Electronic Supplementary Material (ESI) for ChemComm.

Unsymmetrically Substituted Tellurium-Boron based Heterocycles

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Supporting Information

General experimental procedure

All experimental manipulations were conducted using standard Schlenk line techniques or in an O_2-free, N_2-filled MBraun LABmaster SP dry box equipped with a -35 ^oC freezer, in either 4-dram glass vials with screw caps or in flame-dried Schlenk flasks. All proteo solvents (purchased from Caledon Laboratories) were purified using a Grubbs-type column system (Innovative Technologies) and stored over 4 Å sieves or sodium wire in Straus flasks. $CDCl_3$ (Cambridge Isotopes) was dried using CaH_2 and distilled under reduced pressure prior to use. All solvents were also degassed by repeated freeze-pump-thaw cycles prior to use.

Benzyl alcohol, 4-bromobenzyl alcohol, cinnamyl alcohol, 5-norbornene-2-methanol (*exo* + *endo*), 4-methoxyphenol and trimethylsilanol were purchased from Sigma-Aldrich, 1,1-diphenylmethanol and cyclohexanol were purchased from Alfa Aesar, 2-phenoxyethanol and 4-bromophenylacetylene were purchased from TCI chemicals, and 2-hydroxybenzylamine was purchased from Apollo Chemicals. All liquid reagents were de-gassed by repeated freeze-pump-thaw cycles and stored over 4 Å sieves prior to use. All solid reagents were placed under vacuum for 1 h prior to use. Compound 1, was prepared using standard literature procedure.[1]

NMR spectroscopy was performed on either a Bruker Advance III 400 MHz, an Agilent DD2 500 MHz, or an Agilent DD2 600 MHz spectrometer. Unless otherwise stated, all spectra were obtained at room temperature. All NMR spectra were referenced to residual proteo solvent peaks (^1H = 5.32 ppm and ^{13}C = 53.84 ppm for $CHCl_3$) 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)[2]).

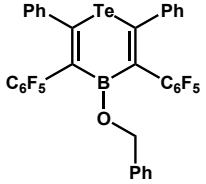
Single-crystal X-ray crystallographic analyses were performed on crystals coated in Paratone-N oil and mounted on a Bruker Kappa Apex II diffractometer. The structure was solved using SHELXS and least square refinements were performed using SHELXL-97. Combustion elemental analyses were performed on a PerkinElmer CHN Analyzer.

General synthetic procedure for compounds 2-11

1 eq. of compound **1** and 1.1 eq. of alkyne were dissolved in 5 ml of acetonitrile. The yellow slurry was then transferred into a 50-ml Schlenk flask equipped with a Teflon tab seal. The solution was heated to 110 ^oC for 16 h, upon which point a crude $^{19}F\{^1H\}$ NMR spectrum was taken to ensure reaction completion. The reaction times of compounds **2-11** vary between 1 to 7 days as outlined in **scheme 2** in the main article. Once the reaction was completed as determined by *in situ* $^{19}F\{^1H\}$ NMR spectra, all volatiles were removed under reduced pressure, and the product was extracted into 5 ml of DCM and filtered through a short plug of celite. The resulting clear yellow or orange solution was

then put under vacuum to remove all volatiles again before pentane was used to either precipitate out or recrystallize the product.

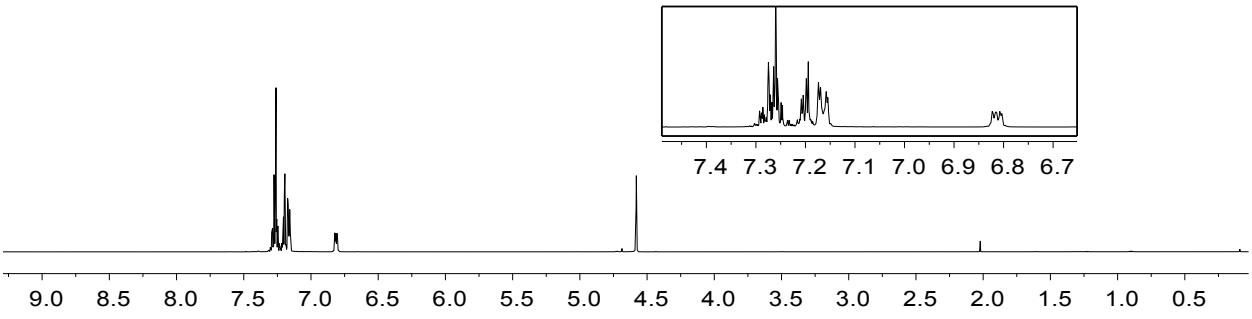
Spectroscopic data of 2



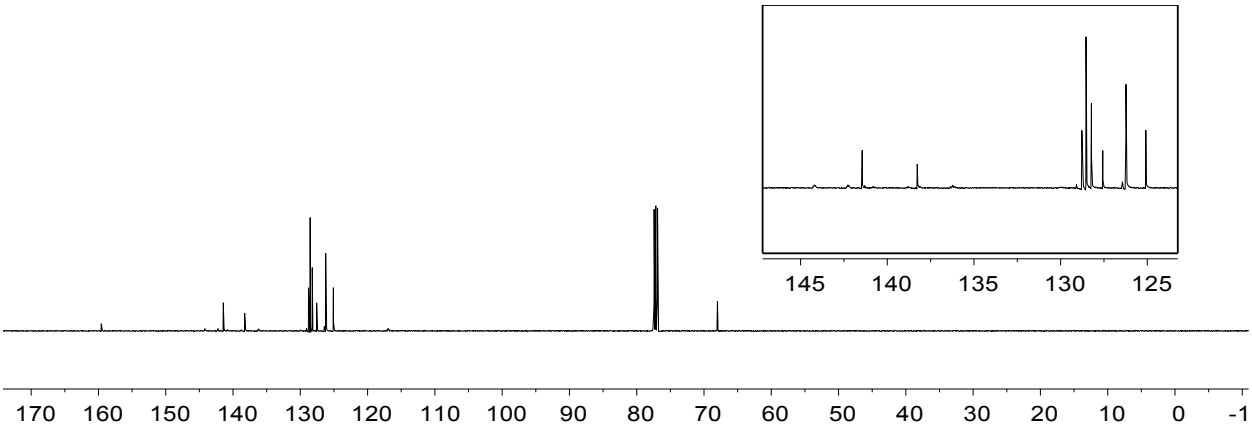
Compound **1** (612.2 mg, 0.727 mmol) was reacted with benzyl alcohol (104.0 mg, 0.9617 mmol) of benzyl alcohol to give compound **2** (478.1 mg, 0.6114 mmol, 85.1% yield), which precipitated out as an off-white powder when triturated with pentane.

^{1}H (500.0 MHz, $CDCl_3$): δ 7.26 (m, 6H, *m*-Ph^{Te} + *p*-Ph^{Te}), 7.20 (m, 3H, *m*-OCH_2*Ph* + *p*-OCH_2*Ph*), 7.17 (m, 4H, *o*-Ph^{Te}), 6.81 (m, 2H, *o*-OCH_2*Ph*), 4.58 (s, 2H, O*C*H_2Ph).
^{11}B{^{1}H} (128 MHz, $CDCl_3$): δ 36.9 (br s, $v_{1/2}$ ≈ 817 Hz)
^{13}C{^{1}H} (125 MHz, $CDCl_3$): δ 159.6 (s, Te*C*=), 141.4 (s, *i*-Ph^{Te}), 138.3 (s, *i*-OCH_2*Ph*), 129.9 (br s, BC=), 128.8 (s, *p*-Ph^{Te}), 128.5 (s, *m*-Ph^{Te}), 128.2 (s, *m*-OCH_2*Ph*), 127.6 (s, *p*-OCH_2*Ph*), 126.2 (s, *o*-Ph^{Te}), 125.1 (s, *o*-OCH_2*Ph*), 68.0 (s, O*C*H_2Ph).
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ -139.0 (m, 4F, *o*-C_6F_5), -156.7 (t, 2F, $^{3}J_{F\text{-}F}$ = 21.5 Hz, *p*-C_6F_5), -163.0 (m, 4F, *m*-C_6F_5)
^{125}Te (158 MHz, $CDCl_3$): δ 773.6 (s)

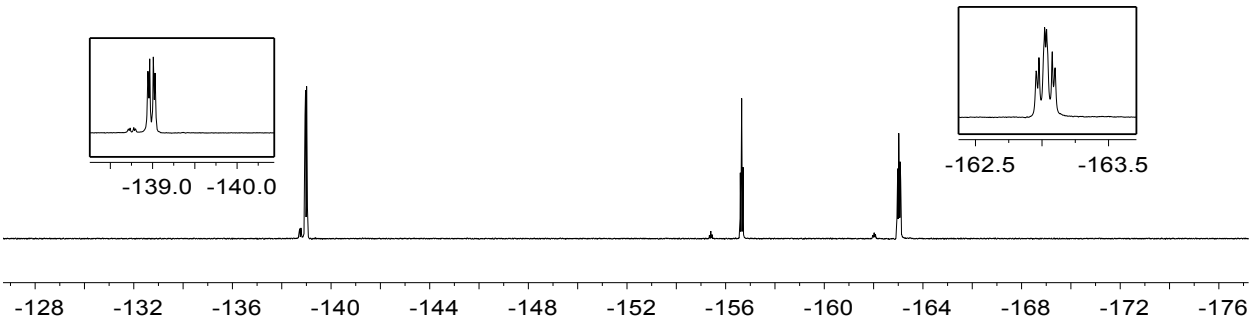
MS (DART+): cal'd for $C_{35}H_{18}OBF_{10}Te$ [M+H^{+}]: 785.03533 amu. Found: 785.03695 amu



^{1}H (500.0 MHz, $CDCl_3$) NMR spectrum of 2

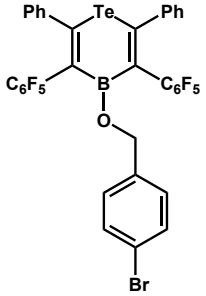


$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectrum of 2



$^{19}F\{^{1}H\}$ (377 MHz, $CDCl_3$) NMR spectrum of 2

Spectroscopic data of 3

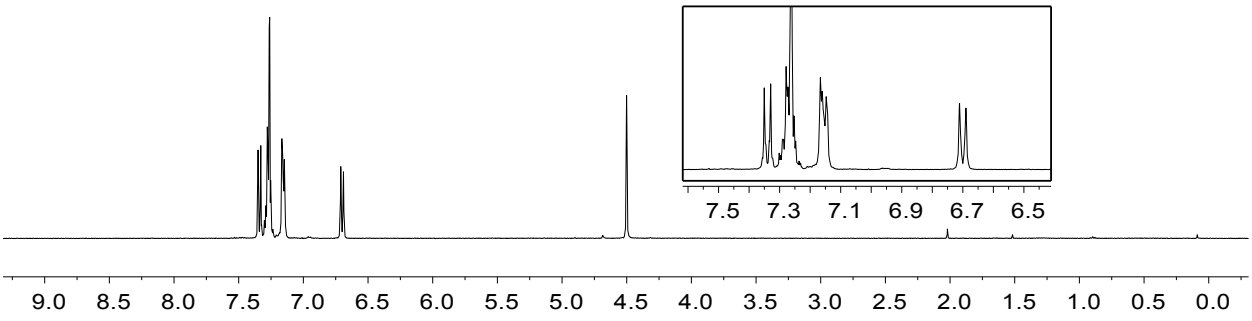


Compound **1** (77.0 mg, 0.0915 mmol) was reacted with 4-bromobenzyl alcohol (20.3 mg, 0.109 mmol) to give compound **3** (48.8 mg, 0.0567 mmol, 61.9% yield), which precipitated out as a white powder when triturated with pentane.

