SUPPORTING INFORMATION

Triphosphiranes as Phosphinidene-Transfer Agents – Synthesis of Regular and Chelating NHC Phosphinidene Adducts

*M.Sc. Jan-Erik Siewert, Dr. André Schumann, M.Sc. Tim Wellnitz, Dr. Fabian Dankert, Dr. habil. Christian Hering-Junghans**

This file includes:

1 Experimental

General Information. If not stated otherwise, all manipulations were carried out under oxygen- and moisture-free conditions under an inert atmosphere of argon using standard Schlenk techniques or an inert atmosphere glovebox (MBraun LABstar ECO). All glassware was heated three times *in vacuo* using a heat gun and cooled under argon atmosphere. Solvents were transferred using syringes, steel- or PE-canulas, which were purged with argon prior to use. Solvents and reactants were either obtained from commercial sources or synthesized as detailed in Table S1.

Table S1: Origin and purification of solvents and reactants.

Substance	Origin	Purification
n-Hexane, THF, Et_2O, CH_2Cl_2, toluene	local trade	purified with the Grubbs-type column system "Pure Solv MD-5"
MeCN	local trade	purified with the Grubbs-type column system "Pure Solv MD-5", stored over molecular sieves.
n-Pentane	local trade	dried over Na/benzophenone/tetraglyme freshly distilled prior to use
CD_2Cl_2	euriso-top	dried over P_4O_{10} and CaH_2 freshly distilled prior to use
C_6D_6	euriso-top	dried over Na freshly distilled prior to use
THF-d_8	euriso-top	dried over Na/benzophenone freshly distilled prior to use
DMSO-d_6	Sigma Aldrich	Used as received
1-Methylimidazole	Sigma Aldrich	Used as received
Methyliodide	Sigma Aldrich	Used as received
2-Iodopropane	Sigma Aldrich	Used as received
N,N'-di-(*iso*-propyl)-imidazolium chloride	Sigma Aldrich	Used as received
N,N'-dimethyl-imidazolium iodide	Synthesized[1]	Dried in vacuo and handled under inert conditions
N,N-dimethylthiourea	Sigma Aldrich	Used as received
1-hydroxybutan-3-one	Sigma Aldrich	Used as received

Substance	Origin	Purification
1,3,4,5-tetramethylimidazolin-2-ylidene	Synthesized[2]	re-crystallized as described in the literature
1,3-(*iso*-propyl)imidazolin-2-ylidene	Synthesized[3]	re-crystallized as described in the literature
1,3-(*iso*-propyl) 4,5-dimethylimidazolin-2-ylidene	Synthesized[4]	re-crystallized as described in the literature

NMR spectra were recorded on Bruker spectrometers (AVANCE 300, AVANCE 400 or Fourier 300) and were referenced internally to the deuterated solvent (^{13}C: CD_2Cl_2 δ_{ref} = 54.0 ppm, C_6D_6 δ_{ref} = 128.4 ppm, THF-d_8 $\delta_{ref,1}$ = 25.4 ppm, $\delta_{ref,2}$ = 67.6 ppm), to protic impurities in the deuterated solvent (^1H: $CHDCl_2$ δ_{ref} = 5.32 ppm, C_6HD_5 δ_{ref} = 7.16 ppm, THF-d_7 $\delta_{ref,1}$ = 1.73 ppm, $\delta_{ref,2}$ = 3.58 ppm, DMSO-d_6 δ_{ref} = 2.50 ppm)[1] or externally (^{31}P: 85% H_3PO_4 δ_{ref} = 0 ppm). All measurements were carried out at ambient temperature unless denoted otherwise. NMR signals were assigned using experimental data (e.g. chemical shifts, coupling constants, integrals where applicable)

IR spectra of crystalline samples were recorded on a Bruker Alpha II FT-IR spectrometer equipped with an ATR unit at ambient temperature under argon atmosphere. Relative intensities are reported according to the following intervals: very weak (vw, 0–10%), weak (w, 10–30%), medium (m, 30–60%), strong (s, 60–90%), very strong (vs, 90–100%).

Elemental analyses were obtained using a Leco Tru Spec elemental analyzer.

Mass spectra were obtained using a Thermo Electron MAT 95-XP (EI) and an Agilent 1200/6210 Time-of-Flight LC-MS (ESI) device.

UV-Vis spectra were acquired on an UV/Vis absorption spectrophotometer UV5 (Mettler Toledo) using Quartz glass cuvettes.

2 Structure elucidation

X-ray Structure Determination: X-ray quality crystals of all samples were selected in Fomblin© Y-1800 perfluoroether (Sigma Aldrich) at ambient temperature. The samples were cooled to 150(2) K during measurement. The data was collected on a Bruker Kappa Apex II diffractometer using Mo K_α radiation (λ = 0.71073 Å) (**1b**, **1c**, **3a**, **3b**, **4b**, **4c**) or Cu K_α radiation (λ = 1.54178 Å) (**2c**, **3c**, **5a**, **6b**, **6c, 8**, **9**). The data for **7** was collected on a STOE IPDS II diffractometer using MoK_α radiation (λ = 0.71073 Å). The structures were solved by intrinsic phasing (SHELXT)[5] and refined by full matrix least squares procedures (SHELXL)[6] within the Olex2 platform (**7**),[7] or using the WinGX platform.[8] Semi-empirical absorption corrections (multiscan and additional spherical absorption correction) were applied to the diffraction data collected with the Bruker device using the SADABS application within the APEX II platform.[9] Semi-empirical absorption corrections (multiscan and additional spherical absorption correction) were applied to the diffraction data recorded with the STOE device using the LANA application within the STOE X-AREA platform.[10] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model. All special refinement details for disordered structures, molecular structure representations (of compounds **6c** and **8**) as well as a compilation of standard crystallographic details are summarized below.

In **1b** the *n*-hexane solvent was not modelled and was rather treated as diffuse contribution to the overall scattering using Platon/SQUEEZE.[11]

In **1c** the isopropyl group in *para*-position was found to be disordered and was split in two parts, which were allowed to refine freely.

In **2c** the C13-15 *i*Pr group was found to be disordered and was split into two parts. The occupancy of each part was allowed to refine freely.

In **3a** one of the isopropyl groups was found to be disordered and was split in two parts and the occupancy of each part was allowed to refine freely.

In **3b** one of isopropyl groups of the Dip (C10-C12) and the I*i*Pr$_2$ (C16-C18) moieties, respectively, were found to be disordered and were split in two parts. The occupancy of each part was allowed to refine freely.

In **3c** one of *o*-*i*Pr groups (C7-C9) of the Tip moiety was found to be disordered and was split in two parts. The occupancy of each part was allowed to refine freely.

In **4c** one of the *i*Pr groups was found to be disordered and the atomic positions of C20 and C21 were split and the occupancy of each part was allowed to refine freely.

In **5a** one of the p-*i*Pr groups (C10-C12) was found to be disordered and was split in two parts. The occupancy of each part was allowed to refine freely and the thermal ellipsoids of C11A/C11B and C12A/C12B were constrained to be equal using the EADP command.

In **6b** the C25-C27 *i*Pr group was found to be disordered and was split in two parts. The occupancy of each part was allowed to refine freely. The thermal ellipsoids of C25A and C25B were treated with EADP.

In **6c** two of the *i*Pr groups (C13-C15; C43-C45) were found to be disordered and were split in two parts. The occupancy of each part was allowed to refine freely.

In **7** the $[GaI_4]^-$ as well as DCM ions/molecules are disordered over various positions. For most of the DCM molecules as well as one $[GaI_4]^-$, the FVAR instruction was sufficient and employed accordingly. For a second, massively disordered $[GaI_4]^-$ ion, the SUMP instruction was used with PARTS 3, 4 and 5 and free variables 3, 4 and 5 (31, 41, 51). FVAR and SUMP were allowed to refine against an occupancy of 1 (see .cif for details). One of the massively disordered $[GaI_4]^-$ ions shares an occupancy site with a further DCM molecule which is included to FVAR5 (51) as it correlates to the position of the $[GaI_4]^-$ in PART5 (with FVAR5). Due to this DCM being just included around 11%

in this crystal moiety, an uneven number of atoms in the unit cell results. To model the disorder, we employed several SADI, ISOR, DELU and in some cases DANG restraints to reach reasonable displacement and suitable atom distances.

In **8** the $GeCl_3$ counter anion was found to be disordered and was split in two parts. The occupancy of each part was allowed to refine freely. The unit cell contains two disordered CH_2Cl_2 molecules. These have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.[11]

In **9** the C19-C21 and C22-24 *i*Pr group were found to be disordered and were split into two parts. The occupancy of each part was allowed to refine freely. The geometry of C19-C21 was modelled using the DFIX and SADI commands.

Overall, the unit cell contains 3.3 molecules of C_6H_5F and 0.5 molecules of *n*-hexane. One of the C_6H_5F is positioned and disordered over a special position with an overall occupancy of 0.9. The *n*-hexane is similarly situated on a center of inversion with an overall occupancy of 0.5 per cell. On the same position a C_6H_5F molecule was found, which is disordered with an occupancy of 0.4 per cell. These values match with the residual electron density found using PLATON/SQUEEZE, which has been applied.[11]

Table S2: Crystallographic details for **1b**, **1c** and **2b**.

Compound	**1b**	**1c**	**2c**
Chem. Formula	$C_{17}H_{25}N_2P$	$C_{20}H_{31}N_2P$	$C_{22}H_{35}N_2P$
Formula weight [g/mol]	288.36	330.44	358.49
Colour	yellow	yellow	yellow
Crystal system	Orthorhombic	monoclinic	orthorhombic
Space group	*Pbca*	*C*2/*c*	$Pna2_1$
a [Å]	8.0396(2)	31.2584(2)	30.2653(7)
b [Å]	15.6897(4)	8.8082(2)	9.5140(2)
c [Å]	58.4856(16)	14.9274(4)	15.0351(4)
α [°]	90	90	90
β [°]	90	107.1280(10)	90
γ [°]	90	90	90
V [Å^3]	7377.3(3)	3927.68(18)	4329.27(18)
Z	16	8	8
$\rho_{calcd.}$ [g/cm^3]	1.038	1.118	1.100
μ [mm^{-1}]	0.143	0.142	1.151
T [K]	150(2)	150(2)	150(2)
Measured reflections	91471	35224	34196
Independent reflections	10753	4744	7020
Reflections with $I > 2\sigma(I)$	9313	3959	6730
R_{int}	0.0442	0.0295	0.0419
F(000)	2496	1440	1568
$R_1(R[F^2>2\sigma(F^2)])$	0.0761	0.0381	0.0326
$wR_2(F^2)$	0.1811	0.1083	0.0844
GooF	1.199	1.019	1.039
No. of Parameters	373	224	497
CCDC #	2289296	2289297	2289298

Table S3: Crystallographic details for **3a**, **3b** and **3c**.

Compound	**3a**	**3b**	**3c**
Chem. Formula	$C_{18}H_{27}N_2P$	$C_{21}H_{33}N_2P$	$C_{24}H_{39}N_2P$
Formula weight [g/mol]	302.38	344.46	386.54
Colour	yellow	yellow	yellow
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	$P2_12_12_1$	$P2_1/n$	*Pbca*
a [Å]	8.8637(9)	10.2794(5)	10.9389(3)
b [Å]	13.6251(14)	14.6603(7)	16.6305(4)
c [Å]	15.3577(16)	15.1574(7)	25.9319(6)
α [°]	90	90	90
β [°]	90	109.1081(9)	90
γ [°]	90	90	90
V [Å^3]	1854.7(3)	2158.35(18)	4717.5(2)
Z	4	4	8
$\rho_{calcd.}$ [g/cm^3]	1.083	1.060	1.088
μ [mm^{-1}]	0.145	0.145	1.087
T [K]	150(2)	150(2)	150(2)
Measured reflections	19113	27210	32203
Independent reflections	5403	6312	4107
Reflections with $I > 2\sigma(I)$	4549	4917	3829
R_{int}	0.0415	0.0340	0.0325
F(000)	656	752	1696
$R_1(R[F^2>2\sigma(F^2)])$	0.0393	0.0460	0.0329
$wR_2(F^2)$	0.0937	0.1266	0.0917
GooF	1.023	1.034	1.063
No. of Parameters	223	259	284
CCDC #	2289299	2289300	2289301

Table S4: Crystallographic details for **4b**, **4c** and **5a**.

Compound	**4b**	**4c**	**5a**
Chem. Formula	$C_{23}H_{37}N_2P$	$C_{26}H_{43}N_2P$	$C_{36}H_{44}N_4P_2$
Formula weight [g/mol]	372.51	414.59	594.69
Colour	yellow	yellow	yellow
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	P-1	$P21/c$
a [Å]	10.4539(9)	16.679(2)	15.3256(7)
b [Å]	15.7979(13)	17.697(2)	27.6449(13)
c [Å]	14.8454(12)	18.581(3)	15.9718(7)
α [°]	90	89.3374(23)	90
β [°]	106.127(2)	73.1646(21)	91.864(2)
γ [°]	90	78.0995(22)	90
V [Å^3]	2355.2(3)	5129.6(12)	6763.3(5)
Z	4	8	8
$\rho_{calcd.}$ [g/cm^3]	1.051	1.074	1.168
μ [mm^{-1}]	0.125	0.121	1.386
T [K]	150(2)	150(2)	150(2)
Measured reflections	59977	77951	69488
Independent reflections	6873	26528	11850
Reflections with $I > 2\sigma(I)$	5553	15031	9471
R_{int}	0.0364	0.0559	0.0734
F(000)	688	1824	2544
$R_1(R[F^2>2\sigma(F^2)])$	0.0369	0.0578	0.0645
w$R_2(F^2)$	0.1094	0.1499	0.1882
GooF	1.066	1.008	1.088
No. of Parameters	245	1110	777
CCDC #	2289302	2289303	2289304

Table S5: Crystallographic details for **6b**, **6c** and **7**.

Compound	**6b**	**6c**	**7**
Chem. Formula	$C_{42}H_{56}N_4P_2$	$C_{48}H_{68}N_4P_2 \cdot (C_6H_6)_2$	$[C_{36}H_{44}GaI_2N_4P_2][GaI_4] \cdot (CH_2Cl_2)_{2.06}$
Formula weight [g/mol]	678.84	919.22	1670.14
Colour	yellow	yellow	colourless
Crystal system	triclinic	triclinic	triclinic
Space group	*P*-1	*P*-1	*P*-1
a [Å]	10.9493(3)	8.3009(2)	14.9427(3)
b [Å]	11.5418(3)	19.0540(5)	17.0844(3)
c [Å]	15.7607(4)	26.0572(8)	23.0489(4)
α [°]	81.3760(10)	84.5600(10)	74.3750(10)
β [°]	80.2230(10)	85.3170(10)	74.2030(10)
γ [°]	85.7660(10)	88.8880(10)	82.8170(10)
V [Å^3]	1938.24(9)	4088.81(19)	5444.13(18)
Z	2	3	4
$\rho_{calcd.}$ [g/cm^3]	1.163	1.120	2.038
μ [mm^{-1}]	1.266	1.020	4.683
T [K]	150(2)	150(2)	150(2)
Measured reflections	28087	50513	73082
Independent reflections	6751	13661	22576
Reflections with $I > 2\sigma(I)$	5893	10821	18054
R_{int}	0.0374	0.0412	0.0184
F(000)	732	1494	3137
$R_1(R[F^2>2\sigma(F^2)])$	0.0393	0.0474	0.0334
w$R_2(F^2)$	0.1101	0.1344	0.0855
GooF	1.035	1.023	1.028
No. of Parameters	465	968	1276
CCDC #	2289305	2289306	2289307

Table S6: Crystallographic details of **8** and **9**.

Compound	**8**	**9**
Chem. Formula	$[C_{36}H_{44}GeClN_4P_2][GeCl_3]$ $\cdot CH_2Cl_2$	$(C_{48}H_{68}N_4P_2GeCl][GeCl_3]$ $\cdot(C_6H_5F)1.65\cdot(C_6H_{14})_{0.25}$
Formula weight [g/mol]	966.60	1230.34
Colour	yellow	Yellow
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a [Å]	8.7735(7)	9.6037(5)
b [Å]	15.3647(12)	16.1076(8)
c [Å]	16.7707(13)	22.4447(10)
α [°]	76.373(3)	110.610(3)
β [°]	89.218(3)	98.326(3)
γ [°]	83.018(2)	93.649(3)
V [Å^3]	2180.5(3)	3190.8(3)
Z	2	2
$\rho_{calcd.}$ [g/cm^3]	1.472	1.281
μ [mm^{-1}]	6.019	3.510
T [K]	150(2)	150(2)
Measured reflections	45394	49376
Independent reflections	7713	11150
Reflections with $I > 2\sigma(I)$	7289	9114
R_{int}	0.0318	0.0525
F(000)	984	1282
$R_1(R[F^2>2\sigma(F^2)])$	0.0263	0.0526
$wR_2(F^2)$	0.0684	0.1524
GooF	1.035	1.018
No. of Parameters	481	652
CCDC #	2289308	2289309

Figure S1: Solid-state structure of **6c** with 50% probability thermal ellipsoids, hydrogen atoms omitted and the *i*Pr-substituents rendered as wire-frame for clarity. Selected bond lengths [Å] and angles [°] of **6c** (one of two independent molecules in the asymmetric unit): P1–C16 1.764(2), N1–C16 1.370(2), C16–N2 1.385(2), P2–C30 1.769(2), N3–C30 1.394(2), C30–N4 1.369(2); C1–P1–C16 104.11(8), N1–C16–P1 136.4(1), N2–C16–P1 119.2(1), N2–C16–N1 104.2(2), N3–C30–P2 119.7(1), N4–C30–P2 136.3(1), N4–C30–N3 104.0(1).

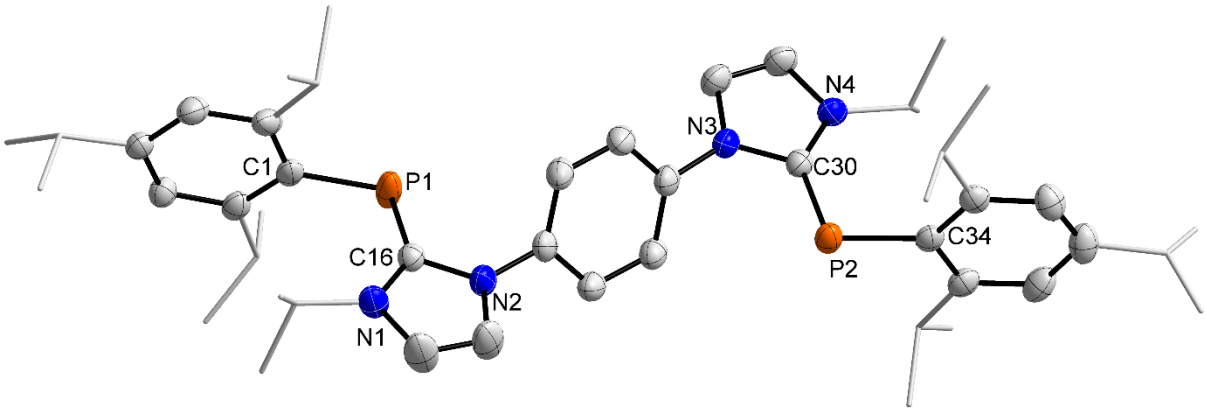
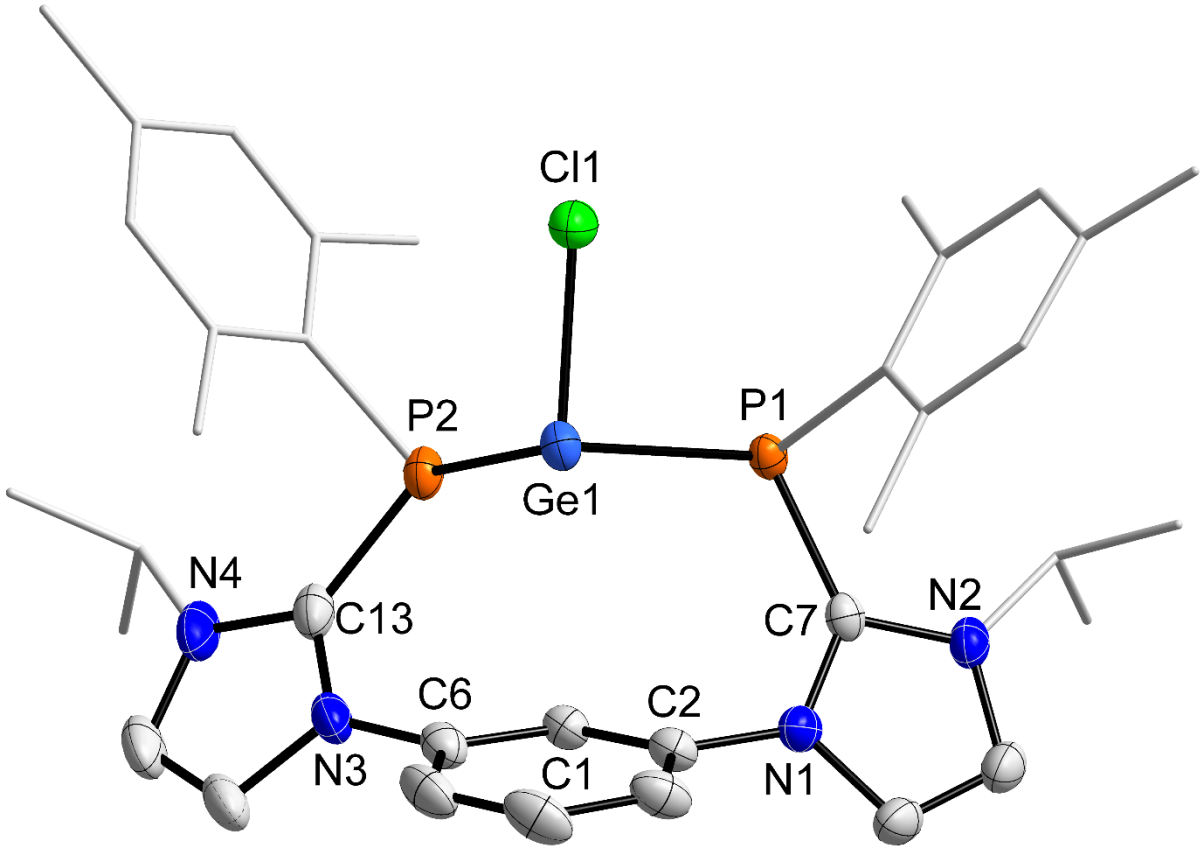
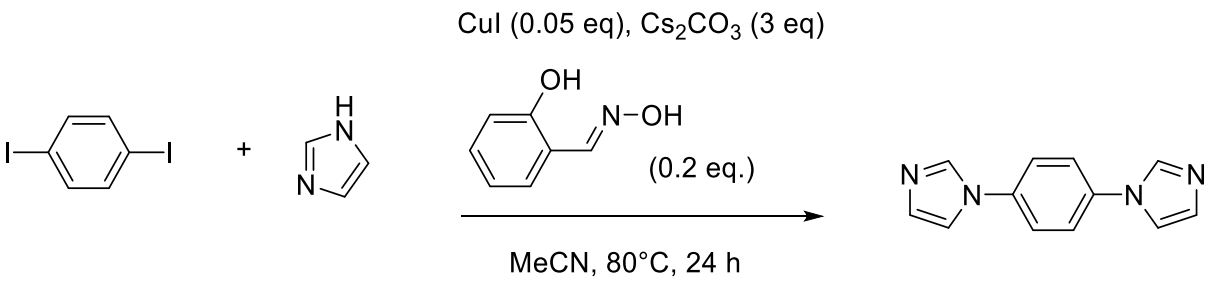


Figure S2: Solid-state structure of the cation in **8** with 50% probability thermal ellipsoids, hydrogen atoms and the $GeCl_3^-$ counter anion omitted and the *i*Pr- and Mes-substituents rendered as wire-frame for clarity. Selected bond lengths [Å] and angles [°]: Ge1−Cl1 2.3072(5), P2−Ge1 2.5226(5), P1−Ge1 2.4893(5), P2−C13 1.829(2), P1−C7 1.836(2), N4−C13 1.357(2), N3−C13 1.355(3), N2−C7 1.351(2), N1−C7 1.356(2), Ge1···C1 3.004(2); C13−P2−Ge1 108.77(6), C7−P1−Ge1 111.01(5), P2−Ge1−P1 92.86(2), P2−Ge1−Cl1 90.09(2), P1−Ge1−Cl1 84.71(2).



3 Syntheses of starting materials

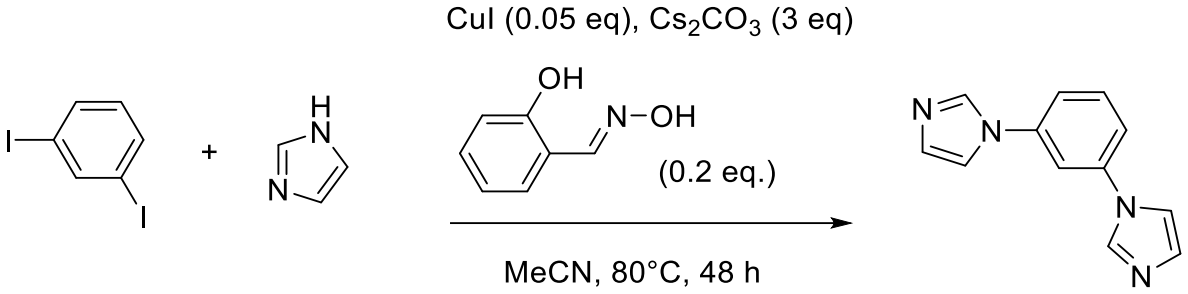
3.1 1,4-Bis(imidazolyl)benzene[12]



1,4-Diiodobenzene (7.49 g, 22.7 mmol), imidazole (3.87 mmol, 56.8 mmol), CuI (0.216g, 1.13 mmol), Cs_2CO_3 (22.2 g, 68.1 mmol) and salicylaldoxime (0.624 g, 4.6 mmol) were dissolved in 15 mL MeCN and refluxed for 22 hrs. The brown suspension was extracted with CH_2Cl_2 (4 x 100 mL). Afterwards the organic phase is washed with distilled H_2O (3 x 100 mL) and brine (1 x 150 mL). The organic phase is dried over $NaSO_4$ and after filtration the volatiles are removed in vacuo, giving 1,4-bis(imidazolyl)benzene as a yellow crystalline solid. Yield: 3.92 g, 18.6 mmol, 82 %.

^{1}H NMR (300.2 MHz, $CDCl_3$) δ = 7.87 (s (br), 2H), 7.51 (s, 4H), 7.29 (s (br), 2H), 7.23 (s (br), 2H) ppm.

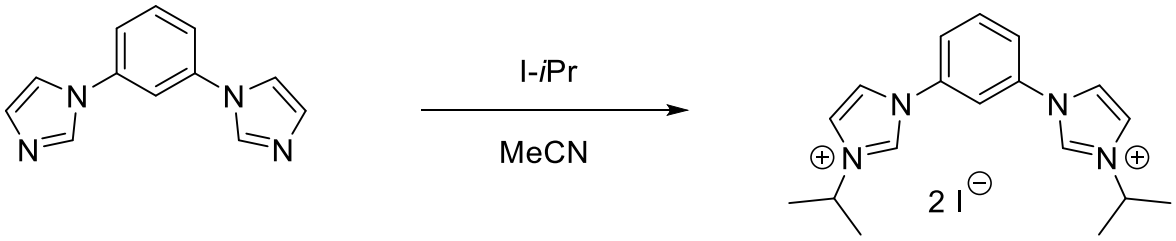
3.2 1,3-Bis(imidazolyl)benzene[13]



1,3-Diiodobenzene (7.49 g, 22.7 mmol), imidazole (3.87 mmol, 56.8 mmol), CuI (0.216 g, 1.13 mmol), Cs_2CO_3 (22.2 g, 68.1 mmol) and salicylaldoxime (0.624 g, 4.6 mmol) were dissolved in 20 mL MeCN and refluxed for 48 h. The brown suspension was extracted with CH_2Cl_2 (3 x 100 mL). Afterwards the organic phase is washed with distilled H_2O (3 x 150 mL) and Brine (1 x 150 mL). The organic phase is dried over $NaSO_4$ and removed in vacuo. The result is neat yellow crystals of 1,3-bis(imidazolyl)benzene (3.53 g, 16.7 mmol, 74 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s (br), 2H), 7.66 – 7.57 (m, 1H), 7.44-7.41 (m, 2H), 7.41-7.39 (m, 1H), 7.34 (s (br), 2H), 7.27 (s (br), 2H) ppm.

3.3 2,6-bis(3-isopropylimidazolium)benzene diiodide[14]

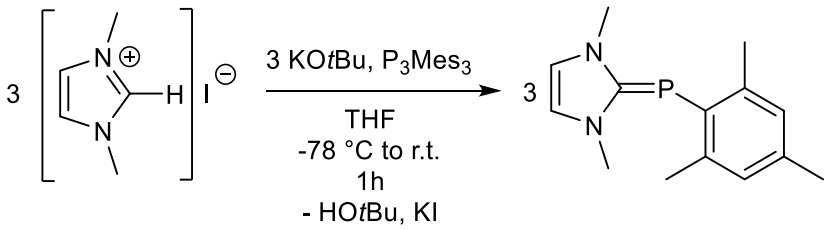


1,3-bis(imidazolyl)benzene (0.500 g, 2.3 mmol) is suspended in MeCN (5 mL). I-*i*Pr (0.850 g, 5 mmol, 2.2 eq.) is added dropwise. The reaction mixture is degassed and heated to 80 °C for 4 days. The volatiles are removed in vacuo and the yellow solid is recrystallized from MeOH and washed with Et_2O (3x 10 mL) resulting in off white 2,6-bis(3-isopropylimidazolium)benzene diiodide (0.772 g, 1.4 mmol, 61 %)

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.96 (s, 1H), 8.46 (q, J = 1.6 Hz, 2H), 8.39 (d, J = 2.1 Hz, 1H), 8.26 (t, J = 1.9 Hz, 2H), 8.11 – 8.04 (m, 2H), 4.77 (hept, $^3J_{HH}$ = 6.7 Hz, 2H), 1.60 (d, $^3J_{HH}$ = 6.7 Hz, 12H) ppm.

4 Syntheses of compounds

4.1 MesP=IMe$_2$ (1a)



A mixture of *N,N'*-dimethylimidazolium iodide (0.250 g, 1.12 mmol), KO*t*Bu (0.130 g, 1.16 mmol) and P_3Mes_3 (0.174 g, 0.39 mmol) was dissolved in THF (20 mL) at −78 °C (dry ice/EtOH). The colour changes to yellow upon slow warming to ambient temperature. The solution was stirred additionally for 1 h at room temperature. Using an external solvent trap, the reaction mixture was evaporated to dryness. The solid residue was triturated in *n*-hexane (10 mL) and the mixture was filtered through a PE-tube equipped with a glass fibre filter. The filtrate was concentrated to incipient crystallization and placed in a freezer at −30 °C for 24 h. MesP=IMe$_2$ (**1a**) was afforded as a yellow crystalline solid. Yield: 0.07 g (0.28 mmol, 25%). The analytical data is in line with those reported in the literature.[15]

^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ = −74.15 ppm. **^{1}H NMR** (400 MHz, C_6D_6) δ = 6.96-6.90 (m, 2H, Ar*H*), 5.65 (s, 2H, ((*H*CN(CH$_3$))$_2$C), 2.69 (s, 6H, ArC*H*$_3$), 2.68 (s, 6H, ArC*H*$_3$), 2.64 (s, 6H, NC*H*$_3$), 2.23 (s, 6H, ArC*H*$_3$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6) δ 170.2 (d, $^1J_{PC}$ = 100.7 Hz, ((H$_2$CN(CH$_3$))$_2$*C*), 143.2 (d, $^2J_{PC}$ = 10.1 Hz, *o*-*C*Ar), 138.8 (d, $^1J_{PC}$ = 45.3 Hz, *i*-*C*Ar), 134.2 (*m*-*C*Ar), 128.2 (*p*-*C*Ar), 118.3 (d, J_{PC} = 3.2 Hz, ((H*C*N(CH$_3$))$_2$C), 35.6 (d, J_{PC} = 10.6 Hz, N-*C*H$_3$), 25.0 (d, J_{PC} = 11.9 Hz, o-Ar-*C*H$_3$), 21.2 (p-Ar-*C*H$_3$) ppm. **MS** (ESI) [MH$^+$] expected: 247.1364, found: 247.1369.

Figure S3: ^{1}H NMR spectrum of MesP=IMe$_2$ (**1a**) (400 MHz, C_6D_6, r.t.).

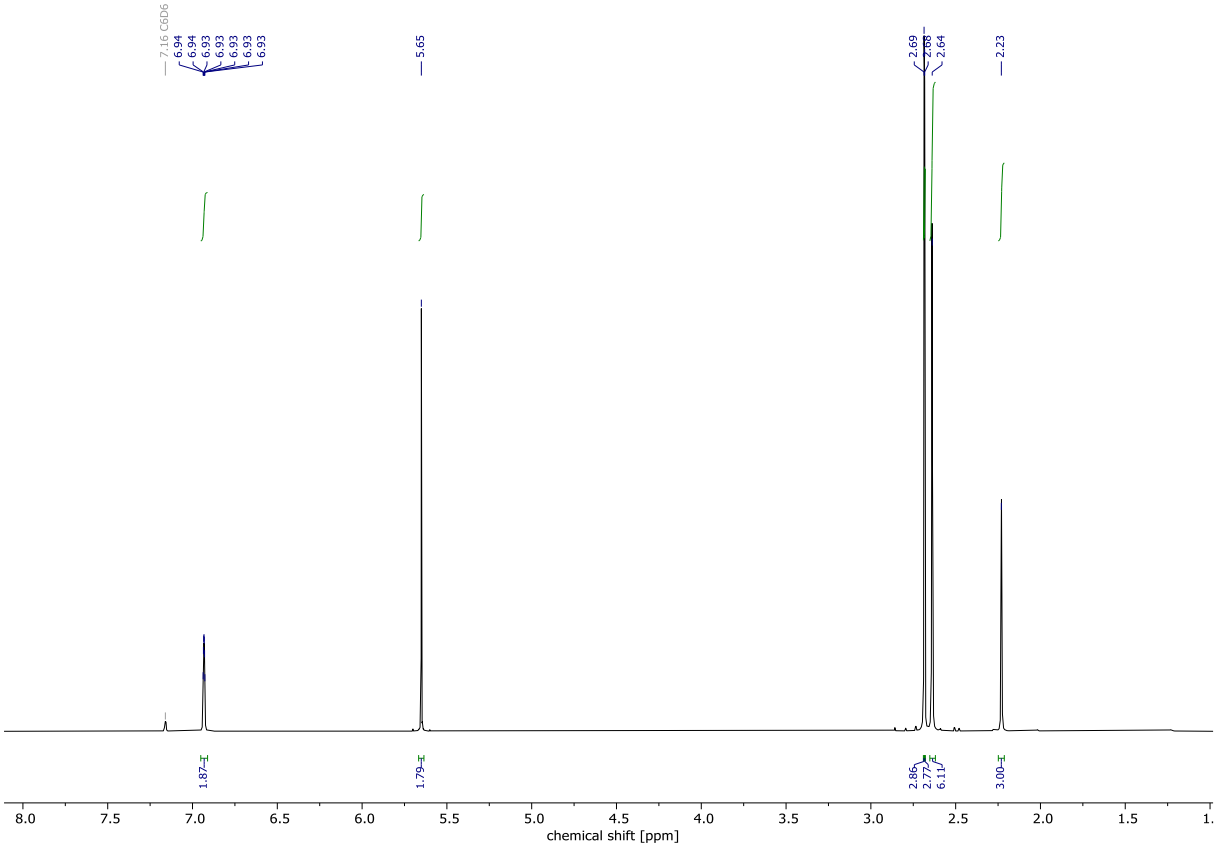


Figure S4: ^{13}C NMR spectrum of MesP=IMe$_2$ (**1a**) (101 MHz, C_6D_6, r.t.).

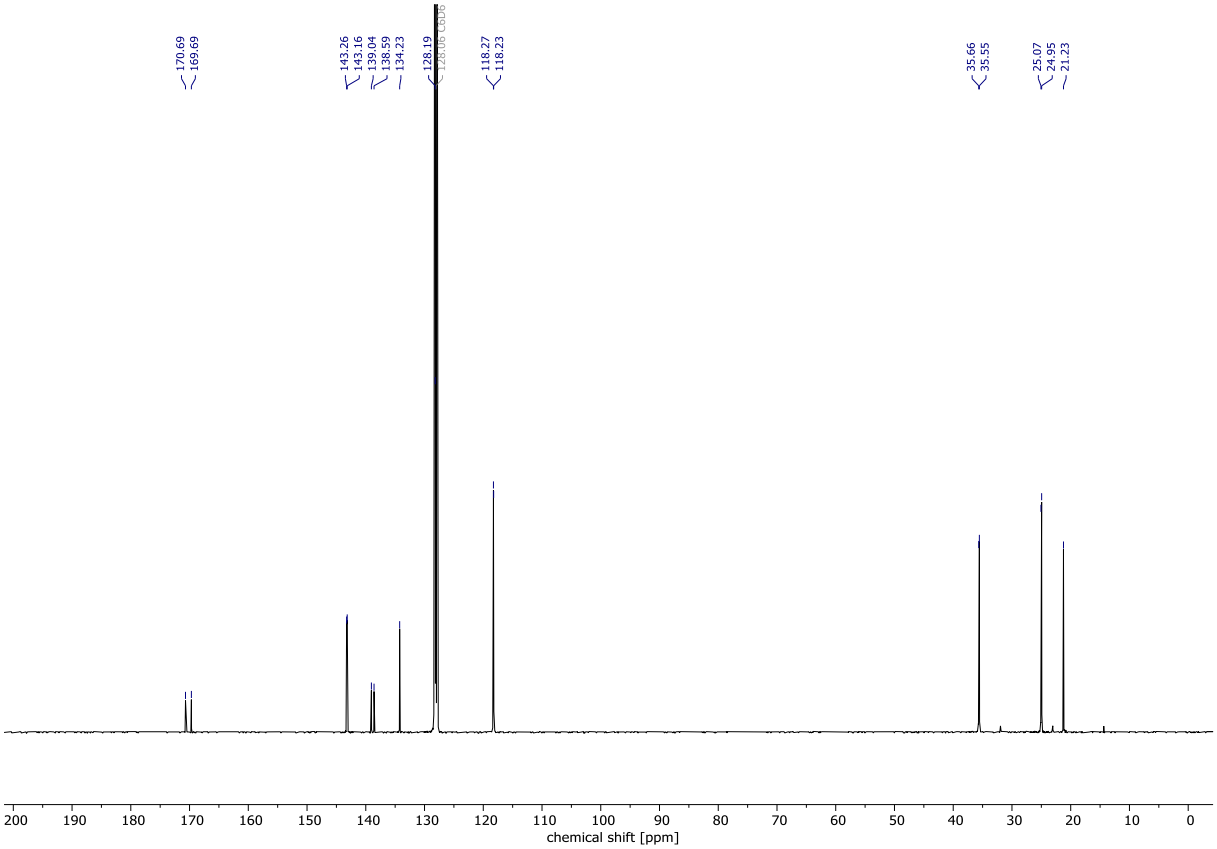
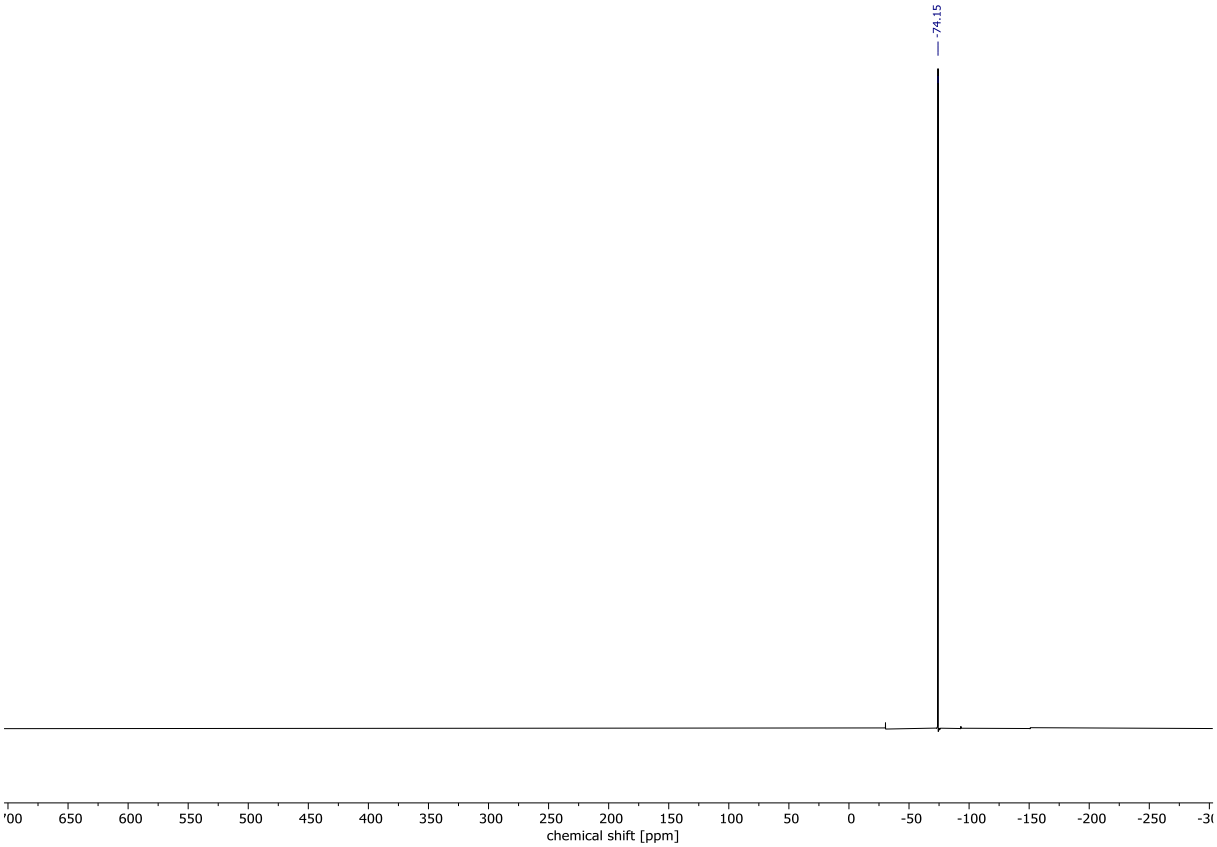
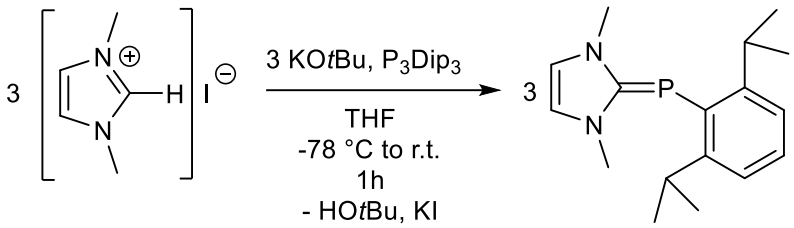


Figure S5: ^{31}P NMR spectrum of MesP=IMe_2 (**1a**) (162 MHz, C_6D_6, r.t.).



4.2 DipP=IMe$_2$ (1b)



A mixture of *N,N'*-dimethylimidazolium iodide (0.037 g, 0.3 mmol), KO*t*Bu (0.034 g, 0.3 mmol) and P_3Dip_3 (0.058 g, 0.1 mmol) was dissolved in THF (5 mL) at −78 °C (dry ice/EtOH). The colour changes to yellow upon slow warming to ambient temperature. The solution was stirred additionally for 1 h at room temperature. Using an external solvent trap, the reaction mixture was evaporated to dryness. The solid residue was triturated in *n*-hexane (10 mL) and the mixture was filtered through a PE-tube equipped with a glass fibre filter. The filtrate was concentrated to incipient crystallization and placed in a freezer at −30 °C for 72 h. DipP=IMe$_2$ (**1b**) was obtained as a yellow crystalline solid. Yield: 0.020 g (0.07 mmol, 23%).

CHN calc. (found) in %: C 70.81 (68.84), H 8.74 (8.45), N 9.71 (8.08). **^{31}P{^{1}H} NMR** (121.5 MHz, C_6D_6): δ = −84.0 ppm. **^{1}H NMR** (300.13 MHz, C_6D_6): δ = 7.29 (m, 1H, Ar*H*), 7.23-7.17 (m, 2H, Ar*H*), 5,51 (s, 2H, ((*H*CN(CH$_3$))$_2$C), 4.70 (hept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 2.67 (d, J_{PH} = 1.6 Hz, 6H, NC*H*$_3$), 1.32 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ = 169.8 (d, $^1J_{PC}$ = 103.7 Hz, ((HCN(CH$_3$))$_2$*C*), 154.9 (d, J_{PC} = 8.1 Hz, *o*-*C*Ar), 139.6 (d, $^1J_{PC}$ = 46.1 Hz, *i*-*C*Ar), 128.1 (*p*-*C*Ar), 123.2 (*m*-*C*Ar), 118.5 (d, J_{PC} = 3.3 Hz, (H*C*N(CH$_3$))$_2$*C*), 36.1 (d, J_{PC} = 11.4 Hz, N-*C*H$_3$), 34.3 (d, J_{PC} = 11.4 Hz, *C*H(CH$_3$)$_2$), 24.8 (CH(*C*H$_3$)$_2$) ppm. **MS** (ESI) [MH$^+$] expected: 289.1833, found: 289.1838.

Single crystals suitable for X-ray diffraction were grown from a saturated *n*-hexane solution at −30 °C.

Figure S6: ^{1}H NMR spectrum of DipP=IMe$_2$ (**1b**) (300.1 MHz, C_6D_6, r.t.).

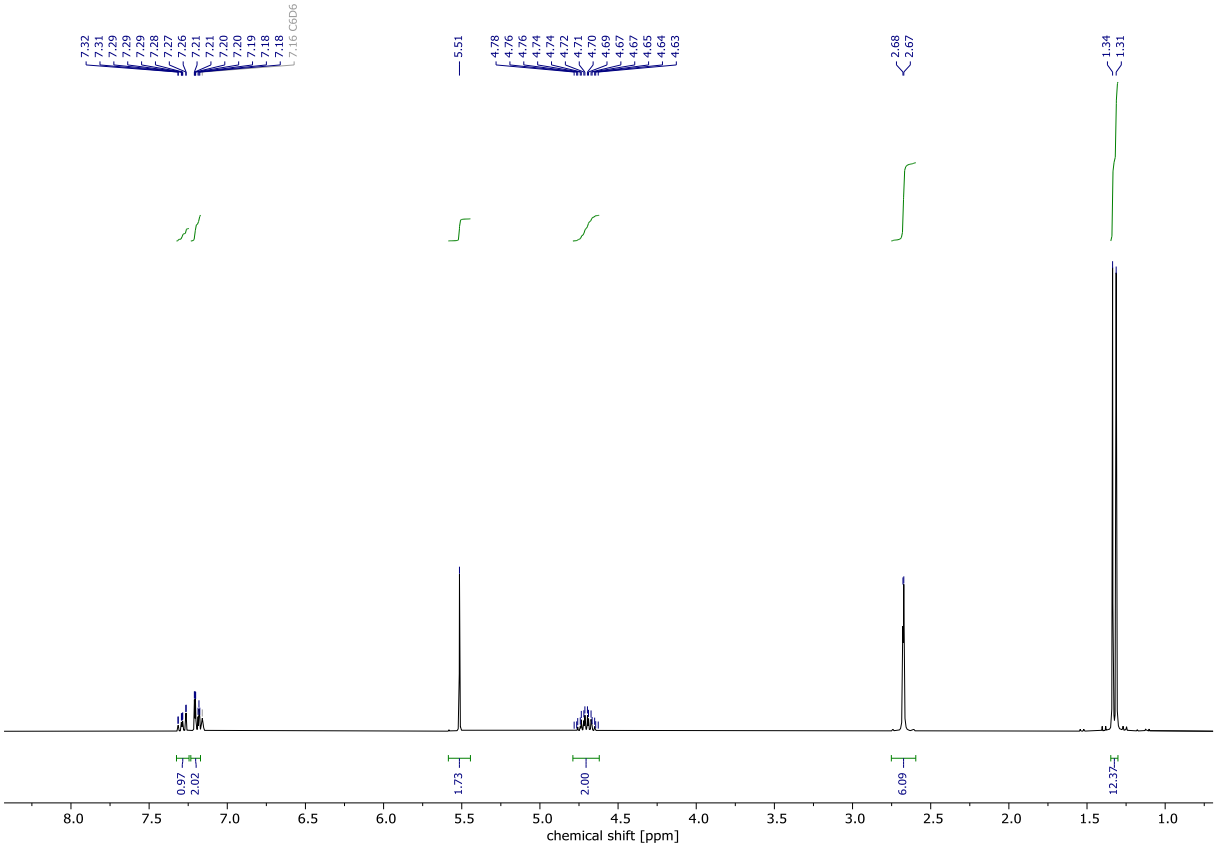


Figure S7: ^{13}C NMR spectrum of DipP=IMe$_2$ (**1b**) (100.1 MHz, C_6D_6, r.t.).

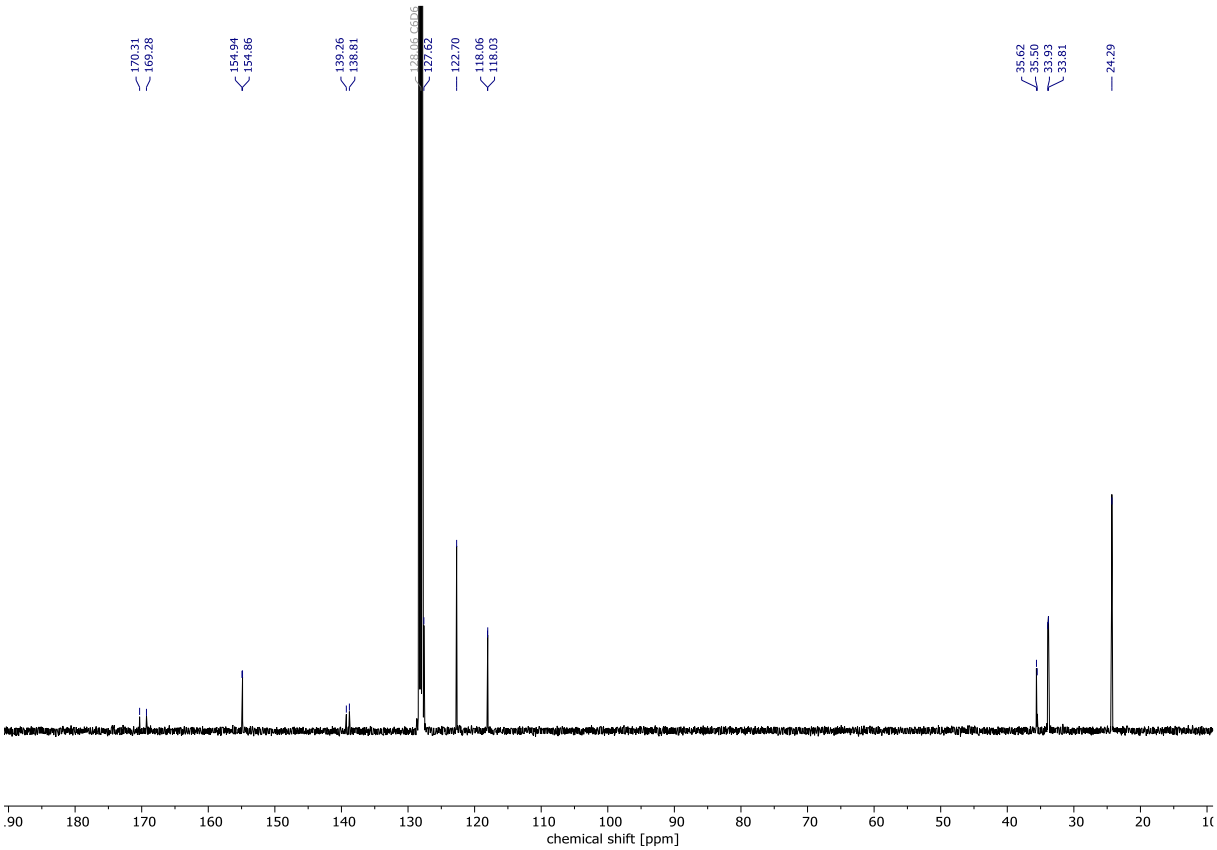
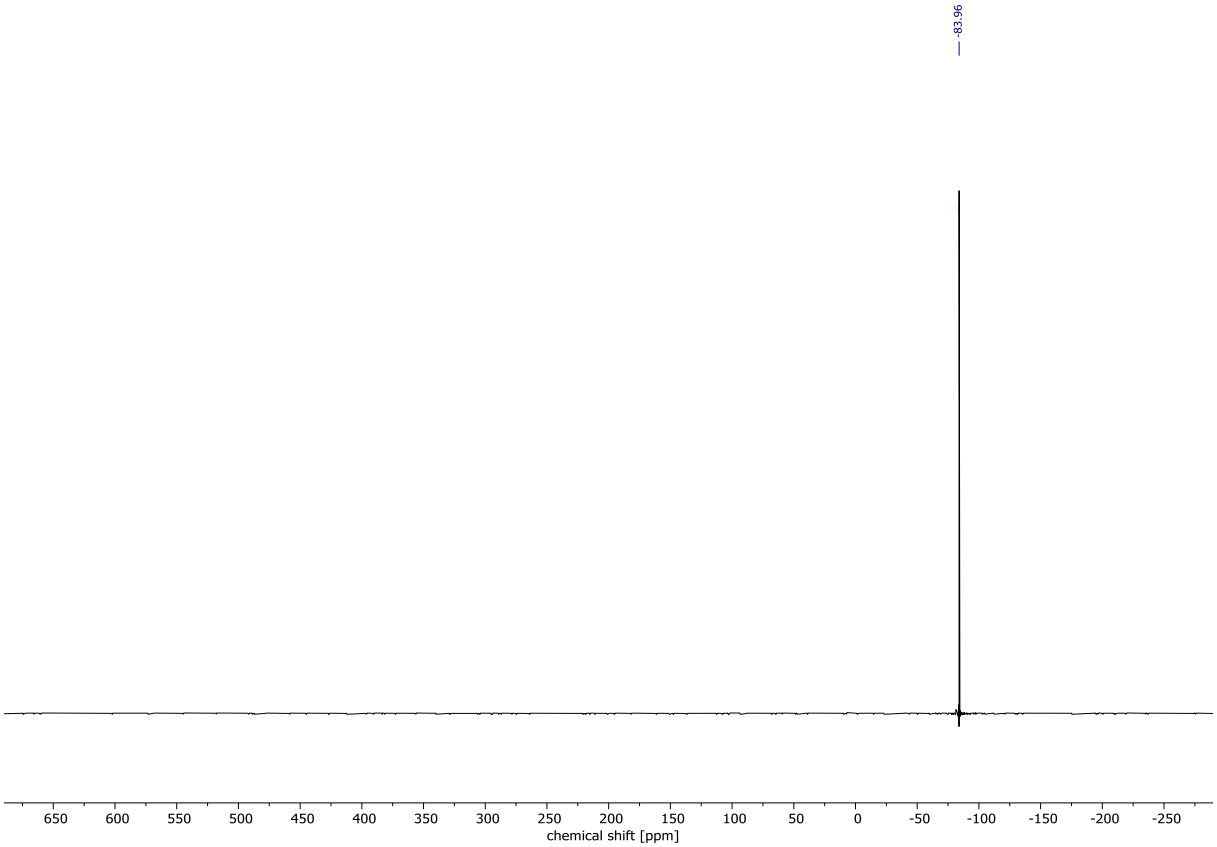
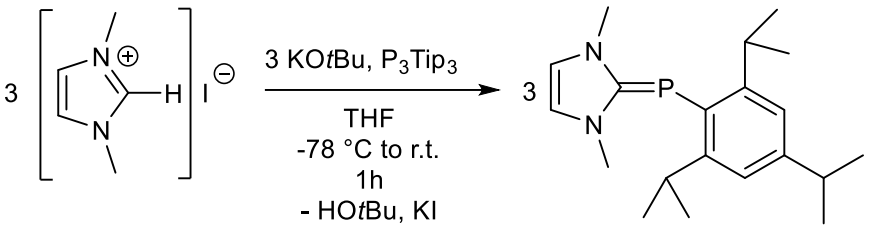


Figure S8: ^{31}P NMR spectrum of DipP=IMe_2 (**1b**) (121 MHz, C_6D_6, r.t.).



