Supporting Information for manuscript

A planar chiral [2.2]paracyclophane derived N-heterocyclic stannylene

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General remarks

All reactions were carried out in flame-dried reaction vessels using standard Schlenk or glove box techniques under argon. Solvents were dried over sodium/benzophenone under argon and were freshly distilled prior to use. All new compounds were fully characterized. NMR-spectra were recorded on a Bruker ARX-300, AV-300, AV-400 MHz or on a Varian Associated, Varian 600 unity plus. ^{1}H, $^{13}C\{^{1}H\}$, and $Sn\{^{1}H\}$ spectra of the stannylene (±)-**4** were recorded on Bruker AVANCE II 200 (QNP-probehead), Bruker AVANCE I 400 (BBO-probehead) or Bruker AVANCE III 400 (BBFO-probehead) spectrometers. Chemical shifts (δ) are quoted in ppm downfield of tetramethylsilane. Coupling constants (*J*) are quoted in Hz.

Infrared spectra were recorded on a Varian Associated FT-IR 3100 Excalibur with ATR unit. The wave numbers (ν) of recorded IR-signals are quoted in cm^{-1}. ESI mass spectra were recorded on a Bruker Daltonics MicroTof.

GC-MS Spectra were recorded on an Agilent Technologies 7890A GC-system with Agilent 5975C VL MSD or 5975 inert Mass Selective Detector (EI) and a HP-5MS column (0.25 mm x 30 m, Film: 0.25 µm). For control of the conversion and characterization of the products, the methods in Table 1.1 were used. The method used starts with the injection temperature T_0, after holding this temperature for 3 min, the column is heated to the temperature T_1 (ramp) and holds the final temperature for the indicated time.

Table 1.1: GC-MS methods.

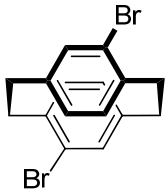
method	T_0 [°C]	ramp/K·min^{-1}	T_1 [°C] /holding time [min]
A	**50**	**40**	**320 / 7**
B	**50**	**40**	**320/ 3**

1. X-ray diffraction studies

All diffraction data were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 153(2) K using graphite monochromated Mo-Ka radiation (λ = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART program package.[1] Structure solutions were found with the SHELXS-97[2] package using the heavy-atom method and were refined with SHELXL-97[3] against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions.

2. Synthesis of stannylene (±)-4

[2.2]Paracyclophane-4,15-dibromide (*pseudo-para*-(±)-2)



Following a literature known procedure,[4] to a solution of [2.2]paracyclophane (**1**) (4.17 g, 20 mmol, 1.0 eq.) in CCl_4 (75 mL) at room temperature was added dropwise elemental bromine (6.78 mL, 132 mmol, 6.6 eq.). The reaction mixture was stirred at 60 °C for 3 h. After reaction control via TLC the mixture was cooled to 0 °C and a solution of aq. $NaHSO_3$ was added until decolorization. The resulting precipitate was removed through filtration, washed with water (3×10 mL) and EtOH (5 mL) and dried under vacuum (6×10^{-2} mbar) over night, leading to pure *pseudo-para*-dibromo[2.2]paracyclophane (*pseudo-para*-(±)-**2**) as light yellow solid (2.27 g, 6.19 mmol, 31%). The obtained analytical data is in agreement with the literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.15 (dd, J = 7.9, 1.8 Hz, 2H, 2×Ar-H), 6.51 (d, J = 1.6 Hz, 2H, 2×Ar-H), 6.44 (d, J = 7.9 Hz, 2H, 2×Ar-H), 3.50 (ddd, J = 11.6, 9.2, 2.5 Hz, 2H, CH_2), 3.19-3.12 (m, 2H, CH_2), 2.98-2.81 (m, 4H, 2×CH_2); **^{13}C NMR (100 MHz, $CDCl_3$):** δ/ppm = 141.3, 138.7, 137.5, 134.3, 128.4, 126.9, 35.5, 33.0; **GC-MS, t_R (method B):** 10.4 min, **(EI) m/z (%):** 367.9 (16), 365.9 (31), 363.9 (16), 185.0 (9), 184.0 (98), 183.0 (10), 182.0 (100), 103.1 (23), 77.0 (25).

