

## *Supporting Information for*

### **Catalytic activity of cyclobutadiene rhodium complexes in hydrosilylation and other transformations of alkynes**

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## General remarks

All reactions were carried out in the argon atmosphere. All products were isolated in air.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured with a Bruker Avance 400 or 300 spectrometer at 20 °C. Chemical shifts are reported in ppm using the residual signals of the solvents as internal standards. Reagents were purchased from Acros or Sigma-Aldrich and used as received. The complex  $[\text{Rh}(\text{cod})(p\text{-xylene})]\text{SbF}_6$  was synthesized similarly to the literature procedure (R. Sumitani, D. Kuwahara, and T. Mochida, *Inorg. Chem.* 2023, **62**, 2169–2180). Column chromatography was carried out using Macherey-Nagel silica gel 60 (0.04–0.063 mm particle size).

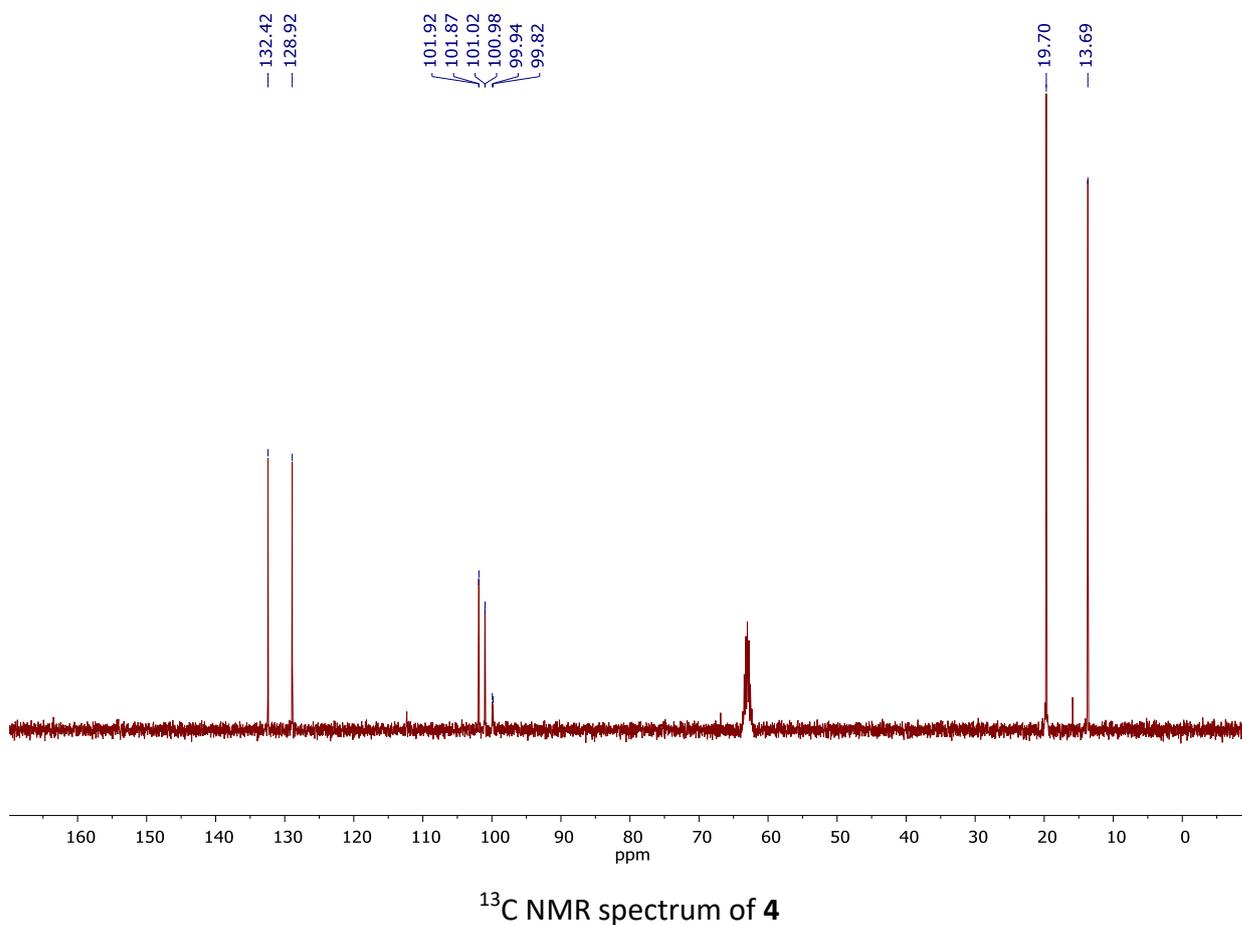
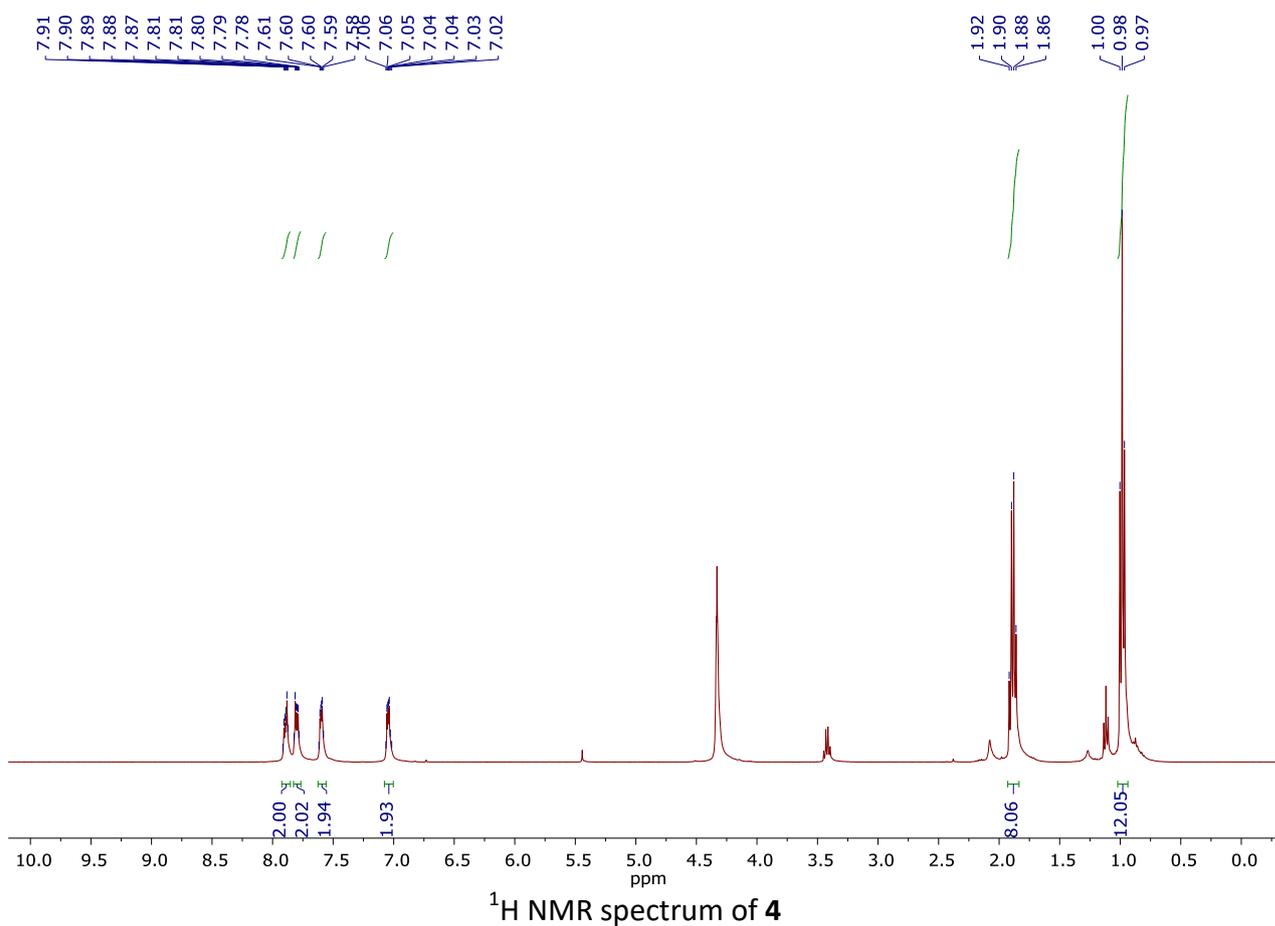
## Synthesis of cyclobutadiene rhodium complexes

### *Synthesis of $[\text{Rh}(\text{C}_4\text{Et}_4)(\text{C}_{10}\text{H}_8)]\text{PF}_6$ (**4**)*

Complex **1a** (52 mg, 0.1 mmol, 1 equiv.) was dissolved in MeCN (1.5 ml) and 5 ml of hexane was added. The 2-phase solution was stirred vigorously (for making layers mixed) for 3 hours. Then hexane phase was carefully decanted and new portion of hexane was added. After another 3 hours this procedure was repeated, and reaction was allowed to stir overnight. On the next morning hexane phase was exchanged the last time. After 3 hours hexane was decanted and MeCN was removed from the reaction flask in vacuo giving complex **3** as yellow powder. The precipitate was washed with 1 ml of  $\text{Et}_2\text{O}$  and 3 ml of hexane, then dried in vacuo. Then naphthalene (600 mg, 4.7 mmol, 47 equiv.) and  $\text{CH}_3\text{NO}_2$  (2 ml) were added to the reaction flask and the reaction mixture was stirred 24 hours. Then  $\text{CH}_3\text{NO}_2$  was removed in vacuo, large amount of  $\text{Et}_2\text{O}$  was added. The product was separated by centrifugation and reprecipitated from 800  $\mu\text{l}$  of dichloromethane by 10 ml of  $\text{Et}_2\text{O}$ . The precipitate was dried in vacuo giving 29.3 mg of complex **4** as yellowish powder (54% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{NO}_2$ )  $\delta$ : 7.91-7.87 (m, 2H, arene), 7.82-7.78 (m, 2H, arene), 7.62-7.58 (m, 2H, arene), 7.06-7.02 (m, 2H, arene), 1.89 (q,  $J = 7.5$  Hz, 8H,  $\text{CH}_2$ ), 0.98 (t,  $J = 7.5$  Hz, 12H,  $\text{CH}_3$ ).  
 $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_3\text{NO}_2$ )  $\delta$ : 132.42 (arene), 128.92 (arene), 101.90 (d,  $J = 4.6$  Hz, arene), 101.00 (d,  $J = 3.7$  Hz, arene), 99.88 (d,  $J = 12.0$  Hz, cyclobutadiene), 19.70 ( $\text{CH}_2$ ), 13.69 ( $\text{CH}_3$ ). Signals of bridgehead carbon atoms of naphthalene were not observed because of their low intensity.

