Supporting Information

Arylallenes and the Halogeno-B(C_6F_5)$_2$ Reagents: Facile Formation of 2-Borylindenes

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Supporting Information: experimental and analytical details

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General Information. All reactions involving air- or moisture-sensitive compounds were carried out under an inert gas atmosphere (Argon) by using Schlenk-type glassware or in a glovebox. All solvents were dried and degassed before use, if necessary for the respective reaction. Chemicals: Unless otherwise noted all chemicals were used as purchased. The following instruments were used for physical characterization of the compounds: elemental analyses: Foss-Heraeus CHNO-Rapid; NMR: Varian UNITY plus NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 151 MHz; ^{11}B, 192 MHz; ^{19}F, 564 MHz; ^{31}P, 243 MHz). NMR chemical shifts are given relative to $SiMe_4$ and referenced to the respective solvent signals (^{1}H and ^{13}C) or external standard [$\delta(BF_3{\cdot}OEt_2) = 0$ for ^{11}B NMR, $\delta(CFCl_3{\cdot}OEt_2) = 0$ for ^{19}F NMR]. NMR assignments were supported by additional 2D NMR experiments.

X-Ray diffraction: Data sets for compounds **6b** and **6c** were collected with a D8 Venture Dual Source 100 CMOS diffractometer. For compounds **6a** and **6d** data sets were collected with a Bruker APEX II CCD diffractometer. Programs used: data collection: APEX3 V2016.1-0 (Bruker AXS Inc., **2016**); cell refinement: SAINT V8.37A (Bruker AXS Inc., **2015**); data reduction: SAINT V8.37A (Bruker AXS Inc., **2015**); absorption correction, SADABS V2014/7 (Bruker AXS Inc., **2014**); structure solution *SHELXT-2015* (Sheldrick, G. M. *Acta Cryst.,* **2015**, *A71*, 3-8); structure refinement *SHELXL-2015* (Sheldrick, G. M. *Acta Cryst.,* **2015**, *C71* (1), 3-8) and graphics, *XP* (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, **1998**). For compounds **6g(pyr)$_3$** and **6g'** data sets were collected with a Nonius Kappa CCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, **2008**, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr*. **2003**, *A59*, 228-234); structure solution SHELXT-2015; structure refinement SHELXL-2015. *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: For compounds **6b** and **6c** the borylindene unit, for compound **6g(pyr)$_3$** four C_6F_5 groups and for compound **6g'** one C_6F_5 group were found disordered

over two positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. Additionally, for compound **6g**(**pyr**)$_3$ two badly disordered dichloromethane molecules were found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (Spek, A.L. (2015). Acta Cryst. C71, 9-18.) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecules. Compound **6g'** was refined as a 2-component inversion twin. CCDC deposition numbers are 1907601 to 1907606.

Materials. $ClB(C_6F_5)_2$ and $BrB(C_6F_5)_2$ were prepared according to procedures described in the literature [A. Ueno, J. Li, C. G. Daniliuc, G. Kehr, G. Erker, *Chem. Eur. J.* **2018**, *24*, 10044–10048]. Arylallenes were prepared according to procedures described in the literatures [J. Kuang, S. Ma, *J. Org. Chem.* **2009**, *74*, 1763-1765]. Phenylacetylene, 4-ethynyltoluene, p-fluorophenylacetylene, 4-ethynylbiphenyl were purchased from Sigma-Aldrich and used as received.

A) Preparation of arylallenes

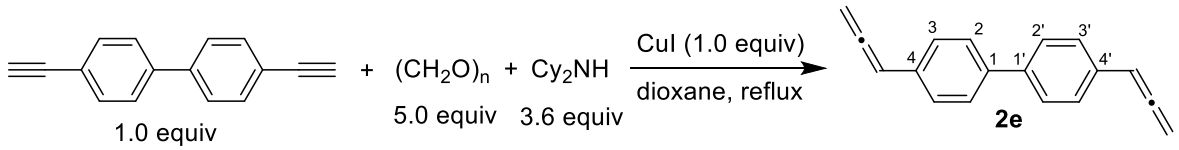
General procedure: According to a modified procedure from the literature [J. Kuang, S. Ma, *J. Org. Chem.* **2009**, *74*, 1763-1765.]: $(CH_2O)_n$ (2.5 equiv), CuI (0.5 equiv), dioxane, terminal mono arylacetylene (1.0 equiv) and dicyclohexylamine (Cy_2NH, 1.8 equiv) were mixed under an Argon atmosphere sequentially into an oven-dried Schlenk tube equipped with a reflux condenser. The resulting mixture was stirred under reflux. After the reaction was complete as monitored by TLC (silica gel, pentane), the reaction mixture was cooled down to room temperature. Column chromatography on silica gel (eluent: pentane) gave the corresponding terminal arylallenes.

Synthesis and characterization of the monoallenes **2a**-**d** were described in our previous publication: X. Tao, C. G. Daniliuc, G. Kehr, G. Erker, *Angew. Chem. Int. Ed.* **2018**, *130*, 14118-14122.

Bis- and tris-allene compounds **2e**-**g** were synthesized by the general procedure with modified molar ratios of starting materials. The NMR spectra of isolated compounds **2e** and **2f** are consistent with those reported in the literature [J.-L. Xia, X. Wu, Y. Liu, G. Chen, S. Jin, G. Yu, S. H. Liu, *Organometallics*, **2009**, *28*, 2701-2706].

Compound **2e**:

Scheme S1.



Following the general procedure: 4,4'-diethynylbiphenyl (0.60 g, 3.0 mmol), paraformaldehyde (0.45g, 15.0 mmol), dicyclohexylamine (2.0 g, 10.8 mmol), CuI (0.57 g, 3.0 mmol) were used as starting materials. After column chromatography (silica gel, eluent: pentane) compound **2e** (310 mg, 1.35 mmol, 45 %) was isolated as pale yellow crystalline material.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ ^{1}H: 7.57 (m, 2H, 2,2'-biphenyl), 7.37 (m, 2H, 3,3'-biphenyl) 6.23 (t, $^4J_{HH}$ = 6.8 Hz, 1H, =CH), 5.20 (d, $^4J_{HH}$ = 6.8 Hz, 2H, =CH_2).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ ^{13}C: 210.3 (=C=), 139.5 (1,1'-biphenyl), 133.4 (4,4'-biphenyl), 127.4 (3,3'-biphenyl), 127.3 (2,2'-biphenyl), 93.7 (=CH), 79.0 (=CH_2).

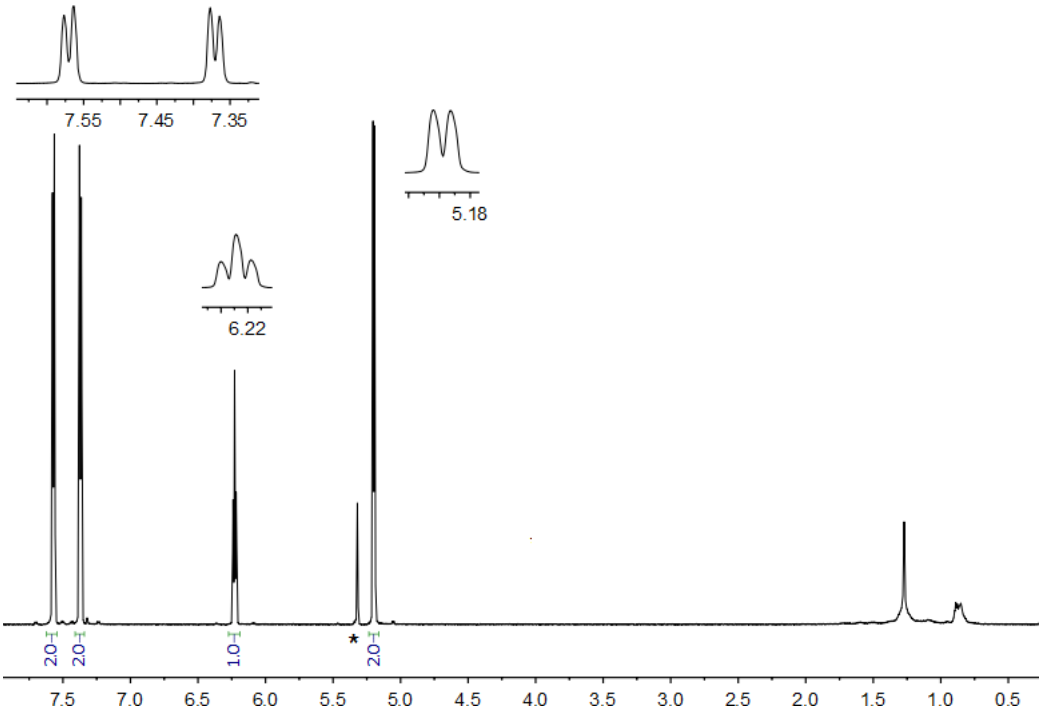


Figure S1. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectrum of compound **2e**.

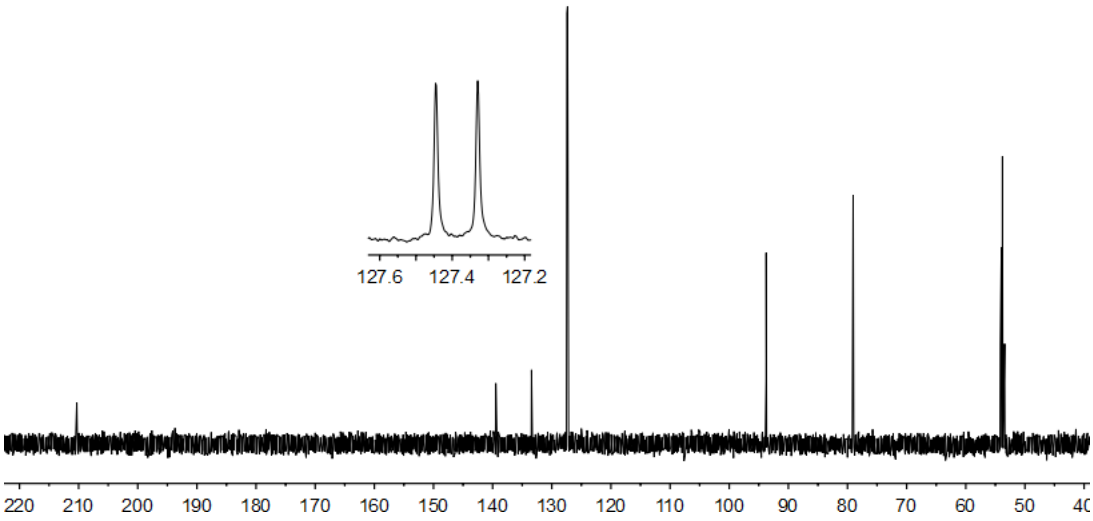
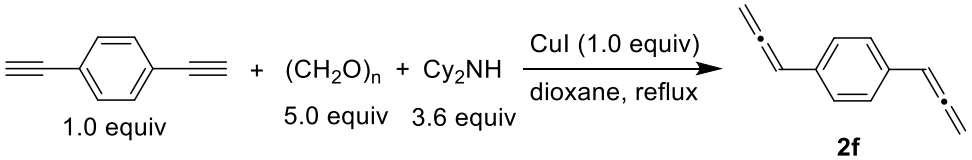


Figure S2. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **2e**.

Compound **2f**:

Scheme S2.



Following the general procedure: 1,4-diethynylbenzene (1.26 g, 10 mmol), paraformaldehyde (1.50 g, 50 mmol), dicyclohexylamine (6.53 g, 36 mmol), CuI (1.90 g, 10 mmol) were used as starting

materials. After column chromatography (silica gel, eluent: pentane) compound **2f** (566 mg, 4.0 mmol, 40 %) was isolated as pale yellow crystalline material.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ ^{1}H: 7.25 (s, 2H, C_6H_4), 6.18 (t, $^{4}J_{HH}$ = 6.7 Hz, 1H, =CH), 5.17 (d, $^{4}J_{HH}$ = 6.7 Hz, 2H, =CH_2).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ ^{13}C: 210.2 (=C=), 139.5 (i-C_6H_4), 127.3 (C_6H_4), 93.9 (=CH), 79.0 (=CH_2).

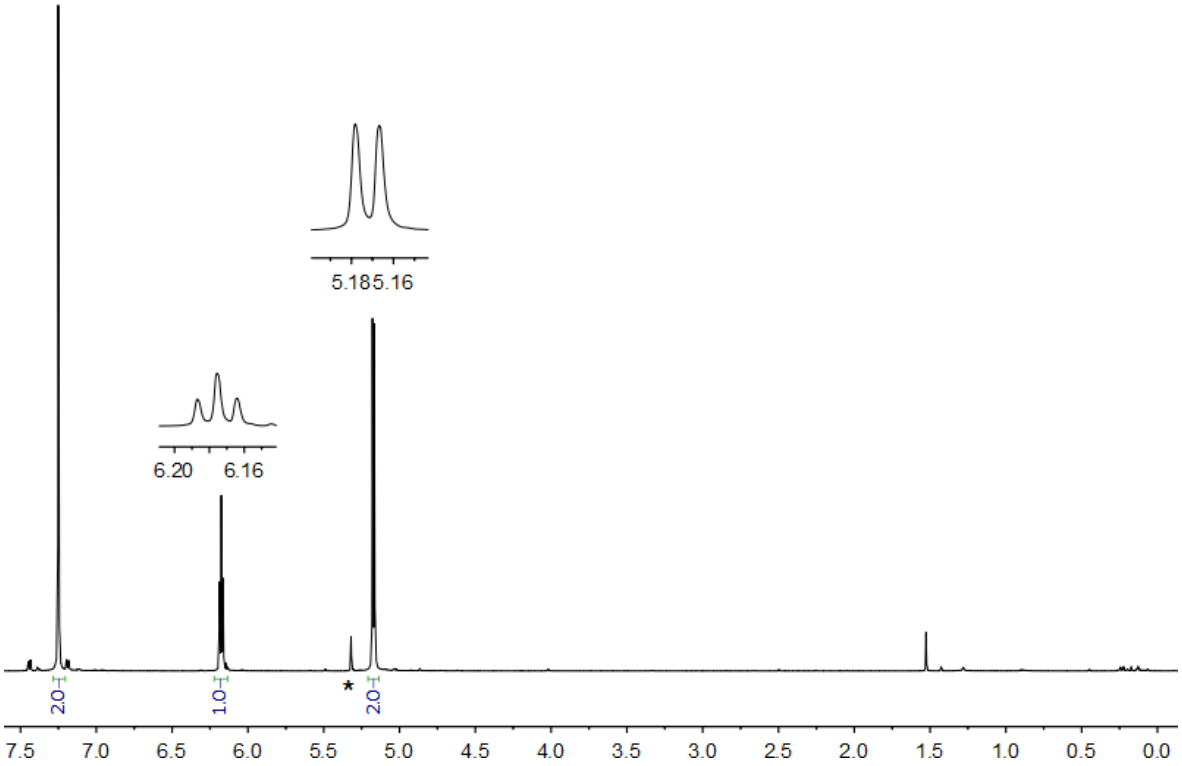


Figure S3. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectrum of compound **2f**.

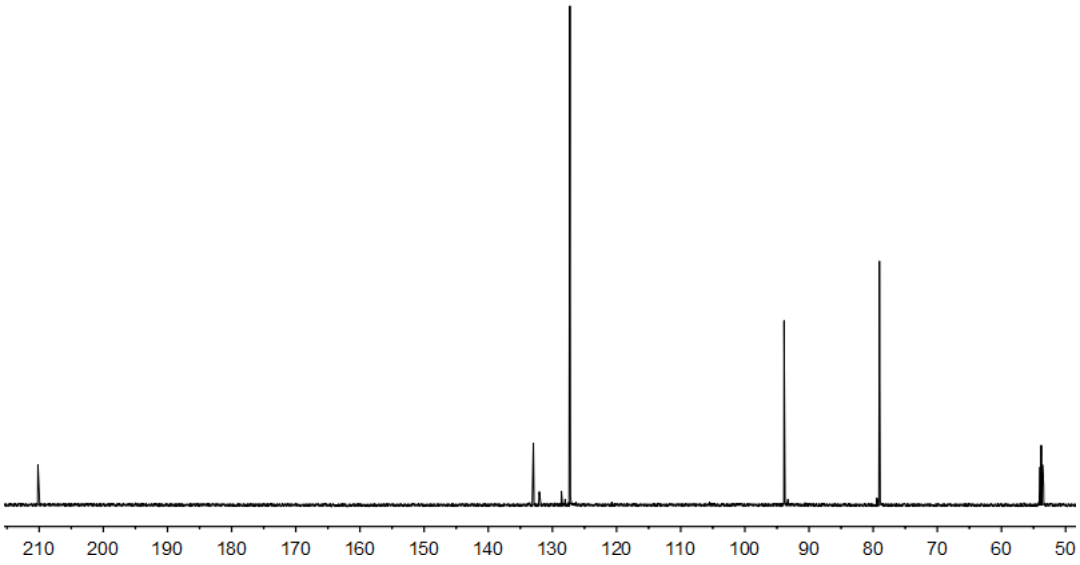
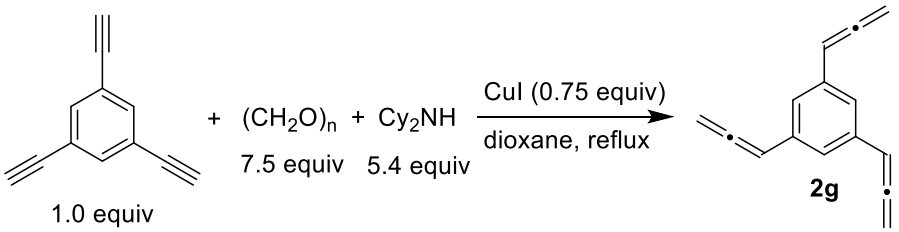


Figure S4. ^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **2f**.

Compound **2g**:

Scheme S3.



Following the general procedure: 1,3,5-trialkynylbenzene (0.52 g, 3.5 mmol), paraformaldehyde (0.75 g, 25 mmol), dicyclohexylamine (3.3 g, 18 mmol), CuI (0.95 g, 5.0 mmol) were used as starting materials. After column chromatography [silica gel, eluent: pentane/CH_2Cl_2 = 9/1 (V/V)] compound **2g** (250 mg, 1.37 mmol, 39 %) was isolated as pale yellow crystalline material.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ ^{1}H: 7.08 (s, 1H, C_6H_3), 6.14 (t, $^4J_{HH}$ = 6.8 Hz, 1H, =CH), 5.17 (d, $^4J_{HH}$ = 6.8 Hz, 2H, =CH_2).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ ^{13}C: 210.1 (=C=), 135.0 (*i*-C_6H_3), 123.9 (C_6H_3), 93.7 (=CH), 79.1 (=CH_2).

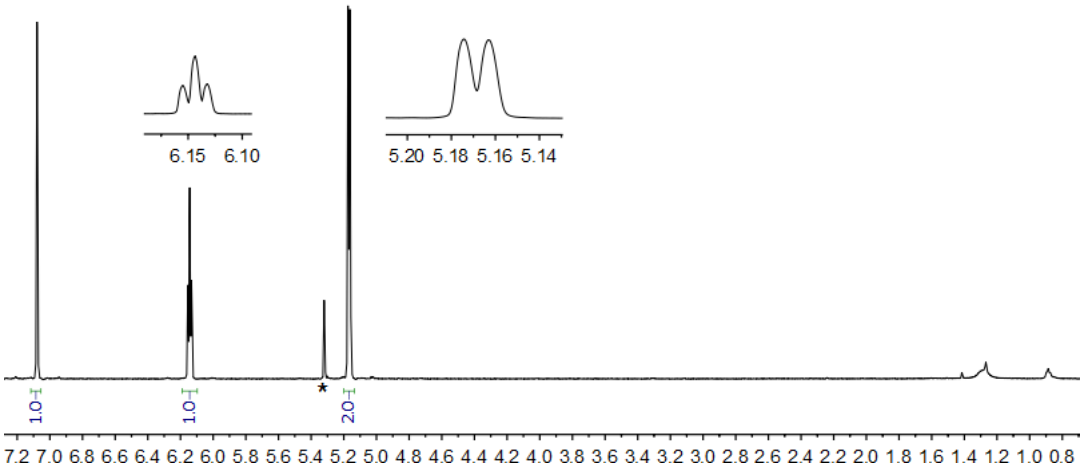


Figure S5. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectrum of compound **2g**.

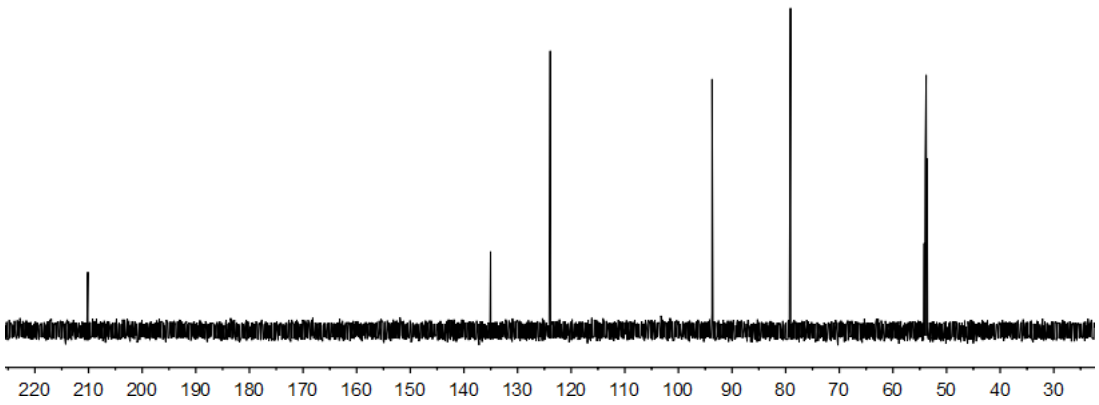
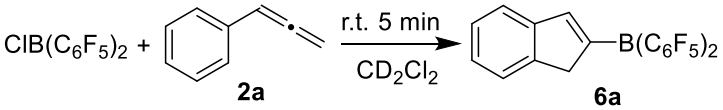


Figure S6. ^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **2g**.

B) Synthesis of compound **6a**

Experiment 1: (reaction of compound **2a** with $ClB(C_6F_5)_2$, NMR scale)

Scheme S4.



A solution of $ClB(C_6F_5)_2$ (38 mg, 0.10 mmol) in CD_2Cl_2 (0.3 mL) was added to a solution of phenylallene (14 mg, 0.12 mmol) in CD_2Cl_2 (0.3 mL) at room temperature. Subsequently, the resulting reaction mixture was characterized by NMR experiments.

A mixture of compounds **2a** (6 mol%, ^1H), **6a** (86 mol%, ^1H) and $ClB(C_6F_5)_2$ (8 mol%, ^{19}F) was obtained.

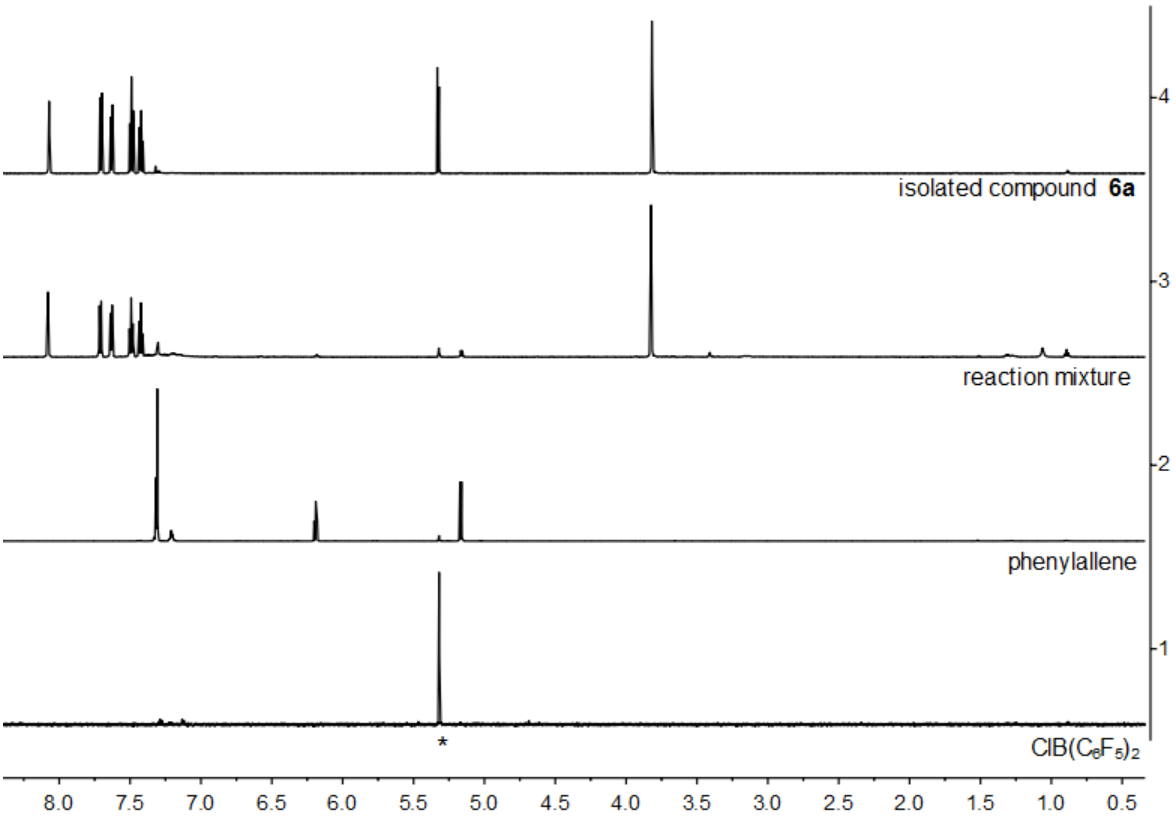


Figure S7. ^1H NMR (600 MHz, 299 K, CD_2Cl_2*) spectra of (1) $ClB(C_6F_5)_2$, (2) phenylallene, (3) reaction mixture, and (4) isolated compound **6a**.

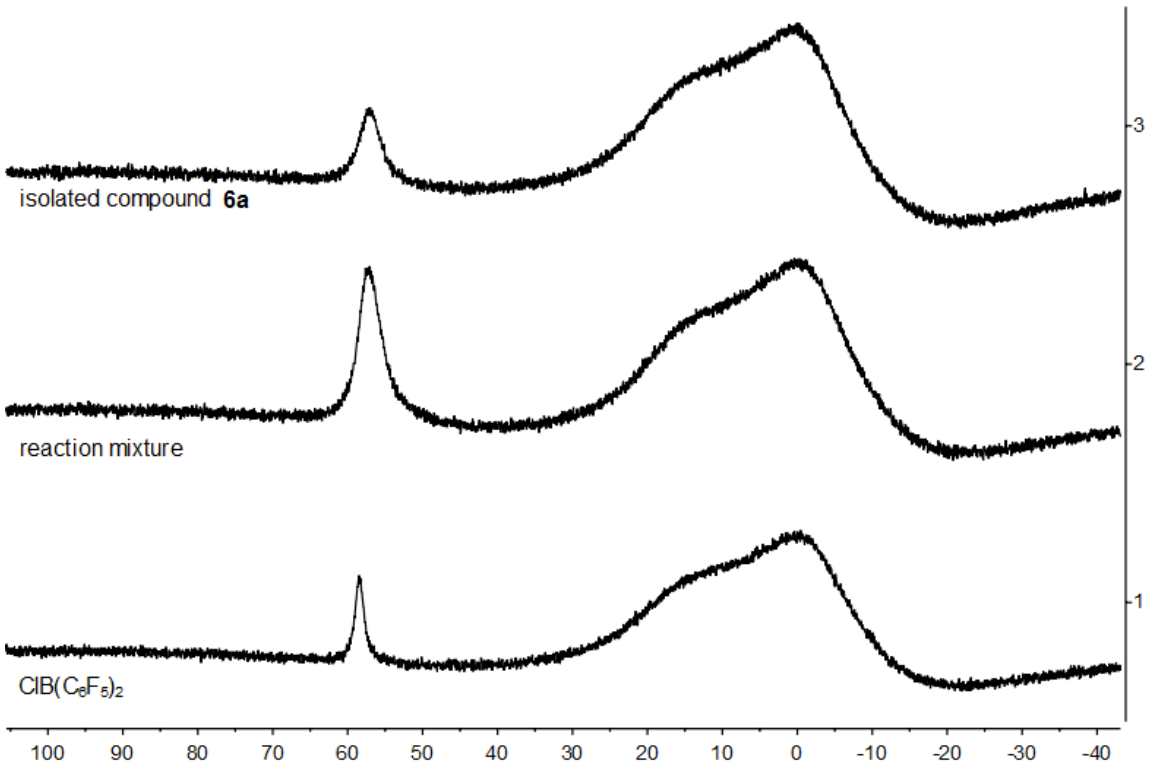


Figure S8. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectra of (1) $ClB(C_6F_5)_2$, (2) reaction mixture, and (3) isolated compound **6a**.

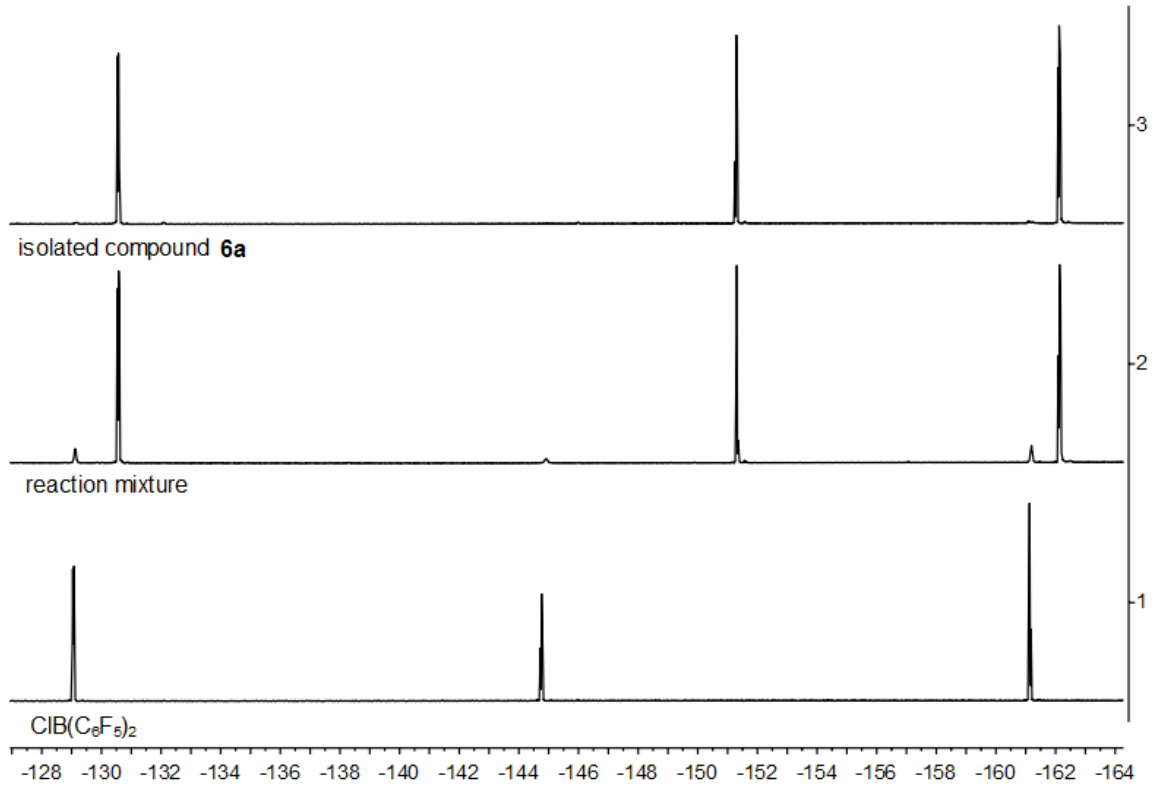
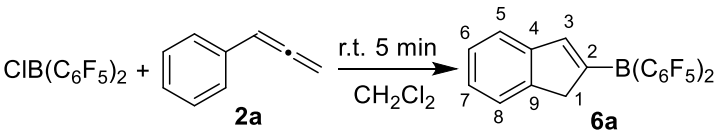


Figure S9. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectra of (1) $ClB(C_6F_5)_2$, (2) reaction mixture, and (3) isolated compound **6a**.

Experiment 2: (reaction of compound **2a** with $ClB(C_6F_5)_2$, preparative scale)

Scheme S5.



A solution of $ClB(C_6F_5)_2$ (152 mg, 0.40 mmol) in CH_2Cl_2 (2 mL) was added to a solution of phenylallene (56 mg, 0.48 mmol) in CH_2Cl_2 (2 mL) at room temperature. After stirring at room temperature for 5 min, all the volatiles were removed in vacuo, the residue was washed carefully with pentane (0.5 ml × 3) and dried in vacuo giving compound **6a** (152 mg, 0.33 mmol, 83%) as white crystalline material.

Anal. Calc. for $C_{21}H_7BF_{10}$: C, 54.82; H, 1.53. Found: C, 54.67; H, 1.49.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ ^{1}H: 8.07 (t, $^4J_{HH}$ = 1.90 Hz, 1H, 3-CH=), 7.71 (dm, $^3J_{HH}$ = 7.6 Hz, 1H, 5-CH=), 7.63 (dm, $^3J_{HH}$ = 7.6 Hz, 1H, 8-CH=), 7.49 (td, $^3J_{HH}$ = 7.6 Hz, J_{HH} = 1.2 Hz, 1H, 7-CH=), 7.42 (tm, $^3J_{HH}$ = 7.6 Hz, 1H, 6-CH=), 3.82 (d, $^4J_{HH}$ = 1.90 Hz, 2H, CH_2).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ ^{13}C: 162.3 (3-CH=), 151.1 (9-C), 151.1 (br, CB)^t, 146.6 (dm, dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 144.0 (4-C), 142.8 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 137.9 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 130.7 (7-CH=), 127.7 (6-CH=), 125.7 (5-CH=), 125.0 (8-CH=), 114.8 (br, i-C_6F_5), 42.2 (CH_2), [^{t} tentative assignment].

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ ^{19}F: −130.6 (m, 2F, *o*), −151.3 (t, $^3J_{FF}$ = 20.0 Hz, 1F, *p*), −162.1 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 10.8].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ ^{11}B: 57.0 ($\nu_{1/2}$ ~ 800 Hz).

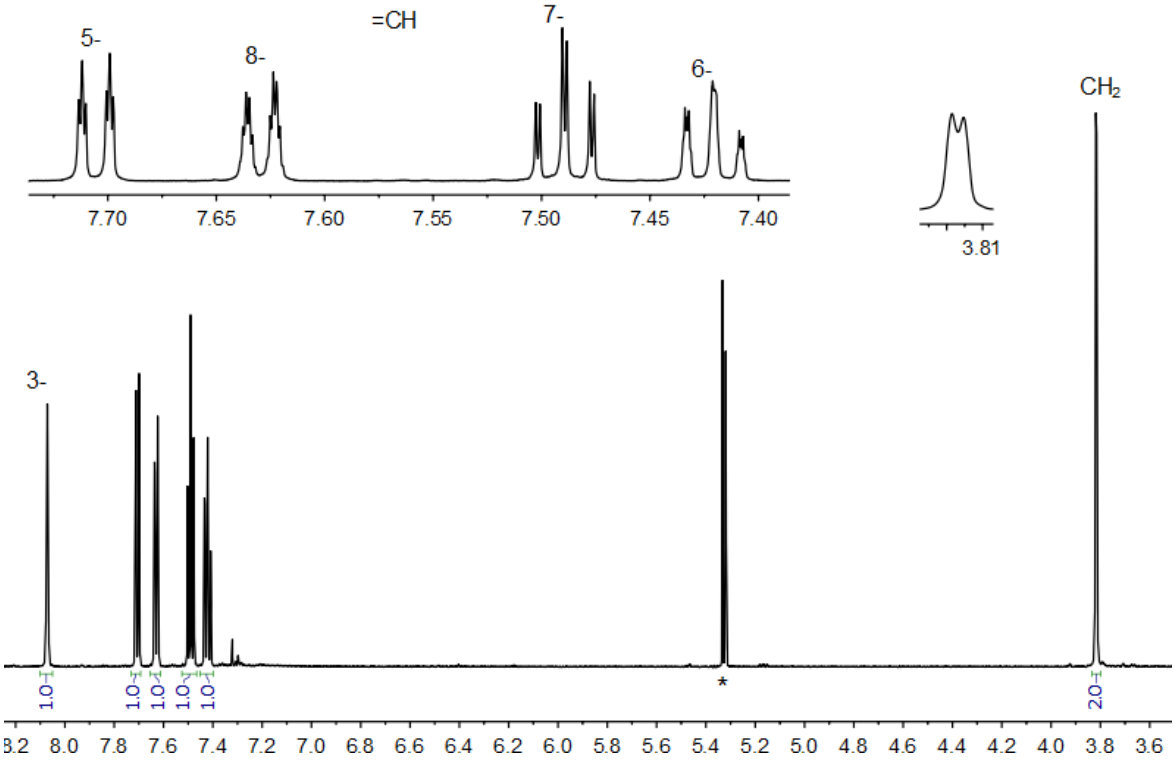


Figure S10. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectrum of compound **6a**.

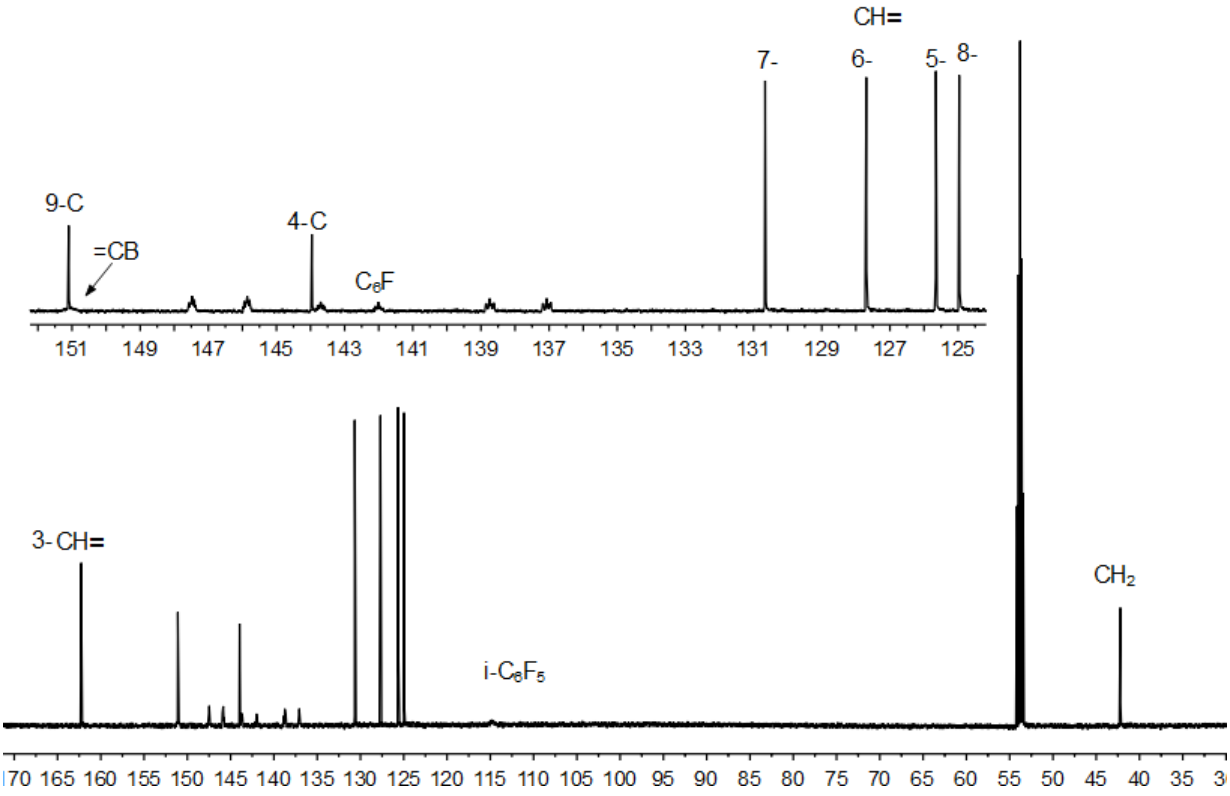


Figure S11. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **6a**.

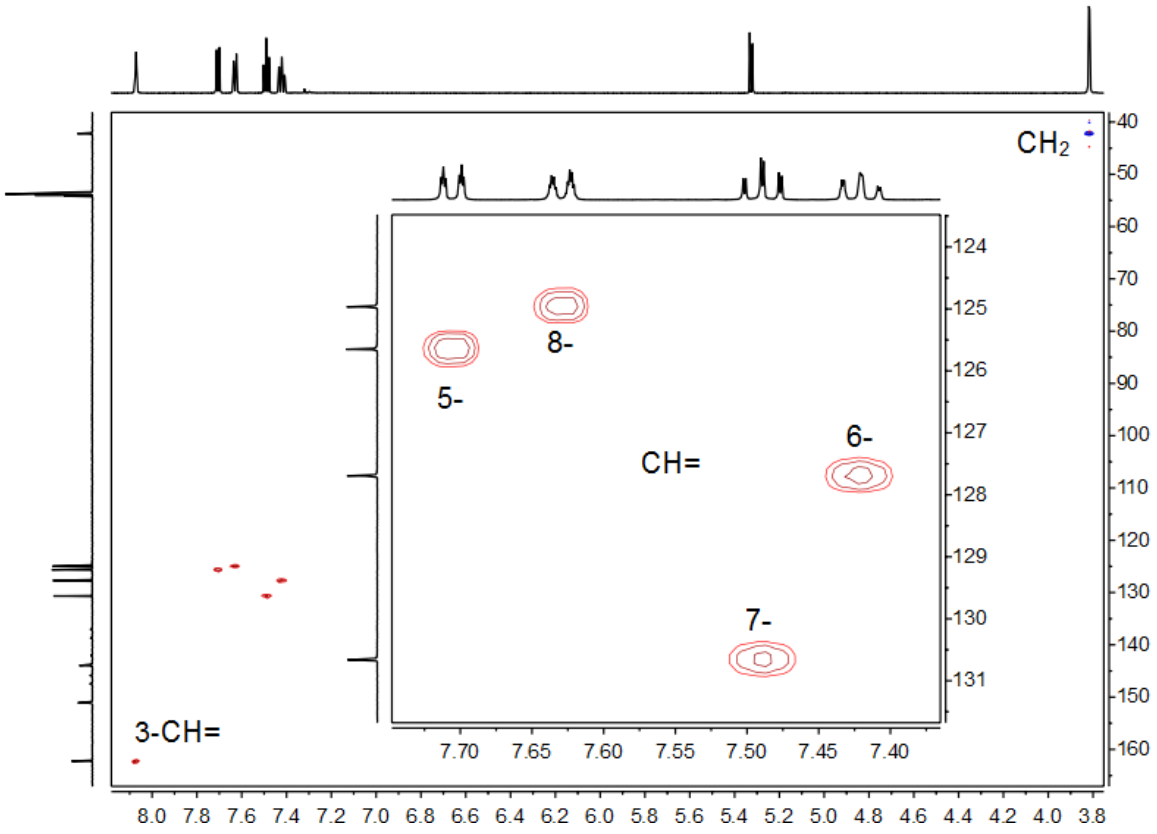


Figure S12. $^{1}H,^{13}C$ GHSQC (600/151 MHz, CD_2Cl_2, 299K) spectrum of compound **6a**.

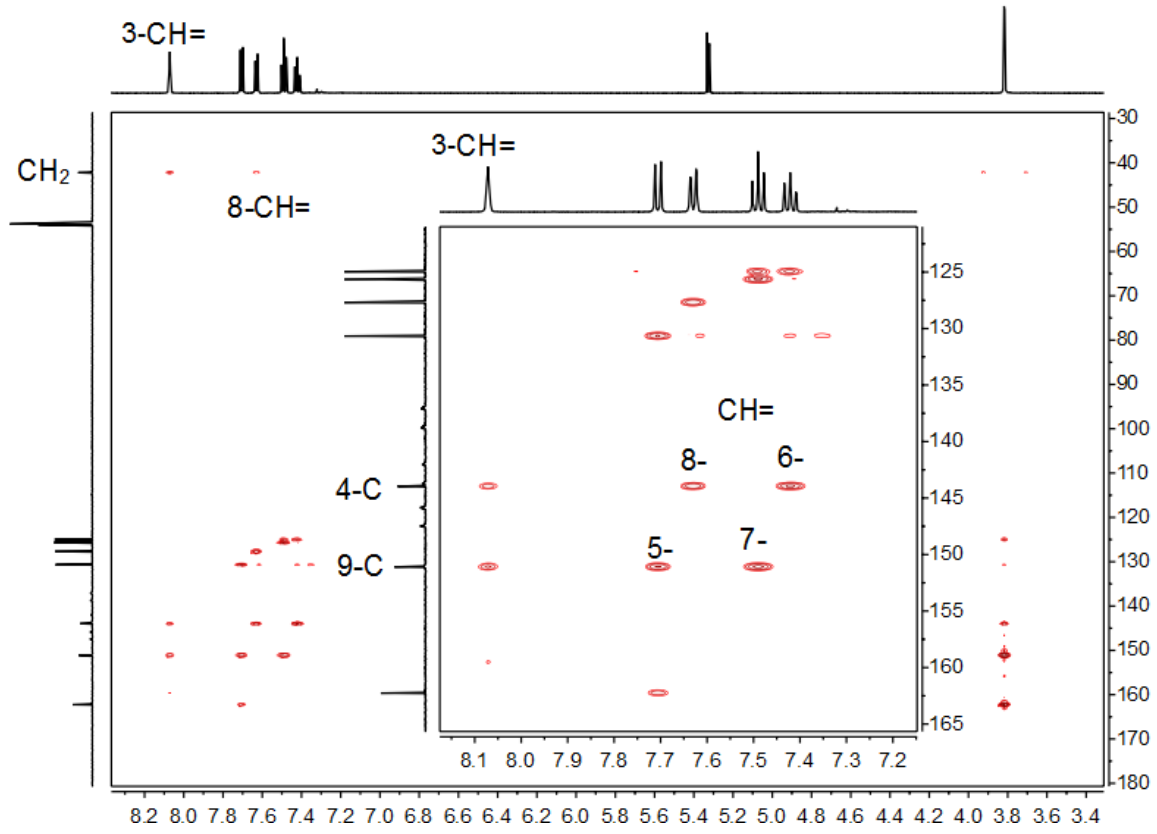


Figure S13. $^{1}H,^{13}C$ GHMBC (600/151 MHz, CD_2Cl_2, 299K) spectrum of compound **6a**.

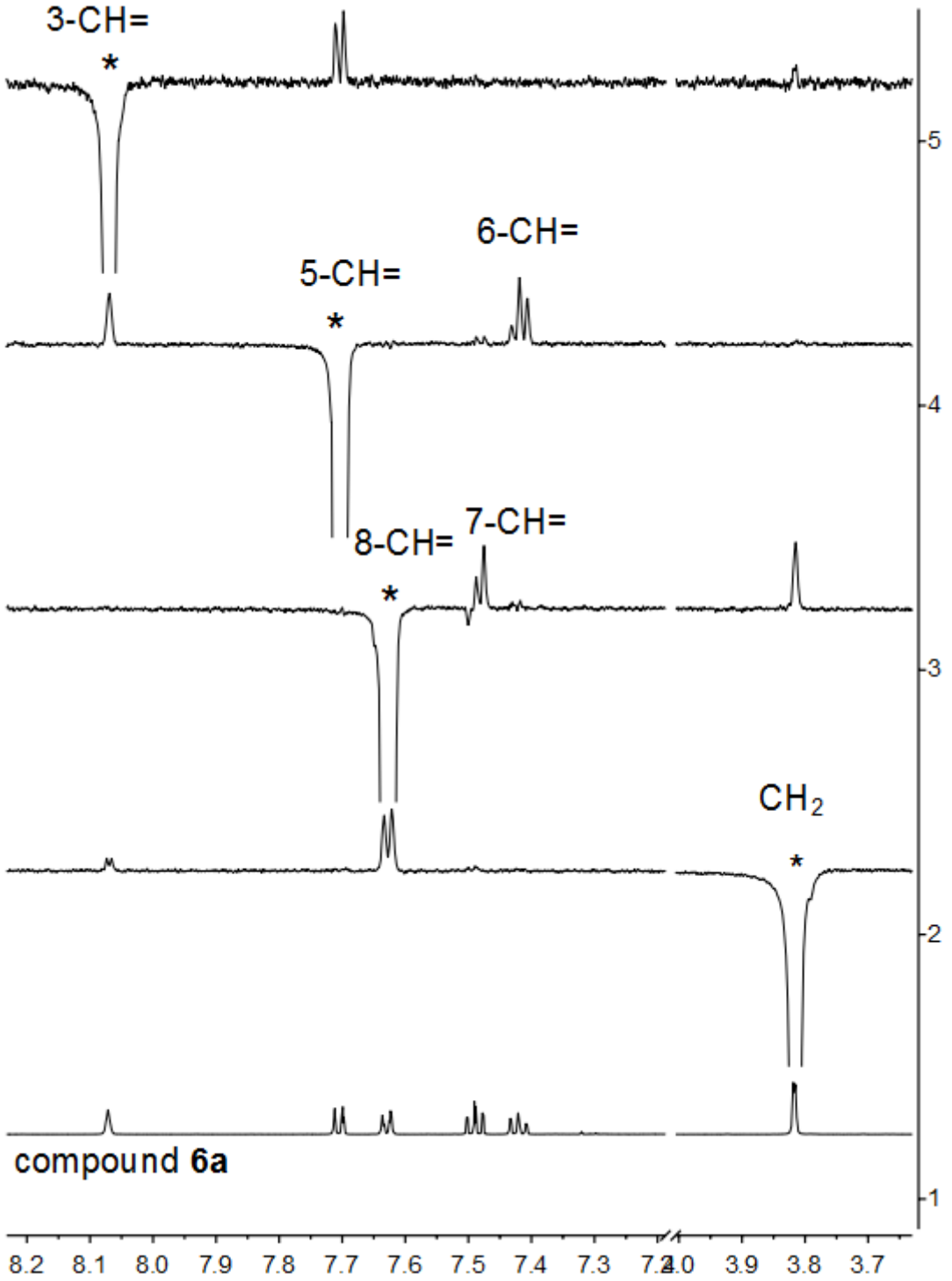


Figure S14. (1) ^{1}H NMR and (2 to 5) ^{1}H{^{1}H} NOESY (600 MHz, 299 K, CD_2Cl_2) spectra of compound **6a**. Irradiation points (*): (2) δ^{1}H 3.82 (CH_2); (3) δ^{1}H 7.63 (8-CH); (4) δ^{1}H 7.71 (5-CH); (5) δ^{1}H 8.07 (=CH).

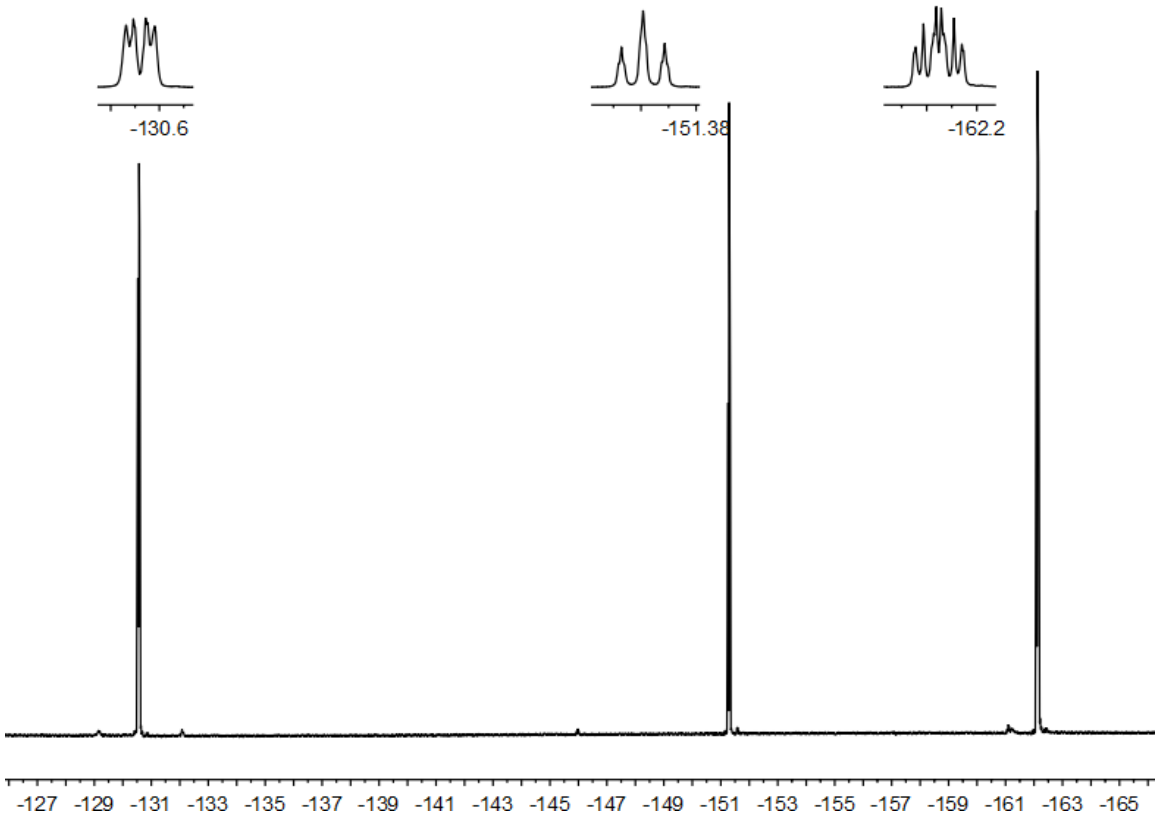


Figure S15. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **6a**.

