Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Frustrated N-heterocyclic carbene-silylium ion Lewis pairs

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1. Experimental Details

Materials and Methods

All operations with air- and moisture-sensitive compounds were performed in a glove box under a dry argon atmosphere (MBraun 200B) or on a high vacuum line using Schlenk techniques. All solvents were distilled from Na/benzophenone or CaH_2, degassed, and stored over molecular sieves (4 Å). The ^{1}H, ^{13}C, ^{29}Si, ^{31}P and ^{19}F NMR spectra were recorded on Bruker DPX 200, Bruker AV 300 and Bruker DRX 400 spectrometers. Tetramethylsilane (TMS) was used as internal standard for ^{1}H, ^{13}C and ^{29}Si. Trichlorofluoromethane ($CFCl_3$) was used as external reference for ^{19}F. H_3PO_4 was used as external reference for ^{31}P. Chemical shifts are reported in ppm (parts per million). Coupling constants (J) are reported in Hertz (Hz), and splitting patterns are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), sept (septet) and br (broad). Elemental analysis was carried out with a Vario Micro Cube System. A Bruker Vertex 70 spectrometer was used for recording the IR spectra. Unless otherwise indicated, all starting materials were obtained from Sigma-Aldrich, ABCR, TCI, Acros or Fluka and were purified if necessary. 1,3-Di-*tert*-butyl-4,5-dimethylimidazolin-2-ylidene[1] (**1b**) trimethylsilyltriflimide,[2] diphenylbutadiyne,[3] $(PPh_3)AuCl$[4] were prepared according to literature procedures. The compounds [(**1b**)$SiMe_3$]X (X = I, OTf, NTf_2) were prepared in Teflon® vials (Figure 1). NMR spectra of [(**1b**)$SiMe_3$]X (X = OTf, NTf_2) were recorded using FEP inserts (WILMAD, 6005-7, O.D. 5 mm).

Figure 1: Teflon vials used for preparation of [(**1b**)$SiMe_3$]X (X = I, OTf, NTf2).

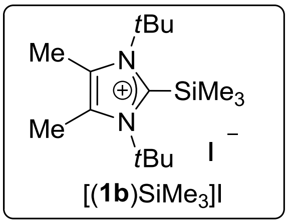
[1] A. A. Grishina, S. M. Polyakova, R. A. Kunetskiy, I. Císařová and I. M. Lyapkalo, *Chem. Eur. J.,* 2011, **17**, 96-100.

[2] B. Mathieu and L. Ghosez, *Tetrahedron*, 2002, **58**, 8219–8226.

[3] a) H. Taniguchi, I. M. Mathai and S. I. Miller, *Org. Synth.*, 1970, **50**, 97-100; b) M. F. Habibi and R. E. Benson, *Org. Synth.*, 1988, **6**, 925-928.

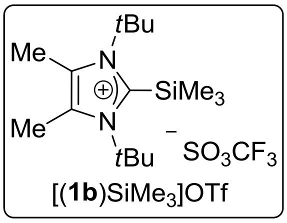
[4] M. I. Bruce, B. K. Nicholson, O. Bin Shawkataly, *Inorg. Synth.* 1989, **26**, 324-328.

Synthesis:



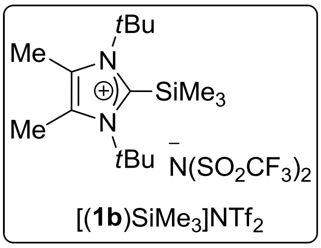
[(**1b**)SiMe$_3$]I

Preparation of [(1b)SiMe$_3$]I: The liquid carbene **1b** (200 mg; 1.0 mmol) was treated with 200 mg (1.0 mmol) Me_3SiI, whereupon the mixture immediately solidified. The yellowish solid was ground in a Teflon® vial to complete the reaction and the product was washed with cold hexane and dried; the yield was quantitative. It is not soluble in common deuterated solvents and decomposed in CD_2Cl_2 **Elemental analysis** (%) calcd for $C_{16}H_{33}IN_2Si$ (408.4 g/mol): C 47.05, H 8.14 found C 47.92, H 8.23.



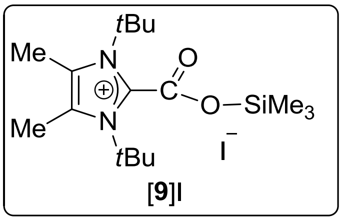
[(**1b**)SiMe$_3$]OTf

Preparation of [(1b)SiMe$_3$]OTf: The liquid carbene **1b** (200 mg; 1.0 mmol) was treated with 214 mg (1.0 mmol) Me_3SiOTf, whereupon the mixture immediately solidified. The colorless solid was ground in a Teflon® vial to complete the reaction and the product was washed with cold hexane and dried; the yield was quantitative. The NMR of [(**1b**)$SiMe_3$]OTf in C_6D_5Br solution showed the free carbene **1b** together with Me_3SiOTf. **Elemental analysis** (%) calcd for $C_{17}H_{33}F_3N_2O_3SSi$ (430.3 g/mol): C 47.42, H 7.72, N 6.51 found C 47.65, H 7.58, N 7.03. **^{1}H NMR** (300 MHz, C_6D_5Br): δ/ppm 0.20 (s, 9H, SiC*H*$_3$), 1.55 (s, 18H, C*H*$_3$), 2.09 (s, 6H, C*H*$_3$); **^{13}C NMR** (75 MHz, C_6D_5Br): δ/ppm -0.3 (Si(*C*H$_3$)$_3$), 12.6 (*C*H$_3$), 31.5 (C(*C*H$_3$)), 56.3 (*C*(CH$_3$)$_3$), 123.6 (*C*=*C*), 210.5 (N$_2$*C*); **^{19}F NMR** (188 MHz, C_6D_5Br): δ/ppm -78.2 (s, 3F).



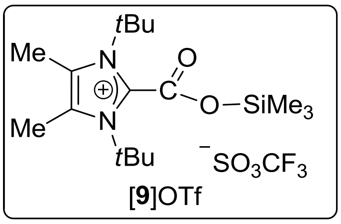
[(**1b**)SiMe$_3$]NTf$_2$

Preparation of [(1b)SiMe$_3$]NTf$_2$: The liquid carbene **1b** (150 mg; 0.7 mmol) was treated with 254 mg (0.7 mmol) Me_3SiNTF_2, whereupon the mixture immediately solidified. The colorless solid was ground in a Teflon® vial to complete the reaction and the product [(**1b**)$SiMe_3$]NTf_2 was washed with cold hexane and dried; the yield was quantitative. Suitable crystals for X-ray diffraction analysis could be obtained from a C_6D_5Br solution at room temperature. **Elemental analysis** (%) calcd for $C_{18}H_{33}F_6N_3O_4S_2Si$ (561.7 g/mol): C 38.49, H 5.92, N 7.48, found C 38.49, H 6.05, N 8.66. **^{1}H NMR** (300 MHz, C_6D_5Br): δ/ppm 0.22 (s, 9H, SiC*H*$_3$), 1.35 (s, 18H, C*H*$_3$), 1.99 (s, 6H, C*H*$_3$); **^{13}C NMR** (75 MHz, C_6D_5Br): δ/ppm 5.3 (Si(*C*H$_3$)$_3$), 12.6 (*C*H$_3$), 30.8 (C(*C*H$_3$)), 64.7 (*C*(CH$_3$)$_3$), 120.3 (q, $^1J_{CF}$ = 322 Hz, CF$_3$), 128.4 (*C*=*C*), 155.9 (N$_2$*C*Si); **^{19}F NMR** (188 MHz, C_6D_5Br): δ/ppm -77.3 (s, 3F); **^{29}Si NMR** (79.5 MHz, C_6D_5Br): δ/ppm 4.50 (s, 1Si).



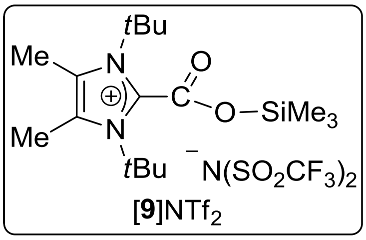
[**9**]I

Preparation of [9]I: A diethyl ether suspension with 589 mg (1.4 mmol) [(**1b**)$SiMe_3$]I was cooled to -78°C and purged with 1 bar of CO_2 for 2 min. After removal of the cooling bath the reaction was slowly warmed to room temperature in a closed system, whereupon a powdery colorless solid precipitated. The mixture was stirred under CO_2 atmosphere for further 3 h to complete the reaction. After removing of the solvent in vacuum the product [**9**]I was obtained as a colorless solid in 90% yield (589 mg). It is not soluble in toluene, is slightly soluble in THF and dissolves with decomposition in CH_2Cl_2. **Elemental analysis** (%) calcd for $C_{17}H_{33}IN_2O_2Si$ (452.4 g/mol): C 45.13, H 7.35 found C 45.43, H 7.45. **FT-IR:** $\tilde{\upsilon}$ = 1707, 1545, 1204 cm^{-1}. **^{1}H NMR** (200 MHz, CD_2Cl_2): δ/ppm 0.44 (s, 9H, $SiC\mathit{H}_3$), 1.77 (s, 18H, $C\mathit{H}_3$), 2.50 (s, 6H, $C\mathit{H}_3$); **^{13}C NMR** (75 MHz, CD_2Cl_2): δ/ppm 0.2 ($Si(\mathit{C}H_3)_3$), 14.6 ($\mathit{C}H_3$), 30.7 ($C(\mathit{C}H_3)$), 65.9 ($\mathit{C}(CH_3)_3$), 129.4 (C=C), 158.9 ($C\mathit{C}O_2$).



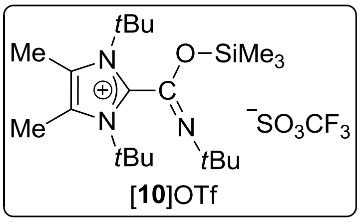
[**9**]OTf

Preparation of [9]OTf: The liquid carbene **1b** (214 mg; 1.0 mmol) was treated with 229 mg (1.0 mmol) Me_3SiOTf; the mixture immediately solidified. The solid was suspended in 3 ml diethyl ether and purged with 1 bar CO_2 for 1 min at room temperature, whereby a voluminous colorless precipitate formed. The mixture was stirred under CO_2 atmosphere for additional 2 h. After removing the solvent in vacuum the expected product [**9**]OTf was isolated as a colorless solid in 92% yield (451mg). It is soluble in THF and dissolves with decomposition in CH_2Cl_2. Crystals suitable for X-ray diffraction analysis were grown from a THF solution at -30°C. **Elemental analysis** (%) calcd for $C_{18}H_{33}F_3N_2O_5SSi$ (474.6) C 45.55, H 7.01 found C 45.28, H 7.01. **FT-IR:** $\tilde{\upsilon}$ = 1761, 1543, 1026 cm^{-1}. **^{1}H NMR** (300 MHz, CD_2Cl_2): δ/ppm 0.47 (s, 9H, $SiC\mathit{H}_3$), 1.78 (s, 18H, $C\mathit{H}_3$), 2.49 (s, 6H, $C\mathit{H}_3$); **^{13}C NMR** (75 MHz, CD_2Cl_2): δ/ppm -0.6 ($Si(\mathit{C}H_3)_3$), 14.3 ($\mathit{C}H_3$), 30.7 ($C(\mathit{C}H_3)$), 66.2 ($\mathit{C}(CH_3)_3$), 129.8 (C=C), 158.9 ($C\mathit{C}O_2$); **^{19}F NMR** (188 MHz, CD_2Cl_2): δ/ppm -78.8 ($SO_3C\mathit{F}_3$).