4.3 TipP=IMe$_2$ (1c)



A mixture of *N,N'*-dimethylimidazolium iodide (0.057 g, 0.26 mmol), KO*t*Bu (0.030 g, 0.3 mmol) and P_3Tip_3 (0.060 g, 0.09 mmol) was dissolved in THF (5 mL) at −78 °C (dry ice/ ethanol). The color changes to yellow upon slow warming to ambient temperature. The solution was stirred for 16 h at room temperature. Using an external solvent trap, the reaction mixture was evaporated to dryness. The solid residue was triturated in *n*-hexane (10 mL) and the mixture was filtered through a PE-tube equipped with a glass fibre filter. The filtrate was concentrated to incipient crystallization and placed in a refrigerator at 5 °C for 24 h. TipP=IMe$_2$ (**1c**) was obtained as a yellow crystalline solid. Yield: 0.040 g (0.12 mmol, 47%).

CHN calc. (found) in %: C 72.69 (72.37), H 9.46 (9.70), N 8.48 (6.73). **^{31}P{^{1}H} NMR** (121.5 MHz, C_6D_6): δ = −84.52 ppm. **^{1}H NMR** (300.13 MHz, C_6D_6): δ = 7.19 (d, J = 1.9 Hz, 2H, Ar<u>*H*</u>), 5.54 (s, 2H, ((<u>*H*</u>CN(CH$_3$))$_2$C), 4.74 (hept-d, J_{PH} = 4,8 Hz, $^3J_{HH}$ = 6.9 Hz, 2H, *o*-C<u>*H*</u>(CH$_3$)$_2$), 2.89 (hept, $^3J_{HH}$ = 6.9 Hz, 1H, *p*-C<u>*H*</u>(CH$_3$)$_2$), 2.71 (d, J_{PH} = 1.7 Hz, 6H, NC<u>*H*</u>$_3$), 1.37 (d, $^3J_{HH}$ = 6.9 Hz, 12H, *o*-CH(C<u>*H*</u>$_3$)$_2$), 1.31 (d, $^3J_{HH}$ = 6.9 Hz, 6H, *p*-CH(C<u>*H*</u>$_3$)$_2$) ppm. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6) δ = 169.9 (d, $^1J_{PC}$ = 104.1 Hz, ((HCN(CH$_3$))$_2$<u>*C*</u>), 154.9 (d, J_{PC} = 8.3 Hz, *o*-<u>*C*</u>Ar), 147.7 (*p*-<u>*C*</u>Ar), 135.8 (d, $^1J_{PC}$ = 44.9 Hz, *i*-<u>*C*</u>Ar), 120.75 (*m*-<u>*C*</u>Ar), 118.0 (d, J = 3.5 Hz, ((H<u>*C*</u>N(CH$_3$))$_2$C), 35.6 (d, J_{PC} = 11.7 Hz, *o*-<u>*C*</u>H(CH$_3$)$_2$), 34.8 (*p*-<u>*C*</u>H(CH$_3$)$_2$), 34.0 (d, J_{PC} = 11.2 Hz, N-<u>*C*</u>H$_3$), 24.5 (*p*-CH(<u>*C*</u>H$_3$)$_2$), 24.4 (*o*-CH(<u>*C*</u>H$_3$)$_2$) ppm. **MS** (ESI) [MH$^+$] expected: 331.2303, found: 331.2301.

Single crystals suitable for X-ray diffraction were grown from a saturated *n*-hexane solution at −30 °C.

Figure S9: ^{1}H NMR spectrum of TipP=IMe$_2$ (**1c**) (300.1 MHz, C_6D_6, r.t.).

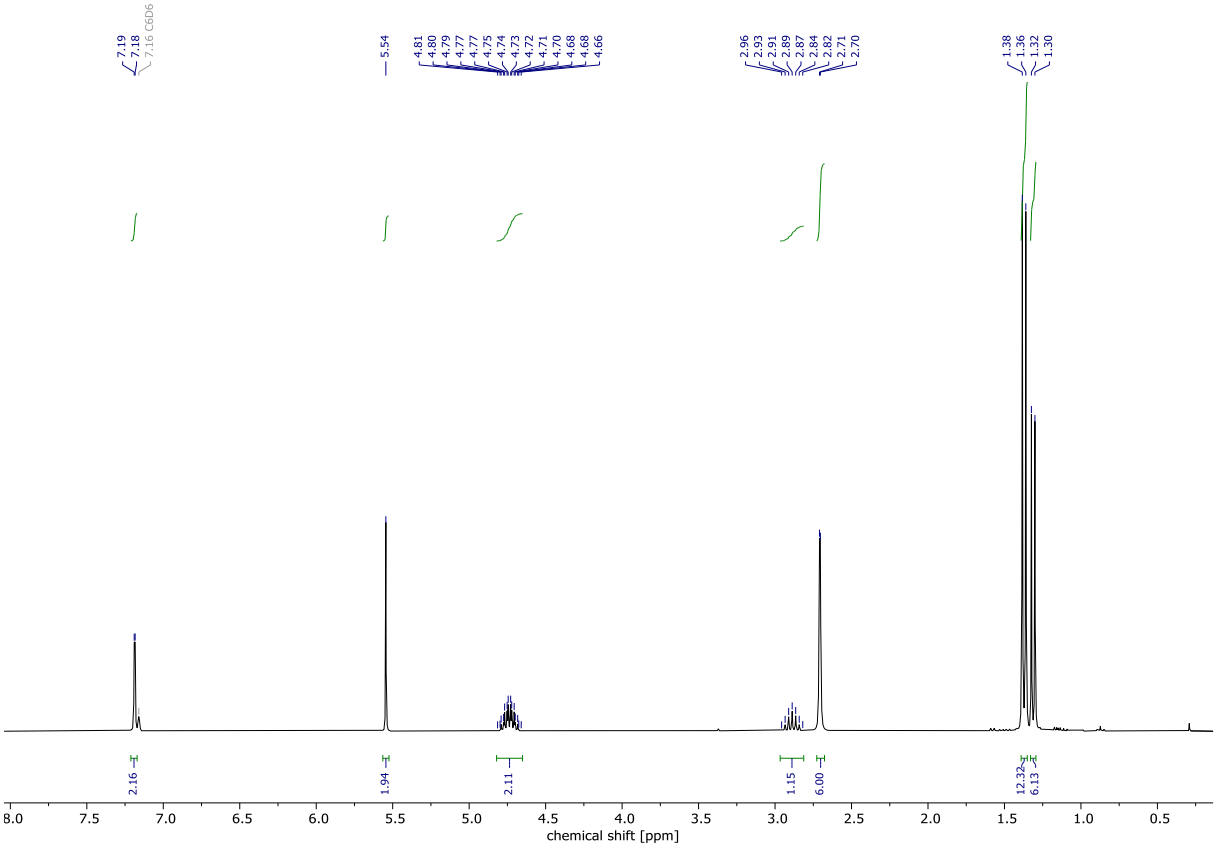


Figure S10: ^{13}C NMR spectrum of TipP=IMe$_2$ (**1c**) (75.5 MHz, C_6D_6, r.t.).

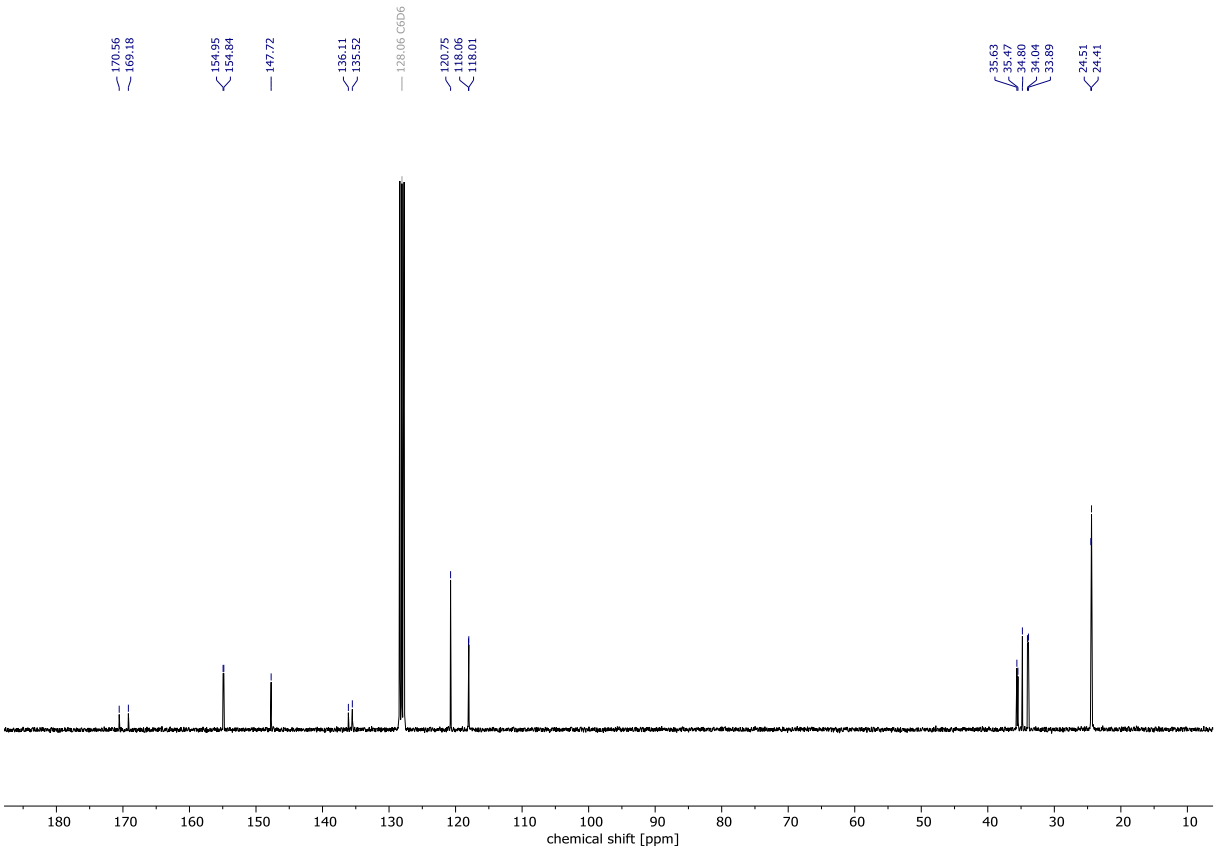
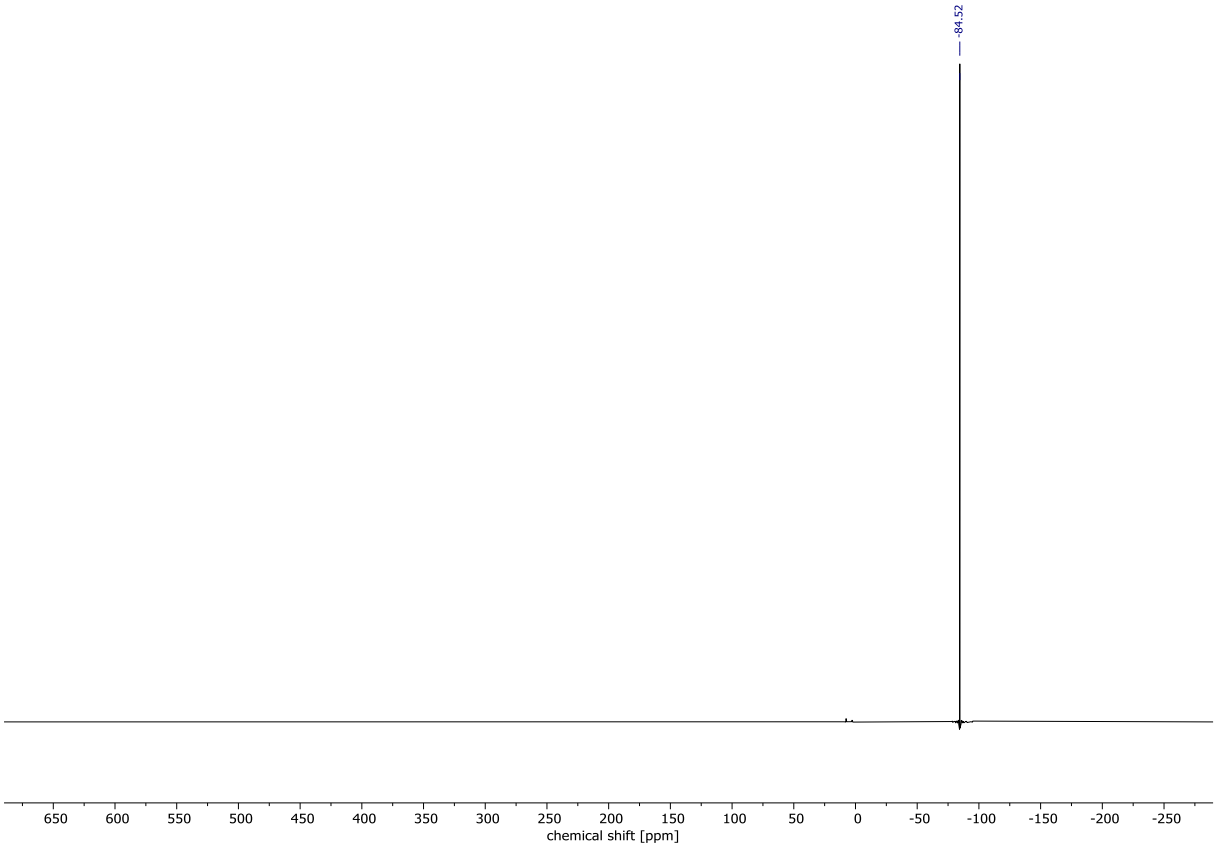
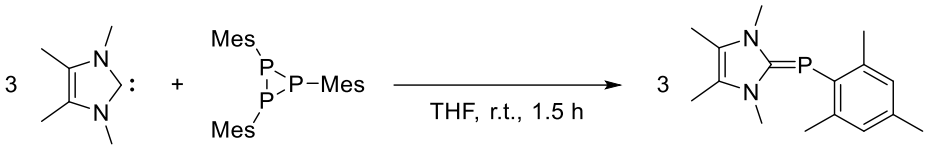


Figure S11: ^{31}P NMR spectrum of TipP=IMe_2 (**1c**) (121.5 MHz, C_6D_6, r.t.).



4.4 MesP=IMe$_4$ (2a)



IMe$_4$ (0.120 g, 0.955 mmol) and P$_3$Mes$_3$ (0.143 mg, 0.319 mmol) were combined in a Schlenk flask and dissolved in THF (5 mL) at ambient temperature, resulting in a turbid orange solution. The reaction mixture was stirred for 1.5 h at room temperature. Subsequently, the solvent was evaporated using an external trap and the solid was extracted with *n*-hexane (10 mL), filtered through a canula fitted with a glass fibre filter and concentrated to incipient crystallization. Standing in a freezer at −30 °C for 24 h resulted in the deposition of yellow crystals of MesP=IMe$_4$ (**2a**). Yield: 0.114 g (0.416 mmol, 45 %). The NMR data agrees with previous reports on **2a**.[16]

^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ [ppm] = −74.87. **^{1}H NMR** (400 MHz, C_6D_6): δ [ppm] = 7.01 (m, 2H, Ar*H*), 2.81 (d, J_{PH} = 0.9 Hz, 6H, NC*H*$_3$), 2.72 (s, 6H, *o*-C*H*$_3$), 2.28 (s, 3H, *p*-C*H*$_3$), 1.24 (s, 6H, CC*H*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6) δ = 169.2 (d, $^1J_{PC}$ = 97.6 Hz, N$_2$*C*=P), 142.5 (d, J = 9.8 Hz, *o*-Ar*C*), 140.6 (d, $^1J_{PC}$ = 48.2 Hz, *i*-Ar*C*), 133.5 (Ar*C*), 121.1 (backbone-*C*CH$_3$), 32.4 (d, J = 11.6 Hz, N*C*H$_3$), 25.0 (d, J = 12.5 Hz, *o*-Ar*C*H$_3$), 21.3 (*p*-Ar*C*H$_3$), 8.5 (backbone-C*C*H$_3$) ppm.

Single crystals suitable for X-ray diffraction were grown from a saturated *n*-hexane solution at −30 °C.

Figure S12: ^{1}H NMR spectrum of MesP=IMe$_4$ (**2a**) (400 MHz, C_6D_6, r.t.).

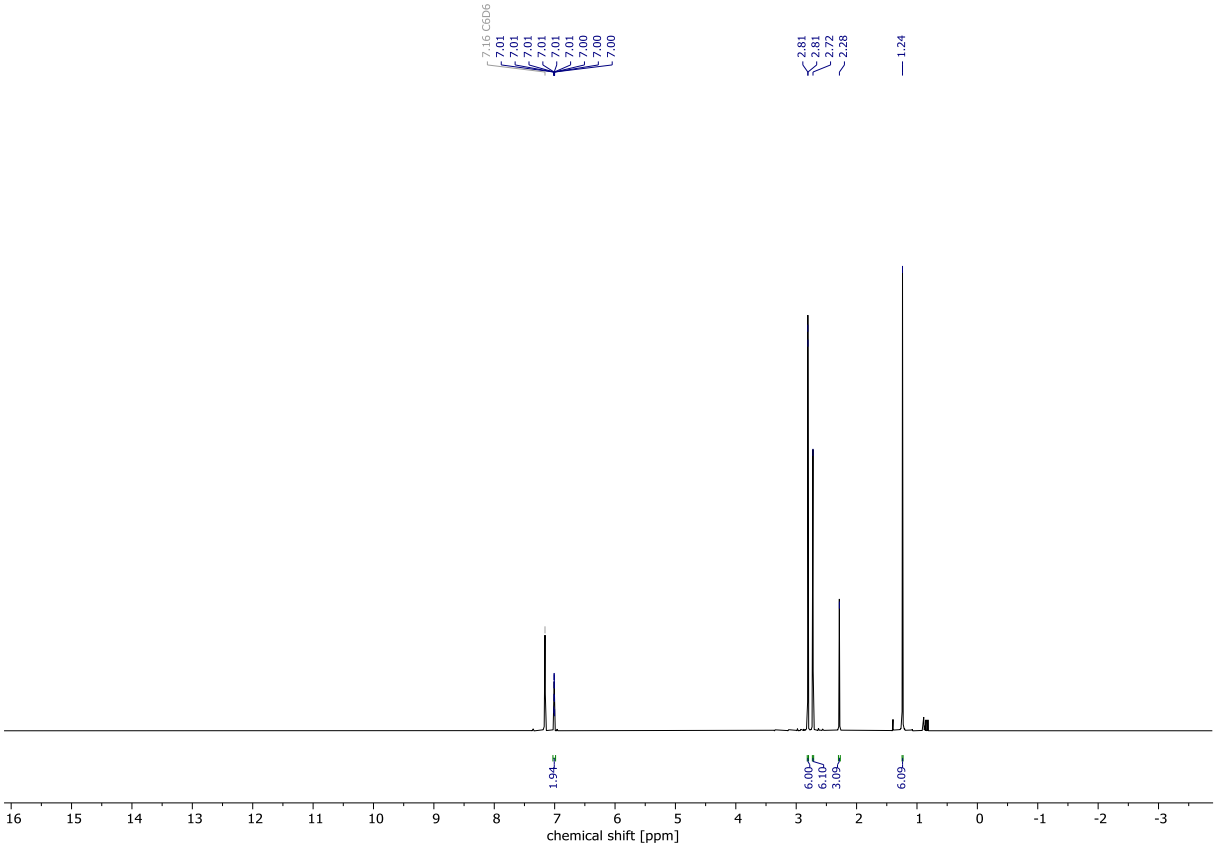


Figure S13: ^{13}C NMR spectrum of MesP=IMe$_4$ (**2a**) (101 MHz, C_6D_6, r.t.).

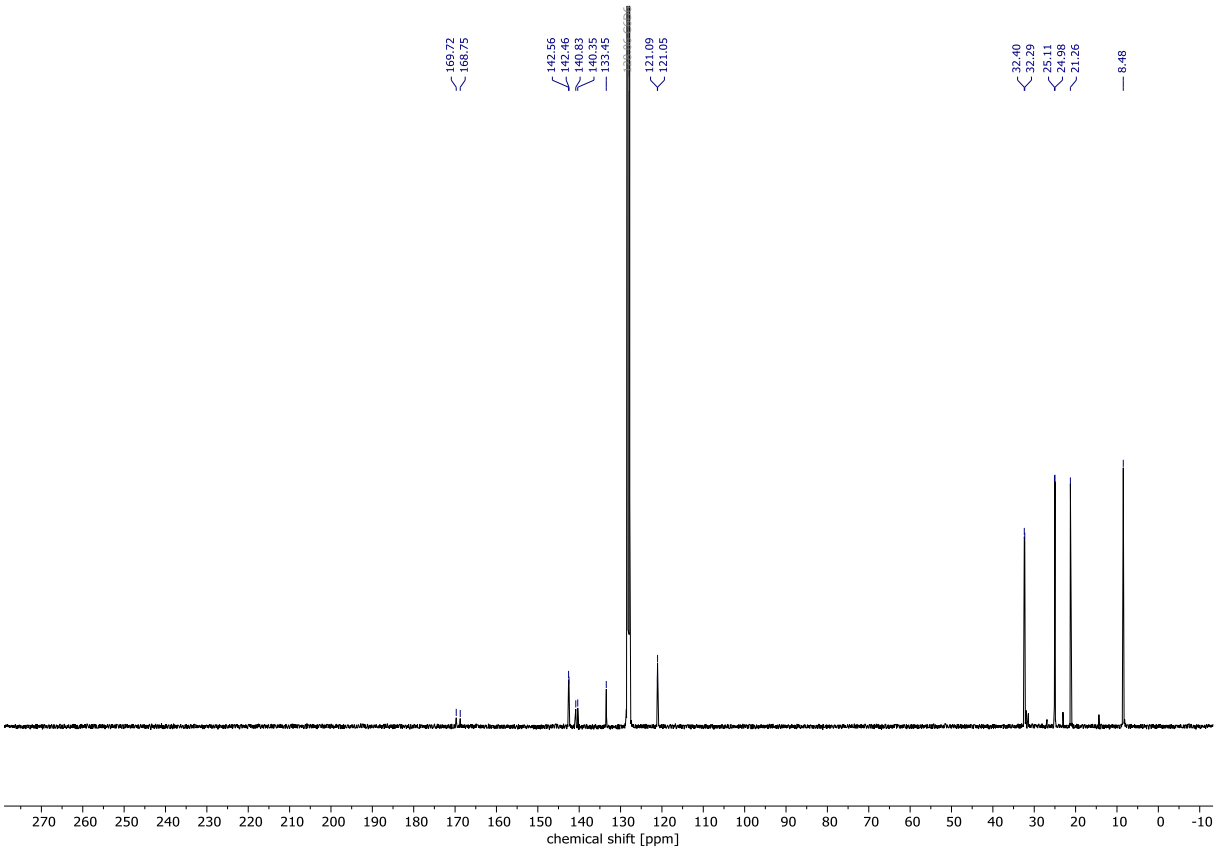
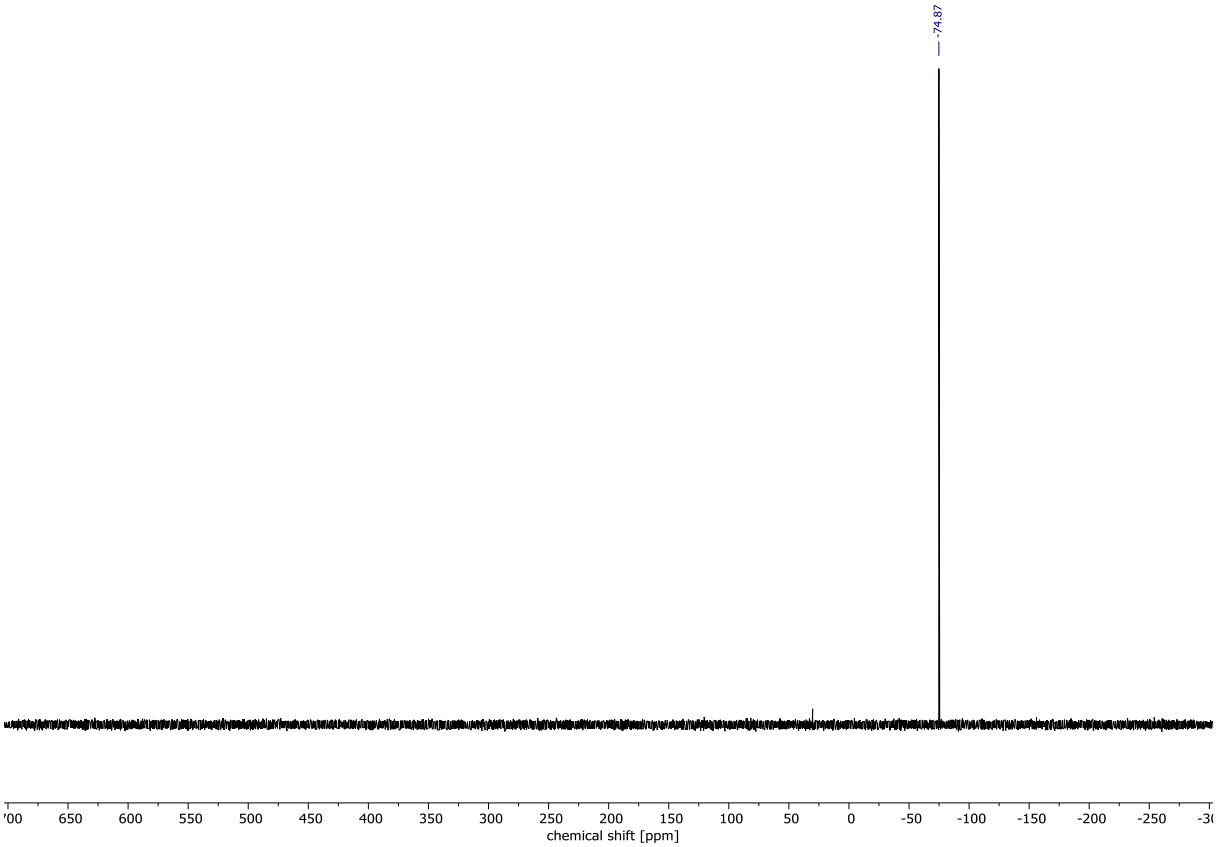


Figure S14: ^{31}P NMR spectrum of MesP=IMe$_4$ (**2a**) (162 MHz, C_6D_6, r.t.).



4.5 DipP=IMe$_4$ (2b)

IMe$_4$ (0.032 g, 0.26 mmol) and P_3Dip_3 (0.049 mmol, 0.086 mmol) were combined in Schlenk flask and dissolved in THF (5 mL) at ambient temperature, resulting in a turbid orange solution. The reaction mixture was stirred for 1.5 h at room temperature. Subsequently, the solvent was evaporated using an external trap and the solid residue was extracted with *n*-hexane (10 mL), filtered through a canula fitted with a glass fibre filter and was concentrated to incipient crystallization. Standing in a freezer at −30 °C for 24 h resulted in the deposition of DipP=IMe$_4$ (**2b**) as a yellow crystalline solid. Yield: 0.036 g (0.114 mmol, 44%). The analytical data agrees with a previous report on **2b**.[17]

CHN calc. (found) in %: C 72.12 (72.34), H 9.24 (9.47), N 8.85 (8.51). **^{31}P{^{1}H} NMR** (C_6D_6, 162 MHz): δ = −86.5 ppm. **^{1}H NMR** (400 MHz, C_6D_6): δ = 7.31 (dd, J = 6.5, 2.4 Hz, 1H, *o*-ArC*H*), 7.24 (d, J = 2.5 Hz, 1H, *p*-ArC*H*), 7.23 – 7.20 (m, 1H, *o'*-ArC*H*), 4.81 (sept-d, $^3J_{HH}$ = 6.9 Hz, $^4J_{HP}$ = 4.8 Hz, 2H, *o*-C*H*(CH$_3$)$_2$), 2.93 (sept, $^3J_{HH}$ = 6.9 Hz, 1 H, *p*-C*H*(CH$_3$)$_2$), 2.81 (d, $^4J_{HP}$ = 1.2 Hz, 6H, NC*H*$_3$), 1.41 (d, $^3J_{HH}$ = 6.9 Hz, 12H, *o*-CH(C*H*$_3$)$_2$), 1.35 (d, $^3J_{HH}$ = 6.9 Hz, 6H, *p*-CH(C*H*$_3$)$_2$), 1.28 (s, 6H, CC*H*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ = 169.2 (d, $^1J_{PC}$ = 103.1 Hz, ((CH$_3$CN(CH$_3$))$_2$*C*), 154.4 (d, J = 8.5 Hz, *o*-*C*Ar), 140.8 (d, $^1J_{PC}$ = 48.5 Hz, *i*-*C*Ar), 127.1 (*p*-*C*Ar), 122.7 (*m*-*C*Ar), 120.7 (d, J_{PC} = 3.5 Hz, ((CH$_3$*C*N(CH$_3$))$_2$C)), 33.9 (d, J = 12.0 Hz, ((CH$_3$CN(*C*H$_3$))$_2$C)), 32.2 (d, J = 12.7 Hz, *C*H(CH$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$), 8.4 ((C*H*$_3$CN(CH$_3$))$_2$C) ppm. **MS** (ESI) [MH$^+$] expected: 317.2147, found: 317.2146.

Figure S15: ^{1}H NMR spectrum of DipP=IMe$_4$ (**2b**) (400 MHz, C_6D_6, r.t.).

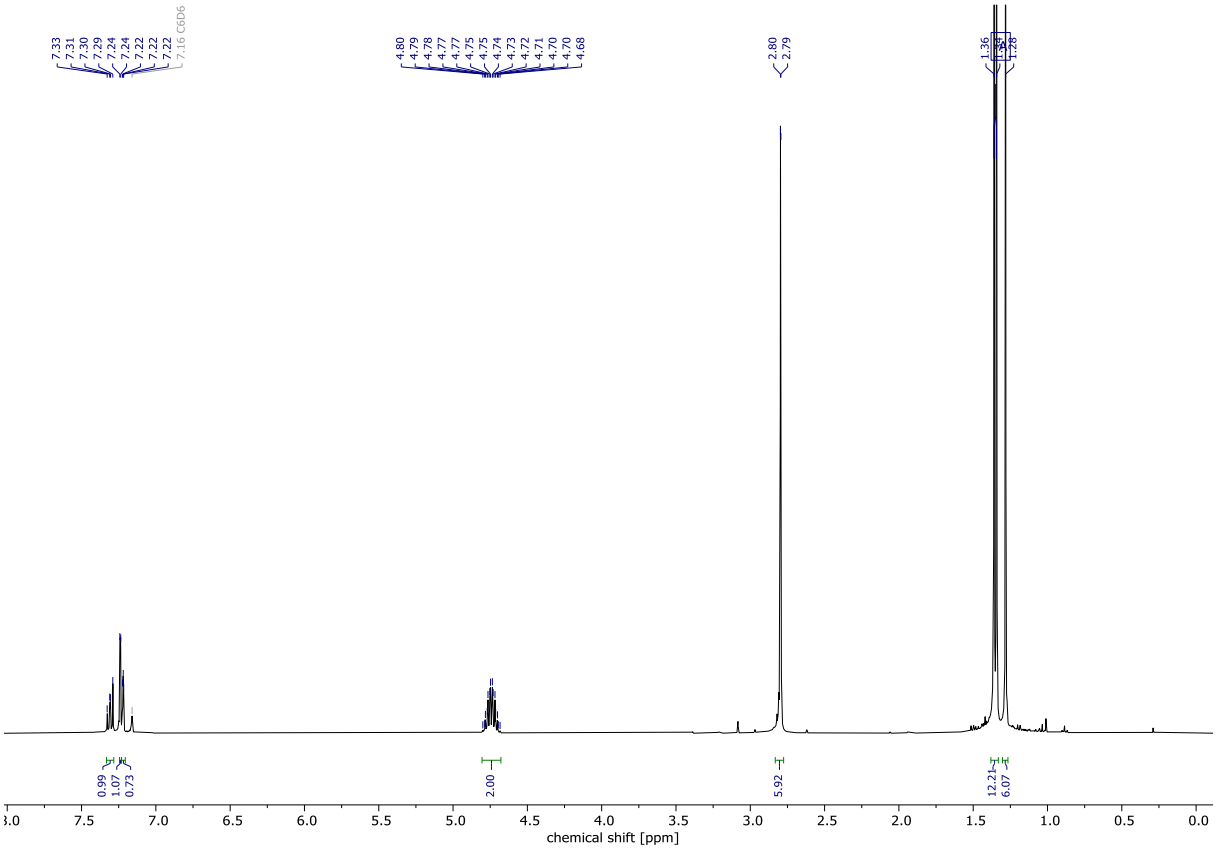


Figure S16: ^{13}C NMR spectrum of DipP=IMe$_4$ (**2b**) (101 MHz, C_6D_6, r.t.).

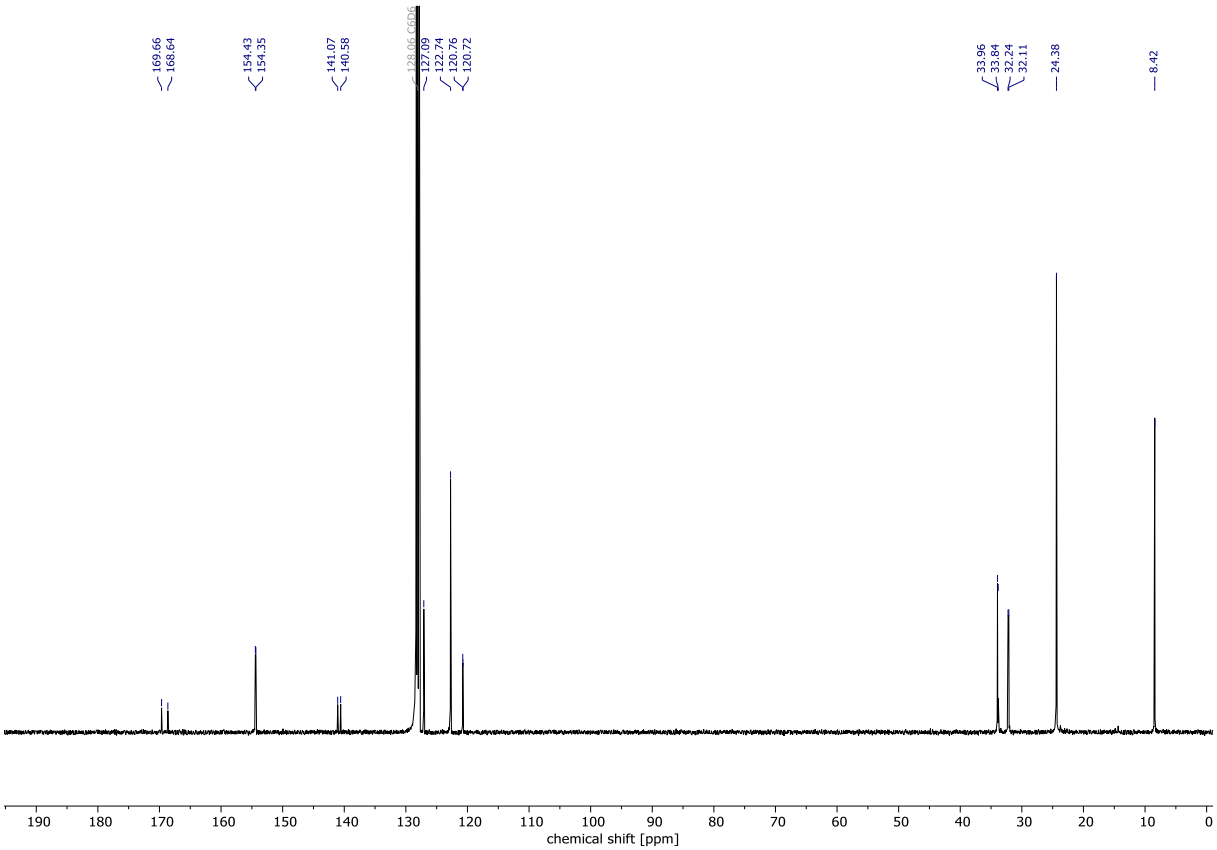
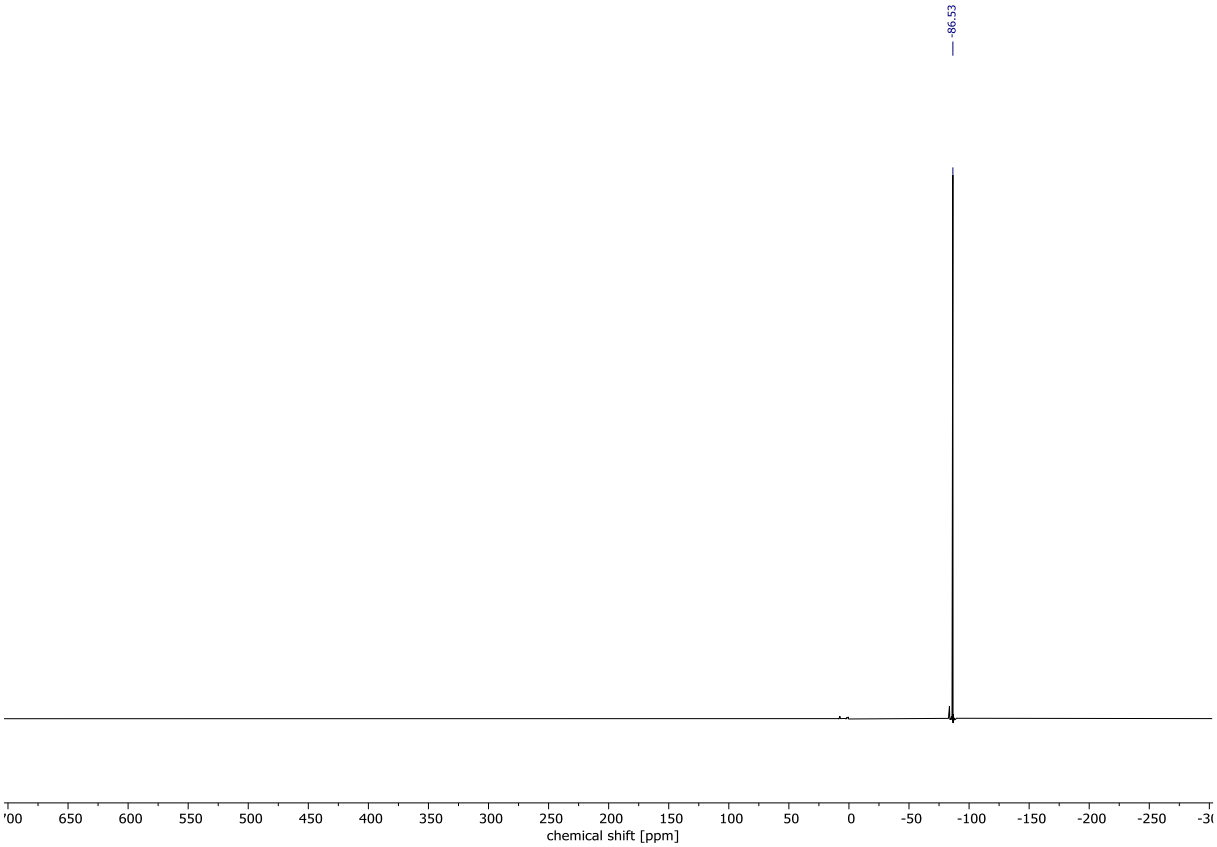
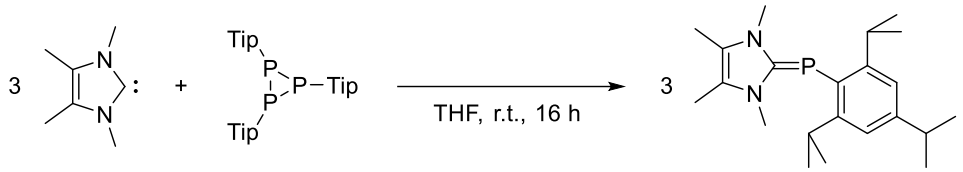


Figure S17: ^{31}P NMR spectrum of DipP=IMe_4 (**2b**) (162 MHz, C_6D_6, r.t.).



4.6 IMe$_4$PTip (2c)



IMe_4 (0.112 g, 0.9 mmol) and P_3Tip_3 (0.211 mmol, 0.3 mmol) were combined and dissolved in THF (5 mL) at ambient temperature, resulting in an orange solution. This solution was stirred for 16 h at room temperature. Subsequently, the solvent was evaporated using an external trap and the solid residue was triturated with *n*-hexane (3 ml). Evaporating the solvent and drying *in vacuo* afforded a bright yellow powder. This powder was extracted with *n*-hexane (10 mL), filtrated through a canula fitted with a glass fibre filter and concentrated to incipient crystallization. Standing in a freezer at −30 °C for 24 h resulted in the deposition of TipP=IMe_4 (**2c**) as a yellow crystalline solid. Yield: 0.216 g (0.60 mmol, 67%).

CHN calc. (found) in %: C 73.71 (69.46), H 9.84 (9.22), N 7.81 (6.92). **^{31}P{^{1}H} NMR** (C_6D_6, 162 MHz): δ [ppm] = −86.74. **^{1}H NMR** (400 MHz, C_6D_6): δ = 7.23 (d, $^4J_{HP}$ = 1.8 Hz, 2H, *m*-ArC*H*), 4.81 (sept-d, $^3J_{HH}$ = 6.9 Hz, $^4J_{HP}$ = 4.8 Hz, 2H, *o*-C*H*(CH$_3$)$_2$), 2.93 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, *p*-C*H*(CH$_3$)$_2$), 2.81 (d, $^4J_{HP}$ = 1.2 Hz, 6H, NC*H*$_3$), 1.41 (d, $^3J_{HH}$ = 6.9 Hz, 12H, *o*-CH(C*H*$_3$)$_2$), 1.35 (d, $^3J_{HH}$ = 6.9 Hz, 6H, *p*-CH(C*H*$_3$)$_2$), 1.28 (s, 6H, CC*H*$_3$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ = 169.3 (d, $^1J_{PC}$ = 104.0 Hz, ((CH$_3$CN(CH$_3$))$_2$*C*), 154.5 (d, J = 8.4 Hz, *o*-Ar*C*), 147.2 (*m*-Ar*C*), 137.5 (d, J = 46.9 Hz *i*-Ar*C*), 120.8 (p-Ar*C*), 120.6 (d, J = 3.5 Hz, ((CH$_3$*C*N(CH$_3$))$_2$C), 34.8 (*p*-*C*H(CH$_3$)$_2$), 34.0 (d, J = 11.5 Hz, *o*-*C*H(CH$_3$)$_2$), 32.1 (d, J = 13.0 Hz, N-*C*H$_3$), 24.6 (*p*-CH(*C*H$_3$)$_2$), 24.5 (*o*-*C*H(CH$_3$)$_2$), 8.4 (((*C*H$_3$CN(CH$_3$))$_2$C) ppm. **MS** (ESI) [MH$^+$] expected: 359.2616, found: 359.2621.

Single crystals suitable for X-ray diffraction were grown from a saturated *n*-hexane solution at −30 °C.

Figure S18: ^{1}H NMR spectrum of TipP=IMe$_4$ (**2c**) (400 MHz, C_6D_6, r.t.).

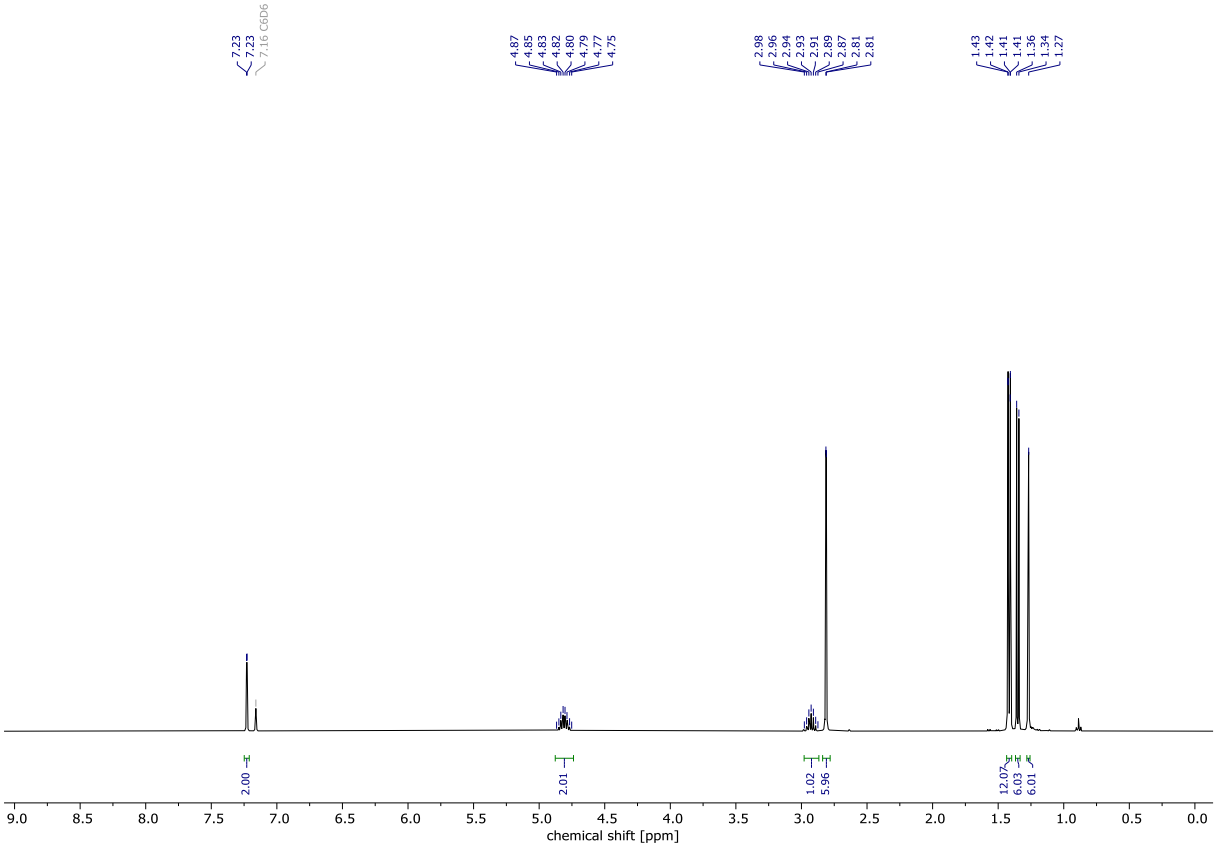


Figure S19: ^{13}C NMR spectrum of TipP=IMe$_4$ (**2c**) (101 MHz, C_6D_6, r.t.).

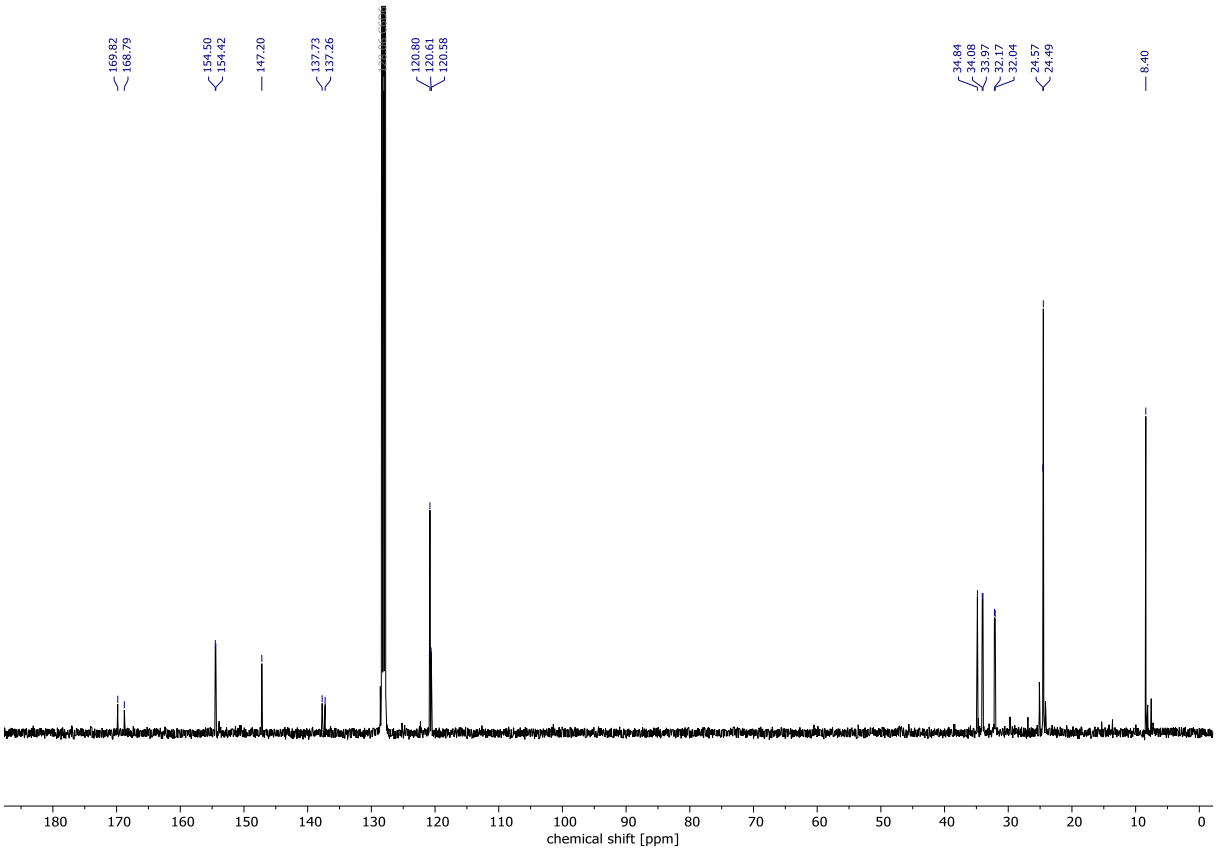
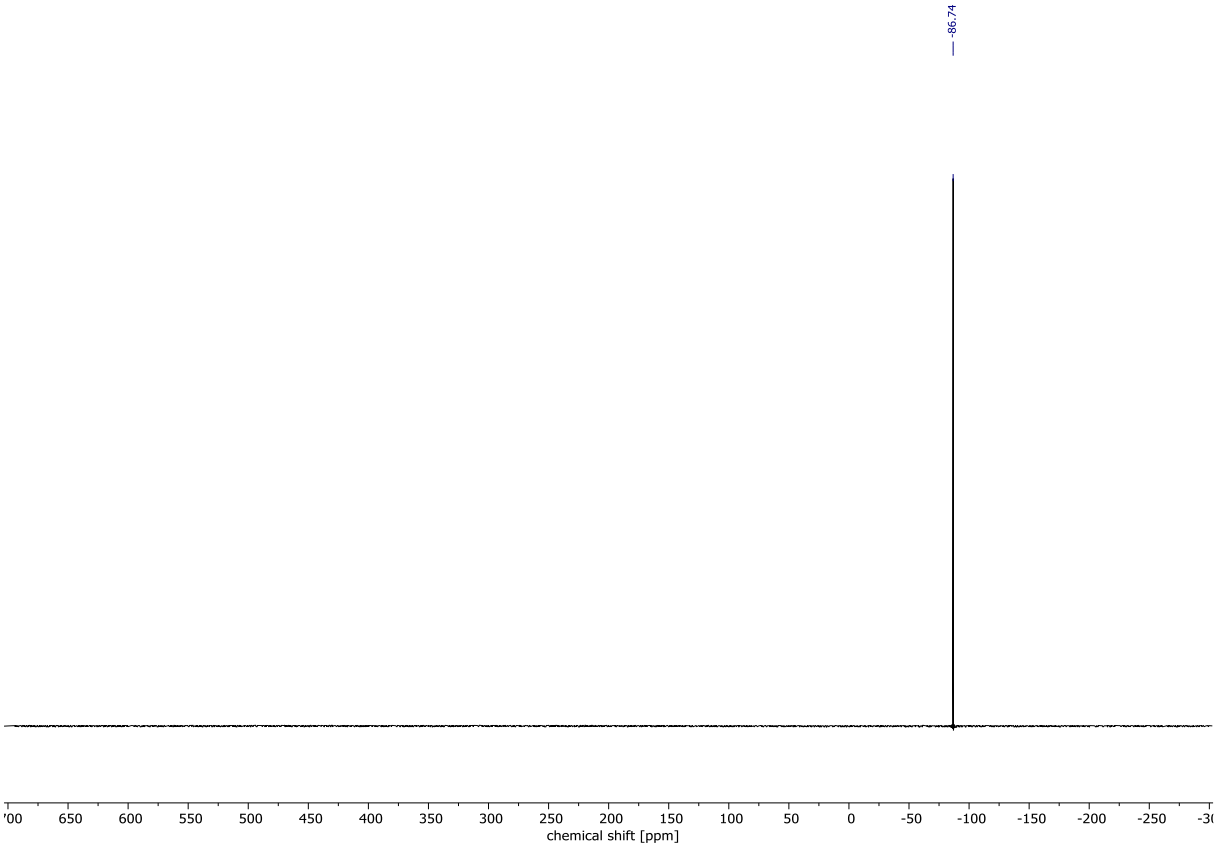
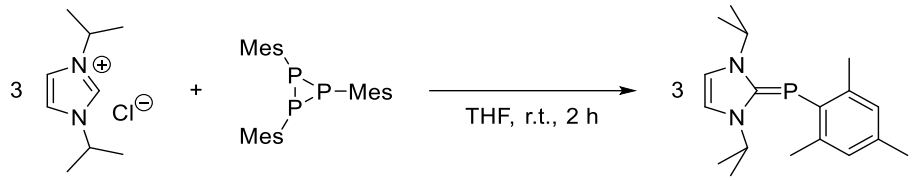


Figure S20: ^{31}P NMR spectrum of TipP=IMe$_4$ (**2c**) (162 MHz, C_6D_6, r.t.).



