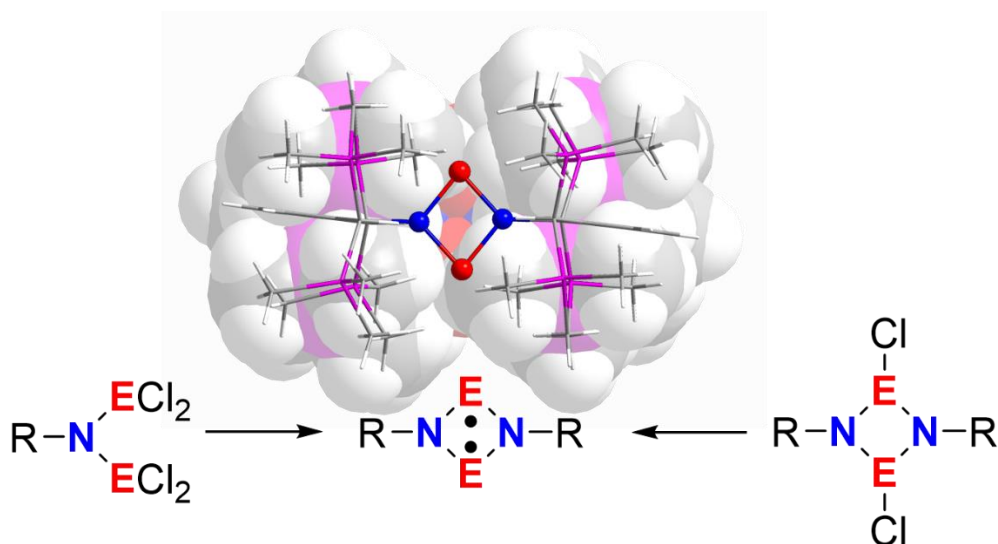


SUPPORTING INFORMATION

$[E(\mu\text{-NBbp})]_2$ (E = P, As) – Group 15 biradicals synthesized from acyclic precursors

Jonas Bresien, Axel Schulz, Lilian Sophie Szych, Alexander Villinger and Ronald Wustrack*



This file includes:

1 Experimental	1
2 Structure Elucidation	3
3 Syntheses of starting materials	7
4 Syntheses of compounds	12
5 Computational details	40
6 Optimized structures (.xyz files)	42
7 References	49

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.

NMR spectra were recorded on Bruker spectrometers AVANCE 250, AVANCE 300 and AVANCE 500 and were referenced internally to the deuterated solvent (^{13}C : CD_2Cl_2 $\delta_{\text{ref}} = 54.0$ ppm; CDCl_3 $\delta_{\text{ref}} = 77.0$ ppm; C_6D_6 $\delta_{\text{ref}} = 128.4$ ppm; THF- d_8 $\delta_{\text{ref},1} = 25.3$ ppm, $\delta_{\text{ref},2} = 67.2$ ppm), to protic impurities in the deuterated solvent (^1H : CHDCl_2 $\delta_{\text{ref}} = 5.32$ ppm, CHCl_3 $\delta_{\text{ref}} = 7.26$ ppm, C_6HD_5 $\delta_{\text{ref}} = 7.16$ ppm, THF- d_7 $\delta_{\text{ref},1} = 1.73$ ppm, $\delta_{\text{ref},2} = 3.58$ ppm) or externally (^{31}P : 85 % H_3PO_4 $\delta_{\text{ref}} = 0$ ppm). All measurements were carried out at ambient temperature unless denoted otherwise. NMR signals were assigned using experimental data (e.g. chemical shifts, coupling constants, integrals where applicable).

IR spectra of crystalline samples were recorded on a Nicolet 380 FT-IR spectrometer equipped with a Smart Orbit ATR unit at ambient temperature.

Raman spectra of crystalline samples were recorded using a LabRAM HR 800 Horiba Jobin YVON Raman spectrometer equipped with an Olympus BX41 microscope with variable lenses. The samples were excited by either an infrared laser (785 nm, 100 mW, air-cooled diode laser), a red laser (633 nm, 17 mW, air-cooled HeNe laser) or a green laser (532 nm, 50 mW, air-cooled, frequency-doubled Nd:YAG solid state laser). All measurements were carried out at ambient temperature unless stated otherwise.

Elemental analyses were obtained using an Elementar vario Micro cube CHNS analyser or a LECO TruSpec Micro CHNS analyser.

Melting points (uncorrected) were determined using a Stanford Research Systems EZ Melt at a heating rate of 5 °C/min.

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

Table S1: Origin and purification of solvents and reactants.

Substance	Origin	Purification
AiBN	local trade	used as received
AsCl ₃	local trade	distilled, degassed, (freeze-pump-thaw)
2-Brom- <i>m</i> -xylol	<i>J&K Chemicals (98 %)</i>	used as received
<i>t</i> -Butyllithium (1.7 M in <i>n</i> -pentane)	<i>Aldrich</i>	used as received
CCl ₄	<i>Abcr GmbH</i>	used as received
C ₆ D ₆	<i>Eurisotop</i>	dried over Na, freshly distilled prior to use
CD ₂ Cl ₂	<i>Eurisotop</i>	used as received
CDCl ₃	<i>Eurisotop</i>	used as received
DBU	Merck, for synthesis	distilled
Et ₂ O, THF	local trade	dried over Na/benzophenone, freshly distilled prior to use
<i>n</i> -hexane	local trade	dried over Na/benzophenone /tetraglyme, freshly distilled prior to use
LiAlH ₄	<i>Abcr GmbH (97 %)</i>	used as received
Mg turnings	<i>Abcr GmbH (for Grignards 99.8 %)</i>	used as received
MgSO ₄	Grüssing (99 %)	used as received
NaHSO ₃ -solution	<i>Sigma Aldrich (ca. 40 %)</i>	used as received
NaOH	<i>VBR (98.8 %)</i>	used as received
NEt ₃	<i>Sigma Aldrich (99 %)</i>	dried over Na, distilled
NBS	<i>Abcr GmbH (99 %)</i>	used as received
PCl ₃	Merck, for synthesis	dried over P ₄ O ₁₀ , distilled, degassed, (freeze-pump-thaw)
(Me) ₃ SiCl	Sigma Aldrich (>98 %)	dried over CaH ₂ , distilled, degassed (freeze-pump-thaw)
Tos-N ₃	Synthesized ¹	recrystallized

2 Structure Elucidation

X-ray Structure Determination:

X-ray quality crystals were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature. The samples were cooled to 123(2) K during measurement if possible. Crystals of **1As_Bbp** were cooled to 213(2) K and crystals of **4_Bbp** to 193(2) K because otherwise they burst into smaller fragments. The data were collected on a Bruker D8 Quest diffractometer using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by iterative methods (SHELXT)² and refined by full matrix least squares procedures (SHELXL)³. Semi-empirical absorption corrections were applied (SADABS).⁴ All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

Table S2: Crystallographic details of **1P_Bbp**, **1As_Bbp** and **2P_Bbp**.

Compound	1P_Bbp	1As_Bbp	2P_Bbp
Chem. formula	C ₄₀ H ₈₂ N ₂ P ₂ Si ₈	C ₄₀ H ₈₂ As ₂ N ₂ Si ₈	C ₄₀ H ₈₂ Cl ₂ N ₂ P ₂ Si ₈
Formula weight [g/mol]	877.73	965.63	948.63
Colour	yellow	olive	colourless
Crystal system	triclinic	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	9.2127 (6)	9.2670(6)	13.3218(9)
<i>b</i> [Å]	12.6045 (9)	12.6666(9)	15.5388(11)
<i>c</i> [Å]	12.8563 (8)	12.9543(9)	14.3474(10)
α [°]	78.439 (2)	78.372(2)	90
β [°]	74.181 (2)	73.259(2)	112.395(2)
γ [°]	71.926 (2)	72.519(2)	90
<i>V</i> [Å ³]	1354.48 (16)	1377.84(16)	2746.0(3)
<i>Z</i>	1	1	2
$\rho_{\text{calc.}}$ [g/cm ³]	1.076	1.164	1.147
μ [mm ⁻¹]	0.28	1.413	0.379
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073	0.71073
<i>T</i> [K]	123(2)	213(2)	123(2)
Measured reflections	69464	60626	74586
Independent reflections	7169	9958	8027
Reflections with <i>I</i> > 2 σ (<i>I</i>)	5363	8141	5644
<i>R</i> _{int.}	0.0732	0.0273	0.1056
<i>F</i> (000)	478	514	1024
<i>R</i> ₁ (<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)])	0.0459	0.0318	0.0401
<i>wR</i> ₂ (<i>F</i> ²)	0.1149	0.087	0.0859
GooF	1.045	1.070	1.033
No. of parameters	247	247	275
CCDC #	1882065	1882064	1882066

Table S3: Crystallographic details of **3P_Bbp**, **3As_Bbp** and **4_Bbp**.

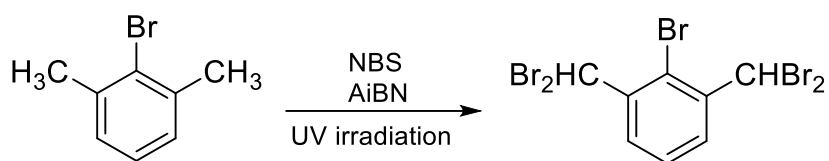
Compound	3P_Bbp	3As_Bbp	4_Bbp
Chem. formula	C ₂₀ H ₄₁ Cl ₄ NP ₂ Si ₄	C ₂₀ H ₄₁ As ₂ Cl ₄ NSi ₄	C ₂₀ H ₄₁ BrSi ₄
Formula weight [g/mol]	611.64	699.54	473.80
Colour	colourless	colourless	colourless
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/n</i>	<i>P2₁/c</i>
<i>a</i> [Å]	20.7415(7)	17.907(2)	8.4553(13)
<i>b</i> [Å]	17.8599(7)	23.513(3)	13.167(2)
<i>c</i> [Å]	17.9973(6)	47.214(6)	12.639(2)
α [°]	90	90	90
β [°]	107.625(1)	99.182(2)	102.629(5)
γ [°]	90	90	90
<i>V</i> [Å ³]	6354.0(4)	19624(4)	1373.1(4)
<i>Z</i>	8	24	2
$\rho_{\text{calc.}}$ [g/cm ³]	1.279	1.421	1.146
μ [mm ⁻¹]	0.64	2.528	1.674
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073	0.71073
<i>T</i> [K]	123(2)	123(2)	193(2)
Measured reflections	236946	295413	18330
Independent reflections	22988	47381	3648
Reflections with $I > 2\sigma(I)$	15023	28476	2330
<i>R</i> _{int.}	0.0792	0.1150	0.0480
<i>F</i> (000)	2576	8592	504
<i>R</i> ₁ (<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)])	0.0408	0.0594	0.0398
w <i>R</i> ₂ (<i>F</i> ²)	0.0942	0.1362	0.1023
GooF	1.019	1.036	1.031
No. of parameters	583	1831	227
CCDC #	1882068	1882067	1882069

Table S4: Crystallographic details of **5_Bbp**, **6_Bbp** and **7P_Bbp**.

Compound	5_Bbp	6_Bbp	7P_Bbp
Chem. formula	C ₂₀ H ₄₁ N ₃ Si ₄	C ₂₀ H ₄₃ NSi ₄	C ₂₀ H ₄₂ Cl ₂ NPSi ₄
Formula weight [g/mol]	435.92	409.91	510.77
Colour	colourless	colourless	colourless
Crystal system	monoclinic	triclinic	orthorhombic
Space group	<i>P2₁/c</i>	<i>P</i> $\bar{1}$	<i>Pbca</i>
<i>a</i> [Å]	15.4585(4)	9.1282(8)	13.9382(8)
<i>b</i> [Å]	7.04160(10)	12.6553(10)	12.5570(5)
<i>c</i> [Å]	25.1492(6)	12.8592(11)	33.8982(14)
α [°]	90	86.649(2)	90
β [°]	95.6170(10)	71.391(2)	90
γ [°]	90	70.322(2)	90
<i>V</i> [Å ³]	2724.41(10)	1323.61(19)	5932.9(5)
<i>Z</i>	4	2	8
$\rho_{\text{calc.}}$ [g/cm ³]	1.063	1.029	1.144
μ [mm ⁻¹]	0.228	0.229	0.44
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073	0.71073
<i>T</i> [K]	123(2)	123(2)	123(2)
Measured reflections	63696	26389	44343
Independent reflections	7938	5892	6643
Reflections with $I > 2\sigma(I)$	5932	4059	5151
<i>R</i> _{int.}	0.0730	0.0512	0.0902
<i>F</i> (000)	952	452	2192
<i>R</i> ₁ (<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)])	0.044	0.0402	0.0747
<i>wR</i> ₂ (<i>F</i> ²)	0.1028	0.0998	0.1549
GooF	1.123	1.024	1.15
No. of parameters	256	246	288
CCDC #	1882070	1882071	1882072

3 Syntheses of starting materials

Synthesis of 1-Bromo-2,6-bis(dibromomethyl)benzene



1-Bromo-2,6-bis(dibromomethyl)benzene is prepared according to modified literature procedure.^{5,6}

The synthesis is carried out under non-inert conditions.

2-Bromo-*m*-xylene (6.69 mL; 9.25 g; 0.05 mol) is added to a suspension of *N*-bromosuccinimide (60 g; 0.34 mol) and azobisisobutyronitrile (AiBN, 10 mg) in CCl₄ (250 mL). The stirred reaction mixture is heated under reflux conditions and UV radiation (Philips, Efbe Schott, 15 W) for approximately 48 hours, reaction progress can easily be traced by ¹H NMR spectroscopy. After completion of the reaction the intensely orange colored suspension is cooled to ambient temperature. The solid succinimide is filtered off and the resulting solution is washed with diluted NaHSO₃ solution to remove traces of bromine. The solvent is removed *in vacuo*, yielding 1-bromo-2,6-bis(dibromomethyl)benzene as yellow flakes. The product can be recrystallized from heptane or purified by column chromatography to remove impurities if necessary. Yield: 22.5 g (0.045 mol; 90 %).

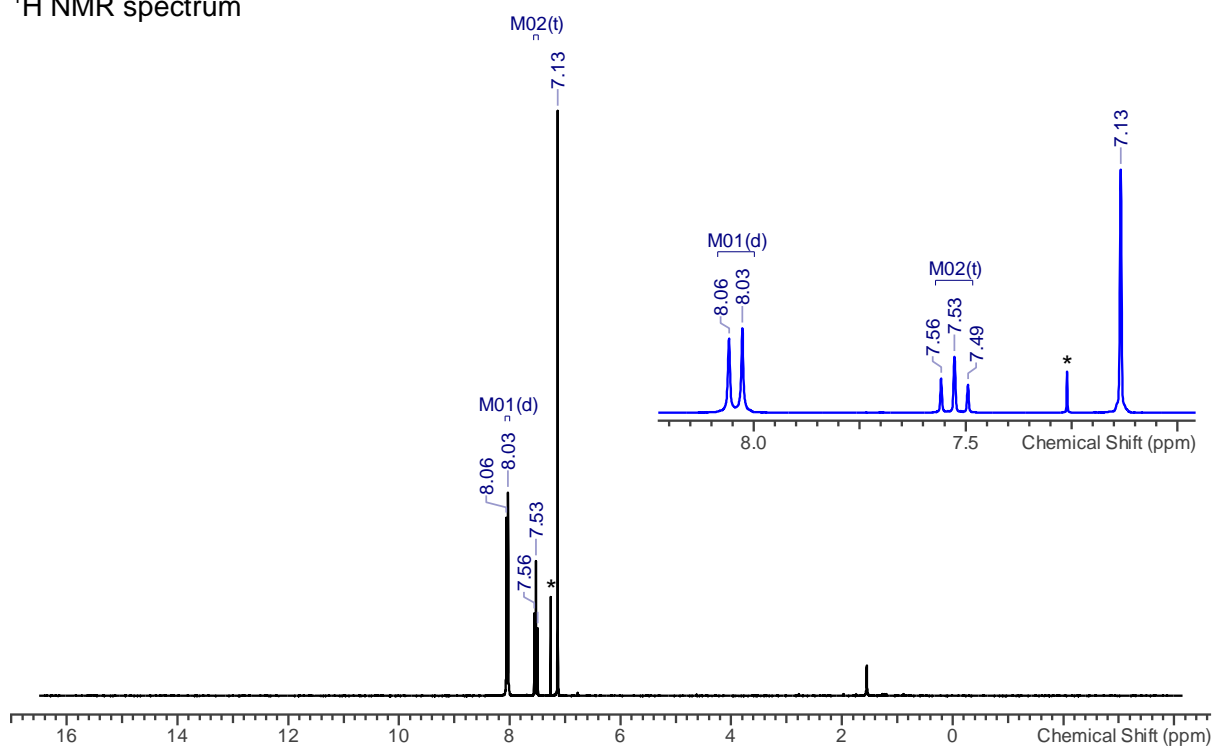
With respect to the poor availability of CCl₄, a substitution of the solvent with benzene is possible but might result in a minor yield reduction.

M(C₈H₅Br₅) = 500.65 g/mol.

Mp. 153 °C. **EA:** calc. (found) in %: C 19.19 (19.34), H 1.01 (0.84). **¹H NMR:** (CDCl₃, 300.0 K, 250.13 MHz): δ = 7.13 (s, 2H, CHBr₂); 7.53 (t, 1H, ³J(¹H,¹H) = 8 Hz, *p*-phenyl-*H*); 8.05 (d, 2H, ³J(¹H,¹H) = 8 Hz, *m*-phenyl-*H*). **¹³C{¹H} NMR:** (CDCl₃, 300.0 K, 62.90 MHz): δ = 39.2 (s, CHBr₂); 117.1 (s, phenyl-C); 129.1 (s, phenyl-C); 132.4 (s, phenyl-C); 140.7 (s, phenyl-C). **IR** (ATR, 32 Scans, cm⁻¹): $\tilde{\nu}$ = 3024 (m), 2346 (w), 1575 (w), 1420 (m), 1290 (w), 1255 (m), 1195 (w), 1148 (m), 1115 (w), 1020 (m), 936 (m), 719 (s), 668 (w), 660 (m), 620 (vs), 561 (m), 480 (m), 425 (w), 406 (m). **Raman:** (633 nm, 10 s, 20 scans, cm⁻¹): $\tilde{\nu}$ = 3148 (1), 3171 (2), 3152 (2), 3122 (5), 3118 (1), 3116 (1), 2322 (1), 1944 (1), 1929 (1), 1921 (1), 1868 (1), 1583 (1), 1571 (3), 1561 (1), 1415 (1), 1285 (2), 1246 (8), 1219 (1), 1214 (1), 1217 (1), 1211 (1), 1188 (2), 1164 (1), 1142 (2), 1116 (1), 1112 (1), 1151 (1), 1146 (1), 1135 (1), 1128 (1), 1115 (4), 971 (1), 954 (1), 929 (1), 926 (1), 811 (1), 779 (1), 769 (3), 722 (1), 715 (1), 713 (1), 695 (1), 692 (1), 673 (2), 653 (11), 631 (9), 619 (2), 611 (1), 589 (1), 519 (2), 519 (1), 472 (1), 399 (1), 348 (1), 334 (1), 331 (1), 313 (8), 232 (1). **MS** (EI, 70 eV, m/z): 80 (Br⁺); 171 ([CHBr₂]⁺); 421 ([C₈H₅Br₄]⁺).

Figure S1: NMR, IR and Raman spectra of 1-Bromo-2,6-bis(dibromomethyl)benzene (solvent signals indicated by asterisks).

^1H NMR spectrum



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum

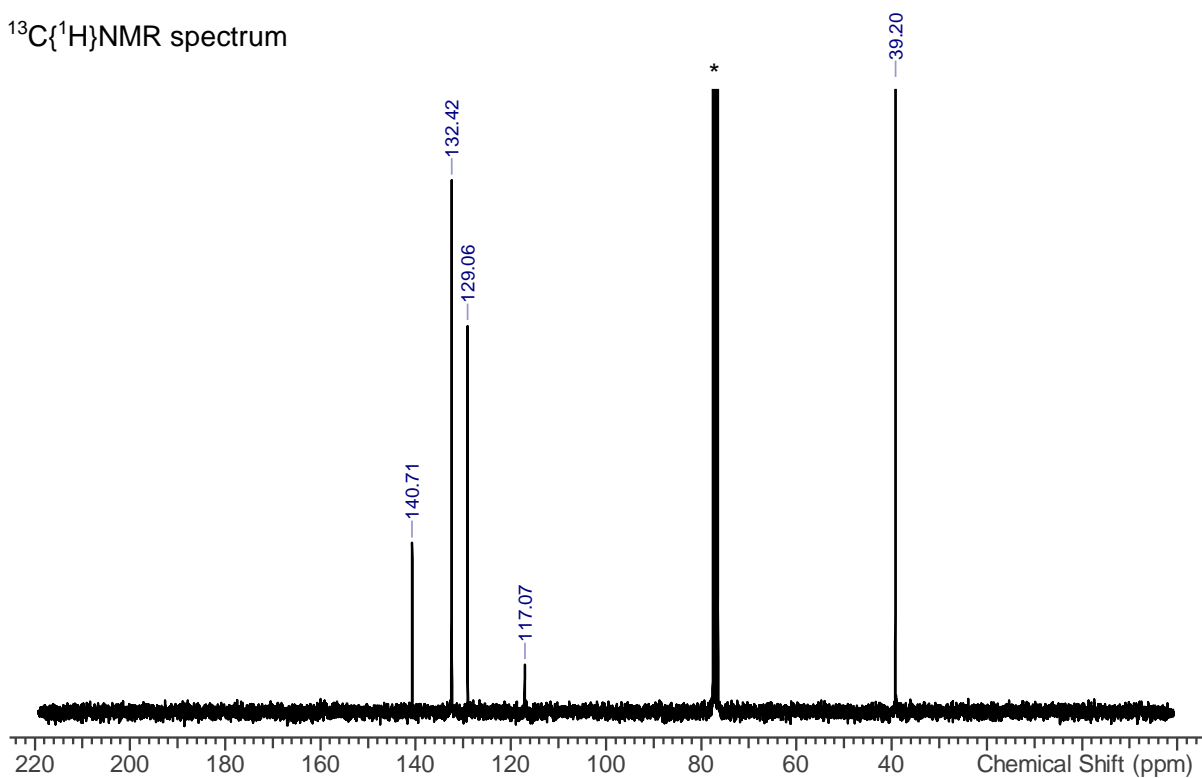
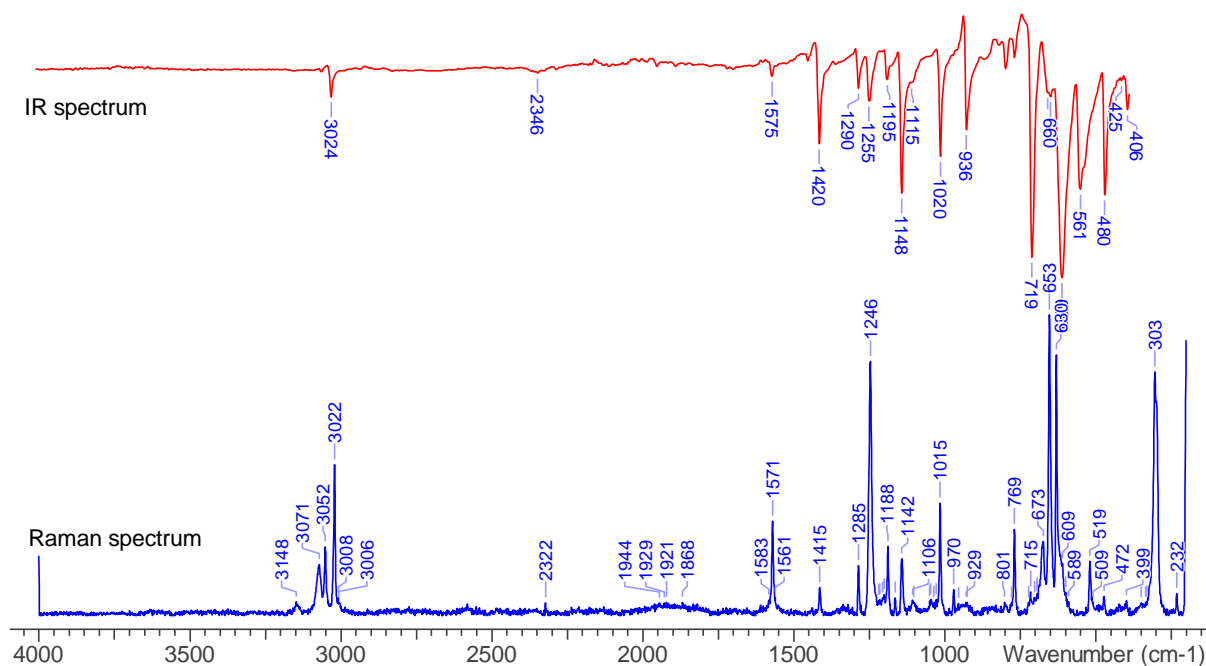
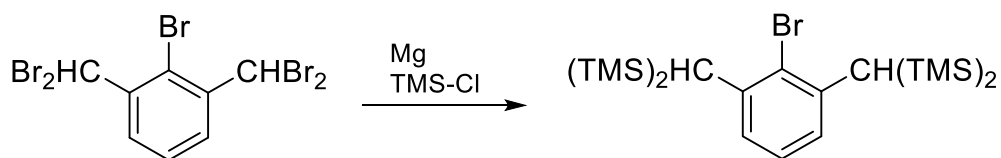


Figure S1 continued



Synthesis of Bbp-Br (4_Bbp)



Bbp-Br is prepared according to a modified literature procedure.⁷

A solution of 1-bromo-2,6-bis(dibromomethyl)benzene (11.16 g; 22 mmol) in THF (100 mL) is added slowly at 50 °C to a stirred suspension of magnesium turnings (2.67 g; 110 mmol) and trimethylchlorosilane (55.8 mL; 47.8 g; 440 mmol) in THF (40 mL). After addition, the reaction mixture is heated to 70 °C and stirred for two hours. Thereafter, the reaction mixture is poured into ice water. The organic phase is separated, the aqueous phase is extracted with Et₂O. The combined organic phases are dried over MgSO₄ and the solvent is removed *in vacuo*. The resulting greenish product is washed with ice-cold ethanol, yielding crystalline, colourless Bbp-Br. Yield: 6.36 g (13.4 mmol; 61 %).