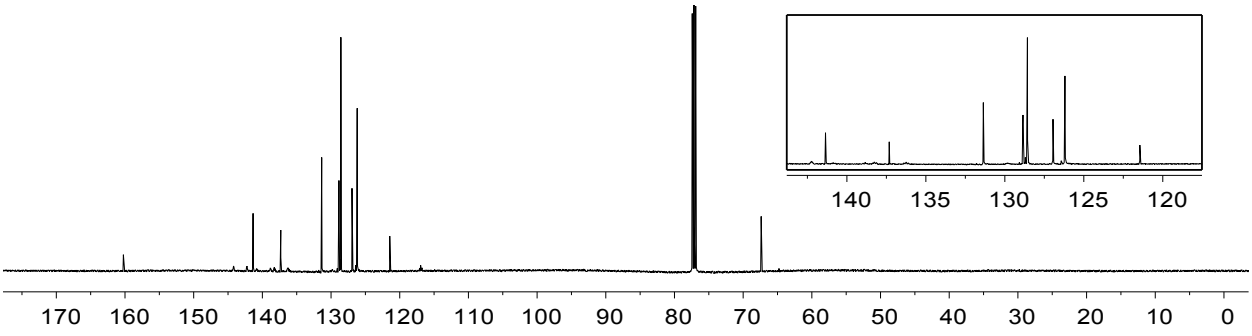
^{1}H (400.0 MHz, $CDCl_3$): δ 7.34 (d, 2H, $^{3}J_{H\text{-}H}$ = 8.4 Hz, *m*-OCH_2*Ar*), 7.28-7.25 (m, 6H, *m*-Ph^{Te} + *p*-Ph^{Te}), 7.16 (m, 4H, *o*-Ph^{Te}), 6.70 (d, 2H, $^{3}J_{H\text{-}H}$ = 8.4 Hz, *o*-OCH_2*Ar*), 4.50 (s, 2H, O*CH*$_2$Ar)
$^{11}B\{^{1}H\}$ (128 MHz, $CDCl_3$): δ 36.3 (br s, $v_{1/2}$ ≈ 1222 Hz)

$^{13}C\{^1H\}$ (125 MHz, $CDCl_3$): δ n.o. (BC=), 160.2 (s, Te*C*=), 141.4 (s, *i*-Ph^{Te}), 137.3 (s, *i*-OCH_2*Ar*), 131.4 (s, *m*-OCH_2*Ar*), 128.9 (s, *p*-Ph^{Te}), 128.6 (s, *m*-Ph^{Te}), 126.9 (s, *o*-OCH_2*Ar*) , 126.2 (s, *o*-Ph^{Te}), 121.5 (s, *o*-OCH_2*Ar*), 67.4 (s, OCH_2Ar).
$^{19}F\{^1H\}$ NMR (377 MHz, $CDCl_3$): δ -138.9 (m, 4F, *o*-C_6F_5), -156.2 (t, 2F, $^3J_{F\text{-}F}$ = 21.0 Hz, *p*-C_6F_5), -162.8 (m, 4F, *m*-C_6F_5)
^{125}Te (158 MHz, $CDCl_3$): δ 777.7 (s)

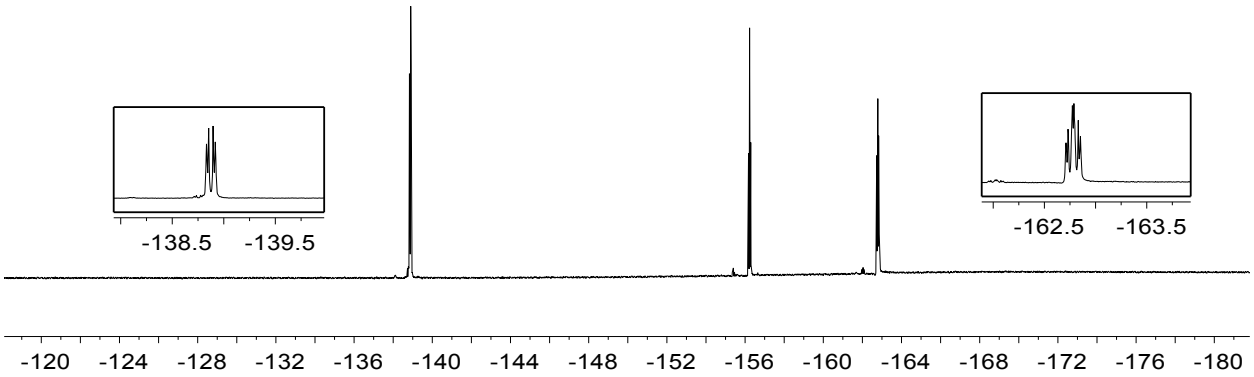
MS (DART+): cal'd for $C_{35}H_{17}BBrF_{10}OTe$ [M+H^+]: 862.94584 amu. Found: 862.94394 amu



^1H (400.0 MHz, $CDCl_3$) NMR spectrum of 3

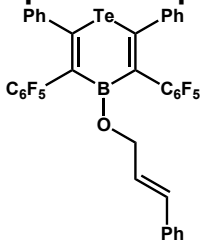


$^{13}C\{^1H\}$ (125 MHz, $CDCl_3$) NMR spectrum of 3



$^{19}F\{^{1}H\}$ (377 MHz, $CDCl_3$) NMR spectrum of 3

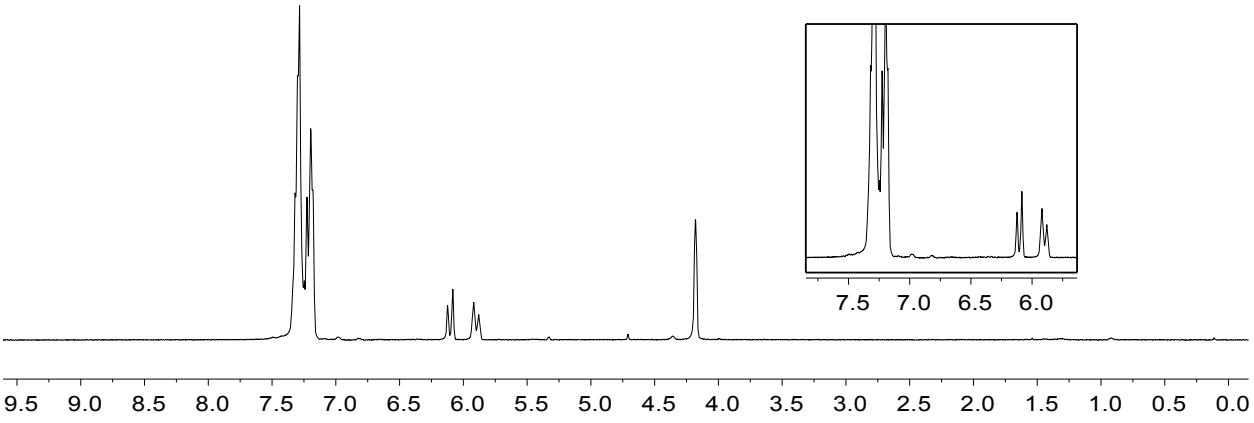
Spectroscopic data of 4



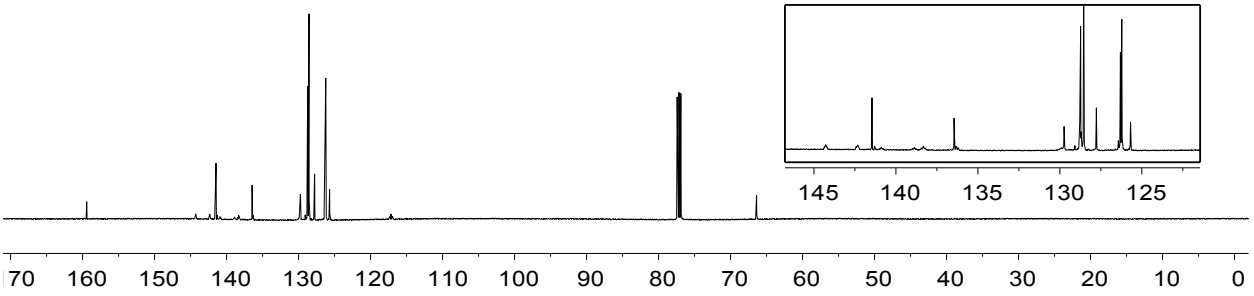
Compound **1** (114.0 mg, 0.1354 mmol) was reacted with cinnamyl alcohol (55.1 mg, 0.411 mmol) of to give compound **4** (83.2 mg, 0.103 mmol, 76.1% yield), which precipitated out as a yellow powder when triturated with pentane.

