

# Phospha-Claisen Type Reactions at Frustrated Lewis Pair Frameworks

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## Supporting Information

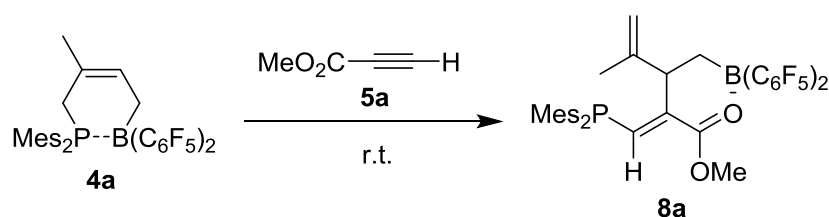
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**General Procedure.** All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Solvents were dried and stored under an argon atmosphere. NMR spectra were recorded on an Agilent DD2-500 MHz ( $^1\text{H}$ : 500 MHz,  $^{13}\text{C}$ : 126 MHz,  $^{19}\text{F}$ : 470 MHz,  $^{11}\text{B}$ : 160 MHz,  $^{31}\text{P}$ : 202 MHz) and on a Agilent DD2-600 MHz ( $^1\text{H}$ : 600 MHz,  $^{13}\text{C}$ : 151 MHz,  $^{19}\text{F}$ : 564 MHz,  $^{11}\text{B}$ : 192 MHz,  $^{31}\text{P}$ : 243 MHz).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR: chemical shifts are given relative to TMS and referenced to the solvent signal.  $^{19}\text{F}$  NMR: chemical shifts are given relative to  $\text{CFCl}_3$  ( $\delta = 0$ , external reference),  $^{11}\text{B}$  NMR: chemical shifts are given relative to  $\text{BF}_3\cdot\text{Et}_2\text{O}$  ( $\delta = 0$ , external reference),  $^{31}\text{P}$  NMR: chemical shifts are given relative to  $\text{H}_3\text{PO}_4$  (85% in  $\text{D}_2\text{O}$ ) ( $\delta = 0$ , external reference). NMR assignments were supported by additional 2D NMR experiments. Elemental analyses were performed on an Elementar Vario El III. Melting points and decomposition points were obtained with a DSC 2010 (TA Instruments).

**X-Ray diffraction:** For compounds **11a**, **12** and **16** 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 (Bruker AXS, **2000**). For compound **8a** data sets were collected with a Kappa CCD APEXII Bruker diffractometer. For compound **8b** data sets were collected with a D8 Venture Dual Source 100 CMOS diffractometer. Programs used: data collection: APEX2 V2014.5-0 (Bruker AXS Inc., **2014**); cell refinement: SAINT V8.34A (Bruker AXS Inc., **2013**); data reduction: SAINT V8.34A (Bruker AXS Inc., **2013**); absorption correction, SADABS V2014/2 (Bruker AXS Inc., **2014**); structure solution SHELXT-2014 (Sheldrick, 2014); structure refinement SHELXL-2014 (Sheldrick, **2014**) and graphics, XP (Bruker AXS Inc., **2014**). *R*-values are given for observed reflections, and  $wR^2$  values are given for all reflections. *Exceptions and special features:* For compound **8b** two badly disordered dichloromethane molecules and for compound **11a** one and a half badly disordered dichloromethane molecules were found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (A. L. Spek *J. Appl. Cryst.*, **2003**, 36, 7-13) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecules.

**Materials.** P/B FLPs **4a-c** [Moquist, P.; Chen, G.-Q.; Mück-Lichtenfeld, C.; Bussmann, K.; Daniliuc, C. G.; Kehr, G.; Erker, G. *Chem. Sci.* **2015**, 6, 816-825.] were prepared according to the literature.

## Synthesis of compound 8a



**Scheme S1**

A solution of compounds **4a** (102.3 mg, 0.15 mmol) and **5a** (12.6 mg, 0.15 mmol) in dichloromethane (3 mL) was stirred at room temperature for 5 h. Then all volatiles were removed in vacuo and compound **8a** (103.6 mg, 90 %) was obtained as a yellow solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **8a** in dichloromethane at -35 °C. **Decomp.** 157 °C. **Anal. Calc.** for C<sub>39</sub>H<sub>34</sub>BF<sub>10</sub>O<sub>2</sub>P: C: 61.12; H: 4.47. Found: C: 60.36; H: 4.50.

**<sup>1</sup>H NMR** (500 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>): δ = 8.23 (dd, <sup>2</sup>J<sub>PH</sub> = 7.1 Hz, <sup>4</sup>J<sub>HH</sub> = 1.4 Hz, 1H, =CH), 6.60 (dm, <sup>4</sup>J<sub>PH</sub> = 3.5 Hz, 4H, *m*-Mes), 4.40 (m, 1H, =CH<sup>E</sup>), 4.35 (s, 1H, =CH<sup>Z</sup>), 3.33 (d, *J* = 0.8 Hz, 3H, OCH<sub>3</sub>), 3.03 (m, 1H, CH), 2.15 (s, 12H, *o*-CH<sub>3</sub><sup>Mes</sup>), 2.01 (s, 6H, *p*-CH<sub>3</sub><sup>Mes</sup>), 1.79 (dd, <sup>2</sup>J<sub>HH</sub> = 15.1 Hz, <sup>3</sup>J<sub>HH</sub> = 6.3 Hz, 1H, CH<sub>2</sub>), 1.59 (dd, <sup>2</sup>J<sub>HH</sub> = 15.1 Hz, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 1H, CH<sub>2</sub>), 1.24 (s, 3H, CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (126 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>): δ = 174.9 (d, <sup>3</sup>J<sub>PC</sub> = 9.5 Hz, C=O), 158.9 (d, <sup>1</sup>J<sub>PC</sub> = 20.5 Hz, =CH), 146.1 (d, <sup>4</sup>J<sub>PC</sub> = 3.0 Hz, C=CH<sub>2</sub>), 143.1 (d, <sup>2</sup>J<sub>PC</sub> = 15.3 Hz, *o*-Mes), 140.0 (d, <sup>4</sup>J<sub>PC</sub> = 0.8 Hz, *p*-Mes), 130.3 (d, <sup>3</sup>J<sub>PC</sub> = 4.8 Hz, *m*-Mes), 128.9 (d, <sup>2</sup>J<sub>PC</sub> = 19.1 Hz, C=CH), 128.0 (*i*-Mes), 110.6 (d, <sup>5</sup>J<sub>PC</sub> = 1.4 Hz, =CH<sub>2</sub>), 56.8 (OCH<sub>3</sub>), 42.3 (d, <sup>3</sup>J<sub>PC</sub> = 3.3 Hz, CH), 23.5 (d, <sup>3</sup>J<sub>PC</sub> = 14.2 Hz, *o*-CH<sub>3</sub><sup>Mes</sup>), 22.2 (br, CH<sub>2</sub>), 20.8 (*p*-CH<sub>3</sub><sup>Mes</sup>), 20.4 (d, <sup>5</sup>J<sub>PC</sub> = 1.0 Hz, CH<sub>3</sub>), [C<sub>6</sub>F<sub>5</sub> not listed].

**<sup>11</sup>B{<sup>1</sup>H} NMR** (160 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>): δ = 3.4 (ν<sub>1/2</sub> ~ 700 Hz).

**<sup>31</sup>P{<sup>1</sup>H} NMR** (202 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>): δ = -28.9 (ν<sub>1/2</sub> ~ 2 Hz).

**<sup>19</sup>F NMR** (470 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>): δ = -134.5 (m, 2F, *o*), -158.5 (t, <sup>3</sup>J<sub>FF</sub> = 20.6 Hz, 1F, *p*), -163.9 (m, 2F, *m*)(C<sub>6</sub>F<sub>5</sub>)[Δδ<sup>19</sup>F<sub>mp</sub> = 5.4], -135.3 (m, 2F, *o*), -159.3 (t, <sup>3</sup>J<sub>FF</sub> = 20.7 Hz, 1F, *p*), -164.7 (m, 2F, *m*)(C<sub>6</sub>F<sub>5</sub>)[Δδ<sup>19</sup>F<sub>mp</sub> = 5.4].

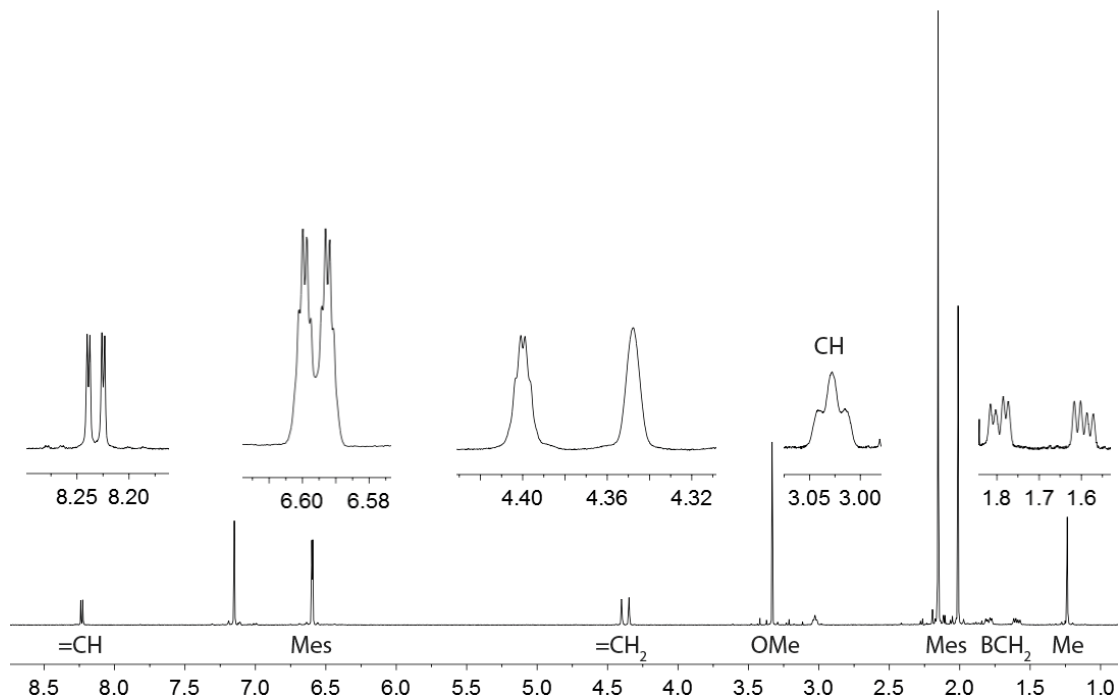
**<sup>1</sup>H, <sup>1</sup>H-GCOSY** (500 MHz / 500 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>)[selected traces]: δ <sup>1</sup>H / δ <sup>1</sup>H = 4.40, 4.35 / 1.24 (=CH<sup>E</sup>, =CH<sup>Z</sup> / CH<sub>3</sub>), 3.03 / 1.79, 1.59 (CH / CH<sub>2</sub>, CH<sub>2</sub>).

**<sup>1</sup>H, <sup>13</sup>C-GHSQC** (500 MHz / 126 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>): δ <sup>1</sup>H / δ <sup>13</sup>C = 8.23 / 158.9 (=CH), 6.60 / 130.3 (*m*-Mes), 4.40, 4.35 / 110.6 (=CH<sub>2</sub>), 3.33 / 56.8 (OCH<sub>3</sub>), 3.03 / 42.3 (CH), 2.15 / 23.5 (*o*-CH<sub>3</sub><sup>Mes</sup>), 2.01 / 20.8 (*p*-CH<sub>3</sub><sup>Mes</sup>), 1.79, 1.59 / 22.2 (CH<sub>2</sub>), 1.24 / 20.4 (CH<sub>3</sub>).

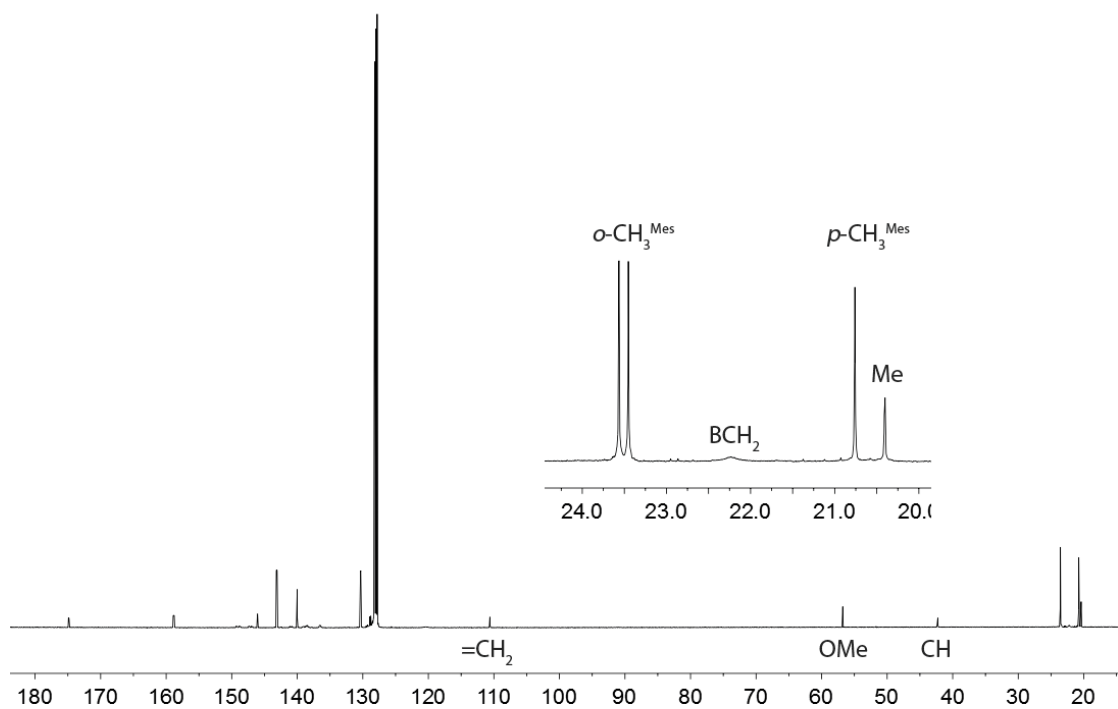
**<sup>1</sup>H, <sup>13</sup>C-GHMBC** (500 MHz / 126 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>)[selected traces]: δ <sup>1</sup>H / δ <sup>13</sup>C = 8.23, 6.60, 2.15 / 128.0 (=CH, *m*-Mes, *o*-CH<sub>3</sub><sup>Mes</sup> / *i*-Mes), 8.23, 3.33, 3.03 / 174.9 (=CH, OCH<sub>3</sub>, CH / C=O), 8.23, 3.03, 1.79, 1.59 / 128.9 (=CH, CH, CH<sub>2</sub>, CH<sub>2</sub> / C=CH), 4.35,

3.03, 1.79, 1.59, 1.24 / 146.1 ( $=CH_2^Z$ , CH,  $CH_2$ ,  $CH_2$ ,  $CH_3$  /  $C=CH_2$ ), 2.15 / 143.1 ( $o-CH_3^{Mes}$  /  $o-Mes$ ), 2.01 / 140.0 ( $p-CH_3^{Mes}$  /  $p-Mes$ ).

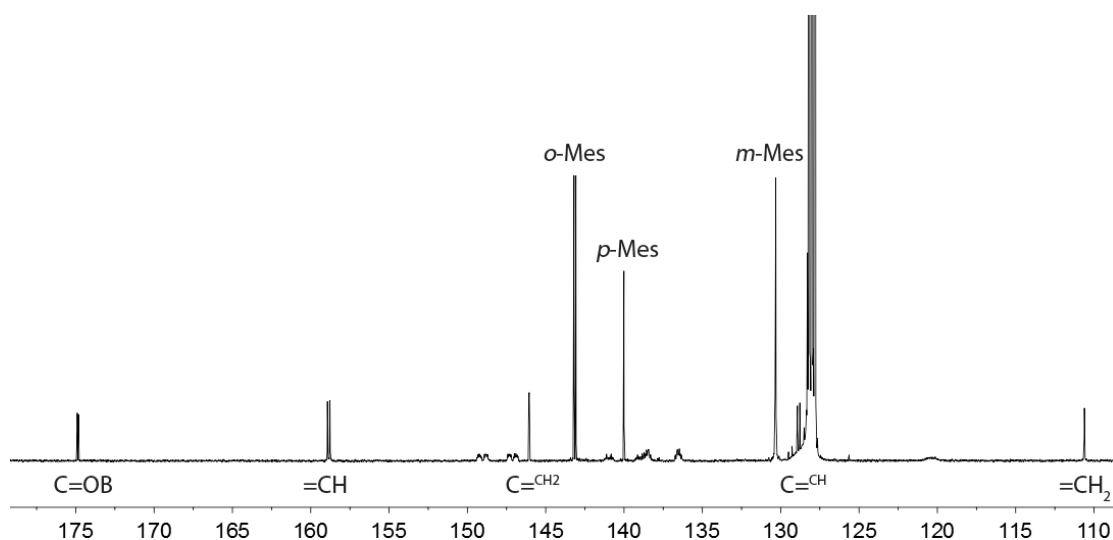
$^{19}F$ ,  $^{19}F$ -GCOSY (470 MHz / 470 MHz, 299 K,  $C_6D_6$ ):  $\delta^{19}F$  /  $\delta^{19}F$  = -163.9 / -134.5, -158.5 ( $m-C_6F_5^a$  /  $o-C_6F_5^a$ ,  $p-C_6F_5^a$ ), -164.7 / -135.3, -159.3 ( $m-C_6F_5^b$  /  $o-C_6F_5^b$ ,  $p-C_6F_5^b$ ).



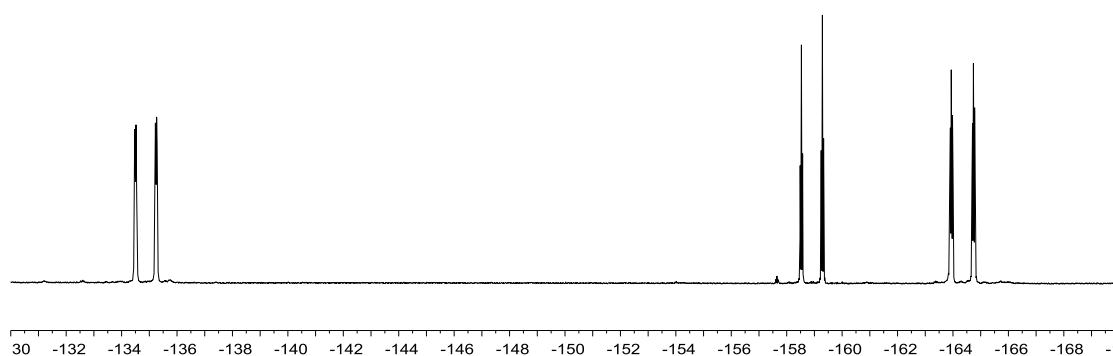
**Figure S1.**  $^1H$  NMR (500 MHz, 299 K,  $C_6D_6$ ) of compound **8a**



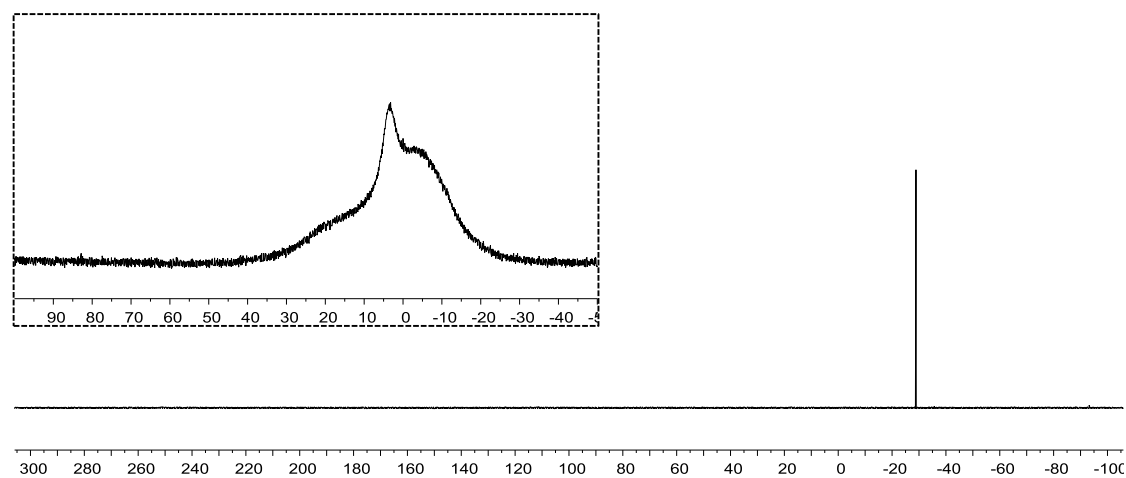
**Figure S2.**  $^{13}C\{^1H\}$  NMR (126 MHz, 299 K,  $C_6D_6$ ) of compound **8a**



**Figure S3.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) of compound **8a**

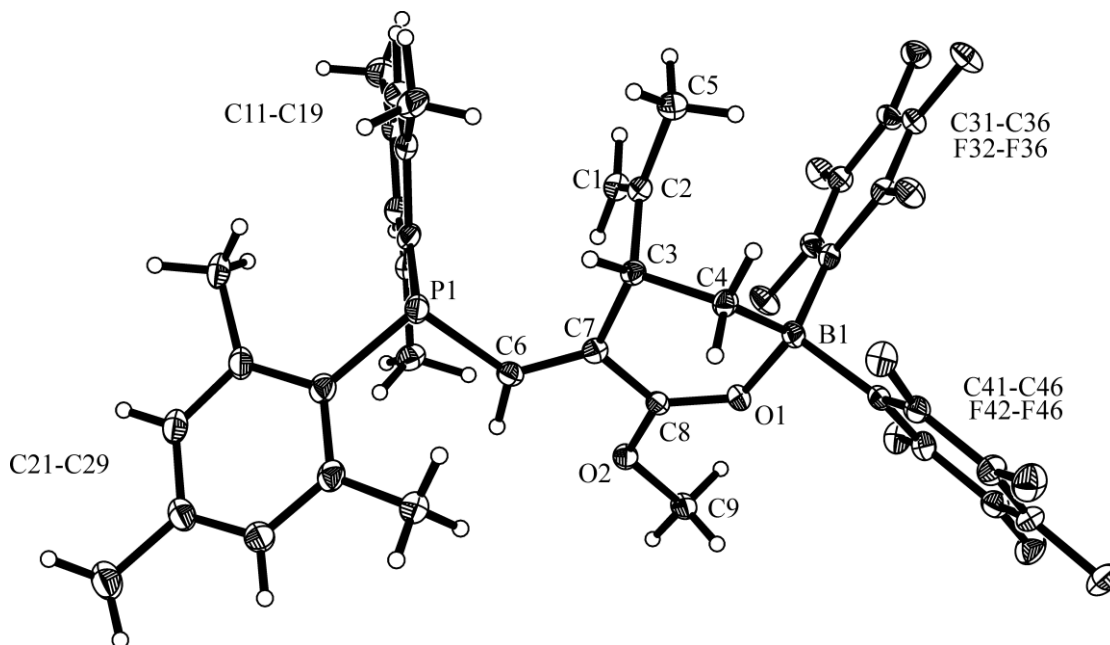


**Figure S4.**  $^{19}\text{F}$  NMR (470 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) of compound **8a**



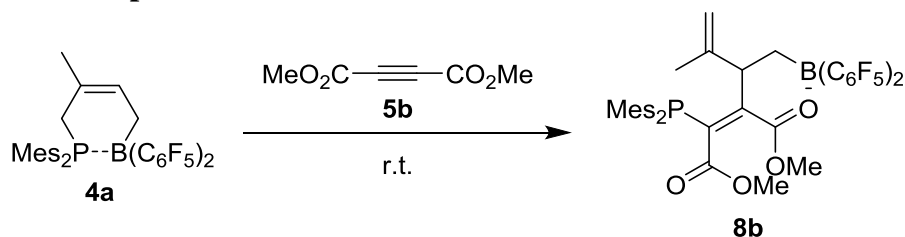
**Figure S5.**  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) of compound **8a**

**X-ray crystal structure analysis of compound 8a:** A yellow plate-like specimen of  $C_{39}H_{34}BF_{10}O_2P$ , approximate dimensions 0.020 mm x 0.100 mm x 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1140 frames were collected. The total exposure time was 25.93 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 31721 reflections to a maximum  $\theta$  angle of  $65.08^\circ$  ( $0.85 \text{ \AA}$  resolution), of which 6011 were independent (average redundancy 5.277, completeness = 99.4%,  $R_{\text{int}} = 9.03\%$ ,  $R_{\text{sig}} = 6.89\%$ ) and 3973 (66.10%) were greater than  $2\sigma(F^2)$ . The final cell constants of  $a = 11.4134(15) \text{ \AA}$ ,  $b = 20.663(3) \text{ \AA}$ ,  $c = 15.422(2) \text{ \AA}$ ,  $\beta = 102.950(8)^\circ$ , volume =  $3544.5(8) \text{ \AA}^3$ , are based upon the refinement of the XYZ-centroids of 4481 reflections above  $20 \sigma(I)$  with  $7.273^\circ < 2\theta < 132.9^\circ$ . Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.849. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8430 and 0.9710. The final anisotropic full-matrix least-squares refinement on  $F^2$  with 486 variables converged at  $R1 = 5.24\%$ , for the observed data and  $wR2 = 13.91\%$  for all data. The goodness-of-fit was 1.065. The largest peak in the final difference electron density synthesis was  $0.258 \text{ e}^-/\text{\AA}^3$  and the largest hole was  $-0.341 \text{ e}^-/\text{\AA}^3$  with an RMS deviation of  $0.065 \text{ e}^-/\text{\AA}^3$ . On the basis of the final model, the calculated density was  $1.436 \text{ g/cm}^3$  and  $F(000)$ , 1576  $e^-$ .



**Figure S6.**

## Synthesis of compound 8b



**Scheme S2**

A solution of compounds **4a** (102.3 mg, 0.15 mmol) and **5b** (21.3 mg, 0.15 mmol) in pentane (3 mL) was stirred at room temperature for 1 h. Then all volatiles were removed in vacuo and the residue was washed with cold pentane (3x1 mL). After drying in vacuo compound **8b** (102.6 mg, 83 %) was obtained as an orange solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **8b** in dichloromethane at -35 °C. **Decomp.** 179 °C. **Anal. Calc.** for  $\text{C}_{41}\text{H}_{36}\text{BF}_{10}\text{O}_4\text{P}$ : C: 59.73; H: 4.40. Found: C: 59.11; H: 4.22.

**$^1\text{H}$  NMR** (500 MHz, 299 K,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 6.61 (dm,  $^4J_{\text{PH}}$  = 3.6 Hz, 4H, *m*-Mes), 4.52 (br, 1H, =CH<sub>2</sub>), 4.41 (m, 1H, =CH<sub>2</sub>), 3.67 (m, 1H, CH), 3.37 (s, 3H, OCH<sub>3</sub><sup>B</sup>), 2.81 (s, 3H, OCH<sub>3</sub>), 2.30 (s, 12H, *o*-CH<sub>3</sub><sup>Mes</sup>), 2.02 (dd,  $^2J_{\text{HH}}$  = 15.2 Hz,  $^3J_{\text{HH}}$  = 5.9 Hz, 1H, CH<sub>2</sub>), 1.99 (s, 6H, *p*-CH<sub>3</sub><sup>Mes</sup>), 1.73 (dd,  $^2J_{\text{HH}}$  = 15.3 Hz,  $^3J_{\text{HH}}$  = 7.5 Hz, 1H, CH<sub>2</sub>), 1.37 (s, 3H, CH<sub>3</sub>).

**$^{13}\text{C}\{^1\text{H}\}$  NMR** (126 MHz, 299 K,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 174.4 (d,  $^3J_{\text{PC}}$  = 7.8 Hz, C=OB), 166.5 (C=O), 162.5 (d,  $^1J_{\text{PC}}$  = 39.8 Hz, =CP), 145.1 (d,  $^4J_{\text{PC}}$  = 1.5 Hz, C=CH<sub>2</sub>), 144.6 (d,  $^2J_{\text{PC}}$  = 18.0 Hz, *o*-Mes), 140.3 (d,  $^4J_{\text{PC}}$  = 1.0 Hz, *p*-Mes), 131.8 (d,  $^2J_{\text{PC}}$  = 34.0 Hz, =C), 130.3 (d,  $^3J_{\text{PC}}$  = 5.4 Hz, *m*-Mes), 126.4 (d,  $^1J_{\text{PC}}$  = 12.4 Hz, *i*-Mes), 111.6 (d,  $^5J_{\text{PC}}$  = 1.8 Hz, =CH<sub>2</sub>), 57.4 (OCH<sub>3</sub><sup>B</sup>), 51.4 (OCH<sub>3</sub>), 45.6 (d,  $^3J_{\text{PC}}$  = 15.7 Hz, CH), 23.2 (d,  $^3J_{\text{PC}}$  = 16.7 Hz, *o*-CH<sub>3</sub><sup>Mes</sup>), 23.1 (br, CH<sub>2</sub>), 20.8 (*p*-CH<sub>3</sub><sup>Mes</sup>), 20.4 (d,  $^5J_{\text{PC}}$  = 2.3 Hz, CH<sub>3</sub>), [ $\text{C}_6\text{F}_5$  not listed].

**$^{11}\text{B}\{^1\text{H}\}$  NMR** (160 MHz, 299 K,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 4.0 ( $\nu_{1/2}$  ~ 750 Hz).

**$^{31}\text{P}\{^1\text{H}\}$  NMR** (202 MHz, 299 K,  $\text{C}_6\text{D}_6$ ):  $\delta$  = -28.2 ( $\nu_{1/2}$  ~ 10 Hz).

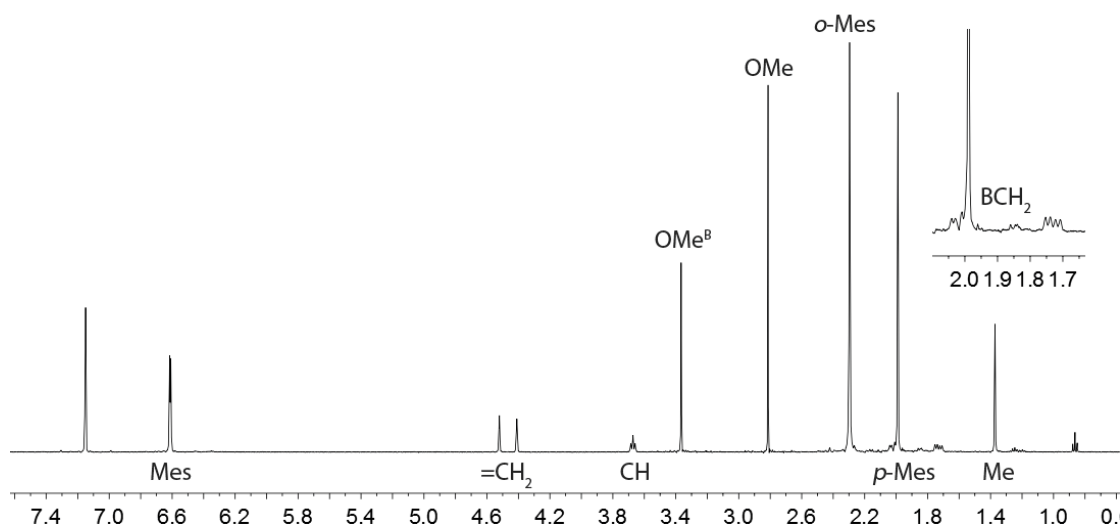
**$^{19}\text{F}$  NMR** (470 MHz, 299 K,  $\text{C}_6\text{D}_6$ ):  $\delta$  = -134.0 (m, 2F, *o*), -158.1 (t,  $^3J_{\text{FF}}$  = 20.6 Hz, 1F, *p*), -163.9 (m, 2F, *m*)( $\text{C}_6\text{F}_5$ )[ $\Delta\delta^{19}\text{F}_{\text{mp}}$  = 5.8], -135.5 (m, 2F, *o*), -159.0 (t,  $^3J_{\text{FF}}$  = 20.7 Hz, 1F, *p*), -164.4 (m, 2F, *m*)( $\text{C}_6\text{F}_5$ )[ $\Delta\delta^{19}\text{F}_{\text{mp}}$  = 5.4].

**$^1\text{H}$ ,  $^1\text{H}$ -GCOSY** (500 MHz / 500 MHz, 299 K,  $\text{C}_6\text{D}_6$ )[selected traces]:  $\delta$   $^1\text{H}$  /  $\delta$   $^1\text{H}$  = 4.52, 4.41 / 1.37 (=CH<sub>2</sub>, =CH<sub>2</sub> / CH<sub>3</sub>), 3.67 / 2.02, 1.73 (CH / CH<sub>2</sub>, CH<sub>2</sub>).

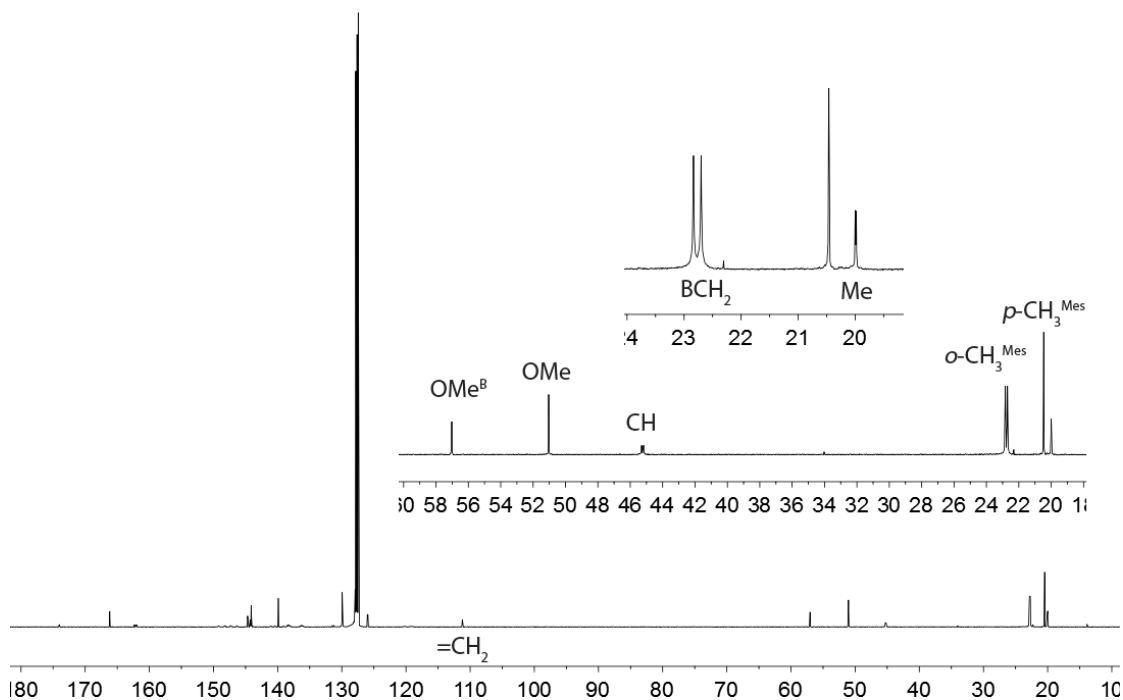
**$^1\text{H}$ ,  $^{13}\text{C}$ -GHSQC** (500 MHz / 126 MHz, 299 K,  $\text{C}_6\text{D}_6$ ):  $\delta$   $^1\text{H}$  /  $\delta$   $^{13}\text{C}$  = 6.61 / 130.3 (*m*-Mes), 4.52, 4.41 / 111.6 (=CH<sub>2</sub>), 3.67 / 45.6 (CH), 3.37 / 57.4 (OCH<sub>3</sub><sup>B</sup>), 2.81 / 51.4 (OCH<sub>3</sub>), 2.30 / 23.2 (*o*-CH<sub>3</sub><sup>Mes</sup>), 2.02, 1.73 (CH<sub>2</sub>), 1.99 / 20.8 (*p*-CH<sub>3</sub><sup>Mes</sup>), 1.37 / 20.4 (CH<sub>3</sub>).

**$^1\text{H}$ ,  $^{13}\text{C}$ -GHMBC** (500 MHz / 126 MHz, 299 K,  $\text{C}_6\text{D}_6$ )[selected traces]:  $\delta\ ^1\text{H} / \delta\ ^{13}\text{C} =$  6.61, 2.30 / 126.4 (*m*-Mes, *o*- $\text{CH}_3^{\text{Mes}}$  / *i*-Mes), 4.52, 3.67, 2.02, 1.73, 1.37 / 145.1 ( $=\text{CH}_2$ , CH,  $\text{CH}_2$ ,  $\text{CH}_2$ ,  $\text{CH}_3 / =\text{C}^{\text{CH}_2}$ ), 3.67, 3.37 / 174.4 (CH,  $\text{OCH}_3^{\text{B}}$  /  $\text{C}=\text{O}$ ), 3.67, 2.02, 1.73 / 131.8 (CH,  $\text{CH}_2$ ,  $\text{CH}_2 / =\text{C}$ ), 3.67 / 162.5 (CH /  $=\text{CP}$ ), 2.81 / 166.5 ( $\text{OCH}_3 / \text{C}=\text{O}$ ), 2.30 / 144.6 (*o*- $\text{CH}_3^{\text{Mes}}$  / *o*-Mes), 1.99 / 140.3 (*p*- $\text{CH}_3^{\text{Mes}}$  / *p*-Mes).

**$^{19}\text{F}$ ,  $^{19}\text{F}$ -GCOSY** (470 MHz / 470 MHz, 299 K,  $\text{C}_6\text{D}_6$ ):  $\delta\ ^{19}\text{F} / \delta\ ^{19}\text{F} =$  -163.9 / -134.0, -158.1 (*m*- $\text{C}_6\text{F}_5^{\text{a}}$  / *o*- $\text{C}_6\text{F}_5^{\text{a}}$ , *p*- $\text{C}_6\text{F}_5^{\text{a}}$ ), -164.4 / -135.5, -159.0 (*m*- $\text{C}_6\text{F}_5^{\text{b}}$  / *o*- $\text{C}_6\text{F}_5^{\text{b}}$ , *p*- $\text{C}_6\text{F}_5^{\text{b}}$ ).

