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Supplementary Information

Synthesis of Mono-, Di-, and Triaminobismuthanes and Observation of C-C Coupling of Aromatic Systems with Bismuth(III) Chloride

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Table of contents

1. General Information....................2
2. Crystallographic Details....................3
3. Numbering Schemes of Compounds....................8
4. Synthesis of Starting Materials....................31
5. Synthesis of Compounds....................38
6. References....................49

1. General Information.

All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques.

Dichloromethane was purified according to a literature procedure,[1] dried over P_4O_{10} and CaH_2 and freshly distilled prior to use. Tetrahydrofurane (thf), Et_2O, *n*-hexane, benzene and toluene were dried over Na/benzophenone and freshly distilled prior to use.

2,6-bis(2,4,6-trimethylphenyl)aniline ($TerNH_2$)[2,3], 2,4,6-tri-*tert*-butylanilin (Mes^*NH_2)[4], *N*-trimethylsilyl-2,6-bis(2,4,6-trimethylphenyl)anilin ($TerN(SiMe_3)H$)**[2]** and *N*-trimethylsilyl-2,4,6-tri-*tert*-butylanilin ($Mes^*N(SiMe_3)H$)[5] were prepared according to a modified literature procedure. Trimethylsilylchloride (TMSCl) (Merk) was dried over CaH_2 and freshly destilled prior to use. $LiN(SiMe_3)_2$ (Aldrich) and *n*-BuLi (2.5M, Acros) were used as received. $BiCl_3$ (99.9%, anhydrous, Alfa Aesar) was sublimed prior to use, if no other information are given.

NMR: ^1H-, $^{13}C\{^1H\}$-, and ^{29}Si-INEPT-NMR spectra were recorded on a Bruker AVANCE 250, a Bruker AVANCE 300 or a Bruker AVANCE 500. The chemical shifts were referenced to solvent signals (CD_2Cl_2: $d\ ^1H = 5.32$, $d\ ^{13}C = 54.0$; d6-benzene: $d\ ^1H = 7.16$, $d\ ^{13}C = 128.4$). The NMR signals were assigned by DEPT and two-dimensional correlation spectra (HSQC and HMBC) using standard pulse sequences (standard Bruker software).

IR: Nicolet 6700 FT-IR spectrometer with a Smart Endurance ATR device was used.

Raman: A LabRAM HR 800 Horiba Jobin Yvon with a High Stability BX40 Microscop (focus 1 μm) and Olympus Mplan 50xNA 0.70 objectivs was used. A infra red laser (785 nm, 100 mW, air cooled diod laser), a red laser (633 nm, 17 mW, HeNe-laser), a green laser (532 nm, 50 mW, air cooled, doubled frequenze Nd:YAG solid state laser) or a blue laser (473 nm, 20 mW, air cooled solid state laser was used.

CHN analyses: Analysator Flash EA 1112 from Thermo Quest was used.

Melting points are uncorrected (EZ-Melt, Stanford Research Systems). Heating-rate 20 °C/min (clearing-points are reported).

DSC: DSC 823e from Mettler-Toledo (Heating-rate 5 °C/min) was used.

2. Crystallographic Details

Table S1. Crystallographic details of TripN($SiMe_3$)H, DmpN($SiMe_3$)Li · 0.5 thf, *p*-TolN($SiMe_3$)Li · thf and **5a_i**.

	TripN($SiMe_3$)H	DmpN($SiMe_3$)Li · 0.5 thf	*p*-TolN($SiMe_3$)Li · thf	**5a_i**
chem. formula	$C_{18}H_{33}NSi$	$C_{22}H_{36}Li_2N_2Si_2 \cdot C_4H_8O$	$C_{10}H_{16}NSiLi \cdot C_4H_8O$	$C_{21}H_{38}BiCl_2NSi$
M [g mol^{-1}]	291.54	470.69	257.37	612.49
color	colorless	colorless	colorless	yellow
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a [Å]	11.5209(6)	11.3711(6)	11.4715(7)	12.8210(6)
b [Å]	12.3140(6)	15.2605(8)	13.3538(7)	17.8386(8)
c [Å]	13.3055(7)	17.1661(9)	11.6454(6)	11.3085(5)
α [°]	90.0	90.0	90.0	90
β [°]	90.088(3)	98.542(3)	119.112(2)	109.114(3)
γ [°]	90.0	90.0	90.0	90
V [Å^3]	1887.6(2)	2945.8(3)	1558.6(2)	2443.8(2)
Z	4	4	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.026	1.061	1.097	1.665
μ [mm^{-1}]	0.12	0.14	0.14	7.49
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	173	173	173	123
measured reflexes	25882	44236	22782	37662
independent reflexes	5427	8581	4540	7792
reflexes with $I > 2\sigma(I)$	4742	5307	2942	4539
$R_{int.}$	0.048	0.056	0.066	0.121
$F(000)$	648	1024	560	1208
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.041	0.049	0.049	0.051
wR_2 (F^2)	0.106	0.142	0.132	0.100
GooF	1.03	1.02	1.02	0.98
parameter	195	378	189	247

Table S2. Crystallographic details of **5a_ii**, **5a** · 1.5 C_7H_8, **8_i** and **8_ii**.

	5a_ii	**5a** · 1.5 C_7H_8	**8_i**	**8_ii**
chem. formula	$C_{21}H_{38}BiCl_2NSi$	$C_{21}H_{38}BiCl_2NSi$ · 1.5 C_7H_8	$C_{42}H_{76}N_2Si_2$	$C_{42}H_{76}N_2Si_2$
M [g mol^{-1}]	612.49	750.70	665.23	665.23
color	yellow	yellow	yellow	yellow
crystal system	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P1$	Cc	$P2_1/n$
a [Å]	25.6910(7)	10.1770(5)	12.1974(3)	10.3047(9)
b [Å]	20.0014(5)	10.7624(5)	16.2449(4)	28.762(3)
c [Å]	29.9643(8)	16.3280(7)	21.8846(6)	14.636(1)
α [°]	90.0	93.750(2)	90.0	90.0
β [°]	90.167(2)	101.264(2)	98.390(2)	94.693(4)
γ [°]	90.0	105.923(2)	90.0	90.0
V [Å^3]	15397.3(7)	1673.2(1)	4289.9(2)	4323.2(6)
Z	24	2	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.585	1.490	1.030	1.022
μ [mm^{-1}]	7.13	5.48	0.11	0.11
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	123	173	153	173
measured reflexes	141038	42741	29914	36515
independent Reflexes	50315	12066	11665	9406
reflexes with $I > 2\sigma(I)$	25220	10988	8667	5337
$R_{int.}$	0.085	0.028	0.036	0.061
$F(000)$	7248	754	1480	1480
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.059	0.021	0.050	0.055
wR_2 (F^2)	0.123	0.049	0.110	0.147
GooF	0.96	1.04	1.01	1.01
parameter	1497	375	442	477

Table S3. Crystallographic details of **5b** · 0.5 C_6H_6, **9b**, **5c** and **9c_i**.

	5b · 0.5 C_6H_6	**9b**	**5c**	**9c_i**
chem. formula	$C_{18}H_{32}BiCl_2NSi \cdot 0.5\ C_6H_6$	$C_{36}H_{64}BiClN_2Si_2$	$C_{15}H_{26}BiCl_2NSi$	$C_{30}H_{52}BiClN_2Si_2$
M [g mol^{-1}]	609.47	825.50	528.34	741.34
color	yellow	yellow	orange	yellow
crystal system	triclinic	triclinic	triclinic	monoclinic
space group	$P1$	$P1$	$P1$	$P2_1/c$
a [Å]	10.1484(5)	9.8401(6)	14.383(2)	11.6699(4)
b [Å]	15.3428(7)	11.5699(8)	16.648(2)	16.0308(5)
c [Å]	16.9799(8)	19.169(1)	19.085(2)	36.1902(11)
α [°]	79.412(2)	94.760(4)	107.659(4)	90.0
β [°]	86.011(2)	101.072(4)	102.886(4)	90.8730(10)
γ [°]	75.179(2)	109.648(4)	101.754(4)	90.0
V [Å^3]	2511.7(2)	1991.2(2)	4059.8(6)	6769.6(4)
Z	4	2	8	8
$\rho_{calc.}$ [g cm^{-3}]	1.612	1.377	1.729	1.455
μ [mm^{-1}]	7.29	4.58	9.00	5.38
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	173	173	173	123
measured reflexes	84282	81351	98637	118191
independent reflexes	17282	17516	25805	24366
reflexes with $I > 2\sigma(I)$	11399	13029	18083	16320
$R_{int.}$	0.060	0.052	0.047	0.069
$F(000)$	1196	844	2032	2992
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.035	0.038	0.032	0.043
wR_2 (F^2)	0.065	0.067	0.061	0.066
GooF	1.01	1.03	1.00	1.01
parameter	479	460	749	701

Table S4. Crystallographic details of **9c_ii**, **5d** · CH_2Cl_2, **12e** and **5e/9e** · 0.5 C_6H_{14}.

	9c_ii	**5d** · CH_2Cl_2	**12e**	**5e/9e**
chem. formula	$C_{30}H_{52}BiClN_2Si_2$	$C_{27}H_{34}BiCl_2NSi \cdot CH_2Cl_2$	$C_{33}H_{54}BiN_3Si_3$	$C_{33}H_{54}Bi_2Cl_3N_3Si_3 \cdot 0.5\ C_6H_{14}$
M [g mol^{-1}]	741.34	765.45	786.04	1144.46
color	yellow	yellow	colourless	yellow
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	$P1$	$P2_1/c$	$P2_1/n$	$C2/c$
a [Å]	9.8262(2)	16.3869(4)	11.1196(4)	41.022(2)
b [Å]	15.8803(3)	8.7559(2)	17.8846(7)	9.1798(3)
c [Å]	23.2517(5)	22.1230(6)	18.8099(7)	24.3117(9)
α [°]	102.676(1)	90.0	90.0	90.0
β [°]	101.007(1)	104.483(2)	91.798(2)	90.767(3)
γ [°]	95.852(1)	90.0	90.0	90.0
V [Å^3]	3435.3(2)	3073.4(1)	3738.9(2)	9154.3(5)
Z	4	4	4	8
$\rho_{calc.}$ [g cm^{-3}]	1.433	1.654	1.396	1.661
μ [mm^{-1}]	5.30	6.14	4.84	7.96
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	173	173	173	173
measured reflexes	106132	56298	65316	68126
independent reflexes	24458	11599	13419	7182
reflexes with $I > 2\sigma(I)$	18241	7394	8960	5019
$R_{int.}$	0.035	0.079	0.063	0.097
$F(000)$	1496	1504	1592	4456
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.043	0.043	0.043	0.037
wR_2 (F^2)	0.088	0.0817	0.083	0.067
GooF	1.10	1.02	1.02	1.03
parameter	689	341	376	469

Table S5. Crystallographic details of **11f**, **12g** and **11g**.

	11f	**12g**	**11g**
chem. formula	$C_{38}H_{54}Bi_2N_4Si_2$	$C_{30}H_{48}BiN_3Si_3$	$C_{34}H_{46}Bi_2N_4Si_2$
M [g mol^{-1}]	1040.99	743.96	984.89
color	yellow	colourless	red
crystal system	orthorhombic	monoclinic	triclinic
space group	$Pna2_1$	$P2_1/n$	$P1$
a [Å]	15.4153(6)	10.8187(9)	8.7707(2)
b [Å]	11.6452(5)	17.560(2)	10.3814(3)
c [Å]	22.130(1)	18.694(2)	11.5042(3)
α [°]	90.0	90.0	111.435(1)
β [°]	90.0	92.585(4)	95.368(1)
γ [°]	90.0	90.0	107.984(1)
V [Å^3]	3972.7(3)	3547.8(5)	901.84(4)
Z	4	4	1
$\rho_{calc.}$ [g cm^{-3}]	1.741	1.393	1.813
μ [mm^{-1}]	8.94	5.09	9.84
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
measured reflexes	52463	57018	29366
independent reflexes	11494	11780	7359
reflexes with $I > 2\sigma(I)$	7065	7519	6209
$R_{int.}$	0.075	0.089	0.047
$F(000)$	2016	1496	472
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.044	0.040	0.029
wR_2 (F^2)	0.072	0.078	0.049
GooF	1.00	1.00	1.01
parameter	429	346	290

3. Numbering schemes of compounds

Scheme S1. Numbering scheme of TripN(SiMe$_3$)H.

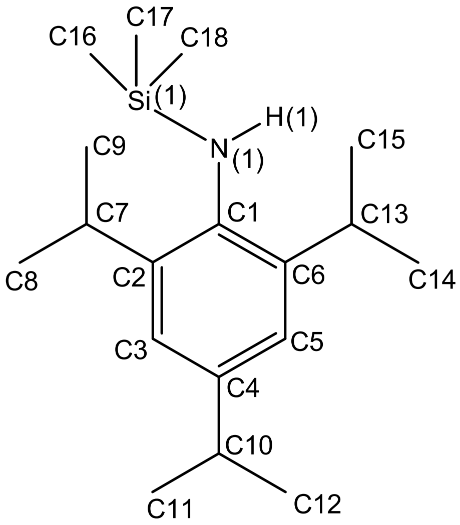


Table S6. Selected bond length (Å), angels (°) and torsion angels (°) of TripN(SiMe$_3$)H.

Si1—N1	1.732(1)	**Si1—N1—H1**	110(2)
N1—C1	1.435(2)	**C11—C10—C4**	113.0(1)
N1—H1	0.77(3)	**C11—C10—C12**	110.4(2)
C1—N1—Si1	127.5(1)	**C4—C10—C12**	111.1(1)
C1—N1—H1	116(2)	**C3—C4—C10—C11**	-60.4(2)

Scheme S2. Numbering scheme of DmpN($SiMe_3$)Li · 0.5 thf.

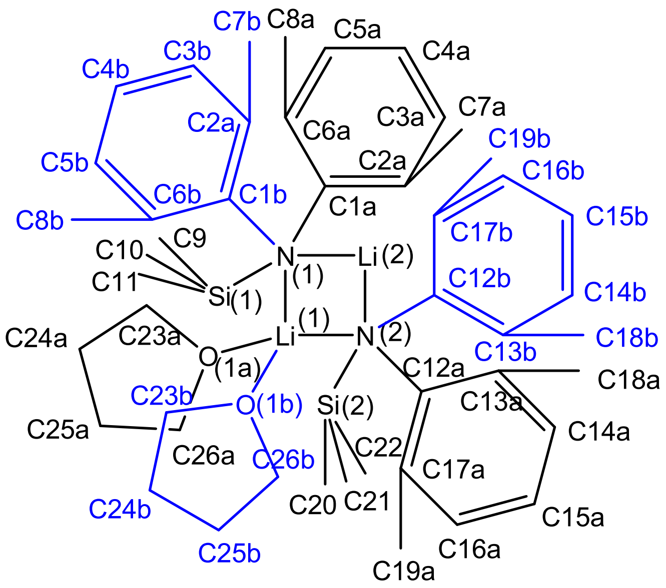


Table S7. Selected bond length (Å), angels (°) and torsion angels (°) of DmpN($SiMe_3$)Li · 0.5 thf.

Li1—O1A	1.947(6)	**O1A—Li1—N1**	129.7(3)
Li1—O1B	1.96(2)	**O1B—Li1—N1**	126.1(9)
Li1—N2	2.032(3)	**C1A—N1—Si1**	118.9(4)
Li1—N1	2.048(3)	**C1B—N1—Si1**	117.1(9)
Si1—N1	1.705(1)	**C1A—N1—Li2**	88.9(4)
N1—C1A	1.378(9)	**C1B—N1—Li2**	95.8(8)
N1—C1B	1.54(2)	**Si1—N1—Li2**	138.4(1)
N1—Li2	1.962(3)	**C1A—N1—Li1**	117.8(4)
Li2—N2	2.882(3)	**C1B—N1—Li1**	111.6(8)
Si2—N2	1.707(1)	**Si1—N1—Li1**	112.5(1)
N2—C12A	1.390(5)	**Li2—N1—Li1**	74.2(1)
N2—C12B	1.47(2)	**Si2—N2—Li2**	103.4(1)
O1A—Li1—N2	121.2(2)	**Li2—N2—Li1**	74.6(1)
O1B—Li1—N2	127.5(7)		

Scheme S3. Numbering scheme of *p*-TolN(SiMe$_3$)Li · thf.

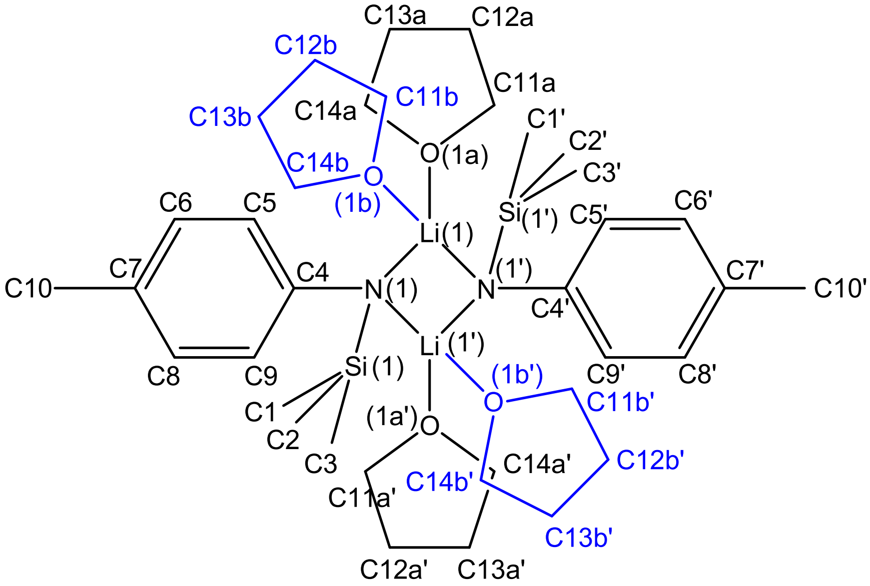


Table S8. Selected bond length (Å), angels (°) and torsion angels (°) of *p*-TolN(SiMe$_3$)Li · thf.

Li1—O1A	1.898(5)	**Si1—N1—Li1**	107.7(1)
Li1—O1B	1.91(2)	**C4—N1—Li1'**	102.1(1)
Li1—N1	2.002(3)	**Si1—N1—Li1'**	121.9(1)
Li1—N1'	2.036(3)	**N1—C4—C5**	124.3(1)
Li1—Li1'	2.432(5)	**N1—C4—C9**	120.8(1)
N1—C4	2.700(3)	**O1A—Li1—N1—C4**	71.9(3)
N1—Si1	3.005(3)	**O1B—Li1—N1—C4**	58.0(1)
O1A—Li1—N1	123.4(3)	**N1'—Li1—N1—C4**	-94.4(2)
O1B—Li1—N1	121.7(1)	**Li1'—Li1—N1—C4**	-94.4(2)
N1—Li1—N1'	105.9(1)	**O1A—Li1—N1—Si1**	-74.7(3)
C4—N1—Si1	120.6(1)	**O1B—Li1—N1—Si1**	88.6(9)
C4—N1—Li1	122.3(1)		

Scheme S4. Numbering scheme of **5a_i**.

