

A Stable Chiral Diaminocyclopropenylidene

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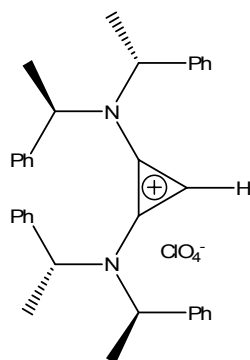
General:

All operations were performed in an atmosphere of dry argon by using Schlenk and vacuum techniques. All solvents were purified by standard methods and distilled prior to use. ¹H and ¹³C NMR spectra were recorded on Bruker DPX 200, Bruker DPX 400 and Bruker AV 600 devices. The chemical shifts are given in ppm relative to TMS. The spin coupling patterns are indicated as s (singlet), d (doublet), m (multiplet), sept (septet) and br (broad, for unresolved signals). Elemental analyses (C, H, N) and IR-spectroscopy analysis were performed on a Elementar Vario EL elemental analyzer and on a Bruker Vertex 70 ATR. ESI-MS in Methanol and EI-MS spectra were recorded on a thermoquest MAT 95 XLT and a Finnigan MAT 90 device. Potassium bis(trimethylsilyl)amide, perchloric acid and tetrafluoroboric acid was received from Aldrich and Merck. The tetrachlorocyclopropene was prepared according to literature procedures.¹

¹(a) Tobey, S. W.; West, R. *J. Am. Chem. Soc.* **1966**, *88*, 2478-2481. (b) Tobey, S. W.; West, R. *J. Am. Chem. Soc.* **1966**, *88*, 2481-2488. (c) West, R.; Sadô, A.; Tobey, S. W. *J. Am. Chem. Soc.* **1966**, *88*, 2488-2494. (d) Weber, W.; De Meijere, A. *Chem. Ber.* **1985**, *118*, 2450-2471. (e) Glück, C.; Poignee, V.; Schwager, H. *Synthesis*, **1987**, *3*, 260-262

Preparation of the Compounds

Bis[bis(*R*-1-phenylethyl)amino]cyclopropenylium-perchlorate, (1)ClO₄

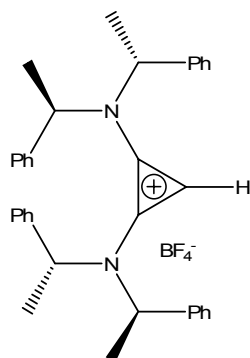


At room temperature (+)-Bis[*R*]-1-phenylethylamine (0.044 mol, 10 g) was added to a stirred solution of tetrachlorocyclopropene (0.01 mol, 1.8 g) in CH₂Cl₂ (60 ml). After 24 hours, perchloric acid (70 % in water, 0.13 ml) was added to the yellow solution at room temperature, and the reaction mixture was subsequently stirred for 8 hours at room temperature. After the addition of triphenylphosphine (0.0115 mol, 3.00 g), water (150 ml) was immediately added to the solution, and the mixture was stirred overnight. The organic layer was separated, washed

with water, dried over MgSO₄ and concentrated under vacuum. The crude oily product was recrystallized at -26°C from CH₂Cl₂/Et₂O/pentane (1/3/1) affording (1)ClO₄ as a white solid.

Yield: 2.92 g, 50%. ¹H NMR (400 MHz, CDCl₃): δ = 1.71 (d, *J* = 7.1, 6H, CH₃CH), 1.77 (d, *J* = 7.1, 6H, CH₃CH), 4.67 (dq, *J* = 7.1, 4H, NCH), 6.72 (m, 4H, CH_{aryl}), 6.89 (m, 4H, CH_{aryl}), 7.10-7.21 (m, 12H, CH_{aryl}), 7.37 (s, 1H, CH_{ring}); ¹³C NMR (100 MHz, CDCl₃): δ = 18.64 (CH₃CH), 18.76 (CH₃CH), 60.11 (NCH) 60.57 (NCH), 102.64 (CH_{ring}), 127.14 (CH_{aryl}), 127.75 (CH_{aryl}), 128.71 (CH_{aryl}), 128.89 (C_{aryl}), 128.95 (CH_{aryl}), 129.05 (CH_{aryl}), 135.38 (C_{ring}), 136.89 (C_{aryl}), 137.27 (C_{aryl}); elemental analysis: theoretical: N 4.78, C 71.82, H 6.37, found: N 4.76, C 71.64, H 6.33; MS (ESI), *m/z* (%): 485,4 (100, [C₃₅H₃₇N₂⁺]), 486,4 (41), 487,4 (10); IR (ATR) cm⁻¹: 1556 (vs, C-N stretching), 1867 (m, ring deformation).

Bis[bis(*R*-1-phenylethyl)amino]cyclopropenylium-tetrafluoroborate, (1)BF₄

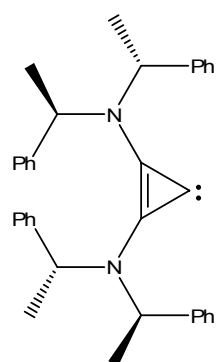


The procedure is analogous to the preparation of (1)ClO₄: (+)-Bis[*R*]-1-phenylethylamine (0.044 mol, 10 g) tetrachlorocyclopropene (0.01 mol, 1.8 g), tetrafluoroboric acid solution (50 wt. % in water, 1.37 ml, 0.879 g) triphenylphosphine (0.0115 mol, 3 g). The resulting product was a white solid of (1)BF₄. Yield: 5.2 g, 90%. ¹H NMR (200 MHz, CDCl₃): δ = 1.82 (d, *J* = 7.1, 6H, CH₃CH), 1.88 (d, *J* = 7.1, 6H, CH₃CH), 4.84 (dq, *J* = 7.1, 4H, NCH), 6.83 (m, 4H, CH_{aryl}), 7.00 (m,

4H, CH_{aryl}), 7.22-7.33(m, 12H, CH_{aryl}), 7.51 (s, 1H, CH_{ring}); ¹³C NMR (50 MHz, CDCl₃): δ = 18.61 (CH₃CH), 60.04 (NCH), 60.55 (NCH), 102.78 (CH_{ring}), 127.14 (CH_{aryl}), 127.75

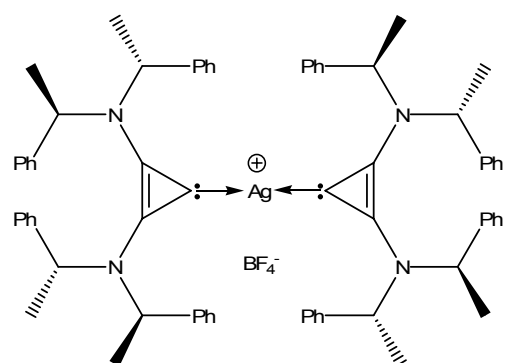
(CH_{aryl}), 128.68 (CH_{aryl}), 128.93 (C_{aryl}), 129.03 (CH_{aryl}), 135.44 (C_{ring}), 136.92 (C_{aryl}), 137.30 (C_{aryl}); IR (ATR) cm^{-1} : 1556 (vs, C-N stretching), 1867 (m, ring deformation); elemental analysis: theoretical: N 4.89, C 73.42, H 6.51, found: N 4.63, C 72.69, H 6.52;

