Electronic Supplementary Material (ESI) for Dalton Transactions.

1,1-Carboboration to Tellurium–Boron Intramolecular Frustrated Lewis Pairs

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Supporting Information

General experimental procedure

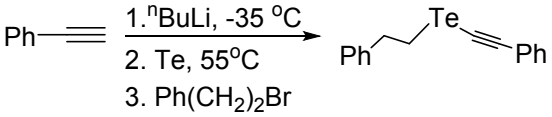
All experimental manipulations were conducted in an O_2-free, N_2-filled MBraun LABmaster SP dry box equipped with a -35 °C freezer. All proteo solvents (purchased from Caledon Laboratories) were purified using a Grubbs-type column system (Innovative Technologies) and stored over 4 Å sieves in Straus flasks. CD_2Cl_2 (purchased from Cambridge Isotopes) was dried over CaH_2 and distilled under reduced pressure. All solvents were degassed by repeated freeze-pump-thaw cycles prior to use.

All chemicals were used as received unless otherwise noted. ^{n}BuLi (1.6 M in hexanes), phenylacetylene, benzaldehyde were purchased from Sigma-Aldrich, 2-bromoethylbenzene was purchased from TCI America, $B(C_6F_5)_3$ was purchased from Boulder Scientific, Elemental tellurium was purchased from Alfa Aesar, resublimed iodine was purchased from ACP Chemicals. BPh_3 was purchased from Strem Chemicals and recrystallized from diethyl ether prior to use. $PhB(C_6F_5)_2$[1] and $CH_3B(C_6F_5)_2$[2] were prepared using standard literature procedure.

NMR spectroscopy was performed on either a Bruker Advance III 400 MHz, an Agilent DD2 500 MHz, or an Agilent DD2 600 MHz. Unless otherwise stated, all spectra were obtained at room temperature. All NMR spectra were referenced to residual proteo solvent peaks of CD_2Cl_2 (^{1}H = 5.32 ppm; ^{13}C = 53.84 ppm) or an external standard (^{19}F: $CFCl_3$ (δ 0.00), ^{11}B: $(Et_2O)BF_3$ (δ 0.00), ^{125}Te: Ph_2Te_2 (δ 420.8)[3]).

Single-crystal X-ray crystallographic analyses were performed on crystals coated in Paratone oil and mounted on a Bruker Kappa Apex II diffractometer. Combustion elemental analyses were performed on a on a PerkinElmer CHN Analyzer. HR-MS was performed on a JEOL AccuTOF equipped with a Direct Analysis in Real Time (DART) ion source.

Preparation of $Ph(CH_2)_2TeCCPh$ 1

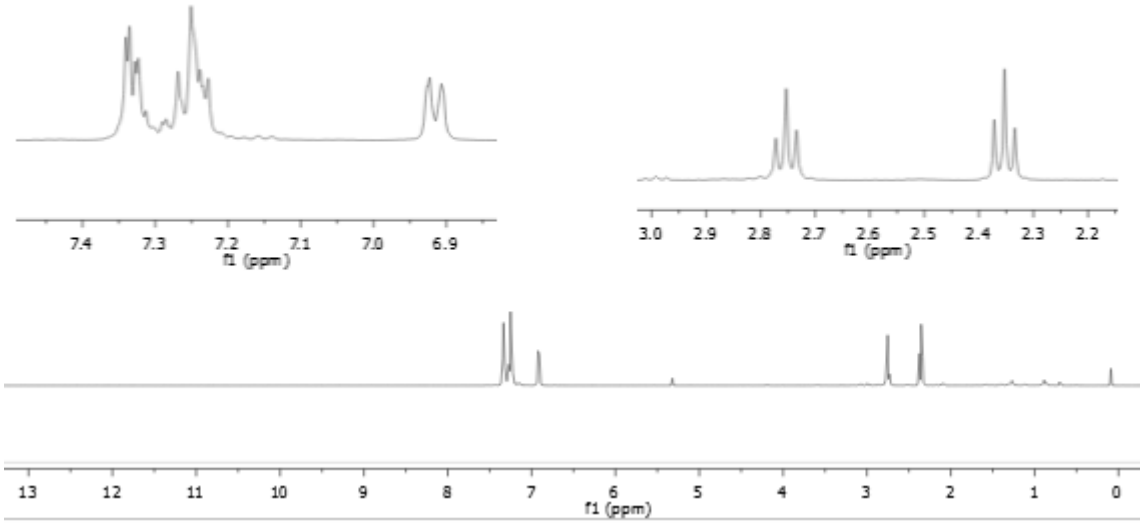


^{1}H (400.0 MHz, CD_2Cl_2): δ 7.43-7.41 (m, 2H, Ar-H), 7.30-7.34 (m, 5H, Ar-H), 7.26-7.23 (m, 3H, Ar-H), 3.27 (t, $^3J_{H-H}$ = 8.0 Hz, 2H, Te*CH*$_2$CH$_2$) 3.13 (t, $^3J_{H-H}$ = 8.0 Hz, 2H, Te*CH*$_2$CH$_2$)
^{13}C{^{1}H} (100.6 MHz, CD_2Cl_2): δ 142.8 (s, *i*-Ph^{Te}), 132.2 (s, *o*-Ph), 129.1 (s, Ar-C), 128.86 (s, Ar-C), 128.85(s, Ar-C), 128.83(s, Ar-C), 127.0 (s, Ar-C), 124.3 (s, *i*-Ph), 112.27 (s, ≡CPh), 45.3 (s, TeC≡), 38.3 (s, TeCH$_2$*CH*$_2$), 11.4 (s, Te*CH*$_2$CH$_2$)
^{125}Te (189.3 MHz, CD_2Cl_2): δ 298.3 (s)
[Note: Ph^{Te} denotes *Ph*$(CH_2)_2$Te]

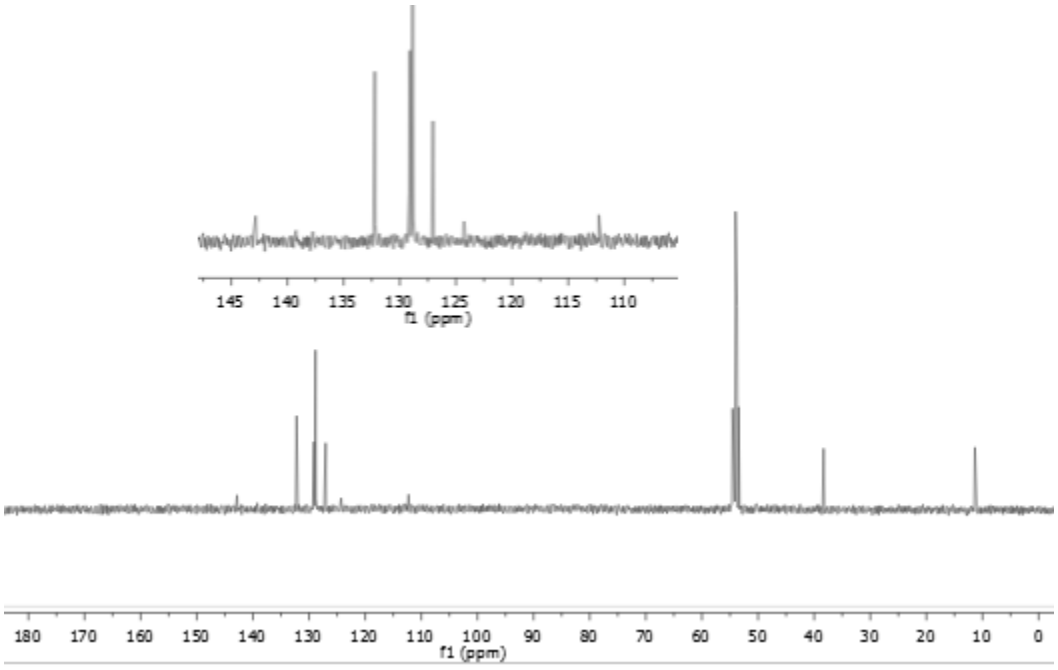
^{n}BuLi (1.9 ml, 1.6 M in hexanes) was added drop-wise to a solution of phenylacetylene (315.9 mg, 3.1 mmol) dissolved in ca. 15 ml THF and cooled to -35 °C. The solution was stirred and kept at this temperature for 30 min, upon which point tellurium powder (391.3 mg, 3.1 mmol) was added and the resulting slurry transferred to a 100-ml flask equipped with a Teflon-valve air-free stopcock seal and heated to 55 °C for 2 h in the dark, giving a clear yellow solution. The solution was then cooled down to room temperature and $Ph(CH_2)_2Br$ (563.0 mg, 3.1mmol)

dissolved in ca. 5ml THF was added to it. No immediate colour change was observed. The mixture was stirred at room temperature for 18 h in the dark to give a dark yellow solution. All volatiles were then removed *in vacuo*, giving a thick, dark red oil. The product was extracted twice with 10 ml of 1:1 mixture of Et_2O:hexanes and passed through a short plug of silica to give a clear yellow solution. All volatiles were then removed *in vacuo* to give a dark orange oil, which was then washed with pentane (5ml x3) to precipitate out compound **1** as a pale yellow solid (753.9 mg, 2.3 mmol, 73% yield).

