

**Supporting information for:**

**Synthesis of  $L_2Ni(OR^F)_2$  ( $R^F=C(CF_3)_3$ ) complexes and their reactivity in ethylene oligomerization.**

Julien Petit,<sup>a,b</sup> Nathalie Saffon-Merceron,<sup>c</sup> Lionel Magna,<sup>\*b</sup> Nicolas Mézailles.<sup>\*a</sup>

<sup>a</sup>Laboratoire Hétérochimie Fondamentale et Appliquée, UMR 5069 CNRS, Université Paul Sabatier, 118 Route de Narbonne ; 31062 Toulouse, France.

<sup>b</sup>IFP Energies Nouvelles Rond-point de l'échangeur de Solaize, BP3, 69360 Solaize, France.

<sup>c</sup>Institut de Chimie de Toulouse ICT – FR2599, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse, France.

## Table of contents

1. Experimental procedures and NMRs
2. X-ray diffraction data
3. UV-vis analyses
4. Catalytic tests
5. C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>D<sub>4</sub> experiments
6. References

## 1. Experimental procedures and NMRs

### *Reagents and solvents*

All the reactions were carried out in the glove box or using standard schlenck techniques under N<sub>2</sub>. The commercial compounds stored under N<sub>2</sub> or Ar were used directly without any further purification, while the non-stored under inert atmosphere, they were degassed before use. All solvents, except *o*-DFB, were taken from MBSPS-800 solvent purification system, then they were degassed and dried using molecular sieves. *o*-DFB was pre-dried over CaH<sub>2</sub> and then filtered and stored on molecular sieve.

### *NMR*

<sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F and <sup>31</sup>P NMR spectra were recorded on Bruker Avance 300 and 400 MHz spectrometers. <sup>1</sup>H and <sup>13</sup>C chemical shifts reported are referenced internally to used solvent while <sup>19</sup>F and <sup>31</sup>P chemical shifts are referenced to an external standard of trichlorofluoromethane and phosphoric acid respectively.

### *Elemental analysis (C, H, N)*

Elemental analysis of **4**, **5**, **9** and **10** powders were carried out by combustion analysis using vario MICRO cube apparatus from Elementar.

### *UV-vis*

UV-Vis analyses of **1**, **4**, **5**, **9** and **10**, solubilized in *ortho*-difluorobenzene, were carried out on a V-630 UV-vis spectrometer (Jacso) Kontron.

### *XRD analysis*

X-ray intensity data of compounds **1**, **3**, **4**, **5**, **7**, **8**, **9**, **10** and **dcpmS** were collected at 193 K on a Bruker D8 VENTURE Photon III-C14 diffractometer and using graphite mono-chromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) for **1**, **3**, **4**, **5**, **9** and **dcpmS** and Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) for **7** and **10** and on a Bruker kappa APEX II Quazar diffractometer equipped with a 30W air-cooled microfocus source using Mo K $\alpha$  radiation (**8**). The semi-empirical absorption corrections were employed [1]. Crystallographic data and refinement details are given in **2**. The structures were solved using an intrinsic phasing method [2], and refined by full matrix least squares procedures on F<sup>2</sup>[3]. All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined isotropically at calculated positions using a riding model with their isotropic displacement parameters constrained to be equal to 1.5 times the equivalent isotropic displacement parameters of their pivot atoms for terminal sp<sup>3</sup> carbon and 1.2 times for all other carbon atoms.

In most of these structures (**3**, **4**, **5**, **7**, **9** and **10**), parts of molecules were disordered. Several restraints (SAME, SADI, SIMU, DELU, ISOR) were applied to refine some moieties of the molecules and to avoid the collapse of the structures during the least-squares refinement by the large anisotropic displacement parameters. H atoms on O (**7** and **8**) were located by difference Fourier map and were refined using the restraints SADI (**7**) or DFIX (**8**).

CCDC-2105366 (**1**), CCDC-2105367 (**3**), CCDC-2105368 (**4**), CCDC-2105369 (**5**), CCDC-2105370 (**7**), CCDC-2105371 (**8**), CCDC-2105372 (**9**), CCDC-2105373 (**10**) and CCDC-2105374 (**dcpmS**) contain the supplementary crystallographic data. These data can be obtained free of charge from <https://www.ccdc.cam.ac.uk/structures/> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; tel: + 44 (0)1223 336408; fax: + 44 (0)1223336033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)

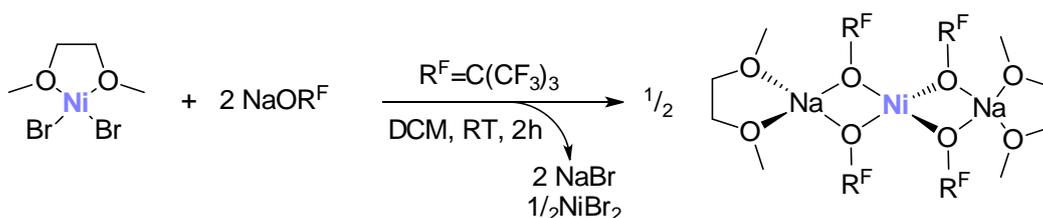
## GC & GC-MS

GC analyses were performed with an Agilent 6850 series II device equipped with an autosampler and fitted with PONA columns.

GC-MS analyses were conducted with an Agilent 6890 N apparatus equipped with a PONA and an Agilent 5975B inert XL EI/CI MSD mass spectrometer.

## Syntheses

### Synthesis of $(\text{DME})_2\text{Na}_2\text{Ni}[\text{OC}(\text{CF}_3)_3]_4$ **1**:



On a suspension of  $(\text{DME})\text{NiBr}_2$  (500mg, 1.62mmol, 1eq.) in DCM (10mL), a solution of  $(\text{THF})_{0.75}\text{NaOC}(\text{CF}_3)_3$  (1.07g, 3.43mmol, 2.1eq.) in DCM (10mL) is added dropwise. It slowly turned from colorless to blue over 3h at RT. White ( $\text{NaBr}$ ) and yellow ( $\text{NiBr}_2$ ) solids precipitated. Solvent is removed under reduced pressure to give a blue solid. This solid is extracted with pentane until the solution is clear. The obtained deep blue solution is stored 4h at  $5^\circ\text{C}$ . After apparition of first crystals, the mixture is put at  $-35^\circ\text{C}$  overnight to give large blue crystals as needles. These latter are washed with pentane ( $3 \times 5\text{mL}$ ) at  $-40^\circ\text{C}$ . Solvent is finally removed under reduced pressure. The product is obtained as a deep blue crystalline solid (730mg, 0.60mmol, 37%).

$^1\text{H NMR}$  (273K, 300,0MHz,  $\text{C}_6\text{D}_6$ ): -5.8 & -4.4 (br, 12H,  $\text{DME-CH}_3$ ), 6.0 (br, 5H,  $\text{CH}_2$ ), 10.5 (br, 5H,  $\text{CH}_2$ ) ppm.  $^{19}\text{F NMR}$  (273K, 282,2 Hz,  $\text{C}_6\text{D}_6$ ): -30 (s,  $\text{C}(\text{CF}_3)_3$ ) ppm.

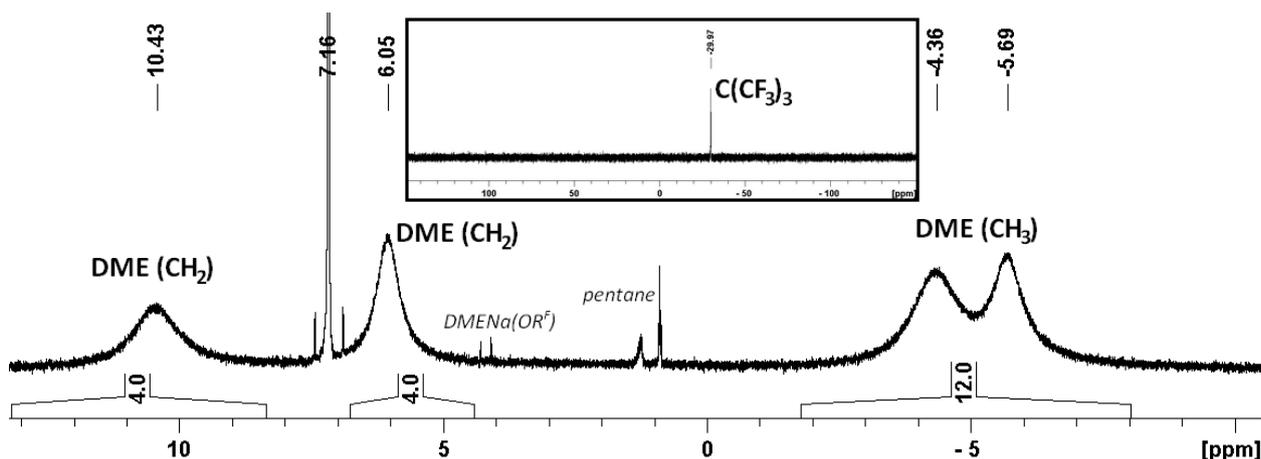
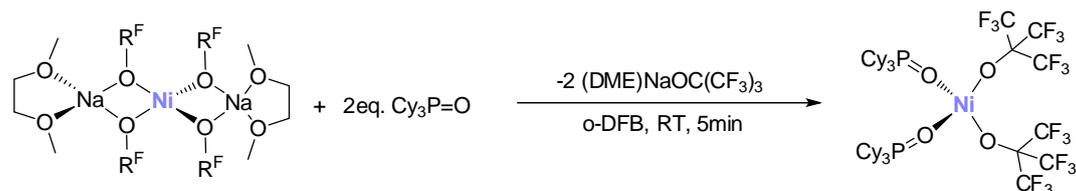


Figure S1 –  $^1\text{H}$  and  $^{19}\text{F}$  (inset) NMR spectra of **1** at  $25^\circ\text{C}$  in  $\text{C}_6\text{D}_6$  (singlet at 7.16ppm).

