Double FLP-Alkyne Exchange Reactions: A Facile Route to Te/B Heterocycles

Fu An Tsao[1], Levy Cao,[1] Stefan Grimme[2]* and Douglas W. Stephan[1]*

[1]Department of Chemistry, 80 St. George St., University of Toronto, Toronto, Ontario, Canada M5S 3H6
[2]Mulliken Center for Theoretical Chemistry, Institut für Physikalische und Theoretische Chemie, Universität Bonn Beringstr. 4, 53115 Bonn, Germany.

Supporting Information

General experimental procedure

All experimental manipulations were conducted using standard Schlenk 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. Deuterated solvents (purchased from Cambridge Isotopes) were dried using appropriate drying agent (CaH_2 for CD_2Cl_2, Na/benzophenone for C_6D_6) and distilled under reduced pressure prior to use. All solvents were also degassed by repeated freeze-pump-thaw cycles prior to use.

Phenylacetylene, 4-ethynylanisole, 4-tert-butylphenylacetylene, 4-trifluoromethylphenylacetylene, 3-chlorophenylacetylene, 3, 5-difluorophenylacetylene, 4-ethynylbiphenyl and ethynylferrocene were purchased from Sigma-Aldrich. 4-bromophenylacetylene and 3-ethynylthiophene were purchased from TCI Chemicals. All alkynes were dried either over 4 Å sieves or CaH_2 prior to use. Compound 1,[1] 2-ethynylfluorene[2] and 2,4-diethynyl-9,9'-dioctylfluorene[3] 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 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 CD_2Cl_2; 1H = 7.16 ppm and 13C = 128.06 ppm for C_6D_6) 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)[4]).

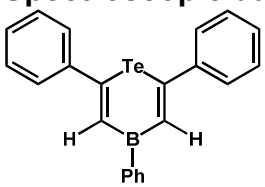
Single-crystal X-ray crystallographic analyses were performed on crystals coated in Paratone-N oil and mounted on a Bruker Kappa Apex II diffractometer. The structure was solved using SHELXS and least square refinements were performed using SHELXL-97. UV-Vis absorption spectra of were recorded on a Varian Cary 5000 UV-vis-NIR spectrophotometer as solutions of CH_2Cl_2 at 298 K in quartz cuvettes. The spectrum of compound 5 could not be obtained as it could only be isolated as a mixture of **5** and diphenylacetylene. Combustion elemental analyses were performed on a PerkinElmer CHN Analyzer. HR-MS was performed on a JEOL AccuTOF equipped with a Direct Analysis in Real Time (DART) ion source or a Waters GC Premier TOF-MS equipped with an EI/CI source.

All computed structures were minimized using the Gaussian 09 program[5] at the B3LYP/SDD level of theory. All minimized structures were found to contain no imaginary frequencies. NICS values were obtained from adding ghost atoms (Bq) in the center of the compounds **1** and **2**, and GIAO method was chosen to perform the NMR calculation

General synthetic procedure for compounds 2-12

1 eq. of compound **1** and 2.2 eq. of alkyne were dissolved in 5 ml of toluene. The orange or yellow solution was then transferred into a 50-ml Schlenk flask equipped with a Teflon tab seal. The solution was heated to 110 ^{o}C for 16 h. The orange or red solution was then filtered through a plug of celite before all volatiles were removed. The resulting dark orange or red oil was triturated or sonicated in a variety of solvent to precipitate out the desired product.

Spectroscopic data of 2



60.8 mg (0.11 mmol) of compound **1** was reacted with 22.5 mg (0.22 mmol) of phenylacetylene to give 29.2 mg (0.07 mmol, 63%) of **2**, which precipitated out as a dark yellow powder when sonicated in minimal amounts of $O(TMS)_2$.

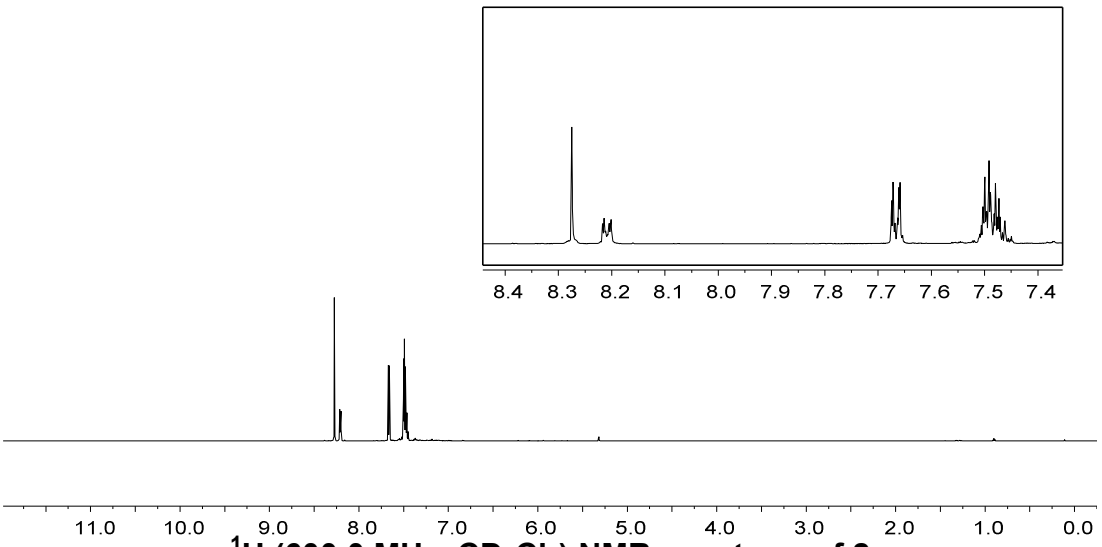
^{1}H (600.0 MHz, CD_2Cl_2): δ 8.28 (s, 2H, *H*(B)C=), 8.22-8.20 (m, 2H, *o*-Ph^{B}), 7.68-7.65 (m, 4H, *o*-Ph), 7.50-7.46 (m, 9H, *m*- *p*-Ph^{B} + *m*- *p*-Ph)

^{11}B{^{1}H} (128.3 MHz, CD_2Cl_2): δ 49.9 (s, $v_{1/2}$ ≈ 790 Hz)

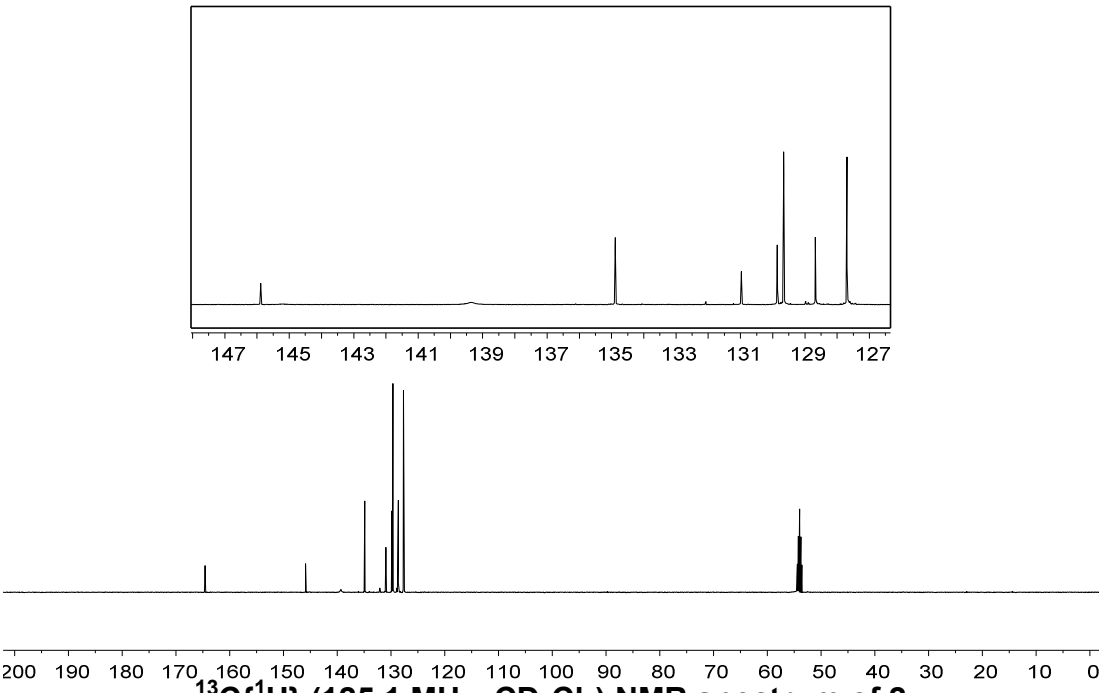
^{13}C{^{1}H} (125.1 MHz, CD_2Cl_2): 164.6 (s, Te*C*=), 145.9 (s, *i*-Ph), 145.2 (br s, *i*-Ph^{B}), 139.3 (br s, =*C*B), 134.9 (s, *o*-Ph^{B}), 131.0 (s, *p*-Ph), 129.9 (s, *p*-Ph^{B}), 129.7 (s, *m*-Ph), 128.7 (s, *m*-Ph^{B}), 127.7 (s, *o*-Ph)

^{125}Te (157.8 MHz, CD_2Cl_2, 193 K): δ 659.7 (s)

Anal. Calc. for $C_{22}H_{17}TeB$: C 62.95 %, H 4.08 %. Found: C 63.23 % H 4.05 %

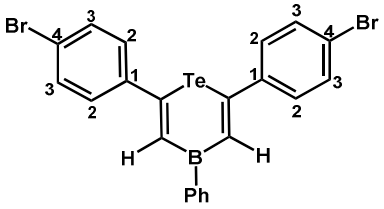


^{1}H (600.0 MHz, CD_2Cl_2) NMR spectrum of 2



^{13}C{^{1}H} (125.1 MHz, CD_2Cl_2) NMR spectrum of 2

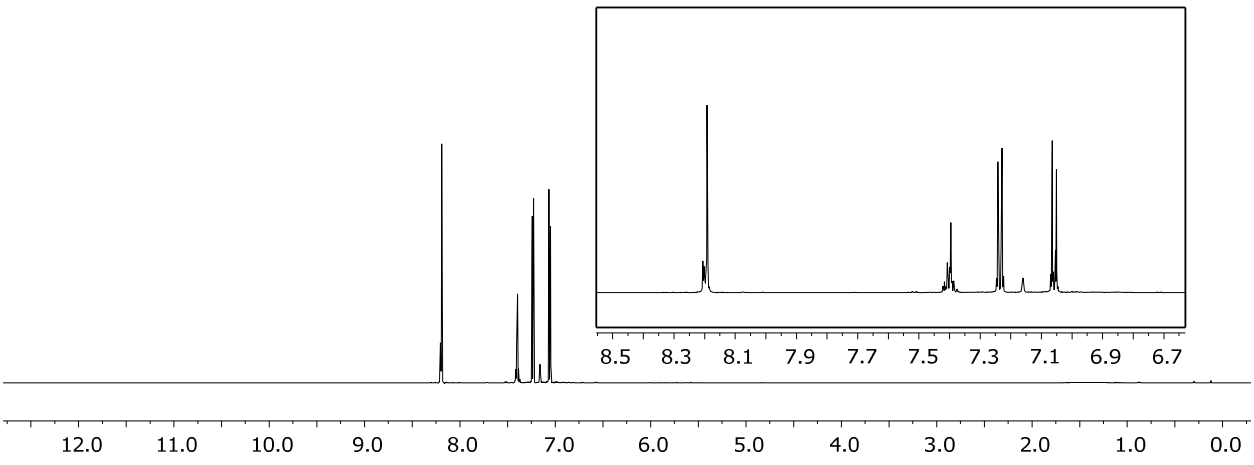
Spectroscopic data of 3



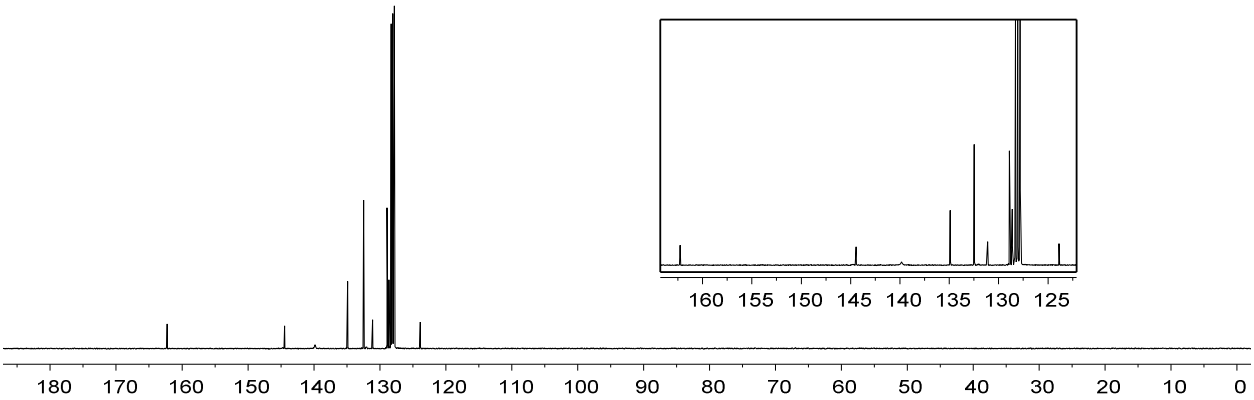
101.9 mg of compound **1** (0.18 mmol) was reacted with 68.8 mg (0.38 mmol) of 4-bromophenylacetylene to give 60.3 mg (0.10 mmol, 58% yield) of **3**, which precipitated out of solution as a bright yellow powder when sonicated in pentane.