Anal. Calc. for $C_{16}H_{14}Te$: C 57.56 %, H 4.23 %. Found: C 57.27 % H 3.81 %

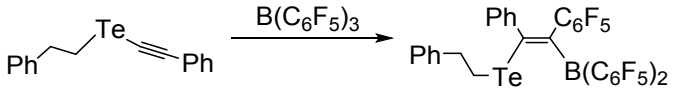


^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of 1



$^{13}C\{^1H\}$ (100.6 MHz, CD_2Cl_2) NMR spectrum of 1

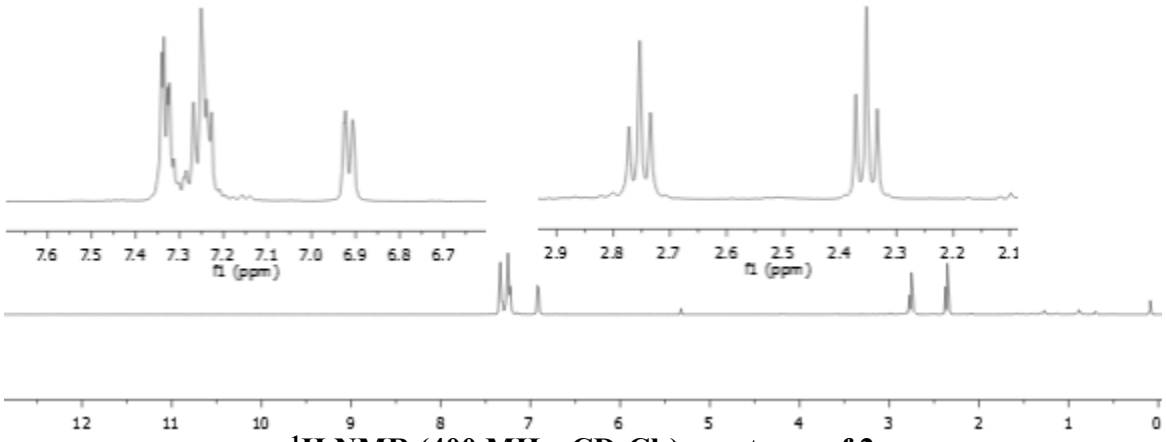
Preparation of compound 2, $Ph(CH_2)_2TeC(Ph)C(C_6F_5)B(C_6F_5)_2$



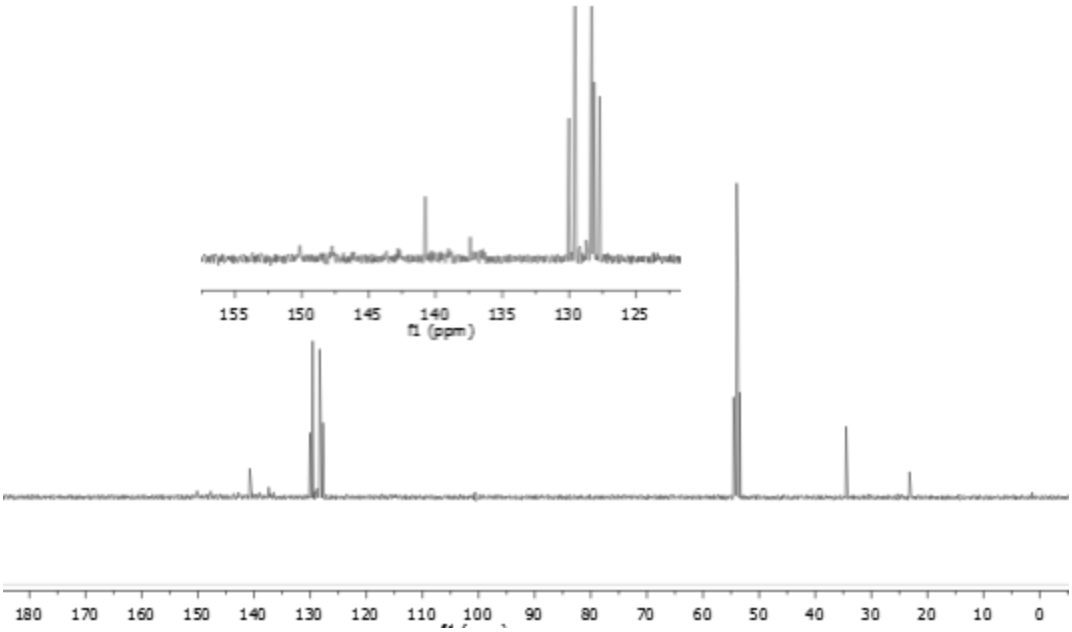
^{1}H (400.0 MHz, CD_2Cl_2): δ 7.34-7.32 (m, 3H, Ar-H), 7.27-7.23 (m, 5H, Ar-H), 6.90 (m, 2H, *o*-Ph^{Te}), 2.75 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, $TeCH_2\mathit{CH_2}$) 2.35 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, $Te\mathit{CH_2}CH_2$)
^{11}B{^{1}H} (128.3 MHz, CD_2Cl_2): δ 1.6 (s, $\nu_{1/2} \approx 720$ Hz)
^{13}C{^{1}H} (100.6 MHz, CD_2Cl_2): δ = n.o. (=CB), 148.9 (dm, $^1J_{C-F} \approx 243$ Hz, *o*-$C_6F_5^B$), 144.9 (dm, $^1J_{C-F} \approx 252$ Hz, *o*-C_6F_5), 141.4 ($^1J_{C-F} \approx 272$ Hz, *p*-$C_6F_5^B$), n.o. (*p*-C_6F_5), 140.8 (s, *i*-Ph^{Te}), 138.4 (dm, $^1J_{C-F} \approx 232$ Hz, *m*-C_6F_5), 137.4(s, *i*-Ph), 136.2 (dm, $^1J_{C-F} \approx 250$ Hz, *m*-$C_6F_5^B$), 130.0 (s, Ar-C), 129.58 (s, Ar-C), 129.56 (s, Ar-C), 128.3 (s, *o*-Ph^{Te}), 128.1 (s, Ar-C), 127.1 (s, *m*-Ph^{Te}), n.o. (*i*-C_6F_5 and *i*-$C_6F_5^B$), 100.6 (s, TeC=), 34.5 (s, $TeCH_2\mathit{CH_2}$), 23.2 (s, $Te\mathit{CH_2}CH_2$)
^{19}F{^{1}H} (376.4 MHz, CD_2Cl_2): δ -130.4 (m, 4F, *o*-$C_6F_5^B$), -138.6 (m, 2F, *o*-C_6F_5), -154.7 (t, 2F, $^3J_{F-F}$ = 20.3 Hz, *p*-$C_6F_5^B$), -155.3 (t, 1F, $^3J_{F-F}$ = 21.1 Hz, *p*-C_6F_5), -162.8 (m, 2F, *m*-C_6F_5), -163.2 (m, 4F, *m*-$C_6F_5^B$)
^{125}Te (157.8 MHz, CD_2Cl_2): δ 467.9 (tt, app quint., $^2J_{Te-H}$ = 103.5 Hz)
[Note: Ph^{Te} denotes $\mathit{Ph}(CH_2)_2Te$, $C_6F_5^B$ denotes $=CB(C_6F_5)_2$ and C_6F_5 denotes $=C(C_6F_5)$]

A solution of $B(C_6F_5)_3$ (157.9 mg, 0.31 mmol) dissolved in ca. 5 ml pentane was added drop-wise to a solution of compound **1** (103.9 mg, 0.31 mmol) in ca. 5 ml pentane at room temperature. The mixture immediately turned orange. The solution was stirred for an additional 30 min at room temperature, then filtered through a short plug of celite before all volatiles were removed *in vacuo*, giving **2** as a bright orange powder (245.6 mg, 0.29 mmol, 94% yield).

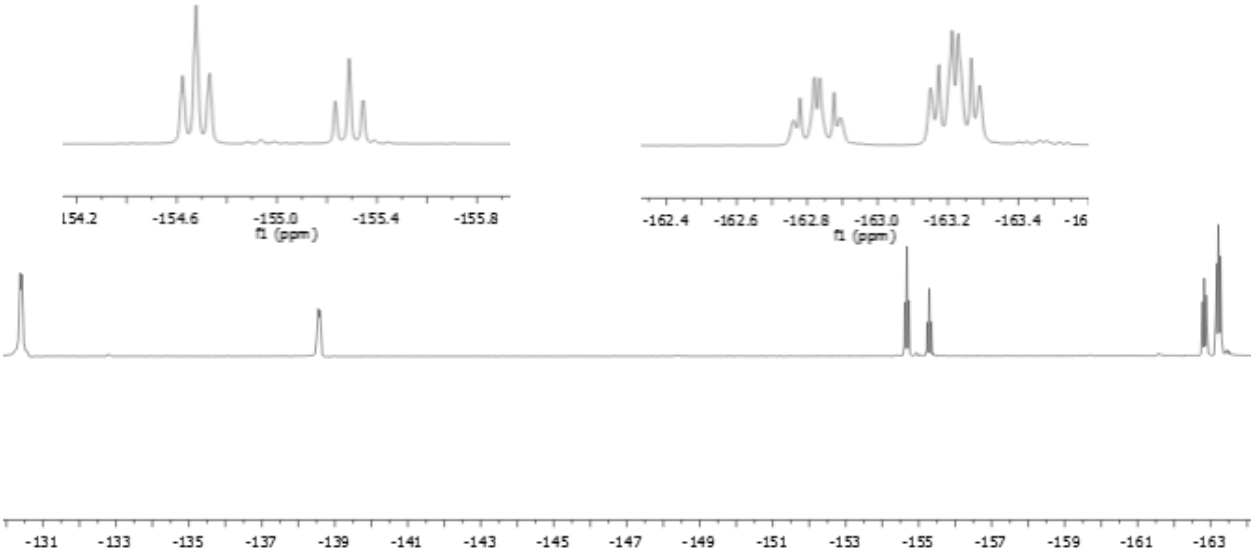
Anal. Calc. for $C_{34}H_{14}BF_{15}Te$: C 48.28 %, H 1.67 %. Found: C 47.76 % H 1.82 %



