SUPPORTING INFORMATION

On 1,3-Phosphaazaallenes and their Diverse Reactivity

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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 or Drybox techniques. All glassware was heated three times *in vacuo* using a heat gun and cooled under argon atmosphere. Solvents were transferred using syringes, which were purged three times 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
Benzene	local trade	dried over Na/benzophenone freshly distilled prior to use, stored over molecular sieves.
n-hexane	Geyer, CHROMASOLV®, for HPLC, ≥97,0% (GC)	purified with the Grubbs-type column system "Pure Solv MD-5" dried over Na/benzophenone/tetraglyme freshly distilled prior to use
n-pentane	local trade	dried over Na/benzophenone/tetraglyme freshly distilled prior to use
Toluene	Fisher Chemical, for HPLC	purified with the Grubbs-type column system "Pure Solv MD-5"
THF	Sigma Aldrich, inhibitor-free, for HPLC, ≥99.9%	purified with the Grubbs-type column system "Pure Solv MD-5" dried over Na/benzophenone freshly distilled prior to use
C_6D_6	euriso-top	dried over Na/benzophenone freshly distilled prior to use
C_7D_8 (toluene-d_8)	euriso-top	dried over Na/benzophenone freshly distilled prior to use
CN*t*Bu	Sigma Aldrich, 98%	freshly distilled and degassed (freeze-pump-thaw) stored over molecular sieves at 5 °C
CNXyl	Sigma Aldrich, 99%	used as received, stored inside a Glovebox
$K[N(SiMe_3)_2]$	Sigma Aldrich, 95%	used as received, stored inside a Glovebox
Kryptofix® 222	Sigma Aldrich, for synthesis	used as received, stored inside a Glovebox

Table S1 continued.

Substance	Origin	Purification
^{Dip}TerPPMe$_3$ (**1c**)[1]	synthesized	
^{Mes}TerPPMe$_3$ (**1b**)[1]	synthesized	
Mes*PPMe$_3$ (**1a**)[1]	synthesized	
HB(C_6F_5)$_2$[2]	synthesized	
B(C_6F_5)$_3$[3]	synthesized	BCl_3 solution (1.0 M in hexanes) was used instead of freshly condensed BCl_3.

NMR spectra were recorded on Bruker spectrometers (AVANCE 300, AVANCE 400 or Fourier 300) and were referenced internally to the deuterated solvent (^{13}C: C_6D_6 δ_{ref} = 128.06 ppm; C_7D_8 δ_{ref} = 20.43 ppm) or to protic impurities in the deuterated solvent (^{1}H: C_6HD_5 δ_{ref} = 7.16 ppm; C_7D_8 δ_{ref} = 2.08 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: weak (w, 0–33%), medium (m, 33–66%), strong (s, 66–100%).

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

Mass spectra were recorded on a Thermo Electron MAT 95-XP sector field mass spectrometer using crystalline samples.

2 Structure elucidation

X-ray Structure Determination: X-ray quality crystals of all compounds were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature or in Fomblin© Y perfluoroether (Sigma Aldrich) at −30 °C under a constant stream of nitrogen. The samples were cooled to 123(2) K during measurement. The data were collected on a Bruker Kappa Apex II diffractometer using Mo K_α radiation (λ = 0.71073 Å) or Cu K_α radiation (λ = 1.54178 Å), or on a STOE-IPDS II diffractometer using Mo Kα radiation (λ = 0.71073 Å). The structures were solved by iterative methods (SHELXT)[4] and refined by full matrix least squares procedures (SHELXL).[5] Semi-empirical absorption corrections were applied (SADABS).[6] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

In **4a** the position of H1 was fixed using the AFIX1 command.

In **6c-crypt** one of the iso-propyl groups (C13-C15) was found to be disordered and was split in two parts. The occupancy of each part was allowed to refine freely. The unit cell also contains two severely disordered benzene molecules. These have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.[7]

Crystals of **7** were of poor quality and the data did not allow a detailed discussion of structural parameters. The crystal data has been added to Table S4.

In **8** one of the para-*t*Bu groups (C12-C14) was found to be disordered and was split in two parts. The occupancy of each part was allowed to refine freely. The position of H1 was fixed using the AFIX1 command.

In **9** One of the C_6F_5 groups (C24-C29) was found to be disordered and was split in two parts and the occupancy of each part was allowed to refine freely. SIMU and DELU

comments were applied to restrain the U_{ij} and the ADPs of the atoms in the minor orientation.

Table S2: Crystallographic details of **3a**, **3e** and **3f**.

Compound	**3a**	**3e**	**3f**
Chem. Formula	$C_{23}H_{38}NP$	$C_{33}H_{34}NP$	$C_{39}H_{46}NP$
Formula weight [g/mol]	359.51	475.88	559.74
Colour	yellow	orange	red
Crystal system	monoclinic	Monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1$/n
a [Å]	11.8225(5)	14.6249(13)	11.2216(15)
b [Å]	9.7226(4)	7.7621(7)	21.266(3)
c [Å]	20.8398(8)	24.362(2)	14.998(2)
α [°]	90	90	90
β [°]	101.3433(17)	104.5246(21)	111.581(2)
γ [°]	90	90	90
V [Å^3]	2348.65(17)	2677.2(4)	3328.3(8)
Z	4	4	4
$\rho_{calcd.}$ [g/cm^3]	1.017	1.180	1.117
μ [mm^{-1}]	1.047	0.124	0.109
T [K]	150(2)	150(2)	150(2)
Measured reflections	35629	45239	84027
Independent reflections	4158	7124	8859
Reflections with $I > 2\sigma(I)$	3731	5345	7167
R_{int}	0.0436	0.0460	0.0428
$F(000)$	792	1016	1208
$R_1(R[F^2>2\sigma(F^2)])$	0.0359	0.0460	0.0398
w$R_2(F^2)$	0.1018	0.1261	0.1065
GooF	1.039	1.020	1.032
No. of Parameters	238	324	380
CCDC #	2086496	2086497	2086498

Table S3: Crystallographic details of **4a-c**.

Compound	**4a**	**4b**	**4c**
Chem. Formula	$C_{19}H_{30}NP$	$C_{25}H_{26}NP$	$C_{31}H_{38}NP$
Formula weight [g/mol]	303.41	371.44	455.59
Colour	colourless	colourless	colourless
Crystal system	orthorhombic	monoclinic	Trigonal
Space group	$P2_12_12_1$	$P2_1/n$	R-3
a [Å]	6.0042(3)	11.3511(7)	26.746(4)
b [Å]	15.3676(6)	12.5307(8)	26.746(4)
c [Å]	19.9448(8)	15.0165(9)	20.118(4)
α [°]	90	90	90
β [°]	90	95.3326(10)	90
γ [°]	90	90	120
V [Å^3]	1840.31(14)	2126.7(2)	12463(4)
Z	4	4	18
$\rho_{calcd.}$ [g/cm^3]	1.095	1.160	1.093
μ [mm^{-1}]	1.256	0.138	0.117
T [K]	150(2)	150(2)	150(2)
Measured reflections	13962	26951	68947
Independent reflections	3113	6205	6358
Reflections with $I > 2\sigma(I)$	3073	5058	4170
R_{int}	0.0266	0.0246	0.0390
F(000)	664	792	4428
$R_1(R[F^2>2\sigma(F^2)])$	0.0359	0.0459	0.0577
w$R_2(F^2)$	0.0962	0.1331	0.1792
GooF	1.109	1.030	0.928
No. of Parameters	200	258	314
CCDC #	2086499	2086500	2086501

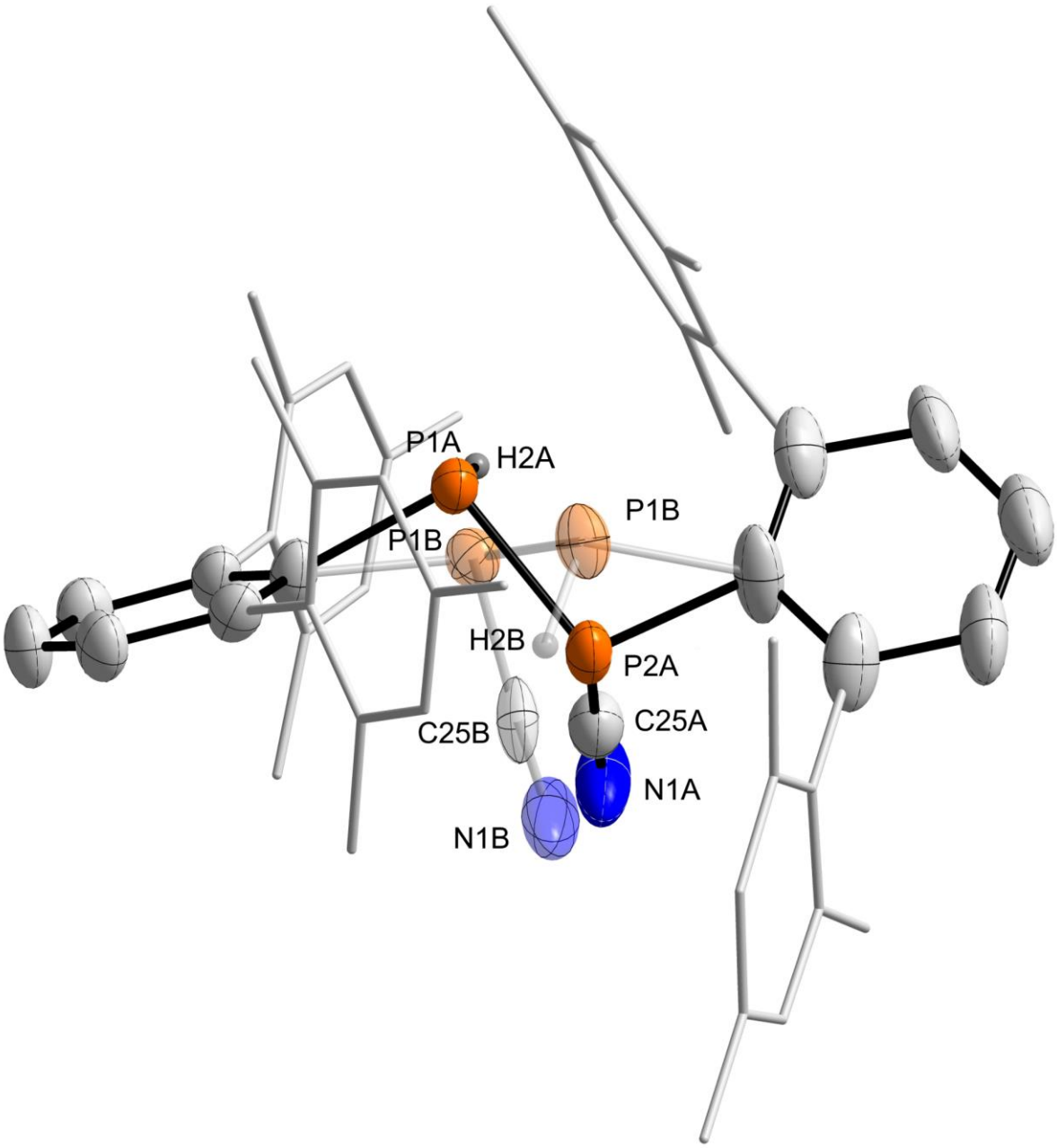
Table S4: Crystallographic details of **5a**, **7** and **6c-crypt**.

Compound	**5a**	**7**	**6c-crypt**
Chem. Formula	$C_{37}H_{30}BF_{15}NP$	$C_{49}H_{52}NP$	$[C_{31}H_{37}NP][KC_{18}H_{36}O_6N_2]\cdot C_6D_6$
Formula weight [g/mol]	815.40	716.85	948.28
Colour	colourless	colourless	Yellow
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$
a [Å]	10.3933(15)	12.792(4)	10.9300(2)
b [Å]	17.413(3)	19.992(6)	22.7400(4)
c [Å]	20.363(3)	16.690(6)	21.6453(4)
α [°]	90	90	90
β [°]	90	106.917(6)	90.0940(10)
γ [°]	90	90	90
V [Å^3]	3685.2(9)	4084(2)	5379.89(17)
Z	4	4	4
$\rho_{calcd.}$ [g/cm^3]	1.470	1.166	1.171
μ [mm^{-1}]	1.256	0.141	1.533
T [K]	150(2)	150(2)	150(2)
Measured reflections	47418	31248	52338
Independent reflections	10755	8919	9370
Reflections with $I > 2\sigma(I)$	8295	3807	8427
R_{int}	0.0418	0.1530	0.0365
$F(000)$	1656	1532	2048
$R_1(R[F^2>2\sigma(F^2)])$	0.0419	0.1125	0.0327
$wR_2(F^2)$	0.0978	0.2952	0.0884
GooF	1.012	1.033	1.034
No. of Parameters	545	526	557
CCDC #	2086502	-	2086503

Table S5: Crystallographic details of **8**, **9** and **10**.

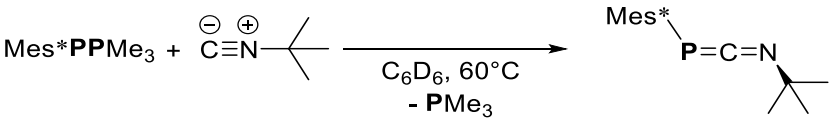
Compound	**8**	**9**	**10**
Chem. Formula	$C_{55}H_{59}BF_{15}NP_2$	$C_{35}H_{39}BF_{10}NP$	$C_{51}H_{47}BF_{10}NP \cdot C_6D_6$
Formula weight [g/mol]	1091.78	705.45	989.82
Colour	colourless	yellow	yellow
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$P2c$
a [Å]	10.3569(3)	18.1837(4)	10.5963(8)
b [Å]	25.3573(8)	9.1923(2)	10.7434(8)
c [Å]	20.2715(6)	22.6189(5)	21.9612(16)
α [°]	90	90	90
β [°]	94.1057(16)	111.1270(10)	98.703(2)
γ [°]	90	90	90
V [Å^3]	5310.1(3)	3526.62(14)	2471.3(3)
Z	4	4	2
$\rho_{calcd.}$ [g/cm^3]	1.366	1.329	1.330
μ [mm^{-1}]	1.539	0.117	0.133
T [K]	150(2)	150(2)	150(2)
Measured reflections	72366	37110	60346
Independent reflections	9256	6227	15075
Reflections with $I > 2\sigma(I)$	7779	5902	11354
R_{int}	0.0324	0.0272	0.0503
$F(000)$	2264	1464	1024
$R_1(R[F^2>2\sigma(F^2)])$	0.0461	0.0335	0.0438
$wR_2(F^2)$	0.1324	0.0902	0.0947
GooF	1.026	1.015	1.017
No. of Parameters	711	579	663
CCDC #	2086504	2086505	2086506

Figure S1: Molecular structure of ^{Mes}**TerP(H)P(CN)**^{Mes}**Ter** (**7**). ORTEPs drawn at 50% probability, all H-atoms (except H1) omitted and Mes-groups rendered as wireframe for clarity. Due to the poor data quality the structural parameters are not discussed.



3 Syntheses of compounds

3.1 Synthesis of Mes*PCN*t*Bu (3a)



A) Mes*PPMe$_3$ (**1a**) (0.030 g, 0.085 mmol) was dissolved in 0.3 mL of C_6D_6. An excess of *tert*-butyl isocyanide (**2a**) (3.0 eq., 0.021 g, 0.026 mmol) in 0.3 mL of C_6D_6 was added and the reaction mixture was allowed to stand for 16 h at room temperature. Regular control by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy showed that the reaction is very slow at room temperature. Subsequently, the reaction mixture was heated to 60 °C overnight, which revealed complete consumption of Mes*PPMe$_3$ (**1a**) and of one equivalent of *tert*-butyl isocyanide (**2a**) to give Mes*P=C=N^{t}Bu (**3a**) accompanied by the release of PMe$_3$ (Figures S2 and S3).

B) Mes*PPMe$_3$ (**1a**) (1.000 g, 2.973 mmol) was suspended in 12 mL of *n*-hexane. *tert*-butyl isocyanide (**2a**) (0.33 mL, 2.973 mmol) was added and the reaction mixture was heated to 60 °C for 16 h. Removal of all volatile components under vacuum yielded Mes*P=C=N^{t}Bu (**3a**) as a yellow solid.

Crystals suitable for single crystal X-ray diffraction (SC-XRD) were obtained by slow evaporation of a saturated solution of **3a** in *n*-pentane.

Yield: 0.939 g (2.612 mmol; 88%).

CHN calculated: C 76.84, H 10.65, N 3.90; found: C 76.63, H 10.51, N 3.20. **^{1}H NMR** (300 MHz, C_6D_6, 298 K): δ = 0.94 (s, 9H, $NC_q(CH_3)_3$), 1.28 (s, 9H, *p*-$C_q(CH_3)_3P$), 1.831-1.833 (m, 18H, *o*-$C_q(CH_3)_3P$), 7.58-7.59 (m, 2H, CH_{Aryl}) ppm. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, 298 K): δ = 30.5 ($NC_q(\underline{C}H_3)_3$), 31.5 (*p*-$C_q(\underline{C}H_3)_3P$), 33.4 (*o*-$C_q(\underline{C}H_3)_3P$), 33.5 (*o*-$C_q(\underline{C}H_3)_3P$),

35.0 (*p*-$\underline{C}_q(CH_3)_3P$), 38.8 (*o*-$\underline{C}_q(CH_3)_3P$), 61.2 (d, $^3J_{P,C}$ = 12.1 Hz, $N\underline{C}_q(CH_3)_3$), 122.2 (CH_{Aryl}), 124.0 (d, $^1J_{P,C}$ = 51.7 Hz, $C_{q,Aryl}P$), 149.8 (*p*-$C_{q,Aryl}P$), 157.3 (d, $^2J_{P,C}$ = 4.0 Hz, *o*-$C_{q,Aryl}P$), 192.2 (d, $^1J_{P,C}$ = 76.8 Hz, P=C=N) ppm. **$^{31}P\{^1H\}$ NMR** (122 MHz, C_6D_6, 298 K): δ = −103.9 ppm. **IR** (ATR, 32 scans, cm^{-1}): ν = 2953 (s), 2905 (m), 2866 (m), 1881 (s), 1798 (w), 1693 (w), 1590 (m), 1530 (w), 1476 (m), 1460 (m), 1405 (w), 1390 (m), 1361 (s), 1281 (w), 1236 (m), 1212 (m), 1183 (s), 1126 (m), 1034 (w), 925 (w), 903 (m), 877 (m), 754 (m), 715 (w), 661 (m), 596 (m), 525 (w), 504 (s), 483 (w), 466 (m). **MS** (CI): expected: m/z = 359; found: m/z = 359 $[M]^+$, 304 $[M - iso\text{-butene} + H]^+$.

Figure S2: Monitoring of the reaction of Mes*$PPMe_3$ (**1a**) with *tert*-butyl isocyanide (**2a**) via ^1H NMR spectroscopy (300 MHz, C_6D_6, rt); 0.80 ppm: PMe_3, 0.88 ppm: *tert*-butyl isocyanide (**2a**). (#: PMe_3, °: *tert*-butyl isocyanide (**2a**))

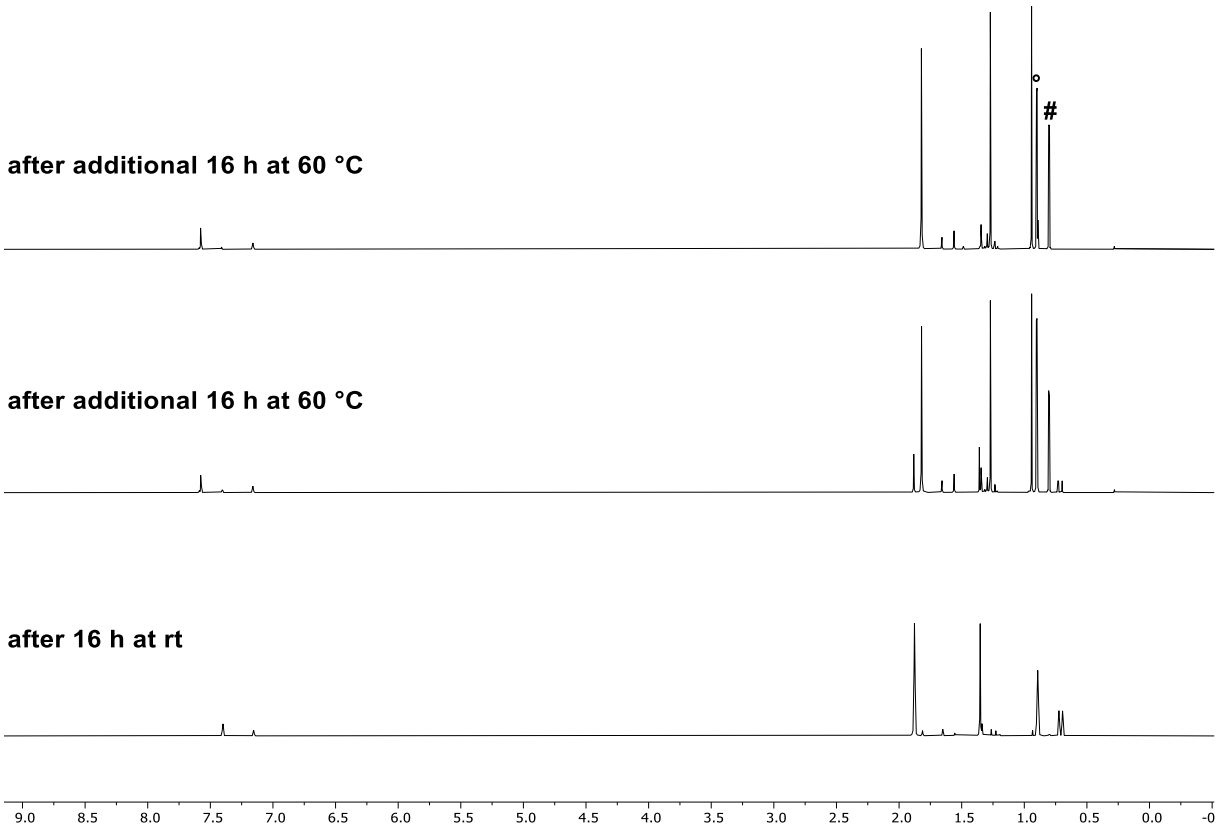


Figure S3: Monitoring of the reaction of Mes*PPMe$_3$ (**1a**) with *tert*-butyl isocyanide (**2a**) via $^{31}P\{^1H\}$ NMR spectroscopy (122 MHz, C_6D_6, rt); −134.3 and 4.2 ppm: Mes*PPMe$_3$ (**1a**), −62.6 ppm: PMe$_3$, −103.8 ppm: Mes*P=C=N*t*Bu (**3a**).

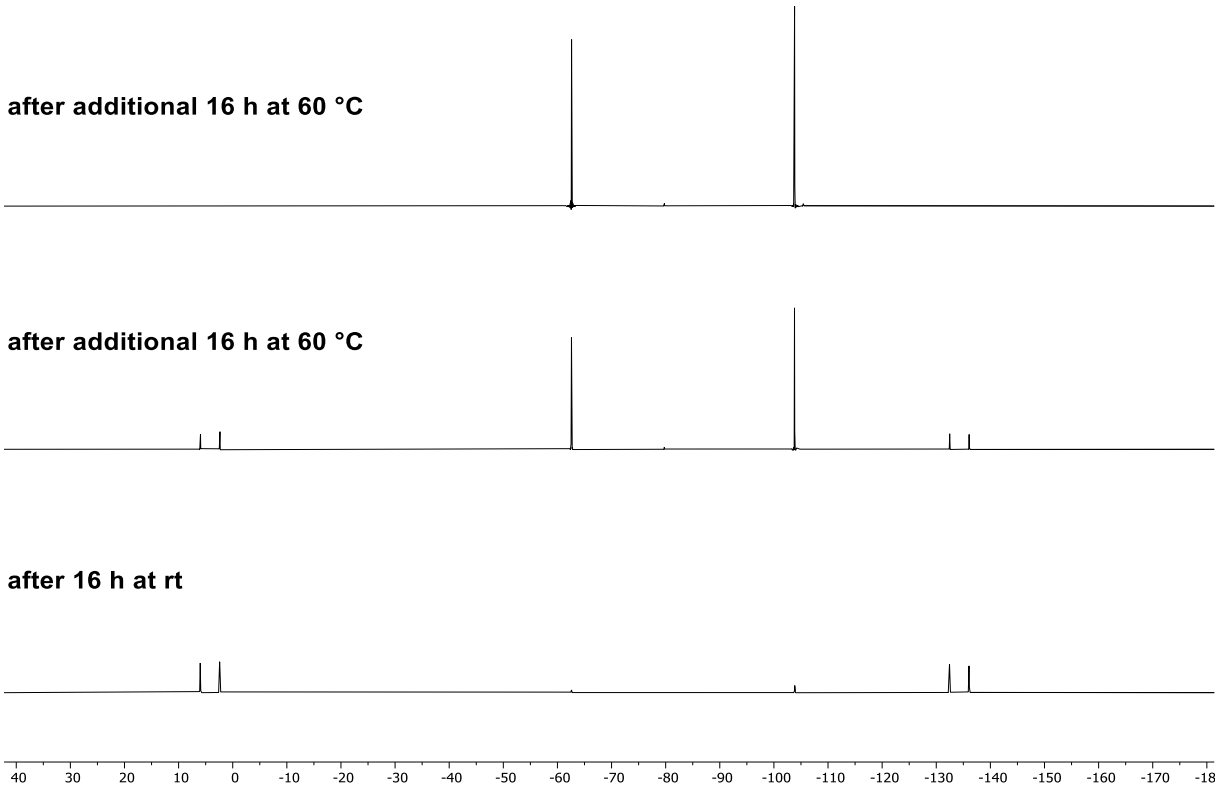


Figure S4: ^{1}H NMR spectrum of Mes*P=C=N*t*Bu (**3a**) (300 MHz, C_6D_6, rt).

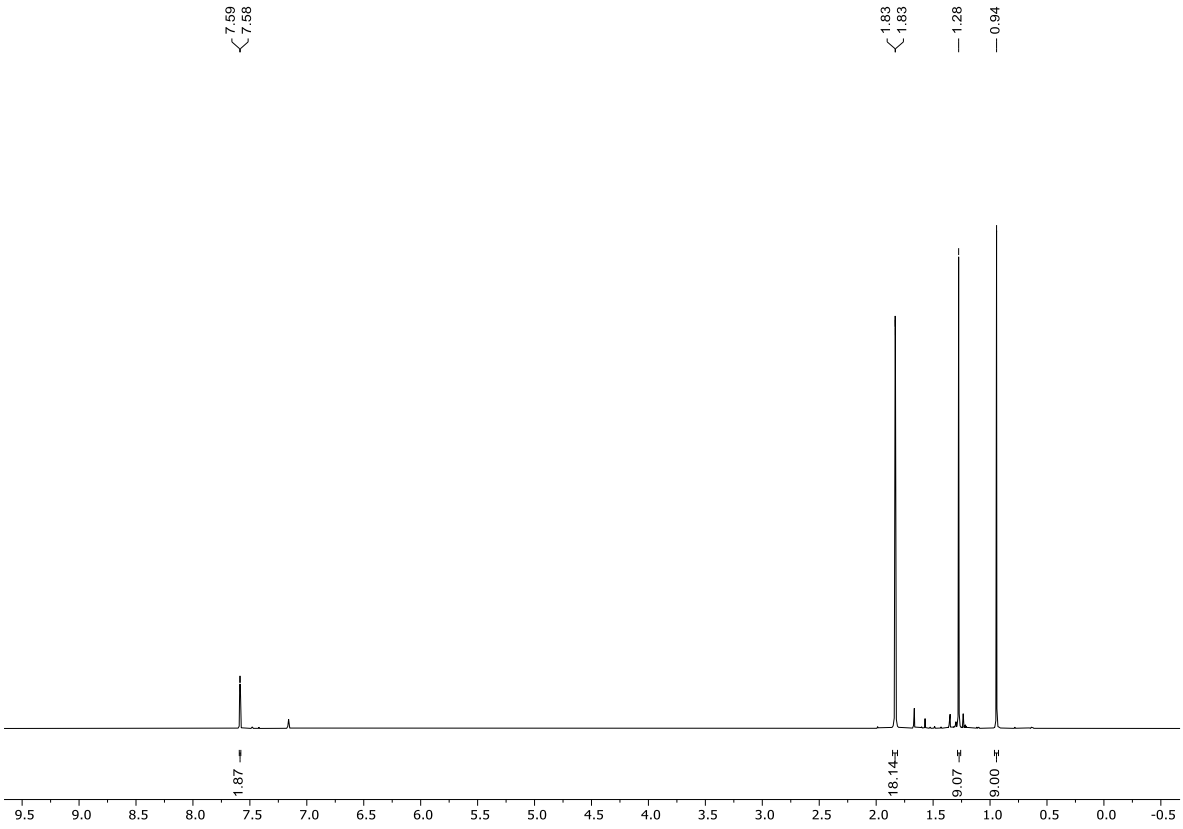


Figure S5: ^{13}C NMR spectrum of Mes*P=C=N*t*Bu (**3a**) (75 MHz, C_6D_6, rt).

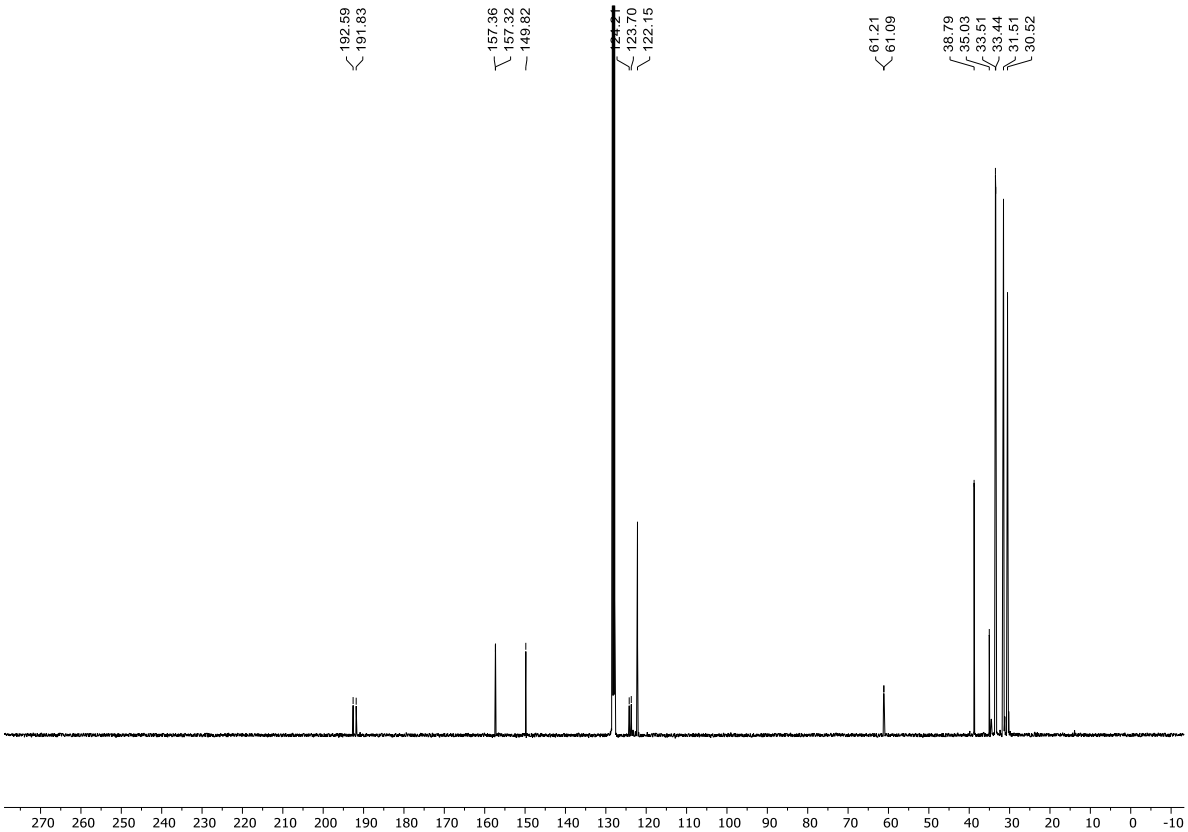
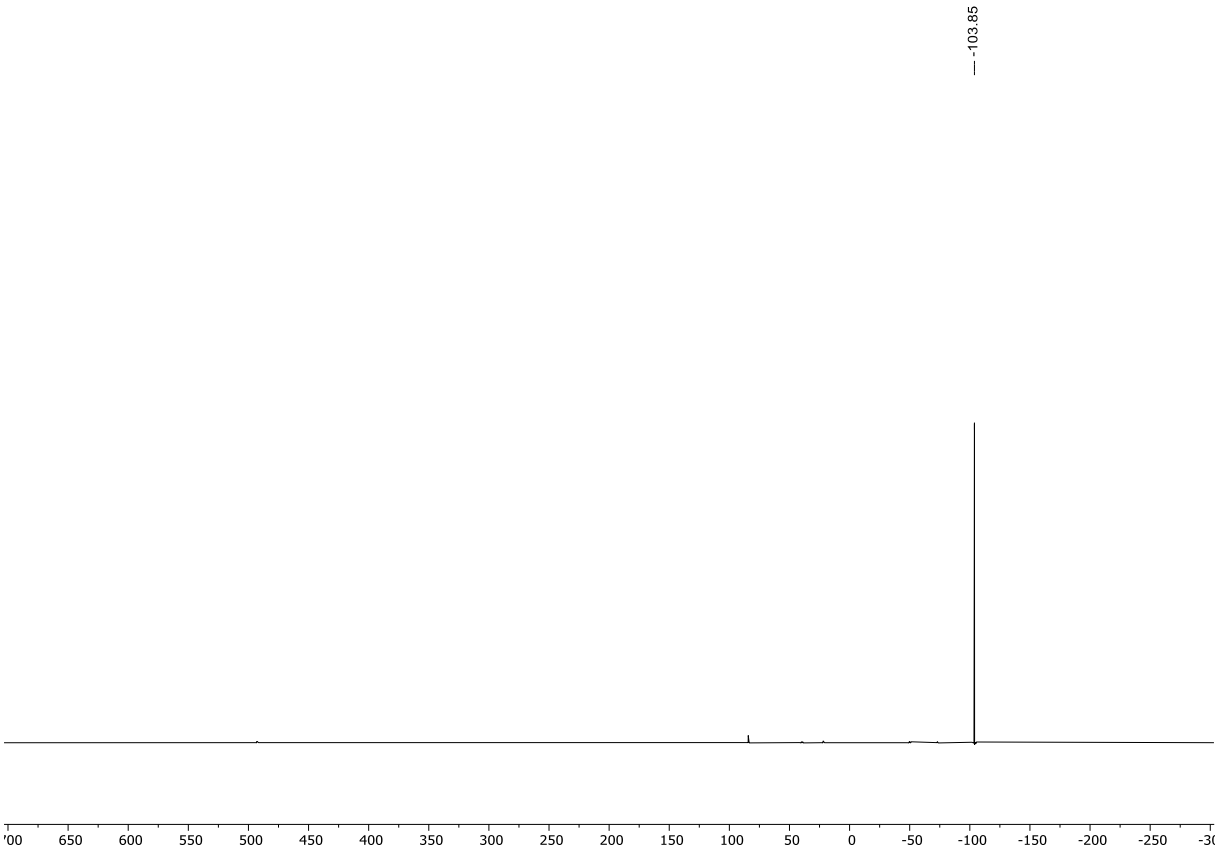
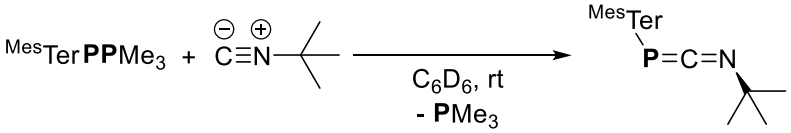


Figure S6: $^{31}P\{^{1}H\}$ NMR spectrum of Mes*P=C=N*t*Bu (**3a**) (122 MHz, C_6D_6, rt).



3.2 Synthesis of ^{Mes}TerPCN*t*Bu (3b)



^{Mes}TerPPMe$_3$ (**1b**) (0.040 g, 0.095 mmol) was dissolved in 0.6 mL of C_6D_6. An excess of *tert*-butyl isocyanide (**2a**) (3 drops with a 1 mL syringe) was added and the reaction mixture was allowed to stand for 5 days at room temperature. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy revealed that mainly ^{Mes}TerP=C=N*t*Bu (**3b**) and PMe$_3$ were formed during the reaction with only approximately 5% of (^{Mes}TerP)$_2$ being formed (determined by integration of the $^{31}P\{^{1}H\}$ NMR signals ($\delta^{31}P\{^{1}H\}_{(TerPPTer)}$ = 492.6 ppm)) (Figures S7 and

S8). All volatile components were removed under vacuum to yield ^{Mes}TerP=C=N*t*Bu (**3b**) as a yellow solid.

Note: When the reaction is performed at higher temperature the amount of (^{Mes}TerP)$_2$ significantly increases.

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.86 (s, 9H, $NC_q(CH_3)_3$), 2.20 (s, 12H, *o*-$CH_3C_6H_3$), 2.23 (s, 6H, *p*-$CH_3C_6H_3$), 6.91-6.92 (m, 4H, CH_{Aryl}), 6.93-6.94 (m, 1H, CH_{Aryl}), 6.96-6.97 (m, 1H, CH_{Aryl}), 7.10-7.13 (m, 1H, CH_{Aryl}) ppm. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, 298 K): δ = 21.1 (d, $J_{P,C}$ = 2.3 Hz, *o*-$\underline{C}H_3C_6H_3$), 21.3 (*p*-$\underline{C}H_3C_6H_3$), 29.5 (d, $J_{P,C}$ = 0.8 Hz, $NC_q(\underline{C}H_3)_3$), 60.5 (d, $^3J_{P,C}$ = 9.9 Hz, $N\underline{C}_q(CH_3)_3$), 128.3 (CH_{Aryl})*, 128.7 (CH_{Aryl}), 128.8 (CH_{Aryl}), 128.9 (CH_{Aryl}), 132.7 (d, $^1J_{P,C}$ = 39.9 Hz, $C_{q,Aryl}P$), 135.9 (*o*-$\underline{C}_{q,Aryl}C_6H_3$), 136.8 (*p*-$\underline{C}_{q,Aryl}C_6H_3$), 140.4 (d, $^3J_{P,C}$ = 4.1 Hz, $C_{q,Aryl}$), 146.9 (d, $^2J_{P,C}$ = 14.0 Hz, *o*-$C_{q,Aryl}P$), 186.6 (d, $^1J_{P,C}$ = 73.0 Hz, P=C=N) ppm. * = overlap with C_6D_6 signal. **^{31}P{^{1}H} NMR** (122 MHz, C_6D_6, 298 K): δ = -125.4 ppm.

Figure S7: Monitoring of the reaction of ^{Mes}TerPPMe$_3$ (**1b**) with *tert*-butyl isocyanide (**2a**) via ^{1}H NMR spectroscopy (300 MHz, C_6D_6, rt); 0.80 ppm: PMe_3, 0.88 ppm: *tert*-butyl isocyanide (**2a**).

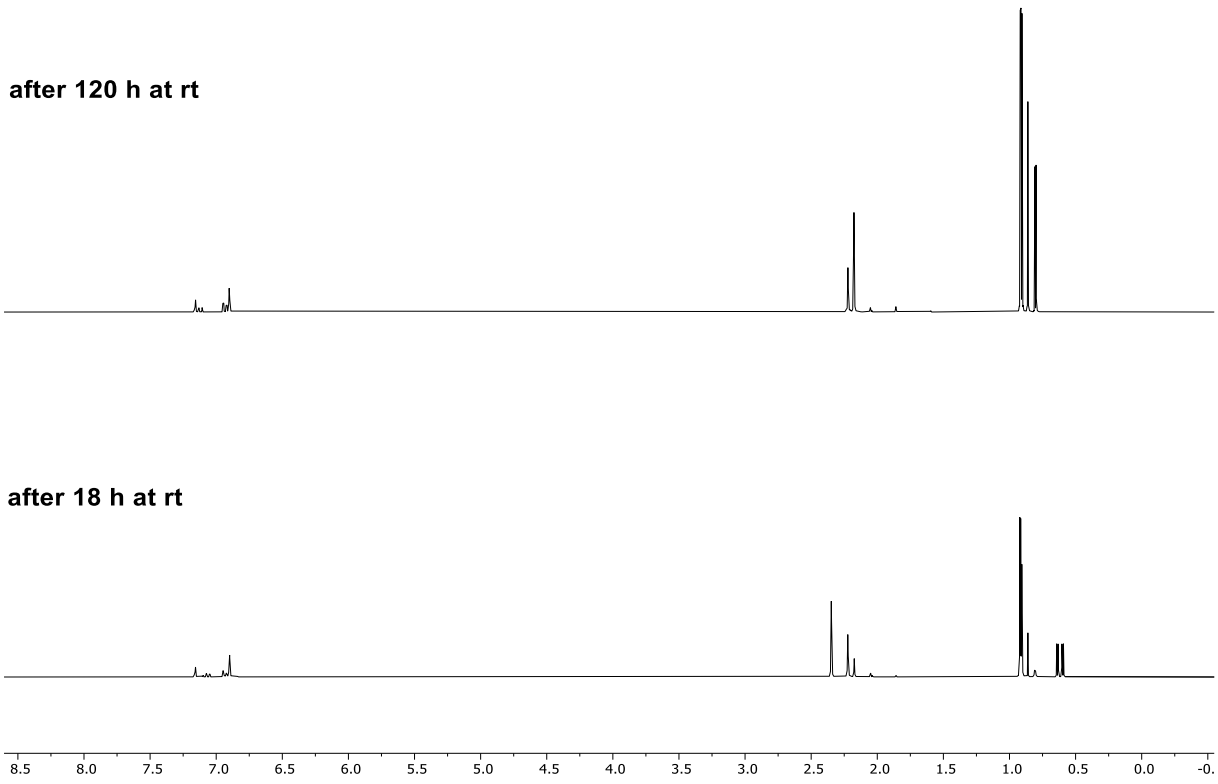


Figure S8: Monitoring of the reaction of ^{Mes}TerPPMe$_3$ (**1b**) with *tert*-butyl isocyanide (**2a**) via $^{31}P\{^1H\}$ NMR spectroscopy (122 MHz, C_6D_6, rt); -114.2 and -2.9 ppm: ^{Mes}TerPPMe$_3$ (**1b**), −62.6 ppm: PMe$_3$, −125.4 ppm: ^{Mes}TerP=C=N*t*Bu (**3b**), 492.6 ppm: (^{Mes}TerP)$_2$.

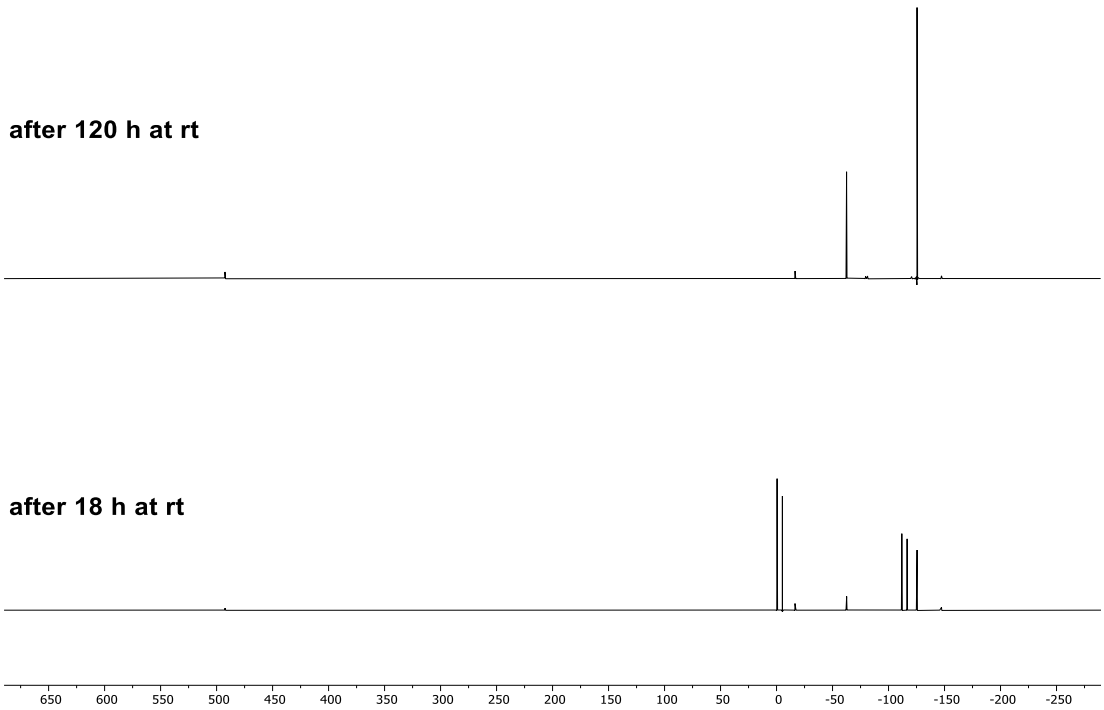


Figure S9: ^{1}H NMR spectrum of ^{Mes}TerP=C=N*t*Bu (**3b**) (300 MHz, C_6D_6, rt).

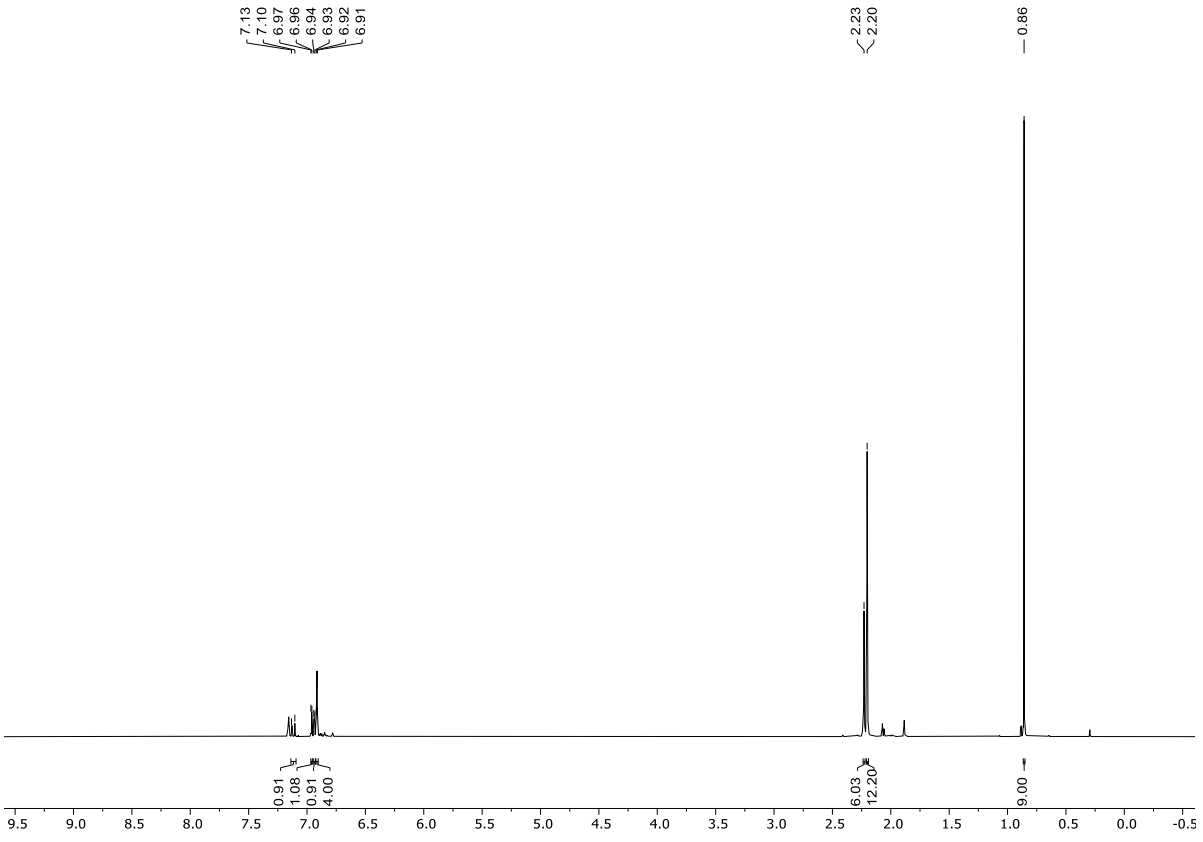


Figure S10: ^{13}C NMR spectrum of ^{Mes}TerP=C=N*t*Bu (**3b**) (75 MHz, C_6D_6, rt).

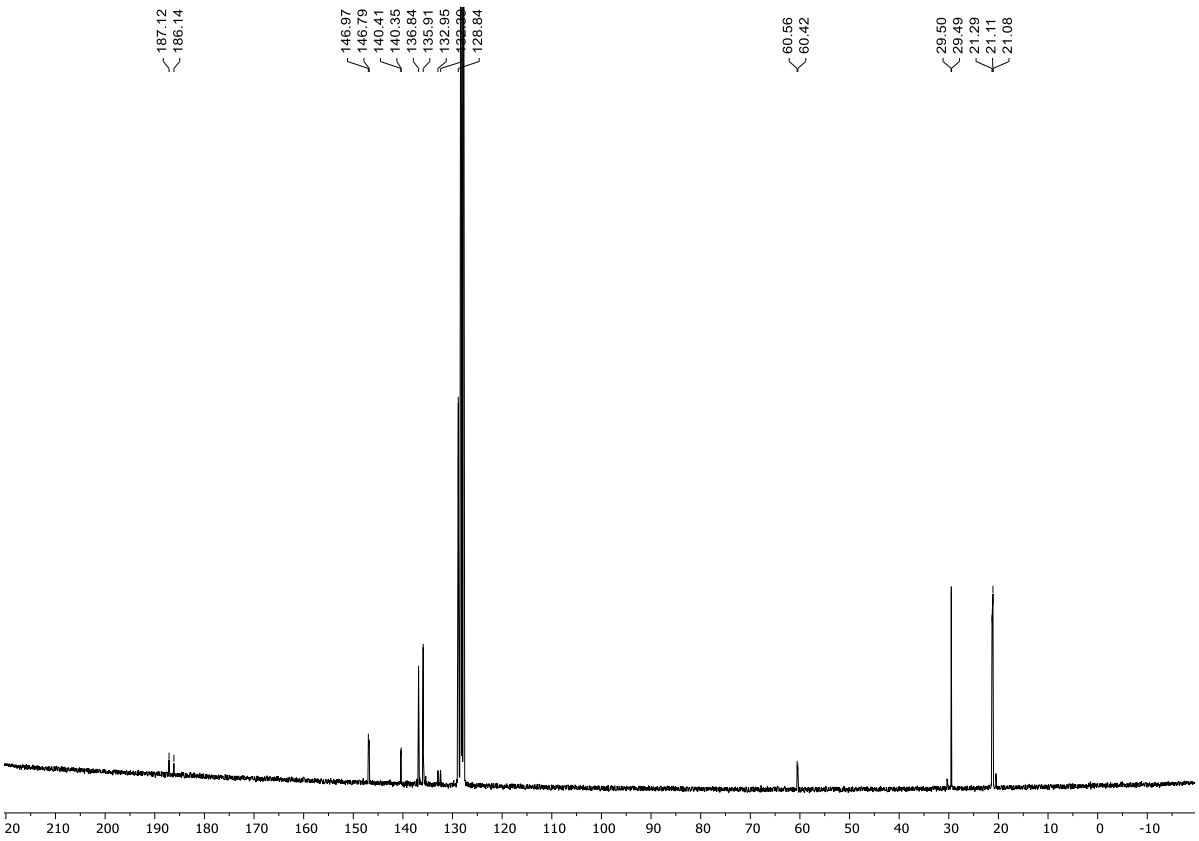
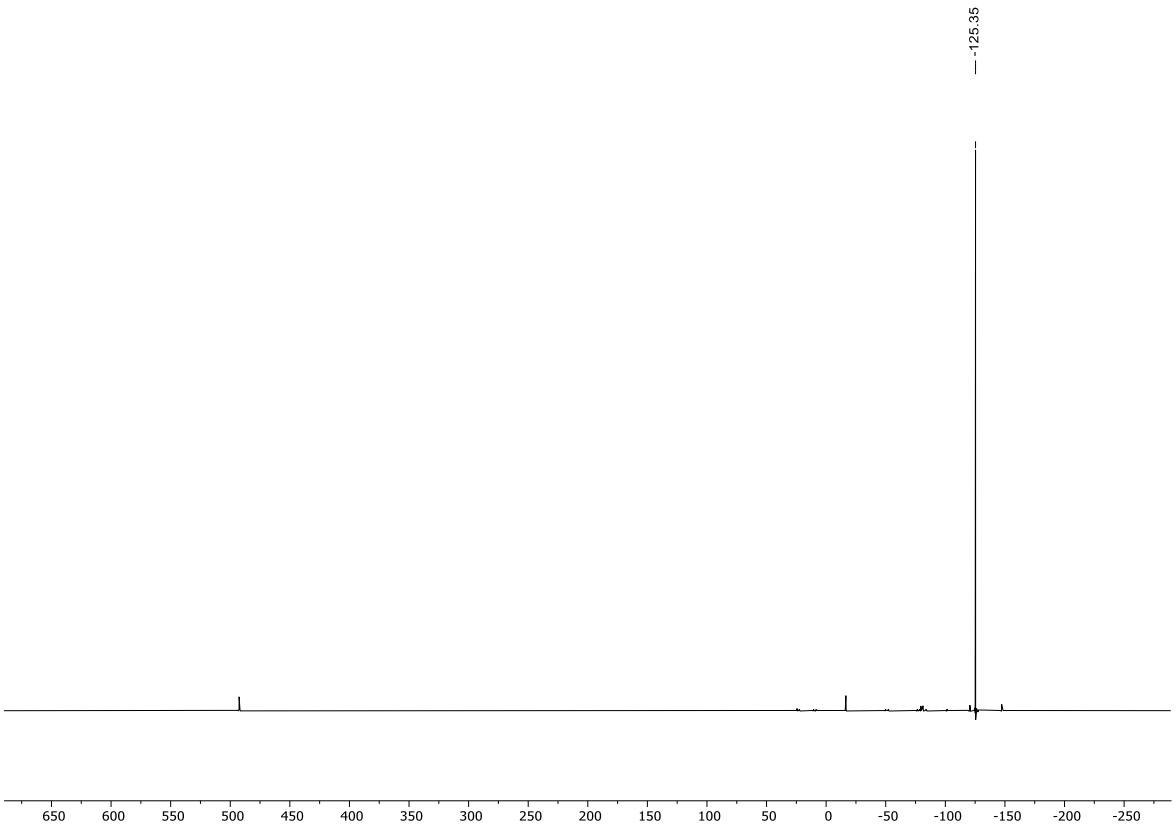
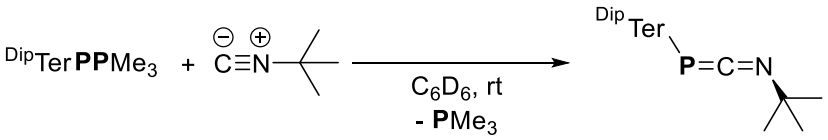


Figure S11: $^{31}P\{^1H\}$ NMR spectrum of ^{Mes}TerP=C=N*t*Bu (**3b**) (122 MHz, C_6D_6, rt).



3.3 Synthesis of ^{Dip}TerPCN*t*Bu (3c)



^{Dip}TerPPMe$_3$ (**1c**) (0.020 g, 0.040 mmol) was dissolved in 0.3 mL of C_6D_6. An excess of *tert*-butyl isocyanide (**2a**) (3.0 eq., 0.010 g, 0.120 mmol) in 0.3 mL of C_6D_6 was added and the reaction mixture was allowed to stand for several hours at room temperature. Regular control by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy verified clean conversion of one equivalent each of both starting materials to give ^{Dip}TerP=C=N*t*Bu (**3c**) as a yellow solid under release of PMe_3 after 40 hours (Figures S12 and S13).

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.78 (s, 9H, $C_q(CH_3)_3$), 1.13 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.45 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 2.97 (hept, $^3J_{H,H}$ = 6.8 Hz, 4H, $CH(CH_3)_2$), 6.98-7.05 (m, 3H, CH_{Aryl}), 7.20-7.21 (m, 2H, CH_{Aryl}), 7.22-7.23 (m, 2H, CH_{Aryl}), 7.29-7.35(m, 2H, CH_{Aryl}) ppm. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, 298 K): δ = 23.84 ($CH(\underline{C}H_3)_2$), 23.86 ($CH(\underline{C}H_3)_2$), 25.2 ($CH(\underline{C}H_3)_2$), 29.8 (d, $^{TS}J_{P,C}$ = 1.5 Hz, $C_q(\underline{C}H_3)_3$), 31.2 ($\underline{C}H(CH_3)_2$), 60.9 (d, $^3J_{P,C}$ = 8.2 Hz, $\underline{C}_q(CH_3)_3$), 123.4 (CH_{Aryl}), 125.9 (CH_{Aryl}), 129.0 (CH_{Aryl}), 129.5 (d, $J_{P,C}$ = 3.5 Hz, CH_{Aryl}), 136.8 (d, $^1J_{P,C}$ = 47.2 Hz, $C_{q,Aryl}P$), 140.7 (d, $^3J_{P,C}$ = 5.7 Hz, *o*-$\underline{C}_{q,Ary}CH(CH_3)_2$), 144.7 (d, $^2J_{P,C}$ = 16.9 Hz, *o*-$\underline{C}_{q,Ary}P$), 147.3 ($\underline{C}_{q,Aryl}CH(CH_3)_2$), 177.9 (d, $^1J_{P,C}$ = 77.9 Hz, P=C=N) ppm. **^{31}P{^{1}H} NMR** (122 MHz, C_6D_6, 298 K): δ = -134.8 ppm. **MS** (ESI-TOF): expected: m/z = 512.3446 $[M+H]^+$; found: m/z = 512.3450.

Figure S12: Monitoring of the reaction of ^{Dip}TerPPMe$_3$ (**1c**) with *tert*-butyl isocyanide (**2a**) via ^{1}H NMR spectroscopy (300 MHz, C_6D_6, rt); 0.80 ppm: PMe$_3$, 0.88 ppm: *tert*-butyl isocyanide (**2a**).

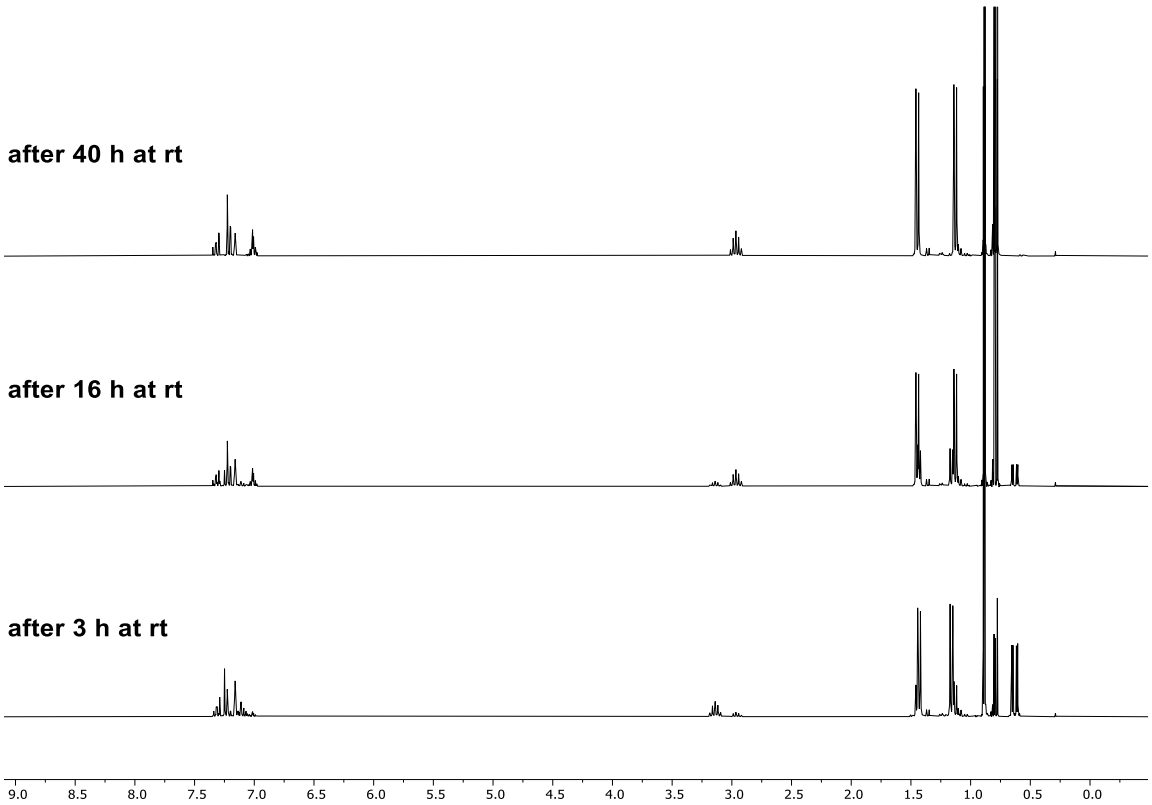


Figure S13: Monitoring of the reaction of ^{Dip}TerPPMe$_3$ (**1c**) with *tert*-butyl isocyanide (**2a**) via ^{31}P{^{1}H} NMR spectroscopy (122 MHz, C_6D_6, rt); −116.3 and −3.1 ppm: ^{Dip}TerPPMe$_3$ (**1c**), −62.6 ppm: PMe$_3$, −134.9 ppm: ^{Dip}TerP=C=N*t*Bu (**3c**).

