SUPPLEMENTARY INFORMATION

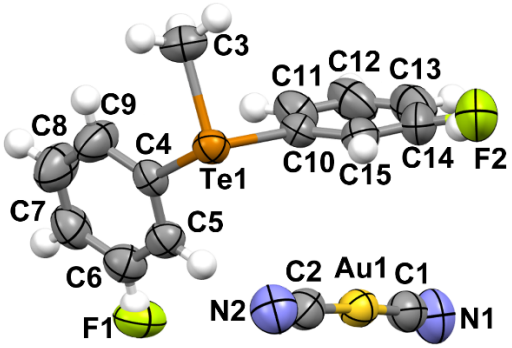


Figure 1. Ellipsoid plot of the asymmetric unit of salt **1** (50% probability).

Table 1. Crystal data and structure refinement for **1.**

Empirical formula	$C_{15}H_{12}AuFN_2Te$
Formula weight	563.83
Temperature/K	298.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.5046(4)
b/Å	13.2604(2)
c/Å	13.3332(3)
α/°	90
β/°	109.638(3)
γ/°	90
Volume/Å^3	1582.71(8)
Z	4
ρ_{calc}g/cm^3	2.366
μ/mm^{-1}	31.743
F(000)	1024.0
Crystal size/mm^3	0.11 × 0.1 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.7 to 133.75
Index ranges	-10 ≤ h ≤ 8, -15 ≤ k ≤ 14, -15 ≤ l ≤ 15
Reflections collected	8706
Independent reflections	2484 [R_{int} = 0.0362, R_{sigma} = 0.0295]
Data/restraints/parameters	2484/0/191
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0428, wR_2 = 0.1127
Final R indexes [all data]	R_1 = 0.0457, wR_2 = 0.1164
Largest diff. peak/hole / e Å^{-3}	1.72/-1.28

Table 2. Bond Lengths for **1.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Au1	C1	1.971(10)		C6	F1	1.268(10)
Au1	C2	1.965(9)		C11	C12	1.376(10)
Te1	C4	2.112(6)		C8	C9	1.399(10)
Te1	C10	2.119(8)		C7	C8	1.348 (20)
Te1	C3	2.116(9)		C15	C14	1.357(20)
C4	C5	1.381(10)		C12	C13	1.337(20)

C4	C9	1.372(10)		C13	C14	1.394 (10)
C10	C11	1.381(10)		C14	F2	1.328(20)
C10	C15	1.388(10)		C1	N1	1.130(10)
C5	C6	1.370(10)		C2	N2	1.142(10)
C6	C7	1.392(10)				

Table 3. Bond Angles for **1**.

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
C1	Au1	C2	176.5(4)		F1	C6	C7	118.0(9)
C4	Te1	C10	95.0(3)		C12	C11	C10	119.2(8)
C3	Te1	C4	97.9(3)		C7	C8	C9	121(1)
C3	Te1	C10	93.6(3)		C4	C9	C8	119 (1)
C5	C4	Te1	117.4(5)		C14	C15	C10	119.2(9)
C9	C4	Te1	122.3(6)		C12	C13	C14	118(1)
C9	C4	C5	120.2(8)		C13	C12	C11	122(1)
C11	C10	Te1	122.2(6)		C8	C7	C6	118.9(9)
C11	C10	C15	119.5(7)		C15	C14	C13	122(1)
C15	C10	Te1	118.2(6)		F2	C14	C15	121 (1)
C6	C5	C4	119.4(7)		F2	C14	C13	116(1)
C7	C6	C5	121.1(8)		N2	C2	Au1	179.1(9)
F1	C6	C5	120.9(9)		N1	C1	Au1	176.3(9)

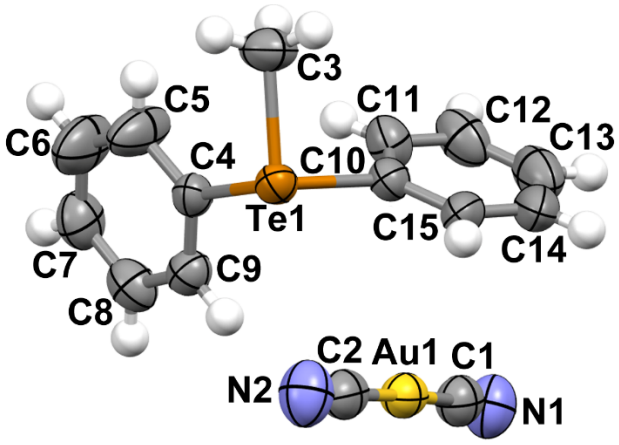


Figure 2. Ellipsoid plot of the asymmetric unit of salt **2** (50% probability)

Table 4. Crystal data and structure refinement for **2**.