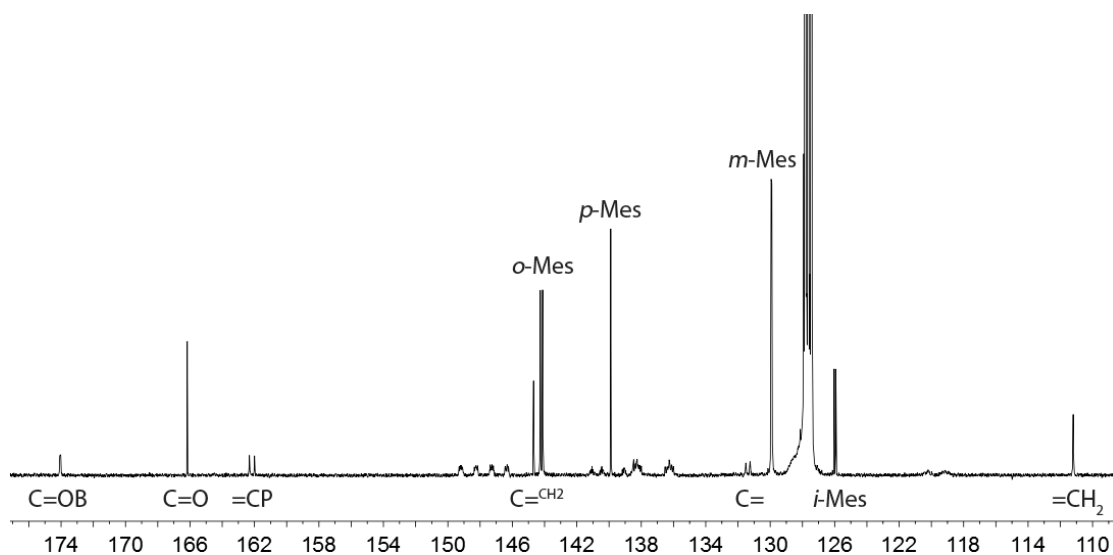


**Figure S7.**  $^1\text{H}$  NMR (500 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) of compound **8b** [admixed with pentane]

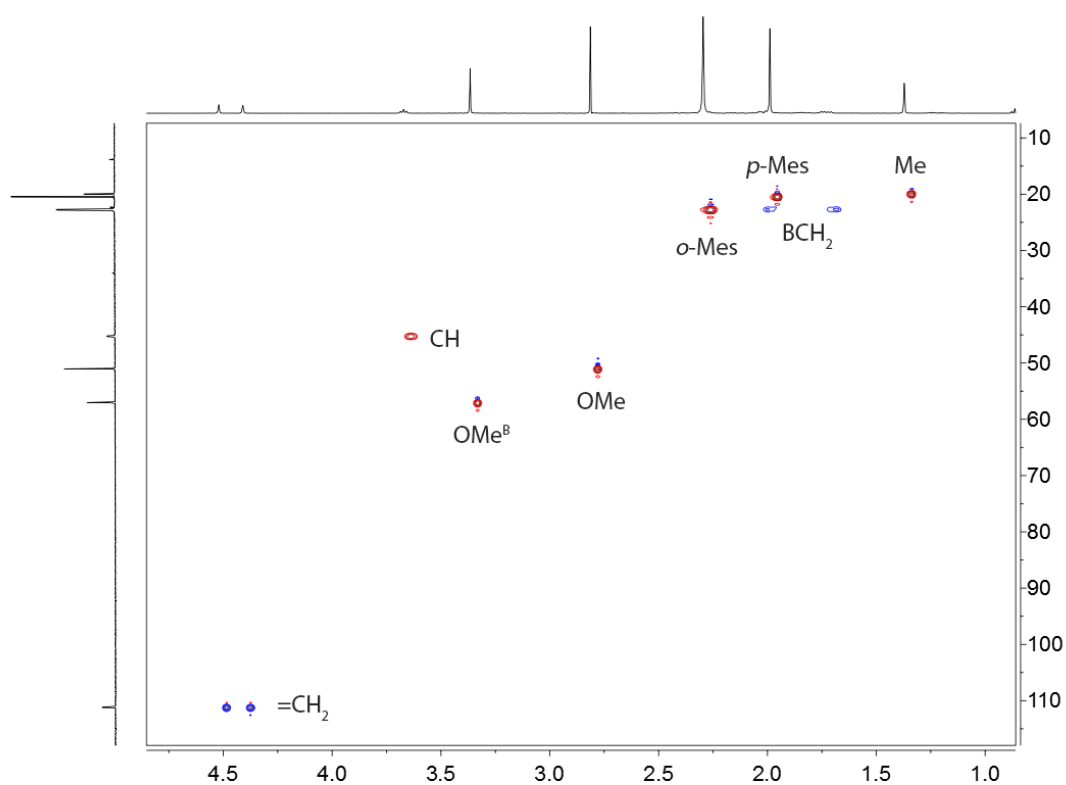


**Figure S8.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) of compound **8b** [admixed with pentane]

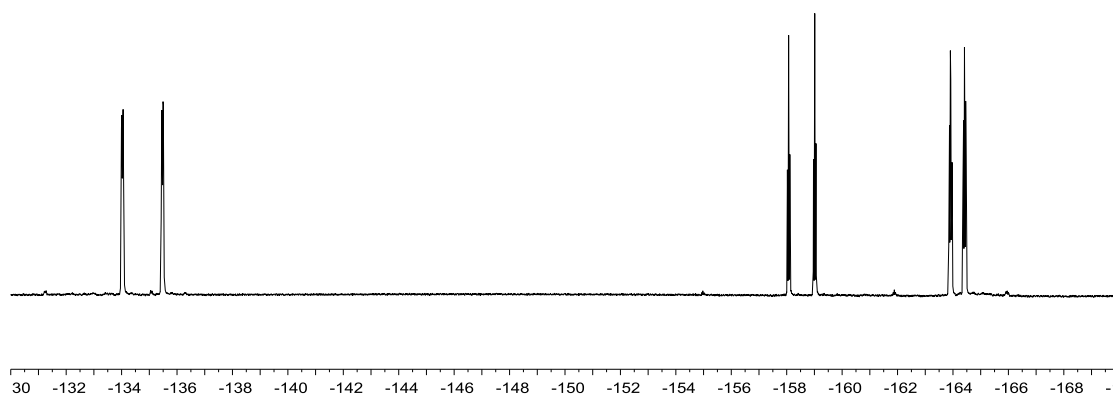




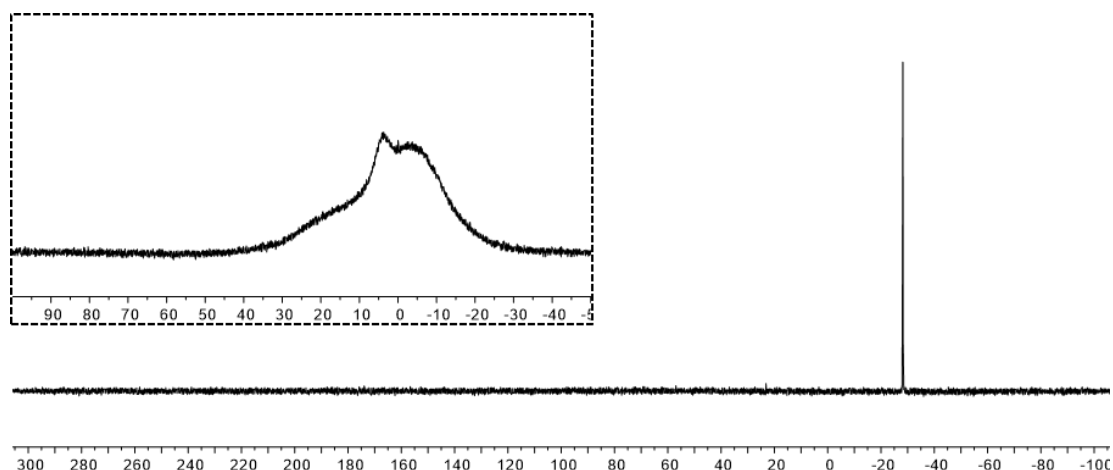
**Figure S9.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) of compound **8b**



**Figure S10.**  $^1\text{H}$ ,  $^{13}\text{C}$ -GHSQC (500 MHz / 126 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) of compound **8b**



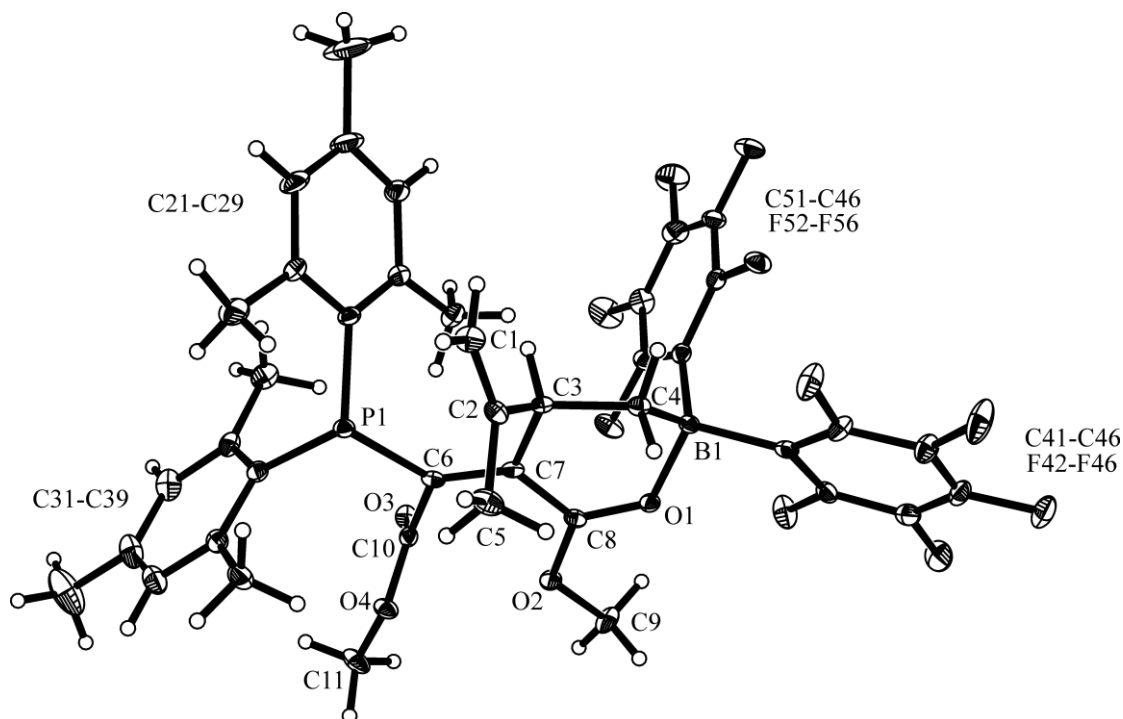
**Figure S11.**  $^{19}\text{F}$  NMR (470 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) of compound **8b**



**Figure S12.**  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) of compound **8b**

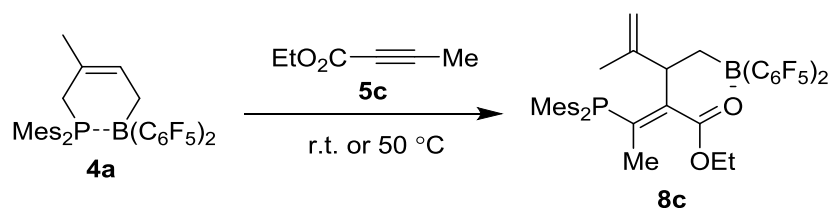
**X-ray crystal structure analysis of compound 8b:** A yellow prism-like specimen of  $\text{C}_{41}\text{H}_{36}\text{BF}_{10}\text{O}_4\text{P}$ , approximate dimensions 0.099 mm x 0.170 mm x 0.257 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 511 frames were collected. The total exposure time was 4.26 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 8176 reflections to a maximum  $\theta$  angle of  $25.35^\circ$  ( $0.83 \text{ \AA}$  resolution), of which 8176 were independent (average redundancy 1.000, completeness = 96.5%,  $R_{\text{int}} = 4.47\%$ ,  $R_{\text{sig}} = 6.73\%$ ) and 5669 (69.34%) were greater than  $2\sigma(F^2)$ . The final cell constants of  $a = 11.3650(5) \text{ \AA}$ ,  $b = 14.8236(7) \text{ \AA}$ ,  $c = 16.1305(7) \text{ \AA}$ ,  $\alpha = 65.606(2)^\circ$ ,  $\beta = 70.053(2)^\circ$ ,  $\gamma = 77.352(2)^\circ$ , volume =  $2316.74(19) \text{ \AA}^3$ , are based upon the refinement of the XYZ-centroids of 5798 reflections above  $20 \sigma(I)$  with  $4.660^\circ < 2\theta < 54.83^\circ$ . Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.931. The calculated minimum and maximum transmission

coefficients (based on crystal size) are 0.9660 and 0.9870. 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,  $C_{41}H_{36}BF_{10}O_4P$ . The final anisotropic full-matrix least-squares refinement on  $F^2$  with 523 variables converged at  $R1 = 5.72\%$ , for the observed data and  $wR2 = 16.48\%$  for all data. The goodness-of-fit was 1.048. The largest peak in the final difference electron density synthesis was  $0.502 \text{ e}^-/\text{\AA}^3$  and the largest hole was  $-0.274 \text{ e}^-/\text{\AA}^3$  with an RMS deviation of  $0.067 \text{ e}^-/\text{\AA}^3$ . On the basis of the final model, the calculated density was  $1.182 \text{ g/cm}^3$  and  $F(000)$ , 848  $e^-$ .



**Figure S13.**

## Synthesis of compound 8c



**Scheme S3**

A solution of compounds **4a** (102.3 mg, 0.15 mmol) and **5c** (16.8 mg, 0.15 mmol) in dichloromethane (3 mL) was heated at 50 °C for 1 day (or alternatively stirred at room temperature for 7 days). Then all volatiles were removed in vacuo and compound **8c** (109.1 mg, 92 %) was obtained as an orange solid. **Decomp.** 173 °C. **Anal. Calc.** for  $\text{C}_{41}\text{H}_{38}\text{BF}_{10}\text{O}_2\text{P}$ : C: 61.98; H: 4.82. Found: C:62.39; H:4.71.

**$^1\text{H}$  NMR** (600 MHz, 299 K,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 6.59 (dm,  $^4J_{\text{PH}}$  = 3.4 Hz, 4H, *m*-Mes), 4.63 (br, 1H, =CH<sub>2</sub>), 4.59 (m, 1H, =CH<sub>2</sub>), 4.06 (q,  $^3J_{\text{HH}}$  = 7.2 Hz, 2H, OEt), 3.44 (m, 1H, CH), 2.10 (dd,  $^2J_{\text{HH}}$  = 15.1 Hz,  $^3J_{\text{HH}}$  = 6.3 Hz, 1H, CH<sub>2</sub>), 2.01 (m, 12H, *o*-CH<sub>3</sub><sup>Mes</sup>), 2.01 (s, 6H, *p*-CH<sub>3</sub><sup>Mes</sup>), 1.70 (d,  $^3J_{\text{PH}}$  = 5.7 Hz, 3H, <sup>P</sup>CH<sub>3</sub>), 1.61 (dd,  $^2J_{\text{HH}}$  = 15.1 Hz,  $^3J_{\text{HH}}$  = 8.9 Hz, 1H, CH<sub>2</sub>), 1.58 (m, 3H, CH<sub>3</sub>), 0.40 (t,  $^3J_{\text{HH}}$  = 7.2 Hz, 3H, OEt).

**$^{13}\text{C}\{^1\text{H}\}$  NMR** (151 MHz, 299 K,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 175.7 (C=OB), 170.3 (d,  $^1J_{\text{PC}}$  = 42.9 Hz, =CP), 148.1 (d,  $^4J_{\text{PC}}$  = 3.6 Hz, C=CH<sub>2</sub>), 142.6 (d,  $^3J_{\text{PC}}$  = 17.0 Hz, *o*-Mes), 139.1 (*p*-Mes), 134.4 (d,  $^2J_{\text{PC}}$  = 24.3 Hz, =C), 131.1 (d,  $^1J_{\text{PC}}$  = 12.5 Hz, *i*-Mes), 130.2 (d,  $^3J_{\text{PC}}$  = 4.6 Hz, *m*-Mes), 110.6 (=CH<sub>2</sub>), 68.2 (OEt), 46.1 (CH), 24.0 (br, CH<sub>2</sub>), 23.1 (br d,  $^3J_{\text{PC}}$  = 16.3 Hz, *o*-CH<sub>3</sub><sup>Mes</sup>), 23.0 (d,  $^2J_{\text{PC}}$  = 2.0 Hz, <sup>P</sup>CH<sub>3</sub>), 20.79 (CH<sub>3</sub>), 20.77 (*p*-CH<sub>3</sub><sup>Mes</sup>), 12.5 (OEt), [ $\text{C}_6\text{F}_5$  not listed].

**$^{11}\text{B}\{^1\text{H}\}$  NMR** (160 MHz, 299 K,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 2.8 ( $\nu_{1/2}$  ~ 500 Hz).

**$^{10}\text{B}\{^1\text{H}\}$  NMR** (54 MHz, 299 K,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 2.8 ( $\nu_{1/2}$  ~ 550 Hz).

**$^{31}\text{P}\{^1\text{H}\}$  NMR** (243 MHz, 299 K,  $\text{C}_6\text{D}_6$ ):  $\delta$  = -11.0 (m).

**$^{19}\text{F}$  NMR** (564 MHz, 299 K,  $\text{C}_6\text{D}_6$ ):  $\delta$  = -134.1 (m, 2F, *o*), -158.3 (t,  $^3J_{\text{FF}}$  = 20.6 Hz, 1F, *p*), -163.8 (m, 2F, *m*)( $\text{C}_6\text{F}_5$ )[ $\Delta\delta^{19}\text{F}_{\text{mp}}$  = 5.5], -135.5 (m, 2F, *o*), -159.2 (t,  $^3J_{\text{FF}}$  = 20.5 Hz, 1F, *p*), -164.5 (m, 2F, *m*)( $\text{C}_6\text{F}_5$ )[ $\Delta\delta^{19}\text{F}_{\text{mp}}$  = 5.3].

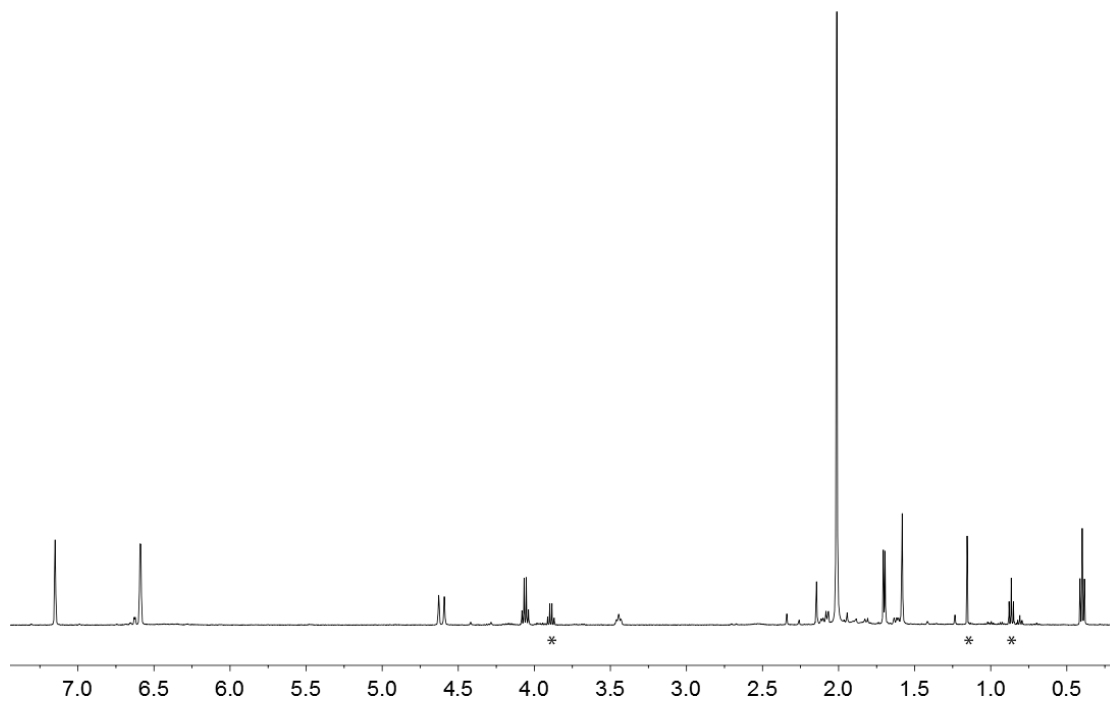
**$^1\text{H}$ ,  $^1\text{H}$ -GCOSY** (600 MHz / 600 MHz, 299 K,  $\text{C}_6\text{D}_6$ )[selected traces]:  $\delta$   $^1\text{H}$  /  $\delta$   $^1\text{H}$  = 4.63, 4.60 / 1.58 (=CH<sub>2</sub>, =CH<sub>2</sub> / CH<sub>3</sub>), 3.44 / 2.10, 1.61 (CH / CH<sub>2</sub>, CH<sub>2</sub>).

**$^1\text{H}$ ,  $^{13}\text{C}$ -GHSQC** (600 MHz / 151 MHz, 299 K,  $\text{C}_6\text{D}_6$ ):  $\delta$   $^1\text{H}$  /  $\delta$   $^{13}\text{C}$  = 6.59 / 130.2 (*m*-Mes), 4.63, 4.59 / 110.6 (=CH<sub>2</sub>), 4.06 / 68.2 (OEt), 3.44 / 46.1 (CH), 2.10, 1.61 / 24.0 (CH<sub>2</sub>), 2.01 / 23.1 (*o*-CH<sub>3</sub><sup>Mes</sup>), 2.01 / 20.77 (*p*-CH<sub>3</sub><sup>Mes</sup>), 1.70 / 23.0 (<sup>P</sup>CH<sub>3</sub>), 1.58 / 20.79 (CH<sub>3</sub>), 0.40 / 12.5 (OEt).

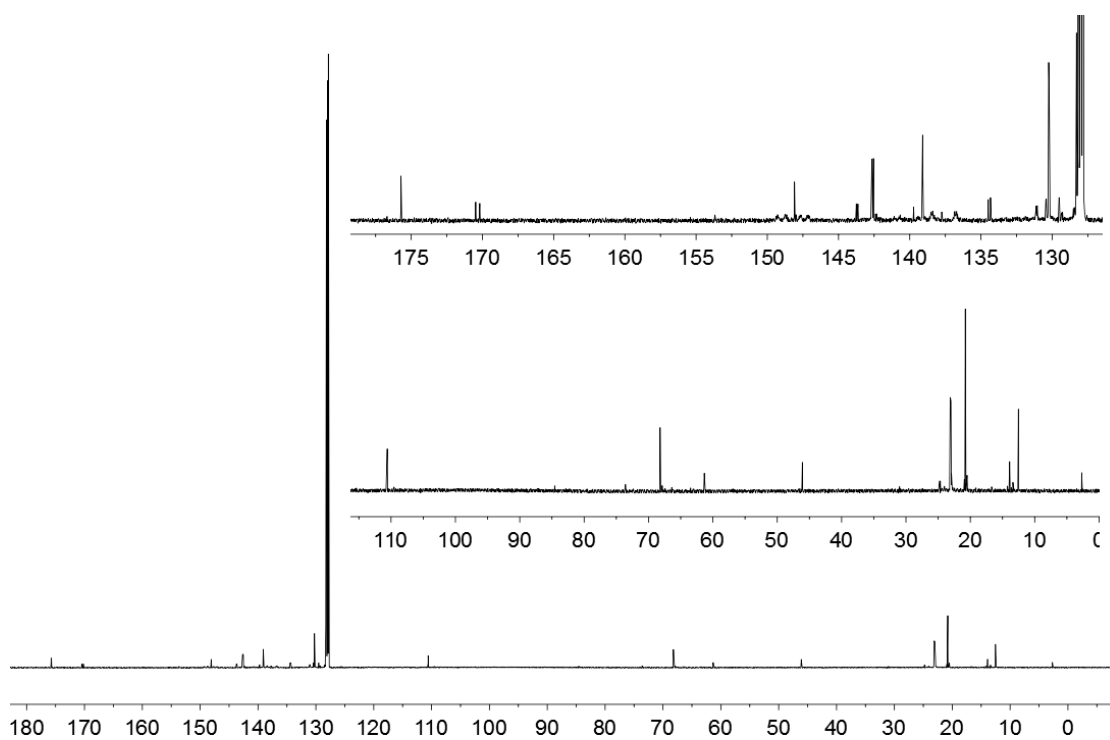
**$^1\text{H}$ ,  $^{13}\text{C}$ -GHMBC** (600 MHz / 151 MHz, 299 K,  $\text{C}_6\text{D}_6$ )[selected traces]:  $\delta$   $^1\text{H}$  /  $\delta$   $^{13}\text{C}$  = 6.59, 2.01 / 131.1 (*m*-Mes, *o*-CH<sub>3</sub><sup>Mes</sup> / *i*-Mes), 4.63, 4.59, 3.44, 2.10, 1.61, 1.58 / 148.1 (=CH<sub>2</sub>, =CH<sub>2</sub>, CH, CH<sub>2</sub>, CH<sub>2</sub>, CH<sub>3</sub> / C=CH<sub>2</sub>), 4.06, 3.44 / 175.7 (OEt, CH / C=OB), 3.44,

2.10, 1.70, 1.61 / 134.4 (CH, CH<sub>2</sub>, <sup>P</sup>CH<sub>3</sub>, CH<sub>2</sub> / =CCH), 3.44, 1.70 / 170.3 (CH, <sup>P</sup>CH<sub>3</sub> / =CP), 2.01 / 139.1 (*p*-CH<sub>3</sub><sup>Mes</sup> / *p*-Mes), 2.01 / 142.6 (*o*-CH<sub>3</sub><sup>Mes</sup> / *o*-Mes).

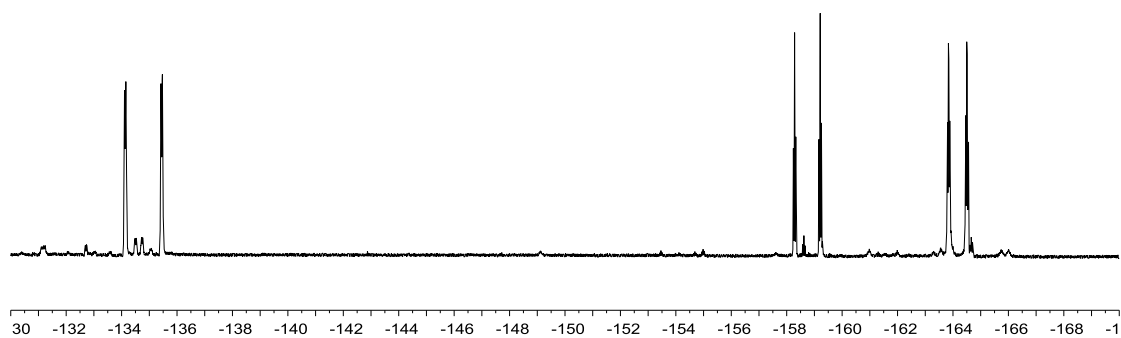
<sup>19</sup>F, <sup>19</sup>F-GCOSY (564 MHz / 564 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>): δ <sup>19</sup>F / δ <sup>19</sup>F = -163.8 / -134.1, -158.3 (*m*-C<sub>6</sub>F<sub>5</sub><sup>a</sup> / *o*-C<sub>6</sub>F<sub>5</sub><sup>a</sup>, *p*-C<sub>6</sub>F<sub>5</sub><sup>a</sup>), -164.5 / -135.5, -159.2 (*m*-C<sub>6</sub>F<sub>5</sub><sup>b</sup> / *o*-C<sub>6</sub>F<sub>5</sub><sup>b</sup>, *p*-C<sub>6</sub>F<sub>5</sub><sup>b</sup>).



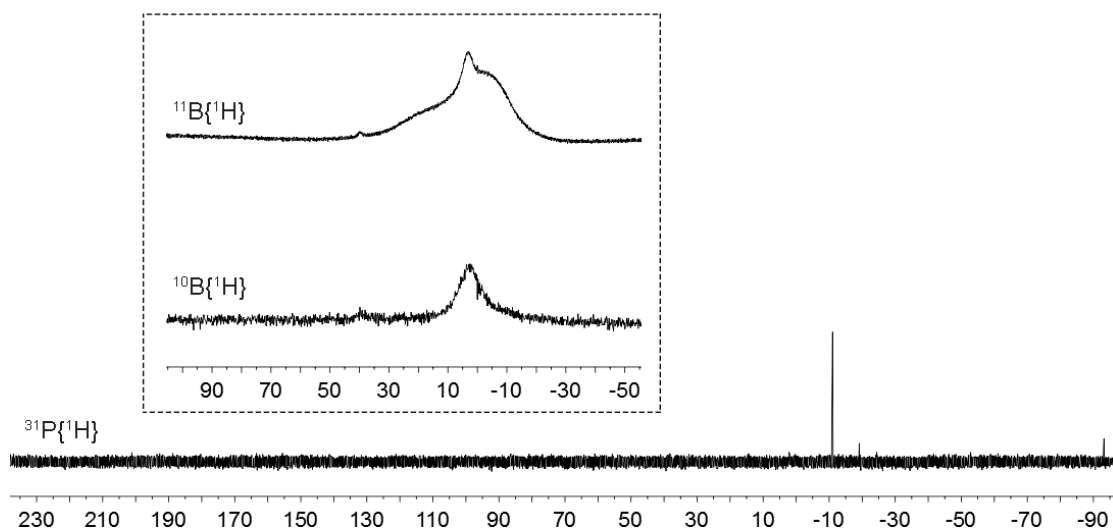
**Figure S14.** <sup>1</sup>H NMR (500 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>) of compound **8c** [admixed with EtO<sub>2</sub>C-C≡C-Me (\*)]



**Figure S15.** <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>) of compound **8c** [admixed with EtO<sub>2</sub>C-C≡C-Me



**Figure S16.**  $^{19}\text{F}$  NMR (470 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) of compound **8c**



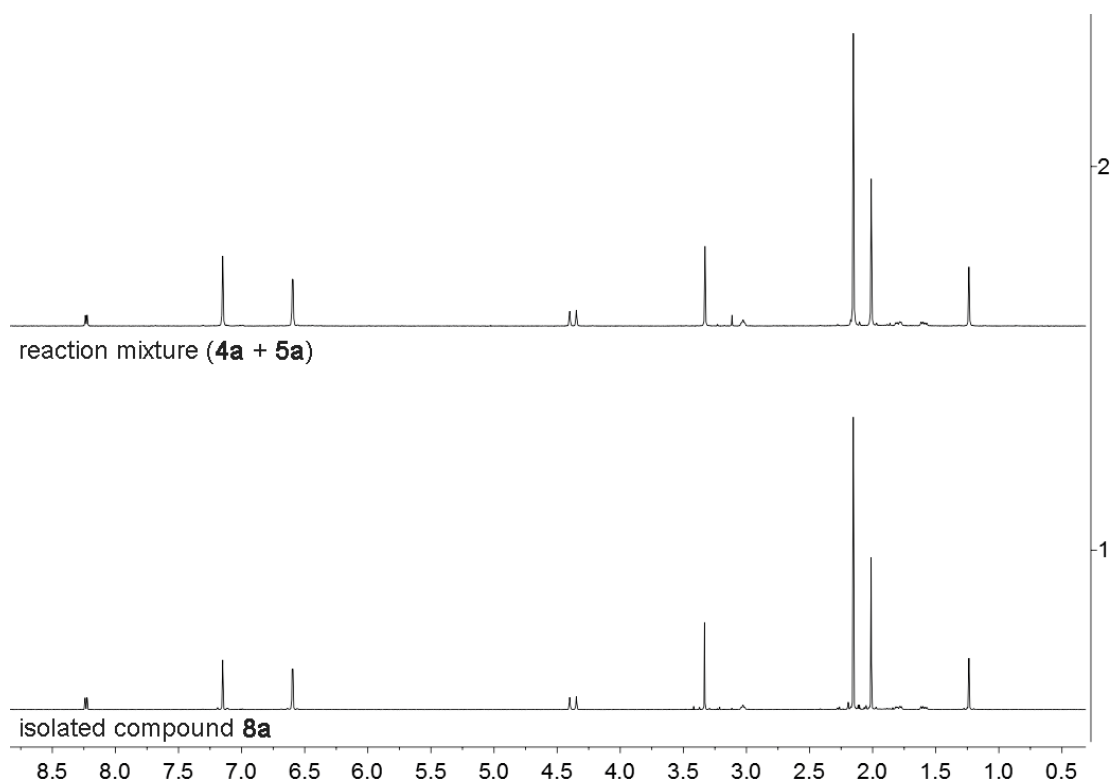
**Figure S17.**  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, 299 K,  $\text{C}_6\text{D}_6$ ),  $^{10}\text{B}\{^1\text{H}\}$  NMR (54 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) of compound **8c**

### Control experiments (4a + 5a,b,c: NMR scale)

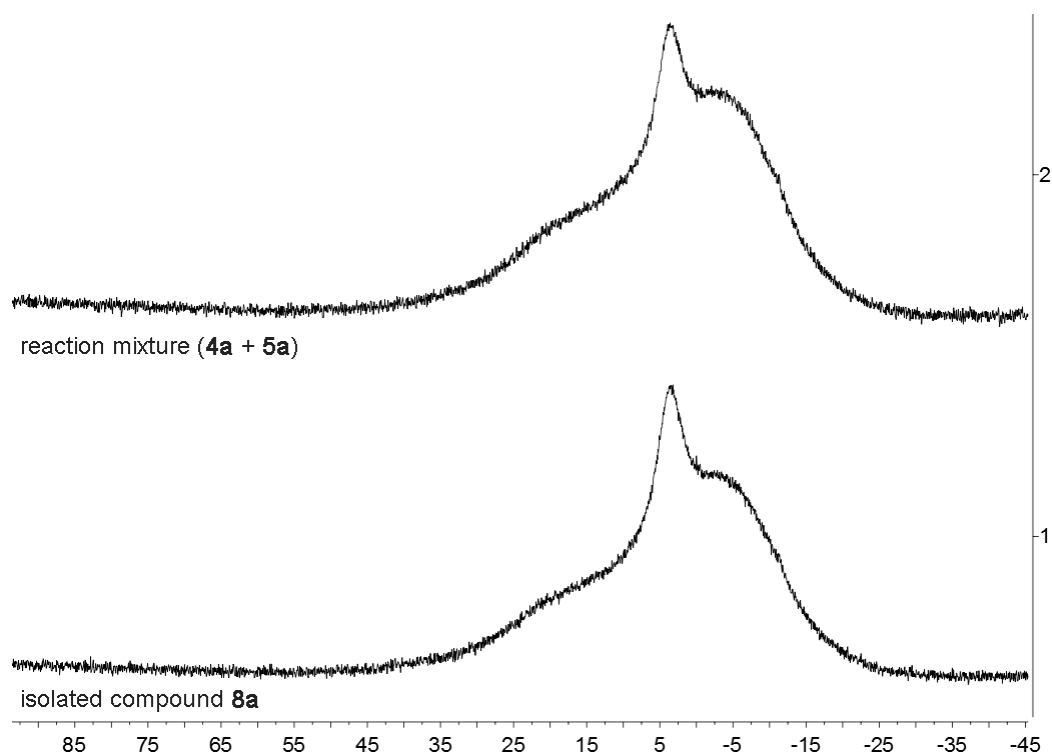
*Reactions of compound 4a with the alkynes 5a, 5b and 5c, respectively, monitored by NMR spectroscopy*

Alkyne **5a** (0.03 mmol, 2.5 mg) [**5b** (0.03 mmol, 4.3 mg), **5c** (0.03 mmol, 3.4 mg)] was added to a solution of compound **4a** (0.03 mmol, 20.5 mg) in C<sub>6</sub>D<sub>6</sub> (0.5 mL). Then the reaction mixture was transferred to a NMR tube and monitored by NMR spectroscopy.

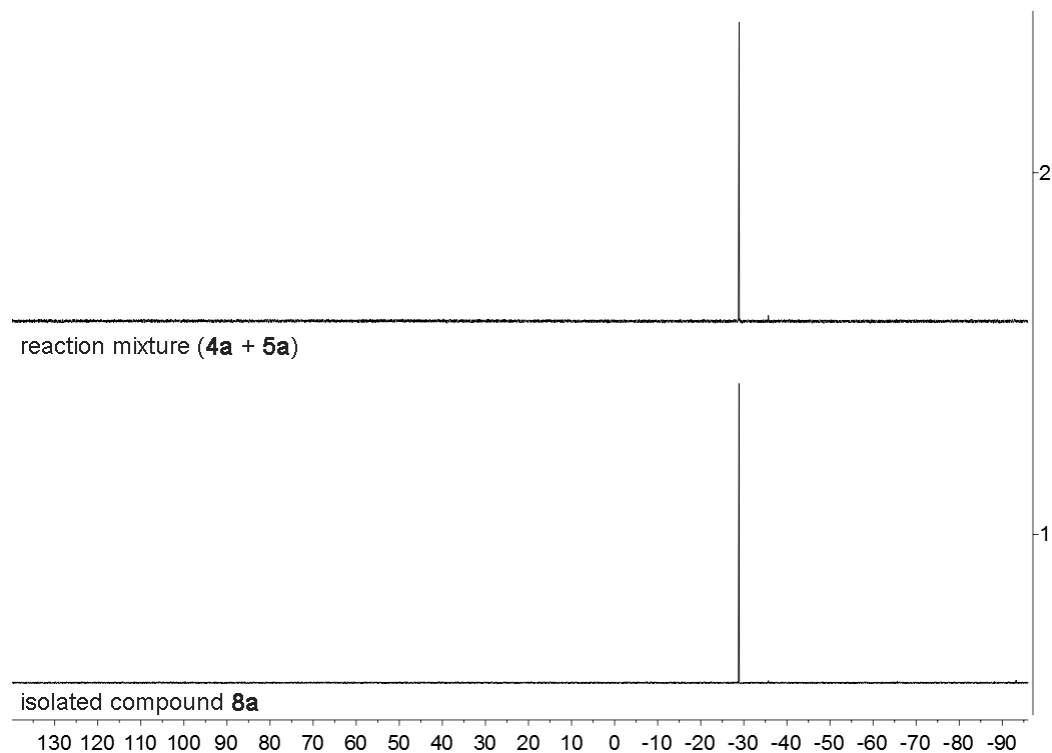
Comment 1: NMR spectra showed that the reactions of compound **4a** with the alkynes **5a** or **5b** were finished in less than 10 min. after mixing the components at r.t. to give compounds **8a** and **8b**, respectively, in quantitative yields.



