Electronic Supplementary Information for

Multinuclear beryllium amide and imide complexes: structure, properties and bonding

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Crystallographic Details

Table S1: Crystal data and details of the structure determination for $[Be(HNMes)_2]_3$ (**1**), $[(py)_2Be(HNMes)_2]$ (**2**) and $[Be(HNDipp)_2]_2$ (**3**).

	$[Be(HNMes)_2]_3$ (**1**) · C_6H_6	$[(py)_2Be(HNMes)_2]$ (**2**)	$[Be(HNDipp)_2]_2$ (**3**)
Empirical formula	$C_{54}H_{72}Be_3N_6$, C_6H_6	$C_{28}H_{34}BeN_4$	$C_{48}H_{72}Be_2N_4$
Relative molecular mass	910.31	435.60	723.11
Crystal system	triclinic	monoclinic	monoclinic
Space group (No.)	$P\bar{1}$ (2)	$I2/a$ (15)	$P2_1/c$ (14)
Radiation / Å	1.54186	1.54186	1.54178
a / Å	14.2365(15)	16.1582(15)	9.5804(3)
b / Å	14.6407(15)	8.6300(5)	16.0927(5)
c / Å	15.7210(18)	17.5982(15)	14.6676(5)
α / deg	63.743(8)	90	90
β / deg	71.969(9)	95.030(7)	102.993(2)
γ / deg	72.777(8)	90	90
V / Å^3	2745.2(6)	2444.5(3)	2203.47(12)
Z	2	4	2
$F(000)$ / e	984	936	792
$\rho_{calc.}$ / g·cm^{-3}	1.101	1.184	1.090
μ / mm^{-1}	0.476	0.531	0.462
ϑ range / °	3.205 – 76.230	5.046 – 76.127	4.137 – 74.576
Range of Miller indices	$-17 \le h \le 17$	$-20 \le h \le 18$	$-11 \le h \le 11$
	$-17 \le k \le 18$	$-10 \le k \le 6$	$-20 \le k \le 20$
	$-19 \le l \le 15$	$-21 \le l \le 22$	$-17 \le l \le 18$
Reflections collected, unique	67425, 11226	15241, 2534	68071, 4499
Restraints, parameters	2052, 927	0, 157	0, 258
R_{int}	0.0661	0.0257	0.0482
R_1 ($I \ge 2\sigma(I)$)	0.0497	0.0380	0.0362
R_1 (*all data*)	0.0942	0.0482	0.0405
wR_2 ($I \ge 2\sigma(I)$)	0.1183	0.1043	0.0946
wR_2 (*all data*)	0.1377	0.1085	0.0978
S	0.838	1.064	1.047
$\Delta\rho_{min}$, $\Delta\rho_{max}$ / e·Å^{-3}	−0.204, 0.201	−0.157, 0.242	−0.180, 0.282

Table S2: Crystal data and details of the structure determination for $[Be(NPh_2)(\mu_2\text{-}HNDipp)]_2$ (**4**) and $[Be(NCPh_2)_2]_3$ (**5**).

	$[Be(NPh_2)(\mu_2\text{-}HNDipp)]_2$ (**4**)	$[Be(NCPh_2)_2]_3$ (**5**)
Empirical formula	$C_{48}H_{56}Be_2N_4$	$C_{78}H_{60}Be_3N_6$
Relative molecular mass	706.98	1108.35
Crystal system	monoclinic	triclinic
Space group (No.)	$P2_1/c$ (14)	$P\bar{1}$ (2)
Radiation / Å	1.54186	1.54186
a / Å	9.4884(9)	9.9415(6)
b / Å	9.8022(7)	15.0952(7)
c / Å	22.2345(19)	23.1922(13)
α / deg	90	71.835(4)
β / deg	99.949(7)	87.988(6)
γ / deg	90	71.142(4)
V / Å^3	2036.9(3)	3121.1(3)
Z	2	2
$F(000)$ / e	760	1164
$\rho_{calc.}$ / g·cm^{-3}	1.153	1.179
μ / mm^{-1}	0.499	0.522
ϑ range / °	4.037 – 76.128	3.243 – 70.070
Range of Miller indices	$-6 \le h \le 11$	$-12 \le h \le 5$
	$-12 \le k \le 12$	$-18 \le k \le 18$
	$-26 \le l \le 27$	$-28 \le l \le 28$
Reflections collected, unique	24532, 4152	70021, 11726
Restraints, parameters	69, 283	0, 785
R_{int}	0.0535	0.0285
R_1 ($I \ge 2\sigma(I)$)	0.0518	0.055
R_1 *(all data)*	0.0640	0.067
wR_2 ($I \ge 2\sigma(I)$)	0.1488	0.157
wR_2 *(all data)*	0.1578	0.165
S	1.061	1.086
$\Delta\rho_{min}$, $\Delta\rho_{max}$ / e·Å^{-3}	−0.223, 0.288	−0.236, 0.315

NMR Spectra

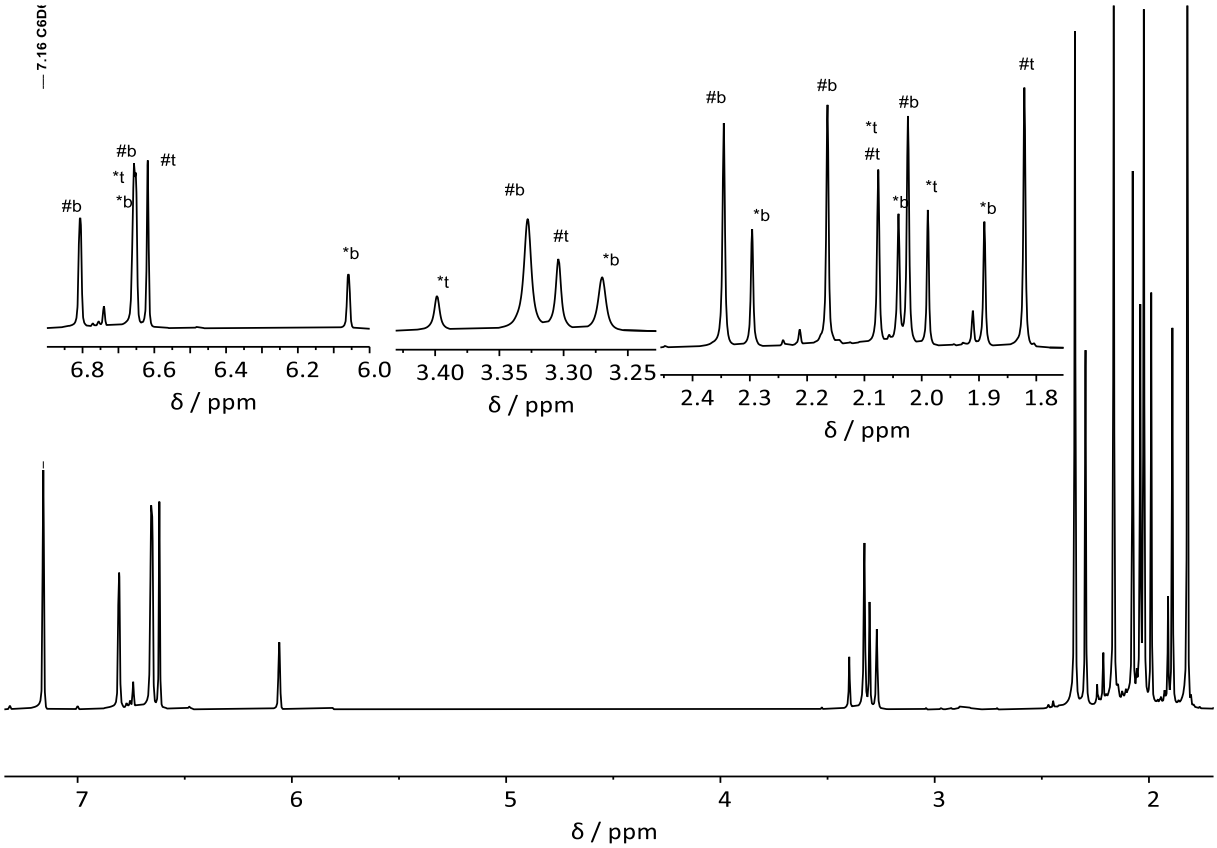

Figure S1. ^{1}H NMR spectrum of $[Be(HNMes)_2]_3$ (**1**) in C_6D_6. The major isomer is annotated with a hash while for the minor one an asterisk is used. Bridging and terminal HNMes units are marked with "b" and "t", respectively.

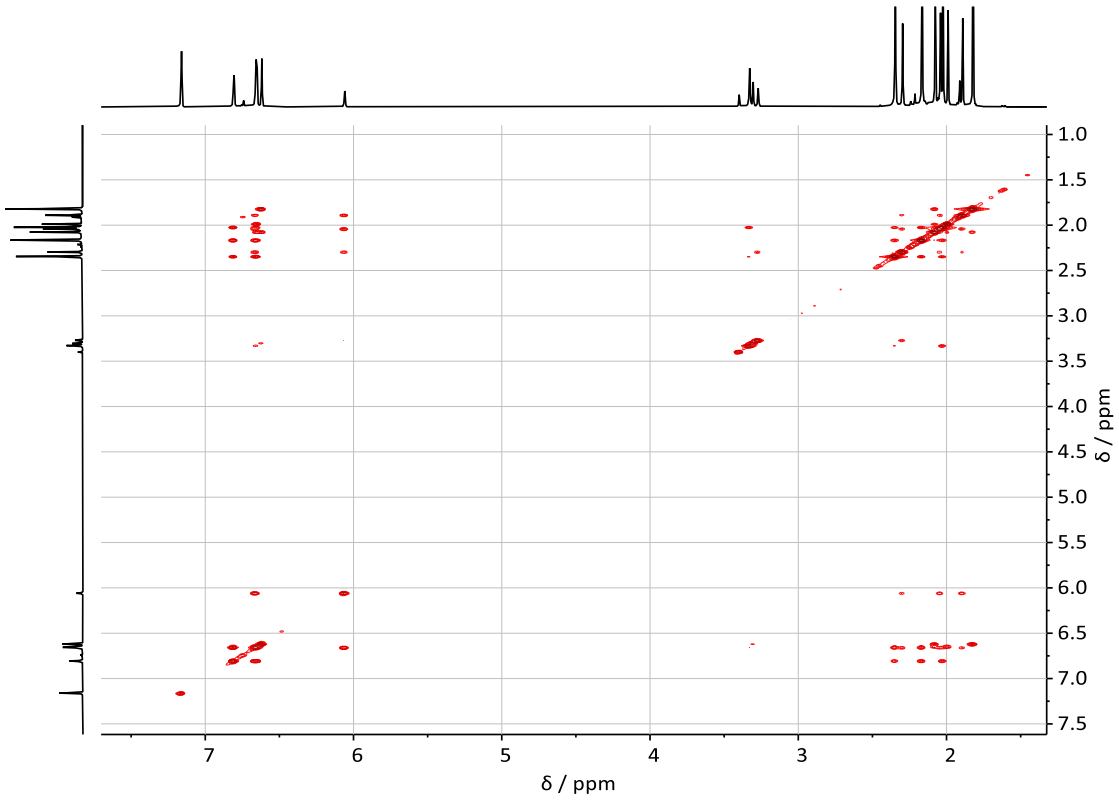

Figure S2. ^{1}H^{1}H COSY NMR spectrum of $[Be(HNMes)_2]_3$ (**1**) in C_6D_6.

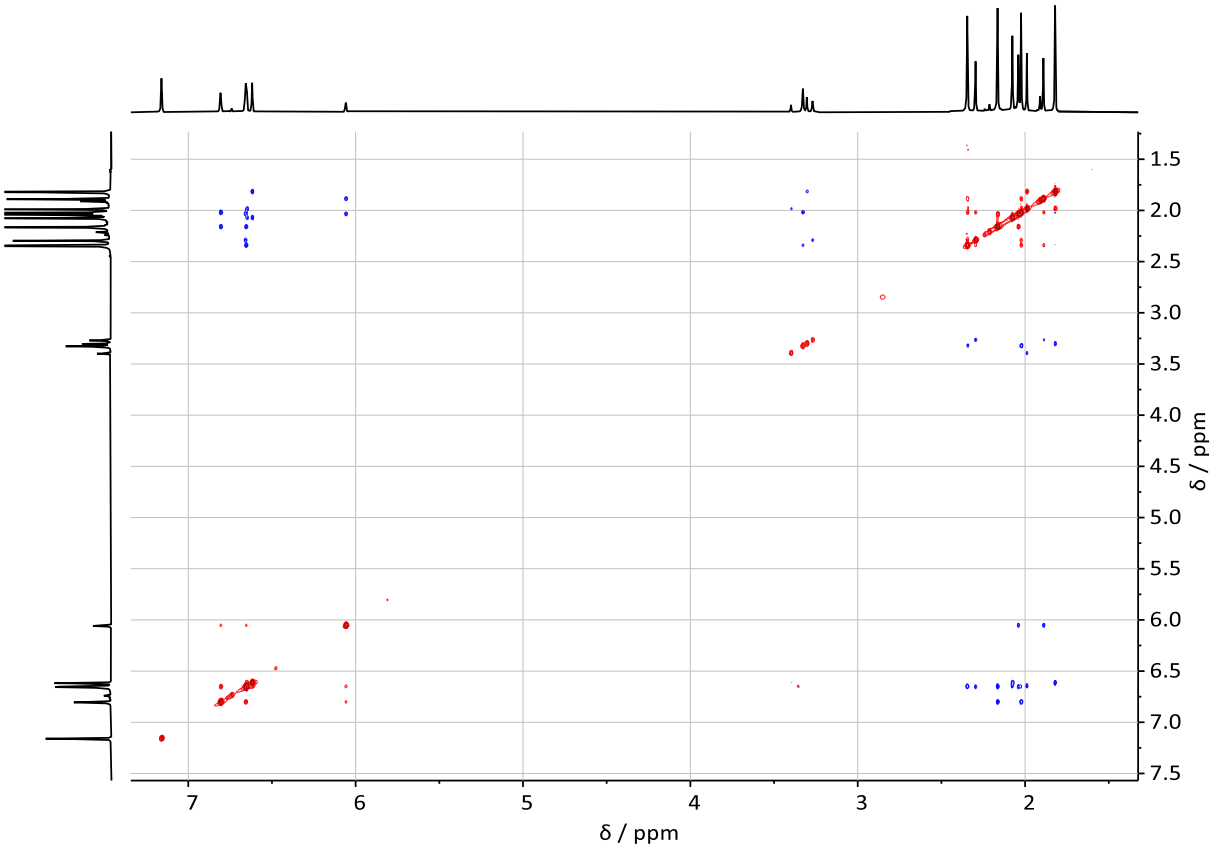

Figure S3. Phaseselective $^{1}H^{1}H$ NOESY NMR spectrum of $[Be(HNMes)_2]_3$ (**1**) in C_6D_6.

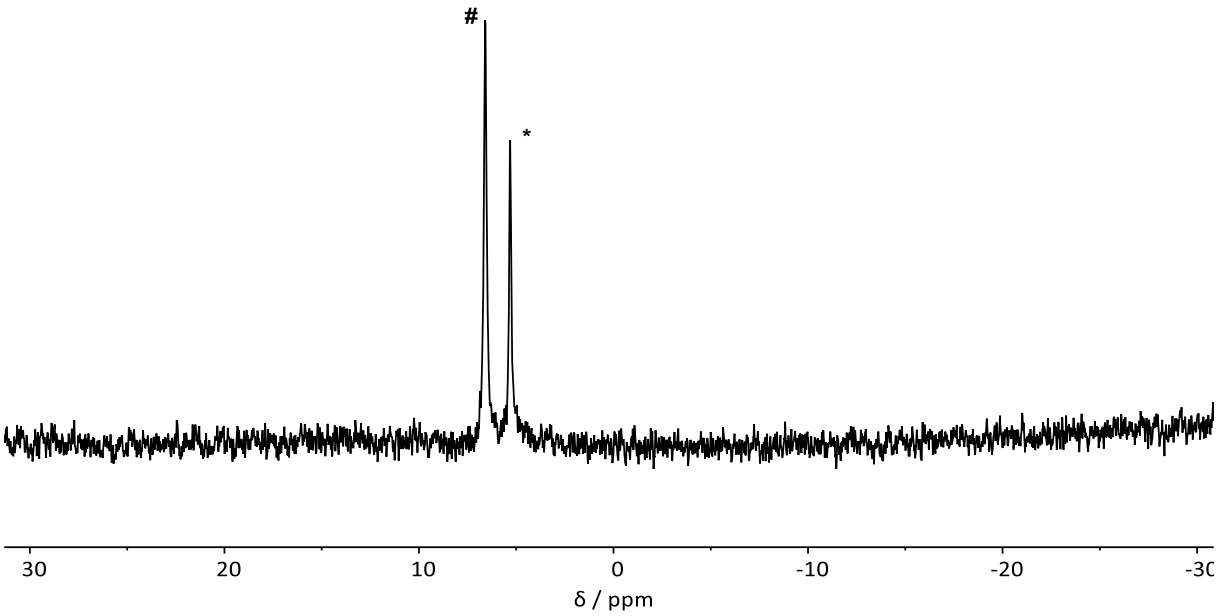

Figure S4. ^{9}Be NMR spectrum of $[Be(HNMes)_2]_3$ (**1**) in C_6D_6. The major isomer is annotated with a hash while for the minor one an asterisk is used.

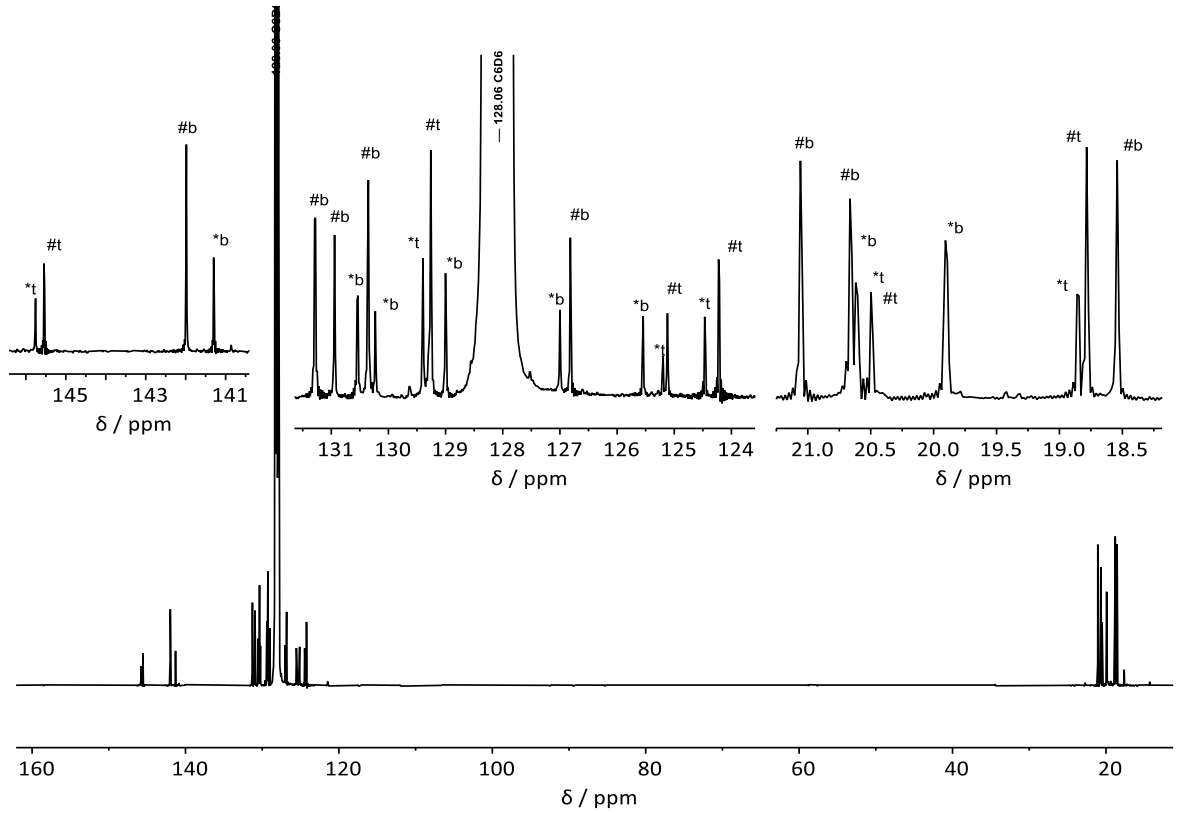

Figure S5. ^{13}C NMR spectrum of $[Be(HNMes)_2]_3$ (**1**) in C_6D_6. The major isomer is annotated with a hash while for the minor one an asterisk is used. Bridging and terminal HNMes units are marked with "b" and "t", respectively.

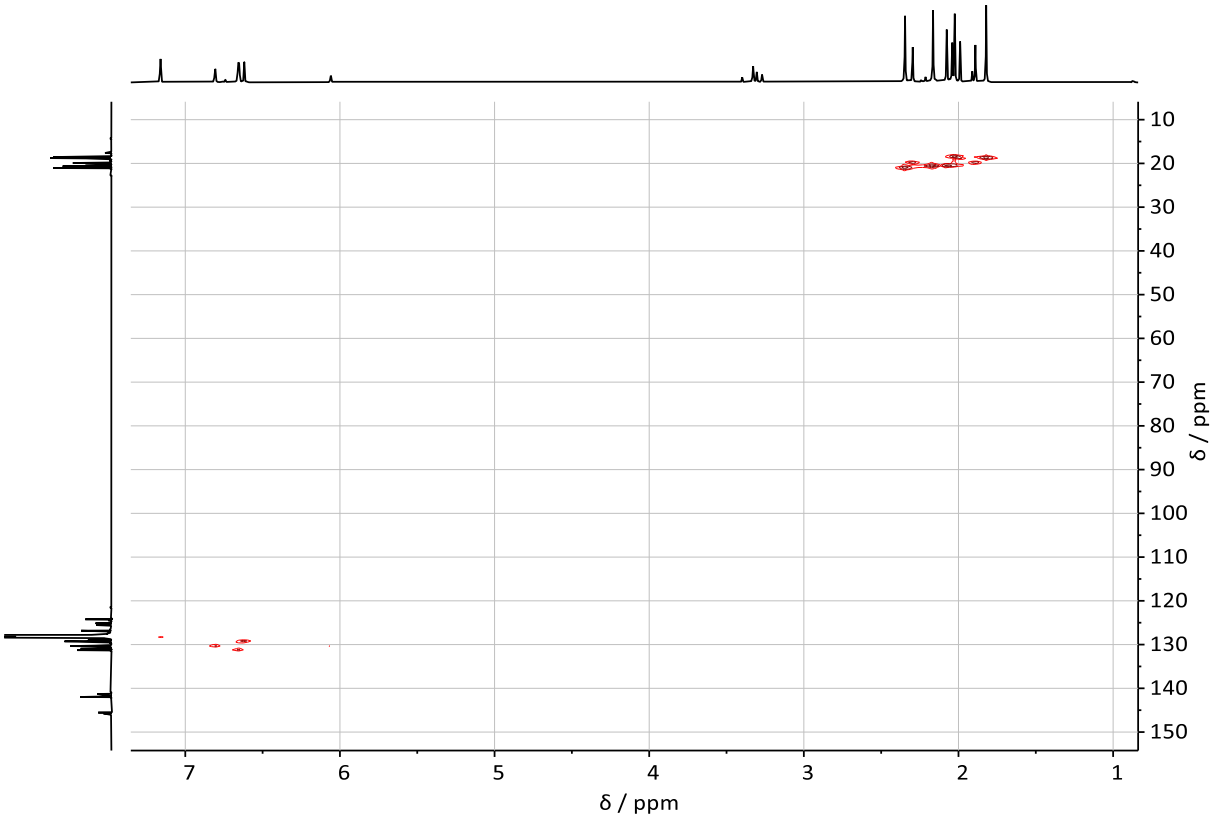

Figure S6. $^{1}H^{13}C$ HMQC NMR spectrum of $[Be(HNMes)_2]_3$ (**1**) in C_6D_6.