^{1}H (600.0 MHz, C_6D_6): δ 8.21-8.19 (m, 4H, *o*-Ph^B + *H*(B)C=), 7.42-7.38 (m, 3H, *m*-, *p*-Ph^B), 7.24 (app dt, 4H, $^{3}J_{H\text{-}H}$ = 8.4 Hz, H^2-Ph), 7.06 (app dt, 4H, $^{3}J_{H\text{-}H}$ = 8.4 Hz, H^3-Ph)
^{11}B{^{1}H} (128.3 MHz, C_6D_6): δ 50.3 (s, $v_{1/2}$ ≈ 1040 Hz)
^{13}C{^{1}H} (100.6 MHz, C_6D_6): δ 162.3 (s, Te*C*=), 144.8 (br s, *i*-Ph^B), 144.4 (s, C^1-Ph), 139.8 (br s, =*C*B), 134.9 (s, *o*-Ph^B), 132.5 (s, C^2-Ph), 131.1 (s, *p*-Ph^B), 128.9 (s, C^3-Ph), 128.6 (s, *m*-Ph^B), 123.9 (s, C^4-Ph)
^{125}Te (157.8 MHz, CD_2Cl_2, 193 K): δ 670.3 (s)
[Note: Ph^B denotes the phenyl ring directly bonded to boron]

Anal. Calc. for $C_{22}H_{15}TeBBr_2$: C 45.75 %, H 2.62 %. Found: C 45.89 % H 2.39 %

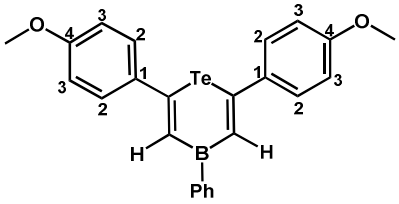


^{1}H (600.0 MHz, C_6D_6) NMR spectrum of 3



$^{13}C\{^{1}H\}$ (100.6 MHz, C6D6) NMR spectrum of 3

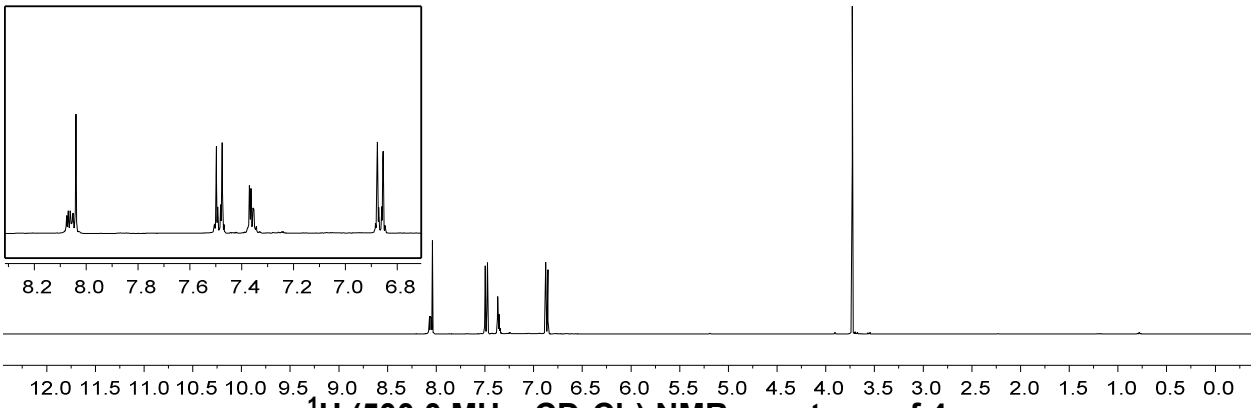
Spectroscopic data of 4



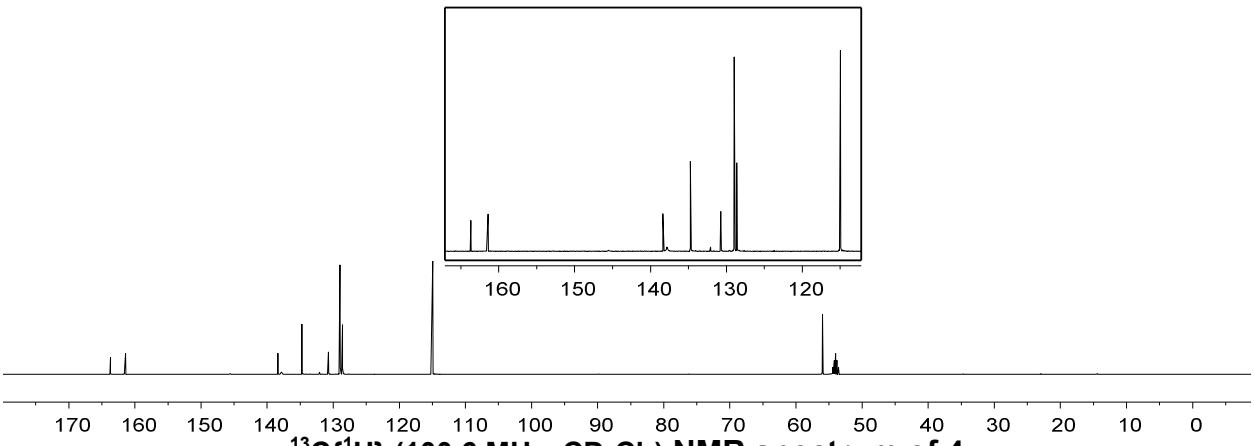
82.5 mg (0.14 mmol) of compound **1** was reacted with 42.8 mg (0.32 mmol) of 4-ethynylanisole to give 40.8 mg (0.09 mmol, 61% yield) of **4**, which precipitated out of solution as a dark yellow powder when sonicated in pentane.

^{1}H (500.0 MHz, CD_2Cl_2): δ 8.21-8.18 (m, 2H, *o*-Ph^B), 8.17 (s, 2H, *H*(B)C=), 7.62 (app dt, 4H, $^{3}J_{H\text{-}H}$ = 11 Hz, H^2-Ph), 7.50-7.48 (m, 3H, *m*-, *p*-Ph^B), 7.00 (app dt, 4H, $^{3}J_{H\text{-}H}$ = 11 Hz, H^3-Ph), 3.86 (s, 6H, -OC*H*$_3$)
$^{11}B\{^{1}H\}$ (128.3 MHz, CD_2Cl_2): δ 49.5 (s, $v_{1/2}$ ≈ 720 Hz)
$^{13}C\{^{1}H\}$ (100.6 MHz, CD_2Cl_2): δ 163.7 (s, Te*C*=), 161.4 (s, C^4-Ph), 145.6 (br s, *i*-Ph^B), 138.4 (s, C^2-Ph), 137.8 (br s, =*C*B), 134.7 (s, *o*-Ph^B), 130.7 (s, *p*-Ph^B), 129.0 (s, C^3-Ph), 128.6 (s, *m*-Ph^B), 115.0 (s, C^1-Ph), 56.0 (s, -O*C*H$_3$)
^{125}Te (157.8 MHz, CD_2Cl_2, 193 K): δ 626.3 (s)
[Note: Ph^B denotes the phenyl ring directly bonded to boron]

MS (EI+): cal'd for $C_{24}H_{21}O_2BTe$ [M+]: 482.0697 amu. Found: 482.0694 amu

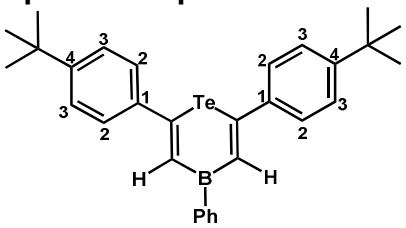


^{1}H (500.0 MHz, CD_2Cl_2) NMR spectrum of 4



^{13}C{^{1}H} (100.6 MHz, CD_2Cl_2) NMR spectrum of 4

Spectroscopic data of 5

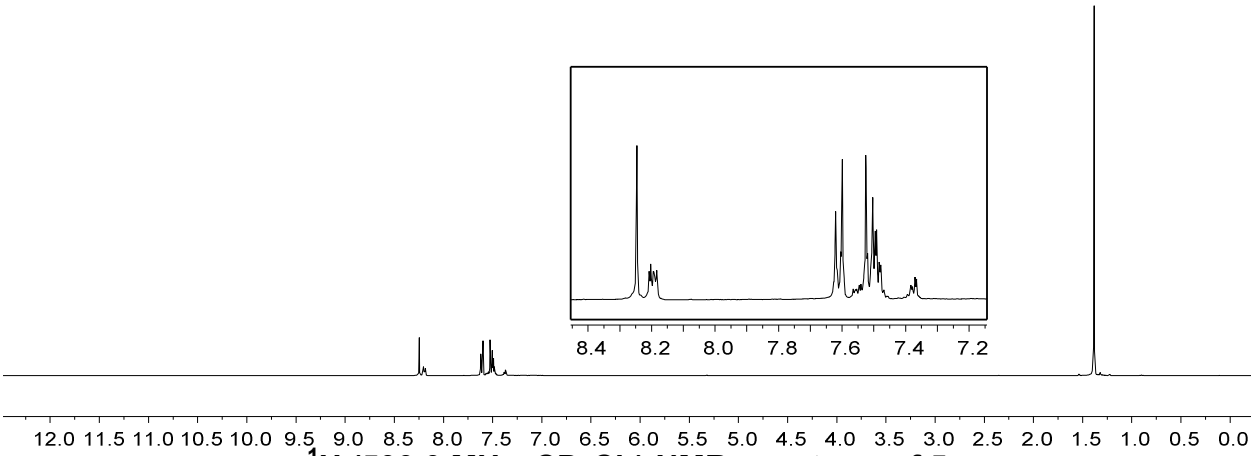


84.5 mg (0.15 mmol) of compound **1** was reacted with 50.2 mg (0.32 mmol) of 4-tert-butylphenylacetylene to give 42.8 mg (0.075 mmol, 50% yield) of **5** and 20% PhCCPh. Compound **5** could only be purified by recrystallization in $O(TMS)_2$, and always co-crystallized with PhCCPh at various ratios as orange crystals.

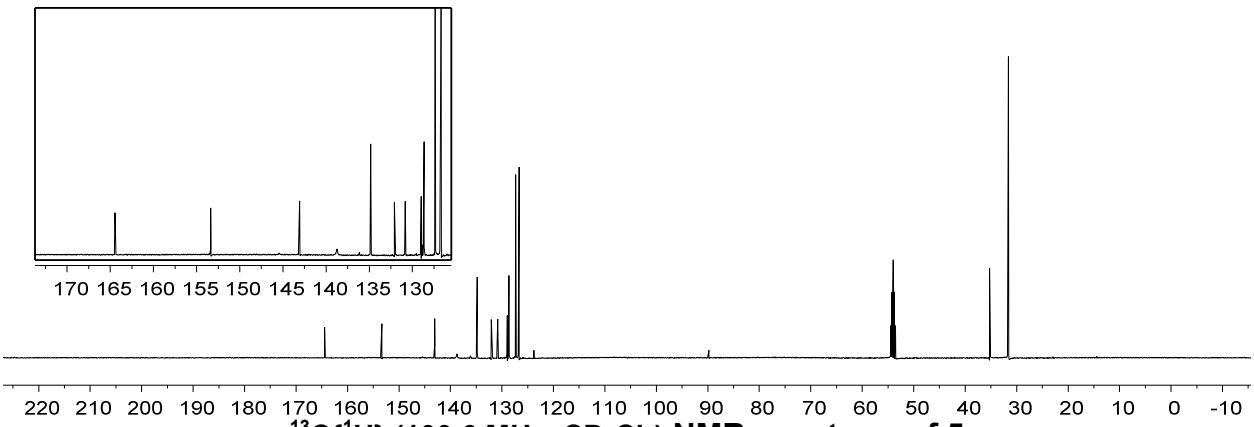
^{1}H (500.0 MHz, CD_2Cl_2): δ 8.25 (s, 2H, *H*(B)C=), 8.21-8.19 (m, 2H, *o*-Ph^B), 7.61 (app dt, 4H, $^{3}J_{H\text{-}H}$ = 8.5 Hz, H^2-Ph), 7.52 (app dt, 4H, $^{3}J_{H\text{-}H}$ = 8.5 Hz, H^3-Ph), 7.50-7.47 (m, 3H, *m*-, *p*-Ph^B), 1.38 (s, 18H, $C(CH_3)_3$)
^{11}B{^{1}H} (128.3 MHz, CD_2Cl_2): δ 49.6 (s, $v_{1/2}$ ≈ 940 Hz)

$^{13}C\{^1H\}$ (100.6 MHz, CD_2Cl_2): δ 164.4 (s, Te*C*=), 153.4 (s, C^4-Ph), 145.4 (br s, *i*-Ph^B), 143.1 (s, C^1-Ph), 138.8 (br s, =*C*B), 134.8 (s, *o*-Ph^B), 132.1 (s, *p*-Ph^B), 130.8 (s, *m*-Ph^B), 127.4, (s, C^2-Ph), 126.7 (s, C^3-Ph), 35.3 (s, $C(CH_3)_3$), 31.6 (s, $C(CH_3)_3$)
^{125}Te (157.8 MHz, CD_2Cl_2, 193 K): δ 649.5 (s)
[Note: Ph^B denotes the phenyl ring directly bonded to boron]

