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Supplementary information for the manuscript

# Catalytic Systems Based on Nickel (II) Complexes with Bis(3,5-dimethylpyrazol-1-yl)methane – Impact of $PPh_3$ on the Formation of Precatalysts and Selective Dimerization of Ethylene

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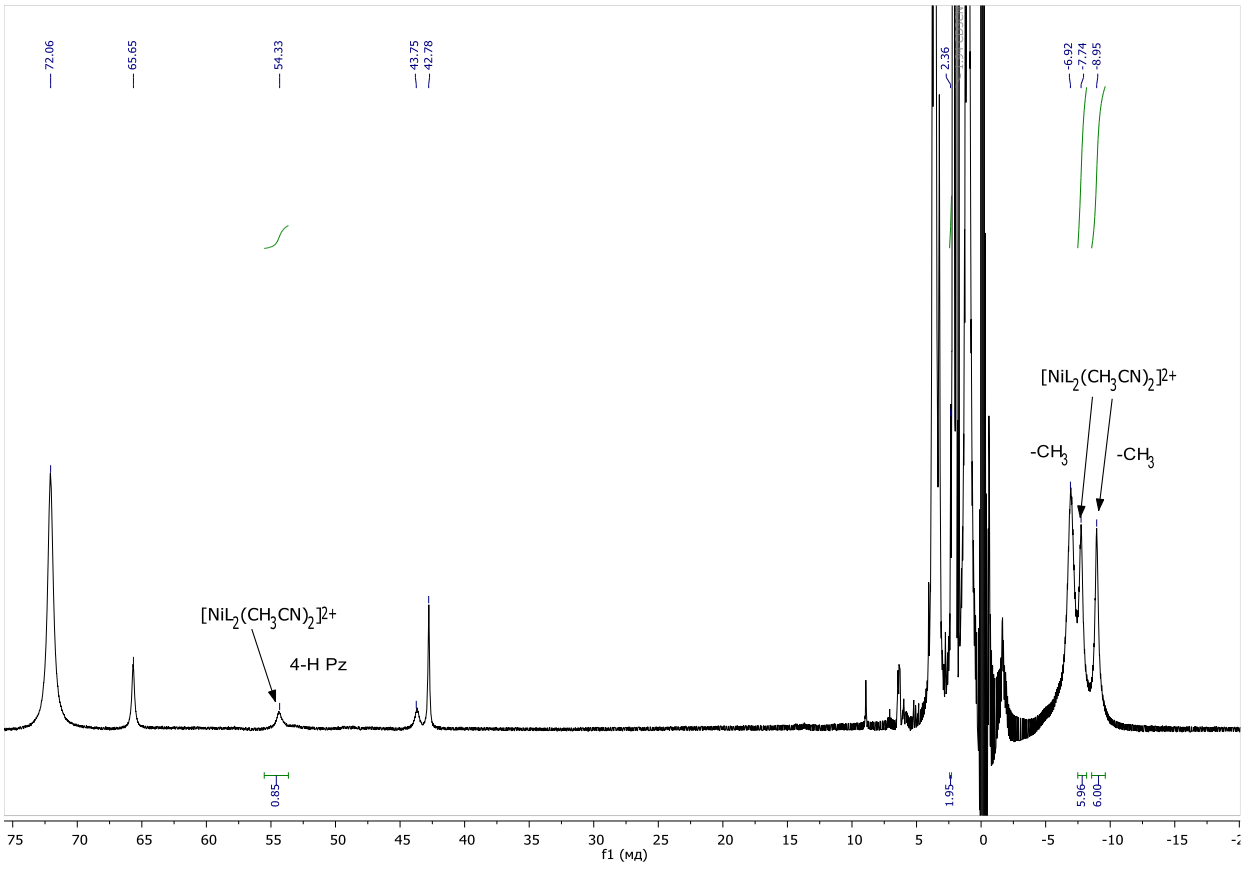