^{1}H (400.0 MHz, $CDCl_3$): δ 7.31-7.22 (m, 9H, *Ar*-H), 7.20-7.15 (m, 6H, *Ar*-H), 6.08 (d, 1H, $^{3}J_{H-H}$ = 15.8 Hz, $OCH_2CHCHPh$), 5.87 (dt, 1H, $^{3}J_{H-H}$ = 15.8 Hz, $^{3}J_{H-H}$ = 5.4 Hz, OCH_2CHPh), 4.15 (m, OCH_2CHPh)
$^{11}B\{^{1}H\}$ (128 MHz, $CDCl_3$): δ 37.2 (br s, $v_{1/2}$ ≈ 997 Hz)
$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$): (C_6F_5 signals not listed, Ar signals tentatively assigned due to closeness in peaks) δ 159.4 (s, Te*C*=), 141.5 (s, *i*-Ph^{Te}), 136.5 (s, *i*-Ph), 129.9 (br s, BC=),129.7 (s, OCH_2CHPh), 128.8, (s, *p*-Ph), 128.7 (s, *p*-Ph^{Te}), 128.5 (s, *m*-Ph^{Te}), 127.8 (s, *m*-Ph), 126.3 (s, *o*-Ph), 126.2 (s, *o*-Ph^{Te}), 125.7 (s, $OCH_2CHCHPh$), 66.4 (s, OCH_2CHPh)
$^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$): δ -138.8 (m, 4F, *o*-C_6F_5), -156.3 (t, 2F, $^{3}J_{F-F}$ = 21.4 Hz, *p*-C_6F_5), -162.8 (m, 4F, *m*-C_6F_5)
^{125}Te (158 MHz, $CDCl_3$): δ 773.3 (s)

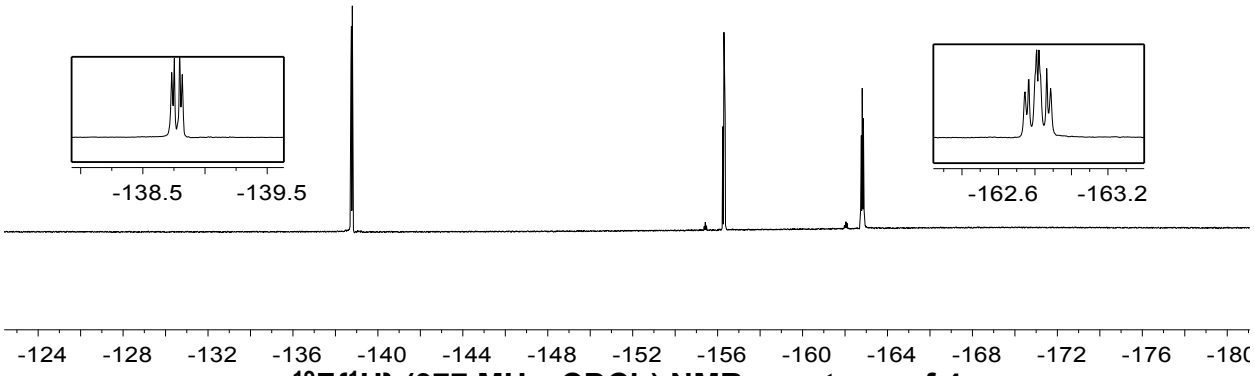
Anal. Calc. for $C_{37}H_{19}BF_{10}OTe$: C 55.00%, H 2.37%. Found: C 54.67% H 2.24%



^{1}H (400.0 MHz, $CDCl_3$) NMR spectrum of 4

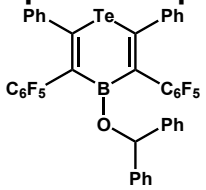


^{13}C{^{1}H} (125 MHz, $CDCl_3$) NMR spectrum of 4



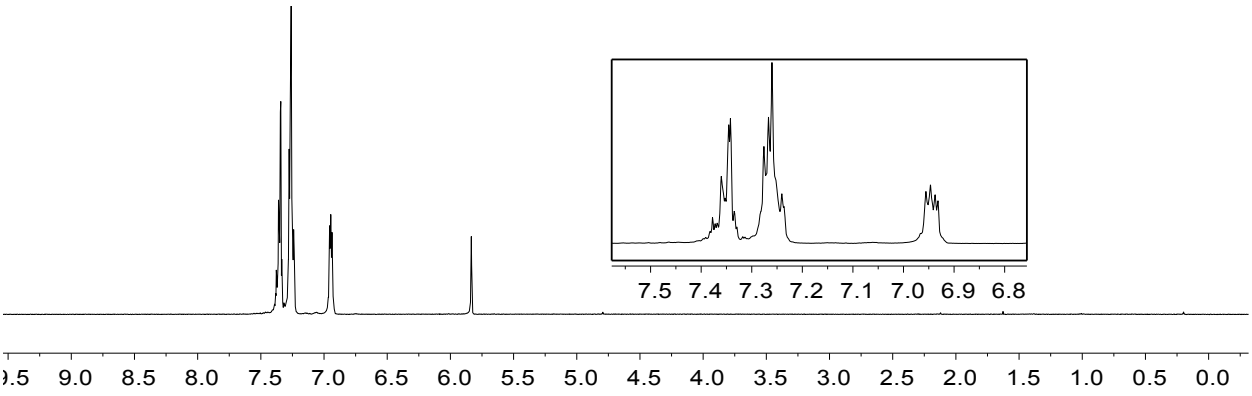
^{19}F{^{1}H} (377 MHz, $CDCl_3$) NMR spectrum of 4

Spectroscopic data of 5

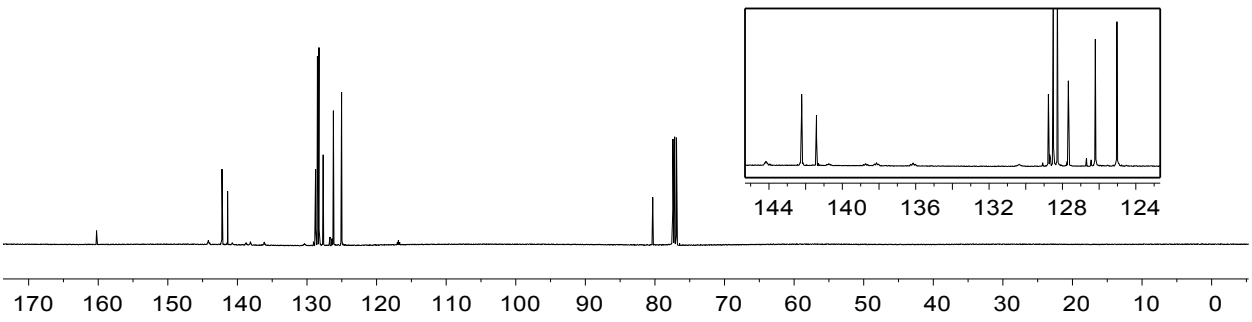


Compound **1** (84.9 mg, 0.101 mmol) was reacted with 1,1-diphenylmethanol (23.6 mg, 0.128 mmol) to give compound **5** (42.8 mg, 0.0498 mmol, 49.4% yield), which precipitated out as a white powder when triturated with pentane.

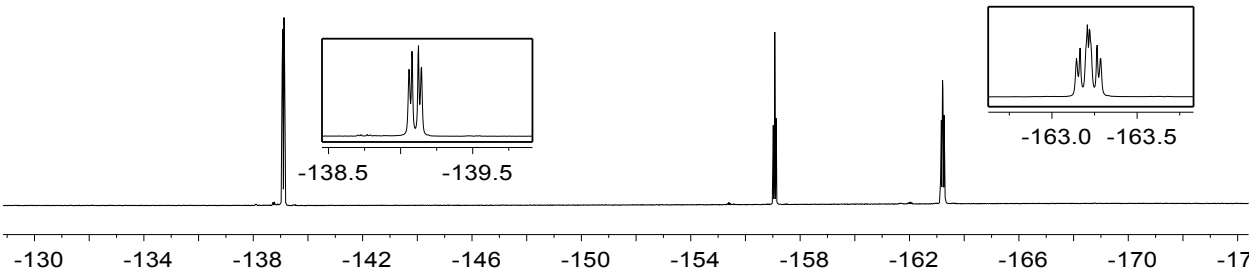
^{1}H (400.0 MHz, $CDCl_3$): δ 7.38-7.33 (m, 6H, *m*-, *p*-Ph), 7.28-7.24 (m, 10H, *m*-, *p*-Ph^{Te} + *o*-Ph), 6.95 (m, 4H, *o*-Ph^{Te}), 5.84 (s, OC*H*Ph_2)
^{11}B{^{1}H} (128 MHz, $CDCl_3$): δ 36.2 (br s, $v_{1/2}$ ≈ 1380 Hz)
^{13}C{^{1}H} (125 MHz, $CDCl_3$): (C_6F_5 signals not listed) δ 160.2 (s, Te*C*=), 142.2 (s, *i*-Ph^{Te}), 141.4 (s, *i*-Ph), 130.4 (br s, BC=), 128.8 (s, *p*-Ph^{Te}), 128.5 (s, *m*-Ph^{Te}), 128.3 (s, *m*-Ph), 127.7 (s, *p*-Ph), 126.2 (s, *o*-Ph^{Te}), 125.0 (s, *o*-Ph), 80.3 (s, OC*H*Ph_2)
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ -139.1 (m, 4F, *o*-C_6F_5), -157.1 (t, 2F, $^{3}J_{F-F}$ = 21.1 Hz, *p*-C_6F_5), -163.2 (m, 4F, *m*-C_6F_5)
^{125}Te (158 MHz, $CDCl_3$): δ 777.7 (s)



^{1}H (400.0 MHz, $CDCl_3$) NMR spectrum of 5

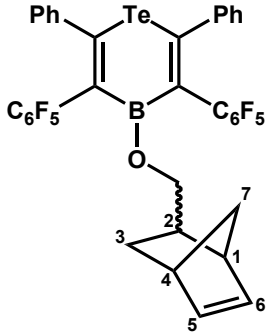


$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectrum of 5



$^{19}F\{^{1}H\}$ (377 MHz, $CDCl_3$) NMR spectrum of 5

Spectroscopic data of 6



Compound **1** (221.1 mg, 0.2626 mmol) was reacted with 5-norbornene-2-methanol (*endo:exo* ≈ *7:3*) (33.3 mg, 0.268 mmol) of to give compound **6** (129.3 mg, 0.1620 mmol, 61.7% yield), which precipitated out as an off-white powder when triturated with pentane. The ratio of endo and exo isomers in **6** is about the same as the starting mixture as confirmed by integration in ^{1}H NMR spectrum.