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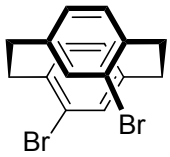
[1] *SMART*, Bruker AXS, 2000.
[2] *SHELXS-97*, G. M. Sheldrick, *Acta Crystallogr.,* 1990, **A46**, 467–473.
[3] *SHELXL-97*, G. M. Sheldrick, *Acta Crystallogr.,* 2008, **A64**, 112–122.
[4] L. Bondarenko, I. Dix, H. Hinrichs and H. Hopf, *Synthesis* 2004, 2751.

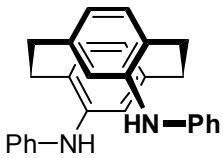
[2.2]Paracyclophane-4,15-dibromide (*pseudo-ortho*-(±)-2)



Slightly modifying a literature known procedure,[4] *pseudo-para*-dibromo-[2.2]paracyclophane (*pseudo-para*-(±)-**2**) (2.2 g, 6.0 mmol, 1.0 eq.) was suspended in a mixture of triglyme (11 mL) and NMP (2.0 mL) and heated under microwave irradiation at 240 °C for 4 h. After cooling to 0 °C the remaining precipitate was filtered off and subjected to the reactions conditions again, with accordingly less solvent (3.6 mL triglyme and 0.8 mL NMP). After repeating this procedure for two more cycles (triglyme/NMP = 1.8 mL/0.38 mL and 0.5 mL/0.1 mL), the residual solvents from the collected filtrates were removed by Kugelrohr distillation. The remaining brown solid was then purified via flash column chromatography (4×12 cm SiO_2, *n*-pentane/CH_2Cl_2 = 100/0→99/1) to yield the pure *pseudo-ortho*-dibromo[2.2]paracyclo-phane (*pseudo-ortho*-(±)-**2**) as a white solid (1.38 g, 3.77 mmol, 63%). The obtained analytical data are in agreement with data reported in the literature.[4]

R_f (*n*-pentane/CH_2Cl_2 = 9/1): 0.38; **^{1}H NMR (300 MHz, $CDCl_3$):** δ/ppm = 7.20 (d, *J* = 1.3 Hz, 2H, 2×Ar-H), 6.57-6.50 (m, 4H, 4×Ar-H), 3.50-3.41 (m, 2H, CH_2), 3.14-2.98 (m, 4H, 2×CH_2), 2.86-2.76 (m, 2H, CH_2); **^{13}C NMR (75 MHz, $CDCl_3$):** δ/ppm = 141.4, 138.8, 135.1, 132.8, 131.7, 126.7, 35.9, 32.6; **GC-MS, t_R (method B):** 10.2 min, **(EI) m/z (%):** 367.9 (14), 365.9 (28), 363.9 (14), 185.0 (9), 184.0 (99), 183.0 (10), 182.0 (100), 103.0 (25), 77.0 (27).

[2.2]Paracyclophane-4,15-*N*,*N*'-diphenyldiamine (*pseudo-ortho*-(±)-3)



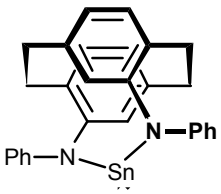
In analogy to the literature,[5] a pressure resistant screw cap reaction tube was charged in a glovebox with $Pd(OAc)_2$ (108 mg, 0.48 mmol, 0.09 eq.), P*t*Bu_3HBF_4 (139 mg, 0.48 mmol, 0.09 eq.) and NaO*t*Bu (1.54 g, 15.99 mmol, 3.0 eq.). Outside the glovebox, toluene (107 mL) was added and oxygen was removed by freeze-thaw-pump-cycle technique. After the addition of *pseudo-ortho*-dibromo[2.2]paracyclophane (*pseudo-ortho*-(±)-**2**) (1.95 g, 5.33 mmol, 1.0 eq.) and aniline (1.45 mL, 15.99 mmol, 3.0 eq.) the reaction mixture was stirred at 110 °C for 20 h. After reaction control via TLC the reaction was stopped through the addition of satd. aq. NH_4Cl. The mixture was extracted with CH_2Cl_2 (3×80 mL) and the combined organic layer was washed with satd. aq. NH_4Cl (80 mL), dried over Na_2SO_4 and residual solvent was removed under reduced pressure. Flash column chromatography (4×10 cm SiO_2, *n*-pentane/CH_2Cl_2 = 5/1→3/1) yielded the desired amine *pseudo-ortho*-(±)-**3** as light yellow solid (1.62 g, 4.15 mmol, 78%).