**Figure S1.** $^1H$ NMR (600 MHz) spectrum of **2** in $CD_3CN$.

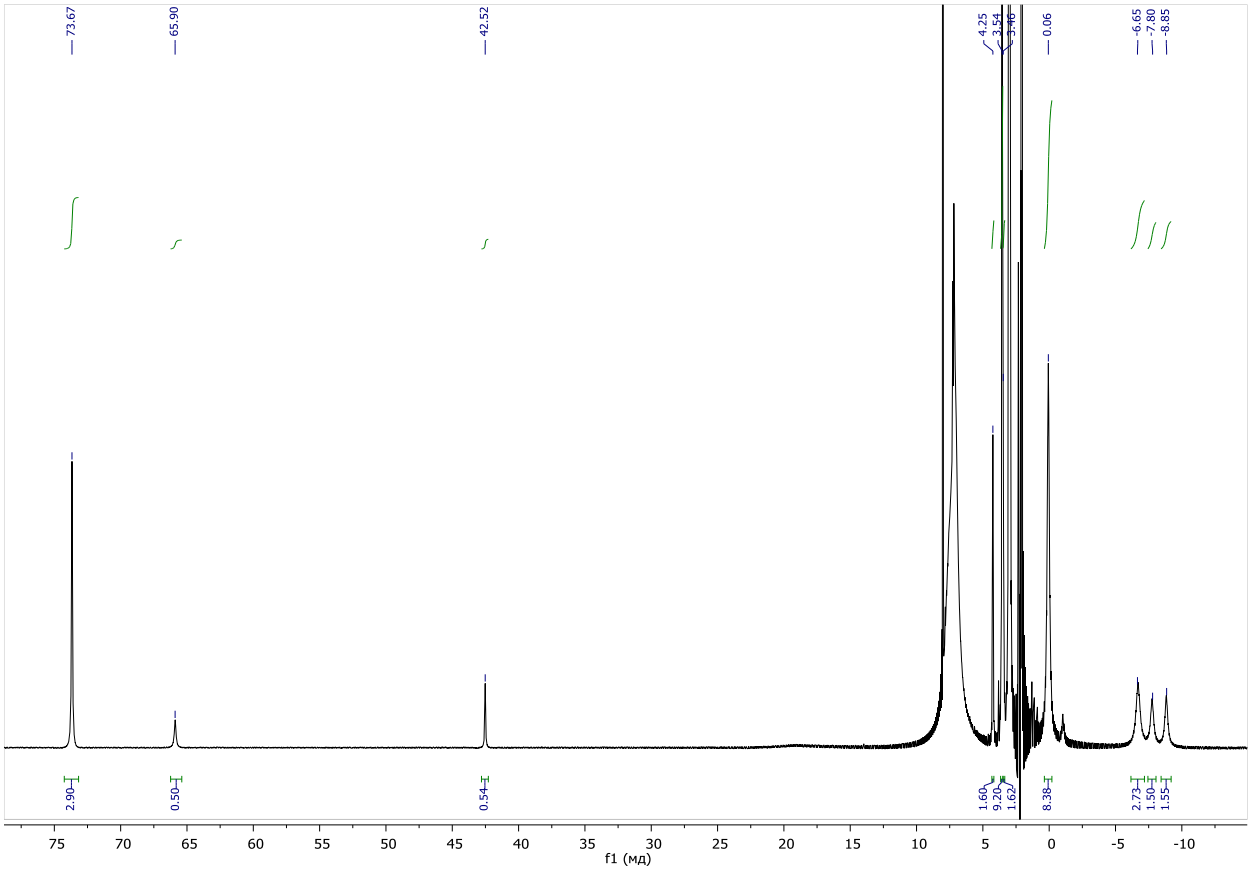


**Figure S2.** $^{1}$H NMR (600 MHz) spectrum of **2** + 1 equiv. $PPh_3$ in aceton-$d_6$.