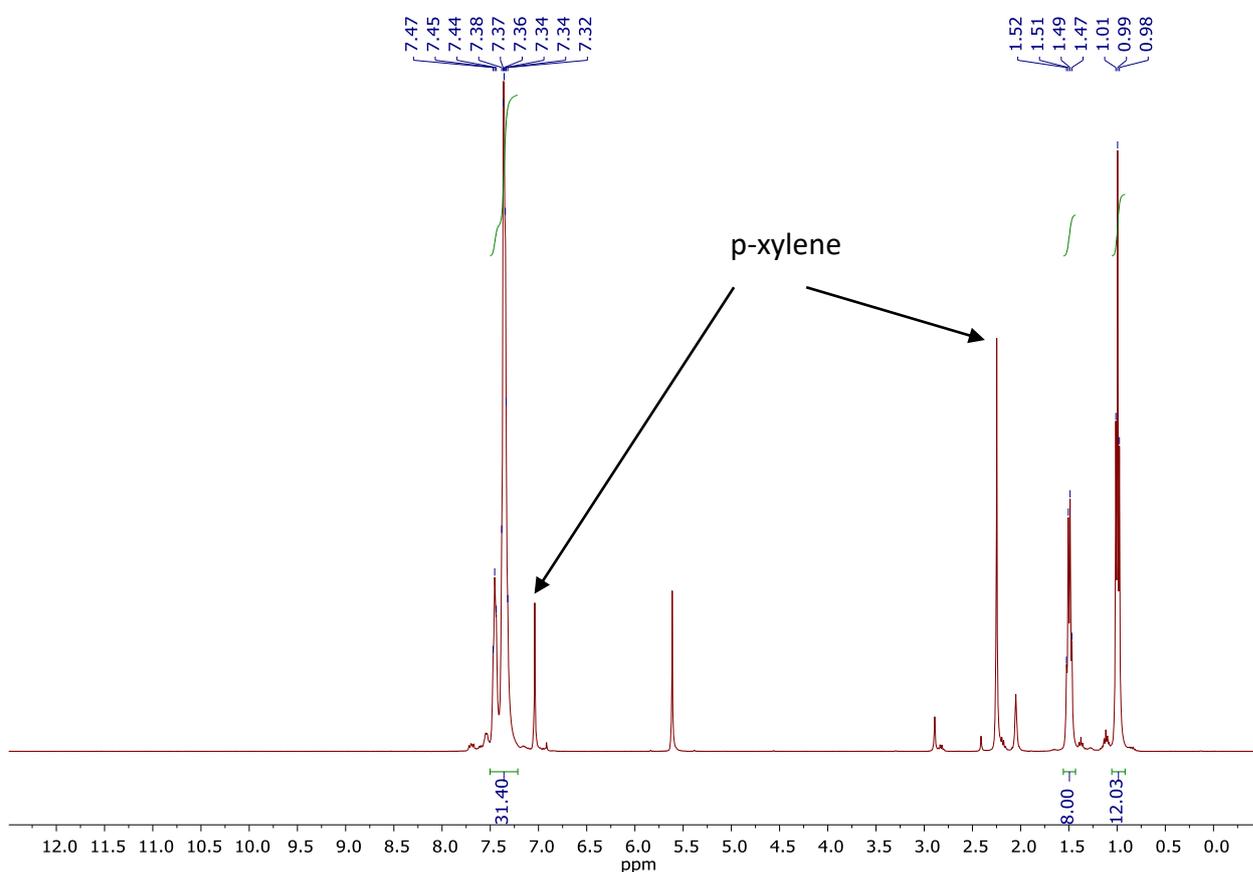
Anal. Calc. for  $\text{C}_{26}\text{H}_{40}\text{F}_6\text{PRh}$ : %C = 48.90, %H = 5.22; found %C = 48.79, %H = 5.32.



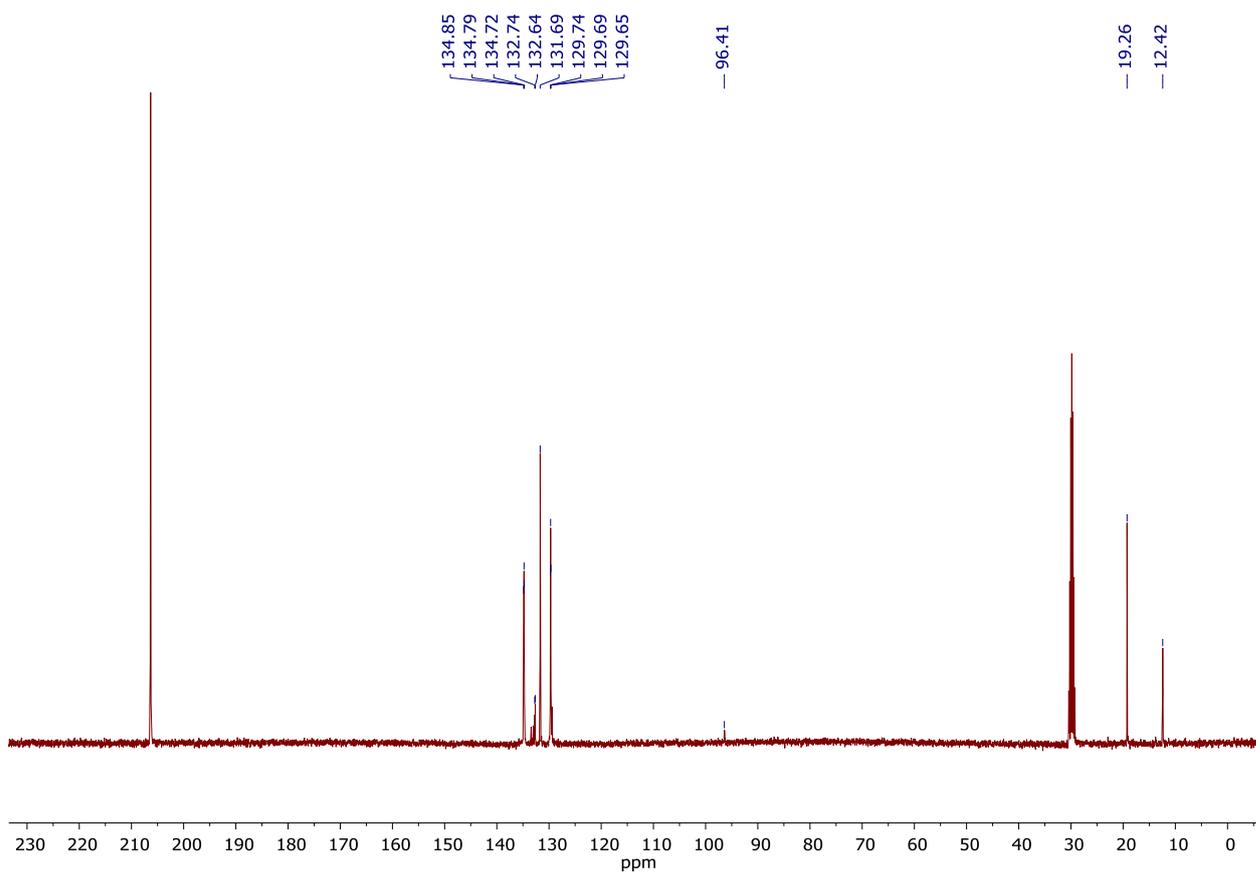
### Synthesis of $[Rh(C_4Et_4)(PPh_3)_2]BF_4$ (**5**)

The mixture of complex **1b** (30 mg, 0.065 mmol, 1 equiv. and  $PPh_3$  (34 mg, 0.13 mmol, 2 equiv.) in 1 ml of acetone was stirred for 3 hours. Intense dark red color appeared during the reaction. The solvent was removed *in vacuo*, the dark red residue was washed with  $Et_2O$  (2x10 ml). The solid was then reprecipitated from minimal amount of dichloromethane by 10 ml of  $Et_2O$  and dried in vacuum to give 51 mg (89% yield) of the product as dark red powder. Crystals suitable for X-ray analysis were obtained by diffusion of  $Et_2O$  vapors into the dichloromethane solution of the complex.

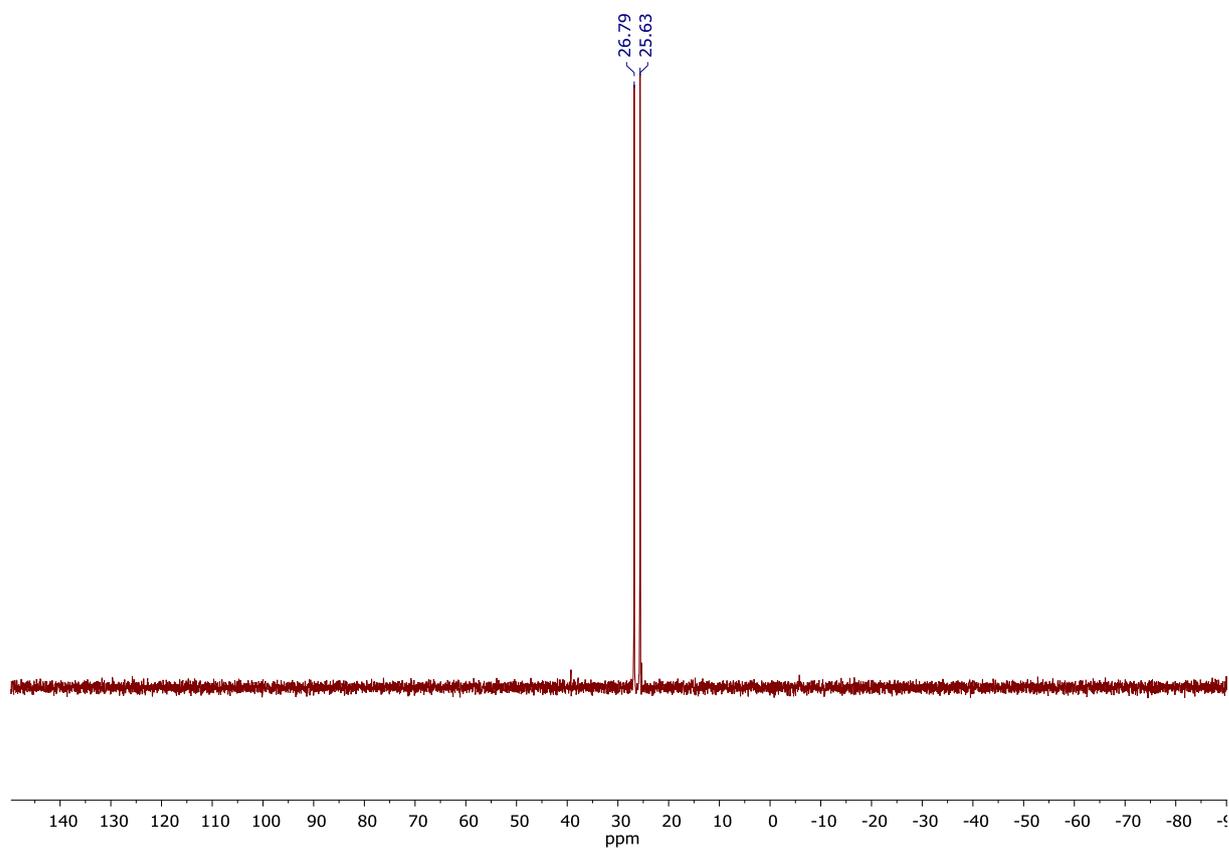
$^1H$  NMR (400 MHz, acetone- $d_6$ )  $\delta$ : 7.47-7.32 (m, 30H, Ph), 1.50 (q,  $J = 7.5$  Hz, 8H,  $CH_2$ ), 0.99 (t,  $J = 7.5$  Hz, 12H,  $CH_3$ ).  $^{13}C$  NMR (101 MHz, acetone- $d_6$ )  $\delta$  134.90 (p,  $J = 7.8$  Hz, Ph), 132.69 (d,  $J = 9.7$  Hz, Ph), 131.69 (s, Ph), 129.69 (t,  $J = 4.8$  Hz, Ph), 96.36 (d,  $J = 8.4$  Hz, cyclobutadiene), 19.26 (s,  $CH_2$ ), 12.42 (s,  $CH_3$ ).  $^{31}P$  NMR (162 MHz, acetone- $d_6$ )  $\delta$ : 26.21 (d,  $J = 187.9$  Hz). HRMS (ESI-TOF,  $m/z$ ) calcd for  $C_{48}H_{50}P_2Rh$ : 791.2442; found 791.2428.