[5] J. Barluenga, A. Jiménez-Aquino, C. Valdés and F. Aznar, *Angew. Chem. Int. Ed.,* 2007, **46**, 1529.

R_f (*n*-pentane/CH_2Cl_2 = 3/1): 0.53; **^{1}H NMR (400 MHz, $CDCl_3$):** δ/ppm = 7.25 -7.21 (m, 4H, 4×Ar-H), 6.83-6.79 (m, 6H, 6×Ar-H), 6.44-6.41 (m, 4H, 4×Ar-H), 6.20 (dd, *J* = 7.8, 1.1 Hz, 2H, 2×Ar-H), 5.47-5.01 (br s, 2H, 2×NH), 2.97-2.86 (m, 4H, 2×CH_2), 2.82-2.73 (m, 2H, CH_2), 2.64-2.57 (m, 2H, CH_2); **^{13}C NMR (100 MHz, $CDCl_3$):** δ/ppm = 143.4, 141.4, 140.7, 135.7, 129.8, 129.3, 126.7, 120.6, 119.7, 117.0, 33.5, 33.0; **ESI-MS:** calculated $[C_{28}H_{26}N_2H]^+$: 391.2169, found: 391.2170; calculated $[C_{28}H_{26}N_2Na]^+$: 413.1988, found: 413.1992; **GC-MS, t_R (method A):** 15.9 min, **(EI) m/z (%):** 391.2 (11), 390.3 (38), 281.1 (17), 208.1 (10), 207.1 (42), 196.1 (18), 195.2 (64), 194.2 (100), 193.1 (31), 192.2 (9), 180.2 (27.0); **ATR-FTIR (cm^{-1}):** 1591, 1562, 1491, 1307, 1285, 1237, 1159, 1026, 883, 792, 741, 692, 661, 616, 582, 510.

^{1}H NMR (200 MHz, THF-d_8): δ = 7.09 (t, 4H, $^3J_{HH}$ = 7.9 Hz, Ph-H_{meta}), 6.80 (d, 4H, $^3J_{HH}$ = 8.0 Hz, Ph-H_{ortho}), 6.77 (s, 2H, NH), 6.70 (t, $^3J_{HH}$ = 7.4 Hz, 2H, Ph-H_{para}), 6.49 (d, $^3J_{HH}$ = 6.49 Hz, 2H, Cyclophane-H), 6.44 (s, 2H, Cyclophane-H) 6.31 (d, $^3J_{HH}$ = 6.4 Hz, 2H, Cyclophane-H), 3.03–2.54 (m, 8H, CH_2) ; **^{13}C NMR (50.3 MHz, THF-d_8):** δ/ppm = 145.9, 142.5, 140.9, 136.5, 133.3 129.6 128.4, 123.3, 119.6, 115.6, 35.0, 34.1.