Empirical formula	$C_{15}H_{13}AuN_2Te$
Formula weight	545.84
Temperature/K	298.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.2490(2)
b/Å	13.2961(2)
c/Å	13.4912(3)
α/°	90
β/°	108.514(2)

γ/°	90
Volume/Å^3	1573.21(6)
Z	4
ρ_{calc}g/cm^3	2.305
μ/mm^{-1}	31.808
F(000)	992.0
Crystal size/mm^3	0.8 × 0.7 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.594 to 133.582
Index ranges	-10 ≤ h ≤ 9, -15 ≤ k ≤ 15, -16 ≤ l ≤ 15
Reflections collected	16022
Independent reflections	2725 [R_{int}= 0.0529, R_{sigma}= 0.0244]
Data/restraints/parameters	2725/0/174
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0400, wR_2 = 0.1075
Final R indexes [all data]	R_1 = 0.0425, wR_2 = 0.1108
Largest diff. peak/hole / e Å^{-3}	1.32/-1.99

Table 5. Bond lengths for **2**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Te1	C4	2.108(5)		C11	C12	1.374(10)
Te1	C10	2.132(6)		C10	C15	1.376(8)
Te1	C3	2.116(6)		C15	C14	1.374(10)
Au1	C1	1.979(8)		C1	N1	1.131(9)
Au1	C2	1.960(9)		C5	C6	1.392(12)
C4	C9	1.374(9)		C2	N2	1.175(10)
C4	C5	1.363(10)		C6	C7	1.357(12)
C9	C8	1.396(10)		C14	C13	1.327(13)
C8	C7	1.360(11)		C13	C12	1.411(12)
C11	C10	1.384(9)				

Table 6. Bond angles for **2**.

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
C4	Te1	C10	95.3(2)		C15	C10	Te1	118.0(5)
C4	Te1	C3	97.2(3)		C15	C10	C11	121.1(6)
C3	Te1	C10	94.0(3)		C14	C15	C10	117.9(7)
C2	Au1	C1	176.8(3)		N1	C1	Au1	177.6(7)
C9	C4	Te1	117.6(4)		C4	C5	C6	119.4(8)
C5	C4	Te1	122.8(5)		N2	C2	Au1	178.2(6)
C5	C4	C9	119.5(6)		C7	C6	C5	121.2(7)
C4	C9	C8	120.4(6)		C6	C7	C8	119.7(7)
C7	C8	C9	119.7(7)		C13	C14	C15	122.6(8)
C12	C11	C10	119.7(7)		C14	C13	C12	120.1(7)
C11	C10	Te1	120.9(4)		C11	C12	C13	118.6(7)

Table 7. Vibrational data for **1**, **2**, **3a** and **3b**

3b		**2**		**3a**		**1**		Assignment
IR	Raman	IR	Raman	IR	Raman	IR	Raman	
3150 w	3150 w	3149 w	3149 w	3154 vw		3149 vw	3149 w	
3090 m	3090 sh			3091 sh				
		3078 m				3078 w	3078 m	
	3065 s	3068 m		3064 w				
3057 s			3055 s			3056 m	3058 s	$\nu_{CH}(C_6)$
		3045 s				3045 m	3042 m	
		3036 sh	3036 w					
3024 sh	3024 vw		3027 m			3026 w		

2997 w 2957 m 2940 s 2926 sh 2874 m 2859 m	3000 vw 2941 m	2992 w 2960 w 2951 w 2945 w 2929 m 2880 vw 2859 vw	 2945 m 2930 s	2998 vw 2953 w 2918 m 2874 w 2850 m		2953 w 2931 sh 2918 s 2874 w 2850 s	2934 m	$\nu_{CH}(CH_3)$
		2158 m 2137 vvs	2158 s 2137 w			2158 vw 2138 vs	2158 vs 2138 vw	ν_{CN}
 1575 w 1481 m 1438 s 1419 w 1396 w 1337 w	 1578 m 1485 w 1438 w	 1573 m 1477 s 1432 s 1419 m 1390 w 1331 m	 1578 m 1478 w 1421 vw 1394 w 1334 vw	1588 s 1576 m 1474 s 1439 m 1426 m 1414 sh 1336 w	1593 m 1577 m 1479 vw 1441 vvw 1336 vw	1585 s 1575 m 1471 s 1435 m 1416 m 1331 w	1590 vw 1576 w 1480 w 	ν_{C-C}
 1286 w 1269 w		1303 w 1269 w	 1270 vw	1308 w 1285 w 1271 w 1227 m	1309 w 1271 w 1229 w	1301 w 1268 m 1229 m	 1268 w 1229 w	β_{CH}
1240 vw		1220 m						
				1218 m	1218 w	1219 s	1219 sh	ν_{C-F}
	1198 w							
1185 w	1185 w	1179 w	1192 w	1185 w	1188 vw	1185 w	1188 w	δ_{CH3}
1163 vw	1164 w	 1094 w 1065 m 1060 m	 1067 w	1166 w	1168 w 1089 w 1059 w	1162 m 1085 m 1060 m	1160 w 1085 w 1060 w	β_{CH}
1046 vs 1031 vs 1015 vs				1044 vs 1028 vs				ν_{B-F}
	1021 m	1018 m	1022 s		1021 m	1020 m	1021 m	β_{CH}
996 vs	1002 s	996 s	1000 vs	995 vs	1000 vs	997 m	999 vs	Ring
976 sh 915 m 867 m		 966 m 911 m 862 s	 918 w 904 w 864 w	 918 m 876 m		 912 w 861 m		γ_{CH}
845 sh		845 m	847 vw	848 s	851 w	847 m	851 w	ρ_{CH3}
		832 w						γ_{CH}
				787 m		779 m		C-F
 743 s 732 s	767 w 	 723 vs	 740 vw	766 w 736 s	767 m	 730 s		γ_{CH}
687 s	 662 s	685 vs	687 vw 660 s	685 sh 676 m 655 w	 678 vw 659 s	683 m 672 s 653 w	 659 m	φ_{C-C}
613 vw	614 w	613 vw	615 w	614 w	614 w		614 w	α_{C-C-C}
543 vw	544 s	539 w	541 vs	544 w	544 s	538 w	539 s	$\nu_{(CH3)-Te}$
520 m	520 sh							δ_{B-F}
				520 m	523 m	521 m	524 w	
				498 vw				C-F
464 m		458 m	461 w	453 vw		453 m	453 w	
444 w		445 s		438 m				
				430 w				C-F
		427 m				425 vs		
				352 vw	352 w			