**Figure S18.** <sup>1</sup>H NMR (500 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>) spectra of (1) isolated compound **8a** and (2) the reaction mixture of the reaction of compounds **4a** with **5a**

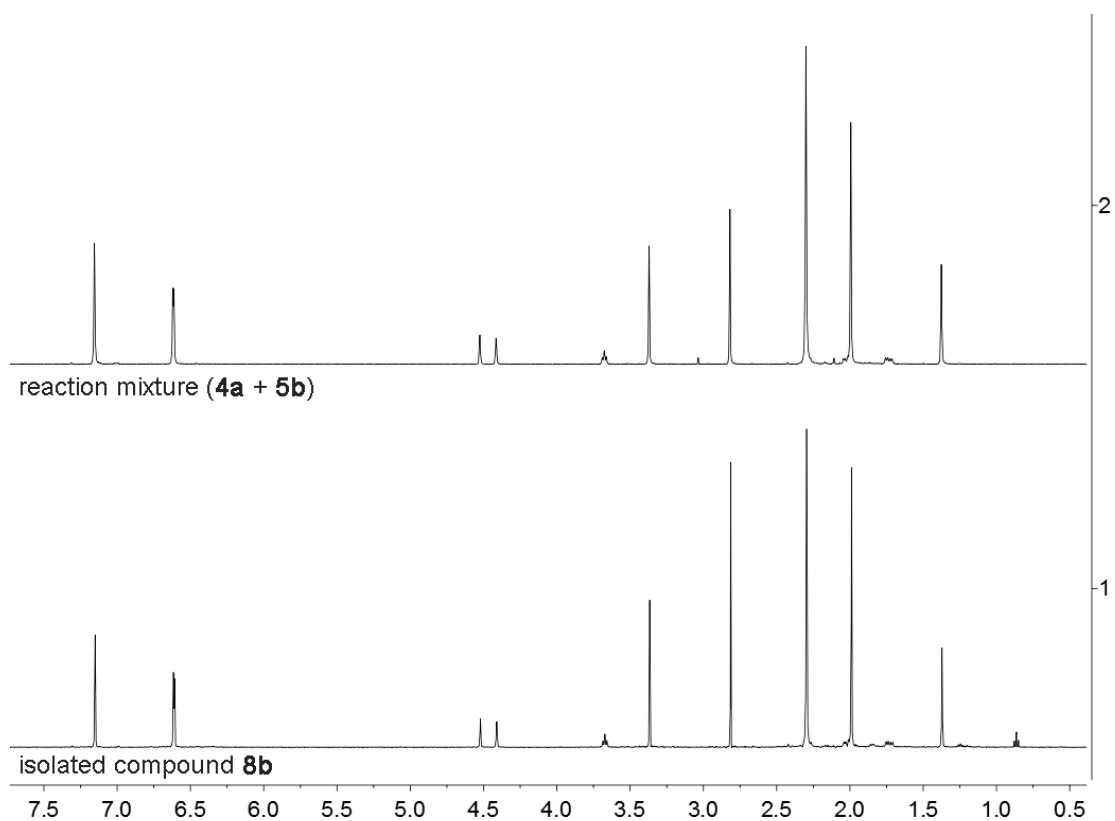


**Figure S19.**  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectra of (1) isolated compound **8a** and (2) the reaction mixture of the reaction of compounds **4a** with **5a**

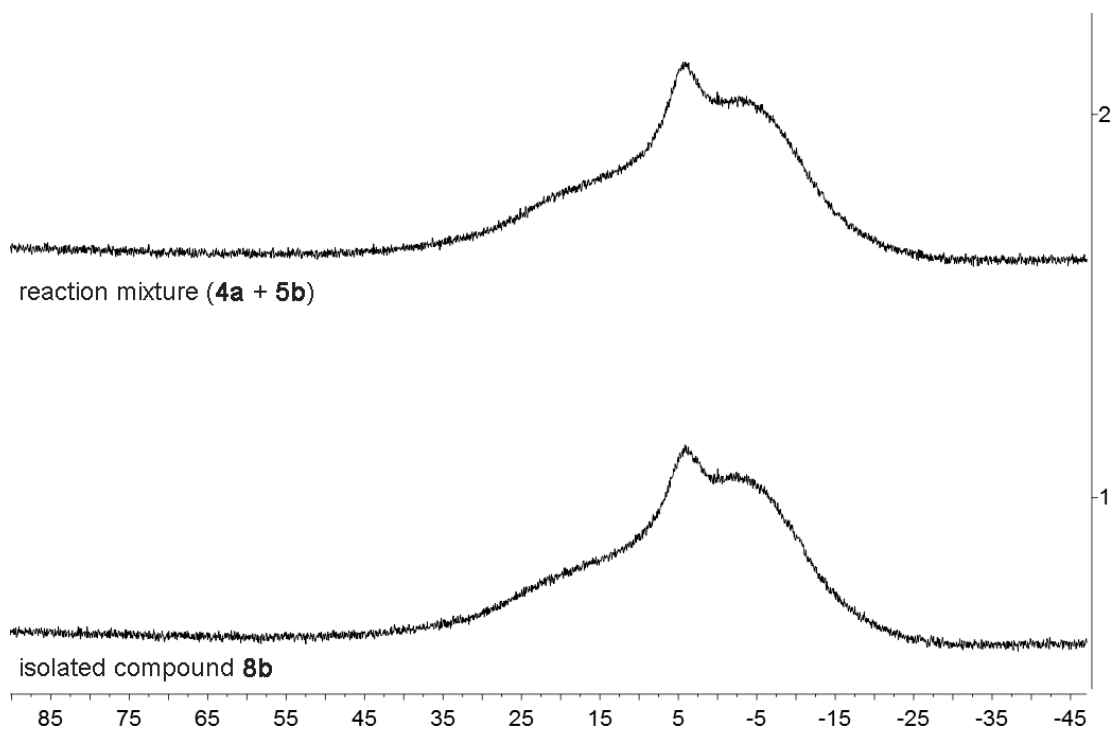


**Figure S20.**  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectra of (1) isolated compound **8a** and (2) the reaction mixture of the reaction of compounds **4a** with **5a**

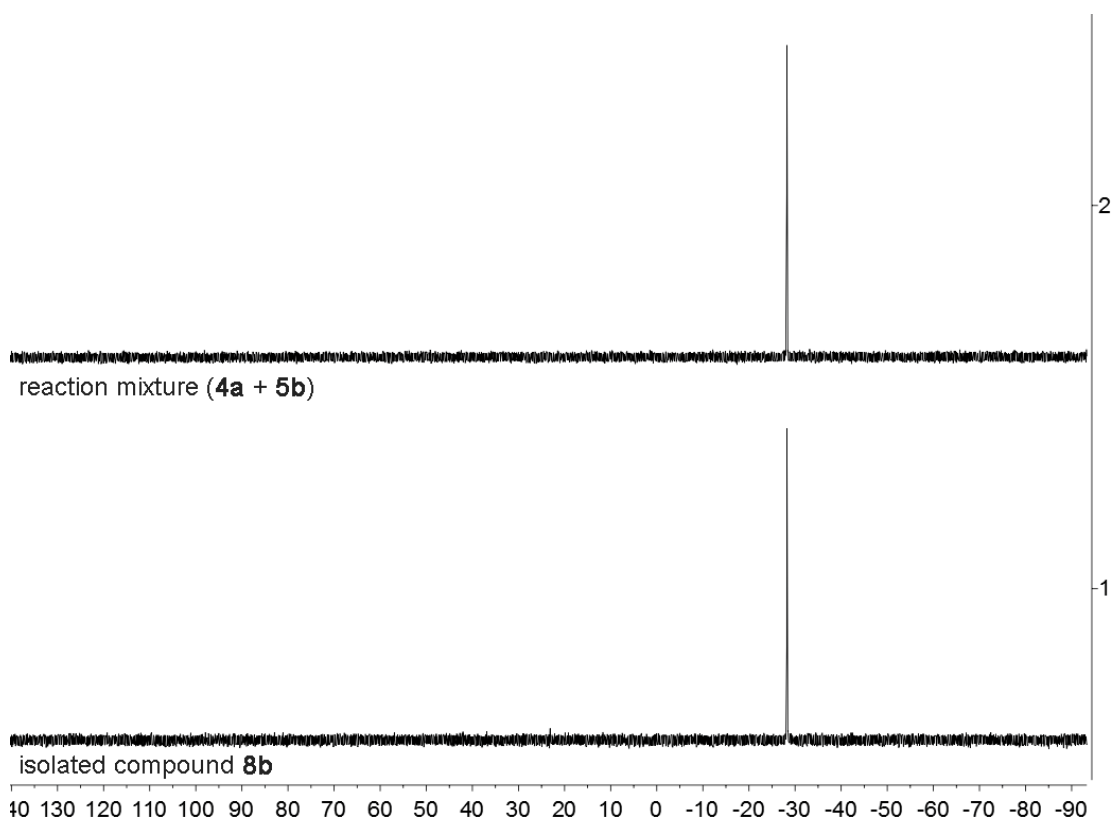




**Figure S21.**  $^1\text{H}$  NMR (500 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectra of (1) isolated compound **8b** and (2) the reaction mixture of the reaction of compounds **4a** with **5b**



**Figure S22.**  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectra of (1) isolated compound **8b** and (2) the reaction mixture of the reaction of compounds **4a** with **5b**

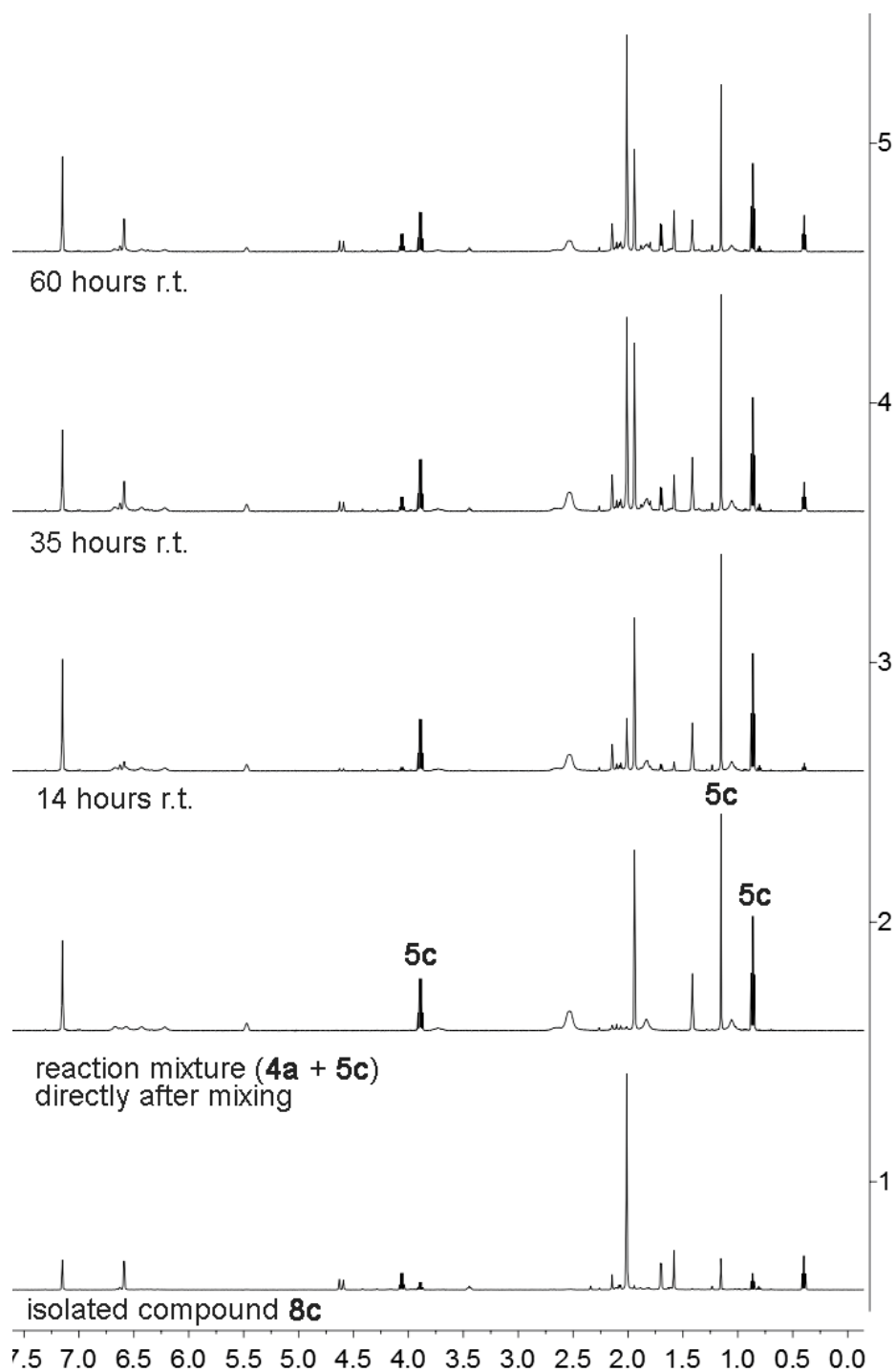


**Figure S23.**  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectra of (1) isolated compound **8b** and (2) the reaction mixture of the reaction of compounds **4a** with **5b**

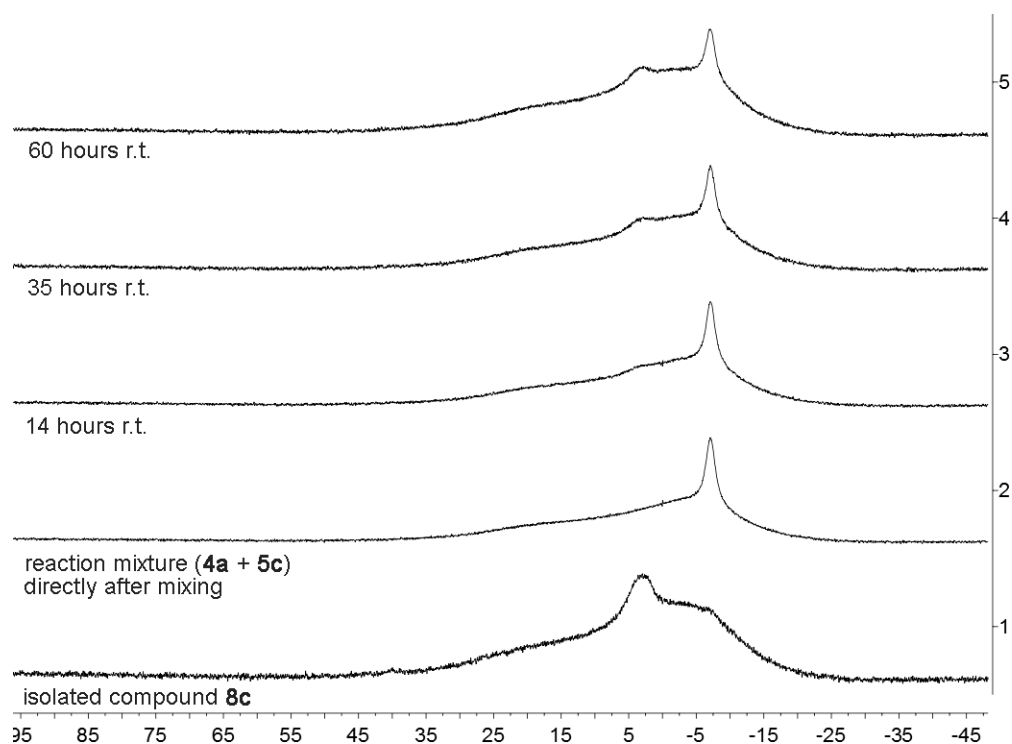
Comment 2: The reaction of compound **4a** with alkyne **5c** was not completed after 60 hours at r.t.:

a) directly after mixing: reaction mixture of compounds **4a** (ca. 53 mol%,  $^1\text{H}$ ) and **5c**, (ca. 47 mol%,  $^1\text{H}$ ) was observed.

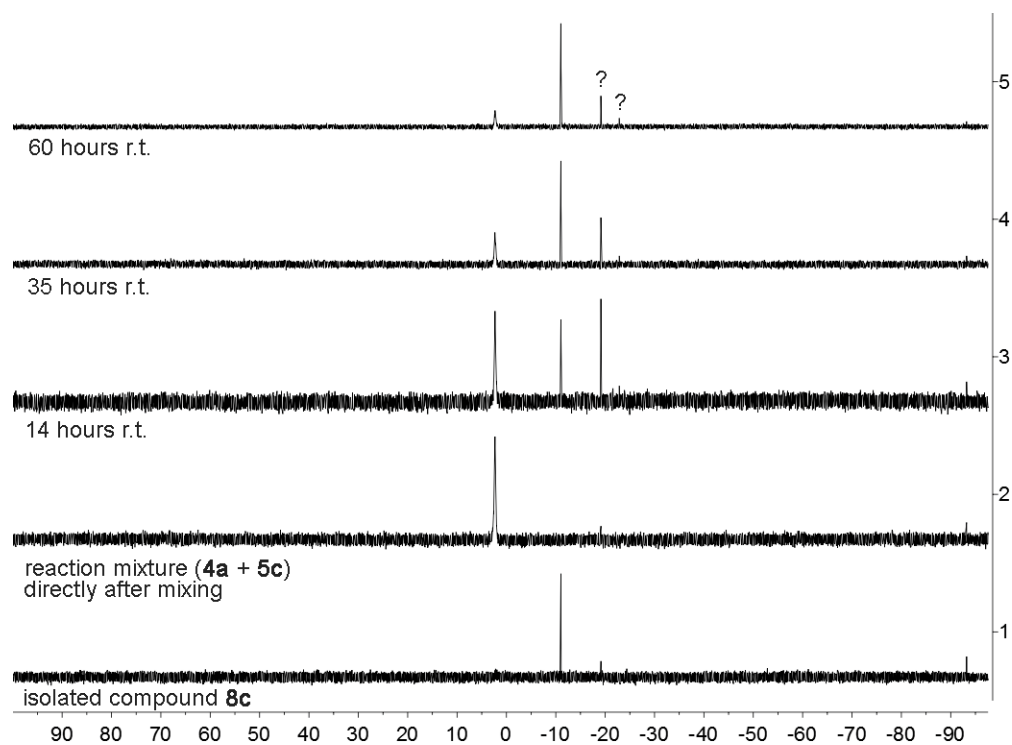
b) after 60 hours r.t.: reaction mixture of compounds **4a** (32 mol%,  $^1\text{H}$ ), **5c** (ca. 40 mol%,  $^1\text{H}$ ), and **8c** (28 mol%,  $^1\text{H}$ ) was observed.



**Figure S24. Figure S51.**  $^1\text{H}$  NMR (500 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectra of (1) isolated compound **8c** and (2 to 5) the reaction mixture of the reaction of compounds **4a** with **5c**

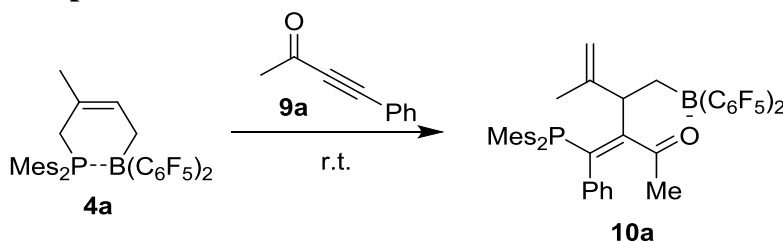


**Figure S25.**  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectra of (1) isolated compound **8c** and (2 to 5) the reaction mixture of the reaction of compounds **4a** with **5c**



**Figure S26.** (1)  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectrum of isolated compound **8c** and (2 to 5)  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectra of the reaction mixture of the reaction of compounds **4a** with **5c** [after 60 hours: **4a** (ca. 48 mol%), **8c** (ca. 41 mol%), ? (ca. 7 and 4 mol%)]

## Synthesis of compound 10a



Scheme S4

A solution of compounds **4a** (102.3 mg, 0.15 mmol) and **9a** (21.6 mg, 0.15 mmol) in dichloromethane (3 mL) was stirred at room temperature for 1 day. Then all volatiles were removed in vacuo and compound **10a** (111.8 mg, 90 %) was obtained as a dark red solid. **Decomp.** 168 °C. **Anal. Calc.** for C<sub>45</sub>H<sub>38</sub>BF<sub>10</sub>OP: C: 65.39; H: 4.63. Found: C: 65.23; H: 4.67.

**<sup>1</sup>H NMR** (600 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>): δ = 7.56 (m, 1H, *o*-Ph), 6.91 (m, 1H, *o*'-Ph), 6.77 (m, 1H, *p*-Ph), 6.74 (m, 1H, *m*-Ph), 6.68 (m, 1H, *m*'-Ph), 6.47 (d, <sup>4</sup>*J*<sub>PH</sub> = 3.6 Hz, 4H, *m*-Mes), 4.33 (s, 1H, =CH<sub>2</sub>), 4.16 (s, 1H, =CH<sub>2</sub>), 3.67 (m, 1H, CH), 2.17 (s, 12H, *o*-CH<sub>3</sub><sup>Mes</sup>), 2.08 (m, 2H, CH<sub>2</sub>), 1.89 (s, 6H, *p*-CH<sub>3</sub><sup>Mes</sup>), 1.63 (d, <sup>5</sup>*J*<sub>PH</sub> = 5.0 Hz, 3H, <sup>O=C</sup>CH<sub>3</sub>), 0.99 (s, 3H, CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>): δ = 206.0 (br, C=O), 173.2 (d, <sup>1</sup>*J*<sub>PC</sub> = 7.8 Hz, =CP), 146.2 (d, <sup>4</sup>*J*<sub>PC</sub> = 1.7 Hz, C=CH<sub>2</sub>), 143.9 (d, <sup>2</sup>*J*<sub>PC</sub> = 15.1 Hz, *o*-Mes), 141.1 (d, <sup>4</sup>*J*<sub>PC</sub> = 2.0 Hz, *p*-Mes), 140.6 (d, <sup>2</sup>*J*<sub>PC</sub> = 19.8 Hz, *i*-Ph), 139.6 (br d, <sup>2</sup>*J*<sub>PC</sub> = 18.6 Hz, =C), 131.9 (d, <sup>5</sup>*J*<sub>PC</sub> = 2.1 Hz, *p*-Ph), 131.5 (d, <sup>3</sup>*J*<sub>PC</sub> = 5.2 Hz, *o*'-Ph), 130.21 (d, <sup>3</sup>*J*<sub>PC</sub> = 19.2 Hz, *o*-Ph), 130.17 (d, <sup>3</sup>*J*<sub>PC</sub> = 7.6 Hz, *m*-Mes), 128.8 (*m*-Ph), 128.6 (*m*'-Ph), 126.0 (d, <sup>1</sup>*J*<sub>PC</sub> = 14.0 Hz, *i*-Mes), 109.6 (=CH<sub>2</sub>), 49.9 (d, <sup>3</sup>*J*<sub>PC</sub> = 8.0 Hz, CH), 28.9 (d, <sup>4</sup>*J*<sub>PC</sub> = 2.1 Hz, <sup>O=C</sup>CH<sub>3</sub>), 23.3 (d, <sup>3</sup>*J*<sub>PC</sub> = 13.7 Hz, *o*-CH<sub>3</sub><sup>Mes</sup>), 23.0 (br, CH<sub>2</sub>), 20.8 (d, *J* = 0.7 Hz, *p*-CH<sub>3</sub><sup>Mes</sup>), 20.6 (CH<sub>3</sub>), [C<sub>6</sub>F<sub>5</sub> not listed].

**<sup>11</sup>B{<sup>1</sup>H} NMR** (192 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>): δ = 2.0 (ν<sub>1/2</sub> ~ 500 Hz).

**<sup>10</sup>B{<sup>1</sup>H} NMR** (64 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>): δ = 2.0 (ν<sub>1/2</sub> ~ 500 Hz).

**<sup>31</sup>P{<sup>1</sup>H} NMR** (243 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>): δ = -4.7 (ν<sub>1/2</sub> ~ 40 Hz).

**<sup>19</sup>F NMR** (564 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>): δ = -133.5 (m, 2F, *o*), -158.9 (t, <sup>3</sup>*J*<sub>FF</sub> = 20.6 Hz, 1F, *p*), -164.2 (m, 2F, *m*)(C<sub>6</sub>F<sub>5</sub>)[Δδ<sup>19</sup>F<sub>mp</sub> = 5.3], -134.9 (m, 2F, *o*), -160.6 (t, <sup>3</sup>*J*<sub>FF</sub> = 20.6 Hz, 1F, *p*), -165.4 (m, 2F, *m*)(C<sub>6</sub>F<sub>5</sub>)[Δδ<sup>19</sup>F<sub>mp</sub> = 4.8].

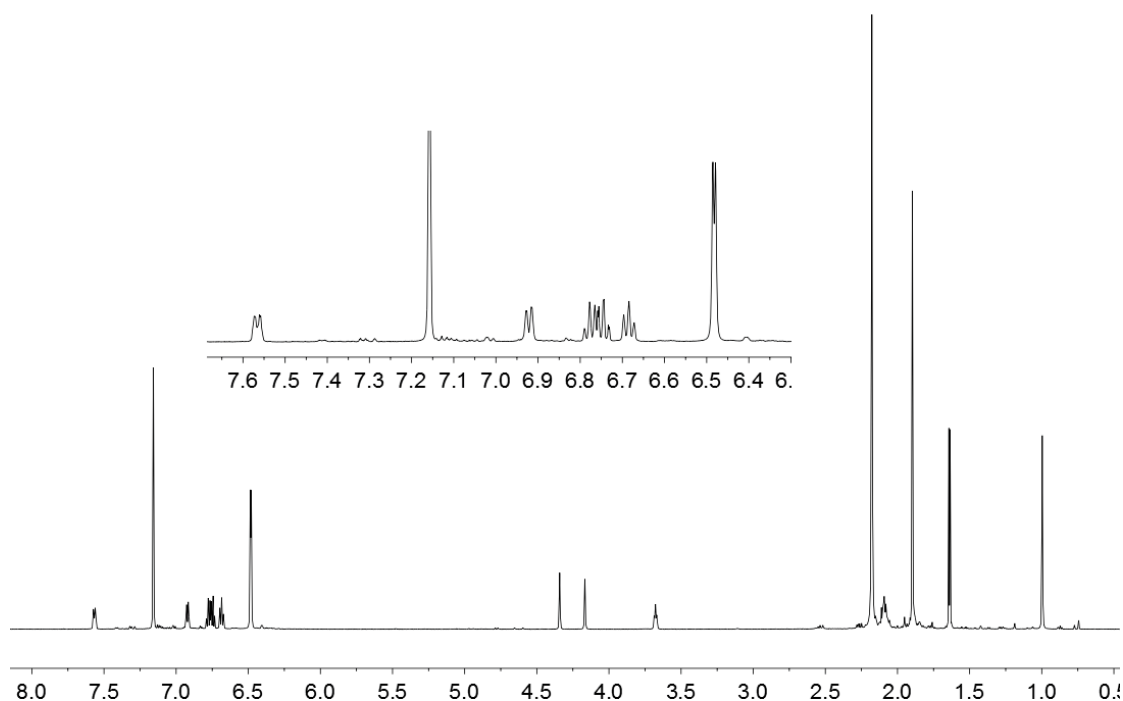
**<sup>1</sup>H, <sup>1</sup>H-GCOSY** (600 MHz / 600 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>)[selected traces]: δ <sup>1</sup>H / δ <sup>1</sup>H = 7.56 / 6.74 (*o*-Ph / *m*-Ph), 6.91 / 6.68 (*o*'-Ph / *m*'-Ph), 4.33, 4.16 / 3.67, 0.99 (=CH<sub>2</sub>, =CH<sub>2</sub> / CH, CH<sub>3</sub>), 3.67 / 2.08 (CH / CH<sub>2</sub>).

**<sup>1</sup>H, <sup>13</sup>C-GHSQC** (600 MHz / 151 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>): δ <sup>1</sup>H / δ <sup>13</sup>C = 7.56 / 130.21 (*o*-Ph), 6.91 / 131.5 (*o*'-Ph), 6.77 / 131.9 (*p*-Ph), 6.74 / 128.8 (*m*-Ph), 6.68 / 128.6 (*m*'-Ph), 6.47 / 130.17 (*m*-Mes), 4.33, 4.16 / 109.6 (=CH<sub>2</sub>), 3.67 / 49.9 (CH), 2.17 / 23.3 (*o*-CH<sub>3</sub><sup>Mes</sup>), 2.08 / 23.0 (CH<sub>2</sub>), 1.89 / 20.8 (*p*-CH<sub>3</sub><sup>Mes</sup>), 1.63 / 28.9 (<sup>O=C</sup>CH<sub>3</sub>), 0.99 / 20.6

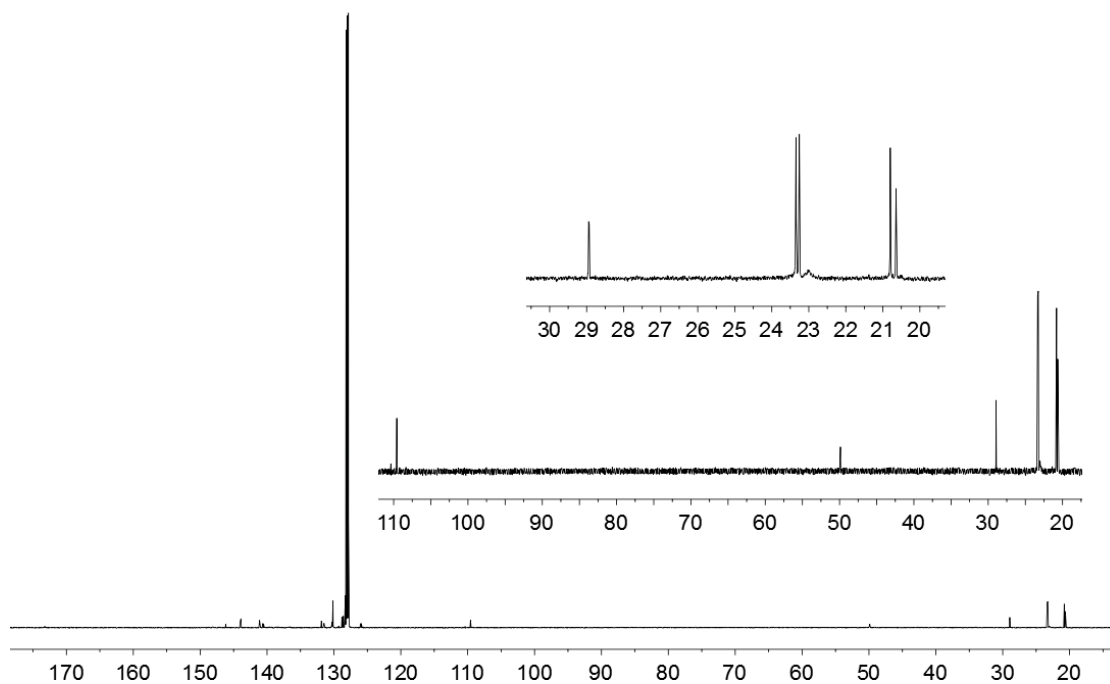
(CH<sub>3</sub>).

**<sup>1</sup>H, <sup>13</sup>C-GHMBC** (600 MHz / 151 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>)[selected traces]:  $\delta$  <sup>1</sup>H /  $\delta$  <sup>13</sup>C = 7.56, 6.91, 3.67 / 173.2 (*o*-Ph, *o'*-Ph, CH / =CP), 6.74, 6.68 / 140.6 (*m*-Ph, *m'*-Ph / *i*-Ph), 6.47, 2.17 / 126.0 (*m*-Mes, *o*-CH<sub>3</sub><sup>Mes</sup> / *i*-Mes<sup>a</sup>), 4.33, 4.16, 3.67, 2.08, 0.99 / 146.2 (=CH<sub>2</sub>, =CH<sub>2</sub>, CH, CH<sub>2</sub>, CH<sub>3</sub> / C=<sup>CH</sup><sub>2</sub>), 3.67, 2.08, 1.63 / 139.6 (CH, CH<sub>2</sub>, <sup>O=C</sup>CH<sub>3</sub> / =C), 3.67, 1.63 / 206.0 (CH, <sup>O=C</sup>CH<sub>3</sub> / C=O), 2.17 / 143.9 (*o*-CH<sub>3</sub><sup>Mes</sup> / *o*-Mes), 1.89 / 141.1 (*p*-CH<sub>3</sub><sup>Mes</sup> / *p*-Mes).

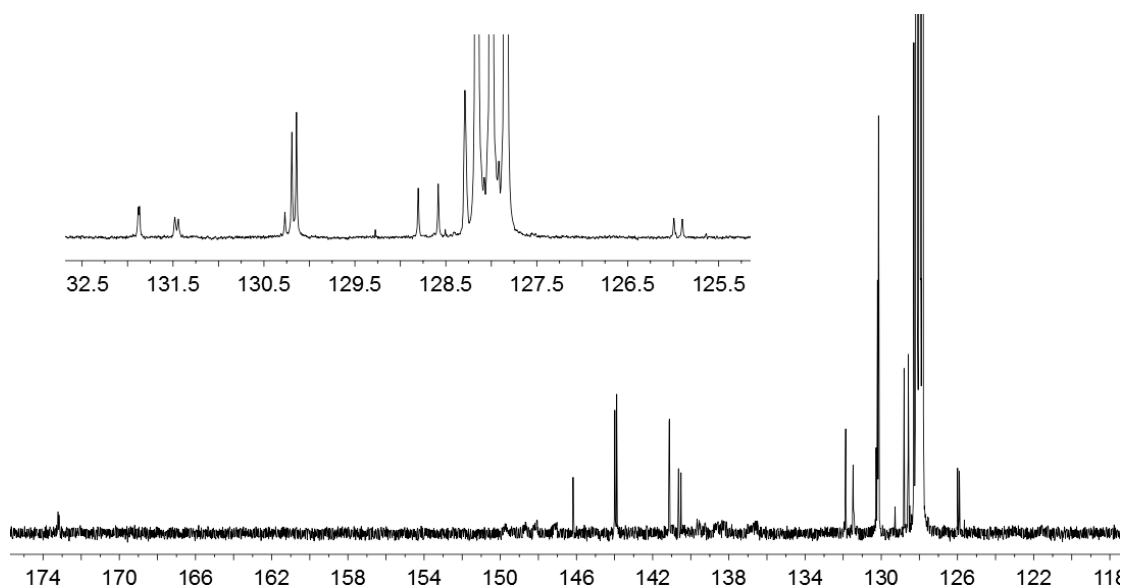
**<sup>19</sup>F, <sup>19</sup>F-GCOSY** (564 MHz / 564 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  <sup>19</sup>F /  $\delta$  <sup>19</sup>F = -164.2 / -133.5, -158.9 (*m*-C<sub>6</sub>F<sub>5</sub><sup>a</sup> / *o*-C<sub>6</sub>F<sub>5</sub><sup>a</sup>, *p*-C<sub>6</sub>F<sub>5</sub><sup>a</sup>), -165.4 / -134.9, -160.6 (*m*-C<sub>6</sub>F<sub>5</sub><sup>b</sup> / *o*-C<sub>6</sub>F<sub>5</sub><sup>b</sup>, *p*-C<sub>6</sub>F<sub>5</sub><sup>b</sup>).



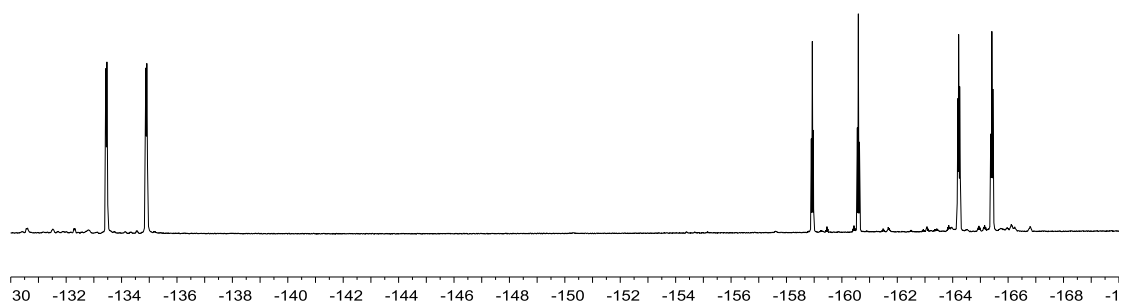
**Figure S27.** <sup>1</sup>H NMR (600 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>) of compound **10a**



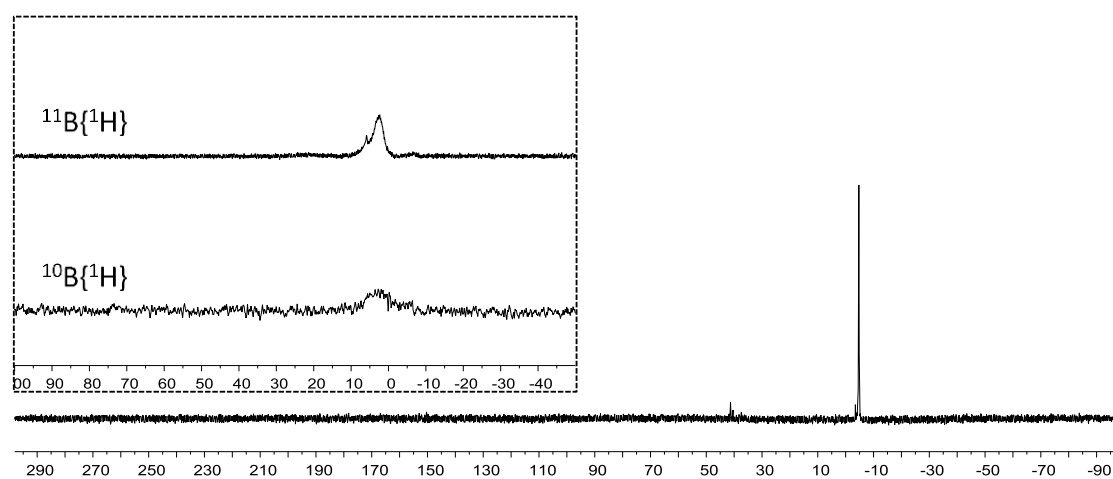
**Figure S28.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) of compound **10a**



**Figure S29.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) of compound **10a**



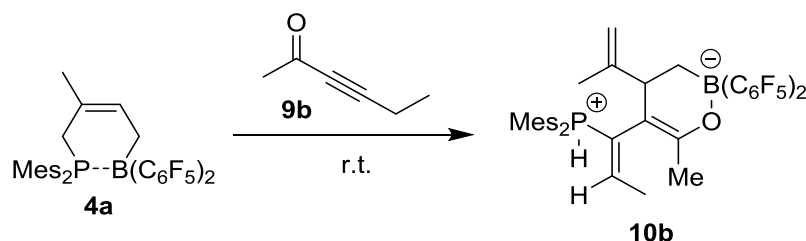
**Figure S30.**  $^{19}\text{F}$  NMR (564 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) of compound **10a**



**Figure S31.**  $^{11}\text{B}\{^1\text{H}\}$  NMR (192 MHz, 299 K,  $\text{C}_6\text{D}_6$ ),  $^{10}\text{B}\{^1\text{H}\}$  NMR (64 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) of compound **10a**



## Synthesis of compound 10b



Scheme S5

A solution of compound **4a** (102.3 mg, 0.15 mmol) and **9b** (14.4 mg, 0.15 mmol) in pentane (3 mL) was stirred at room temperature for 5 days. Then all volatiles were removed in vacuo and the residue was washed with cold pentane (3x1 mL). After drying in vacuo compound **10b** (88.5 mg, 76 %) was obtained as a yellow solid. **Decomp.** 169 °C. **Anal. Calc.** for C<sub>41</sub>H<sub>38</sub>BF<sub>10</sub>O<sub>2</sub>P: C: 61.98; H: 4.82. Found: C: 62.41; H: 4.68.

**<sup>1</sup>H NMR** (500 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = 8.13 (br d, <sup>1</sup>J<sub>PH</sub> = 480.5 Hz, 1H, PH), 7.05 (br, 2H, *m*-Mes<sup>a</sup>), 6.93 (br, 2H, *m*-Mes<sup>b</sup>), 5.87 (dq, <sup>3</sup>J<sub>PH</sub> = 27.3 Hz, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz, 1H, =CH), 4.70 (s, 1H, =CH<sub>2</sub>), 4.59 (s, 1H, =CH<sub>2</sub>), 2.84 (m, 1H, CH), 2.35 (s, 3H, *p*-CH<sub>3</sub><sup>Mes,b</sup>), 2.34 (s, 3H, *p*-CH<sub>3</sub><sup>Mes,a</sup>), 2.24 (br, 12H, *o*-CH<sub>3</sub><sup>Mes,a,b</sup>), 1.93 (ddd, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, <sup>a</sup>J<sub>PH</sub> = 3.7 Hz, <sup>a</sup>J<sub>HH</sub> = 2.0 Hz, <sup>a</sup>3H, =CHCH<sub>3</sub>), 1.78 (m, 3H, <sup>O</sup>-CCH<sub>3</sub>), 1.71 (m, 3H, CH<sub>3</sub>), 1.32 (dd, <sup>2</sup>J<sub>HH</sub> = 13.2 Hz, <sup>3</sup>J<sub>HH</sub> = 5.9 Hz, 1H, CH<sub>2</sub>), 1.16 (dd, <sup>2</sup>J<sub>HH</sub> = 13.2 Hz, <sup>3</sup>J<sub>HH</sub> = 10.0 Hz, 1H, CH<sub>2</sub>), [<sup>a</sup> assignment by <sup>1</sup>H{<sup>1</sup>H} and <sup>1</sup>H{<sup>31</sup>P} NMR experiments].