M(C₂₀H₄₁Si₄Br) = 473.79 g/mol.

Mp. 138 °C. **EA:** calc. (found) in %: C 50.70 (50.68), H 8.72 (8.75). **^1H NMR:** (CD_2Cl_2 , 298.2 K, 300.13 MHz): δ = 0.03 (broad s, 36H, $\text{Si}(\text{CH}_3)_3$); 2.56 (s, 2H, $\text{CH}(\text{Si}(\text{CH}_3)_3)_2$); 6.78 (d, 2H, $^3J(^1\text{H}, ^1\text{H}) = 8$ Hz, *m*-phenyl-*H*); 7.02 (t, 1H, $^3J(^1\text{H}, ^1\text{H}) = 8$ Hz, *p*-phenyl-*H*). **$^{13}\text{C}\{^1\text{H}\}$ NMR:** (CD_2Cl_2 , 298.2 K, 75.48 MHz): δ = 0.4 (s, $\text{Si}(\text{CH}_3)_3$); 29.9 (s, $\text{CH}(\text{Si}(\text{CH}_3)_3)_2$); 124.6 (s, phenyl-C); 126.1 (s, phenyl-C); 129.6 (s, phenyl-C); 144.6 (s, phenyl-C). **^{29}Si INEPT NMR:** (CD_2Cl_2 , 298.2 K, 59.63 MHz): δ = 2.43 (m, $\text{Si}(\text{CH}_3)_3$). **IR** (ATR, 32 Scans, cm^{-1}): $\tilde{\nu}$ = 2952 (w), 2896 (w), 2879 (w), 1571 (w), 1449 (w), 1433 (w), 1402 (w), 1247 (m), 1160 (m), 1039 (m), 1012 (w), 1000 (w), 938 (m), 855 (m), 824 (vs), 771 (m), 763 (m), 748 (m), 719 (m), 684 (m), 655 (m), 616 (m), 585 (w), 501 (w), 418 (m). **Raman:** (633 nm, 10 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3053 (1), 2990 (1), 2949 (3), 2891 (6), 2876 (3), 2819 (1), 2787 (1), 1563 (2), 1558 (2), 1399 (1), 1268 (2), 1226 (6), 1170 (1), 1160 (1), 1090 (1), 1032 (1), 1005 (2), 994 (1), 991 (1), 865 (1), 834 (1), 791 (1), 763 (0), 755 (1), 739 (1), 680 (3), 663 (1), 613 (4), 597 (1), 578 (10), 410 (1), 330 (3), 315 (2), 253 (1), 242 (0), 227 (1). **MS** (EI, 70 eV, m/z): 73 (TMS^+); 473 (M^+).

Single crystals suitable for X-ray diffraction can be grown from saturated diethyl ether solution at ambient temperature.

Figure S2: NMR, IR and Raman spectra of Bbp-Br (solvent signals indicated by asterisks, traces of water in deuterated solvent indicated).

^1H NMR spectrum

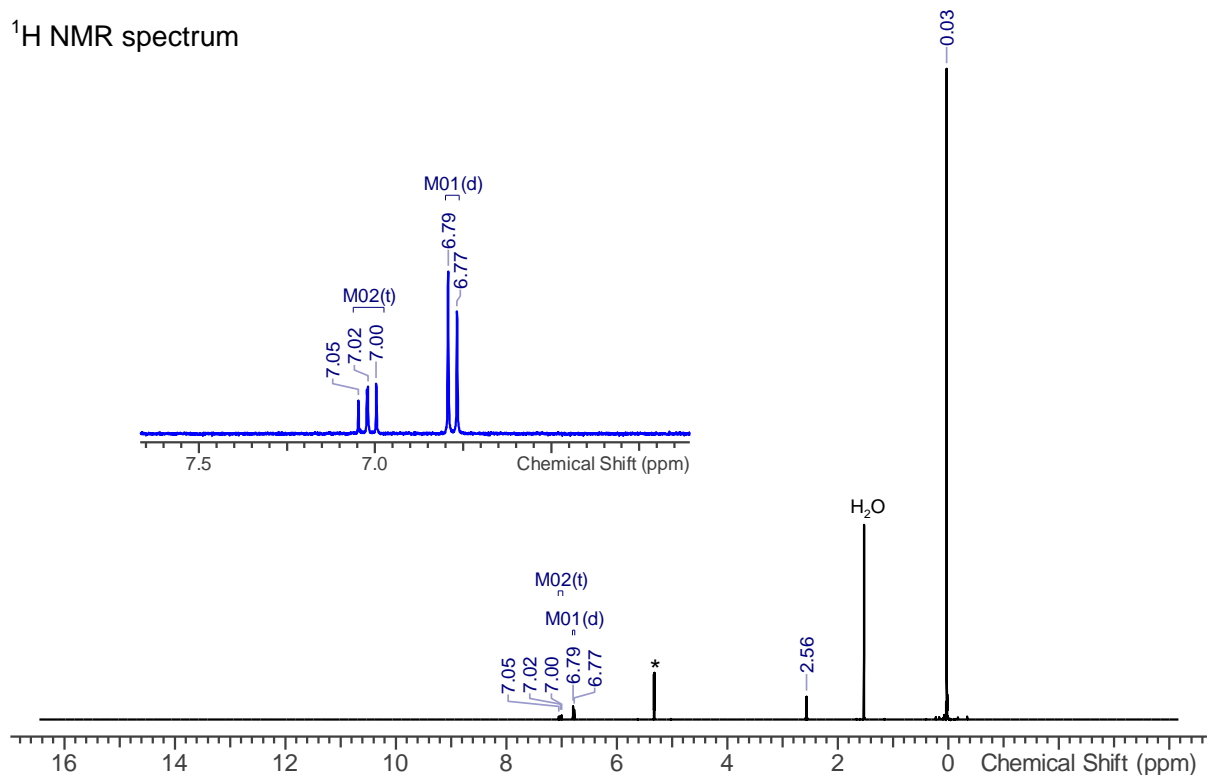
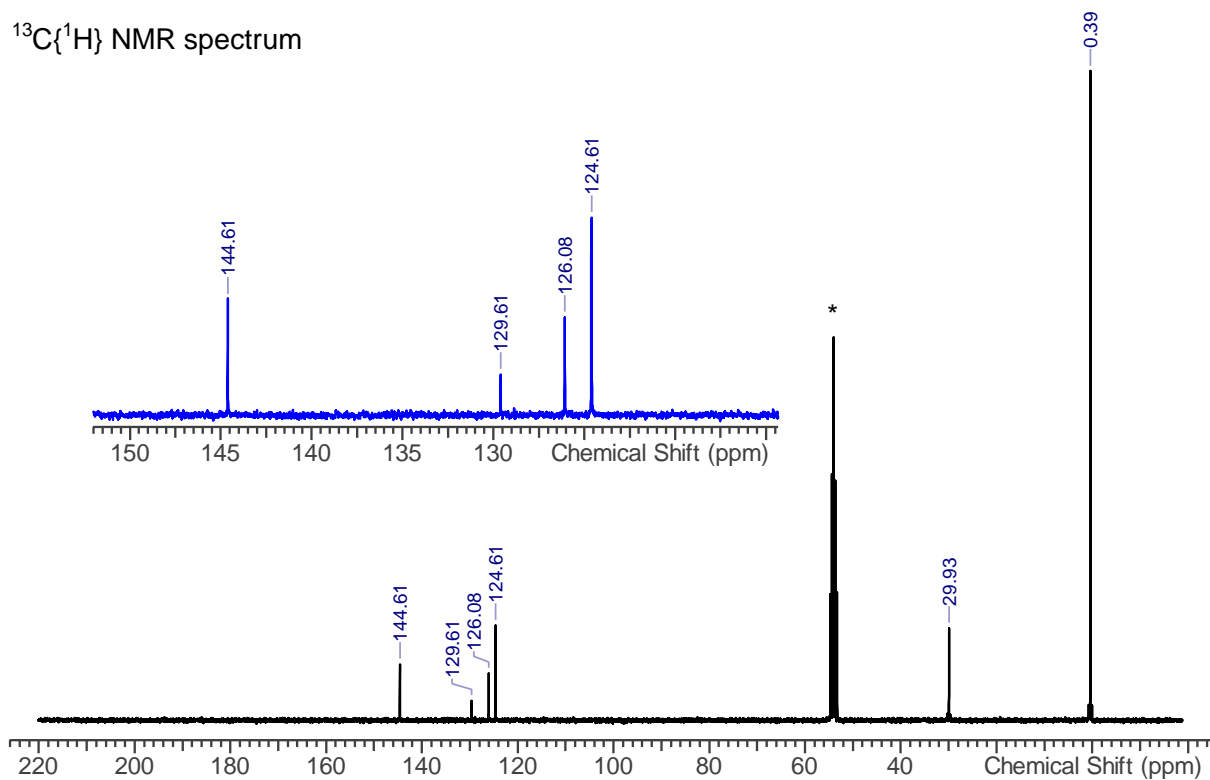


Figure S2 continued.

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



^{29}Si INEPT NMR spectrum

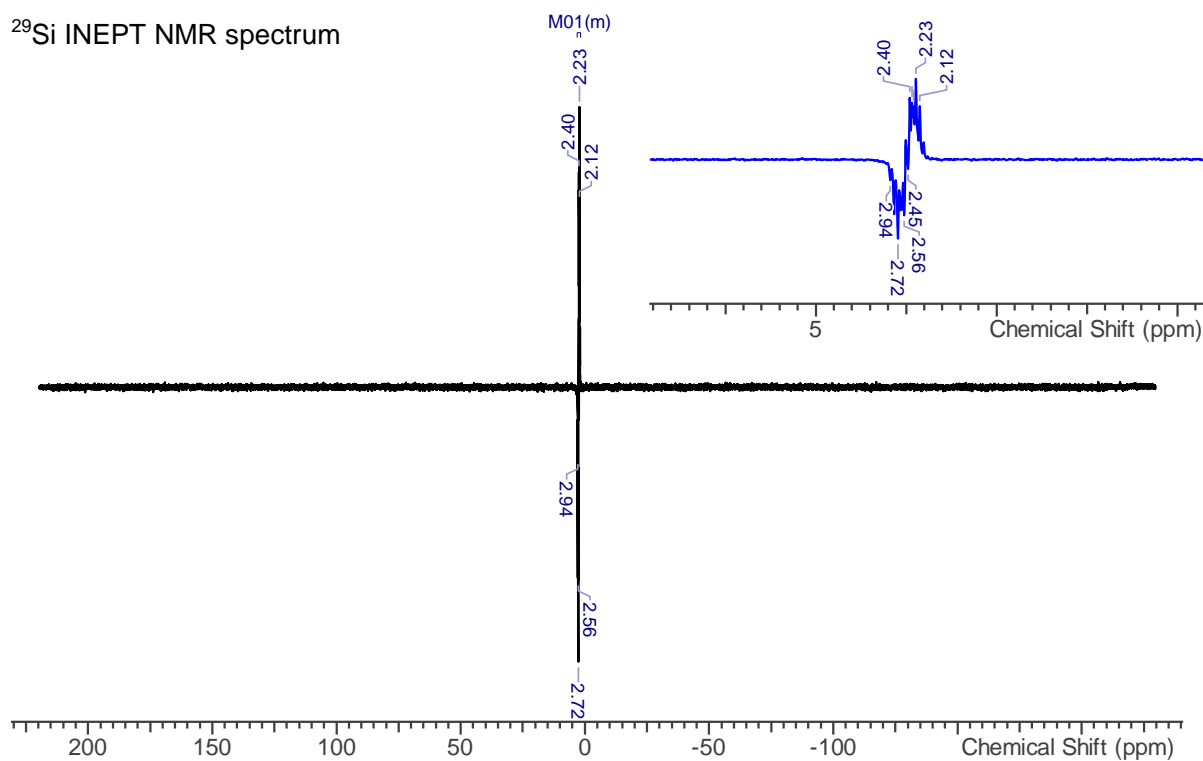
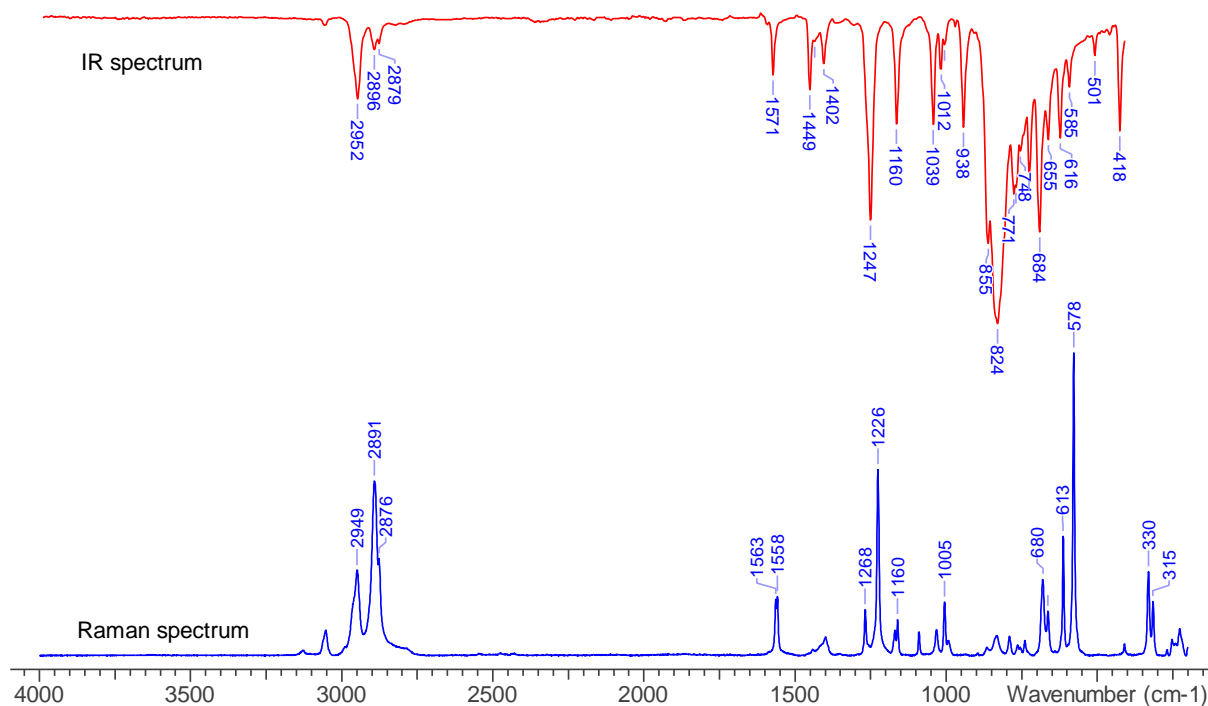
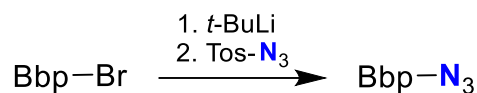


Figure S2 continued.



4 Syntheses of compounds

Synthesis of Bbp-N₃ (5_Bbp)



Bbp-N₃ is prepared according to a modified literature procedure for *Tbt-N₃*.⁸

A solution of *t*-butyllithium (1.7 M in pentane; 4.7 mL; 8 mmol) is added dropwise to a stirred solution of Bbp-Br (1.9 g; 4 mmol) in THF (30 mL) at -70 °C over a period of 5 minutes, yielding a greenish suspension. After stirring for half an hour at -70 °C, tosyl azide (0.79 g; 4 mmol) is added dropwise to the reaction mixture, whereupon the suspension turns beige to light orange. After addition the suspension is stirred at constant temperature for half an hour. The reaction vessel is warmed slowly to ambient temperature, poured on distilled water and extracted with Et₂O. The organic layers are combined and dried over MgSO₄. After separating the inorganic solids by filtration, the solvents are evaporated, yielding product in form of colourless crystals. Bbp-N₃ can be purified by recrystallization from ethanol. Yield: 1.22 g (2.8 mmol; 70 %).

$M(\text{C}_{20}\text{H}_{41}\text{Si}_4\text{N}_3) = 435.90 \text{ g/mol}$

Mp. 100.5 °C. **EA:** calc. (found) in %: C 55.11 (55.15), H 9.48 (9.36), N 9.64 (9.34). **¹H NMR:** (CDCl₃, 298 K, 300.13 MHz): δ = 0.03 (broad s, 36H, Si(CH₃)₃); 2.03 (s, 2H, CH(Si(CH₃)₃)₂); 6.73 (d, 2H, ³J(¹H,¹H) = 8 Hz, *m*-phenyl-*H*); 6.97 (t, 1H, ³J(¹H,¹H) = 8 Hz, *p*-phenyl-*H*). **¹³C{¹H} NMR:** (CDCl₃, 298.2 K, 75.48 MHz): δ = 0.2 (s, Si(CH₃)₃); 23.3 (s, CH(SiMe₃)₂); 124.2 (s, phenyl-C); 125.5 (s, phenyl-C); 135.3 (s, phenyl-C); 138.6 (s, phenyl-C). **²⁹Si INEPT NMR:** (CDCl₃, 298.2 K, 59.63 MHz): δ = 2.25 (m, Si(CH₃)₃). **IR** (ATR, 32 Scans, cm⁻¹): $\tilde{\nu}$ = 3059 (s), 2951 (s), 2895 (s), 2127 (s), 1570 (s), 1448 (s), 1402 (s), 1248 (m), 1161 (m), 1038 (m), 939 (m), 858 (w), 829 (w), 771 (m), 762 (m), 719 (m), 685 (m), 658 (m), 615 (m), 586 (m), 540 (s). **Raman:** (784 nm, 20 s, 20 scans, cm⁻¹): $\tilde{\nu}$ = 2958 (1), 2954 (1), 2952 (1), 2900 (1), 2898 (1), 1575 (1), 1430 (1), 1419 (1), 1406 (1), 1289 (1), 1284 (1), 1245 (1), 1231 (1), 1173 (1), 1166 (1), 1057 (1), 871 (1), 847 (1), 845 (1), 725 (1), 719 (1), 687 (1), 666 (1), 630 (1), 616 (1), 614 (1), 612 (1), 610 (1), 590 (8), 571 (1), 452 (1), 353 (1), 351 (1), 336 (2), 287 (1), 284 (1), 277 (1), 275 (1), 273 (1), 267 (1), 248 (2), 245 (2), 237 (2), 226 (2), 224 (2), 203 (4), 201 (4), 199 (4), 187 (3), 174 (5), 151 (5), 126 (10), 106 (4), 103 (4), 73 (9). **MS** (EI, 70 eV, m/z): 43 ([SiMe]⁺); 73 (TMS⁺); 394 ([Bbp]⁺); 407 ([BbpN]⁺).

Single crystals suitable for X-ray diffraction can be grown from saturated *n*-hexane solution at ambient temperature.

Figure S3: NMR, IR and Raman spectra of Bbp–N₃ (solvent signals indicated by asterisks).

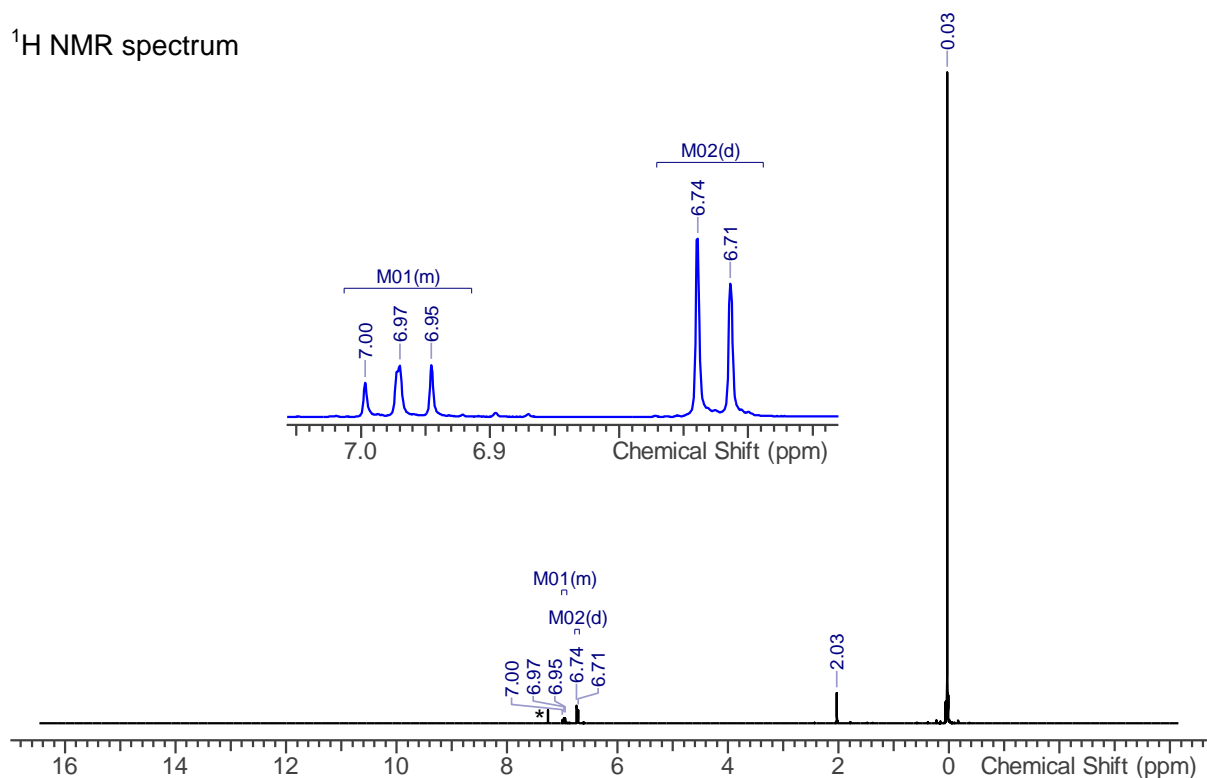
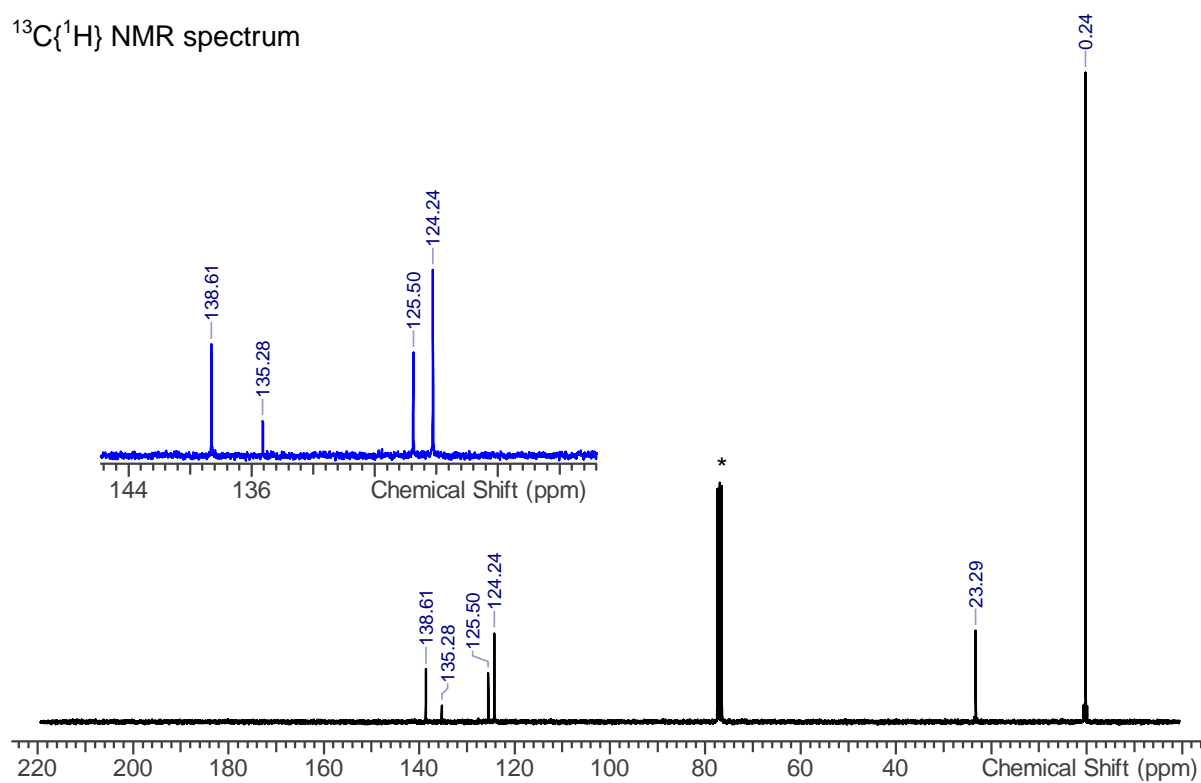


Figure S3 continued.