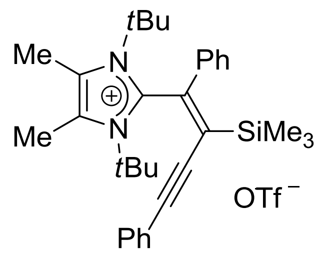
[**9**]NTf_2

Preparation of [9]NTf_2: The liquid carbene **1b** (292 mg; 1.4 mmol) was treated with 496 mg (1.4 mmol) Me_3SiNTf_2; the mixture immediately solidified. The colorless solid was suspended in 7 ml diethyl ether and cooled to -78 °C. The suspension was purged with 1 bar CO_2 for 2 min and the voluminous precipitate was immediately filtered at -78 °C through a tempered frit. The remaining solid was dried in vacuum to yield a 1.6 to 1 mixture of [**9**]NTf_2 and imidazolium trifilimidate, which decomposes at room temperature within a few days. [**9**]NTf_2: **^{1}H NMR** (300 MHz, CD_2Cl_2): δ/ppm 0.64 (s, 9H, SiCH_3), 1.79 (s, 18H, CH_3), 2.46 (s, 6H, CH_3); **^{13}C NMR** (75 MHz, CD_2Cl_2): δ/ppm 6.1 ($Si(CH_3)_3$), 13.5 (CH_3), 31.7 ($C(CH_3)$), 65.7 ($C(CH_3)_3$), 120.3 (q, $^1J_{CF}$ = 322 Hz, CF_3), 129.5 ($C{=}C$), 157.1 (CCO_2); **^{19}F NMR** (188 MHz, CD_2Cl_2): δ/ppm -78.7 ($N(SO_2CF_3)_2$). Imidazolium trifilimidate: **^{1}H NMR** (300 MHz, CD_2Cl_2): δ/ppm 1.71 (s, 18H, CH_3), 2.42 (s, 6H, CH_3), 8.08 (s, 1H, CH); **^{13}C NMR** (75 MHz, CD_2Cl_2): δ/ppm 11.8 (CH_3), 29.5 ($C(CH_3)$), 61.7 ($C(CH_3)_3$), 120.3 (q, $^1J_{CF}$ = 322 Hz, CF_3), 129.6 ($C{=}C$), 135.3 (N_2C); **^{19}F NMR** (188 MHz, CD_2Cl_2): δ/ppm -78.7 (SO_3CF_3).



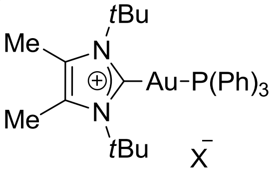
[**10**]OTf

Preparation of [10]OTf: The liquid carbene **1b** (150 mg; 0.7 mmol) was treated with 160 mg (0.7 mmol) Me_3SiOTf; the mixture immediately solidified. The solid was suspended in 5 ml diethyl ether, and 0.7 mmol (71 mg) of *tert*-butylisocyanate were added at room temperature, whereby an immediate reaction was observed. To complete the reaction, the mixture was stirred for further 16 h at room temperature. After removal of the solvent in vacuum 300 mg (yield = 79%) of the expected product [**10**]OTf was obtained. Crystals suitable for X-ray diffraction analysis were obtained from a diethyl ether/CH_2Cl_2 solution at -30°C. **Elemental analysis** (%) calcd for $C_{22}H_{42}F_3N_3O_4SSi$ (529.73 g/mol): C 49.88, H 7.99, N 7.93 found C 50.39, H 8.10, N 8.07. **^{1}H NMR** (300 MHz, CD_2Cl_2): δ/ppm 0.22 (s, 9H, SiCH_3), 1.35 (s, 9H, NCH_3), 1.73 (s, 18H, CH_3), 2.42 (s, 6H, CH_3); **^{13}C NMR** (75 MHz, CD_2Cl_2): δ/ppm -4.1 ($Si(CH_3)_3$), 11.9 (CH_3), 29.6 ($C(CH_3)$), 32.0 (N*t*Bu), 54.6 ($NC(CH_3)_3$), 61.7 ($C(CH_3)_3$), 129.2 ($C{=}C$), the signal for the C_2 carbon atom was not observed; **^{19}F NMR** (188 MHz, CD_2Cl_2): δ/ppm -78.9 (SO_3CF_3).



[**11**]OTf

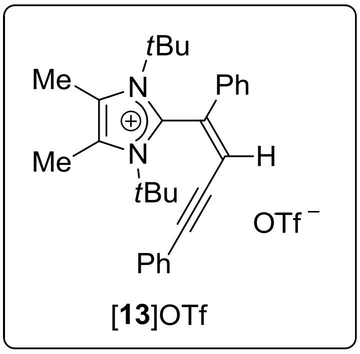
Preparation of [11]OTf: The liquid carbene **1b** (262 mg; 1.26 mmol) was treated with 279 mg (1.26 mmol) Me_3SiOTf; the mixture immediately solidified. The solid was dissolved in 8 ml chlorobenzene, and 255 mg (1.26 mmol) of 1,4-diphenylbutadiyne were added. the yellowish solution was stirred overnight at room temperature. After careful removal of the solvent, the remaining dark solid was washed 4 times with 4 ml of n-hexane and dried in vacuum; 407 mg (yield = 51%) of the 1,2-addition product [**11**]OTf were obtained. Crystals suitable for X-ray diffraction analysis were obtained either from a C_6D_5Br/*n*-hexane solution at room temperature or by diffusion of n-hexane into a THF solution at -30°C. **^{1}H NMR** (600 MHz, CD_2Cl_2): δ/ppm 0.42 (s, 9H, C*H*$_3$), 1.69 (s, 18H, C*H*$_3$), 2.62 (s, 6H, C*H*$_3$), 6.88 (m, 4H, ArH), 6.98 (m, 2H, *p*-ArH), 7.24 (m, 4H, ArH), 8.27 (s, 1H, C*H*); **^{13}C NMR** (150 MHz, CD_2Cl_2): δ/ppm -0.4 (TMS), 14.9 (*C*H$_3$), 31.2 (C(*C*H$_3$)), 66.1 (*C*(CH$_3$)$_3$), 91.9 (*C*≡C), 106.7 (*C*≡C), 106.7, 121.4 3 (q, $^1J_{CF}$ = 321 Hz, *C*F$_3$), 122.2, 128.9, 129.2, 129.3, 129.6, 129.9, 130.1, 130.8, 131.6, 132.7, 137.6, 139.4, 143.5, 146.3; **^{19}F NMR** (188 MHz, CD_2Cl_2): δ/ppm -77.8 (SO$_3$C*F*$_3$). **Elemental analysis (%)** calcd for $C_{33}H_{43}F_3N_2O_3SSi$ (632.3. g/mol): C 58.07, H 7.39, N 7.01 found C 58.06, H 7.26, N 7.53.



[**12**]**X**

Preparation of [12]OTf: The liquid carbene **1b** (38 mg; 0.19 mmol) was treated with 41 mg (0.19 mmol) Me_3SiOTf; the mixture immediately solidified. The solid dissolved in 5 ml C_6H_5Cl, and 92 mg (0.19 mmol) of $(PPh_3)AuCl$ were added at room temperature. The reaction was stirred for 1 h and treated with 5 ml *n*-hexane, whereby a precipitate formed. This was filtered off and dried in vacuum, whereby 127 mg (0.156 mmol, 84%) of the expected product [**12**]OTf were obtained as a voluminous colorless solid. Crystals suitable for X-ray diffraction analysis were obtained from a toluene/CH_2Cl_2 solution at -30°C. **Elemental analysis** (%) calcd for $C_{32}H_{39}AuF_3N_2O_3PS$ (816.66 g/mol): C 47.06, H 4.81, N 3.93 found C 47.47, H 4.73, N 3.63. **^{1}H NMR** (300 MHz, CD_2Cl_2): δ/ppm 1.95 (s, 18H, C*H*$_3$), 2.39 (s, 6H, C*H*$_3$), 7.29-7.64 (m, 15H, C*H*$_{Ar}$); **^{13}C NMR** (75 MHz, CD_2Cl_2): δ/ppm 14.5 (*C*H$_3$), 33.8 (C(*C*H$_3$)), 61.3 (*C*(CH$_3$)$_3$), 121.4 (q, $^1J_{CF}$ = 321 Hz), 128.9 (d, $^1J_{CP}$= 58.4 Hz, *ipso*-*C*$_6$H$_5$), 130.0 (d, $^3J_{CP}$= 11.4 Hz, *m*-*C*$_6$H$_5$), 133.0 (d, $^4J_{CP}$= 2.5 Hz, *p*-*C*$_6$H$_5$), 134.2 (d, $^2J_{CP}$= 13.6 Hz, *o*-*C*$_6$H$_5$), 130.2 (*C*=*C*)**,** 184.3 (d, $^2J_{CP}$= 125.3 Hz, N$_2$*C*Au), **^{31}P NMR** (121 MHz, CD_2Cl_2): δ/ppm 37.5 (P(Ph)$_3$).

Preparation of [12]NTf$_2$: The liquid carbene **1b** (18 mg; 0.08 mmol) was treated with 28 mg (0.08 mmol) Me_3SiNTf_2; the mixture immediately solidified. The solid dissolved in 4 ml C_6H_5Cl, and 39 mg (0.08 mmol) of $(PPh_3)AuCl$ were added at room temperature. The reaction was stirred for 1 h and treated with 8 ml *n*-hexane, whereby a precipitate formed. This was filtered off and dried in vacuum, whereby 57 mg (0.06 mmol, 80%) of the expected product [**12**]NTf$_2$ were obtained as a voluminous colorless solid. Crystals suitable for X-ray diffraction analysis were obtained from a *n*-hexane/CH_2Cl_2 solution at -30°C. **Elemental analysis** (%) calcd for $C_{33}H_{39}AuF_6N_3O_2PS_2$ (947.17g/mol): C 41.82, H 4.15, N 4.43 found C 41.41, H 4.56, N 4.73. **^{1}H NMR** (400 MHz, CD_2Cl_2): δ/ppm 1.96 (s, 18H, CH_3), 2.39 (s, 6H, CH_3), 7.52 (m, 10H, CH_{Ar}; **^{13}C-NMR** (100 MHz, CD_2Cl_2): δ = 14.8 (CH_3), 33.9 ($C(CH_3)_3$), 61.9 ($C(CH_3)_3$), 120.3 (q, $J_{C\text{-}F}$ = 320 Hz, $CF3$), 128.9 (*ipso*-C_6H_5), 130.1 (*m*-C_6H_5), 132.8 (*p*-C_6H_5), 134.5 (*o*-C_6H_5), 129.7 (C=C), 184.4 (d, $^2J_{CP}$= 125.3 Hz, N_2CAu).**^{19}F-NMR** (376 MHz, CD_2Cl_2): δ = -79.4 (CF_3). **^{31}P-NMR** (162 MHz, CD_2Cl_2): δ = 37.6 ($P(Ph)_3$).

