Supporting Information

Using Boryl-substitution and Improved Suzuki-Miyaura Cross-coupling to Access New Phosphorescent Tellurophenes

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1. X-ray structure determinations

X-ray Crystallography. Crystals suitable for X-ray diffraction studies were removed from a vial and immediately coated in a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was then mounted on a glass fiber, and quickly placed in a low temperature stream of nitrogen on an X-ray diffractometer. All data was collected on a Bruker APEX II CCD detector/D8 diffractometer[1] using Cu Kα radiation with the crystals cooled to –100 °C. The data was corrected for absorption using Gaussian integration from the indexing of the crystal faces.[2] Crystal structures were solved using intrinsic phasing SHELXT-2014[3] and refined using full-matrix least-squares on F^2 (SHELXL).[4] The assignment of hydrogen atom positions were based on the sp^2 or sp^3 hybridization geometries of their respective carbon atoms, and were given thermal parameters 20 % greater than those of their parent atoms.

Special refinement conditions for danB-Te-6-Bdan: In the structure of **danB-Te-6-Bdan**, the C11S-C12S distance (carbons of an Et_2O solvent molecule) was constrained by *DFIX* command in *SHELXL* to be 1.4437(11) Å.

Table S1. Crystallographic data for tellurophenes derived from **(^{i}PrO)$_2$B-Te-6-B(O^{i}Pr)$_2$**.

Compound	**catB-Te-6-Bcat**	**(^{t}Bucat)B-Te-6-B(^{t}Bucat)**	**danB-Te-6-Bdan**	**Mes(^{i}PrO)B-Te-6-B(O^{i}Pr)Mes**
formula	$C_{20}H_{16}B_2O_4Te$	$C_{28}H_{32}B_2O_4Te$	$C_{40}H_{54}B_2N_4O_3Te$	$C_{32}H_{44}B_2O_2Te$
form. wt. (g/mol)	469.55	581.75	788.09	609.89
crys. dimes. (mm)	0.45×0.04×0.04	0.29×0.16×0.14	0.23×0.23×0.14	0.12×0.09×0.06
Crystal system	Orthorhombic	Triclinic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)	P21/c (No. 14)	*Pnn*2 (No. 34)
a (Å)	5.07070(10)	12.0209(3)	15.677(6)	10.0095(3)
b (Å)	17.1292(3)	12.9608(3)	13.588(3)	12.3649(4)
c (Å)	20.6984(4)	18.3885(4)	18.6150(19)	12.5793(4)
α (deg)	-	86.3327(10)	-	-
β (deg)	-	77.7639(9)	91.140(15)	-
γ (deg)	-	69.4855(11)	-	-
V (Å^3)	1797.80(6)	2622.13(11)	3964.8(18)	1556.90(8)
Z	4	4	4	2
ρ_{calcd} (g cm^{-3})	1.735	1.474	1.320	1.301
μ (mm^{-1})	13.26	6.204	6.237	7.720
temperature (°C)	−100	−100	−100	−100
$2\theta_{max}$ (deg)	148.13	148.26	149.08	148.15
total data	12381	64505	172797	10692
unique data (R_{int})	3595 (0.0252)	10160 (0.0392)	8062 (0.0391)	3126 (0.0180)
Obs [I > 2σ(I)]	3579	9170	7701	3037
Parameters	246	643	493	171
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]^a	0.0203	0.0220	0.0207	0.0158
wR_2 [all data]^a	0.0490	0.0597	0.0559	0.0399
max/min Δr (e Å^{-3})	1.018/−0.717	0.572/−0.433	0.789/−0.462	0.220/−0.262

$^a R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$

2. Ultraviolet-visible (UV-vis) spectroscopy measurements

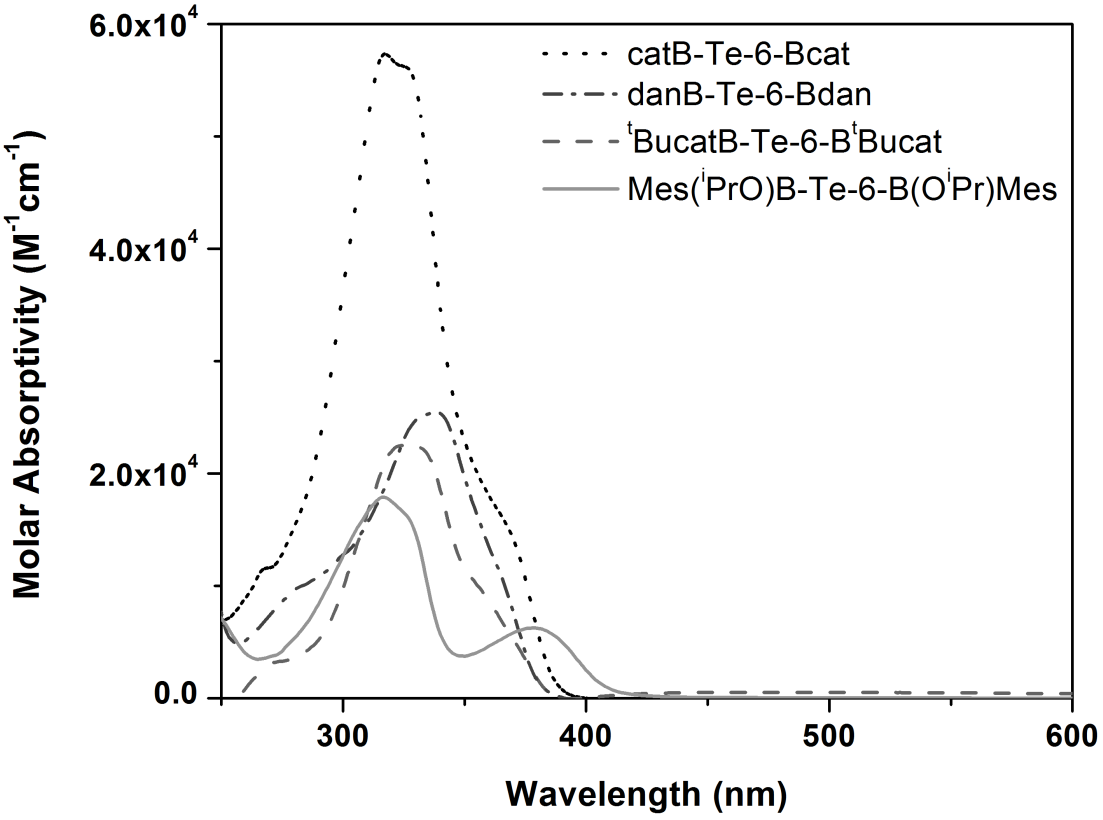

Figure S1. UV-vis absorption spectra recorded in THF, [conc] = 3x 10^{-5} M.

3. Luminescence Images

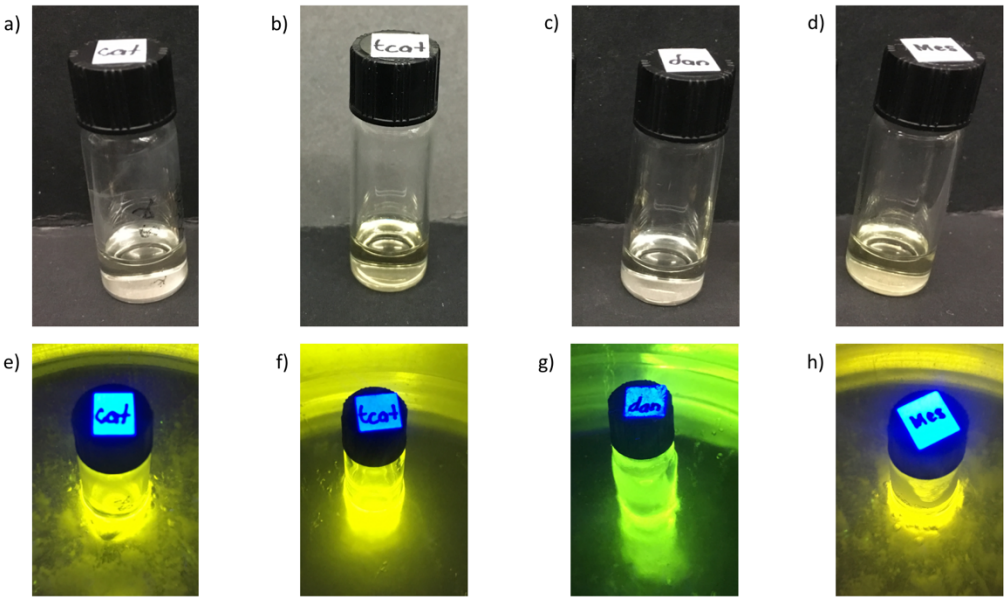

Figure S2. Top: Solutions of a) **catB-Te-6-Bcat**, b) **^{t}BucatB-Te-6-B^{t}Bucat**, c) **danB-Te-6-Bdan** and d) **Mes(^{i}PrO)B-Te-6-B(O^{i}Pr)Mes** in 2-methyltetrahydrofuran (0.01 – 0.02 M) at room temperature. Bottom: 2-Methyltetrahydrofuran solutions of e) **catB-Te-6-Bcat**, f) **^{t}BucatB-Te-6-B^{t}Bucat**, g) **danB-Te-6-Bdan** and h) **Mes(^{i}PrO)B-Te-6-B(O^{i}Pr)Mes** cooled in an $N_{2\,(l)}$ bath and irradiated with a handheld UV lamp (365 nm).

