# Ethene/Alkyne Exchange Reaction at an Intramolecular Frustrated Lewis Pair

Christina Eller, Kathrin Bussmann, Gerald Kehr, Birgit Wibbeling<sup>‡</sup>, Constantin G. Daniliuc<sup>‡</sup>, Gerhard Erker

‡ X-ray crystal structure analysis

General Procedures. 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. The following instruments were used for physical characterization of the compounds: NMR spectra: Varian Inova 500 (<sup>1</sup>H: 500 MHz, <sup>13</sup>C: 126 MHz, <sup>19</sup>F: 470 MHz, <sup>11</sup>B: 160 MHz, <sup>31</sup>P: 202 MHz), Varian UnityPlus 600 (<sup>1</sup>H: 600 MHz, <sup>13</sup>C: 151 MHz, <sup>19</sup>F: 564 MHz, <sup>11</sup>B: 192 MHz, <sup>31</sup>P: 243 MHz) and Bruker AC 200 P (<sup>1</sup>H: 200 MHz, <sup>11</sup>B: 64 MHz). <sup>1</sup>H NMR and <sup>13</sup>C NMR: chemical shifts δ are given relative to TMS and referenced to the solvent signal. <sup>19</sup>F NMR: chemical shifts  $\delta$  are given relative to CFCl<sub>3</sub> (external reference,  $\delta = 0$ ); <sup>11</sup>B NMR: chemical shifts  $\delta$  are given relative to BF<sub>3</sub>·Et<sub>2</sub>O (external reference,  $\delta = 0$ ). NMR assignments are supported by additional 2D NMR experiments. Elemental analyses were performed on a Elementar Vario El III. IR spectra were recorded on a Varian 2100 FT-IR (Excalibur Series). Melting points were obtained with a DSC Q20 (TA Instruments).X-Ray Crystal Structure Analyses. Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, Methods Enzymol. 1997, 276, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, Acta Crystallogr. 2003, A59, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, Acta Crystallogr. 1990, A46, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, Acta Crystallogr. 2008, A64, 112-122) and graphics, XP (BrukerAXS, 2000). Thermal ellipsoids are shown with 30% probability, *R*-values are given for observed reflections, and  $wR^2$  values are given for all reflections. Exceptions and special features: In compound 7 two disordered over two positions t-Bu groups were found in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. For the compound 6 two t-Bu groups disordered over two positions were found in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. (964462 (4), 964463 (7), and 976687 (6)).

**Materials.** Phenyl vinyl sulfide was purchased from *Acros Organics* and used without further purification. Bis(pentafluorophenyl)borane (Parks, D. J.; Spence, R. E. V H.; Piers, W. E., *Angew. Chem.* **1995**, *107*, 895-897; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 809-811; Piers, W. E.; Parks, D. J.; Yap, G. P. A., *Organometallics* **1998**, *17*, 5492-5503) was prepared according to modified literature procedures. B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was obtained from Boulder Scientific company.

## Synthesis of compound 3 (THF-d<sub>8</sub>)



A suspension of bis(pentafluorophenyl)borane (36.0 mg, 0.10 mmol) in *n*-pentane (5 mL) was added to a solution of phenyl vinyl sulfide (14.0 mg, 0.10 mmol) in *n*-pentane (2 mL). The obtained suspension was stirred for four hours at room temperature. Then all volatiles were removed *in vacuo* and the colourless residue was washed with *n*-pentane (2 x 3 mL) and the colourless product **3** (20.0 mg, 36%) was dried *in vacuo*.

**3**: **IR** (KBr):  $\tilde{v}$  [cm<sup>-1</sup>] = 3553 (w), 1646 (m), 1520 (s), 1462 (s), 1379 (w), 1289 (m), 1207 (w), 1161 (w), 1092 (s), 963 (s), 921 (w), 887 (w), 821 (w), 786 (m), 747 (m), 689 (m), 650 (w), 619 (w), 554 (w), 489 (w).