			304 sh 298 m				304 m 300 sh	β_{CN}
	281 m							
		269 w	273 m	269 sh	270 s		269 s	$\nu_{symTe-C}$
262 m	259 m	259 m	261 s	258 w	259 sh	258 m	258 vs	$\nu_{asymTe-C}$
	247 m	245 w	240 w	243 sh	243 s	243 w	243 s	
	231 sh	235 w	234 m					
					211 m		210 s	
	186 w	185 m	185 w					
				166 w	166 m	161 m		

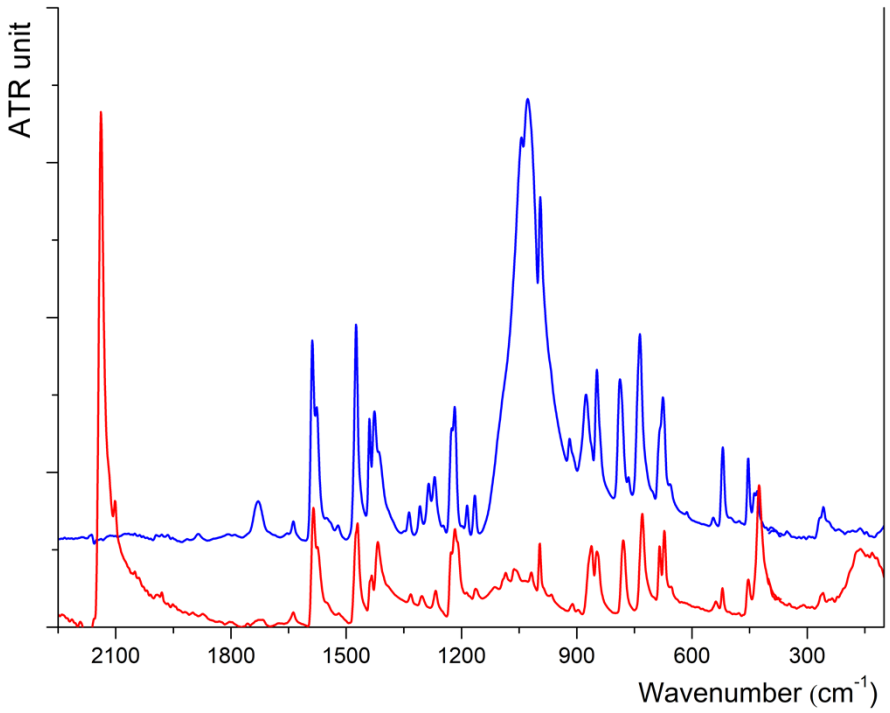


Figure 3. FT-ATR spectra of **1** (in red) and **3a** (in blue).