MS (EI+): cal'd for $C_{30}H_{33}BTe$ [M+]: 534.1738 amu. Found: 534.1722 amu

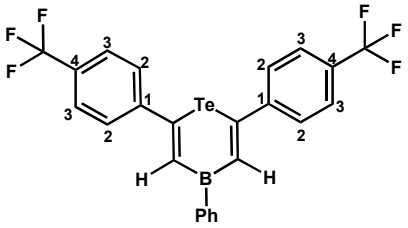


^1H (500.0 MHz, CD_2Cl_2) NMR spectrum of 5



$^{13}C\{^1H\}$ (100.6 MHz, CD_2Cl_2) NMR spectrum of 5

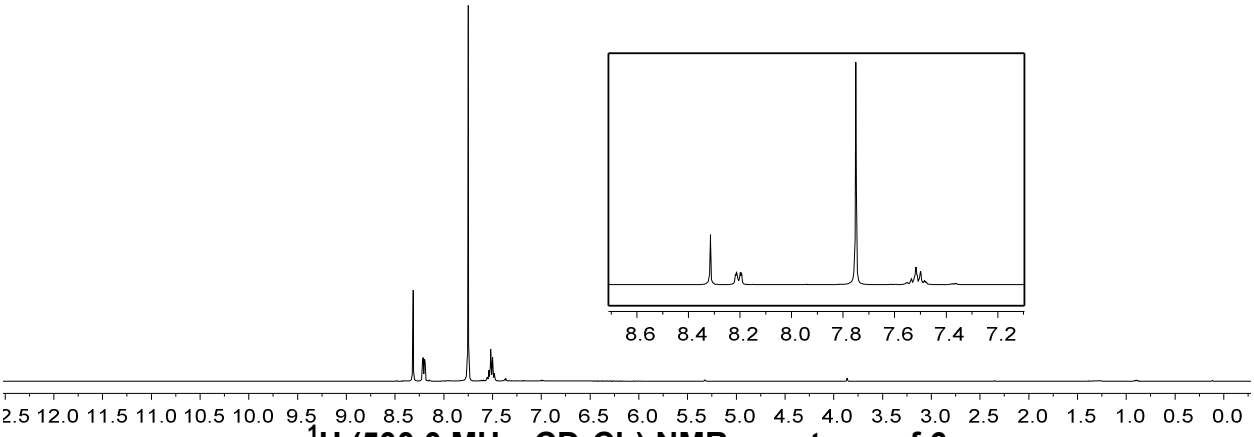
Spectroscopic data of 6



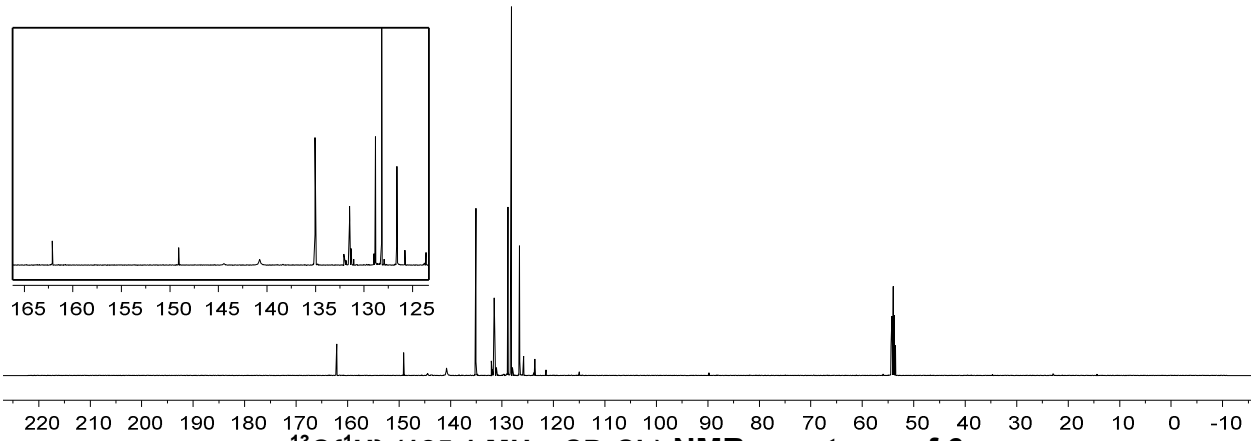
75.9 mg (0.13 mmol) of compound **1** was reacted with 50.5 mg (0.30 mmol) of 4-trifluoromethylphenylacetylene to give 41.6 mg (0.07 mmol, 57% yield) of **6**, which precipitated out as a light yellow powder when sonicated in minimal amounts of pentane.

^{1}H (500.0 MHz, CD_2Cl_2): δ 8.32 (s, 2H, *H*(B)C=), 8.22-8.19 (m, 2H, *o*-Ph^B), 7.75 (app s, 8H, H^2-Ph + H^3-Ph), 7.55-7.48 (m, 3H, *m*-, *p*-Ph^B)
^{11}B{^{1}H} (128.3 MHz, CD_2Cl_2): δ 49.8 (s, $v_{1/2}$ ≈ 800 Hz)
^{13}C{^{1}H} (125.1 MHz, CD_2Cl_2): δ 162.1 (s, Te*C*=), 149.0 (br q, J_{C-F} = 1.2 Hz, C^4-Ph), 144.4 (br s, *i*-Ph^B), 140.8 (br s, =*C*B), 135.1 (s, *o*-Ph^B), 132.1 (s, C^1-Ph), 131.51 (s, *p*-Ph^B), 131.17 (q, J_{C-F} = 31.3 Hz, -*C*F_3), 128.8 (s, *m*-Ph^B), 128.2 (s, C^2-Ph), 126.6 (q, J_{C-F} = 3.6 Hz, C^3-Ph)
^{19}F{^{1}H} (376.4 MHz, CD_2Cl_2): -62.9 (s)
^{125}Te (157.8 MHz, CD_2Cl_2, 193 K): δ 681.1 (s)
[Note: Ph^B denotes the phenyl ring directly bonded to boron]

MS (EI+): cal'd for $C_{24}H_{15}BTeF_6$ [M+]: 558.0233 amu. Found: 558.0234 amu

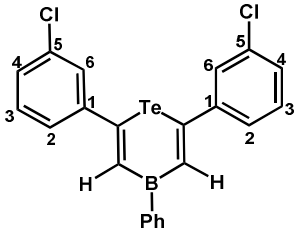


^{1}H (500.0 MHz, CD_2Cl_2) NMR spectrum of 6



$^{13}C\{^{1}H\}$ (125.1 MHz, CD_2Cl_2) NMR spectrum of 6

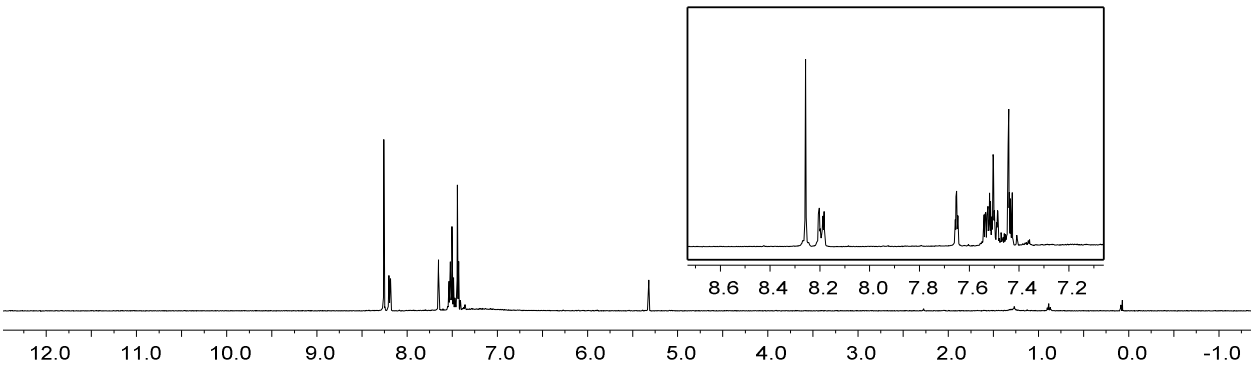
Spectroscopic data of 7



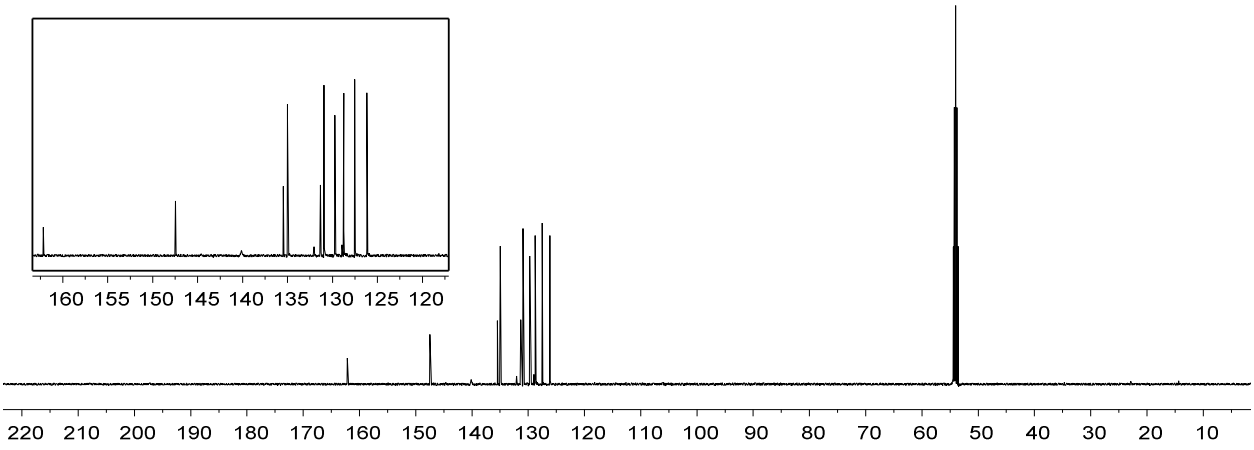
38.5 mg (0.07 mmol) of compound **1** was reacted with 24.3 mg (0.18 mmol) of 3-chlorophenylacetylene to give 21.6 mg (0.04 mmol, 60% yield) of **7**, which precipitated out as a yellow powder when sonicated in minimal amounts of $O(TMS)_2$

^{1}H (500.0 MHz, CD_2Cl_2): δ 8.26 (s, 2H, *H*(B)C=), 8.20-8.19 (m, 2H, *o*-Ph^B), 7.66-7.65 (m, 1H, *p*-Ph^B), 7.54-5.52 (m, 2H, *Ar*-H), 7.44-7.51 (m, 2H, *m*-Ph^B), 7.37-7.36 (m, 2H, *Ar*-H)
$^{11}B\{^{1}H\}$ (128.3 MHz, CD_2Cl_2): δ 50.6 (s, $v_{1/2}$ ≈ 560 Hz)
$^{13}C\{^{1}H\}$ (100.6 MHz, CD_2Cl_2): δ 162.2 (s, Te*C*=), 147.5 (s, C^1-Ph), 144.6 (br s, *i*-Ph^B), 140.1 (br s, =*C*B), 135.5 (s, C^5-Ph), 135.0 (s, *o*-Ph^B), 131.3 (s, *Ar*-C), 131.0 (s, *Ar*-C), 129.7 (s, *Ar*-C), 128.7 (s, *m*-Ph^B), 127.5 (s, *p*-Ph^B), 126.2 (s, *Ar*-C)
^{125}Te (157.8 MHz, CD_2Cl_2, 193 K): δ 675.3 (s)
[Note: Ph^B denotes the phenyl ring directly bonded to boron]

MS (EI+): cal'd for $C_{22}H_{15}BCl_2Te$ [M+]: 489.9706 amu. Found: 489.9700 amu

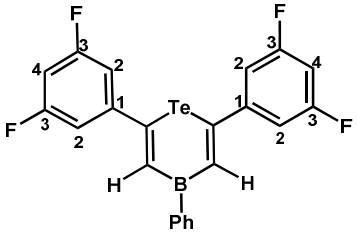


^{1}H (500.0 MHz, CD_2Cl_2) NMR spectrum of 7



^{13}C{^{1}H} (100.6 MHz, CD2Cl2) NMR spectrum of 7

Spectroscopic data of 8

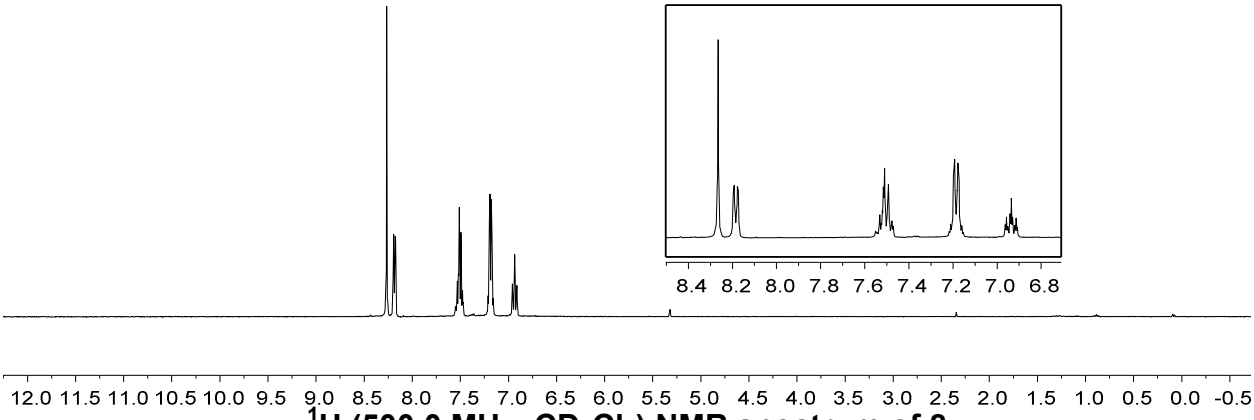


86.4 mg (0.15 mmol) of compound **1** was reacted with 43.9 mg (0.32 mmol) of 3, 5-difluorophenylacetylene to give 34.0 mg (0.07 mmol, 46% yield) of **8**, which precipitated out as a bright yellow powder when sonicated in minimal amounts of $O(TMS)_2$.

