Supporting Information

Arylallenes and the Halogeno-B(C₆F₅)₂ Reagents: Facile Formation of 2-Borylindenones


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Table of Contents

Supporting Information: experimental and analytical details S2
General Information S2
A) Preparation of arylallenes S4
B) Synthesis of compound 6a S8
C) Synthesis of compound 6b S22
D) Synthesis of compound 6c S28
E) Synthesis of compound 6d S38
F) Synthesis of compound 6e S44
G) Synthesis of compounds 6f and 6f’ S48
H) Synthesis of compounds 6g and 6g’ S55
I) Synthesis of compounds 6g(pyr)₃ S73
J) Synthesis of compound 7a S77
K) Synthesis of compounds 7d and 7d’ S80
L) Generation of compounds 6h and 6h’ S82
Photophysical measurements S86
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 [δ(BF$_3$·OEt$_2$) = 0 for $^{11}$B NMR, δ(CFCl$_3$·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$_6$F$_5$ groups and for compound 6g’ one C$_6$F$_5$ 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$_6$F$_5$)$_2$ and BrB(C$_6$F$_5$)$_2$ 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.]: \((\text{CH}_2\text{O})_n\) (2.5 equiv), CuI (0.5 equiv), dioxane, terminal mono arylacetylene (1.0 equiv) and dicyclohexylamine (Cy\(_2\text{NH}\), 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 (0.45 g, 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.

**^1H NMR** (600 MHz, 299 K, CD\(_2\text{Cl}_2\)): \(\delta\ ^1\text{H}: 7.57 \text{ (m, 2H, 2,2’-biphenyl), 7.37 \text{ (m, 2H, 3,3’-biphenyl)}\) \(6.23 \text{ (t, } 4^J_{\text{HH}} = 6.8 \text{ Hz, 1H, } =\text{CH,}\) \(5.20 \text{ (d, } 4^J_{\text{HH}} = 6.8 \text{ Hz, 2H, } =\text{CH}_2\).}

**^13C\{^1H\} NMR** (151 MHz, 299 K, CD\(_2\text{Cl}_2\)): \(\delta\ ^{13}\text{C}: 210.3 \text{ (=C=), 139.5 \text{ (1,1’-biphenyl), 133.4 \text{ (4,4’-biphenyl), 127.4 \text{ (3,3’-biphenyl), 127.3 \text{ (2,2’-biphenyl), 93.7 \text{ (=CH, 79.0 \text{ (=CH}_2\text{).}})}}}

54
Figure S1. $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$*) spectrum of compound 2e.

Figure S2. $^{13}$C($^1$H) NMR (151 MHz, 299 K, CD$_2$Cl$_2$) 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), Cul (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.

\( ^1\text{H NMR} \) (600 MHz, 299 K, CD\(_2\)Cl\(_2\)): \( \delta \ ^1\text{H}: 7.25 \text{ (s, 2H, C} \_6\text{H}_4 \)), 6.18 \text{ (t, } ^4\text{J}_{\text{HH}} = 6.7 \text{ Hz, 1H, } =\text{CH}) \), 5.17 \text{ (d, } ^4\text{J}_{\text{HH}} = 6.7 \text{ Hz, 2H, } =\text{CH}_2 \)).

\( ^{13}\text{C}^{\{^1\text{H}\}} \text{ NMR} \) (151 MHz, 299 K, CD\(_2\)Cl\(_2\)): \( \delta ^{13}\text{C}: 210.2 \text{ (=C=), 139.5 (i-C} \_6\text{H}_4 \)), 127.3 (C\(_6\)H\(_4\)), 93.9 (=CH), 79.0 (=CH\(_2\)).

**Figure S3.** \(^1\text{H NMR} \) (600 MHz, 299 K, CD\(_2\)Cl\(_2\)) spectrum of compound 2f.

**Figure S4.** \(^{13}\text{C}^{\{^1\text{H}\}} \text{ NMR} \) (151 MHz, 299 K, CD\(_2\)Cl\(_2\)) 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$_2$Cl$_2$ = 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$_2$Cl$_2$): $\delta$ $^1$H: 7.08 (s, 1H, C$_6$H$_3$), 6.14 (t, $^4$J$_{HH}$ = 6.8 Hz, 1H, =CH), 5.17 (d, $^4$J$_{HH}$ = 6.8 Hz, 2H, =CH$_2$).

$^{13}$C{$^1$H} NMR (151 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^{13}$C: 210.1 (=C=), 135.0 (t-C$_6$H$_3$), 123.9 (C$_6$H$_3$), 93.7 (=CH), 79.1 (=CH$_2$).

Figure S5. $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$*) spectrum of compound 2g.

Figure S6. $^{13}$C{$^1$H} NMR (151 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 2g.
B) Synthesis of compound 6a

**Experiment 1:** (reaction of compound 2a with ClB(C₆F₅)₂, NMR scale)

**Scheme S4.**

A solution of ClB(C₆F₅)₂ (38 mg, 0.10 mmol) in CD₂Cl₂ (0.3 mL) was added to a solution of phenylallene (14 mg, 0.12 mmol) in CD₂Cl₂ (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(C₆F₅)₂ (8 mol%, ¹⁹F) was obtained.

**Figure S7.** ¹H NMR (600 MHz, 299 K, CD₂Cl₂*) spectra of (1) ClB(C₆F₅)₂, (2) phenylallene, (3) reaction mixture, and (4) isolated compound 6a.
Figure S8. $^{11}$B($^1$H) NMR (192 MHz, 299 K, CD$_2$Cl$_2$) spectra of (1) ClB(C$_6$F$_5$)$_2$, (2) reaction mixture, and (3) isolated compound 6a.

Figure S9. $^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectra of (1) ClB(C$_6$F$_5$)$_2$, (2) reaction mixture, and (3) isolated compound 6a.
**Experiment 2:** (reaction of compound 2a with ClB(C₆F₅)₂, preparative scale)

**Scheme S5.**

\[
\text{ClB(C₆F₅)₂ + } \text{2a} \xrightarrow{\text{r.t. }} \text{5 min} \xrightarrow{\text{CH₂Cl₂}} \text{6a}
\]

A solution of ClB(C₆F₅)₂ (152 mg, 0.40 mmol) in CH₂Cl₂ (2 mL) was added to a solution of phenylallene (56 mg, 0.48 mmol) in CH₂Cl₂ (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 C₂₁H₇BF₁₀: C, 54.82; H, 1.53. Found: C, 54.67; H, 1.49.