Bis[bis(*R*-1-phenylethyl)amino]cyclopropenylidene (**2**)



A mixture of (**1**) BF_4 (1.4 mmol, 800 mg) and potassium bis(trimethylsilyl)amide (1.4 mmol, 280 mg) was cooled to -90°C , and pre-cooled (-60°C) Et_2O was added. The suspension was stirred for 30 min at -85°C and subsequently allowed to warm up to ambient temperature over a period of 3 hours. After evaporation of the solvent under vacuum, hexane (30 ml) was added, and the suspension was stirred for 15 min. After filtration of the suspension, the orange solution was left in a refrigerator at -35°C overnight to obtain an amber colored powder. The solid was isolated by decantation of the mother liquor and dried under vacuum. Crystals were obtained from hexamethyldisiloxane solution at 1°C . Yield: 670 mg, 60%. ^1H NMR (400 MHz, THF-d_8): δ = 1.68 (d, J = 6.7, 12H, CH_3CH), 4.62 (q, J = 7.05, 4H, NCH), 6.94-6.99 (m, 12H, CH_{aryl}), 7.05-7.08 (m, 8H, CH_{aryl}); ^{13}C NMR (100 MHz, THF): δ = 19.96 (CH_3CH), 59.84 (NCH), 127.52 (CH_{aryl}), 128.56 (CH_{aryl}), 128.73 (CH_{aryl}), 142.93 (C_{aryl}), 160.77 (C_{ring}), 188.20 ($\text{C}_{\text{carbene}}$); elemental analysis: theoretical: N 5.78, C 86.73, H 7.49, found: N 5.49, C 85.99, H 7.73; MS (EI), m/z (%): 105 (100, [C_8H_9^+]), 379 (4, [$\text{C}_{27}\text{H}_{27}\text{N}_2^+$]), 484 (2, [M^+]), IR (ATR) cm^{-1} : 1431 (vs, C-N stretching), 1821 (m, ring deformation).

Biscyclopropenylidene-silver(I) complex [(**2**) $_2\text{Ag}$] BF_4 (**3**)

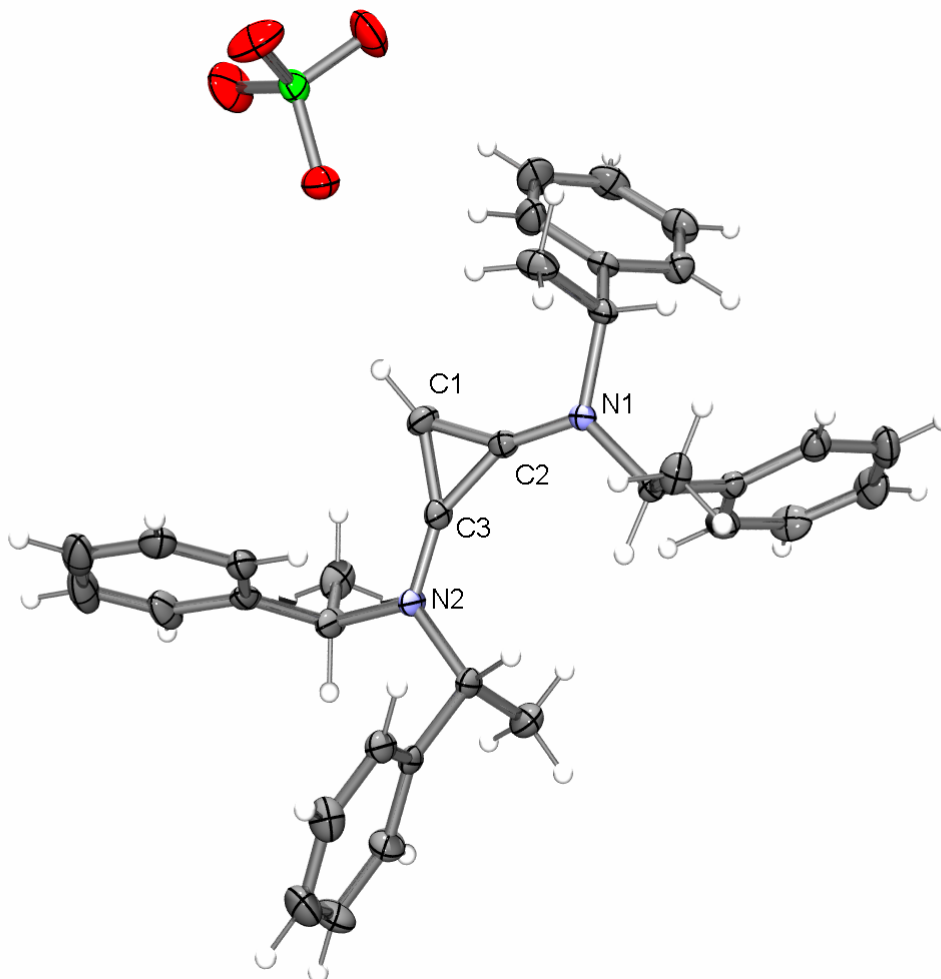


At room temperature, Ag_2O (0.55 mmol, 130 mg), (**1**) BF_4 (1.1 mmol, 640 mg) and a catalytic amount of Me_4BF_4 was added to a stirred solution of CH_2Cl_2 (40 ml). Subsequently, the flask was kept in the dark. After 30 min 1 M NaOH aqueous solution (40 ml) was added to this suspension. The mixture was stirred for 24 hours at room temperature. The organic layer was separated and the aqueous layer washed with CH_2Cl_2 . The organic layers were

combined and dried over MgSO_4 . After concentration under vacuum, a pale yellow solid was obtained. The crude product was precipitated at -26°C from $\text{CH}_2\text{Cl}_2/\text{pentane}$. Crystals were obtained from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}/\text{pentane}$ (1/2/5) at 1°C . ^1H NMR (600 MHz, CDCl_3): $\delta = 1.72$ (broad s, 12H, CH_3CH), $\delta = 1.85$ (broad s, 12H, CH_3CH), 4.61 (broad s, 4H, NCH), 4.91 (broad s, 4H, NCH), 6.74 (broad s, 8H, CH_{aryl}), 7.06-7.11 (broad s, 32H, CH_{aryl}); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 18.94$ (CH_3CH), 19.91 (CH_3CH), 58.45 (NCH), 127.31 (CH_{aryl}), 127.75 (CH_{aryl}), 128.45 (CH_{aryl}), 138.10 (C_{aryl}), 140.12 (C_{aryl}), 146.2 (d, C_{ring}), 150.77 (C_{ring}); elemental analysis: theoretical: N 4.81, C 72.23, H 6.23, found: N 4.62, C 71.24, H 6.73; MS (ESI), m/z (%): 1077.5 (100, $[\text{C}_{70}\text{H}_{72}\text{N}_4\text{Ag}^+]$), 1077.5 (85), 1078.5 (65), 1076.5 (65), 1079.5 (25), 1080.5 (10); IR (ATR) cm^{-1} : 1491 (vs, C-N stretching), 1835 (m, ring deformation)