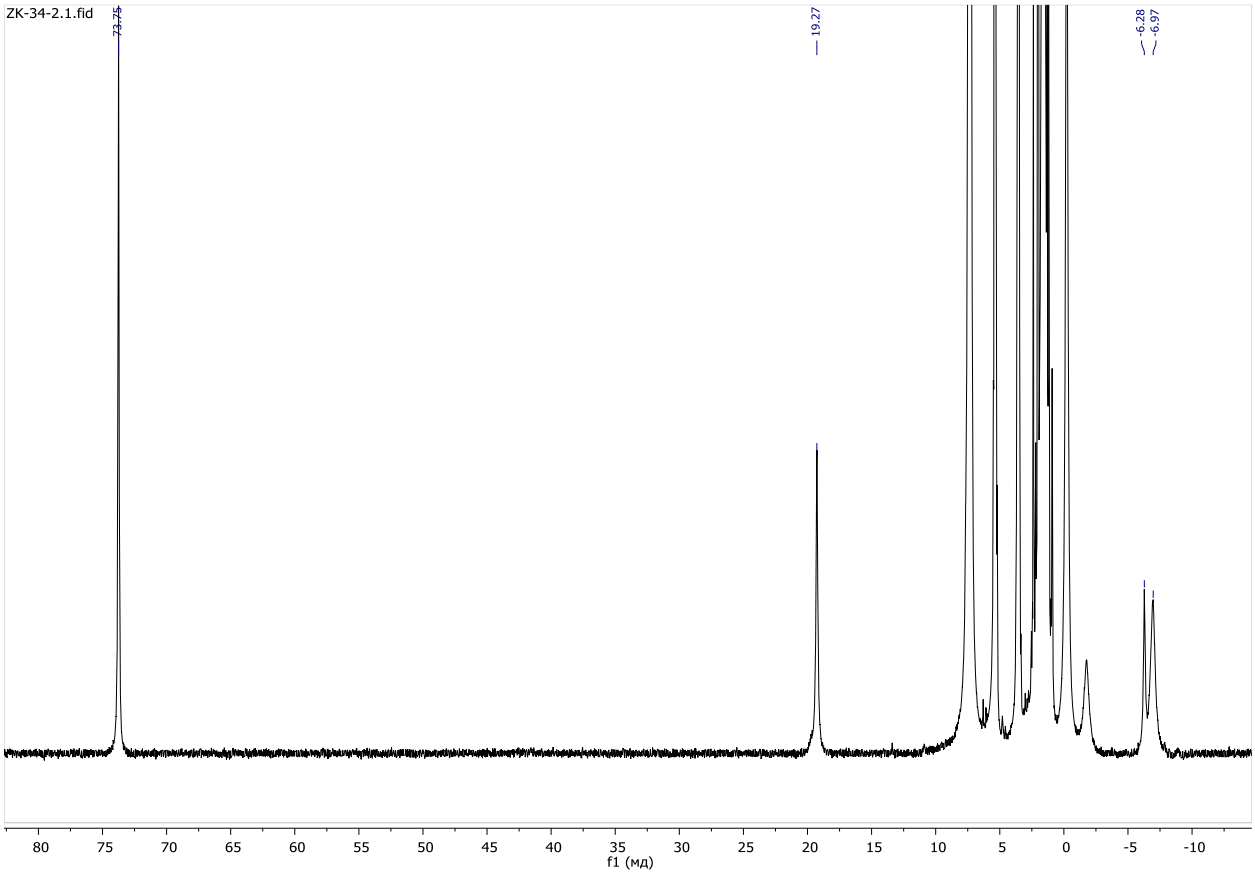


**Figure S3.** $^{1}$H NMR (600 MHz) spectrum of **3** in $CD_2Cl_2$.

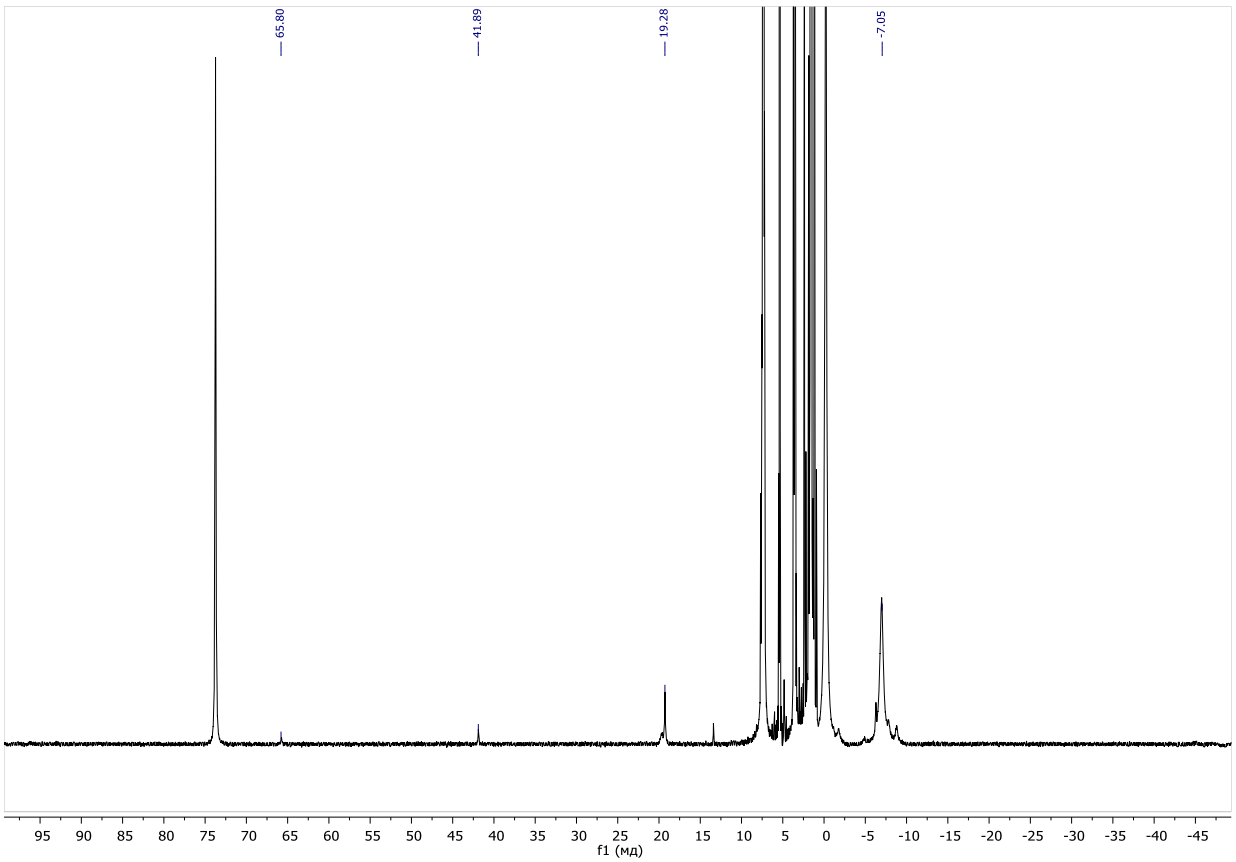