**¹H NMR** (600 MHz, 299 K, CD₂Cl₂): \(δ\) ¹H: 8.07 (t, \(J_{HH} = 1.90\) Hz, 1H, 3-CH=), 7.71 (dm, \(J_{HH} = 7.6\) Hz, 1H, 5-CH=), 7.63 (dm, \(J_{HH} = 7.6\) Hz, 1H, 8-CH=), 7.49 (td, \(J_{HH} = 7.6\) Hz, \(J_{HH} = 1.2\) Hz, 1H, 7-CH=), 7.42 (tm, \(J_{HH} = 7.6\) Hz, 1H, 6-CH=), 3.82 (d, \(J_{HH} = 1.90\) Hz, 2H, CH₂).

**¹³C{¹H} NMR** (151 MHz, 299 K, CD₂Cl₂): \(δ\) ¹³C: 162.3 (3-CH=), 151.1 (9-C), 151.1 (br, CB)\(^t\), 146.6 (dm, \(J_{FC} \sim 240\) Hz, C₆F₅), 144.0 (4-C), 142.8 (dm, \(J_{FC} \sim 250\) Hz, C₆F₅), 137.9 (dm, \(J_{FC} \sim 250\) Hz, C₆F₅), 130.7 (7-CH=), 127.7 (6-CH=), 125.7 (5-CH=), 125.0 (8-CH=), 114.8 (br, i-C₆F₅), 42.2 (CH₂), \[^t\] tentative assignment].

**¹⁹F NMR** (564 MHz, 299 K, CD₂Cl₂): \(δ\) ¹⁹F: −130.6 (m, 2F, o), −151.3 (t, \(J_{FF} = 20.0\) Hz, 1F, p), −162.1 (m, 2F, m)(C₆F₅)[\(Δδ¹⁹F_{m,p} = 10.8\)].

**¹¹B{¹H} NMR** (192 MHz, 299 K, CD₂Cl₂): \(δ\) ¹¹B: 57.0 (\(ν_{1/2} \sim 800\) Hz).
Figure S10. $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$*) spectrum of compound 6a.

Figure S11. $^{13}$C($^1$H) NMR (151 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 6a.
Figure S12. $^1$H,$^{13}$C GHSQC (600/151 MHz, CD$_2$Cl$_2$, 299K) spectrum of compound 6a.

Figure S13. $^1$H,$^{13}$C GHMBC (600/151 MHz, CD$_2$Cl$_2$, 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$_2$Cl$_2$) spectra of compound 6a. Irradiation points (*): (2) $\delta^1$H 3.82 (CH$_2$); (3) $\delta^1$H 7.63 (8-CH); (4) $\delta^1$H 7.71 (5-CH); (5) $\delta^1$H 8.07 (=CH).
Figure S15. $^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 6a.

Figure S16. $^{11}$B$^{[1]}$H NMR (192 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 6a.
The activation energy was estimated by the coalescence of the para fluorine signals (δ -149.7, -150.4) of the two pentafluorophenyl rings:

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

$T_{coal}$ = coalescence temperature [K]: 218 K ($^{19}$F, BC$_6$F$_5$)

$\Delta \nu$ = chemical shift difference [Hz] ($^{19}$F, p-BC$_6$F$_5$, 193 K): 397 Hz

$R = 8.314 \text{ J/(mol·K)}$; 1 J = 0.239 cal

$$\Delta G^* [218 \text{ K, } \Delta \nu (193 \text{ K}) = 397 \text{ Hz}] = 40527 \text{ J/mol} = 9.7 \text{ kcal/mol}.$$
Crystals suitable for the X-ray crystal structure analysis were obtained from diffusion of pentane vapor to a solution of compound 6a in CH₂Cl² at -35 °C.

**X-ray crystal structure analysis of compound 6a (erk9199):** A colorless plate-like specimen of C₂₁H₇BF₁₀, 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%, Rₘᵦ = 3.69%, Rₘᵦ = 2.62%) and 2948 (96.09%) were greater than 2σ(F²). The final cell constants of a = 7.4242(2) Å, b = 10.8667(3) Å, c = 21.4824(5) Å, volume = 1733.13(8) Å³, 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 P2₁2₁2₁, with Z = 4 for the formula unit, C₂₁H₇BF₁₀. The final anisotropic full-matrix least-squares refinement on F² 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/Å³ and the largest hole was -0.145 e/Å³ with an RMS deviation of 0.035 e/Å³. On the basis of the final model, the calculated density was 1.763 g/cm³ and F(000), 912 e⁻. CCDC number: 1907601.

![Figure S18. Crystal structure of compound 6a (thermal ellipsoids: 30 % probability)](image-url)
**Experiment 3:** (reaction of compound 2a with BrB(C₆F₅)₂, NMR scale)

**Scheme S6.**

\[ \text{BrB(C₆F₅)₂} + \text{2a} \xrightarrow{\text{r.t. 5 min CD₂Cl₂}} \text{6a} \]

A solution of BrB(C₆F₅)₂ (42 mg, 0.10 mmol) in CD₂Cl₂ (0.3 mL) was added to a solution of phenylallene (11.6 mg, 0.10 mmol) in CD₂Cl₂ (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%, ¹⁹F), BrB(C₆F₅)₂ (12 mol%, ¹⁹F) and an unknown compound (18 mol%, ¹H) was obtained.

**Reaction mixture after 3 h:** A mixture (dark red solution) of compound 6a (81 mol%, ¹⁹F) and BrB(C₆F₅)₂ (19 mol%, ¹⁹F) was obtained.
Figure S19. $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$*) spectra of (1) BrB(C$_6$F$_5$)$_2$, (2) phenyllallene, (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$_2$Cl$_2$) spectra of (1) BrB(C$_6$F$_5$)$_2$, (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$_2$Cl$_2$) spectra of (1) BrB(C$_6$F$_5$)$_2$, (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(C₆F₅)₂, preparative scale)

Scheme S7.

\[
\text{BrB(C}_{6}\text{F}_{5})_{2} + \overset{\text{r.t. 5 min}}{2a} \rightarrow 6a
\]

A solution of BrB(C₆F₅)₂ (168 mg, 0.40 mmol) in CH₂Cl₂ (1 mL) was added to a solution of phenylallene (56 mg, 0.48 mmol) in CH₂Cl₂ (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, CD₂Cl₂) 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$_2$Cl$_2$) 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$_2$Cl$_2$) 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(C₆F₅)₂, preparative scale)

**Scheme S8.**

A solution of ClB(C₆F₅)₂ (152 mg, 0.40 mmol) in CH₂Cl₂ (2 mL) was added to a solution of p-tolylallene (62 mg, 0.48 mmol) in CH₂Cl₂ (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 C₂₂H₉BF₁₀: C, 55.73; H, 1.91. Found: C, 55.74; H, 2.04.