4.7 MesP=I*i*Pr$_2$ (3a)



A solution of *N,N'*-di-(*iso*-propyl)-imidazolium chloride (100 mg, 0.53 mmol), KO*t*Bu (65 mg, 0.58 mmol) and P_3Mes_3 (80 mg, 0.177 mmol) in THF (5 ml) was stirred at room temperature overnight. The color of the solution quickly turned to bright yellow. Afterwards, the solvent was evaporated to leave a resinoid residue. For extraction of the raw product, *n*-hexane (10 mL) was added, and the mixture was filtered. The filtrate was concentrated. At −30 °C MesP=I*i*Pr$_2$ (**3a**) precipitated from the saturated solution and could be isolated as a yellow powder. Yield: 0.086 g (0.29 mmol, 54%).

The NMR data agrees with a recent report on the synthesis of **3a**. However, in that study **3a** is described as a yellow oil.[18]

CHN calc. (found) in %: C 71.49 (70.12), H 9.00 (8.13), N 9.21 (7.98). **^{31}P{^{1}H} NMR** (C_6D_6, 162.01 MHz): δ = −79.69 ppm. **^{1}H NMR** (400.13 MHz, C_6D_6): δ = 6.97 (s, 2H, Ar*H*), 6.13 (s, 2H, backbone-C*H*), 4.69 (hept.d, $^3J_{HH}$ = 6.7 Hz, J_{PH} = 4.0 Hz, 2H, C*H*$(CH_3)_2$), 2.72 (s, 6H, *o*-C*H*$_3$), 2.23 (s, 3H, *p*-C*H*$_3$), 0.90 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH(C*H*$_3)_2$) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 100.63 MHz): δ = 168.7 (d, J_{PC} = 105.5 Hz, $((H_2CN(C_3H_7))_2C)$, 142.7 (d, J_{PC} = 10.4 Hz, *o*-Ar*C*), 140.23 (d, $^1J_{PC}$ = 48.5 Hz, *i*-Ar*C*), 133.9 (*p*-Ar*C*), 128.6 (*m*-Ar*C*), 114.0 (d, J_{PC} = 3.6 Hz, $H_2CN(C_3H_7))_2C$), 48.9 (d, J_{PC} = 11.3 Hz, N-*C*H$(CH_3)_2$), 25.0 (d, J_{PC} = 12.2 Hz, *o*-Ar*C*H$_3$), 21.6 (N-CH(*C*H$_3)_2$), 21.2 (*p*-Ar*C*H$_3$) ppm. **MS** (ESI) [MO_2H^+] expected: 335.1888, found: 335.1884.

Figure S21: ^{1}H NMR spectrum of MesP=I*i*Pr$_2$ (**3a**) (400.1 MHz, C_6D_6, r.t.).

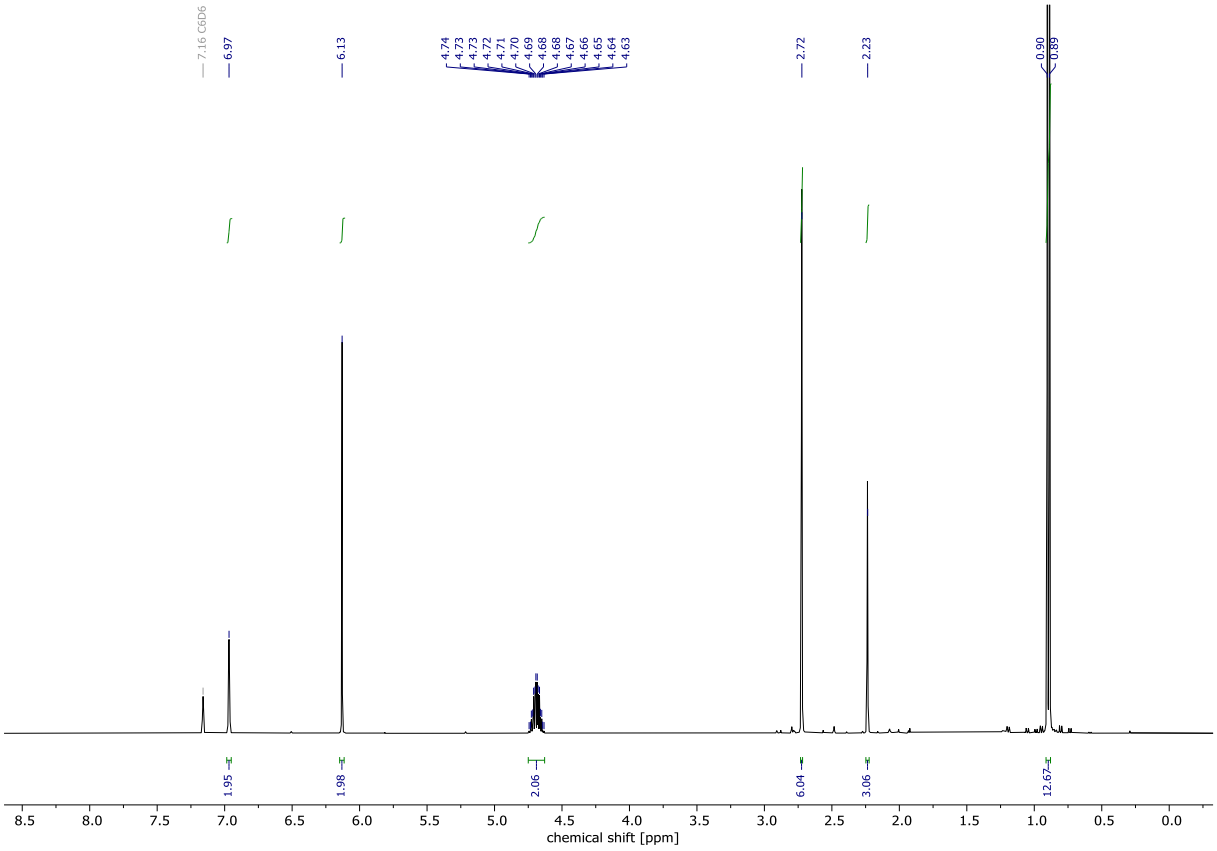


Figure S22: ^{13}C NMR spectrum of MesP=I*i*Pr$_2$ (**3a**) (101 MHz, C_6D_6, r.t.).

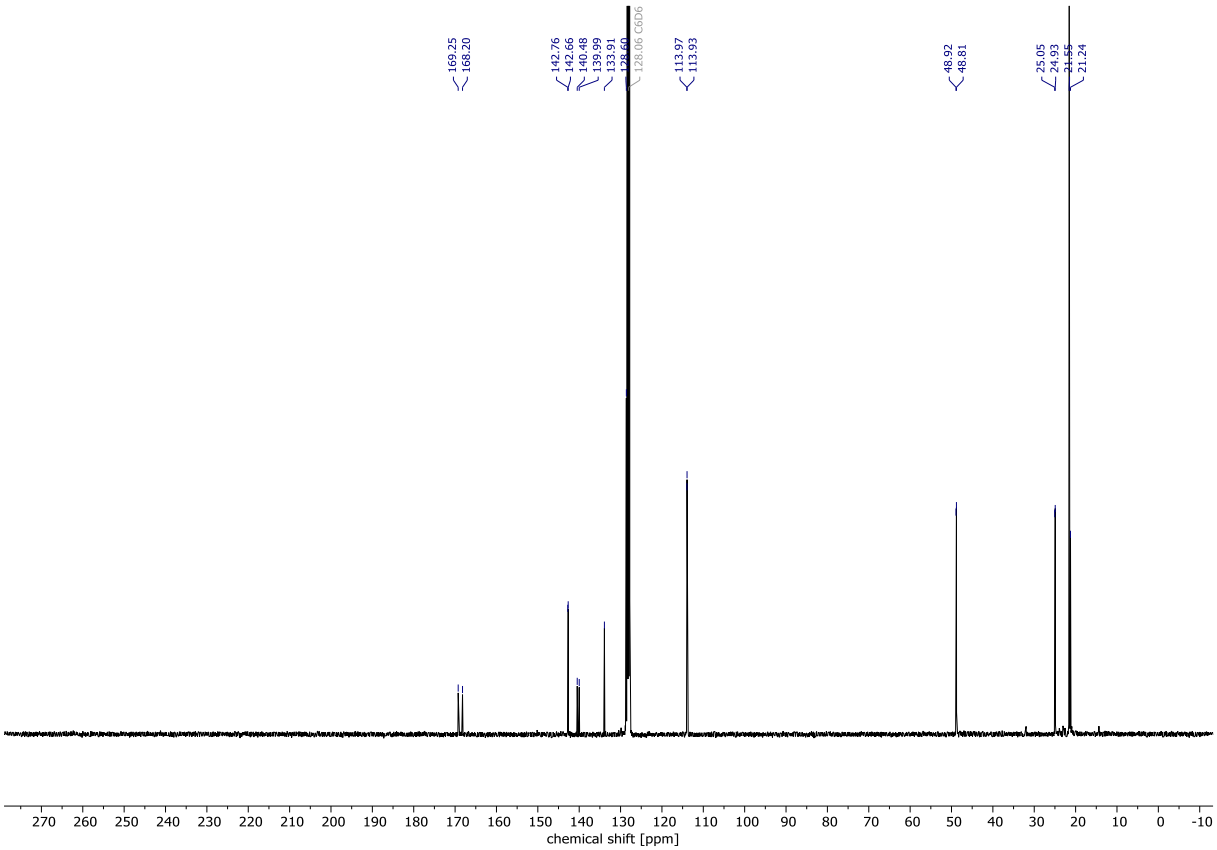
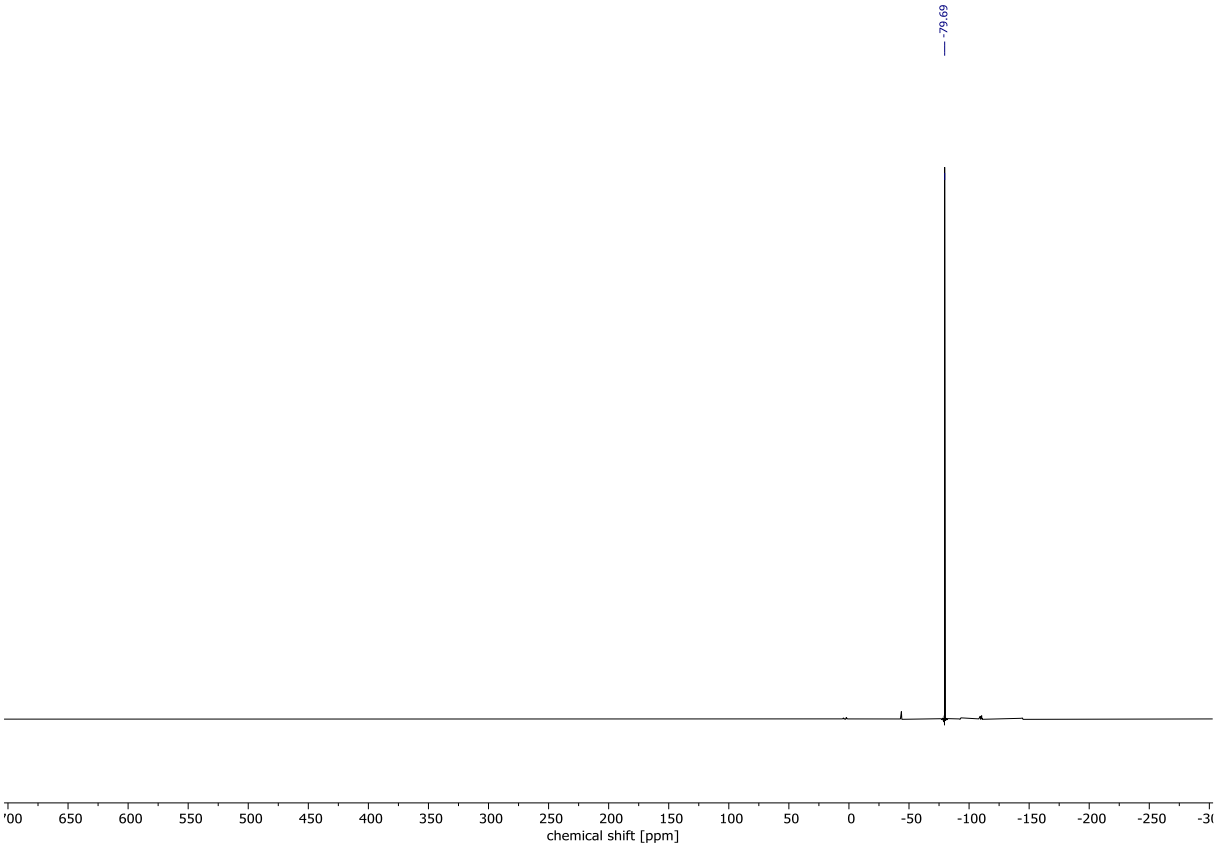
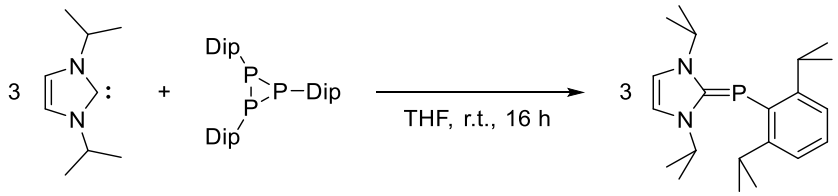


Figure S23: ^{31}P NMR spectrum of MesP=I*i*Pr$_2$ (**3a**) (162 MHz, C_6D_6, r.t.).



4.8 DipP=I*i*Pr$_2$ (3b)



A solution of I*i*Pr (79 mg, 0.52 mmol) and P_3Dip_3 (100 mg, 0.173 mmol) in 10 mL THF was stirred overnight at room temperature. Thus, the colour of the reaction solution changed from red to bright orange. The solvent was evaporated and the resinoid residue was extracted with *n*-hexane (10 mL). After filtration, the solvent was evaporated again. The raw material was recrystallized from *n*-pentane at −30 °C affording DipP=I*i*Pr$_2$ (**3b**) as yellow powder. Yield: 0.145 g (0.42 mmol, 81%).

CHN calc. (found) in %: C 73.22 (71.10), H 9.66 (10.02), N 8.13 (6.95). **^{31}P{^{1}H} NMR** (C_6D_6, 121.5 MHz): δ = −95.00 ppm. **^{1}H NMR** (300.13 MHz, C_6D_6): δ = 7.32-7.24 (m, 1H, *p*-Ar*H*), 7.23-7.18 (m, 2H, *m*-Ar*H*), 6.10 (s, 2H, backbone-C*H*), 4.70 (sept-d, $^4J_{PH}$ = 4.2 Hz, $^3J_{HH}$ = 6.7 Hz, 2H, C*H*(CH$_3$)$_2$), 4.68 (sept-d, $^4J_{PH}$ = 4.8 Hz, $^3J_{HH}$ = 6.9 Hz, 2H, N-C*H*(CH$_3$)$_2$), 1.33 (d, $^3J_{HH}$ = 6.9 Hz, 12H, C*H*), 0.89 (d, $^3J_{HH}$ = 6.7 Hz, 12H, C*H*$_3$) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 75.5 MHz): δ = 168.66 (d, $^1J_{PC}$ = 108.6 Hz, ((HCN(C$_3$H$_7$))$_2$*C*), 154.38 (d, $^3J_{PC}$ = 8.2 Hz, *o*-Ar*C*), 141.29 (d, $^1J_{PC}$ = 50.4 Hz, *i*-Ar*C*), 127.06 (m-Ar*C*), 122.90 (p-Ar*C*, 113.89 (d, J_{PC} = 3.6 Hz, ((H*C*N(C$_3$H$_7$))$_2$C), 48.67 (d, J_{PC} = 11.7 Hz, N*C*H(CH$_3$)$_2$), 34.03 (d, J_{PC} = 11.4 Hz, *C*H(CH$_3$)$_2$), 24.56 (CH(*C*H$_3$)$_2$), 21.68 (CH(*C*H$_3$)$_2$) ppm. **MS** (ESI) [MH$^+$] expected: 345.2459, found: 345.2458.

Single crystals suitable for X-ray diffraction were grown from a saturated *n*-hexane solution at −30 °C.

The exact chemical shifts of the methine CH-protons were obtained by selectively decoupling the CH$_3$-signals at 0.89 and 1.33 ppm, respectively. This gave dublet signals for the methine protons showing only the $^4J_{PH}$ coupling. In the ^{31}P NMR spectrum a complex signal is detected, which ideally should show a ttt signature, which could however not be resolved.

Figure S24: ^{1}H NMR spectrum and excerpt of the $^{1}H\{^{31}P\}$ NMR of DipP=I*i*Pr$_2$ (**3b**) (300.1 MHz, C_6D_6, r.t.).

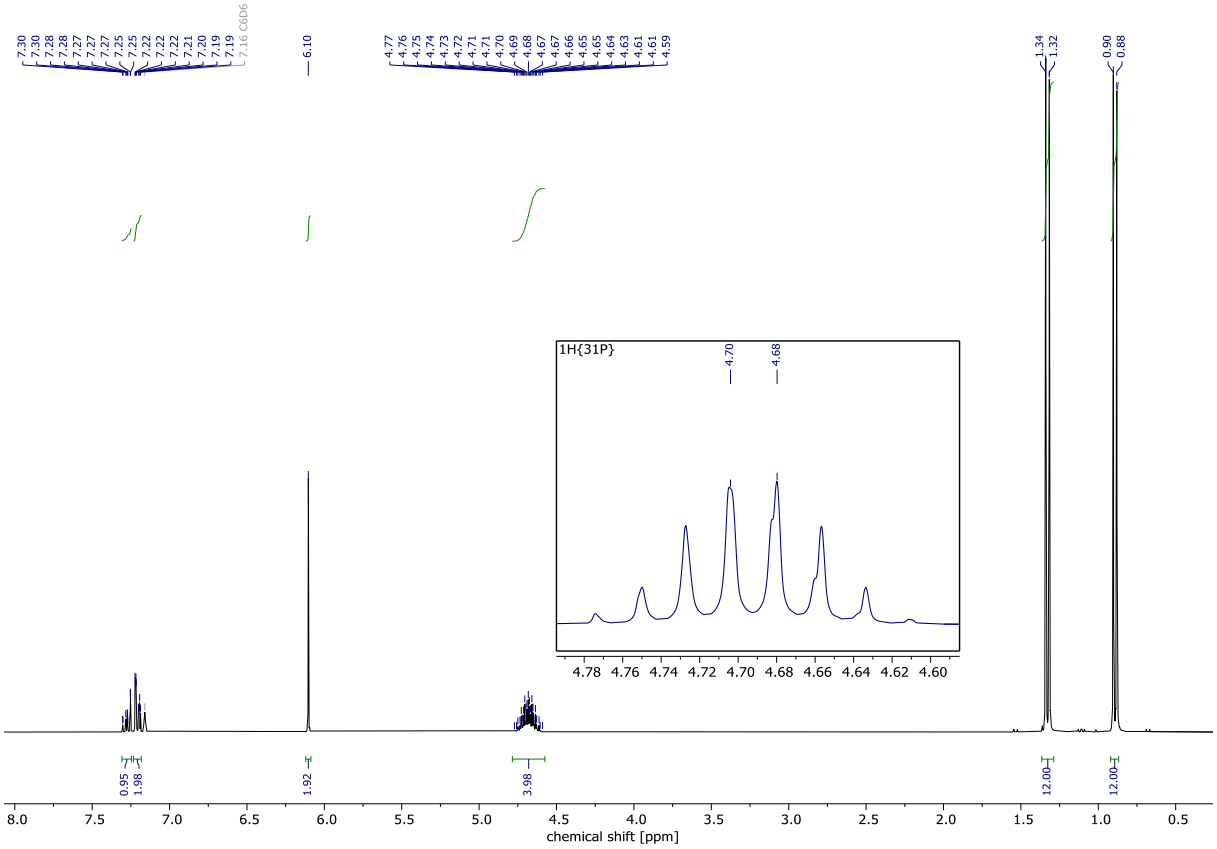


Figure S25: ^{13}C NMR spectrum of DipP=I*i*Pr$_2$ (**3b**) (75.5 MHz, C_6D_6, r.t.).

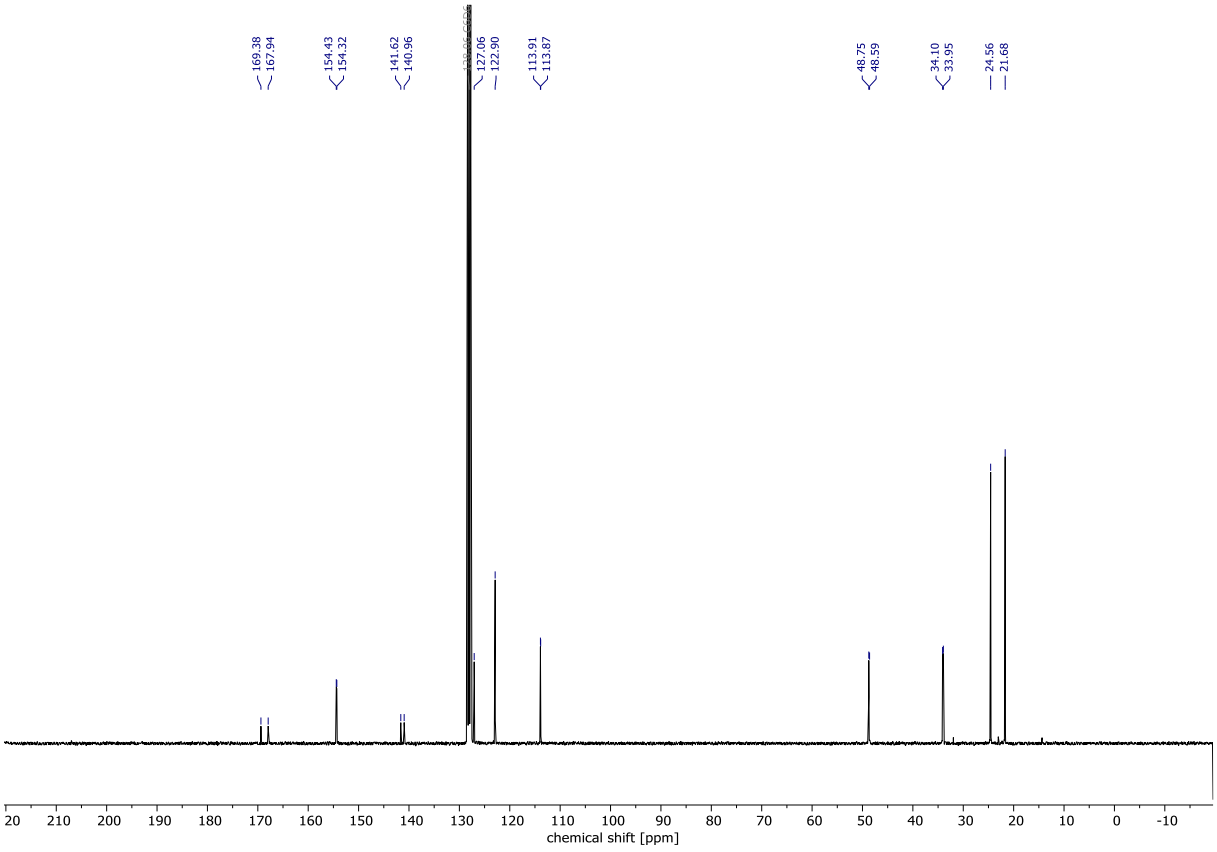
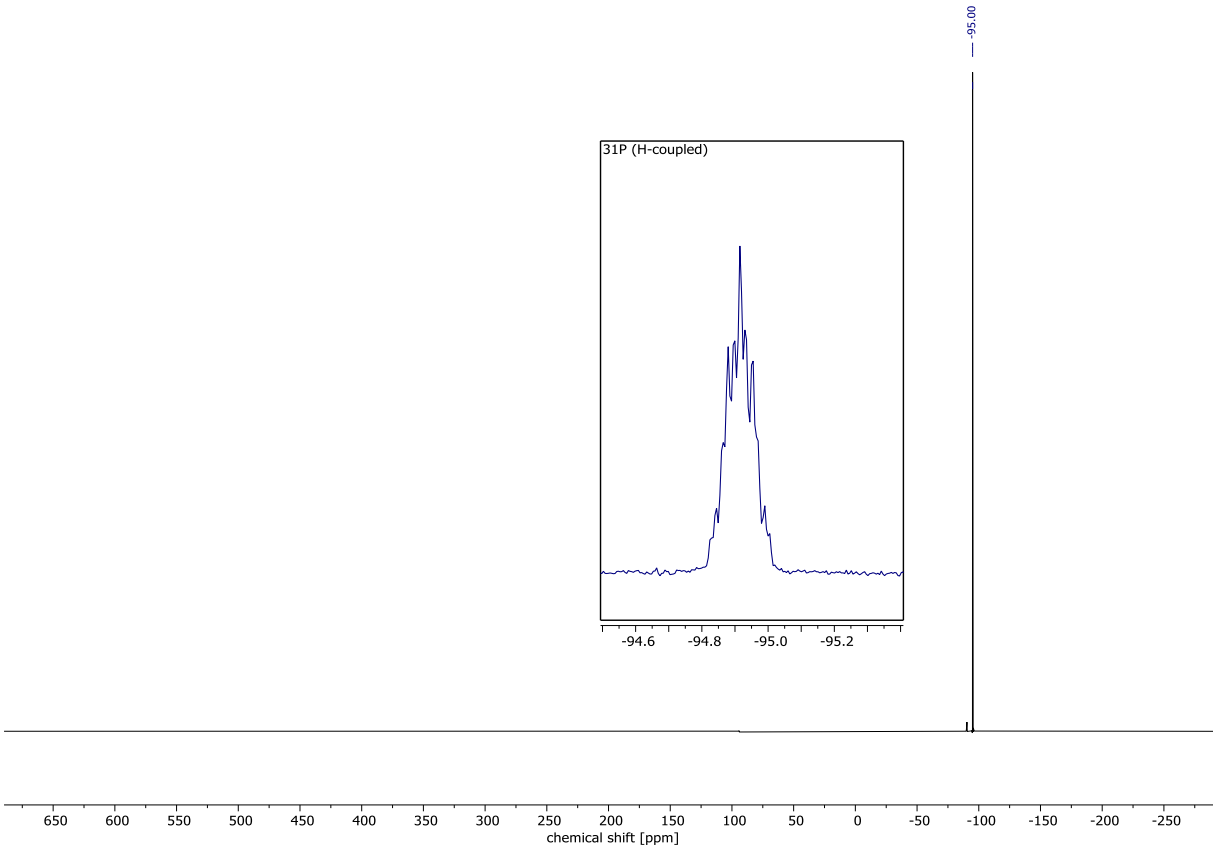


Figure S26: $^{31}P\{^{1}H\}$ NMR and excerpt of the ^{31}P NMR spectrum of DipP=I*i*Pr$_2$ (**3b**) ((121.5 MHz, C_6D_6, r.t.)).



4.9 TipP=I*i*Pr$_2$ (3c)

To a mixture of *N,N'*-di-(*iso*-propyl)-imidazolium chloride (0.080 g, 0.43 mmol), KO*t*Bu (0.049 g, 0.44 mmol) and P_3Tip_3 (0.100 g, 0.142 mmol) pre-cooled THF (10 mL) was added and the reaction mixture was allowed to warm to room temperature and was stirred overnight at room temperature. The colour of the reaction solution changed from yellow to bright orange. Afterwards the solvent was evaporated and the residue was extracted with *n*-hexane (10 mL) and the filtrate was concentrated to incipient crystallization. Storing at −30 °C for 72 h afforded few crystals of TipP=I*i*Pr$_2$ (**3c**). Yield: less than 0.002 g isolated. ^{13}C NMR data obtained directly from the reaction mixture.

^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz): δ = −95.57 ppm. **^{1}H NMR** (300.13 MHz, C_6D_6): δ = 7.18 (d, $^4J_{PH}$ = 1.9 Hz, 2H, *m*-Ar*H*), 6.11 (s, 2H, backbone-C*H*), 4.79-4.65 (m, 4H, NC*H*(CH$_3$)$_2$ and *o*-C*H*(CH$_3$)$_2$), 2.89 (hept, $^3J_{HH}$ = 6.9 Hz, 1H, p-C*H*(CH$_3$)$_2$), 1.33 (d, $^3J_{HH}$ = 6.9 Hz, 12H, C*H*), 1.37 (d, $^3J_{HH}$ = 6.9 Hz, 12H, *o*-CH(C*H*$_3$)$_2$), 1.31 (d, $^3J_{HH}$ = 6.9 Hz, 6H, *p*-CH(C*H*$_3$)$_2$), 0.90 (d, $^3J_{HH}$ = 6.7 Hz, 12H, C*H*$_3$) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 75.5 MHz) δ = 168.92 (d, $^1J_{PC}$ = 109.2 Hz, ((HCN*i*Pr)$_2$*C*), 154.37 (d, $^3J_{PC}$ = 8.4 Hz, *o*-Ar*C*), 147.15 (p-Ar*C*), 138.15 (d, $^1J_{PC}$ = 49.0 Hz, *i*-Ar*C*), 120.88 (m-Ar*C*), 113.88 (d, J_{PC} = 3.6 Hz, ((H*C*N*i*Pr)$_2$C), 48.62 (d, J_{PC} = 11.9 Hz, *C*H(CH$_3$)$_2$), 34.84 (*C*H(CH$_3$)$_2$), 34.10 (d, J_{PC} = 11.2 Hz, *C*H(CH$_3$)$_2$), 24.68 (CH(*C*H$_3$)$_2$), 24.57 (CH(*C*H$_3$)$_2$), 21.72 (CH(*C*H$_3$)$_2$) ppm.

Few single crystals of **3c** suitable for X-ray diffraction were grown from a saturated *n*-hexane solution at −30 °C.

Figure S27: ^{1}H NMR spectrum of the reaction mixture of TipP=I*i*Pr$_2$ (**3c**) in C_6D_6 (300.1 MHz, r.t.).

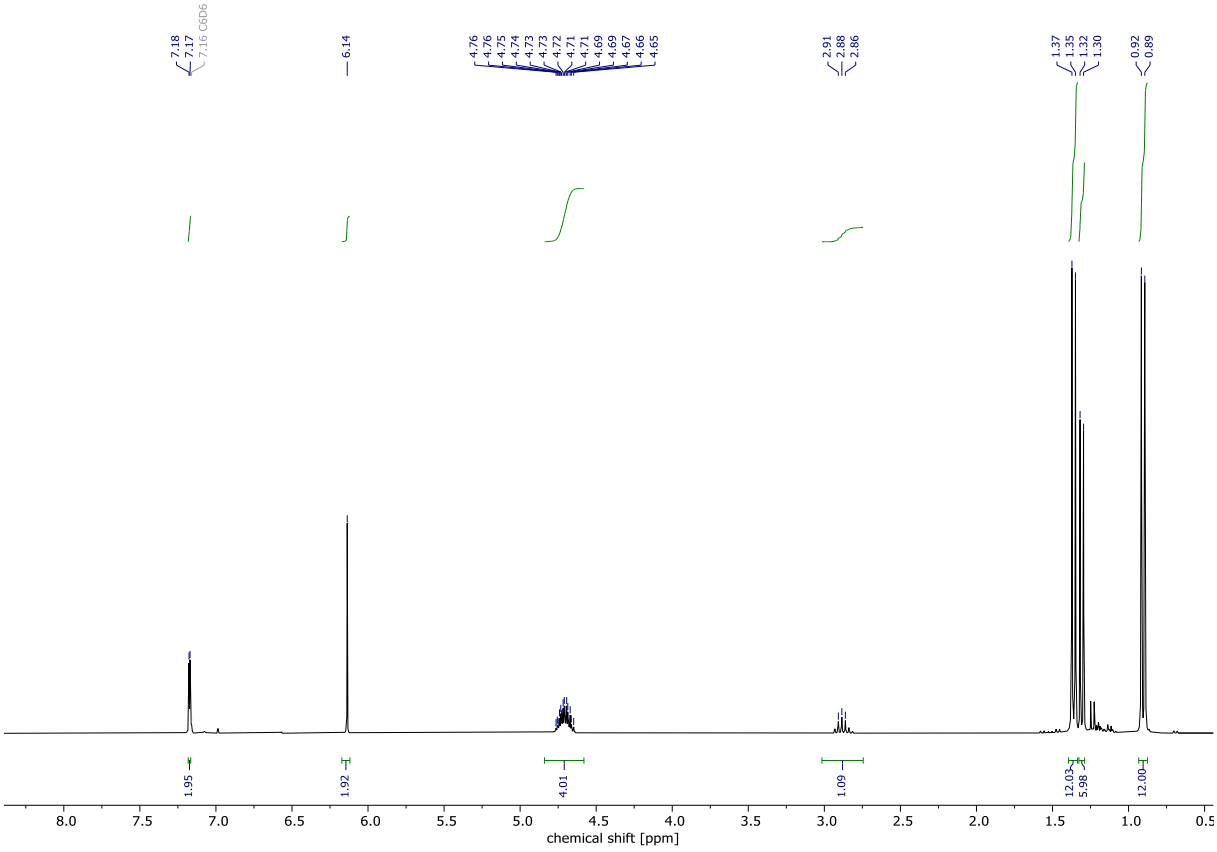


Figure S28: $^{13}C\{^{1}H\}$ NMR spectrum of reaction of containing TipP=I*i*Pr$_2$ (**3c**) in C_6D_6 (75.5 MHz, r.t.).

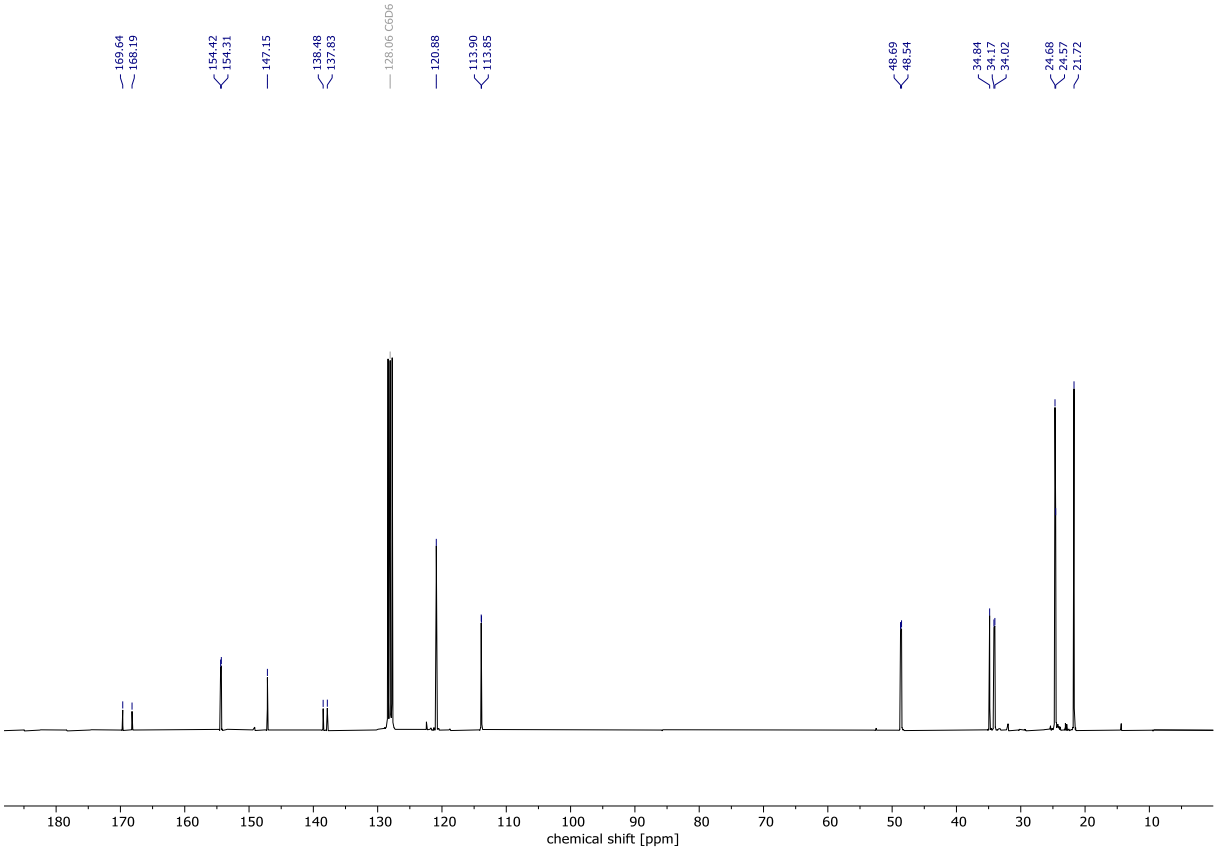
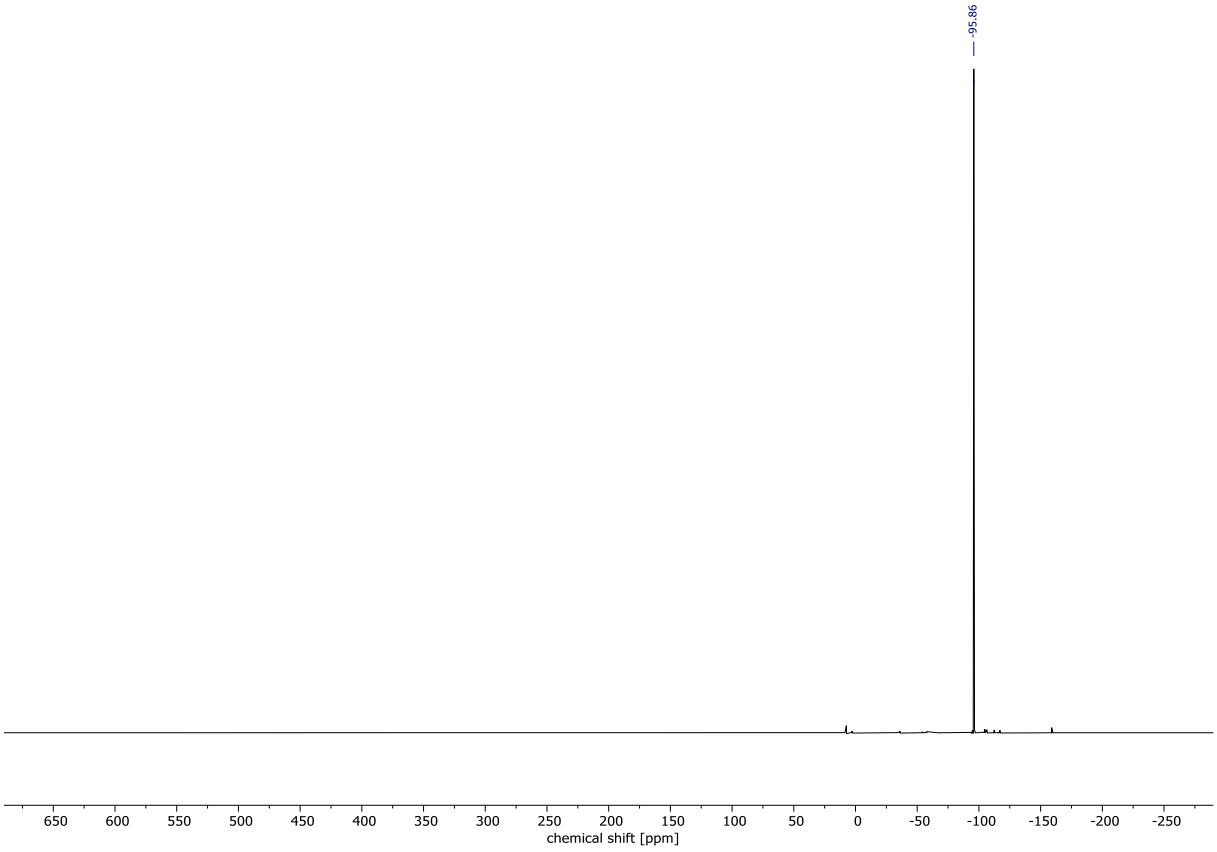
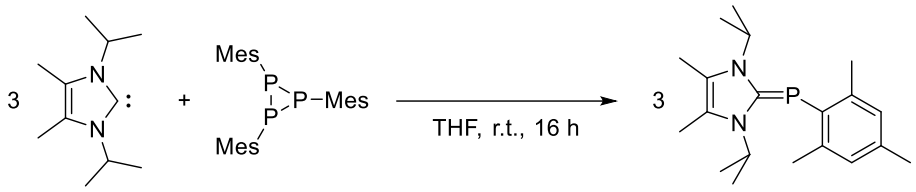


Figure S29: $^{31}P\{^{1}H\}$ NMR spectrum of reaction of containing TipP=I*i*Pr$_2$ (**3c**) in C_6D_6 (121.5 MHz, r.t.).



4.10 MesP=^{Me}I*i*Pr$_2$ (4a)



A mixture of ^{Me}I*i*Pr$_2$ (120 mg, 0.666 mmol) and P_3Mes_3 (100 mg, 0.222 mmol) was dissolved in 5 mL THF and stirred at room temperature overnight giving a yellow solution. The solvent was evaporated, and the solid residue was extracted with *n*-hexane (10 mL). After filtration MesP=^{Me}I*i*Pr$_2$ (**4a**) was obtained as yellow, powdery solid by precipitation from the saturated *n*-hexane solution at −30 °C. Yield: 0.143 g (0.43 mmol, 65%). Crystals suitable for SC-XRD experiments were not obtained.

CHN calc. (found) in %: C 72.69 (71.10), H 9.46 (9.10), N 8.48 (8.32). **^{31}P{^{1}H} NMR** (C_6D_6, 162 MHz): δ [ppm] = -84.97. **^{1}H NMR** (400.13 MHz, C_6D_6): δ = 7.00 (s, 2H, Ar*H*), 5.50 (br, 2H, C*H*$(CH_3)_2$), 2.74 (s, 6H, backbone-C*H*$_3$), 2.29 (s, 3H, *p*-C*H*$_3$), 1.59 (s, 6H, *o*-C*H*$_3$), 1.01 (d, $^3J_{HH}$ = 7.1 Hz, 12H, CH(C*H*$_3$)$_2$) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 100.6 MHz): δ = 171.0 (d, $^1J_{PC}$ = 104.6 Hz, ((H_3C)CN(C_3H_7))$_2$*C*), 143.1 (d, $^1J_{PC}$ = 52.1 Hz, *i*-Ar*C*), 142.0 (d, J_{PC} = 10.6 Hz, *o*-Ar*C*), 133.0 (*m*-Ar*C*), 128.7 (*p*-Ar*C*), 123.1 (((H_3C)*C*N(C_3H_7))$_2$C), 51.1 (d, J_{PC} = 13.9 Hz, N*C*H$(CH_3)_2$), 25.2 (d, J_{PC} = 12.6 Hz, *o*-Ar*C*), 21.3 (*p*-Ar*C*), 20.6 (NCH(*C*H_3)$_2$), 10.3 (((H_3C)CN(C_3H_7))$_2$C) ppm. **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 420 (w), 445 (m), 468 (w), 476 (w), 503 (w), 515 (w), 552 (m), 567 (w), 616 (w), 645 (w), 658 (w), 680 (w), 721 (w), 756 (w), 787 (w), 845 (m), 880 (w), 905 (w), 921 (w), 950 (w), 973 (m), 1006 (m), 1026 (m), 1049 (m), 1078 (m), 1103 (m), 1136 (m), 1169 (m), 1202 (s), 1231 (w), 1253 (m), 1261 (m), 1292 (s), 1309 (vs), 1364 (s), 1397 (w), 1418 (m), 1428 (m), 1459 (s), 1550 (w), 1604 (w), 1635 (w), 2725 (w), 2890 (m), 2929 (m), 2966 (m), 3011 (w). **MS** (ESI) [MH$^+$] expected: 331.2303, found: 331.2299.

Figure S30: ^{1}H NMR spectrum of MesP=^{Me}I*i*Pr$_2$ (**4a**) (400 MHz, C_6D_6, r.t.).

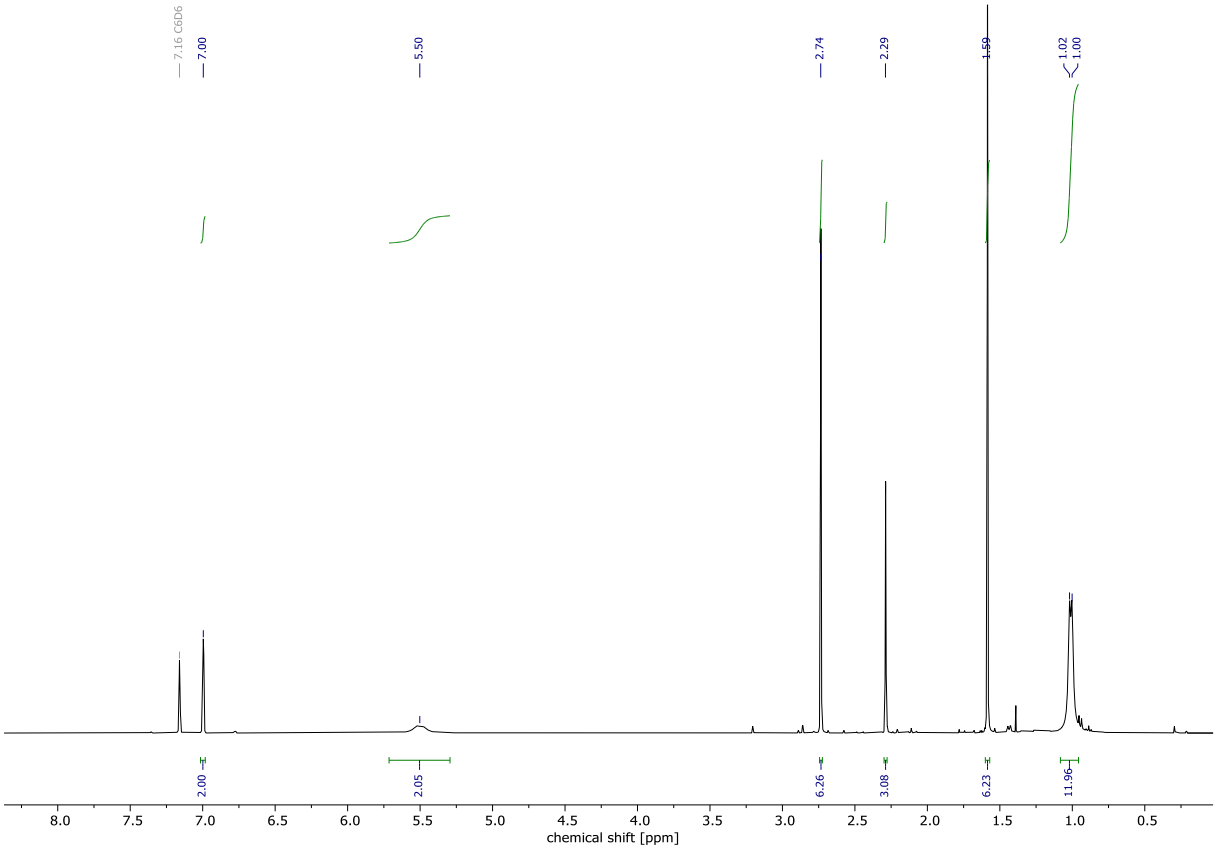


Figure S31: ^{13}C NMR spectrum of MesP=^{Me}I*i*Pr$_2$ (**4a**) (101 MHz, C_6D_6, r.t.).

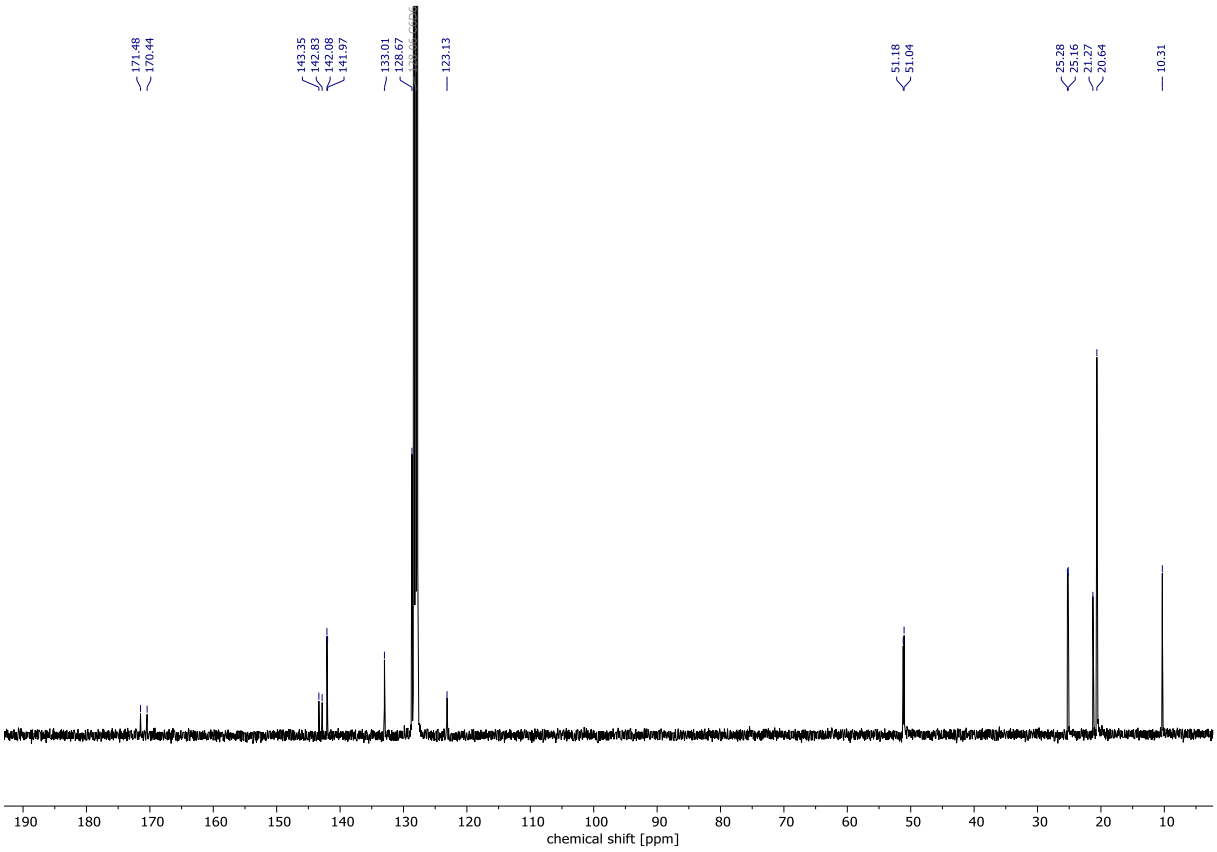


Figure S32: ^{31}P NMR spectrum of MesP=^{Me}I*i*Pr$_2$ (**4a**) (162 MHz, C_6D_6, r.t.).