$^1H$  NMR spectrum of **5**



$^{13}\text{C}$  NMR spectrum of **5**



$^{31}\text{P}$  NMR spectrum of **5**

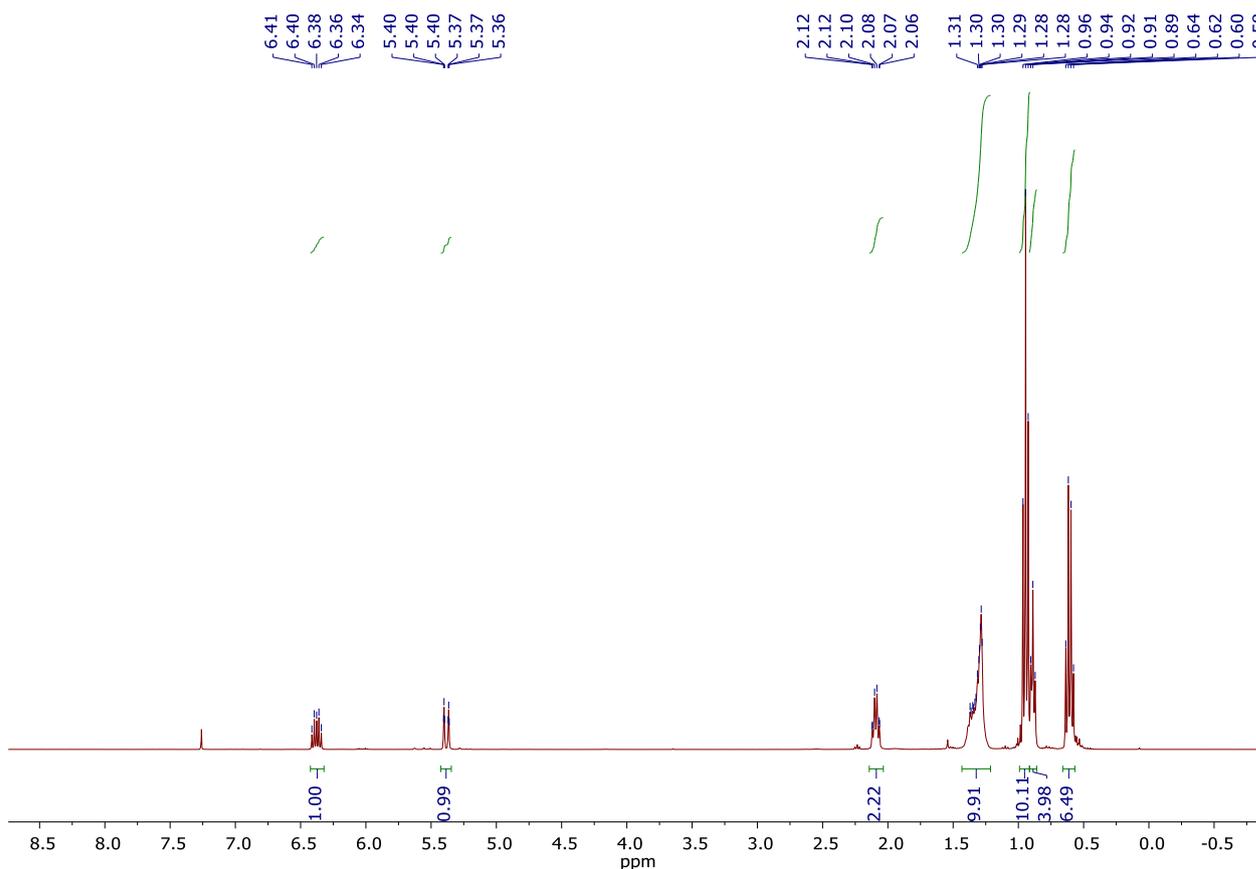
## Hydrosilylation reactions

### Hydrosilylation of 1-octyne with triethylsilane, catalyzed by $[Rh(C_4Et_4)I]_2$ (**21**, entry 2)

Schlenk tube was charged with complex **1b** (2.3 mg, 0.005 mmol, 1 mol.%) and  $NEt_4I$  (2.6 mg, 0.01 mmol, 2 mol.%), degassed and filled with argon several times. Solid reactants were dissolved in 1 ml of dichloromethane, forming dark red solution which was stirred overnight. Then 1-octyne (74  $\mu$ l, 0.5 mmol, 1 equiv.) and triethylsilane (80  $\mu$ l, 0.5 mmol, 1 equiv.) were added to the generated catalyst and the reaction mixture was stirred for 21 hours. The solvent was removed *in vacuo* and the reaction mixture was eluted with hexane through a plug of  $Al_2O_3$  giving 105 mg of product as a mixture of stereoisomers (total yield 93%). The ratio of E- and Z-isomers was determined by NMR spectroscopy with internal standard (dioxane): Z – 96%, E – 4%.

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 6.38 (dt,  $J = 14.4, 7.3$  Hz, 1H,  $CHCH_2$ ), 5.38 (d,  $J = 14.1$  Hz, 1H,  $CHSiEt_3$ ), 2.09 (q,  $J = 7.3$  Hz, 2H,  $CH_2$ ), 1.41-1.21 (m, 8H, alkyl), 0.94 (t,  $J = 7.9$  Hz, 9H,  $SiCH_3$ ), 0.89 (t,  $J = 6.8$  Hz, 3H,  $CH_3$ -alkyl), 0.61 (q,  $J = 7.9$  Hz, 6H,  $SiCH_2$ ).

Cf. to R. Takeuchi, S. Nitta, and D. Watanabe, *J. Org. Chem.*, 1996, **60**, 3045-3051.



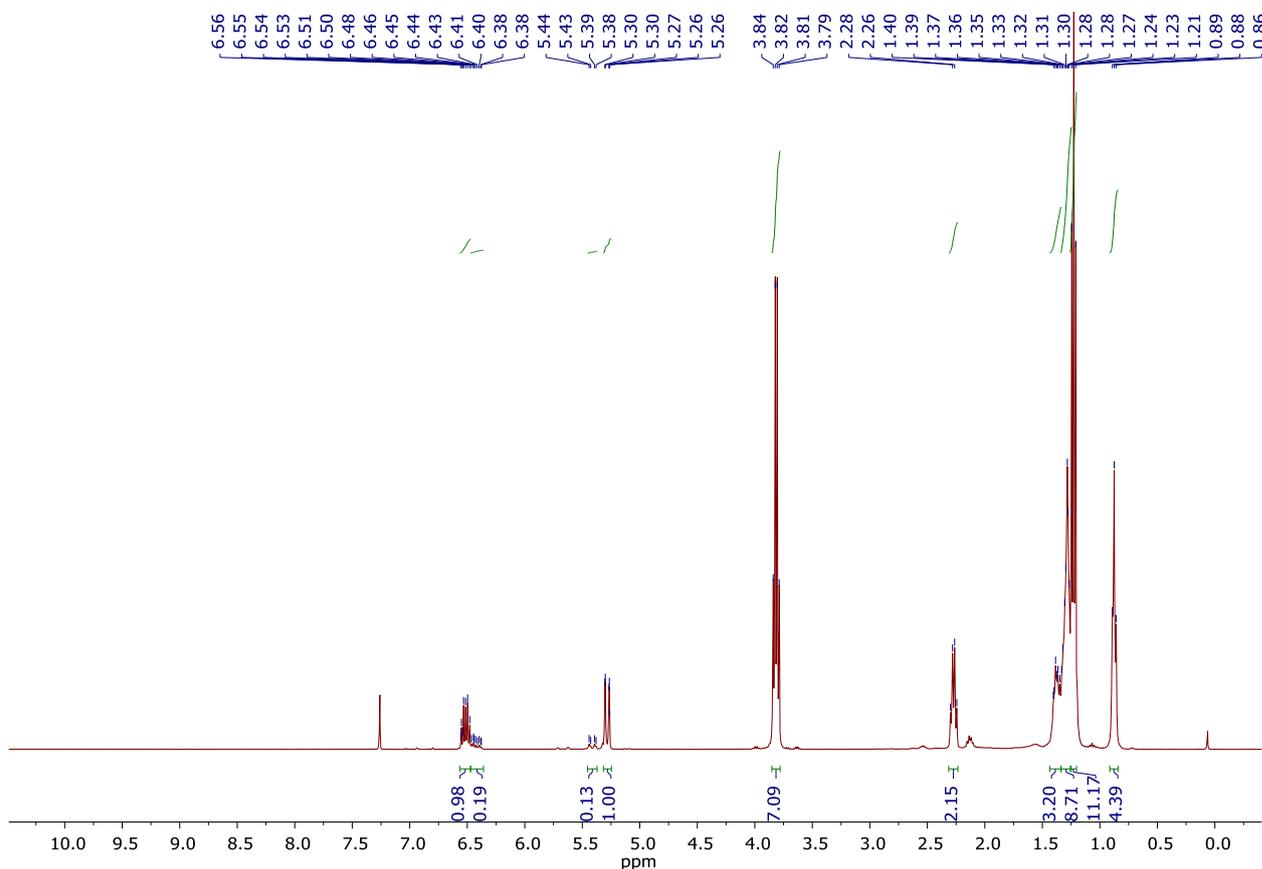
$^1H$  NMR spectrum of 1-octyne hydrosilylation with triethylsilane with  $[Rh(C_4Et_4)I]_2$  (**21**) catalyst

### Hydrosilylation of 1-octyne with triethoxysilane, catalyzed by $[Rh(C_4Et_4)I]_2$ (**2I**)

NMR tube was charged with complex **1a** (1.4 mg, 0.003 mmol, 1 mol.%) and  $NEt_4I$  (1.5 mg, 0.006 mmol, 2 mol.%), degassed and filled with argon several times. Solid reactants were dissolved in 600  $\mu$ l of  $CDCl_3$ , forming dark red solution which was stirred overnight. Then 1-octyne (44  $\mu$ l, 0.3 mmol, 1 equiv.) and triethoxysilane (55  $\mu$ l, 0.3 mmol, 1 equiv.) were added to the generated catalyst and the reaction mixture was stirred overnight. The solvent was removed *in vacuo* and the reaction mixture was eluted with hexane through a plug of  $Al_2O_3$  giving 23 mg of product as a mixture of stereoisomers (total yield 28%). The ratio of E- and Z-isomers was determined by NMR spectroscopy: Z – 88%, E – 12%.