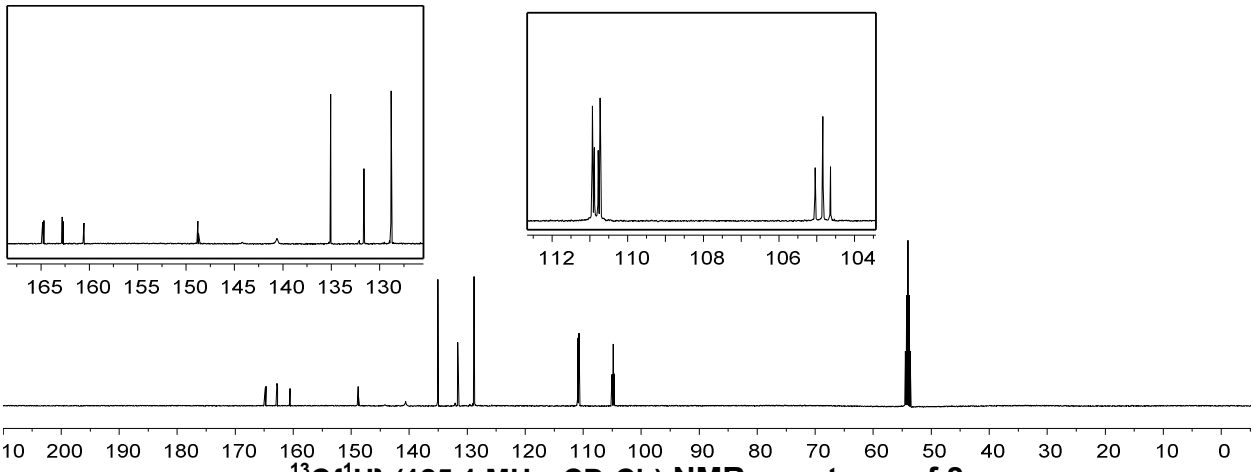
^{1}H (400.0 MHz, CD_2Cl_2): δ 8.27 (s, 2H, *H*(B)C=), 8.20-8.17 (m, 2H, *o*-Ph^B), 7.55-7.47 (m, 3H, *m*-, *p*-Ph^B), 7.19 (m, 4H, H^2-Ph), 6.94 (tt, 2H, $^{3}J_{H\text{-}F}$ = 8.8 Hz, $^{4}J_{H\text{-}H}$ = 2.0 Hz, H^4-Ph)
^{11}B{^{1}H} (128.3 MHz, CD_2Cl_2): δ 50.5 (s, $v_{1/2}$ ≈ 650 Hz)

$^{13}C\{^1H\}$ (125.1 MHz, CD_2Cl_2): δ 163.8 (dd, $^1J_{C\text{-}F}$ = 248.6 Hz, $^3J_{C\text{-}F}$ = 12.9 Hz, C^3-Ph), 160.6 (t, $^4J_{C\text{-}F}$ = 2.5 Hz, Te*C*=), 148.8 (t, $^3J_{C\text{-}F}$ = 9.1 Hz, C^1-Ph), 144.2 (br s, *i*-Ph^B), 140.6 (br s, =*C*B), 135.1 (s, *o*-Ph^B), 131.6 (s, *p*-Ph^B), 128.8 (s, *m*-Ph^B), 110.9 (dd, $^2J_{C\text{-}F}$ = 19.6 Hz, $^4J_{C\text{-}F}$ = 6.4 Hz), 104.8 (t, $^2J_{C\text{-}F}$ = 25.4 Hz, C^4-Ph)
$^{19}F\{^1H\}$ (376.4 MHz, CD_2Cl_2): -109.1 (s)
^{125}Te (157.8 MHz, CD_2Cl_2, 193 K): δ 684.3 (s)
[Note: Ph^B denotes the phenyl ring directly bonded to boron]

MS (DART+): cal'd for $C_{22}H_{13}BF_4Te$ [M^+]: 494.01087 amu. Found: 494.01114 amu

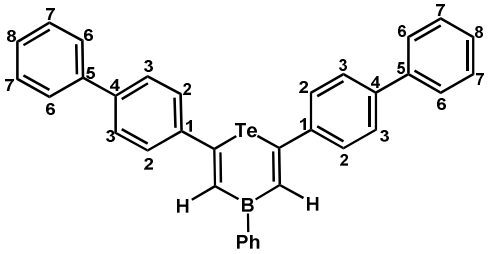


^1H (500.0 MHz, CD_2Cl_2) NMR spectrum of 8



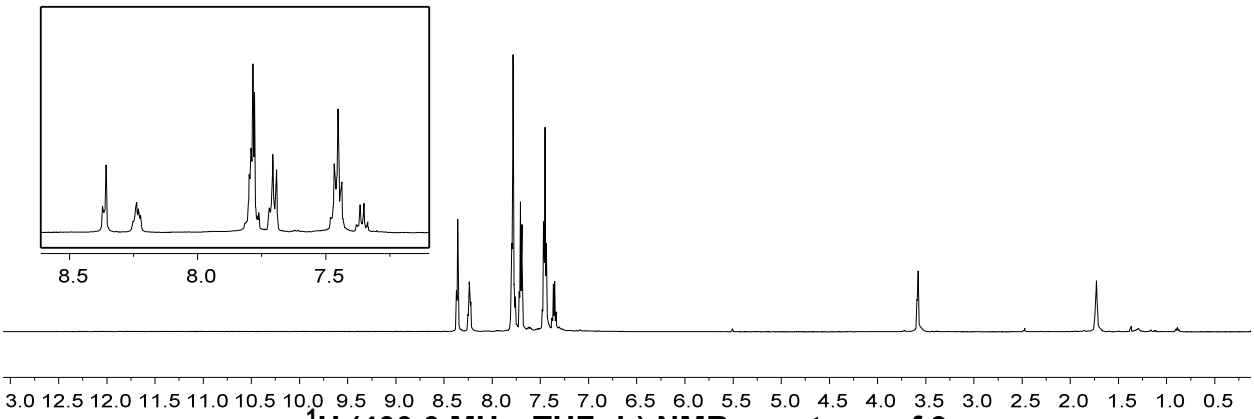
$^{13}C\{^1H\}$ (125.1 MHz, CD_2Cl_2) NMR spectrum of 8

Spectroscopic data of 9

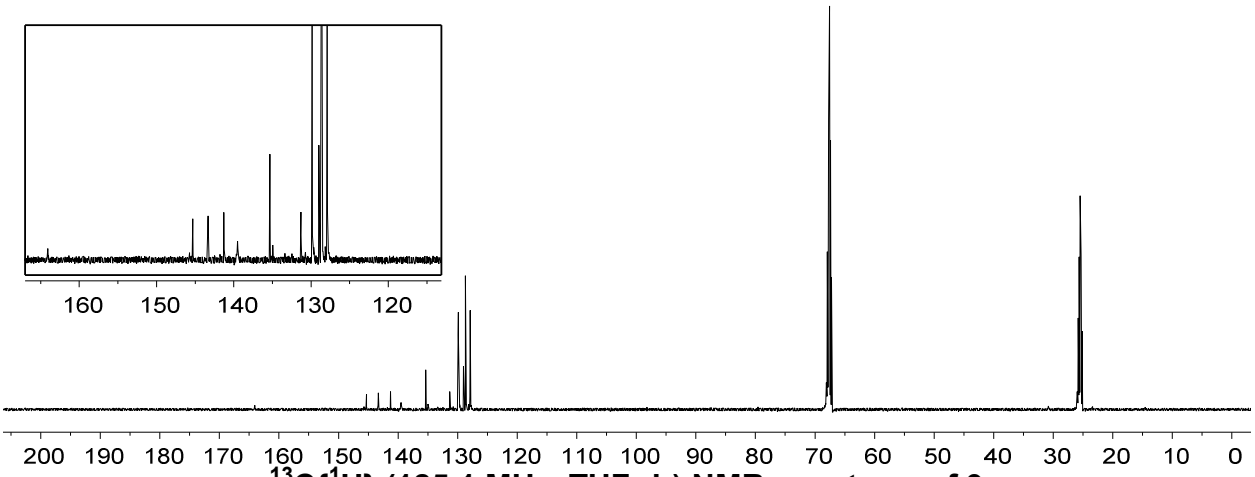


82.5 mg (0.14 mmol) of compound **1** was reacted with 54.1 mg (0.30 mmol) of 4-ethnylbiphenyl to give 58.9 mg (0.10 mmol, 71% yield) of **9**, which precipitated out as a deep yellow powder when triturated with pentane.

^{1}H (400.0 MHz, THF-d$_8$): δ 8.36 (s, 2H, *H*(B)C=),8.24-8.22 (m, 2H, *o*-Ph^{B}), 7.80-7.75 (m, 8H, H^{6}+H^{7}-Ph), 7.70 (dm, 4H, $^{3}J_{H-H}$ = 8.4 Hz, H^{2}-Ph), 7.47-7.44 (m, 7H, H^{3}-Ph + *m*- *p*-Ph^{B}), 7.35 (app tt, 2H, $^{3}J_{H-H}$ = 2.0 Hz, H^{8}-Ph)
^{11}B{^{1}H} (128.3 MHz, THF-d$_8$): (couldn't be observed)
^{13}C{^{1}H} (125.1 MHz, THF-d$_8$): δ 164.1 (br s, Te*C*=) 145.8 (br s, *i*-Ph^{B}), 145.3 (s, C^{1}-Ph), 143.3 (s, C^{5}-Ph), 141.3 (s, C^{4}-Ph), 139.5 (br s, =*C*B), 135.3 (s, *o*-Ph^{B}), 131.3 (s, *p*-Ph^{B}), 129.9 (s, C^{3}-Ph), 129.0 (s, *m*-Ph^{B}), 128.7 (s, C^{6}-Ph+C^{7}-Ph), 128.6 (s, C^{8}-Ph), 127.9 (s, C^{2}-Ph)
^{125}Te (157.8 MHz, THF-d$_8$, 193 K): δ 649.6 (s)
[Note: Ph^{B} denotes the phenyl ring directly bonded to boron]

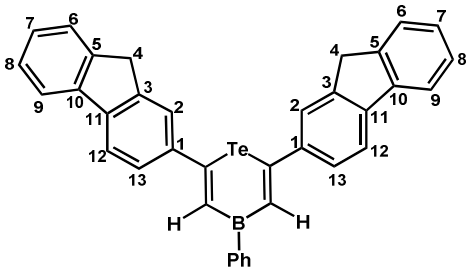


^{1}H (400.0 MHz, THF-d$_8$) NMR spectrum of 9



$^{13}C\{^{1}H\}$ (125.1 MHz, THF-d_8) NMR spectrum of 9

Spectroscopic data of 10



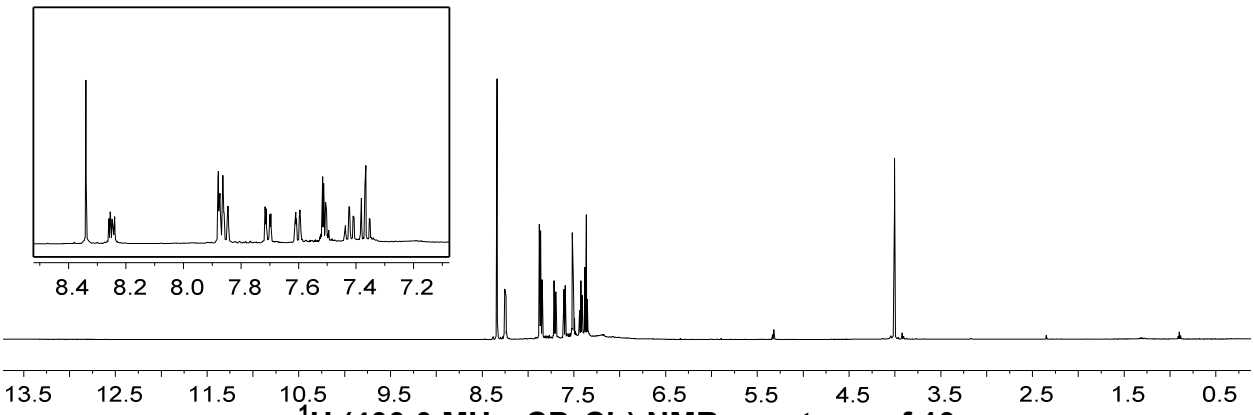
89.5 mg (0.16 mmol) of compound **1** was reacted with 65.4 mg (0.34 mmol) of 2-ethynylfluorene to give 67.6 mg (0.12 mmol, 73 % yield) of **10**, which precipitated out of solution as a yellow-orange solid when triturated with pentane.

