

# **Supporting Information**

## **Reductive Hydrogenation under Single-Site-Control: Generation and Reactivity of a Transient NHC-Stabilized Tantalum(III) Alkoxide**

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## 1) SYNTHETIC PROCEDURES AND NMR SPECTRA

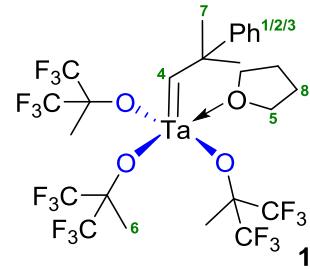
**General Remarks.** All manipulations were carried out under an atmosphere of dry and oxygen-free argon, by means of standard Schlenk or Glovebox techniques. Benzene, toluene, THF as well as the deuterated solvents C<sub>6</sub>D<sub>6</sub>, toluene-*d*<sub>8</sub>, THF-*d*<sub>8</sub>, were refluxed over sodium and purified by distillation. Dichloromethane, acetonitrile and CD<sub>3</sub>CN were refluxed over CaH<sub>2</sub> and purified by distillation. Methanol and CD<sub>3</sub>OD were dried and purified by distillation over magnesium turnings. Pentane, hexane and diethylether were dried and purified by passing the solvents through columns of activated alumina (MB SPS-800 System) and stored over potassium or sodium. Acetone was dried over phosphorus pentoxide and purified by distillation. The compounds Ta(=CHC(CH<sub>3</sub>)<sub>3</sub>)(THF)<sub>2</sub>Cl<sub>3</sub>,<sup>[1]</sup> Ta(=CH(CH<sub>3</sub>)<sub>2</sub>Ph)(THF)<sub>2</sub>Cl<sub>3</sub>,<sup>[2]</sup> LiOCCH<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>,<sup>[3,4]</sup> 1,3-diisopropyl-1H-imidazol-2-ylidene<sup>[5]</sup> and 1,3-diisopropyl-1H-imidazol-2-ylidene-*d*<sub>14</sub><sup>[5,6]</sup> were synthesized according to known procedures. All other chemicals were purchased from commercial suppliers and used as received.

All NMR spectra were recorded at the following spectrometers: Bruker Avance III 600 MHz or Bruker Avance II 400 MHz at room temperature unless noted otherwise. <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced to the residue proton or carbon signals of the lock solvent. In order to calibrate chemical shifts in the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, the following solvents were used: CDCl<sub>3</sub> (<sup>1</sup>H NMR:  $\delta$  (in ppm): 7.26 ppm, <sup>13</sup>C NMR:  $\delta$  (in ppm): 77.36 ppm), CD<sub>2</sub>Cl<sub>2</sub> (<sup>1</sup>H NMR:  $\delta$  (in ppm): 5.32 ppm, <sup>13</sup>C NMR:  $\delta$  (in ppm): 54.24 ppm), CD<sub>3</sub>OD (<sup>1</sup>H NMR:  $\delta$  (in ppm): 3.34 ppm, <sup>13</sup>C NMR:  $\delta$  (in ppm): 49.86 ppm), C<sub>6</sub>D<sub>6</sub> (<sup>1</sup>H NMR:  $\delta$  (in ppm): 7.15 ppm, <sup>13</sup>C NMR:  $\delta$  (in ppm): 128.62 ppm), THF-*d*<sub>8</sub> (<sup>1</sup>H NMR:  $\delta$  (in ppm): 1.79, 3.62, <sup>13</sup>C NMR:  $\delta$  (in ppm): 26.19, 68.03), toluene-*d*<sub>8</sub> (<sup>1</sup>H NMR:  $\delta$  (in ppm): 2.11, 6.96 - 7.01, 7.09, <sup>13</sup>C NMR:  $\delta$  (in ppm): 21.37, 125.66, 128.51, 129.33, 137.84), acetone-*d*<sub>6</sub> (<sup>1</sup>H NMR:  $\delta$  (in ppm): 2.09, <sup>13</sup>C NMR:  $\delta$  (in ppm): 20.51, 205.87). <sup>31</sup>P {<sup>1</sup>H} NMR spectra were referenced to external P(OMe)<sub>3</sub> (141 ppm with respect to 85% H<sub>3</sub>PO<sub>4</sub> at 0.0 ppm). The chemical shift  $\delta$  are given in ppm and coupling constants in Hz. To indicate the signal multiplicities the following abbreviations were used in <sup>1</sup>H NMR, <sup>2</sup>H NMR, <sup>13</sup>C NMR, <sup>19</sup>F NMR and <sup>31</sup>P NMR spectra: singlet (s), doublet (d), triplet (t), quartet (q), quintet (pent), sextet (sext), septet (sept), multiplet (m). All spectra were processed and integrated using TopSpin (Bruker).

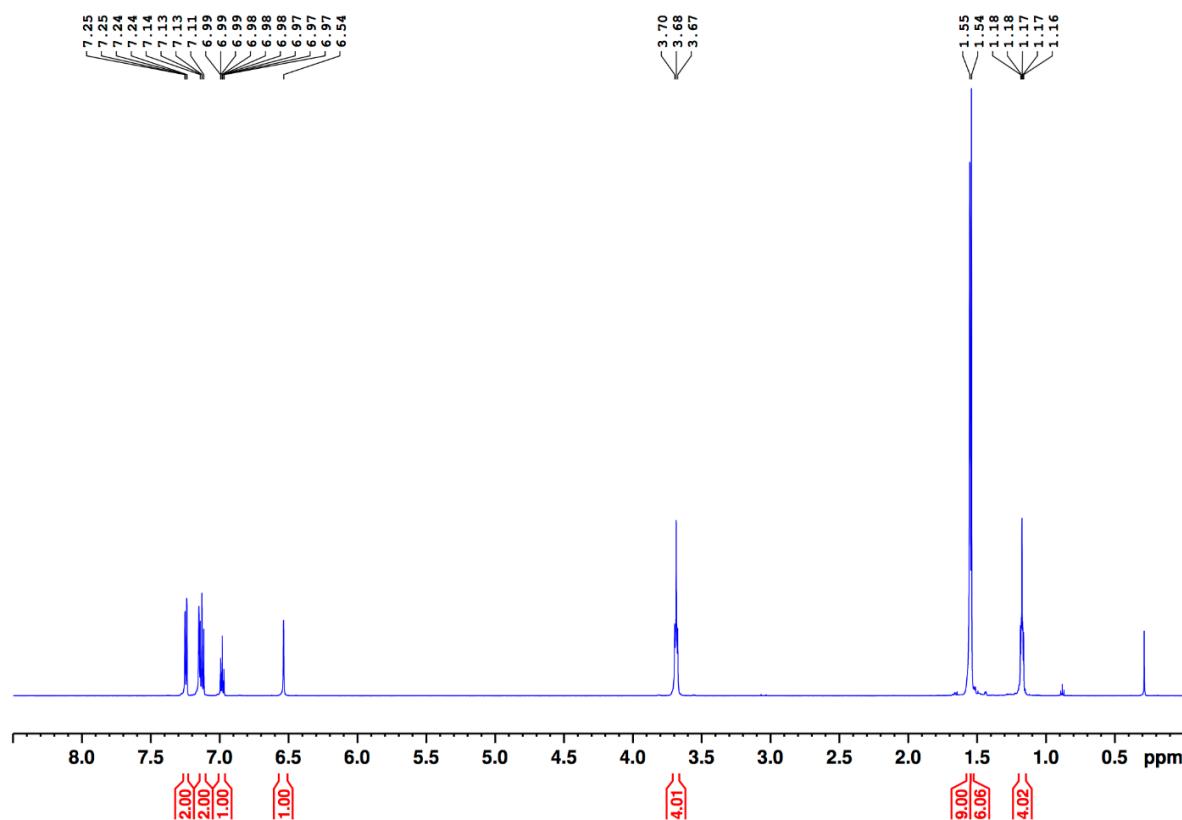
Elemental Analyses were carried out at the Department of Inorganic Chemistry at the University of Heidelberg on a vario MICRO cube.

Mass spectra were recorded at the Department of Organic Chemistry at the University of Heidelberg on a Bruker ApexQe hybrid 9.4 T FT-IVR (HR-ESI, HR-DART) or a JEOL JMS-700 magnetic sector (HR-EI).

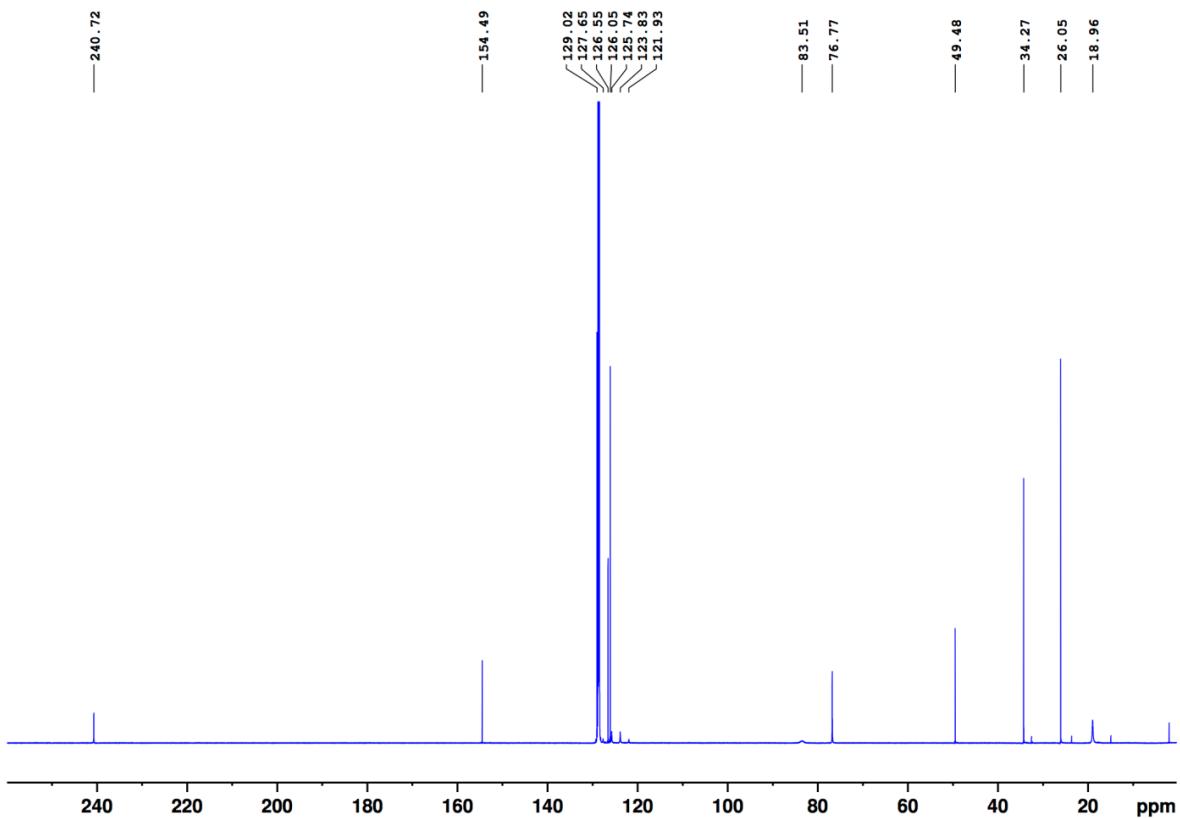
**Synthesis of 1.** In an argon-filled glovebox, 1.0 eq of  $Ta(=CH(CH_3)_2Ph)(THF)_2Cl_3$  (313 mg, 0.56 mmol) was dissolved in 8 ml of  $Et_2O/THF$  (6:1). Then a solution of 3.0 eq of  $LiOCCH_3(CF_3)_2$  (313 mg, 1.67 mmol) in 3 ml of  $Et_2O/THF$  (6:1) was added dropwise under vigorous stirring (the precipitation of  $LiCl$  started immediately). The resulting yellow-orange solution was stirred for 1d. The precipitate was filtered off, the solvent was removed in vacuum and the residue was taken up in pentane.



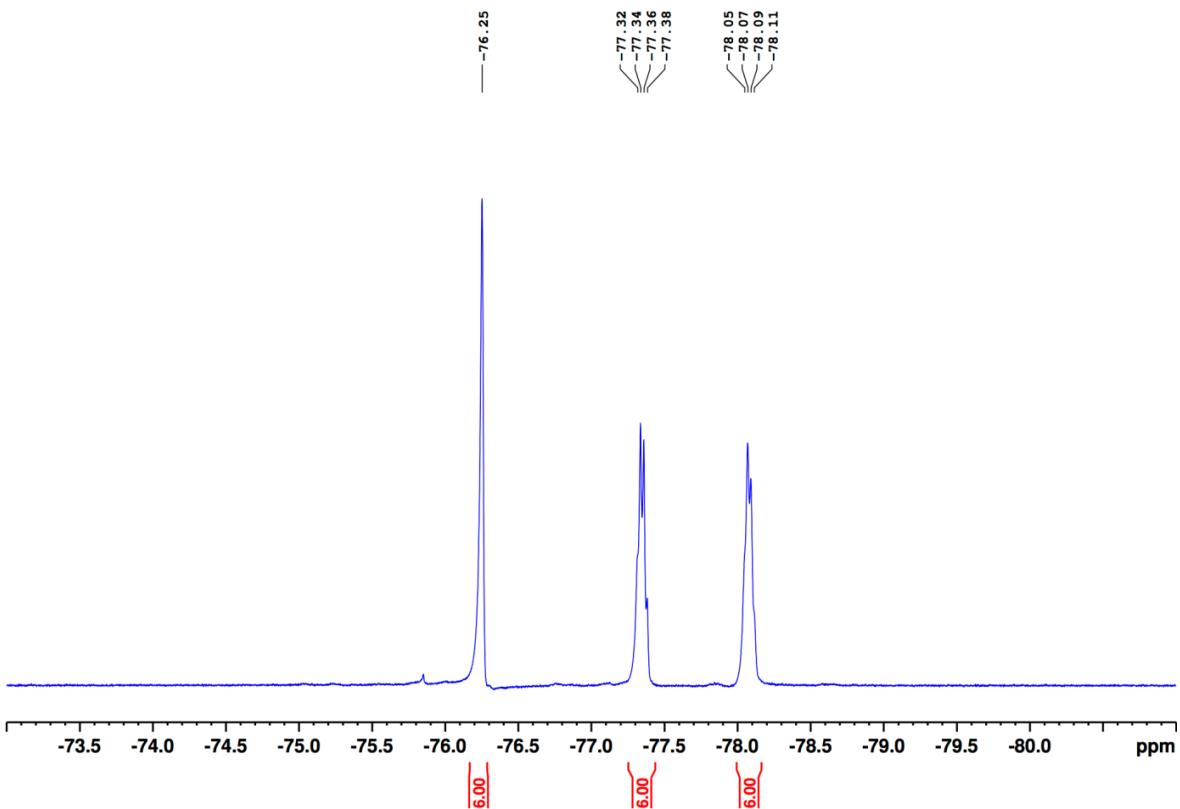
The title compound was isolated by crystallization from a concentrated solution of hexane at -35°C and obtained as a yellow microcrystalline powder (395 mg, 0.43 mmol, 76%). **<sup>1</sup>H NMR** (toluene-*d*<sub>8</sub>, 600 MHz, 25°C): δ (in ppm) = 7.25 - 7.24 (m, 2H, Ar-H<sup>ortho</sup>, H-1/2/3), 7.14 - 7.11 (m, 2H, Ar-H<sup>meta</sup>, H-1/2/3), 6.98 (tt, J<sub>H-H</sub> = 7.3 Hz, J<sub>H-H</sub> = 1.2 Hz, 1H, Ar-H<sup>para</sup>, H-1/2/3), 6.54 (s, 1H, H-4), 3.70 - 3.67 (m, 4H, THF, H-5), 1.55 (s, 9H, H-6), 1.54 (s, 6H, H-7), 1.18 - 1.16 (m, 4H, THF, H-8). **<sup>13</sup>C{<sup>1</sup>H} NMR** (toluene-*d*<sub>8</sub>, 151 MHz, 25°C): δ (in ppm) = 240.72 (s, 1C, C<sup>Alkylidene</sup>), 154.49 (s, 1C, C<sup>Ar</sup>), 129.02 (s, 2C, C<sup>Ar</sup>), 127.65 (s, 1C, C<sup>Ar</sup>), 126.55 (s, 2C, C<sup>Ar</sup>), 124.79 (q: <sup>1</sup>J<sub>C-F</sub> = 293.3 Hz, 6C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 83.51 (brs, 3C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 76.77 (s, 2C, THF), 49.48 (s, 1C, CMe<sub>2</sub>Ph), 34.27 (s, 2C, CMe<sub>2</sub>Ph), 26.05 (s, 2C, THF), 18.96 (s, 3C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>). **<sup>19</sup>F{<sup>1</sup>H} NMR** (toluene-*d*<sub>8</sub>, 376 MHz, 25°C): δ (in ppm) = -76.25 (s, 6F), -77.32 to -77.38 (m, 6F), -78.05 to -78.11 (m, 6F). **Elem. Anal. Calcd.** For C<sub>26</sub>H<sub>29</sub>F<sub>18</sub>O<sub>4</sub>Ta (928.43 g/mol): C, 33.64; H, 3.15. **Found:** C, 33.54; H, 3.19.



**Figure S1:**  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{C}_6\text{D}_6$ , 25°C) of **1**.



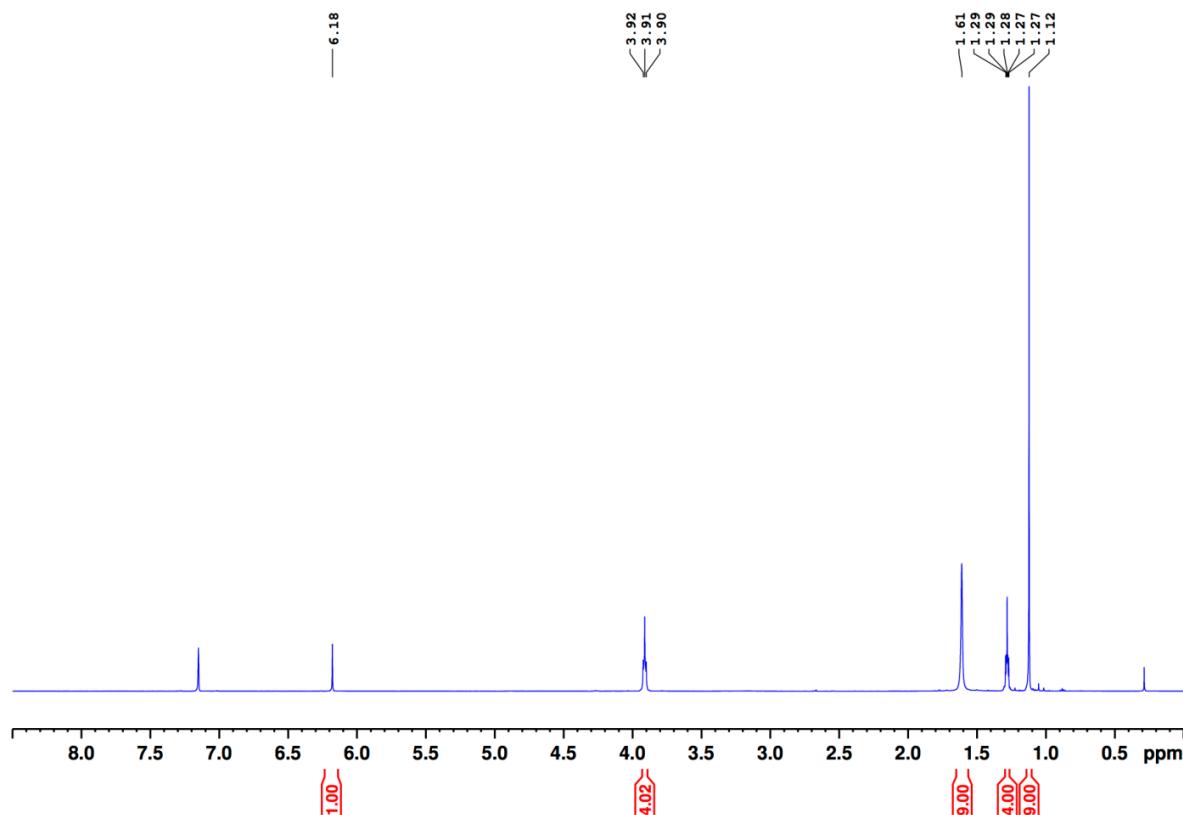
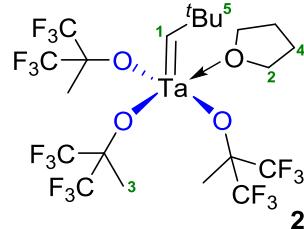
**Figure S2:**  $^{13}\text{C}$  { $^1\text{H}$ } NMR spectrum (151 MHz,  $\text{C}_6\text{D}_6$ , 25°C) of **1**.



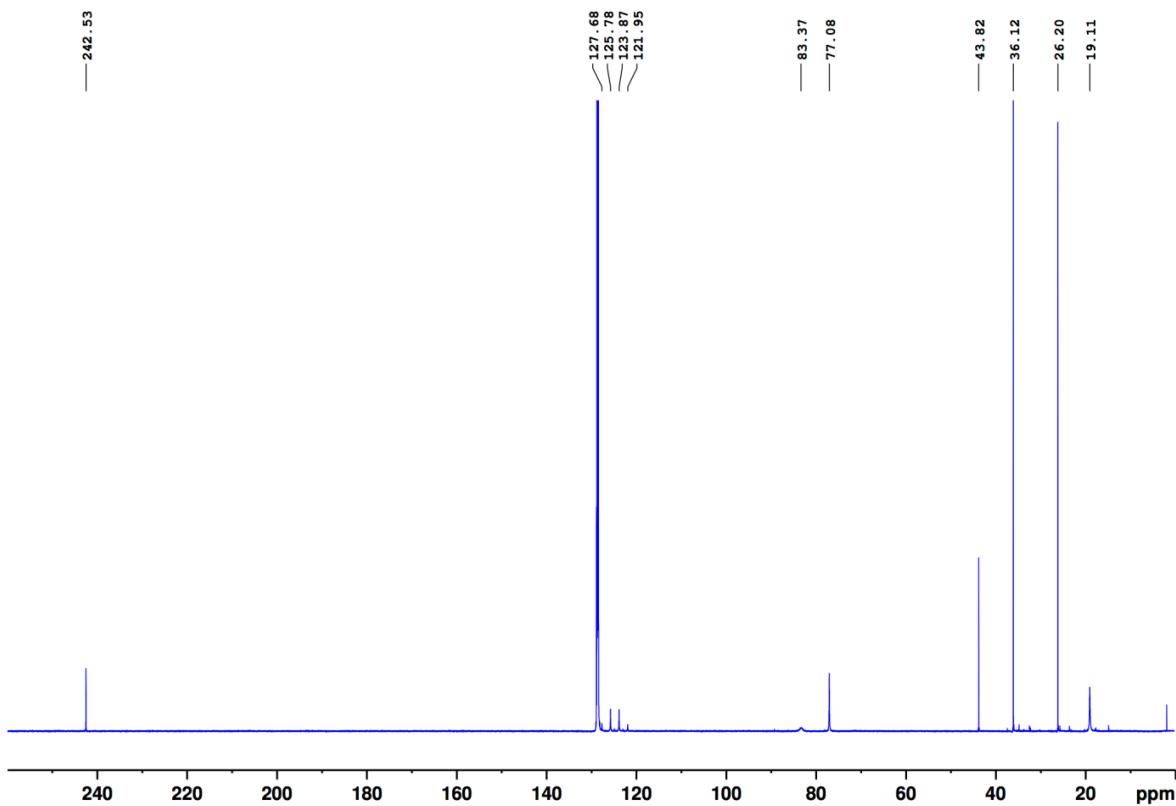
**Figure S3:**  $^{19}\text{F}$  { $^1\text{H}$ } NMR spectrum (376 MHz,  $\text{C}_6\text{D}_6$ , 25°C) of **1**.

**Synthesis of 2.** In an argon-filled glovebox, 1.0 eq of  $\text{Ta}(\text{=CH}(\text{CH}_3)_3)(\text{THF})_2\text{Cl}_3$  (421 mg, 0.84 mmol) was dissolved in 8 ml of  $\text{Et}_2\text{O}/\text{THF}$  (6:1). Then a solution of 3.0 eq of  $\text{LiOCCH}_3(\text{CF}_3)_2$  (473 mg, 2.52 mmol) in 3 ml of  $\text{Et}_2\text{O}/\text{THF}$  (6:1) was added dropwise under vigorous stirring (the precipitation of  $\text{LiCl}$  started immediately). The resulting yellow-orange solution was stirred for 1d. The precipitate was filtered off, the solvent was removed in vacuum and the residue was taken up in pentane.

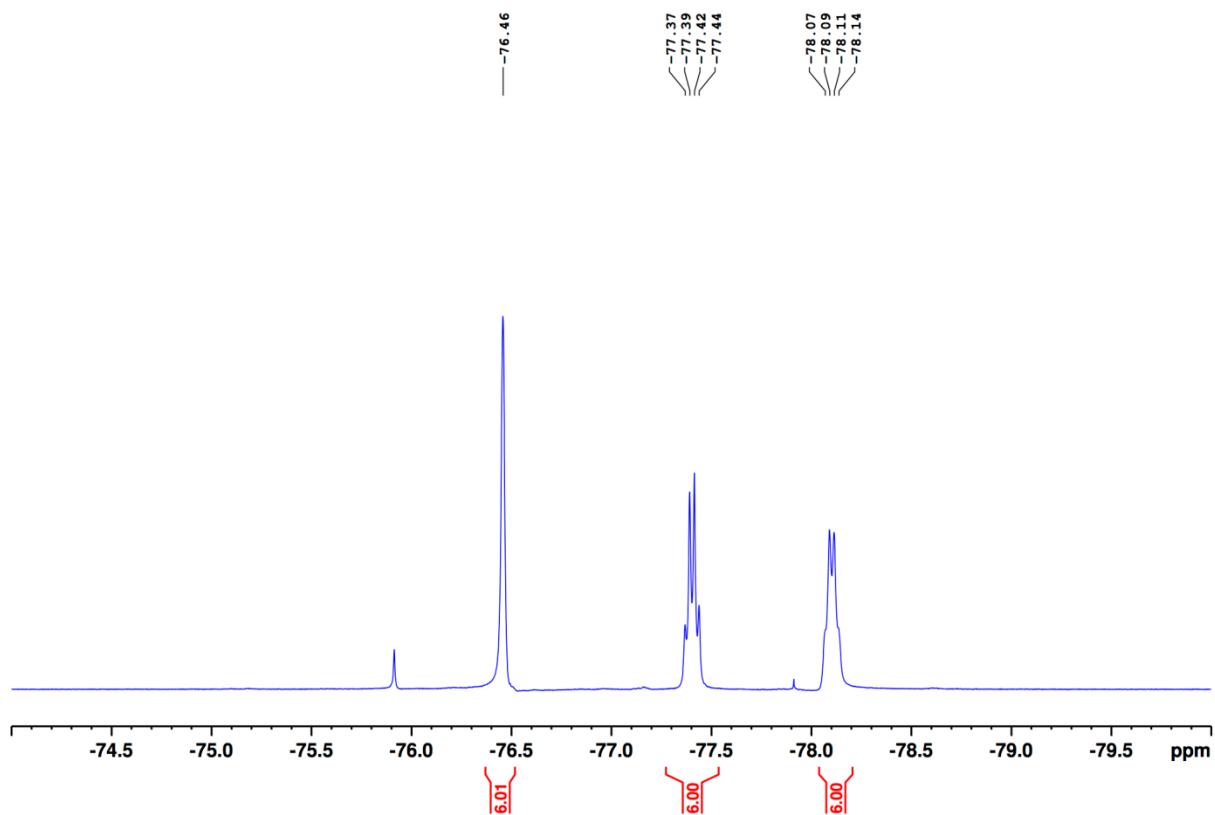
The title compound was isolated by crystallization from a concentrated solution of pentane at  $-35^\circ\text{C}$  and obtained as a yellow microcrystalline powder (582 mg, 0.67 mmol, 80 %).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 600 MHz,  $25^\circ\text{C}$ ):  $\delta$  (in ppm) = 6.18 (s, 1H, H-1), 3.92 - 3.90 (m, 4H, THF, H-2), 1.61 (s, 9H, H-3), 1.29 - 1.27 (m, 4H, THF, H-4), 1.12 (s, 9H, H-5).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 151 MHz,  $25^\circ\text{C}$ ):  $\delta$  (in ppm) = 242.53 (s, 1C,  $\text{C}^{\text{Alkylidene}}$ ), 124.83 (q,  $^1\text{J}_{\text{C-F}} = 288.4$  Hz, 6C,  $\text{OC}(\text{CF}_3)_2\text{CH}_3$ ), 83.37 (brs, 3C,  $\text{OC}(\text{CF}_3)_2\text{CH}_3$ ), 77.08 (s, 2C, THF), 43.83 (s, 1C,  $t\text{Bu}$ ), 36.12 (s, 3C,  $t\text{Bu}$ ), 26.20 (s, 2C, THF), 19.11 (s, 3C,  $\text{CCH}_3(\text{CF}_3)_2$ ).  $^{19}\text{F}\{^1\text{H}\}$  NMR (toluene- $d_8$ , 376 MHz,  $25^\circ\text{C}$ ):  $\delta$  (in ppm) = -76.46 (s, 6F), -77.37 to -77.44 (m, 6F), -78.07 to -78.14 (m, 6F). **Elem. Anal.** **Calcd.** For  $\text{C}_{21}\text{H}_{27}\text{F}_{18}\text{O}_4\text{Ta}$  (866.36 g/mol): C, 29.11; H, 3.14. **Found:** C, 28.67; H, 3.19. Although the carbon value is within the 0.5 limit, consistently low carbon values were obtained upon combustion of several samples. This observation may be related to carbide formation or to incomplete combustion.



**Figure S4:**  $^1\text{H NMR}$  spectrum (600MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ) of **2**.



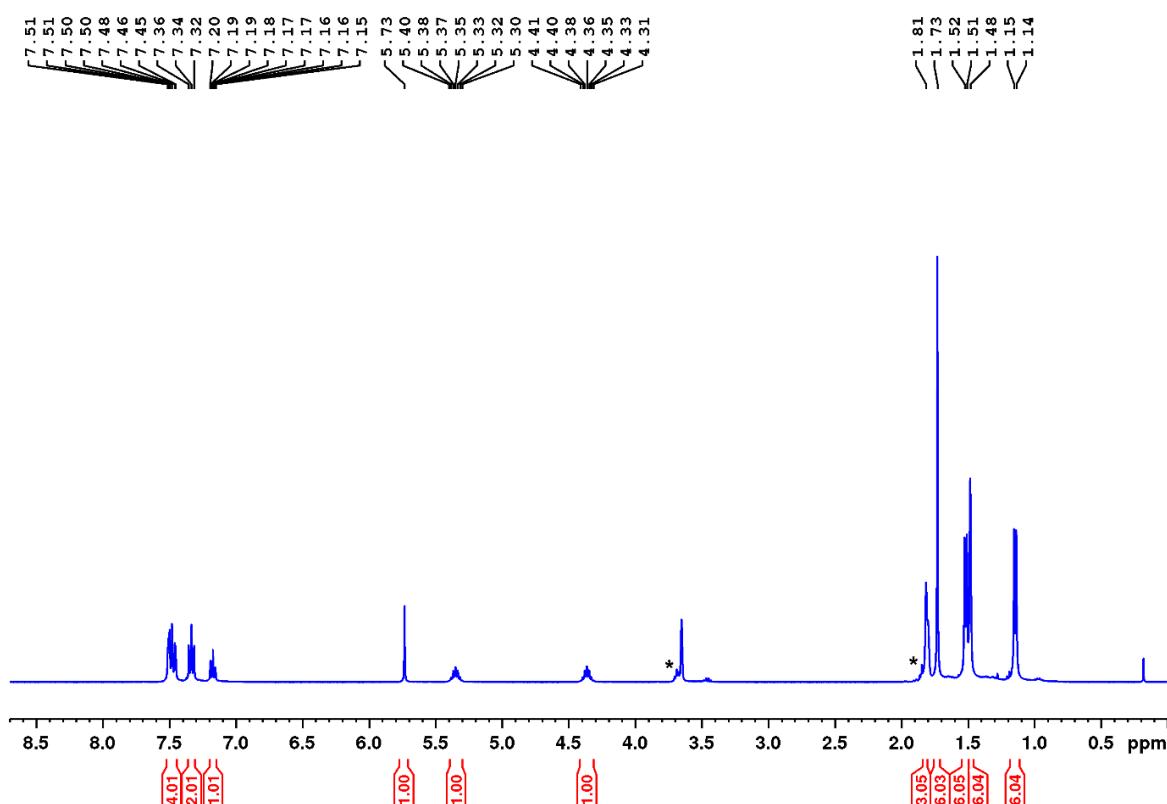
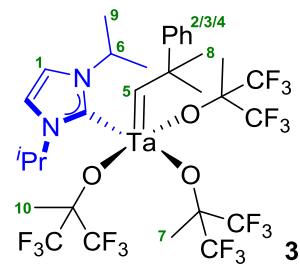
**Figure S5:**  $^{13}\text{C}$  { $^1\text{H}$ } NMR spectrum (151 MHz,  $\text{C}_6\text{D}_6$ , 25°C) of **2**.



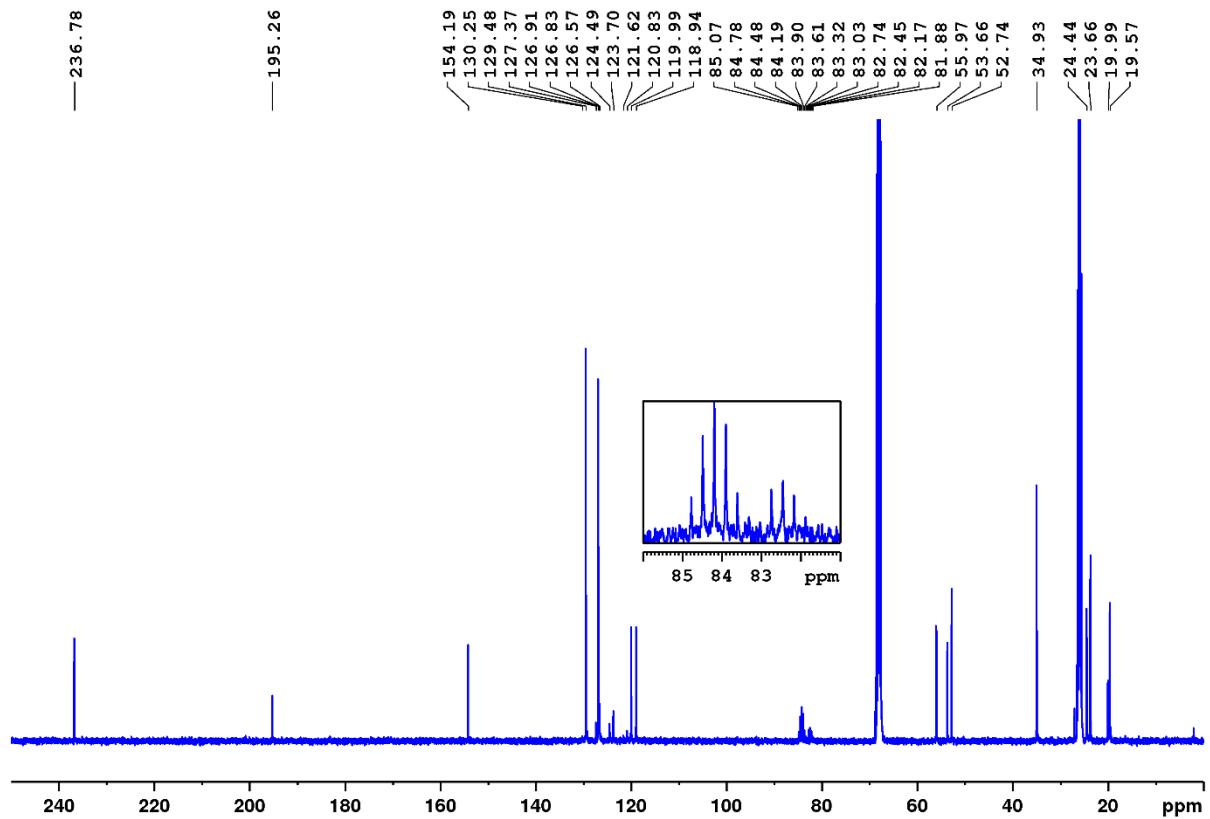
**Figure S6:**  $^{19}\text{F}$  { $^1\text{H}$ } NMR spectrum (376 MHz, toluene- $d_8$ , 25°C) of **2**.

**Synthesis of 3.** In an argon-filled glovebox, 1.0 eq of **1** (618 mg, 0.67 mmol) was dissolved in 5 ml of THF and a solution of 1.0 eq of 1,3-diisopropyl-1H-imidazol-2-ylidene (101 mg, 0.67 mmol) in 1 ml of THF was added dropwise under vigorous stirring. The resulting yellow solution was stirred for 1d. The solvent was removed in vacuum and the residue was taken up in pentane. The title compound was isolated by crystallization from a concentrated solution in pentane at -35°C and obtained as a yellow crystalline solid (450

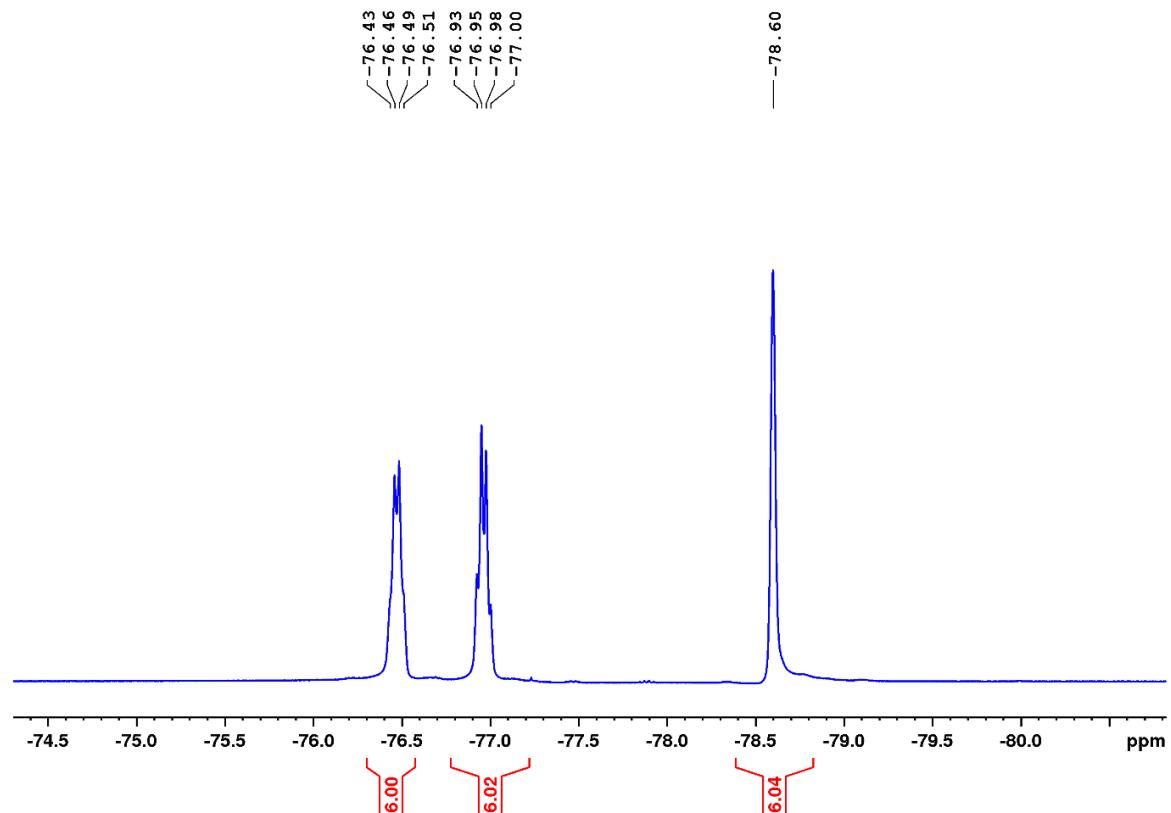
mg, 0.45 mmol, 66%). **<sup>1</sup>H NMR** (THF-d<sub>8</sub>, 400 MHz, 25°C): δ (in ppm) = 7.51 - 7.50 (m, 2H, H-1), 7.45 (m, 2H, Ar-H<sup>ortho</sup>, H-2/3/4), 7.34 (t, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz, 2H, Ar-H<sup>meta</sup>, H-2/3/4), 7.17 (tt, <sup>3</sup>J<sub>H-H</sub> = 7.3 Hz, <sup>5</sup>J<sub>H-H</sub> = 1.2 Hz, 1H, H<sup>para</sup>, H-2/3/4), 5.73 (s, 1H, H-5), 5.35 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, 1H, H-6), 4.36 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, 1H, H-6), 1.81 (s, 3H, H-7), 1.73 (s, 6H, H-8), 1.52 (d, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, 6H, H-9), 1.48 (s, 6H, H-10), 1.14 (d, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, 6H, H-9). **<sup>13</sup>C{<sup>1</sup>H} NMR** (THF-d<sub>8</sub>, 101 MHz, 25°C): δ (in ppm) = 236.78 (s, 1C, C<sup>Alkylidene</sup>), 195.26 (s, 1C, C<sup>Carbene</sup>), 154.19 (s, 1C, C<sup>A'</sup>), 129.48 (s, 2C, C<sup>A'</sup>), 126.91 (s, 2C, C<sup>A'</sup>), 126.83 (s, 1C, C<sup>A'</sup>), 125.93 (q, <sup>1</sup>J<sub>C-F</sub> = 290.2 Hz, 2C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 125.13 (q, <sup>1</sup>J<sub>C-F</sub> = 288.9 Hz, 4C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 119.99 (s, 1C, C<sup>Imidazole</sup>), 118.94 (s, 1C, C<sup>Imidazole</sup>), 84.19 (sept, <sup>2</sup>J<sub>C-F</sub> = 29.4 Hz, 2C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 82.45 (sept, <sup>2</sup>J<sub>C-F</sub> = 28.9 Hz, 1C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 55.97 (s, 1C), 53.66 (s, 1C), 52.74 (s, 1C), 34.93 (s, 2C), 24.44 (s, 2C), 23.66 (s, 2C), 19.99 (s, 1C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 19.57 (s, 2C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>). **<sup>19</sup>F{<sup>1</sup>H} NMR** (THF-d<sub>8</sub>, 376 MHz, 25°C): δ (in ppm) = -76.47 (q, <sup>4</sup>J<sub>F-F</sub> = 9.8 Hz, 6F), -76.96 (q, <sup>4</sup>J<sub>F-F</sub> = 9.8 Hz, 6F), -78.60 (s, 6F). **Elem. Anal. Calcd.** for C<sub>31</sub>H<sub>37</sub>F<sub>18</sub>N<sub>2</sub>O<sub>3</sub>Ta (1008.6 g/mol): C, 36.92; H, 3.70; N, 2.78. **Found:** C, 37.44; H, 3.69; N, 2.83.



**Figure S7:** <sup>1</sup>H NMR spectrum (400 MHz, THF-d<sub>8</sub>, 25°C) of **3** (residual THF signals are labeled with \*).

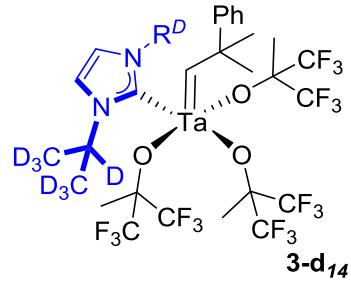


**Figure S8:**  $^{13}\text{C}$  { $^1\text{H}$ } NMR spectrum (101 MHz, THF- $d_8$ , 25°C) of **3**.

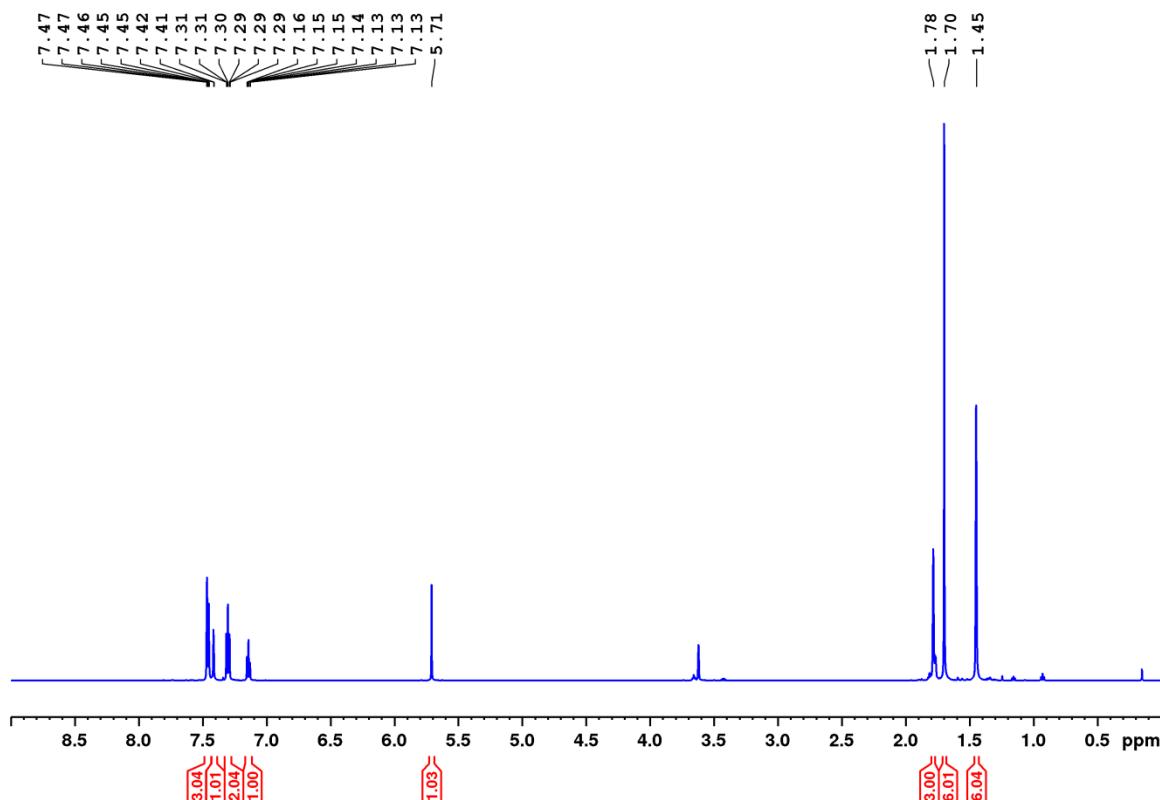


**Figure S9:**  $^{19}\text{F}$  { $^1\text{H}$ } NMR spectrum (376 MHz, THF- $d_8$ , 25°C) of **3**.

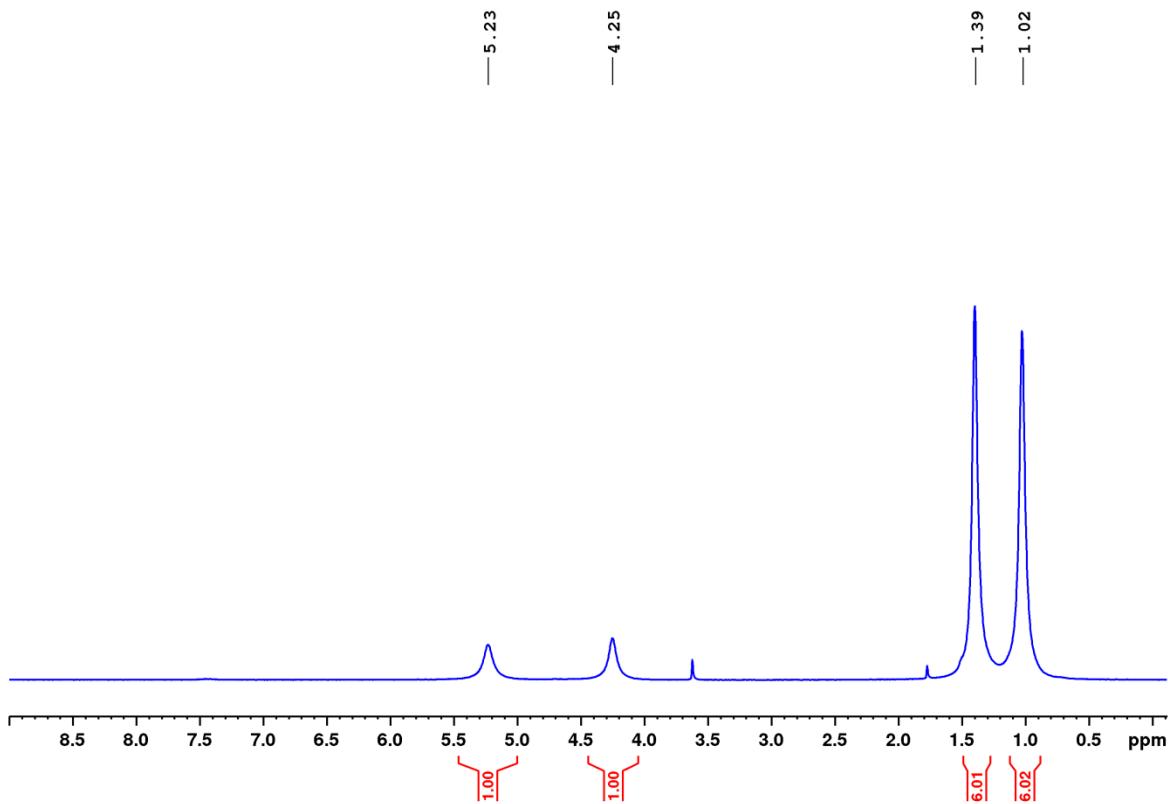
**Synthesis of 3-*d*<sub>14</sub>.** In an argon-filled glovebox, 1.0 eq of **1** (800 mg, 0.86 mmol) was dissolved in 5 ml of THF. Then a solution of 1.0 eq of 1,3-diisopropyl-1H-imidazol-2-ylidene-*d*<sub>14</sub> (144 mg, 0.86 mmol) in 1 ml of THF was added dropwise under vigorous stirring. The resulting yellow solution was stirred for 1d. The solvent was removed in vacuum and the residue was taken up in a mixture of pentane/THF (1:1). The title compound was isolated by crystallization at -35°C and obtained as a yellow microcrystalline solid (702 mg, 0.69 mmol, 80%).



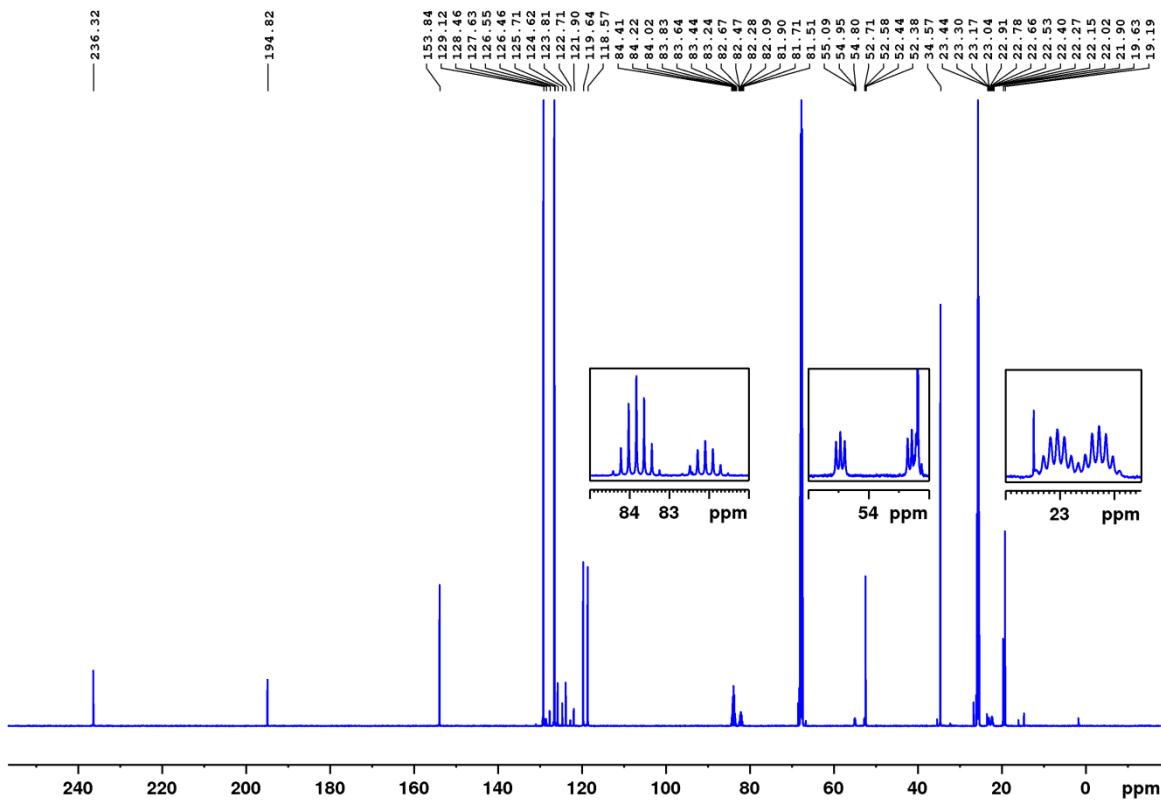
**<sup>1</sup>H NMR** (THF-d<sub>8</sub>, 600 MHz, 25°C): δ (in ppm) = 7.47 - 7.45 (m, 3H), 7.41 (d, <sup>3</sup>J<sub>H-H</sub> = 1.8 Hz, 1H), 7.31 - 7.29 (m, 2H), 7.16 - 7.13 (m, 1H), 5.71 (s, 1H), 1.78 (s, 3H), 1.70 (s, 6H), 1.45 (s, 6H). **<sup>2</sup>H NMR** (THF, 92 MHz, 25°C): 5.23 (s, 1D), 4.25 (s, 1D), 1.39 (s, 6D), 1.02 (s, 6D). **<sup>13</sup>C{<sup>1</sup>H} NMR** (THF-d<sub>8</sub>, 151 MHz, 25°C): δ (in ppm) = 236.32 (s, 1C), 194.82 (s, 1C), 153.84 (s, 1C), 129.12 (s, 2C), 126.55 (s, 2C), 126.54 (q, <sup>1</sup>J<sub>C-F</sub> = 289.0 Hz, 2C), 126.46 (s, 1C), 124.76 (q, <sup>1</sup>J<sub>C-F</sub> = 287.8 Hz, 4C), 119.64 (s, 1C), 118.57 (s, 1C), 83.83 (sept, <sup>2</sup>J<sub>C-F</sub> = 29.4 Hz, 2C), 82.09 (sept, <sup>2</sup>J<sub>C-F</sub> = 29.0 Hz, 1C), 54.95 (t, <sup>1</sup>J<sub>C-D</sub> = 21.8 Hz, 1C), 52.58 (t, <sup>1</sup>J<sub>C-D</sub> = 21.5 Hz, 1C), 52.38 (s, 1C), 34.57 (s, 2C), 23.04 (sept, <sup>1</sup>J<sub>C-D</sub> = 19.1 Hz, 2C), 22.27 (sept, <sup>1</sup>J<sub>C-D</sub> = 19.5 Hz, 2C), 19.63 (s, 1C), 19.19 (s, 2C).



**Figure S10:**  $^1\text{H}$  NMR spectrum (600 MHz, THF- $d_8$ , 25°C) of **3-d<sub>14</sub>**.

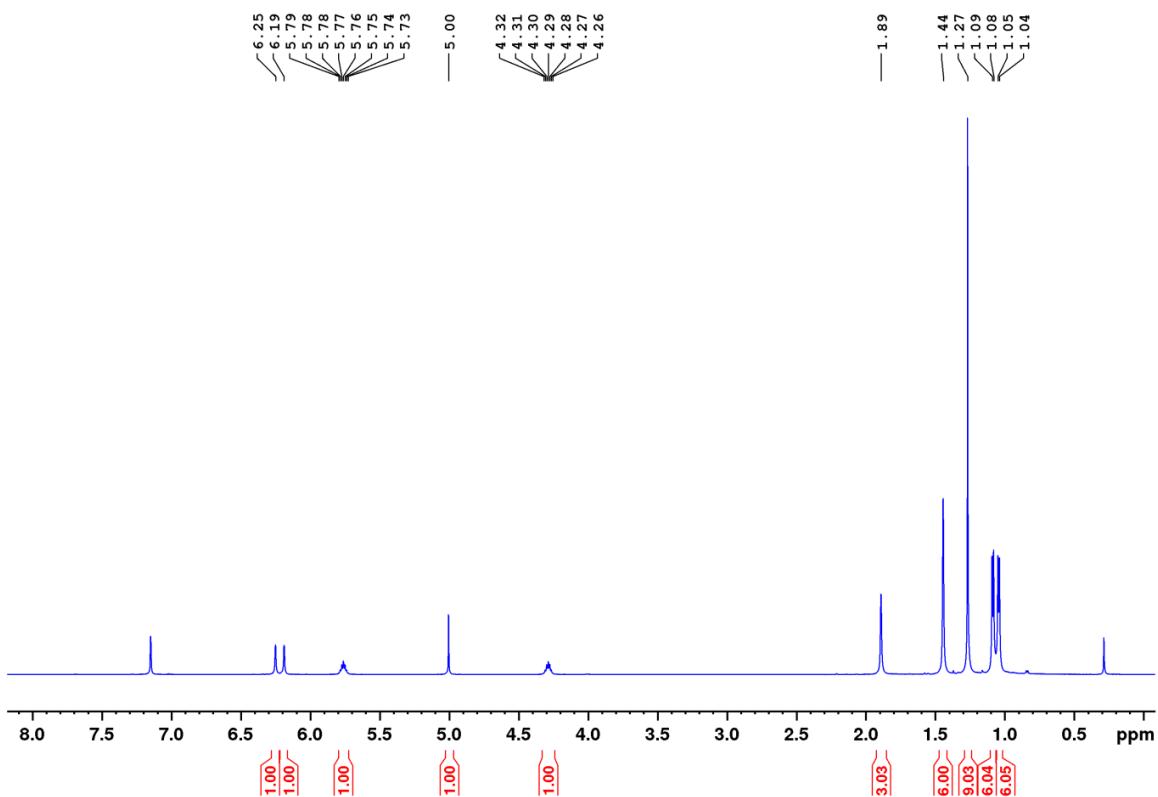
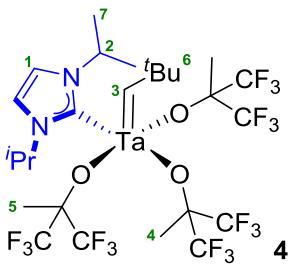


**Figure S11:**  $^{2}\text{H} \{^1\text{H}\}$  NMR spectrum (92 MHz, THF, 25°C) of **3-d<sub>14</sub>**.

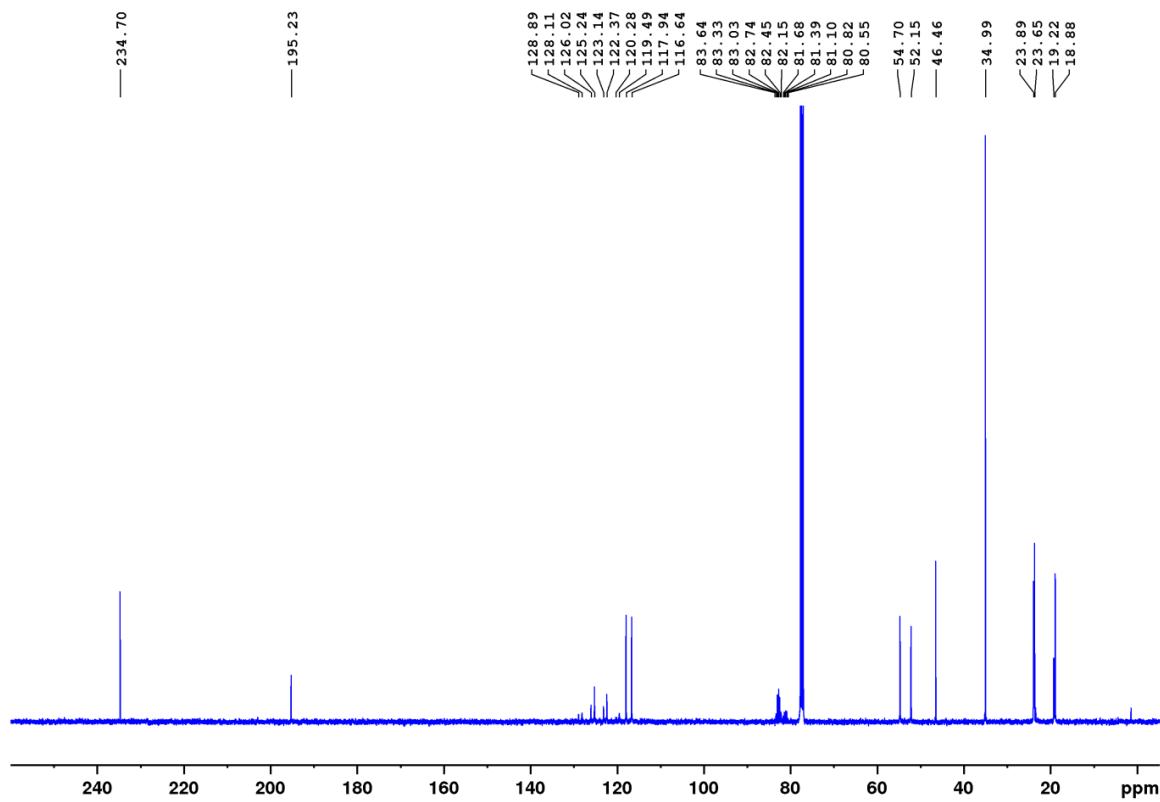


**Figure S12:**  $^{13}\text{C} \ {^1\text{H}}$  NMR spectrum (151 MHz, THF-d<sub>8</sub>, 25°C) of **3-d<sub>14</sub>**.

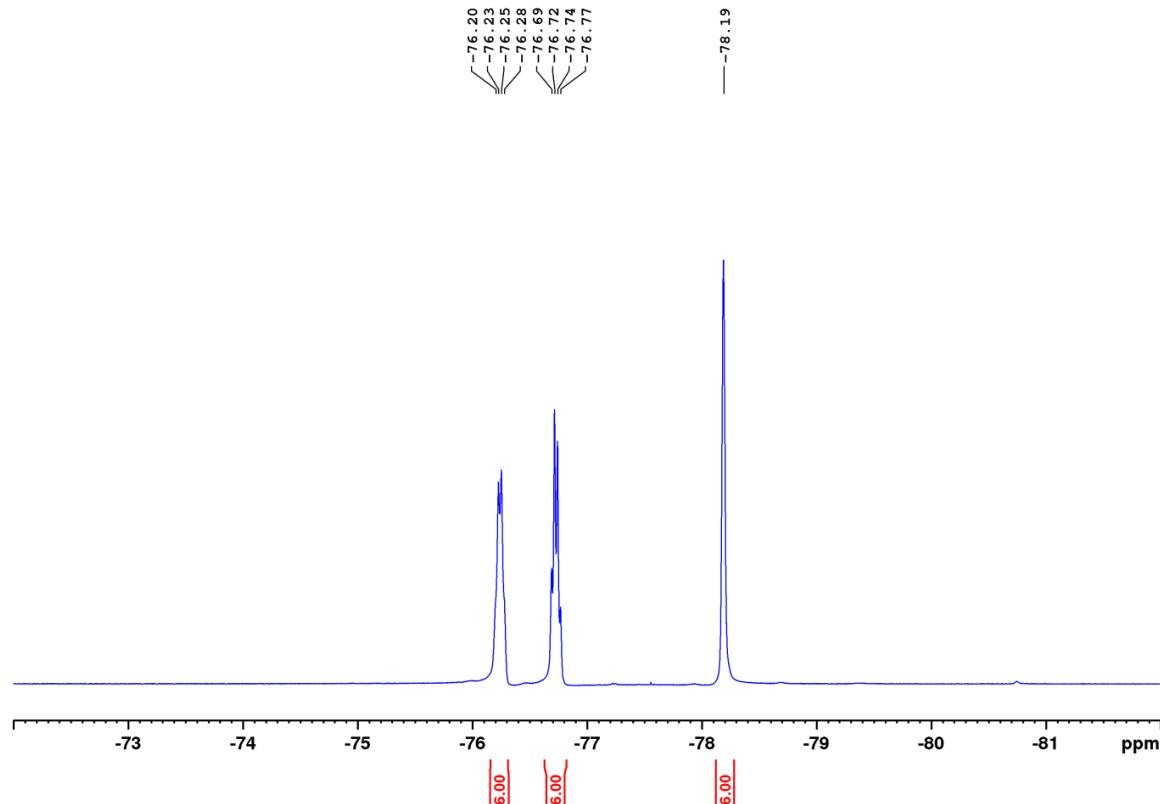
**Synthesis of 4.** In an argon-filled glovebox, 1.0 eq of **2** (600 mg, 0.69 mmol) was dissolved in 5 ml of THF. Then a solution of 1.0 eq of 1,3-diisopropyl-1H-imidazol-2-ylidene (105 mg, 0.69 mmol) in 1 ml of THF was added dropwise under vigorous stirring. The resulting yellow solution was stirred for 1d. The solvent was removed in vacuum and the residue was taken up in pentane. The title compound was isolated by crystallization from a concentrated solution in pentane at -35°C and obtained as a yellow microcrystalline powder (430 mg, 0.45 mmol, 65%). **<sup>1</sup>H NMR** ( $\text{C}_6\text{D}_6$ , 600 MHz, 25°C):  $\delta$  (in ppm) = 6.25 (s, 1H, H-1), 6.19 (s, 1H, H-1), 5.76 (sept,  $^3\text{J}_{\text{H-H}} = 6.6$  Hz, 1H, H-2), 5.00 (s, 1H, H-3), 4.29 (sept,  $^3\text{J}_{\text{H-H}} = 6.6$  Hz, 1H, H-2), 1.89 (s, 3H, H-4), 1.44 (s, 6H, H-5), 1.27 (s, 9H, H-6), 1.09 (d,  $^3\text{J}_{\text{H-H}} = 6.6$  Hz, 6H, H-7), 1.04 (d,  $^3\text{J}_{\text{H-H}} = 6.6$  Hz, 6H, H-7). **<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 101 MHz, 25°C):  $\delta$  (in ppm) = 234.70 (s, 1C,  $\text{C}^{\text{Alkylidene}}$ ), 195.23 (s, 1C,  $\text{C}^{\text{Carbene}}$ ), 124.58 (q,  $^1\text{J}_{\text{C-F}} = 289.5$  Hz, 2C,  $\text{OC}(\text{CF}_3)_2\text{CH}_3$ ), 123.81 (q,  $^1\text{J}_{\text{C-F}} = 288.7$  Hz, 4C,  $\text{OC}(\text{CF}_3)_2\text{CH}_3$ ), 117.98 (s, 1C,  $\text{C}^{\text{Imidazole}}$ ), 116.68 (s, 1C,  $\text{C}^{\text{Imidazole}}$ ), 82.74 (sept,  $^2\text{J}_{\text{C-F}} = 29.5$  Hz, 2C,  $\text{OC}(\text{CF}_3)_2\text{CH}_3$ ), 81.10 (sept,  $^2\text{J}_{\text{C-F}} = 28.6$  Hz, 1C,  $\text{OC}(\text{CF}_3)_2\text{CH}_3$ ), 54.70 (s, 1C), 52.15 (s, 1C), 46.46 (s, 1C,  $^t\text{Bu}$ ), 34.99 (s, 3C,  $^t\text{Bu}$ ), 23.89 (s, 2C), 23.65 (s, 2C), 19.22 (s, 1C,  $\text{OC}(\text{CF}_3)_2\text{CH}_3$ ), 18.88 (s, 2C,  $\text{OC}(\text{CF}_3)_2\text{CH}_3$ ). **<sup>19</sup>F{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 376 MHz, 25°C):  $\delta$  (in ppm) = -76.24 (q,  $^4\text{J}_{\text{F-F}} = 9.7$  Hz, 6F), -76.73 (q,  $^4\text{J}_{\text{F-F}} = 9.7$  Hz, 6F), -78.19 (s, 6F). **Elem. Anal. Calcd.** for  $\text{C}_{26}\text{H}_{35}\text{F}_{18}\text{N}_2\text{O}_3\text{Ta}$  (946.50 g/mol): C, 32.99; H, 3.73; N, 2.96. **Found:** C, 33.26; H, 3.71; N, 3.04.