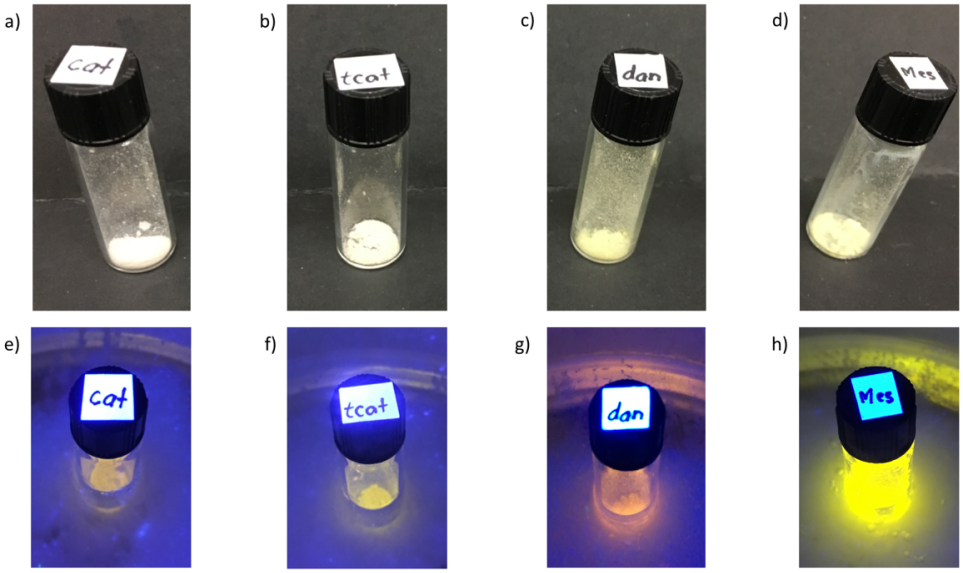

Figure S3. Top: Solid state samples of a) **catB-Te-6-Bcat**, b) **^{t}BucatB-Te-6-B^{t}Bucat**, c) **danB-Te-6-Bdan** and d) **Mes(^{i}PrO)B-Te-6-B(O^{i}Pr)Mes** at room temperature. Bottom: Solid state samples of e) **catB-Te-6-Bcat**, f) **^{t}BucatB-Te-6-B^{t}Bucat**, g) **danB-Te-6-Bdan** and h) **Mes(^{i}PrO)B-Te-6-B(O^{i}Pr)Mes** cooled in an $N_{2\,(l)}$ bath and irradiated with a handheld UV lamp (365 nm).

4. Lifetime measurements

Lifetime measurements were collected on samples sealed in a melting point tube under an N_2 atmosphere. The decay curves were measured using a Horiba PTI QuantaMaster 8075 fluorescence spectrometer equipped with a 75W xenon flash lamp. The resulting decay curve was fitted with the lowest exponential function that gave a suitable reduced chi-square value (χ^2)[13] and a suitable Durbin Watson parameter.[14-16]

Table S2. The photoluminescence decay of **Mes(^{i}PrO)B-Te-6-B(O^{i}Pr)Mes** powder fit with a biexponential, and the resulting parameters.

Number of components	2
Lifetime of component 1 (τ_1)	81. 9517 ± 0.641791 μs
Weight of component 1 (A_1)	0.79
Lifetime of component 2 (τ_2)	160.609 ± 0.378898 μs
Weight of component 2 (A_2)	0.21
Weighted mean lifetime $\left(\frac{\sum A_i\tau_i^2}{\sum A_i\tau_i}\right)$	108.893 μs
χ^2	1.01188
Durbin-Watson parameter	2.03129
Z (run test of the residuals)	–0.00895626

Table S3. The photoluminescence decay of **(^{t}Bucat)B-Te-6-B(^{t}Bucat)** powder fit with a biexponential, and the resulting parameters.

Number of components	2
Lifetime of component 1 (τ_1)	9.1034 ± 0.302457 μs
Weight of component 1 (A_1)	0.61
Lifetime of component 2 (τ_2)	27.9130 ± 0.172553 μs
Weight of component 2 (A_2)	0.39
Weighted mean lifetime $\left(\frac{\sum A_i\tau_i^2}{\sum A_i\tau_i}\right)$	21.5352 μs
χ^2	1.03149
Durbin-Watson parameter	1.86808
Z	–0.0397772

5. NMR Spectra

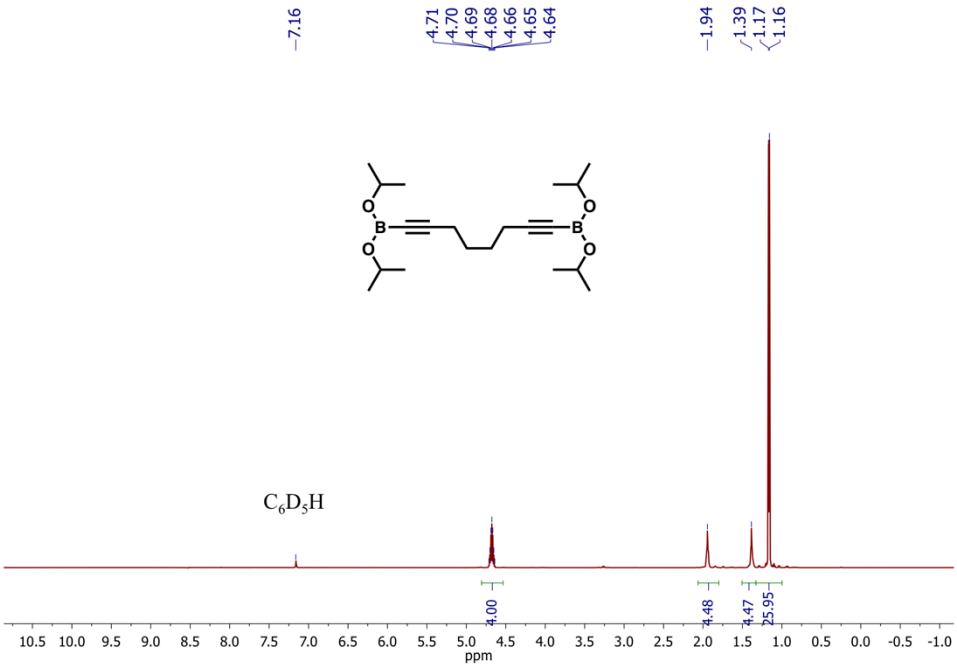

Figure S4. ^{1}H NMR spectrum of 1,8-bis(diisopropyl-1,3,2-dioxaborolan-2-yl)octa-1,7-diyne in C_6D_6.

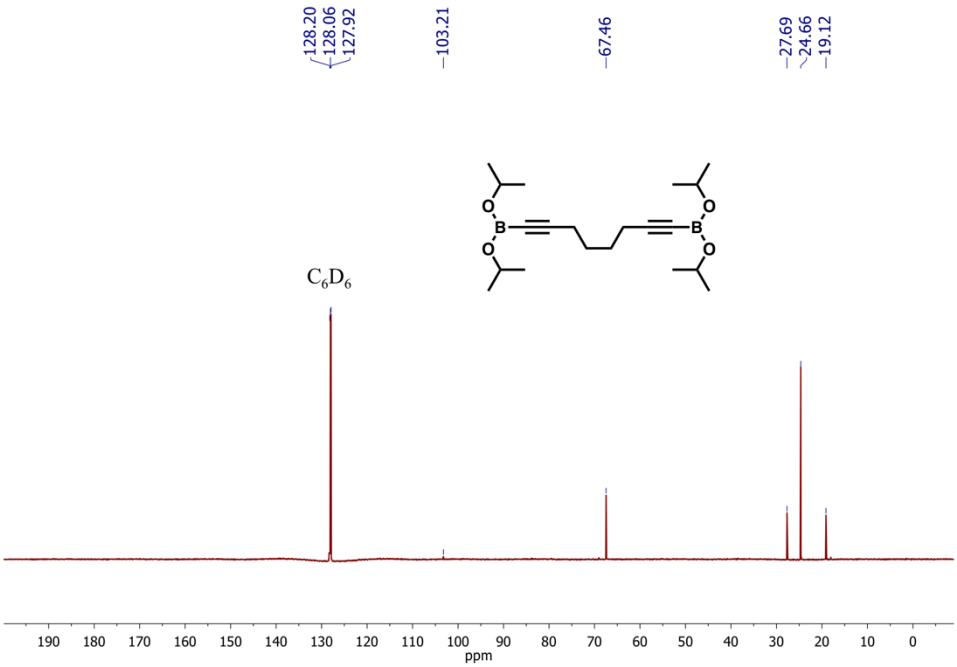

Figure S5. ^{13}C{^{1}H} NMR spectrum of 1,8-bis(diisopropyl-1,3,2-dioxaborolan-2-yl)octa-1,7-diyne in C_6D_6.