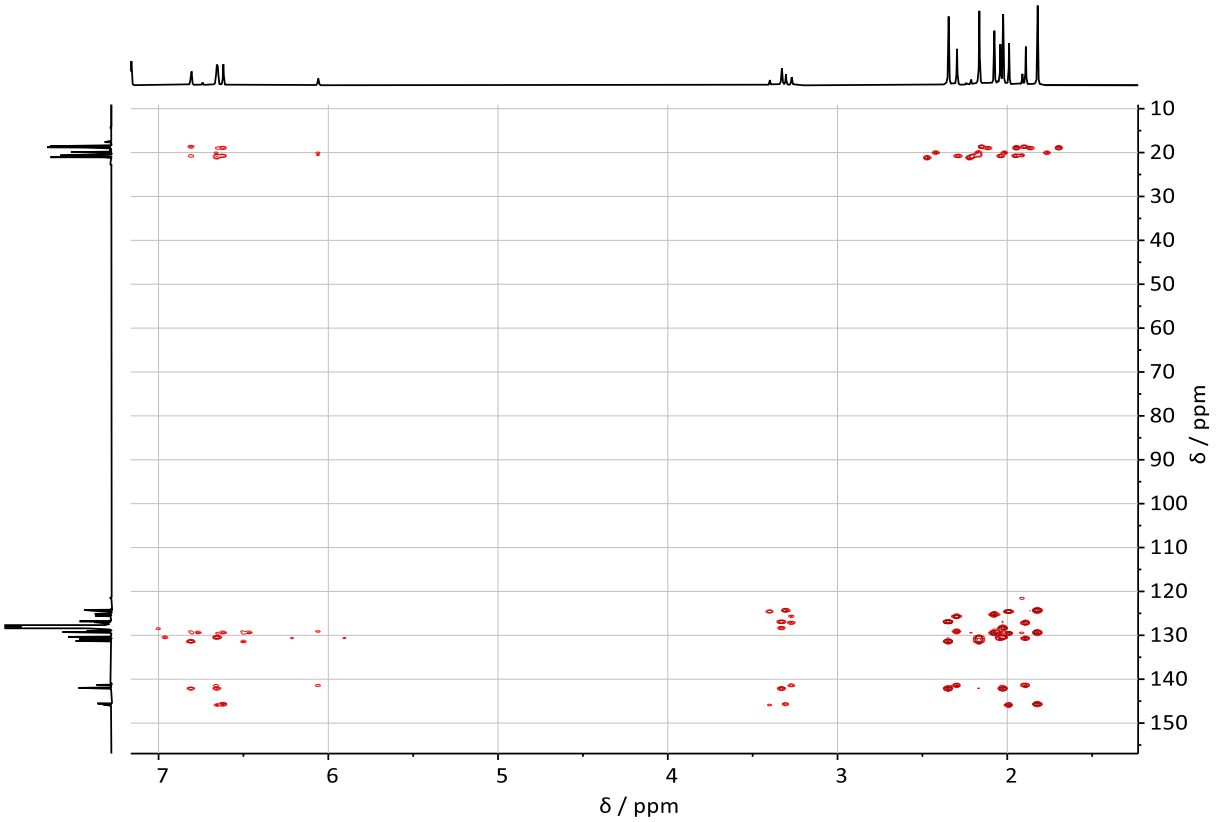

Figure S7. $^{1}H^{13}C$ HMBC NMR spectrum of $[Be(HNMes)_2]_3$ (**1**) in C_6D_6.

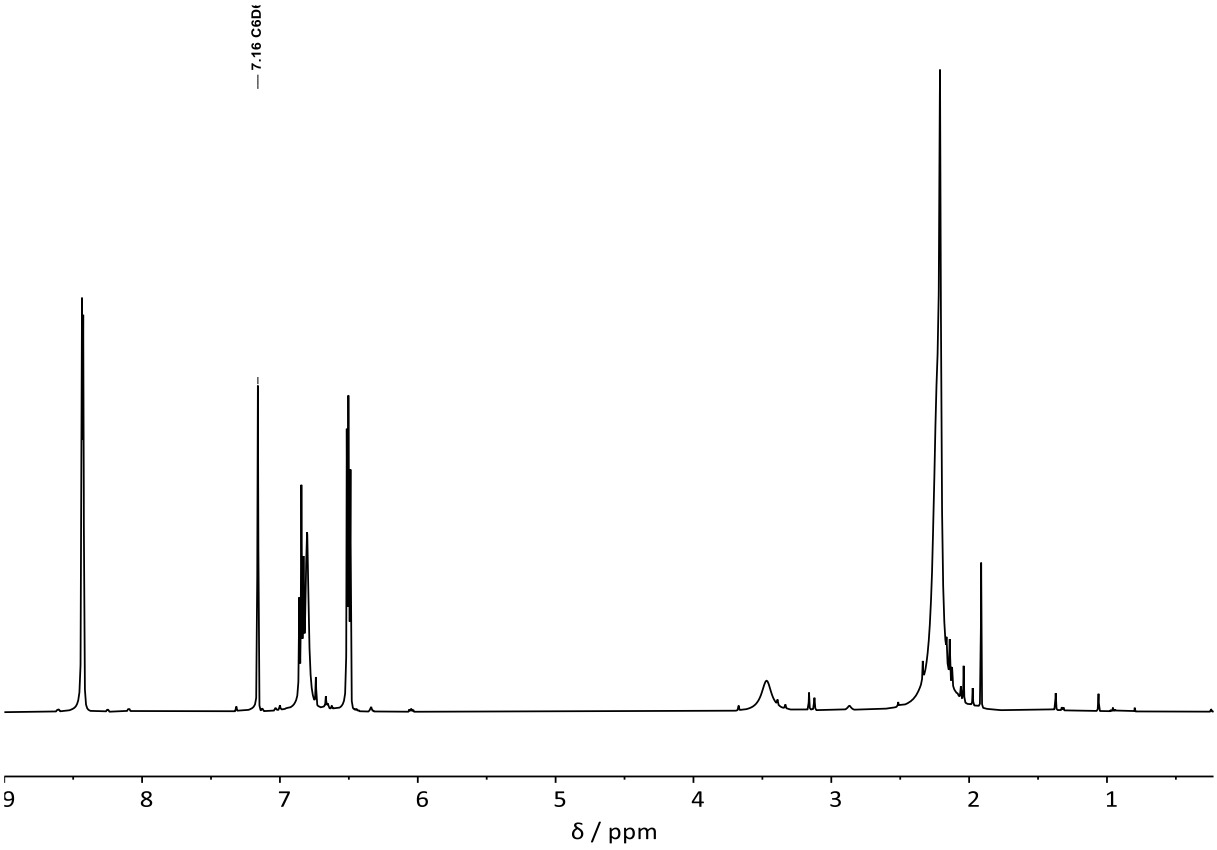

Figure S8. ^{1}H NMR spectrum of $[(py)_2Be(HNMes)_2]$ (**2**) in C_6D_6.

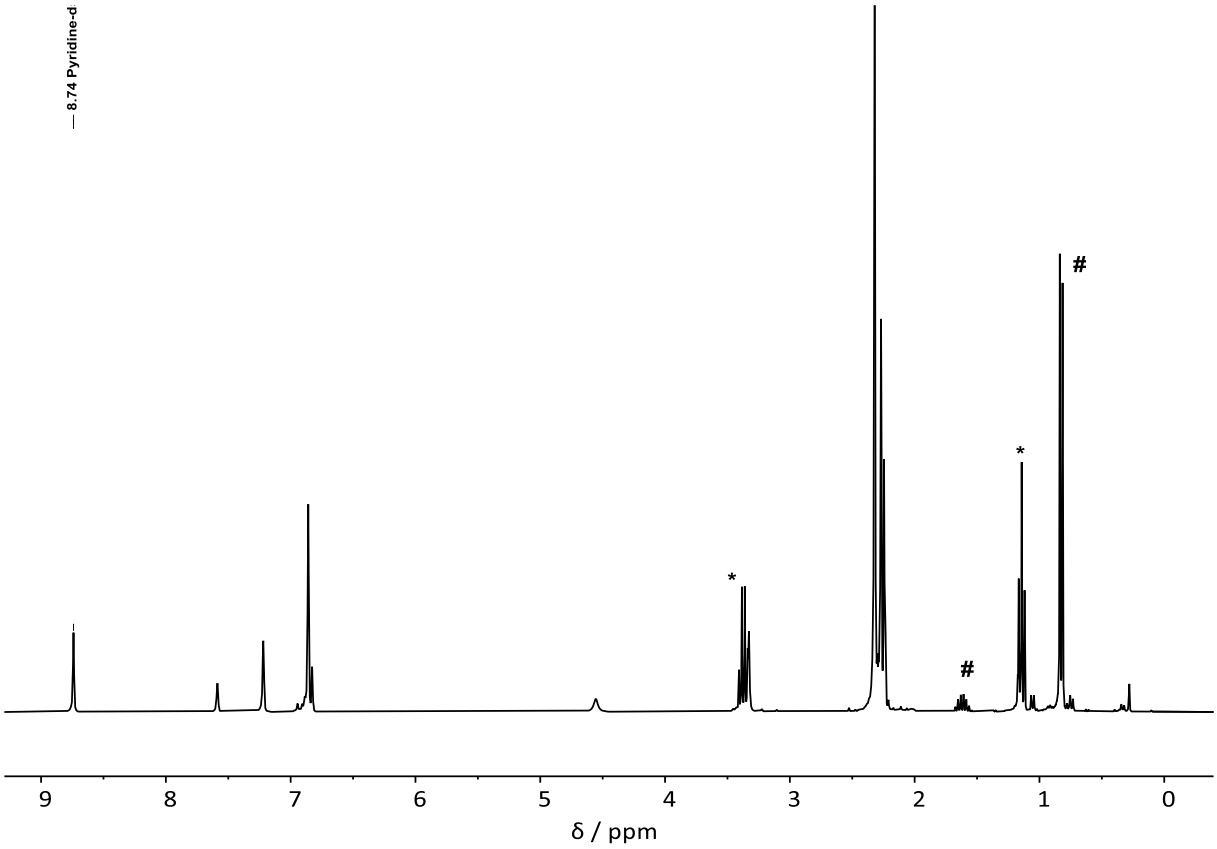

Figure S9. ^{1}H NMR spectrum of [(py)$_2$Be(HNMes)$_2$] (**2**) in py-d$_5$. The signals denoted with an asterisk originate from Et$_2$O and those marked with a hash from isobutene.

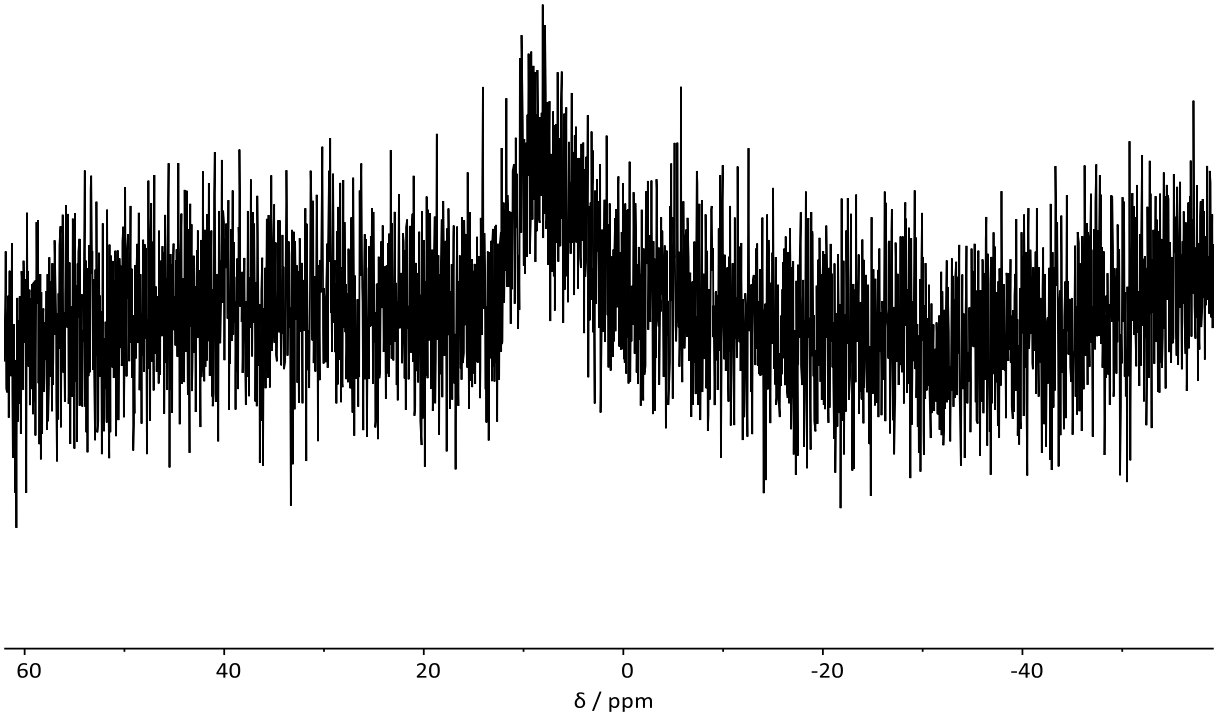

Figure S10. ^{9}Be NMR spectrum of [(py)$_2$Be(HNMes)$_2$] (**2**) in C$_6$D$_6$.

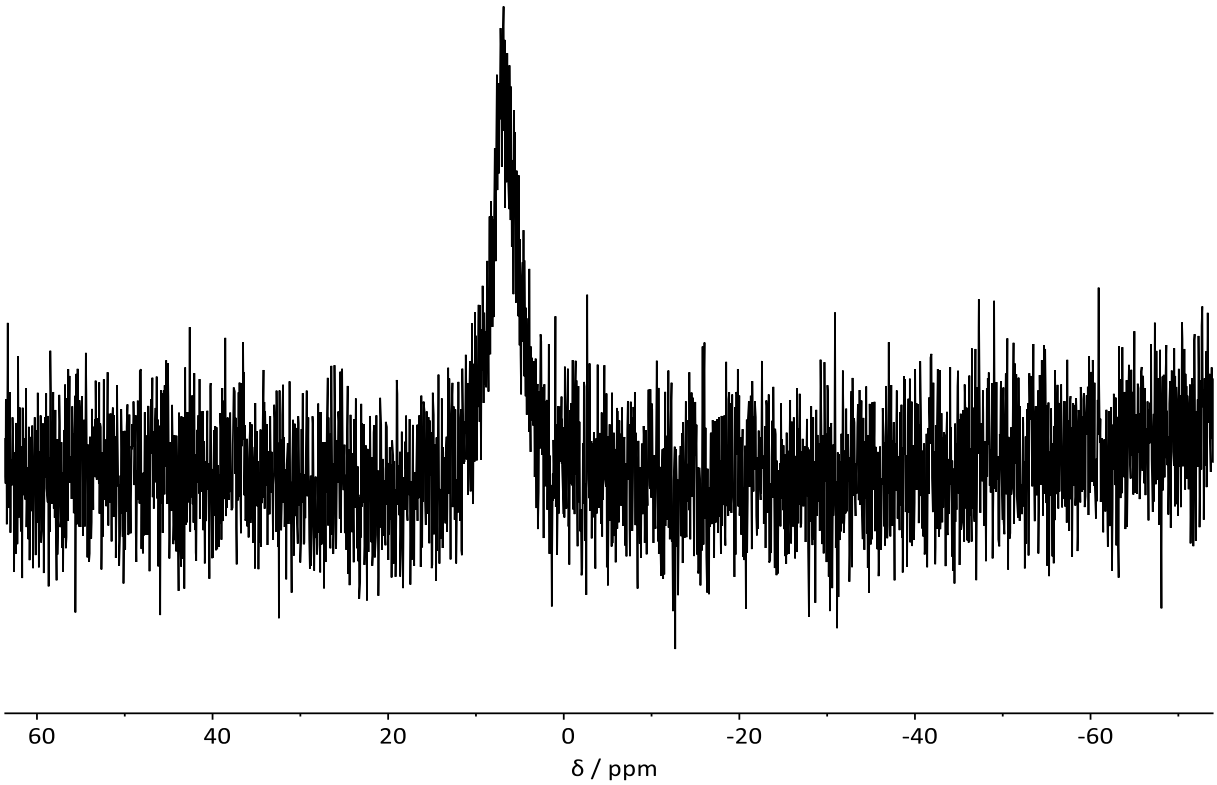

Figure S11. ^{9}Be NMR spectrum of [(py)$_2$Be(HNMes)$_2$] (**2**) in py-d$_5$.

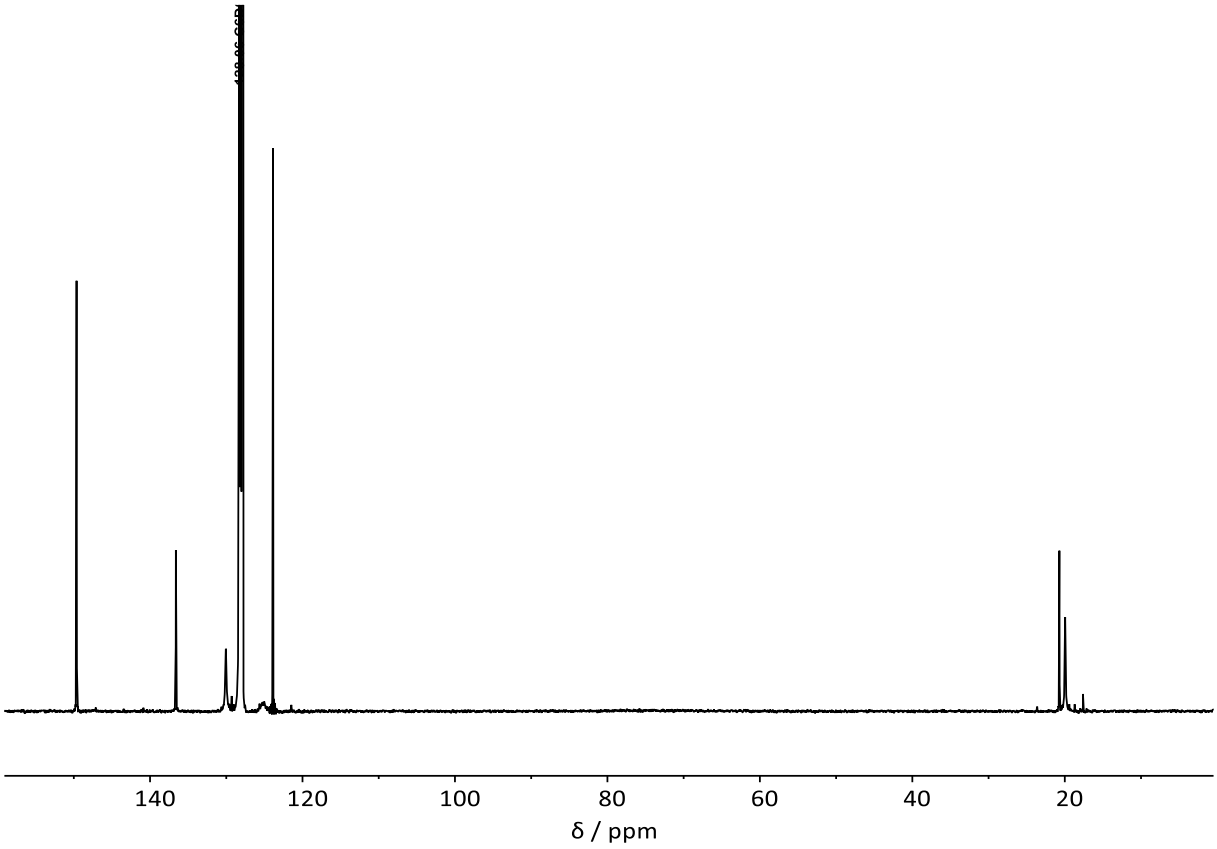

Figure S12. ^{13}C NMR spectrum of [(py)$_2$Be(HNMes)$_2$] (**2**) in C_6D_6.

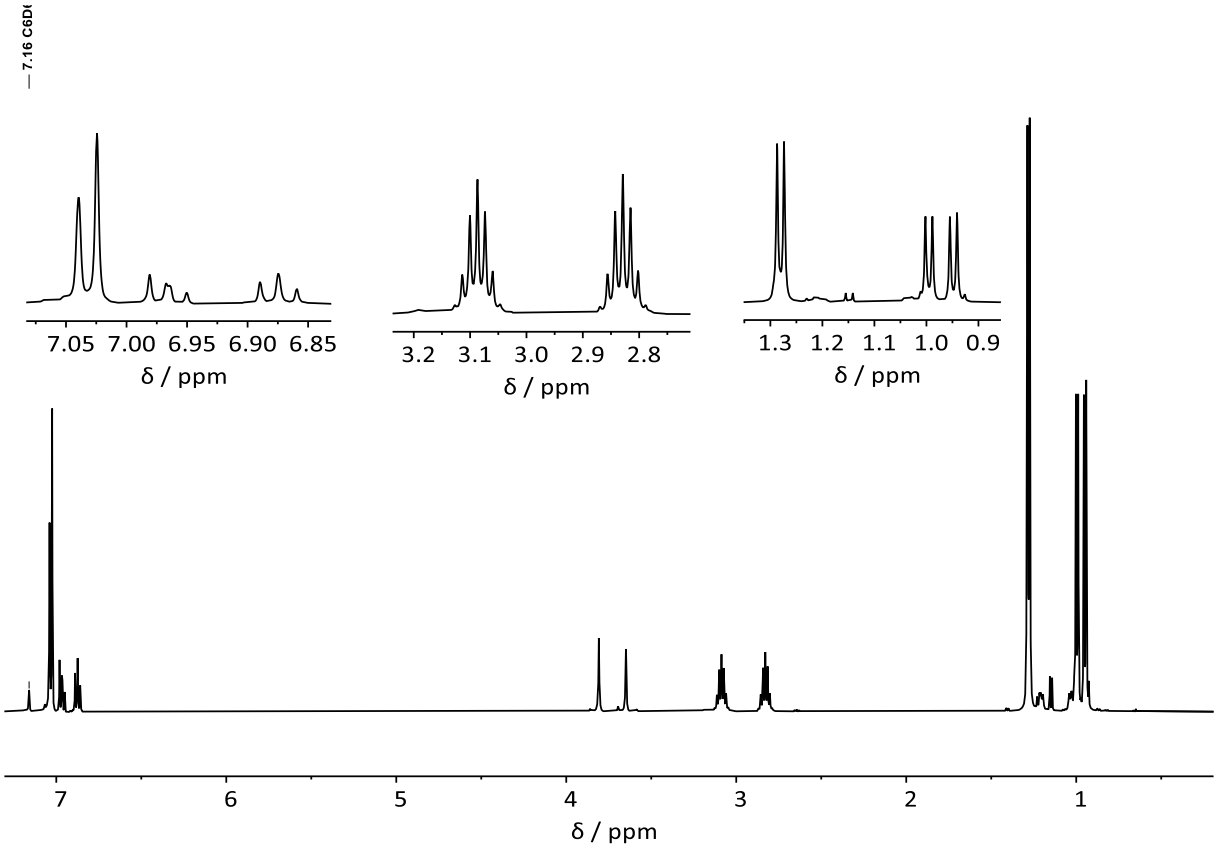

Figure S13. ^{1}H NMR spectrum of $[Be(HNDipp)_2]_2$ (**3**) in C_6D_6.

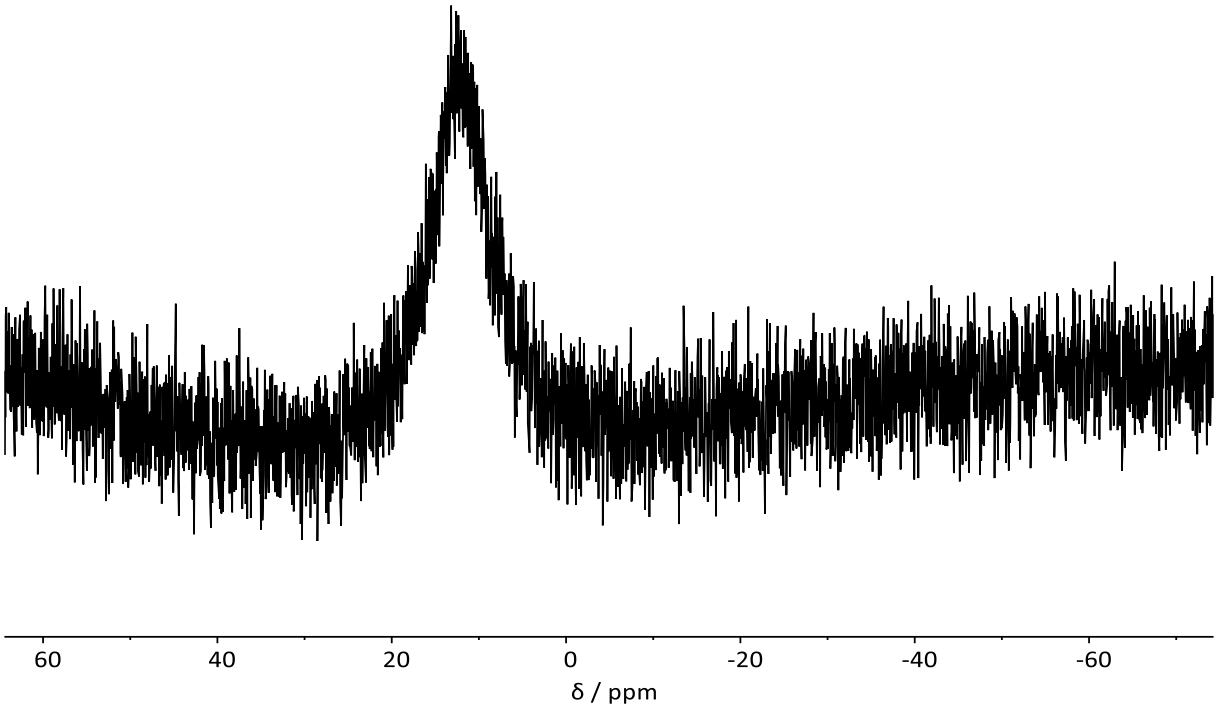

Figure S14. ^{9}Be NMR spectrum of $[Be(HNDipp)_2]_2$ (**3**) in C_6D_6.