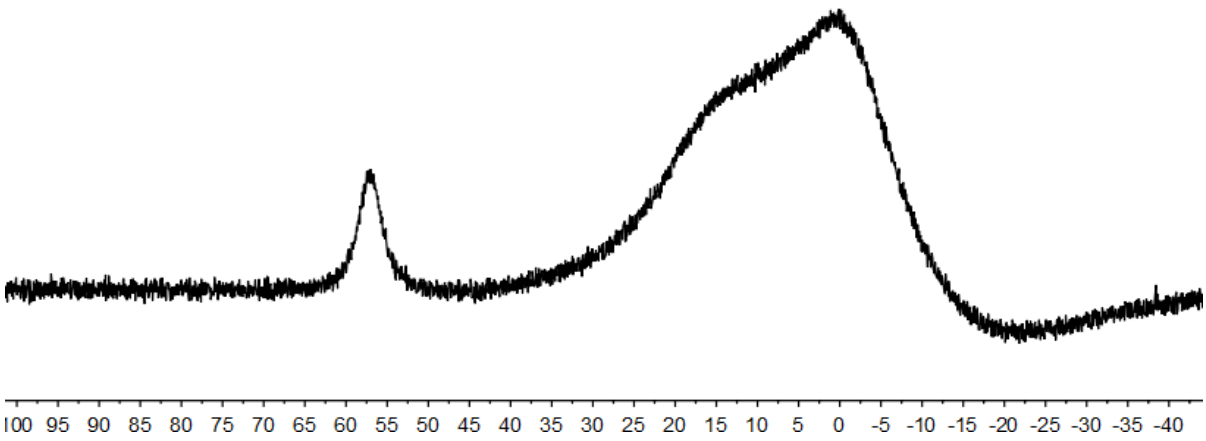


Figure S16. $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of compound **6a**.

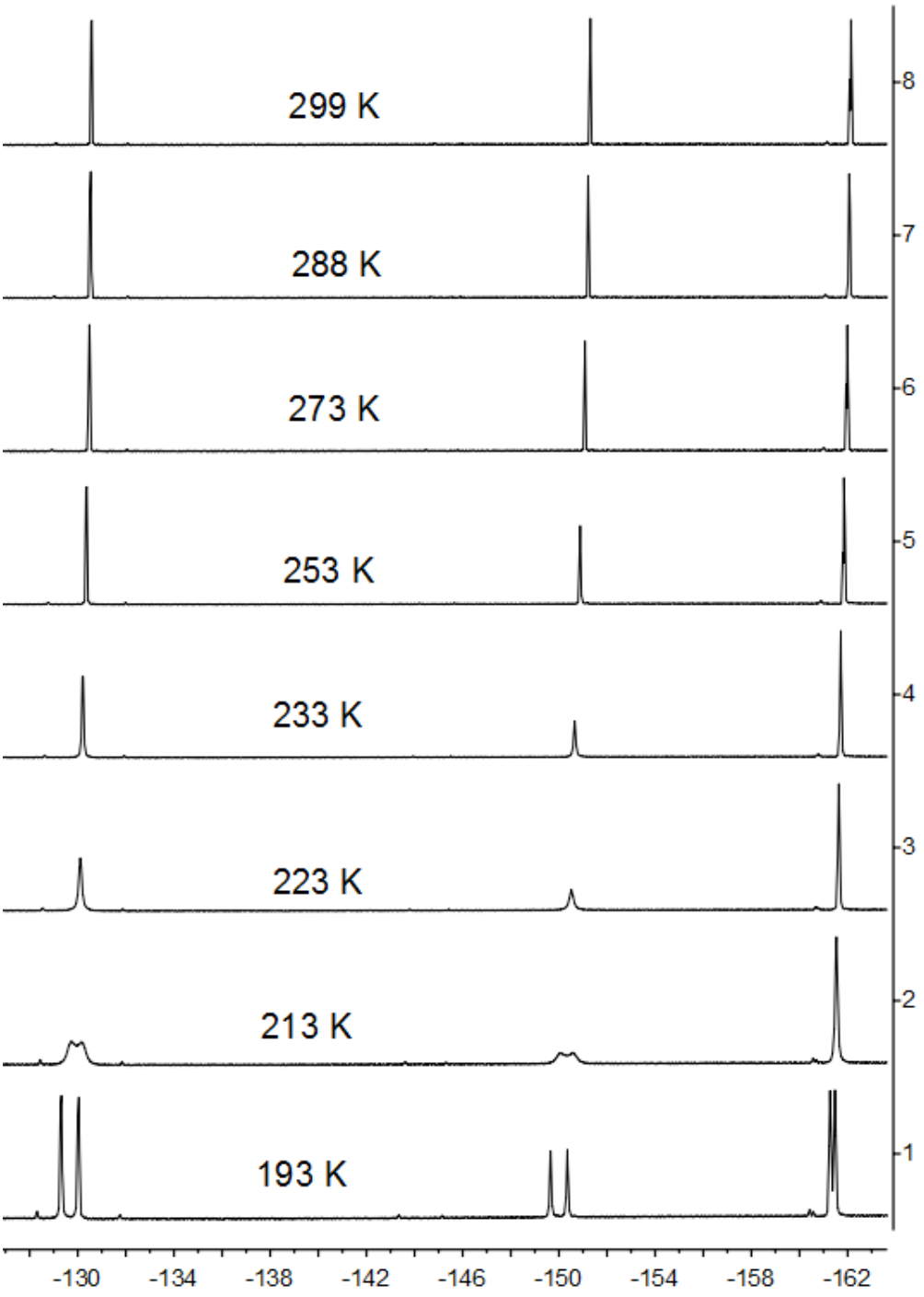


Figure S17. ^{19}F NMR (564 MHz, CD_2Cl_2) spectra of compound **6a** at variable temperature.

The activation energy was estimated by the coalescence of the para fluorine signals (δ -149.7, -150.4) of the two pentafluorophenyl rings:

$\Delta G^{\neq}[T_{coal}, \Delta\nu(T)] = RT_{coal}(22.96 + \ln(T_{coal}/\Delta\nu))$ [J/mol]

T_{coal} = coalescence temperature [K]: 218 K (^{19}F, BC_6F_5)

$\Delta\nu$ = chemical shift difference [Hz] (^{19}F, *p*-BC_6F_5, 193 K): 397 Hz

R = 8.314 J/(mol·K); 1 J = 0.239 cal

$\Delta G^{\neq}$ [218 K, $\Delta\nu$ (193 K) = 397 Hz] = 40527 J/mol = 9.7 kcal/mol.

Crystals suitable for the X-ray crystal structure analysis were obtained from diffusion of pentane vapor to a solution of compound **6a** in CH_2Cl_2 at -35 °C.

X-ray crystal structure analysis of compound 6a (erk9199): A colorless plate-like specimen of $C_{21}H_7BF_{10}$, approximate dimensions 0.070 mm x 0.100 mm x 0.220 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1542 frames were collected. The total exposure time was 17.21 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 15707 reflections to a maximum θ angle of 66.74° (0.84 Å resolution), of which 3068 were independent (average redundancy 5.120, completeness = 99.9%, R_{int} = 3.69%, R_{sig} = 2.62%) and 2948 (96.09%) were greater than $2\sigma(F^2)$. The final cell constants of a = 7.4242(2) Å, b = 10.8667(3) Å, c = 21.4824(5) Å, volume = 1733.13(8) $Å^3$, are based upon the refinement of the XYZ-centroids of 8958 reflections above 20 σ(I) with 8.231° < 2θ < 133.4°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.823. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7200 and 0.8960. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_12_12_1$, with Z = 4 for the formula unit, $C_{21}H_7BF_{10}$. The final anisotropic full-matrix least-squares refinement on F^2 with 289 variables converged at R1 = 2.35%, for the observed data and wR2 = 5.79% for all data. The goodness-of-fit was 1.048. The largest peak in the final difference electron density synthesis was 0.158 $e^-/Å^3$ and the largest hole was -0.145 $e^-/Å^3$ with an RMS deviation of 0.035 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.763 g/cm^3 and F(000), 912 e^-. CCDC number: 1907601.

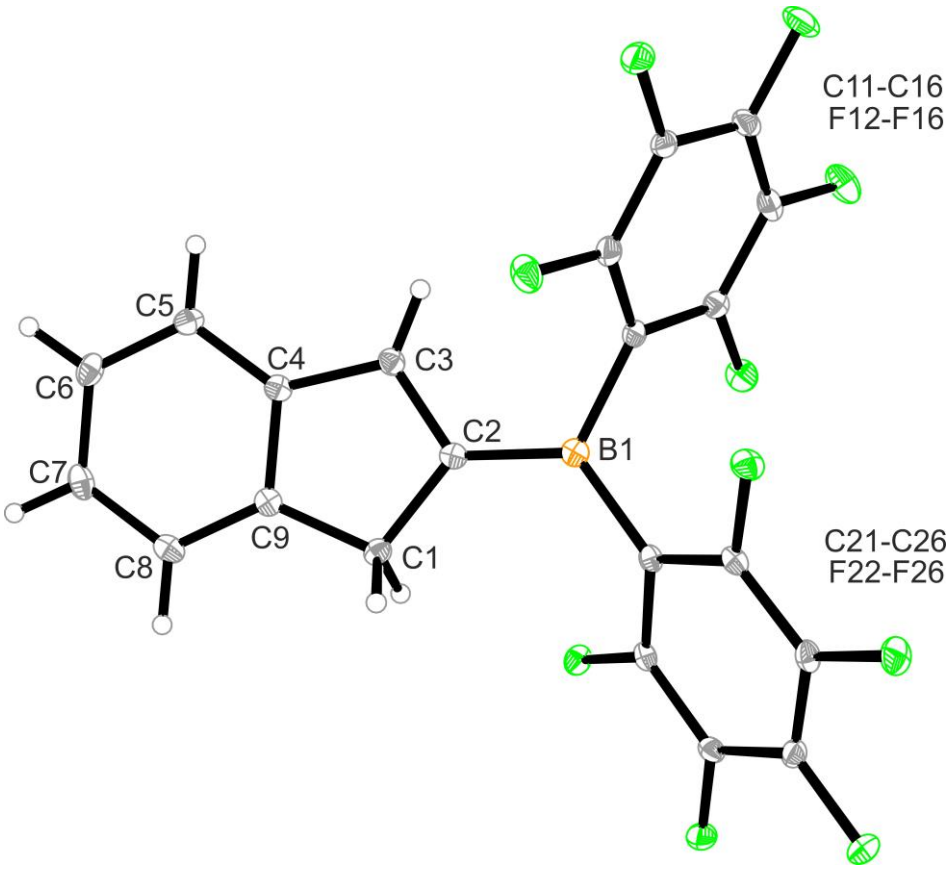
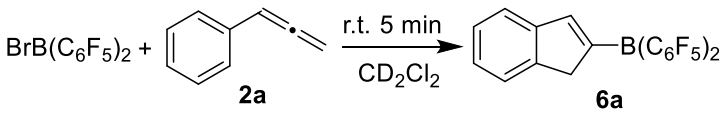


Figure S18. Crystal structure of compound **6a** (thermal ellipsoids: 30 % probability)

Experiment 3: (reaction of compound **2a** with $BrB(C_6F_5)_2$, NMR scale)

Scheme S6.



A solution of $BrB(C_6F_5)_2$ (42 mg, 0.10 mmol) in CD_2Cl_2 (0.3 mL) was added to a solution of phenylallene (11.6 mg, 0.10 mmol) in CD_2Cl_2 (0.3 mL) at room temperature. Subsequently, the resulting reaction mixture was characterized by NMR experiments.

Reaction mixture after 5 min: A mixture (pale yellow solution) of compound **6a** (70 mol%, ^{19}F), $BrB(C_6F_5)_2$ (12 mol%, ^{19}F) and an unknown compound (18 mol%, ^{1}H) was obtained.

Reaction mixture after 3 h: A mixture (dark red solution) of compound **6a** (81 mol%, ^{19}F) and $BrB(C_6F_5)_2$ (19 mol%, ^{19}F) was obtained.

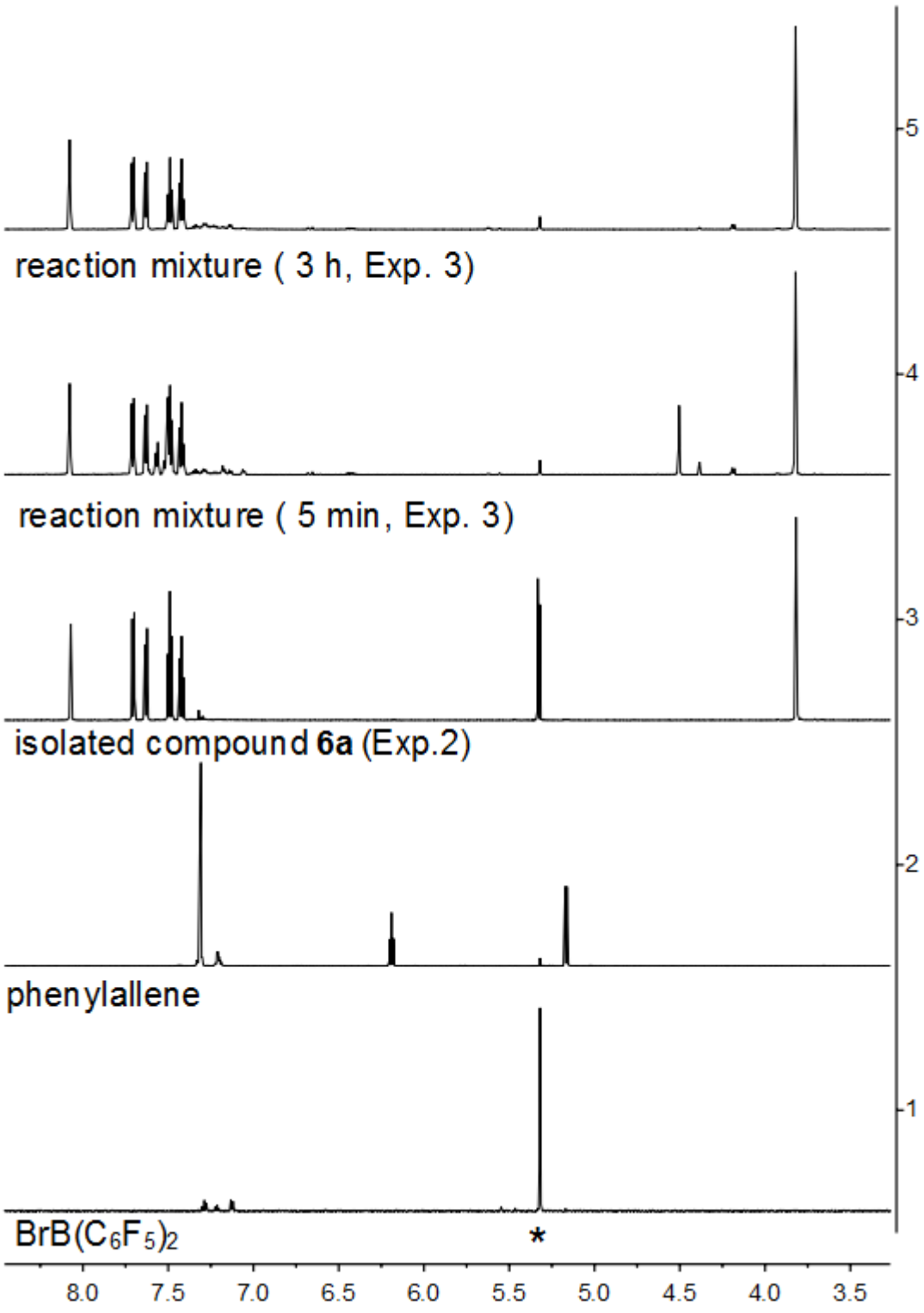


Figure S19. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectra of (1) $BrB(C_6F_5)_2$, (2) phenylallene, (3) isolated compound **6a**, and (4) reaction mixture from Experiment 3 after 5 min, and (5) reaction mixture from Experiment 3 after 3 h.

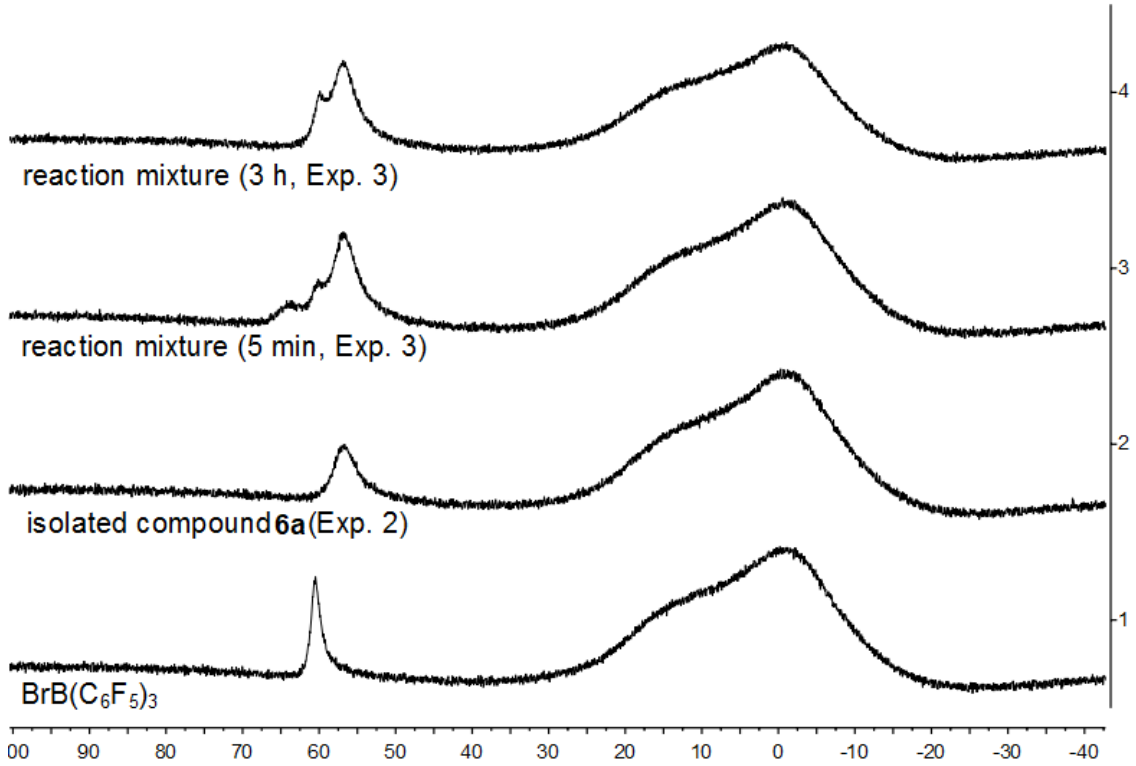


Figure S20. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectra of (1) $BrB(C_6F_5)_2$, (2) isolated compound **6a**, (3) reaction mixture from Experiment 3 after 5 min, and (4) reaction mixture from Experiment 3 after 3 h.

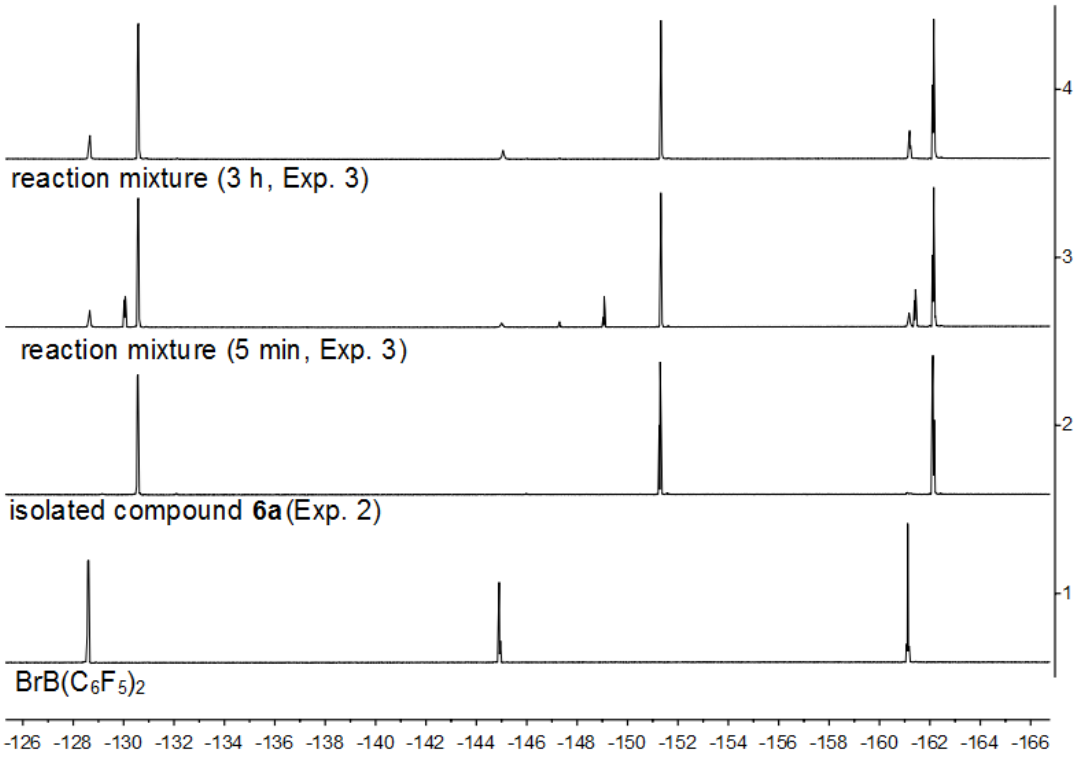
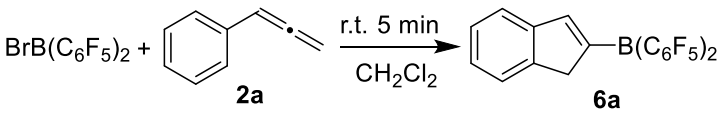


Figure S21. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectra of (1) $BrB(C_6F_5)_2$, (2) isolated compound **6a** from Experiment 2, (3) reaction mixture from Experiment 3 after 5 min, and (4) reaction mixture from Experiment 3 after 3 h.

Experiment 4: (reaction of compound **2a** with $BrB(C_6F_5)_2$, preparative scale)

Scheme S7.



A solution of $BrB(C_6F_5)_2$ (168 mg, 0.40 mmol) in CH_2Cl_2 (1 mL) was added to a solution of phenylallene (56 mg, 0.48 mmol) in CH_2Cl_2 (1 mL) at room temperature. After stirring at room temperature for 5 min, all the volatiles were removed in vacuo. The remaining residue was washed carefully with pentane (0.5 ml × 3) and dried in vacuo giving compound **6a** (125 mg, 0.27 mmol, 68%) as white crystalline material.

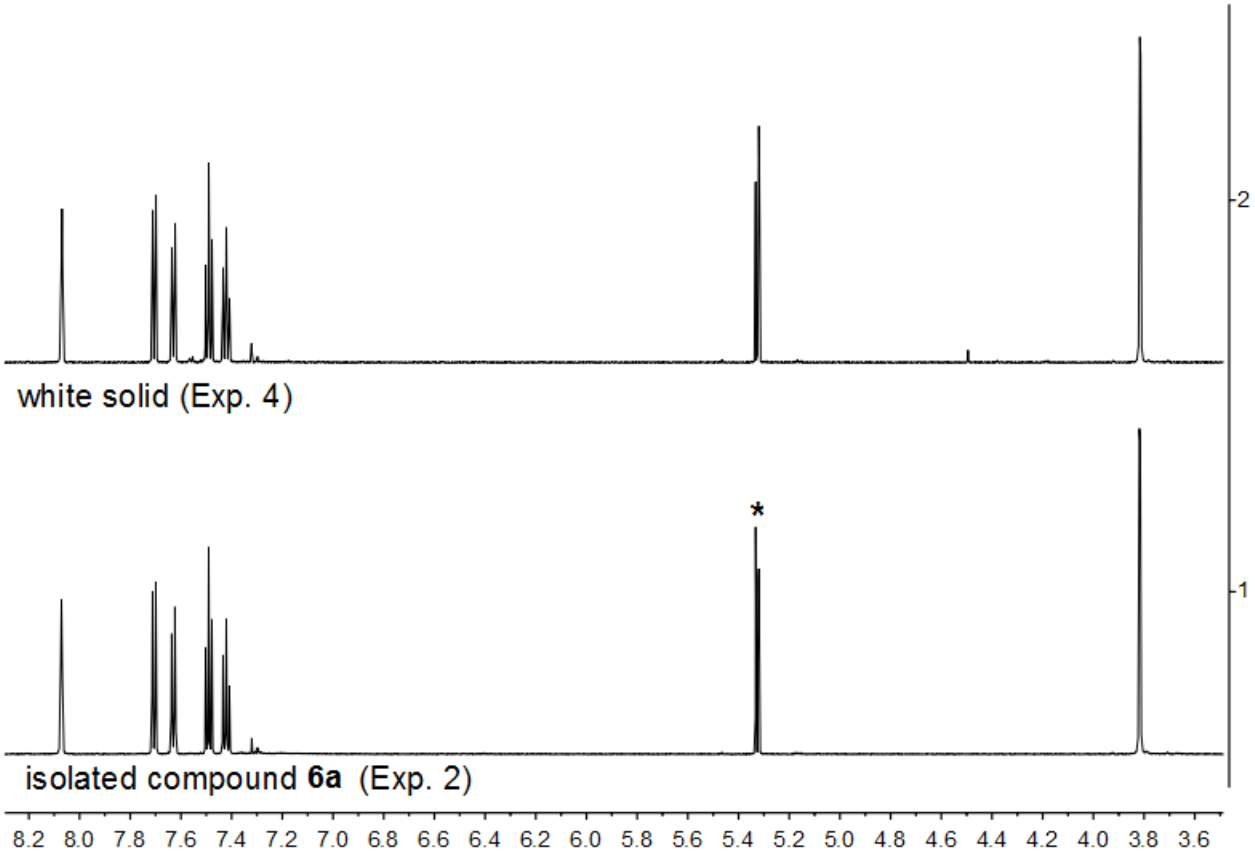


Figure S22. ^1H NMR (600 MHz, 299 K, CD_2Cl_2*) spectra of (1) isolated compound **6a** from Experiment 2 and (2) the white solid from Experiment 4.

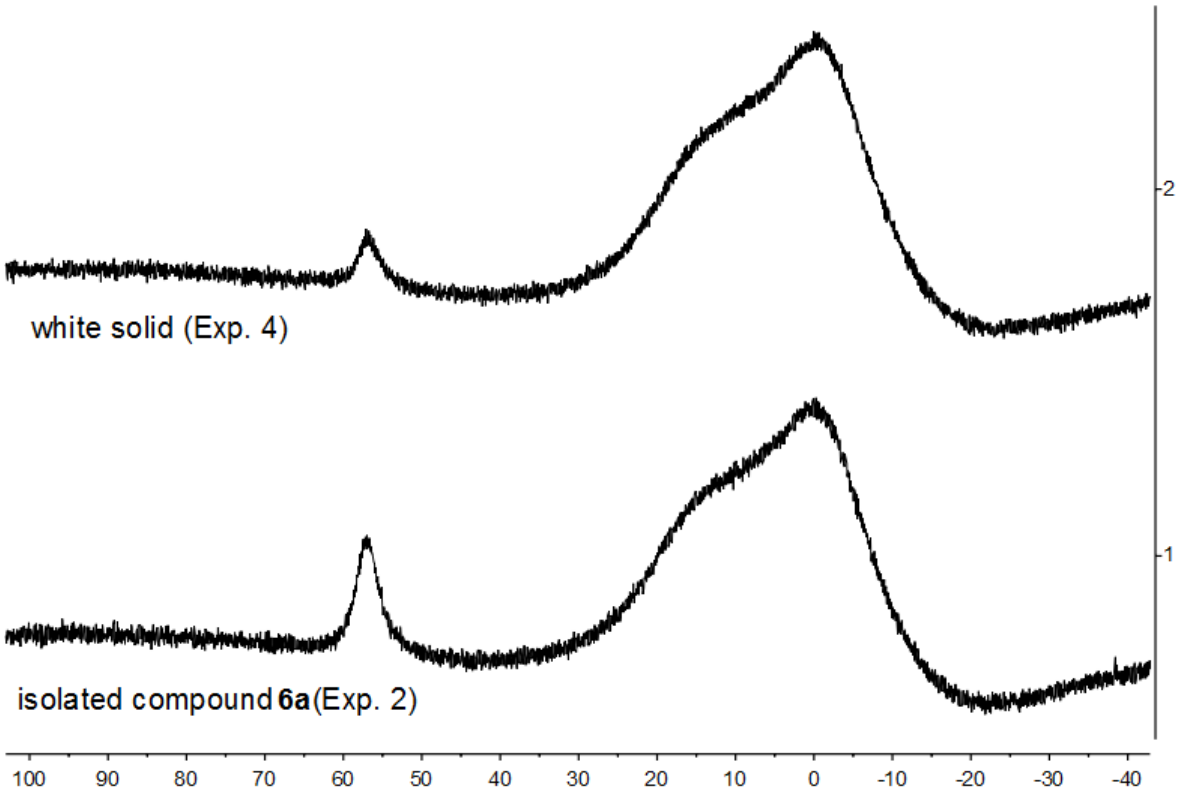


Figure S23. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectra of (1) isolated compound **6a** from Experiment 2 and (2) the white solid from Experiment 4.

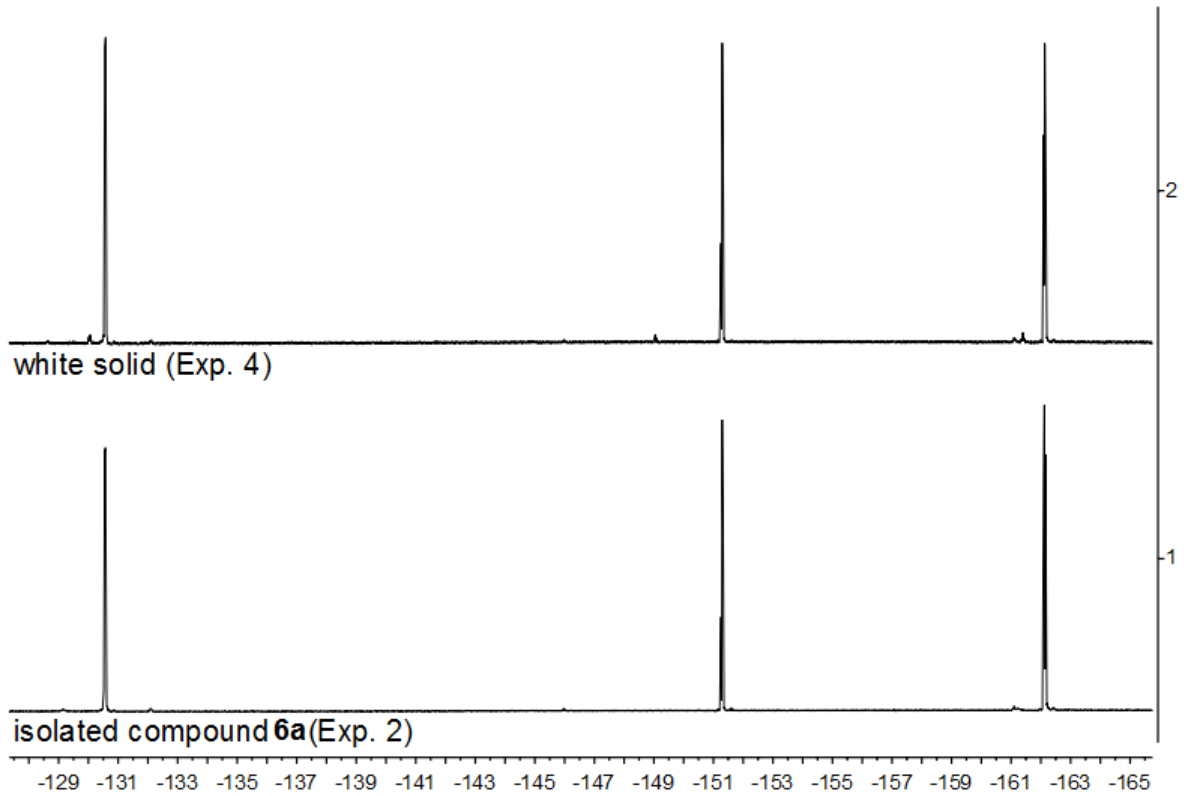
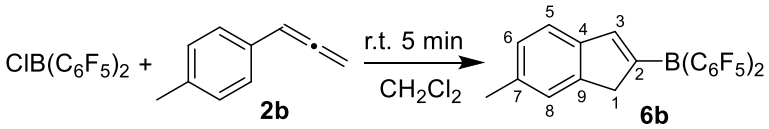


Figure S24. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectra of (1) isolated compound **6a** from Experiment 2 and (2) the white solid from Experiment 4.

C) Synthesis of compound **6b**

Experiment 1: (reaction of compound **2b** with $ClB(C_6F_5)_2$, preparative scale)

Scheme S8.



A solution of $ClB(C_6F_5)_2$ (152 mg, 0.40 mmol) in CH_2Cl_2 (2 mL) was added to a solution of p-tolylallene (62 mg, 0.48 mmol) in CH_2Cl_2 (2 mL) at room temperature. After stirring at room temperature for 5 min, all the volatiles were removed in vacuo, and the remaining residue was dissolved in pentane (1 ml). After storage of this solution at −35 °C for 24 h, a crystalline material precipitated. Part of the crystals were used for X-ray crystal structure analysis and the rest was dried in vacuo to finally give compound **6b** (158 mg, 0.33 mmol, 83%) as a pale yellow crystalline solid.

Anal. Calc. for $C_{22}H_9BF_{10}$: C, 55.73; H, 1.91. Found: C, 55.74; H, 2.04.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ ^{1}H: 8.05 (t, $^4J_{HH}$ = 1.9 Hz, 1H, 3-CH=), 7.59 (d, $^3J_{HH}$ = 7.9 Hz, 1H, 5-CH=), 7.44 (m, 1H, 8-CH=), 7.25 (dm, $^3J_{HH}$ = 7.6 Hz, 1H, 6-CH=), 3.77 (d, $^4J_{HH}$ = 1.90 Hz, 2H, CH_2), 2.47 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ ^{13}C: 162.6 (3-CH=), 151.8 (9-C), 150.3 (br, CB=), 146.6 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 142.6 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 142.0 (7-C), 141.6 (4-C), 137.8 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 128.9 (6-CH=), 125.6 (8-CH=), 125.4 (5-CH=), 114.9 (br, i-C_6F_5), 41.9 (CH_2), 22.2 (CH_3).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ ^{19}F: −130.7 (m, 2F, *o*), −151.7 (t, $^3J_{FF}$ = 20.0 Hz, 1F, *p*), −162.3 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 10.6].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ ^{11}B: 56.0 ($\nu_{1/2}$ ~ 800 Hz).

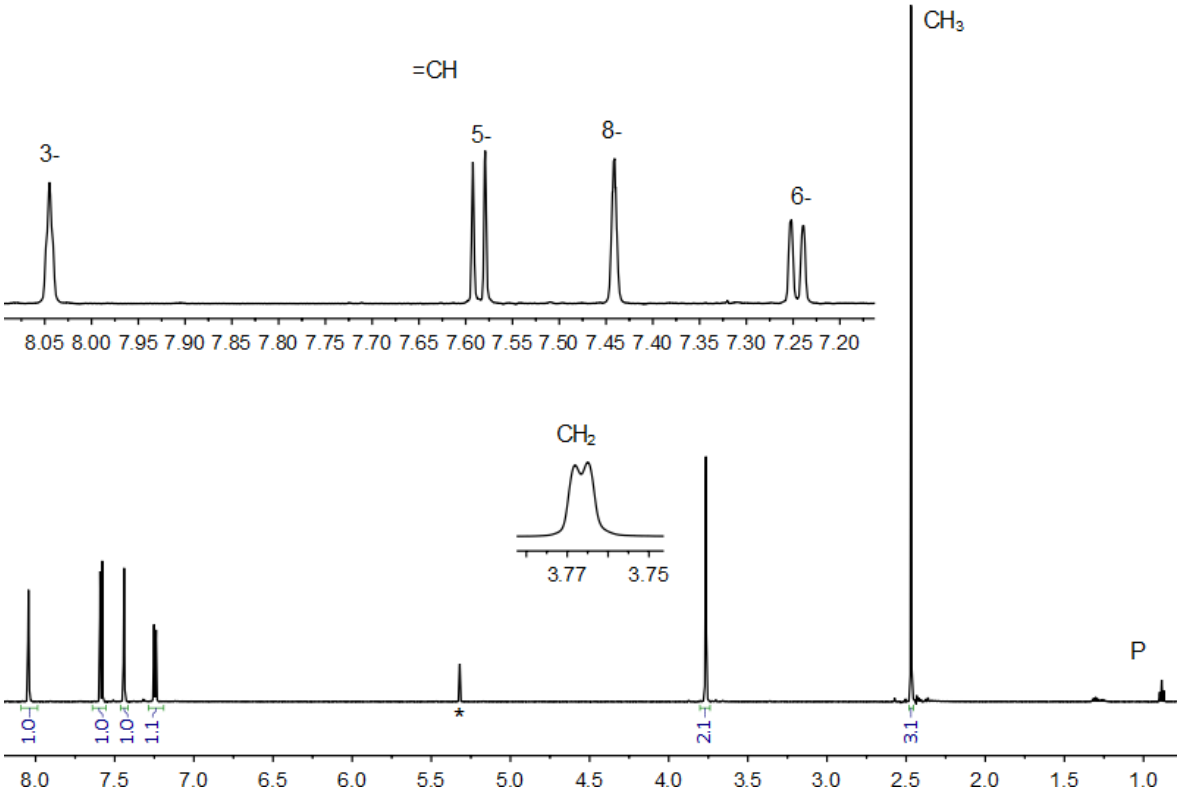


Figure S25. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectrum of compound **6b**. [P: pentane]

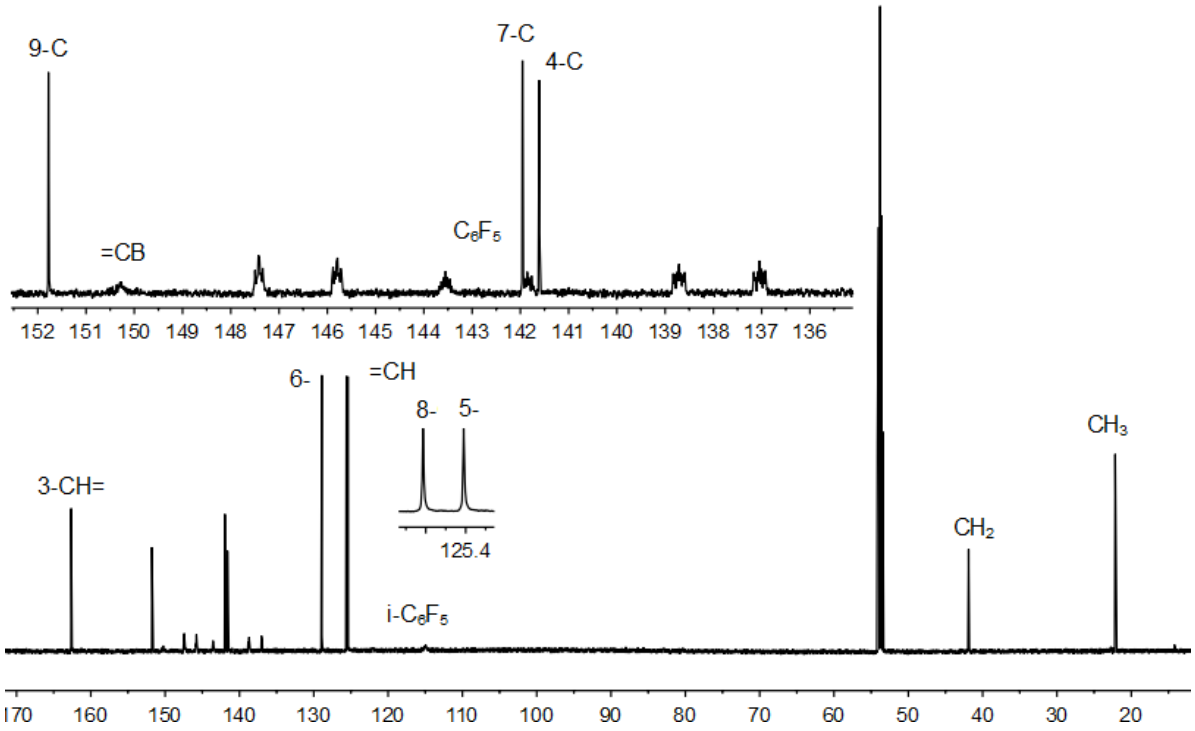


Figure S26. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **6b**.

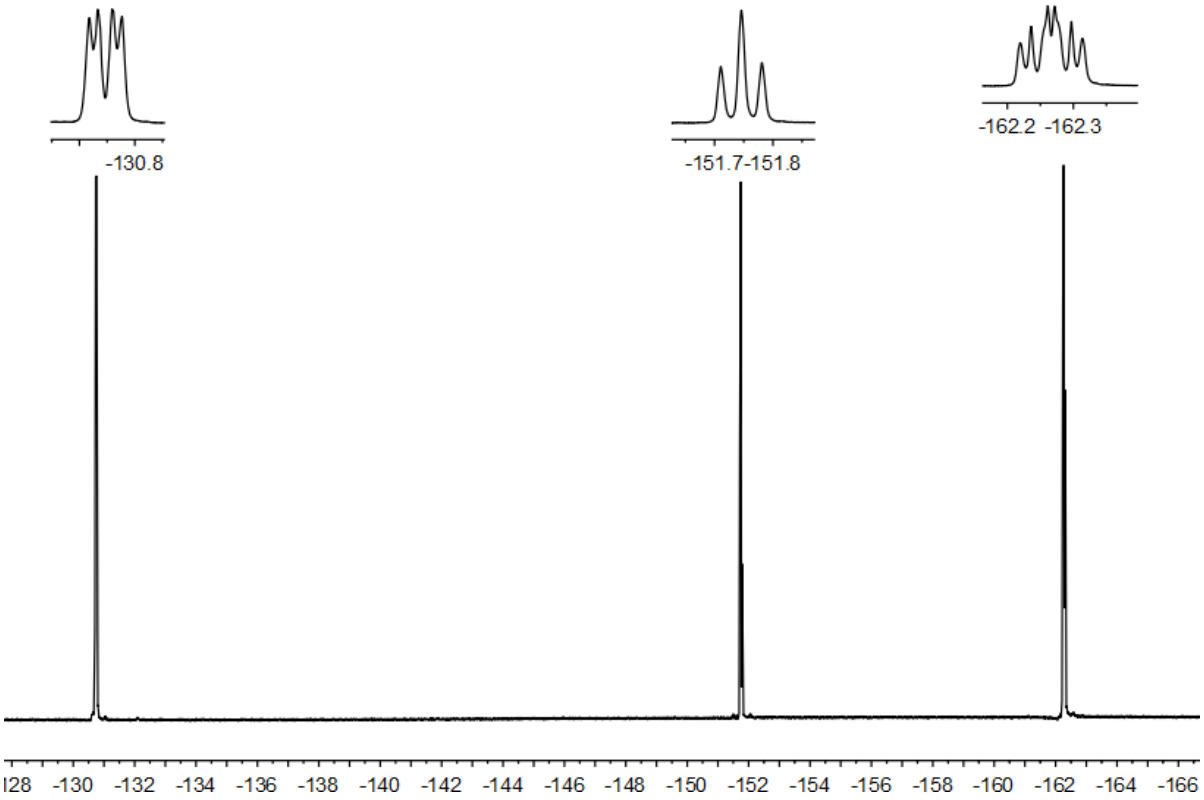


Figure S27. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **6b**.

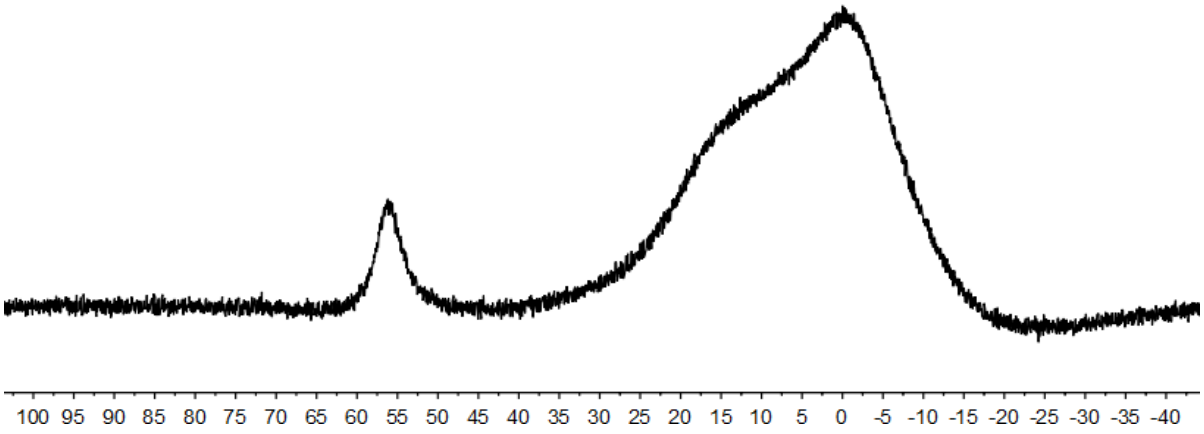


Figure S28. $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of compound **6b**.

X-ray crystal structure analysis of compound 6b (erk9187): A colorless prism-like specimen of $C_{22}H_9BF_{10}$, approximate dimensions 0.073 mm x 0.117 mm x 0.135 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The total exposure time was 5.37 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 39378 reflections to a maximum θ angle of 25.03° (0.84 Å resolution), of which 3336 were independent (average redundancy 11.804, completeness = 99.8%, R_{int} = 11.84%, R_{sig} = 4.90%) and 2793 (83.72%) were greater than $2\sigma(F^2)$. The final cell constants of a = 7.3604(4) Å, b = 11.9863(7) Å, c = 21.4524(13) Å, volume = 1892.62(19) $Å^3$, are based upon the refinement of the XYZ-centroids of 9270 reflections above 20 σ(I) with 5.096° < 2θ < 51.59°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.922. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9780 and 0.9880. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_12_12_1$, with Z = 4 for the formula unit, $C_{22}H_9BF_{10}$. The final anisotropic full-matrix least-squares refinement on F^2 with 391 variables converged at R1 = 5.89%, for the observed data and wR2 = 10.95% for all data. The goodness-of-fit was 1.160. The largest peak in the final difference electron density synthesis was 0.216 $e^-/Å^3$ and the largest hole was -0.270 $e^-/Å^3$ with an RMS deviation of 0.058 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.664 g/cm^3 and F(000), 944 e^-. CCDC number: 1907602.

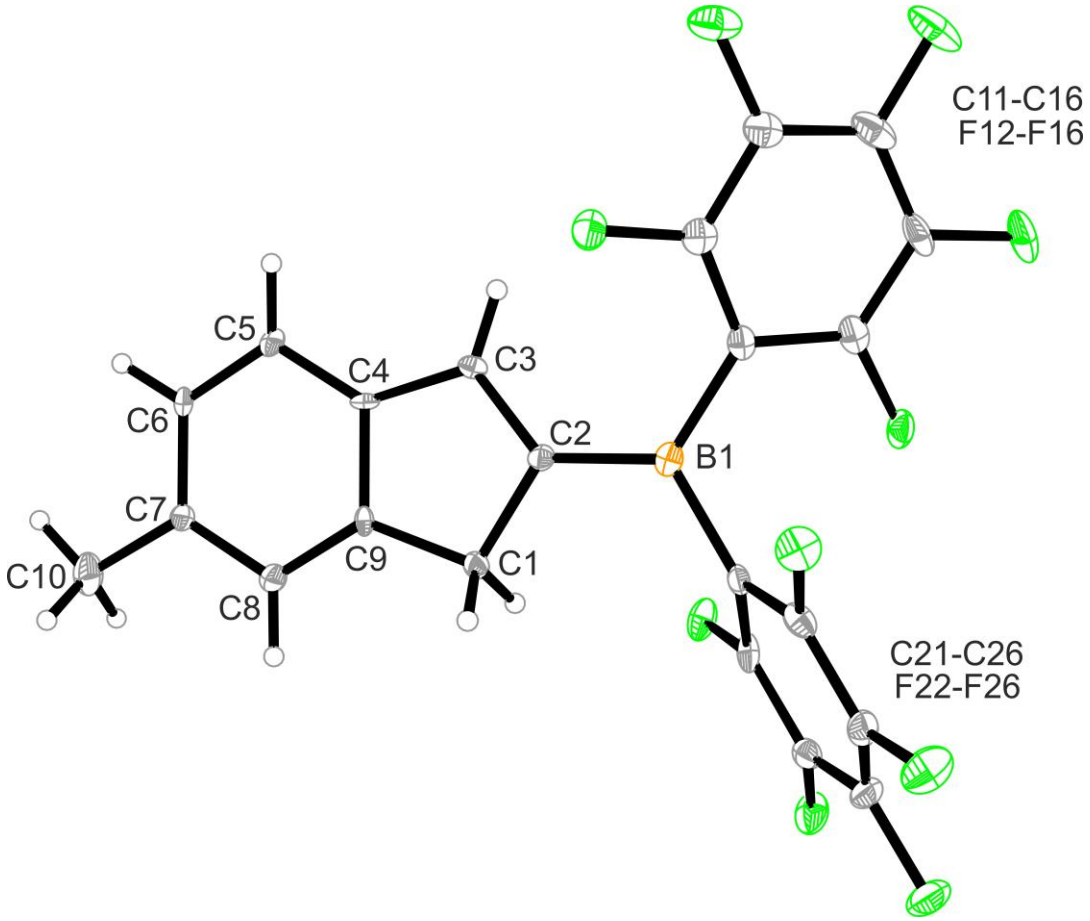
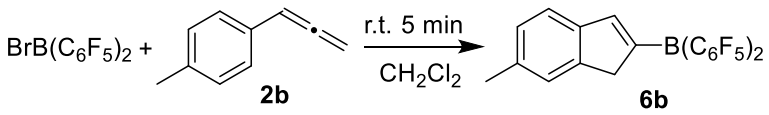


Figure S29. Crystal structure of compound **6b** (thermal ellipsoids: 30 % probability)

Experiment 2: (reaction of compound **2b** with $BrB(C_6F_5)_2$, preparative scale)

Scheme S9.



A solution of $BrB(C_6F_5)_2$ (168 mg, 0.40 mmol) in CH_2Cl_2 1 mL) was added to a solution of p-tolylallene (57 mg, 0.48 mmol) in CH_2Cl_2 (1 mL) at room temperature. After stirring at room temperature for 5 min, all the volatiles were removed in vacuo and the remaining residue was dissolved in pentane (1 mL). After storage of this solution at −35 °C for 24 h, a crystalline material precipitated. The solution was removed by decantation, then the crystalline material was carefully washed with cold pentane and dried in vacuo to give a pale yellow crystalline solid (125 mg, 0.27 mmol, 67%).