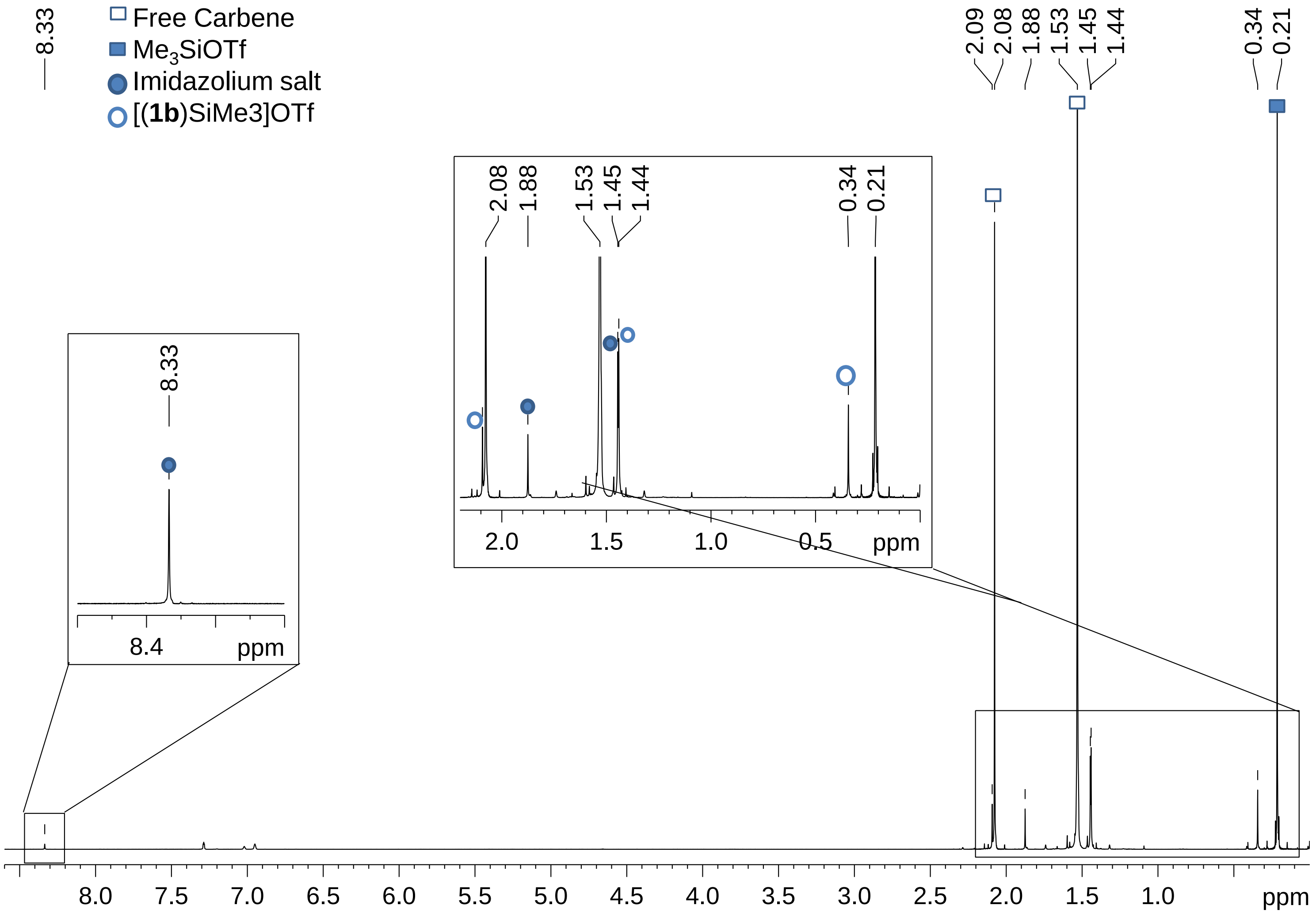


[**13**]OTf

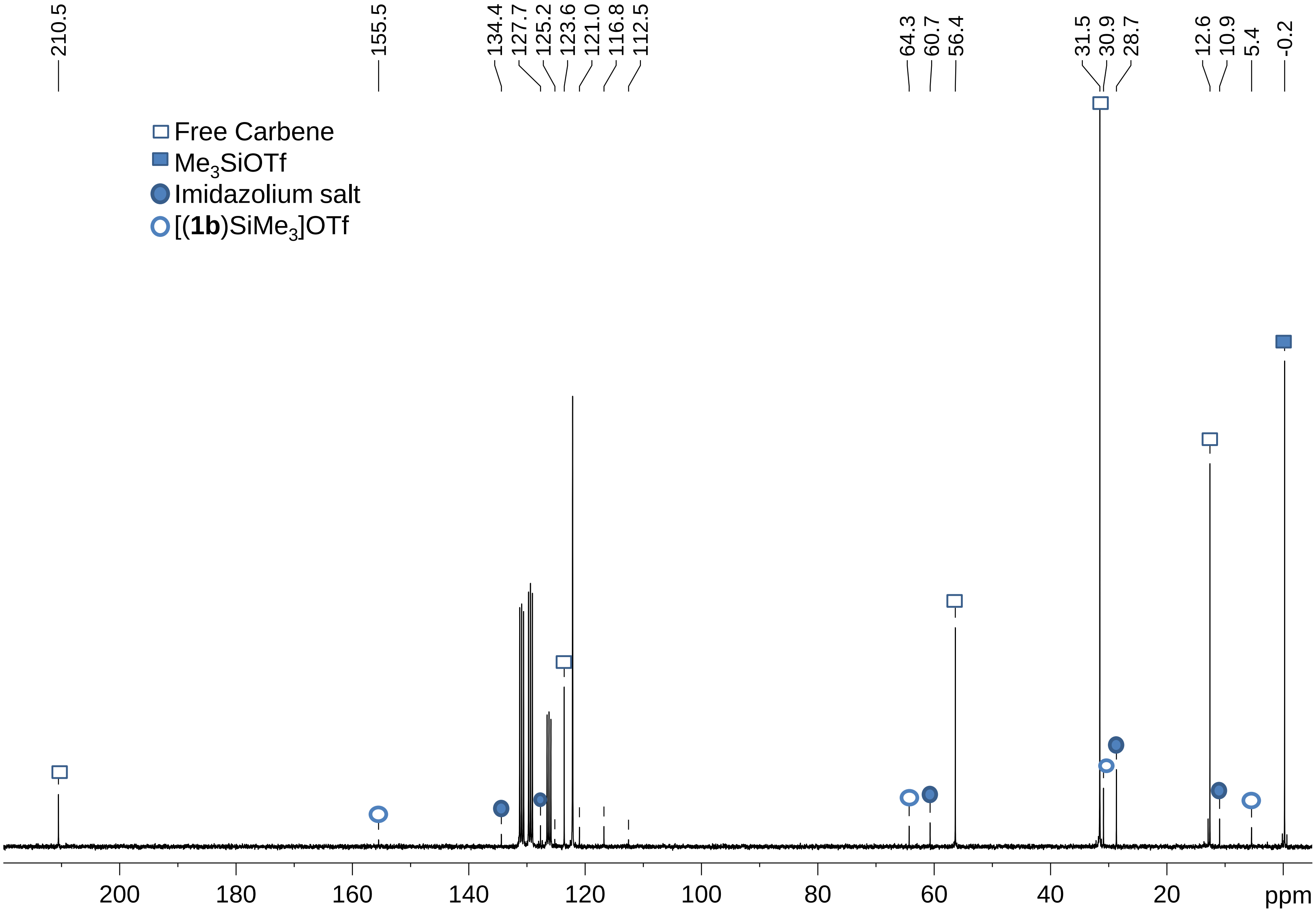
Hydrolysis product of [11]OTf Exposition of [**11**]OTf to air and moisture leads to the loss of the Me_3Si-moiety, which is replaced by a proton. Crystals of [**13**]OTf suitable for X-ray diffraction analysis were obtained either from a CD_2Cl_2 / *n*-hexane solution at 4°C. For structure, see Section 4.

2. NMR spectra

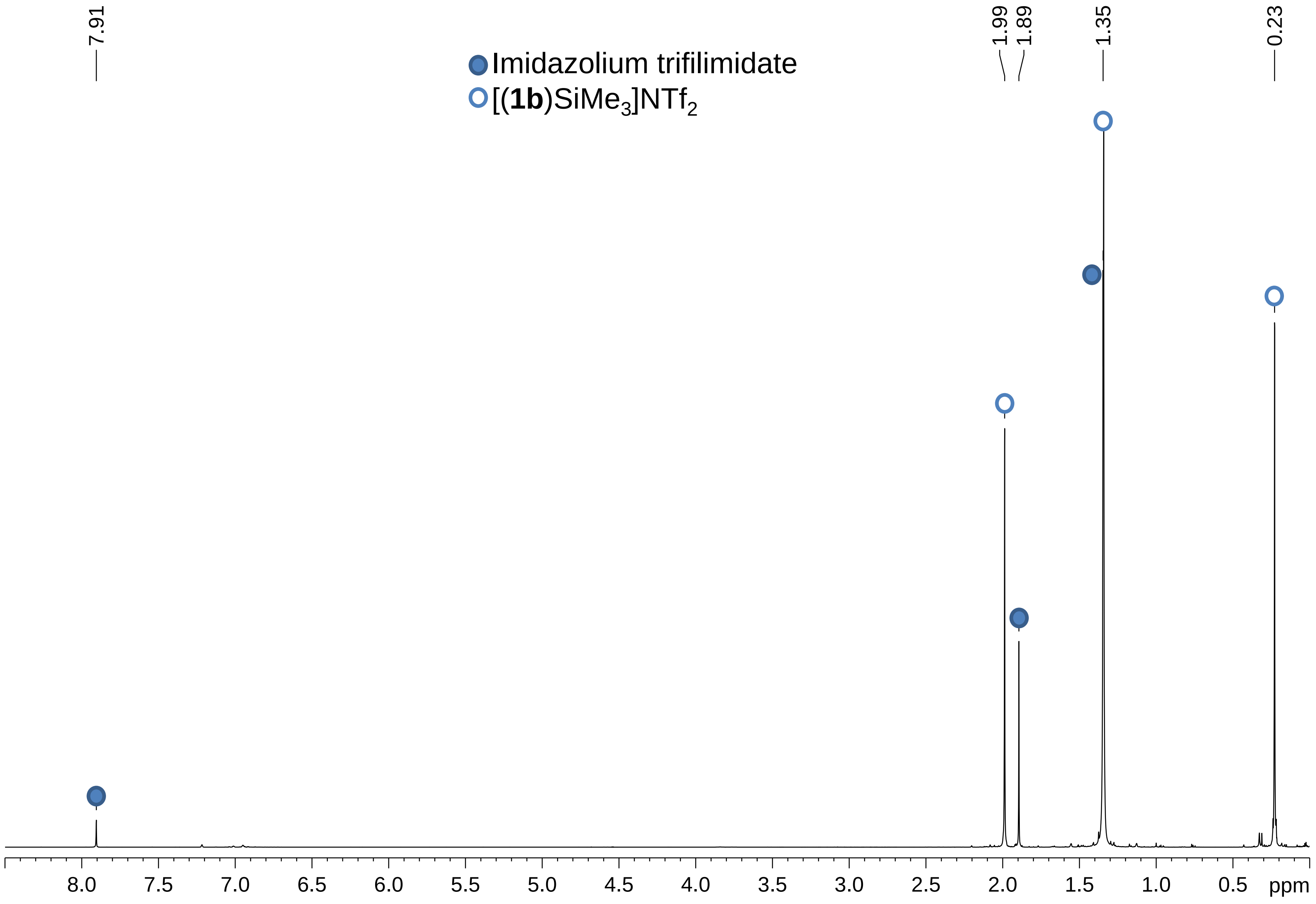
^{1}H NMR of **1b**, Me_3SiOTf and [(**1b**)$SiMe_3$]OTf in C_6D_5Br.



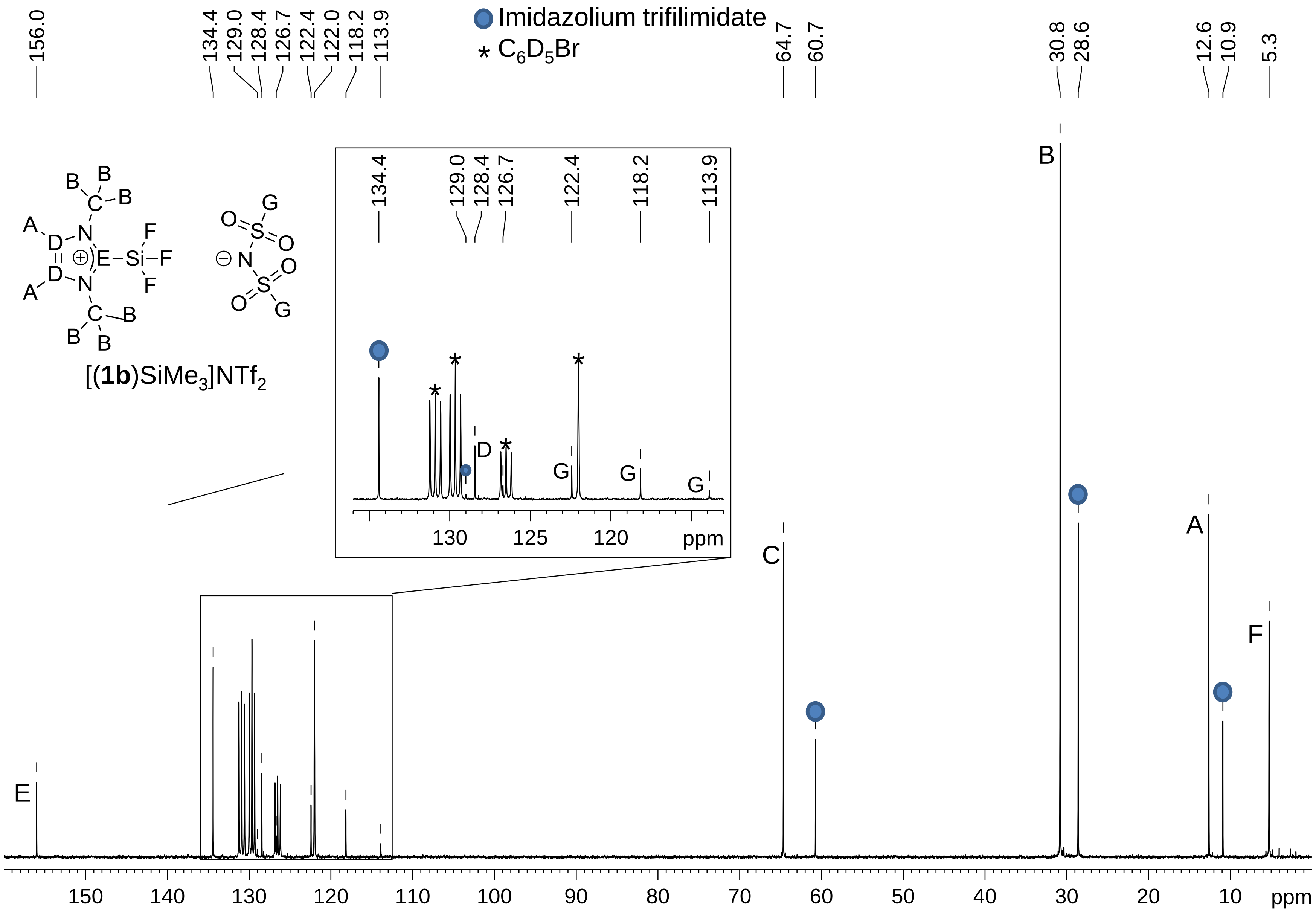
^{13}C NMR of **1b**, Me_3SiOTf and [(**1b**)$SiMe_3$]OTf in C_6D_5Br.