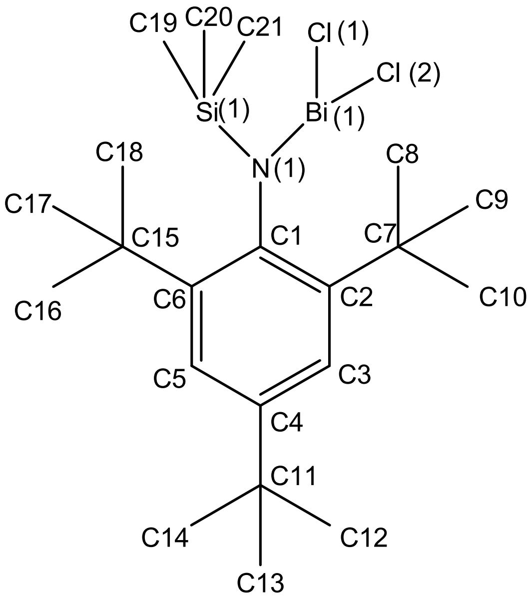


Table S9. Selected bond length (Å), angels (°) and torsion angels (°) of **5a_i**.

Bi1—N1	2.139(5)	**N1—Bi1—Cl1**	103.2(2)
Bi1—Cl1	2.518(2)	**C1—N1—Bi1**	99.7(3)
Bi1—Cl2	2.484(2)	**C1—N1—Si1**	134.6(4)
N1—Si1	1.759(5)	**Si1—N1—Bi1**	125.5(3)
N1—C1	1.451(8)	**C2—C1—N1—Bi1**	-92.8(5)
Cl2—Bi1—Cl1	90.80(6)	**C2—C1—N1—Si1**	92.4(7)
N1—Bi1—Cl2	101.8(2)		

Scheme S5. Numbering scheme of **5a_ii**.

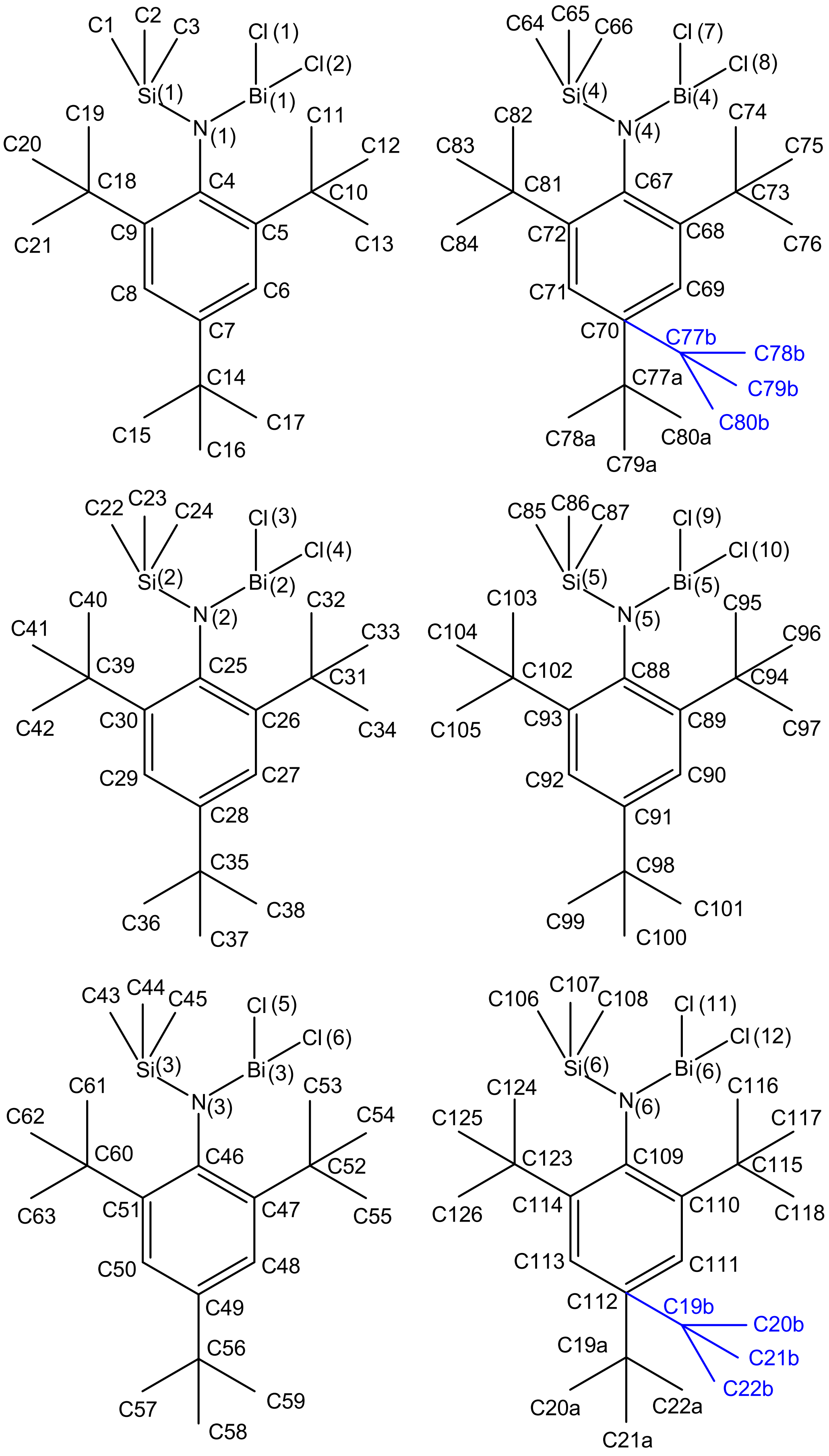


Table S10. Selected bond length (Å), angels (°) and torsion angels (°) of **5a_ii**.

Bi1—N1	2.165(5)	**N2—Bi2—Cl3**	103.6(2)
Bi1—Cl1	2.469(2)	**N2—Bi2—Cl4**	99.9(2)
Bi1—Cl2	2.512(2)	**Cl3—Bi2—Cl4**	89.96(6)
Bi2—N2	2.151(6)	**N3—Bi3—Cl5**	99.5(2)
Bi2—Cl3	2.475(2)	**N3—Bi3—Cl6**	97.5(2)
Bi2—Cl4	2.507(2)	**Cl5—Bi3—Cl6**	91.69(6)
Bi3—N3	2.161(5)	**N4—Bi4—Cl7**	100.2(2)
Bi3—Cl5	2.492(2)	**N4—Bi4—Cl8**	98.6(2)
Bi3—Cl6	2.546(2)	**Cl7—Bi4—Cl8**	92.03(6)
Bi4—N4	2.152(5)	**N5—Bi5—Cl9**	99.2(2)
Bi4—Cl7	2.498(2)	**N5—Bi5—Cl10**	99.8(2)
Bi4—Cl8	2.538(2)	**Cl9—Bi5—Cl10**	91.85(6)
Bi5—N5	2.159(6)	**N6—Bi6—Cl11**	104.2(2)
Bi5—Cl9	2.481(2)	**N6—Bi6—Cl12**	98.6(2)
Bi5—Cl10	2.539(2)	**Cl11—Bi6—Cl12**	90.41(8)
Bi6—N6	2.153(5)	**Bi1—N1—C4—C9**	91.7(6)
Bi6—Cl11	2.452(2)	**Bi2—N2—C25—C26**	87.2(6)
Bi6—Cl12	2.513(2)	**Bi3—N3—C46—C47**	92.9(6)
N1—Bi1—Cl1	103.5(2)	**Bi4—N4—C67—C68**	88.1(6)
N1—Bi1—Cl2	99.2(2)	**Bi5—N5—C88—C89**	88.2(7)
Cl1—Bi1—Cl2	90.22(6)	**Bi6—N6—C109—C110**	92.0(6)

Scheme S6. Numbering scheme of **5a** · 1.5 C_7H_8.

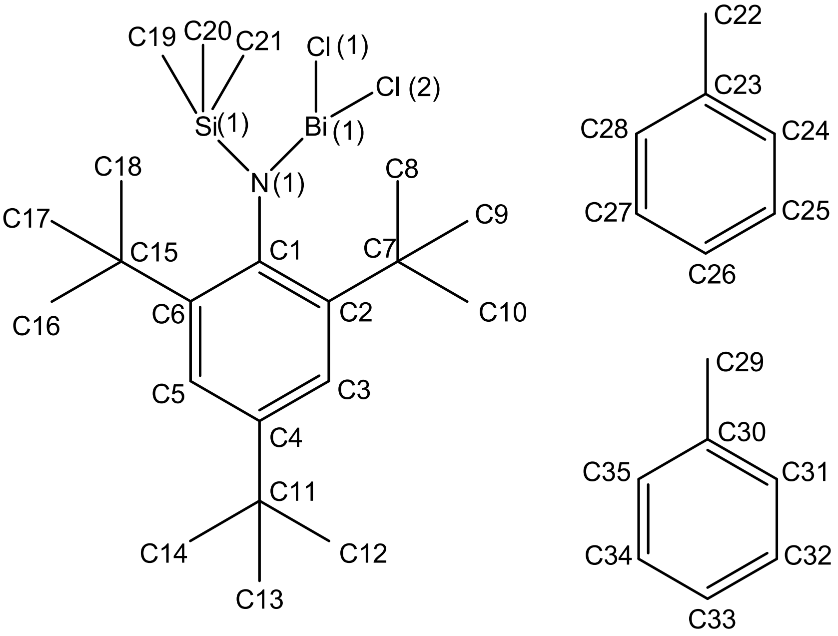


Table S11. Selected bond length (Å), angels (°) and torsion angels (°) of **5a** · 1.5 C_7H_8.

Bi1—N1	2.146(2)	**Si1—N1—Bi1**	126.58(6)
Bi1—Cl1	2.4771(5)	**C1—N1—Si1**	131.7(1)
Bi1—Cl2	2.4920(5)	**C6—C1—C2**	118.4(1)
Si1—N1	1.747(2)	**C6—C1—N1**	120.3(2)
N1—C1	1.449(2)	**C2—C1—N1**	120.8(1)
C1—C6	1.426(2)	**C1—N1—Si1**	131.9(1)
C1—C2	1.432(2)	**Cl1—Bi1—N1—C1**	148.90(7)
N1—Bi1—Cl1	99.82(3)	**Cl2—Bi1—N1—C1**	-118.85(7)
N1—Bi1—Cl2	103.57(3)	**Cl1—Bi1—N1—Si1**	-28.37(8)
Cl1—Bi1—Cl2	89.86(2)	**Cl2—Bi1—N1—Si1**	63.88(8)
C1—N1—Bi1	101.49(8)		

Scheme S7. Numbering scheme of **8_i**.

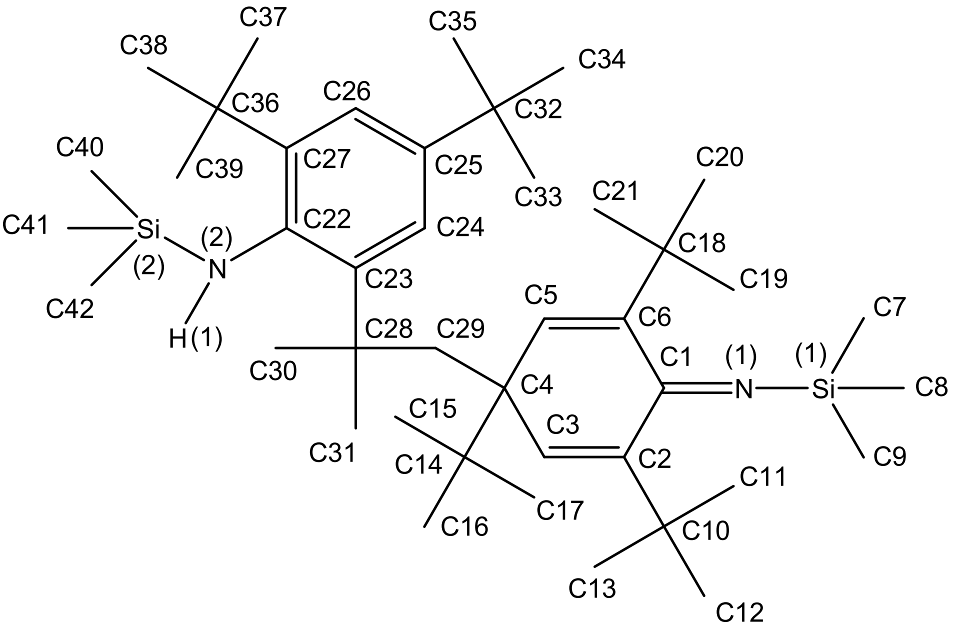


Table S12. Selected bond length (Å), angels (°) and torsion angels (°) of **8_i**.

Si1—N1	1.6885(2)	**C4—C14**	1.617(2)
Si1—C8	1.863(2)	**C5—C6**	1.329(3)
Si1—C7	1.866(2)	**C6—C18**	1.535(3)
Si1—C9	1.878(2)	**C22—C27**	1.421(2)
Si2—N2	1.7317(2)	**C22—C23**	1.426(2)
Si2—C40	1.863(3)	**C23—C24**	1.398(3)
Si2—C41	1.869(3)	**C23—C28**	1.559(2)
Si2—C42	1.881(3)	**C24—C25**	1.384(2)
N1—C1	1.268(2)	**C25—C26**	1.385(3)
N2—C22	1.438(2)	**C25—C32**	1.537(3)
N2—H1	0.78(3)	**C26—C27**	1.387(3)
C1—C2	1.507(2)	**C27—C36**	1.559(3)
C1—C6	1.504(3)	**C28—C30**	1.545(3)
C2—C3	1.336(2)	**C28—C31**	1.536(3)

C2—C10	1.537(3)	**C6—C1—C2**	114.3(2)
C3—C4	1.495(3)	**C1—N1—Si1**	175.8(2)
C4—C5	1.496(3)	**C22—N2—Si2**	135.2(1)
C4—C29	1.565(3)	**C22—N2—H1**	110(2)
C28—C29	1.559(3)	**C3—C4—C5**	109.7(2)
Si2—N2—H1	114(2)	**C3—C4—C29**	111.4(2)
N1—Si1—C8	108.9(1)	**C5—C4—C29**	110.3(1)
N1—Si1—C7	108.1(1)	**C28—C29—C4**	121.2(2)
C8—Si1—C7	112.4(1)	**C2—C1—N1—Si1**	43(2)
N2—Si2—C40	109.7(1)	**C23—C24—C25—C26**	3.0(3)
N2—Si2—C41	111.4(1)	**Si2—N2—C22—C27**	86.7(2)
C40—Si2—C41	110.8(2)	**C3—C4—C5—C6**	17.7(2)
N1—C1—C6	122.0(2)	**C29—C4—C5—C6**	140.7(2)
N1—C1—C2	123.7(2)	**C14—C4—C29—C28**	169.9(2)

Scheme S8. Numbering scheme of **8_ii**.

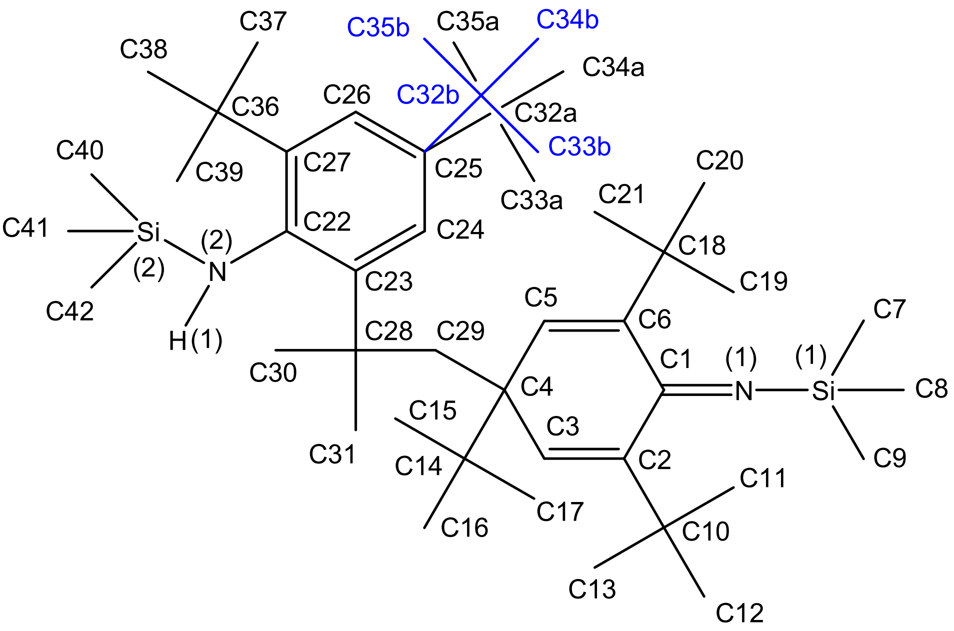


Table S13. Selected bond length (Å), angels (°) and torsion angels (°) of **8_ii**.

Si1—N1	1.678(2)	**C6—C18**	1.533(3)
Si1—C8	1.859(3)	**C22—C27**	1.415(3)
Si1—C7	1.849(3)	**C23—C24**	1.396(3)
Si1—C9	1.862(3)	**C23—C28**	1.551(3)
Si2—N2	1.714(2)	**C24—C25**	1.374(3)
Si2—C40	1.865(3)	**C28—C30**	1.535(3)
C1—C6	1.507(3)	**C22—C23**	1.414(3)
C1—C2	1.499(3)	**N1—Si1—C8**	115.1(1)
C2—C3	1.328(3)	**N1—Si1—C7**	106.6(1)
C2—C10	1.528(3)	**C7—Si1—C8**	108.9(2)
C3—C4	1.493(3)	**N1—C1—C6**	122.7(2)
C4—C5	1.485(3)	**N1—C1—C2**	122.2(2)
Si2—C41	1.867(3)	**C2—C1—C6**	115.0(2)
Si2—C42	1.848(3)	**C5—C4—C3**	109.9(2)
N1—C1	1.267(3)	**C3—C4—C29**	109.4(2)
N2—C22	1.435(3)	**C5—C4—C29**	111.8(2)
N2—H1	0.80(3)	**N2—Si2—C40**	110.2(1)
C25—C26	1.378(3)	**N2—Si2—C41**	110.8(1)
C25—C32A	1.532(6)	**C40—Si2—C41**	103.3(2)
C25—C32B	1.55(2)	**C1—N1—Si1**	174.2(2)
C26—C27	1.385(3)	**C22—N2—Si2**	135.0(2)
C27—C36	1.541(3)	**C22—N2—H1**	113(2)
C28—C31	1.537(3)	**Si2—N2—H1**	110(2)
C28—C29	1.553(3)	**C28—C29—C4**	121.1(2)
C4—C29	1.563(3)	**Si1—N1—C1—C2**	80(2)
C4—C14	1.606(3)	**Si2—N2—C22—C27**	−92.7(3)
C5—C6	1.326(3)	**C3—C4—C5—C6**	18.0(3)

C14—C4—C29—C28	−163.4(2)	**C29—C4—C5—C6**	139.6(2)
C23—C24—C25—C26	−4.3(3)		

Scheme S9. Numbering scheme of **5b** · 0.5 C_6H_6.

