# Evidence for and Evaluation of Fluorine-Tellurium Chalcogen Bonding

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I. General Information

The solvents were purchased from commercial sources and purified according to the standard procedure and freshly distilled under argon prior to use. CH$_2$Cl$_2$, and Et$_2$O were dried by passing through activated alumina under a positive pressure of argon using GlassTechnology GTS100 devices. Anhydrous reactions were carried out in flame-dried glassware and under an argon atmosphere, using standard Schlenk techniques. Analytical TLC was carried out on silica gel 60 F254 plates (layer thickness 0.25 mm) with visualization by ultraviolet light. Chromatography was carried out using silica gel 60 (40–63 μm).

Compounds 1$^1$, 2$^2$ and 4$^3$, 9$^1$ and 12$^2$ were synthesized according the literature. Compound 3 is commercially available.

Data are presented as follows; chemical shift, multiplicity (standard abbreviations), coupling constants (J in Hz), integration, and carbons with same chemical shift (x carbons). Assignments were determined either based on unambiguous chemical shifts or coupling patterns, and COSY, HSQC, HMBC, HMQC, NOESY or DEPT 135 experiments were sometimes needed to fully interpret spectra for related compounds.

The samples NMR experiments were prepared using CDCl$_3$/CD$_2$Cl$_2$ as the solvent that was purchased from Euriso-Top and dried over molecular sieves prior to use. The concentration of the samples was approx. 20 mM. The NMR spectra were recorded on Brucker Avance III spectrometer operating at specified power (Bruker Corporation, Billerica, MA, USA) and performed at 25°C if not specified for characterization. The chemical shifts are given in ppm on the δ scale. The solvent peak was used as reference value. For $^1$H NMR: CDCl$_3$ = 7.26 ppm, CD$_2$Cl$_2$ = 5.32 ppm. For $^{13}$C NMR: CDCl$_3$ = 77.16 ppm, CD$_2$Cl$_2$ = 53.84 ppm.

$^{125}$Te NMR spectra were recorded at 158 MHz on a 500 MHz spectrometer (equipped with a CP BBO 500S1 BBF-H-D-05 Z probe) at 298 K and are referenced externally to diphenylditelluride in CDCl$_3$ at 422 ppm and chemical shift were compared with $^{125}$Te NMR tables. The experiments were performed with a relaxation delay ranging from 1.0 to 1.5 second and a prolonged minimum number of scans (n = 248) to minimize the signal-to-noise ratio.

$^{19}$F NMR spectra were recorded at 282 MHz on a 500 MHz spectrometer (equipped with a CP BBO 500S1 BBF-H-D-05 Z probe) at 298 K and are referenced externally to CFCl$_3$ in CDCl$_3$ at 0.00 ppm and chemical shift were compared with $^{19}$F NMR tables.

Melting point were recorded on a Stuart Scientific melting point apparatus SMP30. High-resolution mass spectra (HRMS) data were recorded on a micrOTOF spectrometer (Bruker Corporation, Billerica, MA, USA) equipped with an orthogonal electrospray interface (ESI) or with atmospheric pressure chemical ionization (APCI). The parent ions [M + H]$^+$, [M + Na]$^+$, [M + K]$^+$ are quoted.

**CAUTION!** Tellurium compounds are toxic so special care should be taken when handling them. All manipulations, including column glassware and vessels cleaning, were performed in a well-ventilated fume hood. Tellurium waste were stored and disposed separately from other chemical waste. Although tellurium compounds are known to have a characteristic unpleasant smell, most of the reported compounds in this work were almost odorless. Particular care has been taken during the treatment of the organotellurium compounds because they are thermosensitive and slightly photosensitive.
II. Experimental procedures and characterizations

A. General procedures

1. General procedure GP1: alkyl-aryltellane synthesis

In a dry Schlenk tube was placed diaryl ditelluride (1 eq.). The Schlenk tube was evacuated and filled with argon before addition of solvent mixture (THF/EtOH 9:1, 5 mL). NaBH₄ (8-9 eq.) was then added portionwise under nitrogen. By the addition of NaBH₄, the reaction mixture changed from orange to transparent pale yellow to colorless solution, which was further stirred for 30 min at room temperature. A solution of eletrophile (2-4 eq. in THF/EtOH 9:1, 2 mL) was slowly added to the reaction mixture under nitrogen and the mixture was stirred for 15 min. The reaction mixture was then quenched with distilled water (15 mL) and extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over anhydrous sodium sulfate, and the solvent was removed in vacuo. The product was purified by alumina column chromatography using pentane or petroleum ether as eluent.

2. General procedure GP2: Diaryltellane synthesis

A mixture of arylboronic acid (1 eq.), diaryl ditelluride (0.5 eq.), iodine (10 mol%), and DMSO (1 mmol, 2 eq.) were placed in a microwave glass tube, which was sealed and placed in a CEM Discover microwave device. A maximum irradiation power of 100W and a temperature of 100 °C were applied for 15 min. When the reaction was completed, the reaction mixture was dissolved in ethyl acetate (15 mL) and washed with an aqueous solution of 10% Na₂S₂O₄ (2 x 10 mL) and brine (2 x 15 mL). Combined organic extracts were dried over MgSO₄, filtered, and concentrated under vacuum. The crude material was purified by chromatography on a silica gel column with pentane-ethyl acetate 99:1 to 80:20 as the eluent.
B. Characterizations

(2-(Fluoromethyl)phenyl)(phenyl)tellane (5a)

Synthesis: According to GP2, starting from 1,2-bis(2-(fluoromethyl)phenyl)ditellane 2 (40 mg, 0.085 mmol), benzeneboronic acid (21 mg, 0.18 mmol), iodine (2 mg, 0.0085 mmol, 10 mol%) and DMSO (20 mg, 0.25 mmol).

Yield 80%, 44 mg.

Aspect: colorless oil; \(^{1}H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.69 (dd, \(J = 8.1, 1.4\) Hz, 2H), 7.66 (d, \(J = 7.7\) Hz, 1H), 7.45 (d, \(J = 7.7\) Hz, 1H), 7.35 – 7.29 (m, 2H), 7.23 (t, \(J = 7.6\) Hz, 2H), 7.14 (t, \(J = 7.6\) Hz, 1H), 5.47 (d, \(J = 47.8\) Hz, 2H); \(^{13}C\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) 140.0 (d, \(J = 16.5\) Hz), 139.1 (d, \(J = 1.7\) Hz), 138.6, 129.8, 129.7 (d, \(J = 2.8\) Hz), 128.5, 128.4 (d, \(J = 8.3\) Hz), 128.3, 117.4 (d, \(J = 4.0\) Hz), 114.4 (d, \(J = 2.7\) Hz), 87.7 (d, \(J = 167.6\) Hz); \(^{19}F\) NMR (282 MHz, CDCl\(_3\)) \(\delta\) -205.3; \(^{125}Te\) NMR (158 MHz, CDCl\(_3\)) \(\delta\) 596.4 (d, \(J = 110.4\) Hz).