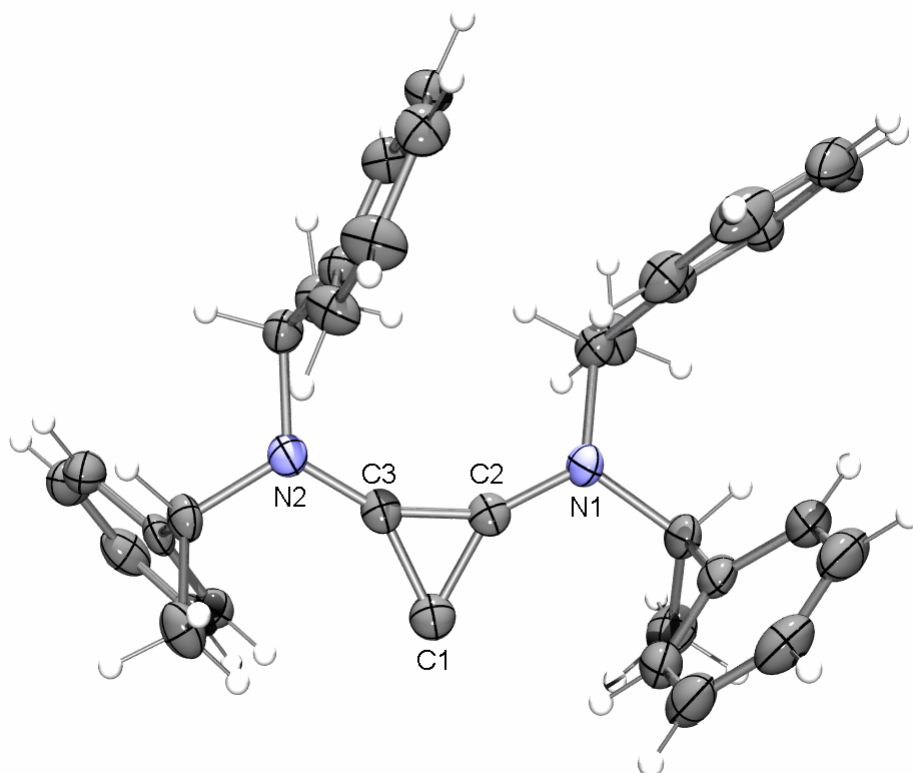
X-ray structures

ORTEP diagram of bis[bis(*R*-1-phenylethyl)amino]cyclopropenylium-perchlorate, (1)ClO₄, with thermal displacement parameters drawn at 50% probability.



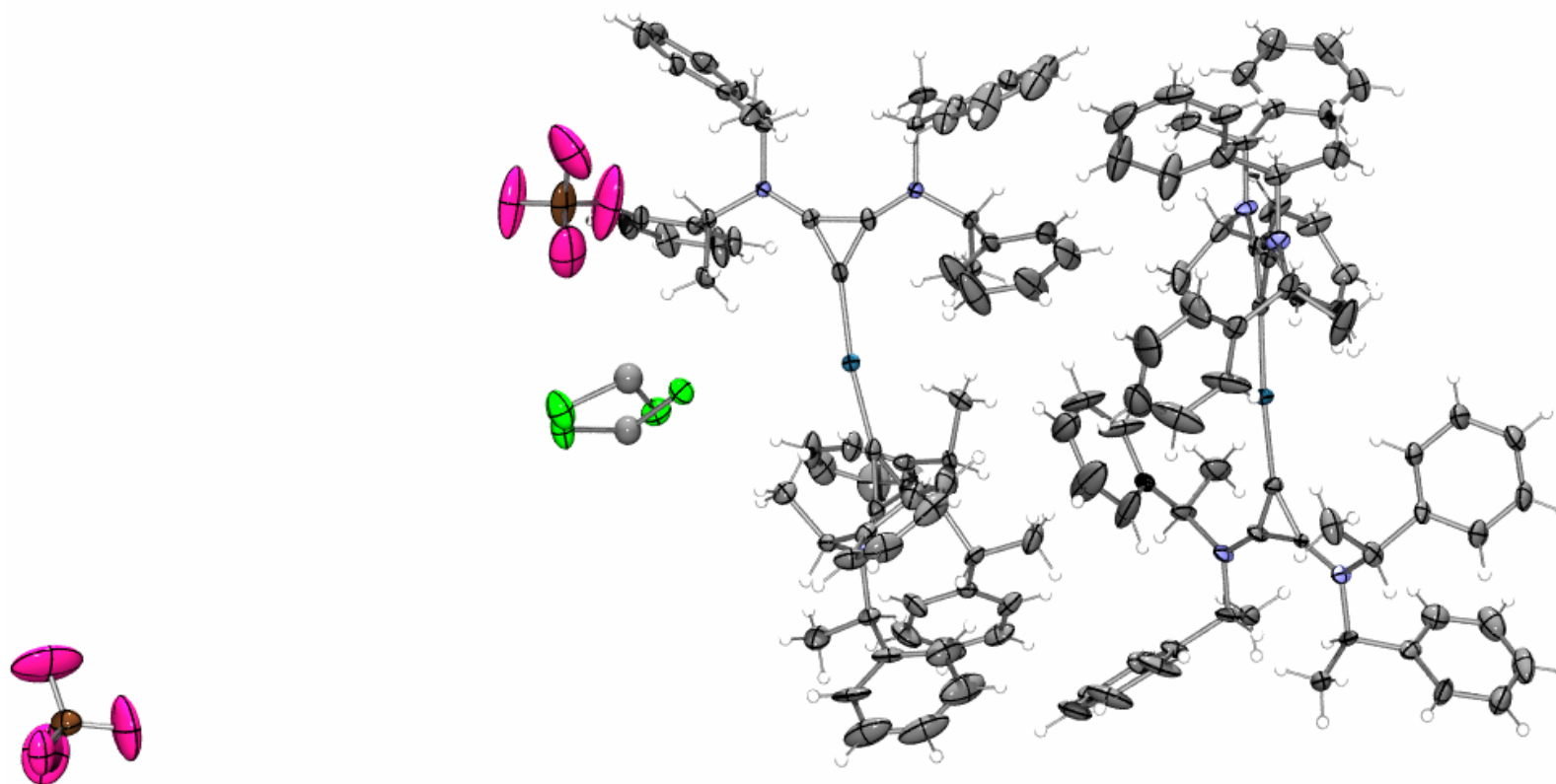
Selected bond lengths [Å] and angles [°]: C1-C2 1.369(3), C1-C3 1.355(3), C2-C3 1.421(2), C2-N1 1.313(2), C3-N2 1.305(2); C2-C1-C3 62.9(14); C1-C2-C3 58.06(13), C1-C3-C2 59.04(13).