^{1}H (500.0 MHz, $CDCl_3$): δ 7.35-7.34 (m, 2H, *p*-Ph^{Te}), 7.29-7.23 (m, 4H, *m*-Ph^{Te}), 7.17 (m, 4H, *o*-Ph^{Te}), 6.01 (m, 1H, *endo* =C*H*), 5.96 (m, 1H, *exo* =C*H*), 5.92 (m, 1H, *exo* =C*H*), 5.61 (m, 1H, *endo* =C*H*), 3.41 (m, 1H, *exo* OCH_2), 3.21 (app t, 1H, *exo* OCH_2), 3.04 (m,

1H, *endo* OCH_2), 2.95 (app t, 1H, *endo* OCH_2), 2.69 (br s, 1H, H^1), 2.36 (br s, 1H, *endo* H^4), 2.22 (br s, 1H, *exo* H^4), 1.96 (m, 1H, *endo* H^2), 1.50 (m, 1H, *endo* H^3), 1.33 (m, 1H, *endo* H^7), 1.29 (m, 1H, *exo* C^2), 1.20 (m, 1H, *exo* H^7), 1.11 (m, 1H, *endo* H^7), 0.96 (m, 1H, *exo* H^3), 0.91 (m, 1H, *exo* H^7), 0.71 (m, 1H, *exo* H^3), 0.12 (m, 1H, *endo* H^3)

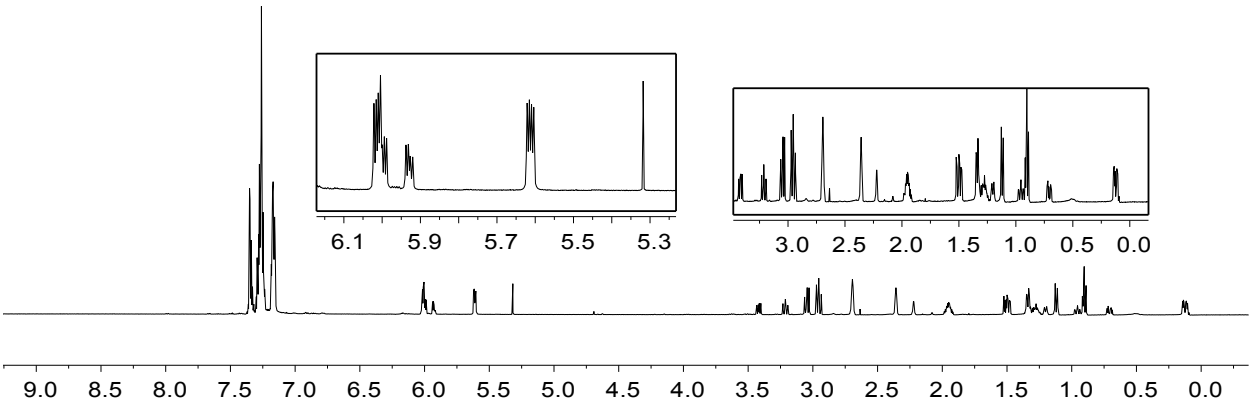
$^{11}B\{^1H\}$ (128 MHz, $CDCl_3$): δ 34.9 (br s, $v_{1/2}$ ≈ 922 Hz)

$^{13}C\{^1H\}$ (125 MHz, $CDCl_3$): δ 158.8 (s, *exo* Te*C*=), 158.4 (s, *endo* Te*C*=), 141.54 (s, *Ar*-C), 141.49 (s, *Ar*-C), 141.2 (s, *Ar*-C), 137.5 (s, *endo* C^5), 136.8 (s, *exo* C^5), 136.2 (s, *exo* C^6), 131.8 (s, *endo* C^6), 129.9 (s, *Ar*-C), 129.7(s, *Ar*-C), 128.8 (s, *Ar*-C), 128.7 (s, *Ar*-C), 128.7 (s, *Ar*-C), 128.5 (s, *Ar*-C), 128.5 (s, *Ar*-C), 126.5 (s, *Ar*-C), 126.3 (s, *Ar*-C), 70.3 (s, *exo* O*C*H_2), 69.7 (s, *endo* O*C*H_2), 49.4 (s, *endo* C^7), 44.8 (s, *exo* C^7), 43.5 (s, *endo* C^4), 43.26 (s, C^{Nor}), 43.28 (s, C^{Nor}), 42.2 (s, C^1), 41.5 (s, C^{Nor}), 41.0 (s, C^{Nor}), 40.5 (s, C^{Nor}), 28.9 (s, *exo* C^3), 28.5 (s, *endo* C^3)

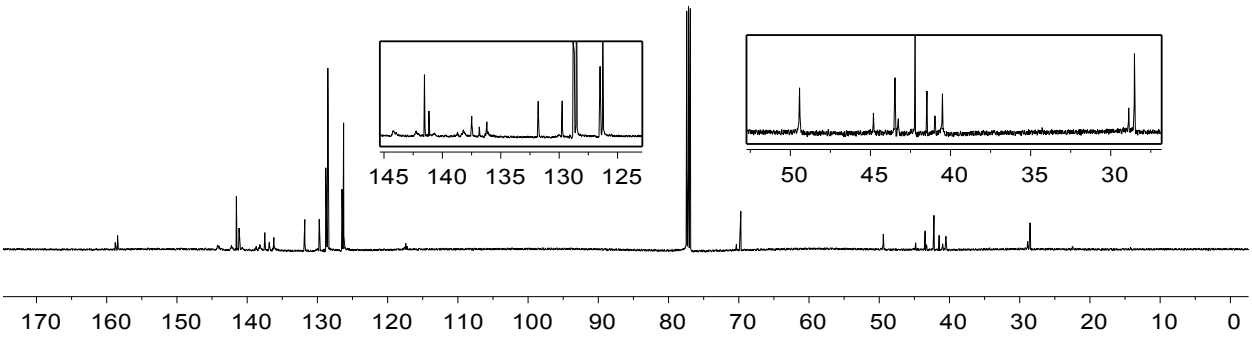
$^{19}F\{^1H\}$ NMR (377 MHz, $CDCl_3$): δ -139.1 (m, 4F, *o*-C_6F_5), -156.8 (t, $^3J_{F\text{-}F}$ = 20.5 Hz, 2F, *exo p*-C_6F_5), -156.7 (t, $^3J_{F\text{-}F}$ = 21.8 Hz, 2F, *endo p*-C_6F_5), -163.2 (m, 4F, *m*-C_6F_5)

^{125}Te (158 MHz, $CDCl_3$): δ 763.5 (s)

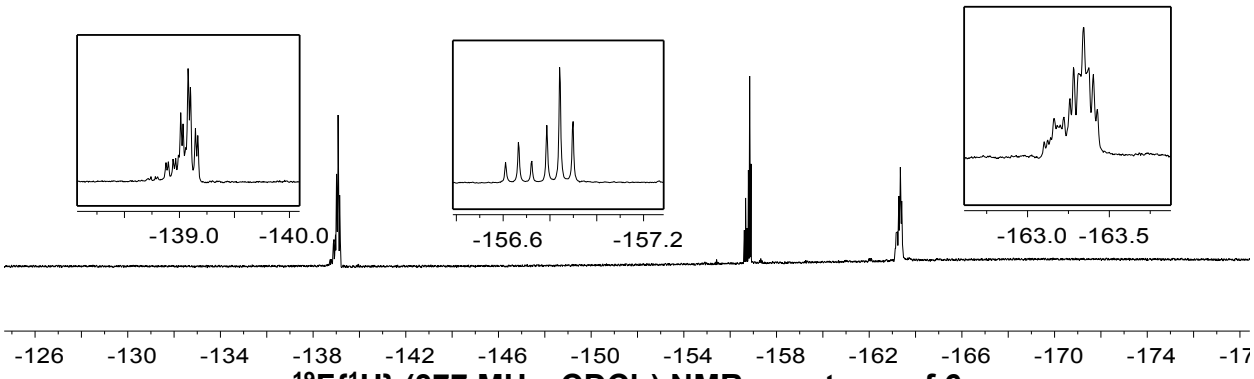
Note: when not specified, the endo- and exo-resonances are too close in chemical shifts to be unambiguously assigned by 2D experiments



^1H (500.0 MHz, $CDCl_3$) NMR spectrum of 6

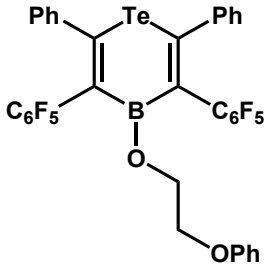


$^{13}C\{^1H\}$ (125 MHz, $CDCl_3$) NMR spectrum of 6



$^{19}F\{^{1}H\}$ (377 MHz, $CDCl_3$) NMR spectrum of 6

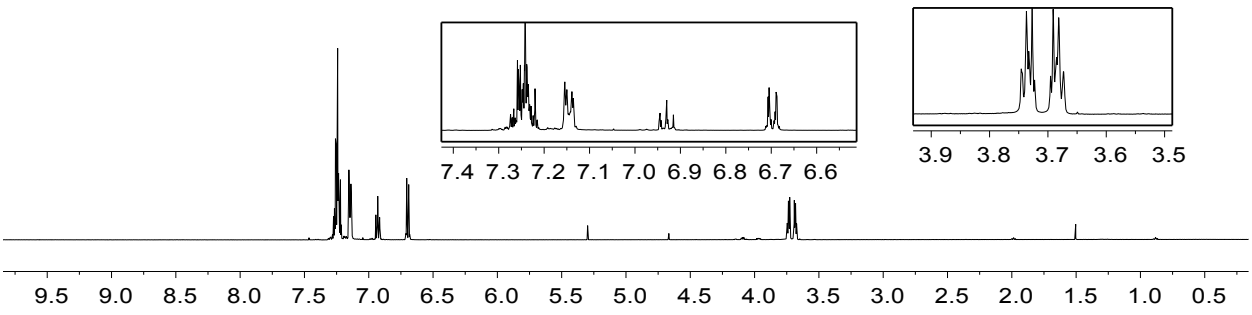
Spectroscopic data of 7



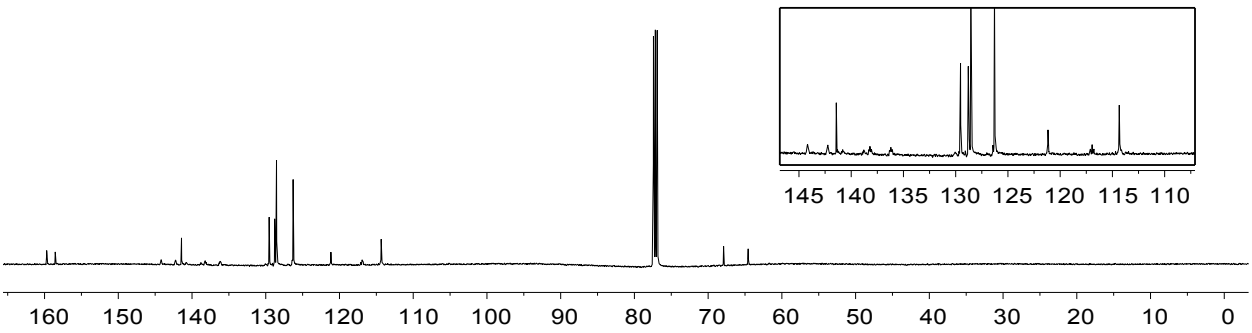
Compound **1** (103.7 mg, 0.1232 mmol) was reacted with 2-phenoxyethanol (51.8 mg, 0.374 mmol) to give compound **7** (62.9 mg, 0.0775 mmol, 62.9% yield), which precipitated out as an off-white powder when triturated with pentane.