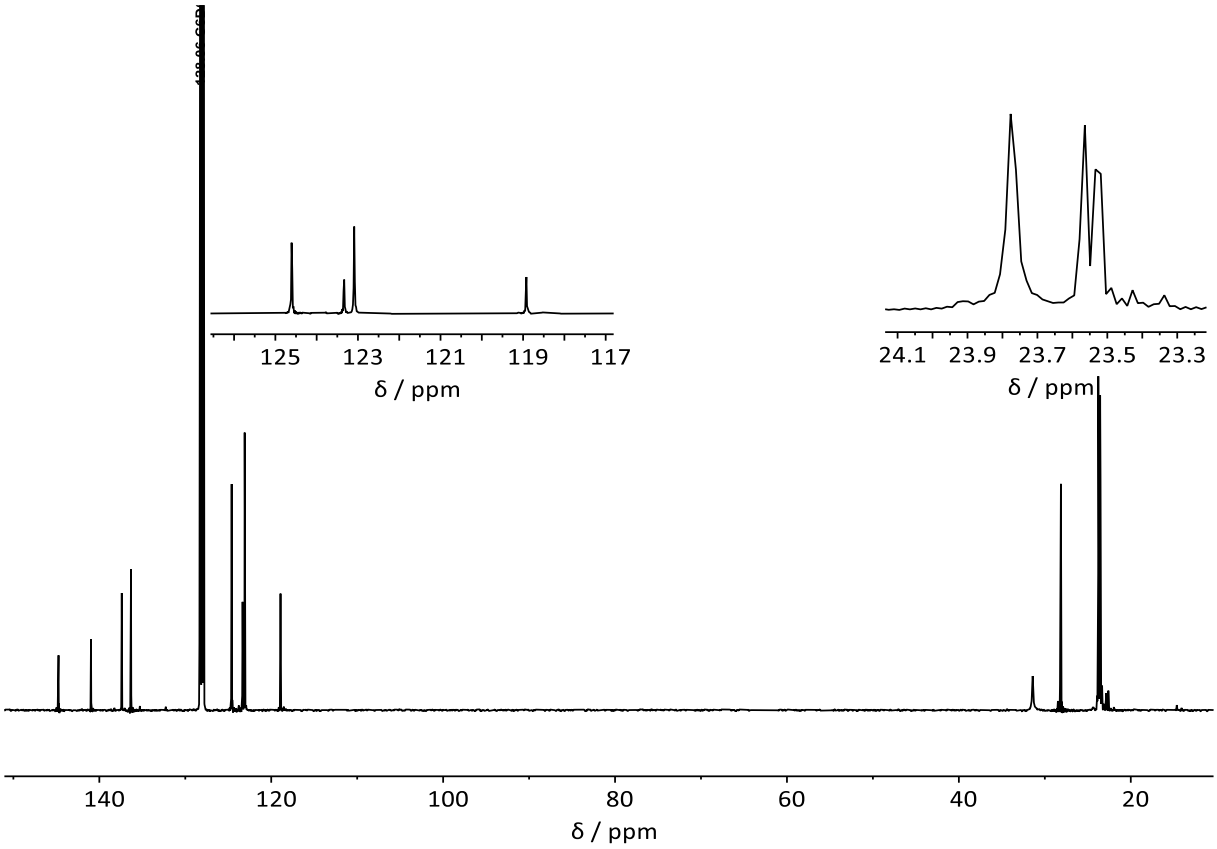

Figure S15. ^{13}C NMR spectrum of $[Be(HNDipp)_2]_2$ (**3**) in C_6D_6.

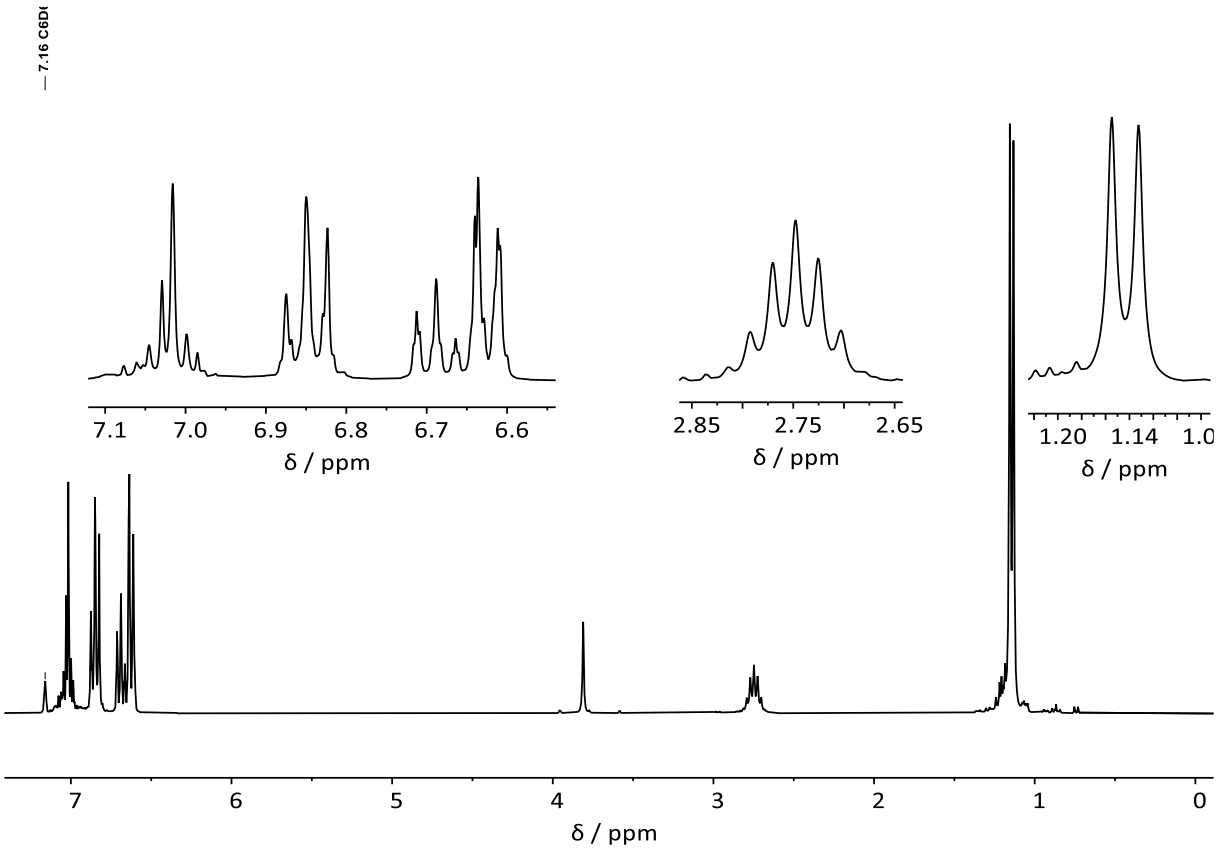

Figure S16. ^{1}H NMR spectrum of $[Be(NPh_2)(\mu_2\text{-}HNDipp)]_2$ (**4**) in C_6D_6.

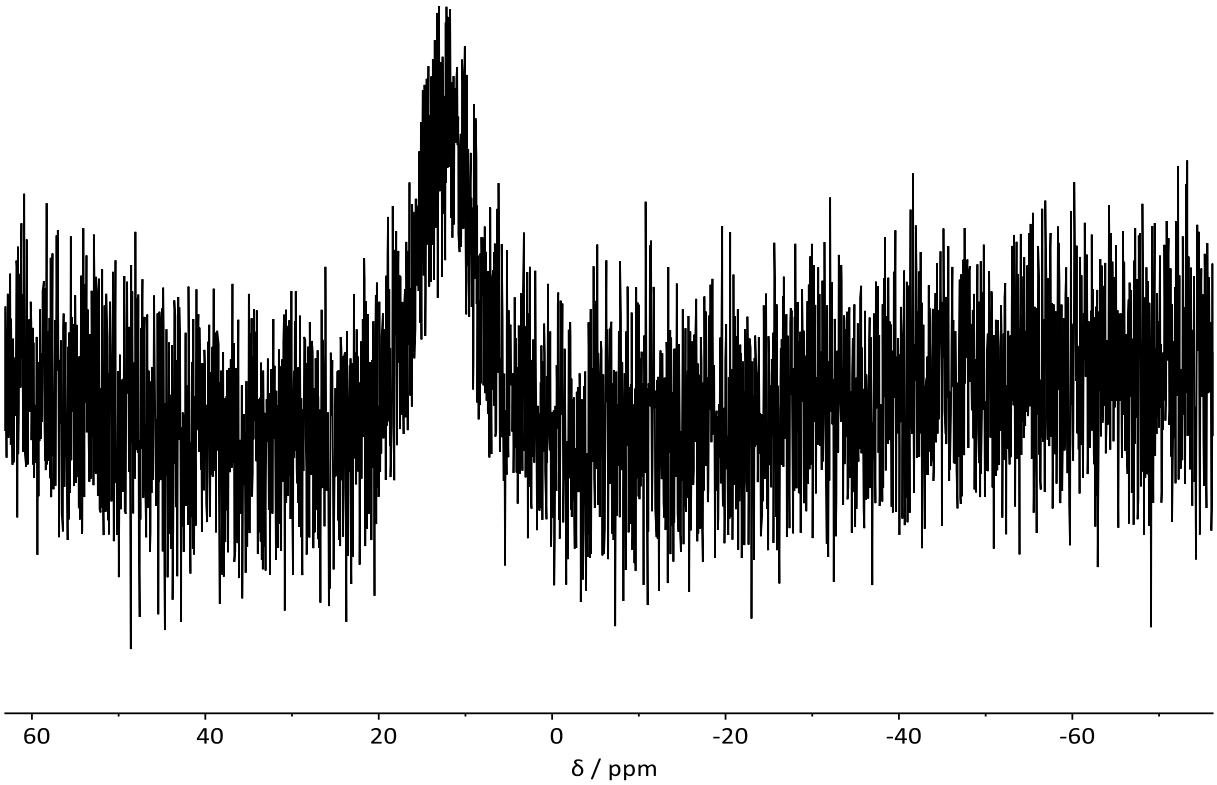

Figure S17. ^{9}Be NMR spectrum of $[Be(NPh_2)(\mu_2\text{-}HNDipp)]_2$ (**4**) in C_6D_6.

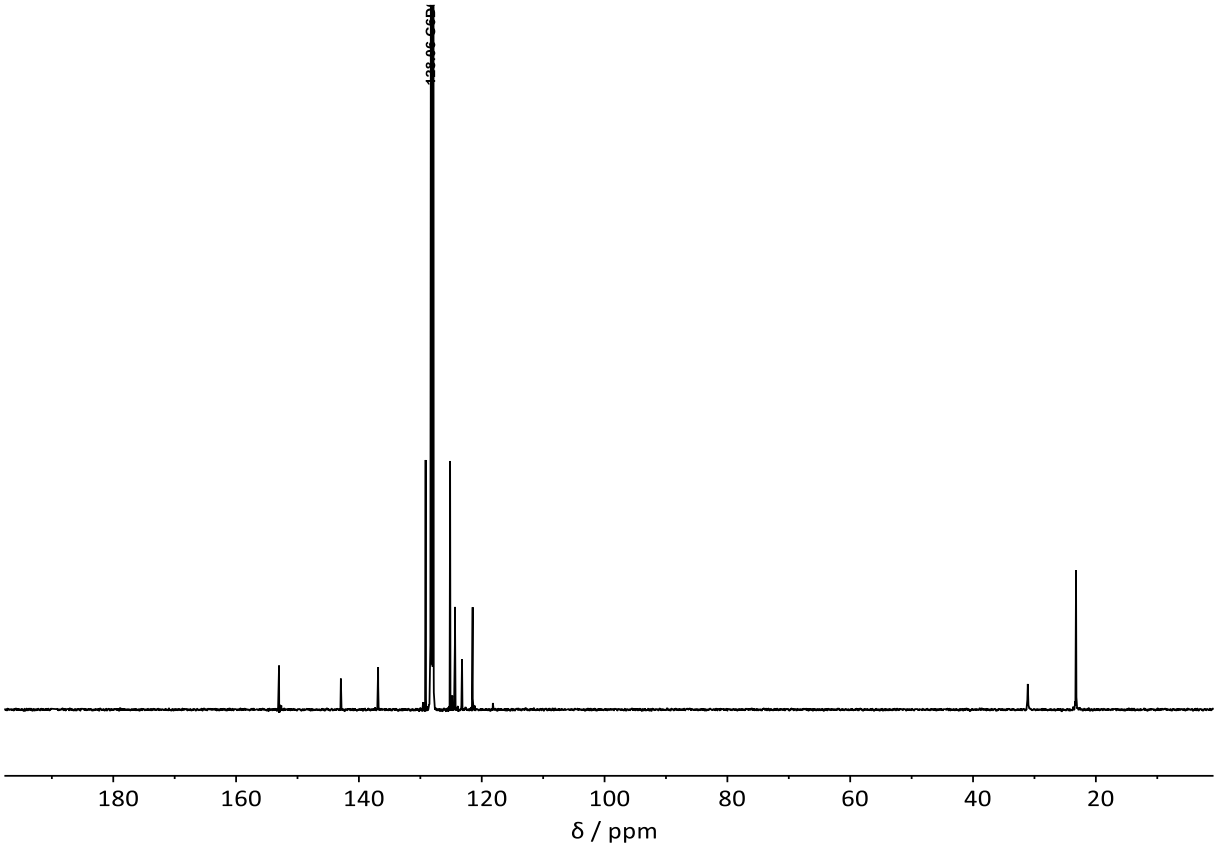

Figure S18. ^{13}C NMR spectrum of $[Be(NPh_2)(\mu_2\text{-}HNDipp)]_2$ (**4**) in C_6D_6.

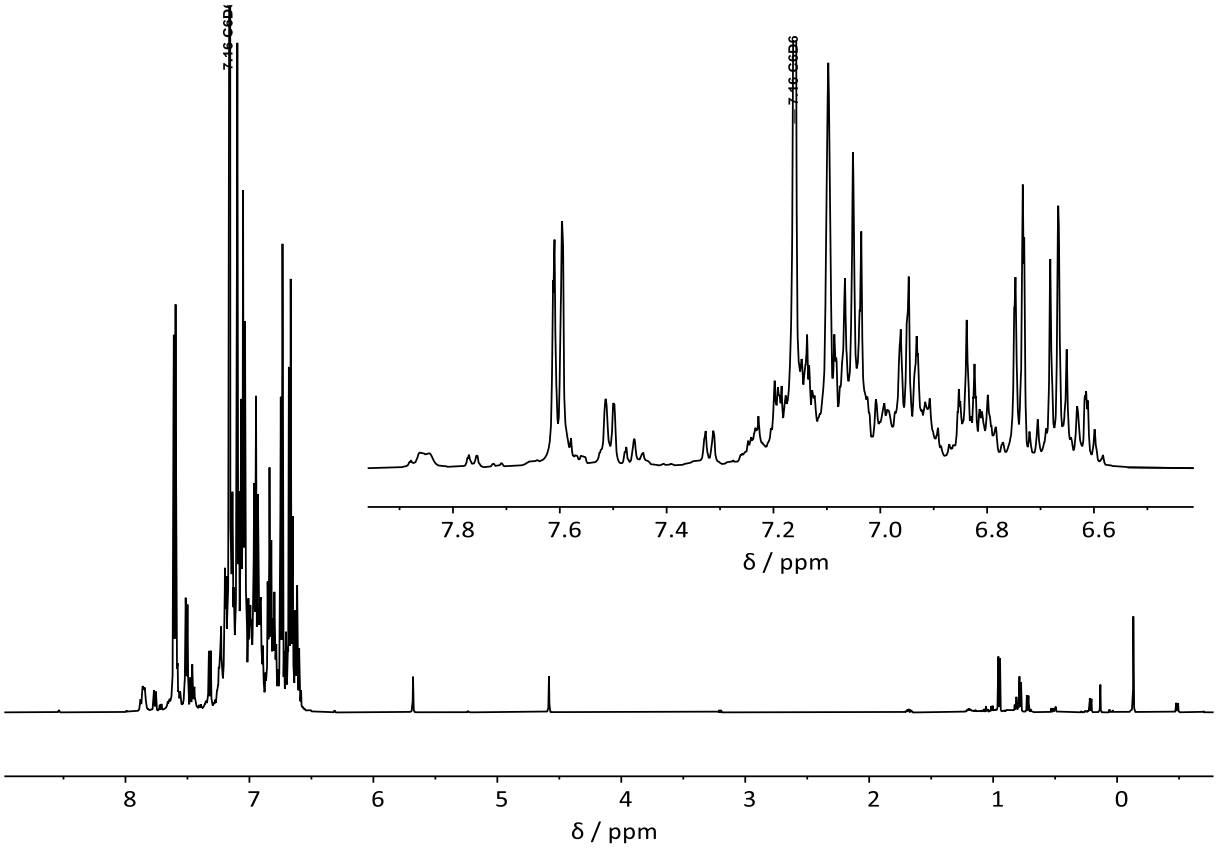

Figure S19. ^{1}H NMR spectrum of $[Be(NCPh_2)_2]_3$ (**5**) in C_6D_6.

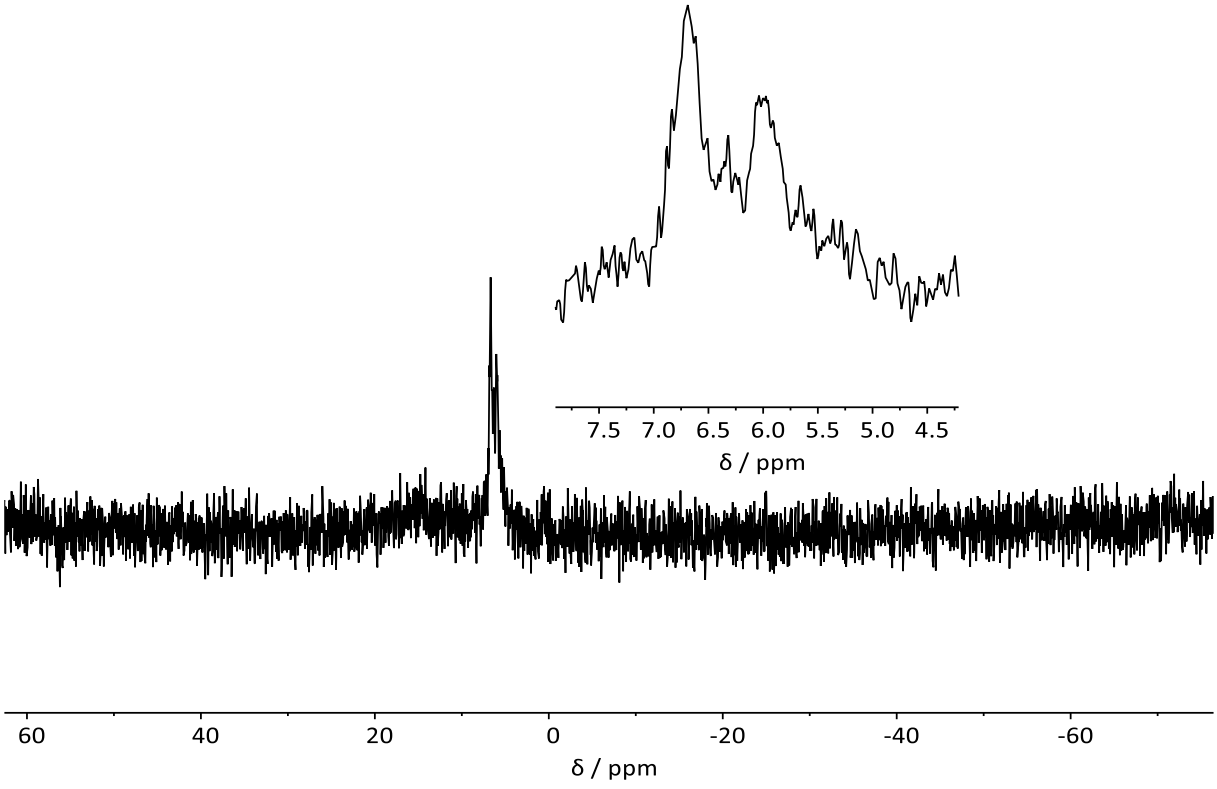

Figure S20. ^{9}Be NMR spectrum of $[Be(NCPh_2)_2]_3$ (**5**) in C_6D_6.

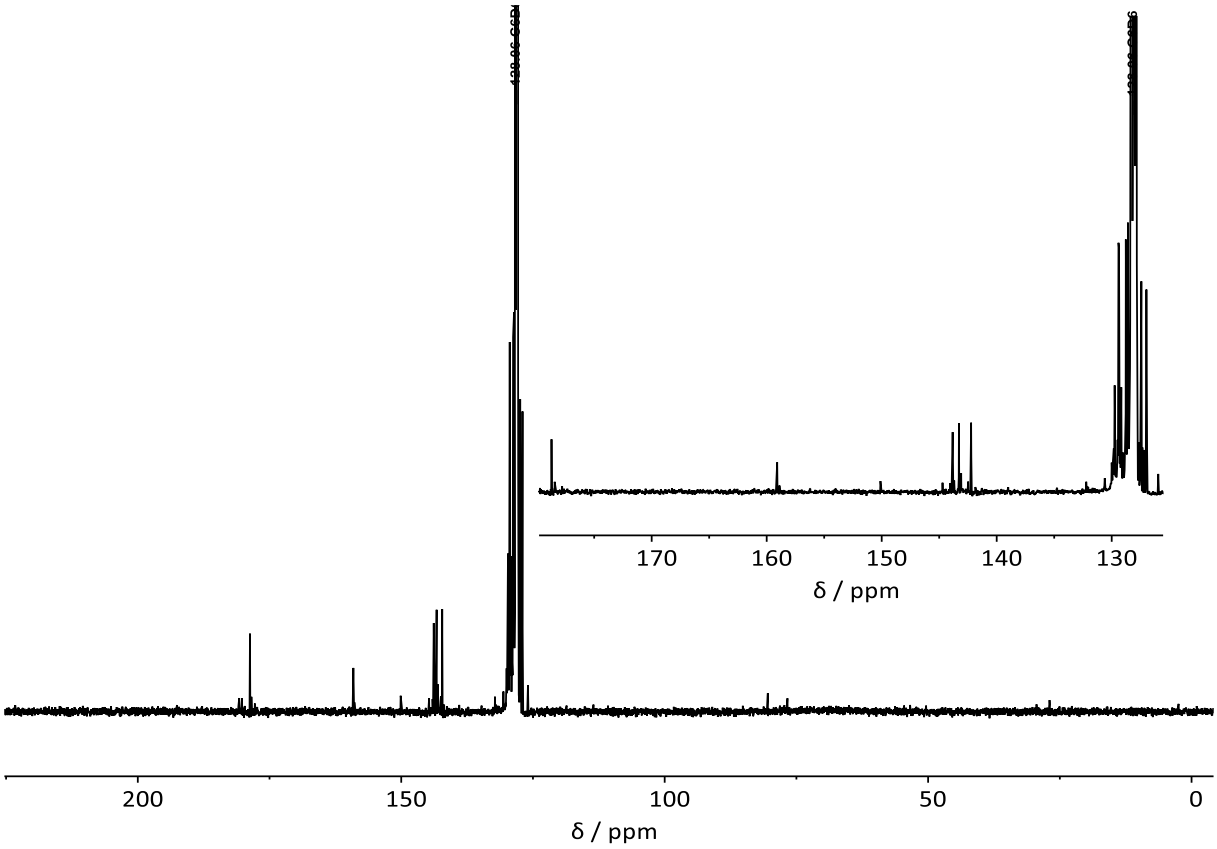

Figure S21. ^{13}C NMR spectrum of $[Be(NCPh_2)_2]_3$ (**5**) in C_6D_6.

IR Spectra

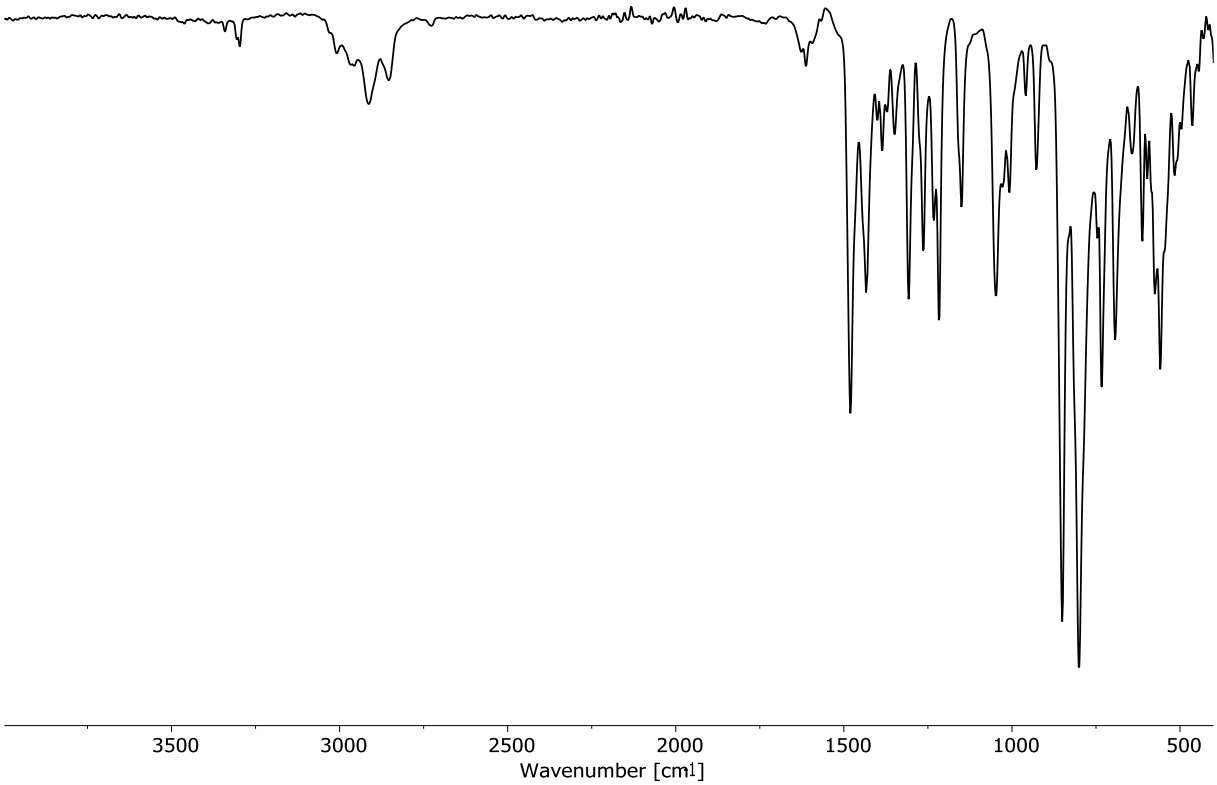

Figure S22. IR spectrum of $[Be(HNMes)_2]_3$ (**1**).