ORTEP diagram of Bis[bis(*R*-1-phenylethyl)amino]cyclopropenyldiene (2) with thermal displacement parameters drawn at 50% probability.

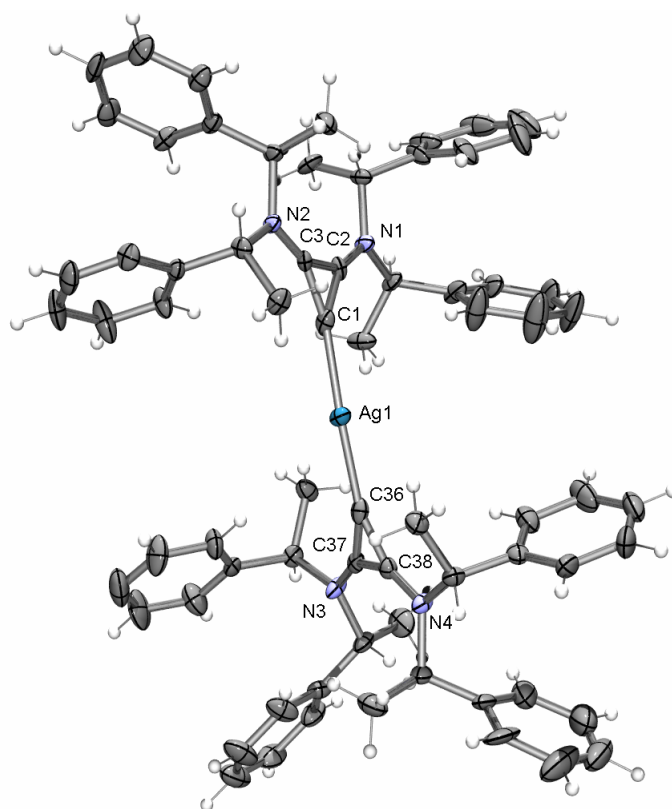


Selected bond lengths [Å] and angles [°]: C1-C2 1.404(4), C1-C3 1.400(4), C2-C3 1.357(3), C2-N1 1.342(3), C3-N2 1.346(3); C2-C1-C3 57.89(18); C1-C2-C3 60.90(19), C1-C3-C2 61.21(18).

ORTEP diagram of $[(2)_2Ag]BF_4 \cdot 0.5CH_2Cl_2$ with thermal displacement parameters drawn at 50% probability.

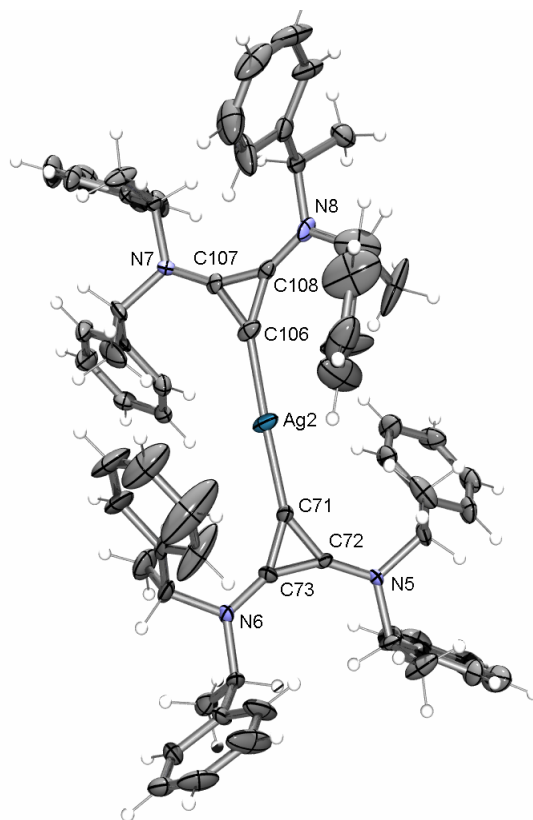


ORTEP diagram of one of the two independent cations in $[(2)_2\text{Ag}]\text{BF}_4 \cdot 0.5\text{CH}_2\text{Cl}_2$ with thermal displacement parameters drawn at 50% probability.



Selected bond lengths [\AA] and angles [$^\circ$]: Ag1-C1 2.060(6), Ag1-C36 2.063(6), C1-Ag1-C36 172.1(2), C1-C2 1.400(8), C1-C3 1.403(8), C2-C3 1.387(7), C2-N1 1.329(7), C3-N2 1.328(7); C2-C1-C3 59.3(4); C1-C2-C3 60.40(4), C1-C3-C2 60.2(4), C36-C37 1.393(8), C36-C38 1.400(8), C37-C38 1.379(8), C37-N3 1.330(7), C38-N4 1.331(7); C37-C36-C38 59.1(4); C36-C37-C38 60.70(4), C36-C38-C37 60.2(4).