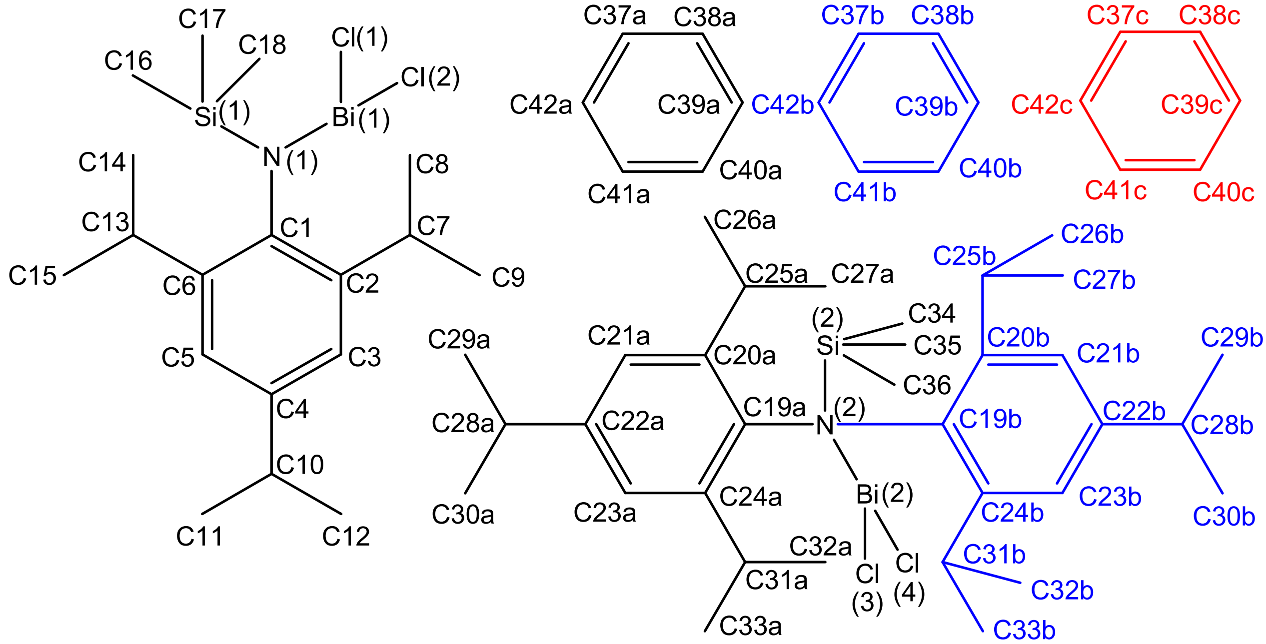


Table S14. Selected bond length (Å), angels (°) and torsion angles (°) of **5b** · 0.5 C_6H_6.

Bi1—N1	2.111(3)	**Cl1—Bi1—Cl2**	93.85(4)
Bi1—Cl1	2.449(1)	**C1—N1—Si1**	120.7(2)
Bi1—Cl2	2.483(1)	**C1—N1—Bi1**	106.1(2)
N1—C1	1.448(4)	**Si1—N1—Bi1**	133.2(1)
N1—Si1	1.756(3)	**N2—Bi2—Cl3**	99.03(7)
N2—Bi2	2.122(3)	**N2—Bi2—Cl4**	101.15(7)
Bi2—Cl3	2.4946(9)	**Cl3—Bi2—Cl4**	88.63(3)
Bi2—Cl4	2.5063(9)	**C19A—N2—Si2**	120.4(4)
N2—Si2	1.757(3)	**C19B—N2—Si2**	121.0(5)
N2—C19A	1.445(7)	**C19A—N2—Bi2**	109.6(4)
N2—C19B	1.482(7)	**C19B—N2—Bi2**	109.3(5)

N1—Bi1—Cl1	97.84(7)	**Si2—N2—Bi2**	129.7(1)
N1—Bi1—Cl2	97.05(7)		

Scheme S10. Numbering scheme of **9b**.

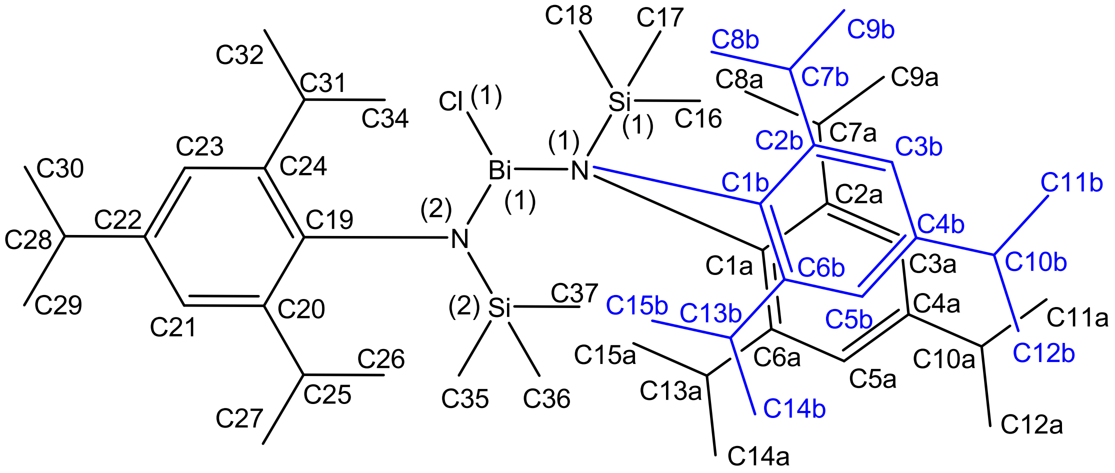


Table S15. Selected bond length (Å), angels (°) and torsion angels (°) of **9b**.

Bi1—N1	2.140(2)	**C1A—N1—Bi1**	110.0(4)
Bi1—Cl1	2.4862(7)	**C1B—N1—Bi1**	103.0(1)
Bi1—N2	2.178(2)	**Si1—N1—Bi1**	131.6(1)
N1—C1A	1.438(5)	**C19—N2—Si2**	119.6(2)
N1—C1B	1.48(2)	**C19—N2—Bi1**	107.4(1)
N1—Si1	1.749(2)	**Si2—N2—Bi1**	123.5(1)
N2—C19	1.446(3)	**N2—Bi1—N1—C1A**	138.5(2)
N2—Si2	1.756(2)	**N2—Bi1—N1—C1B**	147.1(7)
N1—Bi1—N2	108.50(7)	**Cl1—Bi1—N1—C1A**	-122.8(2)
N1—Bi1—Cl1	97.35(5)	**Cl1—Bi1—N1—C1B**	-114.2(7)
N2—Bi1—Cl1	95.83(5)	**N2—Bi1—N1—Si1**	-51.7(2)
C1A—N1—Si1	117.6(4)	**Cl1—Bi1—N1—Si1**	47.0(1)
C1B—N1—Si1	122.7(1)		

Scheme S11. Numbering scheme of **5c.**

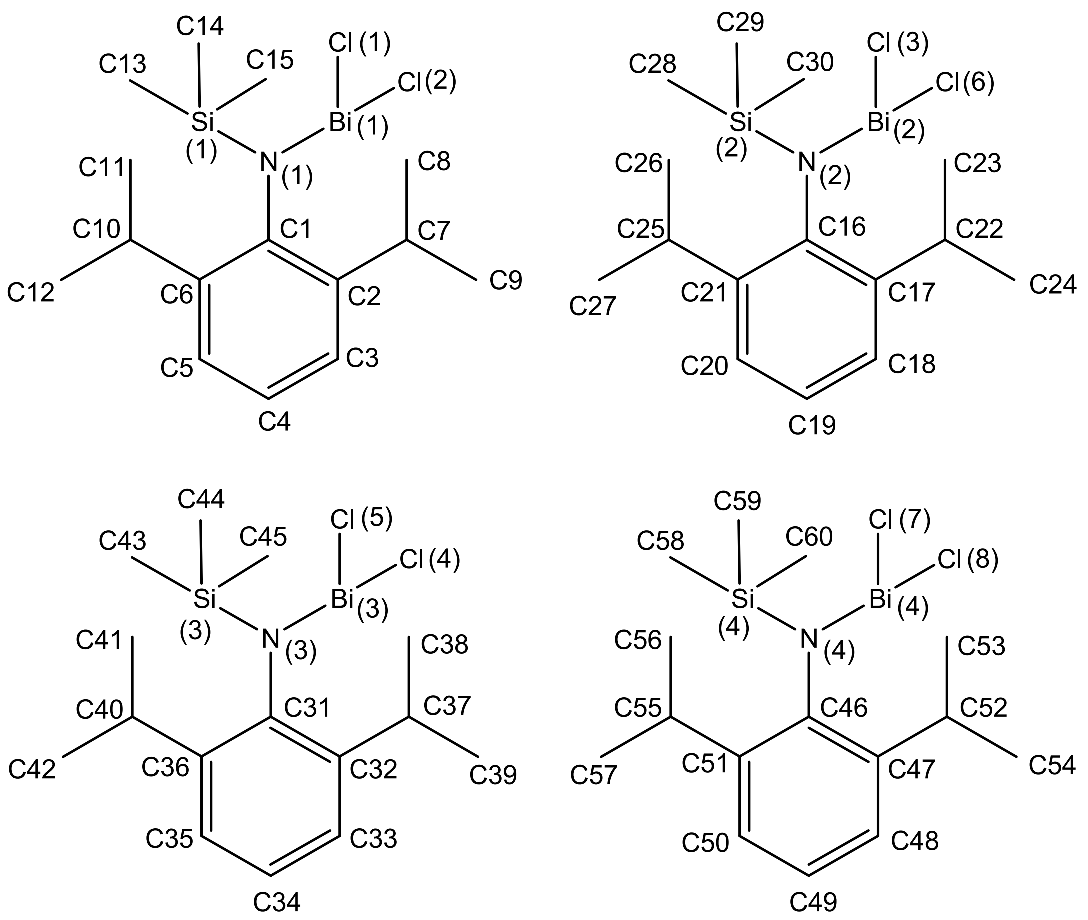


Table S16. Selected bond length (Å), angels (°) and torsion angels (°) of **5c.**

Bi1—N1	2.125(3)	**Bi3—Cl4**	2.6580(8)
Bi1—Cl1	2.4746(9)	**N3—Si3**	1.757(3)
Bi1—Cl2	2.5124(9)	**Bi4—N4**	2.126(3)
N1—Si1	1.754(3)	**Bi4—Cl7**	2.4369(9)
Bi2—N2	2.128(2)	**Bi4—Cl8**	2.515(1)
Bi2—Cl3	2.4687(8)	**N4—Si4**	1.755(3)
Bi2—Cl6	2.6409(8)	**Cl1—Bi1—Cl2**	94.90(3)
N2—Si2	1.755(3)	**N1—Bi1—Cl2**	92.50(7)
Bi3—N3	2.142(2)	**N1—Bi1—Cl1**	95.99(7)
Bi3—Cl5	2.4631(8)	**C1—N1—Bi1**	119.7(2)

C1—N1—Si1	122.6(2)	**Cl3—Bi2—Cl6**	84.24(3)
Si1—N1—Bi1	117.5(2)	**N2—Bi2—Cl6**	101.95(7)
N2—Bi2—Cl3	94.48(7)	**N4—Bi4—Cl7**	94.58(7)
C16—N2—Bi2	108.0(2)	**C46—N4—Bi4**	118.6(2)
C16—N2—Si2	121.6(2)	**C46—N4—Si4**	122.6(2)
Si2—N2—Bi2	130.0(2)	**Si4—N4—Bi4**	118.8(2)
Cl5—Bi3—Cl4	92.16(3)	**C2—C1—N1—Bi1**	-100.9(3)
N3—Bi3—Cl5	93.19(7)	**C2—C1—N1—Si1**	85.0(3)
N3—Bi3—Cl4	96.16(7)	**C17—C16—N2—Bi2**	95.7(3)
C31—N3—Bi3	124.8(2)	**C17—C16—N2—Si2**	-90.2(3)
C31—N3—Si3	122.5(2)	**C32—C31—N3—Bi3**	-91.7(3)
Si3—N3—Bi3	112.7(2)	**C32—C31—N3—Si3**	87.2(3)
Cl7—Bi4—Cl8	97.86(3)	**C47—C46—N4—Bi4**	81.7(3)
N4—Bi4—Cl8	95.89(8)	**C47—C46—N4—Si4**	-95.9(3)

Scheme S12. Numbering scheme of **9c_i.**

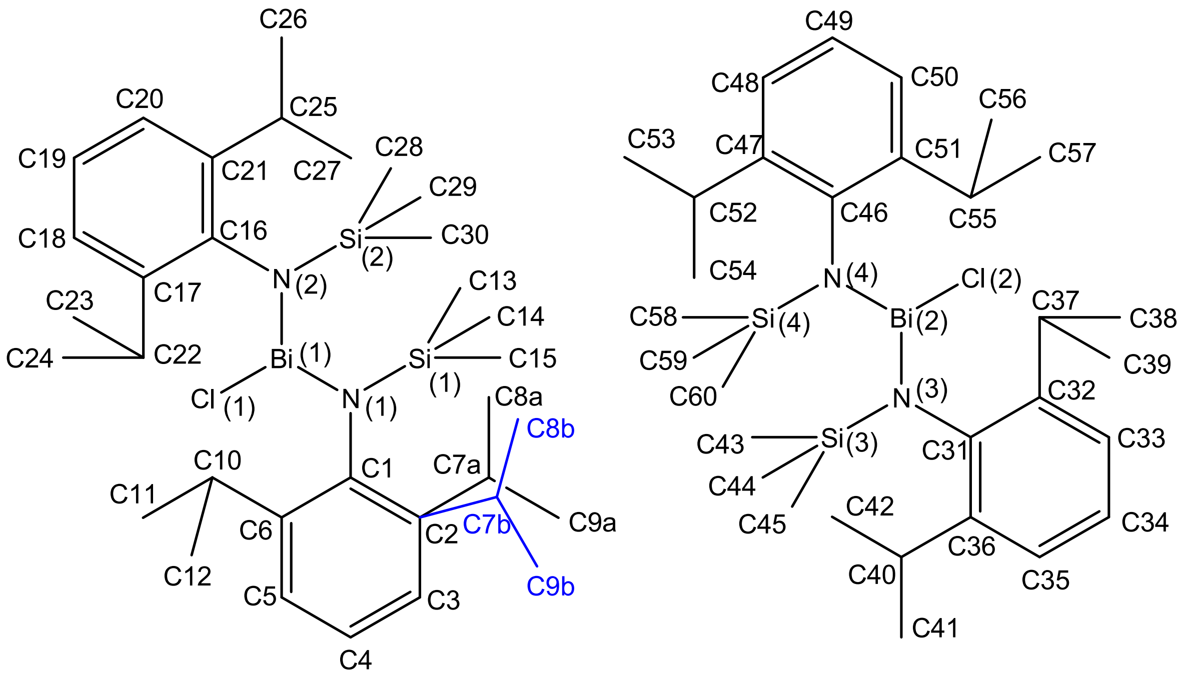


Table S17. Selected bond length (Å), angels (°) and torsion angels (°) of **9c_i**.

Bi1—N1	2.172(2)	**N4—Si4**	1.758(3)
Bi1—N2	2.151(2)	**N4—C46**	1.446(4)
Bi1—Cl1	2.4847(8)	**N2—Bi1—N1**	109.99(9)
N1—Si1	1.761(3)	**N2—Bi1—Cl1**	95.79(7)
N1—C1	1.447(4)	**N1—Bi1—Cl1**	94.69(7)
N2—Si2	1.747(3)	**N3—Bi2—N4**	110.99(9)
N2—C16	1.450(4)	**N4—Bi2—Cl2**	94.19(7)
Bi2—N3	2.150(2)	**N3—Bi2—Cl2**	96.72(7)
Bi2—N4	2.168(2)	**Bi1—N1—C1—C2**	-113.1(3)
Bi2—Cl2	2.4911(8)	**Bi1—N2—C16—C17**	98.9(3)
N3—Si3	1.751(3)	**Bi2—N3—C31—C32**	-75.2(3)
N3—C31	1.454(4)	**Bi2—N4—C46—C47**	64.4(3)

Scheme S13. Numbering scheme of **9c_ii.**

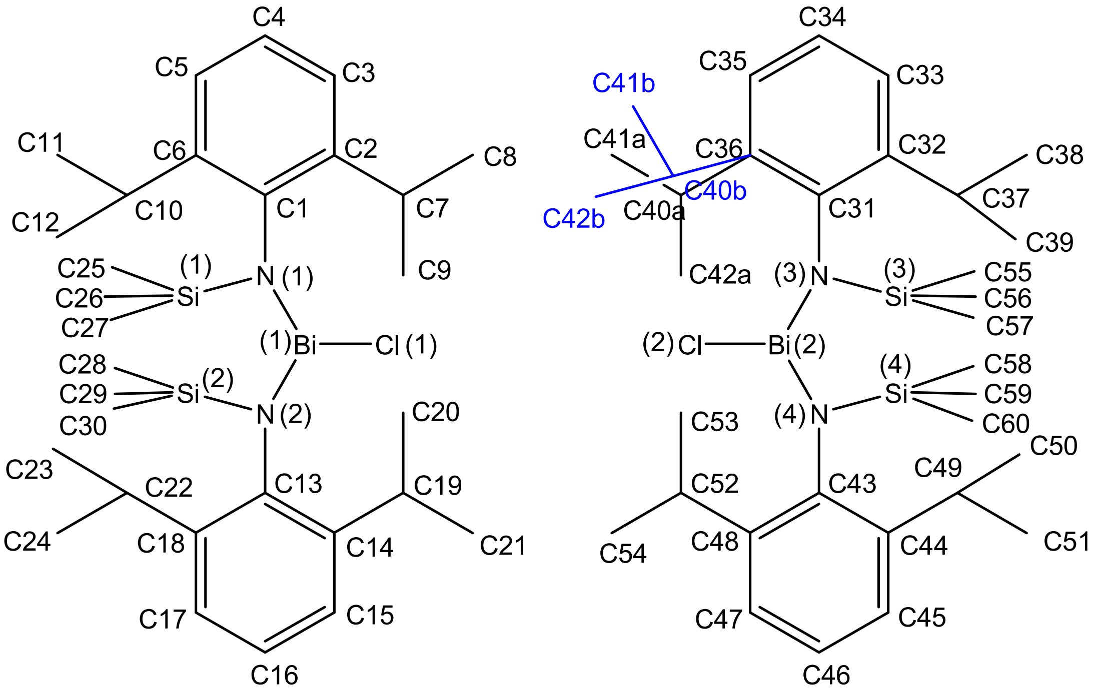


Table S18. Selected bond length (Å), angels (°) and torsion angels (°) of **9c.**

Bi1—N1	2.170(3)	**N2—Bi1—N1**	112.5(2)
Bi1—N2	2.147(3)	**Si1—N1—Bi1**	128.1(2)
Bi1—Cl1	2.497(2)	**C1—N1—Si1**	121.6(2)
N1—Si1	1.752(3)	**C1—N1—Bi1**	105.0(2)
N3—Si3	1.755(3)	**Si2—N2—Bi1**	135.6(2)
N4—Si4	1.750(3)	**C13—N2—Si2**	118.5(2)
Si2—N2	1.755(3)	**C13—N2—Bi1**	105.9(2)
Bi2—N3	2.182(3)	**N3—Bi2—Cl2**	95.17(8)
Bi2—N4	2.148(3)	**Cl2—Bi2—N4**	96.74(8)
Bi2—Cl2	2.477(1)	**N4—Bi2—N3**	110.7(1)
N1—Bi1—Cl1	96.48(9)	**Si3—N3—Bi2**	125.7(2)
N2—Bi1—Cl1	98.6(1)	**C31—N3—Si3**	119.3(2)

C31—N3—Bi2	107.2(2)	**C2—C1—N1—Bi1**	67.0(4)
Si4—N4—Bi2	131.5(2)	**C2—C1—N1—Si1**	-89.1(4)
C43—N4—Si4	118.2(2)	**C14—C13—N2—Bi1**	85.1(3)
C43—N4—Bi2	109.2(2)	**C14—C13—N2—Si2**	-97.4(4)
C32—C31—N3—Bi2	65.8(4)	**C44—C43—N4—Bi2**	96.4(3)
C32—C31—N3—Si3	-85.3(4)	**C44—C43—N4—Si4**	-93.9(4)

Scheme S14. Numbering scheme of **5d** · CH_2Cl_2.