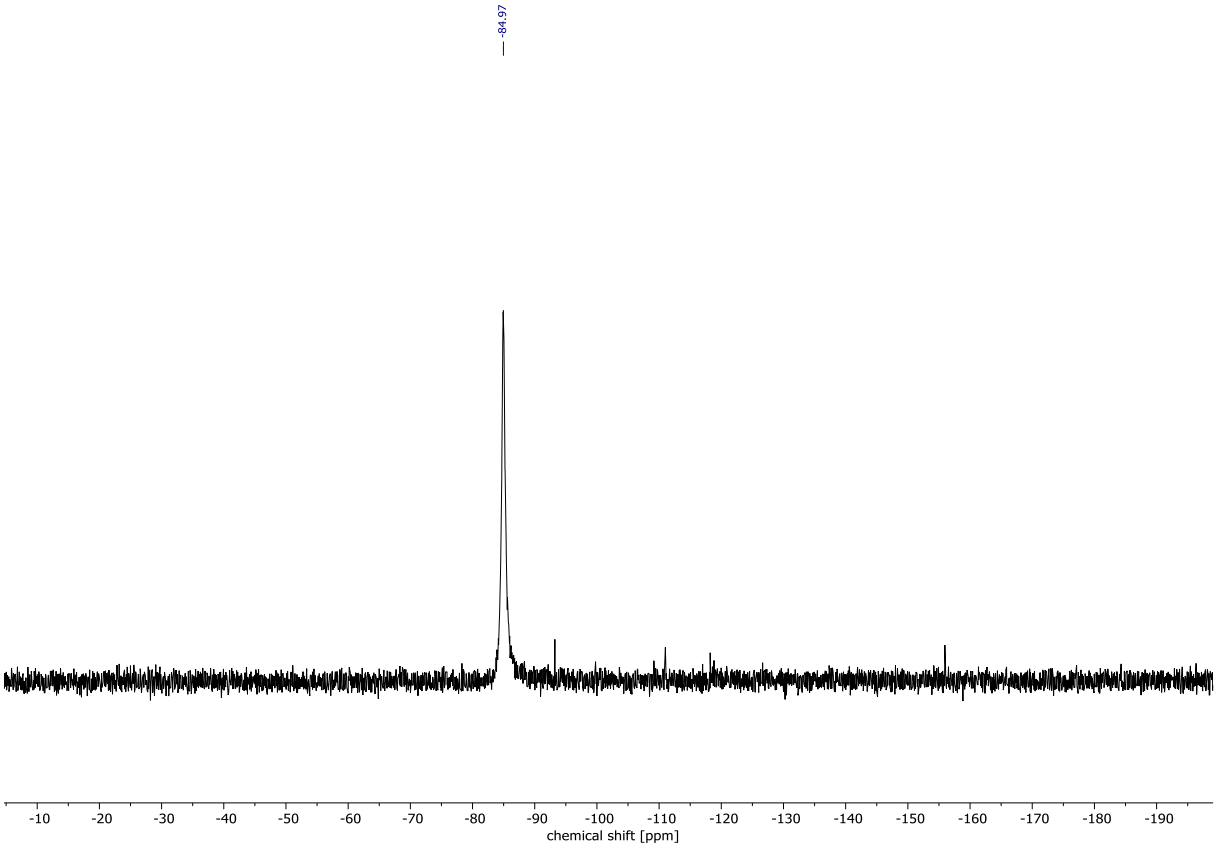
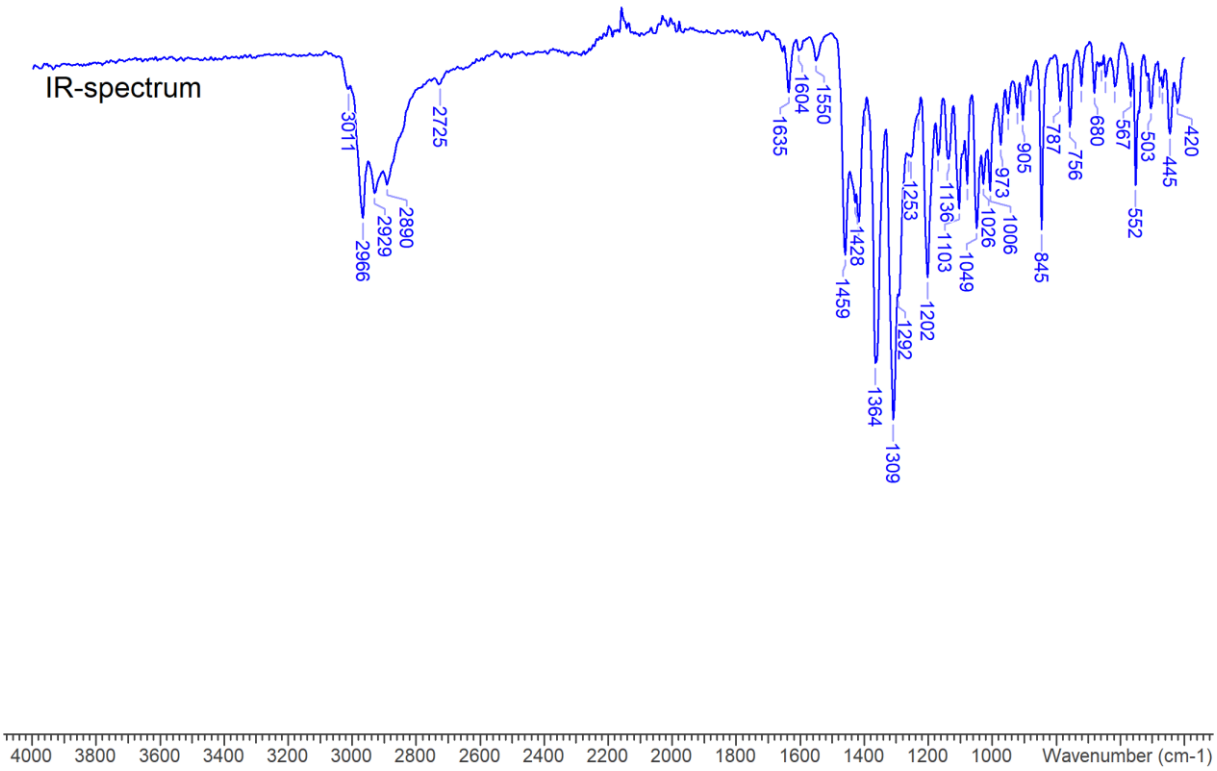
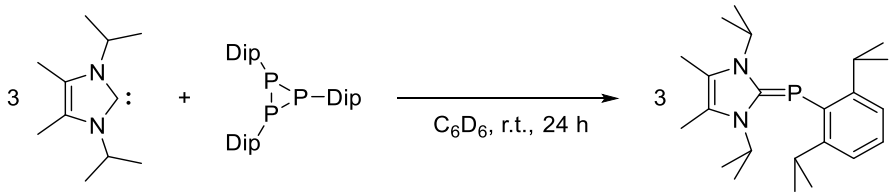


Figure S33: IR spectrum of MesP=^{Me}I*i*Pr$_2$ (**4a**) (solid sample, 32 scans, r.t.).



4.11 DipP=^{Me}I*i*Pr$_2$ (4b)



^{Me}I*i*Pr$_2$ (0.022 g, 0.12 mmol) and P_3Dip_3 (0.023 g, 0.04 mmol) were combined in an NMR tube equipped with a J-Young screw cap and C_6D_6 (0.5 mL) was added and the yellow solution was analyzed by ^{1}H and ^{31}P{^{1}H} spectroscopy after 24 h. Afterwards the NMR tube was brought inside a glovebox and the solution was transferred into a vial and the solvent was evaporated. The sticky residue was extracted with *n*-hexane (1 mL). After filtration, the yellow solution was concentrated to incipient crystallisation. After standing at −30 °C for 24 h, minimal amounts of yellow crystals of DipP=^{Me}I*i*Pr$_2$ (**4b**) were afforded, which precluded collection of comprehensive analytical data.

^{31}P{^{1}H} NMR (C_6D_6, 122 MHz): δ = −101.77 ppm. **^{1}H NMR** (300.2 MHz, C_6D_6): δ = 7.34-7.25 (m, 1H, *p*-ArC*H*), 7.24-7.19 (m, 2H, m-ArC*H*), 5.53 (s (br), 2H, C*H*(CH$_3$)$_2$) Dip, (hept of doublets, $^3J_{HH}$ = 6.9 Hz, J_{PH} = 5.0 Hz, 2H, C*H*(CH$_3$)$_2$ ^{Me}I*i*Pr$_2$), 1.60 (s, 6H, C*H*$_3$-^{Me}I*i*Pr$_2$), 1.32 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.01 (d, $^3J_{HH}$ = 7.1 Hz, 12H, CH(C*H*$_3$)$_2$ ^{Me}I*i*Pr$_2$) ppm.

Single crystals suitable for X-ray diffraction were grown from a saturated *n*-hexane solution at −30 °C.

Figure S34: ^{1}H NMR spectrum of DipP=^{Me}I*i*Pr$_2$ (**4b**) (300.2 MHz, C_6D_6, r.t.).

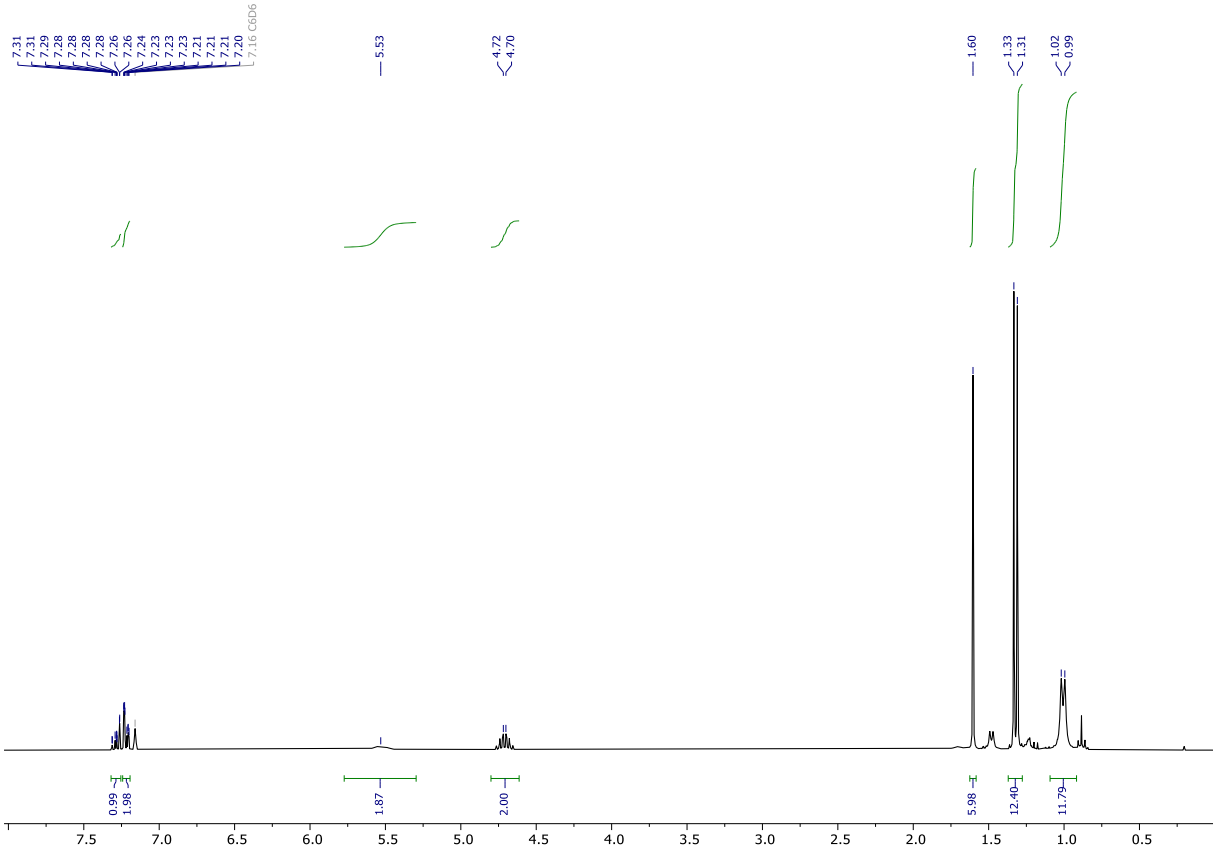
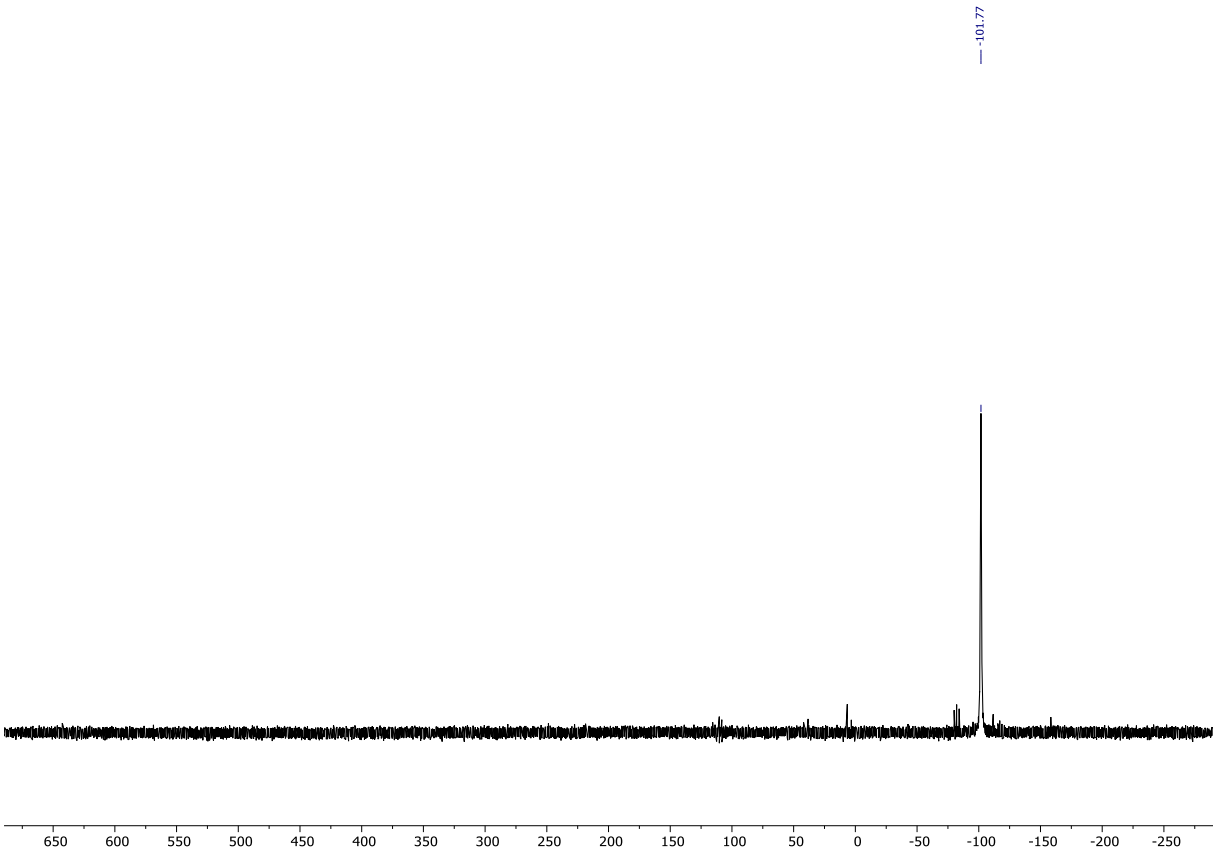
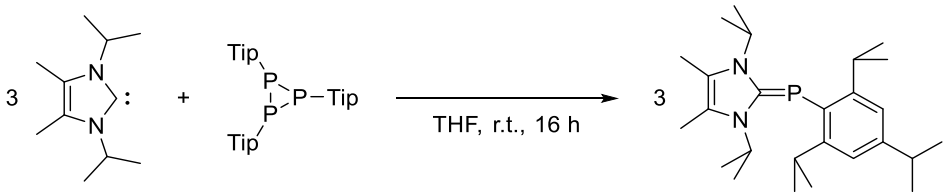


Figure S35: ^{31}P{^{1}H} NMR spectrum of DipP=^{Me}I*i*Pr$_2$ (**4b**) (121.5 MHz, C_6D_6, r.t.).



4.12 TipP=^{Me}I*i*Pr$_2$ (4c)



A solution of ^{Me}I*i*Pr$_2$ (77 mg, 0.427 mmol) and P_3Tip_3 (100 mg, 0.142 mmol) in 10 mL THF was stirred overnight at room temperature. During this time the colour of the reaction solution changed from red to bright orange. The solvent was evaporated, and the sticky residue was extracted with *n*-hexane (5 mL). After filtration, the solvent was evaporated again. The raw material was recrystallized from a saturated *n*-pentane solution at −30 °C affording TipP=^{Me}I*i*Pr$_2$ (**4c**) as yellow powder. Yield: 0.135 g (0.326 mmol, 76%).

CHN calc. (found) in %: C 75.32 (74.38), H 10.45 (10.40), N 6.76 (5.59). **^{31}P{^{1}H} NMR** (C_6D_6, 122 MHz): δ = −102.39 ppm. **^{1}H NMR** (300.13 MHz, C_6D_6): δ = 7.18 (d, $^4J_{HH}$ = 1.9 Hz, 2H, ArC*H*), 5.51 (br, 2H, C*H*(CH$_3$)$_2$), 4.76 (hept., $^3J_{HH}$ = 6.9 Hz, J_{PH} = 5.1 Hz, 2H, C*H*(CH$_3$)$_2$), 2.92 (hept., $^3J_{HH}$ = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 1.61 (s, 6H, C*H*$_3$-backbone), 1.36 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.35 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.01 (d, $^3J_{HH}$ = 7.1 Hz, 12H, CH(C*H*$_3$)$_2$) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 75.5 MHz): δ = 171.6 (d, $^1J_{PC}$ = 107.8 Hz, ((H$_3$C)CN(C$_3$H$_7$))$_2$*C*), 153.8 (d, J_{PC} = 8.3 Hz, *o*-Ar*C*), 146.4 (Ar*C*), 141.5 (d, $^1J_{PC}$ = 52.4 Hz, o-Ar*C*), 123.1 (*C*CH$_3$), 120.9 (*C*CH$_3$), 51.1 (d, J_{PC} = 14.3 Hz, *C*H(CH$_3$)$_2$), 34.9 (*C*H(CH$_3$)$_2$), 34.1 (*C*H(CH$_3$)$_2$), 34.0 (*C*H(CH$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 20.7 (CH(*C*H$_3$)$_2$), 10.3 (N*C*H$_3$). **MS** (ESI) [MH$^+$] expected: 415.3242, found: 415.3233.

Single crystals suitable for X-ray diffraction were grown from a saturated *n*-hexane solution at −30 °C.

Figure S36: ^{1}H NMR spectrum of TipP=^{Me}I*i*Pr$_2$ (**4c**) (300.1 MHz, C_6D_6, r.t.).

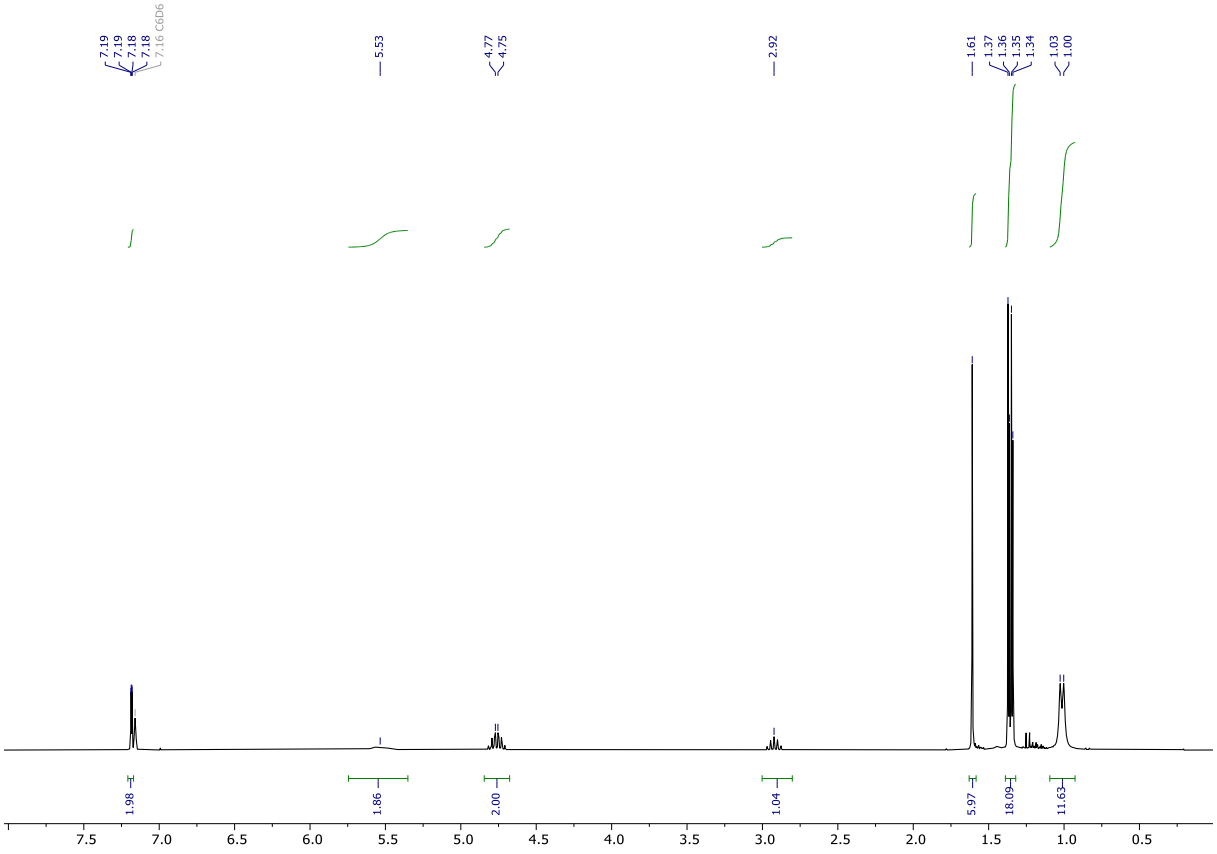


Figure S37: ^{13}C NMR spectrum of TipP=^{Me}I*i*Pr$_2$ (**4c**) (75.5 MHz, C_6D_6, r.t.).

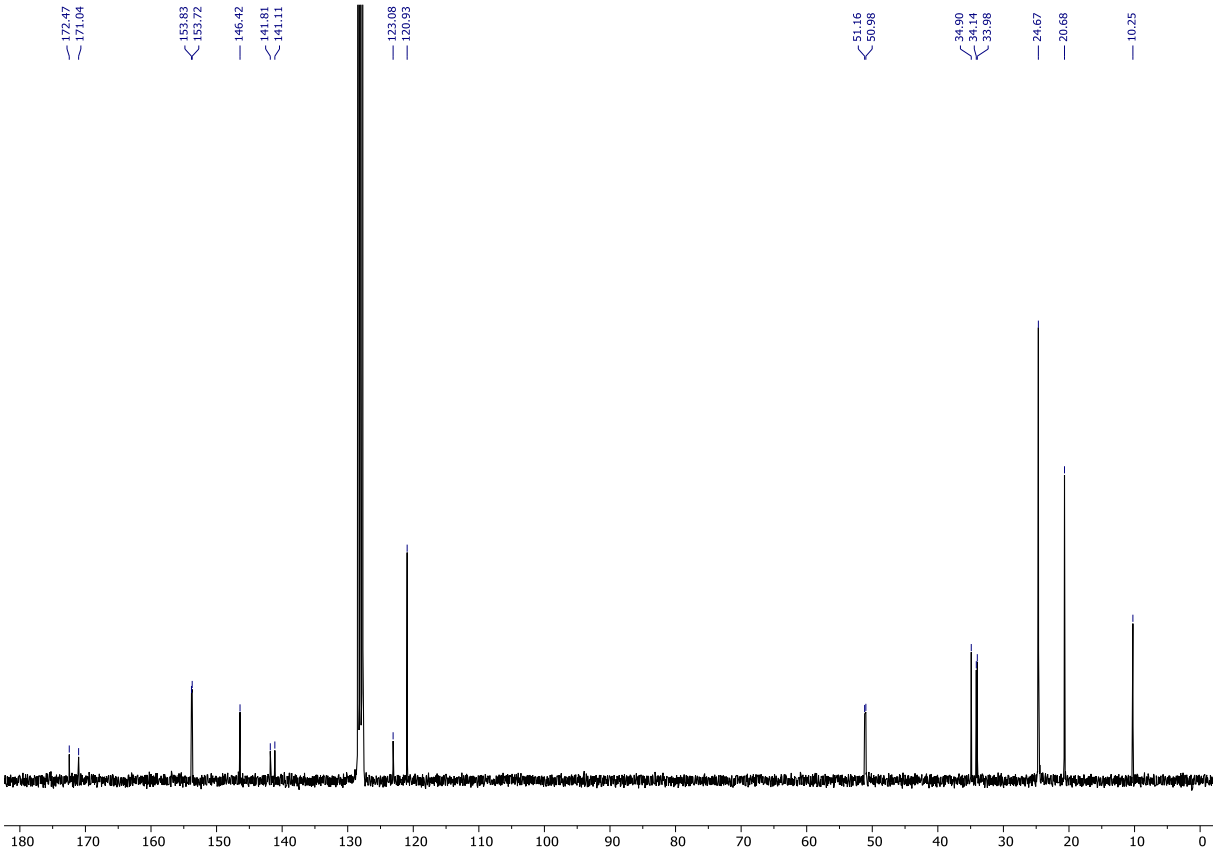
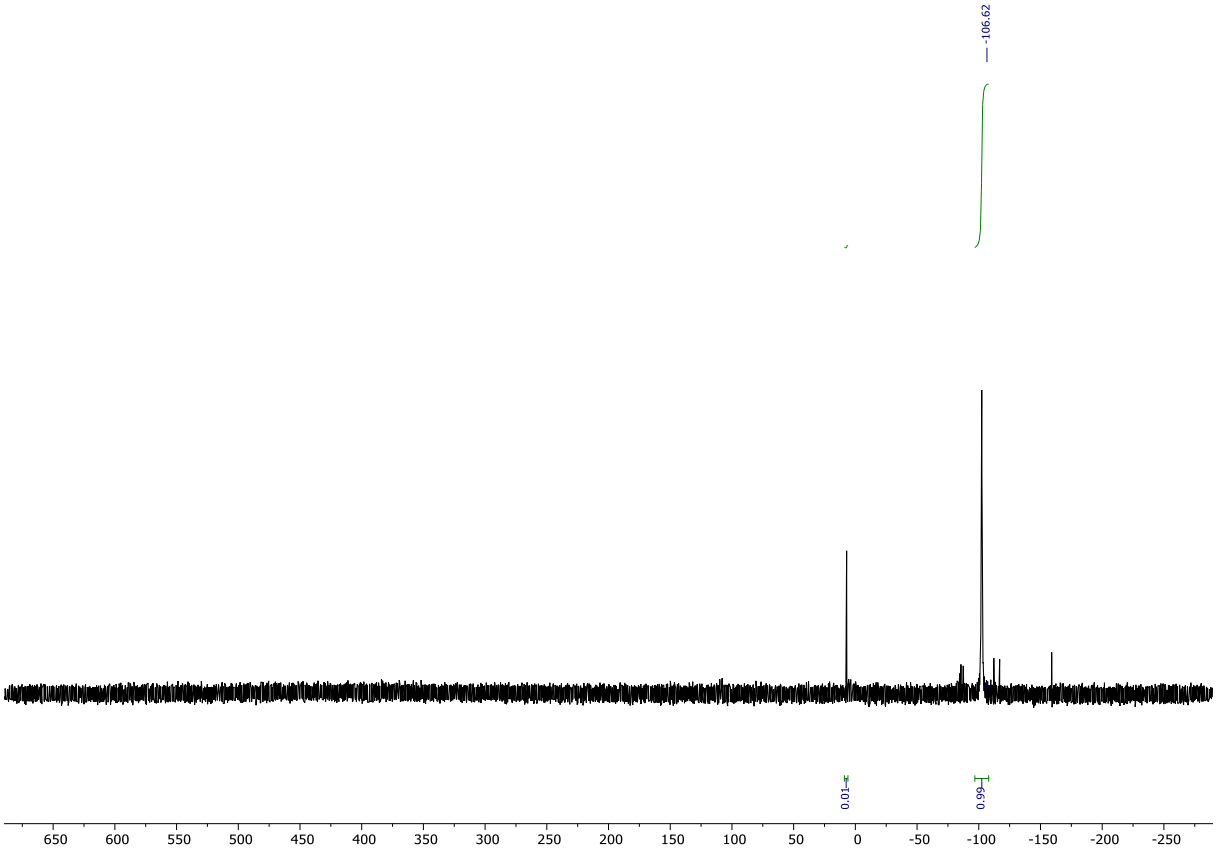
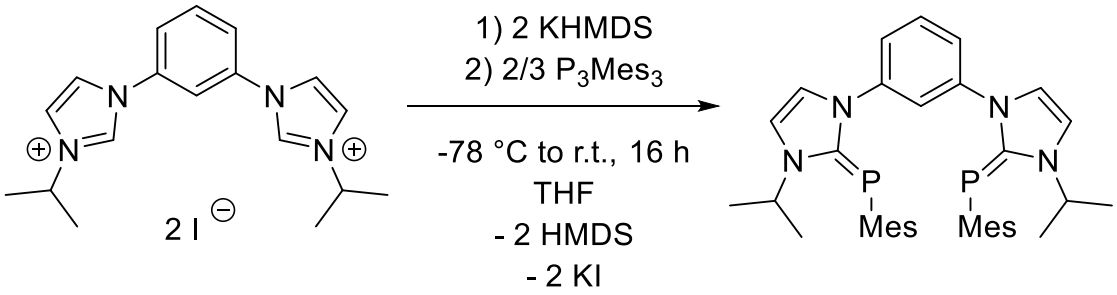


Figure S38: ^{31}P NMR spectrum of TipP=^{Me}I*i*Pr$_2$ (**4c**) (121.5 MHz, C_6D_6, r.t.).



4.13 Synthesis of 5a



1,3-Bis(3-isopropylimidazolium)benzene diiodide (0.427 g, 0.78 mmol) is suspended in THF (4 mL). KHMDS (0.317 mg, 1.59 mmol, 2.05 eq.) is dissolved in THF (20 mL) and added dropwise to the cooled suspension of the bisimidazolium diiodide (−78 °C). The resulting yellow suspension briefly cleared, and a white precipitate slowly formed. The suspension was stirred at low temperatures for 4 h. The resulting NHC is then added to Mes_3P_3 (0.233 g, 0.52 mmol, 0.67 eq.) via canula filtration. The resulting deep yellow solution was stirred overnight at room temperature. Afterwards the solvent was evaporated from the deep red solution, giving a deep red residue that was extracted twice with hot toluene (70 °C, 250 mL, 100 mL) The filtrate was then concentrated to incipient crystallization and placed in the freezer (−30 °C) for 24 h, giving after removal of the supernatant solution **5a** as a yellow crystalline solid. Yield: 0.167 g, 0.314 mmol, 54 %.

CHN calc. (found) in %: C 72.71 (72.86), H 7.46 (7.51), N 9.42 (9.46). **$^{31}P\{^{1}H\}$ NMR** (122 MHz, THF-d_8) δ = −68.40 ppm. **^{1}H NMR** (300 MHz, THF-d_8) δ = 7.16 – 7.13 (m, 1H, Ph*H*), 7.12 (dd, J = 2.4, 1.3 Hz, 2H, CHC*H*N), 6.77 – 6.60 (m, 3H, Ph), 6.50 (dd, J = 2.3, 1.8 Hz, 2H, CHC*H*N), 6.28 (dd, J = 2.0, 0.7 Hz, 4H, Ar*H*), 4.75 (hept, J = 6.6 Hz, 2H, NC*H*$(CH_3)_2$), 2.06 (s, 12H, o-ArCH_3), 1.96 (s, 6H, p-ArCH_3), 1.43 (d, J = 6.7 Hz, 12H, NCH(C$H_3)_2$) ppm. **$^{13}C\{^{1}H\}$ NMR** (75 MHz, THF-d_8) δ = 168.9 (d, $^{1}J_{PC}$ = 104.3 Hz, N_2*C*=P), 142.2 (d, J = 10.0 Hz, *o*-Ar*C*), 138.8 (d, J_{PC} = 45.6 Hz, *i*-Ar*C*), 133.4 (*p*-Ar*C*), 128.6 (d, *J* = 1.4 Hz, Ph*C*H), 128.0 (Ar*C*H), 121.7 (Ph*C*H), 121.0 (Ph*C*H), 120.7 (d, J_{PC} = 4.3 Hz, CH*C*HN), 115.0 (d, *J* = 2.6 Hz, CH*C*HN), 49.3 (d, *J* = 23.6 Hz, N*C*H$(CH_3)_2$), 24.3 (d, *J* =12.0 Hz, NCH(*C*$H_3)_2$), 21.7 (d, J_{PC} = 1.8 Hz, *o*-Ar*C*H_3), 21.2 (*p*-Ar*C*H_3). **MS** (ESI) expected: [MH^+]

595.3120, found: 595.3123. **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 445 (vw), 464 (vw), 486 (vw), 509 (m), 548 (w), 554 (w), 569 (w), 583 (w), 610 (w), 653 (m), 695 (vs), 721 (w), 765 (m), 794 (w), 814 (w), 851 (m), 878 (w), 892 (w), 923 (w), 948 (w), 985 (w), 1010 (w), 1022 (w), 1053 (w), 1076 (w), 1090 (w), 1111 (m), 1117 (m), 1127 (m), 1169 (w), 1208 (s), 1222 (w), 1249 (m), 1270 (s), 1319 (s), 1334 (s), 1369 (m), 1393 (s), 1412 (s), 1428 (w), 1465 (m), 1492 (m), 1513 (w), 1575 (w), 1593 (w), 1608 (w), 2875 (w), 2892 (w), 2910 (w), 2927 (w), 2968 (m), 3018 (w), 3112 (w), 3141 (w), 3174 (w),

Single crystals suitable for X-ray diffraction were grown from a saturated toluene of **5a** solution at −30 °C.

Figure S39: ^{1}H NMR spectrum of **5a** (300.2 MHz, THF-d_8, r.t.).

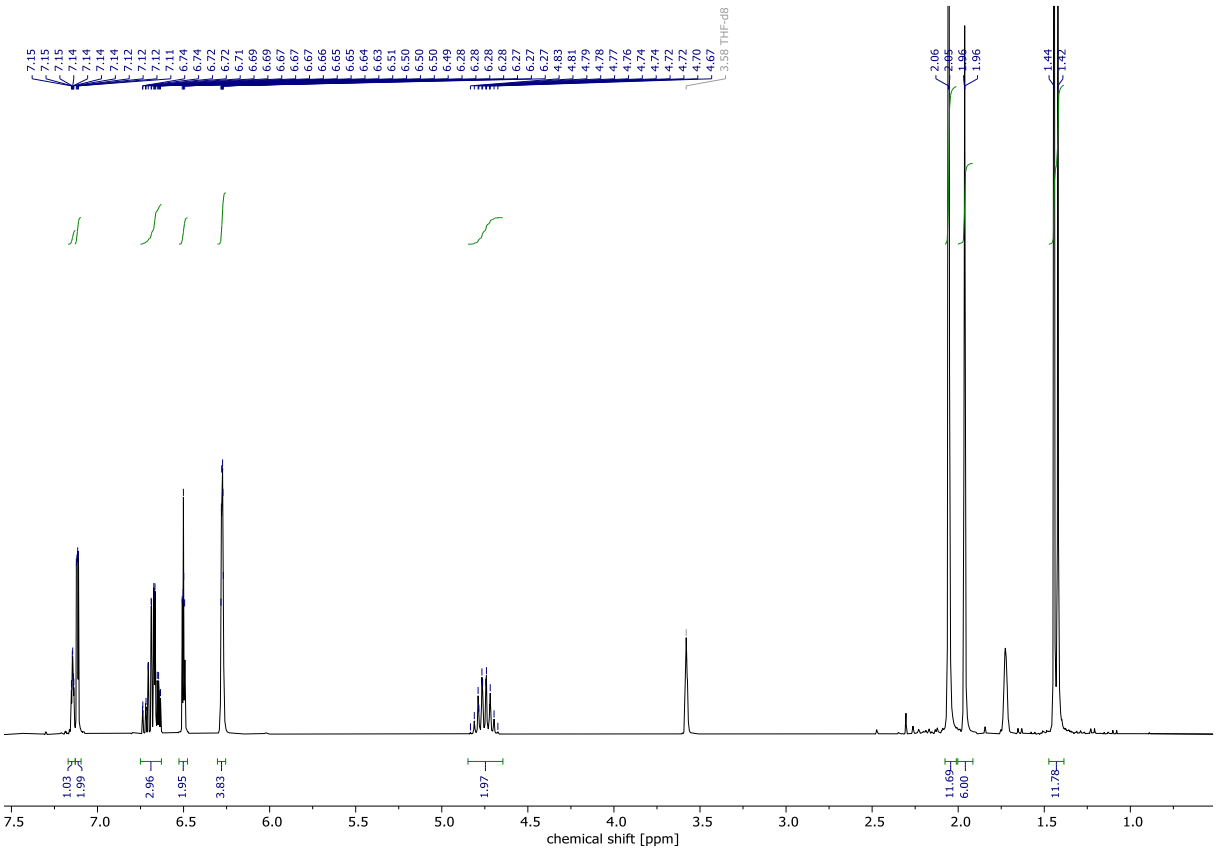


Figure S40: $^{13}C\{^{1}H\}$ NMR spectrum of **5a** (75.5 MHz, THF-d_8, r.t.).

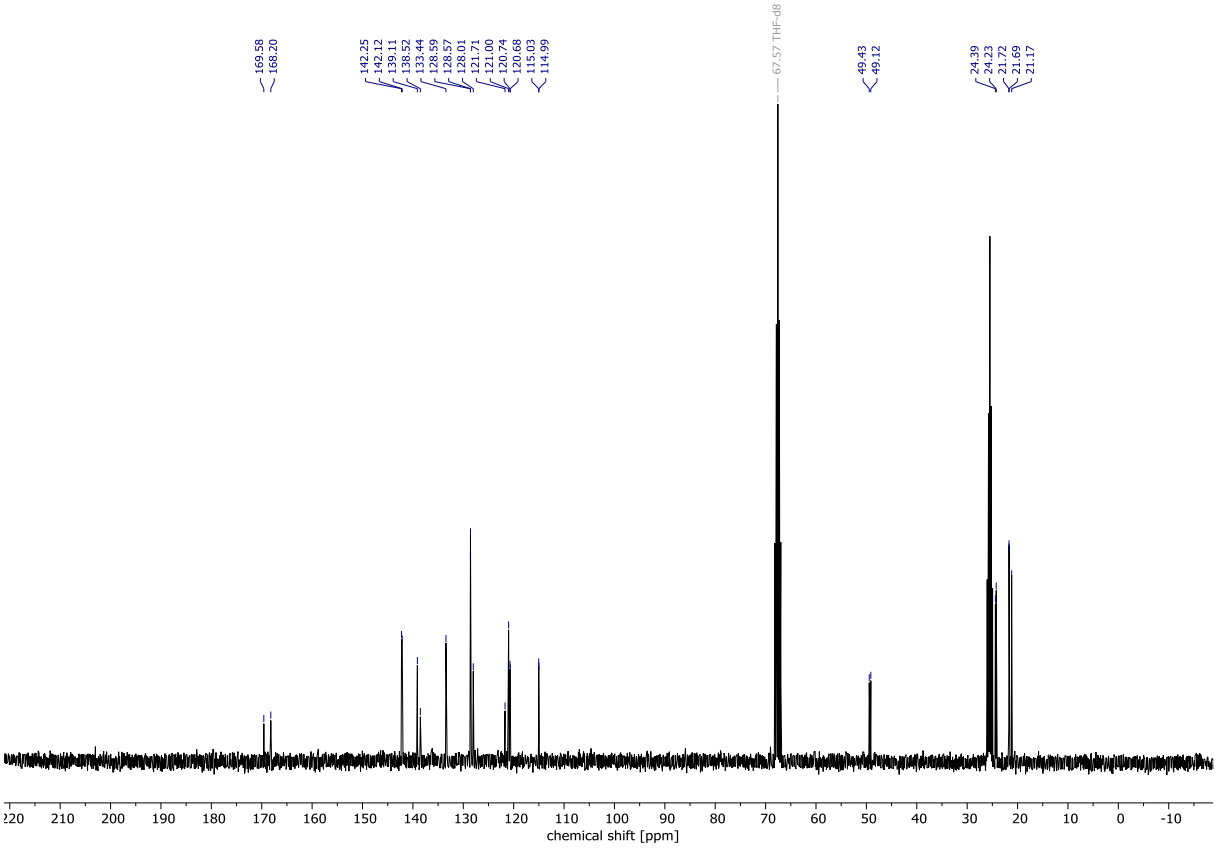


Figure S41: $^{31}P\{^{1}H\}$ NMR spectrum of **5a** (121.5 MHz, THF-d_8, r.t.).

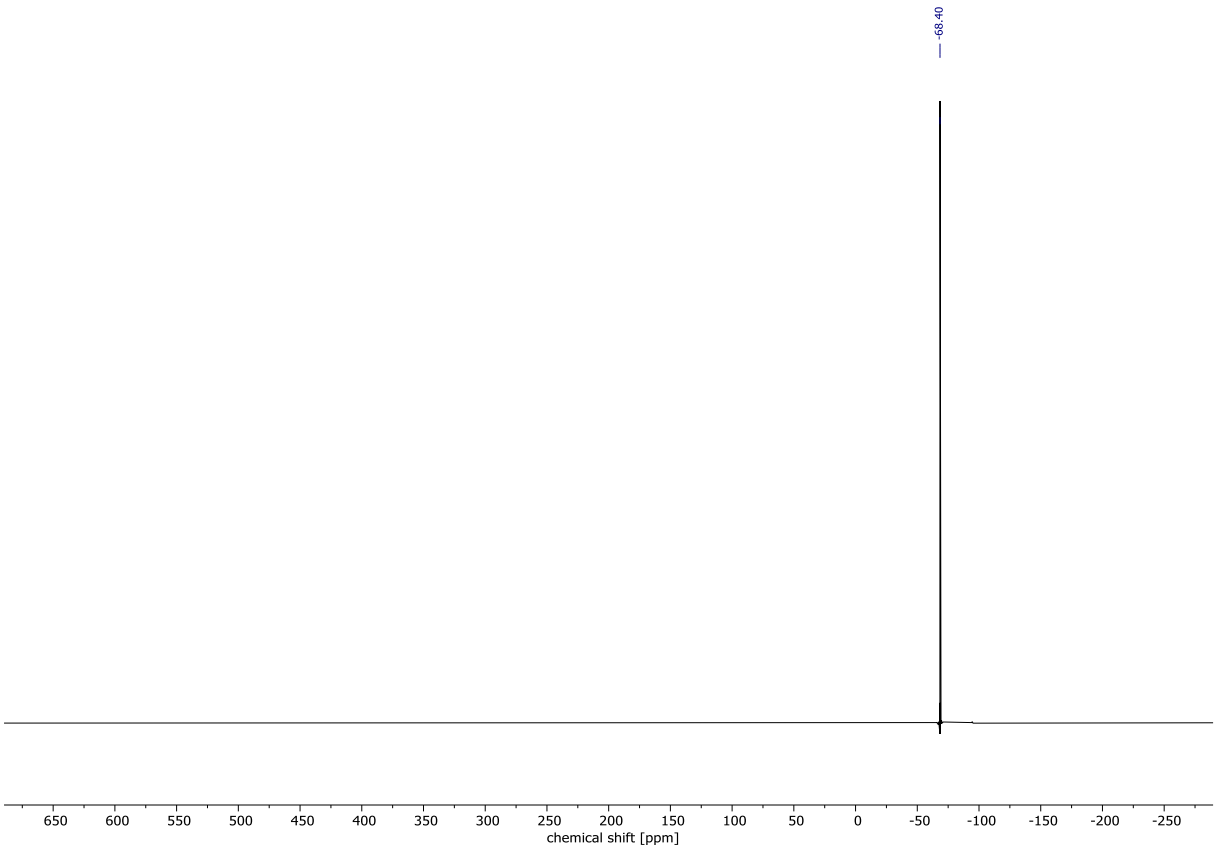
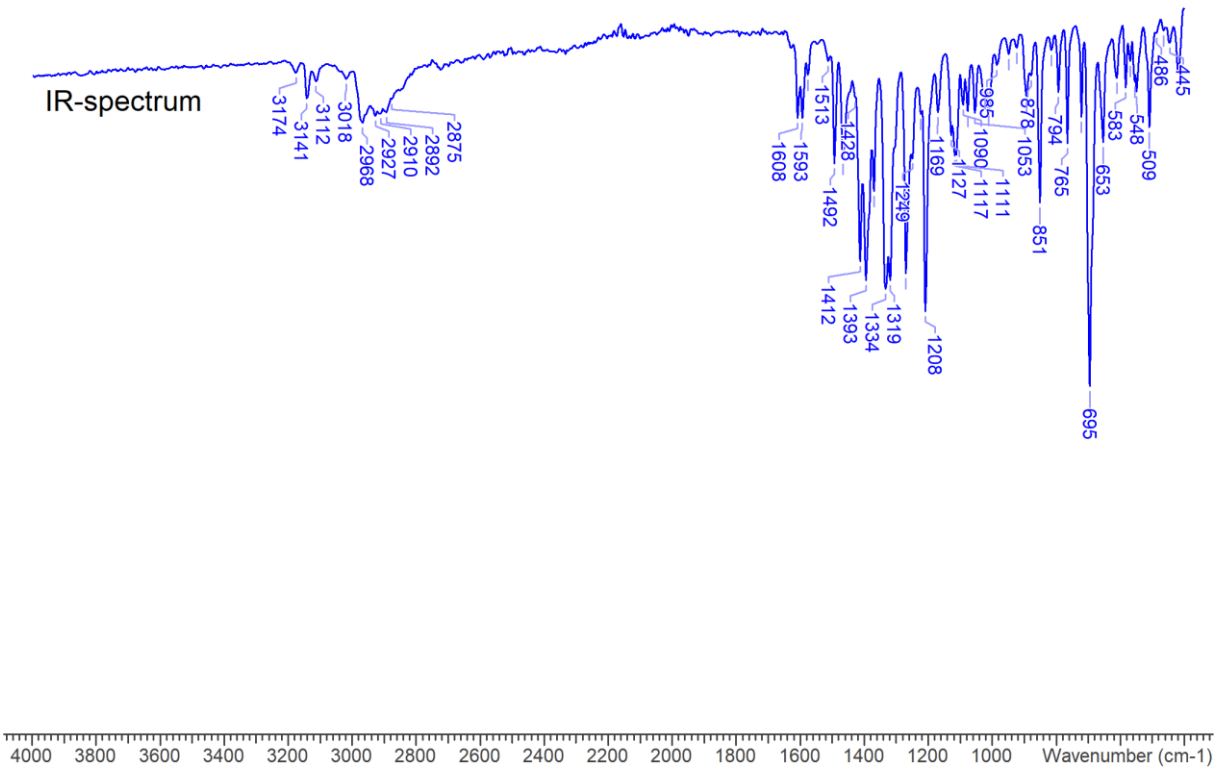
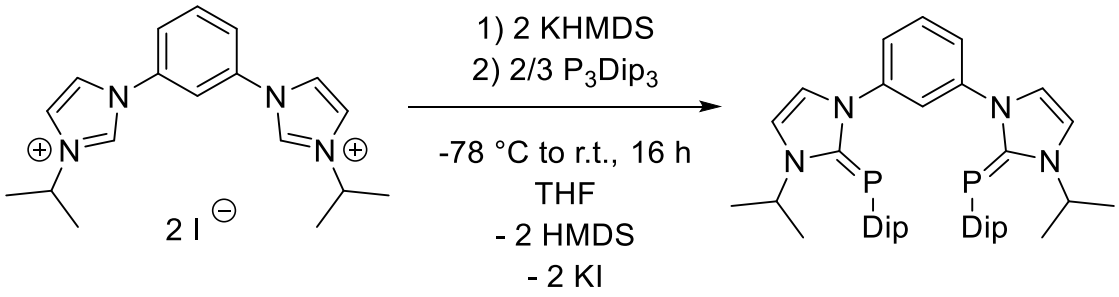


Figure S42: IR spectrum of **5a** (solid sample, 32 scans, r.t.).



4.14 Attempted synthesis of 5b



1,3-Bis(3-isopropylimidazolium)benzene diiodide (0.150 g, 0.27 mmol) was suspended in THF (4 mL). KHMDS (0.111 g, 0.64 mmol, 2.03 eq) was dissolved in THF (20 mL) and added dropwise to the cooled suspension (−78 °C) of the bisimidazolium diiodide and stirred at −70 °C for 2 h and at room temperature for an additional 2 h. This solution containing the free NHC was then added via canula filtration onto Dip_3P_3 (0.105 g, 0.18 mmol, 2/3 eq.). The solution is then stirred at 80 °C for 16 h. THF is removed in vacuo and the red residue is extracted with *n*-hexane (30 mL). *n*-Hexane is then

removed *in vacuo*, resulting in 0.082 g of a red crystalline solid, which contains **5b** and unreacted P_3Dip_3.

$^{31}P\{^1H\}$ NMR (122 MHz, C_6D_6) δ = −85.54 ppm. **MS** (ESI) [MH^+] expected: 679.4058, found: 679.4049.

Crystals suitable for X-ray analysis could not be obtained in <u>*any*</u> solvent.

Figure S43: $^{31}P\{^1H\}$ NMR spectrum of crude **5b** (122 MHz, C_6D_6, r.t.).