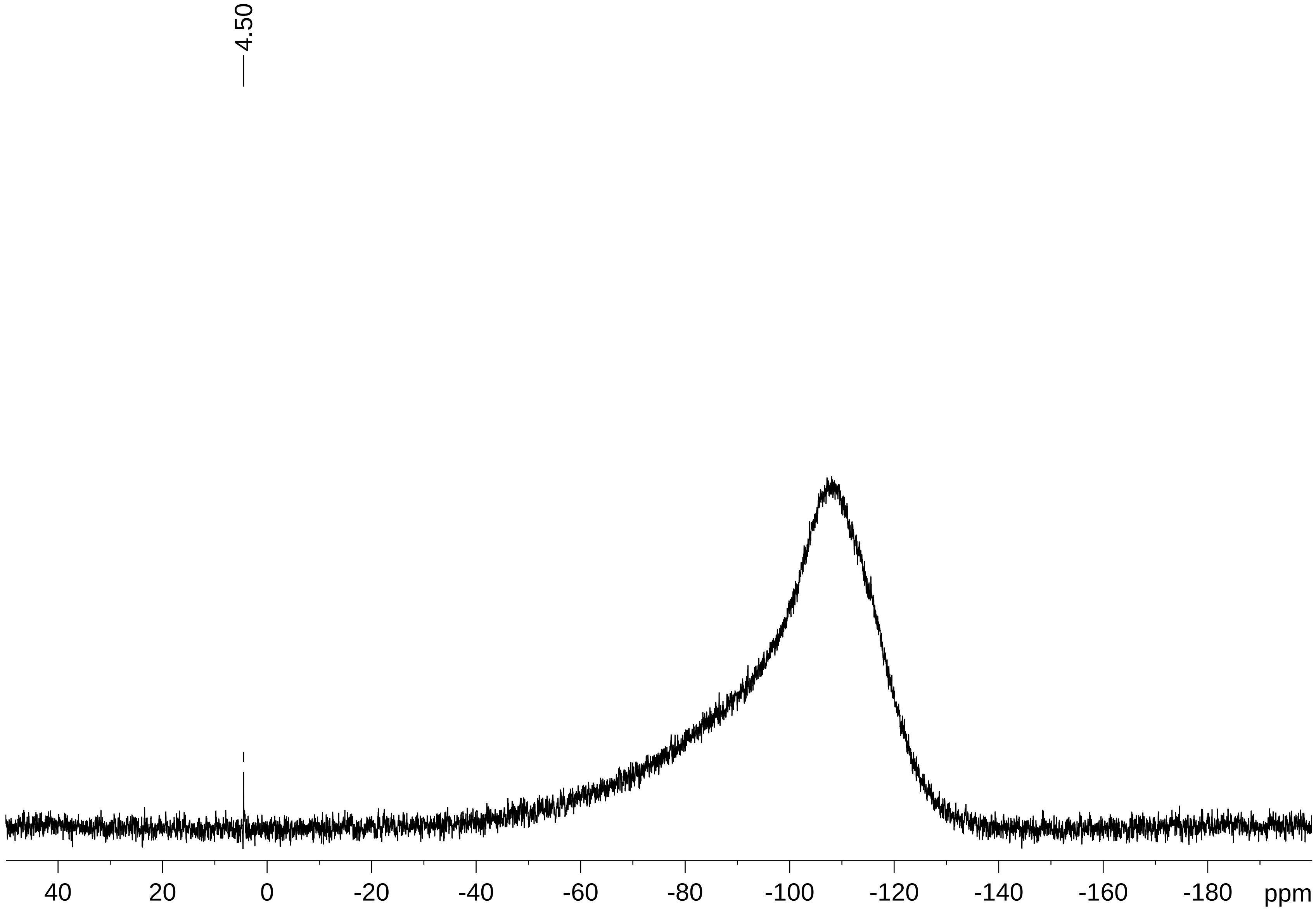
^{1}H NMR of [(**1b**)SiMe$_3$]NTf$_2$ in C$_6$D$_5$Br



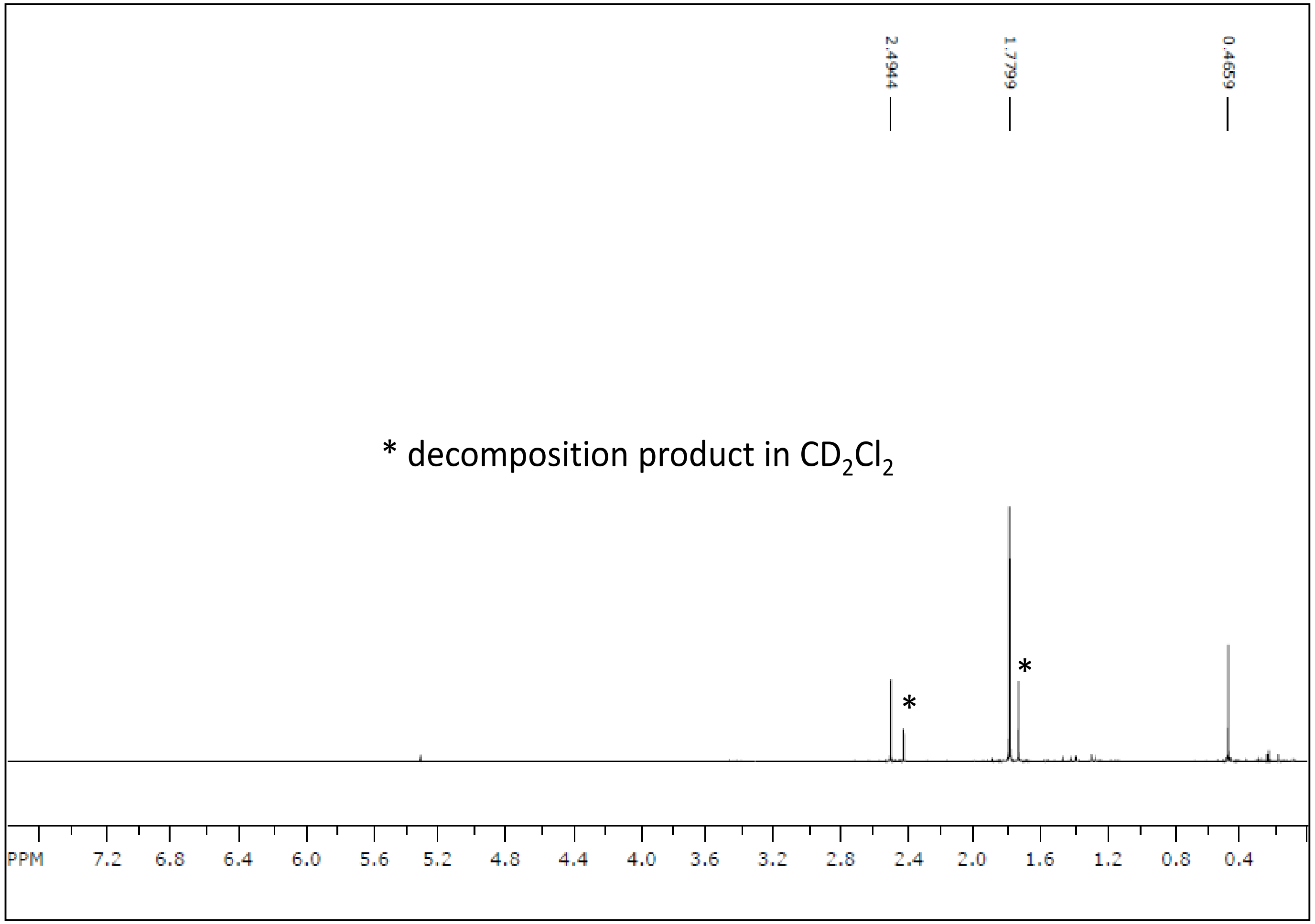
^{13}C NMR of [(**1b**)SiMe$_3$]NTf$_2$ in C_6D_5Br



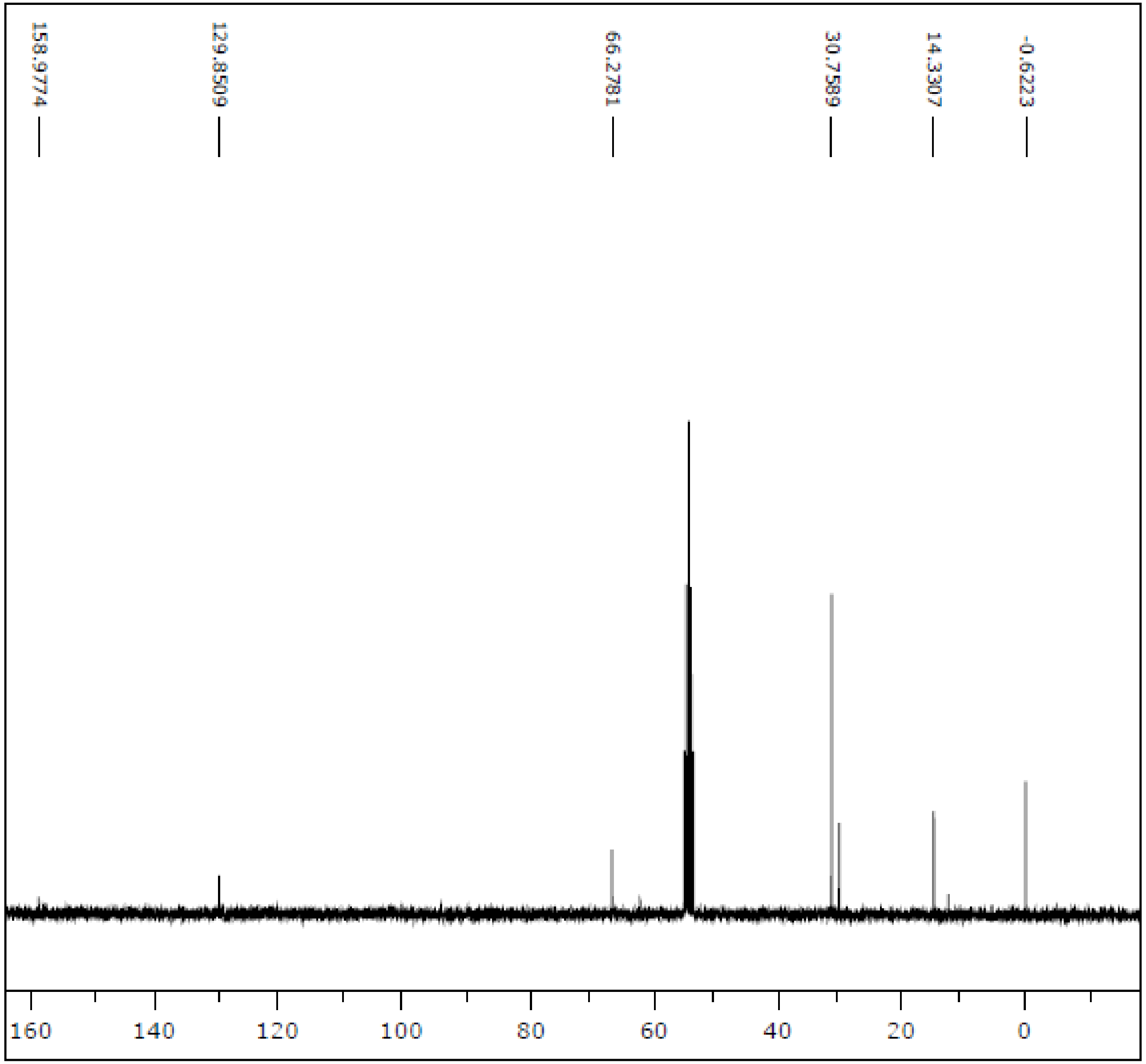
^{29}Si NMR of [(**1b**)SiMe$_3$]NTf$_2$ in C$_6$D$_5$Br