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



^{29}Si INEPT NMR spectrum

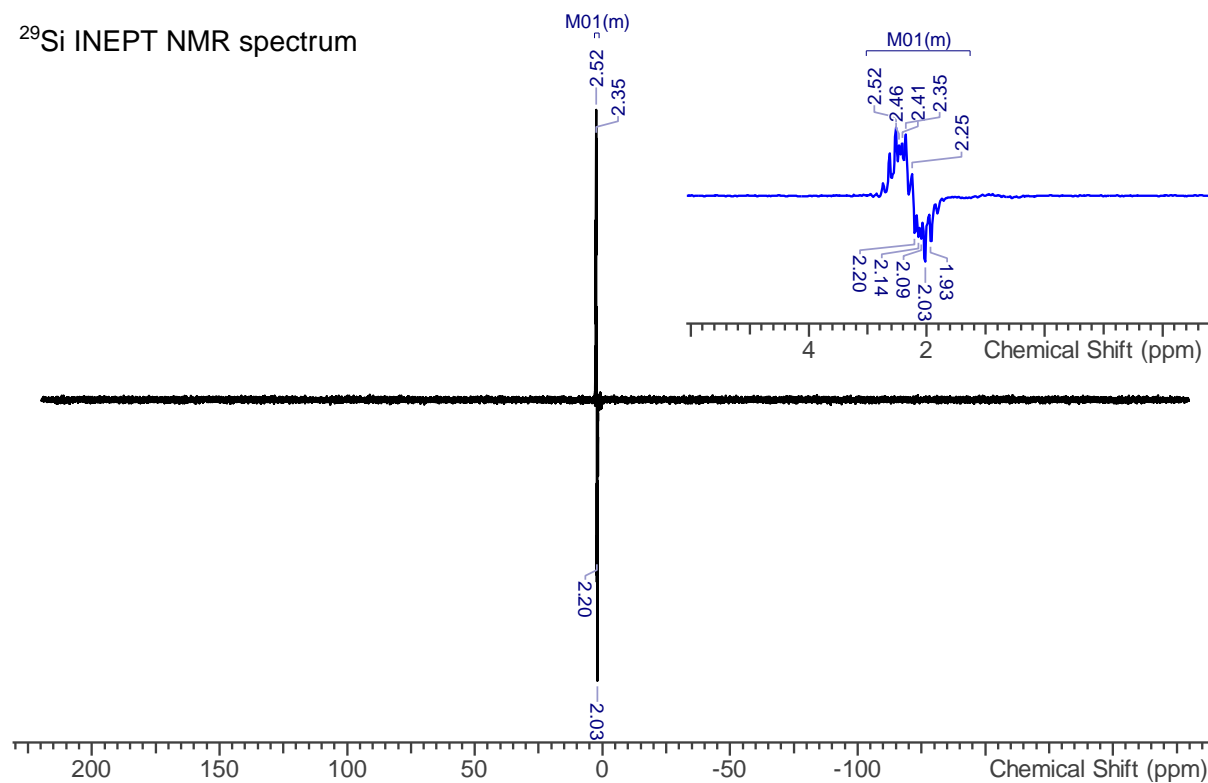
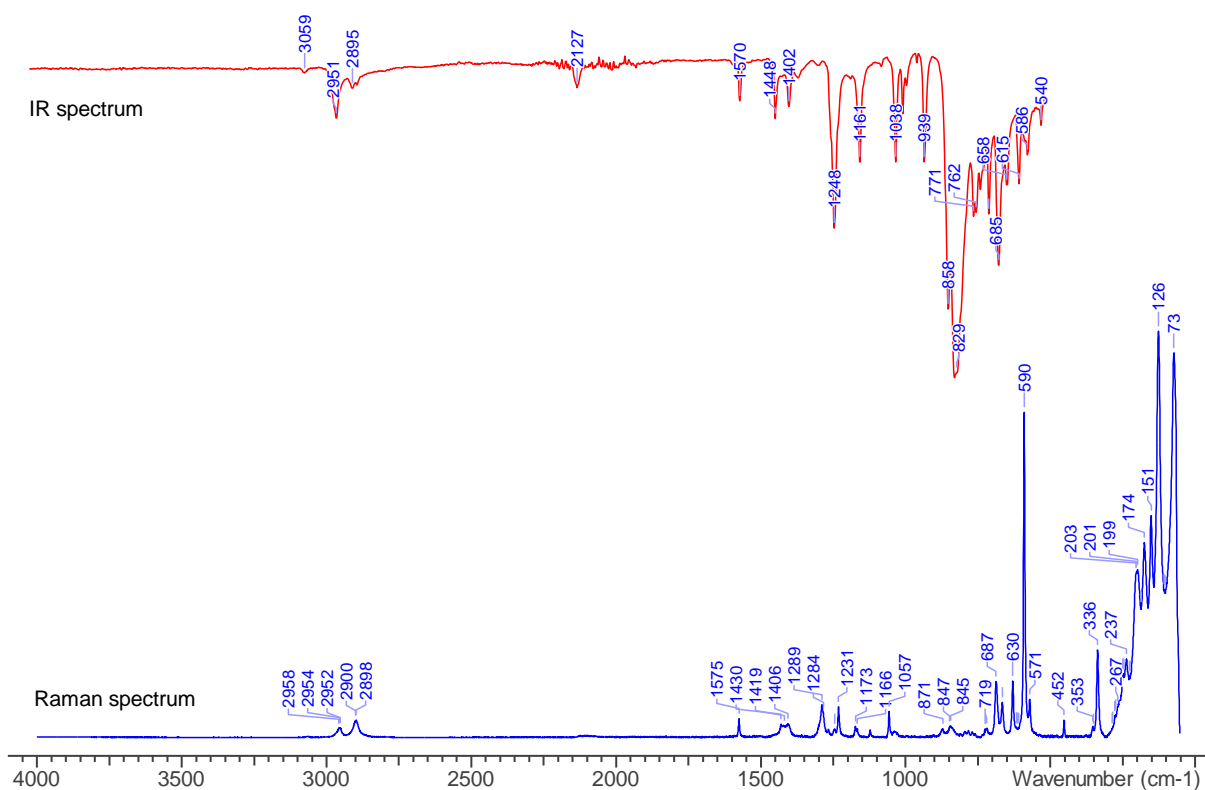
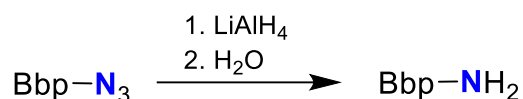


Figure S3 continued.



Synthesis of Bbp-NH₂ (6_Bbp)



Bbp-NH₂ is prepared according to modified literature procedures for *Tbt-NH₂* and *Ter-NH₂*.^{1,8}

A solution of Bbp-N₃ (3.3 g; 7.6 mmol) in Et₂O (50 mL) is slowly added to a stirred suspension of LiAlH₄ (1.53 g; 40 mmol) in Et₂O (50 mL) at -60 °C over a period of 15 minutes. The reaction vessel is warmed to ambient temperature and heated under reflux conditions for two hours. After cooling to -20 °C, aqueous NaOH (10 mL; 0.01 M) is slowly (!) added to the suspension to destroy excess hydrides. Caution: Vigorous H₂ gas evolution! The organic layer is separated and the aqueous layers are extracted with Et₂O. The organic layers are combined and dried over MgSO₄. After separating the inorganic solids by filtration, the solvents are evaporated, yielding colourless crystals. Yield: 2.5 g (6.1 mmol; 80 %).

M (C₂₀H₄₃Si₄N) = 409.91 g/mol

Mp. 89 °C. **EA:** calc. (found) in %: C 58.6 (58.52), H 10.57 (9.79), N 3.42 (3.28). **¹H NMR:** (CDCl₃, 298.2 K, 300.13 MHz): δ = 0.03 (broad s, 36H, Si(CH₃)₃); 1.35 (s, 2H, CH(Si(CH₃)₃)₂); 3.26 (broad s, 2H, NH₂); 6.63 (m, 3H, phenyl-H). **¹³C{¹H} NMR:** (CDCl₃, 300.0 K, 62.90 MHz): δ = 0.3 (s, Si(CH₃)₃); 21.9 (s, CH(SiMe₃)₂); 117.9 (s, phenyl-C); 124.2 (s, phenyl-C); 128.2 (s, phenyl-C); 139.5 (s, phenyl-C). **²⁹Si INEPT NMR:** (CDCl₃, 298.2 K, 59.63 MHz): δ = 2.31 (m, Si(CH₃)₃). **IR** (ATR, 32 Scans, cm⁻¹): $\tilde{\nu}$ = 2955 (vs), 2922 (m), 2868 (m), 1593 (m), 1475 (m), 1461 (m), 1407 (m), 1391 (m), 1360 (s), 1236 (m), 1212 (m), 1187 (m), 1127 (m), 1090 (w), 925 (w), 905 (w), 878 (m), 756 (m), 715 (m), 649 (m), 637 (m), 598 (m), 577 (m), 546 (m), 525 (m), 517 (m), 492 (m), 453 (m). **Raman:** (784 nm, 20 s, 20 scans, cm⁻¹): $\tilde{\nu}$ = 2895 (1), 1582 (1), 1577 (1), 1443 (1), 1405 (1), 1308 (1), 1258 (1), 1222 (2), 1167 (1), 1075 (1), 832 (1), 778 (2), 758 (1), 720 (2), 683 (2), 648 (1), 625 (1), 594 (10), 543 (1), 510 (1), 337 (2), 252 (2), 232 (2), 198 (2), 170 (4), 93 (7). **MS** (EI, 70 eV, m/z): 73 (TMS⁺); 233 ([C₁₃H₂₂Si₂]⁺); 394 ([Bbp]⁺).

Single crystals suitable for X-ray diffraction can be grown from saturated *n*-hexane solution at ambient temperature.

Figure S4: NMR, IR and Raman spectra of Bbp-NH₂ (solvent signals indicated by asterisks).

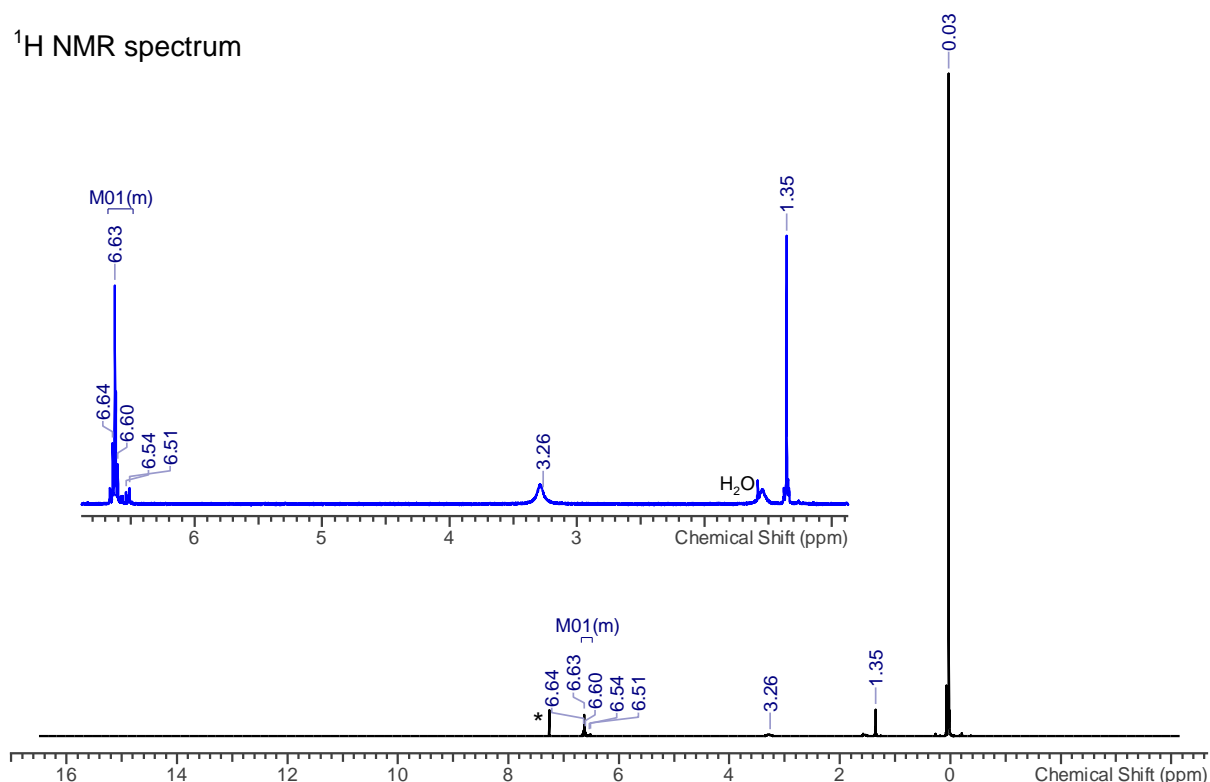


Figure S4 continued.

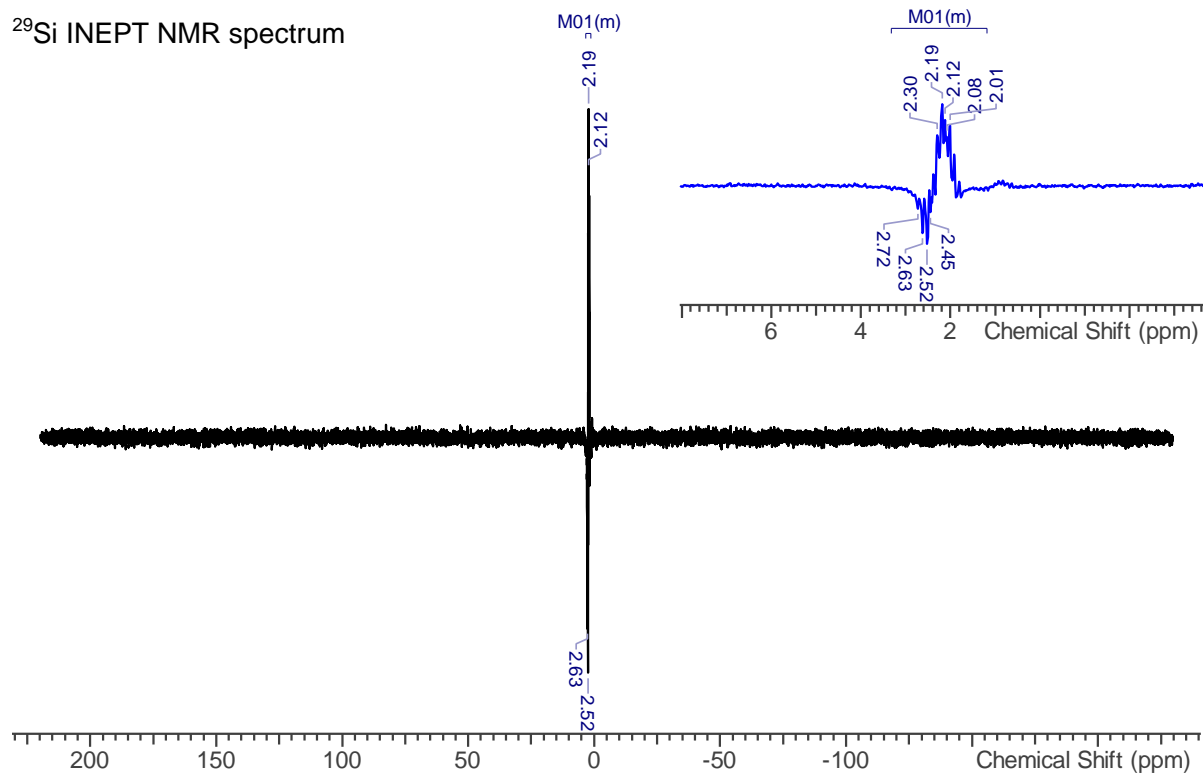
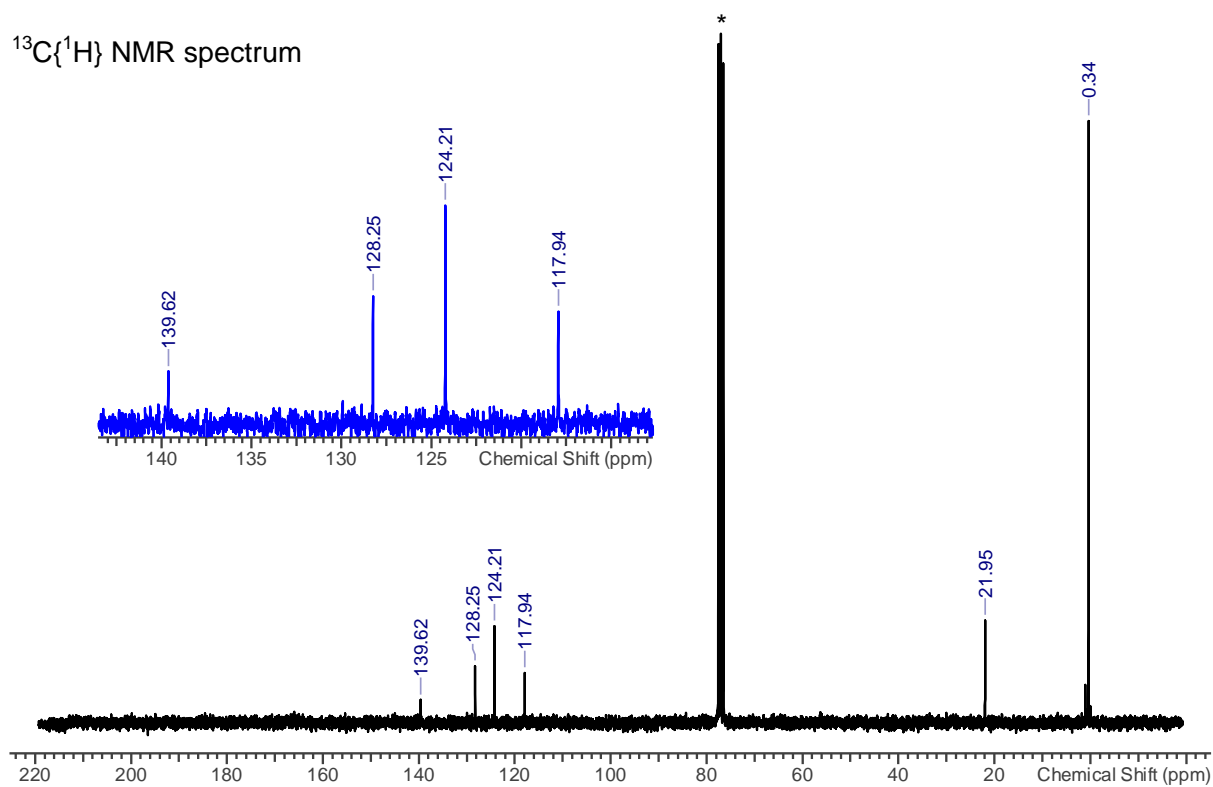
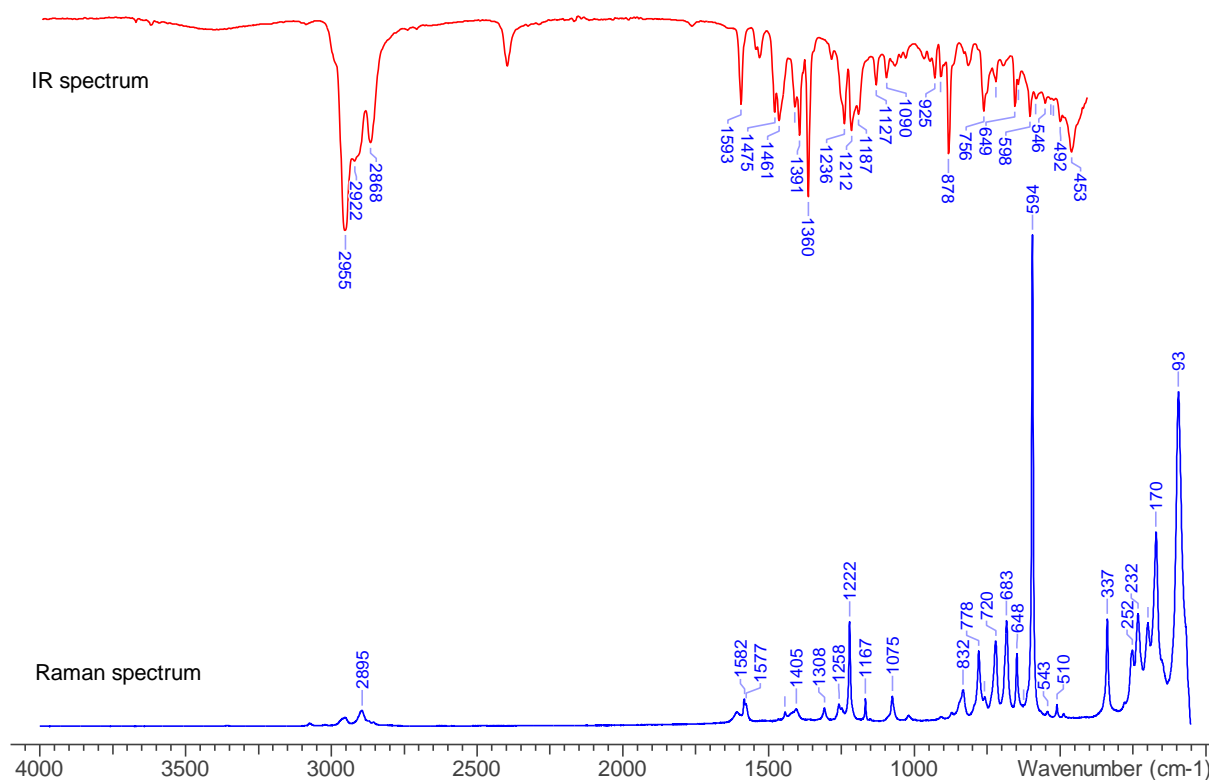
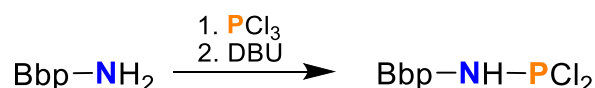


Figure S4 continued.



Synthesis of Bbp-NH-PCl₂ (7_Bbp)



PCl₃ (0.42 g; 3.0 mmol) is added slowly to a stirred solution of Bbp-NH₂ (0.81 g; 2.0 mmol) in Et₂O (20 mL) at -40 °C over a period of 5 minutes. Afterwards, DBU (0.3 g; 2.0 mmol) is added at the same temperature, resulting in formation of a colourless suspension. The reaction vessel is slowly warmed to ambient temperature and stirred for 20 hours. Afterwards, all volatile compounds are removed *in vacuo* and the product is extracted with *n*-hexane using a glass sinter frit. The product is dried *in vacuo*, resulting in a colourless solid. Yield: 0.78 g (1.52 mmol; 76 %).