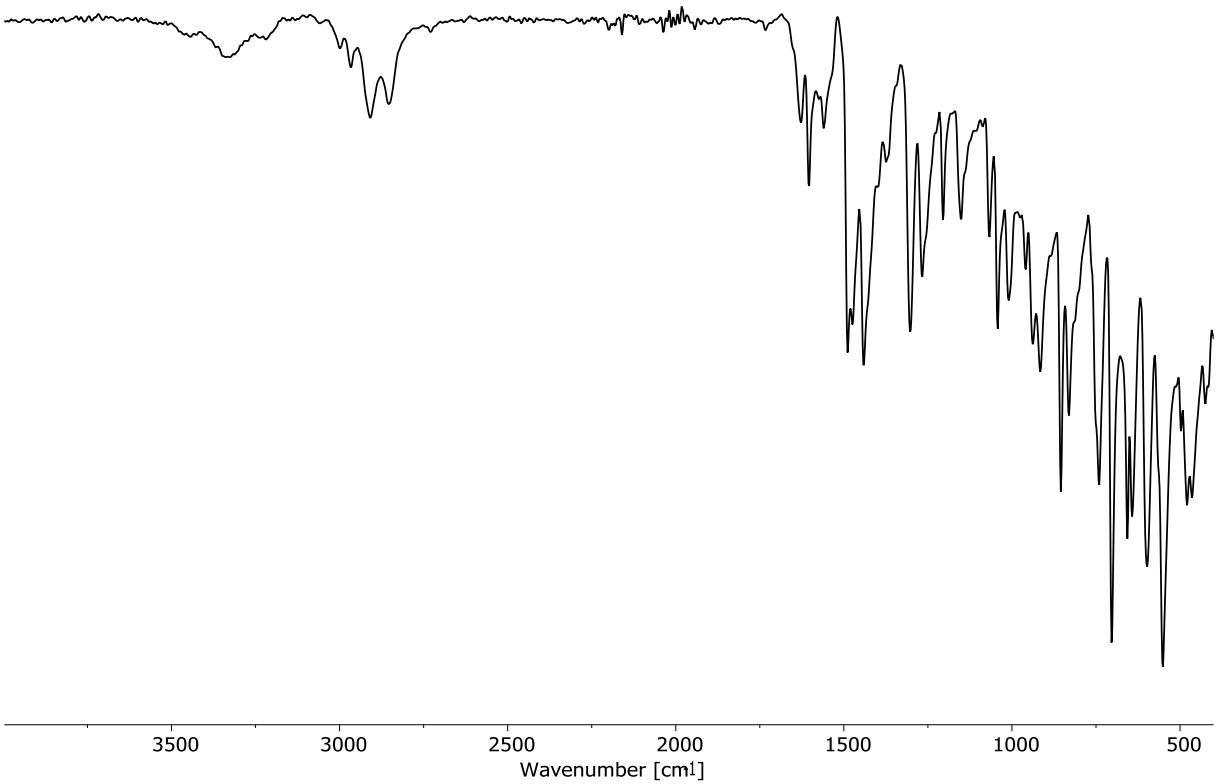

Figure S23. IR spectrum of $[(py)_2Be(HNMes)_2]$ (**2**).

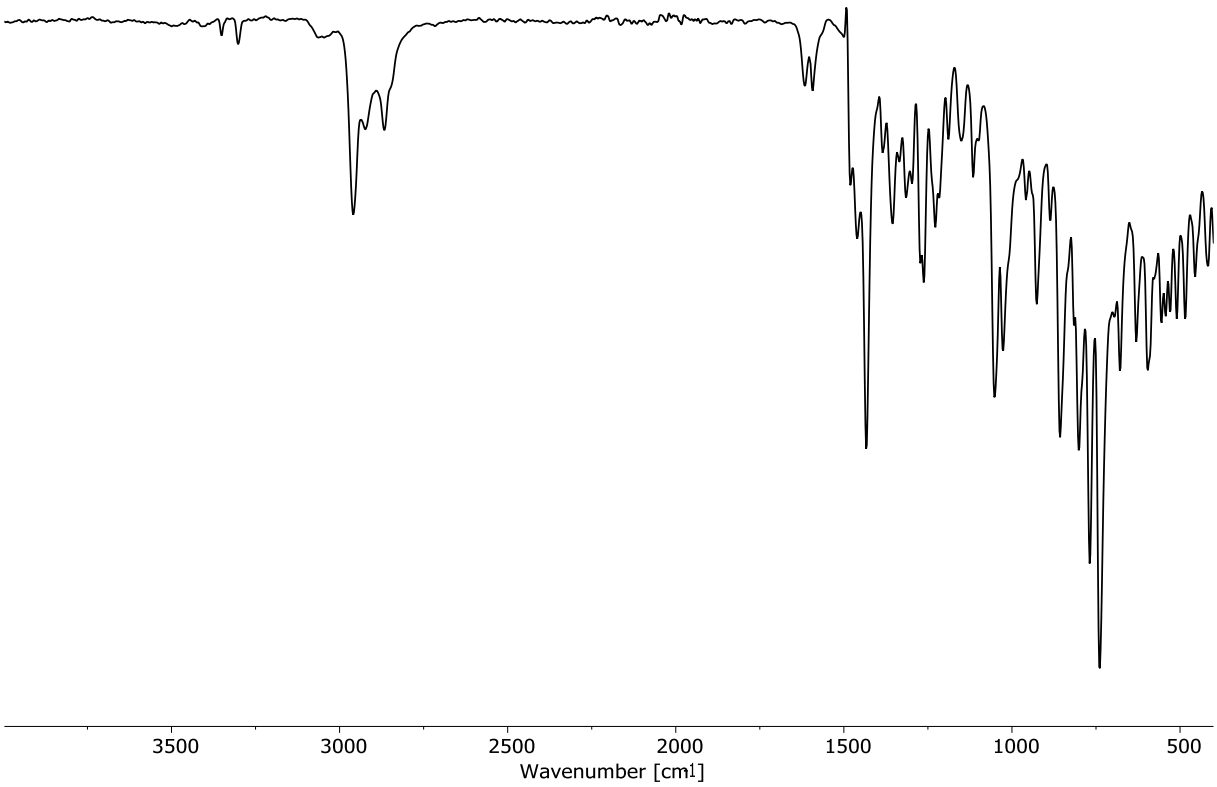

Figure S24. IR spectrum of $[Be(HNDipp)_2]_2$ (**3**).

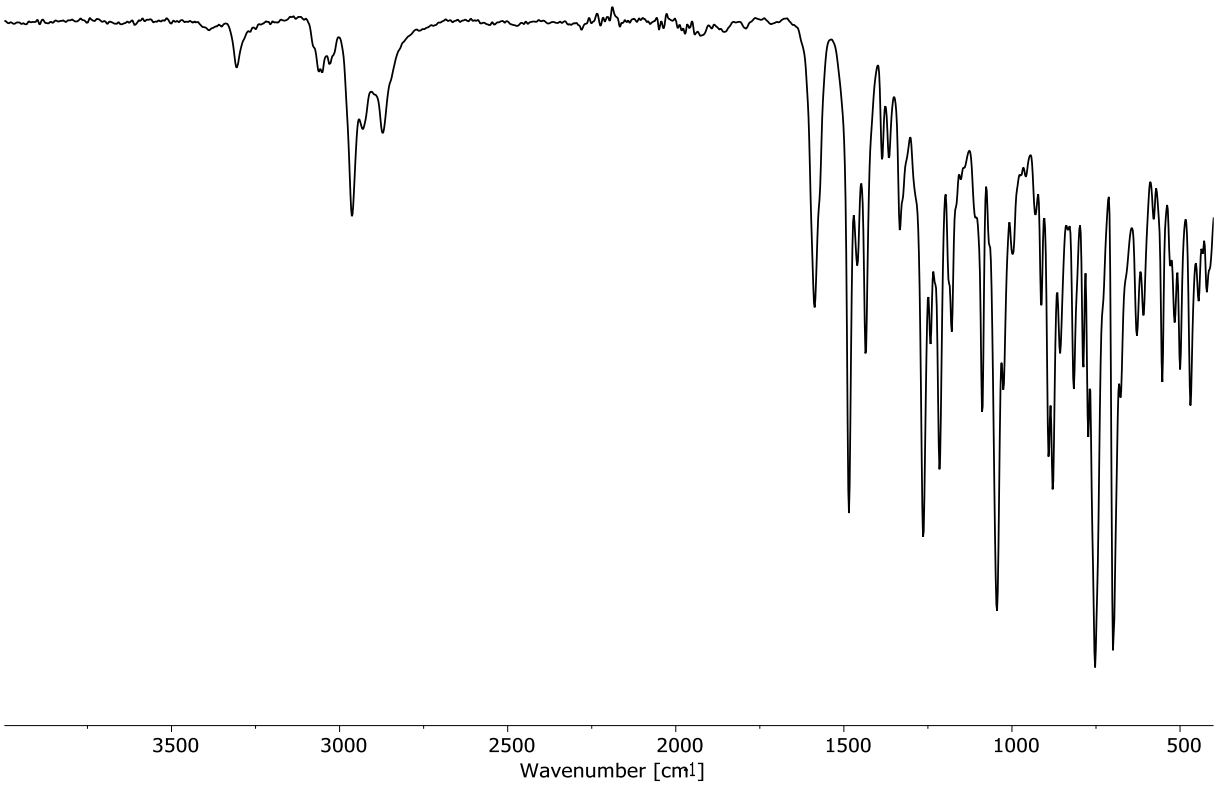

Figure S25. IR spectrum of $[Be(NPh_2)(\mu_2\text{-}HNDipp)]_2$ (**4**).

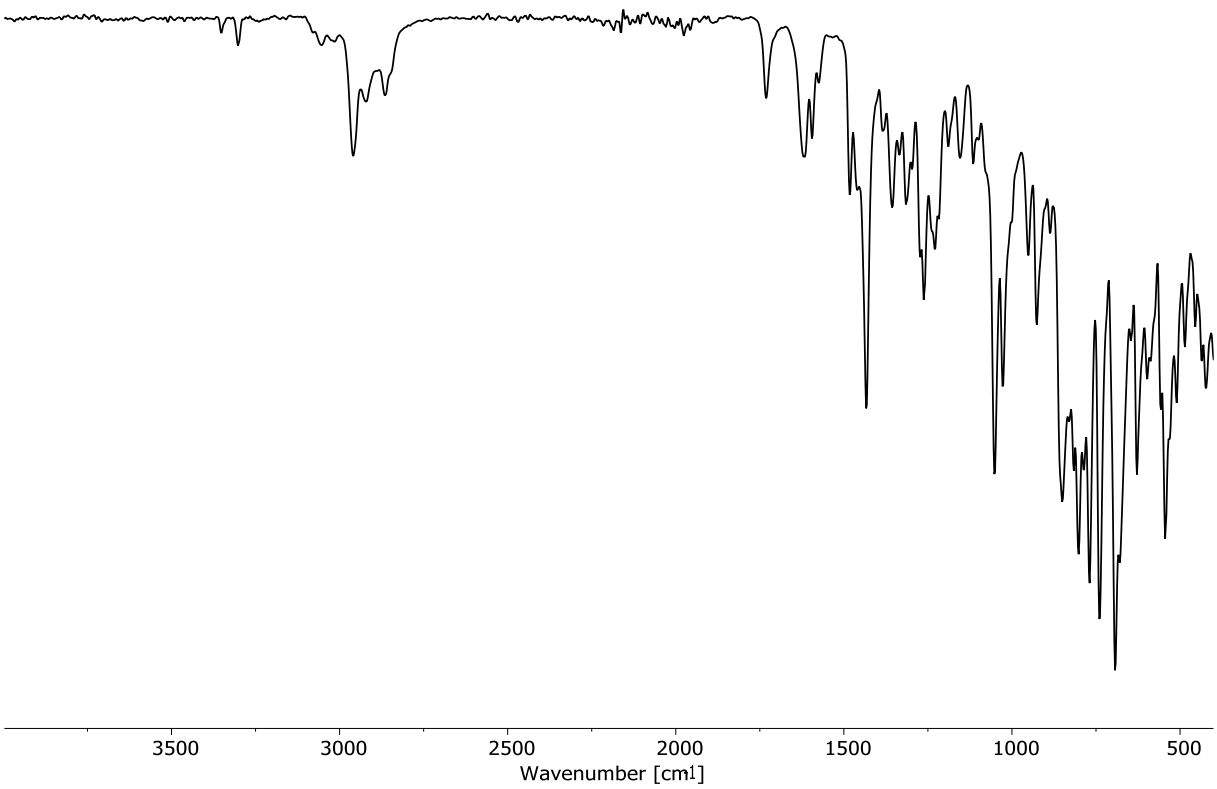

Figure S26. IR spectrum of $[Be(NCPh_2)_2]_3$ (**5**).

Computational results

IAO atomic charges

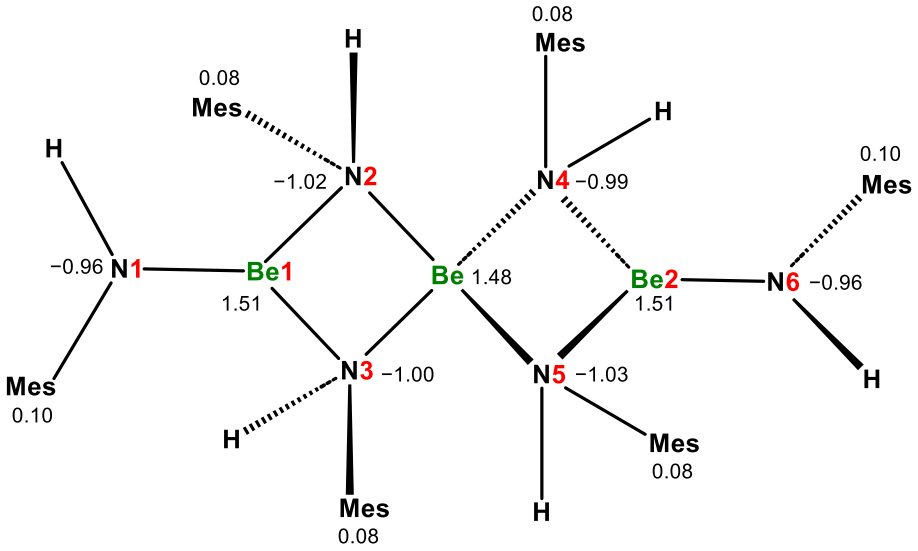

Figure S27. Lewis structure with IAO atomic charge analysis partial charges of selected atoms of complex **1**. The partial charges that are adjacent to the Mes label correspond to the C–N carbon atom.

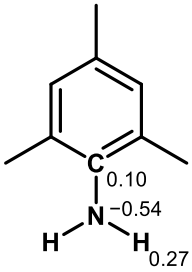

Figure S28. Lewis structure with IAO atomic charge analysis partial charges of selected atoms of free H_2NMes. Due to symmetry, the partial charge of the unlabeled amine proton is the same as that of the labeled proton.

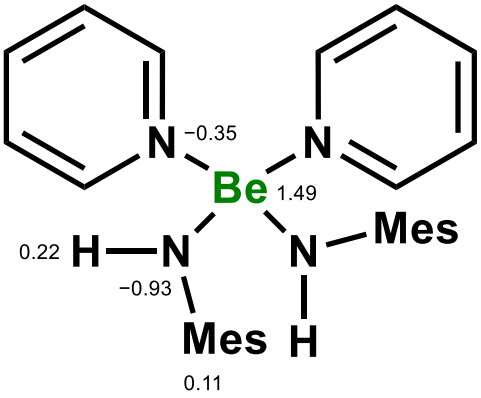

Figure S29. Lewis structure with IAO atomic charge analysis partial charges of selected atoms of complex **2**. The partial charges that are adjacent to the Mes label correspond to the C-N carbon atom. Due to symmetry partial charge of the same ligands are equal.

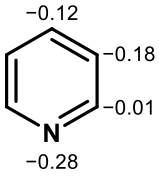

Figure S30. Lewis structure with IAO atomic charge analysis partial charges of selected atoms of free pyridine. Due to symmetry, the partial charges of unlabeled carbon atoms are not given and are equal to the with a mirror symmetry operation connected carbon atoms.

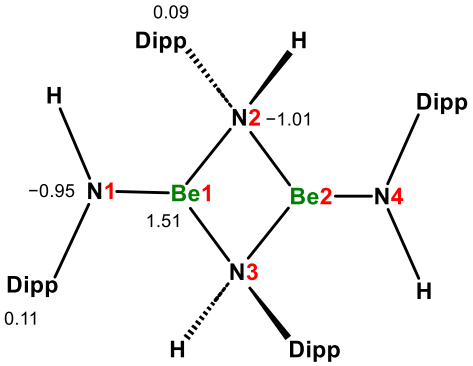

Figure S31. Lewis structure with IAO atomic charge analysis partial charges of selected atoms of complex **3**. The partial charges that are adjacent to the Dipp label correspond to the C-N carbon atom. Due to symmetry partial charge of Be1/Be2, N1/N2 and N2/N3 are equal.

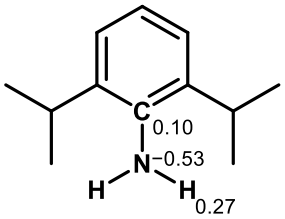

Figure S32. Lewis structure with IAO atomic charge analysis partial charges of selected atoms of free H_2NDipp. Due to symmetry, the partial charge of the unlabeled amine proton is the same as that of the labeled proton.

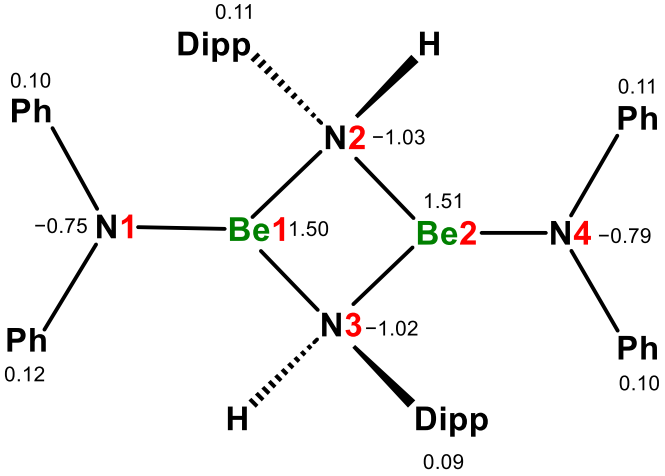

Figure S33. Lewis structure with IAO atomic charge analysis partial charges of selected atoms of complex **4**. The partial charges that are adjacent to the Dipp label correspond to the C-N carbon atom.

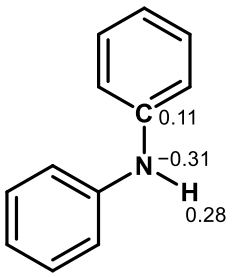

Figure S34. Lewis structure with IAO atomic charge analysis partial charges of selected atoms of free $HNPh_2$. Due to symmetry, the partial charges of unlabeled carbon atoms are not given and are equal to the with a mirror symmetry operation connected carbon atoms.

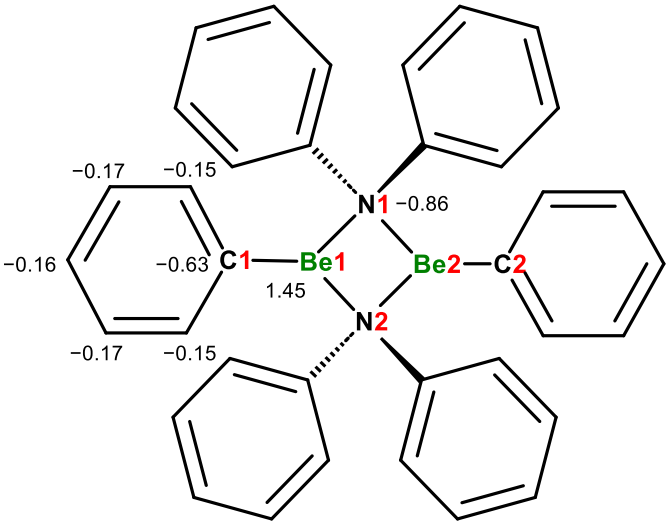

Figure S35. Lewis structure with IAO atomic charge analysis partial charges of selected atoms of $[(NPh_2)BePh]_2$. Due to symmetry partial charge of Be1/Be2, N1/N2 and C1/C2 are equal.

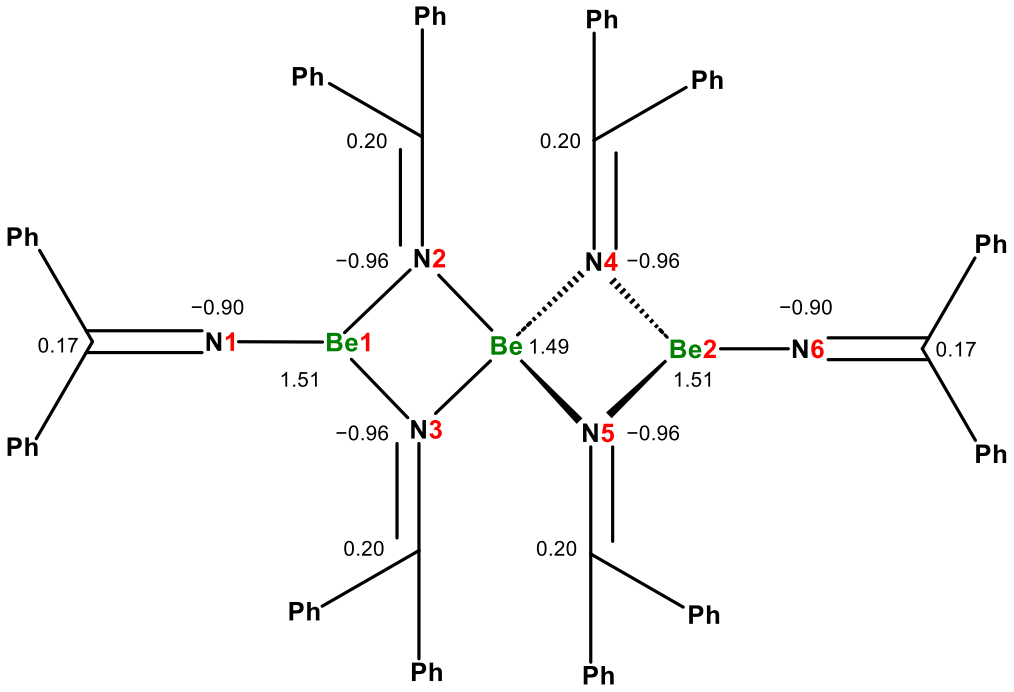

Figure S36. Lewis structure with IAO atomic charge analysis partial charges of selected atoms of complex **5**.

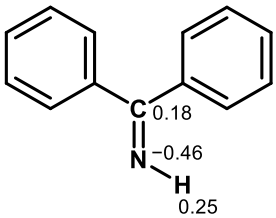

Figure S37. Lewis structure with IAO atomic charge analysis partial charges of selected atoms of free $HNCPh_2$.

LMO analysis

Table S3: Comparison of the orbital contribution in the LMO bonding analysis of complex **1**, **Fig. 4 a, b**. Orbital contribution below 2% are not listed. Labelling scheme according to figure 3.

Bond	Atom + total contribution to LMO	s/p orbital contribution
2 x σ Be–N	N1/6 62%	N 27% 2s, 35% 2p
	Be1/3 38%	Be 15% 2s, 21% 2p
2 x π Be–N	N1/6 89%	N 89% 2p
	Be1/3 11%	Be 8% 2p

Table S4: Comparison of the orbital contribution in the LMO bonding analysis of complex **1**, **Fig. 6 c**. Orbital contribution below 2% are not listed. Labelling scheme according to figure 3.

Bond	Atom + total contribution to LMO	s/p orbital contribution
2e3c σ Be–N–Be	N3 55%	N 16% 2s, 39% 2p
	Be2 25%	Be 4% 2s, 18% 2p
	Be1 20%	Be1 5% 2s, 12% 2p
2e3c σ Be–N–Be	N2 57%	N 19% 2s, 38% 2p
	Be2 29%	Be 8% 2s, 18% 2p
	Be1 14%	Be1 10% 2p
2e3c σ Be–N–Be	N5 56%	N 18% 2s, 38% 2p
	Be2 30%	Be 7% 2s, 20% 2p
	Be3 14%	Be2 10% 2p
2e3c σ Be–N–Be	N4 56%	N 17% 2s, 39% 2p
	Be2 23%	Be 5% 2s, 15% 2p
	Be3 21%	Be2 6% 2s, 12% 2p

Table S5: Comparison of the orbital contribution in the LMO bonding analysis of complex **1**, **Fig. 6 d**. Orbital contribution below 2% are not listed. Labelling scheme according to figure 3.