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 6.51 (dt,  $J = 14.5, 7.4$  Hz, 1H,  $CHCH_2$ ), 6.42 (ddd,  $J = 19.9, 8.2, 4.4$  Hz, 1H, E-isomer  $CHCH_2$ ), 5.41 (dd,  $J = 18.8, 5.6$  Hz, 1H, E-isomer,  $CHSiEt_3$ ), 5.28 (dd,  $J = 14.1, 1.4$  Hz, 1H,  $CHSiEt_3$ ), 3.81 (q,  $J = 6.9$  Hz, 7H, E+Z,  $SiOCH_2$ ), 2.27 (q,  $J = 7.3$  Hz, 2H, E+Z,  $CH_2$ -alkyl), 1.44-1.25 (m, 9H, E+Z, alkyl), 1.23 (t,  $J = 7.0$  Hz, 10H, E+Z,  $SiOCH_3$ ), 0.88 (t,  $J = 6.6$  Hz, 3H, E+Z,  $CH_3$ -alkyl).

Cf. to E. Alacid, and C. Najera, *J. Org. Chem.*, 2008, **73**, 6, 2315–2322.



$^1H$  NMR spectrum of 1-octyne hydrosilylation with triethoxysilane with  $[Rh(C_4Et_4)I]_2$  (**2I**) catalyst

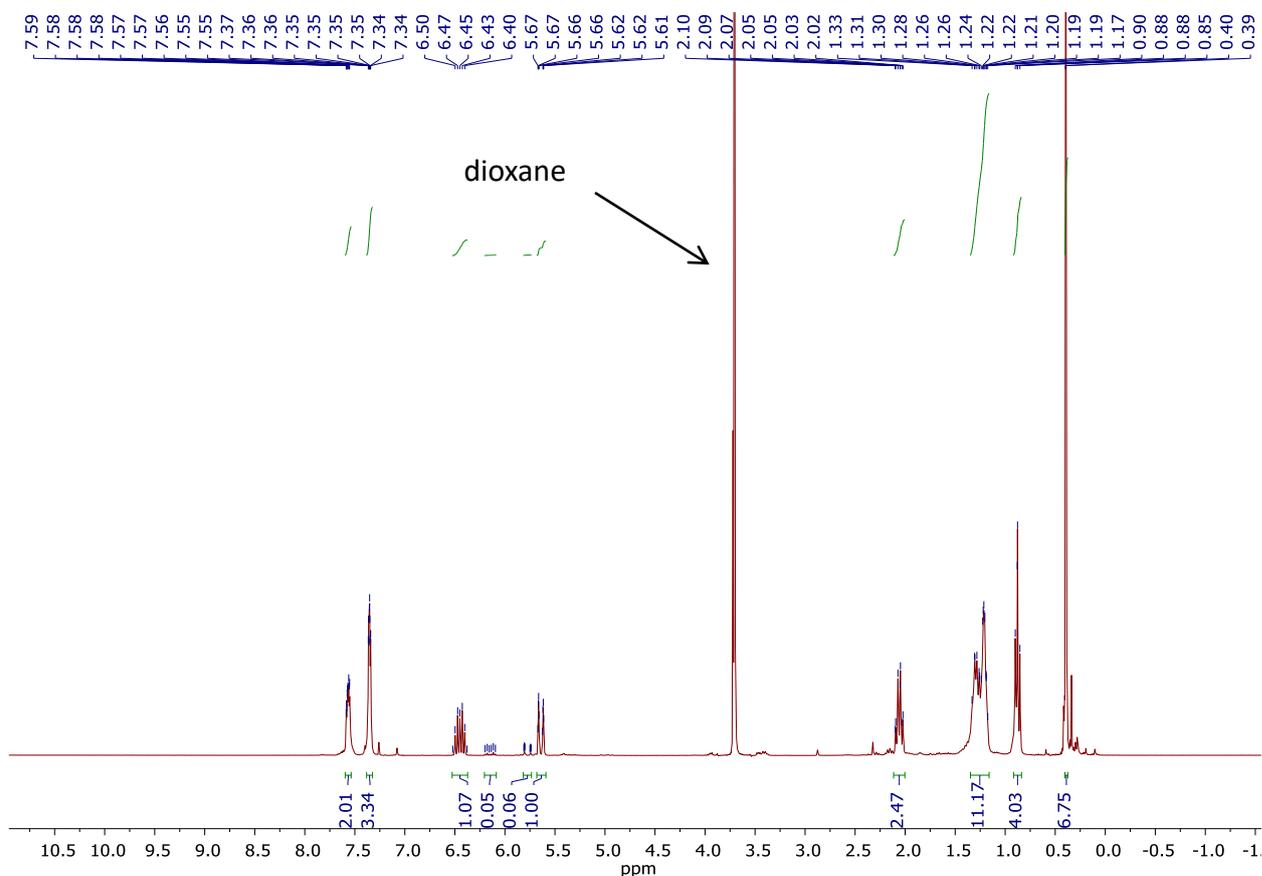
### Hydrosilylation of 1-octyne with dimethylphenylsilane, catalyzed by $[Rh(C_4Et_4)I]_2$ (**2I**)

NMR tube was charged with complex **1a** (1.4 mg, 0.003 mmol, 1 mol.%) and  $NEt_4I$  (1.5 mg, 0.006 mmol, 2 mol.%), degassed and filled with argon several times. Solid reactants were dissolved in 600  $\mu$ l of  $CDCl_3$ , forming dark red solution which was stirred overnight. Then 1-

octyne (44  $\mu$ l, 0.3 mmol, 1 equiv.) and dimethylphenylsilane (46  $\mu$ l, 0.3 mmol, 1 equiv.) were added to the generated catalyst and the reaction mixture was stirred overnight. Then dioxane was added to the NMR tube as an internal standard, total yield and ratio of stereoisomers were determined by NMR spectrum: total yield – 74%; Z – 95%, E – 5%.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.59-7.55 (m, 2H, E+Z, Ph), 7.37-7.34 (m, 3H, E+Z, Ph), 6.55–6.35 (m, 1H, Z-isomer,  $\text{CHCH}_2$ ), 6.15 (dt,  $J = 18.6, 6.2$  Hz, 1H, E-isomer,  $\text{CHCH}_2$ ), 5.77 (dt,  $J = 18.6, 1.1$  Hz, 1H, E-isomer,  $\text{CHSiMe}_2\text{Ph}$ ), 5.64 (dq,  $J = 13.9, 1.1$  Hz, 1H, Z-isomer,  $\text{CHSiMe}_2\text{Ph}$ ), 2.06 (q,  $J = 7.2$  Hz, 2H, E+Z,  $\text{CH}_2$ -alkyl), 1.33-1.17 (m, 8H, E+Z, alkyl), 0.88 (t,  $J = 6.9$  Hz, 3H, E+Z,  $\text{CH}_3$ -alkyl), 0.39 (s, 6H, E+Z,  $\text{SiCH}_3$ ).

Cf. to H. Yoshida, Y. Izumi, Y. Hiraoka, K. Nakanishi, M. Nakamoto, S. Hatano, and M. Abe, *Dalton Trans.*, 2022, **51**, 6543-6546.



$^1\text{H}$  NMR spectrum of 1-octyne hydro-silylation with dimethylphenylsilane with  $[\text{Rh}(\text{C}_4\text{Et}_4)\text{I}]_2$  (**2I**) catalyst