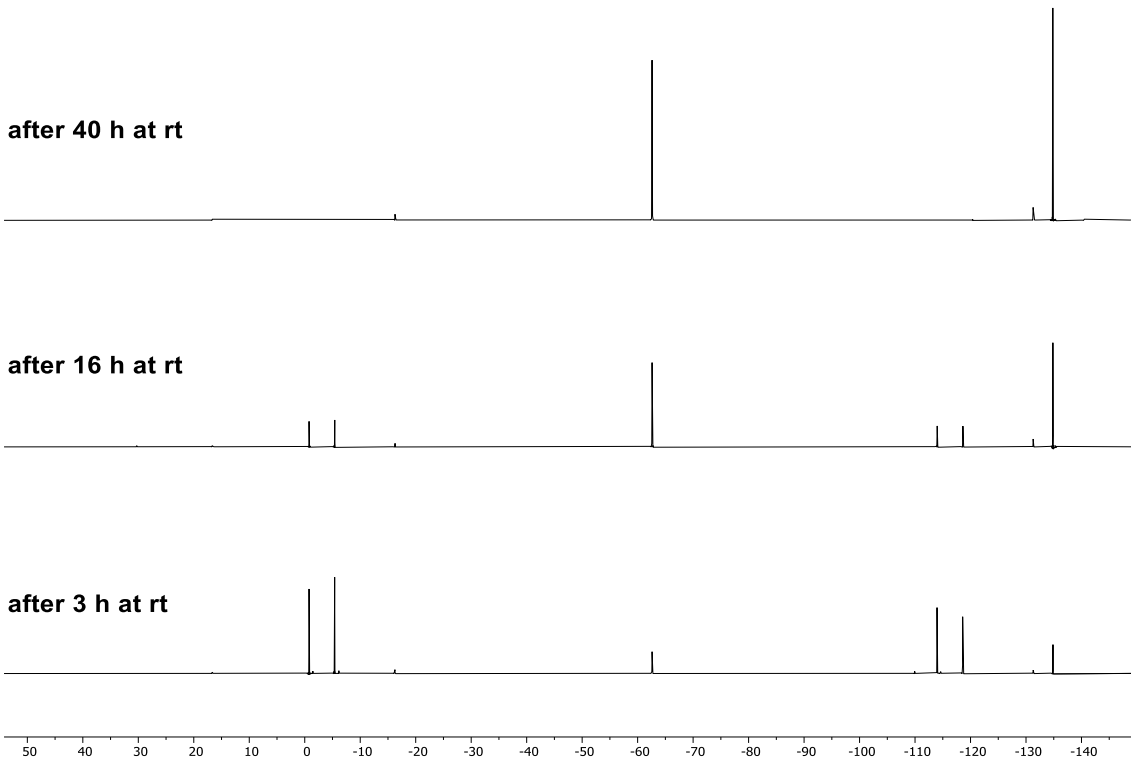


Figure S14: ^{1}H NMR spectrum of ^{Dip}TerP=C=N*t*Bu (**3c**) (300 MHz, C_6D_6, rt).

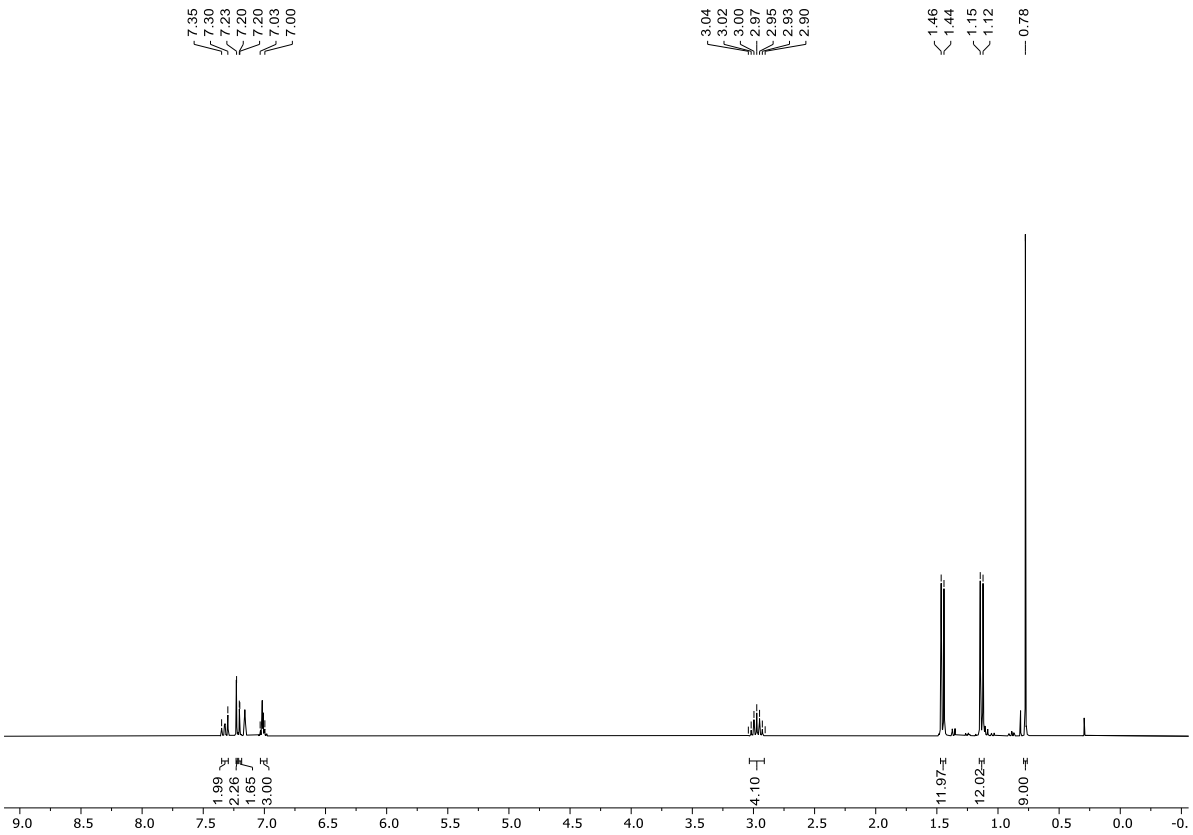


Figure S15: ^{13}C NMR spectrum of ^{Dip}TerP=C=N*t*Bu (**3c**) (75 MHz, C_6D_6, rt).

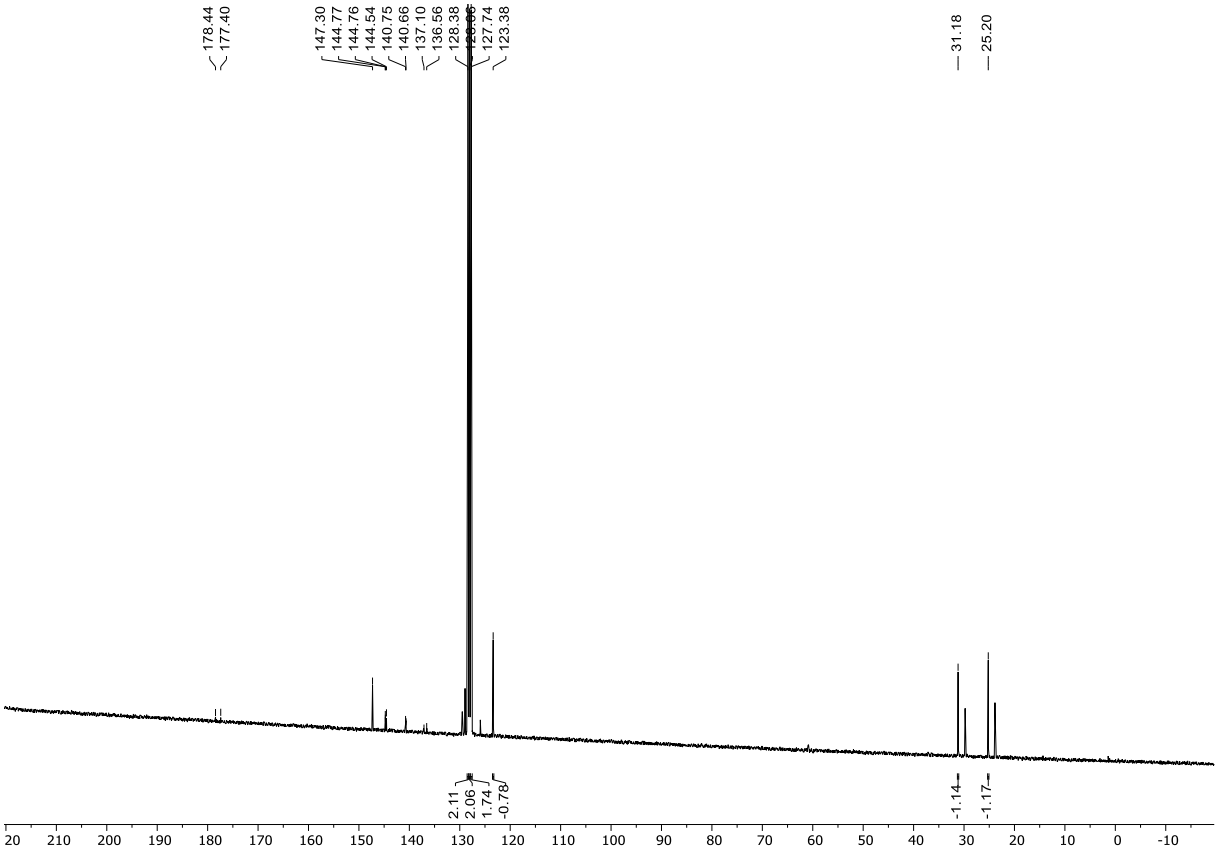
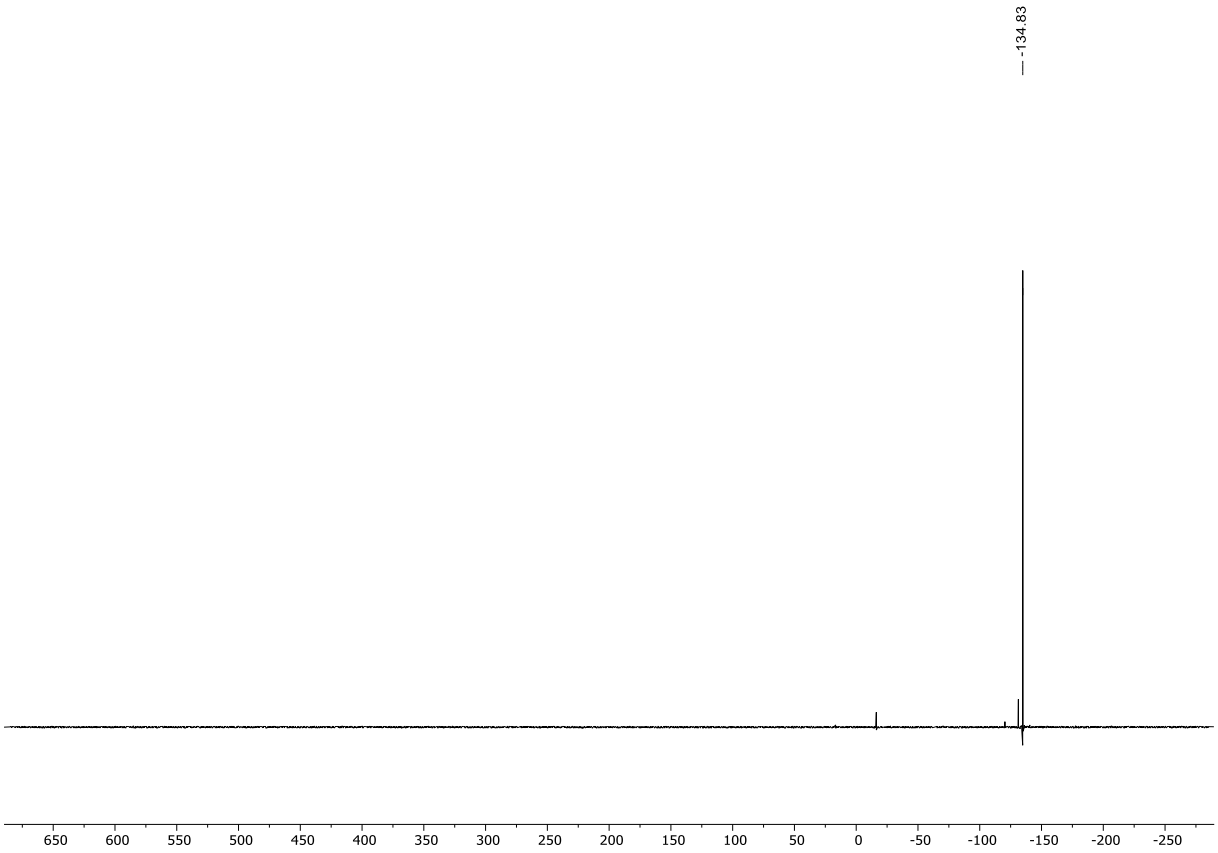
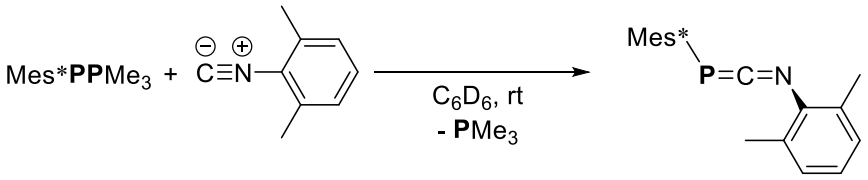


Figure S16: $^{31}P\{^{1}H\}$ NMR spectrum of ^{Dip}TerP=C=N*t*Bu (**3c**) (122 MHz, C_6D_6, rt).



3.4 Synthesis of Mes*PCNXyl (3d)



Mes*PPMe$_3$ (**1a**) (0.030 g, 0.085 mmol) and 2,6-dimethylphenyl isocyanide (**2b**) (0.011 g, 0.085 mmol) were dissolved in 0.6 mL of C_6D_6. The reaction mixture was allowed to stand for several hours at room temperature and the reaction progress was regularly controlled by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. After 40 hours Mes*PPMe$_3$ was completely consumed and Mes*P=C=NXyl (**3d**) has been formed accompanied by formation of Mes*PPMes* (δ^{31}P{^{1}H} = 493.0 ppm) [ratio 1.00 : 0.65 (integration of the respective ^{31}P{^{1}H} NMR signals)]. Consequently, a part of **2b** remains unreacted. At higher reaction temperatures the amount of the diphosphene significantly increases. By using an excess of **2b** the amount of formed Mes*PPMes* can be suppressed but remains at a high level (e. g. the reaction with 5.0 equivalents of **2b** results in a ratio of 1.00 : 0.30, Figure S19). The characteristic NMR signals of **2b** are given below.

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 1.30 (s, 9H, *p*-$C_q(CH_3)_3$P), 1.74 (s, 18H, *o*-$C_q(CH_3)_3$P), 1.86 (s, 6H, CH_3), 6.71-6.72 (m, 3H, CH_{Aryl}), 7.56-7.57 (m, 2H, CH_{Aryl}) ppm. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, 298 K): δ = 191.5 (d, $^1J_{P,C}$ = 78.8 Hz, P=C=N) ppm. **^{31}P{^{1}H} NMR** (122 MHz, C_6D_6, 298 K): δ = -120.6 ppm.

Figure S17: Monitoring of the reaction of Mes*PPMe$_3$ (**1a**) with 2,6-dimethylphenyl isocyanide (**2b**) via ^{1}H NMR spectroscopy (300 MHz, C_6D_6, rt).

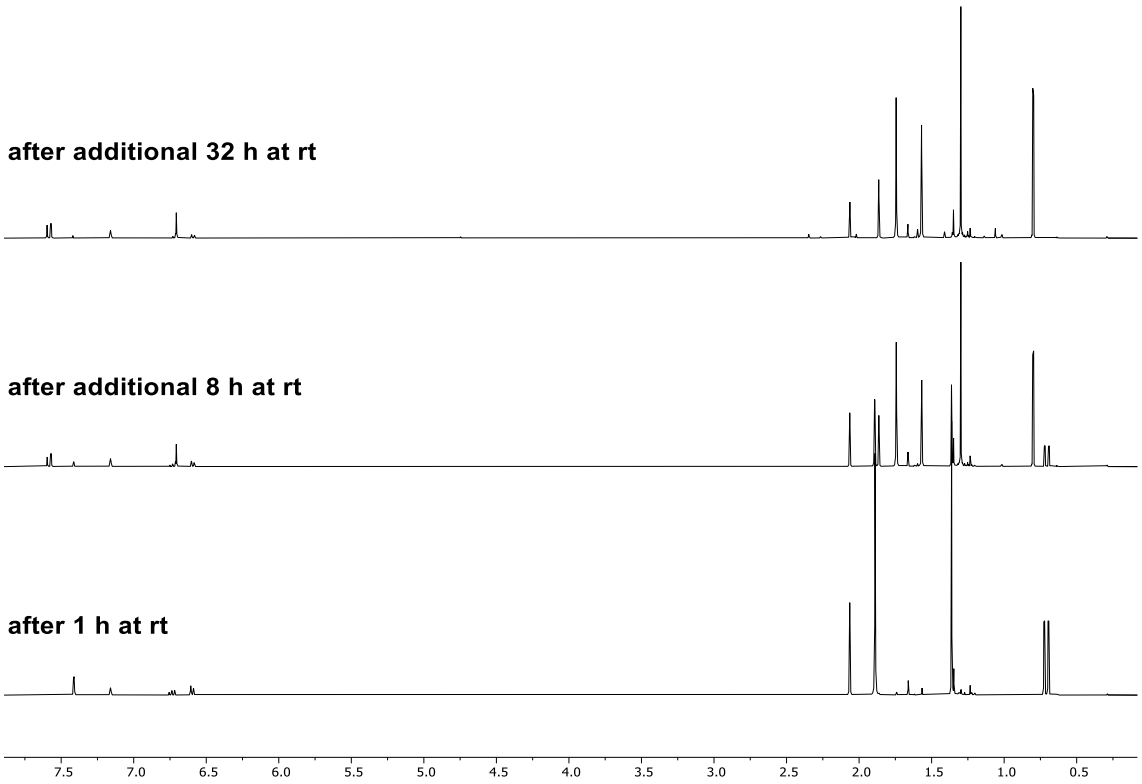


Figure S18: Monitoring of the reaction of Mes*PPMe$_3$ (**1a**) with 2,6-dimethylphenyl isocyanide (**2b**) via ^{31}P{^{1}H} NMR spectroscopy (122 MHz, C_6D_6, rt); -134.3 and 4.1 ppm: Mes*PPMe$_3$ (**1a**), −62.6 ppm: PMe$_3$, −120.6 ppm: Mes*P=C=NXyl (**3d**).

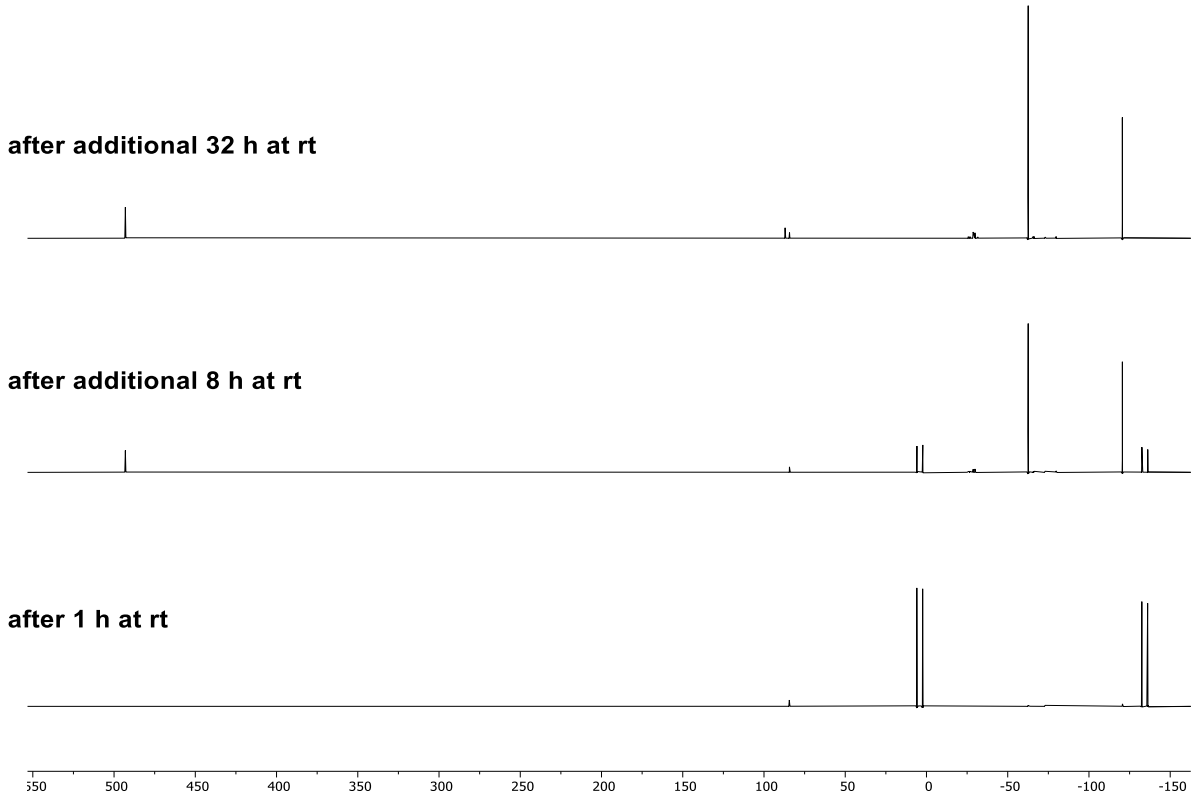


Figure S19: Monitoring of the reaction of Mes*PPMe$_3$ (**1a**) with 5.0 equivalents of 2,6-dimethylphenyl isocyanide (**2b**) via $^{31}P\{^1H\}$ NMR spectroscopy (122 MHz, C_6D_6, rt); −134.3 and 4.1 ppm: Mes*PPMe$_3$ (**1a**), −62.6 ppm: PMe$_3$, −120.6 ppm: Mes*P=C=NXyl (**3d**).

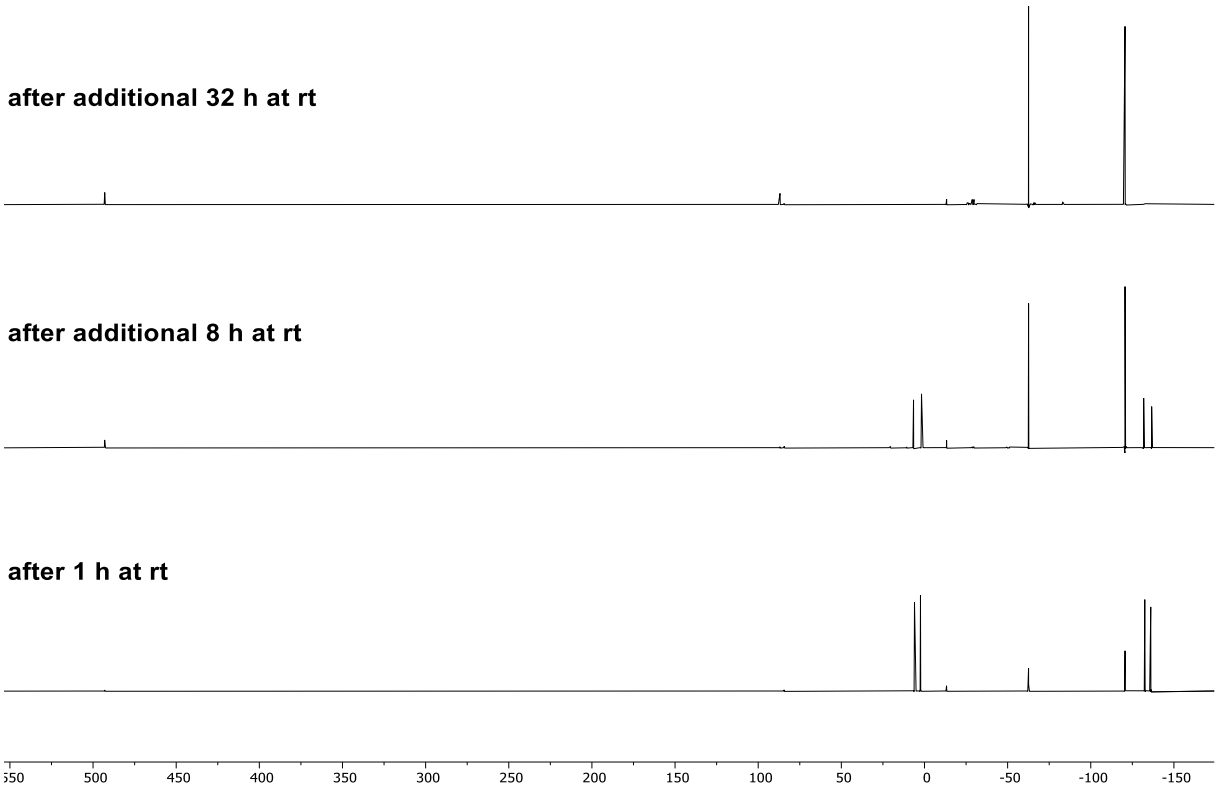
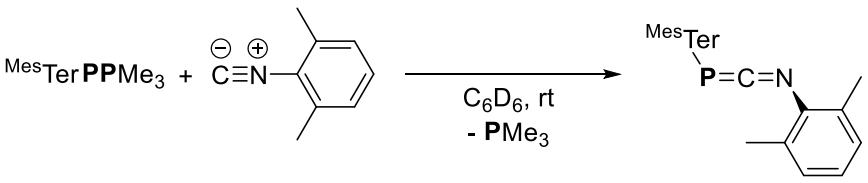


Figure S22: Monitoring of the reaction of Mes*PPMe$_3$ (**1a**) with 5.0 equivalents of 2,6-dimethylphenyl

3.5 Synthesis of MesTerPCNXyl (3e)



^{Mes}TerPPMe$_3$ (**1b**) (0.025 g, 0.059 mmol) was dissolved in 0.3 mL of C_6D_6. 2,6-Dimetyhlphenyl isocyanide (**2b**) (0.008 g, 0.059 mmol) in 0.3 mL of C_6D_6 was added and the reaction mixture was allowed to stand for several hours at room temperature. The reaction already started at room temperature but was heated to 80 °C to allow for the faster formation of ^{Mes}TerP=C=NXyl (**3e)**. Regular control by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy verified conversion of both starting materials to give **3e** under release of PMe$_3$ accompanied by the formation of (^{Mes}TerP)$_2$. Recrystallization from *n*-heptane yielded analytically pure **3e**.

Crystals suitable for SC-XRD were obtained by slow evaporation of a saturated solution of **3e** in *n*-heptane.

Yield: 0.012 g (0.032 mmol; 53%).

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 2.00 (s, 6H, *o*-CH_3N), 2.03 (s, 6H, *p*-$CH_3C_6H_3$), 2.22 (s, 12H, *o*-$CH_3C_6H_3$), 6.62-6.64 (m, 2H, CH_{Aryl}), 6.70-6.74 (m, 1H, CH_{Aryl}), 6.75-6.76 (m, 4H, CH_{Aryl}), 6.93-6.95 (m, 2H, CH_{Aryl}), 7.10-7.14 (m, 1H, CH_{Aryl}) ppm. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, 298 K): δ = 19.0 (*o*-CH_3N), 20.93 (*o*-$\underline{C}H_3C_6H_3$), 20.95 (*o*-$\underline{C}H_3C_6H_3$), 21.2 (*p*-$\underline{C}H_3C_6H_3$), *, 128.6 (CH_{Aryl}), 132.9 (d, $^3J_{P,C}$ = 2.3 Hz, $C_{q,Aryl}$N), 133.5 (d, $^1J_{P,C}$ = 41.7 Hz, $C_{q,Aryl}$P), 136.1 (*o*-$\underline{C}_{q,Aryl}C_6H_3$), 136.3 (d, $^4J_{P,C}$ = 2.9 Hz, *o*-$C_{q,Aryl}$N), 137.2 (*p*-$\underline{C}_{q,Aryl}C_6H_3$), 140.4 (d, $^3J_{P,C}$ = 4.3 Hz, $C_{q,Aryl}$), 146.6 (d, $^2J_{P,C}$ = 15.1 Hz, *o*-$C_{q,Aryl}$P), 183.7 (d, $^1J_{P,C}$ = 78.1 Hz, P=C=N) ppm. * = the other CH_{Aryl} signals are masked by the C_6D_6 signal. **^{31}P{^{1}H} NMR** (122 MHz, C_6D_6, 298 K): δ = −145.4 ppm.

MS (ESI-TOF): expected: m/z = 476.2507 $[M+H]^+$; found: m/z = 476.2504.

Figure S20: ^{1}H NMR spectrum of ^{Mes}TerP=C=NXyl (**3e**) (300 MHz, C_6D_6, rt).

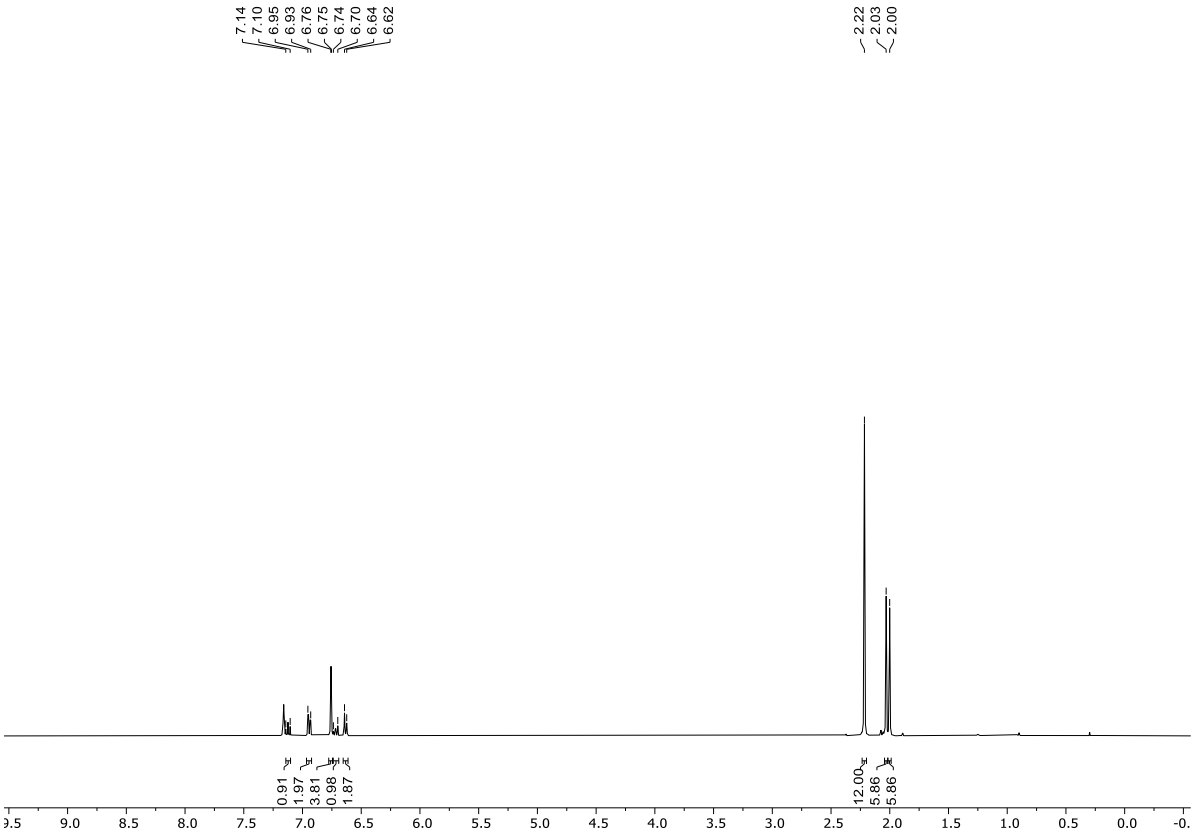


Figure S21: ^{13}C NMR spectrum of ^{Mes}TerP=C=NXyl (**3e**) (75 MHz, C_6D_6, rt).

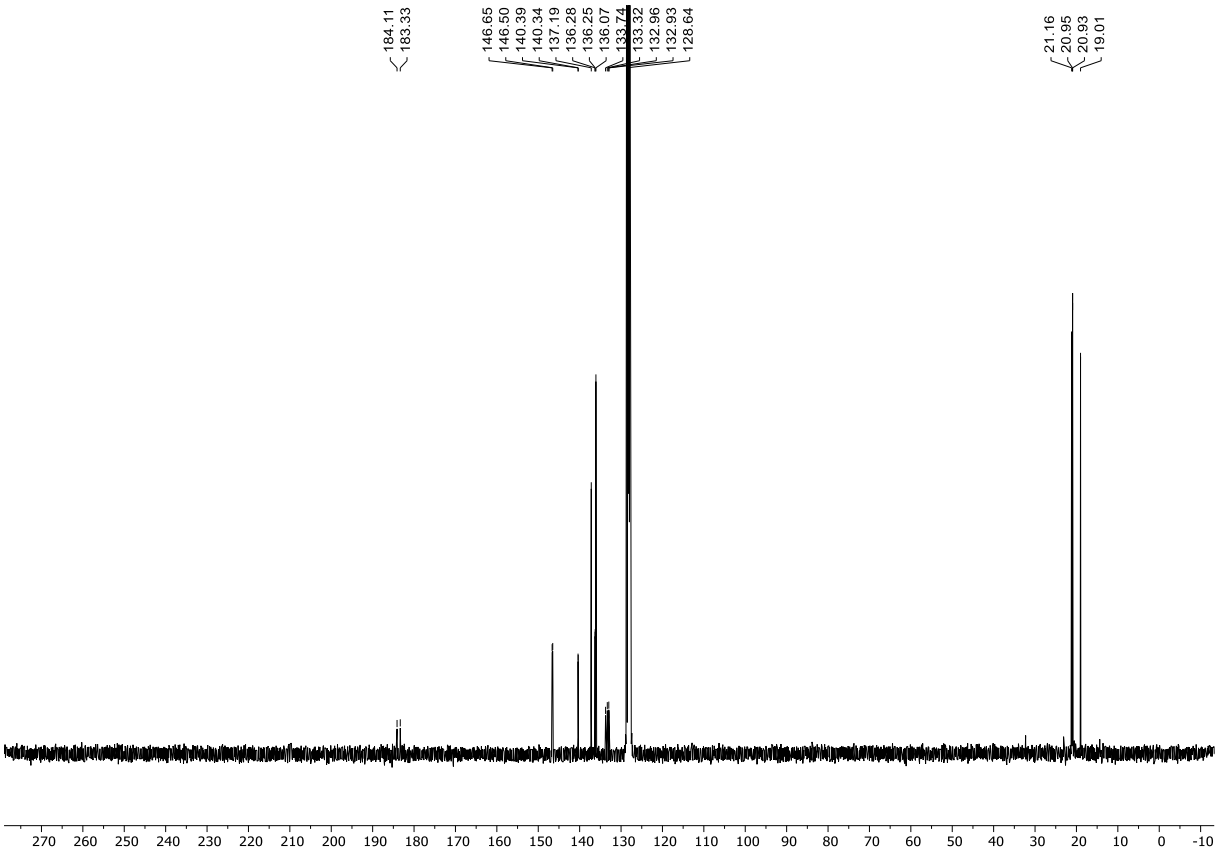
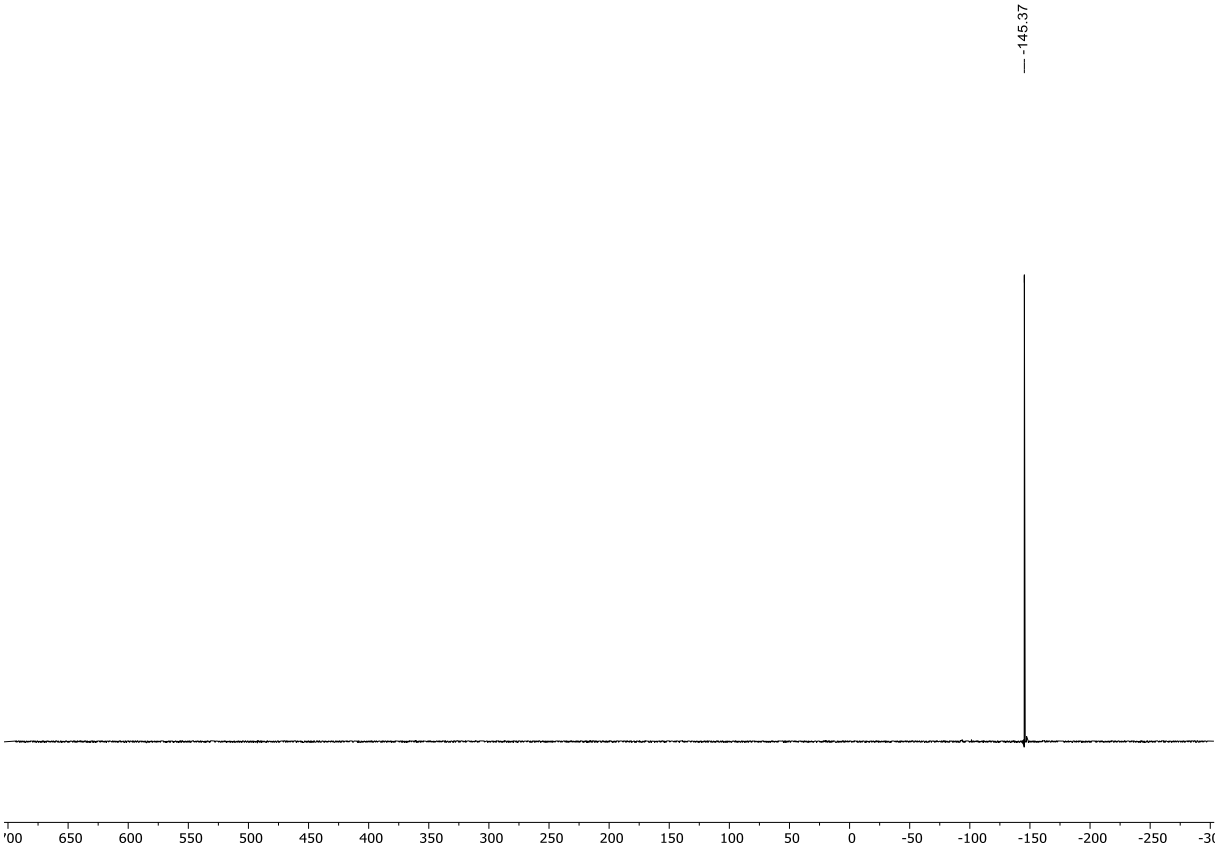
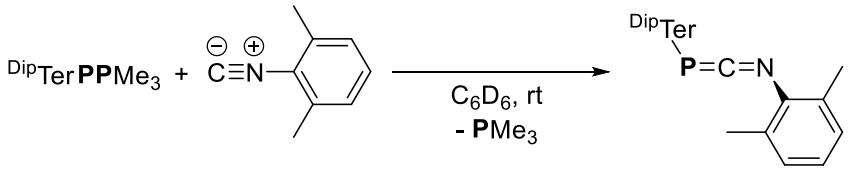


Figure S22: $^{31}P\{^{1}H\}$ NMR spectrum of ^{Mes}TerP=C=NXyl (**3e**) (122 MHz, C_6D_6, rt).



3.6 Synthesis of ^{Dip}TerPCNXyl (3f)



A) ^{Dip}TerPPMe$_3$ (**1c**) (0.019 g, 0.038 mmol) was dissolved in 0.3 mL of C_6D_6 2,6-Dimetyhlphenyl isocyanide (**2b**) (0.005 g, 0.038 mmol) in 0.3 mL of C_6D_6 was added and the reaction mixture was allowed to stand for several hours at room temperature. The reaction already started at room temperature but was heated to 80 °C to allow for the faster formation of ^{Dip}TerP=C=NXyl (**3f**). Regular control verified clean conversion of both starting materials to give **3f** under release of PMe_3.

B) ^{Dip}TerPPMe$_3$ (**1c**) (0.100 g, 0.198 mmol) and 2,6-dimetyhlphenyl isocyanide (**2b**) (0.026 g, 0.198 mmol) were dissolved in 2 mL of benzene and stirred for a prolonged period of time at 80 °C until $^{31}P\{^1H\}$ NMR spectroscopy revealed complete conversion of both starting materials. All volatile components were removed under vacuum to give **3f** as a red solid.

Crystals suitable for SC-XRD were obtained from a saturated solution of **3f** in *n*-pentane at -30 °C.

Yield: 0.077 g (0.138 mmol; 70%).

CHN calculated: C 83.68, H 8.28, N 2.50; found: C 83.55, H 8.13, N 1.96. **^{1}H NMR** (300 MHz, C_6D_6, 298 K): δ = 1.12 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.39 (d, $^3J_{H,H}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 2.06 (s, 6H, $C_{q,Aryl}CH_3$), 2.99 (hept, $^3J_{H,H}$ = 6.8 Hz, 4H CH(CH$_3$)$_2$), 6.61-6.63 (m, 2H, CH_{Aryl}), 6.70-6.74 (m, 1H, CH_{Aryl}), 7.04-7.05 (m, 3H, CH_{Aryl}), 7.14-7.16 (m, 4H, CH_{Aryl})*, 7.23-7.27 (m, 2H, CH_{Aryl}) ppm. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, 298 K): δ = 19.8 ($C_{q,Aryl}\underline{C}H_3$), 23.71 (CH($\underline{C}H_3$)$_2$), 23.73 (CH($\underline{C}H_3$)$_2$), 25.3 (CH($\underline{C}H_3$)$_2$), 31.2 ($\underline{C}$H(CH$_3$)$_2$), 123.2 ($CH_{Aryl}$), 125.9 ($CH_{Aryl}$), 128.4 ($CH_{Aryl}$)*, 128.9 ($CH_{Aryl}$), 129.6 (d, $J_{P,C}$ = 3.1 Hz, CH_{Aryl}), 131.9 ($C_{q,Aryl}\underline{C}H_3$), 136.7 (d, $^1J_{P,C}$ = 44.9 Hz, $C_{q,Aryl}$P), 137.2 (d, $^3J_{P,C}$ = 3.1 Hz, $C_{q,Aryl}$N), 140.8 (d, $^3J_{P,C}$ = 5.2 Hz, *o*-$\underline{C}_{q,Ary}$CH(CH$_3$)$_2$), 144.9 (d, $^2J_{P,C}$ = 16.5 Hz, *o*-$\underline{C}_{q,Ary}$P), 147.1

($\underline{C}_{q,Aryl}CH(CH_3)_2$), 179.6 (d, $^1J_{P,C}$ = 77.2 Hz, P=C=N) ppm. * = overlap with C_6D_6 and C_6D_5H signals, respectively **$^{31}P\{^1H\}$ NMR** (122 MHz, C_6D_6, 298 K): δ = −144.8 ppm.

MS (ESI-TOF): expected: m/z = 560.3446 $[M+H]^+$; found: m/z = 560.3455 $[M+H]^+$.

Figure S23: Monitoring of the reaction of ^{Dip}TerPPMe$_3$ (**1c**) with 2,6-dimethylphenyl isocyanide (**2b**) via ^{1}H NMR spectroscopy (300 MHz, C_6D_6, rt).

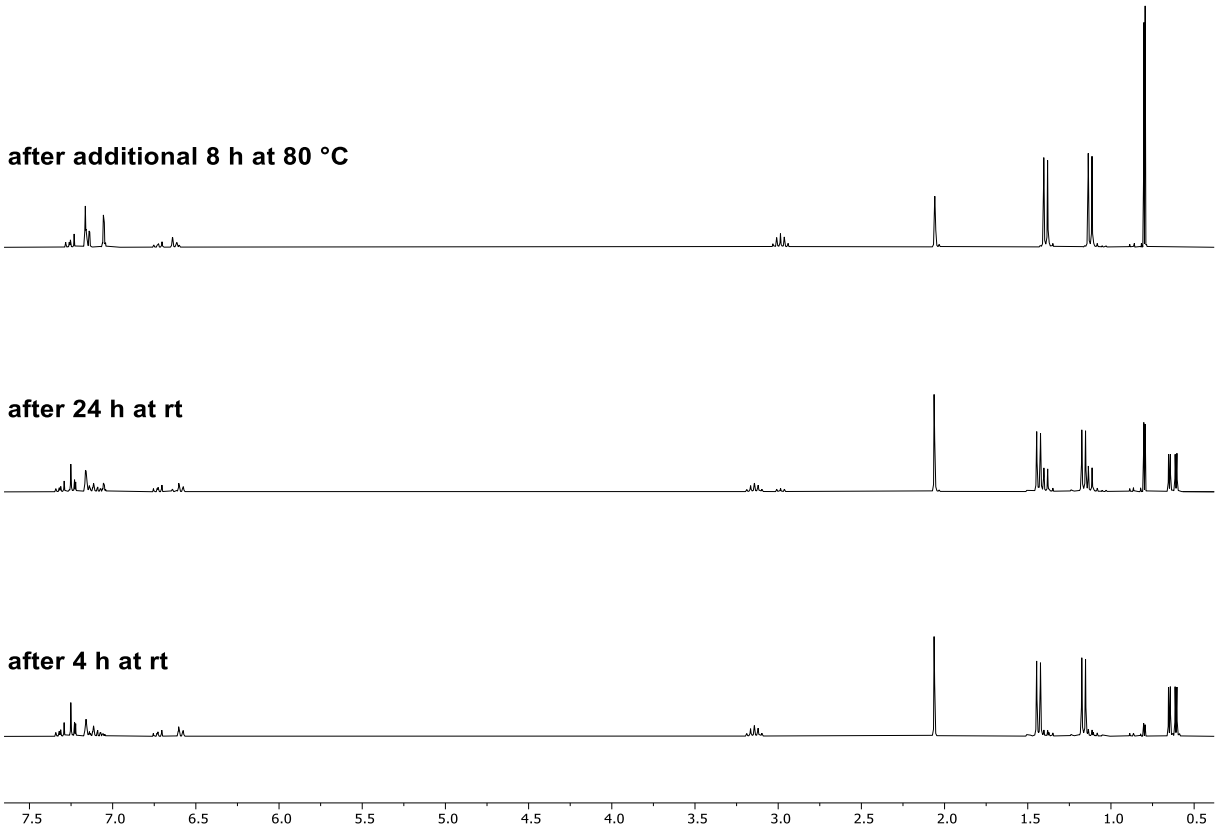


Figure S24: Monitoring of the reaction of ^{Dip}TerPPMe$_3$ (**1c**) with 2,6-dimethylphenyl isocyanide (**2b**) via ^{31}P{^{1}H} NMR spectroscopy (122 MHz, C_6D_6, rt); −116.3 and −3.1 ppm: ^{Dip}TerPPMe$_3$ (**1c**), −62.6 ppm: PMe$_3$, −144.8 ppm: ^{Dip}TerP=C=NXyl (**3f**).

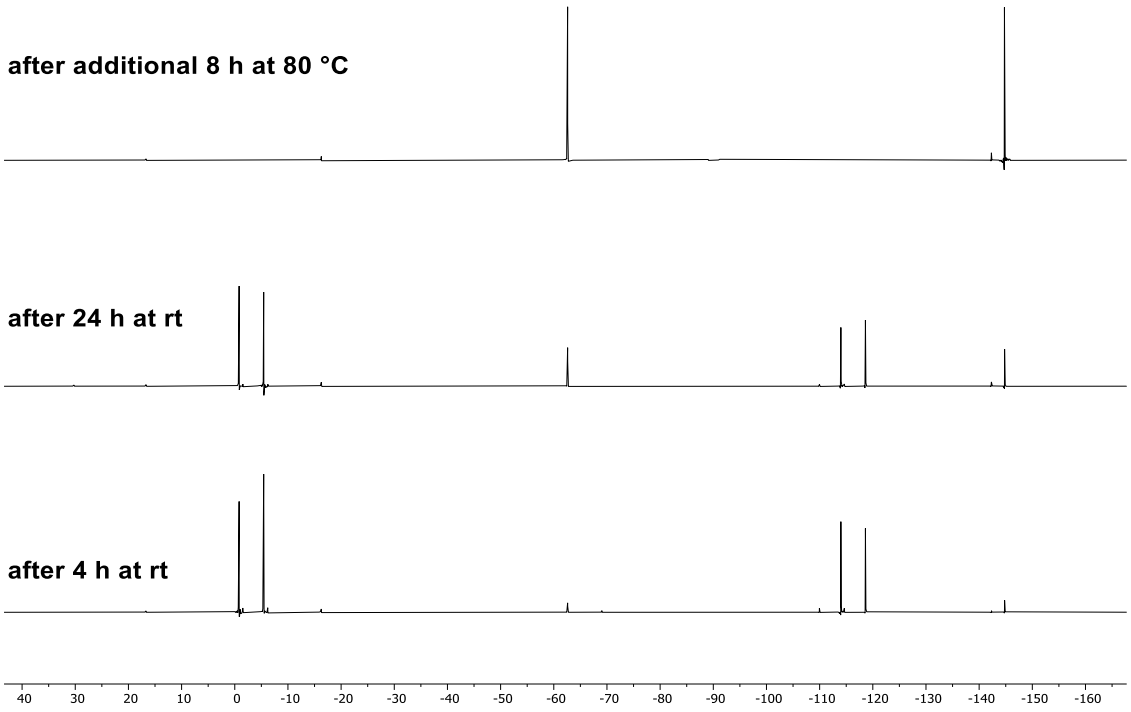


Figure S25: ^{1}H NMR spectrum of ^{Dip}TerP=C=NXyl (**3f**) (300 MHz, C_6D_6, rt).

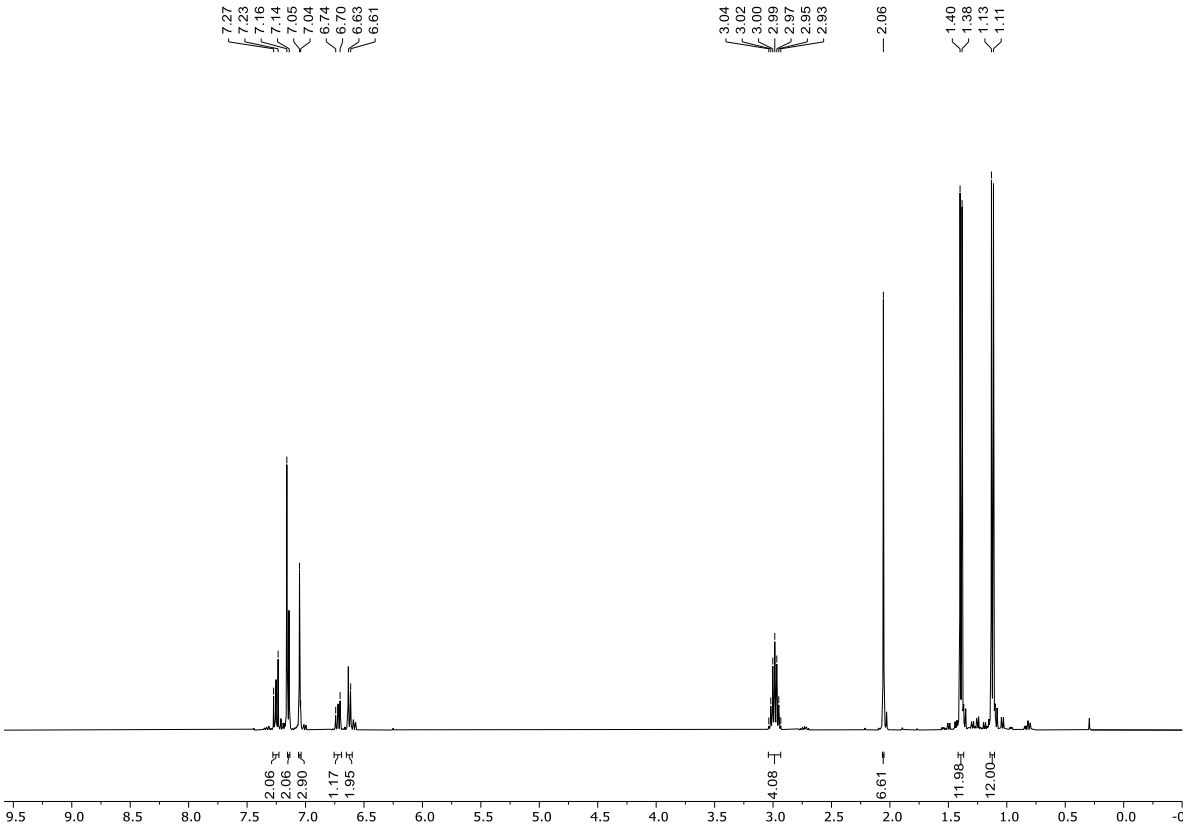


Figure S26: ^{13}C NMR spectrum of ^{Dip}TerP=C=NXyl (**3f**) (75 MHz, C_6D_6, rt).

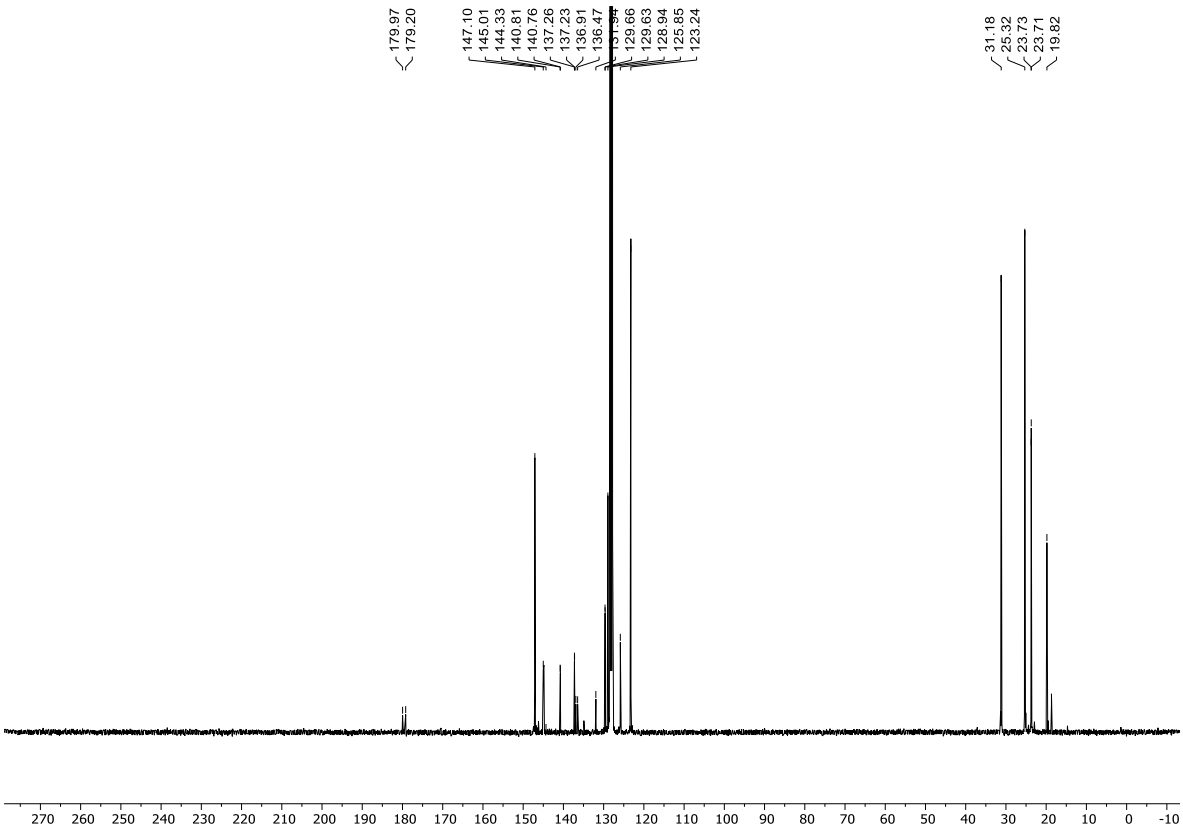
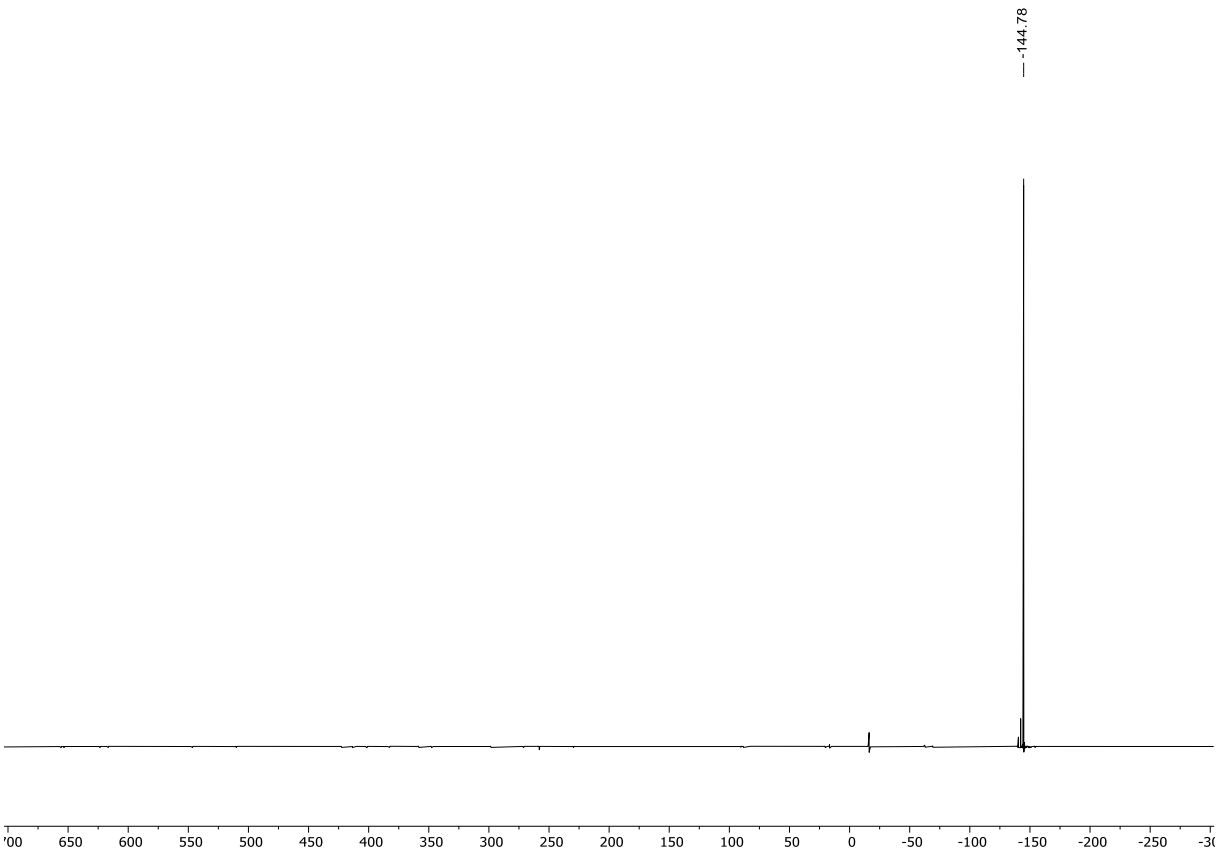
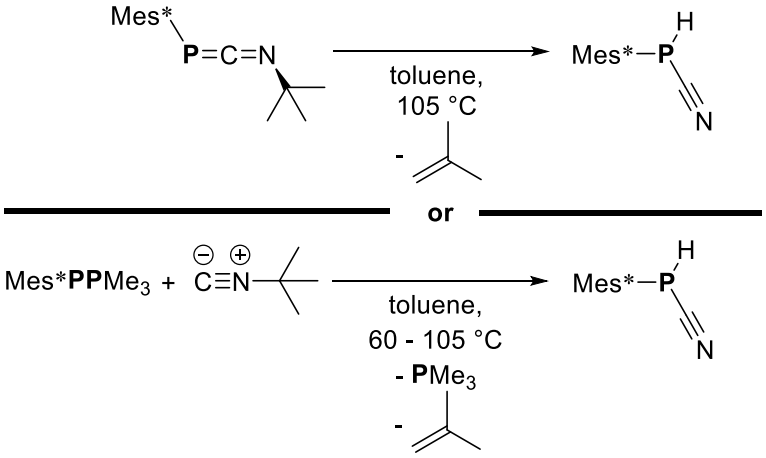


Figure S27: $^{31}P\{^1H\}$ NMR spectrum of ^{Dip}TerP=C=NXyl (**3f**) (122 MHz, C_6D_6, rt).