M(C₂₀H₄₂Si₄PNCl₂) = 510.78 g/mol.

Mp. 106 °C. **EA:** calc. (found) in %: C 47.03 (48.34), H 8.29 (8.26), N 2.74 (2.46). **³¹P{¹H} NMR:** (CD₂Cl₂, 298.6 K, 121.51 MHz): δ = 155.3 (s, PCl₂). **¹H NMR:** (CD₂Cl₂, 298.2 K, 300.13 MHz): δ = 0.4 (broad s, 36H, Si(CH₃)₃); 2.21 (s, 2H, CH(Si(CH₃)₃)₂); 4.72 (broad s, 1H, NH); 6.80 (d, 2H, ³J(¹H,¹H) = 8 Hz, *m*-phenyl-H), 7.06 (td, 1H, ³J(¹H,¹H) = 8 Hz, *J* = 2 Hz, *p*-phenyl-H). **¹³C{¹H} NMR:** (CD₂Cl₂, 298.3 K, 75.48 MHz): δ = 0.6 (s, Si(CH₃)₃); 24.7 (d, *J* = 1 Hz, CH(SiMe₃)₂); 125.0 (d, *J* = 2 Hz, phenyl-C); 127.4 (d, *J*

= 3 Hz, phenyl-C); 133.9 (d, $J = 14$ Hz, phenyl-C); 143.6 (d, $J = 4$ Hz, phenyl-C). ^{29}Si INEPT-NMR: (C_6D_6 , 298.2 K, 59.63 MHz): $\delta = 2.5$ (m, SiMe_3). IR (ATR, 32 Scans, cm^{-1}): $\tilde{\nu} = 3360$ (w), 3061 (w), 2952 (w), 2896 (w), 2661 (w), 2344 (w), 1931 (w), 1599 (w), 1575 (w), 1496 (w), 1457 (w), 1433 (w), 1400 (w), 1317 (w), 1247 (m), 1218 (w), 1189 (w), 1165 (w), 1074 (w), 1045 (w), 1029 (w), 969 (w), 942 (m), 903 (w), 855 (s), 824 (vs), 771 (m), 763 (m), 744 (m), 719 (m), 684 (m), 655 (m), 614 (m), 569 (w), 521 (w), 507 (w), 472 (m), 435 (s). Raman: (633 nm, 20 s, 20 scans, cm^{-1}): $\tilde{\nu} = 2954$ (1), 2900 (1), 2897 (1), 2894 (1), 1361 (1), 1358 (1), 1349 (1), 1340 (2), 1337 (2), 1330 (2), 1309 (3), 1305 (3), 1278 (2), 1264 (1), 1259 (1), 1241 (3), 1233 (5), 1215 (1), 1208 (1), 1166 (1), 1149 (1), 1072 (1), 869 (1), 837 (1), 804 (10), 770 (2), 744 (6), 685 (2), 655 (1), 649 (1), 632 (1), 621 (1), 600 (8), 580 (1), 566 (2), 558 (1), 548 (1), 545 (1), 539 (1), 533 (1), 489 (1), 474 (2), 457 (1), 447 (1), 434 (1), 354 (2), 333 (6), 307 (5), 282 (1), 270 (2), 260 (1). MS (EI, 70 eV, m/z): 73 (TMS^+); 394 (Bbp^+); 409 ($[\text{BbpNH}]^+$); 510 ($[\text{M}]^+$). Single crystals suitable for X-ray diffraction can be grown from saturated *n*-hexane solution at -40 °C.

Figure S5: NMR, IR and Raman spectra of Bbp–NHPCl₂ (solvent signals indicated by asterisks).

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum

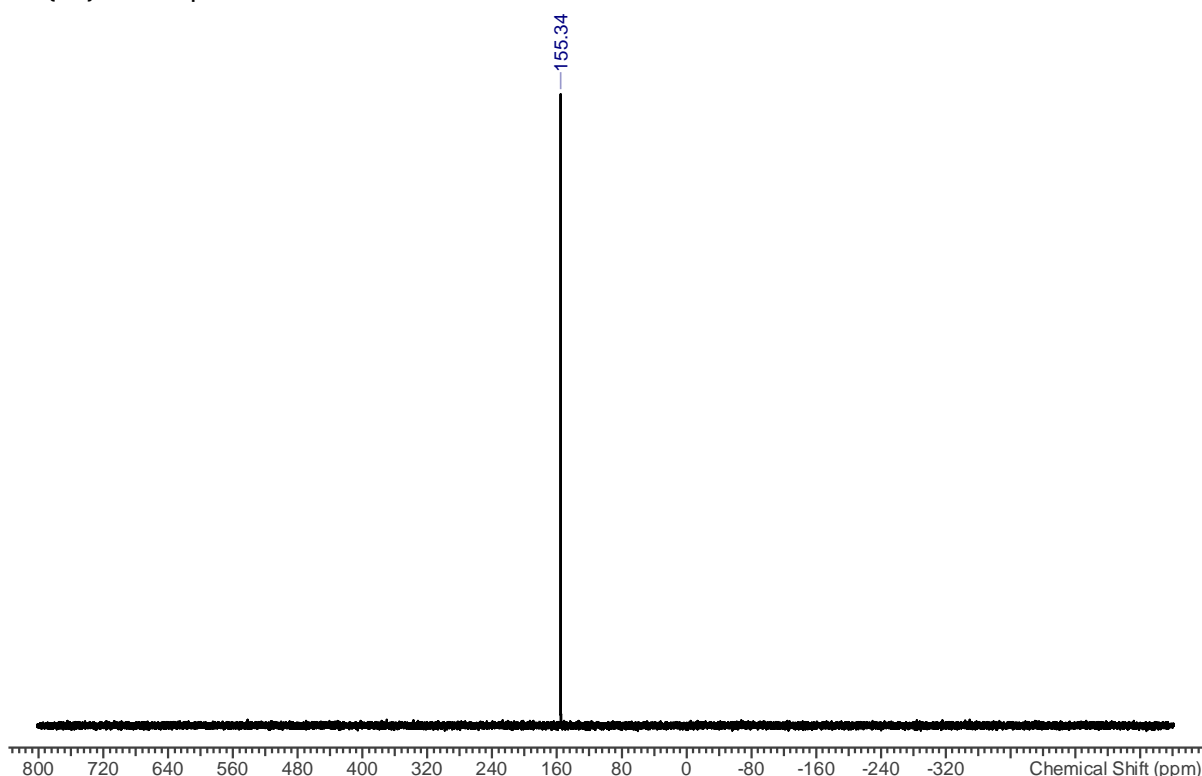
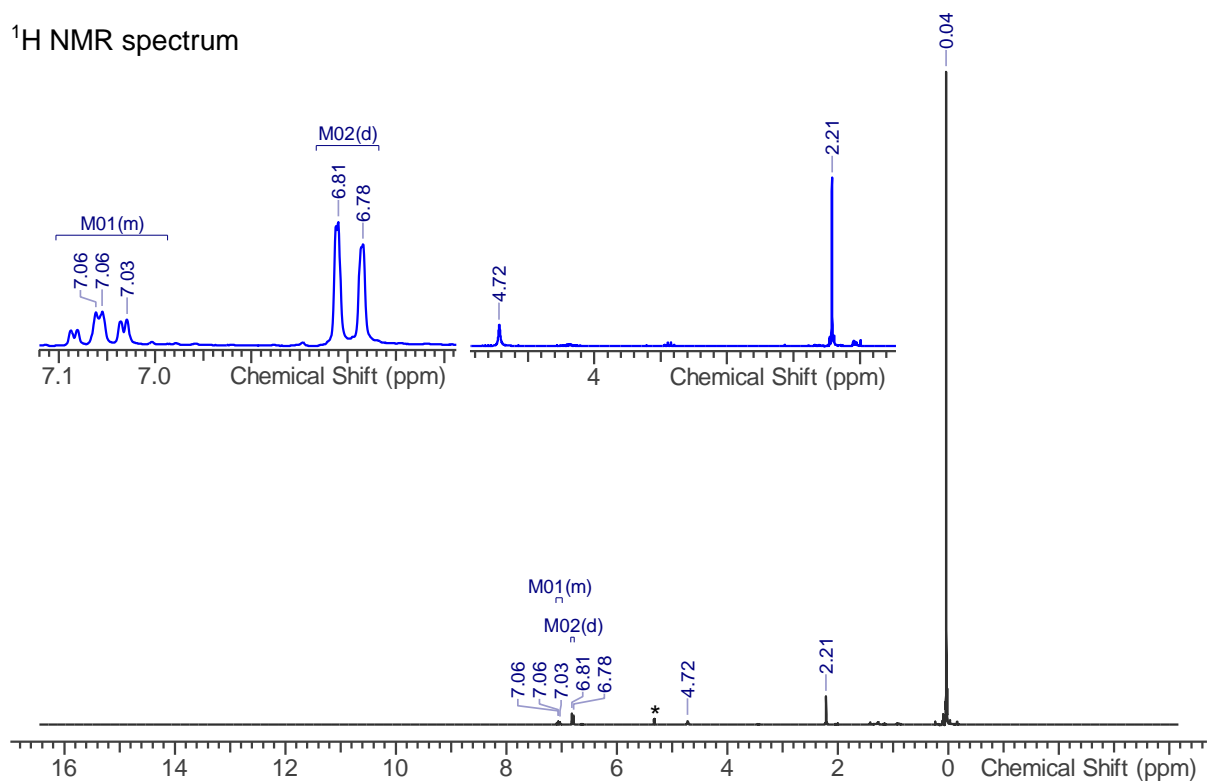


Figure S5 continued.

^1H NMR spectrum



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum

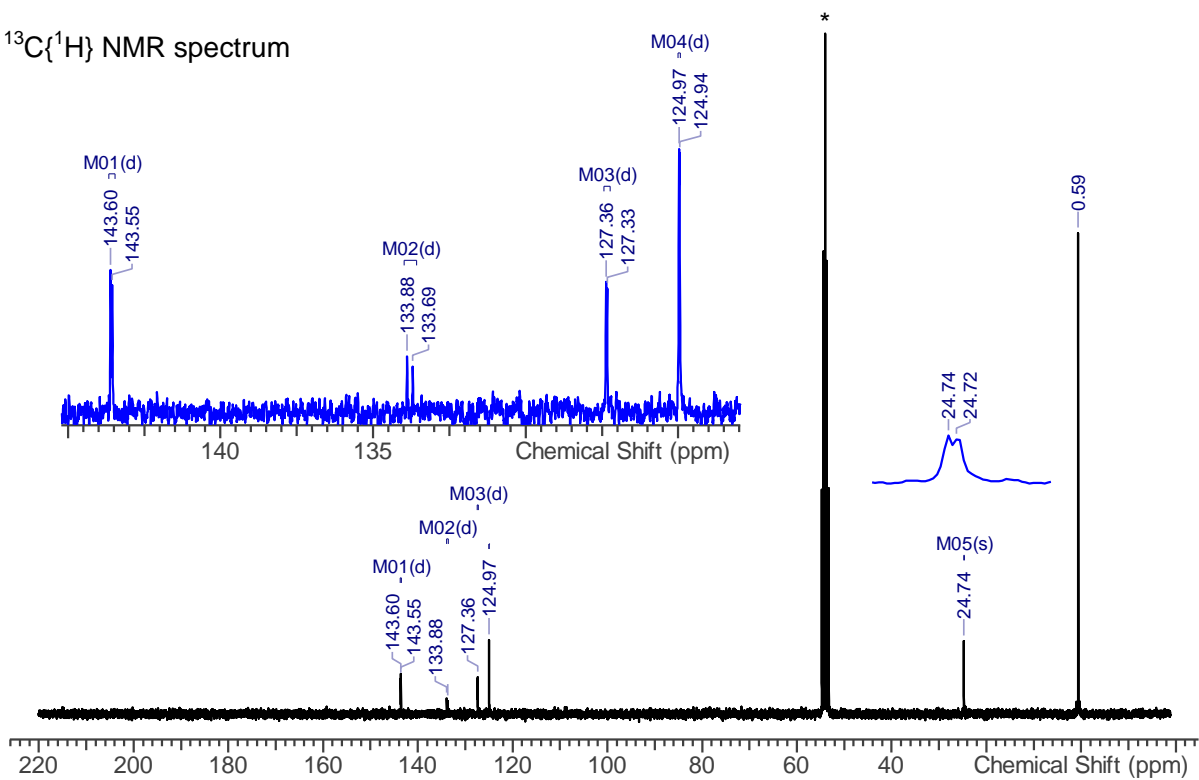
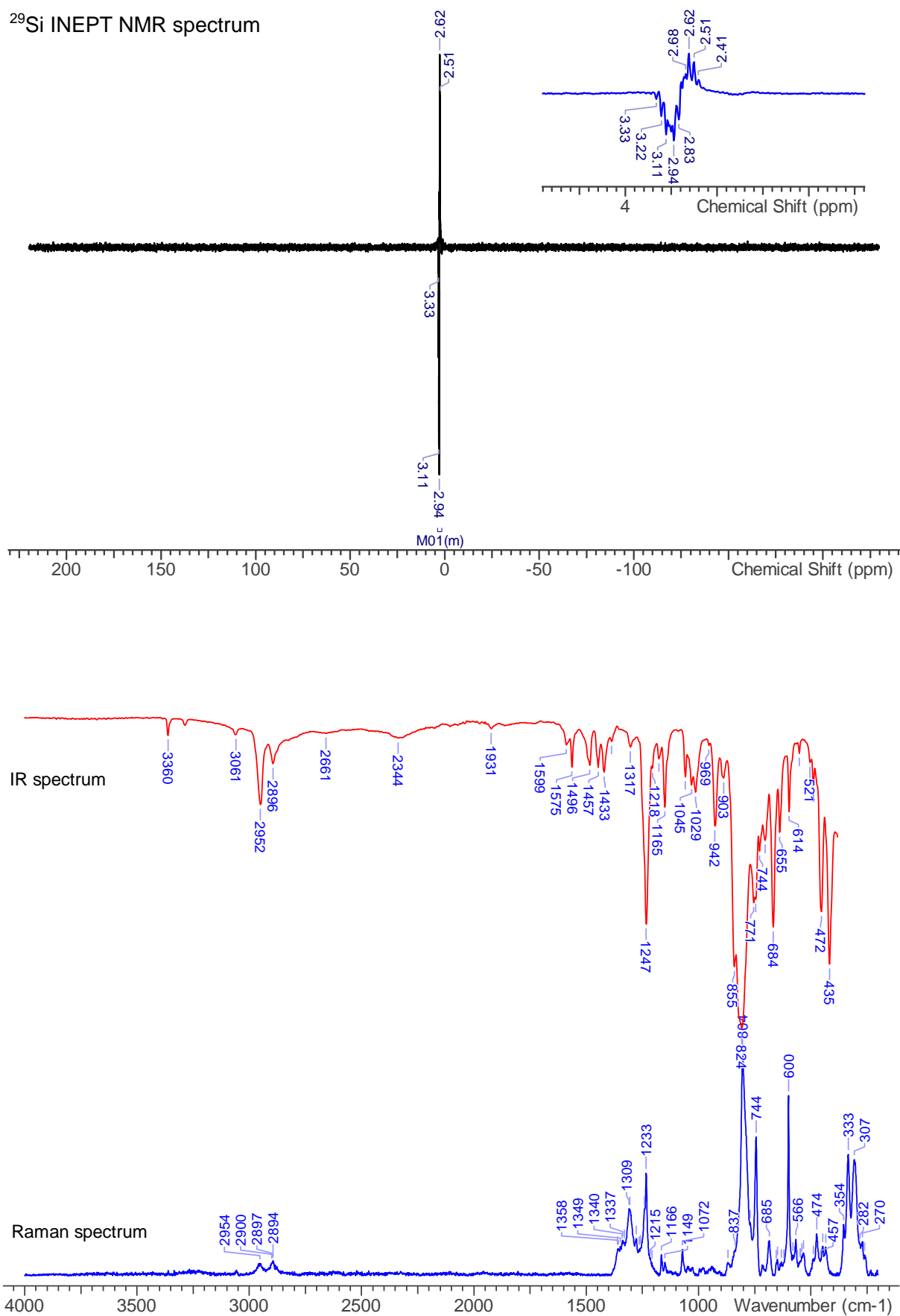
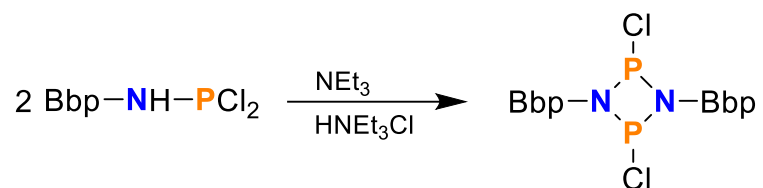


Figure S5 continued.



Synthesis of $[\text{ClP}(\mu\text{-NBbp})_2(\text{2P_Bbp})]$



Et_3N (2.5 mmol, 0.253 g) is added to a solution of Bbp-NH-PCl_2 (1.2 mmol; 0.613 g) in Et_2O (10 mL) at -70°C . The reaction vessel is slowly warmed to ambient temperature, and the mixture is stirred for a week. The solvent is removed *in vacuo* and the remaining orange precipitate is extracted with *n*-hexane by filtration. The desired product can be isolated as colourless crystals by crystallization from concentrated *n*-hexane solution. The product is a mixture of *cis*- and *trans*-isomers, which could not be separated on a larger scale *via* crystallization. Additionally, there are some impurities which could not be removed from the product. Yield: 0.24 g (0.3 mmol; 25 %)

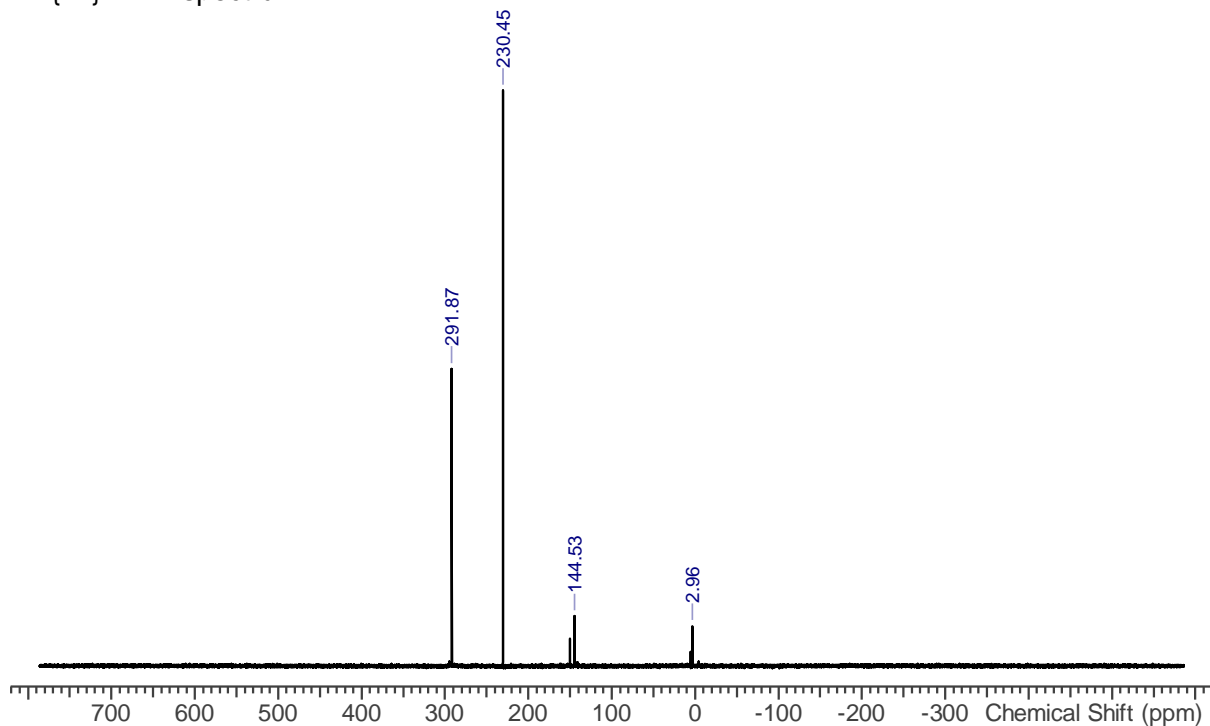
$M(\text{C}_{40}\text{H}_{82}\text{Si}_8\text{P}_2\text{N}_2\text{Cl}_2) = 948.64 \text{ g/mol}$.

Mp. approx. 245°C (decomposition). **EA:** calc. (found) in %: C 50.65 (52.39), H 8.71 (8.71), N 2.95 (2.47). **$^{31}\text{P}\{^1\text{H}\}$ NMR:** (C_6D_6 , 298.1 K, 202.48 MHz): $\delta = 231$ (s, *cis*-PCl), 292 (s, *trans*-PCl). **^1H NMR:** (C_6D_6 , 298.2 K, 500.13 MHz): $\delta = 0.2\text{-}0.35$ (broad s, 36H, $\text{Si}(\text{CH}_3)_3$); 2.84 (s, 1H, *cis*- $\text{CH}(\text{Si}(\text{CH}_3)_3)_2$); 3.07 (s, 1H, *trans*- $\text{CH}(\text{Si}(\text{CH}_3)_3)_2$); 6.94 (m, 3H, phenyl-H). **$^{13}\text{C}\{^1\text{H}\}$ NMR:** (C_6D_6 , 298.1 K, 125.77 MHz): $\delta = 2.0$ (m, $\text{Si}(\text{CH}_3)_3$); 25.2 (s, $\text{CH}(\text{SiMe}_3)_2$); 126.4 (s, phenyl-C); 126.9 (s, phenyl-C); 131.0 (s, phenyl-C); 143.7 (s, phenyl-C). **^{29}Si INEPT NMR:** (C_6D_6 , 298.2 K, 99.36 MHz): $\delta = 2.1$ (m, *trans* 2P_Bbp SiMe_3), 2.8 (m, *trans* 2P_Bbp SiMe_3), 4.4 (m, *cis* 2P_Bbp SiMe_3). **IR** (ATR, 32 Scans, cm^{-1}): $\tilde{\nu} = 3060$ (w), 2953 (w), 2897 (w), 1591 (w), 1574 (w), 1455 (w), 1424 (w), 1245 (m), 1191 (w), 1148 (w), 1084 (w), 1028 (m), 1018 (w), 968 (w), 940 (m), 919 (w), 890 (w), 826 (vs), 771 (m), 760 (m), 717 (m), 682 (m), 655 (m), 614 (m), 581 (w), 540 (w), 525 (w), 507 (m), 453 (m), 408 (m). **Raman:** (784 nm, 30 s, 20 scans, cm^{-1}): $\tilde{\nu} = 3172$ (3), 2906 (3), 2904 (3), 2900 (3), 2896 (3), 1582 (1), 1428 (1), 1312 (1), 1249 (2), 1233 (2), 1172 (1), 1096 (1), 999 (1), 972 (1), 807 (5), 793 (4), 748 (3), 689 (2), 605 (3), 595 (10), 458 (1), 433 (1), 337 (3), 312 (3), 308 (3), 306 (3), 194 (3), 188 (3), 184 (3), 92 (4), 84 (4), 73 (6), 71 (6). **MS** (EI, 70 eV, m/z): 73 (TMS^+); 234 ($[\text{Bbp} - (\text{CH}(\text{TMS})_2]^+$); 394 (Bbp^+); 948 ($[\text{M}]^+$).

Single crystals suitable for X-ray diffraction can be grown from saturated *n*-hexane solution at -40°C .

Figure S6: NMR, IR and Raman spectra of $[\text{ClP}(\mu\text{-NBbp})]_2$ (solvent signals indicated by asterisks). The NMR spectra show traces of impurities, which could not be removed from the product. The side product with a chemical shift of 144.5 ppm could be identified as Bbp-NH-PCl-NH-Bbp. Traces of this side product can be seen in all NMR spectra.