### Melting point (DSC): 176 °C.

*Comment:* To get a sufficient solubility for NMR experiments a drop of THF-d<sub>8</sub> was added to give **3** (THF-d<sub>8</sub>):

<sup>1</sup>**H** NMR (500 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>/TDF):  $\delta$  = 7.32 (m, 2H, *o*-Ph), 7.02 (m, 2H, *m*-Ph), 6.89 (m, 1H, *p*-Ph), 2.79 (m, 2H, SCH<sub>2</sub>), 1.59 (m, 2H, BCH<sub>2</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>/TDF):  $\delta = 148.2$  (dm,  ${}^{1}J_{FC} \sim 239$  Hz, C<sub>6</sub>F<sub>5</sub>), 140.3 (dm,  ${}^{1}J_{FC} \sim 246$  Hz, C<sub>6</sub>F<sub>5</sub>), 138.1 (*i*-Ph), 137.6 (dm,  ${}^{1}J_{FC} \sim 252$  Hz, C<sub>6</sub>F<sub>5</sub>), 129.2 (*o*-Ph), 129.1 (*m*-Ph), 125.9 (*p*-Ph), 116.9 (br, *i*-C<sub>6</sub>F<sub>5</sub>), 31.2 (SCH<sub>2</sub>), 23.8 (br, BCH<sub>2</sub>).

<sup>1</sup>**H**, <sup>1</sup>**H GCOSY** (500 MHz / 500 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>/TDF)[selected traces]:  $\delta$  <sup>1</sup>H /  $\delta$  <sup>1</sup>H = 7.02 / 7.32, 6.89 (*o*-Ph / *m*-Ph, *p*-Ph), 2.79 / 1.59 (SCH<sub>2</sub> / BCH<sub>2</sub>).

<sup>1</sup>**H**,<sup>13</sup>**C GHSQC** (500 MHz / 126 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>/TDF):  $\delta$  <sup>1</sup>H /  $\delta$  <sup>13</sup>C = 7.32 / 129.2 (*o*-Ph), 7.02 / 129.1 (*m*-Ph), 6.89 / 125.9 (*p*-Ph), 2.79 / 31.2 (SCH<sub>2</sub>), 1.59 / 23.8 (BCH<sub>2</sub>).

<sup>1</sup>**H**,<sup>13</sup>**C GHMBC** (500 MHz / 126 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>/TDF)[selected traces]:  $\delta$  <sup>1</sup>H /  $\delta$  <sup>13</sup>C = 7.02 / 138.1, 129.1 (*m*-Ph / *i*-Ph, *m*-Ph), 2.79 / 138.1, 23.8 (SCH<sub>2</sub> / *i*-Ph, BCH<sub>2</sub>).

<sup>19</sup>**F NMR** (470 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>/TDF):  $\delta = -133.3$  (m, 2F, *o*-C<sub>6</sub>F<sub>5</sub>), -156.1 (t, <sup>3</sup>J<sub>FF</sub> = 20.8 Hz, 1F, *p*-C<sub>6</sub>F<sub>5</sub>), -162.8 (m, 2F, *m*-C<sub>6</sub>F<sub>5</sub>). [Δδ<sup>19</sup>F<sub>m,p</sub> = 6.7].

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>/TDF):  $\delta = 6.9 (v_{1/2} \sim 350 \text{ Hz}).$ 



 $^{19}\mathrm{F}$  NMR (470 MHz, 298 K,  $\mathrm{C_6D_6}\,/\mathrm{TDF})$  of 3.



#### Reaction of 3 with tert-butyl isocyanide: synthesis of compound 4



Caution: many alkyl isocyanides are toxic and have to be handled with due care!

A suspension of bis(pentafluorophenyl)borane (40.0 mg, 0.12 mmol) in *n*-pentane (5 mL) was added to a solution of phenyl vinyl sulfide (24.0 mg, 0.12 mmol) in *n*-pentane (1 mL). The resulting suspension was stirred for five minutes at room temperature. Upon the addition of *tert*-butyl isocyanide (14  $\mu$ L, 0.1 mmol, 1.1 eq.) and stirring at room temperature (5 min) a colourless solid precipitated. Stirring was continued overnight at ambient temperature. The solvent of the obtained suspension was removed *via* syringe and the colourless residue was washed with *n*-pentane (2 x 2 mL). Thereafter the residue was dried *in vacuo* overnight to yield the compound **4** (18.0 mg, 28%) as a colourless powder. Crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation of a solution of **4** in dichloromethane at room temperature.