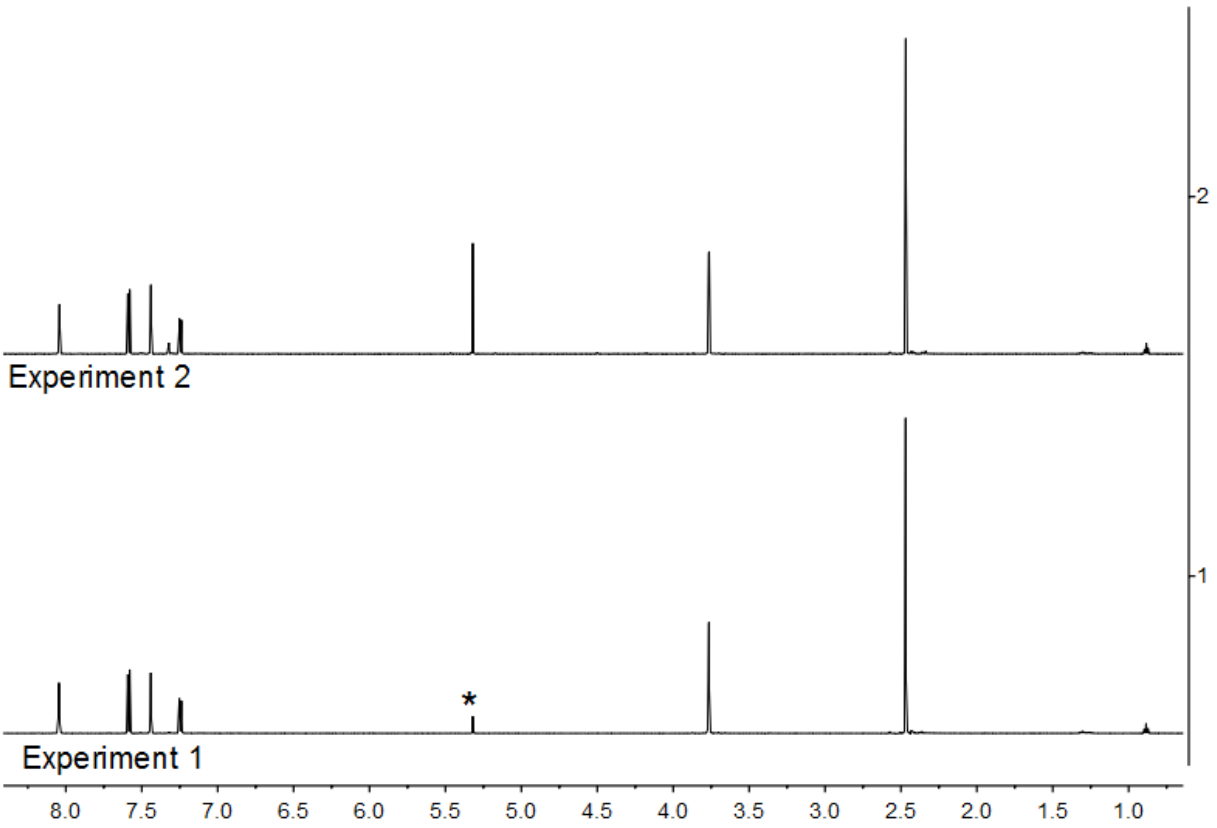


Figure S30. ^1H NMR (600 MHz, 299 K, CD_2Cl_2*) spectra of (1) isolated compound **6b** from Experiment 1 and (2) the yellow solid from Experiment 2.

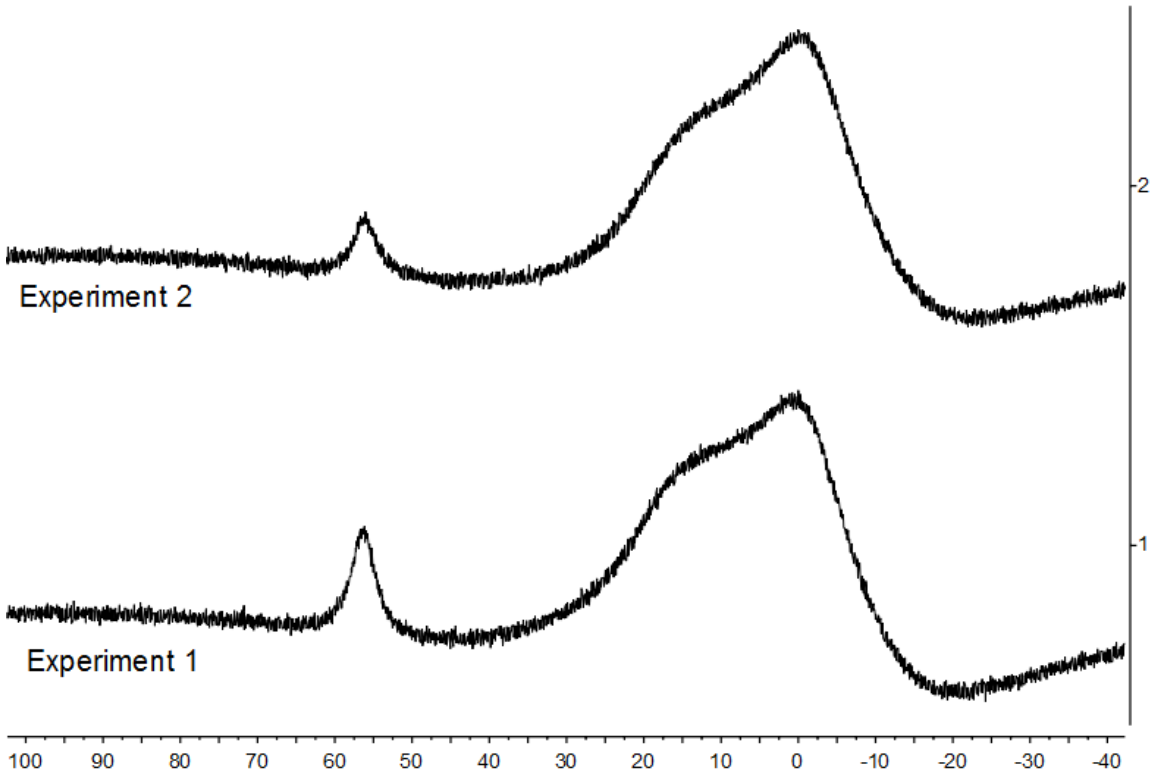


Figure S31. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2*) spectra of (1) isolated compound **6b** from Experiment 1 and (2) the yellow solid from Experiment 2.

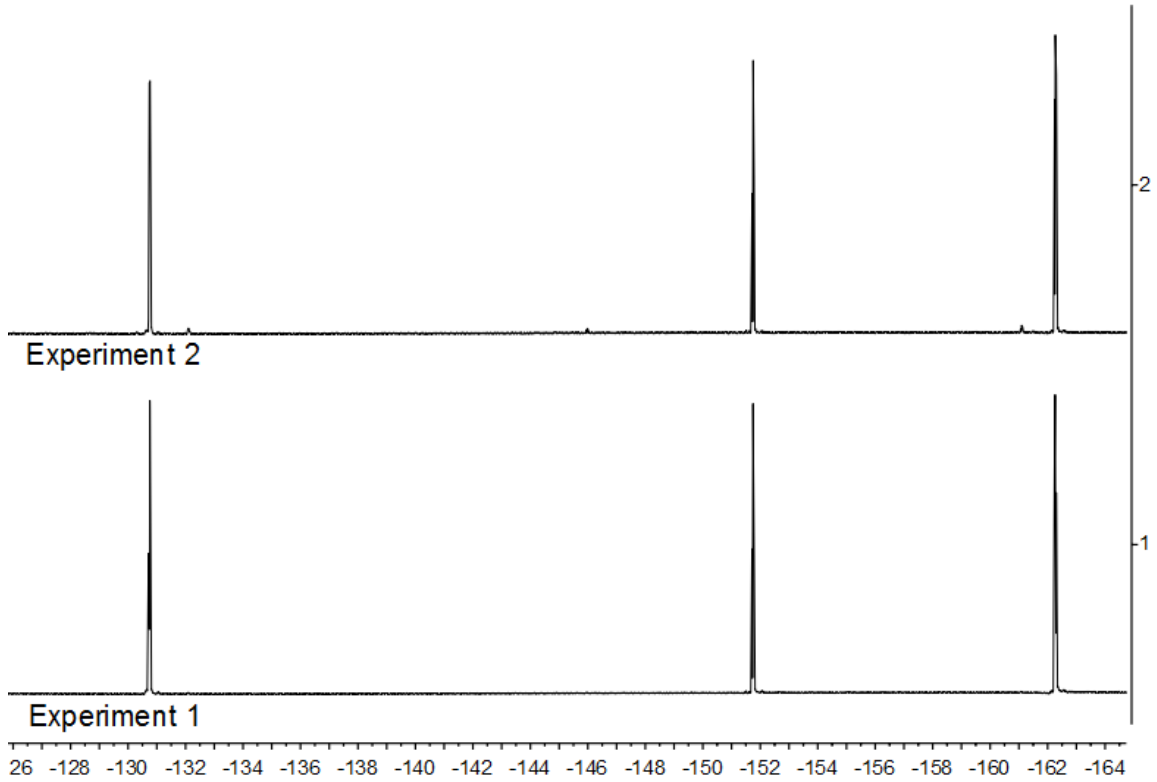
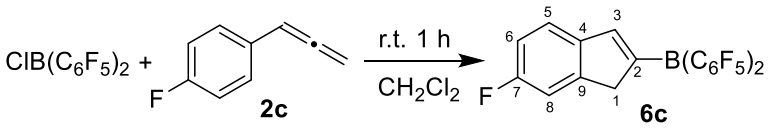


Figure S32. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2*) spectra of (1) isolated compound **6b** from Experiment 1 and (2) the yellow solid from Experiment 2.

D) Synthesis of compound **6c**

Experiment 1: (reaction of compound **2c** with $ClB(C_6F_5)_2$, preparative scale)

Scheme S10.



A solution of $ClB(C_6F_5)_2$ (152 mg, 0.40 mmol) in CH_2Cl_2 (2 mL) was added to a solution of p-fluorophenylallene (64 mg, 0.48 mmol) in CH_2Cl_2 (2 mL) at room temperature. After stirring at room temperature for 1 h, all the volatiles were removed in vacu. The remaining residue was washed with pentane (1 ml × 3) and dried in vacuo to give compound **6c** (155 mg, 0.32 mmol, 81%) as a redish crystalline solid.

Anal. Calc. for $C_{21}H_6BF_{11}$: C, 52.76; H, 1.27. Found: C, 51.89; H, 1.41.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ ^{1}H: 8.02 (t, $^4J_{HH}$ = 1.9 Hz, 1H, 3-CH=), 7.67 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{FH}$ = 5.2 Hz, 1H, 5-CH=), 7.32 (dm, $^3J_{FH}$ = 8.5 Hz, 1H, 8-CH=), 7.15 (ddd, $^3J_{FH}$ = 9.2 Hz, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.3 Hz, 1H, 6-CH=), 3.82 (d, $^4J_{HH}$ = 1.9 Hz, 2H, CH_2).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ ^{13}C: 165.0 (d, $^1J_{FC}$ = 251.6 Hz, CF), 161.3 (3-CH=), 153.8 (d, $^3J_{FC}$ = 9.7 Hz, 9-C), 151.1 (br, CB=), 146.6 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 142.8 (dm, $^1J_{FC}$ ~ 260 Hz, C_6F_5), 140.3 (d, $^4J_{FC}$ = 1.8 Hz, 4-C), 137.9 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 127.0 (d, $^3J_{FC}$ = 9.8 Hz, 5-CH=), 115.6 (d, $^2J_{FC}$ = 24.0 Hz, 6-CH=), 114.7 (br, i-C_6F_5), 112.3 (d, $^2J_{FC}$ = 23.2 Hz, 8-CH=), 42.5 (CH_2).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ ^{19}F: −109.5 (m, 1F, CF), [−130.6 (m, 2F, *o*), −151.2 (t, $^3J_{FF}$ = 20.0 Hz, 1F, *p*), −162.0 (m, 2F, *m*)](C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 10.8].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ ^{11}B: 56.4 ($\nu_{1/2}$ ~ 800 Hz).

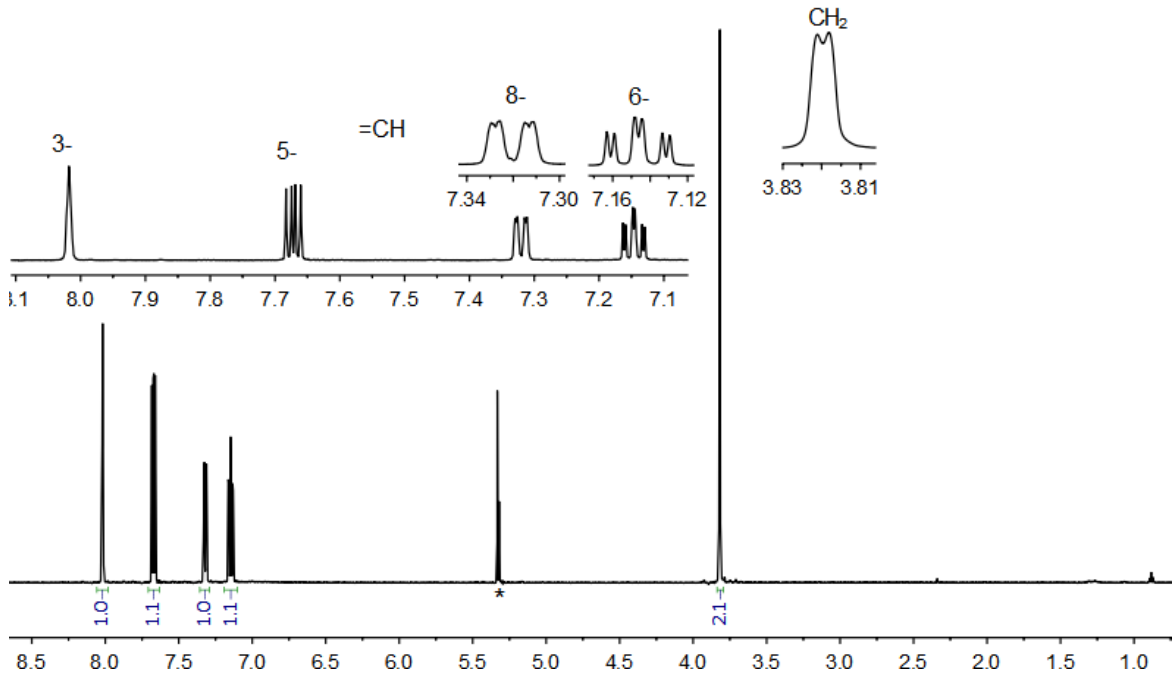


Figure S33. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectrum of compound **6c**.

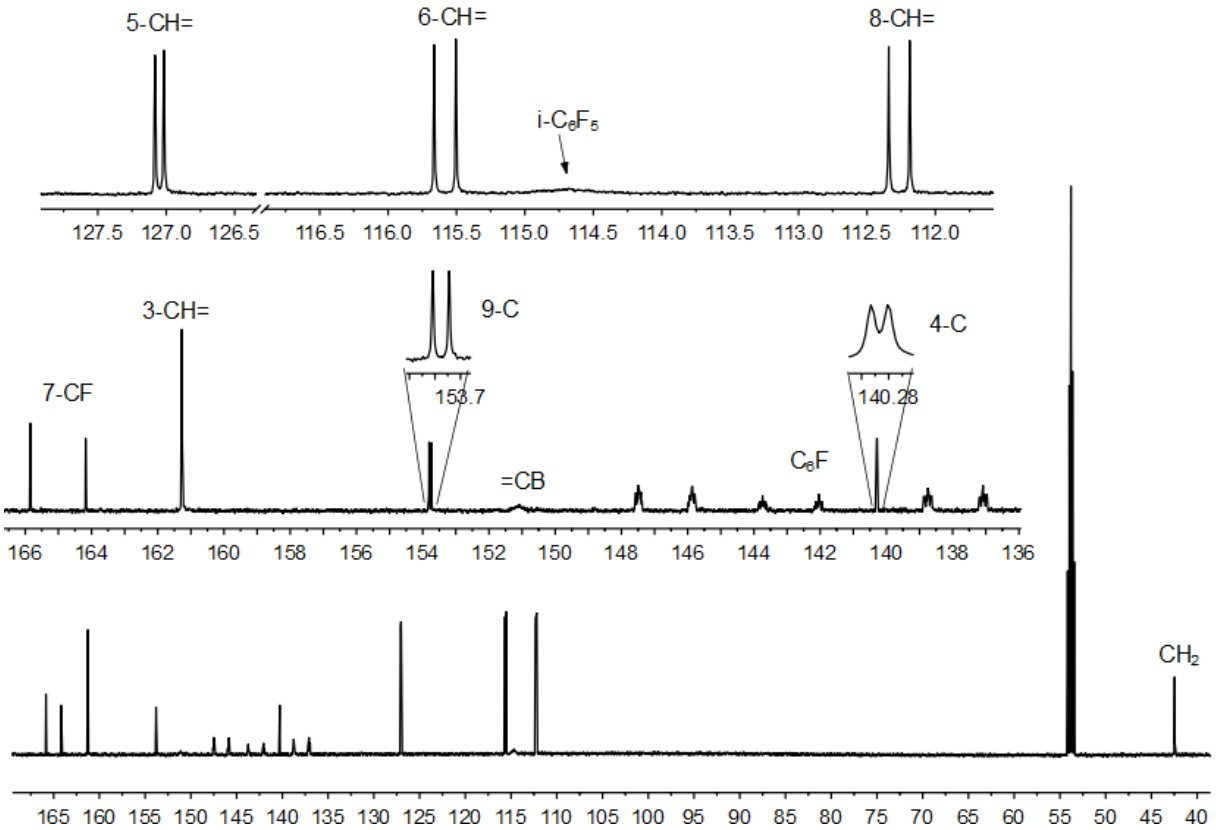


Figure S34. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **6c**.

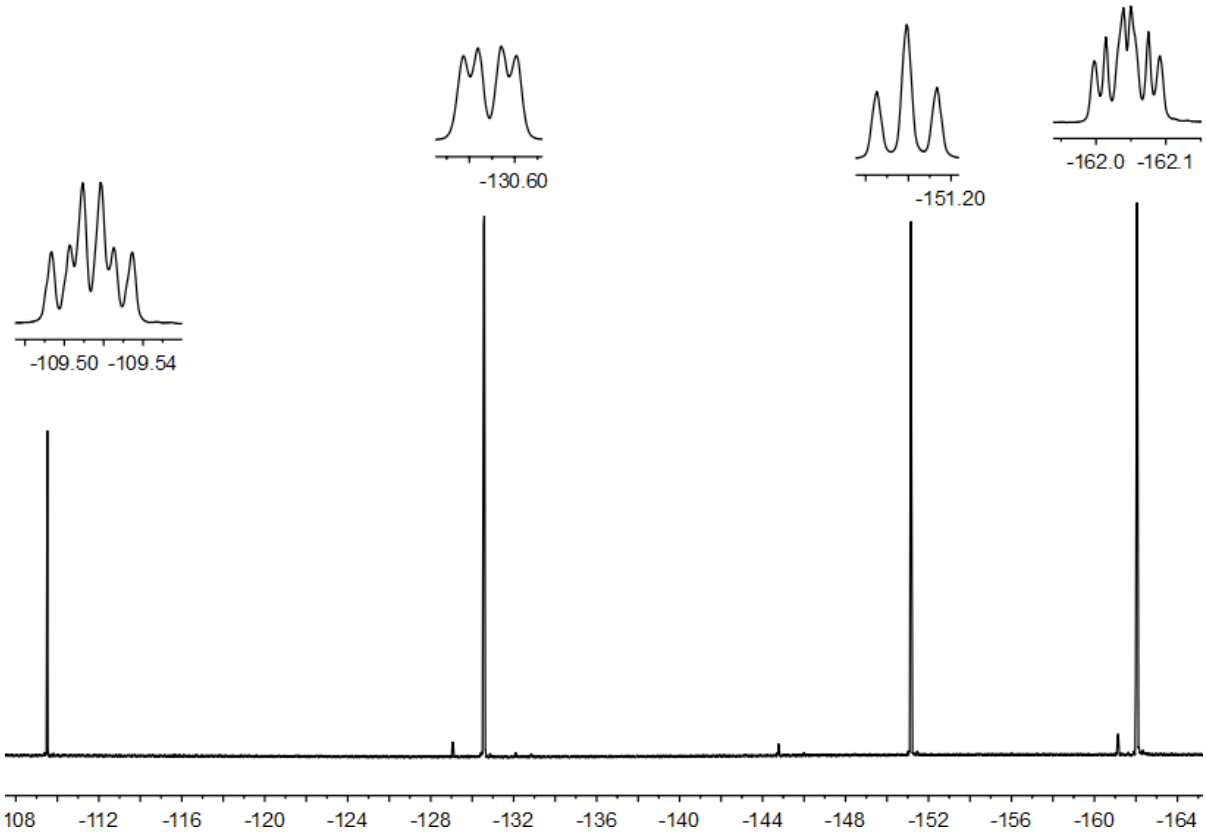


Figure S35. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **6c**.

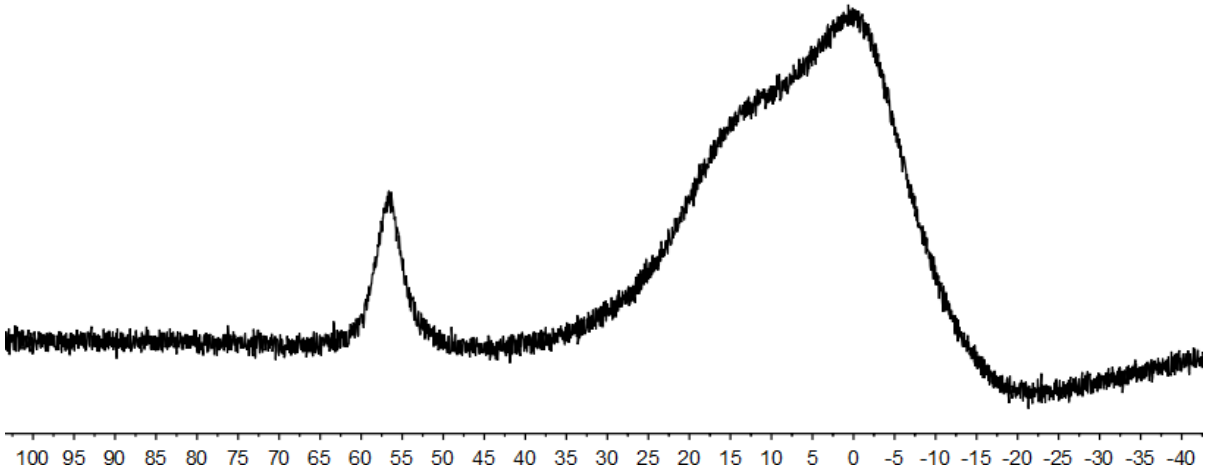


Figure S36. $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of compound **6c**.

Crystals suitable for the X-ray crystal structure analysis were obtained from the diffusion of pentane vapor to a solution of compound **6c** in CH_2Cl_2 at -35 ^oC.

X-ray crystal structure analysis of compound 6c (erk9217): A colorless needle-like specimen of $C_{21}H_6BF_{11}$, approximate dimensions 0.032 mm x 0.067 mm x 0.164 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1026 frames were collected. The total exposure time was 21.62 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 16290 reflections to a maximum θ angle of 66.59° (0.84 Å resolution), of which 3060 were independent (average redundancy 5.324, completeness = 99.4%, R_{int} = 11.47%, R_{sig} = 7.39%) and 2523 (82.45%) were greater than $2\sigma(F^2)$. The final cell constants of a = 7.4593(3) Å, b = 10.9446(4) Å, c = 21.4005(10) Å, volume = 1747.12(13) $Å^3$, are based upon the refinement of the XYZ-centroids of 7034 reflections above 20 σ(I) with 8.263° < 2θ < 136.4°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.847. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7680 and 0.9480. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_12_12_1$, with Z = 4 for the formula unit, $C_{21}H_6BF_{11}$. The final anisotropic full-matrix least-squares refinement on F^2 with 389 variables converged at R1 = 6.70%, for the observed data and wR2 = 14.56% for all data. The goodness-of-fit was 1.163. The largest peak in the final difference electron density synthesis was 0.321 $e^-/Å^3$ and the largest hole was -0.289 $e^-/Å^3$ with an RMS deviation of 0.073 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.818 g/cm^3 and F(000), 944 e^-. CCDC number: 1907603.

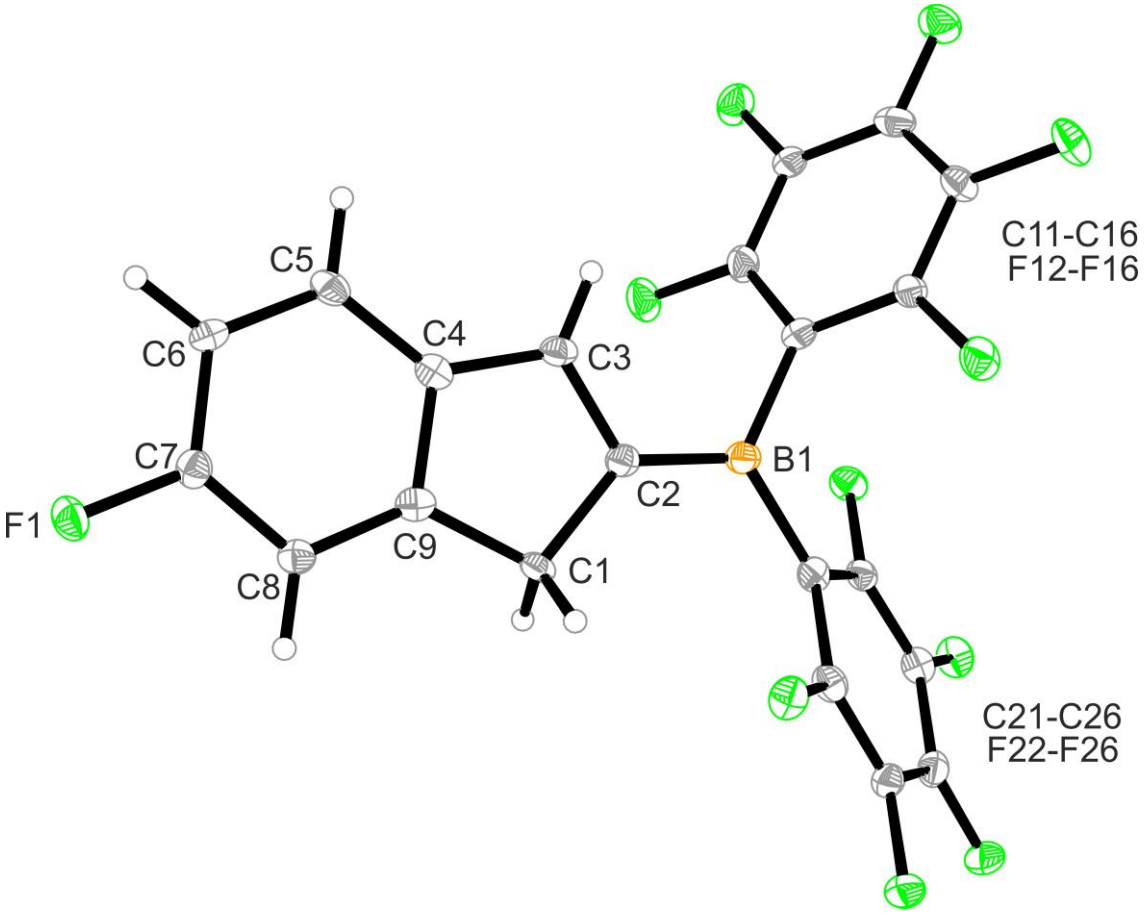
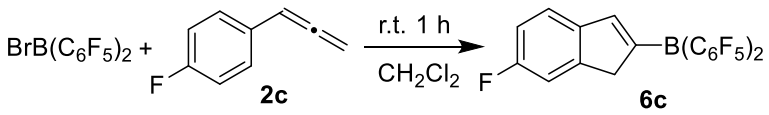


Figure S37. Crystal structure of compound **6c** (thermal ellipsoids: 30 % probability.)

Experiment 2: (reaction of compound **2c** with $BrB(C_6F_5)_2$, preparative scale)

Scheme S11.



A solution of $BrB(C_6F_5)_2$ (168 mg, 0.40 mmol) in CH_2Cl_2 (1 mL) was added to a solution of p-fluorophenylallene (62 mg, 0.44 mmol) in CH_2Cl_2 (1 mL) at room temperature. After stirring at room temperature for 1 hour, all the volatiles were removed in vacuo. The remaining residue was washed with pentane (1 ml × 3) and dried in vacuo to finally give compound **6c** (105 mg, 0.22 mmol, 56%) as redish crystalline material.

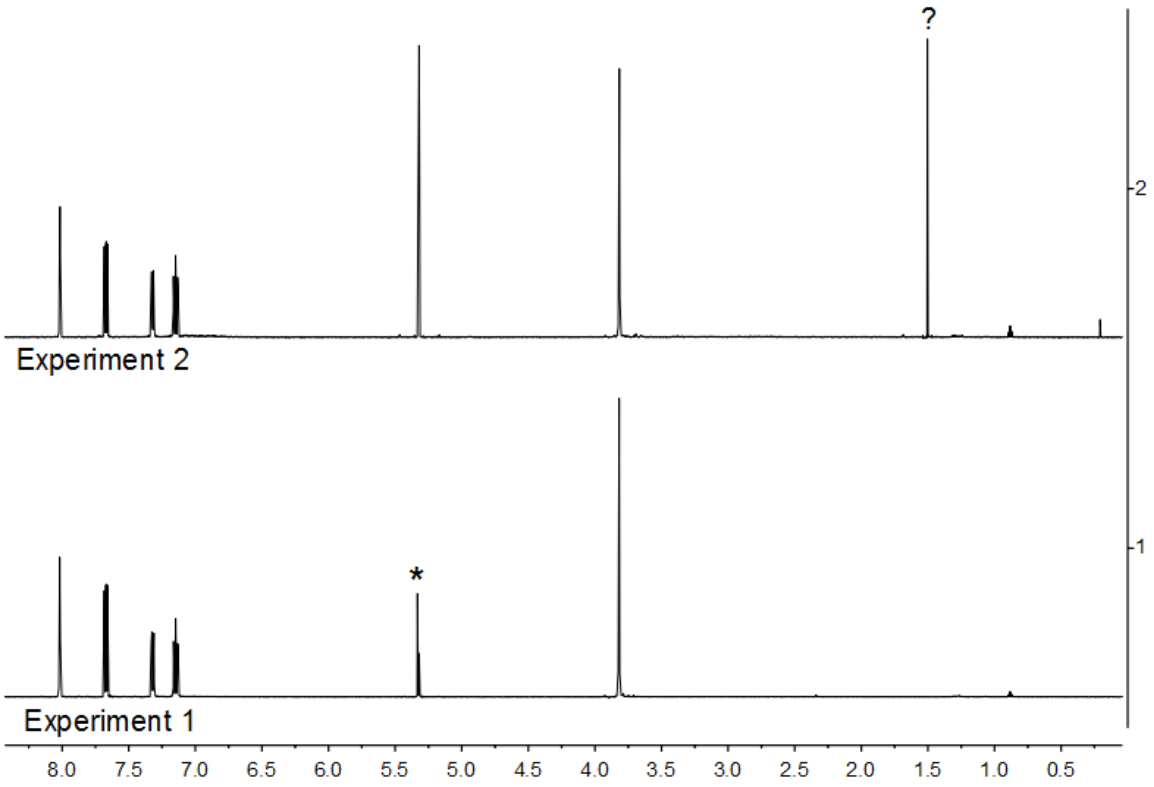


Figure S38. ^1H NMR (600 MHz, 299 K, CD_2Cl_2*) spectra of (1) isolated compound **6c** from Experiment 1 and (2) the redish solid from Experiment 2. [?: unknown signal]

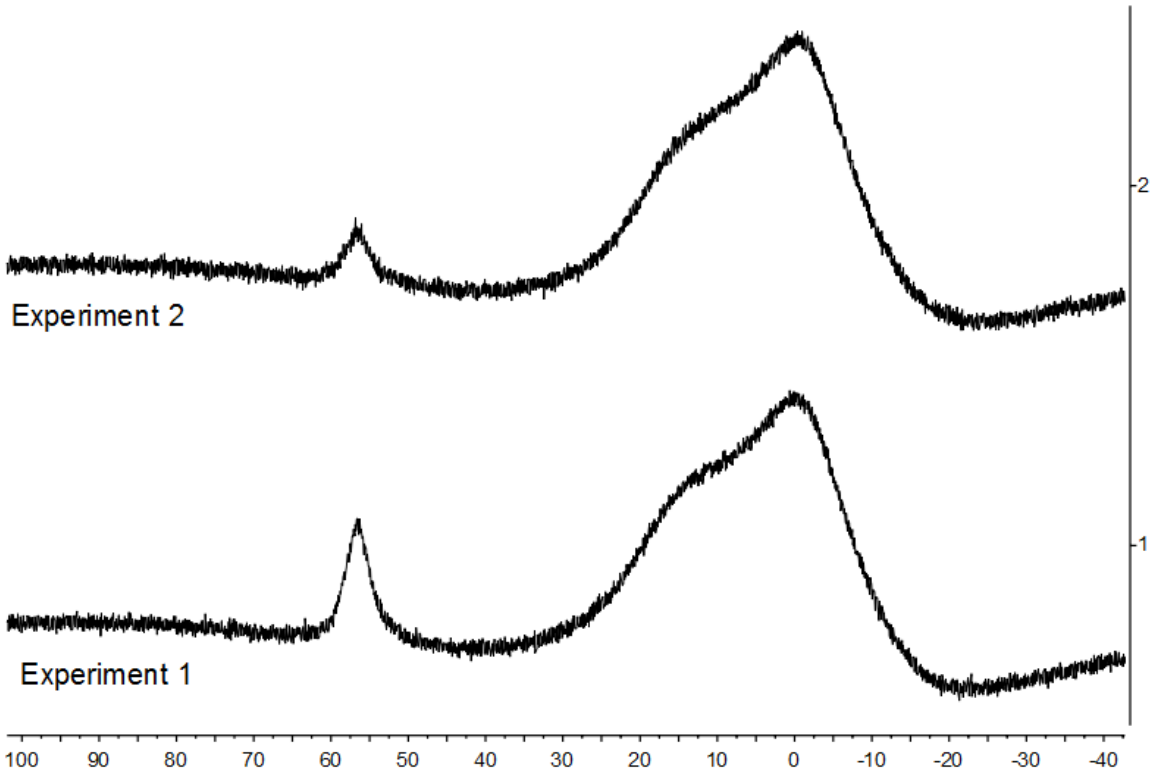


Figure S39. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2*) spectra of (1) isolated compound **6c** from Experiment 1 and (2) the redish solid from Experiment 2.

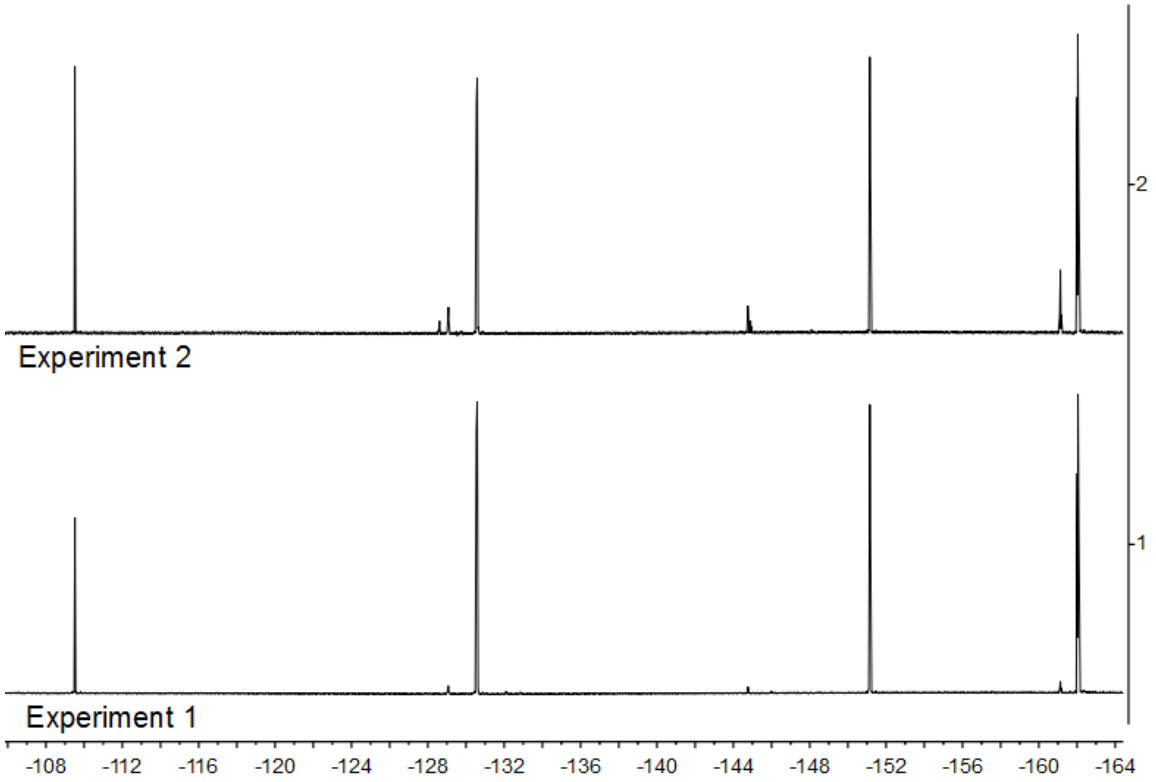
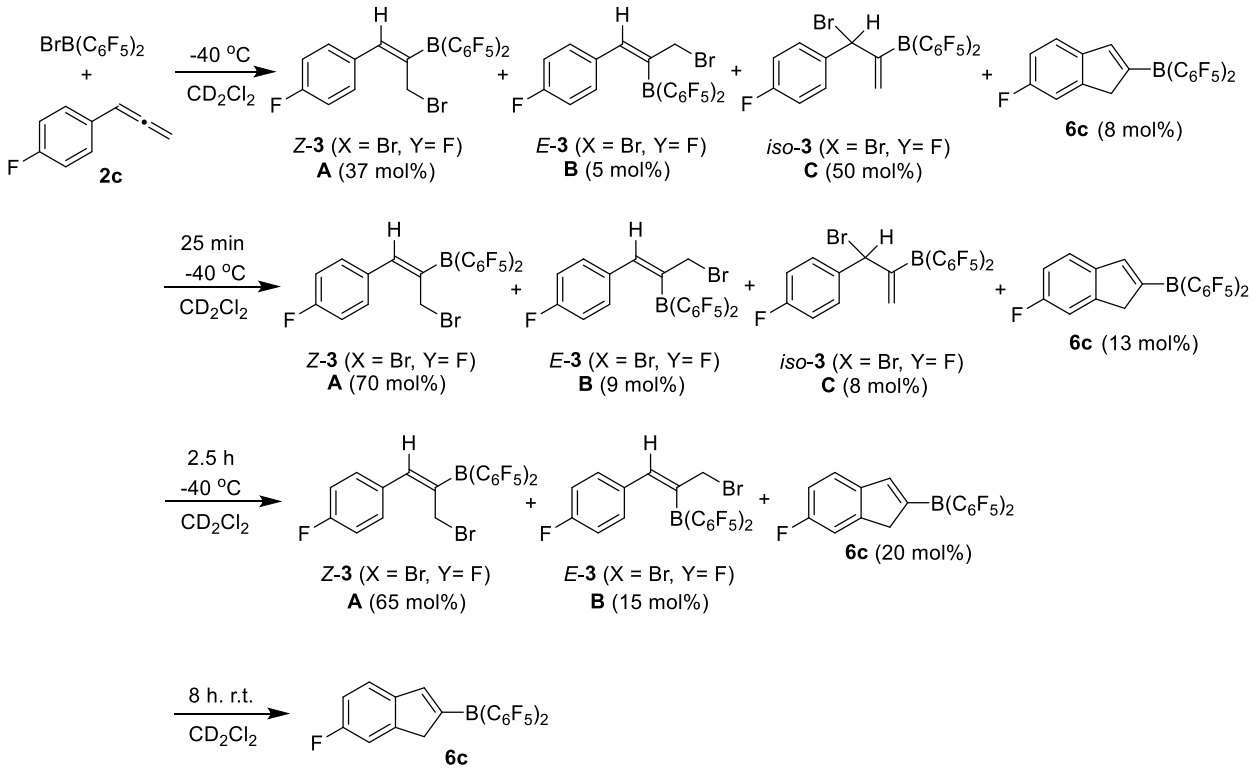


Figure S40. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2*) spectra of (1) isolated compound **6c** from Experiment 1 and (2) the redish solid from Experiment 2.

Experiment 3: (reaction of compound **2c** with $BrB(C_6F_5)_2$, NMR scale)

Scheme S12.



$BrB(C_6F_5)_2$ (42 mg, 0.10 mmol) was placed at the bottom of a Young NMR tube and cooled to -78 °C. Then a solution of compound **2c** (14 mg, 0.10 mmol) in CD_2Cl_2 (0.5 mL) was added to the Young NMR tube at -78 °C. The obtained reaction mixture was characterized by NMR experiments:

(1) immediately after mixing,

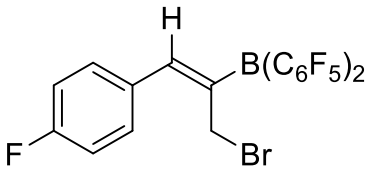
(2) after storage for ca. 25 min at -40 °C,

(3) after storage for ca. 2 hours at -40 °C [comment: a white precipitate was observed after the NMR experiments].

(4) Then after the reaction mixture was stored for ca. 8 hours at room temperature.

The ratios of the main components in the corresponding reactions are given in **Scheme S12**.

NMR data of compound **A**:

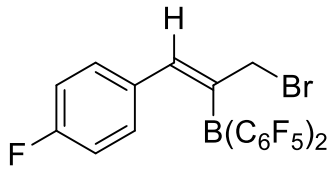


A: *Z*-**3** (X = Br, Y= F)

^{1}H NMR (600 MHz, 233 K, CD_2Cl_2): δ ^{1}H: 7.59 (m, 2H, o-C_6H_4F), 7.43 (s, 1H, CH=), 7.20 (m, 2H, m-C_6H_4F), 4.44 (s, 2H, CH_2).

^{13}C{^{1}H} NMR (151 MHz, 233 K, CD_2Cl_2): δ ^{13}C: 163.6 (d, $^{1}J_{FC}$ = 252.4 Hz, p-C_6H_4F), 156.1 (CH=), 143.3 (br, CB=), 132.8 (d, $^{3}J_{FC}$ = 8.8 Hz, o-C_6H_4F), 130.6 (d, $^{4}J_{FC}$ = 2.9 Hz, i-C_6H_4F), 116.1 (d, $^{2}J_{FC}$ = 21.8 Hz, m-C_6H_4F), 31.2 (CH_2).

NMR data of compound **B**:

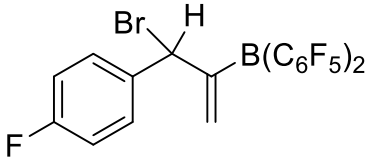


B: *E*-**3** (X = Br, Y= F)

^{1}H NMR (600 MHz, 233 K, CD_2Cl_2): δ ^{1}H: 7.48 (s, 1H, CH=), 6.99 (m, 2H, o-C_6H_4F), 6.85 (m, 2H, m-C_6H_4F), 4.36 (s, 2H, CH_2).

^{13}C{^{1}H} NMR (151 MHz, 233 K, CD_2Cl_2): δ ^{13}C: 163.3 (d, $^{1}J_{FC}$ = 250.2 Hz, p-C_6H_4F), 145.6 (CH=), 144.1 (br, CB=), 133.5 (i-C_6H_4F), 130.8 (o-C_6H_4F), 115.1 (m-C_6H_4F), 37.7 (CH_2).

NMR data of compound **C**:



C: *iso*-**3** (X = Br, Y= F)

^{1}H NMR (600 MHz, 233 K, CD_2Cl_2): δ ^{1}H: [7.33, 7.05](each m, each 2H, C_6H_4F), 6.08 (s, 1H, CHBr), [5.93, 5.88](each s, each 1 H, =CH_2).

^{13}C{^{1}H} NMR (151 MHz, 233 K, CD_2Cl_2) selected resonances: δ ^{13}C: 137.5 (=CH_2), [130.3, 115.6] (o,m-C_6H_4F), 55.6 (CHBr).

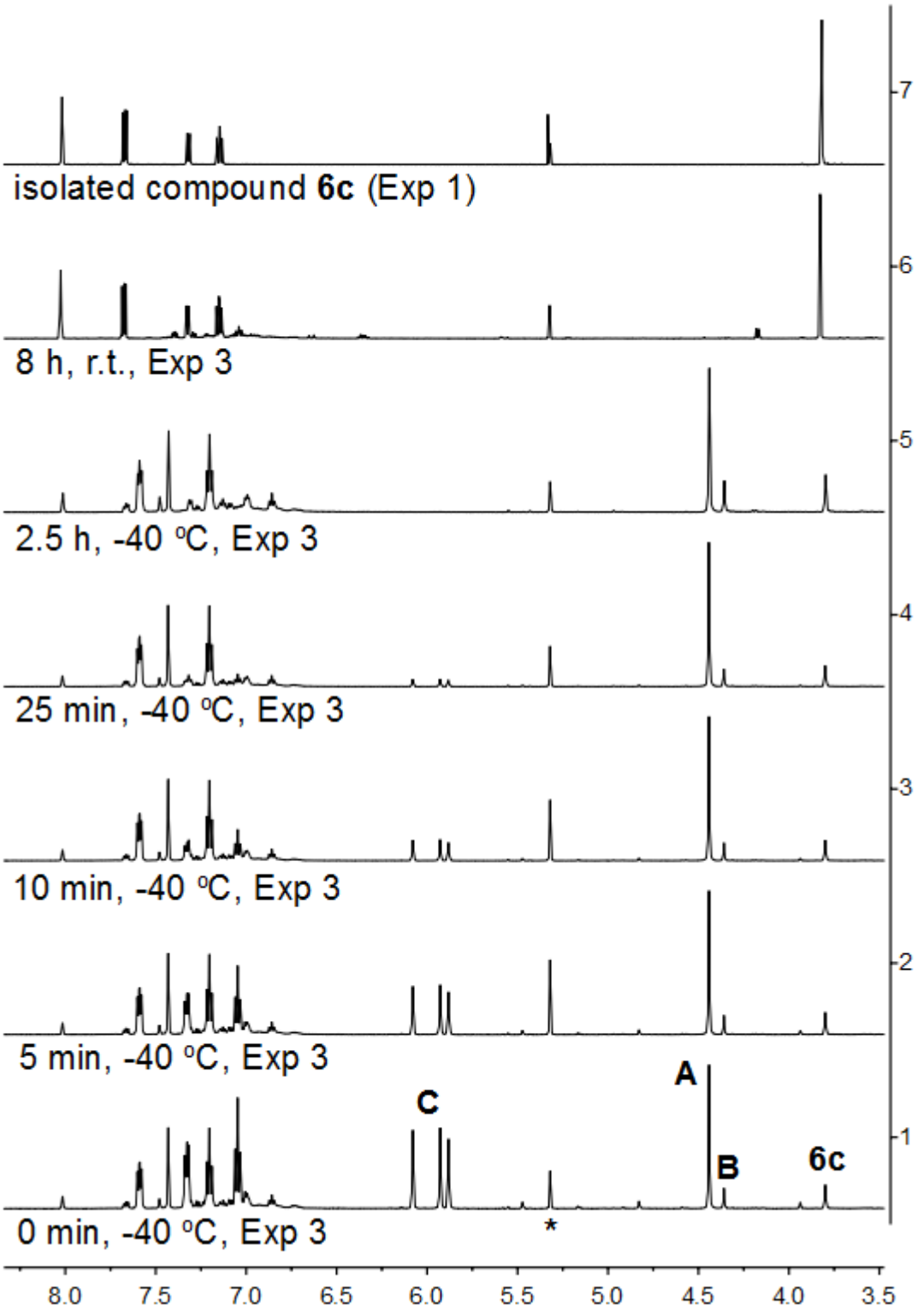


Figure S41. ^{1}H NMR (600 MHz, 233 K, CD_2Cl_2*) spectra of (1-6) the reaction mixture as described in Experiment 3 and (7) the isolated compound **6c** from Experiment 1.

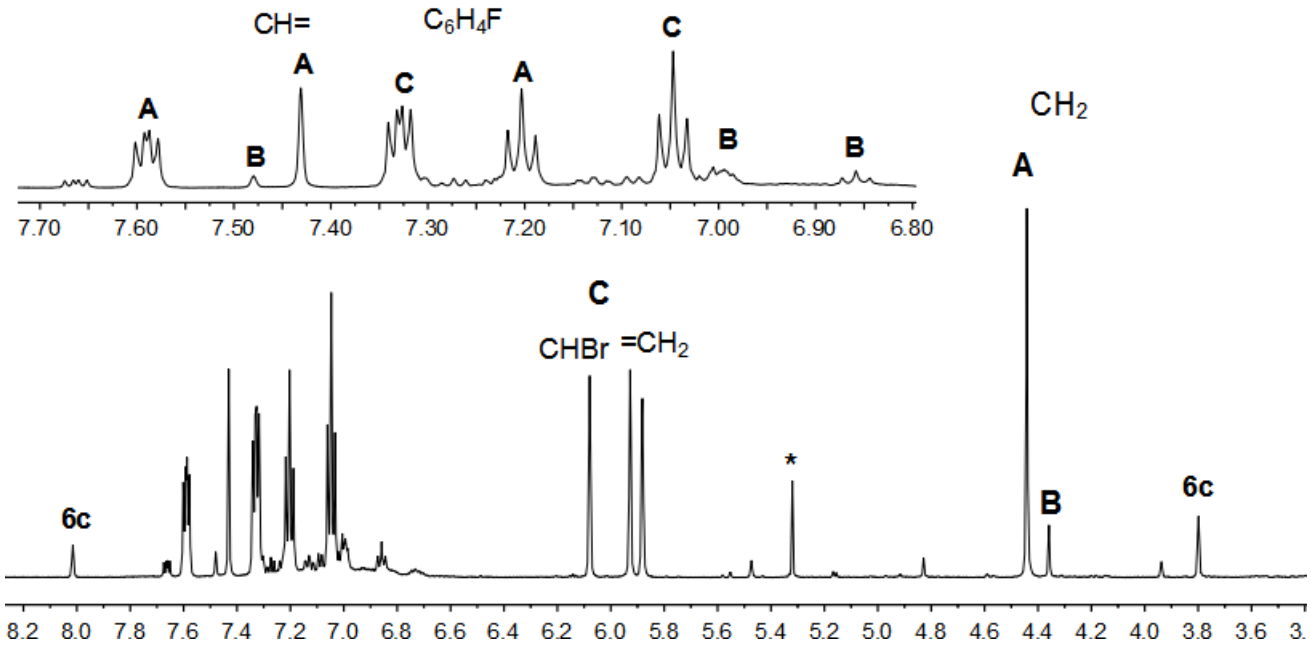


Figure S42. ^{1}H NMR (600 MHz, 233 K, CD_2Cl_2) spectrum of reaction mixture as described in Experiment 3 (0 min, -40 °C).

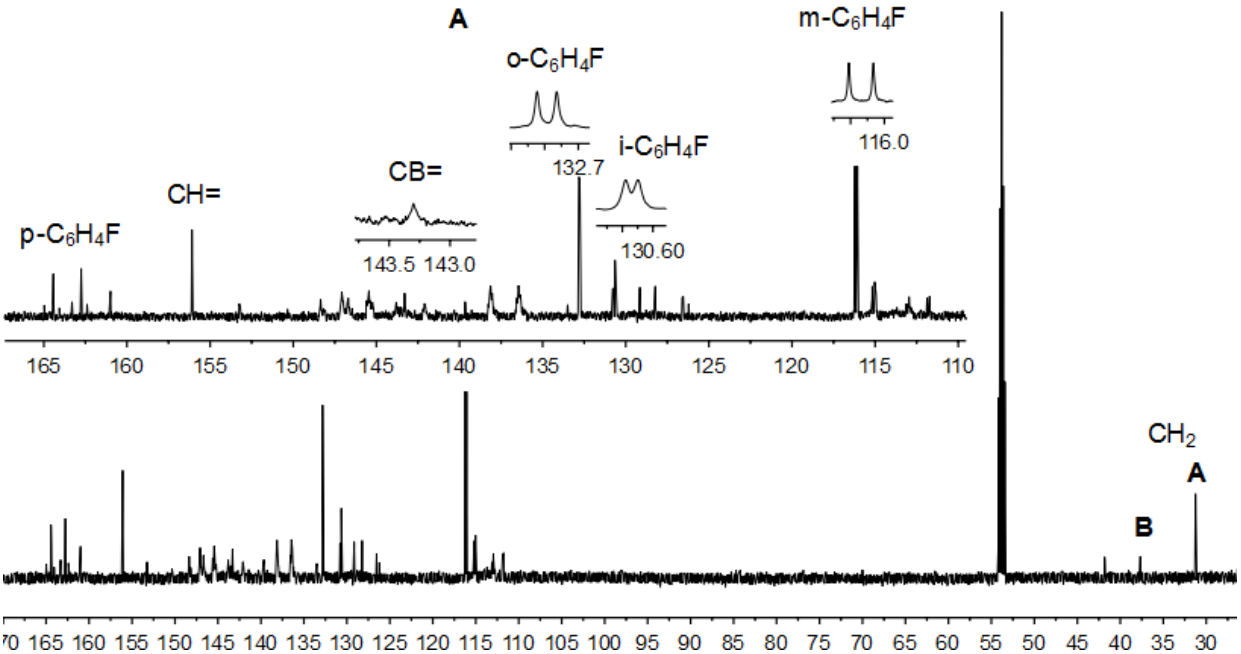
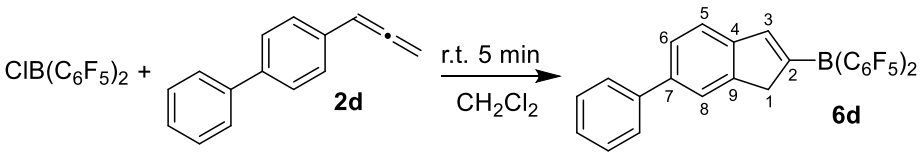


Figure S43. $^{13}C\{^{1}H\}$ NMR (151 MHz, 233 K, CD_2Cl_2) spectrum of reaction mixture as described in Experiment 3 (2.5 h, -40 °C).