^{1}H (400.0 MHz, CD_2Cl_2): δ 8.34 (s, 2H, *H*(B)C=), 8.26-8.23 (m, 2H, *o*-Ph^B), 7.90-7.85 (m, 6H, H^2+H^9+H^{13}), 7.72 (d, 2H, $^3J_{H-H}$ = 9.0 Hz, H^{12}), 7.61 (d, 2H, $^3J_{H-H}$ = 7.2 Hz, H^6), 7.51-7.49 (m, 3H, *m*- *p*-Ph^B), 7.43 (t, 2H, $^3J_{H-H}$ = 7.5 Hz, H^8), 7.37 (t, 2H, $^3J_{H-H}$ = 6.6 Hz, H^7), 4.02 (s, 4H, H^4)

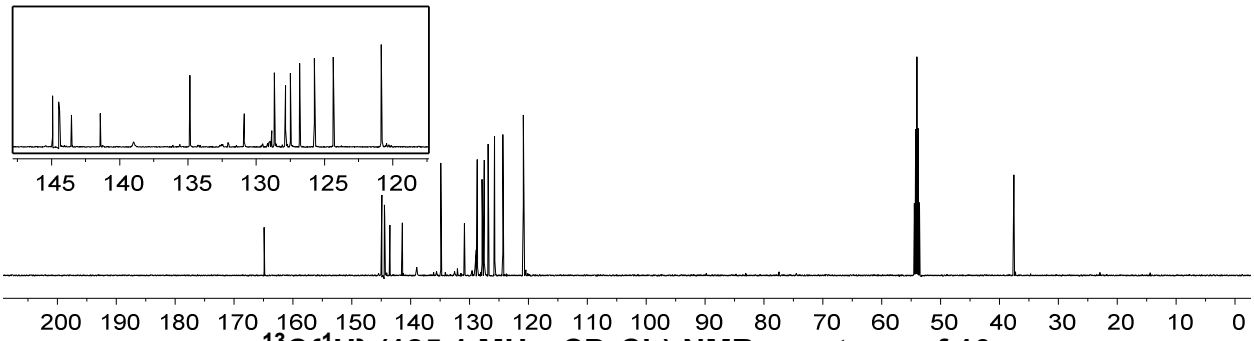
$^{11}B\{^{1}H\}$ (128.3 MHz, CD_2Cl_2): (couldn't be observed)

$^{13}C\{^{1}H\}$ (125.1 MHz, CD_2Cl_2): 164.9 (s, Te*C*=), 145.4 (br s, *i*-Ph^B), 144.9 (s, *Ar*-C), 144.5 (s, C^1), 144.4 (s, *Ar*-C), 143.6 (s, *Ar*-C), 141.4 (s, *Ar*-C), 139.0 (br s, =*C*B), 134.9 (s, *o*-Ph^B), 130.9 (s, *p*-Ph^B), 128.7 (s, *m*-Ph^B), 127.9 (s, C^7), 127.5 (s, C^8), 126.8 (s, C^{12}), 125.7 (s, C^6), 124.4 (s, C^9), 120.9 (s, C^2/C^{13}), 120.8 (s, C^2/C^{13}), 37.5 (s, C^4)

^{125}Te (157.8 MHz, CD_2Cl_2, 193 K): δ 652.4 (s)

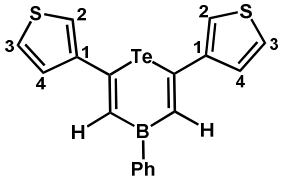


^{1}H (400.0 MHz, CD_2Cl_2) NMR spectrum of 10



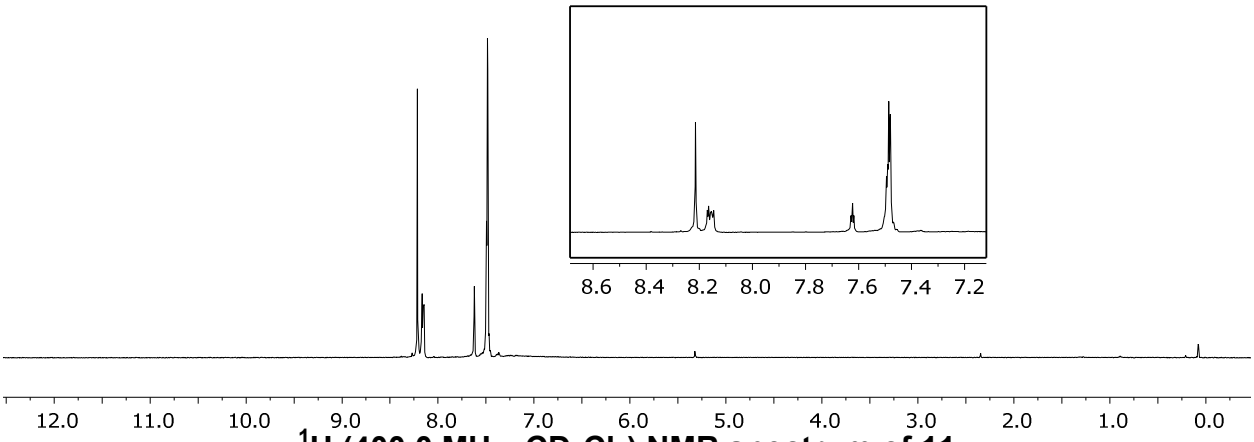
^{13}C{^{1}H} (125.1 MHz, CD_2Cl_2) NMR spectrum of 10

Spectroscopic data of 11

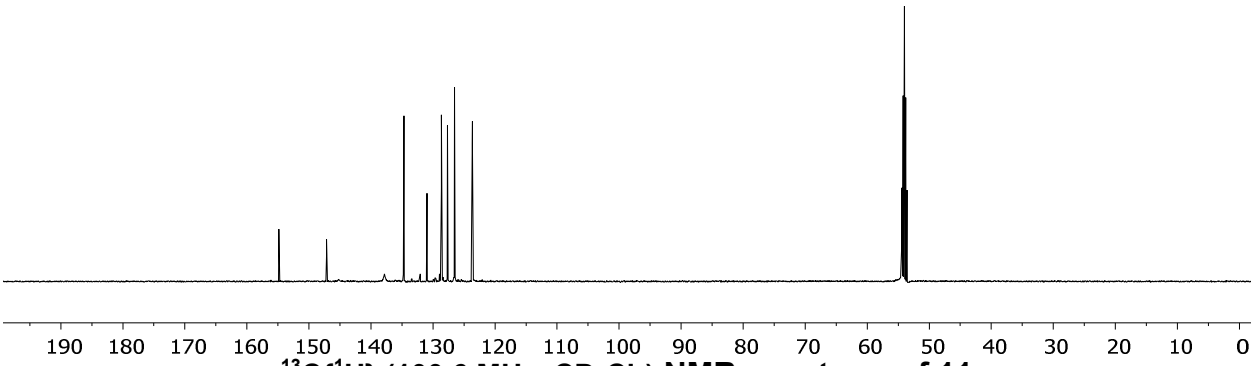


84.6 mg (0.15 mmol) of compound **1** was reacted with 34.1 mg (0.32 mmol) of 3-ethynylthiophene to give 32.1 mg (0.07mmol, 50% yield) of **11**, which precipitated out of solution as a bright yellow powder when sonicated in $O(TMS)_2$.

^{1}H (400.0 MHz, CD_2Cl_2): δ 8.21 (s, 2H, *H*(B)C=), 8.17-8.15 (m, 2H, *o*-Ph^B), 7.62 (t, 1H, $^{3}J_{H\text{-}H}$ = 2.2 Hz), 7.49-7.48 (m, 8H, *Ar*-H)
^{11}B{^{1}H} (128.3 MHz, CD_2Cl_2): δ 50.3 (s, $v_{1/2}$ ≈ 590 Hz)
^{13}C{^{1}H} (100.6 MHz, CD_2Cl_2): δ 154.8 (s, Te*C*=), 147.2 (s, Ar-C), 145.2 (br s, *i*-Ph^B), 137.8 (br s, =*C*B), 134.7 (s, *o*-Ph^B), 131.0 (s, C^1), 128.7 (s, *m*-Ph^B), 127.7 (s, *p*-Ph^B), 126.5 (s, Ar-C), 123.7 (s, Ar-C)
^{125}Te (157.8 MHz, CD_2Cl_2, 193 K): δ 642.0 (s)

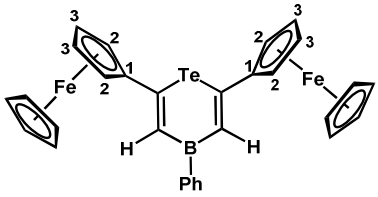


^{1}H (400.0 MHz, CD_2Cl_2) NMR spectrum of 11



^{13}C{^{1}H} (100.6 MHz, CD_2Cl_2) NMR spectrum of 11

Spectroscopic data of 12

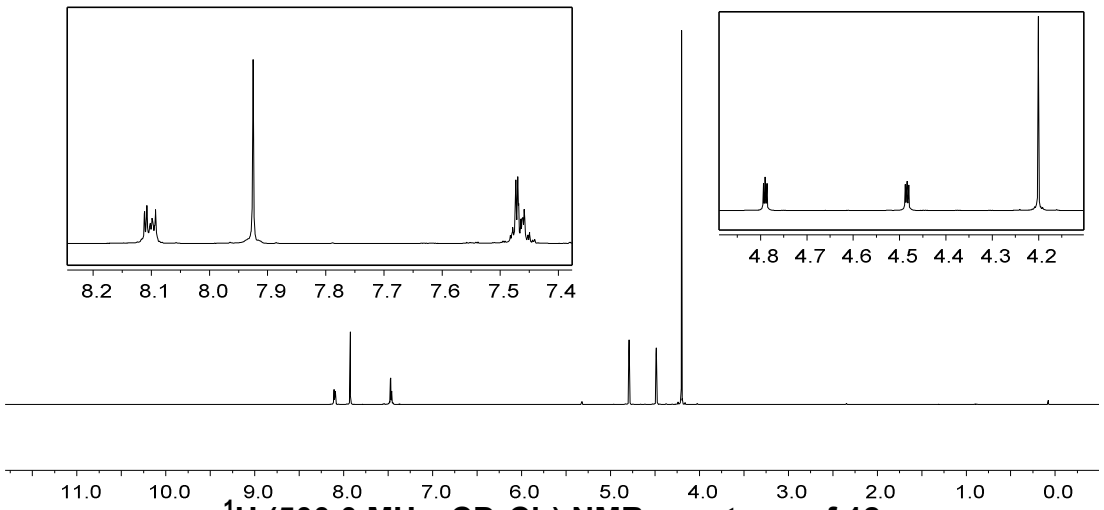


100.5 mg (0.18 mmol) of compound **1** was reacted with 76.8 mg (0.37 mmol) of ethynylferrocene to give 58.7 mg (0.09 mmol, 51% yield) of **12**, which precipitated out as a bright red solid when sonicated in minimal amounts of $O(TMS)_2$.