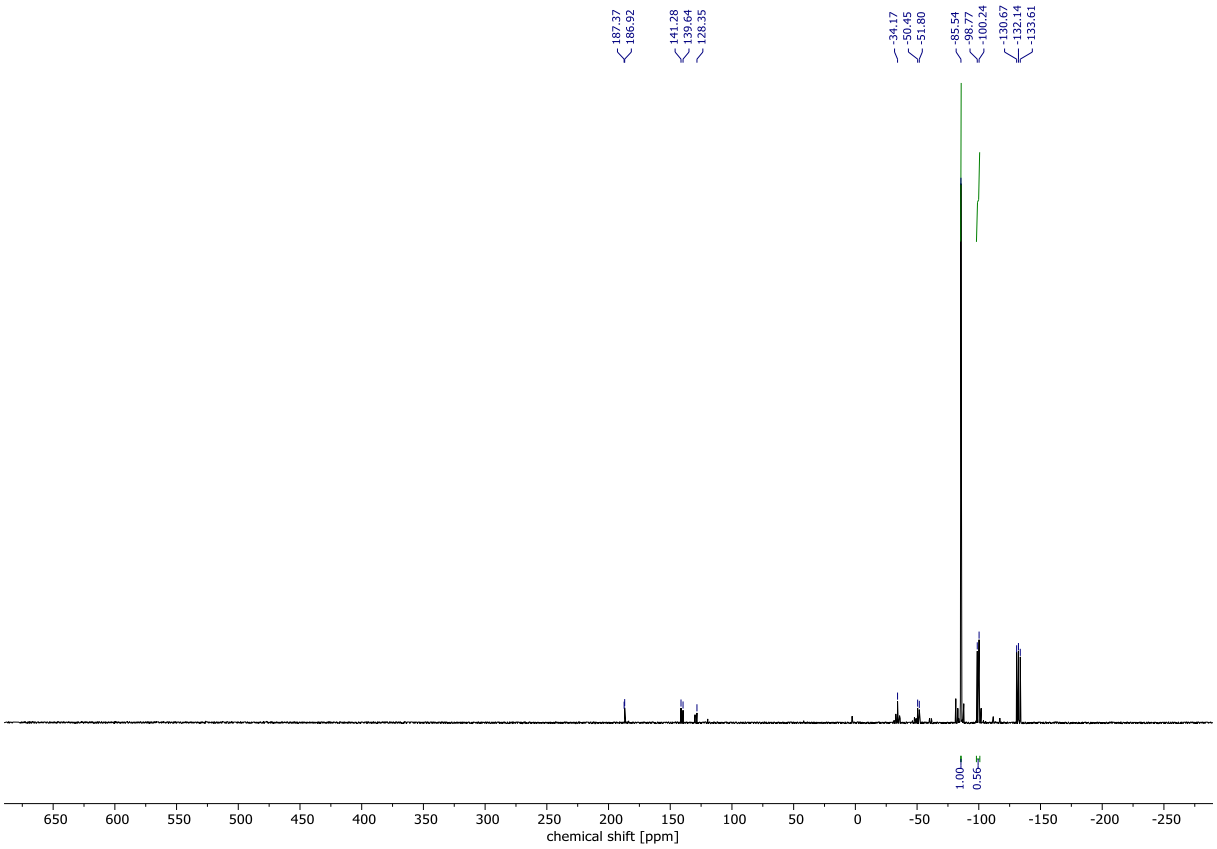
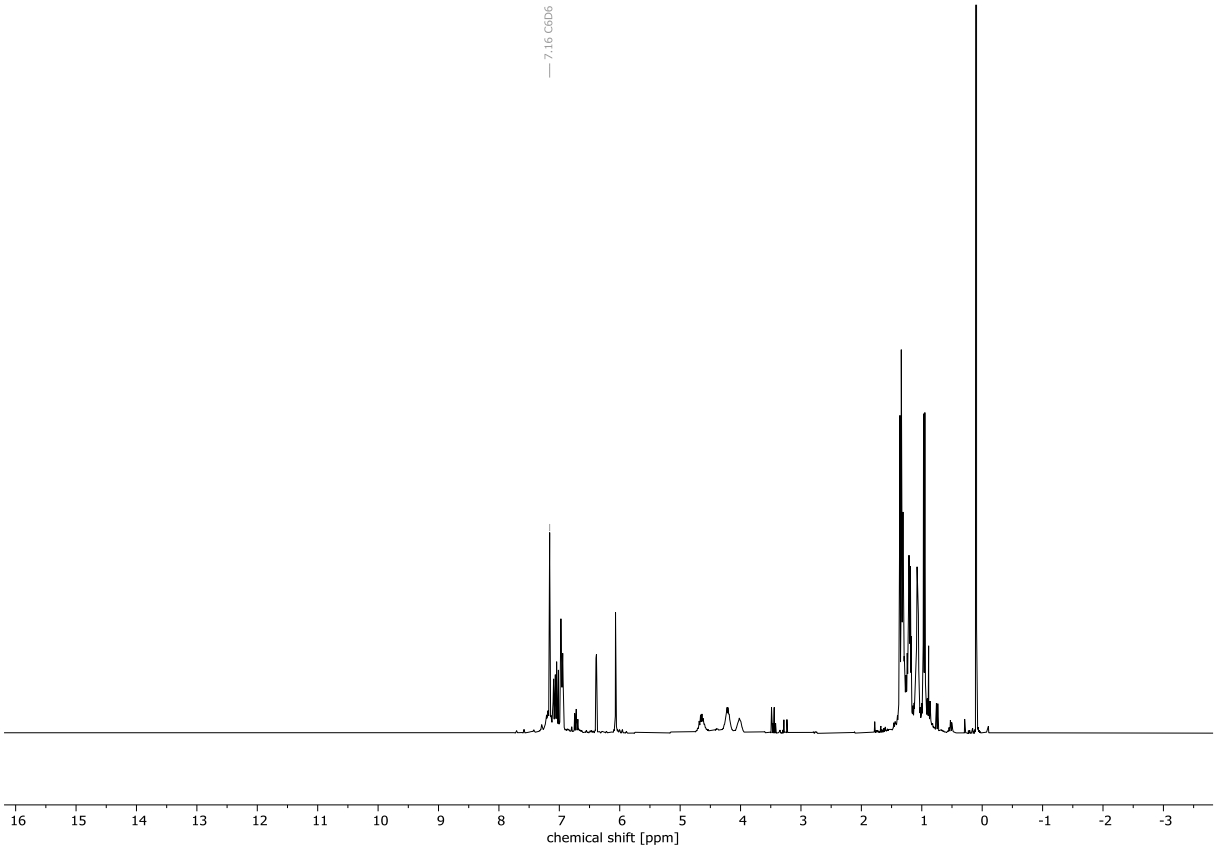
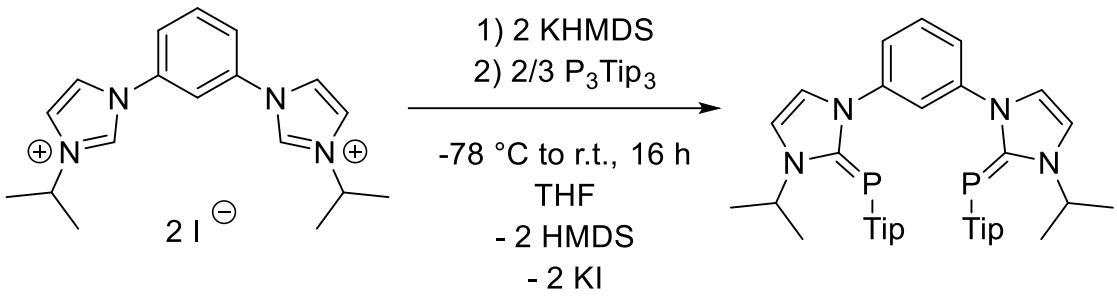


Figure S44: ^{1}H NMR spectrum of crude **5b** (300.2 MHz, C_6D_6, r.t.).

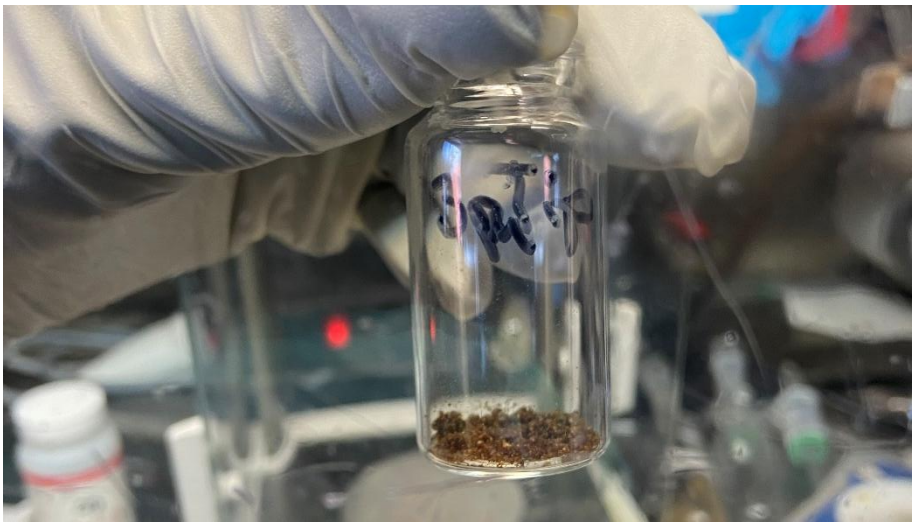


4.15 Attempted synthesis of 5c



1,3-Bis(3-isopropylimidazolium)benzene diiodide (0.300 g, 0.55 mmol) is suspended in THF (4 mL). KHMDS (0.223 g, 1.11 mmol) is dissolved in THF (20 mL) and added dropwise to the cooled suspension of the bisimidazolium diiodide (−78 °C). The resulting yellow suspension turned clear and a white precipitate slowly formed. The suspension was stirred at room temperature for another 4 h. The resulting NHC was then added to Tip_3P_3 (0.252 g, 0.36 mmol) via canula filtration. The resulting deep yellow solution was stirred at 80 °C for 72 h. The solvent of the resulting deep red

solution was removed in vacuo. The deep red residue was extracted twice with *n*-hexane (250 mL, 100 mL). Resulting in 0.231 g red crystals (image below). Analytically pure material could not be obtained. Crystals suitable for X-ray analysis could not be obtained in *any* solvent.



$^{31}P\{^{1}H\}$ NMR (122 MHz, C_6D_6) δ = −84.40 ppm. **MS** (ESI) [MH^+] expected: 763.4998, found: 763.4994.

Figure S45: $^{31}P\{^{1}H\}$ NMR spectrum of crude **5c** (122 MHz, C_6D_6, r.t.).

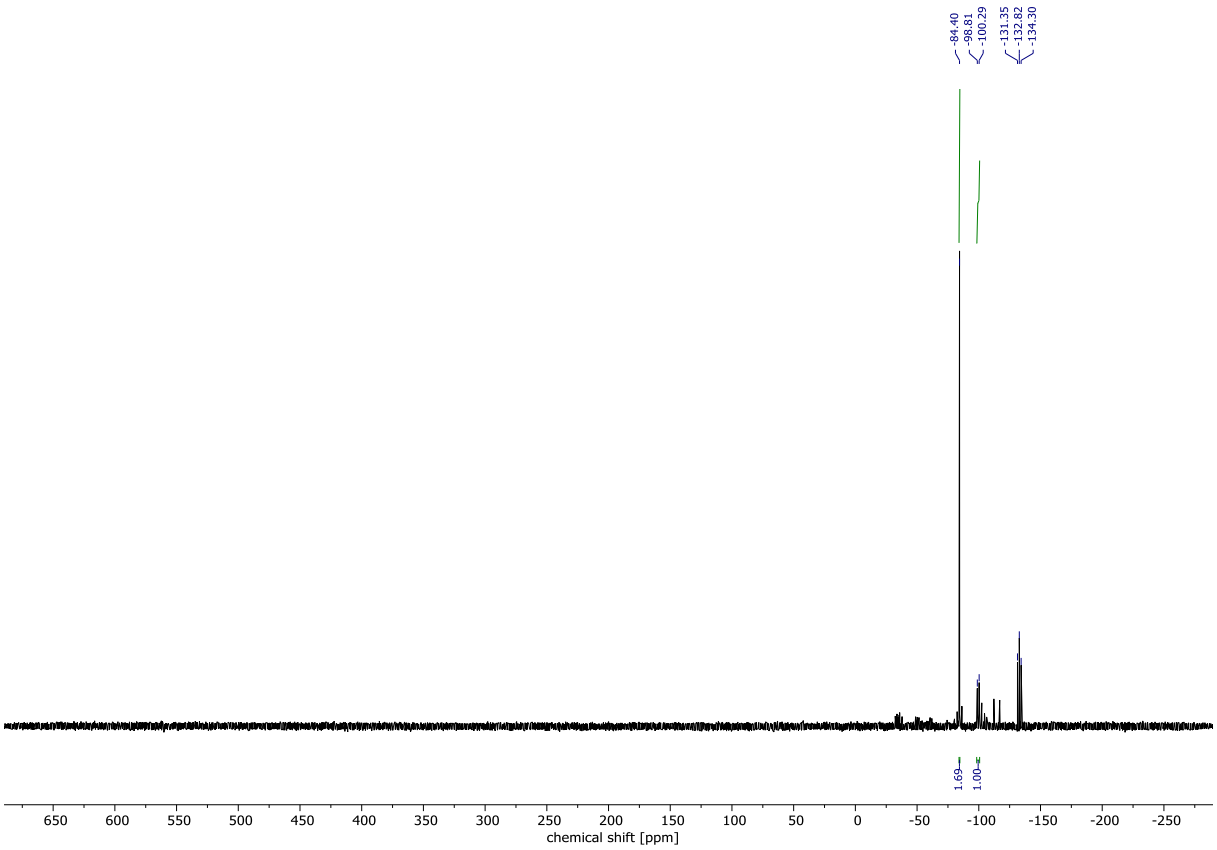
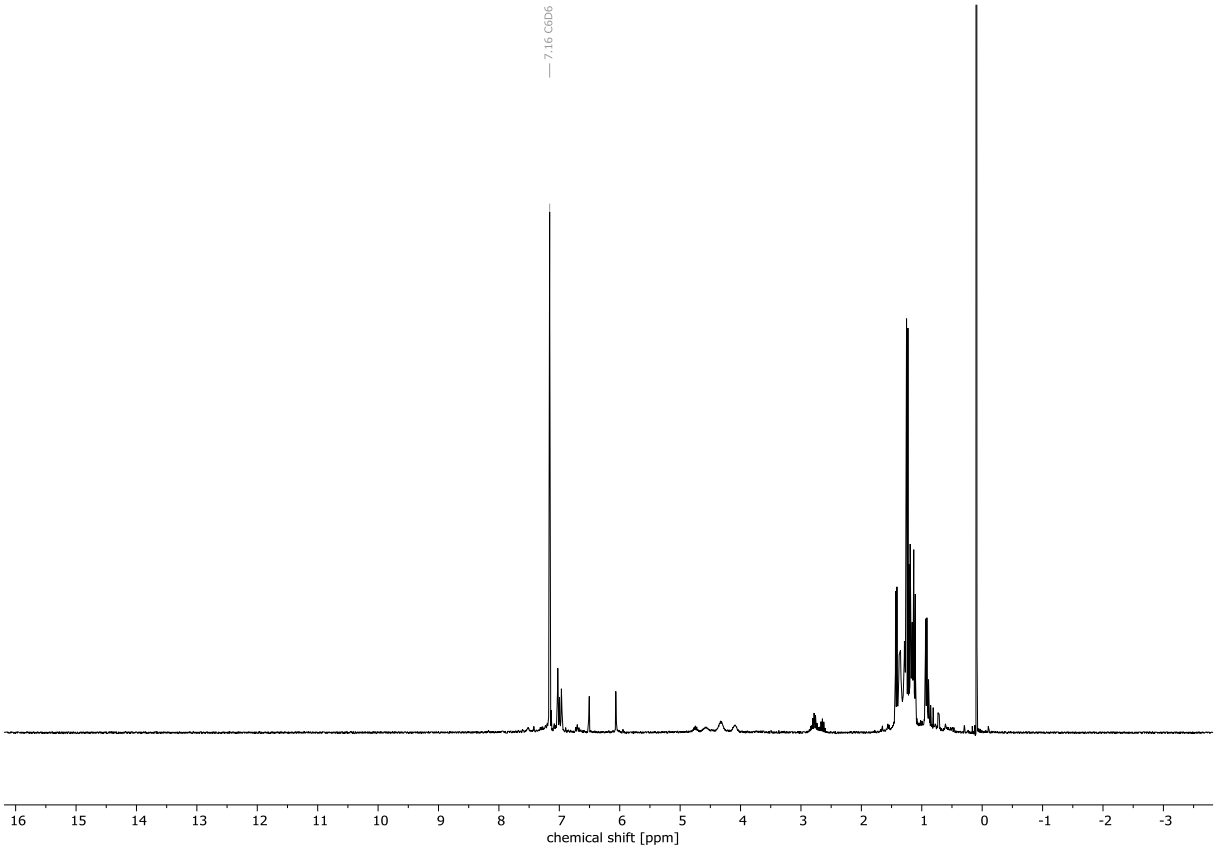
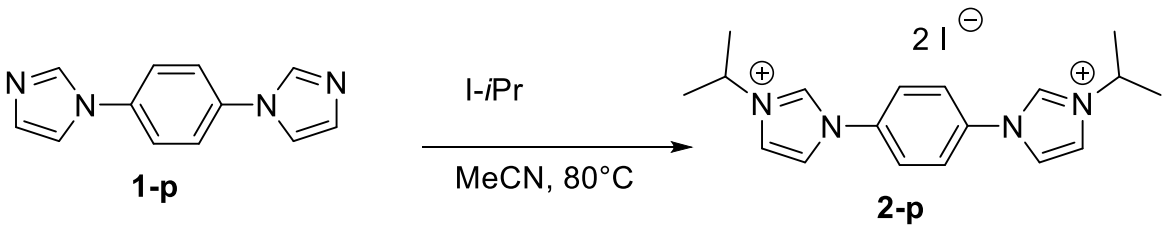


Figure S46: ^{1}H NMR spectrum of crude **5c** (300.2 MHz, C_6D_6, r.t.).



4.16 1,4-Bis(3-isopropylimidazolium)benzene diiodide



1,4-bis(imidazolyl)benzene (2.19 g, 10 mmol) was suspended in MeCN (10 mL) and to this suspension *i*Pr-I (2.6 mL, 27 mmol, 2.7 eq.) was added dropwise. Subsequently the reaction mixture was degassed (3x freeze/pump/thaw) and heated to 80 °C for 8 days. Afterwards the solvent and excess *i*Pr-I were removed in vacuo and the yellow solid was washed with Et_2O (3x 50 mL) resulting in off white 1,4-bis(3-isopropylimidazolium)benzene diiodide. Yield: 4.85 g, 8.81 mmol, 88 %.

CHN calc. C 39.29 N 10.18 H 4.4; found C 39.49 N 9.98 H 5.36. **^{1}H NMR** (300 MHz, DMSO-d6) δ = 9.77 (t, 2H, J = 1.7 Hz, NC*H*N), 8.30 (t, 2H, J = 1.7 Hz, N-C*H*-CH), 8.07 (t, 2H, N-C*H*-CH, J = 1.6 Hz,), 8.00 (s, 4H, Ph-*H*), 4.61 (hept, J = 6.7 Hz, 2H, C*H*-CH_3), 1.46 (d, J = 6.7 Hz, 12H, CH-C*H*$_3$) ppm. **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6) δ = 135.4 (N*C*HN), 134.6 (*i*-*C*Ph), 123.5 (*o*-*C*Ph), 121.8 (N-*C*H-CH), 121.4 (N-*C*H-CH), 53.3 (*C*H-CH_3), 22.3 (CH-*C*H$_3$) ppm. **MS** (ESI) $[M]^{2+}$ expected: 296.2001, observed: 296.1944. **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 447 (w), 526 (m), 557 (w), 625 (s), 637 (m), 647 (m), 759 (m), 804 (vs), 837 (m), 954 (w), 1072 (m), 1092 (m), 1134 (m), 1208 (s), 1317 (w), 1329 (w), 1367 (w), 1424 (m), 1459 (w), 1513 (m), 1554 (s), 2160 (m), 3020 (m), 3053 (m), 3071 (m).

Figure S47: ^{1}H NMR spectrum of 2,5-bis(3-isopropylimidazolium)benzene diiodide (300 MHz, DMSO-d_6, r.t.).

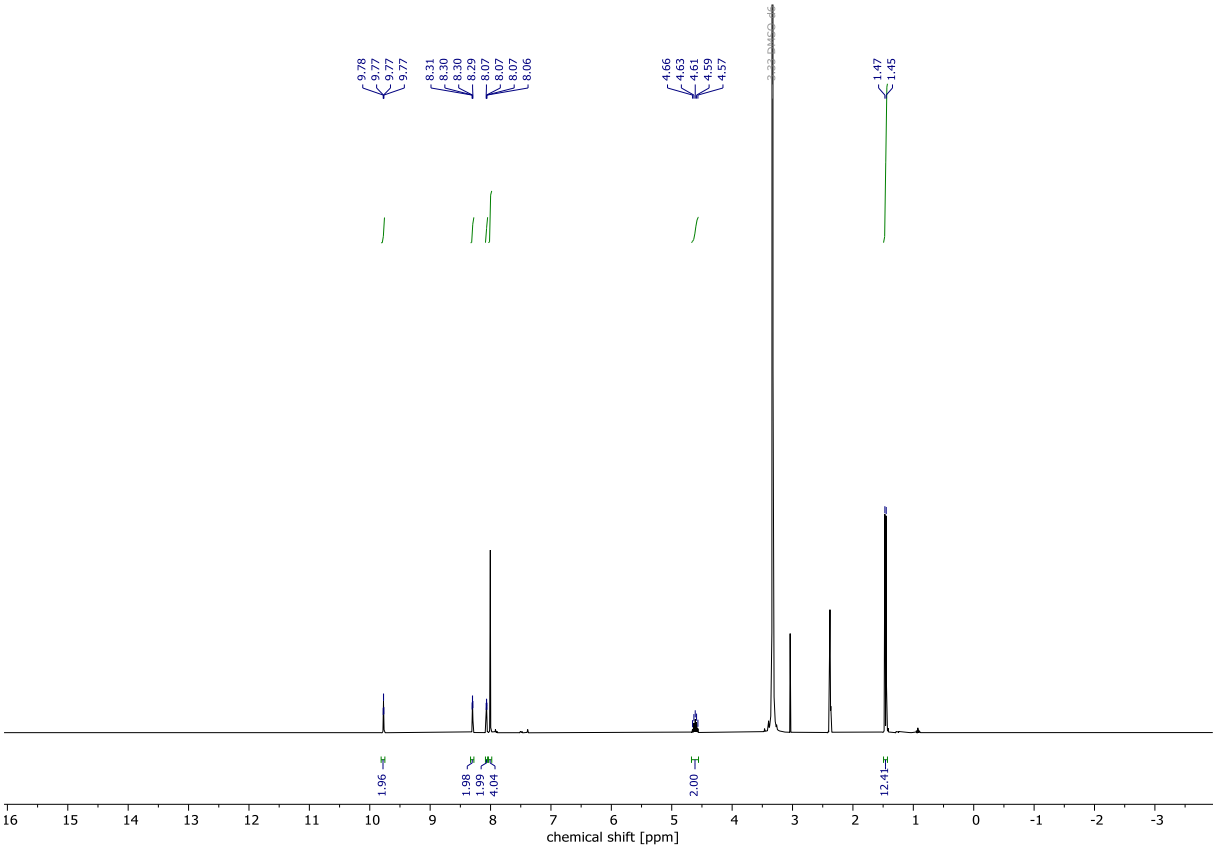


Figure S48: ^{13}C NMR spectrum of 2,5-bis(3-isopropylimidazolium)benzene diiodide (75.5 MHz, DMSO-d_6, r.t.).

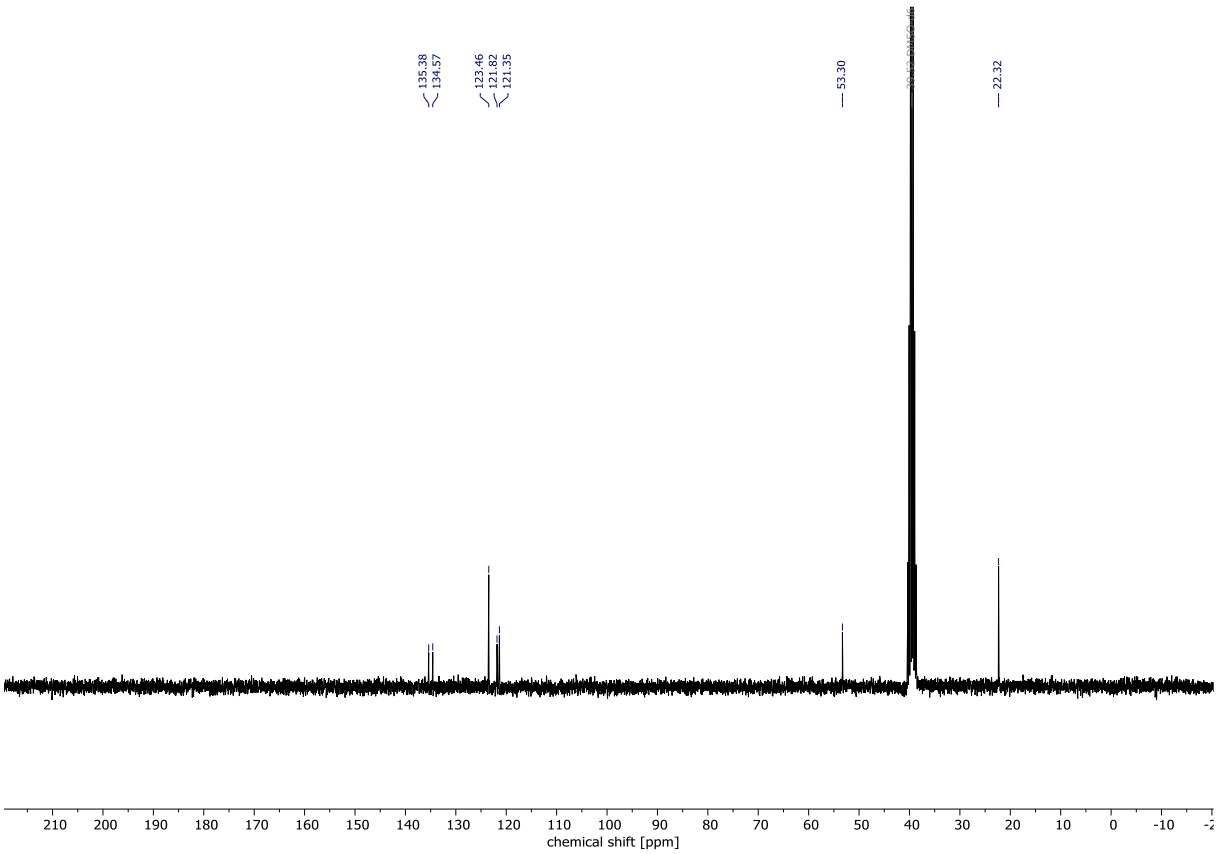
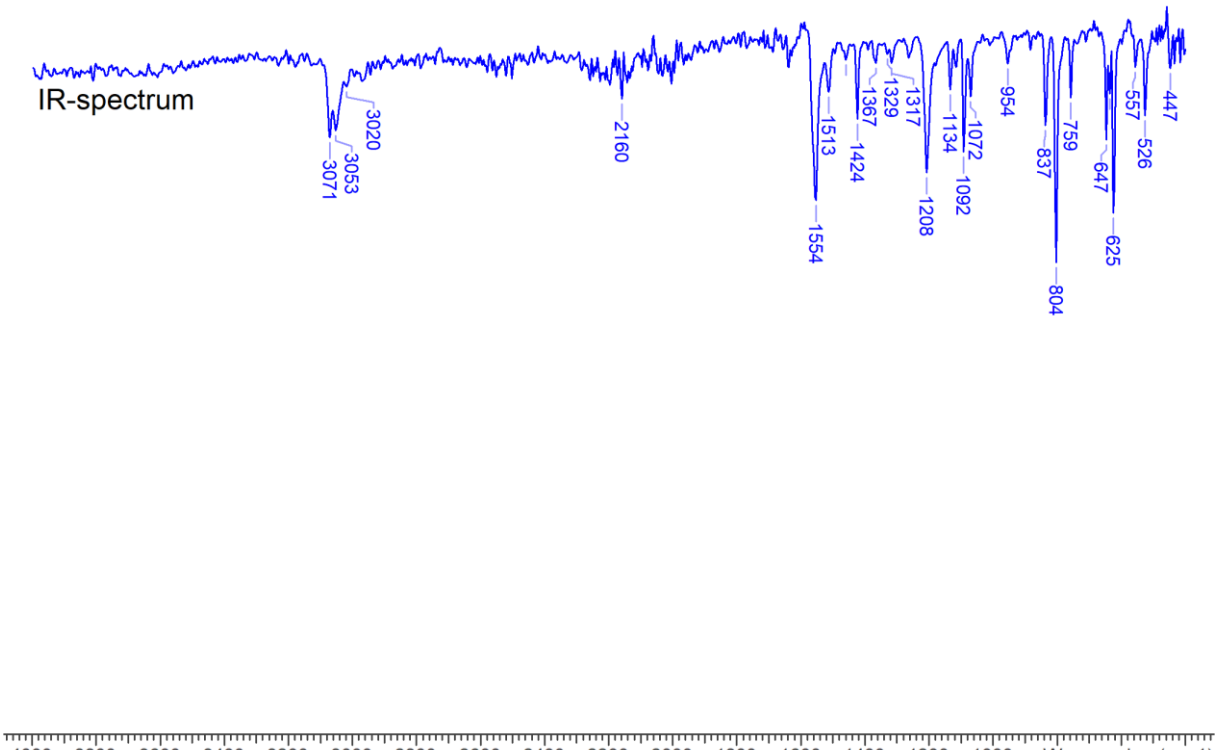
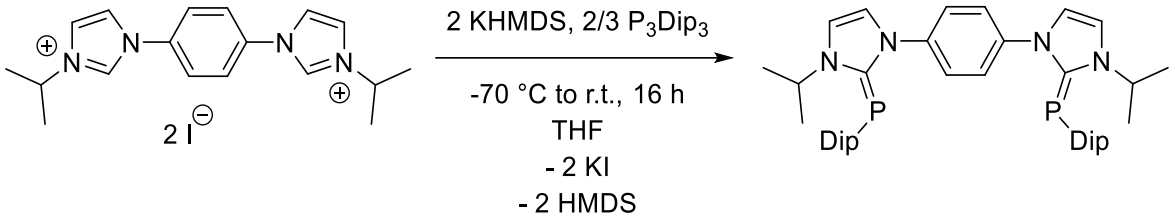


Figure S49: IR spectrum of 2,5-bis(3-isopropylimidazolium)benzene diiodide (solid, 32 scans, r.t.).



4.17 Synthesis of 6b



1,4-Bis(3-isopropylimidazolium)benzene diiodide (0.150 g, 0.27 mmol), Dip_3P_3 (0.105 g, 0.182, 2/3 eq.) and KHMDS (0.111 mg, 0.57 mmol, 2eq.) are suspended in precooled THF (5 mL) and stirred at −70 °C for 1 h. Afterwards the mixture was stirred at 80 °C for 16 h and afterwards the solvent was removed in vacuo. The black/red residue was then extracted with toluene (40 mL), filtered over a G4 frit and afterwards the solvent was evaporated from the filtrate. The residue was redissolved in THF (2 mL), giving deep red solution, which was added dropwise to *n*-hexane (10 mL) with vigorous stirring resulting in the deposition of yellow crystals of **6b**. The yellow crystals were washed with *n*-hexane (2mL) resulting in analytically pure **6b**. Yield: 0.105 g, 0.16 mmol, 57 %.

CHN calc. (found) in %: C 74.31 (74.66), H 8.74 (9.09), N 8.25 (8.54). **^{31}P{^{1}H} NMR** (162 MHz, THF-d_8) δ = −86.90 ppm. **^{1}H NMR** (400 MHz, THF-d_8) δ = 7.01 (d, *J* = 2.4 Hz, 2H, CHC*H*N), 6.83 (t, *J* = 7.4 Hz, 6H, Ar*H*), 6.73 (s, 2H, Ph*H*), 6.71 (s, 2H, Ph*H*), 6.68 (s, 2H, CHC*H*N), 4.57 (s, 2H, NCH$(CH_3)_2$), 3.86 (dd, J = 10.0, 3.0 Hz, 4H, C*H*$(CH_3)_2$), 1.29 (d, J = 6.6 Hz, 12H, CH(C*H*$_3)_2$), 1.05 (dd, J = 9.9, 6.8 Hz, 24H, CH(C*H*$_3)_2$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, THF-d_8) δ = 169.7 (d, $^{1}J_{PC}$ = 108.2 Hz, N_2*C*=P), 154.2 (d, *J* = 8.0 Hz, *o*-Ar*C*), 140.5 (d, $^{1}J_{PC}$ = 49.3 Hz, *i*-Ar*C*), 138.1 (Ar*C*), 127.1 (*i*-Ph*C*), 126.3 (d, *J* = 3.2 Hz, Ar*C*H), 122.4 (Ph*C*H), 120.5 (d, J = 3.9 Hz, N*C*HCH), 115.5 (d, J = 3.3 Hz, N*C*HCH), 49.7 (d, *J* = 18.0 Hz, N*C*H$(CH_3)_2$), 33.9 (d, *J* = 10.3 Hz, *C*H$(CH_3)_2$), 23.5 (CH(*C*H$_3)_2$), 21.7 (CH(*C*H$_3)_2$) ppm. **MS** (ESI) [MH^+] expected: 679.4058, found: 679.4052.

Single crystals suitable for X-ray analysis were grown from a saturated THF solution at room temperature.

Figure S50: ^{1}H NMR spectrum of 3pPDip **6b** (400 Mhz, THF-d_8, r.t.).

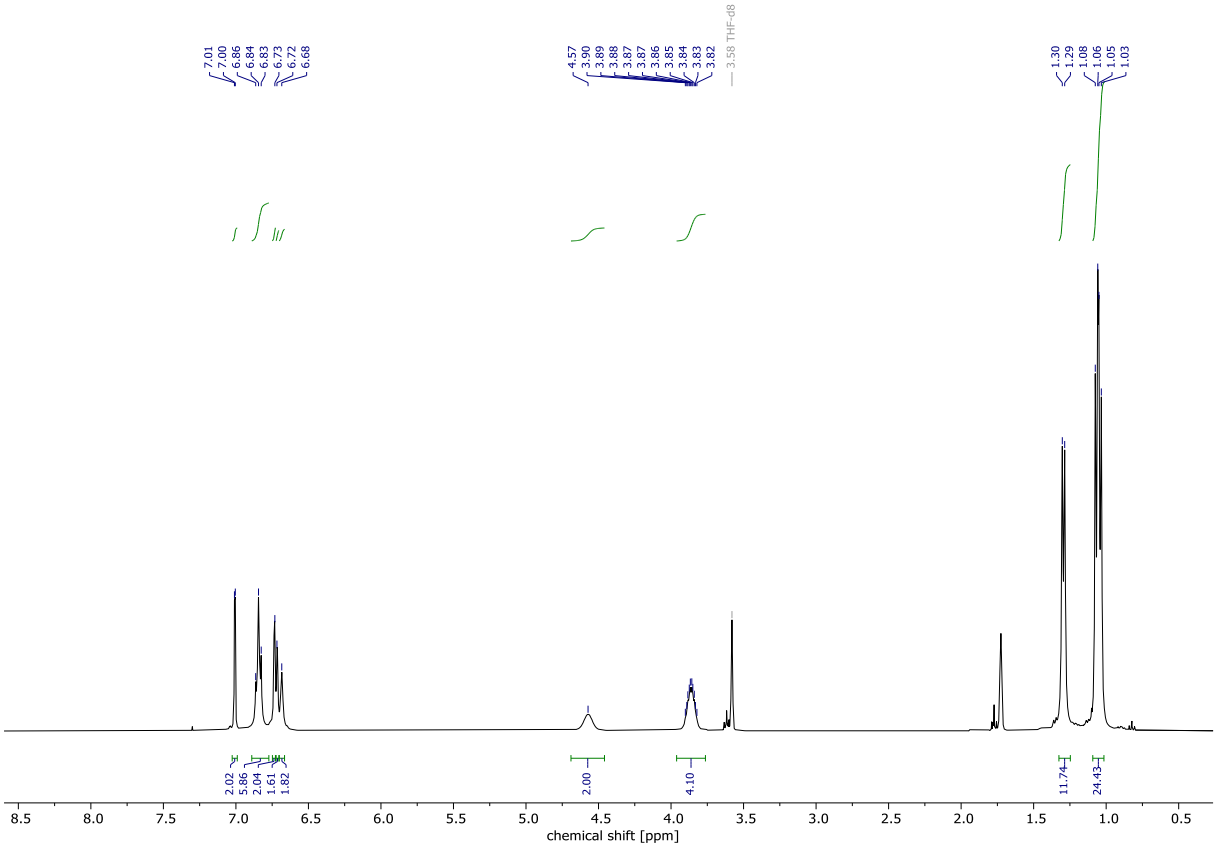


Figure S51: $^{13}C\{^{1}H\}$ NMR spectrum of **6b** (400 Mhz, THF-d_8, r.t.)..

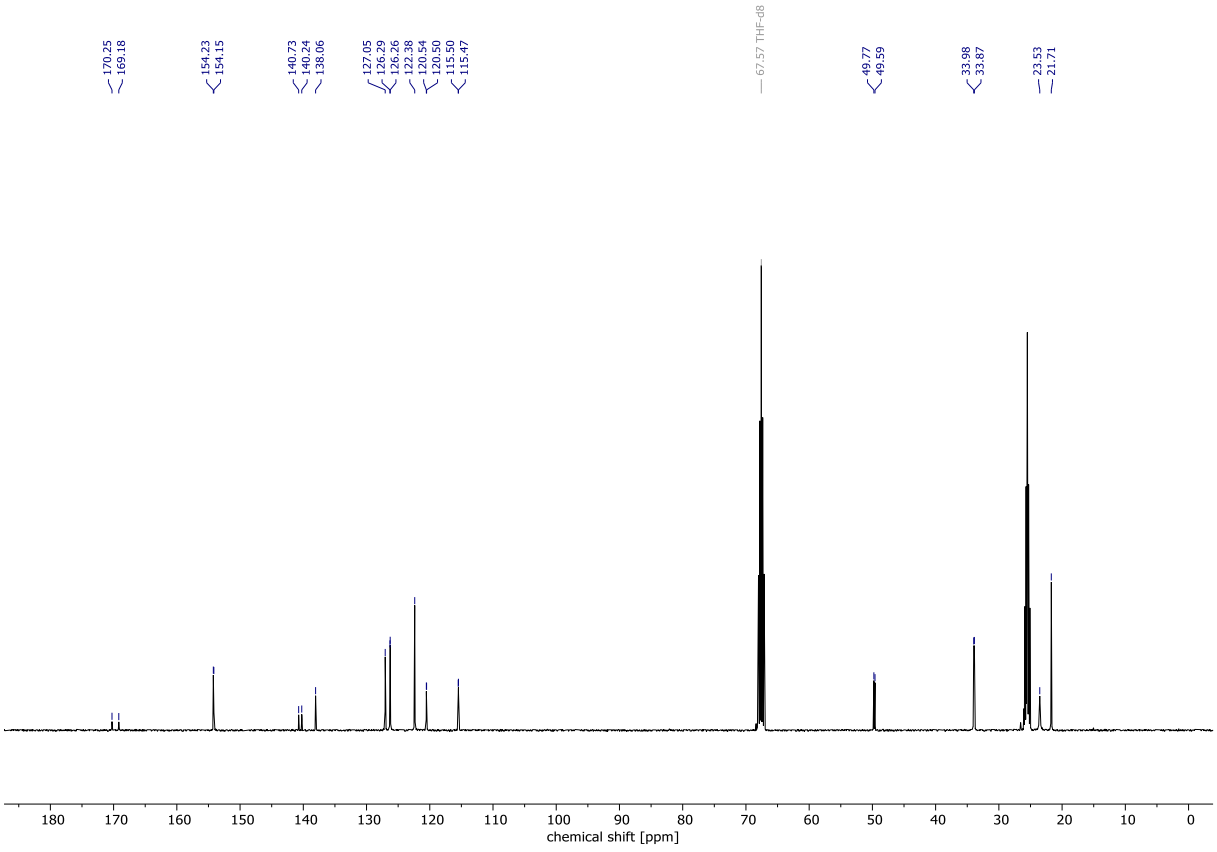
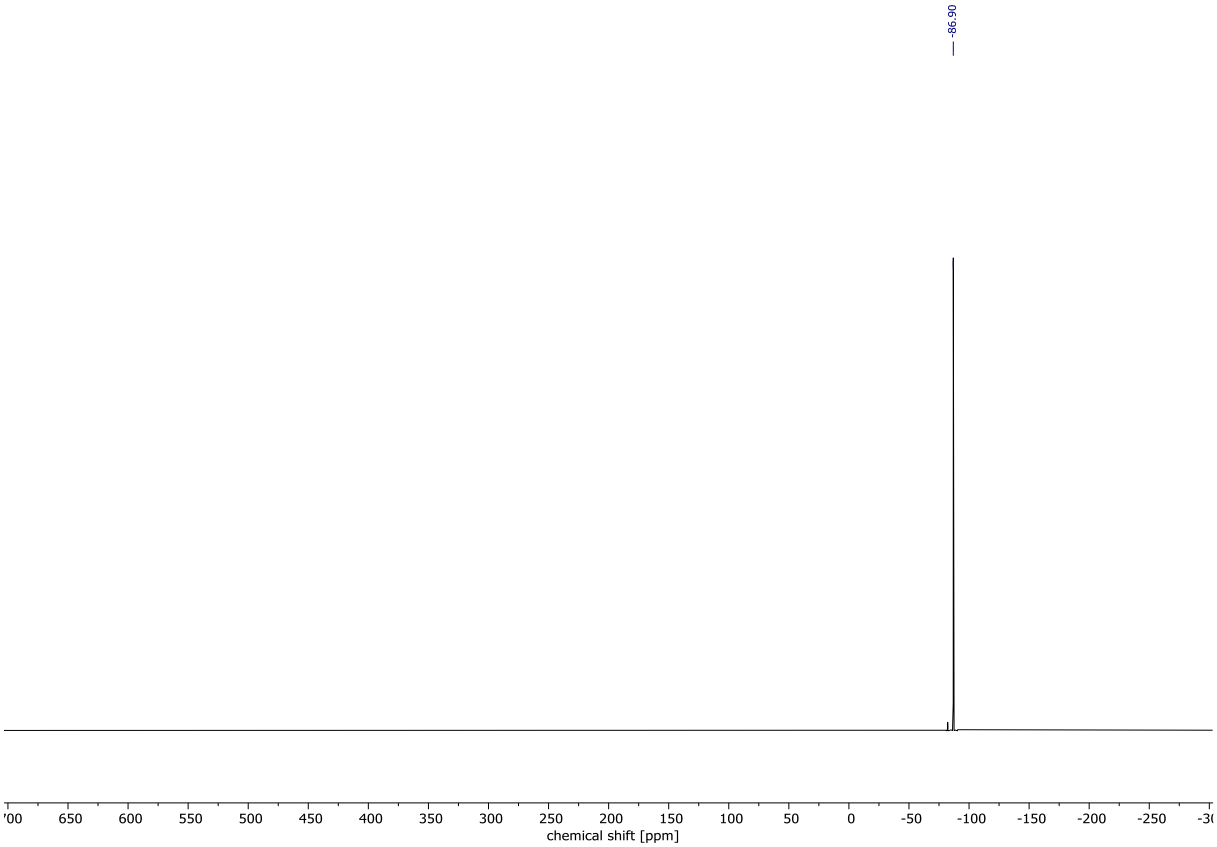
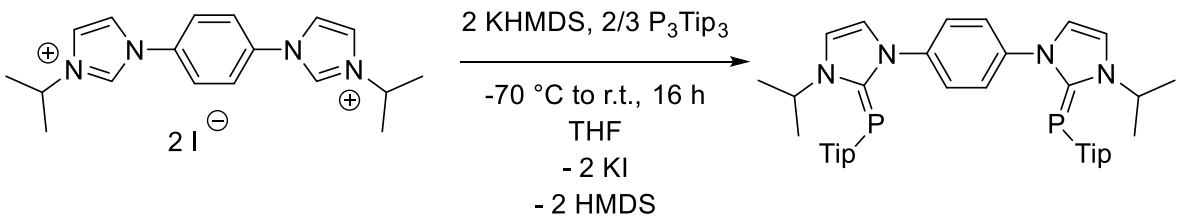


Figure S52: $^{31}P\{^{1}H\}$ NMR spectrum of **6b**.



4.18 Synthesis of 6c



1,4-Bis(3-isopropylimidazolium)benzene diiodide (1 g, 1.820 mmol, 1 eq.) Tip_3P_3 (0.853 g, 1.213 mmol, 0.67 eq.) and KHMDS (0.728 g, 3.640 mmol, 2 eq.) were dissolved in precooled THF and stirred at -70 °C for 1 h. The red suspension is heated to 80 °C overnight. THF is removed in vacou and the resulting red residue is redissolved in tolouene. The red solution is filtred through a G3 frit and afterwards toluene was removed in vacuo. The red residue was washed with MeCN (2 x 5 mL) and HMDSO (3 x 10 mL) resulting in yellow crystals of **6c**. Yield: 0.434 g, 0.57 mmol, 31 %.

CHN calc. (found) in %: C 75.32 (74.38), H 10.45 (10.40), N 6.76 (5.59). **^{31}P{^{1}H} NMR** (C_6D_6, 121.5 MHz): δ = -84.61 ppm. **^{1}H NMR** (400.13 MHz, C_6D_6): δ = 6.94 (s, 4H, Ar*H*), 6.90 (s, 4H, Ph*H*), 6.24 (s, 2H, CHCHN), 6.09 (d, J = 2.3 Hz, 2H, CHCHN), 4.67 (s, 2H, NC*H*$(CH_3)_2$), 4.26 (s, 4H, *o*-C*H*$(CH_3)_2$), 2.76 (p, J = 6.9 Hz, 2H, *p*-C*H*$(CH_3)_2$), 1.36 (d, J = 6.8 Hz, 12H, C*H*$_3$), 1.29 – 1.20 (m, 24H, C*H*$_3$), 0.98 (d, J = 6.7 Hz, 12H, C*H*$_3$) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 75.5 MHz): δ = 170.1 (d, J = 108.8 Hz, N_2C=P), 153.9 (d, J = 8.1 Hz, *o*-Ar*C*), 147.1 (*i*-Ph*C*), 137.6 (*p*-Ar*C*), 136.5 (d, J = 47.1 Hz, *i*-Ar*C*), 125.9 (d, J_{PC} = 3.8 Hz, Ar*C*H), 120.2 (CH*C*HN), 119.5 (Ph*C*H), 114.1 (d, J = 3.4 Hz, CH*C*HN), 48.7 (d, J = 16.5 Hz, N*C*H$(CH_3)_2$), 34.8 (*p*-*C*H$(CH_3)_2$), 33.7 (d, J = 10.0 Hz, *o*-*C*H$(CH_3)_2$), 24.6 (CH(*C*H$_3)_2$), 21.4 (CH(*C*H$_3)_2$) ppm. **MS** (ESI) [MH^+] expected: 763.4998, found: 763.4996. **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 418 (w), 456 (w), 488 (w), 519 (w), 561 (m), 596 (m), 647 (m), 662 (m), 701 (vs), 728 (vw), 759 (m), 837 (s), 876 (m), 934 (m), 946 (m), 1012 (w), 1022 (w), 1037 (w), 1057 (m), 1101 (s), 1117 (m), 1132 (m), 1162 (m), 1210 (vs), 1251 (s), 1303 (vs), 1356 (m), 1379 (s), 1391 (s), 1404 (s), 1461 (m), 1517 (s), 1573 (vw), 1595 (w), 2865 (m), 2929 (m), 2956 (s), 3042 (vw), 3102 (w), 3131 (w).

Figure S53: ^{1}H NMR spectrum of **6c** (400 MHz, C_6D_6, r.t.).

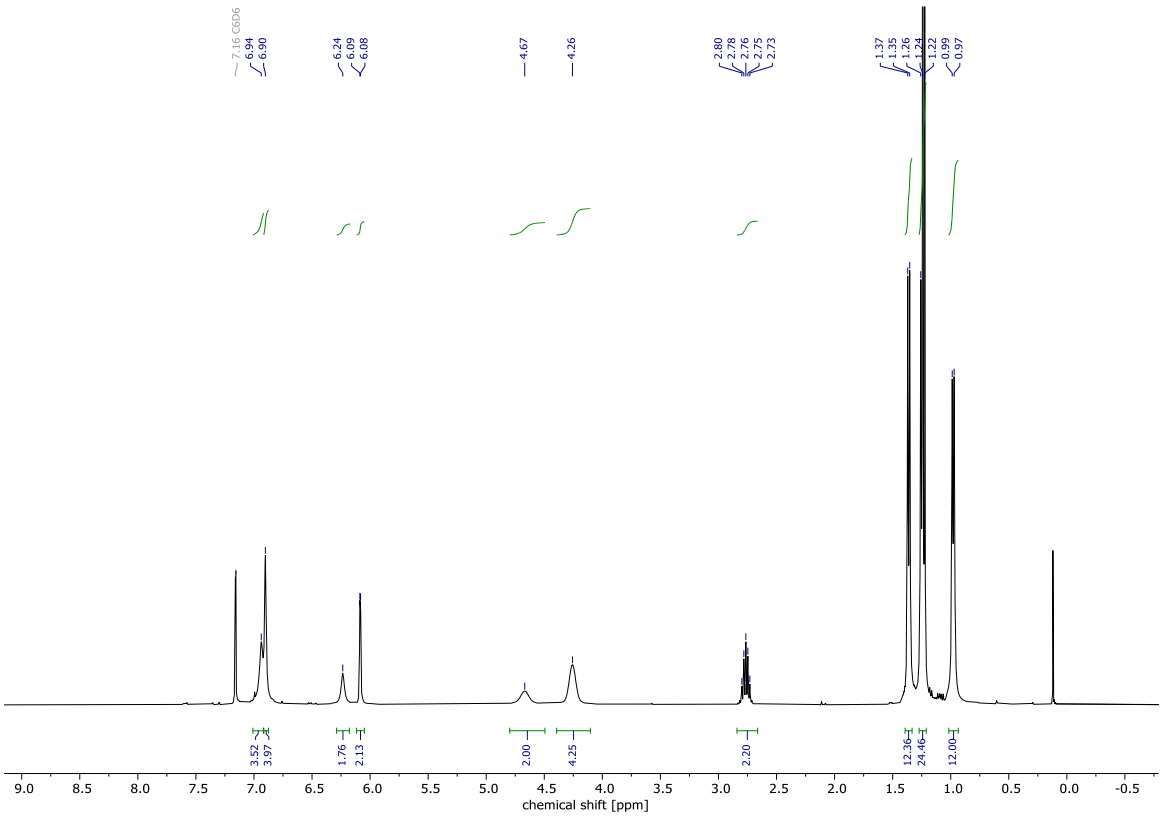


Figure S54: $^{13}C\{^{1}H\}$ NMR spectrum of **6c** (75.5 MHz, C_6D_6, r.t.).

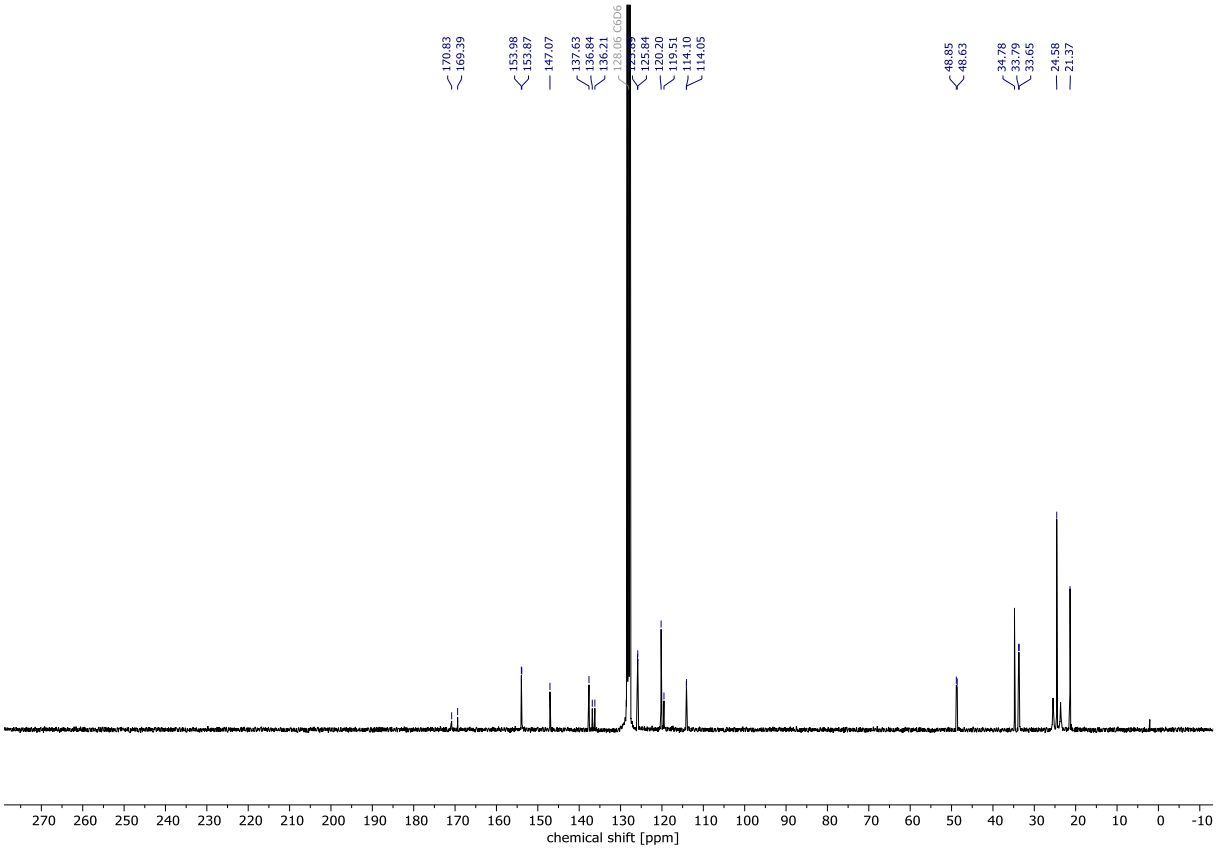


Figure S55: $^{31}P\{^{1}H\}$ NMR spectrum of **6c** (162 MHz, C_6D_6, r.t.).