**<sup>13</sup>C{<sup>1</sup>H} NMR** (126 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = 160.5 (d, <sup>3</sup>J<sub>PC</sub> = 12.4 Hz, =CO), 154.1 (br, C=<sup>CH</sup>), 146.1 (d, <sup>5</sup>J<sub>PC</sub> = 2.7 Hz, *p*-Mes<sup>a</sup>), 145.8 (d, <sup>5</sup>J<sub>PC</sub> = 2.7 Hz, *p*-Mes<sup>b</sup>), 144.5 (d, <sup>2</sup>J<sub>PC</sub> = 9.5 Hz), 143.3 (br)(*o*-Mes)<sup>t</sup>, 143.3 (d, <sup>2</sup>J<sub>PC</sub> = 19.9 Hz, =CH), 131.8 (br, *m*-Mes<sup>a</sup>), 131.5 (d, <sup>3</sup>J<sub>PC</sub> = 10.8 Hz, *m*-Mes<sup>b</sup>), 126.8 (d, <sup>1</sup>J<sub>PC</sub> = 60.3 Hz, =CP), 112.8 (d, <sup>1</sup>J<sub>PC</sub> = 76.8 Hz), 112.6 (d, <sup>1</sup>J<sub>PC</sub> = 79.2 Hz, *i*-Mes<sup>a,b</sup>)<sup>t</sup>, 110.7 (d, <sup>5</sup>J<sub>PC</sub> = 1.5 Hz, =CH<sub>2</sub>), 100.6 (d, <sup>3</sup>J<sub>PC</sub> = 9.5 Hz, =C), 45.3 (CH), 26.1 (br, CH<sub>2</sub>), 23.2 (d, <sup>4</sup>J<sub>PC</sub> = 1.8 Hz, <sup>O</sup>-CCH<sub>3</sub>), 22.2, 22.1 (each br, *o*-CH<sub>3</sub><sup>Mes,a,b</sup>), 21.4 (d, <sup>5</sup>J<sub>PC</sub> = 1.3 Hz, *p*-CH<sub>3</sub><sup>Mes,a</sup>), 21.2 (*p*-CH<sub>3</sub><sup>Mes,b</sup>), 19.8 (d, <sup>3</sup>J<sub>PC</sub> = 18.5 Hz, =CHCH<sub>3</sub>), 19.6 (br, CH<sub>3</sub>), [<sup>t</sup> tentatively assigned; C<sub>6</sub>F<sub>5</sub> not listed].

**<sup>11</sup>B{<sup>1</sup>H} NMR** (160 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = -2.4 (ν<sub>1/2</sub> ~ 160 Hz).

**<sup>31</sup>P{<sup>1</sup>H} NMR** (202 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = -19.8 (ν<sub>1/2</sub> ~ 10 Hz).

**<sup>31</sup>P NMR** (202 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = -19.8 (br dd, <sup>1</sup>J<sub>PH</sub> ~ 480 Hz, <sup>3</sup>J<sub>PH</sub> ~ 26 Hz).

**<sup>19</sup>F NMR** (470 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = -134.8 (m, 2F, *o*), -163.2 (t, <sup>3</sup>J<sub>FF</sub> = 20.3 Hz, 1F, *p*), -166.5 (m, 2F, *m*)(C<sub>6</sub>F<sub>5</sub>)[Δδ<sup>19</sup>F<sub>mp</sub> = 3.3], -135.6 (br m, 2F, *o*), -164.0 (br t, <sup>3</sup>J<sub>FF</sub> = 20.1 Hz, 1F, *p*), -167.3 (br m, 2F, *m*)(C<sub>6</sub>F<sub>5</sub>)[Δδ<sup>19</sup>F<sub>mp</sub> = 3.3].

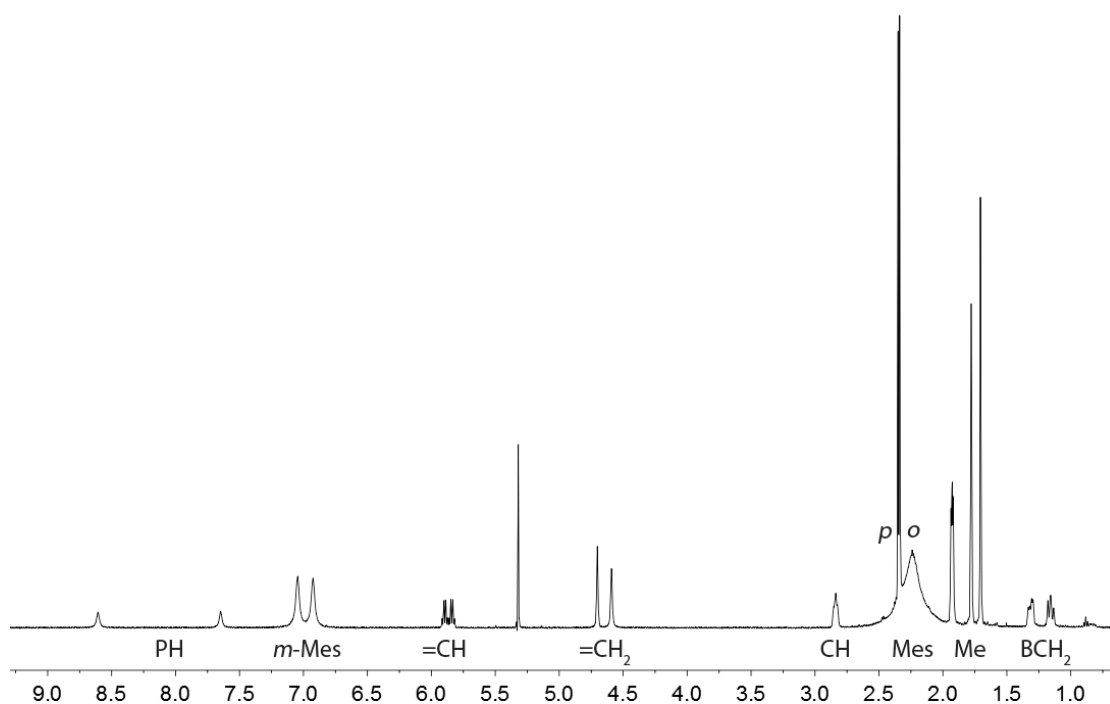
**<sup>1</sup>H, <sup>1</sup>H-GCOSY** (500 MHz / 500 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>)[selected traces]: δ <sup>1</sup>H / δ <sup>1</sup>H = 7.05 / 2.34 (*m*-Mes<sup>a</sup> / *p*-CH<sub>3</sub><sup>Mes,a</sup>), 6.93 / 2.35 (*m*-Mes<sup>b</sup> / *p*-CH<sub>3</sub><sup>Mes,b</sup>), 5.87 / 1.93 (=CH / =CHCH<sub>3</sub>), 4.70, 4.59 / 1.71 (=CH<sub>2</sub>, =CH<sub>2</sub> / CH<sub>3</sub>), 2.84 / 1.32, 1.16 (CH / CH<sub>2</sub>, CH<sub>2</sub>).

**<sup>1</sup>H, <sup>13</sup>C-GHSQC** (500 MHz / 126 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ <sup>1</sup>H / δ <sup>13</sup>C = 7.05 / 131.8

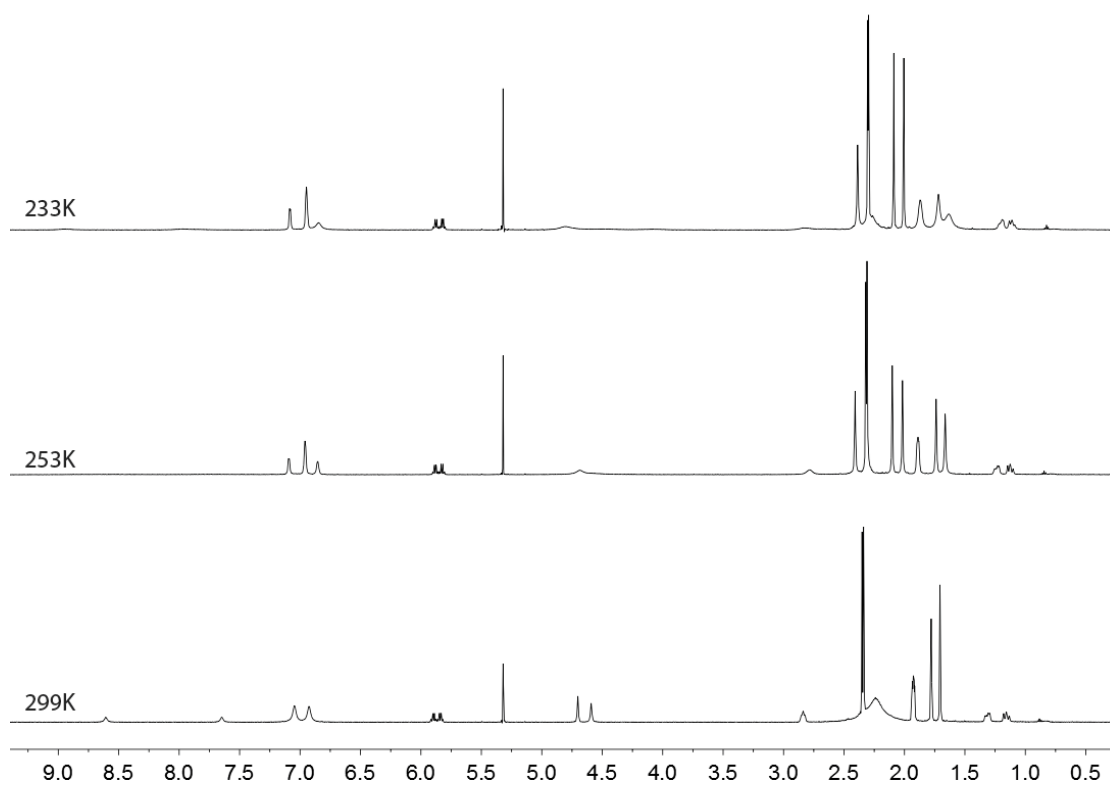
(*m*-Mes<sup>a</sup>), 6.93 / 131.5 (*m*-Mes<sup>b</sup>), 5.87 / 143.3 (=CH), 4.70, 4.59 / 110.7 (=CH<sub>2</sub>), 2.84 / 45.3 (CH), 2.35 / 21.2 (*p*-CH<sub>3</sub><sup>Mes,b</sup>), 2.34 / 21.4 (*p*-CH<sub>3</sub><sup>Mes,a</sup>), 2.24 / 22.2, 22.1 (*o*-CH<sub>3</sub><sup>Mes,a,b</sup>), 1.93 / 19.8 (=CHCH<sub>3</sub>), 1.78 / 23.2 (<sup>O</sup>-CCH<sub>3</sub>), 1.71 / 19.6 (CH<sub>3</sub>), 1.32, 1.16 / 26.1 (CH<sub>2</sub>).

**<sup>1</sup>H, <sup>13</sup>C-GHMBBC** (500 MHz / 126 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>)[selected traces]: δ <sup>1</sup>H / δ <sup>13</sup>C = 5.87, 1.78, 1.32 / 100.6 (=CH, <sup>O</sup>-CCH<sub>3</sub>, CH<sub>2</sub> / =C), 2.35 / 145.8 (*p*-CH<sub>3</sub><sup>Mes,b</sup> / *p*-Mes<sup>b</sup>), 2.34 / 146.1 (*p*-CH<sub>3</sub><sup>Mes,a</sup> / *p*-Mes<sup>a</sup>), 1.93 / 126.8 (=CHCH<sub>3</sub> / =CP), 1.78 / 160.5 (<sup>O</sup>-CCH<sub>3</sub> / =CO), 1.71 / 154.1 (CH<sub>3</sub> / C=CH<sub>2</sub>).

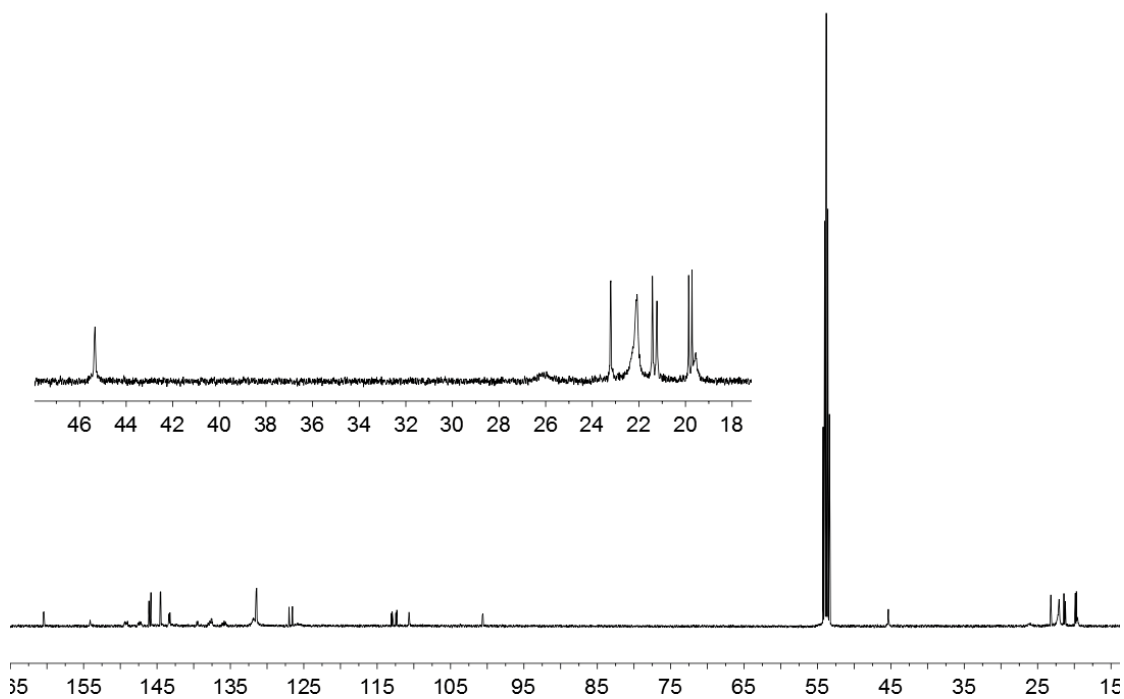
**<sup>19</sup>F, <sup>19</sup>F-GCOSY** (470 MHz / 470 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ <sup>19</sup>F / δ <sup>19</sup>F = -166.5 / -134.8, -163.2 (*m*-C<sub>6</sub>F<sub>5</sub><sup>a</sup> / *o*-C<sub>6</sub>F<sub>5</sub><sup>a</sup>, *p*-C<sub>6</sub>F<sub>5</sub><sup>a</sup>), -167.3 / -135.6, -164.0 (*m*-C<sub>6</sub>F<sub>5</sub><sup>b</sup> / *o*-C<sub>6</sub>F<sub>5</sub><sup>b</sup>, *p*-C<sub>6</sub>F<sub>5</sub><sup>b</sup>).



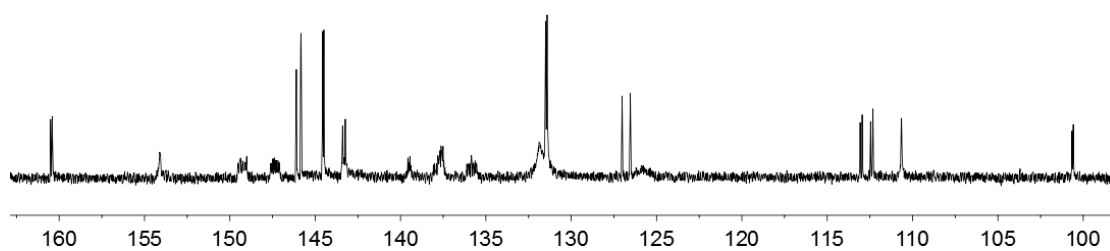
**Figure S32.** <sup>1</sup>H NMR (500 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>) of compound **10b**



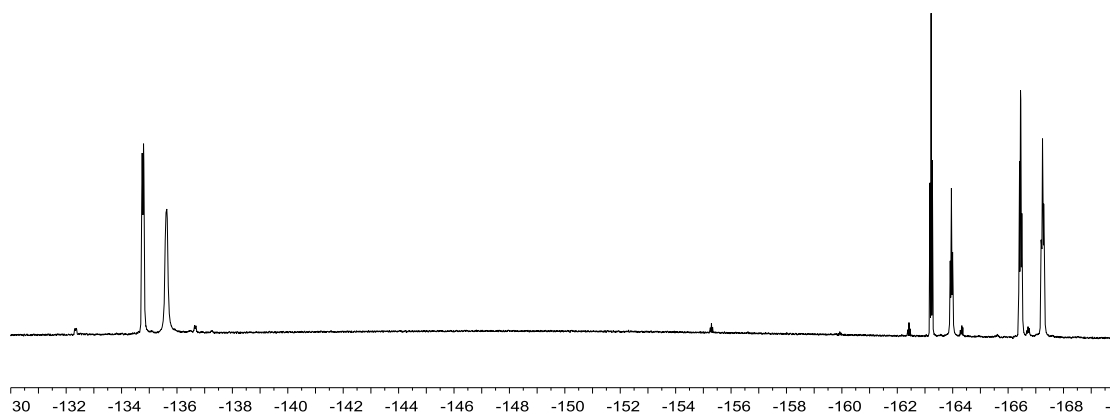
**Figure S33.**  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ) of compound **10b**



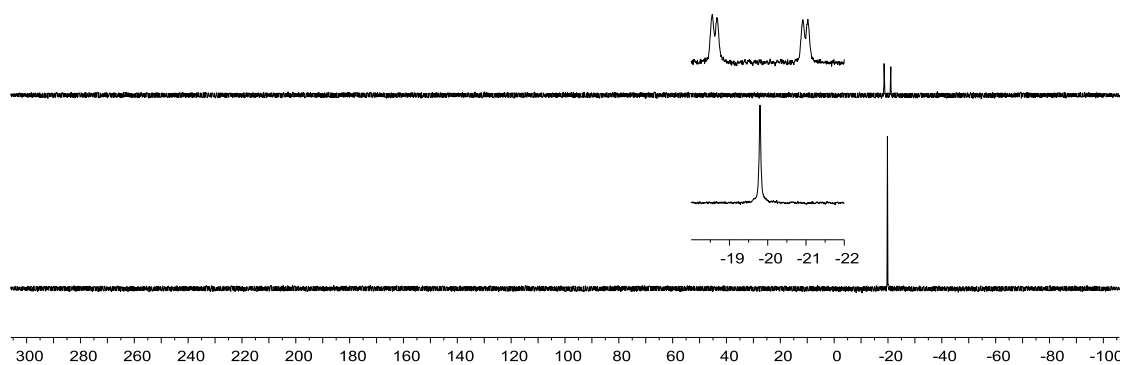
**Figure S34.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) of compound **10b**



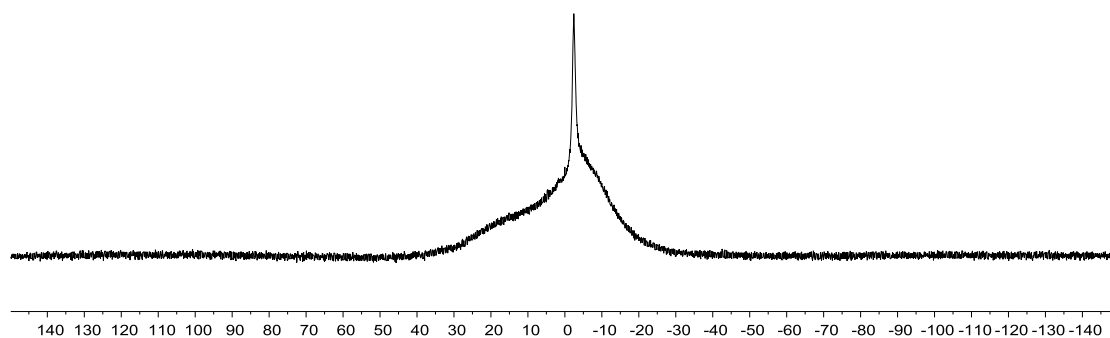
**Figure S35.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) of compound **10b**



**Figure S36.**  $^{19}\text{F}$  NMR (470 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) of compound **10b**

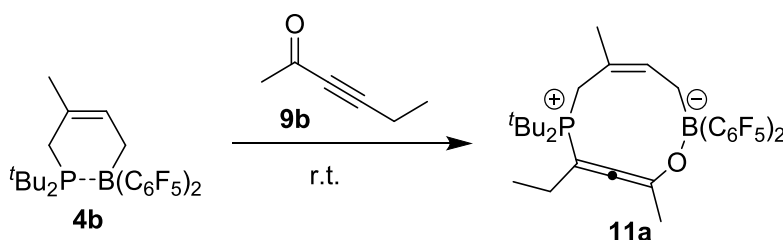


**Figure S37.**  $^{31}\text{P}\{^1\text{H}\}$  and  $^{31}\text{P}$  NMR (202 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) of compound **10b**



**Figure S38.**  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) of compound **10b**

## Synthesis of compound 11a



Scheme S6

A solution of compounds **4b** (111.6 mg, 0.2 mmol) and **9b** (19.2 mg, 0.2 mmol) in pentane (2 mL) was stirred at room temperature for 3 h. Then all volatiles were removed in vacuo and the resulting residue was washed with cold pentane (3x1 mL). After drying in vacuo compound **11a** (106.1 mg, 81 %) was obtained as a light yellow solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **11a** in dichloromethane at -35 °C. **Decomp.** 113 °C. **Anal. Calc.** for C<sub>31</sub>H<sub>34</sub>BF<sub>10</sub>OP: C: 56.90; H: 5.24. Found: C: 56.43; H: 5.16.

**<sup>1</sup>H NMR** (600 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = 5.89 (d, <sup>4</sup>J<sub>PH</sub> = 12.9 Hz, 1H, =CH), 3.54 (t, <sup>2</sup>J<sub>HH</sub> = <sup>2</sup>J<sub>PH</sub> = 15.0 Hz, 1H, PCH<sub>2</sub>), 2.52 (dd, <sup>2</sup>J<sub>HH</sub> = 15.0 Hz, <sup>2</sup>J<sub>PH</sub> = 12.5 Hz, 1H, PCH<sub>2</sub>), 2.35, 1.51 (each m, each 1H, BCH<sub>2</sub>), 2.12, 2.02 (each m, each 1H, Et), 1.90 (m, 3H, CH<sub>3</sub>), 1.86 (d, <sup>5</sup>J<sub>PH</sub> = 5.5 Hz, 3H, <sup>O</sup>-CCH<sub>3</sub>), 1.58 (d, <sup>3</sup>J<sub>PH</sub> = 13.6 Hz, 9H, <sup>t</sup>Bu<sup>a</sup>), 1.41 (d, <sup>3</sup>J<sub>PH</sub> = 14.6 Hz, 9H, <sup>t</sup>Bu<sup>b</sup>), 0.61 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, 3H, Et).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = 225.7 (d, <sup>2</sup>J<sub>PC</sub> = 4.3 Hz, =C=), 139.7 (d, <sup>3</sup>J<sub>PC</sub> = 6.7 Hz, =CH), 135.3 (d, <sup>3</sup>J<sub>PC</sub> = 12.9 Hz, =CO), 115.6 (d, <sup>2</sup>J<sub>PC</sub> = 12.0 Hz, =C<sup>CH<sub>3</sub></sup>), 92.7 (d, <sup>1</sup>J<sub>PC</sub> = 63.1 Hz, =CP), 37.0 (d, <sup>1</sup>J<sub>PC</sub> = 31.9 Hz, <sup>t</sup>Bu<sup>b</sup>), 36.8 (d, <sup>1</sup>J<sub>PC</sub> = 28.9 Hz, <sup>t</sup>Bu<sup>a</sup>), 28.9 (<sup>t</sup>Bu<sup>a</sup>), 28.8 (d, <sup>2</sup>J<sub>PC</sub> = 14.9 Hz, Et), 28.1 (<sup>t</sup>Bu<sup>b</sup>), 28.0 (br, BCH<sub>2</sub>), 27.2 (d, <sup>3</sup>J<sub>PC</sub> = 4.1 Hz, CH<sub>3</sub>), 25.1 (d, <sup>1</sup>J<sub>PC</sub> = 43.9 Hz, PCH<sub>2</sub>), 21.2 (d, <sup>4</sup>J<sub>PC</sub> = 5.2 Hz, <sup>O</sup>-CCH<sub>3</sub>), 11.3 (d, <sup>3</sup>J<sub>PC</sub> = 4.6 Hz, Et), [C<sub>6</sub>F<sub>5</sub> not listed].

**<sup>11</sup>B{<sup>1</sup>H} NMR** (192 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = -1.1 (ν<sub>1/2</sub> ~ 80 Hz).

**<sup>31</sup>P{<sup>1</sup>H} NMR** (243 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = 31.8 (ν<sub>1/2</sub> ~ 2 Hz).

**<sup>19</sup>F NMR** (564 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = -133.0 (m, 2F, *o*), -162.9 (t, <sup>3</sup>J<sub>FF</sub> = 20.2 Hz, 1F, *p*), -167.1 (m, 2F, *m*)(C<sub>6</sub>F<sub>5</sub>)[Δδ<sup>19</sup>F<sub>mp</sub> = 4.2], -134.8 (m, 2F, *o*), -163.5 (t, <sup>3</sup>J<sub>FF</sub> = 20.2 Hz, 1F, *p*), -166.9 (m, 2F, *m*)(C<sub>6</sub>F<sub>5</sub>)[Δδ<sup>19</sup>F<sub>mp</sub> = 3.4].

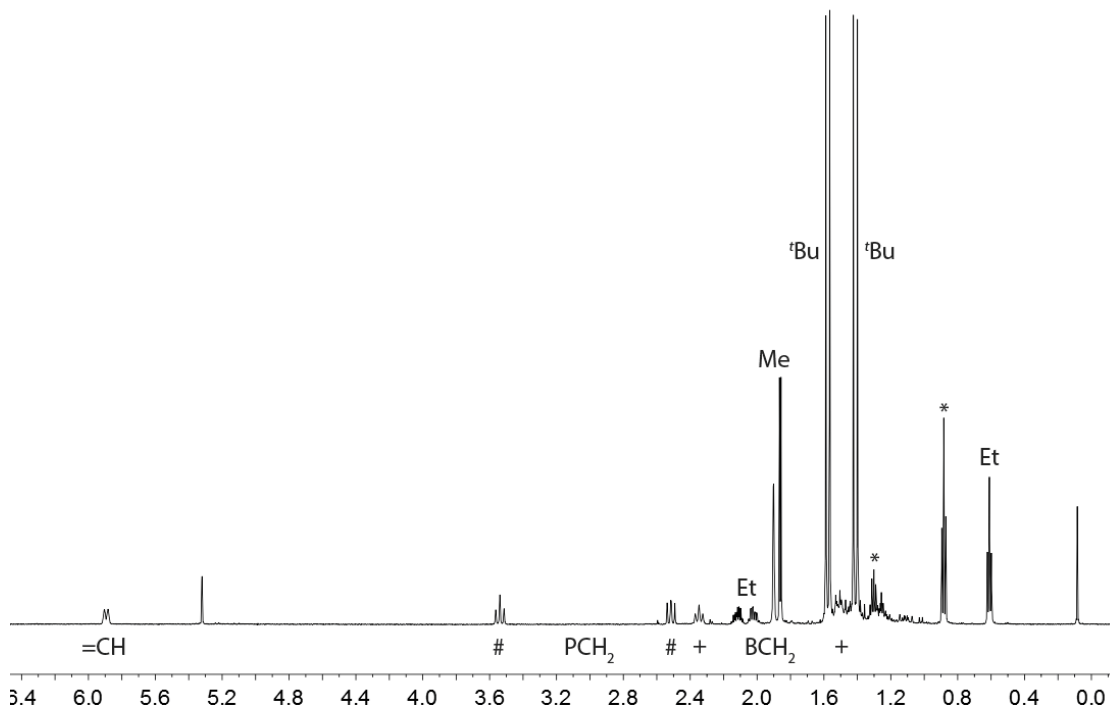
**<sup>1</sup>H, <sup>1</sup>H-GCOSY** (600 MHz / 600 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>)[selected traces]: δ <sup>1</sup>H / δ <sup>1</sup>H = 5.89 / 1.90 (=CH / CH<sub>3</sub>), 3.54 / 2.52 (PCH<sub>2</sub> / PCH<sub>2</sub>), 2.35 / 1.51 (BCH<sub>2</sub> / BCH<sub>2</sub>), 2.12 / 2.02, 0.61 (Et / Et, Et).

**<sup>1</sup>H, <sup>13</sup>C-GHSQC** (600 MHz / 151 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ <sup>1</sup>H / δ <sup>13</sup>C = 5.89 / 139.7 (=CH), 3.54, 2.52 / 25.1 (PCH<sub>2</sub>), 2.35, 1.51 / 28.0 (BCH<sub>2</sub>), 2.12, 2.02 / 28.8 (Et), 1.90 / 27.2 (CH<sub>3</sub>), 1.86 / 21.2 (<sup>O</sup>-CCH<sub>3</sub>), 1.58 / 28.9 (<sup>t</sup>Bu<sup>a</sup>), 1.41 / 28.1 (<sup>t</sup>Bu<sup>b</sup>), 0.61 / 11.3 (Et).

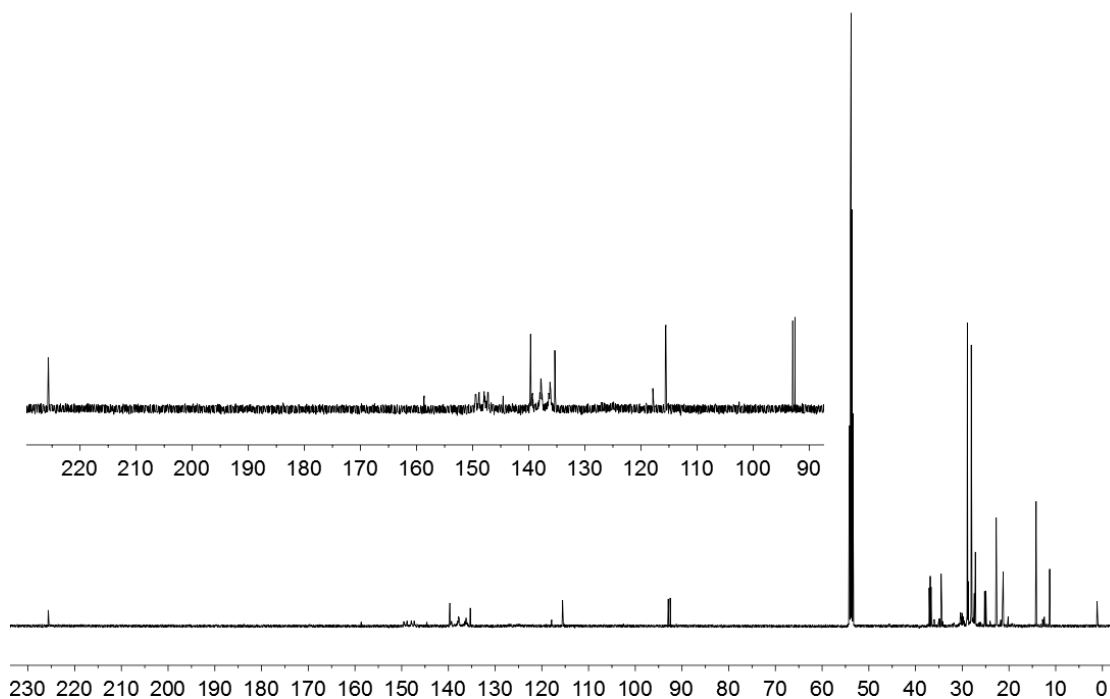
**<sup>1</sup>H, <sup>13</sup>C-GHMBC** (600 MHz / 151 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>)[selected traces]: δ <sup>1</sup>H / δ <sup>13</sup>C = 3.54, 2.52, 2.35, 1.90 / 115.6 (PCH<sub>2</sub>, PCH<sub>2</sub>, BCH<sub>2</sub>, CH<sub>3</sub> / =C<sup>CH<sub>3</sub></sup>), 2.52, 2.12, 2.02,

0.61 / 92.7 (PCH<sub>2</sub>, Et, Et, Et / =CP), 2.12, 2.02, 1.86 / 225.7 (Et, Et, <sup>O</sup>-CCH<sub>3</sub> / =C=), 1.86 / 135.3 (<sup>O</sup>-CCH<sub>3</sub> / =CO), 1.58 / 36.8 (<sup>t</sup>Bu<sup>a</sup> / <sup>t</sup>Bu<sup>a</sup>), 1.41 / 37.0 (<sup>t</sup>Bu<sup>b</sup> / <sup>t</sup>Bu<sup>b</sup>).

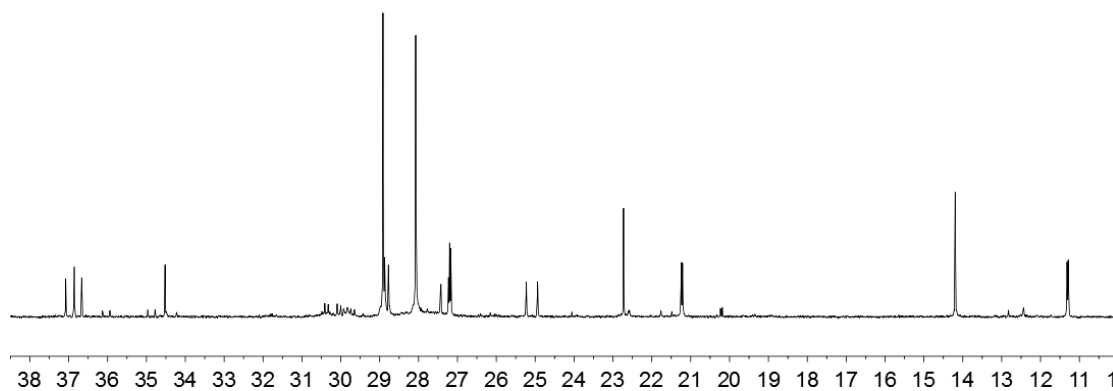
<sup>19</sup>F, <sup>19</sup>F-GCOSY (564 MHz / 564 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ <sup>19</sup>F / δ <sup>19</sup>F = -167.1 / -133.0, -162.9 (*m*-C<sub>6</sub>F<sub>5</sub><sup>a</sup> / *o*-C<sub>6</sub>F<sub>5</sub><sup>a</sup>, *p*-C<sub>6</sub>F<sub>5</sub><sup>a</sup>), -166.9 / -134.8, -163.5 (*m*-C<sub>6</sub>F<sub>5</sub><sup>b</sup> / *o*-C<sub>6</sub>F<sub>5</sub><sup>b</sup>, *p*-C<sub>6</sub>F<sub>5</sub><sup>b</sup>).



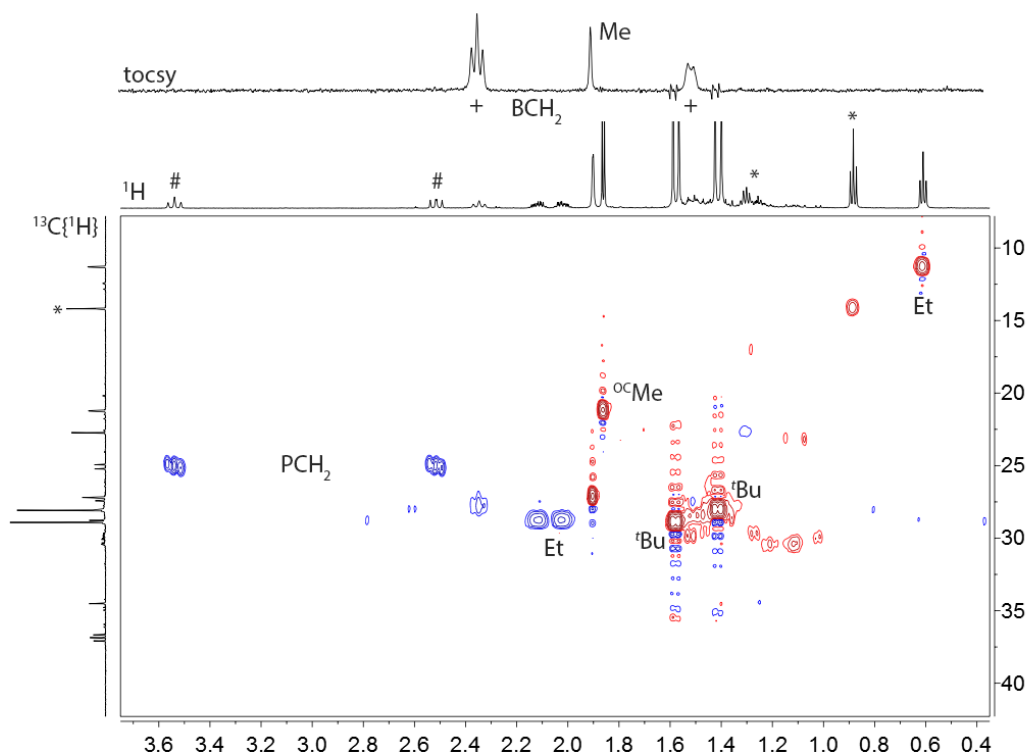
**Figure S39.** <sup>1</sup>H NMR (600 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>) of compound **11a** [admixed with pentane (\*)]



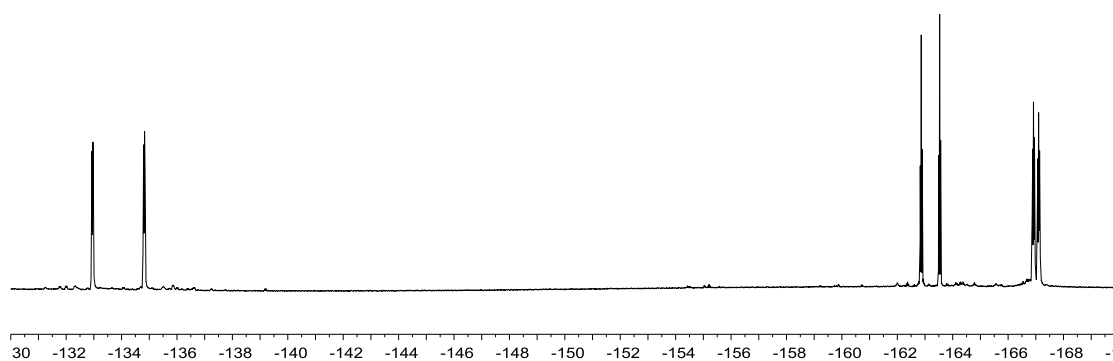
**Figure S40.** <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>) of compound **11a** [admixed with pentane]



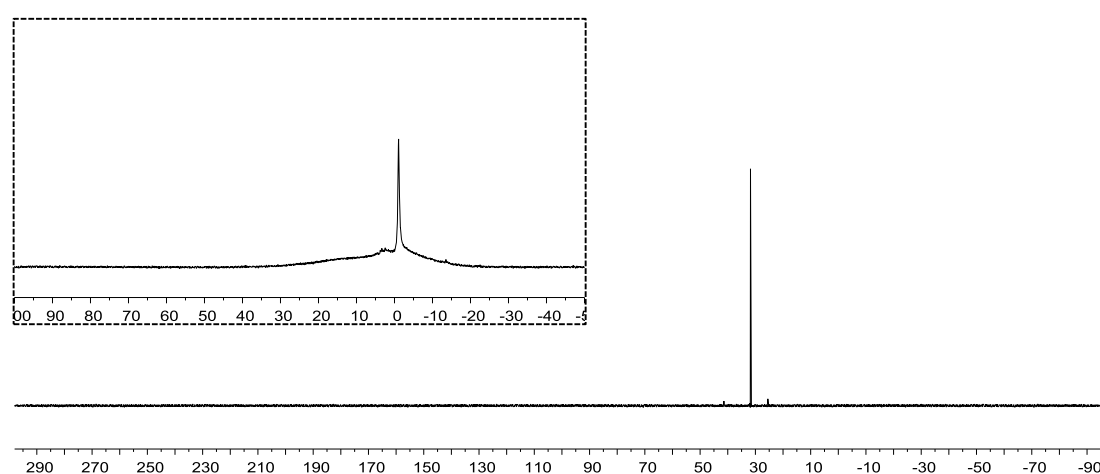
**Figure S41.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) of compound **11a** [admixed with pentane]



**Figure S42.**  $^1\text{H}$ ,  $^{13}\text{C}$ -GHSQC (600 MHz / 151 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) of compound **11a** [admixed with pentane (\*)].  $^1\text{H}$ ,  $^1\text{H}$  tocsy: irradiation at  $\delta^1\text{H}_{\text{irr}} = 2.35$  ( $\text{BCH}_2$ ).