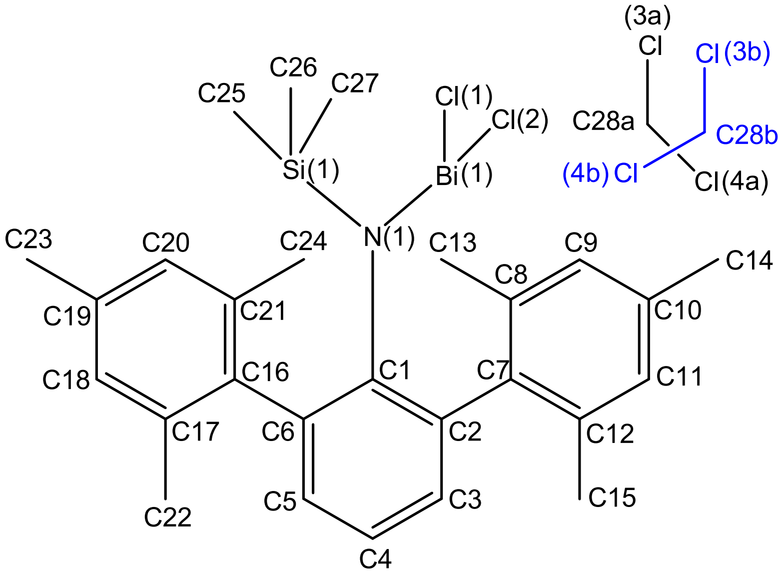


Table S19. Selected bond length (Å), angels (°) and torsion angels (°) of **5d** · CH_2Cl_2.

Bi1—N1	2.176(3)	**N1—C1**	1.415(5)
Bi1—Cl1	2.4846(1)	**C2—C7**	1.496(5)
Bi1—Cl2	2.5170(1)	**C6—C16**	1.500(5)
Si1—N1	1.760(3)	**C1—N1—Si1**	127.0(2)
Si1—C25	1.855(4)	**C1—N1—Bi1**	118.3(2)
Si1—C26	1.869(5)	**Si1—N1—Bi1**	112.42(2)
Si1—C27	1.884(4)	**N1—Bi1—Cl1**	100.31(8)

N1—Bi1—Cl2	94.09(8)	**Cl1—Bi1—Cl2**	87.64(3)

Scheme S15. Numbering scheme of **5e/9e** · 0.5 C_6H_{14}.

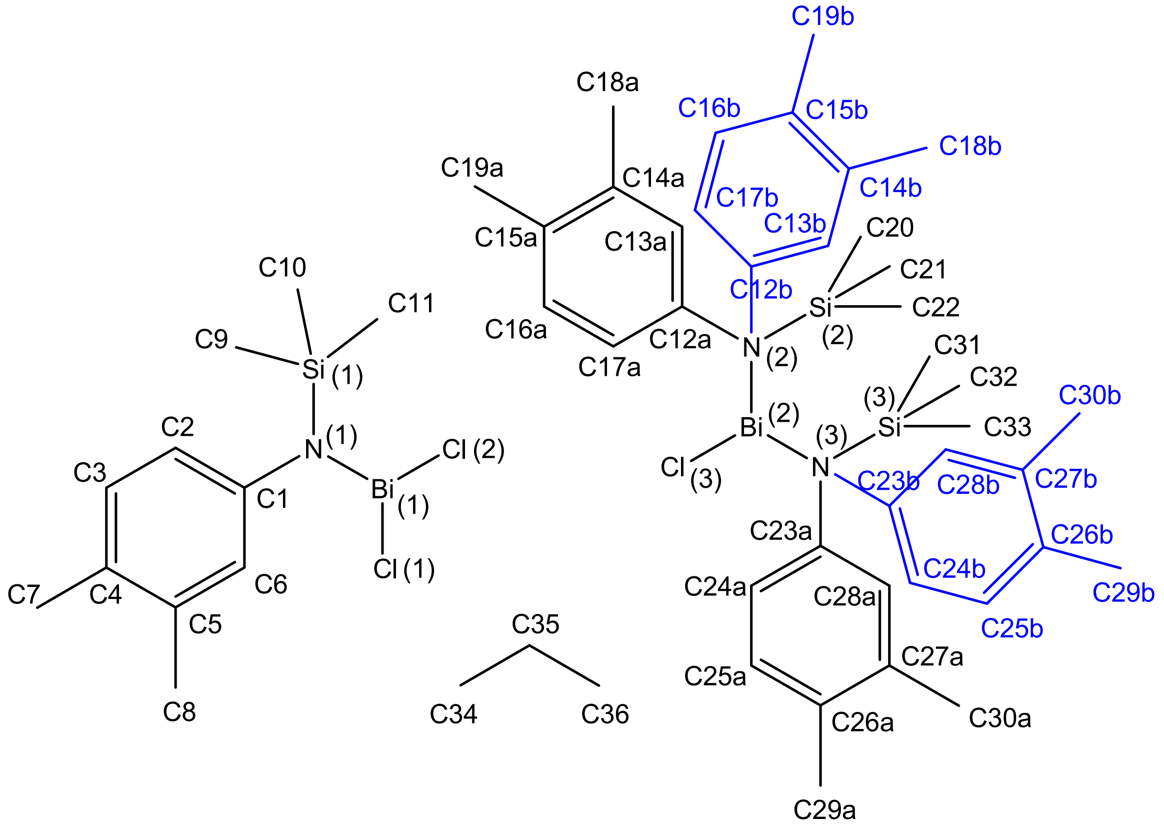


Table S20. Selected bond length (Å), angels (°) and torsion angels (°) of **5e/9e** · 0.5 C_6H_{14}.

Bi1—N1	2.166(6)	**Bi2—Cl3**	2.581(2)
N1—Si1	1.746(6)	**N2—Si2**	1.743(6)
Bi1—Cl1	2.470(2)	**N3—Si3**	1.748(6)
Bi1—Cl2	2.550(2)	**Cl1—Bi1—Cl2**	89.60(7)
Bi2—N2	2.137(6)	**N1—Bi1—Cl2**	94.7(2)
Bi2—N3	2.141(6)	**N1—Bi1—Cl1**	95.2(2)
C1—N1—Bi1	121.3(4)	**C12a—N2—Bi2**	124(1)
C1—N1—Si1	117.8(5)	**C12b—N2—Bi2**	119(1)
Si1—N1—Bi1	120.7(3)	**Si3—N3—Bi2**	120.9(3)

N2—Bi2—Cl3	97.9(2)	**C23a—N3—Si3**	118.5(7)
N3—Bi2—Cl3	94.6(2)	**C23b—N3—Si3**	113(1)
N2—Bi2—N3	95.7(2)	**C23a—N3—Bi2**	115.9(7)
Si2—N2—Bi2	119.2(3)	**C23b—N3—Bi2**	125(1)
C12a—N2—Si2	116(1)	**Si2—N2—Bi2—Cl3**	–97.1(3)
C12b—N2—Si2	120(1)	**Si3—N3—Bi2—Cl3**	–171.2(3)

Scheme S16. Numbering scheme of **12e**.

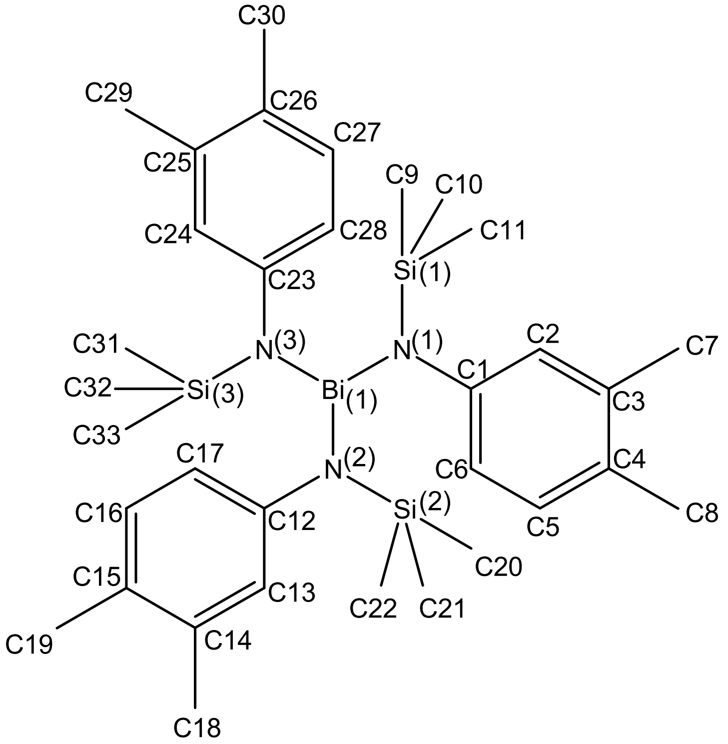


Table S21. Selected bond length (Å), angels (°) and torsion angels (°) of **12e**.

Bi1—N1	2.159(3)	**N2—Bi1—N1**	98.5(1)
Bi1—N2	2.155(3)	**N2—Bi1—N3**	97.9(1)
Bi1—N3	2.155(3)	**C1—N1—Si1**	118.2(2)
N1—C1	1.431(4)	**C1—N1—Bi1**	120.3(2)
N1—Si1	1.728(3)	**Si1—N1—Bi1**	120.4(1)

N2—C12	1.431(4)	**C12—N2—Bi1**	121.0(2)
N2—Si2	1.729(3)	**C12—N2—Si2**	117.4(2)
N3—C23	1.434(4)	**Si2—N2—Bi1**	120.7(2)
N3—Si3	1.728(3)	**C23—N3—Si3**	117.4(2)
N3—Bi1—N1	98.7(1)	**C23—N3—Bi1**	120.6(2)
Si3—N3—Bi1	120.1(2)	**N2—Bi1—N3—C23**	90.6(2)
N1—Bi1—N3—C23	-9.3(3)	**N3—Bi1—N2—C12**	-9.3(3)
N1—Bi1—N2—C12	90.8(3)	**N3—Bi1—N1—C1**	88.2(2)
N2—Bi1—N1—C1	-11.2(2)		

Scheme S17. Numbering scheme of **11f**.

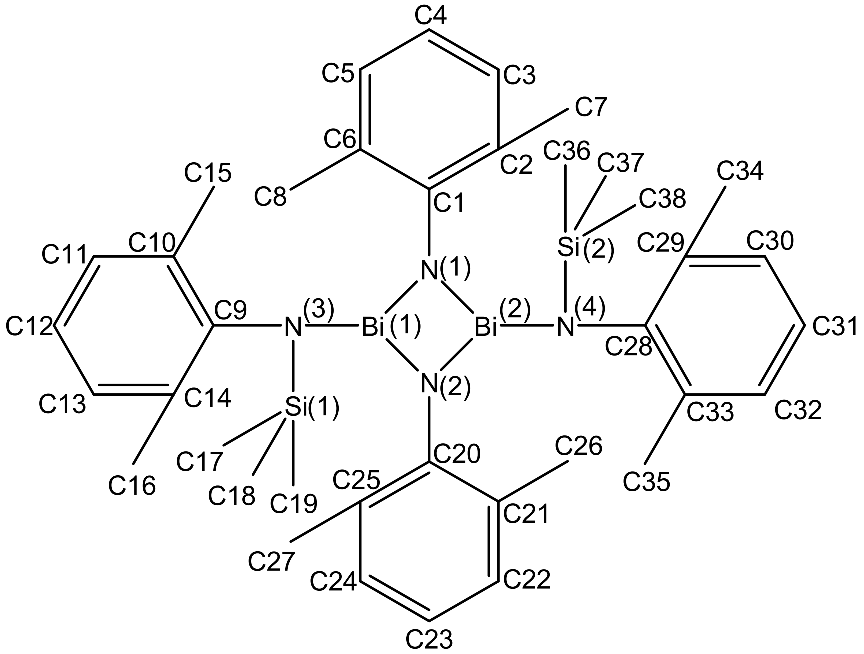


Table S22. Selected bond length (Å), angels (°) and torsion angels (°) of **11f**.

Bi1—N1	2.16(1)	**Bi2—N1**	2.142(7)
Bi1—N2	2.164(7)	**Bi2—N2**	2.154(9)
Bi1—N3	2.176(9)	**Bi2—N4**	2.175(9)

N1—C1	1.41(1)	**C1—N1—Bi2**	126.7(8)
N2—C20	1.41(1)	**C1—N1—Bi1**	130.5(7)
N3—C9	1.41(1)	**Bi2—N1—Bi1**	102.8(4)
N3—Si1	1.73(1)	**C20—N2—Bi2**	129.7(6)
N4—C28	1.44(1)	**C20—N2—Bi1**	127.9(7)
N4—Si2	1.71(1)	**Bi2—N2—Bi1**	102.3(4)
N1—Bi1—N2	77.1(3)	**C9—N3—Si1**	124.7(7)
N1—Bi1—N3	101.7(3)	**C9—N3—Bi1**	118.8(7)
N2—Bi1—N3	99.5(3)	**Si1—N3—Bi1**	116.5(4)
N1—Bi2—N2	77.7(3)	**C28—N4—Si2**	123.2(8)
N1—Bi2—N4	98.7(3)	**C28—N4—Bi2**	118.7(7)
N2—Bi2—N4	102.1(3)	**Si2—N4—Bi2**	118.1(5)

Scheme S18. Numbering scheme of **11g**.

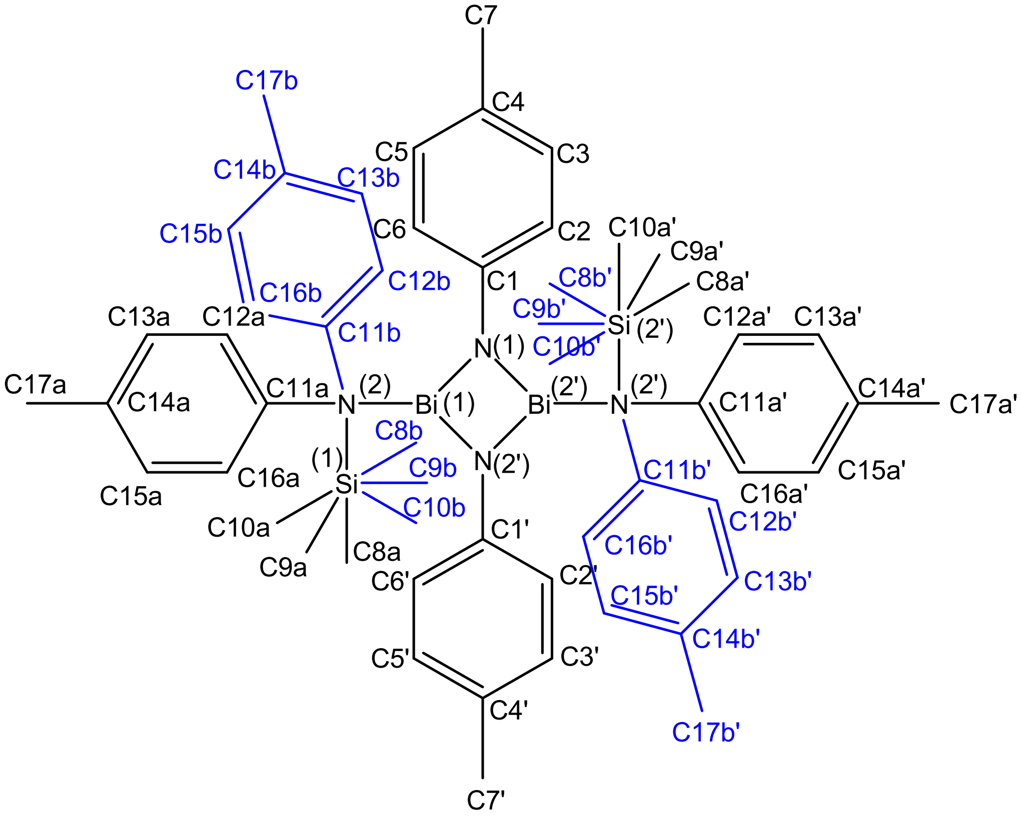


Table S23. Selected bond length (Å), angels (°) and torsion angels (°) of **11g**.

Bi1—N2'	2.137(5)	**N2'—Bi1—N1**	96.7(2)
Bi1—N2	2.147(5)	**N2—Bi1—N1**	97.1(2)
Bi1—N1	2.171(5)	**C4—N1—Si1**	119.5(4)
Si1—N1	1.715(6)	**C4—N1—Bi1**	116.7(4)
N1—C4	1.421(7)	**Si1—N1—Bi1**	122.9(3)
N2—Bi1'	2.137(5)	**C11—N2—Bi1'**	126.2(4)
N2—C11	1.380(8)	**C11—N2—Bi1**	128.8(4)
N2'—Bi1—N2	75.9(2)	**Bi1'—N2—Bi1**	104.1(2)
N2—Bi1—N1—C4	-41.9(5)	**N1—Bi1—N2—Bi1'**	95.1(2)
N2'—Bi1—N2—Bi1'	0.0	**N2'—Bi1—N1—C4**	34.6(5)

Scheme S19. Numbering scheme of **12g**.

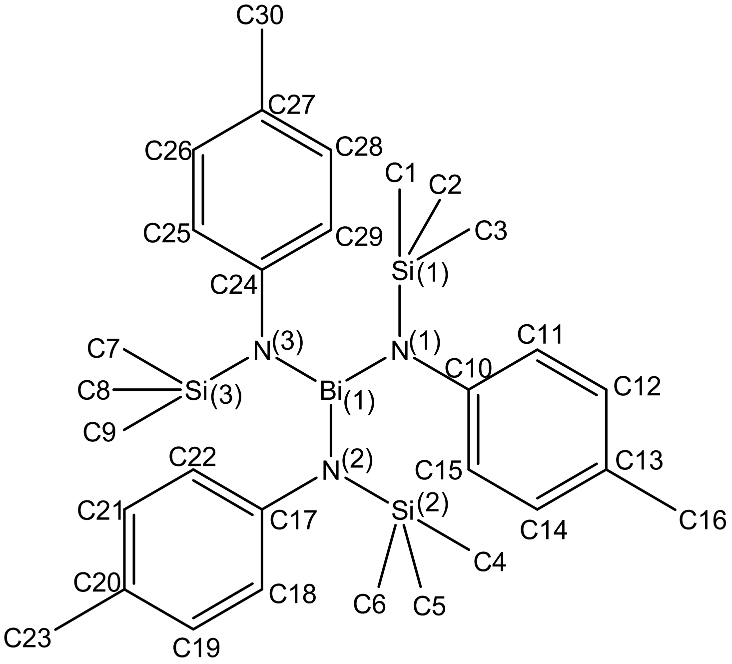


Table S24. Selected bond length (Å), angels (°) and torsion angels (°) of **12g**.