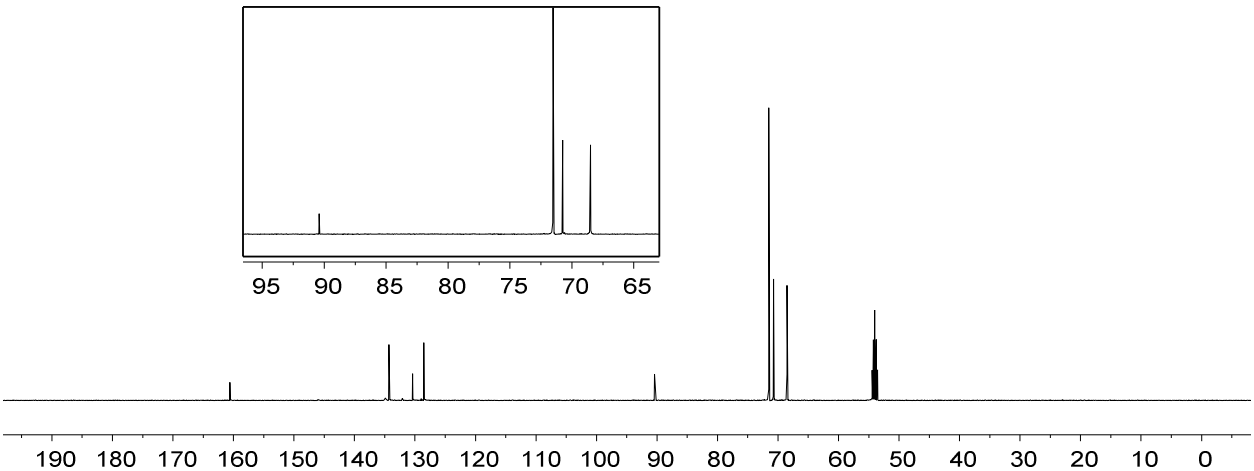
^{1}H (500.0 MHz, CD_2Cl_2): δ 8.11-8.09 (m, 2H, *o*-Ph^B), 7.93 (s, 2H, $^{3}J_{Te\text{-}H}$ = 40 Hz, *H*(B)C=), 7.48-7.45 (m, 3H, *m*-, *p*-Ph^B), 4.79 (t, 4H, $^{3}J_{H\text{-}H}$ = 2.0 Hz, H^3-Cp), 4.48 (t, 4H, $^{3}J_{H\text{-}H}$ = 2.0 Hz, H^2-Cp), 4.20 (s, 10H, Cp')
^{11}B{^{1}H} (128.3 MHz, CD_2Cl_2): δ 48.5 (s, $v_{1/2}$ ≈ 950 Hz)
^{13}C{^{1}H} (125.7 MHz, CD_2Cl_2): δ 160.6 (s, Te*C*=), 146.0 (br s, *i*-Ph^B), 134.9 (br s, =*C*B), 134.3 (s, *o*-Ph^B), 130.4 (s, *p*-Ph^B), 128.5 (s, *m*-Ph^B), 90.4 (s, C^1-Cp), 71.5 (s, Cp'), 70.8 (C^2-Cp), 68.5 (C^3-Cp).
^{125}Te (157.8 MHz, CD_2Cl_2, 193 K): δ 648.0 (s)

[Note: Cp' refers to the cyclopentadiene ring not directly bonded to the central Te-B heterocycle. Ph^B denotes the phenyl ring directly bonded to boron]

MS (DART+): cal'd for $C_{30}H_{26}BFe_2Te$ [$M+H^+$]: 638.98886 amu. Found: 638.98751 amu

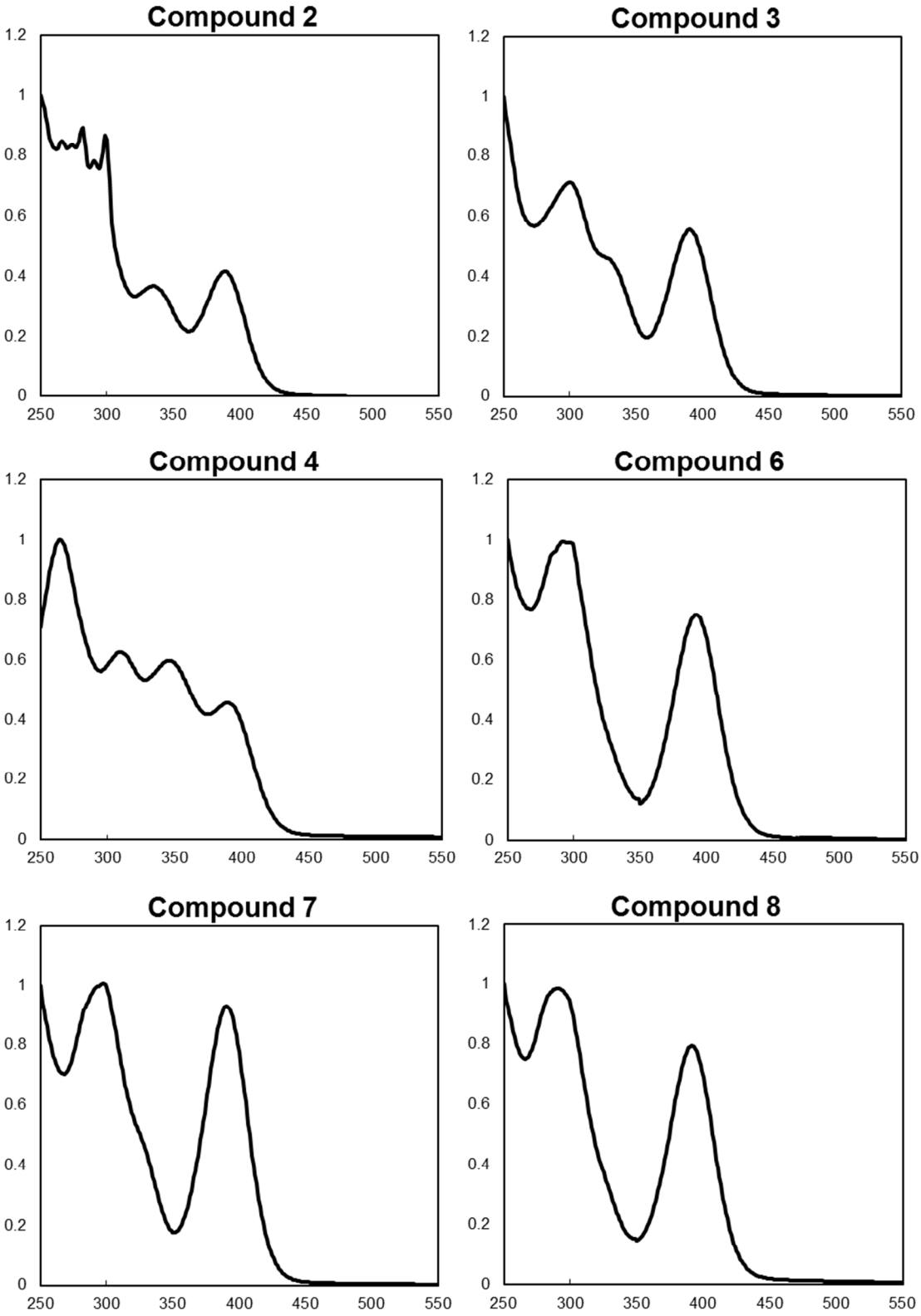


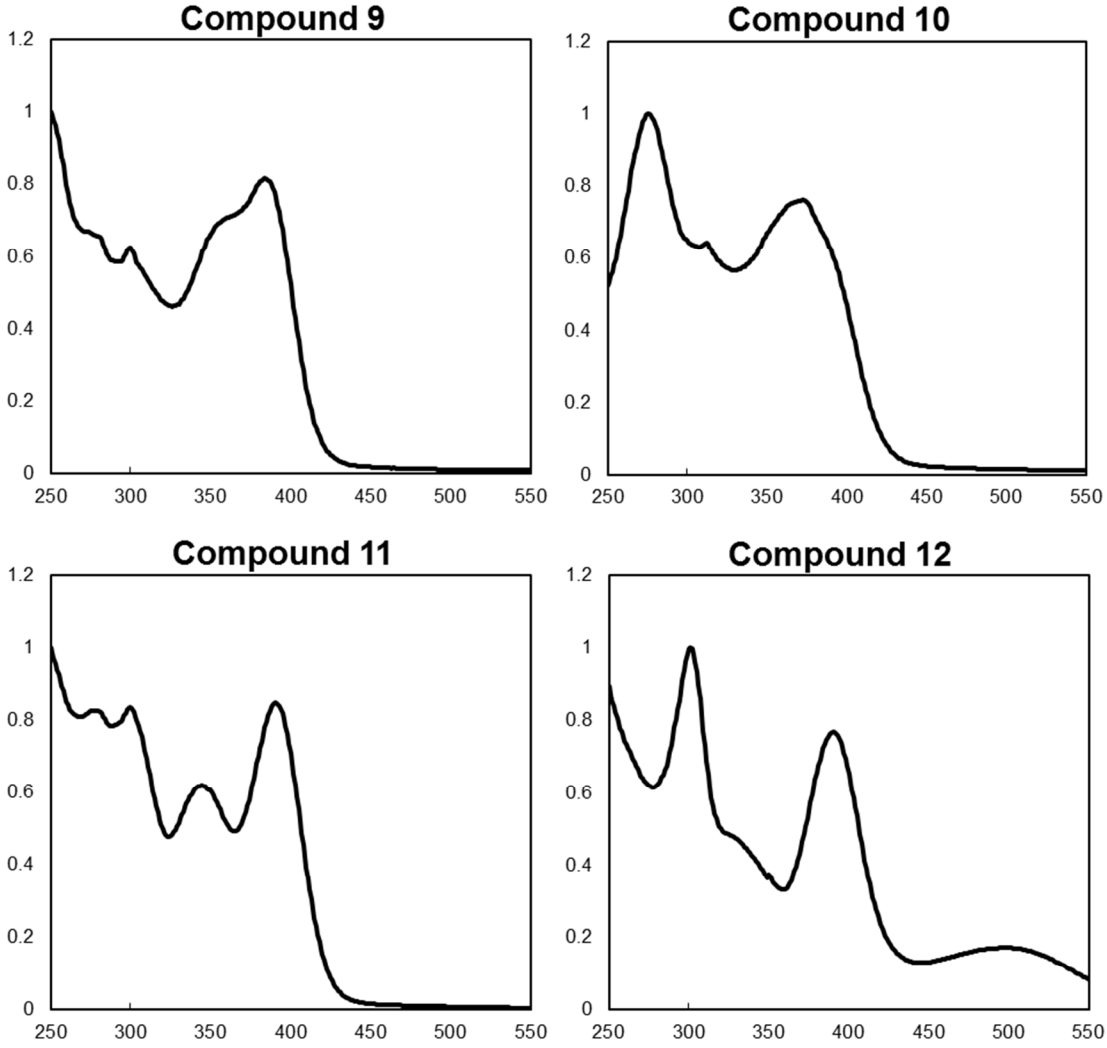
^{1}H (500.0 MHz, CD_2Cl_2) NMR spectrum of 12



$^{13}C\{^1H\}$ (125.7 MHz, CD_2Cl_2) NMR spectrum of 12

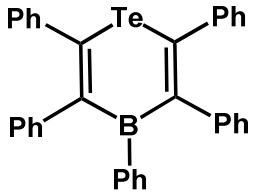
UV-Vis absorption spectra of compounds 2-12

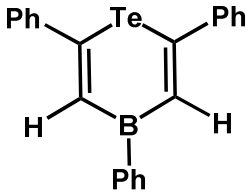



Compound 9
Compound 10
Compound 11
Compound 12
1.2
1
0.8
0.6
0.4
0.2
0
250
300
350
400
450
500
550

NICS Calculations of compounds 1 and 2

Table S1: NICS calculation results (GIAO-B3LYP/SDD)





Entry	NICS(0)	NICS(1)
Compound 1	-2.7721	-2.9294
Compound 2	-2.8631	-3.3500

Table S2: Cartesian coordinates of compounds used for NICS calculation

Compound 1

C	1.577995	-1.04835	0.011908
C	1.387562	0.32149	0.018724
C	-1.38765	0.321402	-0.0184
C	-1.578	-1.04845	-0.01214
C	-0.00016	2.63527	-0.00107
C	-0.57363	3.375581	-1.06725
C	0.573169	3.377014	1.064164
C	-0.56099	4.782391	-1.08117
H	-1.03857	2.849207	-1.89868
C	0.560179	4.783833	1.076389
H	1.038301	2.851739	1.896175
C	-0.0005	5.494508	-0.00281
H	-0.99966	5.318615	-1.92014
H	0.998736	5.321173	1.914709
H	-0.00065	6.582609	-0.00347
C	2.641934	1.169311	0.059196
C	2.980929	2.01454	-1.02105
C	3.498134	1.140062	1.183127
C	4.147726	2.798341	-0.986
H	2.326521	2.064085	-1.88771
C	4.661501	1.930371	1.226731
H	3.251469	0.497489	2.025195
C	4.99437	2.761121	0.139674
H	4.389893	3.441422	-1.82914
H	5.305263	1.894665	2.102954
H	5.893898	3.371803	0.170519
C	-2.64204	1.169256	-0.0576
C	-3.49932	1.140336	-1.1807
C	-2.97989	2.014319	1.023139
C	-4.66265	1.930769	-1.22301

H	-3.25355	0.497936	-2.02316
C	-4.14663	2.798249	0.989395
H	-2.32462	2.06362	1.889174
C	-4.99439	2.761328	-0.13546
H	-5.30726	1.895314	-2.09862
H	-4.38791	3.441203	1.832882
H	-5.89388	3.372113	-0.1653
C	2.900205	-1.75396	-0.05951
C	3.75464	-1.56633	-1.17279
C	3.293672	-2.66262	0.951716
C	4.971092	-2.26275	-1.26592
H	3.462039	-0.87638	-1.95863
C	4.516662	-3.35328	0.861578
H	2.654353	-2.81129	1.81947
C	5.359421	-3.15784	-0.24866
H	5.614182	-2.10692	-2.12876
H	4.807942	-4.03833	1.654283
H	6.302553	-3.69404	-0.32158
C	-2.90009	-1.75425	0.059317
C	-3.75439	-1.56701	1.172753
C	-3.29357	-2.6627	-0.9521
C	-4.97073	-2.26363	1.265883
H	-3.46178	-0.87718	1.958692
C	-4.51645	-3.35355	-0.86196
H	-2.65436	-2.81103	-1.81999
C	-5.35907	-3.15852	0.248459
H	-5.61372	-2.10811	2.128857
H	-4.80775	-4.03843	-1.6548
H	-6.30211	-3.69489	0.321369
B	-4.4E-05	1.052607	-0.00019
Te	0.000127	-2.42898	-0.00059
Bq	0.000041	-0.68819	-0.0004
Bq	0.039139	-0.6883	0.998841