3.7 Synthesis of Mes*P(H)CN (4a)



A) Mes*P=C=N^{t}Bu (**3a**) (0.030 g, 0.083 mmol) was dissolved in 0.6 mL of toluene-d_8 and heated to 105 °C for 16 h resulting mainly in the formation of Mes*P(H)C≡N (**6a**) and *iso*-butene (δ^1H = 1.59 (t, $^4J_{H,H}$ = 1.2 Hz, 6H, CH_3), 4.70 (hept, $^3J_{H,H}$ = 1.2 Hz, 2H, CH_2)). The obtained ^{1}H and ^{31}P{^{1}H} NMR spectra are shown in Figures S28 and S29, respectively.

B) Mes*PPMe$_3$ (**1a**) (0.500 g, 1.419 mmol) was dissolved in 8 mL of toluene followed by addition of *tert*-butyl isocyanide (**2a**) (0.16 mL, 1.419 mmol). The reaction mixture was heated to 60 °C for 16 h for the *in-situ* generation of Mes*P=C=N^{t}Bu (**3a**) and subsequently heated to 105 °C for two days. All volatile components were removed under vacuum. The residue was recrystallized from *n*-hexane and collected in fractions to give Mes*P(H)C≡N (**6a**) as a colorless solid.

Crystals suitable for SC-XRD were obtained by slow evaporation of a saturated solution of **6a** in *n*-hexane at −30 °C.

Yield: 0.325 g (1.071 mmol; 75% (**B**)).

CHN: calculated: C 75.21, H 9.97, N 4.62; found: C 75.97, H 10.34, N 4.15. **^{1}H NMR** (300 MHz, C_6D_6, 298 K): d = 1.21 (s, 9H, p-Cq(CH3)3P), 1.49 (s, 18H, o-Cq(CH3)3P), 5.57 (d, 1JP,C = 252.3 Hz, 1H, PH), 7.53-7.54 (m, 2H, CHAryl) ppm. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, 298 K): δ = 31.2 (*p*-$C_q(\underline{C}H_3)_3P$), 33.5 (d, $J_{P,C}$ = 6.6 Hz, *o*-$C_q(\underline{C}H_3)_3P$), 35.3

(*p*-$\underline{C}_q(CH_3)_3P$), 38.3 (*o*-$\underline{C}_q(CH_3)_3P$), 119.0 (d, $^1J_{P,C}$ = 23.7 Hz, $C_{q,Aryl}P$), 120.8 (d, $^1J_{P,C}$ = 76.3 Hz, PC≡N), 123.5 (d, $^3J_{P,C}$ = 4.7 Hz, CH_{Aryl}), 152.8 (*p*-$C_{q,Aryl}P$), 157.0 (d, $^2J_{P,C}$ = 11.0 Hz, *o*-$C_{q,Aryl}P$) ppm. **$^{31}P\{^1H\}$/31 P NMR** (122 MHz, C_6D_6, 298 K): δ = −105.4 (d, $^1J_{P,H}$ = 252.3 Hz) ppm. **IR** (ATR, 32 scans, cm^{-1}): ν = 2961 (s), 2905 (m), 2869 (m), 2411 (w), 1591 (m), 1536 (w), 1476 (m), 1460 (m), 1407 (m), 1392 (m), 1364 (s), 1283 (w), 1238 (m), 1213 (s), 1194 (m), 1129 (w), 1022 (w), 953 (w), 931 (m), 921 (m), 905 (w), 894 (w), 878 (m), 790 (m), 753 (m), 743 (m), 652 (w), 640 (w), 597 (m), 584 (s), 546 (w), 493 (w), 465 (m), 437 (w), 415 (w). **MS** (CI): expected: m/z = 303; found: m/z = 304 $[M + H]^+$, 277 $[M – CN]^+$.

Figure S28: ^{1}H NMR spectrum obtained after heating Mes*P=C=N^{t}Bu (**3a**) for 16 h to 105 °C (**A**) (300 MHz, toluene-d_8, rt), +: *iso*-butene.

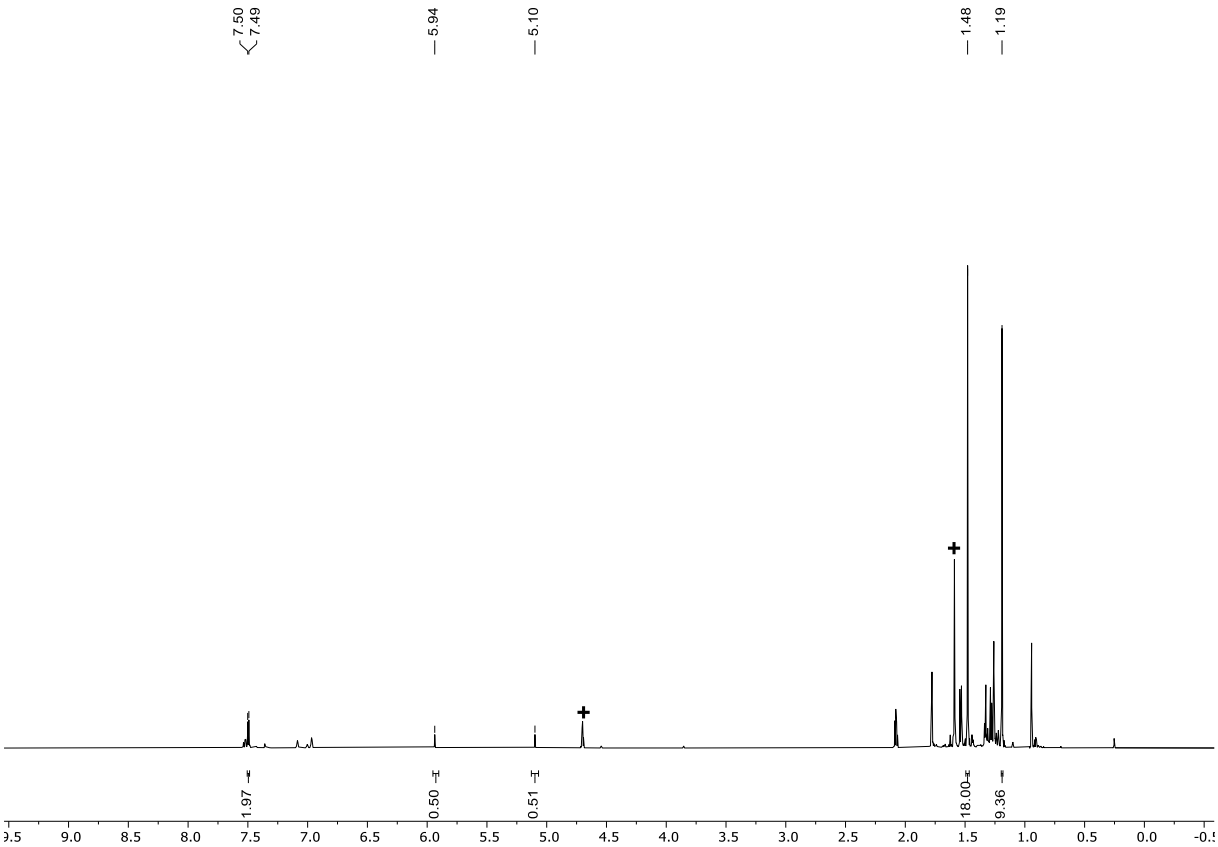


Figure S29: $^{31}P\{^{1}H\}$ NMR spectrum obtained after heating Mes*P=C=N^{t}Bu (**3a**) for 16 h to 105 °C (**A**) (122 MHz, toluene-d_8, rt).

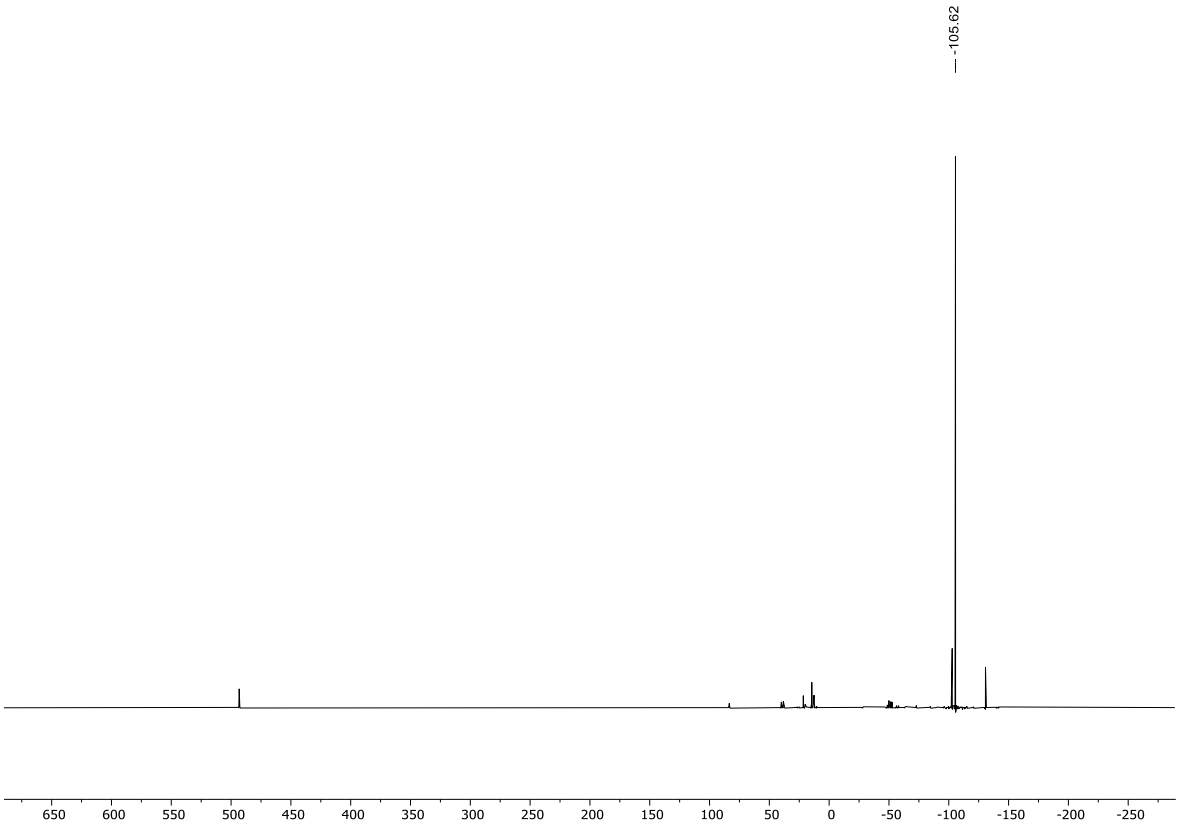


Figure S30: ^{1}H NMR spectrum of Mes*P(H)C≡N (**6a**) (300 MHz, C_6D_6, rt).

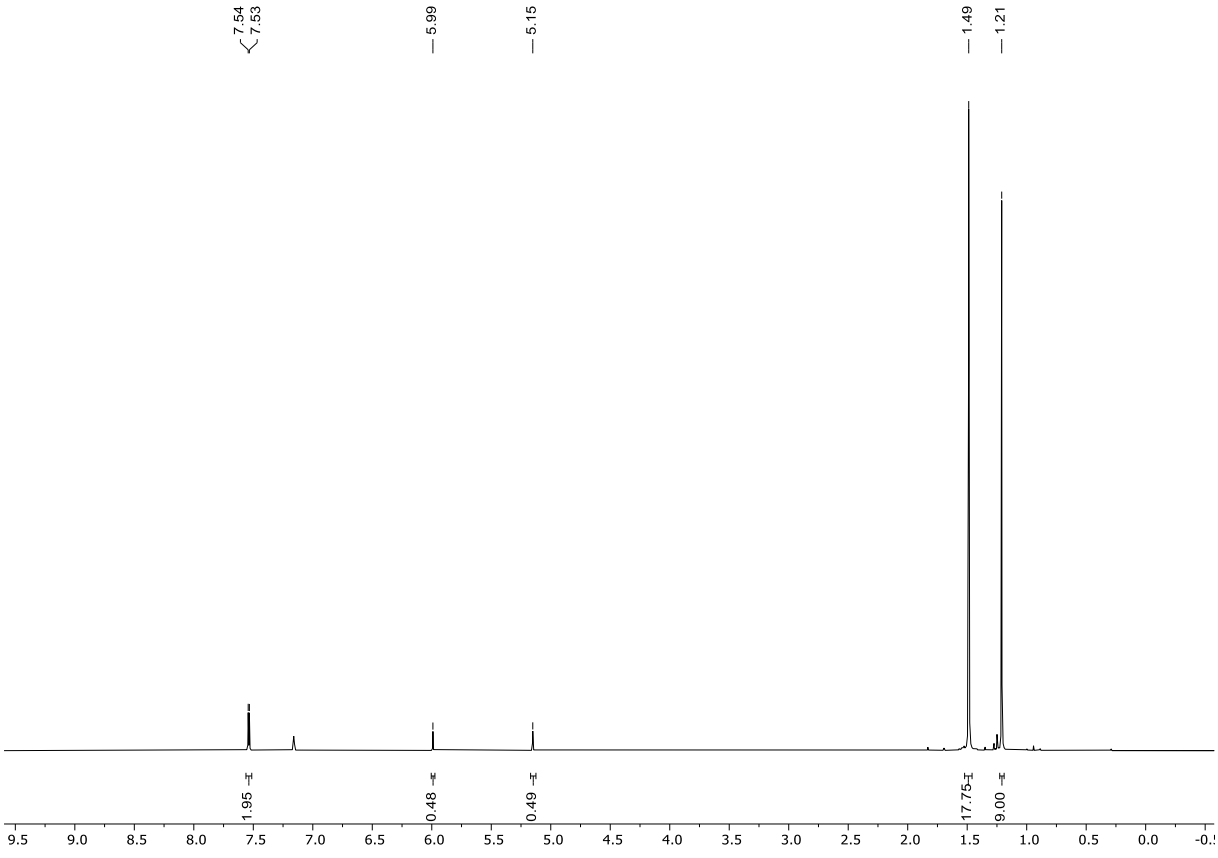


Figure S31: ^{13}C NMR spectrum of Mes*P(H)C≡N (**6a**) (75 MHz, C_6D_6, rt).

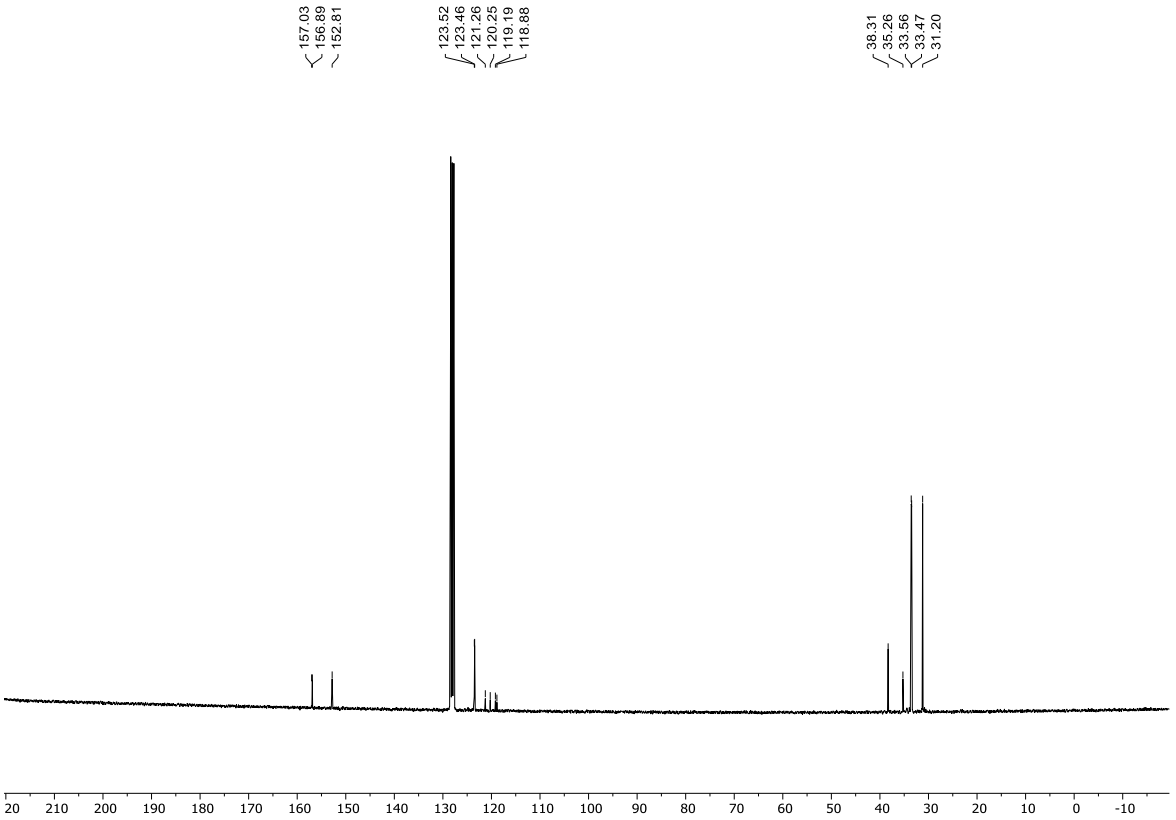
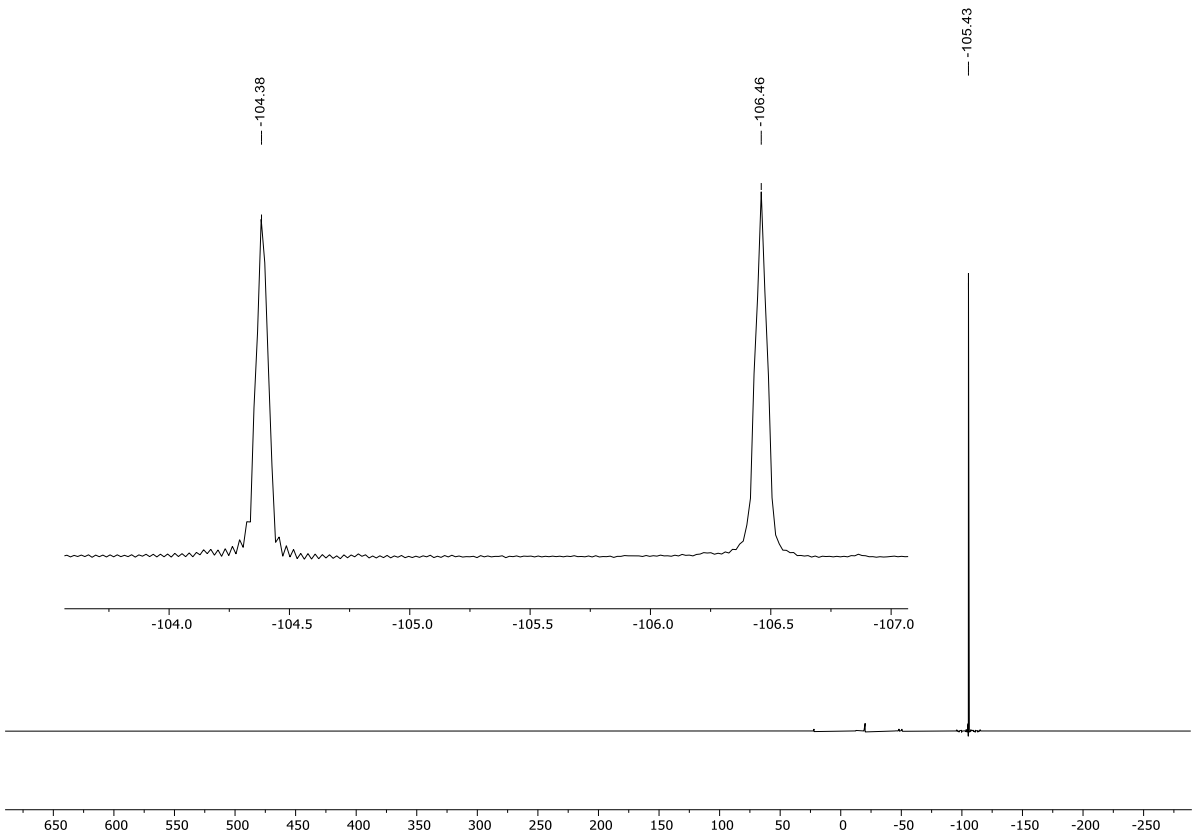
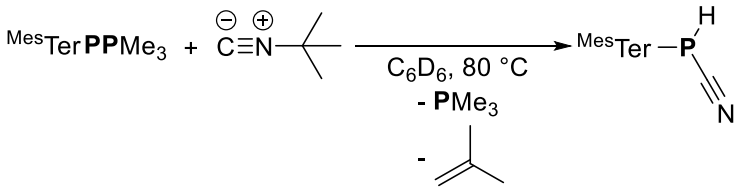


Figure S32: $^{31}P\{^1H\}$ and ^{31}P NMR spectra of Mes*P(H)C≡N (**6a**) (122 MHz, C_6D_6, rt).



3.8 Synthesis of ^{Mes}TerP(H)CN (4b)



^{Mes}TerPPMe$_3$ (**1b**) (0.025 g, 0.060 mmol) was dissolved in 0.3 mL of C_6D_6. An excess of *tert*-butyl isocyanide (**2a**) (3 drops with a 1 mL syringe) in 0.3 mL of C_6D_6 was added and the reaction mixture was heated to 80 °C over night which revealed complete consumption of ^{Mes}TerPPMe$_3$ (**1b**) and of one equivalent of *tert*-butyl isocyanide (**2a**) to give ^{Mes}TerP(H)C≡N (**4b**) accompanied by the release of PMe$_3$ and *iso*-butene (Figures S33-S35). Approximately 10% of (^{Mes}TerP)$_2$ are formed during the course of the heating as indicated by integration of the corresponding $^{31}P\{^1H\}$ NMR signals [$\delta^{31}P\{^1H\}$ (^{Mes}TerP)$_2$ = 492.5 ppm] (Figure S35). Analytically pure **4b** (colorless solid) was obtained by subsequent removal of all volatile components under vacuum and washing of the residue with *n*-hexane (3×1 mL).

Crystals of **4b** suitable for SC-XRD were obtained by filtering of the wash solution through a microfiber filter and storage of the clear filtrate at −30 °C for several days.

Yield: 0.012 g (0.032 mmol; 53%).

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 2.00 (s, 6H, $CH_{3,Mes}$), 2.07 (s, 6H, $CH_{3,Mes}$), 2.17 (s, 6H, $CH_{3,Mes}$), 4.38 (d, $^1J_{P,H}$ = 244.6 Hz, 1H, PH), 6.85-6.87 (m, 6H, CH_{Aryl}), 7.09-7.13 (m, 1H, CH_{Aryl}) ppm. **$^{13}C\{^1H\}$ NMR** (75 MHz, C_6D_6, 298 K): δ = 20.73 ($CH_{3,Mes}$), 20.76 ($CH_{3,Mes}$), 21.2 ($CH_{3,Mes}$), 116.7 (d, $^1J_{P,C}$ = 76.7 Hz, P(H)C≡N), 129.0 (CH_{Aryl}), 129.1 (CH_{Aryl}), 129.2 (CH_{Aryl}), 129.22 (CH_{Aryl}), 131.5 (CH_{Aryl}), 135.4 ($C_{q,Mes}$), 136.2 ($C_{q,Mes}$), 138.0 ($C_{q,Mes}$), 138.1 (d, $^2J_{P,C}$ = 3.0 Hz, *o*-$C_{q,Aryl}$P), 147.7 (d, $^1J_{P,C}$ = 14.4 Hz, $C_{q,Aryl}$P) ppm. **$^{31}P\{^1H\}$/^{31}P NMR** (122 MHz, C_6D_6, 298 K): δ = -120.6 (d, $^1J_{P,H}$ = 244.8 Hz) ppm.

MS (ESI-TOF): expected: m/z = 372.1881 $[M + H]^+$; found: m/z = 372.1872 $[M + H]^+$.

Figure S33: ^{1}H NMR spectrum of the product mixture after 16 h at 80 °C (300 MHz, C_6D_6, rt); #: PMe_3, °: *tert*-butyl isocyanide (**2a**), +: *iso*-butene.

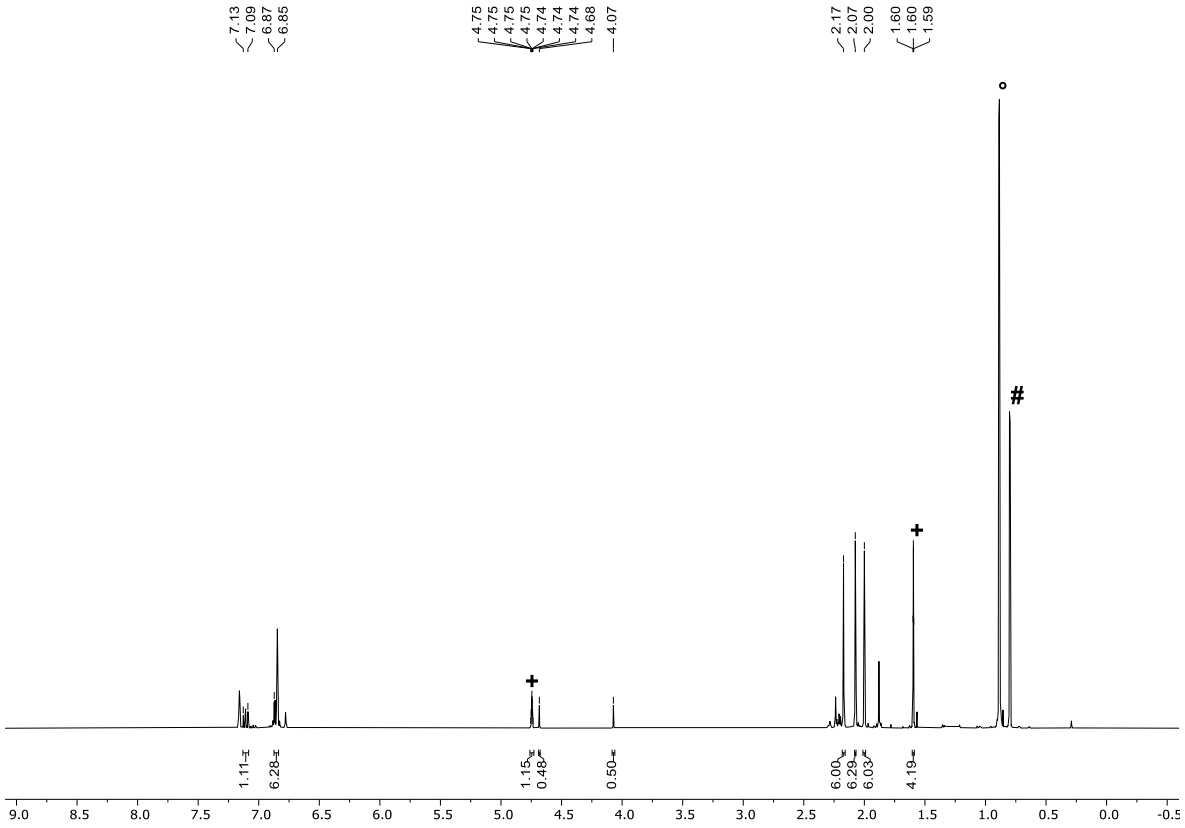


Figure S34: $^{13}C\{^1H\}$ NMR spectrum of the product mixture after 16 h at 80 °C (75 MHz, C_6D_6, rt); #: PMe_3, °: *tert*-butyl isocyanide (**2a**), +: *iso*-butene.

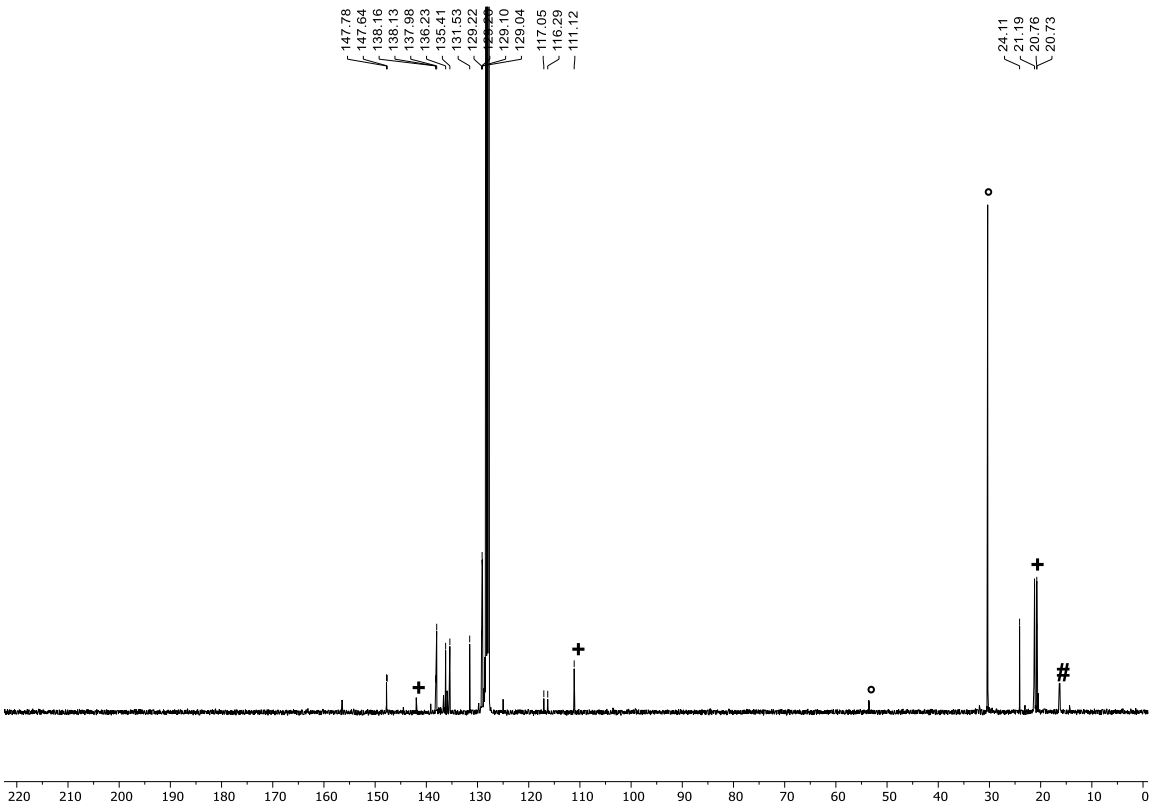


Figure S35: $^{31}P\{^1H\}$ spectrum and excerpt of the ^{31}P NMR spectrum of the product mixture after 16 h at 80 °C (122 MHz, C_6D_6, rt); #: PMe_3, +: $(^{Mes}TerP)_2$.

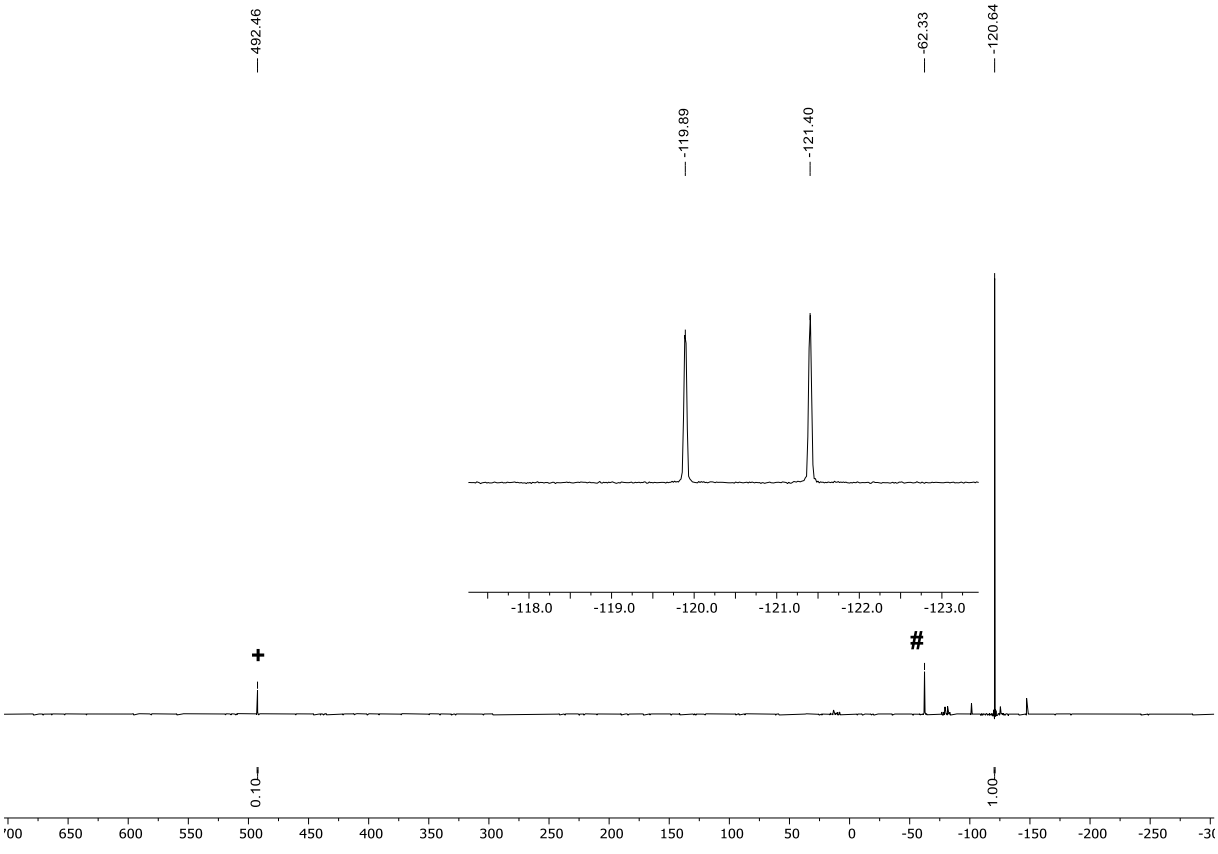


Figure S36: ^{1}H NMR spectrum of TerP(H)C≡N (**4b**) (300 MHz, C_6D_6, rt).

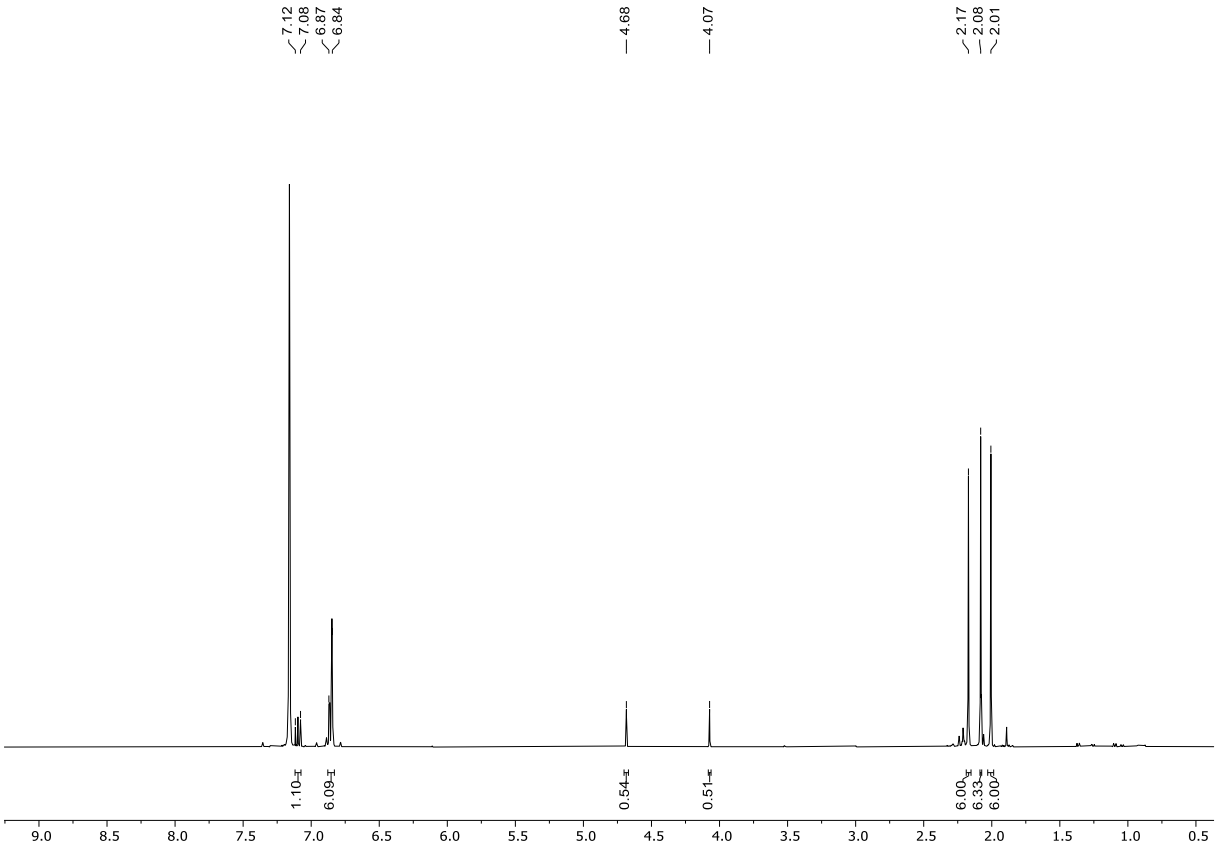
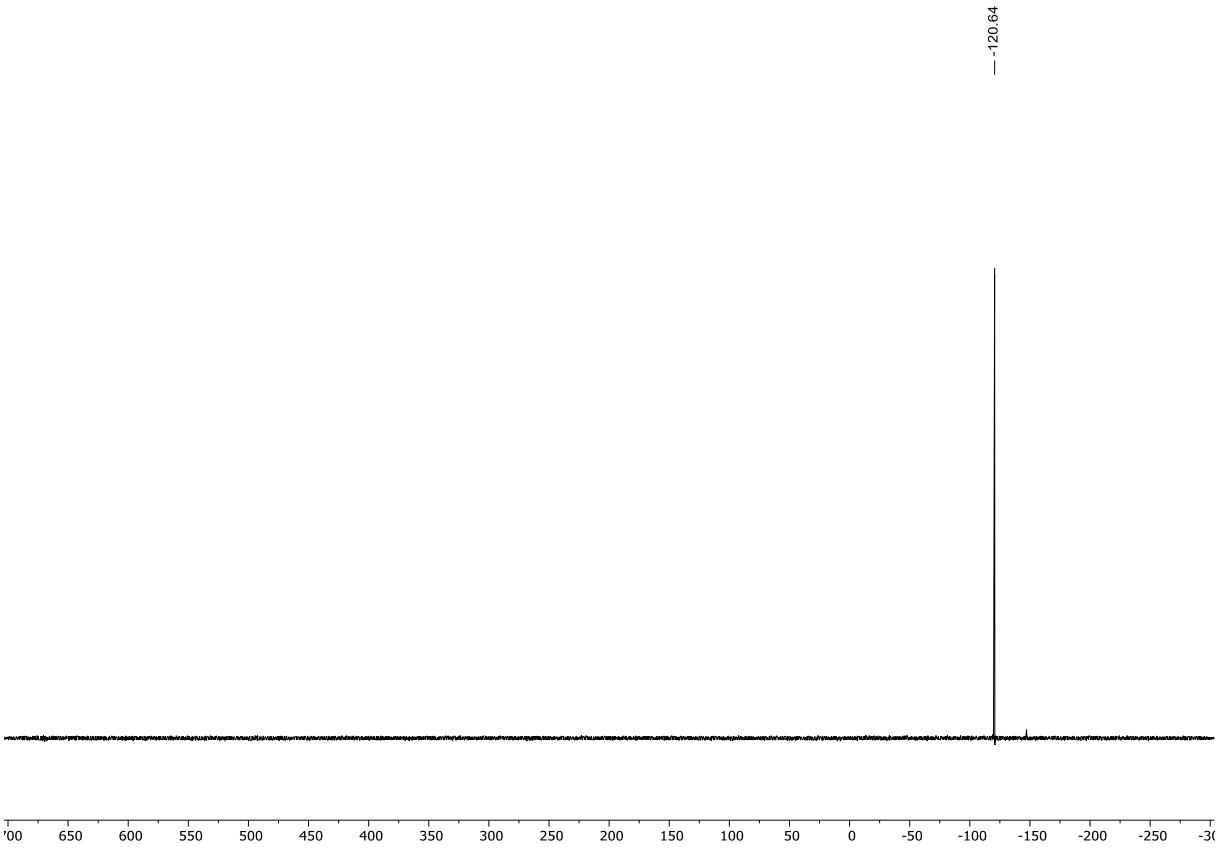
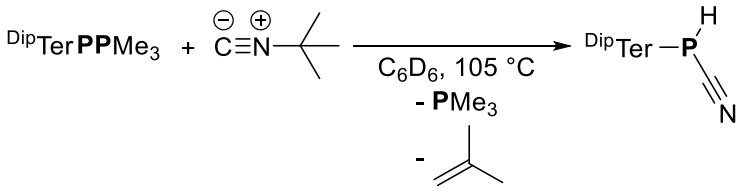


Figure S37: $^{31}P\{^{1}H\}$ spectrum of TerP(H)C≡N (**4b**) (122 MHz, C_6D_6, rt).



3.9 Synthesis of ^{Dip}TerP(H)CN (4c)



^{Dip}TerPPMe$_3$ (**1c**) (0.100 g, 0.198 mmol) was dissolved in 2 mL of toluene. *tert*-Butyl isocyanide (**2a**) (0.016 g, 0.198 mmol) in 1 mL of toluene was added and the reaction mixture was stirred for two days at 105 °C. All volatile components were removed under vacuum and the residue was washed with small amounts of *n*-pentane. Subsequent drying under vacuum yielded ^{Dip}TerP(H)C≡N (**4c**) as a colorless solid.

Crystals of **4c** suitable for SC-XRD were obtained from a saturated solution of **4c** in *n*-pentane at −30 °C.

Yield: 0.064 g (0.140 mmol; 71%).

CHN: calculated: C 81.72, H 8.41, N 3.07; found: C 81.68, H 8.40, N 3.07.**^{1}H NMR** (300 MHz, C_6D_6, 298 K): δ = 0.98-1.02 (m, 12H, CH(C*H*$_3$)$_2$), 1.29 (d, $^3J_{H,H}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.35 (d, $^3J_{H,H}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 2.57 (hept, $^3J_{H,H}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 2.71 (hept, $^3J_{H,H}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 4.35 (d, $^1J_{P,C}$ = 247.2 Hz, 1H, PH), 7.09-7.11 (m, 3H, CH$_{Aryl}$), 7.14-7.20 (m, 4H, CH$_{Aryl}$)*, 7.27-7.32 (m, 2H, CH$_{Aryl}$) ppm. * = overlap with C_6D_5H signal. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, 298 K): δ = 23.2 (d, $J_{P,C}$ = 2.4 Hz, CH(C̲H$_3$)$_2$), 23.4 (d, $J_{P,C}$ = 1.6 Hz, CH(C̲H$_3$)$_2$), 25.6 (CH(C̲H$_3$)$_2$), 25.8 (CH(C̲H$_3$)$_2$), 31.3 (C̲H(CH$_3$)$_2$), 31.4 (d, $J_{P,C}$ = 1.4 Hz, C̲H(CH$_3$)$_2$), 116.6 (d, $^1J_{P,C}$ = 75.3 Hz, PC≡N), 123.7 (d, $J_{P,C}$ = 3.9 Hz, CH$_{Aryl}$), 126.5 (d, $J_{C,P}$ = 4.6 Hz, C$_{q,Aryl}$), 129.7 (CH$_{Aryl}$), 129.8 (CH$_{Aryl}$), 130.4 (d, $J_{P,C}$ = 2.2 Hz, CH$_{Aryl}$), 138.2 (d, $J_{P,C}$ = 3.2 Hz, C$_{q,Aryl}$), 146.6 (d, $J_{P,C}$ = 14.4 Hz, C$_{q,Aryl}$), 146.8 (d, $^1J_{P,C}$ = 61.1 Hz, C$_q$P) ppm. **^{31}P{^{1}H}/^{31}P NMR** (122 MHz, C_6D_6, 298 K): δ = −120.4 (d, $^1J_{P,H}$ = 247.2 Hz) ppm. **IR** (ATR, 32 scans, cm^{-1}): ν = 2962 (s), 2929 (m), 2867 (w), 2310 (w), 1592 (w), 1567 (w), 1458 (m), 1443 (m), 1384 (m), 1363 (m), 1345 (w), 1324 (w), 1249 (w), 1198 (m), 1176 (w), 1118 (w), 1104 (w), 1086 (w), 1056 (m), 1039 (w), 1020 (w), 936 (w), 917 (w),907 (w),

824 (m), 806 (m), 795 (m), 778 (w), 758 (s), 703 (w), 688 (w), 625 (w), 587 (w), 574 (w), 498 (s), 466 (m), 443 (m).

MS (CI): expected: m/z = 456 $[M+H]^+$; found: m/z = 456 $[M+H]^+$.

Figure S38: ^{1}H NMR spectrum of ^{Dip}TerP(H)C≡N (**4c**) (300 MHz, C_6D_6, rt).

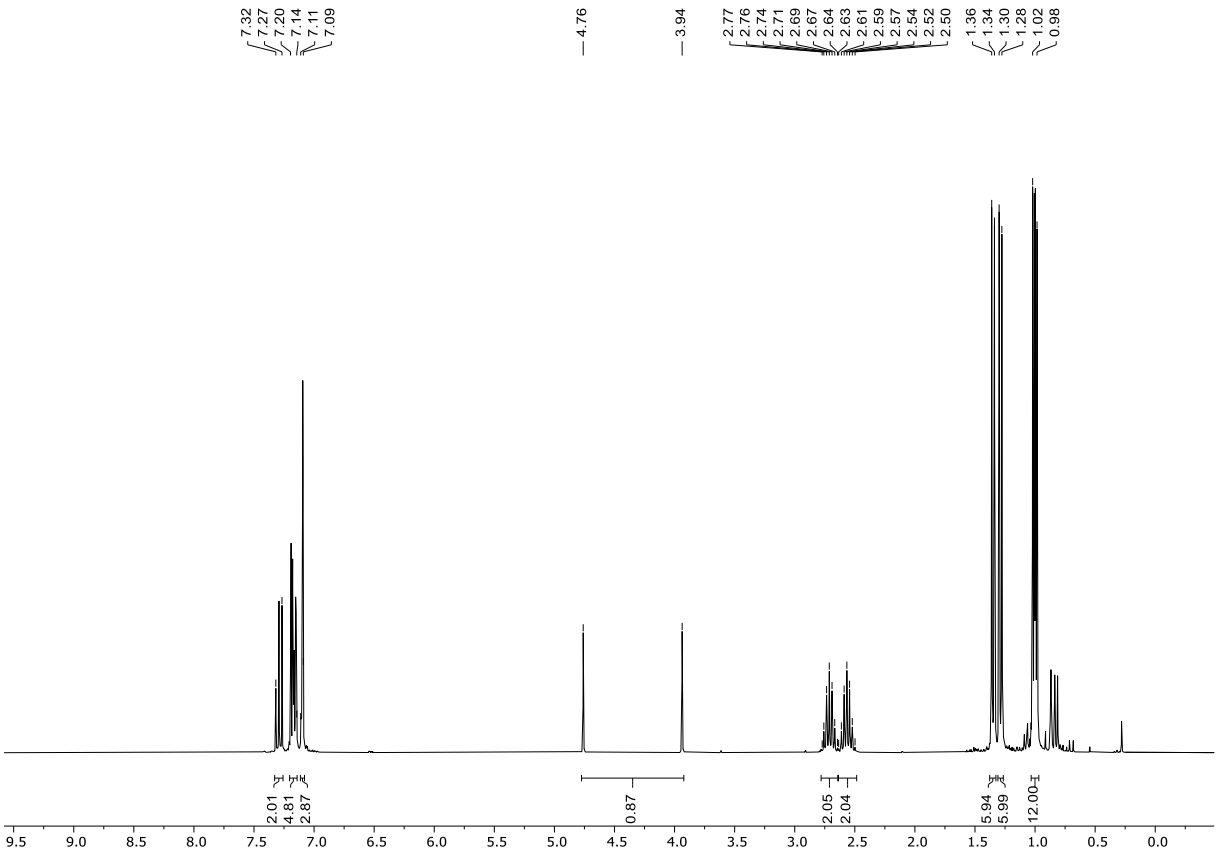


Figure S39: $^{13}C\{^{1}H\}$ NMR spectrum of ^{Dip}TerP(H)C≡N (**4c**) (75 MHz, C_6D_6, rt).

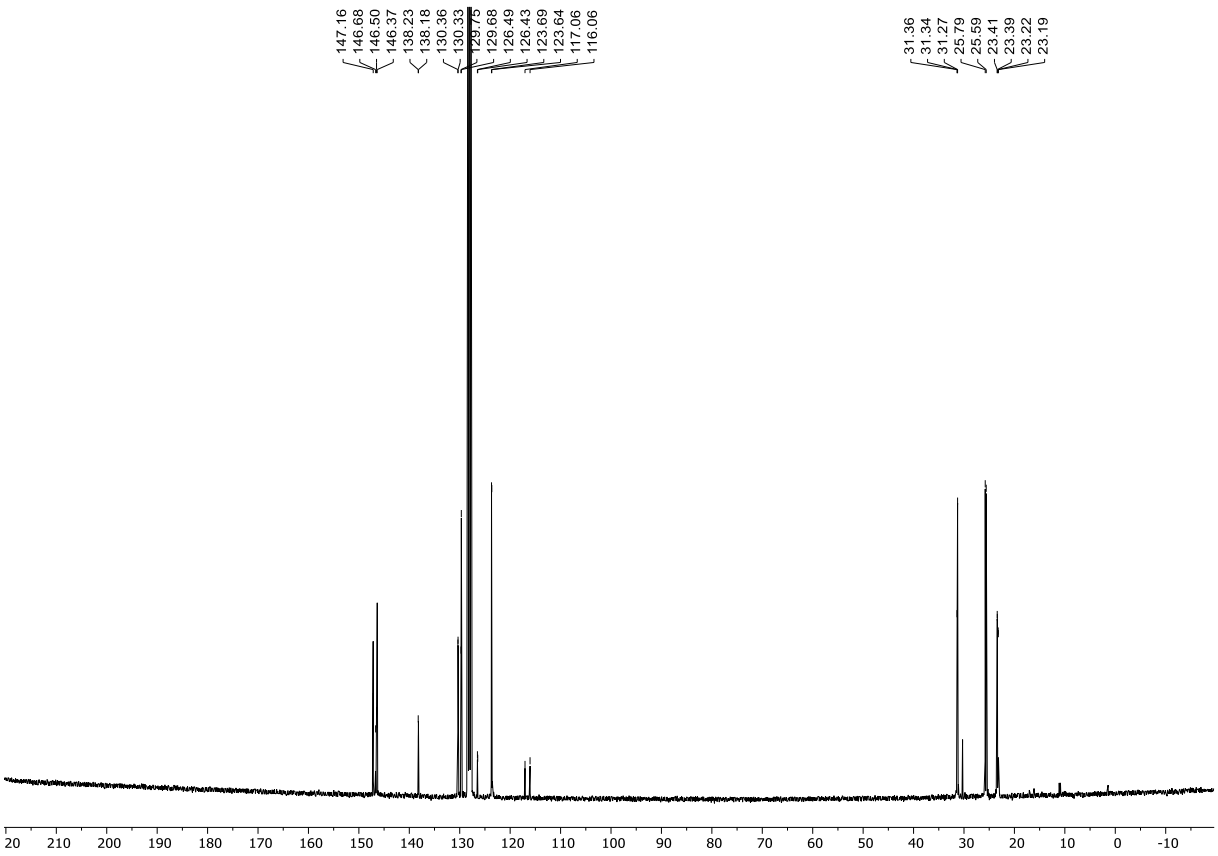
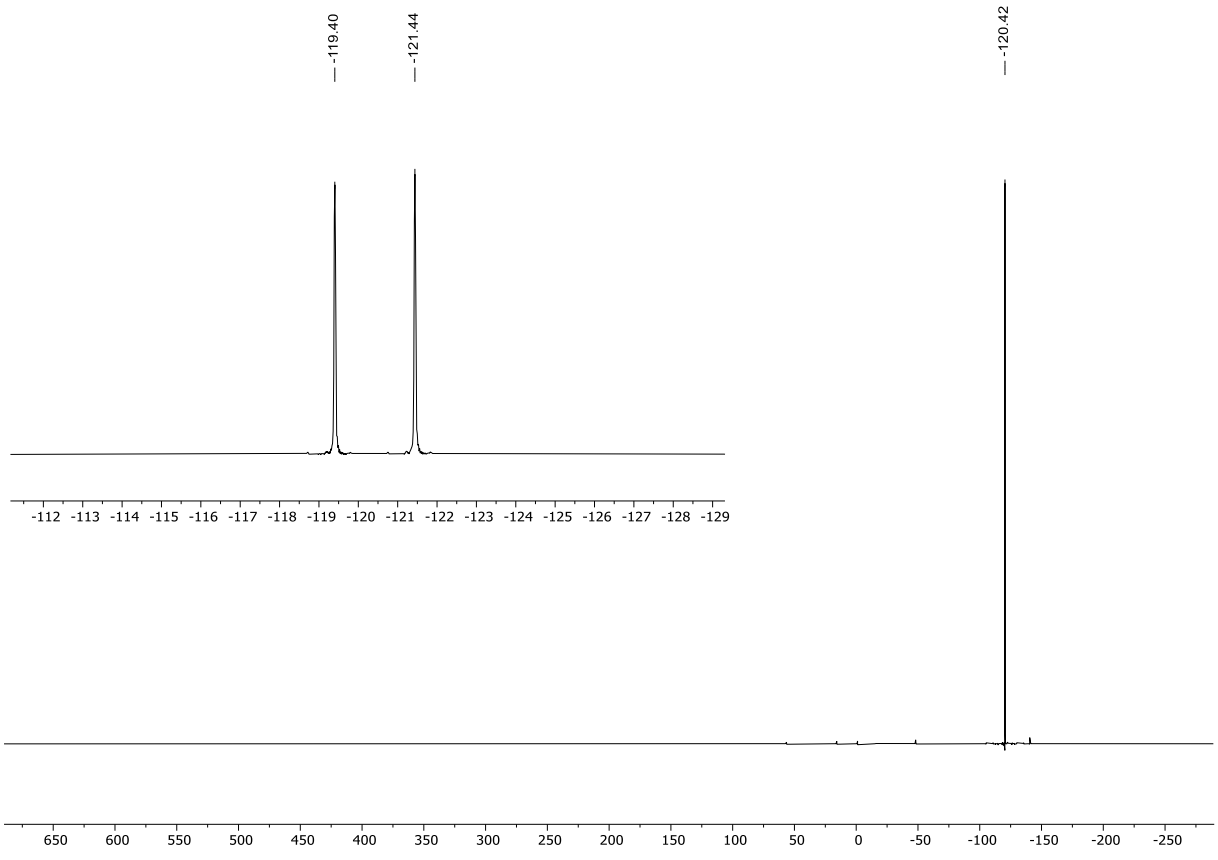
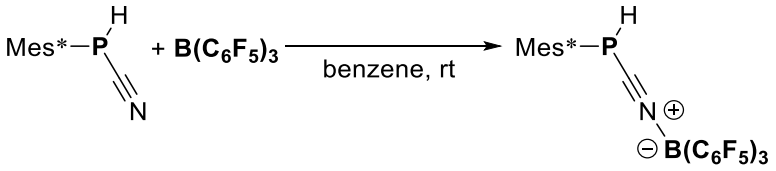


Figure S40: $^{31}P\{^{1}H\}$ and ^{31}P NMR spectrum of ^{Dip}TerP(H)C≡N (**4c**) (122 MHz, C_6D_6, rt).



3.10 Synthesis of Mes*P(H)CNB(C_6F_5)$_3$ (5a)



A) Mes*P(H)C≡N (**4a**) (0.020 g, 0.066 mmol) and B(C_6F_5)$_3$ (0.034 g, 0.066 mmol) were dissolved in 0.6 mL of C_6D_6 and subsequently analyzed by NMR spectroscopy revealing clean conversion of both starting materials to give Mes*P(H)C≡N–B(C_6F_5)$_3$ (**5a**).

B) Mes*P(H)C≡N (**4a**) (0.047 g, 0.155 mmol) and B(C_6F_5)$_3$ (0.079 g, 0.155 mmol) were dissolved in 2 mL of benzene and stirred for 2 h at room temperature. All volatile components were removed under vacuum and the residue was washed with *n*-pentane (3×2 mL). The remaining colorless solid was dried under vacuum to give Mes*P(H)C≡N–B(C_6F_5)$_3$ (**5a**). The combined wash solutions were concentrated to incipient crystallization and stored at 4 °C to give a second crystalline fraction of **5a**. These crystals were suitable for SC-XRD.

Yield: 0.069 g (0.085 mmol; 55% (Route **B**)).

EA: calculated: C 54.50, H 3.71, N 1.72; found: C 54.24, H 3.72, N 1.52. **^{1}H NMR** (300 MHz, C_6D_6, 298 K): δ = 1.18 (s, 9H, *p*-$C_q(CH_3)_3P$), 1.24 (s, 18H, *o*-$C_q(CH_3)_3P$), 5.61 (d, $^1J_{P,H}$ = 260.1 Hz, 1H, PH), 7.48-7.49 (m, 2H, CH_{Aryl}) ppm. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, 298 K): δ = 30.8 (*p*-$C_q(\underline{C}H_3)_3P$), 33.1 (d, $J_{P,C}$ = 6.4 Hz, *o*-$C_q(\underline{C}H_3)_3P$), 35.5 (*p*-$\underline{C}_q(CH_3)_3P$), 37.8 (*o*-$\underline{C}_q(CH_3)_3P$), 110.6 (d, $^1J_{P,C}$ = 23.8 Hz, C_qP), 115.7 (m(br), $B(\underline{C}_qC_5F_5)_3$), 121.0 (d, $^1J_{P,C}$ = 106.8 Hz, PC≡N), 124.2 (d, $^3J_{P,C}$ = 5.0 Hz, CH_{Aryl}), 137.7 (dm, $^1J_{F,C}$ = 243.7 Hz, $B(C_q\underline{C}_5F_5)_3$), 141.0 (dm, $^1J_{F,C}$ = 240.4 Hz, $B(C_q\underline{C}_5F_5)_3$), 148.5 (dm, $^1J_{F,C}$ = 243.2 Hz, $B(C_q\underline{C}_5F_5)_3$), 155.8 (*p*-$C_{q,Aryl}P$), 158.2 (d, $^2J_{P,C}$ = 11.7 Hz, *o*-$C_{q,Aryl}P$) ppm. **^{11}B{^{1}H} NMR** (96 MHz, C_6D_6, 298 K): δ = -10.3 ppm. **^{19}F{^{1}H} NMR** (282 MHz, C_6D_6, 298 K): δ = −133.8 to −134.0 (m, 6F, *m*-$F_{Ar}B$), −155.8 (t, $^3J_{F,F}$ = 20.8 Hz, 3F, *p*-$F_{Ar}B$), −163.3 to −163.5 (m, 6F, *o*-$F_{Ar}B$), ($\Delta\delta^{19}F_{m,p}$ = 7.6 Hz) ppm. **^{31}P{^{1}H}/^{31}P NMR** (122 MHz, C_6D_6, 298 K): δ = −99.2 ($^1J_{P,H}$ = 260.0 Hz) ppm. **IR** (ATR, 32 scans, cm^{-1}): ν = 2971 (w), 2910 (w), 2876 (w),

2265 (w), 1645 (w), 1596 (w), 1567 (w), 1516 (m), 1461 (s), 1416 (w), 1395 (w), 1383 (w), 1366 (w), 1286 (m), 1239 (w), 1212 (w), 1192 (w), 1101 (m), 1031 (w), 975 (s), 926 (w), 905 (w), 882 (w), 867 (w), 805 (s), 772 (m), 758 (s), 740 (m), 731 (w), 723 (w), 681 (s), 654 (w), 616 (w), 600 (w), 577 (w), 498 (w), 475 (w), 446 (w).

Figure S41: ^{1}H NMR spectrum of Mes*P(H)C≡N–B(C_6F_5)$_3$ (**5a**) (300 MHz, C_6D_6, rt).