Bi1—N1	2.150(3)	**N3—Bi1—N2**	98.6(1)
Bi1—N2	2.154(3)	**C10—N1—Si1**	117.6(2)
Bi1—N3	2.162(3)	**C10—N1—Bi1**	121.5(2)
N1—C10	1.440(5)	**Si1—N1—Bi1**	120.0(2)
N1—Si1	1.730(3)	**C17—N2—Bi1**	120.8(2)
N2—C17	1.422(5)	**C17—N2—Si2**	118.7(2)
N2—Si2	1.735(3)	**Si2—N2—Bi1**	119.3(2)
N3—C24	1.425(5)	**N1—Bi1—N2—C17**	-87.2(3)
N3—Si3	1.730(3)	**N3—Bi1—N2—C17**	12.3(3)
C24—N3—Si3	118.5(2)	**N1—Bi1—N3—C24**	13.3(3)
C24—N3—Bi1	120.9(2)	**N2—Bi1—N3—C24**	-86.7(3)
Si3—N3—Bi1	119.7(2)	**N3—Bi1—N1—C10**	-90.4(3)
N1—Bi1—N3	98.0(1)	**N2—Bi1—N1—C10**	9.7(3)
N1—Bi1—N2	98.6(1)		

4. Synthesis of Starting Materials

4.1 Synthesis of lithium *N*-trimethylsilyl-1-amino-2,4,6-tri-*tert*-butylbenzene $Mes^*N(SiMe_3)Li$

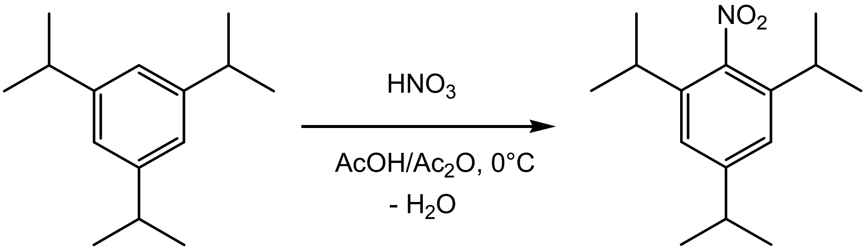
$$\mathrm{Mes^*N(SiMe_3)H} \xrightarrow[\substack{\mathrm{Et_2O,\ r.t.} \\ -\ n\text{-}\mathrm{BuH}}]{1)\ n\text{-}\mathrm{BuLi}} \mathrm{Mes^*N(SiMe_3)Li} \bullet \mathrm{Et_2O}$$

1.668 g (5.00 mmol) of $Mes^*N(SiMe_3)H$ are dissolved in 30 ml Et_2O and a 2.5 M *n*-hexane solution of *n*-BuLi (2.1 ml, 5.25 mmol) is added dropwise at room temperature. The reaction mixture is stirred for 30 min and then filtered. Concentration and storage at 5°C for 3 h yields a first crop of crystals. The supernatant is removed via syringe, concentrated and again stored at 5°C. The colorless crystals are washed with a minimum amount of *n*-hexane and dried *in vacuo* for at least 1.5 h.* Yield: 1.657 g (4.01 mmol, 80.4%) of $Mes^*N(SiMe_3)Li \cdot Et_2O$.

^{1}H-NMR (298.2 K, thf-d_8, 300.13 MHz): 0.09 (s, $^2J(^1H\text{-}^{29}Si) = 5.9$ Hz, 9 H, $Si(C\boldsymbol{H}_3)_3$), 1.12 (t, $^3J(^1H\text{-}^1H) = 7.0$ Hz, 6 H, $O(CH_2C\boldsymbol{H}_3)_2$), 1.22 (s, 9 H, *p*-$C(C\boldsymbol{H}_3)_3$), 1.49 (s, 18 H, *o*-$C(C\boldsymbol{H}_3)_3$), 3.38 (q, $^3J(^1H\text{-}^1H) = 7.0$ Hz, 4 H, $O(C\boldsymbol{H}_2CH_3)_2$), 7.13 (s, 2 H, arom. $C\boldsymbol{H}$). **^{7}Li-NMR** (300.0 K, thf-d_8, 194.36 MHz): -0.27 (s).

* with shorter drying a mixture of the mono- and the dietherate is yielded (amount of Et_2O determined by proton NMR spectroscopy)

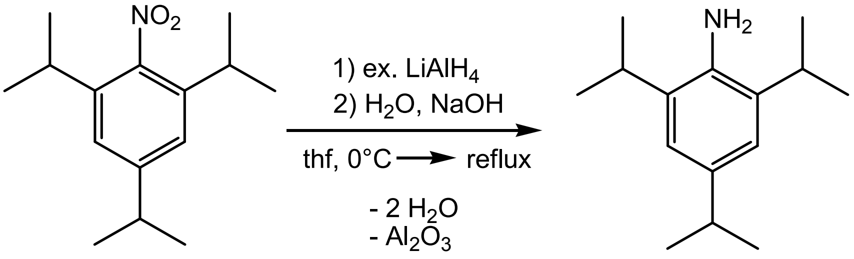
4.2 Synthesis of 1-nitro-2,4,6-triisopropylbenzene $TripNO_2$



Freshly distilled 1,3,5-triisopropylbenzene (42.8 g, 209 mmol) is dissolved in a mixture of 150 ml Ac_2O and 200 ml AcOH and cooled with a water bath. then 13.1 ml (314 mmol) fuming nitric acid are added dropwise. Upon complete addition of HNO_3 the reaction mixture is stirred for another 2 h and is then poured on 1 l deionized water. The resulting yellow solid is filtered off, dried and recrystallized from hot MeOH. After 12 h at 5°C the formed crystals are filtered of and dried *in vacuo*. Yield: 37.3 g (150 mmol, 71.6%).

Mp.: 74°C. **Anal. calc.** (found) in %: C 72.25 (72.18), H 9.30 (9.19), N 5.62 (5.86). **^{1}H-NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): 1.25 (d, $^{3}J(^{1}H-^{1}H)$ = 6.9 Hz, 12 H, *o*-CH(C***H***$_3$)$_2$), 1.26 (d, $^{3}J(^{1}H-^{1}H)$ = 7.0 Hz, 6 H, *p*-CH(C***H***$_3$)$_2$), 2.80 (sept, $^{3}J(^{1}H-^{1}H)$ = 6.9 Hz, 2 H, *o*-C***H***(CH$_3$)$_2$), 2.94 (sept, $^{3}J(^{1}H-^{1}H)$ = 7.0 Hz, 1 H, *p*-C***H***(CH$_3$)$_2$), 7.10 (s, 2 H, arom. ***H***). **^{13}C{^{1}H}-NMR** (298.3 K, CD_2Cl_2, 75.5 MHz): 24.4 (s, *o*-CH(***C***H$_3$)$_2$), 24.4 (s, *p*-CH(***C***H$_3$)$_2$), 30.0 (s, *o*-***C***H(CH$_3$)$_2$), 35.2 (s, *p*-***C***H(CH$_3$)$_2$), 123.0 (s, arom. ***C***H), 139.7 (s, *o*-***C***[CH(CH$_3$)$_2$]), 149.7 (s, ***C***(NO$_2$)), 152.1 (s, *p*-***C***[CH(CH$_3$)$_2$)]). **IR** (ATR, 32 Scans, cm^{-1}): $\tilde{\nu}$ = 2961 (m), 2930 (m), 2871 (m), 1597 (m), 1520 (s), 1463 (s), 1435 (m), 1375 (s), 1364 (s), 1320 (m), 1297 (w), 1274 (w), 1245 (w), 1192 (w), 1173 (w), 1148 (w), 1104 (m), 1082 (w), 1071 (m), 1055 (w), 949 (w), 940 (w), 921 (w), 876 (s), 857 (m), 827 (w), 818 (m), 772 (m), 750 (w), 715 (w), 655 (m), 623 (m), 563 (w). **Raman** (Laser: 632 nm, accumulation time: 15 s, 5 Scans, cm^{-1}): $\tilde{\nu}$ = 3199 (1), 3073 (2), 3062 (2), 3024 (2), 2971 (10), 2939 (8), 2915 (9), 2873 (8), 2763 (1), 2719 (2), 1601 (5), 1524 (2), 1468 (3), 1449 (3), 1379 (7), 1343 (2), 1301 (3), 1276 (4), 1249 (1), 1195 (1), 1150 (1), 1109 (3), 1076 (2), 1058 (7), 1004 (1), 961 (2), 942 (2), 888 (7), 861 (6), 830 (1), 821 (1), 658 (1), 628 (2), 602 (1), 565 (1), 498 (2), 479 (1), 443 (3), 387 (3), 368 (1), 321 (1), 273 (8).

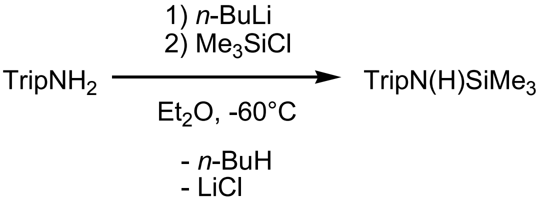
4.3 Synthesis of 1-amino-2,4,6-triisopropylbenzene TripNH$_2$



To a suspension of $LiAlH_4$ (6.86 g, 181 mmol) in 250 ml THF are added 15 g (60 mmol) 1-nitro-2,4,6-triisopropylbenzene in 90 ml Et_2O dropwise. Upon complete addition the reacting mixture is refluxed for 2 h. The reaction is stopped by addition of 100 ml NaOH solution (4 M). The resulting Al_2O_3 is filtered off and the phases are separated. The organic layer is dried with $MgSO_4$ over night and the solvent is removed. From the resulting red oil the corresponding hydrochloride is precipitated by addition of concentrated HCl until no further solid is formed. The orange solid is filtered off and washed with cold *n*-pentane. From the wash solution a second fraction can be obtained by adding again concentrated HCl. The solid is then suspended in 150 ml *n*-pentane and 100 ml of a 4 M solution of NaOH is added. The suspension is vigorously stirred until the solid is completely dissolved. The phases were separated and the organic layer is dried over $MgSO_4$. After the removal of $MgSO_4$ and the solvent, the resulting orange oil is distilled at 10^{-3} mbar. Yield: 5.55 g (25.3 mmol, 42.0%) 1-amino-2,4,6-triisopropylbenze ($TripNH_2$) as colorless to pale yellow oil.

Bp.: 49-52°C (10^{-3} mbar). **Anal. calc.** (found) in %: C 82.13 (80.30), H 11.49 (10.88), N 6.39 (7.30). **^{1}H-NMR** (298.6 K, CD_2Cl_2, 250.13 MHz): 1.22 (d, $^3J(^1H-^1H)$ = 6.9 Hz, 6 H, *o*-CH(C***H***$_3$)$_2$), 1.26 (d, $^3J(^1H-^1H)$ = 6.8 Hz, 12 H, *p*-CH(C***H***$_3$)$_2$), 2.81 (sep, $^3J(^1H-^1H)$ = 6.9 Hz, 1 H, *p*-C***H***(CH$_3$)$_2$), 2.93 (sep, $^3J(^1H-^1H)$ = 6.8 Hz, 2 H, *o*-C***H***(CH$_3$)$_2$), 3.62 (broad, 2 H, N***H***$_2$), 6.88 (s, 2 H, arom. C***H***). **^{13}C{^{1}H}-NMR** (300.0 K, CD_2Cl_2, 62.9 MHz): 23.1 (s, *o*-CH(***C***H$_3$)$_2$), 25.0 (s, *p*-CH(***C***H$_3$)$_2$), 28.8 (s, *p*-***C***H(CH$_3$)$_2$), 34.7 (s, *o*-***C***H(CH$_3$)$_2$), 121.4 (s, arom. ***C***H), 133.2 (s, *o*-***C***[CH(CH$_3$)$_2$]), 139.1 (s, ***C***(NH$_2$)), 139.4 (s, *p*-***C***[CH(CH$_3$)$_2$]). **IR** (ATR, 32 Scans, cm^{-1}): $\tilde{\nu}$ = 3471 (w), 3389 (w), 2956 (s), 2927 (m), 2867 (m), 1759 (w), 1622 (m), 1600 (m), 1471 (s), 1460 (s), 1442 (s), 1381 (m), 1361 (m), 1322 (m), 1302 (m), 1282 (m), 1252 (m), 1228 (w), 1182 (m), 1122 (w), 1098 (w), 1067 (w), 1053 (w), 943 (w), 924 (w), 874 (s), 764 (m), 639 (m), 608 (m), 572 (m), 537 (m).

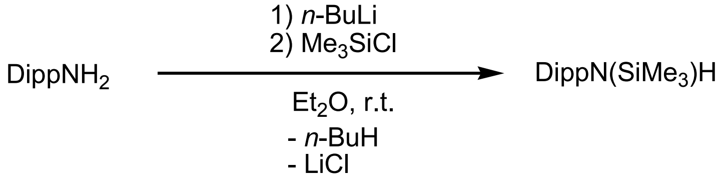
4.4 Synthesis of *N*-trimethylsilyl-1-amino-2,4,6-triisopropylbenzene TripN(SiMe$_3$)H



1-amino-2,4,6-triisopropylbenzene (1.097 g, 5.00 mmol) is dissolved in 15 ml Et_2O and reacted with 2.04 ml (5.10 mmol) of a 2.5 M solution of *n*-BuLi in *n*-hexane at –60°C. After 30 min stirring at this temperature a solution of 0.543 g (5.00 mmol) Me_3SiCl in 5 ml Et_2O is added dropwise. The reaction mixture is stirred and warmed up to room temperature over 2 h. Then the solvent is removed *in vacuo* and the residue is extracted with 10 ml *n*-hexane. Upon filtration (F4) the solvent is removed *in vacuo*. After a Kugelrohr-destillation the clear oil crystallizes upon cooling. Fractional crystallization yields 0.671 g (2.30 mmol, 46.0%) TripN(SiMe$_3$)H as colorless, crystalline blocks.

Mp.: 52°C. **Anal. calc.** (found) in %: C 74.15 (74.35), H 11.41 (11.29), N 4.80 (4.93). **^{1}H-NMR** (300.0 K, CD_2Cl_2, 250.13 MHz): 0.11 (s, $^2J(^1H-^{29}Si)$ = 6.46 Hz, 9 H, $Si(C\boldsymbol{H}_3)_3$), 1.16 (d, $^3J(^1H-^1H)$ = 6.8 Hz, 12 H, *o*-$CH(C\boldsymbol{H}_3)_2$), 1.21 (d, $^3J(^1H-^1H)$ = 6.9 Hz, 6 H, *p*-$CH(C\boldsymbol{H}_3)_2$), 2.17 (broad, 1 H, $N\boldsymbol{H}$), 2.82 (sep, $^3J(^1H-^1H)$ = 6.9 Hz, 1 H, *p*-$C\boldsymbol{H}(CH_3)_2$), 3.39 (sep, $^3J(^1H-^1H)$ = 6.8 Hz, 2 H, *o*-$C\boldsymbol{H}(CH_3)_2$), 6.90 (s, 2 H, arom. $C\boldsymbol{H}$).**^{13}C{^{1}H}-NMR** (300.0, CD_2Cl_2, 62.9 MHz): 1.0 (s, $Si(\boldsymbol{C}H_3)_3$), 24.0 (s, *o*-$CH(\boldsymbol{C}H_3)_2$), 24.5 (s, *p*-$CH(\boldsymbol{C}H_3)_2$), 28.7 (s, *p*-$\boldsymbol{C}H(CH_3)_2$), 34.5 (s, *o*-$\boldsymbol{C}H(CH_3)_2$), 121.3 (s, arom. $\boldsymbol{C}$), 137.8 (s, arom. $\boldsymbol{C}$), 143.9 (s, arom. $\boldsymbol{C}$), 144.7 (s, arom. $\boldsymbol{C}$). **^{29}Si-INEPT-NMR** (300.0 K, CD_2Cl_2, 49.7 MHz): 3.6 (m). **IR** (ATR, 32 Scans, cm^{-1}): $\tilde{\nu}$ = 3379 (w), 2955 (s), 2925 (m), 2865 (w), 1466 (m), 1455 (m), 1403 (w), 1380 (w), 1360 (w), 1333 (m), 1310 (m), 1277 (m), 1261 (m), 1248 (s), 1214 (w), 1178 (m), 1117 (w), 1104 (w), 1067 (w), 1053 (w), 939 (w), 900 (s), 878 (m), 832 (s), 751 (m), 695 (m), 686 (m), 669 (w), 644 (m), 611 (w). **Raman** (Laser: 785 nm, accumulation time: 60 s, 4 Scans, cm^{-1}): $\tilde{\nu}$ = 3020 (1), 2962 (4), 2935 (3), 2903 (5), 2868 (3), 2754 (1), 2711 (1), 1606 (3), 1577 (1), 1465 (3), 1443 (2), 1409 (1), 1382 (1), 1346 (1), 1334 (1), 1312 (2), 1278 (7), 1250 (1), 1216 (1), 1180 (1), 1156 (1), 1119 (1), 1108 (3), 1096 (1), 1069 (1), 1056 (3), 955 (3), 946 (3), 923 (1), 901 (2), 882 (5), 855 (1), 814 (1), 754 (1), 687 (2), 646 (1), 610 (10), 589 (2), 543 (2), 472 (1), 444 (3), 416 (2), 332 (1), 269 (5), 243 (2).

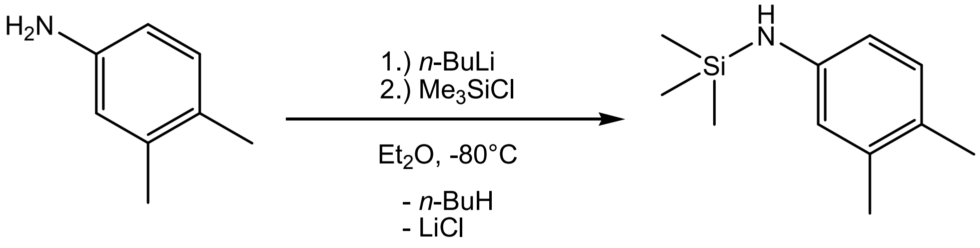
4.5 Synthesis of *N*-trimethylsilyl-1-amino-2,6-diisopropylbenzene DippN($SiMe_3$)H



The synthesis of DippN(SiMe3)H was carried out after a slightly modified literature procedure.[6] To a stirred solution of 1.773 g (10.00 mmol) 1-amino-2,6-diisopropylbenzene ($DippNH_2$) in 15 ml of Et_2O are added 4.20 ml (10.50 mmol) of a 2.5 M *n*-BuLi solution at room temperature. Then a solution of 1.304 g (12.00 mmol) trimethylsilylchloride in 5 ml of diethylether is added dropwise at room temperature. After the reaction mixture is stirred for 2 h at room temperature the solvent is removed *in vacuo* and the residue is extracted with 15 ml *n*-hexane. The colorless solid is filtered of and the residue is again extracted with 5 ml *n*-hexane and filtered. The solvent is removed *in vacuo* from the combined filtrate and the remaining yellow oil is distilled at 10^{-3} mbar. Yield: 1.365 g (5.47 mmol, 54.7 %) DippN($SiMe_3$)H as a colorless oil.