Bond	Atom + total contribution to LMO	s/p orbital contribution
2e3c π Be–N–Be	N4 83%	N 82% 2p
	Be2 8%	Be 8% 2p
	Be3 9%	Be2 6% 2p
2e3c π Be–N–Be	N3 82%	N 81% 2p
	Be2 9%	Be 8% 2p
	Be1 9%	Be1 6% 2p
2 x Be–N	N2/5 87%	N 86% 2p
	Be1/3 13%	Be 5% 2s, 8% 2p

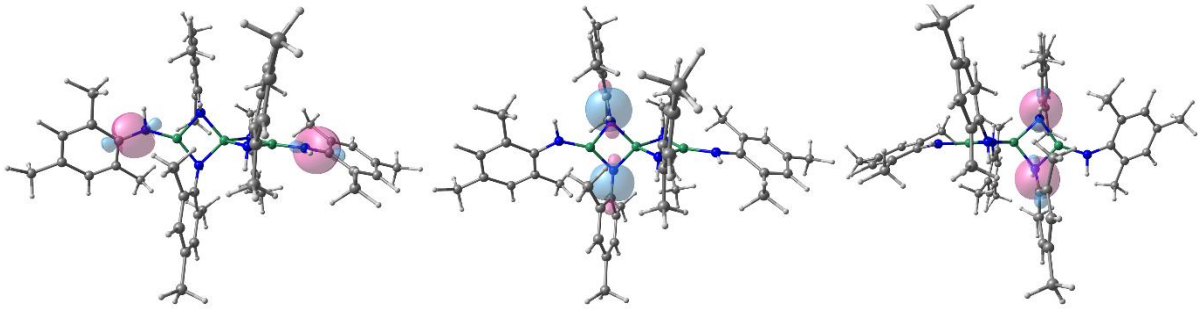

Figure S38. Three sets of LMOs of **1**. Two σ−type LMOs (left) for terminal C–N bond and four σ−type LMOs (middle, right) for central C–N bond. The contour value for LMO isosurface plots is 0.05 a.u. Be: green, N: blue, C: grey, H: white. Red positive phase, blue negative phase.

Table S6: Comparison of the orbital contribution in the LMO bonding analysis of complex **1** in the C–N bond. Orbital contribution below 2% are not listed. Labelling scheme according to figure 3.

Bond	Atom + total contribution to LMO	s/p orbital contribution
2 x σ N−C terminal	N1/6 50%	N 22% 2s, 28% 2p
	C 50%	C 17% 2s, 32% 2p
σ N−C	N3 56%	N 22% 2s, 34% 2p
	C 44%	C 15% 2s, 29% 2p
σ N−C	N2 57%	N 22% 2s, 34% 2p
	C 53%	C 14% 2s, 29% 2p
σ N−C	N5 56%	N 22% 2s, 34% 2p
	C 44%	C 14% 2s, 28% 2p
σ N−C	N4 55%	N 21% 2s, 34% 2p
	C 45%	C 14% 2s, 29% 2p

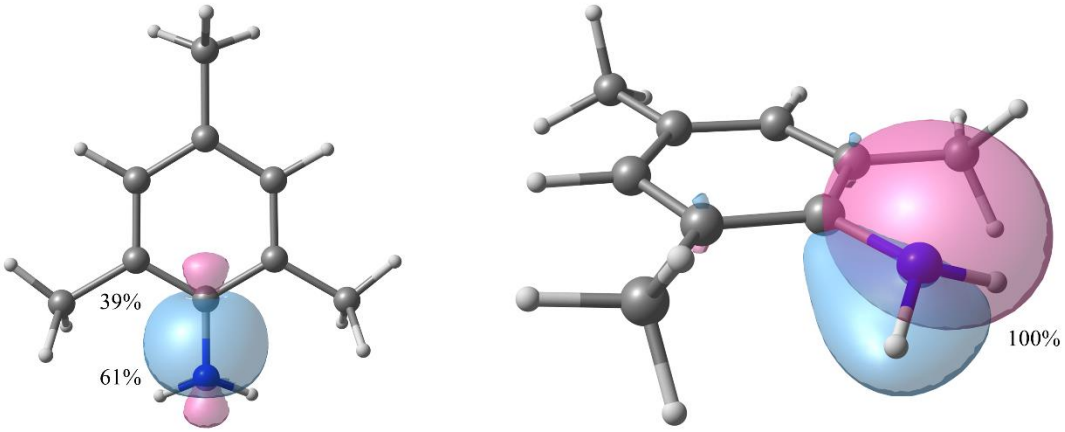

Figure S39. Two LMOs of H_2NMes. One σ−type LMOs (left) and one π−lone pair LMOs (right) for C–N bond of free H_2NMes. The contour value for LMO isosurface plots is 0.05 a.u. N: blue, C: grey, H: white. Red positive phase, blue negative phase.

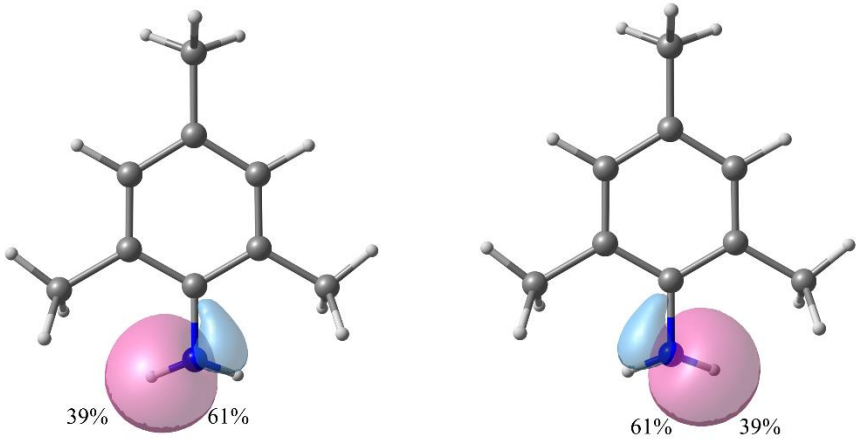

Figure S40. Two LMOs of H_2NMes.Two σ−type LMOs for C–H bond of free H_2NMes. The contour value for LMO isosurface plots is 0.05 a.u. N: blue, C: grey, H: white. Red positive phase, blue negative phase.

Table S7: Comparison of the orbital contribution in the LMO bonding analysis of free H_2NMes. Orbital contribution below 2% are not listed.

Bond	Atom + total contribution to LMO	s/p orbital contribution
σ N−C	N 39%	N 22% 2s, 38% 2p
	C 61%	C 6% 2s, 32% 2p
π−lone pair N	N 100%	N 13% 2s, 87% 2p
2 x σ N−H	N 61%	N 20% 2s, 41% 2p
	H 39%	H 38% 2s

Table S8: Comparison of the orbital contribution in the LMO bonding analysis of complex **2**, **Fig. 6 a, b**. Orbital contribution below 2% are not listed. Labelling scheme according to figure 5.

Bond	Atom + total contribution to LMO	s/p orbital contribution
2 x σ Be–N	N1 74%	N 31% 2s, 42% 2p
	Be 26%	Be 8% 2s, 16% 2p
2 x π Be–N	N1 88%	N 88% 2p
	Be 12%	Be 11% 2p

Table S9: Comparison of the orbital contribution in the LMO bonding analysis of complex **2**, **Fig. 6 c**. Orbital contribution below 2% are not listed. Labelling scheme according to figure 5.

Bond	Atom + total contribution to LMO	s/p orbital contribution
2 x σ Be–N	N2 81%	N 31% 2s, 50% 2p
	Be 19%	Be 15% 2p

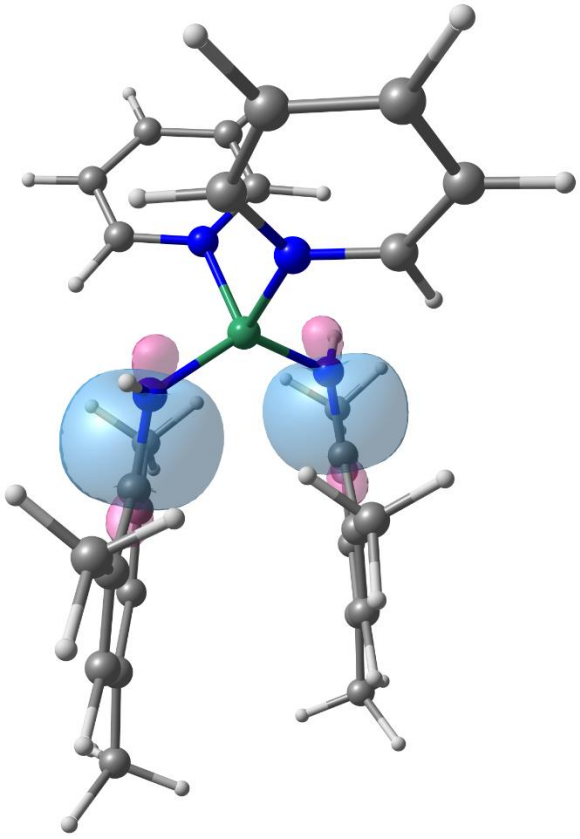

Figure S41. Two sets of LMOs of **2**. Two σ–type LMOs for mesityl ligand C–N bond. The contour value for LMO isosurface plots is 0.05 a.u. N: blue, C: grey, H: white. Red positive phase, blue negative phase.

Table S10: Comparison of the orbital contribution in the LMO bonding analysis of **2** C–N bond. Orbital contribution below 2% are not listed.

Bond	Atom + total contribution to LMO	s/p orbital contribution
2 x σ C–N	N 58%	N 11% 2s, 30% 2p
	C 42%	C 24% 2s, 34% 2p

Table S11: Comparison of the orbital contribution in the LMO bonding analysis of complex **3**, **Fig. 8 a, b**. Orbital contribution below 2% are not listed. Labelling scheme according to figure 7.

Bond	Atom + total contribution to LMO	s/p orbital contribution
2 x σ Be−N	N1 54%	N 25% 2s, 29% 2p
	Be 46%	Be 21% 2s, 23% 2p
2e3c π Be−N−C	N1 87%	N 87% 2p
	Be 7%	Be 5% 2p
	C 7%	C 4% 2p
2e3c π Be−N−C	N1 87%	N 87% 2p
	Be1 7%	Be 5% 2p
	C 5%	C 3% 2p

Table S12: Comparison of the orbital contribution in the LMO bonding analysis of complex **3**, **Fig. 8 c, d**. Orbital contribution below 2% are not listed. Labelling scheme according to figure 7.

Bond	Atom + total contribution to LMO	s/p orbital contribution
2e3c σ Be−N	N2’ 53%	N 16% 2s, 37% 2p
	Be 17%	Be 4% 2s, 10% 2p
	Be’ 30%	Be 10% 2s, 17% 2p
2e3c σ Be−N	N2 53%	N 16% 2s, 37% 2p
	Be 30%	Be 10% 2s, 17% 2p
	Be’ 17%	Be 4% 2s, 10% 2p
2 x π Be−N	N2 85%	N 85% 2p
	Be 15%	Be 4% 2s, 9% 2p

Table S13: Comparison of the orbital contribution in the LMO bonding analysis of complex **3**, **Fig. 8 e**. Orbital contribution below 2% are not listed. Labelling scheme according to figure 7.

Bond	Atom + total contribution to LMO	s/p orbital contribution
2 x σ C−H···Be	C 49%	C 12% 2s, 36% 2p
	H 45%	H 44% 2s
	Be 6%	Be 5% 2p

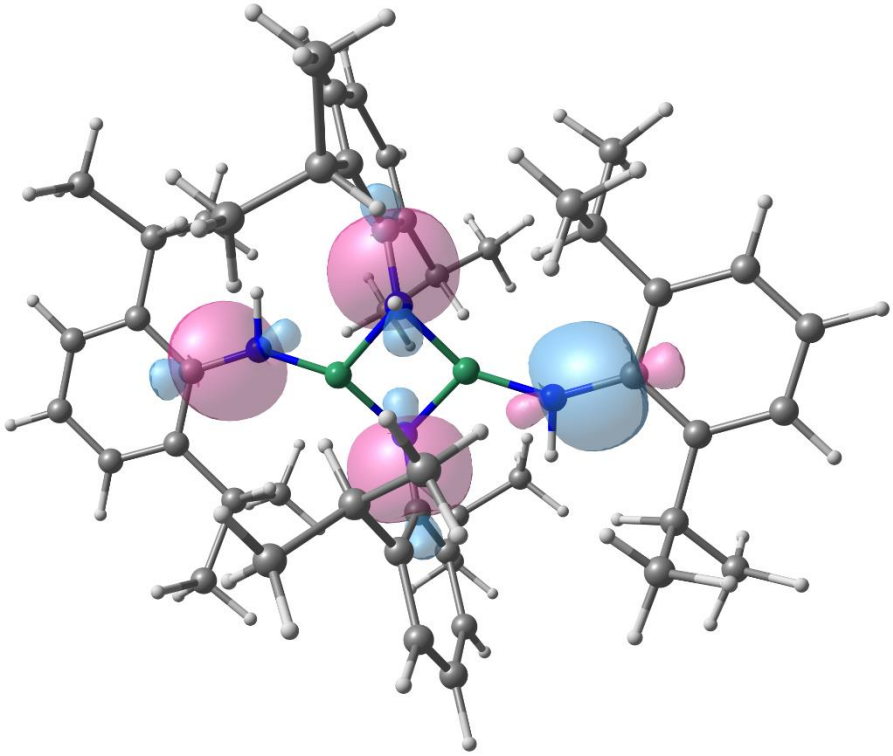

Figure S42. Four sets of LMOs of **3**. Four σ−type LMOs for C–N bond. The contour value for LMO isosurface plots is 0.05 a.u. Be: green, N: blue, C: grey, H: white. Red positive phase, blue negative phase

Table S14: Comparison of the orbital contribution in the LMO bonding analysis of complex **3**. Orbital contribution below 2% are not listed.

Bond	Atom + total contribution to LMO	s/p orbital contribution
2 x σ C−N1/4	N 50%	N 23% 2s, 27% 2p
	C 50%	C 14% 2s, 35% 2p
2 x σ C−N2/3	N 54%	N 21% 2s, 33% 2p
	C 46%	C 15% 2s, 29% 2p

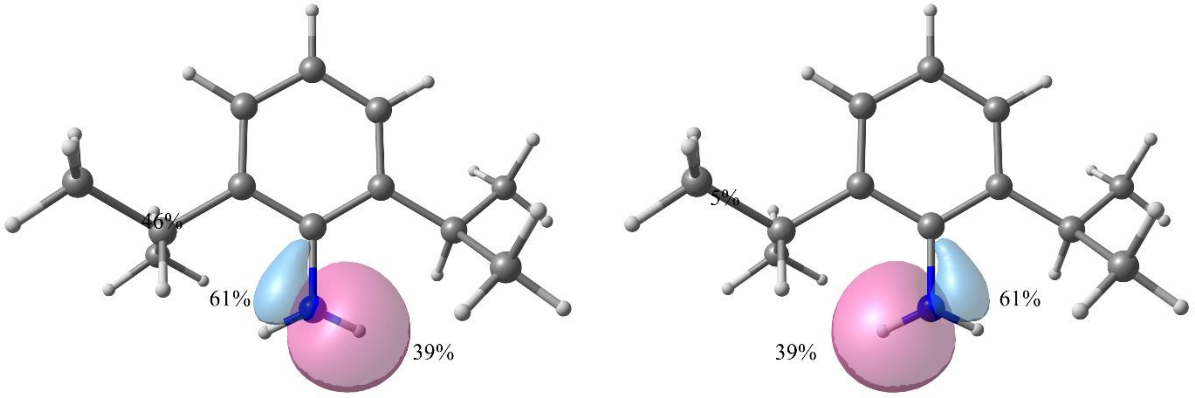

Figure S43. Two LMOs of H_2NDipp.Two σ–type LMOs for C–H bond of free H_2NDipp. The contour value for LMO isosurface plots is 0.05 a.u. N: blue, C: grey, H: white. Red positive phase, blue negative phase.

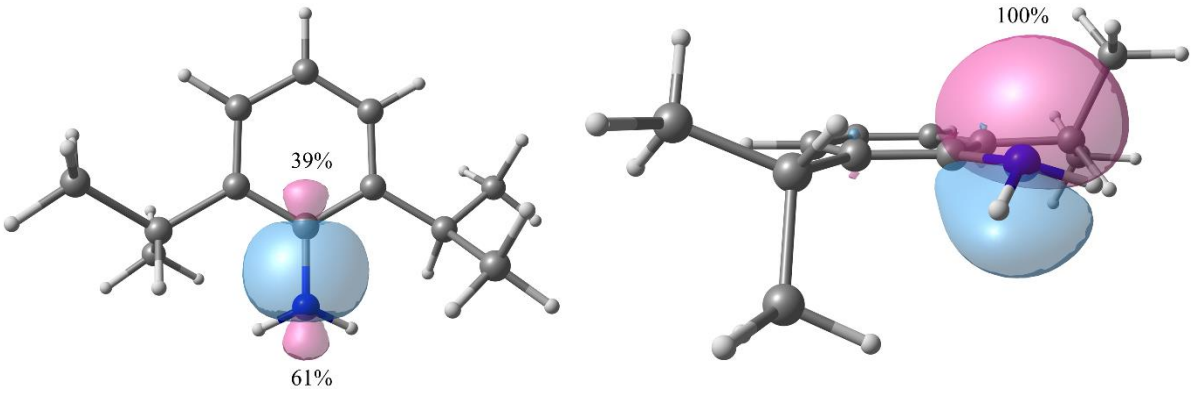

Figure S44. Two LMOs of H_2NDipp. One σ–type (left) and π-lone pair LMOs for C–N bond of free H_2NDipp. The contour value for LMO isosurface plots is 0.05 a.u. N: blue, C: grey, H: white. Red positive phase, blue negative phase.

Table S15: Comparison of the orbital contribution in the LMO bonding analysis of free H_2NDipp. Orbital contribution below 2% are not listed.

Bond	Atom + total contribution to LMO	s/p orbital contribution
σ N–C	N 61%	N 22% 2s, 38% 2p
	C 39%	C 6% 2s, 33% 2p
π–lone pair N	N 100%	N 14% 2s, 86% 2p
2 x σ N–H	N 61%	N 20% 2s, 41% 2p
	H 39%	H 38% 2s

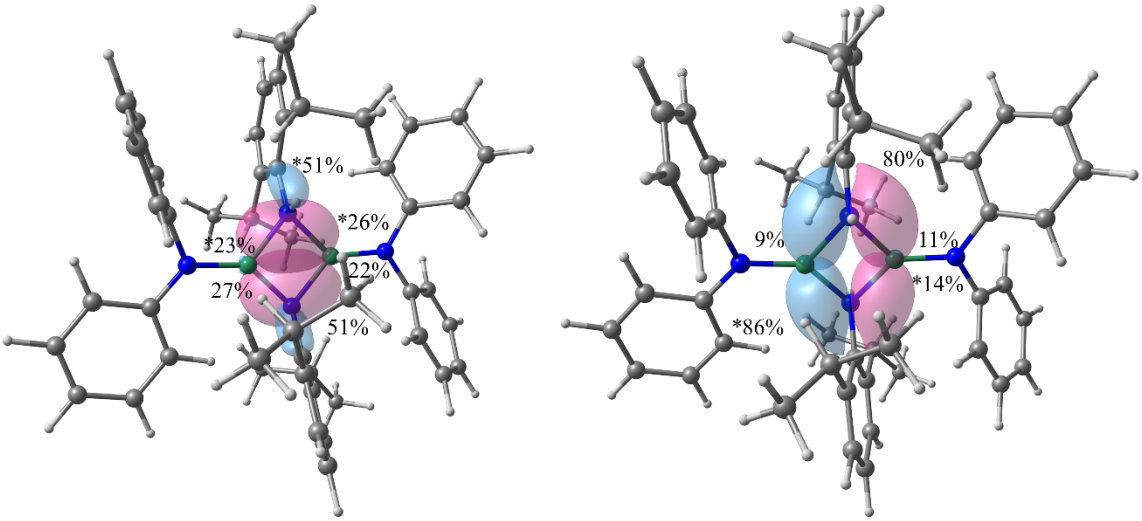

Figure S45. Two sets of LMOs of **4**. Two 2e3c–type LMOs (left) and two π–type LMOs (right) for Be–N(Dipp) bond. The contour value for LMO isosurface plots is 0.05 a.u. Be: green, N: blue, C: grey, H: white. Red positive phase, blue negative phase.

Table S16: Comparison of the orbital contribution in the LMO bonding analysis of complex 2. Orbital contribution below 2% are not listed.

Bond	Atom + total contribution to LMO	s/p orbital contribution
2 x 2e3c σ Be–N–Be	N3/2 51/51%	N3/2 15/15% 2s, 36/37% 2p
	Be1 27/23%	Be1 10/4% 2s 13/14% 2p
	Be2 22/26%	Be2 6/8% 2s 12/14% 2p
2e3c π Be–N–Be	N2 80%	N 80% 2p
	Be1 9%	Be1 7% 2p
	Be2 11%	Be2 8% 2p
π Be–N	N3 86%	N 86% 2p
	Be2 14%	Be2 5% 2s, 8% 2p

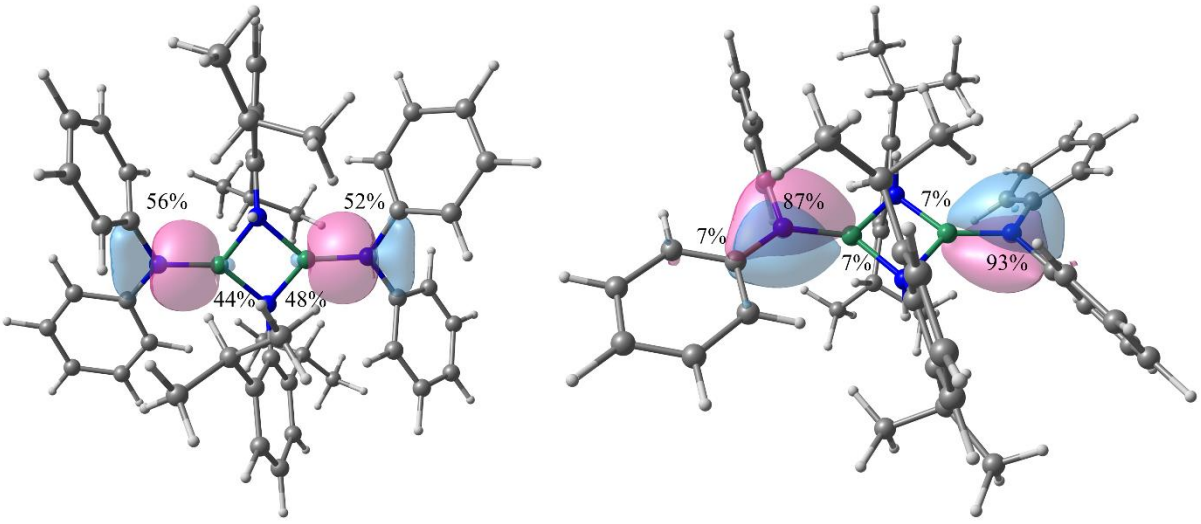

Figure S46. Two sets of LMOs of **4**. Two σ–type LMOs (left) and two π–type LMOs (right) for Be–N(NPh_2) bond. The contour value for LMO isosurface plots is 0.05 a.u. Be: green, N: blue, C: grey, H: white. Red positive phase, blue negative phase.

Table S17: Comparison of the orbital contribution in the LMO bonding analysis of complex **4**. Orbital contribution below 2% are not listed.

Bond	Atom + total contribution to LMO	s/p orbital contribution
σ Be–N	N1 56%	N 25% 2s, 31% 2p
	Be1 44%	Be1 19% 2s 23% 2p
σ Be–N	N4 52%	N 24% 2s, 38% 2p
	Be2 48%	Be2 22% 2s 23% 2p
2e3c π Be–N–C	N1 87%	N 87% 2p
	Be1 7%	Be1 4% 2p
	C 7%	C 4% 2p
π Be–N	N4 93%	N 93% 2p
	Be2 7%	Be2 4% 2p

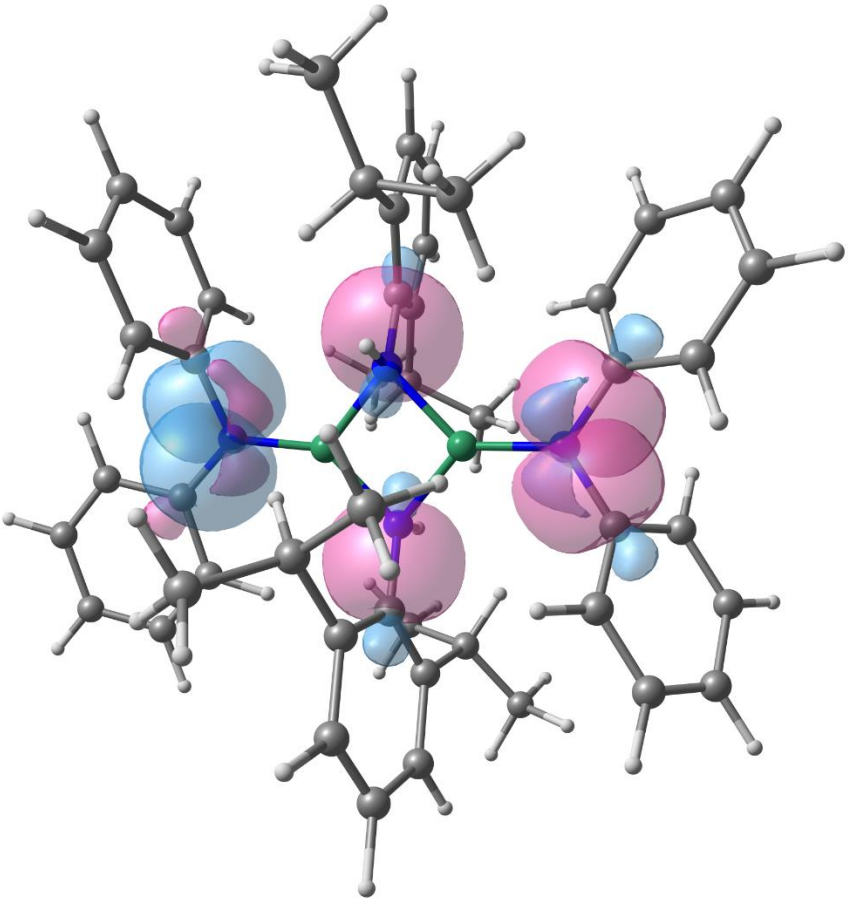

Figure S47. Six sets of LMOs of 1. Four σ–type LMOs for C–N bond. The contour value for LMO isosurface plots is 0.05 a.u. Be: green, N: blue, C: grey, H: white. Red positive phase, blue negative phase

Table S18: Comparison of the orbital contribution in the LMO bonding analysis of complex **4**. Orbital contribution below 2% are not listed.