(3,5-Difluorophenyl)(2-(fluoromethyl)phenyl)tellane (5b)

Synthesis: According to GP2, starting from 1,2-bis(2-(fluoromethyl)phenyl)ditellane 2 (30 mg, 0.063 mmol), (3,5-difluorophenyl)boronic acid (21 mg, 0.13 mmol), iodine (2 mg, 0.0063 mmol, 10 mol%) and DMSO (15 mg, 0.19 mmol).

Yield 83%, 36 mg.

Aspect: colorless oil; \(^{1}H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.80 (d, \(J = 7.6\) Hz, 1H), 7.52 (d, \(J = 7.6\) Hz, 1H), 7.43 (t, \(J = 7.6\) Hz, 1H), 7.23 (t, \(J = 7.6\) Hz, 1H), 7.07 (m, 2H), 6.70 (tt, \(J = 9.0, 2.3\) Hz, 1H), 5.48 (d, \(J = 47.8\) Hz, 2H); \(^{13}C\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) 163.1 (dd, \(J = 253.8, 11.6\) Hz), 140.7 (d, \(J = 1.7\) Hz), 140.7 (d, \(J = 16.6\) Hz), 130.2 (d, \(J = 2.7\) Hz), 129.7, 128.8 (d, \(J = 8.0\) Hz), 119.9 – 119.4 (m), 116.9 (td, \(J = 7.0, 2.8\) Hz), 115.9 (d, \(J = 3.8\) Hz), 103.8 (t, \(J = 25.2\) Hz), 87.9 (d, \(J = 168.0\) Hz); \(^{19}F\) NMR (282 MHz, CDCl\(_3\)) \(\delta\) -109.3, -204.3; \(^{125}Te\) NMR (158 MHz, CDCl\(_3\)) \(\delta\) 644.8 (d, \(J = 108.7\) Hz); MS (APCI): \(m/z\) calcd for (C\(_{12}\)H\(_{11}\)F)Te(C\(_{6}\)H\(_{3}\)F\(_{2}\))(OH): 368.97. [M]+; found: 368.96.
(3,5-Bis(trifluoromethyl)phenyl)(2-(fluoromethyl)phenyl)tellane (5c)

Synthesis: According to GP2, starting from 1,2-bis(2-(fluoromethyl)phenyl)ditellane 2 (40 mg, 0.085 mmol), (3,5-bis(trifluoromethyl)phenyl)boronic acid (46 mg, 0.18 mmol), iodine (2 mg, 0.0085 mmol, 10 mol%) and DMSO (20 mg, 0.26 mmol).

Yield 86%, 66 mg.

Aspects: colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.92 (s, 2H), 7.73 – 7.66 (m, 2H), 7.46 (d, $J = 7.5$ Hz, 1H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.21 – 7.14 (m, 1H), 5.43 (d, $J = 47.8$ Hz, 2H). $^{13}$C NMR 126 MHz, CDCl$_3$ $\delta$ 140.6 (d, $J = 16.3$ Hz), 140.4 (d, $J = 2.0$ Hz), 137.0 (q, $J = 3.7$ Hz), 132.4 (q, $J = 33.3$ Hz), 130.6 (d, $J = 2.9$ Hz), 129.9, 129.3 (d, $J = 7.4$ Hz), 122.9 (q, $J = 273.0$ Hz), 122.0 – 121.9 (m), 117.4 (d, $J = 3.3$ Hz), 116.3 (d, $J = 3.5$ Hz), 87.9 (d, $J = 167.6$ Hz); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -63.0, -202.3; $^{125}$Te NMR (158 MHz, CDCl$_3$) $\delta$ 645.1 (d, $J = 125.8$ Hz); HRMS (ESI–TOF): $m/z$ calcd for C$_{15}$H$_9$F$_7$Te$: 451.9650$. [M]+; found: 451.9634.

(3,5-Dimethoxyphenyl)(2-(fluoromethyl)phenyl)tellane (5d)

Synthesis: According to GP2, starting from 1,2-bis(2-(fluoromethyl)phenyl)ditellane 2 (30 mg, 0.063 mmol), (3,5-dimethoxyphenyl)boronic acid (24 mg, 0.13 mmol), iodine (2 mg, 0.0063 mmol, 10 mol%) and DMSO (15 mg, 0.19 mmol).

Yield 90%, 42 mg.

Aspects: colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.71 (d, $J = 7.6$ Hz, 1H), 7.45 (d, $J = 7.6$ Hz, 1H), 7.34 (t, $J = 7.6$ Hz, 1H), 7.16 (t, $J = 7.6$ Hz, 1H), 6.80 (d, $J = 2.3$ Hz, 2H), 6.37 (t, $J = 2.3$ Hz, 1H), 5.47 (d, $J = 47.8$ Hz, 2H), 3.73 (s, 6H); $^{13}$C NMR 126 MHz, CDCl$_3$ $\delta$ 161.2, 140.1 (d, $J = 16.5$ Hz), 139.4 (d, $J = 1.6$ Hz), 129.8 (d, $J = 2.8$ Hz), 128.7, 128.4 (d, $J = 8.1$ Hz), 117.1 (d, $J = 3.9$ Hz), 116.1, 115.3 (d, $J = 2.7$ Hz), 100.9, 87.8 (d, $J = 167.6$ Hz), 55.5; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -205.3; $^{125}$Te NMR (158 MHz, CDCl$_3$) $\delta$ 622.8 (d, $J = 108.8$ Hz); HRMS (ESI–TOF): $m/z$ calcd for C$_{15}$H$_{16}$FO$_2$Te$: 377.0192$. [M+H]$^+$; found: 377.0163.
(3,5-Di-tert-butylphenyl)(2-(fluoromethyl)phenyl)tellane (5e)

Synthesis: According to GP2, starting from 1,2-bis(2-(fluoromethyl)phenyl)ditellane 2 (35 mg, 0.074 mmol), (3,5-di-tert-butylphenyl)boronic acid (36 mg, 0.16 mmol), iodine (2 mg, 0.0074 mmol, 10 mol%) and DMSO (17 mg, 0.22 mmol).