Stannylene (±)-4

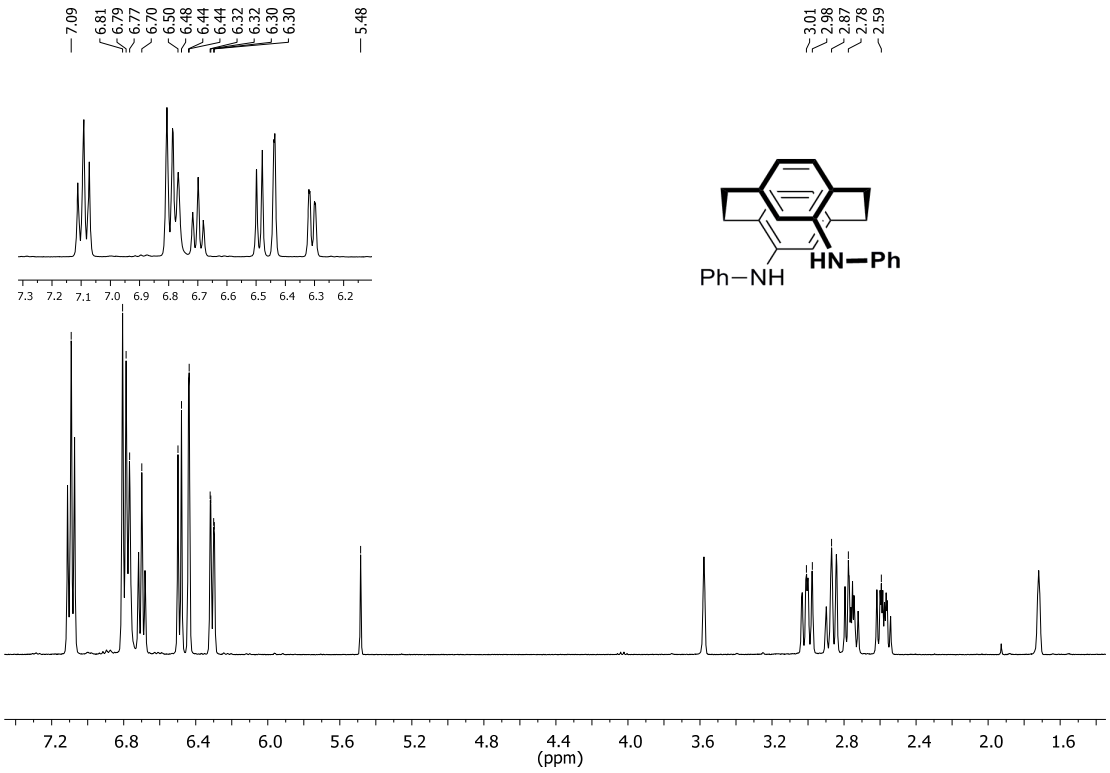


An oven dried Schlenk flask was cooled under argon and charged with diamine (±)-**3** (100 mg, 0.26 mmol, 1.0 eq.) in tetrahydrofuran (20.0 mL). To this was added $Sn[N(SiMe_3)_2]_2$ (112 mg, 0.26 mmol, 1.0 eq.). The reaction mixture was heated for 24 h at 70 °C in an oil bath. After cooling to ambient temperature the solvent was removed in vacuo, the solid residue was taken up in *n*-hexane and the slurry was filtered. Removal of the solvent gave compound (±)-**4** as a bright orange solid (89 mg, 68%). Intense orange Crystals of (±)-**4** were obtained by slow evaporation of a THF solution of the compound under argon for 2 weeks.