Bond	Atom + total contribution to LMO	s/p orbital contribution
σ C–N1	N 49%	N 21% 2s, 28% 2p
	C 51%	C 19% 2s, 31% 2p
σ C–N1	N 55%	N 23% 2s, 31% 2p
	C 45%	C 17% 2s, 27% 2p
σ C–N4	N 49%	N 20% 2s, 28% 2p
	C 51%	C 20% 2s, 30% 2p
σ C–N4	N 50%	N 21% 2s, 28% 2p
	C 50%	C 19% 2s, 30% 2p
σ C–N2	N 57%	N 23% 2s, 33% 2p
	C 43%	C 16% 2s, 26% 2p
σ C–N3	N 56%	N 23% 2s, 33% 2p
	C 44%	C 16% 2s, 27% 2p

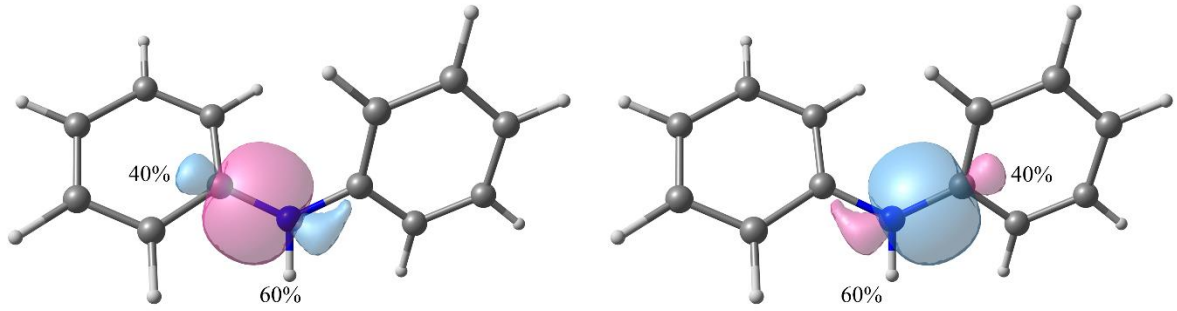

Figure S48. Two LMOs of $HNPh_2$. Two σ−type LMOs for C–N bond of free $HNPh_2$. The contour value for LMO isosurface plots is 0.05 a.u. N: blue, C: grey, H: white. Red positive phase, blue negative phase.

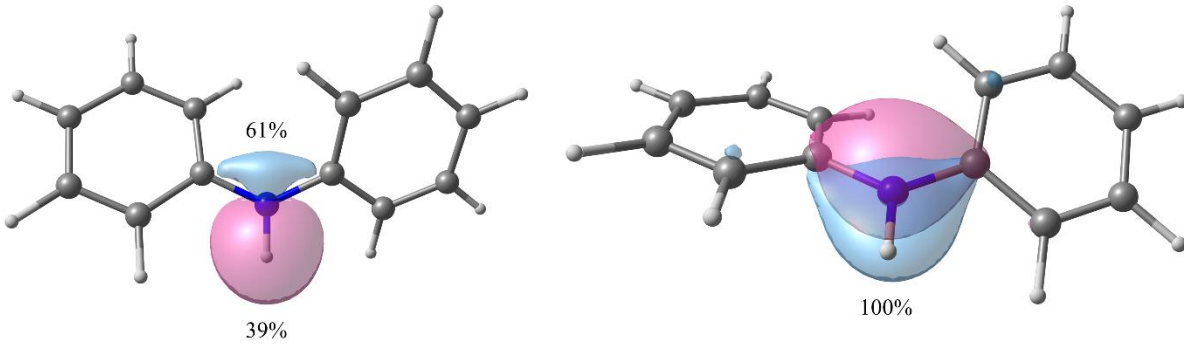

Figure S49. Two LMOs of $HNPh_2$. One σ−type (left) and π-lone pair LMOs for C–H bond of free $HNPh_2$. The contour value for LMO isosurface plots is 0.05 a.u. N: blue, C: grey, H: white. Red positive phase, blue negative phase.

Table S19: Comparison of the orbital contribution in the LMO bonding analysis of free $HNPh_2$. Orbital contribution below 2% are not listed.

Bond	Atom + total contribution to LMO	s/p orbital contribution
2 x σ N−C	N 60%	N 25% 2s, 34% 2p
	C 40%	C 13% 2s, 27% 2p
π−lone pair N	N 100%	N 100% 2p
σ N−H	N 61%	N 22% 2s, 38% 2p
	H 39%	H 38% 2s

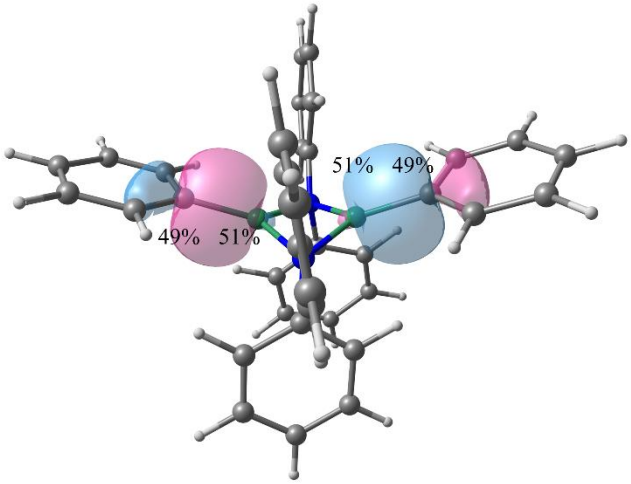

Figure S50. Two sets of LMOs of $[(Ph_2N)BePh]_2$. Two σ−type LMOs for Be–C bond. The contour value for LMO isosurface plots is 0.05 a.u. Be: green, N: blue, C: grey, H: white. Red positive phase, blue negative phase.

Table S20: Comparison of the orbital contribution in the LMO bonding analysis of $[(Ph_2N)BePh]_2$. Orbital contribution below 2% are not listed.

Bond	Atom + total contribution to LMO	s/p orbital contribution
2 x σ Be−C	C 49% Be 59%	C 26% 2s, 22% 2p Be 29% 2s, 21% 2p

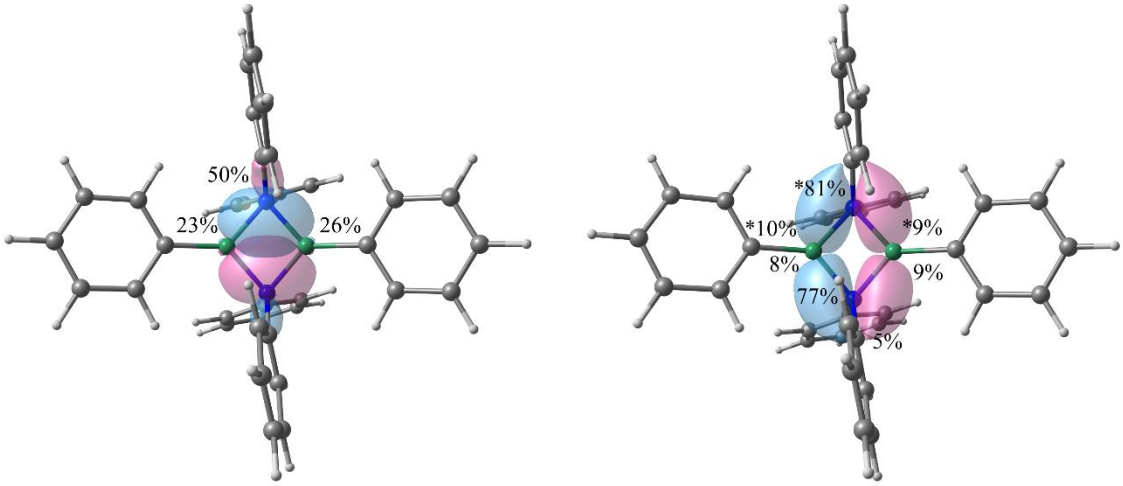

Figure S51. Two sets of LMOs of $[(Ph_2N)BePh]_2$. Two 2e3c−type LMOs (left) and and two π−type LMOs (right) for Be–N bond. The contour value for LMO isosurface plots is 0.05 a.u. Be: green, N: blue, C: grey, H: white. Red positive phase, blue negative phase.

Table S21: Comparison of the orbital contribution in the LMO bonding analysis of $[(Ph_2N)BePh]_2$. Orbital contribution below 2% are not listed.

Bond	Atom + total contribution to LMO	s/p orbital contribution
2 x 2e3c σ Be−N−Be	N 50%	N 14% 2s, 36% 2p
	Be1 23/26%	Be1 5/8% 2s 14% 2p
	Be2 26/23%	Be2 8/5% 2s 14% 2p
2e4c π Be−N(C)−Be	N 77%	N 77% 2p
	Be1 8%	Be1 7% 2p
	Be2 9%	Be2 7% 2p
	C 5%	C 3% 2p
2e3c π Be−N−Be	N 81%	N 81% 2p
	Be1 10%	Be1 8% 2p
	Be2 9%	Be2 7% 2p

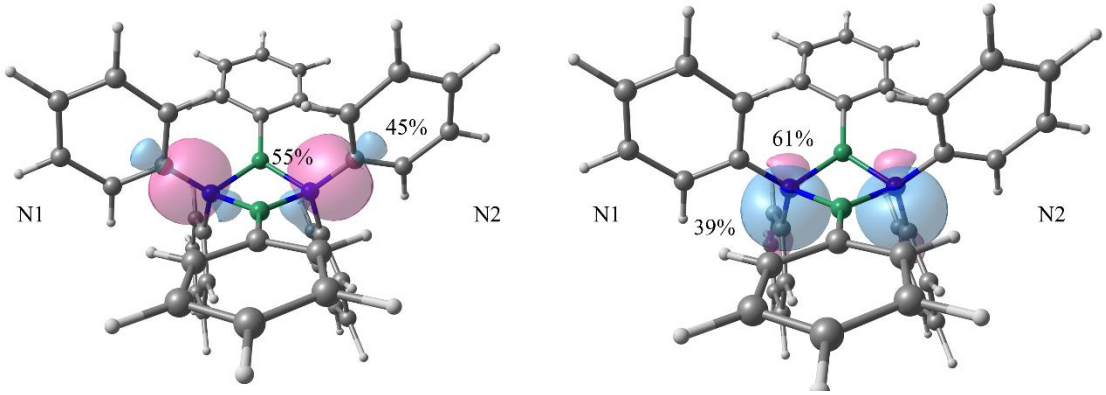

Figure S52. Four sets of LMOs of $[(Ph_2N)BePh]_2$. Two σ−type LMOs (left) and two σ−type LMOs (right) for C–N bond. The contour value for LMO isosurface plots is 0.05 a.u. Be: green, N: blue, C: grey, H: white. Red positive phase, blue negative phase.

Table S22: Comparison of the orbital contribution in the LMO bonding analysis of $[(Ph_2N)BePh]_2$ in the C–N bond. Orbital contribution below 2% are not listed.

Bond	Atom + total contribution to LMO	s/p orbital contribution
2 x σ N−C	N1/2 55%	N 20% 2s, 34% 2p
	C 45%	C 18% 2s, 27% 2p
2 x σ N−C	N1/2 61%	N 21% 2s, 39% 2p
	C 39%	C 12% 2s, 26% 2p

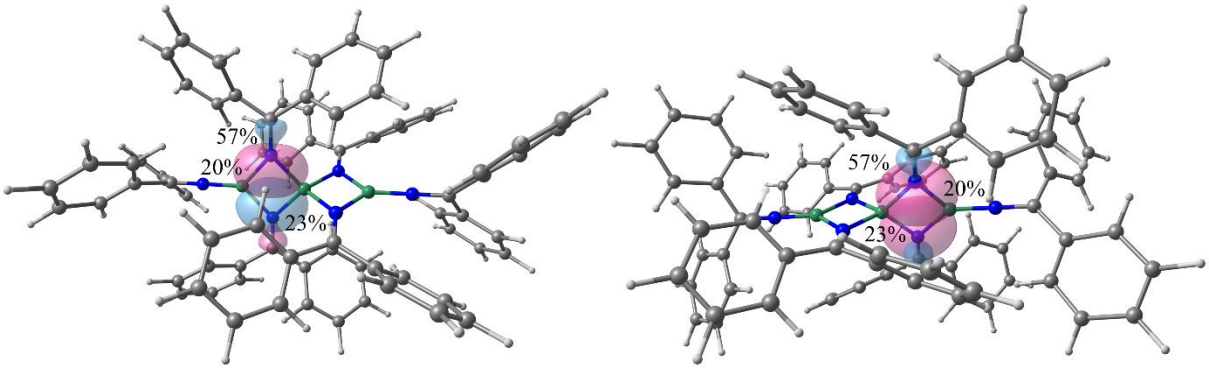

Figure S53. Two sets of LMOs of **5**. Four 2e3c–type LMOs (left and right) for Be–N(CPh_2)–Be bond. The contour value for LMO isosurface plots is 0.05 a.u. Be: green, N: blue, C: grey, H: white. Red positive phase, blue negative phase.

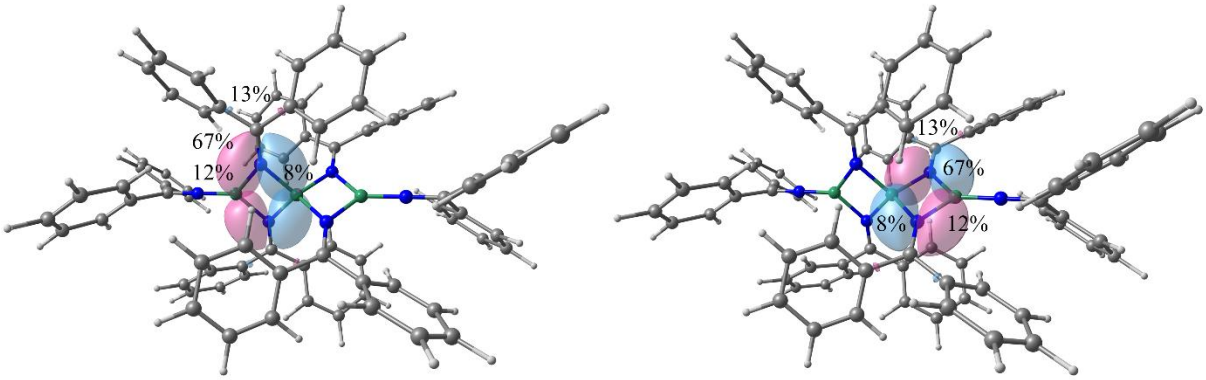

Figure S54. Two sets of LMOs of **5**. Four 2e3c–type LMOs (left and right) for Be–N(CPh2)–Be bond. The contour value for LMO isosurface plots is 0.05 a.u. Be: green, N: blue, C: grey, H: white. Red positive phase, blue negative phase.

Table S23: Comparison of the orbital contribution in the LMO bonding analysis of complex **5**. Be1: Central Atom; Orbital contribution below 2% are not listed.

Bond	Atom + total contribution to LMO	s/p orbital contribution
4 x 2e3c σ Be–N–Be	N 57%	N 43% 2s, 14% 2p
	Be1 23%	Be1 17% 2p
	Be2/3 20%	Be2/3 4% 2s, 13% 2p
4 x 2e3c π Be–N(C)–Be	N 67%	N 67% 2p
	Be1 8%	Be1 3% 2s, 3% 2p
	Be2/3 12%	Be2/3 7% 2s, 4% 2p
	C 13%	C 8% 2p

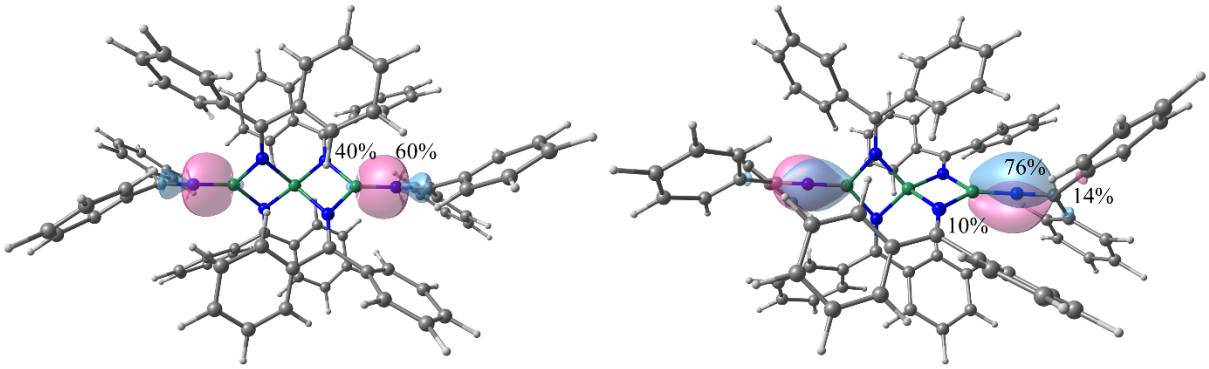

Figure S55. Two sets of LMOs of **5**. Two σ–type LMOs (left) and two π-type LMOs (right) for Be–N(CPh_2) bond. The contour value for LMO isosurface plots is 0.05 a.u. Be: green, N: blue, C: grey, H: white. Red positive phase, blue negative phase.

Table S24: Comparison of the orbital contribution in the LMO bonding analysis of complex **5**. Be1: Central Atom; Orbital contribution below 2% are not listed.

Bond	Atom + total contribution to LMO	s/p orbital contribution
2 σ Be2/3–N	N 60%	N 49% 2s, 11% 2p
	Be2/3 40%	Be2/3 8% 2s, 20% 2p
2 π Be2/3–N–C	N 76%	N 76% 2p
	Be2/3 10%	Be2/3 8% 2p
	C 14%	C 8% 2p

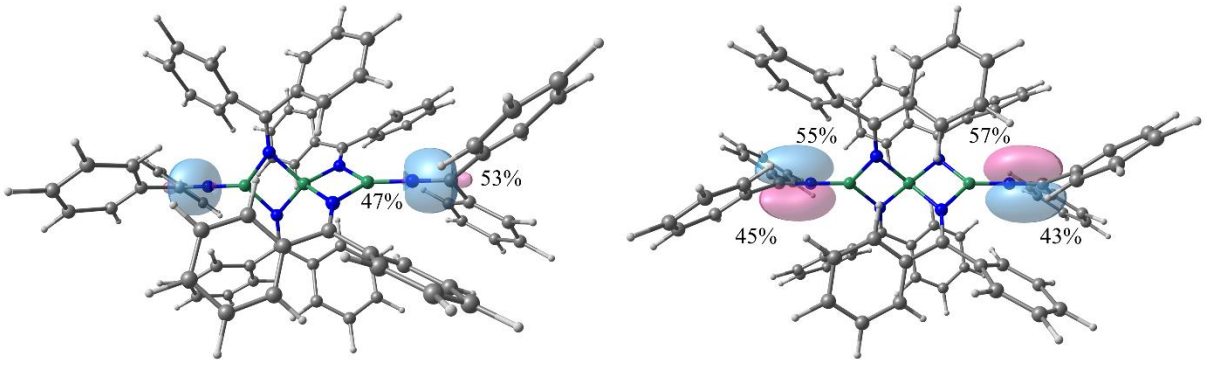

Figure S56. Four sets of LMOs of **5**. Two σ-type and two π-type LMOs for the terminal C–N bonds. The contour value for LMO isosurface plots is 0.05 a.u. Be: green, N: blue, C: grey, H: white. Red positive phase, blue negative phase

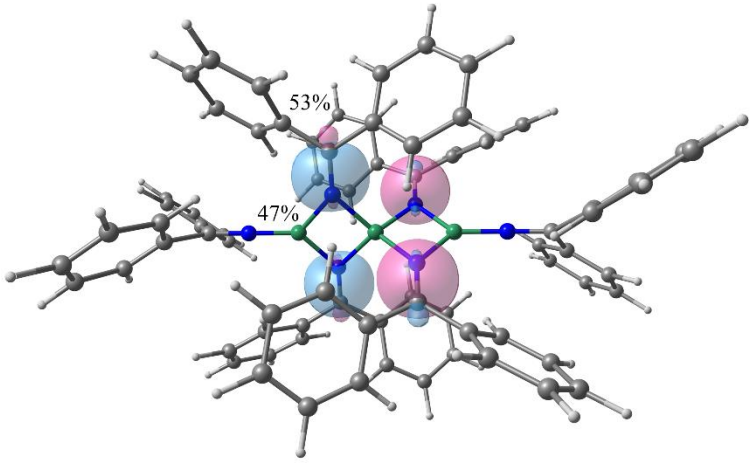

Figure S57. Four sets of LMOs of **5**. Four σ–type LMOs for bridging C–N bonds. The contour value for LMO isosurface plots is 0.05 a.u. Be: green, N: blue, C: grey, H: white. Red positive phase, blue negative phase

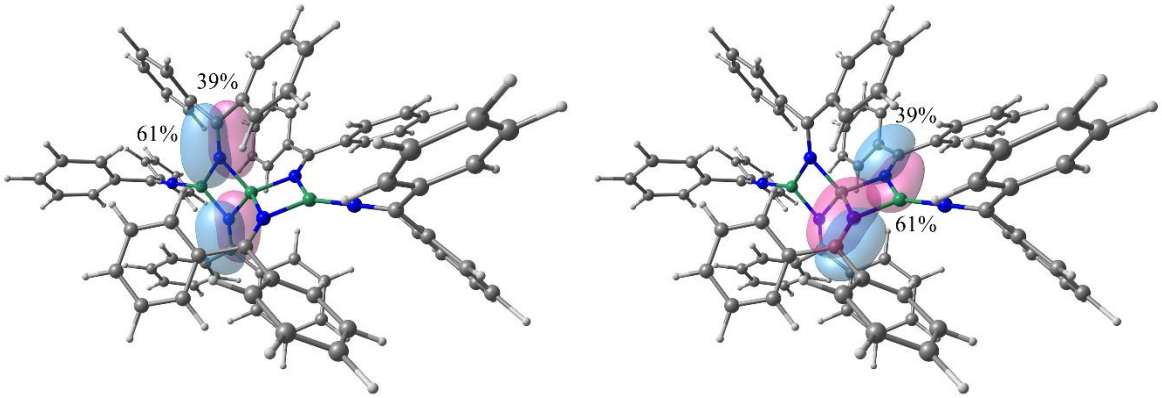

Figure S58. Four sets of LMOs of **5**. Four π–type LMOs for bridging C–N bonds. The contour value for LMO isosurface plots is 0.05 a.u. Be: green, N: blue, C: grey, H: white. Red positive phase, blue negative phase

Table S25: Comparison of the orbital contribution in the LMO bonding analysis of complex **5** in the C–N bond. Orbital contribution below 2% are not listed.

Bond	Atom + total contribution to LMO	s/p orbital contribution
2 x σ N–C terminal	N1/6 47% C 53%	N 28% 2s, 19% 2p C 24% 2s, 27% 2p
π N–C terminal	N1 55% C 45%	N 55% 2p C 43% 2p
π N–C terminal	N6 57% C 43%	N 57% 2p C 41% 2p
4 x σ N–C	N2/3/4/5 47% C 53%	N 26% 2s, 21% 2p C 24% 2s, 28% 2p
4 x π N–C	N2/3/4/5 61% C 39%	N 61% 2p C 37% 2p

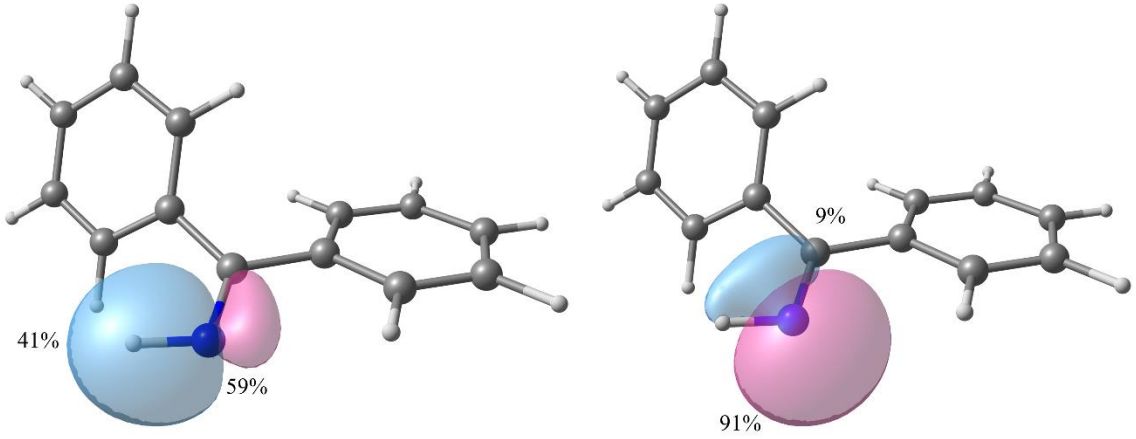

Figure S59. Two LMOs of $HNCPh_2$. One σ–type (left) for N–H bond and π-lone pair (right) LMOs for N–C bond of free ligand $HNCPh_2$. The contour value for LMO isosurface plots is 0.05 a.u. N: blue, C: grey, H: white. Red positive phase, blue negative phase.