^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of 2

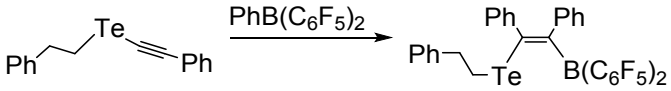


$^{13}C\{^{1}H\}$ NMR (100.6 MHz, CD_2Cl_2) spectrum of 2



$^{19}F\{^{1}H\}$ NMR (376.4 MHz, CD_2Cl_2) spectrum of 2

Preparation of compound 3, $Ph(CH_2)_2TeC(Ph)C(Ph)B(C_6F_5)_2$

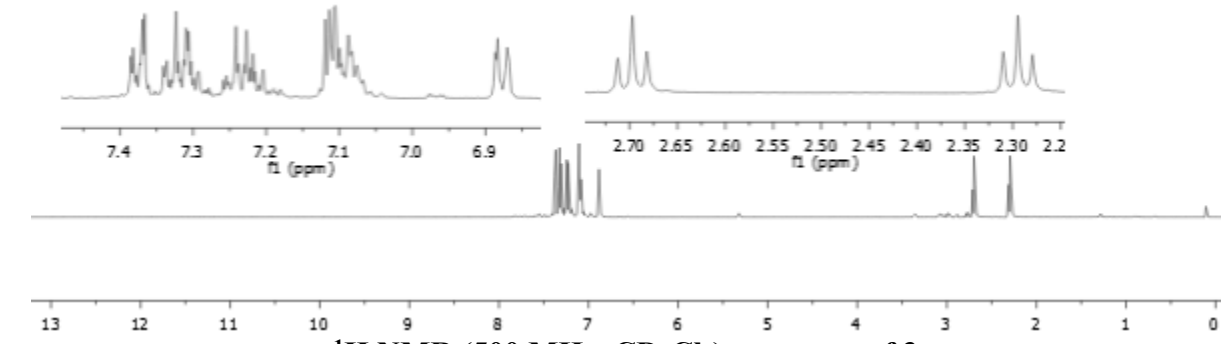


^{1}H (500.0 MHz, CD_2Cl_2): δ 7.37-7.30 (m, 5H, *Ar*-H), 7.23-7.20 (m, 3H, *m, p*-Ph^{Te}), 7.11-7.05 (m, 5H, *Ar*-H), 6.78 (m, 2H, *o*-Ph^{Te}), 2.68 (t, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 2H, $TeCH_2CH_2$) 2.28 (t, $^{3}J_{H\text{-}H}$ = 8.0 Hz, 2H, $TeCH_2CH_2$)

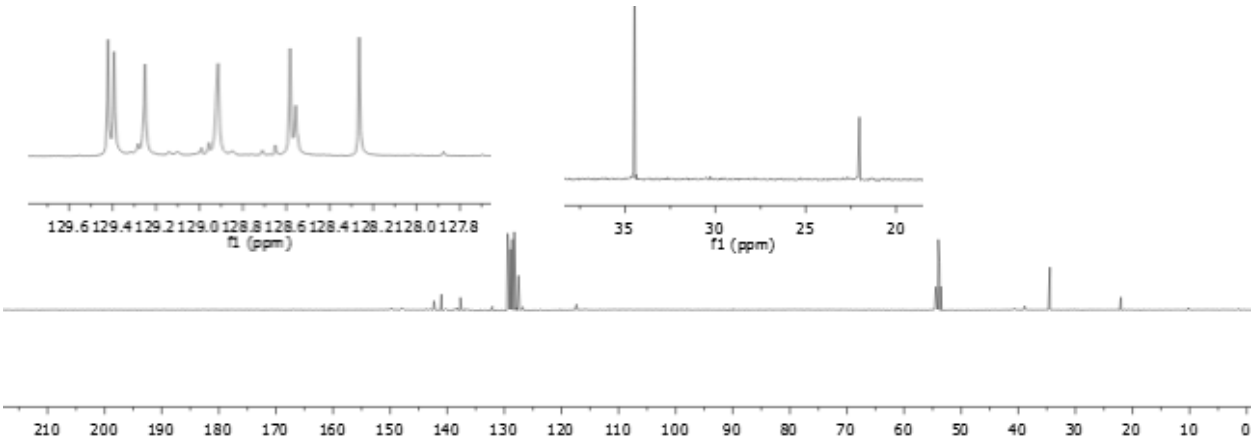
$^{11}B\{^1H\}$ (128.3 MHz, CD_2Cl_2): δ -0.4 (s, $\nu_{1/2} \approx 980$ Hz)
$^{13}C\{^1H\}$ (125.7 MHz, CD_2Cl_2): δ 166.9 (=CB), 142.3 (s, *i*-Ph^{trans}), 148.9 (dm, $^1J_{C-F} \approx 243$ Hz, *o*-C_6F_5), 141.1 (dm, $^1J_{C-F} \approx 230$ Hz, *p*-C_6F_5), 141.0 (s, *i*-Ph^{Te}), 137.7 (s, *i*-Ph), 137.6 (dm, $^1J_{C-F} \approx 246$ Hz, *m*-C_6F_5), 129.42 (s, Ar-C), 129.39 (s, Ar-C), 129.2 (s, Ar-C), 128.9 (s, Ar-C), 128.60 (s, Ar-C), 128.58 (s, Ar-C), 128.56 (s, Ar-C), 128.3 (s, *o*-Ph^{Te}), 127.5 (s, *m*-Ph^{Te}), 117.4 (s, TeC=), 115.4 (br s, *i*-C_6F_5), 34.5 (s, $^2J_{Te-C} = 19.7$ Hz, $TeCH_2\mathit{CH_2}$), 22.0 (s, $^1J_{Te-C} = 166.4$ Hz, $Te\mathit{CH_2}CH_2$)
$^{19}F\{^1H\}$ (376.4 MHz, CD_2Cl_2): δ -130.1 (dd, 4F, $^3J_{F-F} = 22.6$ Hz, $^4J_{F-F} = 6.4$ Hz, *o*-C_6F_5), -155.5 (t, 2F, $^3J_{F-F} = 20.3$ Hz, *p*-C_6F_5), -163.4 (m, 4F, *m*-C_6F_5)
^{125}Te (189.4 MHz, CD_2Cl_2): δ 426.0 (quint, $^3J_{Te-H} = 117.4$Hz)
[Note: Ph^{trans} denotes the phenyl group *trans* to the akyltellurium substituent and Ph^{Te} denotes $\mathit{Ph}(CH_2)_2Te$]

A solution of $PhB(C_6F_5)_2$ (79.2 mg, 0.18 mmol) dissolved in ca. 5 ml pentane was added dropwise to a solution of compound **1** (62.7 mg, 0.19 mmol) in ca. 5 ml pentane at room temperature. The mixture immediately turned a pale light yellow colour. The solution was stirred for an additional 16 h at room temperature, then filtered through a short plug of celite before all volatiles were removed *in vacuo*, giving **3** as an orange oil (104 mg, 0.14 mmol, 73% yield).

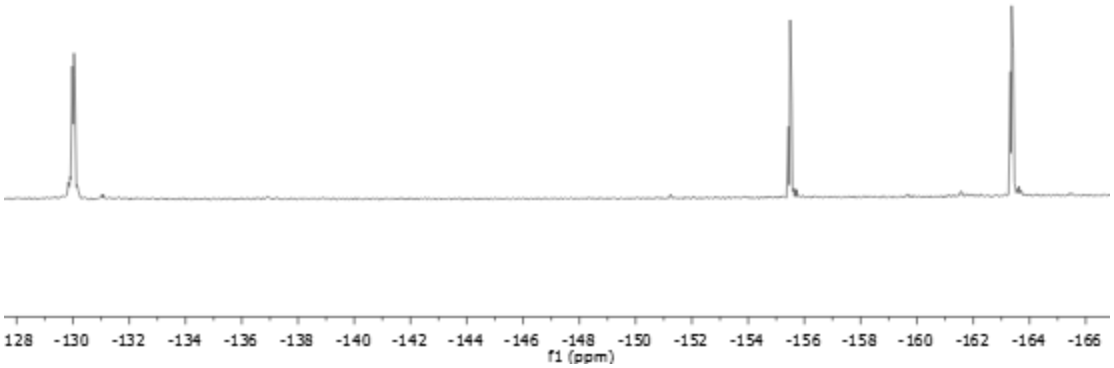
MS (DART+): cal'd for $C_{34}H_{20}BF_{10}Te$: 759.05606 amu, found: 759.05426 amu.