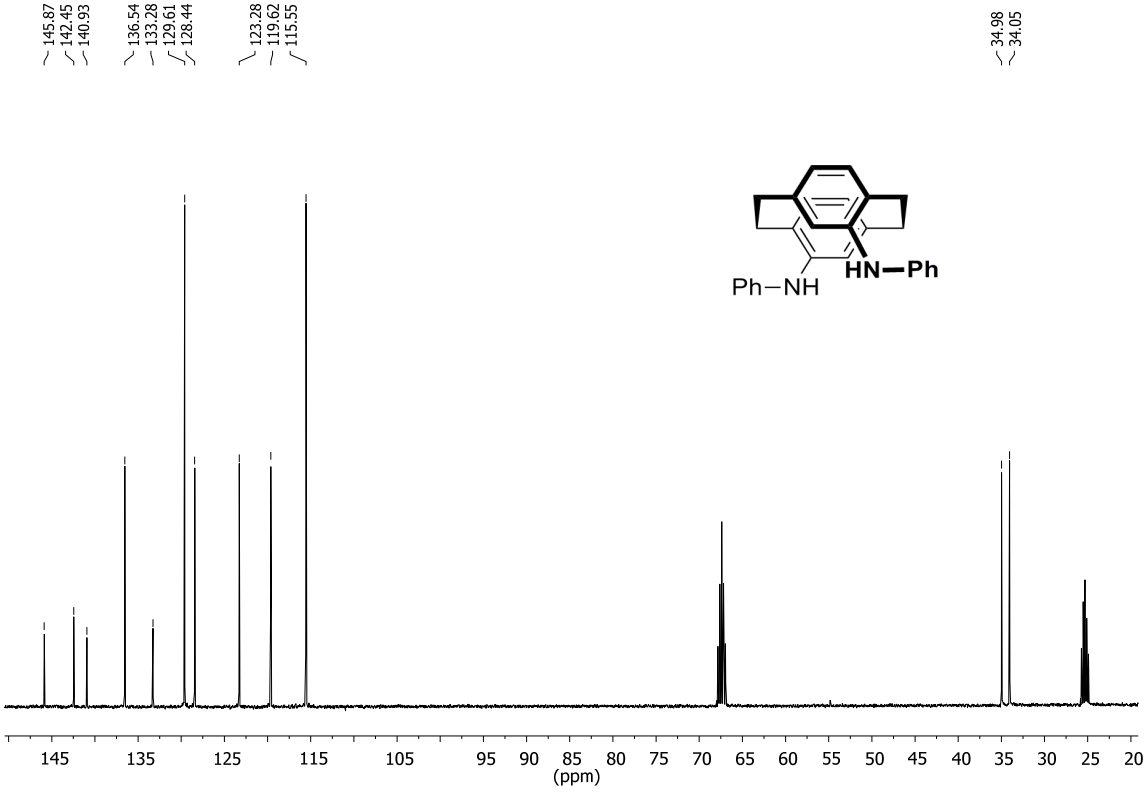
^{1}H NMR (200 MHz, THF-d_8): δ/ppm = 7.05 (t, 4H, $^3J_{HH}$ = 8.2 Hz, Ph-H_{meta}), 7.00 (s, 2H, Cyclophane-H), 6.94 (d, $^3J_{HH}$ = 8.2 Hz, 4H, Ph-H_{ortho}), 6.66 (t, $^3J_{HH}$ = 7.2 Hz, 2H, Ph-H_{para}), 6.44 (d, $^3J_{HH}$ = 7.7 Hz, 2H, Cyclophane-H), 6.32 (d, $^3J_{HH}$ = 7.7 Hz, 2H, Cyclophane-H), 2.94–2.34 (m, 8H, CH_2); **^{13}C NMR (50.3 MHz, THF-d_8):** δ/ppm = 154.3 (Phenyl-*C*N), 150.6 (Cyclophane-*C*N), 142.6 (Cyclophane-*C*CH_2), 136.8 (Cyclophane-*C*CH_2), 134.9 (Cyclophane-CH), 129.9(4) (Cyclophane-CH), 129.9(1) (Phenyl-CH_{meta}) 123.1 (Cyclophane-CH), 119.2 (Phenyl-CH_{para}), 117.2 (Phenyl-CH_{ortho}), 36.9/31.3 (CH_2); **^{119}Sn NMR (149.2 MHz, THF-d_8):** δ/ppm = 41.8; **EI-MS** (70 eV): *m*/*z* = 509 (100 %, $[M+H]^+$) (calculated for $C_{28}H_{24}N_2Sn$, $[M]^+$ 508.10).

