3.2436761
C	-0.9624805	-2.4316064	1.4160562
H	-0.0537337	-1.9431689	1.7589014
C	-2.6308765	-2.7860940	-0.3078904
H	-3.0171218	-2.5723387	-1.3003197
C	-2.8464268	1.3106916	-3.4342807
H	-2.8186623	1.6317892	-4.4718014
C	-3.8992092	1.3289317	-1.2606861
H	-4.6936506	1.6626659	-0.5990785
C	-2.9161337	0.4667728	-0.7762604
H	-2.9552599	0.1373836	0.2583746
C	-3.2936276	-3.6852121	0.5217543
H	-4.1986652	-4.1760990	0.1752555
C	-1.8876422	0.0152772	-1.6208026
C	-3.8691394	1.7510815	-2.5914680
H	-4.6394558	2.4168008	-2.9699315

C   -2.7968079   -3.9551124   1.8025271
H   -3.3191651   -4.6550504   2.4485741

PhNNPh_cis :
24
Energy = -573.0973106577
N   0.6091735   1.9791623   -0.2723710
N   -0.6039840   1.9987362   0.0482087
C   -1.3885769   0.8083627   0.2075056
C   -2.2878335   0.7804159   1.2800732
C   -1.3964344   -0.2167316   -0.7498313
C   -3.1422194   -0.3089228   1.4366616
H   -2.2930819   1.6037272   1.9884362
C   -2.2832834   -1.2797422   -0.6069150
H   -0.7270419   -0.1690215   -1.6021081
C   -3.1439784   -1.3401422   0.4936335
H   -3.8196082   -0.3441136   2.2848946
H   -2.3015462   -2.0664389   -1.3556853
H   -3.8253374   -2.1783861   0.6049136
C   1.3910476   0.7766081   -0.2961352
C   1.3985076   -0.1326722   0.7718303
C   2.2882199   0.6244238   -1.3599467
C   2.2828731   -1.2070797   0.7496438
H   0.7309011   0.0135010   1.6142882
C   3.1398195   -0.4777741   -1.3928022
H   2.2941574   1.3617432   -2.1574307
C   3.1414274   -1.3945295   -0.3381744
H   2.3006884   -1.9034369   1.5830982
H   3.8149238   -0.6115224   -2.2330062
H   3.8211863   -2.2412715   -0.3539575

PhNNPh :
24
Energy = -573.1127088445
N   0.3643792   0.5174922   -0.0081026
N   -0.3644470   -0.5172428   0.0136785
C   -1.7584628   -0.2631477   -0.0153816
C   -2.5765340   -1.4013379   0.0207476
C   -2.3359583   1.0177292   -0.0777049
C   -3.9634811   -1.2664040   -0.0036814
H   -2.1047951   -2.3785779   0.0680650
C   -3.7190981   1.1437368   -0.1023641
H   -1.6890570   1.8878048   -0.1061969
C   -4.5367084   0.0052494   -0.0651471
H   -4.5952850   -2.1492214   0.0246170
H   -4.1706296   2.1307541   -0.1510428
H   -5.6172897   0.1143052   -0.0845778
C   1.7584455   0.2632736   0.0183363
C   2.5763091   1.4020346   -0.0008057
C   2.3362070   -1.0183198   0.0600614
C   3.9632836   1.2670133   0.0215221
H   2.1043727   2.3797957   -0.0330939
C   3.7193843   -1.1444392   0.0818733
H   1.6894814   -1.8888764   0.0742364
C   4.5367675   -0.0053408   0.0626551
H   4.5949139   2.1502852   0.0068046