^{1}H (500.0 MHz, $CDCl_3$): δ 7.27-7.22 (m, 8H, *m*-, *p*-Ph^{Te} + *m*-Ph), 7.15 (m, 4H, *o*-Ph^{Te}), 6.93 (tt, 1H, $^{3}J_{H-H}$ = 7.3 Hz, $^{4}J_{H-H}$ = 1.0 Hz, *p*-Ph^{O}), 6.69 (m, 2H, *p*-Ph^{O}), 3.73 (m, 2H, CH_2), 3.69 (m, 2H, CH_2)
$^{11}B\{^{1}H\}$ (128 MHz, $CDCl_3$): δ 36.4 (br s, $v_{1/2}$ ≈ 1210 Hz)
$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$): δ 159.7 (s, Te*C*=), 158.6 (s, *i*-Ph^{O}), 141.4 (s, *i*-Ph^{Te}), 130.1 (br s, BC=), 129.5 (s, *m*-Ph^{O}), 128.8 (s, *p*-Ph^{Te}), 128.5 (s, *m*-Ph^{Te}), 126.3 (s, *o*-Ph^{Te}), 121.2 (s, *p*-Ph^{O}), 114.3 (s, *o*-Ph^{O}), 67.9 (s, CH_2), 64.6 (s, CH_2)
$^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$): δ -139.0 (m, 4F, *o*-C_6F_5), -156.2 (t, 2F, $^{3}J_{F-F}$ = 20.9 Hz, *p*-C_6F_5), -162.9 (m, 4F, *m*-C_6F_5)
^{125}Te (158 MHz, $CDCl_3$): δ 771.4 (s)

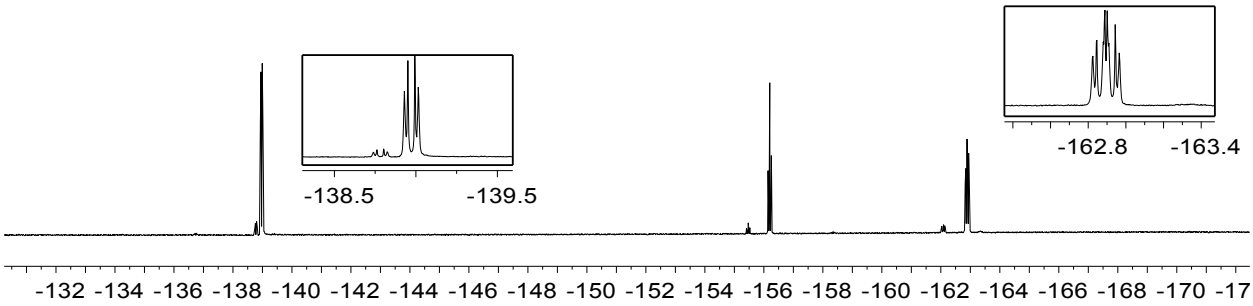
Anal. Calc. for $C_{36}H_{19}BF_{10}O_2Te$: C 53.25%, H 2.36%. Found: C 52.48% H 2.24%



^{1}H (500.0 MHz, $CDCl_3$) NMR spectrum of 7

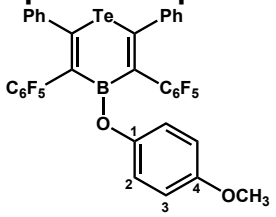


^{13}C{^{1}H} (125 MHz, $CDCl_3$) NMR spectrum of 7



^{19}F{^{1}H} (377 MHz, $CDCl_3$) NMR spectrum of 7

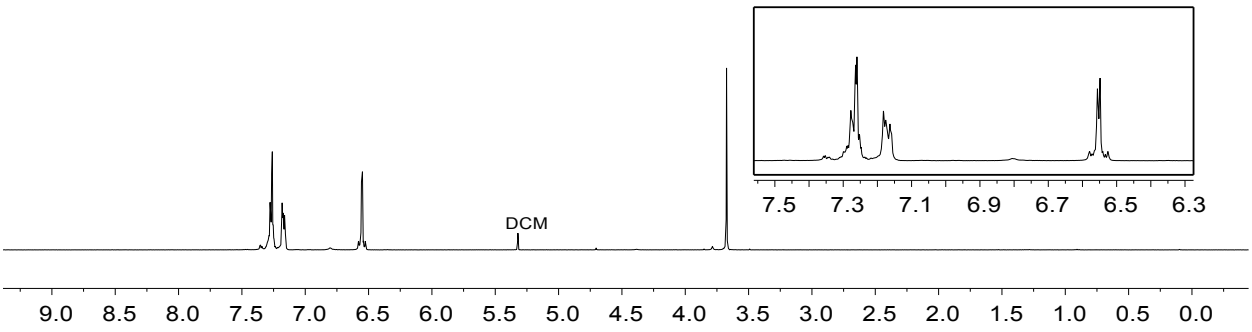
Spectroscopic data of 8



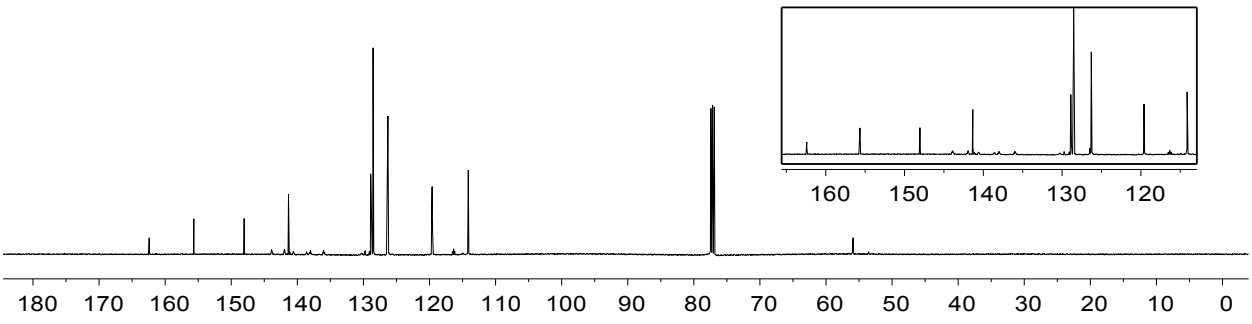
Compound **1** (118.5 mg, 0.1408 mmol) was reacted with 4-methoxyphenol (18.2 mg, 0.147 mmol) to give compound **8** (72.8 mg, 0.0912 mmol, 64.7%) after 7 days of heating at 110 °C. It could be precipitated out as a light yellow powder when triturated with pentane.

^{1}H (400.0 MHz, $CDCl_3$): δ 7.29-7.25 (m, 6H, *m*-, *p*-Ph^{Te}), 7.17 (m, 4H, *o*-Ph^{Te}), 6.55 (app d, 4H, H^2 + H^3), 3.67 (s, 3H, OCH_3)
^{11}B{^{1}H} (128 MHz, $CDCl_3$): δ 35.9 (br s, $v_{1/2}$ ≈ 1200 Hz)
^{13}C{^{1}H} (125 MHz, $CDCl_3$): (C_6F_5 signals not listed) δ 162.4 (s, Te*C*=), 155.7 (s, C^4), 148.1 (s, C^1), 141.3 (s, *i*-Ph^{Te}), 130.3 (br s, BC=), 128.9 (s, *p*-Ph^{Te}), 128.5 (s, *m*-Ph^{Te}), 126.3 (s, *o*-Ph^{Te}), 119.6 (s, C^2), 114.1 (s, C^3), 55.9 (s, O*C*H_3)
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ -133.9 (m, 4F, *o*-C_6F_5), -157.1 (t, 2F, $^{3}J_{F\text{-}F}$ = 20.8 Hz, *p*-C_6F_5), -163.6 (m, 4F, *m*-C_6F_5)
^{125}Te (158 MHz, $CDCl_3$): δ 781.6 (s)

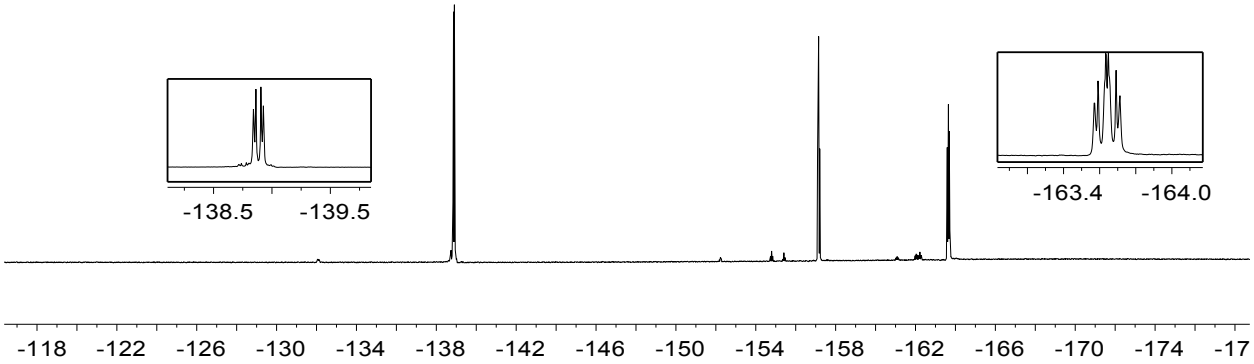
MS (DART+): cal'd for $C_{35}H_{17}O_2BF_{10}Te$ [M^+]: 800.02241 amu. Found: 800.02322 amu