Yield 87%, 54 mg.
aspect colorless oil; \(^{1}H\) NMR (300 MHz, CDCl\(_3\)) \(\delta 7.66 (dt, J = 7.7, 1.4 Hz, 1H)\), 7.54 (d, \(J = 1.8 Hz, 2H\)), 7.47 (d, \(J = 7.7 Hz, 1H\)), 7.37 (t, \(J = 1.8 Hz, 1H\)), 7.33 (tt, \(J = 7.5, 1.2 Hz, 1H\)), 7.14 (tt, \(J = 7.5, 1.6 Hz, 1H\)), 5.49 (d, \(J = 47.9 Hz, 2H\)), 1.29 (s, 18H); \(^{13}C\) NMR (126 MHz, CDCl\(_3\)) \(\delta 152.2, 139.8 (d, J = 16.5 Hz), 138.6 (d, J = 1.7 Hz), 132.9, 129.6 (d, J = 2.8 Hz), 128.3 (d, J = 8.1 Hz), 128.2, 122.5, 117.8 (d, J = 3.8 Hz), 113.7 (d, J = 2.6 Hz), 87.7 (d, J = 167.5 Hz), 35.0, 31.5; \(^{19}F\) NMR (282 MHz, CDCl\(_3\)) \(\delta -205.5\); \(^{125}Te\) NMR (158 MHz, CDCl\(_3\)) \(\delta 594.3 (d, J = 108.5 Hz)\); HRMS (ESI–TOF): \(m/z\) calcd for C\(_{21}\)H\(_{27}\)FTe+: 428.1155. [\(M^+\); found: 428.1161.

Methyl(2-(trifluoromethyl)phenyl)tellane (6a)

Synthesis: According to GP1, starting from sodium borohydride (28 mg, 0.8 mmol), 1,2-bis(2-(trifluoromethyl)phenyl)ditellane 4 (100 mg, 0.18 mmol) and iodomethane (30 µL, 0.44 mmol). The product is unstable and forms side-products.

Yield 67%, 70 mg.
aspect yellow oil; \(^{1}H\) NMR (500 MHz, CDCl\(_3\)) \(\delta 7.65 (d, J = 7.5 Hz, 1H), 7.61 (dd, J = 7.5, 1.5 Hz, 1H), 7.36 – 7.28 (m, 2H), 2.24 (s, 3H); \(^{13}C\) NMR (126 MHz, CDCl\(_3\)) \(\delta 136.2, 133.5 (q, J = 30.4 Hz), 132.0 (q, J = 1.2 Hz), 126.8 (q, J = 5.4 Hz), 126.8, 124.2 (q, J = 274.1 Hz), 112.2 (q, J = 1.4 Hz), -15.2 (q, J = 3.0 Hz); \(^{19}F\) NMR (471 MHz, CDCl\(_3\)) \(\delta -62.0; \(^{125}Te\) NMR (158 MHz, CDCl\(_3\)) \(\delta 369.4 (q, J = 153.3 Hz)\). MS (APCI–TOF): [\(M^+\) \(m/z\) calcd for \(C_7H_4F_3Te(\text{OH})_2\): 308.94, \([M^+]\); found: 308.94, \([M^+]\) \(m/z\) calcd for \(C_7H_4F_3Te^+\): 274.94, \([M^+]\); found: 274.93. 8
Isopropyl(2-(trifluoromethyl)phenyl)tellane (6b)

Synthesis: According to GP1, starting from sodium borohydride (56 mg, 1.5 mmol), 1,2-bis(2-(trifluoromethyl)phenyl)ditellane (100 mg, 0.18 mmol) and 2-iodopropane (44 µL, 0.44 mmol). The product is unstable and forms side-products.

Yield 92%, 105 mg.

aspect yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.95 (d, $J$ = 7.0 Hz, 1H), 7.67 (d, $J$ = 7.0 Hz, 6H), 7.40 – 7.30 (m, 2H), 3.74 (hept, $J$ = 7.0 Hz, 1H), 1.63 (d, $J$ = 7.0 Hz, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 141.1, 135.1 (q, $J$ = 29.8 Hz), 131.9 (d, $J$ = 1.2 Hz), 127.6, 126.7 (q, $J$ = 5.5 Hz), 123.9 (q, $J$ = 274.1 Hz), 111.7 (d, $J$ = 1.9 Hz), 26.2, 17.6 (d, $J$ = 1.7 Hz); $^{19}$F NMR (471 MHz, CDCl$_3$) δ -60.7; $^{125}$Te NMR (158 MHz, CDCl$_3$) δ 720.7 (q, $J$ = 99.5 Hz); MS (APCI–TOF): [M]$^+$ m/z calcd for (C$_7$H$_4$F$_3$)Te(OH)$_2$: 308.94, [M]$^+$; found: 308.94, [M]$^+$ m/z calcd for C$_7$H$_4$F$_3$Te: 274.94, [M]$^+$; found: 274.93.

O-Methyl Te-(2-(trifluoromethyl)phenyl) carbonotelluroate (6c)

Synthesis: According to GP1, starting from sodium borohydride (28 mg, 0.8 mmol), 1,2-bis(2-(trifluoromethyl)phenyl)ditellane (122 mg, 0.22 mmol) and methylchloroformate (43 µL, 0.56 mmol). The product is unstable and forms side-products.

Yield 92%, 137 mg.

aspect pale yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) δ 8.19 (dd, $J$ = 7.5, 2.5 Hz, 1H), 7.73 (dd, $J$ = 7.5, 2.5 Hz, 1H), 7.50 – 7.41 (m, 2H), 3.88 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 158.1 (d, $J$ = 3.1 Hz), 142.8, 134.7 (q, $J$ = 30.1 Hz), 132.7 – 132.1 (m), 129.1, 126.7 (q, $J$ = 5.4 Hz), 123.7 (q, $J$ = 274.0 Hz), 111.6 (d, $J$ = 1.7 Hz), 54.6; $^{19}$F NMR (282 MHz, CDCl$_3$) δ -60.0; $^{125}$Te NMR (158 MHz, CDCl$_3$) δ 795.5 (q, $J$ = 107.4 Hz); MS (APCI–TOF): [M]$^+$ m/z calcd for (C$_7$H$_4$F$_3$)Te(OH)$_2$: 308.94, [M]$^+$; found: 308.94, [M]$^+$ m/z calcd for C$_7$H$_4$F$_3$Te: 274.94, [M]$^+$; found: 274.93.
(Difluoromethyl)(2-(trifluoromethyl)phenyl)tellane (6d)

Synthesis: According to GPX, starting from sodium borohydride (22 mg, 0.56 mmol), 1,2-bis(2-(trifluoromethyl)phenyl)ditellane 4 (62 mg, 0.11 mmol) and dibromodifluoromethane (62 µL, 0.68 mmol). The product is unstable and decompose very quickly.