### Synthesis of $(\text{Cy}_3\text{PO})_2\text{Ni}[\text{OC}(\text{CF}_3)_3]_2$ **4**:



On a solution of  $[(\text{DME})\text{Na}(\mu\text{-OC}(\text{CF}_3)_3)_2]\text{Ni}$  (300mg, 0.24mmol, 1eq.) in *o*-DFB (3mL), a solution of  $\text{Cy}_3\text{PO}$  (200mg, 0.67mmol, 2.8eq.) in *o*-DFB (3mL) is added dropwise. No precipitate or colorshift is observed so the solution stayed deep blue. The solvent is removed under reduced pressure and the obtained blue solid is washed with pentane (3\*5mL, use of ultrasonic bath). This solid is dissolved in a mixture of pentane/*o*-DFB (3/1 ratio). The solution is first put at 5°C over 4h until some blue crystals started to grow. To increase the crystallization rate, the schlenk is put at -35°C over 16h. After filtration, the crystals are washed with pentane (3\*5mL). Solvent is finally removed under reduced pressure. The product is obtained as a deep blue crystalline solid (247mg, 0.22 mmol, 92%).

$^1\text{H NMR}$  (273K, 300,0MHz,  $\text{C}_6\text{D}_6$ ): -6.0 (br, 6H, P-CH-( $\text{CH}_2$ )<sub>2</sub>), -0.9 to -0.4 (br, 36H,  $\text{CH}_2$ ), 1.1 to 1.3 (br, 12H,  $\text{CH}_2$ ), 2.3 (d, 12Hz,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}\{^{31}\text{P}\}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ ): 24.6, 25.7, 29.6 (Cy) 116.8 (br, P-CH-( $\text{CH}_2$ )<sub>2</sub>) ppm.  $^{19}\text{F NMR}$  (273K, 282,2 Hz,  $\text{C}_6\text{D}_6$ ): -11.1 (s,  $\text{C}(\text{CF}_3)_3$ ) ppm.  $^{31}\text{P NMR}$  (273K, 121.4 MHz,  $\text{C}_6\text{D}_6$ ): no signal (paramagnetic) EA: Calculated for  $\text{C}_{44}\text{H}_{66}\text{F}_{18}\text{NiO}_4\text{P}_2$ : C 47.12; H 5.93. Found: C 47.23; H 5.95.

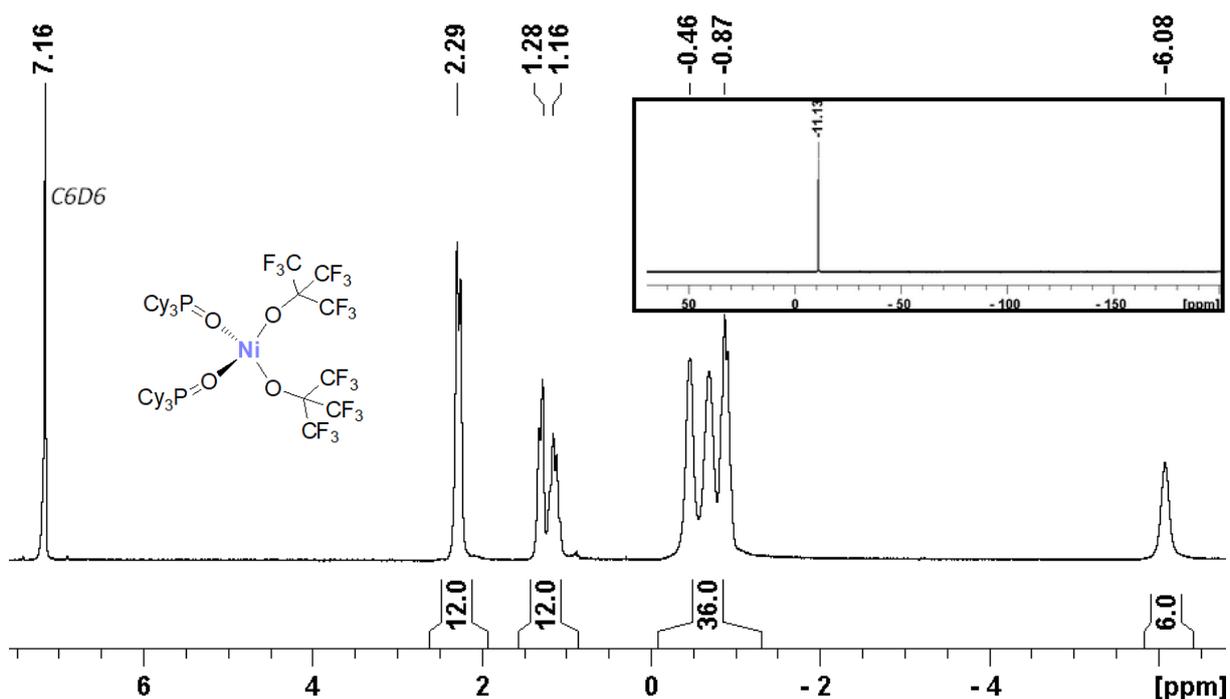


Figure S2 –  $^1\text{H NMR}$  and  $^{19}\text{F}$  (inset) NMR spectra of **4** at 25°C in  $\text{C}_6\text{D}_6$ .

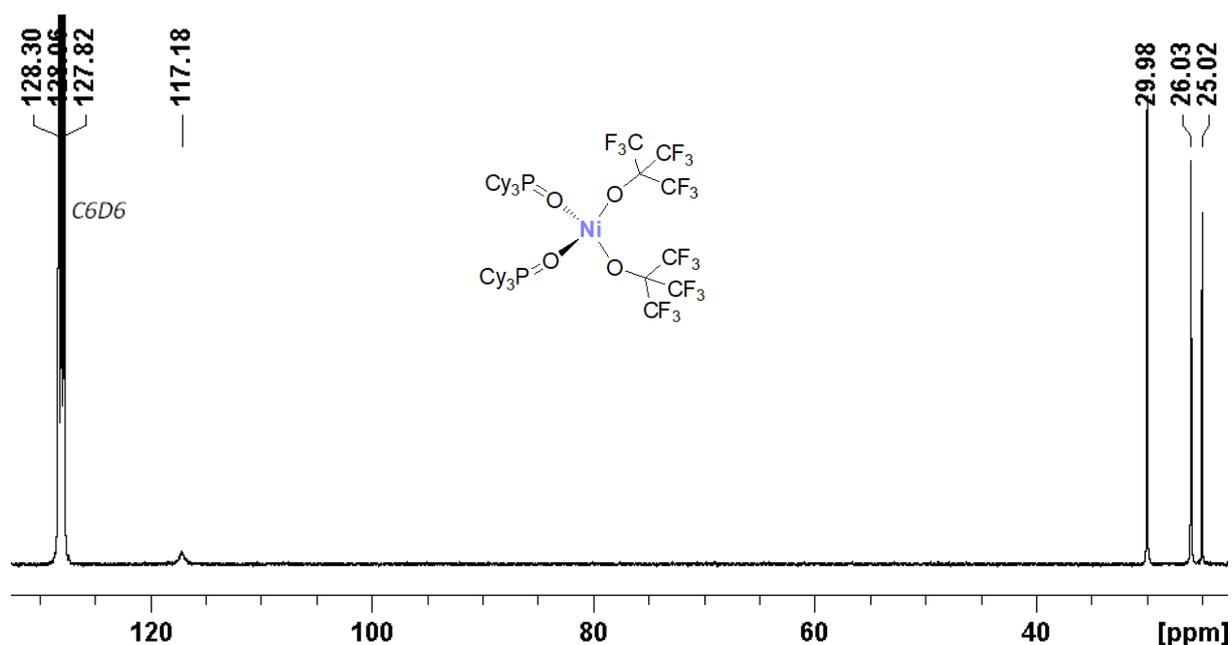
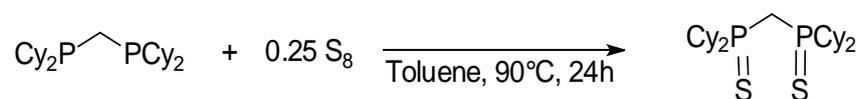


Figure S3 –  $^{13}\text{C}$  NMR (DEPT) of **4** at 25°C in  $\text{C}_6\text{D}_6$ .

Synthesis of bis(dicyclohexylphosphine sulfide)methane dcpmS:



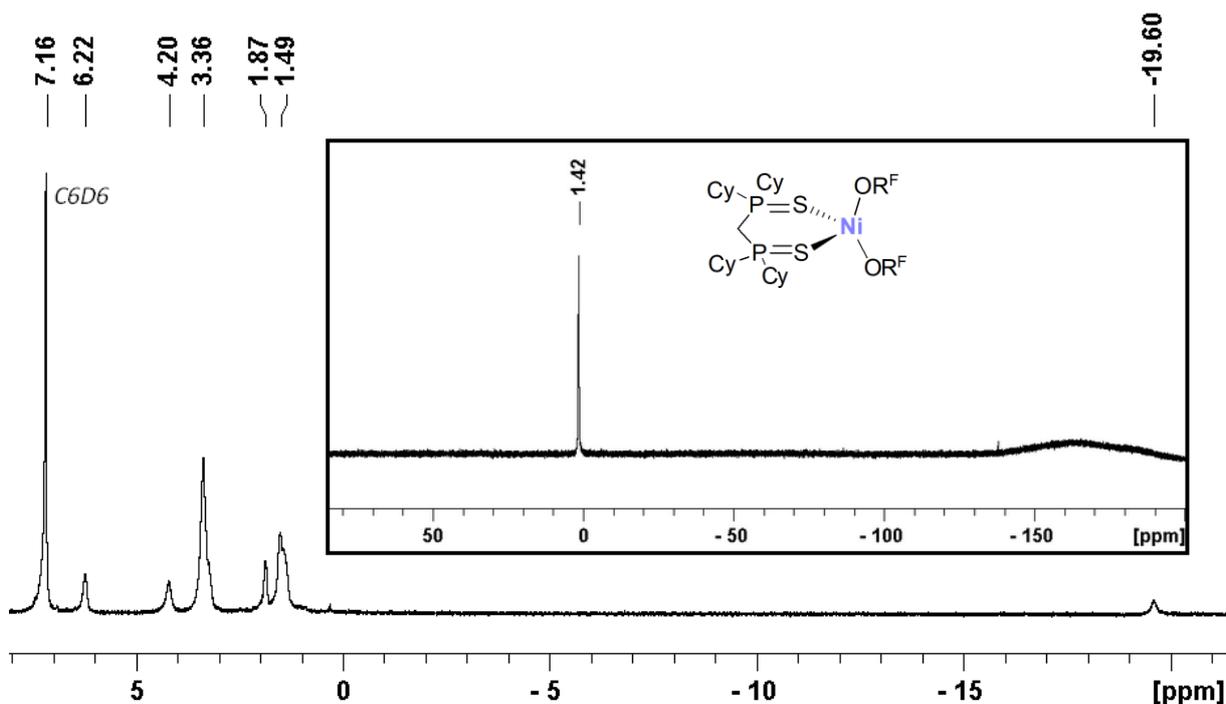
Bis(dicyclohexylphosphino)methane (500mg, 1.22mmol, 1eq.) was dissolved in toluene (20mL). This solution was then added on elemental sulfur  $\text{S}_8$  (78.5mg, 0.31mmol, 0.25eq.) to give a suspension. The mixture was allowed to react at 90°C for 24h. The obtained colorless solution was then filtered through silica and toluene was removed under reduced pressure to give a white powder (570mg, 1.21mmol, 99%).

$^1\text{H}$  NMR (273K, 300,0MHz,  $\text{C}_6\text{D}_6$ ): 2.89-4.26 (m, Cy and  $\text{CH}_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}\{^{31}\text{P}\}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ ): 11.2-14.3 (Cy) 26.5 (dd,  $^1J_{\text{C-P}}$  : 50.0 and 57.1Hz, P- $\text{CH}_2$ -P) ppm.  $^{31}\text{P}$  NMR (273K, 121.4 MHz,  $\text{C}_6\text{D}_6$ ): 56.5 (s, P) ppm.

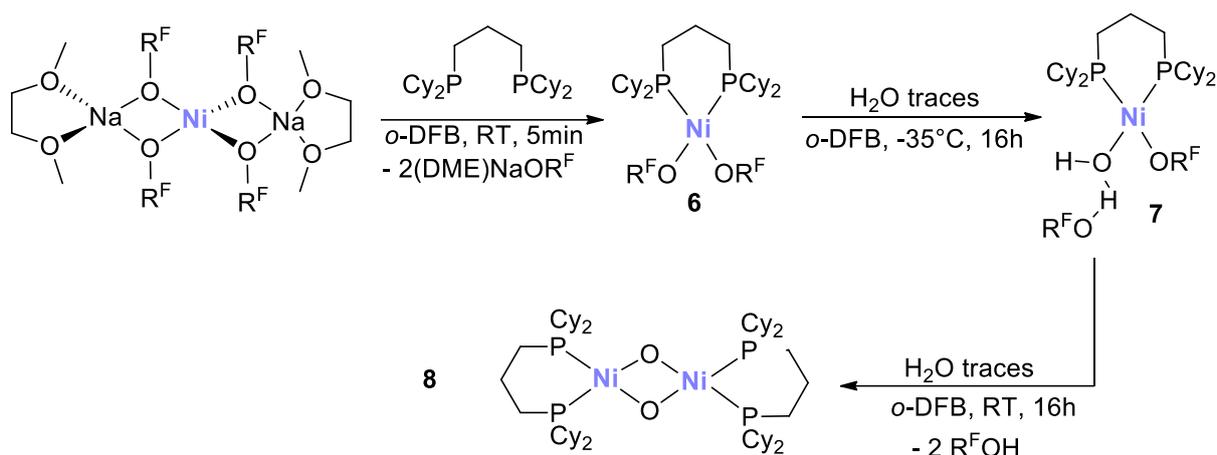


observed (blue). The solvent is removed under reduced pressure and the obtained blue solid is washed with pentane (3\*5mL). This solid is dissolved in a mixture of pentane/*o*-DFB (3/1 ratio). The solution is put at -30°C over 16h. A large amount of blue crystals is observed. They are washed with pentane (3\*5mL). Solvent is finally removed under reduced pressure. The product is obtained as a blue crystalline solid (71mg, 0.071mmol, 88%).

$^1\text{H}$  NMR (273K, 300,0MHz,  $\text{C}_6\text{D}_6$ /*o*-DFB): -19.37, 0.86 to 4.04 ppm.  $^{19}\text{F}$  NMR (273K, 282,2 Hz, THF- $d_8$ ): 1.4 (s,  $\text{C}(\text{CF}_3)_3$ ) ppm. EA: calculated for  $\text{C}_{33}\text{H}_{46}\text{F}_{18}\text{NiO}_2\text{P}_2\text{S}_2$ : C, 39.58; H, 4.63; found: C, 39.74; H, 4.42.



#### Reaction of $(\text{DME})_2\text{Na}_2\text{Ni}[\text{OC}(\text{CF}_3)_3]_4$ **1** with dcpp:



On a solution of  $[(\text{DME})\text{Na}(\mu\text{-OC}(\text{CF}_3)_3)_2\text{Ni}]$  (100mg, 0.081mmol, 1eq.) in *o*-DFB (3mL), a solution of dcpp in *o*-DFB ( $170\mu\text{L}$ ,  $0.48\text{mol}\cdot\text{L}^{-1}$ , 0.081mmol, 1eq.) is added dropwise. A colorshift from deep blue to deep violet is immediately observed. Solvent is removed and a clear purple solution is obtained. Pentane (1mL) is added and gave a suspension. *o*-DFB is then added until full solubilization of solids.

The obtained violet solution is put at  $-35^{\circ}\text{C}$  for 16h. Orange crystals grew up (compound **7**) while the solution was between violet and orange. The solution was allowed to warm up to RT which solubilized back all crystals. Letting this solution at RT over 16 more hours gave new orange crystals (compound **8**). These crystals were insoluble in all tested solvents.

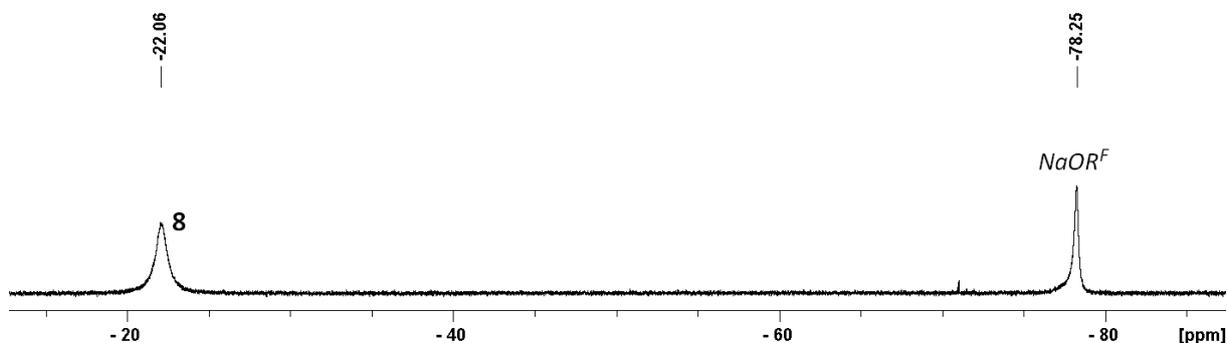


Figure S7 –  $^{19}\text{F}$  NMR of crude solution in *o*-DFB after addition of dcpp on **1**.

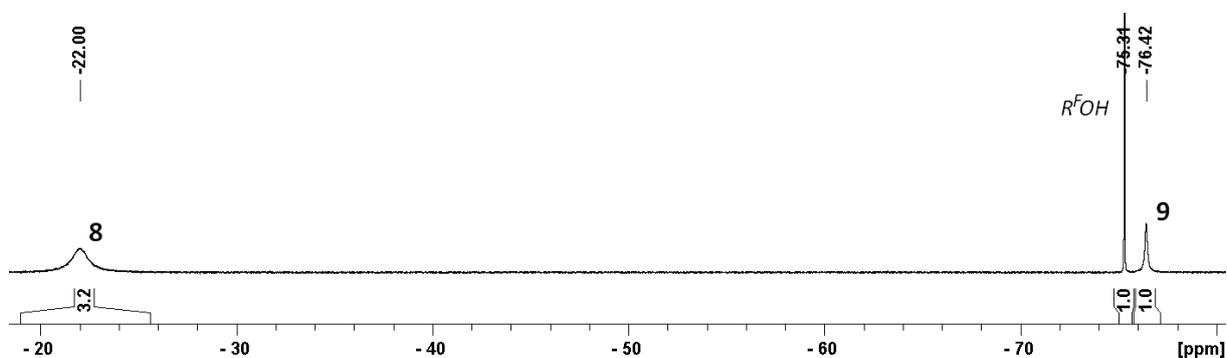
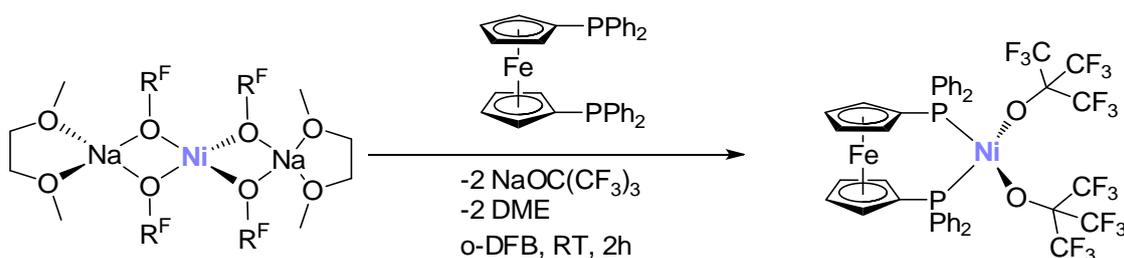


Figure S8 –  $^{19}\text{F}$  NMR spectrum of crystals of **7**. $\text{R}^{\text{F}}\text{OH}$  dissolved in  $\text{C}_6\text{D}_6$ : an equilibrium between **6** and **7** is observed.