E) Synthesis of compound **6d**

Experiment 1: (reaction of compound **2d** with $ClB(C_6F_5)_2$, preparative scale)

Scheme S13.



A solution of $ClB(C_6F_5)_2$ (152 mg, 0.40 mmol) in CH_2Cl_2 (1 mL) was added to a solution of p-biphenylallene (98 mg, 0.51 mmol) in CH_2Cl_2 (1 mL) at room temperature. After stirring at room temperature for 5 min, all the volatiles were removed in vacuo. The remaining residue was washed with pentane (1 ml × 3) and dried in vacuo to finally give compound **6d** (185 mg, 0.33 mmol, 83%) as a pale yellow crystalline material.

Anal. Calc. for $C_{27}H_{11}BF_{10}$: C, 60.48; H, 2.07. Found: C, 60.03; H, 2.07.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ ^{1}H: 8.10 (t, $^4J_{HH}$ = 1.9 Hz, 1H, 3-CH=), 7.86 (m, 1H, 8-CH=), 7.77 (dm, $^3J_{HH}$ = 8.0 Hz, 1H, 5-CH=), 7.68 (dm, $^3J_{HH}$ = 8.0 Hz, 1H, 6-CH=), 7.67 (m, 2H, o-Ph), 7.48 (m, 2H, m-Ph), 7.40 (m, 1H, p-Ph), 3.89 (d, $^4J_{HH}$ = 1.9 Hz, 2H, CH_2).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ ^{13}C: 161.9 (3-CH=), 152.0 (9-C), 151.4 (br, CB=), 146.6 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 143.7 (7-C), 143.2 (4-C), 142.8 (dm, $^1J_{FC}$ ~ 260 Hz, C_6F_5), 141.1 (i-Ph), 137.8 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 129.3 (m-Ph), 128.3 (p-Ph), 127.7 (o-Ph), 114.9 (br, i-C_6F_5), 127.0 (6-CH=), 125.9 (5-CH=), 123.5 (8-CH=), 42.3 (CH_2).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ ^{19}F: −130.5 (m, 2F, *o*), −151.3 (t, $^3J_{FF}$ = 20.0 Hz, 1F, *p*), −162.1 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 10.8].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ ^{11}B: 56.2 ($\nu_{1/2}$ ~ 1200 Hz).

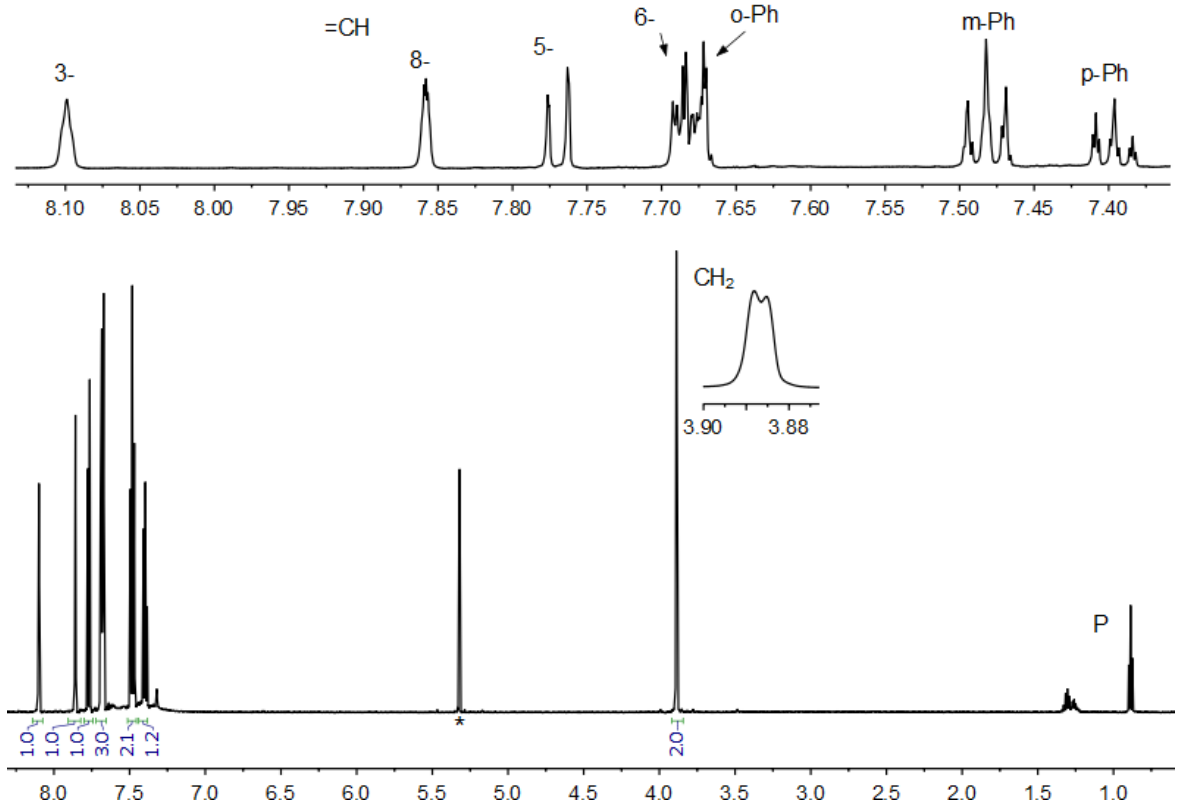


Figure S44. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectrum of compound **6d**.

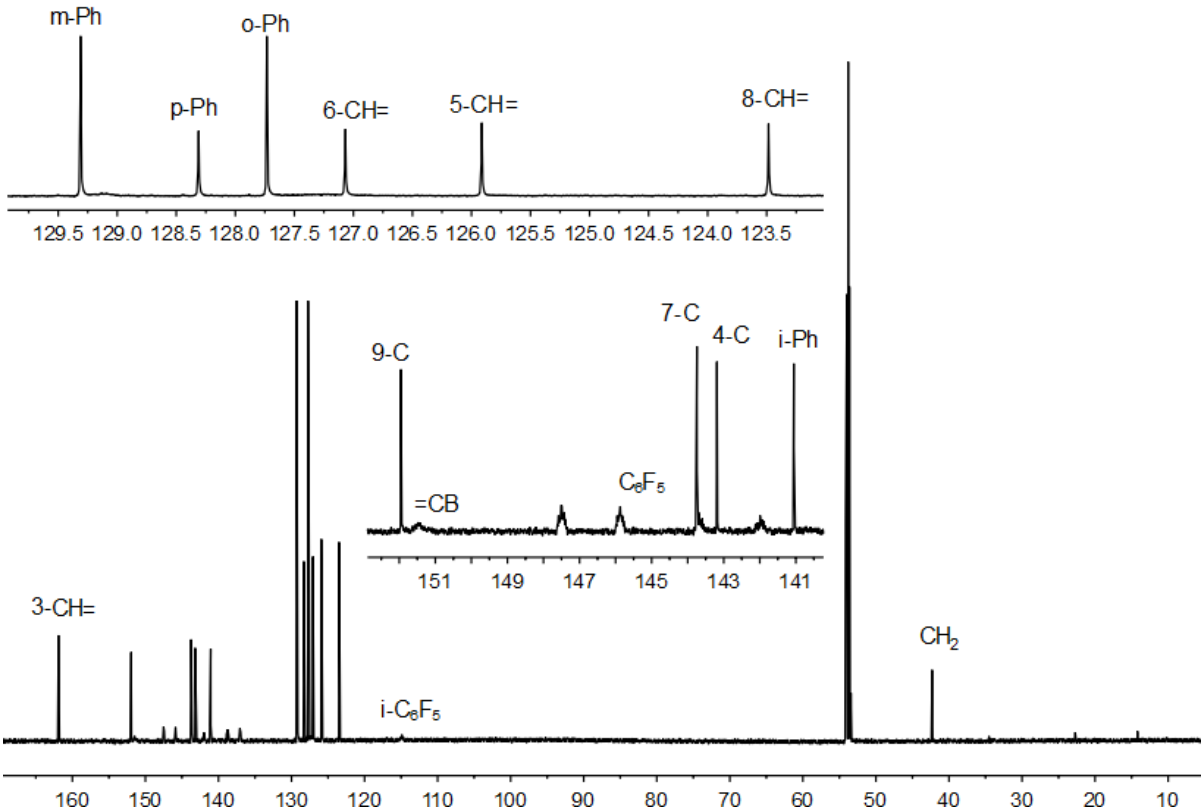


Figure S45. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **6d**.

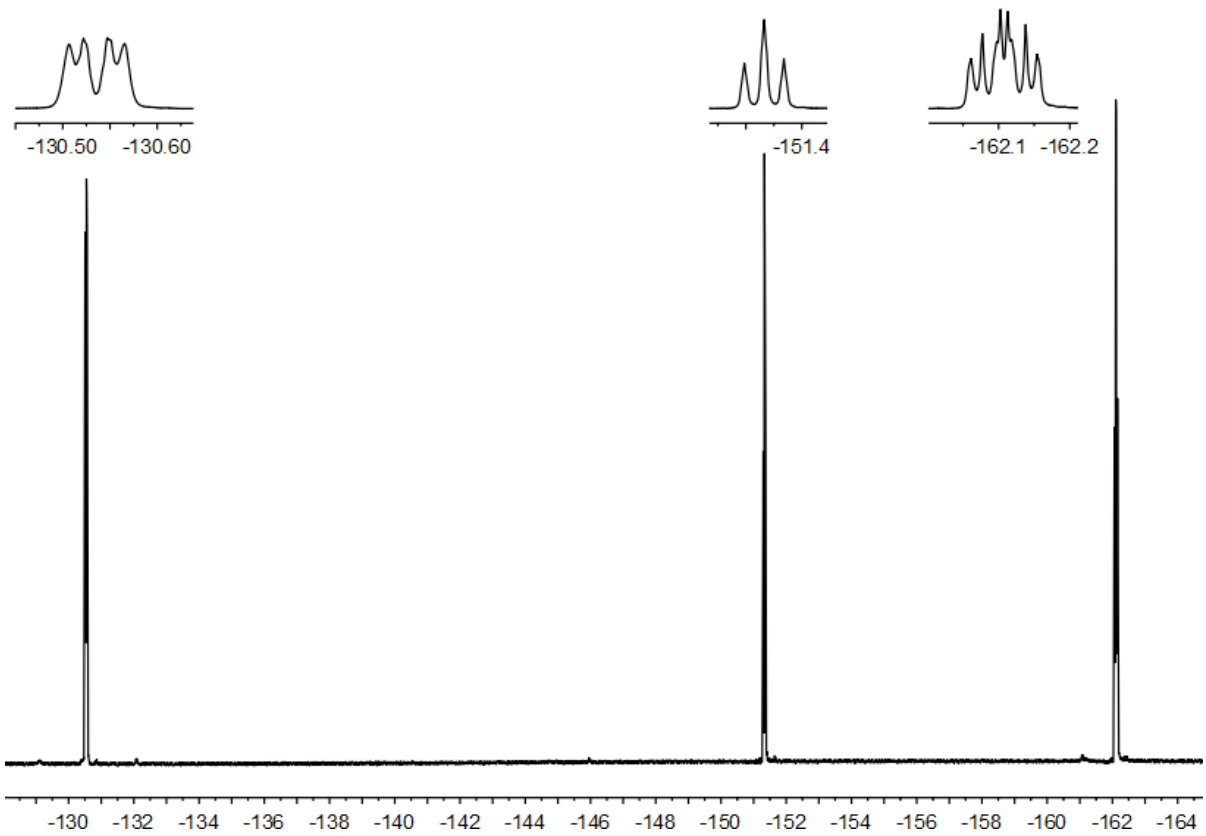


Figure S46. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **6d**.

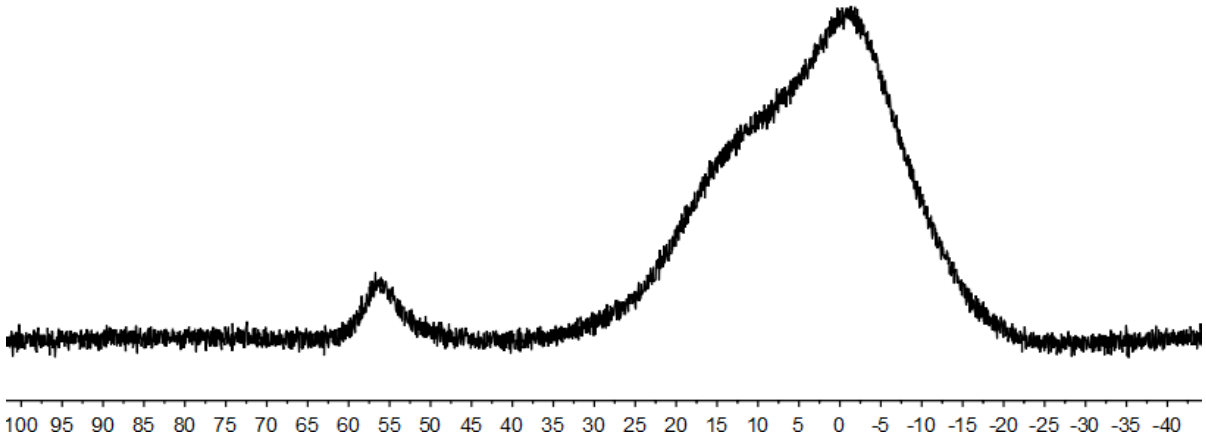


Figure S47. $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of compound **6d**.

Crystals suitable for the X-ray crystal structure analysis were obtained from the diffusion of pentane vapor to a solution of compound **6d** in CH_2Cl_2 at -35 ^oC.

X-ray crystal structure analysis of compound 6d (erk9216): A yellow prism-like specimen of $C_{27}H_{11}BF_{10}$, approximate dimensions 0.080 mm x 0.130 mm x 0.150 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1085 frames were collected. The total exposure time was 18.93 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 40458 reflections to a maximum θ angle of 66.78° (0.84 Å resolution), of which 3786 were independent (average redundancy 10.686, completeness = 99.7%, R_{int} = 7.69%, R_{sig} = 3.24%) and 3037 (80.22%) were greater than 2σ(F^2). The final cell constants of a = 27.821(2) Å, b = 7.5444(6) Å, c = 20.4229(16) Å, volume = 4286.6(6) $Å^3$, are based upon the refinement of the XYZ-centroids of 6523 reflections above 20 σ(I) with 8.659° < 2θ < 133.1°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.829. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8180 and 0.8970. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *Pccn*, with Z = 8 for the formula unit, $C_{27}H_{11}BF_{10}$. The final anisotropic full-matrix least-squares refinement on F^2 with 343 variables converged at R1 = 3.59%, for the observed data and wR2 = 8.77% for all data. The goodness-of-fit was 1.034. The largest peak in the final difference electron density synthesis was 0.216 $e^-/Å^3$ and the largest hole was -0.227 $e^-/Å^3$ with an RMS deviation of 0.049 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.662 g/cm^3 and F(000), 2144 e^-. CCDC number: 1907604.

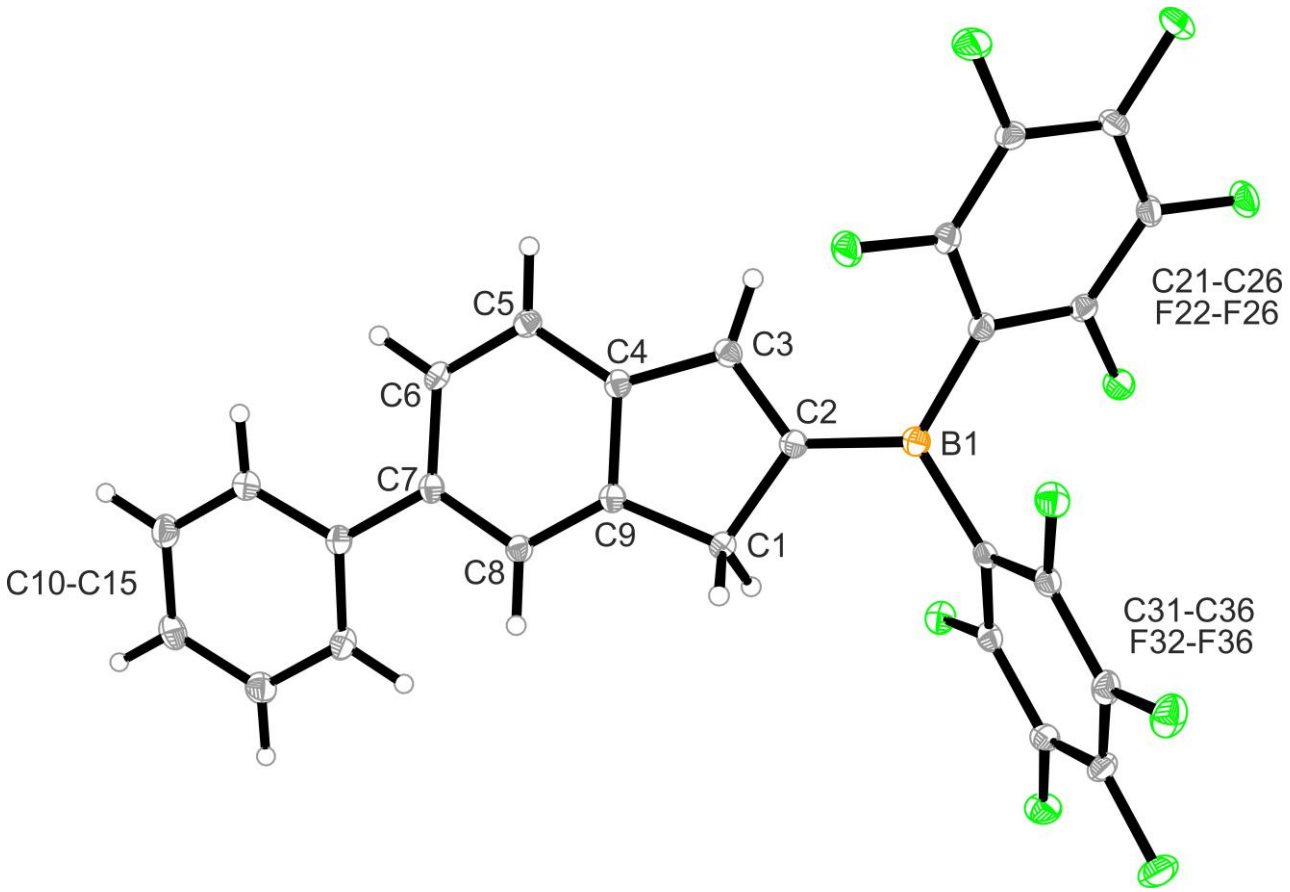
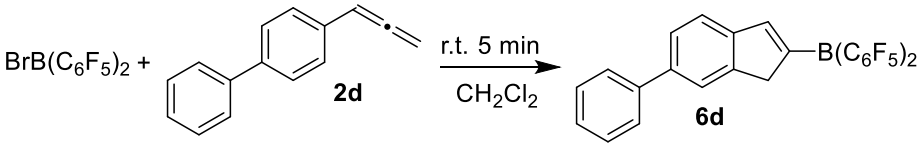


Figure S48. Crystal structure of compound **6d** (thermal ellipsoids: 30 % probability.)

Experiment 2: (reaction of compound **2d** with $BrB(C_6F_5)_2$, preparative scale)

Scheme S14.



A solution of $BrB(C_6F_5)_2$ (152 mg, 0.40 mmol) in CH_2Cl_2 (1 mL) was added to a solution of p-biphenylallene (98 mg, 0.51 mmol) in CH_2Cl_2 (1 mL) at room temperature. After stirring at room temperature for 5 min, all the volatiles were removed in vacuo. The remaining residue was washed with pentane (1 ml × 3) and dried in vacuo to finally give compound **6d** (165 mg, 0.29 mmol, 74%) as a green solid.

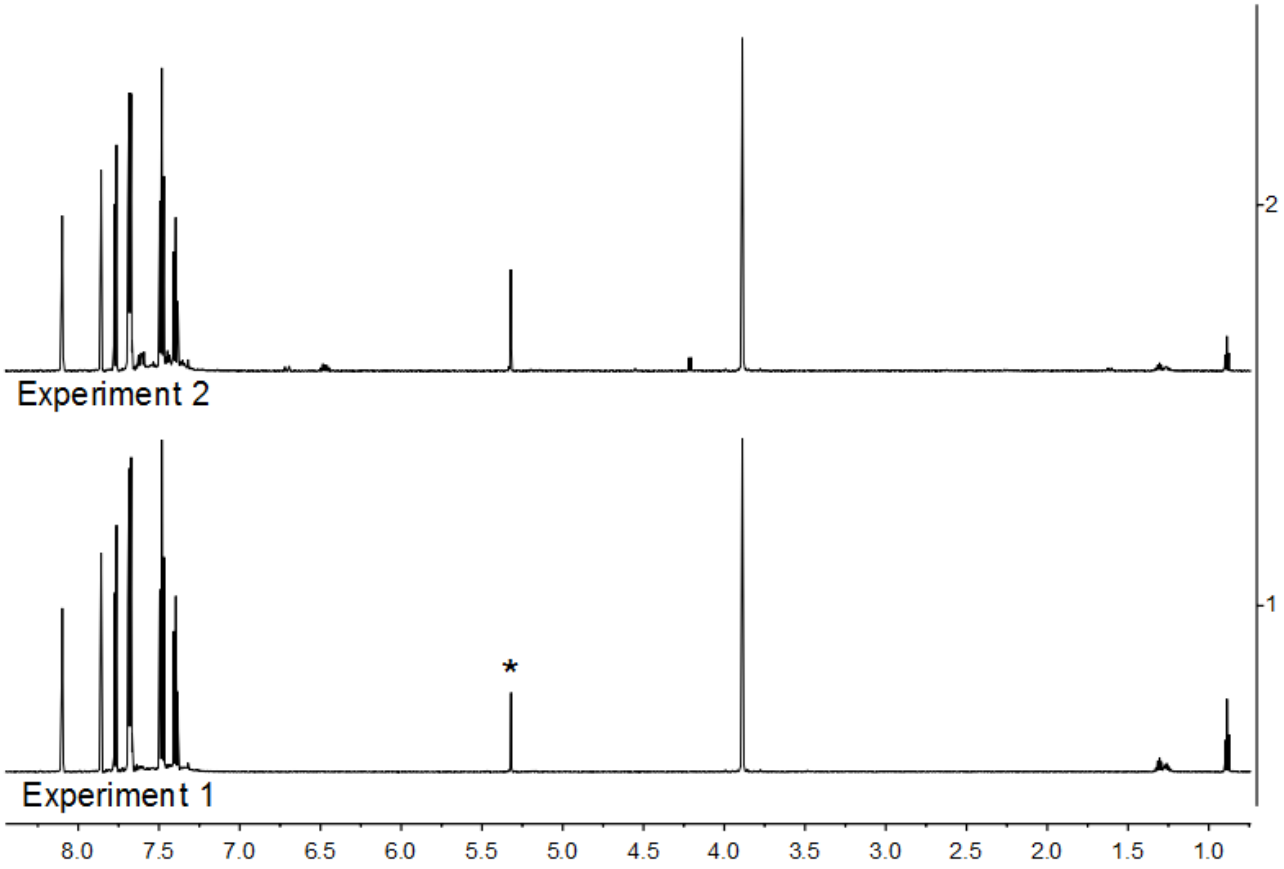


Figure S49. ^1H NMR (600 MHz, 299 K, CD_2Cl_2*) spectra of (1) isolated compound **6d** from Experiment 1 and (2) the green solid from Experiment 2.

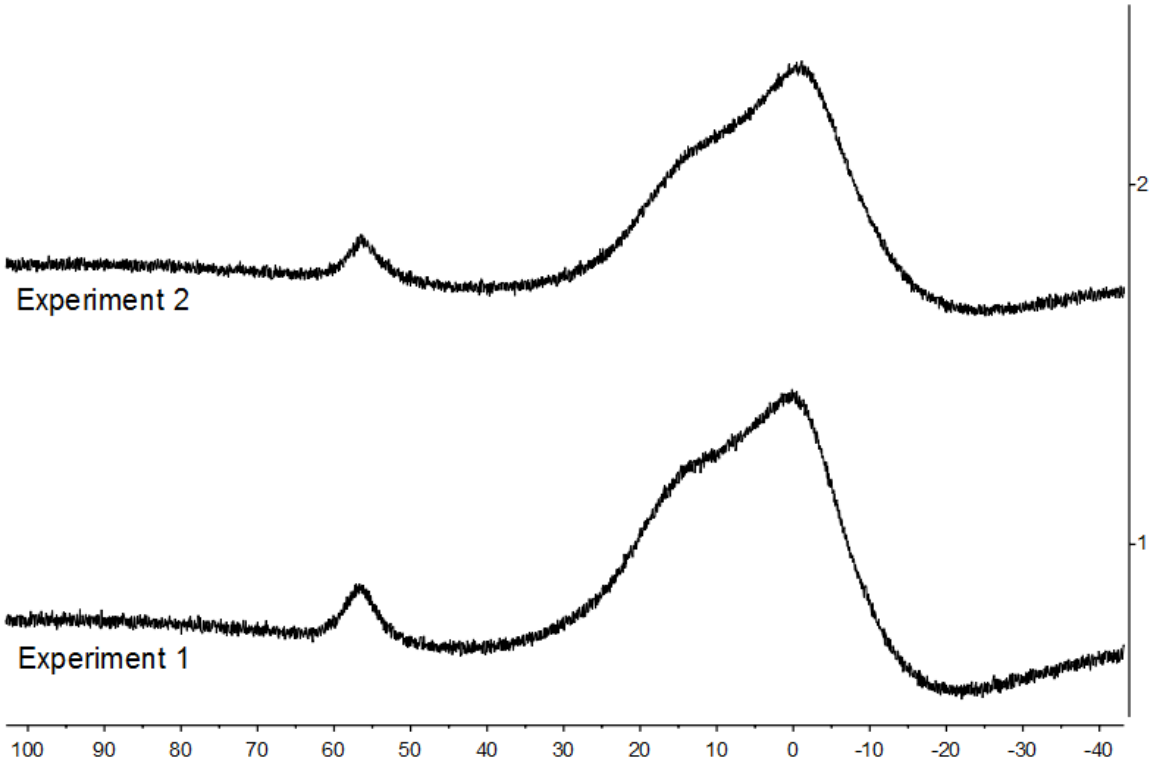


Figure S50. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2*) spectra of (1) isolated compound **6d** from Experiment 1 and (2) the green solid from Experiment 2.

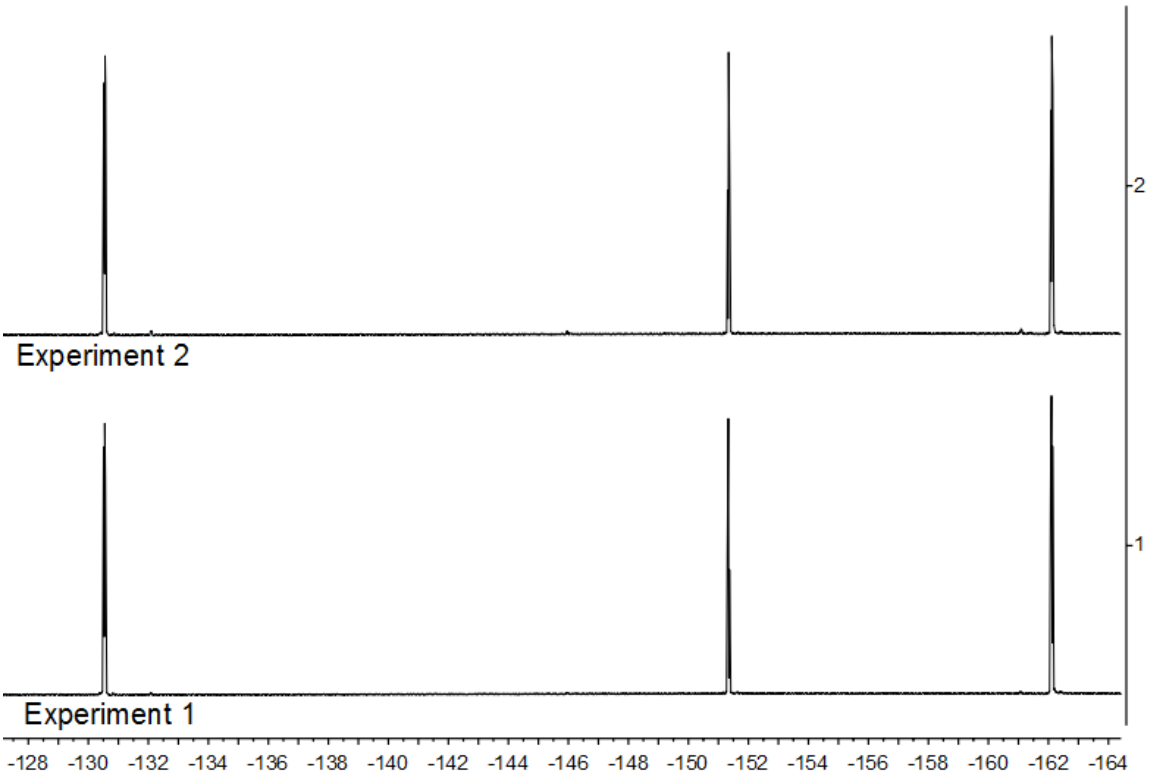
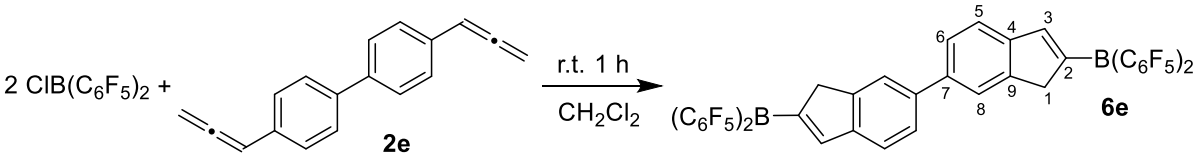


Figure S51. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2*) spectra of (1) isolated compound **6d** from Experiment 1 and (2) the green solid from Experiment 2.

F) Synthesis of compound **6e**

Experiment 1: (reaction of compound **2e** with $ClB(C_6F_5)_2$, preparative scale)

Scheme S15.



A solution of $ClB(C_6F_5)_2$ (152 mg, 0.40 mmol) in CH_2Cl_2 (1 mL) was added to a solution of compound **2e** (50 mg, 0.22 mmol) in CH_2Cl_2 (1 mL) at room temperature. After stirring at room temperature for 1 h, all the volatiles were removed in vacuo. The remaining residue was washed with pentane (1 ml × 3) and dried in vacuo to finally give compound **6e** (141 mg, 0.15 mmol, 77%) as a yellow solid.

Anal. Calc. for $C_{42}H_{12}B_2F_{20}$: C, 54.94; H, 1.32. Found: C, 56.04; H, 1.52.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ ^{1}H: 8.10 (m, 1H, 3-CH=), 7.92 (m, 1H, 8-CH=), 7.80 (d, $^3J_{HH}$ = 8.0 Hz, 1H, 5-CH=), 7.75 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, 6-CH=), 3.91 (d, $^4J_{HH}$ = 1.2 Hz, 2H, CH_2).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ ^{13}C: 161.6 (3-CH=), 151.9 (9-C), 151.8 (br, CB=), 146.6 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 143.7 (4-C), 143.2 (7-C), 142.8 (dm, $^1J_{FC}$ ~ 260 Hz, C_6F_5), 138.0 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 127.4 (6-CH=), 126.0 (5-CH=), 123.8 (8-CH=), 114.9 (br, i-C_6F_5), 42.4 (CH_2).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ ^{19}F: −130.5 (m, 2F, *o*), −151.1 (t, $^3J_{FF}$ = 20.0 Hz, 1F, *p*), −162.0 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 10.9].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ ^{11}B: 56.9 ($\nu_{1/2}$ ~ 1800 Hz).

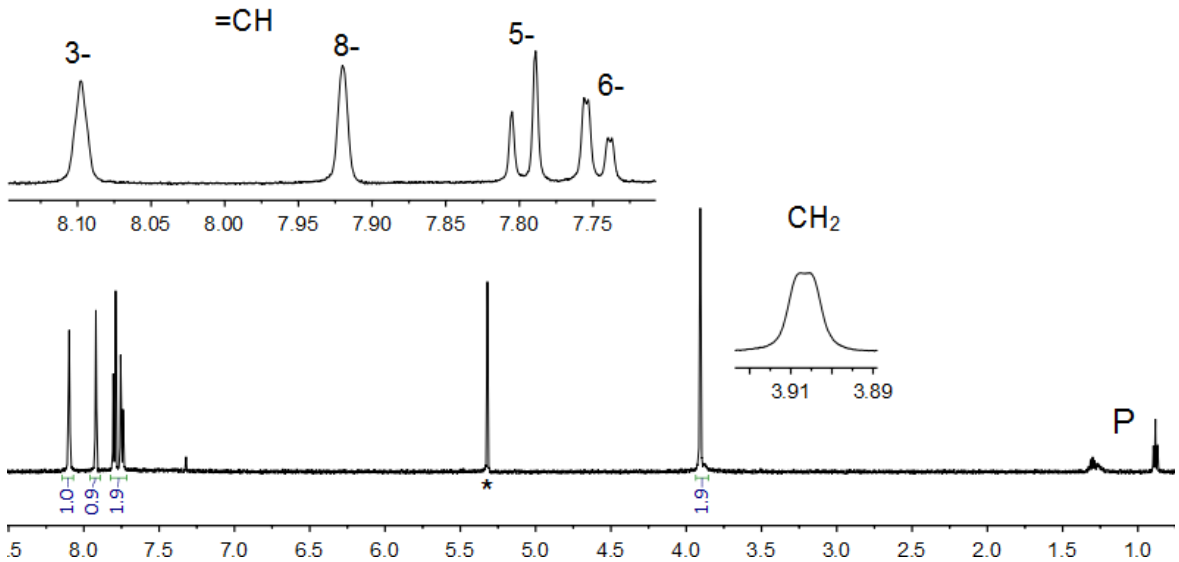


Figure S52. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectrum of compound **6e**. [P: pentane]

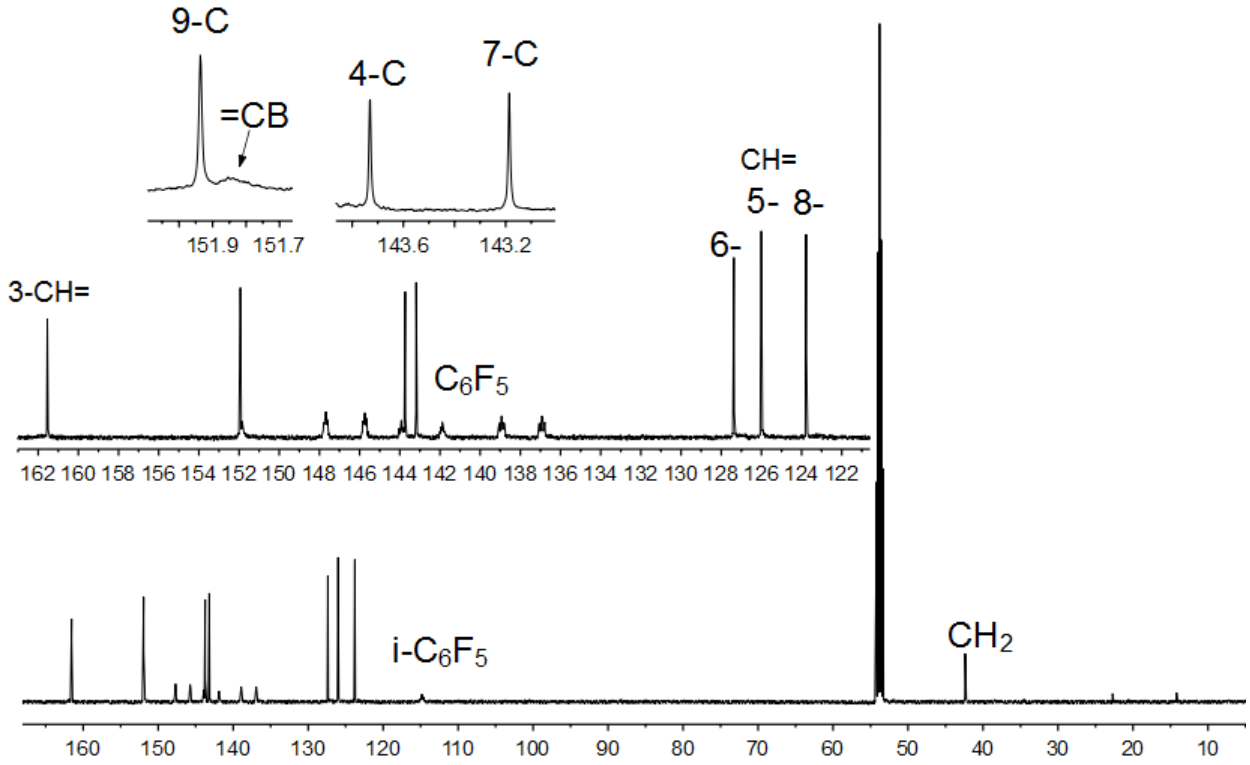


Figure S53. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **6e**.

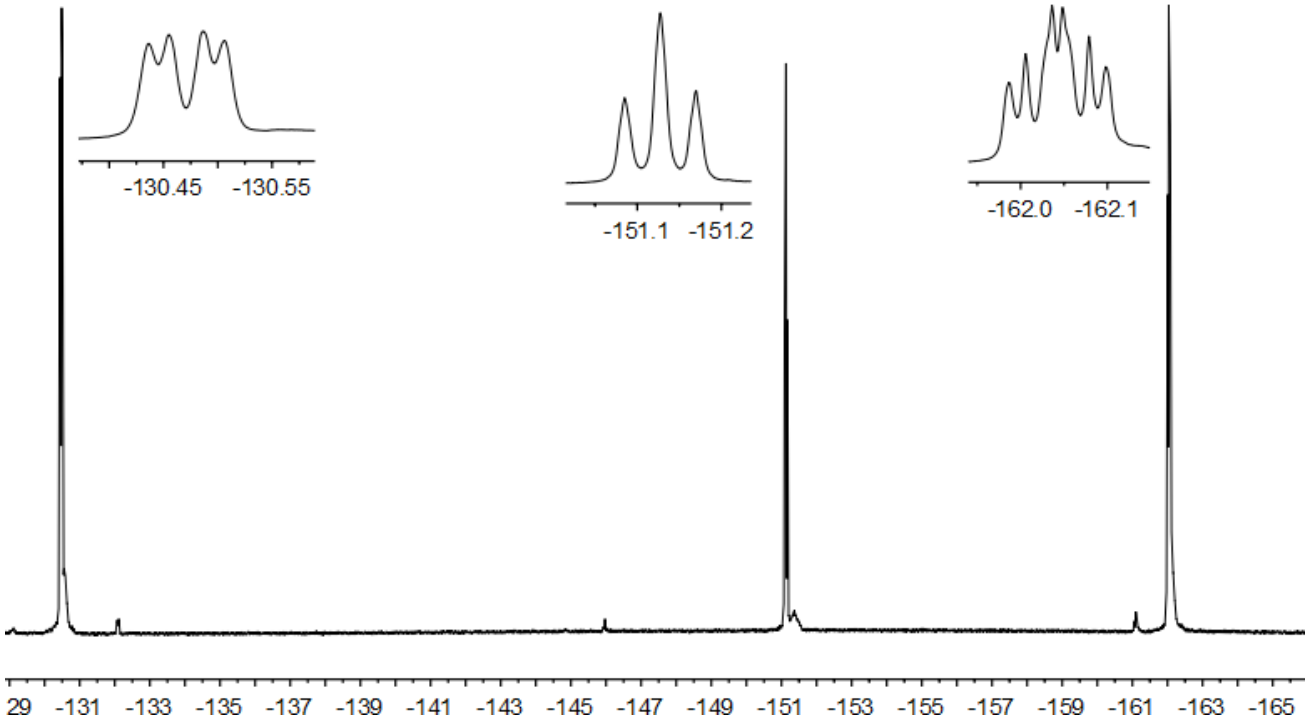


Figure S54. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **6e**.

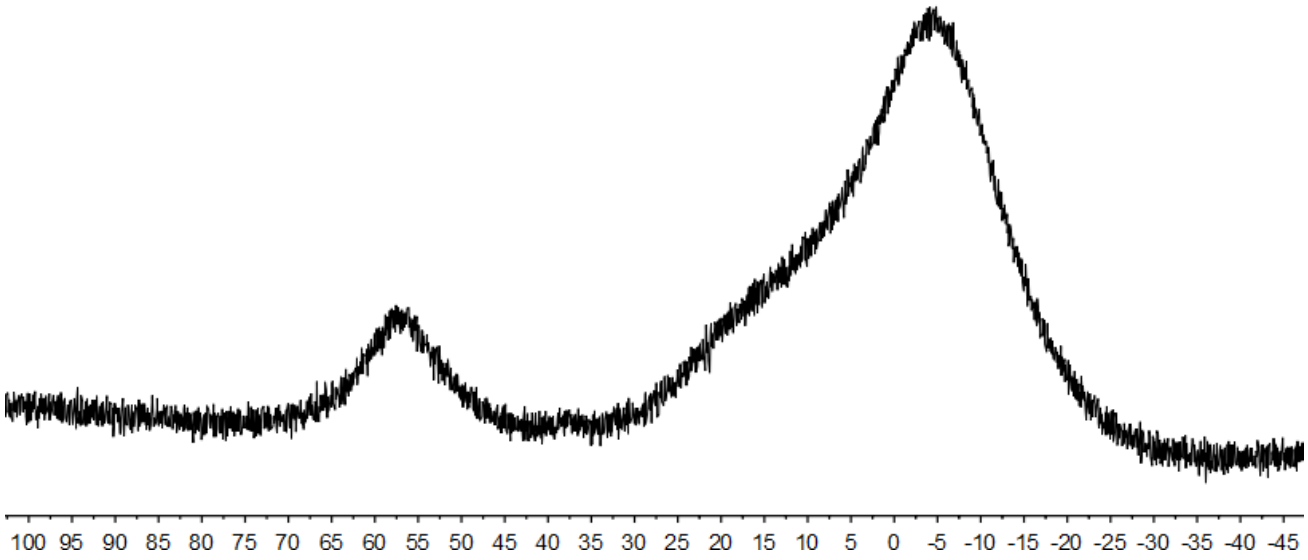
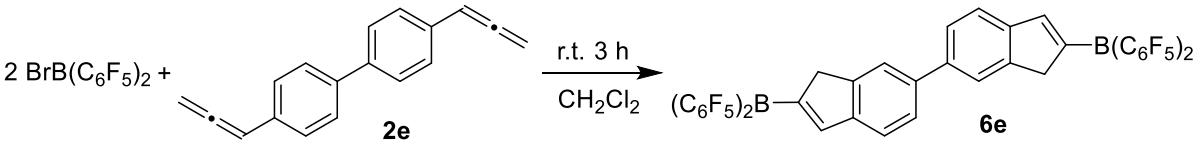


Figure S55. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of compound **6e**.

Experiment 2: (reaction of compound **2e** with $BrB(C_6F_5)_2$, preparative scale)

Scheme S16.



A solution of $BrB(C_6F_5)_2$ (168 mg, 0.40 mmol) in CH_2Cl_2 (1 mL) was added to a solution of compound **2e** (50 mg, 0.22 mmol) in CH_2Cl_2 (1 mL) at room temperature. After stirring at room temperature for 3 h, all the volatiles were removed in vacuo. The remaining residue was washed with pentane (1 ml × 3) and dried in vacuo to finally give compound **6e** (128 mg, 0.14 mmol, 70%) as a yellow solid.

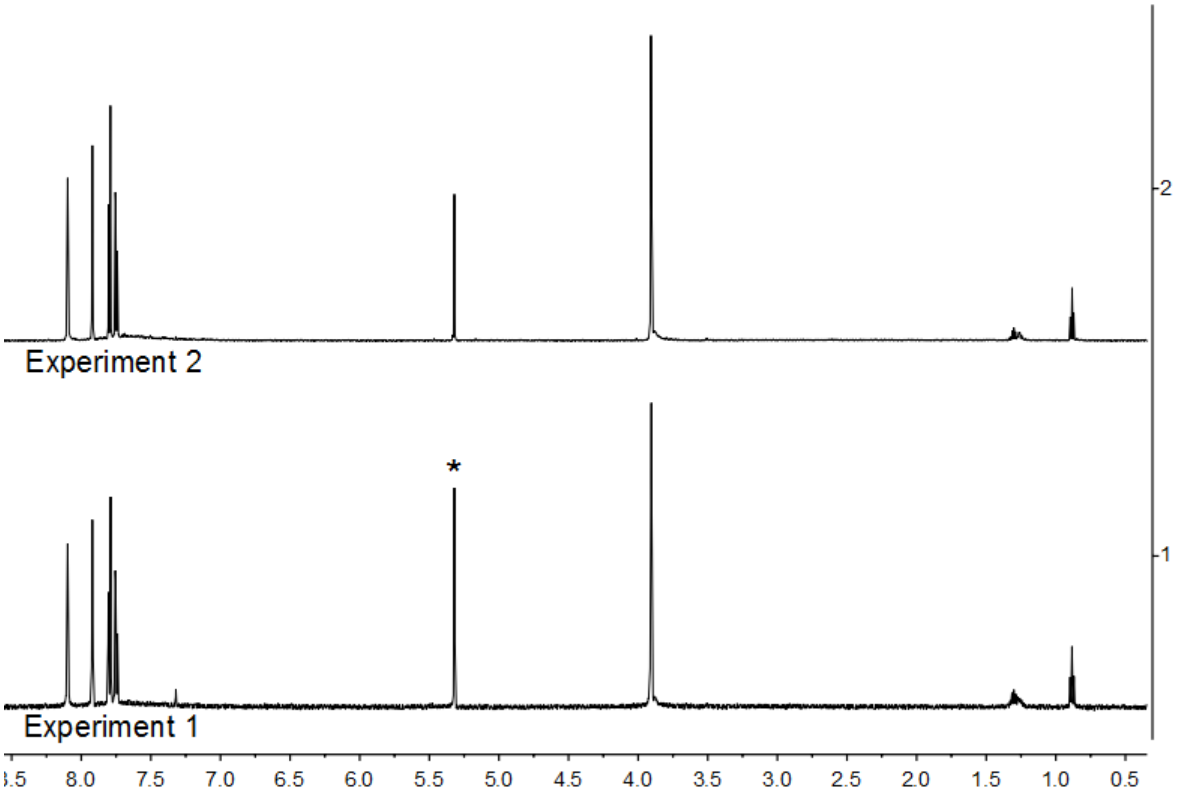


Figure S56. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectra of (1) isolated compound **6e** from Experiment 1 and (2) the yellow solid from Experiment 2.

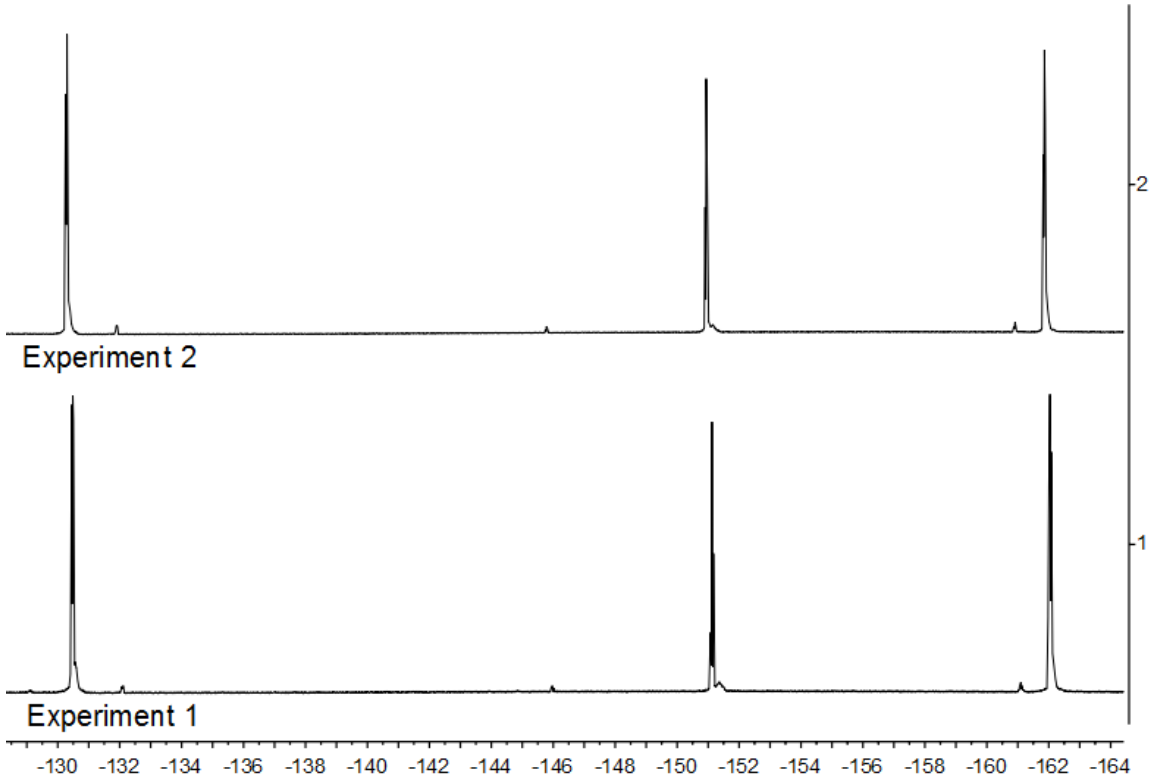


Figure S57. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2*) spectra of (1) isolated compound **6e** from Experiment 1 and (2) the yellow solid from Experiment 2.

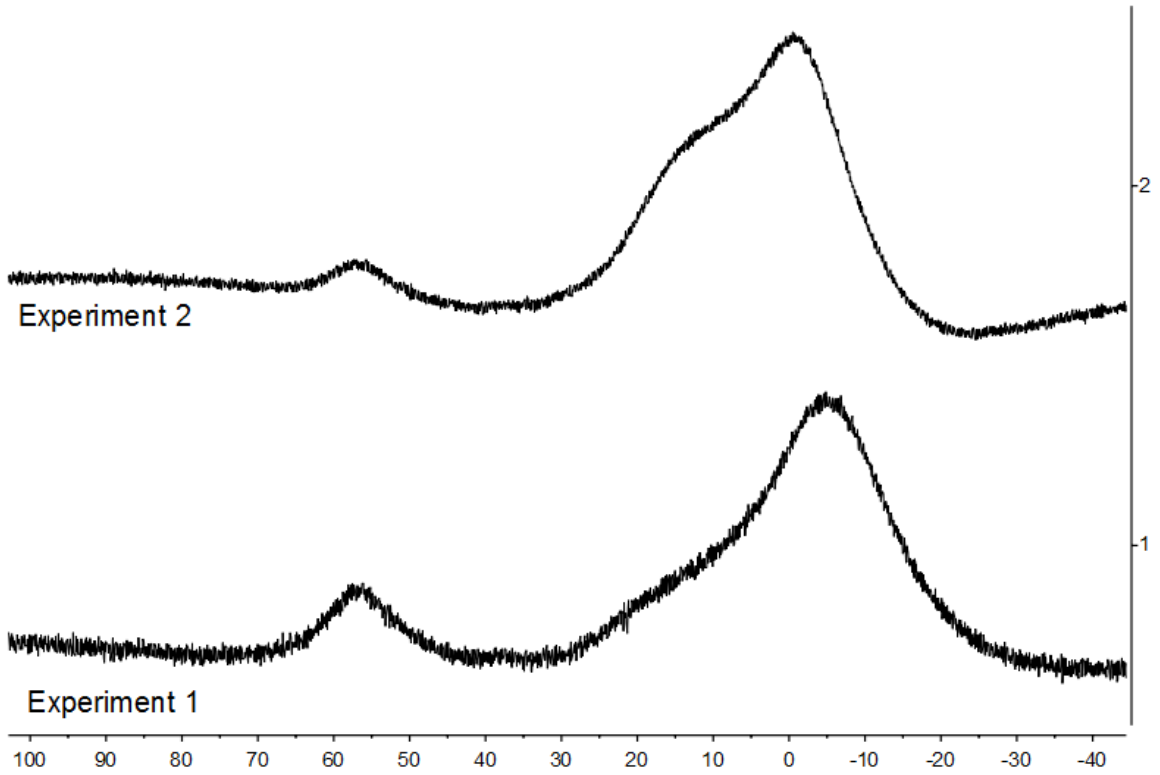
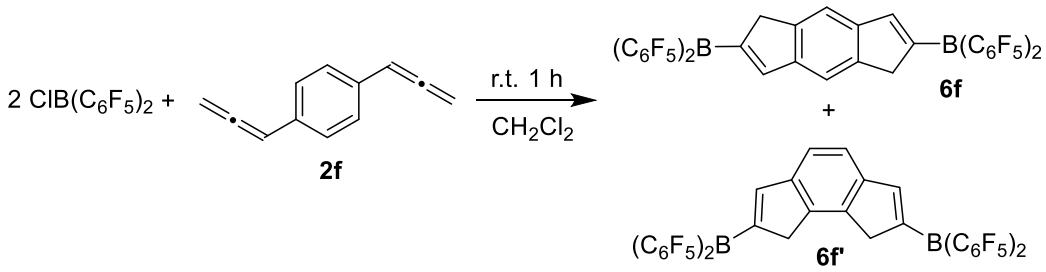


Figure S58. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2*) spectra of (1) isolated compound **6e** from Experiment 1 and (2) the yellow solid from Experiment 2.