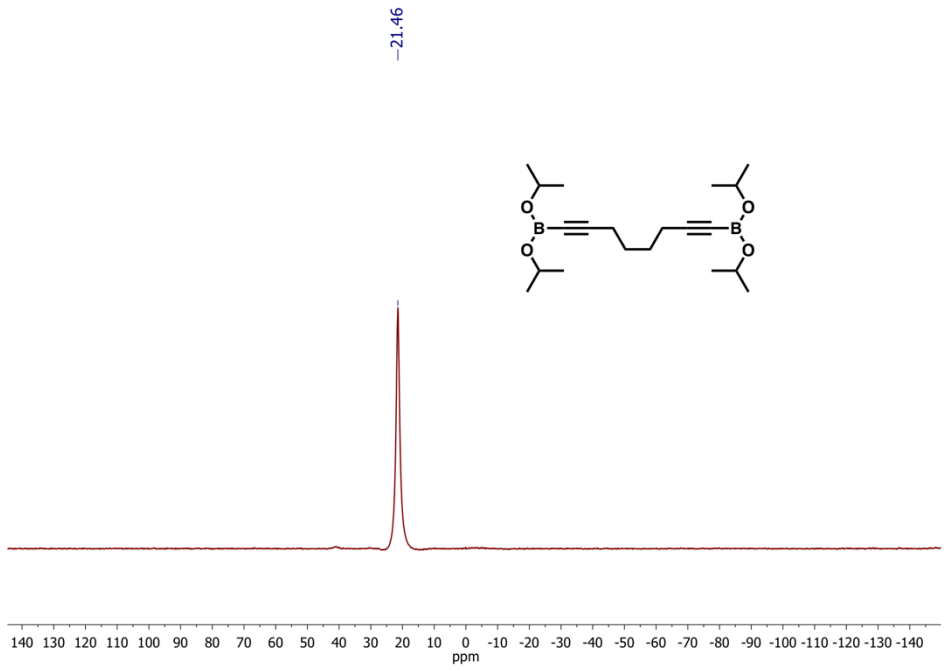

Figure S6. $^{11}B\{^{1}H\}$ NMR spectrum of 1,8-bis(diisopropyl-1,3,2-dioxaborolan-2-yl)octa-1,7-diyne in C_6D_6.

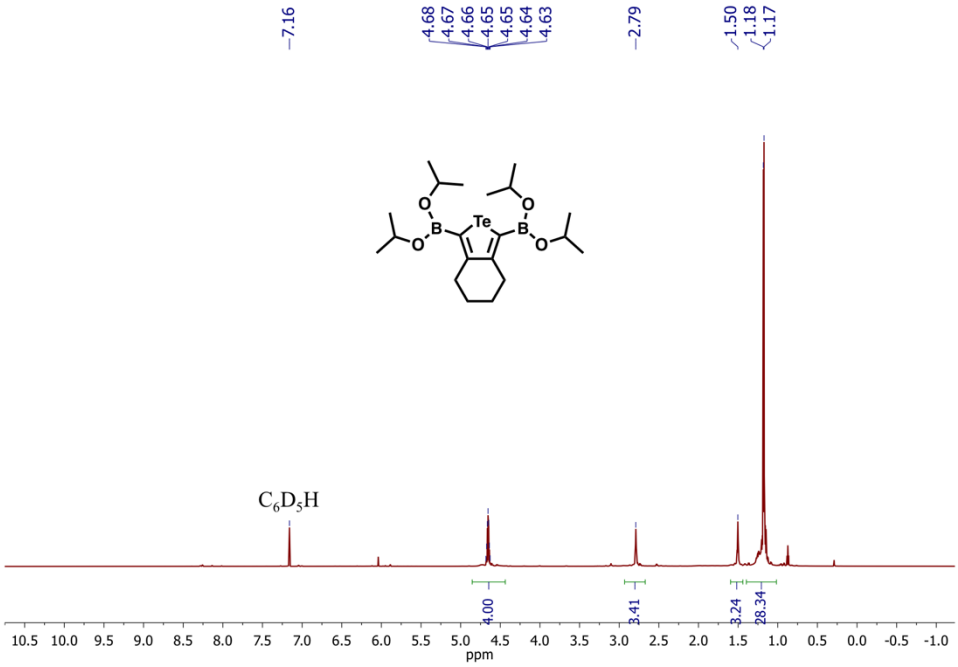

Figure S7. ^{1}H NMR spectrum of **$(^{i}PrO)_2B$-Te-6-$B(O^{i}Pr)_2$** in C_6D_6.

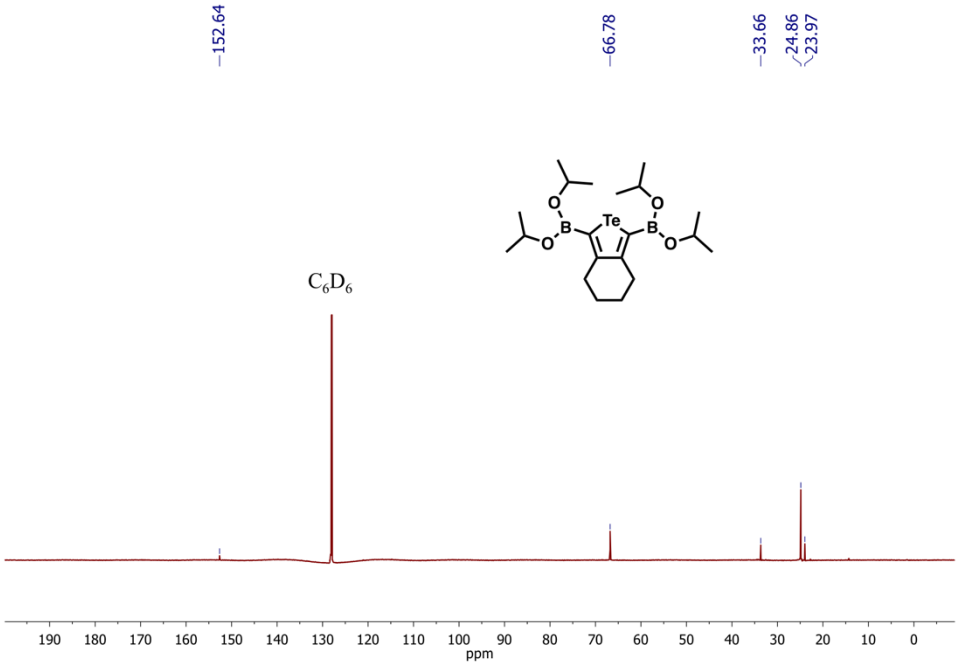

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **(^{i}PrO)$_2$B-Te-6-B(O^{i}Pr)$_2$** in C_6D_6.

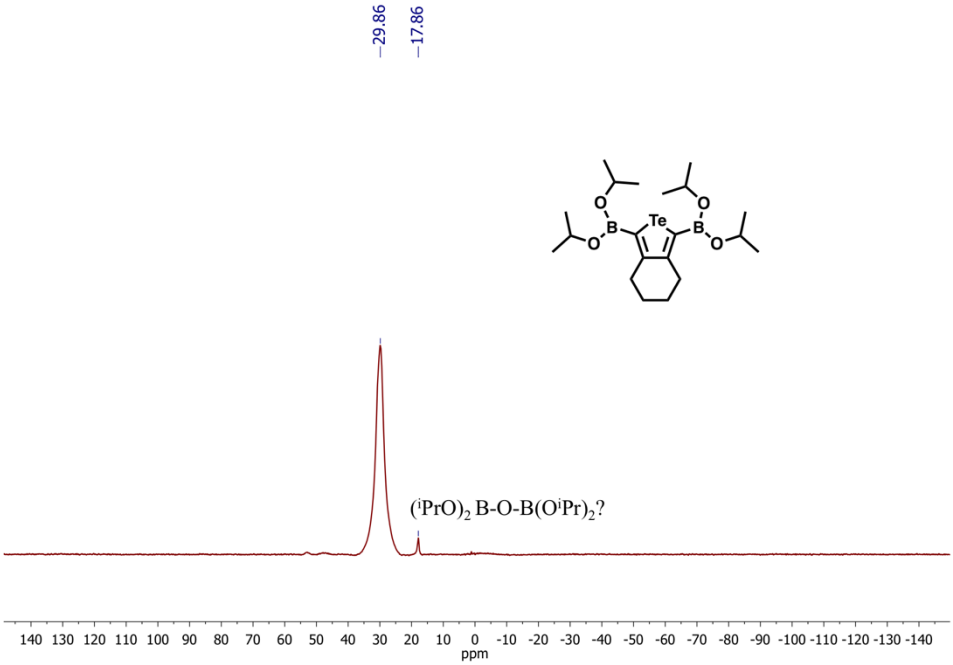

Figure S9. $^{11}B\{^{1}H\}$ NMR spectrum of **(^{i}PrO)$_2$B-Te-6-B(O^{i}Pr)$_2$** in C_6D_6.