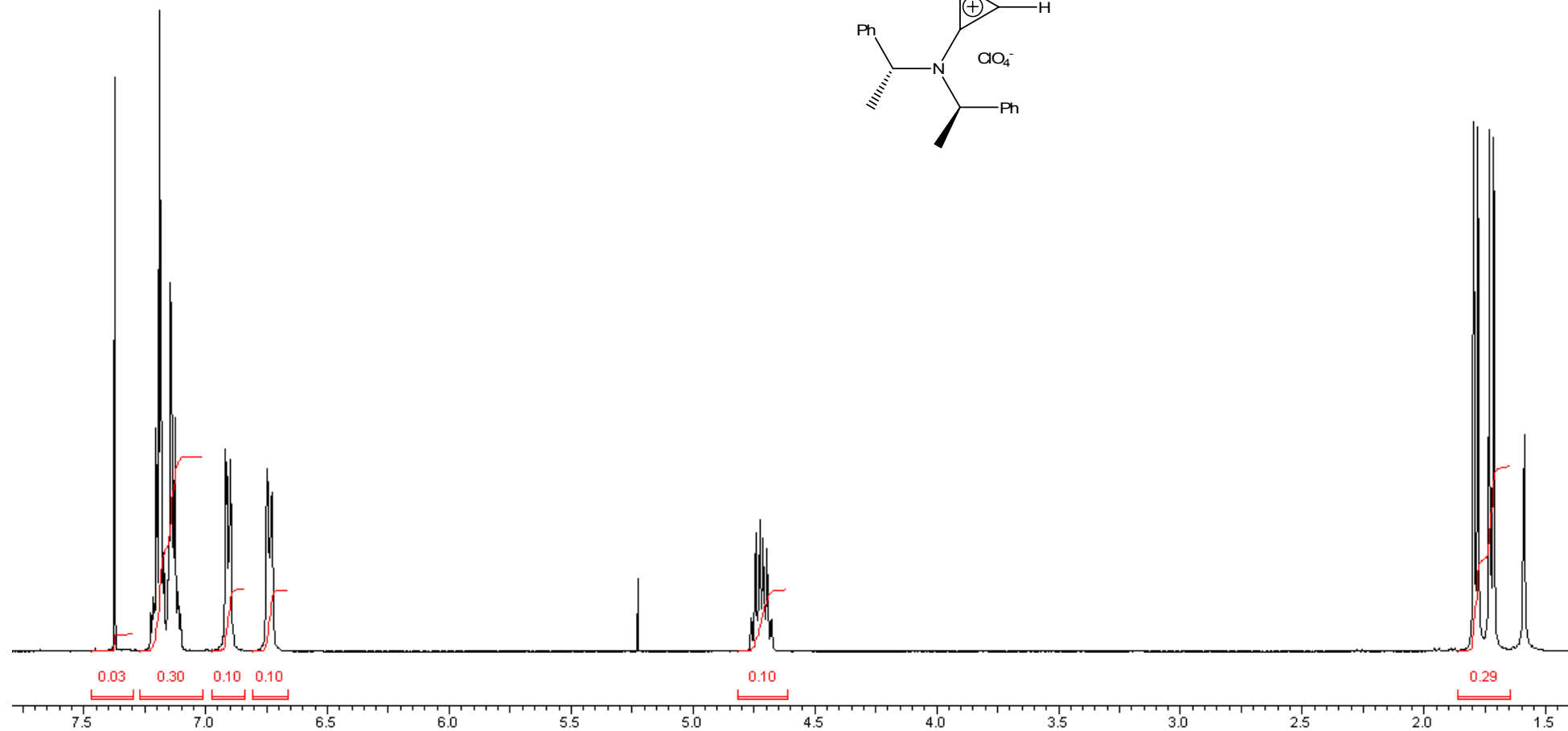
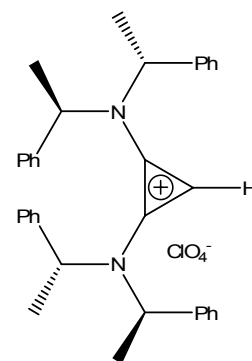
ORTEP diagram of one of the two independent cations in $[(2)_2\text{Ag}]\text{BF}_4 \cdot 0.5\text{CH}_2\text{Cl}_2$ with thermal displacement parameters drawn at 50% probability.



Selected bond lengths [Å] and angles [°]: Ag2-C106 2.072(6), Ag2-C71 2.069(6), C71-Ag2-C106 175.4(2), C71-C72 1.395(8), C71-C73 1.384(8), C72-C73 1.374(8), C72-N5 1.326(7), C73-N6 1.324(7); C72-C71-C73 59.3(4); C71-C72-C73 60.0(4), C71-C73-C72 60.8(4), C106-C107 1.378(8), C106-C108 1.393(9), C107-C108 1.362(8), C107-N7 1.342(7), C108-N8 1.330(7); C107-C106-C108 58.9(4); C106-C107-C108 61.10(4), C106-C108-C107 60.0(4).

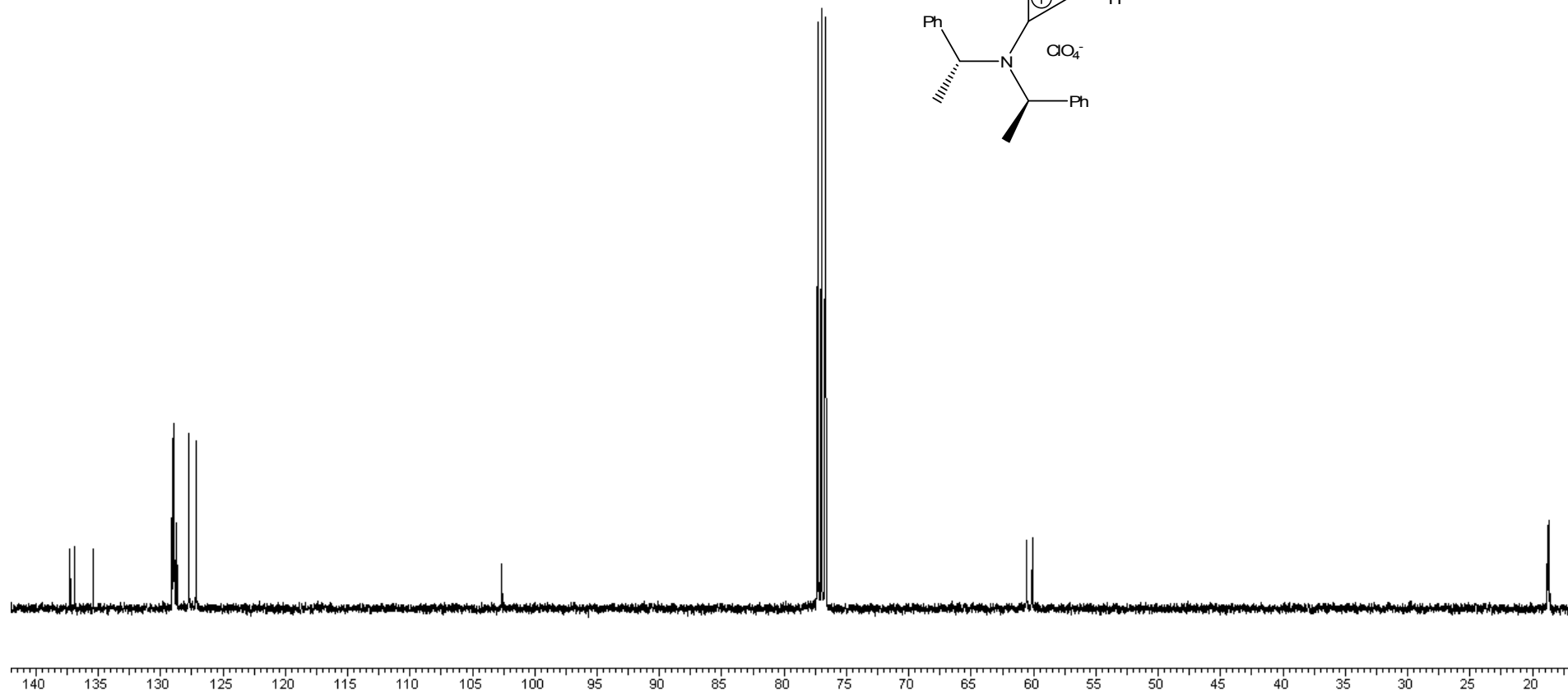
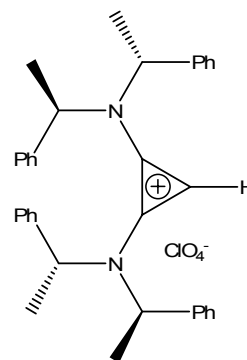
Bis[bis(*R*-1-phenylethyl)amino]cyclopropenylium-perchlorate, (1)ClO₄