Yield 84%, 74 mg.

**aspect** pale yellow oil; \(^1^H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.14 (d, \(J = 8.0\) Hz, 1H), 7.79 (dd, \(J = 7.5, 1.5\) Hz, 1H), 7.61 (t, \(J = 51.5\) Hz, 1H), 7.57 – 7.52 (m, 1H), 7.47 (td, \(J = 7.5, 1.5\) Hz, 1H); \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -60.3, -90.9; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 143.1, 135.3 (d, \(J = 30.1\) Hz), 132.8 (d, \(J = 1.2\) Hz), 129.4, 126.9 (d, \(J = 5.4\) Hz), 126.9 – 118.8 (m), 108.0, 104.0 (tq, \(J = 296.1, 2.7\) Hz).

Phenyl(2-(trifluoromethyl)phenyl)tellane (6e)

Synthesis: According to GP2, starting from 1,2-bis(2-(trifluoromethyl)phenyl)ditellane 4 (40 mg, 0.091 mmol), phenylboronic acid (23 mg, 0.192 mmol), iodine (0.23 mg, 0.000913, 10 mol%) and DMSO (0.29 mg, 0.37 mmol).

Yield 84%, 53 mg.

**aspect** colorless oil; \(^1^H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.91 (d, \(J = 6.5\) Hz, 2H), 7.63 (dd, \(J = 8.0\) Hz, 1H), 7.44 (mt, \(J = 7.5\) Hz, 1H), 7.33 (t, \(J = 7.5\) Hz, 3H), 7.26 (t, \(J = 9.0\) Hz, 1H), 7.16 (t, \(J = 7.5\) Hz, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 141.2, 136.9, 132.6 (q, \(J = 30.6\) Hz), 132.2 (d, \(J = 1.2\) Hz), 130.1, 129.3, 127.0 (q, \(J = 6.3\) Hz), 126.9, 124.3 (q, \(J = 274.7\) Hz), 115.7 (d, \(J = 1.6\) Hz), 113.8 (q, \(J = 4.0\) Hz); \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -61.8; \(^{125}\)Te NMR (189 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 728.2 (q, \(J = 162.1\) Hz); MS (ESI–TOF): \(m/z\) calcd for \(\text{(C}_7\text{H}_4\text{F}_3\text{)Te(C}_6\text{H}_5\text{)(OH)}^+\): 368.97. \([M]^+\); found: 368.97.
(3,5-Bis(trifluoromethyl)phenyl)(2-(trifluoromethyl)phenyl)tellane (6f)

Synthesis: According to GP2, starting from 1,2-bis(2-(trifluoromethyl)phenyl)ditellane 4 (60 mg, 0.11 mmol), (3,5-bis(trifluoromethyl)phenyl)boronic acid (60 mg, 0.23 mmol), iodine (3 mg, 0.011 mmol, 10 mol%) and DMSO (0.17 g, 0.22 mmol). Yield 69%, 70 mg.

aspect colorless oil; ^1H NMR (500 MHz, CDCl₃) δ 8.20 (s, 2H), 7.86 (s, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 7.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H); ^13C NMR (126 MHz, CDCl₃) δ 139.4, 139.1, 133.8 (q, J = 30.5 Hz), 132.9 (d, J = 1.2 Hz), 132.7 (q, J = 33.4 Hz), 128.5, 127.4 (q, J = 5.3 Hz), 125.1, 122.9 (dd, J = 7.3, 3.6 Hz), 122.8 (q, J = 273.3 Hz), 116.4 (t, J = 3.6 Hz), 113.2 (d, J = 1.6 Hz); ^19F NMR (282 MHz, CDCl₃) δ -61.1, -62.9; ^125Te NMR (158 MHz, CDCl₃) δ 779.5 (q, J = 146.9 Hz); MS (MALDI-TOF): m/z calcd for C₁₅H₁₇F₉Te+: 487.95 [+M]+; found: 487.96.

(3,5-Dimethoxyphenyl)(2-(trifluoromethyl)phenyl)tellane (6g)

Synthesis: According to GP2, starting from 1,2-bis(2-(trifluoromethyl)phenyl)ditellane 4 (60 mg, 0.11 mmol), (3,5-dimethoxyphenyl)boronic acid (43 mg, 0.24 mmol), iodine (3 mg, 0.011 mmol, 10 mol%) and DMSO (0.17 g, 0.22 mmol). Yield 55%, 49 mg.

aspect colorless oil; ^1H NMR (500 MHz, CDCl₃) δ 7.64 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 7.5 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 7.19 (t, J = 8.0 Hz, 1H), 7.05 (d, J = 2.5 Hz, 2H), 6.48 (t, J = 2.5 Hz, 1H), 3.79 (s, 6H); ^13C NMR (126 MHz, CDCl₃) δ 161.4, 136.9, 132.5 (q, J = 30.6 Hz), 132.2, 127.0 (q, J = 5.2 Hz), 126.95, 124.3 (q, J = 274.2 Hz), 118.8, 115.7, 114.2 (q, J = 4.2 Hz), 102.2, 55.6; ^19F NMR (282 MHz, CDCl₃) δ -61.8; ^125Te NMR (158 MHz, CDCl₃) δ 760.1 (q, J = 167.1 Hz); HRMS (ESI-TOF): m/z calcd for C₁₅H₁₄F₃O₂Te+: 413.0003. [M+H]+; found: 413.0005.
1,2-Bis(2,6-difluorophenyl)ditellane (7)

Synthesis: According to the literature, starting from grey tellurium powder (0.29 g, 3.7 mmol), 1,3-difluoro-5-iodobenzene (0.24 g, 0.98 mmol) and from t-butyllithium in hexane (1.7 M, 1.2 mL, 2.0 mmol). Yield 17%, 40 mg.

m.p. 82-84°C, aspect red solid; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.33 – 7.26 (m, 2H), 6.94 – 6.87 (m, 4H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.52 (dd, J = 245.3, 8.5 Hz), 132.72 (t, J = 9.9 Hz), 111.01 – 110.41 (m), 84.41 (t, J = 32.9 Hz); $^{19}$F NMR (471 MHz, CDCl$_3$) δ -86.20; $^{125}$Te NMR (158 MHz, CDCl$_3$) δ 215.63 (t, J = 45.5 Hz); HRMS (ESI–TOF): m/z calcd for C$_{12}$H$_6$F$_4$Te$_2$+: 485.8525. [M]$^+$; found: 485.8500.