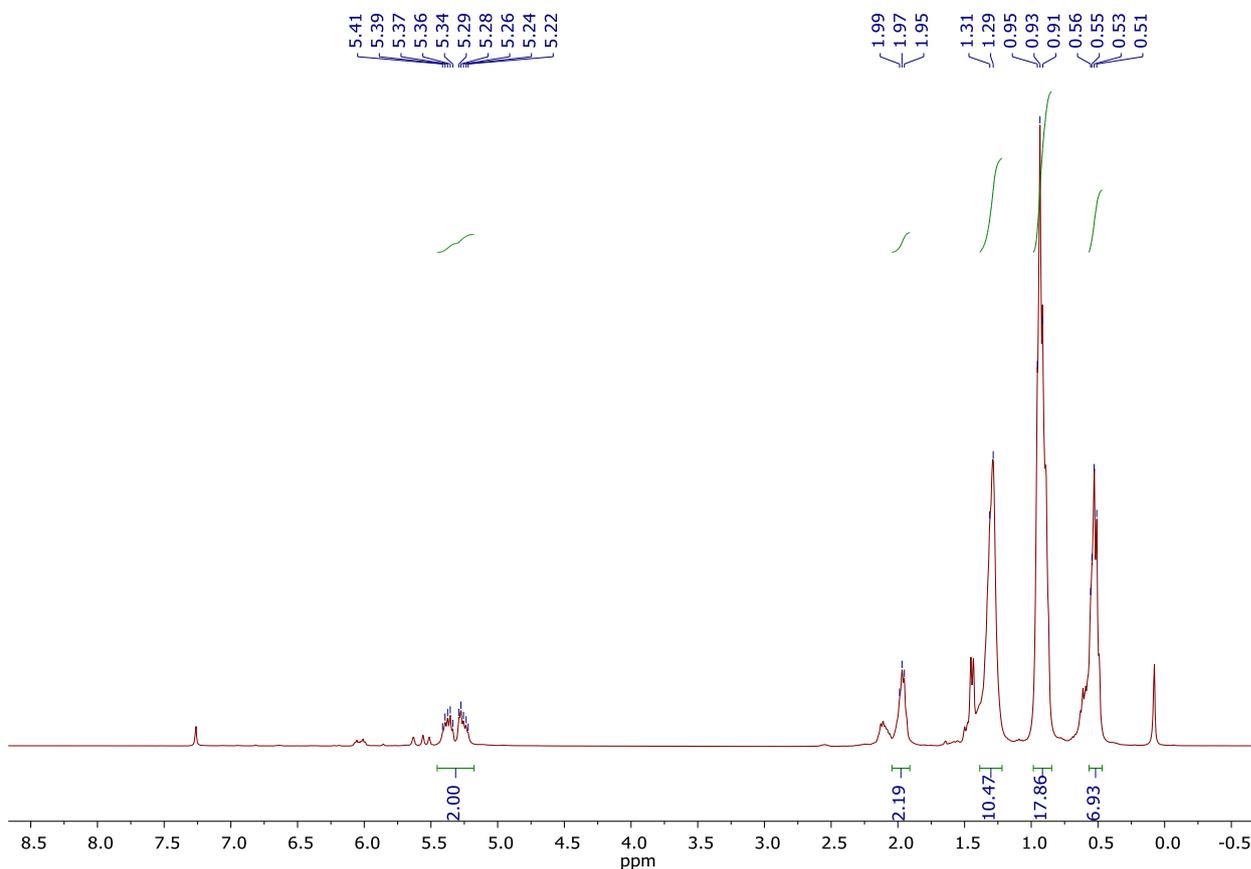
*Hydro-silylation of 1-octyne with triethylsilane, catalyzed by  $[\text{Rh}(\text{C}_4\text{Et}_4)\text{Cl}]_2$  (**2I**, entry 3)*

Schlenk tube was charged with complex **1b** (2.3 mg, 0.005 mmol, 1 mol.%) and  $\text{NBnEt}_3\text{Cl}$  (1.3mg, 0.0055 mmol, 1.1 mol.%), degassed and filled with argon several times. Solid reactants were dissolved in 1 ml of dichloromethane, forming dark red solution which was stirred overnight. Then 1-octyne (74  $\mu$ l, 0.5 mmol, 1 equiv.) and triethylsilane (80  $\mu$ l, 0.5 mmol, 1 equiv.) were added to the generated catalyst and the reaction mixture was stirred for 41 hours. The solvent was removed *in vacuo* and the reaction mixture was eluted with hexane through a plug of  $\text{Al}_2\text{O}_3$  giving 106 mg of product as a mixture of stereoisomers (total yield 94%). The ratio

of isomers was determined by NMR spectroscopy with internal standard (dioxane):  $\alpha$  – 90%, E – 10%. Traces of Z-isomer were detected by mass-spectrometry.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.45-5.20 (m, 2H, =CH<sub>2</sub>), 2.04-1.90 (m, 2H, CH<sub>2</sub>-alkyl), 1.40-1.20 (m, 8H, alkyl), 1.00-0.86 (m, 9H+3H, SiCH<sub>3</sub> +CH<sub>3</sub>-alkyl), 0.53 (m, 6H, SiCH<sub>2</sub>).

Cf. to G. De Bo, G. Berthon-Gelloz, B. Tinant, and I. E. Marko, *Organometallics*, 2006, **25**, 1881-1890.



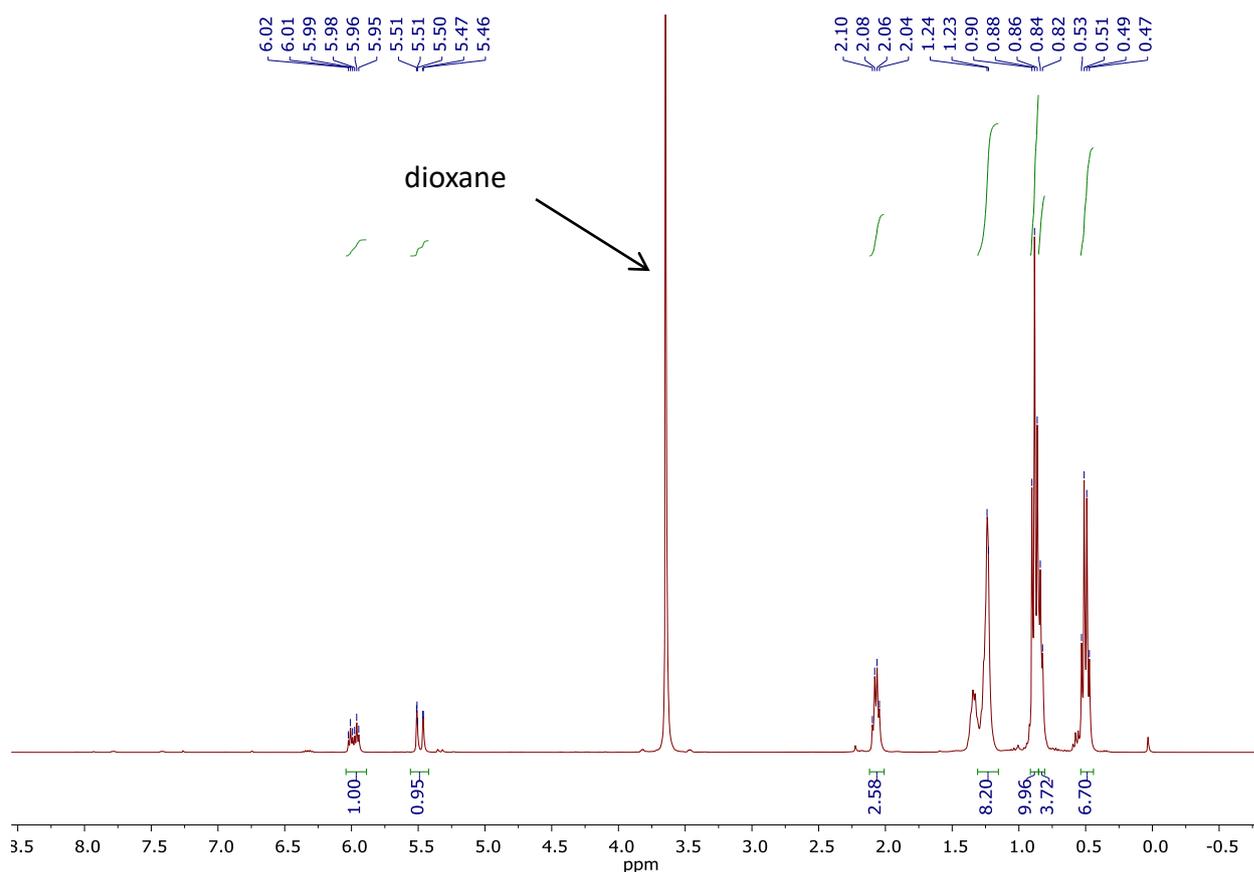
$^1\text{H}$  NMR spectrum of 1-octyne hydrosilylation with  $[\text{Rh}(\text{C}_4\text{Et}_4)\text{Cl}]_2$  (**2Cl**) catalyst

#### *Hydrosilylation of 1-octyne with triethylsilane, catalyzed by $[\text{Rh}(\text{C}_4\text{Et}_4)(\text{PPh}_3)_2]\text{BF}_4$ (**5**, entry 5)*

Schlenk tube was charged with complex **5** (4.4 mg, 0.005 mmol, 1 mol.%), degassed and filled with argon several times. After that 1-octyne (74  $\mu\text{l}$ , 0.5 mmol, 1 equiv.) and triethylsilane (80  $\mu\text{l}$ , 0.5 mmol, 1 equiv.) were added and the reaction mixture was stirred for 1 hour. Then acetone was removed *in vacuo* and the reaction mixture was eluted with hexane through a plug of  $\text{Al}_2\text{O}_3$ . The yield and the ratio of E- and Z-isomers was determined by NMR spectroscopy with internal standard (dioxane). Total yield >99%, E – 94%, Z – 6%.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.98 (dt,  $J = 18.7, 6.2$  Hz, 1H, CHCH<sub>2</sub>), 5.49 (m, 1H, CHSiEt<sub>3</sub>), 2.07 (q,  $J = 7.0$  Hz, 2H, CH<sub>2</sub>-alkyl), 1.30-1.18 (m, 8H, alkyl), 0.88 (t,  $J = 7.9$  Hz, 9H, SiCH<sub>3</sub>), 0.84 (t,  $J = 6.8$  Hz, 3H, CH<sub>3</sub>-alkyl), 0.50 (q,  $J = 7.9$  Hz, 6H, SiCH<sub>2</sub>).

Cf. to R. Takeuchi, S. Nitta, and D. Watanabe, *J. Org. Chem.*, 1996, **60**, 3045-3051.



$^1\text{H}$  NMR spectrum of 1-octyne hydrosilylation with  $[\text{Rh}(\text{C}_4\text{Et}_4)(\text{PPh}_3)_2]\text{BF}_4$  as a catalyst

#### *Hydrosilylation of phenylacetylene with triethylsilane, catalyzed by $[\text{Rh}(\text{C}_4\text{Et}_4)]_2$ (**2**)*