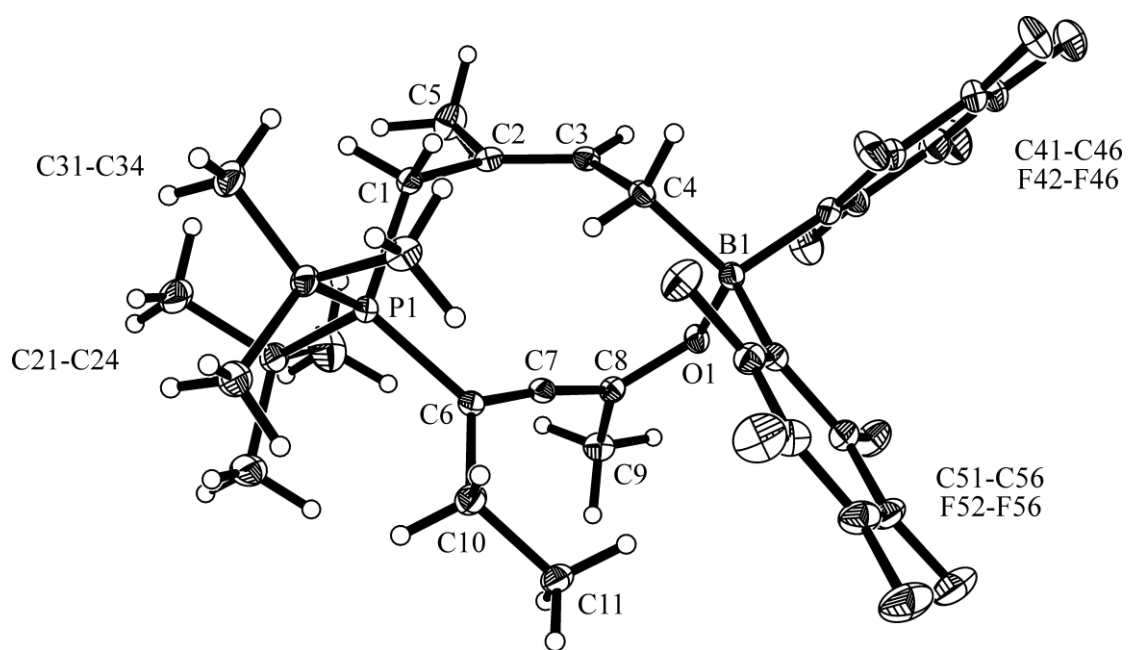
**Figure S43.**  $^{19}\text{F}$  NMR (564 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) of compound **11a**



**Figure S44.**  $^{11}\text{B}\{^1\text{H}\}$  NMR (192 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) of compound **11a**

**X-ray crystal structure analysis of compound 11a:** formula  $\text{C}_{31}\text{H}_{34}\text{BF}_{10}\text{OP}$ ,  $M = 654.36$ , colourless crystal,  $0.18 \times 0.15 \times 0.15$  mm,  $a = 9.1467(2)$ ,  $b = 14.6625(3)$ ,  $c = 14.7129(4)$  Å,  $\alpha = 90.266(1)$ ,  $\beta = 102.873(1)$ ,  $\gamma = 107.489(1)^\circ$ ,  $V = 1829.2(1)$  Å<sup>3</sup>,  $\rho_{\text{calc}} = 1.188$  g cm<sup>-3</sup>,  $\mu = 0.147$  mm<sup>-1</sup>, empirical absorption correction ( $0.974 \leq T \leq 0.978$ ),  $Z = 2$ , triclinic, space group  $P\bar{1}$  (No. 2),  $\lambda = 0.71073$  Å,  $T = 223(2)$  K,  $\omega$  and  $\phi$  scans, 17742 reflections collected ( $\pm h$ ,  $\pm k$ ,  $\pm l$ ), 6342 independent ( $R_{\text{int}} = 0.059$ ) and 4693 observed reflections [ $I > 2\sigma(I)$ ], 400 refined parameters,  $R = 0.086$ ,  $wR^2 = 0.239$ , max. (min.) residual electron density  $0.37$  ( $-0.33$ ) e.Å<sup>-3</sup>, hydrogen atoms were calculated and refined as riding atoms.





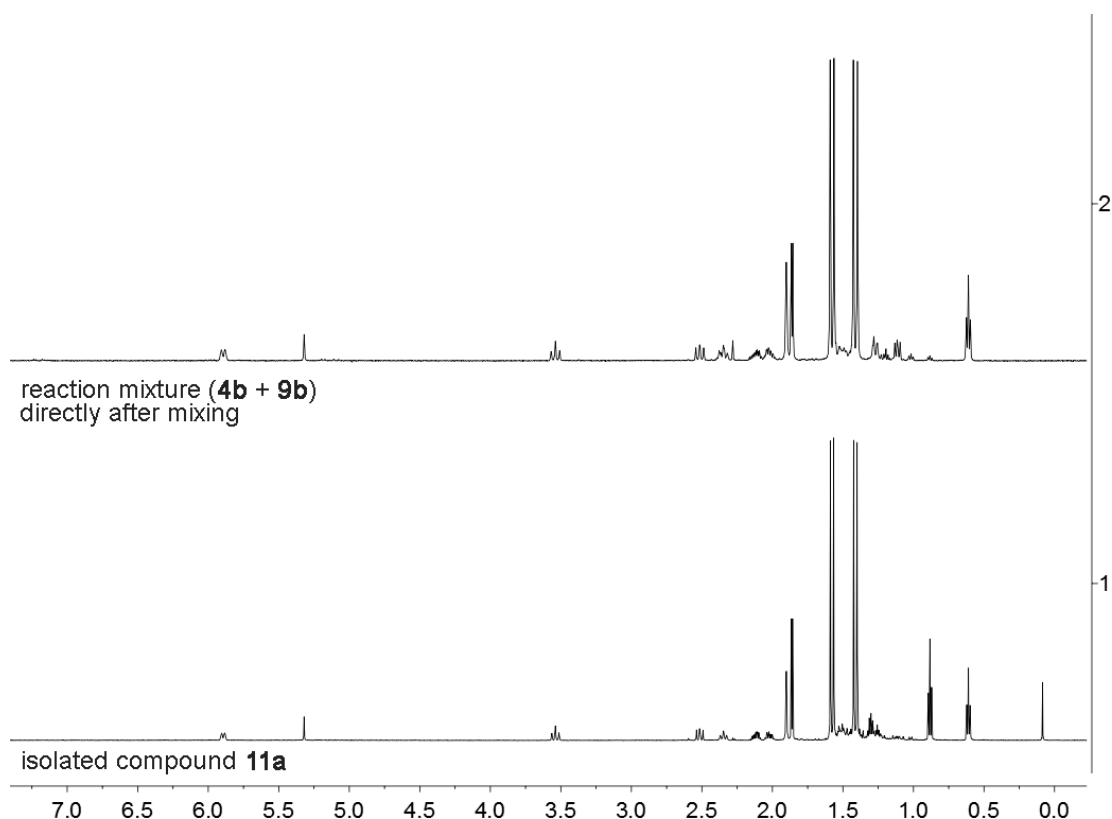
**Figure S45.**

### Control experiments (4b + 9b: NMR scale)

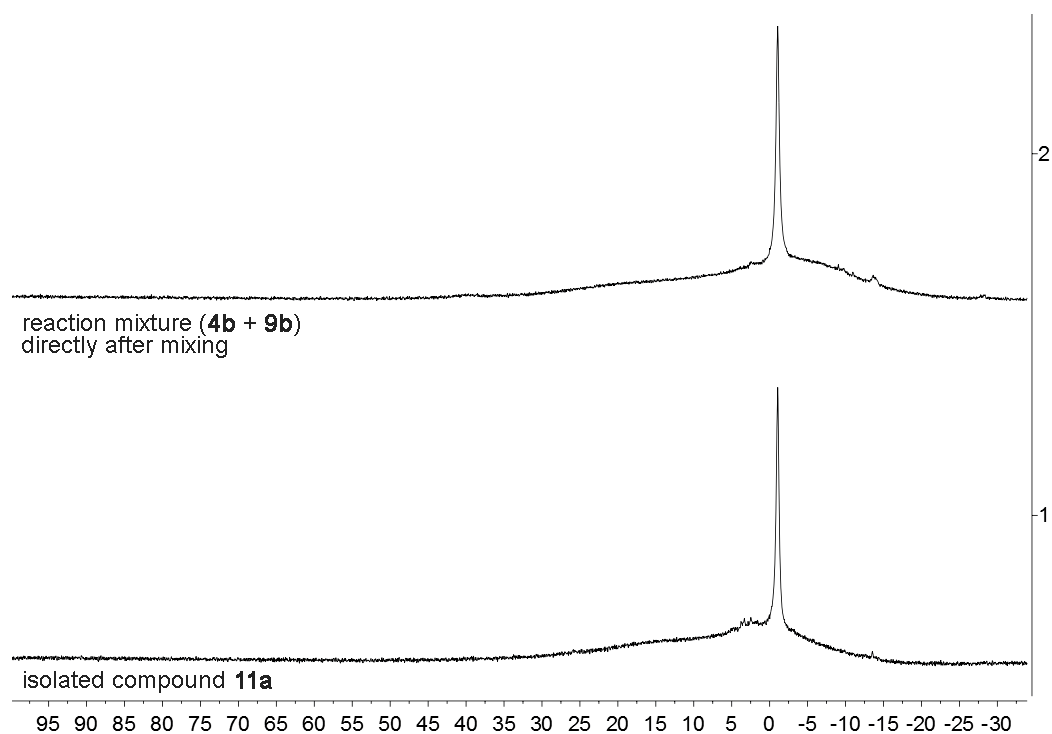
#### *Reactions of compounds 4b with alkyne 9b monitored by NMR spectroscopy*

Alkyne **9b** (0.03 mmol, 2.9 mg) was added to a solution of compound **4b** (0.03 mmol, 16.7 mg) in CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL) [alternatively with C<sub>6</sub>D<sub>6</sub> (0.5 mL)]. The reaction mixture was transferred to a NMR tube and monitored by NMR spectroscopy.

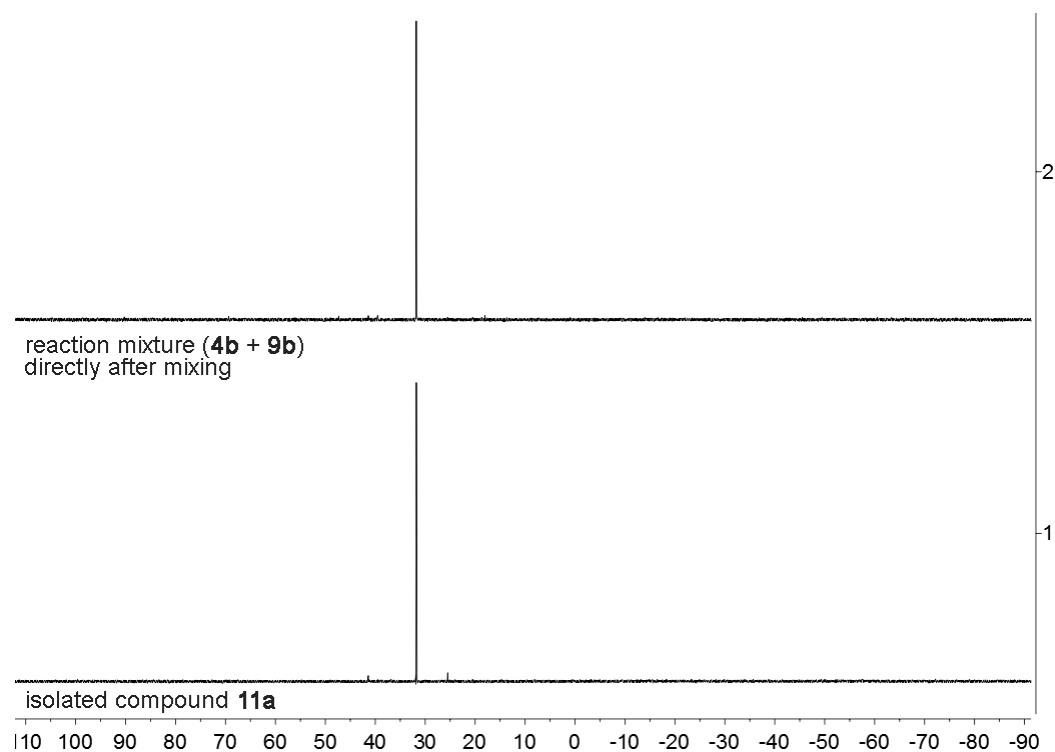
Comment: NMR spectra showed that the reaction of compound **4b** with the alkyne **9b** was finished in less than 10 min. at r.t. after mixing the components to give compound **11a** in quantitative yield.



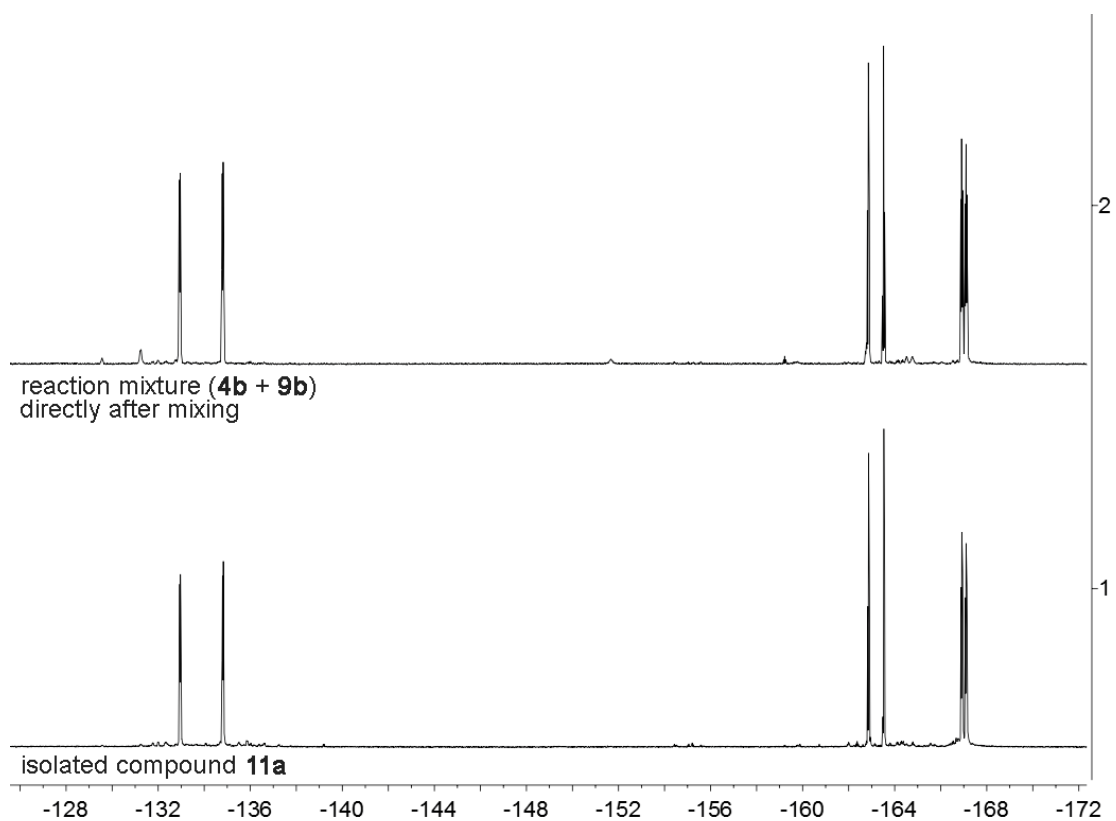
**Figure S46.** (1) <sup>1</sup>H NMR (600 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>) spectrum of isolated compound **11a** and (2) <sup>1</sup>H NMR (500 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>) spectrum of the reaction mixture of the reaction of compounds **4b** with **9b**



**Figure S47.** (1)  $^{11}\text{B}\{^1\text{H}\}\text{NMR}$  (192 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) spectrum of isolated compound **11a** and (2)  $^{11}\text{B}\{^1\text{H}\}\text{NMR}$  (160 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) spectrum of the reaction mixture of the reaction of compounds **4b** with **9b**

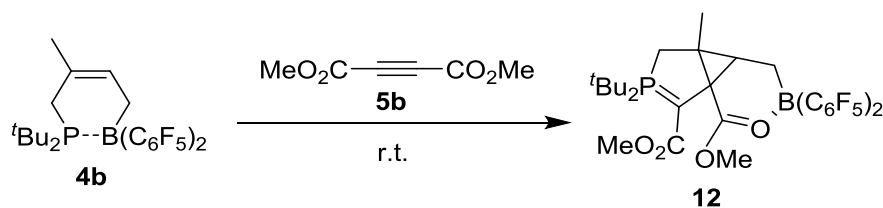


**Figure S48.** (1)  $^{31}\text{P}\{^1\text{H}\}\text{NMR}$  (243 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) spectrum of isolated compound **11a** and (2)  $^{31}\text{P}\{^1\text{H}\}\text{NMR}$  (202 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) spectrum of the reaction mixture of the reaction of compounds **4b** with **9b**



**Figure S49.** (1)  $^{19}\text{F}$ NMR (564 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) spectrum of isolated compound **11a** and (2)  $^{19}\text{F}$ NMR (470 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) spectrum of the reaction mixture of the reaction of compounds **4b** with **9b**

## Synthesis of compound 12



**Scheme S7**

A solution of compounds **4b** (111.6 mg, 0.2 mmol) and **5b** (28.4 mg, 0.2 mmol) in pentane (2 mL) was stirred at room temperature for 3 h. Then all volatiles were removed in vacuo and the resulting residue was washed with cold pentane (3x1 mL). After drying in vacuo compound **12** (119.6 mg, 85 %) was obtained as a light yellow solid (two isomers 85:15 ( $^1\text{H}$ )). Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **12** in dichloromethane at  $-35\text{ }^\circ\text{C}$ . **Decomp.**  $201\text{ }^\circ\text{C}$ . **Anal. Calc.** for  $\text{C}_{31}\text{H}_{32}\text{BF}_{10}\text{O}_4\text{P}$ : C: 53.16; H: 4.61. Found: C: 53.29; H: 4.61.

**$^1\text{H}$  NMR** (500 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = major isomer (85 mol%): 4.07 (s, 3H,  $\text{OCH}_3^{\text{B}}$ ), 2.88 (s, 3H,  $\text{OCH}_3$ ), 2.34 (dd,  $^2J_{\text{HH}} = 15.8\text{ Hz}$ ,  $^2J_{\text{PH}} = 5.9\text{ Hz}$ , 1H,  $\text{PCH}_2$ ), 2.18 (dd,  $^2J_{\text{HH}} = 15.8\text{ Hz}$ ,  $^2J_{\text{PH}} = 10.3\text{ Hz}$ , 1H,  $\text{PCH}_2$ ), 1.97 (m, 1H, CH), 1.96, 0.87 (each m, each 1H,  $\text{BCH}_2$ ), 1.40 (d,  $^3J_{\text{PH}} = 14.7\text{ Hz}$ , 9H,  $^t\text{Bu}^{\text{a}}$ ), 1.39 (d,  $^3J_{\text{PH}} = 14.9\text{ Hz}$ , 9H,  $^t\text{Bu}^{\text{b}}$ ), 1.26 (s, 3H,  $\text{CH}_3$ ); minor isomer (15 mol%): 4.07 (s, 3H,  $\text{OCH}_3^{\text{B}}$ ), 3.28 (s, 3H,  $\text{OCH}_3$ ), 2.43 (dd,  $^2J_{\text{HH}} = 15.8\text{ Hz}$ ,  $^2J_{\text{PH}} = 5.9\text{ Hz}$ , 1H,  $\text{PCH}_2$ ), 2.26 (dd,  $^2J_{\text{HH}} = 15.8\text{ Hz}$ ,  $^2J_{\text{PH}} = 10.2\text{ Hz}$ , 1H,  $\text{PCH}_2$ ), 1.89 (m, 1H, CH), 1.88, 0.84 (each m, each 1H,  $\text{BCH}_2$ ), 1.35 (d,  $^3J_{\text{PH}} = 14.6\text{ Hz}$ , 9H,  $^t\text{Bu}^{\text{a}}$ ), 1.31 (d,  $^3J_{\text{PH}} = 14.8\text{ Hz}$ , 9H,  $^t\text{Bu}^{\text{b}}$ ), 1.25 (s, 3H,  $\text{CH}_3$ ).

**$^{13}\text{C}\{^1\text{H}\}$  NMR** (126 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = major isomer: 187.0 (d,  $^3J_{\text{PC}} = 8.2\text{ Hz}$ ,  $\text{C}=\text{O}^{\text{B}}$ ), 168.2 (d,  $^2J_{\text{PC}} = 25.2\text{ Hz}$ ,  $\text{C}=\text{O}$ ), 57.34 ( $\text{OCH}_3^{\text{B}}$ ), 49.3 (d,  $^4J_{\text{PC}} = 1.7\text{ Hz}$ ,  $\text{OCH}_3$ ), 48.4 (d,  $^1J_{\text{PC}} = 113.0\text{ Hz}$ ,  $\text{C}=\text{P}$ ), 42.40 (CH), 41.1 (d,  $^2J_{\text{PC}} = 21.6\text{ Hz}$ ,  $>\text{C}<$ ), 40.5 (d,  $^2J_{\text{PC}} = 0.8\text{ Hz}$ ,  $\text{C}^{\text{Me}}$ ), 38.8 (d,  $^1J_{\text{PC}} = 35.1\text{ Hz}$ ,  $^t\text{Bu}^{\text{a}}$ ), 35.3 (d,  $^1J_{\text{PC}} = 42.7\text{ Hz}$ ,  $^t\text{Bu}^{\text{b}}$ ), 30.5 (d,  $^1J_{\text{PC}} = 53.1\text{ Hz}$ ,  $\text{PCH}_2$ ), 28.6 (d,  $^2J_{\text{PC}} = 1.0\text{ Hz}$ ,  $^t\text{Bu}^{\text{b}}$ ), 27.4 (d,  $^2J_{\text{PC}} = 1.7\text{ Hz}$ ,  $^t\text{Bu}^{\text{a}}$ ), 16.4 (d,  $^3J_{\text{PC}} = 6.3\text{ Hz}$ ,  $\text{CH}_3$ ), 14.7 (br,  $\text{BCH}_2$ ); minor isomer: 186.4 (d,  $^3J_{\text{PC}} = 8.2\text{ Hz}$ ,  $\text{C}=\text{O}^{\text{B}}$ ), 167.8 (d,  $^2J_{\text{PC}} = 18.9\text{ Hz}$ ,  $\text{C}=\text{O}$ ), 57.29 ( $\text{OCH}_3^{\text{B}}$ ), 48.9 ( $\text{OCH}_3$ ), 47.1 (d,  $^1J_{\text{PC}} = 111.8\text{ Hz}$ ,  $\text{C}=\text{P}$ )<sup>t</sup>, 42.39 (CH), 42.4 (d,  $^2J_{\text{PC}} = 22.9\text{ Hz}$ ,  $>\text{C}<$ )<sup>t</sup>, 38.3 (d,  $^1J_{\text{PC}} = 35.3\text{ Hz}$ ,  $^t\text{Bu}^{\text{a}}$ ), 38.2 (d,  $^2J_{\text{PC}} = 1.2\text{ Hz}$ ,  $\text{C}^{\text{Me}}$ ), 35.5 (d,  $^1J_{\text{PC}} = 43.1\text{ Hz}$ ,  $^t\text{Bu}^{\text{b}}$ ), 32.2 (d,  $^1J_{\text{PC}} = 53.7\text{ Hz}$ ,  $\text{PCH}_2$ ), 28.5 (d,  $^2J_{\text{PC}} = 0.9\text{ Hz}$ ,  $^t\text{Bu}^{\text{b}}$ ), 27.2 (d,  $^2J_{\text{PC}} = 1.6\text{ Hz}$ ,  $^t\text{Bu}^{\text{a}}$ ), 16.1 (d,  $^3J_{\text{PC}} = 6.2\text{ Hz}$ ,  $\text{CH}_3$ ), 14.8 (br,  $\text{BCH}_2$ ), [ $\text{C}_6\text{F}_5$  not listed, <sup>t</sup> tentative assignment].

**$^{11}\text{B}\{^1\text{H}\}$  NMR** (160 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 3.8 ( $\nu_{1/2} \sim 350\text{ Hz}$ ).

**$^{31}\text{P}\{^1\text{H}\}$  NMR** (202 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 80.1 ( $\nu_{1/2} \sim 1\text{ Hz}$ , 83 mol%), 71.1 ( $\nu_{1/2} \sim 0.9\text{ Hz}$ , 17 mol%).

**$^{19}\text{F}$  NMR** (470 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = major isomer (84 mol%): -135.1 (m, 2F, *o*), -160.3 (t,  $^3J_{\text{FF}} = 20.1\text{ Hz}$ , 1F, *p*), -166.1 (m, 2F, *m*)( $\text{C}_6\text{F}_5$ )[ $\Delta\delta^{19}\text{F}_{\text{mp}} = 5.8$ ], -136.3 (m, 2F,

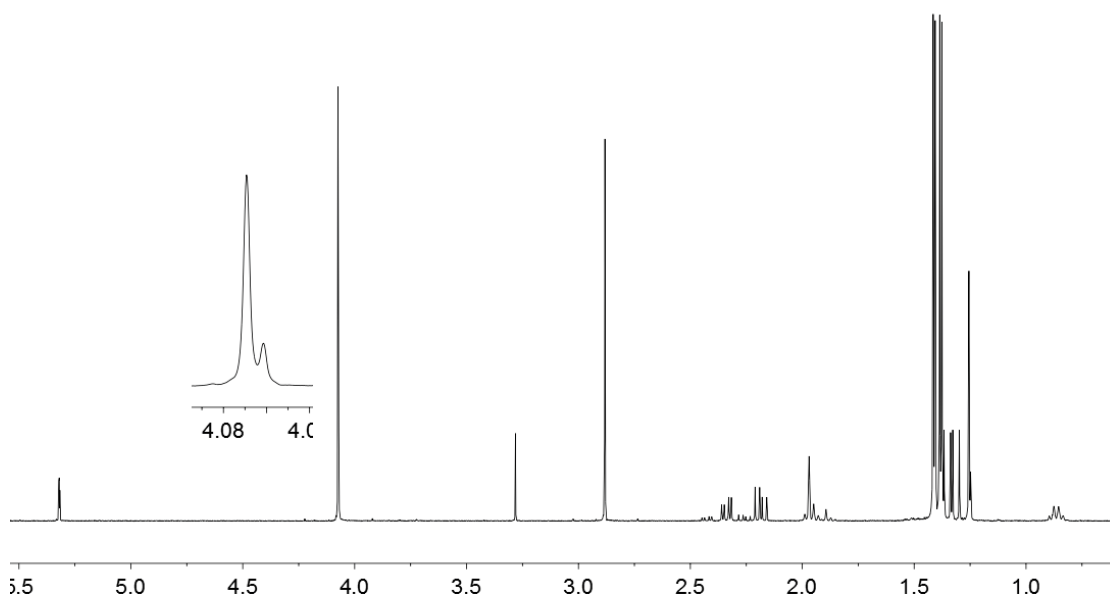
*o*), -161.3 (t,  $^3J_{\text{FF}} = 20.1$  Hz, 1F, *p*), -165.5 (m, 2F, *m*)(C<sub>6</sub>F<sub>5</sub>)[ $\Delta\delta^{19}\text{F}_{\text{mp}} = 4.2$ ]; minor isomer 16 mol%): -135.6 (m, 2F, *o*), -161.6 (t,  $^3J_{\text{FF}} = 20.2$  Hz, 1F, *p*), -167.2 (m, 2F, *m*)(C<sub>6</sub>F<sub>5</sub>)[ $\Delta\delta^{19}\text{F}_{\text{mp}} = 5.6$ ], -136.1 (m, 2F, *o*), -161.4 (t,  $^3J_{\text{FF}} = 20.1$  Hz, 1F, *p*), -165.7 (m, 2F, *m*)(C<sub>6</sub>F<sub>5</sub>)[ $\Delta\delta^{19}\text{F}_{\text{mp}} = 4.3$ ].

**<sup>1</sup>H, <sup>1</sup>H-GCOSY** (500 MHz / 500 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>)[selected traces]:  $\delta^{1\text{H}} / \delta^{1\text{H}} =$  major isomer: 2.34 / 2.18 (PCH<sub>2</sub> / PCH<sub>2</sub>), 1.96 / 0.87 (BCH<sub>2</sub> / BCH<sub>2</sub>); minor isomer: 2.43 / 2.26 (PCH<sub>2</sub> / PCH<sub>2</sub>), 1.88 / 0.84 (BCH<sub>2</sub> / BCH<sub>2</sub>).

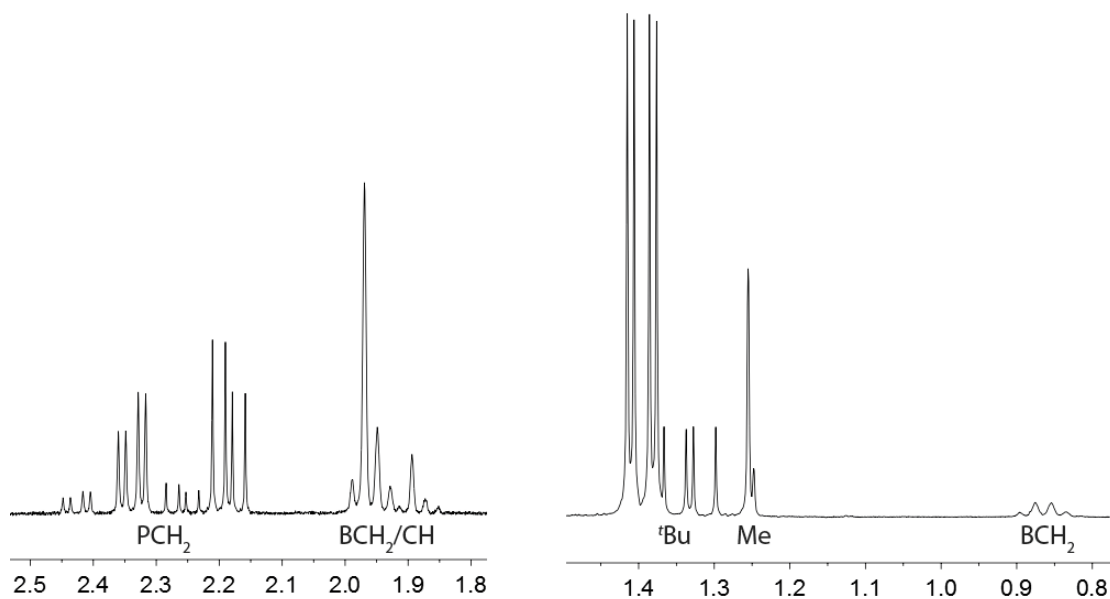
**<sup>1</sup>H, <sup>13</sup>C-GHSQC** (500 MHz / 126 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta^{1\text{H}} / \delta^{13\text{C}} =$  major isomer: 4.07 / 57.34 (OCH<sub>3</sub><sup>B</sup>), 2.88 / 49.3 (OCH<sub>3</sub>), 2.34, 2.18 / 30.5 (PCH<sub>2</sub>), 1.96 / 42.40 (CH), 1.96, 0.87 / 14.7 (BCH<sub>2</sub>), 1.40 / 27.4 (<sup>t</sup>Bu<sup>a</sup>), 1.39 / 28.6 (<sup>t</sup>Bu<sup>b</sup>), 1.26 / 16.4 (CH<sub>3</sub>); minor isomer: 4.07 / 57.29 (OCH<sub>3</sub><sup>B</sup>), 3.28 / 48.9 (OCH<sub>3</sub>), 2.43, 2.26 / 32.2 (PCH<sub>2</sub>), 1.88 / 42.39 (CH), 1.88, 0.84 / 14.7 (BCH<sub>2</sub>), 1.35 / 27.2 (<sup>t</sup>Bu<sup>a</sup>), 1.31 / 28.5 (<sup>t</sup>Bu<sup>b</sup>), 1.25 / 16.1 (CH<sub>3</sub>).

**<sup>1</sup>H, <sup>13</sup>C-GHMBC** (500 MHz / 126 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>)[selected traces]:  $\delta^{1\text{H}} / \delta^{13\text{C}} =$  major isomer: 4.07, 1.96 / 187.0 (OCH<sub>3</sub><sup>B</sup>, CH / C=OB), 2.88 / 168.2 (OCH<sub>3</sub> / C=O), 2.34, 2.18, 1.26, 0.87 / 40.5 (PCH<sub>2</sub>, PCH<sub>2</sub>, CH<sub>3</sub>, BCH<sub>2</sub> / C<sup>Me</sup>), 2.18, 1.96 / 48.4 (PCH<sub>2</sub>, CH / C=P), 1.96, 1.26, 0.87 / 41.1 (CH, CH<sub>3</sub>, BCH<sub>2</sub> / >C<), 1.40 / 38.8 (<sup>t</sup>Bu<sup>a</sup> / <sup>t</sup>Bu<sup>a</sup>), 1.39 / 35.1 (<sup>t</sup>Bu<sup>b</sup> / <sup>t</sup>Bu<sup>b</sup>); minor isomer: 4.07 / 186.4 (OCH<sub>3</sub><sup>B</sup> / C=OB), 3.28 / 167.8 (OCH<sub>3</sub> / C=O), 2.43, 1.25, 0.84 / 38.2 (PCH<sub>2</sub>, CH<sub>3</sub>, BCH<sub>2</sub> / C<sup>Me</sup>), 1.35 / 38.3 (<sup>t</sup>Bu<sup>a</sup> / <sup>t</sup>Bu<sup>a</sup>), 1.31 / 35.5 (<sup>t</sup>Bu<sup>b</sup> / <sup>t</sup>Bu<sup>b</sup>).

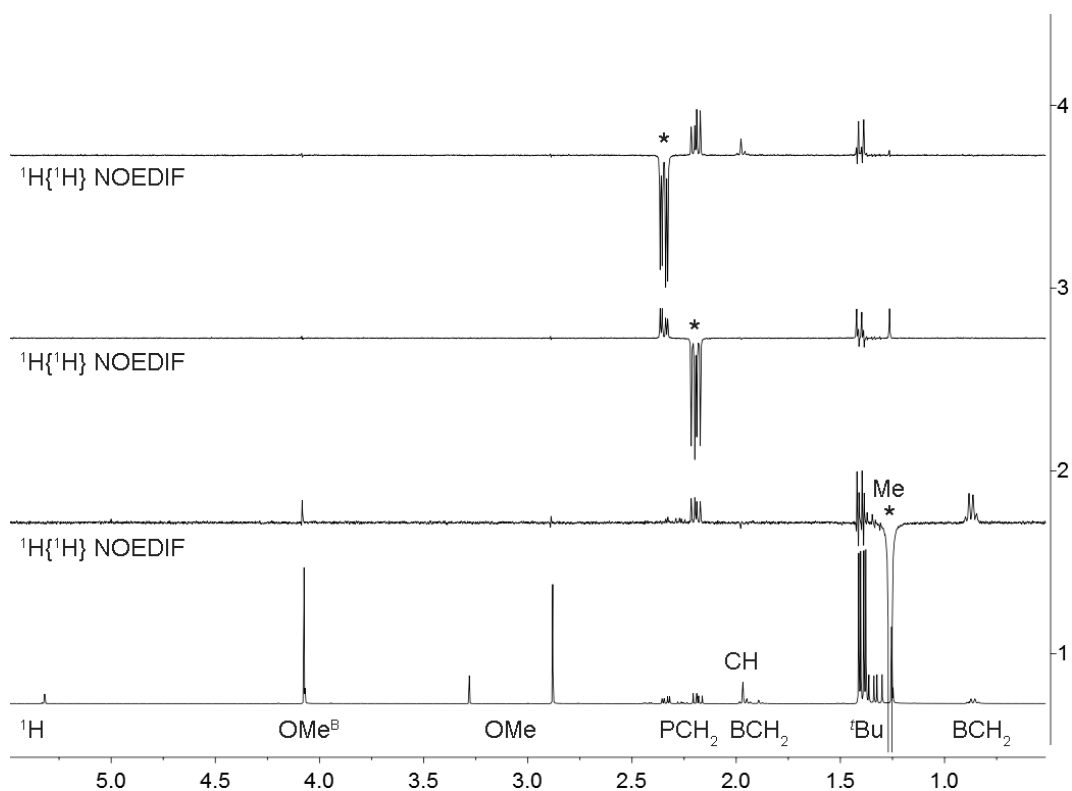
**<sup>19</sup>F, <sup>19</sup>F-GCOSY** (470 MHz / 470 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta^{19\text{F}} / \delta^{19\text{F}} =$  major isomer: -166.1 / -135.1, -160.3 (*m*-C<sub>6</sub>F<sub>5</sub><sup>a</sup> / *o*-C<sub>6</sub>F<sub>5</sub><sup>a</sup>, *p*-C<sub>6</sub>F<sub>5</sub><sup>a</sup>), -165.5 / -136.3, -161.3 (*m*-C<sub>6</sub>F<sub>5</sub><sup>b</sup> / *o*-C<sub>6</sub>F<sub>5</sub><sup>b</sup>, *p*-C<sub>6</sub>F<sub>5</sub><sup>b</sup>); minor isomer: -167.2 / -135.6, -161.6 (*m*-C<sub>6</sub>F<sub>5</sub><sup>a</sup> / *o*-C<sub>6</sub>F<sub>5</sub><sup>a</sup>, *p*-C<sub>6</sub>F<sub>5</sub><sup>a</sup>), -165.7 / -136.1, -161.4 (*m*-C<sub>6</sub>F<sub>5</sub><sup>b</sup> / *o*-C<sub>6</sub>F<sub>5</sub><sup>b</sup>, *p*-C<sub>6</sub>F<sub>5</sub><sup>b</sup>).