**¹H NMR** (600 MHz, 299 K, CD₂Cl₂): δ ¹H: 8.05 (t, ³J_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, CH₂), 2.47 (s, 3H, CH₃).

**¹³C{¹H} NMR** (151 MHz, 299 K, CD₂Cl₂): δ ¹³C: 162.6 (3-CH=), 151.8 (9-C), 150.3 (br, CB=), 146.6 (dm, ¹J_CC ~ 250 Hz, C₆F₅), 142.6 (dm, ¹J_CC ~ 250 Hz, C₆F₅), 142.0 (7-C), 141.6 (4-C), 137.8 (dm, ¹J_CC ~ 250 Hz, C₆F₅), 128.9 (6-CH=), 125.6 (8-CH=), 125.4 (5-CH=), 114.9 (br, i-C₆F₅), 41.9 (CH₂), 22.2 (CH₃).

**¹⁹F NMR** (564 MHz, 299 K, CD₂Cl₂): δ ¹⁹F: −130.7 (m, 2F, o), −151.7 (t, ³J_FF = 20.0 Hz, 1F, p), −162.3 (m, 2F, m)(C₆F₅)[Δδ¹⁹F_m,p = 10.6].

**¹¹B{¹H} NMR** (192 MHz, 299 K, CD₂Cl₂): δ ¹¹B: 56.0 (ν₁/₂ ~ 800 Hz).
Figure S25. $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2^*$) spectrum of compound 6b. [P: pentane]

Figure S26. $^{13}$C($^1$H) NMR (151 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 6b.
Figure S27. $^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 6b.

Figure S28. $^{11}$B($^1$H) NMR (192 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 6b.
X-ray crystal structure analysis of compound 6b (erk9187): A colorless prism-like specimen of C_{22}H_{9}BF_{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 2σ(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 o(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_{9}BF_{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(C₆F₅)₂, preparative scale)

**Scheme S9.**

A solution of BrB(C₆F₅)₂ (168 mg, 0.40 mmol) in CH₂Cl₂ (1 mL) was added to a solution of p-tolylallene (57 mg, 0.48 mmol) in CH₂Cl₂ (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, CD₂Cl₂*) 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$_2$Cl$_2^*$) 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$_2$Cl$_2^*$) 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(C₆F₅)₂, preparative scale)

Scheme S10.

A solution of ClB(C₆F₅)₂ (152 mg, 0.40 mmol) in CH₂Cl₂ (2 mL) was added to a solution of p-fluorophenylallene (64 mg, 0.48 mmol) in CH₂Cl₂ (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 C₂₁H₆BF₁₁: C, 52.76; H, 1.27. Found: C, 51.89; H, 1.41.

¹H NMR (600 MHz, 299 K, CD₂Cl₂): δ ¹H: 8.02 (t, 4JHH = 1.9 Hz, 1H, 3-CH=), 7.67 (dd, 3JHH = 8.5 Hz, 4JFH = 5.2 Hz, 1H, 5-CH=), 7.32 (dm, 3JFH = 8.5 Hz, 1H, 8-CH=), 7.15 (ddd, 3JFH = 9.2 Hz, 3JHH = 8.5 Hz, 4JHH = 2.3 Hz, 1H, 6-CH=), 3.82 (d, 4JHH = 1.9 Hz, 2H, CH₂).

¹³C{¹H} NMR (151 MHz, 299 K, CD₂Cl₂): δ ¹³C: 165.0 (d, ¹JFC = 251.6 Hz, CF), 161.3 (3-CH=), 153.8 (d, ³JFC = 9.7 Hz, 9-C), 151.1 (br, CB=), 146.6 (dm, ¹JFC ~ 240 Hz, C₆F₅), 142.8 (dm, ¹JFC ~ 260 Hz, C₆F₅), 140.3 (d, ⁴JFC = 1.8 Hz, 4-C), 137.9 (dm, ¹JFC ~ 250 Hz, C₆F₅), 127.0 (d, ³JFC = 9.8 Hz, 5-CH=), 115.6 (d, ²JFC = 24.0 Hz, 6-CH=), 114.7 (br, i-C₆F₅), 112.3 (d, ²JFC = 23.2 Hz, 8-CH=), 42.5 (CH₂).

¹⁹F NMR (564 MHz, 299 K, CD₂Cl₂): δ ¹⁹F: −109.5 (m, 1F, CF), [−130.6 (m, 2F, o), −151.2 (t, ³JFF = 20.0 Hz, 1F, p), −162.0 (m, 2F, m)](C₆F₅)[ΔΔ¹⁹Fₚ,m = 10.8].

¹¹B{¹H} NMR (192 MHz, 299 K, CD₂Cl₂): δ ¹¹B: 56.4 (ν₁/₂ ~ 800 Hz).
Figure S33. $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2^*$) spectrum of compound 6c.

Figure S34. $^{13}$C($^1$H) NMR (151 MHz, 299 K, CD$_2$Cl$_2$) 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$_2$Cl$_2$ at -35 °C.
X-ray crystal structure analysis of compound 6c (erk9217): A colorless needle-like specimen of C_{21}H_{6}BF_{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 2σ(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 P_{2_1}2_12_1, with Z = 4 for the formula unit, C_{21}H_{6}BF_{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(C₆F₅)₂, preparative scale)

Scheme S11.

A solution of BrB(C₆F₅)₂ (168 mg, 0.40 mmol) in CH₂Cl₂ (1 mL) was added to a solution of p-fluorophenylallene (62 mg, 0.44 mmol) in CH₂Cl₂ (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, CD₂Cl₂*) 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$_2$Cl$_2^*$) 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$_2$Cl$_2^*$) 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(C₆F₅)₂, NMR scale)

Scheme S12.