¹H NMR



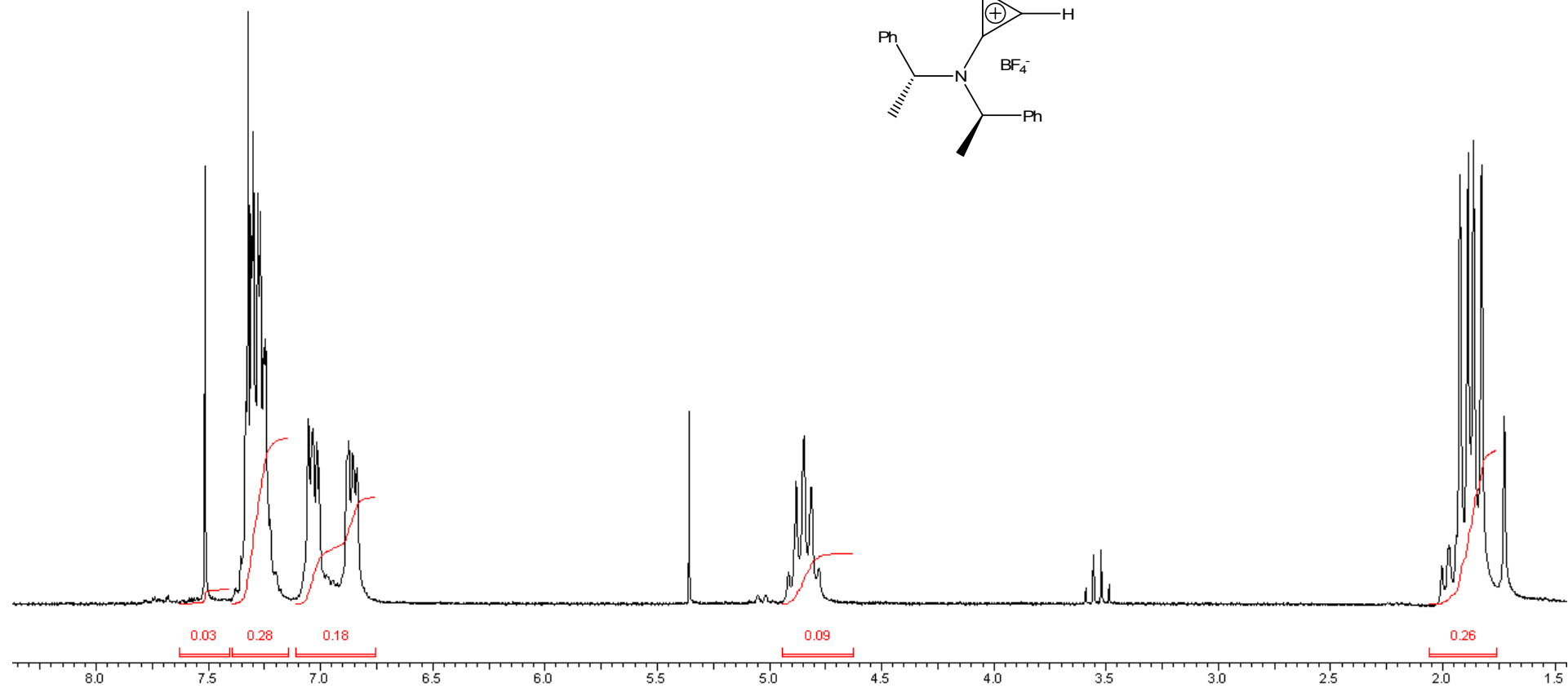
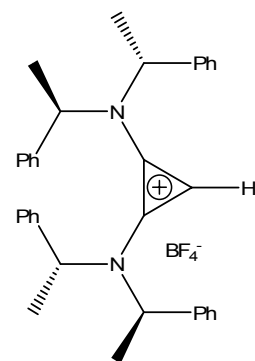
Bis[bis(*R*-1-phenylethyl)amino]cyclopropenylium-perchlorate, (1)ClO₄

¹³C NMR



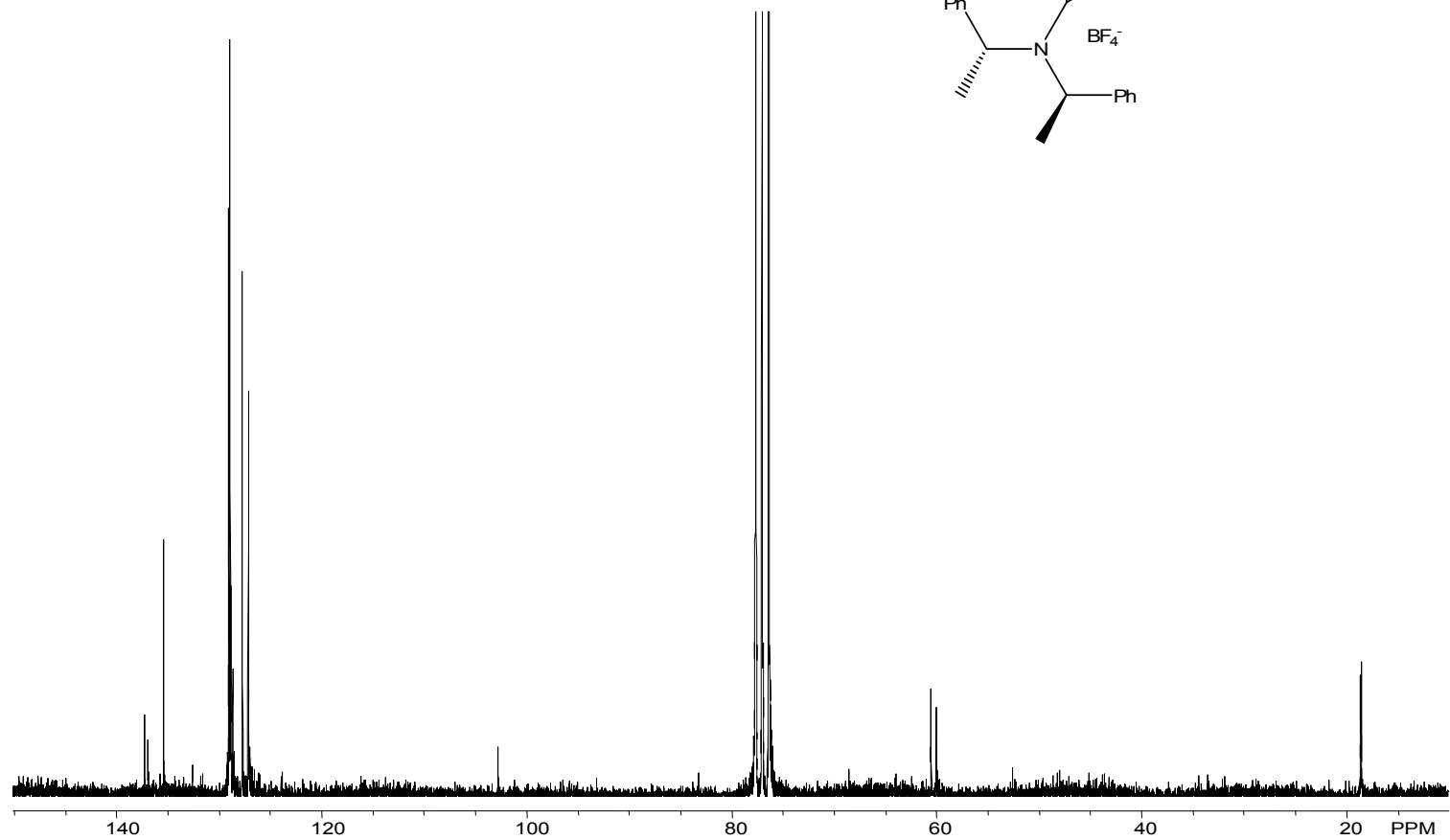
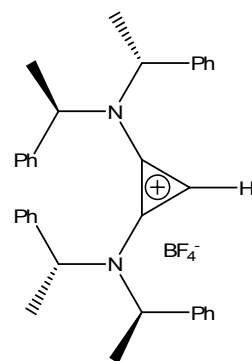
Bis[bis(*R*-1-phenylethyl)amino]cyclopropenylum-tetrafluoroborate, (1)BF₄