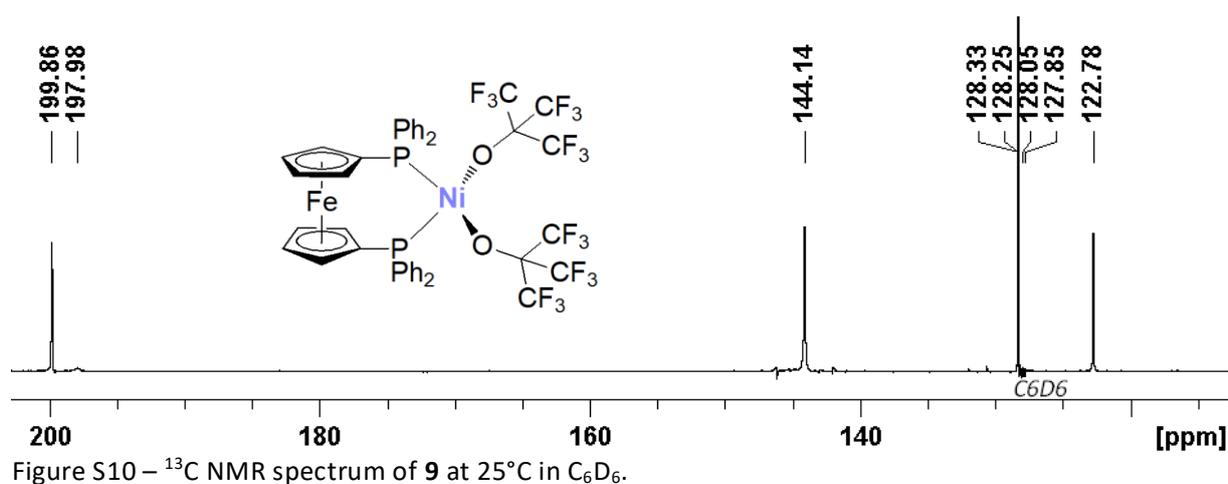
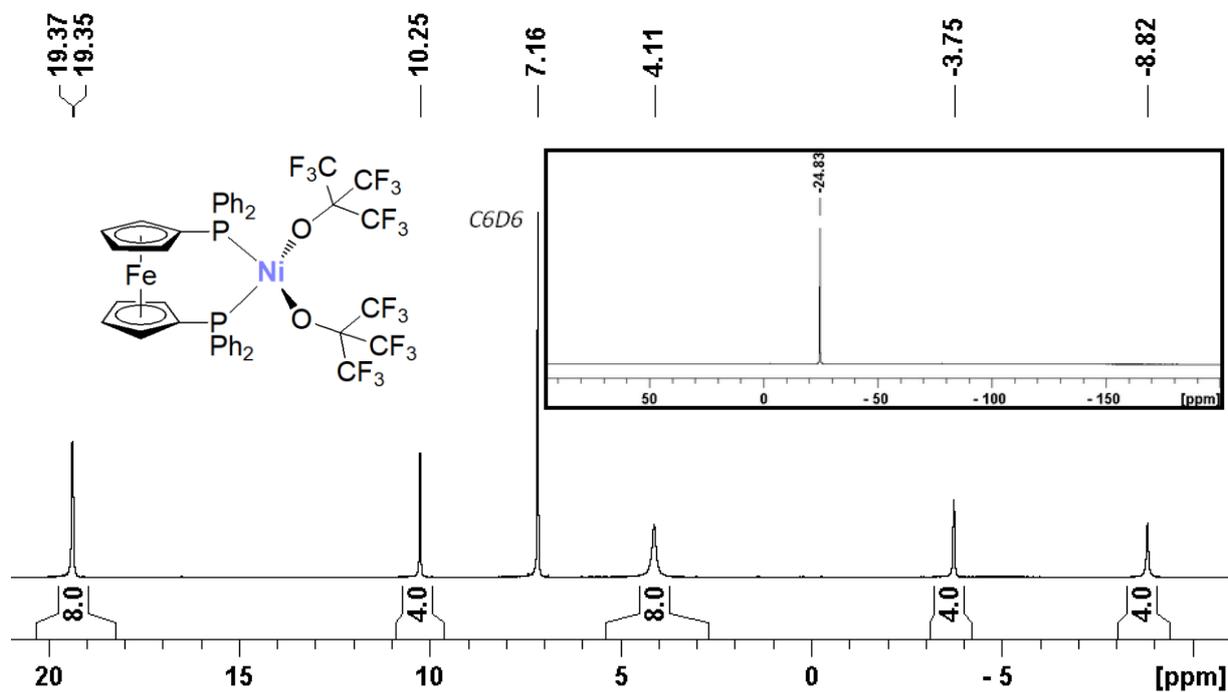
#### Synthesis of $(\text{dppf})\text{Ni}[\text{OC}(\text{CF}_3)_3]_2$ **9**:



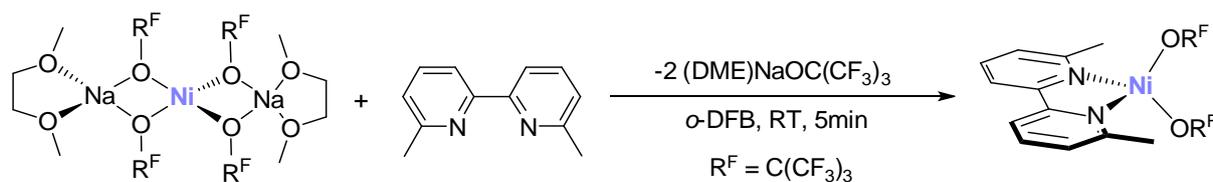
On a solution of  $[(\text{DME})\text{Na}(\mu\text{-OC}(\text{CF}_3)_3)_2]_2\text{Ni}$  (500mg, 0.41mmol, 1eq.) in *o*-DFB (4mL), a solution of dppf (240mg, 0.43mmol, 1.1eq.) in *o*-DFB (4mL) is added dropwise. A deep brown orange solution is obtained that was left to react 2h at RT (dissolution time of the phosphine). Solvent is removed under reduced pressure. The light brown solid is washed with hot HMDSO ( $40^{\circ}\text{C}$ ,  $5 \times 8\text{mL}$ ). The obtained solid is solubilized in  $\text{Et}_2\text{O}$  (5mL) and filtrated (remove excess of dppf). Solvent is removed under reduced pressure to give a light brown solid (370mg, 0.34mmol, 83%).

$^1\text{H}$  NMR (273K, 300,0MHz,  $\text{C}_6\text{D}_6$ ): -8.7 (br, 4H, Cp), -3.6 (t,  $J=7.0\text{Hz}$ , 4H, *p*-Ph), 4.2 (br, 8H, *m*-Ph), 10.4 (br, 4H, Cp), 19.5 (d,  $J=7.0\text{Hz}$ , 8H, *o*-Ph) ppm.  $^{13}\text{C}\{^1\text{H}\}\{^{31}\text{P}\}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ ): 122.45 (Cp) 143.9 (*m*-Ph), 197.5 (Cp), 199.2 (*p*-Ph) ppm.  $^{19}\text{F}$  NMR (273K, 282,2 Hz,  $\text{C}_6\text{D}_6$ ): -24.7 (s,  $\text{C}(\text{CF}_3)_3$ ) ppm.  $^{31}\text{P}$  NMR (273K, 121.4 MHz,  $\text{C}_6\text{D}_6$ ): no signal (paramagnetic) EA: calculated for  $\text{C}_{42}\text{H}_{28}\text{F}_{18}\text{FeNiO}_2\text{P}_2$ : C, 46.57; H,

2.61; found: C, 46.57; H, 2.44.



Synthesis of (6,6'-dimethyl-2,2'-bipyridine)Ni[OC(CF<sub>3</sub>)<sub>3</sub>]<sub>2</sub> **10**:



On a solution of  $[(\text{DME})\text{Na}(\mu\text{-OC}(\text{CF}_3)_3)_2\text{Ni}]$  (1.00g, 0.81mmol, 1eq.) in *o*-DFB (3mL), a solution of 6,6'-

dimethyl-2,2'-bipyridine (165mg, 0.90mmol, 1.1eq.) in *o*-DFB (10mL) is added dropwise. A color change from deep blue to pale orange is observed. An orange/red crystalline precipitation can occur. Solvent is removed under reduced pressure until there is 0.5mL left. Pentane is added (5mL) until the liquid phase is colorless. The mixture is filtrated. This operation is repeated 4 times. One last washing with pentane (5mL) only is done and the obtained red/orange crystalline solid is dried under dynamic vacuum. The product is obtained as an orange crystalline solid (564mg, 0.79mmol, 98%).

$^1\text{H}$  NMR (273K, 300,0MHz, THF- $d_8$ ): 21.8 (s, 2H, Ar-H), 24.5 (br, 6H, CH<sub>3</sub>), 58.6 (s, 2H, Ar-H), 77.5 (s, 2H, Ar-H) ppm.  $^{13}\text{C}\{^1\text{H}\}\{^{31}\text{P}\}$  NMR (125 MHz, THF- $d_8$ ): 41.0, 107.8, 313.6 ppm.  $^{19}\text{F}$  NMR (273K, 282,2 Hz, THF- $d_8$ ): -49 (s, C(CF<sub>3</sub>)<sub>3</sub>) ppm. EA: Calculated for C<sub>20</sub>H<sub>12</sub>F<sub>18</sub>N<sub>2</sub>NiO<sub>2</sub>: C, 33.69; H, 1.70; N, 3.93; found: C, 33.74; H,1.09, N, 3.98.