4-(Fluoromethyl)-1,1'-biphenyl (9)

Selectfluor$^\text{TM}$ (1.26 g, 3.56 mmol), glycine (0.27 g, 3.56 mmol) and 4-methyl-1,1'-biphenyl (0.30 g, 1.78 mmol) were successively added in a mixture of acetonitrile-water (53:47, 20 mL) and were stirred for 5 min. AgNO$_3$ (60 mg, 0.36 mmol, 20 mol%) was added in one portion. The mixture was heated to 35°C for 24 h. Upon completion, the reaction was diluted with ethyl acetate (50 mL) and quenched with NaHCO$_3$ (20 mL). The aqueous phase was extracted with ethyl acetate (3 x 10 mL) and the combined organic layers were washed with brine (80 mL), dried over MgSO$_4$, filtered, and concentrated under vacuum. The crude material was purified by chromatography on a silica gel column with petroleum ether as the eluent to yield the desired fluorinated product 9. Yield 78%, 258 mg. Data were in complete agreement with the literature values.

aspect white solid; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.64 (dd, J = 12.3, 7.7 Hz, 4H), 7.53 – 7.45 (m, 4H), 7.40 (t, J = 7.4 Hz, 1H), 5.45 (d, J = 47.9 Hz, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 141.85 (d, J = 3.2 Hz), 140.70 (d, J = 1.3 Hz), 135.24 (d, J = 17.1 Hz), 128.96, 128.20 (d, J = 5.7 Hz), 127.67, 127.48 (d, J = 1.5 Hz), 127.28 (d, J = 0.9 Hz), 84.53 (d, J = 165.9 Hz); $^{19}$F NMR (282 MHz, CDCl$_3$) δ -206.14.

---

Lithium 2-(trifluoromethyl)benzenetellurolate (10-Li)

To a solution of 4 (9 mg, 0.017 mmol) in THF in a Schlenck tube, under inert atmosphere, LiBH₄ (2M in THF, 85 μL, 0.17 mmol) was added and the mixture was stirred during 2 h, at room temperature (fading of the mixture was observed from red to pale yellow). Then, the solvent was removed using Schlenck line techniques and after 1 h of drying under vacuum, the mixture was solubilized with THF-d₈. The resulting mixture was transferred in a NMR Young tube for NMR monitoring. Intermediate 10-BH₃Li was quantitatively observed. The conversion of 10-BH₃Li into 10-Li was observed after 16 days (87% conversion according to ¹H NMR). Due to their high instability, the species 10-BH₃Li and 10-Li could be only characterized by means of NMR spectroscopy. ¹¹B NMR data of 10-BH₃Li is in complete agreement with the literature value on similar intermediate.⁵

Lithium ((2-(trifluoromethyl)phenyl)tellanyl)trihydroborate (10-BH₃Li)

¹H NMR (300 MHz, THF-d₈) δ 8.35 (d, J = 7.7 Hz, 1H), 7.32 (dd, J = 7.7, 1.6 Hz, 1H), 7.13 – 6.95 (m, 2H); ¹⁹F NMR (471 MHz, THF-d₈) δ -63.43; ¹¹B NMR (96 MHz, THF-d₈) δ -33.98 (q, J = 104.1 Hz); ¹²⁵Te NMR (158 MHz, THF-d₈) δ 9.56.

Lithium 2-(trifluoromethyl)benzenetellurolate (10-Li)

¹H NMR (300 MHz, THF-d₈) δ 8.48 – 8.36 (m, 2H), 7.17 (dd, J = 7.9, 1.6 Hz, 1H), 6.91 – 6.78 (m, 1H), 6.61 – 6.44 (m, 1H); ¹⁹F NMR (282 MHz, THF-d₈) δ -63.12; ¹²⁵Te NMR (158 MHz, THF-d₈) δ 105.77.

---

III. NMR study

A. Variable temperature (VT) NMR of reference probes 4, 6e and 6f

$^{4}J_{\text{Te-F}}$ was extracted from the two satellite peaks of singlet peak in $^{19}$F NMR. As a confirmation of $^{19}$F NMR data, $^{4}J_{\text{Te-F}}$ values were extracted a second time using $^{125}$Te NMR. Data were collected in the temperature range from 193 K to 323 K, in CD$_{2}$Cl$_{2}$ with a sample concentration of 20 mM in standard NMR tube.

1. VT NMR of 4

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$^{4}J_{\text{Te-F}}$ (Hz)</th>
<th>$\delta_{\text{Te}}$ (ppm)</th>
<th>$\delta_{\text{F}}$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>233</td>
<td>167.21</td>
<td>424.77</td>
<td>n.d.</td>
</tr>
<tr>
<td>248</td>
<td>167.16</td>
<td>430.07</td>
<td>-61.76</td>
</tr>
<tr>
<td>260</td>
<td>167.07</td>
<td>435.83</td>
<td>-61.73</td>
</tr>
<tr>
<td>273</td>
<td>166.96</td>
<td>443.44</td>
<td>-61.70</td>
</tr>
<tr>
<td>286</td>
<td>166.80</td>
<td>n.d.</td>
<td>-61.67</td>
</tr>
<tr>
<td>298</td>
<td>166.50</td>
<td>n.d.</td>
<td>-61.64</td>
</tr>
<tr>
<td>308</td>
<td>166.22</td>
<td>n.d.</td>
<td>-61.62</td>
</tr>
</tbody>
</table>

Table S1. VT NMR data for compound 4

Figure S1. NMR data set of 4 for $^{19}$F NMR (A) and $^{125}$Te NMR (B).
## 2. VT NMR of 6e

### Table S2. VT NMR data for compound 6e

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$^4J_{\text{Te-F}}$ (Hz)</th>
<th>$\delta_{\text{Te}}$ (ppm)</th>
<th>$\delta_{\text{F}}$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>233</td>
<td>165.13</td>
<td>713.29</td>
<td>-63.2</td>
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<tr>
<td>253</td>
<td>164.75</td>
<td>717.85</td>
<td>-63.13</td>
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<td>273</td>
<td>163.88</td>
<td>722.47</td>
<td>-63.05</td>
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<tr>
<td>298</td>
<td>162.45</td>
<td>728.93</td>
<td>-62.96</td>
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<td>323</td>
<td>161.90</td>
<td>734.37</td>
<td>-62.86</td>
</tr>
</tbody>
</table>