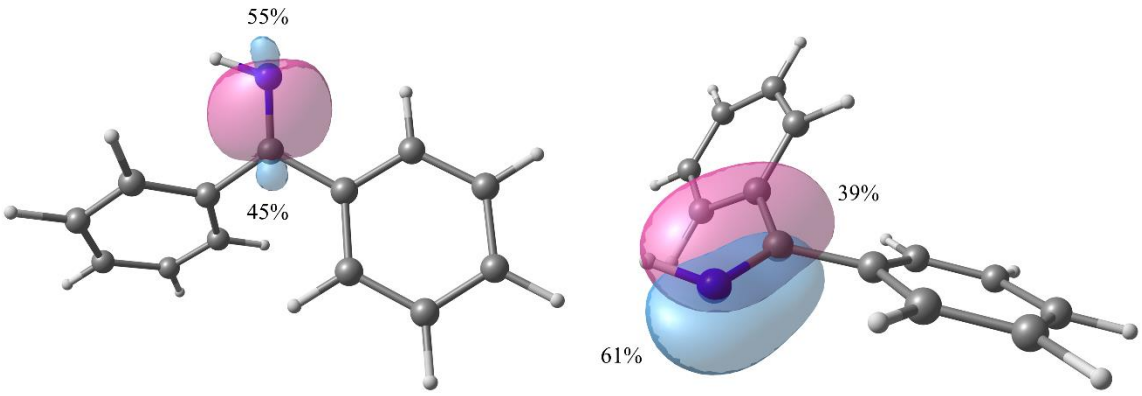

Figure S60. Two LMOs of $HNCPh_2$. One σ–type (left) for N–C bond and π-type (right) LMOs for N–C bond of free $HNCPh_2$. The contour value for LMO isosurface plots is 0.05 a.u. N: blue, C: grey, H: white. Red positive phase, blue negative phase.

Table S26: Comparison of the orbital contribution in the LMO bonding analysis of free $HNCPh_2$. Orbital contribution below 2% are not listed.

Bond	Atom + total contribution to LMO	s/p orbital contribution
σ N–C	N 55%	N 24% 2s, 30% 2p
	C 45%	C 20% 2s, 25% 2p
π N–C	N 61%	N 60% 2p
	C 39%	C 37% 2p
π–lone pair N	N 91%	N 37% 2s, 54% 2p
	C 9%	C 6% 2p
σ N–H	N 59%	N 19% 2s, 40% 2p
	H 41%	H 40% 2s

Table S27: Partial atomic charges (e^-) of selected atoms in complex **1** obtained from Natural Population Analysis (NPA) and Intrinsic Atomic Orbitals (IAO) analysis. If only a single value is specified for a selection of atoms, then the values for each of the atoms will be the same.

Atom	Partial charges / e^- NPA method	Partial charges / e^- IAO method - IBOViewer	Partial charges / e^- IAO method – Turbomole default basis	Partial charges / e^- IAO method – Turbomole correction
Be	1.66	1.48	1.94	1.48
Be1/2	1.67	1.51	1.95	1.51
N2/3/4/5	−1.33/−1.32/−1.32/−1.33	−1.02/−1.00/−0.99/−1.03	−1.24/−1.26/−1.26/−1.25	−1.02/−1.00/−0.99/−1.03
C2/3/4/5	0.14/0.13/0.13/0.14	0.08	0.08	0.08
N1/6	−1.22/−1.22	−0.96/−0.96	−1.14/−1.15	−0.96/−0.96
C1/6	0.15	0.10	0.10	0.10

Table S28: Partial atomic charges (e^-) of selected atoms in the free ligand H_2NMes obtained from Natural Population Analysis (NPA) and Intrinsic Atomic Orbitals (IAO) analysis.

Atom	Partial charges / e^- NPA method	Partial charges / e^- IAO method - IBOViewer	Partial charges / e^- IAO method – Turbomole default basis	Partial charges / e^- IAO method – Turbomole correction
N	−0.79	−0.54	−0.54	−0.54
C	0.15	0.10	0.10	0.10
H	0.38	0.27	0.27	0.27

Table S29: Partial atomic charges (e^-) of selected atoms in complex **2** obtained from Natural Population Analysis (NPA) and Intrinsic Atomic Orbitals (IAO) analysis. Due to symmetry the ligand atoms are equivalent in terms of partial charge.

Atom	Partial charges / e^- NPA method	Partial charges / e^- IAO method - IBOViewer	Partial charges / e^- IAO method – Turbomole default basis	Partial charges / e^- IAO method – Turbomole correction
Be	1.66	1.49	1.96	1.49
N_{py}	−0.57	−0.35	−0.44	−0.35
N_{Mes}	−1.18	−0.93	−1.07	−0.93
C_{Mes}	0.17	0.11	0.11	0.11
H_{Mes}	0.36	0.22	0.22	0.22

Table S30: Partial atomic charges (e^-) of selected atoms in complex **3** obtained from Natural Population Analysis (NPA) and Intrinsic Atomic Orbitals (IAO) analysis. Due to symmetry the ligand atoms are equivalent in terms of partial charge.

Atom	Partial charges / e^- NPA method	Partial charges / e^- IAO method - IBOViewer	Partial charges / e^- IAO method – Turbomole default basis	Partial charges / e^- IAO method – Turbomole correction
Be1/2	1.66	1.51	1.94	1.51
N2/3$_\mu$	−1.35	−1.01	−1.25	−1.01
C$_\mu$	0.16	0.09	0.09	0.09
N1/4	−1.23	−0.95	−1.12	−0.95
C	0.17	0.11	0.11	0.11

Table S31: Partial atomic charges (e^-) of selected atoms in the free ligand H_2NDipp obtained from Natural Population Analysis (NPA) and Intrinsic Atomic Orbitals (IAO) analysis.

Atom	Partial charges / e^- NPA method	Partial charges / e^- IAO method - IBOViewer	Partial charges / e^- IAO method – Turbomole default basis	Partial charges / e^- IAO method – Turbomole correction
N	−0.79	−0.54	−0.54	−0.54
C	0.15	0.10	0.10	0.10
H	0.38	0.27	0.27	0.27

Table S32: Partial atomic charges (e^-) of selected atoms in complex **4** obtained from Natural Population Analysis (NPA) and Intrinsic Atomic Orbitals (IAO) analysis. Due to symmetry the ligand atoms are equivalent in terms of partial charge.

Atom	Partial charges / e^- NPA method	Partial charges / e^- IAO method - IBOViewer	Partial charges / e^- IAO method – Turbomole default basis	Partial charges / e^- IAO method – Turbomole correction
Be1/2	1.66/1.68	1.50/1.51	1.93/1.94	1.50/1.51
N2/3$_\mu$	−1.36/−1.37	−1.03/−1.02	−1.27/−1.27	−1.03/−1.02
C2/3$_\mu$	0.18/0.16	0.11/0.09	0.11/0.10	0.11/0.09
N1/4	−0.98/−1.01	−0.75/−0.79	−0.92/−0.96	−0.75/−0.79
C1	0.14/0.16	0.10/0.12	0.11/0.12	0.10/0.12
C4	0.14/0.14	0.11/0.10	0.11/0.11	0.11/0.10

Table S33: Partial atomic charges (e^-) of selected atoms in the free ligand $HNPh_2$ obtained from Natural Population Analysis (NPA) and Intrinsic Atomic Orbitals (IAO) analysis.

Atom	Partial charges / e^- NPA method	Partial charges / e^- IAO method - IBOViewer	Partial charges / e^- IAO method – Turbomole default basis	Partial charges / e^- IAO method – Turbomole correction
N	−0.55	−0.31	−0.31	−0.31
C	0.15	0.11	0.11	0.11
H	0.39	0.28	0.28	0.28

Table S34: Partial atomic charges (e^-) of selected atoms in complex **5** obtained from Natural Population Analysis (NPA) and Intrinsic Atomic Orbitals (IAO) analysis. Due to symmetry partial charge of Be1/Be2, N1/N2 and C1/C2 are equal.

Atom	Partial charges / e^- NPA method	Partial charges / e^- IAO method - IBOViewer	Partial charges / e^- IAO method – Turbomole default basis	Partial charges / e^- IAO method – Turbomole correction
Be1/2	1.61	1.45	1.95	1.45
N1/2	−1.11	−0.86	−1.08	−0.86
C1/2	−0.72	−0.63	−0.91	−0.63

Table S35: Partial atomic charges (e^-) of selected atoms in complex **6** obtained from Natural Population Analysis (NPA) and Intrinsic Atomic Orbitals (IAO) analysis. Data analysis with IBOViewer was not possible, because the program showed file loading problems and crashed. Two different machines and program versions "v20211019-RevA" and "v20150427" were used without success. If only a single value is specified for a selection of atoms, then the values for each of the atoms will be the same.

Atom	Partial charges / e^- NPA method	Partial charges / e^- IAO method - IBOViewer	Partial charges / e^- IAO method – Turbomole default basis	Partial charges / e^- IAO method – Turbomole correction
Be	1.66	–	1.94	1.49
Be1/2	1.67	–	1.95	1.51
N2/3/4/5	−1.15	–	−1.20	−0.96
C2/3/4/5	0.33	–	0.20	0.20
N1/6	−1.02	–	−1.08	−0.90
C1/6	0.27	–	0.18	0.17

Table S36: Partial atomic charges (e^-) of selected atoms in the free ligand $HNCPh_2$ obtained from Natural Population Analysis (NPA) and Intrinsic Atomic Orbitals (IAO) analysis.

Atom	Partial charges / e^- NPA method	Partial charges / e^- IAO method - IBOViewer	Partial charges / e^- IAO method – Turbomole default basis	Partial charges / e^- IAO method – Turbomole correction
N	−0.59	−0.46	−0.46	−0.46
C	0.26	0.18	0.18	0.18
H	0.34	0.25	0.25	0.25

Table S37: Changes IAO basis for IAO atomic charges.

1 s eigenvalue=-.47325407295449D+01 nsaos=4
0.99186043661042D+00-.10048796341397D-050.18193677767313D-010.19036517991340D-02
2 s eigenvalue=-.30924859523167D+00 nsaos=4
0.21907584757841D-040.56272019570987D+000.22803978978015D+000.31779430523373D+00

Coordinates of Optimized Structures

Table S38: Coordinates of the optimizes structure of **1** in XZY Ångstrom format.

atom	x	y	z
H	−2.9145066	−4.3903692	7.9082250
C	−6.4358764	−0.2113461	−2.8208514
H	−7.1501864	0.3727949	−2.2375441
H	−6.2556669	0.3308130	−3.7545403
H	−6.9066773	−1.1610721	−3.0818809
C	−3.4072402	−3.1664291	6.2036220
C	−3.6645424	−3.9031889	5.0537983
H	−4.1132427	−4.8890721	5.1434525
C	−3.7069900	−3.7170579	7.5649701
H	−3.7977155	−2.9178900	8.3033529
H	−4.6392725	−4.2868485	7.5695909
H	−4.0712749	−5.2260810	2.8676525
C	−3.6537569	−4.2608540	2.5797727
H	−2.7471050	−4.4469984	1.9931087
H	6.0677494	0.8828064	−7.1922094
C	5.4855931	1.8065798	−7.1775051
H	4.9798356	1.9008315	−8.1411198
N	1.7731024	1.9194245	−2.8353832
H	1.1656372	2.7193863	−2.9611295
H	−1.0457724	−1.8005981	−0.3925147
N	−1.4418745	−0.9116682	−0.1011266
H	−3.0179662	−2.2028285	1.6862883
N	−2.4839666	−1.6794394	2.3685671
H	2.1515202	−0.1783628	−0.1052669
N	1.4071325	−0.3380033	−0.7774393
H	−0.5616651	1.1738084	1.9946492
N	−0.1675442	0.2574463	1.8028093
H	−1.0171393	1.4960211	−1.5116379
N	−0.2169647	1.6535289	−0.9061253
C	−0.0193659	−0.9973565	−3.2112773
H	−0.8082157	−0.6299818	−2.5509252
H	0.5265424	−0.1285647	−3.5965987
H	−0.5113215	−1.4720005	−4.0606641
C	0.8193796	4.8739050	0.6009021
H	1.6428398	5.2603709	1.1944686
C	2.4693937	−1.4478959	3.7629380
H	2.8887689	−2.4455749	3.8540011
C	1.4247816	−1.2511096	2.8683979
C	−1.2050870	5.2106834	−0.5861460
H	−1.9967976	5.8656050	−0.9381286
C	0.9108557	−1.9580649	−2.5364107
C	−2.6966051	−0.7576288	−0.7373961
C	−3.5151885	0.3436924	−0.4420761
C	1.6372050	−1.5929716	−1.3944182
C	2.9753681	−0.4238925	4.5505796
C	0.8743288	0.0299850	2.7353851
C	1.3200179	1.0651820	3.5717025
C	0.8526643	3.5386358	0.2194301
C	−1.2165204	3.8822606	−0.9913083
C	−0.2111304	5.7273822	0.2331531
C	−3.1708126	−1.7474899	−1.6132587
C	1.1221900	−3.2118605	−3.0982506
C	2.0453642	−4.1112220	−2.5858763

H	0.5523404	−3.4820701	−3.9825227
C	−0.2066276	3.0192228	−0.5385125
C	−3.1807491	1.2995176	0.6627540
H	−3.2055203	0.7796408	1.6279715
H	−2.2021606	1.7681946	0.5505124
H	−3.9168835	2.1023276	0.7116252
C	2.8066006	−3.6955962	−1.5023367
H	3.5778049	−4.3529541	−1.1117677
C	−4.7164886	0.4936425	−1.1248044
H	−5.3362404	1.3544745	−0.8908049
C	−0.2452364	7.1513698	0.6966179
H	0.7617177	7.5407875	0.8582041
H	−0.7452197	7.7942063	−0.0303740
H	−0.7875951	7.2455568	1.6427520
C	−2.2537791	3.4085479	−1.9643457
H	−2.8475634	2.5699125	−1.5927044
H	−2.9448692	4.2155552	−2.2074787
H	−1.7935347	3.0804927	−2.9036817
C	4.1302388	−0.6533588	5.4764570
H	4.1533795	−1.6844857	5.8339846
H	5.0832747	−0.4600621	4.9739178
H	4.0803545	0.0061204	6.3449323
C	2.0552537	2.7079834	0.5451737
H	1.8047461	1.7622186	1.0294001
H	2.6204581	2.4892128	−0.3686534
H	2.7241766	3.2419324	1.2204376
C	−4.3797073	−1.5537278	−2.2684193
H	−4.7278187	−2.3246267	−2.9496652
C	0.8582440	−2.4174434	2.1203543
H	−0.1560234	−2.6487778	2.4644269
H	0.8158062	−2.2492305	1.0410335
H	1.4665291	−3.3087751	2.2753423
C	−2.4345433	−3.0421256	−1.7809457
H	−2.9548375	−3.6872161	−2.4888856
H	−1.4113019	−2.9181464	−2.1417123
H	−2.3723015	−3.5851917	−0.8306562
C	3.5766068	−2.0116569	0.1705795
H	4.2192447	−2.8368400	0.4776105
H	4.2278179	−1.2080451	−0.1908431
H	3.0747995	−1.6396738	1.0657838
C	2.2198753	−5.4733180	−3.1838166
H	1.5717209	−6.2056842	−2.6921578
H	1.9680756	−5.4756413	−4.2459135
H	3.2477207	−5.8254428	−3.0775520
C	−5.1601261	−0.4242802	−2.0655979
C	2.3673991	0.8197315	4.4501245
H	2.7060039	1.6294152	5.0897915
C	0.6236111	2.3914518	3.5983773
H	1.1511584	3.0865593	4.2516123
H	0.5436954	2.8637219	2.6170180
H	−0.3948602	2.2871585	3.9891009
C	2.6348508	−2.4527635	−0.9075940
Be	−0.0899053	0.1853578	0.0274200
Be	−1.4315831	−0.8346694	1.5929084
Be	1.1775117	1.0687354	−1.6754285
C	−2.5352422	−1.3855221	4.7888318
C	−2.8480066	−1.9081639	6.0375520
H	−2.6564025	−1.2949567	6.9142277

C	−3.3651750	−3.4246659	3.7882362
C	−2.7811265	−2.1499784	3.6374773
C	−1.9667597	−0.0088324	4.6820187
H	−0.8947402	−0.0327184	4.4705384
H	−2.4498925	0.5535095	3.8770274
H	−2.1050383	0.5408635	5.6144324
H	−4.3765197	−3.7816813	1.9075932
C	3.8731306	1.1319743	−3.7926983
C	4.7483680	1.1145727	−4.8709296
H	5.6627534	0.5338438	−4.7812053
C	4.5053938	1.8151635	−6.0434927
C	3.3313795	2.5549953	−6.1083676
H	3.1063268	3.1157398	−7.0118269
C	2.4267204	2.5988977	−5.0590836
C	2.6846631	1.8749575	−3.8770657
C	4.2101066	0.3762545	−2.5500068
H	4.0282457	0.9858344	−1.6592165
H	3.6089860	−0.5316804	−2.4555545
H	5.2594703	0.0771110	−2.5507256
H	6.1948824	2.6374876	−7.1008866
C	1.1679934	3.4005220	−5.1841504
H	1.1116851	4.2020691	−4.4370851
H	1.1037767	3.8694920	−6.1663829
H	0.2772021	2.7762446	−5.0501146

Table S39: Coordinates of the optimizes structure of **2** in XZY Ångstrom format.

atom	x	y	z
H	0.8278084	−2.0392275	−1.1349328
N	0.9732648	−1.1140475	−0.7539215
C	1.2044417	−1.2402305	0.6074399
C	0.9472902	−2.4534520	1.2781370
C	1.0899454	−2.5300731	2.6569812
H	0.8633242	−3.4721373	3.1505033
C	1.7039333	−0.1611570	1.3633275
C	0.5073501	−3.6596405	0.5064730
H	−0.4399558	−3.4922891	−0.0190311
H	0.3683952	−4.5131950	1.1714045
H	1.2458204	−3.9531915	−0.2507636
C	2.1574940	1.0945780	0.6902121
H	3.0504451	0.9089118	0.0826723
H	2.4059980	1.8581511	1.4286368
H	1.3930539	1.5030351	0.0287358
C	−0.4674434	−1.8749263	−3.4815657
N	−1.0039583	−0.9423750	−2.6940100
H	0.6066394	−2.0038998	−3.4033674
C	−1.2230204	−2.6399269	−4.3477273
H	−0.7454967	−3.3900644	−4.9646907
C	−2.5920579	−2.4224848	−4.4025173
H	−3.2153449	−3.0063789	−5.0696396
C	−3.1466022	−1.4471355	−3.5917104
H	−4.2096628	−1.2434147	−3.6020200
C	−2.3170361	−0.7272196	−2.7495613
H	−2.6678105	0.0493253	−2.0772255
Be	0.0000000	0.0000000	−1.4877802
N	−0.9732648	1.1140475	−0.7539215
H	−0.8278084	2.0392275	−1.1349328

N	1.0039583	0.9423750	−2.6940100
C	−1.2044417	1.2402305	0.6074399
C	−0.9472902	2.4534520	1.2781370
C	−1.0899454	2.5300731	2.6569812
H	−0.8633242	3.4721373	3.1505033
C	−1.7039333	0.1611570	1.3633275
C	−0.5073501	3.6596405	0.5064730
H	0.4399558	3.4922891	−0.0190311
H	−0.3683952	4.5131950	1.1714045
H	−1.2458204	3.9531915	−0.2507636
C	−2.1574940	−1.0945780	0.6902121
H	−3.0504451	−0.9089118	0.0826723
H	−2.4059980	−1.8581511	1.4286368
H	−1.3930539	−1.5030351	0.0287358
C	0.4674434	1.8749263	−3.4815657
H	−0.6066394	2.0038998	−3.4033674
C	1.2230204	2.6399269	−4.3477273
H	0.7454967	3.3900644	−4.9646907
C	2.5920579	2.4224848	−4.4025173
H	3.2153449	3.0063789	−5.0696396
C	3.1466022	1.4471355	−3.5917104
H	4.2096628	1.2434147	−3.6020200
C	2.3170361	0.7272196	−2.7495613
H	2.6678105	−0.0493253	−2.0772255
C	1.4922261	−1.4443144	3.4207793
C	1.8153230	−0.2779549	2.7392392
H	2.1683969	0.5827066	3.3012183
C	1.5507715	−1.5155190	4.9162458
H	0.6046374	−1.1958916	5.3669303
H	2.3339813	−0.8670768	5.3163450
H	1.7474100	−2.5333446	5.2612928
C	−1.4922261	1.4443144	3.4207793
C	−1.8153230	0.2779549	2.7392392
H	−2.1683969	−0.5827066	3.3012183
C	−1.5507715	1.5155190	4.9162458
H	−0.6046374	1.1958916	5.3669303
H	−2.3339813	0.8670768	5.3163450
H	−1.7474100	2.5333446	5.2612928

Table S40: Coordinates of the optimizes structure of **3** in XZY Ångstrom format.

atom	x	y	z
H	−0.4061802	−0.0105056	−2.9216276
N	−0.9786219	−0.6340782	−2.3667307
C	−1.8184090	−1.3293090	−3.2191466
C	−1.8083014	−1.0287961	−4.6050789
C	−2.6722785	−2.3471056	−2.7474656
C	−1.1381023	−1.5427771	1.5972440
N	−0.9683743	−0.4736811	0.6871318
C	−0.3163842	−2.6777169	1.4975764
C	−2.1099274	−1.4471802	2.6130919
C	−2.7776473	−2.6235913	−1.2714782
H	−1.8005842	−2.4170114	−0.8258471
C	−3.0530183	−0.2603032	2.6864438
H	−3.3001922	0.0310535	1.6571023
C	−2.6194914	−1.7556669	−5.4631733
H	−2.6054061	−1.5308100	−6.5225364

C	−0.4455268	−3.6788614	2.4522969
H	0.1893873	−4.5544608	2.3898562
C	−0.9598048	0.1087947	−5.1324275
H	0.0107002	0.0828014	−4.6205696
C	0.7077437	−2.8330648	0.3946268
H	0.4287274	−2.1658504	−0.4355818
C	−3.7919249	−1.6728226	−0.6399396
H	−4.7850005	−1.8609431	−1.0560418
H	−3.5426129	−0.6302260	−0.8500948
H	−3.8427480	−1.8180685	0.4415687
C	−2.1996521	−2.4777294	3.5404390
H	−2.9413090	−2.4210679	4.3269480
C	−1.3677821	−3.5817558	3.4765398
H	−1.4505256	−4.3707156	4.2142803
C	−3.4655155	−3.0451698	−3.6475653
H	−4.1150241	−3.8298596	−3.2776617
C	−4.3878119	−0.5938010	3.3397746
H	−4.8475615	−1.4766317	2.8909420
H	−5.0757624	0.2461705	3.2232002
H	−4.2782296	−0.7732720	4.4119555
H	−4.0698409	−3.3242791	−5.6890941
C	−3.4469817	−2.7650880	−5.0012645
C	−2.4233379	0.9516349	3.3726671
H	−2.2081573	0.7232789	4.4197719
H	−3.1117388	1.8005052	3.3514502
H	−1.4866329	1.2596883	2.9046852
C	−3.1214017	−4.0631076	−0.9156874
H	−4.1543932	−4.3090502	−1.1740700
H	−3.0092383	−4.2150464	0.1609279
H	−2.4708513	−4.7711773	−1.4336168
C	2.1098092	−2.4410506	0.8547778
H	2.1336256	−1.4449967	1.3044349
H	2.8150401	−2.4727002	0.0191707
H	2.4625847	−3.1428427	1.6147003
C	0.7159331	−4.2260545	−0.2234601
H	1.0920605	−4.9723656	0.4793683
H	1.3697334	−4.2417994	−1.0982878
H	−0.2840131	−4.5260917	−0.5376219
H	−1.5260898	0.1598618	−7.2345504
C	−0.6367148	0.0146082	−6.6163100
H	−0.1993604	−0.9527278	−6.8730024
H	0.0761042	0.7967108	−6.8888002
C	−1.6107762	1.4574759	−4.8206603
H	−2.5522401	1.5496415	−5.3685181
H	−0.9570081	2.2840612	−5.1092862
H	−1.8318357	1.5602926	−3.7575010
Be	−0.4610484	−0.4729197	−0.9121733
H	−1.7864621	0.1242497	0.7424169
H	0.4061802	0.0105056	2.9216276
N	0.9786219	0.6340782	2.3667307
N	0.9683743	0.4736811	−0.6871318
C	1.8184090	1.3293090	3.2191466
C	1.8083014	1.0287961	4.6050789
C	2.6722785	2.3471056	2.7474656
C	1.1381023	1.5427771	−1.5972440
C	0.3163842	2.6777169	−1.4975764
C	2.1099274	1.4471802	−2.6130919
C	2.7776473	2.6235913	1.2714782