G) Synthesis of compounds **6f** and **6f'**

Experiment 1: (reaction of compound **2f** with $ClB(C_6F_5)_2$, preparative scale)

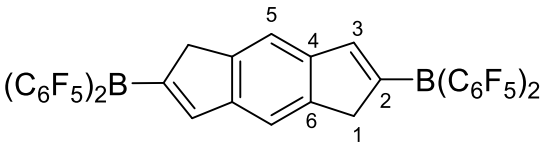
Scheme S17.



A solution of $ClB(C_6F_5)_2$ (190 mg, 0.50 mmol) in CH_2Cl_2 (1 mL) was added to a solution of compound **2f** (38.5 mg, 0.25 mmol) in CH_2Cl_2 (1 mL) at room temperature. After stirring at room temperature for 1 h, all the volatiles were removed in vacuo. The remaining residue was washed with pentane (1 ml × 3) and dried in vacuo to finally give a mixture (195 mg, 0.23 mmol, 93%) of compounds **6f** (59 mol%, ^1H) and **6f'** (41 mol%, ^1H) as a green solid.

Anal. Calc. for $C_{36}H_8B_2F_{20}$: C, 51.35; H, 0.96. Found: C, 51.79; H, 1.09.

NMR data of compound **6f** in the mixture:



6f

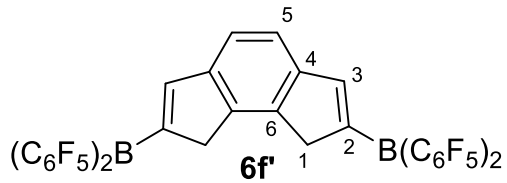
^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ ^{1}H: 8.10 (m, 1H, 3-CH=), 7.88 (m, 1H, 5-CH=), 3.88 (d, $^{4}J_{HH}$ = 1.3 Hz, 2H, CH_2).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ ^{13}C: 161.2 (3-CH=), 153.4 (br, CB=), [150.3, 146.4](4,6-C), 146.7 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 142.9 (dm, $^{1}J_{FC}$ ~ 260 Hz, C_6F_5), 137.9 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 121.2 (5-CH=), 114.6 (br, i-C_6F_5), 41.9 (CH_2).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ ^{19}F: −130.3 (m, 2F, *o*), −150.7 (t, $^{3}J_{FF}$ = 20.0 Hz, 1F, *p*), −161.9 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 11.2].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ ^{11}B: 56.7 ($\nu_{1/2}$ ~ 1500 Hz).

NMR data of compound **6f'** in the mixture:



6f'

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ ^{1}H: 8.12 (m, 1H, 3-CH=), 7.75 (m, 1H, 5-CH=), 3.89 (d, $^{4}J_{HH}$ = 2.0 Hz, 2H, CH_2).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ ^{13}C: 161.7 (3-CH=), 152.5 (br, CB=), 146.7 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), [146.2, 146.1](4,6-C), 142.9 (dm, $^{1}J_{FC}$ ~ 260 Hz, C_6F_5), 137.9 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 125.2 (5-CH=), 114.6 (br, i-C_6F_5), 40.9 (CH_2).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ ^{19}F: −130.3 (m, 2F, *o*), −150.7 (t, $^{3}J_{FF}$ = 20.0 Hz, 1F, *p*), −161.9 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 11.2].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ ^{11}B: 56.7 ($\nu_{1/2}$ ~ 1500 Hz).

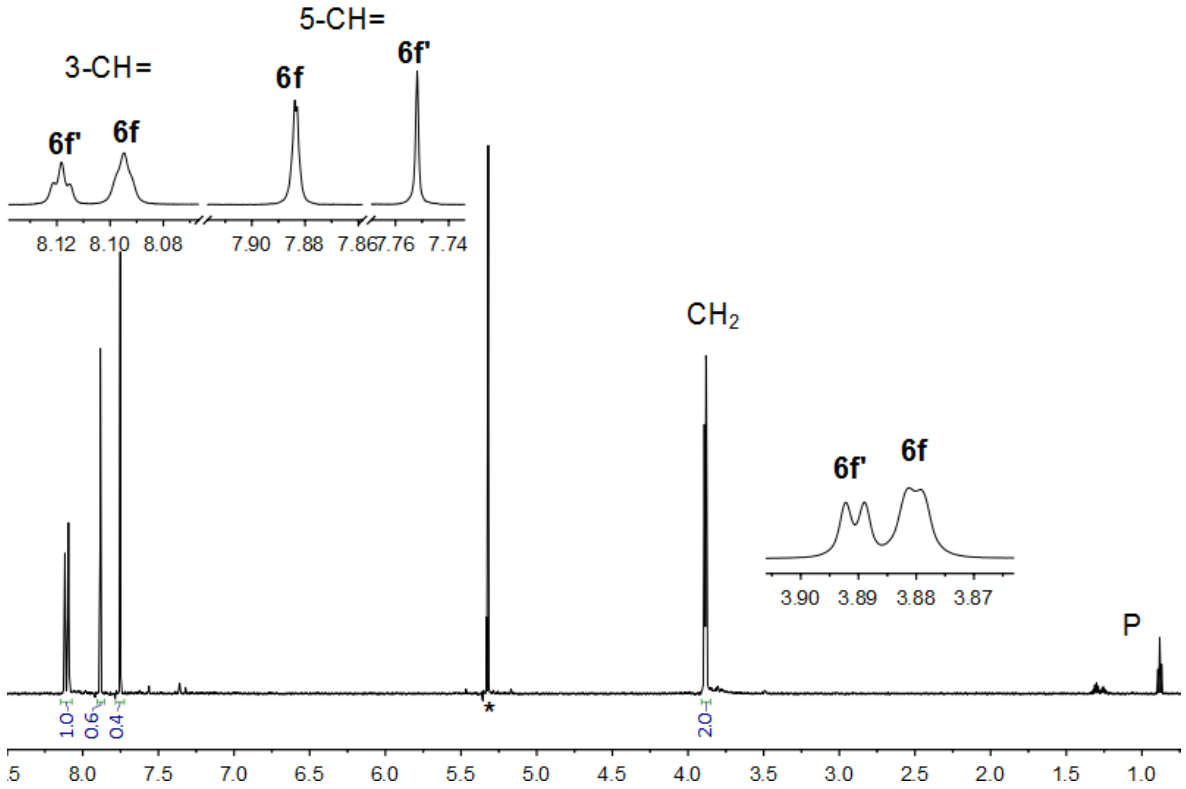


Figure S59. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectrum of the isolated mixture. [P: pentane]

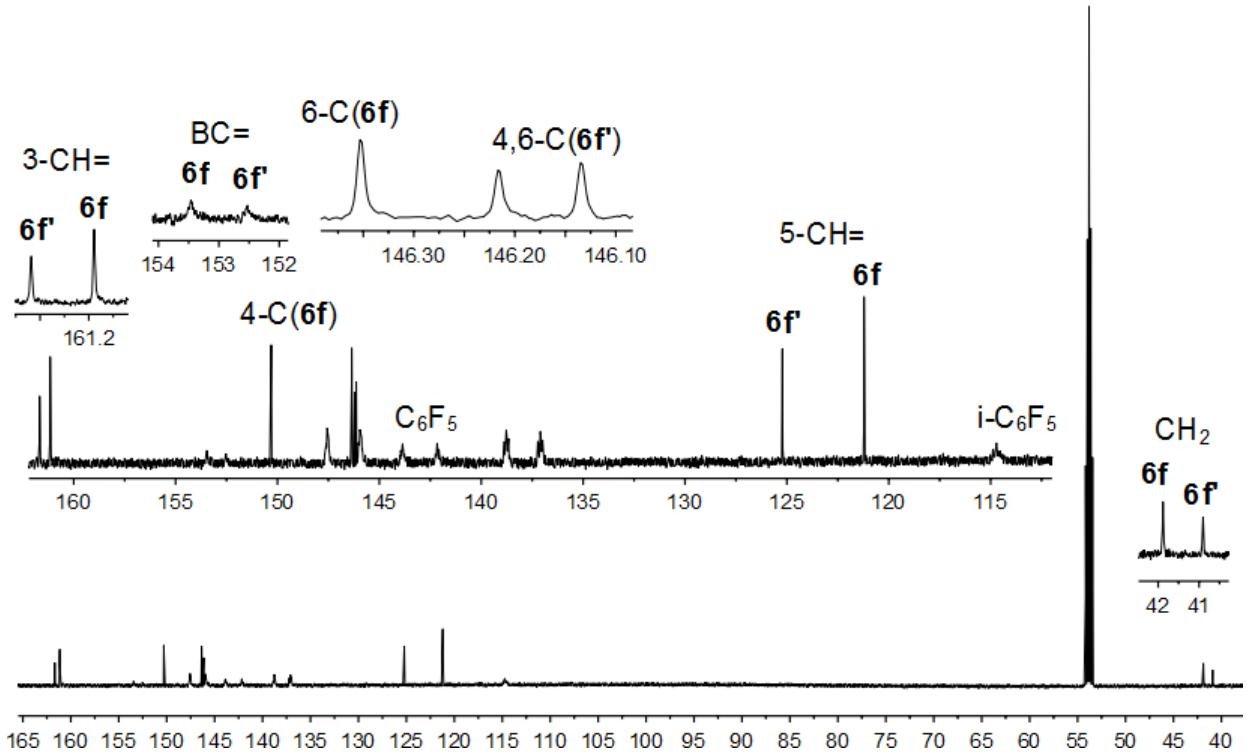


Figure S60. ^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of the isolated mixture.

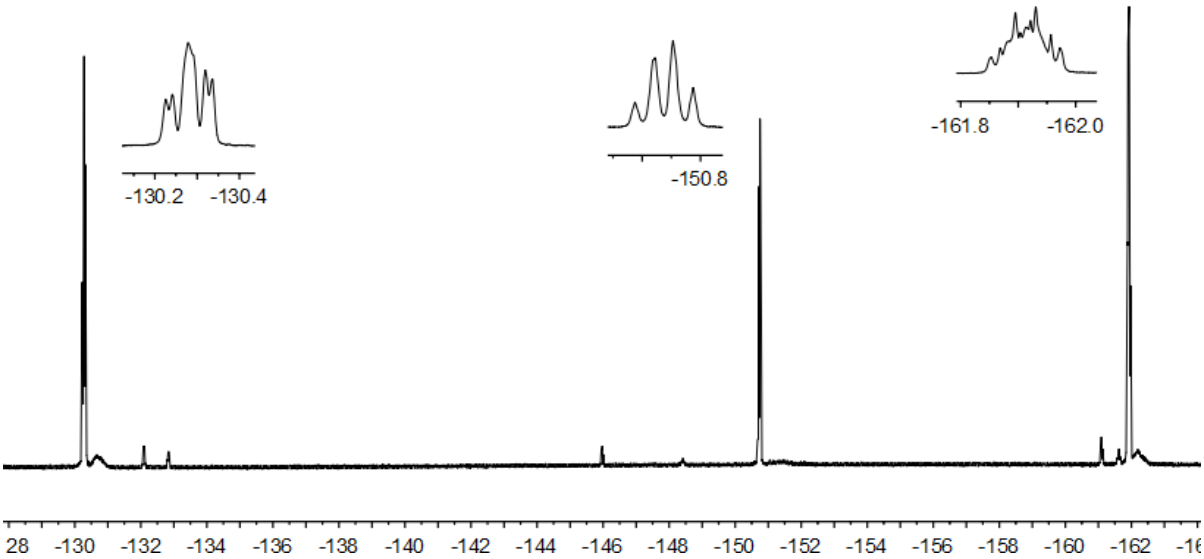


Figure S61. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of the isolated mixture.

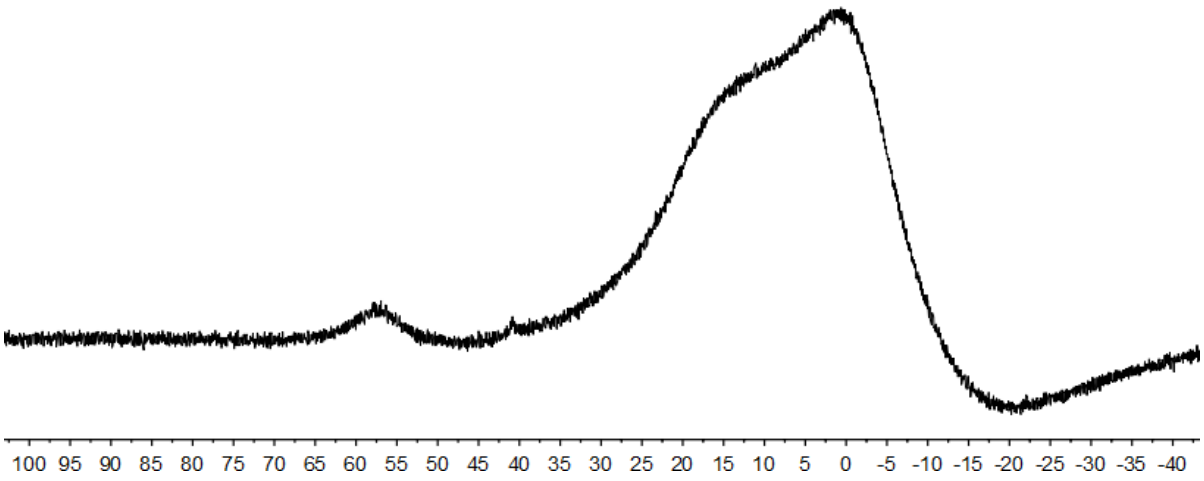


Figure S62. $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of the isolated mixture.

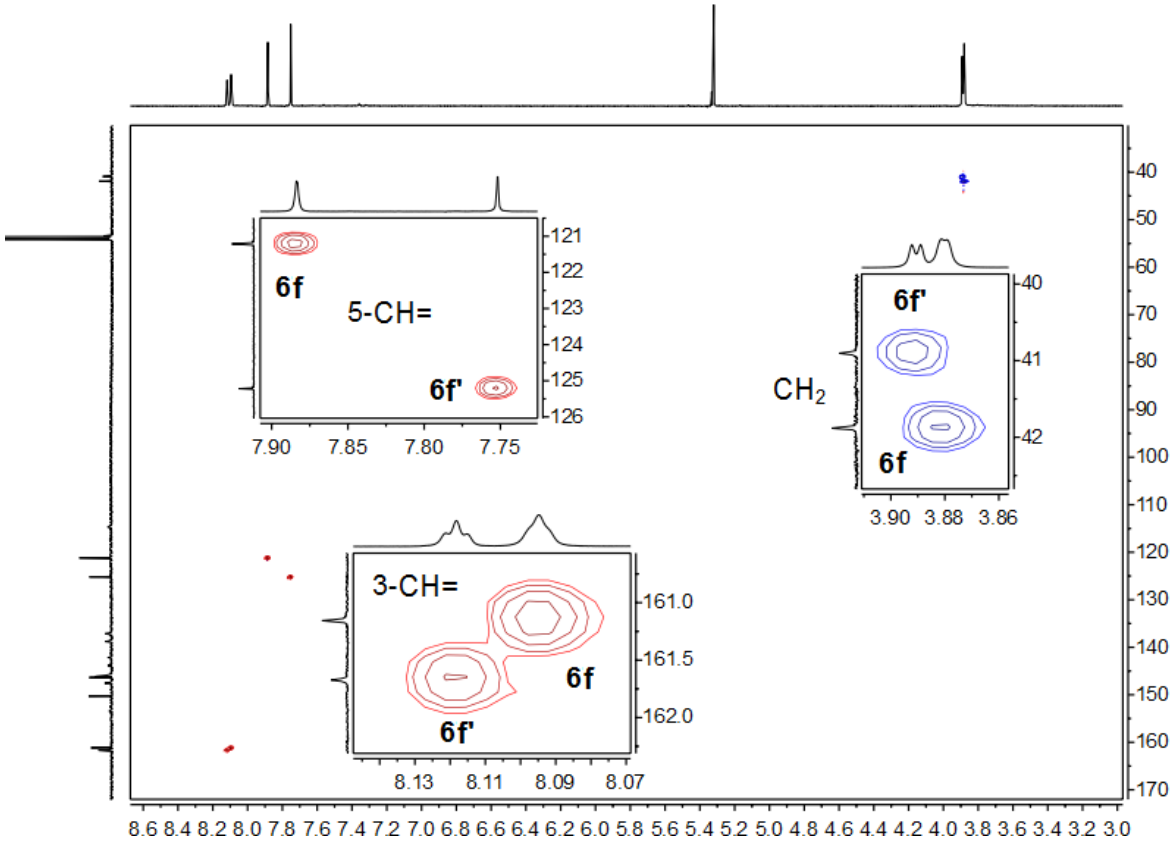


Figure S63. $^{1}H,^{13}C$ GHSQC (600/151 MHz, CD_2Cl_2, 299K) spectrum of the isolated mixture.

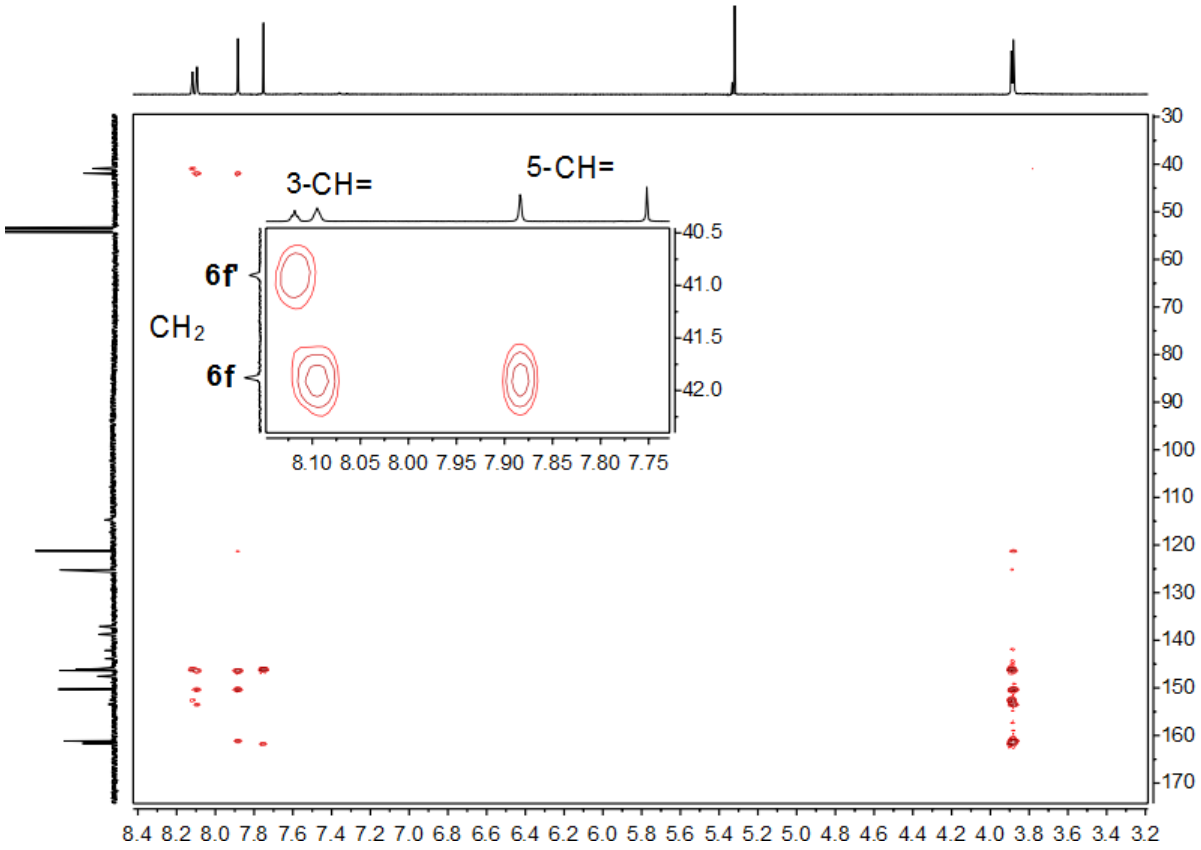
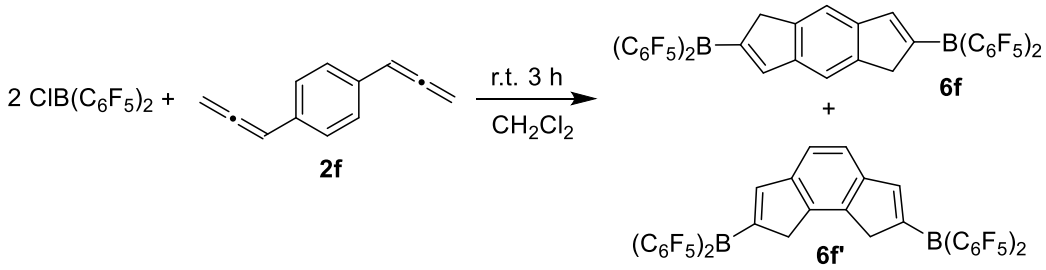


Figure S64. $^{1}H,^{13}C$ GHMBC (600/151 MHz, CD_2Cl_2, 299K) spectrum of the isolated mixture.

Experiment 2: (reaction of compound **2f** with $BrB(C_6F_5)_2$, preparative scale)

Scheme S18.



A solution of $BrB(C_6F_5)_2$ (168 mg, 0.40 mmol) in CH_2Cl_2 (1 mL) was added to a solution of compound **2f** (30.8 mg, 0.20 mmol) in CH_2Cl_2 (1 mL) at room temperature. After stirring at room temperature for 3 h, all the volatiles were removed in vacuo. The remaining residue was washed with pentane (1 ml × 3) and dried in vacuo to finally give a mixture (115 mg, 0.14 mmol, 70%) of compounds **6f** (63 mol%, ^{1}H) and **6f'** (37 mol%, ^{1}H) as a green solid.

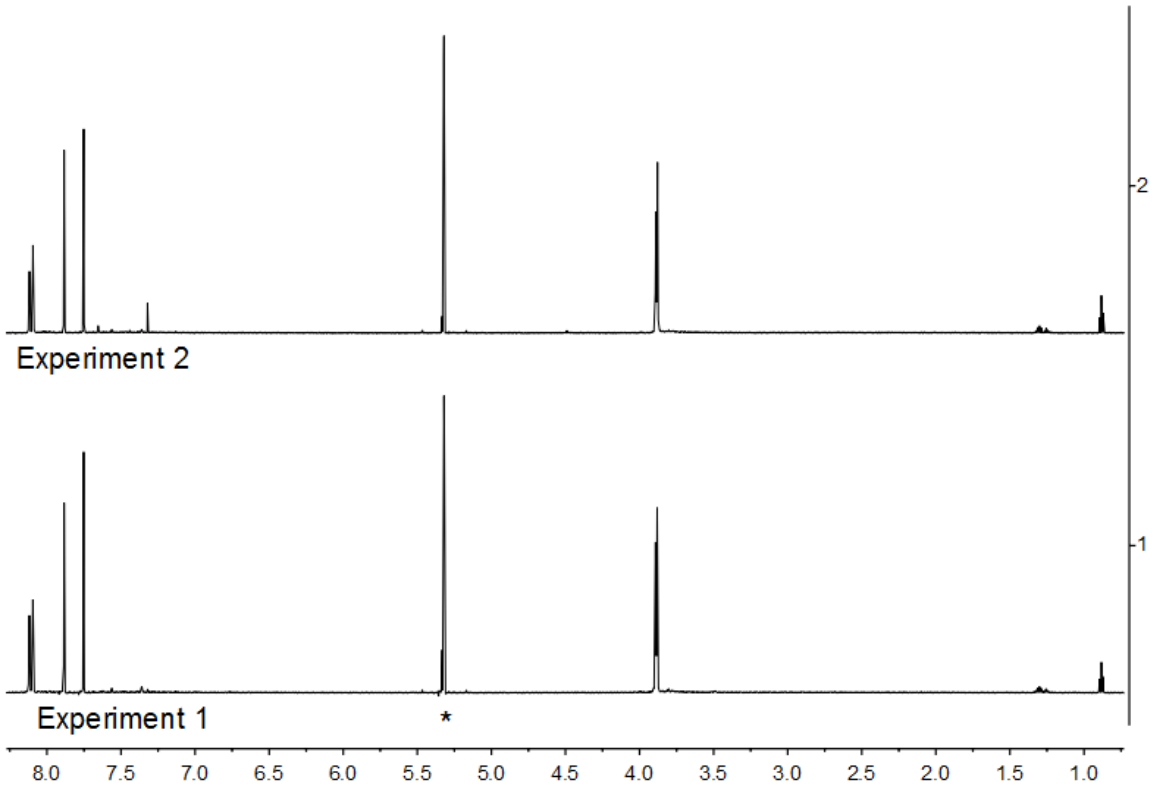


Figure S65. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectra of the isolated mixtures from Experiment 1 (spectrum 1) and Experiment 2 (spectrum 2).

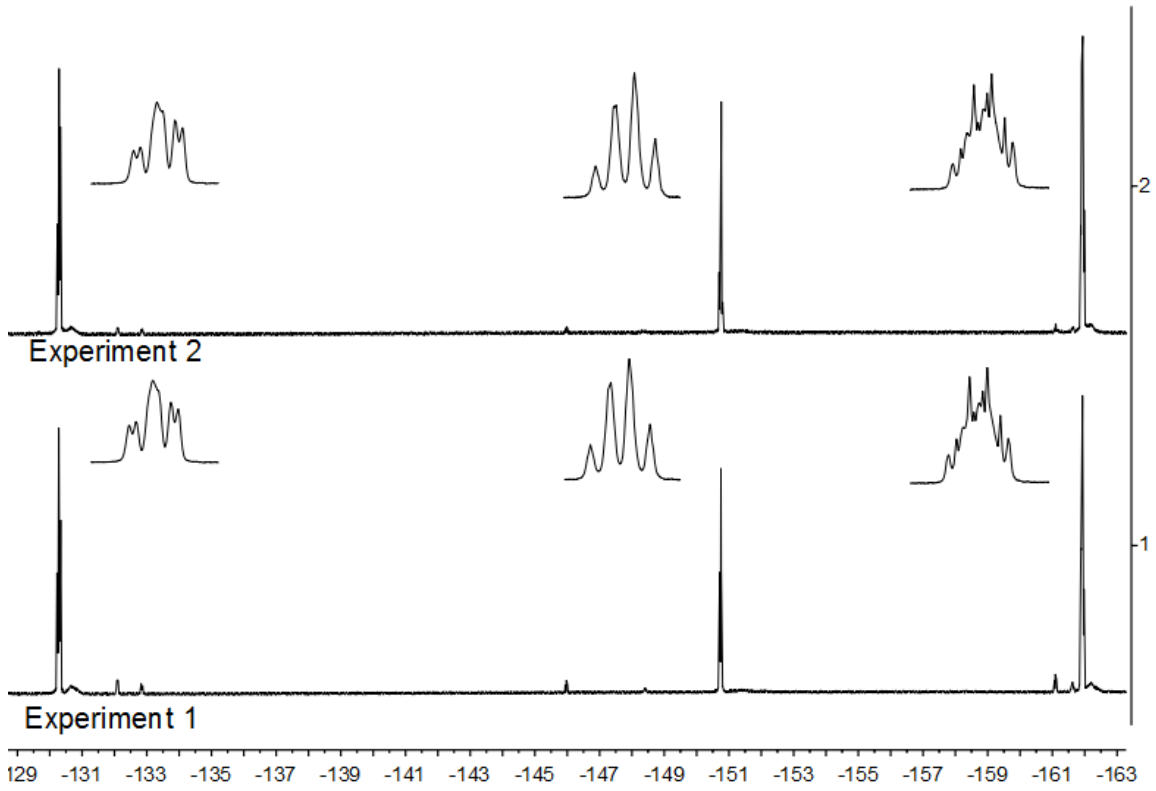


Figure S66. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectra of the isolated mixtures from Experiment 1 (spectrum 1) and Experiment 2 (spectrum 2).

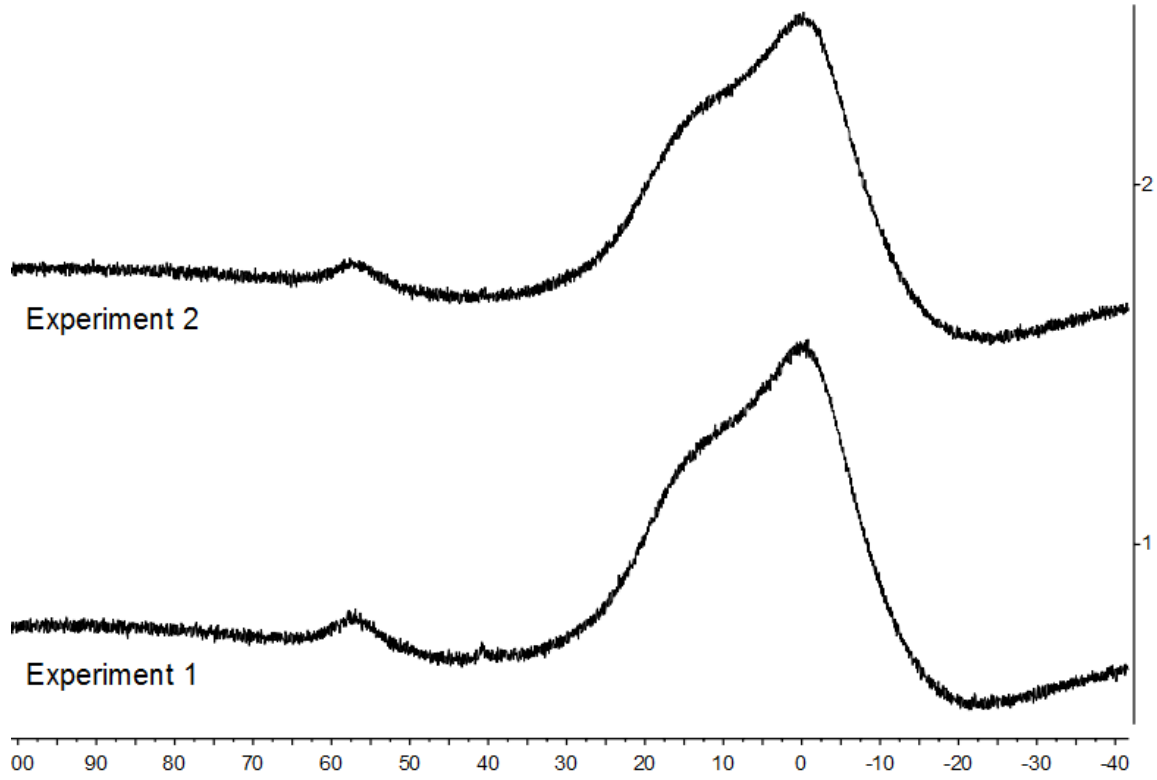
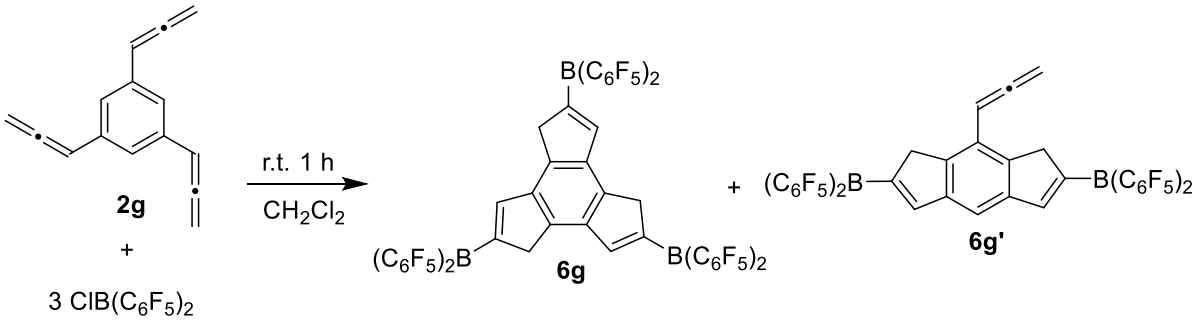


Figure S67. ^{11}B NMR (192 MHz, 299 K, CD_2Cl_2) spectra of the isolated mixtures from Experiment 1 (spectrum 1) and Experiment 2 (spectrum 2).

H) Synthesis of compounds **6g** and **6g'**

Experiment 1: (reaction of compound **2g** with 3 $ClB(C_6F_5)_2$, X-ray crystal structure analysis of **6g'**)

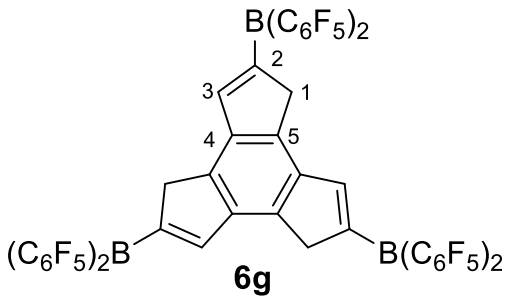
Scheme S19.



A solution of $ClB(C_6F_5)_2$ (114 mg, 0.30 mmol) in CH_2Cl_2 (0.5 mL) was added to a solution of compound **2g** (18.6 mg, 0.10 mmol) in CH_2Cl_2 (0.5 mL) at room temperature. After stirring at room temperature for 1 h, the yellow suspension was filtered. The remaining solid was washed with CH_2Cl_2 (0.5 ml × 3), then with pentane (0.5 ml × 3). Drying in vacuo of the solid gave compound **6g** (25 mg, 0.020 mmol, 20 %) as a yellow powder.

Anal. Calc. for $C_{51}H_9B_3F_{30}$: C, 50.05; H, 0.74. Found: C, 49.24; H, 0.69.

NMR data of compound **6g**: (only slightly soluble in CD_2Cl_2)



^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ ^{1}H: 8.22 (t, $^4J_{HH}$ = 2.0 Hz 1H, CH=), 4.12 (d, $^4J_{HH}$ = 2.0 Hz, 2H, CH_2).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ ^{13}C: 158.3 (CH=), 151.3 (br, CB=), [149.0, 139.6](4,5-C), 41.4 (CH_2). [C_6F_5 not assigned]

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ ^{19}F: −130.1 (m, 2F, *o*), −150.4 (t, $^3J_{FF}$ = 20.0 Hz, 1F, *p*), −161.7 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 11.3].

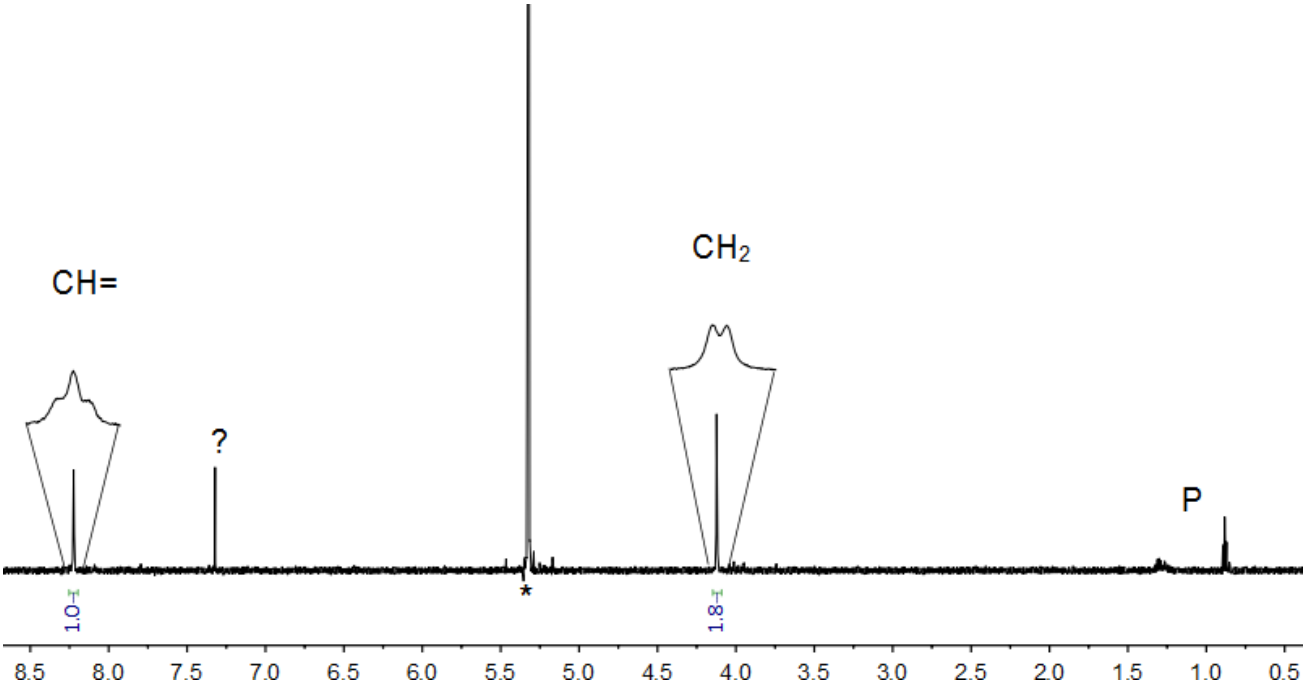


Figure S68. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectrum of the isolated compound **6g**. [?: signal from solvent; P: pentane]

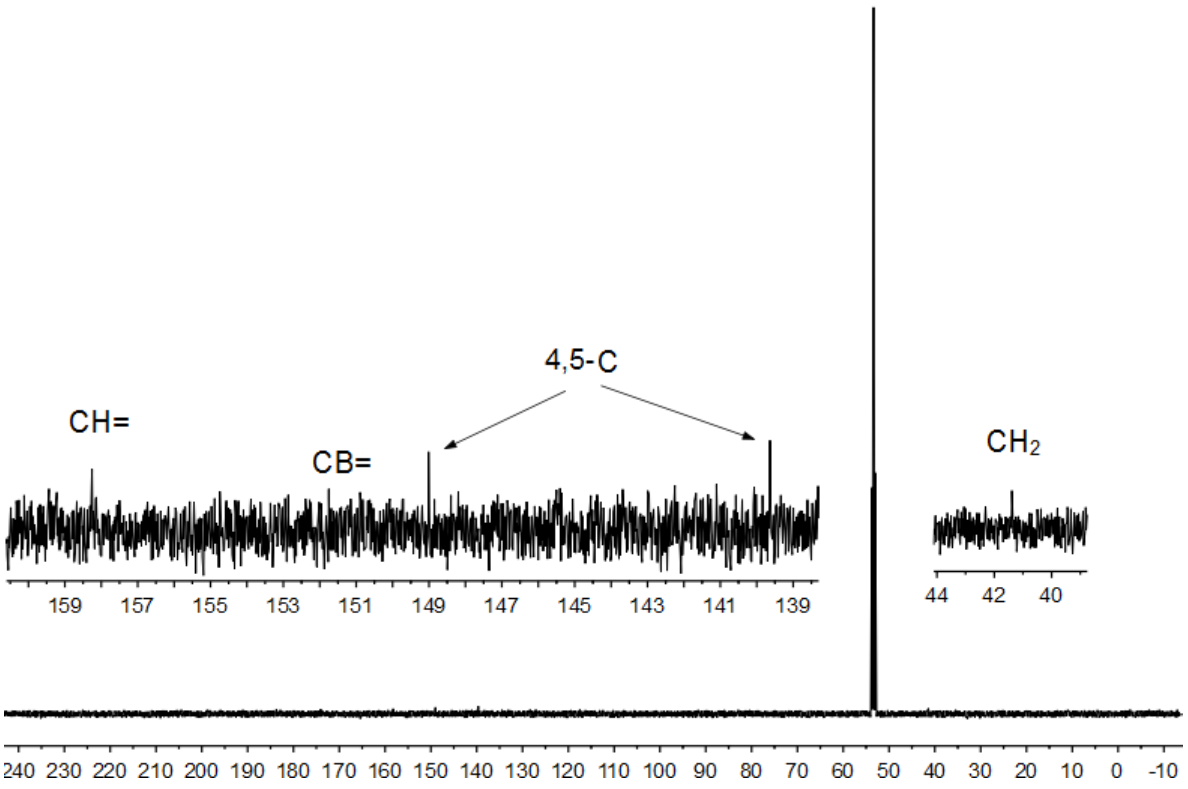


Figure S69. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of the isolated compound **6g**.

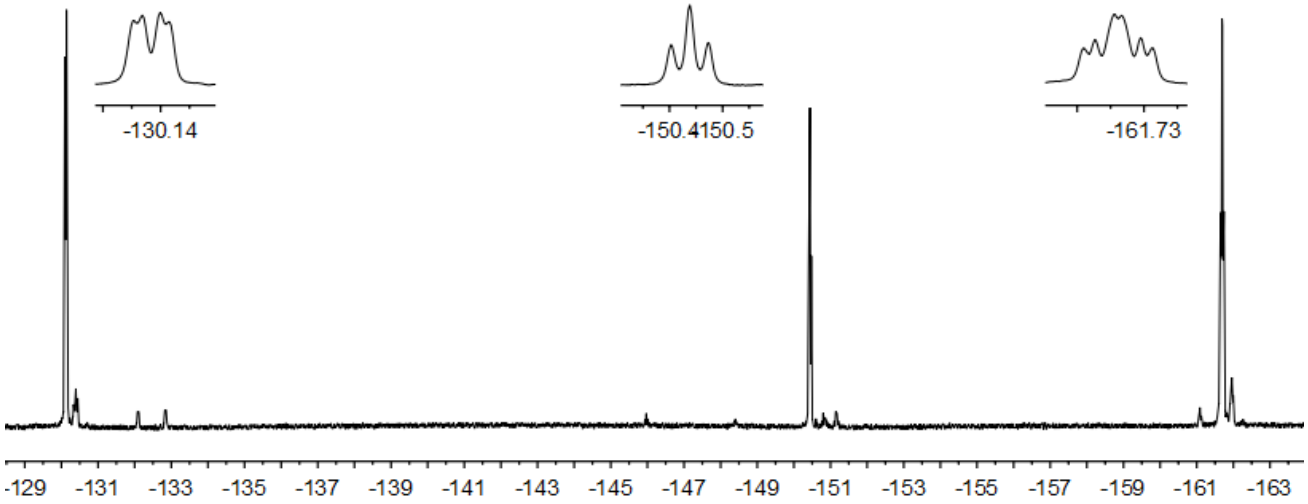


Figure S70. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of the isolated compound **6g**.

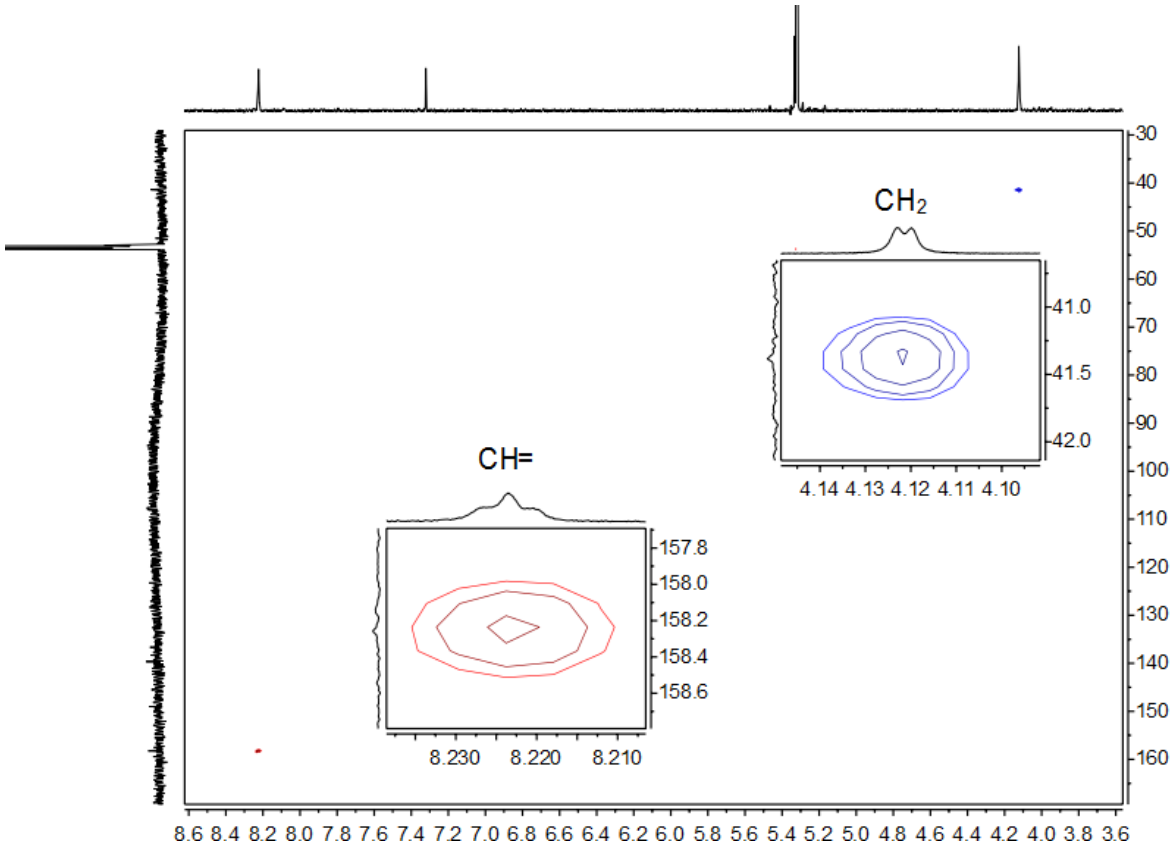


Figure S71. $^{1}H,^{13}C$ GHSQC (600/151 MHz, CD_2Cl_2, 299K) spectrum of the isolated compound **6g**.

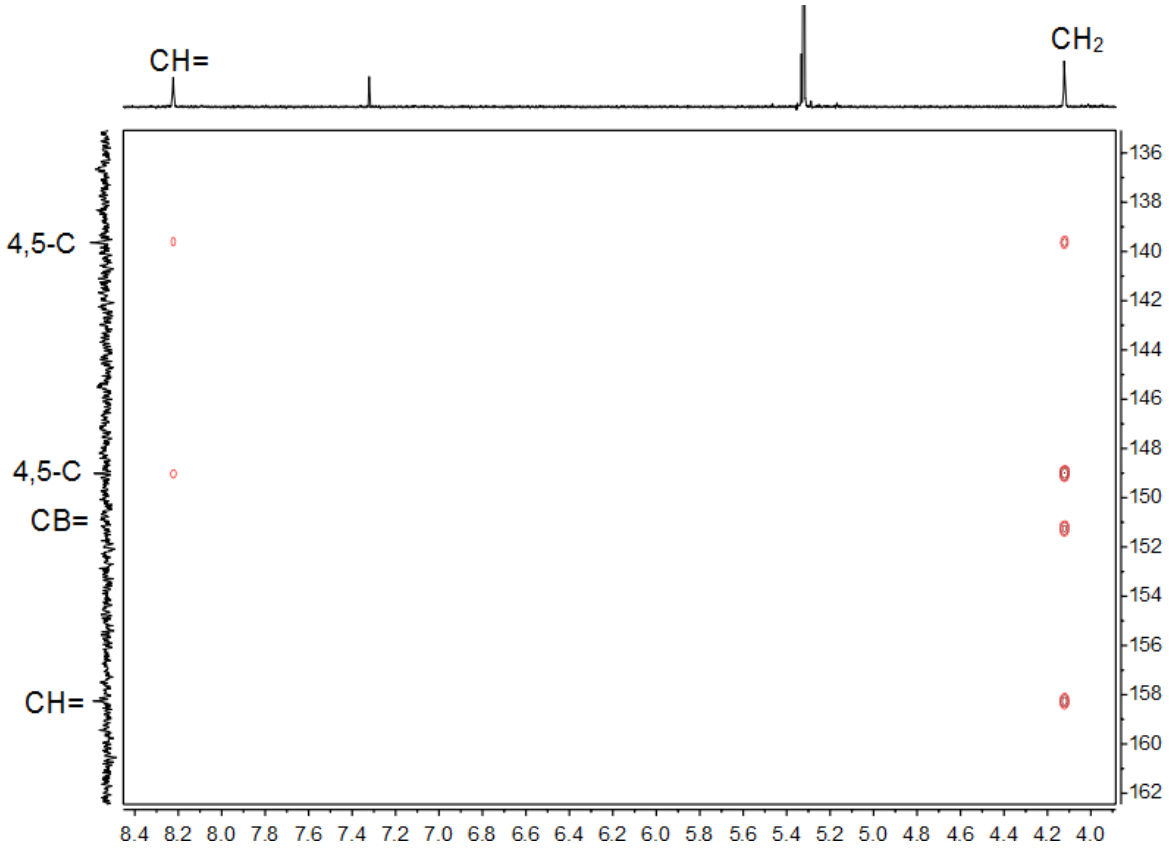


Figure S72. $^{1}H,^{13}C$ GHMBC (600/151 MHz, CD_2Cl_2, 299K) spectrum of the isolated compound **6g**.

The combined filtrates were stored at −35 °C giving compound **6g'** as a few yellow crystals, which were suited for the X-ray crystal structure analysis.

X-ray crystal structure analysis of compound 6g' (erk9249): A yellow plate-like specimen of $C_{39}H_{10}B_2F_{20}$, approximate dimensions 0.020 mm x 0.070 mm x 0.100 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a monoclinic unit cell yielded a total of 5579 reflections to a maximum θ angle of 25.00° (0.84 Å resolution), of which 5579 were independent (average redundancy 1.000, completeness = 99.0%, R_{sig} = 6.19%) and 4058 (72.74%) were greater than $2\sigma(F^2)$. The final cell constants of a = 16.3020(4) Å, b = 31.6317(11) Å, c = 6.8859(3) Å, β = 104.0370(10)°, volume = 3444.8(2) Å^3, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9830 and 0.9970. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *Cc*, with Z = 4 for the formula unit, $C_{39}H_{10}B_2F_{20}$. The final anisotropic full-matrix least-squares refinement on F^2 with 659 variables converged at R1 = 8.10%, for the observed data and wR2 = 16.23% for all data. The goodness-of-fit was 1.145. The largest peak in the final difference electron density synthesis was 0.254 e^-/Å^3 and the largest hole was -0.260 e^-/Å^3 with an RMS deviation of 0.055 e^-/Å^3. On the basis of the final model, the calculated density was 1.697 g/cm^3 and F(000), 1736 e^-. CCDC number: 1907606.

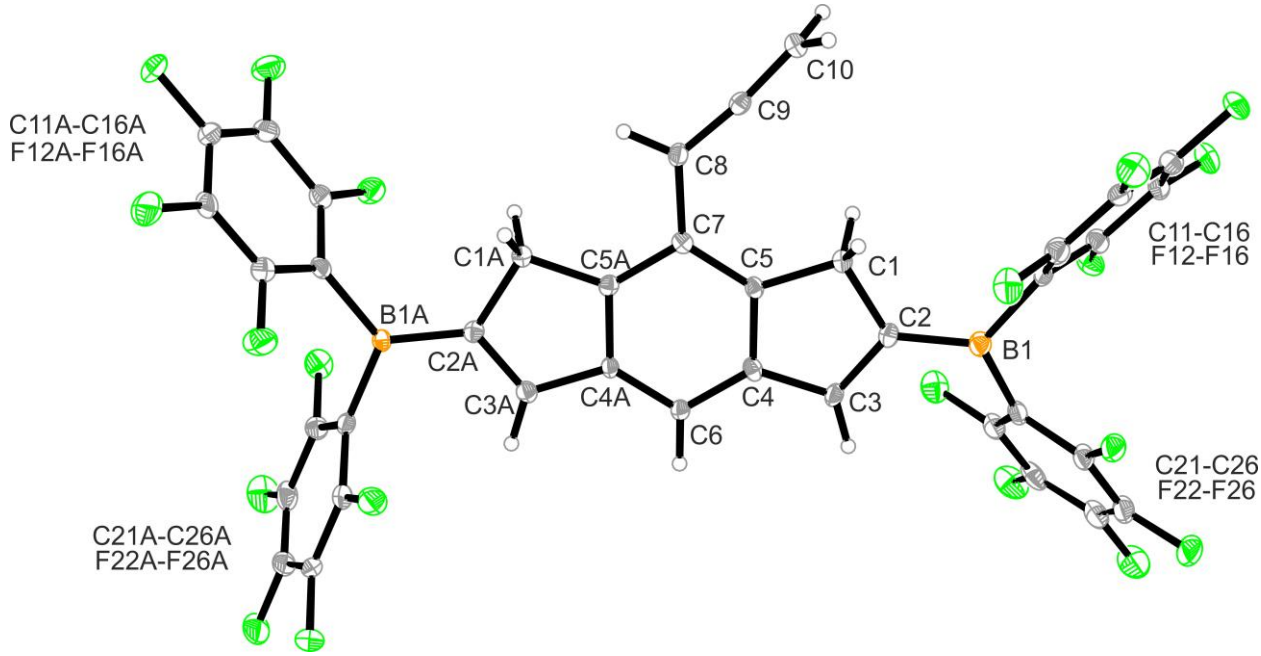
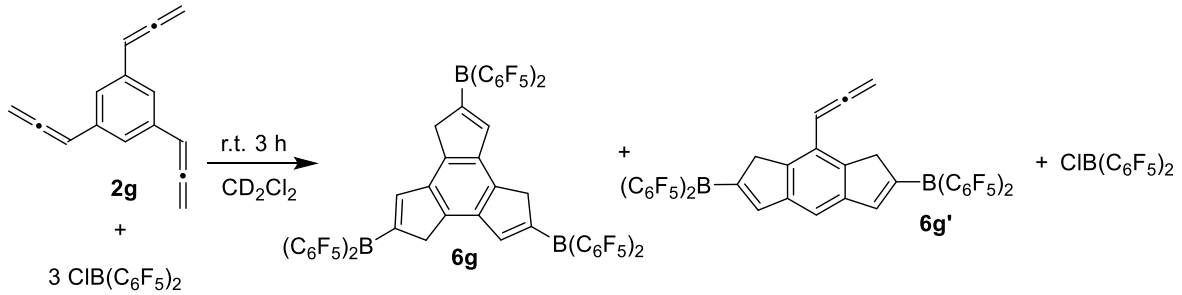


Figure S73. Crystal structure of compound **6g'** (thermal ellipsoids: 15% probability)

Experiment 2: (reaction of compound **2g** with 3 $ClB(C_6F_5)_2$, isolation of compound **6g**, in situ characterization of compound **6g'**)

Scheme S20.