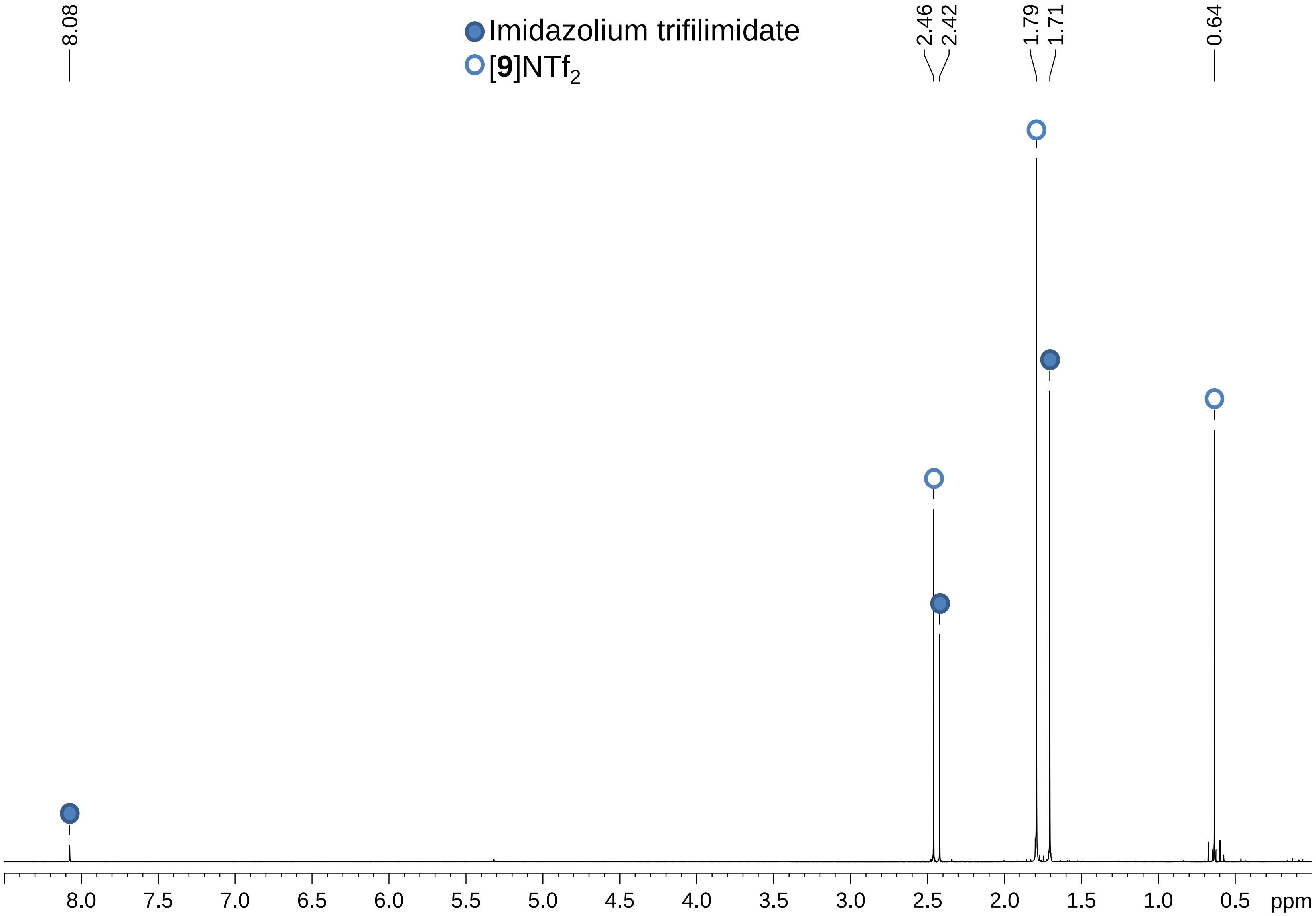
^{1}H NMR of [**9**]OTf in CD_2Cl_2



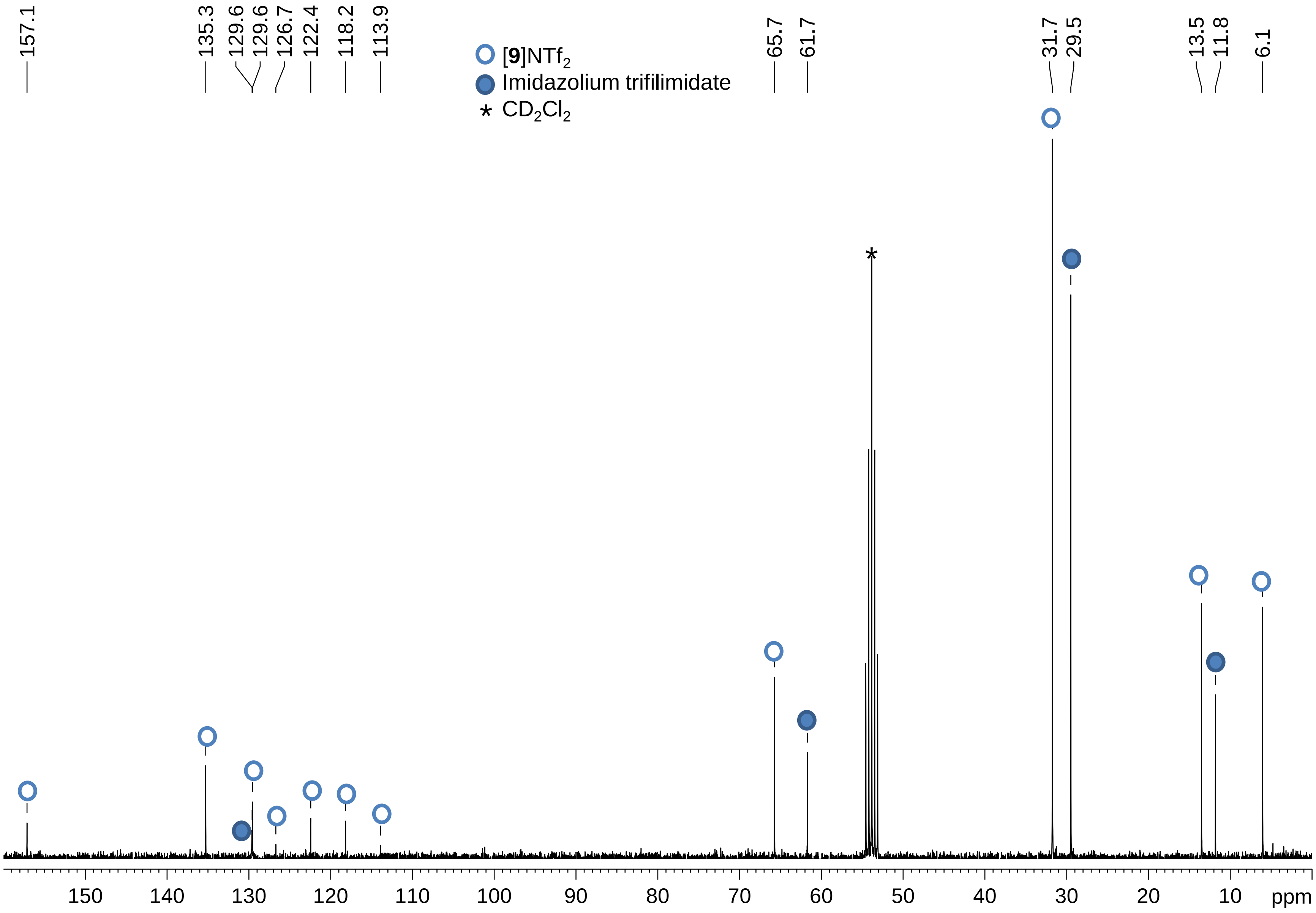
^{13}C NMR of [**9**]OTf in CD_2Cl_2



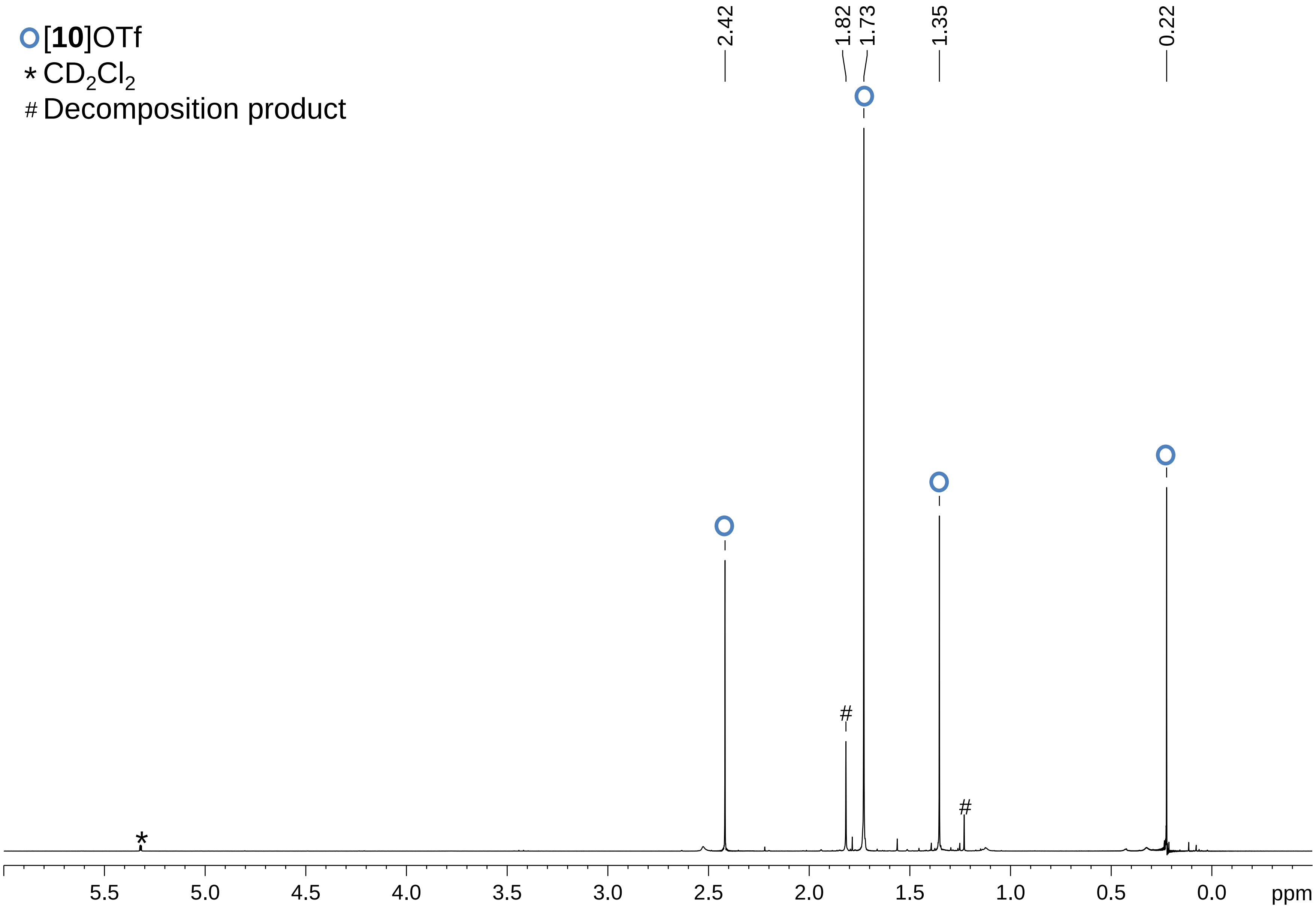
^{1}H NMR of [**9**]NTf$_2$ in CD$_2$Cl$_2$