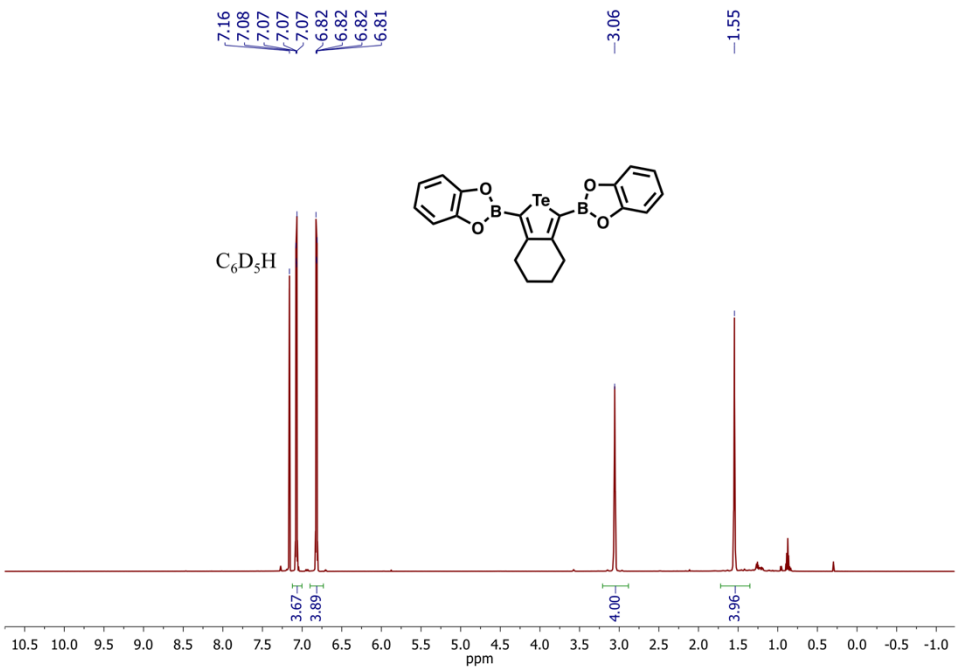

Figure S10. ^{1}H NMR spectrum of **catB-Te-6-Bcat** in C_6D_6.

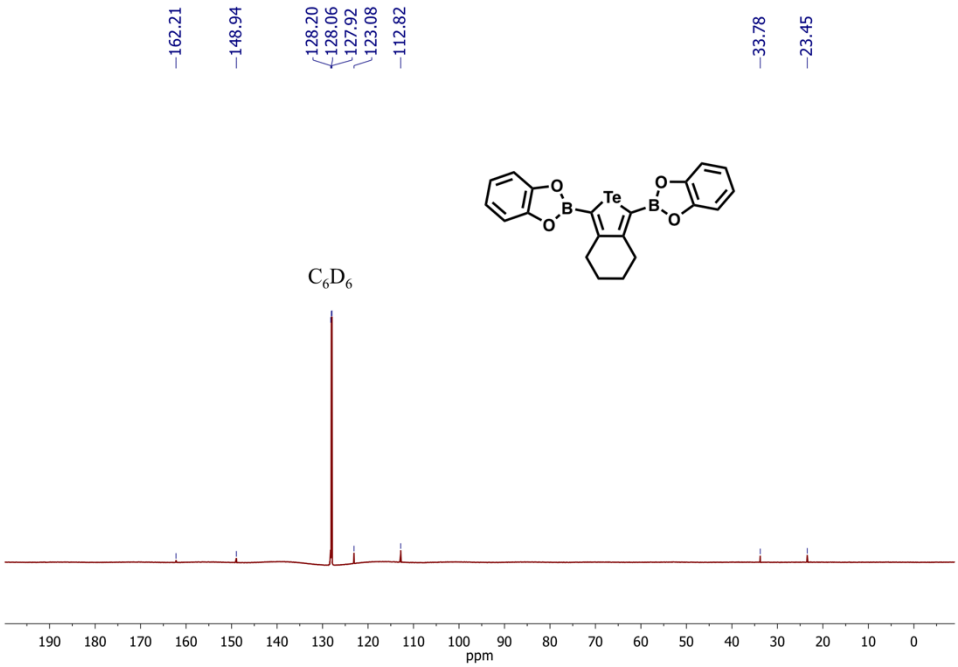

Figure S11. ^{13}C{^{1}H} NMR spectrum of **catB-Te-6-Bcat** in C_6D_6.

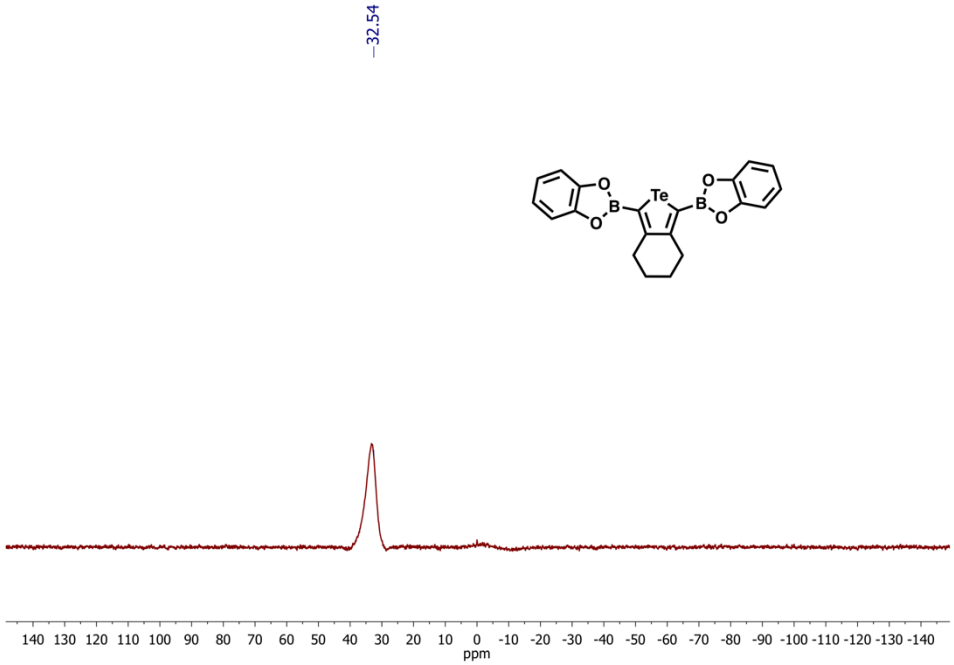

Figure S12. $^{11}B\{^{1}H\}$ NMR spectrum of **catB-Te-6-Bcat** in C_6D_6.

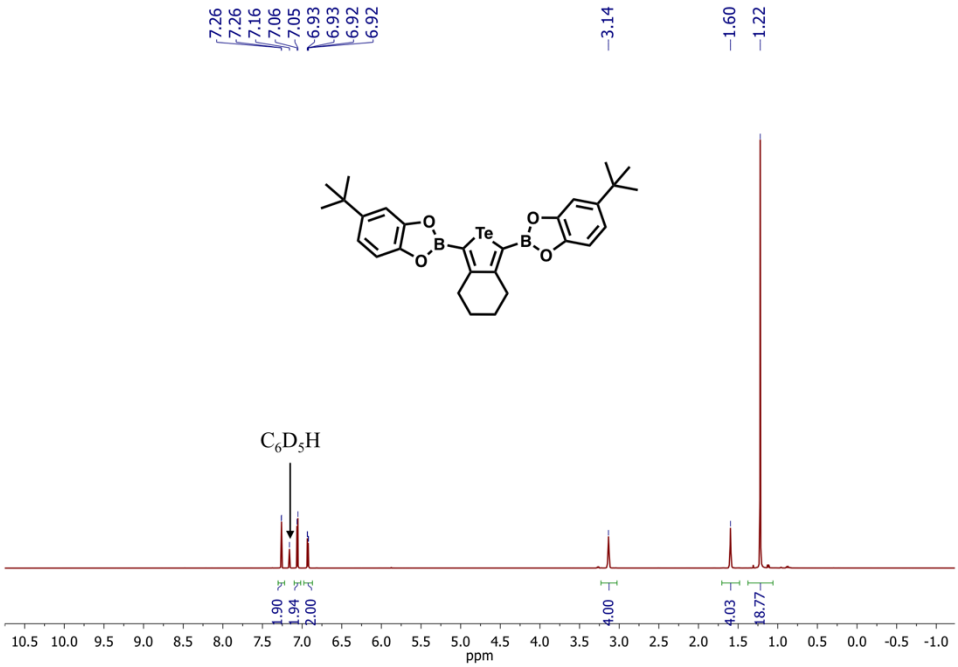

Figure S13. ^{1}H NMR spectrum of **^{t}BucatB-Te-6-B^{t}Bucat** in C_6D_6.

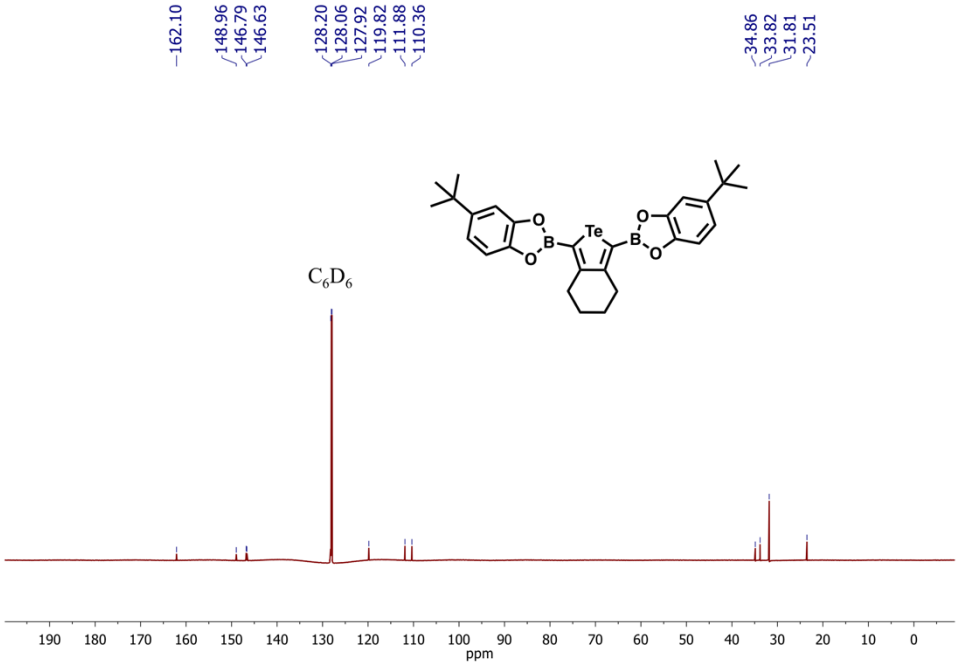

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **^{t}BucatB-Te-6-B^{t}Bucat** in C_6D_6.