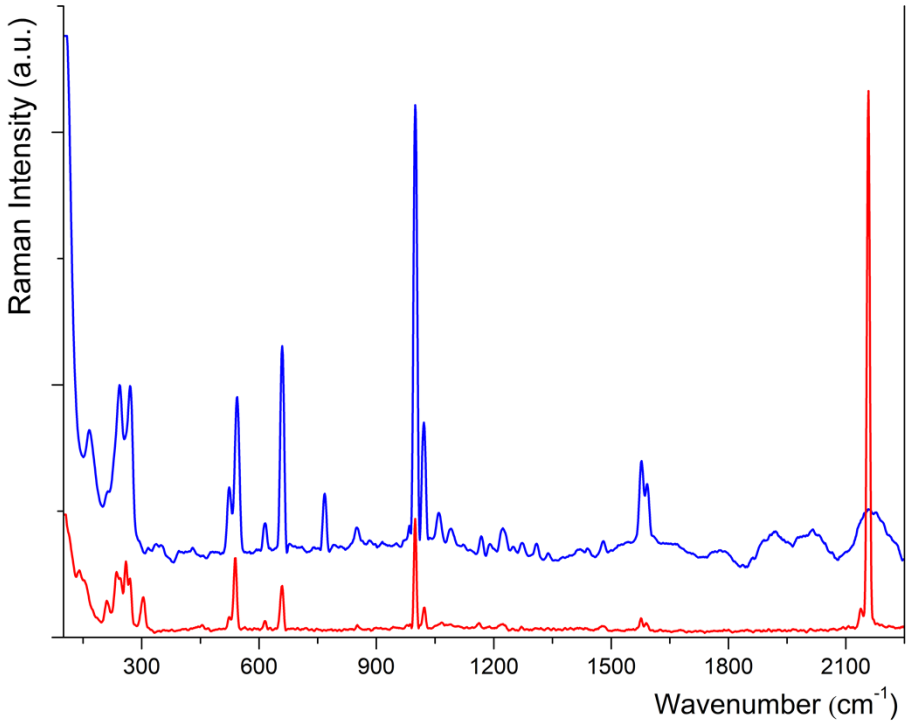


Figure 4. Raman spectra of **1** (in red) and **3a** (in blue).

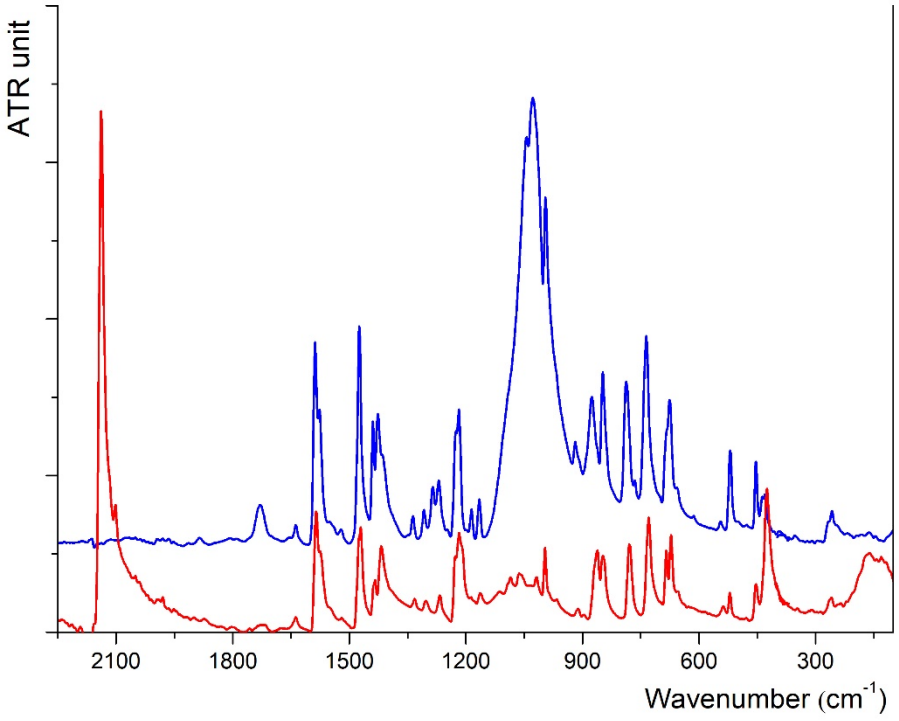


Figure 5. FT-ATR spectra of **2** (in red) and **3b** (in blue).