^{1}H (400.0 MHz, $CDCl_3$) NMR spectrum of 8

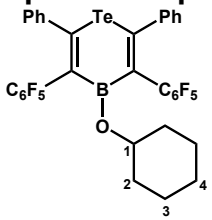


$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectrum of 8



$^{19}F\{^{1}H\}$ (377 MHz, $CDCl_3$) NMR spectrum of 8

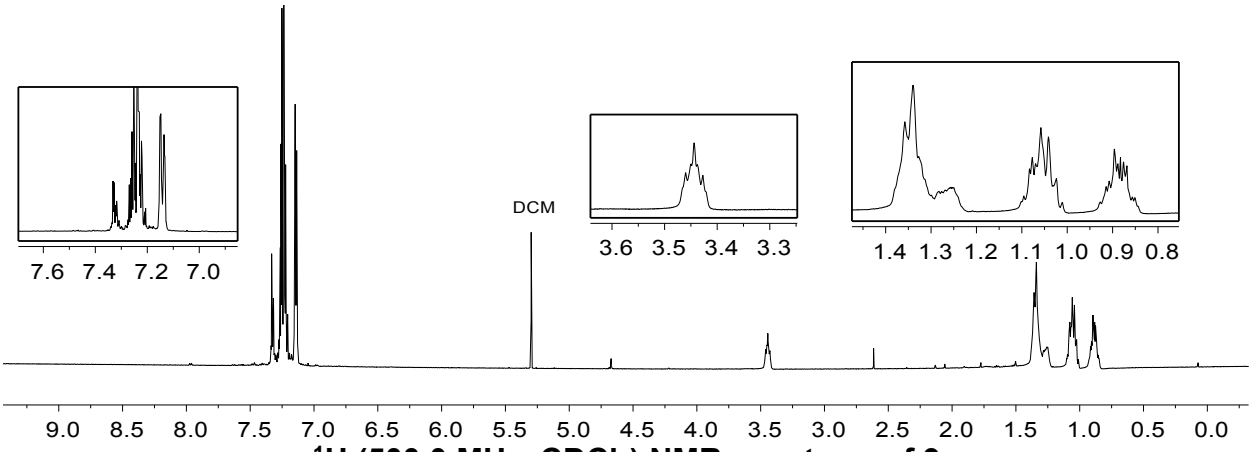
Spectroscopic data of 9



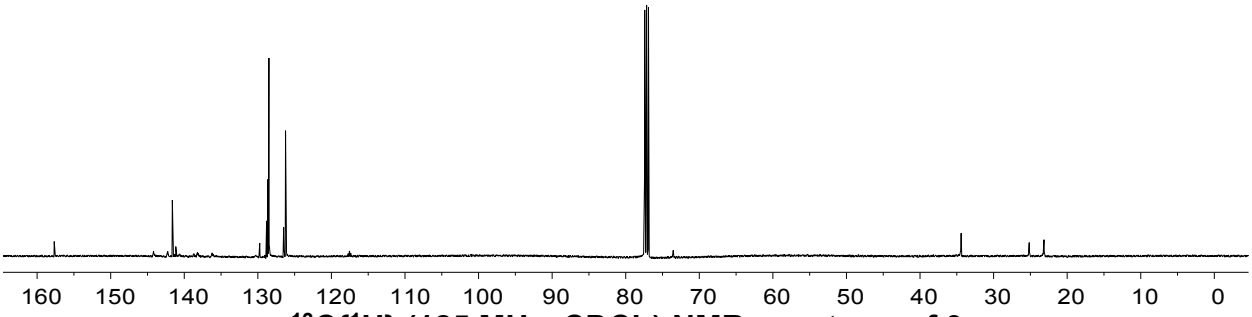
Compound **1** (123.5 mg, 0.1467 mmol) was reacted with cyclohexanol (20.3 mg, 0.203 mmol) to give compound **9** (70.5 mg, 0.0911 mmol, 62.1% yield), which precipitated out as a yellow powder when triturated with pentane.

^{1}H (500.0 MHz, $CDCl_3$): δ 7.35 (m, 1H, *o*-Ph^{Te}), 7.30-7.24 (m, 6H, *m*-, *p*-Ph^{Te}), 7.16 (m, 3H, *o*-Ph^{Te}), 3.46 (br m, 1H, H^1), 1.36 (br m, 5H, H^3 + H^2), 1.08 (br m, 3H, H^2), 0.92 (br m, 2H, H^4)
^{11}B{^{1}H} (128 MHz, $CDCl_3$): δ 35.8 (br s, $v_{1/2}$ ≈ 640 Hz)
^{13}C{^{1}H} (125 MHz, $CDCl_3$): (C_6F_5 signals not listed) δ 157.7 (s, Te*C*=), 141.6 (s, *i*-Ph^{Te}), 130.3 (br s, BC=), 128.6 (s, *p*-Ph^{Te}), 128.5 (s, *m*-Ph^{Te}), 126.2 (s, *o*-Ph^{Te}), 73.6 (s, C^1), 34.4 (s, C^2), 25.2 (s, C^3), 23.2 (s, C^4)
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ -139.1 (m, 4F, *o*-C_6F_5), -156.9 (t, 2F, $^{3}J_{F\text{-}F}$ = 20.5 Hz, *p*-C_6F_5), -163.4 (m, 4F, *m*-C_6F_5)
^{125}Te (158 MHz, $CDCl_3$): δ 754.5 (s)

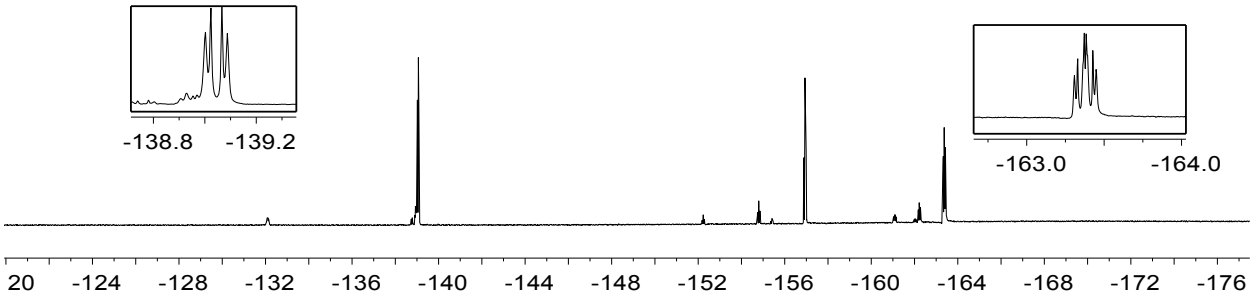
MS (DART+): cal'd for $C_{34}H_{22}OBF_{10}Te$ [M+H^+]: 777.06663 amu. Found: 777.06606 amu



^{1}H (500.0 MHz, $CDCl_3$) NMR spectrum of 9

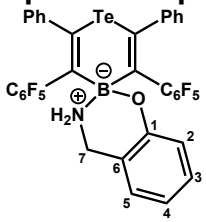


$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectrum of 9



$^{19}F\{^{1}H\}$ (377 MHz, $CDCl_3$) NMR spectrum of 9

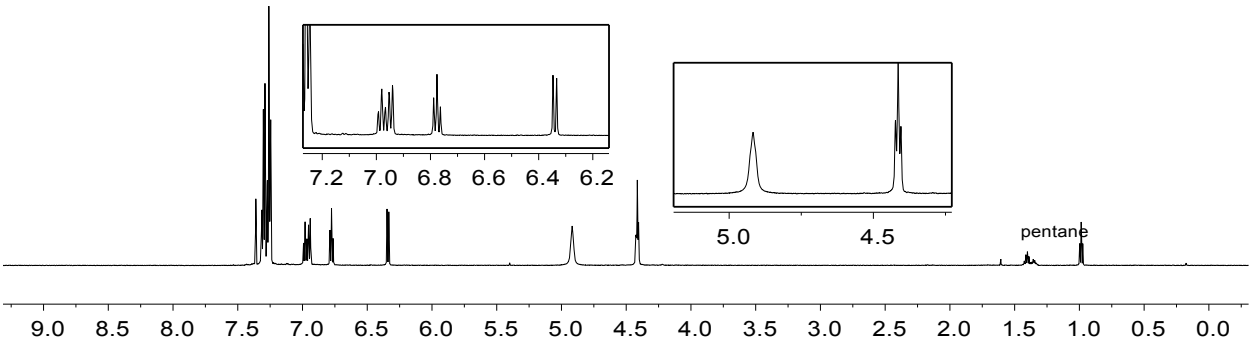
Spectroscopic data of 10



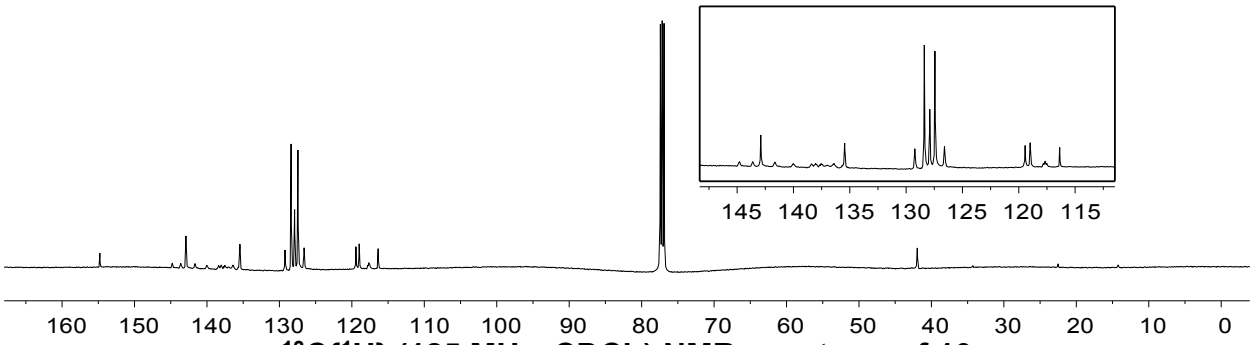
Compound **1** (139.0 mg, 0.1651 mmol) was reacted with 2-hydroxybenzylamine (22.4 mg, 0.1819 mmol) to give compound **10** (86.6 mg, 0.109 mmol, 65.8%) of **10**, which precipitated out as a white powder when triturated with pentane.

^{1}H (600.0 MHz, $CDCl_3$): δ 7.31-7.29 (m, 4H, Ar), 7.27-7.25 (m, 6H, Ar), 6.98 (app t, 1H, H^3), 6.94 (d, 1H, $^{3}J_{H\text{-}H}$ = 7.6 Hz, H^5), 6.78 (app t, 1H, H^4), 6.34 (d, 1H, $^{3}J_{H\text{-}H}$ = 8.1 Hz, H^2), 4.92 (br s, 2H, NH_2), 4.41 (t, 2H, $^{3}J_{H\text{-}H}$ = 5.7 Hz, H^7)
^{11}B{^{1}H} (128 MHz, $CDCl_3$): δ 1.3 (s, $v_{1/2}$ ≈ 290 Hz)
^{13}C{^{1}H} (125 MHz, $CDCl_3$): (C_6F_5 signals not listed) δ 154.8 (s, Te*C*=), 143.2 (1:1:1:1 q, $^{1}J_{C\text{-}B}$ = 150 Hz, BC=), 142.9 (s, *i*-Ph^{Te}), 135.5 (s, C^1), 129.2 (s, C^3), 128.4 (s, *m*-Ph^{Te}), 127.9 (s, *p*-Ph^{Te}), 127.4 (s, *o*-Ph^{Te}), 126.6 (s, C^5), 119.4 (s, C^4), 119.0 (s, C^2), 116.4 (s, C^6), 42.0 (s, C^7)
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ -139.4 (m, 2F, *o*-C_6F_5), -141.5 (m, 2F, *o*-C_6F_5), -158.8 (app t, 2F, *p*-C_6F_5), -163.4 (m, 2F, *m*-C_6F_5), -165.1 (m, 2F, *m*-C_6F_5)
^{125}Te (158 MHz, $CDCl_3$): δ 691.7 (s)

