Supporting Information

Selective Formation of Heterocyclic trans-Cycloalkenes by Alkyne Addition to a Biphenylene-based Phosphane/Borane Frustrated Lewis Pair

Jun Li, Constantin G. Daniliuc, Gerald Kehr and Gerhard Erker*

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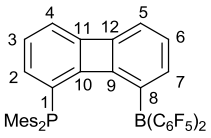
Experimental Procedures

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: melting points: TA-instruments DSC Q-20; 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). NMR chemical shifts are given relative to $SiMe_4$ and referenced to the respective solvent signal (^{1}H and ^{13}C) or an external standard [$\delta(BF_3{\cdot}OEt_2) = 0$ for ^{11}B NMR, $\delta(CFCl_3) = 0$ for ^{19}F NMR]. The assignments of the NMR resonances were supported by additional 1D- and 2D-NMR experiments.
X-Ray diffraction: For compounds **2**, **5**, **7**, **8a**, **8c**, **8d** and **8e** 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 SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*. **1990**, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, **2000**). For compound **8b** data sets were collected with a Bruker APEX II CCD diffractometer. Data sets for the compounds **9** and **10** were collected with a D8 Venture Dual Source 100 CMOS 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, **2015**); structure refinement SHELXL-2015 (Sheldrick, **2015**). *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: For compound **8a** one benzene molecule, for **8b** one half toluene molecule, for **8d** one propyl group and for **9** one dichloromethane molecule 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. For compound **7** two dichloromethane molecules and for compound **8c** one half hexane molecule were found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (Spek, A.L. (**2015**). Acta Cryst. C71, 9-18) as therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecules. CCDC deposition numbers are CCDC 1587986 to 1587995.
Materials: 1,8-dibromobiphenylene[1] and bis(pentafluorophenyl)borane[2] were prepared according to literature procedures

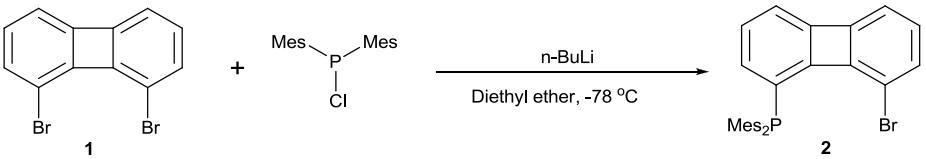
Numbering of the biphenylene ring for the assignment of NMR signals:

Scheme S1. Numbering of the biphenylene ring for the assignment of NMR signals



Preparation of (8-bromobiphenylen-1-yl)dimesitylphosphane 2

Scheme S2. Preparation of compound (8-bromobiphenylen-1-yl)dimesitylphosphane **2**.



n-BuLi (4.0 mL of a 1.6 M solution in hexane, 6.4 mmol) was added dropwise to a suspension of 1,8-dibromobiphenylene (2.0 g, 6.4 mmol) in diethyl ether (40 mL) at -78˚C. The resulting mixture was stirred at -78˚C for a further 2 h. A solution of Mes_2PCl (2.16 g, 7.1mmol) in diethyl ether (20 mL) was then added dropwise at -78 ˚C. The mixture was warmed to room temperature slowly, and stirred overnight. Saturated NH_4Cl solution (50 mL) was added and the aqueous layer was extracted with DCM (20 × 2 mL). The combined organic layer was dried over Na_2SO_4. After chromatography (silica gel, pentane: DCM (20 :1) as eluent), compound (8-bromobiphenylen-1-yl)dimesitylphosphane was obtained as a pale yellow solid (2.0 g, 62%)
Melting point: 188 °C.
Anal. Calc. for $C_{30}H_{28}BrP$: C, 72.15; H, 5.65. Found: C, 71.53; H, 5.65.
^{1}H NMR (600 MHz, 299 K, benzene-d_6): δ ^{1}H: for the mesityl group: 6.73 (d, $^{4}J_{PH}$ = 3.1 Hz, 4H, *m*-Mes), 2.40 (s, 12H, *o*-CH_3^{Mes}), 2.08 (s, 6H, *p*-CH_3^{Mes}); for the P-substituted ring of the biphenylene backbone: 6.61 (dd, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{PH}$ = 3.1 Hz,

1H, 2-CH), 6.31 (dd, $^{3}J_{HH}$ = 8.3, 6.8 Hz, 1H, 3-CH), 6.22 (d, $^{3}J_{HH}$ = 6.8 Hz, 1H, 4-CH); for the Br-substituted ring of the biphenylene backbone: 6.50 (d, $^{3}J_{HH}$ = 8.6 Hz, 1H, 7-CH), 6.13 (d, $^{3}J_{HH}$ = 6.6 Hz, 1H, 5-CH), 6.06 (dd, $^{3}J_{HH}$ = 8.6, 6.6 Hz, 1H, 6-CH).

^{13}C{^{1}H} NMR (151 MHz, 299 K, benzene-d_6) [C_6F_5 not listed]: δ ^{13}C: for the mesityl group: 143.2 (d, $^{2}J_{PC}$ = 16.2 Hz, *o*-Mes), 138.3 (*p*-Mes), 130.7 (d, $^{1}J_{PC}$ = 19.5 Hz, *i*-Mes), 130.6 (d, $^{3}J_{PC}$ = 3.6 Hz, *m*-Mes), 23.4 (d, $^{3}J_{PC}$ = 16.3 Hz, *o*-CH_3^{Mes}), 20.9 (*p*-CH_3^{Mes}); for the P-substituted ring of the biphenylene backbone: 155.8 (d, $^{2}J_{PC}$ = 33.2 Hz, 10-C), 150.0 (d, $^{3}J_{PC}$ = 9.0 Hz, 11-C), 132.1 (2-CH), 130.4 (d, $^{1}J_{PC}$ = 22.1 Hz, 1-C), 129.1 (3-CH), 116.6 (4-CH); for the Br-substituted ring of the biphenylene backbone: 152.8 (12-C), 152.1 (9-C), 132.7 (7-CH), 130.1 (6-CH), 115.7 (5-CH), 111.5 (8-C).

^{31}P{^{1}H} NMR (243 MHz, 299 K, benzene-d_6): δ = -31.5 ($\nu_{1/2}$ ~ 14 Hz).

Figure S1. ^{1}H NMR (600 MHz, 299 K, benzene-d_6) spectrum of compound **2**.

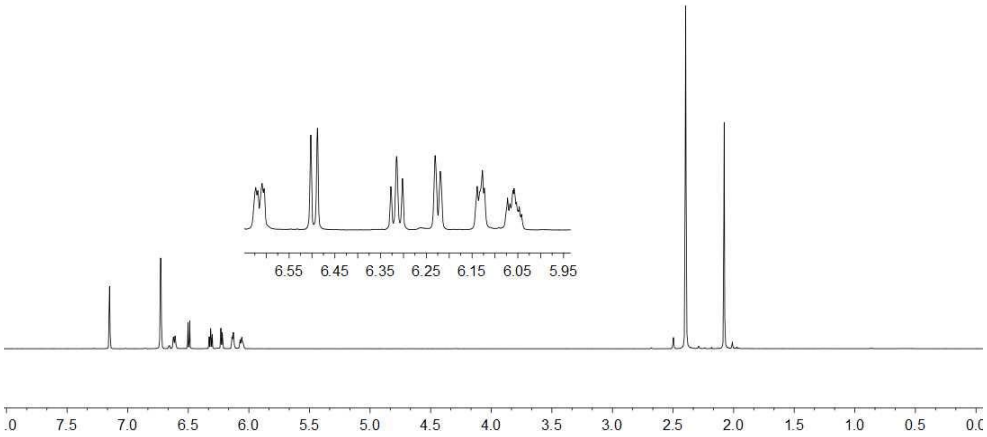


Figure S2. ^{13}C{^{1}H} NMR (151 MHz, 299 K, benzene-d_6) spectrum of compound **2**

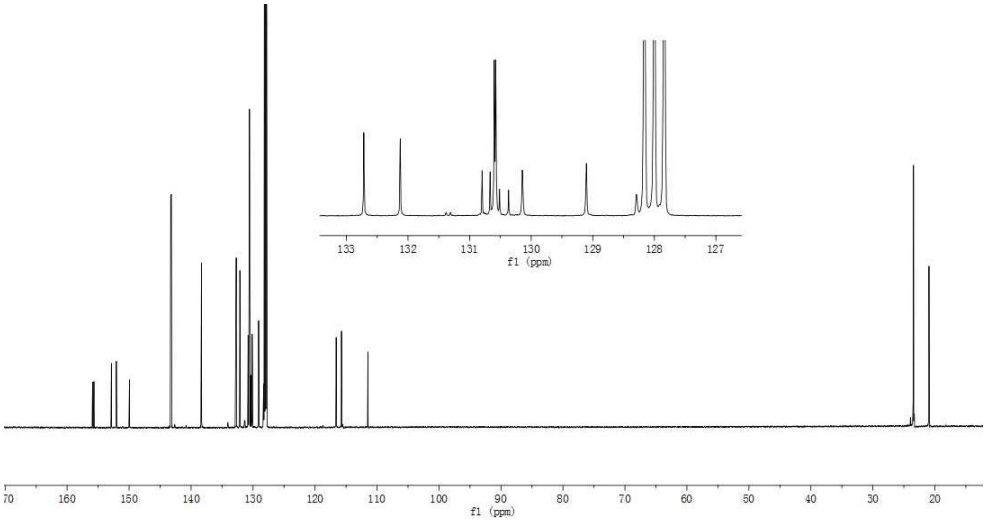
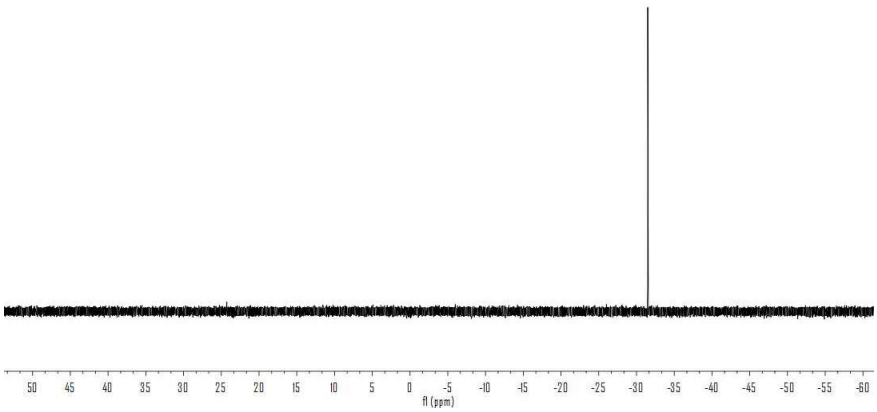


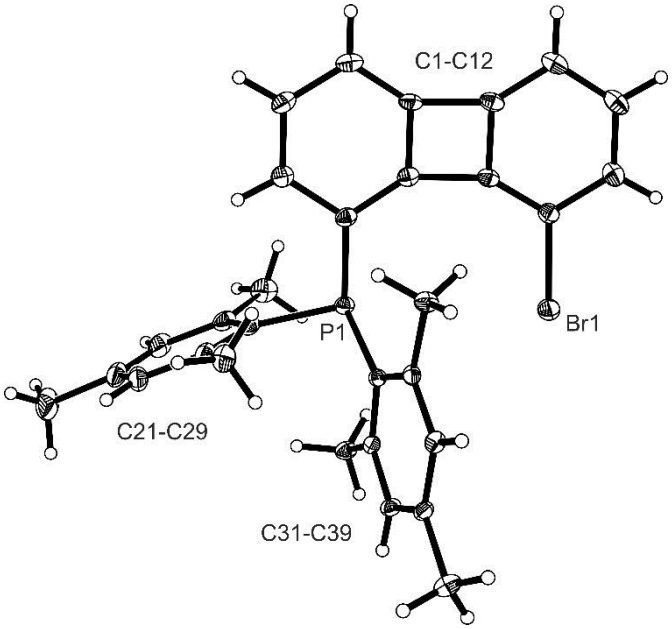
Figure S3. ^{31}P{^{1}H} NMR (243 MHz, 299 K, benzene-d_6) spectrum of compound **2**.



Crystals suitable for the *X*-ray crystal structure analysis were obtained from slow evaporation a solution of compound **2** in benzene-d_6 at 0 °C.

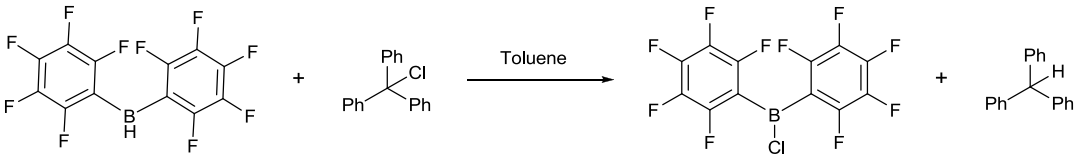
X-ray crystal structure analysis of compound 2 (erk8227): formula $C_{30}H_{28}BrP$, M = 499.40, pale yellow crystal, 0.23 x 0.12 x 0.03 mm, a = 18.8856(4), b = 8.5457(2), c = 15.9422(3) Å, β = 107.321(1)°, V = 2456.2(1) Å^3, ρ_{calc} = 1.350 gcm^{-3}, μ = 1.754 mm^{-1}, empirical absorption correction (0.668 ≤ T ≤ 0.949), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 13982 reflections collected (±h, ±k, ±l), 4158 independent (R_{int} = 0.068) and 2916 observed reflections [I>2σ(I)], 295 refined parameters, R = 0.070, wR^2 = 0.143, max. (min.) residual electron density 0.39 (-0.40) e.Å^{-3}, the hydrogen atoms were calculated and refined as riding atoms.

Figure S4. Crystal structure of compound **2**.



Preparation of chlorobis(pentafluorophenyl)borane 3

Scheme S3. Preparation of chlorobis(pentafluorophenyl)borane **3**.



3

Trityl chloride (2.78 g, 10 mmol) was added in small portions to a suspension of bis(pentafluorophenyl)borane (3.46 g, 10 mmol) in toluene (20 mL). The resulting mixture was stirred several minutes until the red color faded out. Then the volatiles were removed in vacuo and the desired product was obtained by sublimation of the residual solid under full vacuum at 70 - 80 ^{0}C as a white solid (3.0 g, 79%). The NMR was in good agreement with the literature. [2b]

^{11}B{^{1}H} NMR (192 MHz, 299 K, benzene-d_6): δ = 58.1 ($\nu_{1/2}$ ~ 377 Hz).

^{19}F NMR (564 MHz, 299 K, benzene-d_6): δ = -129.6 (m, 2F, *o*-C_6F_5), -144.0 (m, 1F, *p*-C_6F_5), -160.6 (m, 2F, *m*-C_6F_5) [$\Delta\delta$ $^{19}F_{m,p}$ = 16.6].

Figure S5. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, benzene-d_6) spectrum of compound **3**.

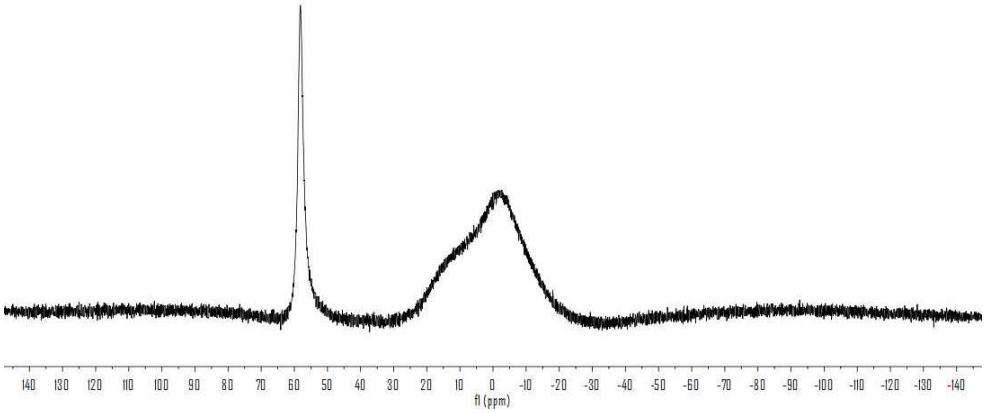
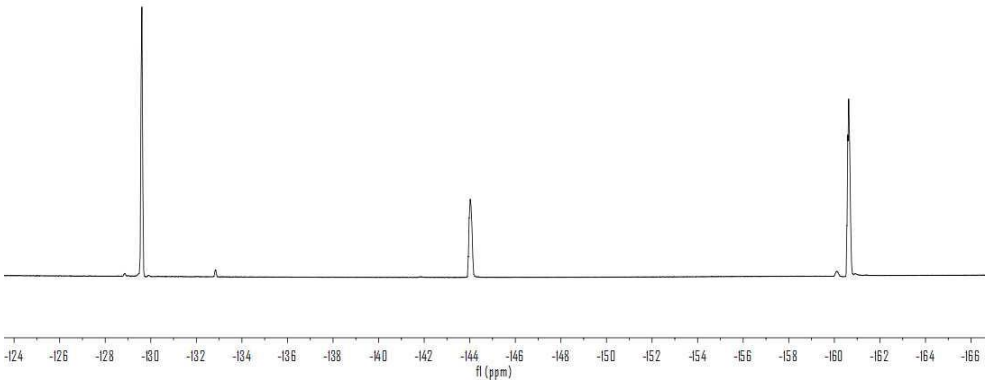
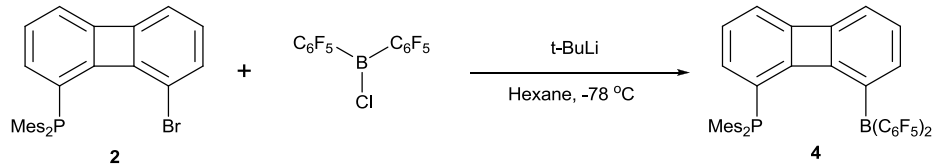


Figure S6. ^{19}F NMR (564 MHz, 299 K, benzene-d_6) spectrum of compound **3**.



Preparation of the FLP 4

Scheme S4. Preparation of FLP **4**



1.2 mL *t*-BuLi (1.7 mol/L in hexane) was added to a suspension of (8-bromobiphenylen-1-yl)dimesitylphosphine (1.0 g, 2 mmol) in hexane (40 mL) in a well dried Schlenk flask at -78 °C. The resulting mixture was allowed to warm to room temperature and stirred for 3h, then cooled down to -78 °C again. A solution of $ClB(C_6F_5)_2$ (760 mg, 2 mmol) in hexane (20.0 mL) was added to the suspension dropwise, the mixture was warmed to room temperature slowly and stirred for further 12h. The precipitate was removed by filtration. The resulting orange solution was contracted to 20 mL and cooled to -78 °C to get the product **4** (810 mg 53% yield) as an orange powder.

Melting point: 173 (with decomposition) °C.

Anal. Calc. for $C_{42}H_{28}BF_{10}P$: C, 65.99; H, 3.69 Found: C, 65.57; H, 3.52.

^{1}H NMR (500 MHz, 299 K, cyclohexane-d_{12}): δ = for the mesityl group: 6.64 (d, $^{4}J_{PH}$ = 2.7 Hz, 4H, *m*-Mes), 2.18 (s, 6H, *p*-CH_3^{Mes}), 1.94 (s, 12H, *o*-CH_3^{Mes}); for the biphenylene backbone: 6.68 (m, 1H, 6-CH), 6.61 (m, 1H, 5-CH), 6.56 (m, 1H, 2-CH), 6.44 (m, 3H, 3-CH, 4-CH, 7-CH).

^{13}C{^{1}H} NMR (126 MHz, 299 K, cyclohexane-d_{12}) [C_6F_5 not listed] : δ = for the mesityl group: 142.4 (d, $^{2}J_{PC}$ = 14.1 Hz, *o*-Mes), 138.7 (*p*-Mes), 130.6 (d, $^{3}J_{PC}$ = 3.6 Hz, *m*-Mes), 130.4 (d, $^{1}J_{PC}$ = 14.2 Hz, *i*-Mes), 23.3 (d, $^{3}J_{PC}$ = 14.9 Hz, *o*-CH_3^{Mes}), 21.0 (*p*-CH_3^{Mes}); for the P-substituted ring of the biphenylene backbone: 160.7 (d, $^{2}J_{PC}$ = 37.8 Hz, 10-C), 152.3 (d, $^{3}J_{PC}$ = 12.7 Hz, 11-C), 134.3 (d, $^{2}J_{PC}$ = 3.4 Hz, 2-CH), 128.8 (3-CH), 127.9 (d, $^{1}J_{PC}$ = 16.2 Hz, 1-C), 117.2 (4-CH); for the B-substituted ring of

the biphenylene backbone: 155.6 (d, $^{3}J_{PC}$ = 8.6 Hz, 9-C), 151.4 (12-C), 135.9 (br, 8-C), 130.0 (7-CH), 128.4 (6-CH), 118.7 (5-CH).
^{11}B{^{1}H} NMR (160 MHz, 299 K, cyclohexane-d_{12}): δ = 63.2 ($\nu_{1/2}$ ~ 2400 Hz).
^{31}P NMR (202 MHz, 299 K, cyclohexane-d_{12}): δ = -33.7 ($\nu_{1/2}$ ~ 21 Hz).
^{19}F NMR (470 MHz, 299 K, cyclohexane-d_{12}): δ = -126.8 (m, 2F, *o*-C_6F_5), -147.0 (m, 1F, *p*-C_6F_5), -162.3 (m, 2F, *m*-C_6F_5). [$\Delta\delta$ ^{19}Fm, p = 15.3].

Figure S7. ^{1}H NMR (500 MHz, 299 K, cyclohexane-d_{12}) spectrum of compound **4**.

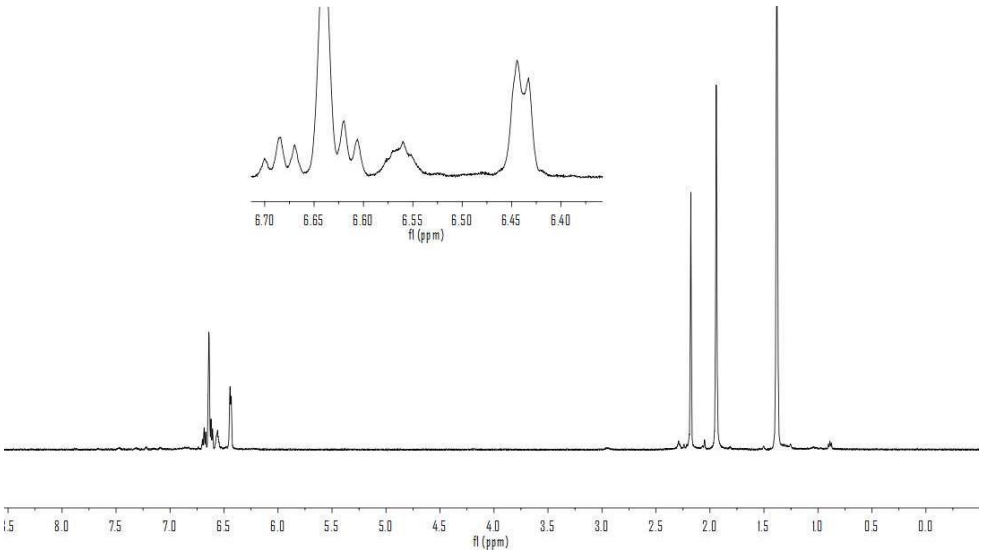


Figure S8. ^{13}C{^{1}H} NMR (126 MHz, 299 K, cyclohexane-d_{12}) spectrum of compound **4**.

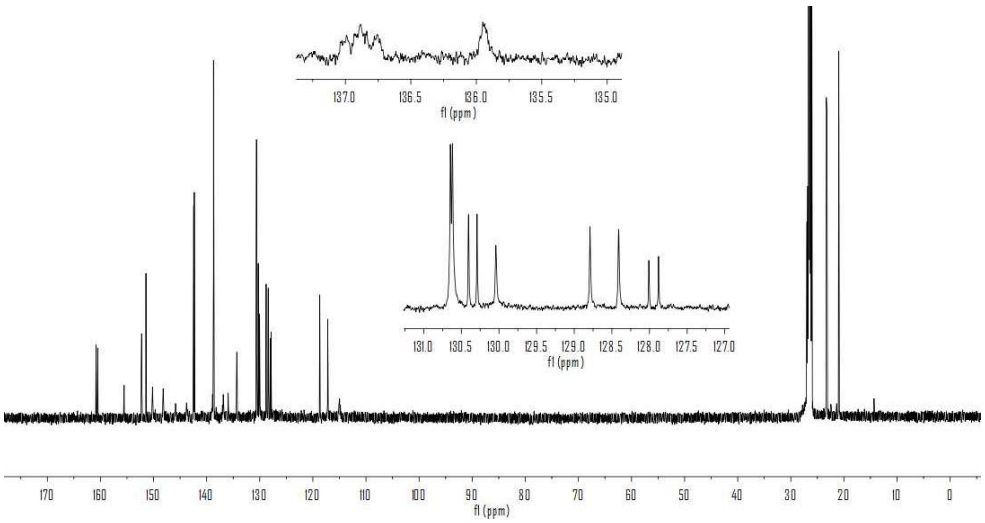


Figure S9. $^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, cyclohexane-d_{12}) spectrum of compound **4**.

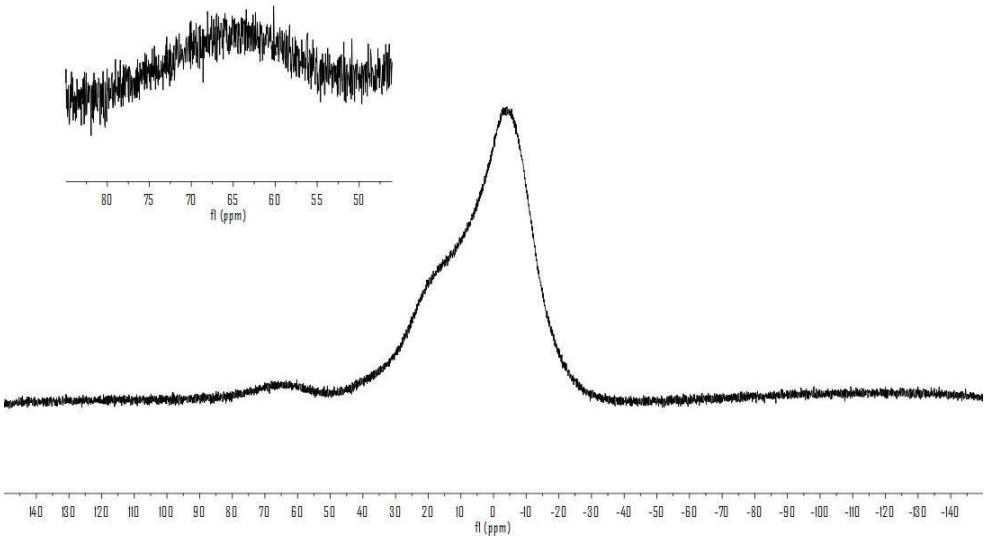


Figure S10. ^{31}P NMR (202 MHz, 299 K, cyclohexane-d_{12}) spectrum of compound **4**.

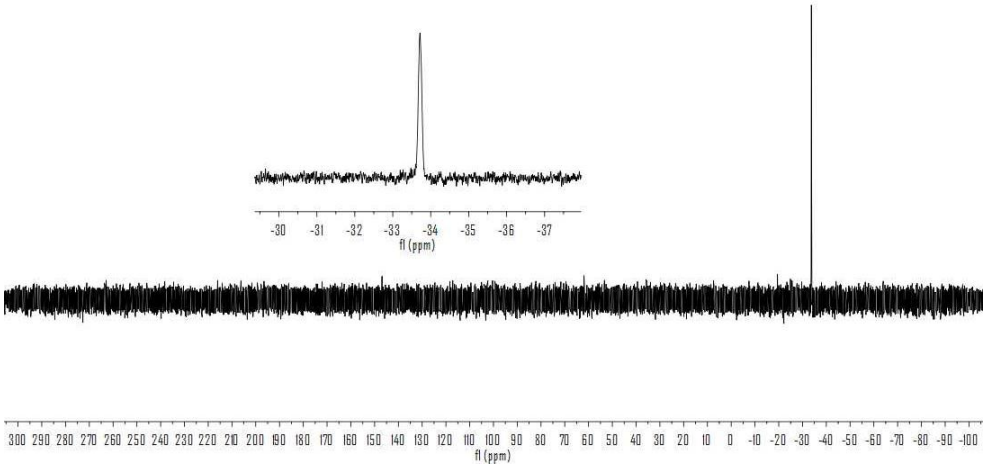
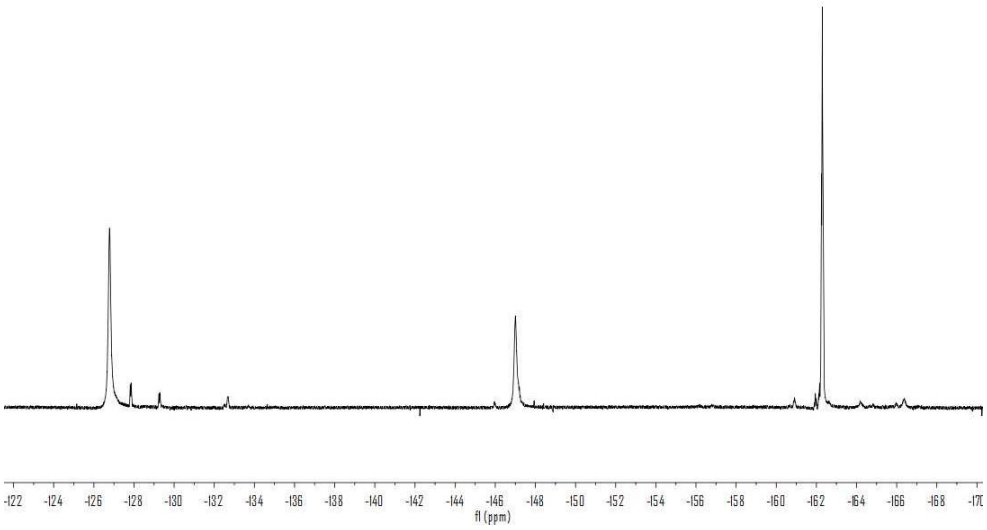
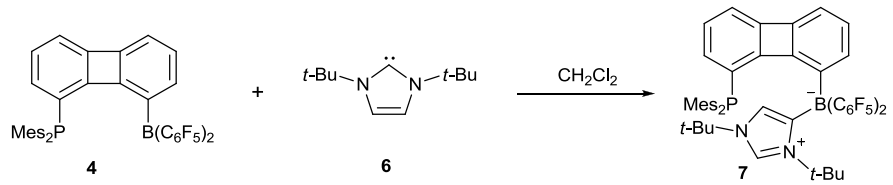


Figure S11. ^{19}F NMR (460 MHz, 299 K, cyclohexane-d_{12}) spectrum of compound **4**.



Preparation of the NHC addition product 7

Scheme S5. Preparation of compound **7**.



Compound **4** (115 mg, 0.15 mmol) was dissolved in CH_2Cl_2 (3 mL), the carbene (27 mg, 0.15 mmol) was added by one portion. The resulting deep orange solution was stirred at room temperature overnight. Then the volatiles were removed via vacuo and the residual solid was washed by pentane (3*5mL) to give compound **7** as a pale yellow powder (116mg, 82% yield).

Melting point: 267 (with decomposition) °C.

Anal. Calc. for $C_{63}H_{52}BF_{10}N_2P$: C, 67.38; H, 5.12; N, 2.97. Found: C, 67.27; H, 5.17; N, 2.97.

^{1}H NMR (500 MHz, 299 K, methylene chloride-d_2): δ = for the mesityl group: 6.75 (m, 1H, *m*-Mes^a), 6.64 (m, 4H, *m*'-Mes^a, *m*-Mes^b, *m*'-Mes^b, overlapping with 6-CH), 2.27 (s, 3H, *p*-CH_3^{Mesa}), 2.22 (s, 3H, *o*-CH_3^{Mesa}), 2.17 (s, 3H, *p*-CH_3^{Mesb}), 1.94 (s, 3H, *o*'-CH_3^{Mesa}), 1.51 (s, 3H, *o*-CH_3^{Mesb}), 1.50 (s, 3H, *o*'-CH_3^{Mesb}); for the biphenylene backbone: several multiplets between 6.90 and 6.35; for the NHC part: 8.09 (d, *J* = 1.9 Hz, 1H, CHN_2), 7.54 (m, 1H, CHN=), 1.48 (s, 9H, CH_3^{tBua}), 1.41 (s, 9H, CH_3^{tBub}).