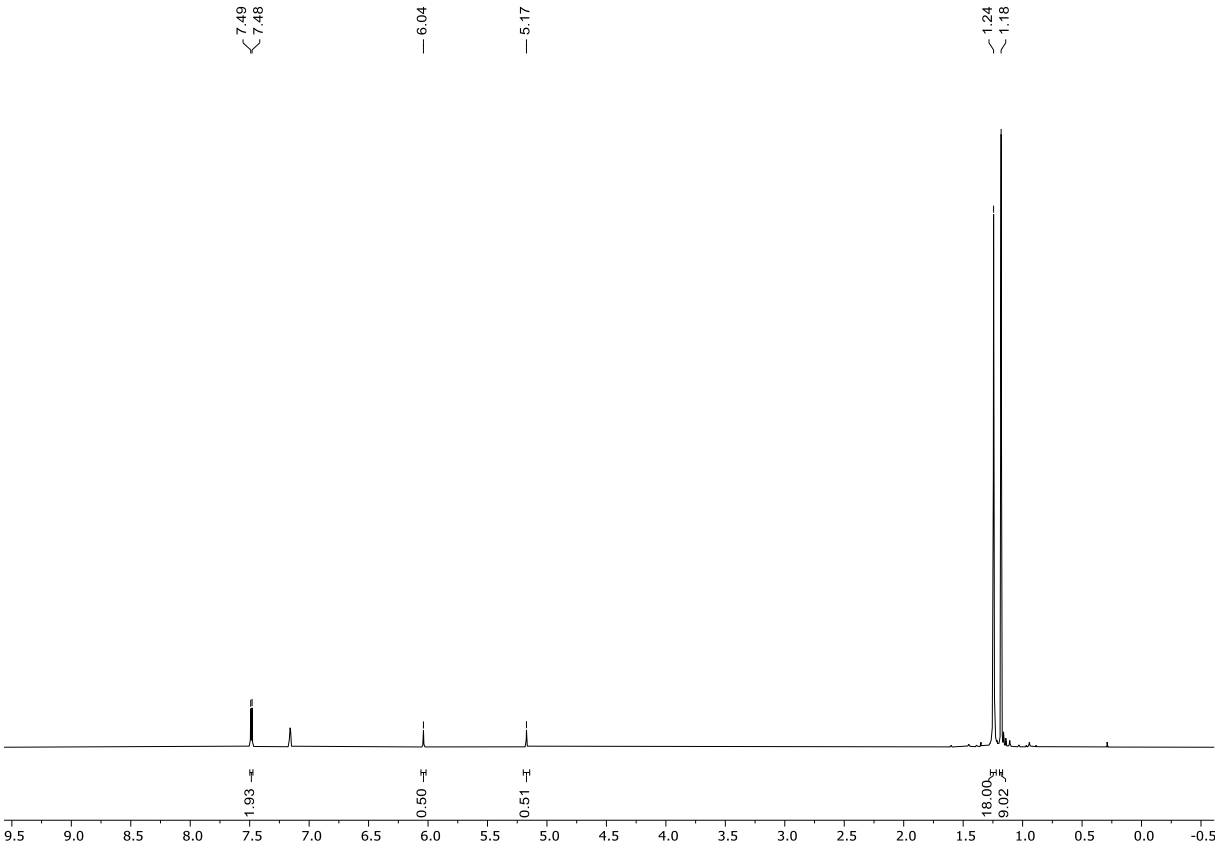


Figure S42: $^{13}C\{^{1}H\}$ NMR spectrum of compound of Mes*P(H)C≡N–B(C_6F_5)$_3$ (**5a**) (75 MHz, C_6D_6, rt).

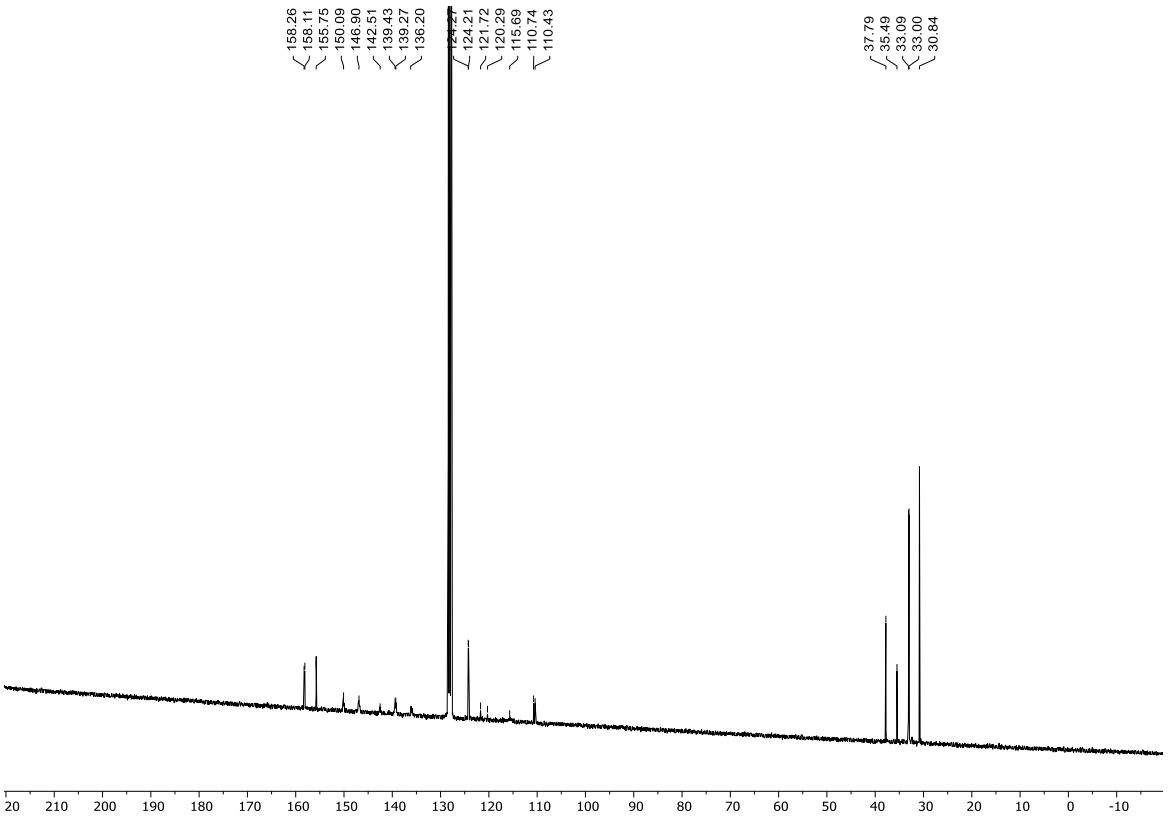


Figure S43: $^{11}B\{^{1}H\}$ NMR spectrum of Mes*P(H)C≡N–B(C_6F_5)$_3$ (**5a**) (96 MHz, C_6D_6, rt).

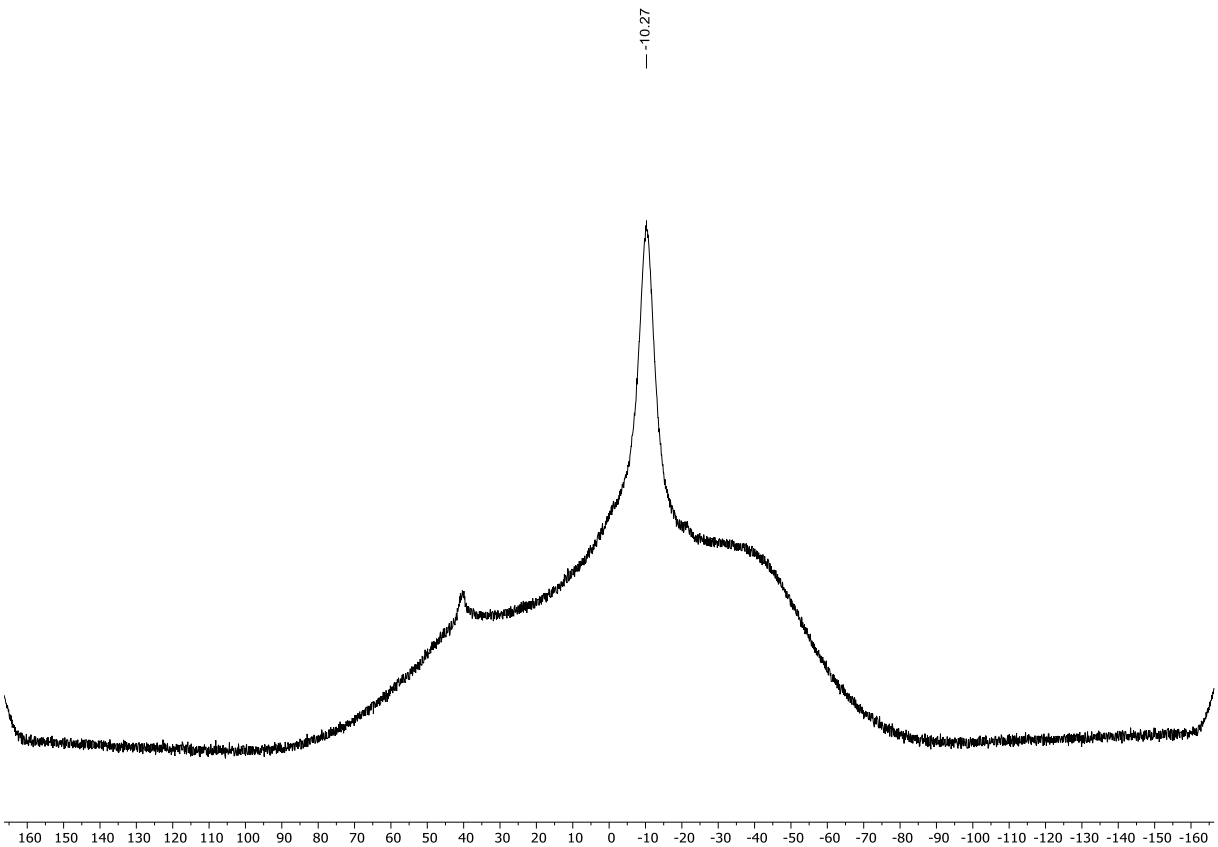


Figure S44: $^{19}F\{^{1}H\}$ NMR spectrum of Mes*P(H)C≡N–B(C_6F_5)$_3$ (**5a**) (282 MHz, C_6D_6, rt).

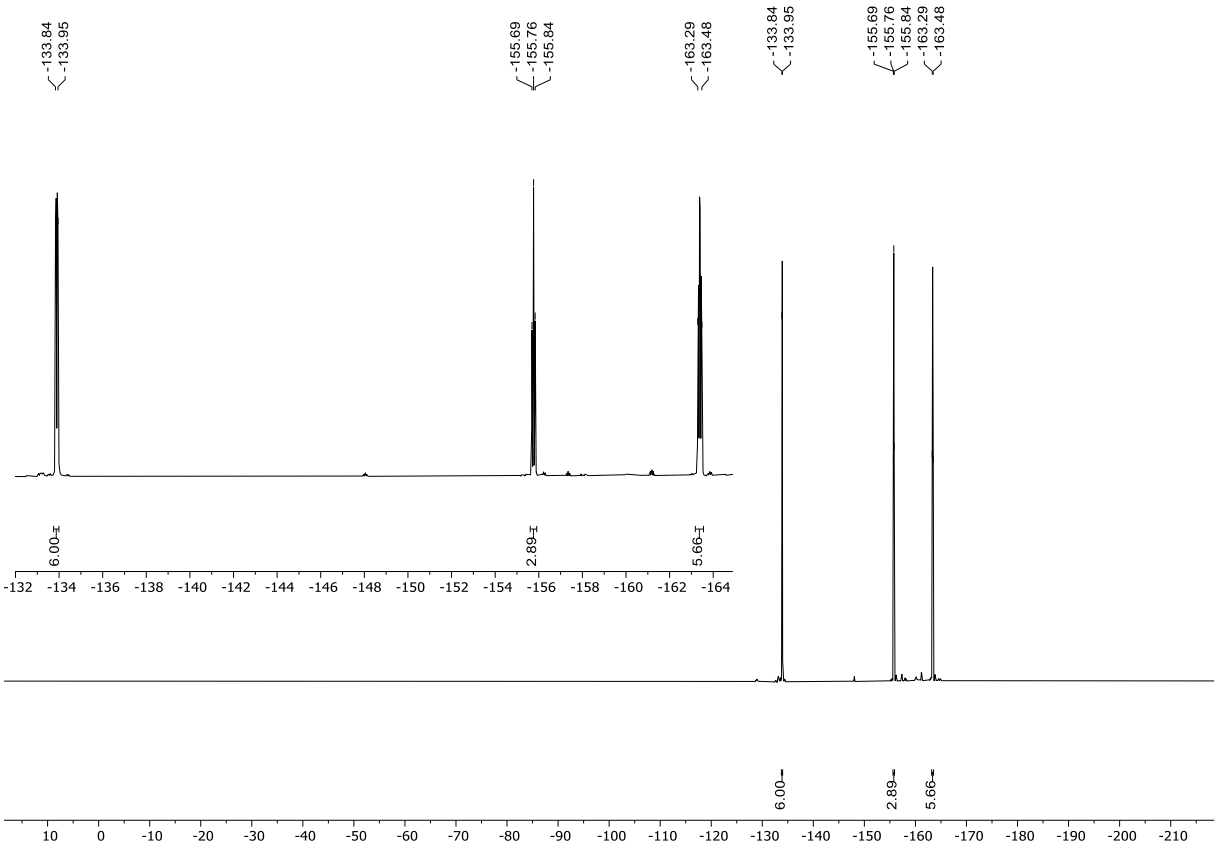
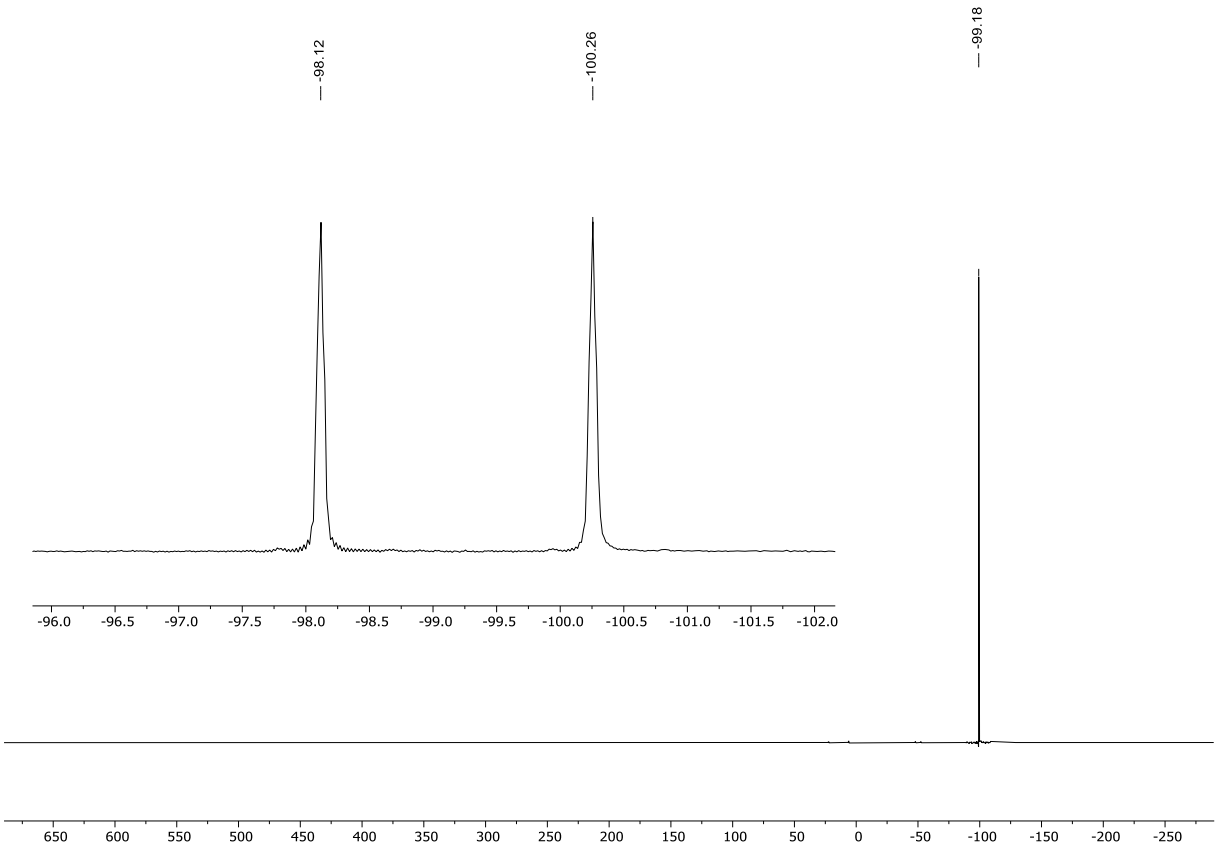
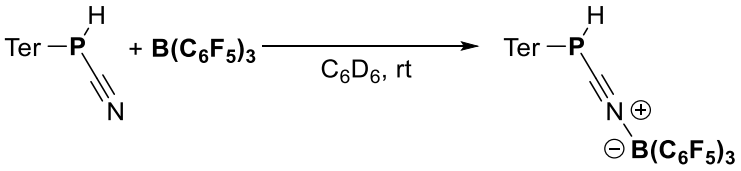


Figure S45: $^{31}P\{^{1}H\}$ and ^{31}P NMR spectra of Mes*P(H)C≡N–B(C_6F_5)$_3$ (**5a**) (122 MHz, C_6D_6, rt).



3.11 Synthesis of ^{Mes}TerP(H)CNB(C_6F_5)$_3$ (5b)



^{Mes}TerP(H)C≡N (**4b**) (0.030 g, 0.081 mmol) and B(C_6F_5)$_3$ (0.041 g, 0.081 mmol) were dissolved in 0.6 mL of C_6D_6 and subsequently analyzed by NMR spectroscopy revealing clean conversion of both starting materials to give ^{Mes}TerP(H)C≡N–B(C_6F_5)$_3$ (**5b**).

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 1.61 (s(br), 6H, $CH_{3,Mes}$), 1.84 (s(br), 6H, $CH_{3,Mes}$), 2.18 (s, 6H, $CH_{3,Mes}$), 4.61 (d, $^1J_{P,H}$ = 251.1 Hz, PH), 6.70-6.79 (m(br), 6H, CH_{Aryl}), 6.99-7.04 (m(br), 1H, CH_{Aryl}) ppm. **^{11}B{^{1}H} NMR** (96 MHz, C_6D_6, 298 K): δ = −9.8 ppm. **^{19}F{^{1}H} NMR** (282 MHz, C_6D_6, 298 K): δ = −133.5 to −133.6 (m, 6F, *m*-F_{Ar}B), −155.7 (t, $^3J_{F,F}$ = 20.8 Hz, 3F, *p*-F_{Ar}B), −163.1 to −163.3 (m, 6F, *o*-F_{Ar}B), ($\Delta\delta^{19}F_{m,p}$ = 7.9 Hz) ppm. **^{31}P{^{1}H}/^{31}P NMR** (122 MHz, C_6D_6, 298 K): δ = −115.1 ($^1J_{P,H}$ = 250.9 Hz) ppm.

Figure S46: ^{1}H NMR spectrum of ^{Mes}TerP(H)C≡N–B(C_6F_5)$_3$ (**5b**) (300 MHz, C_6D_6, rt).

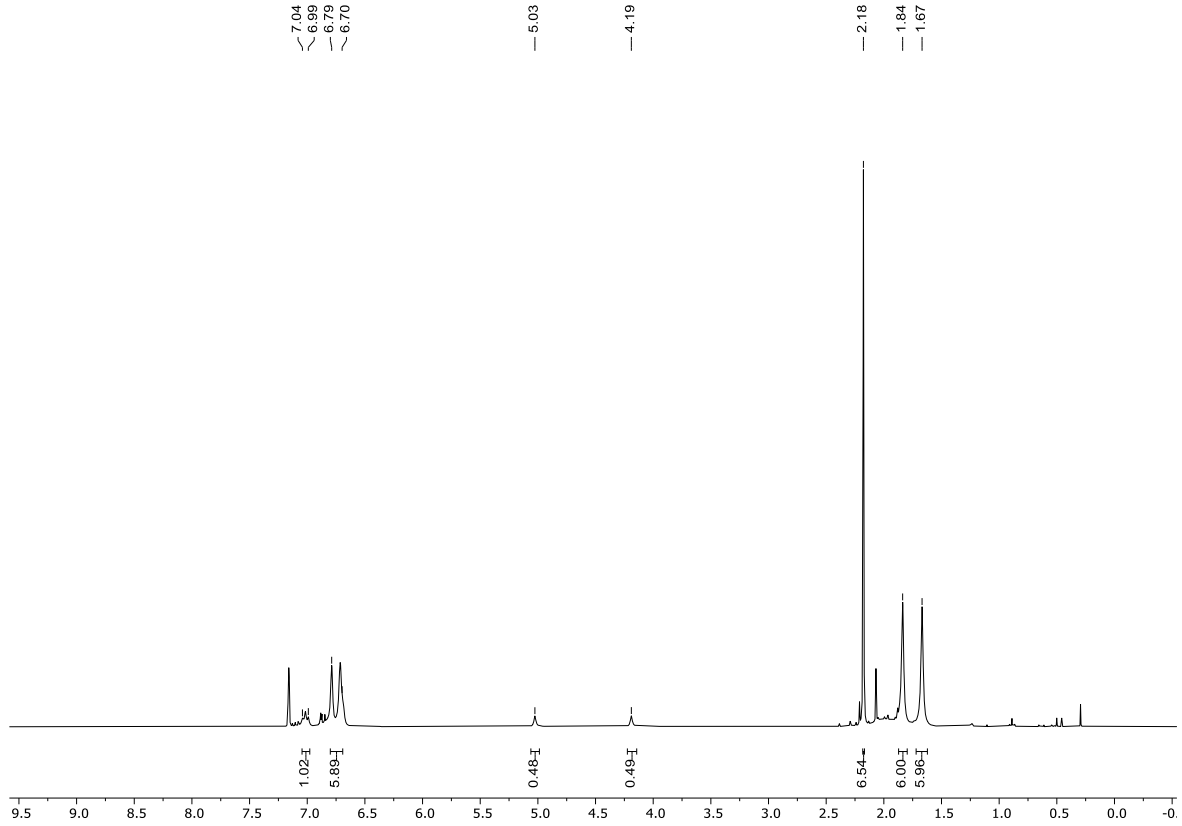


Figure S47: $^{11}B\{^1H\}$ NMR spectrum of ^{Mes}TerP(H)C≡N–B(C_6F_5)$_3$ (**5b**) (96 MHz, C_6D_6, rt).

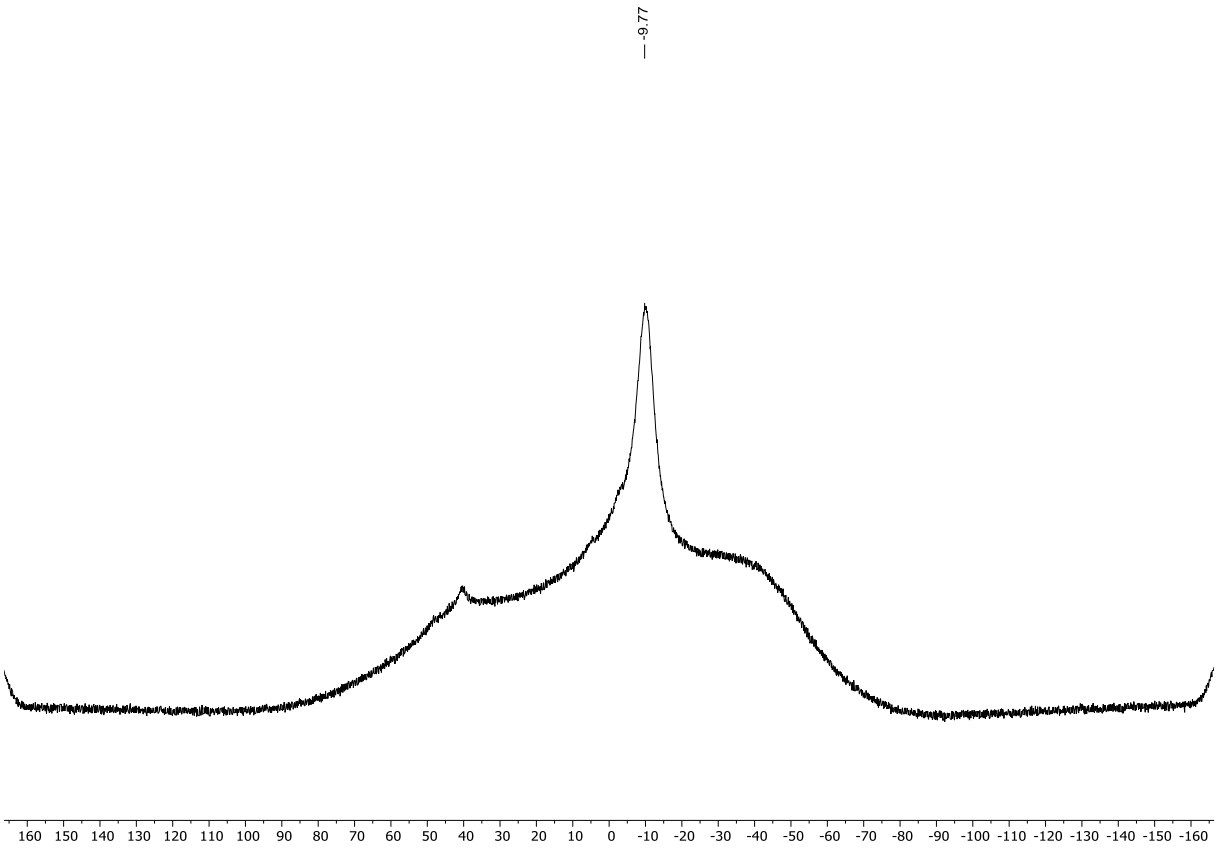


Figure S48: $^{19}F\{^1H\}$ NMR spectrum of ^{Mes}TerP(H)C≡N–B(C_6F_5)$_3$ (**5b**) (282 MHz, C_6D_6, rt).

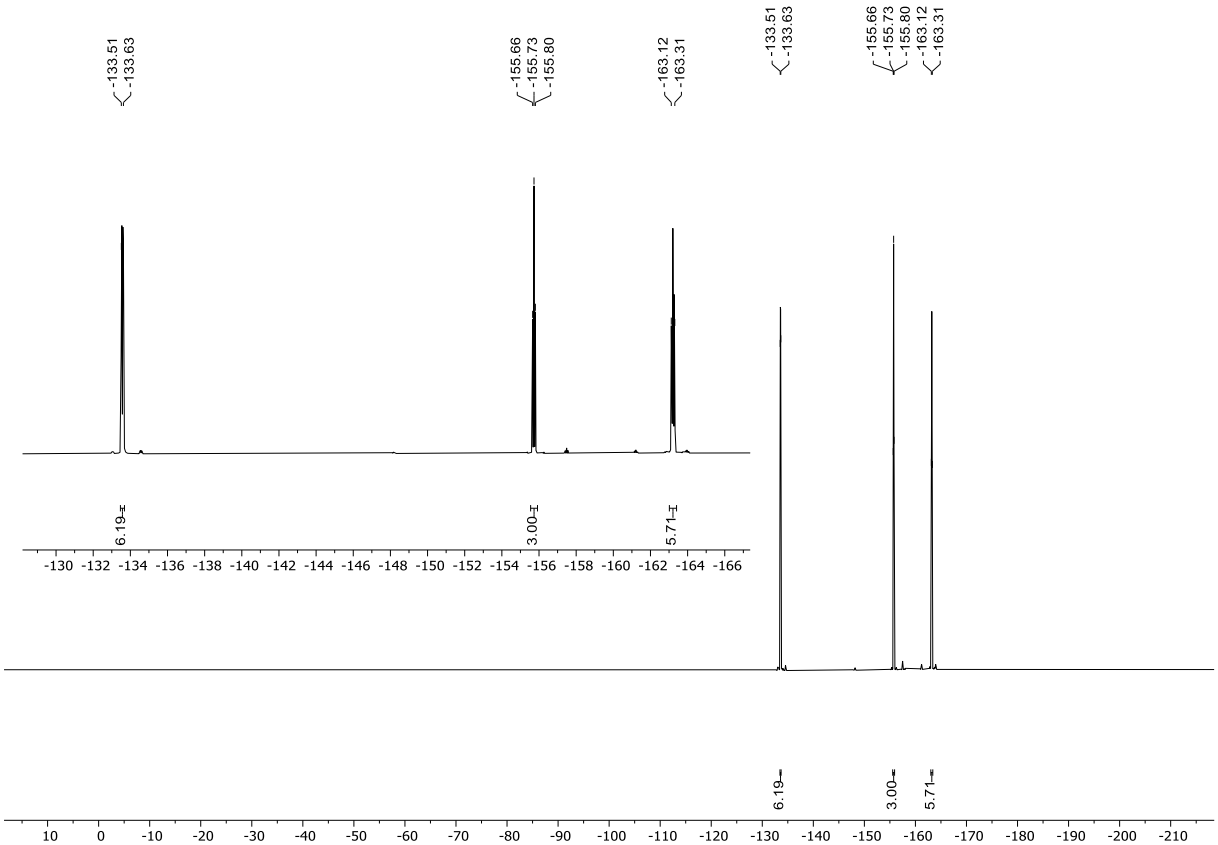
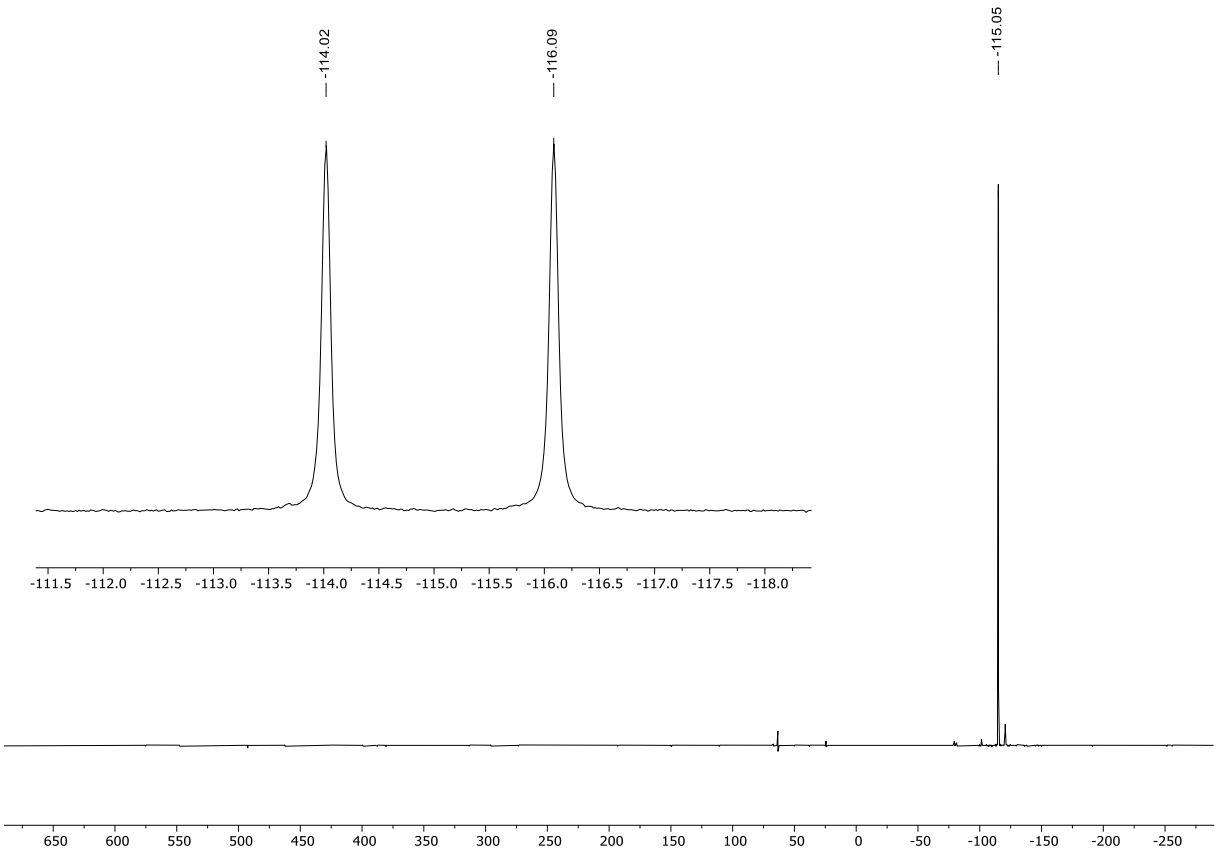
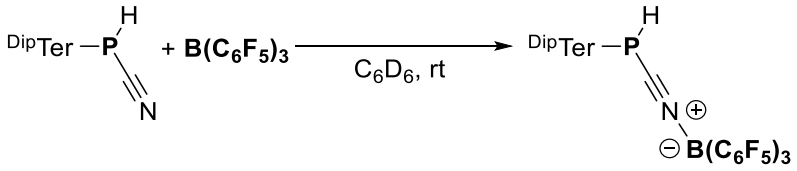


Figure S49: $^{31}P\{^{1}H\}$ and ^{31}P NMR spectra of ^{Mes}TerP(H)C≡N–B(C_6F_5)$_3$ (**5b**) (122 MHz, C_6D_6, rt).



3.12 Synthesis of ^{Dip}TerP(H)CNB(C_6F_5)$_3$ (5c)



^{Dip}TerP(H)C≡N (**4c**) (0.010 g, 0.022 mmol) and B(C_6F_5)$_3$ (0.011 g, 0.022 mmol) were dissolved in 0.6 mL of C_6D_6 and subsequently analyzed by NMR spectroscopy revealing clean conversion of both starting materials to give ^{Dip}TerP(H)C≡N–B(C_6F_5)$_3$ (**5c**).

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.85-0.95 (m, 18H, CH(C*H*$_3$)$_2$), 1.23 (d, $^3J_{P,H}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 2.28 (hept, $^3J_{H,H}$ = 6.7 Hz, 2H, C*H*(CH$_3$)$_2$), 2.56 (hept, $^3J_{H,H}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 5.03 (d, $^1J_{P,H}$ = 256.1 Hz, 1H, PH), 6.85-6.88 (m, 2H, CH$_{Aryl}$), 6.97-7.01 (m, 3H, CH$_{Aryl}$), 7.08-7.09 (m, 2H, CH$_{Aryl}$), 7.18-7.24 (m, 2H, CH$_{Aryl}$) ppm. **^{11}B{^{1}H} NMR** (96 MHz, C_6D_6, 298 K): δ = −9.9 ppm. **^{19}F{^{1}H} NMR** (282 MHz, C_6D_6, 298 K): δ = −133.5 to −133.6 (m, 6F, *m*-F$_{Ar}$B), −155.6 (m(br), 3F, *p*-F$_{Ar}$B), −163.1 to −163.3 (m, 6F, *o*-F$_{Ar}$B), ($\Delta\delta^{19}F_{m,p}$ = 7.6 ppm) ppm. **^{31}P{^{1}H}/^{31}P NMR** (122 MHz, C_6D_6, 298 K): δ = −108.3 ($^1J_{P,H}$ = 256.1 Hz) ppm.

Figure S50: ^{1}H NMR spectrum of ^{Dip}TerP(H)C≡N–B(C_6F_5)$_3$ (**5c**) (300 MHz, C_6D_6, rt).

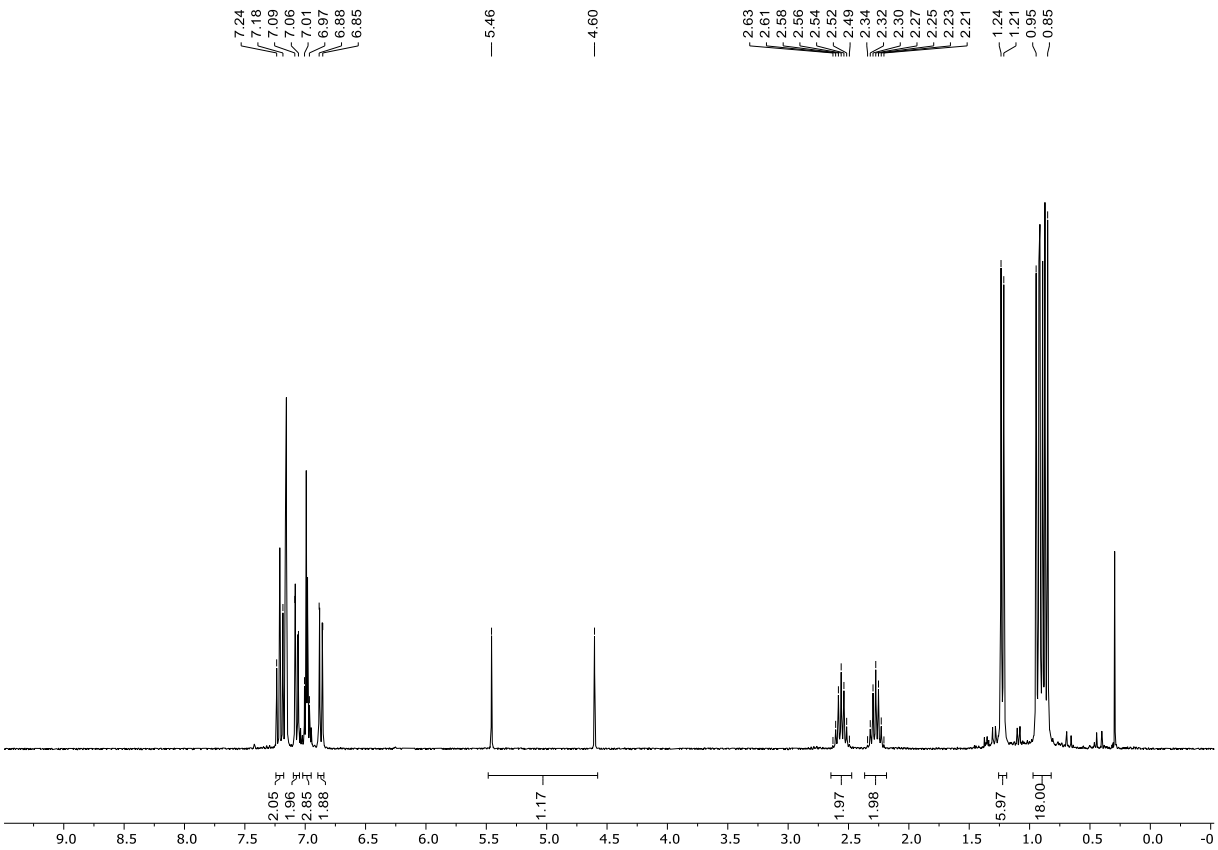


Figure S51: ^{11}B{^{1}H} NMR spectrum of ^{Dip}TerP(H)C≡N–B(C_6F_5)$_3$ (**5c**) (96 MHz, C_6D_6, rt).

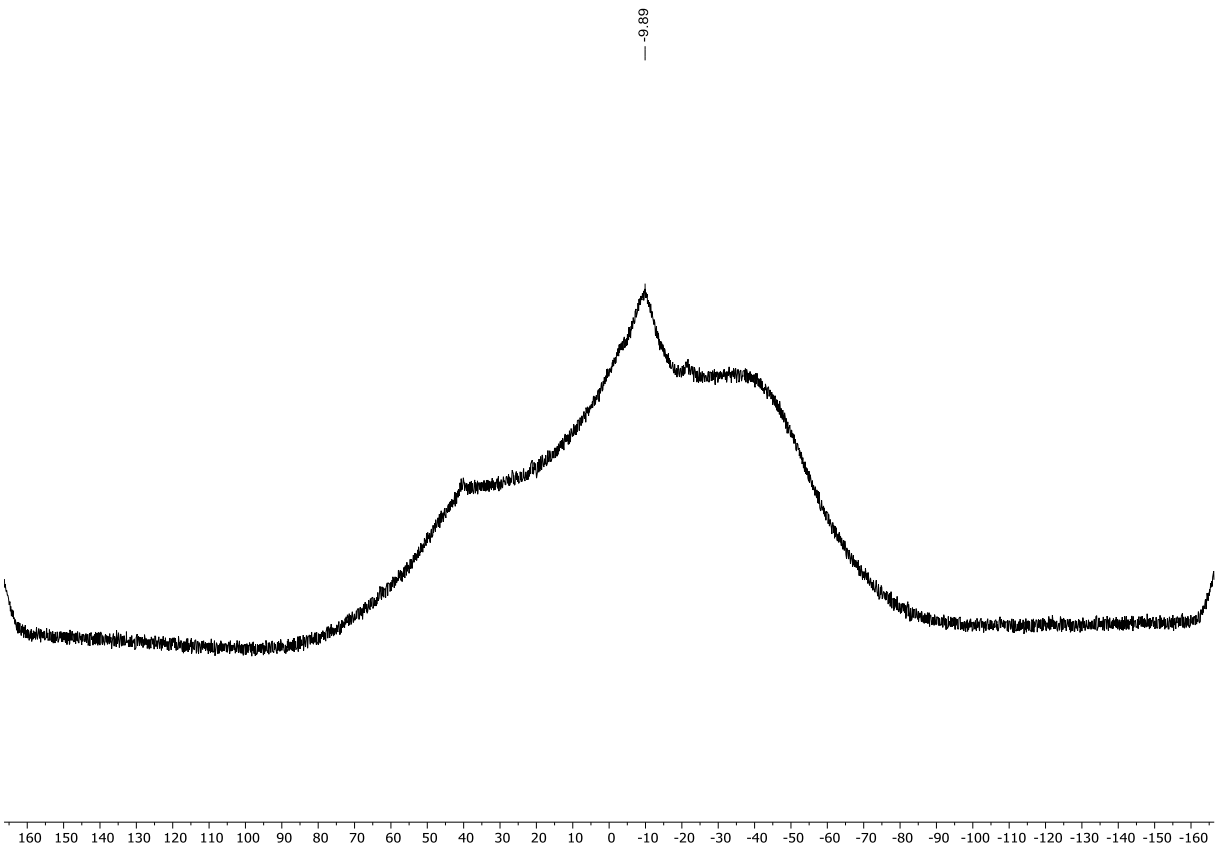


Figure S52: $^{19}F\{^{1}H\}$ NMR spectrum of ^{Dip}TerP(H)C≡N–B(C_6F_5)$_3$ (**5c**) (282 MHz, C_6D_6, rt).

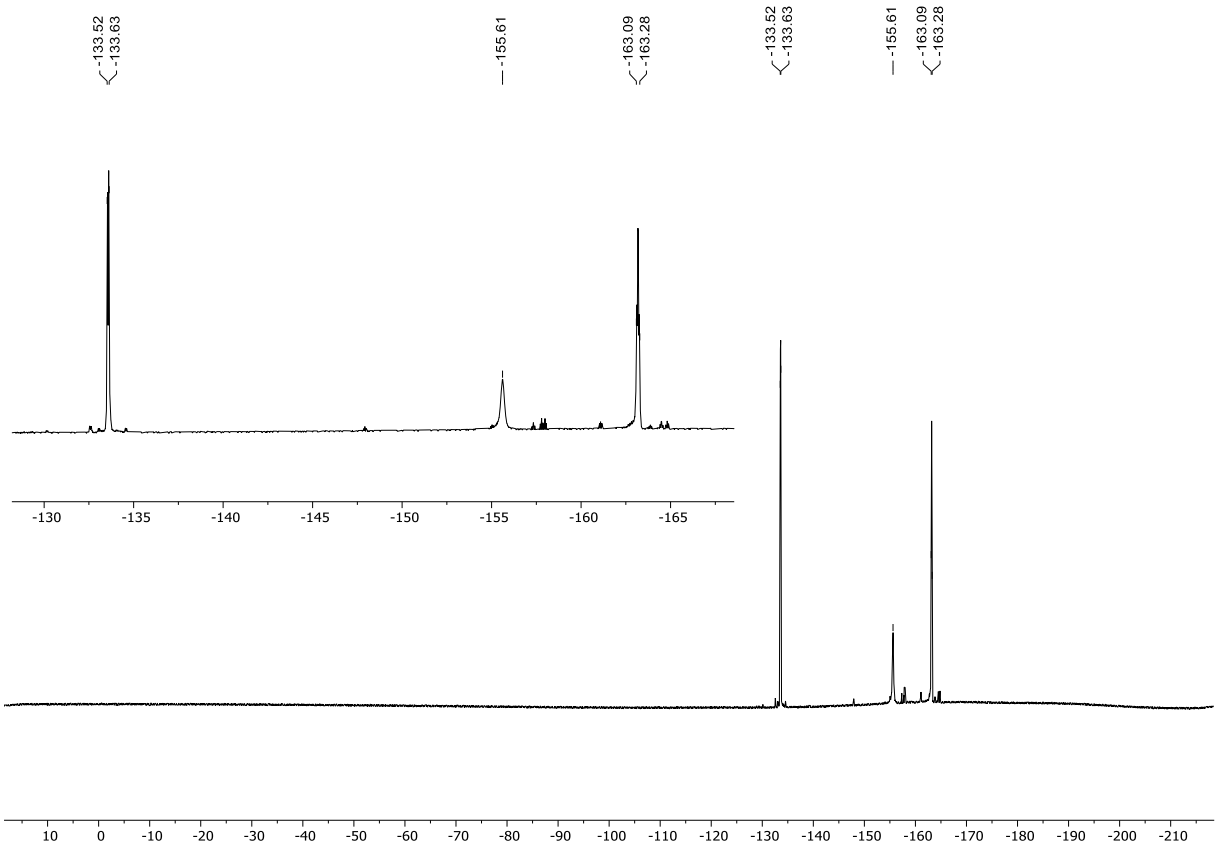
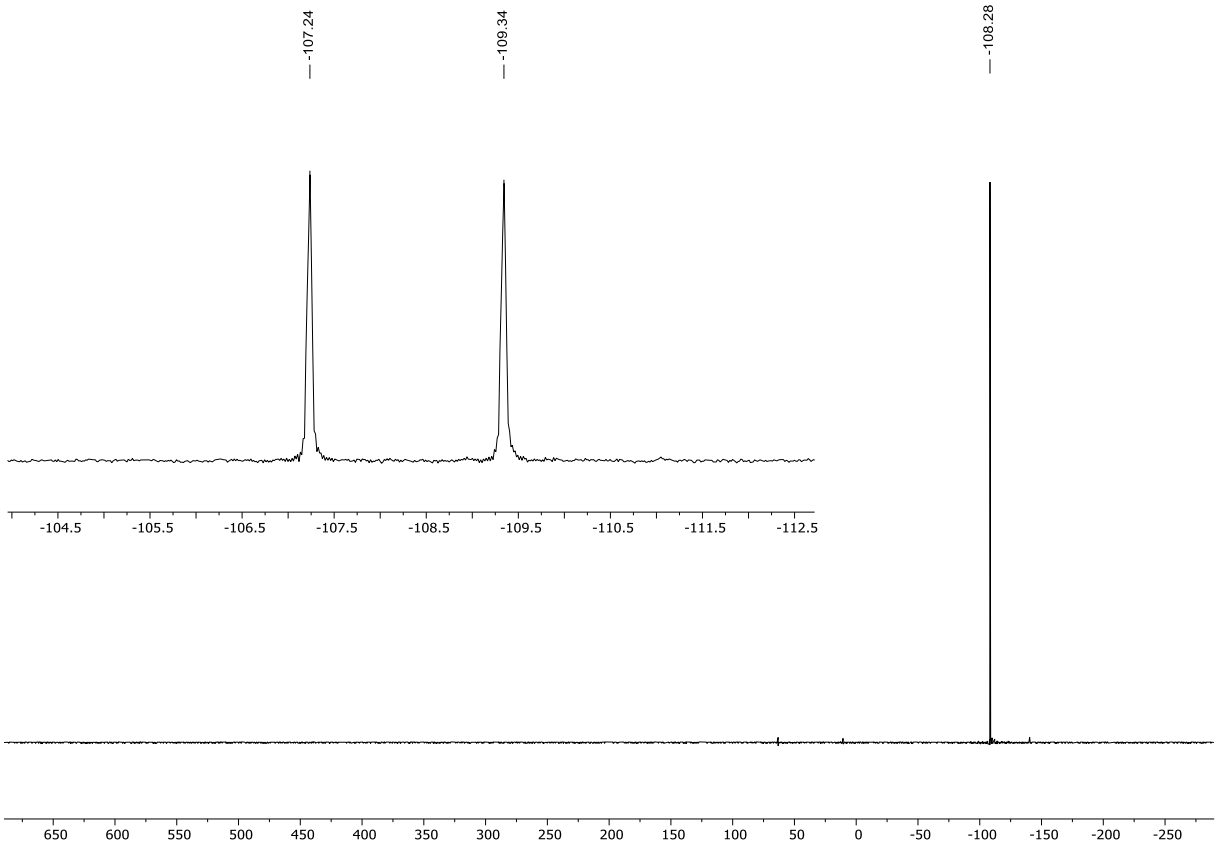
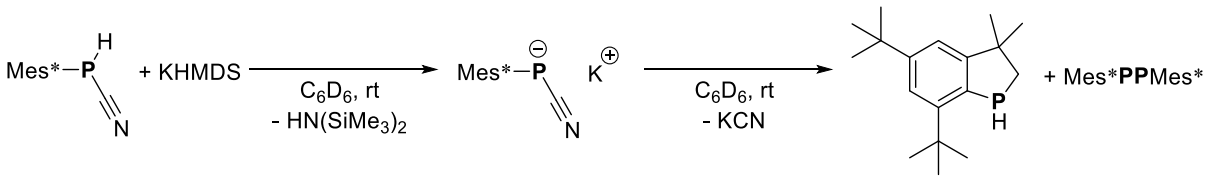


Figure S53: $^{31}P\{^{1}H\}$ and ^{31}P NMR spectra of ^{Dip}TerP(H)C≡N–B(C_6F_5)$_3$ (**5c**) (122 MHz, C_6D_6, rt).



3.13 Reaction of Mes*P(H)CN (4a) with KHMDS



Mes*P(H)C≡N (**4a**) (0.020 g, 0.066 mmol) and K[N(SiMe$_3$)$_2$] (KHMDS) (0.013 g, 0.066 mmol) were dissolved in 0.6 mL of C_6D_6 and subsequently analyzed by NMR spectroscopy revealing conversion of both starting materials to mainly give K[Mes*PCN] (**6a**) and bis(trimethylsilyl)amine ($\delta(^1H)$ = 0.10 ppm). K[Mes*PCN] is not stable in solution and slowly decomposes to mainly give the corresponding phosphaindane ($\delta^{31}P\{^1H\}$ = −79.7 ppm)[8] by intramolecular C–H activation accompanied by release of KCN, which precipitates from the reaction mixture. As another product Mes*PPMes* ($\delta(^{31}P\{^1H\})$ = 493.0 ppm) is formed. These transformations are accompanied by a color change of the solution to orange. Only the signals of K[Mes*PCN] (**6a**) are listed below.

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 1.37 (s, 9H, *p*-$C_q(CH_3)_3$), 1.97 (s, 18H, *o*-$C_q(CH_3)_3$), 7.67-7.68 (m, 2H, CH_{Aryl}) ppm. **^{31}P{^{1}H} NMR** (122 MHz, C_6D_6, 298 K): δ = −146.3 ppm.

Figure S54: Monitoring of the reaction of Mes*P(H)C≡N (**4a**) with KHMDS via ^{1}H NMR spectroscopy (300 MHz, C_6D_6, rt).

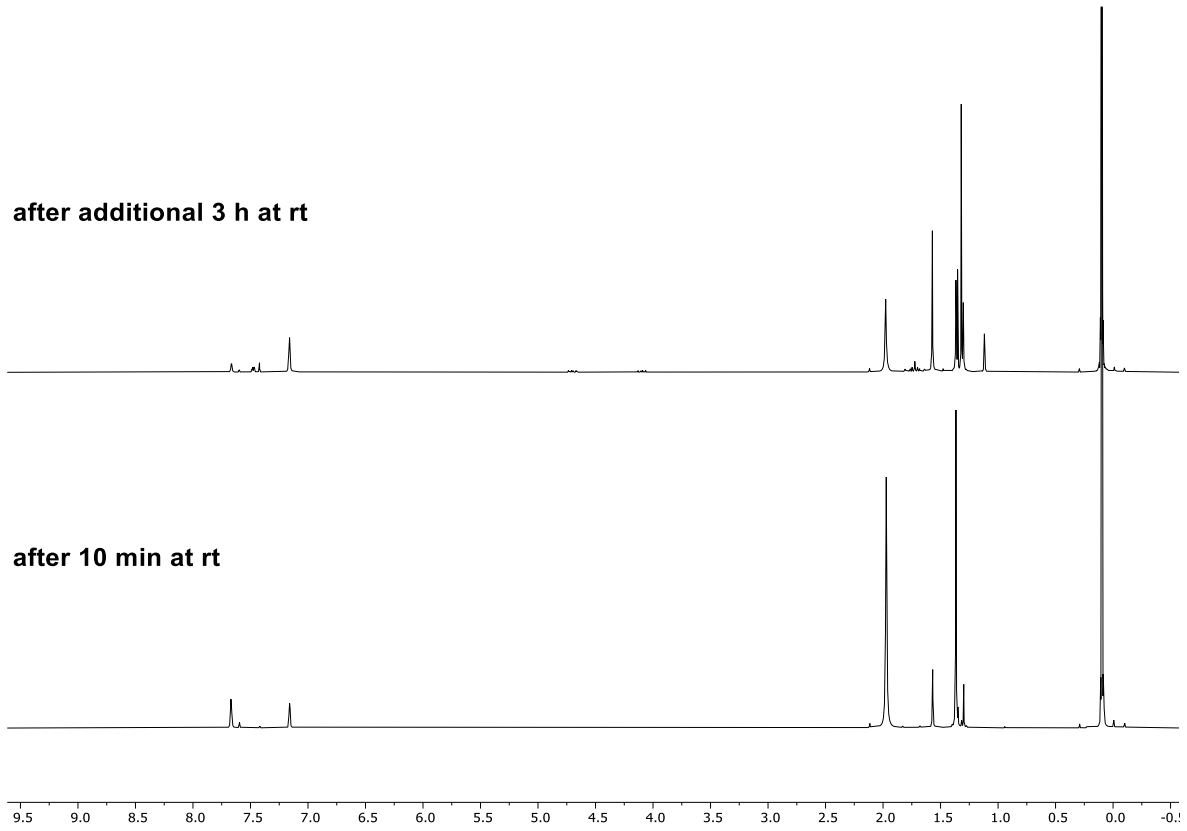


Figure S55: Monitoring of the reaction of Mes*P(H)C≡N (**4a**) with KHMDS via $^{31}P\{^{1}H\}$ NMR (122 MHz, C_6D_6, rt); -146.2 ppm: K[Mes*PCN] (**8a**), −79.7 ppm: phosphaindane, 493.2 ppm: $(Mes*P)_2$.

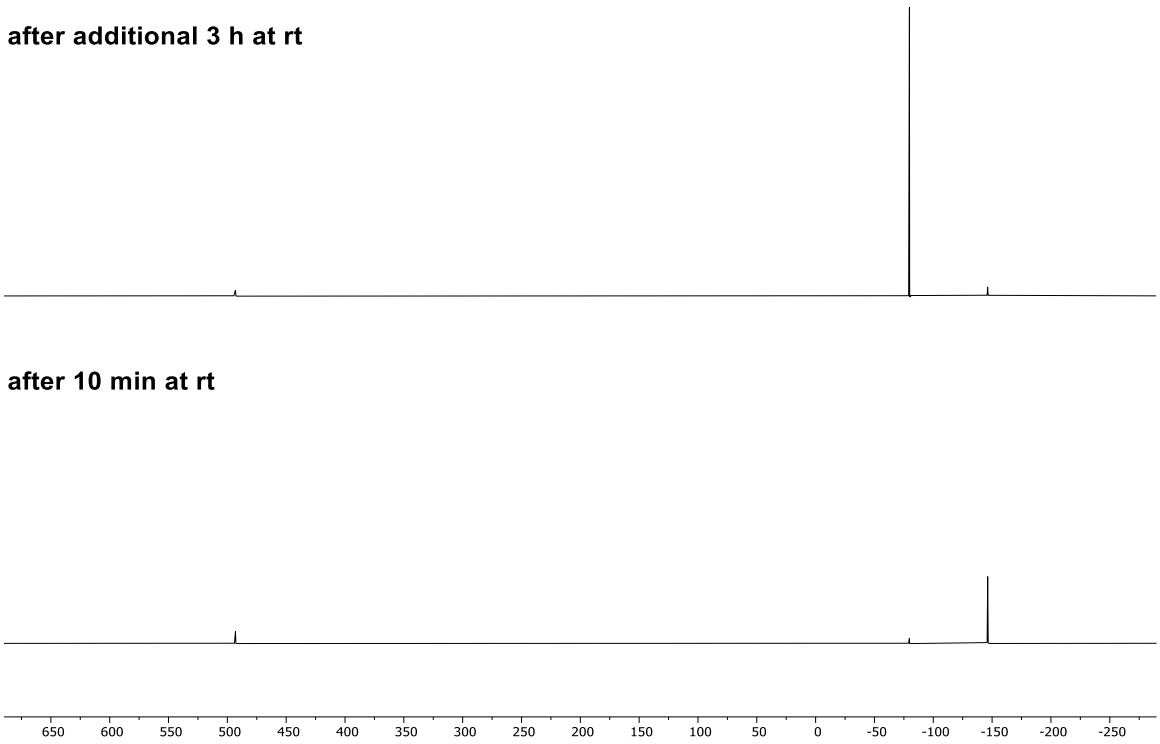


Figure S56: ^{1}H NMR spectrum of K[Mes*PCN] (**6a**) (300 MHz, C_6D_6, rt); 0.10 ppm: bis(trimethylsilyl)amine.

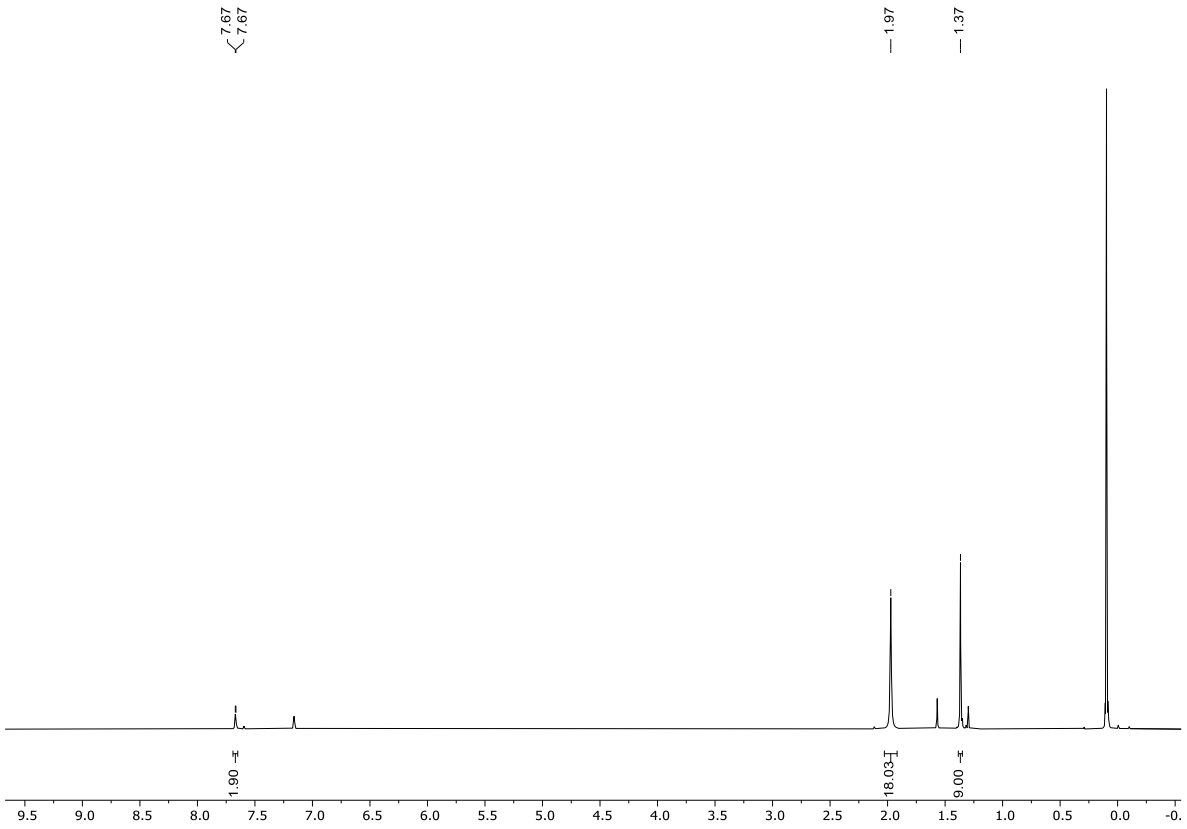
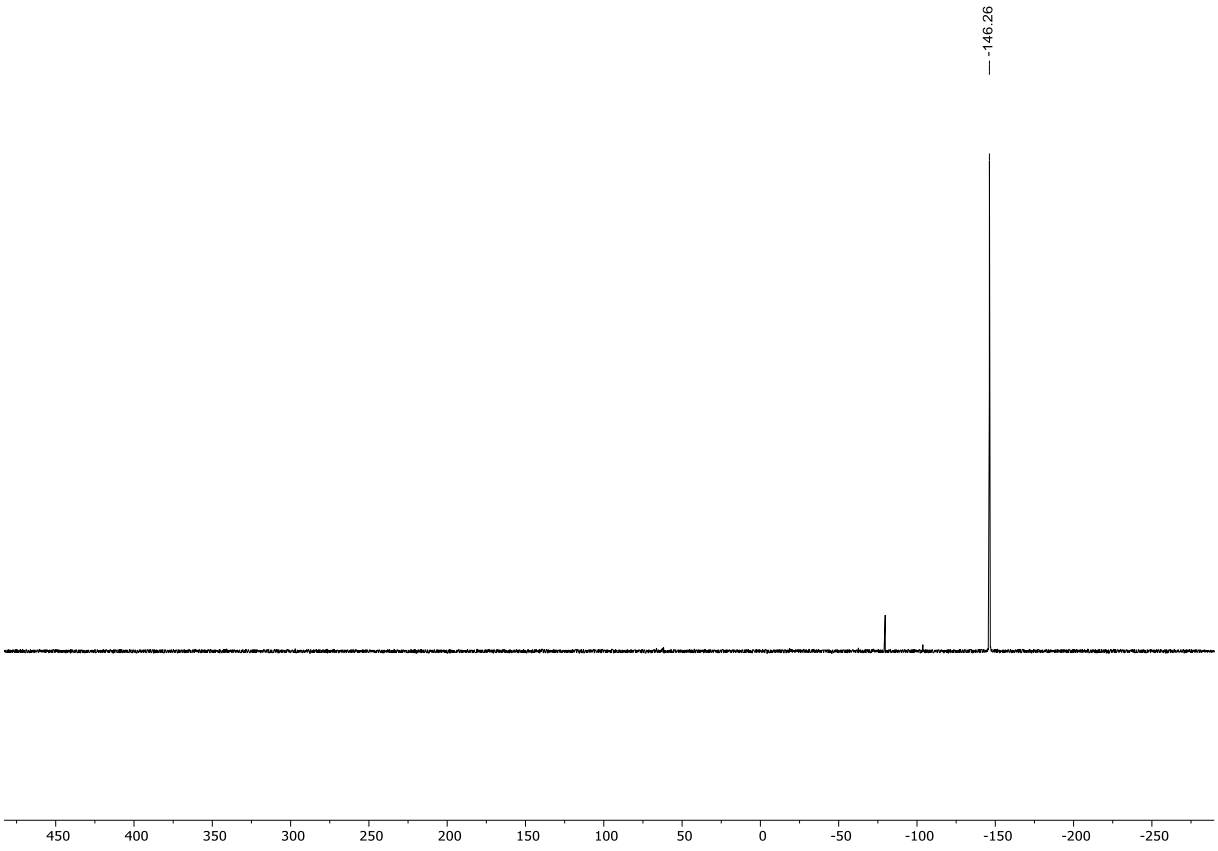
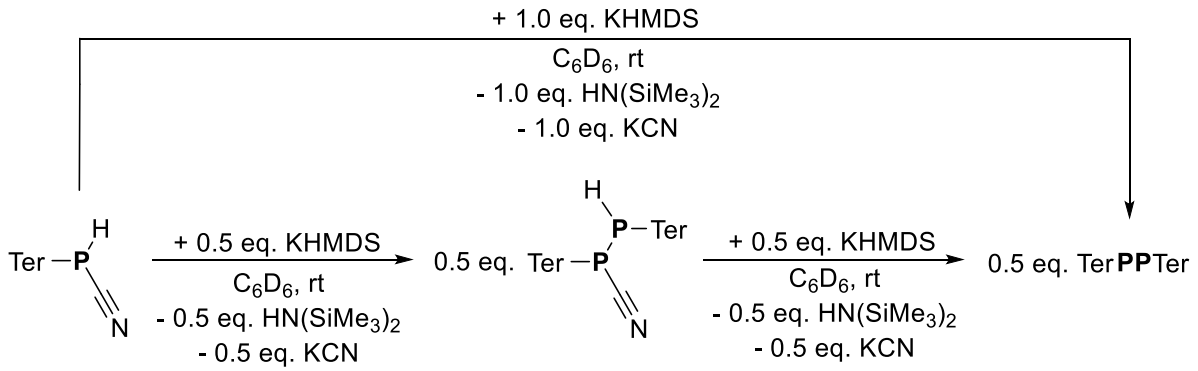


Figure S57: $^{31}P\{^{1}H\}$ NMR spectrum of K[Mes*PCN] (**8a**) (122 MHz, C_6D_6, rt).