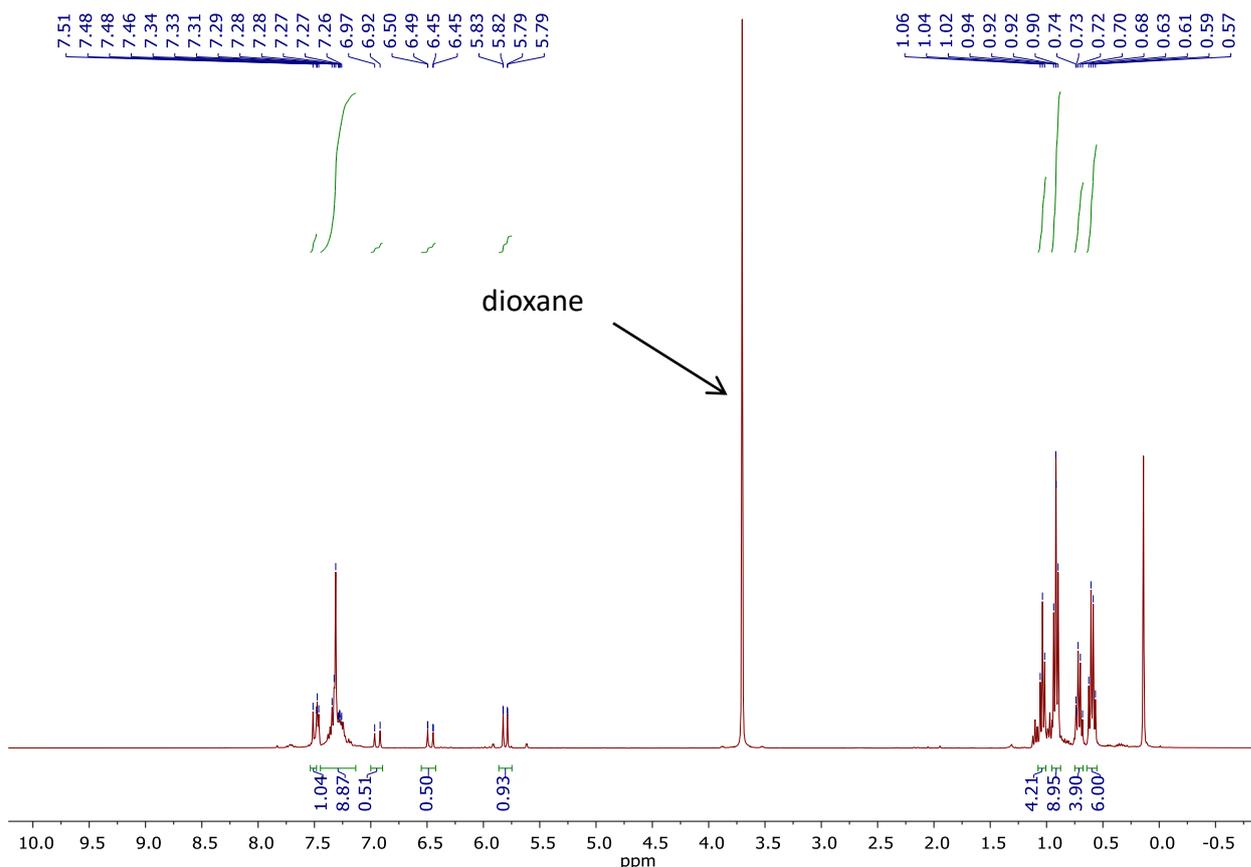
Schlenk tube was charged with complex **1b** (2.3 mg, 0.005 mmol, 1 mol.%) and  $\text{NEt}_4\text{I}$  (2.6 mg, 0.01 mmol, 2 mol.%), degassed and filled with argon several times. Solid reactants were dissolved in 1 ml of dichloromethane, forming dark red solution which was stirred overnight. Then phenylacetylene (55  $\mu\text{l}$ , 0.5 mmol, 1 equiv.) and triethylsilane (80  $\mu\text{l}$ , 0.5 mmol, 1 equiv.) were added to the generated catalyst and the reaction mixture was stirred for 21 hours. The solvent was removed *in vacuo* and the reaction mixture was eluted with hexane through a plug of  $\text{Al}_2\text{O}_3$  giving 105 mg of product as a mixture of stereoisomers (total yield 96%). The ratio of E- and Z-isomers was determined by NMR spectroscopy with internal standard (dioxane): Z – 60%, E – 40%. Traces of  $\alpha$ -isomer (c.a. 5%) were also detected.

Z-Triethyl(2-phenylvinyl)silane.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.38-7.18 (m, 5H, Ph), 5.50 (d,  $J = 15.3$  Hz, 1H, CHPh), 5.81 (d,  $J = 15.3$  Hz, 1H,  $\text{CHSiEt}_3$ ), 0.92 (t,  $J = 7.9$  Hz, 9H,  $\text{SiCH}_3$ ) 0.60 (q,  $J = 7.9$  Hz, 6H,  $\text{SiCH}_2$ ).

Cf. to H. Liang, Y.-X. Ji, R.-H. Wang, Z.-H. Zhang, and B. Zhang, *Org. Lett.* 2019, **21**, 2750–2754.

E-Triethyl(2-phenylvinyl)silane.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.38-7.18 (m, 5H, Ph), 6.94 (d,  $J = 19.4$  Hz, 1H, CHPh), 6.47 (d,  $J = 19.4$  Hz, 1H,  $\text{CHSiEt}_3$ ), 1.04 (t,  $J = 7.9$  Hz, 9H,  $\text{SiCH}_3$ ), 0.71 (q,  $J = 7.9$  Hz, 6H,  $\text{SiCH}_2$ ).

Cf. to N. V. Shvydkiy, K. V. Rimskiy, D. S. Perekalin, *Appl. Organomet. Chem.* 2023, **37**, e7008.



$^1\text{H}$  NMR spectrum of phenylacetylene hydrosilylation with triethylsilane with  $[\text{Rh}(\text{C}_4\text{Et}_4)\text{I}]_2$  (**2I**) catalyst

#### *Hydrosilylation of phenylacetylene with triethylsilane, catalyzed by $[\text{Rh}(\text{C}_4\text{Et}_4)\text{Cl}]_2$ (**2Cl**)*

Schlenk tube was charged with complex **1b** (2.3 mg, 0.005 mmol, 1 mol.%) and  $\text{NBnEt}_3\text{Cl}$  (1.3mg, 0.0055 mmol, 1.1 mol.%), degassed and filled with argon several times. Solid reactants were dissolved in 1 ml of dichloromethane, forming dark red solution which was stirred overnight. Then phenylacetylene (55  $\mu\text{l}$ , 0.5 mmol, 1 equiv.) and triethylsilane (80  $\mu\text{l}$ , 0.5 mmol, 1 equiv.) were added to the generated catalyst and the reaction mixture was stirred for 21 hours. The solvent was removed *in vacuo* and the reaction mixture was eluted with hexane through a plug of  $\text{Al}_2\text{O}_3$  giving 106 mg of product as a mixture of stereoisomers (total yield 97%). The ratio of E- and Z-isomers was determined by NMR spectroscopy with internal standard (dioxane): Z – 40%, E – 40%,  $\alpha$ -isomer – 20%.

Z-Triethyl(2-phenylvinyl)silane.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.38-7.14 (m, 5H, Ph), 5.50 (d,  $J$  = 15.3 Hz, 1H,  $\text{CHPh}$ ), 5.78 (d,  $J$  = 15.3 Hz, 1H,  $\text{CHSiEt}_3$ ), 0.89 (t,  $J$  = 7.9 Hz, 9H,  $\text{SiCH}_3$ ) 0.57 (q,  $J$  = 7.9 Hz, 6H,  $\text{SiCH}_2$ ).

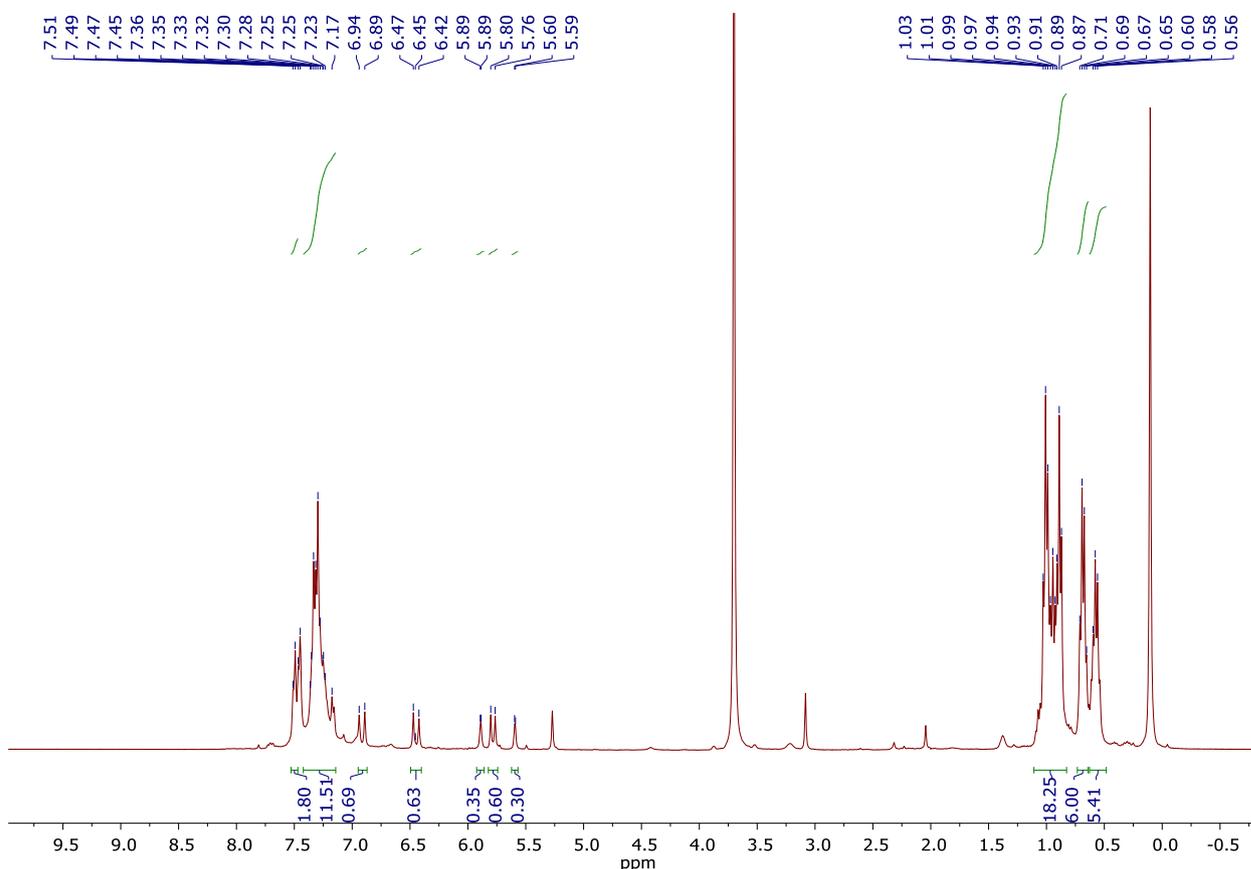
Cf. to H. Liang, Y.-X. Ji, R.-H. Wang, Z.-H. Zhang, and B. Zhang, *Org. Lett.* 2019, **21**, 2750–2754.

E-Triethyl(2-phenylvinyl)silane.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.38-7.14 (m, 5H, Ph), 6.92 (d,  $J$  = 19.4 Hz, 1H,  $\text{CHPh}$ ), 6.45 (d,  $J$  = 19.4 Hz, 1H,  $\text{CHSiEt}_3$ ), 1.01 (t,  $J$  = 7.9 Hz, 9H,  $\text{SiCH}_3$ ), 0.68 (q,  $J$  = 7.9 Hz, 6H,  $\text{SiCH}_2$ ).

Cf. to N. V. Shvydkiy, K. V. Rimskiy, D. S. Perekalin, *Appl. Organomet. Chem.* 2023, **37**, e7008.