^{13}C{^{1}H} NMR (126 MHz, 299 K, methylene chloride-d_2) [C_6F_5 not listed]: δ = for the mesityl group: 142.4 (*o*-Mes^b), 142.1 (*o*-Mes^a), 141.3 (d, $^2J_{PC}$ = 33.0 Hz, *o*'-Mes^b), 141.2 (d, $^2J_{PC}$ = 33.0 Hz, *o*'-Mes^a), 138.2 (*p*-Mes^a), 137.5 (*p*-Mes^b), 132.5 (d, $^1J_{PC}$ = 19.9 Hz, *i*-Mes^b), 132.4 (d, $^3J_{PC}$ = 2.8 Hz, *m*-Mes^a), 131.1 (d, $^1J_{PC}$ = 25.4 Hz, *i*-Mes^a), 130.8 (*m*-Mes^b), 129.39 (d, $^3J_{PC}$ = 8.2 Hz, *m*'-Mes^b), 128.8 (d, $^3J_{PC}$ = 5.0 Hz, *m*'-Mes^a), 24.6 (*o*-CH_3^{Mesa}), 23.0 (d, $^3J_{PC}$ = 29.7 Hz, *o*'-CH_3^{Mesa}), 22.8 (*o*-CH_3^{Mesb}), 21.4 (d, $^3J_{PC}$ = 28.9 Hz, *o*'-CH_3^{Mesb}), 20.85 (*p*-CH_3^{Mesb}), 20.79 (*p*-CH_3^{Mesa}); for the P-substituted ring of the biphenylene backbone: 163.9 (d, $^2J_{PC}$ = 36.8 Hz, 10-C), 151.4 (d, $^3J_{PC}$ = 12.6 Hz, 11-C), 136.1 (d, $^3J_{PC}$ = 1.9 Hz, 2-CH), 127.0 (d, $^1J_{PC}$ = 16.4 Hz, 1-C), 126.49 (3-CH), 114.7 (4-CH); for the B-substituted ring of the biphenylene backbone: 161.1 (d, $^3J_{PC}$ = 7.2 Hz, 9-C), 150.3 (12-C), 143.8 (br, 8-C), 138.5 (d, *J* = 3.4 Hz, 7-CH), 126.53 (6-CH), 114.6 (5-CH); for the NHC part: 148.7 (br, CBN=), 130.0 (CHN=), 129.35 (CHN_2), 61.9 (C^{tBub}), 58.5 (C^{tBua}), 30.9 (CH_3^{tBub}), 30.2 (CH_3^{tBua}).

^{11}B {^{1}H} NMR (160 MHz, 299 K, methylene chloride-d_2): δ = -12.4 ($\nu_{1/2}$ ~ 59 Hz).

^{31}P{^{1}H} NMR (202 MHz, 299 K, methylene chloride-d_2): δ = -27.2 (br 1:1:1:1 q partially relaxed, J_{PB} ~ 4 Hz).

^{19}F NMR (470 MHz, 299 K, methylene chloride-d_2): δ = -123.9 (m, 1F, *o*-$C_6F_5^a$), -133.8 (m, 1F, *o*'-$C_6F_5^a$), -162.2 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), -165.8 (m, 1F, *m*-$C_6F_5^a$), -166.7 (m, 1F, *m*'-$C_6F_5^a$) [$\Delta\delta$ ^{19}F*m, p* = 4.5, 3.6]. -124.7 (m, 1F, *o*-$C_6F_5^b$), -127.4 (m, 1F, *o*'-$C_6F_5^b$), -160.0 (m, 1F, *m*'-$C_6F_5^b$), -161.7 (t, $^3J_{FF}$ = 20.6 Hz, *p*-$C_6F_5^b$), -167.9 (m, 1F, *m*-$C_6F_5^b$) [$\Delta\delta$ ^{19}F*m, p* = 6.2, 1.7].

Figure S12. ^{1}H NMR (500 MHz, 299 K, methylene chloride-d_2) spectrum of compound **7**.

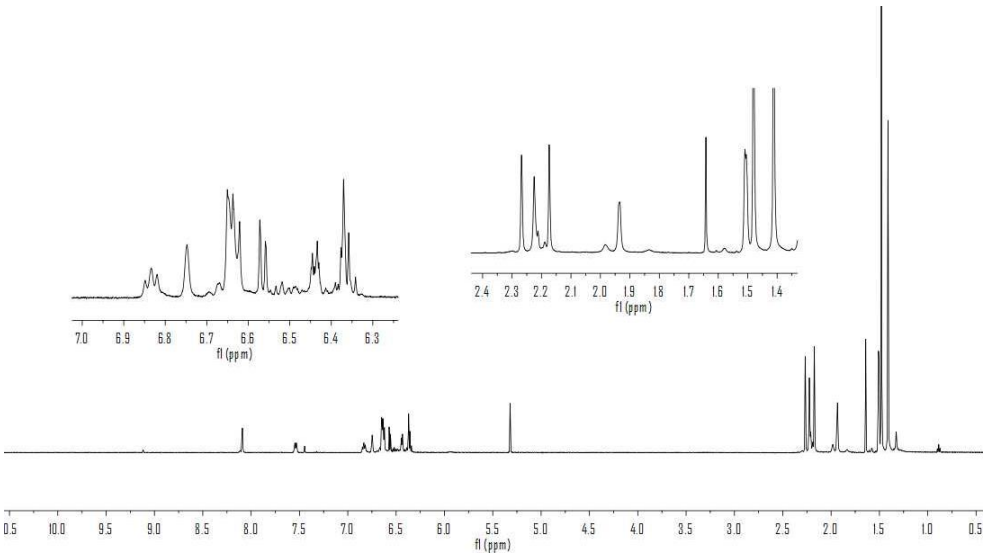


Figure S13. $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, methylene chloride-d_2) spectrum of compound **7**.

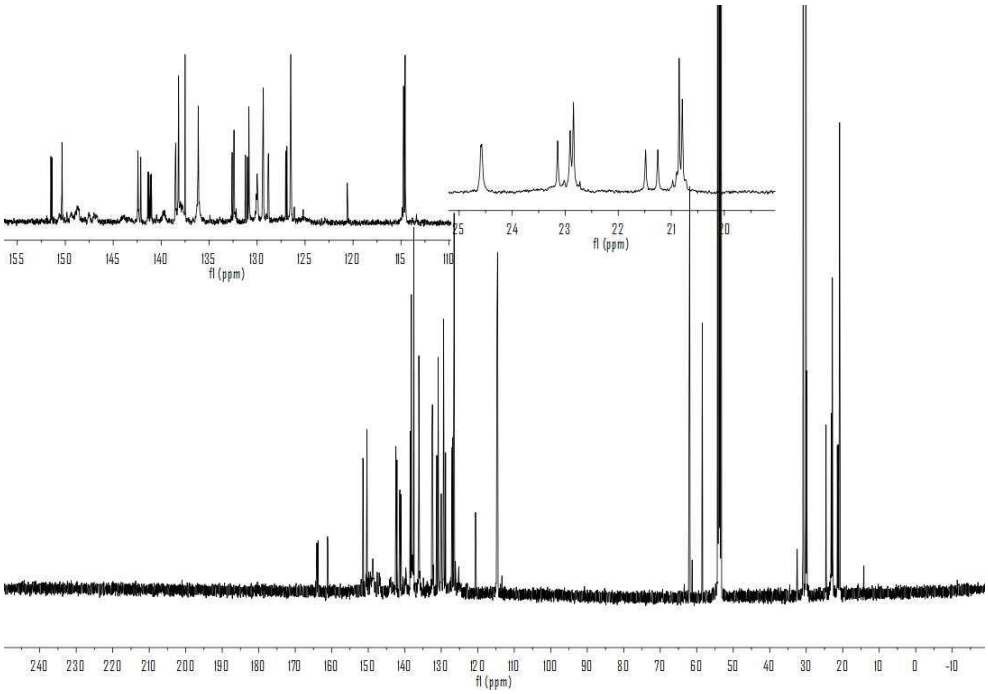


Figure S14. ^{11}B NMR (160 MHz, 299 K, dichloromethane-d_2) spectrum of compound **7**.

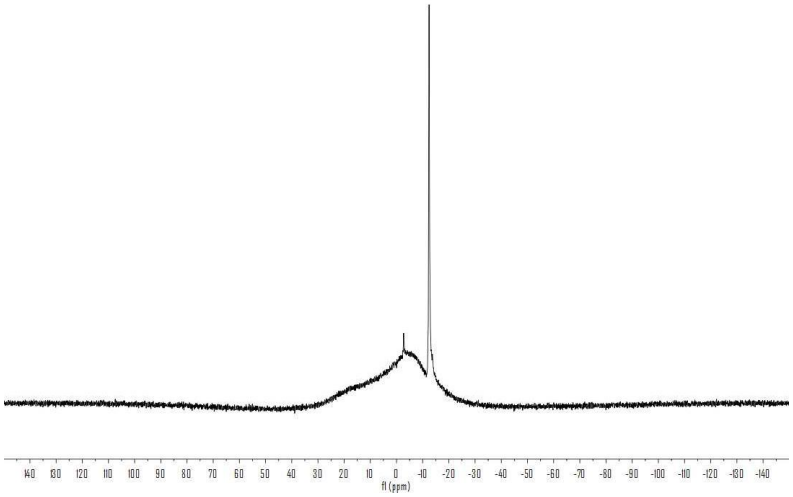


Figure S15. $^{31}P\{^{1}H\}$NMR (202 MHz, 299 K, dichloromethane-d_2) spectrum of compound **7**.

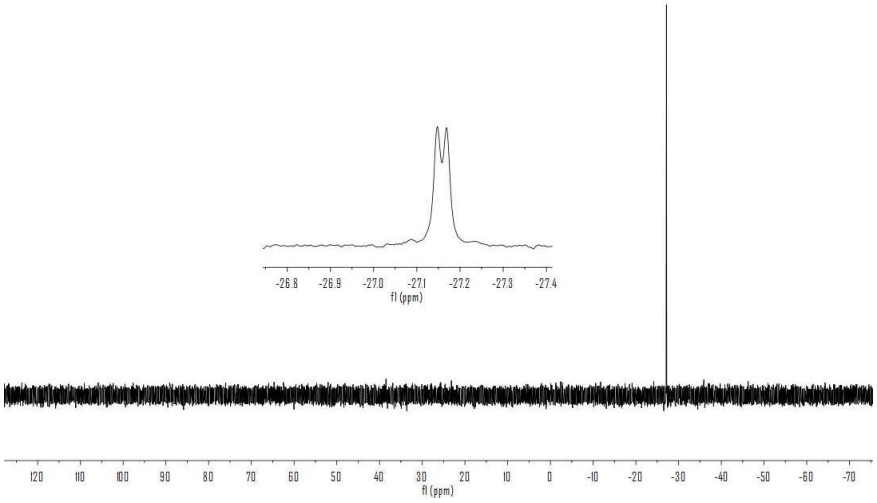
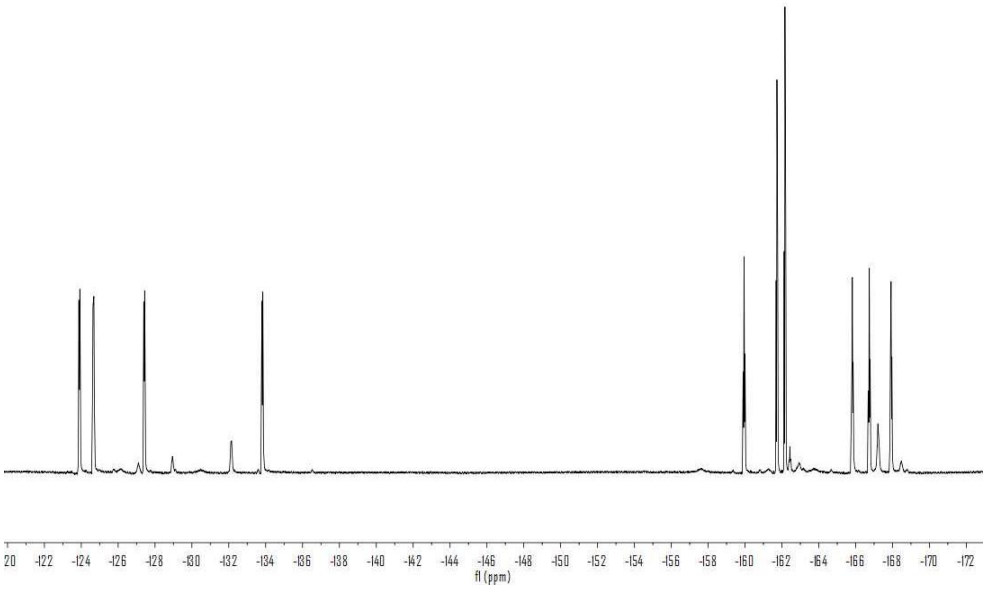


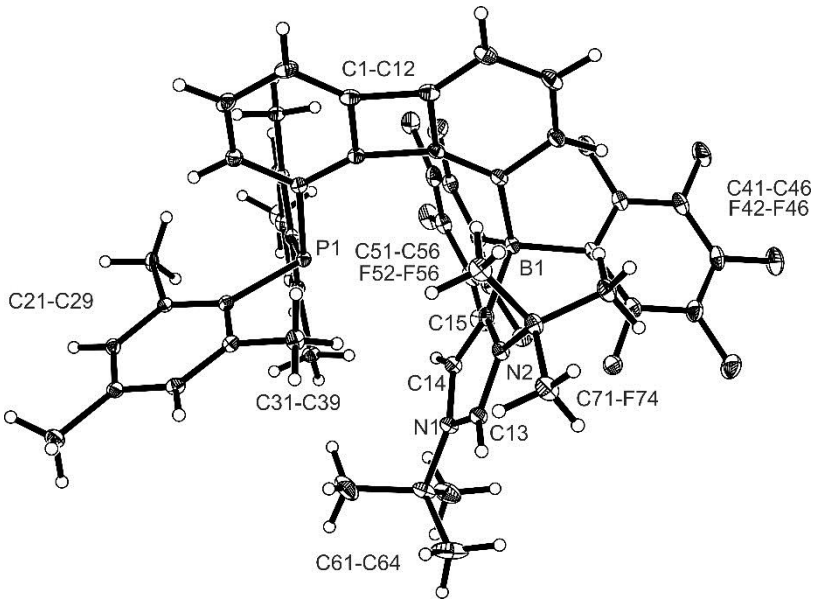
Figure S16. ^{19}F NMR (470 MHz, 299 K, methylene chloride-d_2) spectrum of compound **7**.



Crystals suitable for the *X*-ray crystal structure analysis were obtained from layered pentane on a solution of compound **7** in dichloromethane at room temperature.

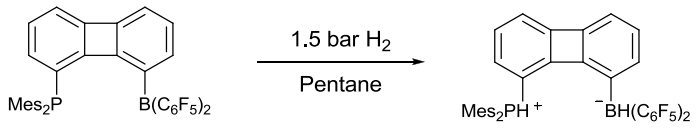
X-ray crystal structure analysis of compound 7 (erk8618): formula $C_{53}H_{48}BF_{10}N_2P$, M = 944.71, colourless crystal, 0.23 x 0.16 x 0.06 mm, a = 11.6758(2), b = 12.5018(2), c = 19.7217(4) Å, α = 90.855(1), β = 106.410(1), γ = 104.165(1)°, V = 2666.6(1) Å^3, ρ_{calc} = 1.177 gcm^{-3}, μ = 0.121 mm^{-1}, empirical absorption correction (0.972 ≤ T ≤ 0.992), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 173(2) K, ω and ϕ scans, 25448 reflections collected (±h, ±k, ±l), 9103 independent (R_{int} = 0.046) and 7307 observed reflections [I>2σ(I)], 620 refined parameters, R = 0.064, wR^2 = 0.163, max. (min.) residual electron density 0.55 (-0.25) e.Å^{-3}, the hydrogen atom at C13 was refined freely; others were calculated and refined as riding atoms.

Figure S17. Structure of compound **7**.



Preparation of the H_2 splitting product 5

Scheme S6. Preparation of compound **5**.



4 **5**

Compound **4** (115 mg, 0.15 mmol) was dissolved in pentane (8 mL) and the resulting solution subjected to three freeze-pump-thaw cycles before backfilling with H_2 (ca. 1.5 bar). The deep orange solution changed to yellow immediately and a pale yellow powder precipitates. The suspension was stirred for further 12h. Then the precipitate was collected by filtration and washed with pentane (2 x 3 mL), dried in vacuo to give compound **5** as a pale yellow powder (64 mg, 56%).
Melting point: 167 °C.
Anal. Calc. for $C_{42}H_{30}BF_{10}P$: C, 65.82; H, 3.95. Found: C, 65.43; H, 3.65.
^{1}H NMR (500 MHz, 299 K, methylene chloride-d_2): δ = for the mesityl group: 6.93 (d, $^4J_{PH}$ = 4.6 Hz, 4H, *m*-Mes), 2.29 (s, 6H, *p*-CH_3^{Mes}), 2.24 (s, 12H, *o*-CH_3^{Mes}); for the P-substituted ring of the biphenylene backbone: 6.72 (m, 2H, 3, 4-CH), 6.33 (m, 1H, 2-CH); for the B-substituted ring of the biphenylene backbone: 6.90 (d, $^3J_{HH}$ = 8.2 Hz, 1H, 7-CH), 6.65 (dd, $^3J_{HH}$ = 8.2, 6.8 Hz, 1H, 6-CH), 6.53 (d, $^3J_{HH}$ = 6.8 Hz, 1H, 5-CH); 9.62 (d, $^1J_{PH}$ ~ 519 Hz, 1H, PH), 3.38 (br 1:1:1:1 q, $^1J_{BH}$ ~ 80 Hz,1H, BH).
^{13}C{^{1}H} NMR (126 MHz, 299 K, methylene chloride-d_2) [C_6F_5 not listed]: δ = for the mesityl group: 146.0 (d, $^4J_{PC}$ = 2.8 Hz, *p*-Mes), 143.6 (d, $^2J_{PC}$ = 10.1 Hz, *o*-Mes), 131.8 (d, $^3J_{PC}$ = 11.3 Hz, *m*-Mes), 112.2 (d, $^1J_{PC}$ = 85.8 Hz, *i*-Mes), 22.0 (d, $^3J_{PC}$ = 8.6 Hz, *o*-CH_3^{Mes}), 21.3 (*p*-CH_3^{Mes}); for the P-substituted ring of the biphenylene backbone: 165.9 (d, $^2J_{PC}$ = 8.8 Hz, 10-C), 154.1 (d, $^3J_{PC}$ = 14.9 Hz, 11-C), 129.7 (d, $^3J_{PC}$ = 10.5 Hz, 3-CH), 127.7 (d, $^2J_{PC}$ = 12.4 Hz, 2-CH), 119.5 (d, $^4J_{PC}$ = 3.1 Hz, 4-CH), 104.0 (d, $^1J_{PC}$ = 85.8 Hz, 1-C); for the B-substituted ring of the biphenylene backbone: 152.6 (9-C), 150.7 (br, 8-C), 149.4 (12-C), 138.5 (7-CH), 129.7 (6-CH), 115.9 (5-CH).
^{11}B NMR (160 MHz, 299 K, methylene chloride-d_2): δ = -20.9 (d, $^1J_{BH}$ ~ 83 Hz).
^{31}P NMR (202 MHz, 299 K, methylene chloride-d_2): δ = -21.6 (d, $^1J_{PH}$ ~ 519 Hz).
^{19}F NMR (470 MHz, 299 K, methylene chloride-d_2): δ = -132.7 (m, 2F, *o*-C_6F_5), -164.4 (t, $^3J_{FF}$ = 20.0 Hz, 1F, *p*-C_6F_5), -166.8 (m, 2F, *m*-C_6F_5) [$\Delta\delta$ ^{19}F*m, p* = 2.4].

Figure S18. ^{1}H NMR (500 MHz, 299 K, methylene chloride-d_2) spectrum of compound **5**.

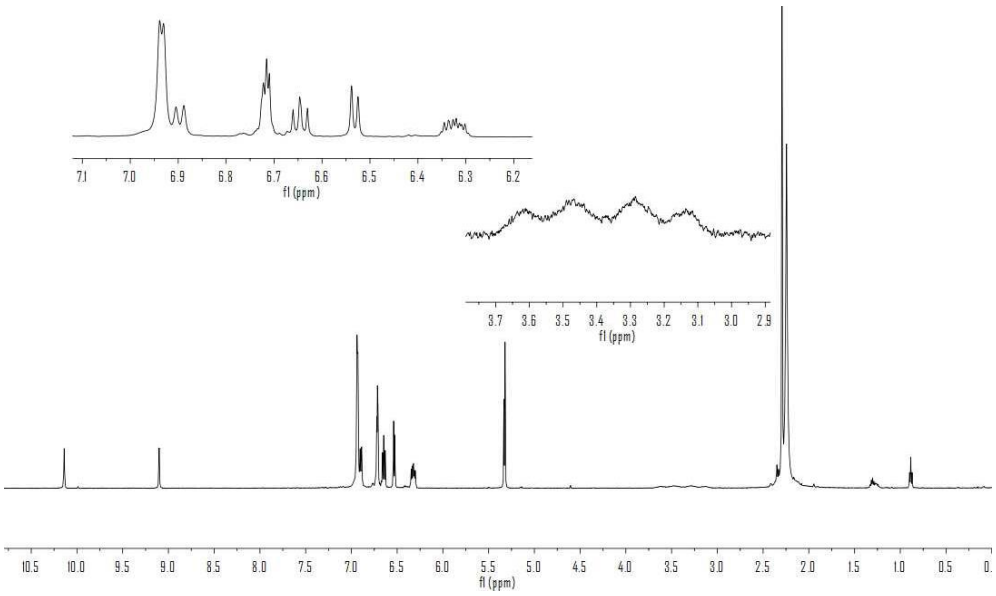


Figure S19. $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, methylene chloride-d_2) spectrum of compound **5**.

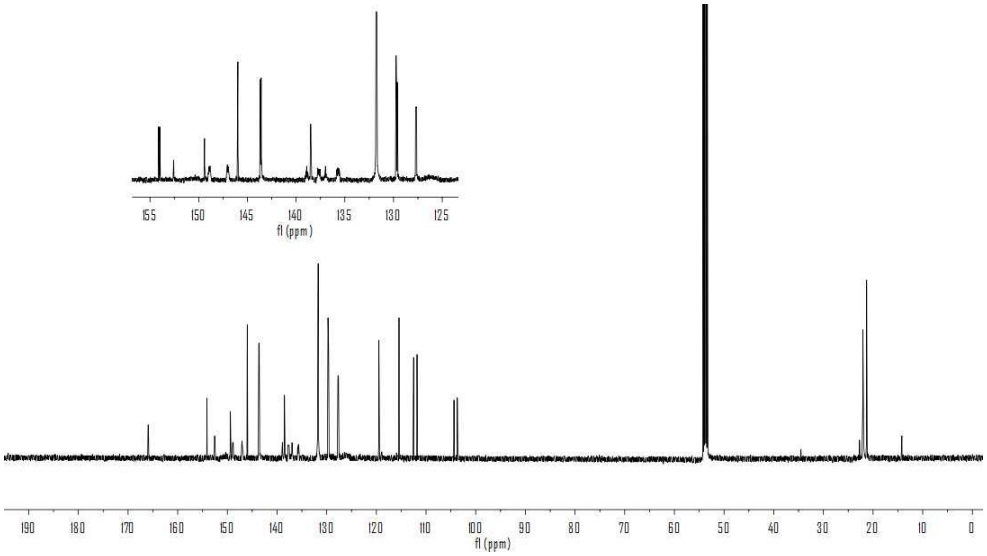


Figure S20. ^{11}B NMR (160 MHz, 299 K, methylene chloride-d_2) spectrum of compound **5**.

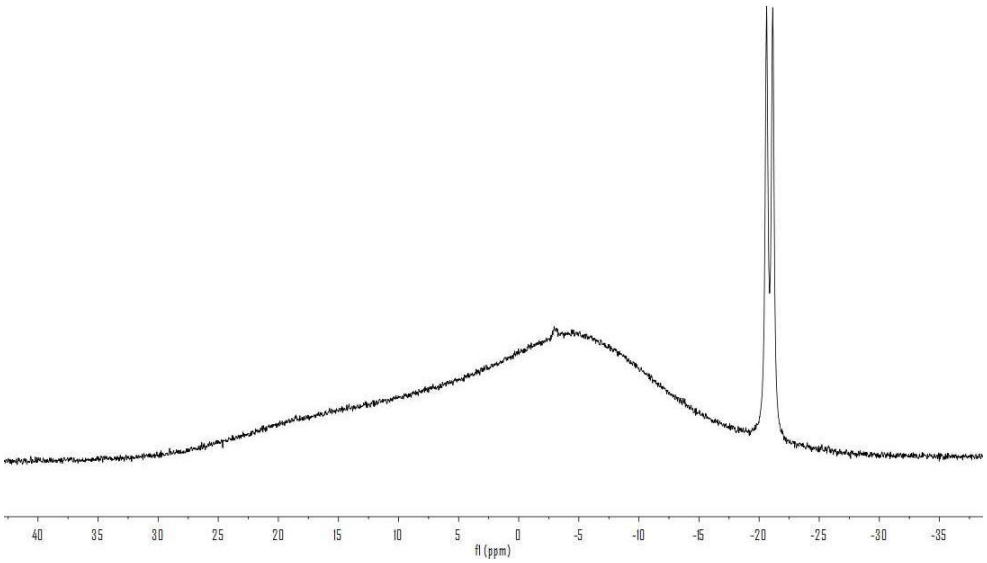


Figure S21. ^{31}P NMR (202 MHz, 299 K, methylene chloride-d_2) spectrum of compound **5**.

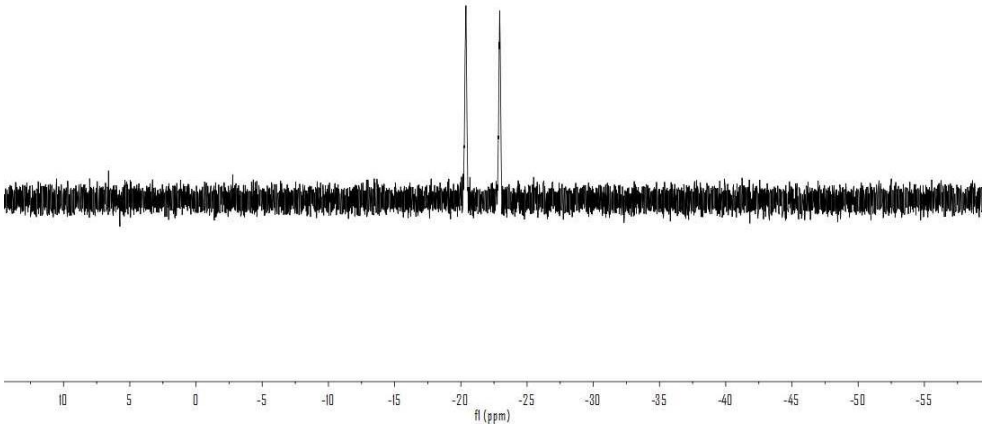
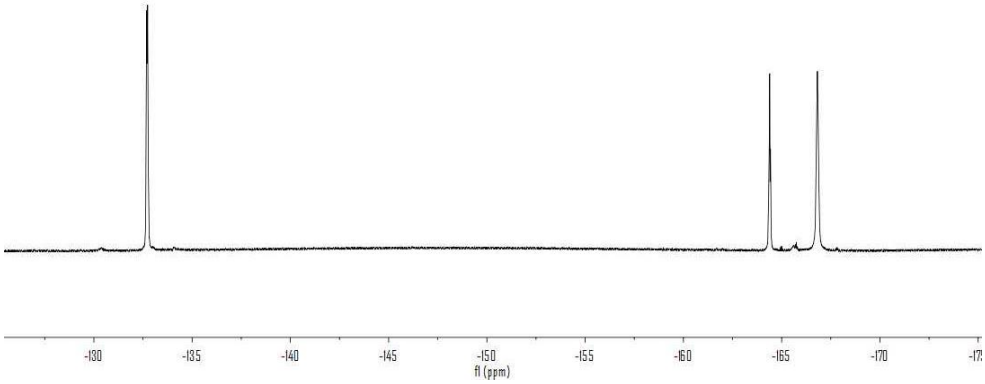


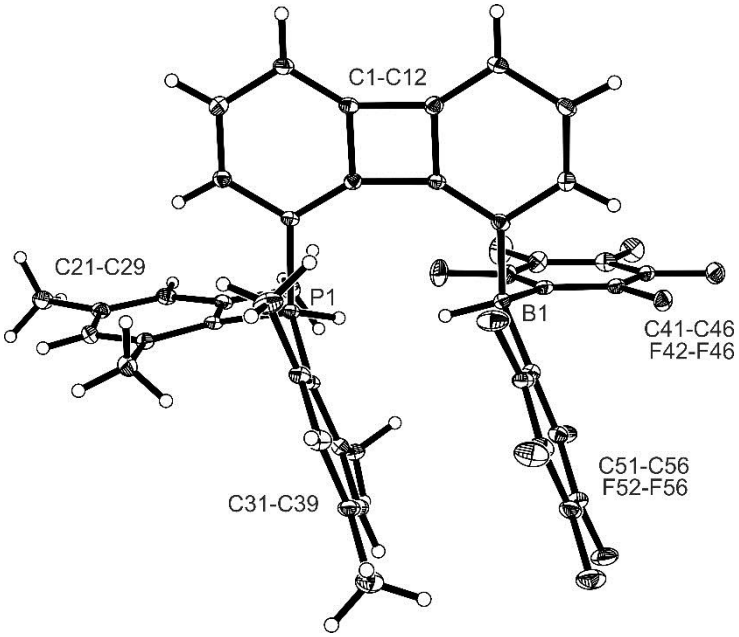
Figure S22. ^{19}F NMR (470 MHz, 299 K, methylene chloride-d_2) spectrum of compound **5**.



Crystals suitable for the *X*-ray crystal structure analysis of compound **5** were obtained from slow evaporation of n-pentane to a solution of compound **5** in CH_2Cl_2 at -35 °C.

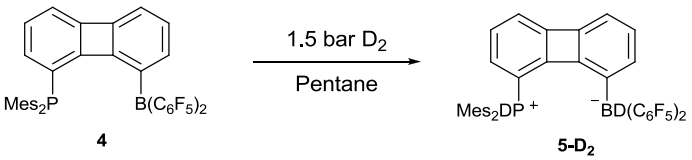
X-ray crystal structure analysis of compound 5 (erk8473): formula $C_{42}H_{30}BF_{10}P$, M = 766.44, pale yellow crystal, 0.18 x 0.12 x 0.04 mm, a = 11.8477(4), b = 12.3022(3), c = 14.0634(5) Å, α = 67.621(2), β = 72.281(2), γ = 67.990(2)°, V = 1725.7(1) Å^3, ρ_{calc} = 1.475 gcm^{-3}, μ = 0.166 mm^{-1}, empirical absorption correction (0.970 ≤ T ≤ 0.993), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 173(2) K, ω and ϕ scans, 15411 reflections collected (±h, ±k, ±l), 5907 independent (R_{int} = 0.068) and 4701 observed reflections [I>2σ(I)], 501 refined parameters, R = 0.081, wR^2 = 0.214, max. (min.) residual electron density 0.43 (-0.51) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Figure S23. Structure of compound **5**.



Preparation of the D_2 addition product 5-D_2

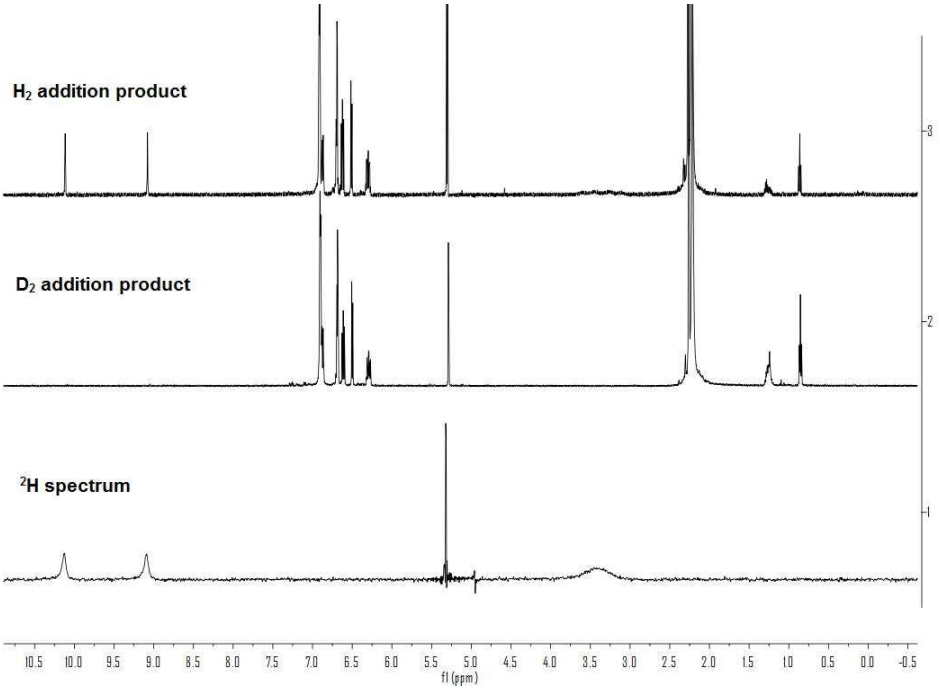
Scheme S7. Preparation of compound **5-D_2**:



4 **5-D_2**

Compound **4** (85 mg) was dissolved in pentane (10 mL) and the resulting solution subjected to three freeze-pump-thaw cycles before backfilling with D_2 (ca. 1.5 bar). The deep orange solution changed to yellow immediately and a pale yellow powder precipitates. Then the precipitate was collected by filtration and washed with pentane (2 x 5 mL), dried in vacuo to give compound **5**-D_2 as a pale yellow powder (41 mg, 48%).

Figure S24. ^{1}H NMR (500 MHz, 299 K, methylene chloride-d_2) and ^{2}H NMR (77 MHz, 299 K, methylene chloride) spectrum of compounds **5** and **5-D_2**.



Catalytic hydrogenation with compound 5

General procedure of catalytic hydrogenation with H_2 addition product:
H_2 addition product (38.3 mg, 0.05 mmol) was added to a solution of substrate (0.5 mmol) in methylene chloride-d_2. The resulting mixture reacted under 10 bar H_2 in the autoclave at room temperature for 24 h. Then the conversion was detected by ^{1}H NMR.

Scheme S8. Catalytic hydrogenation with compound **5**.