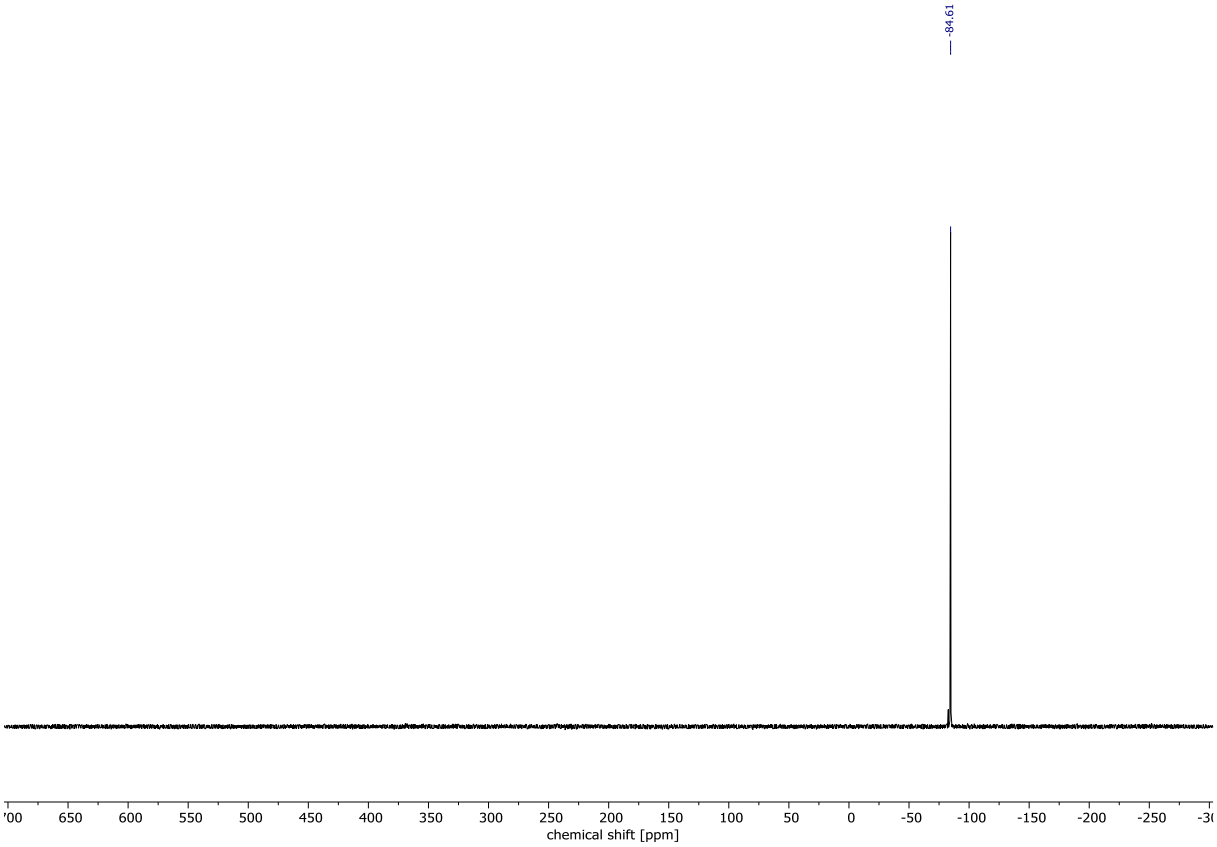
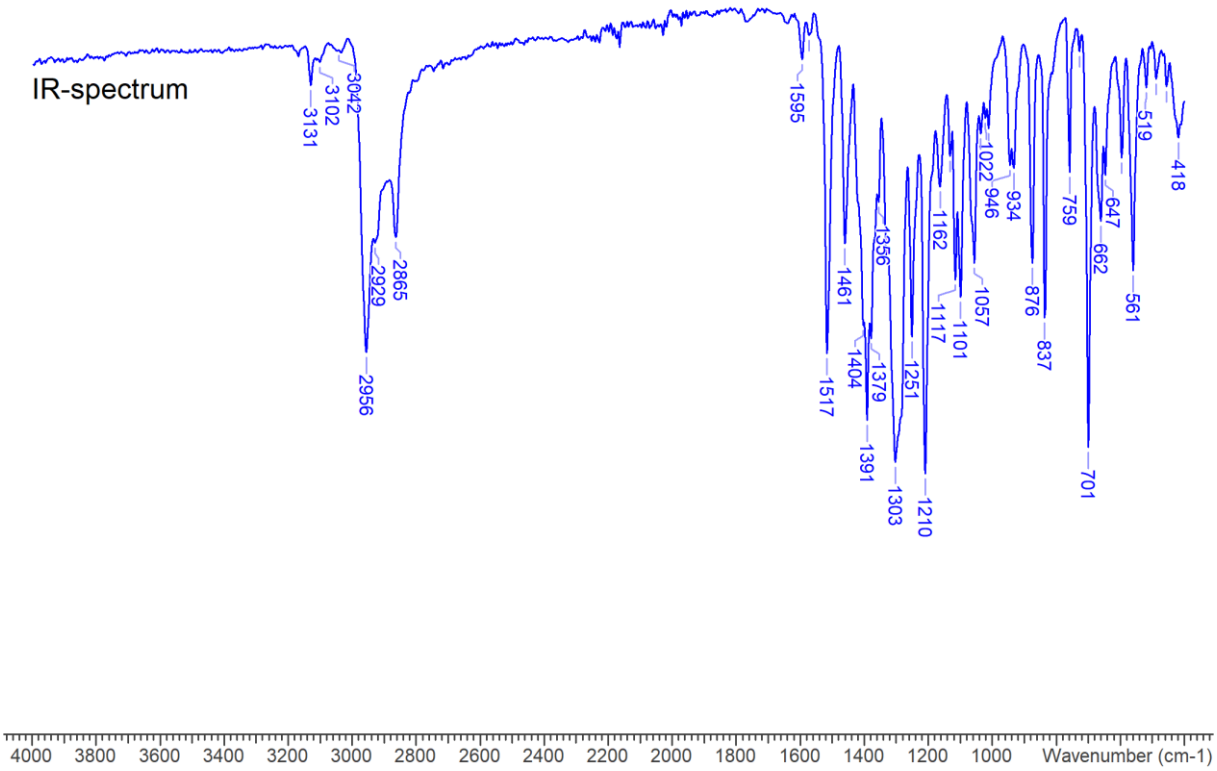
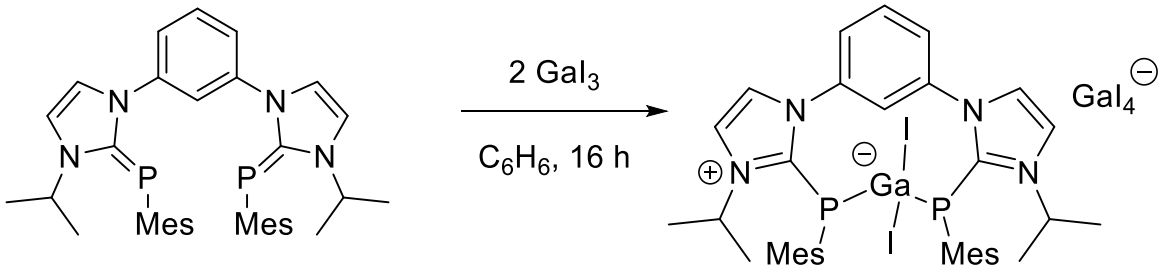


Figure S56: IR spectrum of **6c** (solid sample, 32 scans, r.t.).



4.19 Synthesis of 7



5a (0.035 g, 0.06 mmol) and GaI_3 (0.053 g, 0.12 mmol) were dissolved in C_6H_6 (3 mL) and stirred for 16 h at room temperature resulting in a clear solution and a yellow oil at the bottom of the flask. Subsequently the solvent was removed *in vacuo*. The yellow residue was redissolved in CH_2Cl_2 (1 mL). The product was added dropwise to a stirring solution of hexane (10 mL) resulting in the immediate precipitation of **7** as a white solid. The supernatant *n*-hexane solution was removed via canula filtration, and the white solid was washed with *n*-hexane (5 mL). Resulting in analytically pure **7**. Yield: 0.062 g, 0.04 mmol, 70 %.

CHN calc. (found) in %: C 28.91 (28.19), H 2.97 (3.21), N 3.75 (3.53). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2) δ = -71.89 ppm. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ = 8.07 (dd, J = 8.6, 7.6 Hz, 1H, *i*-Ph*H*), 7.90 (dd, *J* = 8.0, 2.2 Hz, 2H, Ph*H*), 7.73 (d, *J* = 2.3 Hz, 2H, CHC*H*N), 7.72 (d, *J* = 2.1 Hz, 1H, Ph*H*), 7.44 (d, *J* = 2.2 Hz, 2H, CHC*H*N), 6.99 (s, 2H, Ar*H*), 6.88 (s, 2H, Ar*H*), 4.36 (p, J = 6.6 Hz, 2H, NC*H*(CH_3)$_2$), 2.75 (s, 6H, *o'*-ArCH_3), 2.25 (s, 6H, *o*-ArCH_3), 2.07 (s, 6H, *p*-ArCH_3), 1.42 (d, J = 6.7 Hz, 6H, NCH(CH_3)$_2$), 0.81 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, NCH(CH_3)$_2$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2) δ = 154.51 (dd, *J* = 37.5 , 40.6 Hz, N_2C=P), 146.35 (t, *J* = 16.0 Hz, *i*-Ar*C*), 143.68 (Ar*C*), 141.11 (Ar*C*), 137.43 (Ph*C*), 135.60 (Ph*C*H), 130.64 (Ar*C*H), 130.22 (Ar*C*H), 128.44 (Ph*C*H), 127.79 (Ph*C*H), 124.68 (Ar*C*), 123.25 (t, J = 4.5 Hz, CH*C*HN), 120.91 (CH*C*HN), 26.69 (t, J = 13.9 Hz, *C*H(CH_3)$_2$), 24.97 (Ar*C*H_3), 23.92 (CH(*C*H_3)$_2$), 21.28 (Ar*C*H_3), 20.83 (CH(*C*H_3)$_2$). **MS** (ESI) 4mMesGaI_2^+ expected mass: 917.0391, obsevered mass 917.0417. **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 418 (w), 431 (w), 458 (w), 491 (w), 503 (w), 554 (m), 567 (w), 612 (w), 651 (m), 690 (vs), 715 (w), 740 (s), 767 (w), 796 (w), 851 (m), 880 (m), 1004 (w), 1026 (w), 1074 (w), 1119 (m), 1132 (m), 1173 (w), 1206 (s), 1220 (m), 1290 (w), 1317 (m), 1375 (m), 1404 (s), 1433 (m), 1459 (m), 1472 (m), 1496 (m), 1566 (m), 1599 (m), 2914 (w), 2931 (w), 2966 (m), 2974 (m), 3038 (w), 3104 (w), 3133 (w), 3164 (w).

Single crystals suitable for X-ray diffraction were grown by layering a CH_2Cl_2 solution of **7** with *n*-hexane.

Figure S57: ^{1}H NMR spectrum of **7** (400 MHz, CD_2Cl_2, r.t.).

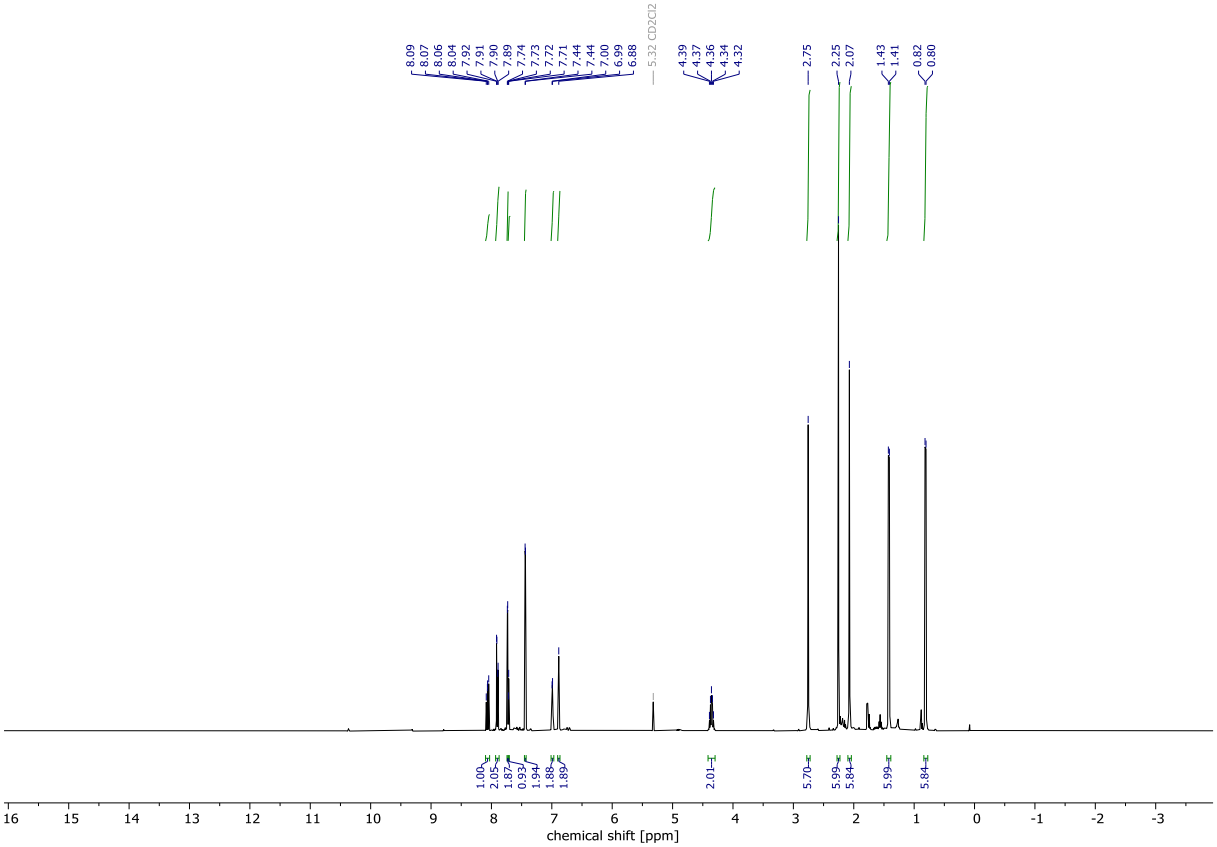


Figure S58: $^{13}C\{^{1}H\}$ NMR spectrum of **7** (101 MHz, CD_2Cl_2, r.t.).

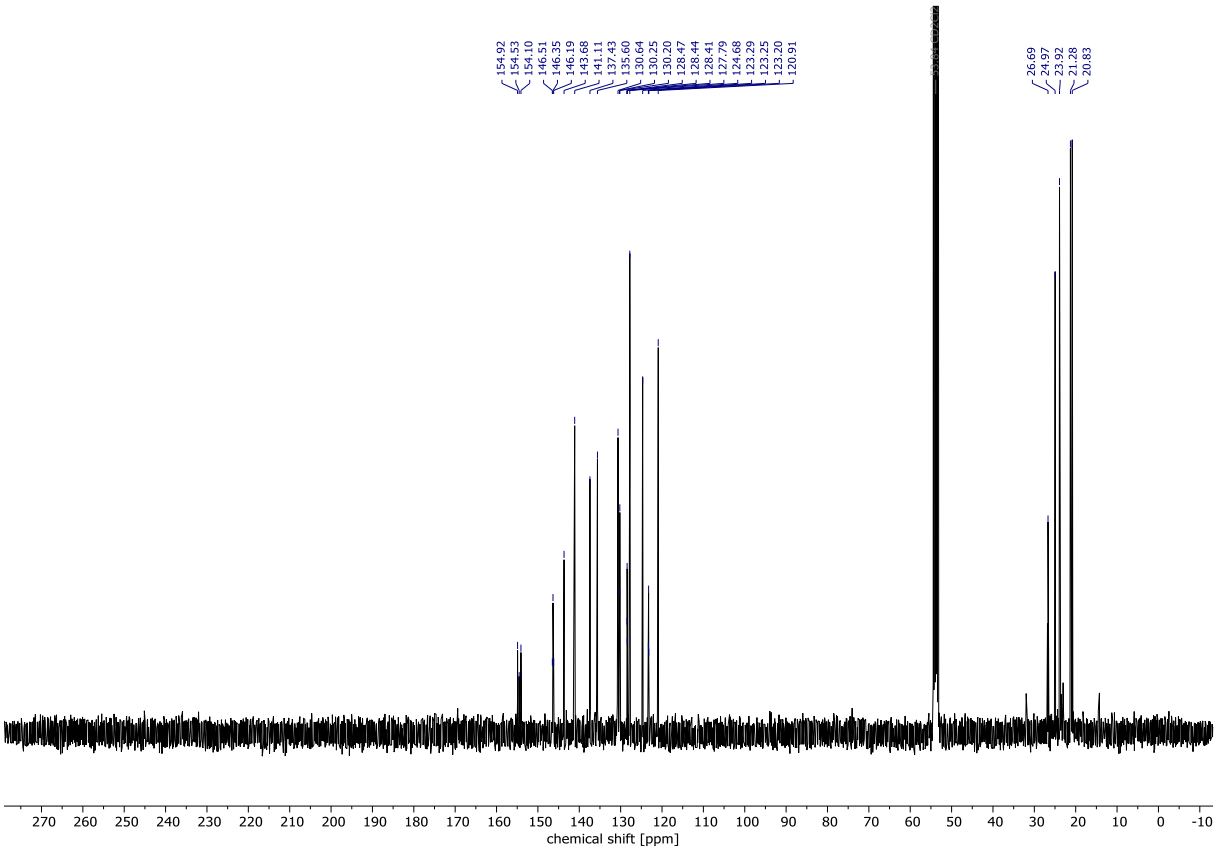


Figure S59: $^{31}P\{^{1}H\}$ NMR spectrum of **7** (162 MHz, CD_2Cl_2, r.t.).

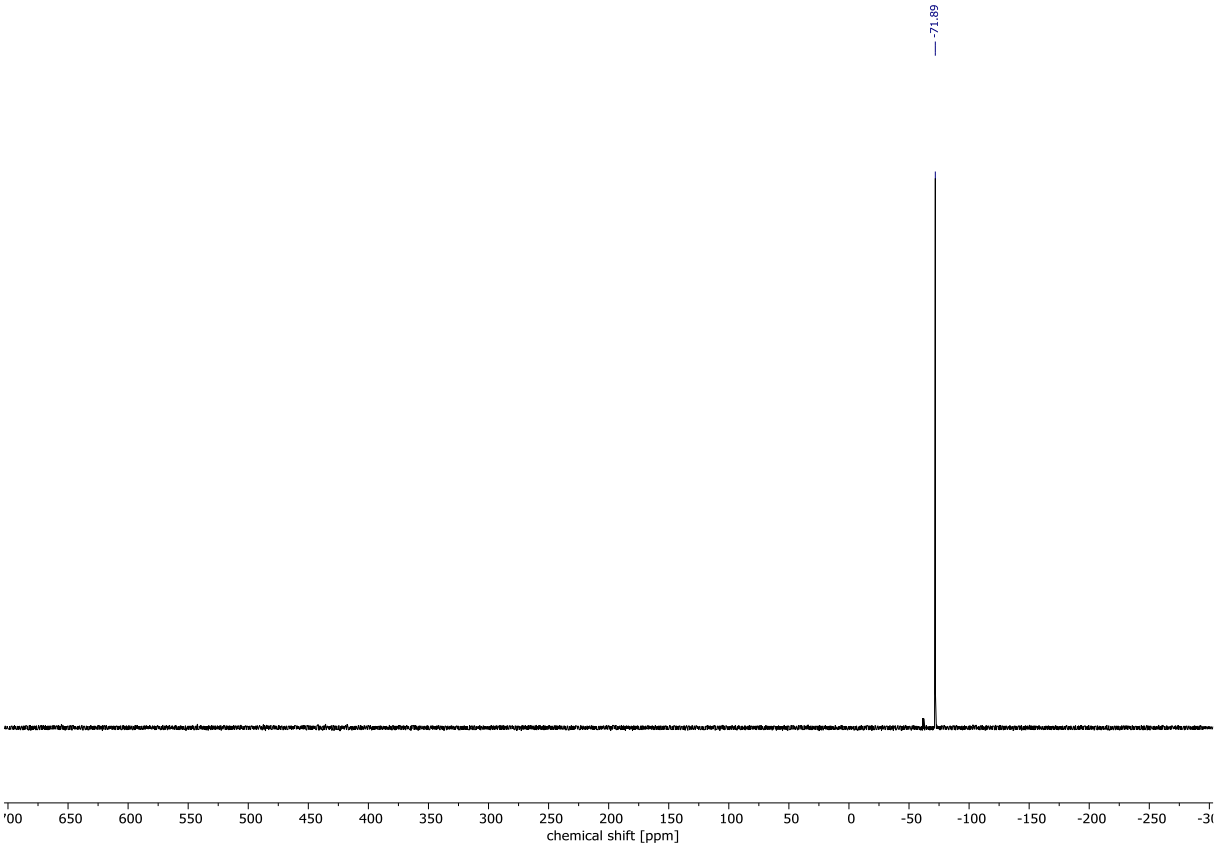
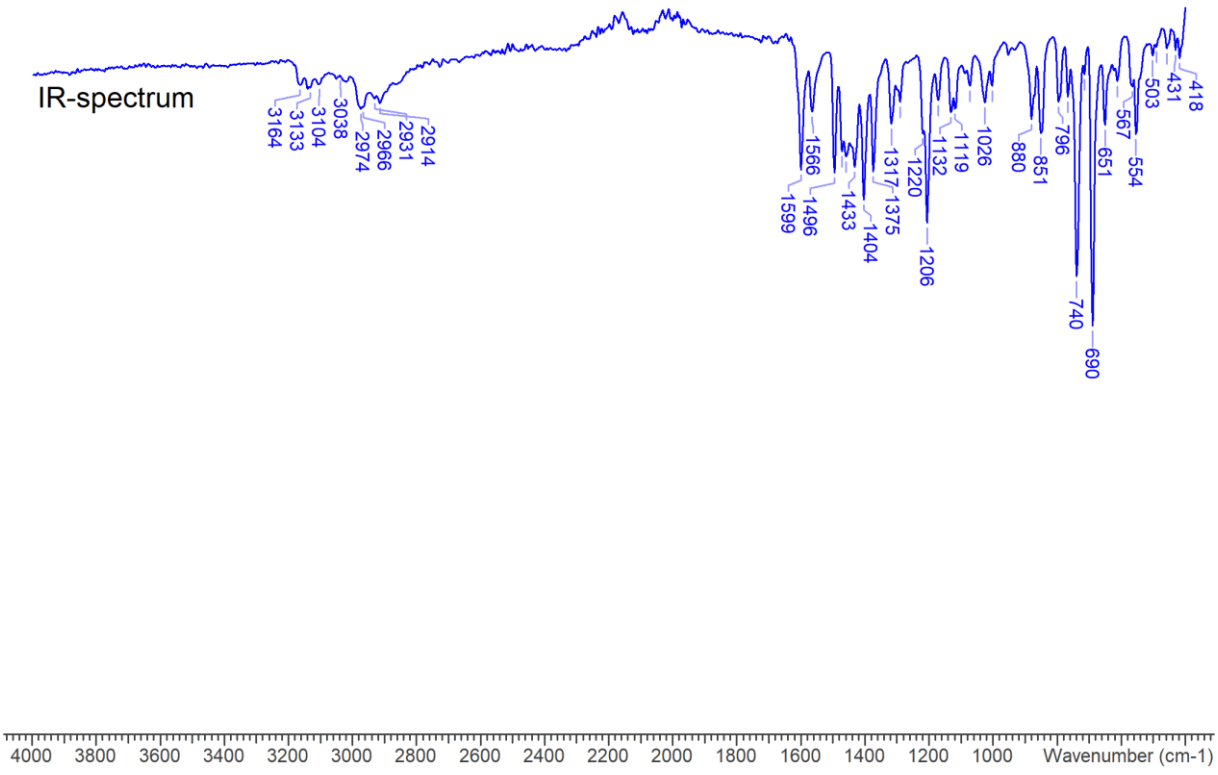
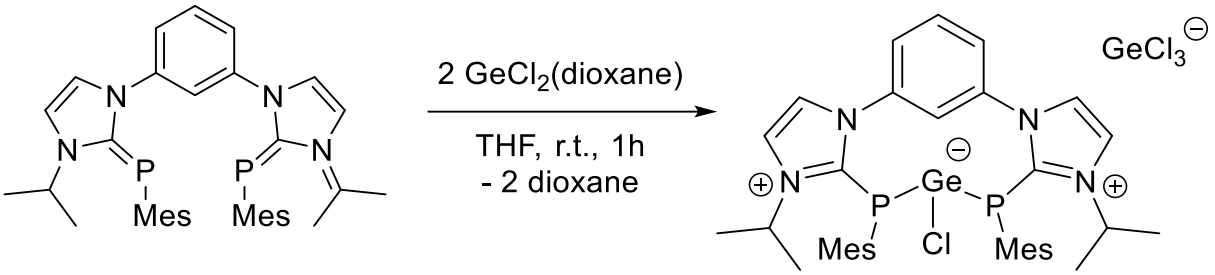


Figure S60: IR spectrum of **7** (solid sample, 32 sans, r.t.).



4.20 Synthesis of 8



5a (0.056 g, 0.095 mmol) and $GeCl_2$(dioxane) (0.044 g, 0.19 mmol) were dissolved in THF (4 mL) and stirred at room temperature for 1 h resulting in a yellow solution. Afterwards the solvent was removed *in vacuo* and the orange residue was redissolved in CH_2Cl_2 (1 mL). The product was added dropwise to *n*-hexane (10 mL) with vigorous stirring resulting in the immediate precipitation of **8** as a yellow solid. The supernatant *n*-hexane solution was removed via canula filtration, and the yellow solid was washed with *n*-hexane (5 mL) giving analytically pure **8**. Yield: 0.066 g, 0.074 mmol, 78 %.

CHN calc. (found) in %: C 49.04 (45.48), H 5.03 (5.21), N 6.35 (6.10). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2) δ = −74.33 ppm. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ = 7.92 (s, 3H, Ph*H*), 7.76 (d, *J* = 2.2 Hz, 2H, CHC*H*N), 7.43 (d, *J* = 2.3 Hz, 2H, CHC*H*N), 7.41 – 7.35 (m, 1H, Ph*H*), 6.97 – 6.90 (m, 2H, Ar*H*), 6.83 – 6.79 (m, 2H, Ar*H*), 4.36 (hept, 2H, $^{3}J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 2.67 (s, 6H), 2.22 (s, 6H), 1.84 (s, 6H), 1.40 (d, J = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 0.76 (d, J = 6.6 Hz, 6H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2) δ = 146.3 (Ar*C*), 142.5 (Ar*C*), 139.5 (Ar*C*), 137.7 (Ar*C*), 133.3 (Ar*C*), 130.1 (Ar*C*H), 129.5 (Ar*C*H), 127.5 (Ar*C*H), 123.8 (CH*C*HN), 120.4 (CH*C*HN), 32.0 (*C*H(CH$_3$)$_2$), 25.7 (t, J = 13.1 Hz, Ar*C*H$_3$), 23.6 (CH(*C*H$_3$)$_2$), 21.1 (Ar*C*H$_3$), 20.7 (Ar*C*H$_3$). **MS** (ESI) 5a·GeCl·(MeOH)$_2^+$ expected: 735.2562, observed: 735.2508.

Single crystals suitable for X-ray diffraction were grown by layering a CH_2Cl_2 of **8** with *n*-hexane.

Figure S61: ^{1}H NMR spectrum of **8** (400 MHz, CD_2Cl_2, r.t.).

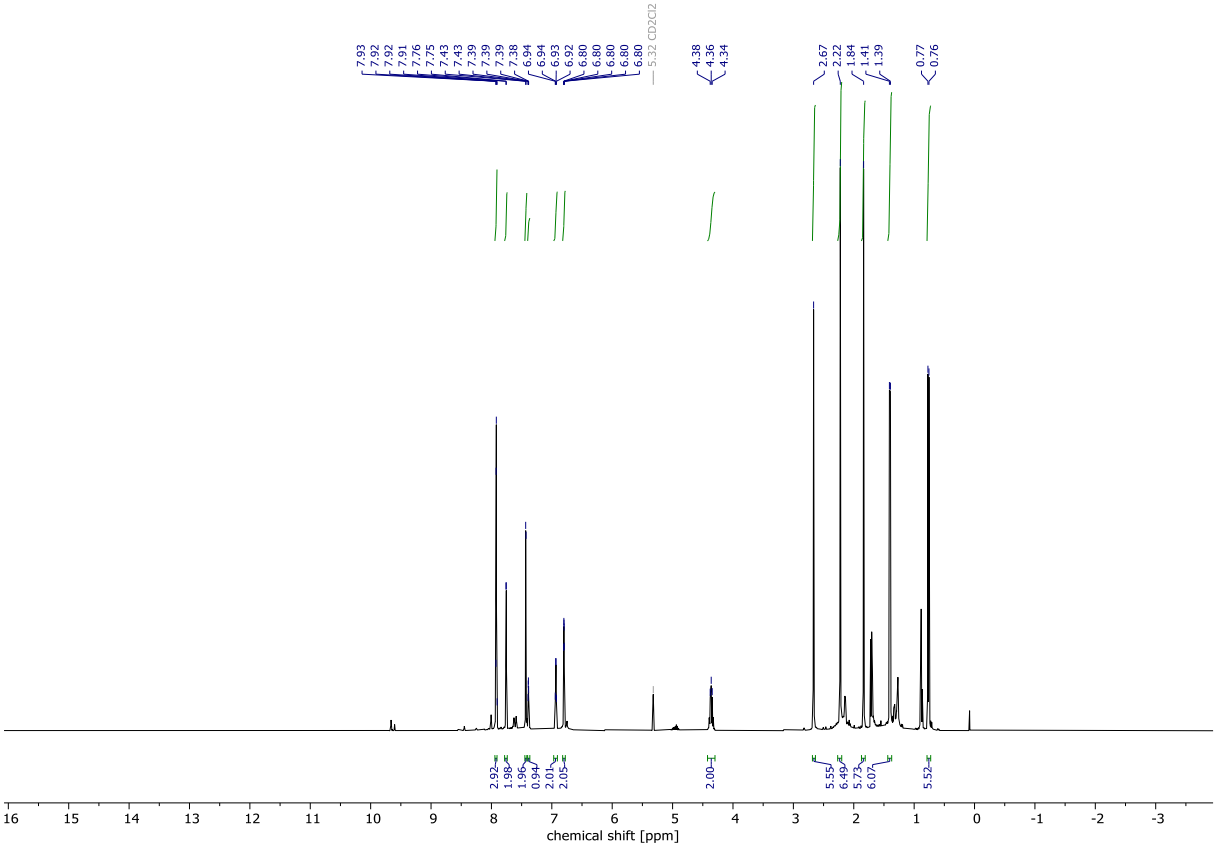


Figure S62: $^{13}C\{^{1}H\}$ NMR spectrum of **8** (101 MHz, CD_2Cl_2, r.t.).

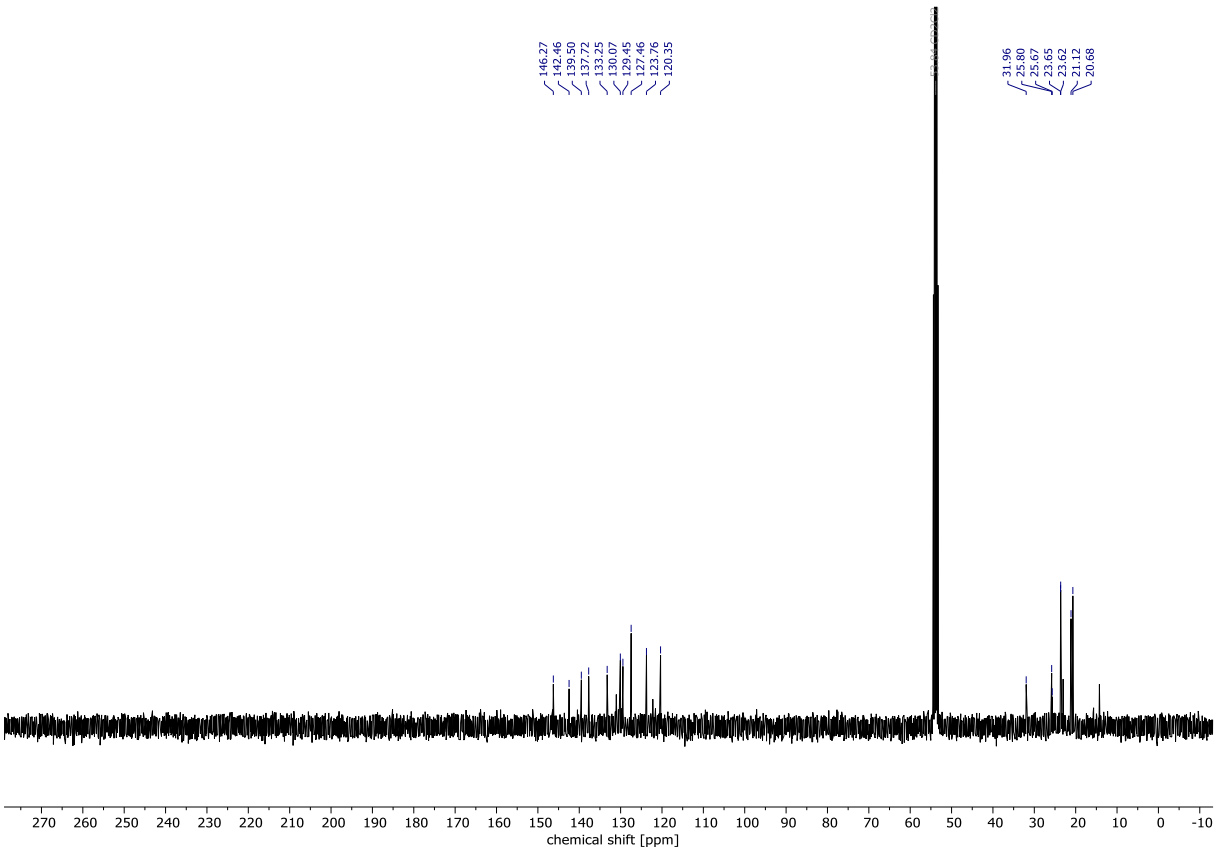
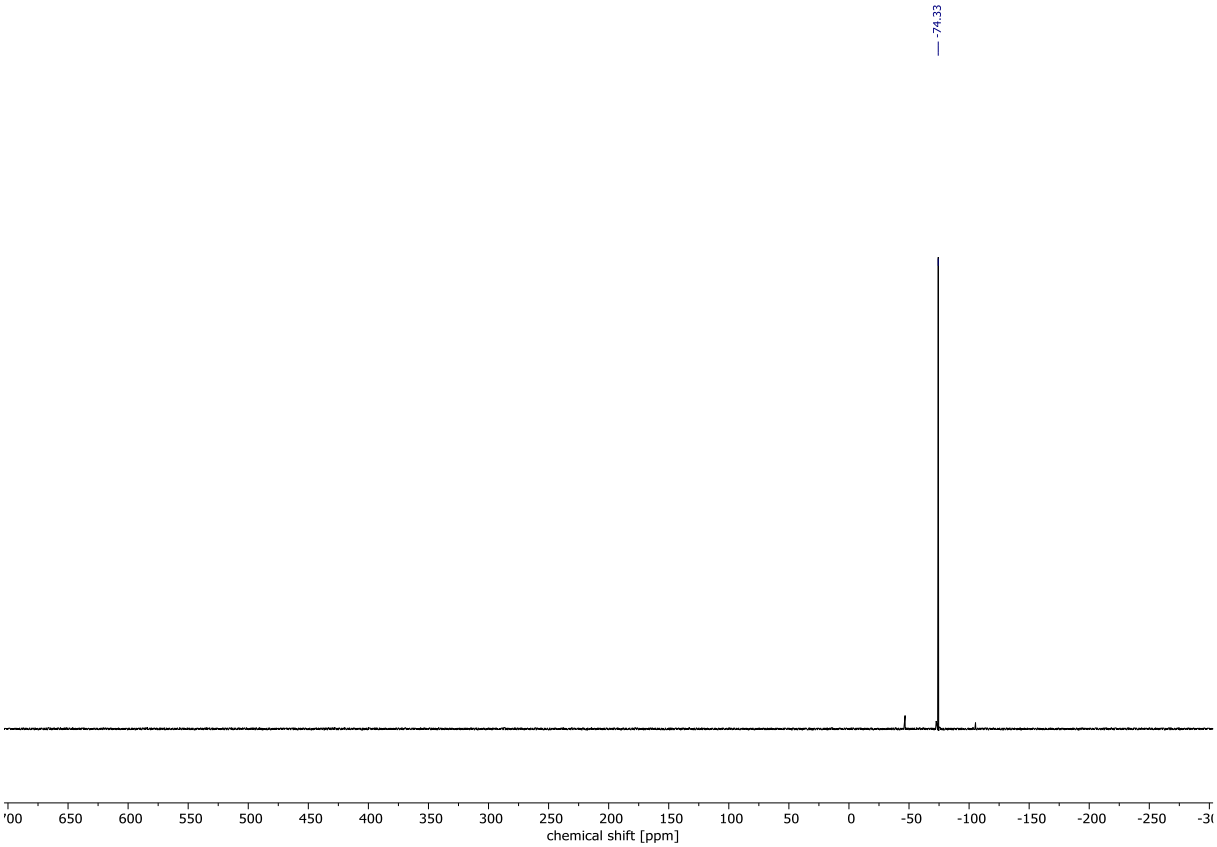
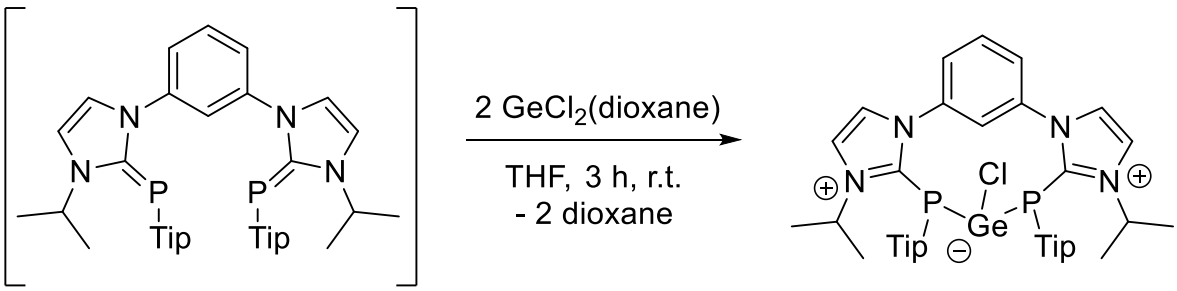


Figure S63: $^{31}P\{^{1}H\}$ NMR spectrum of **8** (162 MHz, CD_2Cl_2, r.t.).



4.21 Synthesis of 9



generated in situ

1,3-Bis(3-isopropylimidazolium)benzene diiodide (0.150 g, 0.27 mmol), KHMDS (111 mg, 0.54 mmol) and Tip_3P_3 (0.125 g, 0.18 mmol) were dissolved in 10 mL THF and heated to 80 °C for 16 h. From the resulting red/orange suspension THF is removed in vacuo and extracted with *n*-hexane (60 mL). *n*-Hexane is removed from the filtrate and to this red material $GeCl_2$·dioxane (0.125 g, 0.54 mmol) is added inside a glove box. After addition of THF (5 mL) the solution is stirred for 3 h resulting in a gold yellow

solution. The solvent is again removed, and the yellow residue is washed with hexane (2 x 10 mL) resulting in yellow powder of **9**. Yield: 0.115 g ,0.11 mmol, 41 %.

^{31}P NMR (122 MHz, CD_2Cl_2) δ = −75.73 ppm. **^{1}H NMR** (300 MHz, CD_2Cl_2) δ = 8.02 – 7.87 (m, 3H, Ph*H*), 7.76 (d, *J* = 2.2 Hz, 2H), 7.44 – 7.36 (m, 1H, Ph*H*), 7.32 (d, *J* = 2.2 Hz, 2H, CHC*H*N), 7.10 (q, *J* = 2.3 Hz, 2H, ArC*H*), 6.90 (d, *J* = 1.8 Hz, 2H, CHC*H*N), 4.52 – 4.28 (m, 4H, C*H*$(CH_3)_2$), 3.02 (hept, J = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 2.85 (hept, $^{3}J_{HH}$ = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 1.37 (d, $^{3}J_{HH}$ = 6.8, Hz, 6H, CH(C*H*$_3)_2$), 1.36 (d, $^{3}J_{HH}$ = 6.8, Hz, 6H, CH(C*H*$_3)_2$) 1.26 – 1.18 (m, 18H, CH(C*H*$_3)_2$), 0.96 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3)_2$), 0.70 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3)_2$), 0.58 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3)_2$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2) δ = 159.3 (d, $^{1}J_{PC}$ = 45.7 Hz, N_2*C*=P), 156.6 (t, *J* = 13.8 Hz, *i*-*C*Ar) 152.9 (*C*Ar), 151.1 (*C*Ar), 137.8 (*C*Ar), 133.4 (*C*ArH), 127.5 (*C*ArH), 124.1 (*C*ArH), 123.3 (*C*ArH), 122.7 (CH*C*HN), 120.1 (CH*C*HN), 35.7 (*C*H$(CH_3)_2$), 34.5 (*C*H$(CH_3)_2$), 34.1 (t, J = 15.2 Hz, (N*C*H$(CH_3)_2$)), 27.3 (CH(*C*H$_3)_2$), 25.2 (CH(*C*H$_3)_2$), 23.9 (d, J = 3.7 Hz, CH(*C*H$_3)_2$), 23.8 (CH(*C*H$_3)_2$), 23.5 (CH(*C*H$_3)_2$), 23.3 (CH(*C*H$_3)_2$), 20.4 (CH(*C*H$_3)_2$). **MS** (ESI) 3mMesGeCl$(MeOH)_2^+$ expected mass: 904.4518, observed mass 904.4503. **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 456 (w), 521 (w), 540 (w), 567 (w), 653 (m), 695 (m), 742 (m), 767 (w), 800 (w), 808 (w), 839 (w), 880 (w), 938 (w), 983 (s), 1123 (s), 1187 (s), 1206 (s), 1233 (vs), 1307 (m), 1360 (w), 1381 (w), 1410 (w), 1461 (w), 1494 (w), 1550 (vw), 1562 (w), 1597 (w), 2867 (w), 2927 (w), 2958 (w), 3048 (vw), 3098 (vw), 3125 (vw), 3147 (vw).

Single crystals of **9** suitable for X-ray diffraction were grown from layering a fluorobenzene solution with *n*-hexane.

Figure S64: ^{1}H NMR spectrum of **9** (300 MHz, CD_2Cl_2, r.t.).

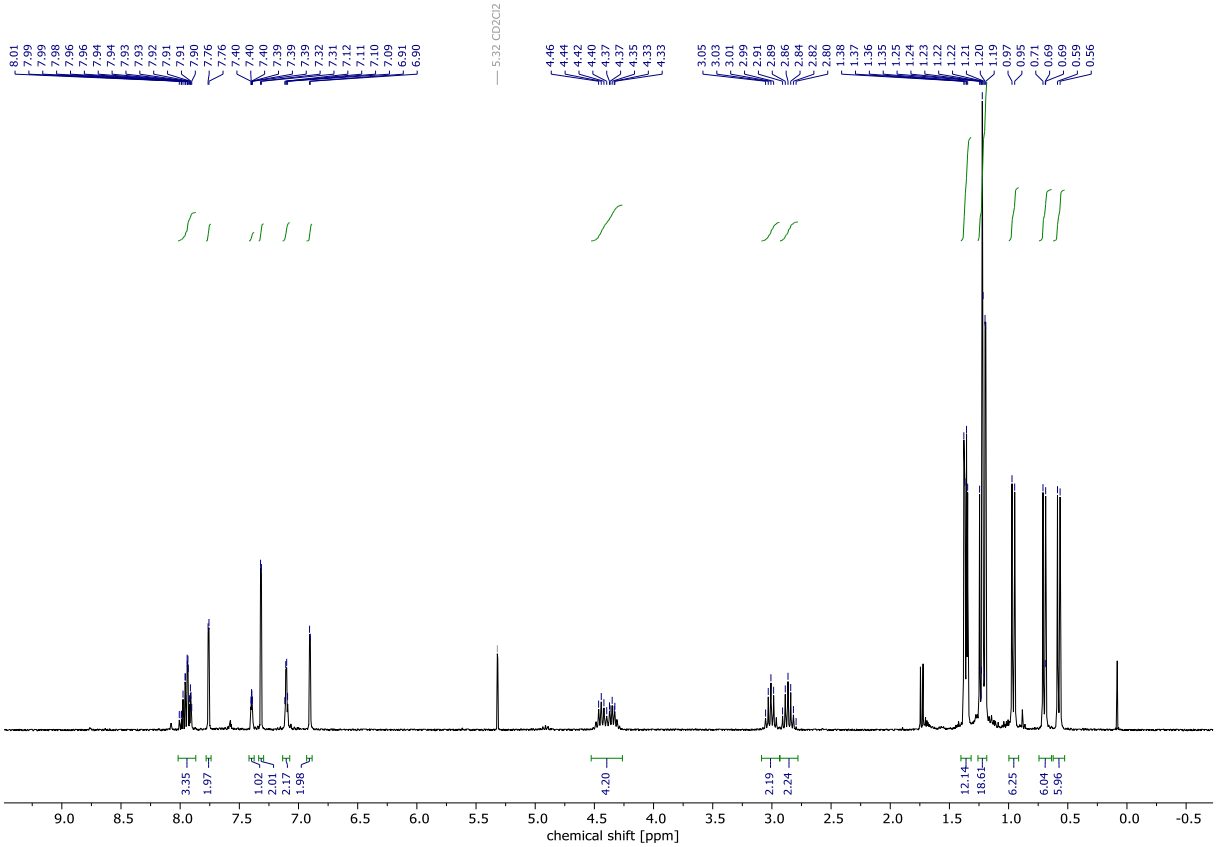


Figure S65: $^{13}C\{^{1}H\}$ NMR spectrum of **9** (100 MHz, CD_2Cl_2, r.t.).

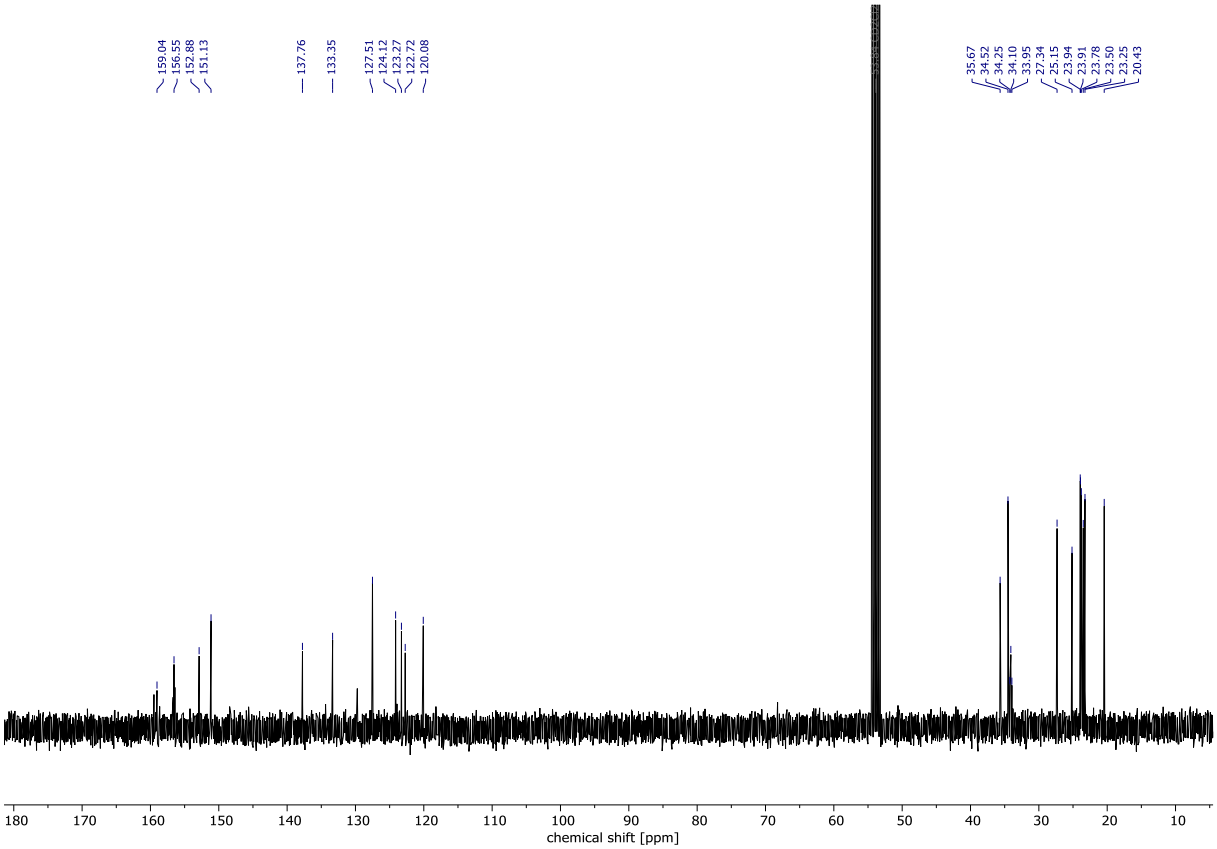


Figure S66: $^{31}P\{^{1}H\}$ NMR spectrum of **9** (122 MHz, CD_2Cl_2, r.t.).

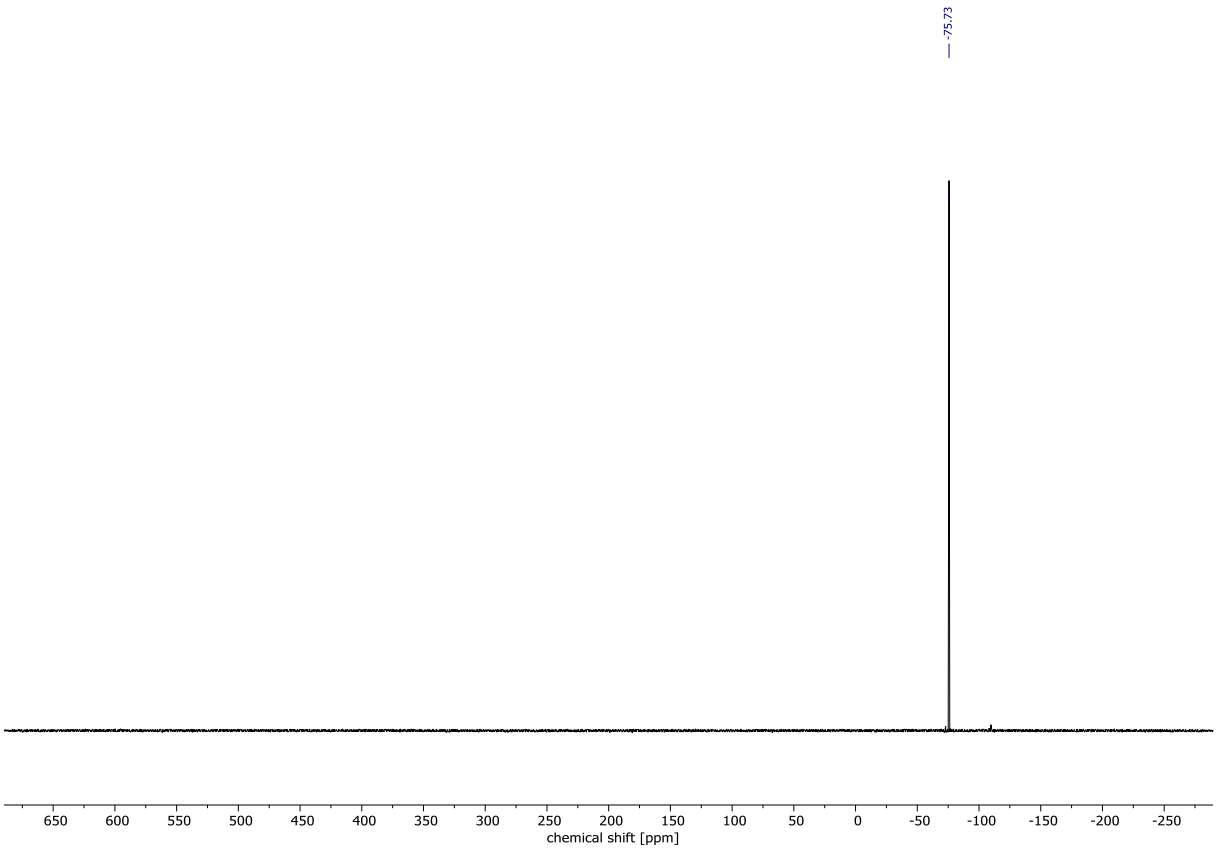
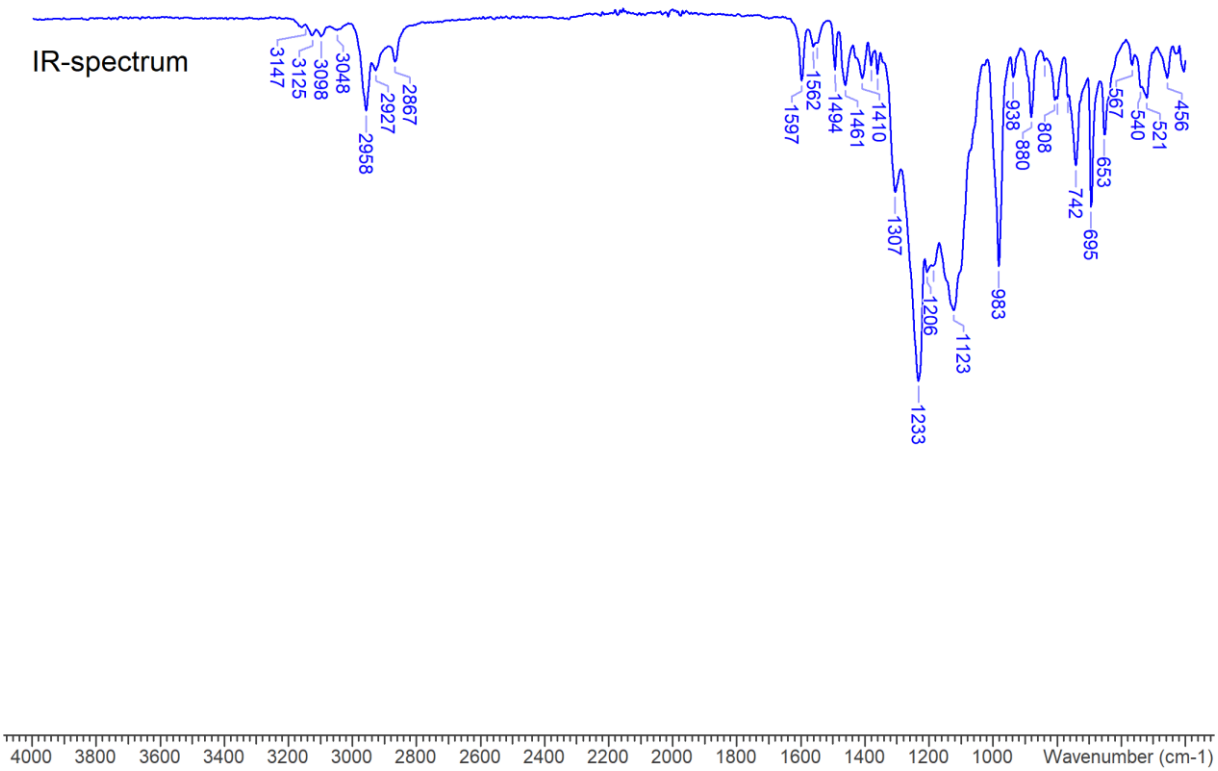


Figure S67: IR spectrum of **9** (solid sample, 32 sans, r.t.).



5 Additional spectroscopic details

5.1 UV-vis data

Figure S68: UV-Vis spectra of **5a** (c = 2.18 µmol/L), in *n*-hexane at room temperature (absorption maxima see Table S7).