BrB(C₆F₅)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 CD₂Cl₂ (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$_2$Cl$_2$): $\delta$ $^1$H: 7.59 (m, 2H, o-C$_6$H$_4$F), 7.43 (s, 1H, CH=), 7.20 (m, 2H, m-C$_6$H$_4$F), 4.44 (s, 2H, CH$_2$).

$^{13}$C($^1$H) NMR (151 MHz, 233 K, CD$_2$Cl$_2$): $\delta$ $^{13}$C: 163.6 (d, $^1$J$_{FC}$ = 252.4 Hz, p-C$_6$H$_4$F), 156.1 (CH=), 143.3 (br, CB=), 132.8 (d, $^3$J$_{FC}$ = 8.8 Hz, o-C$_6$H$_4$F), 130.6 (d, $^4$J$_{FC}$ = 2.9 Hz, i-C$_6$H$_4$F), 116.1 (d, $^2$J$_{FC}$ = 21.8 Hz, m-C$_6$H$_4$F), 31.2 (CH$_2$).

NMR data of compound B:

![Diagram of B](attachment:image.png)

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

$^1$H NMR (600 MHz, 233 K, CD$_2$Cl$_2$): $\delta$ $^1$H: 7.48 (s, 1H, CH=), 6.99 (m, 2H, o-C$_6$H$_4$F), 6.85 (m, 2H, m-C$_6$H$_4$F), 4.36 (s, 2H, CH$_2$).

$^{13}$C($^1$H) NMR (151 MHz, 233 K, CD$_2$Cl$_2$): $\delta$ $^{13}$C: 163.3 (d, $^1$J$_{FC}$ = 250.2 Hz, p-C$_6$H$_4$F), 145.6 (CH=), 144.1 (br, CB=), 133.5 (i-C$_6$H$_4$F), 130.8 (o-C$_6$H$_4$F), 115.1 (m-C$_6$H$_4$F), 37.7 (CH$_2$).

NMR data of compound C:

![Diagram of C](attachment:image.png)

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

$^1$H NMR (600 MHz, 233 K, CD$_2$Cl$_2$): $\delta$ $^1$H: [7.33, 7.05](each m, each 2H, C$_6$H$_4$F), 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$_2$Cl$_2$) selected resonances: $\delta$ $^{13}$C: 137.5 (=CH$_2$), [130.3, 115.6] (o,m-C$_6$H$_4$F), 55.6 (CHBr).
Figure S41. $^1$H NMR (600 MHz, 233 K, CD$_2$Cl$_2$*) 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$_2$Cl$_2$) 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$_2$Cl$_2$) 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(C₆F₅)₂, preparative scale)

**Scheme S13.**

A solution of ClB(C₆F₅)₂ (152 mg, 0.40 mmol) in CH₂Cl₂ (1 mL) was added to a solution of p-biphenylallene (98 mg, 0.51 mmol) in CH₂Cl₂ (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$_₂$Cl$_₂$): $\delta$ $^1$H: 8.10 (t, $^4$J$_{HH}$ = 1.9 Hz, 1H, 3-CH=), 7.86 (m, 1H, 8-CH=), 7.77 (dm, $^3$J$_{HH}$ = 8.0 Hz, 1H, 5-CH=), 7.68 (dm, $^3$J$_{HH}$ = 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, $^4$J$_{HH}$ = 1.9 Hz, 2H, CH$_₂$).

$^{13}$C{$^1$H} NMR (151 MHz, 299 K, CD$_₂$Cl$_₂$): $\delta$ $^{13}$C: 161.9 (3-CH=), 152.0 (9-C), 151.4 (br, CB=), 146.6 (dm, $^1$J$_{FC}$ ~ 250 Hz, C₆F₅), 143.7 (7-C), 143.2 (4-C), 142.8 (dm, $^1$J$_{FC}$ ~ 260 Hz, C₆F₅), 141.1 (i-Ph), 137.8 (dm, $^1$J$_{FC}$ ~ 250 Hz, C₆F₅), 129.3 (m-Ph), 128.3 (p-Ph), 127.7 (o-Ph), 114.9 (br, i-C₆F₅), 127.0 (6-CH=), 125.9 (5-CH=), 123.5 (8-CH=), 42.3 (CH₂).

$^{19}$F NMR (564 MHz, 299 K, CD$_₂$Cl$_₂$): $\delta$ $^{19}$F: −130.5 (m, 2F, o), −151.3 (t, $^3$J$_{FF}$ = 20.0 Hz, 1F, p), −162.1 (m, 2F, m)[C₆F₅][Δδ$^{19}$F$_{m,p}$ = 10.8].

$^{11}$B{$^1$H} NMR (192 MHz, 299 K, CD$_₂$Cl$_₂$): $\delta$ $^{11}$B: 56.2 ($\nu_{1/2}$ ~ 1200 Hz).
Figure S44. $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$*) spectrum of compound 6d.

Figure S45. $^{13}$C($^1$H) NMR (151 MHz, 299 K, CD$_2$Cl$_2$) 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$_2$Cl$_2$ at -35 °C.
**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(C₆F₅)₂, preparative scale)

Scheme S14.

A solution of BrB(C₆F₅)₂ (152 mg, 0.40 mmol) in CH₂Cl₂ (1 mL) was added to a solution of p-biphenylallene (98 mg, 0.51 mmol) in CH₂Cl₂ (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, CD₂Cl₂*) 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$_2$Cl$_2^*$) 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$_2$Cl$_2^*$) 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(C₆F₅)₂, preparative scale)

**Scheme S15.**

A solution of ClB(C₆F₅)₂ (152 mg, 0.40 mmol) in CH₂Cl₂ (1 mL) was added to a solution of compound 2e (50 mg, 0.22 mmol) in CH₂Cl₂ (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 C₄₂H₁₂B₂F₂₂O: C, 54.94; H, 1.32. Found: C, 56.04; H, 1.52.

**¹H NMR** (600 MHz, 299 K, CD₂Cl₂): δ ¹H: 8.10 (m, 1H, 3-CH=), 7.92 (m, 1H, 8-CH=), 7.80 (d, 3J₃H = 8.0 Hz, 1H, 5-CH=), 7.75 (dd, 3J₃H = 8.0 Hz, 4J₄H = 1.3 Hz, 1H, 6-CH=), 3.91 (d, 4J₄H = 1.2 Hz, 2H, CH₂).