**Figure S13:**  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{C}_6\text{D}_6$ , 25°C) of **4**.

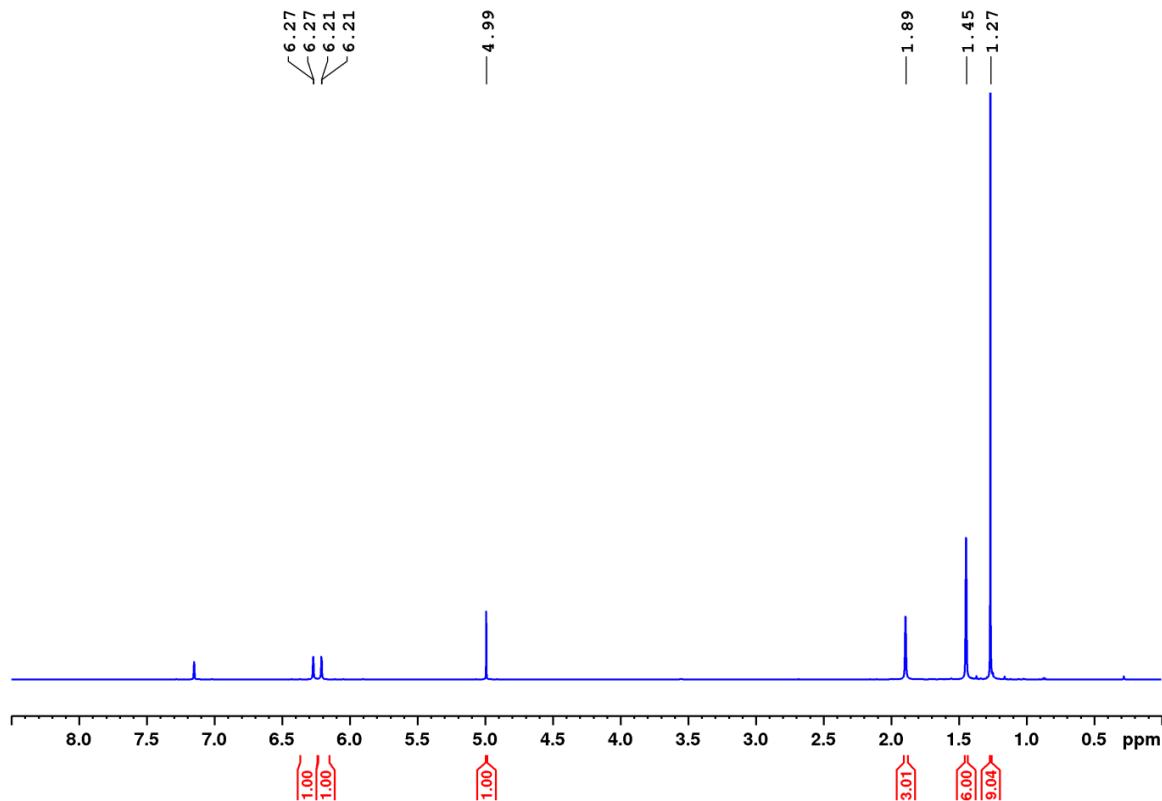
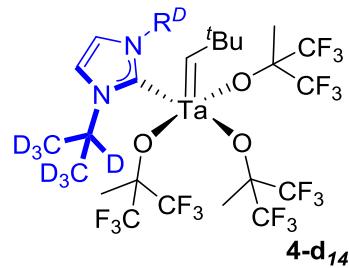


**Figure S14:**  $^{13}\text{C}$  { $^1\text{H}$ } NMR spectrum (101 MHz,  $\text{CDCl}_3$ , 25°C) of **4**.

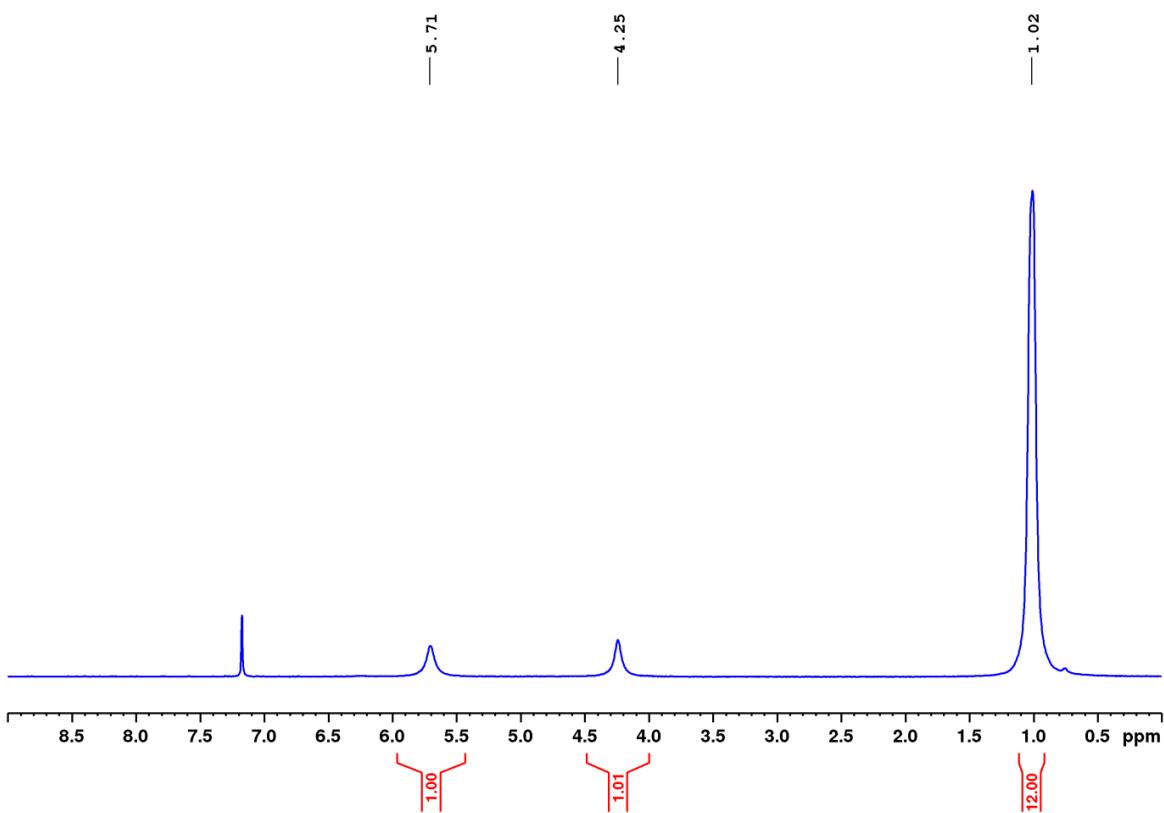


**Figure S15:**  $^{19}\text{F}$  { $^1\text{H}$ } NMR spectrum (376 MHz,  $\text{CDCl}_3$ , 25°C) of **4**.

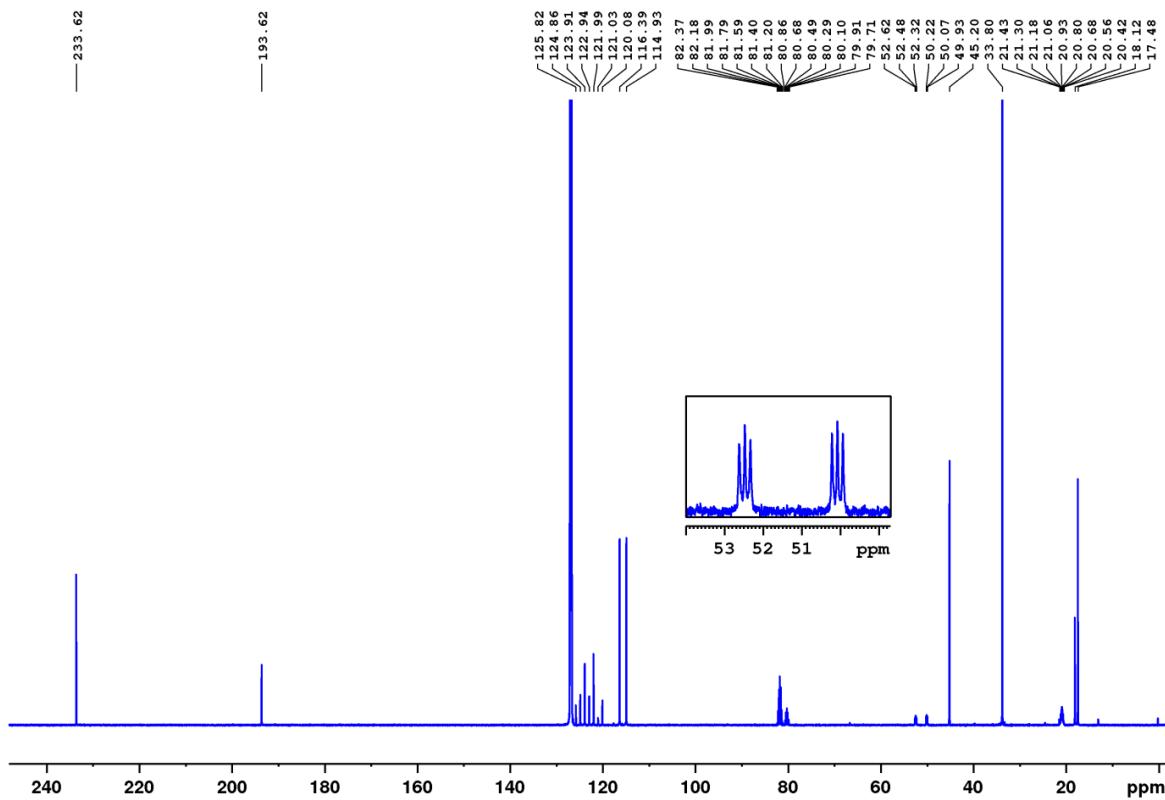
**Synthesis of **4-d<sub>14</sub>**.** In an argon-filled glovebox, 1.0 eq of **2** (552 mg, 0.69 mmol) was dissolved in 5 ml of THF and a solution of 1.0 eq of 1,3-diisopropyl-1H-imidazol-2-ylidene-*d*<sub>14</sub> (105 mg, 0.69 mmol) in 1 ml of THF was added dropwise under vigorous stirring. The resulting yellow solution was stirred for 1d. The solvent was removed in vacuum and the residue was taken up in pentane. The title compound was isolated by crystallization from a concentrated solution in pentane at -35°C and obtained as a yellow microcrystalline powder (449 mg, 0.42 mmol, 61%). **<sup>1</sup>H NMR** ( $C_6D_6$ , 600 MHz, 25°C):  $\delta$  (in ppm) = 6.27 (d,  $^3J_{H-H}$  = 1.7 Hz, 1H), 6.21 (d,  $^3J_{H-H}$  = 1.7 Hz, 1H), 4.99 (s, 1H), 1.89 (s, 3H), 1.45 (s, 6H), 1.27 (s, 9H). **<sup>2</sup>H NMR** ( $C_6H_6$ , 92 MHz, 25°C): 5.71 (s, 1D), 4.25 (s, 1D), 1.02 (s, 12D). **<sup>13</sup>C{<sup>1</sup>H} NMR** ( $C_6D_6$ , 151 MHz, 25°C):  $\delta$  (in ppm) = 233.62 (s, 1C), 193.62 (s, 1C), 123.90 (q,  $^1J_{C-F}$  = 289.1 Hz, 1C), 122.95 (q, 289.5 Hz, 2C), 116.39 (s, 1C), 114.93 (s, 1C), 81.79 (sept,  $^2J_{C-F}$  = 29.2 Hz, 2C), 80.29 (sept,  $^2J_{C-F}$  = 29.2 Hz, 1C), 52.48 (t,  $^1J_{C-D}$  = 22.3 Hz, 1C), 50.07 (t,  $^1J_{C-D}$  = 21.1 Hz, 1C), 45.20 (s, 1C), 33.80 (s, 1C), 21.43 - 20.42 (m, 4C), 18.12 (s, 1C), 17.48 (s, 2C).



**Figure S16:** **<sup>1</sup>H NMR** spectrum (600 MHz,  $C_6D_6$ , 25°C) of **4-d<sub>14</sub>**.

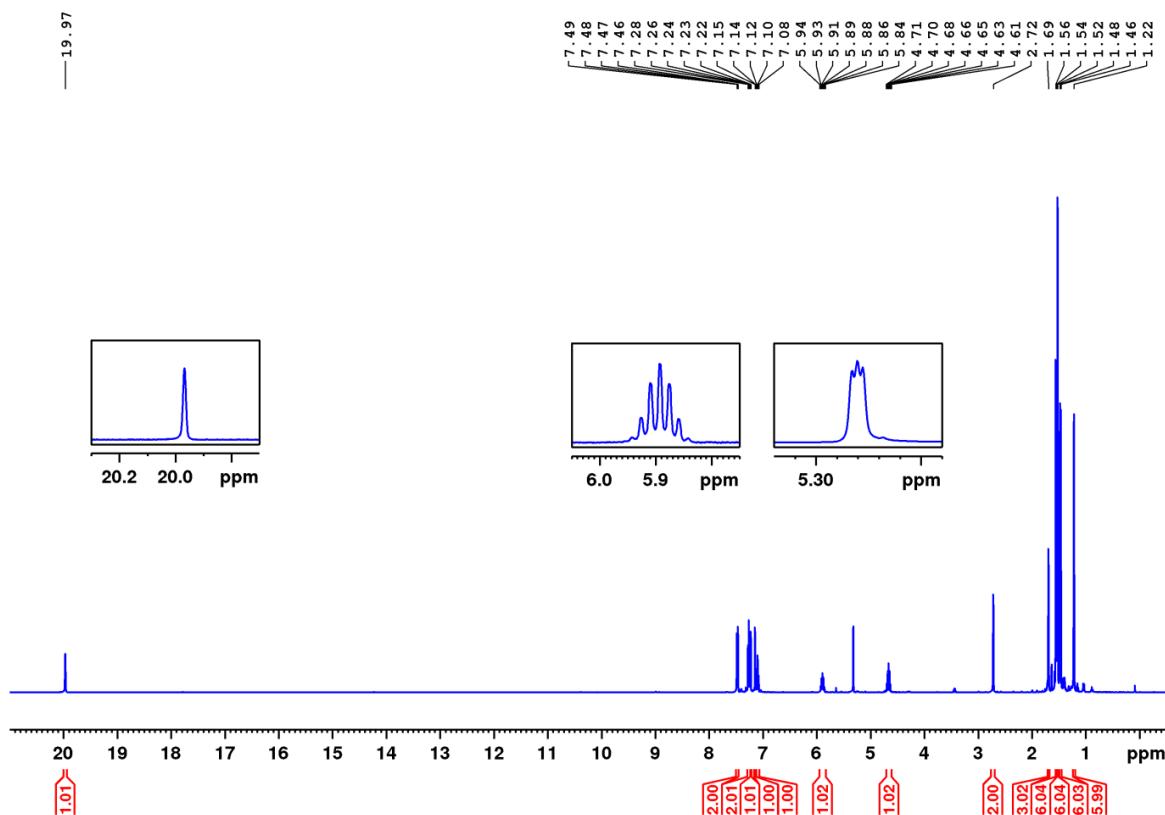
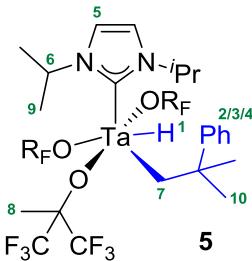


**Figure S17:**  $^2\text{H}$  { $^1\text{H}$ } NMR spectrum (92 MHz,  $\text{C}_6\text{H}_6$ , 25°C) of **4-d<sub>14</sub>**.

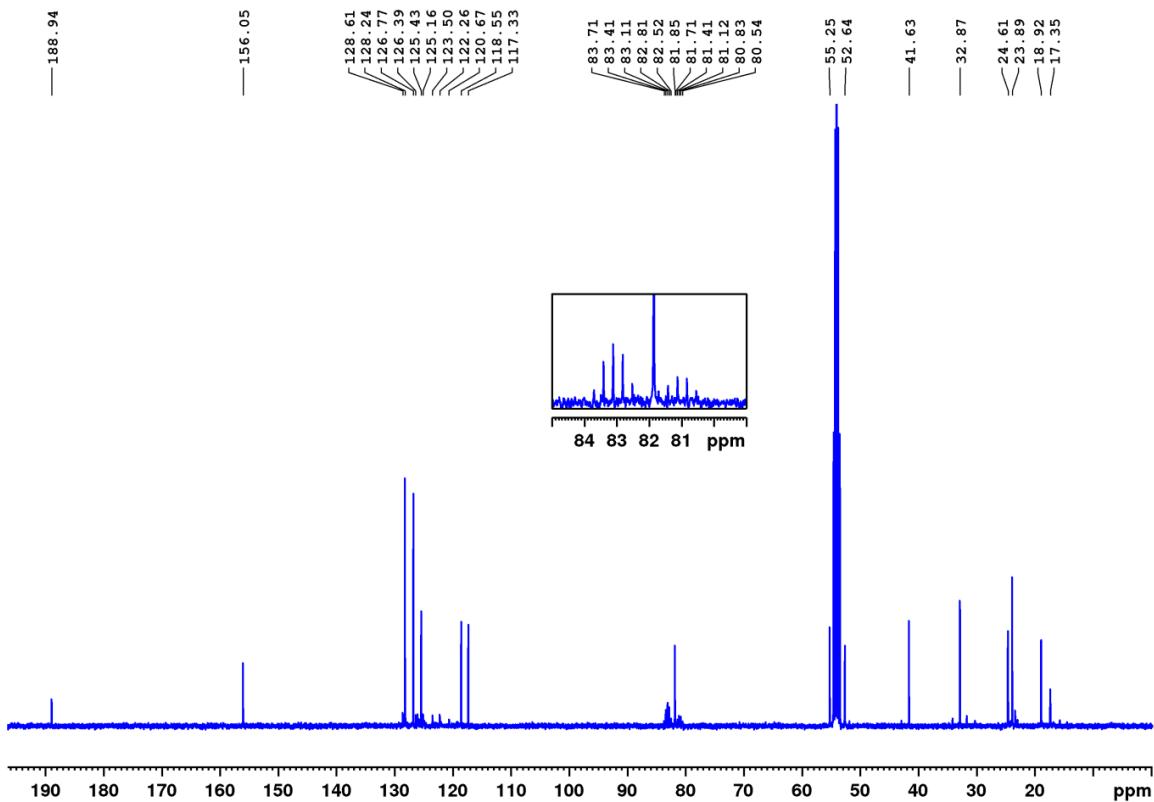


**Figure S18:**  $^{13}\text{C}$  { $^1\text{H}$ } NMR spectrum (151 MHz,  $\text{C}_6\text{D}_6$ , 25°C) of **4-d<sub>14</sub>**.

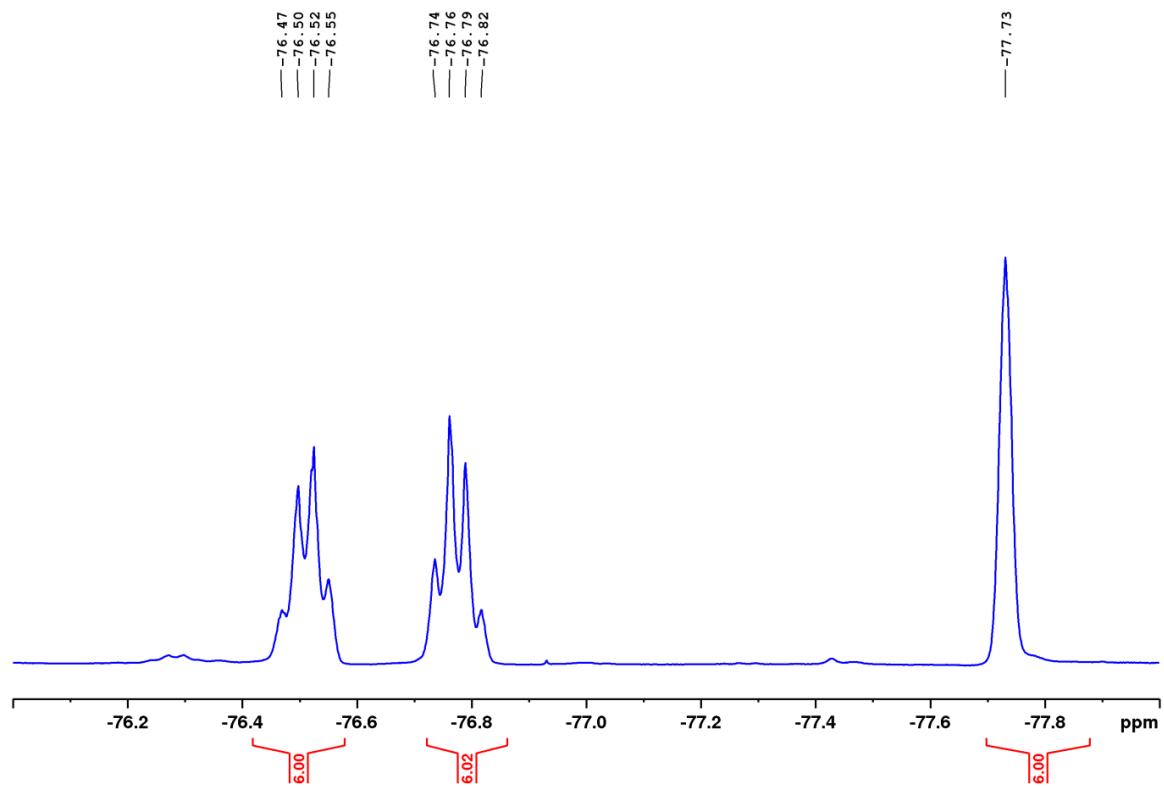
**Synthesis of 5.** A toluene solution (0.23 M) of 1.0 eq of **1** (142 mg, 0.14 mmol) was pressurized with 10 bar H<sub>2</sub> in a high-pressure NMR-tube for 5 min at room temperature. The color of the solution rapidly changed from bright yellow/orange to pale yellow. The tube was transferred in an argon-filled glovebox. A toluene solution (0.14 M) of 1.1 eq of 1,3-diisopropyl-1H-imidazol-2-yliden (21.4 mg, 0.14 mmol) was slowly added and the mixture was stirred for 1h. The solvent was removed in vacuum and the residue was taken up in a 1:6 mixture of Et<sub>2</sub>O/pentane. The title compound was isolated by crystallization at -35°C and obtained as pale-yellow crystals (102 mg, 0.10 mmol, 73%). **<sup>1</sup>H NMR** (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 25°C): δ (in ppm) = 19.97 (s, 1H, H-1), 7.49 - 7.46 (m, 2H, Ar-H<sup>ortho</sup>, H-2/3/4), 7.26 (t, <sup>3</sup>J<sub>H-H</sub> = 8.1 Hz, 2H, Ar-H<sup>meta</sup>, H-2/3/4), 7.23 (d, <sup>3</sup>J<sub>H-H</sub> = 2.0 Hz, 1H, H-5), 7.14 (d, <sup>3</sup>J<sub>H-H</sub> = 2.0 Hz, 1H, H-5), 7.10 (t, <sup>3</sup>J<sub>H-H</sub> = 7.3 Hz, 1H, Ar-H<sup>para</sup>, H-2/3/4), 5.89 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, 1H, H-6), 4.66 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.4 Hz, 1H, H-6), 2.72 (s, 2H, H-7), 1.69 (s, 3H, H-8), 1.55 (d, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, 6H, H-9), 1.52 (s, 6H, H-10), 1.47 (d, <sup>3</sup>J<sub>H-H</sub> = 6.4 Hz, 6H, H-9), 1.22 (s, 6H, H-8). **<sup>13</sup>C{<sup>1</sup>H} NMR** (CD<sub>2</sub>Cl<sub>2</sub>, 101 MHz, 25°C): δ (in ppm) = 189.94 (s, 1C, C<sup>Carbene</sup>), 156.05 (s, 1C, C<sup>Ar</sup>), 128.61 - 120.67 (m, 6C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 128.24 (s, 2C, C<sup>Ar</sup>), 126.77 (s, 2C, C<sup>Ar</sup>), 125.43 (s, 1C, C<sup>Ar</sup>), 118.55 (s, 1C, C<sup>Imidazole</sup>), 117.33 (s, 1C, C<sup>Imidazole</sup>), 83.11 (sept, <sup>2</sup>J<sub>C-F</sub> = 29.6 Hz, 2C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 81.85 (s, 1C, CH<sub>2</sub>), 81.12 (sept, <sup>2</sup>J<sub>C-F</sub> = 29.2 Hz, 1C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 55.25 (s, 1C), 52.64 (s, 1C), 41.63 (s, 1C, CMe<sub>2</sub>Ph), 32.87 (s, 2C, CMe<sub>2</sub>Ph), 24.61 (s, 2C, CH<sub>3</sub>), 23.89 (s, 2C, CH<sub>3</sub>), 18.92 (s, 2C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 17.35 (s, 1C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>). **<sup>19</sup>F{<sup>1</sup>H} NMR** (CD<sub>2</sub>Cl<sub>2</sub>, 376 MHz, 25°C): δ (in ppm) = -76.51 (q, <sup>4</sup>J<sub>F-F</sub> = 10.3 Hz, 6F), -76.77 (q, <sup>4</sup>J<sub>F-F</sub> = 10.3 Hz, 6F), -77.73 (s, 6F). **Elem. Anal. Calcd.** for C<sub>31</sub>H<sub>39</sub>F<sub>18</sub>N<sub>2</sub>O<sub>3</sub>Ta (1010.58 g/mol): C, 36.84; H, 3.89; N, 2.77. **Found:** C, 36.84; H, 3.78; N, 2.94.



**Figure S19:** <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25°C) of **5**.

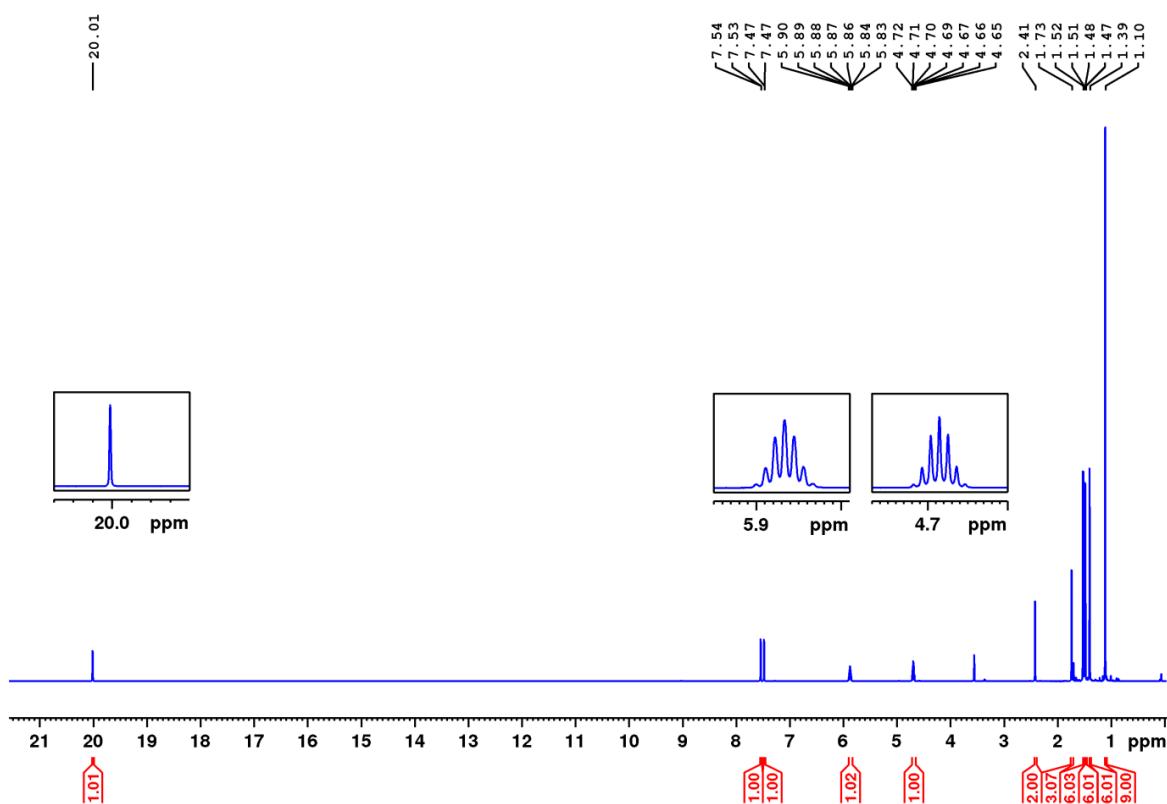
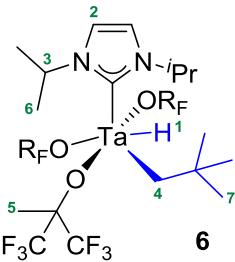


**Figure S20:**  $^{13}\text{C}$  { $^1\text{H}$ } NMR spectrum (101 MHz,  $\text{CD}_2\text{Cl}_2$ , 25°C) of **5**.

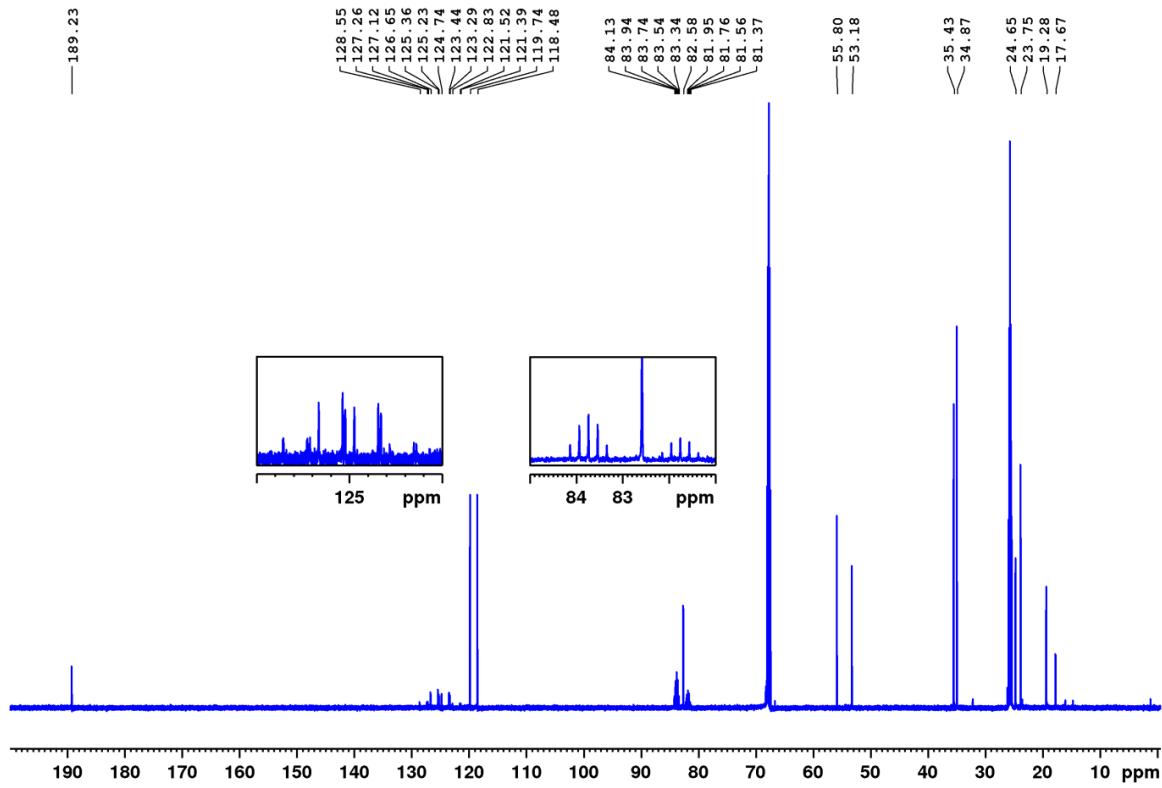


**Figure S21:**  $^{19}\text{F}$  { $^1\text{H}$ } NMR spectrum (376 MHz,  $\text{CD}_2\text{Cl}_2$ , 25°C) of **5**.

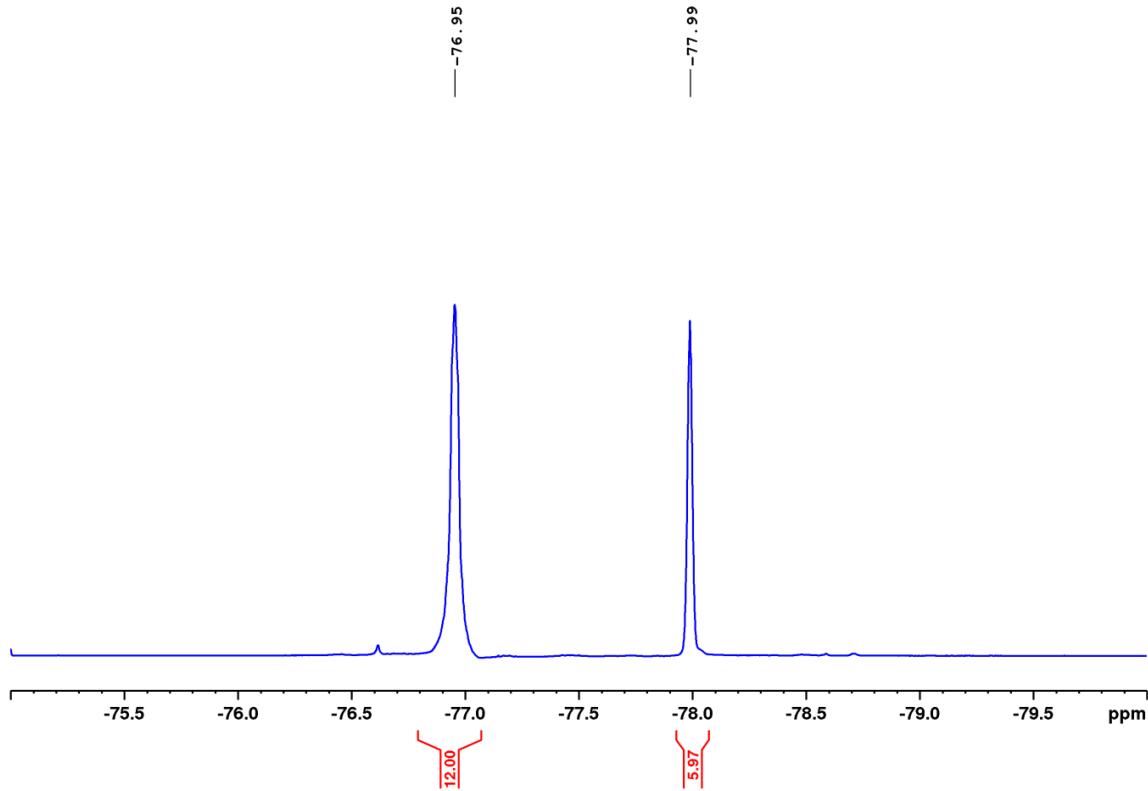
**Synthesis of 6.** A toluene solution (0.27 M) of 1.0 eq of **2** (140 mg, 0.16 mmol) was pressurized with 10 bar H<sub>2</sub> in a high-pressure NMR-tube for 5 min at room temperature. The color of the solution rapidly changed from bright yellow/orange to pale yellow. The tube was transferred in an argon-filled glovebox. A toluene solution (0.18 M) of 1.1 eq of 1,3-diisopropyl-1H-imidazol-2-yliden (26.8 mg, 0.18 mmol) was slowly added and the mixture was stirred for 1h. The solvent was removed in vacuum and the residue was taken up in a 1:6 mixture of Et<sub>2</sub>O/pentane. The title compound was isolated by crystallization at -35°C and obtained as pale-yellow crystals (103 mg, 0.11 mmol, 68%). **<sup>1</sup>H NMR** (THF-*d*<sub>8</sub>, 600 MHz, 25°C): δ (in ppm) = 20.01 (s, 1H, Ta-H, H-1), 7.54 (d, <sup>3</sup>J<sub>H-H</sub> = 1.8 Hz, 1H, H-2), 7.47 (d, <sup>3</sup>J<sub>H-H</sub> = 1.8 Hz, 1H, H-2), 5.87 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz, 1H, H-3), 4.69 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.4 Hz, 1H, H-3), 2.41 (s, 2H, H-4), 1.73 (s, 3H, H-5), 1.52 (d, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz, 6H, H-6), 1.48 (d, <sup>3</sup>J<sub>H-H</sub> = 6.4 Hz, 6H, H-6), 1.39 (s, 6H, H-5), 1.10 (s, 9H, H-7). **<sup>13</sup>C{<sup>1</sup>H} NMR** (THF-*d*<sub>8</sub>, 151 MHz, 25°C): δ (in ppm) = 189.23 (s, 1C, C<sup>Carbene</sup>), 128.55 - 121.39 (m, 6C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 119.74 (s, 1C, C<sup>Imidazole</sup>), 118.49 (s, 1C, C<sup>Imidazole</sup>), 83.74 (sept, <sup>2</sup>J<sub>C-F</sub> = 29.8 Hz, 2C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 82.58 (s, 1C, CH<sub>2</sub>), 81.76 (sept, <sup>2</sup>J<sub>C-F</sub> = 29.4 Hz, 1C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 55.80 (s, 1C), 53.18 (s, 1C), 35.43 (s, 1C, <sup>t</sup>Bu), 34.87 (s, 3C, <sup>t</sup>Bu), 24.65 (s, 2C, CH<sub>3</sub>), 23.75 (s, 2C, CH<sub>3</sub>), 19.28 (s, 2C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 17.66 (s, 1C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>). **<sup>19</sup>F{<sup>1</sup>H} NMR** (THF-*d*<sub>8</sub>, 376 MHz, 25°C): δ (in ppm) = -76.95 (s, 12F), -77.99 (s, 6F). **Elem. Anal. Calcd.** for C<sub>26</sub>H<sub>37</sub>F<sub>18</sub>N<sub>2</sub>O<sub>3</sub>Ta (948.51 g/mol): C, 32.92; H, 3.93; N, 2.95. **Found:** C, 33.15; H, 4.02; N, 3.10.



**Figure S22:** <sup>1</sup>H NMR spectrum (600 MHz, THF-*d*<sub>8</sub>, 25°C) of **6**.



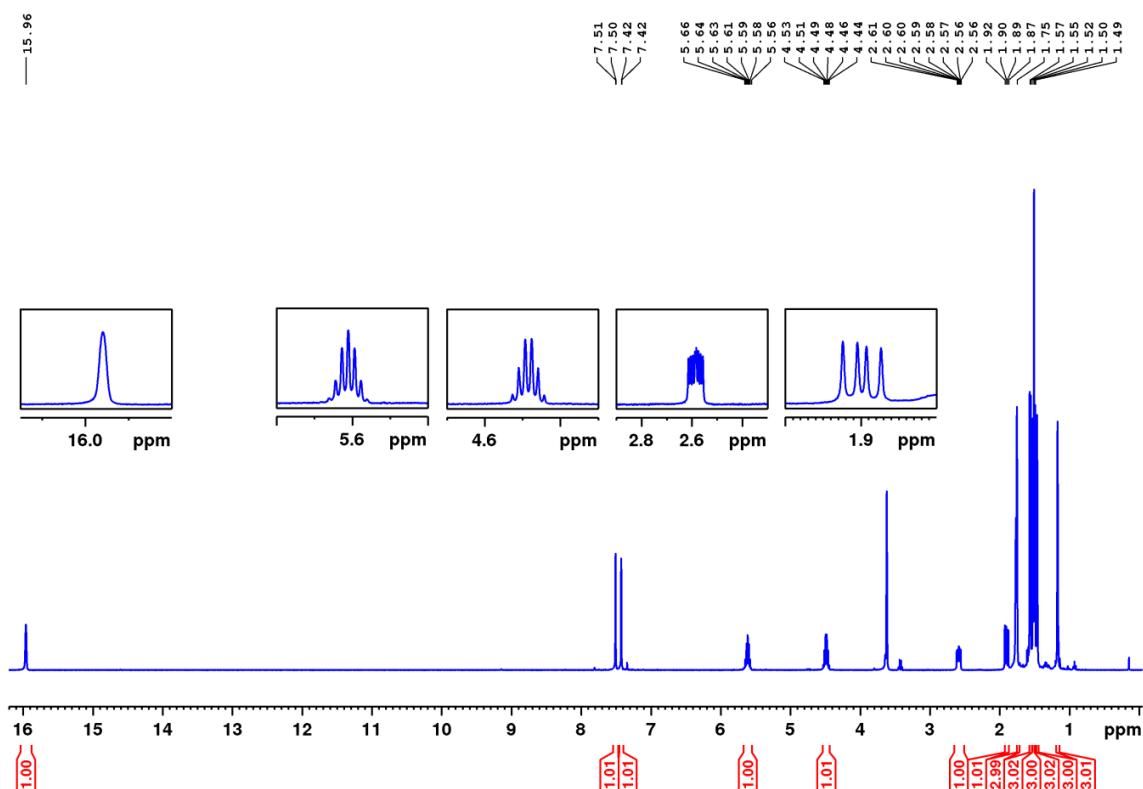
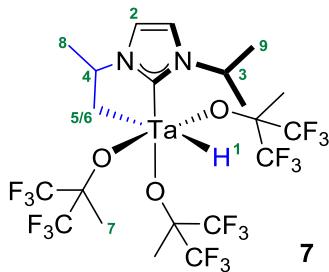
**Figure S23:**  $^{13}\text{C}$  { $^1\text{H}$ } NMR spectrum (151 MHz, THF-*d*<sub>8</sub>, 25°C) of **6**.



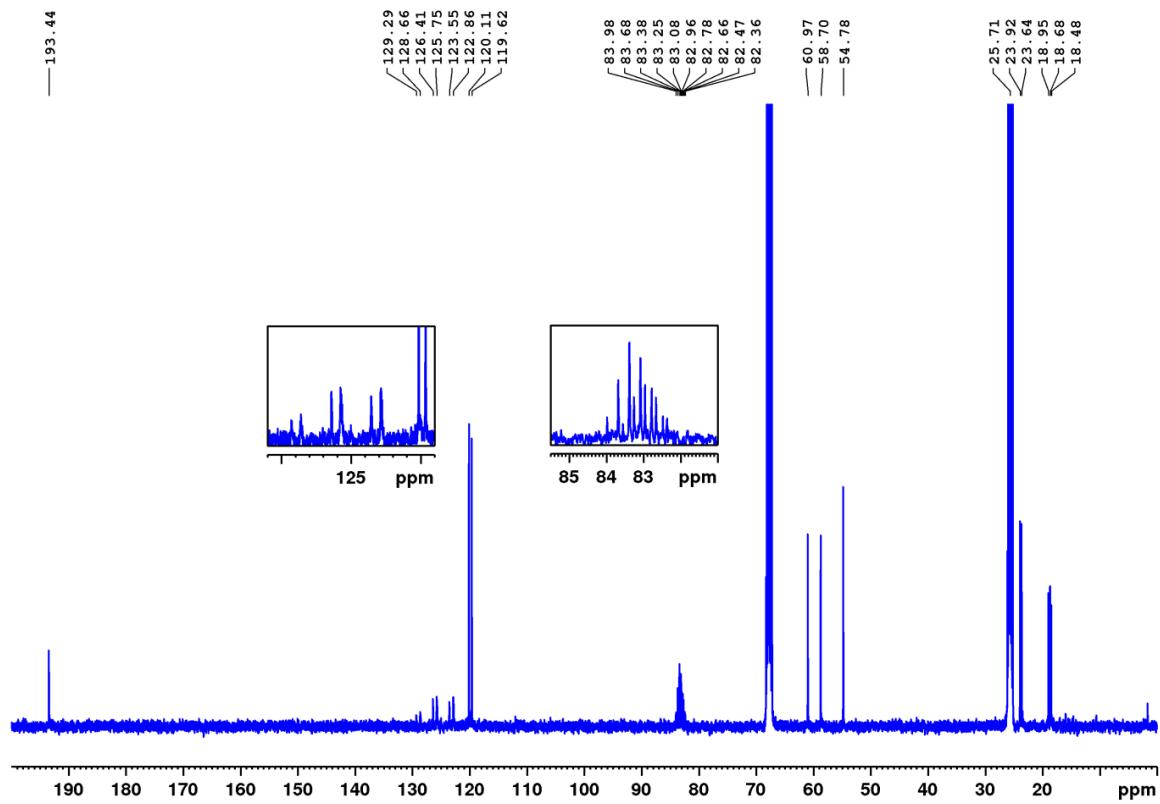
**Figure S24:**  $^{19}\text{F}$  { $^1\text{H}$ } NMR spectrum (376 MHz, THF-*d*<sub>8</sub>, 25°C) of **6**.

**Synthesis of 7.** A THF solution (0.11 M) of 1.0 eq of **4** (65.0 mg, 0.07 mmol) was pressurized with 10 bar H<sub>2</sub> in a high-pressure NMR-tube. The tube was sealed and heated for 48h at 65°C. After cooling to room temperature, the tube was transferred in an argon-filled glovebox. The solvent was removed in vacuum and the residue was taken up in pentane. The title compound was isolated by crystallization from a concentrated solution in pentane at -35°C and obtained as colorless needles (Yield: 38.0 mg 0.04 mmol, 62%).

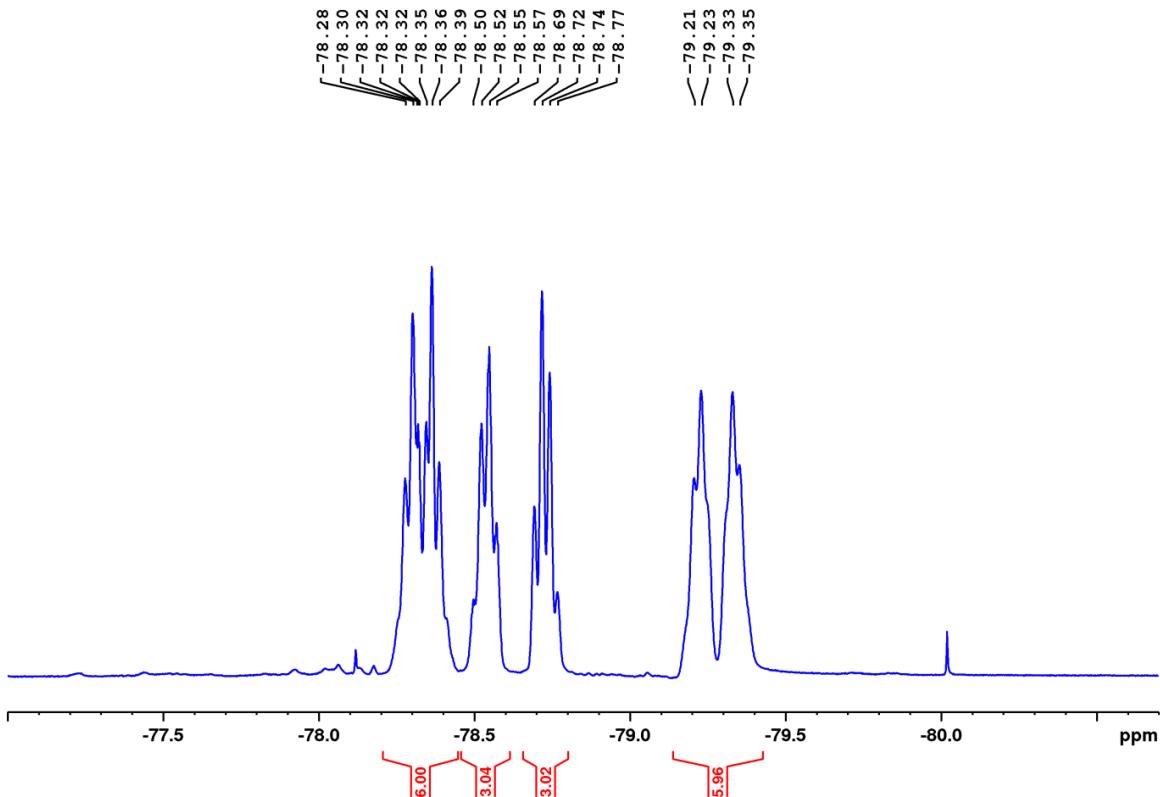
**<sup>1</sup>H NMR** (THF-*d*<sub>8</sub>, 400 MHz, 25°C): δ (in ppm) = 16.01 (s, 1H, Ta-H, H-1), 7.51 (d, <sup>3</sup>J<sub>H-H</sub> = 1.9 Hz, 1H, H-2), 7.43 (d, <sup>3</sup>J<sub>H-H</sub> = 1.9 Hz, 1H, H-2), 5.61 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, 1H, H-3), 4.49 (sext, <sup>3</sup>J<sub>H-H</sub> = 6.4 Hz, 1H, H-4), 2.62 - 2.56 (m, 1H, H-5/6), 1.90 (dd, <sup>2</sup>J<sub>H-H</sub> = 12.7 Hz, <sup>3</sup>J<sub>H-H</sub> = 7.7 Hz, 1H, H-5/6), 1.75 (s, 3H, H-7), 1.56 (d, <sup>3</sup>J<sub>H-H</sub> = 6.4 Hz, 3H, H-8), 1.52 (d, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, 3H, H-9), 1.50 (d, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, 3H, H-9), 1.46 (s, 3H), 1.17 (s, 3H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (THF-*d*<sub>8</sub>, 101 MHz, 25°C): δ (in ppm) = 193.44 (s, 1C, C<sup>Carbene</sup>), 124.98 (q, <sup>1</sup>J<sub>C-F</sub> = 287.8 Hz, 3C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 124.30 (q, <sup>1</sup>J<sub>C-F</sub> = 291.4 Hz, 3C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 120.11 (s, 1C, C<sup>Imidazole</sup>), 119.62 (s, 1C, C<sup>Imidazole</sup>), 83.98 - 82.36 (m, 3C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 60.97 (s, 1C, C<sup>Bridge</sup>), 58.70 (s, 1C), 54.78 (s, 1C), 25.71 (s, 1C, CH<sub>3</sub>), 23.91 (s, 1C, CH<sub>3</sub>), 23.64 (s, 1C, CH<sub>3</sub>), 18.95 (s, 1C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 18.68 (s, 1C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 18.48 (s, 1C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>). **<sup>19</sup>F{<sup>1</sup>H} NMR** (THF-*d*<sub>8</sub>, 376 MHz, 25°C): δ (in ppm) = -78.28 to -78.39 (m, 6F), -78.54 (q, <sup>4</sup>J<sub>F-F</sub> = 9.2 Hz, 3F), -78.73 (q, <sup>4</sup>J<sub>F-F</sub> = 9.2 Hz, 3F), -79.21 to -79.35 (m, 6F). **Elem. Anal. Calcd.** for C<sub>21</sub>H<sub>25</sub>F<sub>18</sub>N<sub>2</sub>O<sub>3</sub>Ta (876.36 g/mol): C, 28.78; H, 2.88; N, 3.20. **Found:** C, 28.95; H, 2.92; N, 3.38.



**Figure S25:** <sup>1</sup>H NMR spectrum (400 MHz, THF-*d*<sub>8</sub>, 25°C) of **7**.

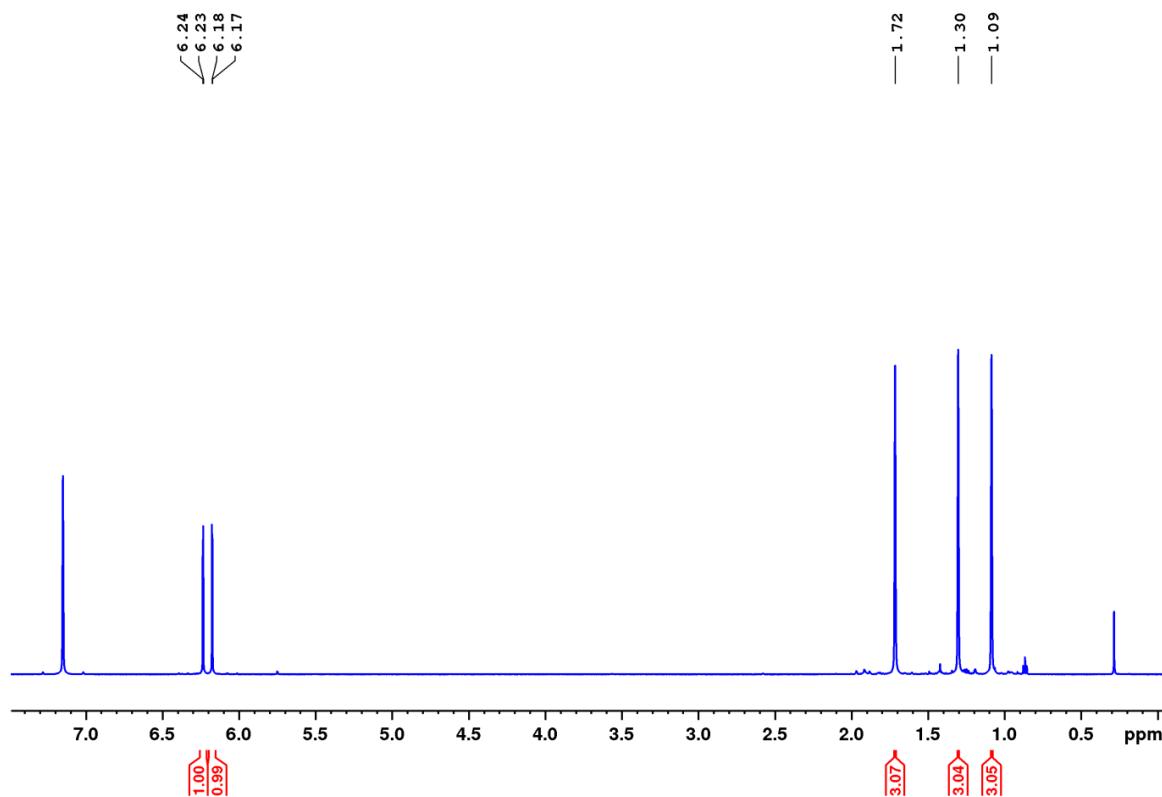
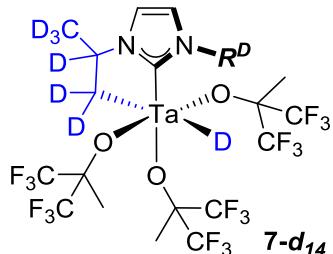


**Figure S26:**  $^{13}\text{C}$  { $^1\text{H}$ } NMR spectrum (101 MHz, THF- $d_8$ , 25°C) of **7**.

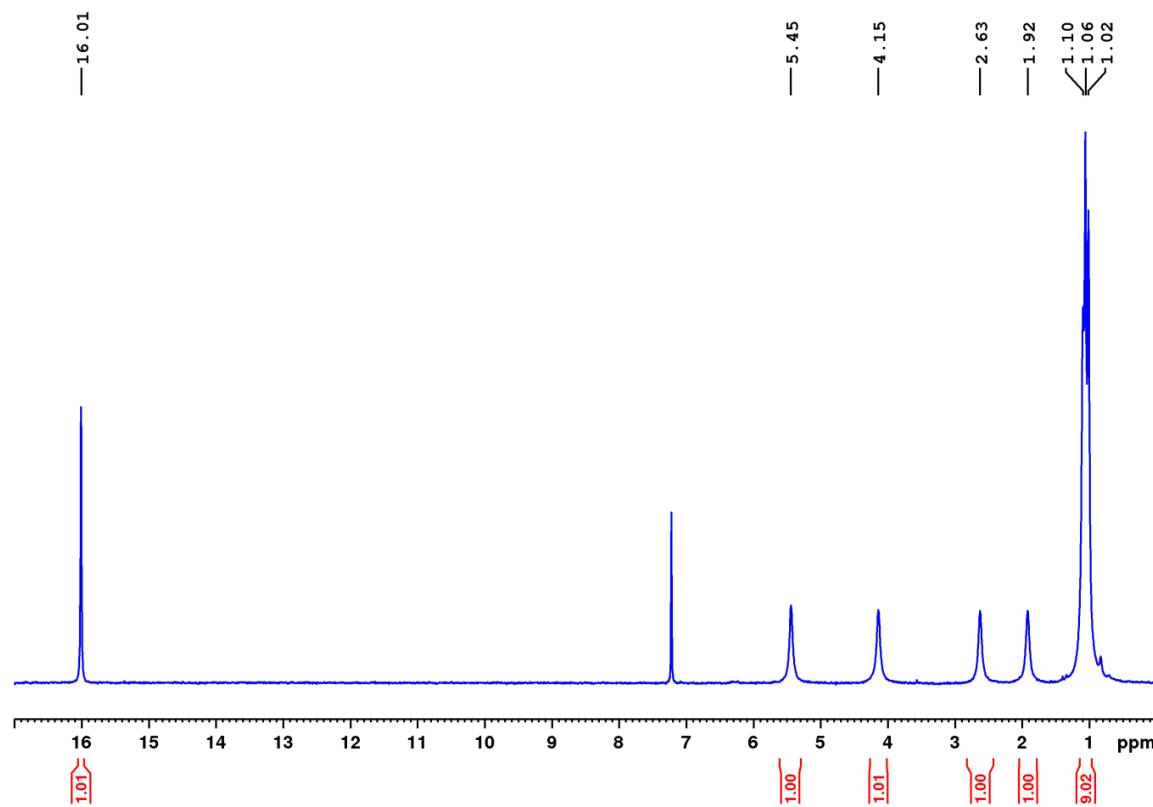


**Figure S27:**  $^{19}\text{F}$  { $^1\text{H}$ } NMR spectrum (376 MHz, THF- $d_8$ , 25°C) of **7**.

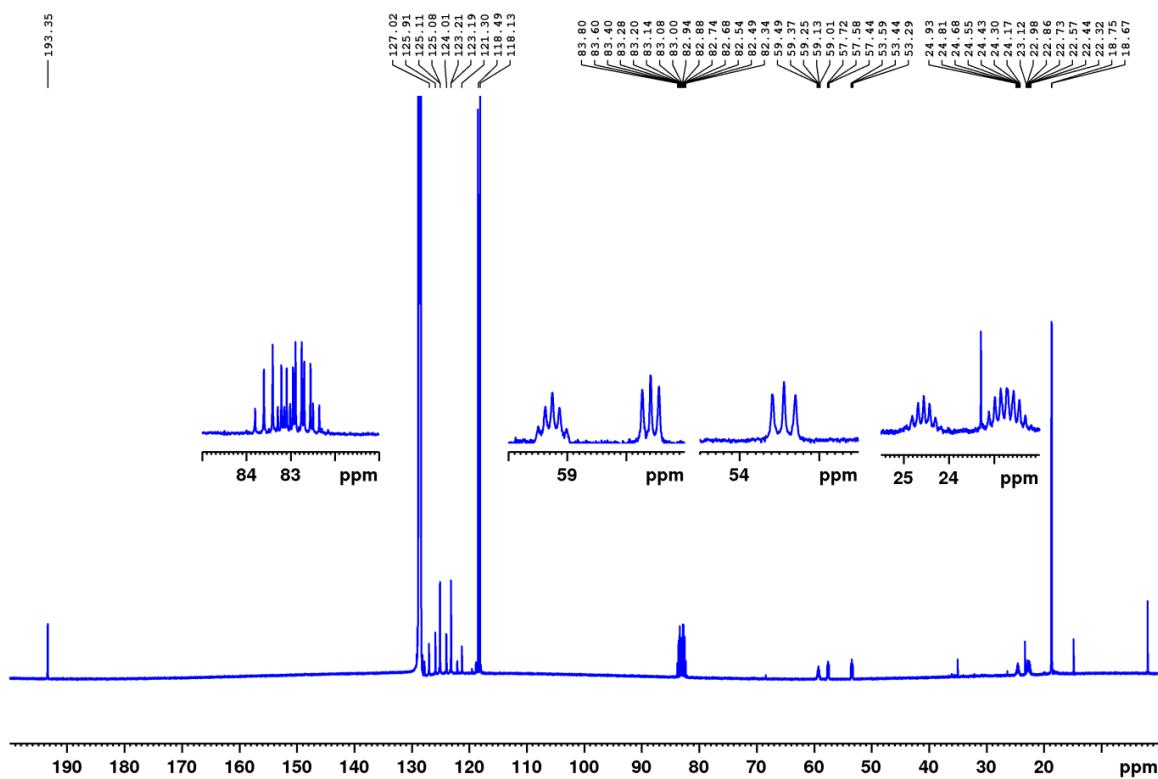
**Synthesis of 7-d<sub>14</sub>.** A THF solution (0.33 M) of 1.0 eq of **4-d<sub>14</sub>** (195 mg, 0.20 mmol) was pressurized with 10 bar H<sub>2</sub> in a high-pressure NMR-tube. The tube was sealed and heated for 1d at 65°C. After cooling to room temperature, the tube was transferred in an argon-filled glovebox. The solvent was removed in vacuum and the residue was taken up in pentane. The title compound was isolated by crystallization from a concentrated solution in pentane at -35°C and obtained as colorless needles (106 mg, 0.12 mmol, 60%). **<sup>1</sup>H NMR** (C<sub>6</sub>D<sub>6</sub>, 600 MHz, 25°C): δ (in ppm) = 6.23 (d, <sup>3</sup>J<sub>H-H</sub> = 1.9 Hz, 1H), 6.17 (d, <sup>3</sup>J<sub>H-H</sub> = 1.9 Hz, 1H), 1.72 (s, 3H), 1.30 (s, 3H), 1.09 (s, 3H). **<sup>2</sup>H NMR** (C<sub>6</sub>H<sub>6</sub>, 92 MHz, 25°C): 16.01 (s, 1D, Ta-D), 5.45 (s, 1D), 4.15 (s, 1D), 2.63 (s, 1D), 1.92 (s, 1D), 1.10 - 1.02 (m, 9D). **<sup>13</sup>C{<sup>1</sup>H} NMR** (C<sub>6</sub>D<sub>6</sub>, 101 MHz, 25°C): δ (in ppm) = 193.35 (s, 1C, C<sup>Carbene</sup>), 124.96 (q, <sup>1</sup>J<sub>C-F</sub> = 287.2 Hz, 2C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 124.16 (q, <sup>1</sup>J<sub>C-F</sub> = 287.8 Hz, 4C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 118.49 (s, 1C, C<sup>Imidazole</sup>), 118.13 (s, 1C, C<sup>Imidazole</sup>), 83.80 - 82.34 (m, 3C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 59.25 (pent, <sup>1</sup>J<sub>C-D</sub> = 17.8 Hz, 1C, C<sup>Bridge</sup>), 57.58 (t, <sup>1</sup>J<sub>C-D</sub> = 20.9 Hz, 1C), 53.44 (t, <sup>1</sup>J<sub>C-D</sub> = 21.9 Hz, 1C), 24.55 (sept, <sup>1</sup>J<sub>C-D</sub> = 18.7 Hz, 1C, CD<sub>3</sub>), 23.12 - 22.32 (m, 2C, CD<sub>3</sub>), 18.74 (s, 1C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 18.67 (s, 2C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>). **<sup>19</sup>F{<sup>1</sup>H} NMR** (C<sub>6</sub>D<sub>6</sub>, 376 MHz, 25°C): δ (in ppm) = -78.33 to -78.47 (m, 6F), -78.59 (q, <sup>4</sup>J<sub>F-F</sub> = 9.3 Hz, 3F), -78.18 (q, <sup>4</sup>J<sub>F-F</sub> = 9.3 Hz, 3F), -79.23 to -79.38 (m, 6F).



**Figure S28:** <sup>1</sup>H NMR spectrum (600 MHz, C<sub>6</sub>D<sub>6</sub>, 25°C) of **7-d<sub>14</sub>**.

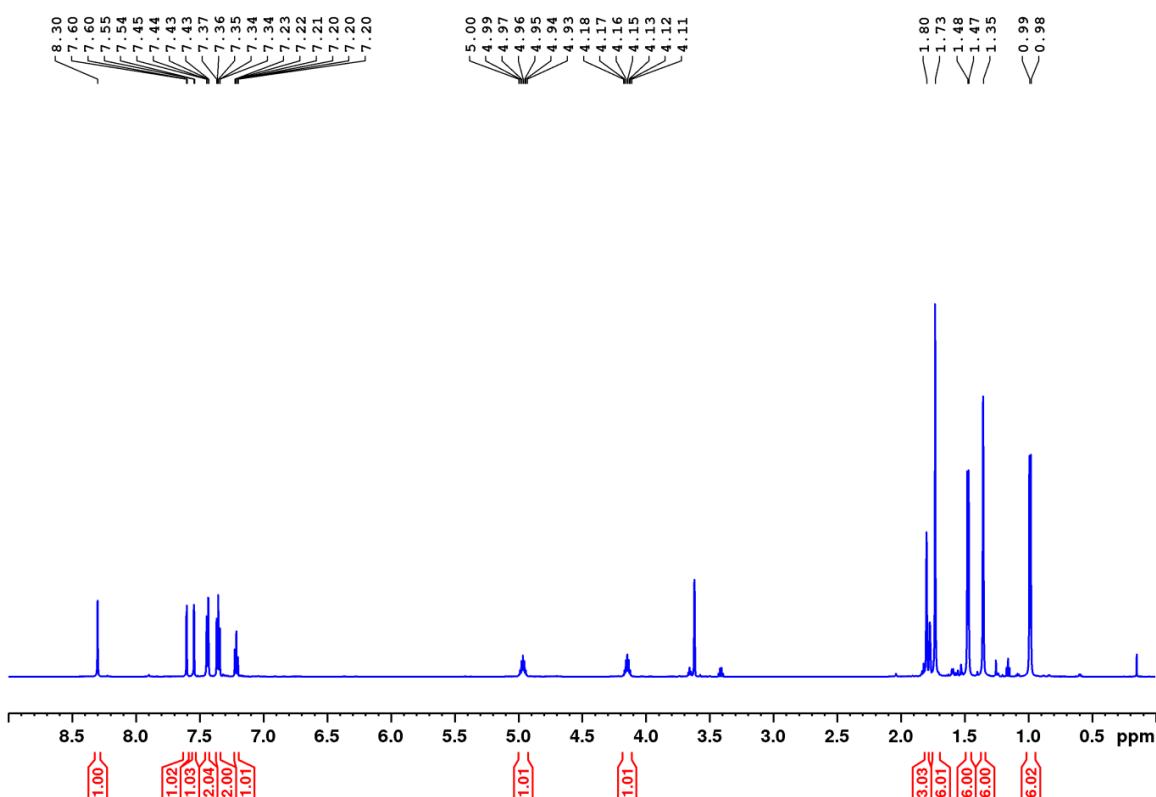
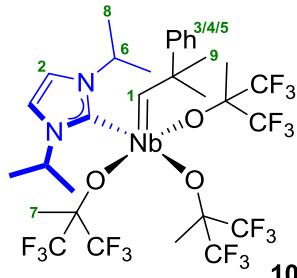


**Figure S29:**  $^2\text{H}$   $\{^1\text{H}\}$  NMR spectrum (92 MHz,  $\text{C}_6\text{H}_6$ , 25°C) of **7-d<sub>14</sub>**.

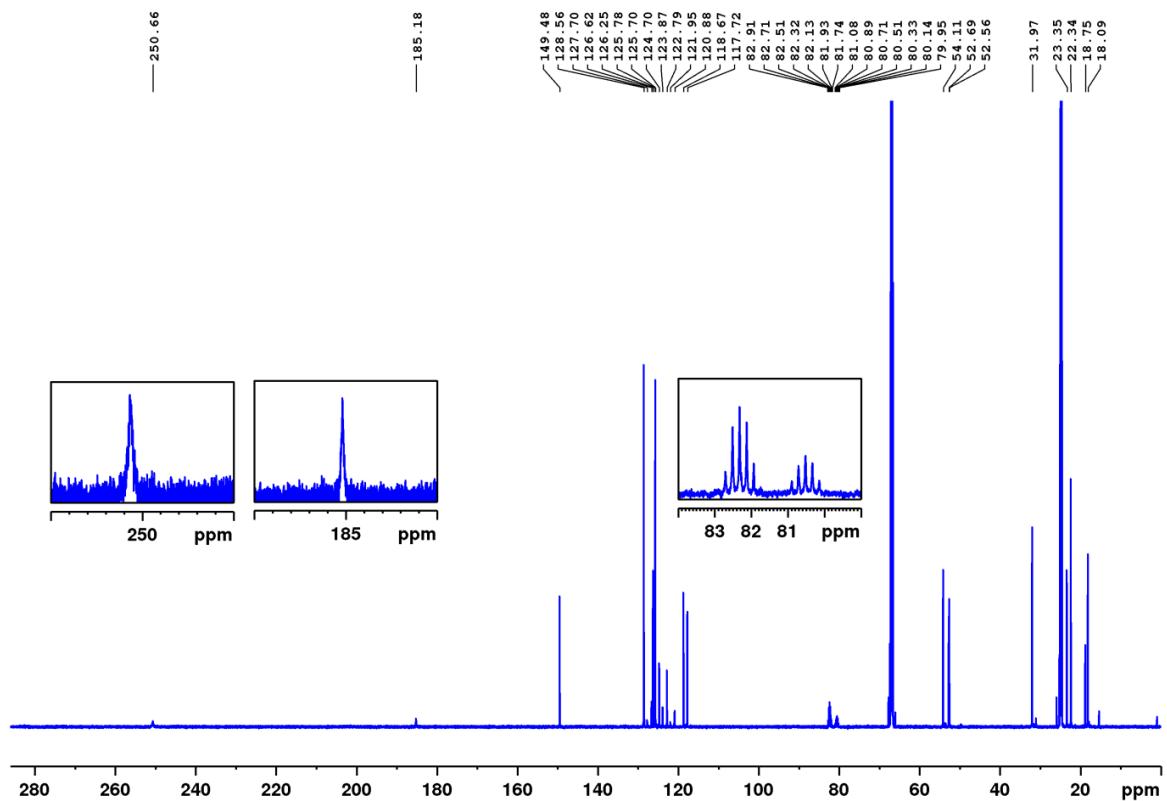


**Figure S30:**  $^{19}\text{F}$   $\{^1\text{H}\}$  NMR spectrum (376 MHz,  $\text{C}_6\text{D}_6$ , 25°C) of **7-d<sub>14</sub>**.