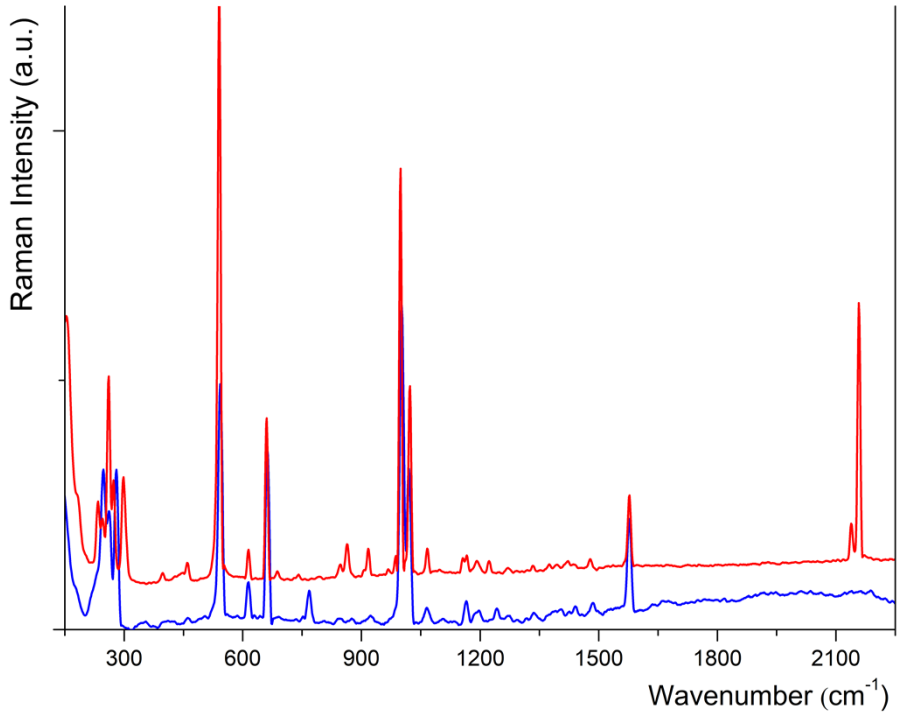
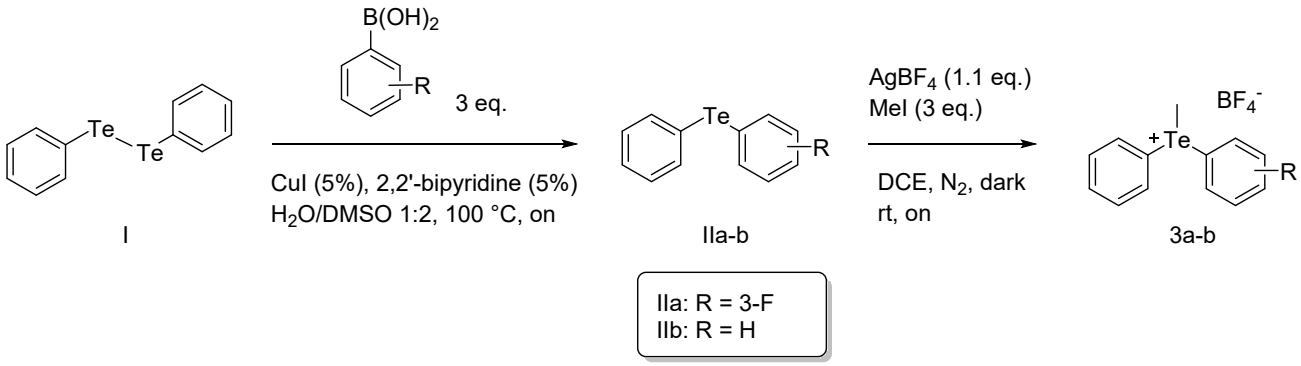


Figure 6. Raman spectra of **2** (in red) and **3b** (in blue).

Synthesis and analysis of compound 3a and 3b



Scheme 1. Synthesis of methyldiaryltelluronium terafluoroborate salts **3a-b**.

General Information

Materials. Unless specified, all reagents were used as received without further purifications. Reactions were monitored by GC-MS analysis and/or by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel coated aluminium plates (60 Merck F254) with UV light (254 nm) as visualizing agent. Chromatographic separations were carried out under pressure on silica gel (40-63 μm, 230-400 mesh) using flash-column techniques.

Instrumentation. ^{1}H NMR (600 MHz), ^{13}C{1H} (150 MHz), ^{19}F NMR (564 MHz), ^{11}B (192 MHz) spectra were recorded on a Jeol ECZR600 spectrometer at room temperature using residual solvent peak as an internal reference. Chemical shifts (δ) are given in parts per million (ppm) and coupling constants (J) in Hertz (Hz). Multiplicities are reported as follows: s (singlet), d (doublet), t (triplet), quint (quintet), sext (sextet), sept (septet), m (multiplet), br (broad). GC analyses were performed on a PerkinElmer Autosystem XL chromatographic system equipped with a methyl silicone capillary column. Mass spectra were obtained on a Shimadzu QP 1000 instrument (EI, 70 eV) and on a Bruker maXis 4G instrument (ESI-TOF, HRMS).

Synthesis of diarytellane

General procedure. Diaryltellane were synthetized following the reported procedure.[1] In a 10 mL capacity round bottom flask, diphenylditelluride **I** (1.0 eq., 100 mg, 0.24 mmol), CuI (0.05 eq., 2 mg, 0.012 mmol), 2,2'-bipyridine (0.05 eq., 2 mg, 0,012 mmol), the appropriate phenylboronic acid (3-fluorophenylboronic acid for **IIa** and phenylboronic acid for **IIb**) (3.0 eq., 0.72 mmol) were sequentially added in H_2O/DMSO 1:2 solution (1 mL). The reaction mixture was stirred at 100°C overnight. Then, reaction mixture was poured in water (5 mL) and extracted with ethyl acetate (3x5 mL). Combined organic layer was dried over (Na_2SO_4) and evaporated under reduced pressure. Crude mixture was purified by column chromatography (pure hexane) to provide the pure diaryltellane.