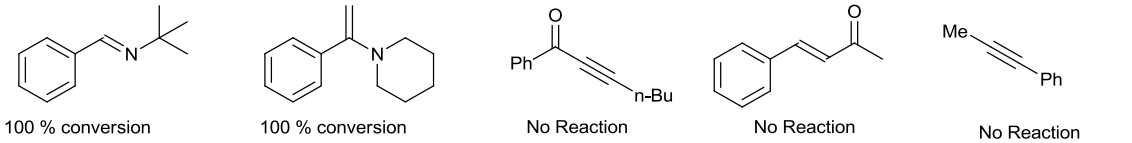


Figure S25. In situ ^{1}H NMR (500 MHz, 299 K, methylene chloride-d_2) spectrum of catalytic hydrogenation product of the imine.

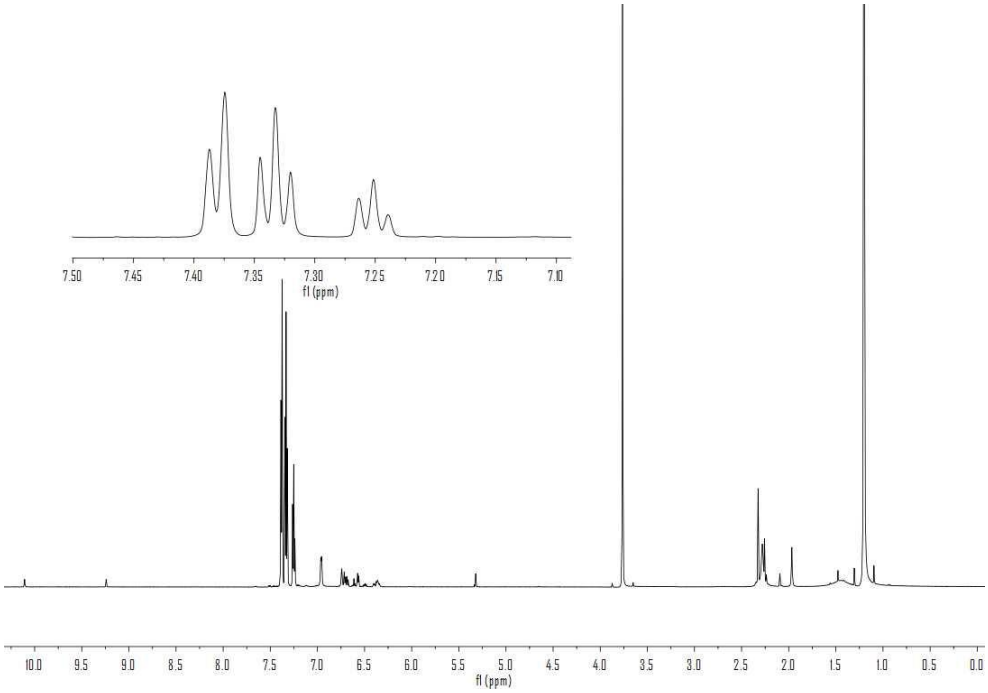
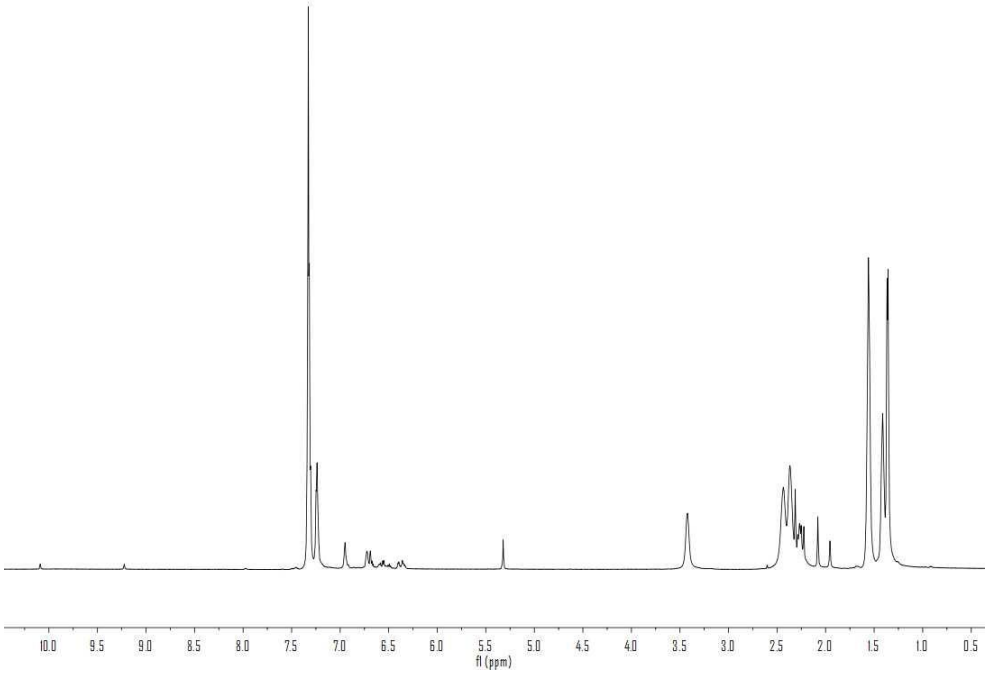
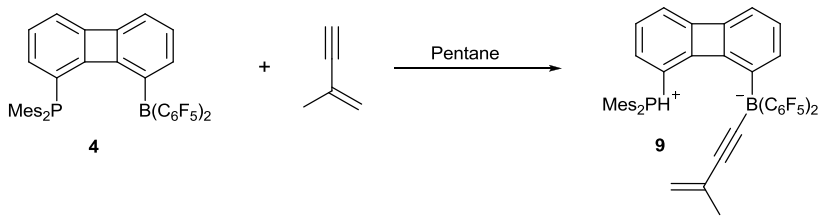


Figure S26. In situ ^{1}H NMR (600 MHz, 299 K, methylene chloride-d_2) spectrum of catalytic hydrogenation product of the enamine.



Preparation of the alkyne CH-splitting product 9

Scheme S9. Preparation of compound **9**.



Compound **4** (115 mg, 0.15 mmol) was dissolved in pentane (10 mL) and the resulting solution was added to the solution of 2-methylbut-1-en-3-yne (19.8 mg, 0.3 mmol) in pentane (2 mL). A pale yellow powder precipitates immediately and the suspension was stirred for further 2h. Then the precipitate was collected by filtration and washed with pentane (2 x 3 mL), dried in vacuo to give compound **9** as a pale yellow powder (75mg, 60% yield).
Decomposition: 142 °C.
HRMS for $C_{47}H_{34}BF_{10}P$: 830.5417. Found: 831.24152 ($[M + H]^+$).
^{1}H NMR (500 MHz, 208 K, methylene chloride-d_2): δ = for the mesityl group: 6.97 (m, 2H, *m*-Mes^a, *m*-Mes^b), 6.94 (m, 1H, *m*´-Mes^a), 6.83(m, 1H, *m*´-Mes^b), 2.48 (s, 3H, *o*-CH_3^{Mesb}); 2.35 (s, 3H, *p*-CH_3^{Mesa}), 2.29 (s, 3H, *o*'-CH_3^{Mesa}), 2.24 (s, 3H, *p*-CH_3^{Mesb}), 2.23 (s, 3H, *o*-CH_3^{Mesa}), 1.40 (s, 3H, *o*'-CH_3^{Mesb}); for the biphenylene backbone: several multiplets from 6.75-6.65 and 6.40-6.30; for the alkynyl part:, 5.00 (m, 1H, =CH_2), 4.86 (m, 1H, =CH_2), 1.81 (s, 3H, CH_3C=); PH: 10.00 (d, $^1J_{PH}$ ~ 514 Hz, 1H).
^{13}C{^{1}H} NMR (126 MHz, 208 K, methylene chloride-d_2) [C_6F_5 not listed]: δ = for the mesityl group: 146.2 (*p*-Mes^a), 145.2 (*p*-Mes^b), 143.9 (d, $^2J_{PC}$ = 9.3 Hz, *o*'-Mes^a), 143.8 (d, $^2J_{PC}$ = 11.0 Hz, *o*-Mes^b), 143.0 (d, $^2J_{PC}$ = 9.2 Hz, *o*'-Mes^b), 142.8 (d, $^2J_{PC}$ = 11.2 Hz, *o*-Mes^a), 132.0 (d, $^3J_{PC}$ = 11.8 Hz, *m*'-Mes^a, *m*'-Mes^b), 130.8 (d, $^3J_{PC}$ = 10.6 Hz, *m*-Mes^b), 130.3 (d, $^3J_{PC}$ = 10.7 Hz, *m*-Mes^a), 111.3 (d, $^1J_{PC}$ = 86.6 Hz, *i*-Mes^b), 110.2 (d, $^1J_{PC}$ = 81.2 Hz, *i*-Mes^a), 23.1 (d, $^3J_{PC}$ = 5.1 Hz, *o*'-CH_3^{Mesa}), 21.9 (d, $^3J_{PC}$ = 9.9 Hz, *o*-CH_3^{Mesb}), 21.7 (d, $^3J_{PC}$ = 4.5 Hz, *o*'-CH_3^{Mesb}), 21.0 (*p*-CH_3^{Mesa}), 20.9 (*p*-CH_3^{Mesb}), 20.8(d, $^3J_{PC}$ = 10.8 Hz, *o*-CH_3^{Mesa}); for the P-substituted ring of the biphenylene backbone: 163.8 (d, $^2J_{PC}$ = 8.4 Hz, 10-C), 152.5 (d, $^3J_{PC}$ = 14.7 Hz, 11-C), 129.2 (d, $^3J_{PC}$ = 10.1 Hz, 3-CH), 128.9 (d, $^2J_{PC}$ = 12.1 Hz, 2-CH), 118.3 (4-CH), 106.0 (d, $^1J_{PC}$ = 81.1 Hz, 1-C); for the B-substituted ring of the biphenylene backbone: 153.1 (9-C), 149.7 (12-C), 147.2 (br, 8-C), 135.8 (7-CH), 129.4 (d, 6-CH, overlapping with C=), 115.3 (5-CH); for the alkynyl part: 129.4 (d, C=, overlapping with 6-CH), 118.8 (=CH_2), 100.2 (C≡), 24.1 (CH_3) (BC≡ not listed).
^{11}B{^{1}H} NMR (160 MHz, 208 K, methylene chloride-d_2): δ = -18.7 ($\nu_{1/2}$ ~ 125 Hz).
^{31}P NMR (202 MHz, 208 K, methylene chloride-d_2): δ = -23.7 (d, $^1J_{PH}$ ~ 514 Hz).
^{19}F NMR (470 MHz, 208 K, methylene chloride-d_2): δ = -129.6 (m, 1F, *o*-C_6F_5), -133.8 (m, 1F, *o*'-C_6F_5), -162.1 (t, $^3J_{FF}$ = 21.1 Hz, 1F, *p*-C_6F_5), -165.4 (m, 1F, *m*'-C_6F_5) -166.4 (m, 1F, *m*-C_6F_5) [$\Delta\delta$ ^{19}F*m, p* = 4.3, 3.3], -130.0 (m, 1F, *o*-C_6F_5), -133.2 (m, 1F, *o*'-C_6F_5), -157.6 (t, $^3J_{FF}$ = 21.7 Hz, 1F, *p*-C_6F_5), -165.1 (m, 1F, *m*'-C_6F_5), -165.4 (m, 1F, *m*-C_6F_5) [$\Delta\delta$ ^{19}F*m, p* = 7.8, 7.5].

Figure S27. ^{1}H NMR (500 MHz, 208 K, methylene chloride-d_2) spectrum of compound **9**.

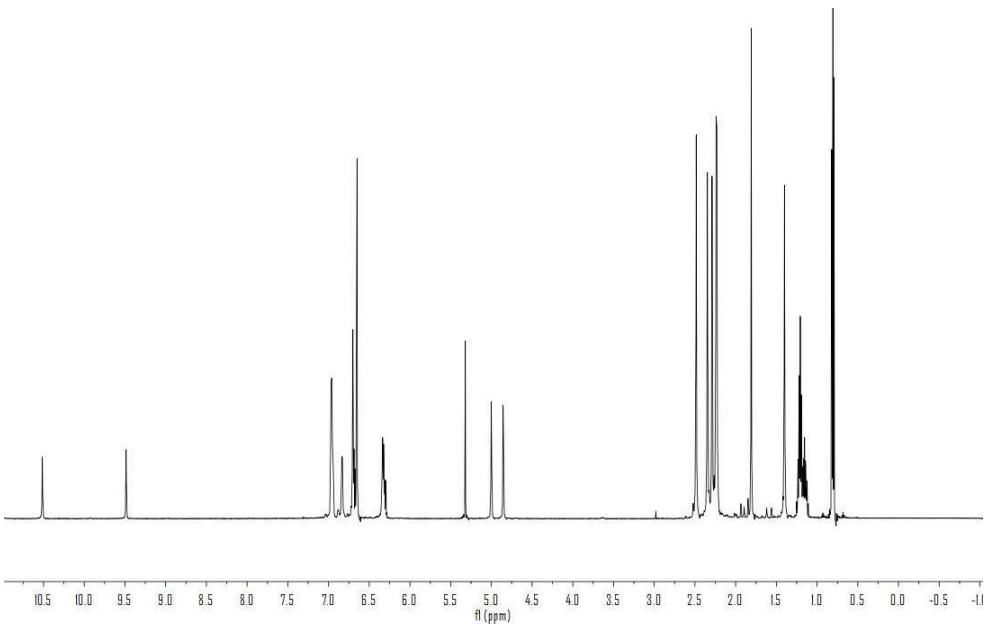


Figure S28. $^{13}C\{^{1}H\}$ NMR (126 MHz, 208 K, methylene chloride-d_2) spectrum of compound **9**.

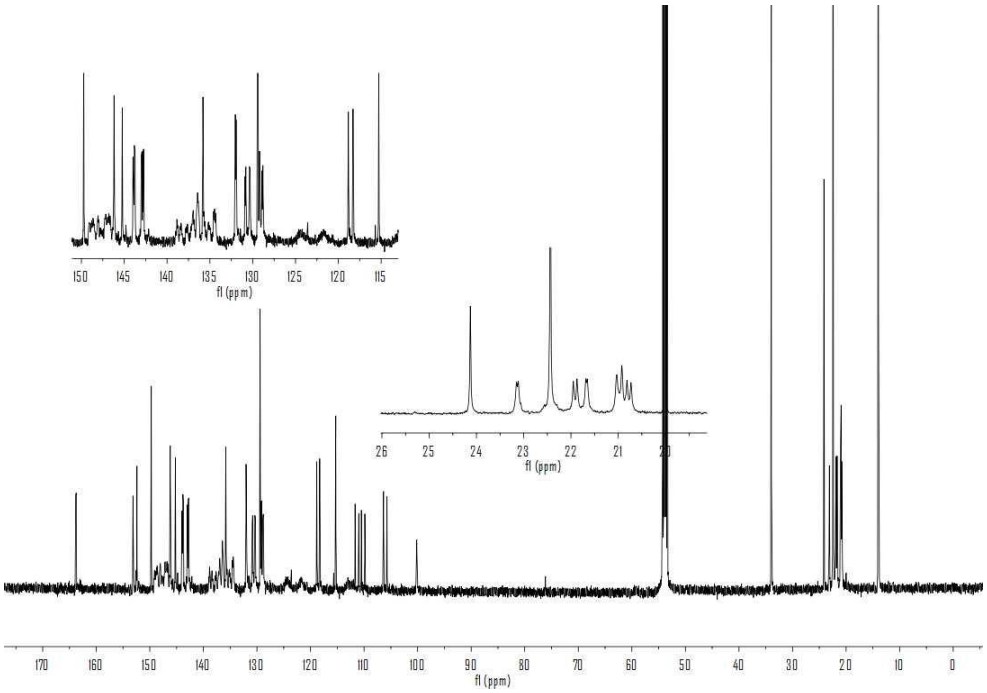


Figure S29. $^{11}B\{^{1}H\}$ NMR (160 MHz, 208 K, methylene chloride-d_2) spectrum of compound **9**.

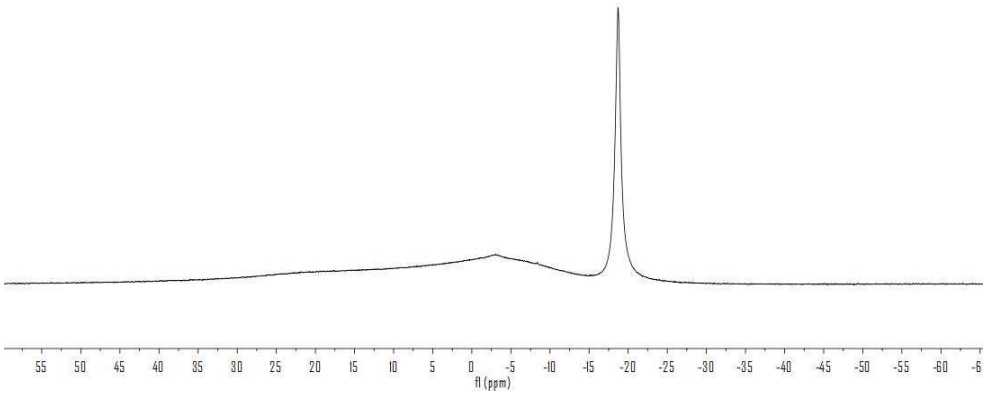


Figure S30. ^{31}P NMR (202 MHz, 208 K, methylene chloride-d_2) spectrum of compound **9**.

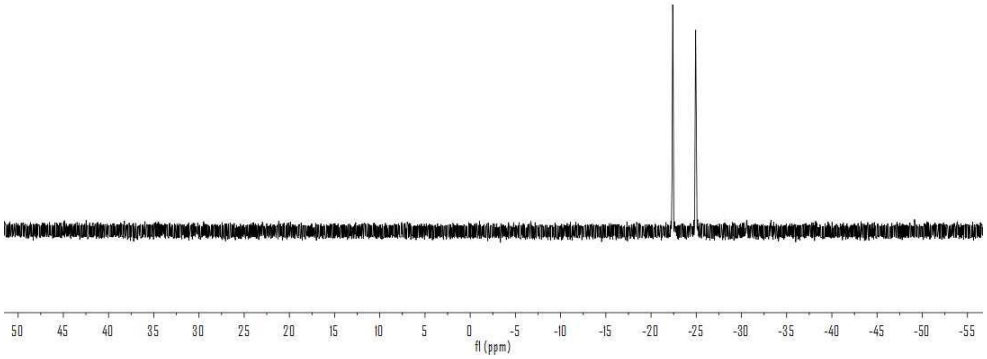
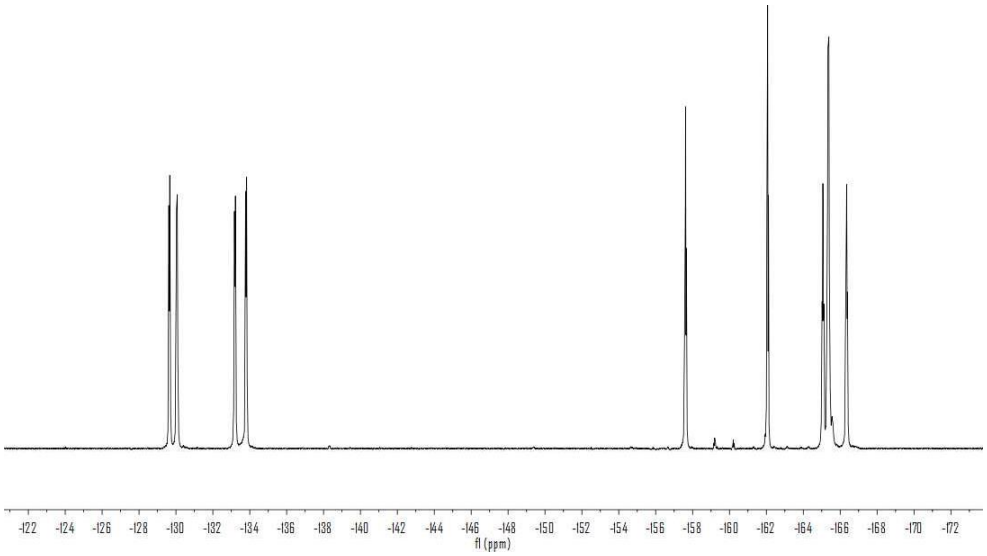


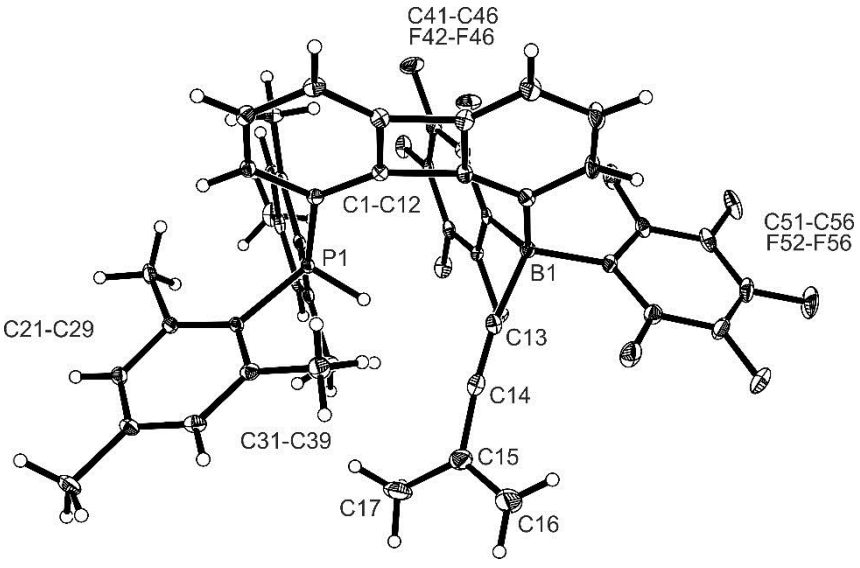
Figure S31. ^{19}F NMR (470 MHz, 208 K, methylene chloride-d_2) spectrum of compound **9**.



Crystals suitable for the *X*-ray crystal structure analysis were obtained from slow evaporation of n-pentane to a solution of compound **9** in CH_2Cl_2 at -35 °C.

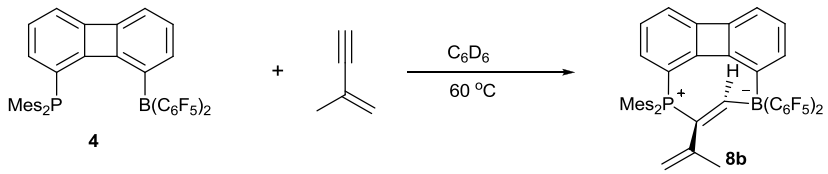
X-ray crystal structure analysis of compound 9 (erk8420): A pale yellow prism-like specimen of $C_{47}H_{34}BF_{10}P \cdot 3 \times CH_2Cl_2$, approximate dimensions 0.127 mm x 0.165 mm x 0.289 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 505 frames were collected. The total exposure time was 7.01 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 39998 reflections to a maximum θ angle of 25.39° (0.83 Å resolution), of which 8823 were independent (average redundancy 4.533, completeness = 99.5%, R_{int} = 4.59%, R_{sig} = 3.42%) and 6991 (79.24%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.5136(5) Å, b = 14.6603(6) Å, c = 16.4813(6) Å, α = 77.3240(10)°, β = 70.5870(10)°, γ = 67.4960(10)°, volume = 2410.36(17) $Å^3$, are based upon the refinement of the XYZ-centroids of 9979 reflections above 20 σ(I) with 5.597° < 2θ < 50.66°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.950. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8770 and 0.9430. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*1 , with Z = 2 for the formula unit, $C_{47}H_{34}BF_{10}P \cdot 3 \times CH_2Cl_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 652 variables converged at R1 = 5.12%, for the observed data and wR2 = 13.14% for all data. The goodness-of-fit was 1.013. The largest peak in the final difference electron density synthesis was 1.070 $e^-/Å^3$ and the largest hole was -0.885 $e^-/Å^3$ with an RMS deviation of 0.070 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.495 g/cm^3 and F(000), 1104 e^-.

Figure S32. Structure of compound **9**.



Preparation of the 1,2-alkyne addition product 8b

Scheme S10. Preparation of compound **8b**.



Compound **4** (38.2 mg, 0.05 mmol) was dissolved in C_6D_6 (1 mL) and 2-methylbut-1-en-3-yne (6.6 mg, 0.1 mmol) was added to the resulting solution via springe. The deep orange solution changed to yellow immediately and the resulting solution reacted at 60 °C for 2 days. Then the volatiles were removed via vacuo and the residual solid was purified by chromatography (silica gel, pentane: DCM (10: 1) as eluent) to give compound **8b** as a pale yellow powder (27mg, 65% yield).

Melting point: 231 (with decomposition) °C.

HRMS for $C_{47}H_{34}BF_{10}P$: 830.5417. Found: 853.22344 ($[M + Na]^+$).

^{1}H NMR (500 MHz, 299 K, toluene-d_8): δ = for the mesityl group: 6.65 (m, 2H, *m*-Mes^a, overlapping with 6-CH), 6.61 (m, 1H, *m*'-Mes^a), 6.53 (m, 1H, *m*-Mes^b), 6.46 (m, 1H, *m*'-Mes^b), 2.29 (s, 3H, *o*'-CH_3^{Mesa}), 2.16 (s, 3H, *o*-CH_3^{Mesa}), 2.13 (s, 3H, *o*-CH_3^{Mesb}), 2.09 (s, 3H, *p*-CH_3^{Mesa}), 1.88 (s, 3H, *p*-CH_3^{Mesb}), 1.66 (s, 3H, *o'*-CH_3^{Mesb}); for the P-substituted ring of the biphenylene backbone: 6.23 (m, 1H, 4-CH), 6.20 (m, 2H, 2, 3-CH); for the B-substituted ring of the biphenylene backbone: 7.63 (d, $^3J_{HH}$ = 8.4 Hz, 1H, 7-CH), 6.65 (m, 2H, 6-CH overlapping with *m*-Mes^a), 6.36 (d, $^3J_{HH}$ = 6.8 Hz, 1H, 5-CH); for the alkenyl part: 8.72 (d, $^3J_{PH}$ = 42.2 Hz, 1H, HC=), 4.96 (s, 1H, H_2C=), 4.46 (s, 1H, H_2C=), 1.36 (s, 3H, CH_3C=).

^{13}C{^{1}H} NMR (126 MHz, 299 K, toluene-d_8) [C_6F_5 not listed]: δ = for the mesityl group: 146.8 (d, $^2J_{PC}$ = 10.5 Hz, *o*-Mes^b), 145.3 (d, $^2J_{PC}$ = 9.2 Hz, *o*'-Mes^b), 145.2 (d, $^2J_{PC}$ = 7.7 Hz, *o*-Mes^a), 144.3 (d, $^4J_{PC}$ = 3.0 Hz, *p*-Mes^a), 143.8 (d, $^4J_{PC}$ = 2.9 Hz, *p*-Mes^b), 132.9 (d, $^3J_{PC}$ = 10.6 Hz, *m*'-Mes^b), 132.7 (d, $^3J_{PC}$ = 7.7 Hz, *m*-Mes^a), 132.6 (d, $^3J_{PC}$ = 7.5 Hz, *m*'-Mes^a), 132.3 (d, $^3J_{PC}$ = 10.8 Hz, *m*-Mes^b), 143.1 (d, $^2J_{PC}$ = 11.3 Hz, *o*'-Mes^a), 124.6 (d, $^1J_{PC}$ = 89.1 Hz, *i*-Mes^a), 115.9 (d, $^1J_{PC}$ = 68.5 Hz, *i*-Mes^b), 27.4 (d, $^3J_{PC}$ = 3.0 Hz, *o*-CH_3^{Mesb}), 25.6 (d, $^3J_{PC}$ = 9.2 Hz, *o*'-CH_3^{Mesa}), 25.1 (d, $^3J_{PC}$ = 3.7 Hz, *o*-CH_3^{Mesa}), 24.8 (d, $^3J_{PC}$ = 3.0 Hz, *o*'-CH_3^{Mesb}), 20.8 (*p*-CH_3^{Mesa}), 20.6 (*p*-CH_3^{Mesb}); for the P-substituted ring of the biphenylene backbone: 165.4 (d, $^2J_{PC}$ = 5.6 Hz, 10-C), 154.9 (d, $^3J_{PC}$ = 12.7 Hz, 11-C), 130.2 (d, $^2J_{PC}$ = 12.4 Hz, 2-CH), 128.2 (d, $^3J_{PC}$ = 1.9 Hz, 3-CH), 117.7(d, $^4J_{PC}$ = 2.9 Hz, 4-CH), 122.9(d, $^1J_{PC}$ = 83.6 Hz, 1-C); for the B-substituted ring of the biphenylene backbone: 153.6 (br, 8-C), 153.1 (d, $^3J_{PC}$ = 4.1 Hz, 9-C), 148.9 (12-C), 140.4 (7-CH), 129.2 (6-CH), 115.6 (5-CH); for the alkenyl part: 178.6 (br, HC=), 138.6 (d, $^2J_{PC}$ = 15.0 Hz, MeC=), 127.8 (d, $^1J_{PC}$ = 24.1, PC=), 122.4 (d, $^3J_{PC}$ = 11.2 Hz, H_2C=), 24.2 (CH_3C=).

^{11}B{^{1}H} NMR (160 MHz, 299 K, toluene-d_8): δ = -14.6 ($\nu_{1/2}$ ~ 45 Hz).

^{31}P NMR (202 MHz, 299 K, toluene-d_8): δ = 8.6 ($\nu_{1/2}$ ~ 89 Hz).

^{19}F NMR (470 MHz, 188 K, toluene-d_8): δ = -128.8, -129.3, -131.8, -134.1 (each br, each 1F, *o*-C_6F_5), -160.6, -161.9 (each br, each 1F, *p*-C_6F_5), -163.8, -165.0, -165.3, -166.1 (each br, each 1F, *m*-C_6F_5).

Figure S32. ^{1}H NMR (500 MHz, 299 K, toluene-d_8) spectrum of compound **8b**.

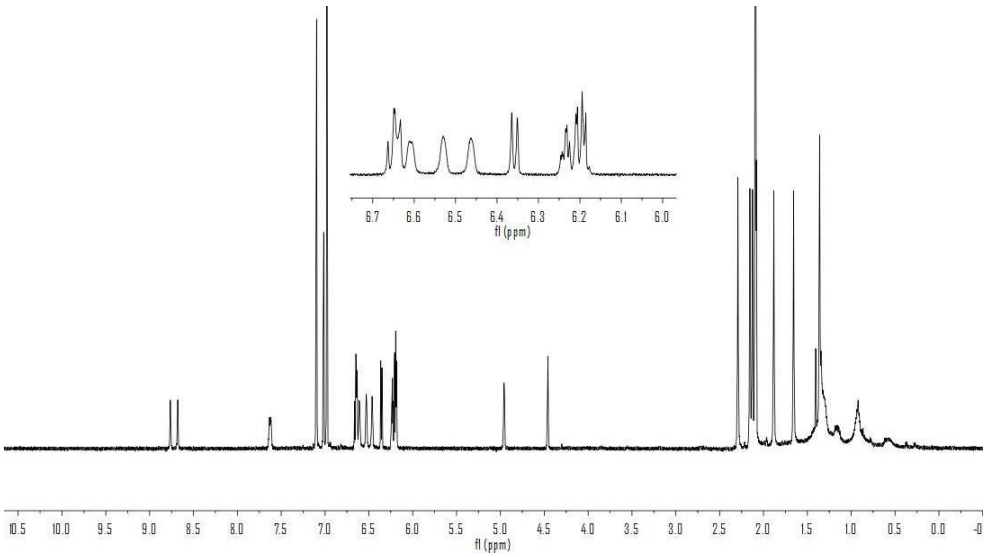


Figure S33. $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, toluene-d_8) spectrum of compound **8b**.

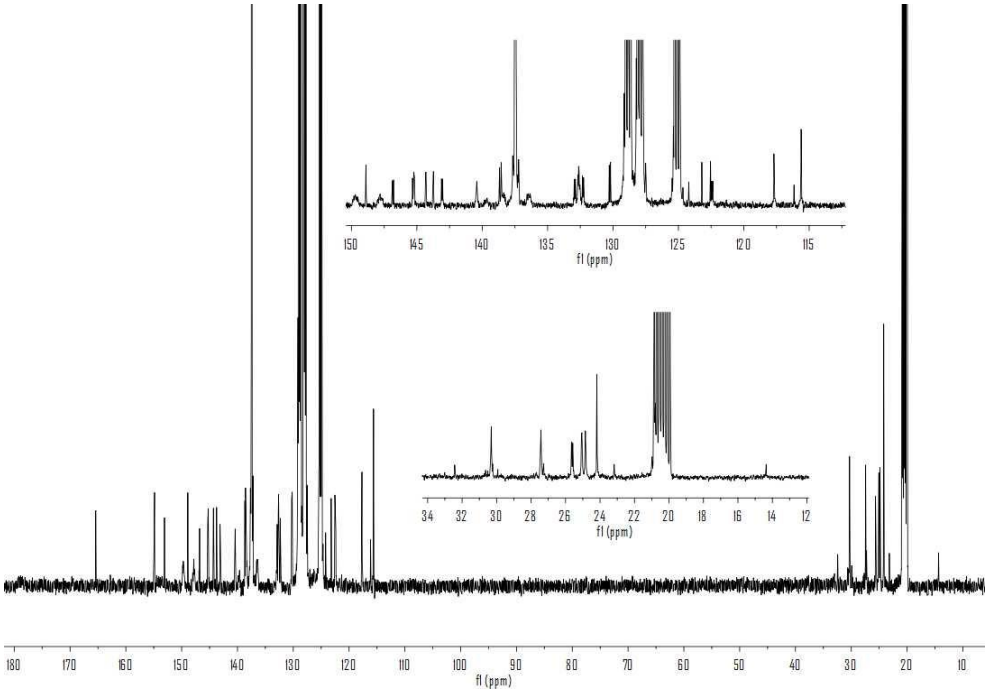


Figure S34. $^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, toluene-d_8) spectrum of compound **8b**.