**Figure S4.** $^{1}$H NMR (600 MHz) spectrum of **4** in $CD_2Cl_2$.

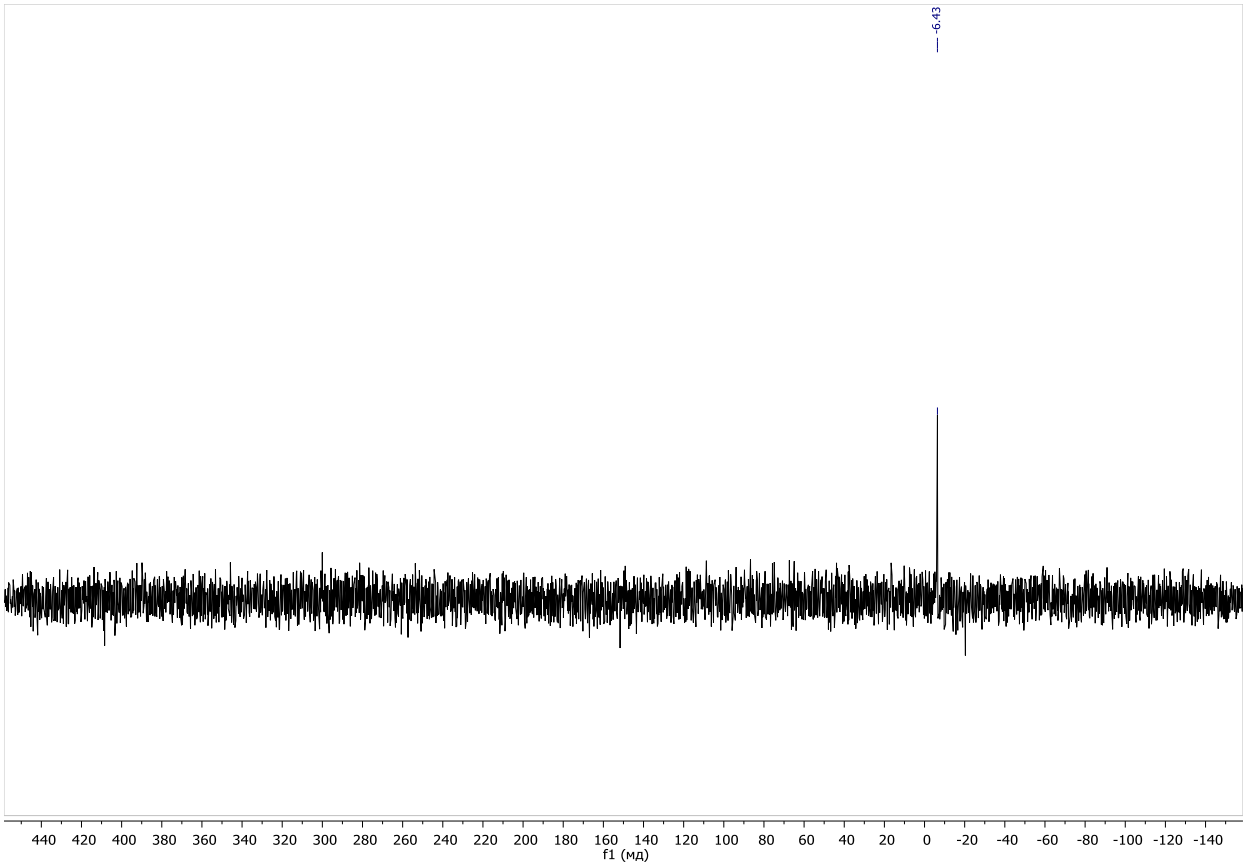


**Figure S5.** $^{31}$P NMR (400 MHz) spectrum of **2** + 1 equiv. $PPh_3$ in toluene-$d_8$.