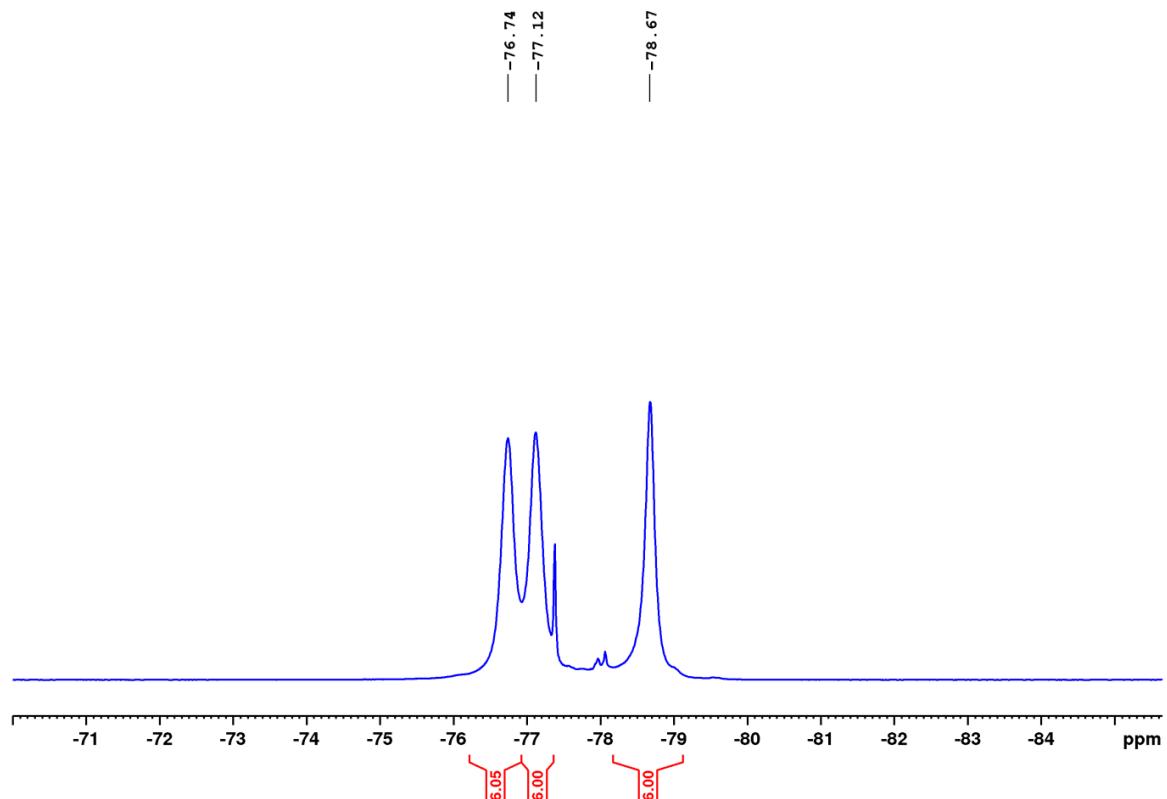
**Synthesis of 10.** In an argon-filled glovebox, 1.0 eq of  $\text{Nb}(\text{=CH}(\text{CH}_3)_2\text{Ph})(\text{THF})_2\text{Cl}_3$  (601 mg, 1.26 mmol) was dissolved in 8 ml of  $\text{Et}_2\text{O}/\text{THF}$  (6:1). Then a solution of 3.0 eq of  $\text{LiOCCH}_3(\text{CF}_3)_2$  (714 mg, 3.79 mmol) in 3 ml of  $\text{Et}_2\text{O}/\text{THF}$  (6:1) was added dropwise under vigorous stirring (the precipitation of  $\text{LiCl}$  started immediately). The resulting yellow-orange solution was stirred for 1d. The precipitate was filtered off, the solvent was removed in vacuum and the residue was taken up in pentane. Removing the pentane in vacuum afforded  $\text{Nb}(\text{=CH}(\text{CH}_3)_2\text{Ph})(\text{OCCH}_3(\text{CF}_3)_2)_3$  as a yellow oil which was used without further purification. This material (1.0 eq, 1.02 g, 1.21 mmol) was dissolved in 5 ml of THF. Then a THF solution of 1.0 eq of 1,3-diisopropyl-1H-imidazol-2-ylidene (186 mg, 1.21 mmol) was added dropwise. The resulting orange solution was stirred for 1d. The solvent was removed in vacuum and the residue was taken up in pentane. The title compound was isolated by crystallization from a concentrated solution in pentane at -35°C and obtained as an orange crystalline solid (614 mg, 0.67 mmol, 55%).  **$^1\text{H NMR}$**  ( $\text{THF-d}_8$ , 600 MHz, -40°C):  $\delta$  (in ppm) = 8.30 (s, 1H, H-1), 7.60 (d,  $^3J_{\text{H-H}} = 2.0$  Hz, 1H, H-2), 7.54 (d,  $^3J_{\text{H-H}} = 2.0$  Hz, 1H, H-2), 7.45 - 7.43 (m, 2H, H-3/4/5), 7.37 - 7.34 (m, 2H, H-3/4/5), 7.23 - 7.20 (m, 1H, H-3/4/5), 4.96 (sept,  $^3J_{\text{H-H}} = 6.6$  Hz, 1H, H-6), 4.15 (sept,  $^3J_{\text{H-H}} = 6.5$  Hz, 1H, H-6), 1.80 (s, 3H, H-7), 1.73 (s, 6H, H-7), 1.47 (d,  $^3J_{\text{H-H}} = 6.5$  Hz, 6H, H-8), 1.35 (s, 6H, H-9), 0.98 (d,  $^3J_{\text{H-H}} = 6.6$  Hz, 6H, H-8).  **$^{13}\text{C}\{^1\text{H}\} \text{NMR}$**  ( $\text{THF-d}_8$ , 151 MHz, -40°C):  $\delta$  (in ppm) = 250.66 (s, 1C), 185.18 (s, 1C), 149.48 (s, 1C), 128.56 (s, 2C), 126.25 (s, 1C), 125.70 (s, 2C), 124.82 (q,  $^1J_{\text{C-F}} = 288.3$  Hz, 2C), 123.75 (q,  $^1J_{\text{C-F}} = 288.9$  Hz, 4C), 118.67 (s, 1C), 117.72 (s, 1C), 82.32 (sept,  $^2J_{\text{C-F}} = 29.2$  Hz, 2C), 80.51 (sept,  $^2J_{\text{C-F}} = 29.2$  Hz, 1C), 54.11 (s, 1C), 52.69 (s, 1C), 52.56 (s, 1C), 31.97 (s, 2C), 23.35 (s, 2C), 22.34 (s, 2C), 18.75 (s, 1C), 18.09 (s, 2C).  **$^{19}\text{F}\{^1\text{H}\} \text{NMR}$**  ( $\text{THF-d}_8$ , 376 MHz, 25°C):  $\delta$  (in ppm) = -76.74 (brs, 6F), -77.12 (brs, 6F), -78.67 (brs, 6F). **Elem. Anal. Calcd.** For  $\text{C}_{31}\text{H}_{37}\text{F}_{18}\text{N}_2\text{NbO}_3$  (920.53 g/mol): C, 40.45; H, 4.05; N, 3.04. **Found:** C, 40.79; H, 4.13; N, 3.19.



**Figure S31:**  $^1\text{H NMR}$  spectrum (600 MHz,  $\text{THF-d}_8$ , -40°C) of **10**.

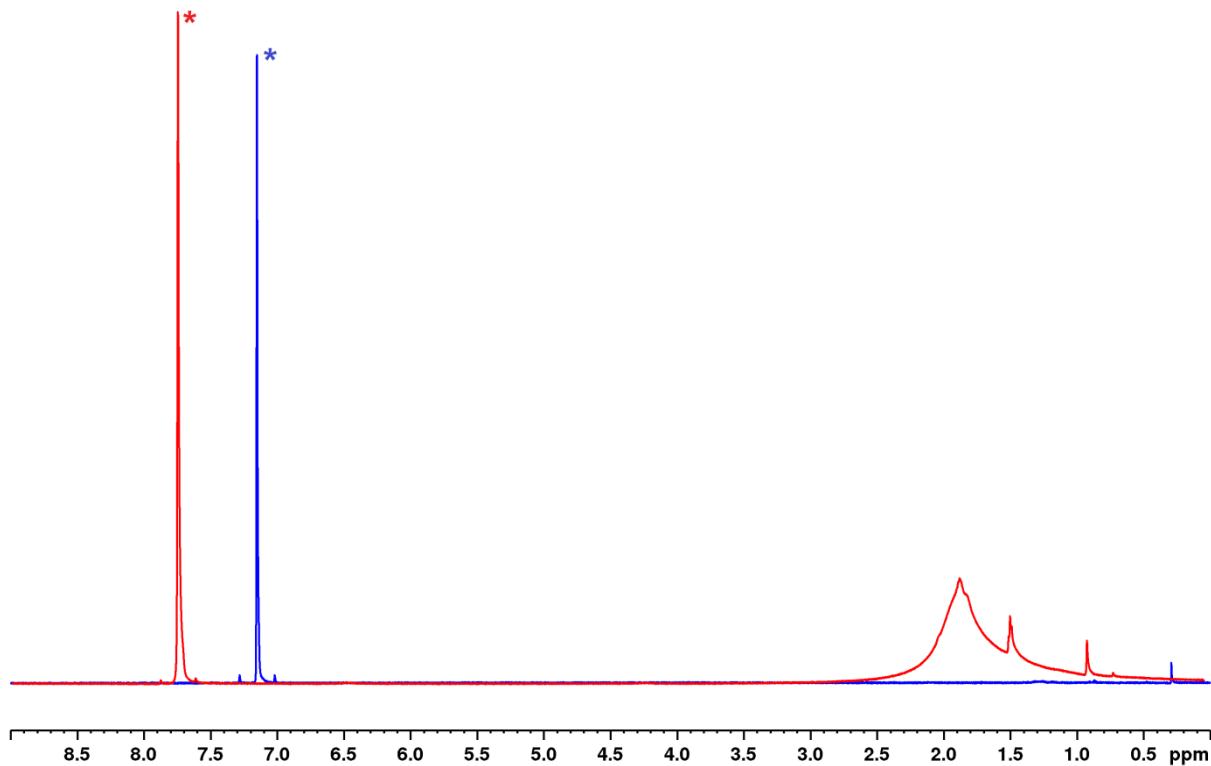
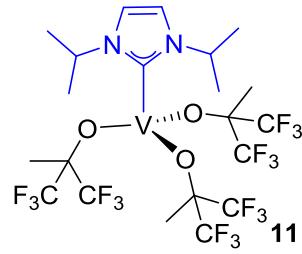


**Figure S32:**  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR spectrum (151 MHz, THF-d<sub>8</sub>, -40°C) of **10**.



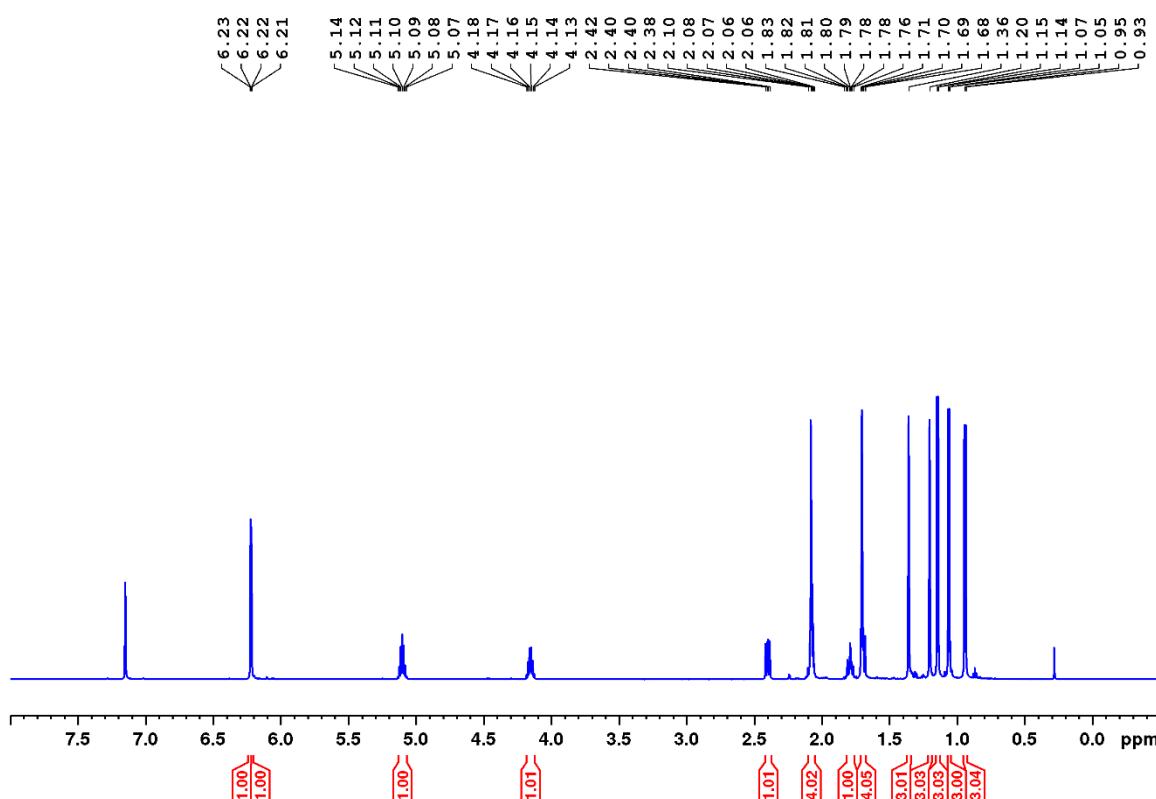
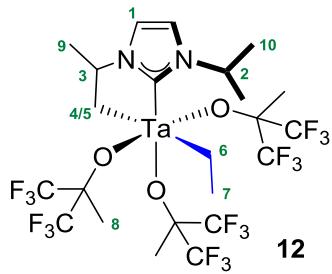
**Figure S33:**  $^{19}\text{F}$  { $^1\text{H}$ } NMR spectrum (376 MHz, THF-d<sub>8</sub>, -40°C) of **10**.

**Synthesis of 11.** In an argon-filled glovebox, 1.0 eq of  $\text{V}(\text{Mes})_3(\text{THF})$  (920 mg, 1.91 mmol) was dissolved in 20 ml of toluene and a toluene solution of 3.5 eq of 1,1,1,3,3-hexafluoro-2-methyl-2-propanol (1.22 g, 6.7 mmol) was added dropwise. The mixture was heated at 50°C for 2h. The solvent was removed in vacuum and the residue was taken up in pentane. Cooling the pentane solution to -40°C led to the formation of crystalline  $\text{V}(\text{OCCH}_3(\text{CF}_3)_2)_3(\text{THF})$ . The synthesis of complex **11** was accomplished by addition of 1.0 eq of 1,3-diisopropyl-1H-imidazol-2-ylidene (149 mg, 0.98 mmol) to a THF solution of 1.0 eq  $\text{V}(\text{OCCH}_3(\text{CF}_3)_2)_3(\text{THF})$  (654 mg, 0.98 mmol) at room temperature. The mixture was stirred for 3h, then the solvent was removed in vacuum and the residue was taken up in a mixture of pentane/HMDSO (1:1). The isolation of the complex **11** was performed by crystallization from a concentrated solution in pentane/HMDSO at -40°C (578 mg, 0.77 mmol, 79%). **Elem. Anal. Calcd.** for  $\text{C}_{21}\text{H}_{25}\text{F}_{18}\text{N}_2\text{O}_3\text{V}$  (746.35 g/mol): C, 33.80; H, 3.38; N, 3.75. **Found:** C, 33.42; H, 3.57; N, 3.87.

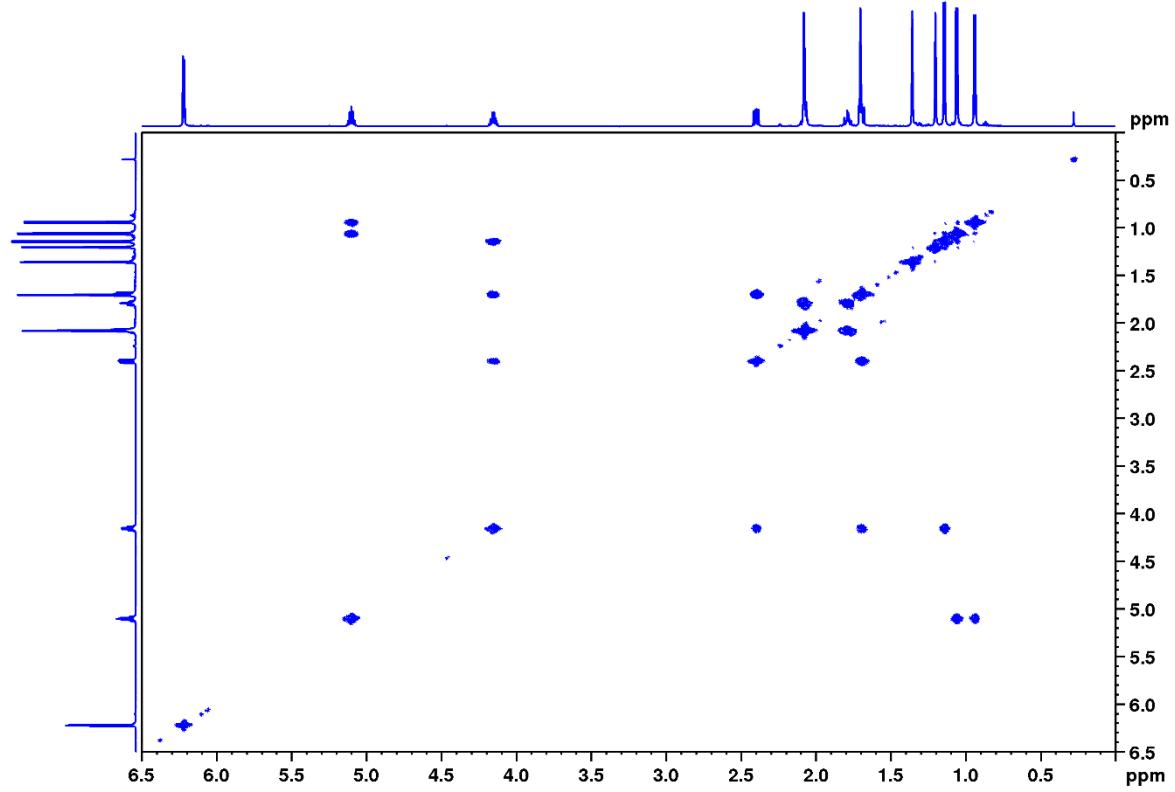


**Figure S34:**  $^1\text{H}$  NMR spectrum of **11** (Evans method for the determination of the magnetic moment in solution. Blue spectrum: pure  $\text{C}_6\text{D}_6$ , the residue signal of  $\text{C}_6\text{D}_5\text{H}$  is labeled with \*. Red spectrum: solution of **11** in  $\text{C}_6\text{D}_6$ , the residue signal of  $\text{C}_6\text{D}_5\text{H}$  is labeled with \*).

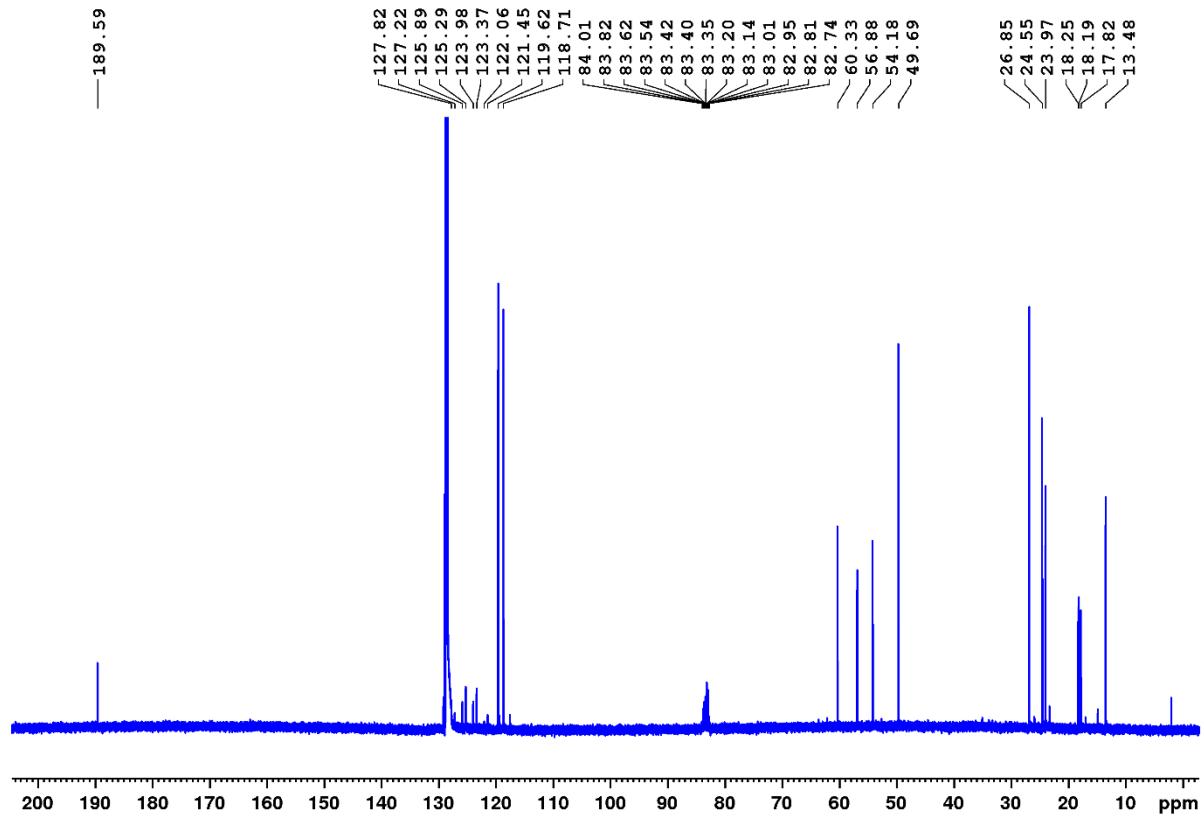
**Synthesis of 12.** A toluene solution (0.16 M) of 1.0 eq of **7** (85 mg, 0.10 mmol) was pressurized with 10 bar C<sub>2</sub>H<sub>4</sub> in a high-pressure NMR-tube for 2 h at 65°C. The tube was transferred in an argon-filled glovebox. The solvent was removed in vacuum and the residue was taken up in pentane. The title compound was isolated by crystallization at -35°C and obtained as a pale yellow crystalline solid (74.3 mg, 0.08 mmol, 82%). **<sup>1</sup>H NMR** (C<sub>6</sub>D<sub>6</sub>, 600 MHz, 25°C): δ (in ppm) = 6.23 (d, <sup>3</sup>J<sub>H-H</sub> = 1.9 Hz, 1H, H-1), 6.22 (d, <sup>3</sup>J<sub>H-H</sub> = 1.9 Hz, 1H, H-1), 5.10 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, 1H, H-2), 4.15 (sext, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 1H, H-3), 2.40 (dd, <sup>2</sup>J<sub>H-H</sub> = 12.3 Hz, <sup>3</sup>J<sub>H-H</sub> = 7.3 Hz, 1H, H-4/5), 2.10 - 2.05 (m, 4H, H-6, H-7), 1.81 - 1.77 (m, 1H, H-6), 1.70 (s, 3H, H-8), 1.70 (dd, <sup>2</sup>J<sub>H-H</sub> = 12.3 Hz, <sup>3</sup>J<sub>H-H</sub> = 7.3 Hz, 1H, H-4/5), 1.36 (s, 3H, H-8), 1.20 (s, 3H, H-8), 1.14 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 3H, H-9), 1.06 (d, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, 3H, H-10), 0.94 (d, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, 3H, H-10). **<sup>13</sup>C{<sup>1</sup>H} NMR** (C<sub>6</sub>D<sub>6</sub>, 151 MHz, 25°C): δ (in ppm) = 189.59 (s, 1C, C<sup>Carbene</sup>), 124.94 (q, <sup>1</sup>J<sub>C-F</sub> = 288.6 Hz, 2C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 124.32 (q, <sup>1</sup>J<sub>C-F</sub> = 289.0 Hz, 4C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 119.62 (s, 1C, C<sup>Imidazole</sup>), 118.71 (s, 1C, C<sup>Imidazole</sup>), 84.01 - 82.74 (m, 3C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 60.33 (s, 1C, C<sup>Bridge</sup>), 56.88 (s, 1C), 54.18 (s, 1C, CH<sub>2</sub><sup>Ethyl</sup>), 49.69 (s, 1C), 26.85 (s, 1C, CH<sub>3</sub>), 24.55 (s, 1C, CH<sub>3</sub>), 23.97 (s, 1C, CH<sub>3</sub>), 18.25 (s, 1C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 18.19 (s, 1C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 17.82 (s, 1C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 13.48 (s, 1C, CH<sub>3</sub><sup>Ethyl</sup>). **<sup>19</sup>F{<sup>1</sup>H} NMR** (C<sub>6</sub>D<sub>6</sub>, 376 MHz, 25°C): δ (in ppm) = -76.71 to -76.77 (m, 6F), -77.17 (s, 6F), -77.20 to -77.30 (m, 6F). **Elem. Anal. Calcd.** for C<sub>23</sub>H<sub>29</sub>F<sub>18</sub>N<sub>2</sub>O<sub>3</sub>Ta (904.42 g/mol): C, 30.54; H, 3.23; N, 3.10. **Found:** C, 31.06; H, 3.62; N, 3.25. Consistently low carbon values were obtained upon combustion of several samples, which may be related to carbide formation or to incomplete combustion. The reported value is 0.52 low in carbon.



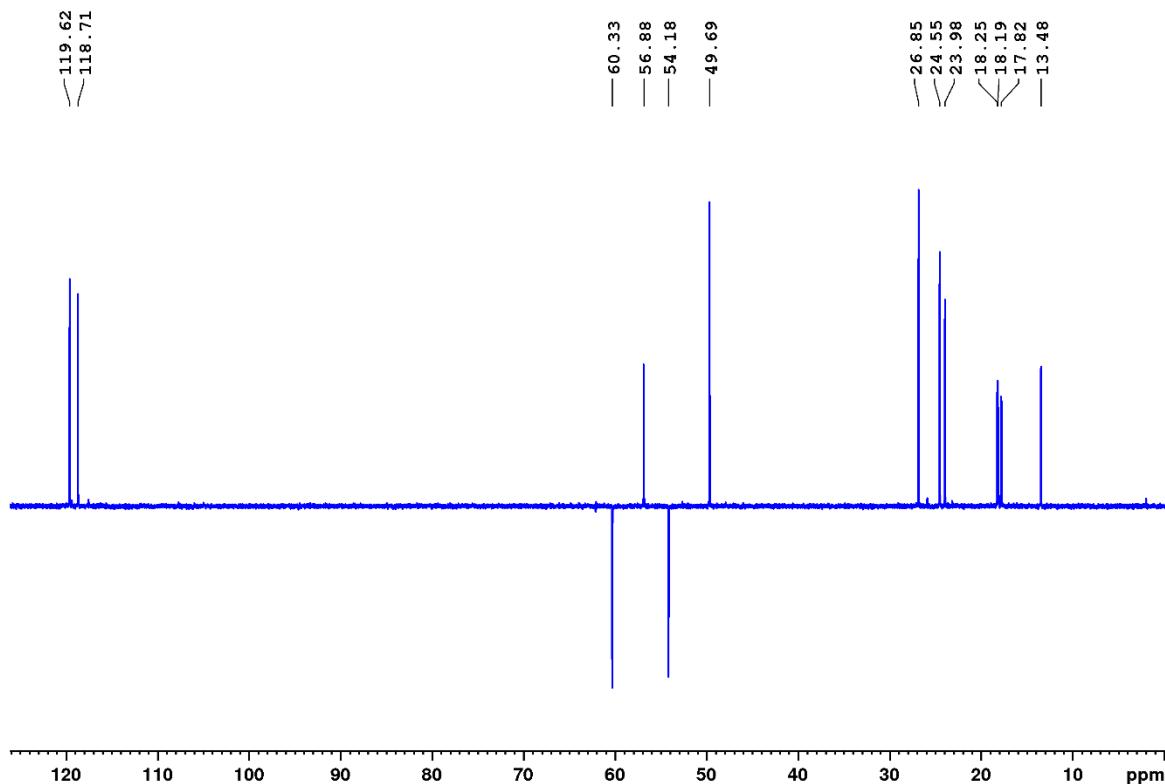
**Figure S35:**  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{C}_6\text{D}_6$ , 25°C) of **12**.



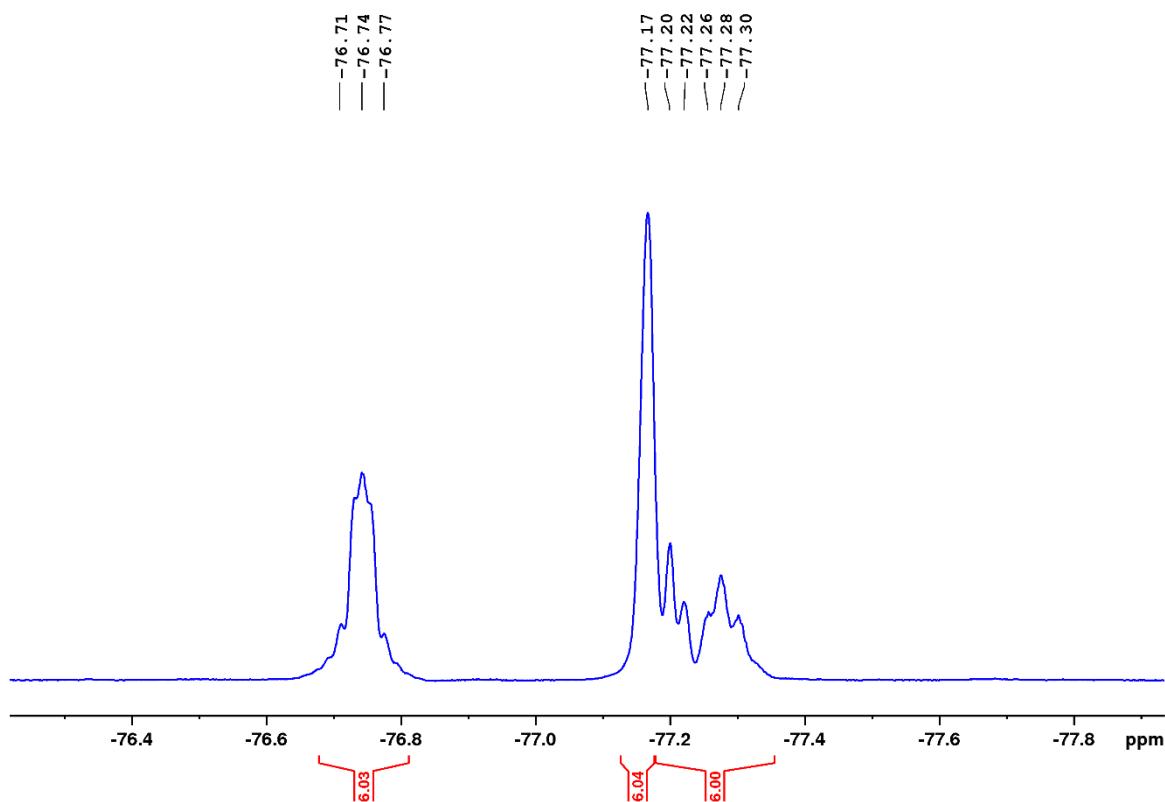
**Figure S36:**  $^1\text{H}/^1\text{H}$  COSY NMR spectrum (600 MHz,  $\text{C}_6\text{D}_6$ , 25°C) of **12**.



**Figure S37:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (151 MHz,  $\text{C}_6\text{D}_6$ , 25°C) of **12**.

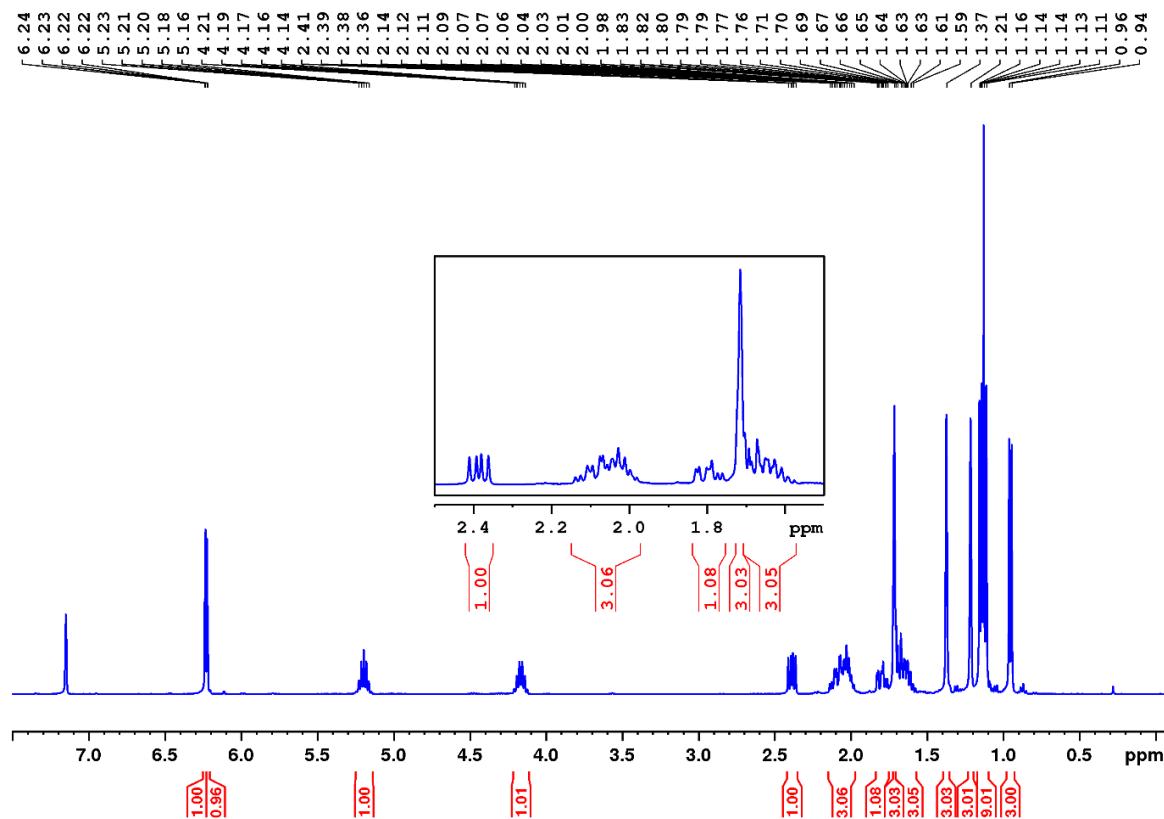
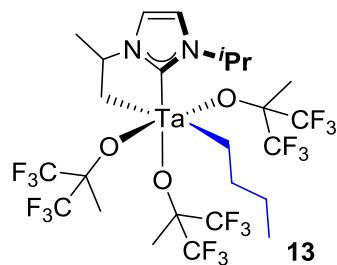


**Figure S38:** Section of the  $^{13}\text{C}\{^1\text{H}\}$  NMR DEPT-135 spectrum (151 MHz,  $\text{C}_6\text{D}_6$ , 25°C) of **12**.

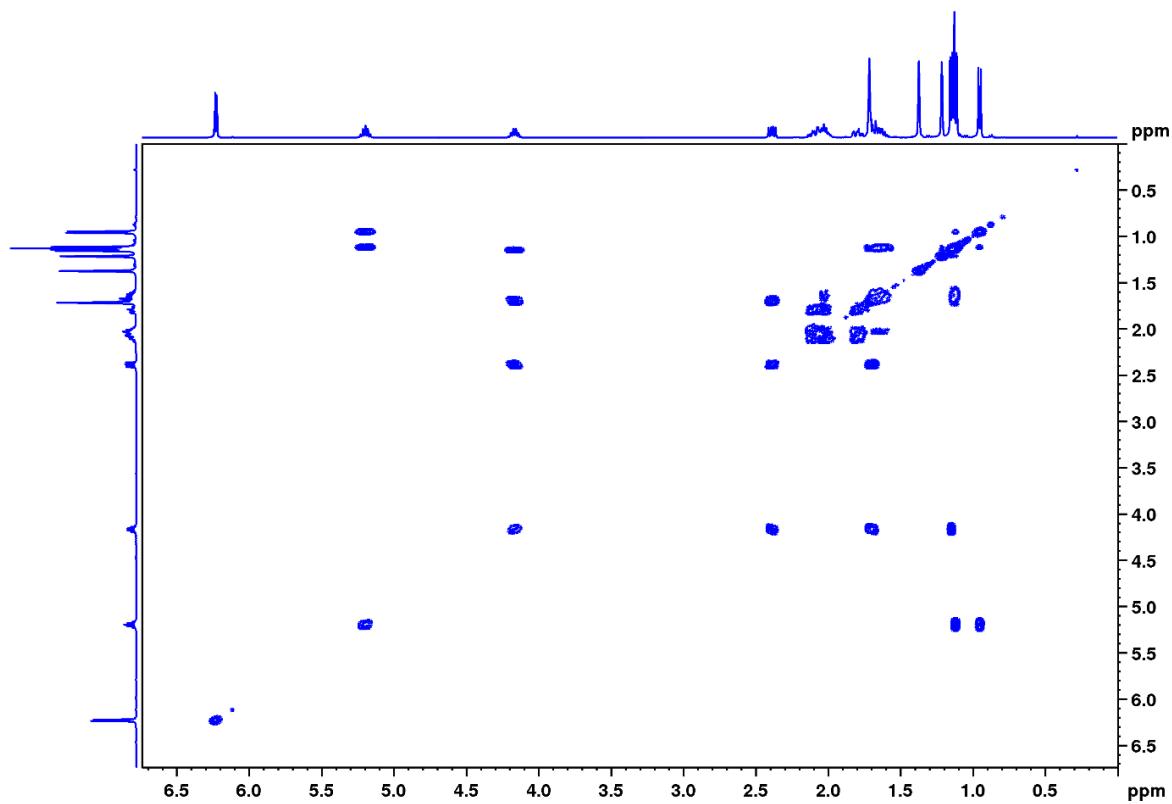


**Figure S39:**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum (376 MHz,  $\text{THF-d}_8$ , 25°C) of **12**.

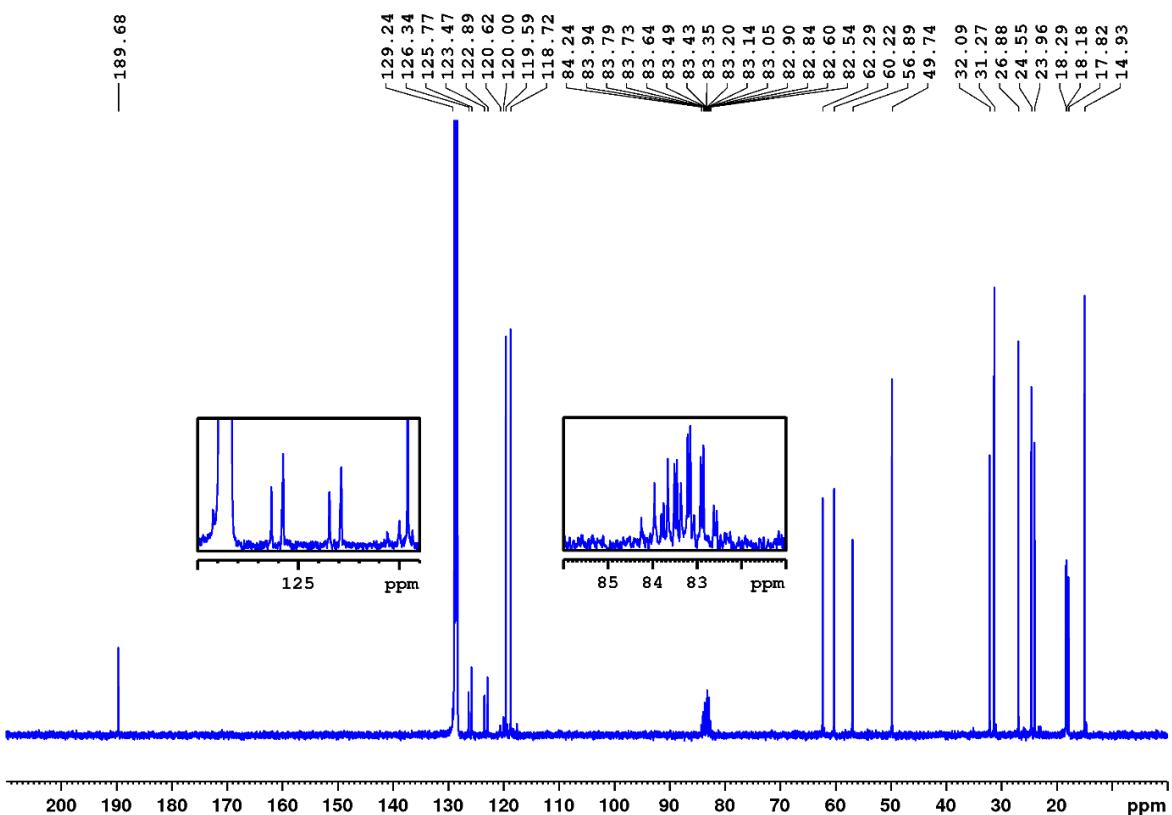
**Synthesis of 13.** A THF solution (0.27 M) of 1.0 eq of **7** (157 mg, 0.18 mmol) was pressurized with 1.8 bar of cis-2-butene in a high-pressure NMR-tube. The tube was sealed and heated for 1d at 65°C. After cooling to room temperature, the tube was transferred in an argon-filled glovebox. The solvent was removed in vacuum and the residue was taken up in pentane. The title compound was isolated by crystallization from a concentrated solution in pentane at -35°C and obtained as yellow crystalline solid (119 mg, 0.13 mmol, 71%).  **$^1\text{H}$  NMR** ( $\text{C}_6\text{D}_6$ , 400 MHz, 25°C):  $\delta$  (in ppm) = 6.24 (d,  $^3\text{J}_{\text{H-H}} = 2.0$  Hz, 1H), 6.22 (d,  $^3\text{J}_{\text{H-H}} = 2.0$  Hz, 1H), 5.20 (sept,  $^3\text{J}_{\text{H-H}} = 6.7$  Hz, 1H), 4.16 (sext,  $^3\text{J}_{\text{H-H}} = 6.9$  Hz, 1H), 2.39 (dd,  $^2\text{J}_{\text{H-H}} = 12.6$  Hz,  $^3\text{J}_{\text{H-H}} = 6.9$  Hz), 2.14 – 1.98 (m, 3H), 1.83 – 1.76 (m, 1H), 1.71 (s, 3H), 1.70 – 1.58 (m, 3H), 1.37 (s, 3H), 1.16 – 1.11 (m, 9H), 0.95 (d,  $^3\text{J}_{\text{H-H}} = 6.7$  Hz, 3H).  **$^{13}\text{C}\{^1\text{H}\}$  NMR** ( $\text{C}_6\text{D}_6$ , 101 MHz, 25°C):  $\delta$  (in ppm) = 189.68 (s, 1C, C<sup>Carbene</sup>), 124.91 (q,  $^1\text{J}_{\text{C-F}} = 289.6$  Hz, 4C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 124.33 (q,  $^1\text{J}_{\text{C-F}} = 289.4$  Hz, 2C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 119.59 (s, 1C, C<sup>Imidazole</sup>), 118.72 (s, 1C, C<sup>Imidazole</sup>), 84.24 – 82.54 (m, 3C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 62.29 (s, 1C, CH<sub>2</sub>), 60.22 (s, 1C, CH<sub>2</sub>), 56.89 (s, 1C, CH), 49.74 (s, 1C, CH), 32.09 (s, 1C, CH<sub>2</sub>), 31.27 (s, 1C, CH<sub>2</sub>), 26.88 (s, 1C, CH<sub>3</sub>), 24.55 (s, 1C, CH<sub>3</sub>), 23.96 (s, 1C, CH<sub>3</sub>), 18.29 (s, 1C, CH<sub>3</sub>), 18.18 (s, 1C, CH<sub>3</sub>), 17.82 (s, 1C, CH<sub>3</sub>), 14.93 (s, 1C, CH<sub>3</sub>).  **$^{19}\text{F}\{^1\text{H}\}$  NMR** ( $\text{C}_6\text{D}_6$ , 376 MHz, 25°C):  $\delta$  (in ppm) = -76.69 to -76.76 (m, 6F), -77.14 (s, 3F), -77.17 to -77.29 (m, 6F). **Elem. Anal. Calcd.** for C<sub>25</sub>H<sub>33</sub>F<sub>18</sub>N<sub>2</sub>O<sub>3</sub>Ta (932.47 g/mol): C, 32.20; H, 3.57; N, 3.00. **Found:** C, 32.37; H, 3.60; N, 3.10.



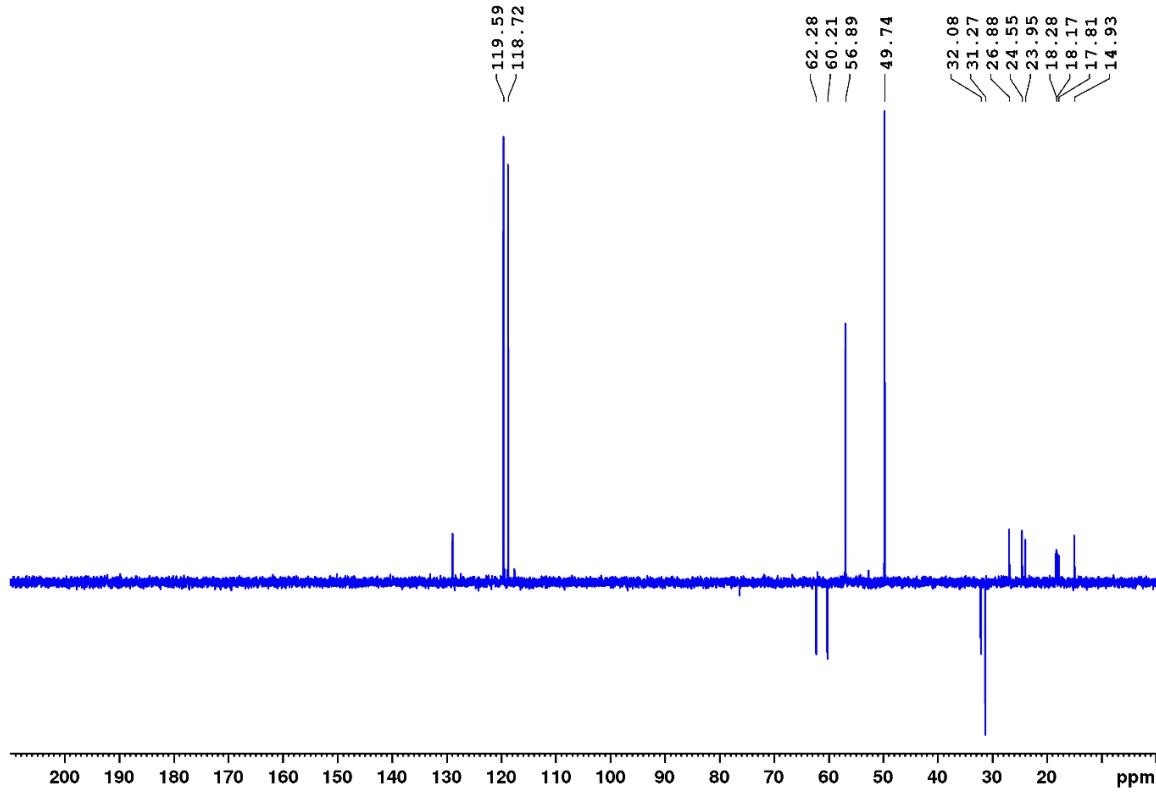
**Figure S40:**  $^1\text{H}$  NMR spectrum (400 MHz  $\text{C}_6\text{D}_6$ , 25°C) of **13**.



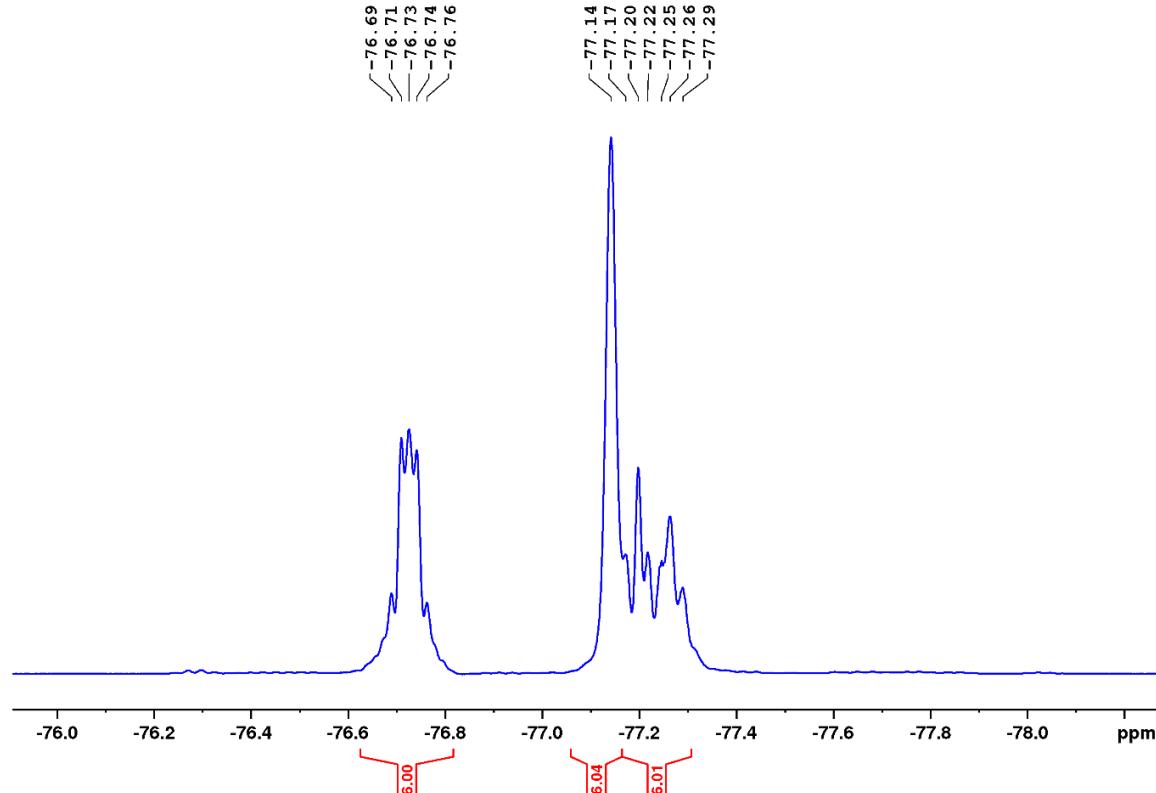
**Figure S41:**  $^1\text{H}/^1\text{H}$  COSY NMR spectrum (400 MHz,  $\text{C}_6\text{D}_6$ , 25°C) of **13**.



**Figure S42:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{C}_6\text{D}_6$ , 25°C) of **13**.



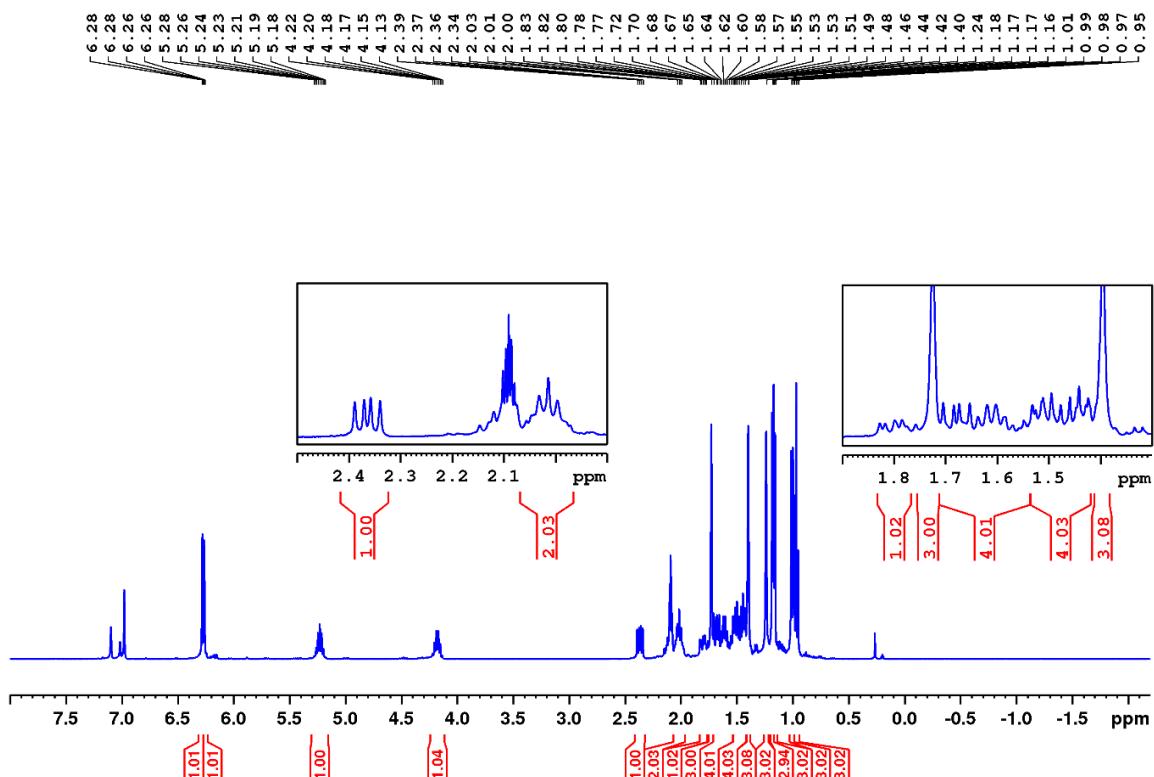
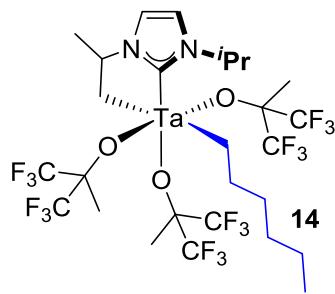
**Figure S43:**  $^{13}\text{C}$   $\{^1\text{H}\}$  DEPT-135 NMR spectrum (101 MHz,  $\text{C}_6\text{D}_6$ , 25°C) of **13**.



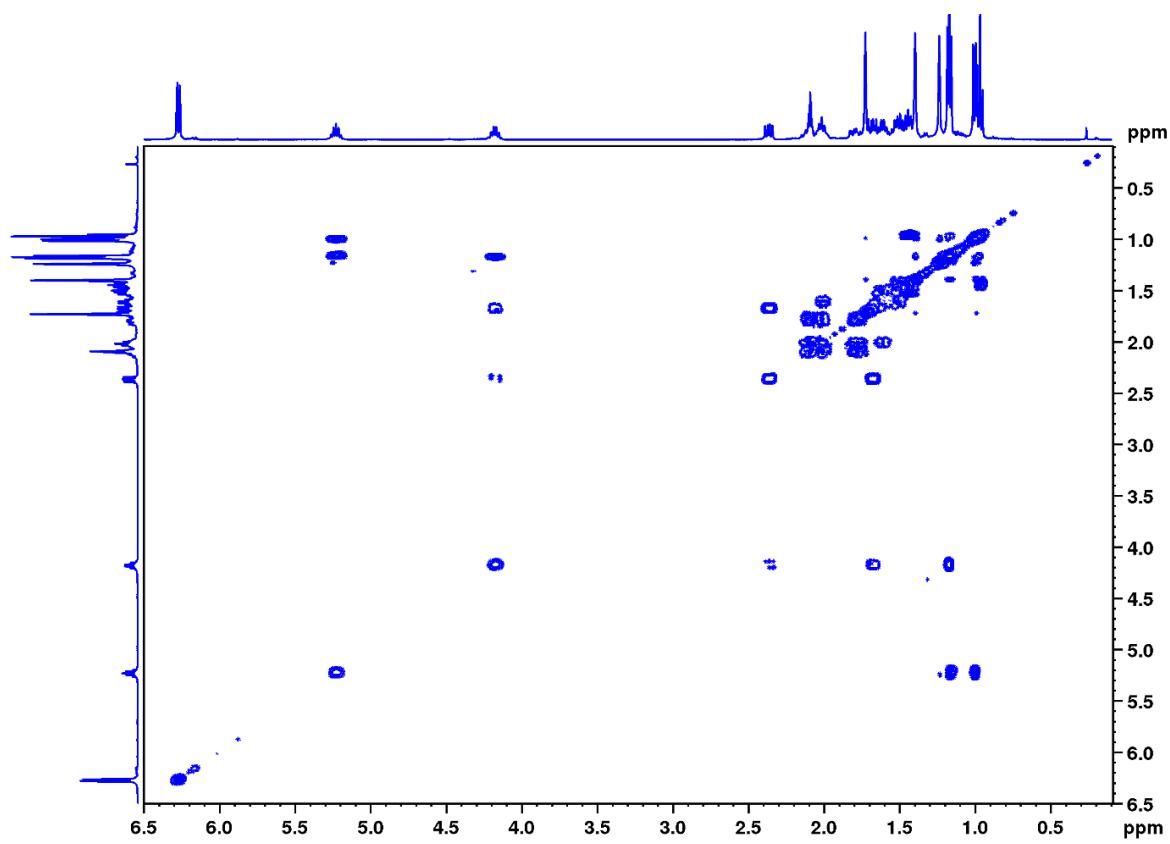
**Figure S44:**  $^{19}\text{F}$   $\{^1\text{H}\}$  NMR spectrum (376 MHz,  $\text{C}_6\text{D}_6$ , 25°C) of **13**.

**Synthesis of 14.** In an argon-filled glovebox, 10.0 eq of cis-3-hexene (108 mg, 1.3 mmol) were added to a THF-solution of 1.0 eq of **7** (115 mg, 0.13 mmol) in a *J. Young* NMR tube. The tube was sealed and heated for 1d at 65°C. After cooling to room temperature, the tube was transferred in an argon-filled glovebox. The solvent was removed in vacuum and the residue was taken up in pentane. The title compound was isolated by crystallization from a concentrated solution in pentane at -35°C and obtained as yellow crystalline solid (98.6 mg, 0.10 mmol, 77%).

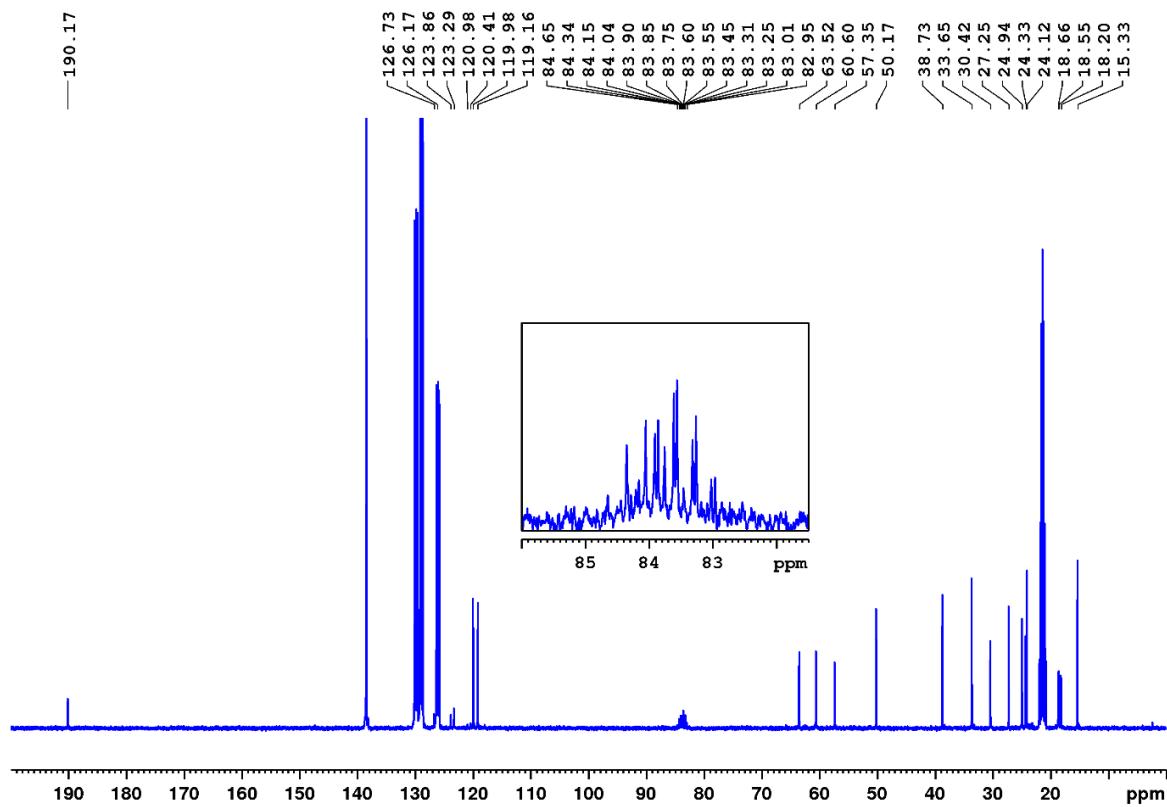
**<sup>1</sup>H NMR** (toluene-*d*<sub>8</sub>, 400 MHz, 25°C): δ (in ppm) = 6.28 (d, <sup>3</sup>J<sub>H-H</sub> = 1.9 Hz, 1H), 6.26 (d, <sup>3</sup>J<sub>H-H</sub> = 1.9 Hz, 1H), 5.23 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz, 1H), 4.18 (sext, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, 1H), 2.36 (dd, <sup>2</sup>J<sub>H-H</sub> = 12.3 Hz, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, 1H), 2.01 (t, <sup>3</sup>J<sub>H-H</sub> = 7.1 Hz, 2H), 1.83 - 1.77 (m, 1H), 1.72 (s, 3H), 1.70 - 1.55 (m, 4H), 1.53 - 1.42 (m, 4H), 1.40 (s, 3H), 1.24 (s, 3H), 1.18 (d, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, 3H), 1.16 (d, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz, 3H), 1.00 (d, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz, 3H), 0.97 (t, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, 3H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (toluene-*d*<sub>8</sub>, 101 MHz, 25°C): δ (in ppm) = 190.17 (s, 1C, C<sup>Carbene</sup>), 125.29 (q, <sup>1</sup>J<sub>C-F</sub> = 288.5 Hz, 2C), 124.73 (q, <sup>1</sup>J<sub>C-F</sub> = 289.7 Hz, 4C), 119.98 (s, 1C, C<sup>Imidazole</sup>), 119.16 (s, 1C, C<sup>Imidazole</sup>), 84.65 - 82.95 (m, 3C), 63.52 (s, 1C, CH<sub>2</sub>), 60.60 (s, 1C, CH<sub>2</sub>), 57.35 (s, 1C, CH), 50.17 (s, 1C, CH), 38.73 (s, 1C, CH<sub>2</sub>), 33.65 (s, 1C, CH<sub>2</sub>), 30.42 (s, 1C, CH<sub>2</sub>), 27.25 (s, 1C, CH<sub>3</sub>), 24.94 (s, 1C, CH<sub>3</sub>), 24.33 (s, 1C, CH<sub>3</sub>), 24.12 (s, 1C), 18.66 (s, 1C, CH<sub>3</sub>), 18.55 (s, 1C, CH<sub>3</sub>), 18.20 (s, 1C, CH<sub>3</sub>), 15.33 (s, 1C, CH<sub>3</sub>). **<sup>19</sup>F{<sup>1</sup>H} NMR** (C<sub>6</sub>D<sub>6</sub>, 376 MHz, 25°C): δ (in ppm) = -76.74 to -76.80 (m, 6F), -77.19 (s, 6F), -77.22 to -77.35 (m, 6F). **Elem. Anal. Calcd.** for C<sub>27</sub>H<sub>37</sub>F<sub>18</sub>N<sub>2</sub>O<sub>3</sub>Ta (960.5 g/mol): C, 33.76; H, 3.88; N, 2.92. **Found:** C, 34.02; H, 3.79; N, 3.02.



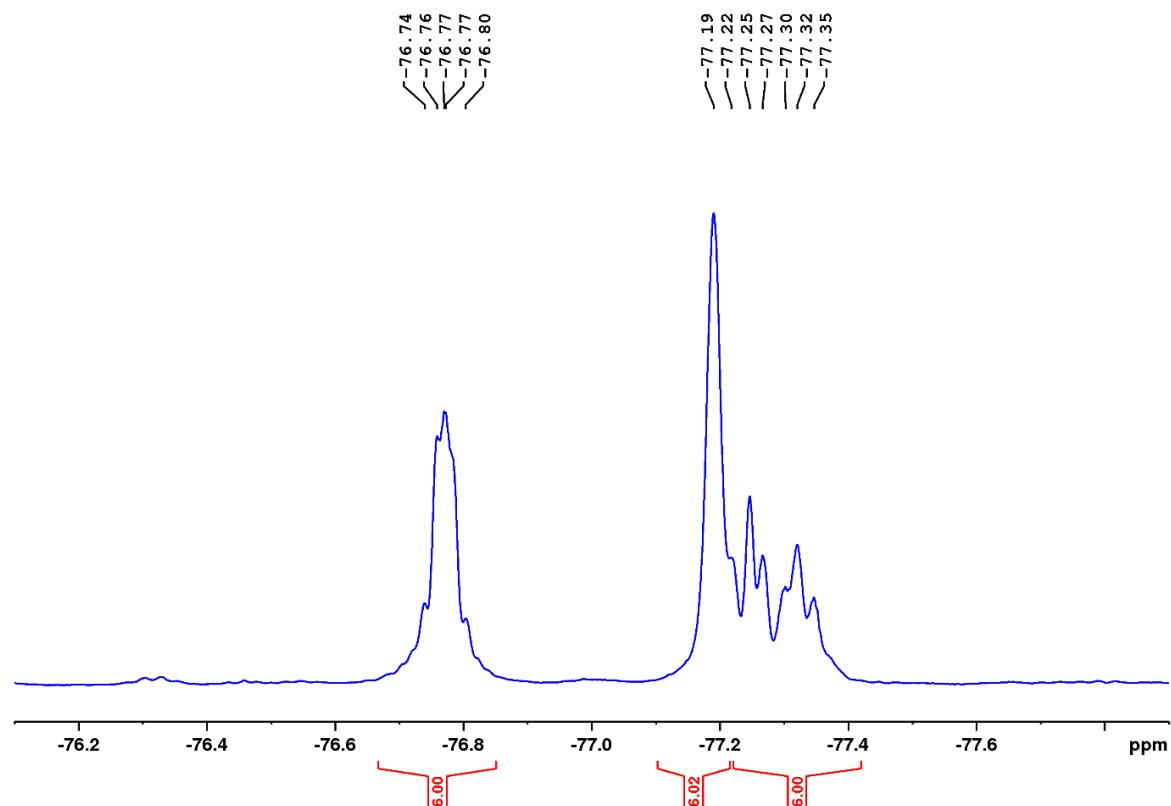
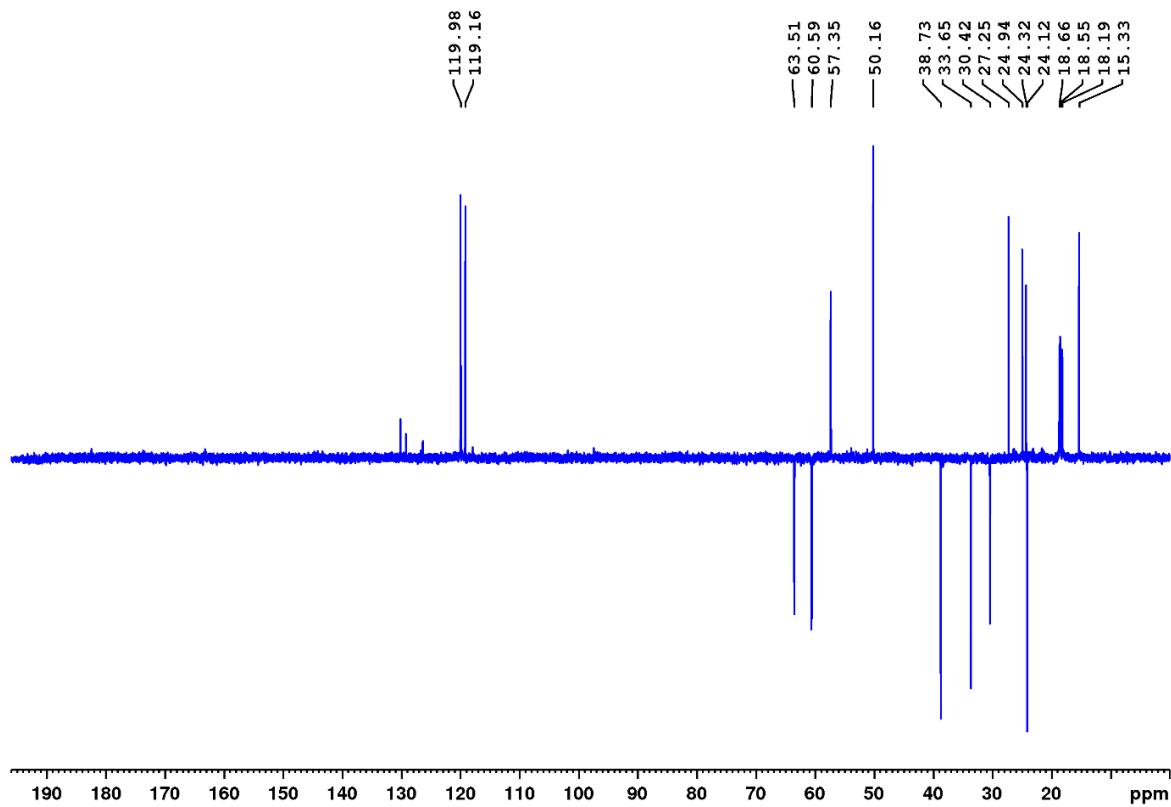
**Figure S45:** <sup>1</sup>H NMR spectrum (400 MHz, toluene-*d*<sub>8</sub>, 25°C) of **14**.