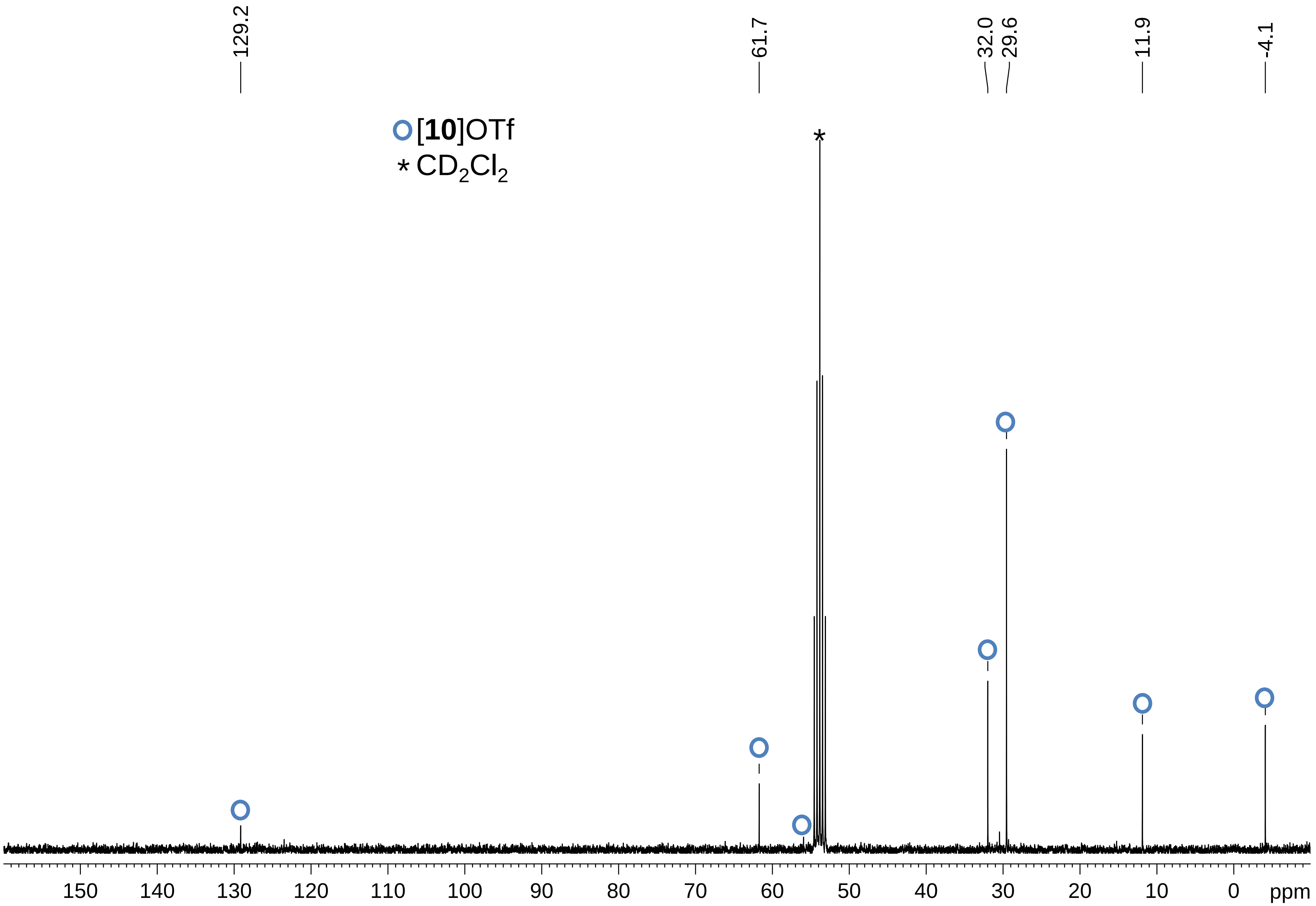
^{13}C NMR of [**9**]NTf$_2$ in CD$_2$Cl$_2$



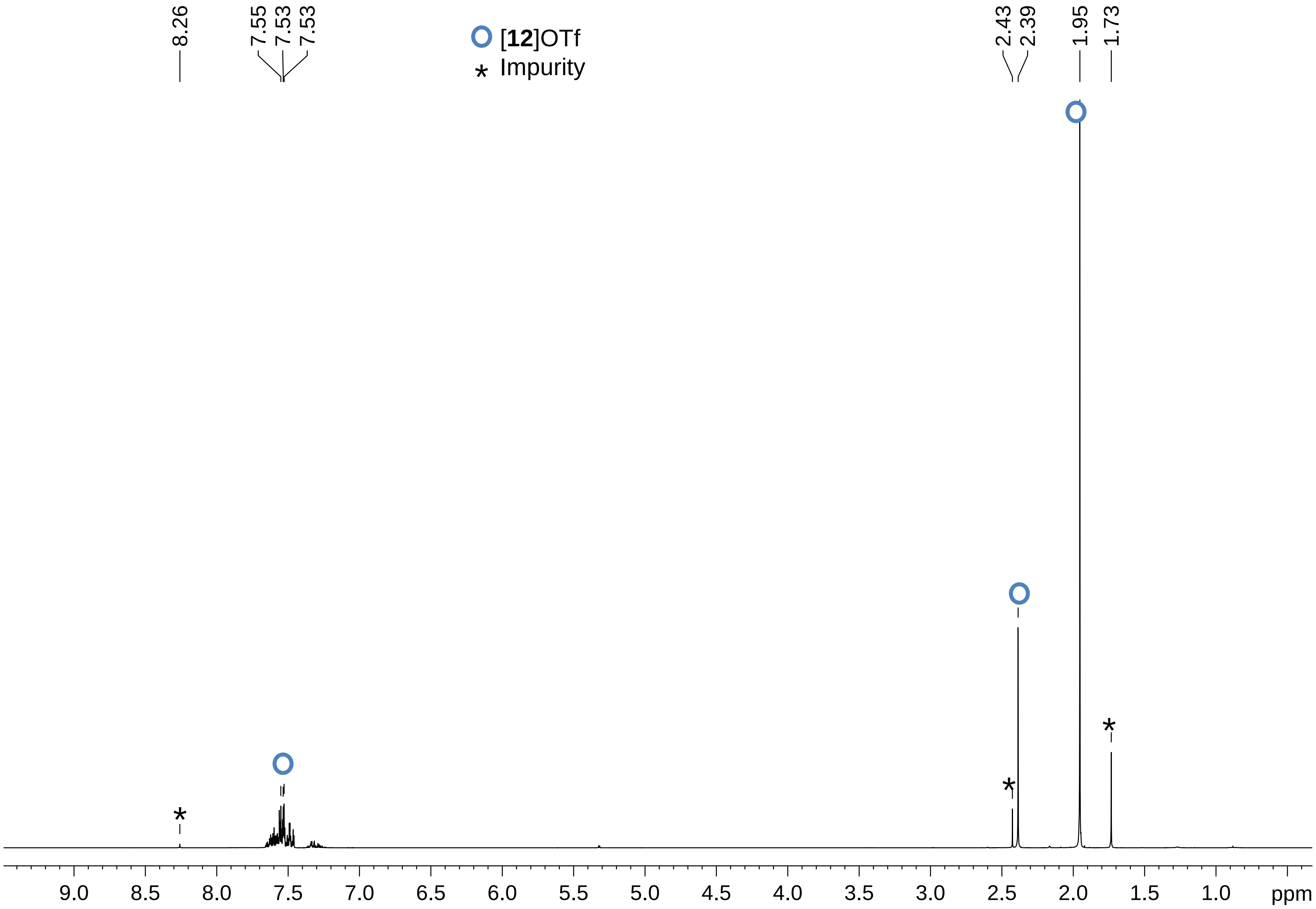
^{1}H NMR of [**10**]OTf in CD_2Cl_2



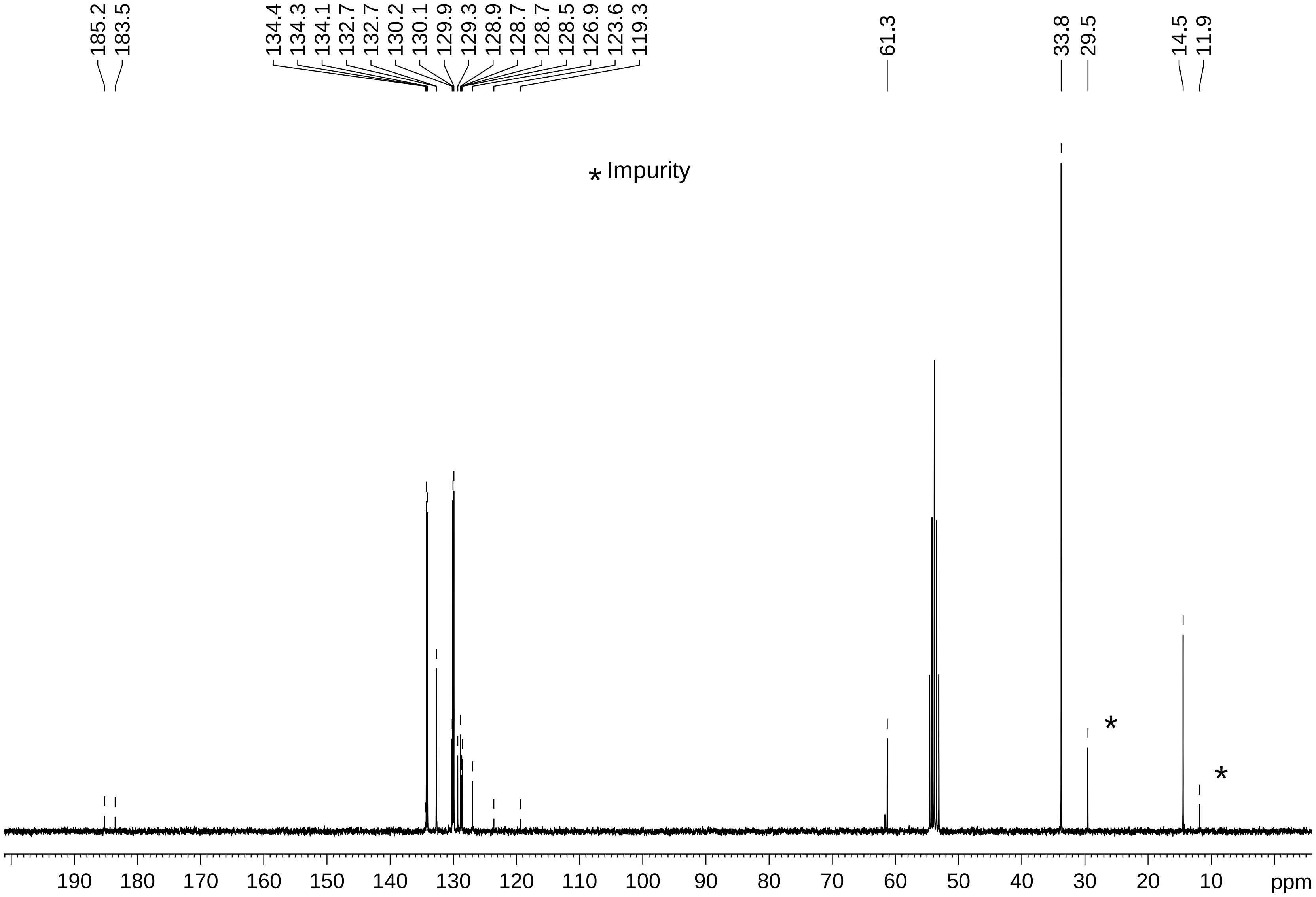
^{13}C NMR of [**10**]OTf in CD_2Cl_2



^{1}H NMR of [**12**]OTf in CD_2Cl_2

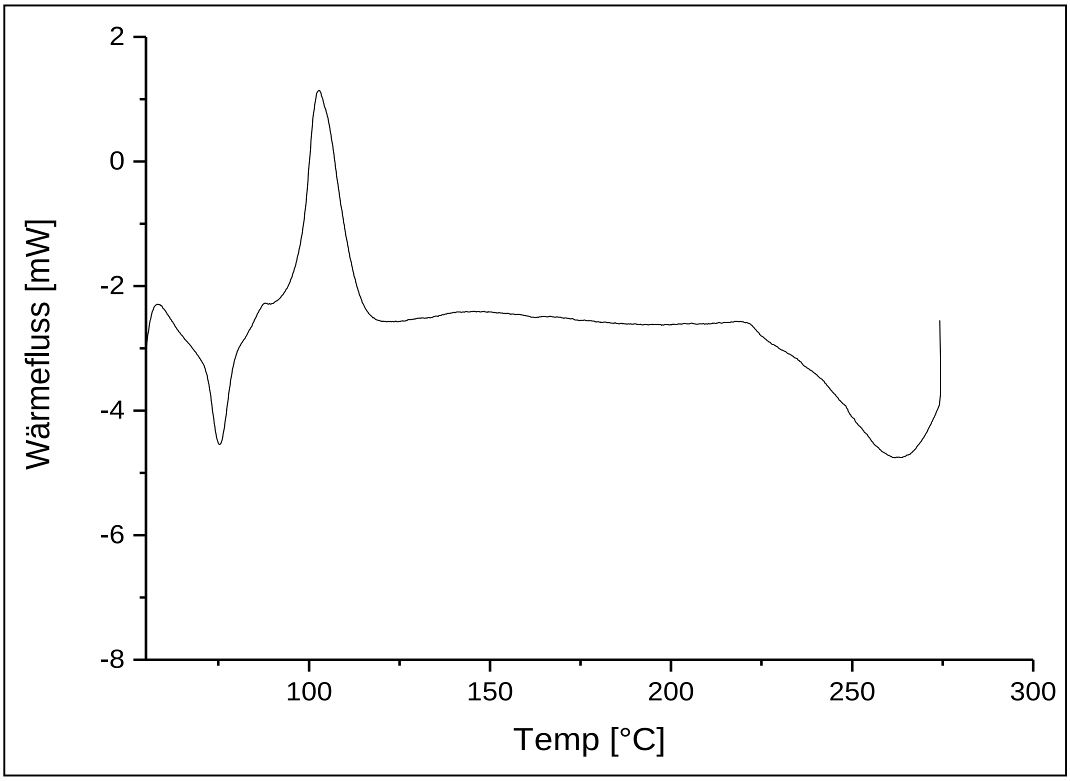


^{13}C NMR of [**12**]OTf in CD_2Cl_2



3. DSC Diagram of [(**1b**)SiMe$_3$]**NTf$_2$**

The DSC measurement was done on a DSC-SP differential-scan-calorimeter from Rheometric Scientific. The measurement was done between 25-275 °C with a heating rate of 5 °C/min.