3. NMR scans

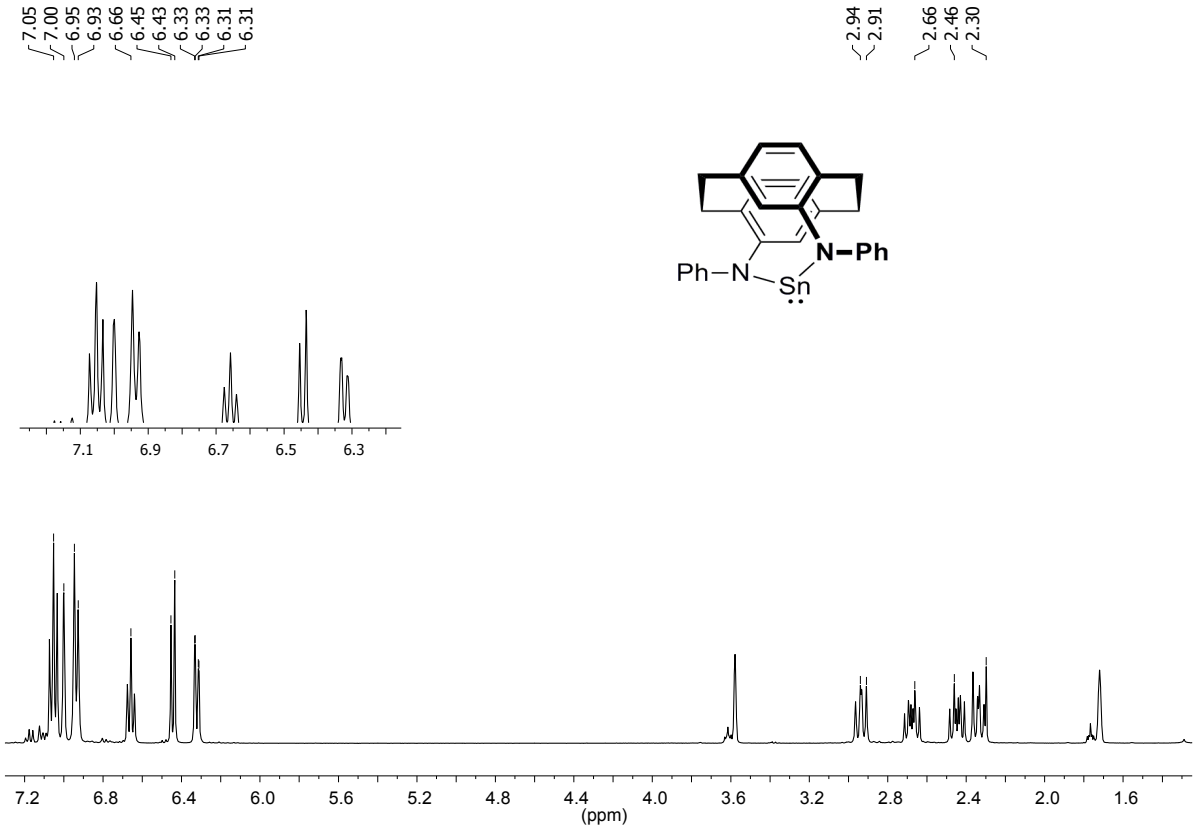
^{1}H NMR of diamine (±)-**3** (THF-d_8)



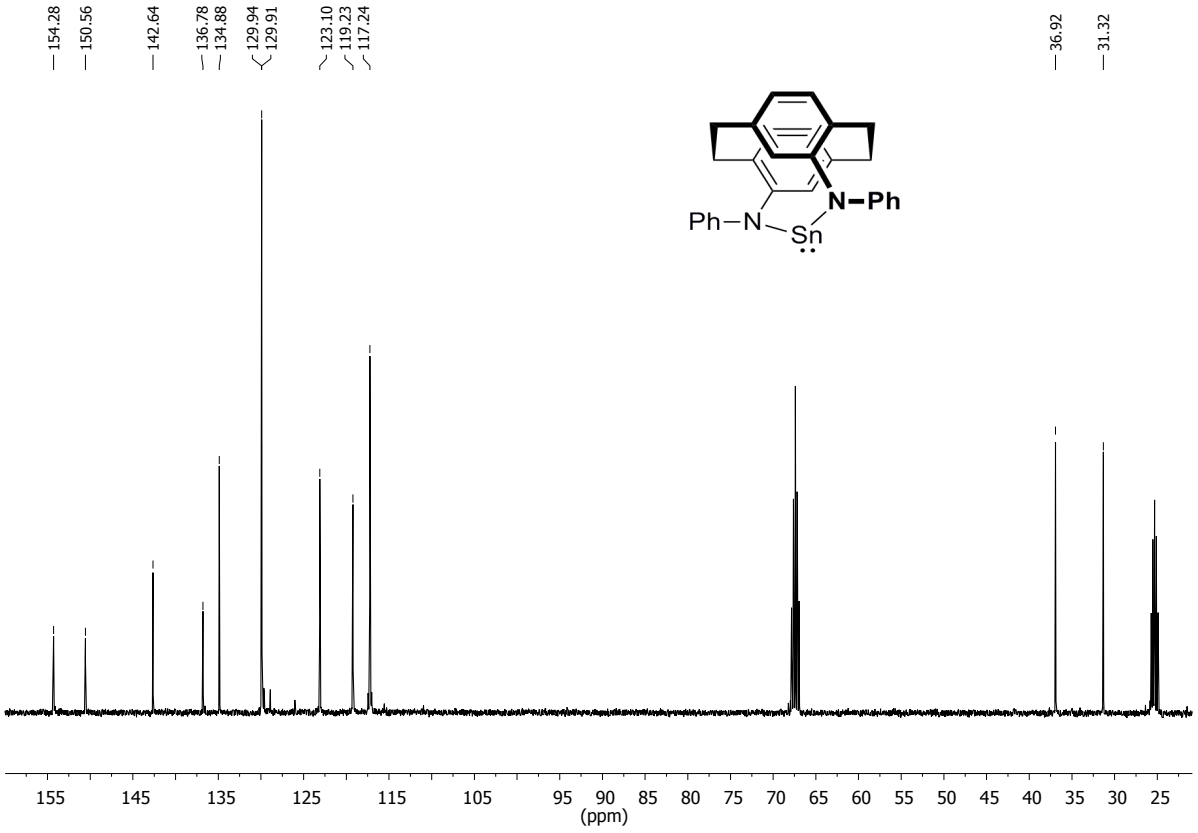
^{13}C{^{1}H} NMR of diamine (±)-**3** (THF-d_8)