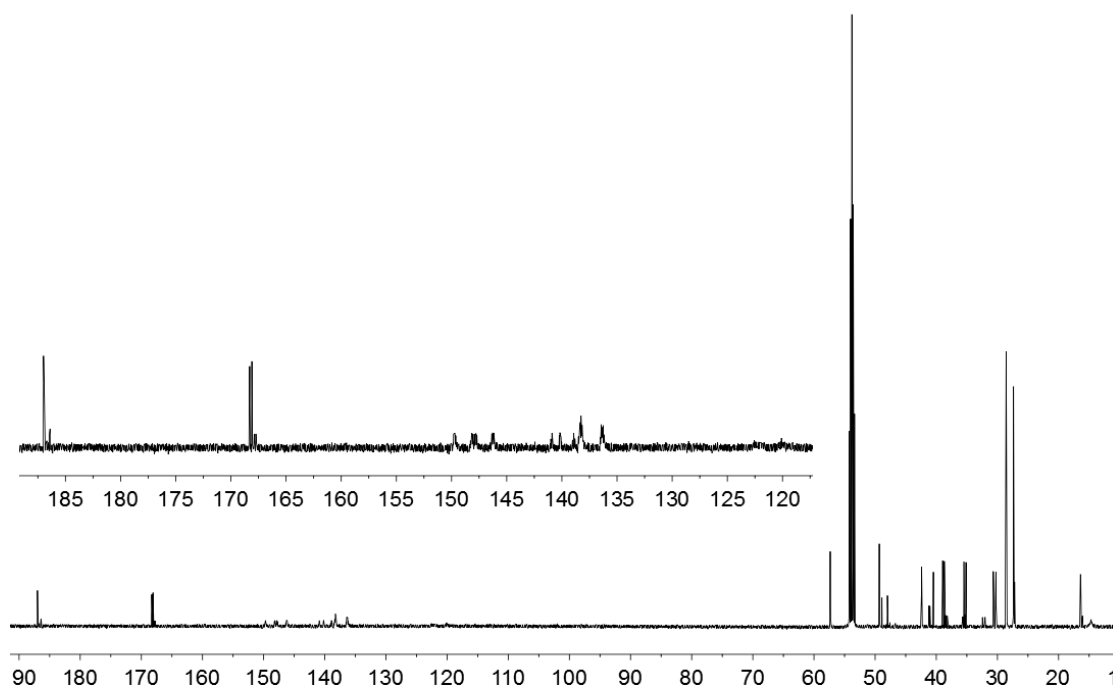
**Figure S50. <sup>1</sup>H NMR (500 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>) of compound 12**



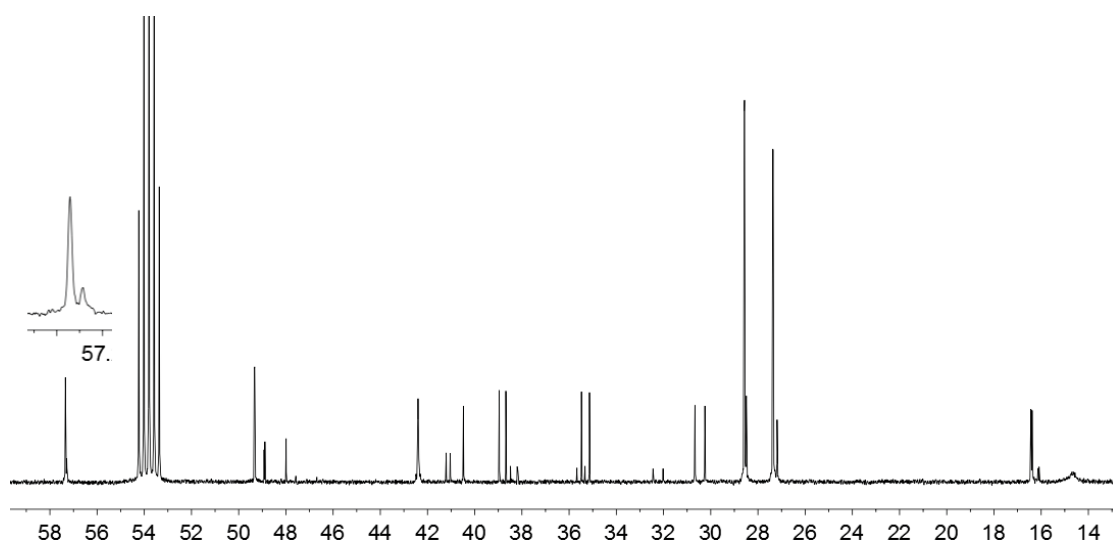
**Figure S51.**  $^1\text{H}$  NMR (500 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) of compound **12**



**Figure S52.** (1)  $^1\text{H}$  NMR (600 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) and (2)  $^1\text{H}\{^1\text{H}\}$  NOEDIF (600 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) spectra of compound **12** [\* irradiation point]

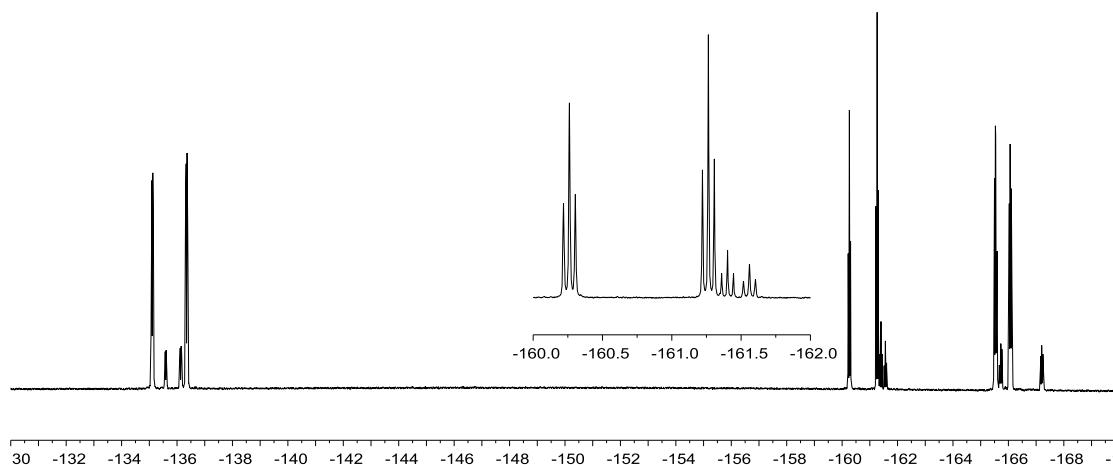


**Figure S53.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) of compound **12**

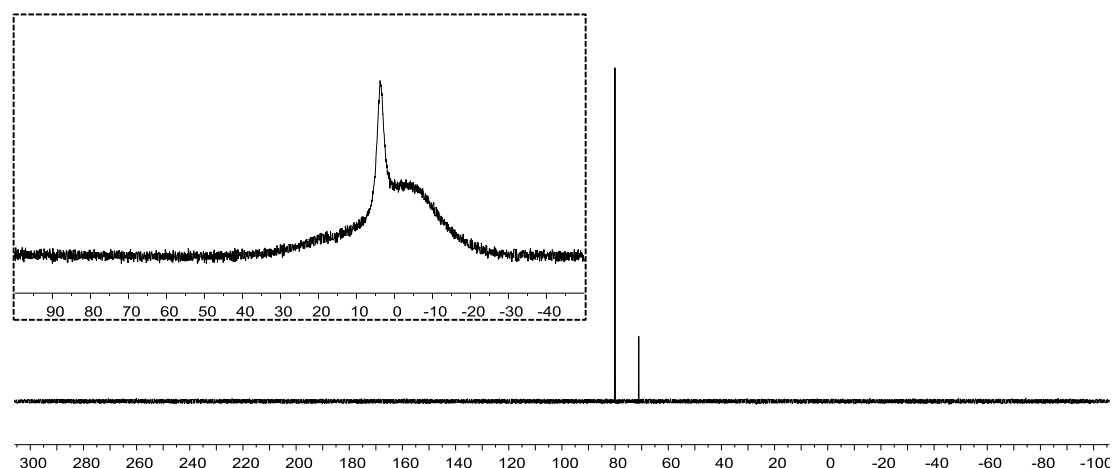


**Figure S54.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) of compound **12**



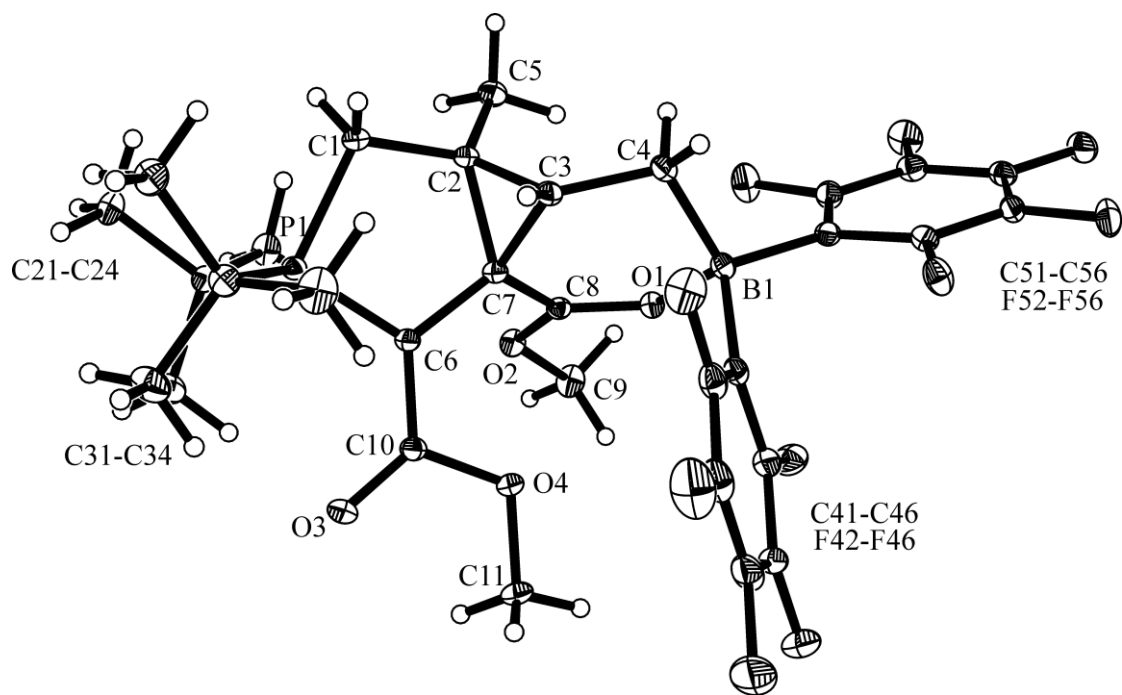


**Figure S55.**  $^{19}\text{F}$  NMR (470 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) of compound **12**



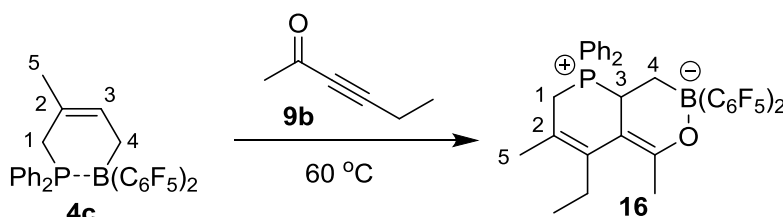
**Figure S56.**  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) of compound **12**

**X-ray crystal structure analysis of compound 12:** formula  $\text{C}_{31}\text{H}_{32}\text{BF}_{10}\text{O}_4\text{P}$ ,  $M = 700.35$ , colourless crystal,  $0.30 \times 0.23 \times 0.15$  mm,  $a = 12.1821(2)$ ,  $b = 18.7258(3)$ ,  $c = 14.2778(2)$  Å,  $\beta = 105.022(1)^\circ$ ,  $V = 3145.7(1)$  Å<sup>3</sup>,  $\rho_{\text{calc}} = 1.479$  gcm<sup>-3</sup>,  $\mu = 0.183$  mm<sup>-1</sup>, empirical absorption correction ( $0.947 \leq T \leq 0.973$ ),  $Z = 4$ , monoclinic, space group  $P2_1/c$  (No. 14),  $\lambda = 0.71073$  Å,  $T = 223(2)$  K,  $\omega$  and  $\phi$  scans, 19786 reflections collected ( $\pm h, \pm k, \pm l$ ), 5602 independent ( $R_{\text{int}} = 0.033$ ) and 4972 observed reflections [ $I > 2\sigma(I)$ ], 433 refined parameters,  $R = 0.048$ ,  $wR^2 = 0.115$ , max. (min.) residual electron density 0.49 (-0.33) e.Å<sup>-3</sup>, hydrogen atoms were calculated and refined as riding atoms.



**Figure S57.**

## Synthesis of compound 16



**Scheme S8**

A solution of compounds **4c** (119.6 mg, 0.2 mmol) and **9b** (19.2 mg, 0.2 mmol) in toluene (2 mL) was stirred at 60 °C for 3 days. Then all volatiles were removed in vacuo and the resulting residue was washed with cold pentane (3x1 mL). After drying in vacuo compound **16** (101.5 mg, 73 %) was obtained as a light yellow solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **16** in dichloromethane at -35 °C. **M.p.** 195 °C. **Anal. Calc.** for C<sub>35</sub>H<sub>26</sub>BF<sub>10</sub>OP: C: 60.54; H: 3.77. Found: C: 60.75; H: 3.93.

**<sup>1</sup>H NMR** (600 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = 7.77, 7.75 (each m, each 1H, *p*-Ph), 7.62 (m, 6H, *m,m,o*-Ph), 7.50 (m, 2H, *o*-Ph), 3.39 (m, 1H, CH), 3.35 (ddm, <sup>2</sup>*J*<sub>HH</sub> = 15.8 Hz, <sup>2</sup>*J*<sub>PH</sub> = 14.8 Hz, 1H, PCH<sub>2</sub>), 2.79 (dd, <sup>2</sup>*J*<sub>HH</sub> = 15.8 Hz, <sup>2</sup>*J*<sub>PH</sub> = 12.1 Hz, 1H, PCH<sub>2</sub>), 2.45 (m), 2.18 (br m)(each 1H, Et), 1.79 (dd, <sup>5</sup>*J*<sub>PH</sub> = 5.6 Hz, <sup>a</sup><sup>5</sup>*J*<sub>HH</sub> = 1.6 Hz, <sup>a</sup> 3H, <sup>O</sup>-CCH<sub>3</sub>), 1.59 (m, 3H, CH<sub>3</sub>), 1.45, 0.83 (each m, each 1H, BCH<sub>2</sub>), 0.72 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz, 3H, Et), [<sup>a</sup> assignment by <sup>1</sup>H{<sup>1</sup>H} and <sup>1</sup>H{<sup>31</sup>P} NMR experiments].

**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = 159.3 (d, <sup>3</sup>*J*<sub>PC</sub> = 11.5 Hz, =CO), 145.0 (d, <sup>3</sup>*J*<sub>PC</sub> = 12.0 Hz, =CEt), 134.59, 134.55 (each d, <sup>4</sup>*J*<sub>PC</sub> = 2.9 Hz, *p*-Ph), 133.8, 133.3 (each d, <sup>2</sup>*J*<sub>PC</sub> = 8.0 Hz, *o*-Ph), 130.2 (d, <sup>3</sup>*J*<sub>PC</sub> = 11.1 Hz), 129.7 (d, <sup>3</sup>*J*<sub>PC</sub> = 11.6 Hz)(*m*-Ph), 121.5 (d, <sup>1</sup>*J*<sub>PC</sub> = 30.9 Hz), 121.0 (d, <sup>1</sup>*J*<sub>PC</sub> = 32.9 Hz)(*i*-Ph), 117.6 (d, <sup>2</sup>*J*<sub>PC</sub> = 11.1 Hz, =CMe), 97.9 (br d, <sup>2</sup>*J*<sub>PC</sub> = 11.2 Hz, =C), 33.0 (d, <sup>1</sup>*J*<sub>PC</sub> = 45.8 Hz, CH), 28.1 (d, <sup>1</sup>*J*<sub>PC</sub> = 49.5 Hz, PCH<sub>2</sub>), 27.6 (d, <sup>4</sup>*J*<sub>PC</sub> = 4.0 Hz, Et), 22.8 (d, <sup>4</sup>*J*<sub>PC</sub> = 2.9 Hz, <sup>O</sup>-CCH<sub>3</sub>), 20.2 (br, BCH<sub>2</sub>), 20.1 (d, <sup>3</sup>*J*<sub>PC</sub> = 6.8 Hz, CH<sub>3</sub>), 12.9 (d, <sup>5</sup>*J*<sub>PC</sub> = 3.1 Hz, Et), [C<sub>6</sub>F<sub>5</sub> not listed].

**<sup>11</sup>B{<sup>1</sup>H} NMR** (192 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = -3.1 (ν<sub>1/2</sub> ~ 90 Hz).

**<sup>10</sup>B{<sup>1</sup>H} NMR** (54 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = -3.1 (ν<sub>1/2</sub> ~ 70 Hz).

**<sup>31</sup>P{<sup>1</sup>H} NMR** (243 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = 27.3 (ν<sub>1/2</sub> ~ 15 Hz).

**<sup>19</sup>F NMR** (564 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = -134.5 (m, 2F, *o*), -162.5 (t, <sup>3</sup>*J*<sub>FF</sub> = 20.2 Hz, 1F, *p*), -166.6 (m, 2F, *m*)(C<sub>6</sub>F<sub>5</sub>)[Δδ<sup>19</sup>F<sub>mp</sub> = 4.1], -136.6 (m, 2F, *o*), -162.9 (t, <sup>3</sup>*J*<sub>FF</sub> = 20.2 Hz, 1F, *p*), -166.5 (m, 2F, *m*)(C<sub>6</sub>F<sub>5</sub>)[Δδ<sup>19</sup>F<sub>mp</sub> = 3.6].

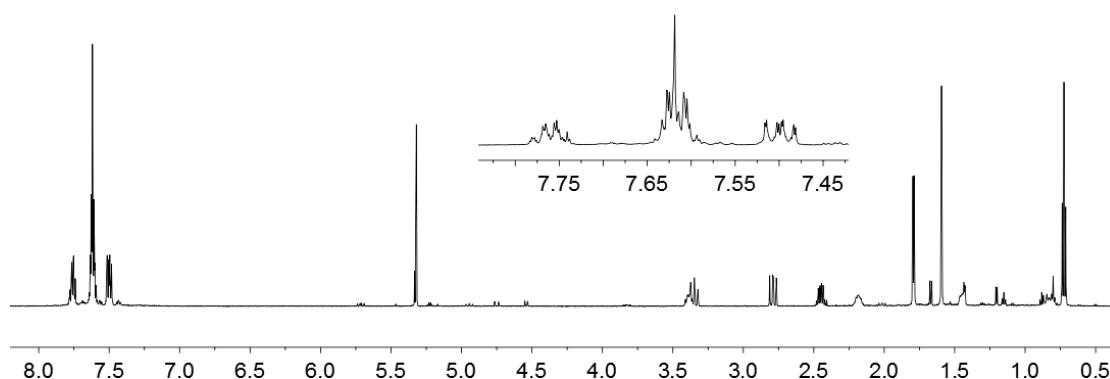
**<sup>1</sup>H, <sup>1</sup>H-GCOSY** (600 MHz / 600 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>)[selected traces]: δ <sup>1</sup>H / δ <sup>1</sup>H = 3.39 / 1.45, 0.83 (CH / BCH<sub>2</sub>, BCH<sub>2</sub>), 3.35 / 2.79, 1.59 (PCH<sub>2</sub> / PCH<sub>2</sub>, CH<sub>3</sub>), 2.45 / 2.18, 0.72 (Et / Et, Et).

**<sup>1</sup>H, <sup>13</sup>C-GHSQC** (600 MHz / 151 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>): δ <sup>1</sup>H / δ <sup>13</sup>C = 7.77 / 134.55 (*p*-Ph<sup>a</sup>), 7.75 / 134.59 (*p*-Ph<sup>b</sup>), 7.62 / 130.2 (*m*-Ph<sup>b</sup>), 7.61 / 129.7 (*m*-Ph<sup>a</sup>), 7.61 / 133.3

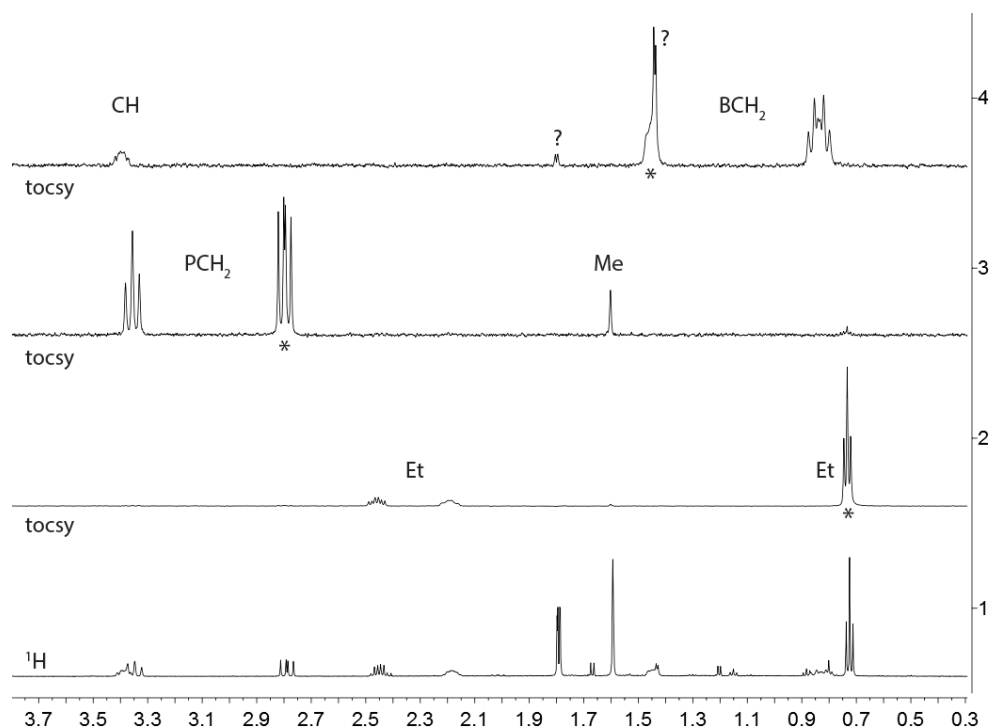
(*o*-Ph<sup>b</sup>), 7.50 / 133.8 (*o*-Ph<sup>a</sup>), 3.39 / 33.0 (CH), 3.35, 2.79 / 28.1 (PCH<sub>2</sub>), 2.45, 2.18 / 27.6 (Et), 1.79 / 22.8 (<sup>O</sup>-CCH<sub>3</sub>), 1.59 / 20.1 (CH<sub>3</sub>), 1.45, 0.83 / 20.2 (BCH<sub>2</sub>), 0.72 / 12.9 (Et).

**<sup>1</sup>H, <sup>13</sup>C-GHMBC** (600 MHz / 151 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>)[selected traces]:  $\delta$  <sup>1</sup>H /  $\delta$  <sup>13</sup>C = 7.62 / 130.2, 121.5 (*m*-Ph<sup>b</sup> / *m*-Ph<sup>b</sup>, *i*-Ph<sup>b</sup>), 7.61 / 129.7, 121.0 (*m*-Ph<sup>a</sup> / *m*-Ph<sup>a</sup>, *i*-Ph<sup>a</sup>), 3.39, 1.79, 1.59 / 159.3 (CH, <sup>O</sup>-CCH<sub>3</sub>, CH<sub>3</sub> / =CO), 3.39, 2.45, 2.18, 1.79, 1.59, 1.45 / 97.9 (CH, Et, Et, <sup>O</sup>-CCH<sub>3</sub>, CH<sub>3</sub>, BCH<sub>2</sub> / =C), 3.35, 2.79, 2.45, 2.18, 1.59, 0.72 / 145.0 (PCH<sub>2</sub>, PCH<sub>2</sub>, Et, Et, CH<sub>3</sub>, Et / =CEt), 3.35, 2.79, 2.45, 2.18, 1.79, 1.59 / 117.6 (PCH<sub>2</sub>, PCH<sub>2</sub>, Et, Et, <sup>O</sup>-CCH<sub>3</sub>, CH<sub>3</sub> / =CMe).

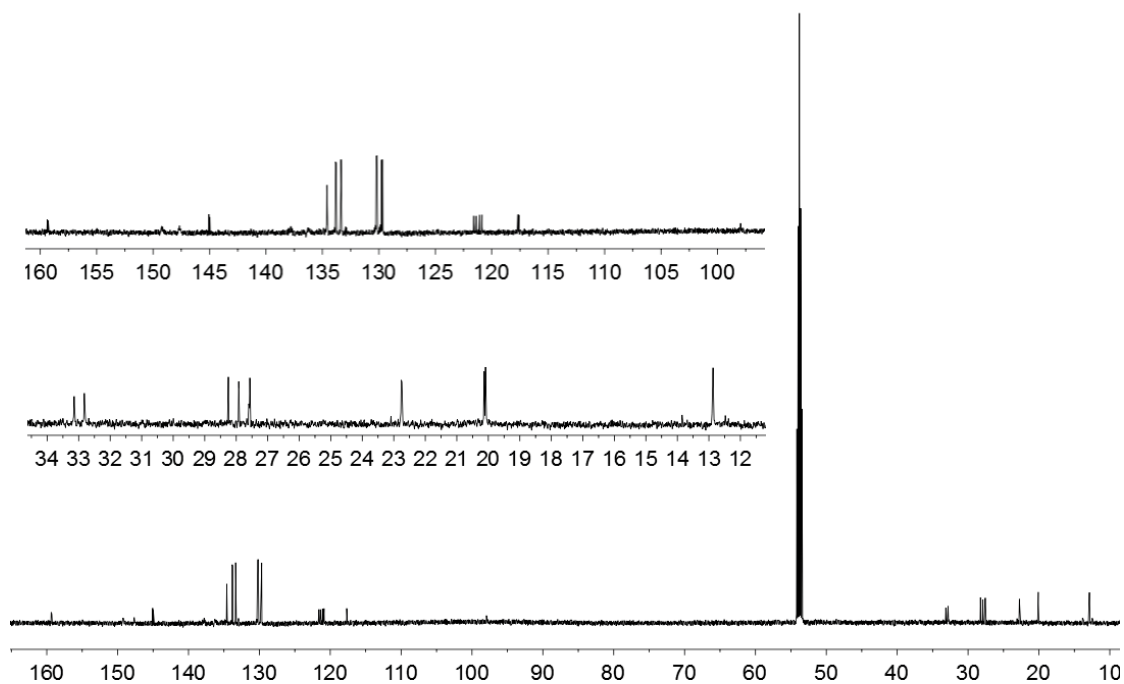
**<sup>19</sup>F, <sup>19</sup>F-GCOSY** (564 MHz / 564 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  <sup>19</sup>F /  $\delta$  <sup>19</sup>F = -166.6 / -134.5, -162.5 (*m*-C<sub>6</sub>F<sub>5</sub><sup>a</sup> / *o*-C<sub>6</sub>F<sub>5</sub><sup>a</sup>, *p*-C<sub>6</sub>F<sub>5</sub><sup>a</sup>), -166.5 / -136.6, -162.9 (*m*-C<sub>6</sub>F<sub>5</sub><sup>b</sup> / *o*-C<sub>6</sub>F<sub>5</sub><sup>b</sup>, *p*-C<sub>6</sub>F<sub>5</sub><sup>b</sup>).



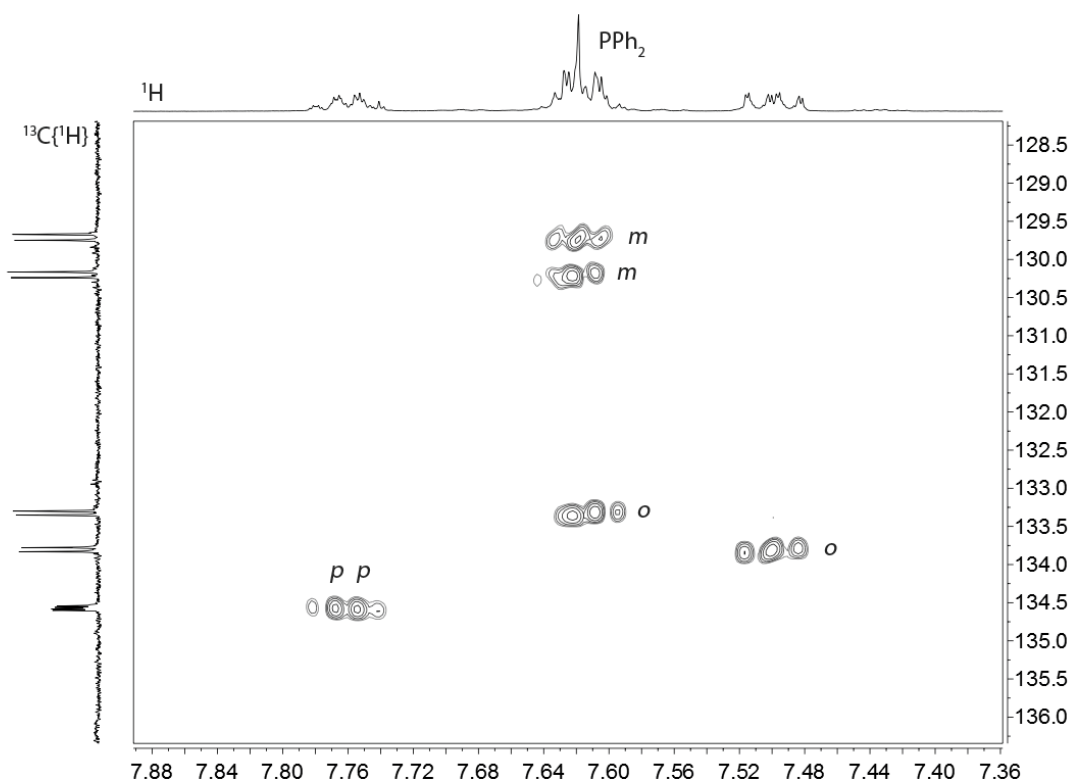
**Figure S58.** <sup>1</sup>H NMR (600 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>) of compound **16**



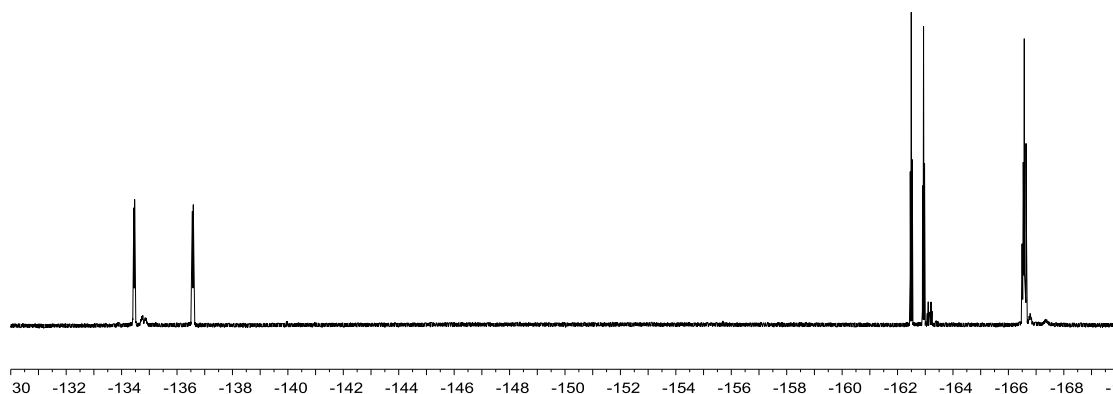
**Figure S59.** (1) <sup>1</sup>H NMR (600 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>) and (2 to 4) <sup>1</sup>H, <sup>1</sup>H-TOCSY (600 MHz / 600 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>) of compound **16**. Irradiation (\*) at (2)  $\delta^1\text{H}_{\text{irr}} = 0.72$  (Et), (3)  $\delta^1\text{H}_{\text{irr}} = 2.79$  (PCH<sub>2</sub>), and (4)  $\delta^1\text{H}_{\text{irr}} = 1.45$  (BCH<sub>2</sub>).



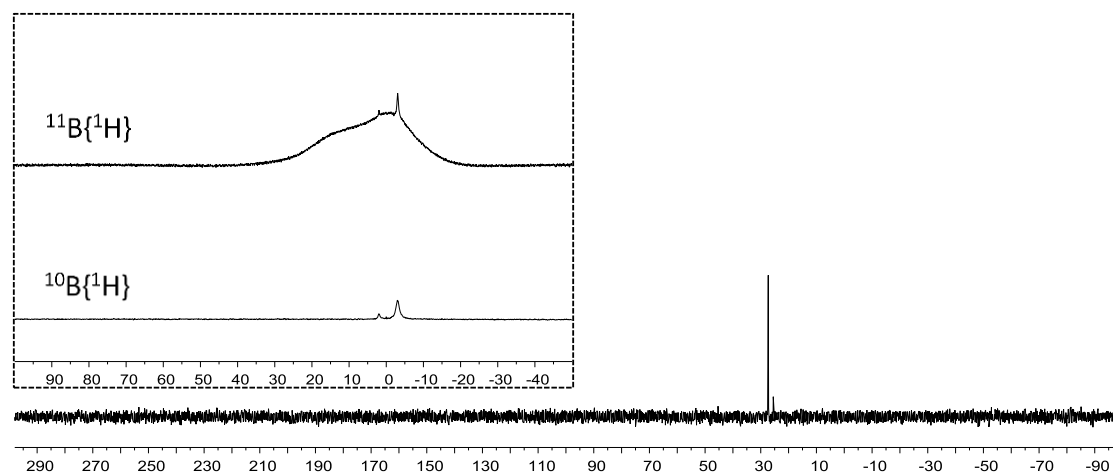
**Figure S60.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) of compound **16**



**Figure S61.**  $^1\text{H}$ ,  $^{13}\text{C}$ -GHSQC (600 MHz / 151 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) of compound **16**

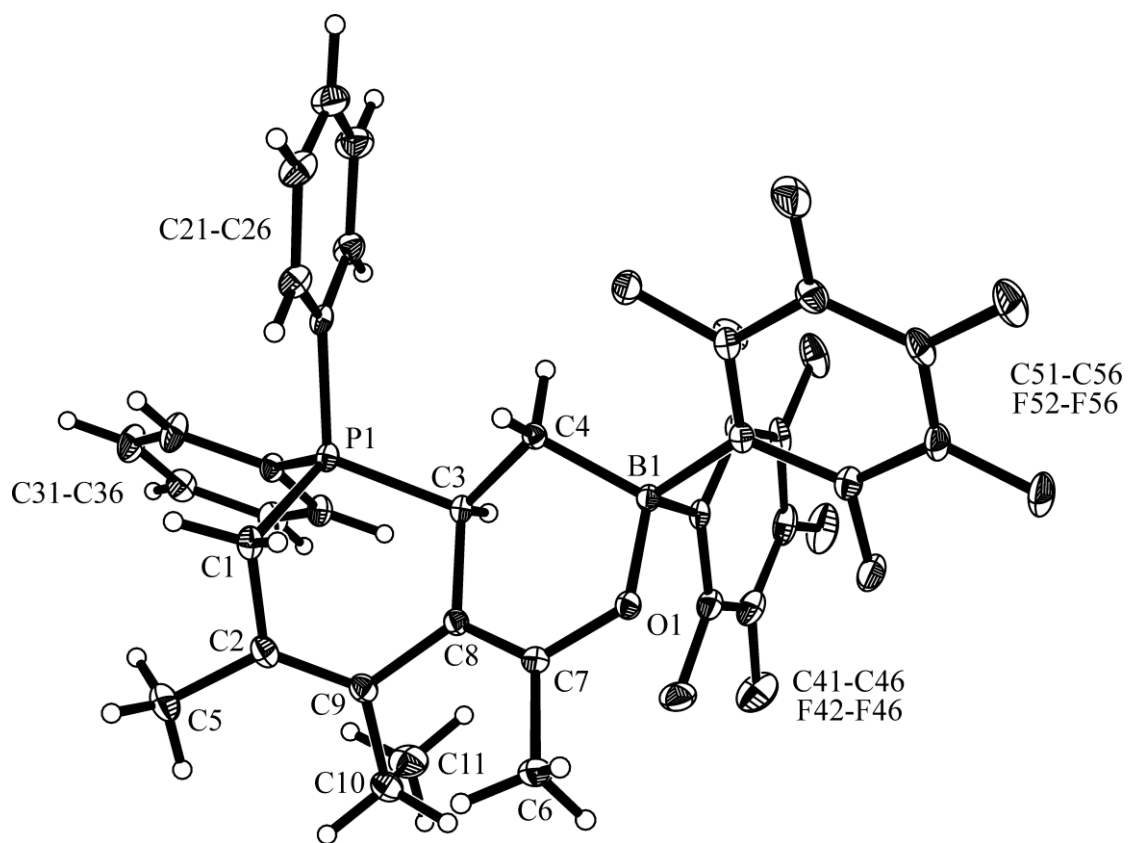


**Figure S62.**  $^{19}\text{F}$  NMR (564 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) of compound **16**



**Figure S63.**  $^{11}\text{B}\{^1\text{H}\}$  NMR (192 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ),  $^{10}\text{B}\{^1\text{H}\}$  NMR (54 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz, 299 K,  $\text{CD}_2\text{Cl}_2$ ) of compound **16**

**X-ray crystal structure analysis of compound 16:** formula  $\text{C}_{35}\text{H}_{26}\text{BF}_{10}\text{OP}$ ,  $M = 694.34$ , colourless crystal,  $0.32 \times 0.15 \times 0.05$  mm,  $a = 10.3933(2)$ ,  $b = 11.7676(2)$ ,  $c = 14.8634(4)$  Å,  $\alpha = 104.124(1)$ ,  $\beta = 101.199(1)$ ,  $\gamma = 111.497(1)^\circ$ ,  $V = 1557.1(1)$  Å<sup>3</sup>,  $\rho_{\text{calc}} = 1.481$  g cm<sup>-3</sup>,  $\mu = 0.178$  mm<sup>-1</sup>, empirical absorption correction ( $0.945 \leq T \leq 0.991$ ),  $Z = 2$ , triclinic, space group  $P\bar{1}$  (No. 2),  $\lambda = 0.71073$  Å,  $T = 223(2)$  K,  $\omega$  and  $\phi$  scans, 14326 reflections collected ( $\pm h$ ,  $\pm k$ ,  $\pm l$ ), 5251 independent ( $R_{\text{int}} = 0.057$ ) and 4479 observed reflections [ $I > 2\sigma(I)$ ], 436 refined parameters,  $R = 0.057$ ,  $wR^2 = 0.121$ , max. (min.) residual electron density  $0.30$  ( $-0.26$ ) e.Å<sup>-3</sup>, hydrogen atoms were calculated and refined as riding atoms.