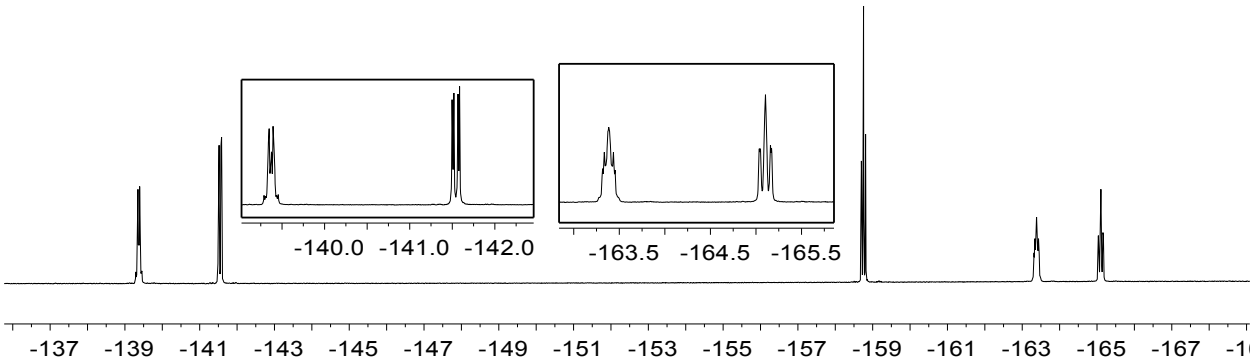
Anal. Calc. for $C_{34}H_{16}BF_{10}NOTe$: C 52.16%, H 2.06%, N 1.79% Found: C 52.22%, H 2.39%, N 1.70%



^{1}H (600.0 MHz, $CDCl_3$) NMR spectrum of 10

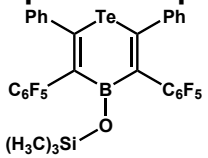


$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectrum of 10



$^{19}F\{^{1}H\}$ (377 MHz, $CDCl_3$) NMR spectrum of 10

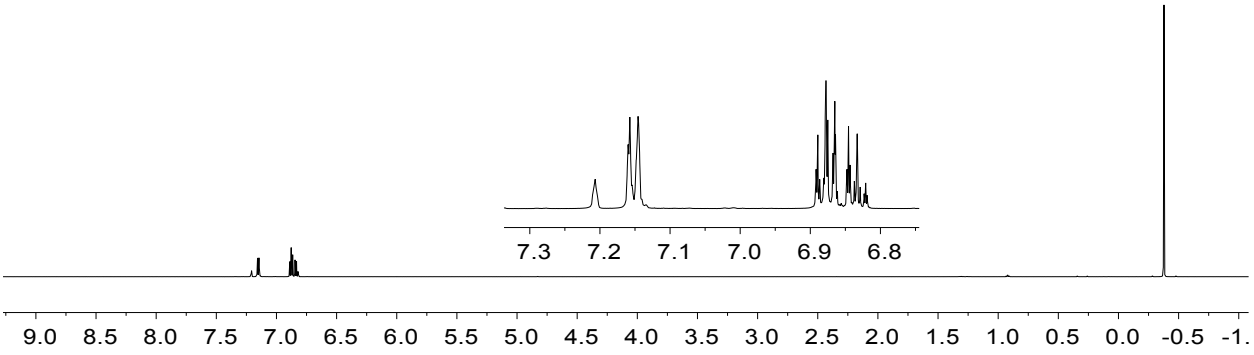
Spectroscopic data of 11



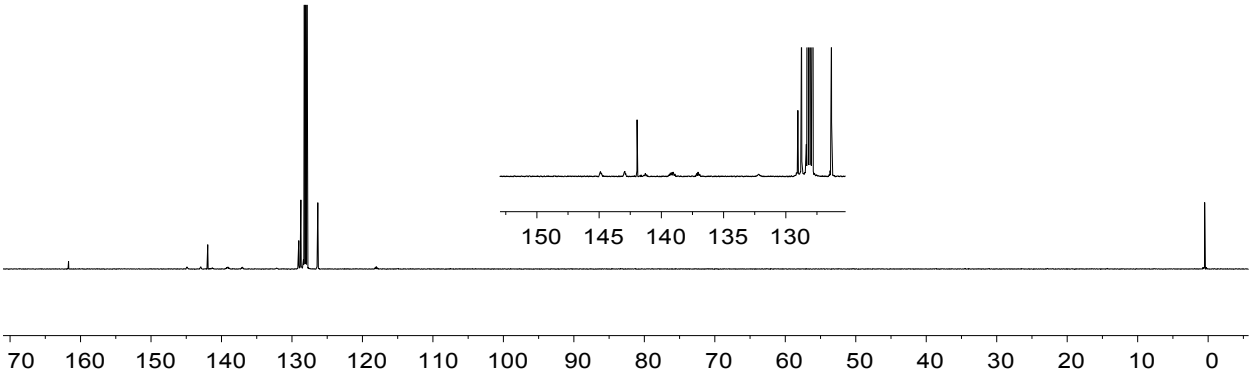
Compound **1** (163.1 mg, 0.1937 mmol) was reacted with trimethylsilanol (21.0 mg, 0.2328 mmol) to give compound **11** (78.3 mg, 0.102 mmol, 52.9% yield), which was purified by recrystallization from pentane.

^{1}H (600.0 MHz, C_6D_6): δ 7.11 (d, 4H, $^{3}J_{H-H}$ = 6.8 Hz, *o*-Ph), 6.85-6.77 (m, 6H, *m*-, *p*-Ph), -0.42 (s, 9H, $Si(CH_3)_3$)
$^{11}B\{^{1}H\}$ (128 MHz, C_6D_6): δ 35.2 (s, $v_{1/2} \approx 820$ Hz)
$^{13}C\{^{1}H\}$ (125 MHz, C_6D_6): (C_6F_5 signals not listed) δ 161.7 (s, Te*C*=),142.0 (s, *i*-Ph^{Te}), 132.2 (br s, BC=), 129.0 (s, *p*-Ph^{Te}), 128.7 (s, *m*-Ph^{Te}), 126.3 (*o*-Ph^{Te})
$^{19}F\{^{1}H\}$ NMR (377 MHz, C_6D_6): δ -139.1 (dd, 4F, *o*-C_6F_5, $^{3}J_{F-F}$ = 24 Hz, $^{4}J_{F-F}$ = 8 Hz), -157.1 (app t, 2F, *p*-C_6F_5, $^{3}J_{F-F}$ = 21 Hz), -163.5 (m, 4F, *m*-C_6F_5)
^{125}Te (158 MHz, C_6D_6): δ 768.4 (s)

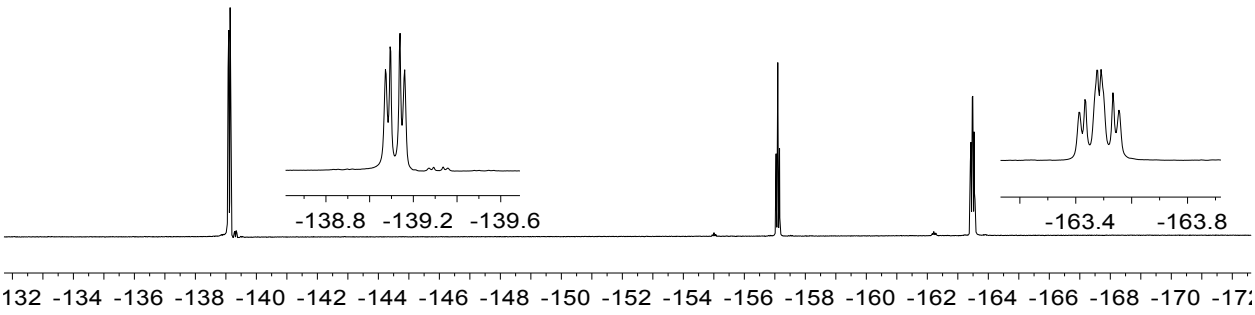
Anal. Calc. for $C_{31}H_{19}BF_{10}SiOTe$: C 48.74%, H 2.51% Found: C 49.25%, H 2.49%



^{1}H (600.0 MHz, C_6D_6) NMR spectrum of 11

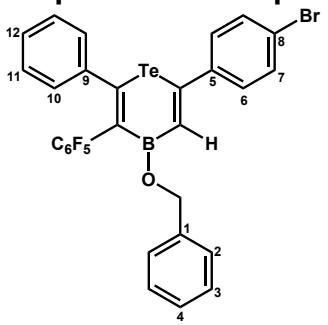


^{13}C{^{1}H} (125 MHz, C_6D_6) NMR spectrum of 11



^{19}F{^{1}H} (377 MHz, C_6D_6) NMR spectrum of 11

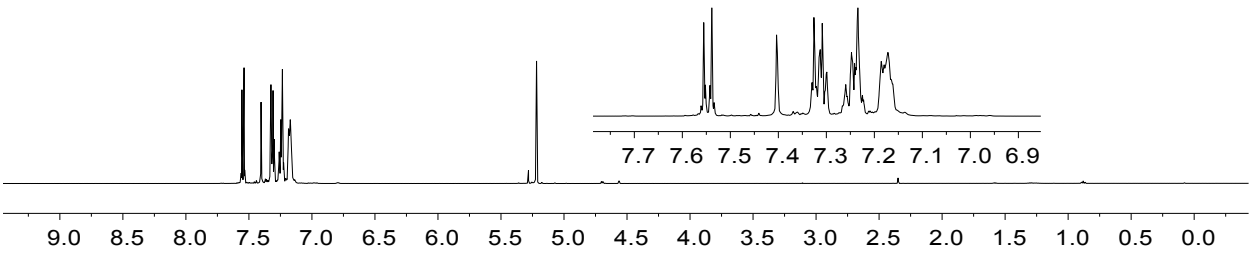
Preparation and spectroscopic data of 12



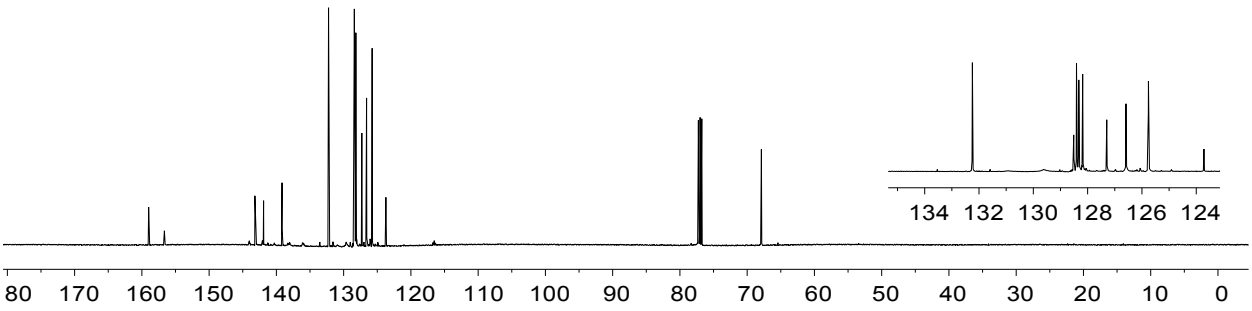
Compound **2** (135.1 mg, 0.1728 mmol) was reacted with 4-ethynylbromobenzene (51.0 mg, 0.282 mmol) in 4 ml of toluene at 110 °C for 16 h, giving a yellow and clear solution. All volatiles were removed under vacuum and the residue was triturated with pentane to give compound **12** (84.7 mg, 0.122 mmol, 70.6% yield) as a yellow powder.