3.14 Reaction of ^{Mes}TerP(H)CN (4b) with KHMDS



^{Mes}TerP(H)C≡N (**4b**) (0.030 g, 0.081 mmol) and KHMDS (0.008 g, 0.040 mmol) were dissolved in 0.6 mL of C_6D_6 and subsequently analyzed by NMR spectroscopy revealing conversion of both starting materials to mainly give ^{Mes}TerP(H)P(CN)^{Mes}Ter (**7**), and hexamethyldisilazane ($\delta(^1H)$ = 0.10 ppm) accompanied by precipitation of KCN. The reaction is accompanied by the formation of approximately 10% of byproduct(s) as determined by integration of the respective $^{31}P\{^1H\}$ NMR signals. All volatile components were removed under vacuum and the colorless solid was suspended in small amounts of *n*-pentane and filtered through a microfiber filter. Storage of the clear solution at −30 °C resulted in the precipitation of colorless crystals of **7**. Despite being of poor quality, the connectivity of **7** could be unambiguously assigned. Repeating the reaction and subsequently adding KHMDS (0.008 g, 0.040 mmol) resulted in the clean conversion to ^{Mes}TerPP^{Mes}Ter ($\delta(^{31}P\{^1H\})$ = 492.5 ppm) (Figure S58). By reacting **4b** with one equivalent of KHMDS, ^{Mes}TerPP^{Mes}Ter is obtained directly. The characteristic ^1H, $^{31}P\{^1H\}$, and ^{31}P NMR shifts of **7** can be clearly assigned and are listed below.

Yield: 0.012 g (**7**, 0.017 mmol; 43%).

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 1.87-1.88 (m, 12H, CH_3), 1.97 (s, 6H, CH_3), 2.21 (s, 6H, CH_3), 2.28 (s, 12H, CH_3), 3.97 (dd, $^1J_{P,H}$ = 216.8 Hz, $^2J_{P,H}$ = 38.5 Hz) ppm.

$^{31}P\{^{1}H\}/^{31}P$ NMR (122 MHz, C_6D_6, 298 K): δ = −78.2 (d, $^{1}J_{P,P}$ = 326.6 Hz), −82.6 (d, $^{1}J_{P,P}$ = 326.5 Hz) / −79.5 (dd, $^{1}J_{P,P}$ = 326.8 Hz, $^{2}J_{P,H}$ = 38.3 Hz), −81.3 (dd, $^{1}J_{P,P}$ = 326.6 Hz, $^{1}J_{P,H}$ = 216.3 Hz) ppm.

MS (ESI-TOF): expected: m/z = 716.3575 $[M+H]^+$, 738.3394 $[m+Na]^+$; found: m/z = 716.3584 $[M+H]^+$, 738.3412 $[M+Na]^+$.

Figure S58: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of TerP(H)P(CN)Ter (**7**) with 0.5 equivalents of KHMDS (middle) and another 0.5 equivalents of KHMDS (top) (122 MHz, C_6D_6, rt).

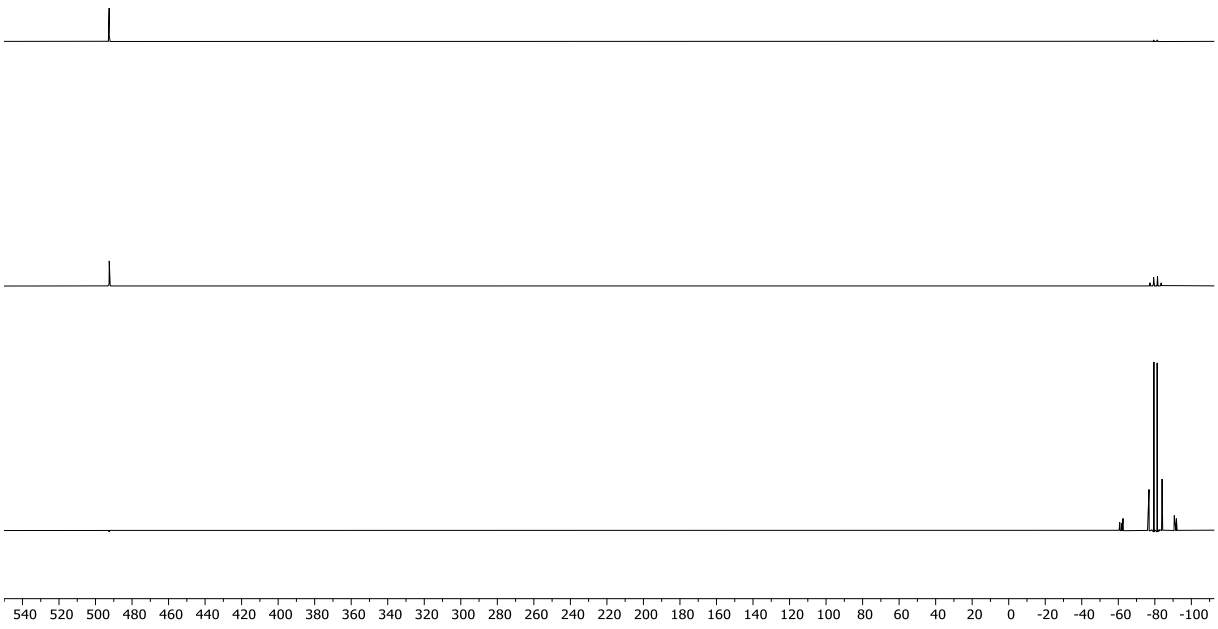


Figure S59: ^{1}H NMR spectrum after the reaction of ^{Mes}TerP(H)CN (**4b**) with KHMDS to give ^{Mes}TerP(H)P(CN)^{Mes}Ter (**7**) (300 MHz, C_6D_6, rt); 0.10 ppm: bis(trimethylsilyl)amine, 0.87 and 1.23 ppm: *n*-pentane.

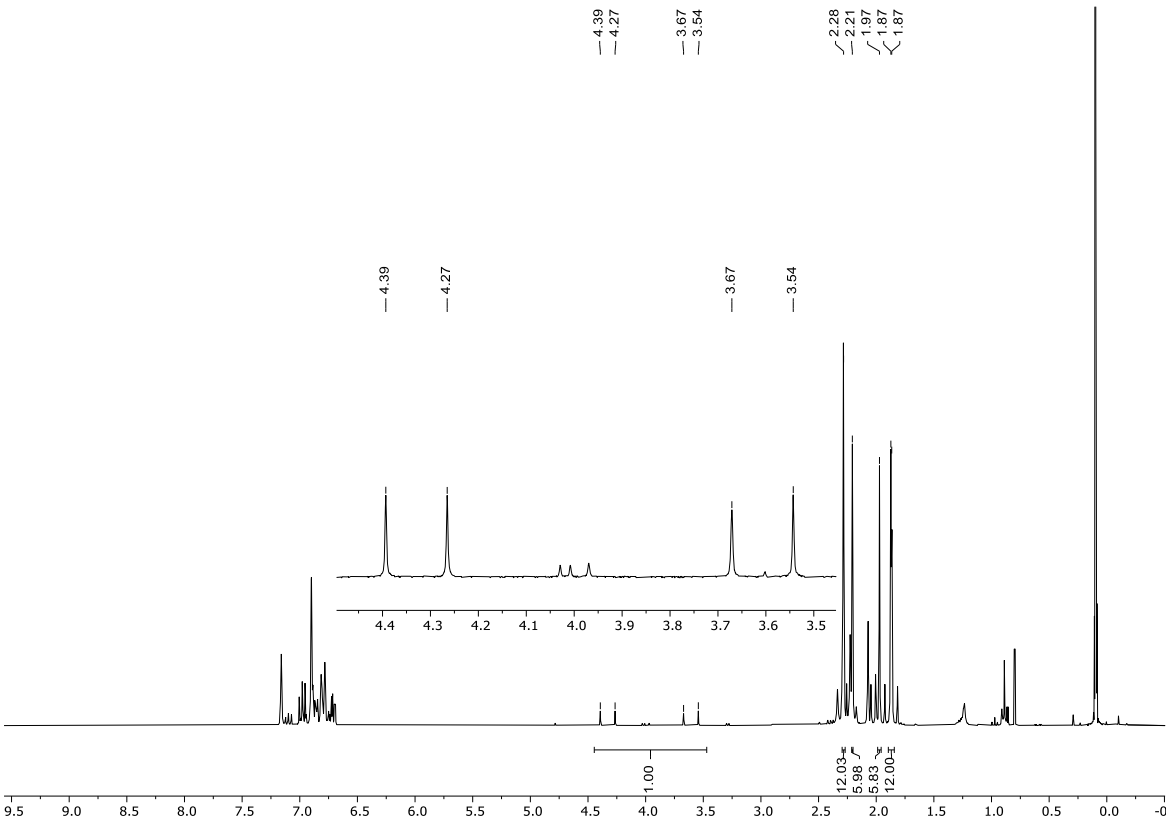
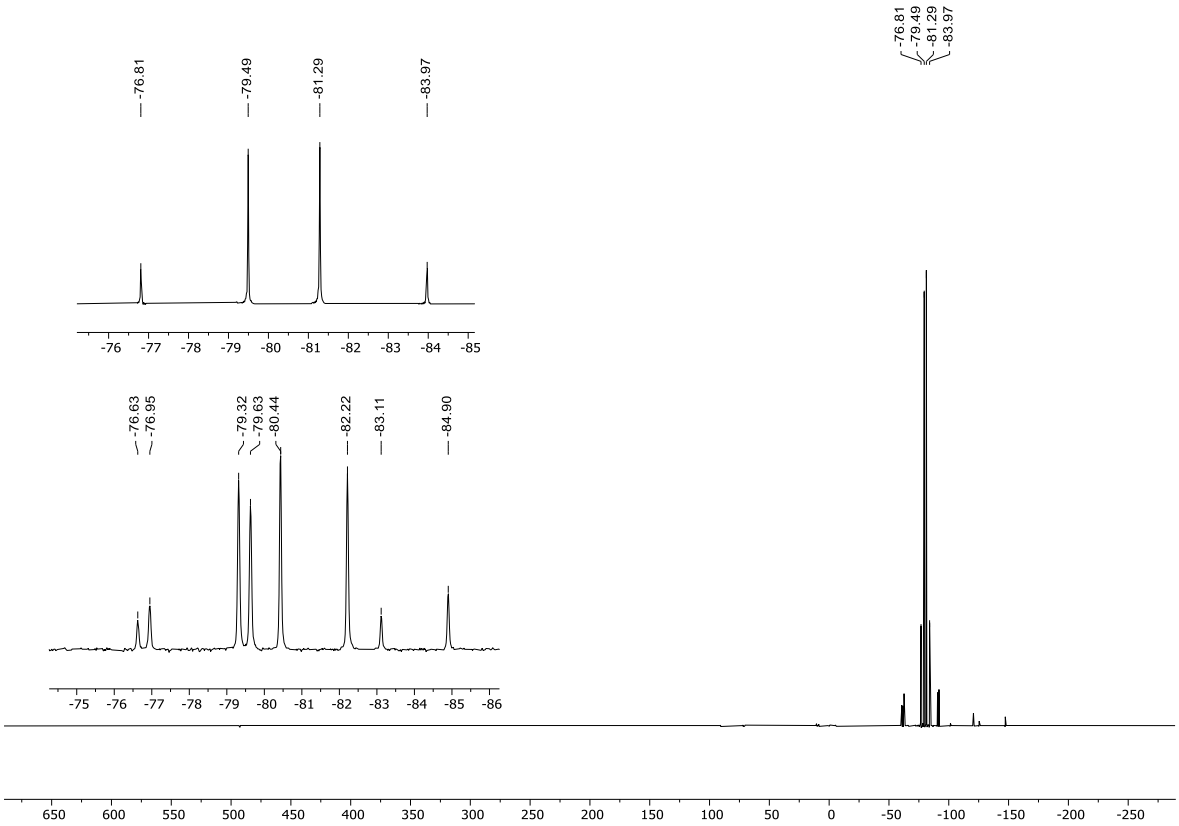
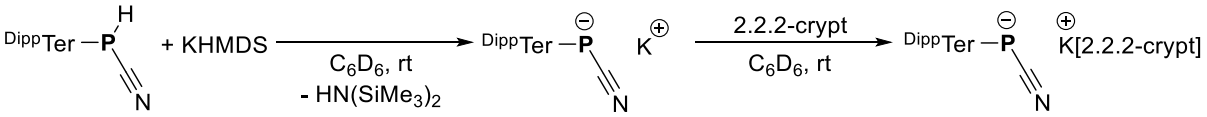


Figure S60: $^{31}P\{^{1}H\}$ (top and bottom) and ^{31}P NMR (middle) spectra after the reaction of TerP(H)CN (**4b**) with KHMDS to give TerP(H)P(CN)Ter (**7**) (122 MHz, C_6D_6, rt).



3.15 Synthesis of [^{Dip}TerPCN]K (6c) and [^{Dip}TerPCN][K-2.2.2-crypt] (6c-crypt)



A) To a solution of ^{Dip}TerP(H)C≡N (**4c**) (0.020 g, 0.044 mmol) in 0.3 mL of C_6D_6 was added potassium hexamethyldisilazide (0.009 g, 0.044 mmol) in 0.3 mL of C_6D_6 which resulted in an immediate color change of the reaction mixture from colorless to yellow. Subsequent analyses by ^{1}H and $^{31}P\{^{1}H\}/^{31}P$ NMR spectroscopy revealed clean conversion to [^{Dip}TerPCN]K (**6c**) accompanied by $HN(SiMe_3)_2$ formation ($\delta(^{1}H)$ =

0.10 ppm) (Figures S61 and S62). **6c** was found to be stable in solution for at least one week.

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 1.14 (d, $^{3}J_{H,H}$ = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.45 (d, $^{3}J_{H,H}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 2.99 (hept, $^{3}J_{H,H}$ = 6.9 Hz, 4H, CH(CH$_3$)$_2$), 6.94-6.98 (m, 2H, CH_{Aryl}), 7.01-7.06 (m, 1H, CH_{Aryl}), 7.18-7.20 (m, 4H, CH_{Aryl}), 7.27-7.32 (m, 2H, CH_{Aryl}) ppm. **^{31}P{^{1}H}** (122 MHz, C_6D_6, 298 K): δ = −142.0 ppm.

B) To a solution ^{Dip}TerP(H)C≡N (**4c**) (0.020 g, 0.044 mmol) in 0.3 mL of C_6D_6 was added KHMDS (0.009 g, 0.044 mmol) in 0.3 mL of C_6D_6, which was accompanied by an immediate color change of the reaction mixture from colorless to yellow. The solution was vigorously shaken for five minutes followed by addition of 2.2.2-cryptand (0.017 g, 0.044 mmol). Subsequent NMR analyses revealed clean conversion to [^{Dip}TerPCN][K-2.2.2-crypt] (**6c-crypt**). The C_6D_6 solution was layered with 0.8 mL of *n*-pentane which yielded yellow crystals of **6c-crypt** suitable for SC-XRD after two days at room temperature. The analytical data of **6c-crypt** are given below.

Yield: 0.021 g (0.024 mmol; 55% (**B**)).

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 1.36 (d, $^{3}J_{H,H}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.74 (d, $^{3}J_{H,H}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 2.07-2.10 (m, 12H, CH_2), 3.07-3.10 (m, 12H, CH_2), 3.20 (s, 12H, CH_2), 3.52 (hept, $^{3}J_{H,H}$ = 7.0 Hz, 4H, CH(CH$_3$)$_2$), 7.01-7.04 (m, 3H, CH_{Aryl}), 7.32-7.34 (m, 6H, CH_{Aryl}) ppm. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, 298 K): δ = 24.9 (d, $J_{P,C}$ = 2.4 Hz, CH(CH_3)$_2$), 25.7 (CH(CH_3)$_2$), 31.1 (CH(CH$_3$)$_2$), 54.3 (CH_2), 67.8 (CH_2), 70.1 (CH_2), 118.2 (CH_{Aryl}), 122.5 (CH_{Aryl}), 127.2 (CH_{Aryl}), 128.6 (CH_{Aryl}), 137.1 (d, $^{1}J_{P,C}$ = 109.4 Hz, PCN), 139.8 (d, $J_{P,C}$ = 18.8 Hz, $C_{q,Aryl}$), 143.6 (d, $J_{P,C}$ = 4.9 Hz, $C_{q,Aryl}$), 148.2 ($C_{q,Aryl}$), 154.6 (d, $^{1}J_{P,C}$ = 60.6 Hz, C_qP) ppm. **^{31}P{^{1}H}** (122 MHz, C_6D_6, 298 K): δ = −120.7 ppm. **IR** (ATR, 32 scans, cm^{-1}): ν = 2957 (m), 2917 (w), 2889 (m), 2865 (m9, 2818 (w), 2053 (m), 1628 (w), 1570 (w), 1475 (w), 1447 (w), 1378 (w), 1356 (s), 1329 (w), 1296 (m), 1259 (m), 1194 (w), 1176 (w), 1131 (m), 1099 (s), 1082 (s), 1056 (m), 1033 (m), 1001 (w), 945 (s), 932 (s), 830 (m), 820 (w), 800 (m), 777 (w), 756 (s), 731 (m), 707 (w), 687 (m), 633 (w), 607 (w), 586 (w), 552 (w), 523 (w), 498 (m), 464 (w), 440 (w), 422 (w). **MS** (ESI-TOF): expected: m/z = 454.2659

$[C_{31}H_{37}NP]^-$, 415.2215 $[K[2.2.2\text{-crypt}]]^+$; found: m/z = 454.2650 $[C_{31}H_{37}NP]^-$, 415.2226 $[K[2.2.2\text{-crypt}]^+$.

Figure S61: ^1H NMR spectrum of [^{Dip}TerPCN]K (**6c**) (300 MHz, C_6D_6, rt); 0.10 ppm: KHMDS.

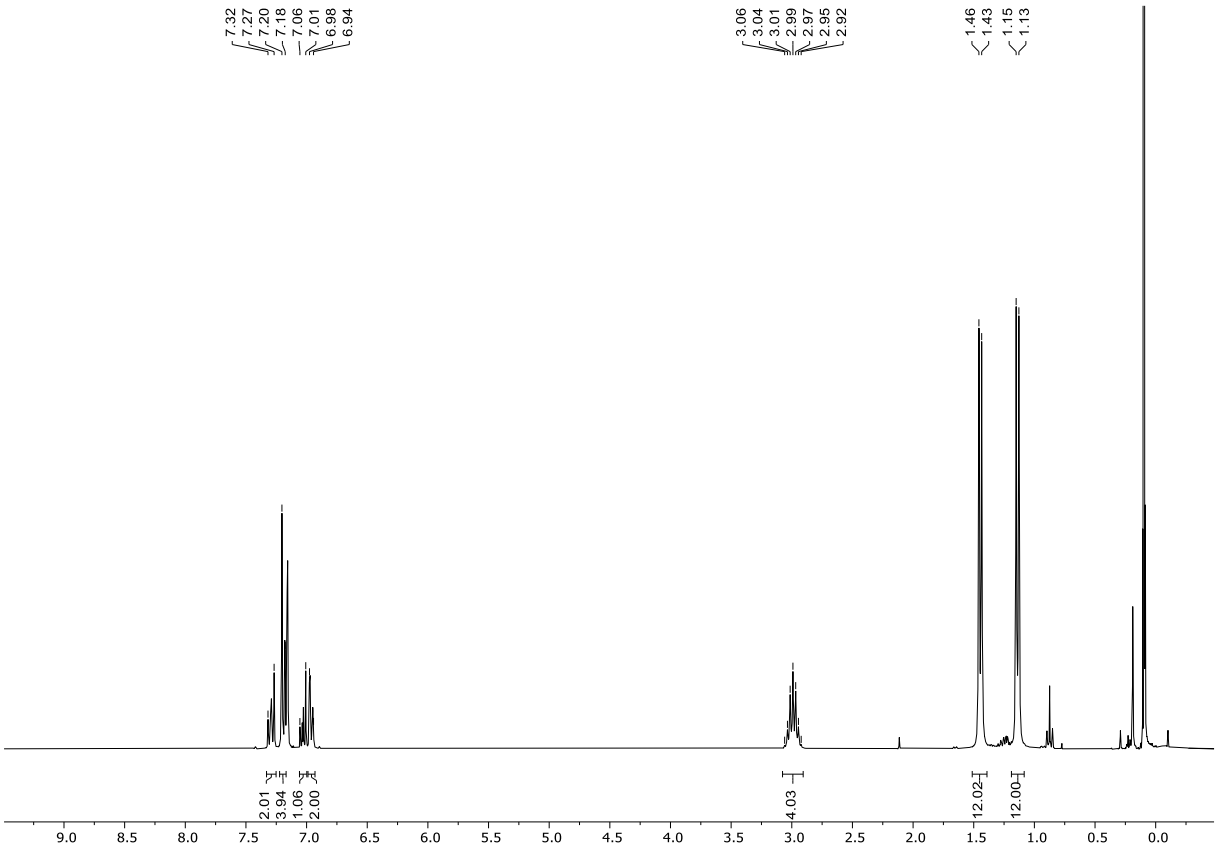


Figure S62: $^{31}P\{^{1}H\}$ NMR spectrum of [^{Dip}TerPCN]K (**6c**) (122 MHz, C_6D_6, rt).

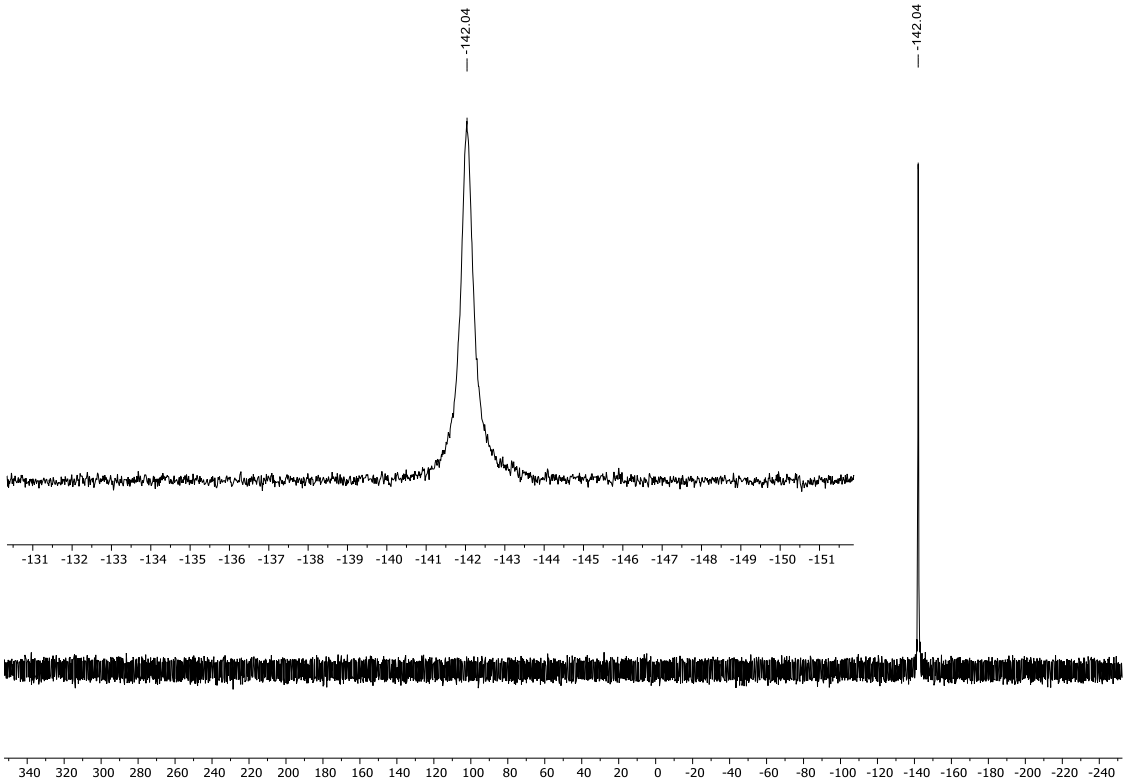


Figure S63: ^{1}H NMR spectrum of [^{Dipp}TerPCN][K-2.2.2-crypt] (**6c-crypt**) (300 MHz, C_6D_6, rt); 0.10 ppm: KHMDS.

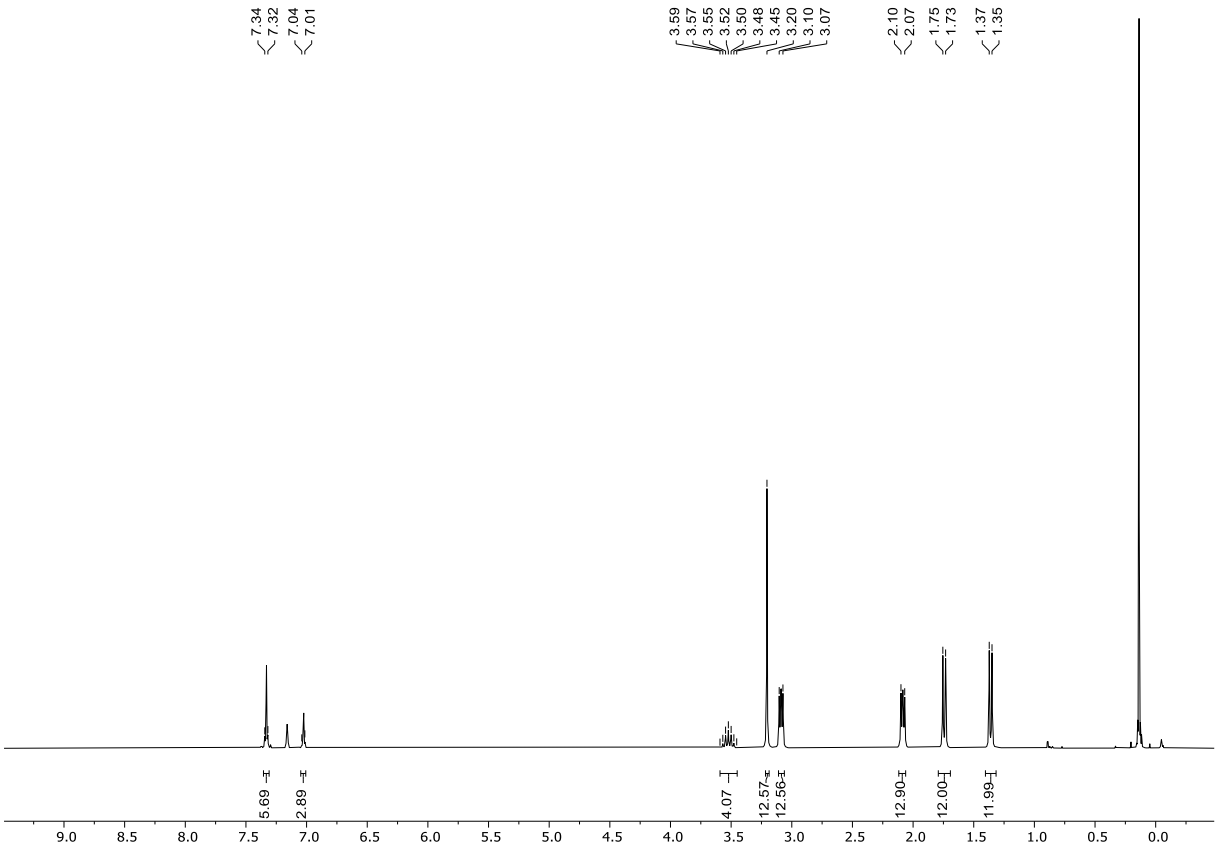


Figure S64: $^{13}C\{^{1}H\}$ NMR spectrum of [^{Dip}TerPCN][K-2.2.2-crypt] (**6c-crypt**) (75 MHz, C_6D_6, rt); 3.0 ppm: KHMDS.

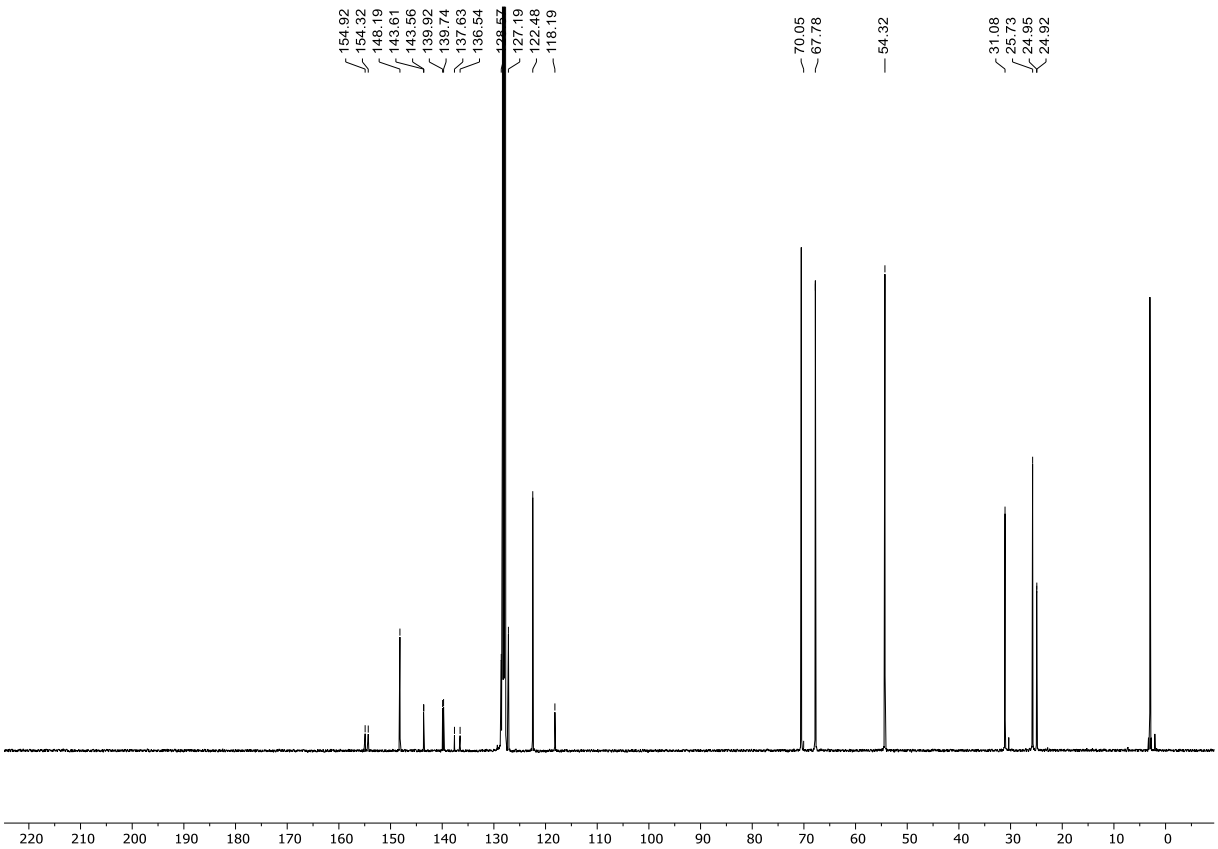
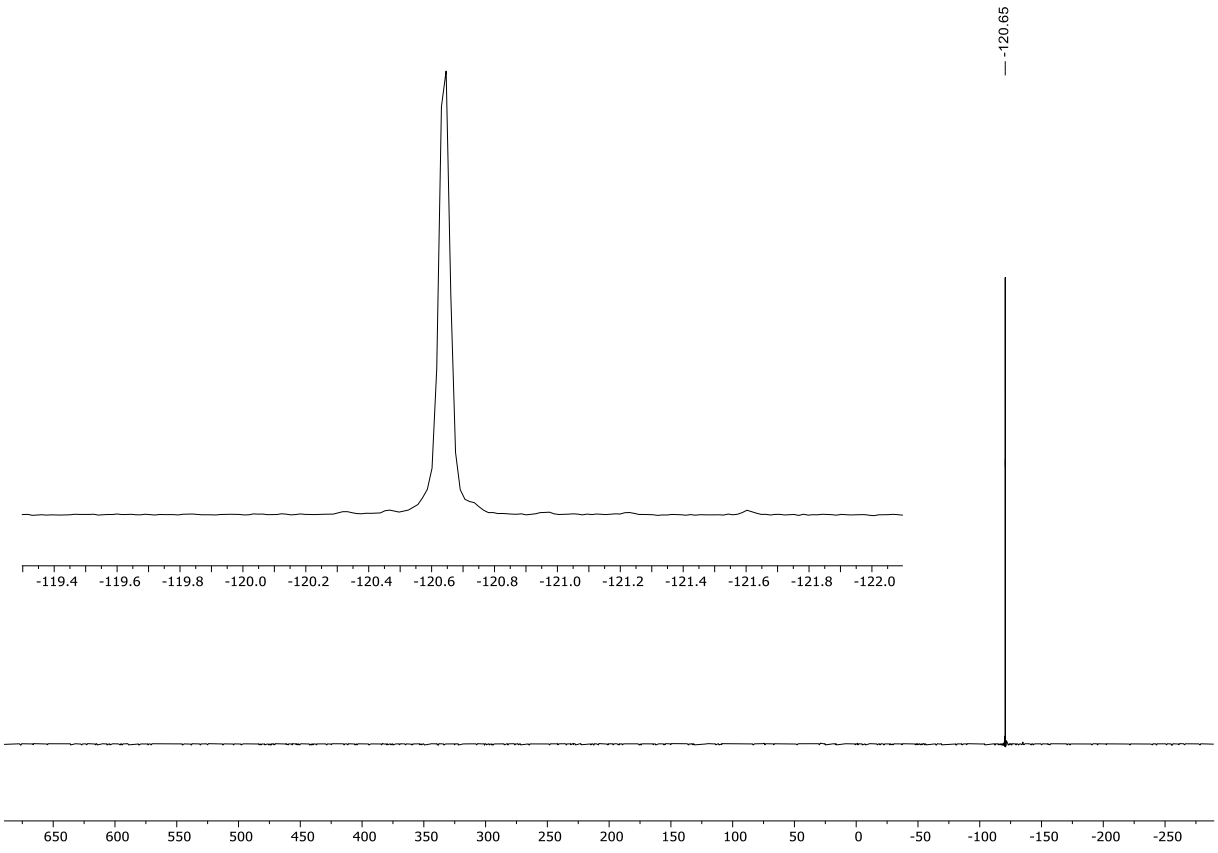
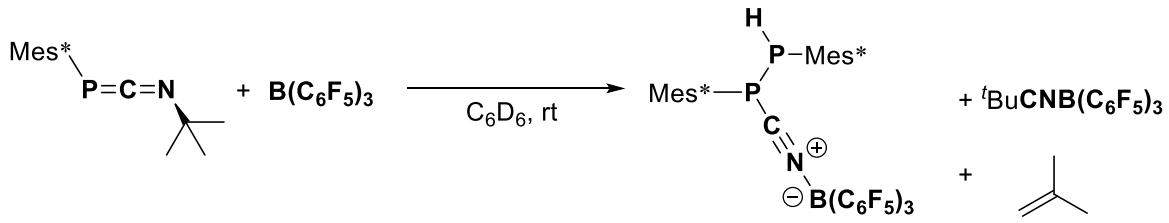


Figure S65: $^{31}P\{^{1}H\}$ NMR spectrum of [^{Dip}TerPCN][K-2.2.2-crypt] (**6c-crypt**) (122 MHz, C_6D_6, rt).



3.16 Reactivity of Mes*PCN*t*Bu (3a) towards $B(C_6F_5)_3$



A) Mes*P=C=N^{t}Bu (**3a**) (0.150 g, 0.417 mmol) ad $B(C_6F_5)_3$ (0.214 g, 0.417 mmol) were dissolved in 15 mL of toluene, which resulted in a color change from yellow to colorless over the course of a few hours. All volatile components were removed under vacuum, and the colorless residue was washed with *n*-pentane (3×3 mL). All volatile components were removed under vacuum to give Mes*P(CNB$(C_6F_5)_3$)P(H)Mes* (**8**) and ^{t}BuCNB$(C_6F_5)_3$ under release of *iso*-butene.

Storing of the combined *n*-pentane wash solutions at −30 °C resulted in the precipitation of colorless crystals suitable for SC-XRD of **8** and ^{t}BuCNB$(C_6F_5)_3$.

B) Mes*P=C=N^{t}Bu (**3a**) (0.020 g, 0.056 mmol) and $B(C_6F_5)_3$ (0.028 g, 0.056 mmol) were dissolved in 0.6 mL of C_6D_6 which results in the precipitation of a colorless solid. The corresponding ^{1}H NMR analyses verifies that *iso*-butene is also formed during this reaction (Figure S73).

The clearly assignable NMR signals of **8** are listed below.

^{1}H NMR (300 MHz, C_6D_6, 298 K): d = 5.44 (d, ^1J = 223.5 Hz, PH) ppm.

^{11}B{^{1}H} NMR (96 MHz, C_6D_6, 298 K): d = −7.9 (very broad) ppm. Assigned by overlaying a sample ^{11}B{^{1}H} NMR spectrum of C_6D_6 in the same NMR tube.

^{31}P{^{1}H}/^{31}P NMR (122 MHz, C_6D_6, 298 K): d = −53.3 (dd, $^1J_{P,P}$ = 247.5 Hz, $^1J_{P,H}$ = 224.0 Hz, PH), −46.8 (d, $^1J_{P,P}$ = 247.5 Hz, P(CNB$(C_6F_5)_3$)) ppm.

Figure S66: ^{1}H NMR spectrum after the reaction of Mes*PCN^{t}Bu (**3a**) with $B(C_6F_5)_3$ (attempt **A**) (300 MHz, C_6D_6, rt); 5.44 ppm: **8**, 0.69 ppm: ^{t}BuCNB$(C_6F_5)_3$.

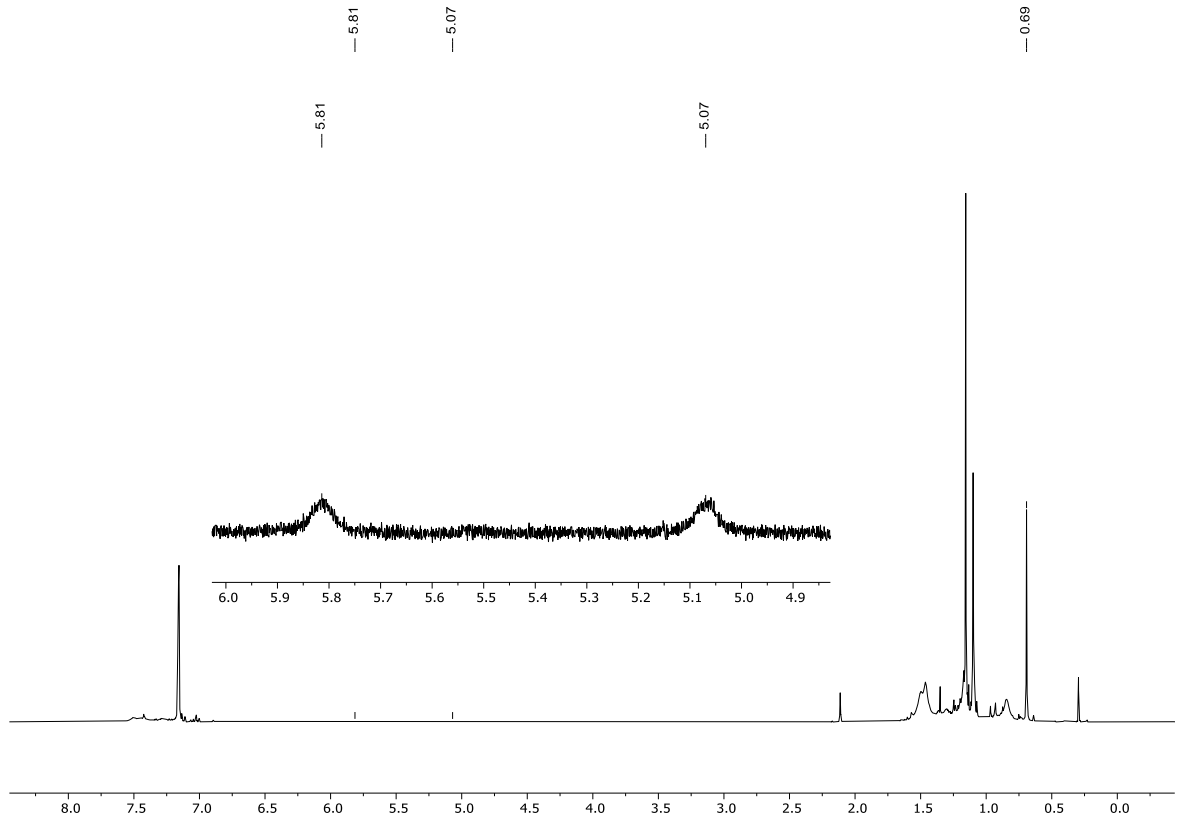


Figure S67: ^{1}H NMR spectrum after the reaction of Mes*PCN^{t}Bu (**3a**) with $B(C_6F_5)_3$ (attempt **B**) (300 MHz, C_6D_6, rt); 1.60, 4.73 ppm: *iso*-butene.

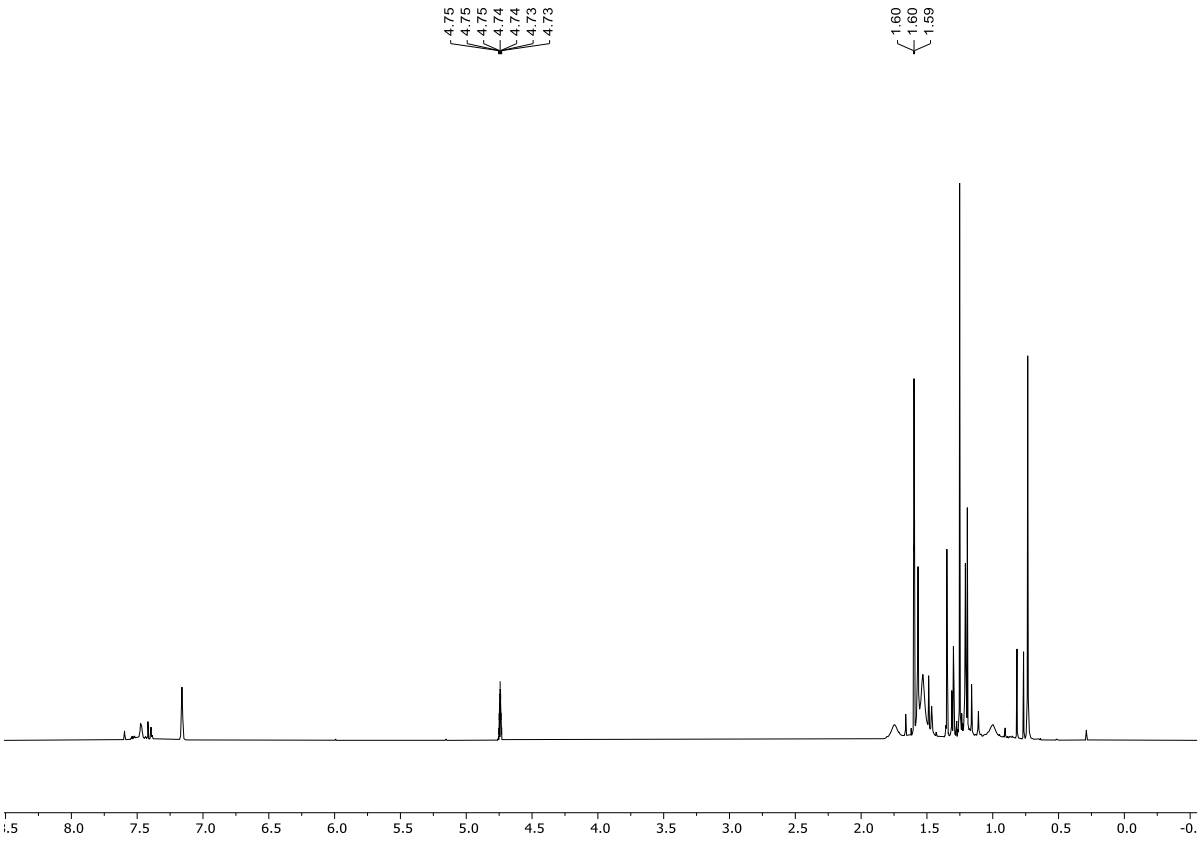


Figure S68: $^{11}B\{^{1}H\}$ NMR spectrum after the reaction of Mes*PCN^{t}Bu (**3a**) with $B(C_6F_5)_3$ (attempt **A**) (96 MHz, C_6D_6, rt); −7.9 ppm: **8**, −20.7 ppm: ^{t}BuCNB$(C_6F_5)_3$.

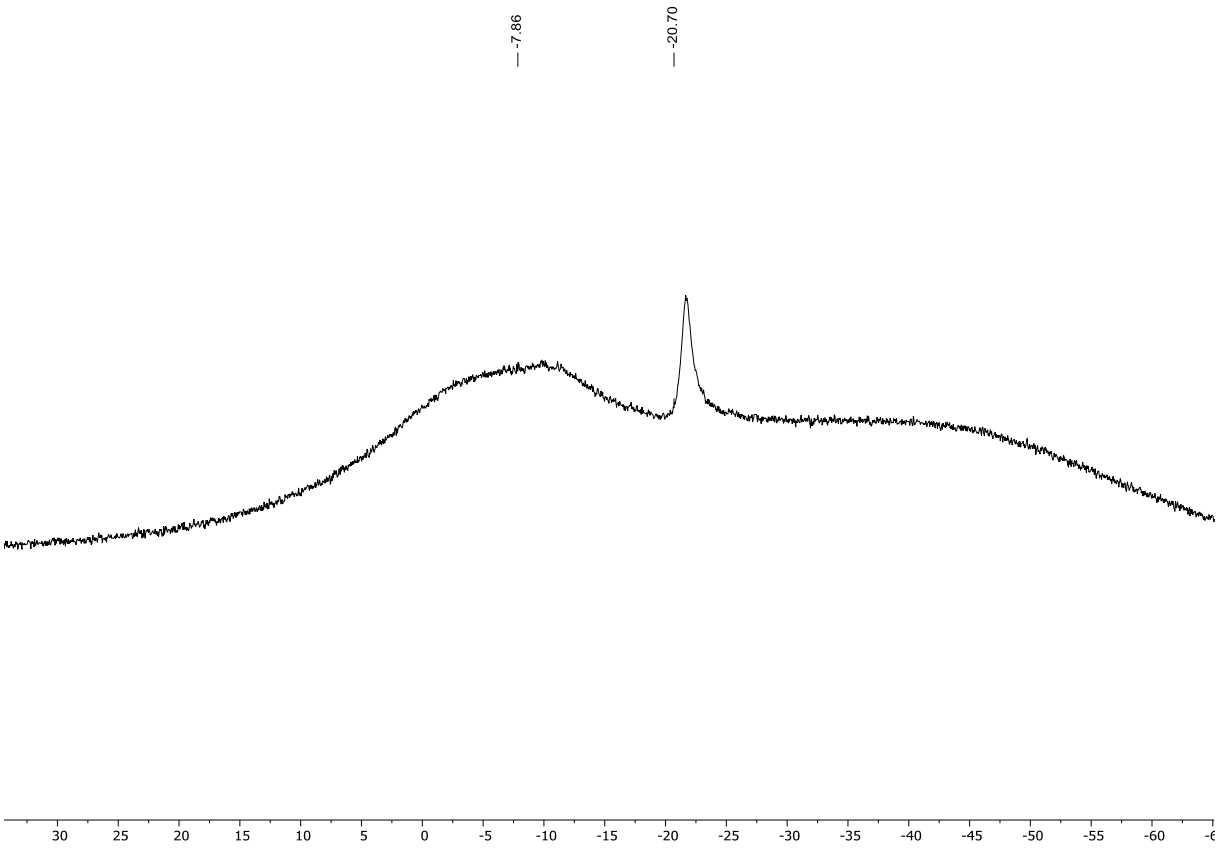


Figure S69: $^{19}F\{^{1}H\}$ NMR spectrum after the reaction of Mes*PCN^{t}Bu (**3a**) with $B(C_6F_5)_3$ (attempt **A**) (282 MHz, C_6D_6, rt).

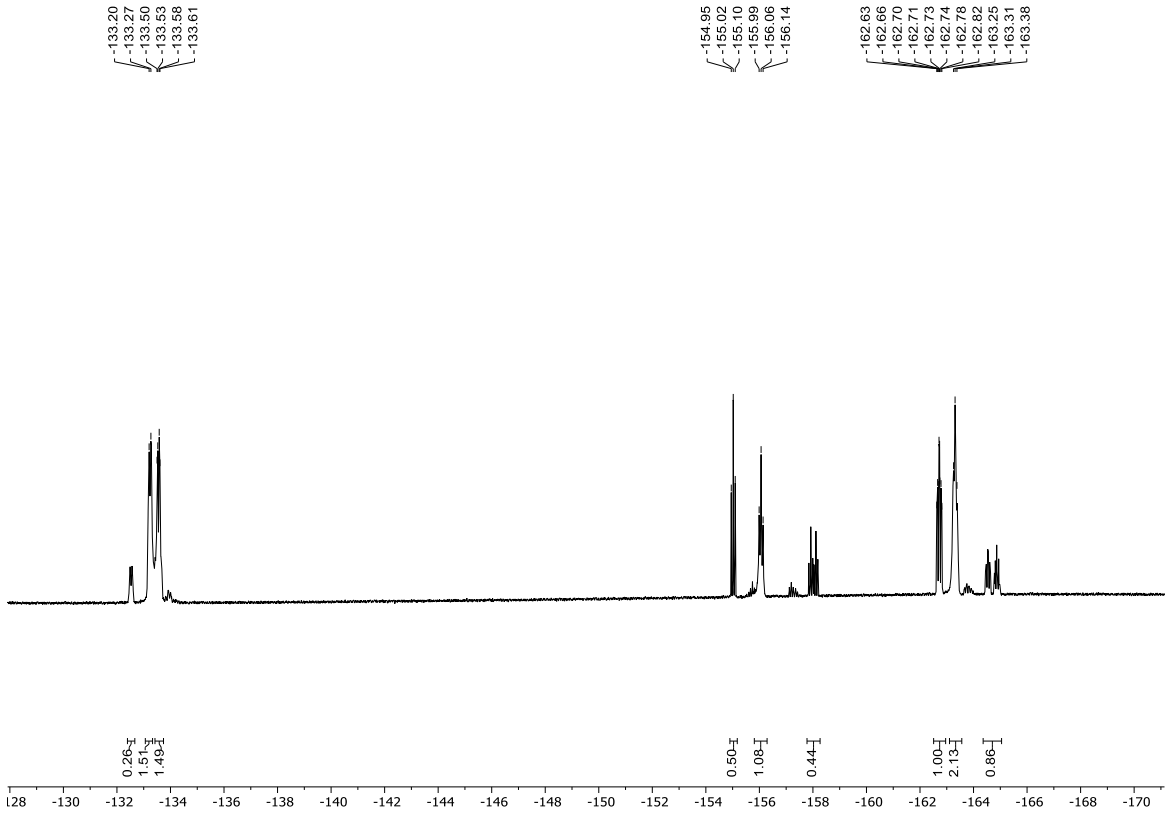


Figure S70: $^{31}P\{^{1}H\}$ NMR spectrum after the reaction of Mes*PCN^{t}Bu (**3a**) with $B(C_6F_5)_3$ (attempt **A**) (122 MHz, C_6D_6, rt).

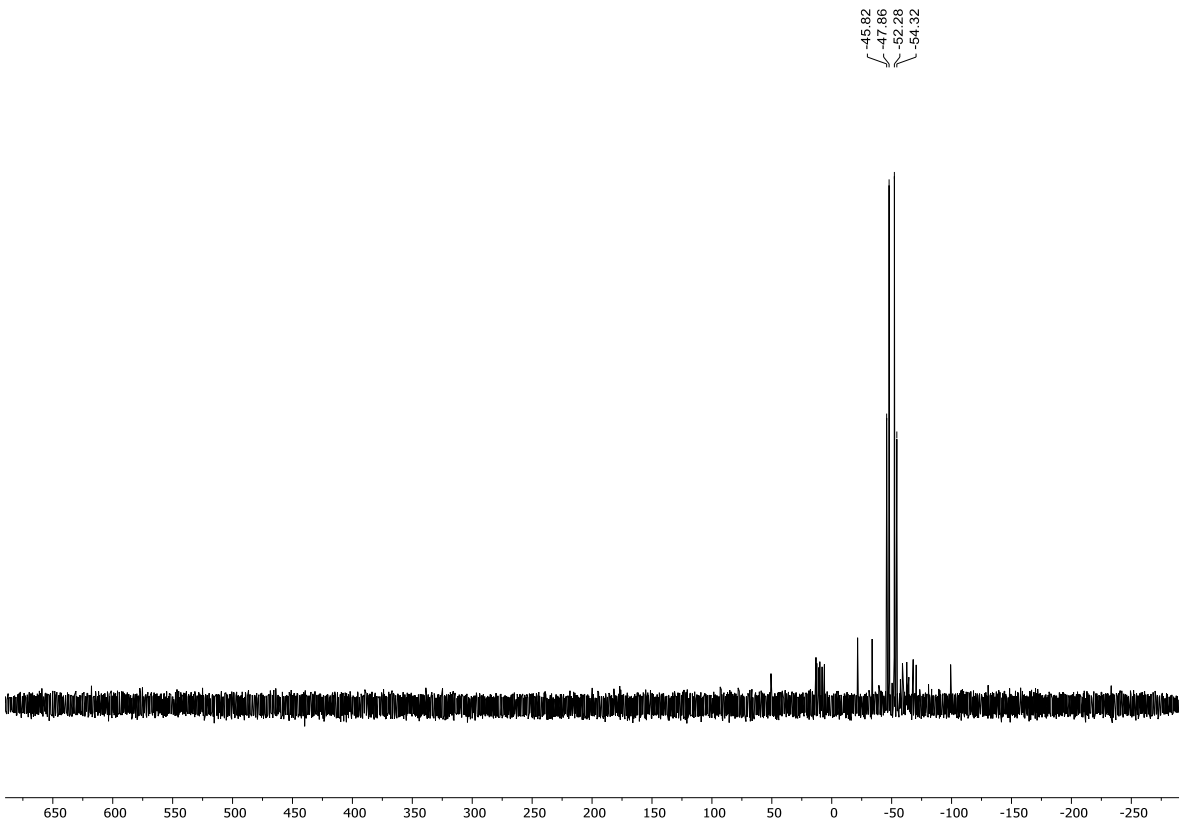
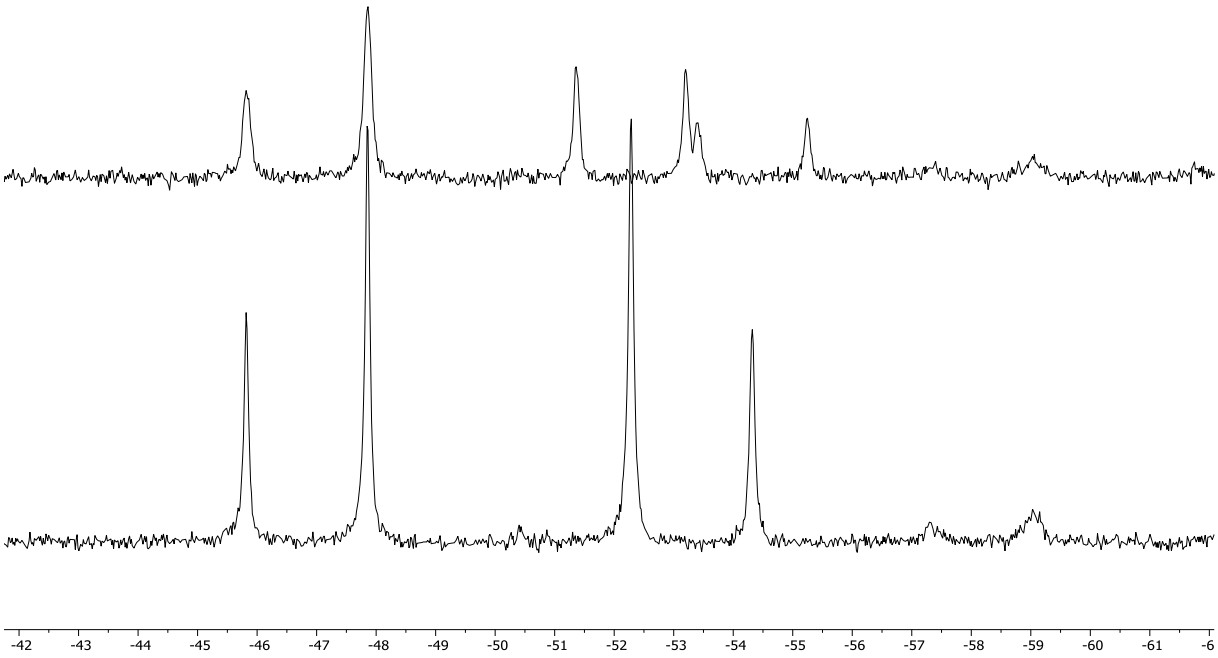
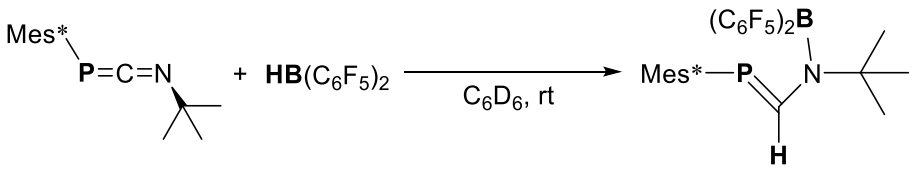


Figure S71: Excerpt of the $^{31}P\{^{1}H\}$ NMR spectrum (bottom) and ^{31}P NMR spectrum (top) after the reaction of Mes*PCN^{t}Bu (**3a**) with $B(C_6F_5)_3$ (attempt **A**) (122 MHz, C_6D_6, rt).