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum



^1H NMR spectrum

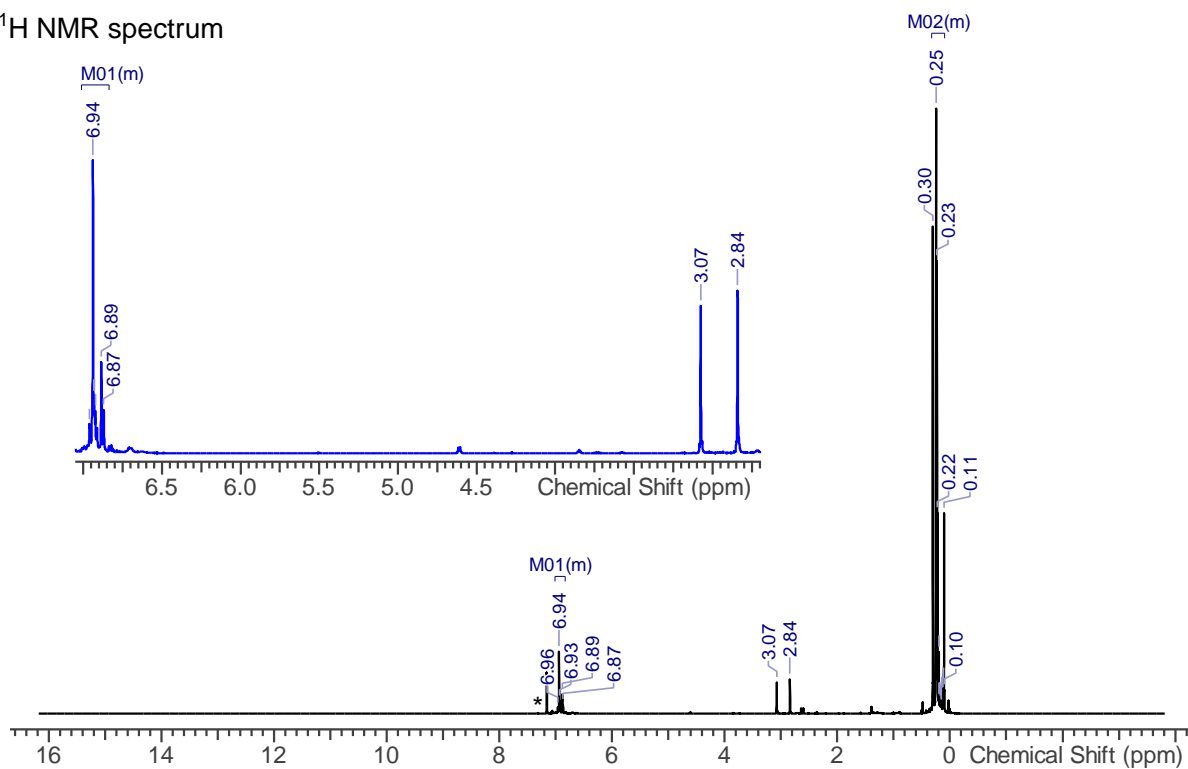


Figure S6 continued.

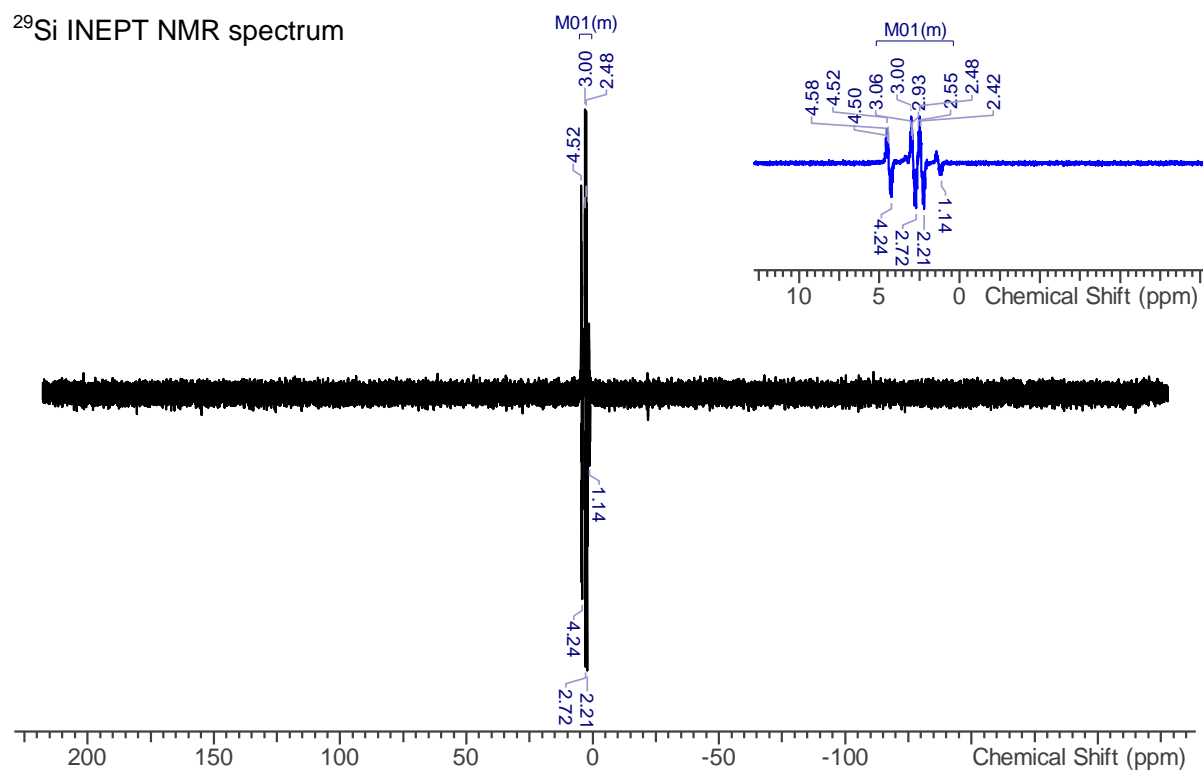
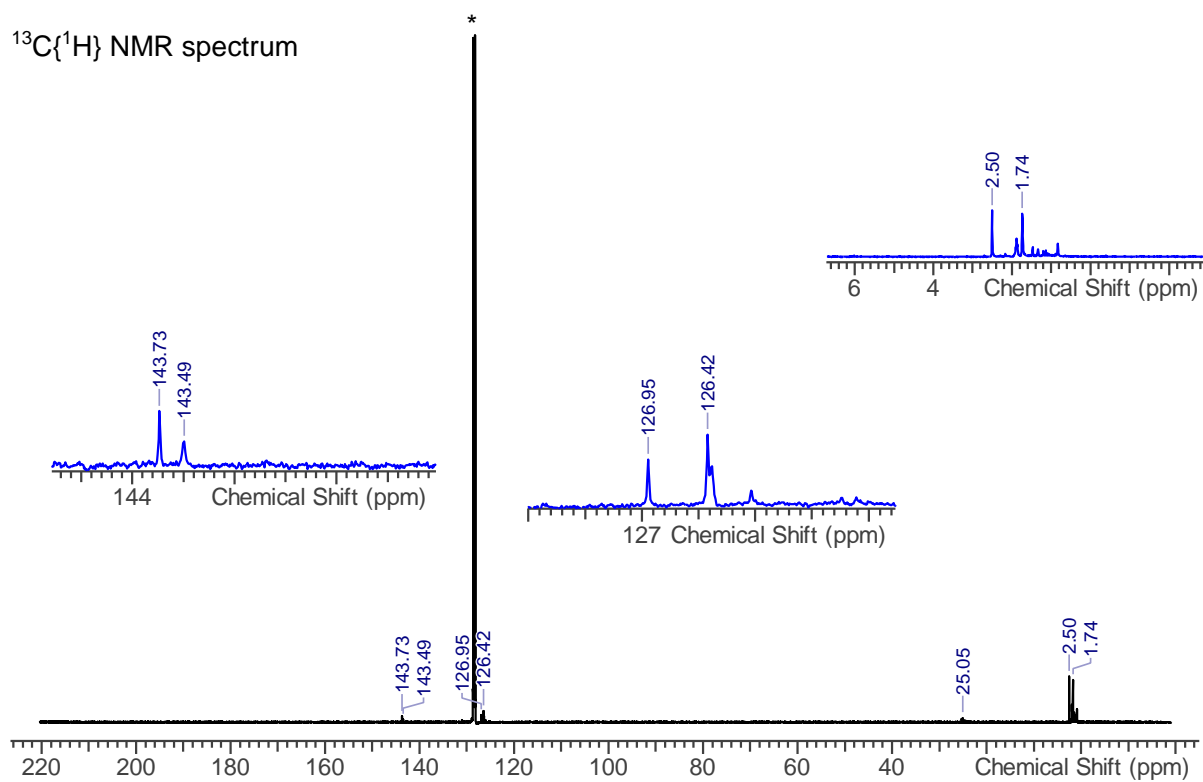
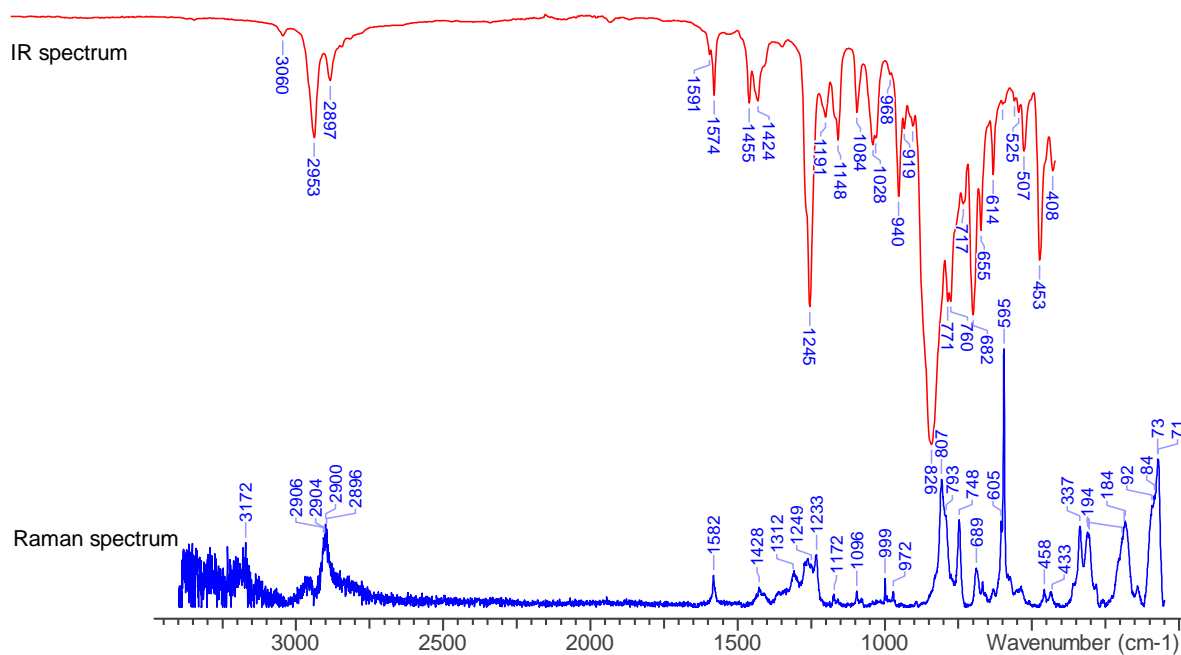
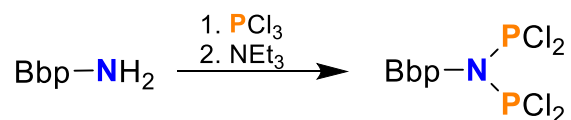


Figure S6 continued.



Synthesis of Bbp-N(PCl₂)₂ (3P_Bbp)



PCl₃ (1.38 g; 10 mmol) is added to a stirred solution of Bbp-NH₂ (1.64 g; 4 mmol) in Et₂O (40 mL) at -60 °C. Subsequently, Et₃N (1.62 g; 16 mmol) is added at constant temperature to the reaction mixture, before the reaction vessel is warmed to ambient temperature. During warming a voluminous yellowish precipitate is formed. All volatile components are removed *in vacuo*, the remaining white precipitate is extracted with *n*-hexane and the resulting suspension is filtered. The solvent of the filtrate is evaporated, yielding the product as colorless solid. Yield: 1.9 g (3.2 mmol; 80 %).

M(C₂₀H₄₁Si₄NP₂Cl₄) = 611.65 g/mol.

Mp. 135 °C (decomposition). **EA:** calc. (found) in %: C 39.27 (39.497), H 6.67 (6.447), N 2.29 (2.209).

³¹P{¹H} NMR: (C₆D₆, 298.0 K, 202.48 MHz): δ = 178.8 (s, PCl₂). **¹H NMR:** (C₆D₆, 298.0 K, 500.13 MHz): δ = 0.15 (broad s, 36H, Si(CH₃)₃); 2.43 (s, 2H, CH(Si(CH₃)₃)₂); 6.82 (m, 3H, phenyl-H). **¹³C{¹H} NMR:** (C₆D₆, 298.0 K, 125.77 MHz): δ = 2.0 (d, *J* = 6 Hz, Si(CH₃)₃); 24.8 (s, CH(SiMe₃)₂); 125.6 (t, *J* = 3 Hz, phenyl-C);

129.5 (t, $J = 4$ Hz, phenyl-C); 136.2 (t, $J = 24$ Hz, phenyl-C); 147.8 (t, $J = 6$ Hz, phenyl-C). ^{29}Si INEPT NMR: (C_6D_6 , 298.2 K, 59.63 MHz): $\delta = 3.83$ (m, SiMe_3). IR (ATR, 32 Scans, cm^{-1}): $\tilde{\nu} = 3065$ (w), 2952 (w), 2896 (w), 2467 (w), 2360 (w), 1618 (w), 1573 (w), 1519 (w), 1455 (w), 1418 (w), 1397 (w), 1249 (m), 1206 (w), 1181 (w), 1156 (m), 1074 (w), 1059 (w), 1024 (m), 983 (w), 963 (w), 936 (m), 909 (m), 833 (vs), 785 (m), 771 (m), 761 (m), 734 (w), 709 (w), 682 (m), 655 (m), 614 (m), 587 (w), 528 (m), 501 (m), 480 (s), 462 (s), 453 (s). Raman: (633 nm, 20 s, 20 scans, cm^{-1}) $\tilde{\nu} = 3071$ (1), 2954 (2), 2899 (8), 2790 (1), 1579 (1), 1573 (1), 1418 (1), 1280 (1), 1249 (1), 1234 (2), 1182 (1), 1076 (1), 1025 (1), 917 (1), 858 (1), 841 (1), 787 (1), 773 (1), 689 (2), 661 (1), 617 (3), 589 (9), 574 (1), 530 (1), 501 (10), 485 (2), 457 (1), 379 (1), 337 (1), 287 (1), 266 (1), 248 (1), 216 (2). MS (EI, 70 eV, m/z): 73 (TMS^+); 86 ($[\text{CH}(\text{TMS})]^+$); 510 ($[\text{BbpNPCl}_2]^+$).

Single crystals suitable for X-ray diffraction can be grown from saturated *n*-hexane solution at ambient temperature.

Figure S7: NMR, IR and Raman spectra of $\text{Bbp-N}(\text{PCl}_2)_2$ (solvent signals indicated by asterisks).

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum

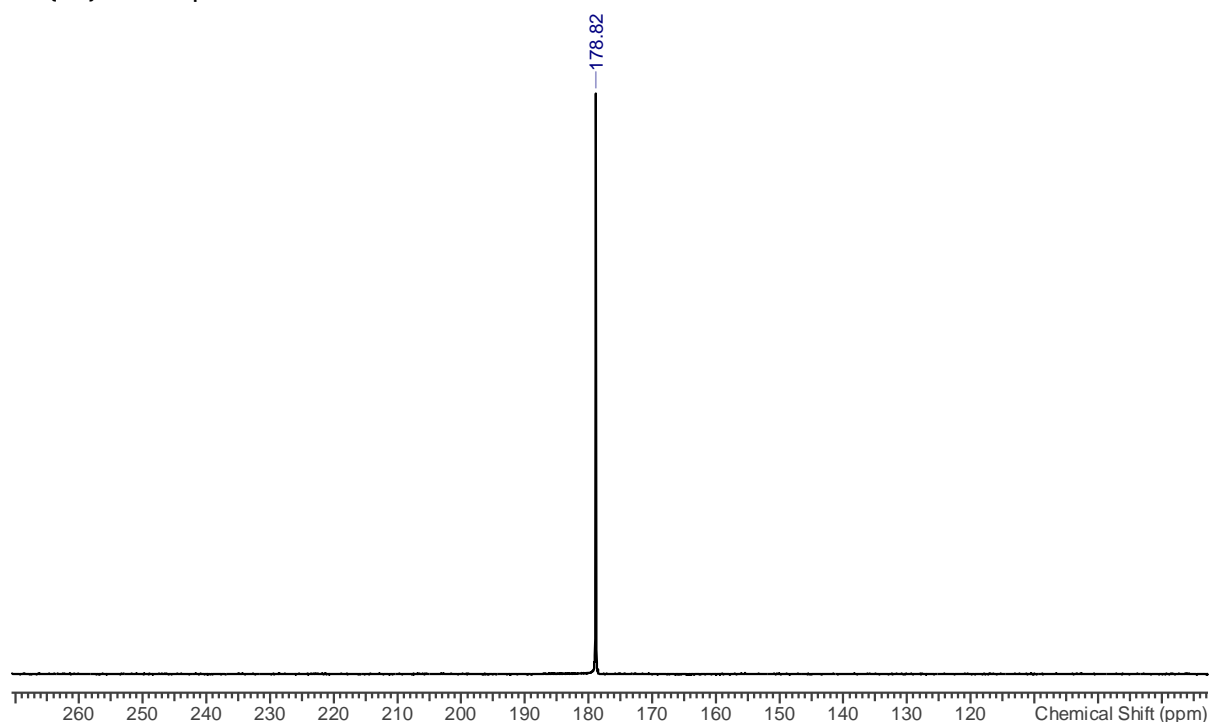
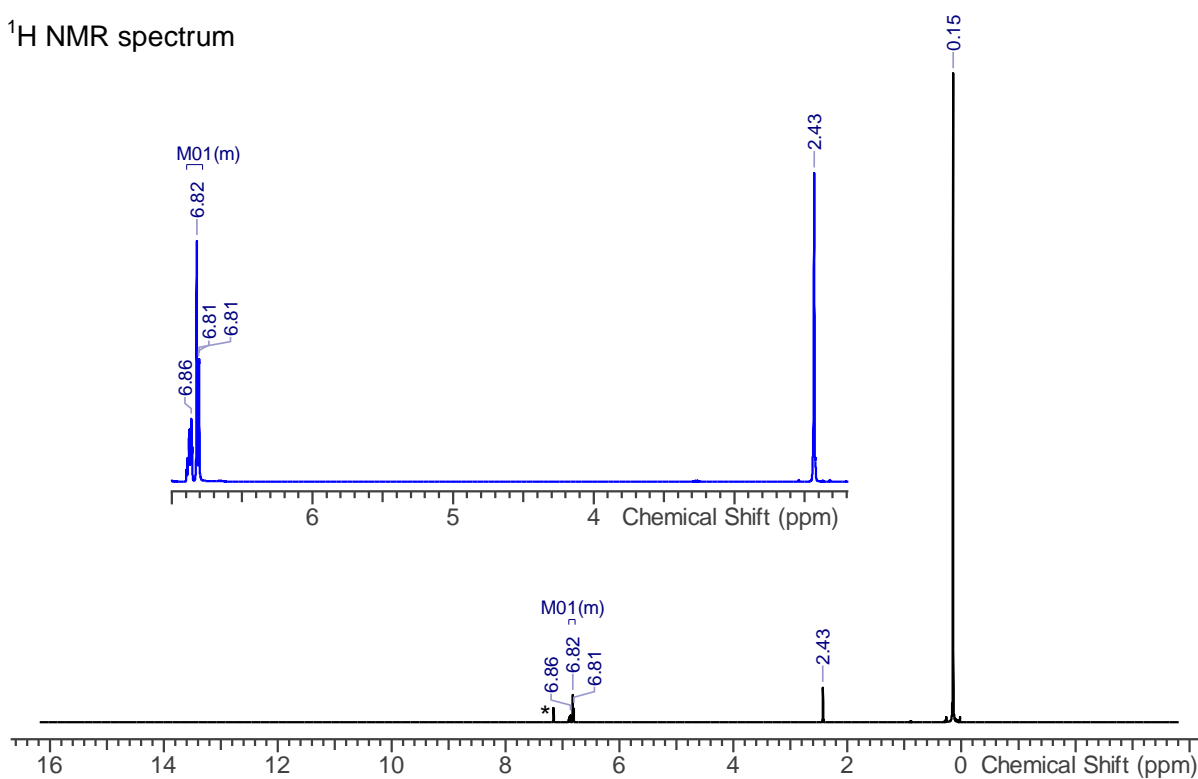


Figure S7 continued.