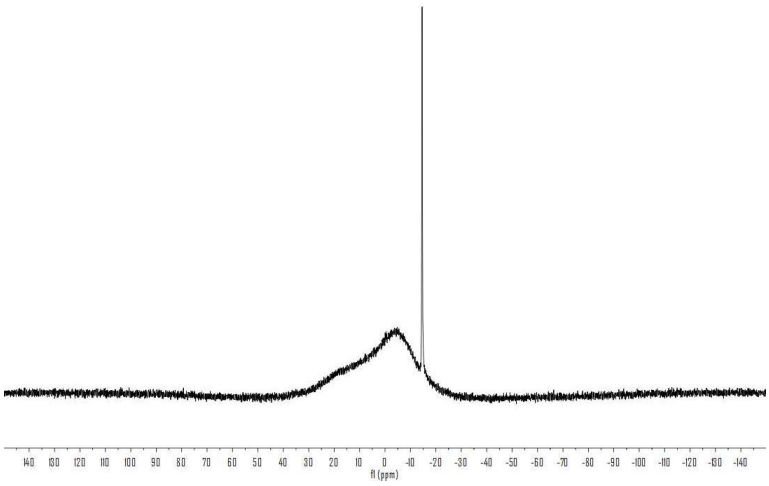


Figure S35. ^{31}P NMR (202 MHz, 299 K, toluene-d_8) spectrum of compound **8b**.

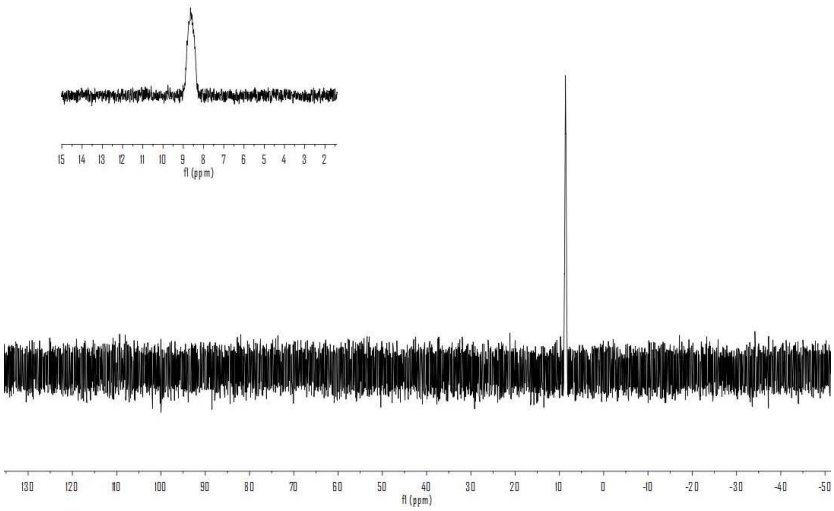
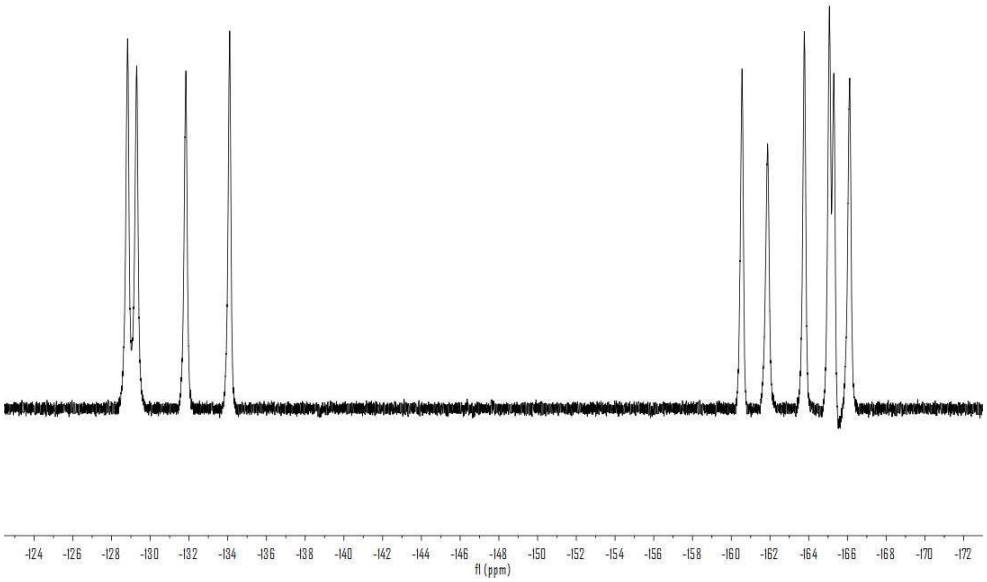


Figure S36. ^{19}F NMR (470 MHz, 188 K, toluene-d_8) spectrum of compound **8b**.



Monitoring the transformation of the CH splitting product 9 to the 1,2-addition product 8b

Figure S37. ^{11}B NMR (C_6D_6) spectra of the thermal rearrangement of compound **9** to compound **8b**.

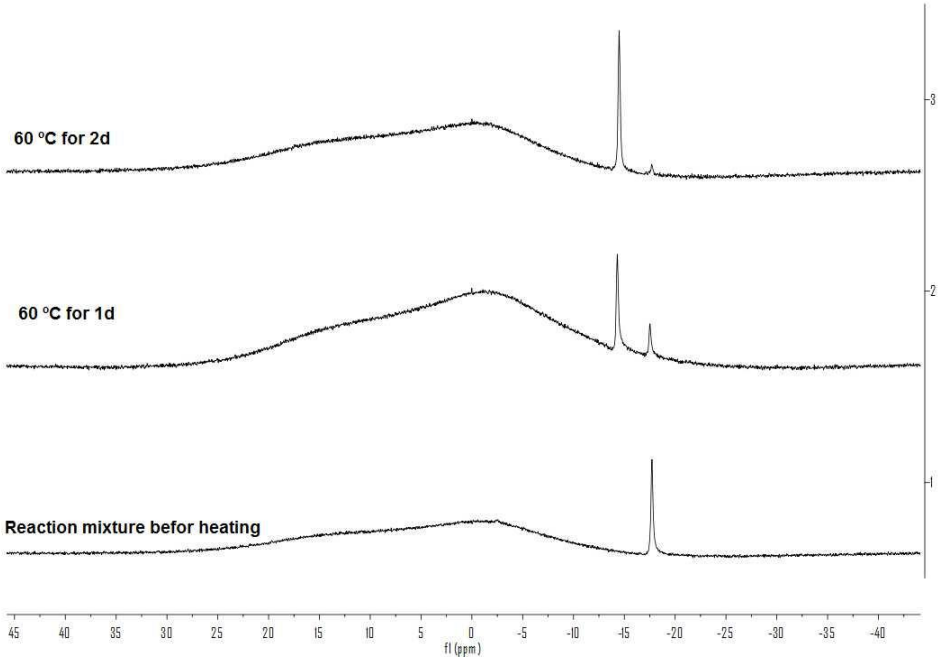
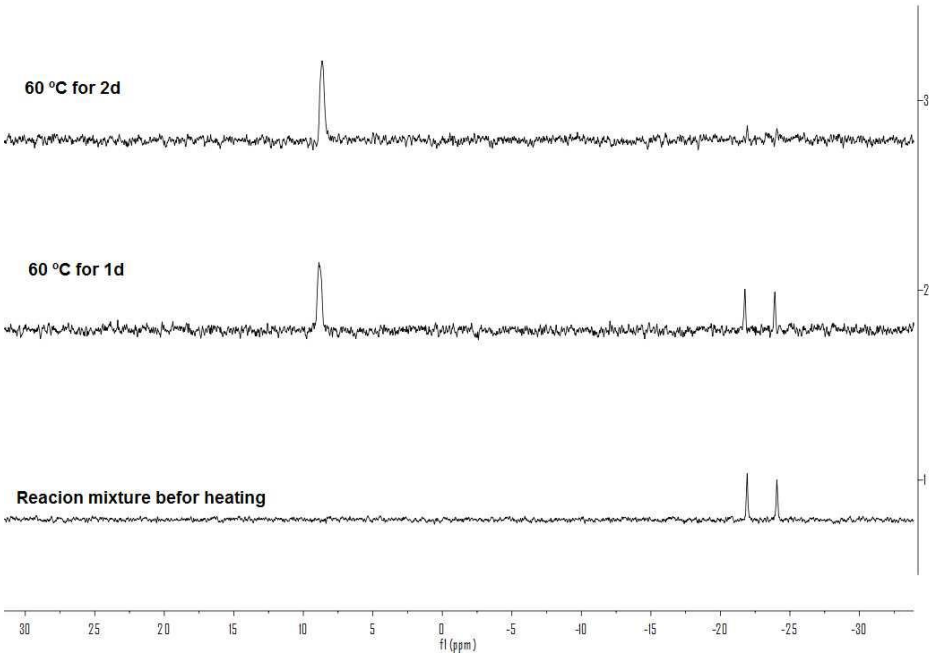
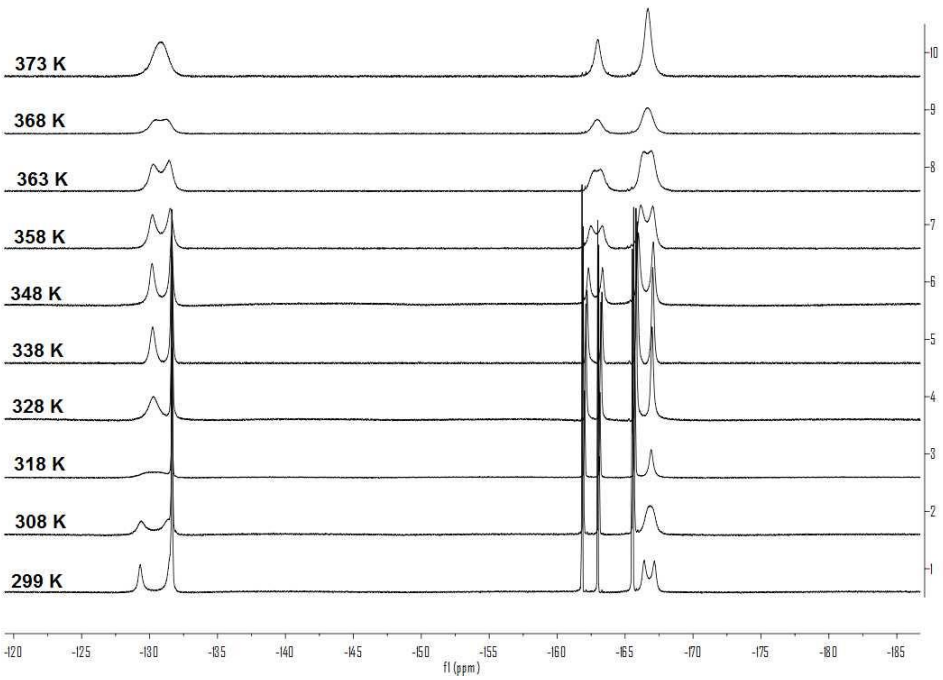


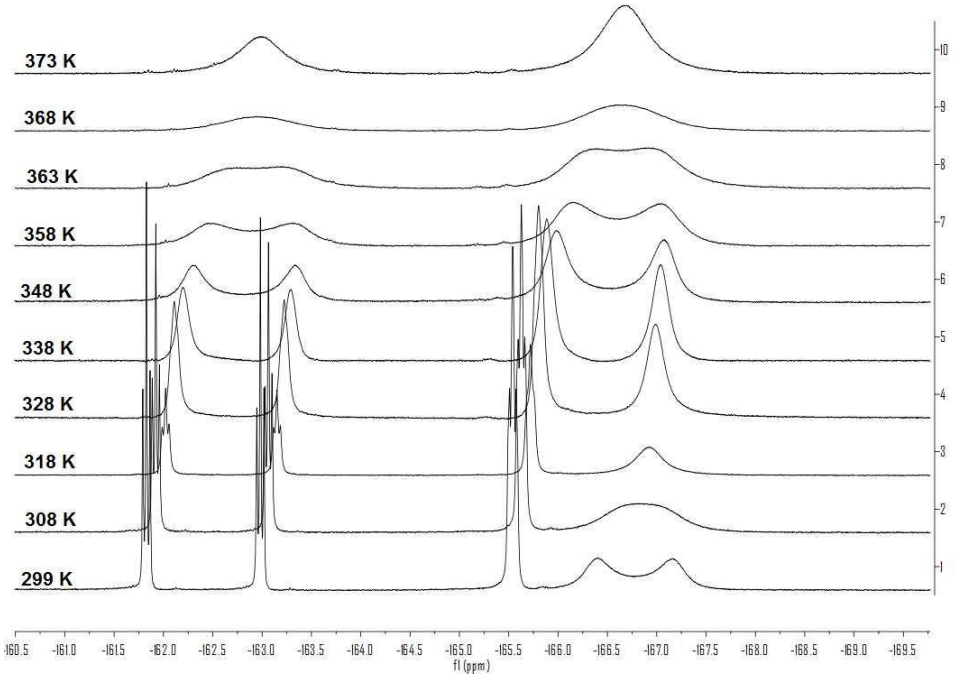
Figure S38. ^{31}P NMR (C_6D_6) spectra of the thermal rearrangement of compound **9** to compound **8b**.



Determining the activation energy of the enantiomerization of compound 8b with dynamic NMR spectroscopy

Figure S39. VT ^{19}F NMR (460 MHz, toluene-d_8) of compound **8b**.

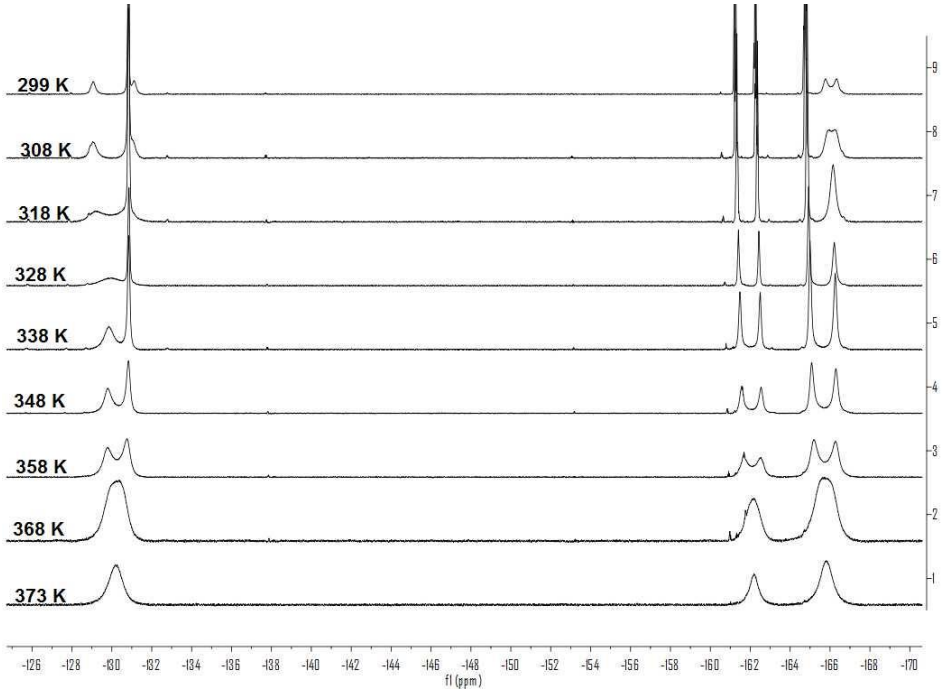


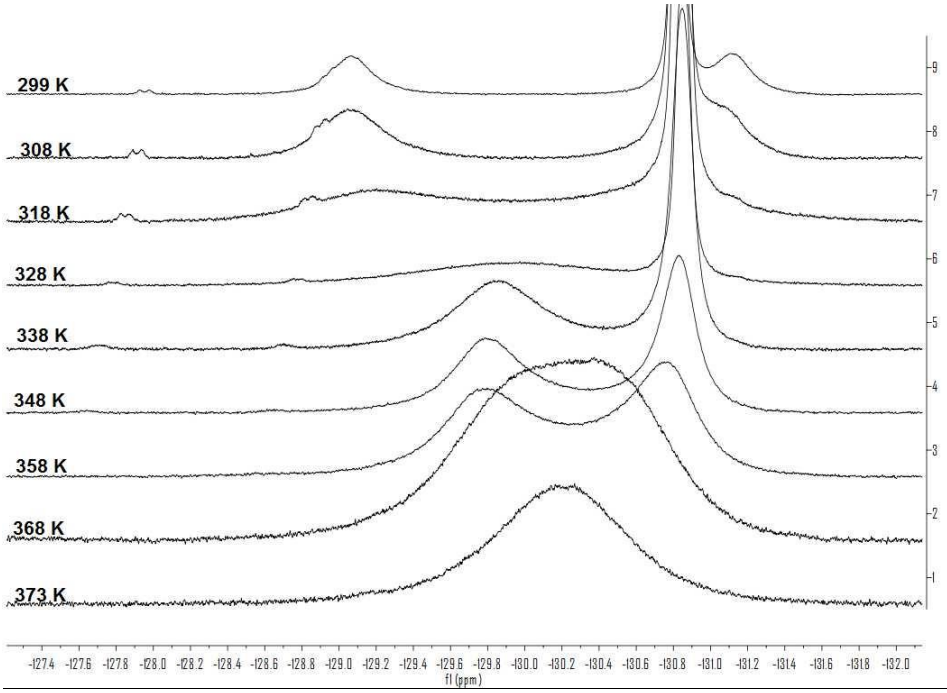


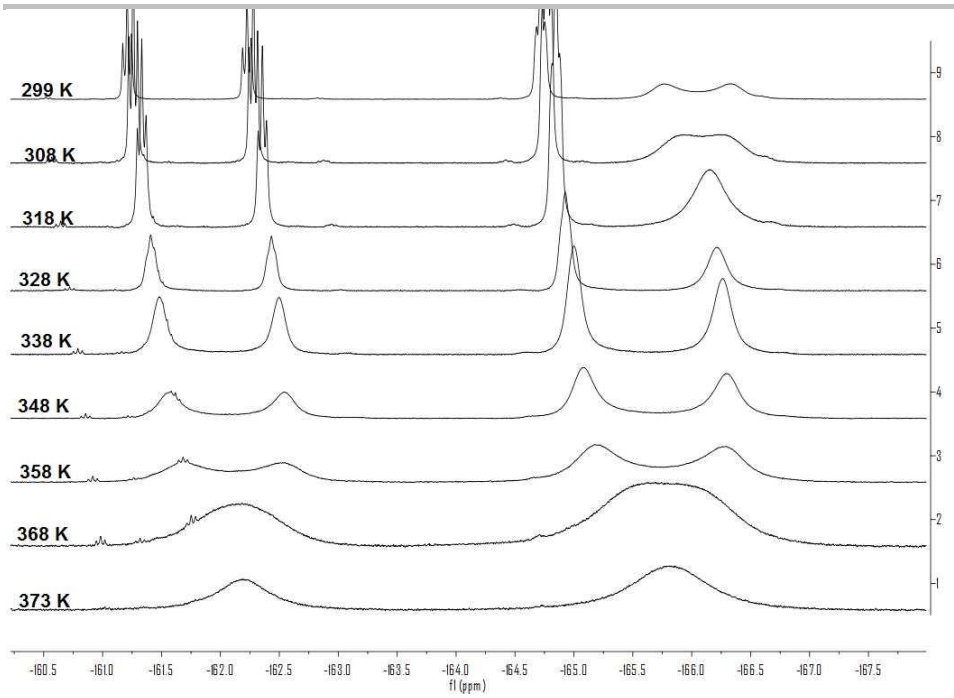
For the enantiomerization process, the activation energy was estimated by the coalescence of the para fluorine signals (δ -161.8, -163.0) of the pentafluorophenyl rings:
$\Delta G^{\neq}$ [T_{coal}, Δν(T)] = $RT_{coal}(22.96 + \ln(T_{coal}/\Delta\nu))$ [J/mol]
Tcoal = coalescence temperature [K]: 363 K (^{19}F, *p*-BC_6F_5)
Δν = chemical shift difference [Hz] (^{19}F, *p*-BC_6F_5, 299 K): 652 Hz
R = 8.314 J/(mol·K); 1 J = 0.239 cal
$\Delta G^{\neq}$ [363 K, Δν(299 K) = 652 Hz] = 67914 J/mol = 16.1 kcal/mol

For the rotation process of one pentafluorophenyl ring, the activation energy was estimated by the coalescence of the meta fluorine signals (δ -166.4, -167.2) of the pentafluorophenyl rings:
$\Delta G^{\neq}$ [T_{coal}, Δν(T)] = $RT_{coal}(22.96 + \ln(T_{coal}/\Delta\nu))$ [J/mol]
Tcoal = coalescence temperature [K]: 308 K (^{19}F, *m*-BC_6F_5)
Δν = chemical shift difference [Hz] (^{19}F, *m*-BC_6F_5, 299 K): 433 Hz
R = 8.314 J/(mol·K); 1 J = 0.239 cal
$\Delta G^{\neq}$ [308 K, Δν(299 K) = 433 Hz] = 57844J/mol = 13.8 kcal/mol.

Figure S40. VT ^{19}F NMR (570 MHz, bromobenzene-d_5) of compound **8b**.







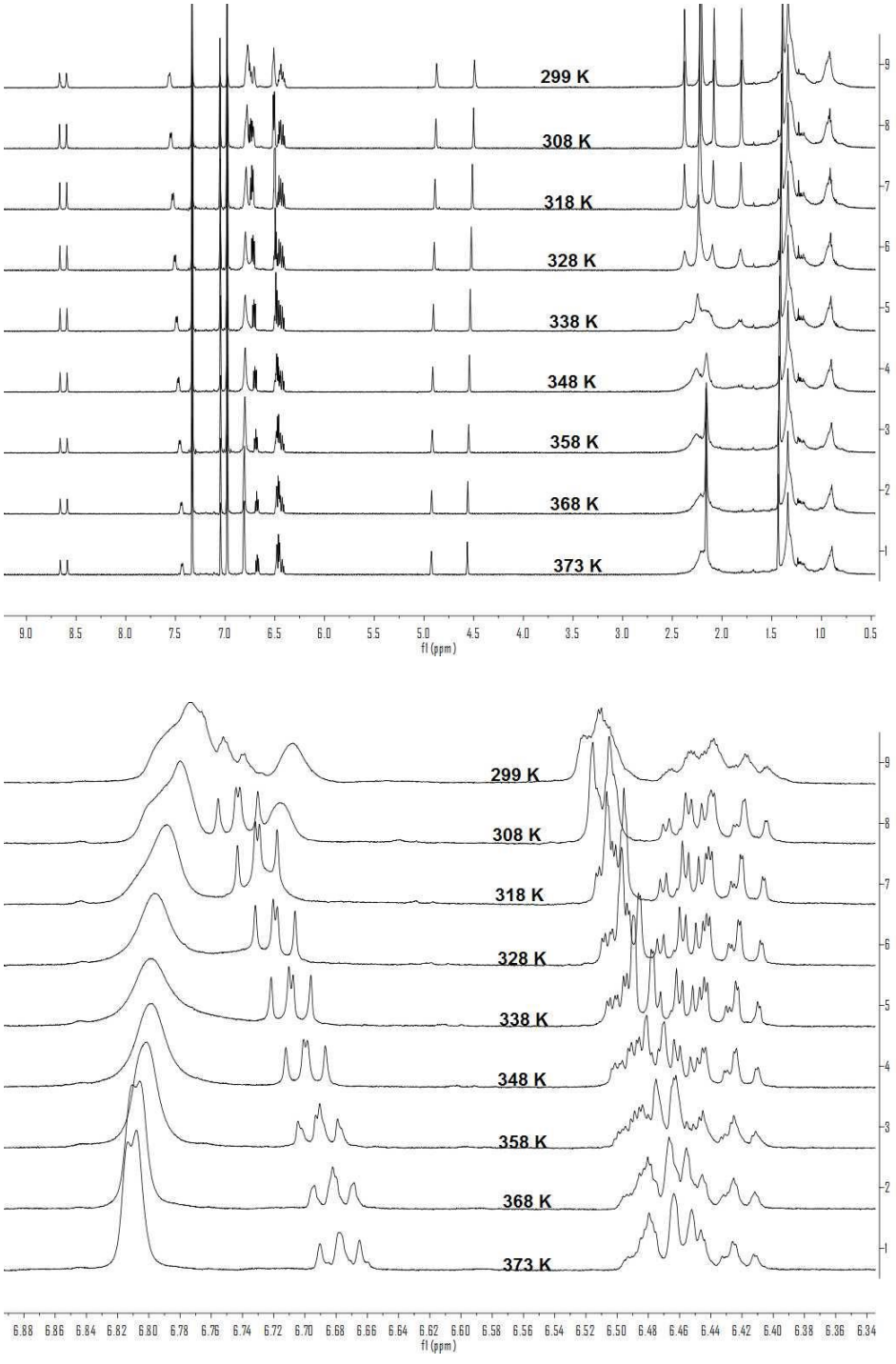
For the enantiomerization process, the activation energy was estimated by the coalescence of the para fluorine signals (δ -161.2, -162.2) of the pentafluorophenyl rings:
$\Delta G^{\neq}$ [T_{coal}, Δν(T)] = $RT_{coal}(22.96 + \ln(T_{coal}/\Delta\nu))$ [J/mol]
Tcoal = coalescence temperature [K]: 368 K (^{19}F, *p*-BC_6F_5)
Δν = chemical shift difference [Hz] (^{19}F, *p*-BC_6F_5, 299 K): 574 Hz
R = 8.314 J/(mol·K); 1 J = 0.239 cal
$\Delta G^{\neq}$ [368 K, Δν(299 K) = 574 Hz] = 68887 J/mol = 16.5 kcal/mol

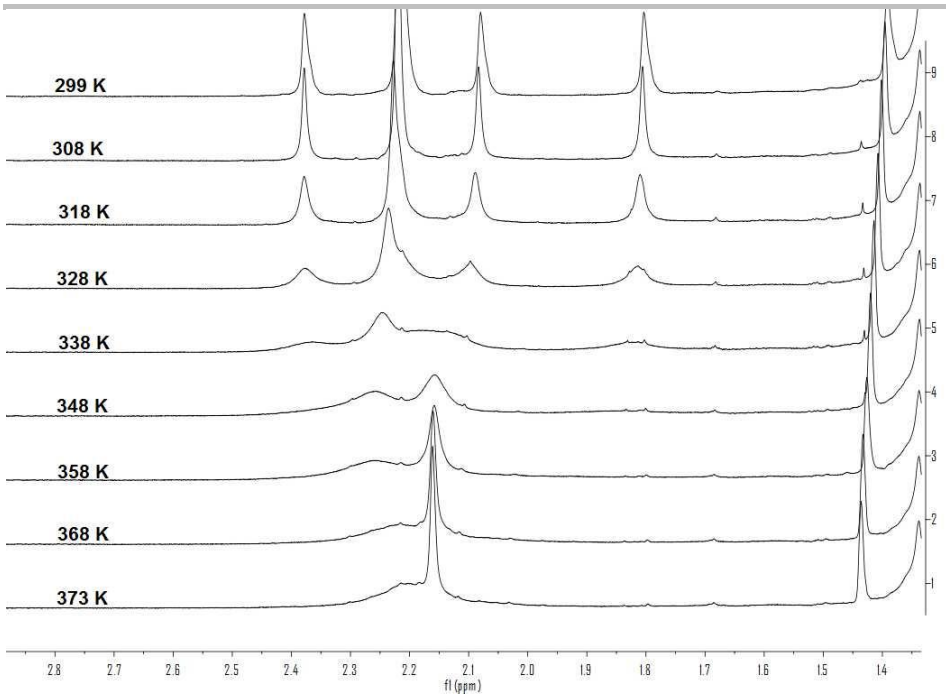
For the enantiomerization process, the activation energy was also estimated by the coalescence of the meta fluorine signals (δ -164.8, -166.1) of the pentafluorophenyl rings:
$\Delta G^{\neq}$ [T_{coal}, Δν(T)] = $RT_{coal}(22.96 + \ln(T_{coal}/\Delta\nu))$ [J/mol]
Tcoal = coalescence temperature [K]: 368 K (^{19}F, *m*-BC_6F_5)
Δν = chemical shift difference [Hz] (^{19}F, *p*-BC_6F_5, 318 K): 740 Hz
R = 8.314 J/(mol·K); 1 J = 0.239 cal
$\Delta G^{\neq}$ [368 K, Δν(318 K) = 740 Hz] = 68110 J/mol = 16.3 kcal/mol

For the rotation process of one pentafluorophenyl ring, the activation energy was estimated by the coalescence of the meta fluorine signal (δ -165.8, -166.3) of the pentafluophenyl rings:
$\Delta G^{\neq}$ [T_{coal}, Δν(T)] = $RT_{coal}(22.96 + \ln(T_{coal}/\Delta\nu))$ [J/mol]
Tcoal = coalescence temperature [K]: 313 K (^{19}F, *m*-BC_6F_5)
Δν = chemical shift difference [Hz] (^{19}F, *m*-BC_6F_5, 299 K): 313 Hz
R = 8.314 J/(mol·K); 1 J = 0.239 cal
$\Delta G^{\neq}$ [308 K, Δν(299 K) = 313 Hz] = 59748 J/mol = 14.3 kcal/mol.

For the rotation process of one pentafluorophenyl ring, the activation energy was also estimated by the coalescence of the ortho fluorine signals (δ -129.0, -131.1) of the pentafluophenyl rings:
$\Delta G^{\neq}$ [T_{coal}, Δν(T)] = $RT_{coal}(22.96 + \ln(T_{coal}/\Delta\nu))$ [J/mol]
Tcoal = coalescence temperature [K]: 328 K (^{19}F, *o*-BC_6F_5)
Δν = chemical shift difference [Hz] (^{19}F, *m*-BC_6F_5, 299 K): 1155 Hz
R = 8.314 J/(mol·K); 1 J = 0.239 cal
$\Delta G^{\neq}$ [328 K, Δν(299 K) = 1155 Hz] = 59178 J/mol = 14.1 kcal/mol.

Figure S41. VT ^{1}H NMR (600 MHz, bromobenzene-d_5) of compound **8b**.



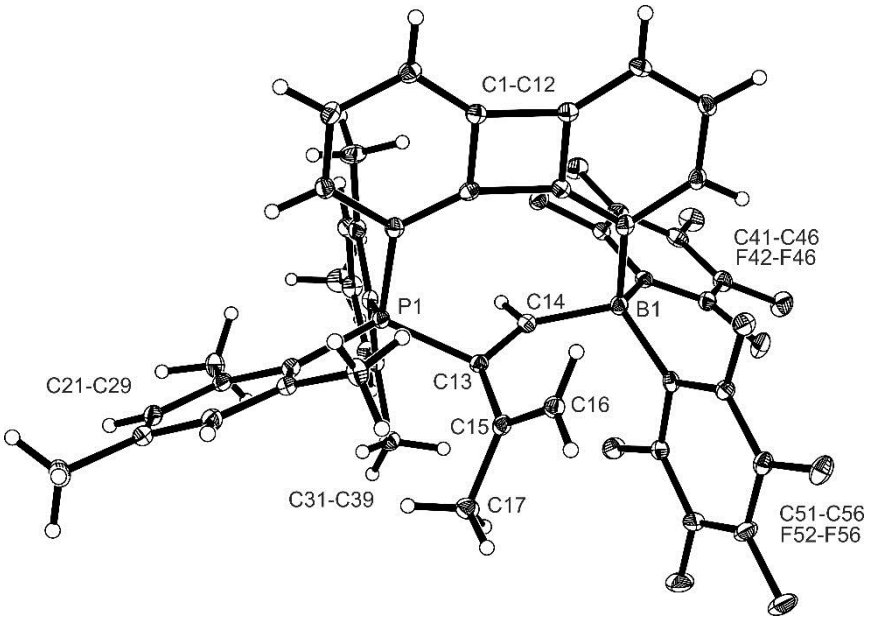


For the enantiomerization process, the activation energy was estimated by the coalescence of the para methyl groups (δ 2.22, 2.07) of the mesityl rings:
$\Delta G^{\neq}$ [T_{coal}, Δν(T)] = $RT_{coal}(22.96 + \ln(T_{coal}/\Delta\nu))$ [J/mol]
Tcoal = coalescence temperature [K]: 338 K (^{1}H, *p*-Mes)
Δν = chemical shift difference [Hz] (^{1}H, *p*-Mes, 299 K): 80.2 Hz
R = 8.314 J/(mol·K); 1 J = 0.239 cal
$\Delta G^{\neq}$ [338 K, Δν(299 K) = 80.2 Hz] = 68563 J/mol = 16.4 kcal/mol

Crystals suitable for the *X*-ray crystal structure analysis were obtained by slow evaporation of the solution of compound **8b** in toluene at room temperature.