Triethyl(1-phenylvinyl)silane ( $\alpha$ -isomer).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.38-7.14 (m, 5H, Ph), 5.89 (d,  $J = 3.1$  Hz, 1H, CH), 5.59 (d,  $J = 3.1$  Hz, 1H, CH), 0.94 (t,  $J = 7.9$  Hz, 9H,  $\text{SiCH}_3$ ), 0.58 (q,  $J = 7.9$  Hz, 6H,  $\text{SiCH}_2$ ).

Cf. to B. G. Rocha, E. A. Valishina, R. S. Chay, M. F. C. G. da Silva, T. M. Buslaeva, A. J. Pombeiro, K. V. Luzyanin, *J. Catal.*, 2014, **309**, 79.



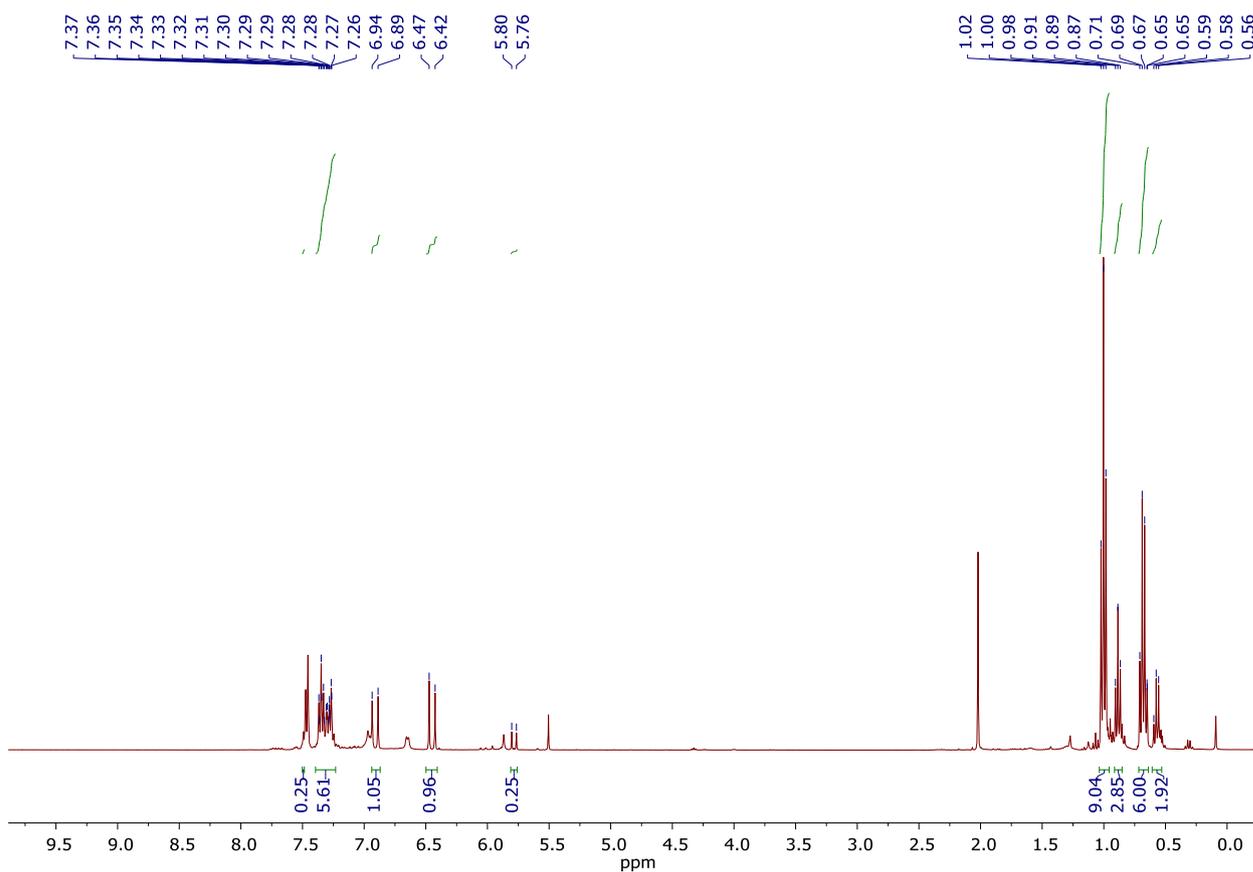
$^1\text{H}$  NMR spectrum of phenylacetylene hydrosilylation with triethylsilane with  $[\text{Rh}(\text{C}_4\text{Et}_4)\text{Cl}]_2$  (**2Cl**) catalyst

#### *Hydrosilylation of phenylacetylene with triethylsilane, catalyzed by $[\text{Rh}(\text{C}_4\text{Et}_4)(\text{PPh}_3)_2]\text{BF}_4$ (**5**)*

Schlenk tube was charged with complex **5** (4.4 mg, 0.005 mmol, 1 mol.%), degassed and filled with argon several times. Solid reactants were dissolved in 1.5 ml of acetone, forming dark red solution. After that phenylacetylene (55  $\mu\text{l}$ , 0.5 mmol, 1 equiv.) and triethylsilane (80  $\mu\text{l}$ , 0.5 mmol, 1 equiv.) were added and the reaction mixture was stirred for 1 hour. Then acetone was removed *in vacuo* and the reaction mixture was eluted with hexane through a plug of  $\text{Al}_2\text{O}_3$ . The major product was the phenylacetylene polymer (c.a. 80%), the yield of hydrosilylation products was less than 20%. The ratio of E- and Z-isomers was determined by NMR spectroscopy: E – 80%, Z – 20%.

E-Triethyl(2-phenylvinyl)silane.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.38-7.14 (m, 5H, Ph), 6.92 (d,  $J = 19.4$  Hz, 1H,  $\text{CHPh}$ ), 6.45 (d,  $J = 19.4$  Hz, 1H,  $\text{CHSiEt}_3$ ), 1.01 (t,  $J = 7.9$  Hz, 9H,  $\text{SiCH}_3$ ), 0.68 (q,  $J = 7.9$  Hz, 6H,  $\text{SiCH}_2$ ).

Cf. to N. V. Shvydkiy, K. V. Rimskiy, D. S. Perekalin, *Appl. Organomet. Chem.* 2023, **37**, e7008.



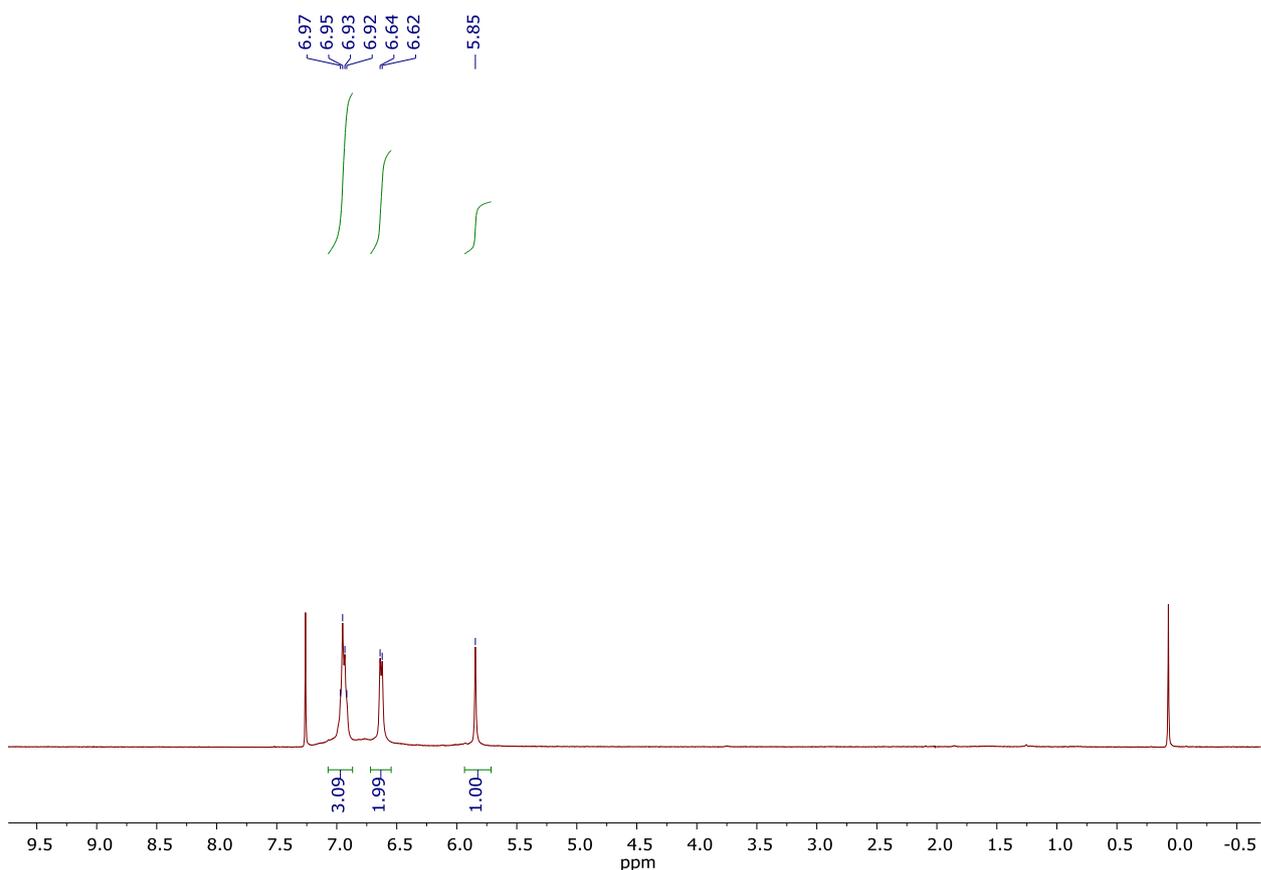
$^1\text{H}$  NMR spectrum of phenylacetylene hydrosilylation with  $[\text{Rh}(\text{C}_4\text{Et}_4)(\text{PPh}_3)_2]\text{BF}_4$  as a catalyst

## Polymerization of phenylacetylene

Schlenk tube was charged with rhodium catalyst (1 mol.% for entries 1-4, 0.1 mol.% for entries 5-6), degassed and filled with argon several times. Then THF (1.5 ml),  $\text{Et}_3\text{N}$  (10  $\mu\text{l}$ , 0.075 mmol, 15 mol.%) and phenylacetylene (55  $\mu\text{l}$ , 0.5 mmol) were added. The reaction mixture was stirred at 30  $^\circ\text{C}$  for 24h. After that it was poured into 20 ml of MeOH with a drop of acetic acid. The yellow precipitate was separated by centrifugation and dried *in vacuo* giving polyphenylacetylene in 8-100% yields.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.94 (m, 3H, Ph), 6.63 (d,  $J = 7.0$  Hz, 2H, Ph), 5.85 (s, 1H, CH).