H   4.1711349   -2.1320350   0.1139544
H   5.6173782   -0.1144935   0.0797552

TSA :
71
Energy = -2643.194518355
P   -2.4025263   -0.0938585   0.1741460
C   -2.9979877   -1.4308208   -0.8906169
C   -2.9161443   1.4338799   -0.6383268
Cl -3.5572692   -0.2046091   1.8750402
C   -2.0695342   -2.1576359   -1.6520036
C   -4.3692537   -1.7096476   -1.0016500
C   -2.7132206   1.5292332   -2.0246243
C   -3.3327538   2.5547302   0.0914281
C   -2.5130753   -3.1555645   -2.5198980
H   -1.0086750   -1.9368876   -1.5756573
C   -4.8016263   -2.7112864   -1.8653140
H   -5.0898130   -1.1501118   -0.4132933
C   -2.9272761   2.7443017   -2.6722564
H   -2.3979143   0.6584163   -2.5921811
C   -3.5536976   3.7612755   -0.5672271
H   -3.4808517   2.4842625   1.1633218
C   -3.8757996   -3.4334669   -2.6252330
H   -1.7936118   -3.7144180   -3.1104958
H   -5.8621719   -2.9279979   -1.9482630
C   -3.3465189   3.8597280   -1.9448522
H   -2.7740217   2.8155432   -3.7447529
H   -3.8830291   4.6274974   -0.0017859
H   -4.2194634   -4.2125420   -3.2988819
H   -3.5160889   4.8045396   -2.4523816
P   0.0211525   -0.0574391   0.2447255
C   0.1117563   -1.1187344   1.7246252
C   -0.0723335   1.6710739   0.8180345
C   0.9114661   -0.7601538   2.8209468
C   -0.5216173   -2.3702084   1.7188197
C   0.1926321   2.6611577   -0.1403255
C   -0.4967926   2.0472244   2.0997369
C   1.0595976   -1.6345652   3.8970460
H   1.4266692   0.1950360   2.8278962
C   -0.3733928   -3.2409901   2.7951193
H   -1.1073183   -2.6790676   0.8579166
C   0.0493328   4.0077853   0.1825863
H   0.5003326   2.3748083   -1.1419701
C   -0.6383411   3.3971991   2.4197451
H   -0.7323161   1.2902131   2.8407245
C   0.4165267   -2.8739152   3.8872233
H   1.6814610   -1.3485194   4.7400344
H   -0.8652134   -4.2088108   2.7777840
C   -0.3632112   4.3771442   1.4642559
H   0.2508582   4.7671077   -0.5668211
H   -0.9727975   3.6819203   3.4129411
H   0.5348604   -3.5543474   4.7251357
H   -0.4791543   5.4272793   1.7156398
N   2.1056772   -0.0940975   0.1118590
N   2.7746811   0.9704864   0.0909513
C   4.1006452   1.0716011   -0.3733178

C	4.4402824	2.3728707	-0.7892576
C	5.0816254	0.0595503	-0.3504054
C	5.7221457	2.6457027	-1.2508748
H	3.6752631	3.1420480	-0.7537233
C	6.3711616	0.3582790	-0.7716430
H	4.8526875	-0.9292759	0.0246343
C	6.6904029	1.6381213	-1.2410639
H	5.9731562	3.6434424	-1.5963261
H	7.1362272	-0.4109345	-0.7343060
H	7.6996928	1.8520218	-1.5792065
C	2.5080359	-1.3498819	-0.4969226
C	2.6090959	-1.4186180	-1.8888408
C	2.6590082	-2.4829492	0.3019258
C	2.8894790	-2.6450864	-2.4855581
H	2.4634590	-0.5259837	-2.4887493
C	2.9531196	-3.7023261	-0.3092142
H	2.5694053	-2.4060935	1.3796770
C	3.0663291	-3.7858526	-1.6976172
H	2.9654208	-2.7091870	-3.5666244
H	3.0888338	-4.5875973	0.3043295
H	3.2857816	-4.7396065	-2.1673583

TSB :
47
Energy = -1377.908260508

P	-0.8403692	0.4159432	0.0325103
C	-0.8919930	-1.3283597	-0.2772630
C	-2.4248911	1.1479598	0.1968069
C	-1.2602440	-2.2045841	0.7592965
C	-0.6367872	-1.8119743	-1.5732084
C	-3.5743117	0.4042965	-0.1298352
C	-2.5192064	2.4857791	0.6276085
C	-1.3436300	-3.5688923	0.4996738
H	-1.4890641	-1.8248752	1.7499108
C	-0.7349244	-3.1784351	-1.8173621
H	-0.3702006	-1.1318880	-2.3744808
C	-4.8223953	1.0064926	-0.0155263
H	-3.4876700	-0.6240056	-0.4650517
C	-3.7753366	3.0685702	0.7386193
H	-1.6209898	3.0429456	0.8719541
C	-1.0784811	-4.0532536	-0.7839576
H	-1.6209718	-4.2512925	1.2962812
H	-0.5425348	-3.5596430	-2.8148025
C	-4.9209034	2.3317440	0.4175677
H	-5.7164493	0.4439620	-0.2626664
H	-3.8643596	4.0966792	1.0736459
H	-1.1469716	-5.1184112	-0.9813585
H	-5.8985048	2.7955067	0.5058677
N	0.3286198	1.1817642	0.9283165
N	0.3867844	1.3223897	-0.7104339
C	1.4554472	0.6958396	-1.4465796
C	1.7142231	1.3009542	-2.6822634
C	2.1996713	-0.4139186	-1.0265345
C	2.7070290	0.7795893	-3.5092330
H	1.1345836	2.1695130	-2.9774319
C	3.2066890	-0.9092853	-1.8530106