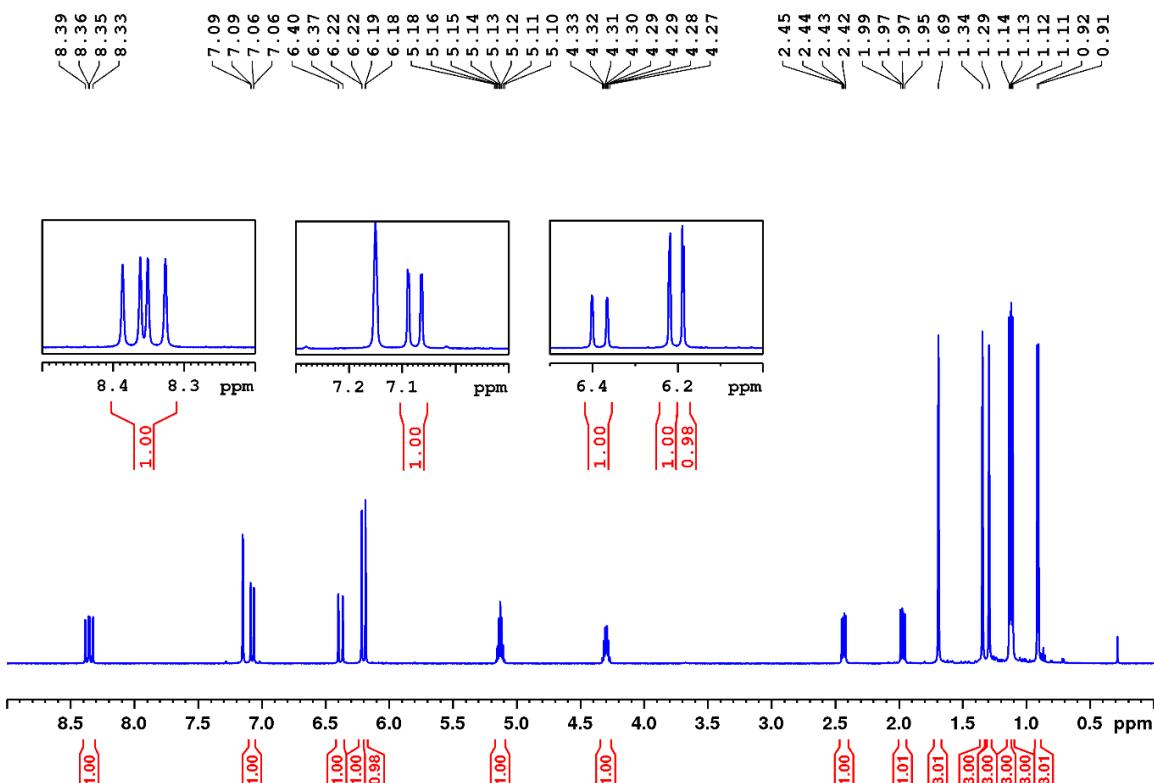
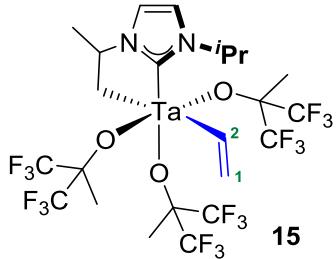
**Figure S46:**  $^1\text{H}/^1\text{H}$  COSY NMR spectrum (400 MHz, toluene- $d_8$ , 25°C) of **14**.



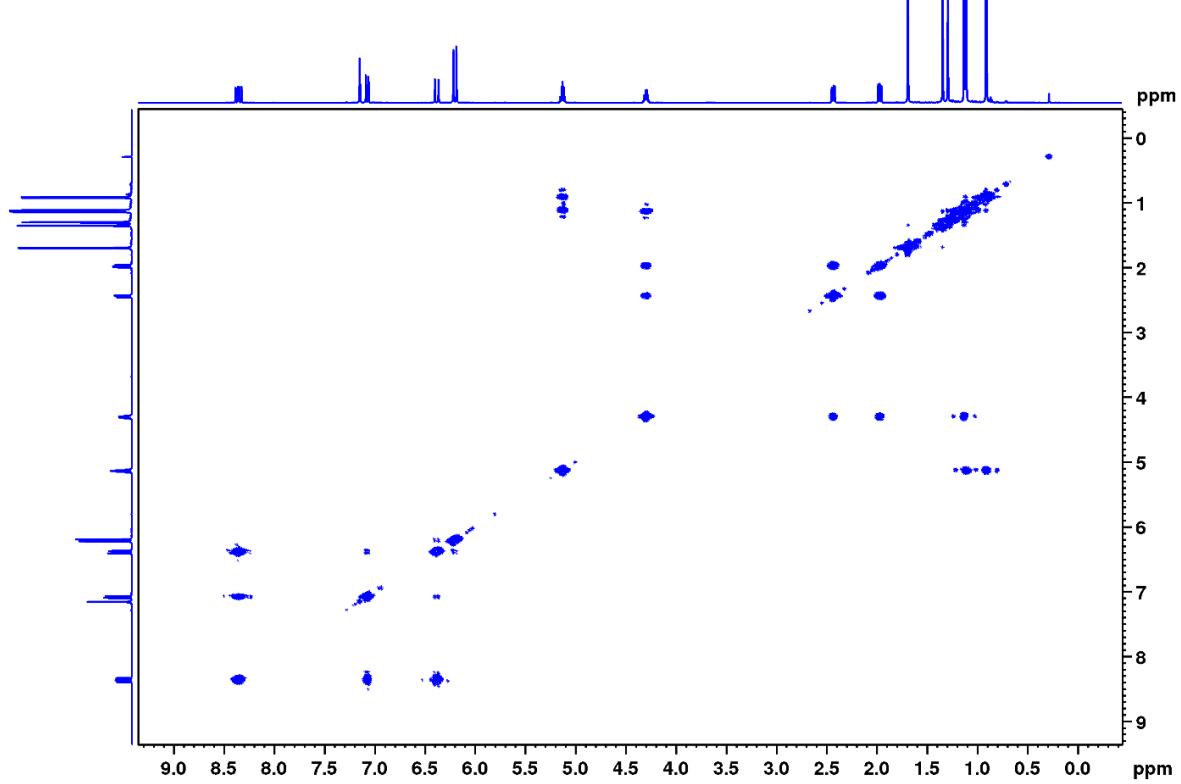
**Figure S47:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz, toluene- $d_8$ , 25°C) of **14**.



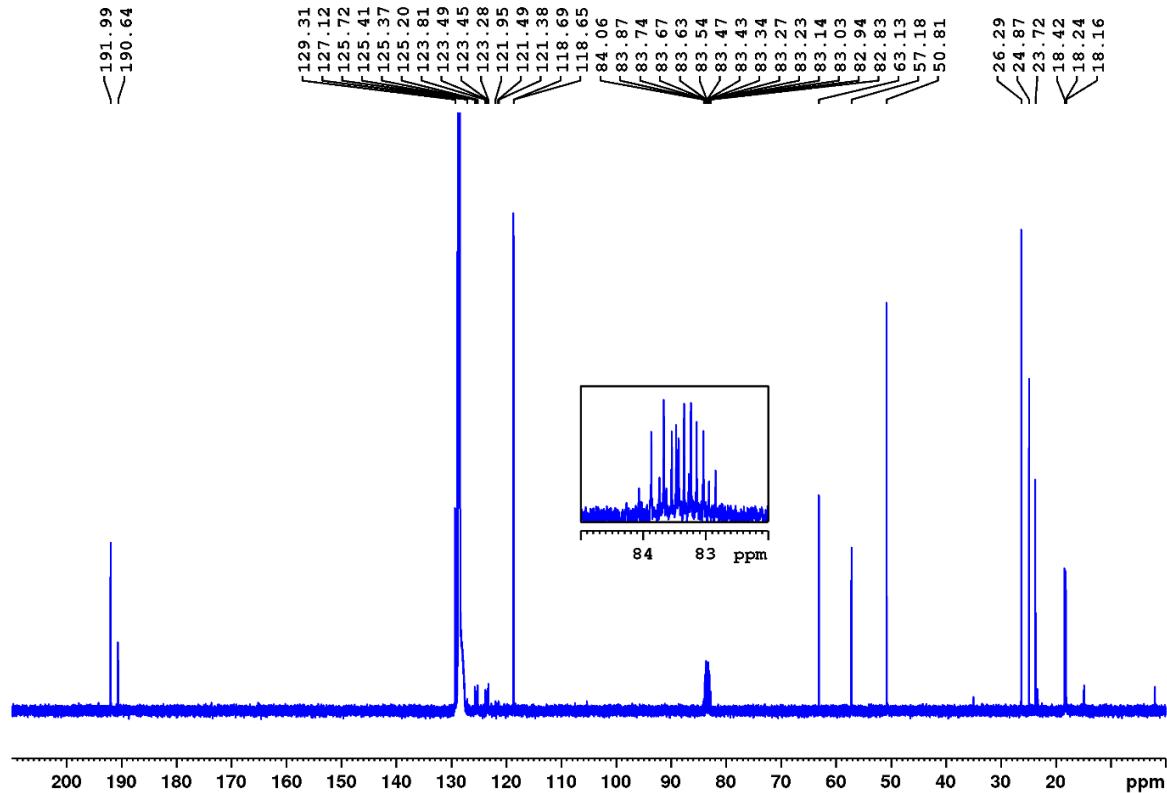
**Synthesis of 15.** A THF solution (0.27 M) of 1.0 eq of **7** (113 mg, 0.13 mmol) was pressurized with 1.5 bar of acetylene in a high-pressure NMR-tube. The tube was sealed and heated for 1d at 60°C. After cooling to room temperature, the tube was transferred in an argon-filled glovebox. The solvent was removed in vacuum and the residue was taken up in pentane. The title compound was isolated by crystallization from a concentrated solution in pentane at -35°C and obtained as pale yellow crystalline solid (64.4 mg, 0.07 mmol, 55%). **<sup>1</sup>H NMR** ( $C_6D_6$ , 600 MHz, 25°C):  $\delta$  (in ppm) = 8.36 (dd,  $J_{H-H} = 21.2$  Hz,  $J_{H-H} = 15.0$  Hz, 1H, H-1), 7.08 (dd,  $J_{H-H} = 15.0$  Hz,  $J_{H-H} = 1.4$  Hz, 1H, H-2), 6.38 (d,  $J_{H-H} = 21.2$  Hz, 1H, H-1), 6.22 (d,  $J_{H-H} = 2.0$  Hz, 1H), 6.19 (d,  $J_{H-H} = 2.0$  Hz, 1H), 5.13 (sept,  $J_{H-H} = 6.7$  Hz, 1H), 4.33 - 4.27 (m, 1H), 2.43 (dd,  $J_{H-H} = 11.8$  Hz,  $J_{H-H} = 6.7$  Hz, 1H), 1.97 (dd,  $J_{H-H} = 12.2$  Hz,  $J_{H-H} = 8.6$  Hz, 1H), 1.69 (s, 3H), 1.35 (s, 3H), 1.29 (s, 3H), 1.13 (d,  $J_{H-H} = 6.5$  Hz, 3H), 1.11 (d,  $J_{H-H} = 6.7$  Hz, 3H), 0.91 (d,  $J_{H-H} = 6.7$  Hz, 3H). **<sup>13</sup>C{<sup>1</sup>H NMR}** ( $C_6D_6$ , 151 MHz, 25°C):  $\delta$  (in ppm) = 191.99 (s, 1C,  $TaCH=CH_2$ ), 190.64 (s, 1C,  $C^{Carbene}$ ), 129.31 (s, 1C,  $TaCH=CH_2$ ), 127.12 - 121.38 (m, 6C,  $OC(CF_3)_2CH_3$ ), 118.69 (s, 1C,  $C^{Imidazol}$ ), 118.65 (s, 1C,  $C^{Imidazol}$ ), 84.06 - 82.83 (m, 3C,  $OC(CF_3)_2CH_3$ ), 63.13 (s, 1C,  $CH_2$ ), 57.18 (s, 1C,  $CH$ ), 50.81 (s, 1C,  $CH$ ), 26.29 (s, 1C,  $CH_3$ ), 24.87 (s, 1C,  $CH_3$ ), 23.72 (s, 1C,  $CH_3$ ), 18.42 (s, 1C,  $CH_3$ ), 18.24 (s, 1C,  $CH_3$ ), 18.16 (s, 1C,  $CH_3$ ). **<sup>19</sup>F{<sup>1</sup>H NMR}** ( $C_6D_6$ , 376 MHz, 25°C):  $\delta$  (in ppm) = -76.25 to -76.33 (m, 3F), -76.38 to -76.46 (m, 3F), -77.16 (br s, 6F), -77.63 (br s, 6F). **Elem. Anal. Calcd.** for  $C_{23}H_{27}F_{18}N_2O_3Ta$  (902.40 g/mol): C, 30.61; H, 3.02; N, 3.10. **Found:** C, 30.22; H, 3.02; N, 3.27.



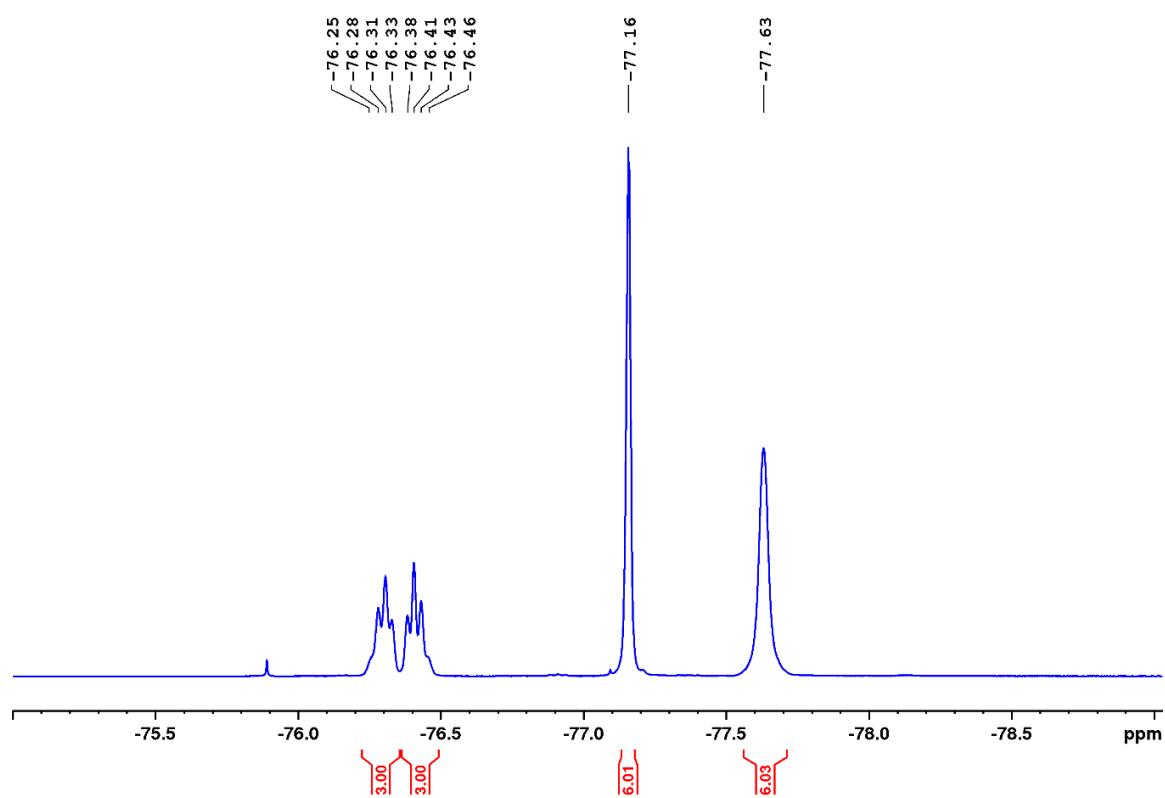
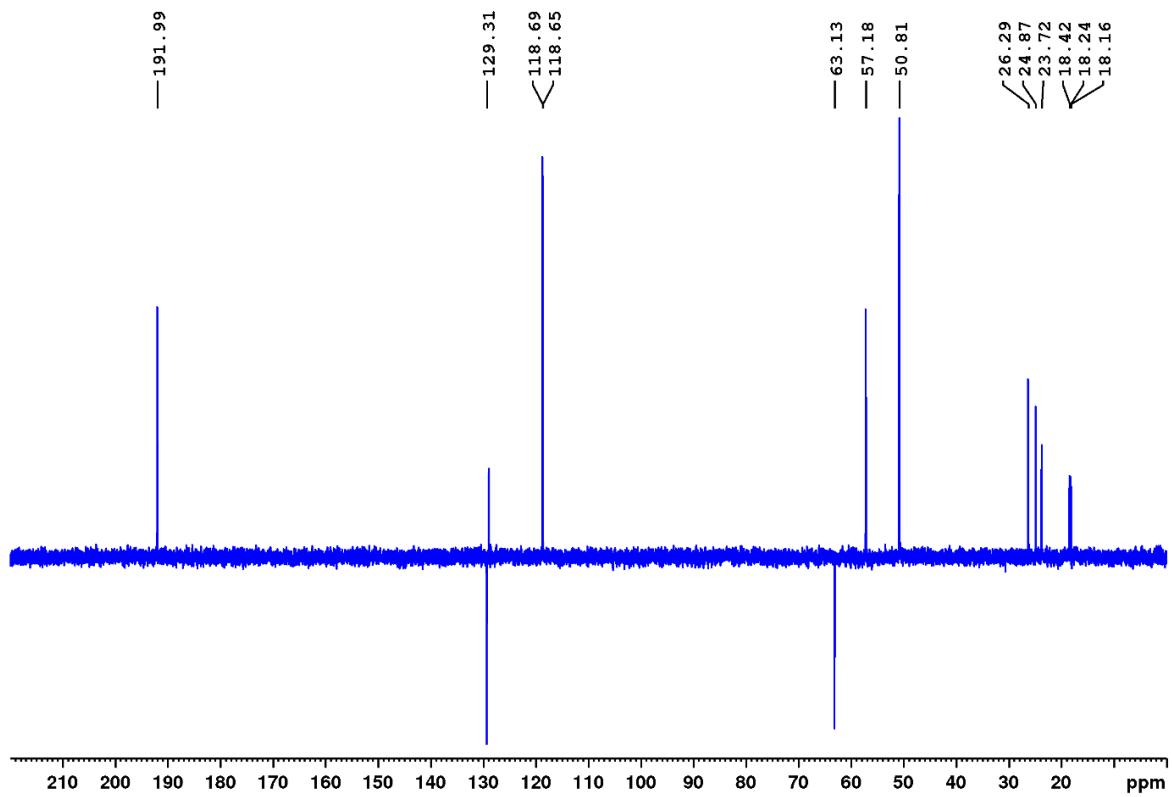
**Figure S50:**  $^1\text{H}$  NMR spectrum (600 MHz  $\text{C}_6\text{D}_6$ , 25°C) of **15**.



**Figure S51:**  $^1\text{H}/^1\text{H}$  COSY NMR spectrum (600 MHz,  $\text{C}_6\text{D}_6$ , 25°C) of **15**.



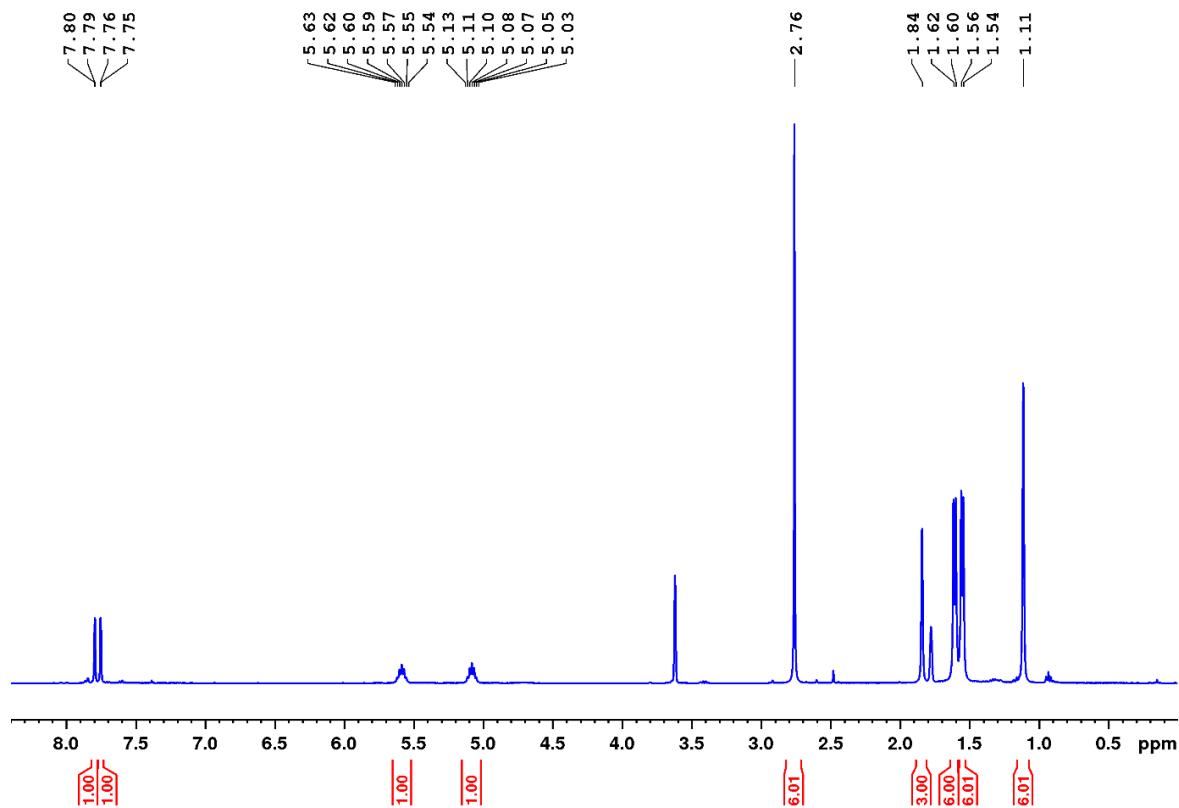
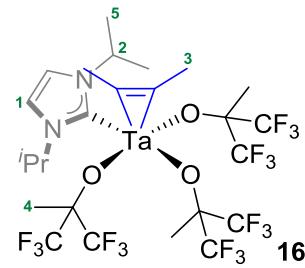
**Figure S52:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (151 MHz,  $\text{C}_6\text{D}_6$ , 25°C) of **15**.



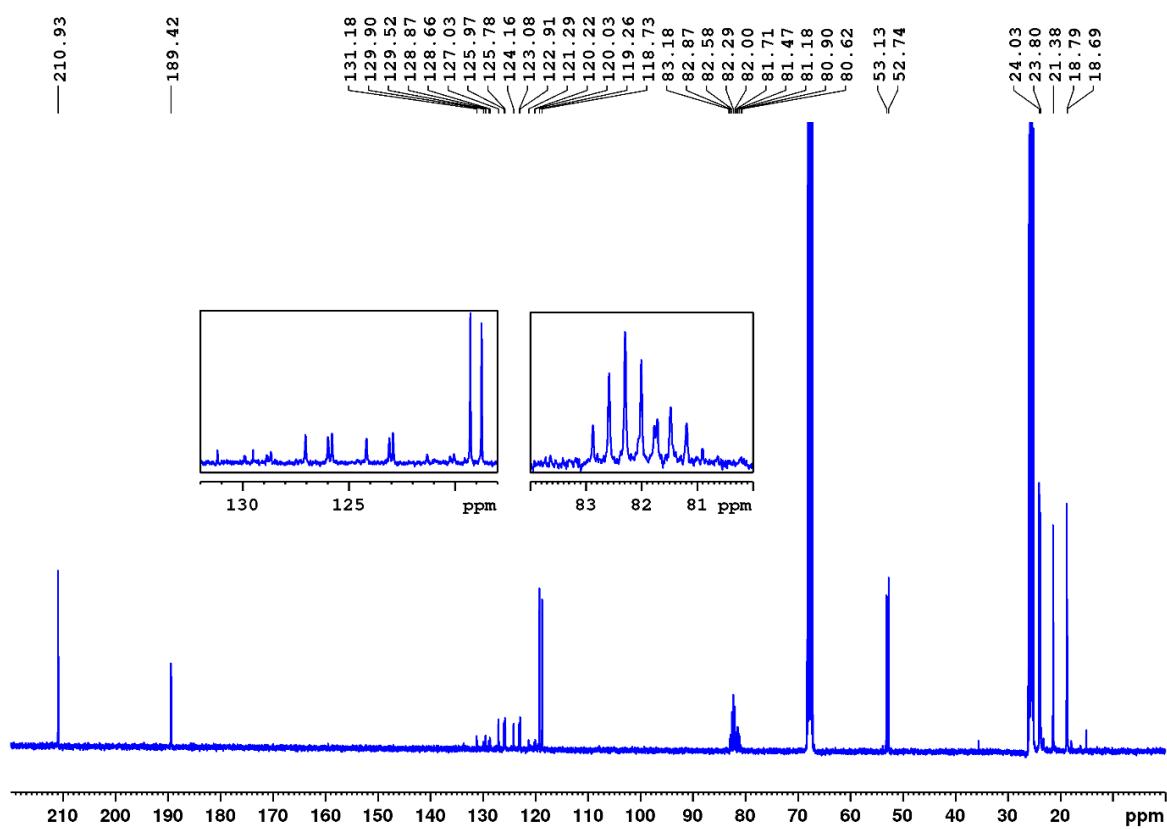
**Figure S54:** <sup>19</sup>F {<sup>1</sup>H} NMR spectrum (376 MHz, C<sub>6</sub>D<sub>6</sub>, 25°C) of **15**.

**Synthesis of 16.** In an argon-filled glovebox, 1.0 eq of **7** (201 mg, 0.23 mmol) was dissolved in 2 ml of THF. Then 10.0 eq of 2-butyne (124 mg, 2.3 mmol) were added and the mixture was stirred for 20 min at room temperature. The solvent was removed in vacuum and the residue was taken up in THF. The solution was then heated at 60°C for 1d. Again the solvent was removed in vacuum and title compound was isolated by crystallization from a concentrated solution in pentane/Et<sub>2</sub>O (10:1) at -35°C

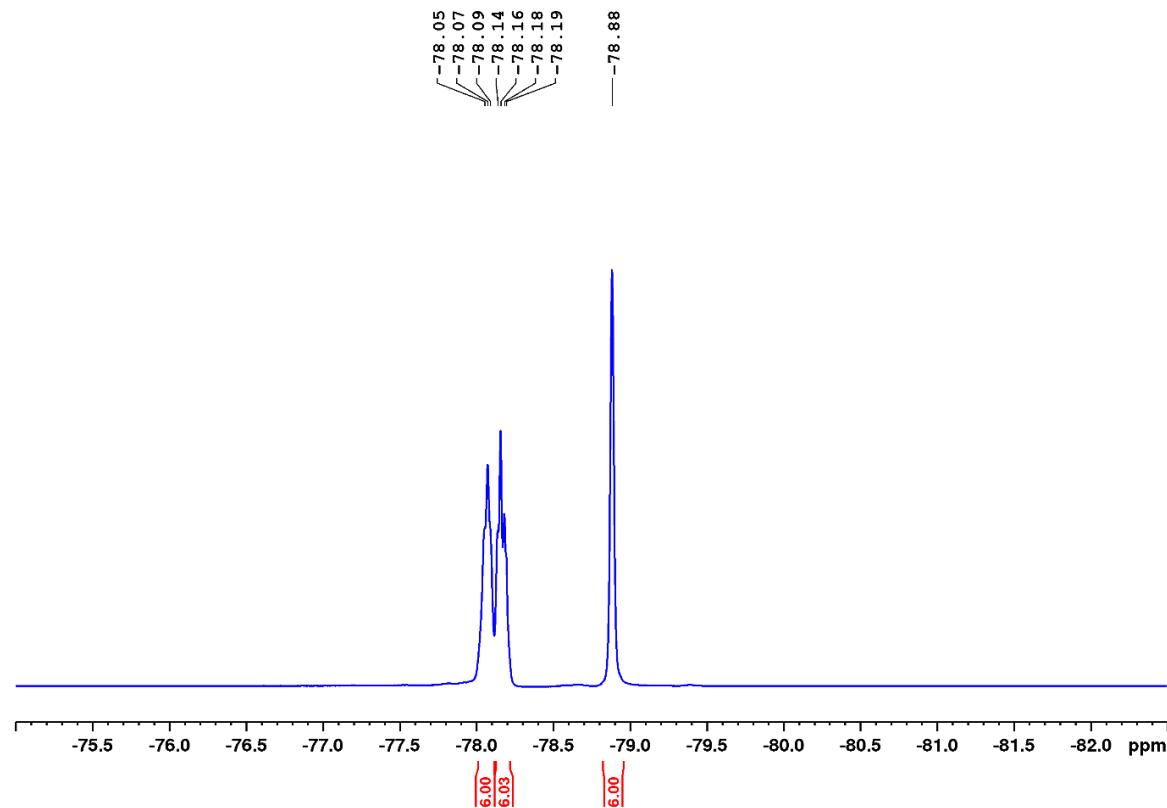
and obtained as a pale yellow crystalline solid (141 mg, 0.15 mmol, 66%). **<sup>1</sup>H NMR** (THF-d<sub>8</sub>, 400 MHz, -60°C): δ (in ppm) = 7.80 (d, <sup>3</sup>J<sub>H-H</sub> = 1.7 Hz, 1H, H-1), 7.75 (d, <sup>3</sup>J<sub>H-H</sub> = 1.7 Hz, 1H, H-1), 5.59 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, 1H, H-2), 5.08 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.4 Hz, 1H, H-2), 2.76 (s, 6H, H-3), 1.84 (s, 3H, H-4), 1.61 (d, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, 6H, H-5), 1.55 (d, <sup>3</sup>J<sub>H-H</sub> = 6.4 Hz, 6H, H-5), 1.11 (s, 6H, H-4). **<sup>13</sup>C{<sup>1</sup>H} NMR** (THF-d<sub>8</sub>, 101 MHz, -60°C): δ (in ppm) = 210.93 (s, 2C, C<sup>Alkyne</sup>), 189.42 (s, 1C, C<sup>Carbene</sup>), 131.18 - 120.03 (m, 6C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 119.26 (s, 1C, C<sup>Imidazole</sup>), 118.73 (s, 1C, C<sup>Imidazole</sup>), 82.29 (sept, <sup>2</sup>J<sub>C-F</sub> = 29.1 Hz, 2C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 81.47 (sept, <sup>2</sup>J<sub>C-F</sub> = 29.0 Hz, 1C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 53.13 (s, 1C, CH), 52.74 (s, 1C, CH), 24.03 (s, 2C, CH<sub>3</sub>), 23.80 (s, 2C, CH<sub>3</sub>), 21.38 (s, 2C, CH<sub>3</sub>), 18.79 (s, 2C, CH<sub>3</sub>), 18.69 (s, 1C, CH<sub>3</sub>). **<sup>19</sup>F{<sup>1</sup>H} NMR** (THF-d<sub>8</sub>, 376 MHz, -60°C): δ (in ppm) = -78.05 to -78.09 (m, 6F), -78.14 to -78.19 (m, 6F), -78.88 (s, 6F). **Elem. Anal. Calcd.** for C<sub>25</sub>H<sub>31</sub>F<sub>18</sub>N<sub>2</sub>O<sub>3</sub>Ta (930.45 g/mol): C, 32.27; H, 3.36; N, 3.01. **Found:** C, 32.51; H, 3.47; N, 3.18.



**Figure S55:** <sup>1</sup>H NMR spectrum (400MHz, THF-d<sub>8</sub>, -60°C) of **16**.



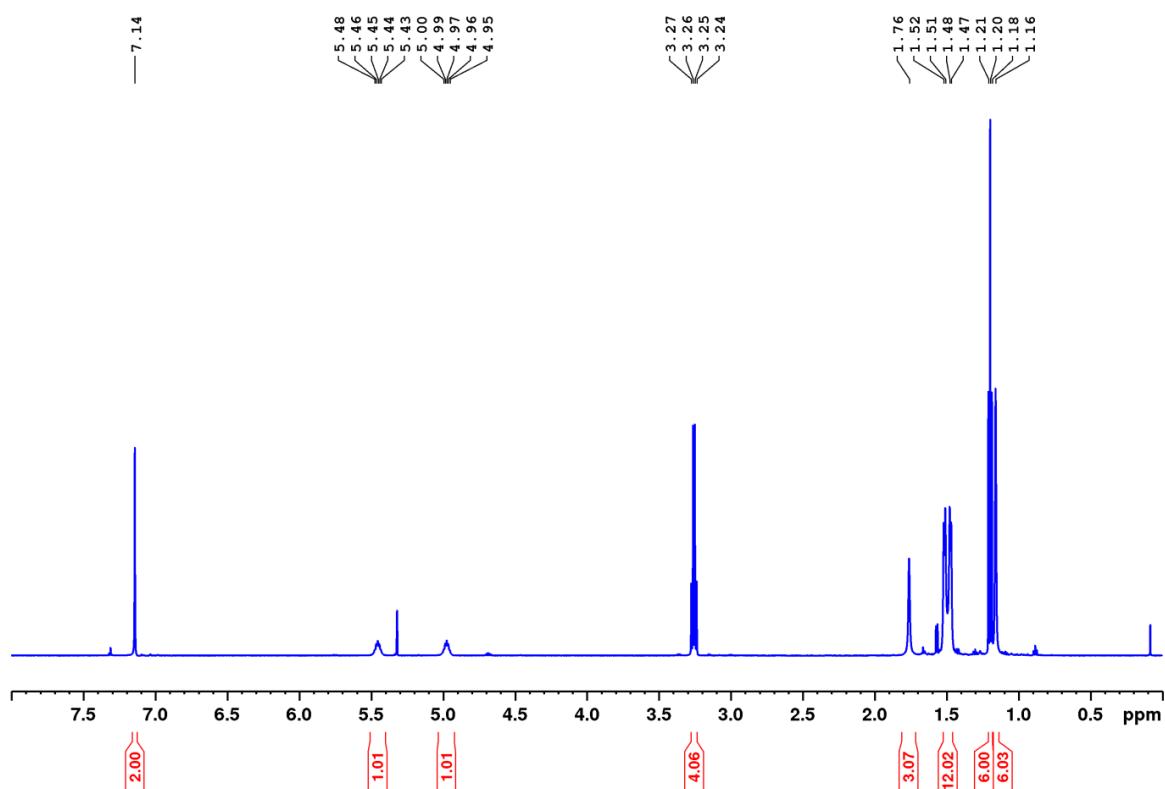
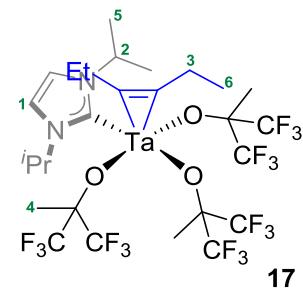
**Figure S56:** <sup>13</sup>C {<sup>1</sup>H} NMR spectrum (101MHz, THF-d<sub>8</sub>, -60°C) of **16**.



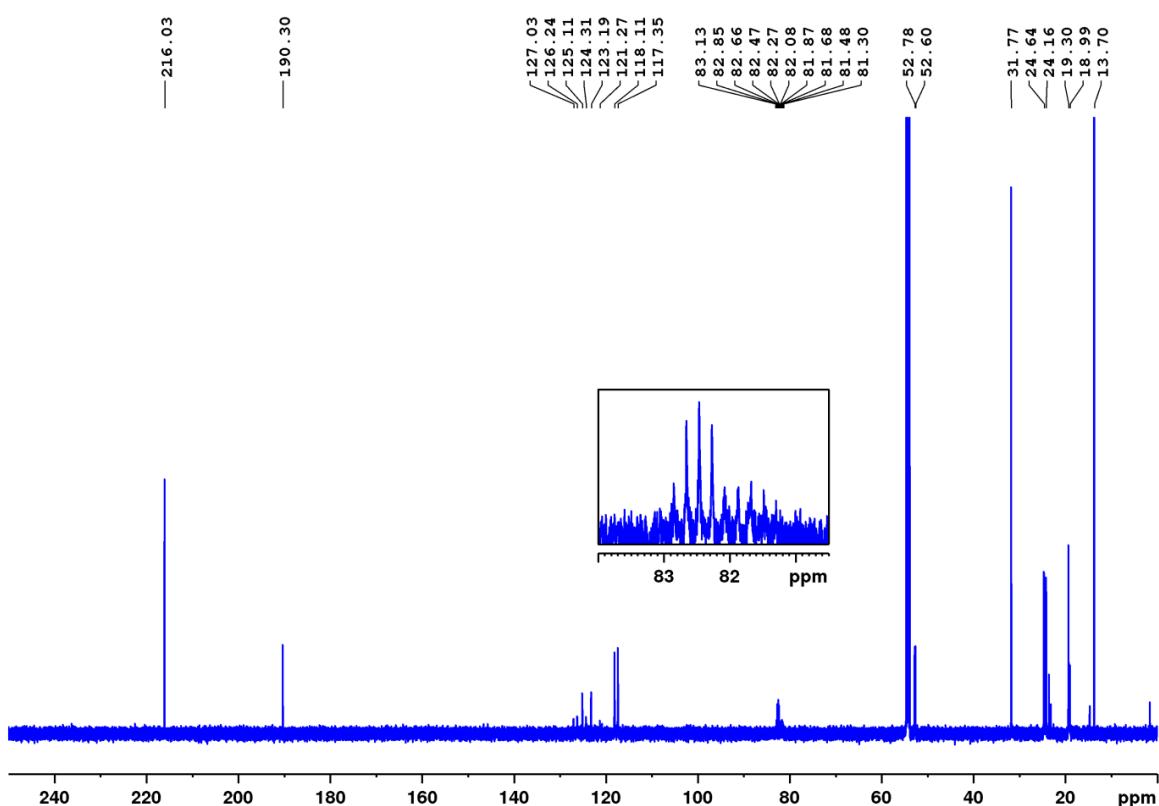
**Figure S57:** <sup>19</sup>F {<sup>1</sup>H} NMR spectrum (376 MHz, THF-d<sub>8</sub>, -60°C) of **16**.

**Synthesis of 17.** In an argon-filled glovebox, 1.0 eq of **7** (112 mg, 0.13 mmol) was dissolved in 2 ml of toluene. Then 10.0 eq of 3-hexyne (108 mg, 13.2 mmol) were added and the mixture was heated at 65°C for 1d. The solvent was removed in vacuum and the residue was taken up in pentane and filtered through a pad of celite. The title compound was isolated by crystallization from a concentrated solution in pentane at -35°C and obtained as a yellow microcrystalline powder (84.7 mg, 0.09 mmol, 68%).

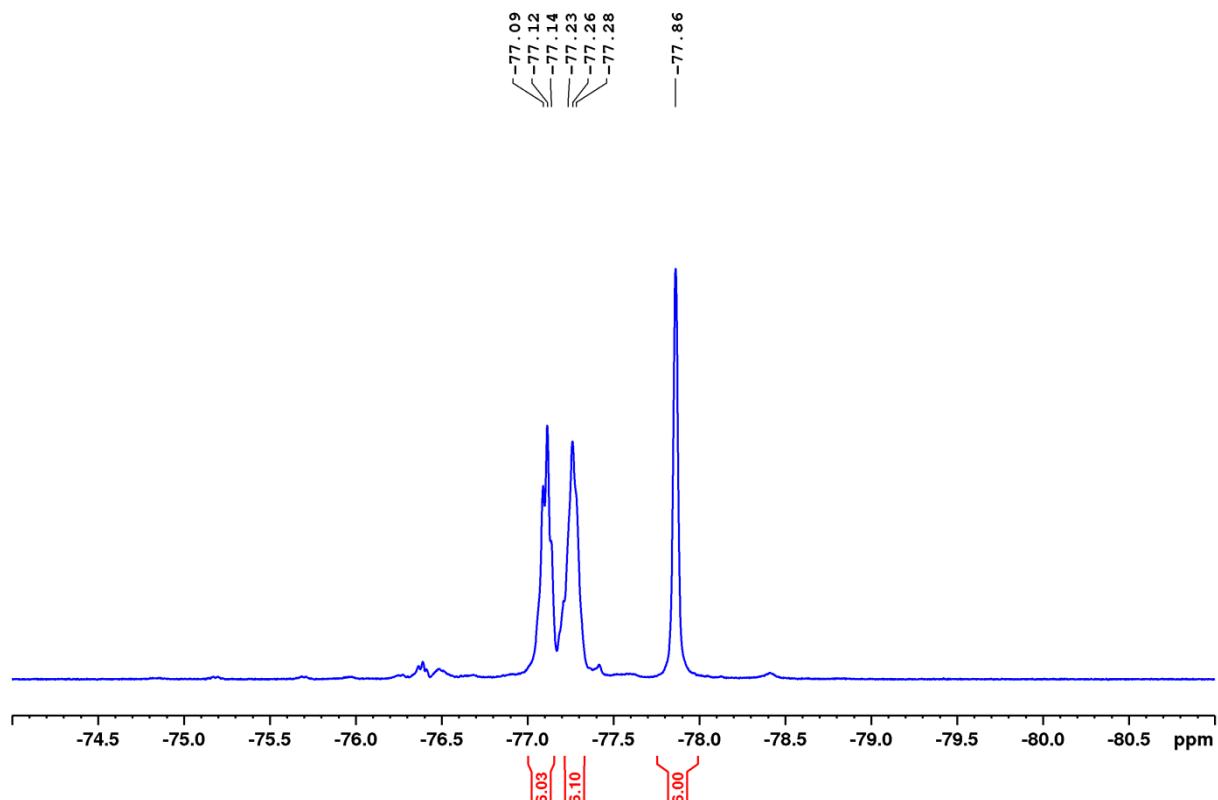
**$^1\text{H}$  NMR** ( $\text{CD}_2\text{Cl}_2$ , 600 MHz, 25°C):  $\delta$  (in ppm) = 7.14 (s, 2H, H-1), 5.45 (sept,  $^3J_{\text{H-H}} = 6.4$  Hz, 1H, H-2), 4.97 (sept,  $^3J_{\text{H-H}} = 6.5$  Hz, 1H, H-2), 3.26 (q,  $^3J_{\text{H-H}} = 7.6$  Hz, 4H, H-3), 1.76 (s, 3H, H-4), 1.51 (d,  $^3J_{\text{H-H}} = 6.5$  Hz, 6H, H-5), 1.47 (d,  $^3J_{\text{H-H}} = 6.4$  Hz, 6H, H-5), 1.20 (t,  $^3J_{\text{H-H}} = 7.6$  Hz, 6H, H-6), 1.16 (s, 6H, H-4).  **$^{13}\text{C}\{^1\text{H}\}$  NMR** ( $\text{CD}_2\text{Cl}_2$ , 151 MHz, 25°C):  $\delta$  (in ppm) = 216.03 (s, 2C, C<sup>Alkyne</sup>), 190.30 (s, 1C, C<sup>Carbene</sup>), 127.03 - 121.27 (m, 6C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 118.11 (s, 1C, C<sup>Imidazole</sup>), 117.35 (s, 1C, C<sup>Imidazole</sup>), 83.13 - 81.30 (m, 3C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 52.78 (s, 1C), 52.60 (s, 1C), 31.77 (s, 2C, CH<sub>2</sub>), 24.64 (s, 2C, CH<sub>3</sub>), 24.16 (s, 2C, CH<sub>3</sub>), 19.30 (s, 2C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 18.99 (s, 1C, OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 13.70 (s, 2C, CH<sub>3</sub>).  **$^{19}\text{F}\{^1\text{H}\}$  NMR** ( $\text{CD}_2\text{Cl}_2$ , 376 MHz, 25°C):  $\delta$  (in ppm) = -77.09 to -77.14 (m, 6F), -77.23 to -77.28 (m, 6F), -77.86 (s, 6F). **Elem. Anal. Calcd.** for  $\text{C}_{27}\text{H}_{35}\text{F}_{18}\text{N}_2\text{O}_3\text{Ta}$  (958.51 g/mol): C, 33.83; H, 3.68; N, 2.92. **Found:** C, 33.72; H, 3.65; N, 2.95.



**Figure S58:**  $^1\text{H}$  NMR spectrum (600MHz,  $\text{CD}_2\text{Cl}_2$ , 25°C) of **17**.

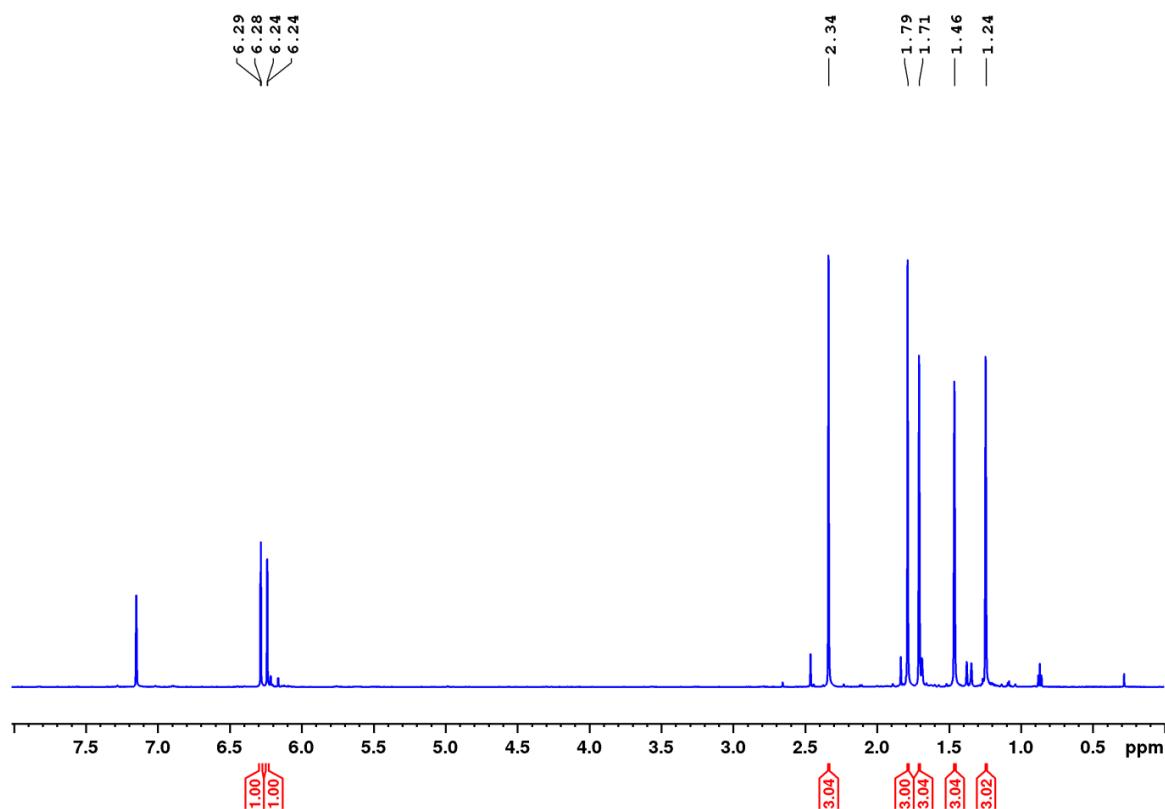
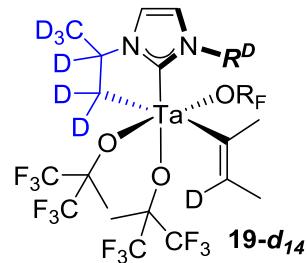


**Figure S59:**  $^{13}\text{C}$  { $^1\text{H}$ } NMR spectrum (151MHz,  $\text{CD}_2\text{Cl}_2$ , 25°C) of **17**.

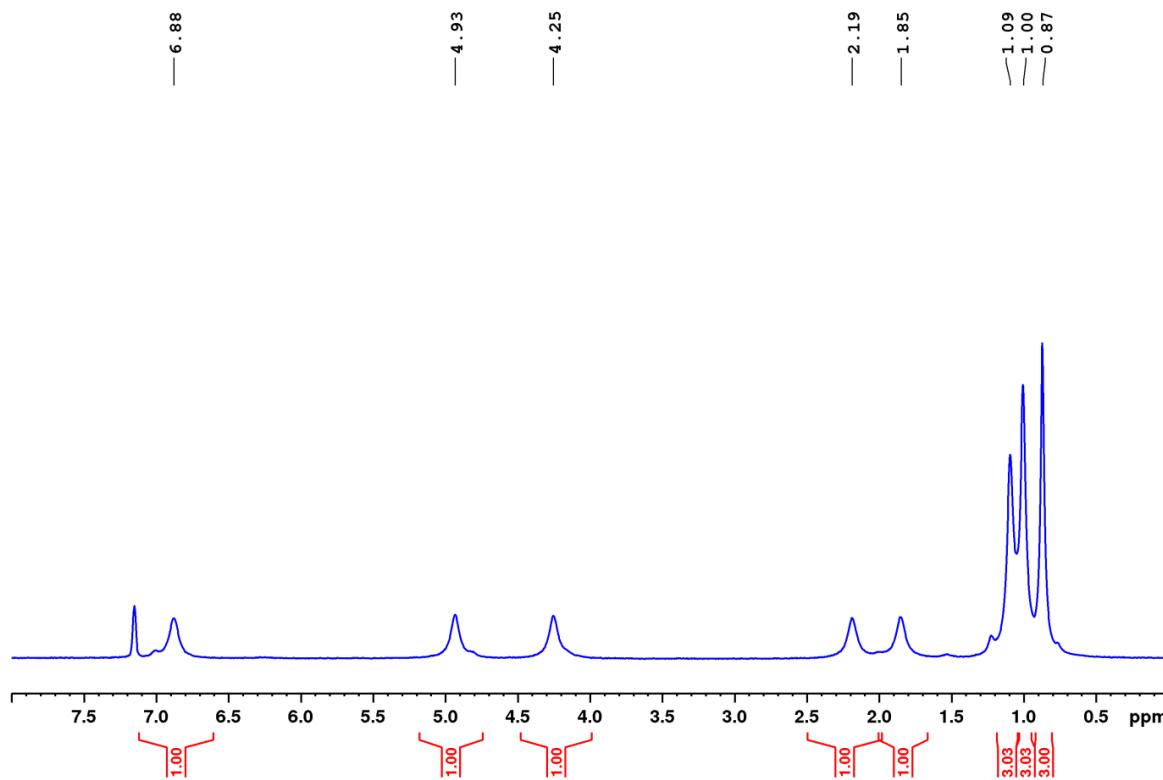


**Figure S60:**  $^{19}\text{F}$  { $^1\text{H}$ } NMR spectrum (376 MHz,  $\text{CD}_2\text{Cl}_2$ , 25°C) of **17**.

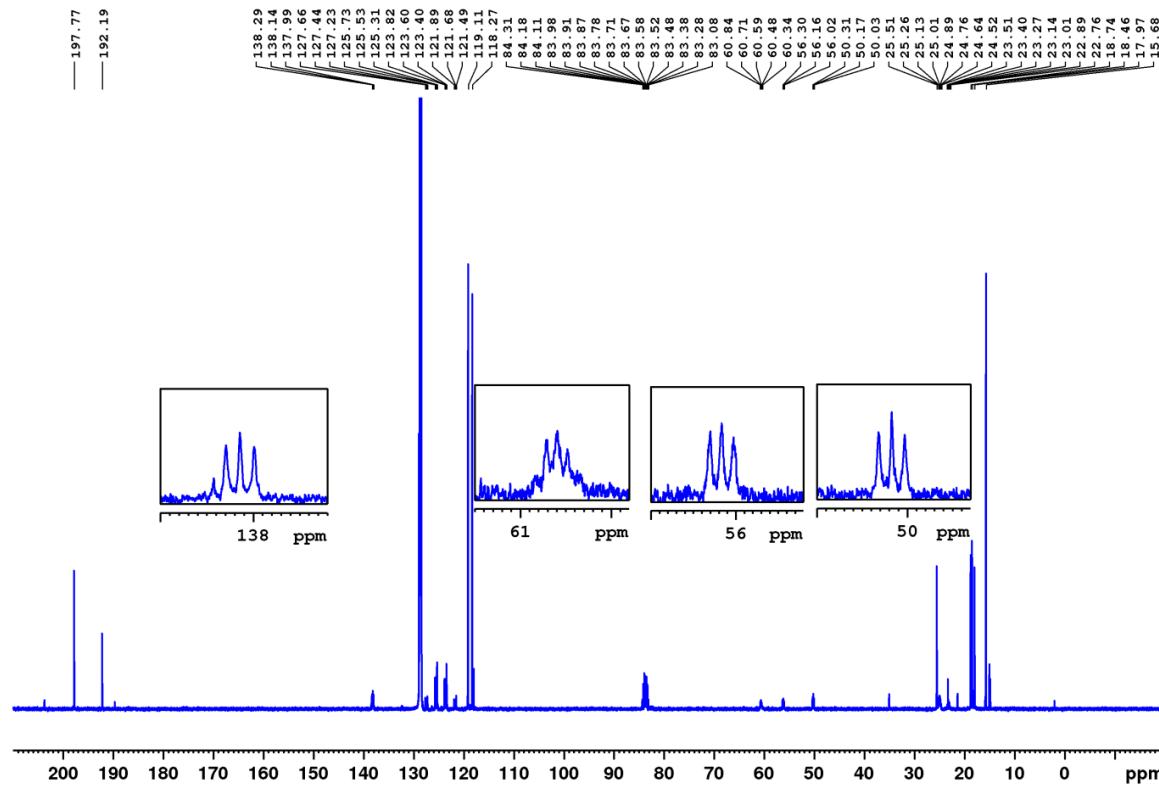
**Synthesis of **19-d<sub>14</sub>**.** In an argon-filled glovebox, 1.0 eq of **7-d<sub>14</sub>** (201 mg, 0.23 mmol) was dissolved in 2 ml of THF. Then 10.0 eq of 2-butyne (124 mg, 2.3 mmol) were added and the mixture was stirred for 20 min at room temperature. The solvent was removed in vacuum and the residue was taken up in pentane. The isolation of the product was performed by crystallization from a concentration solution in pentane (152 mg, 0.16 mmol, 70%). **Note:** complex **19-d<sub>14</sub>** is thermally unstable at room temperature ( $t_{1/2} \approx 1$  d) and was found to rearrange in order to form complex **16-d<sub>14</sub>**. **<sup>1</sup>H NMR** ( $C_6D_6$ , 600 MHz, 25°C):  $\delta$  (in ppm) = 6.29 (d,  $^3J_{H-H}$  = 2.0 Hz, 1H), 6.24 (d,  $^3J_{H-H}$  = 2.0 Hz, 1H), 2.34 (s, 3H), 1.79 (s, 3H), 1.71 (s, 3H), 1.46 (s, 3H), 1.24 (s, 3H). **<sup>13</sup>C{<sup>1</sup>H} NMR** ( $C_6D_6$ , 101 MHz, 25°C):  $\delta$  (in ppm) = 197.77 (s, 1C), 192.19 (s, 1C), 138.14 (t,  $^1J_{C-D}$  = 22.8 Hz, 1C), 124.78 (q,  $^1J_{C-F}$  = 288.5 Hz, 2C), 124.57 (q,  $^1J_{C-F}$  = 291.2 Hz, 2C), 124.36 (q,  $^1J_{C-F}$  = 287.2 Hz, 2C), 119.11 (s, 1C), 118.27 (s, 1C), 84.31 - 83.08 (m, 3C), 60.59 (pent,  $^1J_{C-D}$  = 17.5 Hz, 1C), 56.16 (t,  $^1J_{C-D}$  = 20.8 Hz, 1C), 50.17 (t,  $^1J_{C-D}$  = 21.4 Hz, 1C), 25.51 (s, 1C), 25.26 - 24.52 (m, 2C), 23.14 (sept,  $^1J_{C-D}$  = 18.9 Hz, 1C), 18.74 (s, 1C), 18.46 (s, 1C), 17.97 (s, 1C), 15.68 (s, 1C). **<sup>2</sup>H NMR** ( $C_6H_6$ , 92 MHz, 25°C): 6.88 (s, 1D), 4.93 (s, 1D), 4.25 (s, 1D), 2.19 (s, 1D), 1.85 (s, 1D), 1.09 (s, 3D), 1.00 (s, 3D), 0.87 (s, 3D). **<sup>19</sup>F{<sup>1</sup>H} NMR** ( $C_6D_6$ , 188 MHz, 25°C):  $\delta$  (in ppm) = -75.50 to -75.76 (m, 6F), -76.19 (s, 6F), -77.58 (s, 6F).



**Figure S61:** **<sup>1</sup>H NMR** spectrum (600MHz,  $C_6D_6$ , 25°C) of **19-d<sub>14</sub>**.

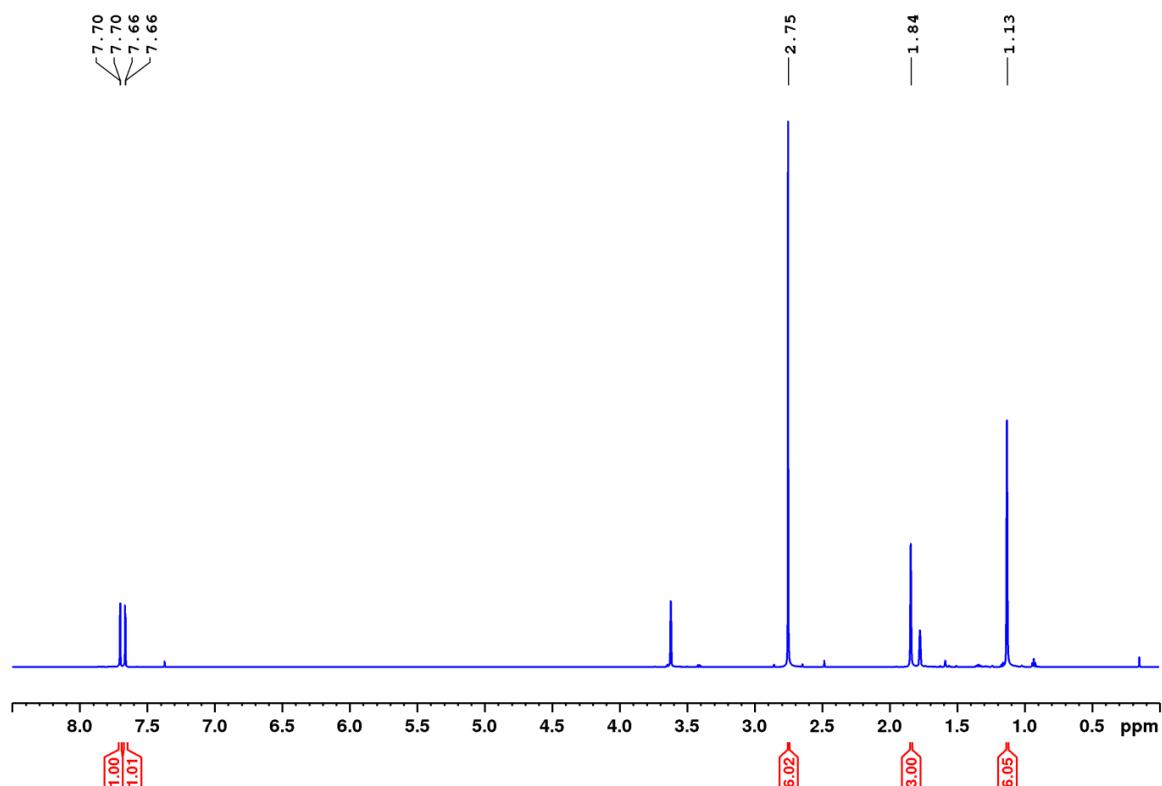
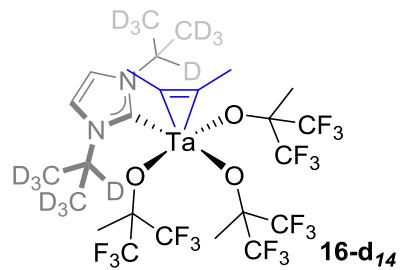


**Figure S62:**  $^2\text{H}$   $\{^1\text{H}\}$  NMR spectrum (92MHz,  $\text{C}_6\text{H}_6$ , 25°C) of **19-d<sub>14</sub>**.

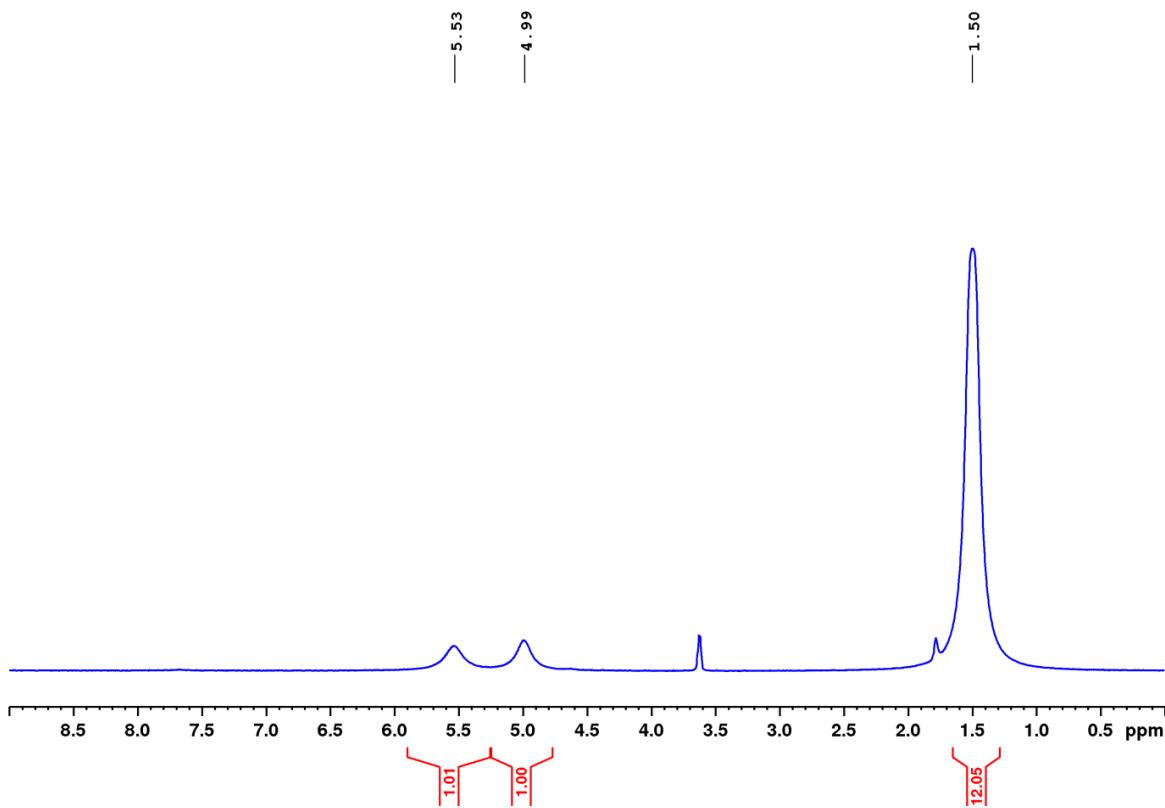


**Figure S63:**  $^{13}\text{C}$  { $^1\text{H}$ } NMR spectrum (101MHz,  $\text{C}_6\text{D}_6$ , 25°C) of **19-d<sub>14</sub>**.

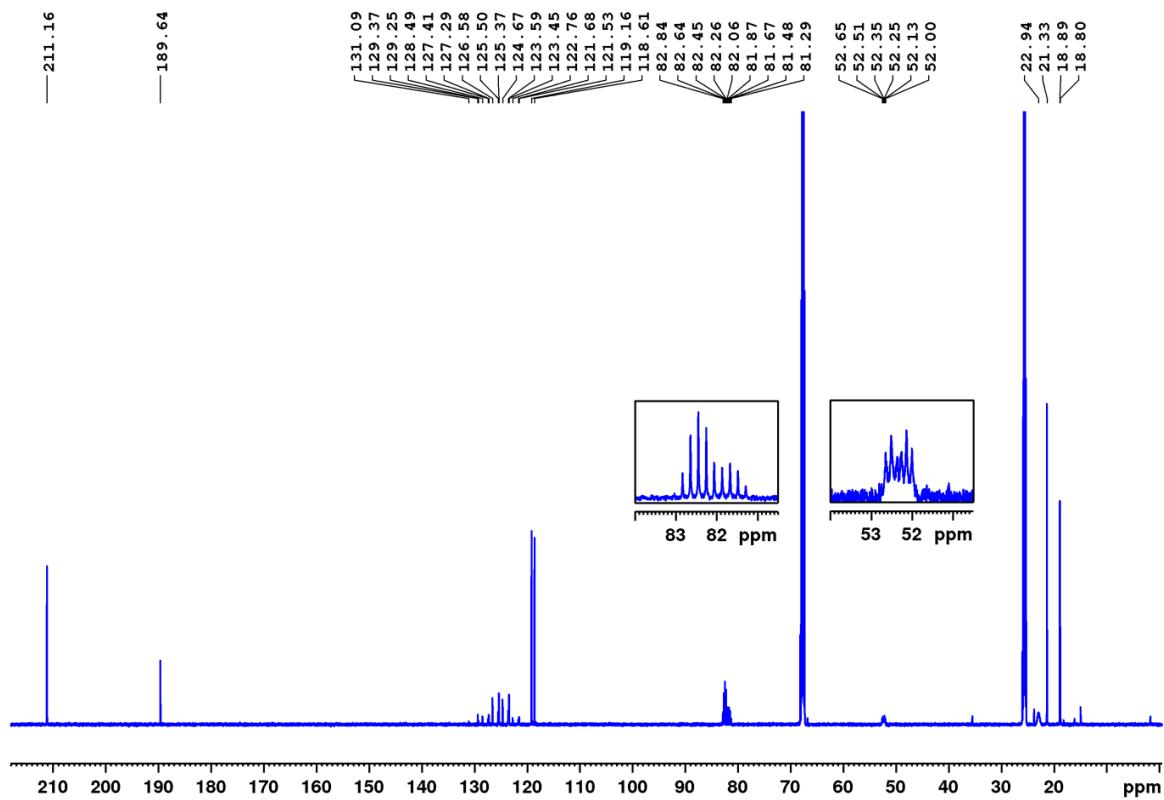
**Synthesis of **16-d<sub>14</sub>**.** In an argon-filled glovebox, 1.0 eq of **19-d<sub>14</sub>** (172 mg, 0.18 mmol) was dissolved in 0.6 ml of THF-*d*<sub>8</sub> and heated in a *J. Young* NMR tube at 60°C for 1d (the reaction was monitored by <sup>19</sup>F{<sup>1</sup>H} NMR spectroscopy until full conversion was observed). The solvent was removed in vacuum and the residue was taken up in pentane. The title compound was isolated by crystallization from a concentrated solution in pentane at -35°C and obtained as a pale yellow crystalline solid (149 mg, 0.16 mmol, 87 %). **<sup>1</sup>H NMR** (THF-*d*<sub>8</sub>, 600 MHz, -40°C): δ (in ppm) = 7.70 (d, <sup>3</sup>J<sub>H-H</sub> = 2.0 Hz, 1H), 7.66 (d, <sup>3</sup>J<sub>H-H</sub> = 2.0 Hz, 1H), 2.75 (s, 6H), 1.84 (s, 3H), 1.13 (s, 6H). **<sup>2</sup>H NMR** (THF, 92 MHz, -40°C): 5.53 (s, 1D), 4.99 (s, 1D), 1.50 (s, 12D). **<sup>13</sup>C{<sup>1</sup>H} NMR** (THF-*d*<sub>8</sub>, 151 MHz, -40°C): δ (in ppm) = 211.16 (s, 1C), 189.64 (s, 1C), 131.09 - 121.53 (m, 6C), 119.16 (s, 1C), 118.61 (s, 1C), 82.45 (sept, <sup>2</sup>J<sub>C-F</sub> = 29.1 Hz, 2C), 81.67 (sept, <sup>2</sup>J<sub>C-F</sub> = 29.4 Hz, 1C), 52.51 (t, <sup>1</sup>J<sub>C-D</sub> = 21.6 Hz, 1C), 52.13 (t, <sup>1</sup>J<sub>C-D</sub> = 21.2 Hz, 1C), 22.94 (brs, 4C), 21.33 (s, 2C), 18.89 (s, 2C), 18.80 (s, 1C).