**IR** (KBr)  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3069 (w), 2992 (w), 2952 (w), 2913 (w), 2844 (w), 2290 (s), 1645 (s), 1585 (m), 1517 (s), 1464 (s), 1374 (s), 1279 (s), 1235 (m), 1187 (m), 1118 (s), 1090 (s), 1026 (m), 990 (s), 967 (s), 945 (s), 875 (m), 836 (m), 785 (s), 736 (s), 690 (s), 568 (w), 534 (m), 509 (w), 471 (m), 432 (w).

**Elemental Analysis** calcd for C<sub>25</sub>H<sub>18</sub>BF<sub>10</sub>NS C 53.12, H 3.21, N 2.48; found C 52.60, H 3.19, N 2.38.

**Exact Mass** calcd for  $C_{25}H_{18}BF_{10}NS$  565.13 g/mol; found  $[4+NH_4]^+$ : 583.14244 g/mol,  $[4+Na]^+$ : 588.09802 g/mol,  $[4+K]^+$ : 604.07294 g/mol.

Melting point (DSC): 139 °C.

<sup>1</sup>**H NMR** (600 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = 7.25 (m, 4H, *o*,*m*-Ph), 7.15 (m, 1H, *p*-Ph), 2.84 (m, 2H, SCH<sub>2</sub>), 1.61 (m, 2H, BCH<sub>2</sub>), 1.61 (s, 9H, tBu).

<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = n.o. (C=N), 148.2 (dm, <sup>1</sup>*J*<sub>FC</sub> ~ 245 Hz, C<sub>6</sub>F<sub>5</sub>), 140.0 (dm, <sup>1</sup>*J*<sub>FC</sub> ~ 246 Hz, C<sub>6</sub>F<sub>5</sub>), 138.2 (*i*-Ph), 137.5 (dm, <sup>1</sup>*J*<sub>FC</sub> ~ 247 Hz, C<sub>6</sub>F<sub>5</sub>), 129.1, 128.8 (*o*,*m*-Ph), 125.8 (*p*-Ph), 117.5 (br, *i*-C<sub>6</sub>F<sub>5</sub>), 61.0 (tBu), 33.0 (SCH<sub>2</sub>), 29.2 (tBu), 20.3 (br, BCH<sub>2</sub>).

<sup>1</sup>**H**,<sup>1</sup>**H GCOSY** (600 MHz / 600 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>)[selected traces]:  $\delta$  <sup>1</sup>H /  $\delta$  <sup>1</sup>H = 7.25 / 7.15 (*o*-Ph, *m*-Ph / *p*-Ph), 2.84 / 1.61 (SCH<sub>2</sub> / BCH<sub>2</sub>).

<sup>1</sup>**H**,<sup>13</sup>**C GHSQC** (600 MHz / 151 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  <sup>1</sup>H /  $\delta$  <sup>13</sup>C = 7.25 / 129.1, 128.8 (*o*,*m*-Ph), 7.15 / 125.8 (*p*-Ph), 2.84 / 33.0 (SCH<sub>2</sub>), 1.61 / 20.3 (BCH<sub>2</sub>), 1.61 / 29.2 (tBu).

<sup>1</sup>H,<sup>13</sup>C GHMBC (600 MHz / 151 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>)[selected traces]:  $\delta$  <sup>1</sup>H /  $\delta$  <sup>13</sup>C = 7.25 / 138.2, 129.1, 128.8, 125.8 (*o*,*m*-Ph / *i*-Ph, *m*,*o*-Ph, *p*-Ph), 2.84 / 138.2, 20.3 (SCH<sub>2</sub> / *i*-Ph, BCH<sub>2</sub>), 1.61 / 117.5, 33.0 (BCH<sub>2</sub> / *i*-C<sub>6</sub>F<sub>5</sub>, SCH<sub>2</sub>).