Bp.: 38.5°C (10^{-3} mbar). **^{1}H-NMR** (298.2 K, CH_2Cl_2, 300.13 MHz): 0.16 (s, 9 H, $Si(C\boldsymbol{H}_3)_3$), 1.21 (m, 12 H, $C_6H_3(CH(C\boldsymbol{H}_3)_2)_2$), 2.37 (broad, 1 H, $N\boldsymbol{H}$), 3.35 – 3.51 (m, 2 H, $C_6H_3(C\boldsymbol{H}(CH_3)_2)_2$), 6.97 – 7.10 (m, 3 H, arom. $C\boldsymbol{H}$). **^{13}C{^{1}H}-NMR** (298.2 K, CD_2Cl_2, 75.5 MHz): 1.1 (s, $^2J(^{13}C\text{-}^{29}Si)$ = 57 Hz, $Si(\boldsymbol{C}H_3)_3$), 24.0 (s, $C_6H_3(CH(\boldsymbol{C}H_3)_2)_2$), 28.7 (s, $C_6H_3(\boldsymbol{C}H(CH_3)_2)_2$), 123.4 (s, Arom. $\boldsymbol{C}$), 123.7 (s, Arom. $\boldsymbol{C}$), 140.5 (s, Arom. $\boldsymbol{C}$), 144.8 (s, Arom. $\boldsymbol{C}$). **^{29}Si-INEPT-NMR** (300.0 K, CD_2Cl_2, 59.6 MHz): 4.0 (m).

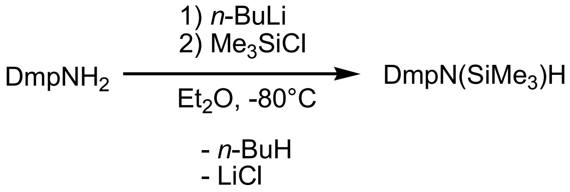
4.6 Synthesis of *N*-trimethylsilyl-3,4-dimethylphenylamin



N-trimethylsilyl-3,4-dimethylphenylamin was prepared after a modified procedure from the literature.[6] 1.176 g (9.7 mmol) of 3,4-dimethylphenylamin are dissolved in 15 ml Et_2O and 3.9 ml (c = 2.5 M, 9.70 mmol) *n*-BuLi in *n*-hexane are added at –80°C. After 15 min at this temperature 1.054 g (9.70 mmol) trimethylsilyl chlorid in 10 ml Et_2O are added and the reaction mixture is brought to room temperature within one hour. The solvent is removed *in vacuo* and the residue is extracted with 10 ml of *n*-hexane and filtrated. Then the solvent is removed *in vacuo* and the remaining oil is distilled at 10^{-3} mbar. Yield: 1.268 g (6.56 mmol, 67.6%).

^{1}H-NMR (298.2 K, CH_2Cl_2, 300.13 MHz): 0.24 (s, 9 H, $Si(C\boldsymbol{H}_3)_3$), 2.12 (s, 3 H, $C_6H_3(C\boldsymbol{H}_3)_2$), 2.15 (s, 3 H, $C_6H_3(C\boldsymbol{H}_3)_2$), 3.32 (broad, 1H, $N\boldsymbol{H}$), 6.37 – 6.86 (m, 3 H, arom. $C\boldsymbol{H}$). **^{13}C{^{1}H}-NMR** (298.2 K, CD_2Cl_2, 62.9 MHz): 0.4 (s, $Si(\boldsymbol{C}H_3)_3$), 18.9 (s, $\boldsymbol{C}H_3$), 20.3 (s, $\boldsymbol{C}H_3$), 113.9 (s, Arom. $\boldsymbol{C}$), 118.3 (s, Arom. $\boldsymbol{C}$), 125.9 (s, Arom. $\boldsymbol{C}$), 130.7 (s, Arom. $\boldsymbol{C}$), 137.8 (s, Arom. $\boldsymbol{C}$), 145.9 (s, Arom. $\boldsymbol{C}$). **^{29}Si-INEPT-NMR** (300.0 K, CD_2Cl_2, 49.7 MHz): 2.4 (m). **IR** (ATR, 32 Scans, cm^{-1}): $\tilde{\nu}$ = 3407 (w), 3380 (w), 3009 (w), 2955 (w), 2919 (w),2897 (w), 2858 (w), 1615 (m), 1581 (w), 1503 (m), 1468 (m), 1437 (m), 1375 (w), 1353 (m),1303 (s), 1276 (m), 1263 (m), 1249 (s), 1215 (m), 1168 (m), 1118 (m), 1010 (m), 956 (m), 870 (s), 835 (s), 803 (s), 768 (m), 749 (m), 702 (m), 686 (m), 617 (m), 578 (w), 564 (w). **Raman** (Laser: 633 nm, accumulation time: 30 s, 4 Scans, cm^{-1}): $\tilde{\nu}$ = 2869 (10), 2836 (8), 2710 (2), 1445 (2),1437 (2), 1425 (3), 1402 (2), 1354 (1), 1279 (4), 1154 (1), 1112 (2), 1046 (2).

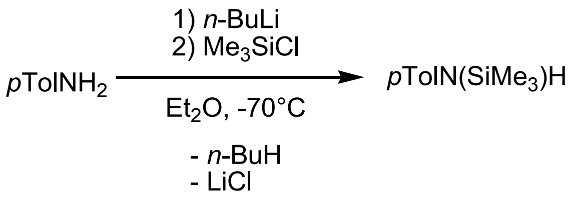
4.7 Synthesis of *N*-trimethylsilyl-2,6-dimethylphenylamin $\mathrm{DmpN(SiMe_3)H}$



$\mathrm{DmpN(SiMe_3)H}$ was prepared after a modified procedure from the literature.[6] 1.212 g (10.0 mmol) freshly distilled 1-amino-2,6-dimethylphenyl are dissolved in 15 ml $\mathrm{Et_2O}$. To the stirred solution 4 ml of a 2.5 M solution of *n*-BuLi (10.0 mmol) in *n*-hexane are added dropwise at –80°C. The reaction mixture is stirred for another 45 min in the cold and then 1.086 g (10.0 mmol) trimethylsilyl chloride are added dropwise. After the reaction mixture is warmed to room temperature and stirred for 1 h at room temperature, the solvent is removed and the residue is extracted with 10 ml *n*-hexane. The solvent is removed *in vacuo* and the resulting oil is distilled at 10^{-3} mbar. Yield: 1.423 g (7.36 mmol, 73.6%).

^{1}H-NMR (298.2 K, $\mathrm{CD_2Cl_2}$, 300.13 MHz): 0.16 (s, 9 H, $\mathrm{Si(C}\boldsymbol{H}_3\mathrm{)_3}$), 2.25 (s, 6 H, $\mathrm{C_6H_3(C}\boldsymbol{H}_3\mathrm{)_2}$), 2.55 (broad, 1 H, $\mathrm{N}\boldsymbol{H}$), 6.75 (t, $^{3}J(^{1}\mathrm{H}\text{-}^{1}\mathrm{H})$ = 7 Hz, 1 H, *p*-C***H***), 6.97 (d, $^{3}J(^{1}\mathrm{H}\text{-}^{1}\mathrm{H})$ = 7 Hz, 2 H, *m*-$\mathrm{(C}\boldsymbol{H}\mathrm{)_2}$). **^{13}C{^{1}H}-NMR** (298.2 K, $\mathrm{CD_2Cl_2}$, 75.5 MHz): 1.4 (s, $\mathrm{Si(}\boldsymbol{C}\mathrm{H_3)_3}$), 20.1 (s, $\mathrm{C_6H_3(}\boldsymbol{C}\mathrm{H_3)_2}$), 121.7 (s, arom. ***C***), 128.7 (s, arom. ***C***), 131.7 (s, arom. ***C***), 144.4 (s, arom. ***C***). **^{29}Si-INEPT-NMR** (300.0 K, $\mathrm{CD_2Cl_2}$, 59.63 MHz): 5.1 (m). **IR** (ATR, 32 Scans, $\mathrm{cm^{-1}}$): $\tilde{\nu}$ = 3361 (w), 3070 (w), 3023 (w), 2953 (w), 2924 (w), 2901 (w), 2856 (w), 2160 (w), 2142 (w), 2107 (w), 1594 (w), 1472 (m), 1429 (m), 1358 (m), 1282 (m), 1261 (m), 1249 (s), 1218 (m), 1194 (w), 1162 (w), 1098 (m), 1030 (w), 985 (w), 900 (s), 834 (s), 761 (s), 698 (m), 682 (m), 648 (m), 611 (m), 557 (m), 544 (m). **Raman** (Laser: 633 nm, accumulation time: 15 s, 4 Scans, $\mathrm{cm^{-1}}$): $\tilde{\nu}$ = 3382 (1), 3363 (1), 3072 (2), 3041 (2), 3006 (2), 2955 (5), 2899 (10), 2730 (1), 1595 (4), 1474 (1), 1442 (2), 1410 (1), 1377 (3), 1260 (6), 1218 (1), 1162 (2), 1099 (3), 985 (2), 900 (1), 847 (1), 743 (2), 733 (1), 681 (1), 649 (2), 610 (10), 544 (7), 505 (1), 469 (1), 424 (1), 337 (1), 292 (2), 255 (1), 234 (2).

4.8 Synthesis of *N*-trimethylsilyl-4-methylphenylamine *p*-TolN($SiMe_3$)H

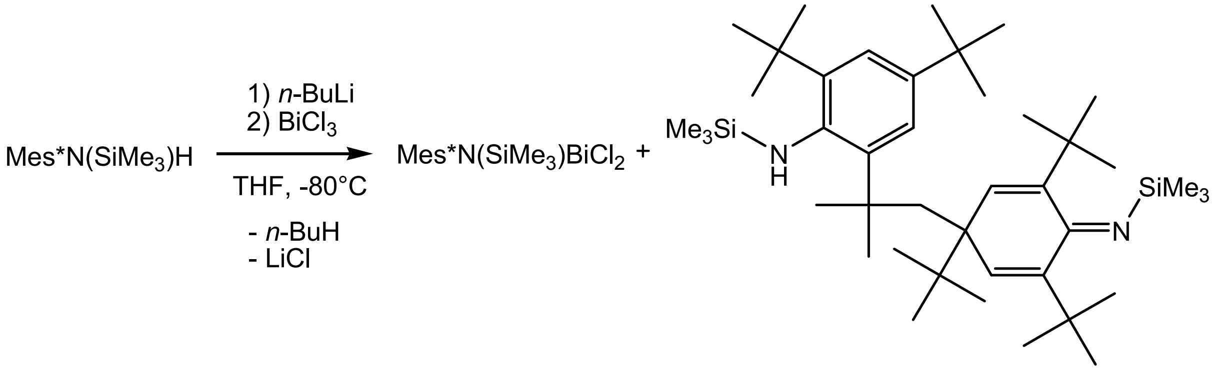


p-TolN($SiMe_3$)H was prepared after a modified procedure from the literature.[6] At –75°C a 2.5 M solution of *n*-BuLi (4 ml, 10 mmol) in *n*-hexane is added to a stirred solution of 1.072 g (10 mmol) 4-methylphenylamin in 20 ml Et_2O. After a half hour at –40°C a solution of 1.086 g (10.0 mmol) trimethylsilyl chloride in 5 ml Et_2O is added at –70°C. The solvent is removed *in vacuo* after the reaction mixture is brought to room temperature and stirred for an hour at this temperature. The residue is extracted with 15 m *n*-hexane and filtrated. then the solvent is removed *in vacuo* and the remaining yellow oil is distilled at 10^{-3} mbar. Yield: 1.210 g (6.74 mmol, 67.4%).

Bp.: 30.5 – 31.0°C (10^{-3} mbar). **^{1}H-NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): 0.24 (s, 9 H, Si(C***H***$_3$)$_3$), 2.20 (s, 3 H, C_6H_4(C***H***$_3$)), 3.38 (broad, 1 H, N***H***), 6.54 - 6.57 (Arom., $^3J(^1H-^1H)$ = 7.9 Hz, 2 H, arom. C***H***), 6.91 - 6.94 (Arom., $^3J(^1H-^1H)$ = 7.7 Hz, 2 H, arom. C***H***). **^{13}C-NMR** (298.2 K, CD_2Cl_2, 75.5 MHz): 0.3 (s, $^1J(^{13}C-^{29}Si)$ = 114 Hz, Si(***C***H$_3$)$_3$), 20.6 (s, C_6H_4(***C***H$_3$), 116.5 (s, arom. ***C***), 127.0 (s, arom. ***C***), 130.2 (s, arom. ***C***), 145.5 (s, arom. ***C***). **^{29}Si-INEPT-NMR** (300.0 K, CD_2Cl_2, 59.63 MHz): 2.5 (m). **IR** (ATR, 8 Scans, cm^{-1}): $\tilde{\nu}$ = 3383 (w), 3031 (w), 3010 (w), 2956 (w), 2918 (w), 2864 (w), 1613 (m), 1582 (w), 1512 (s), 1440 (w), 1366 (m), 1331 (w), 1283 (s), 1263 (m), 1250 (s), 1182 (w), 1121 (w), 1111 (w), 1041 (w), 899 (s), 835 (s), 808 (s), 767 (m), 750 (m), 686 (m), 641 (m), 609 (w). **Raman** (Laser: 473 nm, accumulation time: 8 s, 6 Scans, cm^{-1}): $\tilde{\nu}$ = 3404 (2), 3383 (2), 3053 (4), 3028 (3), 3008 (3), 2954 (5), 2896 (10), 2730 (1), 1610 (7), 1510 (2), 1438 (2), 1407 (2), 1374 (3), 1282 (4), 1259 (2), 1210 (4), 1177 (4), 1009 (1), 898 (1), 847 (3), 789 (5), 763 (2), 695 (2), 681 (1), 636 (3), 603 (5), 375 (2), 334 (2), 310 (2).

5. Synthesis of Compounds

5.1 Reaction of one equivalent of Mes*N(SiMe$_3$)Li (**4a**) with BiCl$_3$



a) To solution of Mes*N(SiMe$_3$)H (0.334 g, 1 mmol) in 15 ml thf *n*-BuLi (0.42 ml, 1.05 mmol) is added at room temperature and stirred for 1 h. Than the solution of Mes*N(SiMe$_3$)Li is added drop wise to a solution of 0.437 g (1.5 mmol) BiCl$_3$* in 20 ml thf at 10°C over a period of 20 min. The solvent of the blackish-greenish solution is removed *in vacuo* and the black residue is extracted with 15 ml toluene. After filtration the filtrate is concentrated to an oil and stored at –24°C. A mixture of **5a**·1.5 C_7H_8 and **8** in a ratio of approximately 1:9 is formed.

*Not sublimed BiCl$_3$

b) To a stirred solution of 0.333 g (1.00 mmol) Mes*N(SiMe$_3$)H in 10 ml thf are added 0.42 ml of *n*-BuLi (c = 2.5 M, 1.05 mmol) and the resulting solution is stirred for 30 min. Then the solution is added dropwise to a solution of 0.347 g (1.10 mmol) of sublimed BiCl$_3$ in 10 ml Et$_2$O. After stirring 1 h at room temperature the solvent is removed *in vacuo* and the black residue (containing approximately 26% **5a**, 53% **8** and 21% Mes*N(SiMe$_3$)H according to the integrals of the trimethylsilyl groups in the proton NMR spectrum) is extracted with 10 ml of toluene and filtered. Afterward the solvent is removed *in vacuo* and then the residue extracted with 3 ml of dichloromethane and filtered. Removal of the solvent *in vacuo* and washing with a minimum amount of *n*-hexane yields 0.213 g (0.32 mmol, 64%) of the C-C coupling (**8**) product.

c) To a stirred solution of 0.333 g (1.00 mmol) Mes*N(SiMe$_3$)H in 20 ml Et$_2$O are added 0.42 ml (1.05 mmol) of a 2.5 M *n*-BuLi solution dropwise. The reaction mixture is stirred for additional 30 min at r.t. and then added to a stirred suspension of 0.347 g (1.10 mmol) $BiCl_3$ in 10 ml Et_2O. Upon complete addition a black suspension is formed which is warmed slowly to room temperature and stirred at ambient temperature for additional 30 min. Then the solvent is removed *in vacuo* and the residue is extracted with 10 ml of toluene. After filtration over a ceolith padded frit the solvent is removed *in vacuo*. This procedure leads to the formation of a mixture of Mes*N($SiMe_3$)H (ca. 15%), the C-C coupling product (**8**, ca. 8%) and Mes*N($SiMe_3$)$BiCl_2$ (**5a**, ca. 77%). The amounts of products are determined by the integrals of the trimethylsilyl groups in the proton NMR spectrum.

d) A solution of 0.827 g (2.00 mmol) Mes*N($SiMe_3$)Li · Et_2O in 8 ml Et_2O is added to a stirred suspension of 0.662 g (2.10 mmol) $BiCl_3$ in 10 ml Et_2O at 80°C. Upon complete addition a black suspension is formed which is stirred and slowly warmed over 45 min to ca. 35°C. Then the solvent is removed *in vacuo* and the residue is extracted with 10 ml of *n*-hexane. After filtration and concentration of the dark solution it is stored at 5°C over night. Yield: 0.435 g (0.71 mmol; 35.5%) **5a** as yellow to orange crystals suitable for single crystals x-ray diffraction.

5a) Mp.: 89°C (Decomp.). **Anal.** calc. % (found): 41.18 (40.74), 6.25 (6.03), 2.29 (2.15). **^{1}H-NMR** (300.0 K, CD_2Cl_2, 250.13 MHz): 0.44 (s, $^2J(^1H-^{29}Si)$ = 6.3 Hz, 9 H, Si(C$\boldsymbol{H}_3$)$_3$), 1.30 (s, 9 H, *p*-C(C$\boldsymbol{H}_3$)$_3$), 1.54 (s, 18 H, *o*-C(C$\boldsymbol{H}_3$)$_3$), 7.57 (s, 2 H, arom. C***H***). **^{13}C{^{1}H}-NMR** (300.0 K, CD_2Cl_2, 75.46 MHz): 6.9 (s, Si(***C***H$_3$)$_3$), 31.7 (s, *p*-C(***C***H$_3$)$_3$), 34.9 (s, *p*-***C***(CH$_3$)$_3$), 35.9 (*o*-C(***C***H$_3$)$_3$), 38.6 (*o*-***C***(CH$_3$)$_3$), 126.0 (s, arom. ***C***), 149.1 (s, arom. ***C***), 152.4 (s, arom. ***C***). **^{29}Si-INEPT-NMR** (300.0 K, CD_2Cl_2, 59.63 MHz): 17.7 (m). **IR** (ATR, 32 Scans, cm^{-1}): 2951 (m), 2906 (w), 2867 (w), 1598 (w), 1494 (w), 1478 (w), 1457 (w), 1434 (w), 1393 (w), 1361 (m), 1351 (w), 1287 (w), 1268 (w), 1256 (m), 1248 (m), 1238 (m), 1219 (w), 1211 (w), 1199 (w), 1175 (m), 1144 (w), 1108 (m), 1051 (w), 1024 (w), 918 (w), 877 (s), 835 (s), 793 (m), 760 (m), 751 (m), 698 (w), 664 (m), 642 (m), 625 (m), 565 (w), 541 (w). **Raman** (Laser: 633 nm, accumulation time: 30 s, 10 scans, cm^{-1}): 2964 (2), 2952 (2), 2935 (2), 2902 (2), 2861 (1), 1597 (3), 1470 (1), 1448 (1), 1400 (1), 1386 (1), 1367 (1), 1358 (1), 1283 (1), 1238 (1), 1173 (3), 1142 (3), 1107 (1), 820 (1), 793 (2), 695 (1), 640 (2), 622 (1), 568 (1), 539 (1), 452 (1), 408 (1), 284 (10), 260 (4).