**¹³C{¹H} NMR** (151 MHz, 299 K, CD₂Cl₂): δ ¹³C: 161.6 (3-CH=), 151.9 (9-C), 151.8 (br, CB₅=), 146.6 (dm, ¹J₁FC ~ 245 Hz, C₆F₅), 143.7 (4-C), 143.2 (7-C), 142.8 (dm, ¹J₁FC ~ 260 Hz, C₆F₅), 138.0 (dm, ¹J₁FC ~ 250 Hz, C₆F₅), 127.4 (6-CH=), 126.0 (5-CH=), 123.8 (8-CH=), 114.9 (br, i-C₆F₅), 42.4 (CH₂).

**¹⁹F NMR** (564 MHz, 299 K, CD₂Cl₂): δ ¹⁹F: −130.5 (m, 2F, o), −151.1 (t, ³J₉F = 20.0 Hz, 1F, p), −162.0 (m, 2F, m)(C₆F₅)[Δδ¹⁹F,m,p = 10.9].

**¹¹B{¹H} NMR** (192 MHz, 299 K, CD₂Cl₂): δ ¹¹B: 56.9 (ν₁/₂ ~ 1800 Hz).

![Figure S52. ¹H NMR (600 MHz, 299 K, CD₂Cl₂*) spectrum of compound 6e. [P: pentane]](image-url)
Figure S53. $^{13}\text{C}({}^1\text{H})$ NMR (151 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 6e.

Figure S54. $^{19}\text{F}$ NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 6e.
Experiment 2: (reaction of compound 2e with BrB(C₆F₅)₂, preparative scale)

Scheme S16.

A solution of BrB(C₆F₅)₂ (168 mg, 0.40 mmol) in CH₂Cl₂ (1 mL) was added to a solution of compound 2e (50 mg, 0.22 mmol) in CH₂Cl₂ (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$_2$Cl$_2$*) 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$_2$Cl$_2$*) 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$_2$Cl$_2$*) 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$_6$F$_5$)$_2$, preparative scale)

Scheme S17.

A solution of ClB(C$_6$F$_5$)$_2$ (190 mg, 0.50 mmol) in CH$_2$Cl$_2$ (1 mL) was added to a solution of compound 2f (38.5 mg, 0.25 mmol) in CH$_2$Cl$_2$ (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%, $^1$H) and 6f’ (41 mol%, $^1$H) as a green solid.

Anal. Calc. for C$_{36}$H$_8$B$_2$F$_{20}$: C, 51.35; H, 0.96. Found: C, 51.79; H, 1.09.

NMR data of compound 6f in the mixture:
$^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^1$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$_2$Cl$_2$): $\delta$ $^{13}$C: 161.2 (3-CH=), 153.4 (br, CB=), [150.3, 146.4] (4,6-C), 146.7 (dm, $^3$J$_{FC}$ ~ 250 Hz, C$_6$F$_5$), 142.9 (dm, $^3$J$_{FC}$ ~ 260 Hz, C$_6$F$_5$), 137.9 (dm, $^3$J$_{FC}$ ~ 250 Hz, C$_6$F$_5$), 121.2 (5-CH=), 114.6 (br, i-C$_6$F$_5$), 41.9 (CH$_2$).

$^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^{19}$F: $-130.3$ (m, 2F, o), $-150.7$ (t, $^3$J$_{FF}$ = 20.0 Hz, 1F, p), $-161.9$ (m, 2F, m) (C$_6$F$_5$) [$\Delta$ $\delta^{19}$F$_{m,p}$ = 11.2].

$^{11}$B($^1$H) NMR (192 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^{11}$B: 56.7 ($\nu_{1/2}$ ~ 1500 Hz).

NMR data of compound 6f' in the mixture:

$^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^1$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$_2$Cl$_2$): $\delta$ $^{13}$C: 161.7 (3-CH=), 152.5 (br, CB=), 146.7 (dm, $^3$J$_{FC}$ ~ 250 Hz, C$_6$F$_5$), [146.2, 146.1] (4,6-C), 142.9 (dm, $^3$J$_{FC}$ ~ 260 Hz, C$_6$F$_5$), 137.9 (dm, $^3$J$_{FC}$ ~ 250 Hz, C$_6$F$_5$), 125.2 (5-CH=), 114.6 (br, i-C$_6$F$_5$), 40.9 (CH$_2$).

$^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^{19}$F: $-130.3$ (m, 2F, o), $-150.7$ (t, $^3$J$_{FF}$ = 20.0 Hz, 1F, p), $-161.9$ (m, 2F, m) (C$_6$F$_5$) [$\Delta$ $\delta^{19}$F$_{m,p}$ = 11.2].

$^{11}$B($^1$H) NMR (192 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^{11}$B: 56.7 ($\nu_{1/2}$ ~ 1500 Hz).
Figure S59. $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$) spectrum of the isolated mixture. [P: pentane]

Figure S60. $^{13}$C($^1$H) NMR (151 MHz, 299 K, CD$_2$Cl$_2$) spectrum of the isolated mixture.
Figure S61. $^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectrum of the isolated mixture.

Figure S62. $^{11}$B($^1$H) NMR (192 MHz, 299 K, CD$_2$Cl$_2$) spectrum of the isolated mixture.
**Figure S63.** $^1$H,$^{13}$C GHSQC (600/151 MHz, CD$_2$Cl$_2$, 299K) spectrum of the isolated mixture.

**Figure S64.** $^1$H,$^{13}$C GHMBC (600/151 MHz, CD$_2$Cl$_2$, 299K) spectrum of the isolated mixture.
**Experiment 2:** (reaction of compound 2f with BrB(C₆F₅)₂, preparative scale)

**Scheme S18.**

A solution of BrB(C₆F₅)₂ (168 mg, 0.40 mmol) in CH₂Cl₂ (1 mL) was added to a solution of compound 2f (30.8 mg, 0.20 mmol) in CH₂Cl₂ (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 x 3) and dried in vacuo to finally give a mixture (115 mg, 0.14 mmol, 70%) of compounds 6f (63 mol%, ¹H) and 6f' (37 mol%, ¹H) as a green solid.

**Figure S65.** ¹H NMR (600 MHz, 299 K, CD₂Cl₂*) 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$_2$Cl$_2$) 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$_2$Cl$_2$) 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(C₆F₅)₂, X-ray crystal structure analysis of 6g’)

Scheme S19.