<sup>19</sup>**F NMR** (564 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = -133.3 (m, 2F, *o*-C<sub>6</sub>F<sub>5</sub>), -158.7 (t, <sup>3</sup>J<sub>FF</sub> = 20.3 Hz, 1F, *p*-C<sub>6</sub>F<sub>5</sub>), -164.3 (m, 2F, *m*-C<sub>6</sub>F<sub>5</sub>). [Δδ<sup>19</sup>F<sub>m,p</sub> = 5.6].

<sup>11</sup>B{<sup>1</sup>H} NMR (64 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = -19.5 (v_{1/2} \sim 100 \text{ Hz}).$ 





**X-ray crystal structure analysis of compound 4:** formula  $C_{25}H_{18}BF_{10}NS$ , M = 565.27, colourless crystal, 0.35 x 0.20 x 0.10 mm, a = 10.6470(10), b = 10.7328(7), c = 12.4320(10)Å,  $\alpha = 99.483(6)$ ,  $\beta = 110.618(5)$ ,  $\gamma = 107.209(5)^{\circ}$ , V = 1211.3(2) Å<sup>3</sup>,  $\rho_{calc} = 1.550$  gcm<sup>-3</sup>,  $\mu = 6$  2.051 mm<sup>-1</sup>, empirical absorption correction (0.533  $\leq$  T  $\leq$  0.821), Z = 2, triclinic, space group  $P\bar{1}$  (No. 2),  $\lambda = 1.54178$  Å, T = 223(2) K,  $\omega$  and  $\varphi$  scans, 13830 reflections collected ( $\pm h$ ,  $\pm k$ ,  $\pm l$ ), [( $\sin\theta$ )/ $\lambda$ ] = 0.59 Å<sup>-1</sup>, 4154 independent ( $R_{int} = 0.033$ ) and 3915 observed reflections [ $I > 2\sigma(I)$ ], 346 refined parameters, R = 0.035,  $wR^2 = 0.099$ , max. (min.) residual electron density 0.26 (-0.23) e.Å<sup>-3</sup>, hydrogen atoms were calculated and refined as riding atoms.



Reaction of 3 with terminal alkynes: synthesis of compound 7



A suspension of bis(pentafluorophenyl)borane (112.2 mg, 0.324 mmol) in dichloromethane (3 mL) was added to a solution of phenyl vinyl sulfide (44.2 mg, 0.324 mmol) in dichloromethane (1 mL). The obtained suspension was stirred for 10 min at room temperature. Thereafter, *p-tert*-butylphenylacetylene (116.7  $\mu$ L, 0.648 mmol, 2.0 eq.) was added. Then the reaction mixture turned immediately red and stirring was continued for

further 3 h at room temperature. Subsequently all volatiles were removed *in vacuo* and the obtained residue was washed with *n*-pentane (3 x 5 mL). The solid was dried *in vacuo* to give compound **7** as a white solid (151.2 mg, 0.196 mmol, 61%).

Crystals suitable for the X-ray crystal structure analysis were obtained by evaporation of a dichloromethane solution of **7** at room temperature.

**IR** (KBr)  $\tilde{v}$  [cm<sup>-1</sup>] = 3074 (w), 2964 (w), 2906 (w), 2869 (w), 1644 (w), 1585 (w), 1558 (w), 1514 (s), 1461 (s), 1402 (w), 1367 (m), 1313 (w), 1272 (m), 1231 (m), 1160 (w), 1082 (s), 1016 (w), 965 (s), 935 (m), 873 (w), 832 (m), 798 (w), 763 (w), 739 (m), 683 (w), 603 (w), 582 (w), 546 (w), 484 (w), 427 (w).