^1H NMR (500 MHz, CD_2Cl_2) spectrum of 3

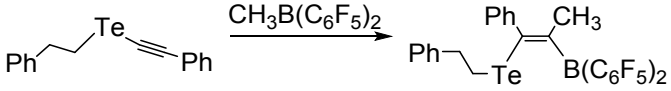


$^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2) spectrum of 3



$^{19}F\{^{1}H\}$ NMR (376.4 MHz, CD_2Cl_2) spectrum of 3

Preparation of compound 4, $Ph(CH_2)_2TeC(Ph)C(CH_3)B(C_6F_5)_2$

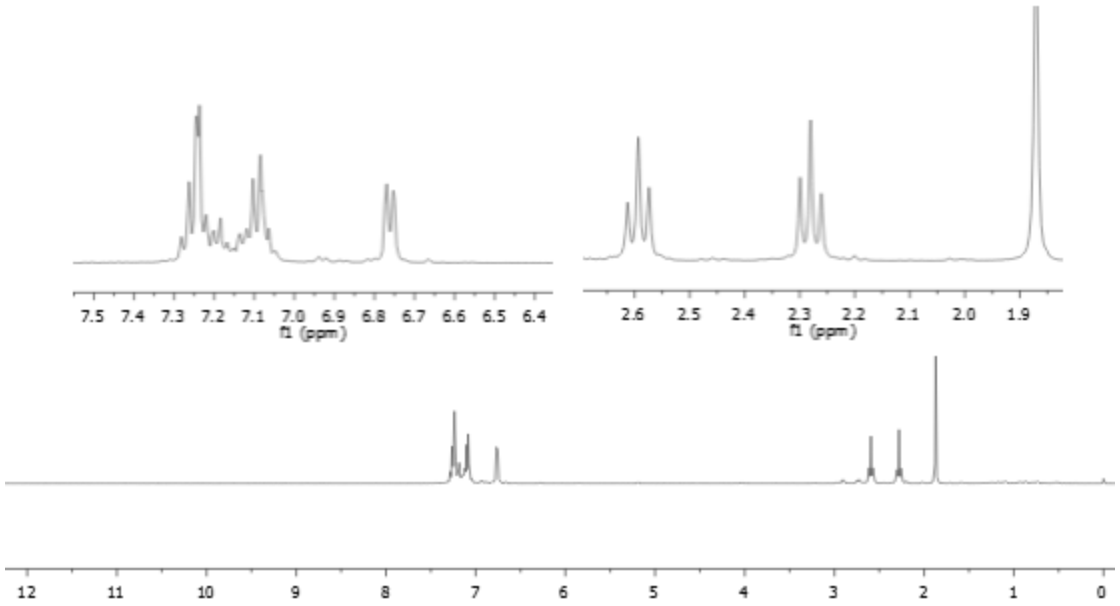


^{1}H (400.0 MHz, CD_2Cl_2): δ 7.40-7.28 (m, 5H, Ph), 7.23-7.18 (m, 3H, *m, p*-Ph^{Te}), 6.88-6.87 (m, 2H, *o*-Ph^{Te}), 2.72 (t, $^{3}J_{H-H}$ = 7.8 Hz, 2H, $TeCH_2CH_2$) 2.40 (t, $^{3}J_{H-H}$ = 7.8 Hz, 2H, $TeCH_2CH_2$), 1.98 (s, 3H, CH_3)
$^{11}B\{^{1}H\}$ (128.3 MHz, CD_2Cl_2): δ -4.5 ($\nu_{1/2} \approx 840$ Hz)
$^{13}C\{^{1}H\}$ (125.7 MHz, CD_2Cl_2): δ 170.2 (br s, =CB), 148.7 (dm, $^{1}J_{C-F} \approx 246$ Hz, *o*-C_6F_5), 141.1 (dm, $^{1}J_{C-F} \approx 252$ Hz, *p*-C_6F_5), 137.8 (dm, $^{1}J_{C-F} \approx 255$ Hz, *m*-C_6F_5), 141.1 (s, *i*-Ph^{Te}), 136.4 (s, *i*-Ph), 129.37 (s, Ar-C), 129.35 (s, Ar-C), 129.2 (s, Ar-C), 128.5 (s, Ar-C), 128.3 (s, *o*-Ph^{Te}), 127.5 (s, *m*-Ph^{Te}), 115.8 (br s, *i*-C_6F_5), 113.8 (s, TeC=), 34.7 (s, $^{2}J_{Te-C}$ = 15.7 Hz, $TeCH_2CH_2$), 23.9 (s, CH_3), 21.9 (s, , $^{1}J_{Te-C}$ = 165.7 Hz, $TeCH_2CH_2$)
$^{19}F\{^{1}H\}$ (376.4 MHz, CD_2Cl_2): δ -130.7 (dd, 4F, $^{3}J_{F-F}$ = 23.7 Hz, $^{4}J_{F-F}$ = 9.0 Hz, *o*-C_6F_5), -156.1 (t, 2F, $^{3}J_{F-F}$ = 20.3 Hz, *p*-C_6F_5), -163.6 (m, 4F, *m*-C_6F_5)
^{125}Te (157.8 MHz, CD_2Cl_2): δ 446.4 (quint., $^{3}J_{Te-H}$ = 131.0 Hz)

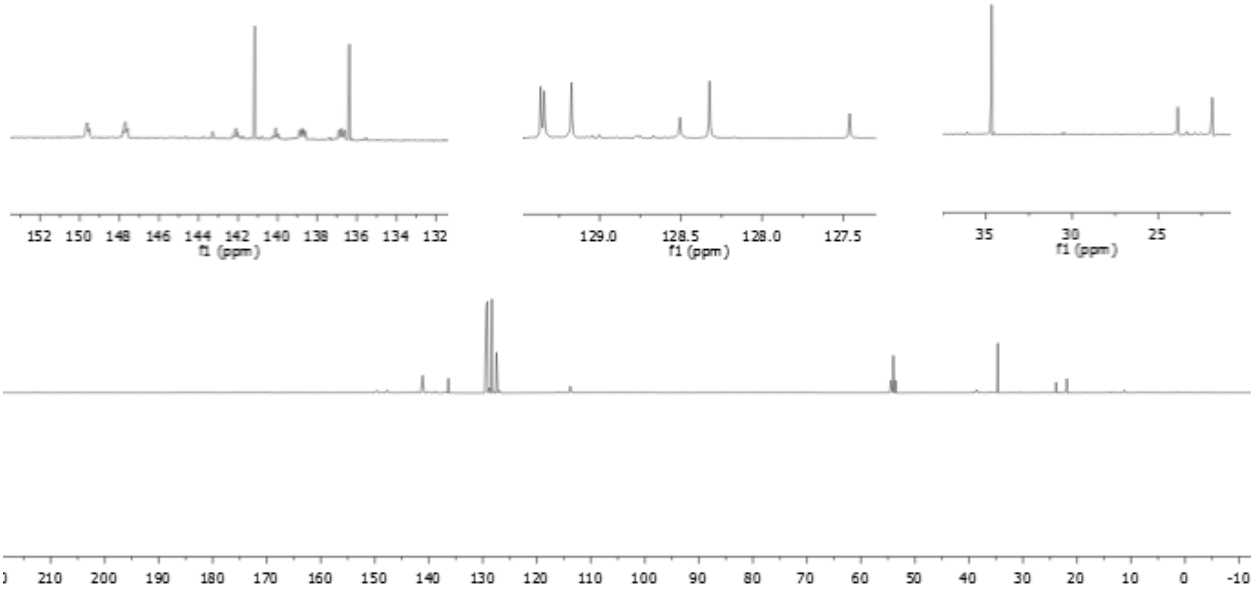
[Note: Ph^{Te} denotes $Ph(CH_2)_2Te$]

A solution of $MeB(C_6F_5)_2$ (68.8 mg, 0.19 mmol) dissolved in ca. 5 ml pentane was added dropwise to a solution of compound 1 (64.0 mg, 0.19 mmol) in ca. 5 ml pentane at room temperature. The mixture immediately turned bright yellow. Stirring was continued for an additional 16 h, then filtered through a short plug of celite before all volatiles were removed *in vacuo*, giving **4** as a thick, orange-yellow oil (114.6 mg, 0.17 mmol, 87% yield).

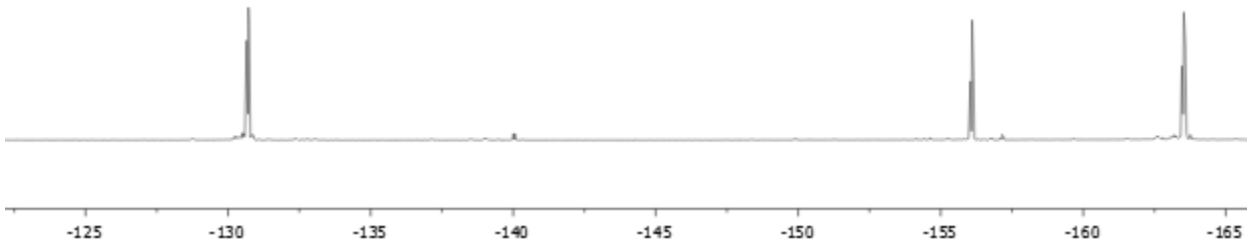
MS (DART+): cal'd for $C_{29}H_{18}BF_{10}Te$: 697.03911 amu, found: 697.04041 amu.



^{1}H NMR (400.0 MHz, CD_2Cl_2) spectrum of 4

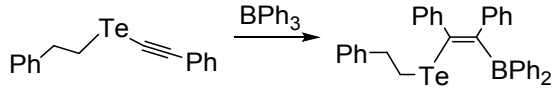


^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2) spectrum of 4



^{19}F{^{1}H} NMR (376.4 MHz, CD_2Cl_2) spectrum of 4

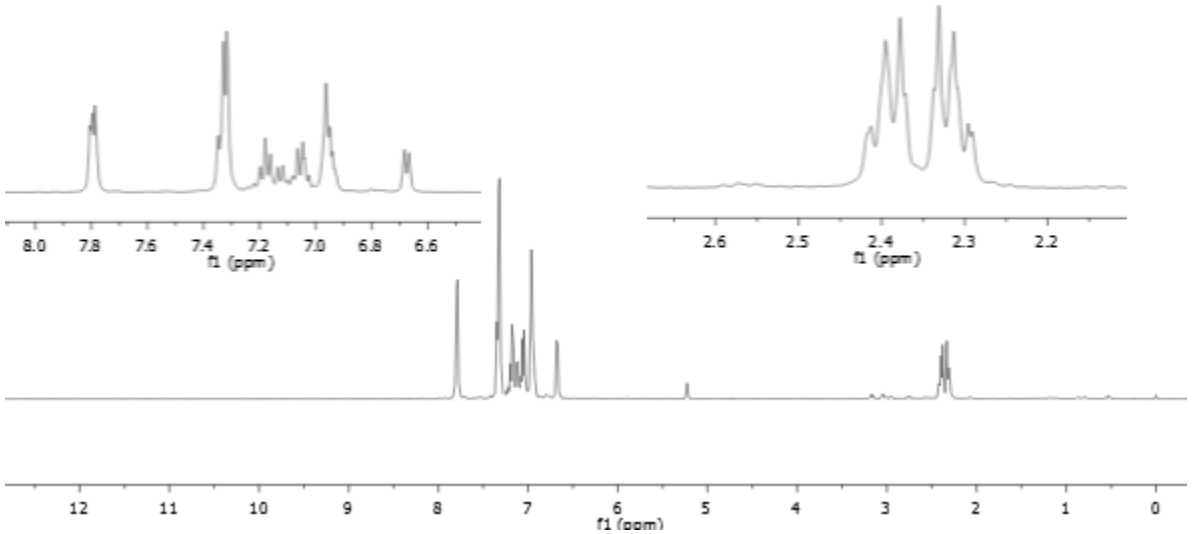
Preparation of compound 5, $Ph(CH_2)_2TeC(Ph)C(Ph)(BPh_2)$