4. X ray crystal structure determinations

Crystals were mounted on glass fibres in inert oil. Intensity measurements were performed at 100 K on Oxford Diffraction diffractometers using monochromated Mo$K\alpha$ or mirror-focussed Cu$K\alpha$ radiation. Absorption corrections were based on multi-scans. The structures were refined anisotropically on F^2 using the program SHELXL-97.[5] Hydrogen atoms were included using a riding model or rigid methyl groups. *Exceptions and special features*: For [(**1b**)SiMe$_3$]NTf$_2$, one SO$_2$CH$_3$ group is disordered over two positions, and the solvent molecule is disordered over an inversion centre. The solvent ring was refined as an ideal hexagon, and appropriate restraints were employed to improve refinement stability, but the dimensions of disordered groups should be interpreted with caution. Similar considerations apply to the one disordered triflate of compound [**10**]OTf and the disordered triflate of [**13**]OTf Compounds [**9**]OTf and [**11**]OTf are achiral and crystallize only by chance in chiral (Sohncke) space groups; the Flack parameters refined to 0.002(11) and 0.000(10) respectively. Compound [**12**]OTf crystallized with disordered solvent (toluene) that could not be satisfactorily refined; it was therefore removed mathematically using SQUEEZE (part of the PLATON package; A. L. Spek, University of Utrecht, Netherlands). The quoted formula, mass and related parameters are based on a nominal solvent content of half a toluene per asymmetric unit. For [**12**]NTf$_2$ the largest difference peak has *x* and *z* coordinates equal to those of the gold atom, which may indicate a small amount of twinning; no twin component could however be identified in the diffraction diagrams.

Crystallographic data are summarized in Tables S1 and S2.

[5]. G. M. Sheldrick, *Acta Cryst.* 2008, *A64*, 112-122.

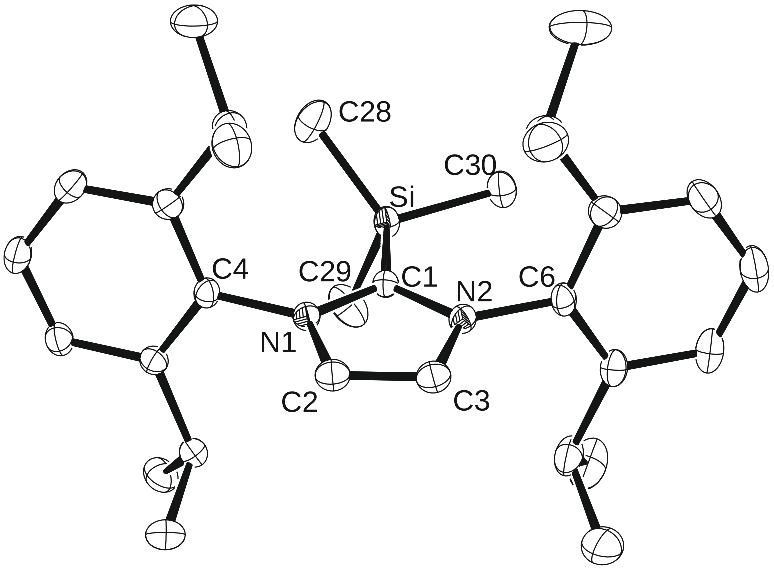
Table S1. Crystallographic data, part 1.

Compound	[(**1b**)$SiMe_3$]NTf_2 · ½C_6D_5Br	**7**	[(**1b**)$SiMe_3$] [$(B(C_6F_5)_3)_2N_3$]	[**9**]OTf	[**10**]OTf
Formula	$C_{21}H_{33}D_{2.5}Br_{0.5}F_6N_3O_4S_2Si$	$C_{31}H_{45}F_3N_2O_3SSi$	$C_{52}H_{33}B_2F_{30}N_5Si$	$C_{18}H_{33}F_3N_2O_5SSi$	$C_{22}H_{42}F_3N_3O_4SSi$
M_r	642.71	610.84	1347.54	474.61	529.74
Habit	colourless prism	colourless block	colourless prism	colourless, irregular	colourless needle
Cryst. size (mm)	0.25×0.12×0.08	0.20×0.15×0.12	0.23×0.20×0.18	0.20×0.15×0.10	0.25×0.10×0.08
Crystal system	triclinic	monoclinic	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$
Temperature (°C)	–173	–173	–173	–173	–173
Cell constants:					
a (Å)	9.3958(2)	9.71654(13)	10.5595(6)	10.6572(3)	18.8522(4)
b (Å)	10.8527(3)	22.4084(2)	14.6325(8)	10.9091(3)	20.4483(3)
c (Å)	14.7369(3)	15.65661(18)	18.5185(10)	20.6522(6)	15.2041(3)
α (°)	92.433(2)	90	97.231(4)	90	90
β (°)	92.837(2)	103.0178(12)	94.146(4)	90	110.952(2)
γ (°)	109.133(2)	90	110.557(6)	90	90
V (Å^3)	1415.23	3321.34	2636.8	2401.03	5473.57
Z	2	4	2	4	8
D_x (Mg m^{-3})	1.502	1.222	1.697	1.313	1.286
μ (mm^{-1})	3.6	1.6	0.20	2.2	1.9
F(000)	664	1304	1348	1008	2272
λ (Å)	1.54184	1.54184	0.71073	1.54184	1.54184
$2\theta_{max}$	152	154	55	154	154
Refl. measured	113557	67865	69215	36236	103018
Refl. indep.	5868	7001	11975	5022	11498
R_{int}	0.050	0.045	0.036	0.041	0.055
Parameters	424	381	822	282	674
Restraints	70	0	0	0	85
$wR2(F^2$, all refl.)	0.079	0.089	0.085	0.060	0.100
$R1(F, >4\sigma(F))$	0.030	0.035	0.036	0.024	0.038
S	1.05	1.03	1.03	1.05	1.03
max. $\Delta\rho$ (e Å^{-3})	0.31	0.28	0.34	0.21	0.52

Table S2. Crystallographic data, part 2.

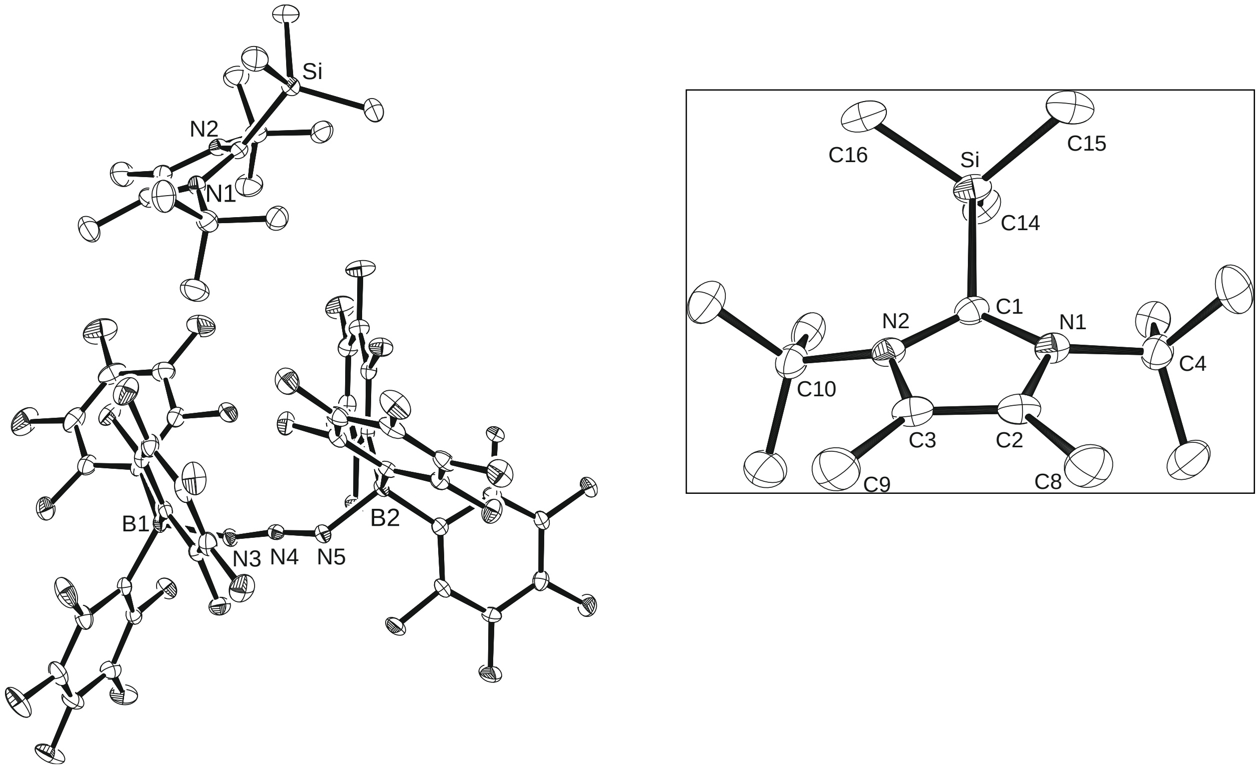
Compound	[**11**]OTf	[**12**]OTf · ½C_7H_8	[**12**]NTf_2	[**13**]OTf
Formula	$C_{33}H_{43}F_3N_2O_3SSi$	$C_{35.5}H_{43}AuF_3N_2O_3PS$	$C_{33}H_{39}AuF_6N_3O_4PS_2$	$C_{30}H_{35}F_3N_2O_3S$
M_r	632.84	862.72	947.73	560.66
Habit	colourless prism	colourless, irregular	colourless prism	yellow block
Cryst. size (mm)	0.28 × 0.10 × 0.03	0.10 × 0.06 × 0.04	0.18 × 0.10 × 0.08	0.31 × 0.21 × 0.20
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
Temperature (°C)	–173	–173	–173	–173
Cell constants:				
a (Å)	9.0006(2)	9.2711(5)	13.3594(4)	8.7510(5)
b (Å)	13.4769(2)	16.7779(8)	14.4701(5)	11.0657(6)
c (Å)	14.1223(2)	22.7298(10)	18.7666(6)	15.6228(8)
α (°)	90	90	90	73.544(5)
β (°)	99.137(2)	96.201(4)	90.246(3)	79.645(5)
γ (°)	90	90	90	83.429(4)
V (Å^3)	1691.29	3514.9	3627.8	1424.00
Z	2	4	4	2
D_x (Mg m^{-3})	1.243	1.630	1.735	1.308
μ (mm^{-1})	1.6	4.3	4.3	1.5
F(000)	672	1724	1880	592
λ (Å)	1.54184	0.71073	0.71073	1.54184
$2\theta_{max}$	152	62	62	152
Refl. measured	38932	93410	122840	28723
Refl. indep.	6988	10522	10993	5870
R_{int}	0.040	0.11	0.11	0.033
Parameters	399	396	459	393
Restraints	1	0	0	67
$wR2(F^2$, all refl.)	0.077	0.075	0.070	0.136
$R1(F, >4\sigma(F))$	0.029	0.045	0.038	0.053
S	1.03	1.07	1.05	1.06
max. $\Delta\rho$ (e Å^{-3})	0.21	1.17	2.81	0.52

X ray crystal structure of 7:



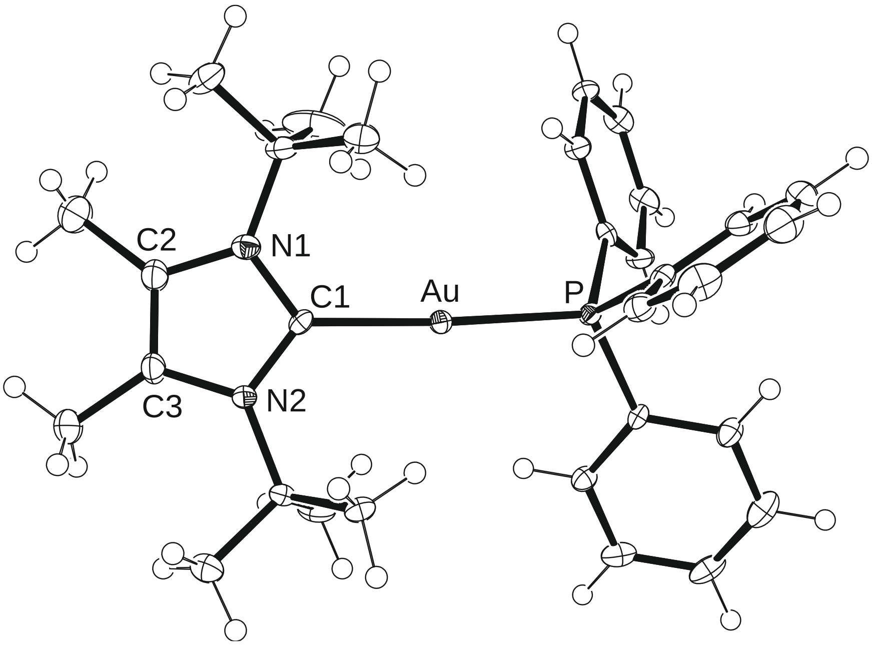
ORTEP plot of the cation of **7**, with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si-C30 1.8491(13), Si-C29 1.8496(15), Si-C28 1.8519(15), Si-C1 1.9330(12), N1-C1 1.3567(15), N1-C2 1.3841(15); C30-Si-C29 109.53(7), C30-Si-C28 109.94(7), C29-Si-C28 112.42(8), C28-Si-C1 110.39, C1-N1-C2 110.19(10). There are two short contacts between anion and cation: H3ΛO2 2.27 and H2ΛO1 2.42 Å.