A solution of compound **2g** (9.3 mg, 0.05 mmol) in CD_2Cl_2 (0.3 mL) was added to a solution of $ClB(C_6F_5)_2$ (57 mg, 0.15 mmol) in CD_2Cl_2 (0.3 mL) at room temperature. After stirring at room temperature for 3 h, the yellow suspension was filtered. The filtrate (a yellow solution) was characterized by NMR experiments [a mixture of compound **6g** (1 mol%, ^1H) compound **6g'** (28 mol%, ^{19}F) and unreacted $ClB(C_6F_5)_2$ (71 mol%, ^{19}F) and other unknown components]. The residual solid was washed with pentane (1 ml × 3) and dried in vacuo to give a yellow solid (21 mg, 0.017 mmol, 34 %), which was characterized as compound **6g** [characterization of this yellow solid see Experiment 3].

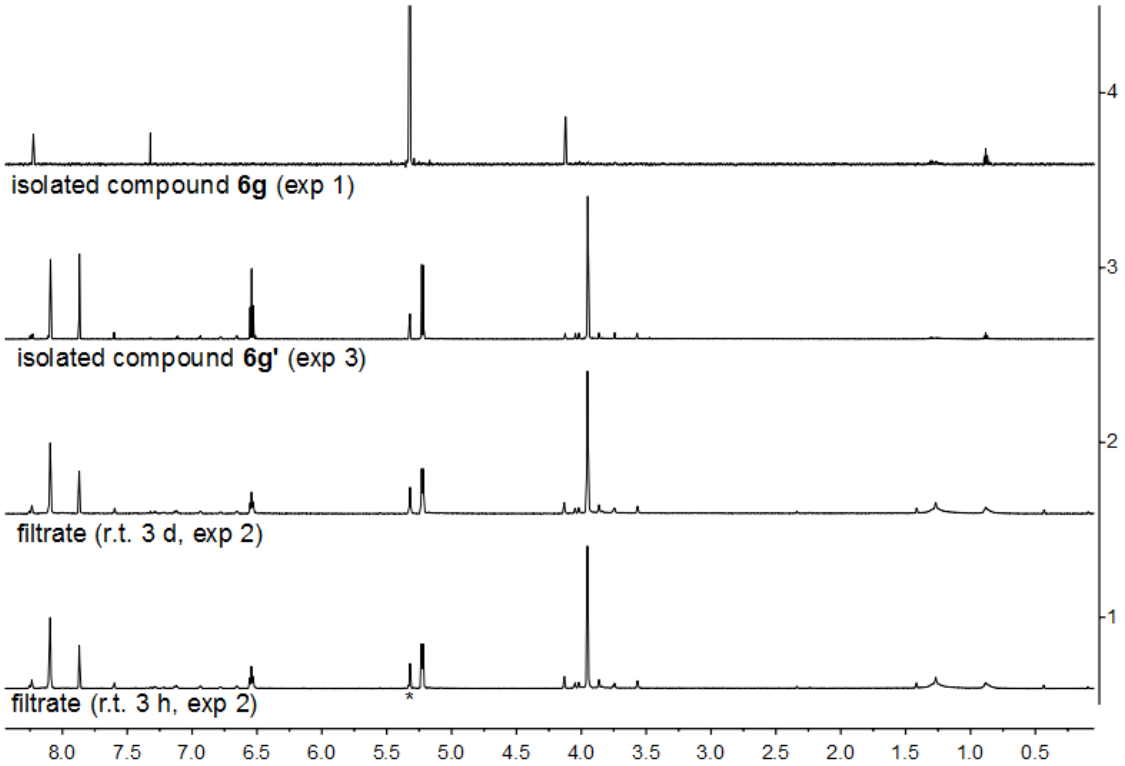


Figure S74. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectra of (1) the filtrate (r.t. 3h) from Experiment 2, (2) the filtrate (r.t. 3d) from Experiment 2, (3) the isolated compound **6g'** from Experiment 3 and (4) the isolated compound **6g**.

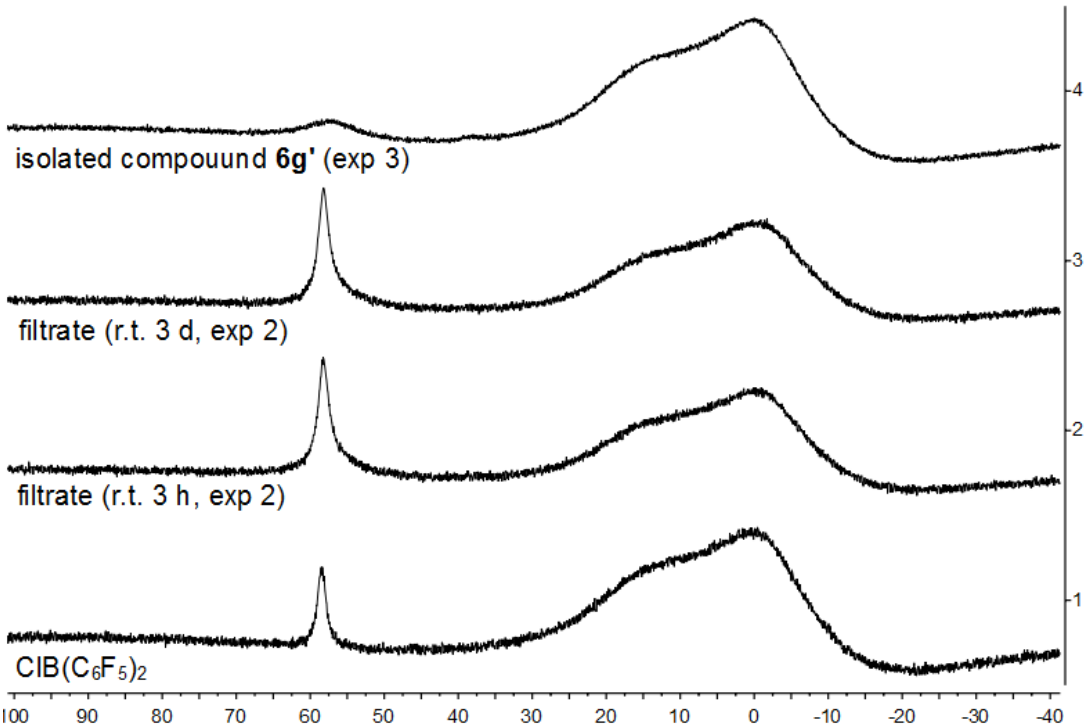


Figure S75. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2*) spectra of (1) the filtrate (r.t. 3h) from Experiment 2, (2) the filtrate (r.t. 3d) from Experiment 2 and (3) the isolated compound **6g'** from Experiment 3.

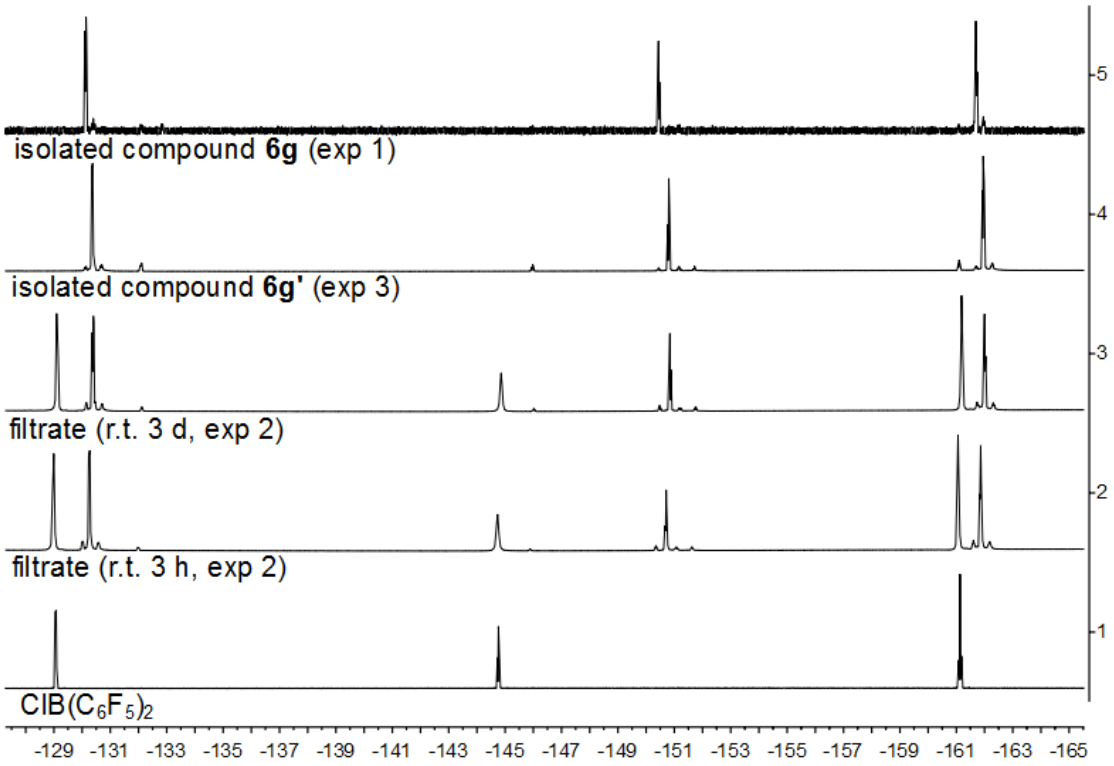
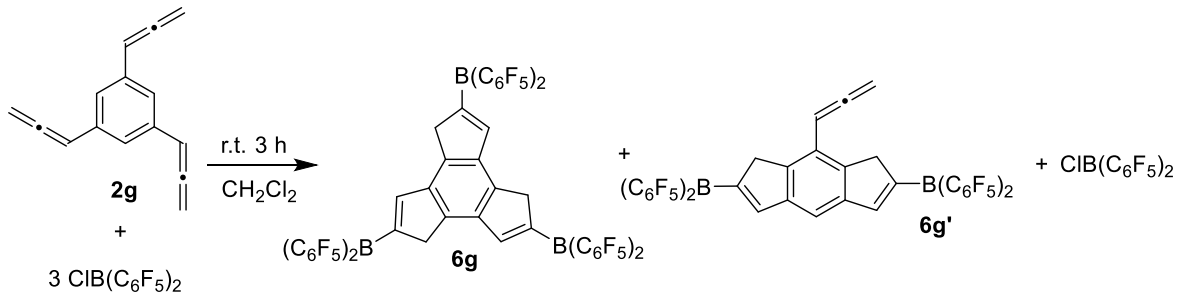


Figure S76. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2*) spectra of (1) the filtrate (r.t. 3h) from Experiment 2, (2) the filtrate (r.t. 3d) from Experiment 2, (3) the isolated compound **6g'** from Experiment 3 and (4) the isolated compound **6g**.

Experiment 3: (reaction of compound **2g** with 3 $ClB(C_6F_5)_2$, isolation of compounds **6g** and **6g'**)

Scheme S21.



A solution of compound **2g** (37.2 mg, 0.20 mmol) in CH_2Cl_2 (1 mL) was added to a solution of $ClB(C_6F_5)_2$ (228 mg, 0.60 mmol) in CH_2Cl_2 (1 mL) at room temperature. After stirring at room temperature for 3 h, the yellow suspension was filtered. The residual solid was washed with pentane (1 ml × 3) and dried in vacuo to give a yellow solid (78 mg, 0.064 mmol, 32 %), which was characterized as compound **6g**.

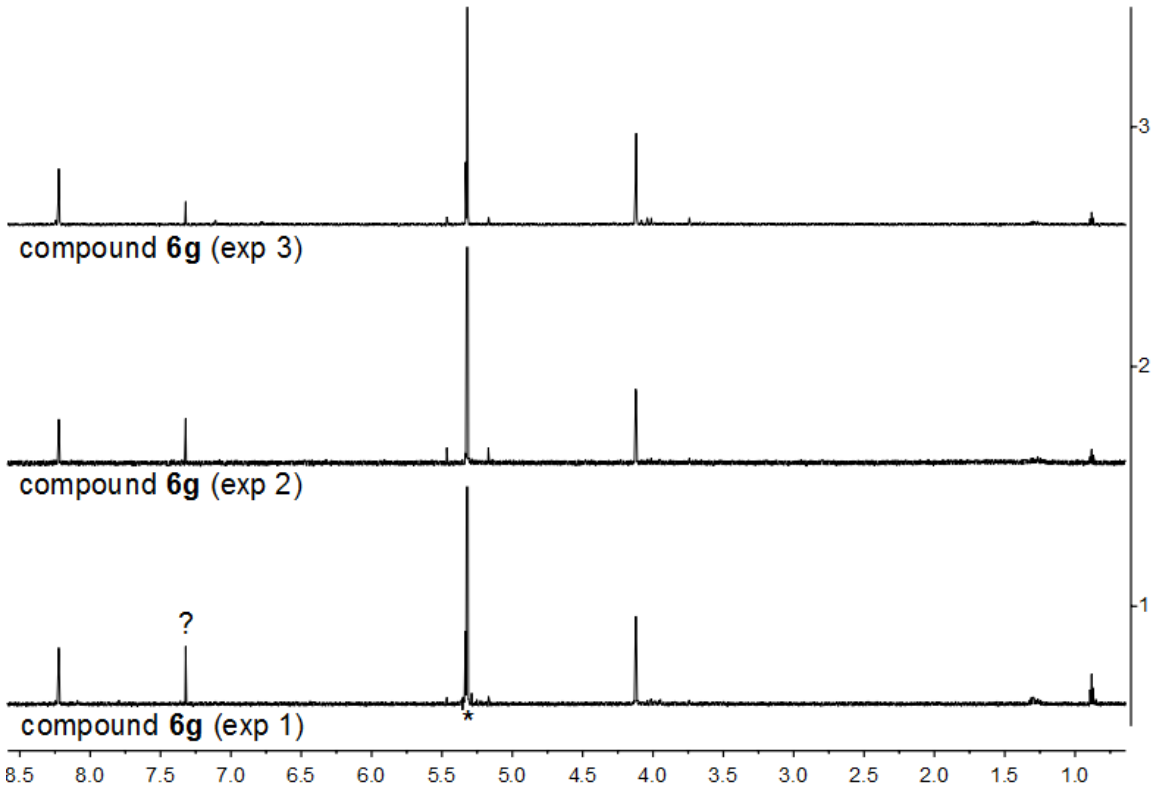


Figure S77. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectra of the isolated compound **6g** from Experiment 1 (Spectrum 1), Experiment 2 (Spectrum 2) and Experiment 3 (Spectrum 3).

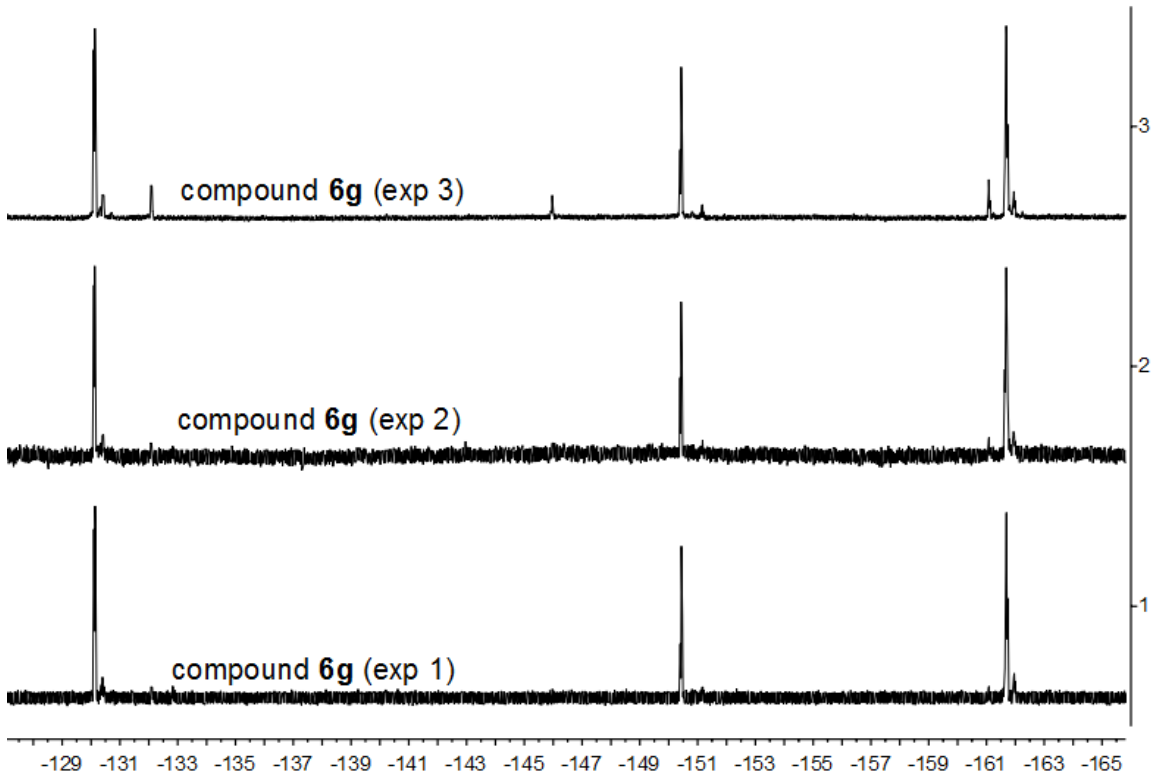
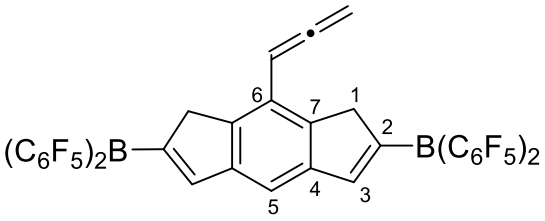


Figure S78. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2*) spectra of the isolated compound **6g** from Experiment 1 (Spectrum 1), Experiment 2 (Spectrum 2) and Experiment 3 (Spectrum 3).

*Isolation of compound **6g'**:* All the volatile in the filtrate (a yellow solution) were removed in vacuo. The remaining residue was washed with pentane (1 mL × 3) and dried in vacuo to give a yellow solid (55 mg, 0.063 mmol, 31 %), which was characterized as compound **6g'**.

NMR data of isolated compound **6g'**:



6g'

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ ^{1}H: 8.09 (t, $^{4}J_{HH}$ = 1.3 Hz, 2H, 3-CH=), 7.87 (s, 1H, 5-CH=), 6.54 (t, $^{4}J_{HH}$ = 7.0 Hz, 1H, CH=), 5.22 (d, $^{4}J_{HH}$ = 7.0 Hz, 2H, CH_2=), 3.95 (d, $^{4}J_{HH}$ = 1.6 Hz, 4H, CH_2).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ ^{13}C: 213.0 (=C=), 161.3 (3-CH=), 151.4 (br, CB=)^{t}, 151.1 (7-C), 146.7 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 144.5 (4-C), 142.9 (dm, $^{1}J_{FC}$ ~ 260 Hz, C_6F_5), 137.9 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 126.6 (6-C), 120.5 (5-CH), 114.7 (br m, i-C_6F_5), 89.3 (CH=), 78.9 (CH_2=), 41.8 (CH_2). [^{t} tentative assignment]

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ ^{19}F: −130.4 (m, 2F, *o*), −150.8 (t, $^{3}J_{FF}$ = 20.0 Hz, 1F, *p*), −162.0 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 11.2].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ ^{11}B: 57.2 ($\nu_{1/2}$ ~ 1300 Hz).

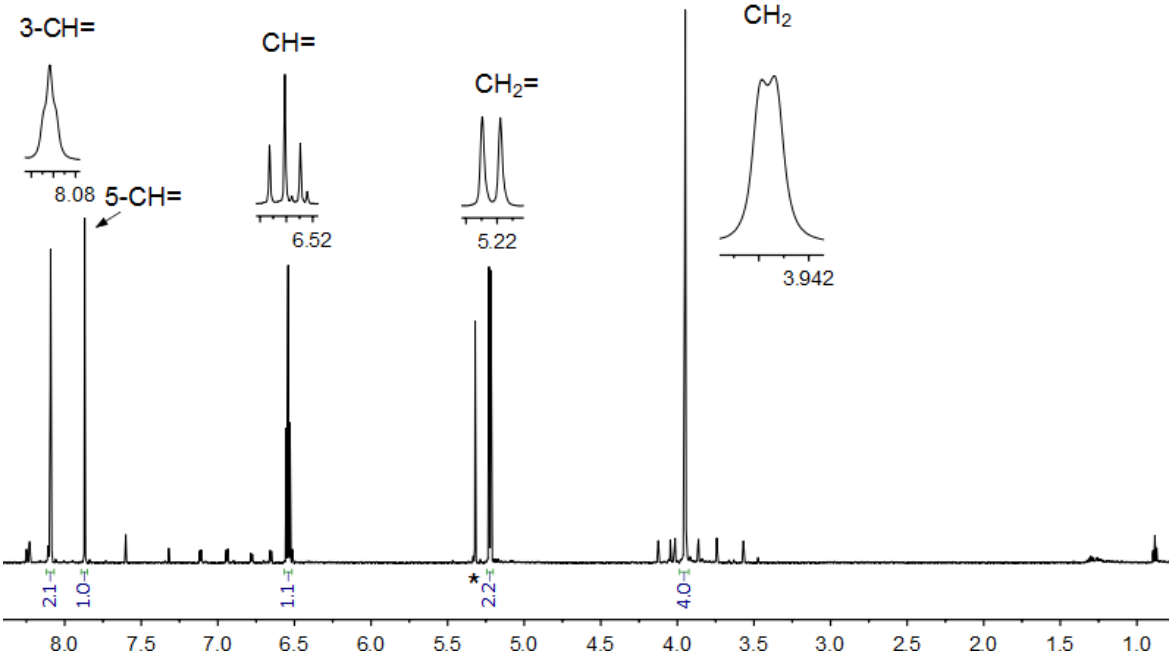


Figure S79. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectrum of the isolated compound **6g'**.

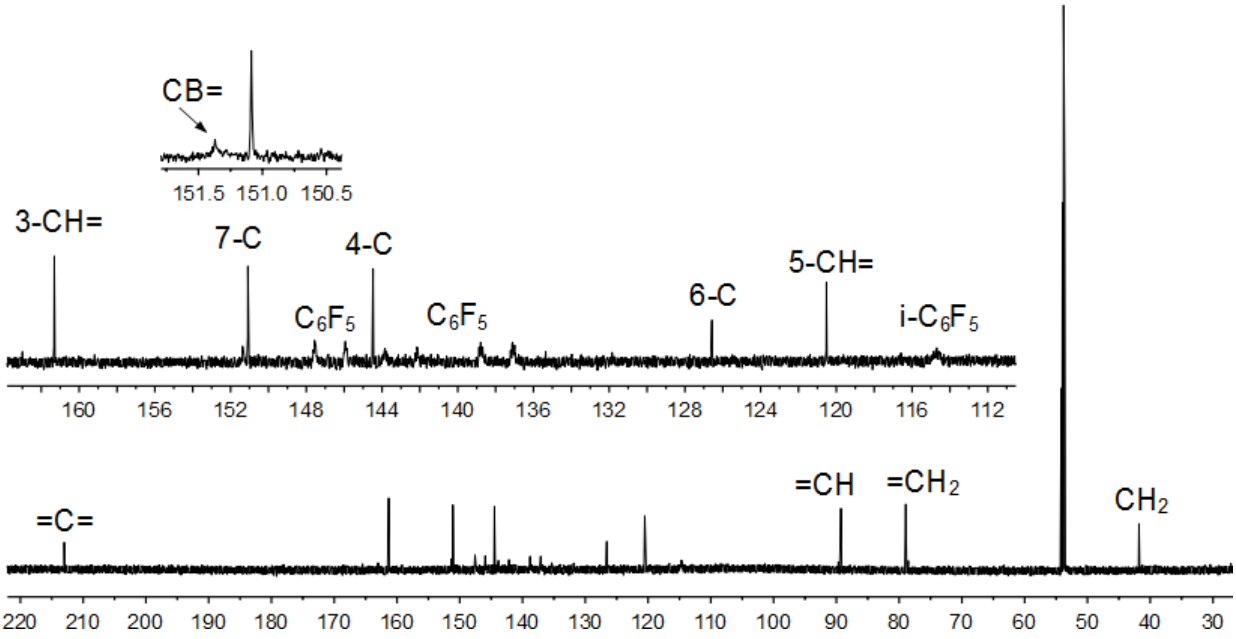


Figure S80. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of the isolated compound **6g'**.

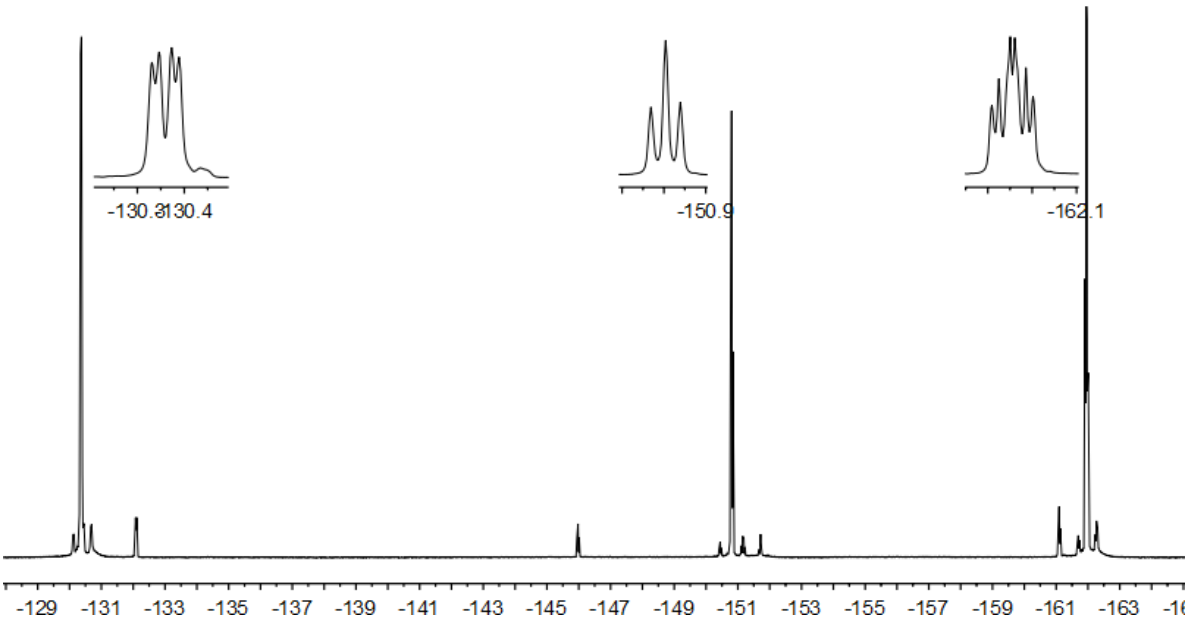


Figure S81. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of the isolated compound **6g'**.

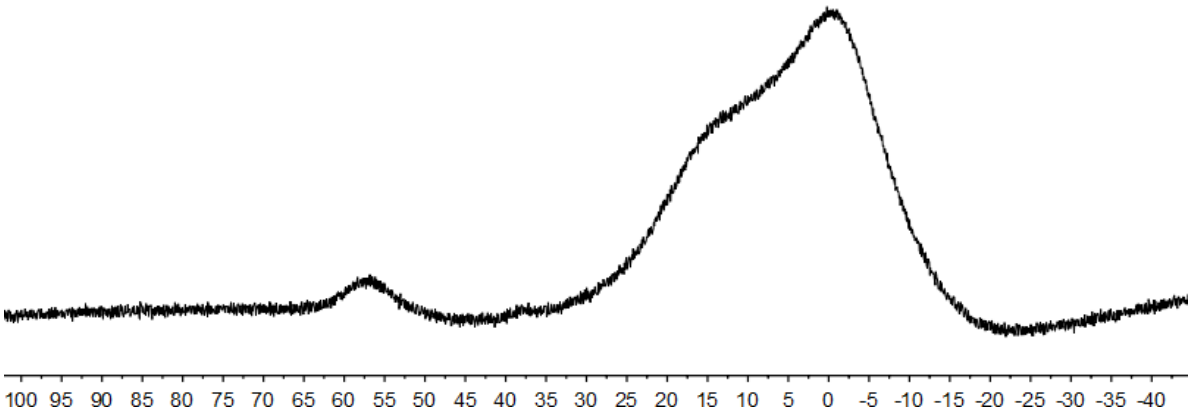
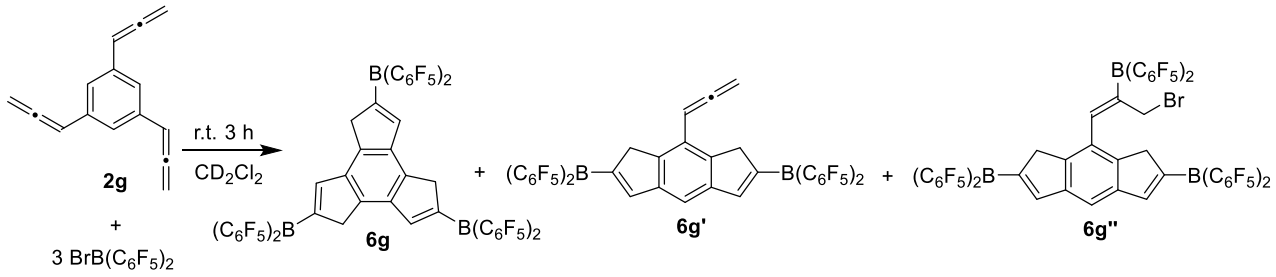


Figure S82. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of the isolated compound **6g'**.

Experiment 4: (reaction of compound **2g** with 3 $BrB(C_6F_5)_2$, NMR scale)

Scheme S22.



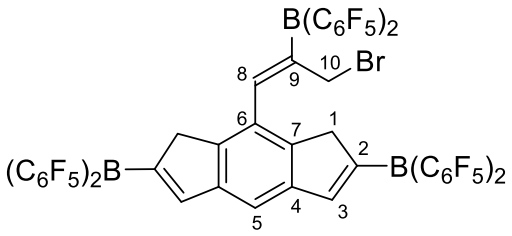
A solution of compound **2g** (9.3 mg, 0.05 mmol) in CD_2Cl_2 (0.3 mL) was added to a solution of $BrB(C_6F_5)_2$ (63.6 mg, 0.15 mmol) in CD_2Cl_2 (0.3 mL) at room temperature. After stirring at room temperature for 3 h, the yellow suspension was filtered. The filtrate was characterized by NMR experiments. The residual solid was washed with pentane (1 ml × 3) and dried in vacuo to give a yellow powder (20 mg, 0.016 mmol, 33%), which was characterized as compound **6g** (see Experiment 5 for characterization).

The filtrate after 3 h: a mixture of compound **6g** (< 1 mol%, ^{1}H), compound **6g'** (ca. 19 mol%, ^{19}F), compound **6g''** (24 mol%, ^{19}F), $BrB(C_6F_5)_2$ (ca. 57 mol%, ^{19}F) and other unknown components.

The filtrate after 7 d: a mixture of compound **6g** (< 1 mol%, ^{1}H), compound **6g''** (ca. 37 mol%, ^{19}F), $BrB(C_6F_5)_2$ (ca. 54 mol%, ^{19}F), an unknown compound (ca. 9 mol%, ^{19}F) and other unknown components.

The filtrate solution was characterized by NMR experiments after 7d.

The NMR data of compound **6g''** in the filtrate solution:



6g''

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ ^{1}H: 8.15 (m, 2H, 3-CH=), 8.01 (s, 1H, 5-CH=), 7.32 (s, 1H, 8-CH=), 4.13 (s, 2H, 10-CH_2), 3.78 (s, 4H, 1-CH_2).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ ^{13}C: 160.8 (3-CH=), 151.4 (br, 2-CB=), 151.0 (7-C), 149.0 (br, 9-CB=), 145.3 (8-CH=), 144.5 (4-C), 129.0 (6-C), 122.0 (5-CH=), 41.2 (1-CH_2), 30.9 (10-CH_2). [C_6F_5 not listed]

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ ^{19}F: [–130.3 (m, 4F, *o*), –150.5 (t, $^{3}J_{FF}$ = 20.0 Hz, 2F, *p*), –161.8 (m, 4F, *m*)]($^{C2}BC_6F_5$)[$\Delta\delta^{19}F_{m,p}$ = 11.4], [–128.5 (m, 2F, *o*), –146.0 (t, $^{3}J_{FF}$ = 20.0 Hz, 1F, *p*), –161.2 (m, 2F, *m*)]($^{C9}C_6F_5$)[$\Delta\delta^{19}F_{m,p}$ = 15.2].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ ^{11}B: 58.1 ($\nu_{1/2}$ ~ 1500 Hz). [tentative assignment]

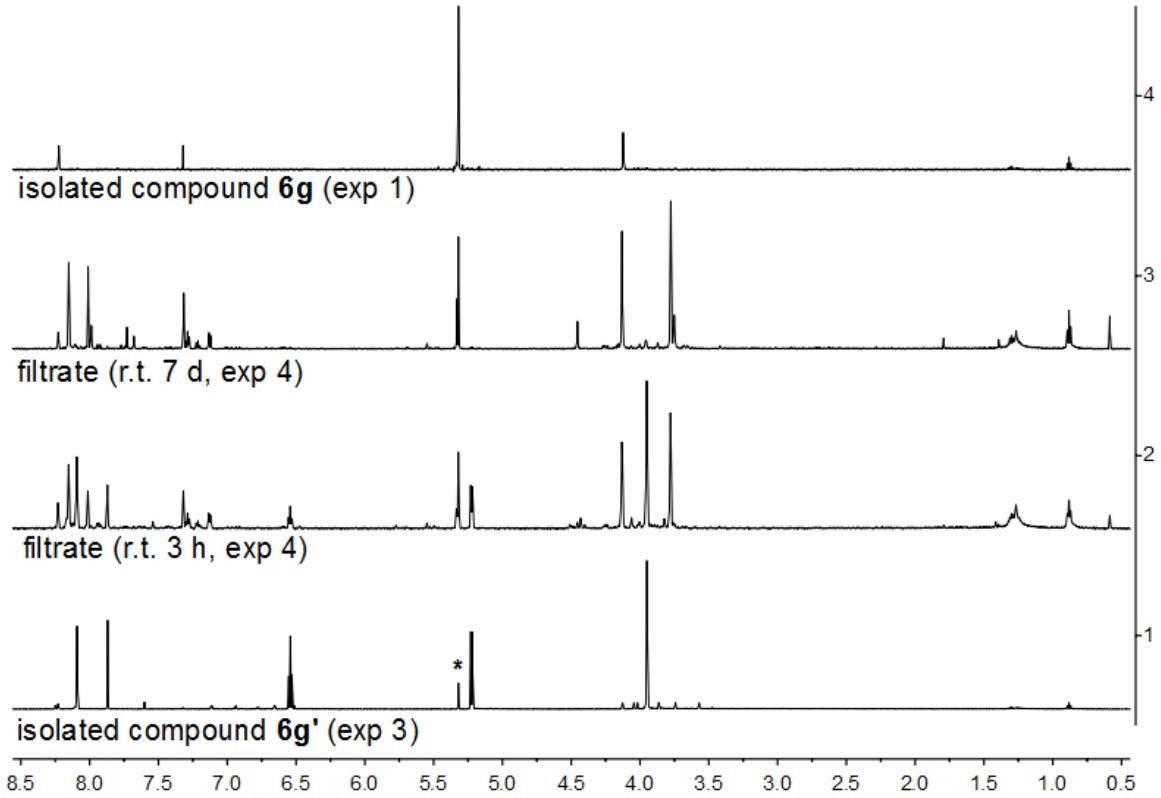


Figure S83. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectra of (1) the isolated compound **6g'** from experiment 3, (2) the filtrate from Experiment 4 (3 h, r.t.), (3) the filtrate from Experiment 4 (7 d, r.t.) and (4) the isolated compound **6g** from Experiment 1.

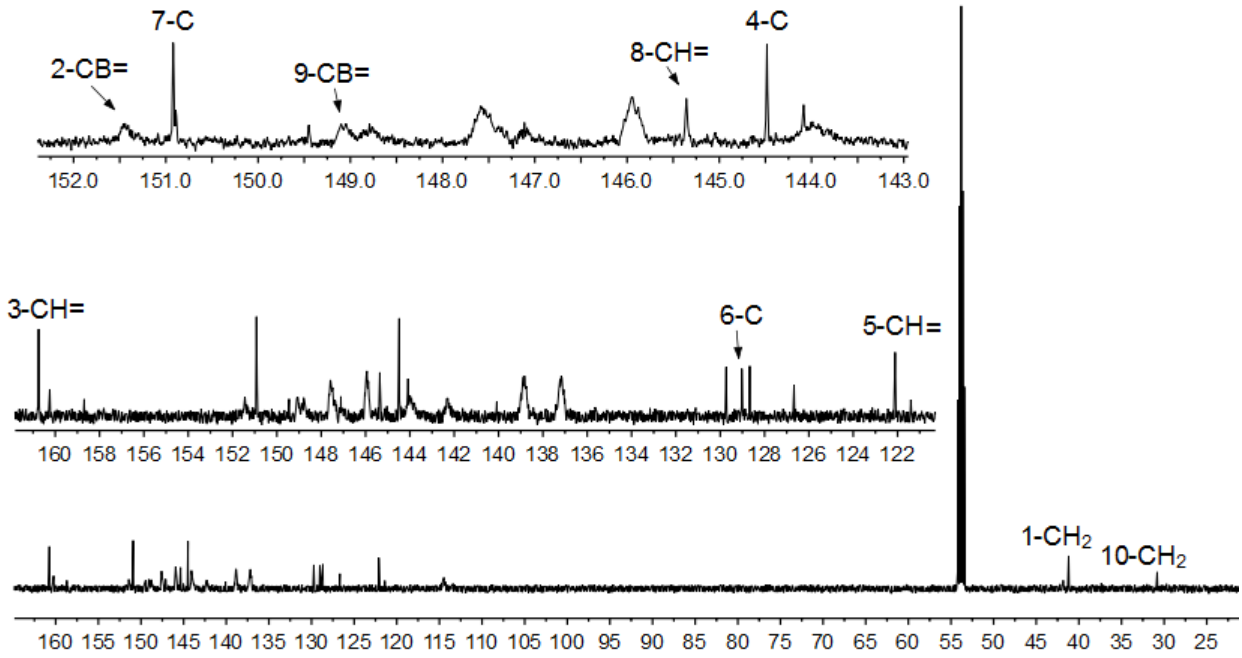


Figure S84. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of the filtrate from Experiment 4 (r.t. 7 d).

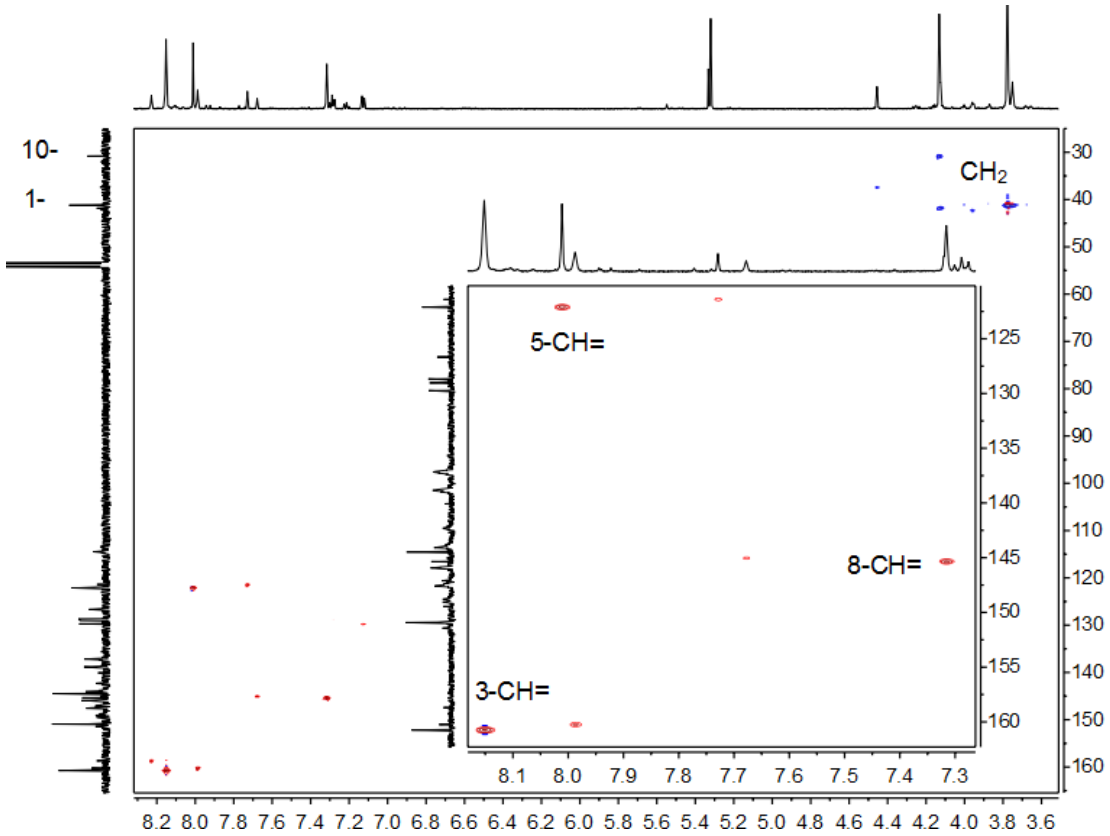


Figure S85. $^{1}H/^{13}C\{^{1}H\}$ GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2) spectrum of the filtrate from Experiment 4 (r.t. 7 d).

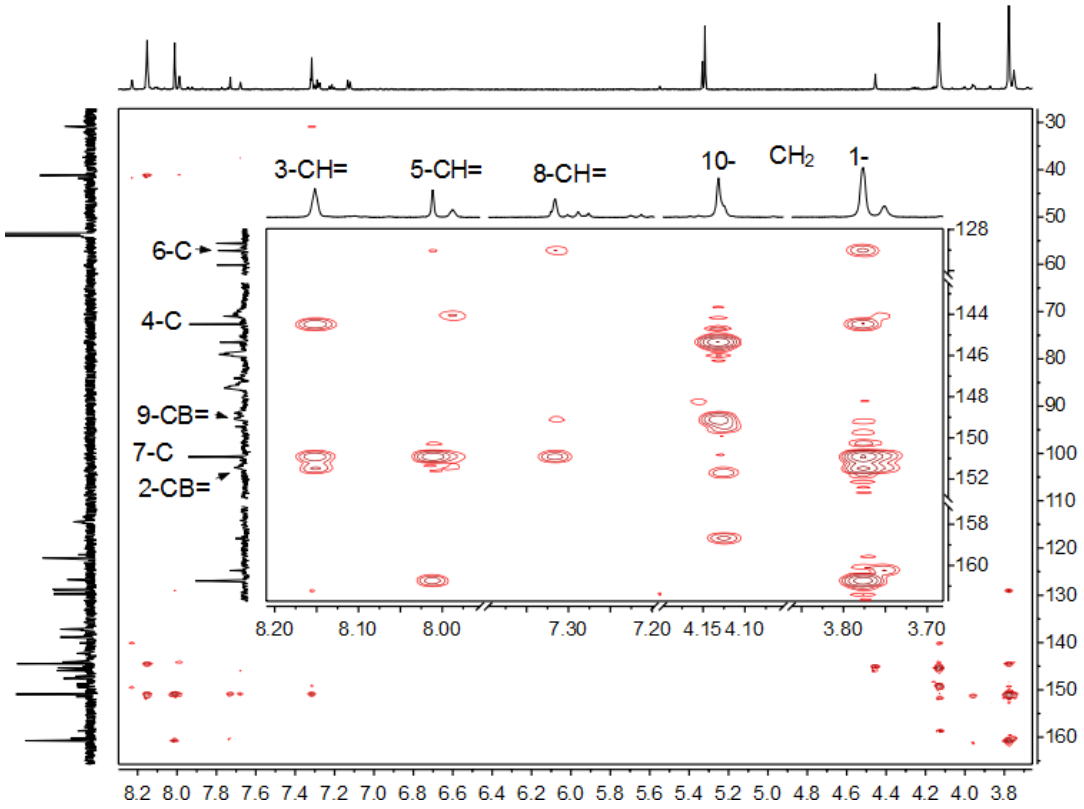


Figure S86. $^{1}H/^{13}C\{^{1}H\}$ GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2) spectrum of the filtrate from Experiment 4 (r.t. 7 d).

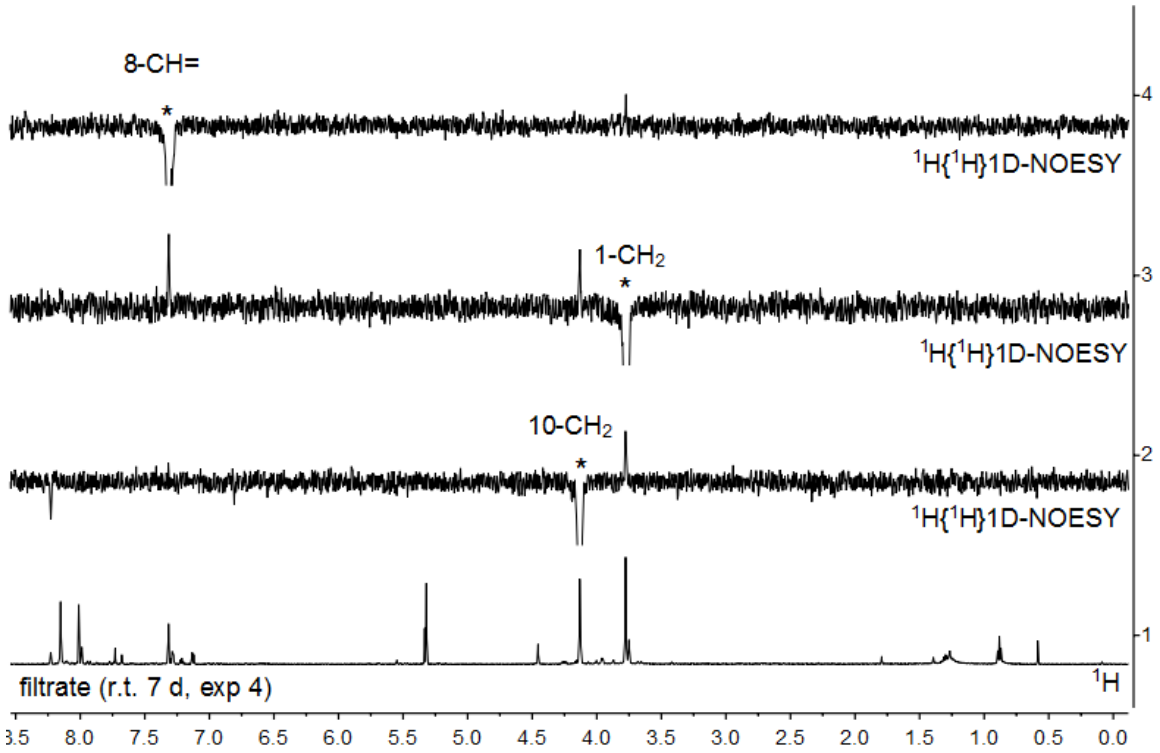


Figure S87. (1) ^{1}H NMR and (2 to 4) $^{1}H\{^{1}H\}$ 1D-NOESY (600 MHz, 299 K, CD_2Cl_2) spectra of the filtrate from Experiment 4 (r.t. 7 d). Irradiation points (*): (2) compound **6g''**: $\delta^{1}H$ 4.13 (10-CH_2); (3) compound **6g''**: $\delta^{1}H$ 3.78 (1-CH_2); (4) compound **6g''**: $\delta^{1}H$ 7.32 (8-CH=).

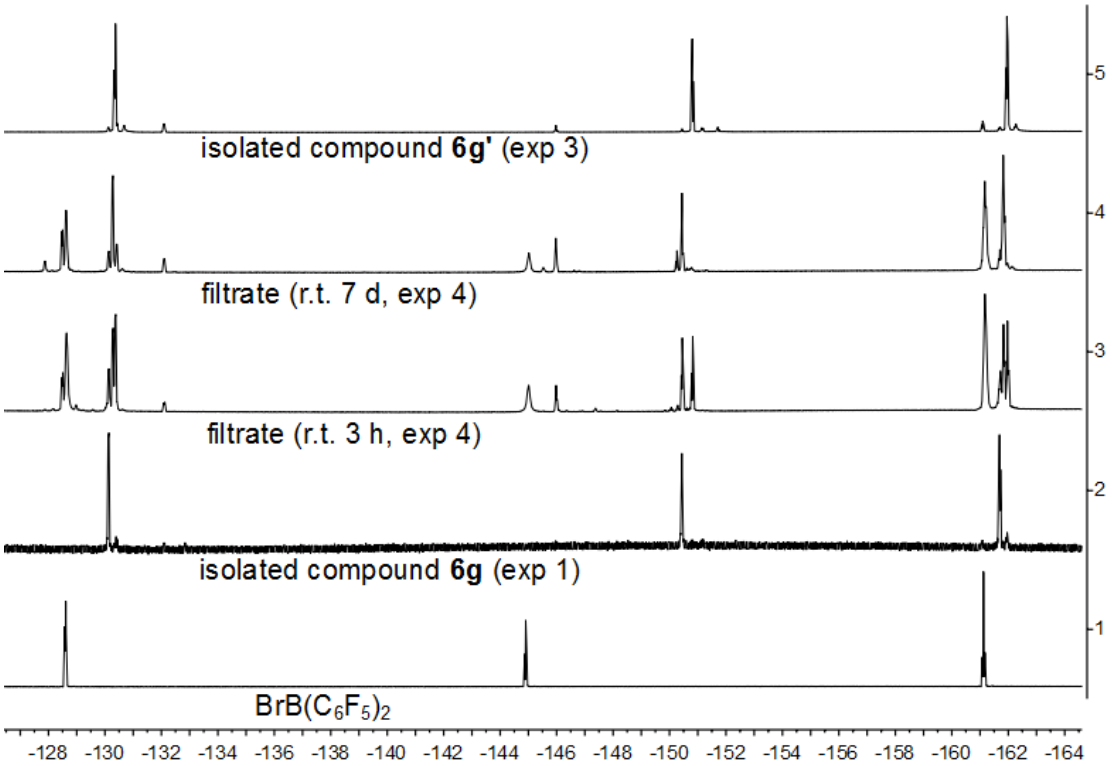


Figure S88. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectra of (1) $BrB(C_6F_5)_2$, (2) the isolated compound **6g** from Experiment 1, (3) the filtrate from Experiment 4 (3 h, r.t.), (4) the filtrate from Experiment 4 (7 d, r.t.) and (5) the isolated compound **6g'** from experiment 3.