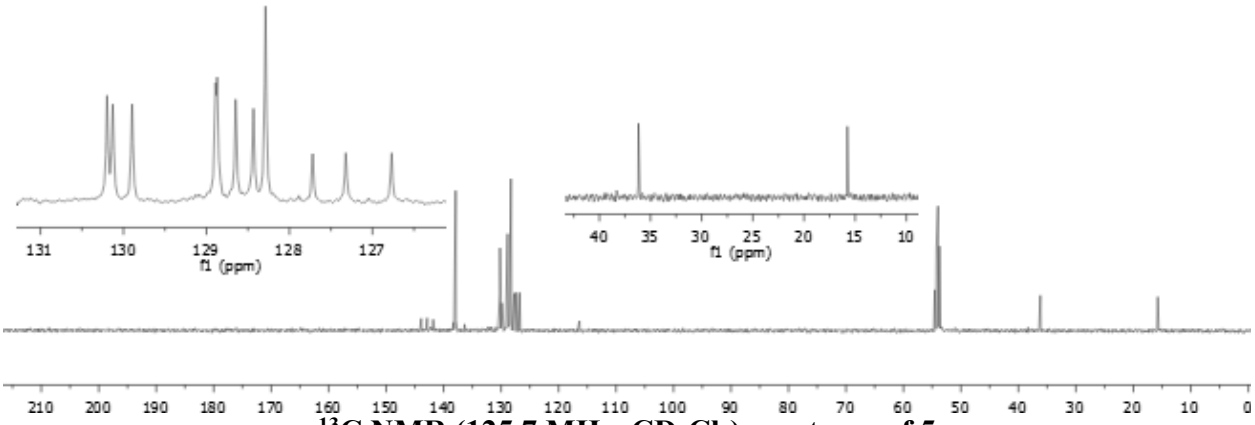
^{1}H (400.0 MHz, CD_2Cl_2): δ 7.90-7.87 (m, 4H, *o*-Ph^B) 7.44-7.41 (m, 8H, *Ar*-H), 7.29-7.21 (m, 3H, *Ar*-H), 7.20-7.17 (m, 3H, *Ar*-H, *m*, *p*-Ph^{Te}), 7.06-7.02 (m, 5H, *Ar*-H), 6.78-6.76 (d, $^3J_{H-H}$ = 6.4 Hz, 2H, *o*-Ph^{Te}), 2.49 (t, $^3J_{H-H}$ = 7.0 Hz, 2H, $TeCH_2CH_2$) 2.41 (t, $^3J_{H-H}$ = 7.0 Hz, 2H, $TeCH_2CH_2$, $^2J_{Te-H}$ = 199.9 Hz),
^{11}B{^{1}H} (128.3 MHz, CD_2Cl_2): δ 42.9 (s, $\nu_{1/2} \approx 1400$ Hz)
^{13}C{^{1}H} (125.7 MHz, CD_2Cl_2): δ n.o. (=CB), 143.9 (s, *i*-Ph^{trans}), 142.9 (s, *i*-Ph^{Te}), 141.8 (s, *i*-Ph), n.o. (i-Ph^B), 137.9 (s, *o*-Ph^B), 130.2 (s, Ar-C), 130.1 (s, *m*-Ph^B), 129.9 (s, Ar-C), 128.89 (s, Ar-C), 128.87 (s, Ar-C), 128.6 (s, Ar-C), 128.4 (s, Ar-C), 128.3 (s, *o*-Ph^{Te}), 127.7 (s, Ar-C), 127.3 (s, Ar-C), 126.8 (s, *m*-Ph^{Te}), 116.4 (s, TeC=), n.o. (*i*-C_6F_5), 36.2 ($TeCH_2CH_2$), 15.8 ($TeCH_2CH_2$)
^{125}Te (157.8 MHz, CD_2Cl_2): δ 426.7 (quint, $^3J_{Te-H}$ = 116.8 Hz)
[Note: Ph^{trans} denotes the phenyl group *trans* to the alkyltellurium substituent, Ph^{Te} denotes $Ph(CH_2)_2Te$ and Ph^B denotes BPh_2]

A solution of BPh_3 (66.1 mg, 0.27 mmol) dissolved in ca. 5 ml pentane was added dropwise to a solution of compound **1** (91.8 mg, 0.27 mmol) in ca. 5 ml pentane at room temperature. The mixture gradually turned lemon yellow and remained clear. The solution was stirred for an additional 16 h at room temperature, then filtered through a short plug of celite before all volatiles were removed *in vacuo*, giving **5** as a viscous bright yellow oil (105.1 mg, 0.18 mmol, 67% yield).

MS (DART+): cal'd for $C_{34}H_{29}BTe$: 578.14245 amu, found: 578.14515 amu

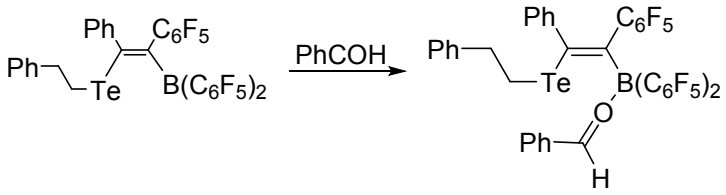


^{1}H NMR (400.0 MHz, CD_2Cl_2) spectrum of 5



^{13}C NMR (125.7 MHz, CD_2Cl_2) spectrum of 5

Preparation of compound 6, $Ph(CH_2)_2TeC(Ph)C(C_6F_5)B(C_6F_5)_2(OCHPh)$

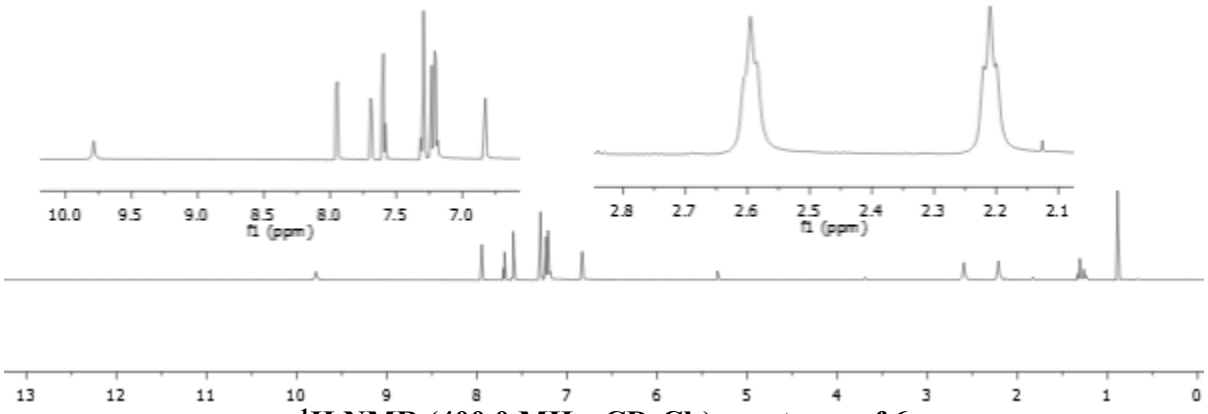


^{1}H (400.0 MHz, CD_2Cl_2): δ 9.80 (br s, 1H, C=OH), 7.94 (m, 2H, *o*-Ph^{CO},), 7.69 (tt, $^{3}J_{H\text{-}H}$ = 7.4 Hz, $^{4}J_{H\text{-}H}$ = 2 Hz, 1H, *p*-Ph^{CO}), 7.593 (t, $^{3}J_{H\text{-}H}$ = 7.4 Hz, 2H *m*-Ph^{CO}), 7.31-7.30 (m, 3H, Ar-H), 7.24-7.20 (m, 5H, Ar-H), 6.84 (m, 2H, *o*-Ph^{Te}), 2.60 (t, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 2H, $TeCH_2\mathit{CH_2}$), 2.22 (t, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 2H, $Te\mathit{CH_2}CH_2$)
^{11}B{^{1}H} (128.3 MHz, CD_2Cl_2): δ 2.1 (s, br, $\nu_{1/2} \approx 2700$ Hz)
^{13}C{^{1}H} (100.6 MHz, CD_2Cl_2): δ =n.o. (=CB), n.o.(COH), 141.2 (s, *i*-Ph^{Te}), 136.0 (s, *p*-Ph^{CO}), 135.8 (s, br, *i*-Ph), 131.1 (s, br, Ar-C), 130.0 (s, *o*-Ph^{CO}), 129.5 (s, *m*-Ph^{CO}), 129.4 (s, br, Ar-C), 129.3 (s, br, Ar-C), 128.3 (s, br, Ar-C), 128.2 (s, *o*-Ph^{Te}), 127.5 (s, *m*-Ph^{Te}), 116.0 (s, br, TeC=), n.o. (*i*-C_6F_5), 34.7 (s,$TeCH_2\mathit{CH_2}$), 22.4 (s, $Te\mathit{CH_2}CH_2$)
^{19}F{^{1}H} (376.4 MHz, CD_2Cl_2, 298 K): δ -130.9 (s, br, 4F, *o*-$C_6F_5^B$), -138.6 (m, 2F, *o*-C_6F_5), -155.3 (s, br, 2F, *p*-$C_6F_5^B$), -156.2 (s, br, 1F, *p*-C_6F_5), -163.4 (m, 6F, *m*-$C_6F_5^B$ + *m*-C_6F_5)
^{19}F{^{1}H} (376.4 MHz, CD_2Cl_2, 193 K): δ -129.2 (s, 1F, *o*-$C_6F_5^B$), -132.7 (s, 1F, *o*-$C_6F_5^B$), -132.9 (s, 1F, *o*-$C_6F_5^B$), -136.3 (s, 1F, *o*-$C_6F_5^B$), -138.7 (s, 1F, *o*-$C_6F_5^B$), -138.6 (s, 1F, *o*-C_6F_5), -140.2 (s, 1F, *o*-C_6F_5), -155.1 (s, 1F, *p*-C_6F_5), -157.1 (s, 1F, *p*-$C_6F_5^B$), -157.7 (s, 1F, *p*-$C_6F_5^B$), -161.3 (s, 1F, *m*-C_6F_5), -162.5 (s, 1F, *m*-C_6F_5), -163.0 (s, 1F, *m*-C_6F_5), -163.5 (s, 1F, *m*-C_6F_5), -164.1 (s, 1F, *m*-$C_6F_5^B$), -164.8 (s, 1F, *m*-$C_6F_5^B$)
^{125}Te (157.8 MHz, CD_2Cl_2, 233 K): δ 400.9 (s, br)
[Note: Ph^{Te} denotes $\mathit{Ph}(CH_2)_2Te$ and Ph^{CO} denotes $\mathit{Ph}COH$]
[Note: ^{13}C resonances of C_6F_5 rings not listed]
[Note: ^{19}F-^{19}F coupling was lost when sample was cooled to 193 K]