Synthesis and analysis of methyldiaryltelluronium terafluoroborate salts (3a and 3b)

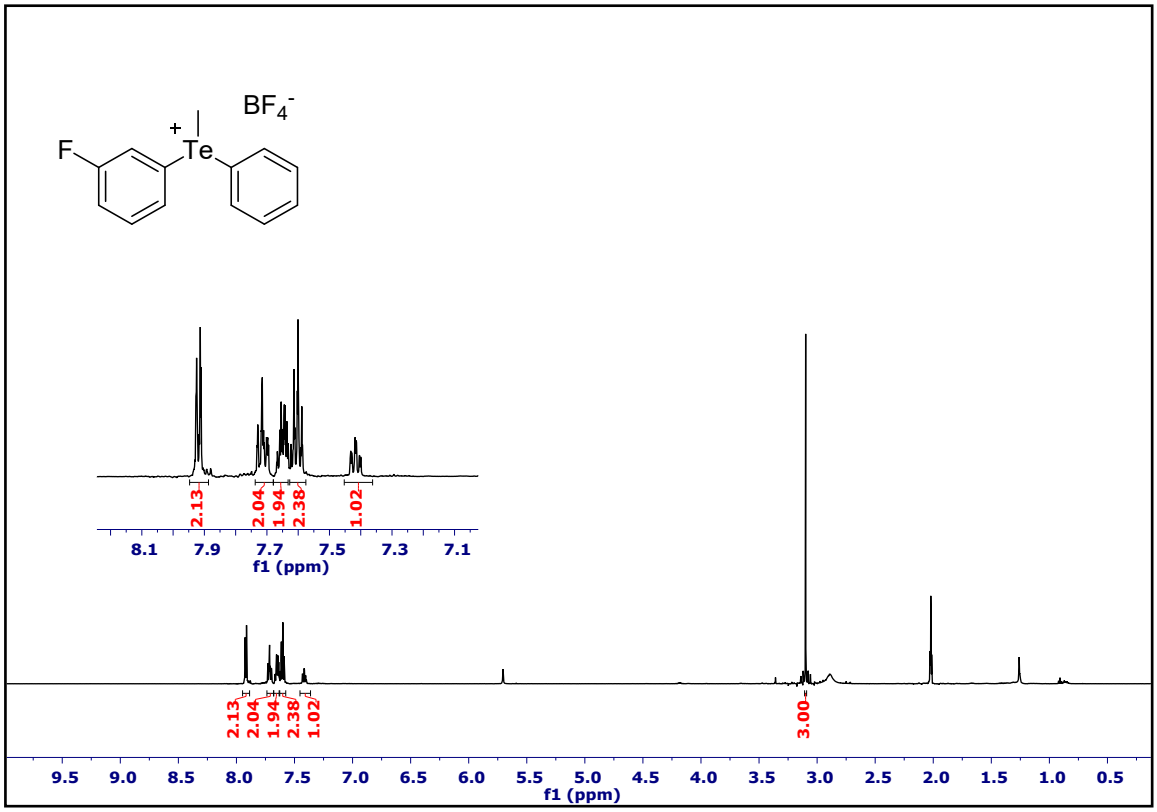
General procedure. Methyldiaryltelluronium tetrafluoroborate salt **3a** and **3b** were synthetized following the reported procedure.[2] In a 10 mL capacity round bottom flask, the selected diaryltellane (1.0 eq., 0.35 mmol), $AgBF_4$ (1.1 eq., 74 mg, 0.38 mmol) were dissolved and stirred in anhydrous DCE (4 mL) under nitrogen. Then MeI (3 eq., 62 µL, 1 mmol) was added and the mixture was stirred overnight, in the dark at room temperature. The mixture was filtrated through a celite pad to remove AgI and it was washed with acetonitrile (15 mL). The filtrate was evaporated under reduced pressure to give crude methyldiaryltelluronium terafluoroborate salt **3a-b**, that was purified by trituration with DCM.

(3-Fluorophenyl)(methyl)(phenyl)telluronium tetrafluoroborate (3a): according to the general procedure starting from fluorophenyl-phenyltellane, white solid (80%, 112 mg). ^{1}H NMR (600 MHz, CD_3COCD_3): δ 7.93-7.91 (m, 2H), 7.73-7.69 (m, 2H), 7.67-7.63 (m, 2H), 7.61-7.59 (m, 2H), 7.43-7.40 (m, 1H), 3.10 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, CD_3COCD_3): δ 162.9 (d, *J* = 250.7 Hz, 1C), 134.3, 132.4, 132.3, 130.7, 130.4 (d, *J* = 4.3 Hz, 1C), 124.6 (d, *J* = 6.3 Hz, 1C), 122.9, 121.1 (d, *J* = 24.4 Hz, C), 119.3 (d, *J* = 20.5 Hz, C), 11.4. ^{19}F (564 MHz, CD_3COCD_3): δ -110.49 (s, 1F), -149.74 (s, 4F). ^{11}B (192 MHz, CD_3COCD_3): δ -1.89 (s, 1B).