*Maximum variation of 2.8% over a temperature range of 90 K*

### Figure S2. NMR data set of 6e for $^{19}$F NMR (A) and $^{125}$Te NMR (B)
3. VT NMR of 6f

Table S3. VT NMR data for compound 6f

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$J_{\text{Tc-F}}$ (Hz)</th>
<th>$\delta_{\text{Tc}}$ (ppm)</th>
<th>$\delta_{\text{F}}$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>193</td>
<td>150.93</td>
<td>750.61</td>
<td>-62.53</td>
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<tr>
<td>233</td>
<td>150.33</td>
<td>758.63</td>
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<tr>
<td>248</td>
<td>150.10</td>
<td>765.51</td>
<td>-62.36</td>
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<tr>
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<td>147.79</td>
<td>772.36</td>
<td>-62.29</td>
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<td>298</td>
<td>144.39</td>
<td>779.4</td>
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<td>308</td>
<td>142.77</td>
<td>782.21</td>
<td>-62.19</td>
</tr>
</tbody>
</table>

Figure S3. NMR data set of 6f for $^{19}$F NMR (A) and $^{125}$Te NMR (B)
B. Variable temperature (VT) NMR of compounds 2, 5a and 5c

Compounds 2, 5a and 5c were dissolved in CD$_2$Cl$_2$ with a concentration of 20 mM and transferred in standard NMR tube. The tube was inserted into a controlled NMR probe and $^1$H, $^{125}$Te and $^{19}$F NMR spectra were collected at various temperature between 193 K and 308 K.

1. VT NMR of 2

![Diagram of compound 2](image)

Table S4. VT NMR data for compound 2

<table>
<thead>
<tr>
<th>T (K)</th>
<th>1/T (K$^{-1}$)</th>
<th>$^4J_{Te-F}$ (Hz)</th>
<th>$\delta_{Te}$ (ppm)</th>
<th>$\delta_{F}$ (ppm)</th>
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</thead>
<tbody>
<tr>
<td>248</td>
<td>0.00403226</td>
<td>155.26</td>
<td>329.84</td>
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<tr>
<td>260</td>
<td>0.00384615</td>
<td>149.71</td>
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<td>-203.16</td>
</tr>
<tr>
<td>273</td>
<td>0.003663</td>
<td>143.11</td>
<td>337.35</td>
<td>-203.19</td>
</tr>
<tr>
<td>286</td>
<td>0.0034965</td>
<td>137.08</td>
<td>349.01</td>
<td>-203.95</td>
</tr>
<tr>
<td>298</td>
<td>0.0033557</td>
<td>131.59</td>
<td>344.69</td>
<td>-203.88</td>
</tr>
<tr>
<td>308</td>
<td>0.00324675</td>
<td>127.64</td>
<td>347.63</td>
<td>-204.13</td>
</tr>
</tbody>
</table>

2. VT NMR of 5a

![Diagram of compound 5a](image)

Table S5. VT NMR data for compound 5a

<table>
<thead>
<tr>
<th>T (K)</th>
<th>1/T (K$^{-1}$)</th>
<th>$^4J_{Te-F}$ (Hz)</th>
<th>$\delta_{Te}$ (ppm)</th>
<th>$\delta_{F}$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>223</td>
<td>0.0044843</td>
<td>152.16</td>
<td>598.73</td>
<td>-203.04</td>
</tr>
<tr>
<td>248</td>
<td>0.00403226</td>
<td>135.61</td>
<td>591.67</td>
<td>-203.90</td>
</tr>
<tr>
<td>273</td>
<td>0.003663</td>
<td>122.54</td>
<td>594.18</td>
<td>-204.78</td>
</tr>
<tr>
<td>298</td>
<td>0.0033557</td>
<td>112.10</td>
<td>597.17</td>
<td>-205.43</td>
</tr>
<tr>
<td>308</td>
<td>0.00324675</td>
<td>108.63</td>
<td>598.49</td>
<td>-205.66</td>
</tr>
</tbody>
</table>

3. TV of 5c

![Diagram of compound 5c](image)

Table S6. VT NMR data for compound 5c

<table>
<thead>
<tr>
<th>T (K)</th>
<th>1/T (K$^{-1}$)</th>
<th>$^4J_{Te-F}$ (Hz)</th>
<th>$\delta_{Te}$ (ppm)</th>
<th>$\delta_{F}$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>0.00384615</td>
<td>142.87</td>
<td>640.80</td>
<td>-202.22</td>
</tr>
<tr>
<td>273</td>
<td>0.003663</td>
<td>136.49</td>
<td>642.79</td>
<td>-202.59</td>
</tr>
<tr>
<td>286</td>
<td>0.0034965</td>
<td>130.32</td>
<td>644.90</td>
<td>-202.93</td>
</tr>
<tr>
<td>298</td>
<td>0.0033557</td>
<td>124.20</td>
<td>646.92</td>
<td>-203.23</td>
</tr>
<tr>
<td>308</td>
<td>0.00324675</td>
<td>119.50</td>
<td>648.69</td>
<td>-203.46</td>
</tr>
</tbody>
</table>
4. NMR data set for 2

Figure S4. VT $^{19}$F NMR of 2

Figure S5. VT $^{125}$Te NMR of 2
5. NMR data set for 5a

Figure S6. VT $^{19}$F NMR of 5a

Figure S7. VT $^{125}$Te NMR of 5a
6. NMR data set for 5c

Figure S8. VT $^{19}$F NMR of 5c

Figure S9. VT $^{125}$Te NMR of 5c
C. Determination of thermodynamic parameters

Optimal values of $^{4}J_{Te-F(syn)}$ leading to a linear fit of the equation below:

\[
\Delta H - T\Delta S = -RT\ln\left(\frac{^{4}J_{Te-F(anti)}}{^{4}J_{Te-F(syn)} - ^{4}J_{Te-F}}\right)
\]

**Compound 2**

For $^{4}J_{Te-F(anti)}$=-20 Hz: $^{4}J_{Te-F(syn)}$=-200 Hz

![Graph showing linear fit of thermodynamic parameters](image)

\[
y = 21.3310x - 7578.9983
\]

$R^2 = 0.9996$
For $^4J_{Te-F}^{\text{anti}} = +20$ Hz: $^4J_{Te-F}^{\text{syn}} = -208$ Hz
Compound 5a

For $^4J_{Te-F(anti)}=-20$ Hz: $^4J_{Te-F(syn)}=-298$ Hz
For $^4J_{Te-F(\text{anti})}=+20$ Hz; $^4J_{Te-F(\text{syn})}=-419.5$ Hz
Compound 5c