3.17 Synthesis of Mes*PC(H)N(*t*Bu)B(C_6F_5)$_2$ (9)



Mes*P=C=N*t*Bu (**3a**) (0.025 g, 0.070 mmol) and $HB(C_6F_5)_2$ (0.024 g, 0.070 mmol) were dissolved in 0.6 mL of C_6D_6. Subsequent NMR analysis revealed complete conversion of both starting materials to give Mes*PC(H)N(*t*Bu)B(C_6F_5)$_2$ (**9**) accompanied by slight formation of byproducts. The solution was transferred into a vial and all volatile components were removed under vacuum to give **9** as a yellow solid.

Crystals suitable for single crystal X-ray diffraction were obtained by layering a C_6D_6 solution of **9** with *n*-hexane and subsequent slow evaporation at room temperature.

Yield: 0.037 g (0.052 mmol; 74%).

CHN: calculated: C 59.59, H 5.57, N 1.99; found: C 59.55, H 5.75, N 1.62. **^{1}H NMR** (300 MHz, C_6D_6, 298 K): δ = 1.01 (s, 9H, $NC_q(CH_3)_3$), 1.24 (s, 9H, *p*-$C_q(CH_3)_3P$), 1.43 (s, 18H, *o*-$C_q(CH_3)_3P$), 7.49-7.50 (m, 2H, CH_{Aryl}), 7.80 (d, $^{2}J_{P,H}$ = 18.5 Hz, PC(H)N) ppm. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, 298 K): δ = 30.2 (d, $^{4}J_{P,C}$ = 2.4 Hz, $NC_q(\underline{C}H_3)_3$), 31.0 (*p*-$C_q(\underline{C}H_3)_3P$), 33.33 (*o*-$C_q(\underline{C}H_3)_3P$), 33.37 (*o*-$C_q(\underline{C}H_3)_3P$), 34.6 (*p*-$\underline{C}_q(CH_3)_3P$), 37.8 (*o*-$\underline{C}_q(CH_3)_3P$), 61.6 (d, $^{3}J_{P,C}$ = 2.9 Hz, $N\underline{C}_q(CH_3)_3$), 121.8 (CH_{Aryl}), 135.5 (d, $^{1}J_{P,C}$ = 56.3 Hz, C_qP), 150.2 (*p*-$C_{q,Aryl}P$), 155.1 (d, $^{2}J_{P,C}$ = 2.2 Hz, *o*-$C_{q,Aryl}P$), 177.5 (d, $^{1}J_{P,C}$ = 37.3 Hz, PC(H)N) ppm. **^{11}B{^{1}H} NMR** (96 MHz, C_6D_6, 298 K): δ = 36.4 ppm. **^{19}F{^{1}H} NMR** (282 MHz, C_6D_6, 298 K): δ = −131.0 to −131.2 (m, 4F, *m*-$F_{Ar}B$), −151.7 (t, $^{3}J_{F,F}$ = 20.6 Hz, 1F, *p*-$F_{Ar}B$), −153.8 (t, $^{3}J_{F,F}$ = 20.5 Hz, 1F, *p*-$F_{Ar}B$) −160.9 to −161.1 (m, 2F, *o*-$F_{Ar}B$), −161.9 to −162.1 (m, 2F, *o*-$F_{Ar}B$) ppm. **^{31}P{^{1}H} NMR** (122 MHz, C_6D_6, 298 K): δ = 228.5 ppm.

Figure S72: ^{1}H NMR spectrum of Mes*PC(H)N(*t*Bu)B(C_6F_5)$_2$ (**9**) (300 MHz, C_6D_6, rt).

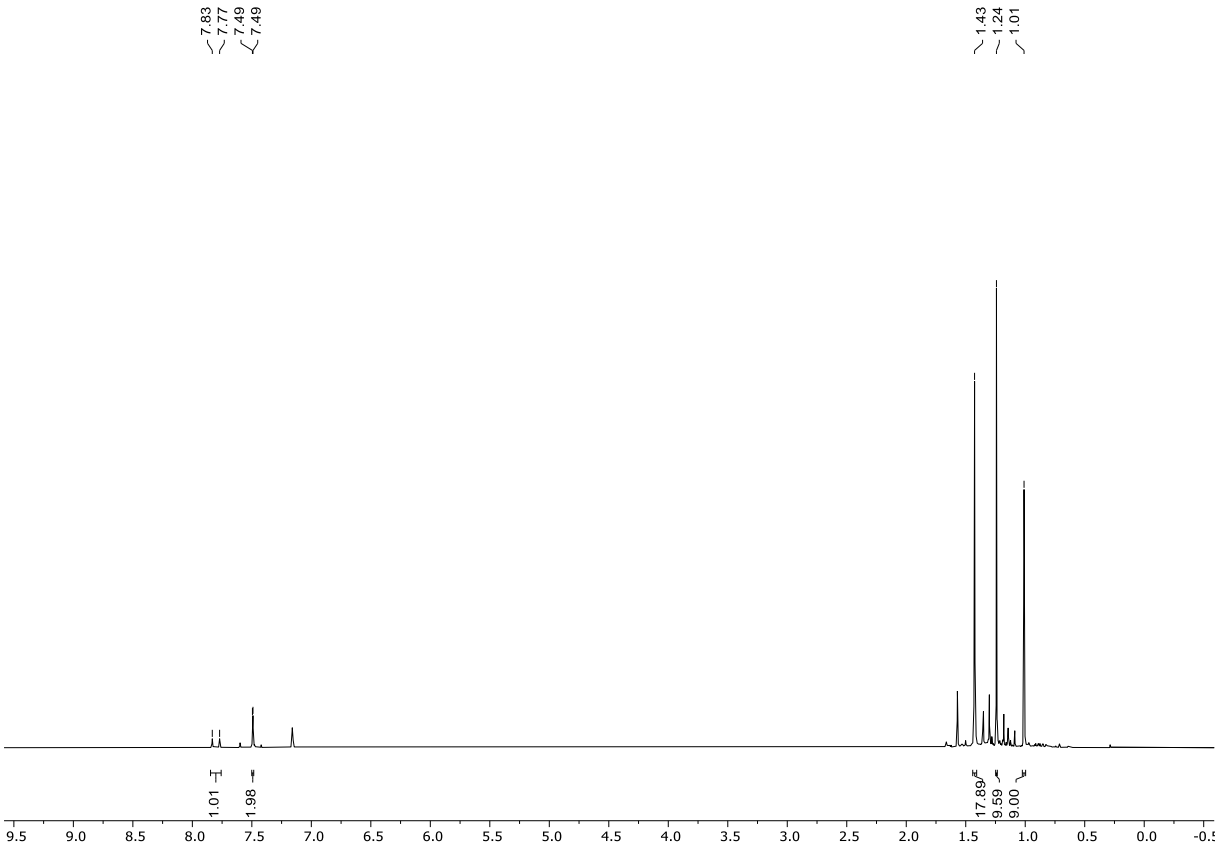


Figure S73: $^{13}C\{^{1}H\}$ NMR spectrum of compound Mes*PC(H)N(*t*Bu)B(C_6F_5)$_2$ (**9**) (75 MHz, C_6D_6, rt).

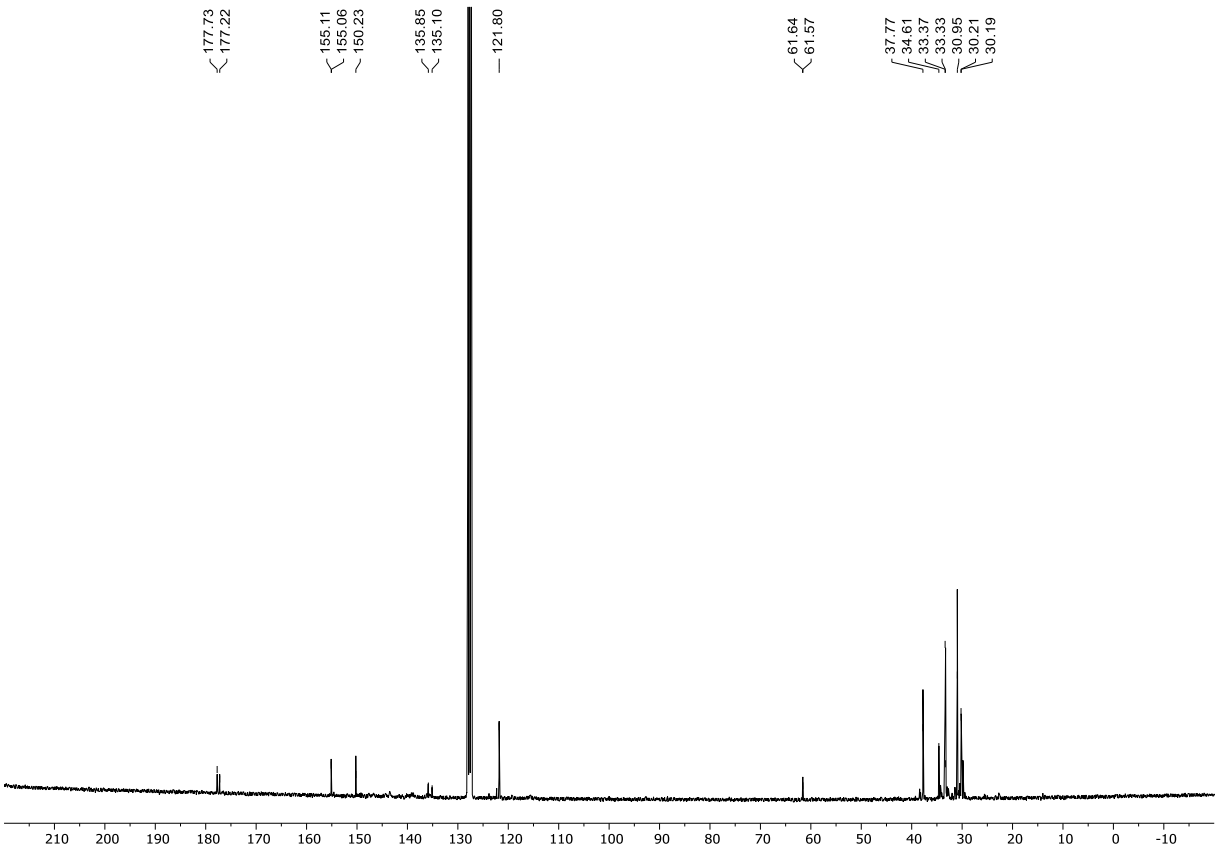


Figure S74: $^{11}B\{^{1}H\}$ NMR spectrum of Mes*PC(H)N(^{t}Bu)B(C_6F_5)$_2$ (**9**) (96 MHz, C_6D_6, rt).

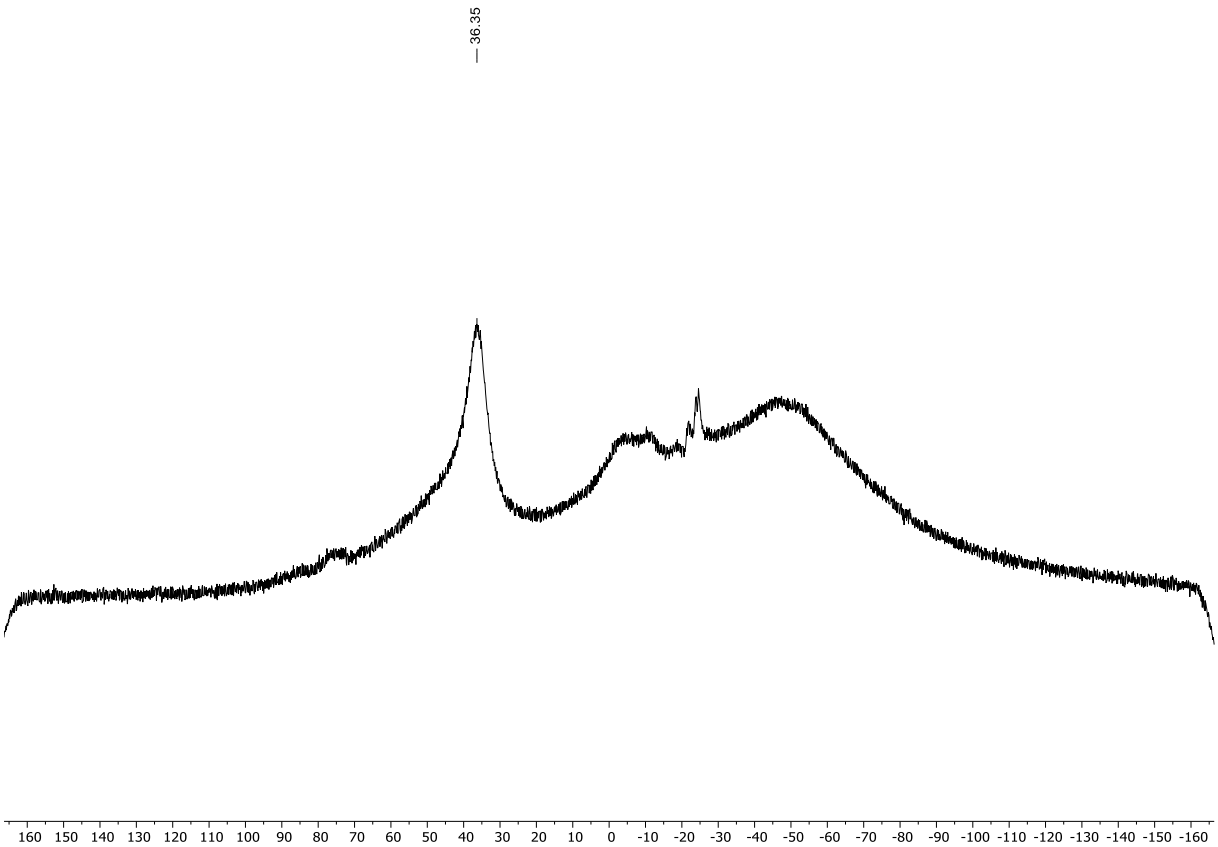


Figure S75: $^{19}F\{^{1}H\}$ NMR spectrum of Mes*PC(H)N(^{t}Bu)B(C_6F_5)$_2$ (**9**) (282 MHz, C_6D_6, rt).

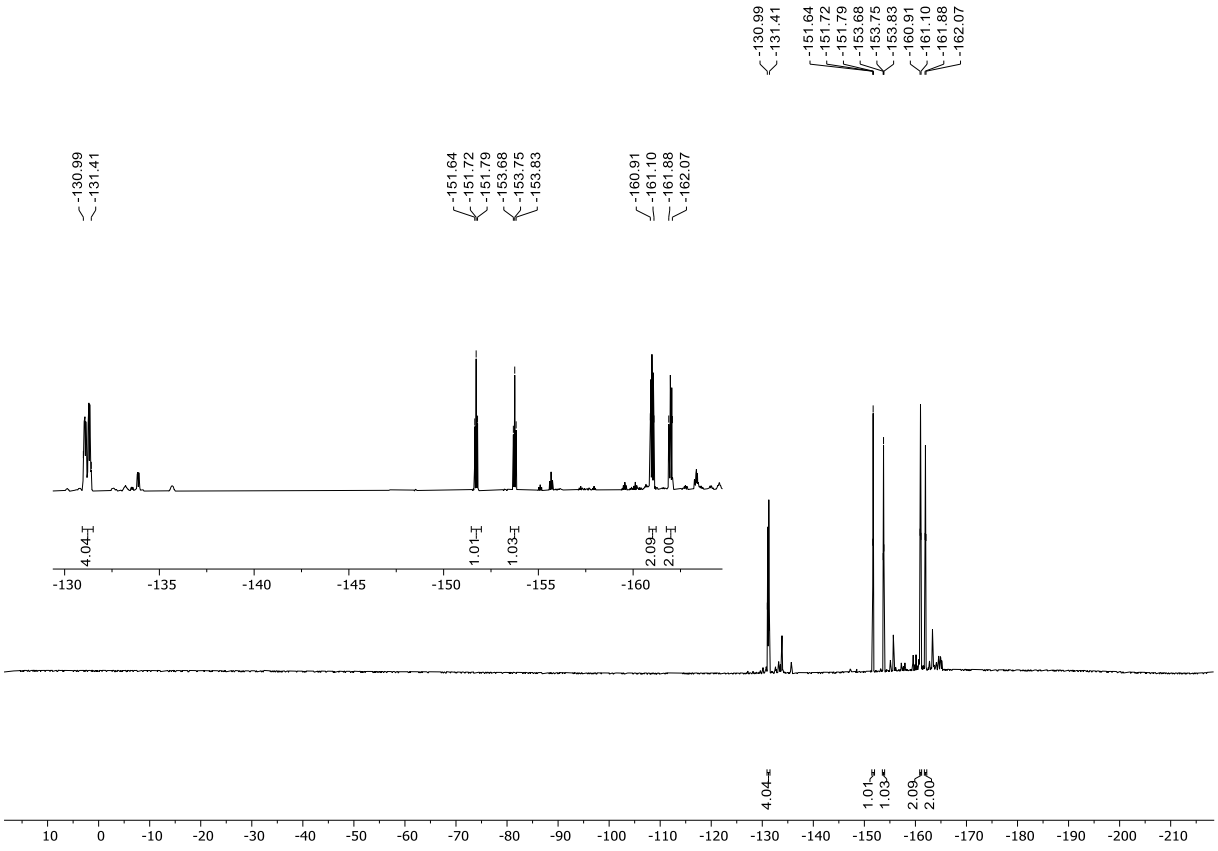
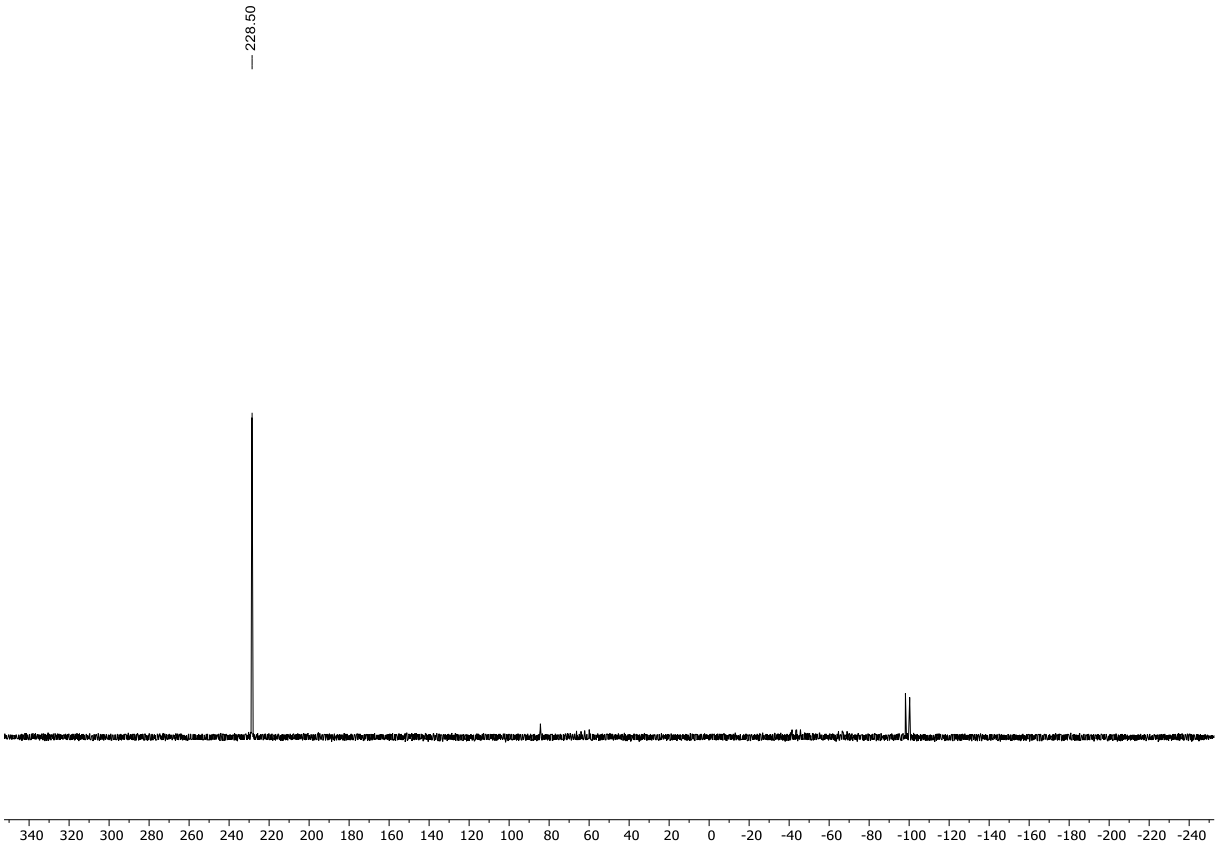
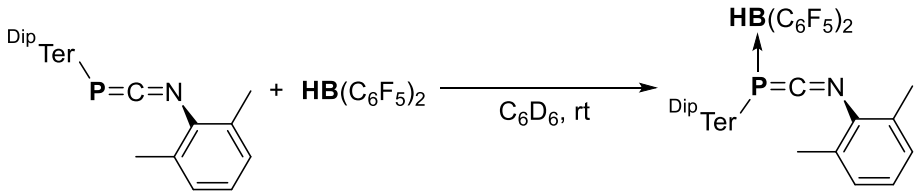


Figure S76: $^{31}P\{^{1}H\}$ NMR spectrum of Mes*PC(H)N(^{t}Bu)B(C_6F_5)$_2$ (**9**) (122 MHz, C_6D_6, rt).



3.18 Synthesis of ^{Dip}TerP(HB(C_6F_5)$_2$)CNXyl (10)



^{Dip}TerP=C=NXyl (**3f**) (0.033 g, 0.059 mmol) and HB(C_6F_5)$_2$ (0.020 g, 0.059 mmol) were dissolved in 0.6 mL of C_6D_6. Subsequent NMR analysis revealed complete conversion of both starting materials to give ^{Dip}Ter(HB(C_6F_5)$_2$)CNXyl (**10**). The solution was transferred into a vial and all volatile components were removed under vacuum to give **10** as a yellow solid.

Crystals suitable for single crystal X-ray diffraction were obtained by layering a C_6D_6 solution of **10** with *n*-hexane and subsequent slow evaporation of the solution at room temperature.

Yield: 0.044 g (0.049 mmol; 83%).

CHN: calculated: C 67.63, H 5.23, N 1.55; found: C 66.92, H 4.85, N 1.26. **^{1}H NMR** (300 MHz, C_6D_6, 298 K): δ = 0.99 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.41 (d, $^3J_{H,H}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.88 (s, 6H, *o*-CH_3N), 2.92 (hept, $^3J_{H,H}$ = 6.9 Hz, CH(CH_3)$_2$), 6.48-6.51 (m, 2H, CH_{Aryl}), 6.66-6.71 (m, 1H, CH_{Aryl}), 6.86 (m(br), 1H, BH), 6.90-6.93 (m, 5H, CH_{Aryl}), 7.05-7.09 (m, 4H, CH_{Aryl}) ppm. **^{11}B{^{1}H} NMR** (96 MHz, C_6D_6, 298 K): δ = −19.3 ppm. **^{19}F{^{1}H} NMR** (282 MHz, C_6D_6, 298 K): δ = −129.1 to −129.2 (m, 4F, *m*-F_{Ar}B), −160.6 (t, $^3J_{F,F}$ = 20.6 Hz, 2F, *p*-F_{Ar}B), −165.1 to −165.3 (m, 4F, *o*-F_{Ar}B), ($\Delta\delta^{19}F_{m,p}$ = 4.6 Hz) ppm. **^{31}P{^{1}H} NMR** (122 MHz, C_6D_6, 298 K): δ = 83.1 ppm.

Figure S77: ^{1}H NMR spectrum of ^{Dip}TerP(HB(C_6F_5)$_2$)CNXyl (**10**) (300 MHz, C_6D_6, rt).

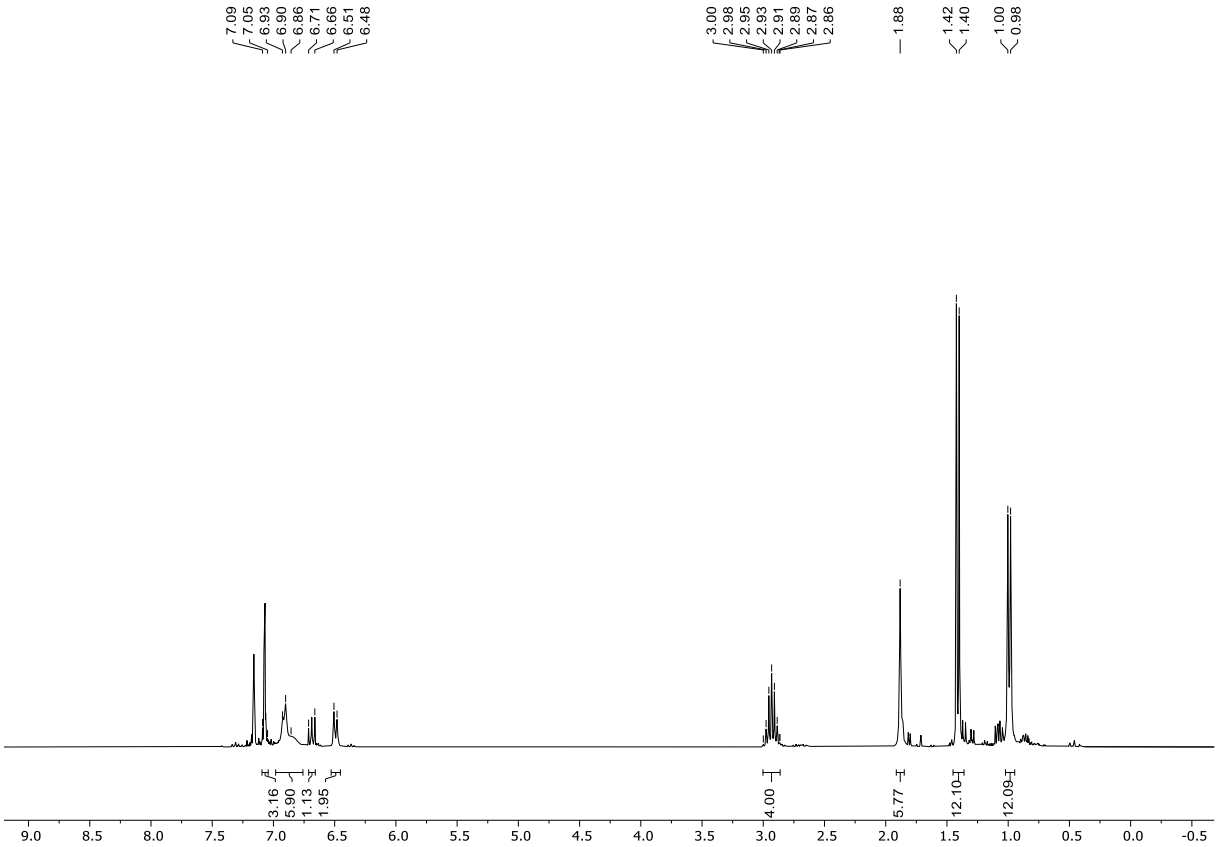


Figure S78: ^{13}C{^{1}H} NMR spectrum of compound ^{Dip}TerP(HB(C_6F_5)$_2$)CNXyl (**10**) (75 MHz, C_6D_6, rt)..

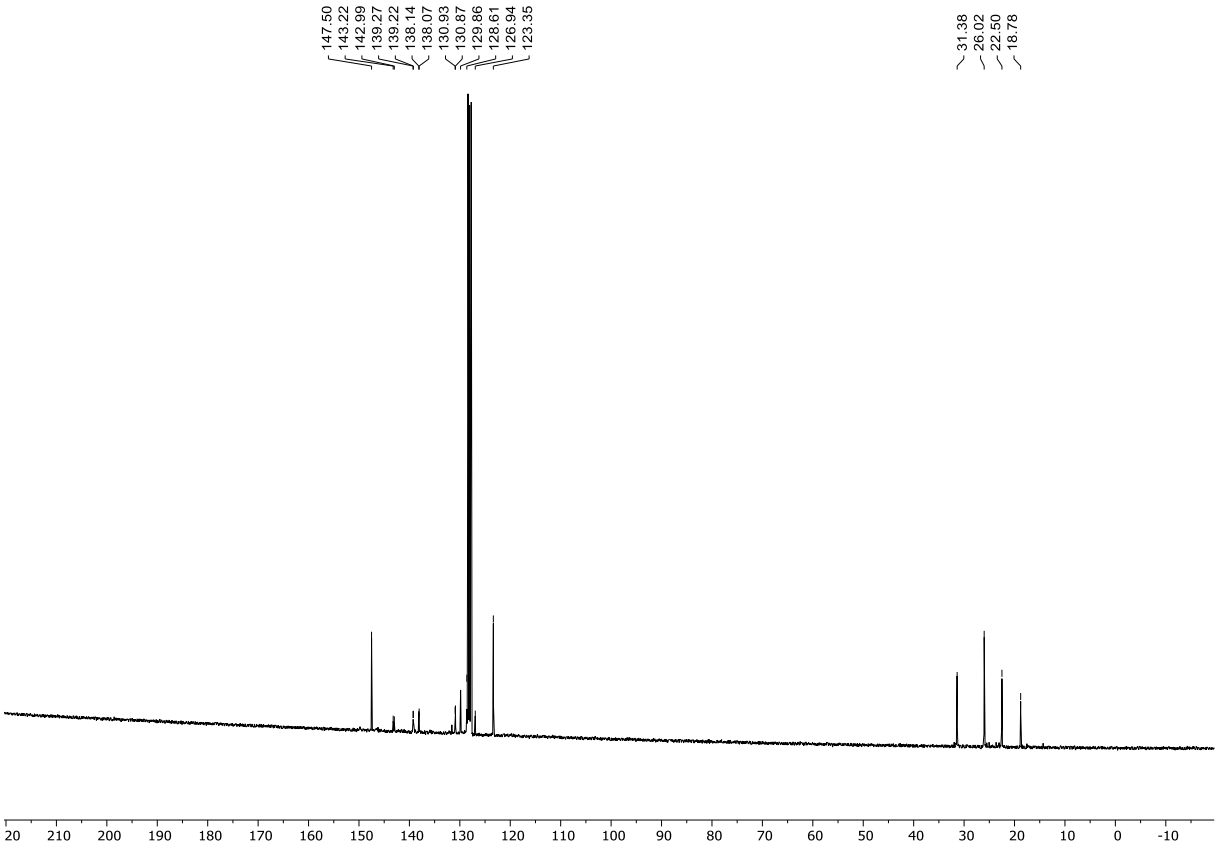


Figure S79: $^{11}B\{^{1}H\}$ NMR spectrum of ^{Dip}TerP(HB(C_6F_5)$_2$)CNXyl (**10**) (96 MHz, C_6D_6, rt).

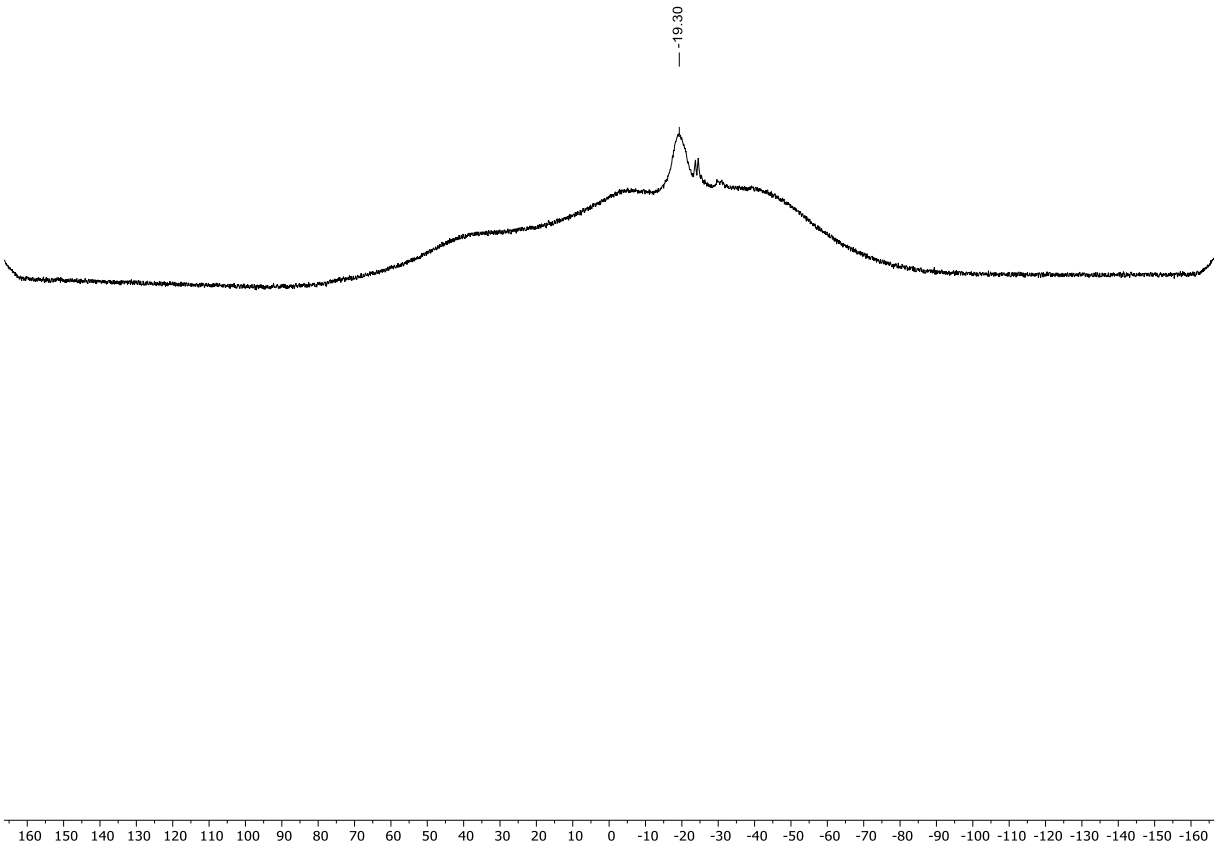


Figure S80: $^{19}F\{^{1}H\}$ NMR spectrum of ^{Dip}TerP(HB(C_6F_5)$_2$)CNXyl (**10**) (282 MHz, C_6D_6, rt).

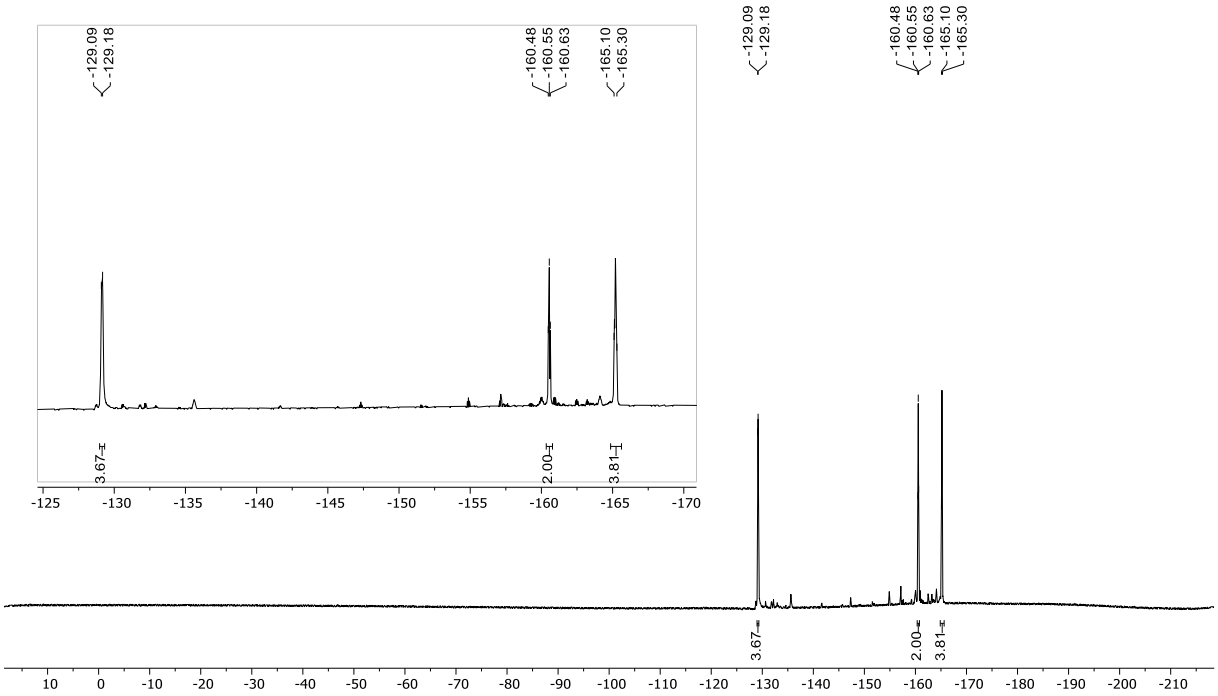
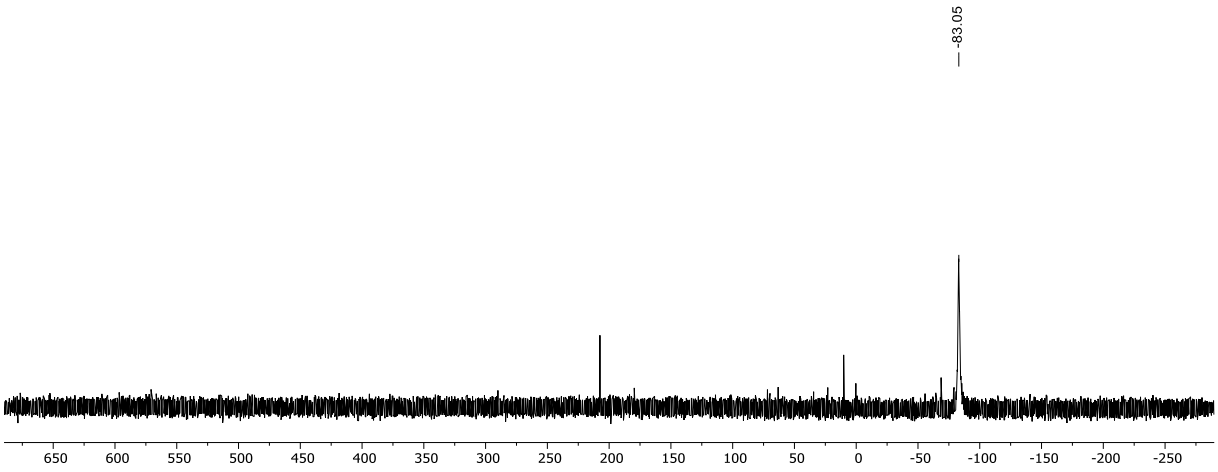


Figure S81: $^{31}P\{^{1}H\}$ NMR spectrum of ^{Dip}TerP(HB(C_6F_5)$_2$)CNXyl (**10**) (122 MHz, C_6D_6, rt).



4 Cyclic Voltammetry (CV)

Cyclic Voltammetry were recorded using a Methrom Autolab PGSTAT204 at 23 °C in THF containing 0.1 M $[N^nBu_4][PF_6]$ at varying scan rates. A standard three-electrode cell configuration was employed using a glassy carbon working electrode, a platinum wire counter electrode, and a silver wire serving as the reference electrode. Formal redox potentials are referenced to the $[FeCp_2]/[FeCp_2]^+$ couple. The $E_{1/2}(ox)$ potential was estimated using difference pulse voltammetry at 0.383 V vs. $[FeCp_2]/[FeCp_2]^+$. Another CV measurement was performed in MeCN as the solvent window is wider at positive potentials compared to THF. This data shows further irreversible oxidation above 0.5 V.

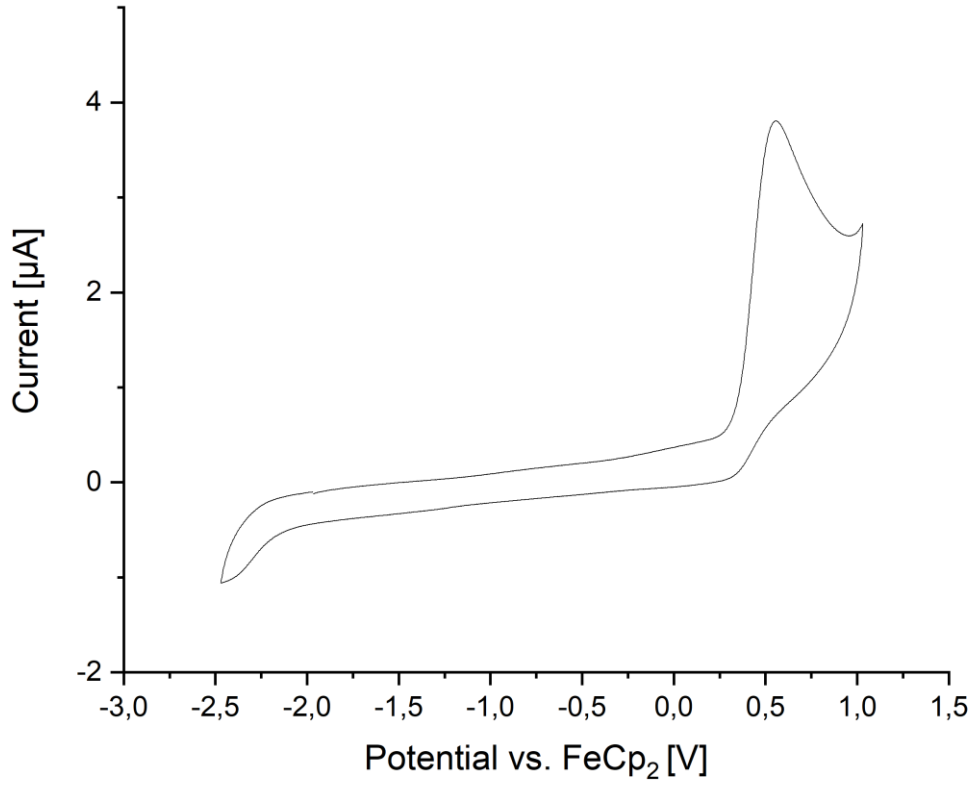


Figure S82: Cyclic voltammogram of **3a** recorded in THF at 100 mV/s. E_{Peak} = 0.469 V vs. $FeCp_2$.

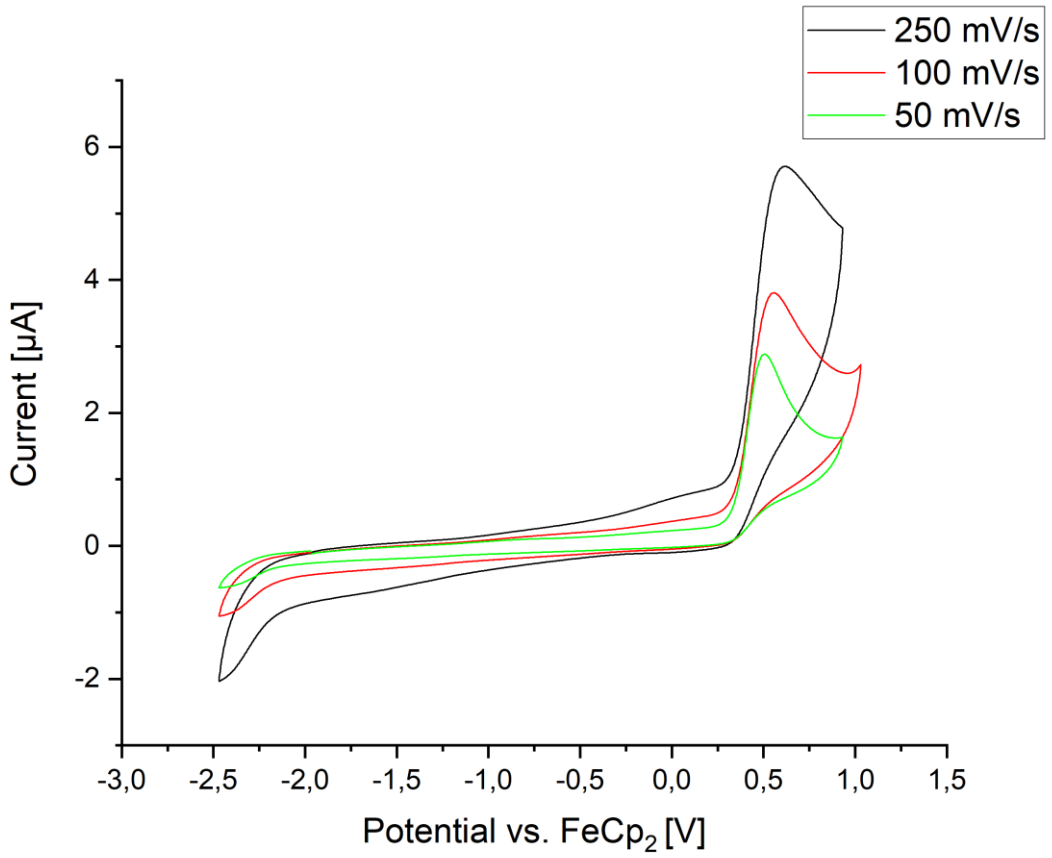


Figure S83: Cyclic voltammogram of **3a** recorded in THF at different scan rates (50, 100 and 250 mV/s).

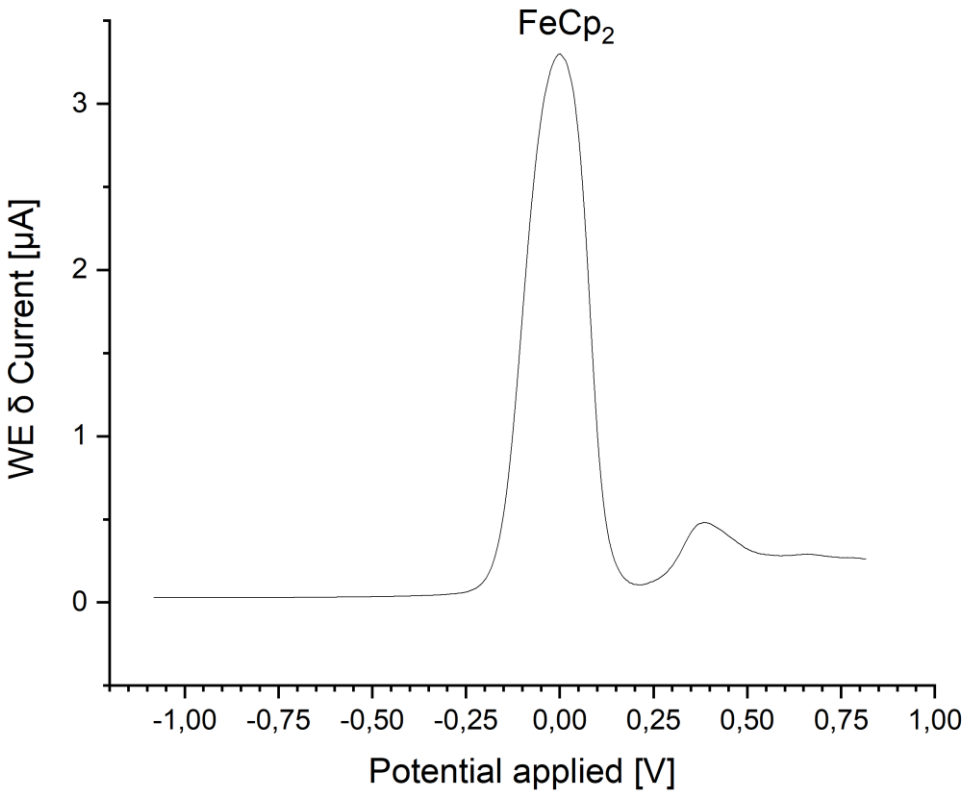


Figure S84: Difference pulse voltammogram of **3a** recorded in THF. $E_{1/2}$(ox) 0.383 V.

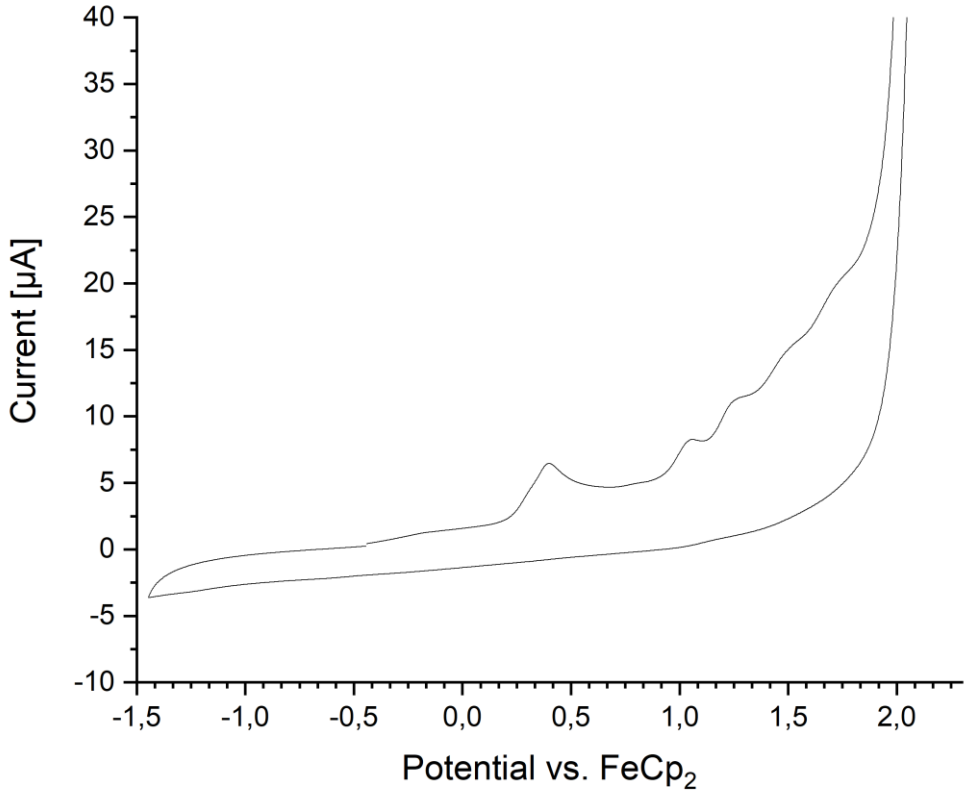


Figure S85: Cyclic voltammogram of **3a** recorded in MeCN at 100 mV/s.

5 Computational details

5.1 General remarks

Computations were carried out using Gaussian09[9] or ORCA 4.2.1[10] and the standalone version of NBO 6.0.[11,12]

Structure optimizations employed the hybrid DFT functional PBE0[13] in conjunction with Grimme's dispersion correction D3(BJ)[14] and the def2-SVP basis set[15] (notation PBE0-D3/def2-SVP). All structures were fully optimized and confirmed as minima by frequency analyses. Calculated frequencies were scaled by 0.950 (as derived from Truhlar's Reduced Scale Factor Optimization model).[16] Partial charges were determined by Natural Population analysis (NPA) using the NBO program. QT-AIM[17] analyses were performed using MultiWfn 3.6[18] employing *Gaussian09* formatted checkpoint files. Chemical shifts and coupling constants were derived by the GIAO method.[19] The calculated absolute shifts ($\sigma_{calc,X}$) were referenced to the experimental absolute shift of 85% H_3PO_4 in the gas phase ($\sigma_{ref,1}$ = 328.35 ppm),[20] using PH_3 ($\sigma_{ref,2}$ = 594.45 ppm) as a secondary standard:[21]

$$\begin{aligned} \delta_{calc,X} &= (\sigma_{ref,1} - \sigma_{ref,2}) - (\sigma_{calc,X} - \sigma_{calc,PH_3}) \\ &= \sigma_{calc,PH_3} - \sigma_{calc,X} - 266.1 \text{ ppm} \end{aligned}$$

At the PBE0-D3/def2-SVP level of theory, σ_{calc,PH_3} amounts to +629.17 ppm.

More accurate estimates of the electronic energy were obtained by single-point DLPNO-CCSD(T)/def2-TZVP[22] computations (notation DLPNO-CCSD(T)/def2-TZVP//PBE-D3/def2-SVP). The T_1 diagnostic was evaluated in each case to ensure reliable results. (Empirically, CCSD(T) results with T_1 values smaller than 0.02 are considered reliable.)[23]

5.2 Summary of calculated data

Table S6. Summary of calculated data, including electronic energies and thermal corrections.

Compd.	NIMAG	ZPE [kcal·mol^{-1}]	E_{tot}[a]	ΔG[b]	$E_{CCSD(T)}$[c]	T_1
1a	0	341,8849	-1503,8422	0,4890	-1503,3024	0,0098
1b	0	335,3170	-1729,7113	0,4699	-1729,1444	0,0101
1c	0	444,5105	-1965,1470	0,6388	-1964,5524	0,0097
3a	0	352,3153	-1293,4137	0,5017	-1293,1084	0,0104
3b	0	346,2996	-1519,2828	0,4855	-1518,9503	0,0107
3c	0	455,0443	-1754,7189	0,6515	-1754,3573	0,0102
3d	0	367,5941	-1445,5721	0,5220	-1445,2430	0,0102
3e	0	361,7001	-1671,4466	0,5070	-1671,0921	0,0106
3f	0	470,6264	-1906,8783	0,6734	-1906,4955	0,0102
4a	0	280,7796	-1136,4617	0,3951	-1136,1899	0,0102
4b	0	274,2852	-1362,3349	0,3756	-1362,0368	0,0105
4c	0	383,2291	-1597,7707	0,5441	-1597,4439	0,0099
5a	0	381,8795	-3340,9832	0,5205		
[6c]$^-$	0	376,2833	-1597,2320	0,5337		
9	0	511,4947	-4030,3942	0,5993		
10	0	545,5351	-3385,4340	0,7744		
(Mes*P)$_2$	0	538,4375	-2086,4160	0,7824	-2085,8039	0,0097
(^{Mes}TerP)$_2$	0	526,9696	-2538,1709	0,7495	-2537,5055	0,0100
PMe$_3$	0	70,6245	-460,6297	0,0833	-460,3989	0,0098
CN*t*Bu	0	81,6717	-250,1866	0,1000	-250,1981	0,0111
CNXyl	0	97,0256	-402,3429	0,1202	-402,3332	0,0111
Isobutene	0	67,6791	-156,9189	0,0805	-156,9066	0,0099
3a_to_4a_TS	1	348,8181	-1293,3502	0,4982	-1293,0454	0,0147
MesPCNMe	0	139,6090	-822,5422	0,1769		

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

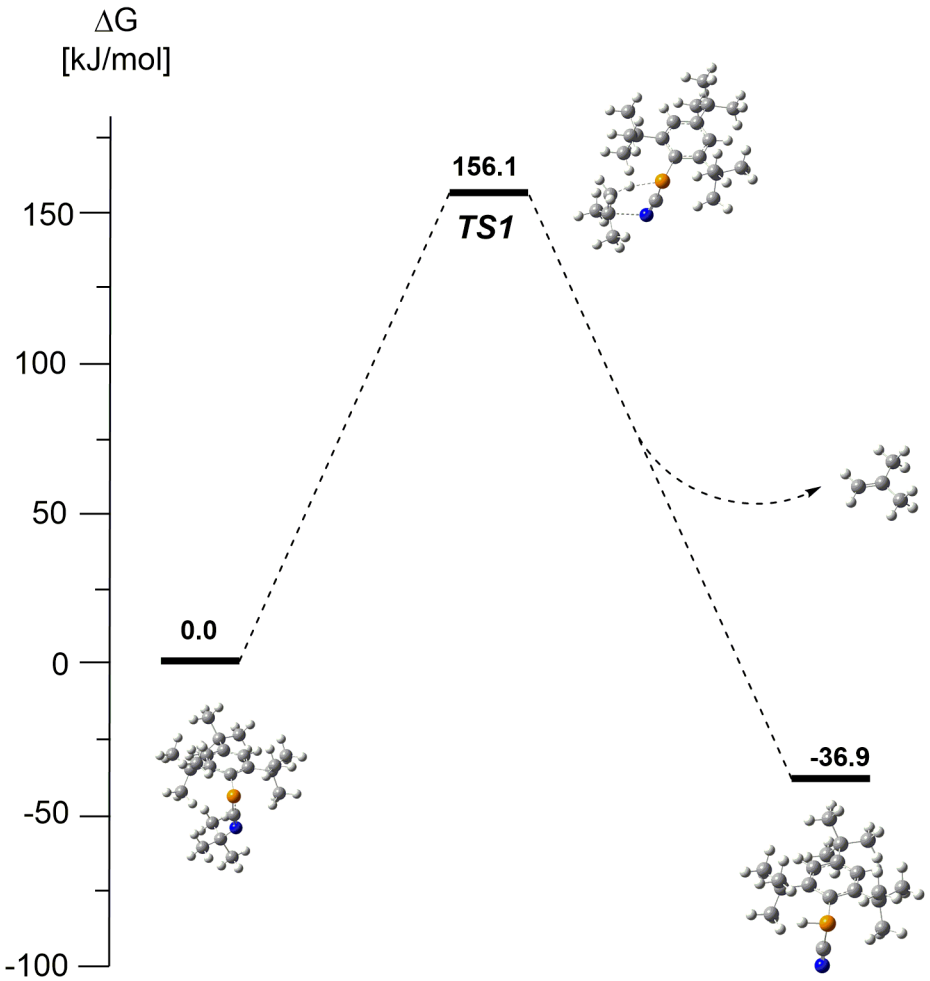
5.3 Thermochemistry

To evaluate the thermodynamic feasibility of the reactions described in the manuscript their respective $\Delta_R G°_{298}$ values were determined on the DLPNO-CCSD(T)/def2-TZVP // PBE0-D3/def2-SVP level of theory. The transformations evaluated have been summarized in Figure S82.

Figure S86: $\Delta_R G°_{298}$ (the DLPNO-CCSD(T)/def2-TZVP // PBE0-D3/def2-SVP) values for the formation of 3a-f and 4a-c, respectively. In addition, potential competing reactions, i.e. the formation of the corresponding diphosphenes, has been evaluated as well.

			$\Delta_R G°_{298}$
Formation of 3a-f:			
Mes*PPMe$_3$ + CN*t*Bu	⟶	Mes*PCN*t*Bu + PMe$_3$	-27.99 kJ/mol
^{Mes}TerPPMe$_3$ + CN*t*Bu	⟶	^{Mes}TerPCN*t*Bu + PMe$_3$	-20.37 kJ/mol
^{Dip}TerPPMe$_3$ + CN*t*Bu	⟶	^{Dip}TerPCN*t*Bu + PMe$_3$	-25.08 kJ/mol
Mes*PPMe$_3$ + CNXyl	⟶	Mes*PCNXyl + PMe$_3$	-26.54 kJ/mol
^{Mes}TerPPMe$_3$ + CNXyl	⟶	^{Mes}TerPCNXyl + PMe$_3$	-34.66 kJ/mol
^{Dip}TerPPMe$_3$ + CNXyl	⟶	^{Dip}TerPCNXyl + PMe$_3$	-29.10 kJ/mol
Competing reactions:			
Mes*PPMe$_3$	⟶	0.5 Mes*P=PMes* + PMe$_3$	-33.67 kJ/mol
^{Mes}TerPPMe$_3$	⟶	0.5 ^{Mes}TerP=P^{Mes}Ter + PMe$_3$	-50.18 kJ/mol
^{Dip}TerPPMe$_3$	⟶	0.5 ^{Dip}TerP=P^{Dip}Ter + PMe$_3$	-35.41 kJ/mol
Formation of 4a-c:			
Mes*PCN*t*Bu	⟶	Mes*P(H)CN + *iso*-butene	-36.93 kJ/mol
^{Mes}TerPCN*t*Bu	⟶	^{Mes}TerP(H)CN + *iso*-butene	-58.87 kJ/mol
^{Dip}TerPCN*t*Bu	⟶	^{Dip}TerP(H)CN + *iso*-butene	-52.78 kJ/mol
Competing reactions:			
Mes*PCN*t*Bu	⟶	0.5 Mes*P=PMes* + CN*t*Bu	-5.68 kJ/mol
^{Mes}TerPCN*t*Bu	⟶	0.5 ^{Mes}TerP=P^{Mes}Ter + CN*t*Bu	-29.82 kJ/mol
^{Dip}TerPCN*t*Bu	⟶	0.5 ^{Dip}TerP=P^{Dip}Ter + CN*t*Bu	-10.33 kJ/mol

Figure S87: Free energy profile of the *iso*-butene elimination from Mes*PCN*t*Bu (**3a**) to give Mes*P(H)CN (**4a**) calculated on the DLPNO-CCSD(T)/def2-TZVP // PBE0-D3/def2-SVP level of theory.



5.4 Summary of calculated NMR data

As described above chemical shifts were derived using the GIAO method.

Table S7. Calculated absolute shifts ($\sigma_{calc,X}$) as obtained from a GIAO calculation at the PBE0-D3/Def2SVP level of theory in the gas phase and chemical shift using H_3PO_4 and PH_3 as standards.