^1H NMR spectrum



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum

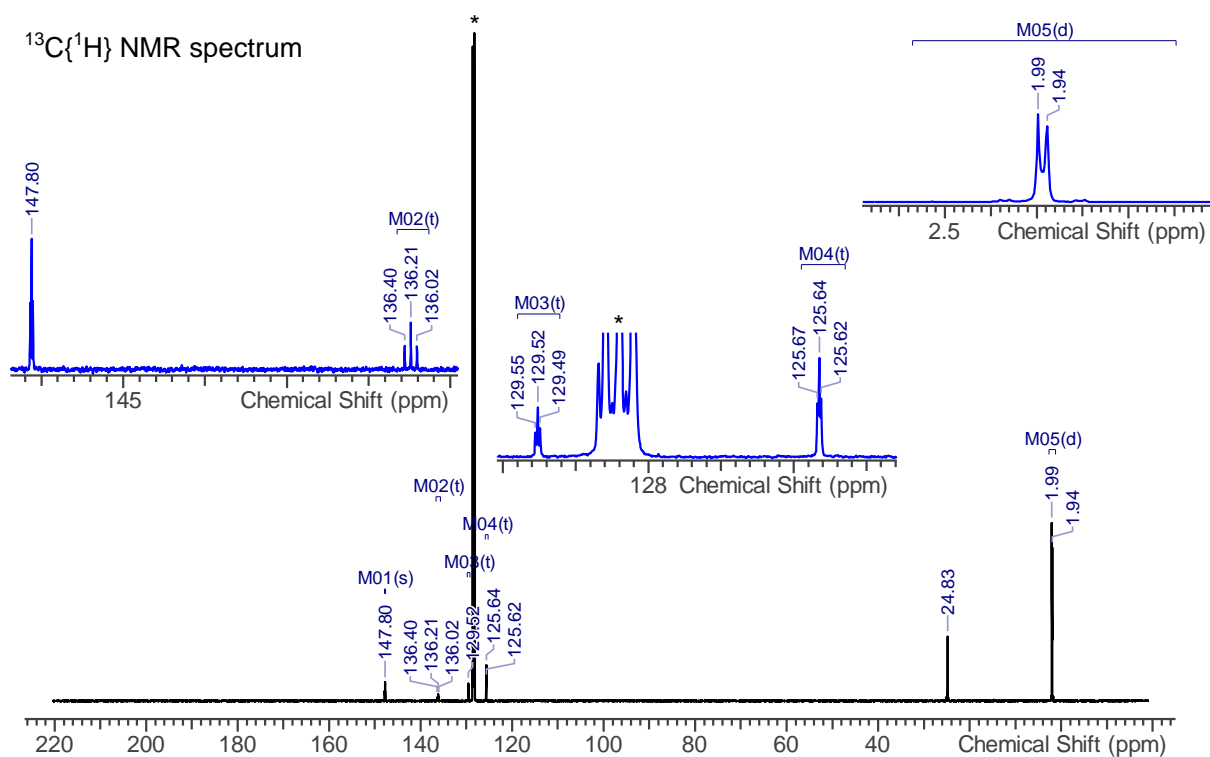
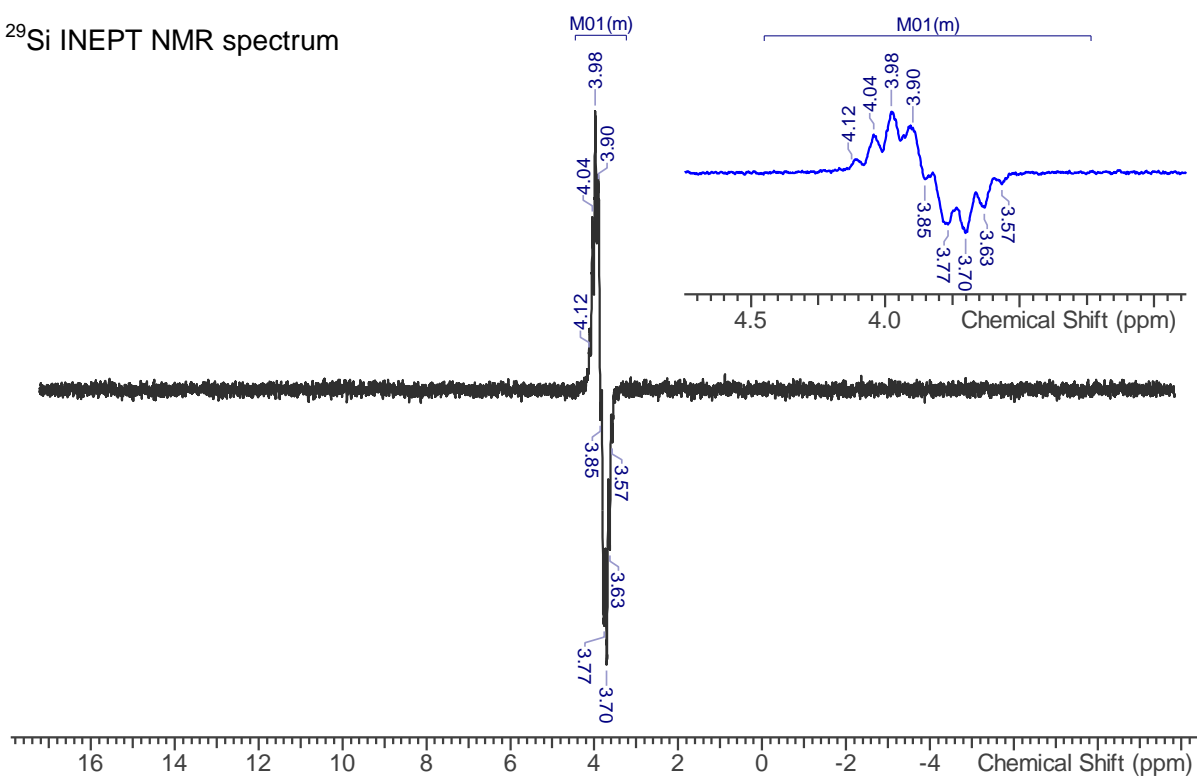
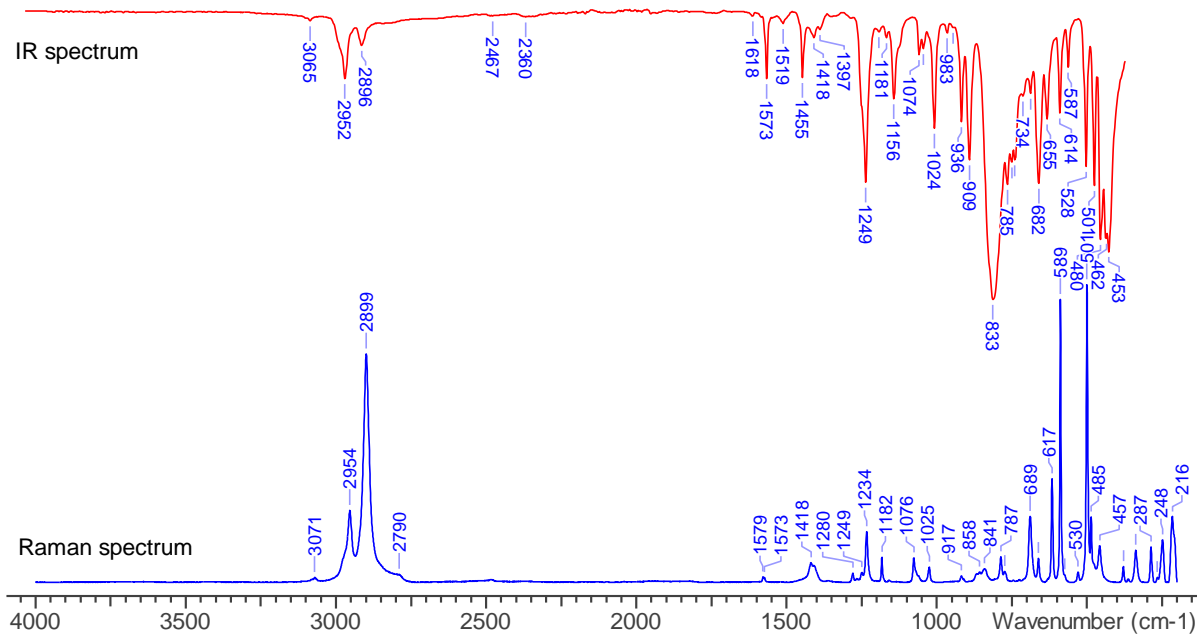


Figure S7 continued.

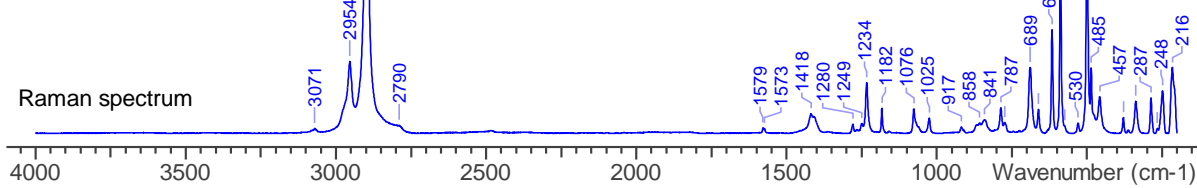
^{29}Si INEPT NMR spectrum



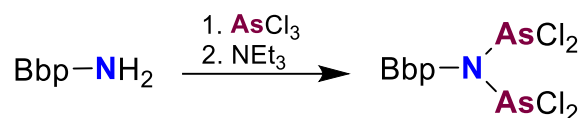
IR spectrum



Raman spectrum



Synthesis of Bbp-N(AsCl₂)₂ (3As_Bbp)



AsCl₃ (1.81 g; 10 mmol) is added to a stirred solution of Bbp-NH₂ (1.64 g; 4 mmol) in Et₂O (40 mL) at -60 °C. Subsequently, Et₃N (1.62 g; 16 mmol) is added at the same temperature to the reaction mixture, before the reaction vessel is warmed to ambient temperature. During warming a voluminous yellow precipitate is formed. All volatile components are removed *in vacuo* and the product is extracted from the white residue by filtration with a glass sinter frit and *n*-hexane. The product is dried *in vacuo*, resulting in bright yellow solid. Yield: 2.4 g (3.4 mmol; 86 %).

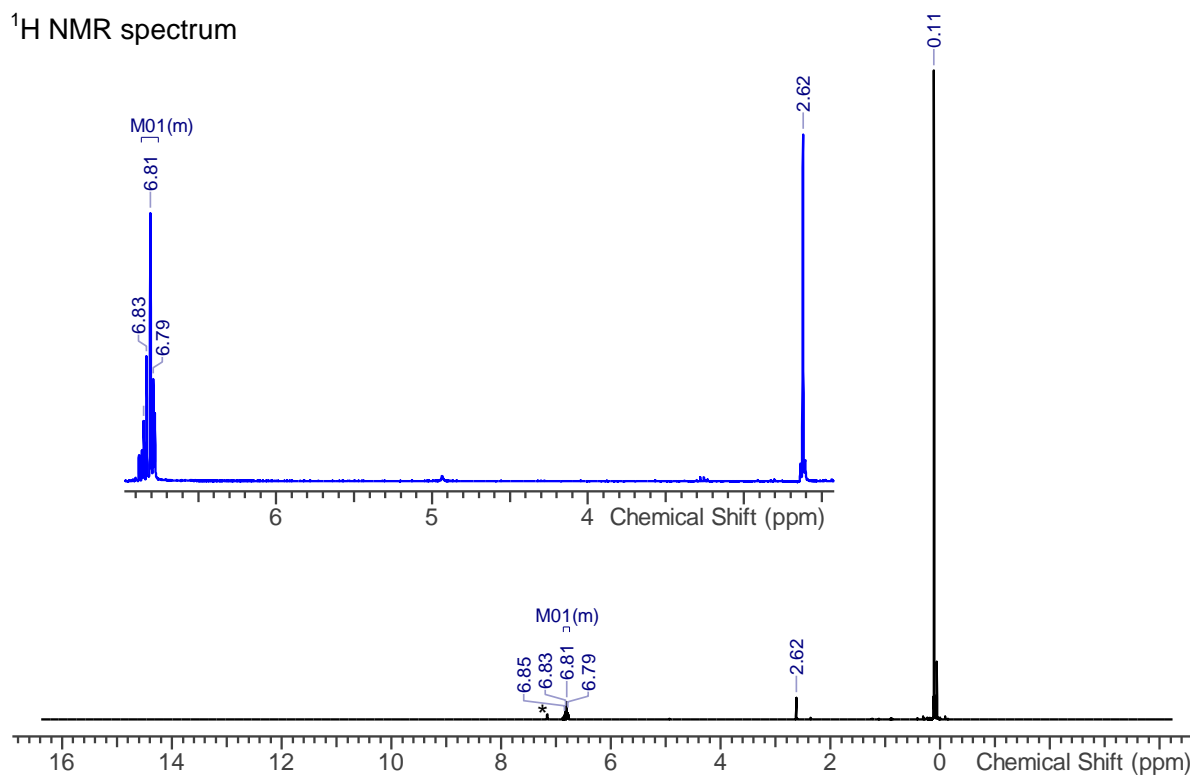
M(C₂₀H₄₁Si₄NA₂Cl₄) = 699.55 g/mol.

Mp.: 235 °C. **EA:** calc. (found) in %: C 34.34 (34.76), H 5.91 (5.79), N 2.00 (1.83). **¹H NMR:** (C₆D₆, 298.2 K, 300.13 MHz): δ = 0.11 (broad s, 36H, Si(CH₃)₃); 2.62 (s, 2H, CH(Si(CH₃)₃)₂); 6.81 (m, 3H, phenyl-H). **¹³C{¹H} NMR:** (C₆D₆, 298.9 K, 75.48 MHz): δ = 2.0 (s, Si(CH₃)₃); 24.7 (s, CH(SiMe₃)₂); 125.7 (s, phenyl-C); 129.0 (s, phenyl-C); 135.8 (s, phenyl-C); 148.7 (s, phenyl-C). **²⁹Si INEPT NMR:** (C₆D₆, 298.2 K, 59.63 MHz): δ = 3.14 (m, SiMe₃). **IR** (ATR, 32 Scans, cm⁻¹): $\tilde{\nu}$ = 3201 (w), 3057 (w), 2954 (w), 2898 (w), 2346 (w), 1738 (w), 1604 (w), 1566 (w), 1548 (w), 1496 (w), 1463 (w), 1453 (w), 1416 (w), 1397 (w), 1367 (w), 1245 (m), 1218 (w), 1181 (w), 1158 (w), 1142 (w), 1072 (w), 1029 (m), 975 (w), 938 (w), 897 (w), 829 (vs), 785 (m), 771 (m), 761 (m), 736 (m), 717 (m), 684 (m), 655 (m), 614 (m), 581 (w), 567 (w), 517 (w), 507 (w), 468 (w), 425 (w). **Raman:** (633 nm, 20 s, 20 scans, cm⁻¹): $\tilde{\nu}$ = 3059 (1), 2958 (1), 2899 (2), 1574 (2), 1413 (1), 1274 (1), 1250 (1), 1242 (1), 1229 (3), 1177 (4), 1140 (1), 1071 (2), 857 (1), 845 (1), 783 (1), 690 (1), 655 (1), 605 (5), 566 (2), 391 (10), 371 (2), 339 (1), 295 (1), 260 (2). **MS** (EI, 70 eV, m/z): 73 (TMS⁺); 306 ([N(AsCl₂)₂]⁺); 481 ([BbpNAs]⁺).

Single crystals suitable for X-ray diffraction can be grown from saturated *n*-hexane solution at ambient temperature.

Figure S8: NMR, IR and Raman spectra of Bbp-N(AsCl₂)₂ (solvent signals indicated by asterisks).

¹H NMR spectrum



¹³C{¹H} NMR spectrum

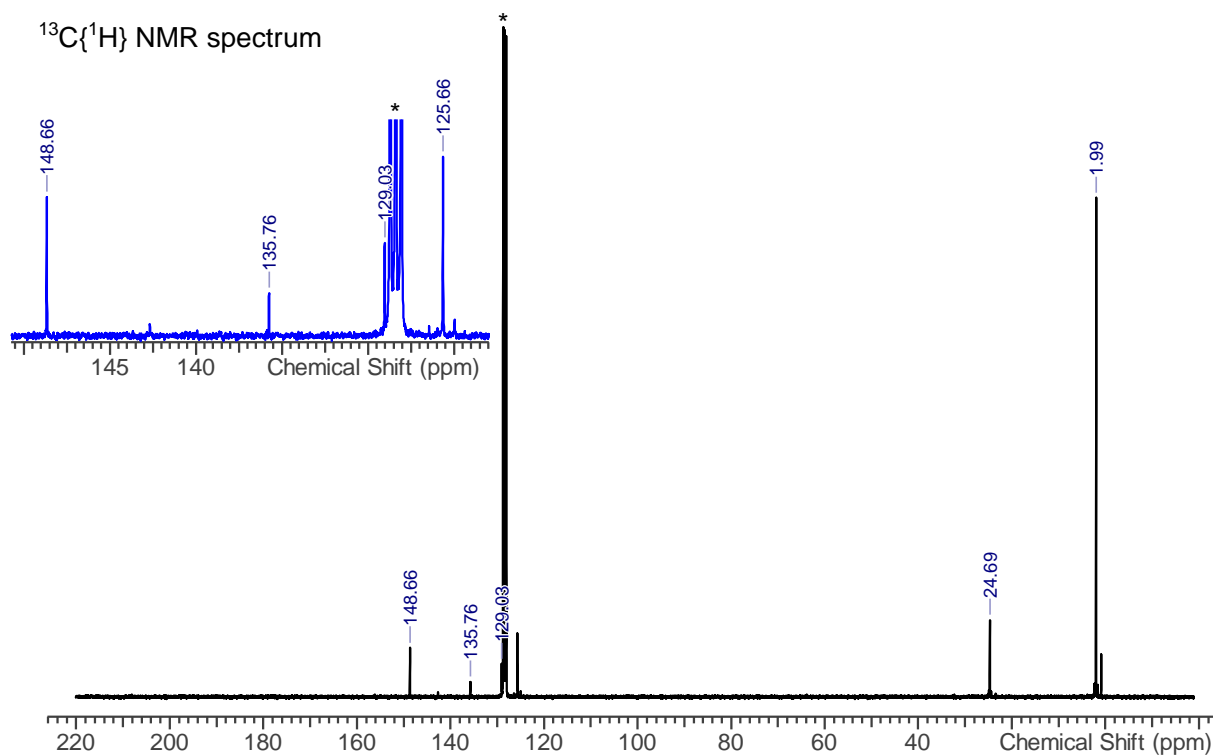
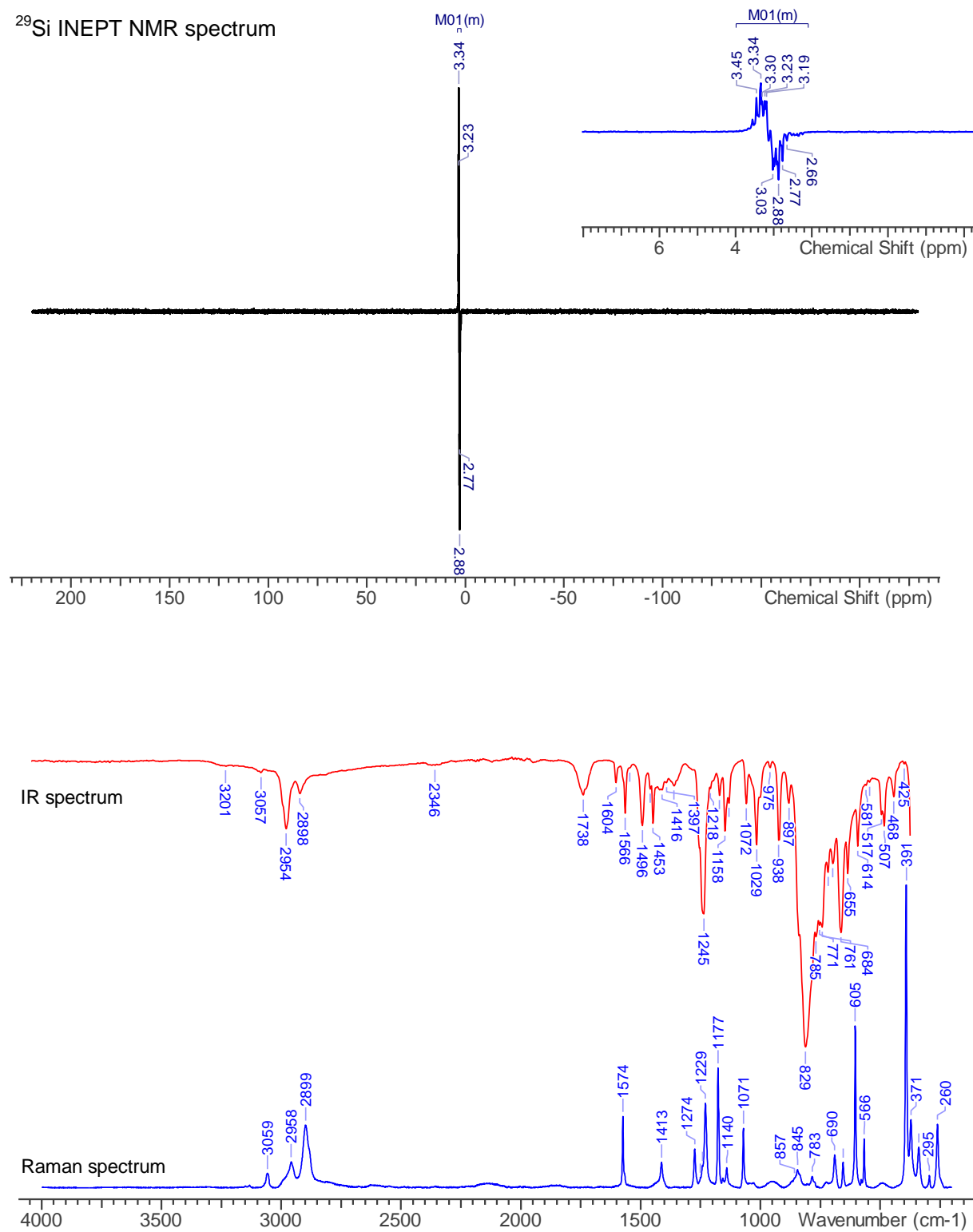
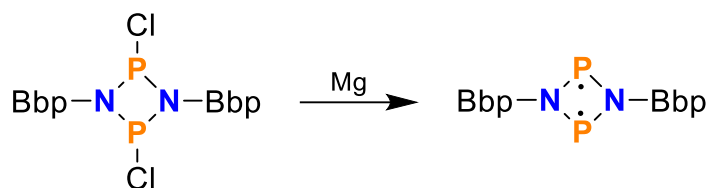


Figure S8 continued.



Synthesis of $[P(\mu\text{-NBbp})]_2$ (1P_Bbp); classical route



A solution of *cis/trans*- $[ClP(\mu\text{-NBbp})]_2$ (1 mmol, 0.95 g) in dimethoxyethane (15 mL) is added to activated magnesium turnings (glass stir bar, stirring for at least a week under inert gas atmosphere), whereupon the solution turns yellow and turbid. The reduction process can easily be traced *via* ^{31}P NMR spectroscopy and takes approximately one day. After completion of the reaction, the solvent is removed *in vacuo* and the product is extracted with *n*-hexane and filtered with a glass sinter frit. The solvent is removed *in vacuo*, resulting in an intensely yellow solid. Yield: 0.18 g (0.2 mmol; 20 %).

$M(C_{40}H_{82}Si_8P_2N_2) = 877.73$ g/mol.

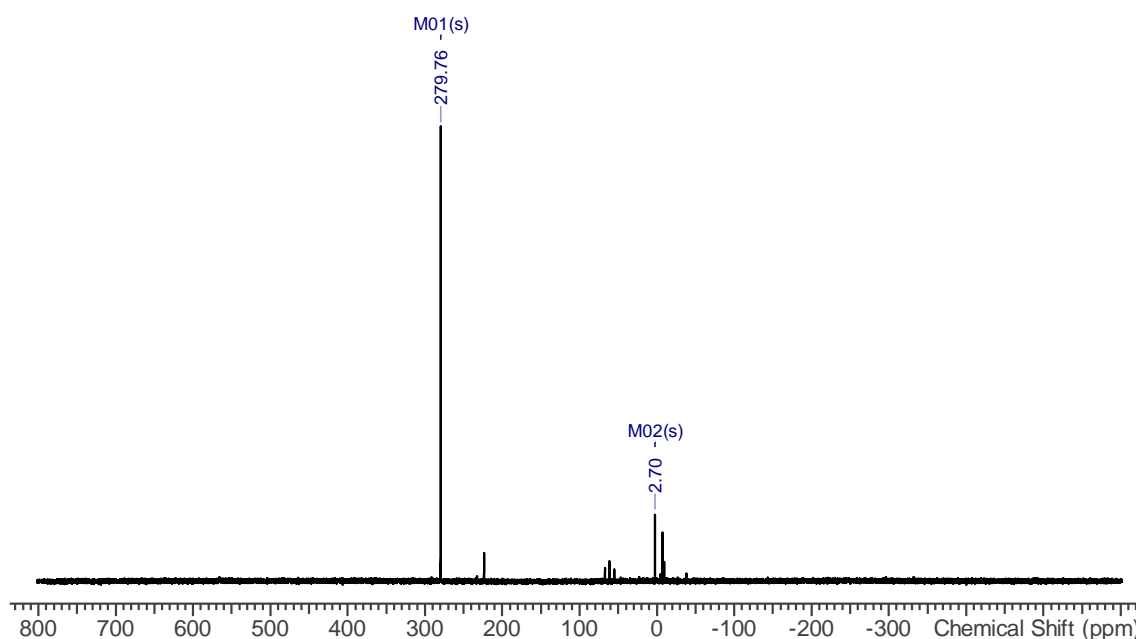
Due to the high sensitivity of the sample, it was not possible to obtain an accurate elemental analysis; the other analytical data prove the successful synthesis of the desired product.

Mp. 152 °C (decomposition). $^{31}P\{^1H\}$ NMR: (C_4D_8O , 299.1 K, 300.13 MHz): $\delta = 279.8$ (s). 1H NMR: (C_4D_8O , 298.4 K, 300.13 MHz): $\delta = 0.12$ (broad s, 36H, $Si(CH_3)_3$); 2.61 (s, 2H, $CH(Si(CH_3)_3)_2$); 6.91 (m, 3H, phenyl-*H*). $^{13}C\{^1H\}$ NMR: (C_4D_8O , 299.1 K, 75.48 MHz): $\delta = 1.3$ (m, $Si(CH_3)_3$); 23.9 (s, $CH(SiMe_3)_2$); 125.7 (s, phenyl-C); 126.8 (s, phenyl-C); 141.7 (s, phenyl-C). ^{29}Si INEPT NMR: (C_6D_6 , 298.2 K, 59.63 MHz): $\delta = 1.92$ (m, $SiMe_3$). IR (ATR, 32 Scans, cm^{-1}): $\tilde{\nu} = 3375$ (w), 2951 (w), 2897 (w), 1574 (w), 1455 (w), 1432 (w), 1245 (m), 1212 (w), 1152 (w), 1100 (w), 1076 (w), 1028 (m), 938 (m), 917 (w), 826 (vs), 771 (m), 760 (m), 746 (m), 721 (m), 684 (m), 657 (m), 614 (m), 468 (m), 451 (m), 437 (m), 412 (m). Raman: (633 nm, 30 s, 20 scans, cm^{-1}): $\tilde{\nu} = 3793$ (1), 3787 (1), 3777 (1), 3773 (1), 3063 (1), 2957 (3), 2900 (6), 2852 (1), 1581 (1), 1437 (1), 1421 (1), 1359 (1), 1336 (1), 1310 (2), 1277 (1), 1268 (1), 1235 (3), 1168 (1), 1077 (1), 999 (1), 941 (1), 806 (10), 773 (2), 746 (6), 689 (1), 598 (5), 575 (1), 553 (1), 543 (1), 536 (1), 469 (1), 356 (2), 336 (5), 308 (6), 261 (1), 237 (1), 234 (1), 208 (2), 179 (5), 130 (1), 79 (5). MS (EI, 70 eV, m/z): 73 (TMS^+); 234 ($[Bbp - (CH(TMS)_2)]^+$); 394 (Bbp^+).

Single crystals suitable for X-ray diffraction can be grown from saturated *n*-hexane solution at -40 °C.