Compound 2

C	1.345568	0.97108	0.037865
C	-1.34683	0.969623	0.014483
C	-1.57692	-0.3833	-0.0284
C	1.577717	-0.38186	0.008387
H	2.262018	1.57138	0.065764
H	-2.26419	1.569165	0.019067
B	-0.0272	1.726957	0.013384
Te	-0.02439	-1.78175	-0.08058
C	2.946882	-0.97418	-0.03567
C	3.298059	-2.11049	0.734265
C	3.93738	-0.39252	-0.86776
C	4.598184	-2.64358	0.681053
H	2.565915	-2.55676	1.404513
C	5.235616	-0.92791	-0.92206
H	3.677567	0.46116	-1.48785
C	5.572911	-2.05594	-0.14804

H	4.850018	-3.50891	1.289378
H	5.978559	-0.47269	-1.57273
H	6.577051	-2.47048	-0.19201
C	-2.94511	-0.97934	-0.01571
C	-3.29473	-2.07338	-0.84525
C	-3.93621	-0.44471	0.846668
C	-4.59397	-2.61068	-0.82026
H	-2.56211	-2.48194	-1.53864
C	-5.23355	-0.98437	0.872626
H	-3.67752	0.374957	1.511509
C	-5.56932	-2.06988	0.0394
H	-4.84465	-3.44262	-1.47396
H	-5.97697	-0.56588	1.546977
H	-6.57276	-2.48783	0.061424
C	-0.05177	3.302564	0.025638
C	-1.18214	4.036563	-0.43066
C	1.05526	4.064306	0.493518
C	-1.20617	5.442449	-0.43066
H	-2.05184	3.503469	-0.80914
C	1.035428	5.470087	0.515316
H	1.941272	3.552807	0.863895
C	-0.09646	6.166636	0.047835
H	-2.08291	5.971196	-0.79875
H	1.89534	6.020158	0.891759
H	-0.11343	7.2545	0.056265
Bq	-0.0258	-0.02695	-0.03358
Bq	-0.05719	-0.0537	0.965566

Theoretical Methods and Technical Details of the Computations

The quantum chemical calculations were carried out with the TURBOMOLE suite of programs.[6] All structures were fully optimized at the dispersion-corrected DFT level using the PBEh-3c density functional.[7] This new compound method contains a modified PBE based hybrid functional together with an efficient valence double-zeta AO basis set. The method also involves an approximate counter-poise correction for BSSE, as well as three-body dispersion effects, see Ref.7 for details. We exploit the efficiency of this method to optimize transition state structures as well as to calculate vibrational harmonic frequencies. Single-point energies were computed with the larger polarized triple-zeta (def2-TZVP) sets by Ahlrichs *et al.*[8] in combination with the accurate PW6B95 hybrid functional.[9] The atom pairwise D3 correction with BJ-damping is included to account for intra- and intermolecular London dispersion interactions.[10] The combined level of theory used in the following is PW6B95-D3//PBEh-3c.

In all DFT treatments, the resolution-of-the-identity approximation has been used[11] for the Coulomb integrals to speed up the computations. The numerical quadrature grid *m4* has been employed for the integration of the exchange-correlation contribution. In the main text, we report pure electronic gas phase energies (termed ΔE) as well as Gibbs free energies at 298.15 K in toluene as a solvent (termed ΔG). The ro-vibrational corrections to the free energy are obtained from a modified rigid rotor, harmonic oscillator statistical treatment[12] based on the harmonic frequencies obtained at the PBEh-3c level (see above). For the entropy, all frequencies with wavenumbers below 100 cm^{-1} were treated as mixed rigid rotors and harmonic oscillators. In two cases very small imaginary modes of about i7 cm^{-1} were obtained computed which were treated as numerical artifacts and used with their absolute value. The harmonic frequencies in PBEh-3c were scaled by a factor of 0.95.

Solvent effects on the thermochemical properties have been obtained by the COSMO-RS method[13] (COSMOtherm software package[14]) based on BP86/TZVP[15] single-point calculations (parametrization from 2014). Solvation contributions to free energies at 298.15 K in toluene solution are computed from the gas phase structures obtained at the above mentioned levels of theory. The computed free energies are then obtained by $\Delta G = \Delta E + \Delta G_{RRHO} + \Delta\delta G_{COSMO\text{-}RS,}$ where the last two terms refer to the above mentioned ro-vibrational and solvation contributions, respectively, to the free energy.

In the main text we discuss only the higher-level PW6B95-D3 based thermochemical data but note in passsing that the more economical PBEh-3c level alone provides very similar reaction energies (see below) that within 1-2 kcal/mol of the PW6B95-D3/def2-TZVP level. Wiberg bond orders are reported to analyse the bonding situation in the transition states and these are based on the PW6B95-D3/def2-TZVP orbitals.

Cartesian coordinates (PBEh-3c) in Bohr

EDUCT

$coord

-0.04347913824729	1.30303403970473	-5.37201682236869	te
-1.29764467151612	-2.00236025645874	-3.67385682788921	c
-1.94670716647166	-2.15906812102269	-1.19706464467932	c
-0.74629196160821	2.70741555042277	0.15695476719686	c
0.06021069812502	3.51002488174946	-2.13874785533266	c
-3.16953164831743	-0.38588860716815	3.37492467163417	c
-1.92805431302988	0.08329504653156	5.65881134384662	c
-3.09474761164859	-0.35637213177135	7.96207203587987	c
-5.57117517051849	-1.21249144159851	8.04222887810459	c
-6.85752317187459	-1.65374188710308	5.80170496115892	c
-5.65412612281827	-1.27417776484562	3.50647141333211	c
-1.25051799706877	-4.12593960481560	-5.49429492375964	c
-2.63348913124919	-4.01514064671210	-7.73397483983543	c
-2.52690645002539	-5.97699414872176	-9.46908827852534	c
-1.01996203524299	-8.06686718806077	-9.00219199472795	c
0.37140216813689	-8.19004369543471	-6.78163838141651	c
0.25463531803811	-6.24228041761132	-5.04100473388482	c
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-5.58053320664387	-8.27886063065537	-0.41746082495586	c
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INTERMEDIATE

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PRODUCT

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TS1

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5.19330173403445	-8.47105734507076	-6.68892668571738	h
3.57958551860696	-4.43656128899341	-5.03081630696064	h
6.51145179533168	-3.92807545745030	1.77678747270295	h
11.00252250423382	-3.93993259630148	0.57579629697564	h
12.48224160052088	-1.32473199806969	-3.00980813932785	h
9.41702132865525	1.31781685517156	-5.35577092068663	h
4.94933632829336	1.36747278007031	-4.11862987356544	h
-4.90673440050693	4.60207545234827	1.73045835646786	h
-5.62748669325352	8.53309201149193	4.11495967730615	h
-2.60258402384489	9.85313701639609	7.42833017023789	h
1.14350806817865	7.19942109114629	8.32385596663173	h
1.87366333354195	3.29950160449868	5.91286371041891	h
-7.61463975731972	-1.03642237611554	0.90052220606535	h
-11.40431884839762	-1.10902104864265	3.57812519747056	h
-11.02206663031625	-0.61182816444753	8.21202666590047	h
-6.79626241185066	-0.06366020250363	10.13665581305510	h
-2.99401746607054	-0.01814762103098	7.46047440925329	h
0.47495130380903	3.10965045927397	-3.78604301258807	h
-4.38951515889913	-0.91002789678675	-5.23511716221452	c
-4.03118816809294	-2.97638419272919	-6.84540946946021	c
-6.04256598629806	-3.94777261054588	-8.19533530367968	c
-8.43480436427013	-2.88612548402529	-7.95727098717932	c
-8.80202442028646	-0.83189589707127	-6.36988555014473	c
-6.79431749502538	0.16235903393903	-5.01808498856745	c
-2.17273727367232	-3.81674827252187	-6.99893741838237	h
-5.75114855008648	-5.54679754887532	-9.43555492923523	h
-10.00603788911143	-3.65941945052919	-9.01177114107335	h
-10.65811594682493	0.00698038277365	-6.19098802451466	h
-7.06406937563890	1.77327577229108	-3.78762228741830	h

TS2

$coord

-1.65171009832751	-4.52604770752016	0.56901783409177	te
2.24277904595423	-4.47842606721013	0.22868310095502	c
3.38578853842124	-2.22832224988783	0.46953760328620	c
-0.31139229715293	0.46350020348481	2.81039185644242	c
-2.06307274218029	-1.38227454524429	2.89747709981785	c
3.96709945698694	2.74500586969477	1.11897449001664	c

3.06194968373680	5.21795084851914	0.86273913764764	c
4.66509511350937	7.27953570588886	0.78315549651702	c
7.25636466544197	6.94254452671165	1.02067059297485	c
8.20918760391075	4.52680730225189	1.34057976150850	c
6.58065151854790	2.46975356846158	1.37247442009594	c
3.42412055228804	-6.83793066243626	-0.63572658705038	c
2.96542647506295	-9.14545570221409	0.55501509770123	c
4.10133184229887	-11.34200515477421	-0.30604841802059	c
5.71106335374059	-11.27383207374199	-2.37379521455306	c
6.17706081665161	-8.99161498588203	-3.57741111361795	c
5.03937717342903	-6.79465393385299	-2.72240727893967	c
5.41587045887418	-2.27212580904053	0.12122175079801	h
-0.75504775477802	2.71113490531566	4.43782961476194	c
-2.89934900392495	4.20428317570897	4.12334855554088	c
-3.29400507176253	6.31376654373858	5.62455176885586	c
-1.55924791767165	6.95054480451759	7.48277796584727	c
0.58015694521314	5.47195567395954	7.81507246210152	c
0.98669743067847	3.38116794031881	6.29329273926652	c
-4.39892833930376	-1.44436758104902	4.42229886052600	c
-6.75607506150436	-1.66139922645492	3.26508775582250	c
-8.94833471480962	-1.73656972278174	4.69851851583923	c
-8.81507503063096	-1.60193986512795	7.31118027385838	c
-6.47623117394337	-1.39320698604626	8.47992145946569	c
-4.28593154726573	-1.31936067390325	7.05112050205098	c
2.14754110774738	0.36786759160241	1.10700207118519	b
0.15943141927766	0.46767958890490	-2.71672757704717	c
-1.51310762440703	-1.12764455054326	-3.18370824436286	c
1.05261847279142	5.54852662029030	0.68800466545324	h
3.89175324327656	9.15692259025752	0.53902613476053	h
8.51761241332990	8.55290400347118	0.96821944121476	h
10.22323048781404	4.23605779208147	1.55760068662835	h
7.39705657737356	0.60977730303185	1.62753344294998	h
1.74562297328226	-9.21229522778160	2.19779184280458	h
3.73701252664813	-13.11146460053342	0.65154203375525	h
6.59411621367400	-12.99067679430619	-3.04634483570467	h
7.41651860116794	-8.92361601849614	-5.20229476902759	h
5.36532107833624	-5.02510011305133	-3.69619972179661	h
-4.26258912292559	3.71403694499856	2.67857957610424	h
-4.96612783582653	7.45807981118625	5.34589209622886	h
-1.86772735453253	8.59404145458583	8.65986063628085	h
1.95217343138969	5.96096832377760	9.25045876677480	h
2.68314018716472	2.26348146345187	6.53327098823557	h
-6.88852640309663	-1.72843422746199	1.21968270220650	h
-10.76259092871484	-1.89230417195967	3.76815291865777	h
-10.52376934103624	-1.65963840912427	8.43245009256582	h
-6.35578523313944	-1.28721814350089	10.51834126657414	h

-2.46752656207473	-1.15166917138665	7.96975926036546	h
1.31392723411250	2.61065096043011	-3.97251341610116	c
-3.50026964723205	-2.09977495447042	-4.75743374770824	c
-3.12377155404488	-4.23112681416882	-6.26922419265940	c
-5.03455997249927	-5.09498552839640	-7.82776806078967	c
-7.35460012911921	-3.86558995341110	-7.88847586421668	c
-7.74466243210861	-1.75352274637696	-6.38800003507994	c
-5.83191423345167	-0.86886462813400	-4.83196420515616	c
-1.31945355477968	-5.19469612369602	-6.21250755208383	h
-4.71617654089695	-6.73792567121782	-9.00255738464425	h
-8.84818683280993	-4.55323285734068	-9.10305995252994	h
-9.54358454762103	-0.78236868169998	-6.43242481137503	h
-6.12704490818153	0.78574851854701	-3.66632759709157	h
-0.13404910315897	4.74291154855086	-4.51315979442066	c
0.94837233218295	6.80982126213663	-5.70147455193359	c
3.47981493527440	6.77006696362760	-6.37527141899364	c
4.92268495516934	4.64045741887419	-5.86203034626797	c
3.85532583125602	2.58044122793171	-4.66000707934379	c
-2.10661504859688	4.78095995470518	-3.97410513406936	h
-0.19454998791641	8.45848688409301	-6.09980961488356	h
4.32731777681885	8.39058369702797	-7.28919989392262	h
6.90262893232250	4.59707443619931	-6.36911238711309	h
4.99834824627028	0.94618490588985	-4.21101653803122	h

Thermochemical data at PBEh-3c level. The various relative energy, enthalpy, and entropy contributions for the reactions are given (kcal/mol, the two leftmost columns are the total values in Hartree).