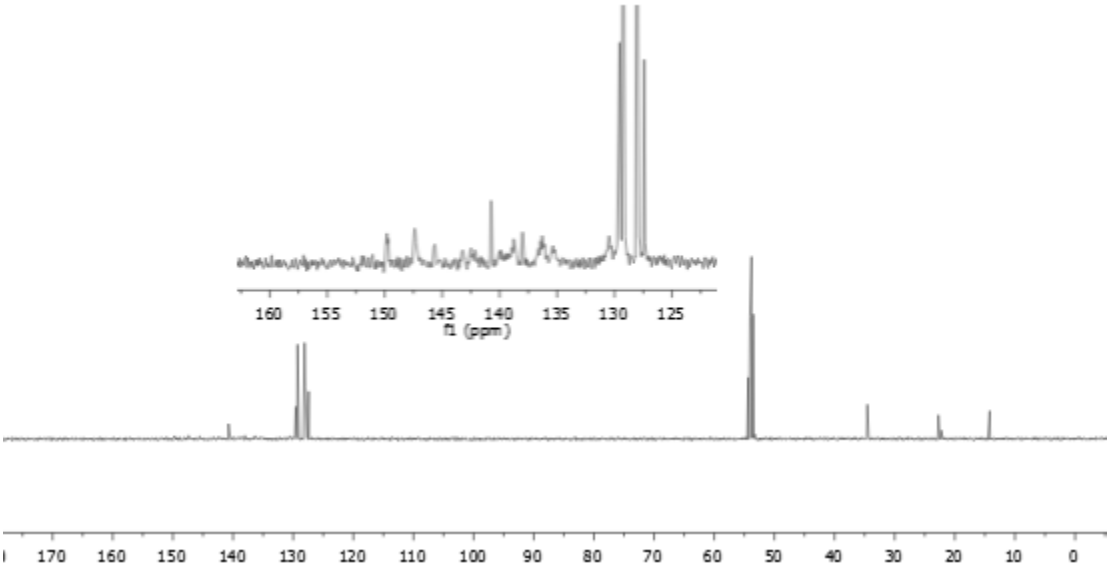
A solution of benzaldehyde (9.5 mg, 0.09 mmol) dissolved in ca. 3 ml dichloromethane (DCM) was added to a stirring solution of compound **2** (75.5 mg, 0.09 mmol) dissolved in ca. 5 ml DCM. The solution was allowed to stir for 3 h before all volatiles were removed in vacuo, leaving a

dark red oil. The oil was dissolved in ca. 3 ml pentane and stored at -35 ^{o}C for 16 h, giving a clear orange supernatant and dark orange crystals. The supernatant was decanted and the crystals were dried under vacuum to give **6** as an orange powder (53.8 mg, 0.06 mmol, 63% yield). Single crystals suitable for X-ray diffraction studies were grown from the slow evaporation of a saturated solution of **6** in DCM. [Note: compound 6 is isolated as 6•pentane as pentane signals show up in the ^{1}H NMR even after being placed under dynamic vacuum for 24 h. Elemental analysis was done using single crystals used for x-ray diffraction analysis]

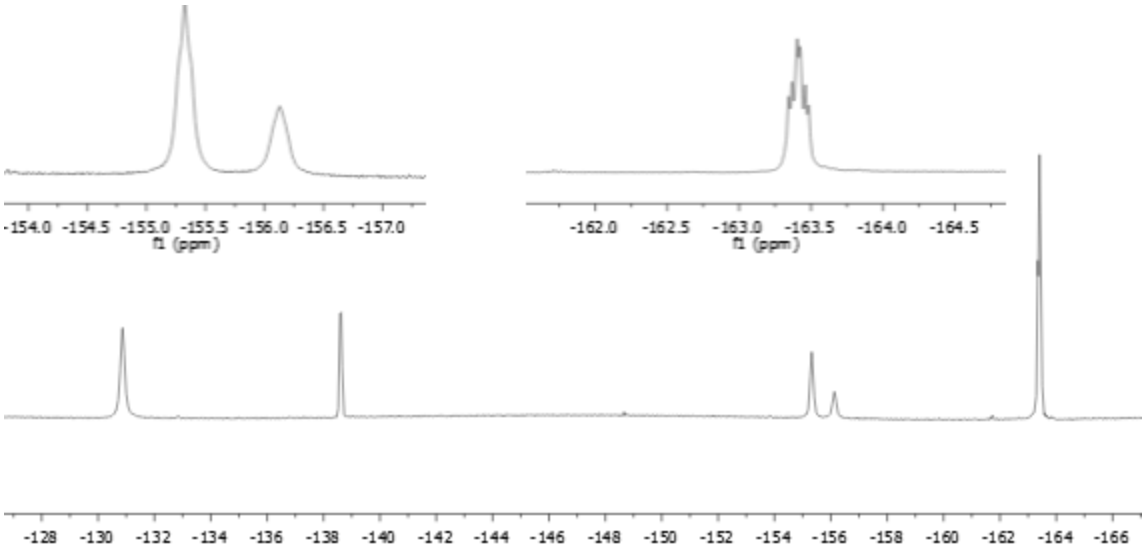
Anal. Calc. for $C_{41}H_{20}BF_{15}OTe$: C 51.73 %, H 2.12 %. Found: C 51.53 % H 1.58 %



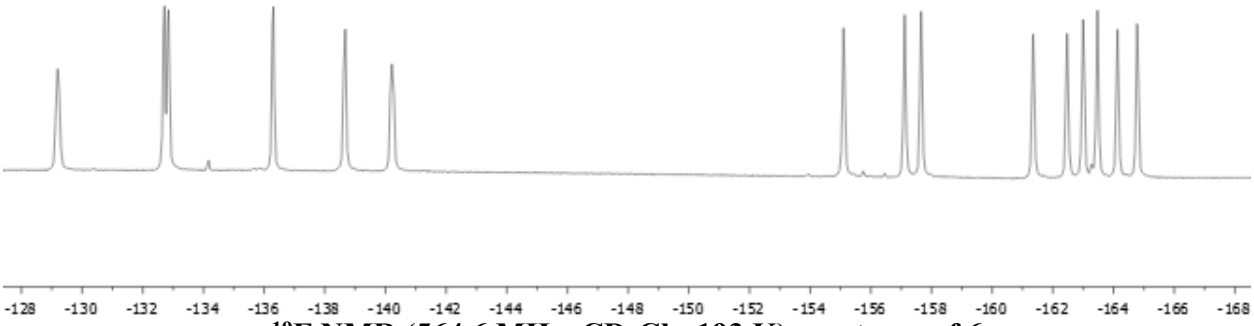
^{1}H NMR (400.0 MHz, CD_2Cl_2) spectrum of 6



^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2) spectrum of 6

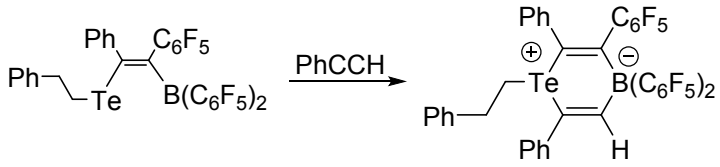


^{19}F NMR (564.6 MHz, CD_2Cl_2, 298 K) spectrum of 6



^{19}F NMR (564.6 MHz, CD_2Cl_2, 193 K) spectrum of 6

Preparation of compound 7



^{1}H (400.0 MHz, CD_2Cl_2): δ 7.68 (s, 1H, HC=), 7.47 (m, 2H, *m*-Ph^{ac}), 7.42-2.44 (m, 6H, Ar-H), 7.26-7.22 (m, 5H, Ar-H), 6.74-6.72 (m, 2H, *o*-Ph^{Te}), 2.84 (m, 1H, Te*CH*$_2$CH$_2$) 2.68 (m, 3H, Te*CH*$_2$CH$_2$ + Te*CH*$_2$'CH$_2$)