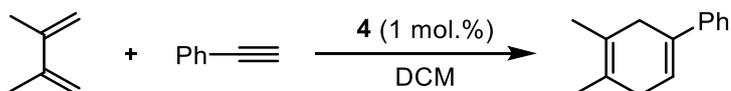
Cf. to I. Saeed, M. Shiotsuki, and T. Masuda, *Macromolecules*, 2006, **39**, 8977-8981.



$^1\text{H}$  NMR spectrum of polyphenylacetylene

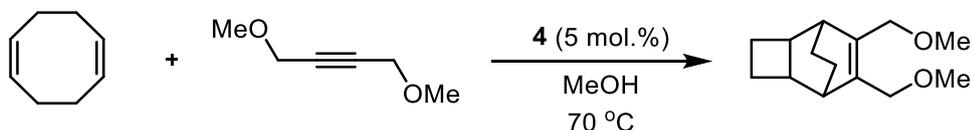
### Catalytic activity of cyclobutadiene rhodium complexes in other alkyne transformations

#### [4+2]-cycloaddition (Diels-Alder reaction) of 2,3-dimethylbutadiene and phenylacetylene



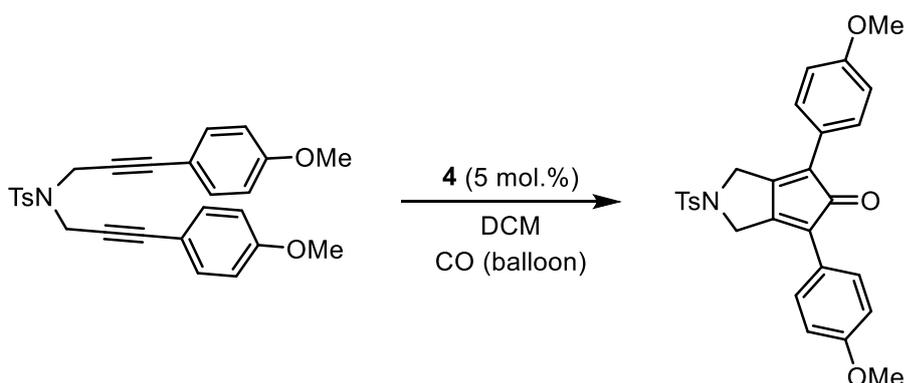
Schlenk tube was charged with complex **4** (2.7 mg, 0.005 mmol, 1 mol.%), degassed and filled with argon several times. Then complex **4** was dissolved in dichloromethane (2 ml), 2,3-dimethylbutadiene (114  $\mu\text{l}$ , 1 mmol, 2 equiv.) and phenylacetylene (55  $\mu\text{l}$ , 0.5 mmol, 1 equiv.) were added and the reaction mixture was stirred for 2 h at room temperature. The resulting solution was filtered through a plug of silica gel (eluent –  $\text{CH}_2\text{Cl}_2$ ). Solvent was evaporated and the residue was analyzed with  $^1\text{H}$  NMR spectroscopy. Desirable product was not detected.

#### [2+2+2]-cycloaddition of 1,5-cyclooctadiene with 1,4-dimethoxy-2-butyne



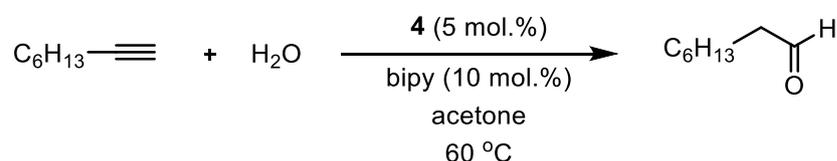
Schlenk tube was charged with complex **4** (8.1 mg, 0.015 mmol, 5 mol.%), degassed and filled with argon several times. Then complex **4** was dissolved in MeOH (3 ml), 1,5-cyclooctadiene (44  $\mu$ l, 0.36 mmol, 1.2 equiv.) and 1,4-dimethoxy-2-butyne (36  $\mu$ l, 0.3 mmol, 1 equiv.) were added and the reaction mixture was stirred for 48 h at 70  $^{\circ}$ C. The solvent was evaporated and residue was purified by column chromatography (eluent - hexane/MTBE 10:1, then hexane/MTBE 5:1). Only trace amounts of the product were determined by  $^1$ H NMR spectroscopy and GC-MS.

*[2+2+1]-cycloaddition of N,N-bis(3-(4-methoxyphenyl)prop-2-yn-1-yl)benzenesulfonamide with CO*



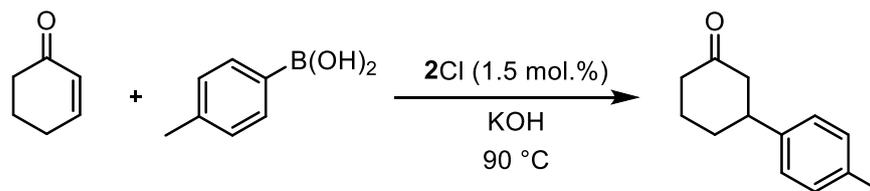
Schlenk tube was charged with complex **4** (8.1 mg, 0.015 mmol, 5 mol.%) and N,N-bis(3-(4-methoxyphenyl)prop-2-yn-1-yl)benzenesulfonamide (138 mg, 0.3 mmol), degassed and filled with CO several times. Then dichloromethane (3 ml) was added in the flow of carbon monoxide. Dark red solution was formed. The reaction mixture was stirred for 18 h at room temperature with balloon with CO connected. Violet solution was evaporated, and the residue was purified by column chromatography (Hex/EA 3:1). The isolated residue (m = 129 mg) was proven to be the starting material.

*Anti-Markovnikov hydration of 1-octyne*



Schlenk tube was charged with complex **4** (8.1 mg, 0.015 mmol, 5 mol.%) and bipyridine (4.7 mg, 0.03 mmol, 10 mol.%), degassed and filled with argon several times. Then acetone (1 ml), 1-octyne (44  $\mu$ l, 0.3 mmol, 1 equiv.), and water (27  $\mu$ l, 1.5 mmol, 5 equiv.) were added and the reaction mixture was stirred overnight at 60  $^{\circ}$ C. The solvent was removed *in vacuo* and the residue was analyzed with  $^1$ H NMR spectroscopy (400 MHz,  $\text{CDCl}_3$ ). The formation of the product was not detected.

1,4-addition of boronic acids to unsaturated ketones



Schlenk tube was charged with complex **1b** (7 mg, 0.015 mmol, 3 mol.%) and NEt<sub>3</sub>BnCl (4 mg, 0.018 mmol, 3.3 mol.%), degassed and filled with argon several times. Then dichloromethane (1 ml) was added and the reaction mixture was stirred for 24h. The solvent was removed *in vacuo* and 2-cyclohexen-1-one (49  $\mu$ l, 0.5 mmol, 1 equiv.), p-tolylboronic acid (102 mg, 0.75 mmol, 1.5 equiv.), 1,4-dioxane (1.5 ml), water (0.2 ml), and KOH (28 mg, 0.5 mmol, 1 equiv.) were added in the flow of argon. The reaction mixture was stirred for 24h at 90 °C. The resulting brown suspension was quenched with excess of saturated aqueous NaHCO<sub>3</sub> solution. The product was extracted with EtOAc (three times), combined organic fractions were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. Yield of the 3-(p-tolyl)cyclohexan-1-one was 31%. Yield was determined by <sup>1</sup>H NMR spectroscopy using 1,4-dioxane as internal standard.

## X-ray crystallography

X-ray diffraction data for  $[(C_4Et_4)Rh(C_{10}H_8)]PF_6$  and  $[(C_4Et_4)Rh(PPh_3)_2]BF_4$  were collected at 100 K with a Bruker Quest D8 CMOS diffractometer, using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ,  $\omega$ -scans). Structures were solved using Intrinsic Phasing with the ShelXT<sup>1</sup> structure solution program in Olex2<sup>2</sup> and then refined with the XL<sup>3</sup> refinement package using Least-Squares minimization against  $F^2$  in the anisotropic approximation for non-hydrogen atoms. Positions of hydrogen atoms were calculated, and they were refined in the isotropic approximation within the riding model. Crystal data and structure refinement parameters are given in Table S1.

Deposition Numbers CCDC 2302268 ( $[(C_4Et_4)Rh(C_{10}H_8)]PF_6$ ) and 2302269 ( $[(C_4Et_4)Rh(PPh_3)_2]BF_4$ ) contain the supplementary crystallographic data for this paper.

**Table S1.** Crystal data and structure refinement parameters for  $[(C_4Et_4)Rh(C_{10}H_8)]PF_6$  and  $[(C_4Et_4)Rh(PPh_3)_2]BF_4$ .

	$[(C_4Et_4)Rh(C_{10}H_8)]PF_6$	$[(C_4Et_4)Rh(PPh_3)_2]BF_4$
Empirical formula	C <sub>22</sub> H <sub>28</sub> F <sub>6</sub> PRh	C <sub>48</sub> H <sub>50</sub> BF <sub>4</sub> P <sub>2</sub> Rh
Formula weight	540.32	878.54
T, K	100	100
Crystal system	Monoclinic	Monoclinic
Space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n
Z	8	4
a, $\text{\AA}$	15.9090(14)	10.7322(2)
b, $\text{\AA}$	17.5486(17)	26.2556(5)
c, $\text{\AA}$	15.8848(16)	14.7421(3)
$\alpha$ , $^\circ$	90	90
$\beta$ , $^\circ$	90.557(6)	96.0350(10)
$\gamma$ , $^\circ$	90	90
V, $\text{\AA}^3$	4434.5(7)	4131.01(14)
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.619	1.413
Linear absorption, $\mu$ (cm <sup>-1</sup> )	8.98	5.43
F(000)	2192	1816
$2\theta_{\text{max}}$ , $^\circ$	52	56

Reflections measured	30655	51256
Independent reflections	7725	9965
Observed reflections [ $I > 2\sigma(I)$ ]	6571	7183
Parameters	617	509
R1	0.0840	0.0428
wR2	0.2683	0.0884
GOF	1.038	1.047
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	1.965/-1.959	0.534/-0.663

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<sup>1</sup> G.M. Sheldrick. *Acta Cryst.* **2015**, *A71*, pp. 3-8

<sup>2</sup> O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann. *J. Appl. Cryst.* **2009**, *42*, pp. 339-341

<sup>3</sup> G.M. Sheldrick. *Acta Cryst.* **2008**, *A64*, pp. 112-122