¹H NMR



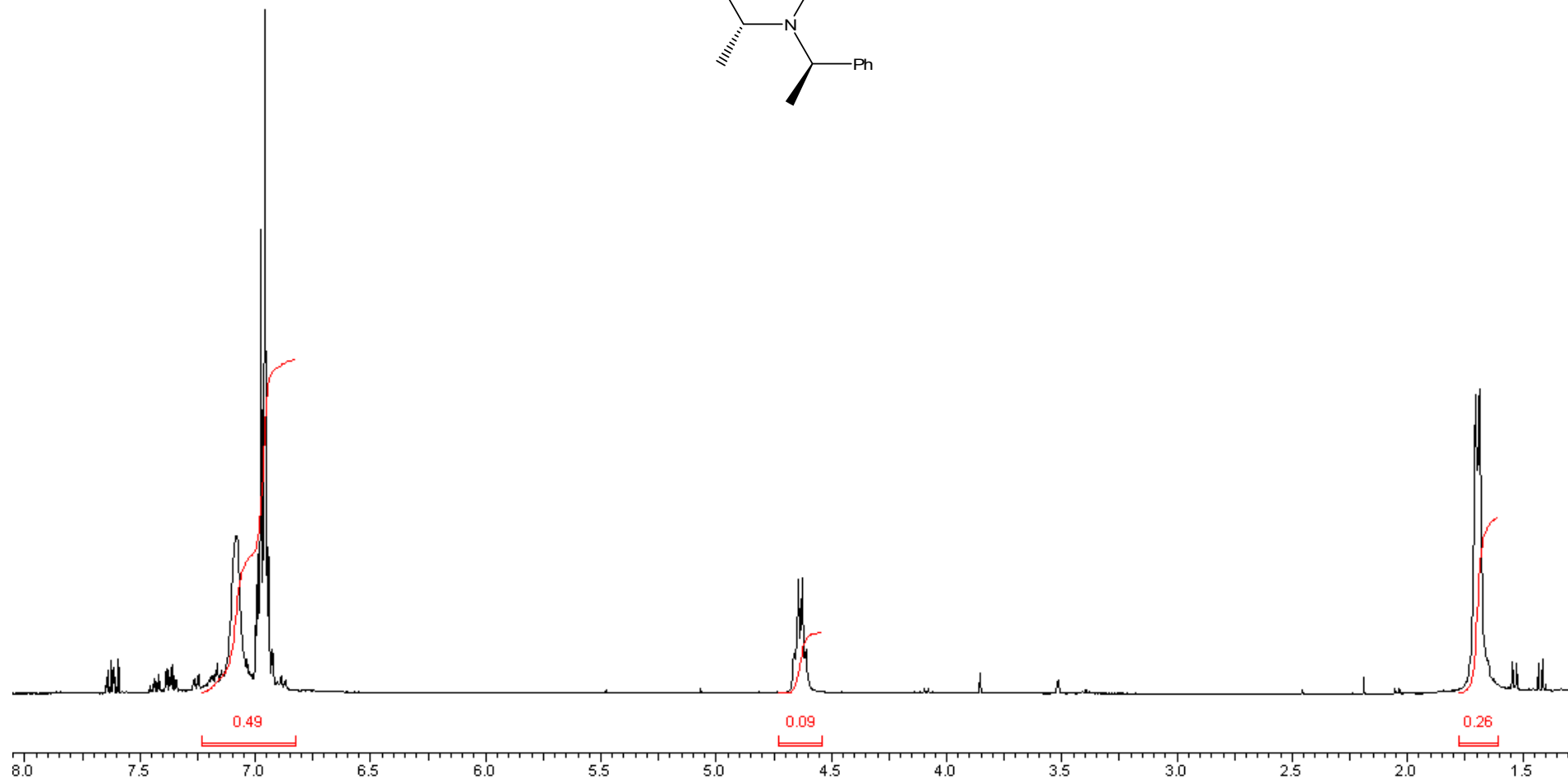
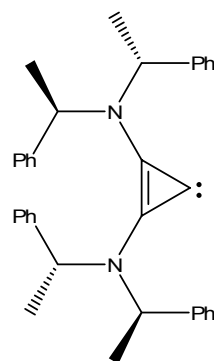
Bis[bis(*R*-1-phenylethyl)amino]cyclopropenylium-tetrafluoroborate, (1)BF₄