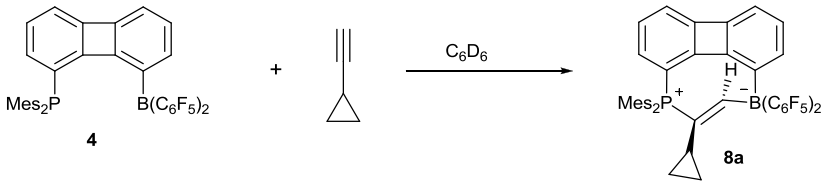
X-ray crystal structure analysis of compound 8b (erk8941): A colorless needle-like specimen of $C_{47}H_{34}BF_{10}P \cdot 2 \times C_7H_8$, approximate dimensions 0.020 mm x 0.080 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1882 frames were collected. The total exposure time was 36.06 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 81755 reflections to a maximum θ angle of 66.71° (0.84 Å resolution), of which 7781 were independent (average redundancy 10.507, completeness = 99.8%, R_{int} = 11.10%, R_{sig} = 4.59%) and 5926 (76.16%) were greater than $2\sigma(F^2)$. The final cell constants of a = 41.3837(18) Å, b = 8.8110(4) Å, c = 24.2497(10) Å, β = 96.346(2)°, volume = 8788.0(7) Å^3, are based upon the refinement of the XYZ-centroids of 8017 reflections above 20 σ(I) with 7.335° < 2θ < 133.0°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.831. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7870 and 0.9750. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *C*2/*c*, with Z = 8 for the formula unit, $C_{47}H_{34}BF_{10}P \cdot 2 \times C_7H_8$. The final anisotropic full-matrix least-squares refinement on F^2 with 617 variables converged at R1 = 4.28%, for the observed data and wR2 = 10.96% for all data. The goodness-of-fit was 1.050. The largest peak in the final difference electron density synthesis was 0.265 e$^-$/Å^3 and the largest hole was -0.384 e$^-$/Å^3 with an RMS deviation of 0.054 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.394 g/cm^3 and F(000), 3804 e$^-$.

Figure S41. Structure of compound **8b**.



Preparation of the 1,2-alkyne addition product 8a

Scheme S11. Preparation of compound **8a**



Ethynylcyclopropane (20 mg, 3.0 mmol) was added to the solution of FLP **4** (115 mg, 0.15 mmol) in C_6D_6 (3 mL). The deep orange solution changed to yellow immediately and a yellow powder precipitates instantaneous. The suspension was stirred for further 12h. Then the volatiles were removed under reduced pressure and the obtained residue was washed with pentane (2 X 3 mL), dried in vacuo to give compound **8a** as a pale yellow powder (90 mg, 72% yield).
Decomposition: 236 °C.
HRMS for $C_{47}H_{34}BF_{10}P$: 830.5417. Found: 853.22337 ($[M + Na]^+$).
^{1}H NMR (500 MHz, 268 K, methylene chloride-d_2): δ = for the mesityl group: 7.05 (m, 2H, *m*-Mes^a, *m*-Mes^b), 6.97 (m, 2H, *m*'-Mes^a, *m*'-Mes^b), 2.36 (s, 3H, *p*-CH_3^{Mesa}), 2.34 (s, 3H, *o*-CH_3^{Mesb}), 2.33 (s, 3H, *p*-CH_3^{Mesb}), 2.29 (s, 3H, *o*-CH_3^{Mesa}), 2.14 (s, 3H, *o*'-CH_3^{Mesa}), 1.92 (s, 3H, *o*'-CH_3^{Mesb});for the P-substituted ring of the biphenylene backbone: 6.66 (m, 3H, 3-CH, 4-CH, overlapping with 6-CH), 6.46 (dd, *J* = 12.4, 8.3 Hz, 1H, 2-CH); for the B-substituted ring of the biphenylene backbone: 7.10 (d, $^3J_{HH}$ = 8.4 Hz, 1H, 7-CH), 6.66 (m, 3H, 6-CH, overlapping with 3-CH, 4-CH), 6.54 (d, $^3J_{HH}$ = 6.7 Hz, 1H, 5-CH); for the alkenyl part: 8.34 (d, $^3J_{PH}$ = 37.9 Hz, 1H, =CH), 1.35 (m, 1H, CH), 0.20 (m, 2H, CH_2^a, CH_2^b), 0.11 (m, 1H, CH_2^a), -0.34 (m, 1H, CH_2^b).
^{13}C{^{1}H} NMR (126 MHz, 268 K, methylene chloride-d_2) [C_6F_5 not listed]: δ = for the mesityl group: 145.9 (d, $^2J_{PC}$ = 10.0 Hz, *o*-Mes^b), 145.1 (d, $^2J_{PC}$ = 7.2 Hz, *o*-Mes^a), 144.38 (d, $^2J_{PC}$ = 11.1 Hz, *o*'-Mes^b), 144.36 (*p*-Mes^b), 144.28 (d, $^4J_{PC}$ = 2.8 Hz, *p*-Mes^a), 142.4 (d, $^2J_{PC}$ = 11.1 Hz, *o*'-Mes^a), 132.6 (d, $^3J_{PC}$ = 5.8 Hz, *m*'-Mes^b), 132.5 (d, $^3J_{PC}$ = 5.0 Hz, *m*-Mes^a), 132.4 (d, $^3J_{PC}$ = 11.2 Hz, *m*'-Mes^a), 131.9 (d, $^3J_{PC}$ = 10.1 Hz, *m*-Mes^b), 123.8 (d, $^1J_{PC}$ = 78.8 Hz, *i*-Mes^a), 115.01 (d, $^1J_{PC}$ = 69.0 Hz, *i*-Mes^b), 26.0 (d, $^3J_{PC}$ = 5.3 Hz, *o*-CH_3^{Mesb}), 25.4 (d, $^3J_{PC}$ = 3.8 Hz, *o*-CH_3^{Mesa}), 24.3 (d, $^3J_{PC}$ = 3.5 Hz, *o*'-CH_3^{Mesb}), 23.8 (d, $^3J_{PC}$ = 10.1 Hz, *o*'-CH_3^{Mesa}), 21.1 (d, $^5J_{PC}$ = 1.5 Hz, *p*-CH_3^{Mesb}), 20.9 (d, $^5J_{PC}$ = 1.6 Hz, *p*-CH_3^{Mesa}); for the P-substituted ring of the biphenylene backbone: 163.1 (d, $^2J_{PC}$ = 4.9 Hz, 10-C), 153.4 (d, $^3J_{PC}$ = 12.6 Hz, 11-C), 131.0 (d, $^2J_{PC}$ = 12.7 Hz, 2-CH), 128.3 (d, $^3J_{PC}$ = 10.5 Hz, 3-CH), 124.5 (d, $^1J_{PC}$ = 79.4 Hz, 1-C), 118.2 (d, $^4J_{PC}$ = 2.9 Hz, 4-CH); for the B-substituted ring of the biphenylene backbone: 152.7 (br, 8-C), 151.6 (d, $^3J_{PC}$ = 4.0 Hz, 9-C), 149.3 (12-C), 137.3 (d, *J* = 9.0 Hz, 7-CH), 128.7 (6-CH), 115.05 (5-CH); for the alkenyl part: 181.7 (br, HC=), 126.2 (d, $^1J_{PC}$ = 70.4 Hz, C=), 13.5 (d, $^2J_{PC}$ = 18.8 Hz, CH), 8.31 (d, $^3J_{PC}$ = 5.9 Hz, CH_2^b), 5.81 (CH_2^a).
^{11}B{^{1}H} NMR (160 MHz, 268 K, methylene chloride-d_2): δ = -14.6 ($\nu_{1/2}$ ~ 64 Hz).

$^{31}P\{^{1}H\}$ NMR (202 MHz, 268 K, methylene chloride-d_2): δ = 6.5 ($\nu_{1/2}$ ~ 48 Hz).
^{19}F NMR (470 MHz, 208 K, methylene chloride-d_2): δ = -128.0, -129.8, -130.2, -133.1 (each m, each 1F， *o*-C_6F_5), 162.9 (t, $^{3}J_{FF}$ = 20.5 Hz, 2F, *p*-C_6F_5), -165.4, -166.0, -166.2, -167.2 (each m, each 1F， *m*-C_6F_5) [$\Delta\delta^{19}F$*m,p* = 4.3, 3.3, 3.1, 2.5].

Figure S42. ^{1}H NMR (500 MHz, 268 K, methylene chloride-d_2) spectrum of compound **8a**.

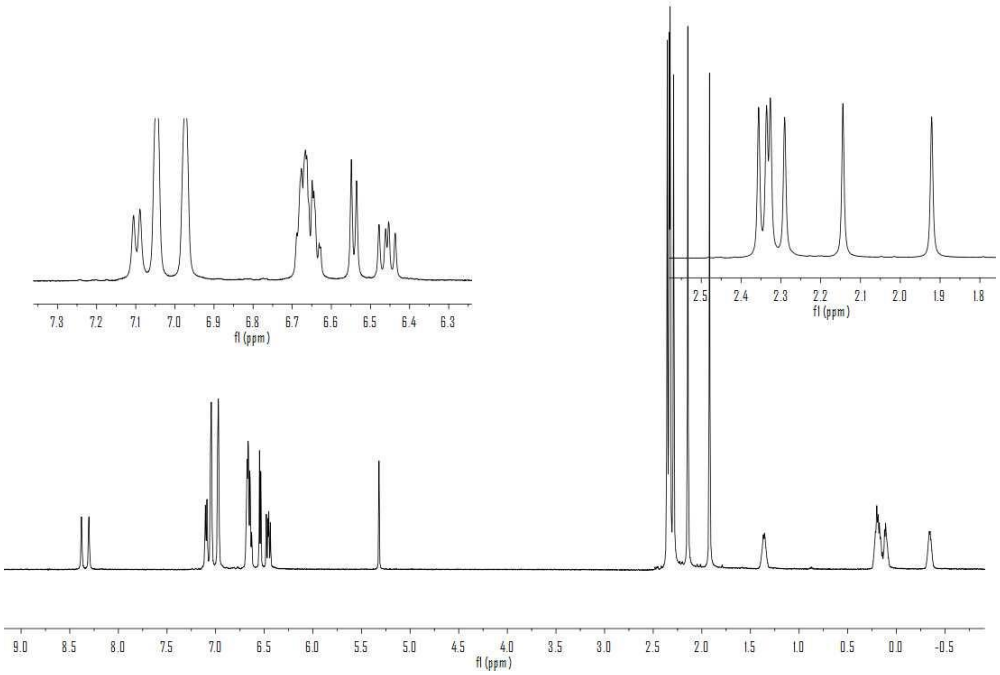


Figure S43. $^{13}C\{^{1}H\}$ NMR (126 MHz, 268 K, methylene chloride-d_2) spectrum of compound **8a**.

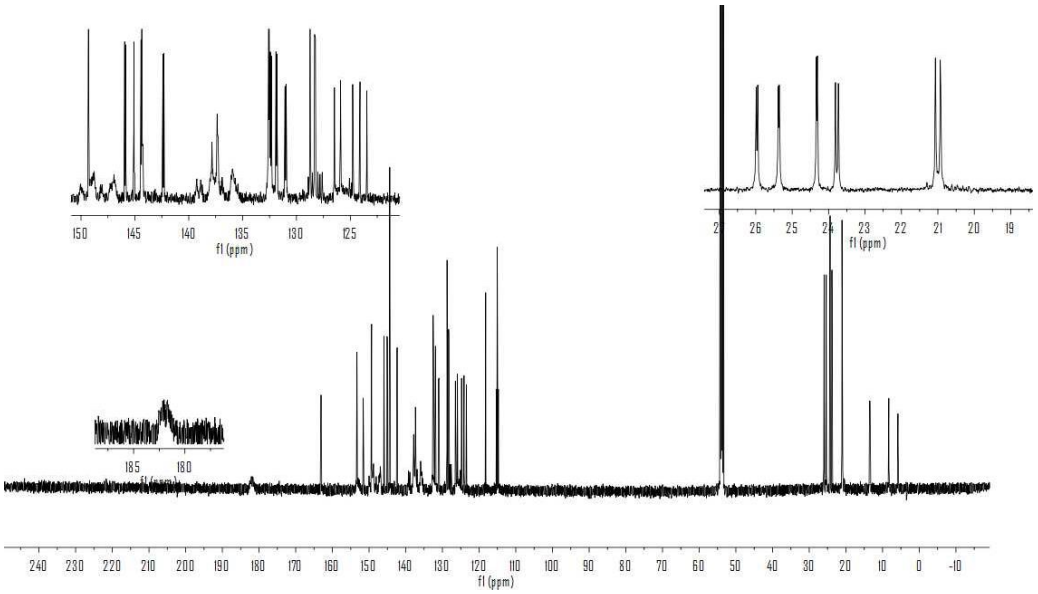


Figure S44. $^{11}B\{^{1}H\}$ NMR (160 MHz, 268 K, methylene chloride-d_2) spectrum of compound **8a**.

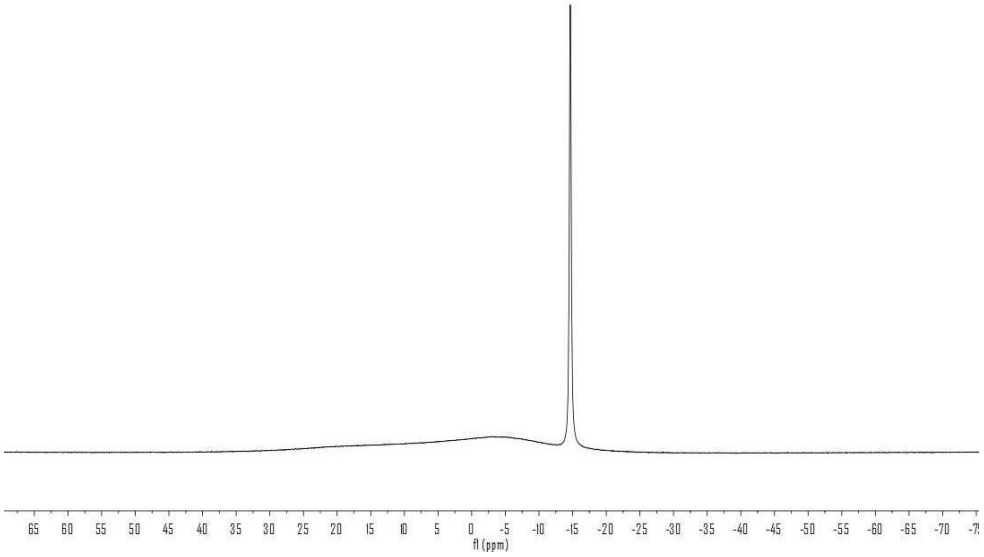


Figure S45. $^{31}P\{^{1}H\}$ NMR (202 MHz, 268 K, methylene chloride-d_2) spectrum of compound **8a**.

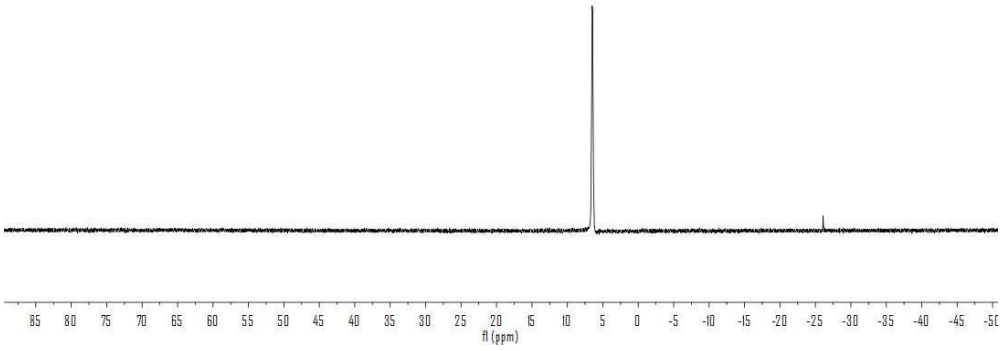
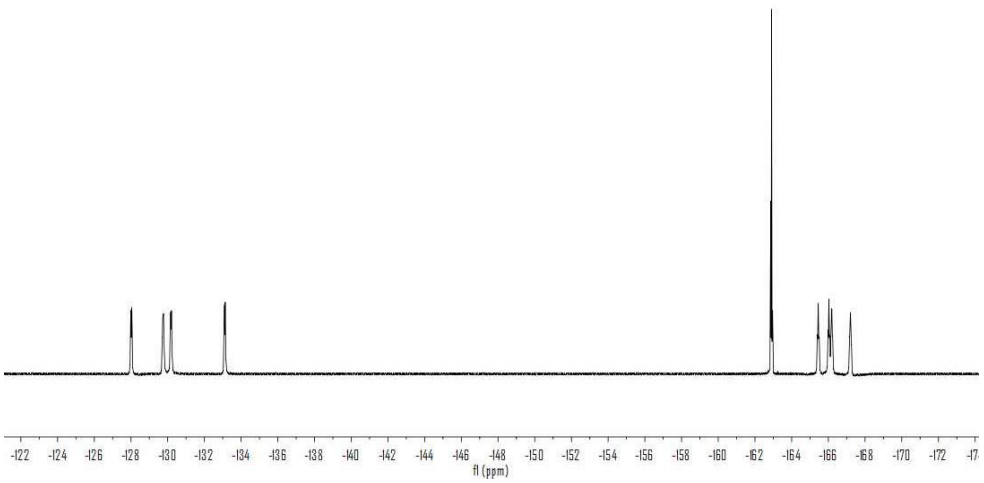
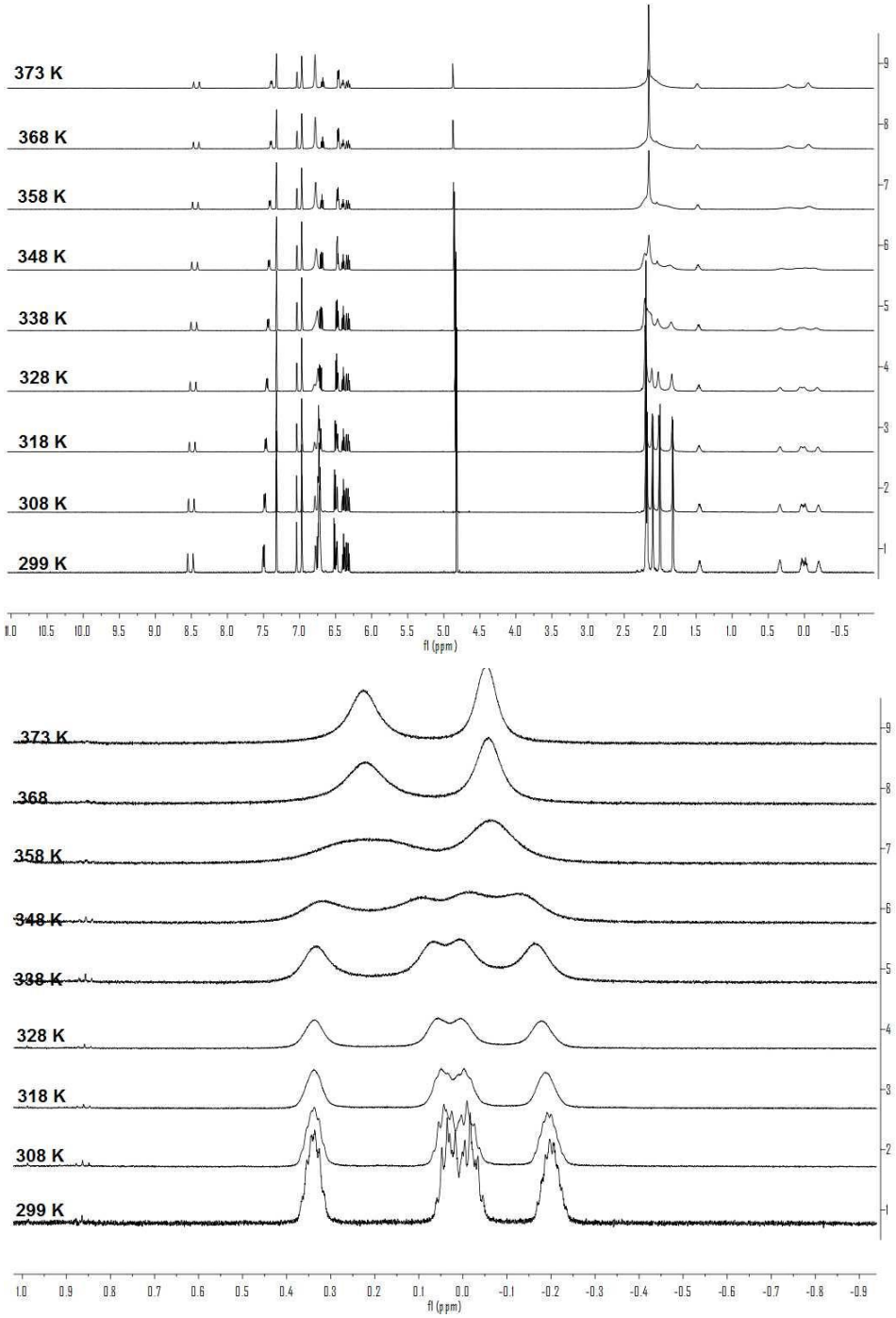


Figure S46. ^{19}F NMR (470 MHz, 268 K, methylene chloride-d_2)) spectrum of compound **8a**.



Determining the activation energy of the enantiomerization reaction of compound 8a by dynamic NMR spectroscopy

Figure S48. VT ^{1}H NMR (500 MHz, bromobenzene-d_5) of compound **8a**.



For the enantiomerization process, the activation energy was estimated by the coalescence of the CH_2 ^{1}H NMR signals (A: δ 0.34, 0.01, B: δ -0.02, -0.20) of the cyclopropyl ring:

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

Tcoal = coalescence temperature [K]: 358 K (CH_2, cyclopropyl ring)

Δν = chemical shift difference [Hz] (CH_2, cyclopropyl ring 299 K): 155 Hz

R = 8.314 J/(mol·K); 1 J = 0.239 cal

$\Delta G^{\neq}$ [358 K, Δν(299 K) = 155 Hz] = 70829 J/mol = 16.9 kcal/mol

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

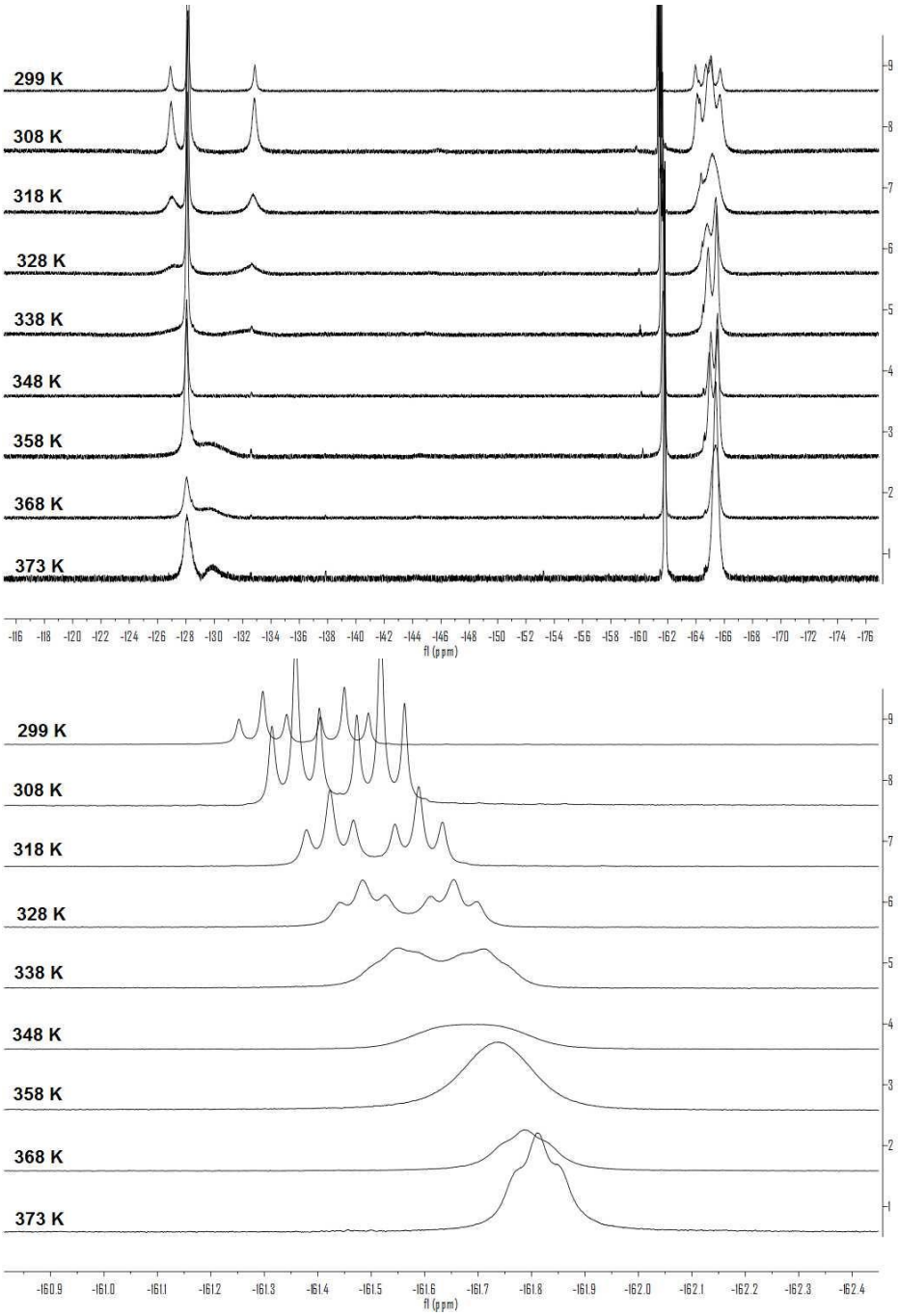
Tcoal = coalescence temperature [K]: 353 K (CH_2, cyclopropyl ring)

Δν = chemical shift difference [Hz] (CH_2, cyclopropyl ring 299 K): 89.5 Hz

R = 8.314 J/(mol·K); 1 J = 0.239 cal

$\Delta G^{\neq}$ [353 K, Δν(299 K) = 89.5 Hz] = 71411 J/mol = 17.1 kcal/mol

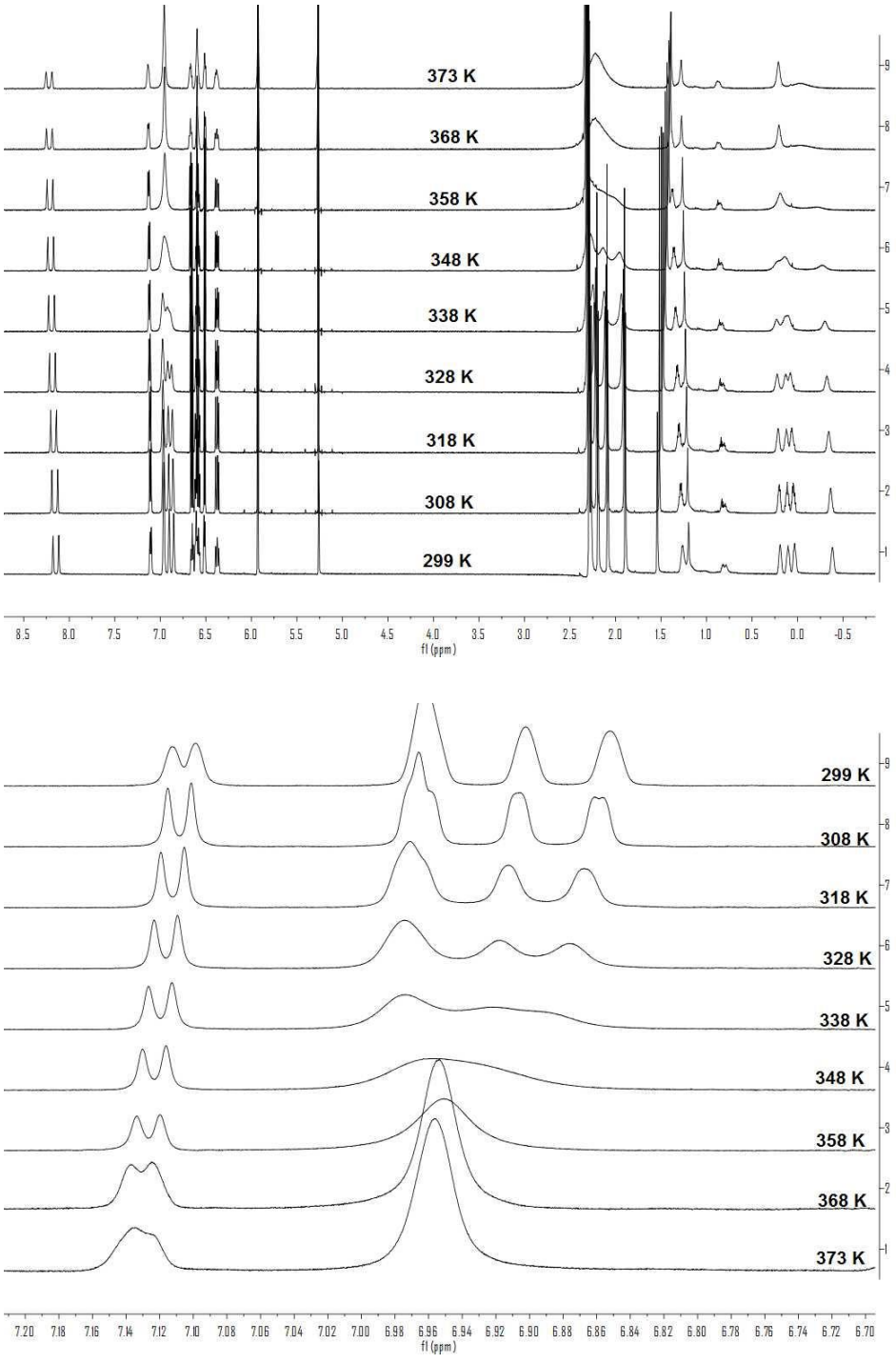
Figure S50. VT ^{19}F NMR (470 MHz, bromobenzene-d_5) of compound **8a**.

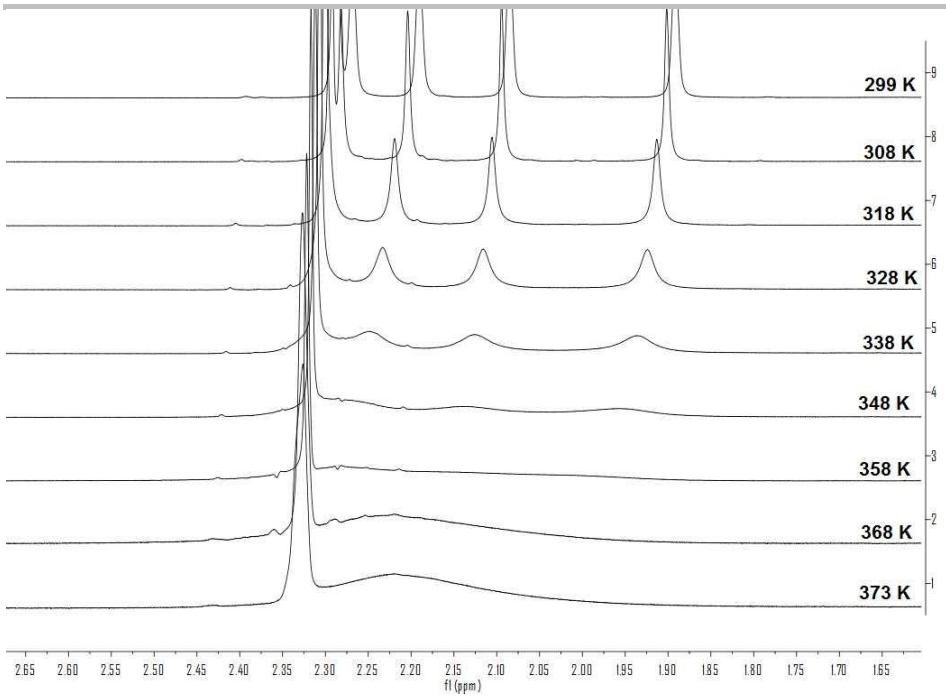


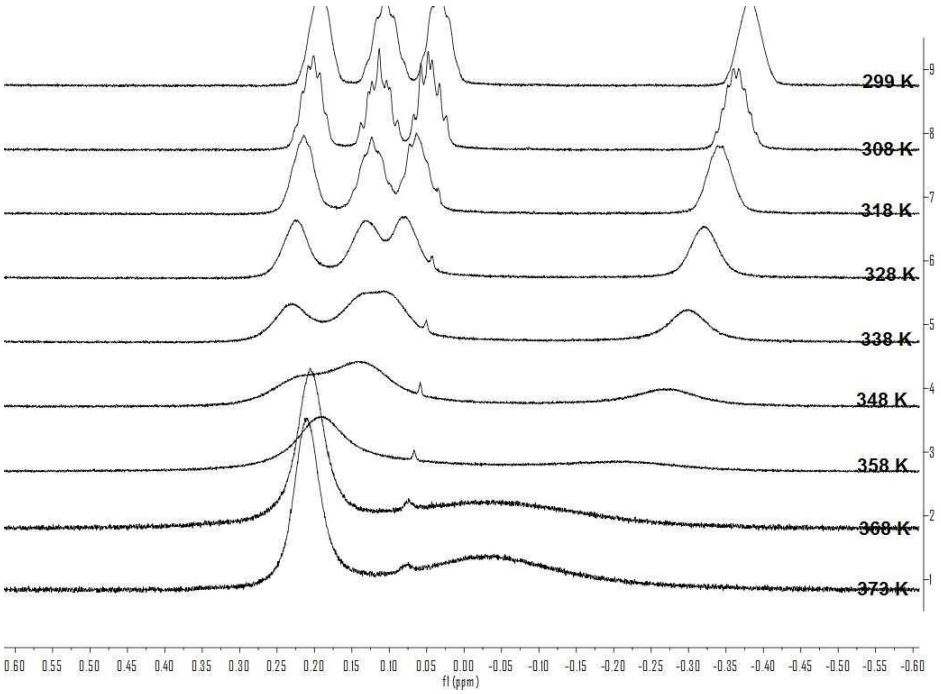
For the enantiomerization process, the activation energy was estimated by the coalescence of the para fluorines signals (δ: -161.30, -161.45) of the pentafluorophenyl rings:
$\Delta G^{\neq}$ [T_{coal}, $\Delta\nu(T)$] = $RT_{coal}(22.96 + \ln(T_{coal}/\Delta\nu))$ [J/mol]
Tcoal = coalescence temperature [K]: 348 K (^{19}F, *p*-BC_6F_5)
$\Delta\nu$ = chemical shift difference [Hz] (^{19}F, *p*-BC_6F_5 299 K): 71.9 Hz
R = 8.314 J/(mol·K); 1 J = 0.239 cal
$\Delta G^{\neq}$ [348 K, $\Delta\nu$(299 K) = 71.9 Hz] = 70992 J/mol = 17.0 kcal/mol

For the rotation process of one perfluorophenyl ring, the activation energy was estimated by the coalescence of the ortho fluorine signals (δ: -126.9, -132.9) of the pentafluorophenyl rings:
$\Delta G^{\neq}$ [T_{coal}, $\Delta\nu(T)$] = $RT_{coal}(22.96 + \ln(T_{coal}/\Delta\nu))$ [J/mol]
Tcoal = coalescence temperature [K]: 348 K (^{19}F, *o*-BC_6F_5)
$\Delta\nu$ = chemical shift difference [Hz] (^{19}F, *o*-BC_6F_5 K): 2753 Hz
R = 8.314 J/(mol·K); 1 J = 0.239 cal
$\Delta G^{\neq}$ [348 K, $\Delta\nu$(299 K) = 2753 Hz] = 60445 J/mol = 14.4 kcal/mol

Figure S51. VT ^{1}H NMR (600 MHz, tetrachloroethane-d_2) of compound **8a**.