Compound	$\sigma_{calc,X}$	$\delta_{calc,X}$	δ_{exp}
Mes*PCNtBu (**3a**)	487.6	-124.4	-103.9
^{Mes}TerPCNtBu (**3b**)	524.3	-161.1	-125.4
^{Dip}TerPCNtBu (**3c**)	528.0	-164.8	-134.8
Mes*PCNXyl (**3d**)	521.0	-157.9	-120.6

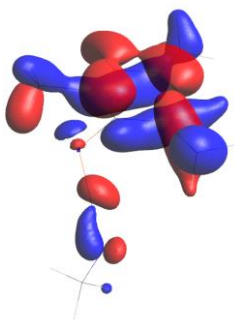
^{Mes}TerPCNXyl (**3e**)	542.5	-179.4	-145.4
DipTerPCNXyl (**3f**)	527.2	-164.1	-144.8
Mes*PHCN (**4a**)	502.3	-139.1	-105.4
^{Mes}TerPHCN (**4b**)	518.0	-154.9	-120.6
^{Dip}TerPHCN (**4c**)	517.7	-154.6	-120.4
Mes*P(H)CNB(C_6F_5)$_3$ (**5a**)	504.0	-140.9	-99.2
[^{Dip}TerPCN]$^-$ (**6c**$^-$)	496.7	-133.6	-120.7
Mes*PC(H)N(B(C_6F_5)$_2$)*t*Bu (**9**)	152.9	210.2	228.5
^{Dip}TerP(HB(C_6F_5)$_2$)CNXyl (**10**)	470.5	-107.4	-83.1

5.5 Bonding and NBO Analysis

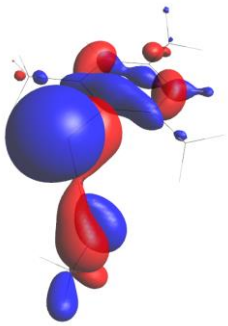
5.5.1 MesPCNMe

The electronic structure of phosphaazaallenes **3a**-**f** was investigated using the truncated model compound MesPCNMe (Mes = 2,4,6-$Me_3C_6H_2$). First the Kohn-Sham orbitals (PBE0-D3/def2-SVP) were inspected and the LUMO+3 to HOMO-4 along with their respective energies are depicted below.

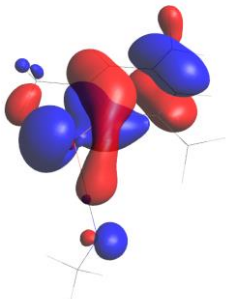
Figure S88. Relevant Kohn-Sham orbitals of MesPCNMe (PBE0-D3/def2-SVP).



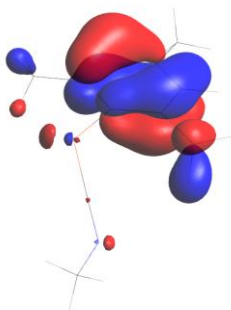
HOMO−4
−9.30 eV



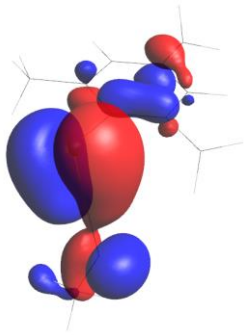
HOMO−3
−7.70 eV



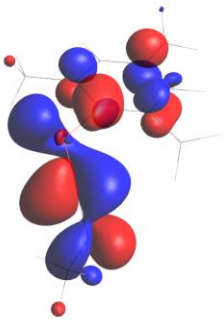
HOMO−2
−6.79 eV



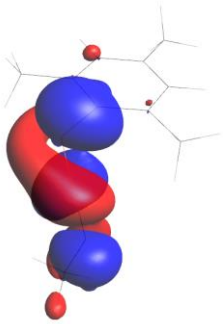
HOMO−1
−6.69 eV



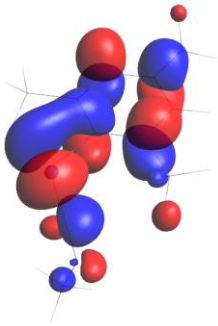
HOMO
−5.84 eV



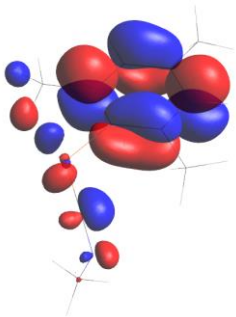
LUMO
−0.70 eV



LUMO+1
−0.45 eV
a



LUMO+2
0.01 eV
b



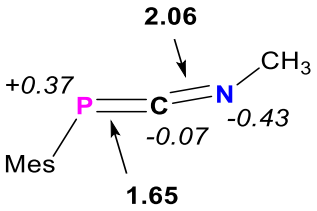
LUMO+3
0.25 eV

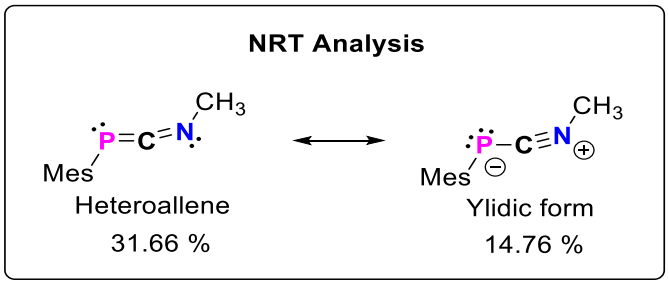
Next an NBO analysis was carried out on the PBE0/def2-SVP level of theory and additionally Wiberg-Bond-Indices (WBI) were determined, NLMOs (Natural localized molecular orbitals) were calculated and an NRT-analysis was carried out. The results of these natural bond orbital analyses for MesPCNMe are summarized below.

This revealed two distinct σ- and π-type NBOs for the P−C (WBI 1.64) and C−N (WBI 2.06) linkages, respectively. Figure S show the corresponding Natural Localized Molecular Orbital, NLMO, and the % of the individual atoms to this NLMO) In addition, a lone pair of electrons (LP) on P with high s-character (s 65.7%, p 34.3%) and a LP on N with rather high p-character (s 20.6%, p 9.4%). The LP on P interacts weakly the π* orbital of the C=N bond, resulting in a resonance stabilization of ca. 12 kcal/mol, whereas the LP on N is delocalized into the P=C π*-orbital, resulting in a resonance stabilization of ca. 58 kcal/mol. Natural resonance theory revealed two leading

resonance structures, with the major being the heteroallene form and the minor relevant resonance being an ylidic form with a $-P^{(-)}-C$ single and $-C\equiv N-^{(+)}$ triple bond, respectively.

In the following the *NPA Charges*, **Wiberg Bond indexes** in **MesPCNMe** are summarized, as well as the results from NRT analysis.





Summary of NBO results:

NPA Charges

N 10 -0.43973

P 11 0.37432

C 9 0.07045

WBIs

N10-C9 2.0561

C9-P11 1.6448

Bonding

18. (1.68849) LP (1) N 10 s(20.50%)p 3.87(79.39%)d 0.01(0.10%)

19. (1.91385) LP (1) P 11 s(65.68%)p 0.52(34.25%)d 0.00(0.07%)

35. (1.99121) BD (1) C 9- N 10

(38.27%) 0.6186* C 9 s(43.88%)p 1.28(56.00%)d 0.00(0.13%)

(61.73%) 0.7857* N 10 s(47.38%)p 1.11(52.49%)d 0.00(0.14%)

36. (1.97469) BD (2) C 9- N 10

(38.55%) 0.6209* C 9 s(0.02%)p99.99(99.80%)d 9.50(0.18%)

(61.45%) 0.7839* N 10 s(0.08%)p99.99(99.77%)d 2.04(0.16%)

37. (1.97476) BD (1) C 9- P 11

(65.55%) 0.8097* C 9 s(55.02%)p 0.82(44.94%)d 0.00(0.04%)

(34.45%) 0.5869* P 11 s(18.36%)p 4.39(80.69%)d 0.05(0.94%)

38. (1.94565) BD (2) C 9- P 11

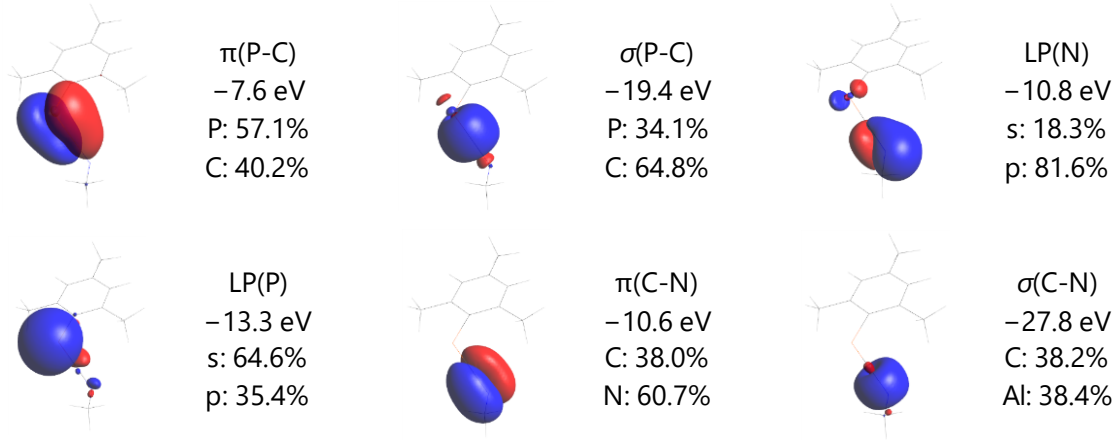
(41.66%) 0.6454* C 9 s(1.03%)p95.54(98.88%)d 0.08(0.08%)

(58.34%) 0.7638* P 11 s(0.05%)p99.99(99.36%)d12.38(0.59%)

2nd order perturbation [kcal/mol]

LP (1) N 10	70. BD*(2) C 9- P 11	58.91
LP (1) P 11	67. BD*(1) C 9- N 10	12.01
LP (1) P 11	68. BD*(2) C 9- N 10	5.25

Figure S89. Selected NLMOs of MesPCNMe (PBE0/def2-SVP).



5.5.2 Mes*P(H)CN (4a)

NPA charges

C 48 -0.03078

N 49 -0.31519

P 50 0.49758

H 51 0.03181

Wiberg Bond Indices

C1-P50 0.9432

C48-N49 2.8792

C48-P50 0.9941

P50-H51 0.9387

Bonding

26. (1.97032) LP (1) N 49 s(49.89%)p 1.00(50.05%)d 0.00(0.06%)

27. (1.91310) LP (1) P 50 s(49.64%)p 1.01(50.30%)d 0.00(0.06%)

79. (1.99743) BD (1) C 48- N 49

(40.71%) 0.6381* C 48 s(46.32%)p 1.16(53.58%)d 0.00(0.10%)

(59.29%) 0.7700* N 49 s(49.42%)p 1.02(50.30%)d 0.01(0.28%)

80. (1.99167) BD (2) C 48- N 49

(46.22%) 0.6798* C 48 s(0.28%)p99.99(99.58%)d 0.52(0.14%)

(53.78%) 0.7334* N 49 s(0.73%)p99.99(98.97%)d 0.41(0.30%)

81. (1.98575) BD (3) C 48- N 49

(47.78%) 0.6912* C 48 s(0.19%)p99.99(99.68%)d 0.68(0.13%)

(52.22%) 0.7226* N 49 s(0.23%)p99.99(99.47%)d 1.35(0.31%)

82. (1.98057) BD (1) C 48- P 50

(63.10%) 0.7944* C 48 s(53.18%)p 0.88(46.78%)d 0.00(0.05%)

(36.90%) 0.6074* P 50 s(15.15%)p 5.53(83.77%)d 0.07(1.08%)

83. (1.96081) BD (1) P 50- H 51

(51.40%) 0.7169* P 50 s(16.70%)p 4.94(82.55%)d 0.05(0.75%)

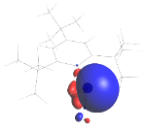
(48.60%) 0.6971* H 51 s(99.74%)p 0.00(0.26%)

2nd Order Perturbation (kcal/mol)

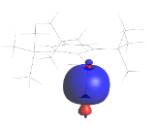
27. LP (1) P 50 135. BD*(1) C 48- N 49 6.56

27. LP (1) P 50 136. BD*(2) C 48- N 49 5.66

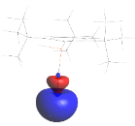
Figure S90. Selected NLMOs of Mes*P(H)CN (PBE0/def2-SVP).



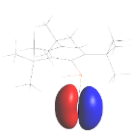
LP(P)
−12.1 eV
s: 48.8%
p: 51.1%



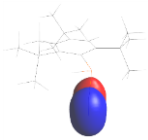
σ(P-C)
−18.2 eV
P: 36.6%
C: 62.5%



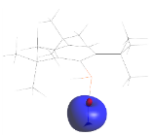
LP(N)
−14.1 eV
s: 50.1%
p: 49.9%



π(C-N)
−9.8 eV
C: 46.1%
N: 53.5%



π(C-N)
−9.9 eV
C: 47.4%
N: 51.8%



σ(C-N)
−28.8 eV
C: 40.7%
N: 59.2%

The NLMOs of **4b** are almost identical and will not be displayed.

5.5.3 ^{Mes}TerP(H)CN (4b)

NPA Charges

P 1 0.51782

N 2 -0.32593

C 52 -0.01981

H 53 0.05494

WBIs

P1-C52 1.0019

P1-H53 0.9402

C52-N2 2.8717

P1-C3 0.9354

Bonding

32. (1.90955) LP (1) P 1 s(51.42%)p 0.94(48.51%)d 0.00(0.07%)

33. (1.97026) LP (1) N 2 s(49.93%)p 1.00(50.01%)d 0.00(0.06%)

34. (1.95392) BD (1) P 1- C 3

(38.85%) 0.6233* P 1 s(18.07%)p 4.49(81.12%)d 0.05(0.82%)

0.0000 0.0000 0.4247 0.0158 0.0000

-0.0343 0.0026 0.0000 -0.5043 -0.0380

0.0000 0.7444 0.0111 0.0122 -0.0170

-0.0558 -0.0169 0.0658

(61.15%) 0.7820* C 3 s(25.63%)p 2.90(74.31%)d 0.00(0.06%)

0.0000 0.5058 -0.0201 0.0354 -0.0089

0.5001 -0.0376 -0.6990 0.0405 0.0018

-0.0020 -0.0200 -0.0052 0.0140

35. (1.98002) BD (1) P 1- C 52

(36.79%) 0.6066* P 1 s(15.14%)p 5.54(83.80%)d 0.07(1.06%)

0.0000 0.0000 0.3883 0.0250 0.0000

0.2428 0.0283 0.0000 0.8106 0.0420

0.0000 0.3453 -0.0154 0.0244 0.0112

0.0680 -0.0706 -0.0167

(63.21%) 0.7950* C 52 s(53.08%)p 0.88(46.88%)d 0.00(0.04%)

0.0000 0.7275 -0.0405 -0.1515 0.0126

-0.6144 0.0410 -0.2578 0.0051 0.0059

0.0030 0.0121 -0.0138 -0.0047

36. (1.95725) BD (1) P 1 - H 53

(52.35%) 0.7236* P 1 s(15.42%)p 5.44(83.83%)d 0.05(0.75%)

0.0000 0.0000 0.3927 -0.0022 0.0000

-0.8885 -0.0051 0.0000 0.1509 -0.0065

0.0000 -0.1568 -0.0391 -0.0407 -0.0001

-0.0029 0.0637 -0.0422

(47.65%) 0.6903* H 53 s(99.71%)p 0.00(0.29%)

0.9986 0.0021 0.0523 -0.0103 0.0049

37. (1.99682) BD (1) N 2 - C 52

(59.30%) 0.7701* N 2 s(49.28%)p 1.02(50.45%)d 0.01(0.27%)

(40.70%) 0.6380* C 52 s(46.24%)p 1.16(53.66%)d 0.00(0.09%)

38. (1.99183) BD (2) N 2 - C 52

(54.16%) 0.7359* N 2 s(1.03%)p96.06(98.67%)d 0.29(0.30%)

(45.84%) 0.6771* C 52 s(0.54%)p99.99(99.32%)d 0.27(0.14%)

39. (1.98460) BD (3) N 2 - C 52

(52.33%) 0.7234* N 2 s(0.11%)p99.99(99.58%)d 2.66(0.30%)

(47.67%) 0.6904* C 52 s(0.09%)p99.99(99.78%)d 1.39(0.13%)

2nd Order Perturbation (kcal/mol)

32. LP (1) P 1 103. BD*(1) N 2 - C 52 7.14

32. LP (1) P 1 104. BD*(2) N 2 - C 52 4.59

5.5.4 Mes*P(H)CNB(C_6F_5)$_3$ (5a)

NPA Charges

B 68 0.55404

N 69 -0.36676

C 49 0.26825

P 1 0.55159

H 85 0.04422

WBIs

B68-N69 0.6625

P1-C49 0.9906

C49-N69 2.5819

Bonding

60. (1.89944) LP (1) P 1 s(52.07%)p 0.92(47.84%)d 0.00(0.08%)

107. (1.97064) BD (1) P 1 - C 49

(34.11%) 0.5841* P 1 s(13.19%)p 6.50(85.70%)d 0.08(1.11%)

(65.89%) 0.8117* C 49 s(53.22%)p 0.88(46.75%)d 0.00(0.03%)

108. (1.95373) BD (1) P 1 - H 85

(51.90%) 0.7204* P 1 s(16.11%)p 5.16(83.12%)d 0.05(0.77%)

159. (1.98399) BD (1) C 49 - N 69

(36.34%) 0.6028* C 49 s(46.49%)p 1.15(53.38%)d 0.00(0.13%)

(63.66%) 0.7979* N 69 s(47.55%)p 1.10(52.32%)d 0.00(0.13%)

160. (1.98354) BD (2) C 49 - N 69

(37.92%) 0.6158* C 49 s(0.02%)p99.99(99.77%)d11.82(0.21%)

(62.08%) 0.7879* N 69 s(0.15%)p99.99(99.71%)d 0.94(0.14%)

161. (1.98084) BD (3) C 49 - N 69

(39.66%) 0.6298* C 49 s(0.02%)p99.99(99.79%)d10.08(0.19%)

(60.34%) 0.7768* N 69 s(0.00%)p 1.00(99.85%)d 0.00(0.14%)

207. (1.96960) BD (1) B 68- N 69

(20.65%) 0.4544* B 68 s(17.79%)p 4.60(81.82%)d 0.02(0.40%)

(79.35%) 0.8908* N 69 s(52.36%)p 0.91(47.63%)d 0.00(0.01%)

209. (0.03518) BD*(1) P 1- C 49

(65.89%) 0.8117* P 1 s(13.19%)p 6.50(85.70%)d 0.08(1.11%)

(34.11%) -0.5841* C 49 s(53.22%)p 0.88(46.75%)d 0.00(0.03%)

261. (0.02584) BD*(1) C 49- N 69

(63.66%) 0.7979* C 49 s(46.49%)p 1.15(53.38%)d 0.00(0.13%)

(36.34%) -0.6028* N 69 s(47.55%)p 1.10(52.32%)d 0.00(0.13%)

262. (0.12540) BD*(2) C 49- N 69

(62.08%) 0.7879* C 49 s(0.02%)p99.99(99.77%)d11.82(0.21%)

(37.92%) -0.6158* N 69 s(0.15%)p99.99(99.71%)d 0.94(0.14%)

263. (0.08564) BD*(3) C 49- N 69

(60.34%) 0.7768* C 49 s(0.02%)p99.99(99.79%)d10.08(0.19%)

(39.66%) -0.6298* N 69 s(0.00%)p 1.00(99.85%)d 0.00(0.14%)

309. (0.04648) BD*(1) B 68- N 69

(79.35%) 0.8908* B 68 s(17.79%)p 4.60(81.82%)d 0.02(0.40%)

(20.65%) -0.4544* N 69 s(52.36%)p 0.91(47.63%)d 0.00(0.01%)

2nd order perturbation (kcal/mol)

60. LP (1) P 1 261. BD*(1) C 49- N 69 6.80

60. LP (1) P 1 262. BD*(2) C 49- N 69 7.29

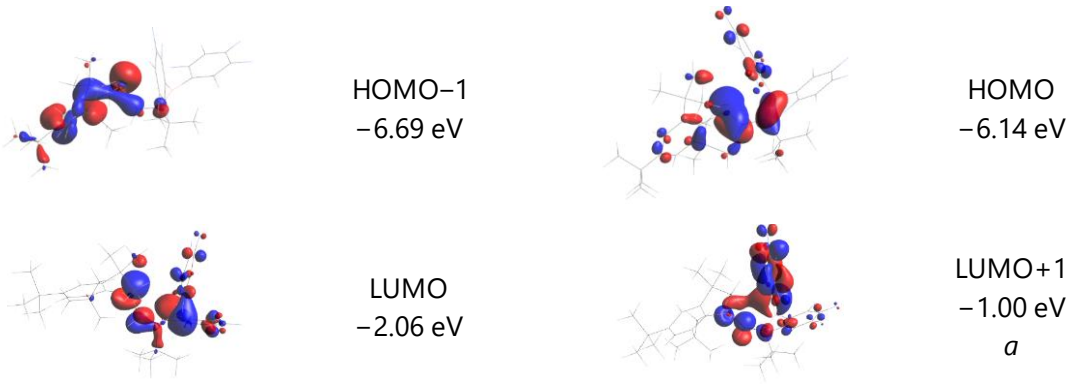
107. BD (1) P 1- C 49 309. BD*(1) B 68- N 69 8.20

5.5.5 Mes*PC(H)N(B(C_6F_5)$_2$)*t*Bu (9)

Compound **9** is best described as a heteroatomic diene with conjugated PC and BN double bonds, respectively. The WBI of the P–C bond (1.68) clearly indicates double bonding, whereas the WBI of the B–N bond (0.98) does not agree with a double bond. However, the π-component of the BN bond is strongly polarized towards N, and can also be understood as interaction of a p-type lone vacancy on B with the p-type LP on

N. Recently Berski et al. have theoretically studied the nature of 25 experimentally established BN molecules using topological analysis of the electron density (AIM) and the NBO method. Topological analysis of the electron density using the QT-AIM approach revealed an electron density ($\rho_{(3,-1)}$ [e/bohr^3]) of 0.198 at the BN bond critical point (BCP), as well as an electron density Laplacian (∇^2 [e/bohr^5]) of 0.651, which corresponds nicely with 9,10-diimino-9,10-dihydro-9,10-diboraanthracene.[24] In agreement with the NBO picture, the Kohn-Sham orbitals show a HOMO and LUMO corresponding to the formulation as heteroatomic diene (Figure S87).

Figure S91. Relevant Kohn-Sham orbitals of Mes*PC(H)N(B(C_6F_5)$_2$)*t*Bu (**9**) (PBE0-D3/def2-SVP).



a

NPA Charges

B 63 0.95710

P 87 0.61693

C 48 -0.39128

N 81 -0.74563

Wiberg Bond Indices

P87-C48 1.6791

N81-C48 1.0468

N81-B63 0.9767

C1-P87 0.9315

Bonding

83. (1.92758) LP (1) P 87 s(62.14%)p 0.61(37.81%)d 0.00(0.05%)

136. (1.97865) BD (1) C 48 - N 81

(36.51%) 0.6042* C 48 s(30.20%)p 2.30(69.61%)d 0.01(0.18%)

(63.49%) 0.7968* N 81 s(30.29%)p 2.30(69.65%)d 0.00(0.06%)

137. (1.97173) BD (1) C 48 - P 87

(63.82%) 0.7989* C 48 s(38.47%)p 1.60(61.44%)d 0.00(0.09%)

(36.18%) 0.6015* P 87 s(21.36%)p 3.64(77.82%)d 0.04(0.82%)

138. (1.91309) BD (2) C 48 - P 87

(54.20%) 0.7362* C 48 s(0.31%)p99.99(99.62%)d 0.23(0.07%)

(45.80%) 0.6767* P 87 s(0.09%)p99.99(99.16%)d 7.93(0.74%)

154. (1.96995) BD (1) B 63 - N 81

(20.48%) 0.4526* B 63 s(32.09%)p 2.11(67.59%)d 0.01(0.32%)

(79.52%) 0.8917* N 81 s(39.11%)p 1.56(60.85%)d 0.00(0.04%)

155. (1.83978) BD (2) B 63 - N 81

(13.90%) 0.3728* B 63 s(0.15%)p99.99(99.48%)d 2.55(0.37%)

(86.10%) 0.9279* N 81 s(0.22%)p99.99(99.77%)d 0.03(0.01%)

Non-Lewis

237. (0.01858) BD*(1) C 48 - P 87

(36.18%) 0.6015* C 48 s(38.47%)p 1.60(61.44%)d 0.00(0.09%)

(63.82%) -0.7989* P 87 s(21.36%)p 3.64(77.82%)d 0.04(0.82%)

238. (0.15521) BD*(2) C 48 - P 87

(45.80%) 0.6767* C 48 s(0.31%)p99.99(99.62%)d 0.23(0.07%)

(54.20%) -0.7362* P 87 s(0.09%)p99.99(99.16%)d 7.93(0.74%)

254. (0.04068) BD*(1) B 63 - N 81

(79.52%) 0.8917* B 63 s(32.09%)p 2.11(67.59%)d 0.01(0.32%)

(20.48%) -0.4526* N 81 s(39.11%)p 1.56(60.85%)d 0.00(0.04%)

255. (0.12907) BD*(2) B 63 - N 81

(86.10%) 0.9279* B 63 s(0.15%)p99.99(99.48%)d 2.55(0.37%)

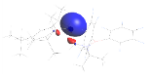
(13.90%) -0.3728* N 81 s(0.22%)p99.99(99.77%)d 0.03(0.01%)

2nd Order Perturbation Theory (kcal/mol)

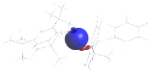
138. BD (2) C 48- P 87 255. BD*(2) B 63- N 81 4.82

155. BD (2) B 63- N 81 238. BD*(2) C 48- P 87 21.97

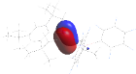
Figure S92. Selected NLMOs of Mes*PC(H)N(B(C_6F_5)$_2$)*t*Bu (**9**) (PBE0/def2-SVP).



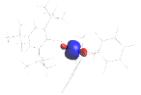
LP(P)
−16.6 eV
s: 61.5%
p: 38.3%



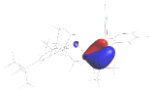
σ(P-C)
−18.7 eV
P: 35.7%
C: 63.0%



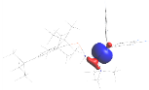
π(P-C)
−8.0 eV
P: 43.8%
C: 51.7%



σ(C-N)
−22.3 eV
C: 36.2%
N: 62.9%



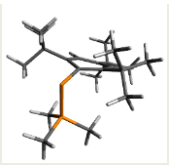
π(N-B)
−9.6 eV
B: 12.8%
N: 79.1%



σ(B-N)
−20.5 eV
B: 20.2%
N: 78.5%

5.6 Optimized structures (.xyz-files)

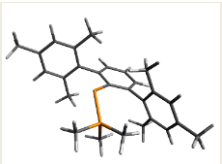
5.6.1 Mes*PPMe$_3$ (1)



```
61
Mes*PPMe3 @ PBE0-D3/def2-SVP
C        0.2346584164      1.2410236160     -0.6144890782
C       -0.4676743255      0.0071056498     -0.7017813725
C        1.5299714218      1.2283335021     -0.0756576836
C        0.2813484369     -1.2053001063     -0.6264159387
C        2.1851641123      0.0520905517      0.2793246109
C        1.5707610096     -1.1469641347     -0.0901499635
H        2.0453003060      2.1750245373      0.0635832742
H        2.1287822599     -2.0736091805      0.0379205355
P       -2.3457968223     -0.0289709590     -0.7156822651
C       -4.2416149124     -0.0849671675      1.7988646127
C       -1.7373217796     -1.4419726653      2.3141292177
C       -1.7955103648      1.3724553063      2.3293027974
H       -4.7285267477      0.8027681963      1.3719470263
H       -4.6902193397     -0.9826609458      1.3512913560
H       -4.3884096860     -0.1007530830      2.8884237361
H       -0.6683543966     -1.5028601018      2.0619223442
H       -1.8517853551     -1.2854228009      3.3974588935
H       -2.2218823165     -2.3801792065      2.0185588756
H       -1.8977382466      1.1982014586      3.4111361717
H       -0.7314176669      1.4825434647      2.0728406565
H       -2.3213415591      2.2923549726      2.0467420334
P       -2.4691283389     -0.0441979074      1.3883558696
C       -0.1951079944     -2.5400233419     -1.2564472054
C       -1.2325577702     -3.3035515506     -0.4246378576
C       -0.7771708417     -2.2407742339     -2.6476693740
C        0.9883327570     -3.4951586007     -1.4714764696
H       -0.8221765112     -3.5800015984      0.5587790215
H       -2.1385521465     -2.6993301825     -0.2859558172
H       -1.5085183185     -4.2352389991     -0.9449636950
H       -0.0460575267     -1.7021285954     -3.2699196244
H       -1.0365919774     -3.1828538072     -3.1570494914
H       -1.6913547432     -1.6345872159     -2.5809649411
H        0.6389100242     -4.3736653114     -2.0348520778
H        1.7999449915     -3.0260015340     -2.0482051238
H        1.4065694294     -3.8680565341     -0.5240063061
C        3.5564372209      0.0330097880      0.9554642271
C        3.4533922894     -0.7659799608      2.2627716066
C        4.5799135889     -0.6343110404      0.0253300455
C        4.0528871208      1.4404299021      1.2885113596
H        2.7267819805     -0.3024026147      2.9482957186
H        3.1291565343     -1.8013970273      2.0806087662
H        4.4294145907     -0.8036717770      2.7728620068
H        4.6617457693     -0.0826824719     -0.9237293165
H        5.5754271536     -0.6563648180      0.4974422225
H        4.2995482277     -1.6707735599     -0.2134220191
H        5.0242705753      1.3827973128      1.8031921869
H        4.1950635691      2.0498104304      0.3830554439
H        3.3532116725      1.9718383649      1.9518539559
C       -0.2905543778      2.5662121632     -1.2257532393
C       -0.8670364772      2.2658609696     -2.6191836590
C       -1.3513782416      3.2823489863     -0.3811755529
```

```
C         0.8582529240      3.5648073756     -1.4328064164
H        -0.1199766151      1.7611445120     -3.2508780557
H        -1.7596290438      1.6277890509     -2.5584136416
H        -1.1602575636      3.2052944293     -3.1149841421
H        -0.9481191840      3.5614128890      0.6044556137
H        -1.6621944543      4.2098620415     -0.8891583917
H        -2.2347850697      2.6444075945     -0.2471010929
H         0.4761414259      4.4367318203     -1.9849925884
H         1.2667755116      3.9410585091     -0.4825223034
H         1.6835685832      3.1310846444     -2.0176832249
```

5.6.2 ^{Mes}TerPPMe$_3$ (1b)



```
63
MesTerPPMe3 @ PBE0-D3/def2-SVP
C        -4.6864369450     -0.3266887973     -1.3731928100
C        -5.3317938082      0.4799382475     -0.4350269837
C        -2.7646035667     -1.7552983951     -2.1540353001
C        -3.4444946086     -0.9122976494     -1.1132907474
C        -4.6958709311      0.7027637530      0.7896794320
C         1.6898646913     -1.2073933990     -2.4066428560
C         3.9766079408     -0.5378524865     -1.6394595674
C         2.6608909935     -0.8705756408     -1.3174047632
C        -2.8277765514     -0.6783295405      0.1283656291
C         4.9343792535     -0.2511013408     -0.6613162604
C        -3.4562136559      0.1375224803      1.0870938085
C        -0.2883372909     -0.6795231790      0.1449306061
C         2.2729955695     -0.9151452208      0.0435867581
C        -2.7699840977      0.4273503486      2.3878469896
C         4.5429502116     -0.3325282594      0.6743060685
C        -1.5200240704     -1.3281523311      0.4384007101
C         0.9089201547     -1.3920249515      0.4079251523
C         3.2369206840     -0.6780487114      1.0449270212
C        -1.5432969559     -2.6028313954      1.0050620171
C         2.9251459779     -0.8287408646      2.5095233086
C         0.8479471132     -2.6665521154      0.9917573697
C        -0.3609797170     -3.2765368584      1.2970340072
H        -5.1612768776     -0.5050407273     -2.3429108697
H         4.2665231513     -0.5112013845     -2.6943955045
H        -5.1784205681      1.3415446791      1.5361804327
H         0.9151851472     -0.4231371359     -2.4805195821
H        -1.7880966450     -1.3254490029     -2.4299480425
H        -1.8183483936      0.9490910020      2.1911913032
H         5.2787519900     -0.1331258972      1.4597119606
H         1.8525799200     -0.7307506232      2.7235066540
H        -2.5121109746     -3.0627559603      1.2181752470
H         1.7859674687     -3.1955770900      1.1795635727
H        -0.3822938319     -4.2741486160      1.7414751010
P        -0.5254385248      0.9476594242     -0.6899836524
C         0.1738464368      3.8862779734     -0.2610680104
H        -0.8032599025      3.9543121756      0.2348717325
H         0.8327186949      4.7016200075      0.0718307476
H         0.0191487231      3.9620946314     -1.3472283440
C         1.1329154588      2.2391083047      1.9168757075
H         1.8299640291      3.0284707489      2.2366388463
H         0.1518052970      2.3869972315      2.3876570732
H         1.5273382943      1.2622660433      2.2201542672
C         2.6137380657      2.4612286651     -0.5477619119
```

```
H         3.2463708841      1.6200625398     -0.2404898900
H         2.5588374120      2.4762152917     -1.6449807325
H         3.0512656287      3.4043859025     -0.1847861623
P         0.9183606020      2.2625320851      0.1096147750
C         6.3302119737      0.1455516115     -1.0448443478
H         6.7114441994     -0.4755503270     -1.8693995689
H         6.3634795985      1.1930306088     -1.3883619446
H         7.0246801172      0.0532481782     -0.1977176498
C        -6.6817335980      1.0730904037     -0.7195651717
H        -6.8856208137      1.1124339883     -1.7993274523
H        -7.4838231033      0.4751949745     -0.2546753624
H        -6.7663576592      2.0944041091     -0.3185364266
H        -2.5659475376     -2.7727442649     -1.7836481062
H        -3.3749444195     -1.8314450109     -3.0646677876
H        -3.3898480499      1.0593368394      3.0393176011
H        -2.5189291372     -0.4963219967      2.9312224140
H         3.4810179221     -0.0926734895      3.1095506881
H         3.2222768266     -1.8270905175      2.8711572289
H         1.1633737135     -2.1495571856     -2.1909149245
H         2.1979850125     -1.3002763924     -3.3763984979
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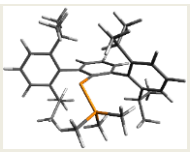
5.6.3 ^{Dip}TerPPMe$_3$ (1c)



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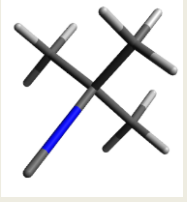
81
DipTerPPMe3 @ PBE0-D3/def2-SVP
C         2.6166090320      3.2132081633     -1.1302924544
C        -1.3038474389      3.2686350149     -2.0347976307
C         4.6968306310      1.0185983066     -0.5498213637
C         5.2830221167     -0.2260510073     -0.7401351259
C         2.8093299260      2.5090901400      0.2122849924
C         3.4323944002      1.1359051936      0.0377880609
C         4.6027013036     -1.3792009875     -0.3573325028
C         3.6044988624      3.3656902002      1.1958245851
C        -1.3850174547      2.7540026285     -0.6029489139
C        -3.7528628528      1.9801218192     -0.9267655077
C        -2.4876560659      1.7332484857     -0.3888025999
C         2.7592379850     -0.0356913852      0.4364944011
C        -4.8374657978      1.1614198114     -0.6300189846
C         3.3365205978     -1.3037808314      0.2245830967
C         2.6903487435     -3.6683660693     -0.4023225870
C        -1.5386365928      3.8940767119      0.4056670807
C         0.2218449364      0.0838594134      0.3925243831
C        -2.3033588158      0.6027092707      0.4468136614
C         2.5972894177     -2.5594166283      0.6410980132
C        -4.6642175614      0.0794562785      0.2219546872
C         1.4395151187      0.0949919688      1.1262520541
C        -0.9736013261      0.3913823256      1.0962101824
C        -3.4096746954     -0.2203470765      0.7692282410
C        -3.9674449199     -2.6716533784      1.1158385504
C         3.0653297671     -3.0422526348      2.0137671918
C         1.4499335543      0.3192290952      2.5041654211
C        -3.3068909552     -1.4196425195      1.6985238614
C        -0.9216249957      0.6284463757      2.4779514428
C         0.2684902568      0.5749696691      3.1912692277
C        -3.9150517936     -1.1214953543      3.0714513420
H         3.5801938591      3.4305469314     -1.6187336435
H         2.0213226940      2.5903542382     -1.8148690588
H        -1.1827146166      2.4300531001     -2.7365558041
```

```
H         2.0908849907      4.1716529652     -0.9917064311
H         5.2295335724      1.9195705689     -0.8654602065
H         6.2735970505     -0.3014073192     -1.1958017828
H        -0.4298438268      3.9278010219     -2.1487506719
H        -2.1917327361      3.8523918198     -2.3262424915
H         4.6260729071      3.5576101898      0.8298191901
H        -3.8981754222      2.8483973542     -1.5729046906
H         5.0671256475     -2.3546561219     -0.5204230033
H         2.3881722960     -3.2947868626     -1.3925393700
H         3.1154534323      4.3410105902      1.3480565328
H        -0.4296504564      2.2571831671     -0.3938314133
H         1.8089422740      2.3633948115      0.6467805086
H        -5.8215885903      1.3760845677     -1.0537974124
H         3.7119269105     -4.0701177340     -0.4914974510
H        -0.7096515765      4.6132475513      0.3066807193
H         3.6884311885      2.8698890451      2.1749116849
H        -2.4835972080      4.4400210535      0.2513700046
H         2.0381518416     -4.5138188370     -0.1295886867
H        -3.6562003859     -2.8614298776      0.0795944144
H         1.5354138030     -2.2797341544      0.7293617023
H        -5.5210966355     -0.5528028222      0.4656309627
H        -1.5342110573      3.5116464343      1.4377312306
H         4.1354045328     -3.3047982763      1.9930482266
H        -5.0651144513     -2.5860125985      1.1182642776
H        -2.2359294790     -1.6309228807      1.8492016633
H         2.4086807227      0.3172059354      3.0291600075
H        -3.7119755154     -3.5575046031      1.7179479088
H         2.9260604755     -2.2617813149      2.7760941153
H         2.5019973768     -3.9340261462      2.3328425748
H        -1.8462236339      0.8990900054      2.9910744518
H        -4.9878763334     -0.8887144597      2.9779444857
H         0.2783337662      0.7657052014      4.2666886356
H        -3.4324548957     -0.2655437283      3.5615584233
H        -3.8162596953     -1.9925217905      3.7384507592
P         0.4701946356     -0.0990058997     -1.4323202031
C        -0.2408977798     -2.2159250406     -3.5534428399
H         0.7338820928     -2.6754459121     -3.3436039099
H        -0.9218124779     -2.9533505146     -4.0033977168
H        -0.0904723023     -1.3830245839     -4.2556977996
C        -1.0480699528     -2.9721896095     -0.8743173153
H        -1.7936604935     -3.7069973232     -1.2122485311
H        -0.0547762616     -3.4365975489     -0.8234907017
H        -1.3125373013     -2.6093843978      0.1272949919
C        -2.6543909723     -1.1585304244     -2.4996935615
H        -3.2346422639     -0.8033782900     -1.6398194873
H        -2.6092321747     -0.3486231879     -3.2413629520
H        -3.1433294398     -2.0408573977     -2.9412738069
P        -0.9384574559     -1.5517677971     -2.0056734687
```

5.6.4 CN*t*Bu (2a)

```
15
CNtBu @ PBE0-D3/def2-SVP
C         2.3512378965     -0.0003515892      0.0002347737
C        -0.2536036457      0.0001987369     -0.0001369492
N         1.1784606140      0.0002131834      0.0002614489
C        -0.7306933133     -0.8196497007     -1.2007080017
C        -0.7312106846     -0.6301294397      1.3098842449
```



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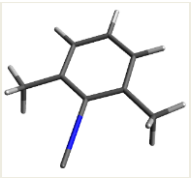
C        -0.7307394311      1.4498363656     -0.1095174001
H        -0.3661745179     -0.3808856490     -2.1405709205
H        -0.3629759840     -1.8537488725     -1.1351112426
H        -1.8300426807     -0.8391550138     -1.2256870392
H        -1.8305202949     -0.6443027898      1.3386056342
H        -0.3649519524     -1.6628407649      1.4000942584
H        -0.3655121775     -0.0555304619      2.1729127286
H        -0.3652658904      2.0441005449      0.7402212071
H        -0.3636951639      1.9099976791     -1.0380875381
H        -1.8300305414      1.4814467926     -0.1127472236
```

5.6.5 CNXyl (2b)



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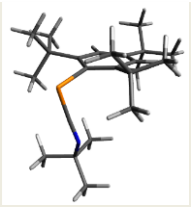
19
CNXyl @ PBE0-D3/def2-SVP
C         2.9916872548     -0.0038851951      0.0000730311
C         0.4366968436     -0.0006289600     -0.0000384804
C        -0.2388121072     -1.2350845702     -0.0000271837
C        -1.6342232742     -1.2057043606      0.0000278392
H        -2.1834011849     -2.1503636358      0.0000755831
C        -2.3252324986      0.0031614401      0.0000318020
H        -3.4175890485      0.0046366846      0.0000867625
C        -1.6309385655      1.2101221912     -0.0000103052
H        -2.1775104054      2.1562877641      0.0000271057
C        -0.2354337287      1.2356812281     -0.0000507481
C         0.5308883928     -2.5187636740     -0.0000184175
H         1.1868367536     -2.5890004653      0.8820826574
H         1.1860781093     -2.5894183618     -0.8826383570
H        -0.1448246125     -3.3839553601      0.0004612809
C         0.5377388087      2.5172740878     -0.0000082292
H        -0.1356682217      3.3842649288     -0.0006138468
H         1.1939978442      2.5856775817     -0.8820083927
H         1.1930154637      2.5861993187      0.8826936243
N         1.8149769368     -0.0024802252     -0.0000060374
```

5.6.6 Mes*PCN*t*Bu (3a)



```
63
Mes*PCNtBu @ PBE0-D3/def2-SVP
C        -0.0321633447      0.2203271837     -1.1096934854
C         0.5172838860     -1.0846195399     -0.9526772042
C         1.6181948194     -1.2291416350     -0.1064104149
H         2.0247758082     -2.2247031697      0.0596918252
C         2.2216196488     -0.1563541334      0.5496544771
C         1.7639324345      1.1172876281      0.2345874982
H         2.2763903524      1.9717111560      0.6661464418
C         0.6669660473      1.3491665984     -0.6078090414
C        -2.4294813982      0.5026140291     -0.2673098805
N        -2.8827688162      0.6809675418      0.8363301706
P        -1.7693528443      0.4077321095     -1.8042366504
C        -3.2613820116     -0.2404653769      1.9101953745
C        -4.0761574028      0.5470625195      2.9306796634
C        -4.0759672906     -1.3997629458      1.3405980446
C        -1.9547562283     -0.7432294261      2.5293433023
H        -3.4953328694      1.4003658162      3.3095138908
H        -4.9976495644      0.9367165158      2.4734851501
H        -4.3536985293     -0.0953879251      3.7792663825
```

```
H       -3.4866688838     -1.9655401877      0.6052349171
H       -4.3763832396     -2.0849577509      2.1473592639
H       -4.9862075149     -1.0291104754      0.8461108947
H       -2.1704565156     -1.4164492685      3.3725680698
H       -1.3558417085     -1.2865985268      1.7830944069
H       -1.3516776554      0.0989654123      2.8990661354
C        0.0157648378     -2.3419902602     -1.7053070771
C       -1.2999907901     -2.8846676046     -1.1269113348
C       -0.1434634867     -2.0287525220     -3.2012021273
C        1.0357983386     -3.4873331282     -1.6180247313
H       -1.1963470047     -3.0847748546     -0.0486483381
H       -2.1306284216     -2.1829571576     -1.2707525852
H       -1.5627443347     -3.8331396968     -1.6223733931
H        0.8054129869     -1.6656859391     -3.6247423831
H       -0.4363377302     -2.9402587233     -3.7459801994
H       -0.9169633043     -1.2737116648     -3.3973096338
H        0.6951360445     -4.3163572983     -2.2562168366
H        2.0324895767     -3.1807227207     -1.9695790640
H        1.1346531974     -3.8877909651     -0.5979923121
C        0.3416905516      2.8215872154     -0.9655598858
C        0.1243160264      2.9646374781     -2.4792586904
C       -0.8736236698      3.3616369727     -0.1946443569
C        1.5219874607      3.7446143719     -0.6212291659
H        1.0061483068      2.6108911082     -3.0353754002
H       -0.7524859155      2.4053082658     -2.8348757229
H       -0.0400476506      4.0235464777     -2.7339669951
H       -0.7765869475      3.1600396496      0.8828903459
H       -0.9435542262      4.4527179727     -0.3324355232
H       -1.8155981327      2.9189572928     -0.5369866732
H        1.3095907315      4.7511600220     -1.0115430991
H        1.6760155787      3.8487624315      0.4632540781
H        2.4635350363      3.4000137981     -1.0751343772
C        3.3614156760     -0.4122145056      1.5362904645
C        3.9052119551      0.8841148143      2.1381440292
C        2.8327895159     -1.2927335692      2.6787163754
C        4.5119370458     -1.1337305822      0.8202495072
H        4.3272800821      1.5475297650      1.3678688745
H        3.1254478117      1.4402595282      2.6804217919
H        4.7090933497      0.6538144643      2.8538494775
H        2.4609142650     -2.2594082726      2.3076772934
H        3.6302656014     -1.4974945889      3.4110772743
H        2.0030864166     -0.7949699023      3.2043435190
H        5.3395636642     -1.3280362455      1.5210884257
H        4.1929894326     -2.1005123805      0.4037916756
H        4.9005605383     -0.5232680108     -0.0091771608
```

5.6.7 ^{Mes}TerPPMe$_3$ (3b)

```
65
MesTerPPMe3 @ PBE0-D3/def2-SVP
C       -0.6740319283     -0.8156235670     -0.2049886415
C        0.4286679474     -1.6345932379     -0.5250410904
C        0.2099530392     -2.8260503965     -1.2301638202
H        1.0723227634     -3.4547217360     -1.4675030155
C       -1.0676130439     -3.2255979692     -1.6051427959
H       -1.2135822270     -4.1611659483     -2.1501157957
C       -2.1573909133     -2.4311617845     -1.2655634100
H       -3.1721744079     -2.7302631410     -1.5403829675
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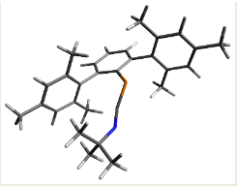

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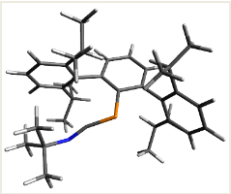
C       -1.9750660284     -1.2348708038     -0.5670913635
C        1.8358742877     -1.3555990331     -0.1205765914
C        2.2505438030     -1.6248375597      1.1984266870
C        3.6056177653     -1.5098217402      1.5191592996
H        3.9232984277     -1.7240744738      2.5440528200
C        4.5627404285     -1.1454806340      0.5696789501
C        4.1272899708     -0.8809077729     -0.7305168539
H        4.8596298401     -0.5926589308     -1.4910337744
C        2.7800958804     -0.9722831298     -1.0917859964
C        1.2594490584     -2.0410631259      2.2443275953
H        1.7642900578     -2.3577814108      3.1673293355
H        0.6241022542     -2.8673069408      1.8906243163
H        0.5845815540     -1.2038752596      2.4916948787
C        6.0069033265     -0.9924506553      0.9474641949
H        6.2896132337     -1.6840874997      1.7543765419
H        6.2104102226      0.0302109744      1.3085927191
H        6.6712472107     -1.1740267916      0.0902041936
C        2.3506176214     -0.6515284400     -2.4954306846
H        3.1952538104     -0.2806965118     -3.0929300310
H        1.5613342415      0.1165795673     -2.4999336069
H        1.9329021039     -1.5311344316     -3.0081402686
C       -3.1711750091     -0.4206127807     -0.2063093017
C       -3.8524205118     -0.6802610214      0.9952552628
C       -4.9829500164      0.0795159417      1.3086164633
H       -5.5110767180     -0.1210429273      2.2455845923
C       -5.4510066909      1.0855872675      0.4631615335
C       -4.7537319238      1.3263682208     -0.7246820137
H       -5.1010973214      2.1142951607     -1.4002142176
C       -3.6207599753      0.5928430315     -1.0747382510
C       -3.3562546372     -1.7364578290      1.9406970747
H       -4.0137719661     -1.8271421229      2.8162843253
H       -2.3414332218     -1.4992394078      2.3002585041
H       -3.2906982331     -2.7207872388      1.4524800979
C       -6.6604539007      1.9018890492      0.8173718732
H       -6.3908519776      2.9568854818      0.9876937015
H       -7.1456588643      1.5290694763      1.7303239455
H       -7.4054313209      1.8869615157      0.0063526864
C       -2.8703830902      0.8936678811     -2.3383798058
H       -2.7602429613     -0.0028020239     -2.9674845203
H       -1.8511647943      1.2445483119     -2.1061864513
H       -3.3753733493      1.6721072823     -2.9268583160
C        0.6345051267      1.5962091680      0.0896283006
N        1.3796477454      2.4431891728     -0.3320543706
P       -0.6356661521      0.7442787739      0.7863109068
C        2.7125837908      2.9365912607      0.0038532317
C        3.2703466545      2.1937073450      1.2129007737
C        3.5967636093      2.7448505881     -1.2260686606
C        2.5490902325      4.4268624907      0.3073044552
H        2.6182955780      2.3336417224      2.0881759156
H        3.3452120900      1.1172026105      1.0101224859
H        4.2723668182      2.5732204803      1.4638919949
H        3.1563099504      3.2445276381     -2.1009132005
H        4.5919812317      3.1746103164     -1.0393466412
H        3.7169337524      1.6771531457     -1.4510196852
H        3.5293151427      4.8704587479      0.5366792530
H        2.1155583702      4.9538297439     -0.5547540785
H        1.8882274770      4.5776541768      1.1736127422
```

5.6.8 ^{Dip}TerPCN*t*Bu (3c)