**Figure S64:** <sup>1</sup>H NMR spectrum (600 MHz, THF-*d*<sub>8</sub>, -40°C) of **16-d<sub>14</sub>**.



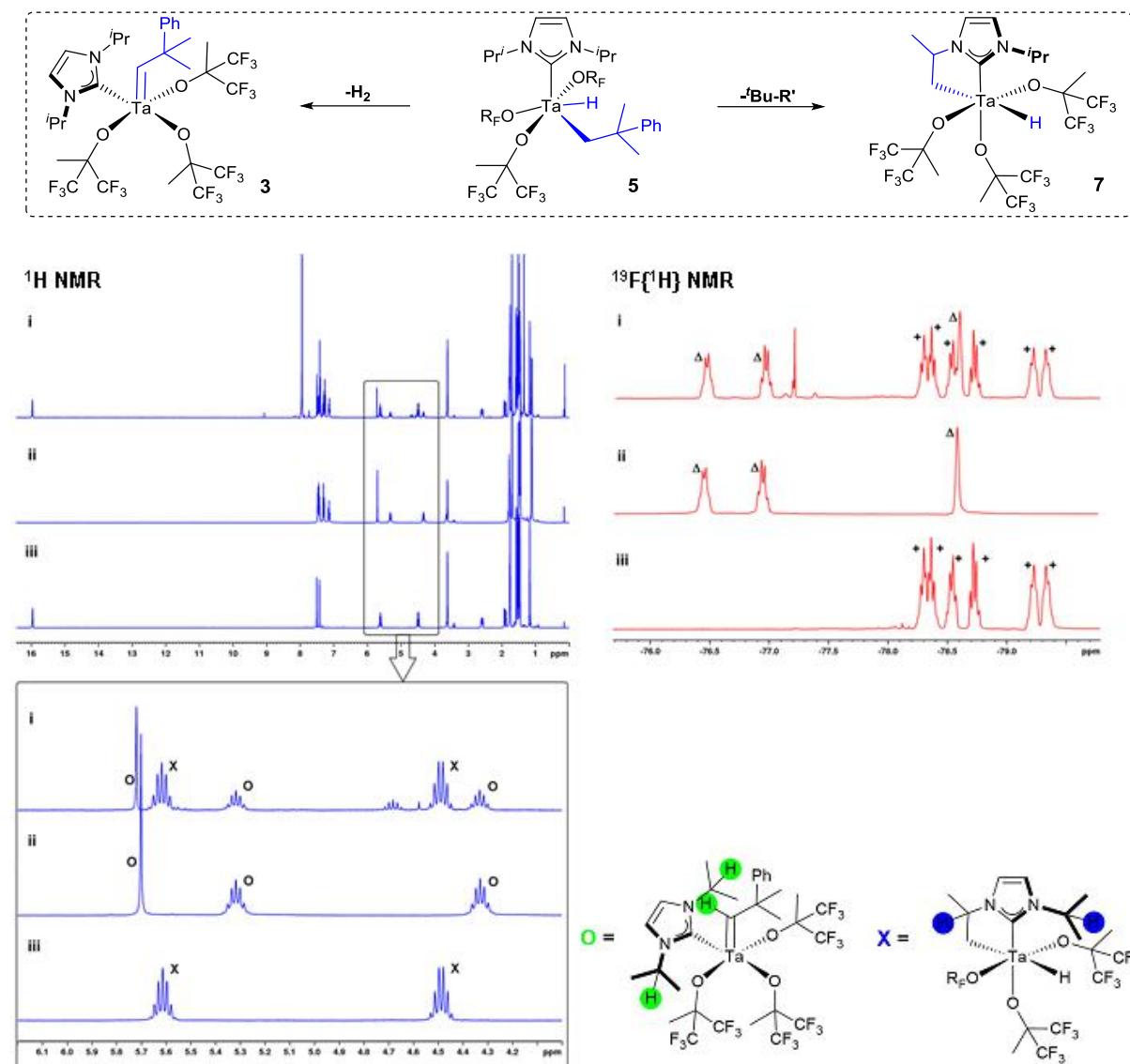
**Figure S65:**  $^2\text{H} \{^1\text{H}\}$  NMR spectrum (92 MHz, THF, -40°C) of **16-d<sub>14</sub>**.



**Figure S66:**  $^{13}\text{C} \{^1\text{H}\}$  NMR spectrum (151MHz, THF, -40°C) of **16-d<sub>14</sub>**.

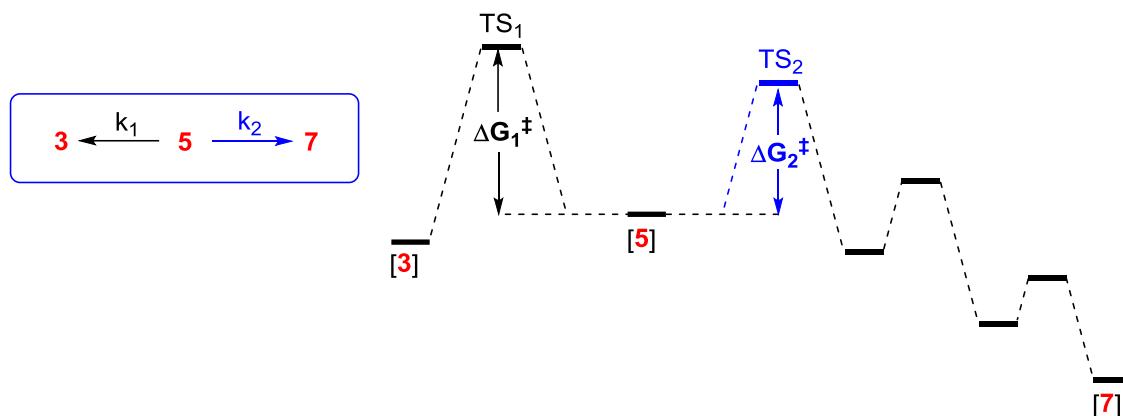
## 2) MECHANISTIC STUDIES

### Thermal conversion of complex 5 to complex 3 and complex 7

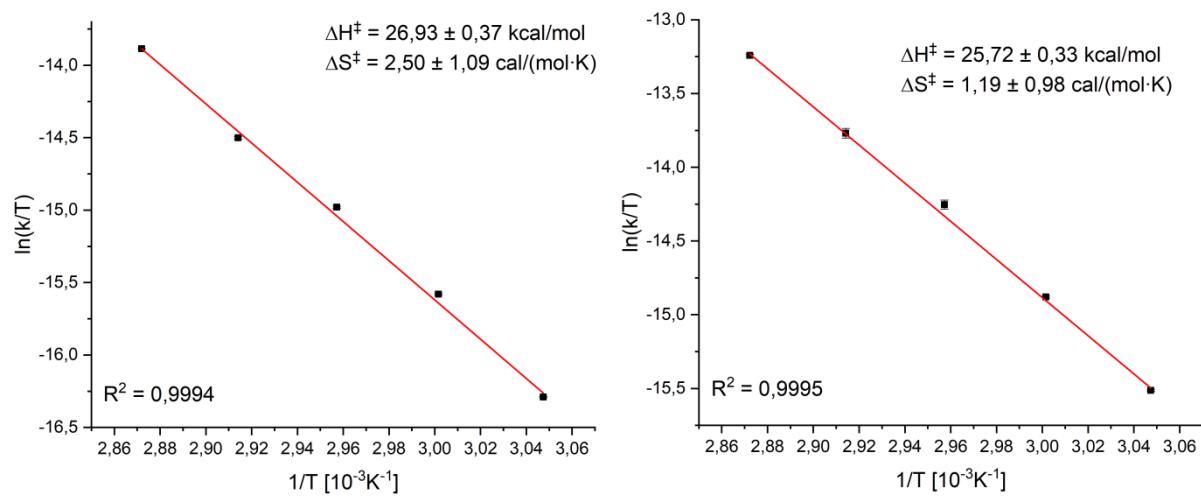


**Figure S67:** i) <sup>1</sup>H NMR (blue)/<sup>19</sup>F{<sup>1</sup>H} NMR (red) of the reaction mixture, after heating a THF-d<sub>8</sub> solution of complex 5 for 18h at 75°C, recorded at 295K. ii) <sup>1</sup>H NMR (blue)/<sup>19</sup>F{<sup>1</sup>H} NMR (red) of the pure complex 3 recorded at 295K in THF-d<sub>8</sub>. iii) <sup>1</sup>H NMR (blue) /<sup>19</sup>F{<sup>1</sup>H} NMR (red) of the pure complex 7 recorded at 295K in THF-d<sub>8</sub>.

### Eyring-Polanyi analysis for the conversion of complex 5 (and 6) to complex 7

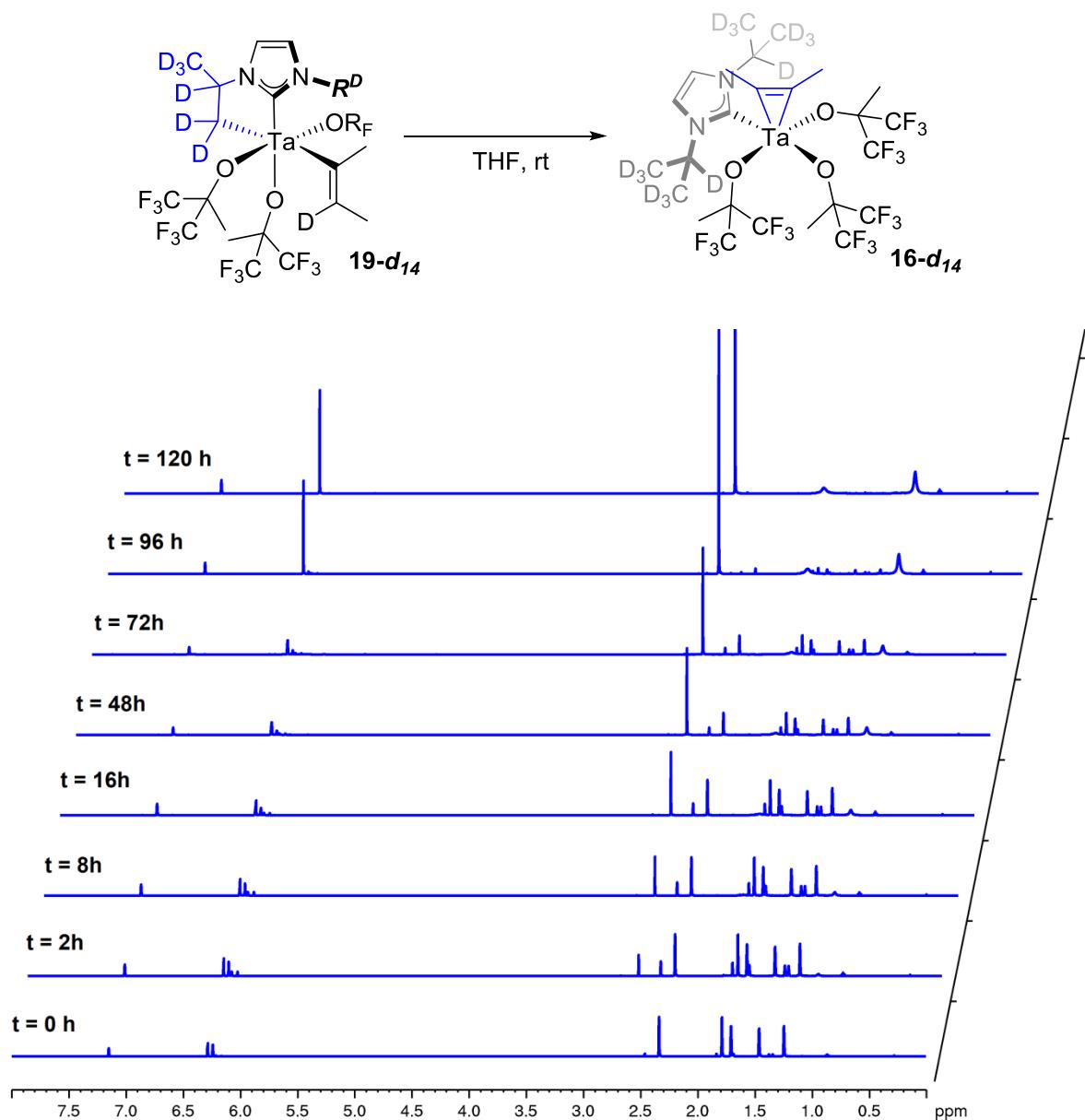


**Figure S68:** Illustration of the schematic reaction profile for the conversion of **5** to **3** and **7**, the Gibbs energy of activation  $\Delta G_2^\ddagger$  (for  $5 \rightarrow 7$ ) is highlighted in blue.



**Figure S69:** Left: linear fit (red line) of the Eyring-Polanyi-Plot for the conversion of **5** into **7**. Right: linear fit (red line) of the Eyring-Polanyi-Plot for the conversion of **6** into **7**.

**Thermal conversion of complex **19-d<sub>14</sub>** to complex **16-d<sub>14</sub>****



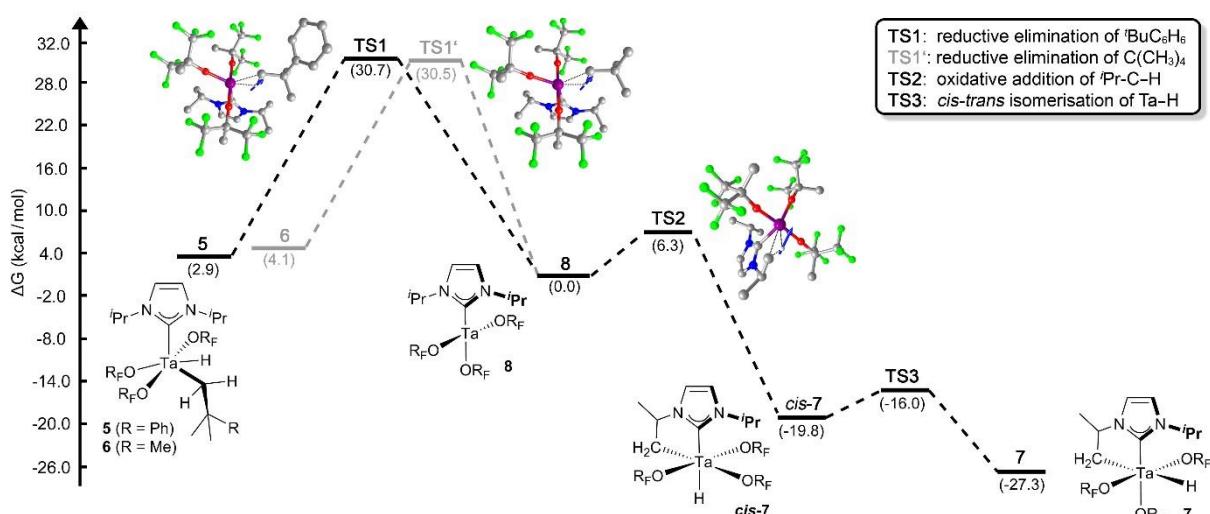
**Figure S70:** <sup>1</sup>H NMR spectra (600 MHz, C<sub>6</sub>D<sub>6</sub>, 25°C) recorded over a period of 5 days (120 h) illustrating the progress of the thermally conversion of complex **19-d<sub>14</sub>** into complex **16-d<sub>14</sub>**.

### 3) COMPUTATIONAL DETAILS

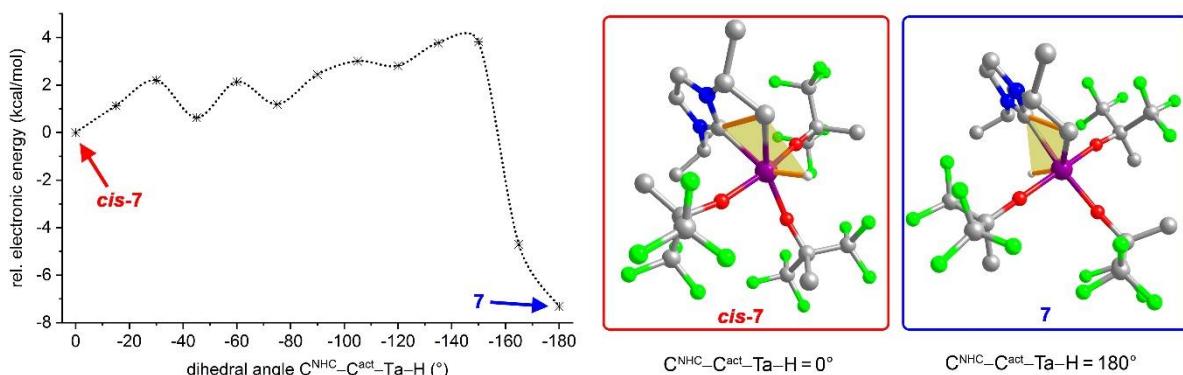
#### Mechanism of the reductive hydrogenation

DFT calculations concerning the reductive hydrogenation (cf. Figure 4 in the article and Figure S71 shown below) were carried out with Gaussian 16 (G16RevB.01)<sup>[7]</sup> using the PBE1PBE functional.<sup>[8,9]</sup> All atoms were described with the valence triple- $\zeta$  basis set Def2-TZVP including polarization functions.<sup>[10]</sup> Dispersion interactions (GD3)<sup>[11]</sup> were taken into account during the geometry optimizations without applying symmetry restrictions. All stationary points were identified as minima or transition states by analytical frequency analysis. All energies were corrected for solvent effects using the polarizable continuum model (PCM for thf)<sup>[12,13]</sup> as implemented in Gaussian.

Optimized coordinates of **5**, **6**, **7**, **cis-7**, **8**, **TS1**, **TS1'** and **TS2** are provided on the following pages. As mentioned in the article, **TS3** was estimated on basis of relaxed potential energy surface scans (PES scans), which may either be carried out by varying the angle  $C^{act}-Ta-H$  or by varying the dihedral angle  $C^{NHC}-C^{act}-Ta-H$  (with  $C^{act}$  = activated carbon atom of the  $iPr$  group,  $C^{NHC}$  = NHC carbon donor atom and H = hydridic hydrogen atom). The latter PES scan is shown in Figure S72.

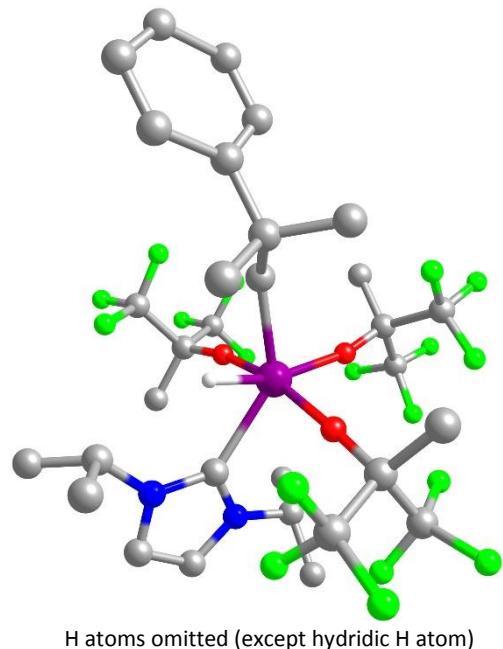


**Figure S71:** Calculated energy profile (PBE1PBE/Def2-TZVP incl. GD3 and PCM for thf) for the conversion of **5** (and **6**) to **7**. Compound **8** was set to 0.0 kcal/mol.



**Figure S72:** PES scan (PBE1PBE/Def2-TZVP incl. GD3 and PCM for thf) leading from **cis-7** to **7** by varying the dihedral angle  $C^{NHC}-C^{act}-Ta-H$  from 0° to 180°. Compound **cis-7** was set to 0.0 kcal/mol.

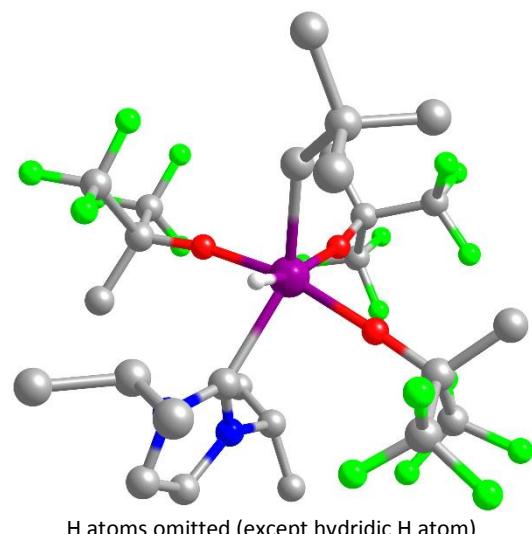
Optimized coordinates of  $(\text{PhMe}_2\text{CCH}_2)(\text{H})\text{Ta}(\text{NHC})(\text{OR}_f)_3$  (PBE1PBE/Def2-TZVP PCM(thf) GD3) (5)



|    |              |              |              |
|----|--------------|--------------|--------------|
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| F  | -3.714110000 | 1.424361000  | -0.348141000 |
| F  | -4.953395000 | 0.885194000  | -2.021745000 |
| F  | -3.954475000 | -1.139914000 | -3.558000000 |
| F  | -1.812144000 | -1.289238000 | -3.715717000 |
| F  | -2.825127000 | -2.185167000 | -2.048975000 |
| F  | 3.945850000  | -0.570013000 | 1.036478000  |
| F  | 3.038265000  | -2.447653000 | 0.518986000  |
| F  | 4.153862000  | -2.261675000 | 2.350810000  |
| F  | 3.074254000  | -0.781218000 | 4.343527000  |
| F  | 2.859266000  | 0.873446000  | 2.983222000  |
| F  | 1.136992000  | 0.096781000  | 4.006864000  |
| F  | -0.116419000 | 3.765073000  | -0.940235000 |
| F  | -0.808524000 | 5.173992000  | 0.532331000  |
| F  | -2.143434000 | 3.670971000  | -0.235974000 |
| F  | -0.862616000 | 2.198082000  | 3.444257000  |
| F  | -1.481743000 | 4.202423000  | 2.957645000  |
| F  | -2.569716000 | 2.512431000  | 2.180156000  |
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| O  | 1.168352000  | -0.616282000 | 1.360812000  |
| O  | -0.435007000 | 1.640487000  | 0.756400000  |
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| N  | -2.018286000 | -2.401367000 | 1.257248000  |
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| C  | -3.941015000 | 0.477487000  | -1.252070000 |
| C  | -2.817725000 | -1.123637000 | -2.852672000 |
| C  | -2.467775000 | 1.347185000  | -3.070831000 |
| H  | -2.355744000 | 2.279787000  | -2.518942000 |
| H  | -3.316239000 | 1.426567000  | -3.748483000 |
| H  | -1.565939000 | 1.166791000  | -3.650102000 |
| C  | 1.986668000  | -1.243710000 | 2.258869000  |
| C  | 2.280580000  | -0.248695000 | 3.410133000  |
| C  | 3.306739000  | -1.624513000 | 1.537231000  |
| C  | 1.370023000  | -2.505563000 | 2.847938000  |
| H  | 0.443053000  | -2.251211000 | 3.356184000  |

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|---|--------------|--------------|--------------|
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| H | 1.144093000  | -3.200617000 | 2.043745000  |
| C | -0.398164000 | 2.915398000  | 1.240887000  |
| C | -1.347603000 | 2.965590000  | 2.463483000  |
| C | -0.885072000 | 3.894677000  | 0.144250000  |
| C | 0.997799000  | 3.340913000  | 1.680403000  |
| H | 1.369920000  | 2.622591000  | 2.405333000  |
| H | 0.993398000  | 4.336382000  | 2.123693000  |
| H | 1.661329000  | 3.339044000  | 0.816994000  |
| C | 1.692525000  | 0.652936000  | -1.160807000 |
| C | 1.964188000  | 0.853740000  | -2.666025000 |
| C | 1.245412000  | 2.104180000  | -3.175021000 |
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| H | 1.605472000  | 3.008720000  | -2.684658000 |
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| H | 1.736793000  | -0.212987000 | -4.542364000 |
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| H | 3.864117000  | -0.718209000 | -3.967462000 |
| C | 5.669678000  | 0.342029000  | -3.573674000 |
| H | 6.275985000  | -0.381169000 | -4.108783000 |
| C | 6.264607000  | 1.441692000  | -2.977852000 |
| H | 7.336873000  | 1.589590000  | -3.039851000 |
| C | 5.465209000  | 2.352651000  | -2.298241000 |
| H | 5.911767000  | 3.219734000  | -1.823402000 |
| C | 4.096044000  | 2.158414000  | -2.220449000 |
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| C | -1.420105000 | -4.412791000 | 0.665953000  |
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| C | -2.308060000 | -3.731668000 | 1.419112000  |
| H | -3.111818000 | -4.088599000 | 2.037428000  |
| C | 0.482330000  | -3.872500000 | -0.845237000 |
| H | 1.147516000  | -3.013097000 | -0.866892000 |
| C | 1.237969000  | -5.080828000 | -0.322109000 |
| H | 1.561624000  | -4.945001000 | 0.710967000  |
| H | 2.128226000  | -5.225000000 | -0.935919000 |
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| C | -0.062812000 | -4.098546000 | -2.242328000 |
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| H | -2.028307000 | -1.839107000 | 3.928114000  |
| H | -2.637164000 | -0.184924000 | 3.766702000  |
| H | -1.054918000 | -0.593849000 | 3.118470000  |
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| H | -4.658154000 | -2.102723000 | 1.281320000  |
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| H | -4.295742000 | -2.430689000 | 2.988717000  |
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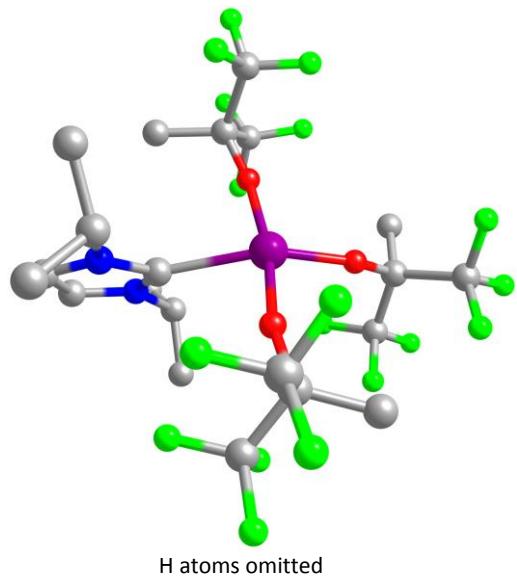
Optimized coordinates of  $(\text{Me}_3\text{CCH}_2)(\text{H})\text{Ta}(\text{NHC})(\text{OR}_f)_3$  (PBE1PBE/Def2-TZVP PCM(thf) GD3) (**6**)



|    |              |              |              |
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| Ta | -0.062409000 | -0.133354000 | -0.058021000 |
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| F  | -4.956885000 | 0.895723000  | -2.012373000 |
| F  | -3.957573000 | -1.131711000 | -3.547123000 |
| F  | -1.815183000 | -1.280567000 | -3.704626000 |
| F  | -2.828338000 | -2.175723000 | -2.037393000 |
| F  | 3.946057000  | -0.592143000 | 1.039764000  |
| F  | 3.027038000  | -2.463614000 | 0.520456000  |
| F  | 4.142993000  | -2.286108000 | 2.352714000  |
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| F  | 2.866009000  | 0.857467000  | 2.986975000  |
| F  | 1.140608000  | 0.088493000  | 4.011117000  |
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| F  | -0.804452000 | 5.176682000  | 0.559441000  |
| F  | -2.138036000 | 3.676528000  | -0.216929000 |
| F  | -0.860926000 | 2.189811000  | 3.459089000  |
| F  | -1.478197000 | 4.196300000  | 2.979569000  |
| F  | -2.566883000 | 2.510061000  | 2.194944000  |
| O  | -1.583957000 | 0.121093000  | -1.222371000 |
| O  | 1.168781000  | -0.620586000 | 1.362854000  |
| O  | -0.430779000 | 1.642002000  | 0.769167000  |
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| N  | -2.017993000 | -2.399091000 | 1.255401000  |
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| C  | -2.820559000 | -1.114528000 | -2.841667000 |
| C  | -2.473557000 | 1.354681000  | -3.064413000 |
| H  | -2.361204000 | 2.288783000  | -2.515061000 |
| H  | -3.323456000 | 1.431682000  | -3.740548000 |
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| C  | 1.981695000  | -1.254268000 | 2.260643000  |
| C  | 2.281764000  | -0.262257000 | 3.413029000  |

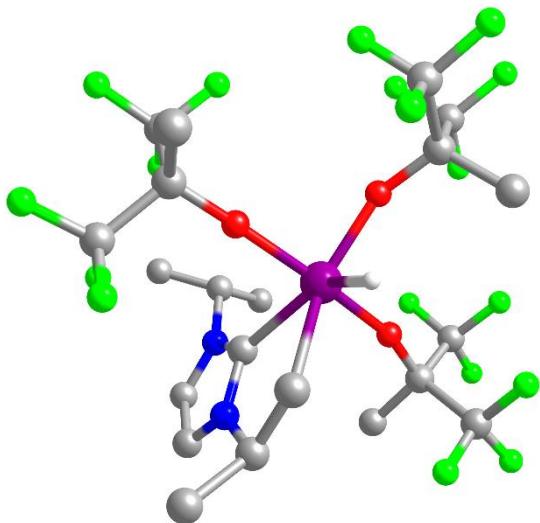
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| H | 2.032225000  | -2.994706000 | 3.554795000  |
| H | 1.125377000  | -3.205437000 | 2.044269000  |
| C | -0.394199000 | 2.914818000  | 1.258511000  |
| C | -1.344506000 | 2.961213000  | 2.480551000  |
| C | -0.879830000 | 3.898796000  | 0.165330000  |
| C | 1.001828000  | 3.337430000  | 1.700679000  |
| H | 1.371277000  | 2.617520000  | 2.425524000  |
| H | 0.999056000  | 4.332507000  | 2.144914000  |
| H | 1.665878000  | 3.334149000  | 0.837708000  |
| C | 1.687168000  | 0.658848000  | -1.166416000 |
| C | 1.945386000  | 0.854715000  | -2.666947000 |
| C | 1.212619000  | 2.091716000  | -3.175137000 |
| H | 0.149135000  | 2.040499000  | -2.947651000 |
| H | 1.331941000  | 2.201297000  | -4.257528000 |
| H | 1.603058000  | 2.994471000  | -2.698489000 |
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| H | 2.034582000  | -1.265121000 | -3.124193000 |
| H | 1.820564000  | -0.219925000 | -4.540124000 |
| H | 0.465653000  | -0.536213000 | -3.439652000 |
| C | 3.449373000  | 1.083163000  | -2.859632000 |
| C | -0.964550000 | -2.224304000 | 0.418108000  |
| C | -1.423282000 | -4.410051000 | 0.659071000  |
| H | -1.318970000 | -5.468421000 | 0.500037000  |
| C | -2.308750000 | -3.729473000 | 1.415491000  |
| H | -3.111565000 | -4.086752000 | 2.034840000  |
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| H | 1.137126000  | -3.007762000 | -0.884496000 |
| C | 1.235619000  | -5.074382000 | -0.333992000 |
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| H | 2.122118000  | -5.219838000 | -0.952957000 |
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| H | -0.824768000 | -4.898729000 | -2.249129000 |
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| C | -2.740217000 | -1.325788000 | 1.956026000  |
| H | -2.709580000 | -0.462339000 | 1.287865000  |
| C | -2.064284000 | -0.968867000 | 3.268091000  |
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| H | -2.636439000 | -0.186023000 | 3.768190000  |
| H | -1.054393000 | -0.592739000 | 3.118232000  |
| C | -4.194214000 | -1.700622000 | 2.182269000  |
| H | -4.657763000 | -2.101526000 | 1.281984000  |
| H | -4.742372000 | -0.806409000 | 2.480487000  |
| H | -4.294467000 | -2.430351000 | 2.988997000  |
| H | 1.877672000  | 1.619570000  | -0.666205000 |
| H | 2.453876000  | -0.026657000 | -0.793788000 |
| H | 0.519060000  | -1.307662000 | -1.235808000 |
| H | 4.019355000  | 0.199009000  | -2.559200000 |
| H | 3.682946000  | 1.297519000  | -3.907900000 |
| H | 3.795396000  | 1.927635000  | -2.256394000 |

**Optimized coordinates of Ta(NHC)(OR<sub>F</sub>)<sub>3</sub> (PBE1PBE/Def2-TZVP PCM(thf) GD3) (8)**



|    |              |              |              |  |
|----|--------------|--------------|--------------|--|
| C  | 0.413672000  | -4.090384000 | 1.858910000  |  |
| C  | -3.261890000 | -1.253500000 | 2.184406000  |  |
| C  | 1.362866000  | -3.367094000 | 0.921930000  |  |
| C  | 2.682651000  | -4.101043000 | 0.779096000  |  |
| C  | 3.930591000  | -0.114427000 | 1.562868000  |  |
| C  | -2.369409000 | 3.075781000  | -0.142293000 |  |
| C  | -0.298548000 | 4.178217000  | 0.724188000  |  |
| C  | -2.936133000 | -2.682985000 | 0.148090000  |  |
| C  | -2.988796000 | -1.249176000 | 0.660114000  |  |
| C  | -0.850461000 | 3.052957000  | -0.184506000 |  |
| C  | 3.235563000  | 0.529546000  | 0.338253000  |  |
| C  | 0.254945000  | -1.987042000 | -0.840822000 |  |
| C  | 0.604449000  | -4.146729000 | -1.339204000 |  |
| C  | -4.126848000 | -0.501081000 | -0.081790000 |  |
| C  | 3.883050000  | 0.056877000  | -0.985509000 |  |
| C  | 3.360190000  | 2.040960000  | 0.446002000  |  |
| C  | -0.385284000 | 3.248610000  | -1.648345000 |  |
| C  | 0.009337000  | -3.570862000 | -2.408496000 |  |
| C  | 0.371458000  | -0.708665000 | -3.884574000 |  |
| C  | -0.739919000 | -1.247337000 | -3.004030000 |  |
| C  | -1.901647000 | -1.800448000 | -3.804026000 |  |
| H  | 0.900756000  | -4.234807000 | 2.824565000  |  |
| H  | -0.496775000 | -3.515278000 | 2.026014000  |  |
| H  | 3.187576000  | -4.122417000 | 1.745104000  |  |
| H  | 0.145992000  | -5.072366000 | 1.461567000  |  |
| H  | 1.553370000  | -2.363157000 | 1.309698000  |  |
| H  | -2.697992000 | 2.899403000  | 0.880321000  |  |
| H  | 2.525162000  | -5.134573000 | 0.462507000  |  |
| H  | -2.077514000 | -3.188765000 | 0.582354000  |  |
| H  | 3.334327000  | -3.606779000 | 0.058902000  |  |
| H  | -3.840746000 | -3.232002000 | 0.405474000  |  |
| H  | -2.765334000 | 4.028430000  | -0.492598000 |  |
| H  | -2.750375000 | 2.275952000  | -0.772312000 |  |
| H  | 0.928778000  | -5.160809000 | -1.183132000 |  |
| H  | -2.822096000 | -2.676744000 | -0.934193000 |  |
| H  | 2.889261000  | 2.370103000  | 1.370281000  |  |
| H  | 4.403787000  | 2.353854000  | 0.440556000  |  |
| H  | 2.839716000  | 2.499533000  | -0.390365000 |  |
| H  | -0.271471000 | -3.991137000 | -3.358342000 |  |
| H  | -0.024299000 | 0.063560000  | -4.546467000 |  |
| H  | 0.800352000  | -1.503139000 | -4.500521000 |  |
| H  | -1.089401000 | -0.441961000 | -2.353388000 |  |
| H  | -1.577600000 | -2.565514000 | -4.513273000 |  |
| H  | -2.670905000 | -2.227388000 | -3.158871000 |  |
| H  | -2.351844000 | -0.989258000 | -4.377794000 |  |
| H  | 1.160336000  | -0.269398000 | -3.271987000 |  |
| F  | -2.359331000 | -2.018163000 | 2.807233000  |  |
| F  | -4.470991000 | -1.748091000 | 2.472013000  |  |
| F  | 3.309820000  | 0.261026000  | 2.683043000  |  |
| F  | -3.182877000 | -0.038122000 | 2.719324000  |  |
| F  | -0.659999000 | 3.950137000  | 1.988511000  |  |
| F  | 3.905802000  | -1.447966000 | 1.527282000  |  |
| F  | 5.209289000  | 0.256781000  | 1.669926000  |  |
| F  | -0.770711000 | 5.381514000  | 0.384690000  |  |
| F  | 1.033135000  | 4.249797000  | 0.700055000  |  |
| F  | -5.274470000 | -1.185208000 | -0.066756000 |  |
| F  | -4.374378000 | 0.702883000  | 0.434047000  |  |
| F  | 3.742630000  | -1.255202000 | -1.182282000 |  |
| F  | 5.188621000  | 0.335993000  | -1.039400000 |  |
| F  | -0.760066000 | 4.437962000  | -2.132506000 |  |
| F  | -3.786711000 | -0.323753000 | -1.362022000 |  |
| F  | -0.930447000 | 2.312777000  | -2.429103000 |  |
| F  | 0.936612000  | 3.158027000  | -1.790079000 |  |
| F  | 3.299077000  | 0.673968000  | -2.016061000 |  |
| N  | 0.752454000  | -3.159859000 | -0.396488000 |  |
| N  | -0.200237000 | -2.255160000 | -2.082624000 |  |
| O  | -1.824615000 | -0.566407000 | 0.447200000  |  |
| O  | -0.339392000 | 1.871984000  | 0.294210000  |  |
| O  | 1.930749000  | 0.116890000  | 0.315760000  |  |
| Ta | 0.017325000  | -0.007185000 | 0.288355000  |  |

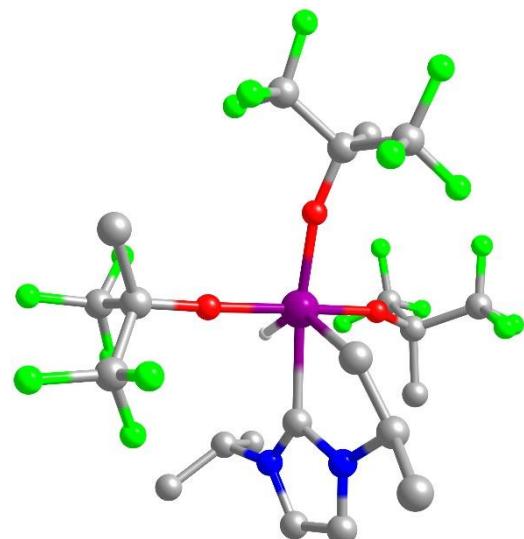
**Optimized coordinates of (H)Ta(NHC<sup>\*</sup>)(OR<sub>F</sub>)<sub>3</sub> (PBE1PBE/Def2-TZVP PCM(thf) GD3) (*cis*-7)**



H atoms omitted (except hydridic H atom)

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | -0.109015000 | -2.055898000 | 3.714753000  |
| C  | -3.753748000 | -0.712979000 | 1.142445000  |
| C  | 1.082047000  | -1.826766000 | 2.800871000  |
| C  | 2.402296000  | -2.107405000 | 3.497154000  |
| C  | 3.574099000  | 1.268253000  | 0.874578000  |
| C  | -2.326945000 | 2.753397000  | -1.145276000 |
| C  | -1.577985000 | 3.507344000  | 1.122392000  |
| C  | -2.636349000 | -2.858545000 | 0.524028000  |
| C  | -2.931536000 | -1.442182000 | 0.048399000  |
| C  | -1.119653000 | 2.913093000  | -0.231653000 |
| C  | 3.190652000  | 0.657632000  | -0.495949000 |
| C  | 0.647258000  | -2.145560000 | 0.356646000  |
| C  | 1.166588000  | -3.983665000 | 1.522139000  |
| C  | -3.730292000 | -1.507441000 | -1.277362000 |
| C  | 3.978618000  | -0.651472000 | -0.752902000 |
| C  | 3.502368000  | 1.658858000  | -1.599002000 |
| C  | -0.100079000 | 3.860076000  | -0.914260000 |
| C  | 0.982973000  | -4.354809000 | 0.233089000  |
| C  | 0.240056000  | -1.590476000 | -2.199072000 |
| C  | 0.321274000  | -3.076461000 | -1.869704000 |
| C  | 1.297524000  | -3.845966000 | -2.741854000 |
| H  | -0.003159000 | -1.446835000 | 4.614020000  |
| H  | -1.042871000 | -1.777562000 | 3.225890000  |
| H  | 2.535179000  | -1.397628000 | 4.314802000  |
| H  | -0.170210000 | -3.103396000 | 4.019903000  |
| H  | 1.083339000  | -0.789007000 | 2.468017000  |
| H  | -3.040625000 | 2.083094000  | -0.672478000 |
| H  | 2.422214000  | -3.112384000 | 3.924755000  |
| H  | -2.079783000 | -2.817844000 | 1.458514000  |
| H  | 3.240059000  | -2.000940000 | 2.808135000  |
| H  | -3.555849000 | -3.420514000 | 0.681077000  |
| H  | -2.805885000 | 3.709900000  | -1.352691000 |
| H  | -1.994456000 | 2.300215000  | -2.078127000 |
| H  | 1.432755000  | -4.571028000 | 2.383787000  |
| H  | -2.029737000 | -3.367575000 | -0.220402000 |
| H  | 2.931728000  | 2.567550000  | -1.417312000 |
| H  | 4.565268000  | 1.895257000  | -1.635310000 |
| H  | 3.190634000  | 1.235889000  | -2.552576000 |
| H  | 1.053583000  | -5.323306000 | -0.230708000 |
| H  | -0.538008000 | -1.451842000 | -2.950910000 |
| H  | 1.175632000  | -1.280516000 | -2.680192000 |
| H  | -0.673189000 | -3.522664000 | -1.980977000 |
| H  | 2.308828000  | -3.453283000 | -2.613804000 |
| H  | 1.305949000  | -4.917002000 | -2.524710000 |
| H  | 1.010500000  | -3.720641000 | -3.786988000 |
| F  | -2.987438000 | -0.530580000 | 2.222450000  |
| F  | -4.821057000 | -1.418947000 | 1.525520000  |
| F  | 2.880548000  | 2.385216000  | 1.082687000  |
| F  | -4.185580000 | 0.485207000  | 0.752534000  |
| F  | -2.452729000 | 2.681949000  | 1.703439000  |
| F  | 3.305179000  | 0.442272000  | 1.889829000  |
| F  | 4.871472000  | 1.578273000  | 0.940143000  |
| F  | -2.182297000 | 4.693617000  | 0.984832000  |
| F  | -0.566502000 | 3.671082000  | 1.978512000  |
| F  | -4.921560000 | -2.090968000 | -1.112272000 |
| F  | -3.936568000 | -0.304187000 | -1.807419000 |
| F  | 3.729887000  | -1.587356000 | 0.164922000  |
| F  | 5.298366000  | -0.449614000 | -0.777268000 |
| F  | -0.629628000 | 5.058215000  | -1.194738000 |
| F  | -3.053315000 | -2.225997000 | -2.177870000 |
| F  | 0.310108000  | 3.331012000  | -2.070687000 |
| F  | 0.988564000  | 4.070543000  | -0.172970000 |
| F  | 3.629726000  | -1.158666000 | -1.938298000 |
| N  | 0.962734000  | -2.625940000 | 1.577348000  |
| N  | 0.674546000  | -3.211585000 | -0.455506000 |
| O  | -1.804642000 | -0.707015000 | -0.187704000 |
| O  | -0.502181000 | 1.726701000  | 0.057304000  |
| O  | 1.858256000  | 0.358687000  | -0.466873000 |
| Ta | -0.000337000 | -0.102875000 | -0.517432000 |
| H  | -0.265211000 | 0.593810000  | -2.100726000 |

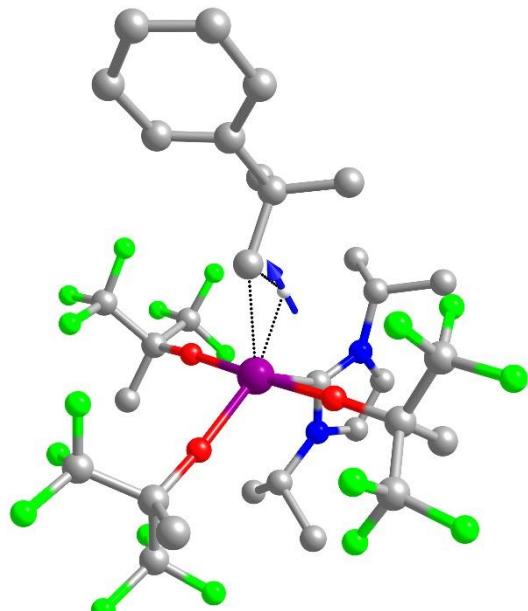
Optimized coordinates of (H)Ta(NHC\*)(OR<sub>F</sub>)<sub>3</sub> (PBE1PBE/Def2-TZVP PCM(thf) GD3) (7)



H atoms omitted (except hydridic H atom)

|   |              |              |              |  |    |              |              |              |
|---|--------------|--------------|--------------|--|----|--------------|--------------|--------------|
| C | -1.558997000 | -4.048145000 | -2.058249000 |  | H  | -1.592423000 | -5.065390000 | -1.659648000 |
| C | 2.799726000  | -1.951920000 | -1.979905000 |  | H  | -2.176523000 | -2.069254000 | -1.544304000 |
| C | -2.304247000 | -3.078606000 | -1.158788000 |  | H  | 2.334988000  | 2.315020000  | -2.259953000 |
| C | -3.785975000 | -3.394817000 | -1.061515000 |  | H  | -3.960913000 | -4.418392000 | -0.721112000 |
| C | -3.588264000 | 1.082295000  | -1.577250000 |  | H  | 1.068166000  | -3.500457000 | -0.479767000 |
| C | 2.812160000  | 2.428000000  | -1.287296000 |  | H  | -4.288590000 | -2.707968000 | -0.380006000 |
| C | 0.986346000  | 4.012930000  | -0.646399000 |  | H  | 2.734605000  | -4.099814000 | -0.326923000 |
| C | 2.039050000  | -3.317632000 | -0.025277000 |  | H  | 3.551722000  | 3.226487000  | -1.338356000 |
| C | 2.531705000  | -1.941641000 | -0.453935000 |  | H  | 3.301899000  | 1.492154000  | -1.030110000 |
| C | 1.739171000  | 2.719631000  | -0.247586000 |  | H  | -2.324576000 | -4.985342000 | 0.863198000  |
| C | -3.002758000 | 1.398585000  | -0.179532000 |  | H  | 1.927559000  | -3.340993000 | 1.057372000  |
| C | -0.988294000 | -2.014235000 | 0.697113000  |  | H  | -2.256365000 | 3.298063000  | -0.821101000 |
| C | -1.793361000 | -4.073433000 | 1.074989000  |  | H  | -3.857238000 | 3.390944000  | -0.052509000 |
| C | 3.832660000  | -1.614620000 | 0.323028000  |  | H  | -2.398709000 | 3.121427000  | 0.930910000  |
| C | -3.904914000 | 0.831699000  | 0.943154000  |  | H  | -0.997379000 | -4.192137000 | 3.133735000  |
| C | -2.881627000 | 2.907336000  | -0.020503000 |  | H  | 0.865534000  | 0.442757000  | 2.503890000  |
| C | 2.401071000  | 2.883297000  | 1.141947000  |  | H  | -0.895255000 | 0.323171000  | 2.552403000  |
| C | -1.142968000 | -3.683025000 | 2.197004000  |  | H  | 1.157420000  | -1.893664000 | 2.741454000  |
| C | 0.014866000  | -0.172927000 | 2.194084000  |  | H  | -1.392320000 | -1.351465000 | 4.330968000  |
| C | 0.118861000  | -1.551348000 | 2.804202000  |  | H  | -0.207994000 | -2.632264000 | 4.672741000  |
| C | -0.340089000 | -1.634381000 | 4.247918000  |  | H  | 0.250557000  | -0.938666000 | 4.845754000  |
| H | -2.019121000 | -4.057927000 | -3.047905000 |  | F  | 1.712335000  | -2.371447000 | -2.631794000 |
| H | -0.515893000 | -3.749099000 | -2.172119000 |  | F  | 3.802819000  | -2.773766000 | -2.305946000 |
| H | -4.239744000 | -3.292215000 | -2.048553000 |  | F  | -2.735669000 | 1.492755000  | -2.518498000 |
|   |              |              |              |  | F  | 3.098704000  | -0.741601000 | -2.450113000 |
|   |              |              |              |  | F  | 0.347500000  | 3.816969000  | -1.804666000 |
|   |              |              |              |  | F  | -3.792602000 | -0.222033000 | -1.768273000 |
|   |              |              |              |  | F  | -4.750829000 | 1.705813000  | -1.785414000 |
|   |              |              |              |  | F  | 1.811132000  | 5.051231000  | -0.816481000 |
|   |              |              |              |  | F  | 0.068499000  | 4.373784000  | 0.252565000  |
|   |              |              |              |  | F  | 4.741739000  | -2.588261000 | 0.220884000  |
|   |              |              |              |  | F  | 4.408170000  | -0.484066000 | -0.088919000 |
|   |              |              |              |  | F  | -3.994335000 | -0.497863000 | 0.904260000  |
|   |              |              |              |  | F  | -5.144927000 | 1.324680000  | 0.889522000  |
|   |              |              |              |  | F  | 3.276246000  | 3.893730000  | 1.172029000  |
|   |              |              |              |  | F  | 3.549606000  | -1.468982000 | 1.620374000  |
|   |              |              |              |  | F  | 3.064628000  | 1.767885000  | 1.457720000  |
|   |              |              |              |  | F  | 1.508018000  | 3.094636000  | 2.110945000  |
|   |              |              |              |  | F  | -3.392764000 | 1.156251000  | 2.134157000  |
|   |              |              |              |  | N  | -1.694208000 | -3.042886000 | 0.173596000  |
|   |              |              |              |  | N  | -0.677292000 | -2.423395000 | 1.942682000  |
|   |              |              |              |  | O  | 1.637230000  | -0.945683000 | -0.182019000 |
|   |              |              |              |  | O  | 0.817293000  | 1.719203000  | -0.161814000 |
|   |              |              |              |  | O  | -1.787693000 | 0.786999000  | -0.075592000 |
|   |              |              |              |  | Ta | -0.059651000 | -0.027449000 | -0.009565000 |
|   |              |              |              |  | H  | -0.558204000 | -1.021076000 | -1.404785000 |

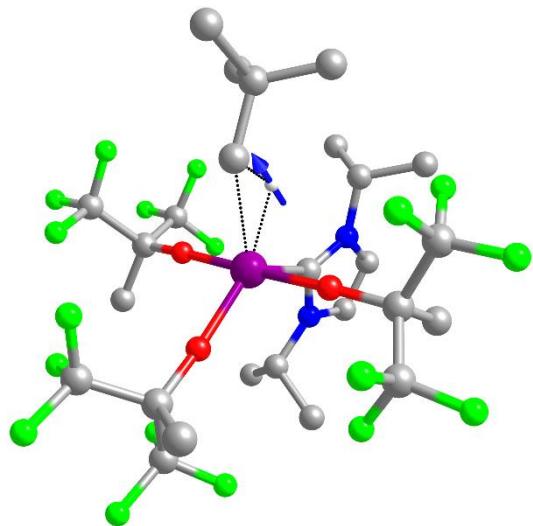
Optimized coordinates of TS1 (reductive elimination of  $t\text{Bu-C}_6\text{H}_5$ ) (PBE1PBE/Def2-TZVP PCM(thf) GD3)



H atoms omitted (except hydridic H atom)

|    |              |              |              |  |
|----|--------------|--------------|--------------|--|
| Ta | 0.244557000  | 0.064718000  | -0.048961000 |  |
| F  | -2.177253000 | -2.040533000 | -2.576350000 |  |
| F  | -0.154883000 | -2.525101000 | -3.113625000 |  |
| F  | -1.592960000 | -4.099610000 | -2.814635000 |  |
| F  | -2.310129000 | -4.699785000 | -0.278867000 |  |
| F  | -1.593649000 | -3.415230000 | 1.293004000  |  |
| F  | -3.027942000 | -2.675219000 | -0.121918000 |  |
| F  | -0.381559000 | 3.933856000  | 1.481217000  |  |
| F  | -0.441147000 | 4.213342000  | -0.649189000 |  |
| F  | 0.887672000  | 5.405947000  | 0.550348000  |  |
| F  | 3.202059000  | 4.322121000  | 1.316326000  |  |
| F  | 1.968112000  | 3.052700000  | 2.543109000  |  |
| F  | 3.397464000  | 2.184938000  | 1.184827000  |  |
| F  | -0.055767000 | -1.651116000 | 3.454695000  |  |
| F  | 1.647021000  | -2.550650000 | 4.414453000  |  |
| F  | 0.969486000  | -3.296083000 | 2.517235000  |  |
| F  | 4.197802000  | -0.889821000 | 1.559582000  |  |
| F  | 3.980727000  | -2.473392000 | 3.003741000  |  |
| F  | 3.138435000  | -2.680818000 | 1.030200000  |  |
| O  | -0.425650000 | -1.707542000 | -0.467961000 |  |
| O  | 0.859043000  | 1.879738000  | 0.257011000  |  |
| O  | 1.375902000  | -0.658692000 | 1.418804000  |  |
| N  | 0.330194000  | 1.021929000  | -3.316906000 |  |
| N  | 1.982285000  | -0.179141000 | -2.696894000 |  |
| C  | -0.762160000 | -2.964362000 | -0.870910000 |  |
| C  | -1.189987000 | -2.908696000 | -2.358955000 |  |
| C  | -1.943948000 | -3.447200000 | 0.008511000  |  |
| C  | 0.393414000  | -3.945290000 | -0.724288000 |  |
| H  | 1.239581000  | -3.579538000 | -1.301375000 |  |
| H  | 0.121527000  | -4.939938000 | -1.075597000 |  |
| H  | 0.684624000  | -3.994405000 | 0.321307000  |  |
| C  | 1.461918000  | 3.101466000  | 0.198627000  |  |
| C  | 2.513411000  | 3.177266000  | 1.332967000  |  |
| C  | 0.372347000  | 4.180737000  | 0.410553000  |  |
| C  | 2.164315000  | 3.350057000  | -1.129985000 |  |
| H  | 2.987966000  | 2.647389000  | -1.239460000 |  |
| H  | 2.550998000  | 4.366725000  | -1.193298000 |  |
| H  | 1.459206000  | 3.177473000  | -1.938337000 |  |
| C  | 2.046247000  | -1.139724000 | 2.507811000  |  |
| C  | 3.350395000  | -1.812830000 | 2.024369000  |  |
| C  | 1.148802000  | -2.179291000 | 3.228124000  |  |
| C  | 2.388117000  | -0.040233000 | 3.505405000  |  |
| H  | 2.997029000  | 0.708520000  | 3.008912000  |  |
| H  | 2.924813000  | -0.429760000 | 4.369964000  |  |
| H  | 1.461897000  | 0.428179000  | 3.837062000  |  |
| C  | -2.044459000 | 0.738373000  | 0.455233000  |  |
| C  | -3.401632000 | 1.290280000  | -0.091948000 |  |
| C  | -3.904137000 | 0.437582000  | -1.256438000 |  |
| H  | -3.173615000 | 0.424264000  | -2.066808000 |  |
| H  | -4.840449000 | 0.841990000  | -1.648140000 |  |
| H  | -4.075719000 | -0.596740000 | -0.961453000 |  |
| C  | -3.210833000 | 2.722535000  | -0.569166000 |  |
| H  | -2.844043000 | 3.370308000  | 0.228712000  |  |
| H  | -4.143715000 | 3.139405000  | -0.956025000 |  |
| H  | -2.475439000 | 2.760970000  | -1.371633000 |  |
| C  | -4.399298000 | 1.209564000  | 1.062331000  |  |
| C  | -4.997388000 | 2.337270000  | 1.619172000  |  |
| H  | -4.768729000 | 3.322442000  | 1.234133000  |  |
| C  | -5.897643000 | 2.232210000  | 2.673652000  |  |
| H  | -6.346183000 | 3.130843000  | 3.083059000  |  |
| C  | -6.220480000 | 0.992247000  | 3.199453000  |  |
| H  | -6.921430000 | 0.908965000  | 4.022273000  |  |
| C  | -5.632877000 | -0.143728000 | 2.657648000  |  |
| H  | -5.872469000 | -1.123645000 | 3.055786000  |  |
| C  | -4.737826000 | -0.032715000 | 1.606238000  |  |
| H  | -4.296331000 | -0.937293000 | 1.204301000  |  |
| C  | 0.796579000  | 0.326879000  | -2.235992000 |  |
| C  | 1.193615000  | 0.960467000  | -4.377544000 |  |
| H  | 1.001378000  | 1.447384000  | -5.318099000 |  |
| C  | 2.235888000  | 0.198785000  | -3.986446000 |  |
| H  | 3.121894000  | -0.095617000 | -4.521702000 |  |
| C  | -0.982337000 | 1.646005000  | -3.438510000 |  |
| H  | -1.405241000 | 1.533998000  | -2.440172000 |  |
| C  | -0.880776000 | 3.117888000  | -3.791749000 |  |
| H  | -0.290223000 | 3.670407000  | -3.062049000 |  |
| H  | -1.881784000 | 3.552740000  | -3.812622000 |  |
| H  | -0.438209000 | 3.262804000  | -4.780408000 |  |
| C  | -1.837134000 | 0.884222000  | -4.437554000 |  |
| H  | -1.432043000 | 0.968404000  | -5.449099000 |  |
| H  | -2.847264000 | 1.297936000  | -4.446236000 |  |
| H  | -1.897171000 | -0.171999000 | -4.174575000 |  |
| C  | 2.923091000  | -1.007344000 | -1.940117000 |  |
| H  | 2.385847000  | -1.300088000 | -1.035114000 |  |
| C  | 4.147080000  | -0.200941000 | -1.546638000 |  |
| H  | 4.647802000  | 0.202291000  | -2.430311000 |  |
| H  | 4.853687000  | -0.837854000 | -1.013885000 |  |
| H  | 3.873564000  | 0.622816000  | -0.886859000 |  |
| C  | 3.289845000  | -2.259221000 | -2.718646000 |  |
| H  | 2.401529000  | -2.771247000 | -3.090281000 |  |
| H  | 3.838233000  | -2.939601000 | -2.064961000 |  |
| H  | 3.934410000  | -2.030368000 | -3.570750000 |  |
| H  | -2.234030000 | -0.241818000 | 0.890104000  |  |
| H  | -1.717092000 | 1.416673000  | 1.245613000  |  |
| H  | -1.423126000 | 0.762934000  | -0.658962000 |  |

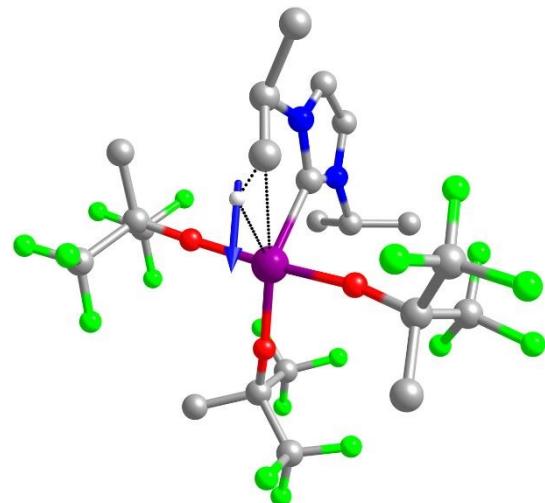
Optimized coordinates of TS1' (reductive elimination of Me<sub>4</sub>C) (PBE1PBE/Def2-TZVP PCM(thf) GD3)



H atoms omitted (except hydridic H atom)

|    |              |              |              |  |
|----|--------------|--------------|--------------|--|
| Ta | 0.248893000  | 0.061856000  | -0.050644000 |  |
| F  | -2.195793000 | -2.064754000 | -2.561759000 |  |
| F  | -0.169370000 | -2.517968000 | -3.111542000 |  |
| F  | -1.582009000 | -4.114056000 | -2.808336000 |  |
| F  | -2.339436000 | -4.675985000 | -0.280518000 |  |
| F  | -1.555615000 | -3.446806000 | 1.303813000  |  |
| F  | -2.996005000 | -2.635591000 | -0.064032000 |  |
| F  | -0.382487000 | 3.940644000  | 1.473930000  |  |
| F  | -0.440348000 | 4.200722000  | -0.659029000 |  |
| F  | 0.885394000  | 5.406254000  | 0.531092000  |  |
| F  | 3.195053000  | 4.327233000  | 1.323019000  |  |
| F  | 1.958826000  | 3.057823000  | 2.547344000  |  |
| F  | 3.396199000  | 2.190093000  | 1.197578000  |  |
| F  | -0.044881000 | -1.679546000 | 3.450428000  |  |
| F  | 1.667386000  | -2.556038000 | 4.414179000  |  |
| F  | 1.008642000  | -3.306674000 | 2.512551000  |  |
| F  | 4.205218000  | -0.851817000 | 1.574725000  |  |
| F  | 4.002060000  | -2.446102000 | 3.008917000  |  |
| F  | 3.170324000  | -2.653024000 | 1.030851000  |  |
| O  | -0.405066000 | -1.715462000 | -0.471603000 |  |
| O  | 0.860314000  | 1.877979000  | 0.260705000  |  |
| O  | 1.379526000  | -0.657957000 | 1.423323000  |  |
| N  | 0.339419000  | 1.041410000  | -3.307050000 |  |
| N  | 1.975508000  | -0.190532000 | -2.703946000 |  |
| C  | -0.755667000 | -2.970919000 | -0.866564000 |  |
| C  | -1.194393000 | -2.918339000 | -2.351685000 |  |
| C  | -1.933539000 | -3.439384000 | 0.026006000  |  |
| C  | 0.393684000  | -3.960223000 | -0.726372000 |  |
| H  | 1.229966000  | -3.616582000 | -1.331050000 |  |
| H  | 0.103695000  | -4.959306000 | -1.049618000 |  |
| H  | 0.708153000  | -3.989451000 | 0.313134000  |  |
| C  | 1.463160000  | 3.099402000  | 0.200162000  |  |
| C  | 2.509126000  | 3.180598000  | 1.339085000  |  |
| C  | 0.371918000  | 4.178885000  | 0.401495000  |  |
| C  | 2.172898000  | 3.342595000  | -1.125566000 |  |
| H  | 2.994617000  | 2.636675000  | -1.228961000 |  |
| H  | 2.563238000  | 4.357819000  | -1.189503000 |  |
| H  | 1.471362000  | 3.170092000  | -1.936905000 |  |
| C  | 2.052640000  | -1.133989000 | 2.512254000  |  |
| C  | 3.367328000  | -1.787797000 | 2.030523000  |  |
| C  | 1.168443000  | -2.189012000 | 3.226588000  |  |
| C  | 2.376909000  | -0.034370000 | 3.515854000  |  |
| H  | 2.976296000  | 0.725039000  | 3.024158000  |  |
| H  | 2.917000000  | -0.420013000 | 4.380055000  |  |
| H  | 1.443472000  | 0.419593000  | 3.847494000  |  |
| C  | -2.043510000 | 0.730923000  | 0.431970000  |  |
| C  | -3.387138000 | 1.277756000  | -0.123544000 |  |
| C  | -3.889308000 | 0.420061000  | -1.277022000 |  |
| H  | -3.163975000 | 0.377580000  | -2.090858000 |  |
| H  | -4.822811000 | 0.824139000  | -1.677960000 |  |
| H  | -4.072934000 | -0.605400000 | -0.951690000 |  |
| C  | -3.241257000 | 2.729387000  | -0.562058000 |  |
| H  | -2.919499000 | 3.357786000  | 0.272087000  |  |
| H  | -4.196081000 | 3.114811000  | -0.930009000 |  |
| H  | -2.506137000 | 2.846133000  | -1.358958000 |  |
| C  | -4.394951000 | 1.213023000  | 1.023308000  |  |
| C  | 0.799565000  | 0.329660000  | -2.234076000 |  |
| C  | 1.197965000  | 0.975077000  | -4.371787000 |  |
| H  | 1.010052000  | 1.472706000  | -5.307536000 |  |
| C  | 2.229587000  | 0.193729000  | -3.991591000 |  |
| H  | 3.108817000  | -0.109680000 | -4.532962000 |  |
| C  | -0.968140000 | 1.678453000  | -3.423332000 |  |
| H  | -1.386669000 | 1.585097000  | -2.421306000 |  |
| C  | -0.854950000 | 3.144253000  | -3.797973000 |  |
| H  | -0.246378000 | 3.700070000  | -3.085828000 |  |
| H  | -1.851340000 | 3.589938000  | -3.808014000 |  |
| H  | -0.427791000 | 3.271402000  | -4.795865000 |  |
| C  | -1.836648000 | 0.912185000  | -4.407362000 |  |
| H  | -1.436459000 | 0.980443000  | -5.422051000 |  |
| H  | -2.843418000 | 1.333885000  | -4.414827000 |  |
| H  | -1.903182000 | -0.140462000 | -4.131163000 |  |
| C  | 2.910066000  | -1.030391000 | -1.952667000 |  |
| H  | 2.369307000  | -1.329925000 | -1.052118000 |  |
| C  | 4.135676000  | -0.232042000 | -1.547572000 |  |
| H  | 4.641452000  | 0.176236000  | -2.426031000 |  |
| H  | 4.837616000  | -0.875571000 | -1.016544000 |  |
| H  | 3.861964000  | 0.587633000  | -0.882579000 |  |
| C  | 3.274338000  | -2.276198000 | -2.741787000 |  |
| H  | 2.385015000  | -2.781635000 | -3.120000000 |  |
| H  | 3.818856000  | -2.964444000 | -2.093114000 |  |
| H  | 3.921853000  | -2.042048000 | -3.590219000 |  |
| H  | -2.248222000 | -0.249302000 | 0.866779000  |  |
| H  | -1.717719000 | 1.408298000  | 1.225193000  |  |
| H  | -1.406074000 | 0.750243000  | -0.678691000 |  |
| H  | -4.058066000 | 1.808780000  | 1.876600000  |  |
| H  | -5.365843000 | 1.601187000  | 0.702069000  |  |
| H  | -4.537297000 | 0.183538000  | 1.363650000  |  |

Optimized coordinates of TS2 (oxidative addition of 'Pr-C-H) (PBE1PBE/Def2-TZVP PCM(thf) GD3)