**Elemental Analysis** calcd for C<sub>42</sub>H<sub>33</sub>BF<sub>10</sub>S C 65.46, H 4.32; found C 64.77, H 4.22.

**Decomposition point (DSC):** 209 °C.

<sup>1</sup>**H** NMR (500 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 7.87$  (br s, 2H, =CH), 7.43 (m, 3H, *o*,*p*-Ph), 7.35 (m, 8H, *o*,*m*-C<sub>6</sub>H<sub>4</sub>), 7.30 (m, 2H, *m*-Ph), 1.27 (s, 18H, tBu).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 157.2$  (br, =CH), 152.8 (*p*-C<sub>6</sub>H<sub>4</sub>), 134.3 (=C)<sup>t</sup>, 133.3 (*p*-Ph), 130.57, 130.56 (*o*,*m*-Ph), 128.9 (*i*-Ph), 127.2, 126.4 (*o*,*m*-C<sub>6</sub>H<sub>4</sub>), 125.9 (*i*-C<sub>6</sub>H<sub>4</sub>)<sup>t</sup>, 34.9 (tBu), 31.2 (tBu), [C<sub>6</sub>F<sub>5</sub> not listed; <sup>t</sup> tentative assignment].

<sup>1</sup>**H**,<sup>1</sup>**H GCOSY** (500 MHz / 500 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>)[selected trace]:  $\delta$  <sup>1</sup>H /  $\delta$  <sup>1</sup>H = 7.43 / 7.30 (*o*,*p*-*Ph* / *m*-Ph).

<sup>1</sup>H{<sup>1</sup>H} NOE-DIFF (500 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>)[selected experiment]:  $\delta^{-1}H_{irr} / \delta^{-1}H_{res} = 7.87 / 7.35$  (=CH / *o*,*m*- C<sub>6</sub>H<sub>4</sub>).

<sup>1</sup>**H**,<sup>13</sup>**C GHSQC** (500 MHz / 126 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  <sup>1</sup>H /  $\delta$  <sup>13</sup>C = 7.87 / 157.2 (=CH), 7.43 / 133.3, 130.55 (*p*,*o*-Ph), 7.35 / 127.2, 126.4 (*o*,*m*-C<sub>6</sub>H<sub>4</sub>), 7.30 / 130.54 (*m*-Ph), 1.27 / 31.2 (tBu).

<sup>1</sup>H,<sup>13</sup>C GHMBC (500 MHz / 126 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>)[selected trace]:  $\delta$  <sup>1</sup>H /  $\delta$  <sup>13</sup>C = 7.87 / 157.2, 134.3, 125.9, 123.9 (=CH / =CH, =C, *i*-C<sub>6</sub>H<sub>4</sub>, *i*-C<sub>6</sub>F<sub>5</sub>), 7.35 / 152.8, 134.3, 125.9, 34.9 (*o*,*m*-C<sub>6</sub>H<sub>4</sub> / *p*-C<sub>6</sub>H<sub>4</sub>, =C, *i*-C<sub>6</sub>H<sub>4</sub>, tBu), 7.30 / 130.57, 130.56, 128.9 (*m*-Ph / o,*m*-Ph, *i*-Ph), 1.27 / 152.8, 34.9, 31.2 (tBu / *p*-C<sub>6</sub>H<sub>4</sub>, tBu, tBu).

<sup>19</sup>**F NMR** (470 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = -133.2$  (m, 2F, *o*), -161.2 (t, <sup>3</sup>*J*<sub>FF</sub> = 20.6 Hz, 1F, *p*), -165.1 (m, 2F, *m*)(C<sub>6</sub>F<sub>5</sub><sup>A</sup>) [Δδ<sup>19</sup>F<sub>m,p</sub> = 3.9], -133.9 (m, 2F, *o*), -161.5 (t, <sup>3</sup>*J*<sub>FF</sub> = 20.2 Hz, 1F, *p*), -165.6 (m, 2F, *m*)(C<sub>6</sub>F<sub>5</sub><sup>B</sup>) [Δδ<sup>19</sup>F<sub>m',p'</sub> = 4.1].