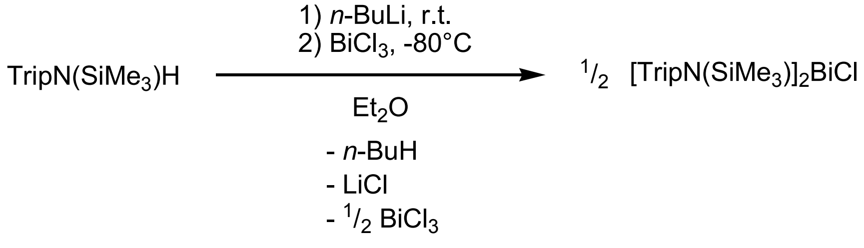
8) Mp: 167°C. **Anal. calc.** (found) in %: C 75.83 (75.43), H 11.52 (11.22), N 4.21 (4.20). **^{1}H-NMR** (299.9 K, CD_2Cl_2, 300.13 MHz): 0.20 (s, $^2J(^1H-^{29}Si)$ = 7.0 Hz, 9 H, Si(C$\boldsymbol{H}_3$)$_3$), 0.22 (s, $^2J(^1H-^{29}Si)$ = 6.6 Hz, 9 H, Si(C$\boldsymbol{H}_3$)$_3$), 0.88 (s, 9 H, C(C$\boldsymbol{H}_3$)$_3$), 0.97 (s, 18 H, C(C$\boldsymbol{H}_3$)$_3$), 1.25 (s, 9 H, C(C$\boldsymbol{H}_3$)$_3$), 1.34 (s, 6 H, C(C$\boldsymbol{H}_3$)$_2$), 1.47 (s, 9 H, C(C$\boldsymbol{H}_3$)$_3$), 2.27 (broad, 1 H, N***H***), 2.77 (s, 2 H, C$\boldsymbol{H}_2$), 6.11 (s, 2 H, C***H***), 7.20 (d, $^3J(^1H-^1H)$ = 2.5 Hz, 1 H, C***H***), 7.29 (d, 1 H, $^3J(^1H-^1H)$ = 2.5 Hz, C***H***). **^{13}C{^{1}H}-NMR**

(298.3 K, CD_2Cl_2, 75.46 MHz): 2.8 (s, $Si(\boldsymbol{C}H_3)_3$), 3.4 (s, $Si(\boldsymbol{C}H_3)_3$), 30.7 (s, $C(\boldsymbol{C}H_3)_3$), 31.9 (s, $C(\boldsymbol{C}H_3)_3$), 32.9 (s, $C(\boldsymbol{C}H_3)_3$), 34.5 (s, $C(\boldsymbol{C}H_3)_2CH_2$), 35.0 (s, $\boldsymbol{C}(CH_3)_3$), 35.2 (s, $\boldsymbol{C}(CH_3)_3$), 37.0 (s, $\boldsymbol{C}(CH_3)_3$), 41.6 (s, $\boldsymbol{C}(CH_3)_3$), 43.6 (s, $\boldsymbol{C}(CH_3)_3$), 46.5 (s, $C(CH_3)_2\boldsymbol{C}H_2$), 48.1 (s, $\boldsymbol{C}(CH_3)_3$), 123.3 (s, $\boldsymbol{C}H$), 123.6 (s, $\boldsymbol{C}H$), 140.2 (s, $\boldsymbol{C}H$), 140.4 (s, $\boldsymbol{C}H$), 145.1 (s), 147.2 (s), 148.1 (s), 148.7 (s), 162.9 (s). ^{29}**Si-INEPT-NMR** (300.0 K, CD_2Cl_2, 59.63 MHz): -19.0 (m), 2.5 (m). **IR** (ATR, 32 Scans, cm^{-1}): $\tilde{\nu}$ = 3402 (w), 3018 (w), 2951 (m), 2906 (w), 2868 (w), 1672 (s), 1653 (m), 1643 (m), 1599 (w), 1475 (w), 1464 (m), 1456 (w), 1425 (m), 1392 (w), 1385 (w), 1362 (m), 1352 (m), 1319 (w), 1286 (w), 1265 (m), 1254 (m), 1240 (m), 1202 (m), 1161 (w), 1149 (w), 1124 (w), 1097 (w), 1063 (w), 1022 (w), 976 (w), 933 (m), 906 (m), 887 (m), 876 (s), 827 (s), 797 (m), 750 (m), 733 (m), 687 (m), 662 (s), 644 (m), 619 (m), 575 (w), 567 (w), 554 (w). **Raman** (Laser: 632 nm, accumulation time: 20 s, 10 Scans, cm^{-1}): $\tilde{\nu}$ = 3400 (1), 3119 (1), 3090 (1), 3051 (2), 3022 (2), 2966 (6), 2954 (7), 2905 (10), 2776 (1), 2765 (1), 2706 (1), 2692 (1), 1672 (3), 1643 (5), 1597 (2), 1467 (3), 1452 (3), 1447 (3), 1405 (2), 1391 (1), 1360 (1), 1347 (1), 1340 (1), 1318 (1), 1287 (1), 1257 (2), 1234 (1), 1200 (3), 1147 (2), 1136 (1), 1112 (1), 1096 (1), 1060 (1), 1020 (1), 1012 (1), 975 (3), 944 (2), 925 (3), 920 (3), 884 (1), 847 (3), 820 (4), 797 (2), 767 (1), 739 (1), 661 (3), 643 (3), 614 (4), 594 (2), 553 (5), 540 (2), 496 (1), 475 (2), 411 (1), 390 (1), 309 (2), 263 (4).

5.2 Reaction of three equivalents of Mes*N($SiMe_3$)Li (**4a**) with $BiCl_3$

0.26 ml (0.65 mmol) of a 2.5 M *n*-BuLi solution are added dropwise to a solution of 0.200 g (0.60 mmol) Mes*N($SiMe_3$)H in 5 ml thf. After 20 min at ambient temperature the reaction mixture is added dropwise at –80°C to a solution of 0.063 g (0.20 mmol) $BiCl_3$ in 5 ml thf. The formed dark solution is stirred for 1 h and then the solvent is removed *in vacuo*. Mes*N($SiMe_3$)H is yielded quantitatively according to proton NMR spectroscopy.

5.3 Reaction of one equivalent of TripN($SiMe_3$)Li (**4b**) with $BiCl_3$



a) 0.292 g (1.00 mmol) TripN(SiMe$_3$)H are dissolved in 10 ml Et$_2$O and to this stirred solution 0.4 ml *n*-BuLi in *n*-hexane (2.5 M, 1.00 mmol) are added at room temperature. After 1.5 h the solution is added dropwise to a suspension of 0.315 g (1.00 mmol) BiCl$_3$* in 10 ml Et$_2$O at –80°C. The reaction mixture is warmed up to room temperature and after 2.5 h at room temperature the solvent is removed. The residue is extracted with 20 ml *n*-hexane and filtered. After the solvent is removed, the formed solid is dissolved in 5 ml benzene and stored in the dark for 1 week. The formed BiCl$_3$ is filtered off during this week several times and the reaction is complete if no further BiCl$_3$ is formed. Crystallization from benzene yields 0.08 g (0.09 mmol, 9.4%) [TripN(SiMe$_3$)]$_2$BiCl (**9b**) as an orange, crystalline solid. (A few crystals of **5b** are obtained by this procedure if the benzene solution is not stored over a week but directly concentrated.)

* not sublimed BiCl$_3$

b) To a stirred solution of 0.292 g (1.00 mmol) TripN(SiMe$_3$)H in 5 ml Et$_2$O are added 0.42 ml (2.5 M, 1.05 mmol) *n*-BuLi solution at room temperature. After 15 min of stirring the reaction mixture is added dropwise at –80°C to a solution of 0.347 g (1.10 mmol) BiCl$_3$ in 5 ml Et$_2$O. A grayish orange Suspension is formed, which is stirred for 30 min and warmed up to approximately –35°C. Afterward the solvent is removed *in vacuo* and the residue extracted with 10 ml *n*-hexane. The clear filtrate is concentrated to initiate crystallization. Storage over night at 5°C yields 0.230 g (0.28 mmol, 55.7%) [TripN(SiMe$_3$)]$_2$BiCl (**9b**) as a yellow crystalline solid.

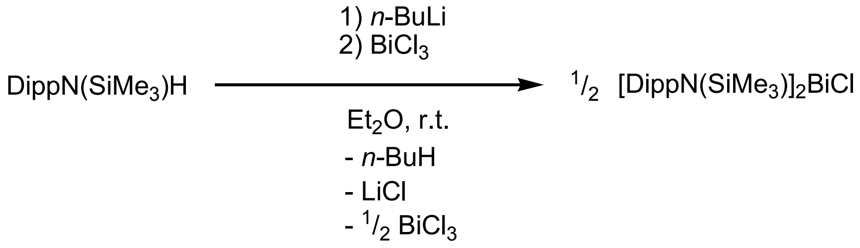
9b) Mp.: 118°C (Decomp.). **Anal. calc.** (found) in %: C 52.38 (50.93), H 7.81 (6.93), N 3.39 (3.09). **^{1}H-NMR** (25°C, CD$_2$Cl$_2$, 250.13 MHz): 0.23 (s, 18 H, Si(C***H***$_3$)$_3$), 0.82 (d, $^3J(^1\mathrm{H}\text{-}^1\mathrm{H})$ = 6.9 Hz, 6 H, *o*-CH(CH$_3$)(C***H***$_3$)), 1.14 (d, $^3J(^1\mathrm{H}\text{-}^1\mathrm{H})$ = 6.8 Hz, 6 H, *o*-CH(C***H***$_3$)(CH$_3$)), 1.16 (d, $^3J(^1\mathrm{H}\text{-}^1\mathrm{H})$ = 6.6 Hz, 6 H, *o*-CH(CH$_3$)(C***H***$_3$)), 1.18 (d, $^3J(^1\mathrm{H}\text{-}^1\mathrm{H})$ = 6.6 Hz, 6 H, *o*-CH(C***H***$_3$)(CH$_3$)), 1.20 (d, $^3J(^1\mathrm{H}\text{-}^1\mathrm{H})$ = 6.9 Hz, 12 H, *p*-CH(C***H***$_3$)$_2$), 2.87 (sep, $^3J(^1\mathrm{H}\text{-}^1\mathrm{H})$ = 6.9 Hz, 2 H, *p*-C***H***(CH$_3$)$_2$), 3.47 (m, $^3J(^1\mathrm{H}\text{-}^1\mathrm{H})$ = 6.9 Hz, 2 H, *o*-C***H***(CH$_3$)(CH$_3$)), 3.50 (m, $^3J(^1\mathrm{H}\text{-}^1\mathrm{H})$ = 6.8 Hz, 2 H, *o*-C***H***(CH$_3$)(CH$_3$)), 6.97 (dd, $^4J(^1\mathrm{H}\text{-}^1\mathrm{H})$ = 6.6 Hz, 4 H, arom. C***H***). **^{13}C{^{1}H}-NMR** (25°C, CD$_2$Cl$_2$, 62.9 MHz): 4.8 (s, Si(***C***H$_3$)$_3$), 24.3 (s), 24.4 (s), 24.7 (s), 25.6 (s), 26.1 (s), 27.6 (s), 27.7 (s), 28.4 (s), 34.1 (s), 122.3 (s, Arom. ***C***), 122.4 (s, arom. ***C***), 138.0 (s, arom. ***C***), 146.6 (s, arom. ***C***), 148.8 (s, arom. ***C***), 150.2 (s, arom. ***C***). **^{29}Si-INEPT-NMR** (300.0 K, CD$_2$Cl$_2$, 49.7 MHz): 12.4 (m). **IR** (ATR, 32 Scans, cm^{-1}): $\tilde{\nu}$ = 3045 (w), 2956 (m), 2929 (m), 2901 (w), 2867 (w), 1603 (w), 1457 (m), 1438 (m), 1381 (w), 1361 (w), 1303 (w), 1279 (w), 1259 (m), 1245 (s), 1198 (w), 1165 (m), 1113 (m), 1100 (w), 1062 (w), 1052 (w), 936 (w), 901 (s), 889 (m), 875 (s), 839 (s), 793 (m), 748 (m), 704 (m), 677 (m), 644 (m), 622 (w), 589 (w), 550 (w), 540 (w). **Raman** (Laser: 785 nm, accumulation time: 45 s, 4 Scans, cm^{-1}): $\tilde{\nu}$ = 2961 (1), 2936

(1), 2905 (2), 2873 (1), 1606 (4), 1460 (1), 1449 (2), 1440 (2), 1411 (1), 1385 (1), 1365 (1), 1264 (5), 1235 (1), 1200 (3), 1169 (4), 1153 (1), 1115 (1), 1102 (2), 1096 (2), 1071 (1), 1057 (1), 1052 (1), 956 (1), 905 (1), 883 (1), 857 (1), 831 (1), 795 (3), 758 (1), 722 (6), 707 (2), 688 (2), 649 (1), 633 (2), 624 (1), 590 (4), 554 (2), 542 (4), 455 (2), 358 (1), 318 (1), 289 (10).

5.4 Reaction of two equivalents of TripN($SiMe_3$)Li (**4b**) with $BiCl_3$

To a stirred solution of 0.146 g (0.50 mmol) TripN($SiMe_3$)H in 5 ml thf are added 0.22 ml (2.5 M, 0.55 mmol) *n*-BuLi solution at room temperature. After 10 min of stirring the reaction mixture is added dropwise at ambient temperature to a solution of 0.079 g (0.25 mmol) $BiCl_3$ in 5 ml thf. A grayish orange suspension is formed, which is stirred for 1 h at room temperature. Afterward the solvent is removed *in vacuo* and the residue extracted with 5 ml benzene. The solvent is removed after filtration. This procedure yields TripN($SiMe_3$)H as the main product besides some unknown side products according to the proton NMR spectrum.

5.5 Reaction of one equivalent of DippN($SiMe_3$)Li (**4c**) with $BiCl_3$



a) To a stirred solution of 0.249 g (1.00 mmol) DippN($SiMe_3$)H in 15 ml thf is added a 2.5 M *n*-BuLi solution in *n*-hexane (0.42 ml, 1.05 mmol). This mixture is stirred for additional 40 min at r.t. and then added dropwise to a stirred suspension of 0.347 g (1.10 mmol) $BiCl_3{}^*$ in 15 ml thf at 0°C. After 1 h stirring at room temperature the solvent is removed in *vacuo* and the oily residue is extracted with 5 ml of toluene and filtered. The solvent is removed in *vacuo*, extracted with 5 ml of *n*-hexane and filtered again. After concentration and storage at 5°C for 24 h few crystals of DippN($SiMe_3$)$BiCl_2$ (**5c**) are obtained. After additional 24 h crystals of [DippN($SiMe_3$)]$_2$BiCl (**9c**) are obtained.

* not sublimed $BiCl_3$

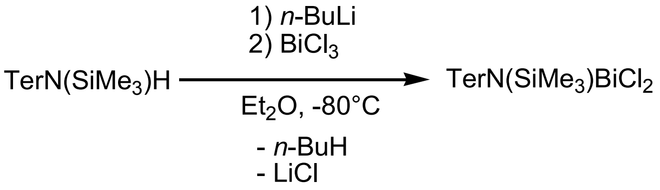
b) To a stirred solution of 0.249 g (1.00 mmol) DippN($SiMe_3$)H in 5 ml Et_2O are added dropwise 0.44 ml (2.5 M, 1.10 mmol) of an *n*-BuLi solution at room temperature. After stirring for 15 min the solution is added dropwise to a suspension of 0.378 g (1.20 mmol) $BiCl_3$ in 5 ml Et_2O at –80°C. The brownish suspension is stirred for 30 min and warmed up to room temperature. Afterward the solvent is removed *in vacuo*, extracted with 10 ml of *n*-hexane and filtered. The filtrate is concentrated and stored at –24°C over night. Yield: 0.235 g (0.32 mmol, 63.4%) of [DippN($SiMe_3$)]$_2$BiCl (**9c**) as yellow crystals by fractional crystallization.

9c) Mp.: 125°C (Decomp.). **Anal. calc.** (found) in %: C 48.60 (47.60), H 7.07 (6.97), N 3.78 (3.12). **^{1}H-NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): 0.29 (s, $^2J(^1H-^{29}Si)$ = 6.4 Hz, 18 H, Si(C***H***$_3$)$_3$), 0.95 (d, $^3J(^1H-^1H)$ = 7.0 Hz, 6 H, CH(CH$_3$)(C***H***$_3$)), 1.20 – 1.26 (m, 18 H, C***H***$_3$), 3.49 – 3.70 (m, 4 H, C***H***(CH$_3$)$_2$), 7.04 (t, $^3J(^1H-^1H)$ = 7.4 Hz, 2 H, arom. *p*-C***H***), 7.19 (d, $^3J(^1H-^1H)$ = 7.4 Hz, 4 H, arom. *m*-C***H***). **^{13}C{^{1}H}-NMR** (298.2 K, CD_2Cl_2, 75.46 MHz): 5.1 (s, Si(***C***H$_3$)$_3$), 25.1 (s, CH(***C***H$_3$)$_2$), 25.8 (s, CH(***C***H$_3$)$_2$), 26.6 (s, CH(***C***H$_3$)$_2$), 27.9 (s), 28.0 (s), 28.5 (s, ***C***H(CH$_3$)$_2$), 124.5 (s, arom. *m*-***C***H), 124.6 (s, arom. *m*-***C***H), 126.8 (s, arom. *p*-***C***H), 141.3 (s, arom. ***C***), 150.0 (s, arom. ***C***), 150.7 (s, arom. ***C***). **^{29}Si-INEPT-NMR** (300.0 K, CD_2Cl_2, 59.63 MHz): 12.5 (m). **Raman** (Laser: 784 nm, accumulation time: 120 s, 10 Scans, cm^{-1}): $\tilde{\nu}$ = 2965 (1), 2945 (1), 2921 (1), 2900 (1), 2863 (1), 1588 (2), 1461 (1), 1433 (2), 1408 (1), 1386 (1), 1365 (1), 1338 (1), 1316 (1), 1312 (1), 1237 (6), 1189 (2), 1175 (2), 1159 (1), 1147 (1), 1133 (1), 1101 (2), 1069 (1), 1040 (2), 1014 (1), 993 (1), 952 (1), 912 (3), 884 (1), 844 (1), 817 (2), 807 (3), 780 (3), 746 (2), 729 (3), 694 (1), 675 (2), 627 (1), 614 (1), 578 (10), 563 (2), 538 (2), 529 (2), 486 (2), 446 (1), 433 (2), 336 (1), 319 (8), 266 (2).