For $J_{Te-F(\text{anti})} = -20$ Hz: $J_{Te-F(\text{syn})} = -174.5$ Hz

\[ y = 29.489x - 10599 \]
\[ R^2 = 0.9998 \]
For \( \Delta J_{\text{Te-F(anti)}} = +20 \text{ Hz} \); \( \Delta J_{\text{Te-F(syn)}} = -179 \text{ Hz} \)

**Table S7.** Thermodynamic parameters of the anti/syn equilibrium for compounds 2, 5a and 5c

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>5a</th>
<th>5c</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta H ) (kJ mol(^{-1}))</td>
<td>-7.58(6)</td>
<td>-6.34(5)</td>
<td>-4.530(7)</td>
</tr>
<tr>
<td>( \Delta S ) (J K(^{-1}) mol(^{-1}))</td>
<td>-21.3(2)</td>
<td>-15.5(2)</td>
<td>-20.67(3)</td>
</tr>
<tr>
<td>( r^2 )</td>
<td>0.99960</td>
<td>0.99942</td>
<td>0.999995</td>
</tr>
<tr>
<td>( \Delta G(298\text{K}) ) (kJ mol(^{-1}))</td>
<td>-1.2</td>
<td>-1.7</td>
<td>+1.6</td>
</tr>
</tbody>
</table>
D. \(^{125}\text{Te}\) Titration experiments with \(\text{Et}_3\text{PO}\)

For pipetting Hamilton®-syringes were used. All experiments were conducted at ambient temperature (298.5 K) and in NMR tubes. For each sample, a set amount of the fluoro-derivative 5c or 6f was weighted on an analytical balance into a volumetric flask and a specific amount of \(\text{Et}_3\text{PO}\) was weighted in another one. They were subsequently diluted carefully in the volumetric flask with the corresponding solvent of titration (dried cyclohexane-\(d_{12}\)). Each mixture was then agitated for at least 5 min to fully dissolve all solids and the solution was mixed thoroughly prior to transferring to NMR tubes. For each titration experiment, the concentration of 5c/6f is kept constant (0.020 M, 0.45 mL before dilution) whereas the concentration of \(\text{Et}_3\text{PO}\) is increased from 0.0 M up to 0.4 M. The NMR tube was manually agitated 5 min before the acquisition of \(^{125}\text{Te}\). \(^1\text{H}\) NMR was systematically recorded to check the homogeneity of the solution in the tube. Throughout each titration experiment all parameters of the NMR spectrometer remained constant.

1) \(^{125}\text{Te}\) NMR in \(\text{C}_6\text{D}_{12}\) of 5c alone and after addition of \(\text{Et}_3\text{PO}\)

![Graph showing \(^{125}\text{Te}\) NMR results](image-url)
2) $^{125}$Te NMR in C$_6$D$_{12}$ of 6f alone and after addition of Et$_3$PO

![NMR Spectra]

Equivalent of OPEt$_3$:
- 10 equivalents
- 5 equivalents
- 1 equivalent
- 0 equivalents

Spectral peaks at:
- 790.7 ppm
- 788.5 ppm
- 786.3 ppm
- 783.7 ppm

Chemical shifts and splitting patterns are marked in the spectra.
IV. Theoretical calculations

A. General information

Molecular geometries of compounds 5a,c and 6e,f were optimized at the DFT level of theory (B3LYP functional completed with D3 dispersion correction\(^6\) Def2TZVPP basis set) using the Gaussian09 software.\(^7\) Conformational analysis was performed by scanning torsion angles about the CH\(_2\)F—Ar and Te—Ar bonds. Frequency calculations were performed in order to check that true energy minima were obtained.

Isosurface of electron density (\(\rho=0.001\) a.u.) mapped with the corresponding total electrostatic potential were calculated and drawn with AIMAll software;\(^8\) characterization of \(V_{S,max}\) extrema of the EP was performed with MultiWfn programs.\(^9\)

Topological analysis of the DFT calculated electron density was performed with AIMAll software.\(^7\)

Spin-spin coupling constants were calculated with ReSpect software\(^10\) using the DFT optimized molecular structures. Due to the presence of heavy Te atom, relativistic four-component Hamiltonian was considered (PBE0 functional) and triple zeta uncontracted Dyall basis sets\(^11\) were employed for all elements. Solvent effects are not included in the calculations.

---


\(^7\) M. J. Frisch et al. Gaussian 09 (Gaussian, Inc., Wallingford CT, 2009).


\(^10\) ReSpect, version 5.1.0 (2019); Relativistic Spectroscopy DFT program of authors M. Repisky, S. Komorovsky, V. G. Malkin, O. L. Malkina, M. Kaupp, K. Ruud, \(i^\)th contributions from R. Bast, U. Ekstrom, M. Kadek, S. Knecht, L. Konecny, E. Malkin, I. Malkin-Ondik, (see http://www.respectprogram.org)

B. Conformational analysis and Electrostatic Potential Surface analysis for 5a, 5c, 6e and 6f

Figure S10. Conformational analysis of 5a, 5c, 6e and 6f
Table S8. $V_{s,max}$ values for 5a and 5c

<table>
<thead>
<tr>
<th>Conformation</th>
<th>$\Delta G$ (kJ/mol)</th>
<th>$\sigma$(CH$_2$FPh-Te)</th>
<th>$\sigma$(Ph-Te)</th>
<th>$\Delta G$ (kJ/mol)</th>
<th>$\sigma$(CH$_2$FPh-Te)</th>
<th>$\sigma$((CF$_3$)$_2$Ph-Te)</th>
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<tbody>
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<td>A</td>
<td>0</td>
<td>12.71</td>
<td>/</td>
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<td>25.95</td>
<td>/</td>
</tr>
<tr>
<td>B</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
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<tr>
<td>F</td>
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<td>14.13</td>
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</table>

Table S9. $V_{s,max}$ values for 6e and 6f

<table>
<thead>
<tr>
<th>Conformation</th>
<th>$\Delta G$ (kJ/mol)</th>
<th>$\sigma$(CH$_2$FPh-Te)</th>
<th>$\sigma$(Ph-Te)</th>
<th>$\Delta G$ (kJ/mol)</th>
<th>$\sigma$(CH$_2$FPh-Te)</th>
<th>$\sigma$((CF$_3$)$_2$Ph-Te)</th>
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<td></td>
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</tr>
<tr>
<td>F</td>
<td>12.67</td>
<td>15.54</td>
<td>15.52</td>
<td></td>
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</tbody>
</table>

NB: $\sigma$(XX-Te) denotes the Te sigma hole in the prolongation of the C$_{XX}$—Te bond.
Figure S11. ESP maps for compounds 5a, 5c, 6e and 6f
C. **Topological analysis of the DFT calculated electron density of 5c.**

The atoms are shown as large spheres (C: grey; F: green; Te: orange; H: white) whereas the bond critical points are shown as small green spheres. The bond path between the F and Te atoms is shown as a dotted line.