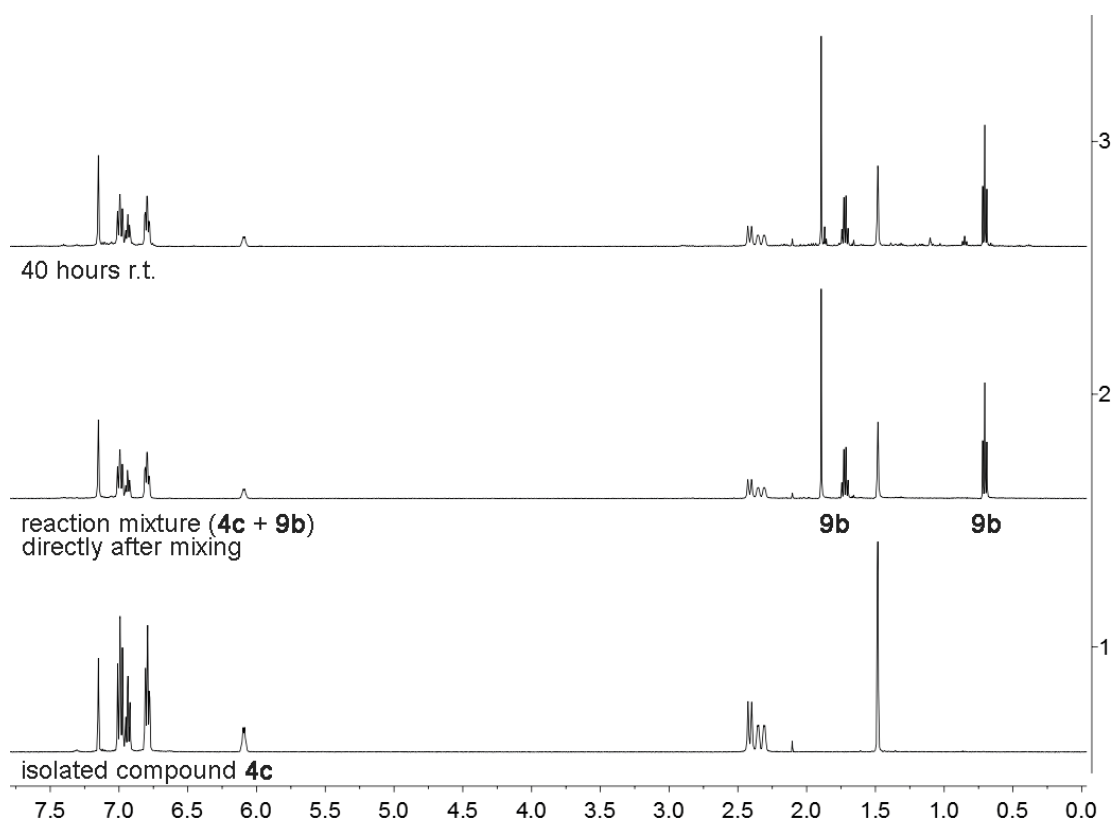
**Figure S64.**

### Control experiments (4c + 9b: NMR scale)

#### *Reactions of compounds 4c with alkyne 9b monitored by NMR spectroscopy*

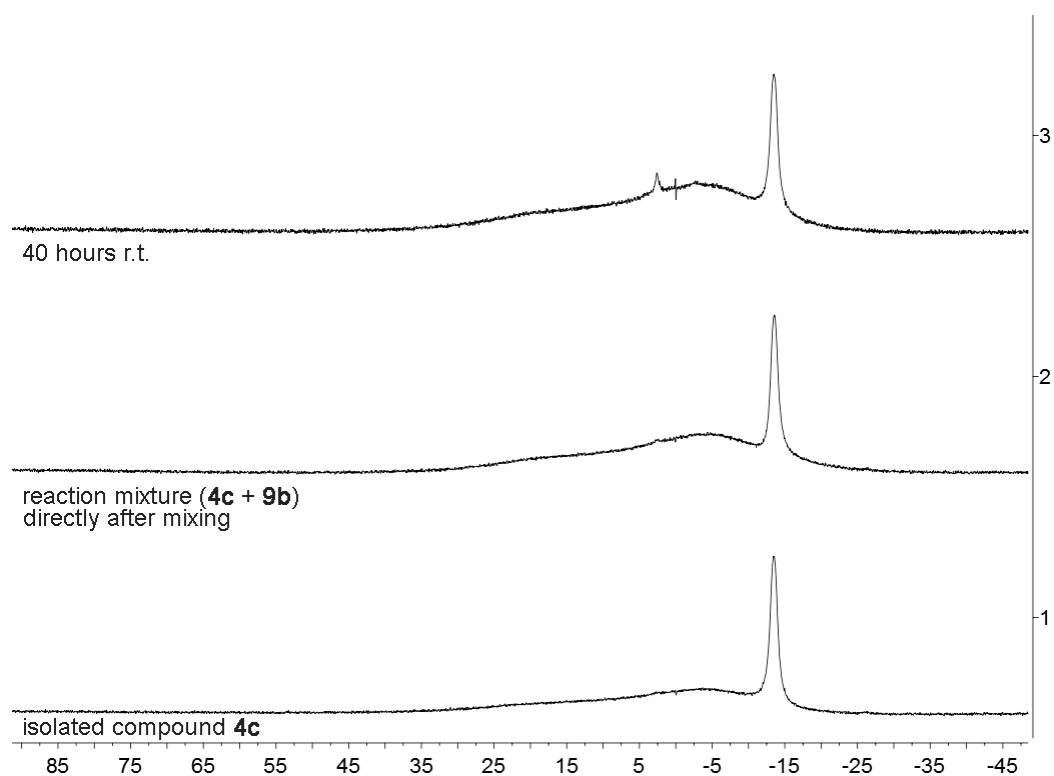
Alkyne **9b** (0.03 mmol, 2.9 mg) was added to a solution of compound **4c** (0.03 mmol, 17.9 mg) in C<sub>6</sub>D<sub>6</sub> (0.5 mL). The reaction mixture was transferred to a NMR tube and monitored by NMR spectroscopy.

Comment: NMR spectra showed that there is no substantial reaction of compound **4c** with the alkyne **9b** at r.t. after 40 hours.

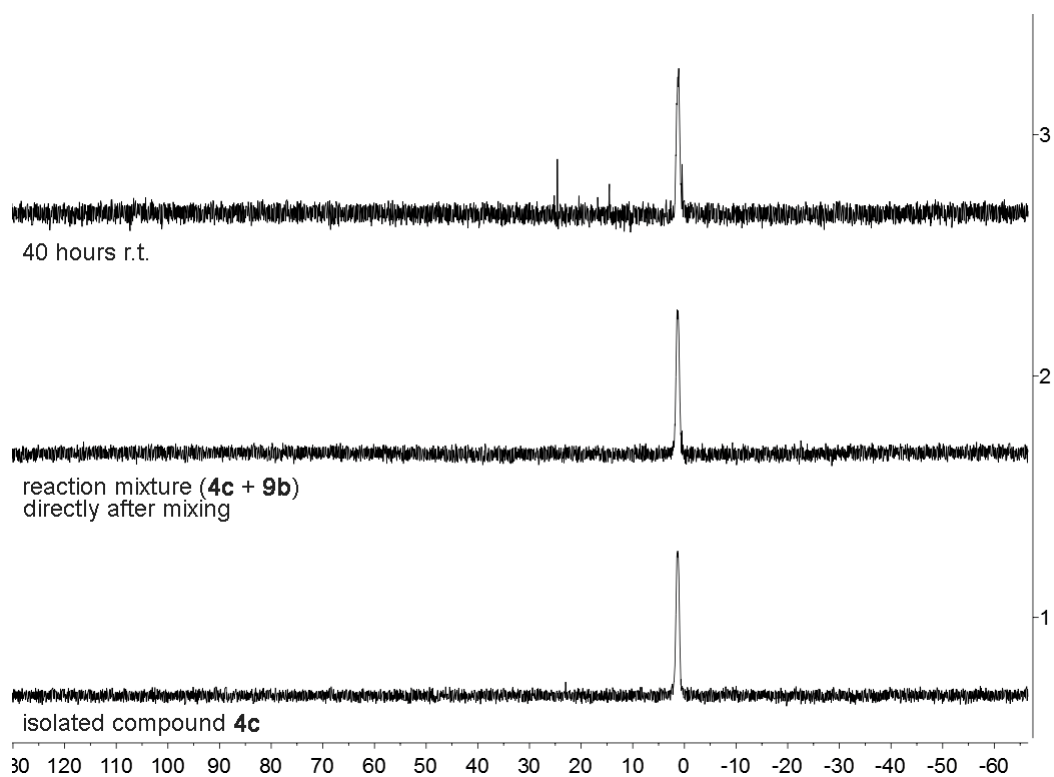


**Figure S65.** <sup>1</sup>H NMR (500 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>) spectra of (1) isolated compound **4c** and (2,3) the reaction mixture of the reaction of compounds **4c** with **9b**





**Figure S66.**  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectra of (1) isolated compound **4c** and (2,3) the reaction mixture of the reaction of compounds **4c** with **9b**



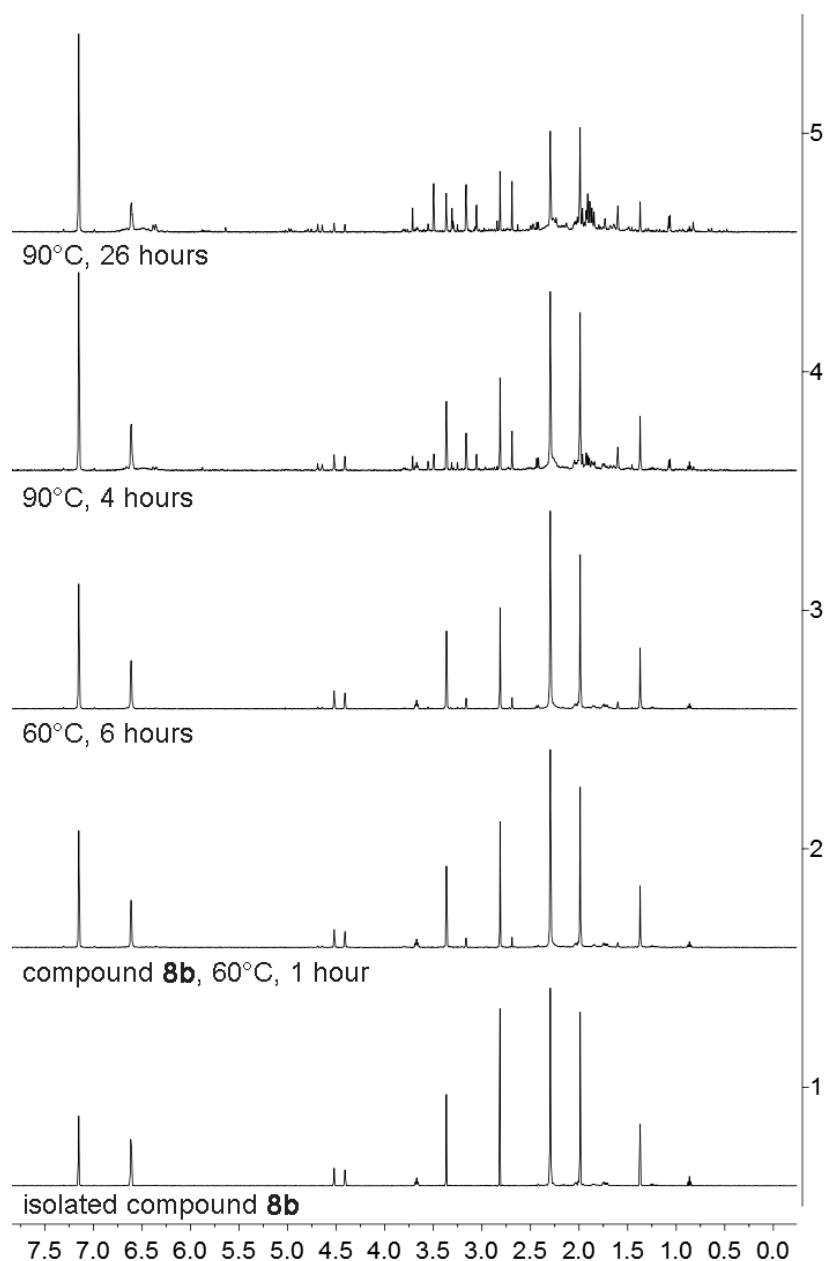
**Figure S67.**  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectra of (1) isolated compound **4c** and (2,3) the reaction mixture of the reaction of compounds **4c** with **9b**

**Control experiments: heating of compounds 8b, 10a, and 11a in C<sub>6</sub>D<sub>6</sub> (NMR scale)**

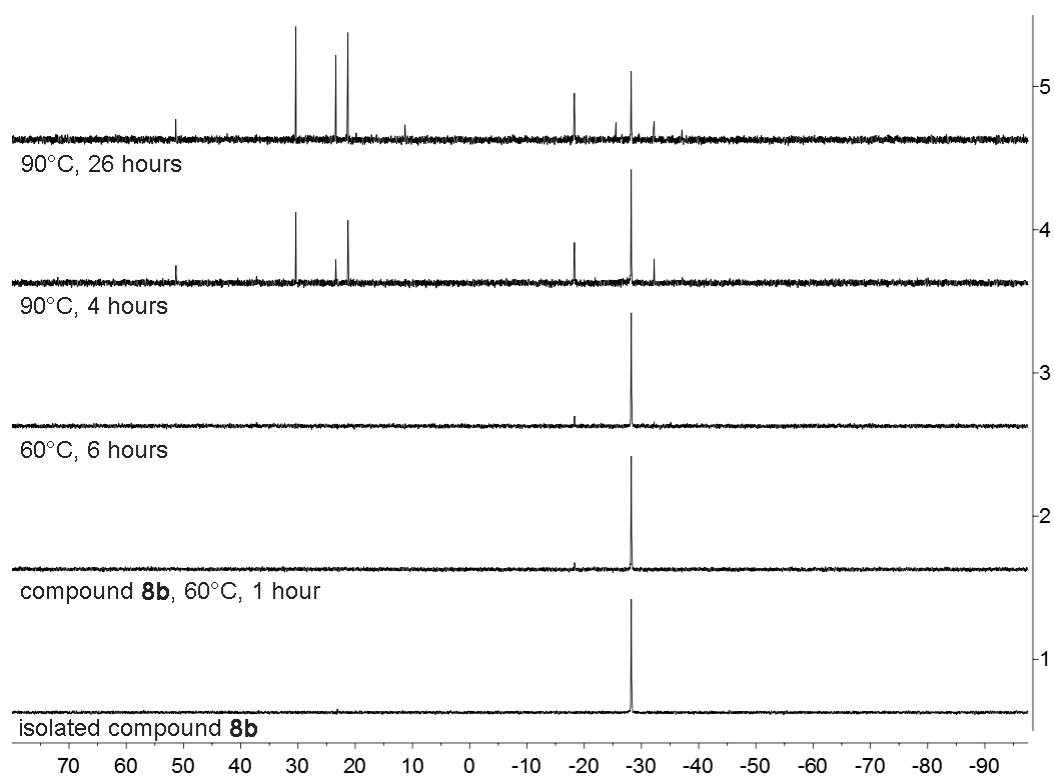
A solution of compound **8b** (0.03 mmol, 24.8 mg) [**10a** (0.03 mmol, 24.8 mg), **11a** (0.03 mmol, 19.6 mg)] in C<sub>6</sub>D<sub>6</sub> (0.5 mL) was transferred to a NMR tube, which was sealed immediately. Then the respective sample was heated and monitored by NMR spectroscopy.

*1) Heating of compound 8b*

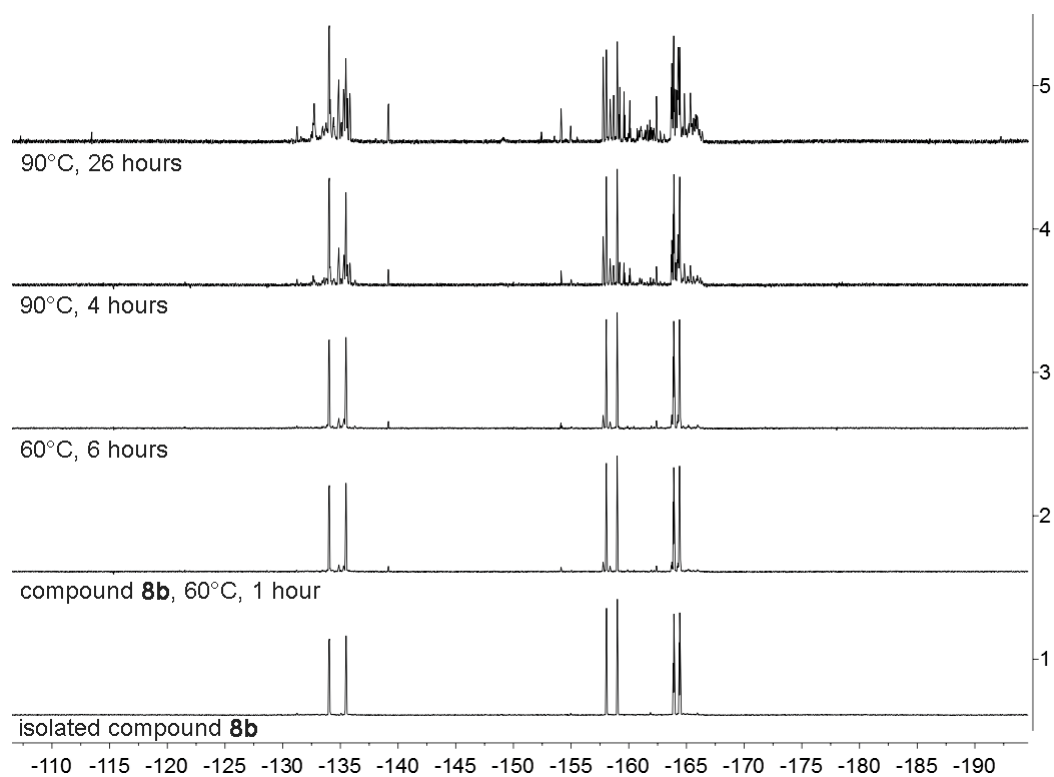
Comment: NMR spectra showed no change after heating a solution of compound **8b** in C<sub>6</sub>D<sub>6</sub> at 60 °C for 6 hours. Subsequent heating at 90 °C for 26 hours gave a complex mixture.



**Figure S68.** <sup>1</sup>H NMR (500 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>) spectra (1) of isolated compound **8b** and (2 to 5) after heating compound **8b**



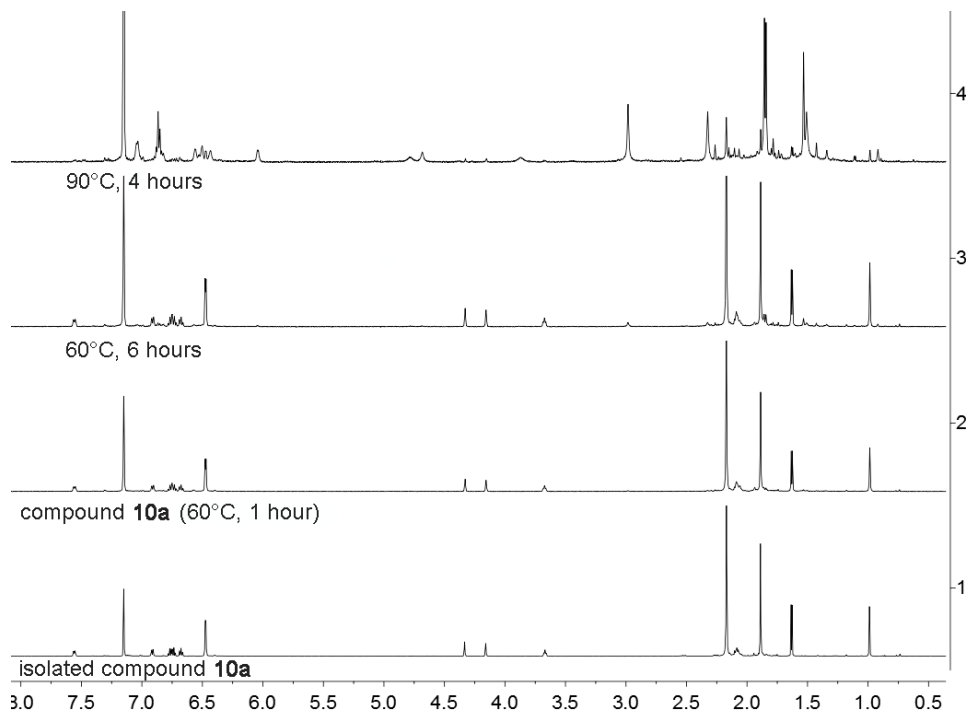
**Figure S69.**  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectra (1) of isolated compound **8b** and (2 to 5) after heating compound **8b**



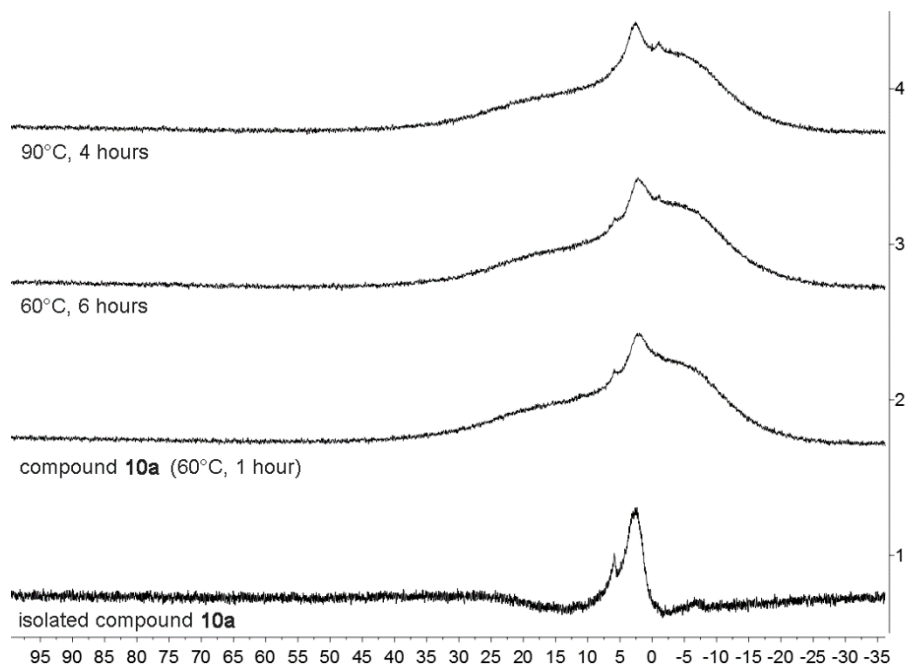
**Figure S70.**  $^{19}\text{F}$  NMR (470 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectra (1) of isolated compound **8b** and (2 to 5) after heating compound **8b**

## 2) Heating of compound **10a**

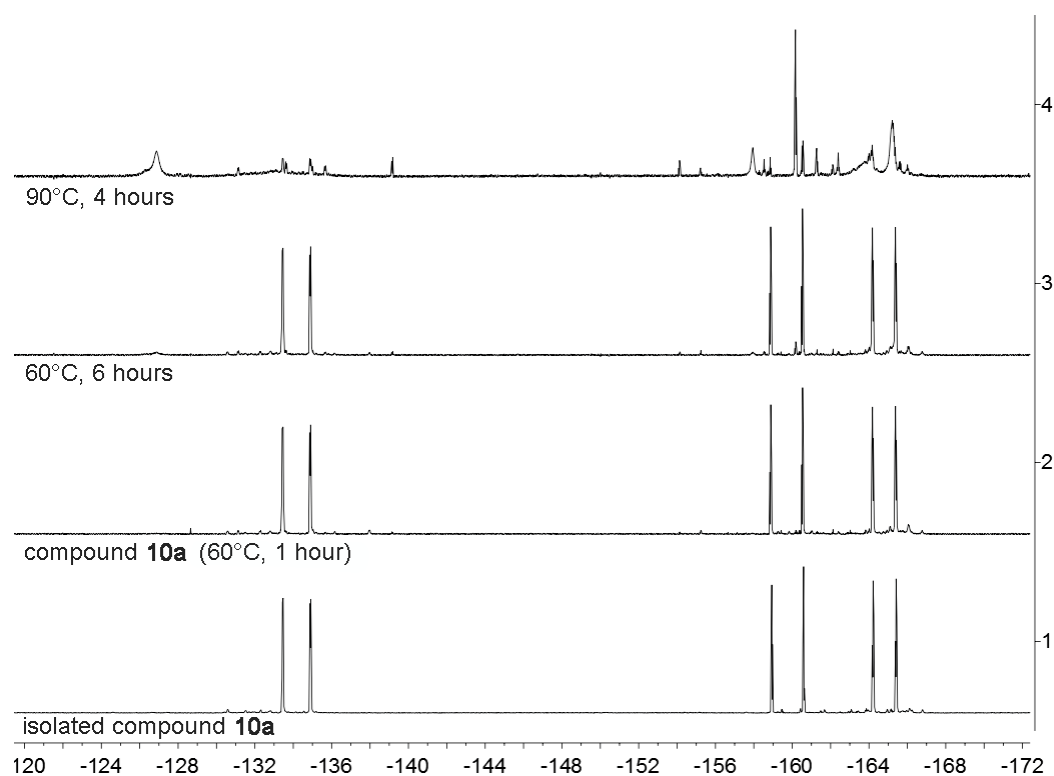
Comment: NMR spectra showed that heating a solution of compound **10a** in C<sub>6</sub>D<sub>6</sub> at 90 °C for 4 hours gave a major compound [ $\delta^{31}\text{P}\{^1\text{H}\}$ : 42.2 ( $\nu_{1/2} \sim 400$  Hz)] which could not be identified yet.



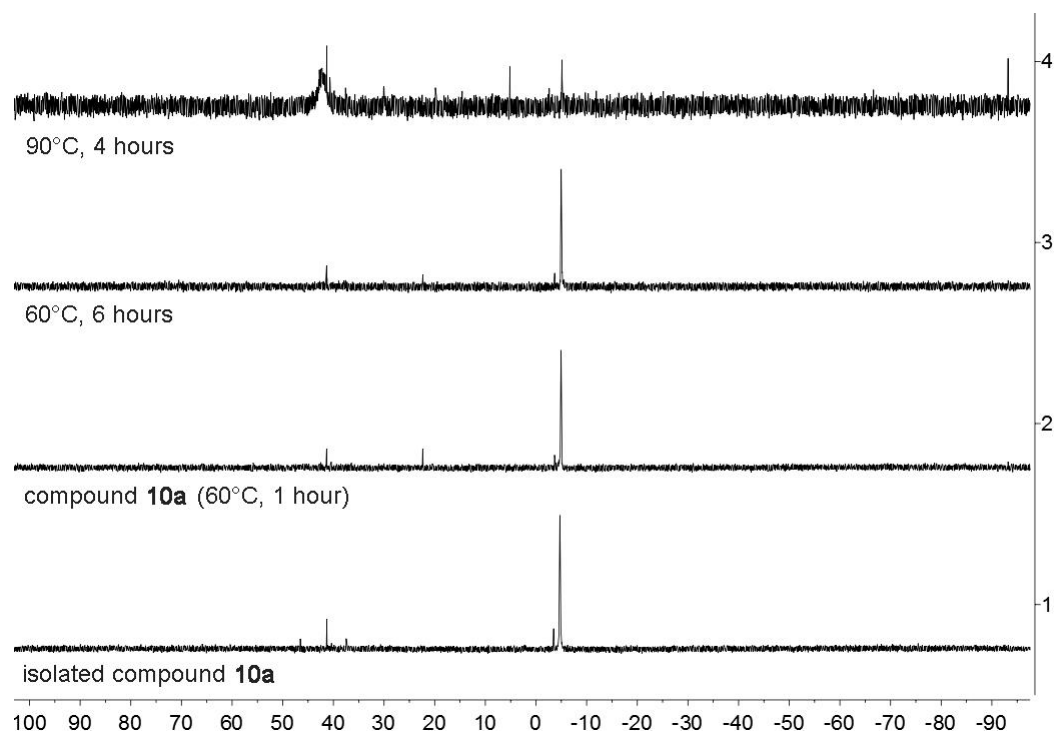
**Figure S71.** (1) <sup>1</sup>H NMR (600 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>) spectrum of isolated compound **10a** and (2 to 4) <sup>1</sup>H NMR (500 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>) spectrum after heating compound **10a**



**Figure S72.** (1) <sup>11</sup>B{<sup>1</sup>H} NMR (192 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>) spectrum of isolated compound **10a** and (2 to 4) <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, 299 K, C<sub>6</sub>D<sub>6</sub>) spectrum after heating compound **10a**



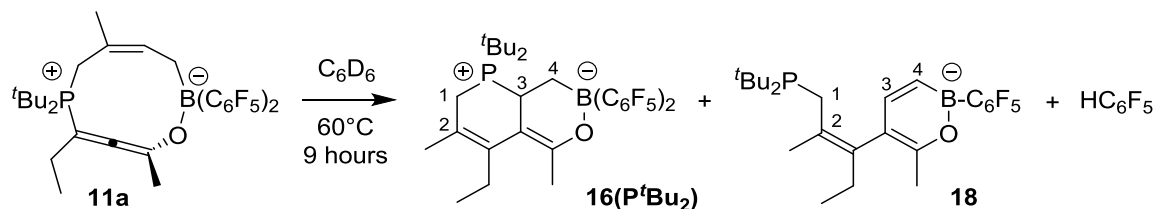
**Figure S73.** (1)  $^{19}\text{F}$  NMR (564 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectrum of isolated compound **10a** and (2 to 4)  $^{19}\text{F}$  NMR (470 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectrum after heating compound **10a**



**Figure S74.** (1)  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectrum of isolated compound **10a** and (2 to 4)  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectrum after heating compound **10a**

### 3) Heating of compound **11a**

Comment: NMR spectra showed that heating a solution of compound **11a** in C<sub>6</sub>D<sub>6</sub> at 60 °C for 9 hours gave two major products [ $\delta^{31}\text{P}\{^1\text{H}\}$ : 47.4 (68 mol%), 24.0 (32 mol%)] which were tentatively assigned as **16**(P<sup>*t*</sup>Bu<sub>2</sub>) and **18** + HC<sub>6</sub>F<sub>5</sub> [ $\delta^1\text{H}(\text{HC}_6\text{F}_5) = 5.81$  (m);  $\delta^{19}\text{F}(\text{HC}_6\text{F}_5) = -139.2$  (m, 2F, *o*), -154.2 (tm,  $^3J_{\text{FF}} = 20.7$  Hz, 1F, *p*), -162.4 (m, 2F, *m*)]

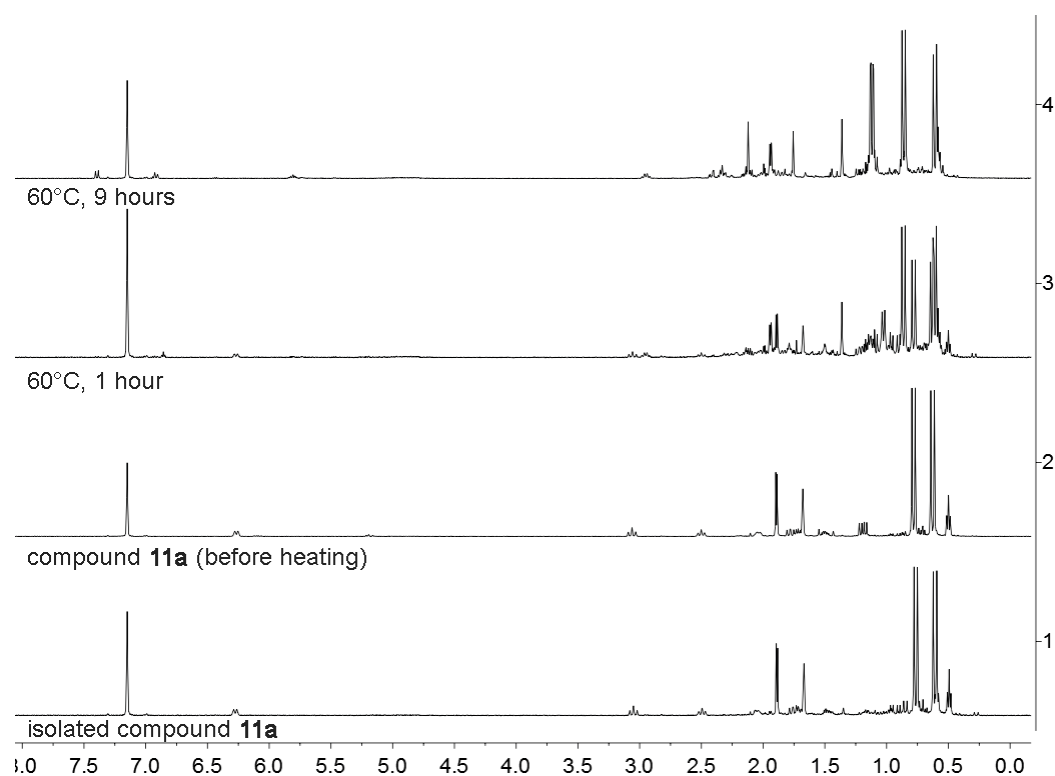


**Scheme S9**

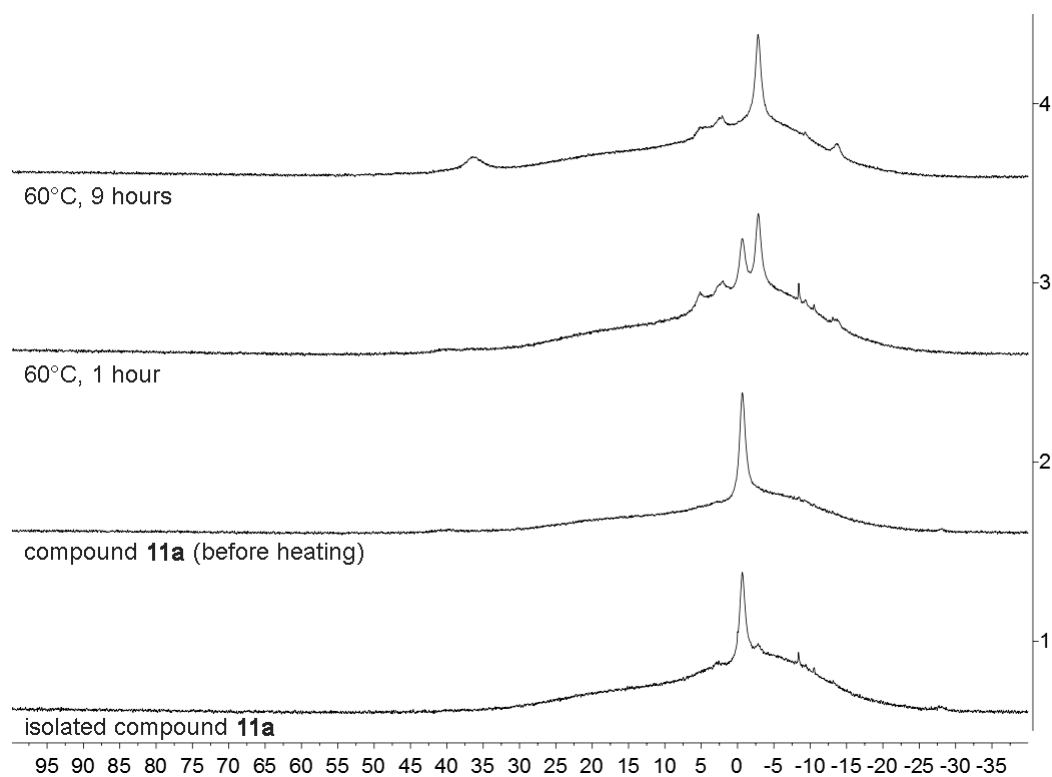
**Table S1.** Selected NMR data<sup>a</sup> in comparison with isolated compound **16** (see above).

	<b>16</b> Ph <sub>2</sub> P (isolated)	<b>16</b> (P <sup><i>t</i></sup> Bu <sub>2</sub> ) <sup><i>t</i></sup> Bu <sub>2</sub> P (68 mol%)	<b>18</b> <sup><i>t</i></sup> Bu <sub>2</sub> P (32 mol%)
$\delta^{31}\text{P}$	27.3	47.4	24.0
$\delta^{19}\text{F}$ , <i>ortho</i>	-134.5/-136.6	-133.8/-135.2	-132.7
<i>para</i>	-162.5/-162.9	-161.7/-161.9	-152.2
<i>meta</i>	-166.5/-166.6	-165.6/-165.7	-163.0
$\delta^{11}\text{B}$	-3.1	-2.9	36.2
$\delta^1\text{H}$			
PCH <sub>2</sub>	3.35/2.79	1.87/1.22	2.42/3.32
BCH <sub>2</sub>	1.45/0.83	2.02/1.81	7.40 <sup>b</sup>
CH	3.39	2.96	6.92 <sup>c</sup>
Et	2.45/2.18	2.14/1.93	2.35/2.33
Et	0.72	0.58	0.87
O-CMe	1.79 <sup>g</sup>	1.94 <sup>h</sup>	2.12
Me	1.59	1.36	1.76
$\delta^{13}\text{C}^{\text{d,e}}$			
=CO	159.3 (11.5)	159.6 (11.4)	156.3 (1.3)
=CEt	145.0 (12.0)	144.9 (8.2)	132.0 (5.0)
=CMe	117.6 (11.1)	116.7 (10.7)	133.6 (11.4)
=C	97.9 (11.2)	101.6 (11.5)	124.5
PCH <sub>2</sub>	28.1 <sup>e</sup> (49.5)	20.9 (41.7)	27.4 (26.0)
BCH <sub>2</sub>	20.2 <sup>f</sup>	19.5 <sup>f</sup>	125.2 <sup>b,f</sup>
CH	33.0 (45.8)	34.3 (39.1)	152.6 <sup>c</sup> (1.3)

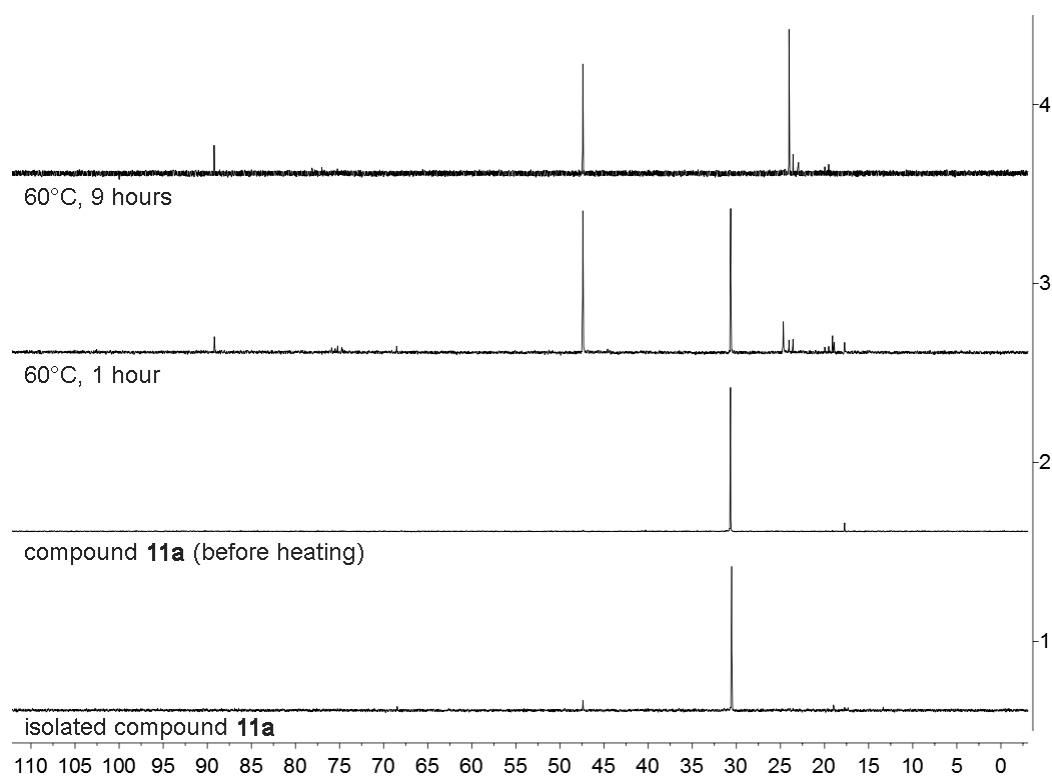
<sup>a</sup> in CD<sub>2</sub>Cl<sub>2</sub> at 299K. <sup>b</sup> =CHB (d,  $^2J_{\text{HH}} = 11.4$  Hz). <sup>c</sup> =CH (br d,  $^2J_{\text{HH}} = 11.4$  Hz). <sup>d</sup> supported by ghsqc and ghmbc experiments. <sup>e</sup>  $^nJ_{\text{XC}}$ : X:  $^{31}\text{P}$ ,  $^{19}\text{F}$  in ( ). <sup>f</sup> broad. <sup>g</sup> dd,  $^5J_{\text{PH}} = 5.6$  Hz,  $^5J_{\text{HH}} = 1.6$  Hz. <sup>h</sup> dd,  $^nJ_{\text{XH}} = 6.2, 1.1$  Hz.