A solution of ClB(C₆F₅)₂ (114 mg, 0.30 mmol) in CH₂Cl₂ (0.5 mL) was added to a solution of compound 2g (18.6 mg, 0.10 mmol) in CH₂Cl₂ (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 CH₂Cl₂ (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 C₅₁H₉B₃F₃₀: C, 50.05; H, 0.74. Found: C, 49.24; H, 0.69.

**NMR data of compound 6g:** (only slightly soluble in CD₂Cl₂)

¹H NMR (600 MHz, 299 K, CD₂Cl₂): δ ¹H: 8.22 (t, 4JHH = 2.0 Hz 1H, CH=), 4.12 (d, 4JHH = 2.0 Hz, 2H, CH₂).

¹³C{¹H} NMR (151 MHz, 299 K, CD₂Cl₂): δ ¹³C: 158.3 (CH=), 151.3 (br, CB=), [149.0, 139.6](4,5-C), 41.4 (CH₂). [C₆F₅ not assigned]

¹⁹F NMR (564 MHz, 299 K, CD₂Cl₂): δ ¹⁹F: −130.1 (m, 2F, o), −150.4 (t, 3JFF = 20.0 Hz, 1F, p), −161.7 (m, 2F, m)(C₆F₅)[Δδ¹⁹F_m,p = 11.3].
Figure S68. $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$) spectrum of the isolated compound 6g. [?: signal from solvent; P: pentane]

Figure S69. $^{13}$C{$^1$H} NMR (151 MHz, 299 K, CD$_2$Cl$_2$) spectrum of the isolated compound 6g.
Figure S70. $^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectrum of the isolated compound 6g.

Figure S71. $^1$H,$^{13}$C GHSQC (600/151 MHz, CD$_2$Cl$_2$, 299K) spectrum of the isolated compound 6g.
Figure S72. $^1$H, $^{13}$C GHMBC (600/151 MHz, CD$_2$Cl$_2$, 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$_2$F$_{20}$, 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%, $R_{\text{sig}}$ = 6.19%) and 4058 (72.74%) were greater than 2σ($F^2$). The final cell constants of $a = 16.3020(4)$ Å, $b = 31.6317(11)$ Å, $c = 6.8859(3)$ Å, $\beta = 104.0370(10)^\circ$, 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$_2$F$_{20}$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 659 variables converged at $R_1 = 8.10\%$, for the observed data and $wR_2 = 16.23\%$ 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.
**Experiment 2:** (reaction of compound 2g with 3 ClB(C₆F₅)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 CD₂Cl₂ (0.3 mL) was added to a solution of ClB(C₆F₅)₂ (57 mg, 0.15 mmol) in CD₂Cl₂ (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%, ¹⁹F) and unreacted ClB(C₆F₅)₂ (71 mol%, ¹⁹F) 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$_2$Cl$_2$*) 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$_2$Cl$_2$*) 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.
Experiment 3: (reaction of compound 2g with 3 ClB(C₆F₅)₂, isolation of compounds 6g and 6g′)

Scheme S21.

A solution of compound 2g (37.2 mg, 0.20 mmol) in CH₂Cl₂ (1 mL) was added to a solution of ClB(C₆F₅)₂ (228 mg, 0.60 mmol) in CH₂Cl₂ (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$_2$Cl$_2$*) 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$_2$Cl$_2$*) 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 x 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':

\[
\begin{align*}
\text{C}_6\text{F}_5\text{B} & \quad \text{B(C}_6\text{F}_5)\text{B} \\
\text{6g'}
\end{align*}
\]

\[\text{H NMR (600 MHz, 299 K, CD}_2\text{Cl}_2): \delta \text{ }^{1}H: 8.09 \text{ (t, }^{1}J_{HH} = 1.3 \text{ Hz, 2H, 3-CH=), 7.87 (s, 1H, 5-CH=), 6.54 (t, }^{1}J_{HH} = 7.0 \text{ Hz, 1H, CH=), 5.22 (d, }^{1}J_{HH} = 7.0 \text{ Hz, 2H, CH}_2=), 3.95 (d, }^{1}J_{HH} = 1.6 \text{ Hz, 4H, CH}_2}.\]

\[\text{C\{H\} NMR (151 MHz, 299 K, CD}_2\text{Cl}_2): \delta \text{ }^{13}C: 213.0 (=C=), 161.3 (3-CH=), 151.4 (br, CB=), 151.1 (7-C), 146.7 (dm, }^{1}J_{FC} \sim 240 \text{ Hz, C}_6\text{F}_5), 144.5 (4-C), 142.9 (dm, }^{1}J_{FC} \sim 260 \text{ Hz, C}_6\text{F}_5), 137.9 (dm, }^{1}J_{FC} \sim 250 \text{ Hz, C}_6\text{F}_5), 126.6 (6-C), 120.5 (5-CH), 114.7 (br m, i-C}_6\text{F}_5), 89.3 (CH=), 78.9 (CH}_2=), 41.8 (CH}_2). [\text{tentative assignment}]\]

\[\text{F NMR (564 MHz, 299 K, CD}_2\text{Cl}_2): \delta \text{ }^{19}F: -130.4 \text{ (m, 2F, o), -150.8 (t, }^{3}J_{FF} = 20.0 \text{ Hz, 1F, p), -162.0 (m, 2F, m)(C}_6\text{F}_5)[\Delta \delta }^{19}F_{m,p} = 11.2].\]

\[\text{B\{H\} NMR (192 MHz, 299 K, CD}_2\text{Cl}_2): \delta \text{ }^{11}B: 57.2 (\nu_{1/2} \sim 1300 \text{ Hz}).\]

\[\text{Figure S79. }^{1}\text{H NMR (600 MHz, 299 K, CD}_2\text{Cl}_2\text{*) spectrum of the isolated compound 6g'.} \]
Figure S80. $^{13}$C$^{1}$H NMR (151 MHz, 299 K, CD$_2$Cl$_2$) spectrum of the isolated compound 6g$^1$.

Figure S81. $^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectrum of the isolated compound 6g$^1$.
Figure S82. $^{11}$B$^{{1H}}$ NMR (192 MHz, 299 K, CD$_2$Cl$_2$) spectrum of the isolated compound 6g'.

Experiment 4: (reaction of compound 2g with 3 BrB(C$_6$F$_5$)$_2$, NMR scale)

Scheme S22.