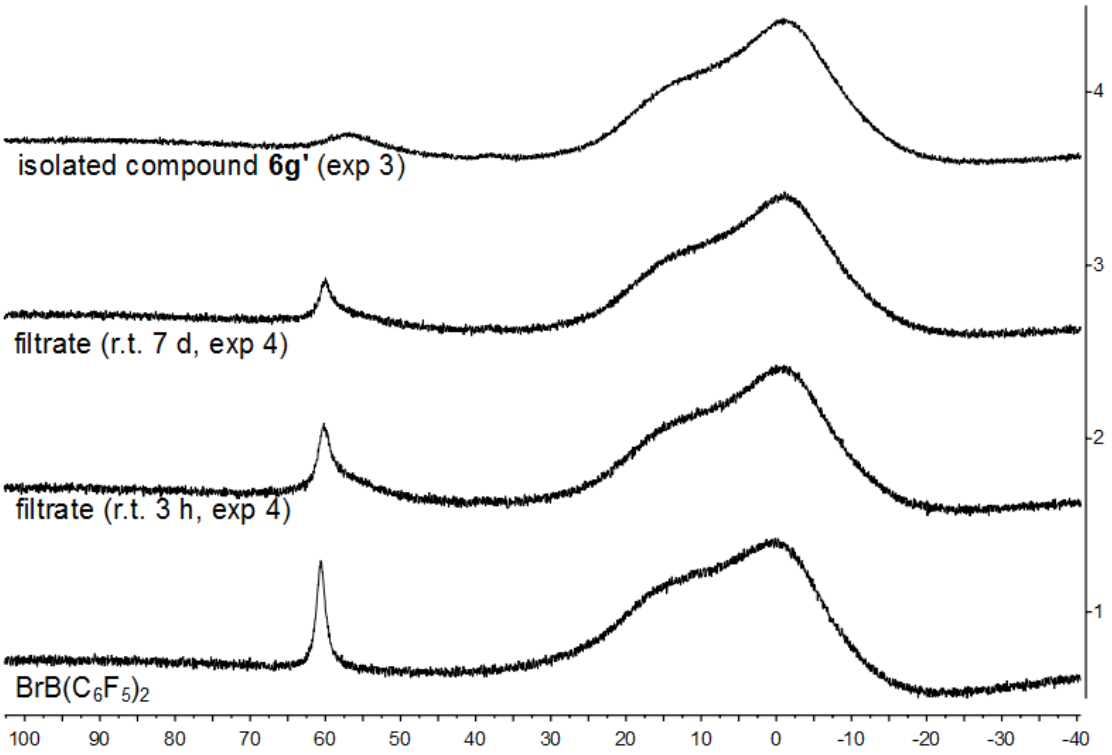
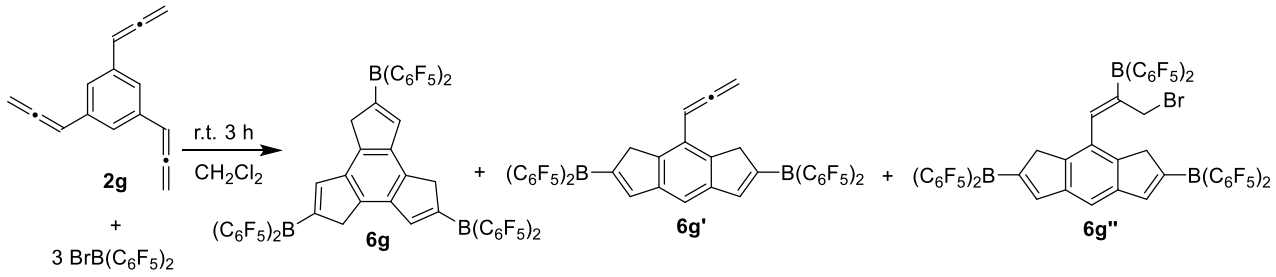


Figure S89. $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectra of (1) $BrB(C_6F_5)_2$, (2) the filtrate from Experiment 4 (3 h, r.t.), (3) the filtrate from Experiment 4 (7 d, r.t.) and (4) the isolated compound **6g'** from experiment 3.

Experiment 5: (reaction of compound **2g** with 3 $BrB(C_6F_5)_2$, preparative scale)

Scheme S23.



A solution of compound **2g** (37.2 mg, 0.20 mmol) in CH_2Cl_2 (1 mL) was added to a solution of $BrB(C_6F_5)_2$ (256 mg, 0.60 mmol) in CH_2Cl_2 (1 mL) at room temperature. After stirring at room temperature for 3 h, the yellow suspension was filtered. The residual solid was washed with pentane (1 mL × 3) and dried in vacuo to give a yellow powder (98 mg, 0.080 mmol, 40%), which was characterized as compound **6g**.

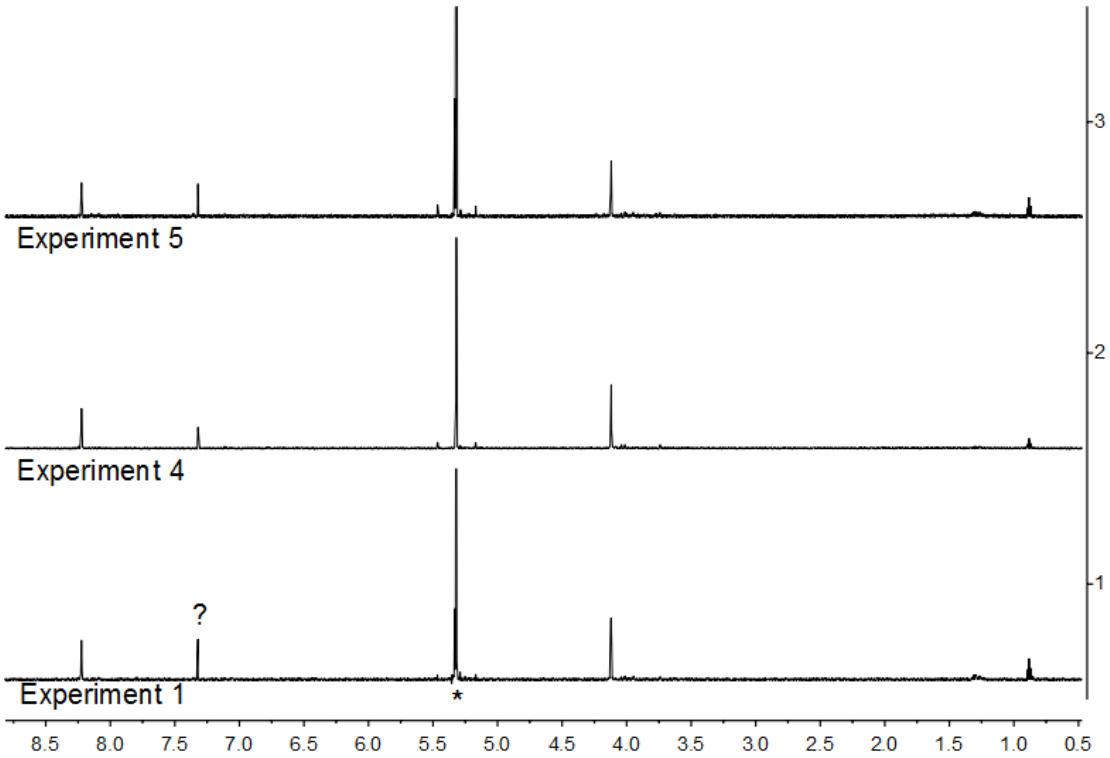


Figure S90. ^1H NMR (600 MHz, 299 K, CD_2Cl_2*) spectra of the isolated compound **6g** from Experiment 1 (spectrum 1), Experiment 4 (spectrum 2) and Experiment 5 (spectrum 3).[?: unknown signal from CD_2Cl_2]

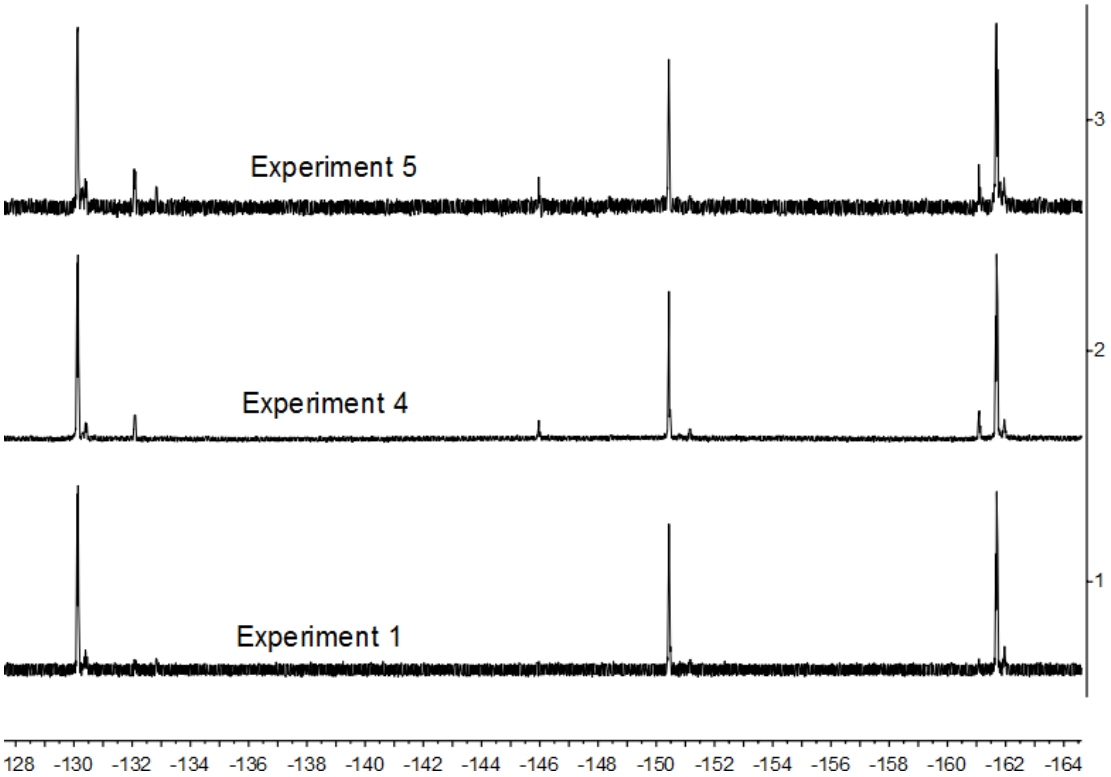


Figure S91. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectra of the isolated compound **6g** from Experiment 1 (spectrum 1), Experiment 4 (spectrum 2) and Experiment 5 (spectrum 3).

*Isolation of compound **6g'':*** All the volatiles in the filtrate (a yellow solution) were removed in vacuo. The residue was dissolved in pentane (1 mL) and stored at −35 °C for 48 h. A yellow precipitate was observed. The solution was removed by decantation. The residue was carefully washed with cold pentane (0.5 mL × 3) and dried in vacuo to give a yellow solid (57 mg, 0.044 mmol, 22%).

The isolated yellow solid was characterized by NMR experiments.

[A mixture of compound **6g'** (23 mol%, ^1H), **6g''** (77 mol%, ^1H) and other unknown components]

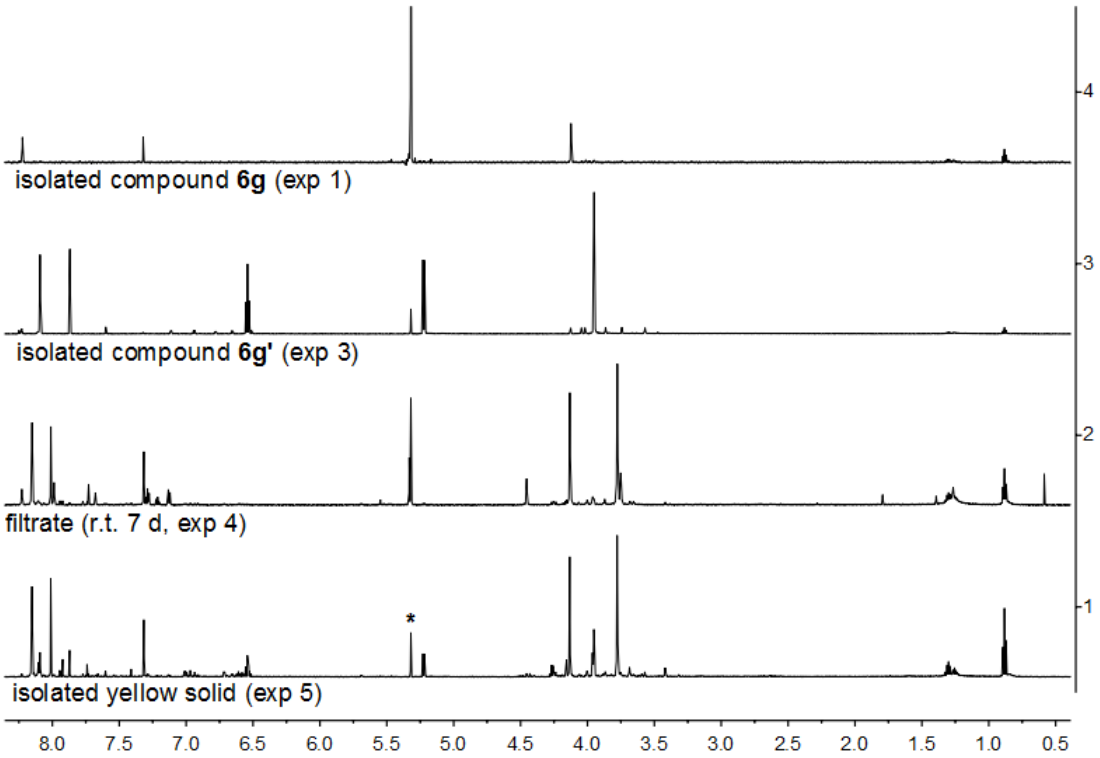


Figure S92. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectra of (1) the isolated yellow solid from Experiment 5, (2) the filtrate from Experiment 4 (r.t. 7 d), (3) the isolated compound **6g'** from Experiment 3 and (4) the isolated compound **6g** from Experiment 1.

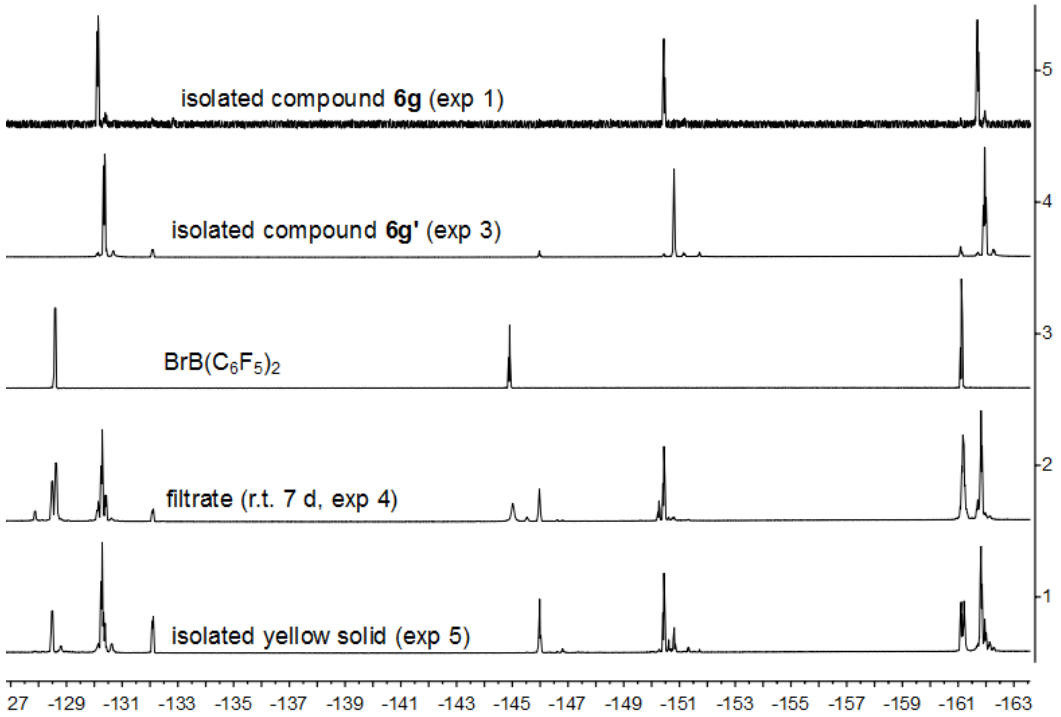


Figure S93. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2*) spectra of (1) the isolated yellow solid from Experiment 5, (2) the filtrate from Experiment 4 (r.t. 7 d), (3) $BrB(C_6F_5)_2$, (4) the isolated compound **6g'** from Experiment 3 and (5) the isolated compound **6g** from Experiment 1.

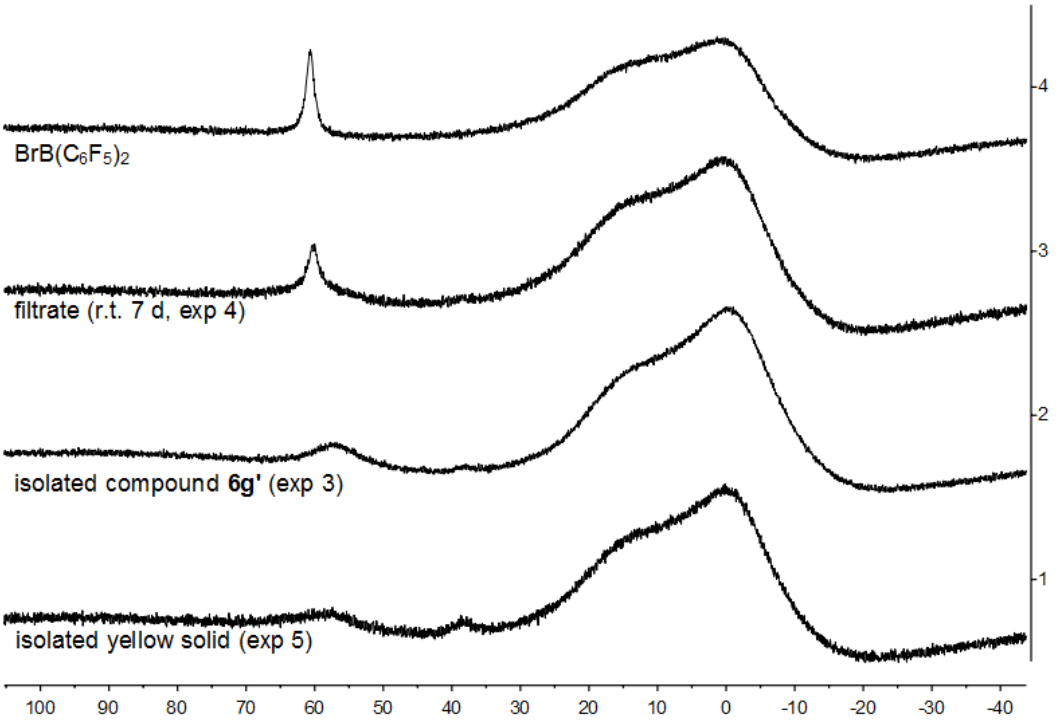
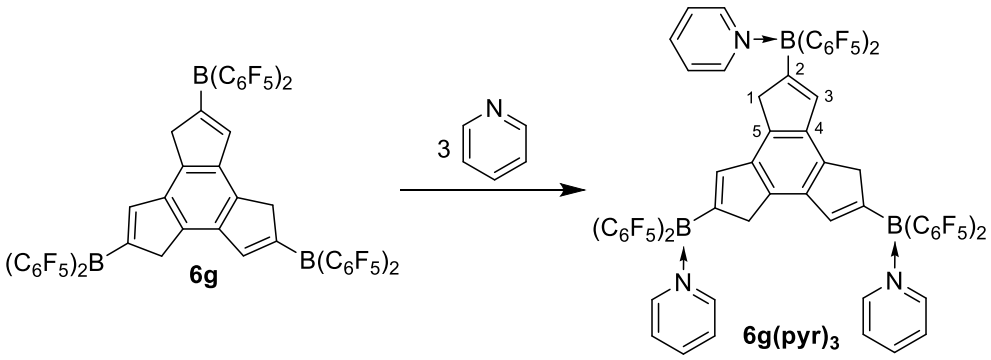


Figure S94. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectra of (1) the isolated yellow solid from Experiment 5, (2) the isolated compound **6g'** from Experiment 3, (3) the filtrate from Experiment 4 (r.t. 7 d) and (4) $BrB(C_6F_5)_2$.

I) Synthesis of compound **6g(pyr)$_3$**

Scheme S24.



Pyridine (20 mg, 0.25 mmol) was added to a suspension of compound **6g** (31 mg, 0.025 mmol) in CH_2Cl_2 (0.5 mL) at room temperature. Then all the volatiles were removed in vacuo. The remaining residue was washed with pentane (1 ml × 3) and dried in vacuo to give compound **6g(pyr)$_3$** (35 mg, 0.024 mmol, 95%) as a pale yellow powder.

Anal. Calc. for $C_{66}H_{24}B_3F_{30}N_3$: C, 54.25; H, 1.66; N, 2.88. Found: C, 54.73; H, 2.04; N, 2.76.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ ^{1}H: 8.83 (m, 2H, o-Py), 8.15 (m, 1H, p-Py), 7.69 (m, 2H, m-Py), 6.70 (t, $^{4}J_{HH}$ = 1.4 Hz, 1H, CH=), 3.31 (s, 2H, CH_2).

$^{13}C\{^1H\}$ NMR (151 MHz, 299 K, CD_2Cl_2): δ ^{13}C: 154.8 (br, CB=), 148.1 (dm, $^1J_{FC}$ ~ 240, C_6F_5), 147.1 (o-Py), 142.4 (p-Py), 140.0 (dm, $^1J_{FC}$ ~ 250, C_6F_5), 139.9 and 133.8 (C), 137.6 (dm, $^1J_{FC}$ ~ 250, C_6F_5), 132.8 (CH=), 126.4 (m-Py), 121.0 (br, i-C_6F_5), 41.5 (CH_2).

$^{11}B\{^1H\}$ NMR (192 MHz, 299 K, CD_2Cl_2): δ ^{11}B: −2.1.

$^{10}B\{^1H\}$ NMR (54 MHz, 299 K, CD_2Cl_2): δ ^{10}B: −2.1 ($\nu_{1/2}$ ~ 300 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ ^{19}F: −131.1 (m, 2F, *o*), −159.0 (t, $^3J_{FF}$ = 20.0 Hz, 1F, *p*), −164.2 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 5.2].

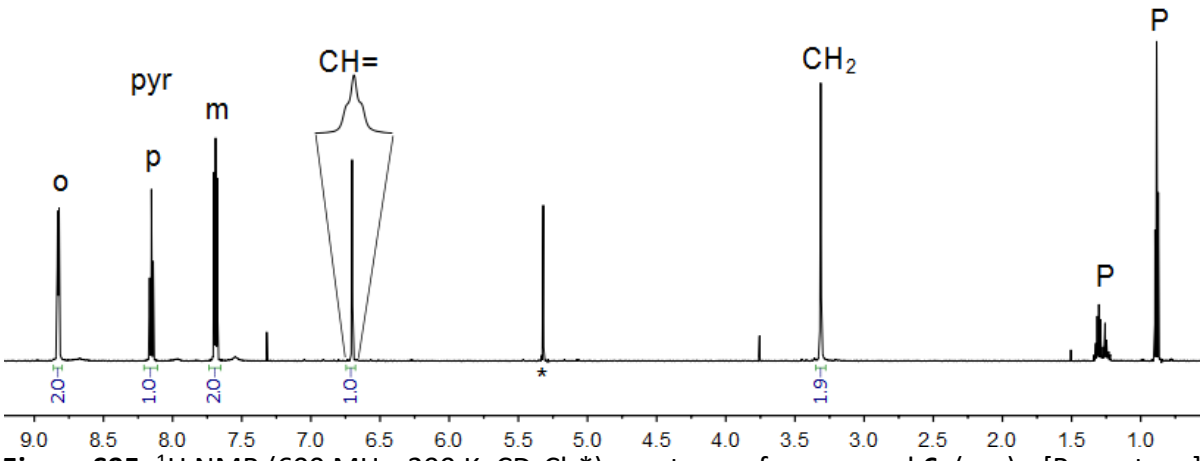


Figure S95. ^1H NMR (600 MHz, 299 K, CD_2Cl_2*) spectrum of compound **6g(pyr)$_3$**. [P: pentane]

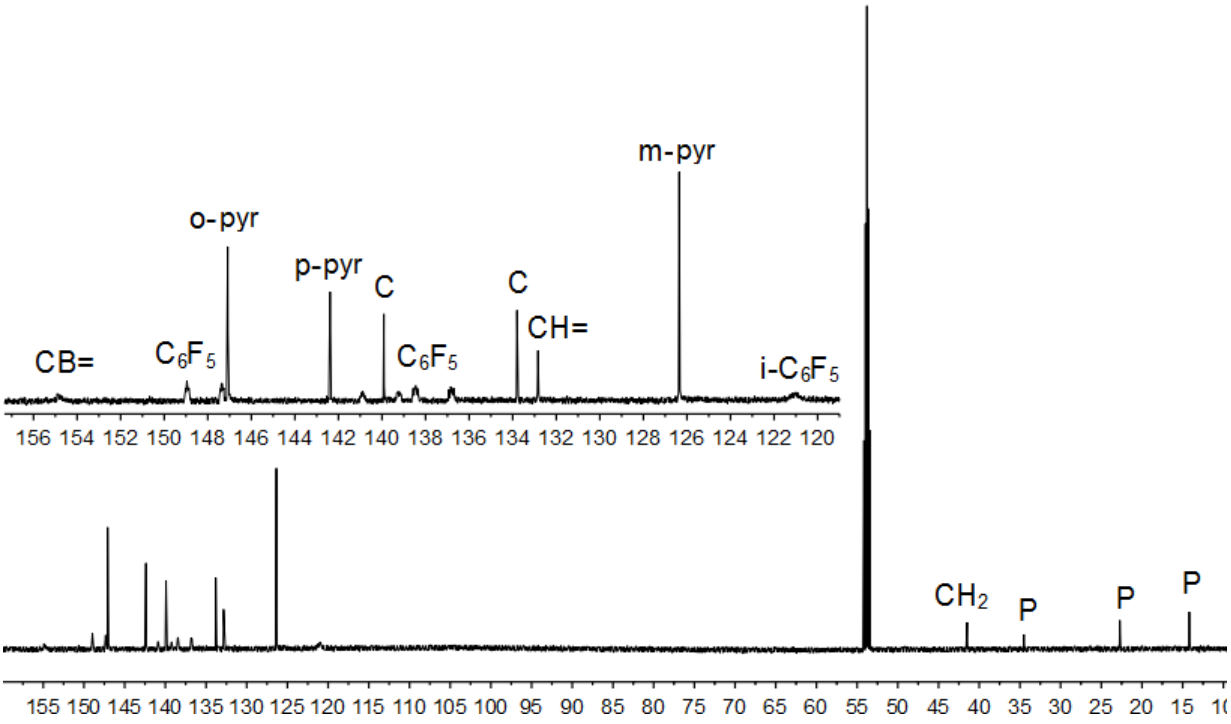


Figure S96. $^{13}C\{^1H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **6g(pyr)$_3$**. [P: pentane]

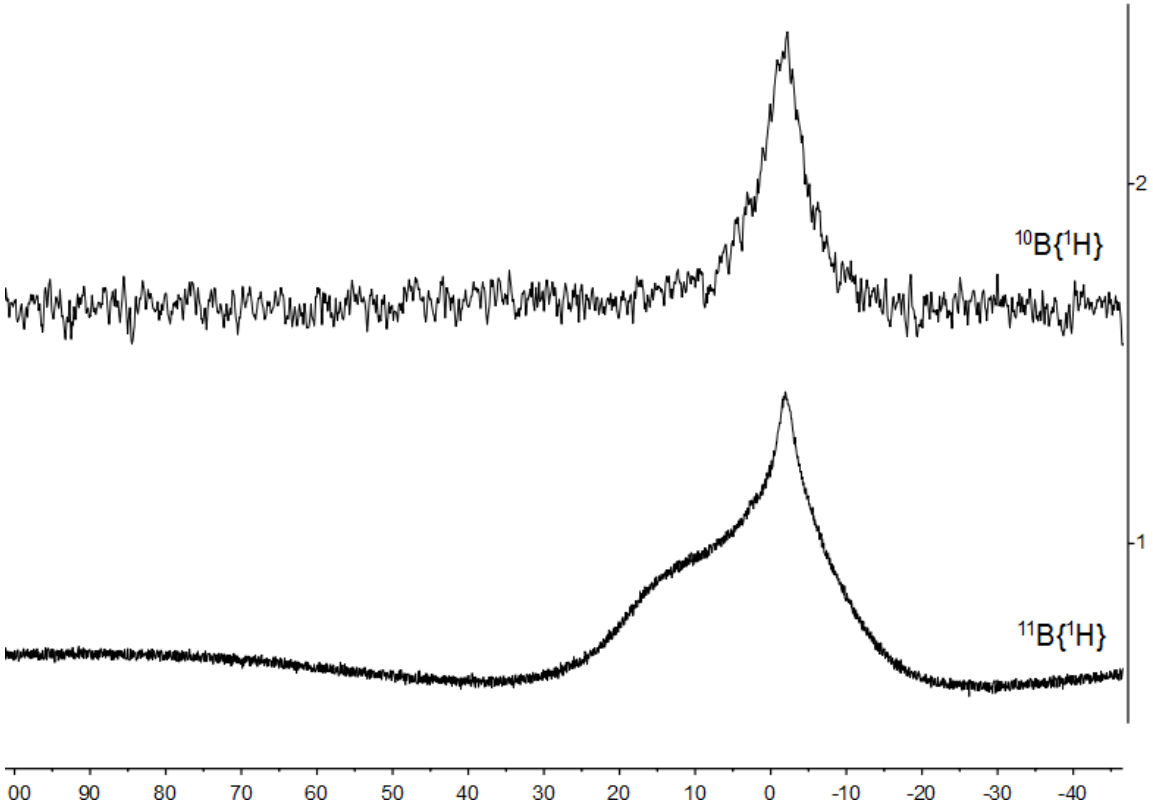


Figure S97. Spectrum 1: $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of compound **6g**(**pyr**)$_3$ and Spectrum 2: $^{10}B\{^1H\}$ NMR (54 MHz, 299 K, CD_2Cl_2) spectrum of compound **6g**(**pyr**)$_3$.

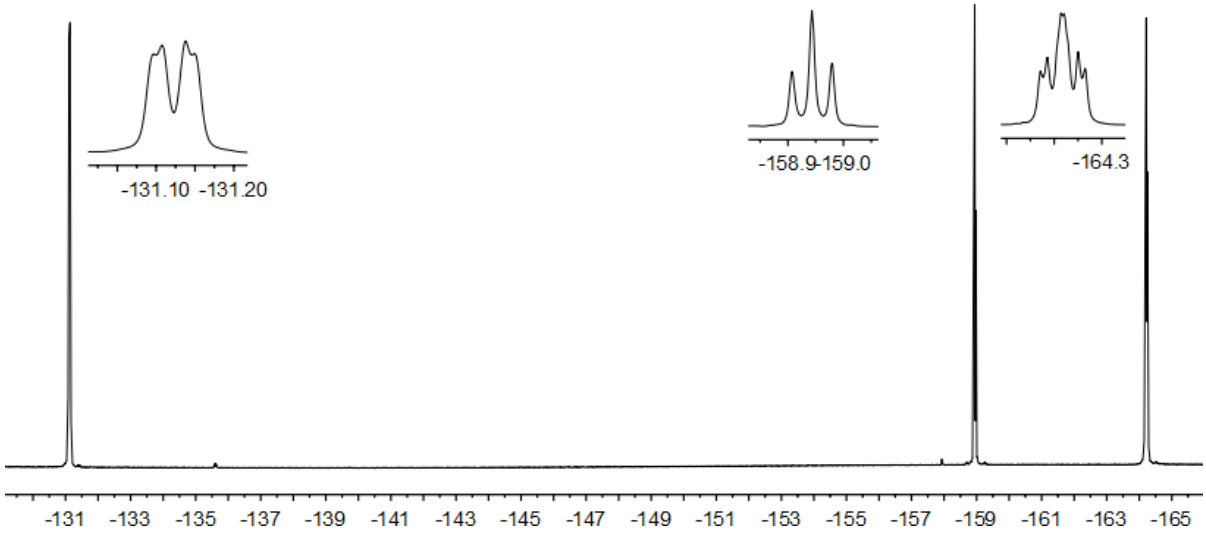
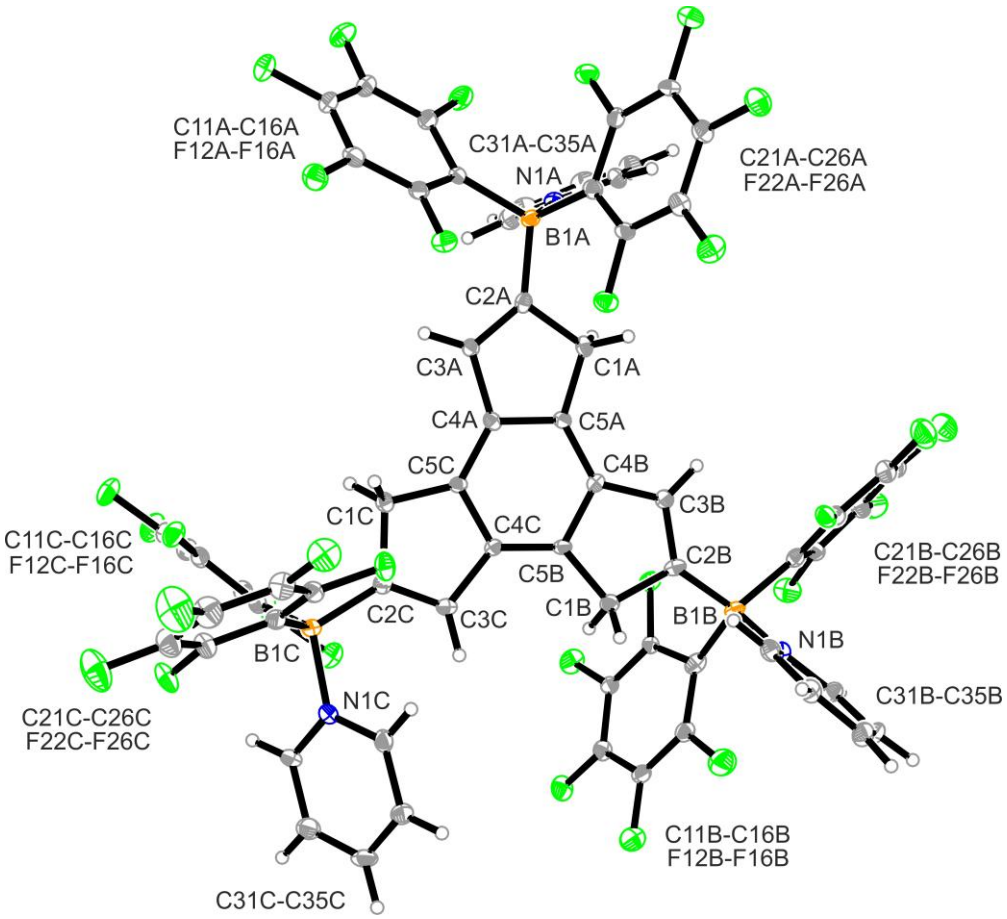


Figure S98. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **6g**(**pyr**)$_3$.

Crystals suitable for X-ray crystal structure analysis were obtained from diffusion of pentane vapor to a solution of compound **6g**(**pyr**)$_3$ in CH_2Cl_2 at room temperature.

X-ray crystal structure analysis of compound 6g(pyr)$_3$ (erk9457): A pale yellow needle-like specimen of $C_{66}H_{24}B_3F_{30}N_3$, approximate dimensions 0.020 mm x 0.040 mm x 0.100 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a monoclinic unit cell yielded a total of 19029 reflections to a maximum θ angle of 25.00° (0.84 Å resolution), of which 11481 were independent (average redundancy 1.657, completeness = 97.6%, R_{int} = 8.06%, R_{sig} = 10.43%) and 6701 (58.37%) were greater than 2σ(F^2). The final cell constants of a = 18.2599(7) Å, b = 26.5169(9) Å, c = 13.8464(4) Å, β = 95.1620(10)°, volume = 6677.2(4) Å^3, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9860 and 0.9970. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_{66}H_{24}B_3F_{30}N_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 1302 variables converged at R1 = 12.24%, for the observed data and wR2 = 25.99% for all data. The goodness-of-fit was 1.151. The largest peak in the final difference electron density synthesis was 1.028 e^-/Å^3 and the largest hole was -0.325 e^-/Å^3 with an RMS deviation of 0.072 e^-/Å^3. On the basis of the final model, the calculated density was 1.454 g/cm^3 and F(000), 2904 e^-. CCDC number: 1907605.



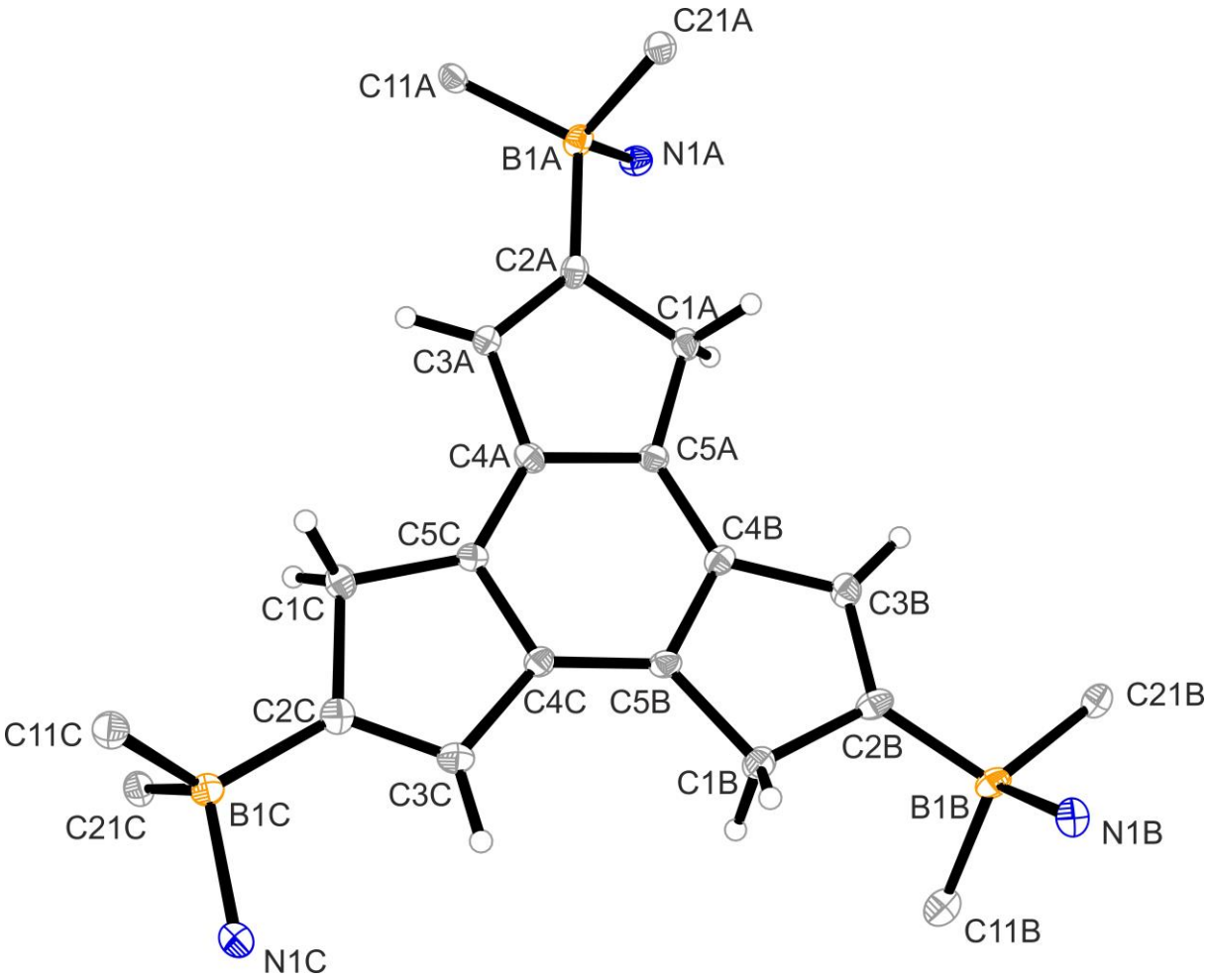
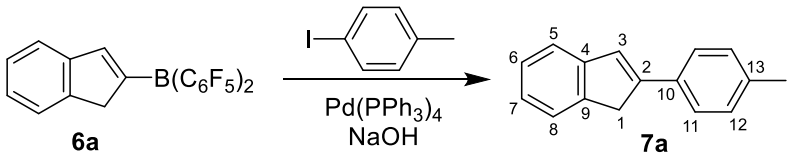


Figure S99. Crystal structure of compound **6g(pyr)$_3$** (thermals ellipsoids: 15 % probability).

J) Synthesis of compound **7a**

Scheme S25.



$Pd(PPh_3)_4$ (35 mg, 0.032 mmol) and aqueous NaOH (3 M, 6 mL) were added to a solution of compound **6a** (150 mg, 0.32 mmol) in THF (20 mL) at room temperature. The resulting reaction mixture was then stirred for 18 h at 65 °C. After cooling down to room temperature, pentane (10 mL) was added to the reaction mixture and the phases were separated. The aqueous phase was washed with pentane (10mL × 3) and all the organic phases were combined and dried over Na_2SO_4. All the volatiles were removed by rotation evaporator and the residue was purified via column chromatography (silica gel, pentane) giving compound **7a** (61 mg, 0.30 mmol, 94%) as a white solid.

Solid **7a** shows a blue fluorescence.

HRMS (EI) *m/z*: Calc. for $C_{16}H_{14}$ $[M]^+$: 206.10900, Found: 206.10909.

NMR data of isolated compound **7a**:

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ ^{1}H: 7.55 (m, 2H, 11-CH=), 7.47 (m, 1H, 8-CH=), 7.38 (m, 1H, 5-CH=), 7.25 (m, 1H, 6-CH=), 7.20 (m, 2H, 12-CH=), 7.19 (m, 1H, 3-CH=), 7.16 (m, 1H, 7-CH=), 3.78 (m, 2H, CH_2), 2.37 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2)[selected resonances]: δ ^{13}C: 147.0 (2-C), 145.9 (4-C), 143.5 (9-C), 138.0 (13-C), 133.5 (10-C), 129.7 (12-CH=), 126.9 (6-CH=), 125.9 (11-CH=), 125.8 (3-CH=), 124.9 (7-CH=), 124.0 (8-CH=), 121.1 (5-CH=), 39.4 (CH_2), 21.3 (CH_3).

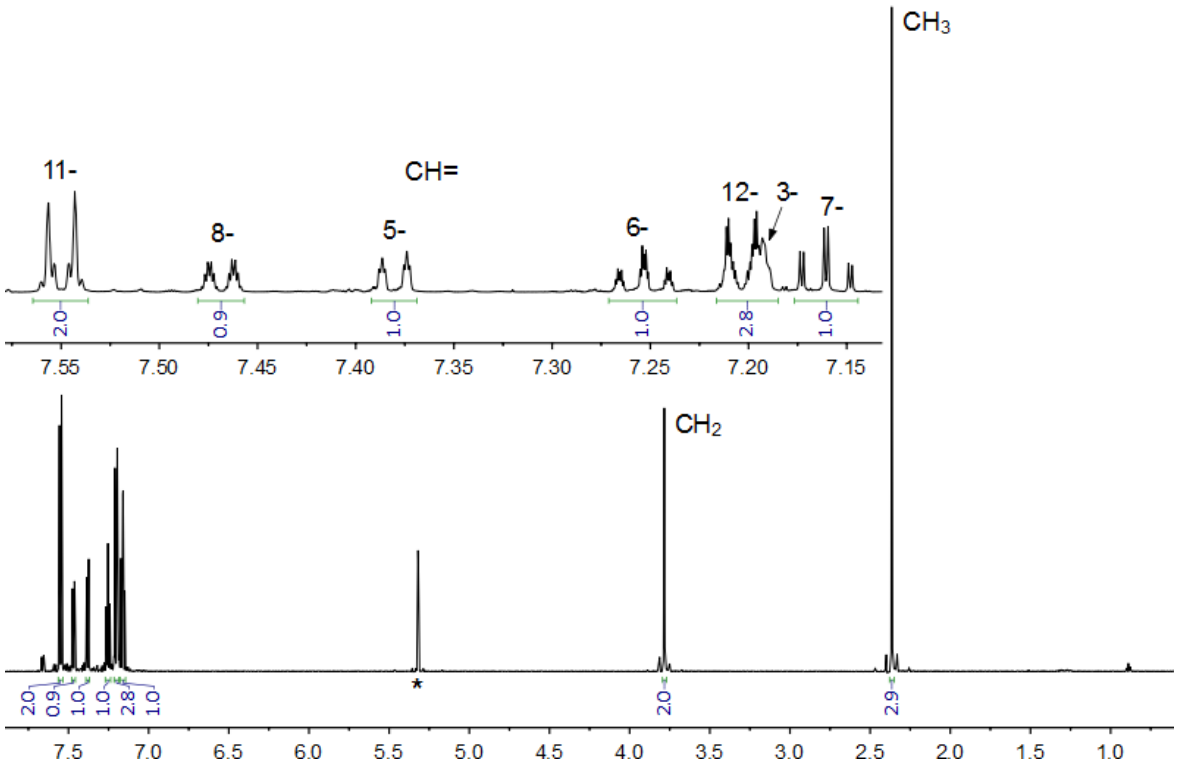


Figure S100. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectrum of compound **7a**.

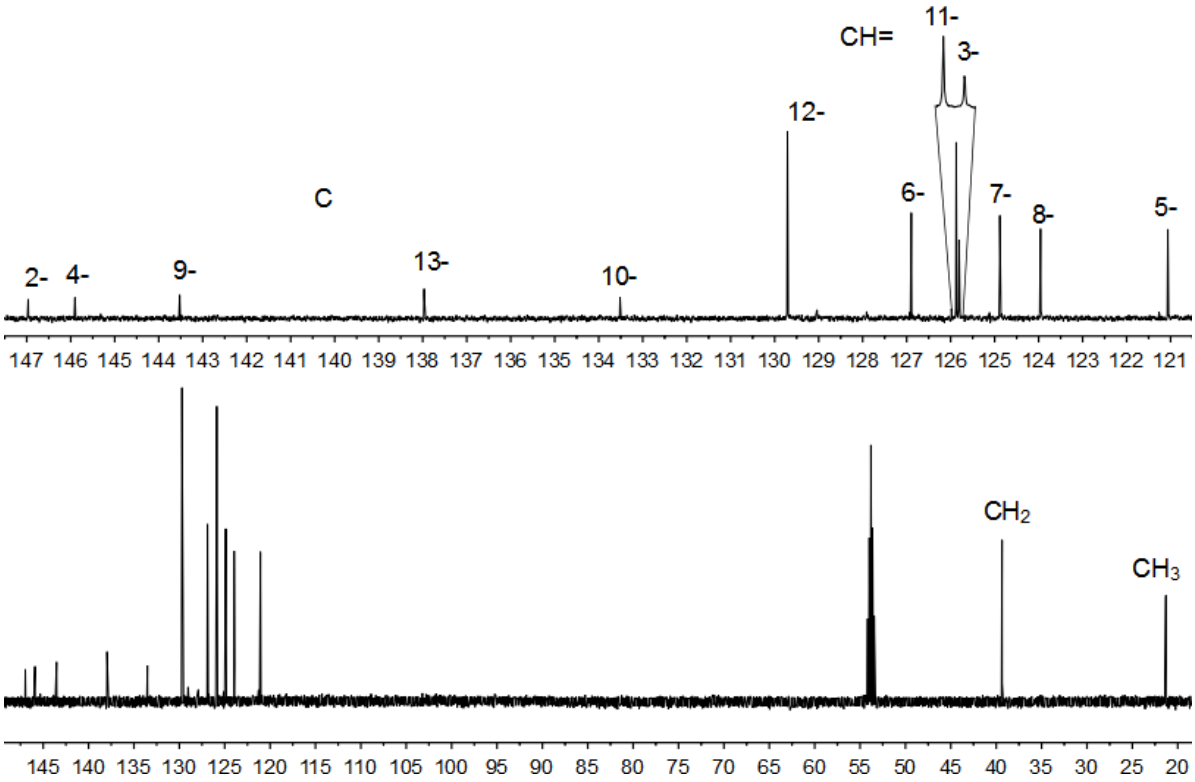


Figure S101. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **7a**.

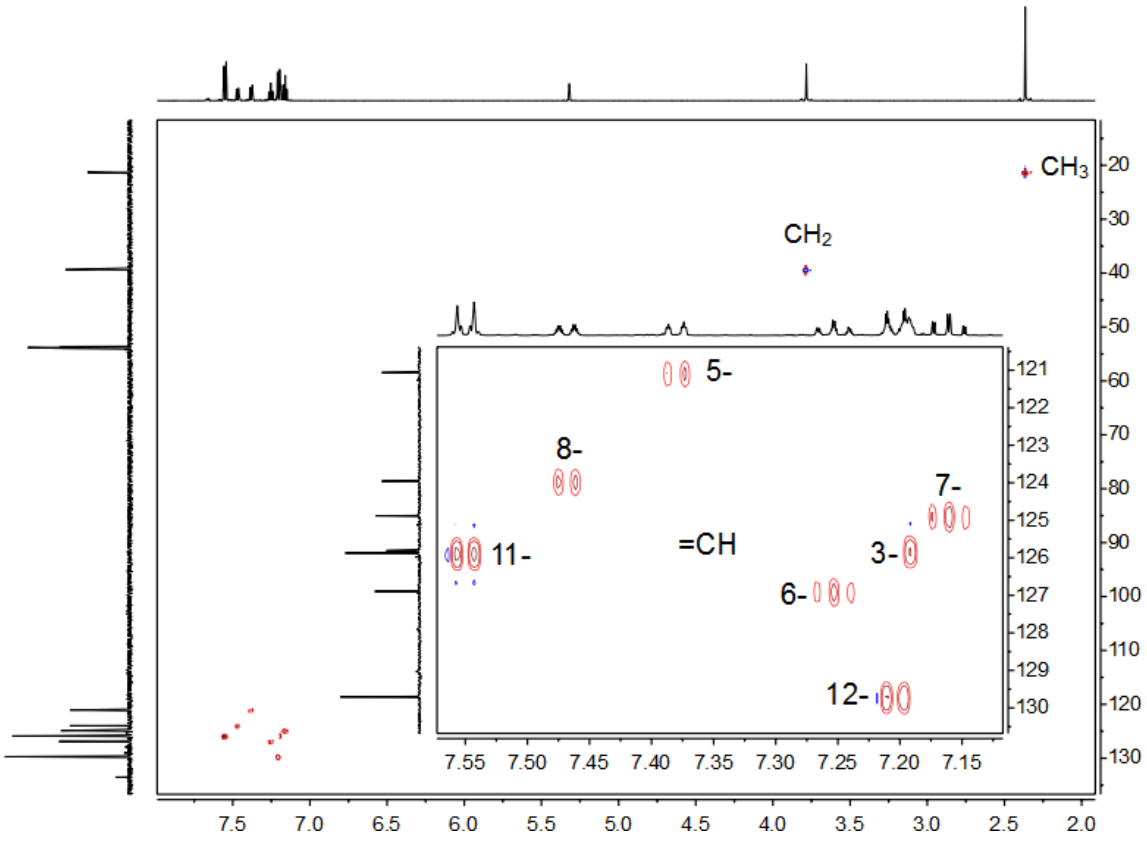
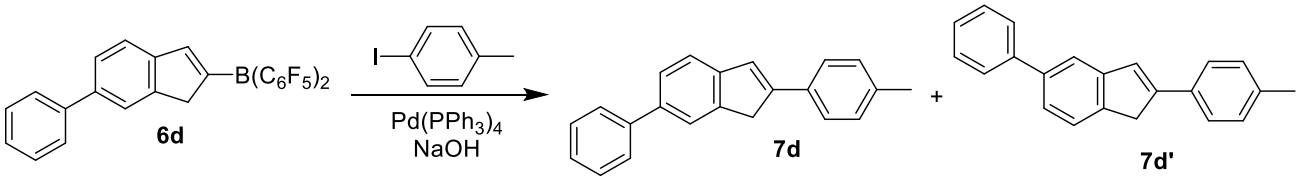


Figure S102. $^{1}H/^{13}C$ GHSQC (600/151 MHz, 299 K, CD_2Cl_2) spectrum of compound **7a**.

K) Synthesis of compound **7d** and **7d'**

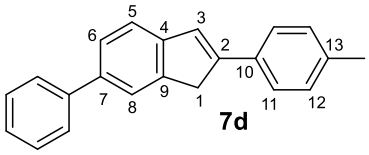
Scheme S26.



$Pd(PPh_3)_4$ (50 mg, 0.044 mmol) and aqueous NaOH (3 M, 8 mL) were added to a solution of compound **6d** (236 mg, 0.44 mmol) in THF (30 mL) at room temperature. The resulting reaction mixture was then stirred for 18 h at 65 °C. After cooling down to room temperature, pentane (10 mL) was added to the reaction mixture and the phased were separated. The aqueous phase was washed with pentane (10mL × 3) and all the organic phase were combined and dried over Na_2SO_4. All the volatiles were removed by rotation evaporator and the residue was purified via column chromatography [silica gel, pentane: CH_2Cl_2 = 9:1(V:V)] giving a mixture of compound **7d** (58 mol%) and **7d'** (42 mol%) (103 mg, 0.37 mmol, 83%) as a white solid.

HRMS (EI) ***m/z***: Calc. for $C_{22}H_{18}$ $[M]^+$: 282.14030, Found: 282.14049.

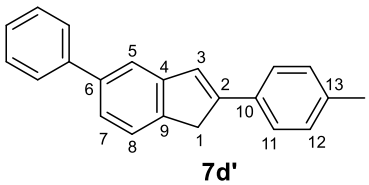
NMR data of compound **7d**:



^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ ^{1}H: 7.73 (m, 1H, 8-CH=), 7.65 (m, 2H, o-Ph), 7.57 (m, 2H, 11-CH=), 7.53 (m, 1H, 6-CH=), 7.45 (m, 2H, m-Ph), 7.45 (m, 1H, 5-CH=), 7.33 (m, 1H, p-Ph), 7.23 (m, 1H, 3-CH=), 7.22 (m, 2H, 12-CH=), 3.86 (m, 2H, CH_2), 2.37 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2)[selected resonances]: δ ^{13}C: 147.5 (2-C), 145.3 (4-C), 144.3 (9-C), 142.0 (i-Ph), 138.1 (13-C), 137.9 (7-C), 133.5 (10-C), 129.7 (12-CH=), 129.1 (m-Ph), 127.3 (o-Ph), 127.2 (p-Ph), 126.0 (6-CH=), 125.9 (11-CH=), 125.5 (3-CH=), 122.7 (8-CH=), 121.3 (5-CH=), 39.6 (CH_2), 21.3 (CH_3).