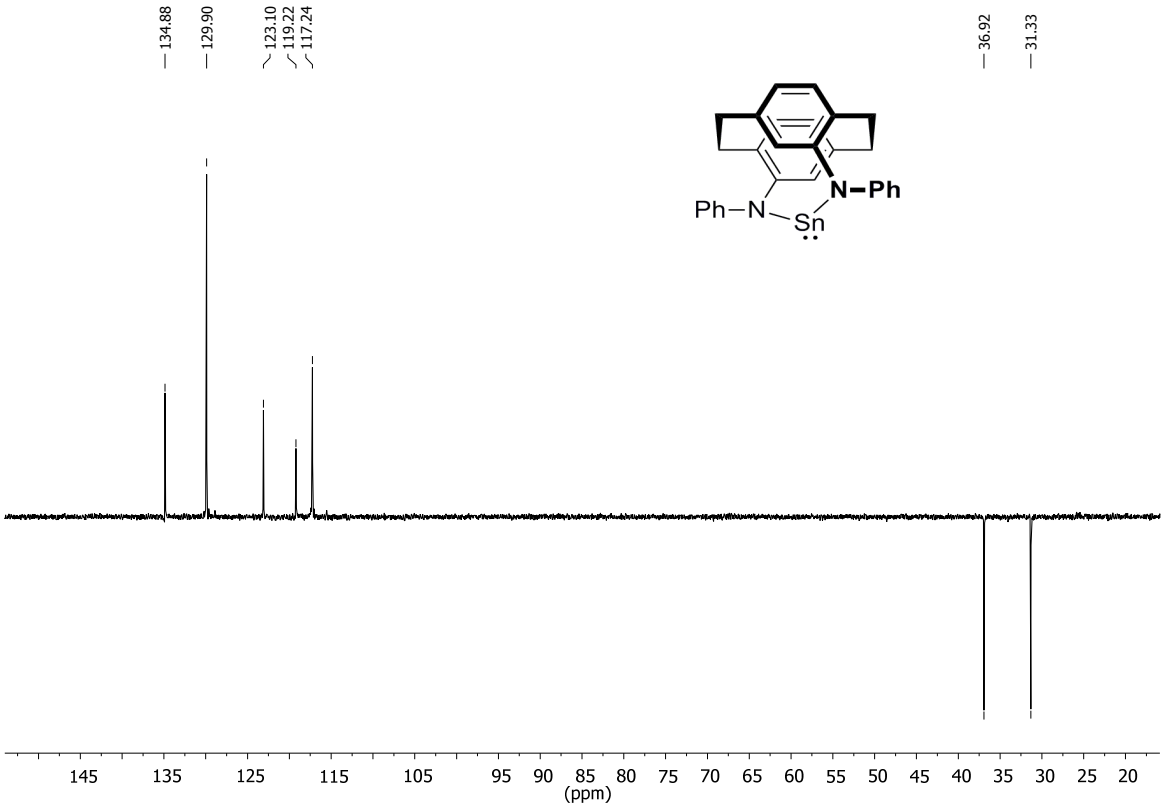
^{1}H NMR of stannylene (±)-**4** (THF-d_8)



^{13}C{^{1}H} NMR of stannylene (±)-**4** (THF-d_8)



$^{13}C\{^{1}H\}$ Dept NMR of stannylene (±)**-4** (THF-d_8)



^{119}Sn NMR of stannylene (±)**-4** (THF-d_8)