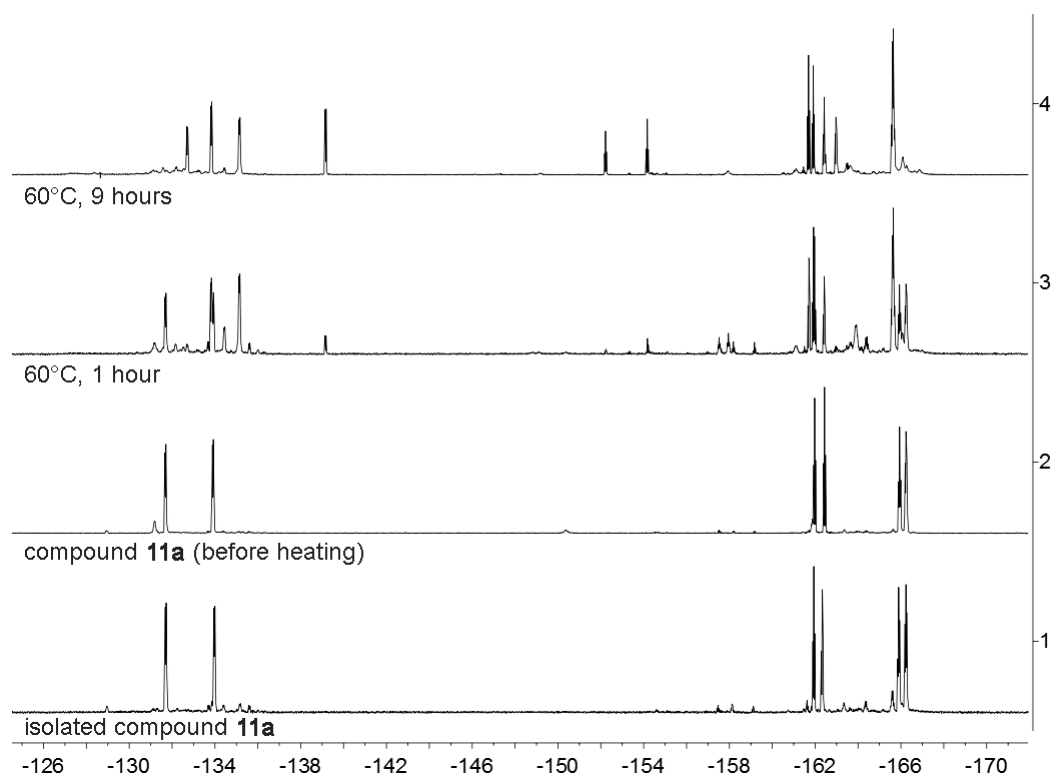
**Figure S75.**  $^1\text{H}$  NMR (500 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectra (1) of isolated compound **11a** and (2 to 4) after heating compound **11a**



**Figure S76.**  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectra (1) of isolated compound **11a** and (2 to 4) after heating compound **11a**



**Figure S77.**  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectra (1) of isolated compound **11a** and (2 to 4) after heating compound **11a**



**Figure S78.**  $^{19}\text{F}$  NMR (470 MHz, 299 K,  $\text{C}_6\text{D}_6$ ) spectra (1) of isolated compound **11a** and (2 to 4) after heating compound **11a**



## DFT Calculations

### Methods

All calculations were performed with the TURBOMOLE 7.0<sup>1</sup> and ORCA 3.0.3<sup>2</sup> (only for PES scans) programs. The structures were optimized without any geometry constraints using the TPSS functional<sup>3</sup> and an atom-pairwise dispersion correction (D3).<sup>4</sup> A flexible triple zeta basis set (def2-TZVP)<sup>5</sup> was used in all calculations (def2-SVP in the PES scans). For the calculation of zero point vibrational energies and free enthalpy contributions, a rotor approximation was applied for vibrational modes with wave numbers below 100 cm<sup>-1</sup>.<sup>6</sup> Single point calculations were performed with TPSS-D3 and the hybrid functional PW6B95(-D3).<sup>7</sup> Free energies of solvation were obtained with the COSMO-RS model<sup>8</sup> for 298 K using pentane as solvent.

### Results

**Table S2.** DFT-calculated electronic energies (TPSS-D3 and PW6B95-D3) after geometry optimization with TPSS-D3. Zero point vibrational energies (ZPE), enthalpic and free energy corrections for 298 K (H(298K), G(298K) with TPSS-D3). G<sub>SOLV</sub>(298K): COSMO-RS calculated free energy of solvation for 298 K in pentane. For all calculations the def2-TZVP basis set was used.

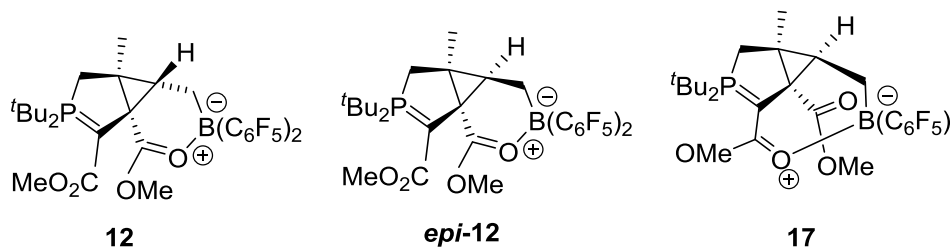
	TPSS-D3	ZPE	H(298K)	G(298K)	PW6B95-D3	G <sub>SOLV</sub> (298K)
	[E <sub>h</sub> ]	[kcal/mol]	[kcal/mol]	[kcal/mol]	[E <sub>h</sub> ]	[kcal/mol]
<b>4b</b>	-2334.080516	289.496	314.266	250.625	-2336.395262	-11.671
<b>5b</b>	-533.392485	70.449	78.090	47.208	-533.930166	-3.197
<b>(4b·5b)</b>	-2867.456263	359.563	392.776	311.647	-2870.303904	-16.861
<b>9b</b>	-308.797619	75.571	81.708	54.498	-309.120594	-2.182
<b>7d</b>	-2867.492867	361.017	393.373	314.099	-2870.343042	-22.425
<b>TS 7d-13a</b>	-2867.481301	360.616	392.445	314.330	-2870.325889	-19.857
<b>13a</b>	-2867.507479	360.706	392.628	314.049	-2870.351562	-20.189
<b>TS 13a-8d</b>	-2867.494697	361.308	393.100	315.363	-2870.335547	-17.258
<b>8d</b>	-2867.532094	361.502	393.902	314.042	-2870.384244	-18.306
<b>12</b>	-2867.558134	363.153	394.586	317.372	-2870.416554	-18.593
<b>epi-12</b>	-2867.499064	362.786	394.155	317.533	-2870.355202	-20.932
<b>17</b>	-2867.558553	363.346	394.628	318.047	-2870.417775	-20.782
<b>11a</b>	-2642.914211	367.136	397.621	322.642	-2645.550205	-21.264
<b>13a-analogue</b>	-2642.893052	367.065	396.903	323.034	-2645.517117	-21.610
<b>8d-analogue</b>	-2642.922403	366.965	397.504	322.200	-2645.557525	-16.017
<b>12-analogue</b>	-2642.916554	367.508	397.339	323.194	-2645.552361	-19.027

**Table S3.** DFT-calculated relative energies and free energies of intermediates in the phospha-Claisen reaction (Scheme 6) with respect to the reactants **4b+5b**.

$$\Delta G_{\text{sol}} = \Delta E_{\text{PW6B95}} + \Delta G_{\text{THERMO}} + \Delta G_{\text{SOLV}}$$

	$\Delta E_{\text{TPSS}}$ (TPSS-D3) <sup>a</sup> [kcal/mol]	$\Delta E_{\text{PW6B95}}$ (PW6B95-D3) <sup>a</sup> [kcal/mol]	$\Delta G_{\text{sol}}$ [kcal/mol]
<b>4b+5b</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>
<b>(4b·5b)</b>	+10.5	+13.5	+25.3
<b>7d</b>	-12.5	-11.1	-2.3
<b>TS 7d-13a</b>	-5.2	-0.3	+11.2
<b>13a</b>	-21.6	-16.4	-5.5
<b>TS13a-8d</b>	-13.6	-6.4	+8.8
<b>8d</b>	-37.1	-36.9	-24.1
<b>12</b>	-53.4	-57.2	-41.4
<i>epi-12</i>	-16.4	-18.7	-5.1
<b>17</b>	-53.7	-58.0	-43.7

<sup>a</sup> def2-TZVP basis set

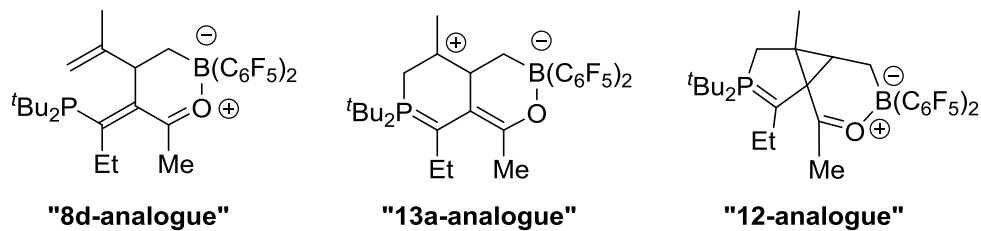


**Table S4.** DFT-calculated relative energies and free energies of intermediates in the phospha-Claisen reaction of **4b** and **9b** (Scheme 5) with respect to the reactants **4b+9b**.

$$\Delta G_{\text{sol}} = \Delta E_{\text{PW6B95}} + \Delta G_{\text{THERMO}} + \Delta G_{\text{SOLV}}$$

	$\Delta E_{\text{TPSS}}$ (TPSS-D3) <sup>a</sup> [kcal/mol]	$\Delta E_{\text{PW6B95}}$ (PW6B95-D3) <sup>a</sup> [kcal/mol]	$\Delta G_{\text{sol}}$ [kcal/mol]
<b>4b+9b</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>
<b>11a</b>	-22.6	-21.6	-11.5
<b>13a-analogue</b>	-9.4	-0.8	9.4
<b>8d-analogue</b>	-27.8	-26.2	-11.2
<b>12-analogue</b>	-24.1	-22.9	-10.0

<sup>a</sup> def2-TZVP basis set



**Figure S79:** DFT-optimized structures of intermediates in the phospha-Claisen reaction of **4b**, (TPSS-D3/def2-TZVP). Bond lengths in Å. (Colors: orange = P, yellow = F, rose = B)

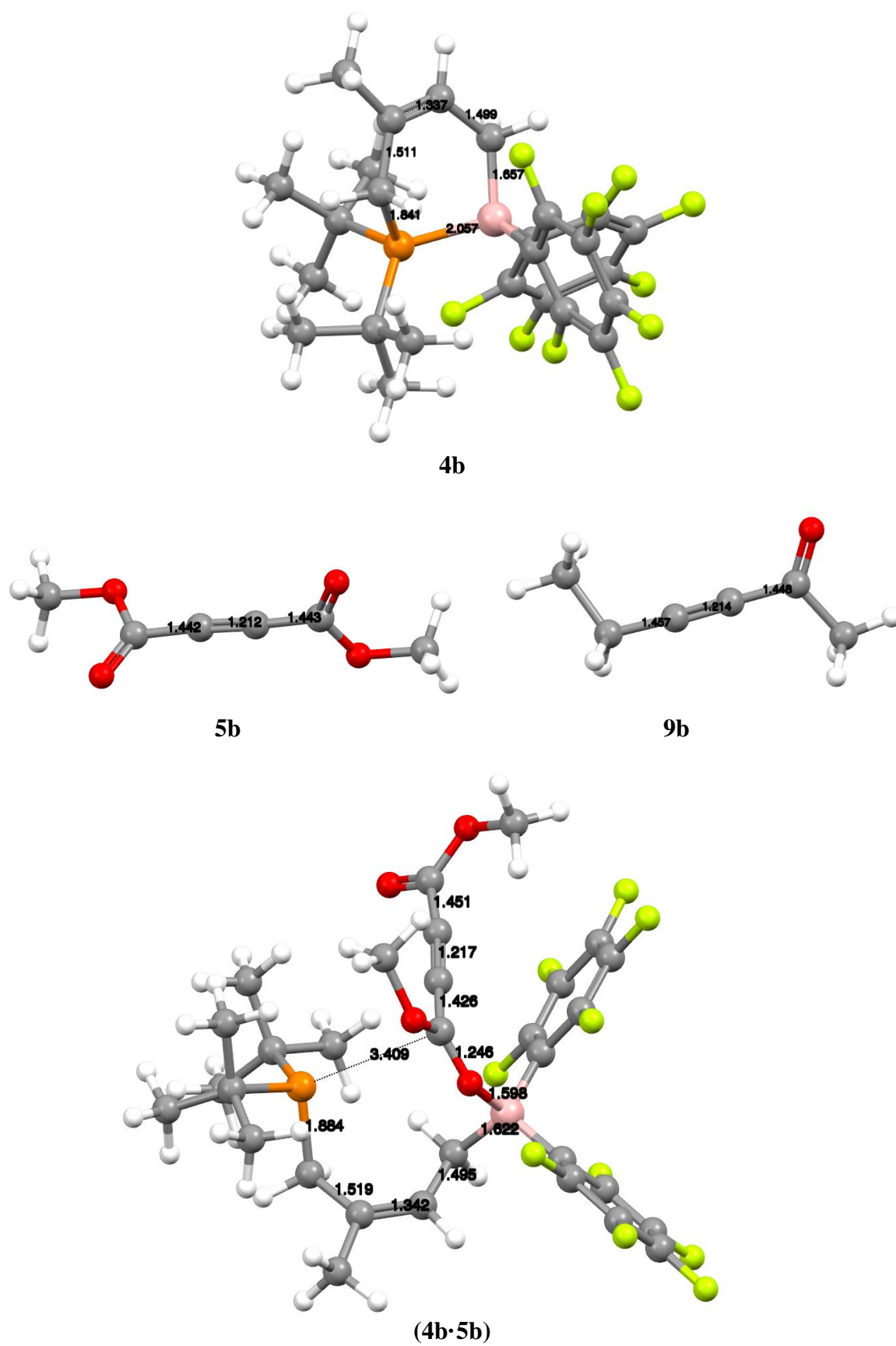
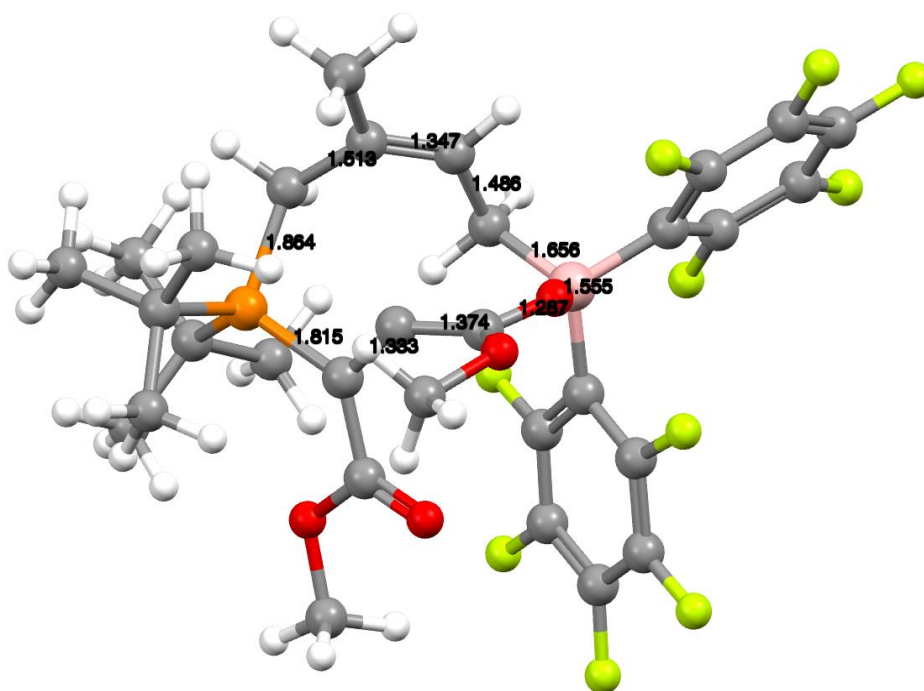
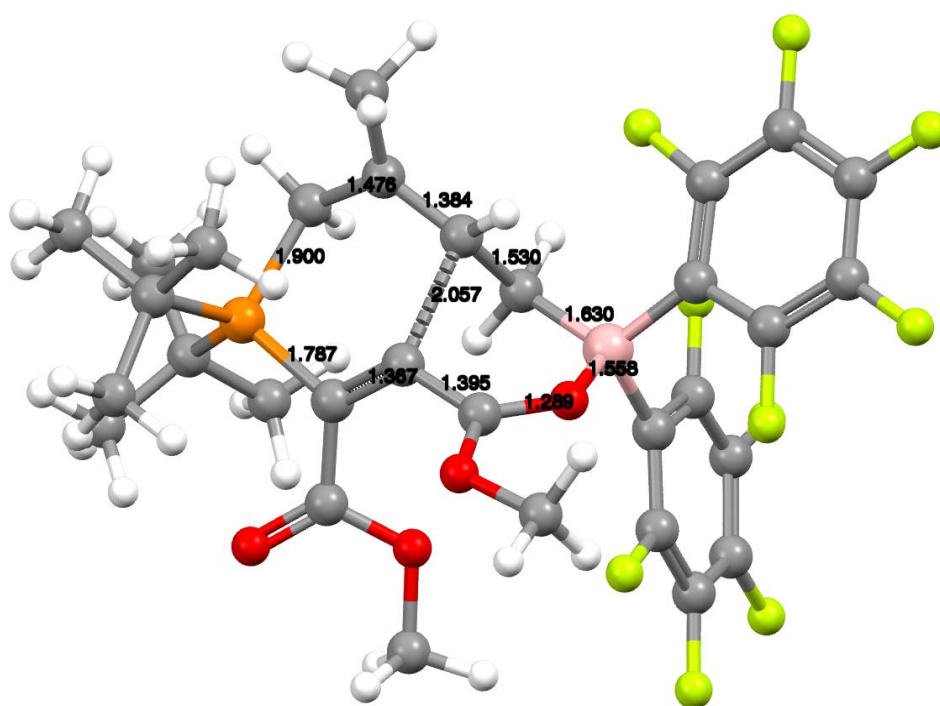


Figure S79 (continued)

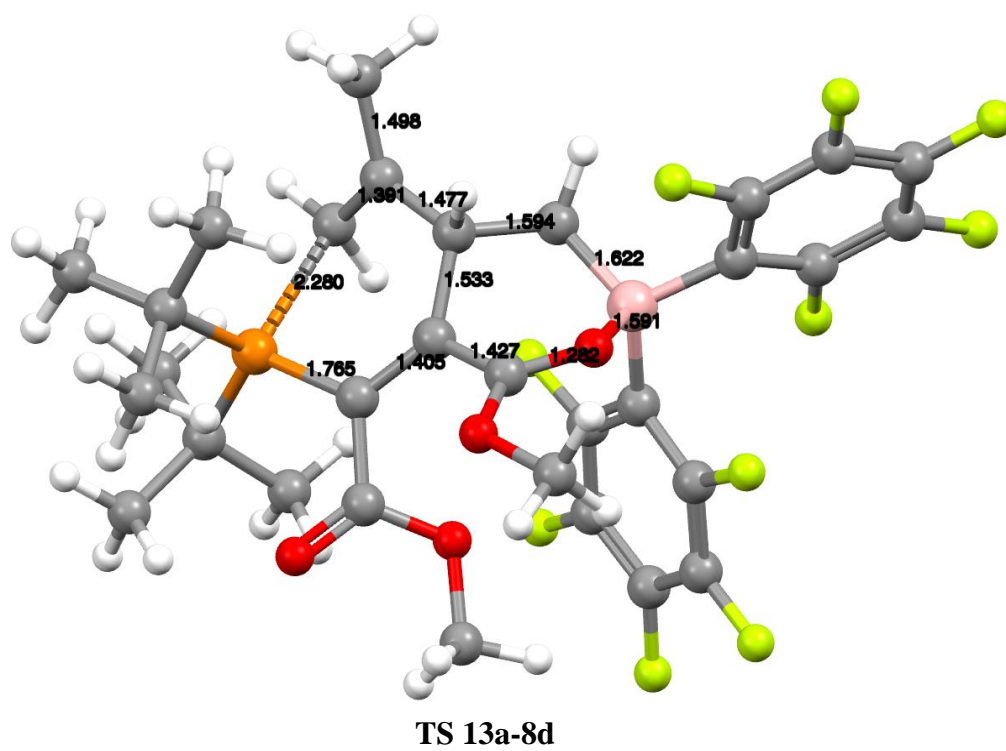
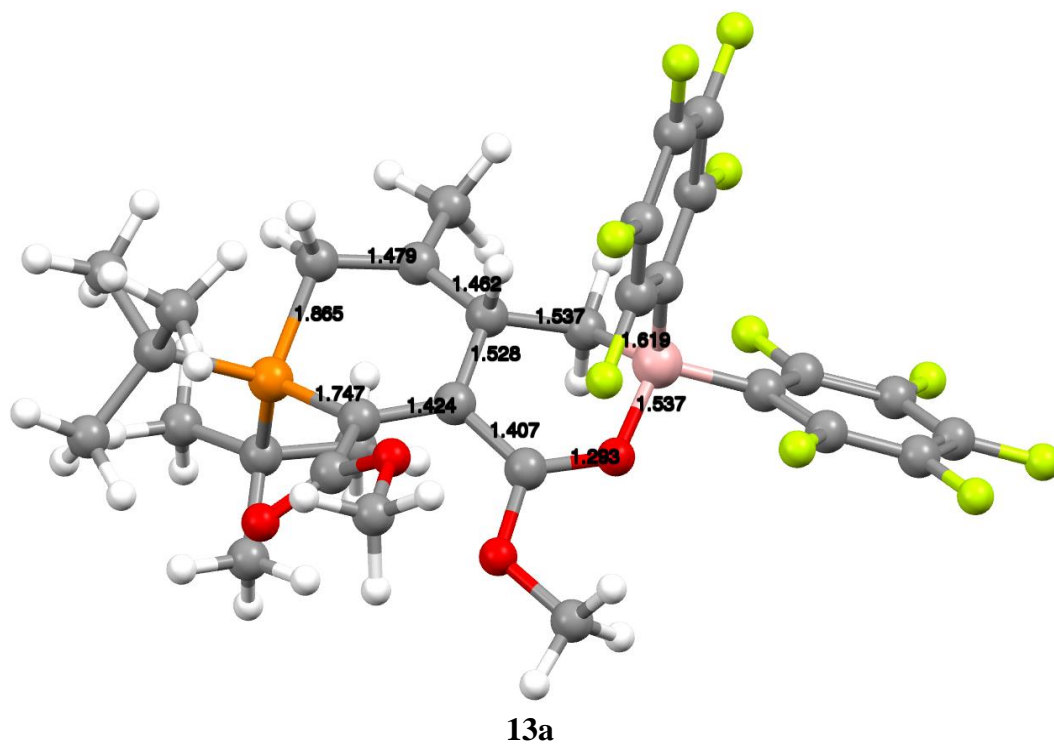


7d



TS 7d-13a

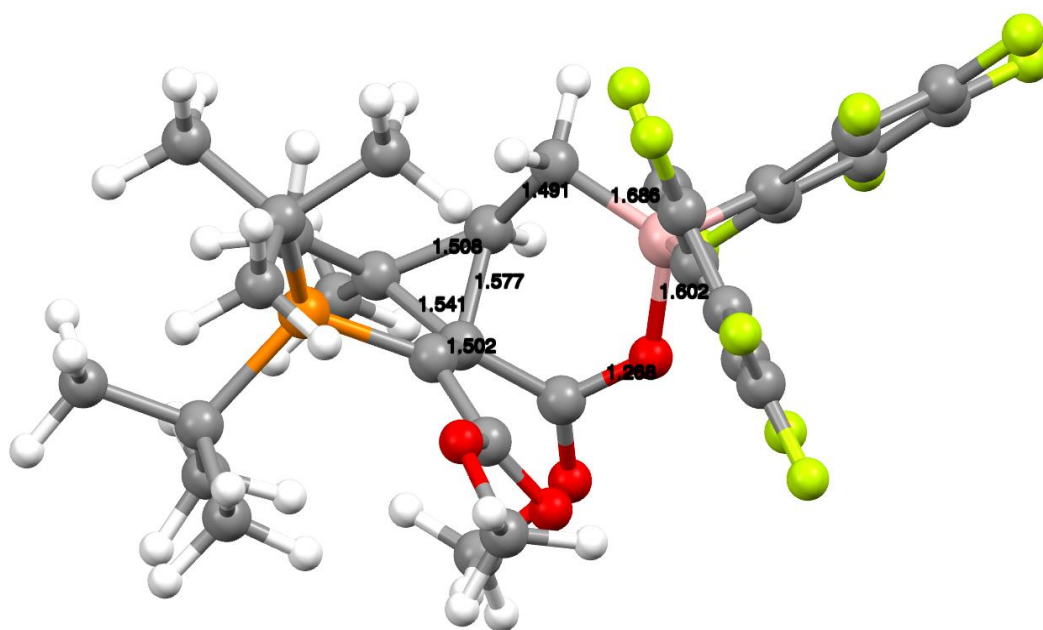
Figure S79 (continued)



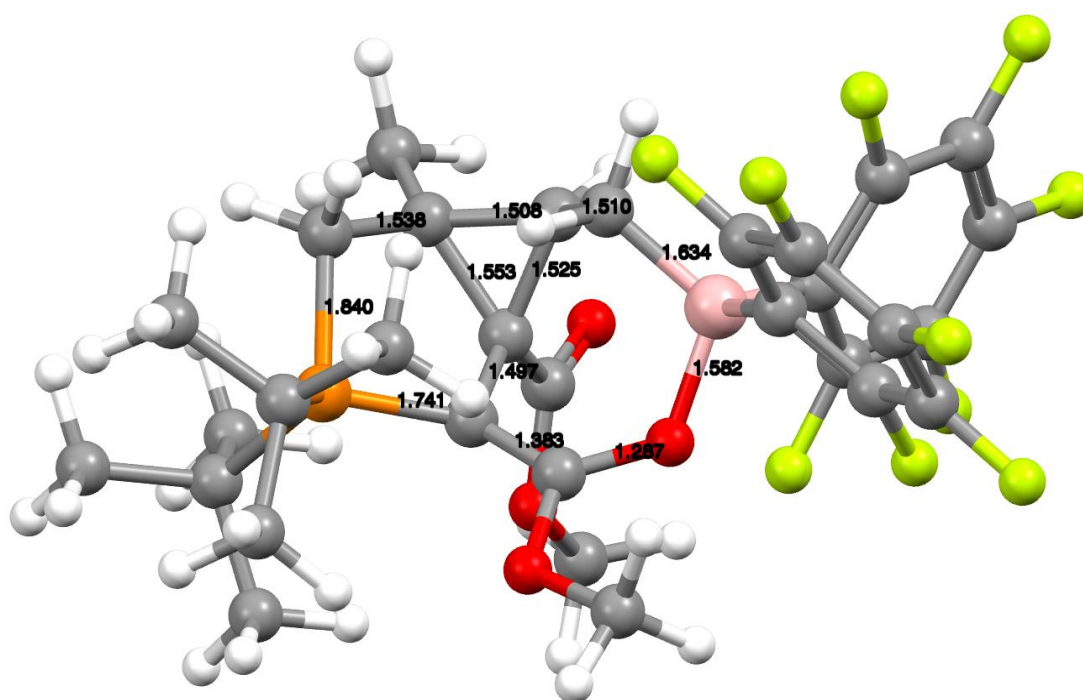
[illegible]

S62

Figure S79 (continued)



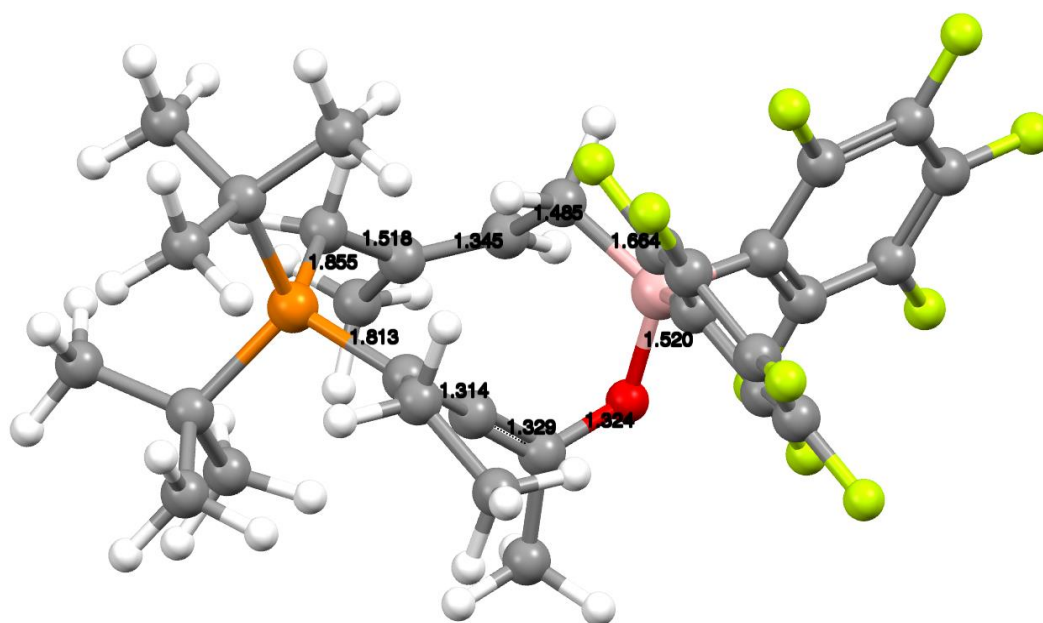
*epi*-12



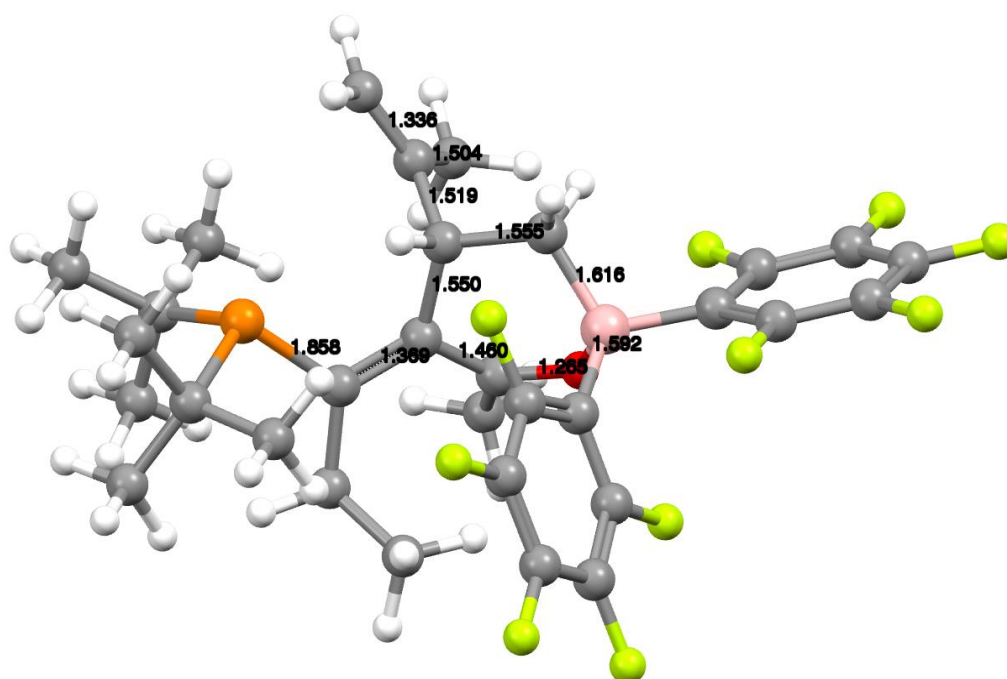
17



**Figure S79** (continued)



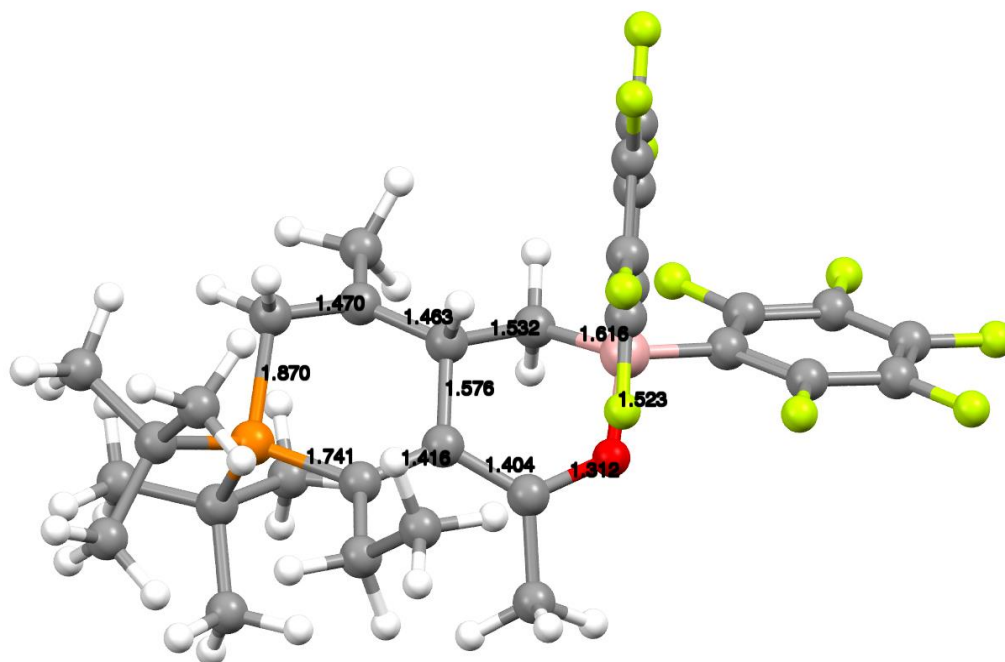
**11a**



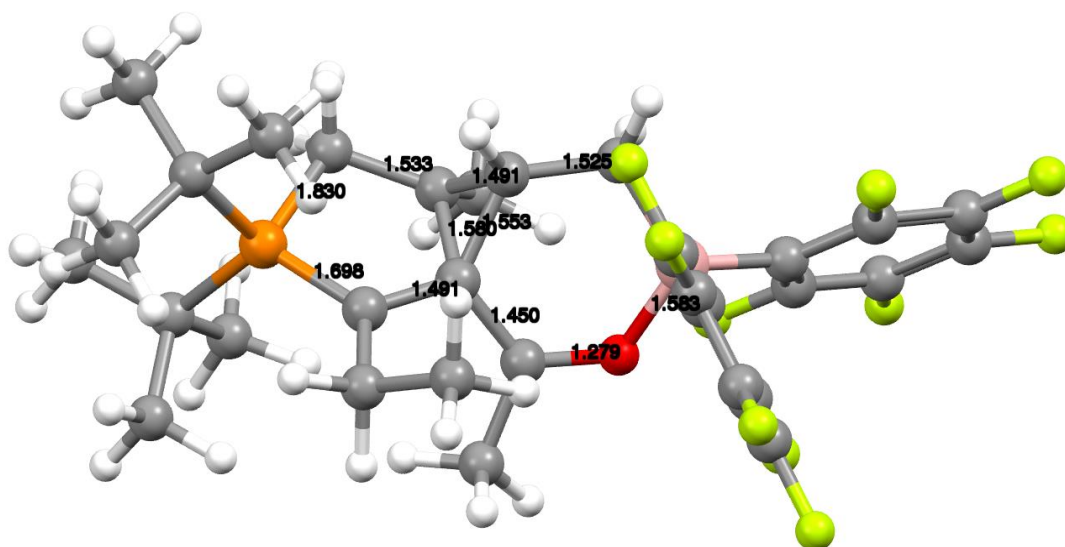
**"8d-analogue"**



**Figure S79** (continued)

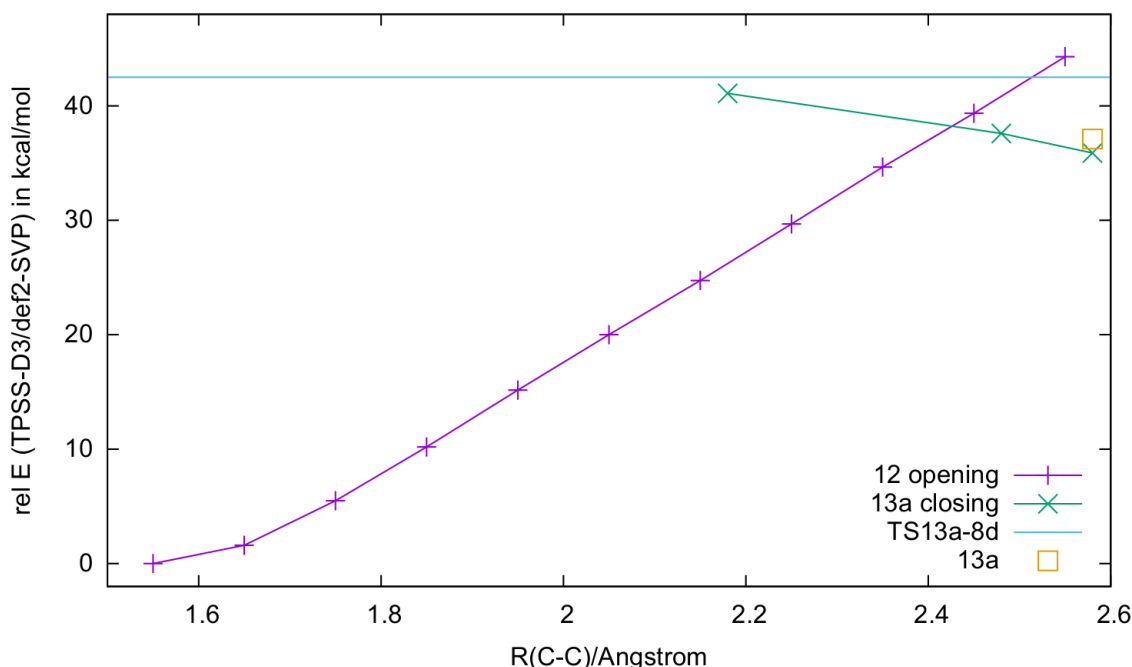


**"13a-analogue"**



**"12-analogue"**

**Figure S80:** Relaxed Potential Energy Surface (PES) scans (TPSS-D3/def2-SVP) for the C-C bond formation of the central cyclopropyl ring of **12** from **13a**. In the two scans, the C-C bond was (a) varied from 1.55 Å to 2.55 Å (opening from **12**) and (b) from 2.58 Å to 2.18 Å (closing from **13a**). The energies of **TS13a-8d** and of **13a** are depicted as a blue line and yellow square, respectively.



As can be seen from the curves in Figure S80, the reaction seems to involve the crossing of two electronic states which have a high probability of interconversion at a C-C distance of ca. 2.4 Å. The spin-restricted single reference method used for all other intermediates and transition structures of the mechanism is not capable of locating this transition state (**TS13a-12**). However, the crossing point of the two PES scans lies well below the transition structure **TS13a-8d**, which has a relative energy  $\Delta E$  of +42.5 kcal/mol with this basis set.

- <sup>1</sup> TURBOMOLE V7.0 2015, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>
- <sup>2</sup> F. Neese, The ORCA program system, *Wiley Interdisciplinary Reviews: Computational Molecular Science*, **2012**, 2, 73-78.
- <sup>3</sup> J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, *Phys. Rev. Lett.*, **2003**, 91, 146401.
- <sup>4</sup> a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* 2010, **132**, 154104. b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, 32, 1456–1465.
- <sup>5</sup> F. Weigend; R. Ahlrichs. *Phys. Chem. Chem. Phys.* **2005**, 7, 3297–3305.
- <sup>6</sup> S. Grimme, *Chem. Eur. J.* **2012**, 18, 9955-9964.
- <sup>7</sup> Y. Zhao, D. G. Truhlar, *J. Phys. Chem. A* **2005**, 109, 5656-5667.
- <sup>8</sup> a) A. Klamt, *J. Phys. Chem.* **1995**, 99, 2224-2235. b) F. Eckert and A. Klamt, COSMOtherm, Version C3.0; COSMOlogic GmbH & Co. KG, Leverkusen, Germany, **2013**.