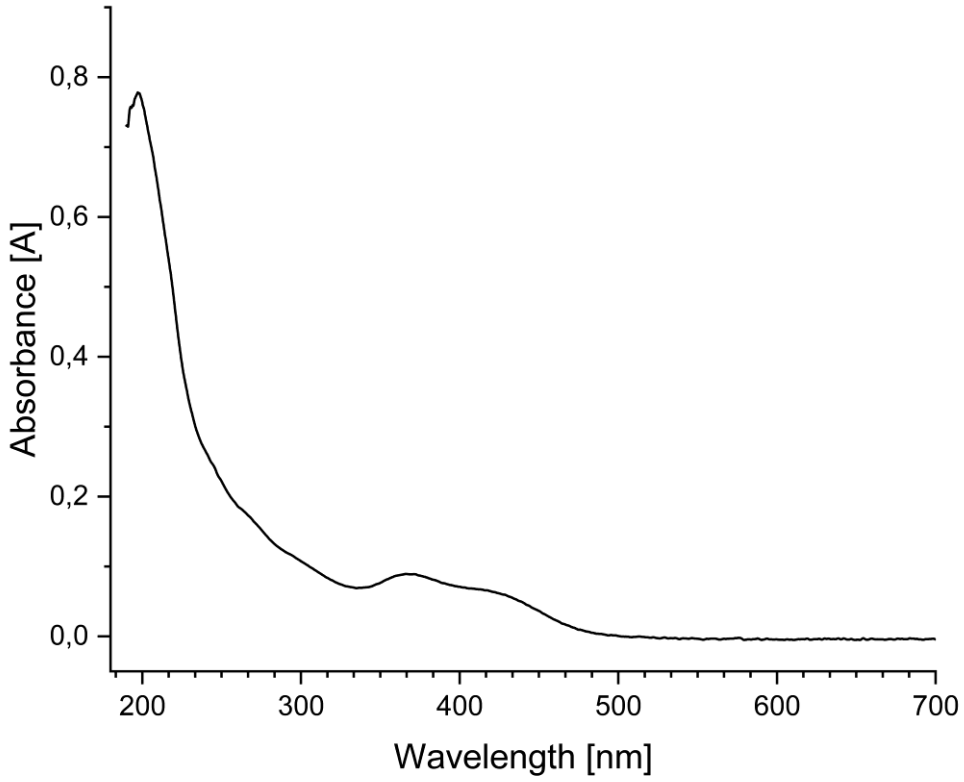


Table S7. Absorption maxima λ_{max} and experimental extinction coefficients ε for **5a**.

Compound 5a	**λ_{max} [nm]**	**ε [l·mol^{-1}·cm^{-1}]**
	366	20842.8
	435	6417.7

Figure S69: UV-Vis spectra of **6c** (c = 2.88 µmol/L), in *n*-hexane at room temperature (absorption maxima see Table S8).

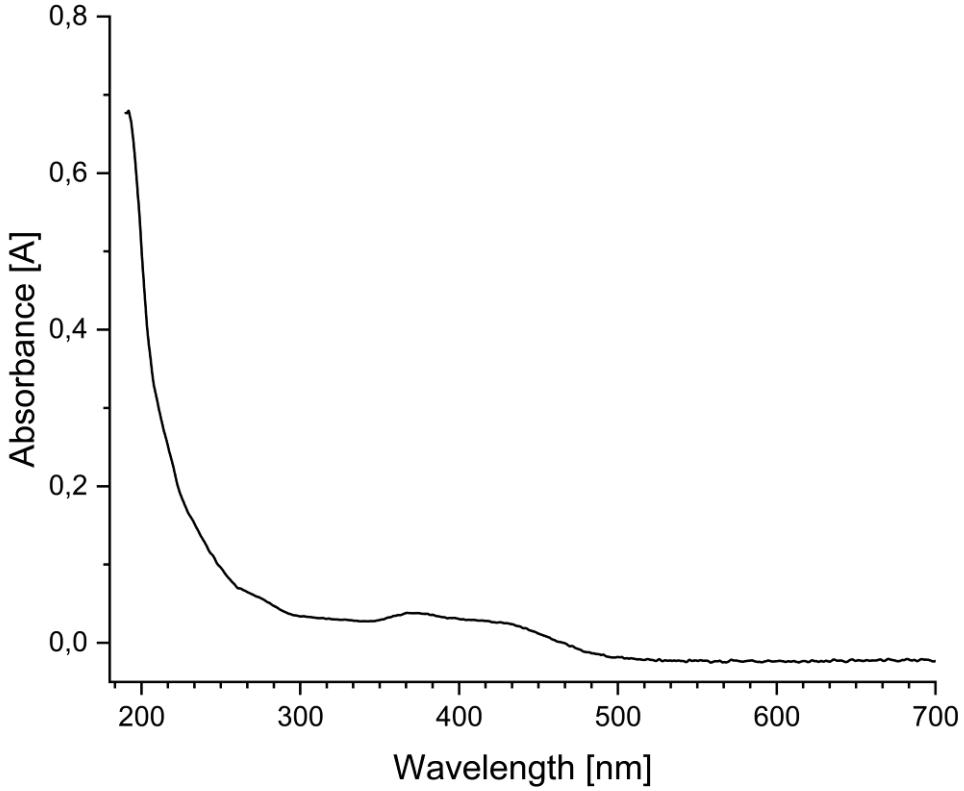
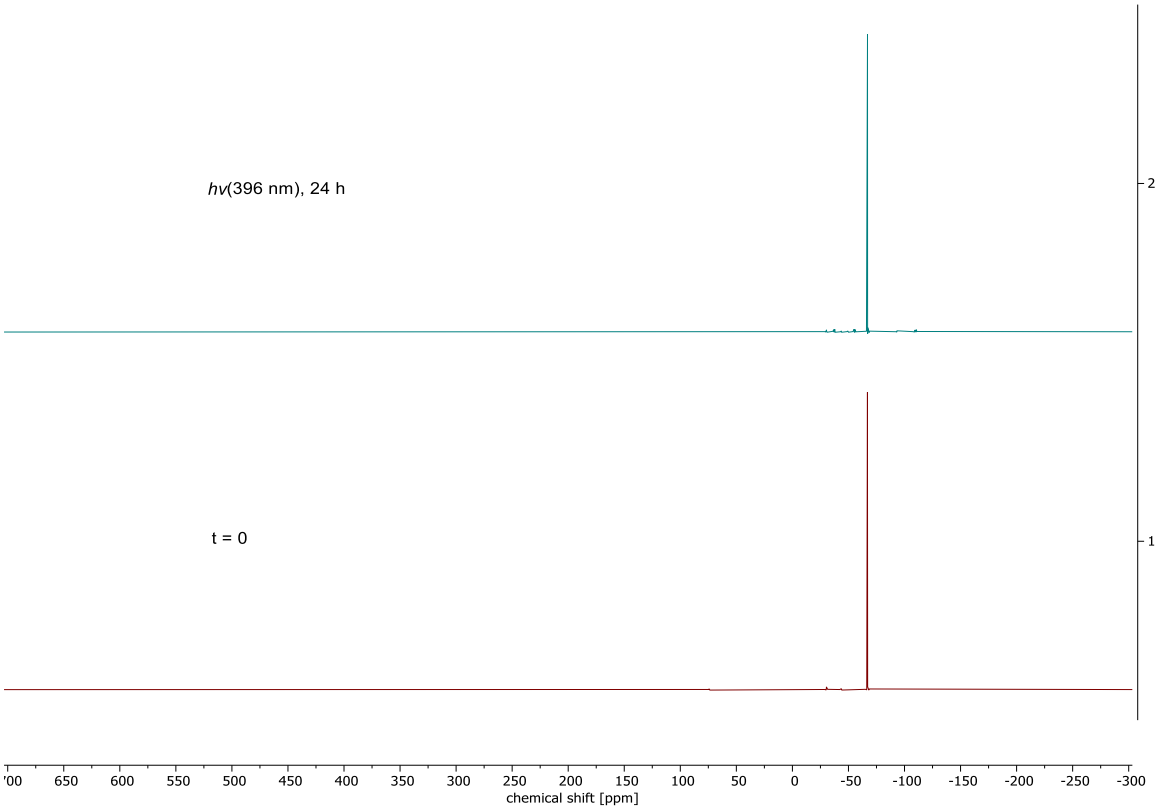


Table S8. Absorption maxima λ_{max} and experimental extinction coefficients ε for **6c**.

Compound 6c	**λ_{max} [nm]**	**ε [l·mol^{-1}·cm^{-1}]**
	369	13191.0
	439	7194.4

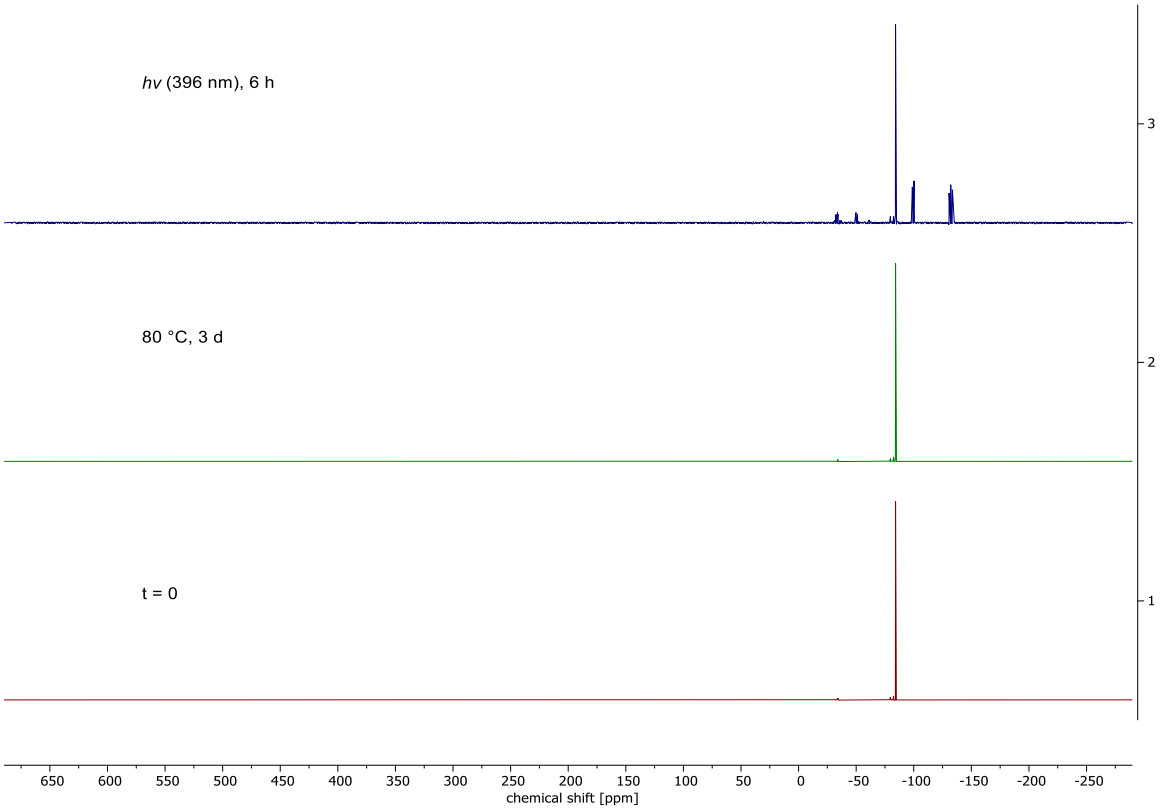
5.2 Irradiation of 5a

Figure S70: $^{31}P\{^{1}H\}$ NMR spectra of **5a** (0.023 g in 0.5 mL C_6D_6) after 24 h of irradiation with an LED (396 nm).



5.3 Irradiation of 6b

Figure S71: $^{31}P\{^{1}H\}$ NMR spectra of **6b** (0.031 g in 0.5 mL C_6D_6) after 80 °C for 3 days (in absence of light) and after 6 h of irradiation with an LED (396 nm) at room temperature.



5.4 Irradiation of 6c

Figure S72: $^{31}P\{^{1}H\}$ NMR spectra of **6c** (22 mg in 0.5 mL C_6D_6) after 24 h of irradiation with an LED (396 nm).

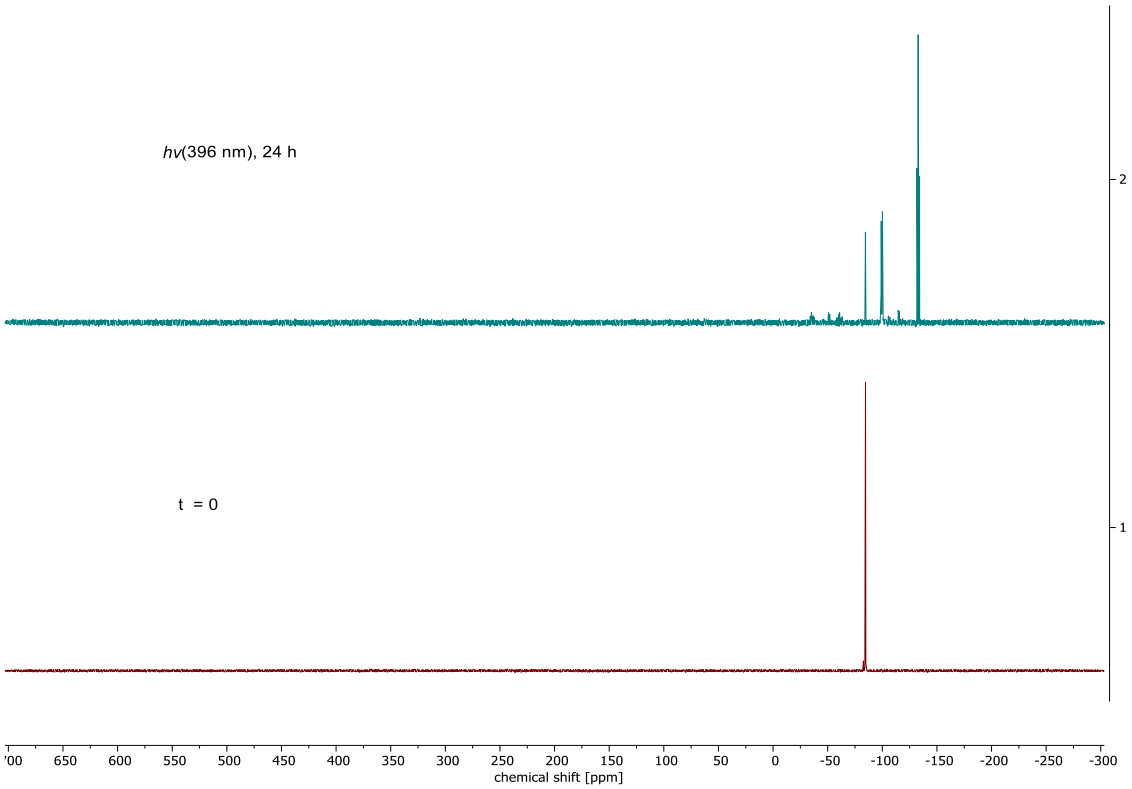


Figure S73: ^{1}H NMR spectra of **6c** (22 mg in 0.5 mL C_6D_6) after 24 h of irradiation with an LED (396 nm).

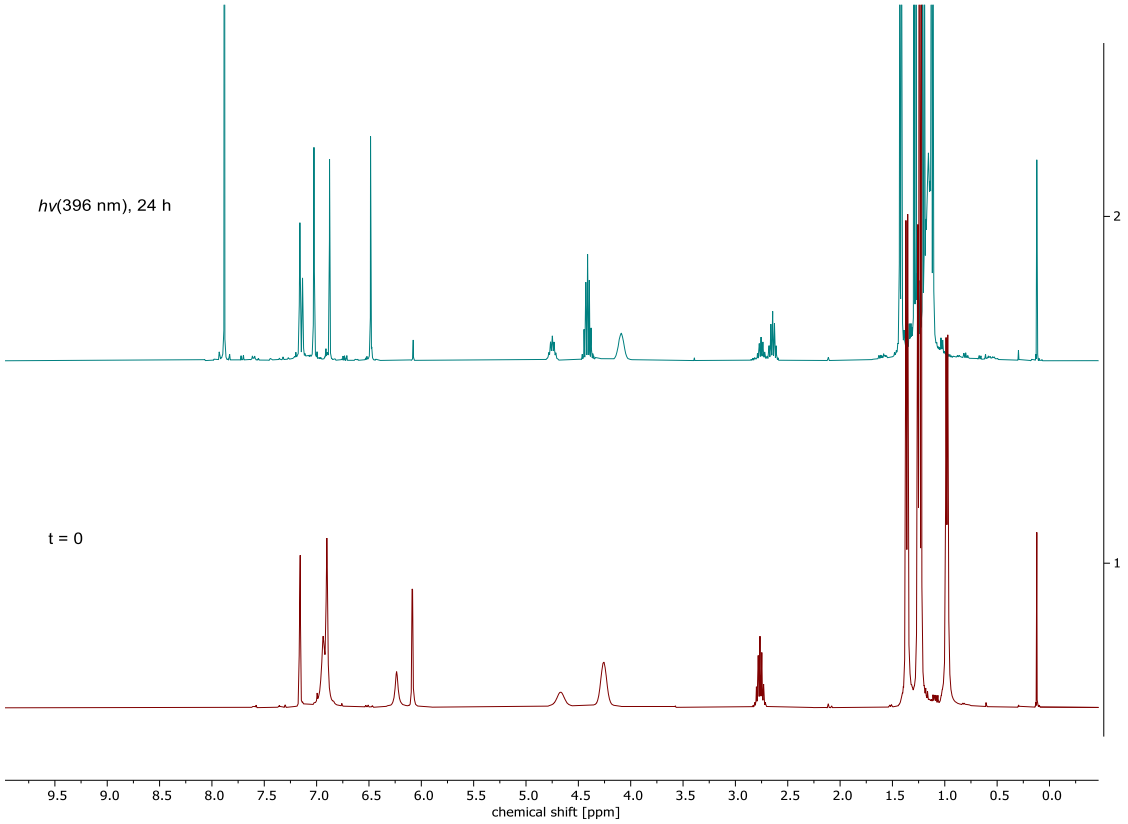
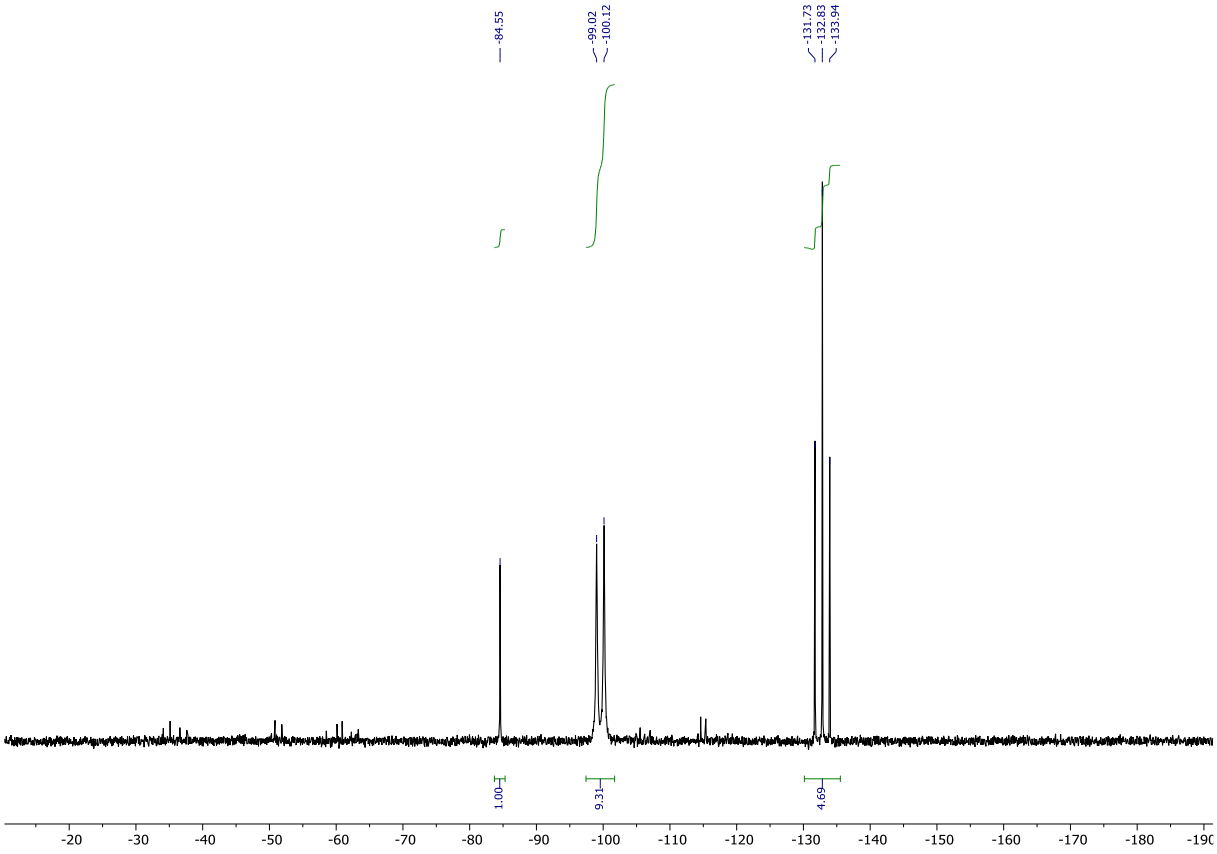


Figure S74: ^{31}P{^{1}H} NMR spectrum of **6c** (22 mg in 0.5 mL C_6D_6) after 24 h of irradiation with an LED (396 nm), showing nearly quantitative conversion to P_3Tip_3.



6 Computational details

6.1 General remarks

Computations were carried out using Gaussian09,[19] Gaussian16[20] and with the standalone version of NBO 6.0.[21]

Structure optimizations employed the hybrid DFT functional PBE0[22] in conjunction with Grimme's dispersion correction D3(BJ)[23] and the def2-SVP basis set[24] (notation PBE0-D3/def2-SVP). All structures were fully optimized and confirmed as minima by frequency analyses. NBO analyses were carried out at the PBE0-D3/def2-TZVP level of theory. Partial charges were determined by Natural Population analysis using the NBO program. Wiberg bond indices (WBIs) were also determined using NBO.

Chemical shifts and coupling constants were derived by the GIAO method at the PBE0-D3/def2-TZVP level of theory using the PBE0-D3/def2-SVP optimized structures.[25] The calculated absolute shifts ($\sigma_{calc,X}$) were referenced to the experimental absolute shift of 85% H3PO4 in the gas phase ($\sigma_{ref,1}$ = 328.35 ppm),[26] using PH_3 ($\sigma_{ref,2}$ = 594.45 ppm) as a secondary standard:[27]

$$\delta_{calc,X} = (\sigma_{ref,1} - \sigma_{ref,2}) - (\sigma_{calc,X} - \sigma_{calc,PH3}) = \sigma_{calc,PH3} - \sigma_{calc,X} - 266.1 \text{ ppm}$$

At the PBE0-D3/def2-TZVP level of theory, $\sigma_{calc,PH3}$ amounts to +567.77 ppm.

Interaction region indicator (IRI) analysis was carried with MultiWfn3.8[28] using the Gaussian16 formatted checkpoint files obtained at the PBE0-D3/def2-TZVP using the PBE0-D3/def2-SVP geometries (*vide supra*). IRI is a real space function defined as follows:[29]

$$\mathrm{IRI}(\mathbf{r}) = \frac{|\nabla\rho(\boldsymbol{r})|}{[\rho(\boldsymbol{r})]^a}$$

In here *a* is a modifiable parameter and a = 1.1 is adopted for the standard definition of IRI, which can be understood as the gradient norm of the electron density weighted by the scaled electron density. In analogy to NCI analysis,[30] the *sign(λ2)p* function can be mapped on IRI isosurfaces by different colours, which help to visualize the nature of interaction regions revealed by IRI analysis. The coloring palette has been provided by T. Lu for use in publications.[29]

Please note that all computations were carried out for single, isolated molecules in the gas phase (ideal gas approximation). There may well be significant differences between gas phase and condensed phase.

6.2 Summary of calculated data

Table S9. Summary of calculated data, including electronic energies and thermal.

Cmpd.	PG	Opt. method	E_{tot}[a]	ΔG[b]	E_{single}[c]	NIMAG
1a	C_1	PBE0-D3 def2-SVP	−994.3442	0.2581	−995.1433	0
1b	C_i		−1112.0029	0.3382	−1112.9785	0
5a	C_1		−2296.6538	0.6543	−2298.5602	0
6c	C_i		−2767.5116	0.9648	−2769.9076	0
[7]$^+$	C_1		−4816.4663	0.6482	−4818.6366	0
[8]$^+$	C_1		−4832.9782	0.6517	−4835.3027	0
[9]$^+$	C_1		−5303.8718	0.9762	−5306.6797	0

[a] Total SCF energy in a.u.; [b] thermal correction to Gibbs energy in a.u. (298 K unless stated otherwise); [c] single-point PBE0-D3/def2-TZVP energy.

6.3 Calculated electronic excitations

Table S10. Calculated electronic excitations of **5a** (PBE0-D3/def2-TZVP).

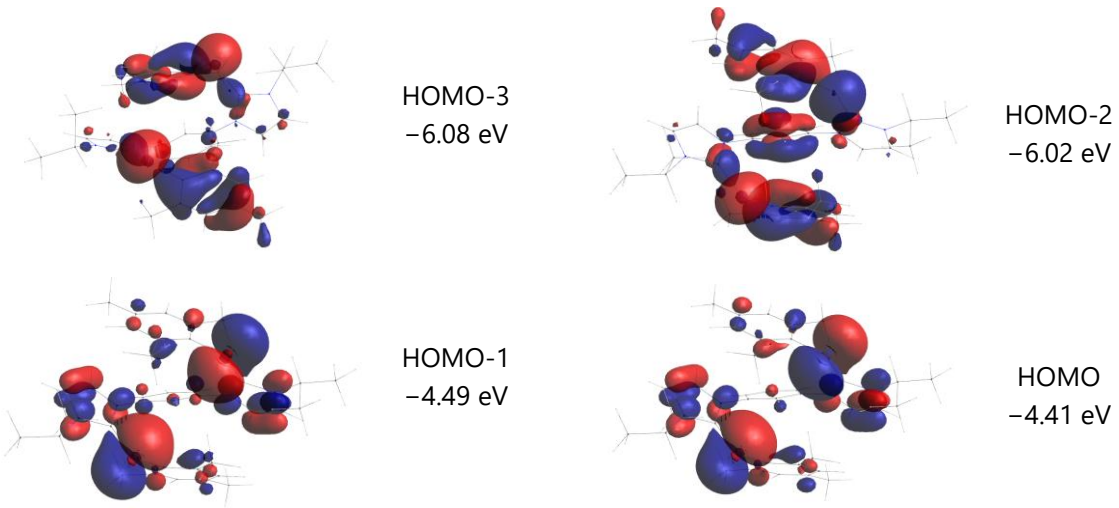
State	λ [nm]	Oscillator strength	Main excitation
S1	444	0.0374	HOMO→LUMO
S2	425	0.0225	HOMO-1→LUMO HOMO→LUMO+1
S3	415	0.0002	HOMO-1→LUMO HOMO→LUMO+1

Table S11. Calculated electronic excitations of **6c** (PBE0-D3/def2-TZVP).

State	λ [nm]	Oscillator strength	Main excitation
S1	484	0.2106	HOMO→LUMO
S2	463	0.0002	HOMO-1→LUMO HOMO-1→LUMO+1
S3	416	0.2126	HOMO-1→LUMO+1 HOMO→LUMO+2

6.4 KS-Orbitals of compounds 5a and 6c.

Figure S75. Relevant Kohn-Sham orbitals of **5a** (PBE0-D3/def2-TZVP, isosurface value: 0.03).



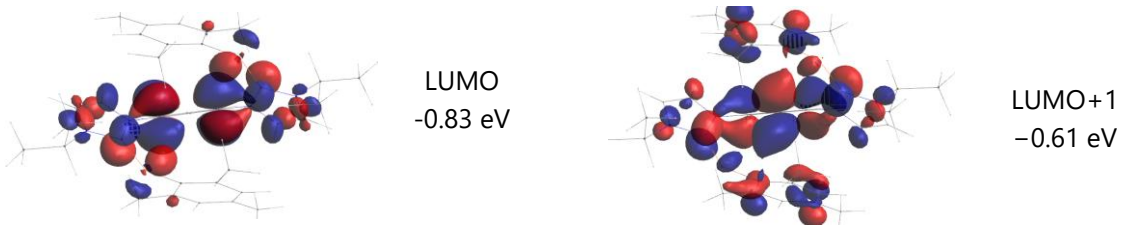
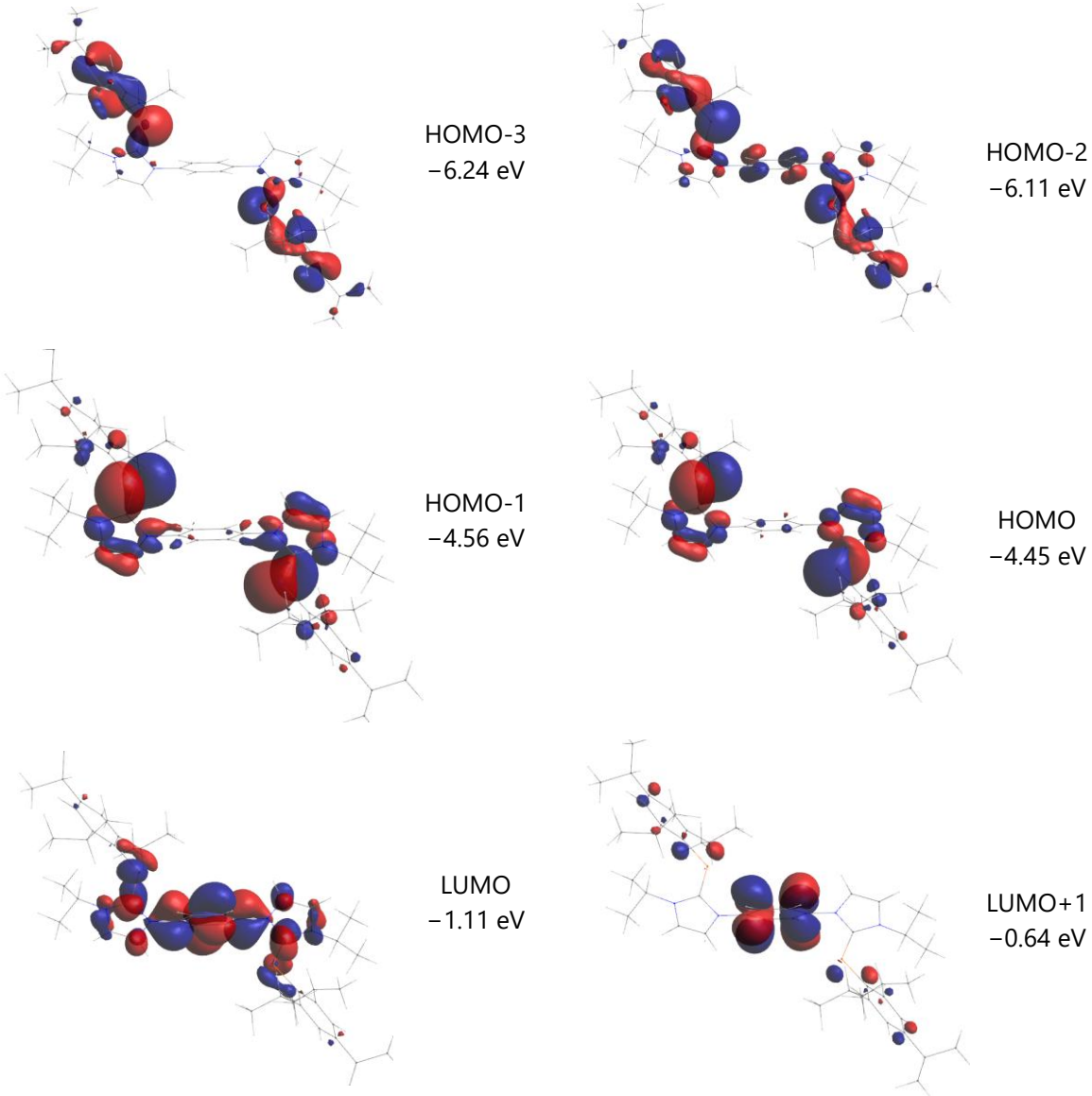
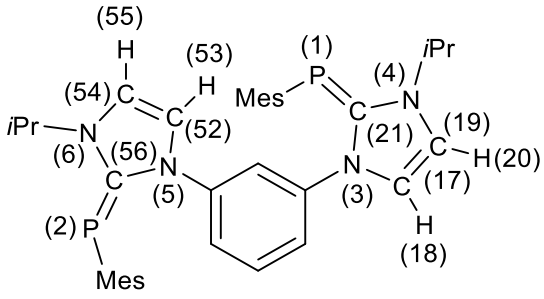


Figure S76. Relevant Kohn-Sham orbitals of **6c** (PBE0-D3/def2-TZVP, isosurface value: 0.03).



6.5 NBO analysis of compound **5a** and the cations in **[7]**$^+$, **[8]**$^+$ and **[9]**$^+$.

5a



Numbering Scheme of **5a** for NBO calculations.

NPA Charges

P 1	0.20723
P 2	0.20723
N 3	-0.38228
N 4	-0.35677
N 5	-0.38227
N 6	-0.35677
C 7	-0.19685
H 8	0.27306
C 17	-0.08201
H 18	0.24255
C 19	-0.08930
H 20	0.23530
C 21	0.11472
C 52	-0.08202
H 53	0.24255
C 54	-0.08930
H 55	0.23530
C 56	0.11471

Bond Analysis

51. (1.92341) LP (1) P 1	s(65.29%)p 0.53(34.65%)d 0.00(0.06%)	f 0.00(0.00%)
52. (1.92341) LP (1) P 2	s(65.29%)p 0.53(34.65%)d 0.00(0.06%)	f 0.00(0.00%)
53. (1.57409) LP (1) N 4	s(0.00%)p 1.00(99.94%)d 0.00(0.03%)	f 0.00(0.03%)

54. (1.57410) LP (1) N 6   s(0.00%)p 1.00(99.94%)d 0.00(0.03%) f 0.00(0.03%)

57. (1.95877) BD (1) P 1- C 21 (*Wiberg Bond Index P1-C21:* ***1.29***)

(33.24%)   0.5766* P 1 s(16.12%)p 5.16(83.19%)d 0.04(0.68%) f 0.00(0.01%)

(66.76%)   0.8171* C 21 s(41.08%)p 1.43(58.68%)d 0.00(0.16%) f 0.00(0.08%)

58. (1.89234) BD (2) P 1- C 21

(65.58%)   0.8098* P 1 s(0.24%)p99.99(99.40%)d 1.45(0.34% f 0.06(0.01%)

(34.42%)   0.5867* C 21 s(0.55%)p99.99(99.14%)d 0.42(0.23%) f 0.14(0.08%)

60. (1.95877) BD (1) P 2- C 56 (*Wiberg Bond Index P2-C56:* ***1.29***)

(33.24%)   0.5766* P 2 s(16.12%)p 5.16(83.19%)d 0.04(0.68%) f 0.00(0.01%)

(66.76%)   0.8171* C 56 s(41.09%)p 1.43(58.68%)d 0.00(0.16%) f 0.00(0.08%)

61. (1.89235) BD (2) P 2- C 56

(65.58%)   0.8098* P 2 s(0.24%)p99.99(99.40%)d 1.45(0.34%) f 0.06(0.01%)

(34.42%)   0.5867* C 56 s(0.55%)p99.99(99.14%)d 0.42(0.23%) f 0.14(0.08%)

2nd Order Perturbation

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol
51. LP (1) P 1	169. BD*(1) N 3- C 21	14.97
52. LP (1) P 2	176. BD*(1) N 5- C 56	14.97
53. LP (1) N 4	161. BD*(2) P 1- C 21	65.98
53. LP (1) N 4	193. BD*(2) C 17- C 19	38.76
54. LP (1) N 6	164. BD*(2) P 2- C 56	65.97
54. LP (1) N 6	229. BD*(2) C 52- C 54	38.76

NLMOs

NLMO / Occupancy / Percent from Parent NBO / Atomic Hybrid Contributions

51. (2.00000) 96.1293% LP (1) P 1

96.133% P 1 s(64.80%)p 0.54(35.14%)d 0.00(0.06%) f 0.00(0.00%)

1.250% C 21 s(13.53%)p 6.32(85.46%)d 0.05(0.68%) f 0.02(0.32%)

52. (2.00000) 96.1298% LP (1) P 2

96.133% P 2 s(64.80%)p 0.54(35.14%)d 0.00(0.06%) f 0.00(0.00%)

1.249% C 56 s(13.53%)p 6.32(85.47%)d 0.05(0.68%) f 0.02(0.32%)

53. (2.00000) 75.9003% LP (1) N 4

4.996% P 1 s(0.06%)p99.99(99.71%)d 3.99(0.23%) f 0.08(0.00%)

75.944% N 4 s(0.03%)p99.99(99.90%)d 0.94(0.03%) f 1.01(0.04%)

2.825% C 17 s(0.16%)p99.99(99.25%)d 2.99(0.49%) f 0.59(0.10%)

2.788% C 19 s(0.01%)p 1.00(97.94%)d 0.02(2.01%) f 0.00(0.04%)

11.026% C 21 s(0.07%)p99.99(99.42%)d 6.75(0.48%) f 0.46(0.03%)

54. (2.00000) 75.9003% LP (1) N 6

4.996% P 2 s(0.06%)p99.99(99.71%)d 4.00(0.23%) f 0.08(0.00%)

75.944% N 6 s(0.03%)p99.99(99.90%)d 0.94(0.03%) f 1.01(0.04%)

2.826% C 52 s(0.17%)p99.99(99.24%)d 2.93(0.49%) f 0.58(0.10%)

2.788% C 54 s(0.01%)p 1.00(97.94%)d 0.02(2.01%) f 0.00(0.04%)

11.026% C 56 s(0.07%)p99.99(99.42%)d 6.76(0.48%) f 0.46(0.03%)

57. (2.00000) 97.9238% BD (1) P 1- C 21

32.703% P 1 s(17.91%)p 4.54(81.42%)d 0.04(0.66%) f 0.00(0.01%)

65.422% C 21 s(40.83%)p 1.44(58.93%)d 0.00(0.16%) f 0.00(0.08%)

58. (2.00000) 94.5027% BD (2) P 1- C 21

63.264% P 1 s(0.15%)p99.99(99.51%)d 2.30(0.34%) f 0.09(0.01%)

31.464% C 21 s(1.00%)p98.92(98.69%)d 0.24(0.23%) f 0.08(0.08%)

60. (2.00000) 97.9238% BD (1) P 2- C 56

32.703% P 2 s(17.91%)p 4.55(81.42%)d 0.04(0.66%) f 0.00(0.01%)

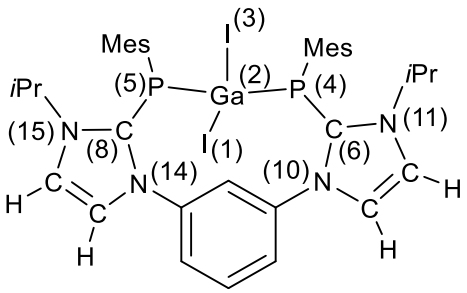
65.422% C 56 s(40.83%)p 1.44(58.93%)d 0.00(0.16%) f 0.00(0.08%)

61. (2.00000) 94.5065% BD (2) P 2- C 56

63.248% P 2 s(0.15%)p99.99(99.50%)d 2.30(0.34%) f 0.09(0.01%)

31.483% C 56 s(1.00%)p99.14(98.69%)d 0.24(0.23%) f 0.08(0.08%)

[7]$^+$



Numbering Scheme of **[7]$^+$** for NBO calculations.

NPA charges

I 1 -0.29532

Ga 2 0.53244

I 3 -0.27781

P 4 0.25789

P 5 0.25911

C 6 0.19175

C 8 0.19136

N 10 -0.34168

N 11 -0.31391

N 14 -0.34161

N 15 -0.31416

Bond Analysis

89. (1.80891) LP (1) P 4 s(48.90%)p 1.04(50.97%)d 0.00(0.12%)f 0.00(0.00%)

90. (1.80843) LP (1) P 5 s(49.01%)p 1.04(50.86%)d 0.00(0.12%)f 0.00(0.00%)

93. (1.94881) BD (1) I 1-Ga 2 (WBI: ***0.89***)

(73.18%) 0.8554* I 1 s(21.43%)p 3.65(78.13%)d 0.02(0.42%) f 0.00(0.02%)

(26.82%) 0.5179*Ga 2 s(25.99%)p 2.83(73.58%)d 0.01(0.36%) f 0.00(0.07%)

94. (1.93983) BD (1)Ga 2- I 3 (WBI: ***0.87***)

(26.46%) 0.5144*Ga 2 s(20.35%)p 3.89(79.21%)d 0.02(0.38%) f 0.00(0.05%)

(73.54%) 0.8576* I 3 s(22.17%)p 3.49(77.37%)d 0.02(0.45%) f 0.00(0.02%)

95. (1.87351) BD (1)Ga 2- P 4 (WBI: ***0.68***)

(26.21%) 0.5120*Ga 2 s(26.76%)p 2.72(72.93%)d 0.01(0.29%) f 0.00(0.02%)

(73.79%) 0.8590* P 4 s(17.32%)p 4.75(82.36%)d 0.02(0.31%) f 0.00(0.01%)

96. (1.87208) BD (1)Ga 2- P 5 (WBI: ***0.68***)

(26.20%) 0.5119*Ga 2 s(26.74%)p 2.73(72.96%)d 0.01(0.29%) f 0.00(0.02%)

(73.80%) 0.8591* P 5 s(17.18%)p 4.80(82.51%)d 0.02(0.31%) f 0.00(0.01%)

97. (1.96324) BD (1) P 4- C 6 (WBI: ***1.00***)

(33.34%) 0.5774* P 4 s(14.72%)p 5.74(84.52%)d 0.05(0.75%) f 0.00(0.01%)

(66.66%) 0.8164* C 6 s(39.94%)p 1.50(59.85%)d 0.00(0.14%) f 0.00(0.07%)

99. (1.96327) BD (1) P 5- C 8 (WBI: ***1.01***)

(33.35%) 0.5775* P 5 s(14.73%)p 5.74(84.51%)d 0.05(0.75%) f 0.00(0.01%)

(66.65%) 0.8164* C 8 s(39.94%)p 1.50(59.84%)d 0.00(0.14%) f 0.00(0.07%)

2nd Order Perturbation

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol
LP (1) P 4	200. BD*(1) I 1-Ga 2	9.37
LP (1) P 4	209. BD*(2) C 6- N 10	15.13
LP (1) P 5	200. BD*(1) I 1-Ga 2	9.24
LP (1) P 5	215. BD*(2) C 8- N 14	15.24
BD (1)Ga 2- P 5	216. BD*(1) C 8- N 15	6.95
BD (1)Ga 2- P 4	210. BD*(1) C 6- N 11	6.97
BD (1) P 4- C 6	221. BD*(1) N 10- C 19	4.28
BD (1) P 4- C 6	222. BD*(1) N 11- C 20	4.60
BD (1) P 5- C 8	230. BD*(1) N 14- C 27	4.27
BD (1) P 5- C 8	231. BD*(1) N 15- C 28	4.58
BD (1) C 18- C 34	*201. BD*(1)Ga 2- I 3*	*1.02*
BD (2) C 18- C 34	*201. BD*(1)Ga 2- I 3*	*1.59*
BD (1) C 26- C 34	*201. BD*(1)Ga 2- I 3*	*1.02*

NLMOs

NLMO / Occupancy / Percent from Parent NBO / Atomic Hybrid Contributions

89. (2.00000) 90.0329% LP (1) P 4

1.878% Ga 2 s(0.10%)p99.99(98.34%) d14.43(1.42%)

90.199% P 4 s(45.60%)p 1.19(54.28%) d 0.00(0.12%)

3.254% C 6 s(2.35%)p40.99(96.42%) d 0.47(1.10%)

90. (2.00000) 90.0226% LP (1) P 5

1.822% Ga 2 s(0.09%)p99.99(98.32%) d16.80(1.44%)

90.193% P 5 s(45.68%)p 1.19(54.20%) d 0.00(0.12%)

3.292% C 8 s(2.42%)p39.85(96.36%) d 0.45(1.10%)

95. (2.00000) 93.6025% BD (1)Ga 2- P 4

25.785% Ga 2 s(47.74%)p 1.09(52.03%)d 0.00(0.20%) f 0.00(0.04%)

69.249% P 4 s(21.25%)p 3.69(78.44%)d 0.01(0.31%)

1.270% C 6 s(5.93%)p15.73(93.20%)d 0.12(0.71%) f 0.03(0.16%)

96. (2.00000) 93.5340% BD (1)Ga 2- P 5

25.596% Ga 2 s(47.03%)p 1.12(52.74%)d 0.00(0.20%) f 0.00(0.04%)

69.298% P 5 s(21.17%)p 3.71(78.52%)d 0.01(0.31%) f 0.00(0.01%)

1.297% C 8 s(5.86%)p15.90(93.26%)d 0.12(0.72%) f 0.03(0.16%)

97. (2.00000) 98.1523% BD (1) P 4- C 6

32.793% P 4 s(16.60%)p 4.98(82.66%)d 0.04(0.73%) f 0.00(0.01%)

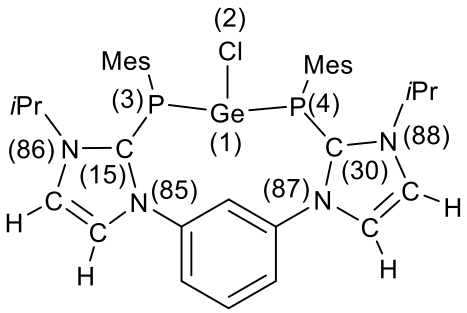
65.430% C 6 s(39.11%)p 1.55(60.67%)d 0.00(0.14%) f 0.00(0.07%)

99. (2.00000) 98.1536% BD (1) P 5- C 8

32.799% P 5 s(16.63%)p 4.97(82.64%)d 0.04(0.73%) f 0.00(0.01%)

65.425% C 8 s(39.11%)p 1.55(60.67%)d 0.00(0.14%) f 0.00(0.07%)

[8]$^+$



Numbering Scheme of **[8]**$^+$ for NBO calculations.

NPA Charges

Ge 1 0.41988

Cl 2 -0.47427

P 3 0.31868

P 4 0.31867

C 15 0.18546

C 30 0.18546

N 85 -0.35205

N 86 -0.31885

N 87 -0.35205

N 88 -0.31884

Bond Analysis

70. (1.97317) LP (1)Ge 1 s(85.84%)p 0.16(14.12%)d 0.00(0.04%)f 0.00(0.00%)

74. (1.85159) LP (1) P 3 s(56.40%)p 0.77(43.46%)d 0.00(0.14%)f 0.00(0.00%)

75. (1.85159) LP (1) P 4 s(56.40%)p 0.77(43.46%)d 0.00(0.14%)f 0.00(0.00%)

78. (1.97383) BD (1)Ge 1-Cl 2 (WBI: ***0.71***)

(20.04%) 0.4477*Ge 1 s(5.04%)p18.63(93.95%)d 0.19(0.95%)f 0.01(0.06%)

(79.96%) 0.8942*Cl 2 s(23.52%)p 3.23(76.06%)d 0.02(0.42%)f 0.00(0.01%)

79. (1.87096) BD (1)Ge 1- P 3 (WBI: ***0.71***)

(28.62%) 0.5350*Ge 1 s(4.65%)p20.39(94.83%)d 0.11(0.51%)f 0.00(0.02%)

(71.38%) 0.8449* P 3 s(11.98%)p 7.32(87.63%)d 0.03(0.38%)f 0.00(0.01%)

80. (1.87097) BD (1)Ge 1- P 4 (WBI: ***0.71***)

(28.62%) 0.5350*Ge 1 s(4.65%)p20.39(94.83%)d 0.11(0.51%)f 0.00(0.02%)

(71.38%) 0.8449* P 4 s(11.98%)p 7.32(87.63%)d 0.03(0.38%)f 0.00(0.01%)

81. (1.96161) BD (1) P 3- C 15 (WBI: ***1.00***)

(32.38%) 0.5691* P 3 s(13.81%)p 6.18(85.38%)d 0.06(0.80%)f 0.00(0.01%)

(67.62%) 0.8223* C 15 s(40.38%)p 1.47(59.41%)d 0.00(0.15%)f 0.00(0.07%)

83. (1.96161) BD (1) P 4- C 30 (WBI: ***1.00***)

(32.38%) 0.5691* P 4 s(13.81%)p 6.18(85.38%)d 0.06(0.80%)f 0.00(0.01%)

(67.62%) 0.8223* C 30 s(40.38%)p 1.47(59.41%)d 0.00(0.15%)f 0.00(0.07%)

2nd order perturbation

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol
LP (1) P 3	207. BD*(2) C 15- N 85	12.13
LP (1) P 3	267. BD*(1) C 65- C 66	8.45
LP (1) P 4	226. BD*(2) C 30- N 87	12.13
LP (1) P 4	246. BD*(1) C 45- C 52	8.45
BD (1)Ge 1- P 3	208. BD*(1) C 15- N 86	7.72
BD (1)Ge 1- P 4	227. BD*(1) C 30- N 88	7.72
BD (1) P 3- C 15	212. BD*(1) C 16- N 85	4.59
BD (1) P 3- C 15	214. BD*(1) C 18- N 86	4.68
BD (1) P 4- C 30	231. BD*(1) C 31- N 87	4.59
BD (1) P 4- C 30	233. BD*(1) C 33- N 88	4.68

NLMOs

NLMO / Occupancy / Percent from Parent NBO / Atomic Hybrid Contributions

70. (2.00000) 98.6528% LP (1)Ge 1

98.653% Ge 1 s(85.79%)p 0.17(14.18%)d 0.00(0.04%)f 0.00(0.00%)

74. (2.00000) 92.2312% LP (1) P 3

0.555% Ge 1 s(11.36%)p 7.40(83.99%)d 0.35(3.95%)f 0.06(0.70%)

92.362% P 3 s(53.36%)p 0.87(46.50%)d 0.00(0.14%)f 0.00(0.00%)

3.012% C 15 s(3.26%)p29.25(95.42%)d 0.36(1.17%)f 0.04(0.15%)

75. (2.00000) 92.2345% LP (1) P 4

0.555% Ge 1 s(11.05%)p 7.63(84.29%)d 0.36(3.95%)f 0.06(0.70%)

92.365% P 4 s(53.37%)p 0.87(46.49%)d 0.00(0.14%) f 0.00(0.00%)

3.008% C 30 s(3.27%)p29.18(95.41%)d 0.36(1.17%)f 0.04(0.15%)

78. (2.00000) 98.6814% BD (1)Ge 1-Cl 2 (WBI 0.7125)

19.951% Ge 1 s(6.30%)p14.73(92.78%)d 0.14(0.86%)f 0.01(0.06%)

78.899% Cl 2 s(23.66%)p 3.21(75.92%)d 0.02(0.42%)f 0.00(0.01%)

79. (2.00000) 93.4381% BD (1)Ge 1- P 3 (WBI 0.7127)

26.728% Ge 1 s(5.52%)p17.03(93.99%)d 0.09(0.48%)f 0.00(0.02%)

66.996% P 3 s(15.61%)p 5.38(84.01%)d 0.02(0.37%)f 0.00(0.01%)

1.906% C 15 s(4.73%)p19.97(94.43%)d 0.15(0.69%)f 0.03(0.15%)

80. (2.00000) 93.4409% BD (1)Ge 1- P 4 (WBI 0.7127)

26.714% Ge 1 s(5.48%)p17.15(94.02%)d 0.09(0.48%)f 0.00(0.02%)

67.009% P 4 s(15.62%)p 5.38(83.99%)d 0.02(0.37%)f 0.00(0.01%)

1.934% C 30 s(4.64%)p20.37(94.53%)d 0.15(0.68%)f 0.03(0.15%)

81. (2.00000) 98.0703% BD (1) P 3- C 15 (WBI 0.9985)

31.844% P 3 s(16.07%)p 5.18(83.16%)d 0.05(0.77%)f 0.00(0.01%)

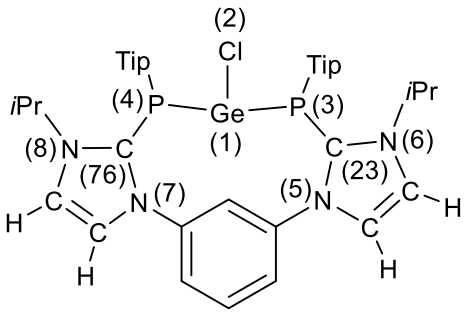
66.304% C 15 s(39.60%)p 1.52(60.18%)d 0.00(0.15%)f 0.00(0.07%)

83. (2.00000) 98.0706% BD (1) P 4- C 30 (WBI 0.9985)

31.844% P 4 s(16.07%)p 5.18(83.16%)d 0.05(0.77%)f 0.00(0.01%)

66.305% C 30 s(39.60%)p 1.52(60.18%)d 0.00(0.15%)f 0.00(0.07%)

[9]$^+$



Numbering Scheme of **[9]**$^+$ for NBO calculations.