A solution of compound 2g (9.3 mg, 0.05 mmol) in CD$_2$Cl$_2$ (0.3 mL) was added to a solution of BrB(C$_6$F$_5$)$_2$ (63.6 mg, 0.15 mmol) in CD$_2$Cl$_2$ (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$_6$F$_5$)$_2$ (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$_6$F$_5$)$_2$ (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:
$^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^1$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$_2$Cl$_2$): $\delta$ $^{13}$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$_6$F$_5$ not listed]

$^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^{19}$F: [-130.3 (m, 4F, o), -150.5 (t, $^{3}$J$_{FF}$ = 20.0 Hz, 2F, p), -161.8 (m, 4F, m)]($^{2}$BC$_6$F$_5$)[Δ$\delta^{19}$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)]($^{2}$BC$_6$F$_5$)[Δ$\delta^{19}$F$_{m,p}$ = 15.2].

$^{11}$B{$^1$H} NMR (192 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^{11}$B: 58.1 (ν$_{1/2}$ ~ 1500 Hz). [tentative assignment]

Figure S83. $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$*) 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$_2$Cl$_2$) 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$_2$Cl$_2$) 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$_2$Cl$_2$) 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$_2$Cl$_2$) spectra of the filtrate from Experiment 4 (r.t. 7 d). Irradiation points (*): (2) compound 6g'': $^\delta$H 4.13 (10-CH$_2$); (3) compound 6g'': $^\delta$H 3.78 (1-CH$_2$); (4) compound 6g'': $^\delta$H 7.32 (8-CH=).
Figure S88. $^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectra of (1) BrB(C$_6$F$_5$)$_2$, (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($^1$H) NMR (192 MHz, 299 K, CD$_2$Cl$_2$) spectra of (1) BrB(C$_6$F$_5$)$_2$, (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(C₆F₅)₂, preparative scale)

**Scheme S23.**

A solution of compound 2g (37.2 mg, 0.20 mmol) in CH₂Cl₂ (1 mL) was added to a solution of BrB(C₆F₅)₂ (256 mg, 0.60 mmol) in CH₂Cl₂ (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, CD₂Cl₂*) spectra of the isolated compound 6g from Experiment 1 (spectrum 1), Experiment 4 (spectrum 2) and Experiment 5 (spectrum 3).[?: unknown signal from CD₂Cl₂]
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 x 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$_2$Cl$_2$*) 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$_2$Cl$_2$*) spectra of (1) the isolated yellow solid from Experiment 5, (2) the filtrate from Experiment 4 (r.t. 7 d), (3) BrB(C$_6$F$_5$)$_2$, (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$_2$Cl$_2$) spectra of (1) the isolated yellow solid from Experiment 5, (2) the isolated compound 6g$^1$ from Experiment 3, (3) the filtrate from Experiment 4 (r.t. 7 d) and (4) BrB(C$_6$F$_5$)$_2$.

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$_2$Cl$_2$ (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$_3$F$_{30}$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$_2$Cl$_2$): $\delta$ $^1$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($^1$H) NMR (151 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^{13}$C: 154.8 (br, CB=), 148.1 (dm, $^1$J$_{FC} \sim$ 240, C$_6$F$_5$), 147.1 (o-Py), 142.4 (p-Py), 140.0 (dm, $^1$J$_{FC} \sim$ 250, C$_6$F$_5$), 139.9 and 133.8 (C), 137.6 (dm, $^1$J$_{FC} \sim$ 250, C$_6$F$_5$), 132.8 (CH=), 126.4 (m-Py), 121.0 (br, i-C$_6$F$_5$), 41.5 (CH$_2$).

$^{11}$B($^1$H) NMR (192 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^{11}$B: $-$2.1.

$^{10}$B($^1$H) NMR (54 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^{10}$B: $-$2.1 ($\nu_{1/2}$ $\sim$ 300 Hz).

$^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^{19}$F: $-$131.1 (m, 2F, o), $-$159.0 (t, $^3$J$_{FF}$ = 20.0 Hz, 1F, p), $-$164.2 (m, 2F, m)(C$_6$F$_5$)[$\Delta\delta^{19}$F$_{m,p}$ = 5.2].

Figure S95. $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2^*$) spectrum of compound 6g(pyr)$_3$. [P: pentane]

Figure S96. $^{13}$C($^1$H) NMR (151 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 6g(pyr)$_3$. [P: pentane]
Figure S97. Spectrum 1: $^{11}$B($^1$H) NMR (192 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 6g(pyr)$_3$ and Spectrum 2: $^{10}$B($^1$H) NMR (54 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 6g(pyr)$_3$.

Figure S98. $^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) 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$_2$Cl$_2$ at room temperature.
X-ray crystal structure analysis of compound 6g(pyr)₃ (erk9457): A pale yellow needle-like specimen of C₆₆H₂₄B₃F₃₀N₃, 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(F²). 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) Å³, are based upon the refinement of the XYZ-centroids of reflections above 20 o(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 P2₁/c, with Z = 4 for the formula unit, C₆₆H₂₄B₃F₃₀N₃. The final anisotropic full-matrix least-squares refinement on F² 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/Å³ and the largest hole was -0.325 e/Å³ with an RMS deviation of 0.072 e/Å³. On the basis of the final model, the calculated density was 1.454 g/cm³ and F(000), 2904 e⁻. CCDC number: 1907605.
J) Synthesis of compound 7a

Scheme S25.

Pd(PPh₃)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 (10 mL × 3) and all the organic phases were combined and dried over Na₂SO₄. 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:**

**{^1H} NMR (600 MHz, 299 K, CD$_2$Cl$_2$):** $\delta$ {^1H}: 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$_3$).

**{^{13C}{^1H}} NMR (151 MHz, 299 K, CD$_2$Cl$_2$):** [selected resonances]: $\delta$ {^{13C}}: 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.** {^1H} NMR (600 MHz, 299 K, CD$_2$Cl$_2$*) spectrum of compound 7a.
Figure S101. $^{13}$C($^1$H) NMR (151 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 7a.

Figure S102. $^1$H/$^{13}$C GHSQC (600/151 MHz, 299 K, CD$_2$Cl$_2$) 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 phases were separated. The aqueous phase was washed with pentane (10 mL × 3) and all the organic phase were combined and dried over Na$_2$SO$_4$. All the volatiles were removed by rotation evaporator and the residue was purified via column chromatography [silica gel, pentane: CH$_2$Cl$_2$ = 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$_2$Cl$_2$): 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$_2$Cl$_2$)[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$_2$Cl$_2$): 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, CH2), 2.37 (s, 3H, CH3).