X ray crystal structure of [(**1b**)SiMe$_3$]**[(C$_6$F$_5$)$_3$BN$_3$B(C$_6$F$_5$)$_3$]**



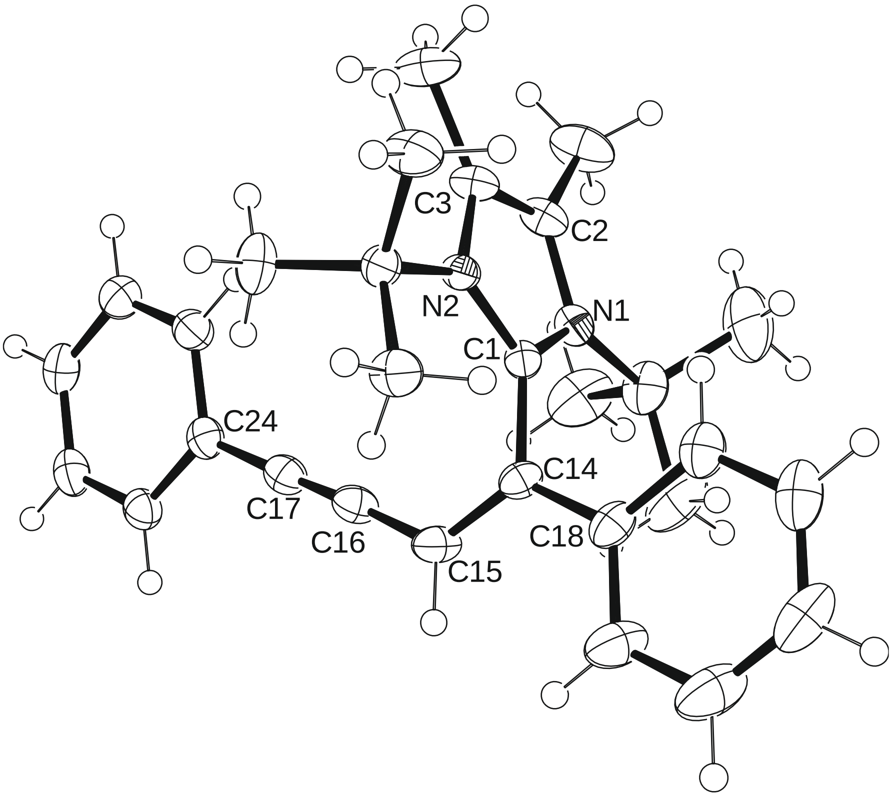
ORTEP plot of [(**1b**)SiMe$_3$]**[(C$_6$F$_5$)$_3$BN$_3$B(C$_6$F$_5$)$_3$]**with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Inset: The cation [(**1b**)SiMe$_3$]$^+$. Selected bond lengths (Å) and angles (°): Si-C16 1.866(2), Si-C14 1.8674(18), Si-C15 1.872(2), Si-C1 1.9680(17), B1-N3 1.655(2), B2-N5 1.619(2), N1-C1 1.373(2), N1-C2 1.392(2), N4-N5 1.1695(17), N3-N4 1.1753(17); C16-Si-C14 110.25(9), C16-Si-C15 100.62(9), C14-Si-C15 112.28(9), C16-Si-C1 110.37(8), C14-Si-C1 113.33(8), C15-Si-C1 109.28(8), N3-N4-N5 172.23(15), N4-N5-B2 134.01(14), N4-N3-B1 127.58(13).

X-Ray crystal structure of [**12**]OTf:



ORTEP plot of the cation of [**12**]OTf with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity Selected bond lengths [Å] and angles: Au-C1 2.063(4), Au-P 2.2777(10), N1-C1 1.353(5), N1-C2 1.397(5), N1-C4 1.529(5), N2-C1 1.362(5); C1-Au-P 176.52(11), N1-C1-N2 106.6(3), N1-C1-Au 125.5(3), N2-C1-Au 126.8(3).

X-Ray crystal structure of [13]OTf:



ORTEP plot of the cation of [**13**]OTf with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity Selected bond lengths [Å] and angles: C1-C14 1.492(2), C14-C15 1.349(2), C14-C18 1.478(2), C15-C16; N1-C1-N2 108.73(13), C14-C15-C1 116.50(14), C15-C16-C17 176.86(18).

5. Computational Details

All computations were performed using the density functional methods B97-D, M05-2X, M06-2X and M06-L as implemented in the Gaussian09 program.[6] For all elements (C, H, N, O, Si, P, S, F and I) the all-electron triple-ζ basis set (6-311G**) was used,[7] whereas for the 4d transition metal gold the Stuttgart-Köln MCDHF RSC ECP was applied.[8]

Energies for all optimized structures

Compounds	Method	**E(0 K)[a] / [Ha]**	**H(298 K)[b] / [Ha]**	**G(298 K)[b] / [Ha]**
$(Me_3Si)^+$	B97-D	-408.8239	-408.814844	-408.857752
	M05-2X	-408.866137	-408.865193	-408.906891
	M06-2X	-408.81443	-408.805529	-408.848437
Me_3SiI	B97-D	-7332.618934	-7332.608808	-7332.653926
	M05-2X	-7328.815872	-7328.805885	-7328.850706
	M06-2X	-7329.072195	-7329.062186	-7329.107063
Me_3SiNTf_2	B97-D	-2236.024722	-2236.000956	-2236.077189
	M05-2X	-2236.483901	-2236.461245	-2236.534886
	M06-2X	-2236.163095	-2236.140433	-2236.213793
Me_3SiOTf	B97-D	-1370.44259	-1370.425884	-1370.486162
	M05-2X	-1370.725273	-1370.709214	-1370.768008
	M06-2X	-1370.52154	-1370.505203	-1370.565316
Me_4ImC: (**1c**)	B97-D	-383.080368	-383.069006	-383.114589
	M05-2X	-383.290338	-383.27927	-383.324352
	M06-2X	-383.175175	-383.164058	-383.209278
Me_2*t*Bu_2ImC: (**1b**)	B97-D	-618.697087	-618.678347	-618.740194
	M05-2X	-619.028286	-619.009949	-619.071408
	M06-2X	-618.832636	-618.814447	-618.875357
$(Me_4ImC\text{-}SiMe_3)^+$	B97-D	-792.049928	-792.030653	-792.095318
	M05-2X	-792.31026	-792.291648	-792.354409
	M06-2X	-792.136537	-792.117832	-792.181279
$(Me_2$*t*$Bu_2ImC\text{-}SiMe_3)^+$	B97-D	-1027.642889	-1027.616802	-1027.69388
	M05-2X	-1028.018322	-1027.992657	-1028.068819
	M06-2X	-1027.765997	-1027.740223	-1027.816716
$(Me_4ImC\text{-}SiMe_3)I$ [C]	B97-D	-7715.740656	-7715.719446	-7715.789485
	M05-2X	-7712.142223	-7712.121551	-7712.191268
	M06-2X	-7712.284278	-7712.263582	-7712.332688
$(Me_4ImC\text{-}SiMe_3)NTf_2$ [C]	B97-D	-2619.164314	-2619.128857	-2619.231224
	M05-2X	-2619.830784	-2619.796825	-2619.895028
	M06-2X	-2619.395883	-2619.362622	-2619.458398
$(Me_4ImC\text{-}SiMe_3)OTf$ [C]	B97-D	-1753.565663	-1753.538153	-1753.622231
	M05-2X	-1754.053954	-1754.026739	-1754.110184
	M06-2X	-1753.737383	-1753.711076	-1753.792173
$(Me_2$*t*$Bu_2ImC\text{-}SiMe_3)I$ [A]	B97-D	-7951.326588	-7951.297634	-7951.384501
$(Me_2$*t*$Bu_2ImC\text{-}SiMe_3)I$ [TS]		-7951.299712	-7951.272411	-7951.35318
$(Me_2$*t*$Bu_2ImC\text{-}SiMe_3)I$ [B]		-7951.300241	-7951.271691	-7951.357745
$(Me_2$*t*$Bu_2ImC\text{-}SiMe_3)I$ [C]	B97-D	-7951.324562	-7951.296381	-7951.379333
	M05-2X	-7947.844118	-7947.816217	-7947.898767
	M06-2X	-7947.907203	-7947.879434	-7947.961468
$(Me_2$*t*$Bu_2ImC\text{-}SiMe_3)NTf_2$ [A]	B97-D	-2854.733468	-2854.690425	-2854.80931
$(Me_2$*t*$Bu_2ImC\text{-}SiMe_3)NTf_2$ [TS]		-2854.718079	-2854.67675	-2854.788301
$(Me_2$*t*$Bu_2ImC\text{-}SiMe_3)NTf_2$ [B]		-2854.730848	-2854.689	-2854.802977
$(Me_2$*t*$Bu_2ImC\text{-}SiMe_3)NTf_2$ [C]	B97-D	-2854.751861	-2854.709584	-2854.823646
	M05-2X	-2855.529992	-2855.48912	-2855.59981
	M06-2X	-2855.017842	-2854.977262	-2855.08667
$(Me_2$*t*$Bu_2ImC\text{-}SiMe_3)OTf$ [A]	B97-D	-1989.155176	-1989.118826	-1989.223567
$(Me_2$*t*$Bu_2ImC\text{-}SiMe_3)OTf$ [TS]		-1989.131746	-1989.097563	-1989.194851
$(Me_2$*t*$Bu_2ImC\text{-}SiMe_3)OTf$ [B]		-1989.131527	-1989.097146	-1989.193406
$(Me_2$*t*$Bu_2ImC\text{-}SiMe_3)OTf$ [C]	B97-D	-1989.153484	-1989.118518	-1989.216573
	M05-2X	-1989.753896	-1989.719664	-1989.817362
	M06-2X	-1989.361355	-1989.32824	-1989.420349
$(Me_2$*t*$Bu_2ImC\text{-}Au\text{-}PPh_3)^+$ [A]	B97-D	-1790,320906	-1790,282616	-1790,39423
$(Me_2$*t*$Bu_2ImC\text{-}Au\text{-}PPh_3)^+$ [TS]		-1790,315926	-1790,278442	-1790,387475
$(Me_2$*t*$Bu_2ImC\text{-}Au\text{-}PPh_3)^+$ [B]		-1790,320241	-1790,282732	-1790,391014
$(Me_2$*t*$Bu_2ImC\text{-}Au\text{-}PPh_3)^+$ [A]	M06-L	-1790,816612	-1790,779161	-1790,887218
$(Me_2$*t*$Bu_2ImC\text{-}Au\text{-}PPh_3)^+$ [TS]		-1790,814873	-1790,77776	-1790,886376
$(Me_2$*t*$Bu_2ImC\text{-}Au\text{-}PPh_3)^+$ [B]		-1790,815515	-1790,77829	-1790,885391

[a] DFT energy incl. ZPE.

[b] standard conditions T = 298.15 K and p = 1 atm.

[6] Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[7] X. Cao and M. Dolg, *J. Chem. Phys.*, 2001, **115**, 7348.

[8] Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.2.2 [https://bse.pnl.gov/bse/portal]. a) The Role of Databases in Support of Computational Chemistry Calculations, D. Feller, *J. Comp. Chem.,* 1996, **17**, 1571-1586. b) Basis Set Exchange: A Community Database for Computational Sciences, K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li and T. L. Windus, *J. Chem. Inf. Model.*, 2007, **47**, 1045-1052.