H	1.8005842	2.4170114	0.8258471
C	3.0530183	0.2603032	−2.6864438
H	3.3001922	−0.0310535	−1.6571023
C	2.6194914	1.7556669	5.4631733
H	2.6054061	1.5308100	6.5225364
C	0.4455268	3.6788614	−2.4522969
H	−0.1893873	4.5544608	−2.3898562
C	0.9598048	−0.1087947	5.1324275
H	−0.0107002	−0.0828014	4.6205696
C	−0.7077437	2.8330648	−0.3946268
H	−0.4287274	2.1658504	0.4355818
C	3.7919249	1.6728226	0.6399396
H	3.5426129	0.6302260	0.8500948
H	3.8427480	1.8180685	−0.4415687
C	2.1996521	2.4777294	−3.5404390
H	2.9413090	2.4210679	−4.3269480
C	1.3677821	3.5817558	−3.4765398
H	1.4505256	4.3707156	−4.2142803
C	3.4655155	3.0451698	3.6475653
C	4.3878119	0.5938010	−3.3397746
H	4.8475615	1.4766317	−2.8909420
H	5.0757624	−0.2461705	−3.2232002
H	4.2782296	0.7732720	−4.4119555
C	3.4469817	2.7650880	5.0012645
C	2.4233379	−0.9516349	−3.3726671
H	2.2081573	−0.7232789	−4.4197719
H	3.1117388	−1.8005052	−3.3514502
H	1.4866329	−1.2596883	−2.9046852
C	3.1214017	4.0631076	0.9156874
H	4.1543932	4.3090502	1.1740700
H	3.0092383	4.2150464	−0.1609279
H	2.4708513	4.7711773	1.4336168
C	−2.1098092	2.4410506	−0.8547778
H	−2.1336256	1.4449967	−1.3044349
H	−2.8150401	2.4727002	−0.0191707
H	−2.4625847	3.1428427	−1.6147003
C	−0.7159331	4.2260545	0.2234601
H	−1.0920605	4.9723656	−0.4793683
H	−1.3697334	4.2417994	1.0982878
H	0.2840131	4.5260917	0.5376219
C	0.6367148	−0.0146082	6.6163100
H	0.1993604	0.9527278	6.8730024
H	−0.0761042	−0.7967108	6.8888002
C	1.6107762	−1.4574759	4.8206603
H	2.5522401	−1.5496415	5.3685181
H	0.9570081	−2.2840612	5.1092862
H	1.8318357	−1.5602926	3.7575010
Be	0.4610484	0.4729197	0.9121733
H	1.7864621	−0.1242497	−0.7424169
H	1.5260898	−0.1598618	7.2345504
H	4.7850005	1.8609431	1.0560418
H	4.1150241	3.8298596	3.2776617
H	4.0698409	3.3242791	5.6890941

Table S41: Coordinates of the optimizes structure of **4** in XZY Ångstrom format.

atom	x	y	z

N	1.2128949	−1.3107362	−2.0894933
C	2.3054621	−2.1682153	−2.1740275
N	0.9527108	−0.4681877	0.8310167
C	1.1987104	−1.5522795	1.7150965
C	0.4063788	−1.1870679	−3.2529579
C	3.0311484	−2.5051855	−1.0232607
H	2.7200189	−2.1206267	−0.0617475
C	2.1542844	−1.4053221	2.7340110
C	0.4744914	−2.7439488	1.5724750
C	4.1265138	−3.3453962	−1.0871619
H	4.6564787	−3.5866249	−0.1720003
C	2.7319120	−2.7186912	−3.3898446
H	2.1979020	−2.4803854	−4.3009257
C	2.9136110	−0.1045417	2.8875546
H	2.1960309	0.7100572	2.7199574
C	2.3704949	−2.4694597	3.5978000
H	3.0971136	−2.3690104	4.3937117
C	0.5130623	−0.0792992	−4.0857097
H	1.2542576	0.6759942	−3.8573452
C	4.5417777	−3.8846080	−2.2977248
C	3.8312486	−3.5608656	−3.4429295
H	4.1344977	−3.9675841	−4.4016669
C	−0.5441188	−2.1620578	−3.5544188
H	−0.6142899	−3.0358064	−2.9157190
C	0.7173308	−3.7764624	2.4704536
H	0.1674169	−4.7041366	2.3736411
C	1.6570761	−3.6488268	3.4762768
H	1.8358565	−4.4680087	4.1625112
C	4.0402694	0.0082568	1.8565081
H	3.7020158	−0.1306172	0.8262994
C	3.4675922	0.1223878	4.2860091
H	2.6859133	0.0257938	5.0406218
C	−0.3234495	0.0654109	−5.1828779
H	−0.2373642	0.9459504	−5.8089008
C	−1.3757602	−2.0230508	−4.6541167
H	−2.1127432	−2.7878296	−4.8721280
C	−1.2701485	−0.9050868	−5.4710282
H	−1.9240539	−0.7927240	−6.3279408
Be	0.6395683	−0.5643644	−0.8310626
H	1.6940969	0.2117536	0.9705064
C	−0.5671426	−2.9058205	0.4887205
C	−0.6676822	−4.3260932	−0.0506495
H	−1.3375338	−4.3491270	−0.9134862
H	−1.0787675	−5.0145745	0.6911909
H	0.3096313	−4.6968318	−0.3643176
H	−0.2465973	−2.3095581	−0.3759710
C	−1.9382230	−2.4020699	0.9345842
H	−2.6590028	−2.4558375	0.1138895
H	−1.9174767	−1.3692165	1.2968130
H	−2.3175627	−3.0149411	1.7564035
N	−0.7392480	0.4205600	−0.8448963
N	−1.1865843	1.2198119	1.9954973
C	−2.2575439	2.1191503	1.8061428
C	−0.9092433	1.5512171	−1.6841746
C	−0.7947884	1.0492260	3.3422435
C	−2.2129394	3.1095590	0.8276670
H	−1.3220174	3.2305774	0.2272599

C	−2.1171204	1.7191624	−2.3816152
C	0.1280272	2.4868392	−1.8117387
C	−3.2998098	3.9430628	0.6088247
H	−3.2387490	4.6952981	−0.1694366
C	−3.4120631	2.0150146	2.5886380
H	−3.4537933	1.2575418	3.3630844
C	−3.1852521	0.6455022	−2.3430309
H	−2.6671054	−0.3224268	−2.4086152
C	−2.2972985	2.8788099	−3.1209861
H	−3.2253370	3.0270692	−3.6580471
C	−0.6769663	−0.2142437	3.9149543
H	−0.9211491	−1.0902778	3.3290389
C	−4.4452660	3.8222515	1.3783843
H	−5.2923738	4.4768053	1.2110574
C	−4.4896733	2.8554201	2.3759629
H	−5.3772702	2.7497447	2.9898596
C	−0.5034989	2.1650659	4.1340253
H	−0.6070718	3.1537719	3.7011447
C	−0.1026159	3.6354540	−2.5599986
H	0.6845547	4.3733095	−2.6560622
C	−1.3114136	3.8477888	−3.1954190
H	−1.4749777	4.7510077	−3.7710425
C	−4.0005475	0.6791107	−1.0494814
H	−4.7212024	−0.1425208	−1.0334175
H	−4.5510495	1.6191736	−0.9738754
H	−3.3844672	0.6088294	−0.1524631
C	−4.1209667	0.6823148	−3.5428600
H	−4.7595183	−0.2036894	−3.5378101
H	−4.7789395	1.5545485	−3.5124317
H	−3.5657616	0.6964214	−4.4819825
C	−0.2591332	−0.3625708	5.2299088
H	−0.1683076	−1.3592708	5.6462115
C	−0.0971624	2.0154133	5.4474614
H	0.1255521	2.8947110	6.0415894
C	0.0310999	0.7483622	6.0046405
H	0.3498121	0.6321950	7.0338119
Be	−0.4576405	0.4877837	0.8226273
H	−1.5385739	−0.1898700	−0.9891465
C	1.4779406	2.2725458	−1.1610691
H	1.6401535	1.1879655	−1.0831067
C	1.5591629	2.8784087	0.2387770
H	2.5244065	2.6560362	0.7027881
H	1.4597625	3.9651332	0.1789339
H	0.7691555	2.5265649	0.9086529
C	2.6432641	2.7696469	−2.0082627
H	3.5880700	2.4418033	−1.5694197
H	2.6679643	3.8603906	−2.0565953
H	2.5914416	2.3860090	−3.0283796
H	5.3989042	−4.5450227	−2.3452527
H	4.7930770	−0.7614530	2.0437040
H	4.5294356	0.9833566	1.9237942
H	3.8837884	1.1295390	4.3570737
H	4.2730158	−0.5784660	4.5202179

Table S42: Coordinates of the optimizes structure of [(Ph_2N)BePh]2 in XZY Ångstrom format.

atom	x	y	z

N	−0.7307039	−0.1058673	−1.0551535
Be	0.8058224	−0.5808247	−0.4876309
H	0.8173417	−2.0652959	−2.9274371
C	1.7089038	−2.3091506	−2.3552072
Be	−0.8782206	0.3047206	0.5988809
C	2.6121879	−3.2131381	−2.8968383
H	2.4265244	−3.6516974	−3.8716084
H	3.2607397	−1.6882792	0.5795786
C	3.0661890	−2.0980194	−0.4088301
C	0.8234727	−1.6517930	2.3801216
C	1.1700564	−0.3162262	2.1855376
H	0.3263732	−2.1999147	1.5860281
C	1.1318984	−2.2935451	3.5655134
H	0.8544594	−3.3329868	3.6952650
C	1.7987518	−1.6164762	4.5768666
H	2.0425553	−2.1195182	5.5045507
C	2.1529130	−0.2909247	4.3825772
H	2.6762774	0.2509558	5.1620210
C	1.8425325	0.3604030	3.1980251
H	2.1196227	1.3979594	3.0601959
C	2.7123053	1.6363675	0.2222297
C	1.4030260	1.5857064	0.6916991
H	3.2727557	0.7148379	0.1128624
C	3.2790040	2.8530213	−0.1197861
C	2.5435580	4.0243176	−0.0016407
H	2.9846909	4.9735421	−0.2816780
C	1.2426513	3.9761310	0.4750801
H	0.6621558	4.8858911	0.5709390
C	0.6764435	2.7618076	0.8323964
H	−0.3380365	2.7206657	1.2172808
C	−2.2358249	0.4713955	1.6037075
C	−2.0957460	0.8467269	2.9471760
H	−1.1014454	0.9933488	3.3616187
C	−3.1901447	1.0284412	3.7812882
H	−3.0444424	1.3182532	4.8165418
C	−4.4728838	0.8328606	3.2899929
H	−5.3319171	0.9705422	3.9375661
C	−4.6504434	0.4532957	1.9667806
H	−5.6505972	0.2914654	1.5787921
C	−3.5462684	0.2774539	1.1451783
H	−3.7146074	−0.0353999	0.1173185
C	−0.6843219	1.1313032	−1.7909938
C	−1.7430682	2.0308921	−1.7069962
H	−2.6164866	1.7690751	−1.1205841
C	−1.6651300	3.2545144	−2.3512122
H	−2.4901751	3.9530589	−2.2750637
C	−0.5309250	3.5910698	−3.0771979
H	−0.4670303	4.5539520	−3.5699893
C	0.5202124	2.6918859	−3.1695878
H	1.4086714	2.9466383	−3.7348745
C	0.4401832	1.4598171	−2.5383742
H	1.2559751	0.7477146	−2.6179722
C	−1.5521767	−1.1301006	−1.6012878
C	−2.0308663	−1.0864928	−2.9067698
H	−1.8051453	−0.2338026	−3.5346596
C	−2.7910064	−2.1346309	−3.4040818
H	−3.1554084	−2.0856761	−4.4238343

C	−3.0823177	−3.2360582	−2.6151891
H	−3.6753350	−4.0521666	−3.0093769
C	−2.6089314	−3.2782898	−1.3113071
H	−2.8338074	−4.1269544	−0.6761607
C	−1.8544056	−2.2346951	−0.8074183
H	−1.5133642	−2.2665065	0.2224746
N	0.7865098	0.3142750	0.9700618
C	1.9067192	−1.7185624	−1.0992530
C	3.7520409	−3.5603221	−2.1860586
H	4.4601573	−4.2683076	−2.6026799
C	3.9777767	−3.0016514	−0.9356996
H	4.8633895	−3.2749099	−0.3717402
H	4.2963358	2.8838777	−0.4919733

Table S43: Coordinates of the optimizes structure of **5** in XZY Ångstrom format.

atom	x	y	z
C	−4.2885329	3.3922331	−2.2182405
C	−3.2924726	4.0318976	−2.9518346
H	−4.0198771	2.9487169	−1.2658615
C	−5.5869357	3.3379781	−2.6945848
H	−6.3587626	2.8531722	−2.1070502
C	−5.9022647	3.9066238	−3.9228059
H	−6.9172720	3.8579760	−4.3004419
C	−4.9157704	4.5441390	−4.6605998
H	−5.1568867	4.9878575	−5.6200350
C	−3.6198449	4.6192959	−4.1703735
H	−2.8497851	5.1247724	−4.7426276
C	−3.9990200	5.1922749	1.5064035
H	−4.5649726	6.1167413	1.4973013
C	−4.5692502	4.0345050	2.0172796
H	−5.5810232	4.0518072	2.4055691
C	−3.8432774	2.8543247	2.0346272
H	−4.2826527	1.9504768	2.4418107
H	−2.2003034	−5.8411317	3.6836767
C	−1.1552201	−5.6957716	3.9339128
C	−0.6482520	−6.2033775	5.1241621
C	0.6940059	−6.0331875	5.4296310
H	−1.2980342	−6.7363955	5.8089184
H	1.0935842	−6.4263175	6.3576862
C	−1.8913863	4.0110895	−2.4333274
N	−1.4422330	3.0136504	−1.8364608
C	−1.0476475	5.2244708	−2.6535797
C	0.3122496	5.0598764	−2.9044258
H	0.7011839	4.0510010	−2.9861823
C	0.9283052	0.3747365	−2.5773621
N	0.2838404	0.6969343	−1.5343543
C	1.9038425	−0.7475943	−2.5755915
C	2.7239030	−0.9756383	−1.4730870
H	2.6774621	−0.2980637	−0.6301413
C	3.5831900	−2.0609650	−1.4447598
H	4.2088821	−2.2334578	−0.5772977
C	3.6226110	−2.9424004	−2.5167730
H	4.2823449	−3.8018673	−2.4864878
C	2.8109193	−2.7239800	−3.6205088
H	2.8327284	−3.4139882	−4.4560116
C	1.9675401	−1.6245211	−3.6569814

H	1.3336127	−1.4516190	−4.5189824
C	0.7378089	1.0926828	−3.8649973
C	1.8376263	1.4673898	−4.6352384
H	2.8342546	1.1825727	−4.3167665
C	1.6626040	2.2171152	−5.7873589
H	2.5248735	2.5251214	−6.3673372
C	0.3844504	2.5695138	−6.1982156
H	0.2470427	3.1521037	−7.1019335
C	−0.7163532	2.1714385	−5.4528065
H	−1.7178221	2.4375027	−5.7709466
C	−0.5400503	1.4436861	−4.2883195
H	−1.3949471	1.1429675	−3.6975954
C	−1.8076389	1.5292430	1.4374430
N	−1.1587448	1.1943032	0.4013040
C	−2.5525996	2.8135196	1.5095387
C	−1.9864677	3.9803181	1.0059224
H	−0.9802838	3.9524438	0.6094353
C	−2.7026884	5.1650542	1.0117077
H	−2.2485275	6.0667310	0.6171543
C	−1.8516101	0.6612604	2.6440345
C	−1.9172134	−0.7245716	2.5206609
H	−1.9819800	−1.1653114	1.5340156
C	−1.8894248	−1.5354708	3.6426295
H	−1.9309209	−2.6125638	3.5330621
C	−1.7810676	−0.9684847	4.9053317
C	−1.7161832	0.4108217	5.0396804
C	−1.7666979	1.2221615	3.9169650
H	−1.7172337	2.2999955	4.0201640
C	−0.8394166	−2.4592957	−0.9404780
N	−0.2401536	−1.6868072	−0.1336146
C	−0.6174364	−3.9289088	−0.9240693
C	−1.6952072	−4.8084802	−1.0134252
H	−2.6960630	−4.4141645	−1.1498592
C	−1.4940446	−6.1753279	−0.9068195
H	−2.3403406	−6.8508991	−0.9531055
C	−0.2100344	−6.6769593	−0.7446251
H	−0.0519316	−7.7464974	−0.6663587
C	0.8703231	−5.8077766	−0.6873475
H	1.8765540	−6.1926607	−0.5675580
C	0.6667646	−4.4408225	−0.7684605
H	1.5051051	−3.7595248	−0.7113700
C	−1.7901470	−1.9378293	−1.9581121
C	−1.7933682	−2.4611425	−3.2498088
H	−1.1301360	−3.2836748	−3.4912806
C	−2.6144006	−1.9174692	−4.2253130
H	−2.5893394	−2.3150190	−5.2332969
C	−3.4634723	−0.8653555	−3.9136544
H	−4.1057420	−0.4388971	−4.6755268
C	−3.4837683	−0.3525939	−2.6235940
H	−4.1380107	0.4755260	−2.3789596
C	−2.6470312	−0.8821958	−1.6557850
H	−2.6472930	−0.4713291	−0.6542638
C	1.7285957	0.5636990	2.0933820
N	1.1245843	−0.2001522	1.2817675
C	2.4421540	0.0302731	3.2831830
C	1.8711545	−0.9838781	4.0454177
H	0.8818278	−1.3421245	3.7941496

C	2.5616135	−1.5298352	5.1139627
C	3.8370520	−1.0781063	5.4223957
C	4.4113754	−0.0612766	4.6721503
H	5.4067494	0.2952625	4.9106185
C	3.7104513	0.5022011	3.6179629
H	4.1528770	1.3029200	3.0358215
C	1.7477777	2.0388464	1.9067241
C	1.8546734	2.5932029	0.6334828
H	1.9705640	1.9383181	−0.2207010
C	1.8030798	3.9651747	0.4542653
H	1.8777241	4.3842484	−0.5420494
C	1.6288840	4.8013794	1.5488305
H	1.5703555	5.8742415	1.4060779
C	1.5224444	4.2596948	2.8216194
H	1.3782482	4.9083746	3.6778221
C	1.5970769	2.8873743	3.0018882
H	1.5150888	2.4623666	3.9956006
C	1.8677171	−4.0282770	2.4305308
N	1.4042747	−3.0351298	1.8374925
C	1.0225374	−4.8332266	3.3632766
C	−0.3266913	−5.0069898	3.0650964
H	−0.7037795	−4.5967646	2.1348605
C	1.5288399	−5.3639417	4.5461216
H	2.5802116	−5.2378755	4.7800214
C	3.2864256	−4.4528773	2.2313161
C	4.2613633	−3.4741613	2.0551903
H	3.9634266	−2.4339180	2.1254295
Be	−0.8553103	1.8241240	−1.1035925
Be	0.0027518	0.0020273	0.0050558
Be	0.8521243	−1.8277137	1.1071930
H	−1.7413681	−1.6042303	5.7822863
H	−1.6236230	0.8571396	6.0230020
H	2.1041622	−2.3190360	5.6995677
H	4.3833652	−1.5158270	6.2500215
C	1.1372756	6.1609586	−3.0550219
H	2.1913191	6.0217081	−3.2685721
C	0.6155672	7.4435016	−2.9358699
H	1.2623926	8.3064753	−3.0459103
H	−1.1487679	8.6149708	−2.5891640
C	−0.7374872	7.6162994	−2.6841405
C	−1.5680083	6.5118533	−2.5584931
H	−2.6275855	6.6460544	−2.3706594
C	5.5762234	−3.8286875	1.8076257
H	6.3309570	−3.0589139	1.6901422
C	5.9297826	−5.1692869	1.7124632
H	6.9578034	−5.4479280	1.5106279
C	4.9645255	−6.1504092	1.8849380
H	5.2354998	−7.1975471	1.8101759
C	3.6516307	−5.7939377	2.1580746
H	2.8979496	−6.5603519	2.3014864

Table S44: Coordinates of the optimizes structure of H_2NMes in XZY Ångstrom format.

atom	x	y	z
C	−0.5907469	1.0547203	−0.4155425
C	0.3766500	0.2368890	−1.0130539
C	−1.0582943	0.7295858	0.8496911

H	−1.8057463	1.3730238	1.3056959
C	−0.6048695	−0.3833226	1.5459439
C	0.3536939	−1.1770327	0.9290761
H	0.7316961	−2.0534797	1.4482878
C	0.8513721	−0.8927168	−0.3343434
C	−1.1050992	2.2577167	−1.1419006
H	−0.3091895	2.9853153	−1.3437688
H	−1.5463918	1.9863470	−2.1067299
H	−1.8691474	2.7686584	−0.5559234
C	1.8793557	−1.7723114	−0.9737848
H	2.1234667	−2.6170451	−0.3295420
H	1.5283351	−2.1701272	−1.9317938
N	0.8215276	0.5128223	−2.3018392
H	0.7343076	1.4739370	−2.5879695
H	1.7242978	0.1326518	−2.5335681
C	−1.1515818	−0.7322335	2.8973758
H	−0.4047947	−1.2433529	3.5085906
H	−1.4750385	0.1599703	3.4374588
H	−2.0178559	−1.3971951	2.8185721
H	2.8140534	−1.2328206	−1.1709323

Table S45: Coordinates of the optimizes structure of pyridine in XZY Ångstrom format.

atom	x	y	z
C	0.0000000	0.0000000	−1.1875644
C	−1.1905597	0.0000000	−0.4796224
C	−1.1347786	0.0000000	0.9066676
N	0.0000000	0.0000000	1.5975498
C	1.1347786	0.0000000	0.9066676
C	1.1905597	0.0000000	−0.4796224
H	0.0000000	0.0000000	−2.2716173
H	−2.1474043	0.0000000	−0.9875080
H	−2.0507421	0.0000000	1.4912789
H	2.0507421	0.0000000	1.4912789
H	2.1474043	0.0000000	−0.9875080

Table S46: Coordinates of the optimizes structure of H_2NDipp in XZY Ångstrom format.

atom	x	y	z
C	0.0881083	−0.9773903	−0.7861065
C	0.3459025	0.1459708	0.0200729
C	−1.2110925	−1.4580539	−0.8634735
H	−1.4197823	−2.3257524	−1.4772671
C	−2.2458794	−0.8568352	−0.1682254
H	−3.2545111	−1.2450203	−0.2427437
C	−1.9773836	0.2444834	0.6258016
H	−2.7884245	0.7134220	1.1688202
C	−0.6941281	0.7614620	0.7414439
C	−0.3955073	1.9357020	1.6461969
H	0.2964177	2.6032484	1.1112639
C	−1.6126266	2.7832153	1.9855154
H	−2.3164078	2.2370404	2.6185819
H	−1.3040060	3.6726083	2.5395596
H	−2.1431036	3.1068614	1.0876024
C	0.2965305	1.4692161	2.9289538
H	1.1812485	0.8669963	2.7163048

H	0.5969118	2.3220331	3.5438276
H	−0.3909288	0.8539346	3.5150920
C	1.2161644	−1.6177494	−1.5630695
H	2.1116689	−1.5731358	−0.9305088
C	1.4985833	−0.8416824	−2.8523253
H	1.6599015	0.2241242	−2.6711623
H	2.3790664	−1.2372158	−3.3658690
H	0.6444244	−0.9239982	−3.5292698
C	0.9881685	−3.0881508	−1.8828034
H	0.1761943	−3.2237197	−2.6016258
H	1.8882927	−3.5175928	−2.3287589
H	0.7457091	−3.6595518	−0.9847129
N	1.6518257	0.6098150	0.1511407
H	1.7384529	1.5543739	0.4868238
H	2.2502103	0.4413417	−0.6390796

Table S47: Coordinates of the optimizes structure of $HNPh_2$ in XZY Ångstrom format.

atom	x	y	z
N	0.9542560	0.2406909	0.4468964
H	1.8498823	0.4444667	0.8545442
C	0.0800640	−0.4723655	1.2526772
C	−0.9399440	−1.2752307	0.7379673
H	−1.0719572	−1.3589247	−0.3325314
C	−1.7604335	−1.9912633	1.5935265
H	−2.5445687	−2.6107147	1.1728827
C	−1.5811212	−1.9399436	2.9678173
H	−2.2264311	−2.5049774	3.6288818
C	−0.5560796	−1.1579855	3.4810763
H	−0.3948666	−1.1063167	4.5518335
C	0.2601299	−0.4266580	2.6377939
H	1.0474009	0.1970155	3.0492356
C	0.7733426	0.6891135	−0.8523816
C	−0.4868778	0.9607685	−1.3891777
H	−1.3721166	0.8215303	−0.7829917
C	−0.6032845	1.4402240	−2.6830965
H	−1.5909453	1.6469606	−3.0796826
C	0.5190792	1.6740713	−3.4637197
H	0.4183659	2.0509774	−4.4739186
C	1.7735411	1.4241369	−2.9259175
H	2.6645980	1.6038537	−3.5165872
C	1.9017712	0.9306927	−1.6403826
H	2.8861953	0.7198782	−1.2347458

Table S48: Coordinates of the optimizes structure of $HNCPh_2$ in XZY Ångstrom format.

atom	x	y	z
C	−0.3460482	1.1425810	−0.3318600
C	−0.8695221	−0.0782710	−1.0002754
C	−0.0126217	−1.1016142	−1.4004629
C	−0.5035741	−2.1989362	−2.0891626
C	−1.8596528	−2.2992547	−2.3653206
C	−2.7224333	−1.2926984	−1.9566577
C	−2.2289495	−0.1864429	−1.2842291
N	−0.6880315	2.3199197	−0.6796658
H	−1.3266308	2.2836943	−1.4733718

H	0.1754078	−2.9801788	−2.4105240
H	−2.2441636	−3.1630920	−2.8948557
H	−3.7843565	−1.3713981	−2.1584391
H	−2.9036364	0.5964690	−0.9552143
C	0.6212357	0.9825879	0.7798567
C	0.6633571	−0.1793211	1.5474171
H	−0.0118264	−0.9963132	1.3227543
C	1.5506322	−0.2898310	2.6070614
C	2.4126712	0.7546004	2.9027656
C	2.3781167	1.9159125	2.1407118
C	1.4859899	2.0314303	1.0905474
H	1.0460232	−1.0266468	−1.1806773
H	1.5672275	−1.1947143	3.2032956
H	3.1119317	0.6653754	3.7262323
H	3.0519763	2.7338077	2.3683552
H	1.4368777	2.9323342	0.4917189