For the enantiomerization process, the activation energy was estimated by the coalescence of the CH_2 ^1H NMR signals (A: δ 0.19, 0.04, B: δ 0.10, -0.38) of the cyclopropyl ring:

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

Tcoal = coalescence temperature [K]: 353 K (CH_2, cyclopropyl ring)

Δν = chemical shift difference [Hz] (CH_2, cyclopropyl ring 299 K): 96.0 Hz

R = 8.314 J/(mol·K); 1 J = 0.239 cal

$\Delta G^{\neq}$ [353 K, Δν(299 K) = 96.0 Hz] = 71250 J/mol = 17.0 kcal/mol

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

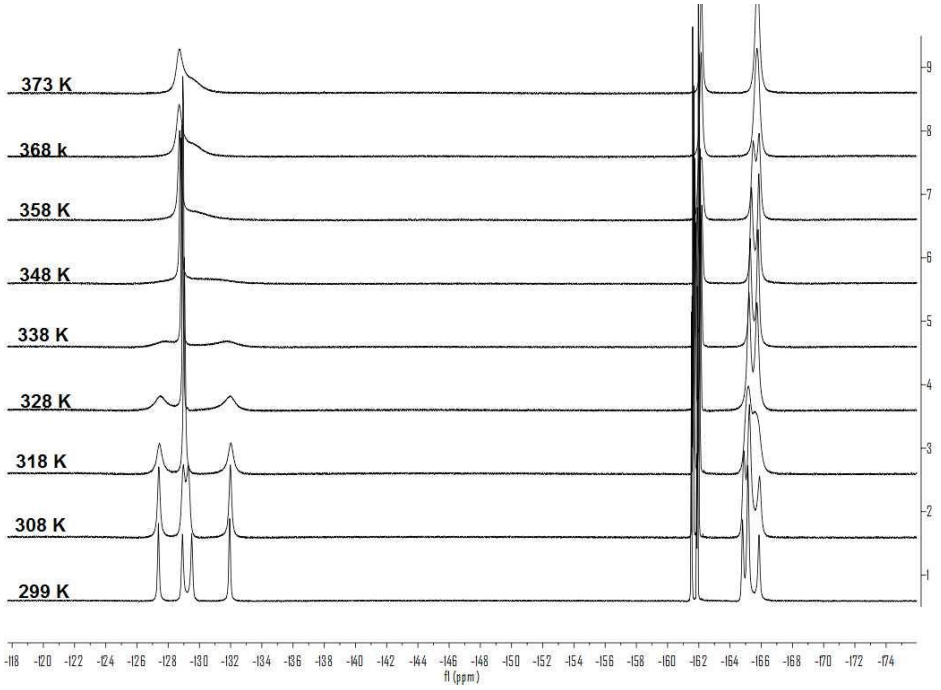
Tcoal = coalescence temperature [K]: 368 K (CH_2, cyclopropyl ring)

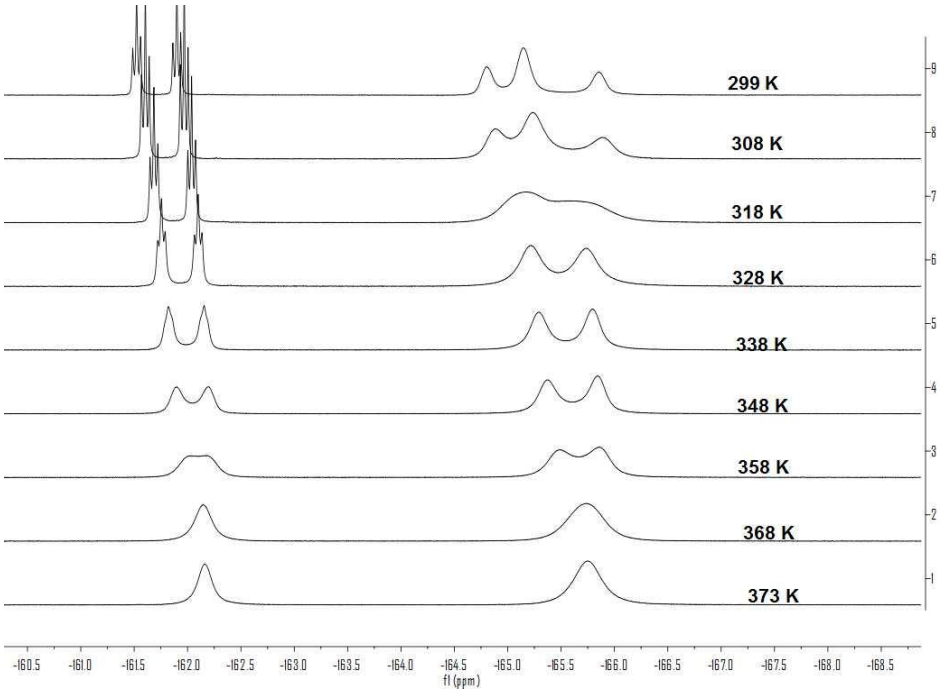
Δν = chemical shift difference [Hz] (CH_2, cyclopropyl ring 299 K): 292 Hz

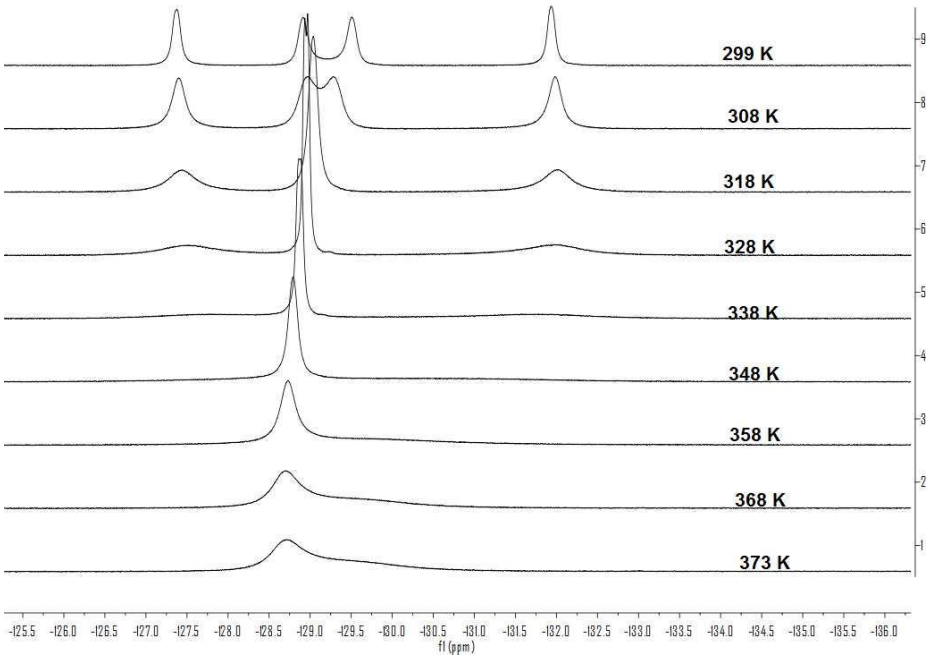
R = 8.314 J/(mol·K); 1 J = 0.239 cal

$\Delta G^{\neq}$ [368 K, Δν(299 K) = 292 Hz] = 70955 J/mol = 17.0 kcal/mol

Figure S52. VT ^{19}F NMR (560 MHz,tetrachloroethane-d_2) of compound **8a**.







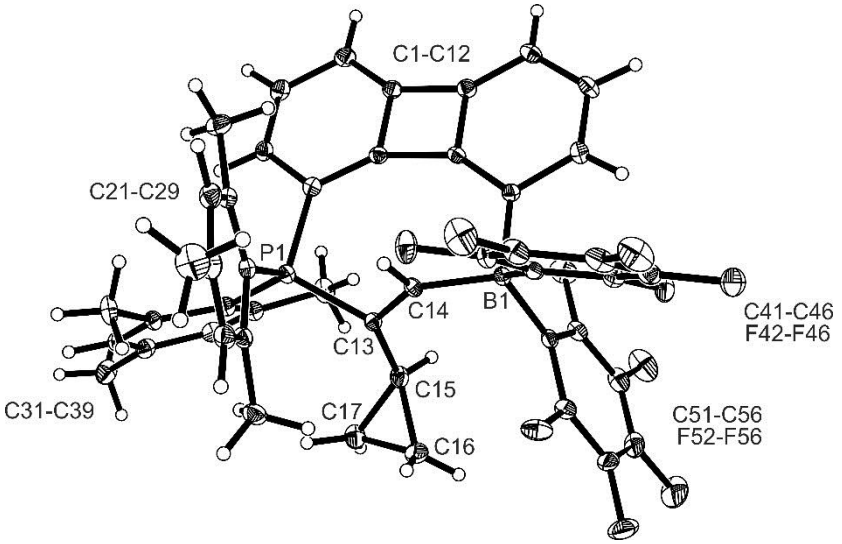
For the enantiomerization process, the activation energy was estimated by the coalescence of the para fluorine signals (δ: -161.5, -161.9) of the pentafluorophenyl rings:
$\Delta G^{\neq}$ [T_{coal}, Δν(T)] = RT_{coal}(22.96 + ln(T_{coal}/Δν)) [J/mol]
Tcoal = coalescence temperature [K]: 363 K (^{19}F, *p*-BC_6F_5)
Δν = chemical shift difference [Hz] (^{19}F, *p*-BC_6F_5 299 K): 213 Hz
R = 8.314 J/(mol·K); 1 J = 0.239 cal
$\Delta G^{\neq}$ [363 K, Δν(299 K) = 213 Hz] = 70901 J/mol = 16.9 kcal/mol

For the rotation process of one perfluorophenyl ring, the activation energy was estimated by the coalescence of the ortho fluorine signals (δ: -127.4, -131.9) of the pentafluorophenyl rings:
$\Delta G^{\neq}$ [T_{coal}, Δν(T)] = RT_{coal}(22.96 + ln(T_{coal}/Δν)) [J/mol]
Tcoal = coalescence temperature [K]: 348 K (^{19}F, *o*-BC_6F_5)
Δν = chemical shift difference [Hz] (^{19}F, *o*-BC_6F_5 K): 2572 Hz
R = 8.314 J/(mol·K); 1 J = 0.239 cal
$\Delta G^{\neq}$ [348 K, Δν(299 K) = 2572 Hz] = 60642 J/mol = 14.5 kcal/mol

For the rotation process of the other perfluorophenyl ring, the activation energy was estimated by the coalescence of the ortho fluorine signals (δ: -128.9, -129.5) of the pentafluorophenyl rings:
$\Delta G^{\neq}$ [T_{coal}, Δν(T)] = RT_{coal}(22.96 + ln(T_{coal}/Δν)) [J/mol]
Tcoal = coalescence temperature [K]: 313 K (^{19}F, *o*-BC_6F_5)
Δν = chemical shift difference [Hz] (^{19}F, *o*-BC_6F_5 K): 323 Hz
R = 8.314 J/(mol·K); 1 J = 0.239 cal
$\Delta G^{\neq}$ [313 K, Δν(299 K) = 323 Hz] = 59666 J/mol = 14.3 kcal/mol

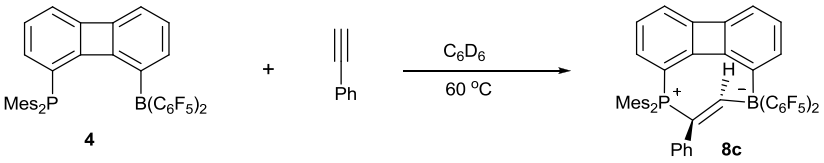
Crystals suitable for the *X*-ray crystal structure analysis were obtained from reaction solution directly.
X-ray crystal structure analysis of compound 8a (erk8366): formula $C_{47}H_{34}BF_{10}P \cdot 2 \times C_6H_6$, *M* = 499.40, pale yellow crystal, 0.12 x 0.06 x 0.02 mm, *a* = 22.7843(3), *b* = 8.4334(2), *c* = 27.6135(5) Å, *β* = 113.888(1)°, *V* = 4851.4(2) Å^3, ρ_{calc} = 1.351 gcm^{-3}, μ = 0.135 mm^{-1}, empirical absorption correction (0.984 ≤ T ≤ 0.997), *Z* = 4, monoclinic, space group *P*2/*c* (No. 13), λ = 0.71073 Å, *T* = 223(2) K, ω and ϕ scans, 39200 reflections collected (±*h*, ±*k*, ±*l*), 8435 independent (R_{int} = 0.097) and 5171 observed reflections [*I*>2σ(*I*)], 703 refined parameters, *R* = 0.082, wR^2 = 0.158, max. (min.) residual electron density 0.29 (-0.24) e.Å^{-3}, the hydrogen atoms were calculated and refined as riding atoms.

Figure S53. Structure of compound **8a**.



Preparation of the 1,2-alkyne addition product 8c

Scheme S12. Preparation of compound **8c**.



Ethynylbenzene (31 mg, 3.0 mmol) was added to the solution of FLP **4** (115 mg, 0.15 mmol) in C_6D_6 (3 mL). The deep orange solution changed to yellow immediately and the mixture was stirred for further 48 h at 60 °C. Then the volatiles were removed under reduced pressure and the obtained residue was washed with pentane (2 x 3 mL), dried in vacuo to give compound **8c** as a pale yellow powder (65 mg, 50% yield).

Melting point: 247 °C (with decomposition).

HRMS for $C_{50}H_{34}BF_{10}P$: 866.5738. Found: 889.22312([M+Na]$^+$).

^{1}H NMR (600 MHz, 258 K, methylene chloride-d_2): δ = for the mesityl group: 7.13 (d, $^4J_{PH}$ = 4.5 Hz, 1H, *m*-Mes^a), 7.04 (d, $^4J_{PH}$ = 4.4 Hz, 1H, *m*'-Mes^a), 6.92 (m, 1H, *m*-Mes^b), 6.60 (m, 2H, *m*'-Mes^b, overlapping with 5-CH), 2.64 (s, 3H, *o*-CH_3^{Mesa}), 2.38 (s, 3H, *p*-CH_3^{Mesa}), 2.31 (s, 3H, *o*'-CH_3^{Mesa}), 2.22 (s, 3H, *p*-CH_3^{Mesb}), 1.89 (s, 3H, *o*-CH_3^{Mesb}), 1.08 (s, 3H, *o*'-CH_3^{Mesb}); for the P-substituted ring of the biphenylene backbone: 6.70 (m, 2H, 4-CH, overlapping with 6-CH), 6.66 (m 1H, 3-CH), 6.46 (dd, *J* = 12.6, 8.5 Hz, 1H, 2-CH); for the B-substituted ring of the biphenylene backbone: 7.21 (t, *J* = 7.3 Hz, 1H, 7-CH), 6.70 (m, 2H, 6-CH, overlapping with 4-CH), 6.60 (m, 2H, 5-CH, overlapping with *m*'-Mes^b); for the alkenyl part: 8.65 (d, $^3J_{PH}$ = 40.9 Hz, 1H, HC=), 7.01 (t, $^3J_{HH}$ = 4.4 Hz, 1H, *p*-Ph), 6.97 (m, 2H, *o*-Ph), 6.86 (m, 2H, *m*-Ph).

^{13}C{^{1}H} NMR (151 MHz, 258 K, methylene chloride-d_2) [C_6F_5 not Listed]: δ = for the mesityl group: 146.7 (d, $^2J_{PC}$ = 9.9 Hz, *o*'-Mes^b), 145.25 (d, $^2J_{PC}$ = 3.9 Hz, *o*'-Mes^a), 145.19 (d, $^2J_{PC}$ = 6.3 Hz, *o*-Mes^b), 144.5 (d, $^4J_{PC}$ = 2.8 Hz, *p*-Mes^a), 144.1 (d, $^4J_{PC}$ = 3.0 Hz, *p*-Mes^b), 142.7 (d, $^2J_{PC}$ = 11.0 Hz, *o*-Mes^a), 132.7 (d, $^3J_{PC}$ = 10.9 Hz, *m*-Mes^b), 132.43 (d, $^3J_{PC}$ = 6.8 Hz, *m*-Mes^a), 132.36 (d, $^3J_{PC}$ = 7.1 Hz, *m*'-Mes^a), 131.9 (d, $^3J_{PC}$ = 11.0 Hz, *m*'-Mes^b), 123.75 (d, $^1J_{PC}$ = 86.7 Hz, *i*-Mes^a), 112.9 (d, $^1J_{PC}$ = 70.8 Hz, *i*-Mes^b), 25.8 (d, $^3J_{PC}$ = 9.6 Hz, *o*-CH_3^{Mesa}), 25.2 (m, *o*'-CH_3^{Mesa}, *o*-CH_3^{Mesb}), 23.8 (d, $^3J_{PC}$ = 3.5 Hz, *o*'-CH_3^{Mesb}), 20.9 (*p*-CH_3^{Mesa}), 20.8 (*p*-CH_3^{Mesb}); for the P-substituted ring of the biphenylene backbone: 163.6 (d, $^2J_{PC}$ = 5.5 Hz, 10-C), 153.7 (d, $^3J_{PC}$ = 12.6 Hz, 11-C), 130.8 (d, $^2J_{PC}$ = 12.2 Hz, 2-CH), 128.8 (d, $^3J_{PC}$ = 10.5 Hz, 3-CH), 123.66 (d, $^1J_{PC}$ = 82.6 Hz, 1-C), 118.6 (d, $^4J_{PC}$ = 2.9 Hz, 4-CH); for the B-substituted ring of the biphenylene backbone: 153.4 (d, $^3J_{PC}$ = 4.0 Hz, 9-C), 152.1 (br, 8-C), 149.1 (12-C), 139.2 (7-CH), 127.9 (6-CH), 115.3 (5-CH); for the alkenyl part: 177.6 (br, HC=), 134.9 (d, $^2J_{PC}$ = 16.5 Hz, *i*-Ph), 130.5 (br, *o*-Ph), 127.5 (*p*-Ph), 126.4 (*m*-Ph), 126.0 (d, $^1J_{PC}$ = 71.0 Hz, C=).

^{11}B{^{1}H} NMR (192 MHz, 258 K, methylene chloride-d_2): δ = -15.2 ($\nu_{1/2}$ ~ 57 Hz).

^{31}P{^{1}H} NMR (243 MHz, 258 K, methylene chloride-d_2): δ = 11.8 ($\nu_{1/2}$ ~ 46 Hz).

^{19}F NMR (564 MHz, 198 K, methylene chloride-d_2): δ = -129.2 (m, 1F,), -132.4 (m, 1F, *o*'-$C_6F_5^a$), -161.5 (m, 1F, *p*-$C_6F_5^a$), -164.8 (m, 1F, *m*-$C_6F_5^a$), -165.5 (m, 1F, *m*'-$C_6F_5^a$) $\Delta\delta^{19}$F*m,p* = 4.0, 3.3], -132.0 (m, 1F, *o*-$C_6F_5^b$), -132.7 (m, 1F, *o*'-$C_6F_5^b$), -163.3 (m, 1F, *p*-$C_6F_5^b$), -167.0 (d, 1F, *m*'-$C_6F_5^b$), -167.2 (m, 1F, *m*-$C_6F_5^b$) $\Delta\delta^{19}$F*m,p* = 3.9, 3.7].

Figure S54. ^{1}H NMR (600 MHz, 258 K, methylene chloride-d_2) spectrum of compound **8c**.

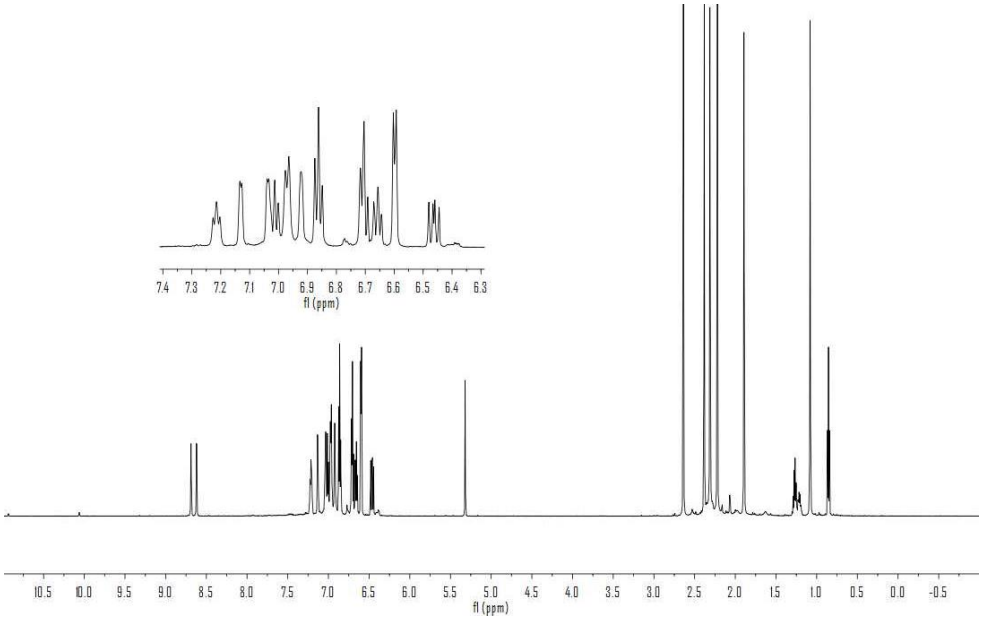


Figure S55. ^{13}C{^{1}H} NMR (160 MHz, 258 K, methylene chloride-d_2) spectrum of compound **8c**.

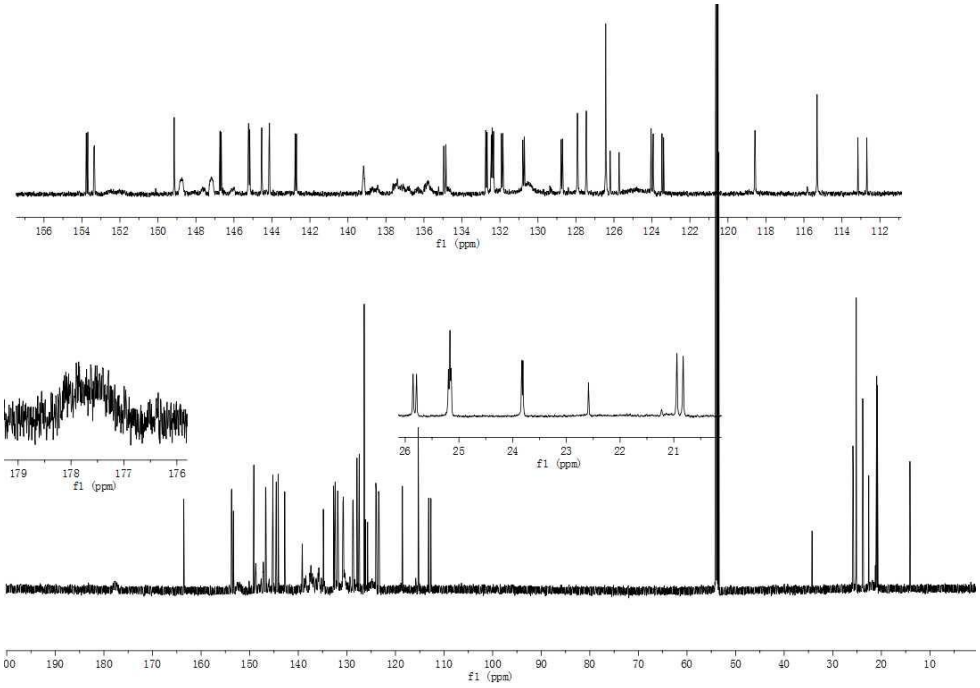


Figure S56. $^{11}B\{^{1}H\}$ NMR (192 MHz, 258 K, methylene chloride-d_2) spectrum of compound **8c**.

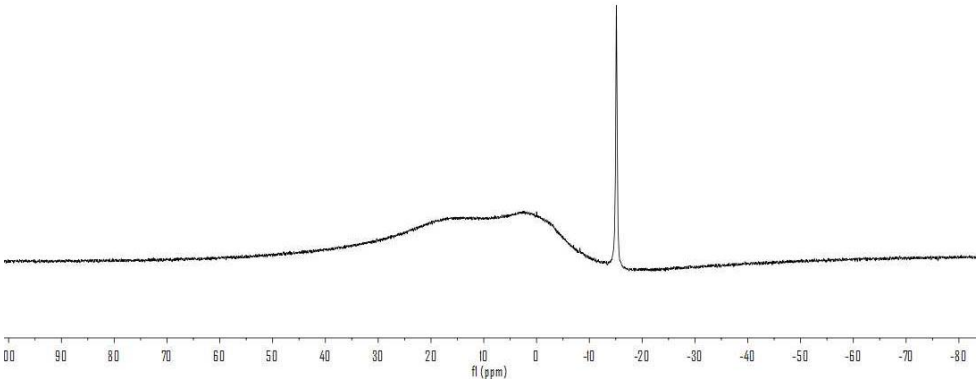


Figure S57. $^{31}P\{^{1}H\}$ NMR (243 MHz, 258 K, methylene chloride-d_2) spectrum of compound **8c**.

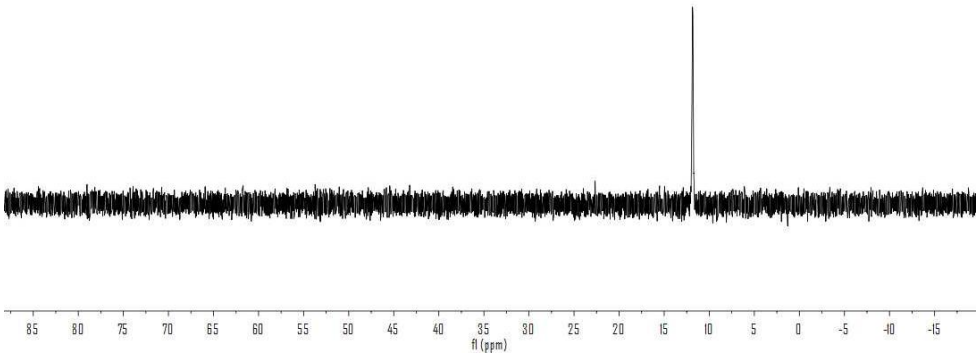
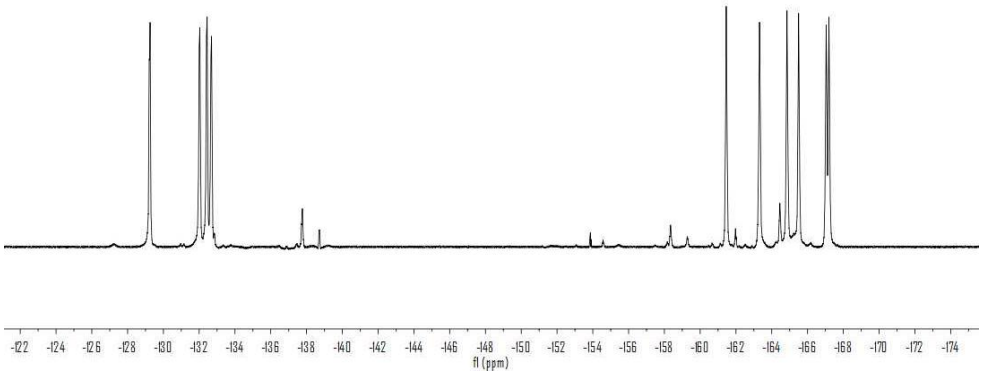
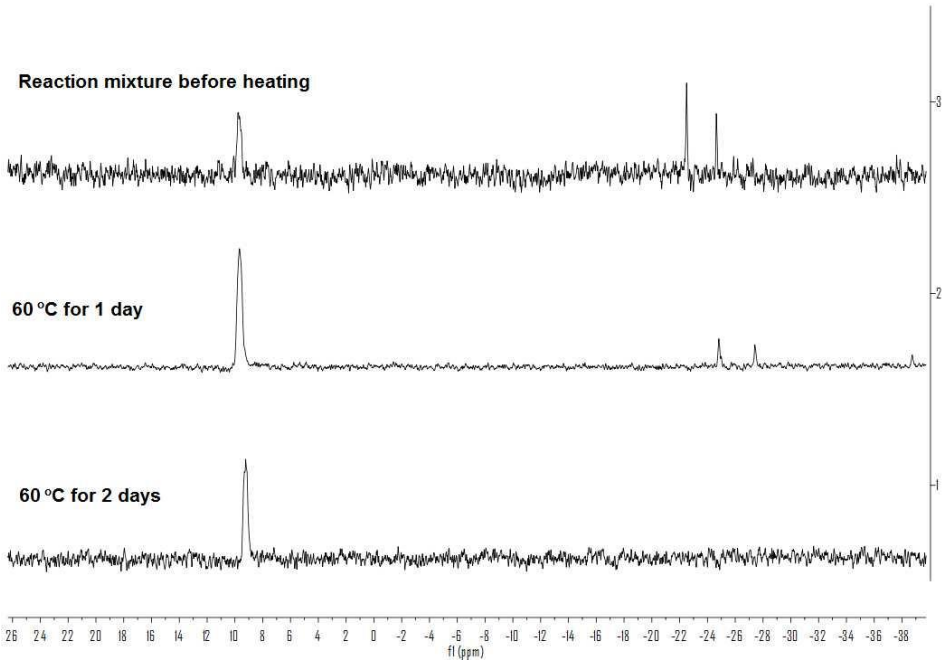


Figure S58. ^{11}F NMR (564 MHz, 198 K, methylene chloride-d_2) spectrum of compound **8c**.



Monitoring the transformation of the phenylacetylene CH activation product to the 1,2-addition product:

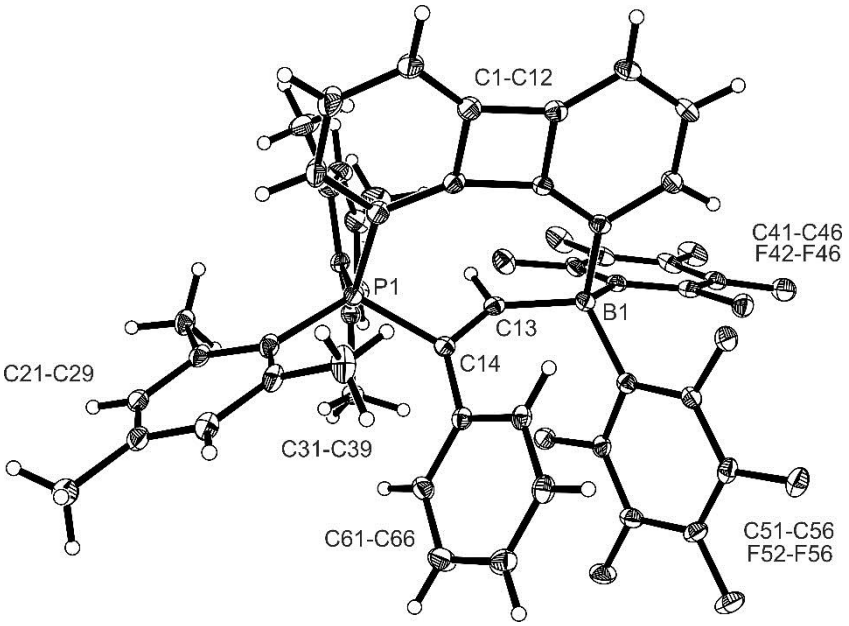
Figure S59. ^{31}P NMR (C_6D_6) spectrum of compound **8c**.



Crystals suitable for the *X*-ray crystal structure analysis were obtained from layered n-pentane on a solution of compound **8c** in toluene at room temperature.