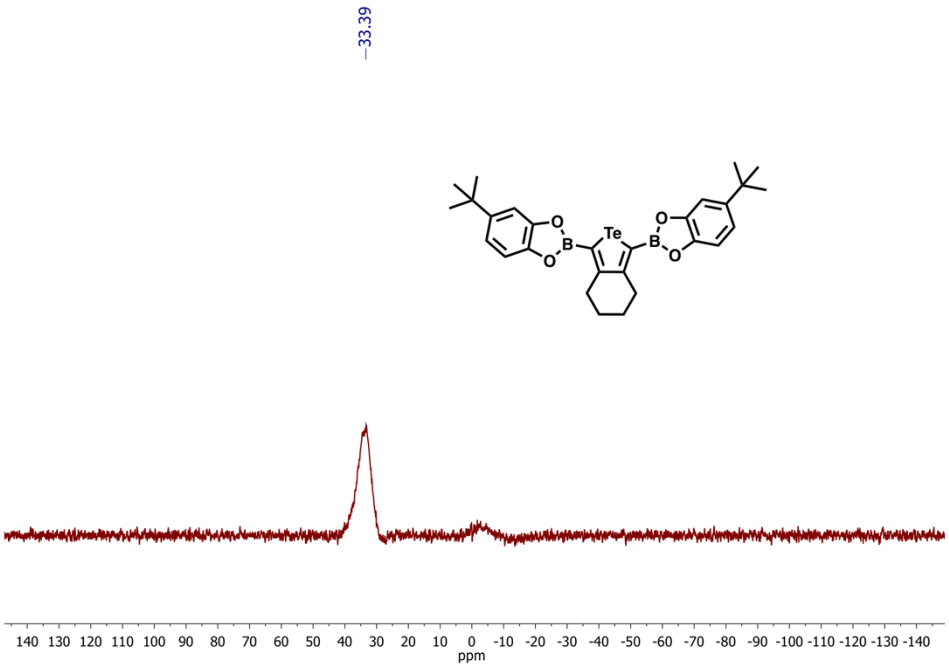

Figure S15. $^{11}B\{^{1}H\}$ NMR spectrum of **^{t}BucatB-Te-6-B^{t}Bucat** in C_6D_6.

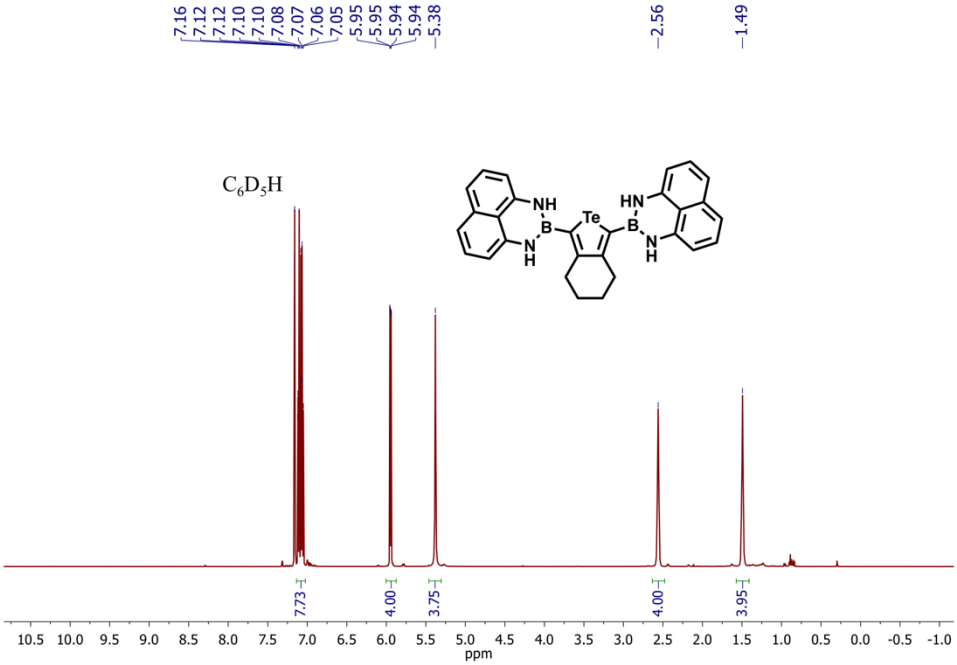

Figure S16. ^{1}H NMR spectrum of **danB-Te-6-Bdan** in C_6D_6.

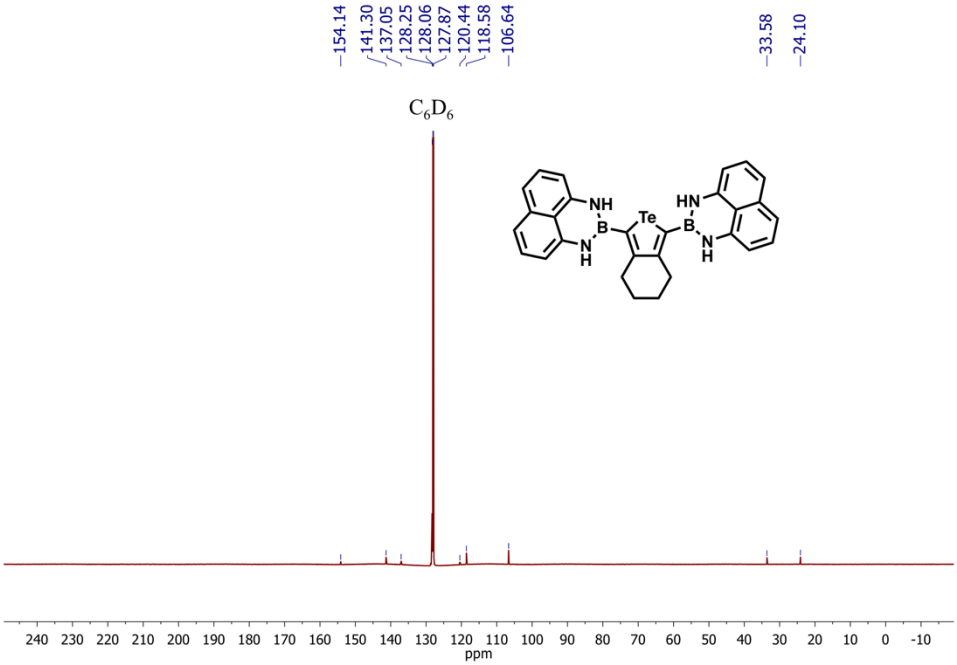

Figure S17. ^{13}C{^{1}H} NMR spectrum of **danB-Te-6-Bdan** in C_6D_6.

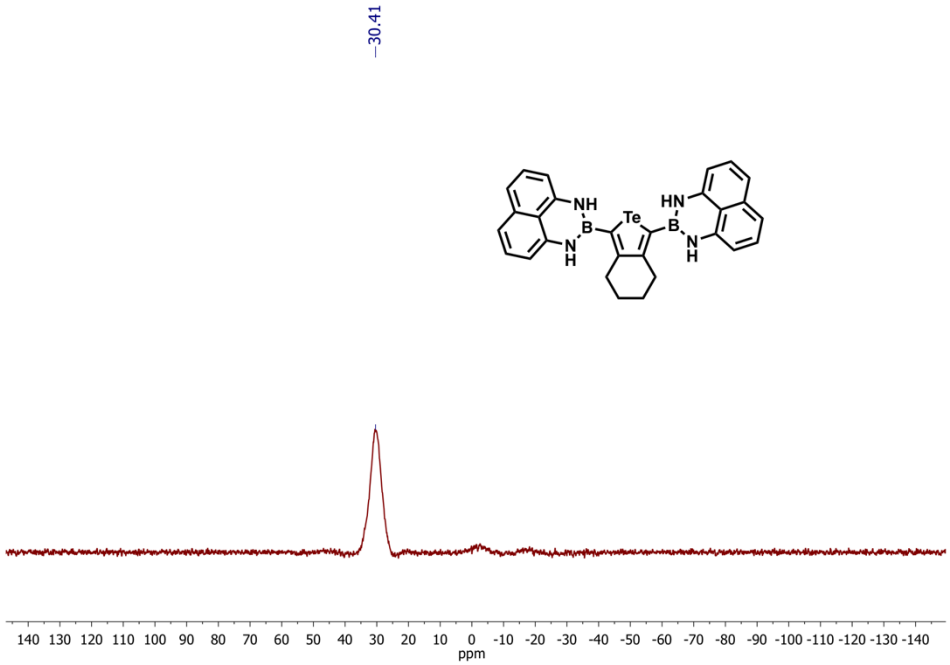

Figure S18. $^{11}B\{^{1}H\}$ NMR spectrum of **danB-Te-6-Bdan** in C_6D_6.