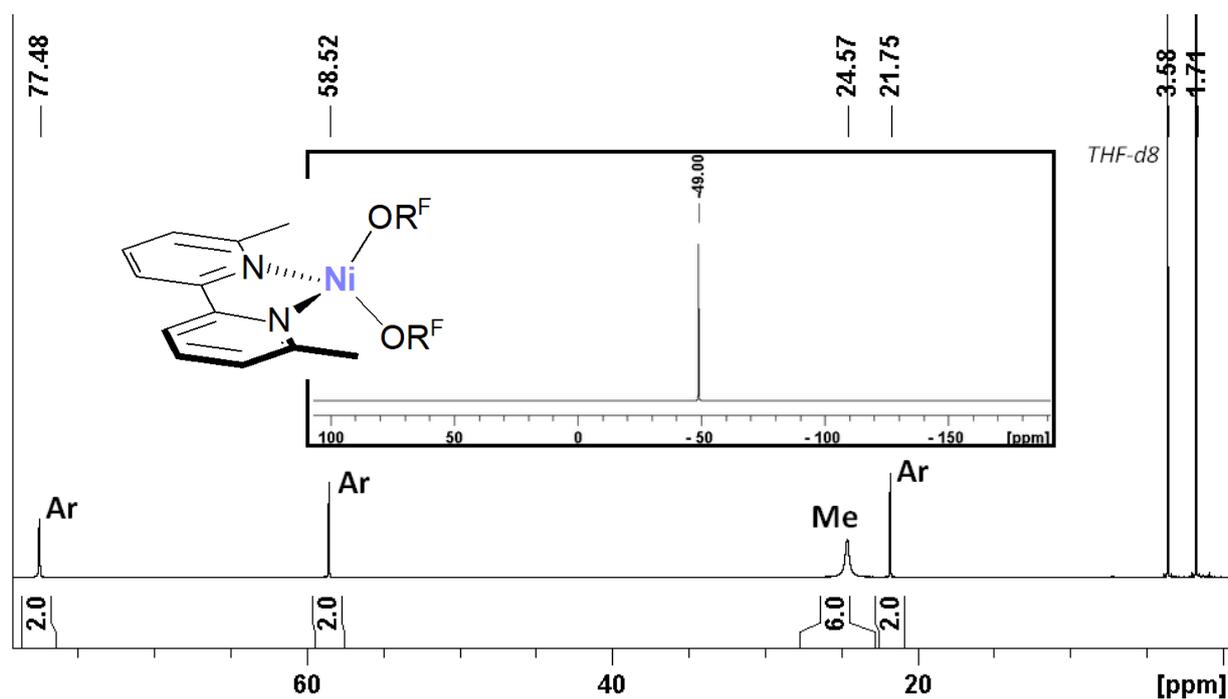


Figure S11 –  $^1\text{H}$  and  $^{19}\text{F}$  (inset) NMR spectra of **10** at 25°C in THF- $d_8$ .

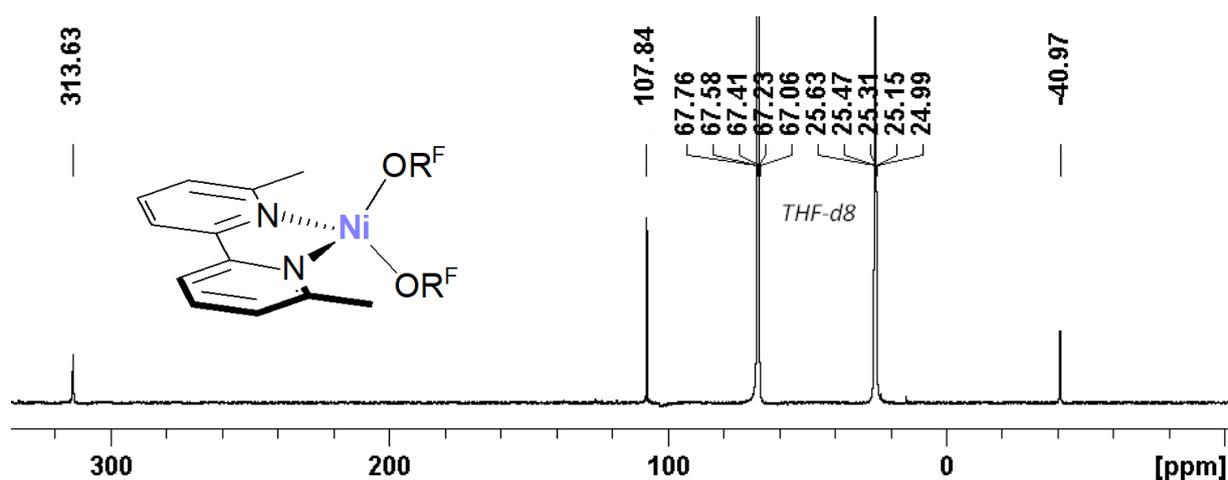


Figure S12 –  $^{13}\text{C}$  NMR of **10** at 25°C in THF- $d_8$ .

Reaction between complex **1** and 2 equivalents of PCy<sub>3</sub>:

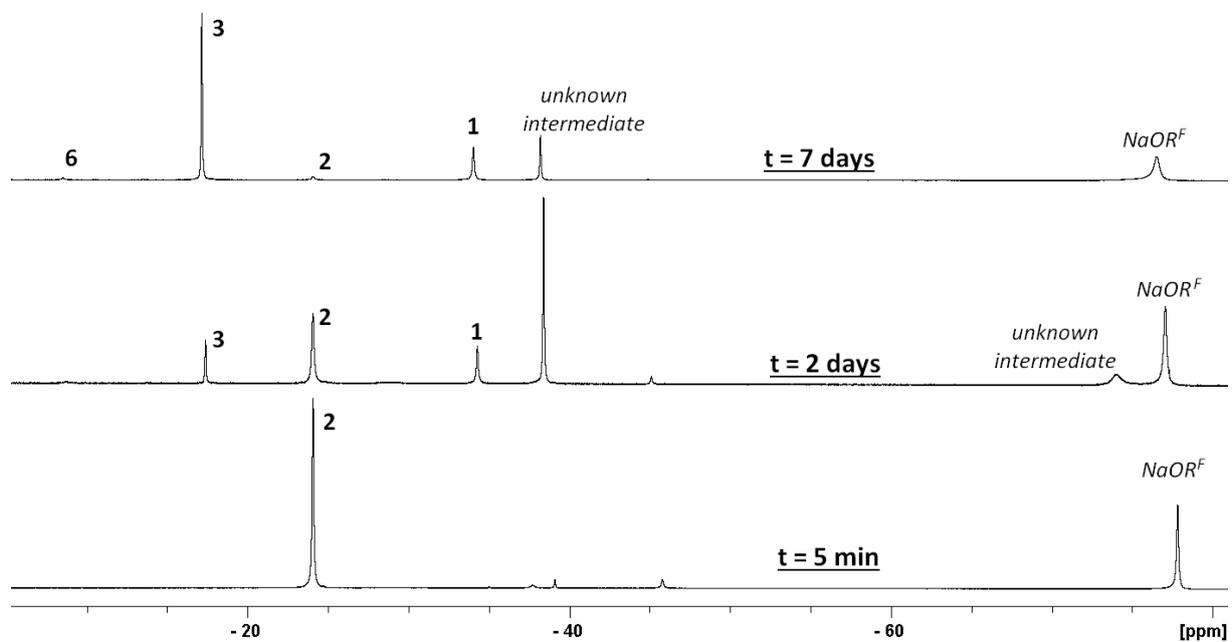
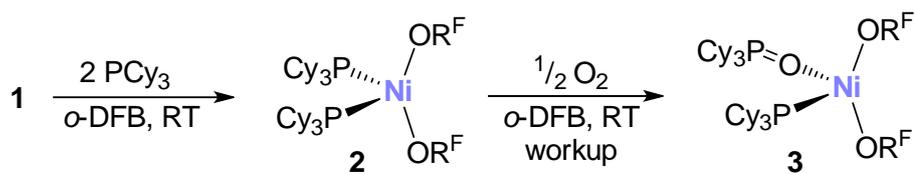


Figure S13 – <sup>19</sup>F NMR after addition of 2 Cy<sub>3</sub>P on **1** in o-DFB at RT. Formation of compound **2** and then **3** overtime in a closed NMR J. Young tube.