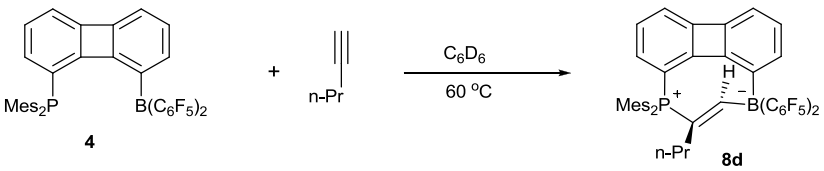
X-ray crystal structure analysis of compound 8c (erk8598): A colorless plate-like specimen of $C_{50}H_{34}BF_{10}P$, approximate dimensions 0.030 mm x 0.180 mm x 0.220 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1415 frames were collected. The total exposure time was 32.49 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 60594 reflections to a maximum θ angle of 66.87° (0.84 Å resolution), of which 14488 were independent (average redundancy 4.182, completeness = 99.0%, R_{int} = 6.01%, R_{sig} = 4.99%) and 11039 (76.19%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.3724(3) Å, b = 14.8949(3) Å, c = 23.4627(5) Å, α = 75.9580(10)°, β = 83.4140(10)°, γ = 65.3740(10)°, volume = 4120.83(16) $Å^3$, are based upon the refinement of the XYZ-centroids of 9915 reflections above 20 σ(I) with 6.685° < 2θ < 133.4°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.800. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7630 and 0.9620. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P\bar{1}$, with Z = 4 for the formula unit, $C_{50}H_{34}BF_{10}P$. The final anisotropic full-matrix least-squares refinement on F^2 with 1129 variables converged at R1 = 4.35%, for the observed data and wR2 = 11.39% for all data. The goodness-of-fit was 1.062. The largest peak in the final difference electron density synthesis was 0.328 $e^-/Å^3$ and the largest hole was -0.365 $e^-/Å^3$ with an RMS deviation of 0.051 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.397 g/cm^3 and F(000), 1776 e

Figure S60. Structure of compound **8c**.



Preparation of the 1,2-alkyne addition product 8d

Scheme S13. Preparation of compound **8d**.



Pent-1-yne (20 mg, 3.0 mmol) was added to the solution of FLP **4** (115 mg, 0.15 mmol) in C_6D_6 (3 mL). The deep orange solution changed to yellow immediately and the mixture was stirred for further 48 h at 60 °C. Then the volatiles were removed under reduced pressure and the obtained residue was washed with pentane (2 x 3 mL), dried in vacuo to give compound **8d** as a pale yellow powder (56 mg, 45% yield).

Melting point: 251 °C.

HRMS for $C_{47}H_{36}BF_{10}P$: 832.5575. Found: 855.23873 ($[M+Na]^+$).

^{1}H NMR (500 MHz, 228 K, methylene chloride-d_2): δ = for the mesityl group: 7.06 (d, $^4J_{PH}$ = 4.5 Hz, 1H, *m*-Mes^a), 7.03 (m, 1H, *m*-Mes^b), 6.99 (m, 1H, *m*'-Mes^b), 6.93 (d, $^4J_{PH}$ = 4.5 Hz, 1H, *m*'-Mes^a), 2.32 (s, 3H, *p*-CH_3^{Mesa}), 2.30 (s, 3H, *p*-CH_3^{Mesb}), 2.28 (s, 3H, *o*'-CH_3^{Mesa}), 2.24 (s, 3H, *o*-CH_3^{Mesa}), 2.15 (s, 3H, *o*-CH_3^{Mesb}), 1.96 (s, 3H, *o*'-CH_3^{Mesb}); for the P-substituted ring of the biphenylene backbone: 6.65 (m, 2H, 4-CH overlapping with 6-CH), 6.61 (m, 1H, 3-CH), 6.37 (dd, *J* = 12.4, 8.5 Hz, 1H, 2-CH); for the B- substituted ring of the biphenylene backbone: 7.00 (d, $^3J_{HH}$ = 8.3 Hz,1H, 7-CH), 6.65 (m, 2H, 6-CH, overlapping with 4-CH), 6.53 (d, $^3J_{HH}$ = 6.7 Hz, 1H, 5-CH); for the alkenyl part: 7.89 (d, $^3J_{PH}$ ~ 40 Hz, 1H, HC=), 1.93 (m, 1H, CH_2C=) 1.81 (m, 1H, CH_2C=), 1.34 (m, 1H, CH_2CH_3), 0.90 (m, 1H, CH_2CH_3), 0.20 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (126 MHz, 228 K, methylene chloride-d_2) [C_6F_5 not listed]: δ = for the mesityl group: 143.72 (d, $^2J_{PC}$ = 11.8 Hz, *o*'-Mes^b), 143.70 (d, $^4J_{PC}$ = 1.8 Hz, *p*-Mes^b), 143.6 (d, $^2J_{PC}$ = 2.9 Hz, *o*-Mes^b), 132.2 (d, $^3J_{PC}$ = 11.3 Hz, *m*'-Mes^a), 132.0 (d, $^3J_{PC}$ = 10.1 Hz, *m*'-Mes^b), 131.6 (d, $^3J_{PC}$ = 10.1 Hz, *m*-Mes^b), 131.2 (d, $^3J_{PC}$ = 11.4 Hz, *m*-Mes^a), 143.4 (d, $^2J_{PC}$ = 3.4 Hz, *o*'-Mes^a), 143.3 (*p*-Mes^a), 142.3 (d, $^2J_{PC}$ = 12.9 Hz, *o*-Mes^a), 123.00 (d, $^1J_{PC}$ = 90.5 Hz, *i*-Mes^a), 115.8 (d, $^1J_{PC}$ = 71.4 Hz, *i*-Mes^b), 24.6 (d, $^3J_{PC}$ = 3.3 Hz, *o*'-CH_3^{Mesa}), 24.3 (d, $^3J_{PC}$ = 9.6 Hz, *o*-CH_3^{Mesa}), 24.0 (d, $^3J_{PC}$ = 3.8 Hz, *o*'-CH_3^{Mesb}), 23.8 (d, $^3J_{PC}$ = 6.2 Hz, *o*-CH_3^{Mesb}), 20.9 (d, $^5J_{PC}$ = 1.4 Hz, *p*-CH_3^{Mesb}), 20.8 (d, $^5J_{PC}$ = 1.5 Hz, *p*-CH_3^{Mesa}); for the P-substituted ring of the biphenylene backbone: 161.8 (d, $^2J_{PC}$ = 3.5 Hz, 10-C), 152.9 (d, $^3J_{PC}$ = 11.8 Hz, 11-C), 130.4 (d, $^2J_{PC}$ = 13.8 Hz, 2-CH), 128.3 (d, $^3J_{PC}$ = 10.9 Hz, 3-CH), 122.97 (d, $^1J_{PC}$ = 82.0 Hz, 1-C), 118.0 (d, $^4J_{PC}$ = 2.8 Hz, 4-CH); for the B-substituted ring of the biphenylene backbone: 153.9 (br, 8-C), 151.8 (9-C), 149.0 (12-C), 135.3 (d, *J* = 13.7 Hz, 7-CH), 129.2 (6-CH), 114.8 (5-CH); for the alkenyl part: 179.8 (br, HC=), 125.1 (d, $^1J_{PC}$ = 69.6 Hz, C=), 30.7 (d, $^2J_{PC}$ = 14.9 Hz, CH_2C=), 26.0 (CH_2CH_3), 13.8 (CH_3).

^{11}B{^{1}H} NMR (160 MHz, 228 K, methylene chloride-d_2): δ = -14.9 ($\nu_{1/2}$ ~ 61 Hz).

$^{31}P\{^{1}H\}$ NMR (202 MHz, 228 K, methylene chloride-d_2): δ = 5.3 ($\nu_{1/2}$ ~ 48 Hz).
^{19}F NMR (470 MHz, 228 K, methylene chloride-d_2): δ = -126.8, -129.1, -130.2, -132.4, (each m, each 1F, *o*-C_6F_5), -161.5 (t, $^{3}J_{FF}$ = 20.8 Hz), -162.2 (t, $^{3}J_{FF}$ = 21.2 Hz) (each 1F, *p*-C_6F_5), -165.5 (m, 3F), -166.5 (m, 1F) (*m*-C_6F_5) [$\Delta\delta^{19}$F*m,p* = 5.0, 4.0, 3.3].

Figure S61. ^{1}H NMR (500 MHz, 228 K, methylene chloride-d_2) spectrum of compound **8d**.

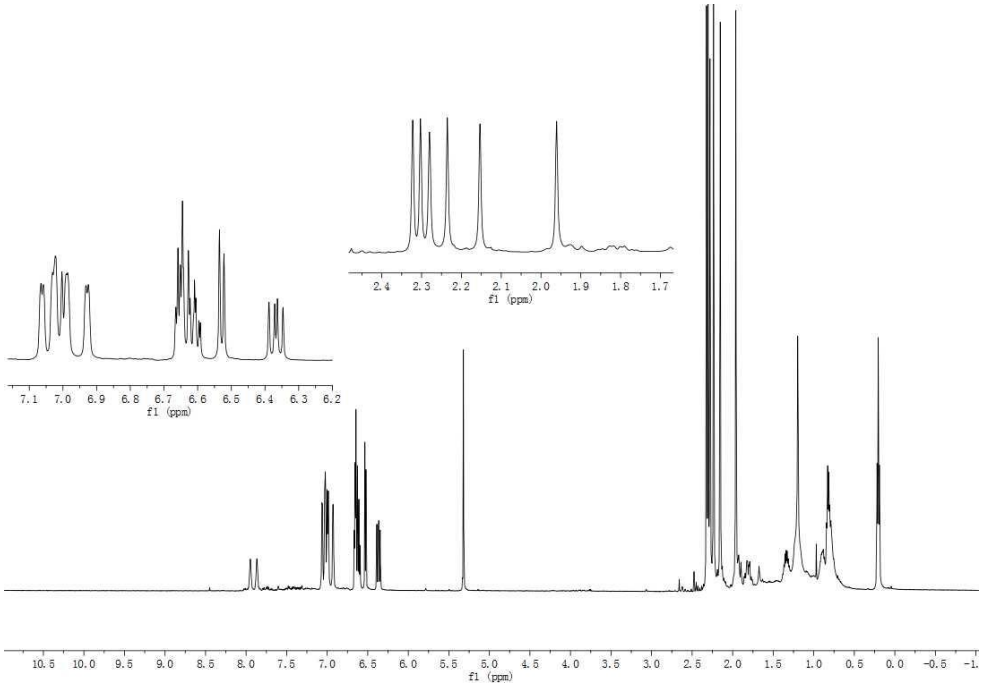


Figure S62. $^{13}C\{^{1}H\}$ NMR (126 MHz, 228 K, methylene chloride-d_2) spectrum of compound **8d**.

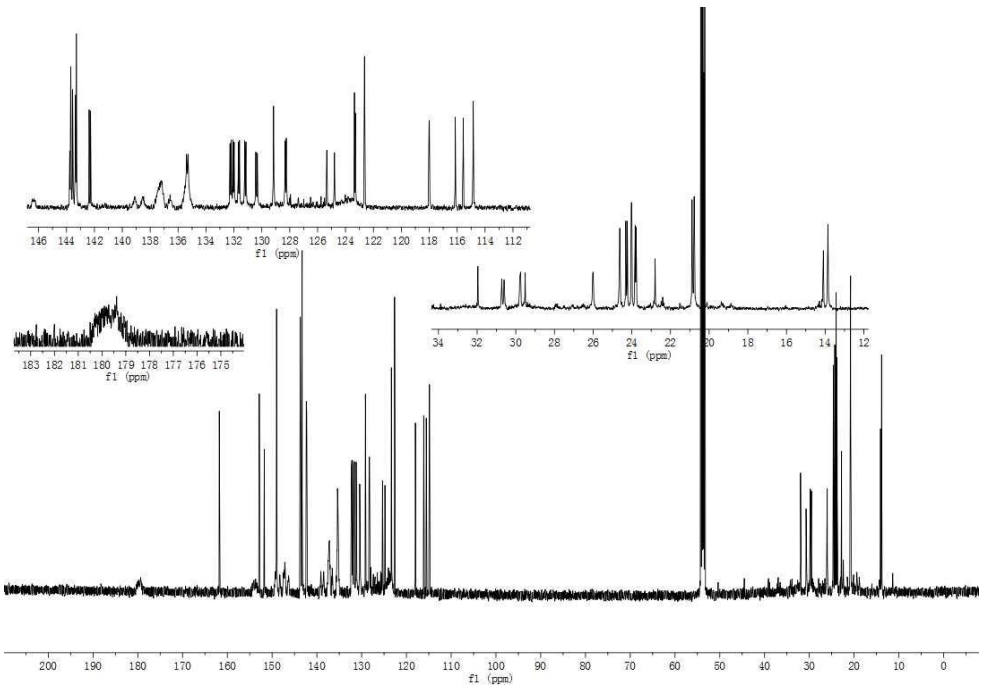


Figure S61. ^{13}B {^{1}H} NMR (160 MHz, 228 K, methylene chloride-d_2) spectrum of compound **8d**.

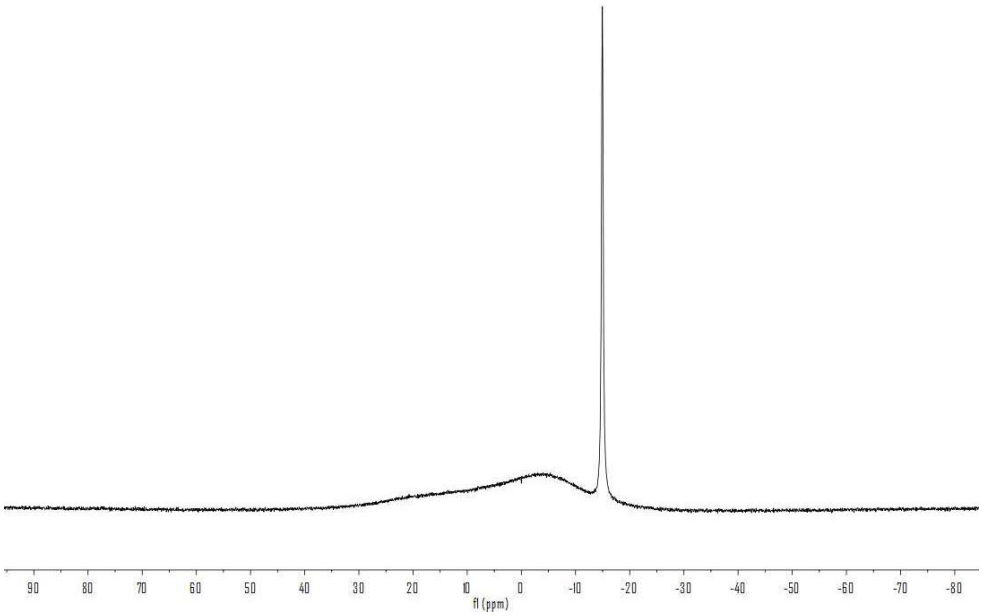


Figure S64. ^{31}P\{^{1}H\} NMR (202 MHz, 228 K, methylene chloride-d_2) spectrum of compound **8d**.

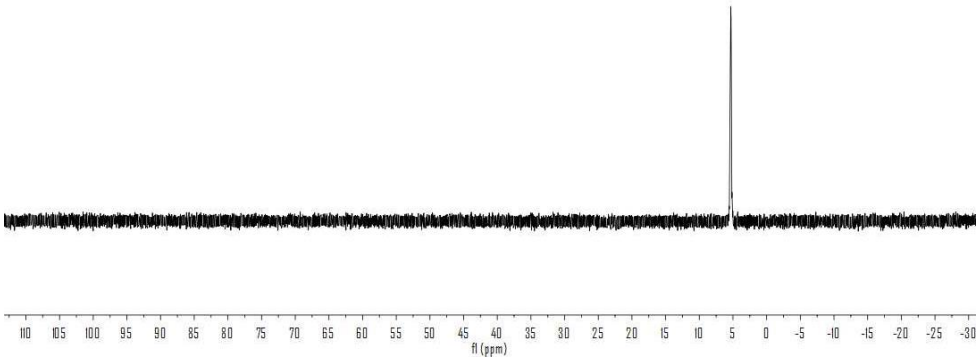
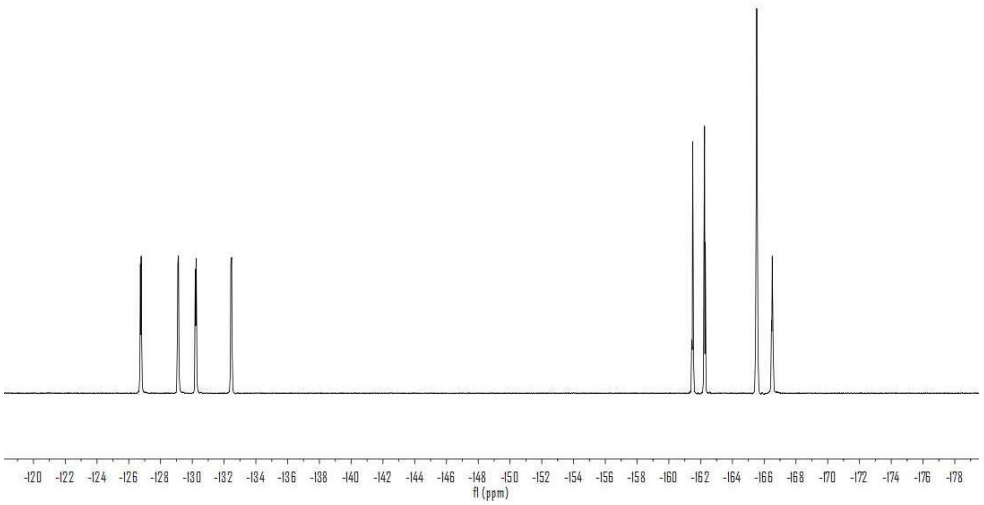


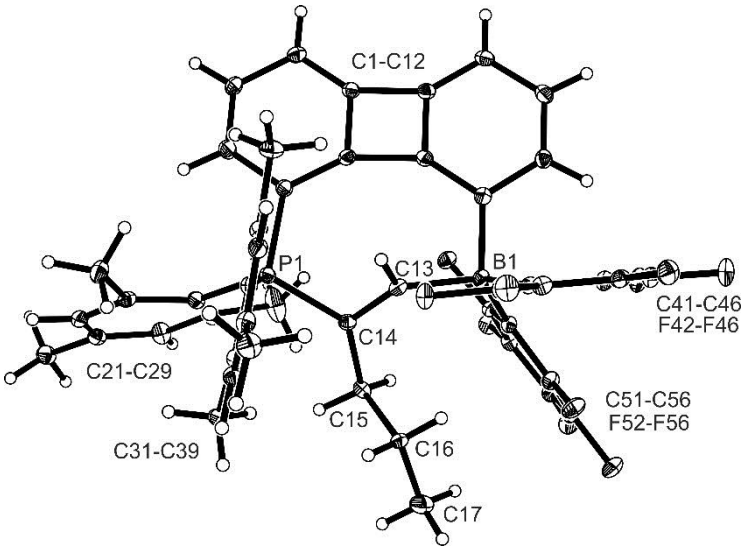
Figure S65. ^{19}F NMR (470 MHz, 228 K, methylene chloride-d_2) spectrum of compound **8d**.



Crystals suitable for the *X*-ray crystal structure analysis were obtained from layered n-pentane on a solution of compound **8d** in toluene at room temperature.

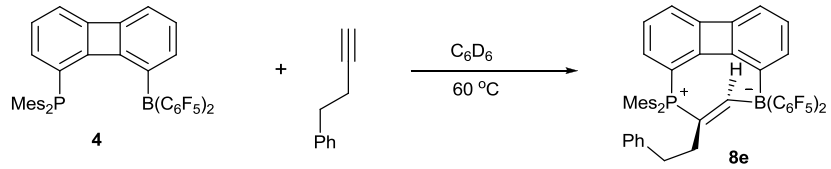
X-ray crystal structure analysis of compound 8d (erk8620): formula $C_{47}H_{36}BF_{10}P$, M = 832.54, colourless crystal, 0.24 x 0.10 x 0.05 mm, a = 13.0923(2), b = 11.9735(2), c = 24.9266(5) Å, β = 98.327(1)°, V = 3866.3(1) Å^3, ρ_{calc} = 1.430 gcm^{-3}, μ = 0.155 mm^{-1}, empirical absorption correction (0.963 ≤ T ≤ 0.992), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 173(2) K, ω and ϕ scans, 21505 reflections collected (±h, ±k, ±l), 6682 independent (R_{int} = 0.057) and 5093 observed reflections [I>2σ(I)], 568 refined parameters, R = 0.062, wR^2 = 0.139, max. (min.) residual electron density 0.32 (-0.29) e.Å^{-3}, the hydrogen atoms were calculated and refined as riding atoms

Figure S66. Structure of compound **8d**.



Preparation of the 1,2-alkyne addition product 8e

Scheme S14. Preparation of compound **8e**.



But-3-ynylbenzene (39 mg, 3.0 mmol) was added to the solution of FLP **4** (115 mg, 0.15 mmol) in C_6D_6 (3 mL). The deep orange solution changed to yellow immediately and the mixture was stirred for further 48 h at 60 °C. Then the volatiles were removed under reduced pressure and the obtained residue was washed with pentane (2 x 3 mL), dried in vacuo to give compound **8e** as a pale yellow powder (24 mg, 13% yield).

Melting point: 259°C.

HRMS for $C_{52}H_{38}BF_{10}P$: 894.6269. Found: 917.25469 ([M+ Na]$^+$)

^{1}H NMR (500 MHz, 299 K, methylene chloride-d_2): δ = for the mesityl group: 7.12 (m, 4H, *m*-Mes^a, overlapping with *m*-Ph, *p*-Ph,), 7.07 (m, 1H, *m*-Mes^b), 7.04 (d, m, 2H, *m*'-Mes^b,overlapping with 7-CH), 6.95 (m, 1H, *m*'-Mes^a), 2.39 (m, 4H, *o*-CH_3^{Mesa}, overlapping with CH_2Ph,), 2.36 (s, 3H, *p*-CH_3^{Mesa}), 2.35 (s, 3H, *o*'-CH_3^{Mesa}), 2.34 (s, 3H, *p*-CH_3^{Mesb}), 2.28 (m, 4H, *o*'-CH_3^{Mesb}, overlapping with CH_2C=), 2.05 (s, 3H, *o*-CH_3^{Mesb}); for the P-substituted ring of the biphenylene backbone: 6.66 (m, 5H, 3-CH, 4-CH, overlapping with *o*-Ph, 6-CH), 6.41 (ddd, J = 12.4, 8.1, 1.3 Hz, 1H, 2-CH); for the B-substituted ring of the biphenylene backbone: 7.04 (d, m, 2H, 7-CH, overlapping with *m*'-Mes^b), 6.66 (m, 5H, 6-CH, overlapping with *o*-Ph, 3-CH, 4-CH), 6.55 (d, $^3J_{HH}$ = 6.8 Hz, 1H, 5-CH); for the alkenyl part: 7.94 (d, $^3J_{PH}$ = 40.2 Hz, 1H, HC=), 7.12 (m, 4H, *m*-Ph, *p*-Ph, overlapping with *m*-Mes^a), 6.66 (m, 5H, *o*-Ph, overlapping with 3-CH, 4-CH, 6-CH), 2.68 (m, 2H, CH_2C=, CH_2Ph), 2.39 (m, 4H, CH_2Ph, overlapping with *o*-CH_3^{Mesa}), 2.28 (m, 4H, CH_2C=, overlapping with *o*'-CH_3^{Mesb}).

^{13}C{^{1}H} NMR (126 MHz, 299 K, methylene chloride-d_2) [C_6F_5 not listed]: δ = for the mesityl group: 144.52 (d, $^2J_{PC}$ = 4.9 Hz, *o*-Mes^b), 144.48 (*p*-Mes^a), 144.2 (d, $^2J_{PC}$ = 3.0 Hz, *o*'-Mes^a), 144.1 (d, $^2J_{PC}$ = 3.5 Hz, *o*'-Mes^b), 144.0 (*p*-Mes^b), 142.9 (d, $^2J_{PC}$ = 12.6 Hz, *o*-Mes^a), 132.9 (d, $^3J_{PC}$ = 11.5 Hz, *m*'-Mes^a), 132.7 (d, $^3J_{PC}$ = 10.1 Hz, *m*-Mes^b), 132.4 (d, $^3J_{PC}$ = 10.2 Hz, *m*'-Mes^b), 132.0 (d, $^3J_{PC}$ = 11.4 Hz, *m*-Mes^a), 124.3 (d, $^1J_{PC}$ = 81.7 Hz, *i*-Mes^a), 116.8 (d, $^1J_{PC}$ = 70.5 Hz, *i*-Mes^b), 24.9 (d, $^3J_{PC}$ = 3.5 Hz,

o'-CH_3^{Mesa}), 24.7 (d, $^3J_{PC}$ = 9.3 Hz, o-CH_3^{Mesa}), 24.3 (d, $^3J_{PC}$ = 6.2 Hz, o'-CH_3^{Mesb}), 24.1 (d, $^3J_{PC}$ = 4.0 Hz, o-CH_3^{Mesb}), 21.2 (d, $^5J_{PC}$ = 1.5 Hz, *p*-CH_3^{Mesb}), 21.0 (d, $^5J_{PC}$ = 1.5 Hz, *p*-CH_3^{Mesa}); for the P-substituted ring of the biphenylene backbone: 163 (d, $^2J_{PC}$ = 3.5 Hz, 10-C), 153.8 (d, $^3J_{PC}$ = 11.9 Hz, 11-C), 130.7 (d, $^2J_{PC}$ = 13.8 Hz, 2-CH), 128.8 (d, $^3J_{PC}$ = 10.9 Hz, 3-CH), 123.5 (d, $^1J_{PC}$ = 90.9 Hz, 1-C), 118.2 (d, $^4J_{PC}$ = 2.9 Hz, 4-CH); for the B-substituted ring of the biphenylene backbone: 154.5 (br, 8-C), 152.3 (9-C), 149.3 (12-C), 136.8 (d, *J* = 7.1 Hz, 7-CH), 129.5 (6-CH), 115.2 (5-CH); for the alkenyl part: 181.4 (br, HC=), 141.20 (d, $^4J_{PC}$ = 1.5 Hz, *i*-Ph), 128.4 (*m*-Ph), 127.3 (*o*-Ph), 126.2 (*p*-Ph), 124.1 (d, $^1J_{PC}$ = 72.4 Hz, C=), 37.0 (d, $^3J_{PC}$ = 4.5 Hz, CH_2Ph), 29.2 (d, $^2J_{PC}$ = 16.1 Hz, CH_2C=),

$^{31}P\{^1H\}$ NMR (202 MHz, 299 K, methylene chloride-d_2): δ = 6.6 (br 1:1:1:1 q partially relaxed, J_{PB} ~ 15 Hz).

$^{11}B\{^1H\}$ NMR (160 MHz, 299 K, methylene chloride-d_2) -14.7 (d, J_{PB} ~ 15 Hz)

^{19}F NMR (470 MHz, 203 K, methylene chloride-d_2): δ = -126.6, -132.4 (each m, each 1F, *o*-$C_6F_5^a$), -161.8 (t, $^3J_{FF}$ = 21.3 Hz, 1F, *p*-$C_6F_5^a$), -165.2 (m, 2F, *m*-$C_6F_5^a$) [$\Delta\delta^{19}Fm,p$ = 3.4]. -129.5 (m, 1F, *o*-$C_6F_5^b$), -130.6 (m, 1F, *o*'-$C_6F_5^b$), -161.2 (t, $^3J_{FF}$ = 21.2 Hz, 1F, *p*-$C_6F_5^b$), -164.6 (m, 1F, *m*'-$C_6F_5^b$), -165.7 (m, 1F, *m*-$C_6F_5^b$) [$\Delta\delta^{19}Fm,p$ = 4.5, 3.4].

Figure S67. ^{1}H NMR (500 MHz, 299 K, methylene chloride-d_2) spectrum of compound **8e**.

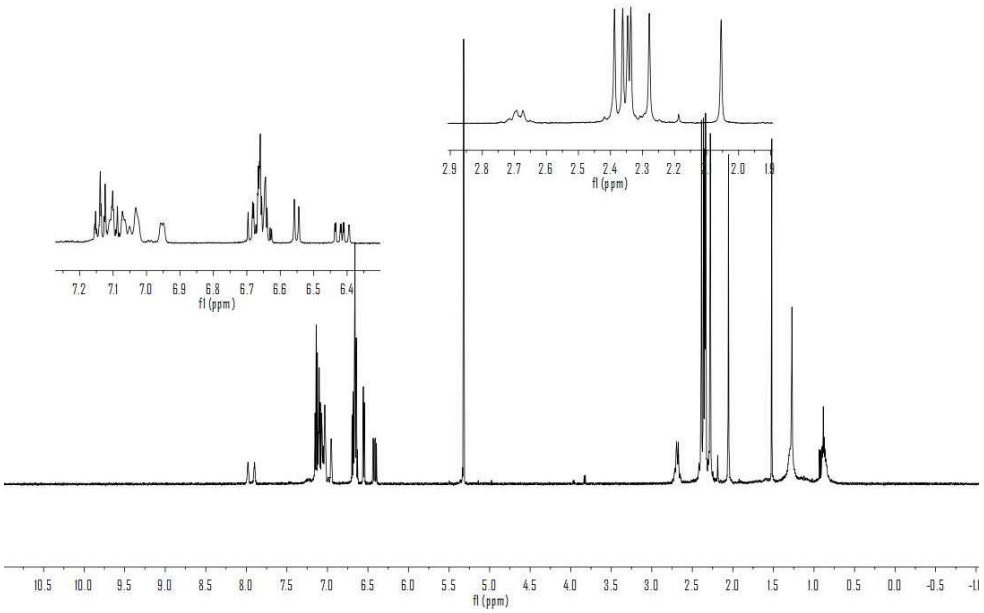


Figure S68. $^{13}C\{^1H\}$ NMR (126 MHz, 299 K, methylene chloride-d_2) spectrum of compound **8e**.

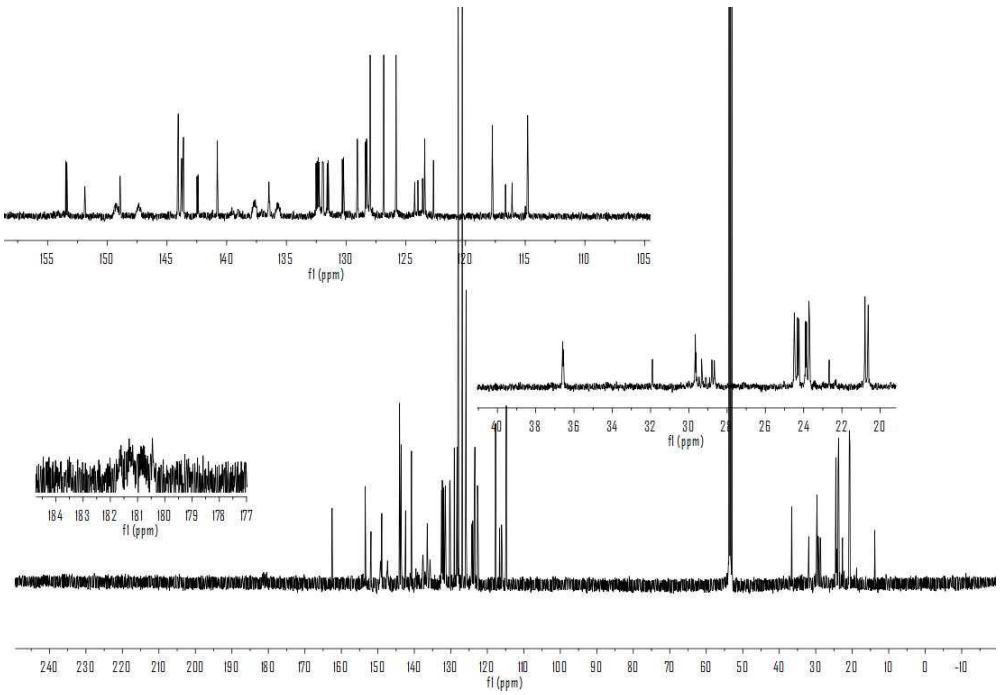


Figure S69. $^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, methylene chloride-d_2) spectrum of compound **8e**.

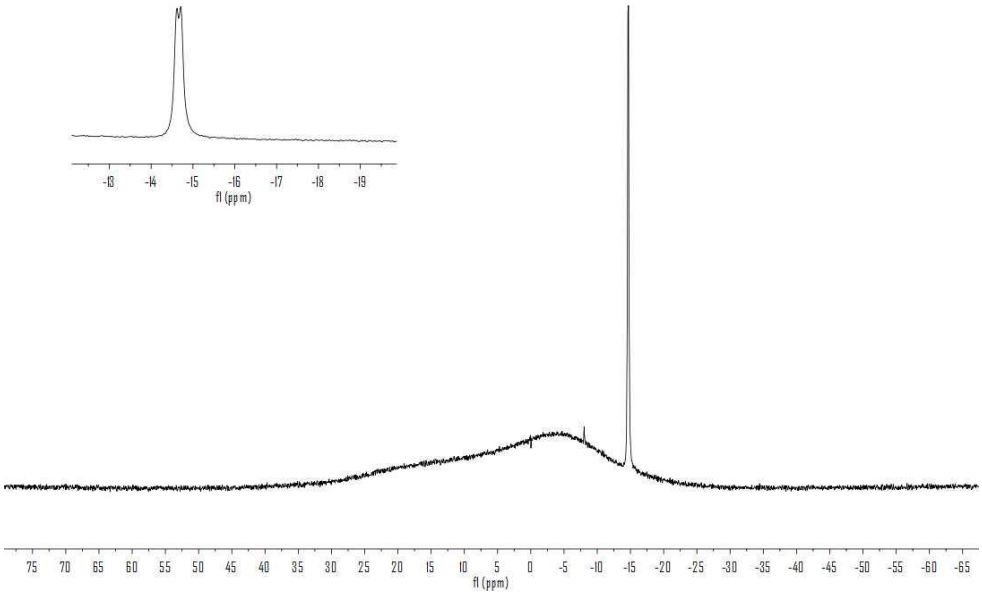


Figure S70. $^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, methylene chloride-d_2) spectrum of compound **8e**.