Figure S9: NMR, IR and Raman spectra of $[\text{P}(\mu\text{-NBbp})]_2$ (solvent signals indicated by asterisks, traces of dimethoxyethane indicated by cross). The ^{31}P NMR spectrum shows impurities due to decomposition of the highly sensitive compound during measurement. We used crystalline material for all the NMR measurements, which was also used for single crystal measurements. These X-ray measurements showed no signs of decomposition. We therefore assume that the decomposition takes place during the workup and/or measurement process because the substances are very sensitive towards oxygen and moisture. The decomposition product of 1P_Bbp with a chemical shift of about 3 ppm was identified as Bbp-NH-PO-NH-Bbp.

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum



^1H NMR spectrum

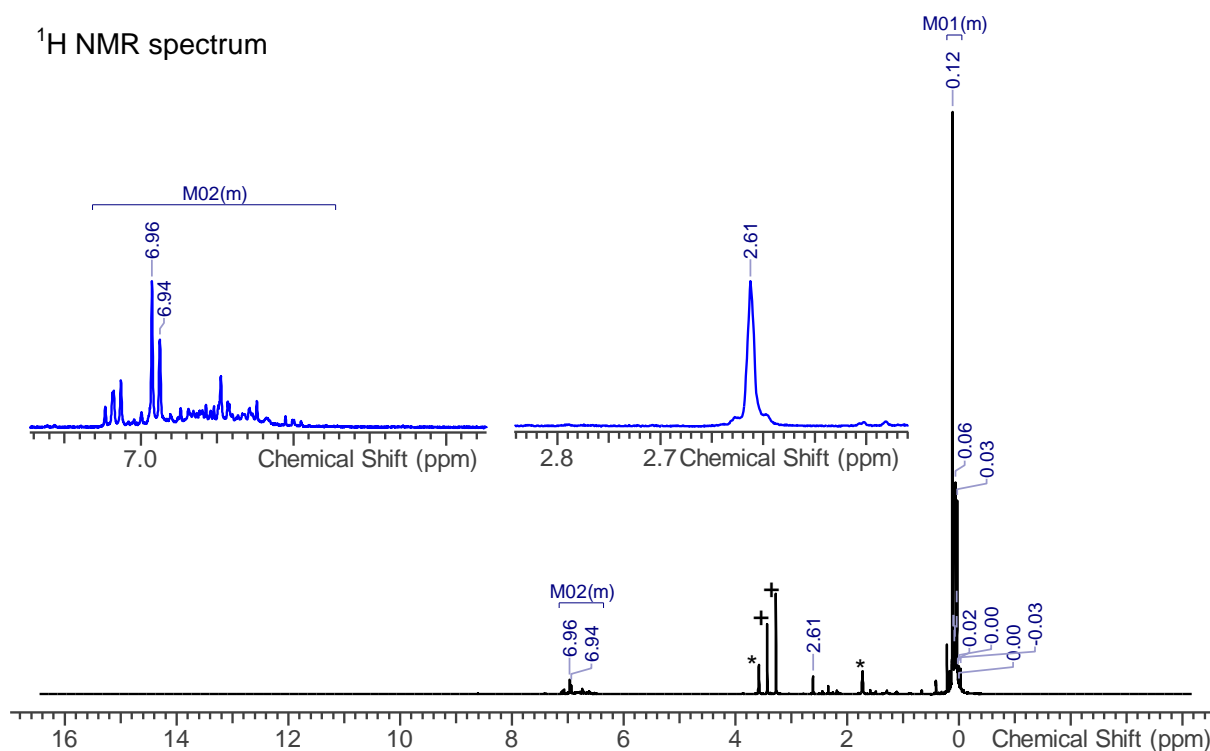
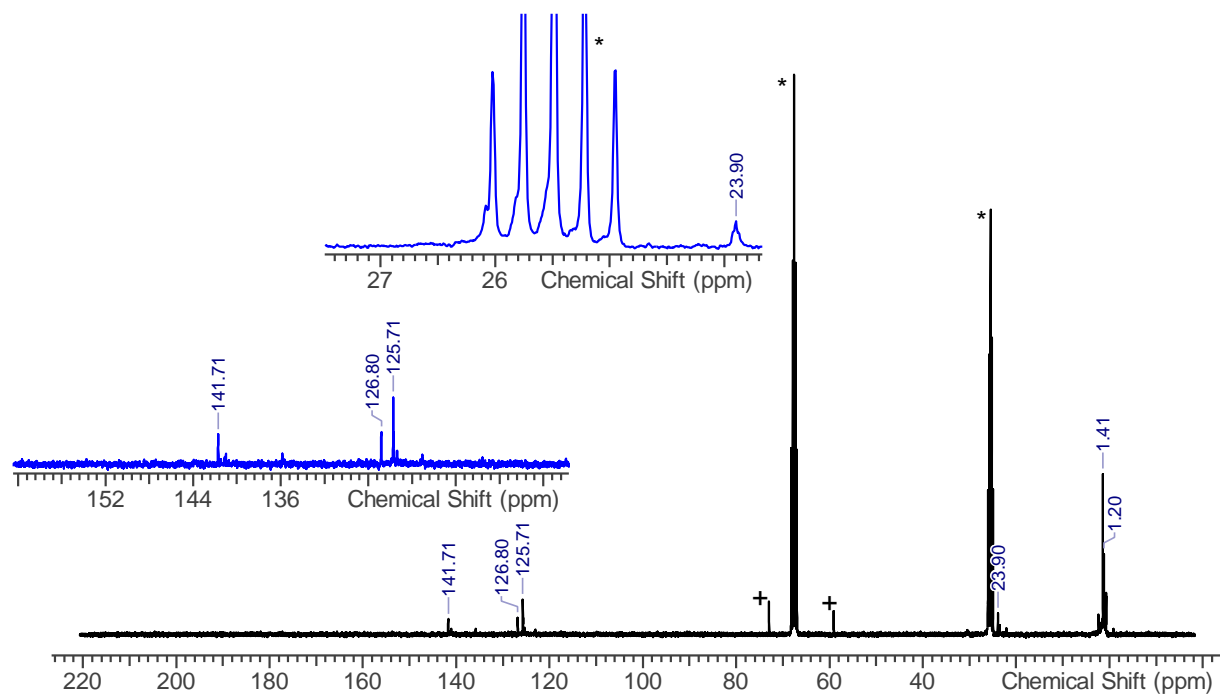


Figure S10 continued.

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



^{29}Si INEPT NMR spectrum

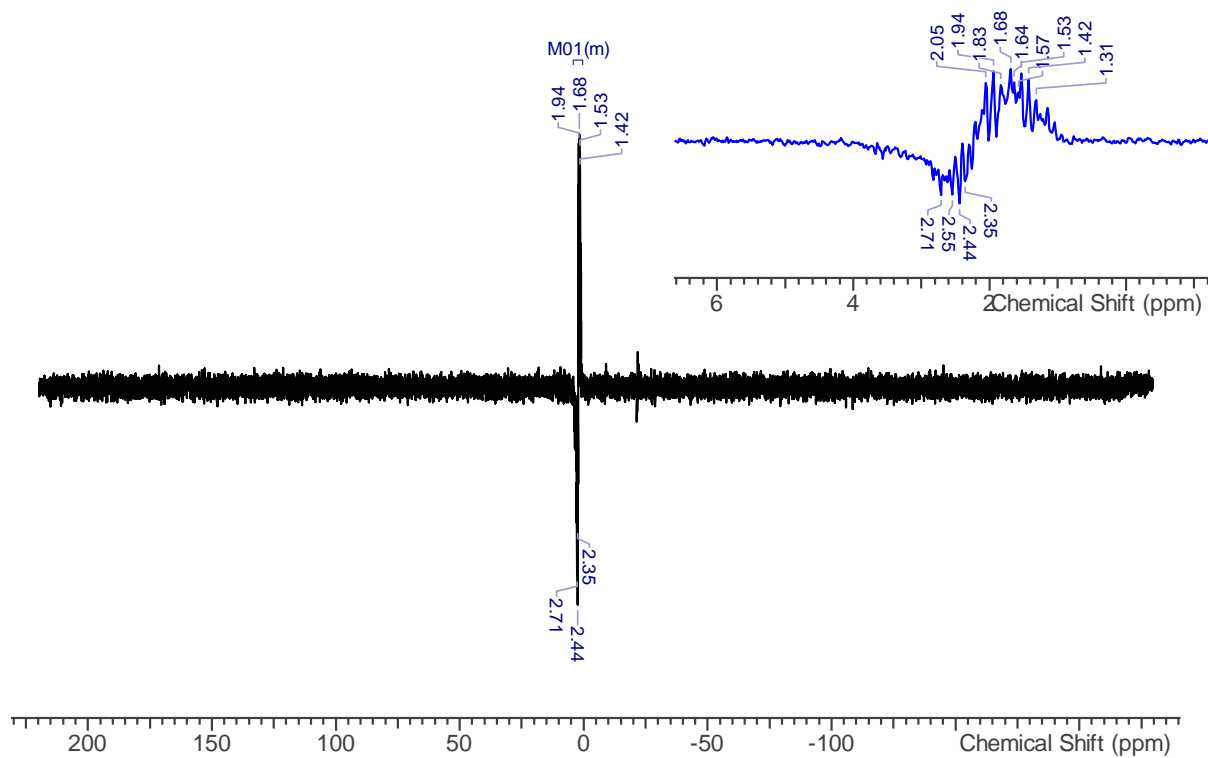
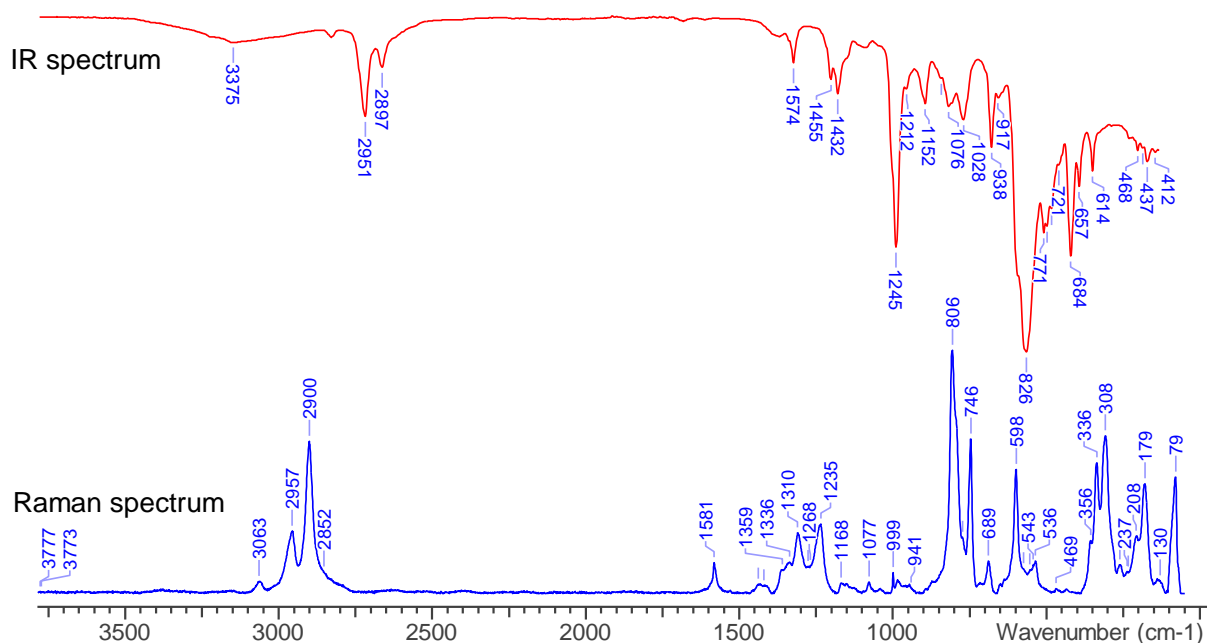
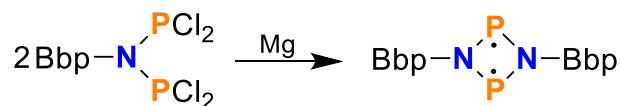


Figure S10 continued.



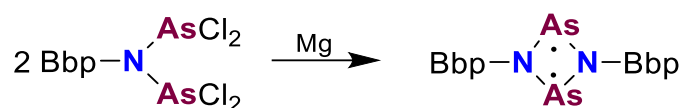
Synthesis of $[P(\mu\text{-NBbp})]_2$ (1P_Bbp); new route



$\text{Bbp-N}(\text{PCl}_2)_2$ (1.3 mmol; 0.794 g) is dissolved in dimethoxyethane (20 mL). The colourless solution is added to an excess of magnesium turnings. After addition, the solution quickly turns slightly yellow, the colouration intensifies rapidly during the progress of the reaction from orange and light red to a very dark reddish-brown; in addition, an onset of turbidity and a slight temporary warming of the reaction flask can be observed. The solution is stirred at room temperature for approx. 8 hours (control of reaction *via* ^{31}P NMR spectroscopy), followed by removal of the solvent *in vacuo* and addition of *n*-hexane to the resulting brown residue. The resulting reddish-brown suspension is filtered off *via* a glass sinter frit, the clear yellow filtrate is concentrated *in vacuo*. At low temperature ($-40\text{ }^\circ\text{C}$), the product can be crystallized selectively as yellow crystals and the supernatant solution can be removed with a syringe. Yield: (0.5 g; 0.58 mmol; 45 %), yield is depending on reaction time and amount of magnesium turnings used.

Analytical data: see above, (Synthesis of $[P(\mu\text{-NBbp})]_2$ (1P_Bbp); classical route). The purity of 1P_Bbp synthesized on the new route and on the common route is comparable after crystallization.

Synthesis of $[\text{As}(\mu\text{-NBbp})]_2$ (1As_Bbp)



$\text{Bbp-N}(\text{AsCl}_2)_2$ (1 mmol; 0.7 g) is dissolved in dimethoxyethane (20 mL), the light-yellow solution is added to an excess of magnesium turnings. After only a few minutes of stirring (glass stir bar) at ambient temperature, the yellow colour of the solution intensifies. After ten hours to one day of stirring, the reaction solution shows an intense dark red-brownish colour. The solvent is removed *in vacuo*, resulting in a brownish precipitate. This is extracted with *n*-hexane, which results in a reddish solution after filtration, from which the product can be isolated as yellow-greenish crystals at low temperature (-40°C). Yield: (0.28 g; 0.3 mmol; 30 %), yield is depending on reaction time and amount of magnesium turnings used.

$M(\text{C}_{40}\text{H}_{82}\text{Si}_8\text{As}_2\text{N}_2) = 965.63 \text{ g/mol}$.

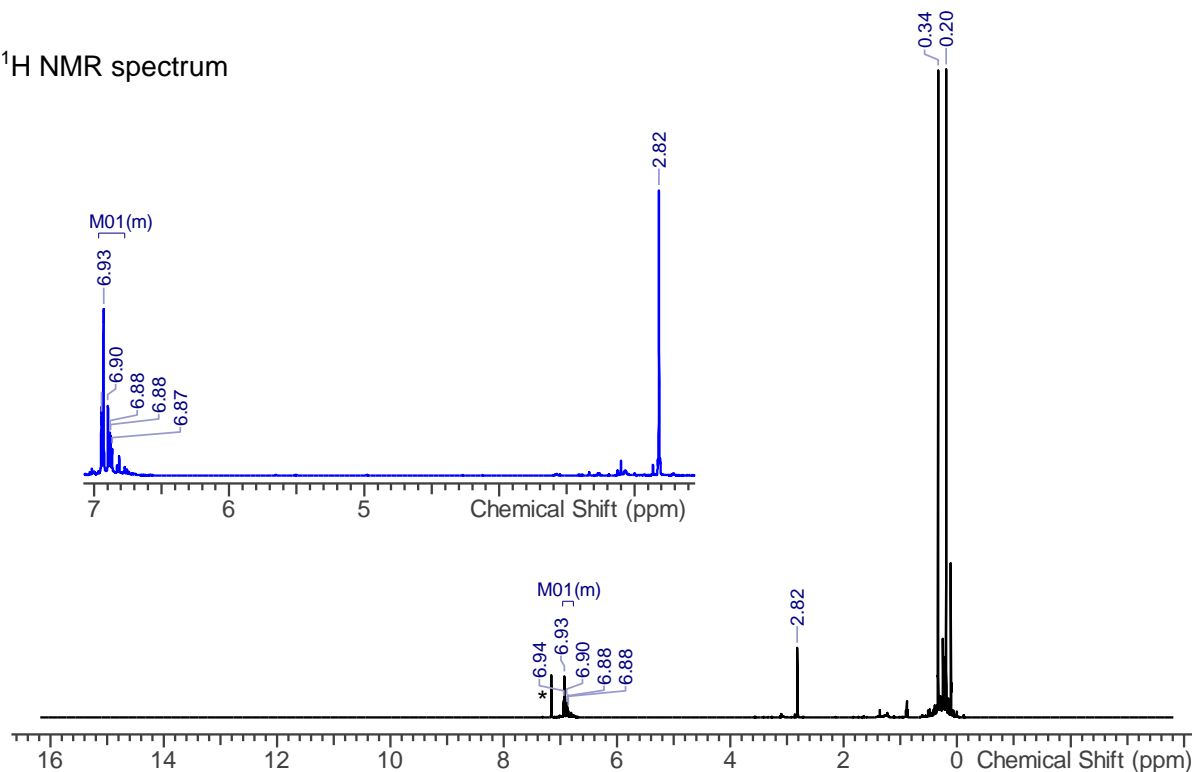
Due to the high sensitivity of the sample, it was not possible to obtain an accurate elemental analysis; the other listed analysis methods prove the successful synthesis of the desired product.

Mp. 145°C (decomposition). **$^1\text{H NMR}$:** (C_6D_6 , 298.2 K, 500.13 MHz): $\delta = 0.20$ (m, 18H, $\text{Si}(\text{CH}_3)_3$); 0.34 (m, 18H, $\text{Si}(\text{CH}_3)_3$); 2.82 (s, 2H, $\text{CH}(\text{Si}(\text{CH}_3)_3)_2$); 6.90 (m, 3H, phenyl-*H*). **$^{13}\text{C}\{^1\text{H}\}$ NMR:** (C_6D_6 , 298.2 K, 125.77 MHz): $\delta = 2.0$ (m, $\text{Si}(\text{CH}_3)_3$); 2.5 (m, $\text{Si}(\text{CH}_3)_3$); 25.3 (s, $\text{CH}(\text{SiMe}_3)_2$); 125.5 (s, phenyl-*C*); 126.1 (s, phenyl-*C*); 135.8 (s, phenyl-*C*); 143.1 (s, phenyl-*C*). **$^{29}\text{Si INEPT NMR}$:** (C_6D_6 , 298.1 K, 99.36 MHz): $\delta = 1.51$ (m, SiMe_3); 4.80 (m, SiMe_3). **IR** (ATR, 32 Scans, cm^{-1}): $\tilde{\nu} = 2949$ (w), 2897 (w), 2864 (w), 1570 (w), 1451 (w), 1418 (w), 1304 (w), 1241 (s), 1189 (m), 1142 (m), 1080 (m), 1022 (w), 1010 (w), 983 (m), 933 (m), 911 (w), 824 (vs), 791 (m), 771 (m), 760 (m), 682 (m), 655 (m), 641 (m), 614 (m), 554 (m), 507 (m), 451 (w), 422 (w). **Raman:** (532 nm, 20 s, 20 scans, cm^{-1}): 3064 (1), 2952 (3), 2899 (7), 2847 (2), 1578 (2), 1425 (1), 1271 (1), 1258 (4), 1228 (5), 1152 (1), 1085 (3), 1027 (2), 935 (7), 790 (1), 742 (1), 689 (1), 661 (1), 614 (2), 583 (10), 347 (4), 271 (1), 182 (3), 157 (1), 113 (3), 92 (3), 66 (2). **MS** (EI, 70 eV, m/z): 73 (TMS^+); 407 ($[\text{BbpN}]^+$); 965 ($[\text{As}(\mu\text{-NBbp})]_2^+$).

Single crystals suitable for X-ray diffraction can be grown from saturated *n*-hexane solution at -40°C .

Figure S10: NMR, IR and Raman spectra of $[\text{As}(\mu\text{-NBbp})_2]$ (solvent signals indicated by asterisks). The observation of two anisochronic $\text{Si}(\text{CH}_3)_3$ groups is unexpected. The NMR spectra were measured from crystalline samples which are undoubtedly 1As_Bbp and the spectral features were observed repeatedly and reproducibly for different samples. We therefore assume that the $\text{CH}(\text{Si}(\text{CH}_3)_3)_2$ groups are not freely rotating but are locked in a position breaking the expected molecular C_{2v} symmetry.