NPA charges

Ge 1 0.39368

Cl 2 -0.47603

P 3 0.31735

P 4 0.31579N

N 5 -0.35450

N 6 -0.32000

N 7 -0.35448

N 8 -0.31652

C 23 0.18176

C 76 0.18621

Bond Analysis

82. (1.96818) LP (1)Ge 1 s(85.85%)p 0.16(14.12%)d 0.00(0.04%) f 0.00(0.00%)

86. (1.84337) LP (1) P 3 s(55.82%)p 0.79(44.05%)d 0.00(0.13%) f 0.00(0.00%)

87. (1.84462) LP (1) P 4 s(55.24%)p 0.81(44.63%)d 0.00(0.12%) f 0.00(0.00%)

90. (1.97619) BD (1)Ge 1-Cl 2 (WBI: ***0.72***)

(20.08%) 0.4481*Ge 1 s(4.80%)p19.66(94.30%)d 0.18(0.85%) f 0.01(0.06%)

(79.92%) 0.8940*Cl 2 s(24.99%)p 2.99(74.61%)d 0.02(0.39%) f 0.00(0.01%)

91. (1.86802) BD (1)Ge 1- P 3 (WBI: ***0.70***)

(28.43%) 0.5332*Ge 1 s(4.64%)p20.47(94.93%)d 0.09(0.42%) f 0.00(0.01%)

(71.57%) 0.8460* P 3 s(12.26%)p 7.13(87.38%)d 0.03(0.34%) f 0.00(0.01%)

92. (1.88427) BD (1)Ge 1- P 4 (WBI: ***0.73***)

(29.12%) 0.5396*Ge 1 s(4.91%)p19.27(94.64%)d 0.09(0.43%) f 0.00(0.02%)

(70.88%) 0.8419* P 4 s(13.31%)p 6.48(86.28%)d 0.03(0.40%) f 0.00(0.01%)

93. (1.96090) BD (1) P 3- C 23 (WBI: ***1.01***)

(32.37%) 0.5690* P 3 s(13.75%)p 6.21(85.46%)d 0.06(0.78%) f 0.00(0.01%)

(67.63%) 0.8224* C 23 s(40.52%)p 1.46(59.26%)d 0.00(0.15%) f 0.00(0.07%)

95. (1.96045) BD (1) P 4- C 76 (WBI: ***0.99***)

(32.41%) 0.5693* P 4 s(13.60%)p 6.29(85.60%)d 0.06(0.79%) f 0.00(0.01%)

(67.59%) 0.8221* C 76 s(40.41%)p 1.47(59.38%)d 0.00(0.14%) f 0.00(0.07%)

2nd order perturbation

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol
86. LP (1) P 3	244. BD*(2) N 6- C 23	10.83
86. LP (1) P 3	280. BD*(1) C 34- C 41	8.44
87. LP (1) P 4	251. BD*(2) N 8- C 76	10.68
87. LP (1) P 4	333. BD*(1) C 87- C 88	8.54
91. BD (1)Ge 1- P 3	243. BD*(1) N 6- C 23	7.68
92. BD (1)Ge 1- P 4	250. BD*(1) N 8- C 76	8.01
93. BD (1) P 3- C 23	240. BD*(1) N 5- C 19	4.54
93. BD (1) P 3- C 23	242. BD*(1) N 6- C 21	4.56
95. BD (1) P 4- C 76	247. BD*(1) N 7- C 72	4.52
95. BD (1) P 4- C 76	249. BD*(1) N 8- C 74	4.70

NLMOs

NLMO / Occupancy / Percent from Parent NBO / Atomic Hybrid Contributions

82. (2.00000) 98.4009% LP (1)Ge 1

98.401% Ge 1 s(85.78%)p 0.17(14.19%)d 0.00(0.04%) f 0.00(0.00%)

86. (2.00000) 91.7642% LP (1) P 3

0.579% Ge 1 s(10.07%)p 8.52(85.78%)d 0.35(3.50%) f 0.06(0.65%)

91.925% P 3 s(52.48%)p 0.90(47.39%)d 0.00(0.13%) f 0.00(0.00%)

1.095% N 6 s(0.65%)p99.99(99.04%)d 0.38(0.25%) f 0.11(0.07%)

3.176% C 23 s(2.74%)p34.99(95.98%)d 0.42(1.14%) f 0.05(0.14%

87. (2.00000) 91.9100% LP (1) P 4

0.546% Ge 1 s(11.00%)p 7.70(84.64%)d 0.33(3.65%) f 0.06(0.71%)

92.026% P 4 s(52.32%)p 0.91(47.55%)d 0.00(0.13%) f 0.00(0.00%)

1.019% N 8 s(0.46%)p99.99(99.17%)d 0.62(0.28%) f 0.18(0.08%)

3.048% C 76 s(2.90%)p33.07(95.87%)d 0.38(1.10%) f 0.05(0.14%)

91. (2.00000) 93.2841% BD (1)Ge 1- P 3

26.494% Ge 1 s(5.44%)p17.29(94.15%)d 0.07(0.39%) f 0.00(0.01%)

67.104% P 3 s(16.20%)p 5.15(83.46%)d 0.02(0.34%) f 0.00(0.01%)

92. (2.00000) 94.1253% BD (1)Ge 1- P 4

27.385% Ge 1 s(5.72%)p16.41(93.86%)d 0.07(0.41%) f 0.00(0.02%)

66.997% P 4 s(16.97%)p 4.87(82.63%)d 0.02(0.39%) f 0.00(0.01%)

93. (2.00000) 98.0337% BD (1) P 3- C 23

31.828% P 3 s(15.91%)p 5.24(83.33%)d 0.05(0.75%) f 0.00(0.01%)

66.280% C 23 s(39.68%)p 1.51(60.09%)d 0.00(0.15%) f 0.00(0.07%)

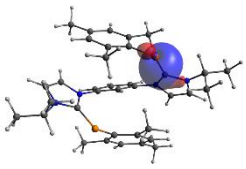
95. (2.00000) 98.0104% BD (1) P 4- C 76

31.852% P 4 s(15.85%)p 5.26(83.38%)d 0.05(0.76%) f 0.00(0.01%)

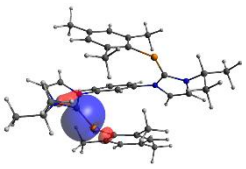
66.232% C 76 s(39.66%)p 1.52(60.13%)d 0.00(0.14%) f 0.00(0.07%)

6.6 NLMOs of compound **5a** and the cations in **[7]**$^+$, **[8]**$^+$ and **[9]**$^+$.

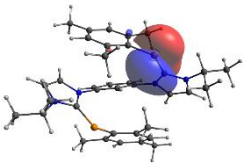
Figure S77. Selected NLMOs of **5a** (point group C_1, PBE0-D3/def2-TZVP).



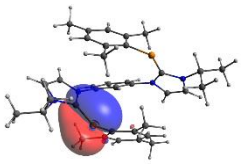
σ(P1-C_{NHC})
−16.8 eV
Ge: 26.7%
P: 67.0%
C_{NHC}: 1.9%



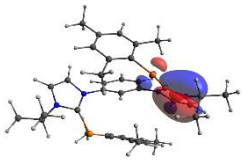
σ(P2-C_{NHC})
−16.8 eV
Ge: 26.7%
P: 67.0%
C_{NHC}: 1.9%



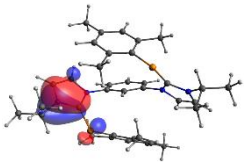
π(C_{NHC}-P1)
−6.8 eV
P: 31.8%
C_{NHC}: 66.3%



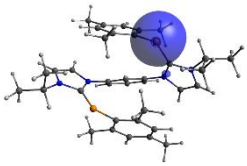
π (C_{NHC}-P2)
−6.8 eV
P: 31.8 %
C_{NHC}: 66.3 %



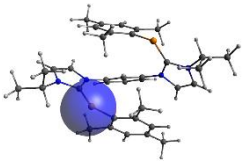
LP(N1)
−9.8 eV
Ge: 20.0%
Cl: 78.9%



LP(N2)
−9.8 eV
P: 92.4 %
C_{NHC}: 3.0%

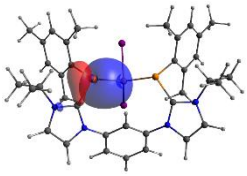


LP(P1)
−12.2 eV
P: 92.4%
C_{NHC}: 3.0%

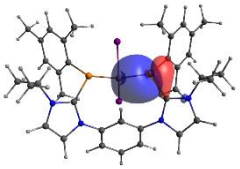


LP(P2)
−12.2 eV
Ge: 98.7 %

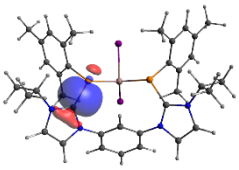
Figure S78. Selected NLMOs of **[7]**$^+$ (point group C_1, PBE0-D3/def2-TZVP).



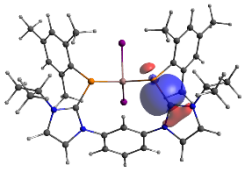
σ(Ga-P1)
−14.8 eV
Ga: 25.8%
P: 69.2%
C_{NHC}: 1.3%



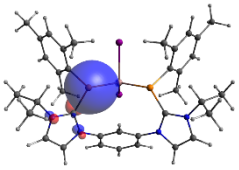
σ(Ga-P2)
−14.8 eV
Ga: 25.6%
P: 69.3%
C_{NHC}: 1.3%



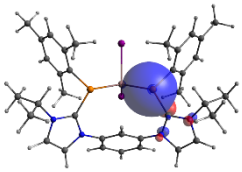
σ(C_{NHC}-P1)
−20.0 eV
P: 32.8%
C_{NHC}: 65.4%



σ(C_{NHC}-P2)
−20.0 eV
P: 32.8 %
C_{NHC}: 65.4 %

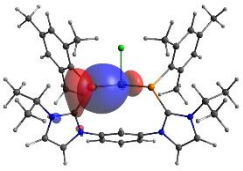


LP(P1)
−13.8 eV
P: 90.2 %
C_{NHC}: 3.3%

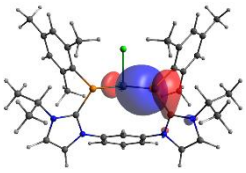


LP(P2)
−13.8 eV
P: 90.2%
C_{NHC}: 3.3%

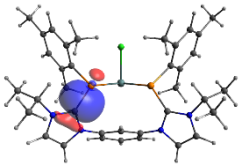
Figure S79. Selected NLMOs of **[8]**$^+$ (point group C_1, PBE0-D3/def2-TZVP).



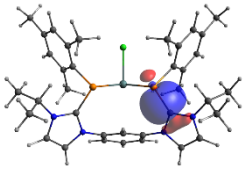
σ(Ge-P1)
−12.9 eV
Ge: 26.7%
P: 67.0%
C_{NHC}: 1.9%



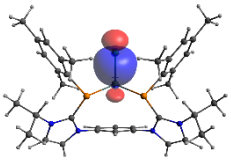
σ(Ge-P2)
−12.9 eV
Ge: 26.7%
P: 67.0%
C_{NHC}: 1.9%



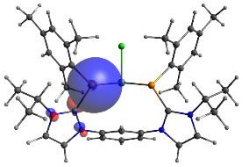
σ(C_{NHC}-P1)
−19.7 eV
P: 31.8%
C_{NHC}: 66.3%



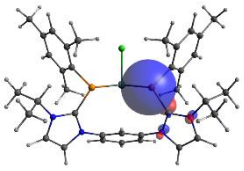
σ(C_{NHC}-P2)
−19.7 eV
P: 31.8 %
C_{NHC}: 66.3 %



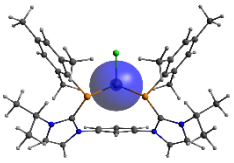
σ(Ge-Cl)
−12.9 eV
Ge: 20.0%
Cl: 78.9%



LP(P1)
−14.2 eV
P: 92.4 %
C_{NHC}: 3.0%

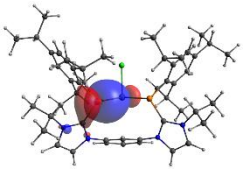


LP(P2)
−14.2 eV
P: 92.4%
C_{NHC}: 3.0%

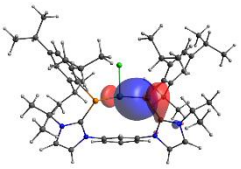


LP(Ge)
−14.5 eV
Ge: 98.7 %

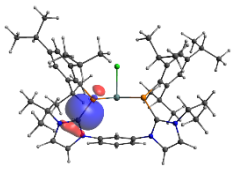
Figure S80. Selected NLMOs of **[9]**$^+$ (point group C_1, PBE0-D3/def2-TZVP).



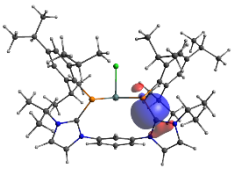
σ(Ge-P1)
−13.0 eV
Ga: 26.5%
P: 67.1%



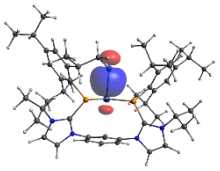
σ(Ge-P2)
−13.2 eV
Ga: 27.4%
P: 67.0%



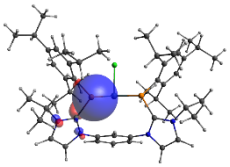
$\sigma(C_{NHC}$-P1)
−19.6 eV
P: 31.8%
C_{NHC}: 66.3%



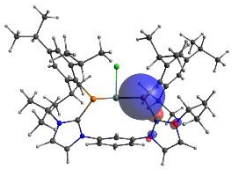
$\sigma(C_{NHC}$-P2)
−19.6 eV
P: 31.9 %
C_{NHC}: 66.2 %



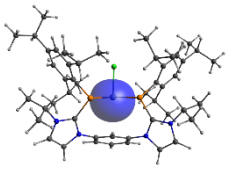
σ(Ge-Cl)
−19.1 eV
Ge: 20.0%
Cl: 79.0%



LP(P1)
−14.2 eV
P: 91.9 %
C_{NHC}: 3.2%



LP(P2)
−14.1 eV
P: 92.0%
C_{NHC}: 3.0%



LP(Ge)
−14.4 eV
Ge: 98.4 %

6.7 Calculation of the NMR chemical shift of **1a** and **1b**.

Among the series of simple NHCPs the Mes-substituted derivatives all show a significant deshielding of the phosphorus atom with $\delta(^{31}P\{^1H\})$ values that are ca. 15 ppm more positive than the respective Dip- and Tip-derivatives when the same NHC is bound to phosphorus. This difference is nicely reproduced by GIAO calculation and revealed $\delta_{calc}(^{31}P)$ values for **1a** (−68.9 ppm) and **1b** (−88.1 ppm), which show the same deshielding of the P atom in the gas phase. According to a theoretical study by Koley and co-workers the theoretical ^{31}P NMR shift of NHCPs is closely related to the NPA charge at the dicoordinate P atom, with more positive values correlating with a deshielded ^{31}P NMR signal.[31] The NPA charges for **1a** (+0.18) and **1b** (+0.17) correspond well with this assumption.

6.8 Optimized structures (.xyz-files)

6.8.1 1a

```
36
1a @ PBE0-D3/def2-SVP
P         0.7742700000      1.4042790000     -0.5312490000
N         3.1929570000      0.1006690000     -0.2682750000
N         1.7187700000     -0.8033100000      1.0535890000
C        -0.8588670000      0.5755820000     -0.3373920000
C        -1.9009930000      1.2772400000      0.3206850000
C        -3.1687400000      0.7048190000      0.4193070000
H        -3.9559920000      1.2565200000      0.9433570000
C        -3.4617350000     -0.5502080000     -0.1228010000
C        -2.4383040000     -1.2186200000     -0.7914330000
H        -2.6469030000     -2.1936150000     -1.2437140000
C        -1.1520240000     -0.6796120000     -0.9224160000
C        -1.6580430000      2.6273910000      0.9324030000
H        -1.3847120000      3.3729700000      0.1681820000
H        -0.8116750000      2.5987360000      1.6372760000
H        -2.5521680000      2.9911890000      1.4589300000
C        -4.8398430000     -1.1348620000     -0.0101340000
H        -5.2071940000     -1.1031040000      1.0277700000
H        -4.8631610000     -2.1812860000     -0.3464350000
H        -5.5631150000     -0.5720940000     -0.6233610000
C        -0.1250040000     -1.4572580000     -1.6930070000
H         0.4672210000     -0.7832590000     -2.3315850000
H        -0.6016860000     -2.2264370000     -2.3175310000
H         0.5952760000     -1.9682800000     -1.0316610000
C         1.8716640000      0.1736010000      0.1008530000
C         3.8391430000     -0.8878350000      0.4443670000
H         4.8935860000     -1.1070350000      0.3038360000
C         2.9191410000     -1.4597290000      1.2573900000
H         3.0137990000     -2.2769810000      1.9665180000
C         3.7820830000      0.9473870000     -1.2685180000
H         3.0476850000      1.0920900000     -2.0781640000
H         4.6924830000      0.4744470000     -1.6595750000
H         4.0318850000      1.9408700000     -0.8625170000
C         0.5452600000     -0.9843050000      1.8701050000
H         0.1481730000      0.0017970000      2.1513820000
H         0.8290210000     -1.5386770000      2.7740770000
H        -0.2510910000     -1.5251180000      1.3382960000
```

6.8.2 1b

```
45
1b @ PBE0-D3/def2-SVP
C        -0.9131860000      0.1854430000     -0.2652620000
C        -0.8280490000      1.5895140000     -0.0666660000
C        -1.9250750000      2.2716300000      0.4720710000
H        -1.8629750000      3.3509990000      0.6303960000
C        -3.1015320000      1.6063030000      0.7973780000
H        -3.9485350000      2.1580940000      1.2136490000
C        -3.1949480000      0.2367770000      0.5839380000
H        -4.1234150000     -0.2805520000      0.8365440000
C        -2.1203790000     -0.4895510000      0.0580200000
```

```
C         0.3936100000      2.3943450000     -0.4862700000
H         1.2420690000      1.6958130000     -0.5266160000
C         0.7654540000      3.5143880000      0.4830210000
H         0.0182570000      4.3239830000      0.4975960000
H         1.7231030000      3.9701610000      0.1857880000
H         0.8749690000      3.1441710000      1.5147240000
C         0.1979370000      2.9317780000     -1.9060130000
H         0.0255920000      2.1049830000     -2.6114500000
H         1.0869510000      3.4899100000     -2.2426120000
H        -0.6690980000      3.6105950000     -1.9550500000
C        -2.2823920000     -1.9815010000     -0.1831430000
H        -1.2627050000     -2.4051300000     -0.1702260000
C        -3.1024880000     -2.6990780000      0.8861000000
H        -2.7252570000     -2.4894840000      1.8994600000
H        -3.0593580000     -3.7881730000      0.7280960000
H        -4.1670830000     -2.4152710000      0.8610000000
C        -2.8504490000     -2.2401980000     -1.5805230000
H        -2.9334960000     -3.3213850000     -1.7778020000
H        -2.2029770000     -1.8040290000     -2.3563080000
H        -3.8537100000     -1.7956930000     -1.6872480000
C         1.7731360000     -0.7305370000      0.0115610000
C         3.9173010000     -1.0086910000      0.6808410000
H         4.9778900000     -1.2182250000      0.5748310000
C         3.1872260000     -0.6841650000      1.7730000000
H         3.4864600000     -0.5559110000      2.8093690000
C         3.4020700000     -1.3137080000     -1.7588960000
H         3.0446070000     -2.3113610000     -2.0627010000
H         4.4926570000     -1.2663960000     -1.8744630000
H         2.9185540000     -0.5733560000     -2.4178020000
C         0.7690820000     -0.3368540000      2.2737310000
H        -0.0200420000     -1.0700580000      2.0556410000
H         0.3272090000      0.6662740000      2.1910130000
H         1.1317410000     -0.4913220000      3.2983420000
P         0.4304260000     -0.7581150000     -1.1365440000
N         3.0539430000     -1.0267250000     -0.3948300000
N         1.8743860000     -0.5207430000      1.3657830000
```

6.8.3 5a

```
86
5a @ PBE0-D3/def2-SVP
P        -1.9041430000      1.9286130000     -1.4736640000
P         1.9040400000     -1.9283830000     -1.4739050000
N        -4.0071380000      0.3109420000     -0.7802320000
N        -2.4339790000      0.0827810000      0.7149020000
N         4.0070200000     -0.3107330000     -0.7803350000
N         2.4338960000     -0.0828400000      0.7148750000
C        -2.3418910000      3.2798230000      1.4270860000
C         2.5174530000      4.2439610000      2.1538940000
C         1.0842770000      2.1249040000     -2.1635970000
C        -0.9352790000      3.1895180000      0.9132370000
C         0.0997870000      3.6910940000      1.7046200000
C         1.4271890000      3.7063470000      1.2725680000
C         1.6984850000      3.2232070000     -0.0071830000
C         0.7022970000      2.6796160000     -0.8213480000
C        -0.6319600000      2.6248290000     -0.3510880000
C        -6.2295090000      0.7744460000     -1.7286550000
C        -4.3206420000     -0.0293080000     -3.1890850000
```

```
C       -4.7283800000      0.7713100000     -1.9594690000
C       -2.7462850000      0.7564330000     -0.4509870000
C       -4.4617450000     -0.5942500000      0.1563270000
C       -3.4988400000     -0.7285690000      1.0927640000
C       -1.0843950000     -2.1248430000     -2.1636840000
C       -2.5171880000     -4.2442900000      2.1537490000
C        2.3420400000     -3.2797810000      1.4267520000
C       -0.7023080000     -2.6796300000     -0.8214970000
C       -1.6984030000     -3.2233860000     -0.0073310000
C       -1.4270030000     -3.7065970000      1.2723740000
C       -0.0995830000     -3.6912620000      1.7043550000
C        0.9354030000     -3.1895360000      0.9129560000
C        0.6319730000     -2.6247840000     -0.3513110000
C        6.2294350000     -0.7743620000     -1.7286080000
C        4.3207390000      0.0297090000     -3.1891180000
C        4.7283280000     -0.7710600000     -1.9595620000
C        2.7461890000     -0.7562840000     -0.4511330000
C        4.4616320000      0.5943280000      0.1563500000
C        3.4987560000      0.7284640000      1.0928470000
C       -1.1999290000      0.0551770000      1.4050330000
C       -1.2055300000      0.0543160000      2.8025820000
C       -0.0000330000     -0.0002360000      3.4933440000
C        1.2054580000     -0.0546790000      2.8025710000
C        1.1998480000     -0.0553240000      1.4050170000
C       -0.0000410000     -0.0000260000      0.7032430000
H       -2.4236260000      4.0494800000      2.2079530000
H       -3.0375080000      3.5175320000      0.6075790000
H       -2.6857450000      2.3293190000      1.8658810000
H        2.5597000000      3.7028140000      3.1139270000
H        3.5024760000      4.1602930000      1.6721010000
H        2.3547420000      5.3065570000      2.3969390000
H        2.1428260000      2.3280350000     -2.3807030000
H        0.9336870000      1.0315490000     -2.2069350000
H        0.4761160000      2.5546330000     -2.9744400000
H       -0.1452890000      4.1013920000      2.6896630000
H        2.7262820000      3.2468320000     -0.3804150000
H       -6.4951810000      1.3247000000     -0.8141180000
H       -6.7253120000      1.2649000000     -2.5782230000
H       -6.6404870000     -0.2452940000     -1.6590540000
H       -4.6218830000     -1.0842310000     -3.0869410000
H       -4.8002710000      0.3819190000     -4.0896080000
H       -3.2312850000      0.0141340000     -3.3318650000
H       -4.3830120000      1.8140570000     -2.0954660000
H       -5.4291990000     -1.0784040000      0.0783390000
H       -3.4390040000     -1.3740230000      1.9620360000
H       -2.1430490000     -2.3276540000     -2.3805720000
H       -0.9334570000     -1.0315430000     -2.2070950000
H       -0.4765370000     -2.5548020000     -2.9746410000
H       -2.3542860000     -5.3068130000      2.3969760000
H       -2.5595580000     -3.7029950000      3.1136980000
H       -3.5022140000     -4.1608780000      1.6719220000
H        2.4238790000     -4.0495730000      2.2074750000
H        3.0376730000     -3.5172570000      0.6071920000
H        2.6857840000     -2.3293190000      1.8657250000
H       -2.7262150000     -3.2470660000     -0.3805140000
H        0.1455850000     -4.1016140000      2.6893530000
H        6.4949440000     -1.3247090000     -0.8140830000
H        6.7252730000     -1.2648090000     -2.5781600000
H        6.6405160000      0.2453300000     -1.6588900000
H        4.6219700000      1.0846230000     -3.0868190000
```

```
H        4.8004600000     -0.3813980000     -4.0896480000
H        3.2313940000     -0.0137060000     -3.3320180000
H        4.3828760000     -1.8137640000     -2.0956930000
H        5.4290580000      1.0785480000      0.0783860000
H        3.4389140000      1.3737910000      1.9622130000
H       -2.1510330000      0.1145550000      3.3442380000
H       -0.0000320000     -0.0003190000      4.5851180000
H        2.1509680000     -0.1150010000      3.3442070000
H       -0.0000500000      0.0000440000     -0.3840480000
```

6.8.4 6c

```
122
6c @ PBE0-D3/def2-SVP
P       -1.2579430000     -3.2118340000     -2.2713790000
P        1.2579430000      3.2118340000      2.2713790000
N        1.0751690000     -2.4192210000     -0.9215560000
N        1.2659720000     -4.4438580000     -1.7131560000
N       -1.0751690000      2.4192210000      0.9215560000
N       -1.2659720000      4.4438580000      1.7131560000
C       -0.2269140000     -0.3996070000     -1.3200240000
C        0.7601780000     -0.7947090000      0.8520700000
C        0.5390870000     -1.1990640000     -0.4668540000
C        1.1289300000     -6.8996480000     -1.8331130000
C        2.1936390000     -5.5401920000     -3.7004640000
C        1.1339870000     -5.5932810000     -2.6084500000
C        0.3920550000     -3.3862890000     -1.6450340000
C        2.3235950000     -2.8955090000     -0.5475070000
C        2.4311610000     -4.1524310000     -1.0301100000
C       -1.1693440000     -5.6952170000      1.6328570000
C       -2.7791020000     -3.8871380000      0.9285920000
C       -1.6281350000     -4.7943630000      0.4910690000
C       -2.6990420000     -9.9800530000     -2.2532030000
C       -5.0276460000     -9.0082720000     -2.1601460000
C       -3.6019460000     -8.9223520000     -1.6177710000
C       -3.4614460000     -4.2858620000     -4.9316390000
C       -1.8872730000     -6.1110160000     -5.6767760000
C       -2.2047080000     -5.0877730000     -4.5915660000
C       -2.0102030000     -5.5387850000     -0.7792850000
C       -2.5766590000     -6.8124860000     -0.6693180000
C       -3.0168320000     -7.5354530000     -1.7770410000
C       -2.8814990000     -6.9456750000     -3.0334750000
C       -2.3166480000     -5.6795030000     -3.1988020000
C       -1.8632500000     -4.9568230000     -2.0653880000
C        0.2269140000      0.3996070000      1.3200240000
C       -0.7601780000      0.7947090000     -0.8520700000
C       -0.5390870000      1.1990640000      0.4668540000
C       -1.1289300000      6.8996480000      1.8331130000
C       -2.1936390000      5.5401920000      3.7004640000
C       -1.1339870000      5.5932810000      2.6084500000
C       -0.3920550000      3.3862890000      1.6450340000
C       -2.3235950000      2.8955090000      0.5475070000
C       -2.4311610000      4.1524310000      1.0301100000
C        1.1693440000      5.6952170000     -1.6328570000
C        2.7791020000      3.8871380000     -0.9285920000
C        1.6281350000      4.7943630000     -0.4910690000
```

```
C         2.6990420000      9.9800530000      2.2532030000
C         5.0276460000      9.0082720000      2.1601460000
C         3.6019460000      8.9223520000      1.6177710000
C         3.4614460000      4.2858620000      4.9316390000
C         1.8872730000      6.1110160000      5.6767760000
C         2.2047080000      5.0877730000      4.5915660000
C         2.0102030000      5.5387850000      0.7792850000
C         2.5766590000      6.8124860000      0.6693180000
C         3.0168320000      7.5354530000      1.7770410000
C         2.8814990000      6.9456750000      3.0334750000
C         2.3166480000      5.6795030000      3.1988020000
C         1.8632500000      4.9568230000      2.0653880000
H        -0.3728400000     -0.6955830000     -2.3592920000
H         1.3267250000     -1.4348440000      1.5306210000
H         2.0825720000     -7.0656560000     -1.3060700000
H         0.9749690000     -7.7424410000     -2.5224740000
H         0.3096670000     -6.9087260000     -1.1009860000
H         2.1575330000     -4.5768270000     -4.2299120000
H         2.0111080000     -6.3406080000     -4.4325500000
H         3.2101610000     -5.6793760000     -3.2998110000
H         0.1512230000     -5.4683090000     -3.0752400000
H         3.0277270000     -2.2812340000      0.0048830000
H         3.2575990000     -4.8541620000     -0.9693220000
H        -1.9911280000     -6.3007420000      2.0470220000
H        -0.7771200000     -5.0824360000      2.4592130000
H        -0.3712100000     -6.3836850000      1.3140420000
H        -3.0305790000     -3.1766730000      0.1271630000
H        -2.5034370000     -3.3084080000      1.8249720000
H        -3.6766340000     -4.4815260000      1.1641200000
H        -0.7838580000     -4.1367840000      0.2417810000
H        -3.0961600000    -10.9936800000     -2.0841650000
H        -1.6815670000     -9.9356350000     -1.8359750000
H        -2.6194690000     -9.8292790000     -3.3418400000
H        -5.6796890000     -8.2603360000     -1.6848640000
H        -5.4581880000    -10.0057620000     -1.9784420000
H        -5.0528620000     -8.8294540000     -3.2469160000
H        -3.6440620000     -9.1275970000     -0.5340300000
H        -4.3509980000     -4.9366940000     -4.9392080000
H        -3.3729040000     -3.8136690000     -5.9233080000
H        -3.6307390000     -3.4904670000     -4.1902640000
H        -2.7276030000     -6.7990900000     -5.8627240000
H        -1.0084610000     -6.7209380000     -5.4143060000
H        -1.6745720000     -5.6010780000     -6.6291320000
H        -1.3696540000     -4.3647220000     -4.5479640000
H        -2.6871360000     -7.2650940000      0.3193180000
H        -3.2194440000     -7.4930850000     -3.9168850000
H         0.3728400000      0.6955830000      2.3592920000
H        -1.3267250000      1.4348440000     -1.5306210000
H        -2.0825720000      7.0656560000      1.3060700000
H        -0.9749690000      7.7424410000      2.5224740000
H        -0.3096670000      6.9087260000      1.1009860000
H        -2.1575330000      4.5768270000      4.2299120000
H        -2.0111080000      6.3406080000      4.4325500000
H        -3.2101610000      5.6793760000      3.2998110000
H        -0.1512230000      5.4683090000      3.0752400000
H        -3.0277270000      2.2812340000     -0.0048830000
H        -3.2575990000      4.8541620000      0.9693220000
H         1.9911280000      6.3007420000     -2.0470220000
H         0.7771200000      5.0824360000     -2.4592130000
H         0.3712100000      6.3836850000     -1.3140420000
```

```
H         3.0305790000      3.1766730000     -0.1271630000
H         2.5034370000      3.3084080000     -1.8249720000
H         3.6766340000      4.4815260000     -1.1641200000
H         0.7838580000      4.1367840000     -0.2417810000
H         3.0961600000     10.9936800000      2.0841650000
H         1.6815670000      9.9356350000      1.8359750000
H         2.6194690000      9.8292790000      3.3418400000
H         5.6796890000      8.2603360000      1.6848640000
H         5.4581880000     10.0057620000      1.9784420000
H         5.0528620000      8.8294540000      3.2469160000
H         3.6440620000      9.1275970000      0.5340300000
H         4.3509980000      4.9366940000      4.9392080000
H         3.3729040000      3.8136690000      5.9233080000
H         3.6307390000      3.4904670000      4.1902640000
H         2.7276030000      6.7990900000      5.8627240000
H         1.0084610000      6.7209380000      5.4143060000
H         1.6745720000      5.6010780000      6.6291320000
H         1.3696540000      4.3647220000      4.5479640000
H         2.6871360000      7.2650940000     -0.3193180000
H         3.2194440000      7.4930850000      3.9168850000
```

6.8.5 $[7]^+$

```
89
[7]+ @ PBE0-D3/def2-SVP
I         0.0038300692      0.5115213536     -2.8982953412
Ga       -0.0004444767     -0.1993005765     -0.4473839943
I        -0.0054628678     -2.7515407691     -0.3780690102
P         1.8589582993      0.1744983773      1.0488643113
P        -1.8618656253      0.1890786853      1.0453685190
C         2.7817518135      1.7312960917      0.8780061461
C         3.1446423232     -1.0190524148      0.4955164641
C        -2.7910890554      1.7380756349      0.8459744887
C        -3.1395390864     -1.0224338518      0.5139667757
N         2.4247012399      2.9048677644      0.2869959457
N         4.0034496768      1.9495093939      1.4184764776
C         3.8725030620     -0.8753379552     -0.7067010960
C         3.3504054245     -2.1512182570      1.3188904811
N        -2.4289584758      2.9068444953      0.2480478132
N        -4.0202460418      1.9587438802      1.3685042788
C        -3.8662714871     -0.9071498347     -0.6929133627
C        -3.3314583299     -2.1440826833      1.3535768777
C         1.2011502404      3.1912367786     -0.3667526292
C         3.4425038386      3.8328589312      0.4261730944
C         4.4291867587      3.2262359612      1.1284285599
C         4.7464530013      1.0305907692      2.3026036535
C         3.7413105916      0.3162978509     -1.6097289525
C         4.7847535935     -1.8731378354     -1.0603497745
C         4.2767004832     -3.1148627065      0.9200235996
C         2.5950534112     -2.3522754013      2.6014825015
C        -1.1949595973      3.1923101510     -0.3859491737
C        -3.4508133602      3.8336639368      0.3648234951
C        -4.4449318709      3.2317113154      1.0602621586
C        -4.7712560821      1.0502238787      2.2566583768
C        -4.7656048135     -1.9206950758     -1.0314156507
C        -3.7394430882      0.2670596532     -1.6190342267
C        -4.2458631523     -3.1256114756      0.9685011532
C        -2.5690325719     -2.3201895139      2.6356259781
```

```
C       -0.0021317322      2.8740966601      0.2619648017
C        1.2204010193      3.8447762136     -1.5974815429
H        3.3537630063      4.8448856242      0.0430190606
H        5.3890070721      3.6089119410      1.4624061923
H        4.0961835956      0.1530524380      2.4026468696
C        6.0516580655      0.5966212457      1.6607240349
C        4.9188489767      1.6661160173      3.6733862571
H        4.3488491493      1.1645969384     -1.2486732377
H        4.0950003289      0.0763659111     -2.6213112954
H        2.7018806844      0.6595456969     -1.6979568745
H        5.3413694285     -1.7648069157     -1.9955890181
C        5.0001417721     -3.0024418344     -0.2692832156
H        4.4309502471     -3.9898272478      1.5575798721
H        2.9615641915     -3.2396582606      3.1347536311
H        2.6788019698     -1.4837240908      3.2742759434
H        1.5204869893     -2.4964302580      2.4050719300
C       -1.1935012008      3.8460016663     -1.6168028875
H       -3.3595494691      4.8421577634     -0.0268865806
H       -5.4098318886      3.6154228580      1.3780162867
H       -4.1268335131      0.1696643801      2.3658547870
C       -4.9460383715      1.6976275940      3.6215887144
C       -6.0758780830      0.6177281824      1.6125941507
H       -5.3159660650     -1.8378520399     -1.9730616162
C       -4.9727046535     -3.0379164456     -0.2198551052
H       -2.7013134752      0.6124877035     -1.7141799395
H       -4.0925940543      0.0062438084     -2.6256100717
H       -4.3492271300      1.1205954090     -1.2746831018
H       -4.3842172690     -3.9962113951      1.6154311703
H       -1.4942498700     -2.4600265015      2.4367325177
H       -2.6562718321     -1.4416402203      3.2947706857
H       -2.9269128318     -3.2016877903      3.1842965401
H       -0.0101114831      2.4429329399      1.2663080629
H        2.1720526834      4.0616087126     -2.0852460308
C        0.0184166399      4.1804281838     -2.2109643429
H        6.5604440651     -0.1186392467      2.3217932595
H        5.8718166092      0.0955119796      0.6998584537
H        6.7317263976      1.4485174073      1.5037112198
H        5.5826977839      2.5437827068      3.6438128766
H        3.9502893017      1.9718211772      4.0948216628
H        5.3720920814      0.9341196739      4.3565085185
C        5.9498147897     -4.0791713527     -0.6990479606
H       -2.1367583046      4.0635268371     -2.1202707885
H       -5.6038559820      2.5794330684      3.5817830153
H       -5.4069070203      0.9740582601      4.3085971051
H       -3.9773710831      2.0004852672      4.0448430663
H       -5.8941257678      0.1094150731      0.6558521247
H       -6.5901768391     -0.0908297117      2.2766438389
H       -6.7521142725      1.4710133390      1.4469307171
C       -5.9585597076     -4.0984694401     -0.6075180469
H        0.0264068754      4.6717416781     -3.1851535003
H        5.4131651229     -4.8620139845     -1.2603467864
H        6.7381752686     -3.6872252412     -1.3568609673
H        6.4261631789     -4.5666031840      0.1635675744
H       -6.9823338753     -3.8036284682     -0.3228321671
H       -5.9597363860     -4.2668269784     -1.6940754232
H       -5.7408426043     -5.0537985947     -0.1104418181
```

6.8.6 $[8]^+$

```
88
[8]+ @ PBE0-D3/def2-SVP
Ge      -0.0000049529      0.1933877192     -1.0872630076
Cl      -0.0000112996      2.4074286471     -0.6042818213
P       -1.7619975616     -0.0055864814      0.6916317484
P        1.7619768707     -0.0055567896      0.6916362252
C       -0.0000134987     -2.7327486863     -0.1360965170
H       -0.0000327260     -2.4573133941      0.9209820348
C       -1.1973873565     -2.9133293186     -0.8263386064
C       -1.2074404376     -3.3269847769     -2.1580409599
H       -2.1574673953     -3.4470477404     -2.6819044723
C        0.0000380915     -3.5492486766     -2.8137405757
H        0.0000574856     -3.8589677092     -3.8601796520
C        1.2074920165     -3.3269824644     -2.1579953290
H        2.1575402313     -3.4470442479     -2.6818205871
C        1.1973858907     -2.9133287365     -0.8262931607
C       -2.7573938818     -1.5131534611      0.4738701920
C       -3.4631112744     -3.5795687367     -0.0786992064
H       -3.3937391429     -4.5760006092     -0.5050965073
C       -4.4497497595     -2.9722661497      0.6255598993
H       -5.4269160043     -3.3413783176      0.9228784154
C       -4.7349341735     -0.7983987854      1.8596561411
H       -4.0535986525      0.0503116978      2.0025131007
C       -4.9746549096     -1.4632695978      3.2060124805
H       -5.6673905852     -2.3155512386      3.1299695040
H       -5.4243698153     -0.7346757792      3.8950580075
H       -4.0316496572     -1.8148540354      3.6490449998
C       -6.0021589882     -0.2985409890      1.1898246257
H       -5.7726806039      0.2195270757      0.2485833130
H       -6.5056103524      0.4180182736      1.8536277544
H       -6.7075393479     -1.1202199155      0.9887970624
C        2.7573703229     -1.5131392050      0.4739313925
C        3.4630649979     -3.5795888666     -0.0785361817
H        3.3936902099     -4.5760306506     -0.5049100681
C        4.4496901424     -2.9722808820      0.6257370149
H        5.4268385328     -3.3414006012      0.9231045910
C        4.7348911196     -0.7983566417      1.8597293158
H        4.0535532808      0.0503568823      2.0025568002
C        6.0021248563     -0.2985235108      1.1898958212
H        6.7075009825     -1.1202132584      0.9888980506
H        6.5055736275      0.4180513969      1.8536842282
H        5.7726593839      0.2195209494      0.2486388575
C        4.9745999599     -1.4631854745      3.2061083092
H        4.0315928183     -1.8147660915      3.6491398707
H        5.4242984822     -0.7345654617      3.8951366009
H        5.6673465577     -2.3154613896      3.1301023592
C        3.0031005118      1.2184766134      0.0869600171
C        3.2026402193      2.3671941239      0.8878986536
C        4.1178676689      3.3335585972      0.4705664583
H        4.2712449731      4.2165201068      1.0975305748
C        4.8305370742      3.2151000989     -0.7248756608
C        4.6014267961      2.0849808548     -1.5100352526
H        5.1377160244      1.9787480698     -2.4575302562
C        3.7000173065      1.0842067870     -1.1342436195
C        2.4402994737      2.5830651979      2.1635067731
H        2.5329909208      1.7294402725      2.8537810973
H        1.3661689563      2.6998004623      1.9500165362
```

```
H        2.7869647752      3.4882293586      2.6800345876
C        5.7764503036      4.2905006151     -1.1675459742
H        5.2259939166      5.1133365341     -1.6530151189
H        6.5106794467      3.9131133222     -1.8928653130
H        6.3210151384      4.7240545758     -0.3162067472
C        3.5374583756     -0.0953739014     -2.0512949630
H        3.8684734305      0.1584061609     -3.0674307329
H        2.4899389893     -0.4273752802     -2.1121664925
H        4.1441342052     -0.9570263000     -1.7222573798
C       -3.0031063487      1.2184818047      0.0870099127
C       -3.7000117924      1.0842819725     -1.1342110433
C       -4.6013713648      2.0851047775     -1.5099805569
H       -5.1376517929      1.9789279583     -2.4574865991
C       -4.8304497970      3.2152062095     -0.7247822927
C       -4.1178090890      3.3335862414      0.4706825122
H       -4.2711714333      4.2165242079      1.0976826550
C       -3.2026252859      2.3671686599      0.8879950221
C       -3.5374764258     -0.0952761486     -2.0512950265
H       -4.1440556435     -0.9569768696     -1.7222134687
H       -2.4899379045     -0.4272097525     -2.1122730688
H       -3.8686143504      0.1584953950     -3.0673921559
C       -5.7762894337      4.2906701106     -1.1674490924
H       -6.5106215018      3.9133195849     -1.8926825140
H       -5.2257781341      5.1134080630     -1.6530238345
H       -6.3207338807      4.7243440305     -0.3160917015
C       -2.4403189368      2.5829510967      2.1636391203
H       -2.7869525300      3.4881176757      2.6801843712
H       -1.3661732585      2.6996308187      1.9502010497
H       -2.5330943485      1.7293102060      2.8538848160
N       -2.4199399680     -2.6737969060     -0.1547490209
N       -3.9978788325     -1.7182749403      0.9735053757
N        2.4199149379     -2.6737985041     -0.1546557820
N        3.9978400173     -1.7182599117      0.9736030036
```

6.8.7 $[9]^+$

```
124
[9]+ @ PBE0-D3/def2-SVP
Ge       0.0174544537     -0.5432762195     -1.0064875306
Cl      -0.0608914493      1.7223582886     -1.0673852543
P       -1.8211697548     -0.5394316625      0.7294411795
P        1.6768609817     -0.2961915798      0.8469299446
N       -2.4070791309     -3.2584866714      0.0331538029
N       -4.0772815710     -2.2544170838      0.9727743333
N        2.4032411938     -3.0719063338      0.5413214125
N        3.8556239284     -1.9232927326      1.6552885595
C       -0.0048831297     -3.2474752451      0.3222799738
H       -0.1267085154     -2.8577273410      1.3355248174
C       -1.1149755312     -3.5363534906     -0.4719152633
C       -0.9675655785     -4.0853412415     -1.7450439727
H       -1.8508535217     -4.2877712408     -2.3536895163
C        0.3098916099     -4.3303014723     -2.2399717525
H        0.4332117127     -4.7459101184     -3.2414580558
C        1.4317690968     -3.9913601578     -1.4886727603
H        2.4371355496     -4.1231518738     -1.8923619385
C        1.2645449238     -3.4424493122     -0.2176007050
C       -3.4405877303     -4.1764899412      0.0996647618
H       -3.3264393804     -5.1992350551     -0.2471173492
```

```
C       -4.4838984221     -3.5393055427      0.6839785601
H       -5.4761031317     -3.9036818233      0.9327872957
C       -2.8058964391     -2.0595038774      0.5482857444
C       -4.8851184858     -1.3021674865      1.7570198773
H       -4.2124459080     -0.4561270115      1.9379508937
C       -5.2528981644     -1.9185291270      3.0977087235
H       -5.9594230602     -2.7561648254      2.9923452232
H       -5.7391272763     -1.1561720880      3.7226070136
H       -4.3597658370     -2.2763286345      3.6302143876
C       -6.0815421842     -0.8107629632      0.9626267465
H       -5.7623395817     -0.3140548159      0.0364891853
H       -6.6396288196     -0.0781221307      1.5623070227
H       -6.7690553517     -1.6342564642      0.7126505242
C       -3.0562629295      0.6663586947      0.0643516835
C       -3.4572335180      1.7238253319      0.9211527473
C       -4.3889053610      2.6504086704      0.4569741110
H       -4.6992697887      3.4617798170      1.1179055537
C       -4.9416927683      2.5729626228     -0.8238001486
C       -4.5224142782      1.5353225464     -1.6509913812
H       -4.9395324288      1.4718451315     -2.6600713457
C       -3.5842589878      0.5808670316     -1.2434602971
C       -2.8803667591      1.8785971132      2.3182160851
H       -2.6364608186      0.8626286903      2.6774696233
C       -3.8440882039      2.4983204260      3.3239493264
H       -3.4183778771      2.4418386385      4.3369807947
H       -4.8165291820      1.9811449568      3.3342812098
H       -4.0333083208      3.5630548518      3.1171928431
C       -1.5600569930      2.6463967451      2.2627355273
H       -0.8444560941      2.1607990262      1.5838883298
H       -1.1038430451      2.7129303543      3.2629694109
H       -1.7199045839      3.6691994811      1.8870526083
C       -5.9680826748      3.5791466968     -1.2939663987
H       -6.2202240785      3.3147746055     -2.3350349084
C       -5.4041775772      4.9993352319     -1.2994053191
H       -4.4905951437      5.0644431477     -1.9085899831
H       -6.1406651428      5.7078145909     -1.7082905571
H       -5.1526359218      5.3349126728     -0.2808178002
C       -7.2512441639      3.4866972794     -0.4679591106
H       -7.6692465325      2.4687036953     -0.4900019523
H       -7.0674532993      3.7521984920      0.5854350428
H       -8.0156601679      4.1775609906     -0.8553576526
C       -3.1882631202     -0.4804854697     -2.2540964236
H       -2.3895633441     -1.0892462474     -1.8024173444
C       -2.5971231661      0.1458009322     -3.5173163882
H       -2.1964806199     -0.6356885468     -4.1816240079
H       -1.7815856909      0.8396883715     -3.2664490209
H       -3.3552315048      0.7075522193     -4.0846050978
C       -4.3434635330     -1.4249544956     -2.5850002719
H       -4.7330632780     -1.9283977475     -1.6875072069
H       -4.0186059946     -2.2002269511     -3.2971063998
H       -5.1830919117     -0.8848547099     -3.0499009706
C        3.4137413005     -3.9448672832      0.9010167979
H        3.3783531727     -5.0006621173      0.6491340719
C        4.3229559106     -3.2169823293      1.5950301506
H        5.2553297442     -3.5203354500      2.0618347442
C        2.6826404996     -1.8142416081      0.9890096594
C        4.5078397325     -0.8499582300      2.4240353286
H        3.8000553578     -0.0131576451      2.3724595641
C        4.6566010291     -1.2678517098      3.8779584345
H        3.6915428986     -1.5780038581      4.3041064067
```

```
H         5.0279117219     -0.4138579866      4.4620226384
H         5.3788147486     -2.0891753091      4.0035420129
C         5.8120949395     -0.4272463118      1.7723769968
H         6.5492208516     -1.2458347417      1.7734501523
H         6.2431070769      0.4131560854      2.3342067196
H         5.6466684820     -0.0927729282      0.7392385039
C         2.9752796234      0.8073593219      0.1189464309
C         3.7157886923      0.4649678698     -1.0399464900
C         4.7570160716      1.2997147660     -1.4469419039
H         5.3298487644      1.0265604815     -2.3372768258
C         5.0828753742      2.4749545694     -0.7677010726
C         4.2965149946      2.8262909551      0.3260007273
H         4.5110135998      3.7656530289      0.8434067516
C         3.2391086677      2.0309957571      0.7781379553
C         3.4066866751     -0.7354083193     -1.9158302174
H         2.5540306838     -1.2655222030     -1.4670750540
C         4.5715076460     -1.7195180623     -1.9992605395
H         5.4613986200     -1.2548131115     -2.4513176840
H         4.3082267551     -2.5858310695     -2.6271902848
H         4.8660615022     -2.0921767282     -1.0061295528
C         2.9447985822     -0.2819592746     -3.3013776907
H         2.1151589472      0.4361726433     -3.2201035276
H         2.5987186354     -1.1423973671     -3.8954404545
H         3.7578222805      0.2077216873     -3.8595264515
C         6.2384961442      3.3431099653     -1.2123116884
H         6.2611347156      4.2141621778     -0.5357427893
C         6.0394108941      3.8654169929     -2.6344715039
H         6.8550512519      4.5493475566     -2.9146097951
H         5.0879479822      4.4088149179     -2.7312715464
H         6.0319188031      3.0428054980     -3.3671953442
C         7.5697375102      2.6060976147     -1.0650256849
H         7.6141172214      1.7270917417     -1.7279995240
H         7.7217863150      2.2562130795     -0.0325815671
H         8.4119973337      3.2635868178     -1.3295885763
C         2.4055367275      2.5536677317      1.9351775500
H         1.6227821032      1.8060578878      2.1438942169
C         1.7021738612      3.8534761198      1.5437365117
H         2.4261343523      4.6598284651      1.3475305941
H         1.0401442276      4.1911335764      2.3554808552
H         1.0952450320      3.7116592950      0.6385916924
C         3.2217766113      2.7303666375      3.2147955256
H         3.6848224645      1.7874720571      3.5441854086
H         2.5792504440      3.0872465778      4.0341717369
H         4.0287005473      3.4682533582      3.0833652324
```

7 References

1 M. Koy, I. Elser, J. Meisner, W. Frey, K. Wurst, J. Kästner and M. R. Buchmeiser, *Chem. Eur. J.*, 2017, **23**, 15484.

2 C. Barnett, M. L. Cole and J. B. Harper, *Eur. J. Inorg. Chem.*, 2021, **2021**, 4954

3 T. B. Rauchfuss, in *Inorganic Syntheses*; Wiley: Hoboken, NJ, 2010; p 78. https://doi.org/10.1002/9780470651568.ch4

4 S. J. Ryan, S. D. Schimler, D. C. Bland and M. Sanford, *Org. Lett.*, 2015, **17**, 1866.

5 G. M. Sheldrick, *Acta Cryst. A*, 2015, **71**, 3–8.

6 G. M. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3–8.

7 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.

8 L. J. Farrugia*, J. Appl. Cryst.*, 2012, **45**, 849.

9 SADABS within APEX2; Bruker AXS Inc.: Madison, WI, 2014.

10 X-AREA and LANA; Stoe & Cie: Darmstadt, Germany, 2020.

11 A. L. Spek, *Acta Cryst.*, 2015, **C71**, 9–18

12 S. M. Walter, F. Kniep, E. Herdtweck and S. M. Huber, *Angew. Chem. Int. Ed.*, 2011, **50**, 7187.

13 J. Cho, T. K. Hollis, E. Valente, J. M. Trate, *J. Organomet. Chem.*, 2011, **696**, 373.

14 M. Raynal, C. S. J. Cazin, C. Vallee, H. Olivier-Bourbiqou, P. Braunstein, *Chem. Commun.* 2008, 3983.

15 A. K. Adhikari, T. Grell, P. Lönnecke and E. Hey-Hawkins, *Eur. J. Inorg. Chem.*, 2016, **2016**, 620.

16 K. Pal, O. B. Hemming, B. M. Day, T. Pugh, D. J. Evans and R. A. Layfield, *Angew. Chem. Int. Ed.*, 2016, **55**, 1690

17 J.-E. Siewert, A. Schumann and C. Hering-Junghans, *Dalton Trans.*, 2021, **50**, 15111

18 L. Werner, G. Horrer, M. Philipp, K. Lubitz, M. W. Kuntze-Fechner and U. Radius, *Z. anorg. allg. Chem.*, 2021, **647**, 881

19 *Gaussian 09, Revision E.01*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2013**.

20 Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji,

X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

21 a) E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis and F. Weinhold, *NBO 6.0*, Theoretical Chemistry Institute, University of Wisconsin, Madison, 2013; b) J. E. Carpenter and F. Weinhold, *J. Mol. Struct.: THEOCHEM*, 1988, **169**, 41.

22 a) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865; b) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396; c) C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158.

23 a) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104; b) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456.

24 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.

25 a) F. London, *J. Phys. Radium*, 1937, **8**, 397; b) R. McWeeny, *Phys. Rev.*, 1962, **126**, 1028; c) R. Ditchfield, *Mol. Phys.*, 1974, **27**, 789; d) K. Wolinski, J. F. Hinton and P. Pulay, *J. Am. Chem. Soc.*, 1990, **112**, 8251; e) J. R. Cheeseman, G. W. Trucks, T. A. Keith and M. J. Frisch, *J. Chem. Phys.*, 1996, **104**, 5497.

26 C. J. Jameson, A. De Dios and A. Keith Jameson, *Chem. Phys. Lett.*, 1990, **167**, 575.

27 C. van Wüllen, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2137–2144.

28 T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580.

29 T. Lu, and Q. Chen, *Chem. Methods*, 2021, **1**, 231.

30 E. R. Johnson, E. R.; Keinan, S.; Mori-Sánchez, P.; Contreras-García, J.; Cohen, A. J.; Yang, W. Revealing Noncovalent Interactions. *J. Am. Chem. Soc.*, 2010, **132**, 6498−6506.

31 S. Dutta, B. Maity, D. Thirumalai and D. Koley, *Inorg. Chem.*, 2018, **57**, 3993.