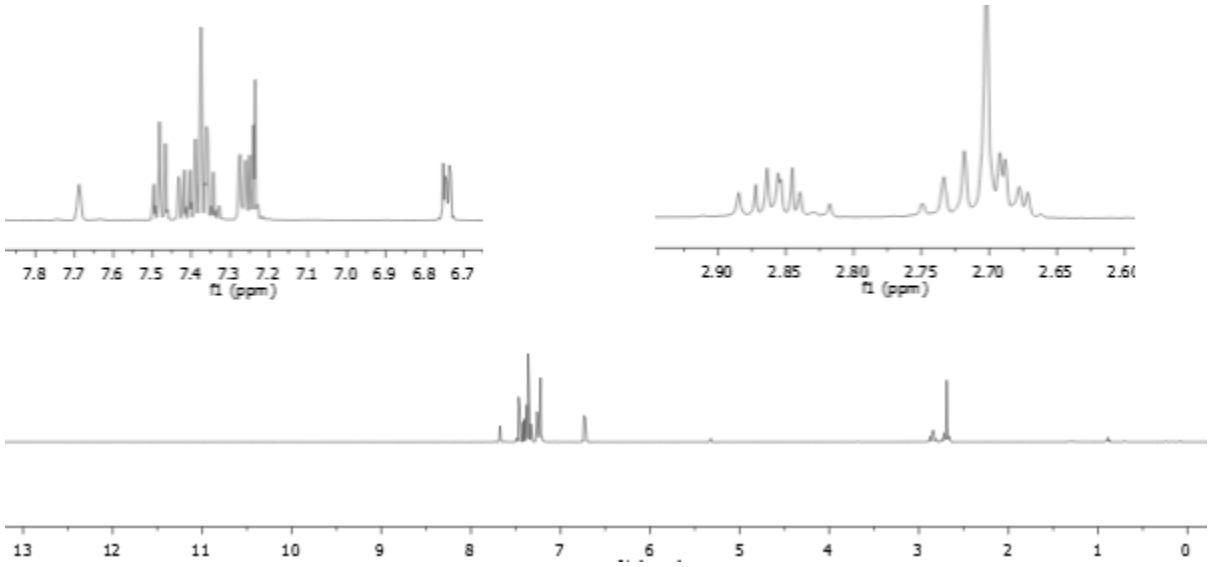
^{11}B{^{1}H} (128.3 MHz, CD_2Cl_2): δ -10.8 (s, $\nu_{1/2} \approx 25$ Hz)

^{13}C{^{1}H} (125.7 MHz, CD_2Cl_2): δ 161.5 (1:1:1:1 q, $^{1}J_{C\text{-}B}$ = 53.4 Hz, TeC=*C*H), 153.9 (1:1:1:1 q, $^{1}J_{C\text{-}B} \approx 43$ Hz, =CB), 148.7 (dm, $^{1}J_{C\text{-}F} \approx 240$ Hz, *o*-$C_6F_5^B$), 142.9 (dm, $^{1}J_{C\text{-}F} \approx 247$ Hz, *o*-C_6F_5), 142.5 (dm, $^{1}J_{C\text{-}F} \approx 243$ Hz, *p*-$C_6F_5^B$), 139.5 (dm, $^{1}J_{C\text{-}F} \approx 228$ Hz, *p*-C_6F_5), 137.5 (dm, $^{1}J_{C\text{-}F} \approx 230$ Hz, *m*-$C_6F_5^B$), 137.0 (dm, $^{1}J_{C\text{-}F} \approx 241$ Hz, *m*-C_6F_5), 139.8 (s, *o*-Ph^{ac}), 139.7 (s, *i*-Ph^{Te}), 138.3 (s, *i*-Ph), 130.7 (s, *i*-Ph^{ac}), 130.2 (s, Ar-C), 130.03 (s, Ar-C), 130.00 (s, Ar-C), 129.6 (s, Ar-C), 129.4

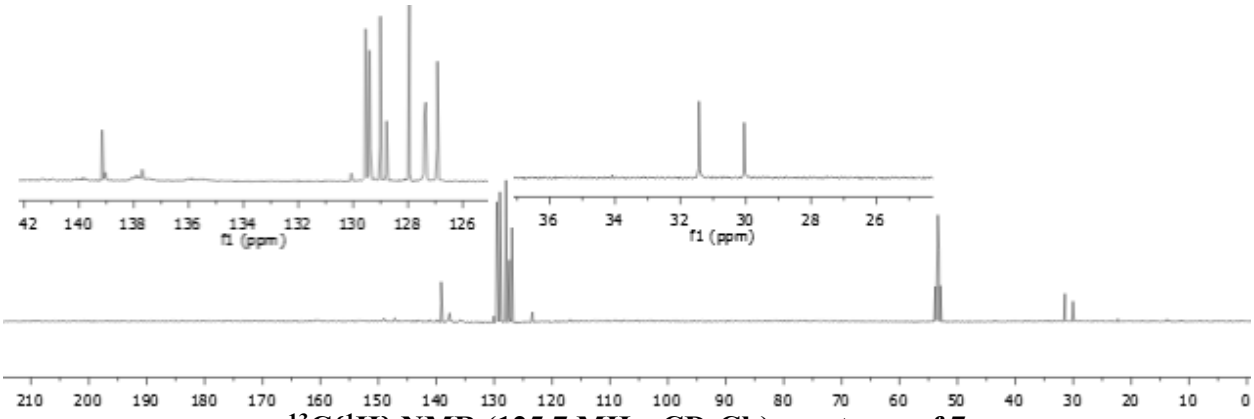
(s, *m*-Ph^{Te}), 128.6 (s, *o*-Ph^{Te}), 128.03 (s, Ar-C), 127.97 (s, Ar-C),127.5 (s, Ar-C), 124.0 (s, Te*C*=CH), 117.5, (s, TeC=), n.o. (*i*-C_6F_5 and *i*-$C_6F_5^B$), 32.1 (s, $TeCH_2CH_2$), 30.7 (s, $TeCH_2CH_2$)
$^{19}F\{^1H\}$ (376.4 MHz, CD_2Cl_2): δ -130.4 (m, 2F, *o*-$C_6F_5^B$), -131.7 (m, 2F, *o*-$C_6F_5^{B'}$), -138.6 (m, 1F, *o*-C_6F_5), -139.6 (m, 1F, *o'*-C_6F_5), -157.5 (t, $^3J_{F-F}$ = 21.1 Hz 1F, *p*-C_6F_5), -159.9 (t, $^3J_{F-F}$ = 20.3 Hz, 1F, *p*-$C_6F_5^B$), -160.6 (t, $^3J_{F-F}$ = 20.3 Hz, 1F, *p*-$C_6F_5^{B'}$), -163.6 (m, 1F, *m*-C_6F_5), -164.8 (m, 3F, *m'*-C_6F_5 + *m*-$C_6F_5^B$), -165.5 (m, 2F, *m*-$C_6F_5^{B'}$)
^{125}Te (157.8 MHz, CD_2Cl_2, 233 K): δ 472.8 (br)
[Note: Ph^{Te} denotes $Ph(CH_2)_2Te$ and Ph^{ac} denotes *Ph*C=CH; $C_6F_5^B$ denotes $=CB(C_6F_5)_2$ and C_6F_5 denotes $=C(C_6F_5)$]

Phenylacetylene (0.05 ml, 0.45 mmol, excess) was added to a solution of compound **2** (100.3 mg, 0.12 mmol) dissolved in ca. 5 ml pentane. The mixture immediately turned orange yellow and remained clear. The solution was stirred for 10 min. and then was allowed to stand at room temperature for 16 h, giving a clear yellow supernatant and bright orange crystals. The supernatant was removed and the orange crystals dried under vacuum to give analytically pure product (98.9 mg, 0.10 mmol, 87% yield). Single crystals suitable for x-ray diffraction studies were grown from letting a dilute pentane solution of **7** stand at room temperature for 1 d.

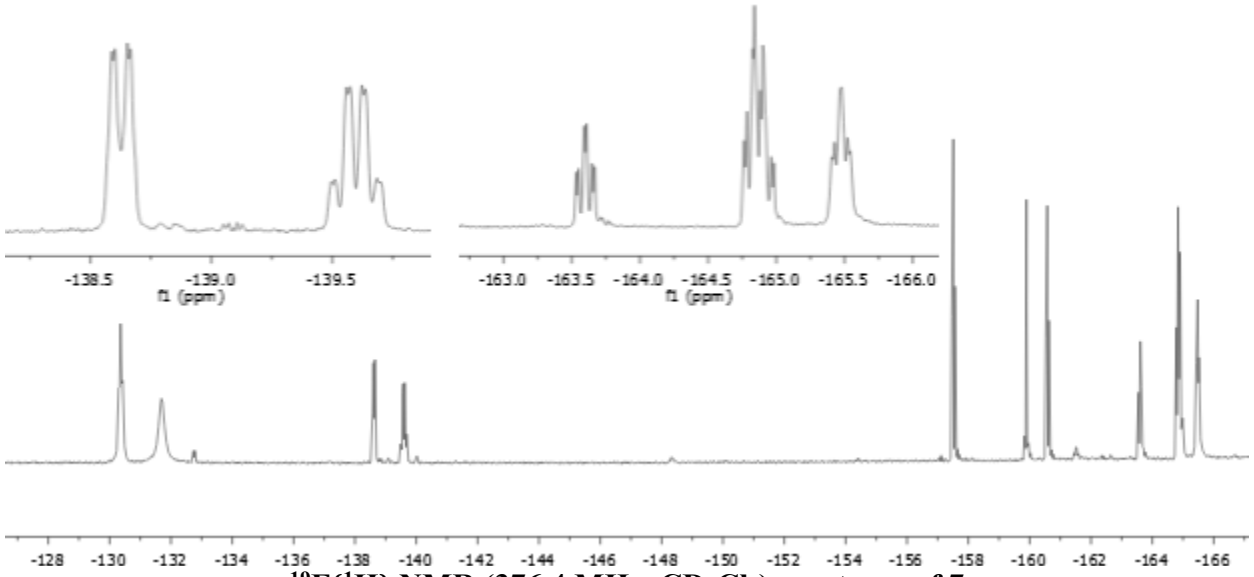
Anal. Calc. for $C_{42}H_{20}BF_{15}Te$: C 53.21 %, H 2.13 %. Found: C 52.97 % H 1.93 %



^1H NMR (400.0 MHz, CD_2Cl_2) spectrum of 7

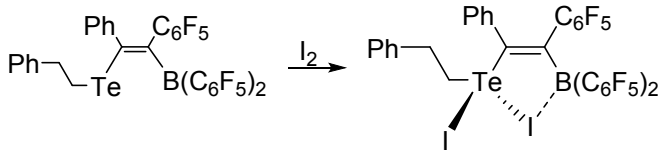


$^{13}C\{^{1}H\}$ NMR (125.7 MHz, CD_2Cl_2) spectrum of 7



$^{19}F\{^{1}H\}$ NMR (376.4 MHz, CD_2Cl_2) spectrum of 7

Preparation of compound 8



^{1}H (400.0 MHz, CD_2Cl_2): δ 7.37-7.32 (m, 5H, Ar-H), 7.28-7.24 (m, 3H, Ar-H), 7.07 (d, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 2H, *o*-Ph), 4.11 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 2H, Te*CH*$_2$CH$_2$), 3.41 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 2H, TeCH$_2$*CH*$_2$)