$^{13}$C{^1H} NMR (151 MHz, 299 K, CD2Cl2)[selected resonances]: $\delta$ $^{13}$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 (CH2), 21.3 (CH3).

Figure S103. $^1$H NMR (600 MHz, 299 K, CD2Cl2*) 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, CD2Cl2) 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-Methylphenyllallene (6.5 mg, 0.05 mmol) and ClB(C₆F₅)₂ (19 mg, 0.05 mmol) were dissolved in CD₂Cl₂ (0.5 mL) at room temperature. The resulting reaction mixture was then characterized by NMR experiments within 5 min: a mixture of compounds 6h (48 mol%, ᵃ⁻¹H), 6h’ (26 mol%, ᵃ⁻¹H) and ClB(C₆F₅)₂ (26 mol%, ᵃ⁻¹F).

Figure S105. ᵃ⁻¹H NMR (600 MHz, 299 K, CD₂Cl₂*) spectra of (1) m-methylphenyllallene and (2) the reaction mixture.
Figure S106. $^{11}$B($^1$H) NMR (192 MHz, 299 K, CD$_2$Cl$_2$) spectra of (1) ClB(C$_6$F$_5$)$_2$ and (2) the reaction mixture.

Figure S107. $^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectra of (1) ClB(C$_6$F$_5$)$_2$ and (2) the reaction mixture.
NMR data of compound 6h:

![structure](image)

**1H NMR** (600 MHz, 299 K, CD$_2$Cl$_2$): 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$_3$).

**13C{1H} NMR** (151 MHz, 299 K, CD$_2$Cl$_2$)[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$_3$).

**11B{1H} NMR** (192 MHz, 299 K, CD$_2$Cl$_2$): δ $^{11}$B: 57.9 (v$_{1/2}$ ~ 600 Hz).

**19F NMR** (564 MHz, 299 K, CD$_2$Cl$_2$): δ $^{19}$F: −130.6 (m, 2F, o), −151.5 (m, 1F, p), −162.2 (m, 2F, m)(C$_6$F$_5$)[Δδ$^{19}$F$_{m,p}$ = 10.7].

NMR data of compound 6h’:

![structure](image)

**1H NMR** (600 MHz, 299 K, CD$_2$Cl$_2$): 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$_3$).

**13C{1H} NMR** (151 MHz, 299 K, CD$_2$Cl$_2$)[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$_3$).

**11B{1H} NMR** (192 MHz, 299 K, CD$_2$Cl$_2$): δ $^{11}$B: 57.9 (v$_{1/2}$ ~ 600 Hz).

**19F NMR** (564 MHz, 299 K, CD$_2$Cl$_2$): δ $^{19}$F: −130.6 (m, 2F, o), −151.5 (m, 1F, p), −162.2 (m, 2F, m)(C$_6$F$_5$)[Δδ$^{19}$F$_{m,p}$ = 10.7].
Figure S108. $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$*) 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$_2$Cl$_2$) spectrum of reaction mixture: compound 6h labeled in blue and compound 6h' labeled in red.
Photophysical measurements

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**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 dissolved in dry dichloromethane (DCM) in quartz tubes (c $\approx$ 1.0×10^{-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, $\lambda_{em} = 650$ nm) and emission (in blue, $\lambda_{ex} = 300$ nm) spectra for compounds 6a-d and 6g. All spectra were recorded in fluid dichloromethane at room temperature [c $\approx 10 \mu M$]. The asterisks (*) denote decomposition products.
Figure S111. Normalized fluorescence excitation (in red, $\lambda_{em} = 550$ nm) and emission (in blue, $\lambda_{ex} = 300$ 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:

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

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

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

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:

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

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

Figure S120. Left: Time-resolved luminescence decay of compound 6d including the instrument response function (red) and the residuals at RT ($\lambda_{ex} = 375$ nm, $\lambda_{em} = 510$ nm). Right: Fitting parameters including pre-exponential factors and confidence limits.
Figure S121. Left: Time-resolved luminescence decay of compound 6g including the instrument response function (red) and the residuals at RT ($\lambda_{ex} = 375$ nm, $\lambda_{em} = 510$ 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).

<table>
<thead>
<tr>
<th>Observable</th>
<th>6a</th>
<th>6b</th>
<th>6c</th>
<th>6d</th>
<th>6g</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ^max_{ex} ± 5 / nm^[a]</td>
<td>365</td>
<td>373</td>
<td>370</td>
<td>390</td>
<td>360</td>
</tr>
<tr>
<td>λ^max_{em} ± 5 / nm^[a]</td>
<td>550</td>
<td>580</td>
<td>555</td>
<td>550</td>
<td>510</td>
</tr>
<tr>
<td>Φ_F ± 2 / %^[a]</td>
<td>21</td>
<td>9</td>
<td>17</td>
<td>25</td>
<td>14</td>
</tr>
<tr>
<td>λ^max_{ex} ± 5 / nm^[b]</td>
<td>380</td>
<td>400</td>
<td>375</td>
<td>440</td>
<td>400</td>
</tr>
<tr>
<td>λ^max_{em} ± 5 / nm^[b]</td>
<td>450</td>
<td>435</td>
<td>450</td>
<td>510</td>
<td>510</td>
</tr>
<tr>
<td>Φ_F ± 2 / %^[b]</td>
<td>55^[c]</td>
<td>29</td>
<td>31</td>
<td>50^[c]</td>
<td>18^[c]</td>
</tr>
</tbody>
</table>

| τ / ns (relative amplitude as %)^[a] | 25.1 ±0.1 (94) 19.8 ±0.1 (98) 6.7 ±1 (6) 14 ±2 (2) 15.8 ±0.1 (88) |
| | 10.8 ±0.1 (94) 19.8 ±0.1 (98) 6.7 ±1 (6) 14 ±2 (2) 15.8 ±0.1 (88) |

| τ / ns (relative amplitude as %)^[b] | 7.4 ±0.1 (8) 6.7 ±0.2 (5) 9.0 ±0.1 (23) 13.7 ±0.1 (23) 11.2 ±0.1 (10) |
| | 1.9 ±0.1 (32) 2.0 ±0.1 (33) 4.4 ±0.1 (46) 7.8 ±0.1 (58) 2.9 ±0.1 (36) |