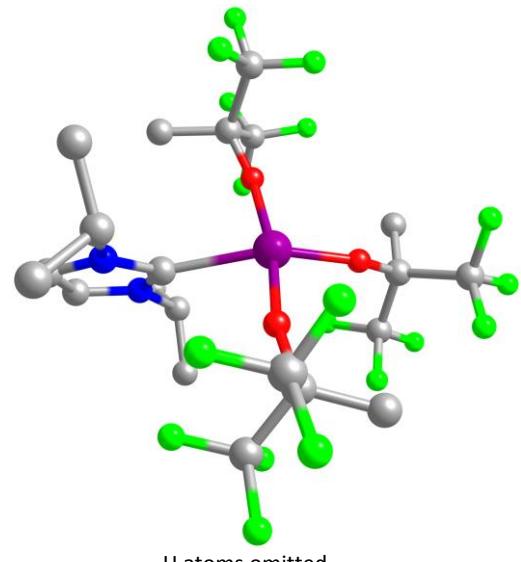
|   |              |              |              |
|---|--------------|--------------|--------------|
| C | -0.877737000 | -0.124530000 | 4.016931000  |
| C | -4.029080000 | -0.375661000 | 0.561508000  |
| C | 0.356475000  | -0.402805000 | 3.177848000  |
| C | 1.638069000  | -0.361112000 | 3.989135000  |
| C | 3.902077000  | 0.360763000  | 0.393120000  |
| C | -1.855228000 | 3.312262000  | -0.719663000 |
| C | -0.546652000 | 3.065568000  | 1.394482000  |
| C | -3.512823000 | -2.439642000 | -0.733147000 |
| C | -3.263660000 | -0.938512000 | -0.661796000 |
| C | -0.506296000 | 2.902498000  | -0.142916000 |
| C | 3.206555000  | -0.001505000 | -0.942324000 |
| C | 0.109197000  | -1.834881000 | 1.141484000  |
| C | 0.140277000  | -2.892920000 | 3.119746000  |
| C | -3.765308000 | -0.294749000 | -1.978372000 |
| C | 3.840029000  | -1.278556000 | -1.549068000 |
| C | 3.373075000  | 1.144924000  | -1.929645000 |
| C | 0.581295000  | 3.824499000  | -0.749112000 |
| C | -0.025728000 | -3.834724000 | 2.160343000  |
| C | 0.315363000  | -2.722171000 | -1.374671000 |
| C | -0.213498000 | -3.727704000 | -0.362323000 |
| C | 0.485225000  | -5.071857000 | -0.490435000 |
| H | -0.795985000 | 0.865888000  | 4.467228000  |
| H | -1.778668000 | -0.150147000 | 3.402915000  |
| H | 1.762563000  | 0.635969000  | 4.414852000  |
| H | -0.980846000 | -0.855248000 | 4.823125000  |

|    |              |              |              |
|----|--------------|--------------|--------------|
| H  | 0.416353000  | 0.337425000  | 2.379956000  |
| H  | -2.622739000 | 2.659769000  | -0.314346000 |
| H  | 1.611541000  | -1.076282000 | 4.815271000  |
| H  | -3.162528000 | -2.899675000 | 0.189436000  |
| H  | 2.504017000  | -0.579487000 | 3.364106000  |
| H  | -4.571461000 | -2.661659000 | -0.861488000 |
| H  | -2.096160000 | 4.348795000  | -0.486611000 |
| H  | -1.825005000 | 3.181251000  | -1.800290000 |
| H  | 0.212594000  | -2.995652000 | 4.188805000  |
| H  | -2.958702000 | -2.848768000 | -1.575916000 |
| H  | 2.966704000  | 2.051988000  | -1.490607000 |
| H  | 4.419851000  | 1.303502000  | -2.186550000 |
| H  | 2.809043000  | 0.909319000  | -2.830855000 |
| H  | -0.127278000 | -4.902593000 | 2.243634000  |
| H  | 0.088677000  | -3.137719000 | -2.363845000 |
| H  | 1.402051000  | -2.688004000 | -1.308539000 |
| H  | -1.284252000 | -3.877816000 | -0.514040000 |
| H  | 1.552357000  | -4.971856000 | -0.278810000 |
| H  | 0.062301000  | -5.826076000 | 0.177306000  |
| H  | 0.369139000  | -5.437320000 | -1.511754000 |
| F  | -3.543459000 | -0.927377000 | 1.678683000  |
| F  | -5.334820000 | -0.655474000 | 0.513395000  |
| F  | 3.291199000  | 1.405214000  | 0.950982000  |
| F  | -3.906585000 | 0.944851000  | 0.688157000  |
| F  | -1.505927000 | 2.287936000  | 1.905389000  |
| F  | 3.860254000  | -0.641123000 | 1.276589000  |
| F  | 5.186387000  | 0.689270000  | 0.220980000  |
| F  | -0.811901000 | 4.322939000  | 1.767498000  |
| F  | 0.598901000  | 2.709763000  | 1.981865000  |
| F  | -5.065556000 | -0.525460000 | -2.188441000 |
| F  | -3.580467000 | 1.023635000  | -2.008658000 |
| F  | 3.699923000  | -2.347999000 | -0.761340000 |
| F  | 5.144983000  | -1.128962000 | -1.793283000 |
| F  | 0.295088000  | 5.122295000  | -0.591245000 |
| F  | -3.094738000 | -0.812949000 | -3.011184000 |
| F  | 0.680195000  | 3.597065000  | -2.062207000 |
| F  | 1.790826000  | 3.622113000  | -0.220978000 |
| F  | 3.245578000  | -1.566350000 | -2.711028000 |
| N  | 0.219541000  | -1.683363000 | 2.481958000  |
| N  | -0.032482000 | -3.167038000 | 0.967045000  |
| O  | -1.945538000 | -0.625365000 | -0.508429000 |
| O  | -0.188824000 | 1.610138000  | -0.446438000 |
| O  | 1.895810000  | -0.257309000 | -0.667427000 |
| Ta | -0.026990000 | -0.351111000 | -0.505287000 |
| H  | -0.062960000 | -1.551010000 | -1.864996000 |

## Comparison of (NHC) $Ta^{III}(OR_F)_3$ (8) to its niobium and vanadium homologs

For the comparison of the trivalent complexes (NHC)M(OR<sub>F</sub>)<sub>3</sub> (M = V, Nb, Ta), each complex was optimized in its S = 0 and S = 1 spin state using Gaussian 16 (G16RevB.01).<sup>[7]</sup> All atoms were described with the PBE1PBE functional<sup>[8,9]</sup> in conjunction with the valence triple- $\zeta$  basis set Def2-TZVP including polarization functions.<sup>[10]</sup> Dispersion interactions (GD3)<sup>[11]</sup> and solvation effects (PCM for thf)<sup>[12,13]</sup> were taken into account during the geometry optimizations. Optimized coordinates are provided below. The final single-point energies of the optimized structures were calculated with DLPNO-CCSD(T)<sup>[14]</sup> using ORCA (version 4.2.1).<sup>[15,16]</sup> The cc-pVTZ-DK basis set<sup>[17-19]</sup> was employed and the required auxiliary basis sets were generated via AUTOAUX<sup>[20]</sup>. Second-order Douglas-Kroll-Hess scalar relativistic corrections were used (DKH2).<sup>[21,22]</sup>

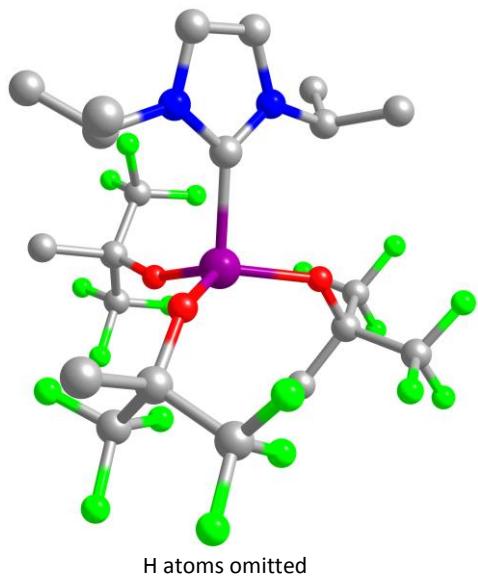
### Optimized coordinates of Ta(NHC)(OR<sub>F</sub>)<sub>3</sub> (S = 0, PBE1PBE/Def2-TZVP PCM(thf) GD3)



H atoms omitted

|    |              |              |              |
|----|--------------|--------------|--------------|
| H  | 0.145992000  | -5.072366000 | 1.461567000  |
| H  | 1.553370000  | -2.363157000 | 1.309698000  |
| H  | -2.697992000 | 2.899403000  | 0.880321000  |
| H  | 2.525162000  | -5.134573000 | 0.462507000  |
| H  | -2.077514000 | -3.188765000 | 0.582354000  |
| H  | 3.334327000  | -3.606779000 | 0.058902000  |
| H  | -3.840746000 | -3.232002000 | 0.405474000  |
| H  | -2.765334000 | 4.028430000  | -0.492598000 |
| H  | -2.750375000 | 2.275952000  | -0.772312000 |
| H  | 0.928778000  | -5.160809000 | -1.183132000 |
| H  | -2.822096000 | -2.676744000 | -0.934193000 |
| H  | 2.889261000  | 2.370103000  | 1.370281000  |
| H  | 4.403787000  | 2.353854000  | 0.440556000  |
| H  | 2.839716000  | 2.499533000  | -0.390365000 |
| H  | -0.271471000 | -3.991137000 | -3.358342000 |
| H  | -0.024299000 | 0.063560000  | -4.546467000 |
| H  | 0.800352000  | -1.503139000 | -4.500521000 |
| H  | -1.089401000 | -0.441961000 | -2.353388000 |
| H  | -1.577600000 | -2.565514000 | -4.513273000 |
| H  | -2.670905000 | -2.227388000 | -3.158871000 |
| H  | -2.351844000 | -0.989258000 | -4.377794000 |
| H  | 1.160336000  | -0.269398000 | -3.271987000 |
| F  | -2.359331000 | -2.018163000 | 2.807233000  |
| F  | -4.470991000 | -1.748091000 | 2.472013000  |
| F  | 3.309820000  | 0.261026000  | 2.683043000  |
| F  | -3.182877000 | -0.038122000 | 2.719324000  |
| F  | -0.659999000 | 3.950137000  | 1.988511000  |
| F  | 3.905802000  | -1.447966000 | 1.527282000  |
| F  | 5.209289000  | 0.256781000  | 1.669926000  |
| F  | -0.770711000 | 5.381514000  | 0.384690000  |
| F  | 1.033135000  | 4.249797000  | 0.700055000  |
| F  | -5.274470000 | -1.185208000 | -0.066756000 |
| F  | -4.374378000 | 0.702883000  | 0.434047000  |
| F  | 3.742630000  | -1.255202000 | -1.182282000 |
| F  | 5.188621000  | 0.335993000  | -1.039400000 |
| F  | -0.760066000 | 4.437962000  | -2.132506000 |
| F  | -3.785711000 | -0.323753000 | -1.362022000 |
| F  | -0.930447000 | 2.312777000  | -2.429103000 |
| F  | 0.936612000  | 3.158027000  | -1.790079000 |
| F  | 3.299077000  | 0.673968000  | -2.016061000 |
| N  | 0.752454000  | -3.159859000 | -0.396488000 |
| N  | -0.200237000 | -2.255160000 | -2.082624000 |
| O  | -1.824615000 | -0.566407000 | 0.447200000  |
| O  | -0.339392000 | 1.871984000  | 0.294210000  |
| O  | 1.930749000  | 0.116890000  | 0.315760000  |
| Ta | 0.017325000  | -0.007185000 | 0.288355000  |

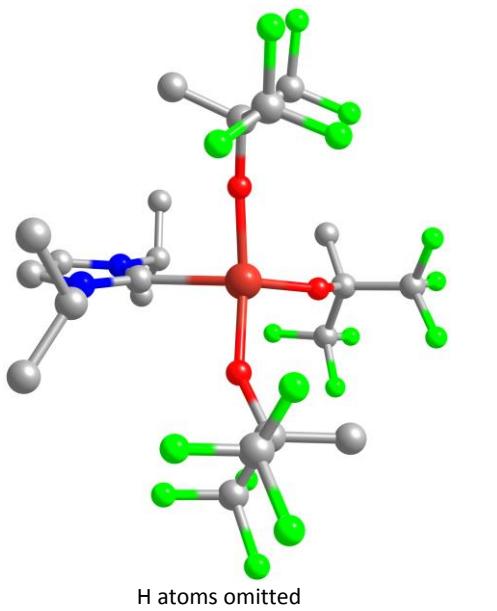
**Optimized coordinates of Ta(NHC)(OR<sub>F</sub>)<sub>3</sub> (S = 1, PBE1PBE/Def2-TZVP PCM(thf) GD3)**



|    |             |              |              |
|----|-------------|--------------|--------------|
| Ta | 5.986549000 | 8.098888000  | 13.853561000 |
| N  | 7.257188000 | 11.014930000 | 13.347206000 |
| N  | 6.715372000 | 10.745191000 | 15.410014000 |
| C  | 6.741281000 | 10.081879000 | 14.208100000 |
| C  | 7.553547000 | 12.186305000 | 13.996702000 |
| H  | 7.974514000 | 13.039555000 | 13.493683000 |
| C  | 7.213051000 | 12.017818000 | 15.291131000 |
| H  | 7.281422000 | 12.698346000 | 16.122126000 |
| C  | 7.474258000 | 10.826793000 | 11.915465000 |
| H  | 6.982922000 | 9.888440000  | 11.676145000 |
| C  | 6.825581000 | 11.944294000 | 11.118310000 |
| H  | 5.770632000 | 12.046881000 | 11.376389000 |
| H  | 6.898656000 | 11.714164000 | 10.053983000 |
| H  | 7.322060000 | 12.902948000 | 11.286228000 |
| C  | 8.955495000 | 10.683633000 | 11.616212000 |
| H  | 9.500480000 | 11.589468000 | 11.894913000 |
| H  | 9.101451000 | 10.513929000 | 10.548323000 |
| H  | 9.376694000 | 9.836252000  | 12.159473000 |
| C  | 6.200286000 | 10.206313000 | 16.664291000 |
| H  | 5.710195000 | 9.269714000  | 16.396642000 |
| C  | 5.170728000 | 11.142567000 | 17.272286000 |
| H  | 5.629985000 | 12.067586000 | 17.628195000 |
| H  | 4.697785000 | 10.656634000 | 18.127393000 |
| H  | 4.397558000 | 11.401197000 | 16.546720000 |

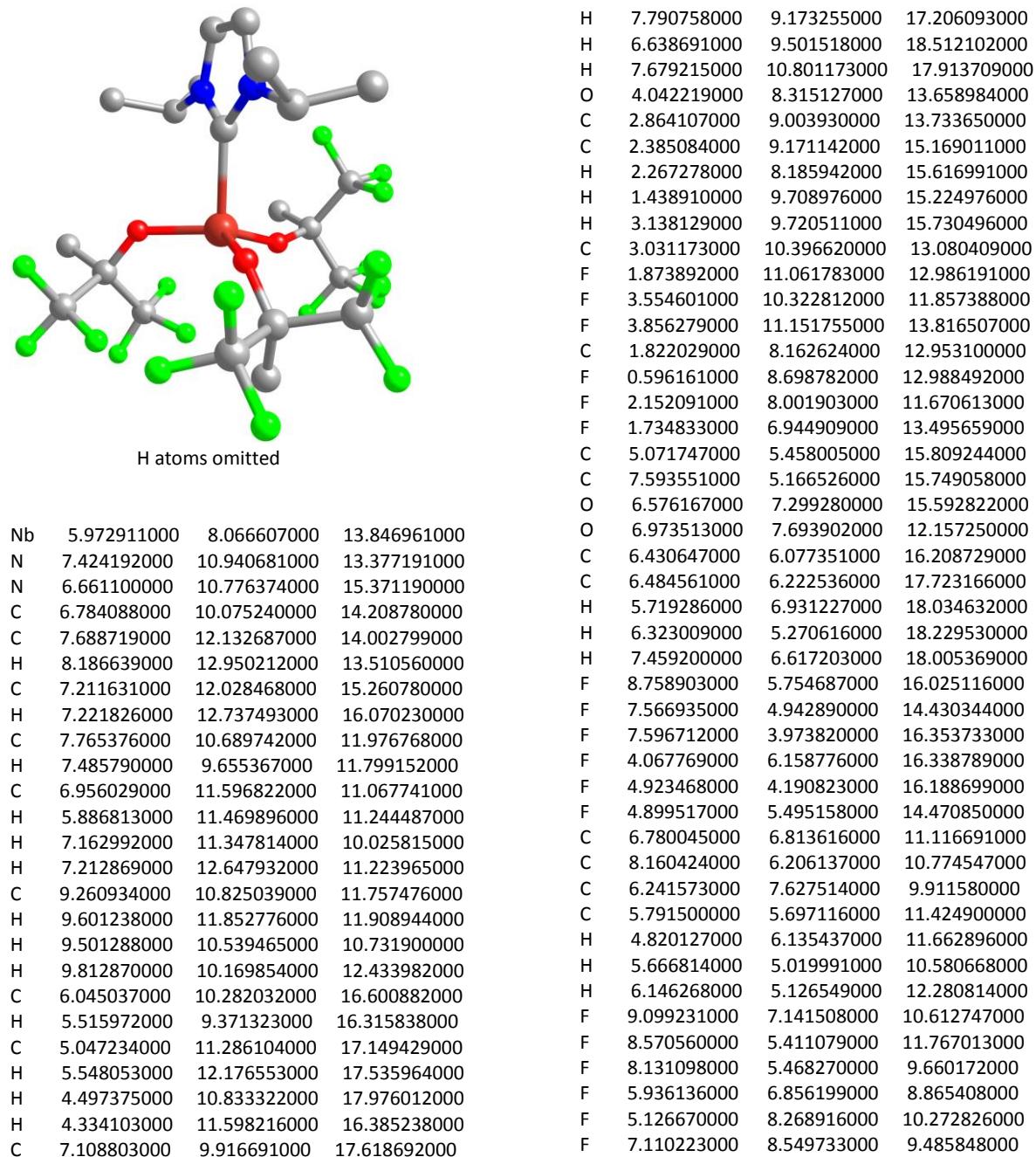
|   |             |              |              |
|---|-------------|--------------|--------------|
| C | 7.336048000 | 9.891609000  | 17.619843000 |
| H | 8.031417000 | 9.184177000  | 17.166552000 |
| H | 6.940020000 | 9.451260000  | 18.536820000 |
| H | 7.880419000 | 10.801178000 | 17.886736000 |
| O | 4.056770000 | 8.284125000  | 13.654735000 |
| C | 2.879174000 | 8.985761000  | 13.631641000 |
| C | 2.298763000 | 9.166602000  | 15.025999000 |
| H | 2.115405000 | 8.185593000  | 15.461794000 |
| H | 1.368361000 | 9.733993000  | 15.009948000 |
| H | 3.024783000 | 9.692041000  | 15.644037000 |
| C | 3.112895000 | 10.369800000 | 12.977709000 |
| F | 1.969624000 | 11.004878000 | 12.700440000 |
| F | 3.806630000 | 10.275834000 | 11.842909000 |
| F | 3.811704000 | 11.159010000 | 13.800572000 |
| C | 1.898195000 | 8.142855000  | 12.777868000 |
| F | 0.672428000 | 8.673066000  | 12.725646000 |
| F | 2.323949000 | 7.989110000  | 11.521482000 |
| F | 1.779010000 | 6.923377000  | 13.308142000 |
| C | 5.016969000 | 5.463912000  | 15.902278000 |
| C | 7.520182000 | 5.091636000  | 15.766007000 |
| O | 6.564413000 | 7.255086000  | 15.570115000 |
| O | 7.052410000 | 7.755646000  | 12.190748000 |
| C | 6.405784000 | 6.057701000  | 16.231187000 |
| C | 6.524542000 | 6.256711000  | 17.735586000 |
| H | 5.807917000 | 7.014244000  | 18.047161000 |
| H | 6.334825000 | 5.333994000  | 18.283790000 |
| H | 7.528389000 | 6.609910000  | 17.966857000 |
| F | 8.708376000 | 5.682533000  | 15.894436000 |
| F | 7.384395000 | 4.747366000  | 14.480349000 |
| F | 7.556923000 | 3.961355000  | 16.477999000 |
| F | 4.052658000 | 6.191917000  | 16.468030000 |
| F | 4.867523000 | 4.205926000  | 16.313676000 |
| F | 4.783005000 | 5.482291000  | 14.575846000 |
| C | 6.860140000 | 6.831499000  | 11.183708000 |
| C | 8.209866000 | 6.116400000  | 10.958247000 |
| C | 6.439404000 | 7.622038000  | 9.919782000  |
| C | 5.788103000 | 5.792493000  | 11.486876000 |
| H | 4.834783000 | 6.294901000  | 11.661560000 |
| H | 5.659420000 | 5.088595000  | 10.665639000 |
| H | 6.068884000 | 5.232797000  | 12.378109000 |
| F | 9.198169000 | 6.962554000  | 10.668094000 |
| F | 8.564392000 | 5.465085000  | 12.068530000 |
| F | 8.147049000 | 5.214980000  | 9.969857000  |
| F | 6.201076000 | 6.830647000  | 8.869079000  |
| F | 5.311987000 | 8.293302000  | 10.178484000 |
| F | 7.350116000 | 8.520829000  | 9.540192000  |

**Optimized coordinates of Nb(NHC)(OR<sub>F</sub>)<sub>3</sub> (*S* = 0, PBE1PBE/Def2-TZVP PCM(thf) GD3)**

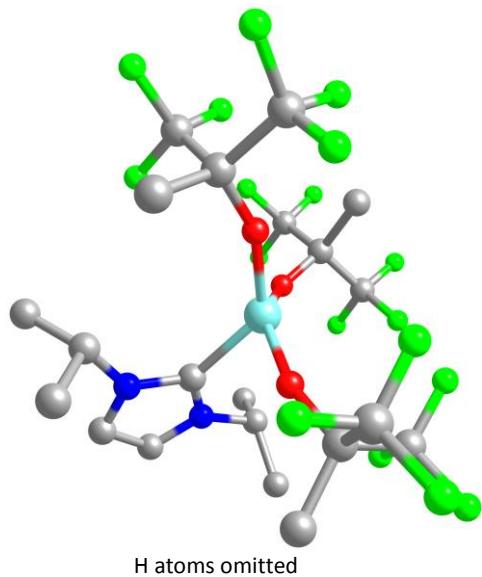


|   |              |              |              |    |              |              |              |
|---|--------------|--------------|--------------|----|--------------|--------------|--------------|
| C | 0.562776000  | -4.477480000 | 1.220762000  | H  | 0.505158000  | -5.439279000 | 0.706023000  |
| C | -2.365750000 | -1.213316000 | 2.678651000  | H  | 1.450033000  | -2.541998000 | 0.971836000  |
| C | 1.397803000  | -3.488264000 | 0.429095000  | H  | -2.789154000 | 2.408066000  | -0.745087000 |
| C | 2.810444000  | -3.989076000 | 0.192946000  | H  | 2.802166000  | -4.937357000 | -0.349463000 |
| C | 3.427411000  | -0.354869000 | 2.286504000  | H  | -2.411870000 | -3.187524000 | 0.795657000  |
| C | -2.067802000 | 2.573574000  | -1.542703000 | H  | 3.390634000  | -3.262427000 | -0.375720000 |
| C | -0.814071000 | 4.028049000  | 0.053589000  | H  | -4.090154000 | -2.854324000 | 1.270198000  |
| C | -3.237644000 | -2.484264000 | 0.702110000  | H  | -2.399753000 | 3.405775000  | -2.162630000 |
| C | -2.780634000 | -1.115847000 | 1.190290000  | H  | -2.012430000 | 1.672449000  | -2.151317000 |
| C | -0.702009000 | 2.836038000  | -0.926377000 | H  | 0.876167000  | -5.102638000 | -1.788012000 |
| C | 3.096211000  | 0.478739000  | 1.025414000  | H  | -3.510912000 | -2.412301000 | -0.349180000 |
| C | 0.264984000  | -1.950050000 | -1.179932000 | H  | 2.065860000  | 1.986461000  | 2.139616000  |
| C | 0.555895000  | -4.077066000 | -1.852763000 | H  | 3.788720000  | 2.345815000  | 1.892435000  |
| C | -3.934418000 | -0.099037000 | 1.014891000  | H  | 2.631801000  | 2.512400000  | 0.551525000  |
| C | 4.240718000  | 0.387363000  | -0.010487000 | H  | -0.413370000 | -3.762818000 | -3.811544000 |
| C | 2.892564000  | 1.930453000  | 1.432281000  | H  | -0.574248000 | -0.089307000 | -5.108772000 |
| C | 0.320626000  | 3.153638000  | -2.043994000 | H  | -0.342141000 | -1.836439000 | -5.191677000 |
| C | -0.077839000 | -3.416973000 | -2.848937000 | H  | -0.641436000 | -0.161747000 | -2.641365000 |
| C | -0.170834000 | -0.951194000 | -4.574524000 | H  | -2.590942000 | -2.199296000 | -3.841026000 |
| C | -0.851612000 | -1.064234000 | -3.224647000 | H  | -2.804527000 | -1.281635000 | -2.336174000 |
| C | -2.350381000 | -1.264643000 | -3.328062000 | H  | -2.793656000 | -0.444503000 | -3.896098000 |
| H | 1.022187000  | -4.641999000 | 2.196522000  | H  | 0.905102000  | -0.810809000 | -4.455107000 |
| H | -0.449501000 | -4.104849000 | 1.377752000  | F  | -1.326353000 | -2.047154000 | 2.800641000  |
| H | 3.304388000  | -4.154071000 | 1.150644000  | F  | -3.350503000 | -1.693042000 | 3.444784000  |
|   |              |              |              | F  | 2.418730000  | -0.277046000 | 3.157551000  |
|   |              |              |              | F  | -1.992595000 | -0.041159000 | 3.188574000  |
|   |              |              |              | F  | -1.636763000 | 3.710709000  | 1.054473000  |
|   |              |              |              | F  | 3.610944000  | -1.648861000 | 2.013780000  |
|   |              |              |              | F  | 4.527493000  | 0.079857000  | 2.908252000  |
|   |              |              |              | F  | -1.306863000 | 5.124657000  | -0.532843000 |
|   |              |              |              | F  | 0.361831000  | 4.357217000  | 0.593724000  |
|   |              |              |              | F  | -5.034422000 | -0.458854000 | 1.684961000  |
|   |              |              |              | F  | -3.600028000 | 1.125704000  | 1.418962000  |
|   |              |              |              | F  | 4.445030000  | -0.862899000 | -0.432856000 |
|   |              |              |              | F  | 5.401192000  | 0.842923000  | 0.472054000  |
|   |              |              |              | F  | 0.009428000  | 4.272564000  | -2.710646000 |
|   |              |              |              | F  | -4.265387000 | -0.011690000 | -0.277401000 |
|   |              |              |              | F  | 0.352713000  | 2.161792000  | -2.939406000 |
|   |              |              |              | F  | 1.560515000  | 3.299459000  | -1.575612000 |
|   |              |              |              | F  | 3.937243000  | 1.121271000  | -1.082669000 |
|   |              |              |              | N  | 0.752944000  | -3.167120000 | -0.845233000 |
|   |              |              |              | N  | -0.239848000 | -2.123910000 | -2.423949000 |
|   |              |              |              | O  | -1.714680000 | -0.659610000 | 0.468031000  |
|   |              |              |              | O  | -0.249175000 | 1.772747000  | -0.186054000 |
|   |              |              |              | O  | 1.986197000  | -0.056984000 | 0.423140000  |
|   |              |              |              | Nb | 0.091992000  | -0.105623000 | 0.083295000  |

**Optimized coordinates of Nb(NHC)(OR<sub>F</sub>)<sub>3</sub> (*S* = 1, PBE1PBE/Def2-TZVP PCM(thf) GD3)**

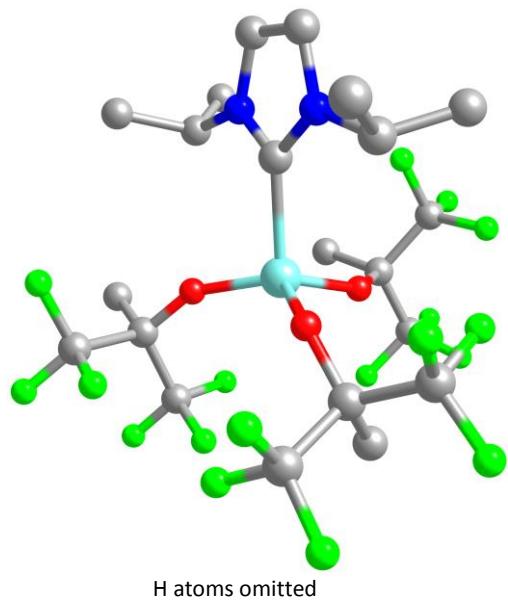


Optimized coordinates of V(NHC)(OR<sub>F</sub>)<sub>3</sub> (*S* = 0, PBE1PBE/Def2-TZVP PCM(thf) GD3)



|   |              |              |              |  |
|---|--------------|--------------|--------------|--|
| C | 0.603668000  | -4.604179000 | 1.047599000  |  |
| C | -1.849988000 | -1.344888000 | 2.818370000  |  |
| C | 1.350829000  | -3.484189000 | 0.347317000  |  |
| C | 2.804674000  | -3.833392000 | 0.087960000  |  |
| C | 3.023449000  | -0.410329000 | 2.422309000  |  |
| C | -1.800014000 | 2.375999000  | -2.147101000 |  |
| C | -0.899430000 | 3.836828000  | -0.347032000 |  |
| C | -3.208078000 | -2.344727000 | 0.965013000  |  |
| C | -2.513446000 | -1.077514000 | 1.446193000  |  |
| C | -0.572967000 | 2.644378000  | -1.279659000 |  |
| C | 2.745876000  | 0.474137000  | 1.182391000  |  |
| C | 0.218887000  | -1.907230000 | -1.230161000 |  |
| C | 0.500445000  | -4.021780000 | -1.938268000 |  |
| C | -3.552695000 | 0.065776000  | 1.555137000  |  |
| C | 4.029167000  | 0.640880000  | 0.333182000  |  |
| C | 2.280423000  | 1.842119000  | 1.659781000  |  |
| C | 0.629196000  | 2.981903000  | -2.192762000 |  |
| C | -0.115718000 | -3.340846000 | -2.930563000 |  |
| C | -0.238574000 | -0.818870000 | -4.595946000 |  |
| C | -0.904894000 | -0.984901000 | -3.244030000 |  |
| C | -2.401885000 | -1.207251000 | -3.341236000 |  |
| H | 1.042513000  | -4.771200000 | 2.032282000  |  |
| H | -0.449279000 | -4.354720000 | 1.179868000  |  |
| H | 3.304958000  | -4.052152000 | 1.031609000  |  |
| H | 0.673138000  | -5.537785000 | 0.484731000  |  |
| H | 1.305257000  | -2.581356000 | 0.955494000  |  |
| H | -2.557493000 | 1.894515000  | -1.530536000 |  |
| H | 2.883327000  | -4.716908000 | -0.550211000 |  |
| H | -2.466683000 | -3.133676000 | 0.849600000  |  |
| H | 3.321094000  | -3.002485000 | -0.393410000 |  |
| H | -3.978995000 | -2.673748000 | 1.660745000  |  |
| H | -2.204667000 | 3.297333000  | -2.565006000 |  |
| H | -1.541744000 | 1.716361000  | -2.971842000 |  |
| H | 0.814148000  | -5.050145000 | -1.887522000 |  |
| H | -3.660339000 | -2.150042000 | -0.006116000 |  |
| H | 1.353735000  | 1.727018000  | 2.221538000  |  |
| H | 3.025820000  | 2.317241000  | 2.296640000  |  |
| H | 2.082618000  | 2.473256000  | 0.798344000  |  |
| H | -0.443479000 | -3.664922000 | -3.903289000 |  |
| H | -0.652706000 | 0.056972000  | -5.098660000 |  |
| H | -0.412522000 | -1.684923000 | -5.238634000 |  |
| H | -0.710675000 | -0.097098000 | -2.641950000 |  |
| H | -2.628330000 | -2.122146000 | -3.893796000 |  |
| H | -2.845341000 | -1.278242000 | -2.346461000 |  |
| H | -2.866743000 | -0.371668000 | -3.867674000 |  |
| H | 0.837369000  | -0.675931000 | -4.483679000 |  |
| F | -0.918273000 | -2.296526000 | 2.686908000  |  |
| F | -2.727398000 | -1.770602000 | 3.731770000  |  |
| F | 1.893792000  | -0.574768000 | 3.118126000  |  |
| F | -1.239841000 | -0.268077000 | 3.312324000  |  |
| F | -1.977484000 | 3.550430000  | 0.385921000  |  |
| F | 3.465555000  | -1.628577000 | 2.103967000  |  |
| F | 3.924434000  | 0.133513000  | 3.247646000  |  |
| F | -1.167616000 | 4.958173000  | -1.029520000 |  |
| F | 0.091600000  | 4.115836000  | 0.500292000  |  |
| F | -4.550218000 | -0.237254000 | 2.393111000  |  |
| F | -3.014249000 | 1.210813000  | 1.967771000  |  |
| F | 4.502520000  | -0.524500000 | -0.115895000 |  |
| F | 5.017577000  | 1.238321000  | 1.010086000  |  |
| F | 0.356805000  | 3.966897000  | -3.056770000 |  |
| F | -4.095396000 | 0.292897000  | 0.354734000  |  |
| F | 0.959084000  | 1.904680000  | -2.914632000 |  |
| F | 1.715118000  | 3.343634000  | -1.508164000 |  |
| F | 3.765937000  | 1.394666000  | -0.735769000 |  |
| N | 0.692212000  | -3.131561000 | -0.911375000 |  |
| N | -0.272318000 | -2.055458000 | -2.479867000 |  |
| O | -1.556522000 | -0.673465000 | 0.561700000  |  |
| O | -0.235675000 | 1.594839000  | -0.471695000 |  |
| O | 1.835036000  | -0.172242000 | 0.381728000  |  |
| V | 0.055609000  | -0.155010000 | -0.034262000 |  |

**Optimized coordinates of V(NHC)(OR<sub>F</sub>)<sub>3</sub> (S = 1, PBE1PBE/Def2-TZVP PCM(thf) GD3)**

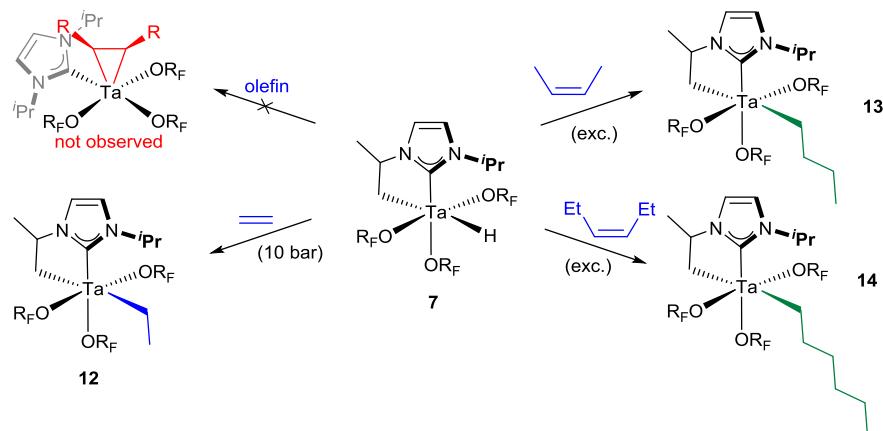


|   |              |              |             |   |              |              |              |
|---|--------------|--------------|-------------|---|--------------|--------------|--------------|
| V | 0.119601000  | -0.107439000 | 0.206100000 | C | 2.104207000  | -3.133280000 | 2.827874000  |
| N | -1.529208000 | -0.701961000 | 2.821286000 | H | 2.482734000  | -2.117905000 | 2.951202000  |
| N | -0.161549000 | -2.301438000 | 2.451387000 | H | 2.899382000  | -3.754231000 | 2.411554000  |
| C | -0.549515000 | -1.094500000 | 1.978092000 | H | 1.846253000  | -3.534242000 | 3.810920000  |
| C | -1.747459000 | -1.639180000 | 3.798298000 | O | -1.055665000 | -0.613177000 | -1.123903000 |
| H | -2.489694000 | -1.516843000 | 4.567995000 | C | -1.490950000 | -1.696424000 | -1.833725000 |
| C | -0.881706000 | -2.648565000 | 3.566742000 | C | -0.525388000 | -2.874185000 | -1.812569000 |
| H | -0.723357000 | -3.570115000 | 4.099134000 | H | 0.448547000  | -2.537656000 | -2.162816000 |
| C | -2.294336000 | 0.544533000  | 2.731563000 | H | -0.868639000 | -3.696111000 | -2.440025000 |
| H | -1.862254000 | 1.077247000  | 1.889420000 | H | -0.426512000 | -3.235209000 | -0.790109000 |
| C | -3.755396000 | 0.249022000  | 2.449145000 | C | -2.849456000 | -2.148713000 | -1.244136000 |
| H | -3.865060000 | -0.335076000 | 1.534088000 | F | -3.367879000 | -3.198837000 | -1.891345000 |
| H | -4.296911000 | 1.187977000  | 2.325747000 | F | -3.765655000 | -1.180340000 | -1.255257000 |
| H | -4.216798000 | -0.301214000 | 3.272736000 | F | -2.681588000 | -2.516319000 | 0.033086000  |
| C | -2.094350000 | 1.375725000  | 3.985209000 | C | -1.663172000 | -1.217931000 | -3.296725000 |
| H | -2.506238000 | 0.876539000  | 4.865598000 | F | -2.156884000 | -2.172053000 | -4.094336000 |
| H | -2.606842000 | 2.331470000  | 3.869932000 | F | -2.468558000 | -0.158640000 | -3.395611000 |
| H | -1.034287000 | 1.571252000  | 4.156460000 | F | -0.476524000 | -0.856570000 | -3.793317000 |
| C | 0.900323000  | -3.149469000 | 1.903482000 | C | 3.096912000  | -0.147598000 | -1.862779000 |
| H | 1.181271000  | -2.685603000 | 0.960037000 | C | 3.997554000  | 0.188362000  | 0.495750000  |
| C | 0.384438000  | -4.554186000 | 1.648588000 | O | 1.861171000  | -0.724663000 | 0.101063000  |
| H | 0.182199000  | -5.082709000 | 2.582636000 | O | -0.227561000 | 1.690224000  | 0.567071000  |
| H | 1.140007000  | -5.121754000 | 1.103161000 | C | 3.124539000  | -0.706045000 | -0.420552000 |
| H | -0.532821000 | -4.541338000 | 1.056959000 | C | 3.726457000  | -2.105968000 | -0.458320000 |
|   |              |              |             | H | 3.105343000  | -2.743990000 | -1.085643000 |
|   |              |              |             | H | 4.742140000  | -2.097818000 | -0.852832000 |
|   |              |              |             | H | 3.741952000  | -2.511777000 | 0.550761000  |
|   |              |              |             | F | 4.066887000  | -0.351195000 | 1.717931000  |
|   |              |              |             | F | 3.494918000  | 1.412989000  | 0.636484000  |
|   |              |              |             | F | 5.252408000  | 0.314735000  | 0.048802000  |
|   |              |              |             | F | 2.318386000  | -0.920510000 | -2.628697000 |
|   |              |              |             | F | 4.304607000  | -0.112670000 | -2.430335000 |
|   |              |              |             | F | 2.592165000  | 1.088611000  | -1.918794000 |
|   |              |              |             | C | -0.479870000 | 2.791412000  | -0.217677000 |
|   |              |              |             | C | 0.603070000  | 3.847127000  | 0.104357000  |
|   |              |              |             | C | -1.879654000 | 3.327676000  | 0.174370000  |
|   |              |              |             | C | -0.479842000 | 2.519076000  | -1.717142000 |
|   |              |              |             | H | -1.243885000 | 1.778334000  | -1.944652000 |
|   |              |              |             | H | -0.672771000 | 3.426570000  | -2.288297000 |
|   |              |              |             | H | 0.489466000  | 2.123366000  | -2.013668000 |
|   |              |              |             | F | 0.700901000  | 4.097495000  | 1.411541000  |
|   |              |              |             | F | 1.796052000  | 3.413035000  | -0.304886000 |
|   |              |              |             | F | 0.374940000  | 5.014722000  | -0.510228000 |
|   |              |              |             | F | -2.235761000 | 4.407292000  | -0.529681000 |
|   |              |              |             | F | -2.801059000 | 2.385416000  | -0.053146000 |
|   |              |              |             | F | -1.964069000 | 3.651849000  | 1.468014000  |

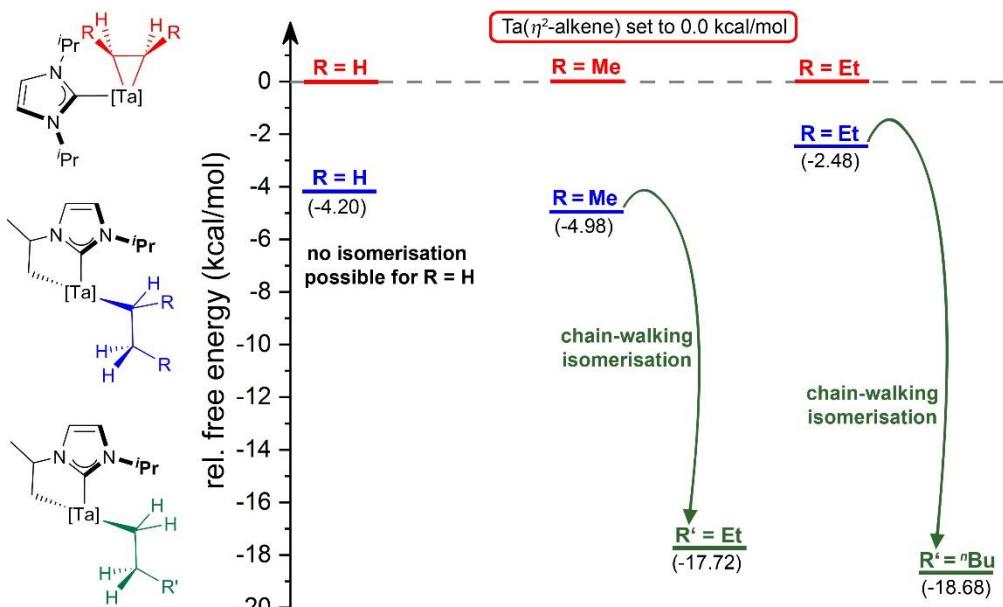
### Reactions of 7 with alkenes and isomerisations to the *n*-alkyl complexes

DFT calculations concerning the products of the reaction of **7** with alkenes (see Figure S73) were carried out with Gaussian 16 (G16RevB.01)<sup>[7]</sup> using the PBE1PBE functional.<sup>[8,9]</sup> All atoms were described with the valence triple- $\zeta$  basis set Def2-TZVP including polarization functions.<sup>[10]</sup> Energies and structures were neither corrected for dispersion effects nor for solvation effects. All stationary points were identified as minima by analytical frequency analysis.

Optimized coordinates of for all complexes shown in Figure S74 are provided on the following pages.

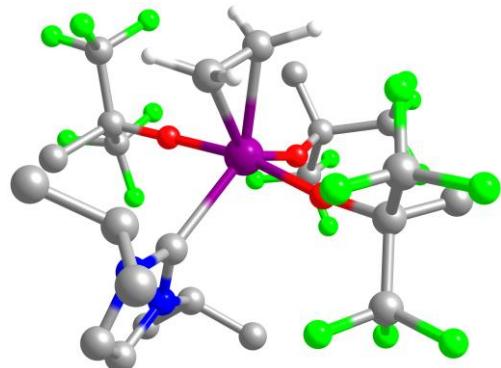


**Figure S73:** Reactions of **7** with olefins to afford the alkyl complexes **12**, **13** and **14** ( $\eta^2$ -alkene species were not observed experimentally).



**Figure S74:** Computational comparison (PBE1PBE/Def2-TZVP) of the *sec*- and *n*-alkyl complexes (highlighted in blue and in green, respectively), which result from the reaction of **7** with ethylene, *cis*-2-butene and *cis*-3-hexyne, respectively. The  $\eta^2$ -alkene complexes (highlighted in red) were not observed in the experiments and were set to 0.0 kcal/mol in the calculations.

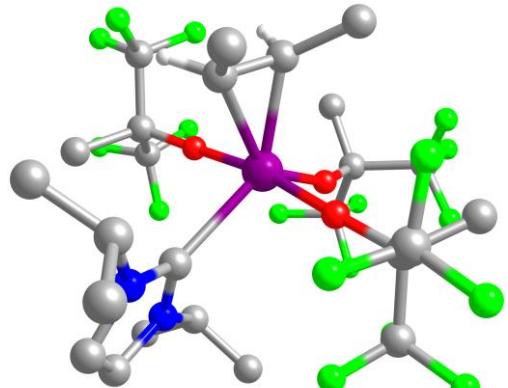
**Optimized coordinates of Ta(NHC)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)(OR<sub>F</sub>)<sub>3</sub> (PBE1PBE/Def2-TZVP)**



H atoms omitted (except  $\eta^2$ -olefine H atoms)

|   |              |              |              |    |              |              |              |
|---|--------------|--------------|--------------|----|--------------|--------------|--------------|
| C | -1.432766000 | -4.632614000 | -1.043870000 | H  | 3.209578000  | -3.860842000 | -0.086920000 |
| C | 3.234905000  | -1.854593000 | -1.902745000 | H  | 3.152605000  | 3.517883000  | -1.333243000 |
| C | -2.181873000 | -3.446857000 | -0.459782000 | H  | 3.146887000  | 1.770342000  | -1.010234000 |
| C | -3.648677000 | -3.764654000 | -0.224668000 | H  | -2.235331000 | -4.559047000 | 2.073539000  |
| C | -3.900150000 | 0.558816000  | -1.467203000 | H  | 2.134044000  | -3.125066000 | 1.116558000  |
| C | 2.525121000  | 2.631389000  | -1.242626000 | H  | -2.646158000 | 2.937897000  | -1.280902000 |
| C | 0.553181000  | 3.983756000  | -0.531484000 | H  | -4.127041000 | 3.054463000  | -0.305159000 |
| C | 2.386562000  | -3.161687000 | 0.057598000  | H  | -2.530243000 | 3.052020000  | 0.476483000  |
| C | 2.749788000  | -1.763436000 | -0.429070000 | H  | -0.777461000 | -3.159379000 | 3.922500000  |
| C | 1.474852000  | 2.797486000  | -0.151855000 | H  | 0.169312000  | 0.963372000  | 3.969250000  |
| C | -3.133028000 | 1.126999000  | -0.243424000 | H  | -1.101065000 | -0.231121000 | 4.282741000  |
| C | -0.758527000 | -1.889775000 | 0.904598000  | H  | 1.028355000  | -0.418375000 | 2.093909000  |
| C | -1.656411000 | -3.658709000 | 1.965652000  | H  | 0.821108000  | -1.840754000 | 4.781189000  |
| C | 3.901698000  | -1.212937000 | 0.457948000  | H  | 1.931065000  | -2.314790000 | 3.478949000  |
| C | -3.842470000 | 0.717522000  | 1.072986000  | H  | 2.066469000  | -0.726035000 | 4.232581000  |
| C | -3.117040000 | 2.646557000  | -0.343852000 | F  | 2.336487000  | -2.507870000 | -2.643826000 |
| C | 2.174896000  | 3.074846000  | 1.202355000  | F  | 4.388545000  | -2.521845000 | -2.001564000 |
| C | -0.938397000 | -2.970403000 | 2.876133000  | F  | -3.237907000 | 0.849722000  | -2.586162000 |
| C | -0.459424000 | 0.199074000  | 3.509400000  | F  | 3.409633000  | -0.656919000 | -2.452673000 |
| C | 0.417454000  | -0.868710000 | 2.879908000  | F  | -0.117886000 | 3.689921000  | -1.650382000 |
| C | 1.359685000  | -1.486336000 | 3.898875000  | F  | -4.033552000 | -0.769786000 | -1.414299000 |
| H | -1.911462000 | -4.947494000 | -1.973010000 | F  | -5.123454000 | 1.078310000  | -1.581393000 |
| H | -0.398455000 | -4.372870000 | -1.271233000 | F  | 1.238494000  | 5.106495000  | -0.765286000 |
| H | -4.130231000 | -3.953165000 | -1.185599000 | F  | -0.350812000 | 4.259344000  | 0.411190000  |
| H | -1.436413000 | -5.484479000 | -0.358098000 | F  | 4.894821000  | -2.095139000 | 0.594859000  |
| H | -2.096844000 | -2.602349000 | -1.137492000 | F  | 4.426747000  | -0.086773000 | -0.016149000 |
| H | 2.020500000  | 2.449674000  | -2.190683000 | F  | -3.770419000 | -0.594808000 | 1.304701000  |
| H | -3.780656000 | -4.661753000 | 0.386302000  | F  | -5.131288000 | 1.059069000  | 1.080480000  |
| H | 1.516144000  | -3.507587000 | -0.494944000 | F  | 2.901849000  | 4.195302000  | 1.180756000  |
| H | -4.164566000 | -2.933580000 | 0.255508000  | F  | 3.436724000  | -0.955432000 | 1.684922000  |
|   |              |              |              | F  | 3.001520000  | 2.067722000  | 1.498418000  |
|   |              |              |              | F  | 1.309113000  | 3.175943000  | 2.213434000  |
|   |              |              |              | F  | -3.264049000 | 1.330217000  | 2.110748000  |
|   |              |              |              | N  | -1.539804000 | -2.985997000 | 0.776039000  |
|   |              |              |              | N  | -0.393809000 | -1.899294000 | 2.214540000  |
|   |              |              |              | O  | 1.695348000  | -0.893346000 | -0.365662000 |
|   |              |              |              | O  | 0.704498000  | 1.675593000  | 0.020022000  |
|   |              |              |              | O  | -1.868172000 | 0.599276000  | -0.237618000 |
|   |              |              |              | Ta | -0.073910000 | -0.075660000 | -0.471888000 |
|   |              |              |              | H  | -1.092146000 | 0.685850000  | 2.769391000  |
|   |              |              |              | C  | -0.614448000 | -1.193665000 | -2.287544000 |
|   |              |              |              | C  | -0.016725000 | 0.113070000  | -2.599909000 |
|   |              |              |              | H  | 0.985651000  | 0.137976000  | -3.020434000 |
|   |              |              |              | H  | -0.050501000 | -2.080954000 | -2.559469000 |
|   |              |              |              | H  | -0.658133000 | 0.889454000  | -3.009759000 |
|   |              |              |              | H  | -1.667993000 | -1.293374000 | -2.536428000 |

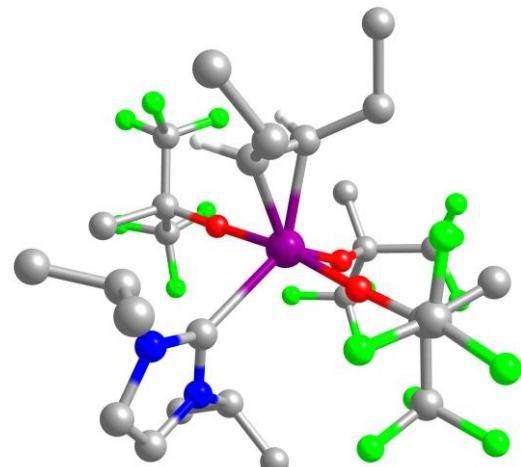
**Optimized coordinates of Ta(NHC)( $\eta^2$ -C<sub>2</sub>H<sub>2</sub>Me<sub>2</sub>)(OR<sub>f</sub>)<sub>3</sub> (PBE1PBE/Def2-TZVP)**



H atoms omitted (except  $\eta^2$ -olefinic H atoms)

|   |              |              |              |    |              |              |              |
|---|--------------|--------------|--------------|----|--------------|--------------|--------------|
| C | -1.211409000 | -4.682495000 | -0.649545000 | H  | -2.110937000 | -4.433668000 | 2.529180000  |
| C | 3.472403000  | -1.667912000 | -1.763411000 | H  | 2.313447000  | -2.996966000 | 1.210627000  |
| C | -2.067936000 | -3.559687000 | -0.088626000 | H  | -2.847732000 | 2.307309000  | -1.949882000 |
| C | -3.477106000 | -4.034545000 | 0.223322000  | H  | -4.137450000 | 2.843292000  | -0.851697000 |
| C | -4.236144000 | 0.162193000  | -0.900826000 | H  | -2.434629000 | 3.053722000  | -0.402625000 |
| C | 2.438542000  | 2.660893000  | -1.219221000 | H  | -0.627977000 | -2.880901000 | 4.229445000  |
| C | 0.419114000  | 3.990687000  | -0.608721000 | H  | 0.342960000  | 1.069684000  | 4.179863000  |
| C | 2.608919000  | -3.021021000 | 0.162319000  | H  | -0.823231000 | -0.194162000 | 4.594452000  |
| C | 2.897826000  | -1.603046000 | -0.316519000 | H  | 1.072345000  | -0.226610000 | 2.191634000  |
| C | 1.320551000  | 2.799795000  | -0.194428000 | H  | 1.155902000  | -1.700738000 | 4.864156000  |
| C | -3.122575000 | 1.026442000  | -0.254155000 | H  | 2.161668000  | -2.133052000 | 3.469374000  |
| C | -0.647018000 | -1.875191000 | 1.111786000  | H  | 2.322509000  | -0.548732000 | 4.227435000  |
| C | -1.531588000 | -3.548239000 | 2.336643000  | F  | 2.715111000  | -2.444020000 | -2.541304000 |
| C | 3.987036000  | -0.977687000 | 0.604215000  | F  | 4.703586000  | -2.188393000 | -1.777160000 |
| C | -3.389957000 | 1.195187000  | 1.262542000  | F  | -4.087149000 | 0.140812000  | -2.227531000 |
| C | -3.141926000 | 2.402352000  | -0.907082000 | F  | 3.533941000  | -0.468722000 | -2.335296000 |
| C | 1.930763000  | 3.066284000  | 1.205650000  | F  | -0.171928000 | 3.724100000  | -1.777998000 |
| C | -0.800772000 | -2.785847000 | 3.172311000  | F  | -4.207957000 | -1.101832000 | -0.477284000 |
| C | -0.294776000 | 0.286438000  | 3.766802000  | F  | -5.455436000 | 0.642483000  | -0.651355000 |
| C | 0.561952000  | -0.720680000 | 3.020054000  | F  | 1.112900000  | 5.121015000  | -0.766173000 |
| C | 1.609028000  | -1.322937000 | 3.944449000  | F  | -0.549864000 | 4.239343000  | 0.275212000  |
| H | -1.702798000 | -5.130778000 | -1.515126000 | F  | 5.004021000  | -1.816684000 | 0.819781000  |
| H | -0.237928000 | -4.308803000 | -0.967932000 | F  | 4.495812000  | 0.149119000  | 0.109183000  |
| H | -3.989519000 | -4.260500000 | -0.713103000 | F  | -3.403983000 | 0.025205000  | 1.907604000  |
| H | -1.060680000 | -5.468936000 | 0.095169000  | F  | -4.544031000 | 1.810488000  | 1.515847000  |
| H | -2.110159000 | -2.744242000 | -0.804612000 | F  | 2.662179000  | 4.183182000  | 1.237942000  |
| H | 1.997619000  | 2.474138000  | -2.197695000 | F  | 3.463178000  | -0.691986000 | 1.797069000  |
| H | -3.477655000 | -4.949869000 | 0.821337000  | F  | 2.732417000  | 2.054652000  | 1.550046000  |
| H | 1.783234000  | -3.422173000 | -0.420971000 | F  | 1.001214000  | 3.165151000  | 2.157726000  |
| H | -4.052285000 | -3.271628000 | 0.747692000  | F  | -2.419846000 | 1.937304000  | 1.801656000  |
| H | 3.478692000  | -3.667999000 | 0.052488000  | N  | -1.431682000 | -2.978262000 | 1.094388000  |
| H | 3.051382000  | 3.560712000  | -1.267856000 | N  | -0.264609000 | -1.775611000 | 2.415439000  |
| H | 3.063509000  | 1.812556000  | -0.953663000 | O  | 1.780308000  | -0.809953000 | -0.294837000 |
|   |              |              |              | O  | 0.550639000  | 1.666810000  | -0.090850000 |
|   |              |              |              | O  | -1.916046000 | 0.384749000  | -0.406044000 |
|   |              |              |              | Ta | -0.065931000 | -0.167824000 | -0.502531000 |
|   |              |              |              | H  | -1.026152000 | 0.757131000  | 3.115877000  |
|   |              |              |              | C  | -0.335555000 | -1.490159000 | -2.288501000 |
|   |              |              |              | C  | 0.115082000  | -0.122253000 | -2.637669000 |
|   |              |              |              | C  | -1.570324000 | -2.022141000 | -2.992724000 |
|   |              |              |              | H  | -2.493425000 | -1.510144000 | -2.722031000 |
|   |              |              |              | H  | -1.466113000 | -1.926437000 | -4.080670000 |
|   |              |              |              | C  | -0.723079000 | 0.764104000  | -3.529052000 |
|   |              |              |              | H  | -0.415366000 | 1.809643000  | -3.462764000 |
|   |              |              |              | H  | -1.784463000 | 0.714444000  | -3.284021000 |
|   |              |              |              | H  | -0.625644000 | 0.461062000  | -4.579052000 |
|   |              |              |              | H  | -1.716587000 | -3.086363000 | -2.797375000 |
|   |              |              |              | H  | 1.175073000  | -0.037835000 | -2.880493000 |
|   |              |              |              | H  | 0.466419000  | -2.221933000 | -2.346700000 |

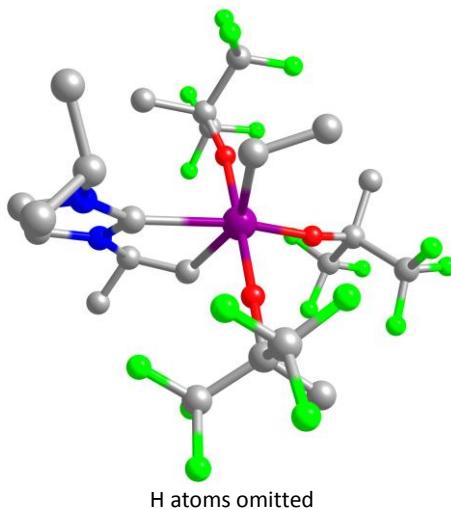
**Optimized coordinates of Ta(NHC)( $\eta^2$ -C<sub>2</sub>H<sub>2</sub>Et<sub>2</sub>)(OR<sub>F</sub>)<sub>3</sub> (PBE1PBE/Def2-TZVP)**



H atoms omitted (except  $\eta^2$ -olefinic H atoms)

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.527735000  | -5.126639000 | -0.729461000 |
| C  | -3.487045000 | -1.740183000 | 1.506572000  |
| C  | 1.379990000  | -3.877036000 | -0.564979000 |
| C  | 2.857722000  | -4.224150000 | -0.513801000 |
| C  | 4.225045000  | 0.029716000  | 0.600465000  |
| C  | -2.411627000 | 2.619553000  | 1.432143000  |
| C  | -0.362108000 | 3.957597000  | 0.956393000  |
| C  | -2.720688000 | -2.875701000 | -0.587255000 |
| C  | -2.957359000 | -1.516965000 | 0.060406000  |
| C  | -1.295070000 | 2.841458000  | 0.420459000  |
| C  | 3.101888000  | 1.029300000  | 0.220396000  |
| C  | 0.540305000  | -1.691314000 | -1.496141000 |
| C  | 1.311261000  | -3.231349000 | -2.954557000 |
| C  | -4.046257000 | -0.758612000 | -0.752345000 |
| C  | 3.328371000  | 1.546412000  | -1.221858000 |
| C  | 3.165714000  | 2.218309000  | 1.170478000  |
| C  | -1.904128000 | 3.275396000  | -0.938006000 |
| C  | 0.863567000  | -2.187576000 | -3.677408000 |
| C  | 0.640766000  | 0.863390000  | -4.022456000 |
| C  | -0.291988000 | -0.045702000 | -3.242093000 |
| C  | -1.500641000 | -0.415151000 | -4.089989000 |
| H  | 0.668287000  | -5.777519000 | 0.135475000  |
| H  | -0.532817000 | -4.886301000 | -0.806628000 |
| H  | 3.052261000  | -4.856972000 | 0.354037000  |
| H  | 0.814099000  | -5.694318000 | -1.618809000 |
| H  | 1.086963000  | -3.354198000 | 0.341328000  |
| H  | -1.970926000 | 2.306800000  | 2.378054000  |
| H  | 3.167281000  | -4.780450000 | -1.403150000 |
| H  | -1.913524000 | -3.370396000 | -0.051946000 |
| H  | 3.475720000  | -3.331764000 | -0.432145000 |
| H  | -3.613074000 | -3.499850000 | -0.555574000 |
| H  | -2.995230000 | 3.526195000  | 1.590821000  |
| H  | -3.064642000 | 1.827551000  | 1.076127000  |
| H  | 1.756065000  | -4.158829000 | -3.270364000 |
| H  | -2.419142000 | -2.734442000 | -1.624852000 |
| H  | 2.892851000  | 1.893062000  | 2.171273000  |
| H  | 4.168807000  | 2.644113000  | 1.191056000  |
| H  | 2.461922000  | 2.979679000  | 0.846508000  |
| H  | 0.842276000  | -2.033827000 | -4.741952000 |
| H  | 0.115017000  | 1.787329000  | -4.268711000 |
| H  | 0.944870000  | 0.393488000  | -4.961481000 |
| H  | -0.634835000 | 0.472004000  | -2.342308000 |
| H  | -1.186405000 | -0.797812000 | -5.064319000 |
| H  | -2.122946000 | -1.165294000 | -3.606951000 |
| H  | -2.110402000 | 0.472627000  | -4.262429000 |
| F  | -2.689817000 | -2.578993000 | 2.172160000  |
| F  | -4.709583000 | -2.280169000 | 1.503090000  |
| F  | 4.149070000  | -0.280234000 | 1.895009000  |
| F  | -3.545983000 | -0.609591000 | 2.205131000  |
| F  | 0.214911000  | 3.555956000  | 2.094480000  |
| F  | 4.146257000  | -1.108137000 | -0.089996000 |
| F  | 5.439730000  | 0.543151000  | 0.388690000  |
| F  | -1.024206000 | 5.085454000  | 1.228256000  |
| F  | 0.618385000  | 4.266680000  | 0.106062000  |
| F  | -5.096184000 | -1.537836000 | -1.028443000 |
| F  | -4.506316000 | 0.320370000  | -0.121812000 |
| F  | 3.422231000  | 0.549474000  | -2.108894000 |
| F  | 4.431484000  | 2.285500000  | -1.332841000 |
| F  | -2.602299000 | 4.409771000  | -0.846523000 |
| F  | -3.540664000 | -0.358160000 | -1.918870000 |
| F  | -2.735442000 | 2.330244000  | -1.384377000 |
| F  | -0.974426000 | 3.448822000  | -1.880883000 |
| F  | 2.298955000  | 2.311604000  | -1.586030000 |
| N  | 1.099862000  | -2.918625000 | -1.636202000 |
| N  | 0.389805000  | -1.263748000 | -2.781527000 |
| O  | -1.816205000 | -0.762264000 | 0.102902000  |
| O  | -0.557581000 | 1.707707000  | 0.186641000  |
| O  | 1.890559000  | 0.380645000  | 0.263549000  |
| Ta | 0.040011000  | -0.176768000 | 0.334576000  |
| H  | 1.531848000  | 1.118350000  | -3.458382000 |
| C  | 0.425075000  | -1.727768000 | 1.891617000  |
| C  | -0.084591000 | -0.455913000 | 2.459800000  |
| C  | 1.754812000  | -2.293125000 | 2.377740000  |
| H  | 2.458459000  | -2.483633000 | 1.562648000  |
| H  | 2.262297000  | -1.559140000 | 3.005545000  |
| C  | 0.689024000  | 0.369244000  | 3.465106000  |
| H  | 0.356472000  | 1.410325000  | 3.418637000  |
| H  | 1.752583000  | 0.385403000  | 3.213804000  |
| C  | 1.578661000  | -3.577037000 | 3.180151000  |
| H  | 2.534924000  | -3.953860000 | 3.554972000  |
| H  | 0.918671000  | -3.417257000 | 4.036845000  |
| H  | 1.125367000  | -4.367885000 | 2.573015000  |
| C  | 0.520025000  | -0.140057000 | 4.893175000  |
| H  | 1.063418000  | 0.486692000  | 5.606080000  |
| H  | -0.534377000 | -0.139349000 | 5.182756000  |
| H  | 0.887262000  | -1.163678000 | 4.996328000  |
| H  | -0.335854000 | -2.508268000 | 1.867865000  |
| H  | -1.141914000 | -0.478352000 | 2.726950000  |

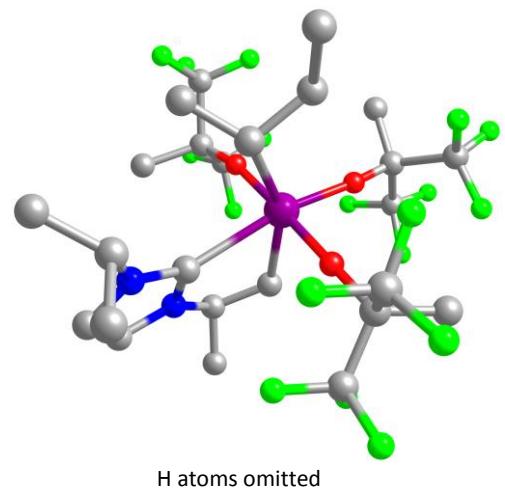
**Optimized coordinates of Ta(NHC\*)(Et)(OR<sub>F</sub>)<sub>3</sub> (PBE1PBE/Def2-TZVP)**



|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.268204000  | 0.184791000  | -3.044143000 |
| C | -1.800085000 | -4.279996000 | -2.058356000 |
| C | -0.481670000 | -0.785709000 | -2.120045000 |
| C | 3.223408000  | -1.971920000 | -1.691449000 |
| C | -2.452746000 | -3.191217000 | -1.222912000 |
| C | -3.953856000 | -3.394599000 | -1.091510000 |
| C | -3.682870000 | 1.233349000  | -1.339156000 |
| C | 2.993349000  | 2.448271000  | -1.034030000 |
| C | 1.045528000  | 3.981913000  | -0.727418000 |
| C | 2.112110000  | -3.346643000 | 0.072272000  |
| C | 2.633185000  | -1.950591000 | -0.254902000 |
| C | 1.770287000  | 2.728104000  | -0.170262000 |
| C | -2.962652000 | 1.459031000  | 0.016175000  |
| C | -1.077254000 | -2.074970000 | 0.588437000  |
| C | -1.992705000 | -4.085181000 | 1.037578000  |
| C | 3.747659000  | -1.584020000 | 0.765250000  |
| C | -3.781021000 | 0.838460000  | 1.178273000  |
| C | -2.823301000 | 2.957744000  | 0.252080000  |
| C | 2.216533000  | 2.971232000  | 1.294296000  |
| C | -1.355477000 | -3.676747000 | 2.155011000  |
| C | 0.018475000  | -0.243488000 | 2.138509000  |
| C | -0.027281000 | -1.613597000 | 2.759948000  |
| C | -0.592340000 | -1.635845000 | 4.171020000  |
| H | 0.122370000  | -0.086754000 | -4.096016000 |
| H | -2.242985000 | -4.294531000 | -3.055965000 |
| H | -0.086786000 | 1.212971000  | -2.933221000 |
| H | 1.345928000  | 0.187453000  | -2.867503000 |
| H | -0.728104000 | -4.108126000 | -2.167837000 |

|    |              |              |              |
|----|--------------|--------------|--------------|
| H  | -4.413216000 | -3.329325000 | -2.079508000 |
| H  | -0.163772000 | -1.808231000 | -2.327436000 |
| H  | -1.544437000 | -0.708277000 | -2.356121000 |
| H  | -1.947920000 | -5.267608000 | -1.612946000 |
| H  | -2.275253000 | -2.228850000 | -1.687675000 |
| H  | 2.676534000  | 2.321683000  | -2.068653000 |
| H  | -4.199589000 | -4.376763000 | -0.679675000 |
| H  | 1.255249000  | -3.560328000 | -0.563517000 |
| H  | -4.400268000 | -2.628069000 | -0.457681000 |
| H  | 2.879384000  | -4.103514000 | -0.087835000 |
| H  | 3.712975000  | 3.264593000  | -0.978539000 |
| H  | 3.463384000  | 1.527872000  | -0.697645000 |
| H  | -2.562373000 | -4.978638000 | 0.849529000  |
| H  | 1.792586000  | -3.383673000 | 1.112327000  |
| H  | -2.296400000 | 3.405356000  | -0.588125000 |
| H  | -3.797796000 | 3.433173000  | 0.360791000  |
| H  | -2.236193000 | 3.121740000  | 1.153555000  |
| H  | -1.259355000 | -4.148487000 | 3.116966000  |
| H  | 0.938733000  | 0.270567000  | 2.434094000  |
| H  | -0.818111000 | 0.359599000  | 2.506276000  |
| H  | 0.982114000  | -2.035732000 | 2.783279000  |
| H  | -1.624994000 | -1.278818000 | 4.177211000  |
| H  | -0.559725000 | -2.627249000 | 4.630721000  |
| H  | 0.002149000  | -0.966371000 | 4.794485000  |
| F  | 2.313700000  | -2.437586000 | -2.552142000 |
| F  | 4.292874000  | -2.767868000 | -1.777109000 |
| F  | -2.916681000 | 1.683926000  | -2.332465000 |
| F  | 3.585414000  | -0.762502000 | -2.112136000 |
| F  | 0.523674000  | 3.701102000  | -1.924732000 |
| F  | -3.929208000 | -0.058138000 | -1.580305000 |
| F  | -4.847350000 | 1.880583000  | -1.404062000 |
| F  | 1.876851000  | 5.013940000  | -0.886578000 |
| F  | 0.045177000  | 4.391235000  | 0.054232000  |
| F  | 4.666573000  | -2.546985000 | 0.872251000  |
| F  | 4.381273000  | -0.456006000 | 0.451596000  |
| F  | -3.870342000 | -0.489153000 | 1.091740000  |
| F  | -5.022748000 | 1.324077000  | 1.232648000  |
| F  | 2.988219000  | 4.054851000  | 1.409387000  |
| F  | 3.209934000  | -1.416902000 | 1.976833000  |
| F  | 2.924162000  | 1.925564000  | 1.730249000  |
| F  | 1.182956000  | 3.118314000  | 2.122216000  |
| F  | -3.191677000 | 1.117260000  | 2.345125000  |
| N  | -1.822477000 | -3.100553000 | 0.096857000  |
| N  | -0.822267000 | -2.452973000 | 1.861188000  |
| O  | 1.659879000  | -0.992106000 | -0.190586000 |
| O  | 0.882192000  | 1.686196000  | -0.178095000 |
| O  | -1.745662000 | 0.837851000  | -0.034090000 |
| Ta | -0.028223000 | -0.025454000 | -0.076660000 |