## 2. X-Ray diffraction data

|  | 1  | 3   | 4   | 5  |
|--|--|---|---|--|
| Formula  | C <sub>24</sub> H <sub>20</sub> F <sub>36</sub> Na <sub>2</sub> NiO <sub>8</sub> | C <sub>44</sub> H <sub>66</sub> F <sub>18</sub> NiO <sub>3</sub> P <sub>2</sub> | C <sub>44</sub> H <sub>66</sub> F <sub>18</sub> NiO <sub>4</sub> P <sub>2</sub> | C <sub>33</sub> H <sub>46</sub> F <sub>18</sub> NiO <sub>2</sub> P <sub>2</sub> S <sub>2</sub> |
| M <sub>r</sub>                                   | 1225.09  | 1105.61   | 1121.61   | 1001.47  |
| Crystal system                                   | Monoclinic   | Monoclinic  | Monoclinic  | Monoclinic   |
| Space Group                                      | C2/c   | C2/c  | C2/c  | P2 <sub>1</sub> /n   |
| <i>a</i> (Å)                                     | 17.0534(8)   | 12.8185(9)  | 12.8482(6)  | 10.8806(3)   |
| <i>b</i> (Å)                                     | 14.4848(7)   | 19.9410(14)   | 20.0004(10)   | 19.8249(6)   |
| <i>c</i> (Å)                                     | 17.2581(7)   | 39.216(3)   | 19.7418(8)  | 19.6350(5)   |
| α (°)  | 90   | 90  | 90  | 90   |
| β (°)  | 104.5279(16)   | 94.418(3)   | 98.019(2)   | 93.8525(10)  |
| γ (°)  | 90   | 90  | 90  | 90   |
| <i>V</i> (Å <sup>3</sup> )                       | 4126.7(3)  | 9994.5(12)  | 5023.4(4)   | 4225.8(2)  |
| <i>Z</i>   | 4  | 8   | 4   | 4  |
| ρ <sub>calc</sub> (g.cm <sup>-3</sup> )          | 1.972  | 1.470   | 1.483   | 1.574  |
| μ (mm <sup>-1</sup> )                            | 0.698  | 0.557   | 0.557   | 0.743  |
| <i>F</i> (000)                                   | 2408   | 4592  | 2328  | 2048   |
| Crystal size (mm <sup>3</sup> )                  | 0.25x0.16x0.12   | 0.40x0.25x0.10  | 0.50x0.40x0.40  | 0.30x0.25x0.16   |
| T (K)  | 193(2) K   | 193(2)  | 193(2)  | 193(2)   |
| Meads reflns                                     | 62538  | 100321  | 83499   | 132812   |
| Unique reflns (Rint)                             | 5093 (0.0329)  | 10378 (0.0482)  | 7467 (0.0333)   | 10487 (0.0356)   |
| Data/restraints/parameters                       | 5093/0/323   | 10378/2326/1229   | 7467/279/385  | 10487/150/579  |
| GOF on F <sup>2</sup>                            | 1.038  | 1.075   | 1.038   | 1.030  |
| R <sub>1</sub> <sup>a</sup> [I>2σ(I)]            | 0.0258   | 0.0706  | 0.0302  | 0.0359   |
| wR <sub>2</sub> <sup>b</sup> [all data]          | 0.0670   | 0.1947  | 0.0798  | 0.1015   |
| Largest diff. peak and hole (e.Å <sup>-3</sup> ) | 0.406 & -0.207   | 0.581 & -0.452  | 0.404 & -0.391  | 0.588 & -0.454   |

|  | <b>7</b>                                 | <b>8</b>                              | <b>9</b>  | <b>10</b>                    | <b>dcpmS</b>         |
|--|--|---------------------------------------|---|------------------------------|----------------------|
| Formula  | $C_{31}H_{50}F_9NiO_2P_2,$<br>$C_4HF_9O$ | $C_{70}H_{104}F_{36}Ni_2O_6$<br>$P_4$ | $C_{42}H_{28}F_{18}FeNiO_2P_2,$<br>$\frac{1}{2}(C_7H_{16})$ | $C_{20}H_{12}F_{18}N_2NiO_2$ | $C_{25}H_{46}P_2S_2$ |
| $M_r$  | 982.40                                   | 1966.83                               | 1133.24   | 713.03                       | 472.68               |
| Crystal system                                   | Monoclinic                               | Triclinic                             | Monoclinic  | Monoclinic                   | Triclinic            |
| Space Group                                      | $P2_1/n$                                 | $P\bar{1}$                            | $P2_1/c$  | $C2/c$                       | $P\bar{1}$           |
| $a$ (Å)  | 11.7078(3)                               | 12.8670(9)                            | 19.9430(9)  | 17.9800(6)                   | 10.9137(5)           |
| $b$ (Å)  | 18.0949(5)                               | 13.5301(9)                            | 11.0349(6)  | 7.8957(2)                    | 11.2079(5)           |
| $c$ (Å)  | 20.8155(6)                               | 14.2551(10)                           | 21.4325(12)   | 17.9499(6)                   | 11.8939(5)           |
| $\alpha$ (°)                                     | 90                                       | 107.718(3)                            | 90  | 90                           | 100.8071(17)         |
| $\beta$ (°)                                      | 105.8882(19)                             | 113.600(3)                            | 100.9799(19)  | 100.1320(17)                 | 111.2083(17)         |
| $\gamma$ (°)                                     | 90                                       | 97.333(3)                             | 90  | 90                           | 97.0703(18)          |
| $V$ (Å <sup>3</sup> )                            | 4241.3(2)                                | 2075.9(3)                             | 4630.3(4)   | 2508.51(14)                  | 1302.99(10)          |
| $Z$  | 4  | 1                                     | 4   | 4                            | 2                    |
| $\rho_{calc}$ (g.cm <sup>-3</sup> )              | 1.539                                    | 1.573                                 | 1.626   | 1.888                        | 1.205                |
| $\mu$ (mm <sup>-1</sup> )                        | 2.412                                    | 0.660                                 | 0.900   | 2.628                        | 0.338                |
| $F(000)$   | 2020                                     | 1012                                  | 2284  | 1408                         | 516                  |
| Crystal size (mm <sup>3</sup> )                  | 0.20x0.16x0.12                           | 0.20x0.16x0.04                        | 0.30x0.20x0.12  | 0.60x0.20x0.05               | 0.25x0.15x0.08       |
| T (K)  | 193(2) K                                 | 193(2)                                | 193(2)  | 193(2)                       | 193(2)               |
| Meas reflns                                      | 94647                                    | 74524                                 | 143011  | 24396                        | 29019                |
| Unique reflns (Rint)                             | 8382 (0.1158)                            | 8058 (0.106)                          | 11486 (0.0651)  | 2371 (0.0532)                | 6456 (0.0328)        |
| Data/restraints/parameters                       | 8382/1007/766                            | 8058/2/539                            | 11486/603/785   | 2371/267/269                 | 6456/0/262           |
| GOF on F <sup>2</sup>                            | 1.012                                    | 1.042                                 | 1.046   | 1.027                        | 1.052                |
| $R_1^a$ [ $I > 2\sigma(I)$ ]                     | 0.0556                                   | 0.0700                                | 0.0367  | 0.0473                       | 0.0339               |
| $wR_2^b$ [all data]                              | 0.1633                                   | 0.2058                                | 0.1022  | 0.1339                       | 0.856                |
| Largest diff. peak and hole (e.Å <sup>-3</sup> ) | 0.525 & -0.328                           | 0.814 & -0.780                        | 0.417 & -0.487  | 0.627 & -0.414               | 0.372 & -0.194       |

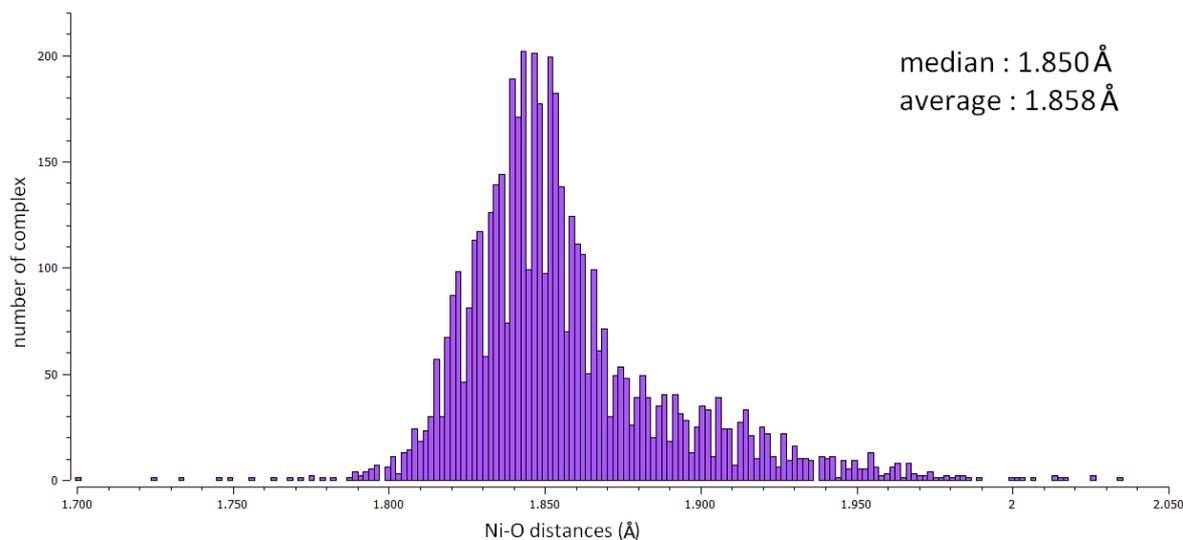


Figure S14 - Histogram summarizing the different lengths of X-type nickel-oxygen bonds reported in the CCDC database

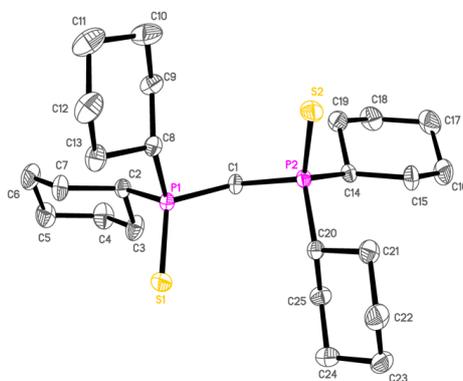


Figure S15 - Molecular structure of **dcpms** ligand in crystalline state. Thermal ellipsoids drawn at 50% probability and H atoms omitted for clarity. Distances [Å] and angles [°]: P1-S1 = 1.9580(5) ; P2-S2 : 1.9564(5) ; P1-C1 : 1.8376(13) ; P2-C1 : 1.8407(12) ; P1-C1-P2 : 123.82(7).

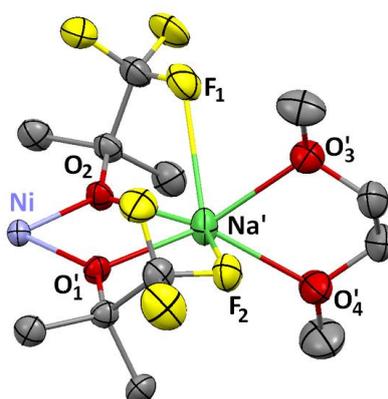


Figure S16 – Zoom on Na side of molecular structure of **1** in crystalline state (*cf* figure 1 in paper). Thermal ellipsoids are drawn at 50% probability level and H atoms with some fluorine atoms are omitted for clarity. Distances [Å]: Na'-O'<sub>1</sub> : 2.3297(10) ; Na'-O'<sub>3</sub> : 2.3789 (12) ; Na'-F<sub>1</sub> : 2.7478(12) ; Na'-F<sub>2</sub> : 2.7620(11).