¹³C NMR



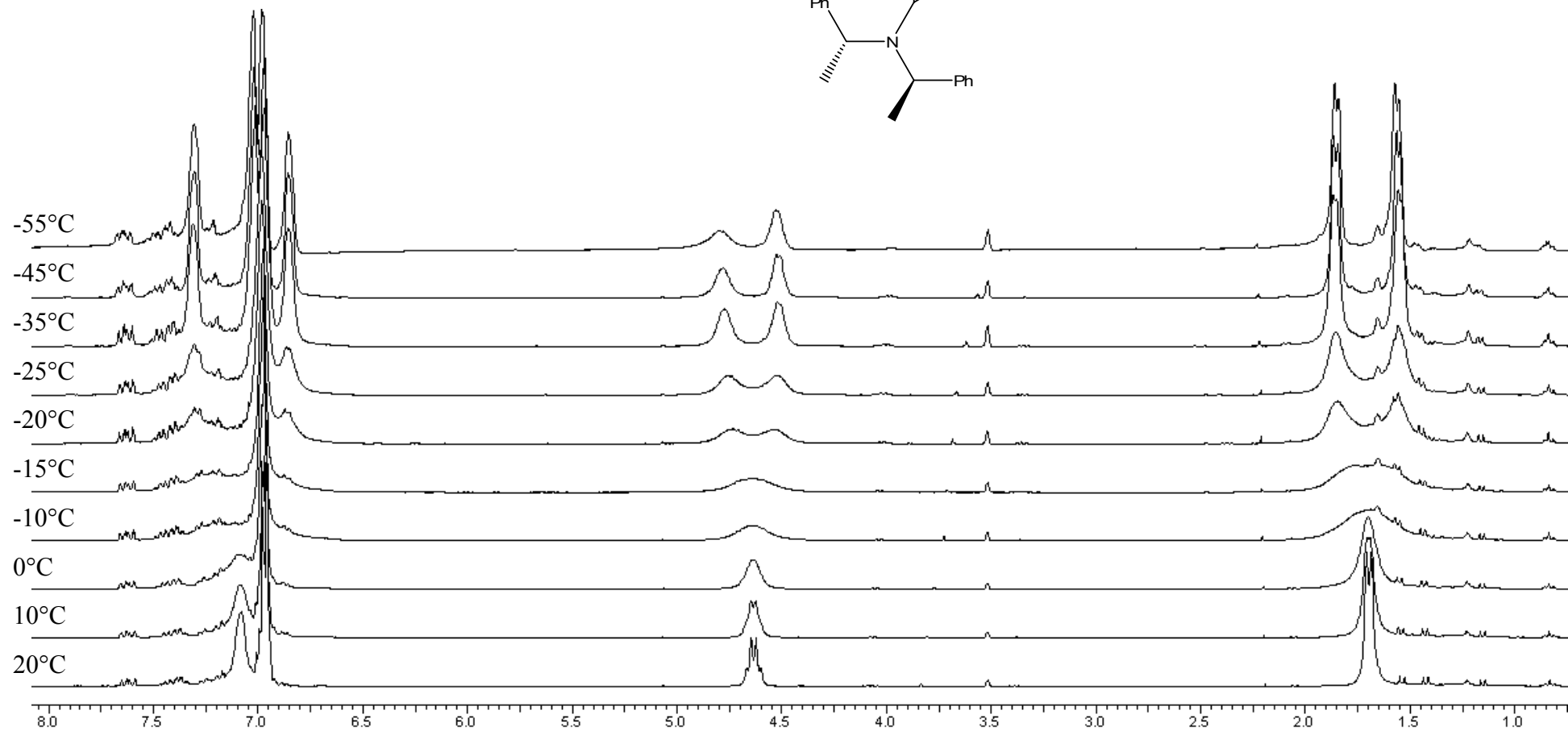
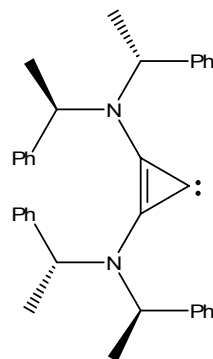
Bis[bis(*R*-1-phenylethyl)amino]cyclopropenyliene (2)

¹H NMR



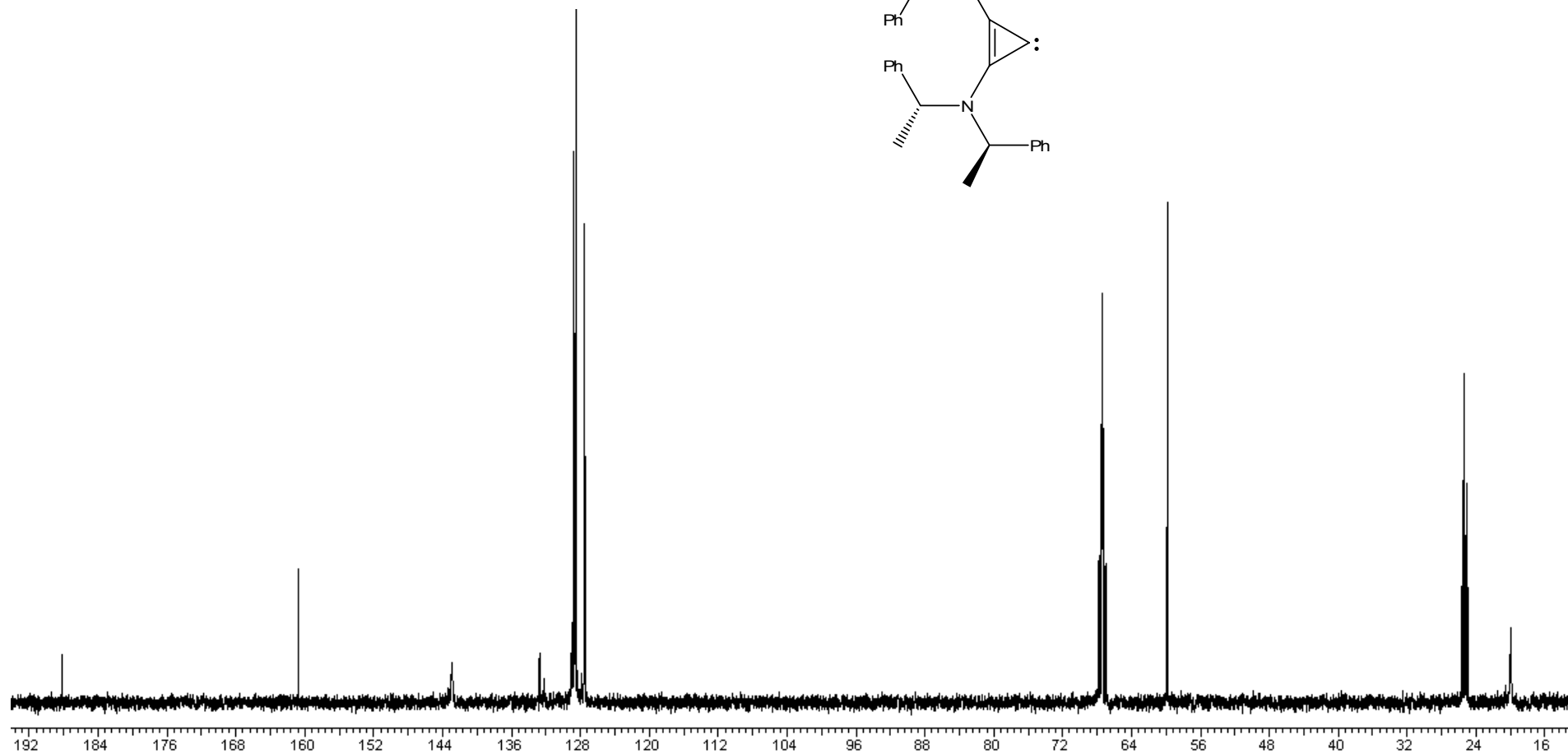
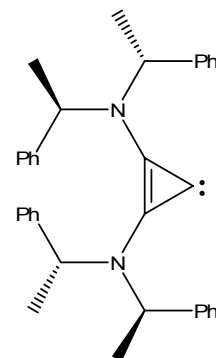
Bis[bis(*R*-1-phenylethyl)amino]cyclopropenyliene (2)

Variable-temperature ^1H NMR study



Bis[bis(*R*-1-phenylethyl)amino]cyclopropenyliene (2)

^{13}C NMR



[(2)₂Ag]BF₄ (3)

¹³C NMR