^{1}H (500.0 MHz, $CDCl_3$): δ 7.57 (m, 2H, H^{6}-Ph), 7.43 (s, 1H, *H*(B)C=), 7.35-7.33 (m, H^{7}-Ph+Ar, 4H), 7.29-7.25 (m, 4H, Ar), 7.21-7.19 (br m, 4H, Ar), 5.24 (s, 2H, BOC*H*$_2$)
^{11}B{^{1}H} (128 MHz, $CDCl_3$): δ 38.6 (s, $v_{1/2}$ ≈ 920 Hz)
^{13}C{^{1}H} (125 MHz, $CDCl_3$): (C_6F_5 signals not listed) δ 159.0 (s, Te*C*=), 156.7 (s, Te*C*=), 143.2 (s, Ar), 141.9 (s, Ar), 139.2 (s, Ar), 132.2 (s, C^{6}), 130.9 (br s, =*C*B), 129.6 (br s, =*C*B), 128.5 (s, Ar), 128.4 (s, Ar), 128.3 (s, Ar), 128.2 (s, Ar), 127.3 (s, Ar), 126.6 (s, Ar), 125.8 (s, Ar), 123.7 (s, Ar), 67.9 (s, O*C*H$_2$Ph)
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ -139.8 (m, 2F, *o*-C_6F_5), -157.8 (app t, 1F, *p*-C_6F_5), --164.0 (m, 2F, *m*-C_6F_5)
^{125}Te (158 MHz, $CDCl_3$): δ 681.7 (s)

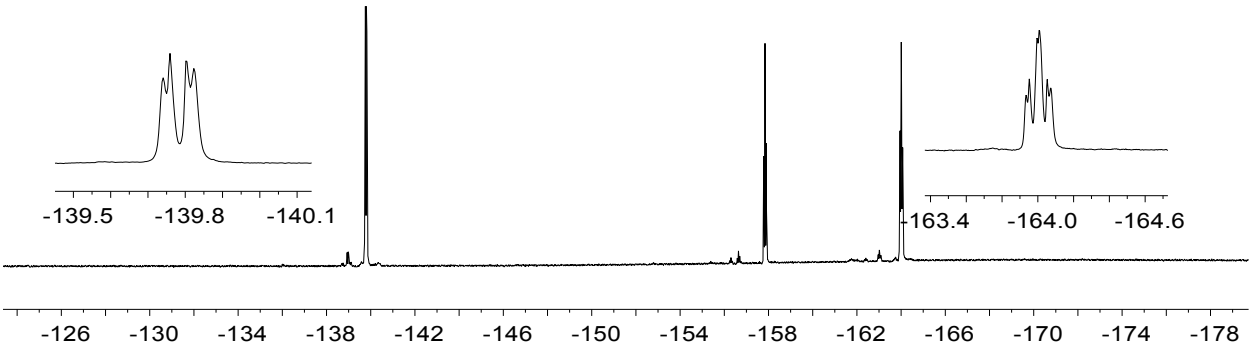
Anal. Calc. for $C_{29}H_{17}BBrF_5OTe$: C 50.14%, H 2.47% Found: C 50.32%, H 2.40%



^{1}H (600.0 MHz, $CDCl_3$) NMR spectrum of 12

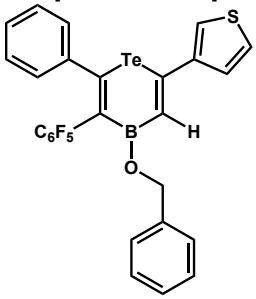


$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectrum of 12



$^{19}F\{^{1}H\}$ (377 MHz, $CDCl_3$) NMR spectrum of 12

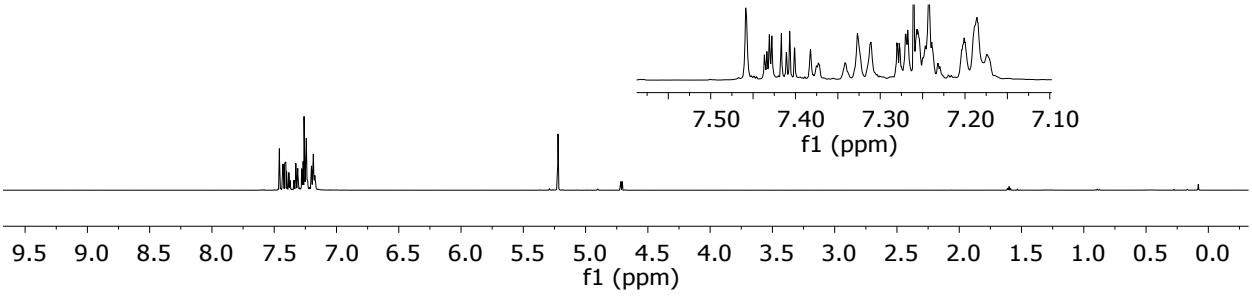
Preparation Spectroscopic data of 13



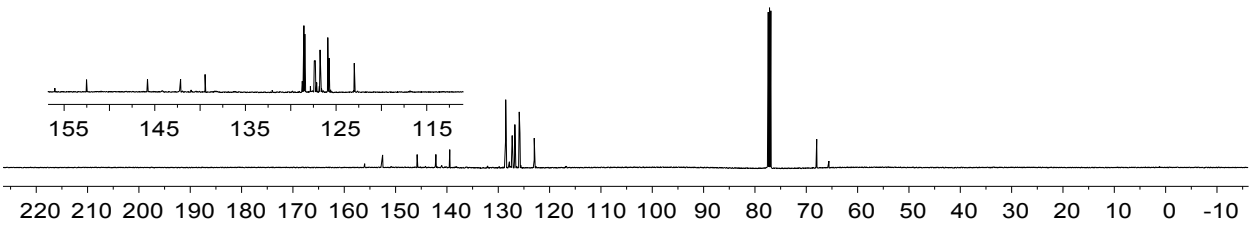
Compound **2** (116.3 mg, 0.1487 mmol) was reacted with 3-ethynylthiophene (51.0 mg, 0.472 mmol) in 4 ml of toluene at 110 ^{o}C for 16 h, giving a brownish-yellow and clear solution. After all volatiles were removed under vacuum, the residue was dissolved in 3 ml of pentane and passed through a plug of silica. 5 ml more of pentane was used to rinse out the C_6F_5CCPh from the silica plug. 5 ml of DCM was then used to extract 13 from the silica, giving again a clear and brownish yellow solution. All volatiles were removed again to give compound **13** (73.0 mg, 0.117, 78.9% yield) as a light yellow sticky solid.

^{1}H (600.0 MHz, $CDCl_3$): δ 7.46 (s, 1H, *H*(B)C=), 7.43 (m, 1H, Ar^S), 7.41 (m, 1H, Ar^S), 7.32 (app d, 2H, Ar), 7.28-7.23 (m, 6H, Ar), 7.20-7.17 (m, 4H, Ar), 5.22 (s, 2H, BOCH_2)
^{11}B{^{1}H} (128 MHz, $CDCl_3$): δ 38.4 (s, $v_{1/2}$ ≈ 600 Hz)
^{13}C{^{1}H} (125 MHz, $CDCl_3$): (C_6F_5 signals not listed) δ 156.0 (s, Te*C*=), 152.5 (s, Te*C*=), 145.8 (s, Ar), 142.2 (s, Ar), 139.5 (s, Ar), 128.6 (s, Ar), 128.6 (s, Ar), 128.5 (s, Ar), 127.4 (s, Ar), 127.3 (s, Ar), 126.8 (s, Ar), 125.9 (s, Ar), 125.8 (s, Ar), 123.0 (s, Ar), 68.0 (s, OCH_2Ph)
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ -139.8 (m, 2F, *o*-C_6F_5), -158.1 (app t, 1F, *p*-C_6F_5), --164.2 (m, 2F, *m*-C_6F_5)
^{125}Te (158 MHz, $CDCl_3$): δ 633.6 (s)

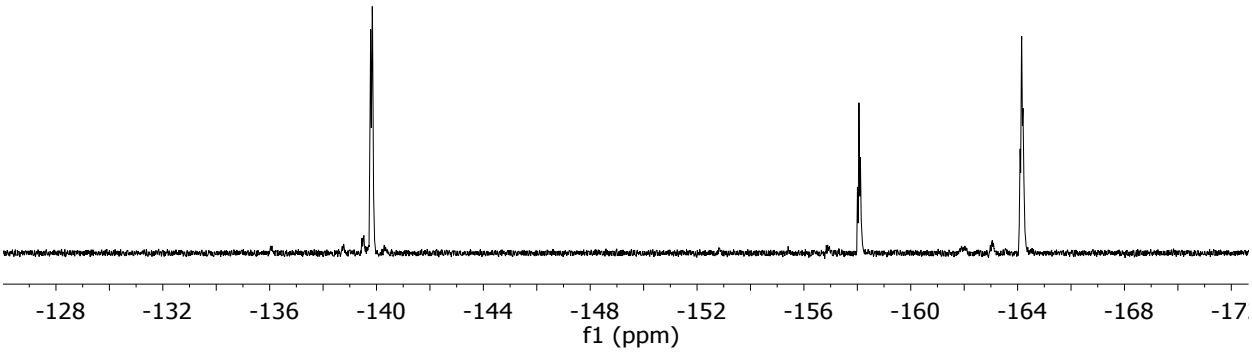
MS (DART+): cal'd for $C_{27}H_{17}OBF_5STe$ [M+H^+]: 625.00755 amu. Found: 625.00837 amu



^{1}H (500.0 MHz, $CDCl_3$) NMR spectrum of 13



^{13}C{^{1}H} (125 MHz, $CDCl_3$) NMR spectrum of 13



$^{19}F\{^{1}H\}$ (377 MHz, $CDCl_3$) NMR spectrum of 13

References

[1] F. A. Tsao, A. J. Lough, D. W. Stephan, *Chem. Commun. (Cambridge, U. K.)* **2015**, *51*, 4287-4289.

[2] P. Granger, S. Chapelle, W. R. McWhinnie, A. Al-Rubaie, *J. Organomet. Chem.* **1981**, *220*, 149-158.