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83
DipTerPCNtBu @ PBE0-D3/def2-SVP
C         0.6219546361      0.0816675222     -0.5555623385
C        -0.3758347277      0.4718847202     -1.4733787082
C        -0.0122002998      0.7944434715     -2.7872032859
H        -0.7980921325      1.1045826178     -3.4803163601
C         1.3115152537      0.7468339167     -3.2101404384
H         1.5705065389      1.0004734528     -4.2404856588
C         2.3019887760      0.3986806175     -2.2980726001
H         3.3534062086      0.3829094259     -2.5952719931
C         1.9739524596      0.0790373533     -0.9792693009
C        -1.8148953906      0.6447469811     -1.1247763270
C        -2.2309105771      1.8545773470     -0.5288777834
C        -3.6006522997      2.0902149465     -0.3775727134
H        -3.9396978146      3.0306740152      0.0642667585
C        -4.5389256337      1.1518592461     -0.7961540209
C        -4.1163733360     -0.0511645107     -1.3522823144
H        -4.8582541804     -0.7876048298     -1.6719625787
C        -2.7556096974     -0.3275670738     -1.5191595483
C        -1.2285383942      2.9148202806     -0.1119808496
H        -0.2293991157      2.4585205584     -0.1636239466
C        -2.3169884468     -1.6403873632     -2.1427690644
H        -1.2216419081     -1.6954165646     -2.0412852322
C         3.0739961075     -0.2149656486     -0.0134608596
C         3.6610957672      0.8514865732      0.6980354488
C         4.7092445727      0.5718807983      1.5799942417
H         5.1751740395      1.3875477102      2.1391495082
C         5.1647397550     -0.7295851527      1.7572577054
C         4.5683499609     -1.7761953437      1.0612787769
H         4.9257408166     -2.7975739210      1.2141243320
C         3.5144186138     -1.5405237393      0.1751613247
C         3.1734296745      2.2795350674      0.5321814902
H         2.3253230408      2.2572826048     -0.1689167051
C         2.8691544043     -2.6931590978     -0.5696176132
H         1.9622652370     -2.2987531749     -1.0538039054
C        -1.1615023736     -0.9052720652      1.3966244275
N        -2.1361445437     -1.4662437748      1.8196973827
P         0.4299491341     -0.3719188005      1.2169810369
C        -3.3222155726     -1.1700380020      2.6125240909
C        -3.4492122975      0.3323827430      2.8423452444
C        -4.5375642725     -1.7209590541      1.8720808198
C        -3.1334040440     -1.9087461010      3.9399083742
H        -2.5604559905      0.7210703898      3.3617555242
H        -3.5520348317      0.8622207741      1.8857417041
H        -4.3328799941      0.5476303319      3.4613445952
H        -4.4273732473     -2.8000633663      1.6917788735
H        -5.4430832147     -1.5562464567      2.4742314699
H        -4.6611973618     -1.2147339865      0.9056278470
H        -4.0164362199     -1.7558944656      4.5778731927
H        -3.0039514288     -2.9870922133      3.7694395723
H        -2.2485592350     -1.5318378404      4.4736238274
C         2.4243570842     -3.8097589014      0.3722457256
C         3.7880891106     -3.2117798347     -1.6754034689
C         4.2499365521      3.1668600929     -0.0904900038
C         2.6522990501      2.8551966675      1.8484541052
C        -2.6434191867     -1.6760837791     -3.6357430935
C        -2.9007306835     -2.8519266592     -1.4182430840
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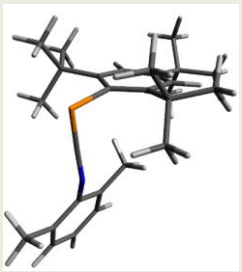
C        -1.2438342402      4.0871809313     -1.0928864574
C        -1.4301103062      3.3756655822      1.3288847971
H         1.7589035048     -3.4153605563      1.1546212125
H         1.8778720399     -4.5871323703     -0.1844385452
H         3.2802430197     -4.2985205550      0.8645935465
H         4.0480633636     -2.4109625507     -2.3842071923
H         4.7285722781     -3.6065763486     -1.2582794921
H         3.3026832026     -4.0232502443     -2.2405730883
H         5.9868035357     -0.9315908366      2.4485131083
H        -5.6063473483      1.3574209003     -0.6826309151
H        -0.4823667634      4.8347178758     -0.8194697169
H        -1.0345426435      3.7474342038     -2.1184776980
H        -2.2245645094      4.5897701441     -1.0989884527
H        -2.3994929205      3.8793287283      1.4724502297
H        -1.3778147813      2.5227686935      2.0212926791
H        -0.6425836200      4.0903008279      1.6142377381
H         3.8692668206      4.1878469096     -0.2518303740
H         5.1369647092      3.2395216429      0.5590869021
H         4.5799888590      2.7681154089     -1.0617848184
H         2.2443088201      3.8667893664      1.6933051899
H         1.8525712785      2.2230857501      2.2632935605
H         3.4506007738      2.9307426460      2.6040127359
H        -2.1713687800     -0.8386239739     -4.1701795559
H        -2.2878158122     -2.6137307525     -4.0911441987
H        -3.7302966835     -1.6103014375     -3.8049871095
H        -3.9985675143     -2.8908630578     -1.5052269051
H        -2.5055497487     -3.7830355212     -1.8534270798
H        -2.6447154486     -2.8381567327     -0.3492460125
```

5.6.9 Mes*PCNXyl (3d)



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67
Mes*PCNXyl @ PBE0-D3/def2-SVP
C         0.8592314679      1.1016398158     -0.6852305034
C         1.0940888750     -0.0663631056     -1.4692844800
C         1.9246544220     -1.0529337846     -0.9319224561
H         2.0873948077     -1.9656929665     -1.5000030846
C         2.5504551816     -0.9368825504      0.3078418881
C         2.3971512531      0.2661182665      0.9850561024
H         2.9269708773      0.3998839183      1.9223681277
C         1.5862469731      1.3100328432      0.5181703885
C        -1.6302946891      1.4237902899     -0.2871640082
N        -2.4174535707      0.8402667463      0.3984757735
P        -0.5079595571      2.2959476255     -1.1819710644
C         0.5265569387     -0.3145278997     -2.8908050600
C        -0.9762874931     -0.6423395370     -2.8655762191
C         0.8060032735      0.8942517223     -3.7973125371
C         1.2137930247     -1.5115006978     -3.5670781755
H        -1.1872331603     -1.4646013252     -2.1636220543
H        -1.5856765413      0.2210083321     -2.5761048771
H        -1.3022493502     -0.9647521338     -3.8674847952
H         1.8857163459      1.1049178675     -3.8402707460
H         0.4580918364      0.6813829353     -4.8205231470
H         0.2901108849      1.8042762064     -3.4623422794
H         0.8530970076     -1.5855808766     -4.6036498061
H         2.3078364170     -1.3974612102     -3.6019556156
H         0.9773519543     -2.4676575755     -3.0765334752
C         1.5818869445      2.6229876123      1.3417257054
```

```
C         1.8610412783      3.8262924506      0.4282167037
C         0.2643294777      2.8167926582      2.1098151517
C         2.7000570339      2.6289614674      2.3961289251
H         2.8196268096      3.6999211656     -0.0981554690
H         1.0741483983      3.9802771391     -0.3229078627
H         1.9197830759      4.7467016088      1.0303973126
H         0.0288127538      1.9256299708      2.7121751073
H         0.3572008520      3.6735633462      2.7963859446
H        -0.5811675725      3.0115638969      1.4406319790
H         2.7214423284      3.6159326356      2.8816471775
H         2.5370888268      1.8850355647      3.1903937569
H         3.6919336166      2.4540506620      1.9526377996
C         3.3827044169     -2.0986697643      0.8520813842
C         4.0224470909     -1.7679914195      2.2008857238
C         2.4672400335     -3.3181627155      1.0356080465
C         4.5002682491     -2.4399815599     -0.1439875832
H         4.7127843078     -0.9137324446      2.1282047688
H         3.2660671190     -1.5340787154      2.9655476100
H         4.6012936922     -2.6323540172      2.5603747618
H         1.9937164028     -3.6176575946      0.0887476709
H         3.0414264886     -4.1795124956      1.4128785712
H         1.6645443874     -3.0991517791      1.7564235422
H         5.1119970596     -3.2740534350      0.2352674681
H         4.0990117938     -2.7396542637     -1.1233105326
H         5.1610838020     -1.5741468283     -0.3030304856
C        -3.2457032529     -0.2336250979      0.6394567489
C        -4.6335235052     -0.0895893124      0.4548825687
C        -2.6643649202     -1.4291279522      1.1096829019
C        -5.4423825841     -1.1909697758      0.7369609887
C        -3.5193519583     -2.4995088152      1.3748647772
C        -4.8957825867     -2.3885746188      1.1915477325
H        -6.5224814214     -1.1008815524      0.5952445859
H        -3.0893022831     -3.4371521584      1.7365227115
H        -5.5462013314     -3.2387372118      1.4080951690
C        -5.1927842897      1.2087236817     -0.0397473385
H        -4.8744994603      2.0485882004      0.5985070851
H        -4.8397762172      1.4349426413     -1.0592198489
H        -6.2904927262      1.1852273458     -0.0585853278
C        -1.1833942865     -1.5189545556      1.3128700638
H        -0.6263921098     -1.3785748174      0.3723540038
H        -0.8243397824     -0.7328922086      1.9966074725
H        -0.9028698653     -2.4949852814      1.7303976282
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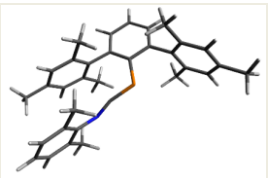
5.6.10 ^{Mes}TerPCNXyl (3e)



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69
MesTerPCNXyl @ PBE0-D3/def2-SVP
C        -1.4010181965      0.9507916823      0.0061077875
C        -0.5139712610      2.0487930132     -0.0262268846
C        -1.0276913491      3.3497492977      0.0104110113
H        -0.3238373058      4.1860020815     -0.0162184037
C        -2.3969151660      3.5884260361      0.0692036230
H        -2.7780045562      4.6117947376      0.0960167903
C        -3.2738012292      2.5086706136      0.0855096948
H        -4.3541817686      2.6702918531      0.1252557938
C        -2.7943745261      1.1972080342      0.0523573377
C         0.9606148465      1.8868207546     -0.1206858152
C         1.5577591097      1.6826784543     -1.3787432175
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C         2.9461816133      1.5548130215     -1.4549260290
H         3.4101777312      1.3890428845     -2.4320016152
C         3.7568991361      1.6350263324     -0.3205582725
C         3.1413472849      1.8583277899      0.9129578033
H         3.7612867560      1.9328279556      1.8115788677
C         1.7556609714      1.9806378410      1.0349206136
C         0.7103370620      1.5849363123     -2.6131460381
H         1.3291521850      1.4754721015     -3.5146320098
H         0.0731699867      2.4743468517     -2.7337103865
H         0.0301843681      0.7191472963     -2.5512915620
C         5.2395218398      1.4348365519     -0.4192187263
H         5.6333128430      1.7939346020     -1.3812466014
H         5.4859022765      0.3630033764     -0.3406931499
H         5.7730297021      1.9558648651      0.3889162280
C         1.1188329208      2.1627289090      2.3819163683
H         1.8711320633      2.1553584971      3.1830778132
H         0.3917667342      1.3592757087      2.5812316888
H         0.5600229319      3.1089690800      2.4442908034
C        -3.7672084342      0.0671690885      0.0600460802
C        -4.2745822873     -0.4242920853     -1.1561167678
C        -5.1981229733     -1.4719952590     -1.1285165251
H        -5.5930528293     -1.8530252861     -2.0751643689
C        -5.6271221576     -2.0438170593      0.0704329096
C        -5.1069690029     -1.5392064955      1.2653679478
H        -5.4296180361     -1.9741400899      2.2163247440
C        -4.1816306808     -0.4951524405      1.2824878677
C        -3.8139181549      0.1563176154     -2.4618863001
H        -4.3127145218     -0.3295761443     -3.3117614334
H        -2.7258605083      0.0292933754     -2.5845384113
H        -4.0101519072      1.2381101568     -2.5156269920
C        -6.5959113737     -3.1907762780      0.0792991801
H        -6.0682402038     -4.1505694287      0.2088002298
H        -7.1605753115     -3.2504197618     -0.8621214634
H        -7.3165632055     -3.1038830679      0.9062832488
C        -3.6134174193      0.0070823649      2.5772536203
H        -3.7623689499      1.0916083145      2.6914444949
H        -2.5252859048     -0.1678219205      2.6132332783
H        -4.0710917005     -0.5003423189      3.4376627985
C         0.6654694124     -0.9193371668      0.2853339684
C         3.0331981376     -1.6787971723      0.2774422640
C         3.3444036025     -2.0383664283     -1.0516987220
C         4.6498366363     -2.4515602059     -1.3240674324
H         4.9100672597     -2.7357328965     -2.3468314749
C         5.6124794538     -2.5077430718     -0.3191073787
H         6.6278187485     -2.8340925089     -0.5557073595
C         5.2831489605     -2.1514145076      0.9867875173
H         6.0383545505     -2.2004711769      1.7750850241
C         3.9904575137     -1.7389376699      1.3106397142
C         2.3020539495     -1.9792083323     -2.1213108281
H         1.9183376495     -0.9548413115     -2.2394158413
H         1.4323644794     -2.6091777382     -1.8754089846
H         2.7082260853     -2.3122300748     -3.0855040608
C         3.6025531942     -1.3686498872      2.7077591288
H         4.4480716010     -1.4858787258      3.3987426404
H         2.7690061518     -1.9947395669      3.0620424125
H         3.2516506279     -0.3265253239      2.7547401798
N         1.7545818733     -1.2977657164      0.6209111145
P        -0.9852113047     -0.8414049483     -0.0652922478
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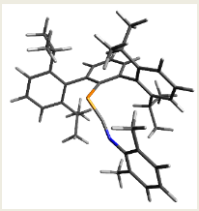
5.6.11 ^{Dip}TerPCNXyl (3f)



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87
DipTerPCNXyl @ PBE0-D3/def2-SVP
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C         2.3687776391     -0.0298430742      0.8955884716
C         2.8801140241      0.4289013045      2.1135896564
H         3.8548168379      0.0640603455      2.4467503979
C         2.1714916285      1.3526493570      2.8731267524
H         2.5845920170      1.7266923188      3.8127833344
C         0.9367457264      1.8088259027      2.4227575826
H         0.3872958012      2.5564335399      2.9989857463
C         0.3798247249      1.3441218251      1.2247105168
C         3.1800007483     -0.9739845827      0.0726655231
C         4.1881532927     -0.4660326368     -0.7710019954
C         4.9528783468     -1.3669814338     -1.5188169854
H         5.7338494745     -0.9889170057     -2.1835675847
C         4.7293126287     -2.7358814789     -1.4336160258
H         5.3379262312     -3.4272175707     -2.0218302544
C         3.7237583604     -3.2257424770     -0.6058268283
H         3.5496913651     -4.3030220327     -0.5513691753
C         2.9309753676     -2.3601555855      0.1505406587
C         4.4226571459      1.0265733194     -0.9200773693
H         3.7676999816      1.5373257626     -0.1979690931
C         4.0177870135      1.5088928384     -2.3137635669
H         4.6453306077      1.0505079833     -3.0948222682
H         4.1250715382      2.6024171819     -2.3944484223
H         2.9708946017      1.2498374117     -2.5339538487
C         5.8591976378      1.4186618113     -0.5813722689
H         6.5807662162      0.9621702941     -1.2775592329
H         6.1298732086      1.0985605918      0.4362746856
H         5.9879236451      2.5107863911     -0.6416004035
C         1.8461998262     -2.9111668465      1.0564230521
H         1.2035877893     -2.0652701415      1.3454205053
C         2.4529578423     -3.4804592591      2.3391392703
H         3.1254204268     -4.3247948966      2.1169670664
H         1.6657796140     -3.8436868124      3.0189869038
H         3.0396652334     -2.7179571038      2.8734543818
C         0.9532597913     -3.9299906408      0.3529589558
H         0.5294730819     -3.5096955484     -0.5709570348
H         0.1180191283     -4.2229785029      1.0082937923
H         1.5007159922     -4.8496905057      0.0924143678
C        -0.9444908751      1.9000600910      0.8152656739
C        -0.9896880381      2.9672431044     -0.1066909778
C        -2.2241710767      3.5595044220     -0.3900693628
H        -2.2711604782      4.3951531393     -1.0922811951
C        -3.3931972760      3.0982963165      0.2053356108
H        -4.3509226350      3.5686870118     -0.0305844745
C        -3.3432888431      2.0286887614      1.0919238523
H        -4.2677384279      1.6628084745      1.5430999485
C        -2.1273422841      1.4177104406      1.4177516900
C         0.2734537956      3.5148032568     -0.7446562043
H         1.0744485582      2.7804959225     -0.5730164073
C         0.1410497268      3.6853413122     -2.2554090318
H        -0.1751248348      2.7435531831     -2.7286089489
H         1.1083981548      3.9768132086     -2.6934277558
H        -0.5877584482      4.4673085843     -2.5218213869
C         0.6994266133      4.8141921344     -0.0605934590
H         1.6387462312      5.1950393625     -0.4921300824
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H         0.8578019486      4.6603223620      1.0175497261
H        -0.0693536882      5.5949170148     -0.1785940618
C        -2.0966377767      0.2912417409      2.4375193460
H        -1.1644854937     -0.2732687154      2.2694477591
C        -2.0594783605      0.8419512708      3.8651025664
H        -1.1821092908      1.4783644200      4.0378676905
H        -2.0299361644      0.0196698874      4.5973910738
H        -2.9589225336      1.4451461992      4.0683056724
C        -3.2630134914     -0.6827446035      2.2932121550
H        -4.2164214205     -0.2268450477      2.6032968438
H        -3.1047482620     -1.5612750742      2.9376034127
H        -3.3846065444     -1.0292367371      1.2595145652
C        -0.8248793420     -0.8688272922     -1.0019120581
C        -3.1694515160     -1.5996291874     -1.1678260783
C        -3.8604768802     -2.7308112680     -0.6859750081
C        -5.2471143633     -2.7638839016     -0.8294253976
H        -5.8005434244     -3.6271593682     -0.4519135121
C        -5.9242149955     -1.7162153985     -1.4491464932
H        -7.0107433359     -1.7578710536     -1.5556767022
C        -5.2213916572     -0.6197583708     -1.9416029149
H        -5.7552827919      0.1952307582     -2.4366676617
C        -3.8338640875     -0.5344297313     -1.8140346998
C        -3.1096161208     -3.8370462364     -0.0129329911
H        -3.7649949600     -4.6953680487      0.1865601638
H        -2.6850971836     -3.4985738311      0.9461676155
H        -2.2601246833     -4.1705817465     -0.6272617649
C        -3.0694466441      0.6327355316     -2.3465718341
H        -3.7400772753      1.3520153604     -2.8342469387
H        -2.3104850071      0.3135000270     -3.0794104000
H        -2.5300205750      1.1601895326     -1.5466398636
N        -1.7967319862     -1.5843610491     -0.9989461680
P         0.6395392636     -0.1027489315     -1.2702451942
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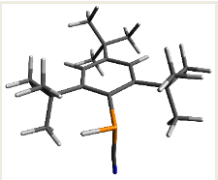
5.6.12 Mes*P(H)CN (4a)



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51
Mes*P(H)CN @ PBE0-D3/def2-SVP
C        -0.8937889780     -0.0312458026     -0.2544553046
C        -0.2468998907      1.2367625171     -0.2241801457
C         1.1413194173      1.2619458488     -0.0367399130
H         1.6407036048      2.2226807973      0.0179201932
C         1.9109471289      0.1141260075      0.0855358907
C         1.2559666543     -1.1085859916     -0.0460199179
H         1.8595503427     -2.0107413777      0.0012758649
C        -0.1219863037     -1.2332125159     -0.2247169870
C        -0.9525990659      2.6052045329     -0.4240922426
C        -1.6303219735      2.6476877364     -1.8047499840
H        -2.0859526358      3.6374590829     -1.9658809567
H        -2.4264646806      1.8993671970     -1.9116199354
H        -0.8895546502      2.4794231587     -2.6013453176
C        -1.9586904280      2.9141041980      0.6988395918
H        -1.5128170049      2.7410868258      1.6897290209
H        -2.8801514263      2.3220201019      0.6323207467
H        -2.2624159254      3.9709730078      0.6412798756
C         0.0519336659      3.7682251424     -0.4127063822
H         0.8176916868      3.6702433414     -1.1963279649
H         0.5560430589      3.8776835429      0.5592966362
H        -0.4944059275      4.7034991211     -0.6036682033
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C         3.4197070062      0.1450539711      0.3286372119
C         3.9564141575      1.5724364005      0.4414009337
H         3.7942681594      2.1462204958     -0.4838900440
H         5.0405577766      1.5479919960      0.6287224792
H         3.4887570964      2.1206628929      1.2733996407
C         4.1351561106     -0.5523438298     -0.8376651948
H         3.8249404029     -1.6028332813     -0.9395838890
H         5.2253767849     -0.5400626904     -0.6805822478
H         3.9201622801     -0.0444423945     -1.7903627405
C         3.7265103888     -0.5952484542      1.6388724294
H         3.2193873868     -0.1147607376      2.4893998424
H         4.8100162859     -0.5909405019      1.8371952145
H         3.3970913217     -1.6441964178      1.6018782646
C        -0.6732283092     -2.6667372692     -0.4310875700
C        -1.3666613345     -2.7691189882     -1.8028617104
H        -1.7955547257     -3.7748505151     -1.9354915002
H        -0.6304212915     -2.6070455033     -2.6048958109
H        -2.1734411226     -2.0441944791     -1.9622512826
C        -1.5728042051     -3.1199991598      0.7332591877
H        -2.4960024341     -2.5456864853      0.8548565800
H        -1.0237751467     -3.0466539498      1.6839755099
H        -1.8594827086     -4.1734960788      0.5888838970
C         0.4538726653     -3.7119655881     -0.4854755647
H         0.0090892907     -4.6961348265     -0.6945981095
H         0.9937161191     -3.7970710153      0.4691727929
H         1.1809845511     -3.5041370446     -1.2841589617
C        -3.0150461952     -0.1642181136      1.5370703976
N        -3.2369243195     -0.1843386254      2.6766757041
P        -2.7493619878      0.0098778217     -0.2281653258
H        -3.0677995430     -1.3370850594     -0.5020880015
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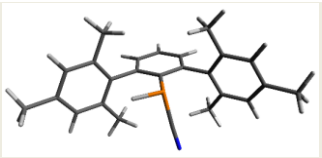
5.6.13 MesTerP(H)CN (4b)



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53
PH3 @ PBE0-D3/def2-SVP
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N         0.7611897376      3.2314311531     -0.1386288681
C        -0.0355197819     -0.4328078256      0.2882640792
C        -1.2746190555     -0.8226240946      0.8327215789
C        -1.2820516510     -1.6827713196      1.9373089435
H        -2.2439678342     -1.9845830000      2.3591079310
C        -0.0938014307     -2.1406787615      2.4977689334
H        -0.1196262432     -2.8095508416      3.3613220381
C         1.1268116061     -1.7419255261      1.9606199827
H         2.0663300782     -2.0908979132      2.3959264354
C         1.1708031446     -0.8927682799      0.8522609393
C        -2.5716382034     -0.3406793087      0.2821488381
C        -3.2283808857     -1.0813520294     -0.7165667213
C        -4.4434894979     -0.6087464048     -1.2183436471
H        -4.9542513817     -1.1855408621     -1.9952071902
C        -5.0203824299      0.5754440289     -0.7546310835
C        -4.3501583338      1.2884450642      0.2428037136
H        -4.7879617621      2.2161438818      0.6232121093
C        -3.1333731347      0.8535284087      0.7720452153
C        -2.6228538205     -2.3493913590     -1.2474848274
H        -1.6384936020     -2.1643536259     -1.7083321133
H        -3.2689612633     -2.8118003316     -2.0060542964
H        -2.4523160773     -3.0828756429     -0.4444960362
```

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C       -6.3098525156      1.0851322068     -1.3301133455
H       -6.9211850676      1.5876976595     -0.5663004606
H       -6.9067245596      0.2719321280     -1.7673449661
H       -6.1197359196      1.8203559597     -2.1298854039
C       -2.4280246633      1.6552833312      1.8272991298
H       -2.1741810606      1.0373445944      2.7017014203
H       -3.0476808023      2.4967442506      2.1660023622
H       -1.4800645182      2.0695749875      1.4480014860
C        2.4773460164     -0.4544647775      0.2863286459
C        3.0212631225     -1.1199920623     -0.8287787007
C        4.2352845454     -0.6719178442     -1.3534238661
H        4.6581527937     -1.1891790084     -2.2198262090
C        4.9199999583      0.4134169978     -0.8032613947
C        4.3689647361      1.0427047891      0.3153636277
H        4.8948992259      1.8888983625      0.7669328343
C        3.1612573551      0.6260801440      0.8774821813
C        2.3062448160     -2.2829297550     -1.4523049720
H        2.9430765496     -2.7901625137     -2.1898528817
H        1.3923761929     -1.9489669820     -1.9729055354
H        1.9917655593     -3.0188035386     -0.6971084203
C        6.2003111931      0.9087137650     -1.4102253613
H        6.0097978200      1.7620474418     -2.0823582102
H        6.6957642554      0.1269183014     -2.0035588660
H        6.9049050366      1.2544772586     -0.6395010093
C        2.6169827687      1.3082092985      2.0992450910
H        2.6797855833      0.6516003869      2.9819700267
H        1.5588199936      1.5793844655      1.9763184109
H        3.1753713103      2.2282362531      2.3180596338
C        0.4630461093      2.1864301635     -0.5479212683
H       -1.2892552134      0.8582848493     -1.4111584912
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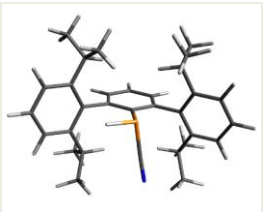
5.6.14 ^{Dip}TerP(H)CN (4c)



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71
DipTerPHCN @ PBE0-D3/def2-SVP
C        0.0487341335      0.0544269295      0.2314564678
C        1.2705225730     -0.0150328673      0.9280534933
C        1.2523241583      0.0317187905      2.3276048688
H        2.2018623944     -0.0190163720      2.8656382757
C        0.0559587467      0.1642269398      3.0230116298
H        0.0604480437      0.2142271151      4.1142943205
C       -1.1467346041      0.2440303167      2.3267038229
H       -2.0882013108      0.3694720391      2.8651077121
C       -1.1690922512      0.1814066651      0.9313107166
C        2.5820440446     -0.0965864665      0.2229131303
C        3.3018782764      1.0896858984     -0.0250730421
C        4.5239321066      1.0003752798     -0.6999811964
H        5.0920614883      1.9095216102     -0.9106024038
C        5.0237904105     -0.2295026825     -1.1105549330
H        5.9803840340     -0.2823821798     -1.6361408907
C        4.3057718068     -1.3944031163     -0.8570769652
H        4.7067167725     -2.3545455345     -1.1876920257
C        3.0767534753     -1.3514989416     -0.1940553165
C        2.7521351992      2.4480483372      0.3743010621
H        1.9164914296      2.2739128929      1.0691838906
C        2.1835655950      3.1878805515     -0.8379478124
H        2.9643151245      3.3797339071     -1.5912685209
H        1.7549438834      4.1574223211     -0.5387824414
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H         1.3851171516      2.6115703283     -1.3307148877
C         3.7797209774      3.3008831375      1.1144646741
H         4.1843256428      2.7688573948      1.9886262102
H         3.3196029189      4.2370111818      1.4667738569
H         4.6278365330      3.5776810770      0.4687398942
C         2.3074638286     -2.6262077456      0.0994673358
H         1.2465167877     -2.3484838625      0.2053978521
C         2.7559395653     -3.2224038080      1.4355109882
H         3.8221093154     -3.4984125220      1.4006991291
H         2.1767386851     -4.1287640997      1.6720358698
H         2.6206432039     -2.5082641368      2.2609832733
C         2.3910095801     -3.6586689711     -1.0199234246
H         2.1125461454     -3.2261847209     -1.9916320055
H         1.6974126263     -4.4887244282     -0.8193216002
H         3.4007312777     -4.0900291694     -1.1085702644
C        -2.4636605836      0.2770130495      0.1929896055
C        -2.8556919509      1.5218548436     -0.3471296439
C        -4.0737254419      1.6019370932     -1.0265956559
H        -4.3947860756      2.5566661768     -1.4485588313
C        -4.8828053147      0.4812063884     -1.1746535067
H        -5.8306359859      0.5596263347     -1.7128296275
C        -4.4852083473     -0.7406721984     -0.6448754706
H        -5.1250775687     -1.6153893494     -0.7745035663
C        -3.2760986308     -0.8689260632      0.0453115686
C        -2.0076926820      2.7661636605     -0.1544339705
H        -0.9890115644      2.4357769665      0.1017201459
C        -1.8970218677      3.6184203876     -1.4150737094
H        -1.5543148752      3.0165719983     -2.2699652256
H        -1.1754018586      4.4354667005     -1.2597067359
H        -2.8579477910      4.0827264605     -1.6868796980
C        -2.5231772871      3.5817747760      1.0324691419
H        -3.5524037158      3.9306620503      0.8512421674
H        -1.8893781146      4.4659868319      1.2054805292
H        -2.5308819432      2.9815719690      1.9546052117
C        -2.8855024133     -2.2036769166      0.6568182118
H        -1.7889796830     -2.2002928813      0.7751515226
C        -3.5066929546     -2.3579422912      2.0480827092
H        -4.6064566996     -2.3557415173      1.9805278886
H        -3.2137814898     -1.5445703627      2.7260752220
H        -3.1974563253     -3.3100123546      2.5072762105
C        -3.2471404559     -3.4045336118     -0.2136164525
H        -2.8337538249     -4.3233581435      0.2298997475
H        -2.8383811039     -3.3094792244     -1.2285296680
H        -4.3374874660     -3.5449817726     -0.2822012933
C        -0.4785143565     -1.5321807578     -2.0118091938
N        -0.8057838079     -2.5933652988     -2.3503770998
P        -0.0302734889      0.1535969397     -1.6100333722
H         1.3514108919     -0.0591294029     -1.8744337639
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5.6.15 Mes*P(H)CNB(C_6F_5)$_3$ (5a)

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85
Mes*P(H)CNB(C6F5)3 @ PBE0-D3/def2-SVP
P         1.2463335495     -0.4723347526     -3.1805835259
C         2.6075891112     -0.2290457470     -1.9543667168
C         3.0336810594     -1.4047187010     -1.2707821821
C         3.9687483945     -1.2488551053     -0.2418832490
H         4.2908152956     -2.1255940572      0.3070405751
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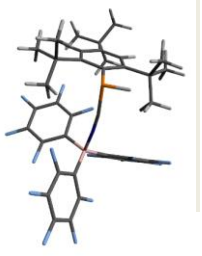

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C         4.4962567049     -0.0195395537      0.1269986247
C         4.0853762571      1.0973019861     -0.5962977808
H         4.5088731838      2.0580484390     -0.3199594408
C         3.1514843093      1.0510962961     -1.6296868815
C         2.5762305990     -2.8546605051     -1.5932121464
C         1.0565993581     -3.0617766544     -1.4487993794
H         0.4683774369     -2.6368204369     -2.2717965810
H         0.6804855566     -2.6483853296     -0.5022524370
H         0.8337550038     -4.1394137063     -1.4506999034
C         3.2111405092     -3.8684113580     -0.6282967033
H         2.9067509103     -3.6926632303      0.4149378235
H         4.3093733445     -3.8707327261     -0.6778825498
H         2.8708799400     -4.8765876095     -0.9045686723
C         3.0462763660     -3.2368256491     -3.0068371115
H         2.7647466510     -4.2783877012     -3.2271051400
H         4.1407858205     -3.1539374055     -3.0850618433
H         2.6004278513     -2.6068561902     -3.7892527607
C         5.4777703574      0.1490718671      1.2853608872
C         4.8354810657      1.0678689064      2.3369449576
H         3.8853433988      0.6465611064      2.6945671855
H         5.5099829616      1.1893464929      3.1990168160
H         4.6292281897      2.0695699497      1.9311420023
C         5.8232792056     -1.1854291317      1.9472541200
H         4.9324520218     -1.6764172772      2.3639016204
H         6.3064537163     -1.8787406314      1.2415418445
H         6.5270562642     -1.0148269612      2.7756105691
C         6.7746294398      0.7852432653      0.7641961521
H         7.2490354841      0.1474333307      0.0025265764
H         6.5971915063      1.7732003701      0.3138406430
H         7.4900282882      0.9208065649      1.5903587594
C         2.8059117164      2.3962824182     -2.3199047795
C         3.1776745382      2.3547607720     -3.8133374147
H         2.8678739965      3.2896068316     -4.3057165131
H         2.7326059037      1.5256457527     -4.3772273831
H         4.2684766513      2.2599324650     -3.9236283274
C         1.3392056524      2.8006700680     -2.0709450749
H         1.0870115162      2.6708187125     -1.0079267127
H         0.5962316601      2.2482335158     -2.6552178223
H         1.1944738550      3.8627228777     -2.3202386268
C         3.6313548703      3.5588773893     -1.7418059850
H         3.3842081428      4.4734033563     -2.3003422782
H         4.7145004242      3.3971980621     -1.8409264906
H         3.3973660600      3.7505069771     -0.6842292842
C        -0.0576036718     -0.1053084272     -2.0069256343
C        -0.9157514673     -0.9761292427      1.1291483521
C         0.4348075873     -0.7562090582      1.4131817738
C         1.2068936335     -1.6383615882      2.1589947542
C         0.6354462789     -2.8159921930      2.6313474851
C        -0.7092330343     -3.0679742667      2.3876375254
C        -1.4606492128     -2.1458855213      1.6556415736
C        -3.1950875376     -0.4026354228     -0.3122973697
C        -3.3760396470     -1.4800038957     -1.1794766236
C        -4.6234635396     -1.9149254620     -1.6120897655
C        -5.7633758694     -1.2566127850     -1.1569981548
C        -5.6329298775     -0.1878532188     -0.2768832449
C        -4.3615937580      0.2163661018      0.1317674231
C        -1.6186774925      1.6170090973      0.6204300290
C        -1.6770307840      2.6543880036     -0.3067483016
C        -1.5352504090      3.9959916807      0.0346202595
C        -1.3678010129      4.3390421674      1.3724802941
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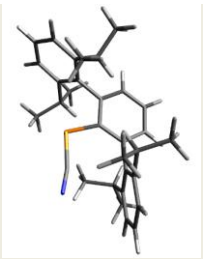
C       -1.3393243892      3.3363945584      2.3382787911
C       -1.4683799098      2.0044671617      1.9498986037
B       -1.7052875822      0.0640200624      0.1396530917
N       -0.8151848791     -0.0117229552     -1.1447044581
F        1.0439544940      0.3376288900      0.9528788631
F        2.4851958788     -1.3888053474      2.4149407198
F        1.3719844656     -3.6816894126      3.3046430157
F       -1.2669557493     -4.1748535665      2.8475043306
F       -2.7402206685     -2.4522033203      1.4832424496
F       -2.3180873309     -2.1748256143     -1.6094882721
F       -4.7374619101     -2.9440414196     -2.4366446531
F       -6.9598887182     -1.6509894286     -1.5526188464
F       -6.7120366133      0.4338310770      0.1690010432
F       -4.3170408101      1.2292888310      0.9912253402
F       -1.8627675444      2.3869034137     -1.6032278570
F       -1.5528873033      4.9367053577     -0.8978581814
F       -1.2368009142      5.6058447358      1.7238163041
F       -1.1929423526      3.6561399644      3.6137249453
F       -1.4481605672      1.0984369125      2.9226922785
H        1.1481061891      0.8009010157     -3.7811589213
```

5.6.16 [DipTerPCN]⁻ (6c⁻)



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70a
DipTerPCN- @ PBE0-D3/def2-SVP
P        0.3195515811      0.0814217813     -1.6122480318
N       -2.2625940570      0.0440550091     -2.9848074431
C        0.0806623125     -0.0533472280      0.1852905359
C       -1.1134068224     -0.0519032528      0.9621349450
C       -1.0526352440     -0.1477625472      2.3579842867
H       -1.9983740671     -0.1378358357      2.9091791616
C        0.1520160217     -0.2475153127      3.0461918405
H        0.1722308271     -0.3202839142      4.1360309093
C        1.3330263443     -0.2391171588      2.3033375640
H        2.3045921427     -0.3042757338      2.8029345972
C        1.3080605309     -0.1409238642      0.9152904164
C       -2.4762339029      0.0767873801      0.3707699441
C       -3.3061305063     -1.0590507027      0.2544924766
C       -4.6009224162     -0.8957709213     -0.2432990886
H       -5.2517623596     -1.7652881918     -0.3574230921
C       -5.0738686140      0.3595191032     -0.6105989272
H       -6.0885837865      0.4671700434     -1.0038426500
C       -4.2497018779      1.4715964499     -0.4964774647
H       -4.6202390406      2.4511633283     -0.8074638238
C       -2.9444659362      1.3474189377     -0.0163584177
C       -2.7680510081     -2.4405870656      0.5853622121
H       -2.0799699223     -2.3225153324      1.4372316767
C       -3.8437732482     -3.4357209563      1.0076936895
H       -4.4724886841     -3.0380755639      1.8201035263
H       -4.5068651045     -3.7058830347      0.1695718508
H       -3.3776768207     -4.3693383934      1.3609834430
C       -1.9448362300     -2.9880474311     -0.5833250121
H       -1.1074576217     -2.3199168130     -0.8341476216
H       -1.5339454210     -3.9821243380     -0.3383398639
H       -2.5671493943     -3.0786338748     -1.4877269037
C       -2.0385576517      2.5603971936      0.0802489002
H       -1.0054133538      2.1816270495      0.0674597942
C       -2.2480836952      3.2950029521      1.4038791666
```

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H       -1.5597178062      4.1521989664      1.4921418397
H       -2.0665900100      2.6242310465      2.2573556630
H       -3.2800694231      3.6766974670      1.4840840848
C       -2.1714612590      3.4949755795     -1.1180071186
H       -2.0754992798      2.9301350289     -2.0569878250
H       -1.3800842530      4.2611942521     -1.0905689311
H       -3.1393866833      4.0239980088     -1.1293706383
C        2.6116631195     -0.1123504757      0.1889668850
C        3.1881289526     -1.3165302450     -0.2628361201
C        4.4450584448     -1.2775458659     -0.8727135644
H        4.9057028284     -2.2068177103     -1.2195267392
C        5.1119717331     -0.0698687829     -1.0565970561
H        6.0945534875     -0.0543311420     -1.5368690774
C        4.5185644929      1.1187877767     -0.6450849613
H        5.0357599703      2.0680882324     -0.8129995254
C        3.2631857862      1.1178053963     -0.0284552916
C        2.4577188338     -2.6344739910     -0.0915186417
H        1.4336567830     -2.3887022405      0.2277718032
C        3.0957376601     -3.4781703825      1.0113302693
H        4.1388353210     -3.7376887440      0.7634904466
H        2.5394183654     -4.4185531914      1.1584992718
H        3.1031269107     -2.9337176909      1.9680608651
C        2.3399513351     -3.4013266391     -1.4058605013
H        3.3225968553     -3.7272176976     -1.7864297897
H        1.8578920337     -2.7682695794     -2.1656850464
H        1.7216372265     -4.3033163187     -1.2685629081
C        2.6149045839      2.4265584879      0.3816678026
H        1.6154090083      2.1784751590      0.7693436969
C        3.3890630738      3.1041244891      1.5109486178
H        3.4669578424      2.4424298723      2.3873798637
H        2.8872233876      4.0330112037      1.8279571616
H        4.4132683145      3.3662400735      1.1967216992
C        2.4121269787      3.3541435853     -0.8149607831
H        3.3720161909      3.6694397646     -1.2575121111
H        1.8701448356      4.2644300173     -0.5094266601
H        1.8183375508      2.8416591767     -1.5870839304
C       -1.3092454910      0.0497096291     -2.3043235429
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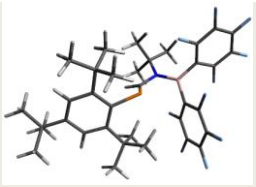
5.6.17 Mes*PC(H)NB(C_6F_5)$_2$*t*Bu (9)



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87
Mes*PC(H)NB(C6F5)2tBu @ PBE0-D3/def2-SVP
C       -2.6681361069     -0.3413607704     -0.5698845725
C       -3.4271299866     -1.5113588148     -0.8618158953
C       -4.7744808298     -1.5349002842     -0.4822925167
H       -5.3501002174     -2.4364772320     -0.6654613319
C       -5.4129986967     -0.4555955800      0.1191754133
C       -4.6777964919      0.7188807921      0.2568891239
H       -5.1836573957      1.5963224225      0.6556337809
C       -3.3304293236      0.8262863766     -0.0965219535
C       -2.8769701664     -2.7418051203     -1.6276173170
C       -2.2490568203     -2.2890836891     -2.9558324403
H       -1.3772059735     -1.6339180025     -2.8159081491
H       -2.9862705916     -1.7478837545     -3.5682475725
H       -1.9053316697     -3.1661988701     -3.5263369757
C       -1.8610550528     -3.5447562161     -0.7992332396
H       -1.6107568210     -4.4807886328     -1.3233587106
H       -2.2824110979     -3.8083362879      0.1835920744
```

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H       -0.9237211407     -2.9991882201     -0.6327671447
C       -3.9980015857     -3.7229164871     -1.9998738241
H       -3.5716438477     -4.5312553794     -2.6123618980
H       -4.7920445124     -3.2422747614     -2.5907128722
H       -4.4565515652     -4.1934562621     -1.1171662561
C       -6.8739211819     -0.4982958684      0.5698276595
C       -7.5029324332     -1.8756672919      0.3569705334
H       -6.9673495877     -2.6593804572      0.9143889577
H       -7.5186505309     -2.1597434817     -0.7062456914
H       -8.5446922759     -1.8673668828      0.7116597352
C       -7.6810393524      0.5336565981     -0.2315849128
H       -7.6421342441      0.3108160614     -1.3088578687
H       -7.2965059606      1.5540759411     -0.0870477531
H       -8.7369498170      0.5252161682      0.0827525302
C       -6.9462587009     -0.1584424243      2.0655211567
H       -7.9911735510     -0.1749593187      2.4141050378
H       -6.5390634009      0.8413478924      2.2768944837
H       -6.3744576972     -0.8864152852      2.6613105570
C       -2.6841340229      2.2259341682      0.0275831931
C       -1.9738442217      2.3715143848      1.3796319335
H       -1.1630131163      1.6440369026      1.4928802060
H       -2.6838081291      2.2173890570      2.2066808651
H       -1.5411017331      3.3790216716      1.4847154938
C       -1.7100130077      2.5020429337     -1.1229701923
H       -1.3575777749      3.5439897241     -1.0730587272
H       -2.1940506910      2.3492016120     -2.0996165840
H       -0.8127957392      1.8650215429     -1.0904274556
C       -3.7455815385      3.3359276865     -0.0538307748
H       -4.4067657056      3.3607156751      0.8241942269
H       -4.3694360319      3.2401716789     -0.9556133651
H       -3.2384369143      4.3114912599     -0.0930976165
C       -0.3881710745     -0.6242251768      0.8825974622
H       -1.1576980234     -0.7204156124      1.6537178557
C        1.1125564717     -1.7139435032      2.4663907094
C        0.3080859991     -1.1495584524      3.6469123204
H       -0.7769939906     -1.1659688727      3.4782370747
H        0.6109517984     -0.1133546640      3.8574911831
H        0.5012034691     -1.7589107915      4.5413009197
C        0.6201412093     -3.1107869095      2.0919047946
H       -0.4437613848     -3.0976590020      1.8158663461
H        0.7453178557     -3.7996722123      2.9403292256
H        1.1876845696     -3.5017199642      1.2354295726
C        2.5681191962     -1.7861241105      2.9205649173
H        2.6048293515     -2.3343836288      3.8724791379
H        2.9906210316     -0.7849162603      3.0936562050
H        3.2090149261     -2.3194569051      2.2095406710
B        1.9742431578     -0.1279578256      0.5864706955
C        1.7478828761      1.3260955728      0.0046000495
C        2.0312719135      1.6655941480     -1.3176518519
C        1.9123084637      2.9668256417     -1.7957497063
C        1.5078191590      3.9754102804     -0.9222249980
C        1.2425106040      3.6786107231      0.4116712274
C        1.3752301846      2.3663735076      0.8537128640
F        2.3964775259      0.7202659399     -2.1747027076
F        2.1577675764      3.2529376292     -3.0626166491
F        1.3562854289      5.2097949715     -1.3647693672
F        0.8424299116      4.6356495593      1.2339747163
F        1.1390015206      2.1250270862      2.1404176920
C        3.4023603604     -0.7417780624      0.3142165737
C        4.5745782708     -0.0710337268      0.6528481497
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C         5.8352568672     -0.5586338417      0.3228046890
C         5.9318858954     -1.7533035505     -0.3903074381
C         4.7797854344     -2.4477260101     -0.7562243779
C         3.5373287642     -1.9311433411     -0.3987347862
N         0.9352380000     -0.7892913122      1.2983091655
F         4.5061977062      1.0579110243      1.3509852693
F         6.9320835251      0.0878817729      0.6757366938
F         7.1175066898     -2.2291858351     -0.7164124503
F         4.8790014884     -3.5762778154     -1.4361374600
F         2.4564768231     -2.6142287876     -0.7644875117
P        -0.8234315555     -0.4401433383     -0.7378542398
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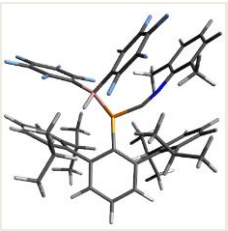
5.6.18 ^{Dip}TerP(HB(C_6F_5)$_2$)CNXyl (10)



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111
DipTerP(HBCF10)CNXyl @ PBE0-D3/def2-SVP
H         1.3333936779     -0.5164847458      1.5866074539
P         0.2775908988      0.6494511813     -0.4134441822
B         0.8184133945     -1.0296259945      0.6232498714
N        -2.4511098655     -0.1328108859     -0.7613404367
C         0.5481230488      2.2529504639      0.4342316769
C         1.8863226560      2.5529215231      0.7780425553
C         2.1865456723      3.8216753742      1.2860276610
H         3.2251641498      4.0469672683      1.5353014428
C         1.2027679192      4.7885268916      1.4541539330
H         1.4597634019      5.7730173194      1.8508235438
C        -0.1046722805      4.5016545082      1.0786799227
H        -0.8845208996      5.2628093412      1.1616555757
C        -0.4425064601      3.2518008296      0.5531474383
C         3.0065960395      1.5864179397      0.5657787183
C         3.5940927037      0.9354323086      1.6742506034
C         4.6697414676      0.0740110218      1.4481686160
H         5.1248790479     -0.4509692461      2.2902559595
C         5.1546013177     -0.1467935443      0.1639394029
H         5.9867704092     -0.8377511755      0.0080569753
C         4.5790433622      0.5053541743     -0.9195417943
H         4.9760590972      0.3333353298     -1.9216148704
C         3.5068065796      1.3856360258     -0.7416756983
C         3.1221326858      1.1911795205      3.0961025330
H         2.1321300731      1.6703107256      3.0331673025
C         2.9564685537     -0.0777097656      3.9291942132
H         3.9164718089     -0.5935866049      4.0864187627
H         2.2636592378     -0.7853276956      3.4581082902
H         2.5594130404      0.1803175729      4.9231712273
C         4.0720535594      2.1635957913      3.8011232162
H         3.7087424067      2.3972325400      4.8142875715
H         4.1800642052      3.1097693441      3.2520023667
H         5.0768384200      1.7216873978      3.8965179810
C         2.9820986432      2.1863320117     -1.9222031303
H         1.9409506617      2.4668018695     -1.7002256900
C         2.9639135954      1.4082952404     -3.2335964140
H         3.9796890010      1.1915157861     -3.5992588915
H         2.4623418582      1.9992095427     -4.0151223840
H         2.4260275644      0.4559375459     -3.1331488747
C         3.7776390038      3.4861639376     -2.0622037765
H         3.7337651755      4.0836910076     -1.1397081521
H         3.3809475592      4.1009379406     -2.8860378560
H         4.8371945574      3.2727127222     -2.2755476642
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C       -1.8212467078      3.0329465403      0.0423876629
C       -2.0454973769      3.1602765252     -1.3486923127
C       -3.3241107731      2.8914445125     -1.8451630040
H       -3.5166456614      2.9695963289     -2.9178021625
C       -4.3576374334      2.5410525916     -0.9849798691
H       -5.3509241993      2.3250050953     -1.3859355930
C       -4.1426061107      2.4966474005      0.3913459002
H       -4.9800217773      2.2728892155      1.0529907505
C       -2.8797796793      2.7405684385      0.9333754973
C       -0.9547395824      3.6623470649     -2.2779250563
H       -0.0083933140      3.6425444600     -1.7180446847
C       -0.7544786487      2.8016736367     -3.5209040350
H       -1.6595969192      2.7554644858     -4.1474325138
H       -0.4615797032      1.7767537791     -3.2497140352
H        0.0502466630      3.2206920308     -4.1440919610
C       -1.2266852315      5.1236853511     -2.6412289804
H       -0.4101536932      5.5283730338     -3.2593835315
H       -1.3129286173      5.7474527684     -1.7388707395
H       -2.1652838031      5.2249560520     -3.2095050871
C       -2.6344083731      2.6864196345      2.4327962965
H       -1.9460642968      3.5158380152      2.6632304807
C       -3.8941207500      2.9014438080      3.2630904655
H       -4.5919674360      2.0530624943      3.1770988305
H       -4.4310669836      3.8156945076      2.9679323259
H       -3.6305294068      2.9905033426      4.3274101010
C       -1.9246329162      1.4000339480      2.8560391970
H       -2.5649109535      0.5197357608      2.6957679309
H       -1.6747245716      1.4289734219      3.9269513327
H       -0.9881496564      1.2402320092      2.3060219318
C       -1.4364333388      0.4166383588     -0.5373981826
C       -3.4871496571     -0.8567471291     -1.2944681116
C       -3.3919213768     -1.2212421094     -2.6571476416
C       -4.4096120122     -2.0146568181     -3.1805255016
H       -4.3568558439     -2.3165875422     -4.2289686090
C       -5.4739871637     -2.4329881973     -2.3845673239
H       -6.2568591225     -3.0625199208     -2.8134453054
C       -5.5389535087     -2.0663976065     -1.0450877588
H       -6.3670618107     -2.4129352969     -0.4224495474
C       -4.5491781987     -1.2705933822     -0.4669370297
C       -2.2261210207     -0.7797666570     -3.4794899335
H       -2.3228771784     -1.1264409651     -4.5160854300
H       -1.2822016410     -1.1730673510     -3.0709846976
H       -2.1417227329      0.3170318202     -3.4873428597
C       -4.6255665957     -0.8879919211      0.9763446231
H       -4.9406457488     -1.7458529153      1.5865395870
H       -5.3616643270     -0.0827950073      1.1266307016
H       -3.6612520173     -0.5270581594      1.3519943150
C        1.9175763434     -1.8347542735     -0.2441769877
C        2.9285548581     -2.5012120884      0.4483057014
C        3.9857896045     -3.1539773373     -0.1788320720
C        4.0501826548     -3.1691430692     -1.5679785958
C        3.0453635195     -2.5490532218     -2.3026417754
C        2.0033925880     -1.9141814706     -1.6323858016
F        2.9280644802     -2.5176920584      1.7788424469
F        4.9501797388     -3.7214670971      0.5325405581
F        5.0605969078     -3.7624382721     -2.1835959433
F        3.0913662965     -2.5527657227     -3.6280924823
F        1.0764978340     -1.3453801820     -2.4129597237
C       -0.4591707742     -1.8973449515      1.0753191182
C       -0.9115142184     -1.8814512623      2.3962100162
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C       -2.0279493791     -2.5975542286      2.8238065264
C       -2.7278363555     -3.3815293525      1.9116811506
C       -2.3063655478     -3.4416534403      0.5875608058
C       -1.1880894537     -2.7064771388      0.2042653086
F       -0.2936729048     -1.1497129404      3.3183541506
F       -2.4485244221     -2.5140491126      4.0778149340
F       -3.8247738020     -4.0218197619      2.2901888069
F       -2.9912807885     -4.1523832418     -0.2952562892
F       -0.8619071149     -2.7541888724     -1.0886290098
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5.6.19 PMe_3

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13
PMe3 @ PBE0-D3/def2-SVP
P        0.4081449799      0.4407317039     -0.0000000000
C       -1.3833579708      0.9017187461     -0.0000000000
H       -1.6044991788      1.5136971271      0.8878215684
H       -1.6044991788      1.5136971271     -0.8878215684
H       -2.0486067957      0.0220885876      0.0000000000
C        0.4081449799     -0.7570259914     -1.4097867740
H        0.2592249751     -0.2116312056     -2.3542559264
H        1.3873806542     -1.2565593010     -1.4664690879
H       -0.3776863754     -1.5250389928     -1.3152104823
C        0.4081449799     -0.7570259914      1.4097867740
H        1.3873806542     -1.2565593010      1.4664690879
H        0.2592249751     -0.2116312056      2.3542559264
H       -0.3776863754     -1.5250389928      1.3152104823
```

5.6.20 C_4H_8 (*iso*-butene)

```
12
C4H8 @ PBE0-D3/def2-SVP

C        0.0000000305      0.1210067966      0.0000103739
C       -1.2699012132     -0.6770537842     -0.0000160353
C        1.2699009168     -0.6770542869      0.0000126581
C        0.0000003244      1.4589455374      0.0000000708
H       -2.1608228604     -0.0338192379      0.0001591461
H       -1.3194435401     -1.3362391061     -0.8834782565
H       -1.3193850925     -1.3364431727      0.8833353151
H        2.1608228233     -0.0338201170     -0.0001972266
H        1.3194660725     -1.3362249983      0.8834842309
H        1.3193613695     -1.3364583231     -0.8833293354
H        0.9334122063      2.0289694952     -0.0000004615
H       -0.9334113067      2.0289698921     -0.0000158178
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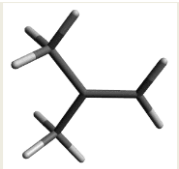

5.6.21 Mes*PPMes*

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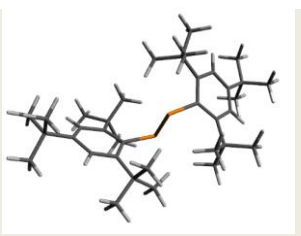
96
Mes*PPMes* @ PBE0-D3/def2-SVP
P       -0.9827788676      0.2765596843      0.4343491262
C       -0.7829264376      2.1196849152      0.2575461107
C       -0.1381984020      2.9458753573      1.2188829580
C        0.3549684491      4.1834138017      0.7957865973
C        0.1592804013      4.6874713595     -0.4859367379
C       -0.6668785531      3.9490192923     -1.3298633886
```



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C       -1.1721405659      2.6897165620     -0.9930152504
C        0.0022465669      2.6427904130      2.7283249818
C        1.4343865184      2.2006463028      3.0590948478
C       -0.3011139756      3.9225166530      3.5333719686
C       -1.0113665815      1.6104209205      3.2262355749
C        0.7829264376      6.0237739192     -0.8894974303
C        2.3088935014      5.9191644224     -0.7540172856
C        0.2589071237      7.1327330760      0.0346067230
C        0.4509253429      6.4010465765     -2.3336509936
C       -2.1741260420      2.0288777517     -1.9713546546
C       -2.6270465815      3.0095432761     -3.0627553994
C       -3.4457776622      1.6215894277     -1.2086846337
C       -1.5697948961      0.8212913724     -2.6999223001
H        0.9120048715      4.7884005929      1.5111666494
H       -0.9250741145      4.3676617960     -2.2975821851
H        2.1543731110      2.9915548970      2.7983690785
H        1.5364632726      1.9875640774      4.1354705477
H        1.7217263981      1.3024573380      2.4959096640
H       -1.2837903633      4.3386963978      3.2641762578
H       -0.3135617756      3.6814254220      4.6073866015
H        0.4520462551      4.7096893673      3.3927239746
H       -0.8362692835      0.6039824181      2.8277193473
H       -0.9503363888      1.5292741621      4.3225703150
H       -2.0392027346      1.9036824413      2.9623544118
H        2.7068815413      5.1278454037     -1.4074940290
H        2.7871144635      6.8710855859     -1.0354182465
H        2.6105786502      5.6836463799      0.2773474863
H        0.5136585411      6.9415878124      1.0875673692
H        0.6956133518      8.1051924007     -0.2440477970
H       -0.8365637177      7.2155993693     -0.0351013036
H       -0.6313887968      6.5328206444     -2.4848275344
H        0.9387775922      7.3535897348     -2.5907208151
H        0.8070367460      5.6407220648     -3.0454602478
H       -1.8095744873      3.2870595207     -3.7448693506
H       -3.4053705955      2.5256779511     -3.6714760649
H       -3.0572891523      3.9301025671     -2.6405175017
H       -3.8963070827      2.4962691711     -0.7151371809
H       -4.1857412871      1.2028787236     -1.9090509070
H       -3.2544900341      0.8588824597     -0.4407486773
H       -1.3102881870      0.0017407830     -2.0146088005
H       -2.2902549011      0.4244218009     -3.4332663678
H       -0.6559734809      1.1123639041     -3.2385816654
P        0.9827788676     -0.2765596843      0.4343491262
C        0.7829264376     -2.1196849152      0.2575461107
C        0.1381984020     -2.9458753573      1.2188829580
C        1.1721405659     -2.6897165620     -0.9930152504
C       -0.3549684491     -4.1834138017      0.7957865973
C       -0.0022465669     -2.6427904130      2.7283249818
C        0.6668785531     -3.9490192923     -1.3298633886
C        2.1741260420     -2.0288777517     -1.9713546546
C       -0.1592804013     -4.6874713595     -0.4859367379
H       -0.9120048715     -4.7884005929      1.5111666494
C       -1.4343865184     -2.2006463028      3.0590948478
C        0.3011139756     -3.9225166530      3.5333719686
C        1.0113665815     -1.6104209205      3.2262355749
H        0.9250741145     -4.3676617960     -2.2975821851
C        2.6270465815     -3.0095432761     -3.0627553994
C        3.4457776622     -1.6215894277     -1.2086846337
C        1.5697948961     -0.8212913724     -2.6999223001
C       -0.7829264376     -6.0237739192     -0.8894974303
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H       -2.1543731110     -2.9915548970      2.7983690785
H       -1.5364632726     -1.9875640774      4.1354705477
H       -1.7217263981     -1.3024573380      2.4959096640
H        1.2837903633     -4.3386963978      3.2641762578
H        0.3135617756     -3.6814254220      4.6073866015
H       -0.4520462551     -4.7096893673      3.3927239746
H        0.8362692835     -0.6039824181      2.8277193473
H        0.9503363888     -1.5292741621      4.3225703150
H        2.0392027346     -1.9036824413      2.9623544118
H        1.8095744873     -3.2870595207     -3.7448693506
H        3.4053705955     -2.5256779511     -3.6714760649
H        3.0572891523     -3.9301025671     -2.6405175017
H        3.8963070827     -2.4962691711     -0.7151371809
H        4.1857412871     -1.2028787236     -1.9090509070
H        3.2544900341     -0.8588824597     -0.4407486773
H        1.3102881870     -0.0017407830     -2.0146088005
H        2.2902549011     -0.4244218009     -3.4332663678
H        0.6559734809     -1.1123639041     -3.2385816654
C       -2.3088935014     -5.9191644224     -0.7540172856
C       -0.2589071237     -7.1327330760      0.0346067230
C       -0.4509253429     -6.4010465765     -2.3336509936
H       -2.7068815413     -5.1278454037     -1.4074940290
H       -2.7871144635     -6.8710855859     -1.0354182465
H       -2.6105786502     -5.6836463799      0.2773474863
H       -0.5136585411     -6.9415878124      1.0875673692
H       -0.6956133518     -8.1051924007     -0.2440477970
H        0.8365637177     -7.2155993693     -0.0351013036
H        0.6313887968     -6.5328206444     -2.4848275344
H       -0.9387775922     -7.3535897348     -2.5907208151
H       -0.8070367460     -5.6407220648     -3.0454602478
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5.6.22 ^{Mes}TerPP^{Mes}Ter

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100
MesTerPPMesTer @ PBE0-D3/def2-SVP
P       -1.1494141352     -0.1876984790     -0.1823077481
P        0.8256251432      0.2182675768      0.0882417209
C        1.2095081393      0.0515077509      1.8806143897
C        2.6034098125     -0.0036336397      2.1363852240
C        3.0745822877     -0.0676178239      3.4493337331
C        2.1847956992     -0.0777408950      4.5191501280
C        0.8145619158     -0.0384369225      4.2759354093
C        0.3116760966      0.0199845917      2.9729758663
C       -1.1615324891      0.0318862519      2.7736916349
C       -1.8339539724      1.2565187661      2.5931431820
C       -3.2023387100      1.2367457210      2.3228496665
C       -3.9197108814      0.0390887579      2.2329611070
C       -3.2344061556     -1.1577229794      2.4407237203
C       -1.8618778228     -1.1853370813      2.7046459687
C       -1.1362499261     -2.4947153799      2.8115774580
C       -5.3856354724      0.0532785350      1.9101825419
C       -1.0758963659      2.5496054976      2.6115066101
C        3.5724721952     -0.0290325321      1.0015090208
C        3.9464895765     -1.2649379543      0.4418319390
C        4.8273896128     -1.2747641877     -0.6412628361
C        5.3429331472     -0.0950835170     -1.1830880623
C        4.9486410820      1.1185228918     -0.6147017121
C        4.0698347459      1.1738500887      0.4684823955
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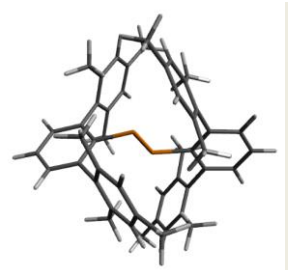

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C         3.6010638938      2.4934642144      1.0071826631
C         6.3099776661     -0.1319430612     -2.3307493879
C         3.3624384698     -2.5459446073      0.9637594450
C        -1.1264730226     -0.0193218467     -2.0267454269
C        -1.2012440370     -1.2220199417     -2.7552235462
C        -1.2993165125     -1.1799355420     -4.1471800751
C        -1.3317391895      0.0468159295     -4.8088996849
C        -1.2647941927      1.2352161978     -4.0850687470
C        -1.1641661247      1.2214677823     -2.6889842389
C        -1.1117117091      2.4872885841     -1.9046315100
C         0.0924529237      3.2118713876     -1.8103098214
C         0.1316449000      4.3503007195     -1.0024079871
C        -0.9896589915      4.8000921230     -0.3003430464
C        -2.1788514410      4.0836203625     -0.4369445218
C        -2.2606001808      2.9309261065     -1.2229334709
C        -3.5546681815      2.1733074631     -1.3098543887
C        -0.9061615857      5.9956716461      0.6029047911
C         1.3295563917      2.7534180729     -2.5261578407
C        -1.1491912458     -2.4973070729     -1.9817425884
C        -2.3215086574     -3.0139285835     -1.3952713003
C        -2.2258886325     -4.1413817005     -0.5757925291
C        -1.0034512864     -4.7636093709     -0.3181956529
C         0.1429952839     -4.2428902348     -0.9250406970
C         0.0943756859     -3.1202664154     -1.7531797600
C         1.3513205719     -2.5499394825     -2.3363448019
C        -0.9132831573     -5.9365048716      0.6139574720
C        -3.6449628686     -2.3359603705     -1.5978456909
H         4.1528348310     -0.1130470702      3.6219989114
H         2.5584218915     -0.1229298531      5.5449533728
H         0.1058757882     -0.0561462934      5.1079777735
H        -3.7216614269      2.1869942823      2.1655368609
H        -3.7754282708     -2.1055091574      2.3653473166
H        -1.8418154713     -3.3364242399      2.8391082727
H        -0.4968826139     -2.5406944868      3.7051743977
H        -0.4803474851     -2.6402127962      1.9363061315
H        -5.5768908049      0.5897201663      0.9670465880
H        -5.9645841255      0.5654159462      2.6955084171
H        -5.7857918159     -0.9649765684      1.8061744338
H        -1.7579904783      3.4096606404      2.6501440765
H        -0.4720189397      2.6511287589      1.6931864795
H        -0.3842848765      2.6046531884      3.4649020207
H         5.1120273973     -2.2353473946     -1.0814665222
H         5.3279140396      2.0549821693     -1.0350656399
H         2.5331422337      2.6472963517      0.7718403761
H         3.6921212099      2.5450632786      2.1023622411
H         4.1663405605      3.3276756177      0.5689511515
H         6.1430056936     -1.0113631630     -2.9695845389
H         7.3508534124     -0.1829361751     -1.9689927303
H         6.2262826284      0.7679534320     -2.9573608946
H         2.2731401725     -2.5788578951      0.7928627398
H         3.5118033618     -2.6499956370      2.0489908196
H         3.8094731775     -3.4179411472      0.4662958368
H        -1.3507046414     -2.1159565496     -4.7094236621
H        -1.4137764685      0.0771922372     -5.8980613645
H        -1.2986066901      2.1970359437     -4.6035788434
H         1.0721931097      4.9034169998     -0.9191086416
H        -3.0755270595      4.4281793800      0.0875228474
H        -4.3954705292      2.7883399480     -0.9589666288
H        -3.5180642426      1.2695407271     -0.6771449455
H        -3.7663372921      1.8411822579     -2.3364927334
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H       -1.8800310353      6.4966827625      0.7025482773
H       -0.5859293048      5.6976235375      1.6159733758
H       -0.1766455874      6.7319600823      0.2350975631
H        2.1568955770      3.4612234665     -2.3769089919
H        1.1592775909      2.6422220556     -3.6072082656
H        1.6537654552      1.7691284097     -2.1507975294
H       -3.1366406452     -4.5396945441     -0.1183514188
H        1.1099972225     -4.7217083575     -0.7431865998
H        1.5820047500     -1.5738664808     -1.8715301315
H        2.2099088725     -3.2133192429     -2.1632052797
H        1.2582220975     -2.3682989136     -3.4168873490
H       -1.8712404970     -6.4712599781      0.6862925250
H       -0.6435263651     -5.6055047924      1.6312858856
H       -0.1430794289     -6.6523135677      0.2910378251
H       -3.6919671400     -1.4044380994     -1.0071735877
H       -4.4741389973     -2.9793381585     -1.2721022517
H       -3.8063678545     -2.0575682424     -2.6492677167
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5.6.23 MesPCNMe

```
27
MesPCNMe @ PBE0-D3/def2-SVP
C       -0.1349116051      0.3034441709     -0.5007080444
C       -0.9987492506      1.2982254867      0.0056347578
C       -2.2681908627      0.9292186463      0.4547197806
H       -2.9315663156      1.7036547848      0.8519570382
C       -2.7106219669     -0.3947651359      0.4156267889
C       -1.8410442749     -1.3595821447     -0.0930911574
H       -2.1683197033     -2.4029520514     -0.1359629570
C       -0.5621931723     -1.0397227856     -0.5603225891
C        2.4708499270     -0.0240558035     -0.1315725234
N        3.2235294843     -0.6891314231      0.5380793713
P        1.5033136331      0.8437130923     -1.1856675524
C        3.8832751573     -0.4590177298      1.7889149911
C       -0.5750700541      2.7375188643      0.0851062178
C        0.3119126351     -2.1321350156     -1.1039450916
C       -4.0925412530     -0.7602974602      0.8733120056
H       -0.2652760535     -3.0543253789     -1.2591265619
H        0.7701972703     -1.8370266610     -2.0605665922
H        1.1451686893     -2.3649493965     -0.4210934562
H       -1.3822039517      3.3641742610      0.4895923533
H        0.3126051672      2.8572995383      0.7260388452
H       -0.2994834256      3.1358041695     -0.9048631541
H       -4.1461947630     -1.8092105933      1.1986691930
H       -4.4227029832     -0.1241476248      1.7076520889
H       -4.8237463389     -0.6323273984      0.0574800211
H        3.5417823249     -1.2089678017      2.5179434335
H        4.9661459941     -0.6021241489      1.6587928450
H        3.6928915279      0.5503353112      2.1898937977
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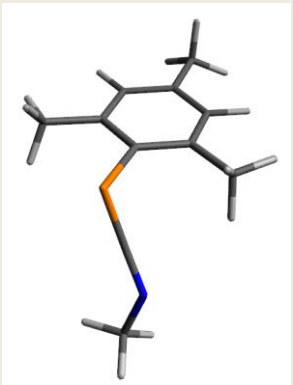
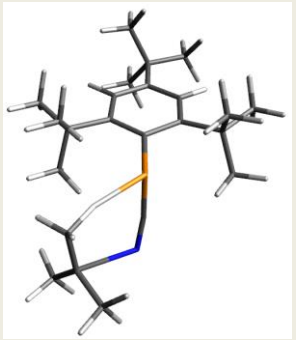


5.6.24 3a to 4a (TS)



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63
3a to 4a TS @ PBE0-D3/def2-SVP
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C        1.8184208009     -1.3942627837     -0.1047306287
H        2.0810128089     -2.4494446507     -0.1024345335
C        2.8009965015     -0.4757397021      0.2522781410
C        2.4608600932      0.8676964511      0.1806485929
H        3.2268720322      1.5990621740      0.4124720625
C        1.1871729399      1.3270662373     -0.1850588711
C       -2.2638043170      0.9878081361      0.8309972233
N       -3.0593511759      0.9043405070      1.6934755479
P       -1.5589136844      0.9996487724     -0.7539435183
C       -4.8142338653     -0.3998468405      0.5132514313
C       -5.6812559277      0.7976416016      0.6860575386
C       -4.2392132628     -0.6717162859     -0.7553395301
C       -4.8588903573     -1.4365392431      1.5807733229
H       -5.6345465138      1.1876805531      1.7112886370
H       -5.4134181225      1.6001443202     -0.0148359239
H       -6.7287604123      0.5058127349      0.4776865715
H       -3.1087633782     -0.1928688573     -0.8072730554
H       -4.0397443275     -1.7282042521     -0.9705917048
H       -4.7018210208     -0.1388106685     -1.5970382776
H       -5.8350723431     -1.9561897587      1.5210244799
H       -4.0728138230     -2.1926815508      1.4615325948
H       -4.7816766926     -0.9876933311      2.5797699108
C       -0.4529870316     -2.1684297457     -0.8217385166
C       -1.4675824132     -2.3510637178      0.3153652978
C       -1.1108360319     -1.9021075623     -2.1847347327
C        0.2586523673     -3.5209449986     -0.9801703256
H       -0.9449757443     -2.6791450354      1.2268132606
H       -1.9978343011     -1.4277975372      0.5679274847
H       -2.2071378837     -3.1257075001      0.0533694709
H       -0.3438307723     -1.8907617437     -2.9742189776
H       -1.8298364392     -2.7020150372     -2.4237940502
H       -1.6476924482     -0.9463177324     -2.2336981451
H       -0.4792462605     -4.2714029007     -1.3024848447
H        1.0514904908     -3.4857986413     -1.7424905286
H        0.6945402228     -3.8839987489     -0.0380221914
C        1.0310991339      2.8655317841     -0.3433213334
C        0.6283009843      3.1996849181     -1.7899464421
C        0.0346189601      3.4709192259      0.6594098889
C        2.3587334535      3.6015911660     -0.1002559199
H        1.3812893589      2.8174901296     -2.4964234633
H       -0.3477975370      2.7763392355     -2.0610164246
H        0.5634629595      4.2922034015     -1.9172631129
H        0.2547679144      3.1348731828      1.6843537923
H        0.1121989696      4.5696764441      0.6371517694
H       -1.0053773221      3.2103483945      0.4347787562
H        2.1988920857      4.6753987053     -0.2766215462
H        2.7170408653      3.4921764702      0.9345514931
H        3.1550935995      3.2724168010     -0.7841657600
C        4.1889722261     -0.9638755676      0.6684383717
C        5.1268861483      0.1918227401      1.0180476766
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C         4.0517166020     -1.8674156729      1.9026370464
C         4.8128640424     -1.7617278188     -0.4858687704
H         5.2903008063      0.8604251488      0.1591404271
H         4.7393273021      0.7940524836      1.8538255608
H         6.1080608945     -0.2045803104      1.3206127995
H         3.4130939157     -2.7399489360      1.6999544814
H         5.0390553896     -2.2404406935      2.2191479362
H         3.6068247497     -1.3154663924      2.7447322270
H         5.8136317759     -2.1266148136     -0.2042247038
H         4.2025465899     -2.6361909065     -0.7564673919
H         4.9169049754     -1.1347631551     -1.3847229252s
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