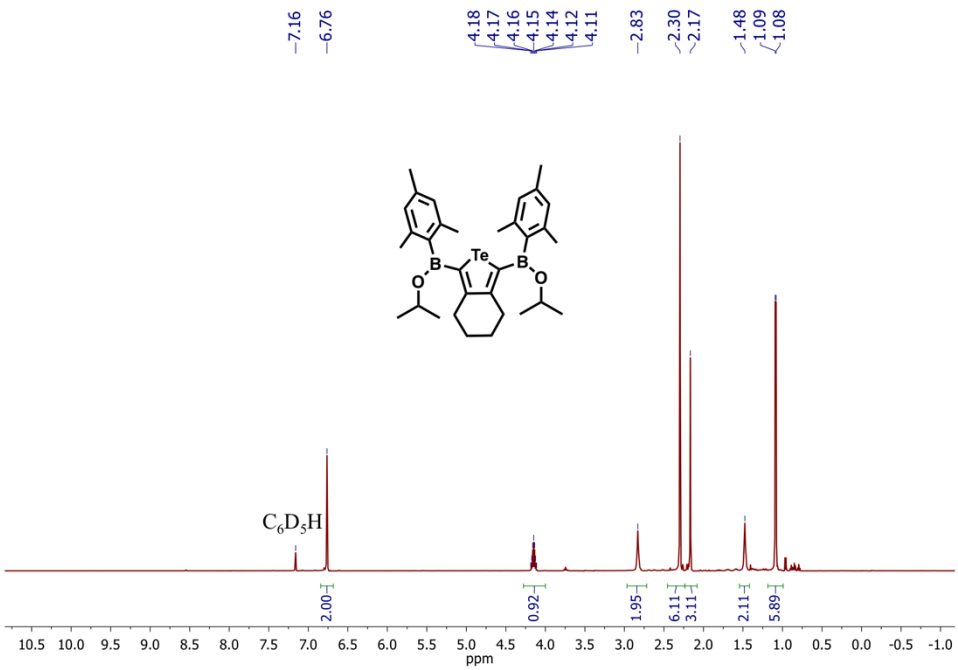

Figure S19. ^{1}H NMR spectrum of **Mes(^{i}PrO)B-Te-6-B(O^{i}Pr)Mes** in C_6D_6.

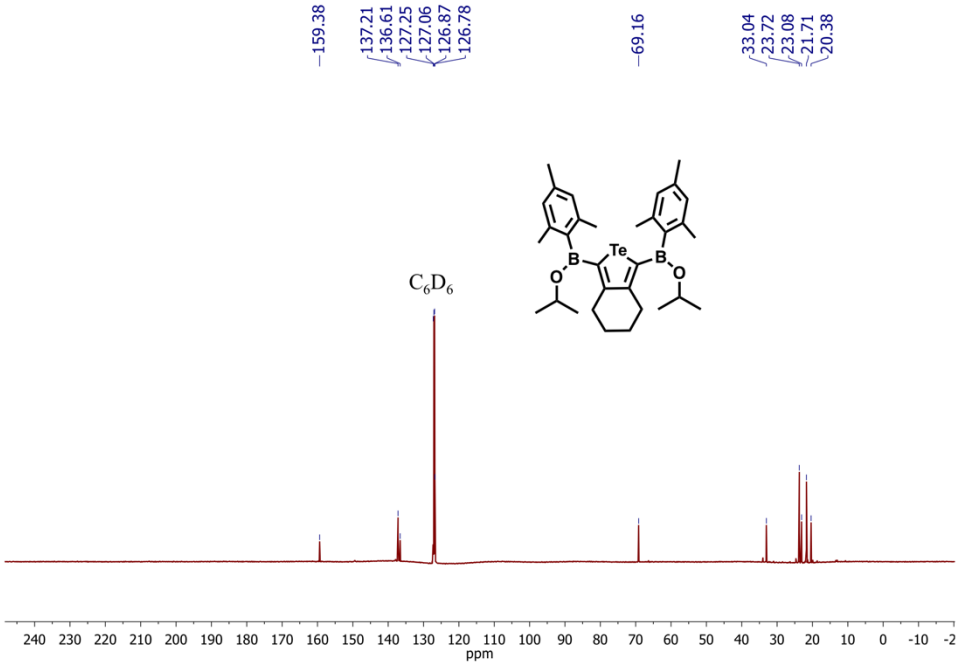

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of **Mes(ⁱPrO)B-Te-6-B(OⁱPr)Mes** in C_6D_6.

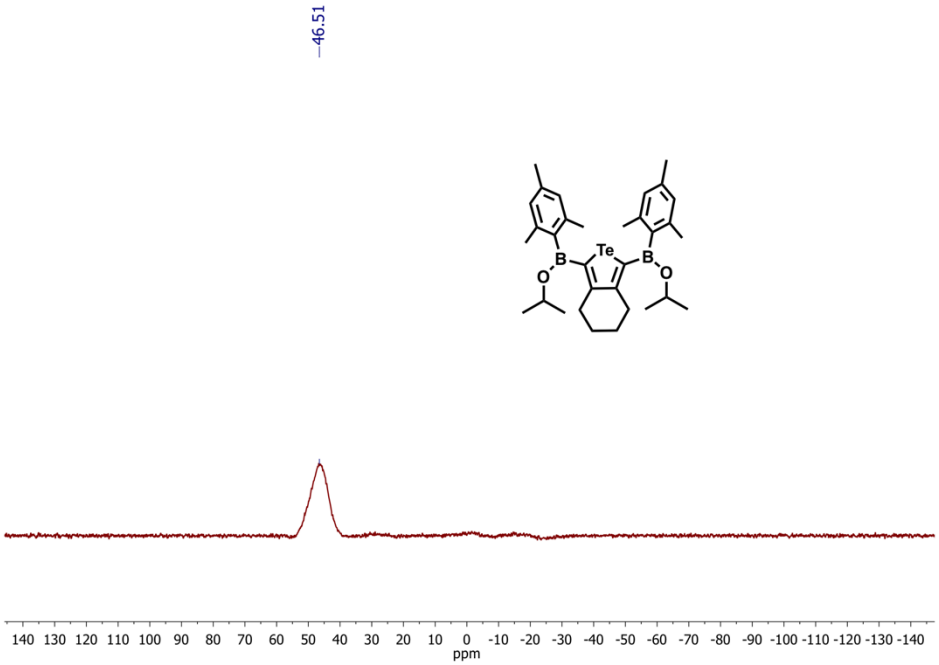

Figure S21. $^{11}B\{^{1}H\}$ NMR spectrum of **Mes(ⁱPrO)B-Te-6-B(OⁱPr)Mes** in C_6D_6.