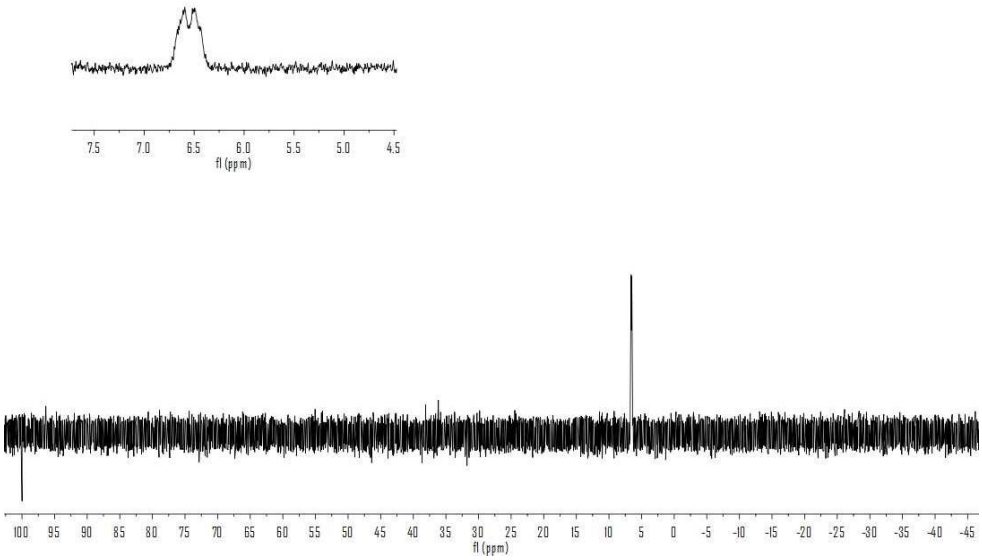
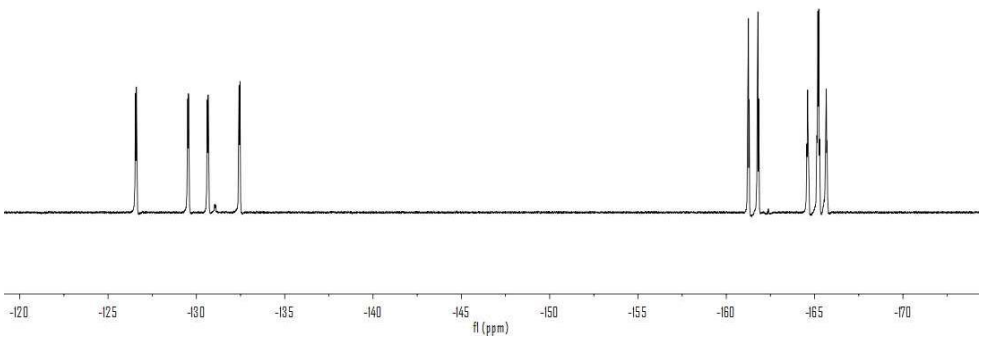


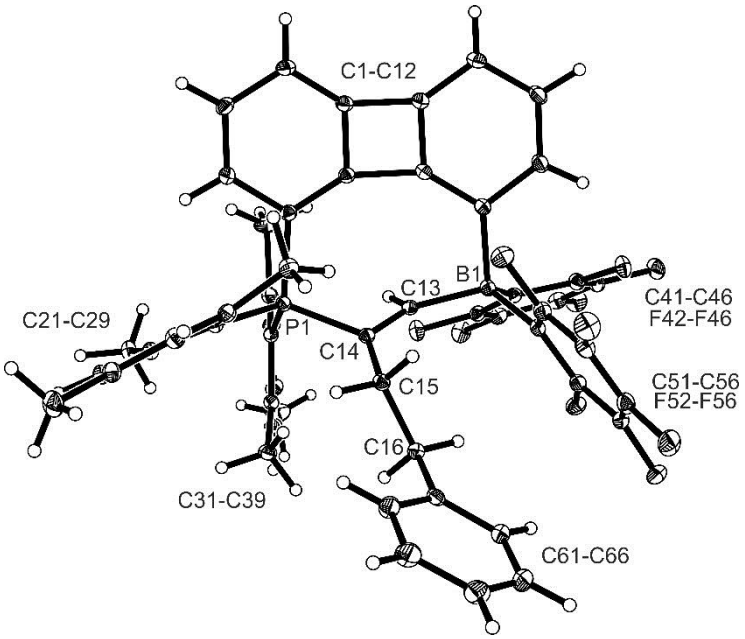
Figure S71. ^{19}F NMR (470 MHz, 203 K, methylene chloride-d_2) spectrum of compound **8e**.



Crystals suitable for the *X*-ray crystal structure analysis were obtained from layered n-pentane on a solution of compound **8e** in methylene chloride at -35 °C.

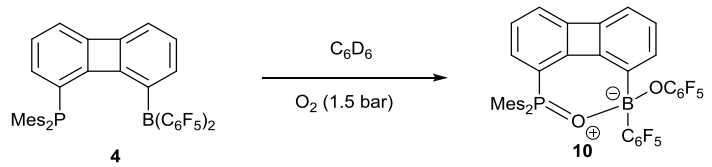
X-ray crystal structure analysis of compound 8e (erk8588): formula $C_{52}H_{38}BF_{10}P$, M = 894.60, colourless crystal, 0.15 x 0.13 x 0.07 mm, a = 14.5964(3), b = 18.8664(3), c = 15.7176(4) Å, β = 104.493(1)°, V = 4190.6(2) Å^3, ρ_{calc} = 1.418 gcm^{-3}, μ = 0.148 mm^{-1}, empirical absorption correction (0.978 ≤ T ≤ 0.989), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 173(2) K, ω and ϕ scans, 34103 reflections collected (±h, ±k, ±l), 8490 independent (R_{int} = 0.061) and 6848 observed reflections [I>2σ(I)], 583 refined parameters, R = 0.050, wR^2 = 0.128, max. (min.) residual electron density 0.37 (-0.33) e.Å^{-3}, the hydrogen atoms were calculated and refined as riding atoms.

Figure S72. Structure of **8e**.



Reaction of compound 4 with dioxygen: preparation of compound 10

Scheme S15. Preparation of compound **10**.



Compound **4** (115 mg, 0.15 mmol) was dissolved in C_6D_6 (2 mL) and the resulting solution subjected to three freeze-pump-thaw cycles before backfilling with O_2 (ca. 1.5 bar). The deep orange solution fades out slowly. The resulting mixture was stirred for 2h. Then the volatiles were removed in vacuo and the residual was washed by pentane (3 mL x 2) to give compound **10** as a pale yellow powder (45 mg, 38 %).

Melting point: 217 °C.

Anal. Calc. for: C, 63.34; H, 3.54. Found: C, 59.86; H, 3.36.

^{1}H NMR (500 MHz, 299 K, toluene-d_8): δ = for the mesityl group: 6.54 (m, 2H, *m*-Mes^a), 6.33 (d, $^4J_{PH}$ = 4.6 Hz, 2H, *m*-Mes^b), 2.28 (very br., 6H, *o*-CH_3^{Mesa}), 2.06 (br, 6H, *o*-CH_3^{Mesb}), 1.95 (s, 3H, *p*-CH_3^{Mesa}), 1.92 (s, 3H, *p*-CH_3^{Mesb}); for the P-substituted ring of the biphenylene backbone: 6.29 (m, 1H, 2-CH), 6.22 (m, 2H, 3, 4-CH); for the B-substituted ring of the biphenylene backbone: 6.68 (d, $^3J_{HH}$ = 8.0 Hz, 1H, 7-CH), 6.42 (dd, $^3J_{HH}$ = 8.0, 6.8 Hz, 1H, 6-CH), 6.36 (d, $^3J_{HH}$ = 6.8 Hz, 1H, 5-CH).

^{13}C{^{1}H} NMR (126 MHz, 299 K, toluene-d_8) [C_6F_5 not listed]: δ = for the mesityl group: 143.8 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Mes^b), 143.3 (d, $^4J_{PC}$ = 3.0 Hz, *p*-Mes^a), 141.9 (m, *o*-Mes^a, *o*-Mes^b, overlapping with 8-C,), 132.0 (br, *m*-Mes^a), 131.50 (m, *m*-Mes^b), 123.8 (d, $^1J_{PC}$ = 104.3 Hz, *i*-Mes^b), 123.6 (d, $^1J_{PC}$ = 110.9 Hz, *i*-Mes^a), 23.5 (br, *o*-CH_3^{Mesa}), 23.1 (br, *o*-CH_3^{Mesb}), 20.8 (*p*-CH_3^{Mesa}), 20.55 (*p*-CH_3^{Mesb}); for the P-substituted ring of the biphenylene backbone: 162.3 (d, $^2J_{PC}$ = 4.6 Hz, 10-C), 153.2 (d, $^3J_{PC}$ = 12.2 Hz,

11-C), 129.2 (d, $^{3}J_{PC}$ = 10.2 Hz, 3-CH), 125.1 (2-CH), 120.1 (d, $^{4}J_{PC}$ = 3.0 Hz, 4-CH), 119.2 (d, $^{1}J_{PC}$ = 102.2 Hz, 1-C); for the B-substituted ring of the biphenylene backbone: 151.0 (d, $^{3}J_{PC}$ = 6.0 Hz, 9-C), 150.2 (12-C), 141.9 (m, 8-C,overlapping with *o*-Mes[a], *o*-Mes[b]), 132.8 (7-CH), 130.1 (6-CH), 118.6 (5-CH).
$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, toluene-d_8): δ = 8.2 ($\nu_{1/2}$ ~ 482 Hz).
$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, toluene-d_8): δ = 39.6 ($\nu_{1/2}$ ~ 9.9 Hz).
^{19}F NMR (470 MHz, 299 K, toluene-d_8): δ = -130.1 (m, 2F, *o*-C_6F_5), -159.3 (m, 1F, *p*-C_6F_5), -165.2 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}Fm,p$ = 5.9]. -156.4 (m, 2F, *o*-OC_6F_5), -166.8 (m, 2F, *m*-OC_6F_5), -170.4 (m, 1F, *p*-OC_6F_5).

Figure S73. ^{1}H NMR (500 MHz, 299 K, toluene-d_8) spectrum of compound **10**.

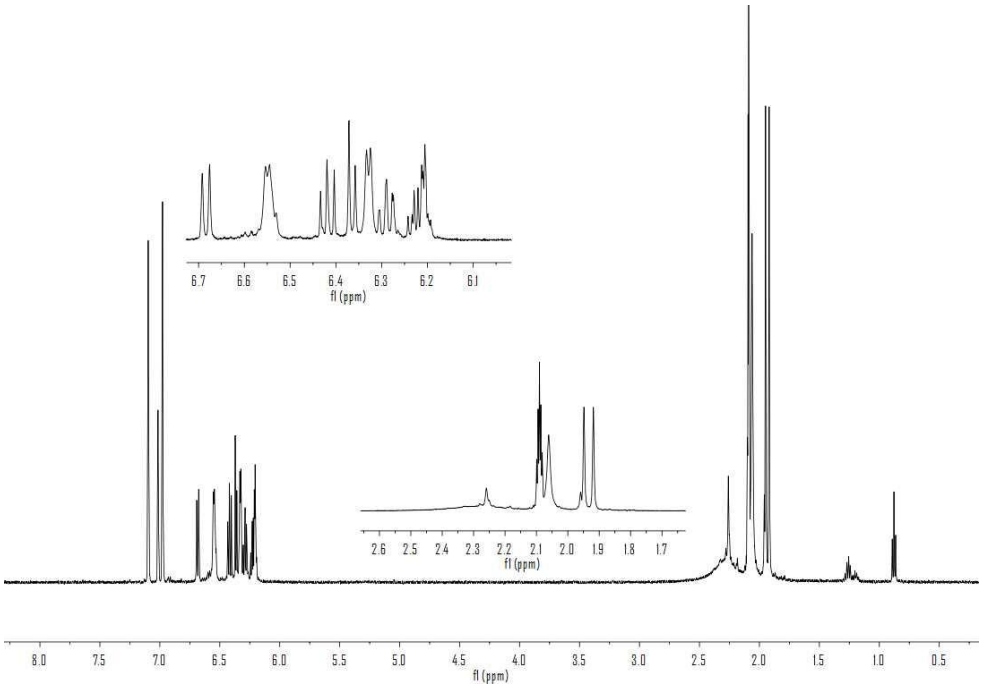


Figure S74. $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, toluene-d_8) spectrum of compound **10**.

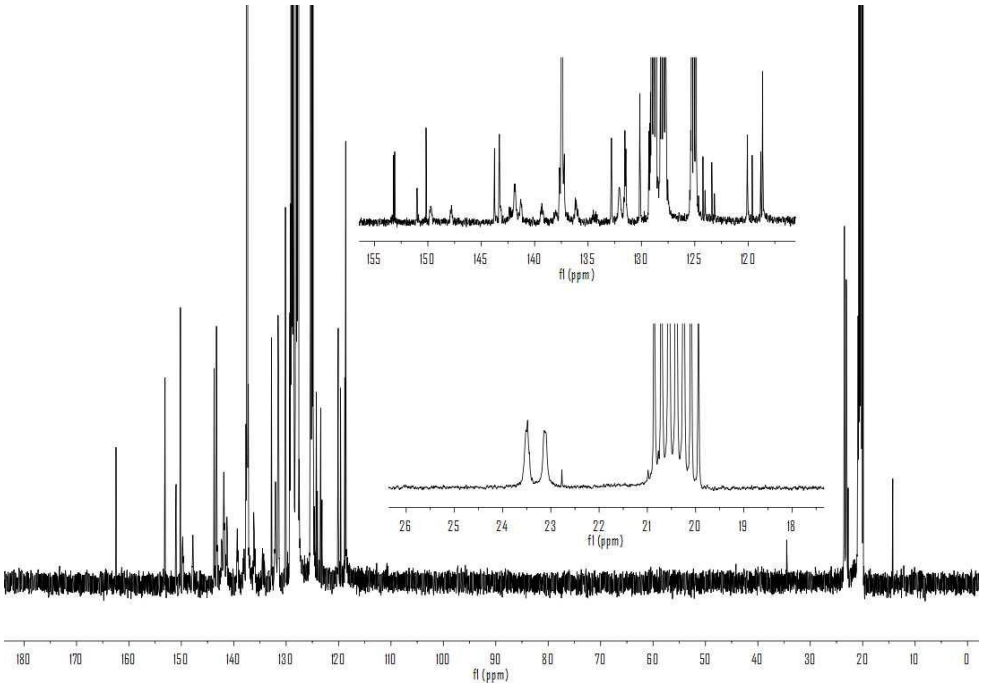


Figure S75. $^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, toluene-d_8) spectrum of compound **10**.

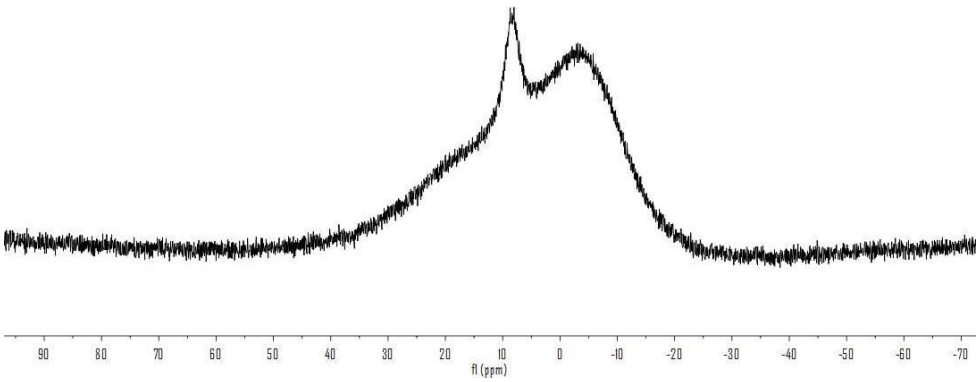


Figure S76. $^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, toluene-d_8) spectrum of compound **10**.

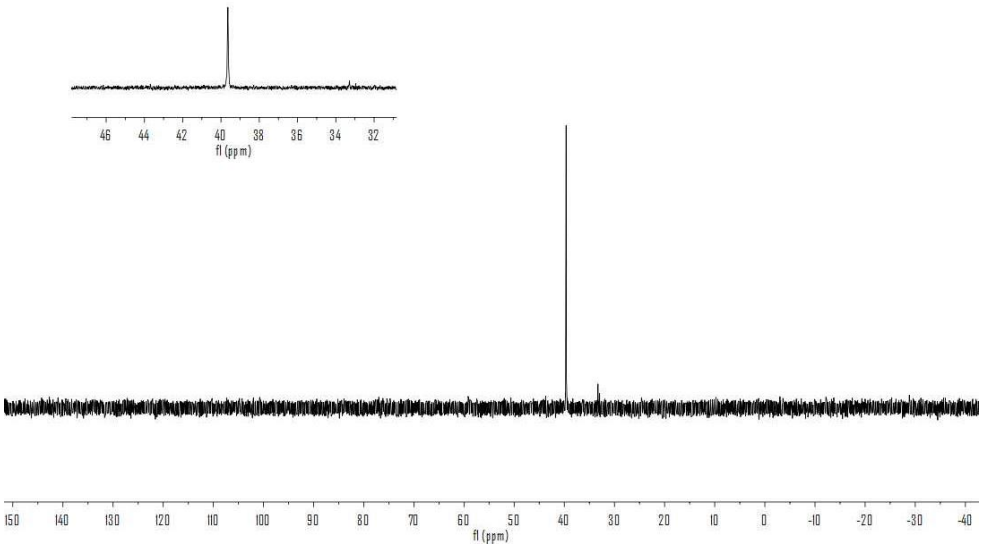
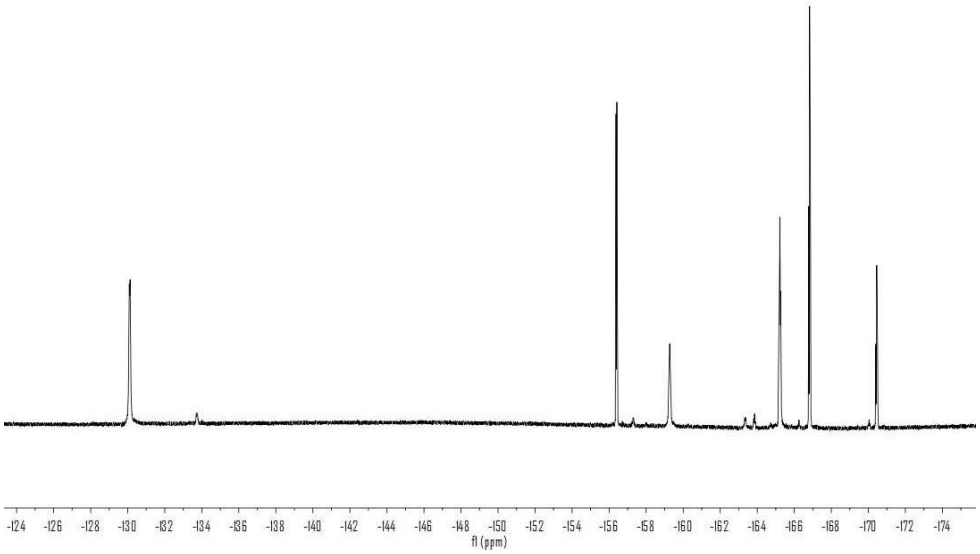


Figure S77. ^{19}F NMR (470 MHz, 299 K, toluene-d_8) spectrum of compound **10**.



Dynamic NMR spectroscopy of compound 10

In low temperature, this compound was split into two diastereoisomers.

Figure S78. VT $^{31}P\{^{1}H\}$ NMR (202 MHz, toluene-d_8) spectrum of compound **10**.

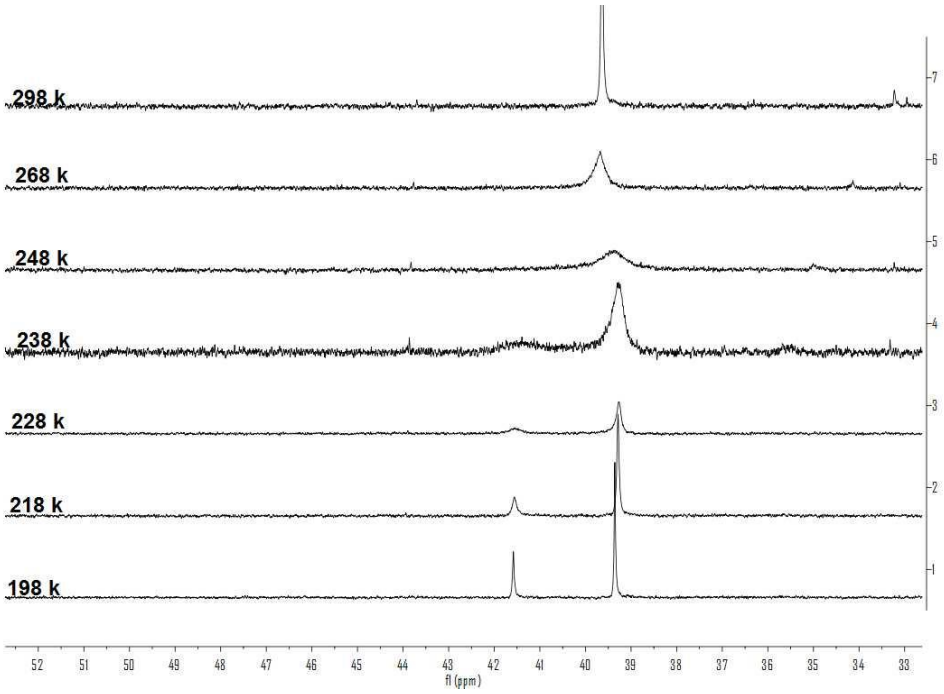
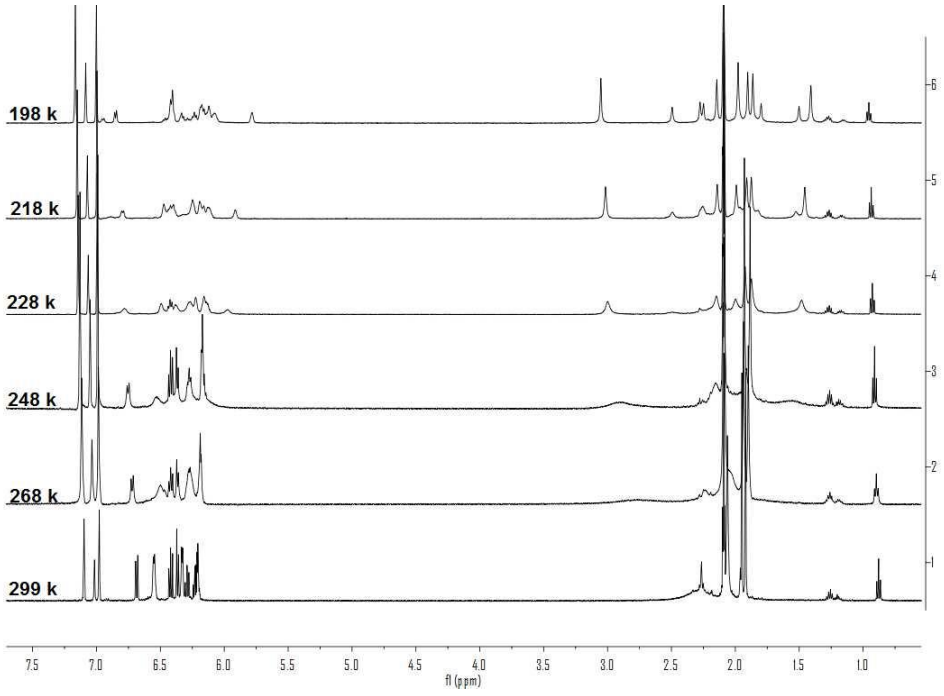


Figure S79. VT ^{1}H NMR (500 MHz, toluene-d_8) spectrum of compound **10**.



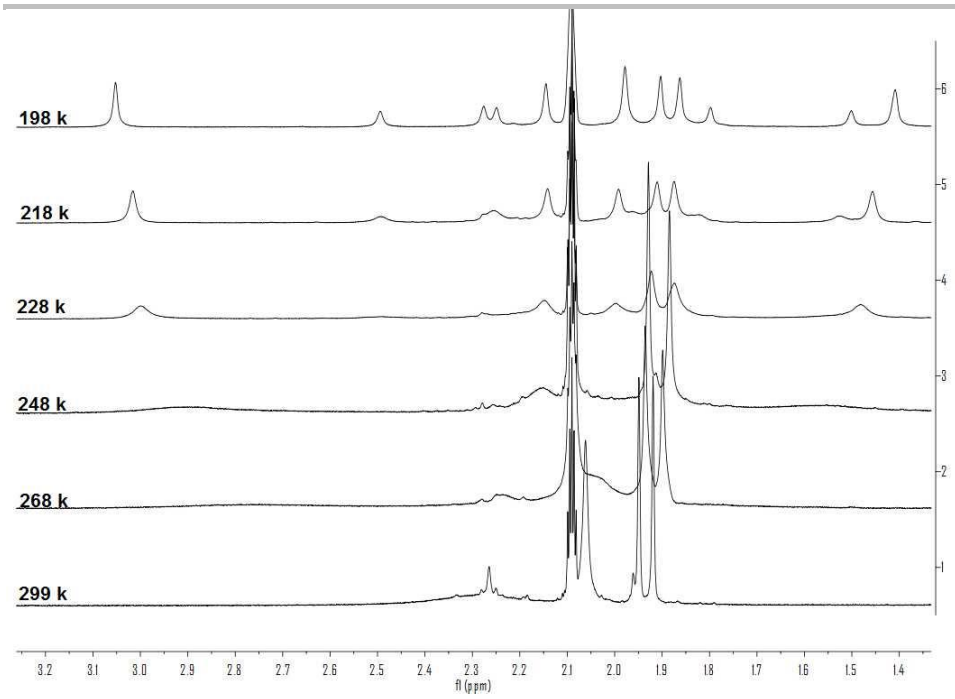
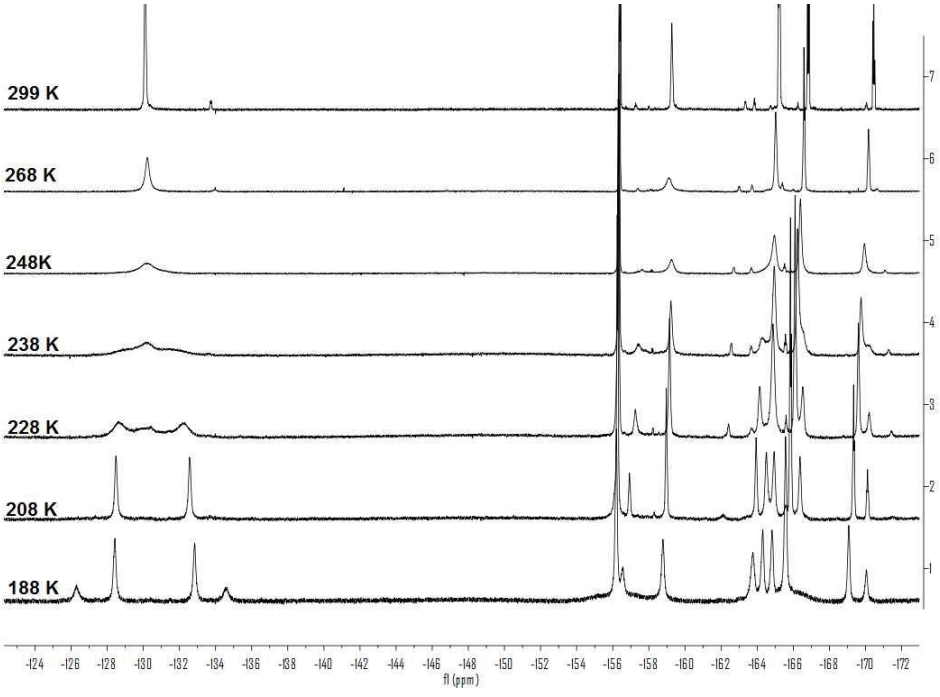
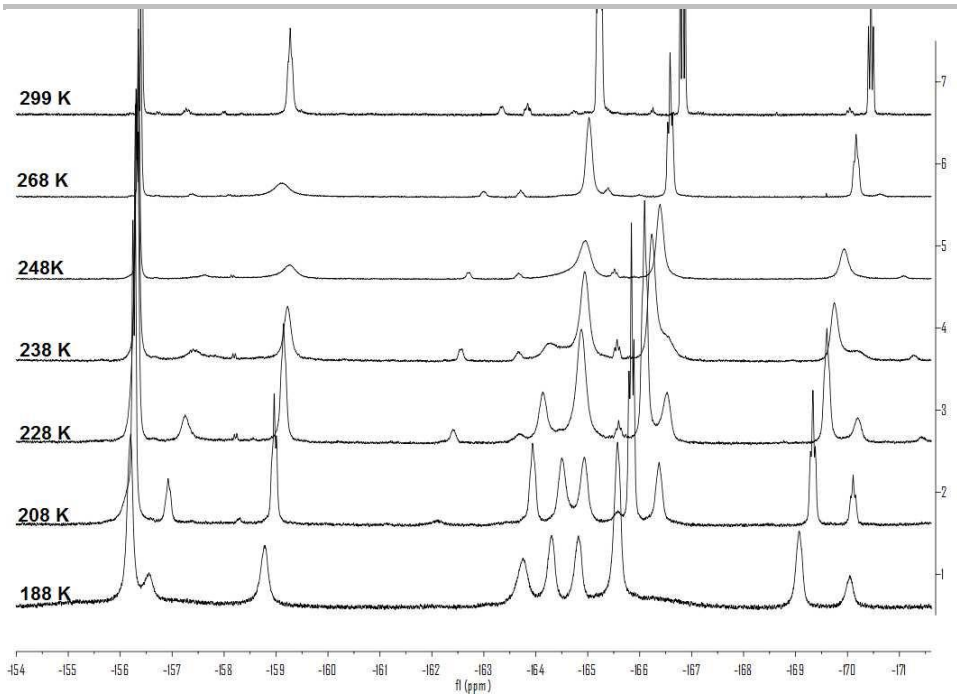


Figure S80. VT ^{19}F NMR (470 MHz, toluene-d_8) spectrum of compound **10**.

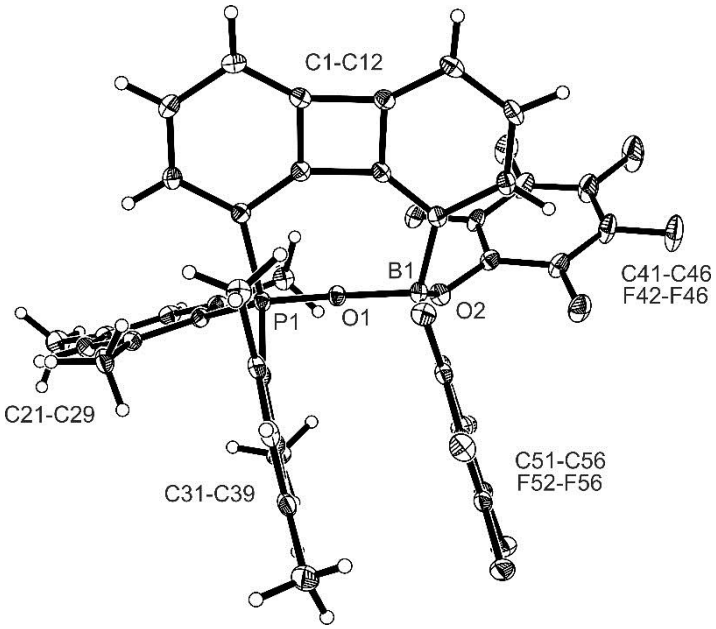




Crystals suitable for the *X*-ray crystal structure analysis were obtained from slow diffusion n-pentane to a solution of compound **10** in dichloromethane at -35 °C.

X-ray crystal structure analysis of compound 10 (erk8533): A pale yellow prism-like specimen of $C_{42}H_{28}BF_{10}O_2P$, approximate dimensions 0.200 mm x 0.233 mm x 0.240 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1641 frames were collected. The total exposure time was 21.73 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 71730 reflections to a maximum θ angle of 26.49° (0.80 Å resolution), of which 7092 were independent (average redundancy 10.114, completeness = 99.6%, R_{int} = 4.12%, R_{sig} = 2.16%) and 5772 (81.39%) were greater than $2\sigma(F^2)$. The final cell constants of a = 20.1789(11) Å, b = 14.4682(8) Å, c = 23.7982(13) Å, β = 98.115(2)°, volume = 6878.4(7) $Å^3$, are based upon the refinement of the XYZ-centroids of 9979 reflections above 20 σ(I) with 4.695° < 2θ < 52.79°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.952. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9590 and 0.9660. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *C*2/*c*, with Z = 8 for the formula unit, $C_{42}H_{28}BF_{10}O_2P$. The final anisotropic full-matrix least-squares refinement on F^2 with 511 variables converged at R1 = 3.98%, for the observed data and wR2 = 10.18% for all data. The goodness-of-fit was 1.024. The largest peak in the final difference electron density synthesis was 0.407 $e^-/Å^3$ and the largest hole was -0.340 $e^-/Å^3$ with an RMS deviation of 0.049 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.538 g/cm^3 and F(000), 3248 e^-.

Figure S81. Structure of compound **10**.



References

1 S. M. Kilyanek, X. Fang and R. F. Jordan, *Organometallics*, **2009**, *28*, 300-305.
2 (*a*) D. J. Parks, R. E. von H. Spence and W. E. Piers, *Angew. Chem. Int. Ed. Engl.*, **1995**, *34*, 809-811; (*b*) D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, **1998**, *17*, 5492–5503.