![Figure S12. Topological analysis of 5c](image)

**Table S10.** Topological analysis of the DFT calculated electron density: properties at the Te···F bond critical point.

<table>
<thead>
<tr>
<th>Compound</th>
<th>DI$^a$</th>
<th>$\rho(r)$ a.u.</th>
<th>$\nabla^2\rho(r)$ a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>0.06</td>
<td>0.0092$^b$</td>
<td>+0.0378</td>
</tr>
<tr>
<td>5c</td>
<td>0.07</td>
<td>0.0097</td>
<td>+0.0387</td>
</tr>
<tr>
<td>6e</td>
<td>0.08</td>
<td>0.0113</td>
<td>+0.0464</td>
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<tr>
<td>6f</td>
<td>0.08</td>
<td>0.0116</td>
<td>+0.0471</td>
</tr>
</tbody>
</table>

$^a$ Delocalization index between F and Te atoms.

$^b$ For comparison, $\rho(r)$=0.1192 a.u. and $\nabla^2\rho(r)$=+0.0073 a.u. for the Te-C$_{Ph}$ bond.

D. **NMR Calculations**

Spin-spin coupling constants were calculated along the potential energy scan of the C-C-C-F torsion angle in 10-Te anions in vacuum (Fig. S13). The obtained results show that when F is *anti* to Te the coupling lies between +10 and +30 Hz i.e. +20 Hz on average. As soon as F approaches Te atom (C-C-C-F<100°) the algebraic Te-F coupling sharply decreases to zero and continues to decrease down to ~-130Hz in the syn conformation. Such large negative value of the coupling is a signature of a direct Te-F coupling (kind of long $^1J_{Te-F}$), an exchange interaction (mediating the coupling) taking place between the involved atoms when they approach each other.
Fig. S13. Relative relativistic energy and calculated algebraic $J_{Te\cdots F}$ as a function of the C-C-C-F torsion angle (syn: 0°; anti: 180°).

Coupling constants were also computed with the same level of theory for the three conformations found for compounds 5a & 5c (Table S11).

**Table S11.** Calculated coupling constants for 5a, 5c, 6e and 6f

<table>
<thead>
<tr>
<th>Conformation</th>
<th>5a</th>
<th>5c</th>
<th>6e</th>
<th>6f</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-253.6</td>
<td>-245.6</td>
<td>(-425.8; -13.6; -57.2) -165.6</td>
<td>(-12.4; -418; -53.8) -161.7</td>
</tr>
<tr>
<td>B</td>
<td>-34.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-13.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>19.0</td>
<td>19.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>-15.1</td>
<td>-19.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>-8.9</td>
<td></td>
<td>(-29.2; -2.1; -6.3) -12.5</td>
<td></td>
</tr>
</tbody>
</table>

Again a large negative coupling is obtained for the syn conformation, displaying a Te\cdots F direct intramolecular $\sigma$-hole interaction.

In conclusion, $J$ coupling constants in eq. 1 have to be considered as algebraic values, and $4J_{Te\cdots F(syn)}$ is larger in absolute value than $4J_{Te\cdots F(anti)}$, the first one being clearly negative (due to a kind of long $1J$ interaction) while the second one may be either positive or negative and of smaller amplitude.
V. NMR Spectra

A. Compound 1

$^1$H NMR

$^{13}$C NMR
B. Compound 2

$^1$H NMR

$^{13}$C NMR
$^{125}\text{Te NMR}$

$^{79}\text{F NMR}$
Non decoupled $^{19}$F NMR

$J_{(\text{F-H})} = 28.2 \text{ Hz}$
C. Compound 4

NMR spectra

\(^1\text{H}\) NMR spectra

\(^{13}\text{C}\) NMR spectra
D. Compound 5a

NMR spectra $^1$H

$^1$H NMR

$^1$C NMR
E. Compound 5b

$^1$H NMR

$^{13}$C NMR
$^{19}$F NMR

$\text{pH-62-2003079-19F.10.b.fd}$
F. Compound 5c

$^1$H NMR

$^{13}$C NMR
G. Compound 5d

$^1$H NMR

$^{13}$C NMR
$^{125}$Te NMR

$^{19}$F NMR
H. Compound 5e

$^1$H NMR

$^{13}$C NMR
I. Compound 6a

$^1$H NMR

$^{13}$C NMR
J. Compound 6b

$^1$H NMR

$^{13}$C NMR
$^{125}\text{Te} \text{ NMR}$

$^{13}\text{C},^{125}\text{Te} \text{ HMQC NMR}$
K. Compound 6c

$^1$H NMR

$^{13}$C NMR
$^{125}\text{Te} \text{ NMR}$

$^7$F$_7$, TeCOOME$_2$.9d
$^{125}$Te
L. Compound 6d

$^1$H NMR

$^{13}$C NMR
M. Compound 6e

$^1$H NMR

$^{13}$C NMR
N. Compound 6f

$^1$H NMR

$^{13}$C NMR
$^{19}$F NMR

$^{125}$Te NMR
O. Compound 6g

$^1$H NMR

$^{13}$C NMR
$^{19}$F NMR

$^{125}$Te NMR
P. Compound 7

$^1$H NMR

$^{13}$C NMR
$^{19}$F NMR

$^{125}$Te NMR
Q. **Compound 9**

**$^1H$ NMR**

$p$-36-191205.11.jpg

**$^{13}C$ NMR**

$p$-36-191205.11.jpg
$^{19}$F NMR

p-36-191205-16.10.34d
R. Intermediates 10-BH$_3$Li and 10-Li

$^1$H NMR (THF-$d_8$, 298 K, after 1h)

$^{11}$B NMR (THF-$d_8$, 298 K, after 1h)
$^{125}$Te NMR (THF-d$_8$, 298 K, after 1h)

$^{19}$F NMR (THF-d$_8$, 298 K, 1h)
$^1$H NMR (THF-d$_8$, 298 K, after 16 days)

$^{11}$B NMR (THF-d$_8$, 298 K, after 16 days)
$^{125}$Te NMR (THF-d$_8$, 298 K, after 16 days)

$^{19}$F NMR (THF-d$_8$, 298 K, after 16 days)