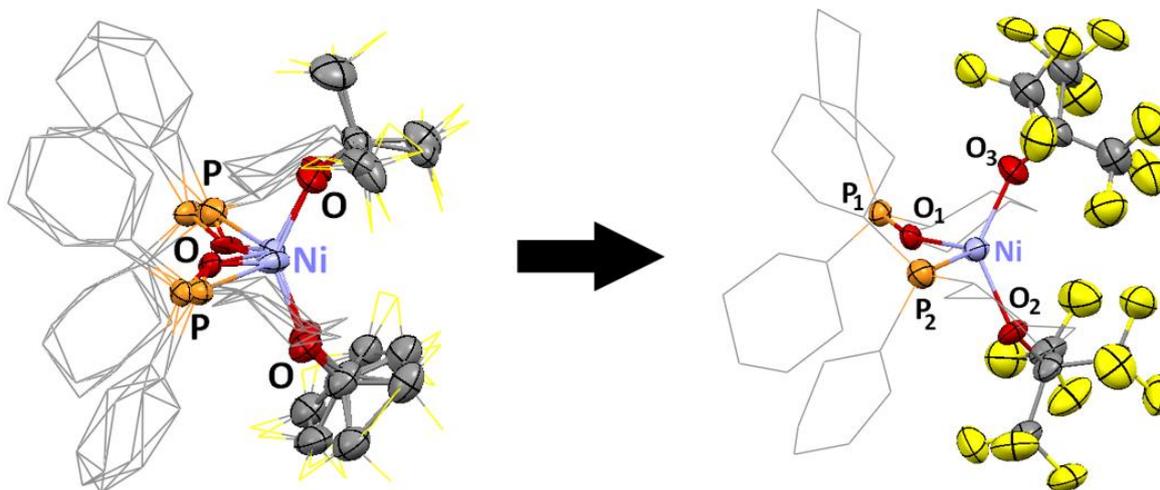


Figure S17 – Left: Disordered molecular structure of **3**. Right: after treatment. Only one part of the molecule is shown. Molecular structure of **3** in crystalline state. Distances [Å] and angles [°] : Ni-O<sub>1</sub> : 1.989(3) ; Ni-O<sub>2</sub> : 1.949(4) ; Ni-O<sub>3</sub> : 1.964(8) ; Ni-P<sub>2</sub> : 2.510(3) ; P<sub>1</sub>-O<sub>1</sub> : 1.531(4) ; Ni-O<sub>6</sub> : 1.992(5) ; O<sub>1</sub>-Ni-P<sub>2</sub> : 107.35(11) ; O<sub>2</sub>-Ni-O<sub>3</sub> : 130.0(6).

### 3. UV-vis analysis

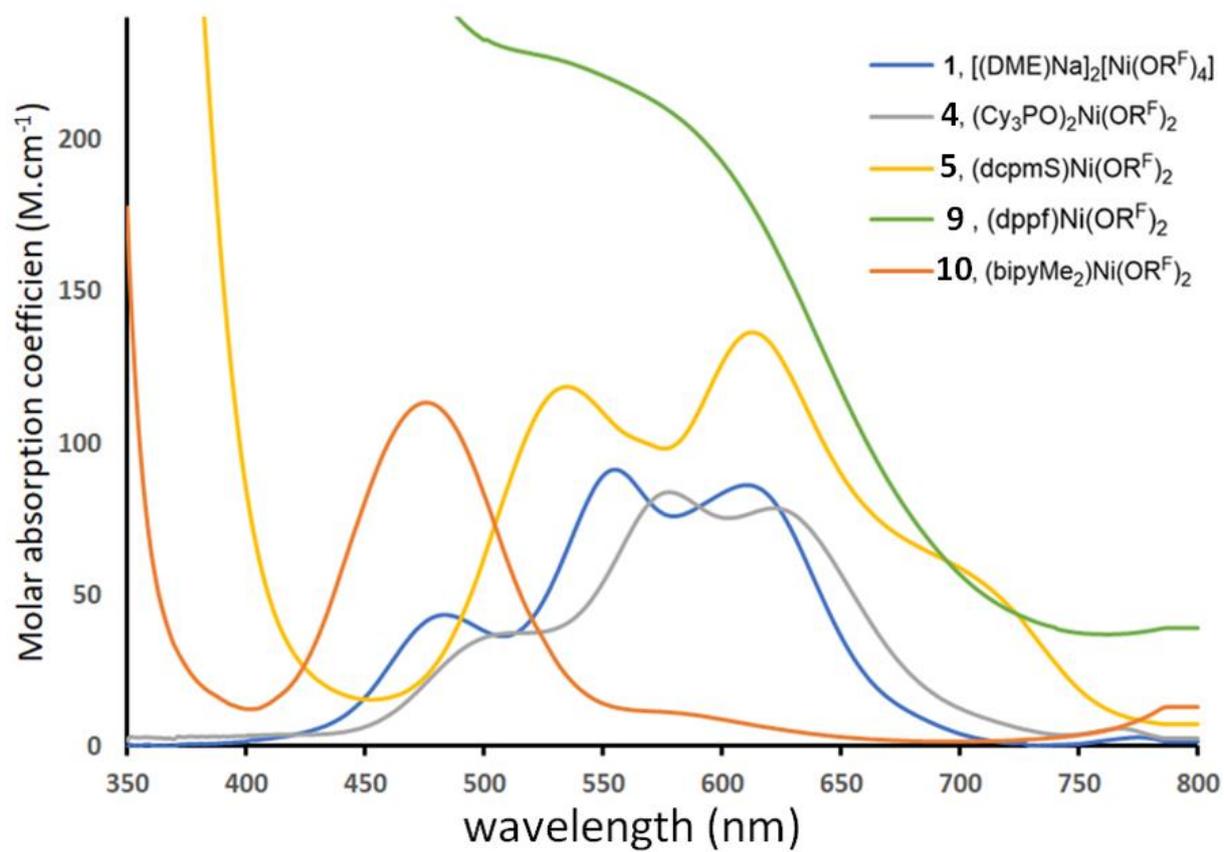


Figure S18 – UV-vis spectra of compounds 1, 4, 5, 9, 10 in *o*-DFB.

## 4. Catalytic tests

Studies were performed in a 6-parallel semi-batch autoclaves equipment (Figure S19). The reactors were placed under an inert atmosphere of nitrogen before the *o*-DFB (or cyclohexane), the complex and  $\text{Al}(\text{OR}^{\text{F}})_3$  (or  $\text{AlEt}_3$ ) were added. The total volume of solutions introduced was 20mL. The ethylene pressure was immediately increased to 20 bar and the temperature stayed at 25°C. The mechanical stirring was then set to 2000 rpm and the ethylene uptake was measured. The test was stopped after 1h or after 15 to 17g of ethylene was consumed, whichever occurred first. After quenching with (2-ethyl-hexyl)amine, the autoclave was depressurized. The liquid phase was collected (by pipette after the autoclave was opened) and weighed. After quenching with a 10%  $\text{H}_2\text{SO}_4$  solution in water (1 mL), the organic layer was analyzed by GC analyses (performed with an Agilent 6850 series II device equipped with an autosampler and fitted with PONA columns).



Figure S19 – Equipment used for catalyst screening consisting of 6 parallelized 100mL reactor (www.top-industrie.com).

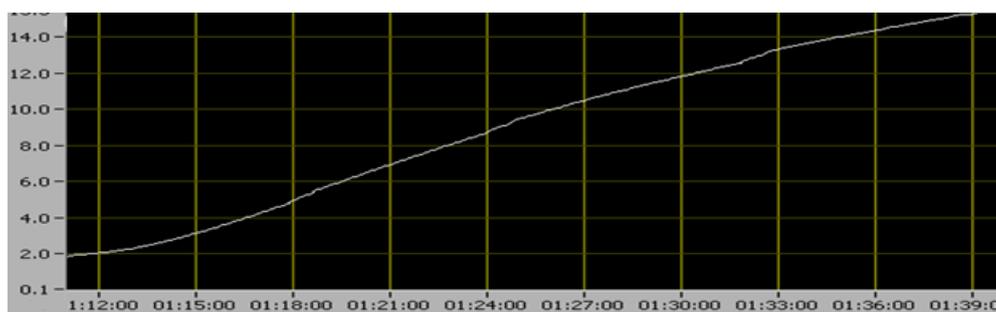


Figure S20 – Usual consumption of  $10/2\text{Al}(\text{OR}^{\text{F}})_3$  system at 25°C in *o*-DFB (20mL) and under 20 bar of ethylene. Y-axis : ethylene consumed (g). x-axis : time (h : min : s).

## 5. C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>D<sub>4</sub> experiments

### *Preparation of C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>D<sub>4</sub> mixture*

Thanks to the set-up described on Figure S21, the mixture of C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>D<sub>4</sub> (1/1) is created. An bottle of pure C<sub>2</sub>D<sub>4</sub> is taken for that experiment. The pressure is controlled out of this bottle and then, ethylene (C<sub>2</sub>H<sub>4</sub>) is slowly added until the pressure is doubled compared to the initial measured pressure. The mixture is then checked by <sup>1</sup>H and <sup>2</sup>D NMR, using a mixture of a 1/1 amount of toluene and toluene-*d*<sub>8</sub> in C<sub>6</sub>D<sub>6</sub>.