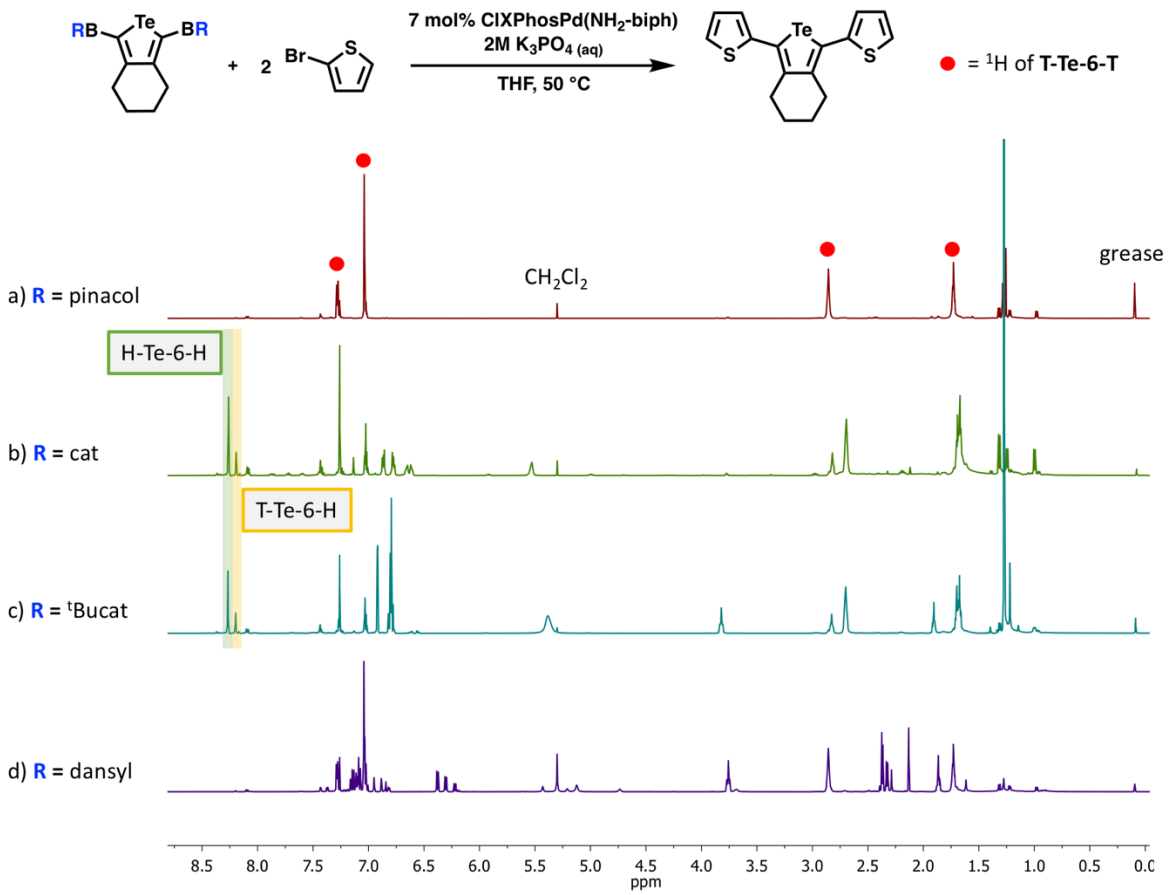

Figure S22. ^{1}H NMR spectrum ($CDCl_3$) of the attempted Suzuki-Miyaura cross coupling reactions between borylated tellurophenes and 2 equiv. of 2-bromothiophene. a) coupling with **pinB-Te-6-B-pin** (16 hrs), b) coupling with **catB-Te-6-Bcat** (40 hrs), c) coupling with **^{t}BucatB-Te-6-B^{t}Bucat** (40 hrs), d) **danB-Te-6-Bdan** (16 hrs). All reactions were worked up by diluting with *ca*. 3 mL of CH_2Cl_2, drying over $MgSO_4$ and filtering before removing all volatiles. In the above spectra **T** = thienyl group.

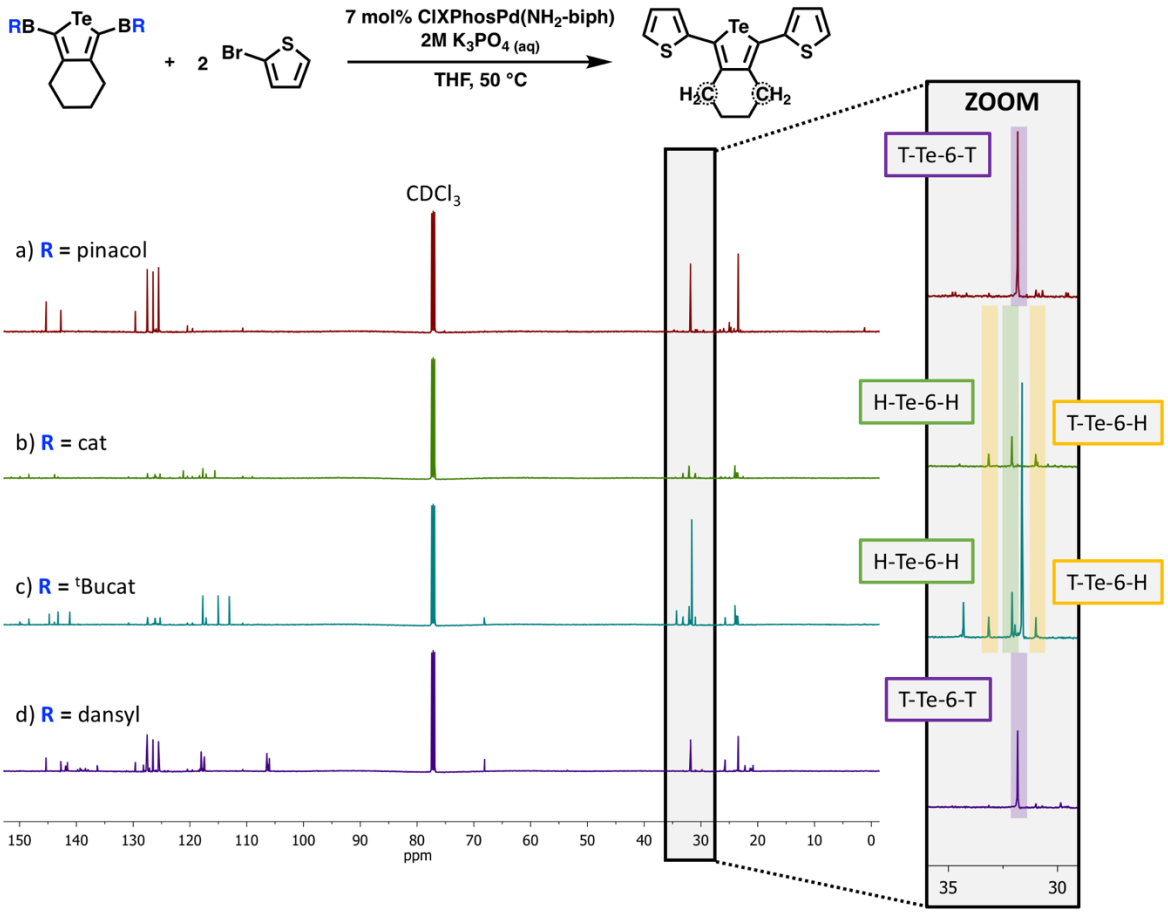

Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of attempted Suzuki-Miyaura cross coupling reactions between borylated tellurophenes and 2-bromothiophene to produce **thienyl-Te-6-thienyl** (**T-Te-6-T**). a) coupling with **pinB-Te-6-B-pin** (16 hrs), b) coupling with **catB-Te-6-Bcat** (40 hrs), c) coupling with **^{t}BucatB-Te-6-B^{t}Bucat** (40 hrs), d) **danB-Te-6-Bdan** (16 hrs). All reactions were worked up by diluting with *ca*. 3 mL of CH_2Cl_2, drying over $MgSO_4$ and filtering before removing all volatiles. In the above spectra **T** = thienyl group.

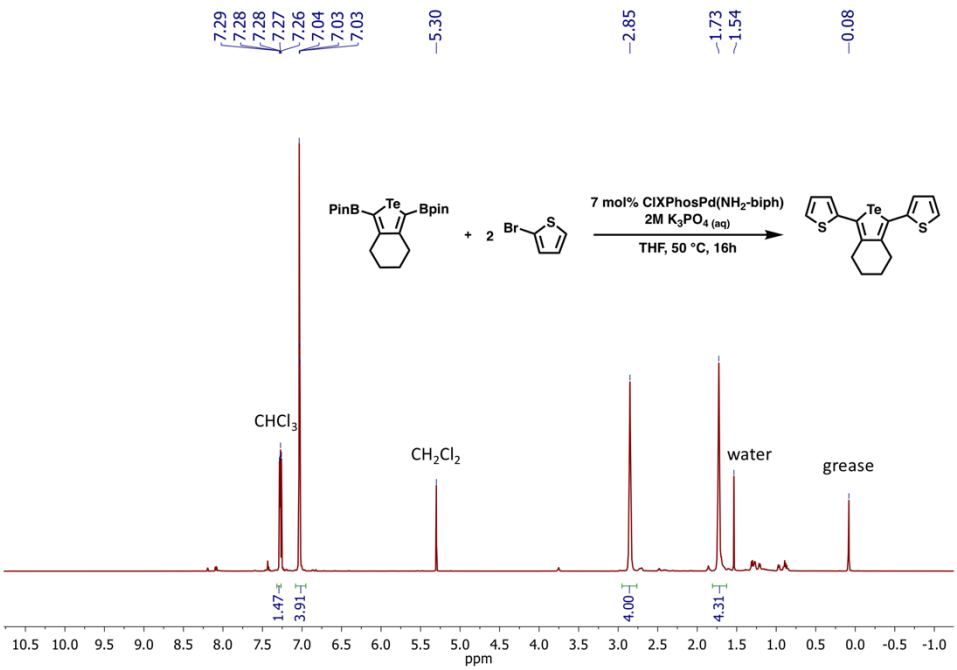

Figure S24. ^{1}H NMR spectrum of **thienyl-Te-6-thienyl** (**T-Te-6-T**) in $CDCl_3$ produced via the Suzuki-Miyaura cross coupling of **pinB-Te-6-Bpin** and 2 equiv. 2-bromothiophene.