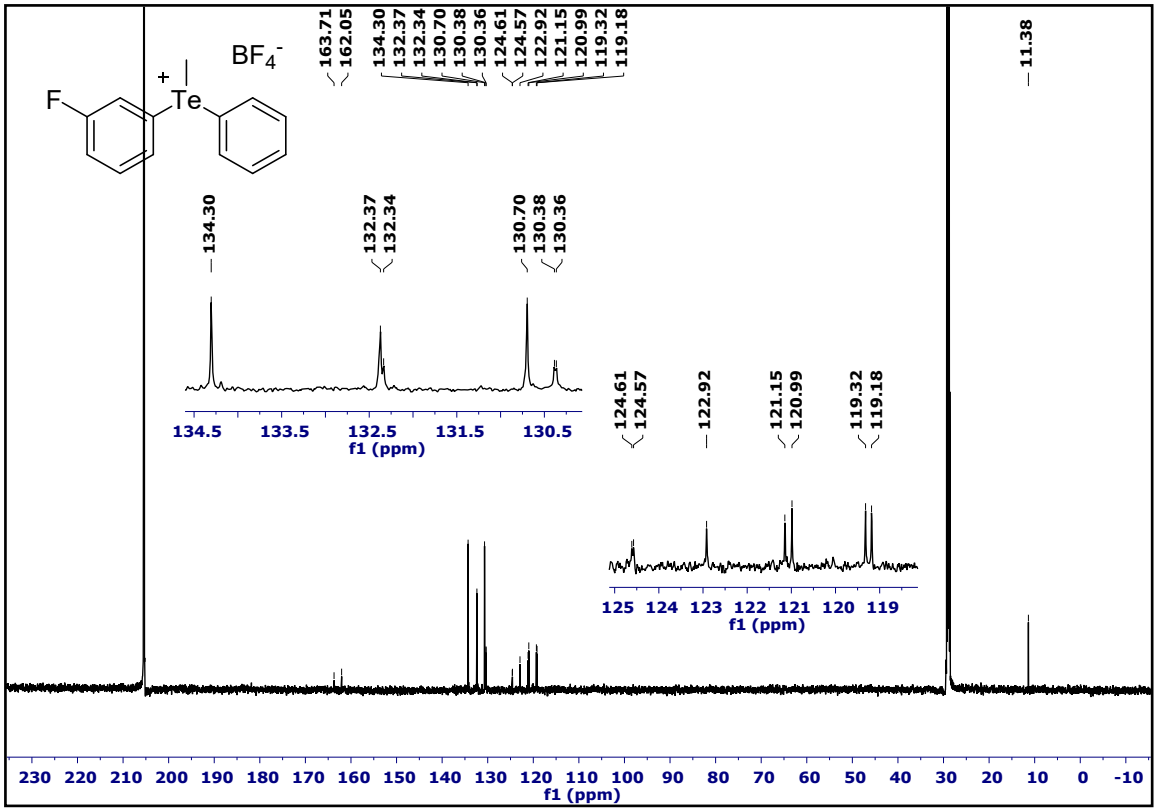
Methyldiphenyltelluronium tetrafluoroborate (3b): according to the general procedure starting from diphenyltellane, white solid (90%, 121 mg). ^{1}H NMR (600 MHz, MeOD): δ 7.72-7.71 (m, 4H), 7.59-7.56 (m, 2H), 7.54-7.51 (m, 4H), 2.74 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, MeOD): δ 133.7, 131.7, 130.2, 124.1, 10.7. ^{19}F (564 MHz, MeOD): δ -154.4 (s, 4F). ^{11}B (192 MHz, MeOD): δ -2.11 (s, 1B).[2]

(3-Fluorophenyl)(methyl)(phenyl)telluronium tetrafluoroborate (3a)

^{1}H NMR (600 MHz, CD_3COCD_3)