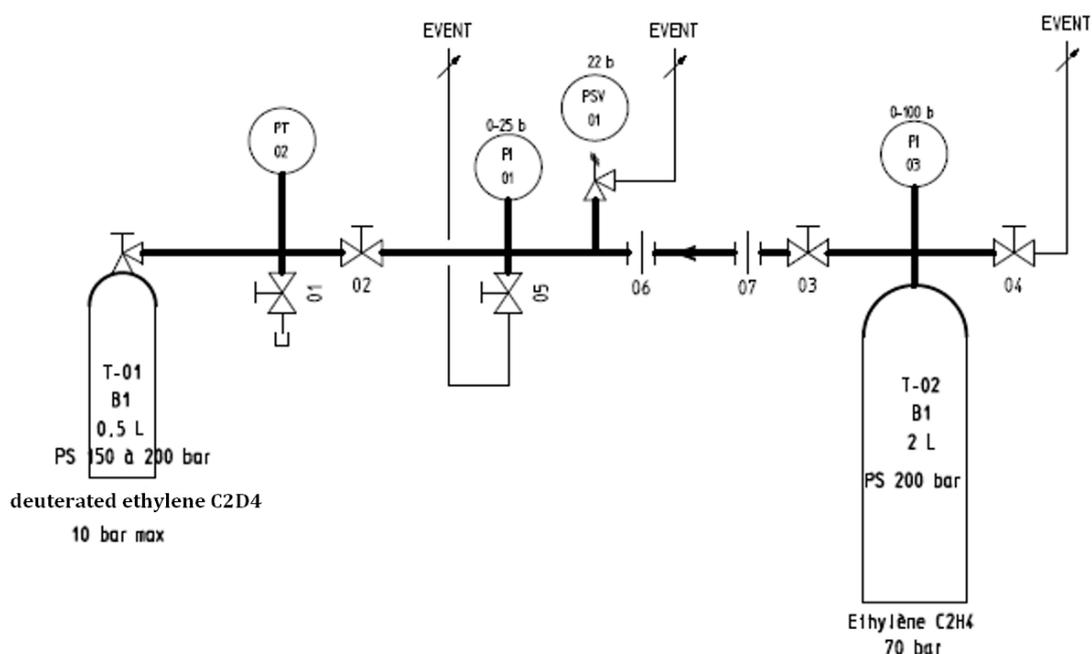


Figure S21 – Process diagram of the montage used to create the 1 to 1 mixture of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>D<sub>4</sub>.

### *Preparation of the catalytic solution*

First of all, three schlenk tubes are prepared. In a 10mL schlenk is added a solution of complex **7** (11mg, 15μmol, 1 eq.) in *o*-DFB (2mL). In another 10mL schlenk, is added a 0.5mL solution of AlEt<sub>3</sub> in fluorobenzene (0.121M, 61μmol, 2eq.). Finally, a solution of R<sup>F</sup>OH (26μL, 186mmol, 3.1eq.) in *o*-DFB (5.5mL).

The AlEt<sub>3</sub> solution is cooled down to -30°C and the solution of **10** at -10°C. At first, the R<sup>F</sup>OH solution is added on the AlEt<sub>3</sub> solution to give a colorless solution. This mixture is let to react not more than 1min. Half of the obtained solution (3mL) is then added on the solution of **10** at -10°C to give a pale orange solution. 0.5mL from this last solution was then added in a pressurized NMR tube and kept at -10°C until addition of ethylene.

### *Analyses*

1<sup>st</sup> tests were made with C<sub>2</sub>D<sub>4</sub> (2.5b, RT) to determine the reaction time. The consumption of ethylene was followed by <sup>2</sup>D NMR (Figure S22). After 5 min, all ethylene is consumed. And only butenes are observed. The GC-MS analysis was then done directly after ethylene addition.

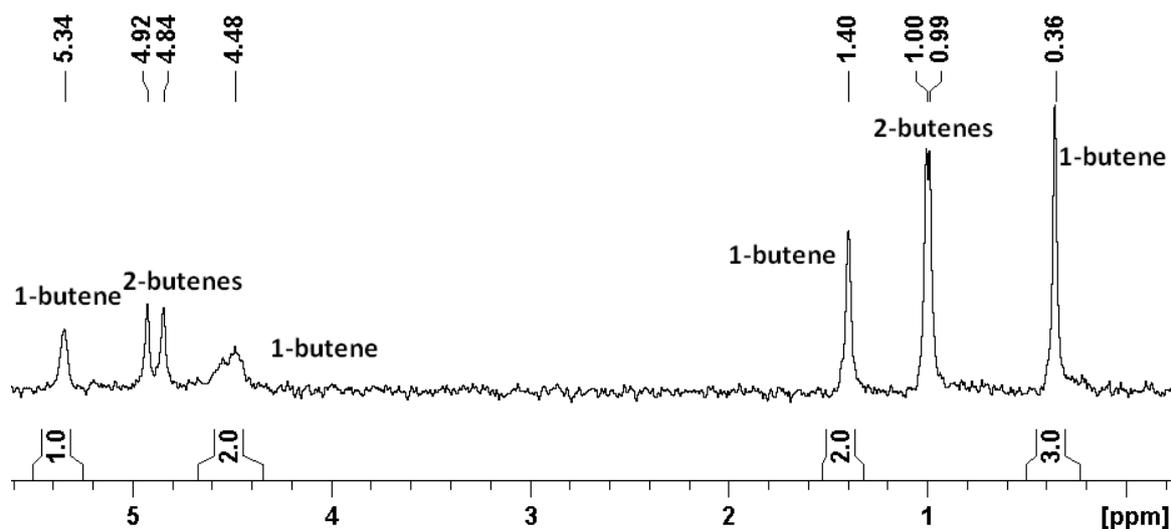


Figure S22 – <sup>2</sup>D NMR of butenes obtained after catalysis under C<sub>2</sub>D<sub>4</sub>.

After addition of the 1/1 mixture of ethylenes (2.5b, 0°C), no color shift is detected. The gas phase is taken with a gas syringe and directly inserted in the GC-MS apparatus. Typical GC is shown on Figure S23. Typical MS spectrum of 1-butene is shown in the paper.

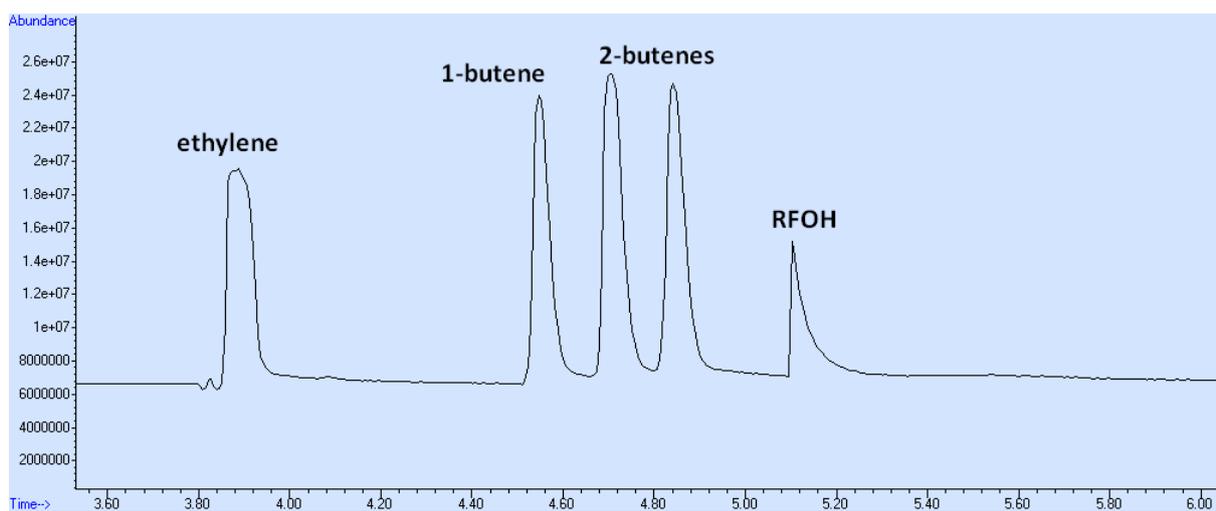


Figure S23 – Typical GC obtained after catalysis under C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>D<sub>4</sub> (1/1) with **10**/2Al(OR<sup>F</sup>)<sub>3</sub>.

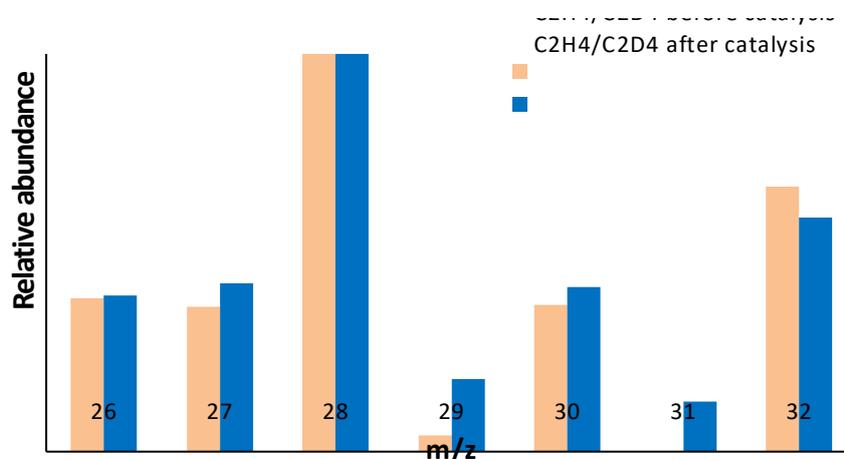


Figure S24 – Mass spectrum of C<sub>2</sub>D<sub>4</sub>/C<sub>2</sub>H<sub>4</sub> (1/1) fraction before (pale orange) and after (blue)

catalysis.

## 6. References

- [1] SADABS, Program for data correction, Bruker-AXS
- [2] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8.
- [3] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8
- [4] I. E. Soshnikov, N. V. Semikolenova, J. Ma, K. Q. Zhao, V. A. Zakharov, K. P. Bryliakov, C. Redshaw, E. P. Talsi, *Organometallics* **2014**, *33*, 1431–1439.
- [5] T. Agapie, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2007**, *129*, 14281–14295.