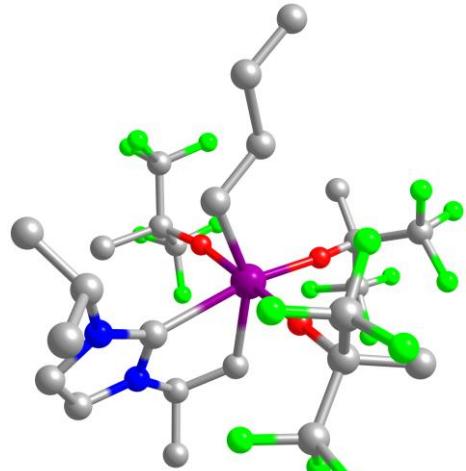
**Optimized coordinates of Ta(NHC\*)(2-butyl)(OR<sub>F</sub>)<sub>3</sub> (PBE1PBE/Def2-TZVP)**



H atoms omitted

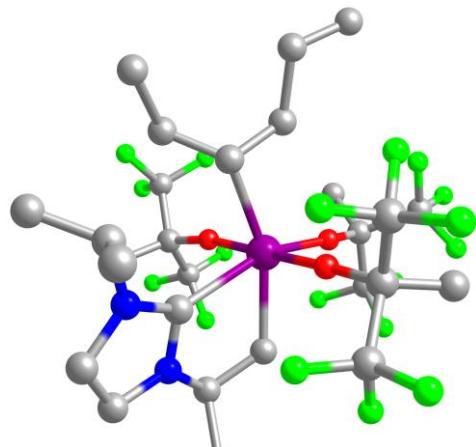
|   |              |              |              |    |              |              |              |
|---|--------------|--------------|--------------|----|--------------|--------------|--------------|
| C | 0.118525000  | 0.441351000  | 2.933748000  | H  | -3.044806000 | -4.117942000 | -0.112515000 |
| C | 2.495312000  | -4.455109000 | 1.762613000  | H  | -3.857736000 | 3.132941000  | 0.855846000  |
| C | 0.621864000  | -0.751748000 | 2.097133000  | H  | -3.566624000 | 1.404698000  | 0.572862000  |
| C | -3.453654000 | -2.003978000 | 1.488625000  | H  | 2.905427000  | -4.839683000 | -1.054461000 |
| C | 2.772403000  | -3.138633000 | 1.052491000  | H  | -1.830884000 | -3.437766000 | -1.209383000 |
| C | 4.263488000  | -2.951564000 | 0.814171000  | H  | 2.086544000  | 3.523045000  | 0.350054000  |
| C | 3.676797000  | 1.498918000  | 1.050037000  | H  | 3.469732000  | 3.612277000  | -0.758145000 |
| C | -3.125456000 | 2.329671000  | 0.930449000  | H  | 1.861007000  | 3.153331000  | -1.361687000 |
| C | -1.211451000 | 3.909197000  | 0.710864000  | H  | 1.445520000  | -4.066216000 | -3.242644000 |
| C | -2.225949000 | -3.403518000 | -0.194987000 | H  | -1.014054000 | 0.173942000  | -2.439918000 |
| C | -2.687642000 | -1.986432000 | 0.128264000  | H  | 0.731855000  | 0.342339000  | -2.534685000 |
| C | -1.877703000 | 2.638908000  | 0.113342000  | H  | -0.943610000 | -2.145271000 | -2.777079000 |
| C | 2.832823000  | 1.602637000  | -0.248189000 | H  | 1.561644000  | -1.227277000 | -4.254054000 |
| C | 1.184257000  | -2.082429000 | -0.645203000 | H  | 0.550577000  | -2.623954000 | -4.686594000 |
| C | 2.253490000  | -3.995013000 | -1.193154000 | H  | -0.101742000 | -0.993165000 | -4.805246000 |
| C | -3.687237000 | -1.527767000 | -0.977061000 | F  | -2.846394000 | -2.798355000 | 2.372823000  |
| C | 3.615099000  | 1.011976000  | -1.451367000 | F  | -4.697535000 | -2.472068000 | 1.347117000  |
| C | 2.551301000  | 3.073913000  | -0.524526000 | F  | 2.957807000  | 1.929697000  | 2.086876000  |
| C | -2.272648000 | 2.898878000  | -1.363524000 | F  | -3.533669000 | -0.792005000 | 2.029538000  |
| C | 1.540214000  | -3.614216000 | -2.271386000 | F  | -0.686094000 | 3.622496000  | 1.904560000  |
| C | -0.069597000 | -0.298014000 | -2.155446000 | F  | 4.049237000  | 0.244154000  | 1.318824000  |
| C | 0.036461000  | -1.660352000 | -2.782824000 | F  | 4.782805000  | 2.242050000  | 0.995312000  |
| C | 0.550020000  | -1.638173000 | -4.214045000 | F  | -2.090657000 | 4.897540000  | 0.890749000  |
| H | 2.955622000  | -4.435876000 | 2.752122000  | F  | -0.227412000 | 4.389084000  | -0.051338000 |
| H | 1.427462000  | -4.632031000 | 1.889946000  | F  | -4.572612000 | -2.481461000 | -1.277005000 |
| H | 4.782707000  | -2.916292000 | 1.773957000  | F  | -4.372664000 | -0.440306000 | -0.623600000 |
| H | 2.924092000  | -5.301141000 | 1.219409000  | F  | 3.786746000  | -0.306475000 | -1.354689000 |
| H | 2.404579000  | -2.317113000 | 1.656442000  | F  | 4.821037000  | 1.566715000  | -1.587705000 |
| H | -2.842540000 | 2.201298000  | 1.974883000  | F  | -3.032626000 | 3.989342000  | -1.493905000 |
| H | 4.681339000  | -3.783929000 | 0.241831000  | F  | -3.032708000 | -1.241303000 | -2.102495000 |
| H | -1.435993000 | -3.680887000 | 0.499366000  | F  | -2.970847000 | 1.864309000  | -1.837370000 |
| H | 4.468646000  | -2.025772000 | 0.280455000  | F  | -1.208952000 | 3.048328000  | -2.152757000 |
|   |              |              |              | F  | 2.944553000  | 1.238226000  | -2.585635000 |
|   |              |              |              | N  | 2.034064000  | -3.058648000 | -0.213468000 |
|   |              |              |              | N  | 0.914049000  | -2.451611000 | -1.919294000 |
|   |              |              |              | O  | -1.642591000 | -1.103105000 | 0.198393000  |
|   |              |              |              | O  | -0.973028000 | 1.611075000  | 0.139637000  |
|   |              |              |              | O  | 1.684688000  | 0.879254000  | -0.070947000 |
|   |              |              |              | Ta | 0.008726000  | -0.068781000 | 0.051728000  |
|   |              |              |              | H  | -0.978415000 | 0.429874000  | 2.966555000  |
|   |              |              |              | C  | 0.653833000  | 0.450133000  | 4.363373000  |
|   |              |              |              | H  | 0.296371000  | 1.326971000  | 4.909750000  |
|   |              |              |              | H  | 0.337838000  | -0.436916000 | 4.916668000  |
|   |              |              |              | H  | 1.746913000  | 0.476928000  | 4.365470000  |
|   |              |              |              | C  | 0.164274000  | -2.061946000 | 2.718355000  |
|   |              |              |              | H  | 0.798603000  | -2.376971000 | 3.555357000  |
|   |              |              |              | H  | -0.845902000 | -1.962249000 | 3.114395000  |
|   |              |              |              | H  | 0.140943000  | -2.885868000 | 2.003673000  |
|   |              |              |              | H  | 1.714778000  | -0.687344000 | 2.120209000  |
|   |              |              |              | H  | 0.400688000  | 1.391190000  | 2.469472000  |

**Optimized coordinates of Ta(NHC\*)(1-butyl)(OR<sub>F</sub>)<sub>3</sub> (PBE1PBE/Def2-TZVP)**



|   |              |              |              |    |              |              |              |
|---|--------------|--------------|--------------|----|--------------|--------------|--------------|
| C | -0.335344000 | 0.251344000  | 2.870411000  | H  | 2.273132000  | -2.156914000 | 1.649035000  |
| C | 1.818081000  | -4.201374000 | 2.076857000  | H  | -2.747529000 | 2.332984000  | 1.733462000  |
| C | 0.446935000  | -0.723341000 | 1.979859000  | H  | 4.256810000  | -4.307541000 | 0.769288000  |
| C | -3.231875000 | -1.967108000 | 1.475931000  | H  | -1.212438000 | -3.571503000 | 0.468731000  |
| C | 2.478143000  | -3.131673000 | 1.222883000  | H  | 4.438070000  | -2.564455000 | 0.493174000  |
| C | 3.985167000  | -3.315941000 | 1.140280000  | H  | -2.814582000 | -4.149962000 | -0.038813000 |
| C | 3.649881000  | 1.308499000  | 1.218341000  | H  | -3.758775000 | 3.226041000  | 0.579238000  |
| C | -3.031018000 | 2.422034000  | 0.685304000  | H  | -3.477348000 | 1.484805000  | 0.363545000  |
| C | -1.093577000 | 3.971773000  | 0.394080000  | H  | 2.669571000  | -4.988870000 | -0.780660000 |
| C | -2.050508000 | -3.390383000 | -0.201350000 | H  | -1.697143000 | -3.460769000 | -1.228643000 |
| C | -2.596537000 | -1.989661000 | 0.058621000  | H  | 2.257057000  | 3.434410000  | 0.358277000  |
| C | -1.783359000 | 2.690981000  | -0.145912000 | H  | 3.783048000  | 3.452912000  | -0.550806000 |
| C | 2.965767000  | 1.479205000  | -0.163477000 | H  | 2.247799000  | 3.093117000  | -1.373995000 |
| C | 1.141311000  | -2.098358000 | -0.665011000 | H  | 1.423366000  | -4.255750000 | -3.112893000 |
| C | 2.094481000  | -4.110395000 | -1.016630000 | H  | -0.845149000 | 0.156700000  | -2.650703000 |
| C | -3.682522000 | -1.673171000 | -1.008066000 | H  | 0.912206000  | 0.263446000  | -2.674695000 |
| C | 3.825531000  | 0.833376000  | -1.281093000 | H  | -0.853288000 | -2.161260000 | -2.917577000 |
| C | 2.812519000  | 2.967242000  | -0.452330000 | H  | 1.784184000  | -1.422789000 | -4.263461000 |
| C | -2.182608000 | 2.880865000  | -1.631768000 | H  | 0.747266000  | -2.799110000 | -4.698505000 |
| C | 1.485307000  | -3.749660000 | -2.165710000 | H  | 0.172122000  | -1.151951000 | -4.937327000 |
| C | 0.071463000  | -0.335802000 | -2.310213000 | F  | -2.343255000 | -2.386806000 | 2.381563000  |
| C | 0.150212000  | -1.726347000 | -2.880920000 | F  | -4.291881000 | -2.775874000 | 1.558009000  |
| C | 0.755765000  | -1.791751000 | -4.273752000 | F  | 2.848989000  | 1.779267000  | 2.174517000  |
| H | 2.231231000  | -4.173593000 | 3.086855000  | F  | -3.624322000 | -0.748966000 | 1.840405000  |
| H | 0.004827000  | 1.279776000  | 2.698432000  | F  | -0.608396000 | 3.736881000  | 1.616337000  |
| H | -1.401880000 | 0.240641000  | 2.620437000  | F  | 3.907826000  | 0.029642000  | 1.508692000  |
| H | 0.740833000  | -4.043401000 | 2.148955000  | F  | 4.802343000  | 1.975609000  | 1.295008000  |
| H | 4.415369000  | -3.210106000 | 2.137854000  | F  | -1.943170000 | 4.996472000  | 0.492027000  |
| H | 0.138469000  | -1.745565000 | 2.209278000  | F  | -0.073138000 | 4.369898000  | -0.367156000 |
| H | 1.502711000  | -0.624470000 | 2.243618000  | F  | -4.588674000 | -2.649063000 | -1.106781000 |
| H | 1.994422000  | -5.201322000 | 1.671081000  | F  | -4.336077000 | -0.540989000 | -0.756463000 |
|   |              |              |              | F  | 3.927985000  | -0.489598000 | -1.150155000 |
|   |              |              |              | F  | 5.062438000  | 1.333053000  | -1.314437000 |
|   |              |              |              | F  | -2.962930000 | 3.949924000  | -1.807825000 |
|   |              |              |              | F  | -3.109422000 | -1.545503000 | -2.208180000 |
|   |              |              |              | F  | -2.862236000 | 1.812507000  | -2.056901000 |
|   |              |              |              | F  | -1.123289000 | 3.014858000  | -2.428832000 |
|   |              |              |              | F  | 3.267636000  | 1.068183000  | -2.472817000 |
|   |              |              |              | N  | 1.884459000  | -3.096061000 | -0.116408000 |
|   |              |              |              | N  | 0.928486000  | -2.523694000 | -1.930590000 |
|   |              |              |              | O  | -1.632242000 | -1.022566000 | -0.010057000 |
|   |              |              |              | O  | -0.883105000 | 1.661430000  | -0.074982000 |
|   |              |              |              | O  | 1.756553000  | 0.842077000  | -0.127180000 |
|   |              |              |              | Ta | 0.048623000  | -0.040122000 | -0.102793000 |
|   |              |              |              | C  | -0.190885000 | -0.056963000 | 4.358711000  |
|   |              |              |              | H  | 0.872481000  | -0.035980000 | 4.623197000  |
|   |              |              |              | H  | -0.532065000 | -1.082162000 | 4.541849000  |
|   |              |              |              | C  | -0.961638000 | 0.908530000  | 5.243671000  |
|   |              |              |              | H  | -2.031896000 | 0.878945000  | 5.019717000  |
|   |              |              |              | H  | -0.838668000 | 0.668948000  | 6.302829000  |
|   |              |              |              | H  | -0.621954000 | 1.937404000  | 5.094454000  |

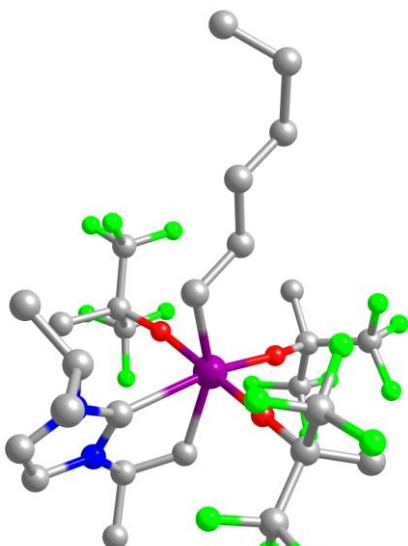
**Optimized coordinates of Ta(NHC\*)(3-hexyl)(OR<sub>F</sub>)<sub>3</sub> (PBE1PBE/Def2-TZVP)**



H atoms omitted

|   |              |              |              |    |              |              |              |
|---|--------------|--------------|--------------|----|--------------|--------------|--------------|
| C | 0.079799000  | 0.478225000  | 2.700611000  | H  | -3.562699000 | 1.284010000  | 0.596485000  |
| C | 2.532449000  | -4.480343000 | 1.335630000  | H  | 3.053259000  | -4.635103000 | -1.504075000 |
| C | 0.683787000  | -0.747329000 | 1.986258000  | H  | -1.713003000 | -3.446899000 | -1.367339000 |
| C | -3.327448000 | -2.195250000 | 1.426418000  | H  | 1.950169000  | 3.556092000  | 0.261881000  |
| C | 2.807710000  | -3.112187000 | 0.731034000  | H  | 3.333780000  | 3.729318000  | -0.836463000 |
| C | 4.300363000  | -2.883120000 | 0.547700000  | H  | 1.748004000  | 3.219822000  | -1.459453000 |
| C | 3.644673000  | 1.583237000  | 0.904300000  | H  | 1.540945000  | -3.786447000 | -3.629310000 |
| C | -3.152248000 | 2.247475000  | 0.884300000  | H  | -1.139192000 | 0.235588000  | -2.504981000 |
| C | -1.320852000 | 3.893833000  | 0.487464000  | H  | 0.586408000  | 0.519130000  | -2.646315000 |
| C | -2.080176000 | -3.471212000 | -0.342053000 | H  | -0.950734000 | -2.041630000 | -2.994697000 |
| C | -2.605505000 | -2.093424000 | 0.045863000  | H  | 1.468043000  | -0.905343000 | -4.464959000 |
| C | -1.974203000 | 2.579321000  | -0.023853000 | H  | 0.519147000  | -2.324629000 | -4.961013000 |
| C | 2.776479000  | 1.683036000  | -0.378283000 | H  | -0.217742000 | -0.725958000 | -4.966013000 |
| C | 1.200769000  | -2.002743000 | -0.899930000 | F  | -2.659414000 | -2.994148000 | 2.261231000  |
| C | 2.358775000  | -3.817091000 | -1.582405000 | F  | -4.553923000 | -2.711860000 | 1.305349000  |
| C | -3.660419000 | -1.650072000 | -1.012536000 | F  | 2.930962000  | 1.978954000  | 1.959556000  |
| C | 3.558279000  | 1.142295000  | -1.604810000 | F  | -3.442624000 | -1.007567000 | 2.014154000  |
| C | 2.437374000  | 3.148056000  | -0.620996000 | F  | -0.689702000 | 3.663246000  | 1.642350000  |
| C | -2.479921000 | 2.785195000  | -1.475854000 | F  | 4.056318000  | 0.336402000  | 1.148317000  |
| C | 1.619328000  | -3.399434000 | -2.629013000 | F  | 4.728214000  | 2.358448000  | 0.842802000  |
| C | -0.160065000 | -0.191902000 | -2.279833000 | F  | -2.225886000 | 4.848333000  | 0.714549000  |
| C | 0.002503000  | -1.504890000 | -2.991730000 | F  | -0.421948000 | 4.394267000  | -0.361845000 |
| C | 0.479962000  | -1.370338000 | -4.429100000 | F  | -4.510756000 | -2.635050000 | -1.313546000 |
| H | 3.004376000  | -4.551311000 | 2.316358000  | F  | -4.381920000 | -0.606904000 | -0.602642000 |
| H | 1.463698000  | -4.659169000 | 1.459378000  | F  | 3.794706000  | -0.167355000 | -1.526034000 |
| H | 4.791968000  | -2.899854000 | 1.522426000  | F  | 4.732863000  | 1.755508000  | -1.762079000 |
| H | 2.945603000  | -5.279175000 | 0.714695000  | F  | -3.285448000 | 3.846482000  | -1.577650000 |
| H | 2.405975000  | -2.336070000 | 1.373350000  | F  | -3.056798000 | -1.301891000 | -2.148596000 |
| H | -2.800929000 | 2.185011000  | 1.913977000  | F  | -3.173824000 | 1.716889000  | -1.874115000 |
| H | 4.751816000  | -3.668994000 | -0.063590000 | F  | -1.480865000 | 2.950209000  | -2.341864000 |
| H | -1.256628000 | -3.730272000 | 0.319811000  | F  | 2.851499000  | 1.346855000  | -2.720922000 |
| H | 4.500982000  | -1.921036000 | 0.080298000  | N  | 2.097779000  | -2.962772000 | -0.540806000 |
| H | -2.857758000 | -4.230889000 | -0.264375000 | N  | 0.937635000  | -2.298125000 | -2.194865000 |
| H | -3.930879000 | 3.006894000  | 0.820468000  | O  | -1.605297000 | -1.159011000 | 0.116638000  |
|   |              |              |              | O  | -1.030550000 | 1.588431000  | -0.026747000 |
|   |              |              |              | O  | 1.656858000  | 0.917181000  | -0.199219000 |
|   |              |              |              | Ta | 0.003342000  | -0.067819000 | -0.066710000 |
|   |              |              |              | H  | -1.017400000 | 0.425335000  | 2.660152000  |
|   |              |              |              | C  | 0.276561000  | -2.061030000 | 2.648017000  |
|   |              |              |              | H  | -0.744122000 | -1.961105000 | 3.022133000  |
|   |              |              |              | H  | 0.225655000  | -2.862014000 | 1.903530000  |
|   |              |              |              | C  | 1.162687000  | -2.537152000 | 3.798748000  |
|   |              |              |              | H  | 0.859722000  | -3.531534000 | 4.140459000  |
|   |              |              |              | H  | 2.214043000  | -2.596095000 | 3.504425000  |
|   |              |              |              | H  | 1.116569000  | -1.867985000 | 4.657382000  |
|   |              |              |              | C  | 0.479390000  | 0.693506000  | 4.163727000  |
|   |              |              |              | H  | 1.569411000  | 0.632974000  | 4.249516000  |
|   |              |              |              | H  | 0.070497000  | -0.113735000 | 4.776920000  |
|   |              |              |              | C  | -0.008387000 | 2.026481000  | 4.706993000  |
|   |              |              |              | H  | 0.265700000  | 2.152069000  | 5.757382000  |
|   |              |              |              | H  | 0.418853000  | 2.862818000  | 4.147945000  |
|   |              |              |              | H  | -1.097145000 | 2.107285000  | 4.637990000  |
|   |              |              |              | H  | 1.772950000  | -0.632549000 | 2.034736000  |
|   |              |              |              | H  | 0.357621000  | 1.399461000  | 2.173903000  |

**Optimized coordinates of Ta(NHC\*)(1-hexyl)(OR<sub>F</sub>)<sub>3</sub> (PBE1PBE/Def2-TZVP)**



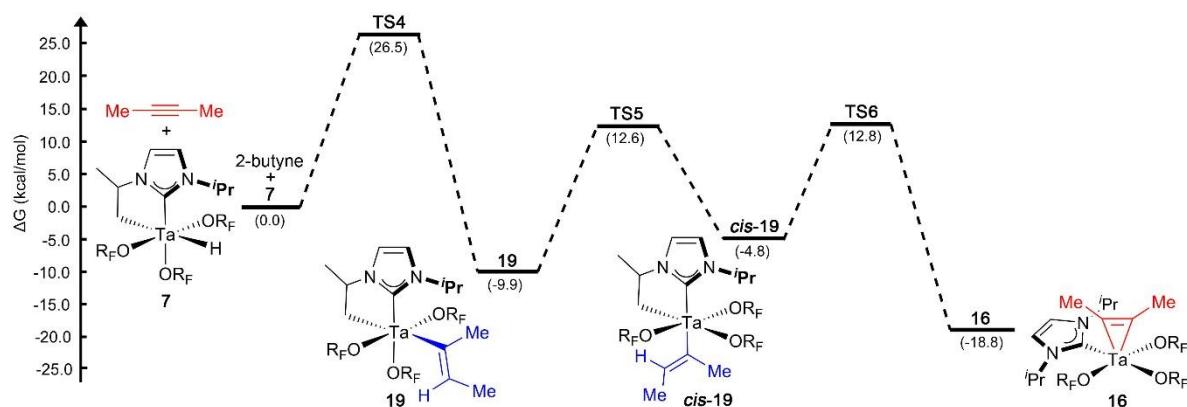
H atoms omitted

|   |              |              |              |    |              |              |              |
|---|--------------|--------------|--------------|----|--------------|--------------|--------------|
| C | -0.720728000 | 0.148383000  | 2.551056000  | H  | 4.091604000  | -4.412494000 | 1.019329000  |
| C | 1.474601000  | -4.312783000 | 1.921609000  | H  | -1.238582000 | -3.552350000 | -0.140126000 |
| C | 0.183780000  | -0.805359000 | 1.758629000  | H  | 4.338254000  | -2.663101000 | 0.858090000  |
| C | -3.374796000 | -1.952987000 | 0.605516000  | H  | -2.747688000 | -4.073701000 | -0.921049000 |
| C | 2.278756000  | -3.221512000 | 1.234853000  | H  | -3.679862000 | 3.284036000  | -0.107078000 |
| C | 3.776698000  | -3.432896000 | 1.387933000  | H  | -3.390659000 | 1.547501000  | -0.348774000 |
| C | 3.492929000  | 1.188471000  | 1.633063000  | H  | 2.762709000  | -4.998045000 | -0.792528000 |
| C | -2.986888000 | 2.463149000  | 0.075195000  | H  | -1.445994000 | -3.357351000 | -1.885860000 |
| C | -1.009756000 | 3.988158000  | 0.143985000  | H  | 2.280623000  | 3.378854000  | 0.666706000  |
| C | -1.956867000 | -3.324187000 | -0.925122000 | H  | 3.936316000  | 3.414691000  | 0.024203000  |
| C | -2.518035000 | -1.924983000 | -0.689903000 | H  | 2.555469000  | 3.123883000  | -1.058686000 |
| C | -1.623692000 | 2.740657000  | -0.544933000 | H  | 1.925730000  | -4.139287000 | -3.260433000 |
| C | 3.047315000  | 1.439372000  | 0.168546000  | H  | -0.306287000 | 0.307223000  | -2.978015000 |
| C | 1.283627000  | -2.079710000 | -0.796273000 | H  | 1.431985000  | 0.365405000  | -2.703745000 |
| C | 2.248144000  | -4.097223000 | -1.078707000 | H  | -0.317824000 | -1.998924000 | -3.342176000 |
| C | -3.412350000 | -1.537619000 | -1.901312000 | H  | 2.517002000  | -1.274667000 | -4.209682000 |
| C | 4.072799000  | 0.833694000  | -0.824864000 | H  | 1.537978000  | -2.603595000 | -4.868590000 |
| C | 2.958256000  | 2.942375000  | -0.064240000 | H  | 1.041562000  | -0.933204000 | -5.122210000 |
| C | -1.788457000 | 2.992404000  | -2.065629000 | F  | -2.651153000 | -2.432524000 | 1.621508000  |
| C | 1.840555000  | -3.674664000 | -2.293996000 | F  | -4.445248000 | -2.741527000 | 0.476018000  |
| C | 0.529751000  | -0.224554000 | -2.512171000 | F  | 2.549859000  | 1.625282000  | 2.468099000  |
| C | 0.674348000  | -1.591853000 | -3.124589000 | F  | -3.804392000 | -0.744453000 | 0.960074000  |
| C | 1.496931000  | -1.615362000 | -4.402759000 | F  | -0.721510000 | 3.699693000  | 1.416220000  |
| H | 1.718990000  | -4.336621000 | 2.985217000  | F  | 3.687826000  | -0.107502000 | 1.895054000  |
| H | -0.340768000 | 1.174939000  | 2.483285000  | F  | 4.623075000  | 1.830620000  | 1.932218000  |
| H | -1.730557000 | 0.171786000  | 2.127383000  | F  | -1.851838000 | 5.023713000  | 0.150525000  |
| H | 0.402159000  | -4.135617000 | 1.826082000  | F  | 0.120431000  | 4.395718000  | -0.435357000 |
| H | 4.041115000  | -3.379994000 | 2.445623000  | F  | -4.303164000 | -2.489062000 | -2.192144000 |
| H | -0.173661000 | -1.829318000 | 1.886305000  | F  | -4.083191000 | -0.404934000 | -1.703727000 |
| H | 1.182398000  | -0.741536000 | 2.197416000  | F  | 4.138205000  | -0.495859000 | -0.747811000 |
| H | 1.700732000  | -5.298018000 | 1.504738000  | F  | 5.303453000  | 1.310888000  | -0.628682000 |
| H | 2.020265000  | -2.261921000 | 1.666260000  | F  | -2.522435000 | 4.079222000  | -2.316575000 |
| H | -2.867540000 | 2.328419000  | 1.149689000  | F  | -2.650591000 | -1.367354000 | -2.985609000 |
|   |              |              |              | N  | 1.910824000  | -3.116601000 | -0.179751000 |
|   |              |              |              | N  | 1.273121000  | -2.446793000 | -2.097481000 |
|   |              |              |              | O  | -1.541996000 | -0.976573000 | -0.555725000 |
|   |              |              |              | O  | -0.756957000 | 1.693606000  | -0.377929000 |
|   |              |              |              | O  | 1.842595000  | 0.823062000  | -0.027120000 |
|   |              |              |              | Ta | 0.143511000  | -0.024520000 | -0.327349000 |
|   |              |              |              | C  | -0.830357000 | -0.225711000 | 4.027199000  |
|   |              |              |              | H  | 0.174233000  | -0.233727000 | 4.468915000  |
|   |              |              |              | H  | -1.206899000 | -1.251752000 | 4.100157000  |
|   |              |              |              | C  | -1.722563000 | 0.720584000  | 4.817676000  |
|   |              |              |              | H  | -2.735745000 | 0.697553000  | 4.395877000  |
|   |              |              |              | H  | -1.359060000 | 1.745272000  | 4.677348000  |
|   |              |              |              | C  | -1.796069000 | 0.423437000  | 6.311229000  |
|   |              |              |              | H  | -2.349309000 | 1.230306000  | 6.803599000  |
|   |              |              |              | H  | -0.784075000 | 0.450860000  | 6.732651000  |
|   |              |              |              | C  | -2.452391000 | -0.905565000 | 6.651942000  |
|   |              |              |              | H  | -3.463824000 | -0.960317000 | 6.238222000  |
|   |              |              |              | H  | -1.888089000 | -1.752261000 | 6.254362000  |
|   |              |              |              | H  | -2.529216000 | -1.042825000 | 7.733238000  |

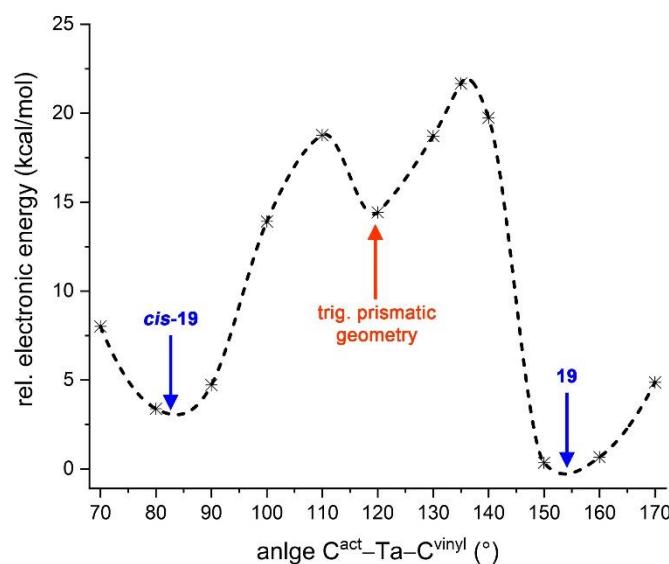
## Vinyl and $\eta^2$ -alkyne complexes 15 - 20 and mechanism of the reaction of 7 with 2-butyne

DFT calculations for complexes **15** - **20** and the DFT modeling studies for the reaction of **7** with 2-butyne (*cf.* Figure 8 in the article, see Figure S75 for a simplified version) were carried out with Gaussian 16 (G16RevB.01)<sup>[7]</sup> using the PBE1PBE functional.<sup>[8,9]</sup> All atoms were described with the valence triple- $\zeta$  basis set Def2-TZVP including polarization functions.<sup>[10]</sup> Dispersion interactions (GD3)<sup>[11]</sup> were taken into account during the geometry optimizations without applying symmetry restrictions. All stationary points were identified as minima or transition states by analytical frequency analysis. All energies were corrected for solvent effects using the polarizable continuum model (PCM for thf)<sup>[12,13]</sup> as implemented in Gaussian.

Optimized coordinates of **15** - **20**, *cis*-**19** **TS4** and **TS6** are provided on the following pages. The transition state **TS5** for the isomerization **19**  $\rightarrow$  *cis*-**19** was estimated via a PES scan (see Figure S76).

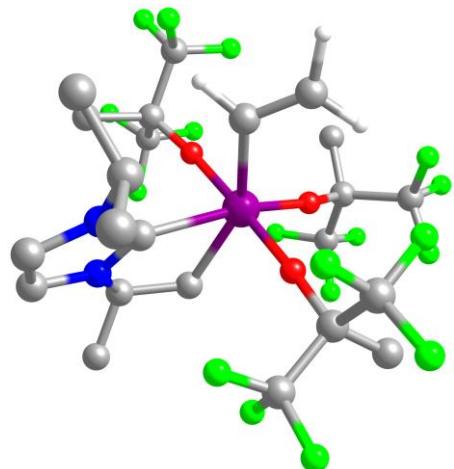


**Figure S75:** Calculated energy profile (PBE1PBE/Def2-TZVP PCM(thf) GD3) for the reaction of **7** with 2-butyne. The  $\Delta G$  values (kcal/mol) provided in parenthesis were referenced to 2-butyne + **7** (set to 0.0 kcal/mol).



**Figure S76:** Relaxed potential energy surface scan (PES scan) along the  $C^{act}$ -Ta- $C^{vinyl}$  angle with  $C^{act}$  = activated carbon atom of the NHC-*i*Pr group and  $C^{vinyl}$  = metal-bonded carbon atom of the vinylidic ligand in *cis*-**19** or **19**.

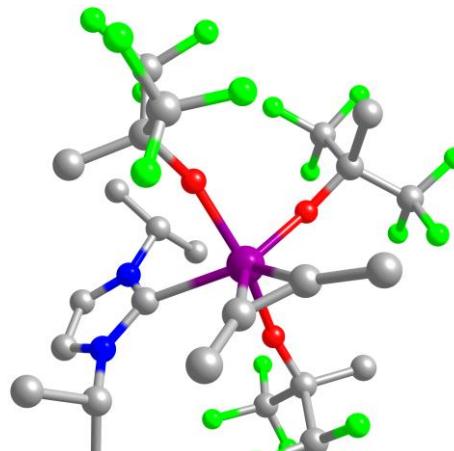
**Optimized coordinates of Ta(NHC\*)( $\eta^1$ -CH=CH<sub>2</sub>)(OR<sub>F</sub>)<sub>3</sub> (PBE1PBE/Def2-TZVP PCM (thf) GD3) (15)**



H atoms omitted (except vinylic H atoms)

|   |              |              |              |    |              |              |              |
|---|--------------|--------------|--------------|----|--------------|--------------|--------------|
| C | -0.526868000 | 0.055729000  | -3.040277000 | H  | -2.191185000 | -2.006467000 | -1.780028000 |
| C | -1.782753000 | -4.057471000 | -2.269949000 | H  | 2.680633000  | 2.169305000  | -2.048798000 |
| C | -0.296377000 | -0.851971000 | -2.088279000 | H  | -4.205719000 | -4.150693000 | -0.944323000 |
| C | 3.257546000  | -1.890825000 | -1.686047000 | H  | 1.261714000  | -3.499791000 | -0.611195000 |
| C | -2.416664000 | -2.996328000 | -1.386944000 | H  | -4.365161000 | -2.409515000 | -0.646112000 |
| C | -3.925061000 | -3.157825000 | -1.303897000 | H  | 2.881876000  | -4.084792000 | -0.170947000 |
| C | -3.714001000 | 1.329177000  | -1.209027000 | H  | 3.714207000  | 3.193756000  | -1.025749000 |
| C | 2.993350000  | 2.376840000  | -1.026304000 | H  | 3.454327000  | 1.481865000  | -0.617767000 |
| C | 1.059556000  | 3.946180000  | -0.823787000 | H  | -2.609651000 | -4.917286000 | 0.583836000  |
| C | 2.126805000  | -3.324256000 | 0.025082000  | H  | 1.814037000  | -3.396278000 | 1.065084000  |
| C | 2.660540000  | -1.924526000 | -0.252676000 | H  | -2.262809000 | 3.388936000  | -0.241678000 |
| C | 1.763467000  | 2.716753000  | -0.198437000 | H  | -3.759318000 | 3.330854000  | 0.716548000  |
| C | -2.952718000 | 1.400328000  | 0.138258000  | H  | -2.198007000 | 2.904945000  | 1.455884000  |
| C | -1.051357000 | -2.048858000 | 0.508687000  | H  | -1.310755000 | -4.251601000 | 2.911244000  |
| C | -2.022349000 | -4.049586000 | 0.830432000  | H  | 1.004455000  | 0.160468000  | 2.427518000  |
| C | 3.768544000  | -1.591491000 | 0.782157000  | H  | -0.750560000 | 0.297438000  | 2.524016000  |
| C | -3.732336000 | 0.647568000  | 1.246476000  | H  | 0.983084000  | -2.153844000 | 2.714419000  |
| C | -2.792790000 | 2.857814000  | 0.545351000  | H  | -1.624498000 | -1.388427000 | 4.098818000  |
| C | 2.184117000  | 3.011242000  | 1.261282000  | H  | -0.602554000 | -2.782854000 | 4.510936000  |
| C | -1.386671000 | -3.721715000 | 1.978084000  | H  | 0.001071000  | -1.144499000 | 4.755935000  |
| C | 0.065098000  | -0.315273000 | 2.127264000  | F  | 2.389334000  | -2.400528000 | -2.563488000 |
| C | -0.016292000 | -1.710078000 | 2.697021000  | F  | 4.378502000  | -2.616522000 | -1.774522000 |
| C | -0.601208000 | -1.771798000 | 4.097094000  | F  | -3.026425000 | 1.984842000  | -2.146533000 |
| H | -2.172515000 | -3.972060000 | -3.285748000 | F  | 3.543878000  | -0.654179000 | -2.085863000 |
| H | -0.697680000 | -3.948677000 | -2.309276000 | F  | 0.588040000  | 3.621567000  | -2.030786000 |
| H | -4.352425000 | -3.033108000 | -2.300325000 | F  | -3.877695000 | 0.076827000  | -1.634955000 |
| H | -2.012402000 | -5.061521000 | -1.903916000 | F  | -4.922684000 | 1.893423000  | -1.135939000 |
|   |              |              |              | F  | 1.891384000  | 4.979863000  | -0.982667000 |
|   |              |              |              | F  | 0.024949000  | 4.374077000  | -0.097128000 |
|   |              |              |              | F  | 4.680395000  | -2.562220000 | 0.883281000  |
|   |              |              |              | F  | 4.416221000  | -0.461020000 | 0.490605000  |
|   |              |              |              | F  | -3.853485000 | -0.655071000 | 0.992438000  |
|   |              |              |              | F  | -4.960181000 | 1.141963000  | 1.423162000  |
|   |              |              |              | F  | 2.986658000  | 4.076119000  | 1.351420000  |
|   |              |              |              | F  | 3.222163000  | -1.435733000 | 1.990492000  |
|   |              |              |              | F  | 2.848702000  | 1.963548000  | 1.757534000  |
|   |              |              |              | F  | 1.136699000  | 3.224075000  | 2.059174000  |
|   |              |              |              | F  | -3.087098000 | 0.763875000  | 2.411136000  |
|   |              |              |              | N  | -1.815646000 | -3.017507000 | -0.050753000 |
|   |              |              |              | N  | -0.819008000 | -2.497096000 | 1.759386000  |
|   |              |              |              | O  | 1.700312000  | -0.961537000 | -0.155925000 |
|   |              |              |              | O  | 0.859697000  | 1.693915000  | -0.172015000 |
|   |              |              |              | O  | -1.742763000 | 0.789140000  | -0.031391000 |
|   |              |              |              | Ta | -0.012109000 | -0.037920000 | -0.075345000 |
|   |              |              |              | H  | -0.019551000 | -1.848693000 | -2.422335000 |
|   |              |              |              | H  | -0.456487000 | -0.175927000 | -4.103347000 |
|   |              |              |              | H  | -0.799258000 | 1.084766000  | -2.813957000 |

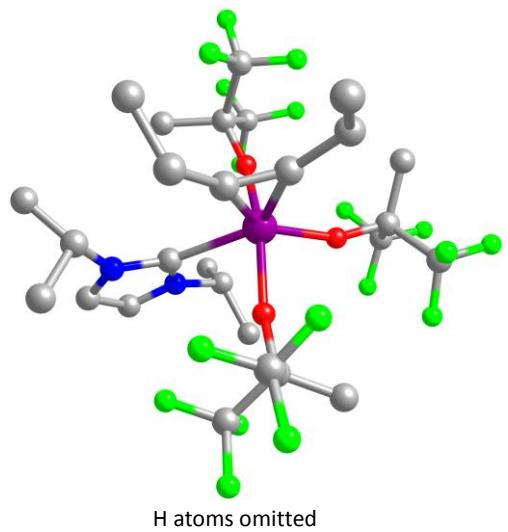
**Optimized coordinates of Ta(NHC)( $\eta^2$ -C<sub>2</sub>Me<sub>2</sub>)(OR<sub>F</sub>)<sub>3</sub> (PBE1PBE/Def2-TZVP PCM(thf) GD3) (**16**)**



H atoms omitted

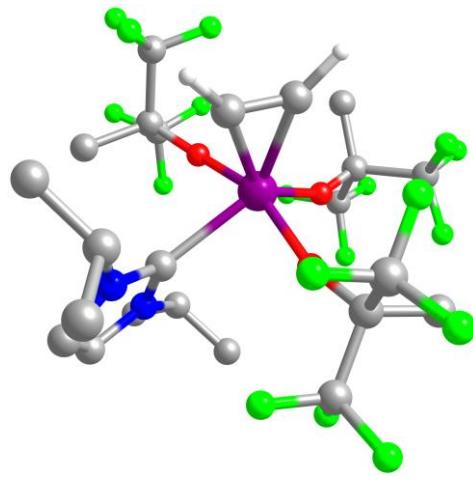
|    |              |              |              |   |              |              |              |
|----|--------------|--------------|--------------|---|--------------|--------------|--------------|
| C  | -1.630673000 | -4.626838000 | -0.958602000 | H | 3.007114000  | -3.871289000 | -0.151186000 |
| C  | 3.117047000  | -1.748268000 | -1.815938000 | H | 3.328384000  | 3.293503000  | -1.112188000 |
| C  | -2.250654000 | -3.347478000 | -0.422015000 | H | 3.093743000  | 1.550224000  | -0.839554000 |
| C  | -3.749494000 | -3.493234000 | -0.228447000 | H | -2.380226000 | -4.526624000 | 2.073647000  |
| C  | -3.811831000 | 0.759123000  | -1.265570000 | H | 2.062581000  | -3.141100000 | 1.162797000  |
| C  | 2.597248000  | 2.486539000  | -1.078100000 | H | -2.262638000 | 2.959960000  | -0.869169000 |
| C  | 0.753755000  | 4.034863000  | -0.419267000 | H | -3.822527000 | 3.228794000  | -0.055935000 |
| C  | 2.255404000  | -3.120792000 | 0.091336000  | H | -2.334189000 | 3.003789000  | 0.892977000  |
| C  | 2.702071000  | -1.723772000 | -0.318333000 | H | -0.809931000 | -3.293332000 | 3.950225000  |
| C  | 1.520133000  | 2.745453000  | -0.035648000 | H | 0.403692000  | 0.783696000  | 4.065327000  |
| C  | -3.067179000 | 1.193093000  | 0.022396000  | H | -0.935847000 | -0.332801000 | 4.382375000  |
| C  | -0.731595000 | -1.927654000 | 0.976794000  | H | 1.195019000  | -0.658451000 | 2.212281000  |
| C  | -1.744781000 | -3.662311000 | 1.991684000  | H | 0.825393000  | -2.109768000 | 4.864007000  |
| C  | 3.929448000  | -1.321491000 | 0.543347000  | H | 1.914838000  | -2.637102000 | 3.565183000  |
| C  | -3.884342000 | 0.815438000  | 1.282450000  | H | 2.160291000  | -1.079515000 | 4.360547000  |
| C  | -2.869887000 | 2.701803000  | -0.004273000 | F | 2.187875000  | -2.361269000 | -2.551905000 |
| C  | 2.184469000  | 2.911102000  | 1.353604000  | F | 4.265275000  | -2.412339000 | -2.006530000 |
| C  | -0.967721000 | -3.058296000 | 2.912951000  | F | -3.135618000 | 1.168430000  | -2.340913000 |
| C  | -0.271240000 | 0.058313000  | 3.607893000  | F | 3.275111000  | -0.523998000 | -2.316205000 |
| C  | 0.534686000  | -1.063835000 | 2.978990000  | F | 0.107265000  | 3.844781000  | -1.574844000 |
| C  | 1.403441000  | -1.776552000 | 3.999230000  | F | -3.936109000 | -0.566290000 | -1.358370000 |
| H  | -2.069510000 | -4.874488000 | -1.926418000 | F | -5.039514000 | 1.284348000  | -1.345591000 |
| H  | -0.552392000 | -4.524213000 | -1.086528000 | F | 1.569014000  | 5.082477000  | -0.590512000 |
| H  | -4.218705000 | -3.659258000 | -1.199664000 | F | -0.159206000 | 4.388095000  | 0.488142000  |
| H  | -1.817237000 | -5.462233000 | -0.278863000 | F | 4.870057000  | -2.271415000 | 0.572125000  |
| H  | -2.053099000 | -2.522641000 | -1.101744000 | F | 4.510158000  | -0.198484000 | 0.113161000  |
| H  | 2.123206000  | 2.388547000  | -2.052899000 | F | -4.088276000 | -0.500349000 | 1.383755000  |
| H  | -3.991401000 | -4.349913000 | 0.405124000  | F | -5.079167000 | 1.412054000  | 1.319611000  |
| H  | 1.328740000  | -3.348344000 | -0.430281000 | F | 3.048842000  | 3.933055000  | 1.388849000  |
| H  | -4.180832000 | -2.596347000 | 0.211801000  | F | 3.547288000  | -1.115373000 | 1.806111000  |
| N  | -1.591689000 | -2.956857000 | 0.824481000  | F | 2.863100000  | 1.803935000  | 1.664414000  |
| N  | -0.351226000 | -2.007986000 | 2.279459000  | F | 1.293459000  | 3.108230000  | 2.328359000  |
| O  | 1.736889000  | -0.776861000 | -0.127825000 | F | -3.218930000 | 1.193878000  | 2.377854000  |
| O  | 0.618015000  | 1.727085000  | 0.079637000  | N | -1.591689000 | -2.956857000 | 0.824481000  |
| O  | -1.883390000 | 0.519926000  | 0.086684000  | N | -0.351226000 | -2.007986000 | 2.279459000  |
| Ta | -0.088319000 | -0.060747000 | -0.392523000 | O | 1.736889000  | -0.776861000 | -0.127825000 |
| H  | -0.876726000 | 0.574997000  | 2.864331000  | C | -0.441455000 | -1.038423000 | -2.228833000 |
| C  | -0.161291000 | 0.240438000  | -2.422279000 | C | -0.763530000 | -2.118418000 | -3.198393000 |
| C  | -1.848519000 | -2.257782000 | -3.257987000 | H | -0.413570000 | -1.872378000 | -4.206097000 |
| C  | -0.027545000 | 1.130395000  | -3.599289000 | C | -0.551656000 | 2.075786000  | -3.443865000 |
| H  | 1.024774000  | 1.378981000  | -3.768364000 | H | -0.410062000 | 0.662835000  | -4.512642000 |
| H  | -0.335619000 | -3.079367000 | -2.910322000 | H | -0.335619000 | -3.079367000 | -2.910322000 |

**Optimized coordinates of Ta(NHC)( $\eta^2$ -C<sub>2</sub>Et<sub>2</sub>)(OR<sub>F</sub>)<sub>3</sub> (PBE1PBE/Def2-TZVP PCM(thf) GD3) (17)**



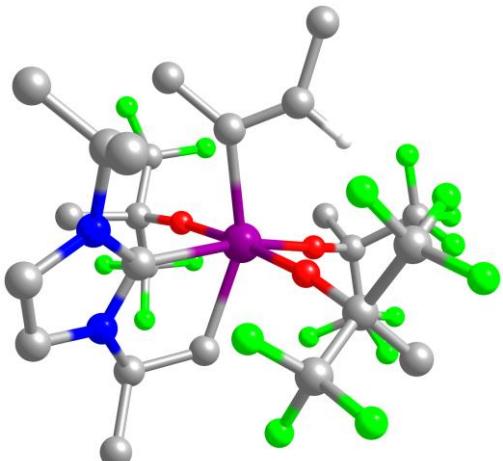
|   |              |              |              |    |              |              |              |
|---|--------------|--------------|--------------|----|--------------|--------------|--------------|
| C | 1.174305000  | -5.054554000 | -0.052417000 | H  | 2.103520000  | -4.305958000 | -2.744891000 |
| C | -3.202608000 | -1.761218000 | 1.586030000  | H  | -2.000206000 | -3.045378000 | -1.383336000 |
| C | 1.752015000  | -3.649019000 | -0.071850000 | H  | 2.328748000  | 3.094082000  | 0.407455000  |
| C | 3.263513000  | -3.653678000 | 0.059546000  | H  | 3.905193000  | 3.178422000  | -0.411005000 |
| C | 3.704922000  | 0.914325000  | 1.176987000  | H  | 2.418393000  | 2.878529000  | -1.341508000 |
| C | -2.588755000 | 2.502519000  | 1.090713000  | H  | 0.861278000  | -2.561959000 | -4.458228000 |
| C | -0.691452000 | 4.048551000  | 0.586122000  | H  | -0.176249000 | 1.464060000  | -4.028738000 |
| C | -2.280029000 | -3.071566000 | -0.331107000 | H  | 1.115357000  | 0.317152000  | -4.425189000 |
| C | -2.730385000 | -1.685311000 | 0.109572000  | H  | -1.079395000 | -0.131801000 | -2.342935000 |
| C | -1.472094000 | 2.801926000  | 0.101469000  | H  | -0.800064000 | -1.222247000 | -5.171725000 |
| C | 3.064569000  | 1.183149000  | -0.209175000 | H  | -1.923241000 | -1.858295000 | -3.951815000 |
| C | 0.608224000  | -1.793990000 | -1.287824000 | H  | -2.069098000 | -0.190668000 | -4.519096000 |
| C | 1.547207000  | -3.407083000 | -2.543512000 | F  | -2.253457000 | -2.312132000 | 2.344173000  |
| C | -3.907727000 | -1.230543000 | -0.791408000 | F  | -4.304033000 | -2.510798000 | 1.723037000  |
| C | 3.961221000  | 0.607556000  | -1.334721000 | F  | 2.916870000  | 1.397698000  | 2.139626000  |
| C | 2.932042000  | 2.687959000  | -0.401197000 | F  | -3.470086000 | -0.560028000 | 2.097864000  |
| C | -2.093224000 | 3.072402000  | -1.291772000 | F  | -0.050603000 | 3.761655000  | 1.725087000  |
| C | 0.934687000  | -2.549921000 | -3.385237000 | F  | 3.877012000  | -0.387270000 | 1.416279000  |
| C | 0.443080000  | 0.657602000  | -3.633971000 | F  | 4.897832000  | 1.505880000  | 1.310731000  |
| C | -0.445135000 | -0.478295000 | -3.162018000 | F  | -1.494563000 | 5.089797000  | 0.835091000  |
| C | -1.359623000 | -0.979276000 | -4.265809000 | F  | 0.230536000  | 4.460200000  | -0.287223000 |
| H | 1.390103000  | -5.519030000 | 0.911185000  | F  | -4.875570000 | -2.149783000 | -0.869342000 |
| H | 0.092519000  | -5.045239000 | -0.194446000 | F  | -4.469129000 | -0.095428000 | -0.371023000 |
| H | 3.549066000  | -4.182232000 | 0.970942000  | F  | 4.058030000  | -0.722047000 | -1.281433000 |
| H | 1.617227000  | -5.681560000 | -0.829823000 | F  | 5.202753000  | 1.103065000  | -1.303890000 |
| H | 1.316552000  | -3.069000000 | 0.736744000  | F  | -2.931295000 | 4.116468000  | -1.283585000 |
| H | -2.155951000 | 2.349348000  | 2.077092000  | F  | -3.465640000 | -1.019975000 | -2.033943000 |
| H | 3.729656000  | -4.168318000 | -0.784622000 | F  | -2.790001000 | 2.004192000  | -1.690232000 |
| H | -1.405331000 | -3.345461000 | 0.254694000  | F  | -1.173013000 | 3.307451000  | -2.229811000 |
| H | 3.655491000  | -2.639025000 | 0.108803000  | F  | 3.445220000  | 0.913080000  | -2.529069000 |
| H | -3.063531000 | -3.814322000 | -0.185407000 | N  | 1.328712000  | -2.933832000 | -1.273685000 |
| H | -3.314154000 | 3.313947000  | 1.137907000  | N  | 0.354210000  | -1.580442000 | -2.604680000 |
| H | -3.083115000 | 1.584456000  | 0.785109000  | O  | -1.744383000 | -0.747143000 | 0.009189000  |
|   |              |              |              | O  | -0.590729000 | 1.772078000  | -0.053370000 |
|   |              |              |              | O  | 1.856454000  | 0.555187000  | -0.275691000 |
|   |              |              |              | Ta | 0.083113000  | -0.067015000 | 0.275641000  |
|   |              |              |              | H  | 1.042348000  | 1.052116000  | -2.815246000 |
|   |              |              |              | C  | 0.752457000  | -1.044185000 | 2.026044000  |
|   |              |              |              | C  | 0.030126000  | 0.025866000  | 2.327342000  |
|   |              |              |              | C  | 1.512889000  | -2.017544000 | 2.869647000  |
|   |              |              |              | H  | 2.367026000  | -2.422196000 | 2.322006000  |
|   |              |              |              | H  | 1.930796000  | -1.496157000 | 3.735705000  |
|   |              |              |              | C  | -0.394059000 | 0.794984000  | 3.525629000  |
|   |              |              |              | H  | -1.480370000 | 0.672740000  | 3.620750000  |
|   |              |              |              | H  | -0.244492000 | 1.860796000  | 3.326202000  |
|   |              |              |              | C  | 0.634433000  | -3.164851000 | 3.361985000  |
|   |              |              |              | H  | 1.221254000  | -3.874110000 | 3.950263000  |
|   |              |              |              | H  | -0.180387000 | -2.792064000 | 3.985290000  |
|   |              |              |              | H  | 0.179647000  | -3.709745000 | 2.531037000  |
|   |              |              |              | C  | 0.283532000  | 0.420416000  | 4.836746000  |
|   |              |              |              | H  | -0.100736000 | 1.033553000  | 5.655808000  |
|   |              |              |              | H  | 0.108309000  | -0.626817000 | 5.091792000  |
|   |              |              |              | H  | 1.362827000  | 0.577894000  | 4.779089000  |

**Optimized coordinates of Ta(NHC)( $\eta^2$ -C<sub>2</sub>H<sub>2</sub>)(OR<sub>F</sub>)<sub>3</sub> (PBE1PBE/Def2-TZVP PCM (thf) GD3) (**18**)**



|   |              |              |              |    |              |              |              |
|---|--------------|--------------|--------------|----|--------------|--------------|--------------|
| C | -1.495163000 | -4.125808000 | -1.799214000 | H  | -3.906197000 | -4.508861000 | -0.531698000 |
| C | 3.076776000  | -1.834155000 | -1.849767000 | H  | 1.279531000  | -3.414608000 | -0.443055000 |
| C | -2.307198000 | -3.112333000 | -1.012561000 | H  | -4.329502000 | -2.799518000 | -0.300657000 |
| C | -3.772222000 | -3.498152000 | -0.924163000 | H  | 2.959583000  | -3.935531000 | -0.179821000 |
| C | -3.771180000 | 1.007857000  | -1.303248000 | H  | 3.259199000  | 3.289139000  | -1.372186000 |
| C | 2.576778000  | 2.454053000  | -1.217105000 | H  | 3.140839000  | 1.563378000  | -0.952465000 |
| C | 0.722823000  | 3.972650000  | -0.512524000 | H  | -2.616611000 | -4.624488000 | 1.303266000  |
| C | 2.211622000  | -3.182667000 | 0.066693000  | H  | 2.033923000  | -3.199472000 | 1.139712000  |
| C | 2.663585000  | -1.790160000 | -0.353313000 | H  | -2.392095000 | 3.170181000  | -0.484538000 |
| C | 1.572901000  | 2.742722000  | -0.110126000 | H  | -3.922905000 | 3.180655000  | 0.420704000  |
| C | -3.067761000 | 1.216422000  | 0.061940000  | H  | -2.383736000 | 2.854581000  | 1.252608000  |
| C | -0.849975000 | -1.955938000 | 0.662734000  | H  | -1.130524000 | -3.704097000 | 3.410812000  |
| C | -1.956568000 | -3.777936000 | 1.370339000  | H  | 0.260585000  | 0.273342000  | 4.133504000  |
| C | 3.887183000  | -1.383508000 | 0.510997000  | H  | -1.185406000 | -0.748066000 | 4.188218000  |
| C | -3.885301000 | 0.561294000  | 1.202492000  | H  | 1.061191000  | -0.953179000 | 2.124036000  |
| C | -2.944437000 | 2.709232000  | 0.331393000  | H  | 0.465601000  | -2.657374000 | 4.578496000  |
| C | 2.333000000  | 3.023307000  | 1.208650000  | H  | 1.592549000  | -3.122055000 | 3.292217000  |
| C | -1.221871000 | -3.326350000 | 2.408216000  | H  | 1.885653000  | -1.669675000 | 4.253331000  |
| C | -0.430518000 | -0.315189000 | 3.527327000  | F  | 2.130176000  | -2.432267000 | -2.578381000 |
| C | 0.339936000  | -1.407067000 | 2.804736000  | F  | 4.207898000  | -2.527800000 | -2.034255000 |
| C | 1.110372000  | -2.275756000 | 3.783701000  | F  | -3.044211000 | 1.563516000  | -2.273364000 |
| H | -1.911663000 | -4.237167000 | -2.802138000 | F  | 3.263598000  | -0.619223000 | -2.360180000 |
| H | -0.456925000 | -3.804561000 | -1.892854000 | F  | -0.003619000 | 3.681414000  | -1.596619000 |
| H | -4.200512000 | -3.478325000 | -1.927384000 | F  | -3.919244000 | -0.284240000 | -1.607039000 |
| H | -1.515794000 | -5.103520000 | -1.311109000 | F  | -4.983353000 | 1.569964000  | -1.341481000 |
| H | -2.230054000 | -2.137510000 | -1.489011000 | F  | 1.474051000  | 5.038616000  | -0.814416000 |
| H | 2.030776000  | 2.254255000  | -2.137824000 | F  | -0.131023000 | 4.347515000  | 0.443339000  |
|   |              |              |              | F  | 4.824845000  | -2.335163000 | 0.555085000  |
|   |              |              |              | F  | 4.472135000  | -0.266023000 | 0.074757000  |
|   |              |              |              | F  | -3.964744000 | -0.764524000 | 1.076105000  |
|   |              |              |              | F  | -5.132123000 | 1.035824000  | 1.274525000  |
|   |              |              |              | F  | 3.139072000  | 4.088683000  | 1.117272000  |
|   |              |              |              | F  | 3.493478000  | -1.164664000 | 1.769214000  |
|   |              |              |              | F  | 3.095281000  | 1.973120000  | 1.523484000  |
|   |              |              |              | F  | 1.510948000  | 3.231596000  | 2.239979000  |
|   |              |              |              | F  | -3.298416000 | 0.808337000  | 2.377274000  |
|   |              |              |              | N  | -1.722682000 | -2.926267000 | 0.319873000  |
|   |              |              |              | N  | -0.548736000 | -2.217776000 | 1.958954000  |
|   |              |              |              | O  | 1.708165000  | -0.832017000 | -0.172390000 |
|   |              |              |              | O  | 0.726923000  | 1.698994000  | 0.139035000  |
|   |              |              |              | O  | -1.849320000 | 0.606050000  | 0.014513000  |
|   |              |              |              | Ta | -0.070291000 | -0.021493000 | -0.434305000 |
|   |              |              |              | H  | -0.928882000 | 0.358692000  | 2.831523000  |
|   |              |              |              | C  | -0.354701000 | -0.905604000 | -2.318515000 |
|   |              |              |              | C  | -0.129375000 | 0.382219000  | -2.458326000 |
|   |              |              |              | H  | -0.044007000 | 1.089257000  | -3.276814000 |
|   |              |              |              | H  | -0.534609000 | -1.719380000 | -3.013478000 |

**Optimized coordinates of Ta(NHC\*)( $\eta^1$ -MeC=CHMe)(OR<sub>F</sub>)<sub>3</sub> (PBE1PBE/Def2-TZVP PCM(thf) GD3) (**19**)**

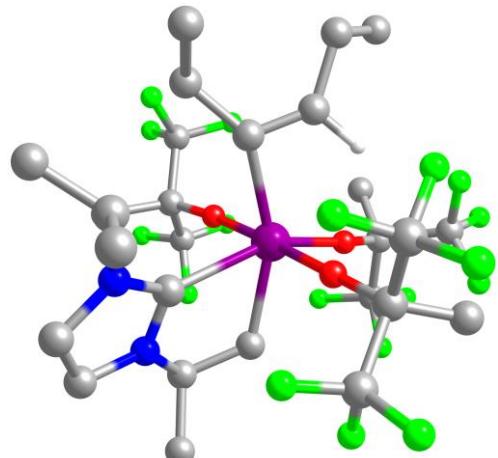


H atoms omitted (except vinylic H atom)

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.674176000  | 0.346915000  | 2.808694000  |
| C | 1.786319000  | -4.355135000 | 2.304711000  |
| C | 0.203744000  | -0.724883000 | 2.150013000  |
| C | -3.749445000 | -1.618953000 | 1.298604000  |
| C | 2.269667000  | -3.122839000 | 1.556743000  |
| C | 3.785446000  | -3.020389000 | 1.587476000  |
| C | 3.706150000  | 1.611387000  | 0.726045000  |
| C | -2.910565000 | 2.524084000  | 0.766638000  |
| C | -0.819153000 | 3.864065000  | 0.937219000  |
| C | -2.544135000 | -3.199000000 | -0.235549000 |
| C | -2.896132000 | -1.734812000 | -0.002276000 |
| C | -1.565189000 | 2.788975000  | 0.107432000  |
| C | 2.907406000  | 1.228052000  | -0.545820000 |
| C | 0.981761000  | -2.190996000 | -0.410598000 |
| C | 2.061237000  | -4.144130000 | -0.692763000 |
| C | -3.763755000 | -1.237728000 | -1.194646000 |
| C | 3.733806000  | 0.251847000  | -1.425056000 |
| C | 2.620244000  | 2.485248000  | -1.354359000 |
| C | -1.787639000 | 3.268982000  | -1.346345000 |
| C | 1.466684000  | -3.840799000 | -1.867777000 |
| C | -0.062907000 | -0.486030000 | -2.141377000 |
| C | 0.035249000  | -1.900837000 | -2.653221000 |
| C | 0.633233000  | -2.017032000 | -4.044637000 |
| H | 2.040337000  | -4.263727000 | 3.362108000  |
| H | 0.706560000  | -4.477443000 | 2.220229000  |
| H | 4.119282000  | -3.022464000 | 2.626872000  |
| H | 2.267168000  | -5.260585000 | 1.925773000  |
| H | 1.853551000  | -2.221801000 | 2.001437000  |
| H | -2.737330000 | 2.157337000  | 1.776966000  |
| H | 4.254625000  | -3.870099000 | 1.085217000  |
| H | -1.827767000 | -3.511028000 | 0.521021000  |

|    |              |              |              |
|----|--------------|--------------|--------------|
| H  | 4.131598000  | -2.101619000 | 1.119944000  |
| H  | -3.426420000 | -3.836287000 | -0.182389000 |
| H  | -3.519651000 | 3.426503000  | 0.806226000  |
| H  | -3.433988000 | 1.755956000  | 0.206098000  |
| H  | 2.675729000  | -4.985161000 | -0.421407000 |
| H  | -2.085710000 | -3.313169000 | -1.215974000 |
| H  | 2.081684000  | 3.193399000  | -0.731588000 |
| H  | 3.541423000  | 2.942899000  | -1.714347000 |
| H  | 1.991437000  | 2.223527000  | -2.203166000 |
| H  | 1.462636000  | -4.369580000 | -2.804502000 |
| H  | -0.981815000 | -0.013500000 | -2.496160000 |
| H  | 0.769431000  | 0.100191000  | -2.538743000 |
| H  | -0.959232000 | -2.353954000 | -2.669434000 |
| H  | 1.659809000  | -1.644500000 | -4.053312000 |
| H  | 0.625452000  | -3.040800000 | -4.425880000 |
| H  | 0.041107000  | -1.406246000 | -4.727780000 |
| F  | -3.262547000 | -2.402909000 | 2.261906000  |
| F  | -5.018078000 | -1.998796000 | 1.101336000  |
| F  | 2.973129000  | 2.433530000  | 1.482081000  |
| F  | -3.770754000 | -0.374779000 | 1.769425000  |
| F  | -0.577643000 | 3.391278000  | 2.162737000  |
| F  | 4.008398000  | 0.546459000  | 1.471131000  |
| F  | 4.846153000  | 2.246811000  | 0.445190000  |
| F  | -1.536284000 | 4.983965000  | 1.073246000  |
| F  | 0.357611000  | 4.208735000  | 0.410065000  |
| F  | -4.754588000 | -2.084923000 | -1.487769000 |
| F  | -4.314560000 | -0.043353000 | -0.958237000 |
| F  | 3.922944000  | -0.930002000 | -0.842830000 |
| F  | 4.935685000  | 0.749443000  | -1.731246000 |
| F  | -2.505426000 | 4.394957000  | -1.406898000 |
| F  | -3.019449000 | -1.121654000 | -2.293698000 |
| F  | -2.452005000 | 2.332001000  | -2.029047000 |
| F  | -0.640585000 | 3.486280000  | -1.992455000 |
| F  | 3.099929000  | 0.021859000  | -2.579338000 |
| N  | 1.759115000  | -3.131159000 | 0.183146000  |
| N  | 0.828214000  | -2.647498000 | -1.672729000 |
| O  | -1.790050000 | -0.943229000 | 0.119159000  |
| O  | -0.780293000 | 1.674517000  | 0.054370000  |
| O  | 1.764410000  | 0.605822000  | -0.128659000 |
| Ta | -0.016885000 | -0.114869000 | 0.057227000  |
| H  | 1.104830000  | 1.175130000  | 2.247629000  |
| C  | 0.675372000  | 0.575242000  | 4.286607000  |
| H  | 1.699009000  | 0.715140000  | 4.651076000  |
| H  | 0.133524000  | 1.495508000  | 4.528894000  |
| H  | 0.222217000  | -0.245732000 | 4.842045000  |
| C  | -0.401211000 | -1.873179000 | 2.904732000  |
| H  | 0.279695000  | -2.279168000 | 3.659049000  |
| H  | -1.306347000 | -1.559069000 | 3.429442000  |
| H  | -0.683639000 | -2.688922000 | 2.241834000  |

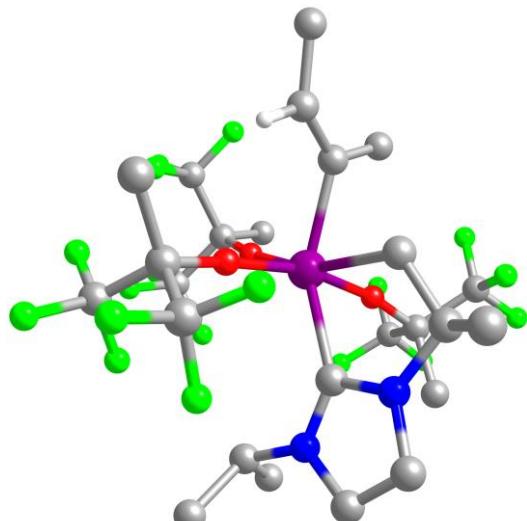
**Optimized coordinates of  $\text{Ta}(\text{NHC}^*)(\eta^1\text{-EtC=CHEt})(\text{OR}_f)_3$  (PBE1PBE/Def2-TZVP PCM(thf) GD3) (**20**)**