<sup>19</sup>**F**,<sup>19</sup>**F GCOSY** (470 MHz / 470 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>)[selected traces]:  $\delta^{19}F / \delta^{19}F = -165.1 / -133.2, -161.2 (m-C_6F_5^A / o-C_6F_5^A, p-C_6F_5^A), -165.6 / -133.9, -161.5 (m-C_6F_5^B / o-C_6F_5^B, p-C_6F_5^B).$ 

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = -17.0 (v_{1/2} \sim 30 \text{ Hz}).$ 





**X-ray crystal structure analysis of compound 7:** formula  $C_{42}H_{33}BF_{10}S$ , M = 770.55, colourless crystal, 0.10 x 0.03 x 0.03 mm, a = 11.6658(1), b = 12.1737(1), c = 15.0272(1) Å,  $\alpha = 102.447(1)$ ,  $\beta = 109.041(1)$ ,  $\gamma = 102.988(1)^{\circ}$ , V = 1866.6(3) Å<sup>3</sup>,  $\rho_{calc} = 1.371$  gcm<sup>-3</sup>,  $\mu = 1.477$  mm<sup>-1</sup>, empirical absorption correction (0.866  $\leq T \leq 0.957$ ), Z = 2, triclinic, space group  $P\bar{1}$  (No. 2),  $\lambda = 1.54178$  Å, T = 223(2) K,  $\omega$  and  $\varphi$  scans, 23865 reflections collected ( $\pm h$ ,  $\pm k$ ,  $\pm l$ ), [( $\sin\theta$ )/ $\lambda$ ] = 0.60 Å<sup>-1</sup>, 6398 independent ( $R_{int} = 0.085$ ) and 4491 observed reflections [ $I > 2\sigma(I)$ ], 543 refined parameters, R = 0.052,  $wR^2 = 0.142$ , max. (min.) residual electron density 0.28 (-0.24) e.Å<sup>-3</sup>, hydrogen atoms were calculated and refined as riding atoms.



## **Generation of compound 6**



A suspension of bis(pentafluorophenyl)borane (37.4 mg, 0.11 mmol) in dichloromethane (1 mL) was added to a solution of phenyl vinyl sulfide (14.7 mg, 0.11 mmol) in d<sub>2</sub>-dichloromethane (1 mL). The obtained suspension was stirred for 10 min at room temperature and then *p-tert*-butylphenylacetylene (17.5  $\mu$ L, 0.10 mmol, 0.9 eq.) was added. The yellow reaction solution was promptly characterized by NMR experiments. The major component was assigned as compound **6** (> 90% conversion; isolated yield: 33.3 mg, 69%). Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of **6** in dichloromethane at -40 °C.

[Comment: After the characterization of compound **6** by NMR experiments a second equivalent of *p-tert*-butylphenylacetylene (17.5  $\mu$ L, 0.1 mmol, 0.9 eq.) was added to give compound **7** (isolated yield: 52 mg, 0.07 mmol, 63%; NMR data are consistent to those given above)]

<sup>1</sup>**H** NMR (500 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 7.73 (br s, 1H, =CH), 7.50 (m, 2H, *o*-C<sub>6</sub>H<sub>4</sub>), 7.38 (m, 2H, *m*-C<sub>6</sub>H<sub>4</sub>), 7.26 (m, 1H, *p*-Ph), 7.19 (m, 2H, *m*-Ph), 7.11 (m, 2H, *o*-Ph), 1.29 (s, 9H, tBu).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 153.4$  (*p*-C<sub>6</sub>H<sub>4</sub>), 149.1 (br, =CH), 135.9 (br, =CS), 130.3 (*i*-C<sub>6</sub>H<sub>4</sub>), 129.9 (*p*-Ph), 129.5 (*m*-Ph), 129.2 (*i*-Ph)<sup>t</sup>, 128.5 (*o*-Ph), 126.2 (*m*-C<sub>6</sub>H<sub>4</sub>), 125.2 (*o*-C<sub>6</sub>H<sub>4</sub>), 35.1 (tBu), 31.2 (tBu), [C<sub>6</sub>F<sub>5</sub> not listed; <sup>t</sup> tentatively assigned].