$^{11}B\{^{1}H\}$ (128.3 MHz, CD_2Cl_2): δ 5.94 (s, $\nu_{1/2} \approx 720$ Hz)

$^{13}C\{^{1}H\}$ (100.6 MHz, CD_2Cl_2): δ =154.6 (br s, =CB), 148.4 (dm, $^{1}J_{C\text{-}F} \approx 245$ Hz, *o*-$C_6F_5^{B}$), 142.3 (dm, $^{1}J_{C\text{-}F} \approx 252$ Hz, *o*-C_6F_5), 142.0 ($^{1}J_{C\text{-}F} \approx 258$ Hz, *p*-$C_6F_5^{B}$), n.o. (*p*-C_6F_5), 143.4 (s, TeC=), 138.8 (s, *i*-Ph), 138.5 (s, *i*-Ph^{Te}), 138.3 (s, Ar-C), 137.8 (dm, $^{1}J_{C\text{-}F} \approx 232$ Hz, *m*-C_6F_5), 137.3 (dm,

$^{1}J_{C\text{-}F}$ ≈ 250 Hz, *m*-$C_6F_5^B$), 130.7 (s, *o*-Ph), 130.6 (s, *m*-Ph), 130.0 (s, Ar-C), 129.3 (s, Ar-C), 128.7 (s, Ar-C), 118.0 (br s, *i*-$C_6F_5^B$), 116.8 (br s, *i*-C_6F_5), 44.8 (s, Te*CH*$_2$CH$_2$), 32.6 (s, TeCH$_2$*CH*$_2$)

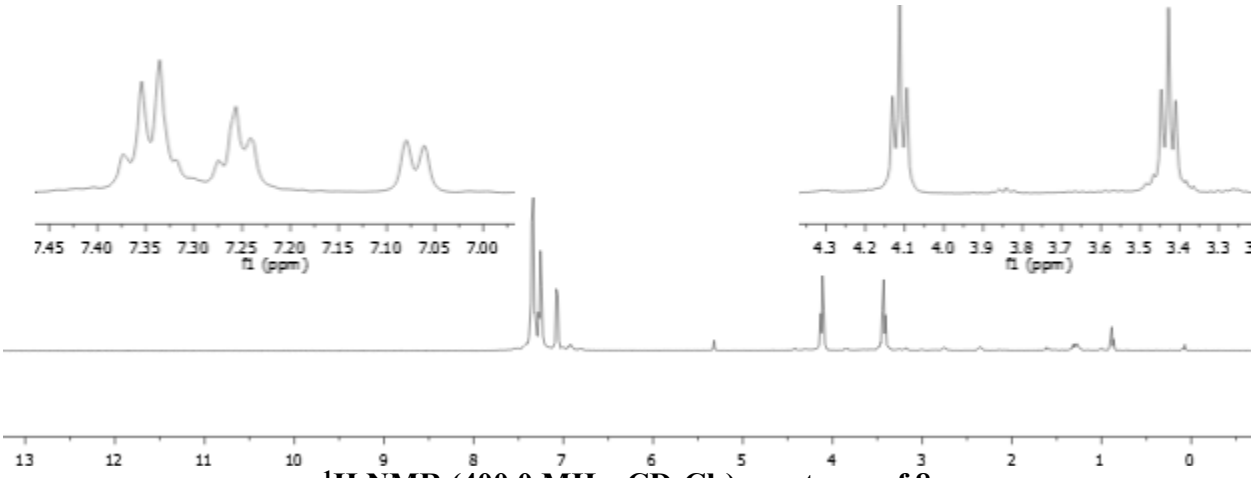
^{19}F{^{1}H} (376.4 MHz, CD_2Cl_2): δ -124.9 (s, br, 4F, *o*-$C_6F_5^B$), -136.4 (s, br, 2F, *o*-C_6F_5), -153.3 (app t, $^{3}J_{F\text{-}F}$ = 20.3 Hz, 2F, *p*-$C_6F_5^B$), -154.8 (app t, $^{3}J_{F\text{-}F}$ = 21.1 Hz, 1F, *p*-C_6F_5), -162.9 (m, 2F, *m*-C_6F_5), -163. 1 (m, 4F, *p*-$C_6F_5^B$)

^{125}Te (157.8 MHz, CD_2Cl_2): δ 955.1 (quint, $^{3}J_{Te\text{-}H}$ = 25.5 Hz)

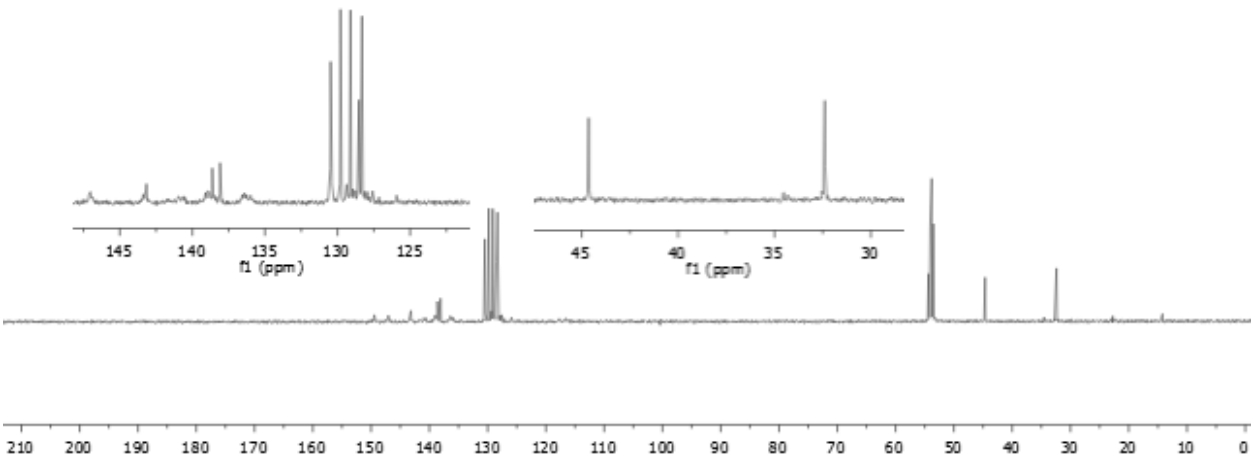
[Note: Ph^{Te} denotes *Ph*(CH$_2$)$_2$Te, $C_6F_5^B$ denotes =CB(C_6F_5)$_2$ and C_6F_5 denotes =C(C_6F_5)]

To a solution of compound **1** (50.9 mg, 0.15 mmol) in ca. 5 ml of toluene was added a slurry of B(C_6F_5)$_3$ (79.2 mg, 0.15 mmol) in ca. 5 ml of pentane at room temperature. The resulting clear yellow solution was stirred at room temperature for 10 min. before a solution of I_2 (40.1 mg, 0.16 mmol) in ca. 5 ml toluene was added. The solution was allowed to stir in the dark for 15 h before all volatiles were removed *in vacuo*, leaving a dark red oil. The oil was re-dissolved in minimal amount of pentane and stored at -35 °C for 18 h to give small orange crystals of **8** (49.8 mg, 4.5 mmol, 30% yield), which were then dried under vacuum. Single crystals suitable for X-ray diffraction studies were grown from the slow evaporation of a saturated pentane solution of **8** at room temperature.

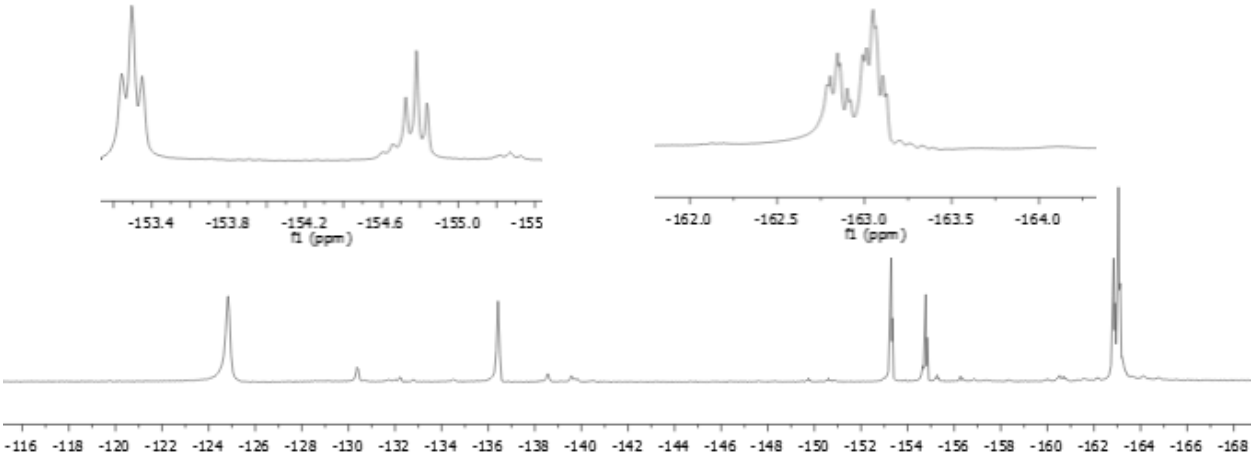
Anal. Calc. for $C_{34}H_{14}BF_{15}I_2Te$: C 37.14 %, H 1.28 %. Found: C 37.46 % H 1.47 %



^{1}H NMR (400.0 MHz, CD_2Cl_2) spectrum of 8



$^{13}C\{^{1}H\}$ NMR (125.7 MHz, CD_2Cl_2) spectrum of 8



$^{19}F\{^{1}H\}$ NMR (376.4 MHz, CD_2Cl_2) spectrum of 8