H atoms omitted (except vinylic H atom)

|   |              |              |              |    |              |              |              |
|---|--------------|--------------|--------------|----|--------------|--------------|--------------|
| C | 0.252872000  | 0.262420000  | 2.622590000  | H  | -3.481973000 | 1.145079000  | 0.612354000  |
| C | 2.597128000  | -4.366199000 | 1.181849000  | H  | 3.158217000  | -4.428101000 | -1.693652000 |
| C | 0.453525000  | -0.898115000 | 1.976489000  | H  | -1.576583000 | -3.397673000 | -1.522137000 |
| C | -3.174023000 | -2.308684000 | 1.345041000  | H  | 1.823544000  | 3.490973000  | 0.544192000  |
| C | 2.854518000  | -2.981760000 | 0.607608000  | H  | 3.263274000  | 3.826437000  | -0.442395000 |
| C | 4.345470000  | -2.730845000 | 0.449256000  | H  | 1.745968000  | 3.301904000  | -1.209549000 |
| C | 3.618103000  | 1.548791000  | 1.091715000  | H  | 1.607510000  | -3.539862000 | -3.780569000 |
| C | -3.134518000 | 2.126298000  | 0.923358000  | H  | -1.162140000 | 0.364642000  | -2.437881000 |
| C | -1.373572000 | 3.863189000  | 0.557017000  | H  | 0.557366000  | 0.702438000  | -2.575314000 |
| C | -1.918143000 | -3.474723000 | -0.490961000 | H  | -0.925371000 | -1.870494000 | -3.060442000 |
| C | -2.519034000 | -2.144036000 | -0.056130000 | H  | 1.463856000  | -0.599251000 | -4.463600000 |
| C | -1.979383000 | 2.538246000  | 0.021404000  | H  | 0.548168000  | -2.010096000 | -5.040113000 |
| C | 2.776822000  | 1.725574000  | -0.197546000 | H  | -0.226711000 | -0.429347000 | -4.957908000 |
| C | 1.230273000  | -1.883877000 | -0.980891000 | F  | -2.371122000 | -2.990250000 | 2.163577000  |
| C | 2.440026000  | -3.627930000 | -1.739112000 | F  | -4.328654000 | -2.983477000 | 1.282024000  |
| C | -3.623919000 | -1.733735000 | -1.070582000 | F  | 2.903224000  | 1.940612000  | 2.149061000  |
| C | 3.582427000  | 1.298995000  | -1.450229000 | F  | -3.423743000 | -1.134210000 | 1.921579000  |
| C | 2.385511000  | 3.189340000  | -0.336735000 | F  | -0.705776000 | 3.624204000  | 1.691337000  |
| C | -2.507670000 | 2.759160000  | -1.418125000 | F  | 3.971723000  | 0.280595000  | 1.299823000  |
| C | 1.681546000  | -3.189781000 | -2.766306000 | F  | 4.735213000  | 2.282253000  | 1.072780000  |
| C | -0.170578000 | -0.046052000 | -2.244744000 | F  | -2.309395000 | 4.776196000  | 0.833824000  |
| C | 0.014857000  | -1.313477000 | -3.031919000 | F  | -0.512313000 | 4.424820000  | -0.294570000 |
| C | 0.486019000  | -1.087332000 | -4.458445000 | F  | -4.449401000 | -2.746020000 | -1.355943000 |
| H | 3.005000000  | -4.429409000 | 2.191194000  | F  | -4.373522000 | -0.722136000 | -0.623779000 |
| H | 1.532235000  | -4.596759000 | 1.224154000  | F  | 3.906095000  | 0.005707000  | -1.434701000 |
| H | 4.821645000  | -2.764751000 | 1.431100000  | F  | 4.712433000  | 1.997500000  | -1.588539000 |
| H | 3.087137000  | -5.134125000 | 0.578321000  | F  | -3.353370000 | 3.795370000  | -1.487323000 |
| H | 2.428709000  | -2.210565000 | 1.243780000  | F  | -3.071982000 | -1.344920000 | -2.219430000 |
| H | -2.774257000 | 2.057699000  | 1.948216000  | F  | -3.170182000 | 1.677153000  | -1.834379000 |
| H | 4.810858000  | -3.499176000 | -0.172976000 | F  | -1.527578000 | 2.981771000  | -2.293703000 |
| H | -1.060717000 | -3.689467000 | 0.143676000  | F  | 2.849759000  | 1.506897000  | -2.548368000 |
| H | 4.539711000  | -1.756820000 | 0.006970000  | N  | 2.157788000  | -2.822885000 | -0.664875000 |
| H | -2.640106000 | -4.287289000 | -0.415883000 | N  | 0.970174000  | -2.127503000 | -2.284576000 |
| H | -3.957306000 | 2.838925000  | 0.878461000  | O  | -1.586657000 | -1.153738000 | 0.009074000  |
|   |              |              |              | O  | -0.991010000 | 1.602871000  | -0.008919000 |
|   |              |              |              | O  | 1.686916000  | 0.913033000  | -0.096082000 |
|   |              |              |              | Ta | 0.036992000  | -0.069619000 | -0.027538000 |
|   |              |              |              | H  | 0.291542000  | 1.210071000  | 2.070866000  |
|   |              |              |              | C  | 0.465448000  | -2.187866000 | 2.751637000  |
|   |              |              |              | H  | -0.457096000 | -2.258163000 | 3.336184000  |
|   |              |              |              | H  | 0.438090000  | -3.038472000 | 2.070289000  |
|   |              |              |              | C  | 1.643156000  | -2.331109000 | 3.716114000  |
|   |              |              |              | H  | 1.642146000  | -3.319871000 | 4.181721000  |
|   |              |              |              | H  | 2.606190000  | -2.194044000 | 3.221208000  |
|   |              |              |              | H  | 1.593705000  | -1.587094000 | 4.511823000  |
|   |              |              |              | C  | -0.054940000 | 0.488261000  | 4.076207000  |
|   |              |              |              | H  | 0.821676000  | 0.947497000  | 4.550529000  |
|   |              |              |              | H  | -0.217005000 | -0.466177000 | 4.580081000  |
|   |              |              |              | C  | -1.267161000 | 1.384501000  | 4.291938000  |
|   |              |              |              | H  | -1.435972000 | 1.558575000  | 5.357029000  |
|   |              |              |              | H  | -1.135219000 | 2.355501000  | 3.810293000  |
|   |              |              |              | H  | -2.167498000 | 0.920743000  | 3.881390000  |

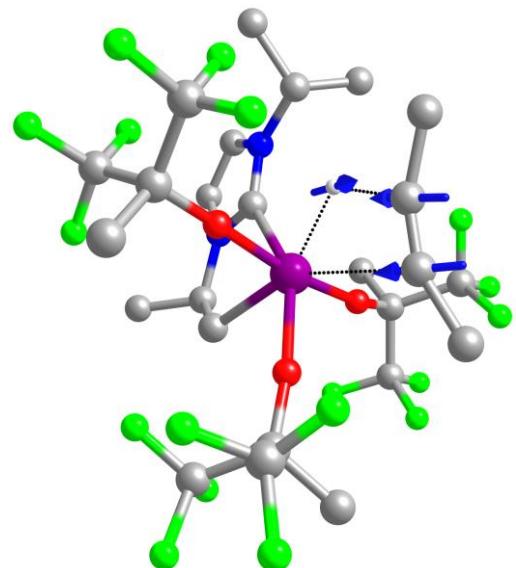
**Optimized coordinates of Ta(NHC\*)(*cis*- $\eta^1$ -MeC=CHMe)(OR<sub>F</sub>)<sub>3</sub> (PBE1PBE/Def2-TZVP PCM(thf) GD3) (*cis*-19)**



H atoms omitted (except vinylic H atom)

|   |              |               |              |    |               |              |              |
|---|--------------|---------------|--------------|----|---------------|--------------|--------------|
| C | -0.520950000 | -1.184361000  | 3.890773000  | H  | -4.202515000  | -2.117560000 | 1.543697000  |
| C | -3.788777000 | 0.547951000   | 1.276398000  | H  | -1.430731000  | 4.689581000  | 0.643531000  |
| C | 0.629336000  | -1.1549841000 | 2.969455000  | H  | -1.948164000  | 3.383043000  | -0.443113000 |
| C | 1.802092000  | -2.130749000  | 3.739707000  | H  | 0.100434000   | -4.297407000 | 3.043786000  |
| C | 3.793758000  | 0.161817000   | 0.624598000  | H  | -2.895145000  | -2.690022000 | 0.496239000  |
| C | -1.451178000 | 3.609834000   | 0.497236000  | H  | 3.582535000   | 1.007988000  | -2.001305000 |
| C | 0.580834000  | 3.184310000   | 1.874677000  | H  | 4.921401000   | -0.138004000 | -1.772489000 |
| C | -3.217659000 | -1.880182000  | 1.145816000  | H  | 3.499795000   | -0.614432000 | -2.716408000 |
| C | -3.245256000 | -0.575995000  | 0.357478000  | H  | -0.642941000  | -5.320515000 | 0.603391000  |
| C | -0.044666000 | 3.028563000   | 0.465016000  | H  | -1.169710000  | -1.650633000 | -2.740744000 |
| C | 3.148468000  | -0.544646000  | -0.595720000 | H  | 0.527796000   | -1.957878000 | -2.493854000 |
| C | -0.035161000 | -2.122327000  | 0.623129000  | H  | -1.875690000  | -3.370922000 | -1.393134000 |
| C | -0.028116000 | -3.808869000  | 2.093468000  | H  | 0.910224000   | -4.372558000 | -2.119208000 |
| C | -4.196133000 | -0.768632000  | -0.854733000 | H  | -0.488826000  | -5.395660000 | -1.732429000 |
| C | 3.368951000  | -2.077250000  | -0.506853000 | H  | -0.505120000  | -4.389515000 | -3.181057000 |
| C | 3.839608000  | -0.039074000  | -1.856742000 | F  | -2.938732000  | 0.745481000  | 2.290395000  |
| C | 0.791233000  | 3.795624000   | -0.590149000 | F  | -4.976149000  | 0.238416000  | 1.805555000  |
| C | -0.390688000 | -4.314611000  | 0.890561000  | F  | 3.804221000   | 1.478433000  | 0.439318000  |
| C | -0.433688000 | -1.891037000  | -1.971855000 | F  | -3.924604000  | 1.711493000  | 0.643677000  |
| C | -0.786965000 | -3.254138000  | -1.394657000 | F  | -0.063257000  | 2.388731000  | 2.736822000  |
| C | -0.179749000 | -4.429582000  | -2.140388000 | F  | 3.132218000   | -0.078502000 | 1.757586000  |
| H | -0.159898000 | -0.517415000  | 4.675438000  | F  | 5.060471000   | -0.226405000 | 0.812019000  |
| H | -1.314944000 | -0.667388000  | 3.353796000  | F  | 0.483104000   | 4.433089000  | 2.343342000  |
| H | 2.193608000  | -1.370430000  | 4.416930000  | F  | 1.868111000   | 2.842825000  | 1.909061000  |
| H | -0.937054000 | -2.075408000  | 4.367583000  | F  | -5.396900000  | -1.216321000 | -0.469580000 |
| H | 0.967690000  | -0.658613000  | 2.444571000  | F  | -4.395010000  | 0.346789000  | -1.552000000 |
| H | -2.011204000 | 3.149110000   | 1.307313000  | F  | 2.944209000   | -2.594396000 | 0.648154000  |
| H | 1.495819000  | -2.986308000  | 4.345923000  | F  | 4.654540000   | -2.411984000 | -0.643893000 |
| H | -2.512842000 | -1.791787000  | 1.968100000  | F  | 1.007637000   | 5.068430000  | -0.226888000 |
| H | 2.603778000  | -2.441093000  | 3.071172000  | F  | -3.682251000  | -1.675127000 | -1.689780000 |
|   |              |               |              | F  | 0.141364000   | 3.824890000  | -1.755873000 |
|   |              |               |              | F  | 1.977575000   | 3.235091000  | -0.808964000 |
|   |              |               |              | F  | 2.697154000   | -2.682820000 | -1.487236000 |
|   |              |               |              | N  | 0.192366000   | -2.465897000 | 1.909874000  |
|   |              |               |              | N  | -0.378226000  | -3.263990000 | 0.012527000  |
|   |              |               |              | O  | -2.016443000  | -0.184037000 | -0.098051000 |
|   |              |               |              | O  | -0.022789000  | 1.696942000  | 0.164303000  |
|   |              |               |              | O  | 1.805332000   | -0.277141000 | -0.600034000 |
|   |              |               |              | Ta | -0.1222545000 | -0.135003000 | -0.548322000 |
|   |              |               |              | C  | -0.338074000  | 0.718629000  | -2.559696000 |
|   |              |               |              | C  | 0.697079000   | 0.842568000  | -3.395317000 |
|   |              |               |              | H  | 1.647170000   | 0.416174000  | -3.094044000 |
|   |              |               |              | C  | -1.711190000  | 1.226356000  | -2.895442000 |
|   |              |               |              | H  | -1.723268000  | 1.876389000  | -3.773501000 |
|   |              |               |              | H  | -2.385797000  | 0.388486000  | -3.093165000 |
|   |              |               |              | H  | -2.155567000  | 1.779437000  | -2.065294000 |
|   |              |               |              | C  | 0.742930000   | 1.508413000  | -4.735611000 |
|   |              |               |              | H  | 1.517390000   | 2.283020000  | -4.753549000 |
|   |              |               |              | H  | 1.010196000   | 0.786424000  | -5.515827000 |
|   |              |               |              | H  | -0.199967000  | 1.972606000  | -5.023748000 |

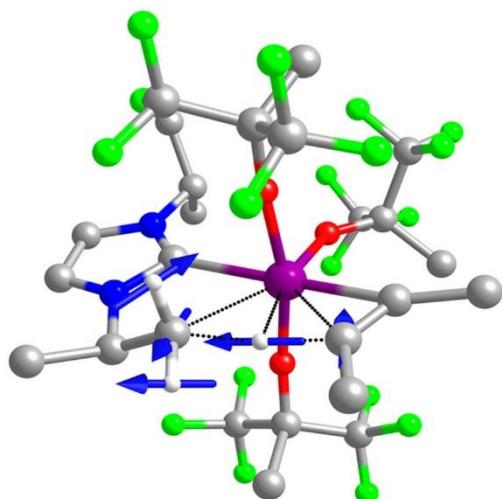
**Optimized coordinates for TS4 (insertion of 2-butyne into Ta-H of 7) (PBE1PBE/Def2-TZVP PCM(thf) GD3)**



H atoms omitted (except hydridic H atom)

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.957186000  | -4.502306000 | -1.228357000 |
| C  | 3.947223000  | -0.865631000 | -1.295308000 |
| C  | -0.306575000 | -3.937577000 | -0.605447000 |
| C  | -1.414250000 | -4.970523000 | -0.500972000 |
| C  | -3.575354000 | -1.159054000 | -1.480509000 |
| C  | 1.139586000  | 4.086749000  | -0.259173000 |
| C  | -1.254328000 | 3.930004000  | -0.992921000 |
| C  | 3.466893000  | -1.810836000 | 0.958672000  |
| C  | 3.336321000  | -0.560579000 | 0.097218000  |
| C  | -0.176882000 | 3.342045000  | -0.026264000 |
| C  | -3.158719000 | -0.364491000 | -0.219148000 |
| C  | 0.099215000  | -2.026865000 | 0.991451000  |
| C  | 0.197424000  | -4.110998000 | 1.822577000  |
| C  | 4.088458000  | 0.609988000  | 0.777826000  |
| C  | -3.530798000 | -1.147262000 | 1.065352000  |
| C  | -3.902792000 | 0.963712000  | -0.213611000 |
| C  | -0.638056000 | 3.670210000  | 1.425288000  |
| C  | 0.426865000  | -3.256977000 | 2.845669000  |
| C  | 0.132900000  | 0.369374000  | 2.068828000  |
| C  | 0.565534000  | -0.731441000 | 3.007839000  |
| C  | -0.150056000 | -0.720352000 | 4.347739000  |
| H  | 0.731787000  | -4.924690000 | -2.209535000 |
| H  | 1.710591000  | -3.723184000 | -1.352726000 |
| H  | -1.707842000 | -5.276889000 | -1.506351000 |
| H  | 1.377827000  | -5.297856000 | -0.608179000 |
| H  | -0.663857000 | -3.104810000 | -1.205864000 |
| H  | 1.372111000  | 4.109161000  | -1.321414000 |
| H  | -1.089850000 | -5.866230000 | 0.033758000  |
| H  | 2.882982000  | -2.612276000 | 0.509515000  |
| H  | -2.289463000 | -4.558109000 | 0.001162000  |
| H  | 4.506051000  | -2.125516000 | 1.044164000  |
| H  | 1.096217000  | 5.112241000  | 0.107212000  |
| H  | 1.928122000  | 3.547734000  | 0.263067000  |
| H  | 0.152874000  | -5.186088000 | 1.812559000  |
| H  | 3.074448000  | -1.608404000 | 1.951840000  |
| H  | -3.655577000 | 1.508652000  | -1.121599000 |
| H  | -4.980902000 | 0.817325000  | -0.158433000 |
| H  | -3.567593000 | 1.548645000  | 0.639886000  |
| H  | 0.624354000  | -3.447969000 | 3.885887000  |
| H  | 0.754815000  | 1.246684000  | 2.240339000  |
| H  | -0.894918000 | 0.660724000  | 2.303907000  |
| H  | 1.643061000  | -0.653227000 | 3.188572000  |
| H  | -1.224579000 | -0.855641000 | 4.202912000  |
| H  | 0.213560000  | -1.491589000 | 5.031345000  |
| H  | 0.011775000  | 0.248710000  | 4.822263000  |
| F  | 3.253376000  | -1.845532000 | -1.882117000 |
| F  | 5.217454000  | -1.276358000 | -1.207667000 |
| F  | -3.208765000 | -0.486669000 | -2.574168000 |
| F  | 3.923944000  | 0.183817000  | -2.113855000 |
| F  | -1.121322000 | 3.415438000  | -2.216372000 |
| F  | -2.996035000 | -2.362290000 | -1.546797000 |
| F  | -4.895541000 | -1.349216000 | -1.550426000 |
| F  | -1.157551000 | 5.260633000  | -1.119708000 |
| F  | -2.505685000 | 3.668138000  | -0.597285000 |
| F  | 5.385918000  | 0.346212000  | 0.959104000  |
| F  | 3.999818000  | 1.744178000  | 0.081295000  |
| F  | -2.918266000 | -2.329189000 | 1.148705000  |
| F  | -4.845915000 | -1.372145000 | 1.154699000  |
| F  | -1.034977000 | 4.947860000  | 1.546715000  |
| F  | 3.555959000  | 0.844196000  | 1.981052000  |
| F  | 0.365463000  | 3.501887000  | 2.293735000  |
| F  | -1.650738000 | 2.905627000  | 1.832542000  |
| F  | -3.173040000 | -0.440878000 | 2.140943000  |
| N  | -0.008246000 | -3.347681000 | 0.701302000  |
| N  | 0.349097000  | -2.000160000 | 2.314775000  |
| O  | 2.046511000  | -0.158406000 | -0.074895000 |
| O  | -0.064736000 | 2.008700000  | -0.228744000 |
| O  | -1.809070000 | -0.187105000 | -0.251109000 |
| Ta | 0.114537000  | -0.023689000 | -0.119193000 |
| H  | 0.113753000  | -1.447292000 | -1.186517000 |
| C  | 0.751363000  | 0.548114000  | -2.556342000 |
| C  | 0.295938000  | -0.571395000 | -2.762346000 |
| C  | -0.141137000 | -1.753312000 | -3.502407000 |
| H  | 0.503376000  | -2.608267000 | -3.289907000 |
| H  | -1.168384000 | -2.026318000 | -3.261063000 |
| H  | -0.086798000 | -1.534646000 | -4.571982000 |
| C  | 1.471296000  | 1.785740000  | -2.837384000 |
| H  | 2.080205000  | 2.090002000  | -1.987896000 |
| H  | 2.128962000  | 1.625320000  | -3.695027000 |
| H  | 0.783664000  | 2.593077000  | -3.078594000 |

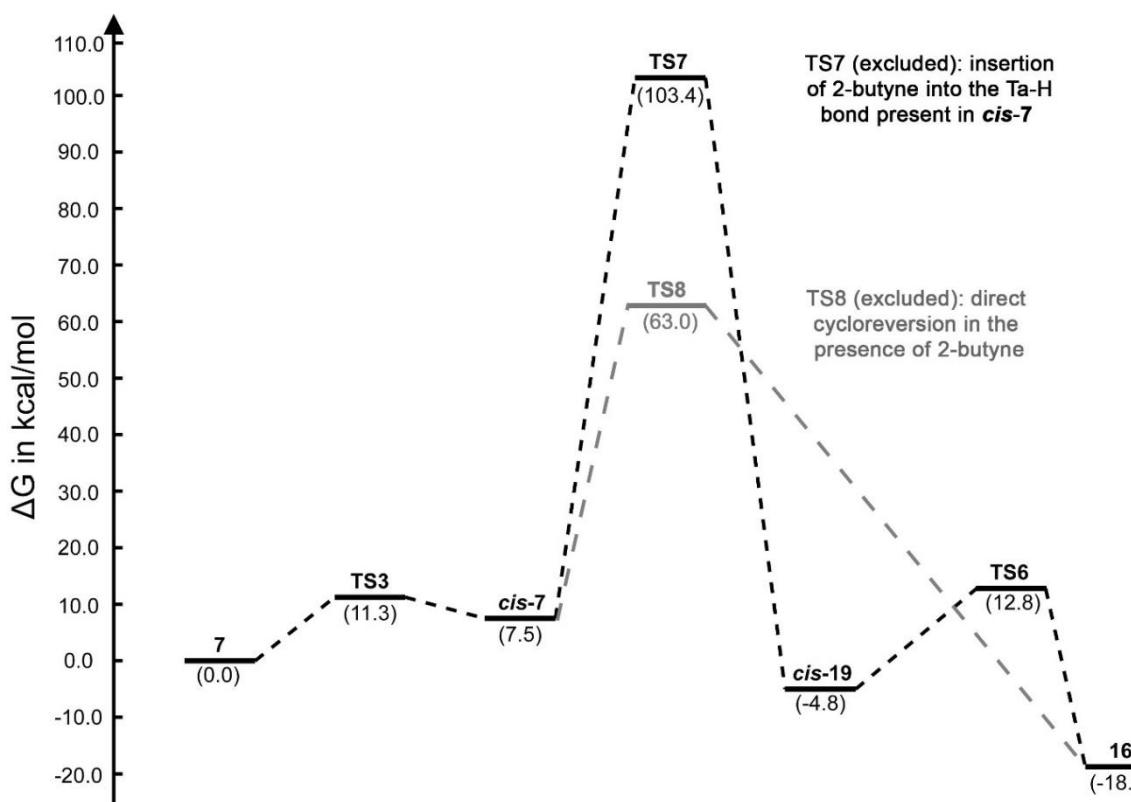
Optimized coordinates for TS6 (H-shift for the reaction *cis*-19→16) (PBE1PBE/Def2-TZVP PCM(thf) GD3)



H atoms omitted (except "moving" H atoms)

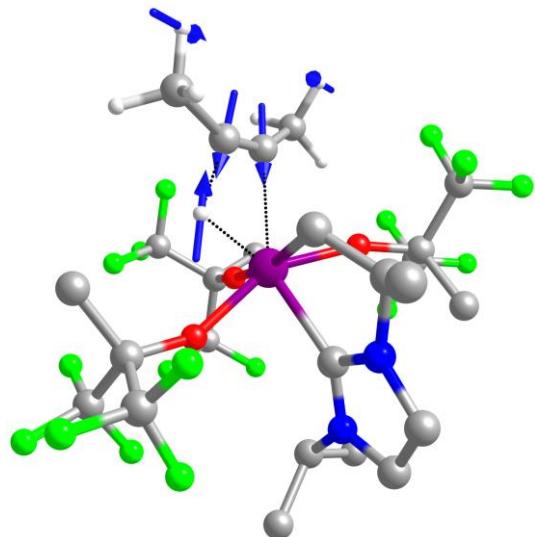
|   |              |              |              |    |              |              |              |
|---|--------------|--------------|--------------|----|--------------|--------------|--------------|
| C | 0.221462000  | 2.715057000  | 3.686661000  | H  | -4.797979000 | -0.613014000 | 1.965420000  |
| C | -4.075789000 | 0.576142000  | -0.325373000 | H  | -1.278930000 | 3.644261000  | -2.479855000 |
| C | 1.097915000  | 1.770376000  | 2.881704000  | H  | -1.214845000 | 1.868768000  | -2.477829000 |
| C | 2.563720000  | 1.896563000  | 3.258522000  | H  | 0.884058000  | 0.256024000  | 5.195776000  |
| C | 4.088481000  | -0.293254000 | 0.085897000  | H  | -3.331628000 | -1.550667000 | 2.282121000  |
| C | -1.316555000 | 2.750811000  | -1.857528000 | H  | 3.101558000  | 0.788988000  | -2.209120000 |
| C | -0.550272000 | 3.835129000  | 0.231375000  | H  | 4.257334000  | -0.478716000 | -2.675627000 |
| C | -3.719623000 | -0.647753000 | 1.815096000  | H  | 2.513864000  | -0.699306000 | -2.958060000 |
| C | -3.358915000 | -0.630578000 | 0.333386000  | H  | -0.057498000 | -2.279952000 | 4.757376000  |
| C | -0.201771000 | 2.743209000  | -0.820584000 | H  | -0.419274000 | -3.668218000 | 0.129251000  |
| C | 3.067115000  | -0.903948000 | -0.905893000 | H  | 1.045311000  | -2.887438000 | 0.659032000  |
| C | 0.220814000  | -0.429031000 | 2.073455000  | H  | -1.688948000 | -2.643999000 | 1.957492000  |
| C | 0.583742000  | -0.226384000 | 4.281909000  | H  | 0.801423000  | -4.139471000 | 2.880985000  |
| C | -3.846854000 | -1.943929000 | -0.333813000 | H  | -0.760719000 | -4.078109000 | 3.727092000  |
| C | 3.304762000  | -2.433021000 | -1.020739000 | H  | -0.640612000 | -4.875827000 | 2.164893000  |
| C | 3.260389000  | -0.283276000 | -2.282776000 | F  | -3.732686000 | 1.702093000  | 0.304402000  |
| C | 1.126828000  | 3.139847000  | -1.509812000 | F  | -5.407536000 | 0.470703000  | -0.253521000 |
| C | 0.121426000  | -1.476516000 | 4.065764000  | F  | 3.938011000  | 1.029843000  | 0.138165000  |
| C | -0.034328000 | -2.756365000 | 0.603836000  | F  | -3.754898000 | 0.721835000  | -1.609817000 |
| C | -0.604594000 | -2.744898000 | 2.005846000  | F  | -1.519248000 | 3.398244000  | 1.035685000  |
| C | -0.277615000 | -4.029450000 | 2.749187000  | F  | 3.928739000  | -0.758357000 | 1.327348000  |
| H | 0.527085000  | 3.745250000  | 3.505030000  | F  | 5.353392000  | -0.538305000 | -0.275637000 |
| H | -0.826763000 | 2.613508000  | 3.403402000  | F  | -0.990412000 | 4.966575000  | -0.334274000 |
| H | 2.909139000  | 2.907088000  | 3.032947000  | F  | 0.491046000  | 4.173367000  | 1.002513000  |
| H | 0.315141000  | 2.522333000  | 4.758285000  | F  | -5.134378000 | -2.192744000 | -0.080642000 |
| H | 0.978248000  | 1.964605000  | 1.818718000  | F  | -3.689391000 | -1.936698000 | -1.657657000 |
| H | -2.278442000 | 2.712430000  | -1.353751000 | F  | 3.275146000  | -3.056829000 | 0.160781000  |
| H | 2.715957000  | 1.719982000  | 4.326658000  | F  | 4.478297000  | -2.721609000 | -1.589590000 |
| H | -3.257449000 | 0.216493000  | 2.289011000  | F  | 1.116433000  | 4.410188000  | -1.940248000 |
| H | 3.175265000  | 1.191016000  | 2.697516000  | F  | -3.145729000 | -2.981664000 | 0.137769000  |
|   |              |              |              | N  | 0.635646000  | 0.393591000  | 3.057161000  |
|   |              |              |              | N  | -0.085318000 | -1.578915000 | 2.713821000  |
|   |              |              |              | O  | -2.018728000 | -0.497043000 | 0.130378000  |
|   |              |              |              | O  | -0.034066000 | 1.553611000  | -0.166902000 |
|   |              |              |              | O  | 1.820481000  | -0.668104000 | -0.404135000 |
|   |              |              |              | Ta | -0.115724000 | -0.466801000 | -0.302087000 |
|   |              |              |              | C  | -0.362496000 | -0.527504000 | -2.439534000 |
|   |              |              |              | C  | -0.478215000 | -1.771145000 | -2.037096000 |
|   |              |              |              | H  | -0.373784000 | -2.251143000 | -0.691778000 |
|   |              |              |              | C  | -0.432575000 | -0.003560000 | -3.828362000 |
|   |              |              |              | H  | -0.254904000 | -0.790167000 | -4.569414000 |
|   |              |              |              | H  | -1.430729000 | 0.401915000  | -4.024743000 |
|   |              |              |              | H  | 0.277442000  | 0.805405000  | -4.002434000 |
|   |              |              |              | C  | -0.707861000 | -3.082138000 | -2.702317000 |
|   |              |              |              | H  | 0.066503000  | -3.807397000 | -2.440379000 |
|   |              |              |              | H  | -1.666582000 | -3.509111000 | -2.395310000 |
|   |              |              |              | H  | -0.719309000 | -2.965741000 | -3.788523000 |

In the article text, it is mentioned that alternative pathways for the reaction between **7** and 2-butyne were considered and modelled *in silico*. In view of the plausible isomerization of **7** to *cis*-**7** under the employed reaction conditions, *cis*-**7** was probed as a possible starting point of the reaction. It was found that the insertion of 2-butyne into the Ta–H bond of *cis*-**7** is not feasible at the employed reaction temperature (65°C). A direct cycloreversion in the presence of a coordinating 2-butyne ligand was excluded for that reason as well. The excluded pathways via *cis*-**7** are shown in Figure S77. Optimized coordinates of the respective transitions states **TS7** and **TS8** are provided on the following pages.



**Figure S77:** Alternative mechanistic scenario (excluded) for the formation of **16** from **7** via *cis*-**7** (PBE1PBE/Def2-TZVP PCM(thf) GD3). The  $\Delta G$  values (kcal/mol) provided in parenthesis were referenced to 2-butyne + **7** (set to 0.0 kcal/mol).

Optimized coordinates for TS7 (excluded) (PBE1PBE/Def2-TZVP PCM (thf) GD3)

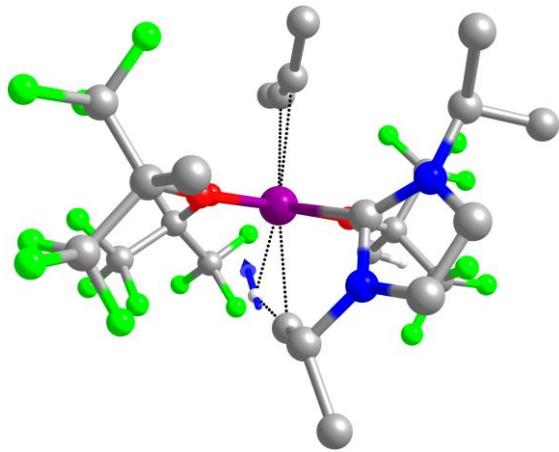


H atoms omitted (except "moving" H atoms)

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | -0.273210000 | -0.525542000 | 4.002262000  |
| C | -3.756648009 | 0.740958000  | 1.302110009  |
| C | 0.784977991  | -0.986270991 | 3.017155000  |
| C | 2.041675000  | -1.449931991 | 3.737517000  |
| C | 4.070393991  | 0.107144000  | 0.139790991  |
| C | -1.142568000 | 3.705970991  | 0.505663000  |
| C | 0.976933000  | 3.080383009  | 1.636696009  |
| C | -3.198005018 | -1.668362009 | 1.438545018  |
| C | -3.276018009 | -0.484374009 | 0.470504018  |
| C | 0.202070009  | 3.015860000  | 0.296111018  |
| C | 3.076435000  | -0.723159000 | -0.722432026 |
| C | -0.097926018 | -1.896607982 | 0.847729000  |
| C | 0.079202009  | -3.345613991 | 2.540792000  |
| C | -4.354403000 | -0.837373000 | -0.597472991 |
| C | 3.374606000  | -2.236883000 | -0.515168009 |
| C | 3.319967018  | -0.385180000 | -2.187733018 |
| C | 0.974617000  | 3.769289000  | -0.817713991 |
| C | -0.388845991 | -4.025085991 | 1.468889000  |
| C | -0.530968000 | -2.147368009 | -1.758369009 |
| C | -0.981985000 | -3.330061000 | -0.916995000 |
| C | -0.549349000 | -4.682605000 | -1.454753991 |
| H | 0.138315000  | 0.262461000  | 4.636940009  |
| H | -1.149362000 | -0.125162000 | 3.496179009  |
| H | 2.481205000  | -0.603028000 | 4.263760000  |
| H | -0.586482000 | -1.348554000 | 4.649906000  |
| H | 1.050129991  | -0.168092991 | 2.347139000  |
| H | -1.693056000 | 3.186993000  | 1.287532009  |
| H | 1.814896000  | -2.215647991 | 4.483143000  |
| H | -2.406438018 | -1.494644009 | 2.162934018  |

|    |              |              |              |
|----|--------------|--------------|--------------|
| H  | 2.779457991  | -1.843795000 | 3.041792000  |
| H  | -4.138197018 | -1.804017009 | 1.969037009  |
| H  | -1.009265009 | 4.746803991  | 0.793647974  |
| H  | -1.720685000 | 3.663582956  | -0.413091000 |
| H  | 0.304744009  | -3.690701000 | 3.535566000  |
| H  | -2.977549009 | -2.581610009 | 0.891957018  |
| H  | 3.016454026  | 0.643653000  | -2.368978018 |
| H  | 4.370625009  | -0.500756009 | -2.452642035 |
| H  | 2.724630009  | -1.044157000 | -2.819360018 |
| H  | -0.643799982 | -5.064263991 | 1.359280991  |
| H  | -1.279734000 | -1.977022044 | -2.537776018 |
| H  | 0.391766009  | -2.427515000 | -2.274568991 |
| H  | -2.073266000 | -3.327928000 | -0.844350000 |
| H  | 0.539482000  | -4.756907009 | -1.495233991 |
| H  | -0.935567000 | -5.517888000 | -0.864801991 |
| H  | -0.935055991 | -4.791265000 | -2.469043991 |
| F  | -2.843218009 | 1.035568000  | 2.234929009  |
| F  | -4.909607009 | 0.509447009  | 1.940404009  |
| F  | 4.014990000  | 1.394406000  | -0.195871009 |
| F  | -3.934154000 | 1.844639991  | 0.574026000  |
| F  | 0.310645009  | 2.388057009  | 2.568026009  |
| F  | 3.810815982  | 0.020781000  | 1.444369991  |
| F  | 5.340897991  | -0.284363000 | -0.036672000 |
| F  | 1.105989000  | 4.330183009  | 2.096994009  |
| F  | 2.198690009  | 2.557468009  | 1.558724009  |
| F  | -5.503434009 | -1.254682000 | -0.046231000 |
| F  | -4.660792000 | 0.180733000  | -1.402239991 |
| F  | 3.337258000  | -2.598217991 | 0.770278991  |
| F  | 4.569983000  | -2.599280000 | -0.992357000 |
| F  | 1.216176000  | 5.045462000  | -0.494556000 |
| F  | -3.912684000 | -1.830085000 | -1.375944991 |
| F  | 0.254245000  | 3.779743991  | -1.944573991 |
| F  | 2.143256000  | 3.203268000  | -1.109406000 |
| F  | 2.465176000  | -2.973511000 | -1.157337009 |
| N  | 0.262578991  | -2.043626991 | 2.140545000  |
| N  | -0.475323000 | -3.118972991 | 0.444585000  |
| O  | -2.114160009 | -0.159638009 | -0.157183965 |
| O  | 0.092273026  | 1.697717991  | -0.058757956 |
| O  | 1.807652991  | -0.461737000 | -0.281863079 |
| Ta | -0.134416035 | -0.184803982 | -0.681685035 |
| C  | -1.375503815 | 1.071028850  | -2.566677692 |
| C  | -0.520204745 | 0.471652903  | -3.219307718 |
| H  | 0.686381859  | -0.151680912 | -2.232537176 |
| C  | -2.505135912 | 1.988071859  | -2.404596044 |
| H  | -2.177236877 | 2.997575833  | -2.667831123 |
| H  | -3.322768797 | 1.716347771  | -3.077028159 |
| H  | -2.886959088 | 1.996381009  | -1.388088097 |
| C  | 0.157977000  | -0.062002947 | -4.408461000 |
| H  | 1.172479000  | 0.328917018  | -4.499581159 |
| H  | 0.213506982  | -1.153303965 | -4.373045159 |
| H  | -0.412467194 | 0.227286194  | -5.295733841 |

Optimized coordinates for TS8 (excluded) (PBE1PBE/Def2-TZVP PCM(thf) GD3)



H atoms omitted (except hydridic H atom)

|   |              |              |              |    |              |              |              |
|---|--------------|--------------|--------------|----|--------------|--------------|--------------|
| C | -2.360686000 | -4.305897000 | -1.856825000 | H  | 2.825257000  | 4.492633000  | -1.371883000 |
| C | 3.368403000  | -1.895044000 | -1.498961000 | H  | 2.790248000  | 2.953499000  | -2.262310000 |
| C | -2.688222000 | -3.033970000 | -1.085334000 | H  | -2.688065000 | -4.799482000 | 0.980155000  |
| C | -4.181573000 | -2.984757000 | -0.791659000 | H  | 1.802124000  | -3.376335000 | 1.194581000  |
| C | -3.861210000 | 1.184203000  | -1.112148000 | H  | -2.567715000 | 3.429317000  | -0.487267000 |
| C | 2.208312000  | 3.636747000  | -1.646483000 | H  | -3.941381000 | 3.340838000  | 0.633777000  |
| C | 0.792554000  | 3.822255000  | 0.377440000  | H  | -2.277142000 | 3.136777000  | 1.228942000  |
| C | 2.120402000  | -3.294815000 | 0.157014000  | H  | -1.160935000 | -4.040365000 | 3.122030000  |
| C | 2.649846000  | -1.889613000 | -0.120194000 | H  | -1.002107000 | 0.250359000  | 2.530309000  |
| C | 1.703334000  | 2.859019000  | -0.424326000 | H  | 0.420852000  | 0.915559000  | 1.295757000  |
| C | -3.017900000 | 1.437002000  | 0.164160000  | H  | 1.140897000  | -1.897303000 | 2.538087000  |
| C | -1.076312000 | -1.972913000 | 0.572758000  | H  | -1.293451000 | -1.519191000 | 4.330956000  |
| C | -2.060366000 | -3.936070000 | 1.114431000  | H  | -0.035109000 | -2.762318000 | 4.513692000  |
| C | 3.720242000  | -1.541055000 | 0.965118000  | H  | 0.367140000  | -1.066520000 | 4.746215000  |
| C | -3.692431000 | 0.783110000  | 1.399665000  | F  | 2.618831000  | -2.512619000 | -2.417841000 |
| C | -2.954761000 | 2.939647000  | 0.402113000  | F  | 4.532018000  | -2.559050000 | -1.441773000 |
| C | 2.951002000  | 2.494831000  | 0.418652000  | F  | -3.271125000 | 1.754875000  | -2.164033000 |
| C | -1.313317000 | -3.560909000 | 2.171792000  | F  | 3.618067000  | -0.673298000 | -1.952443000 |
| C | -0.010156000 | -0.113413000 | 2.260396000  | F  | -0.270884000 | 4.151950000  | -0.367953000 |
| C | 0.113677000  | -1.568654000 | 2.685915000  | F  | -3.988808000 | -0.113571000 | -1.389563000 |
| C | -0.240603000 | -1.751594000 | 4.153245000  | F  | -5.090635000 | 1.700392000  | -1.025554000 |
| H | -2.818192000 | -4.262186000 | -2.846943000 | F  | 1.394575000  | 4.974886000  | 0.707364000  |
| H | -1.289347000 | -4.457725000 | -1.977417000 | F  | 0.326090000  | 3.293334000  | 1.515274000  |
| H | -4.731110000 | -2.910940000 | -1.731787000 | F  | 4.455614000  | -2.615591000 | 1.284928000  |
| H | -2.769425000 | -5.181232000 | -1.346960000 | F  | 4.568522000  | -0.590194000 | 0.582771000  |
| H | -2.404179000 | -2.147036000 | -1.649606000 | F  | -3.653488000 | -0.547804000 | 1.360996000  |
| H | 1.353443000  | 3.984968000  | -2.222908000 | F  | -4.971663000 | 1.144715000  | 1.534827000  |
| H | -4.507880000 | -3.896975000 | -0.286832000 | F  | 3.626630000  | 3.573060000  | 0.855769000  |
| H | 1.258394000  | -3.472720000 | -0.481198000 | F  | 3.135016000  | -1.123216000 | 2.087190000  |
| H | -4.443115000 | -2.132394000 | -0.171568000 | F  | 3.800316000  | 1.790007000  | -0.329581000 |
| H | 2.876369000  | -4.054938000 | -0.034716000 | F  | 2.662953000  | 1.762302000  | 1.498765000  |
|   |              |              |              | N  | -3.060921000 | 1.162789000  | 2.516437000  |
|   |              |              |              | O  | -1.913176000 | -2.965393000 | 0.154830000  |
|   |              |              |              | O  | -0.742577000 | -2.366302000 | 1.827482000  |
|   |              |              |              | O  | 1.660266000  | -0.950731000 | -0.135094000 |
|   |              |              |              | O  | 1.024755000  | 1.750280000  | -0.819360000 |
|   |              |              |              | O  | -1.784504000 | 0.879477000  | -0.021388000 |
|   |              |              |              | Ta | -0.035606000 | 0.037948000  | -0.109266000 |
|   |              |              |              | H  | 0.695720000  | 0.433043000  | 2.897765000  |
|   |              |              |              | C  | -0.315622000 | -0.760893000 | -2.535991000 |
|   |              |              |              | C  | -0.393901000 | 0.451569000  | -2.643936000 |
|   |              |              |              | C  | -0.193600000 | -2.148871000 | -2.975636000 |
|   |              |              |              | H  | -1.121420000 | -2.478368000 | -3.445084000 |
|   |              |              |              | H  | 0.602444000  | -2.213987000 | -3.718268000 |
|   |              |              |              | C  | -0.505172000 | 1.819819000  | -3.123431000 |
|   |              |              |              | H  | 0.455039000  | 2.152038000  | -3.517788000 |
|   |              |              |              | H  | -0.802279000 | 2.504534000  | -2.333597000 |
|   |              |              |              | H  | -1.248057000 | 1.846630000  | -3.924350000 |
|   |              |              |              | H  | 0.046733000  | -2.825815000 | -2.161681000 |

## 4) CRYSTALLOGRAPHIC DATA

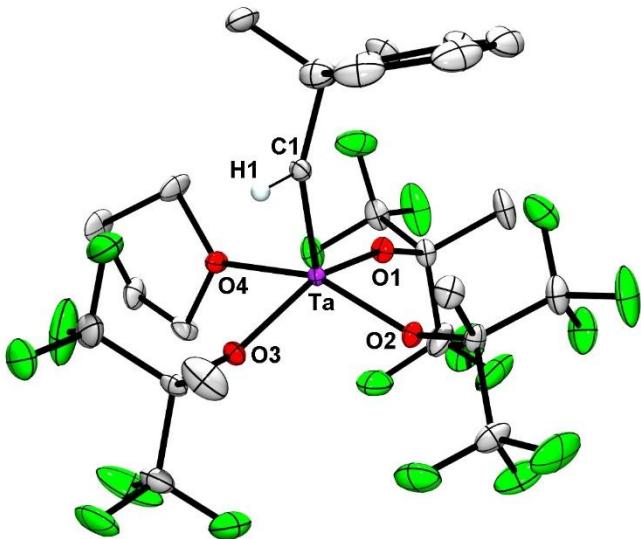
Crystal data and details of the structure determinations are compiled in Tables S1 - S4. Full shells of intensity data were collected at low temperature with a Bruker AXS Smart 1000 CCD diffractometer (Mo- $K_{\alpha}$  radiation, sealed X-ray tube, graphite monochromator; compounds **1** and **12**) or an Agilent Technologies Supernova-E CCD diffractometer (Mo- or Cu- $K_{\alpha}$  radiation, microfocus X-ray tubes, multi-layer mirror optics; all other compounds).

Detector frames (typically  $\omega$ -, occasionally  $\varphi$ -scans, scan width 0.4...1°) were integrated by profile fitting.<sup>[23-25]</sup> Data were corrected for air and detector absorption, Lorentz and polarization effects<sup>[24,25]</sup> and scaled essentially by application of appropriate spherical harmonic functions.<sup>[25-29]</sup> Absorption by the crystal was treated with a semiempirical multiscan method (as part of the scaling procedure), and augmented by a spherical correction,<sup>[25-29]</sup> or numerically (Gaussian grid).<sup>[29,30]</sup> For datasets collected with the microfocus tubes an illumination correction was performed as part of the numerical absorption correction.<sup>[29]</sup> The structures were solved by the charge flip procedure (compounds **2**, **11** and **12**),<sup>[31]</sup> by ab initio dual space methods involving difference Fourier syntheses (VLD procedure)<sup>[32]</sup> or by the heavy atom method combined with structure expansion by direct methods applied to difference structure factors<sup>[33]</sup> and refined by full-matrix least squares methods based on  $F^2$  against all unique reflections.<sup>[34]</sup> All non-hydrogen atoms were given anisotropic displacement parameters.

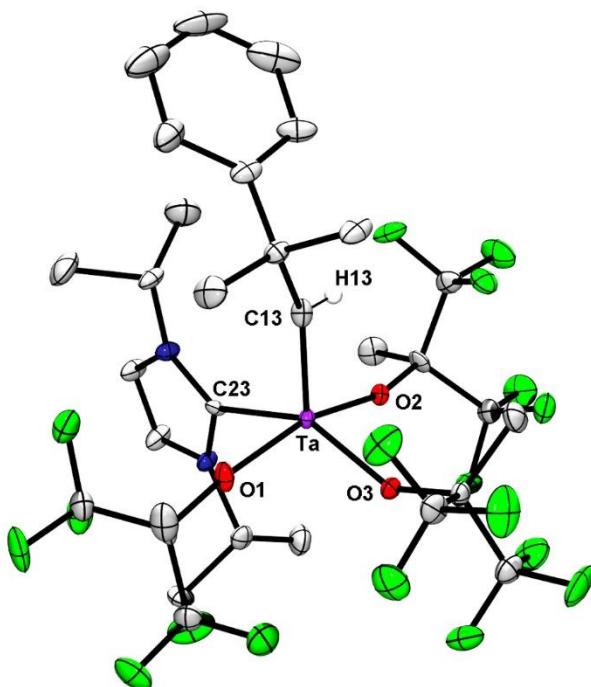
Hydrogen atoms were generally input at calculated positions and refined with a riding model.<sup>[35]</sup> Some hydrogen atoms (hydrides, those involved in agostic MHC interactions and the methylene hydrogens of the Ta-Ethyl groups in complex **12**) were located from difference Fourier syntheses and fully refined. Split atom models were used to refine disordered groups and/or solvent molecules. When found necessary, suitable geometry and adp restraints were applied.<sup>[35,36]</sup>

Crystals of **3** were non-merohedral twins. The twin law (2-fold rotation around reciprocal [001]) was established with the diffractometer software.<sup>[25]</sup> The structure was solved with a de-twinned reflection subset and refined against all single and composite reflections involving the major domain (refined twin fractions 0.65:0.35). After convergence of the refinement of **12**, a difference Fourier map still showed significant residual electron density maxima. Examination of the largest differences  $|F_{\text{obs}} - F_{\text{calc}}|$  indicated some pseudo-merohedral twinning. A twofold twin axis was detected along reciprocal [100].<sup>[37]</sup> Refinement with the corresponding twin matrix converged with only a small proportion (0.016) of the second twin individual, but gave significantly better residuals and a smoother difference map.

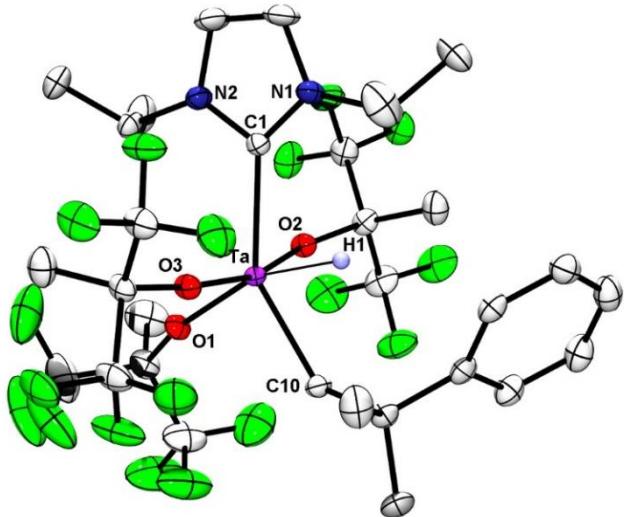
CCDC 2068255 - 2068261 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre's and FIZ Karlsruhe's joint Access Service via <https://www.ccdc.cam.ac.uk/structures/?>.



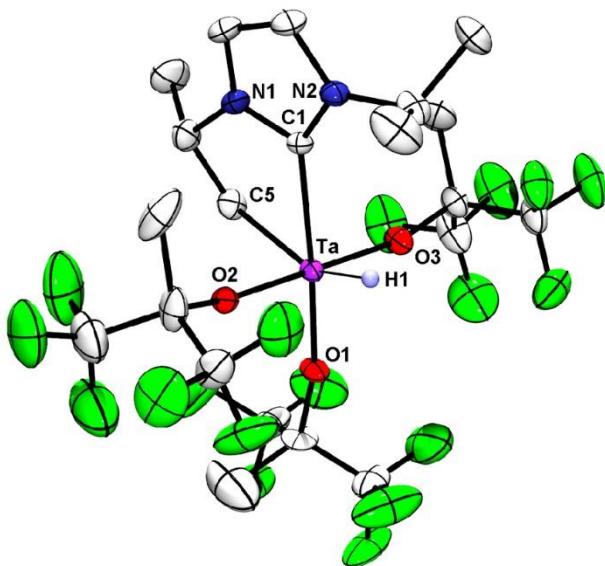
**Figure S78:** ORTEP plot of the molecular structure of **1** (displacement ellipsoids drawn at 50% probability, hydrogen atoms except H1 omitted, disorder of the thf ligand not shown). Selected bond lengths ( $\text{\AA}$ ) and angles ( $^{\circ}$ ): Ta-C1 1.907(2), Ta-O1 1.9044(14), Ta-O2 1.9515(14), Ta-O3 1.9406(15), Ta-O4 2.2068(16), C1-Ta-O3 104.80(8), O3-Ta-O2 91.62(7).



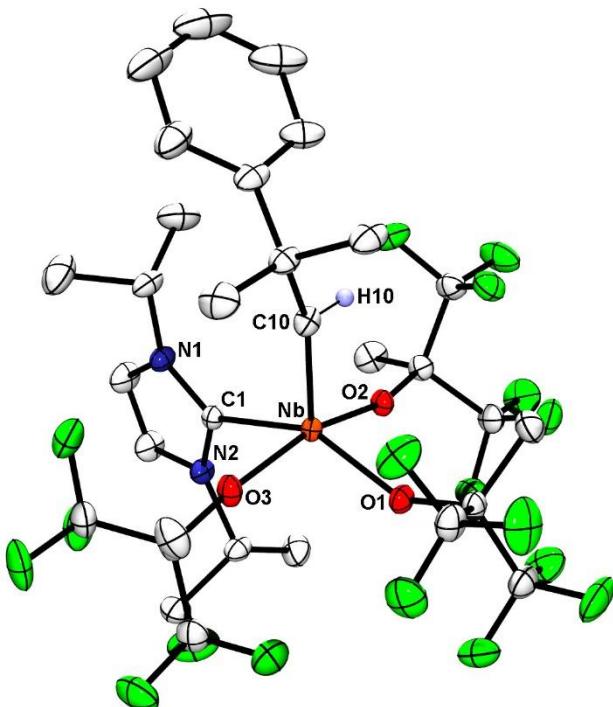
**Figure S79:** ORTEP plot of the molecular structure of **3** (displacement ellipsoids drawn at 50% probability, hydrogen atoms except H13 omitted). Selected bond lengths ( $\text{\AA}$ ) and angles ( $^{\circ}$ ): C23-Ta 2.319(4), C13-Ta 1.924(4), O1-Ta 1.908(3), O2-Ta 1.944(3), O3-Ta 1.989(3), C23-Ta-C13 102.09(19), C23-Ta-O1 85.13(15), C23-Ta-O2 84.04(15), O1-Ta-O3 89.07(14), O3-Ta-O2 89.66(14).



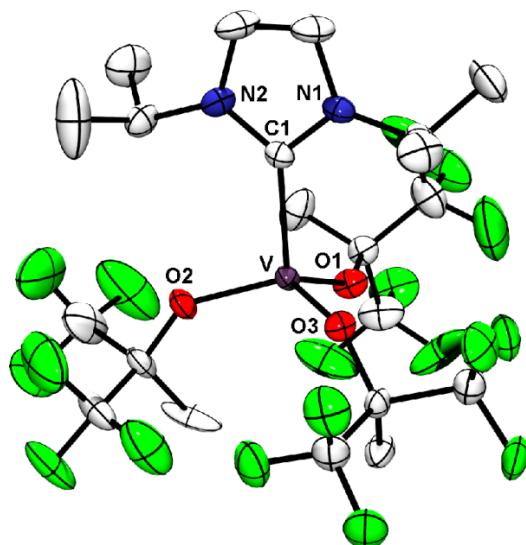
**Figure S80:** ORTEP plot of the molecular structure of **5** (displacement ellipsoids drawn at 50% probability, hydrogen atoms except H1 omitted). Selected bond lengths ( $\text{\AA}$ ) and angles ( $^{\circ}$ ): Ta-C1 2.3066(19), Ta-O1 1.9792(14), Ta-O2 1.9467(14), Ta-O3 1.9074(14), Ta-C10 2.188(2), Ta-H1 1.65(3), C1-Ta-O3 85.56(6), O2-Ta-O3 166.35(6), C1-Ta-H1 73.7(11), C10-Ta-H1 69.5(11).



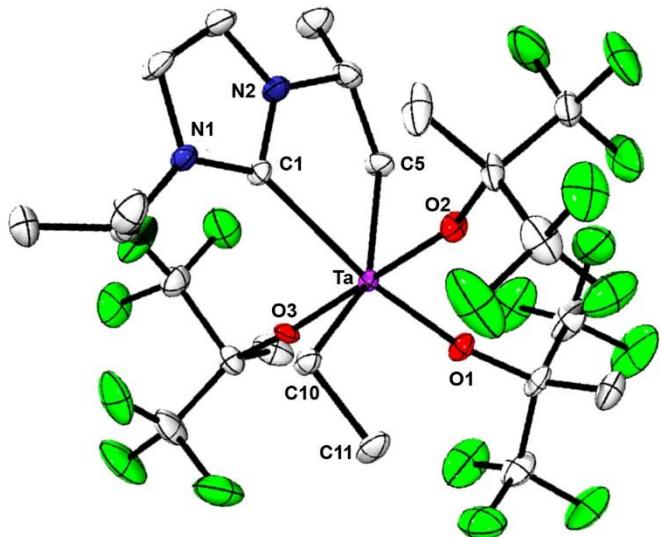
**Figure S81:** ORTEP plot of the molecular structure of **7** (displacement ellipsoids drawn at 50% probability, hydrogen atoms except H1 omitted, disorder of a  $\text{OC}(\text{Me})(\text{CF}_3)_2$  ligand not shown). Selected bond lengths ( $\text{\AA}$ ) and angles ( $^{\circ}$ ), values in square brackets refer to the second disordered set: Ta-C1 2.289(4), Ta-O1 1.925(8) [1.950(16)], Ta-O2 1.916(3), Ta-O3 1.907(3), Ta-C5 2.201(5), Ta-H1 1.60(7), C1-Ta-O3 90.71(15), O2-Ta-O3 174.87(16), C1-Ta-H1 81(2), C5-Ta-H1 152(2).



**Figure S82:** ORTEP plot of the molecular structure of **10** (displacement ellipsoids drawn at 50% probability, hydrogen atoms except H10 omitted). Selected bond lengths ( $\text{\AA}$ ) and angles ( $^{\circ}$ ): Nb-C1 2.3407(13), Nb-C10 1.9270(15), Nb-O1 2.0028(9), Nb-O2 1.9587(9), Nb-O3 1.9112(10), C1-Nb-O3 85.25(4), C1-Nb-O2 83.57(4), O3-Nb-O1 89.46(4), O1-Nb-O2 90.11(4), C1-Nb-C10 101.69(5).



**Figure S83:** ORTEP plot of the molecular structure of **11** (displacement ellipsoids drawn at 50% probability, hydrogen atoms omitted, disorder of two  $\text{OC}(\text{Me})(\text{CF}_3)_2$  ligands not shown). Selected bond lengths ( $\text{\AA}$ ) and angles ( $^{\circ}$ ), values in square brackets refer to the second disordered set: V-C1 2.143(2), V-O1 1.8399(17), V-O2 1.853(10) [1.844(9)], V-O3 1.866(6) [1.852(13)], C1-V-O1 108.60(8), O2-V-O1 114.2(8) [116.6(8)], O3-V-O1 109.6(6) [108.9(13)].



**Figure S84:** ORTEP plot of the molecular structure of **12** (only one of the two independent molecules is shown, displacement ellipsoids drawn at 50% probability, hydrogen atoms omitted, disorder of a  $\text{OC}(\text{Me})(\text{CF}_3)_2$  ligand not shown). Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ), values in square brackets refer to the second disordered set: Ta-C1 2.356(3) [2.378(3)], Ta-O1 1.936(3) [1.925(2)], Ta-O2 1.934(3) [1.922(2)], Ta-O3 1.903(3) [1.912(2)], Ta-C5 2.212(3) [2.214(4)], Ta-C10 2.217(3) [2.218(4)], C1-Ta-O3 90.36(11) [92.25(10)], O2-Ta-O3 177.10(10) [177.51(10)], C1-Ta-C10 82.51(11) [82.24(11)], C5-Ta-C10 152.97(12) [152.86(12)].

**Table S1:** Details of the crystal structure determinations of **1** and **3**.

| compound                                       | <b>1</b>  | <b>3</b>   |
|--|---|--|
| Formula  | C <sub>26</sub> H <sub>29</sub> F <sub>18</sub> O <sub>4</sub> Ta | C <sub>31</sub> H <sub>37</sub> F <sub>18</sub> N <sub>2</sub> O <sub>3</sub> Ta |
| M <sub>r</sub>                                 | 928.44  | 1008.57  |
| crystal system                                 | triclinic   | monoclinic   |
| space group                                    | P -1  | P 2 <sub>1</sub> /c  |
| a /Å   | 9.506(4) <sup>a</sup>   | 12.4863(3)   |
| b /Å   | 9.724(4) <sup>a</sup>   | 12.7636(3)   |
| c /Å   | 18.326(9) <sup>a</sup>  | 23.2444(6)   |
| α /°   | 76.908(9) <sup>a</sup>  |  |
| β /°   | 80.943(14) <sup>a</sup>   | 92.461(2)  |
| γ /°   | 80.122(10) <sup>a</sup>   |  |
| V /Å <sup>3</sup>                              | 1613.1(13) <sup>a</sup>   | 3701.03(16)  |
| Z  | 2   | 4  |
| F <sub>000</sub>                               | 904   | 1984   |
| d <sub>c</sub> /Mg·m <sup>-3</sup>             | 1.912   | 1.810  |
| X-radiation, λ /Å                              | Mo-K <sub>α</sub> , 0.71073                                       | Mo-K <sub>α</sub> , 0.71073  |
| μ /mm <sup>-1</sup>                            | 3.543   | 3.096  |
| max., min. transmission factors                | 0.746, 0.637 <sup>b</sup>   | 1.000, 0.557 <sup>c</sup>  |
| data collect. temperature /K                   | 100(1)  | 120(1)   |
| θ range /°                                     | 2.2 to 32.5   | 2.3 to 32.4 °  |
| index ranges (indep. set) h,k,l                | ±14, ±14, ±27   | ±18, ±19, ±34  |
| reflections measured                           | 41921   | 94534  |
| unique [R <sub>int</sub> ]                     | 10847 [0.037]   | 15523 [0.079]  |
| observed [ <i>I</i> ≥2σ( <i>I</i> )]           | 9879  | 12381  |
| parameters refined [restraints]                | 470 [138]   | 510 [0]  |
| GooF on F <sup>2</sup>                         | 1.057   | 1.005  |
| R indices [F>4σ(F)] R(F), wR(F <sup>2</sup> )  | 0.0230, 0.0481  | 0.0381, 0.0871   |
| R indices (all data) R(F), wR(F <sup>2</sup> ) | 0.0283, 0.0497  | 0.0530, 0.0910   |
| diff. density: max, min /e·Å <sup>-3</sup>     | 1.484, -0.765   | 1.240, -0.952  |
| deposition number CCDC                         | 2068255   | 2068256  |

<sup>a</sup> standard uncertainties include systematic error contributions from Monte Carlo simulations. <sup>b</sup> semi-empirical absorption correction. <sup>c</sup> numerical absorption correction.

**Table S2:** Details of the crystal structure determinations of **5** and **7**.

| compound                                       | <b>5</b>   | <b>7</b>   |
|--|--|--|
| Formula  | C <sub>31</sub> H <sub>39</sub> F <sub>18</sub> N <sub>2</sub> O <sub>3</sub> Ta | C <sub>21</sub> H <sub>25</sub> F <sub>18</sub> N <sub>2</sub> O <sub>3</sub> Ta |
| M <sub>r</sub>                                 | 1010.59  | 876.38   |
| crystal system                                 | monoclinic   | orthorhombic   |
| space group                                    | P 2 <sub>1</sub> /c  | P 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> <sup>b</sup>                      |
| a /Å   | 10.46441(8)  | 10.35678(7)  |
| b /Å   | 18.50732(13)   | 15.00746(10)   |
| c /Å   | 19.65718(15)   | 19.36701(15)   |
| β /°   | 100.0149(7)  |  |
| V /Å <sup>3</sup>                              | 3748.96(5)   | 3010.19(4)   |
| Z  | 4  | 4  |
| F <sub>000</sub>                               | 1992   | 1696   |
| d <sub>c</sub> /Mg·m <sup>-3</sup>             | 1.790  | 1.934  |
| X-radiation, λ /Å                              | Mo-K <sub>α</sub> , 0.71073  | Mo-K <sub>α</sub> , 0.71073  |
| μ /mm <sup>-1</sup>                            | 3.056  | 3.790  |
| max., min. transmission factors <sup>a</sup>   | 1.000, 0.560   | 1.000, 0.507   |
| data collect. temperature /K                   | 120(1)   | 120(1)   |
| θ range /°                                     | 2.2 to 34.2  | 2.2 to 34.7  |
| index ranges (indep. set) h,k,l                | ±15, ±29, 29 ... 31  | ±16, ±23, -30 ... 31   |
| reflections measured                           | 111328   | 122746   |
| unique [R <sub>int</sub> ]                     | 14952 [0.050]  | 12675 [0.043]  |
| observed [ I ≥2σ( I )]                         | 12825  | 12208  |
| parameters refined [restraints]                | 517 [144]  | 510 [444]  |
| GooF on F <sup>2</sup>                         | 1.039  | 1.068  |
| R indices [F>4σ(F)] R(F), wR(F <sup>2</sup> )  | 0.0277, 0.0597   | 0.0298, 0.0820   |
| R indices (all data) R(F), wR(F <sup>2</sup> ) | 0.0359, 0.0628   | 0.0318, 0.0833   |
| diff. density: max, min /e·Å <sup>-3</sup>     | 1.268, -0.776  | 1.735, -0.725  |
| deposition number CCDC                         | 2068257  | 2068258  |

<sup>a</sup> numerical absorption correction. <sup>b</sup> Inversion (racemic) twin.

**Table S3:** Details of the crystal structure determinations of **10** and **11**.

| compound                                       | <b>10</b>   | <b>11</b>   |
|--|---|---|
| Formula  | C <sub>31</sub> H <sub>37</sub> F <sub>18</sub> N <sub>2</sub> NbO <sub>3</sub> | C <sub>21</sub> H <sub>25</sub> F <sub>18</sub> N <sub>2</sub> O <sub>3</sub> V |
| M <sub>r</sub>                                 | 920.53  | 746.37  |
| crystal system                                 | monoclinic  | orthorhombic  |
| space group                                    | P 2 <sub>1</sub> /c   | P bca   |
| a /Å   | 12.50243(9)   | 18.19821(11)  |
| b /Å   | 12.80912(8)   | 17.31168(11)  |
| c /Å   | 23.1774(2)  | 18.48571(14)  |
| β /°   | 92.3514(7)  |   |
| V /Å <sup>3</sup>                              | 3708.63(5)  | 5823.77(7)  |
| Z  | 4   | 8   |
| F <sub>000</sub>                               | 1856  | 2992  |
| d <sub>c</sub> /Mg·m <sup>-3</sup>             | 1.649   | 1.703   |
| X-radiation, λ /Å                              | Cu-K <sub>α</sub> , 1.54184 Å   | Cu-K <sub>α</sub> , 1.54184 Å   |
| μ /mm <sup>-1</sup>                            | 3.811   | 4.207   |
| max., min. transmission factors <sup>a</sup>   | 1.000, 0.559  | 1.000, 0.488  |
| data collect. temperature /K                   | 120(1)  | 120(1)  |
| θ range /°                                     | 3.5 to 71.3   | 4.3 to 71.2   |
| index ranges (indep. set) h,k,l                | ±15, ±15, -26 ... 28  | ±22, ±21, -22 ... 21  |
| reflections measured                           | 180191  | 158136  |
| unique [R <sub>int</sub> ]                     | 7164 [0.049]  | 5628 [0.061]  |
| observed [ I ≥2σ( I )]                         | 6808  | 5311  |
| parameters refined [restraints]                | 509 [0]   | 613 [830]   |
| GooF on F <sup>2</sup>                         | 1.035   | 1.049   |
| R indices [F>4σ(F)] R(F), wR(F <sup>2</sup> )  | 0.0202, 0.0482  | 0.0502, 0.1423  |
| R indices (all data) R(F), wR(F <sup>2</sup> ) | 0.0217, 0.0490  | 0.0523, 0.1447  |
| diff. density: max, min /e·Å <sup>-3</sup>     | 0.405, -0.453   | 1.491, -0.484   |
| deposition number CCDC                         | 2068259   | 2068260   |

<sup>a</sup> numerical absorption correction.

**Table S4:** Details of the crystal structure determinations of **12**.

| compound                                       | <b>12</b>  |
|--|--|
| Formula  | C <sub>23</sub> H <sub>29</sub> F <sub>18</sub> N <sub>2</sub> O <sub>3</sub> Ta |
| M <sub>r</sub>                                 | 904.43   |
| crystal system                                 | triclinic  |
| space group                                    | P -1   |
| a /Å   | 12.236(7) <sup>a</sup>   |
| b /Å   | 13.628(8) <sup>a</sup>   |
| c /Å   | 19.730(11) <sup>a</sup>  |
| α /°   | 109.531(10) <sup>a</sup>   |
| β /°   | 90.761(14) <sup>a</sup>  |
| γ /°   | 90.010(9) <sup>a</sup>   |
| V /Å <sup>3</sup>                              | 3100(3) <sup>a</sup>   |
| Z  | 4  |
| F <sub>000</sub>                               | 1760   |
| d <sub>c</sub> /Mg·m <sup>-3</sup>             | 1.938  |
| X-radiation, λ /Å                              | Mo-K <sub>α</sub> , 0.71073  |
| μ /mm <sup>-1</sup>                            | 3.683  |
| max., min. transmission factors <sup>b</sup>   | 0.435, 0.379   |
| data collect. temperature /K                   | 100(1)   |
| θ range /°                                     | 1.7 to 30.0  |
| index ranges (indep. set) h,k,l                | -17 ... 16, ±19, ±27   |
| reflections measured                           | 74407  |
| unique [R <sub>int</sub> ]                     | 18094 [0.039]  |
| observed [ $I \geq 2\sigma(I)$ ]               | 15850  |
| parameters refined [restraints]                | 1049 [876]   |
| GooF on F <sup>2</sup>                         | 1.076  |
| R indices [F>4σ(F)] R(F), wR(F <sup>2</sup> )  | 0.0283, 0.0632   |
| R indices (all data) R(F), wR(F <sup>2</sup> ) | 0.0367, 0.0677   |
| diff. density: max, min /e·Å <sup>-3</sup>     | 2.154, -1.262  |
| deposition number CCDC                         | 2068261  |

<sup>a</sup> standard uncertainties include systematic error contributions from Monte Carlo simulations. <sup>b</sup> semi-empirical absorption correction.

## 5) REFERENCES

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