^1H NMR spectrum



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum

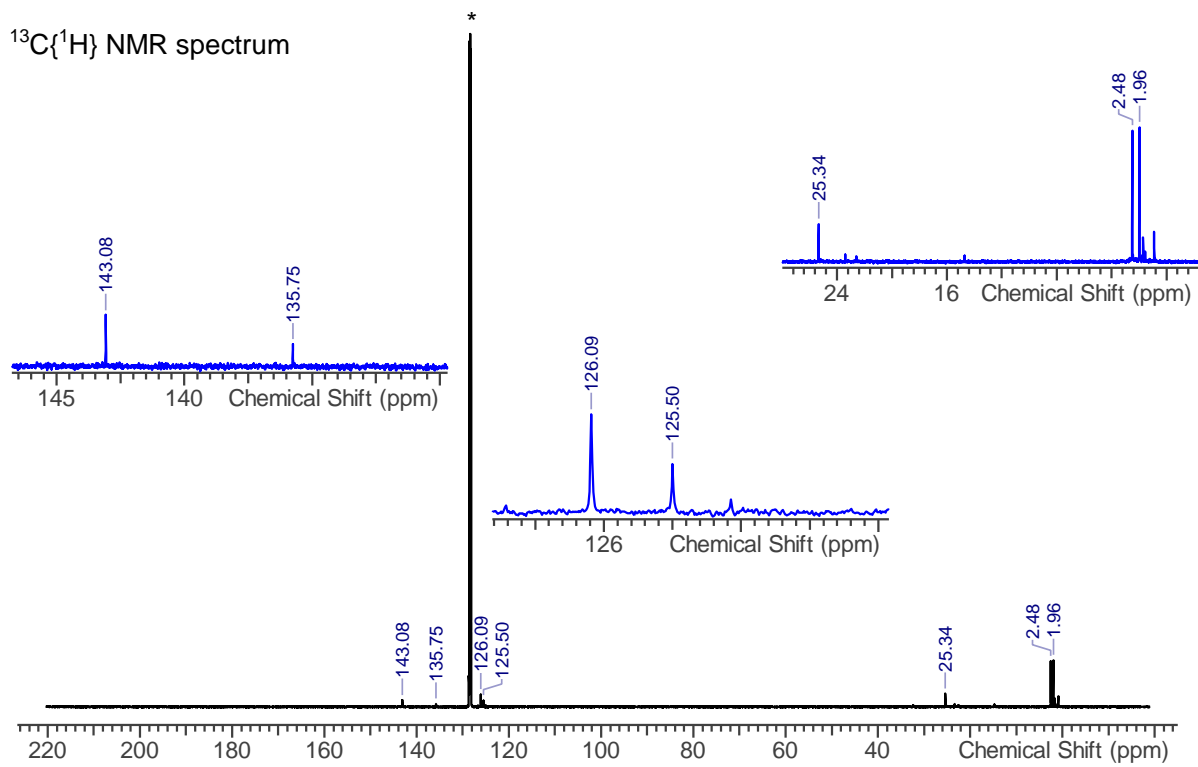
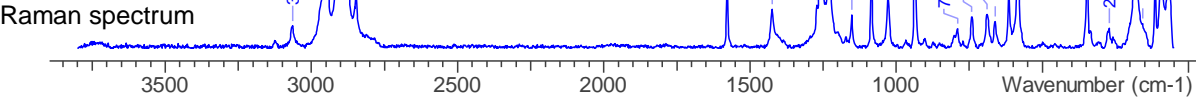
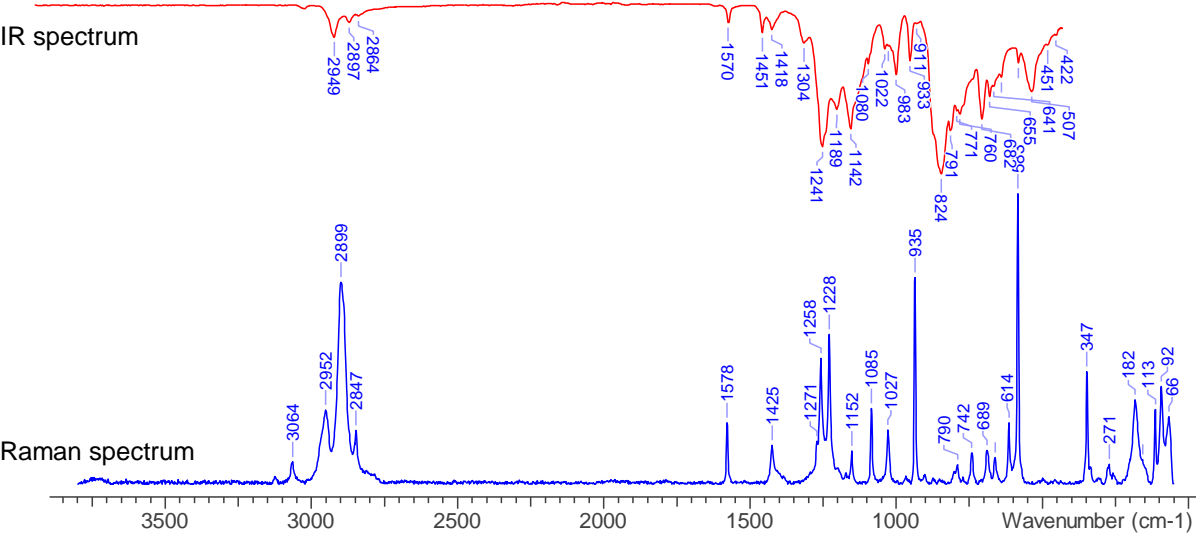
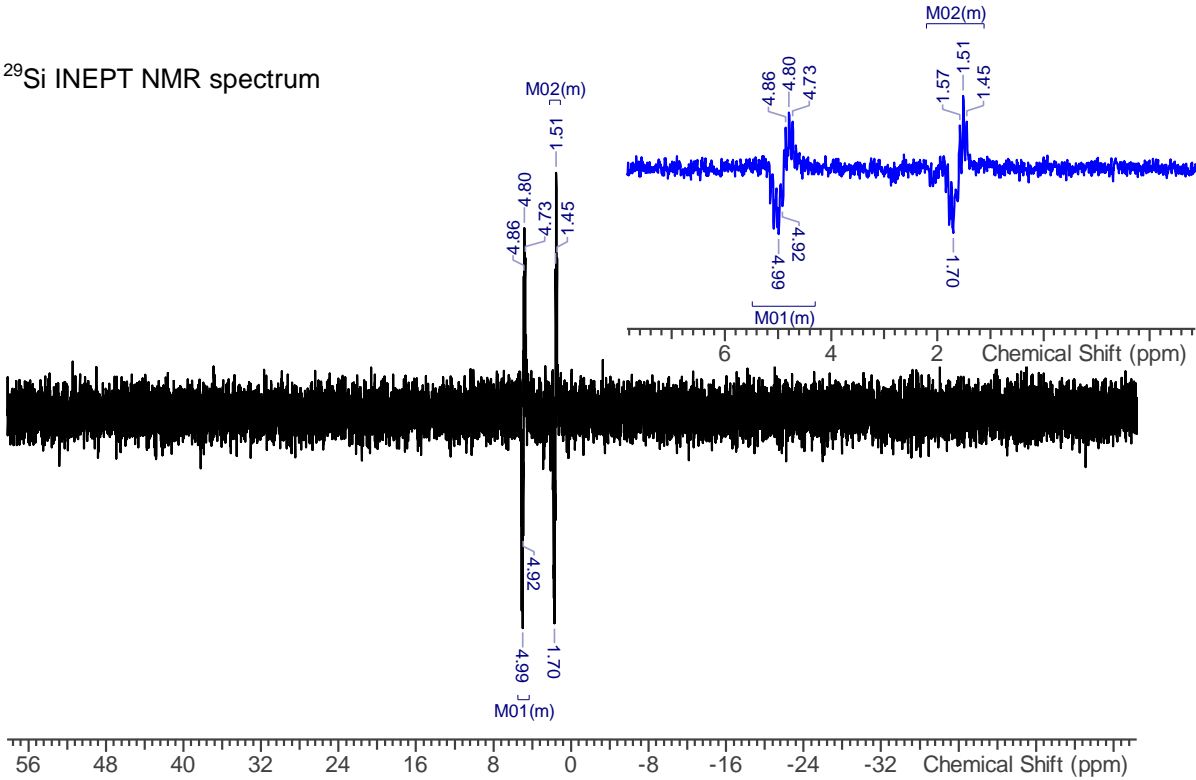


Figure S10 continued.



5 Computational details

Electronic structure computations were carried out using Gaussian 09⁹ or ORCA 4.0.1.^{10,11} NBO analyses were performed using NBO 6.0.^{12–15} Multiwfn¹⁶ was used to calculate and plot the ELF and results of the AIM analysis.

Since biradicals require multi-determinantal wave functions, they cannot be properly described by typical single-reference methods such as HF, DFT or coupled cluster theory. A qualitatively correct wave function can be obtained by multi-configurational SCF (MCSCF) methods which describe non-dynamic correlation, *e.g.* Complete Active Space SCF (CASSCF);^{17–25} better descriptions including dynamic correlation require expensive multi-reference perturbation (MRPT) or multi-reference configuration-interaction (MRCI) calculations, which limit the size of the systems that can be computed.

As we have previously shown,²⁶ the PBE functional^{27–30} is suitable to predict structural and spectroscopic parameters of PN biradicals, even though DFT methods usually fail to reproduce experimental energies due to neglect of non-dynamic correlation. Inclusion of dispersion (DFT-D3 (BJ))^{31,32} is essential to produce meaningful results. As NMR data could be predicted particularly well with the PBE-D3 method, it was used to estimate the structures of the biradicals discussed here. The basis sets def2-TZVP and def2-SVP (including fully relativistic effective core potentials for 5th and 6th row atoms)³³ were applied (notation: PBE-D3/def2-TZVP or PBE-D3/def2-SVP).

For closed shell species, the hybrid functional PBE0 in combination with empirical dispersion correction (D3(BJ)) and the def2-SVP basis set was used (notation: PBE0-D3/def2-SVP).

All structures were fully optimized and confirmed as minima by frequency analyses. Chemical shifts and coupling constants were derived by the GIAO method.^{34–38} The calculated absolute shifts ($\sigma_{\text{calc},X}$) were referenced to the experimental absolute shift of 85 % H₃PO₄ in the gas phase ($\sigma_{\text{ref},1} = 328.35$ ppm),³⁹ using PH₃ ($\sigma_{\text{ref},2} = 594.45$ ppm) as a secondary standard.⁴⁰

$$\begin{aligned}\delta_{\text{calc},X} &= (\sigma_{\text{ref},1} - \sigma_{\text{ref},2}) - (\sigma_{\text{calc},X} - \sigma_{\text{calc},\text{PH}_3}) \\ &= \sigma_{\text{calc},\text{PH}_3} - \sigma_{\text{calc},X} - 266.1 \text{ ppm}\end{aligned}$$

At the PBE0-D3/def2-SVP level of theory, $\sigma_{\text{calc},\text{PH}_3}$ amounts to 629.17 ppm. At the PBE-D3/def2-SVP level of theory, $\sigma_{\text{calc},\text{PH}_3}$ amounts to 617.22 ppm.

CAS(6,4)/def2-SVP single point calculations using the PBE-D3/def2-SVP geometries were carried out to obtain qualitatively correct wave functions of the biradicals **1P_Bbp** and **1As_Bbp**. The Active

Space was chosen to include all four π -type orbitals, which contain a total of 6 electrons. Furthermore, the model systems **1E_H** (E = P, As, Sb, Bi; D_{2h} symmetry) were optimized at the PBE-D3/def2-TZVP level of theory. These structures were used in multi-reference CISD single point calculations including the Davidson1 correction for the disconnected quadruples (MRCI+Q/def2-TZVP, using CAS(6,4)/def2-TZVP reference wave functions) to include the effects of dynamic correlation. Due to the inclusion of dynamic correlation, the relative weights of the reference determinants are lowered; however, the same trend for the biradical character is observed (Table S 5).

Table S5: Calculated properties that describe the multi-reference character of the biradicals.

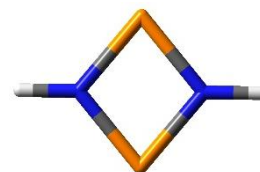
Compound	β [%] CAS	β [%] MRCI	$\epsilon(\pi_1)$ [eV]	$\epsilon(\pi_2)$ [eV]	$\epsilon(\pi_3)$ [eV]	$\epsilon(\pi_4)$ [eV]
1P_H	0.22	0.17	-14.8	-11.1	-5.8	+1.3
1As_H	0.28	0.19	-13.6	-10.5	-5.4	+0.5
1Sb_H	0.36	0.27	-12.4	-10.1	-4.8	-0.4
1Bi_H	0.39	0.30	-11.4	-9.4	-4.4	-0.4

ELF/AIM analysis was done using the CAS(6,4) as well as the PBE-D3 densities, which led to basically identical results.

6 Optimized structures (.xyz files)

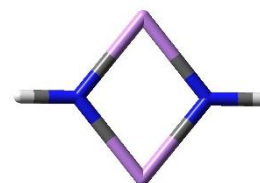
6.1 Optimized structure 1P_H (PBE-D3/def2-TZVP)

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N	0.00000	0.00000	1.09604
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P	-0.00000	1.31763	-0.00000
P	-0.00000	-1.31763	-0.00000



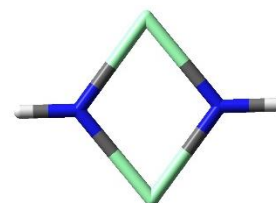
6.2 Optimized structure 1As_H (PBE-D3/def2-TZVP)

H	0.00000	-0.00000	2.17558
H	0.00000	-0.00000	-2.17558
N	0.00000	-0.00000	1.16033
N	0.00000	-0.00000	-1.16033
As	-0.00000	1.43902	-0.00000
As	-0.00000	-1.43902	-0.00000



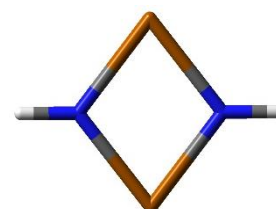
6.3 Optimized structure 1Sb_H (PBE-D3/def2-TZVP)

H	0.00000	0.00000	2.26966
H	0.00000	-0.00000	-2.26966
N	0.00000	0.00000	1.25200
N	0.00000	-0.00000	-1.25200
Sb	0.00000	1.60682	-0.00000
Sb	-0.00000	-1.60682	-0.00000

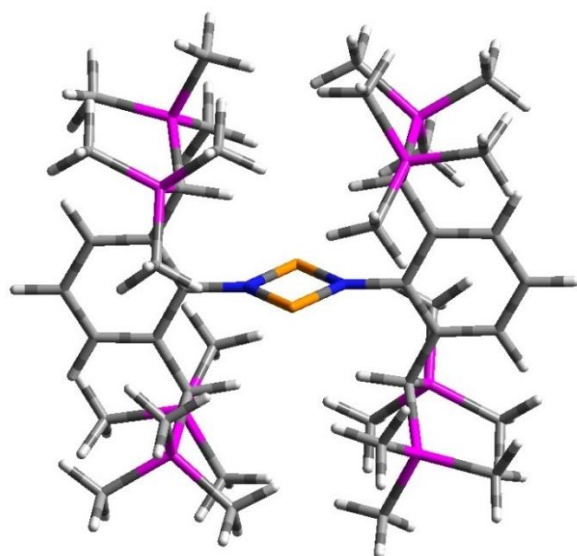


6.4 Optimized structure 1Bi_H (PBE-D3/def2-TZVP)

H	0.00000	-0.00000	2.31887
H	0.00000	0.00000	-2.31887
N	0.00000	-0.00000	1.29902
N	0.00000	0.00000	-1.29902
Bi	0.00000	1.69437	-0.00000
Bi	-0.00000	-1.69437	-0.00000



6.5 Optimized structure 1P_Bbp (PBE-D3/def2-SVP)

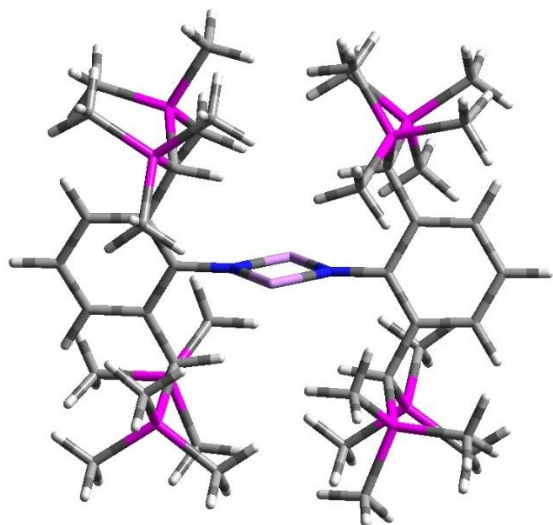


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C	0.00258	-4.80752	0.22757
C	0.00884	-4.09522	2.54185
C	-0.02324	-3.46781	-0.22123
H	-0.01757	-5.61663	-0.51408
C	-0.01279	-2.73480	2.16056
C	0.00001	-2.43468	0.76431
C	-0.15750	-3.17938	-1.69397
C	-0.12044	-1.66560	3.21710
N	0.00064	-1.07356	0.34380
Si	1.37223	-3.73672	-2.70771
Si	-1.88998	-3.75874	-2.30935
Si	1.43883	-1.57684	4.33287
Si	-1.83379	-1.76974	4.09252
P	1.32909	0.00639	0.01374
P	-1.32909	-0.00639	-0.01374
C	1.06225	-3.39532	-4.54640
C	1.79355	-5.57669	-2.53145
C	-2.42787	-2.76360	-3.82649
C	-1.93541	-5.59899	-2.76887
C	1.83925	-3.19129	5.24456
C	1.20071	-0.22693	5.64127
C	-2.30558	-0.09229	4.83013
N	-0.00064	1.07356	-0.34380
H	0.66606	-2.37673	-4.72250
H	0.33918	-4.12266	-4.96861
H	2.00773	-3.49085	-5.11898
H	2.62414	-5.81816	-3.22756
H	0.94025	-6.23651	-2.78432
H	2.13405	-5.82254	-1.50635
H	-3.47052	-3.03650	-4.09202
H	-1.79357	-2.95442	-4.71345
H	-2.41208	-1.67594	-3.61768
H	-2.96623	-5.87522	-3.07412
H	-1.65342	-6.25308	-1.91977
H	-1.26290	-5.82820	-3.62040

H	2.12345	-3.99954	4.54200
H	2.70580	-3.01058	5.91489
H	2.16724	0.00245	6.13505
H	0.49117	-0.55786	6.42664
H	0.81452	0.71491	5.20639
H	-2.31521	0.69744	4.05378
H	-1.62247	0.22787	5.63991
H	-3.32916	-0.15431	5.25474
C	-0.00001	2.43468	-0.76431
C	0.02324	3.46781	0.22123
C	0.01279	2.73480	-2.16056
C	-0.00258	4.80752	-0.22757
C	0.15750	3.17938	1.69397
C	-0.00884	4.09522	-2.54185
C	0.12044	1.66560	-3.21710
H	0.01757	5.61663	0.51408
C	-0.02717	5.11825	-1.58983
Si	-1.37223	3.73672	2.70771
Si	1.88998	3.75874	2.30935
H	0.00551	4.34640	-3.61019
Si	-1.43883	1.57684	-4.33287
Si	1.83379	1.76974	-4.09252
H	0.14133	0.66993	-2.71775
H	-0.04240	6.17016	-1.91365
C	-1.06225	3.39532	4.54640
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C	2.42787	2.76360	3.82649
C	1.93541	5.59899	2.76887
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C	-1.20071	0.22693	-5.64127
C	1.87488	3.05338	-5.48849
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H	-0.33918	4.12266	4.96861
H	-2.00773	3.49085	5.11898
H	-2.62414	5.81816	3.22756
H	-0.94025	6.23651	2.78432
H	-2.13405	5.82254	1.50635
H	3.47052	3.03650	4.09202
H	1.79357	2.95442	4.71345
H	2.41208	1.67594	3.61768
H	2.96623	5.87522	3.07412
H	1.65342	6.25308	1.91977
H	1.26290	5.82820	3.62040
H	-2.12345	3.99954	-4.54200
H	-1.00022	3.55270	-5.87132
H	-2.70580	3.01058	-5.91489
H	-2.16724	-0.00245	-6.13505
H	-0.49117	0.55786	-6.42664
H	-0.81452	-0.71491	-5.20639
H	2.89691	3.09324	-5.91970
H	1.17754	2.78936	-6.30948
H	1.62275	4.07299	-5.13520
H	2.31521	-0.69744	-4.05378
H	1.62247	-0.22787	-5.63991
H	3.32916	0.15431	-5.25474

C	-1.87488	-3.05338	5.48849
H	1.00022	-3.55270	5.87132
H	0.04240	-6.17016	1.91365
H	-0.00551	-4.34640	3.61019
H	-2.89691	-3.09324	5.91970
H	-1.17754	-2.78936	6.30948
H	-1.62275	-4.07299	5.13520
H	0.18132	2.07617	1.84592
H	-0.14133	-0.66993	2.71775
H	-0.18132	-2.07617	-1.84592
C	-3.14057	-3.43676	-0.92669
H	-2.90836	-4.03223	-0.02177
H	-3.13624	-2.36495	-0.63741
H	-4.16733	-3.69405	-1.25927
C	-3.13037	-2.21571	2.78943
H	-3.12711	-1.46363	1.97272
H	-2.93600	-3.20772	2.33606
H	-4.14653	-2.22937	3.23474
C	2.86156	-2.75462	-2.07576
H	2.66655	-1.66256	-2.07478
H	3.08933	-3.04667	-1.02941
H	3.76485	-2.95051	-2.68955
C	2.91682	-1.18655	3.21573
H	3.09765	-2.03148	2.51902
H	2.74124	-0.28338	2.59592
H	3.84130	-1.03059	3.80913
C	-2.91682	1.18655	-3.21573
H	-2.74124	0.28338	-2.59592
H	-3.09765	2.03148	-2.51902
H	-3.84130	1.03059	-3.80913
C	-2.86156	2.75462	2.07576
H	-3.08933	3.04667	1.02941
H	-2.66655	1.66256	2.07478
H	-3.76485	2.95051	2.68955
C	3.14057	3.43676	0.92669
H	3.13624	2.36495	0.63741
H	2.90836	4.03223	0.02177
H	4.16733	3.69405	1.25927
C	3.13037	2.21571	-2.78943
H	2.93600	3.20772	-2.33606
H	3.12711	1.46363	-1.97272
H	4.14653	2.22937	-3.23474

6.6 Optimized structure 1As_Bbp (PBE-D3/def2-SVP)



C	-0.11302	5.42352	0.16006
C	1.09332	4.73343	0.30540
C	-1.29208	4.71607	-0.08776
C	1.15192	3.32489	0.21719
H	2.02034	5.28832	0.50353
C	-1.30270	3.30638	-0.18435
C	-0.06501	2.60954	-0.01709
C	2.47868	2.63195	0.38666
C	-2.61209	2.58910	-0.38495
N	-0.04950	1.19075	-0.02567
Si	3.60679	2.98180	-1.12544
Si	3.21215	2.91115	2.14123
Si	-3.39033	2.95350	-2.10335
Si	-3.73578	2.81695	1.15758
C	5.23688	2.03734	-0.92647
C	4.01387	4.81509	-1.38389
C	4.33906	1.46100	2.60111
C	4.23343	4.50441	2.28615
C	-3.52133	4.80206	-2.50308
C	-5.13548	2.22361	-2.23059
C	-4.81557	1.27442	1.33016
N	0.01660	-1.19578	0.03799
H	5.06438	0.96984	-0.68738
H	5.85829	2.47447	-0.11826
H	5.82568	2.07992	-1.86568
H	4.70261	4.90693	-2.24988
H	4.51184	5.27373	-0.50722
H	3.10418	5.40369	-1.61504
H	4.67921	1.56868	3.65207
H	5.24028	1.40637	1.95945
H	3.80188	0.49542	2.52049
H	4.60696	4.61002	3.32598
H	3.64375	5.41274	2.04967
H	5.11539	4.48217	1.61412
H	-2.52532	5.27918	-2.58872
H	-4.03628	4.91568	-3.48013
H	-5.51949	2.37241	-3.26121
H	-5.84313	2.72087	-1.53665

H	-5.15397	1.13734	-2.01789
H	-4.16222	0.37958	1.37284
H	-5.51471	1.14477	0.48167
H	-5.40963	1.30736	2.26636
C	0.07639	-2.61345	0.03330
C	-1.12313	-3.37401	0.20047
C	1.32989	-3.26319	-0.19589
C	-1.03812	-4.78156	0.11021
C	-2.46747	-2.72255	0.39251
C	1.34732	-4.67367	-0.27218
C	2.61473	-2.49963	-0.38317
H	-1.95744	-5.37406	0.20757
C	0.17877	-5.42621	-0.12645
Si	-3.23771	-3.12346	2.10596
Si	-3.57058	-2.99842	-1.15721
H	2.30285	-5.18032	-0.46490
Si	3.78658	-2.78753	1.10801
Si	3.32713	-2.74653	-2.15165
H	2.39673	-1.40866	-0.33512
H	0.21577	-6.52353	-0.20387
C	-5.01067	-2.46293	2.22740
C	-3.30058	-4.97699	2.49942
C	-4.69155	-1.48806	-1.34769
C	-4.61987	-4.57508	-1.05314
C	4.28587	-4.59779	1.36777
C	5.37052	-1.77415	0.87457
C	4.44839	-4.26939	-2.30596
C	4.33539	-1.22557	-2.65279
H	-5.07018	-1.37567	2.02830
H	-5.69384	-2.97773	1.52190
H	-5.39682	-2.63871	3.25296
H	-3.82101	-5.11350	3.47060
H	-3.86054	-5.55304	1.73573
H	-2.28829	-5.41660	2.59397
H	-5.29278	-1.55068	-2.27773
H	-5.38574	-1.36165	-0.49472
H	-4.05993	-0.57856	-1.41105
H	-5.24339	-4.67095	-1.96628
H	-3.98846	-5.48413	-0.98594
H	-5.30292	-4.56522	-0.17984
H	3.41631	-5.22454	1.64774
H	4.76406	-5.04423	0.47393
H	5.01746	-4.64650	2.20161
H	5.97808	-1.79232	1.80263
H	5.99393	-2.18828	0.05580
H	5.15267	-0.71445	0.63779
H	4.80939	-4.35630	-3.35190
H	5.33874	-4.18867	-1.64996
H	3.92114	-5.21189	-2.05611
H	3.72753	-0.30251	-2.57564
H	5.23970	-1.09361	-2.02726
H	4.66540	-1.32351	-3.70783
C	-4.83413	4.35989	1.05621
H	-4.11021	5.35954	-1.74742
H	-0.13529	6.52070	0.24447
H	-2.24042	5.25999	-0.18944

H	-5.46799	4.42875	1.96465
H	-5.50937	4.33270	0.17708
H	-4.23286	5.28975	0.99997
H	-2.32565	-1.61833	0.41963
H	-2.41918	1.49258	-0.40876
H	2.31927	1.53095	0.34005
C	1.78095	2.97777	3.37937
H	1.08939	3.81563	3.15969
H	1.19361	2.03640	3.34439
H	2.16077	3.10034	4.41464
C	-2.63246	2.93763	2.69096
H	-1.99604	2.03125	2.77574
H	-1.96187	3.81894	2.64364
H	-3.24452	3.01172	3.61348
C	2.66963	2.39706	-2.66369
H	2.32050	1.34913	-2.55388
H	1.77201	3.03086	-2.82035
H	3.29967	2.46180	-3.57438
C	-2.27875	2.15411	-3.41217
H	-1.23957	2.53676	-3.32805
H	-2.24404	1.05164	-3.29197
H	-2.64025	2.37857	-4.43703
C	2.85133	-2.23687	2.65981
H	2.45482	-1.20600	2.55104
H	1.98433	-2.90792	2.83288
H	3.49723	-2.26968	3.56101
C	-2.16313	-2.28300	3.41985
H	-1.10965	-2.62514	3.33935
H	-2.17036	-1.17997	3.29857
H	-2.51932	-2.52064	4.44355
C	-2.45571	-3.09783	-2.68356
H	-1.85211	-2.17039	-2.77720
H	-1.75415	-3.95377	-2.62362
H	-3.06085	-3.20460	-3.60748
C	1.87589	-2.92916	-3.35556
H	1.25472	-3.81533	-3.11552
H	1.21890	-2.03528	-3.31298
H	2.24002	-3.03001	-4.39888
As	-0.03142	-0.04206	-1.43561
As	-0.00923	0.03633	1.44760

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