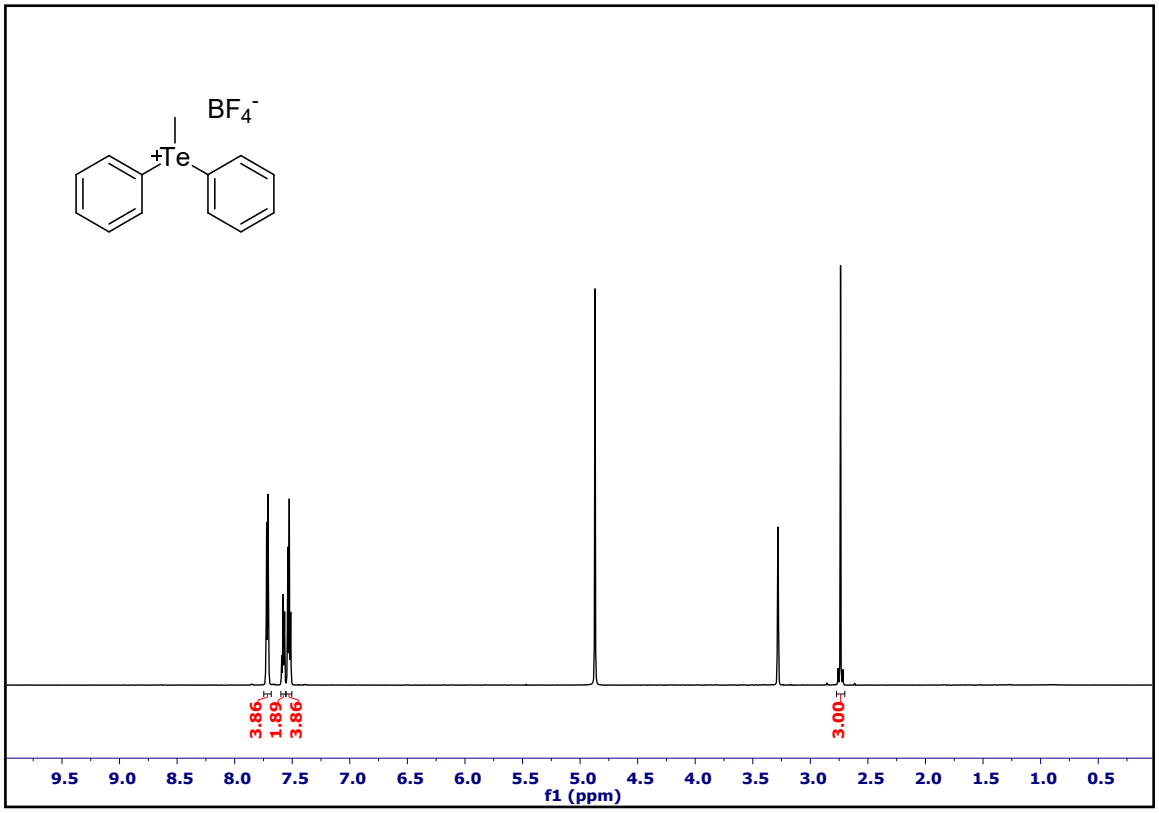


^{13}C NMR (150 MHz, CD_3COCD_3)

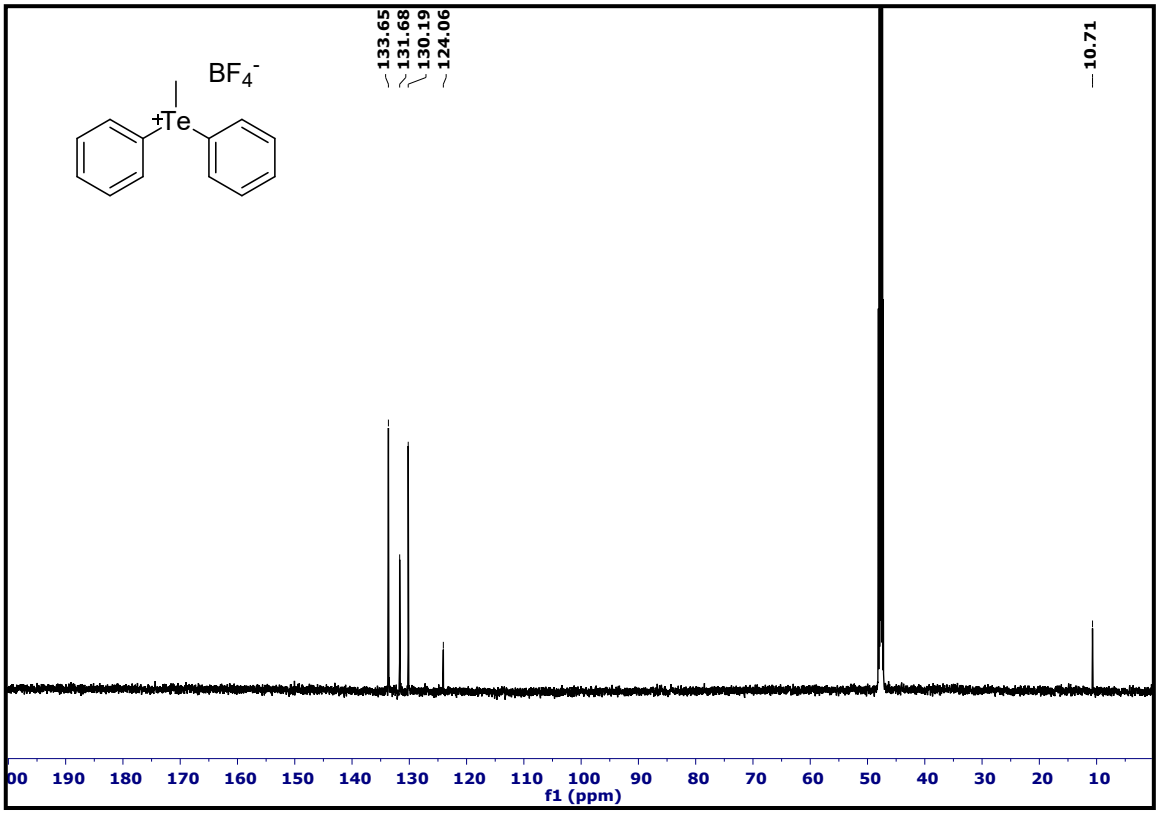


Methyldiphenyltelluronium tetrafluoroborate (3b)

^{1}H NMR (600 MHz, MeOD)



^{13}C NMR (150 MHz, MeOD)



Reference

[1] A. Kumar, S. Kumar, *Tetrahedron* **2014**, *70*, 1763-1772.

[2] R. Weiss, E. Aubert, P. Pale, V. Mamane, *Angew. Chem. In. Ed.* **2021**, *133*, 19430-19435.