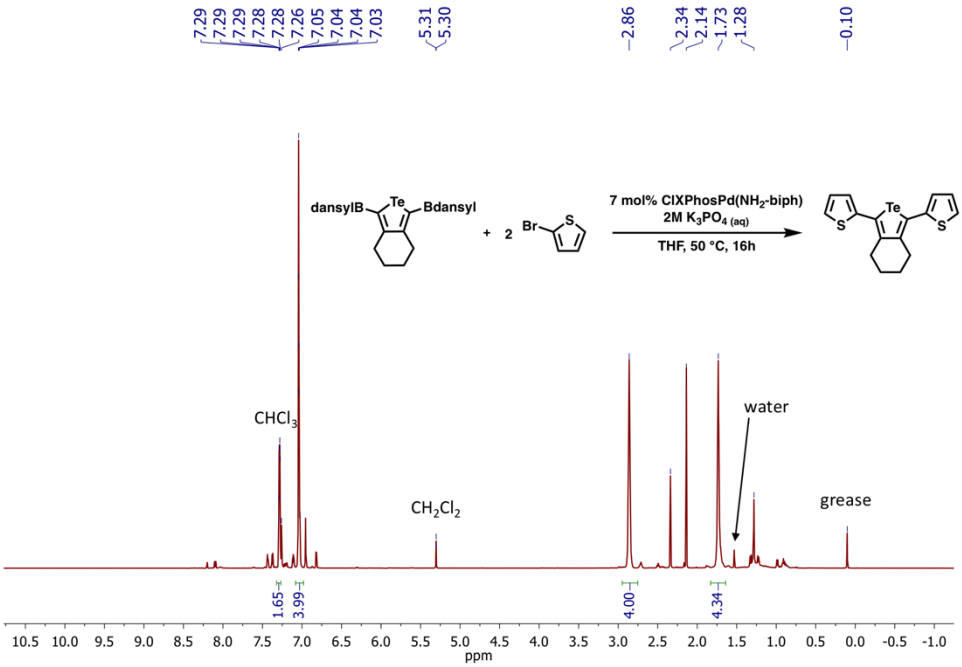

Figure S25. ^{1}H NMR spectrum of **thienyl-Te-6-thienyl** (**T-Te-6-T**) in $CDCl_3$ produced via the Suzuki-Miyaura cross coupling of **danB-Te-6-Bdan** and 2 equiv. 2-bromothiophene.

6. Time dependent density functional theory (TD-DFT) computations for Mes(^{i}PrO)B-Te-6-B(O^{i}Pr)Mes

All computations have been carried out with the Gaussian16 software package.[5] Geometry optimizations of the gas-phase structures have been performed using density functional theory (DFT) with the hybrid density functional (B3LYP)[6,7] in combination with the basis set cc-pVDZ (for C, H, B, O, N)[8] as well as the basis set cc-pVDZ(-PP) for Te.[9] The cc-PVDZ-PP basis set uses the corresponding effective core potential (ECP) accounting for 28 electrons. The use of the cc-PVDZ and cc-PVDZ-PP basis sets will hereafter be referred to as cc-PVDZ(-PP). The basis sets as well as the ECP for the Te atom were obtained from the Basis Set Exchange Library.[10,11] Initial molecular geometries were taken from the experimentally obtained X-ray structures. Subsequent frequency analysis confirmed all obtained structures to be local minima on the potential energy surface. The optimized geometry of the S_0 ground state was determined at the B3LYP level of theory. The phosphorescence energy was calculated by computing the optimized geometry of the lowest lying triplet state (T_1) using UB3LYP (spin-unrestricted B3LYP) with the same basis sets as specified above. Subsequent TD-DFT calculations were used to predict the vertical excitation energies of the first 10 singlet and first ten triplet sates using the B3LYP functional as well as the cc-PVDZ(-PP) basis sets starting from the B3LYP optimized gas-phase S_0 geometry. The presented molecule orbitals (MOs) were extracted from the Gaussian16 checkpoint-files and are visualized with VMD.[12]

Table S4. TD-DFT calculated excited states of **Mes(^{i}PrO)B-Te-6-B(O^{i}Pr)Mes** at the B3LYP/ccpVDZ(-PP) level of theory.

Excited State	Energy (eV) Oscillator Strength	Wavelength (nm)	Transition
T1	2.4463 0.0000	506.8	142 – 144 HOMO-1 to LUMO
T2	2.4934 0.0000	497.3	143 – 144 HOMO to LUMO
S1	3.4273 0.0577	361.8	143 – 144 HOMO to LUMO
T3	3.5688 0.0000	347.4	140 – 146 HOMO-3 to LUMO+2
T4	3.5691 0.0000	347.4	141 – 146 HOMO-2 to LUMO+2
T5	3.8094 0.0000	325.5	141 – 144 HOMO-2 to LUMO
T6	3.8548 0.0000	321.6	140 – 144 HOMO-3 to LUMO
S2	3.8633 0.0046	320.9	141 – 144 HOMO-2 to LUMO
S3	3.8876 0.0001	318.9	140 – 144 HOMO-3 to LUMO
T7	3.8956 0.0000	318.3	143 – 145 HOMO to LUMO+1
S4	3.9338 0.3590	315.2	142 – 144 HOMO-1 to LUMO
T8	4.0703 0.0000	304.6	139 – 144 HOMO-4 to LUMO
T9	4.0723 0.0000	304.5	138 – 144 HOMO-5 to LUMO
S5	4.0831 0.0021	303.7	139 – 144 HOMO-4 to LUMO
S6	4.0847 0.0001	303.5	138 – 144 HOMO-5 to LUMO
S7	4.2622 0.0000	290.9	143 – 145 HOMO to LUMO+1
T10	4.4234 0.0000	280.3	138 – 146 HOMO-5 to LUMO+2
S8	4.7159 0.0030	262.9	143 – 146 HOMO to LUMO+2
S9	4.7350 0.0000	261.9	137 – 144 HOMO-6 to LUMO
S10	4.7407 0.0014	261.5	142 – 145 HOMO-1 to LUMO+1

Table S5. Coordinates for the optimized structure of **Mes(^{i}PrO)B-Te-6-B(O^{i}Pr)Mes** in the ground state (S_0).

Atom	Coordinates		
	X	Y	Z
Te	0.403955945	0.230358186	1.22239863
O	1.010759912	4.31293258	-0.324681636
C	0.529998639	1.867729981	-0.074677582
C	0.420632011	1.444619295	-1.396749948
C	0.499526979	2.436957755	-2.550324858
H	1.557191849	2.735907035	-2.674747283
H	-0.026601767	3.361211619	-2.277791663
C	-0.021314303	1.88598964	-3.880947155
H	-1.124260662	1.807856386	-3.852624245
H	0.22468247	2.59158818	-4.691760423
C	1.283045405	5.67920875	0.046763567
H	1.354430814	5.742708715	1.145712911
C	0.13117618	6.554823203	-0.438264913
H	0.320699677	7.611252187	-0.188342742
H	0.016172208	6.471972769	-1.531409094
H	-0.818257833	6.258430898	0.032745539
C	2.615123346	6.076679455	-0.58243871
H	2.87160029	7.115335586	-0.318486723
H	3.426685766	5.420656453	-0.233004804
H	2.560954135	5.999898112	-1.680610975
C	0.722296228	3.493390133	2.122142215
C	-0.512394158	3.712094323	2.788117876
C	-0.536733147	3.880559386	4.176350956
H	-1.497633243	4.047763785	4.673313627
C	0.633253912	3.831976874	4.948022591
C	1.84379949	3.610460657	4.286811458
H	2.769444505	3.561832002	4.868715939
C	1.90600121	3.445954179	2.893928591
C	-1.811774032	3.748083587	2.011531418
H	-2.664624771	3.979166748	2.66687037
H	-2.012182709	2.779725812	1.523495932
H	-1.79056011	4.505660205	1.210733786
C	0.573253754	4.003200042	6.447255392
H	0.093806599	4.957465489	6.723492638
H	1.577325155	3.987669556	6.896776545
H	-0.018201251	3.199569095	6.918463621

C	3.256283034	3.242607023	2.238499104
H	3.987384149	2.826437455	2.948386642
H	3.669827216	4.198274796	1.870443524
H	3.198620929	2.559937111	1.3765864
B	0.762562857	3.28128154	0.543037014
O	-0.310768407	-3.03775271	-1.647741152
C	0.202539443	-0.838175614	-0.565602144
C	0.253023512	0.029315383	-1.653613992
C	0.111095034	-0.487315972	-3.08002328
H	-0.953829179	-0.731479774	-3.252728368
H	0.64143957	-1.443385946	-3.180002688
C	0.573288576	0.506260303	-4.149873978
H	1.676980337	0.578768091	-4.147687328
H	0.283136648	0.133895949	-5.146347016
C	-0.577094538	-4.449003544	-1.775267512
H	-0.597047605	-4.900657842	-0.769072673
C	0.54291266	-5.084158717	-2.594363229
H	0.356211806	-6.161889876	-2.728753644
H	0.606876645	-4.616115012	-3.590303994
H	1.516077855	-4.96686308	-2.094047901
C	-1.940813694	-4.607681413	-2.441151515
H	-2.193573342	-5.674391571	-2.552953275
H	-2.72922313	-4.126391479	-1.842925507
H	-1.937904599	-4.14404551	-3.441074156
C	0.10006184	-3.141697508	0.913942291
C	1.362876729	-3.57265429	1.399112633
C	1.451286287	-4.22465302	2.633310897
H	2.433092875	-4.549636457	2.99205843
C	0.319518105	-4.464504247	3.425951585
C	-0.918930322	-4.032408239	2.945089103
H	-1.815600634	-4.202448539	3.549129593
C	-1.045413001	-3.382780299	1.706929265
C	2.623765962	-3.318158834	0.600263324
H	3.504571642	-3.760214914	1.089130106
H	2.80932648	-2.237743606	0.480558342
H	2.558157898	-3.740697655	-0.416007179
C	0.448766138	-5.158333649	4.761059105
H	0.932396537	-6.144169592	4.656043561
H	-0.532780708	-5.312793546	5.233476051
H	1.068791962	-4.570323583	5.459264705

C	-2.42332159	-2.970936927	1.231585348
H	-3.116427214	-2.841515231	2.07686689
H	-2.862094015	-3.73620987	0.567039884
H	-2.400488881	-2.025413325	0.667918405
B	-0.01289173	-2.381028409	-0.482055096

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