<sup>1</sup>H{<sup>1</sup>H} TOCSY (500 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>)[selected experiments]:  $\delta^{-1}H_{irr} / \delta^{-1}H_{res} = 7.50 / 7.38 (o-C_6H_4 / m-C_6H_4), 7.11 / 7.26, 7.19 (o-Ph / p,m-Ph).$ 

<sup>1</sup>H{<sup>1</sup>H} NOE-DIFF (500 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>)[selected experiment]:  $\delta^{-1}H_{irr} / \delta^{-1}H_{res} = 7.73 / 7.50$  (=CH / *o*-C<sub>6</sub>H<sub>4</sub>).

<sup>1</sup>**H**,<sup>13</sup>**C GHSQC** (500 MHz / 126 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  <sup>1</sup>H /  $\delta$  <sup>13</sup>C = 7.73 / 149.1 (=CH), 7.50 / 125.2 (*o*-C<sub>6</sub>H<sub>4</sub>), 7.38 / 126.2 (*m*-C<sub>6</sub>H<sub>4</sub>), 7.26 / 129.9 (*p*-Ph), 7.19 / 129.5 (*m*-Ph), 7.11 / 128.5 (*o*-Ph), 1.29 / 31.2 (tBu).

<sup>1</sup>**H**,<sup>13</sup>**C GHMBC** (500 MHz / 126 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>)[selected trace]:  $\delta$  <sup>1</sup>H /  $\delta$  <sup>13</sup>C = 7.50 / 125.2, 135.9, 153.4 (*o*-C<sub>6</sub>H<sub>4</sub> / *o*-C<sub>6</sub>H<sub>4</sub>, =CS, *p*-C<sub>6</sub>H<sub>4</sub>), 7.38 / 35.1, 126.2, 130.3 (*m*-C<sub>6</sub>H<sub>4</sub> / tBu, *m*-C<sub>6</sub>H<sub>4</sub>, *i*-C<sub>6</sub>H<sub>4</sub>), 7.19 / 129.5, 129.2 (*m*-Ph / *m*-Ph, *i*-Ph).

<sup>19</sup>**F NMR** (470 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = -131.5 (m, 2F, *o*), -155.3 (t, <sup>3</sup>*J*<sub>FF</sub> = 20.0 Hz, 1F, *p*), -164.1 (m, 2F, *m*)(C<sub>6</sub>F<sub>5</sub>) [Δδ<sup>19</sup>F<sub>m,p</sub> = 8.8].

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, 299 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 15.7 (v_{1/2} \sim 500 \text{ Hz}).$ 





**X-ray crystal structure analysis of compound 6:** formula  $C_{30}H_{19}BF_{10}S$ , M = 612.32, pale yellow crystal, 0.10 x 0.02 x 0.01 mm, a = 14.0405(12), b = 14.1582(12), c = 16.0389(9) Å,  $\alpha = 70.793(5)$ ,  $\beta = 80.041(5)$ ,  $\gamma = 69.281(3)^{\circ}$ , V = 2810.4(4) Å<sup>3</sup>,  $\rho_{calc} = 1.447$  gcm<sup>-3</sup>,  $\mu = 1.808$  mm<sup>-1</sup>, empirical absorption correction (0.839  $\leq T \leq 0.982$ ), Z = 4, triclinic, space group  $P\bar{1}$  (No. 2),  $\lambda = 1.54178$  Å, T = 223(2) K,  $\omega$  and  $\varphi$  scans, 28498 reflections collected ( $\pm h$ ,  $\pm k$ ,  $\pm l$ ), [( $\sin\theta$ )/ $\lambda$ ] = 0.59 Å<sup>-1</sup>, 8081 independent ( $R_{int} = 0.172$ ) and 3343 observed reflections [ $I > 2\sigma(I)$ ],

843 refined parameters, R = 0.069,  $wR^2 = 0.203$ , max. (min.) residual electron density 0.31 (-0.32) e.Å<sup>-3</sup>, hydrogen atoms were calculated and refined as riding atoms.