NMR data of compound **7d'**:



^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ ^{1}H: 7.65 (m, 2H, o-Ph), 7.62 (m, 1H, 5-CH=), 7.57 (m, 2H, 11-CH=), 7.54 (m, 1H, 8-CH=), 7.45 (m, 2H, m-Ph), 7.42 (m, 1H, 7-CH=), 7.35 (m, 1H, p-Ph), 7.25 (m,

1H, 3-CH=), 7.22 (m, 2H, 12-CH=), 3.84 (m, 2H, CH_2), 2.37 (s, 3H, CH_3).

$^{13}C\{^1H\}$ NMR (151 MHz, 299 K, CD_2Cl_2)[selected resonances]: δ ^{13}C: 147.7 (2-C), 146.6 (4-C), 142.7 (9-C), 142.1 (i-Ph), 140.2 (6-C), 138.1 (13-C), 133.4 (10-C), 129.7 (12-CH=), 129.1 (m-Ph), 127.5 (o-Ph), 127.4 (p-Ph), 125.9 (11-CH=), 125.7 (3-CH=), 124.2 (8-CH=), 124.0 (7-CH=), 119.7 (5-CH=), 39.1 (CH_2), 21.3 (CH_3).

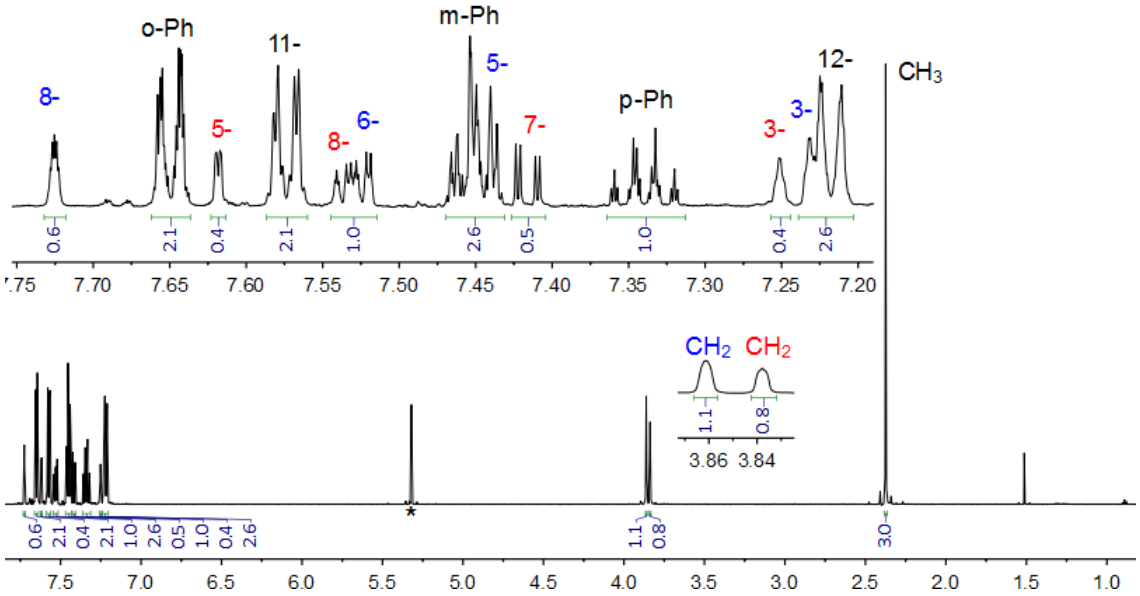


Figure S103. ^1H NMR (600 MHz, 299 K, CD_2Cl_2*) spectrum of isolated mixture of compounds **7d** (labeled in blue) and **7d'** (labeled in red).

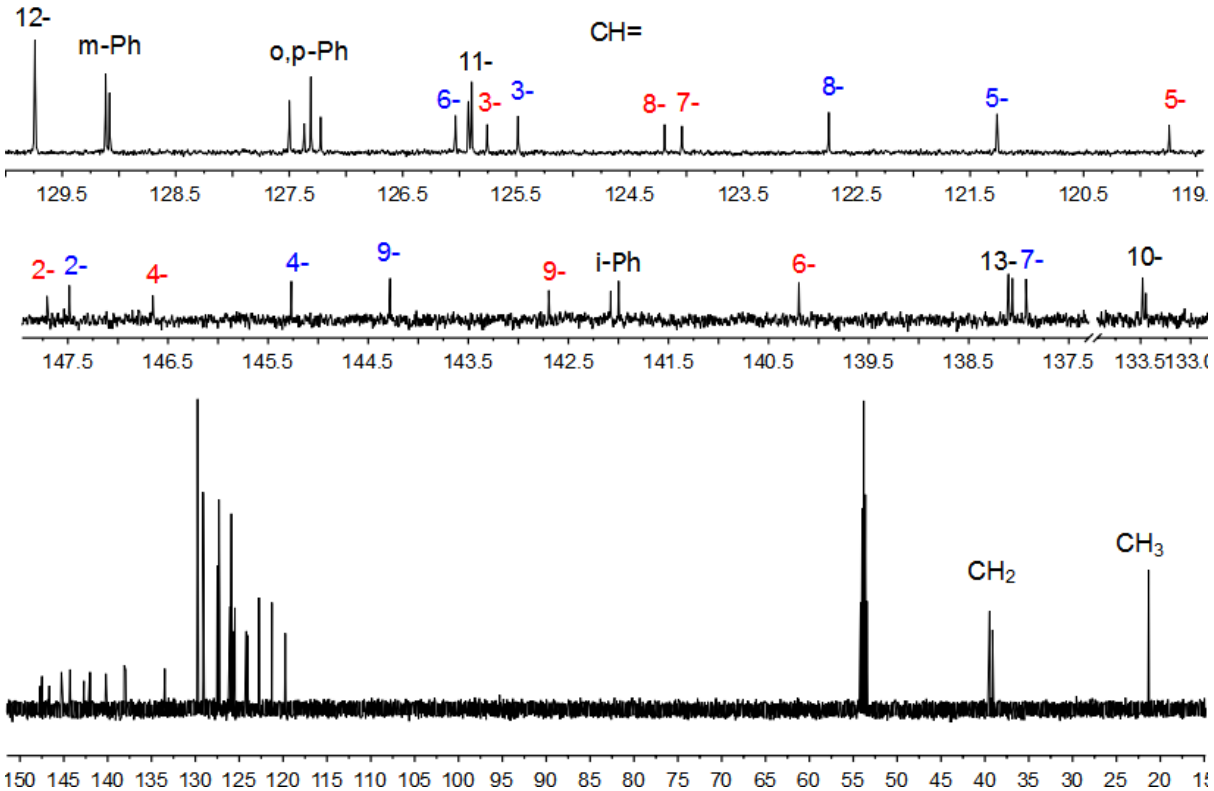
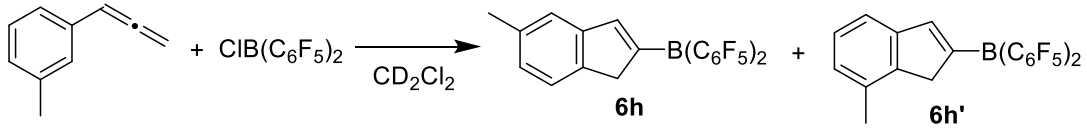


Figure S104. $^{13}C\{^1H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of isolated mixture of compounds **7d** (labeled in blue) and **7d'** (labeled in red).

L) Generation of compounds **6h** and **6h'**

Scheme S27.



m-Methylphenylallene (6.5 mg, 0.05 mmol) and $ClB(C_6F_5)_2$ (19 mg, 0.05 mmol) were dissolved in CD_2Cl_2 (0.5 mL) at room temperature. The resulting reaction mixture was then characrerized by NMR experiments within 5 min: a mixture of compounds **6h** (48 mol%, ^1H), **6h'** (26 mol%, ^1H) and $ClB(C_6F_5)_2$ (26 mol%, ^{19}F).

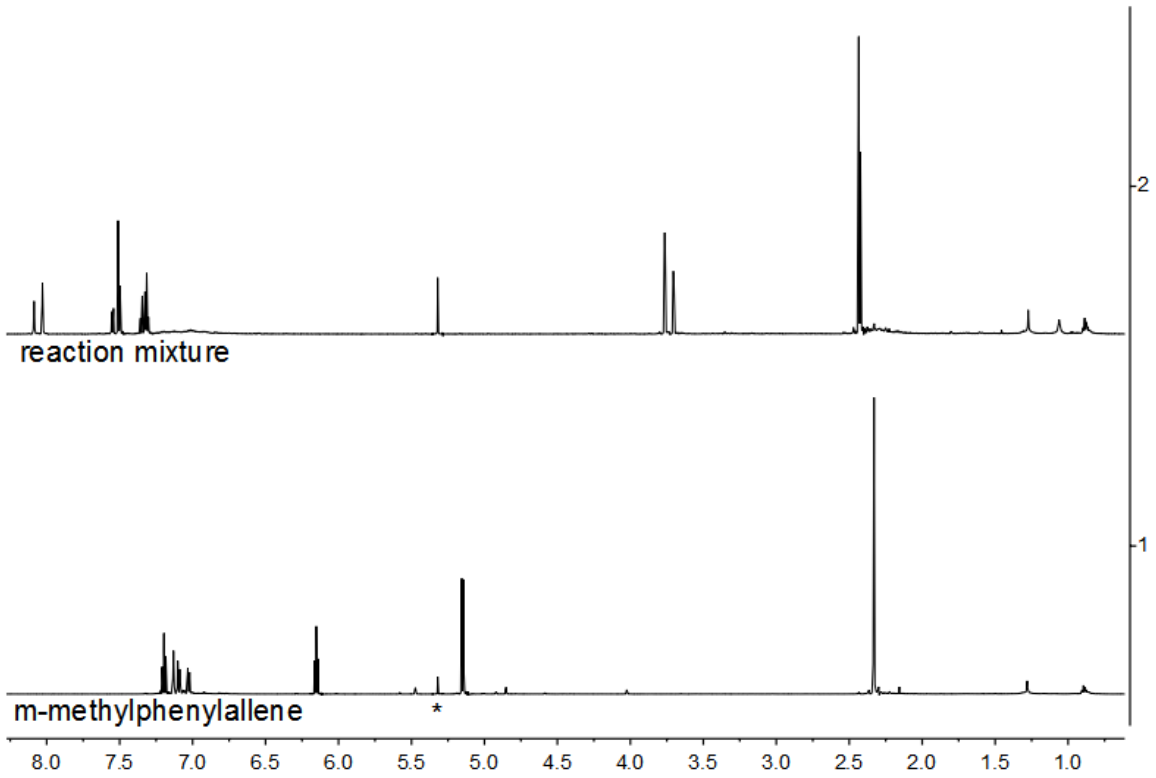


Figure S105. ^1H NMR (600 MHz, 299 K, CD_2Cl_2*) spectra of (1) m-methylphenylallene and (2) the reaction mixture.

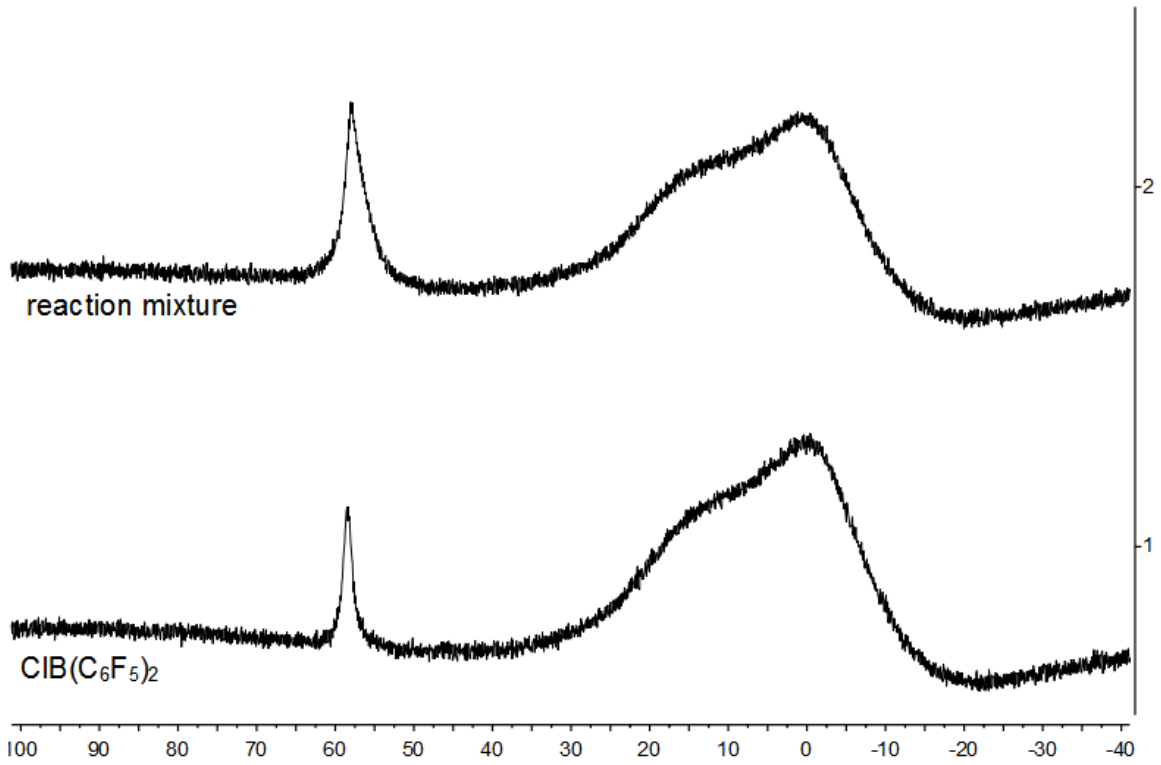


Figure S106. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectra of (1) $ClB(C_6F_5)_2$ and (2) the reaction mixture.

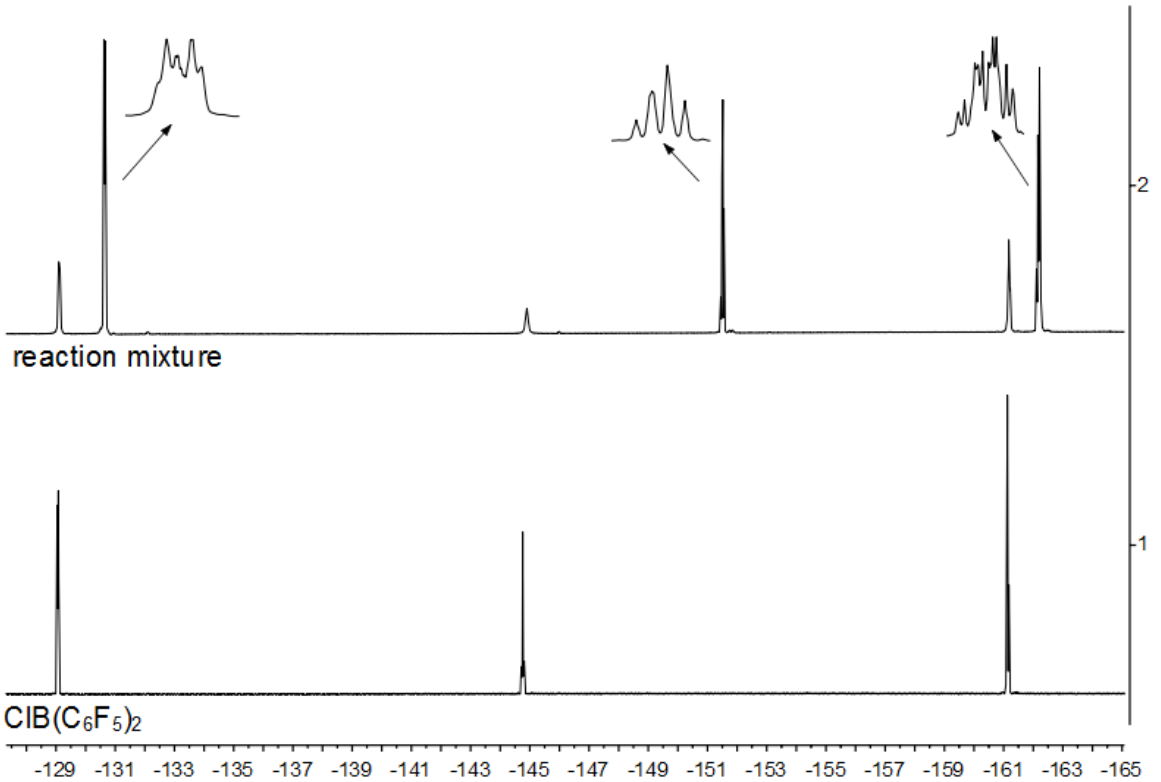
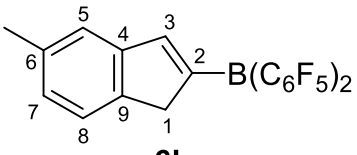


Figure S107. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectra of (1) $ClB(C_6F_5)_2$ and (2) the reaction mixture.

NMR data of compound **6h**:



6h

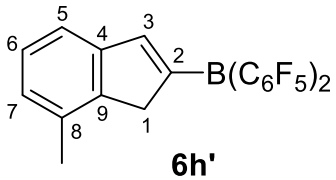
^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ ^{1}H: 8.03 (t, $^{4}J_{HH}$ = 1.9 Hz, 1H, 3-CH=), 7.51 (m, 1H, 5-CH=), 7.50 (m, 1H, 8-CH=), 7.32 (m, 1H, 7-CH=), 3.76 (d, $^{4}J_{HH}$ = 1.9 Hz, 2H, CH_2), 2.44 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2)[selected resonances]: δ ^{13}C: 162.8 (3-CH=), 151.4 (br, CB=), 148.5 (9-C), 144.3 (4-C), 137.7 (6-C), 132.0 (7-CH=), 125.9 (5-CH=), 124.6 (8-CH=), 41.8 (CH_2), 21.4 (CH_3).

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ ^{11}B: 57.9 ($\nu_{1/2}$ ~ 600 Hz)

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ ^{19}F: −130.6 (m, 2F, *o*), −151.5 (m, 1F, *p*), −162.2 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 10.7].

NMR data of compound **6h'**:



6h'

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ ^{1}H: 8.09 (t, $^{4}J_{HH}$ = 2.0 Hz, 1H, 3-CH=), 7.55 (m, 1H, 5-CH=), 7.35 (m, 1H, 6-CH=), 7.31 (m, 1H, 7-CH=), 3.71 (d, $^{4}J_{HH}$ = 2.0 Hz, 2H, CH_2), 2.42 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2)[selected resonances]: δ ^{13}C: 162.8 (3-CH=), 151.0 (br, CB=), 150.0 (9-C), 143.6 (4-C), 134.7 (8-C), 131.7 (7-CH=), 128.0 (6-CH=), 123.3 (5-CH=), 41.2 (CH_2), 18.8 (CH_3).

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ ^{11}B: 57.9 ($\nu_{1/2}$ ~ 600 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ ^{19}F: −130.6 (m, 2F, *o*), −151.5 (m, 1F, *p*), −162.2 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 10.7].

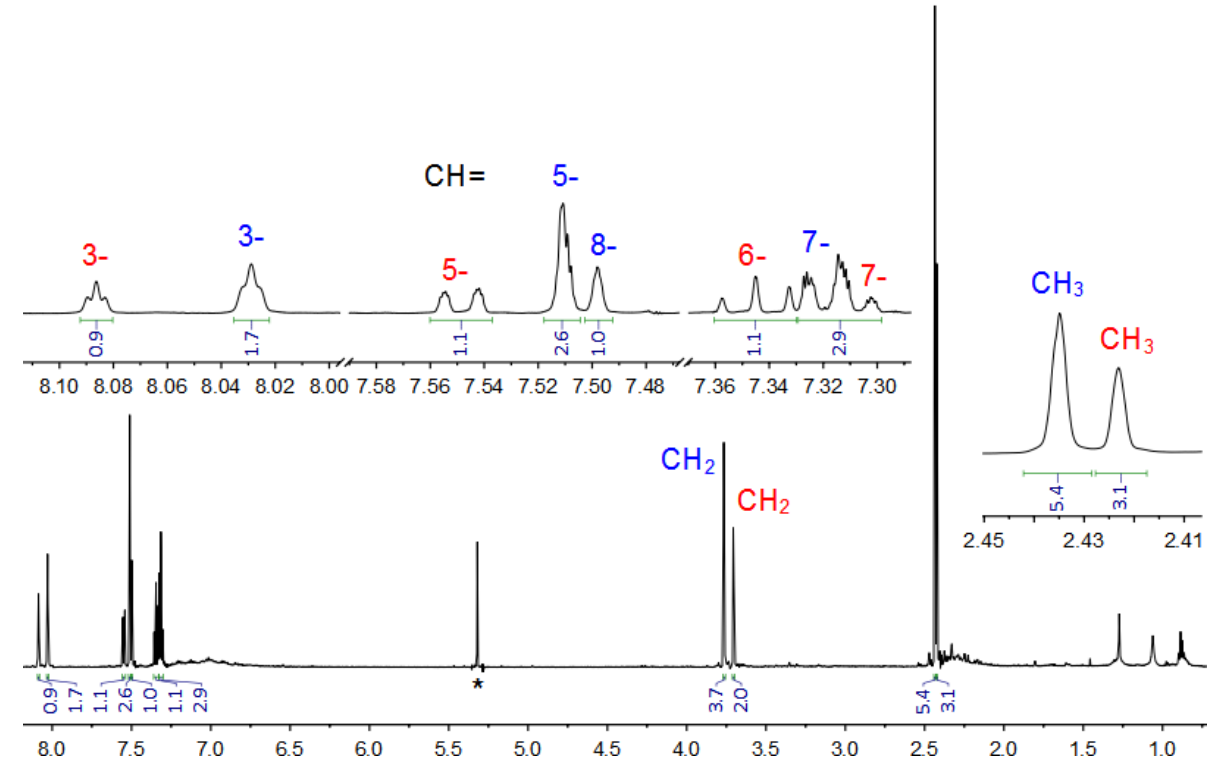


Figure S108. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2*) spectrum of reaction mixture: compound **6h** labeled in blue and compound **6h'** labeled in red.

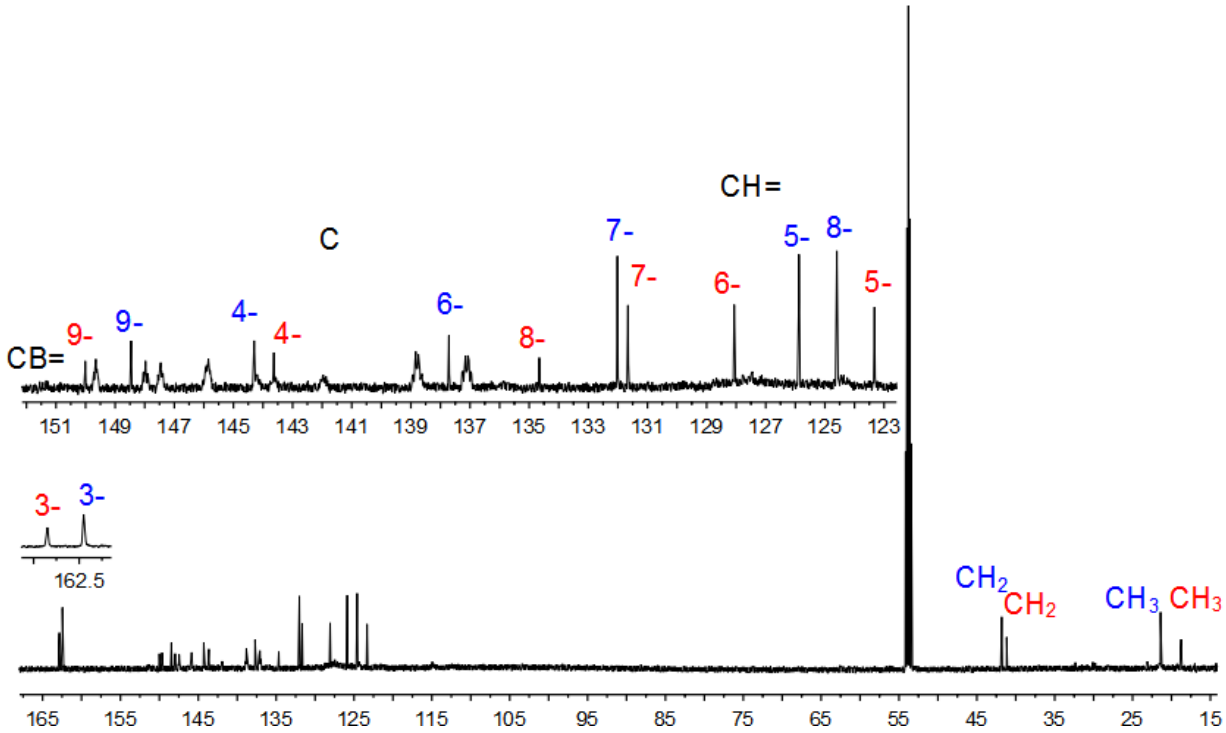


Figure S109. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of reaction mixture: compound **6h** labeled in blue and compound **6h'** labeled in red.

Photophysical measurements

Kateryna Soloviova, Cristian Strassert

Institut für Anorganische und Analytische Chemie - CeNTech, Westfälische Wilhelms-Universität Münster, Heisenbergstrasse 11, D-48149 Münster Germany.

General information: Fluorescence lifetimes were recorded on a FluoTime300 spectrometer from PicoQuant equipped with diode lasers (pulse width < 80 ps) operated by a computer-controlled laser driver PDL-820 (repetition rate up to 80 MHz, burst mode for slow and weak decays), two emission monochromators (Czerny-Turner, selectable gratings blazed at 500 nm with 2.7 nm/mm dispersion and 1200 grooves/mm, or blazed at 1250 nm with 5.4 nm/mm dispersion and 600 grooves/mm), and a PMA Hybrid 40 (transit time spread FWHM < 120 ps, 300 – 720 nm) detector, in TCSPC mode with a PicoHarp 300 (minimum base resolution 4 ps). Lifetime analysis was performed using the commercial FluoFit software. The quality of the fit was assessed by minimizing the reduced chi squared function ($\chi 2$) and visual inspection of the weighted residuals and their autocorrelation. Luminescence quantum yields were measured with a Hamamatsu Photonics absolute PL quantum yield measurement system (C9920-02) equipped with a L9799-01 CW Xenon light source (150 W), monochromator, C7473 photonic multi-channel analyzer, integrating sphere and employing U6039-05 PLQY measurement software (Hamamatsu Photonics, Ltd., Shizuoka, Japan).

Sample preparation: In a dark glovebox the compounds **6a**-**d** and **6g** were dissoved in dry dichloromethane (DCM) in quartz tubes ($c \approx 1.0\times10^{-5}$ mol/L), which were sealed with rubber septa and teflon tape. For solid samples, a small amount of compounds **6a**-**d** and **6g** was placed at the bottom of the quartz tubes, which were sealed with rubber septa and teflon tape. The samples were protected by aluminium foil during delivery.

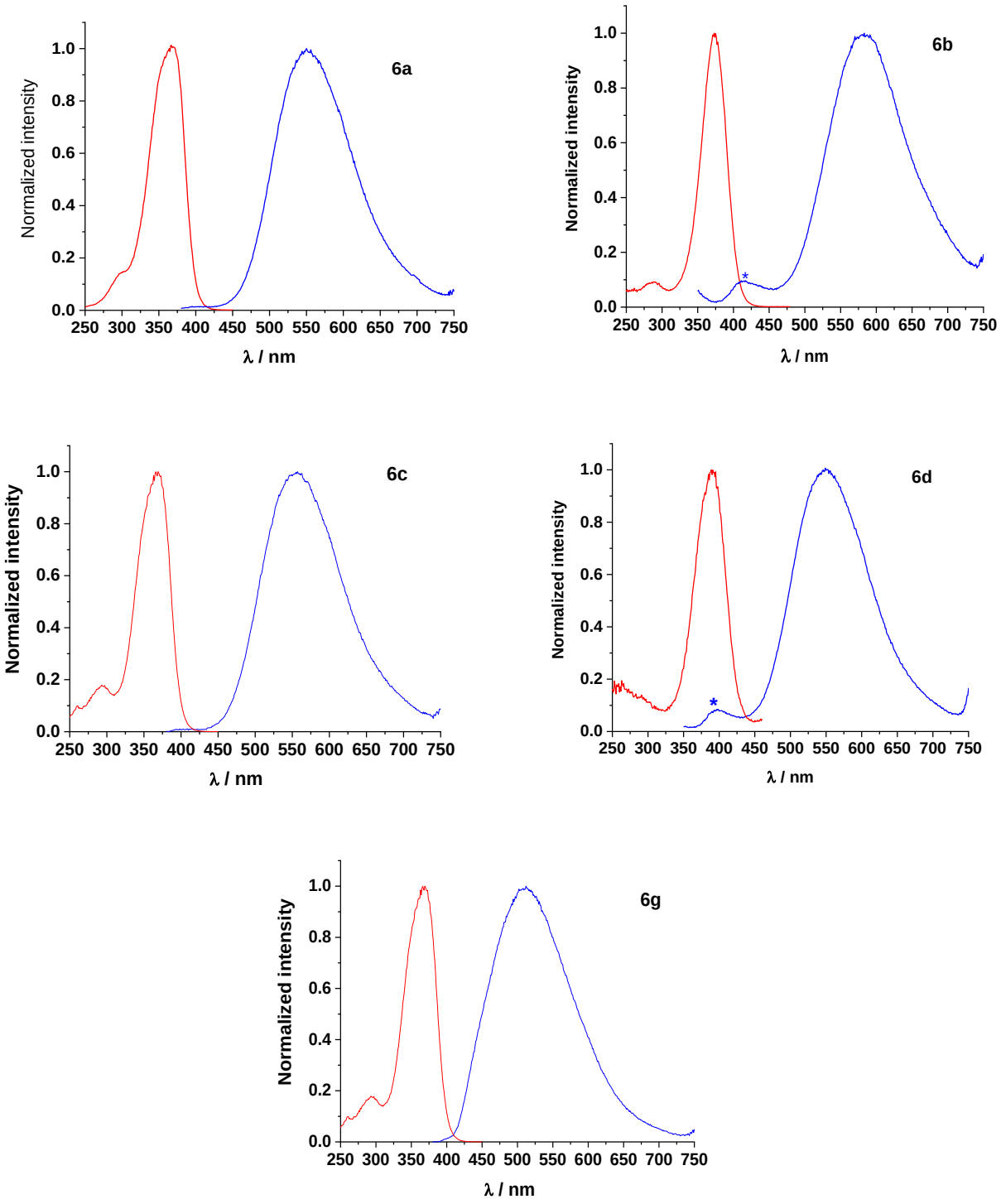


Figure S110. Normalized fluorescence excitation (in red, λ_{em} = 650 nm) and emission (in blue, λ_{ex} = 300 nm) spectra for compounds **6a**-**d** and **6g**. All spectra were recorded in fluid dichloromethane at room temperature [c ≈ 10 µM]. The asterisks (*) denote decomposition products.

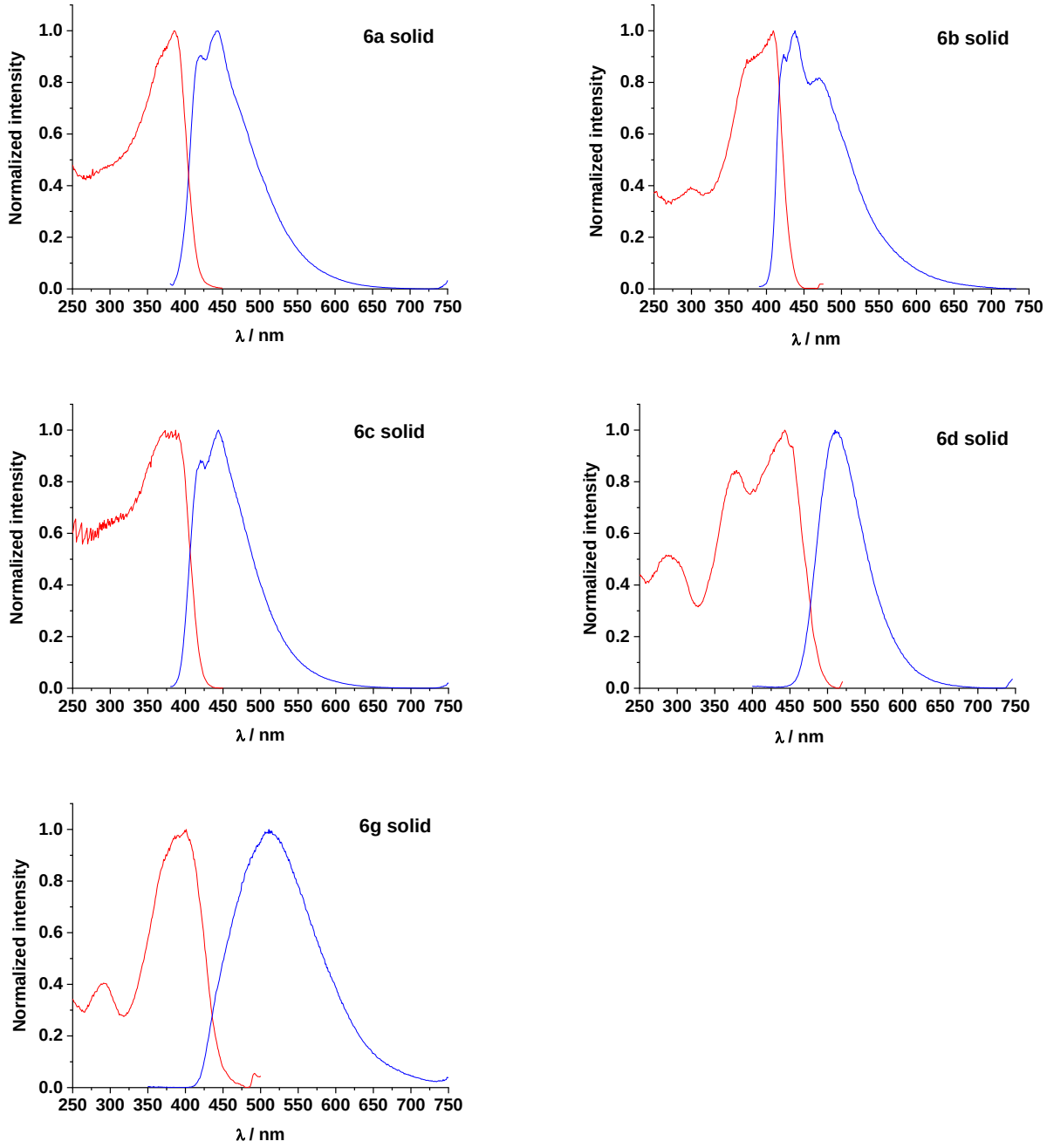
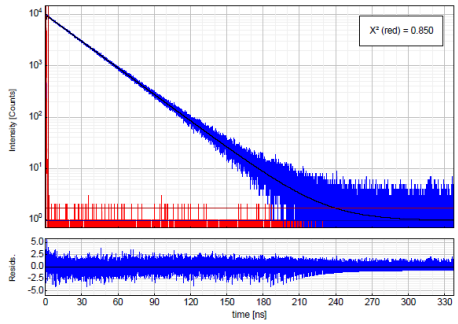


Figure S111. Normalized fluorescence excitation (in red, λ_{em} = 550 nm) and emission (in blue, λ_{ex} = 300 nm) spectra for compounds **6a**-**d** and **6g**. All spectra were recorded as amorphous solids at room temperature.

Time-resolved luminescence decays

Samples in dichloromethane solution:



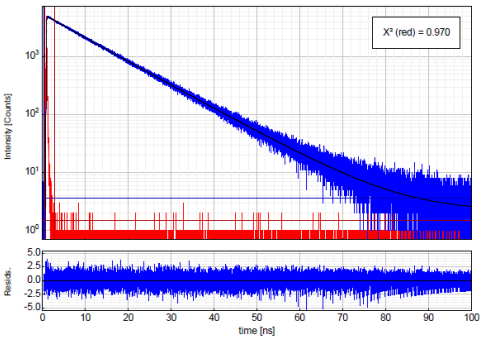
Parameter	Value	Conf. Lower	Conf. Upper
A_1 [Cnts]	9840.5	-53.6	+53.6
τ_1 [ns]	25.1319	-0.0954	+0.0954
Bkgr. Dec [Cnts]	0.972	-0.360	+0.360
Bkgr. IRF [Cnts]	1.68	-4.47	+4.47
Shift IRF [ns]	0.28121	-0.00632	+0.00632
A Scat [Cnts]	12690	-5510	+5510

Average Lifetime:

$\tau_{Av.1}$=25.1319 ns (intensity weighted)

$\tau_{Av.2}$=25.1319 ns (amplitude weighted)

Figure S112. Left: Time-resolved luminescence decay of compound **6a** including the instrument response function (red) and the residuals at RT (λ_{ex} = 375 nm, λ_{em} = 550 nm). Right: Fitting parameters including pre-exponential factors and confidence limits.



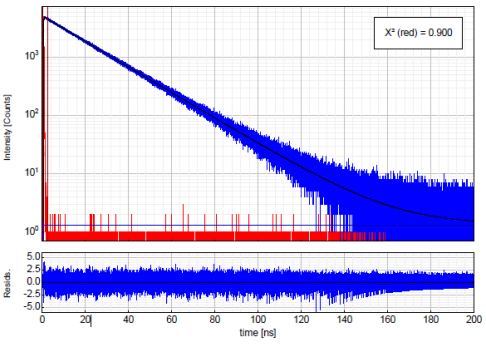
Parameter	Value	Conf. Lower	Conf. Upper
A_1 [Cnts]	-1.965	-0.741	+0.741
τ_1 [ns]	432.979	---	---
A_2 [Cnts]	4790.4	-33.7	+33.7
τ_2 [ns]	10.8052	-0.0521	+0.0521
A_3 [Cnts]	323.7	-53.0	+53.0
τ_3 [ns]	6.259	-0.994	+0.994
Bkgr. Dec [Cnts]	3.666	-0.600	+0.600
Bkgr. IRF [Cnts]	1.51	-2.02	+2.02
Shift IRF [ns]	-0.00840	-0.00537	+0.00537
A Scat [Cnts]	8430	-7830	+7830

Average Lifetime:

$\tau_{Av.1}$=3.847 ns (intensity weighted)

$\tau_{Av.2}$=10.355 ns (amplitude weighted)

Figure S113. Left: Time-resolved luminescence decay of compound **6b** including the instrument response function (red) and the residuals at RT (λ_{ex} = 375 nm, λ_{em} = 580 nm). Right: Fitting parameters including pre-exponential factors and confidence limits.



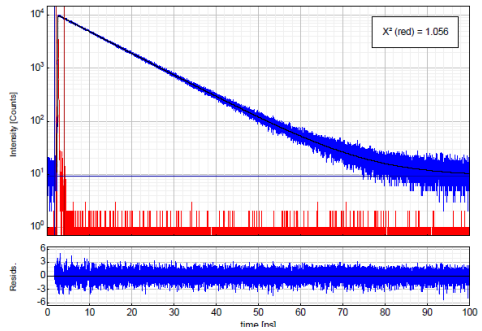
Parameter	Value	Conf. Lower	Conf. Upper
A_1 [Cnts]	4992.9	-34.0	+34.0
τ_1 [ns]	19.7452	-0.0946	+0.0946
Bkgr. Dec [Cnts]	1.335	-0.481	+0.481
Bkgr. IRF [Cnts]	-0.171	-7.04	+7.04
Shift IRF [ns]	0.04385	-0.00693	+0.00693
A Scat [Cnts]	28800	-12000	+12000

Average Lifetime:

$\tau_{Av.1}$=19.7452 ns (intensity weighted)

$\tau_{Av.2}$=19.7452 ns (amplitude weighted)

Figure S114. Left: Time-resolved luminescence decay of compound **6c** including the instrument response function (red) and the residuals at RT (λ_{ex} = 375 nm, λ_{em} = 555 nm). Right: Fitting parameters including pre-exponential factors and confidence limits.



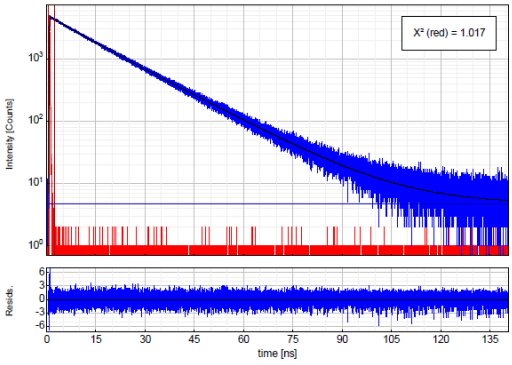
Parameter	Value	Conf. Lower	Conf. Upper
A_1 [Cnts]	167.8	-37.1	+37.1
τ_1 [ns]	13.83	-1.74	+1.74
A_2 [Cnts]	9919.5	-50.5	+50.5
τ_2 [ns]	10.4798	-0.0386	+0.0386
Bkgr. Dec [Cnts]	9.31	-1.04	+1.04
Bkgr. IRF [Cnts]	-0.99	-2.77	+2.77
Shift IRF [ns]	-0.01081	-0.00349	+0.00349
A Scat [Cnts]	98400	-14000	+14000

Average Lifetime:

$\tau_{Av.1}$=10.55 ns (intensity weighted)

$\tau_{Av.2}$=10.54 ns (amplitude weighted)

Figure S115. Left: Time-resolved luminescence decay of compound **6d** including the instrument response function (red) and the residuals) at RT (λ_{ex} = 375 nm, λ_{em} = 550 nm). Right: Fitting parameters including pre-exponential factors and confidence limits.



Parameter	Value	Conf. Lower	Conf. Upper
A_1 [Cnts]	4300.0	-32.5	+32.5
τ_1 [ns]	15.7482	-0.0909	+0.0909
A_2 [Cnts]	561.2	-60.4	+60.4
τ_2 [ns]	7.227	-0.855	+0.855
Bkgr. Dec [Cnts]	4.756	-0.772	+0.772
Bkgr. IRF [Cnts]	-1.56	-3.68	+3.68
Shift IRF [ns]	0.01841	-0.00573	+0.00573
A Scat [Cnts]	70600	-12800	+12800

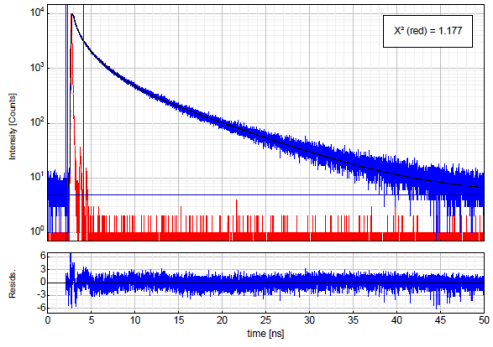
Average Lifetime:

$\tau_{Av.1}$=15.2667 ns (intensity weighted)

$\tau_{Av.2}$=14.7644 ns (amplitude weighted)

Figure S116. Left: Time-resolved luminescence decay of compound **6g** including the instrument response function (red) and the residuals at RT (λ_{ex} = 375 nm, λ_{em} = 510 nm). Right: Fitting parameters including pre-exponential factors and confidence limits.

Solid samples:



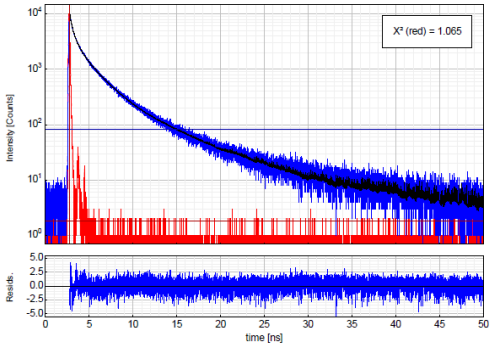
Parameter	Value	Conf. Lower	Conf. Upper
A_1 [Cnts]	997.6	---	---
τ_1 [ns]	7.4055	-0.0841	+0.0841
A_2 [Cnts]	4130.5	-77.1	+77.1
τ_2 [ns]	1.9154	-0.0305	+0.0305
A_3 [Cnts]	7634	-247	+247
τ_3 [ns]	0.4261	-0.0152	+0.0152
Bkgr. Dec [Cnts]	4.959	-0.881	+0.881
Bkgr. IRF [Cnts]	-3.77	-4.28	+4.28
Shift IRF [ns]	0.04195	-0.00277	+0.00277
A Scat [Cnts]	-6680	-8220	+8220

Average Lifetime:

$\tau_{Av.1}$=3.8404 ns (intensity weighted)

$\tau_{Av.2}$=1.4537 ns (amplitude weighted)

Figure S117. Left: Time-resolved luminescence decay of compound **6a** including the instrument response function (red) and the residuals at RT (λ_{ex} = 375 nm, λ_{em} = 445 nm). Right: Fitting parameters including pre-exponential factors and confidence limits.



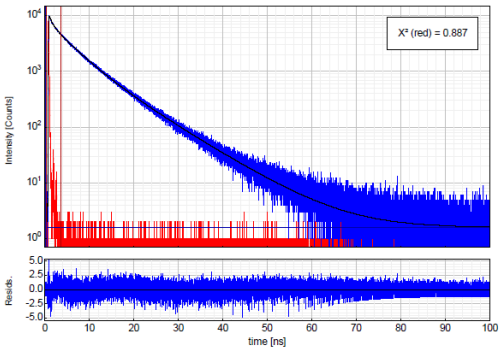
Parameter	Value	Conf. Lower	Conf. Upper
A_1 [Cnts]	2452.1	-70.1	+70.1
τ_1 [ns]	6.677	-0.156	+0.156
A_2 [Cnts]	17225	-213	+213
τ_2 [ns]	2.0262	-0.0235	+0.0235
A_3 [Cnts]	32352	-937	+937
τ_3 [ns]	0.4046	-0.0120	+0.0120
Bkgr. Dec [Cnts]	81.388	-0.624	+0.624
Bkgr. IRF [Cnts]	1.8233	-0.0133	+0.0133
Shift IRF [ns]	0.022321	-0.000213	+0.000213
A Scat [Cnts]	953100	-55100	+55100

Average Lifetime:

$\tau_{Av.1}$=2.879 ns (intensity weighted)

$\tau_{Av.2}$=1.237 ns (amplitude weighted)

Figure S118. Left: Time-resolved luminescence decay of compound **6b** including the instrument response function (red) and the residuals at RT (λ_{ex} = 375 nm, λ_{em} = 470 nm). Right: Fitting parameters including pre-exponential factors and confidence limits.



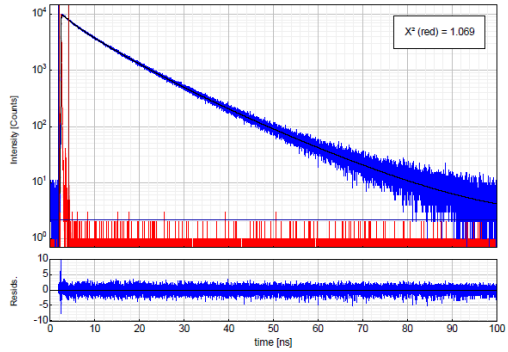
Parameter	Value	Conf. Lower	Conf. Upper
A_1 [Cnts]	2461.3	-33.7	+33.7
τ_1 [ns]	9.0371	-0.0724	+0.0724
A_2 [Cnts]	5030.6	-70.4	+70.4
τ_2 [ns]	4.4169	-0.0548	+0.0548
A_3 [Cnts]	3312	-247	+247
τ_3 [ns]	0.7032	-0.0635	+0.0635
Bkgr. Dec [Cnts]	1.572	-0.406	+0.406
Bkgr. IRF [Cnts]	-1.16	-3.15	+3.15
Shift IRF [ns]	-0.00477	-0.00311	+0.00311
A Scat [Cnts]	86800	-12700	+12700

Average Lifetime:

$\tau_{Av.1}$=6.4283 ns (intensity weighted)

$\tau_{Av.2}$=4.3309 ns (amplitude weighted)

Figure S119. Left: Time-resolved luminescence decay of compound **6c** including the instrument response function (red) and the residuals at RT (λ_{ex} = 375 nm, λ_{em} = 445 nm). Right: Fitting parameters including pre-exponential factors and confidence limits.



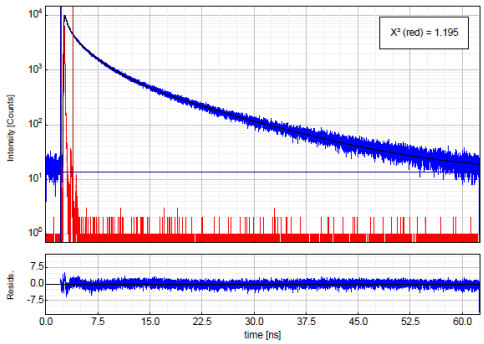
Parameter	Value	Conf. Lower	Conf. Upper
A_1 [Cnts]	2389.1	-32.4	+32.4
τ_1 [ns]	13.720	-0.117	+0.117
A_2 [Cnts]	6014.5	-59.3	+59.3
τ_2 [ns]	7.7848	-0.0647	+0.0647
A_3 [Cnts]	1974	-136	+136
τ_3 [ns]	2.406	-0.195	+0.195
Bkgr. Dec [Cnts]	2.209	-0.835	+0.835
Bkgr. IRF [Cnts]	-5.02	-3.33	+3.33
Shift IRF [ns]	0.04636	-0.00403	+0.00403

Average Lifetime:

$\tau_{Av.1}$=9.788 ns (intensity weighted)

$\tau_{Av.2}$=8.128 ns (amplitude weighted)

Figure S120. Left: Time-resolved luminescence decay of compound **6d** including the instrument response function (red) and the residuals at RT (λ_{ex} = 375 nm, λ_{em} = 510 nm). Right: Fitting parameters including pre-exponential factors and confidence limits.



Parameter	Value	Conf. $_{Lower}$	Conf. $_{Upper}$
A_1 [Cnts]	1194.6	-18.0	+18.0
τ_1 [ns]	11.151	-0.111	+0.111
A_2 [Cnts]	4337.5	-70.7	+70.7
τ_2 [ns]	2.9214	-0.0426	+0.0426
A_3 [Cnts]	6373	-256	+256
τ_3 [ns]	0.4997	-0.0230	+0.0230
Bkgr. $_{Dec}$ [Cnts]	13.43	-1.37	+1.37
Bkgr. $_{IRF}$ [Cnts]	-7.17	-5.28	+5.28
Shift $_{IRF}$ [ns]	-0.02318	-0.00322	+0.00322

Average Lifetime:

$\tau_{Av.1}$=6.414 ns (intensity weighted)

$\tau_{Av.2}$=2.451 ns (amplitude weighted)

Figure S121. Left: Time-resolved luminescence decay of compound **6g** including the instrument response function (red) and the residuals at RT (λ_{ex} = 375 nm, λ_{em} = 510 nm). Right: Fitting parameters including pre-exponential factors and confidence limits.

Table S1. Photophysical data with experimental uncertainties for compounds **6a**-**d** and **6g** at room temperature in fluid dichloromethane (c ≈ 10 µM) and in the solid state, including photoluminescence quantum yields (Φ_F, as percentages), fluorescence excitation (λ_{ex}) and emission (λ_{em}) maxima as well as time-resolved fluorescence decay components (τ) with pre-exponential factors (as percentages).

Observable	6a	6b	6c	6d	6g
λ^{max}_{Ex} ± 5 / nm[a]	365	373	370	390	360
λ^{max}_{Em} ± 5 / nm[a]	550	580	555	550	510
Φ_F ± 2 / %[a]	21	9	17	25	14
λ^{max}_{Ex} ± 5 / nm[b]	380	400	375	440	400
λ^{max}_{Em} ± 5 / nm[b]	450	435	450	510	510
Φ_F ± 2 / %[b]	55[c]	29	31	50[c]	18[c]
τ / ns (relative amplitude as %)[a]	25.1 ±0.1	433 ±1 (rise time) 10.8 ±0.1 (94) 6 ±1 (6)	19.8 ±0.1	14 ±2 (2) 10.5 ±0.1 (98)	15.8 ±0.1 (88) 7.20 ±0.9 (12)
τ / ns (relative amplitude as %)[b]	7.4 ±0.1 (8) 1.9 ±0.1 (32) 0.4 ±0.1 (60)	6.7 ±0.2 (5) 2.0 ±0.1 (33) 0.4 ±0.1 (62)	9.0 ±0.1 (23) 4.4 ±0.1 (46) 0.7 ±0.1 (31)	13.7 ±0.1 (23) 7.8 ±0.1 (58) 2.4 ±0.2 (19)	11.2 ±0.1 (10) 2.9 ±0.1 (36) 0.5 ±0.1 (54)

[a]Measured in fluid solution. [b]Measured in the solid state. [c]Average value of three independent measurements.