H	1.9989855	-0.8944031	-0.0773523
C	3.4593879	-0.3210814	-3.0934753
H	2.8982161	1.2425010	-4.4723994
H	3.7900048	-1.7646381	-1.5264572
H	4.2426091	-0.7172477	-3.7323078
C	1.4319861	0.7316013	1.6879852
C	1.2842906	-0.3041327	2.6179256
C	2.6488422	1.4141336	1.5619612
C	2.3639789	-0.6529413	3.4268731
H	0.3365923	-0.8231530	2.7122120
C	3.7240683	1.0385544	2.3621163
H	2.7429941	2.2196638	0.8416982
C	3.5868236	0.0080527	3.2957249
H	2.2483063	-1.4504722	4.1542916
H	4.6712007	1.5588974	2.2591447
H	4.4284551	-0.2777845	3.9185921

TSC :
71
Energy = -2643.274467815

P	-1.2968359	0.7905386	0.2787710
Cl	-1.0774489	2.1209059	1.8096614
P	1.2768472	-0.2802354	0.1582214
C	-2.3516161	1.7487560	-0.8337899
N	0.0376284	0.5228060	-0.7129775
C	0.1057612	0.8053481	-2.1314957
C	4.9685662	2.4204125	0.3674140
H	5.8390426	3.0644965	0.4460702
C	0.9242632	1.8375721	-2.5907648
H	1.4665573	2.4551463	-1.8837669
C	-3.2539315	-0.4618256	1.7850265
H	-3.3955967	0.4951406	2.2761213
C	2.0735620	-4.1834477	-2.0897138
H	2.2358997	-5.1154718	-2.6226613
C	4.0099161	0.2469100	-0.0802060
H	4.1356145	-0.7994076	-0.3380012
C	2.7297048	0.7678264	0.1565700
C	0.6462545	-0.6218098	2.8220768
N	0.4050188	-0.4437289	1.4573201
C	1.6579194	-1.7908643	-0.7244723
C	-0.6085288	0.0048866	-3.0234975
H	-1.2357756	-0.7962098	-2.6472804
C	1.8364920	-0.1312496	4.8806831
H	2.6389092	0.3896698	5.3961119
C	-0.0557068	-1.6270515	4.9189617
H	-0.7322658	-2.2804544	5.4632356
C	5.1257579	1.0772466	0.0251613
H	6.1159522	0.6731210	-0.1598880
C	0.3134490	1.2729306	-4.8619706
H	0.3936249	1.4568820	-5.9289294
C	-2.7494250	3.7585763	-2.1198379
H	-2.4644708	4.7688727	-2.3960686
C	2.5778136	2.1189479	0.5176020
H	1.5883953	2.5180588	0.7236976
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H	-1.1116326	3.5213045	-0.7511643

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C   -3.4873764    1.1576613   -1.4030931
H   -3.7753122    0.1482573   -1.1291095
C    1.2788031   -3.0066574   -0.1357772
H    0.8165924   -3.0028566    0.8467461
C   -4.0323342   -1.5595716    2.1533693
H   -4.7795487   -1.4470383    2.9324264
C    1.6728883    0.0493905    3.5086710
H    2.3366004    0.7115749    2.9615131
C   -2.8842864   -2.9360137    0.5251995
H   -2.7408641   -3.8949406    0.0373485
C    2.4478953   -2.9728764   -2.6795877
H    2.8968541   -2.9638886   -3.6678320
C   -2.0960265   -1.8513520    0.1550379
H   -1.3306576   -1.9690125   -0.6051340
C   -4.2487451    1.8697446   -2.3296563
H   -5.1281511    1.4091212   -2.7684484
C   -2.2833445   -0.6158519    0.7894441
C    3.6937273    2.9412295    0.6164347
H    3.5745044    3.9850409    0.8887911
C   -0.2159568   -1.4646799    3.5442576
H   -1.0066554   -1.9848281    3.0130833
C    0.9720523   -0.9649904    5.5950582
H    1.0988191   -1.0971646    6.6654467
C    1.4940676   -4.2016875   -0.8191170
H    1.2104776   -5.1445619   -0.3621437
C   -0.5090528    0.2468417   -4.3917949
H   -1.0681774   -0.3694405   -5.0886862
C    2.2475115   -1.7744486   -1.9998114
H    2.5394487   -0.8345945   -2.4584262
C   -3.8483358   -2.7929337    1.5278262
H   -4.4535026   -3.6450112    1.8212373
C   -3.8798135    3.1653363   -2.6900689
H   -4.4741862    3.7171465   -3.4120063
C    1.0307725    2.0641846   -3.9625996
H    1.6668529    2.8650907   -4.3262382
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