5.6 Reaction of two equivalents of DippN($SiMe_3$)Li (**4c**) with $BiCl_3$

To a stirred solution of 0.125 g (0.50 mmol) DippN($SiMe_3$)H in 5 ml thf are added 0.22 ml (0.55 mmol) of a 2.5 M *n*-BuLi solution at room temperature. The reaction mixture is stirred for 30 min and then added to a solution of 0.079 g (0.25 mmol) $BiCl_3$ in 5 ml thf at –80°C. The clear yellow solution is warmed up to room temperature and stirred for 1 h. The solvent is removed *in vacuo*. According to ^{1}H NMR spectroscopy a mixture of products is formed from which no substance could be isolated.

5.7 Reaction of one equivalent of TerN($SiMe_3$)Li (**4d**) with $BiCl_3$



$$\text{TerN(SiMe}_3\text{)H} \xrightarrow[\text{Et}_2\text{O, -80°C}]{\text{1) }n\text{-BuLi; 2) BiCl}_3} \text{TerN(SiMe}_3\text{)BiCl}_2 \quad - n\text{-BuH} \quad - \text{LiCl}$$

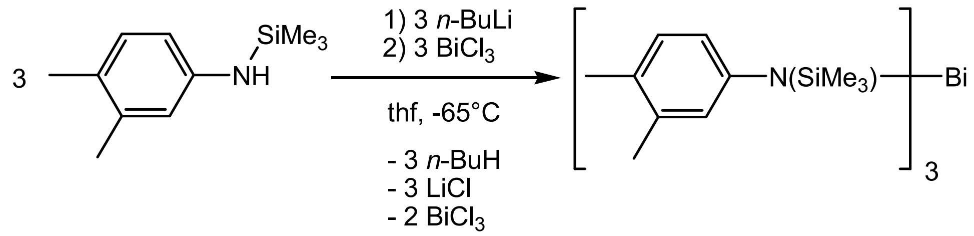
To a stirred solution of 1.205 g (3.00 mmol) TerN($SiMe_3$)H in 20 ml Et_2O 1.26 ml (3.15 mmol) of a 2.5 M solution of *n*-BuLi in *n*-hexane are added at –80°C. The reaction mixture is warmed to room temperature and stirred for 1 h. Then the reaction mixture is added dropwise at –80°C to a stirred suspension of 1.041 g (3.30 mmol) $BiCl_3$ in 40 ml Et_2O. The formed suspension is stirred at this temperature for 1 h, warmed up and stirred additional 2.5 h at room temperature. The solvent is removed *in vacuo* and the residue is dried for ½ h. After extraction with a mixture of 16 ml CH_2Cl_2 and 4 ml *n*-pentane the suspension is stored for 2 h at 5°C and then filtrated through ceolit at 0°C to 5°C. Upon concentration the red solution is stored at room temperature over night for crystallization. The crude product is dissolved in 16 ml CH_2Cl_2 and 4 ml *n*-pentane again. Fractional crystallization yields 706 mg (1.04 mmol, 34.6%) TerN($SiMe_3$)$BiCl_2$ · CH_2Cl_2 (**5d** · CH_2Cl_2) as red crystal blocks. Upon drying *in vacuo* a partial loss of solvent molecules is observed in the elemental analysis and the proton NMR spectrum.

5d · 0.8 CH_2Cl_2**) Mp.:** 155°C (Decomp.). **Anal. calc.** (found) in %: C 44.61 (44.94), H 4.76 (4.76), N 1.87 (2.04). **^{1}H-NMR** (298.2 K, C_6D_6, 300.13 MHz): 0.10 (s, 9 H, Si(C***H***$_3$)$_3$), 2.15 (s, 6 H, C***H***$_3$), 2.19 (s, 6 H, C***H***$_3$), 2.21 (s, 6 H, C***H***$_3$), 4.28 (s, 1.6 H, C***H***$_2$Cl$_2$), 6.73 (m, 1 H, *p*-C***H***), 6.80 (s, 2 H, Mes-C***H***), 6.85 (s, 2 H, Mes-C***H***), 6.95 (m, 2 H, *m*-C***H***). **^{13}C-NMR** (298.2 K, C_6D_6, 75.5 MHz): 5.8 (s, Si(***C***H$_3$)$_3$), 21.4 (s, ***C***H$_3$), 22.5 (s, ***C***H$_3$), 23.1 (s, ***C***H$_3$), 53.7 (s, CH_2Cl_2), 123.1 (s, arom. ***C***), 130.0 (s, arom. ***C***), 130.6 (s, arom. ***C***), 132.7 (s, arom. ***C***), 136.1 (s, arom. ***C***), 138.7 (s, arom. ***C***), 139.0 (s, arom. ***C***), 139.7 (s, arom. ***C***), 140.3 (s, arom. ***C***), 148.9 (s, arom. ***C***). **^{29}Si-INEPT-NMR** (299.4 K, CD_2Cl_2, 59.63 MHz): 13.5 (m).

5.6 Reaction of two equivalents of TerN($SiMe_3$)Li (**4d**) with $BiCl_3$

A stirred solution of 0.119 g (0.30 mmol) TerN($SiMe_3$)H in 5 ml thf is reacted with 0.13 ml (0.32 mmol) of a 2.5 M *n*-BuLi solution at room temperature. After 30 min stirring at ambient temperature the reaction mixture is added dropwise at –80°C to a stirred solution of 0.047 g (0.15 mmol) $BiCl_3$ in 2 ml thf. The resulting brown suspension is warmed to room temperature and the solvent is removed *in vacuo*. A NMR experiment revealed that they main product of the reaction is the starting material $TerN(SiMe_3)H$ besides a minimum amount of unidentified byproducts.

5.7 Reaction of one equivalent of lithium *N*-trimethylsilyl-3,4-dimethylanilid ($DpN(SiMe_3)Li$, **4e**) with $BiCl_3$

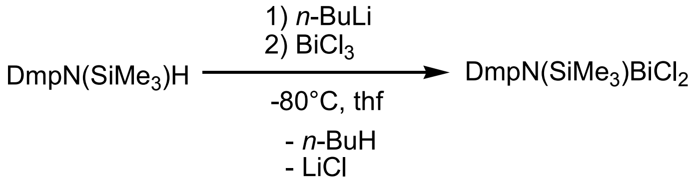


0.193 g (1.00 mmol) *N*-trimethylsilyl-3,4-dimethylphenylamine are dissolved in 10 ml thf. To the stirred solution 0.4 ml (1.00 mmol) of a 2.5 M solution of *n*-BuLi in *n*-hexane is added at –65°C. The clear, orange solution is warmed to room temperature and slowly added to a suspension of 0.315 g (1.00 mmol) $BiCl_3$ in 5 ml thf at –65°C. After 1 h at this temperature the reaction mixture is brought to room temperature and is stirred for 2 h. then the solvent is removed *in vacuo* and the residue is extracted with 20 ml *n*-hexane and filtered. Afterward the solution is concentrated and fractional crystallization yields 0.201 g (0.26 mmol, 76.7%) of **12e** as colorless to pale yellow crystals.

12e) Mp.: 144°C. **Anal. calc.** (found): C 45.51 (45.59), H 6.32 (5.88), N 4.82 (4.67). **^{1}H-NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): 0.03 (s, 9 H, $Si(C\boldsymbol{H}_3)_3$), 1.92 (s, 3 H, $C_6H_3(C\boldsymbol{H}_3)$), 2.30 (s, 3 H, $C_6H_3(C\boldsymbol{H}_3)$), 5.26 - 6.86 (arom, 3 H, $C_6\boldsymbol{H}_3$). **^{13}C{^{1}H}-NMR** (298.2 K, CD_2Cl_2, 75.5 MHz): 2.3 (s, $Si(\boldsymbol{C}H_3)_3$), 19.1 (s, $C_6H_3(\boldsymbol{C}H_3)(CH_3)$), 20.0 (s, $C_6H_3(CH_3)(\boldsymbol{C}H_3)$), 128.8 (s, arom. ***C***), 130.4 (s, arom. ***C***), 131.7 (s, arom. ***C***), 134.4 (s, arom. ***C***), 135.6 (s, arom. ***C***), 146.1 (s, arom. ***C***). **^{29}Si-INEPT-NMR** (298.2 K, CD_2Cl_2, 59.63 MHz): 3.5 (m). **IR** (ATR, 32 Scans, cm^{-1}): $\tilde{\nu}$ = 3062 (w), 3045 (w), 3012 (w), 2942 (w), 2918 (w), 2888 (w), 2861 (w), 2724 (w), 1600 (w), 1563 (w), 1488 (m), 1448 (w), 1415 (w), 1397 (w), 1381 (w), 1354 (w), 1305 (w), 1282 (w), 1258 (m), 1242 (m), 1202 (m), 1157 (w), 1117 (w), 1009 (w), 994 (w), 958 (m), 936 (w), 905 (m), 879 (w), 857 (s), 826 (s), 798 (m), 772 (m), 745 (m), 702 (m), 678 (m), 622 (w), 582 (w), 564 (s). **Raman** (Laser: 633 nm, accumulation time: 15 s, 4 Scans, cm^{-1}): $\tilde{\nu}$ = 3046 (2), 3013 (1), 2951 (2), 2942 (2), 2918 (3), 2894 (3), 1599 (5), 1564 (2), 1493 (1), 1447 (1), 1399 (1), 1379 (2), 1368 (1), 1281 (2), 1250 (10), 1201 (2), 1157 (4), 1116 (3), 959 (1), 934 (1), 915 (1), 905 (1), 834 (1), 828 (1), 776 (4), 745 (7), 722 (2), 702 (3), 679

(2), 623 (2), 583 (3), 564 (2), 519 (5), 480 (2), 447 (1), 359 (2), 351 (3), 291 (4), 258 (2), 243 (2).

5.8 Reaction of one equivalent of DmpN(SiMe$_3$)Li (**4f**) with BiCl$_3$



$$\mathrm{DmpN(SiMe_3)H} \xrightarrow[\substack{-80°\mathrm{C,\ thf} \\ -\ n\text{-}\mathrm{BuH} \\ -\ \mathrm{LiCl}}]{\substack{1)\ n\text{-}\mathrm{BuLi} \\ 2)\ \mathrm{BiCl_3}}} \mathrm{DmpN(SiMe_3)BiCl_2}$$

0.097 g (0.50 mmol) DmpN(SiMe$_3$)H dissolved in 5 ml thf are reacted with 0.22 ml (0.55 mmol) of a 2.5 M *n*-BuLi solution. The formed solution is added dropwise at –80°C to a solution of 0.158 g (0.50 mmol) BiCl$_3$ in 5 ml thf. The reaction mixture is brought to ambient temperature and stirred for 1 h. Afterward the solvent is removed *in vacuo* and the residue is dried for 1 h. The residue is investigated by means of NMR spectroscopy. Only broad resonances are observed in the proton NMR spectrum, which cannot be proper assigned to any known substance.

5.9 Reaction of three equivalents of DmpN(SiMe$_3$)Li (**4f**) with BiCl$_3$

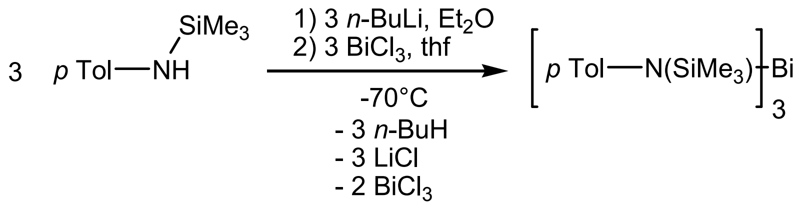
a) To a stirred solution of 0.193 g (1.00 mmol) DmpN(SiMe$_3$)H in 10 ml Et$_2$O 0.4 ml *n*-BuLi in *n*-hexane (2.5 M, 1.00 mmol) are added dropwise at –80°C. During 1 h the reaction mixture is warmed up to room temperature and added slowly to a suspension of 0.105 g (0.33 mmol) BiCl$_3$* in 40 ml thf at –80°C. The reaction mixture is warmed up to room temperature. and stirred for 20 h. Then the solvent is removed *in vacuo* and the residue is extracted with 10 ml *n*-hexane. The filtrate is concentrated and stored at –24°C over night. A few red crystals of [DmpN(SiMe$_3$)BiNDmp]$_2$ (**11f**) are formed, which could be isolated by crystal picking.

* Not sublimed BiCl$_3$

b) To a stirred solution of 0.116 g (0.60 mmol) DmpN(SiMe$_3$)H in 5 ml thf are added 0.26 ml (0.65 mmol) of a 2.5 M *n*-BuLi solution. The formed solution is added dropwise to a solution of 0.063 g (0.20 mmol) BiCl$_3$ in 5 ml thf at ambient temperature. An orange solution is formed and stirred for 1 h. Upon removal of the solvent *in vacuo* the resulting orange oil is examined by means of NMR spectroscopy. A complex mixture is formed containing different DmpN(SiMe$_3$) species which can not, beside DmpN(SiMe$_3$)H, be identified.

11f) ^{1}H-NMR (298.2 K, CD$_2$Cl$_2$, 300.13 MHz): 0.15 (s, 18 H, Si(C***H***$_3$)$_3$), 2.15 (s, 12 H, *o*-(C***H***$_3$)$_2$), 2.23 (s, 12 H, *o*-(C***H***$_3$)$_2$), 6.57 (arom., 2 H, *p*-C***H***), 6.74 (arom., 2 H, *p*-C***H***), 6.90 (arom., 4 H, *m*-C***H***), 6.96 (arom., 4 H, *m*-C***H***). **Raman** (Laser: 785 nm, accumulation time: 30 s, 4 Scans, cm^{-1}): $\tilde{\nu}$ = 3057 (1), 3032 (1), 2899 (1), 2850 (1), 1589 (6), 1463 (2), 1406 (2), 1372 (1), 1253 (10), 1227 (4), 1161 (1), 1111 (3), 1094 (2), 976 (1), 947 (1), 884 (1), 841 (1), 794 (1), 755 (1), 732 (1), 714 (1), 658 (2), 624 (1), 553 (6), 531 (10), 513 (5), 352 (2), 339 (2), 309 (3), 274 (3), 258 (2), 243 (2), 228 (2).

5.10 Reaction of one equivalents of *p*-TolN(SiMe$_3$)Li (**4g**) with BiCl$_3$



a) To a solution of 0.179 g (1.00 mmol) *p*-TolN(SiMe$_3$)H in 10 ml Et$_2$O 0.4 ml (c = 2.5 M, 1.00 mmol) of an *n*-BuLi solution in *n*-hexane are added at –70°C. The reaction mixture is brought to room temperature and is added to a solution of 0.315 g (1.00 mmol) of sublimed BiCl$_3$ in 15 ml thf at –70°C. The reaction mixture is brought to room temperature and after the removal of the solvent *in vacuo* the residue is extracted with 10 ml *n*-hexane and filtered. The solvent is removed *in vacuo*. This procedure leads to a mixture of products from which [*p*-TolN(SiMe$_3$)]$_3$Bi (**12g**) and *p*-TolN(SiMe$_3$)H could be identified by proton NMR spectroscopy. Fractionated crystallization from a concentrated *n*-hexane solution at 5°C yields 0.030 g (0.04 mmol, 12.2%) [*p*-TolN(SiMe$_3$)]$_3$Bi (**12g**) as pale yellow crystals.

5.11 Reaction of three equivalents of *p*-TolN(SiMe$_3$)Li (**4g**) with BiCl$_3$

0.269 g (1.50 mmol) *p*-TolN(SiMe$_3$)H in 5 ml thf are reacted with 0.60 ml (2.5 M, 1.5 mmol) *n*-BuLi at room temperature. The resulting clear solution is added dropwise to a solution of 0.158 g (0.5 mmol) BiCl$_3$* in 5 ml thf at –80°C. The reaction mixture is brought to ambient temperature and stirred for 1 h. After the solvent is evaporated *in vacuo* the residue is extracted with 5 ml CH$_2$Cl$_2$ and filtered. The solvent is removed *in vacuo*. Yield: *p*-Tol(SiMe$_3$)H (35%) and [*p*-TolN(SiMe$_3$)]$_3$Bi (**12g**, 65%). All yields of the crude product are determined by ^{1}H-NMR integrals of the trimethylsilyl groups.

* Sublimed $BiCl_3$, if not sublimed $BiCl_3$ is used the yield of $[p\text{-TolN(SiMe}_3)]_3\text{Bi}$ is lower (ca. 30%) and the four-membered ring **11g** is formed in traces as a side-product beside *p*-TolN($SiMe_3$)Li.

12g) Mp.: 116°C. **Anal. calc.** (found): C 48.43 (47.14), H 6.50 (6.56), N 5.65 (5.48). **^{1}H-NMR** (300.0 K, CD_2Cl_2, 250.13 MHz): 0.03 (s, 9 H, Si(C***H***$_3$)$_3$), 2.39 (s, 3 H, C_6H_4(C***H***$_3$)), 5.75 - 6.87 (arom, 4 H, C_6***H***$_4$). **^{13}C{^{1}H}-NMR** (300.0 K, CD_2Cl_2, 62.9 MHz): 2.3 (s, Si(***C***H$_3$)$_3$), 20.8 (s, C_6H_4(***C***H$_3$)), 128.5 (s, Arom. ***C***), 132.8 (s, Arom. ***C***), 133.1 (s, Arom. ***C***), 145.9 (s, Arom. ***C***). **^{29}Si-INEPT-NMR** (298.4 K, CD_2Cl_2, 59.63 MHz): 3.9 (m). **IR** (ATR, 32 Scans, cm^{-1}): $\tilde{\nu}$ = 3015 (w), 2953 (w), 2917 (w), 2894 (w), 2862 (w), 1614 (w), 1568 (w), 1514 (m), 1498 (m), 1444 (w), 1416 (w), 1367 (w), 1288 (m), 1258 (m), 1244 (m), 1220 (s), 1182 (w), 1170 (m), 1121 (w), 1103 (w), 1040 (w), 1017 (w), 961 (w), 940 (m), 920 (m), 902 (s), 835 (s), 821 (s), 768 (m), 744 (m), 701 (m), 677 (m), 642 (m), 619 (m), 538 (m). **Raman** (Laser: 784 nm, accumulation time: 50 s, 4 Scans, cm^{-1}): $\tilde{\nu}$ = 2956 (1), 2942 (1), 2920 (1), 2896 (1), 1604 (3), 1498 (2), 1403 (1), 1375 (2), 1297 (1), 1260 (1), 1227 (8), 1219 (10), 1208 (4), 1169 (5), 920 (1), 902 (1), 849 (1), 839 (1), 822 (1), 788 (1), 772 (7), 744 (1), 723 (3), 701 (3), 680 (2), 641 (2), 620 (4), 537 (8), 502 (3), 446 (1), 416 (1), 348 (4), 331 (2), 289 (9), 260 (2), 246 (2), 210 (6).

6. General procedure for checking for C-C coupling products

A dried reaction mixture is suspended in ca. 5 ml of dest. H_2O and stirred at room temperature for ca. 15 min. Afterward the suspension is extracted with ca. 5 ml of diethylether. The organic phase is separated and the solvent is removed. The residue is extracted with ca. 0.5 ml of CD_2Cl_2 and examined by NMR spectroscopy.

7. References

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