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thermo reader tmer3 for: EDUCT -> TS1

-1908.32212	-1908.29497	17.03	E_gas(tot)
-0.09903	-0.10068	-1.03	H_solv
-0.07679	-0.07792	-0.71	G_solv
-0.02224	-0.02277	-0.33	TS_solv
0.62212	0.61986	-1.42	H_rovib
0.51592	0.51679	0.55	G_rovib
0.10621	0.10307	-1.97	TS_rovib
-1907.70000	-1907.67512	15.62	H_tot_gas
-1907.80620	-1907.77819	17.58	G_tot_gas
0.43913	0.43887	-0.16	E->G_solution
-1907.79903	-1907.77580	14.58	H_tot_solution
0.08396	0.08031	-2.29	TS_tot_solution
0.28161	0.26935	-7.69	S_tot_solution
-1907.88299	-1907.85610	16.87	G_tot_solution

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thermo reader tmer3 for: EDUCT -> INTERMEDIATE

-1908.32212	-1908.33308	-6.88	E_gas(tot)
-0.09903	-0.10009	-0.67	H_solv
-0.07679	-0.07754	-0.47	G_solv
-0.02224	-0.02255	-0.20	TS_solv
0.62212	0.62219	0.04	H_rovib
0.51592	0.52036	2.79	G_rovib
0.10621	0.10183	-2.75	TS_rovib
-1907.70000	-1907.71089	-6.84	H_tot_gas
-1907.80620	-1907.81272	-4.09	G_tot_gas
0.43913	0.44282	2.32	E->G_solution
-1907.79903	-1907.81099	-7.50	H_tot_solution
0.08396	0.07928	-2.94	TS_tot_solution
0.28161	0.26589	-9.86	S_tot_solution
-1907.88299	-1907.89026	-4.56	G_tot_solution

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thermo reader tmer3 for: EDUCT -> TS2

-1908.32212	-1908.29725	15.61	E_gas(tot)
-0.09903	-0.10046	-0.89	H_solv
-0.07679	-0.07769	-0.56	G_solv
-0.02224	-0.02277	-0.33	TS_solv
0.62212	0.62076	-0.86	H_rovib
0.51592	0.51775	1.15	G_rovib
0.10621	0.10301	-2.00	TS_rovib
-1907.70000	-1907.67649	14.75	H_tot_gas
-1907.80620	-1907.77950	16.76	G_tot_gas
0.43913	0.44006	0.58	E->G_solution
-1907.79903	-1907.77695	13.86	H_tot_solution
0.08396	0.08024	-2.33	TS_tot_solution
0.28161	0.26914	-7.83	S_tot_solution
-1907.88299	-1907.85719	16.19	G_tot_solution

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thermo reader tmer3 for: EDUCT -> PROD

-1908.32212	-1908.33758	-9.70	E_gas(tot)
-0.09903	-0.10294	-2.45	H_solv
-0.07679	-0.07946	-1.68	G_solv
-0.02224	-0.02348	-0.77	TS_solv
0.62212	0.62334	0.76	H_rovib
0.51592	0.51651	0.37	G_rovib
0.10621	0.10683	0.39	TS_rovib
-1907.70000	-1907.71424	-8.94	H_tot_gas
-1907.80620	-1907.82107	-9.33	G_tot_gas
0.43913	0.43704	-1.31	E->G_solution
-1907.79903	-1907.81718	-11.39	H_tot_solution
0.08396	0.08335	-0.38	TS_tot_solution

0.28161	0.27956	-1.28	S_tot_solution
-1907.88299	-1907.90054	-11.01	G_tot_solution

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thermo reader tmer3 for: INTERMEDIATE -> TS1

-1908.33308	-1908.29497	23.91	E_gas(tot)
-0.10009	-0.10068	-0.37	H_solv
-0.07754	-0.07792	-0.24	G_solv
-0.02255	-0.02277	-0.13	TS_solv
0.62219	0.61986	-1.46	H_rovib
0.52036	0.51679	-2.24	G_rovib
0.10183	0.10307	0.78	TS_rovib
-1907.71089	-1907.67512	22.45	H_tot_gas
-1907.81272	-1907.77819	21.67	G_tot_gas
0.44282	0.43887	-2.48	E->G_solution
-1907.81099	-1907.77580	22.08	H_tot_solution
0.07928	0.08031	0.65	TS_tot_solution
0.26589	0.26935	2.17	S_tot_solution
-1907.89026	-1907.85610	21.43	G_tot_solution

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thermo reader tmer3 for: INTERMEDIATE -> TS2

-1908.33308	-1908.29725	22.48	E_gas(tot)
-0.10009	-0.10046	-0.23	H_solv
-0.07754	-0.07769	-0.09	G_solv
-0.02255	-0.02277	-0.13	TS_solv
0.62219	0.62076	-0.90	H_rovib
0.52036	0.51775	-1.64	G_rovib
0.10183	0.10301	0.74	TS_rovib
-1907.71089	-1907.67649	21.59	H_tot_gas
-1907.81272	-1907.77950	20.85	G_tot_gas
0.44282	0.44006	-1.73	E->G_solution
-1907.81099	-1907.77695	21.36	H_tot_solution
0.07928	0.08024	0.61	TS_tot_solution
0.26589	0.26914	2.04	S_tot_solution
-1907.89026	-1907.85719	20.75	G_tot_solution

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thermo reader tmer3 for: INTERMEDIATE -> PROD

-1908.33308	-1908.33758	-2.82	E_gas(tot)
-0.10009	-0.10294	-1.79	H_solv
-0.07754	-0.07946	-1.21	G_solv
-0.02255	-0.02348	-0.58	TS_solv
0.62219	0.62334	0.72	H_rovib
0.52036	0.51651	-2.42	G_rovib
0.10183	0.10683	3.14	TS_rovib
-1907.71089	-1907.71424	-2.10	H_tot_gas
-1907.81272	-1907.82107	-5.24	G_tot_gas
0.44282	0.43704	-3.63	E->G_solution

-1907.81099	-1907.81718	-3.89	H_tot_solution
0.07928	0.08335	2.56	TS_tot_solution
0.26589	0.27956	8.58	S_tot_solution
-1907.89026	-1907.90054	-6.45	G_tot_solution

Thermochemical data at PW6B95-D3// PBEh-3c level. The various relative energy, enthalpy, and entropy contributions for the reactions are given (kcal/mol, the two leftmost columns are the total values in Hartree). These values are discussed in the main text.

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thermo reader tmer3 for: EDUCT -> TS1

-1914.96244	-1914.93492	17.27	E_gas(tot)
-0.09903	-0.10068	-1.03	H_solv
-0.07679	-0.07792	-0.71	G_solv
-0.02224	-0.02277	-0.33	TS_solv
0.62212	0.61986	-1.42	H_rovib
0.51592	0.51679	0.55	G_rovib
0.10621	0.10307	-1.97	TS_rovib
-1914.34032	-1914.31506	15.85	H_tot_gas
-1914.44652	-1914.41814	17.81	G_tot_gas
0.43913	0.43887	-0.16	E->G_solution
-1914.43935	-1914.41575	14.81	H_tot_solution
0.08396	0.08031	-2.29	TS_tot_solution
0.28161	0.26935	-7.69	S_tot_solution
-1914.52331	-1914.49605	17.11	G_tot_solution

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thermo reader tmer3 for: EDUCT -> INTERMEDIATE

-1914.96244	-1914.96792	-3.44	E_gas(tot)
-0.09903	-0.10009	-0.67	H_solv
-0.07679	-0.07754	-0.47	G_solv
-0.02224	-0.02255	-0.20	TS_solv
0.62212	0.62219	0.04	H_rovib
0.51592	0.52036	2.79	G_rovib
0.10621	0.10183	-2.75	TS_rovib
-1914.34032	-1914.34573	-3.39	H_tot_gas
-1914.44652	-1914.44756	-0.65	G_tot_gas
0.43913	0.44282	2.32	E->G_solution
-1914.43935	-1914.44582	-4.06	H_tot_solution
0.08396	0.07928	-2.94	TS_tot_solution
0.28161	0.26589	-9.86	S_tot_solution
-1914.52331	-1914.52510	-1.12	G_tot_solution

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thermo reader tmer3 for: EDUCT -> TS2

-1914.96244	-1914.93790	15.40	E_gas(tot)

-0.09903	-0.10046	-0.89	H_solv
-0.07679	-0.07769	-0.56	G_solv
-0.02224	-0.02277	-0.33	TS_solv
0.62212	0.62076	-0.86	H_rovib
0.51592	0.51775	1.15	G_rovib
0.10621	0.10301	-2.00	TS_rovib
-1914.34032	-1914.31714	14.54	H_tot_gas
-1914.44652	-1914.42015	16.55	G_tot_gas
0.43913	0.44006	0.58	E->G_solution
-1914.43935	-1914.41760	13.65	H_tot_solution
0.08396	0.08024	-2.33	TS_tot_solution
0.28161	0.26914	-7.83	S_tot_solution
-1914.52331	-1914.49784	15.98	G_tot_solution

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thermo reader tmer3 for: EDUCT -> PROD

-1914.96244	-1914.97674	-8.97	E_gas(tot)
-0.09903	-0.10294	-2.45	H_solv
-0.07679	-0.07946	-1.68	G_solv
-0.02224	-0.02348	-0.77	TS_solv
0.62212	0.62334	0.76	H_rovib
0.51592	0.51651	0.37	G_rovib
0.10621	0.10683	0.39	TS_rovib
-1914.34032	-1914.35340	-8.21	H_tot_gas
-1914.44652	-1914.46023	-8.60	G_tot_gas
0.43913	0.43704	-1.31	E->G_solution
-1914.43935	-1914.45635	-10.66	H_tot_solution
0.08396	0.08335	-0.38	TS_tot_solution
0.28161	0.27956	-1.28	S_tot_solution
-1914.52331	-1914.53970	-10.28	G_tot_solution

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thermo reader tmer3 for: INTERMEDIATE -> TS1

-1914.96792	-1914.93492	20.70	E_gas(tot)
-0.10009	-0.10068	-0.37	H_solv
-0.07754	-0.07792	-0.24	G_solv
-0.02255	-0.02277	-0.13	TS_solv
0.62219	0.61986	-1.46	H_rovib
0.52036	0.51679	-2.24	G_rovib
0.10183	0.10307	0.78	TS_rovib
-1914.34573	-1914.31506	19.24	H_tot_gas
-1914.44756	-1914.41814	18.46	G_tot_gas
0.44282	0.43887	-2.48	E->G_solution
-1914.44582	-1914.41575	18.87	H_tot_solution
0.07928	0.08031	0.65	TS_tot_solution
0.26589	0.26935	2.17	S_tot_solution
-1914.52510	-1914.49605	18.22	G_tot_solution

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thermo reader tmer3 for: INTERMEDIATE -> TS2

-1914.96792	-1914.93790	18.83	E_gas(tot)
-0.10009	-0.10046	-0.23	H_solv
-0.07754	-0.07769	-0.09	G_solv
-0.02255	-0.02277	-0.13	TS_solv
0.62219	0.62076	-0.90	H_rovib
0.52036	0.51775	-1.64	G_rovib
0.10183	0.10301	0.74	TS_rovib
-1914.34573	-1914.31714	17.94	H_tot_gas
-1914.44756	-1914.42015	17.20	G_tot_gas
0.44282	0.44006	-1.73	E->G_solution
-1914.44582	-1914.41760	17.71	H_tot_solution
0.07928	0.08024	0.61	TS_tot_solution
0.26589	0.26914	2.04	S_tot_solution
-1914.52510	-1914.49784	17.10	G_tot_solution

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thermo reader tmer3 for: INTERMEDIATE -> PROD

-1914.96792	-1914.97674	-5.54	E_gas(tot)
-0.10009	-0.10294	-1.79	H_solv
-0.07754	-0.07946	-1.21	G_solv
-0.02255	-0.02348	-0.58	TS_solv
0.62219	0.62334	0.72	H_rovib
0.52036	0.51651	-2.42	G_rovib
0.10183	0.10683	3.14	TS_rovib
-1914.34573	-1914.35340	-4.82	H_tot_gas
-1914.44756	-1914.46023	-7.95	G_tot_gas
0.44282	0.43704	-3.63	E->G_solution
-1914.44582	-1914.45635	-6.60	H_tot_solution
0.07928	0.08335	2.56	TS_tot_solution
0.26589	0.27956	8.58	S_tot_solution
-1914.52510	-1914.53970	-9.16	G_tot_solution

Wiberg bond orders (>0.07) of B and Te atoms (PW6B95/def2-TVP//PBEh-3c)

TS1 (c37 and c38 are the alkyne carbon atoms)

te c 5 1.102 c 2 1.081 c 38 0.156 b 36 0.122 c 65 0.117
b c 3 1.020 c 4 1.012 c 6 0.960 c 37 0.422 te 1 0.122 c 38 0.112

TS2 (c32 and c33 are the alkyne carbon atoms)

te c 5 1.112 c 2 1.069 c 33 0.290 c 32 0.137 b 31 0.085
b c 3 1.076 c 4 1.025 c 6 0.986 c 32 0.339 c 33 0.098 te 1 0.085

INTERMEDIATE

te c 2 1.006 c 5 0.996 c 38 0.958
b c 6 0.894 c 4 0.873 c 37 0.864 c 3 0.852

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