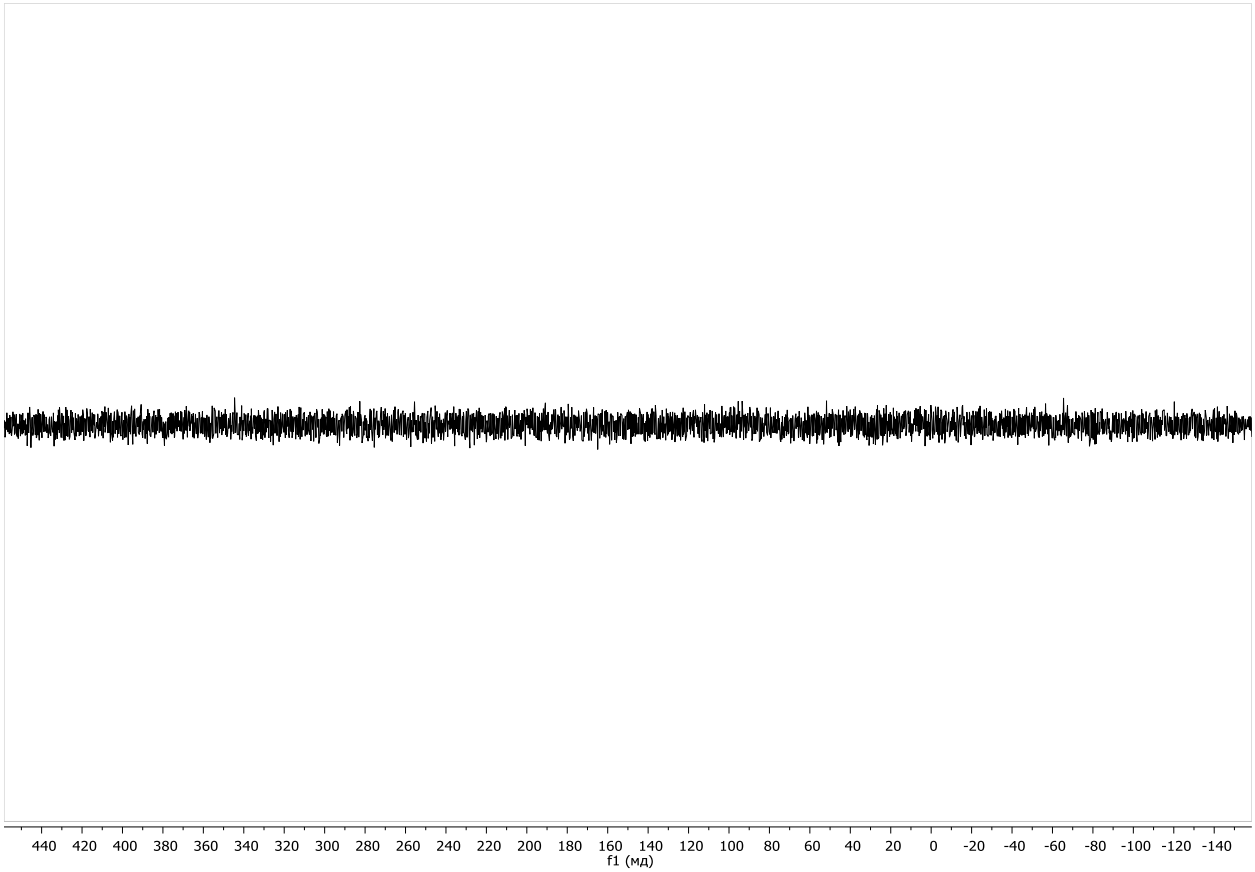


**Figure S6.** $^{31}$P NMR (400 MHz) spectrum of **2** + 1 equiv. $PPh_3$ + 10 equiv. $Et_2AlCl$ in toluene-$d_8$.

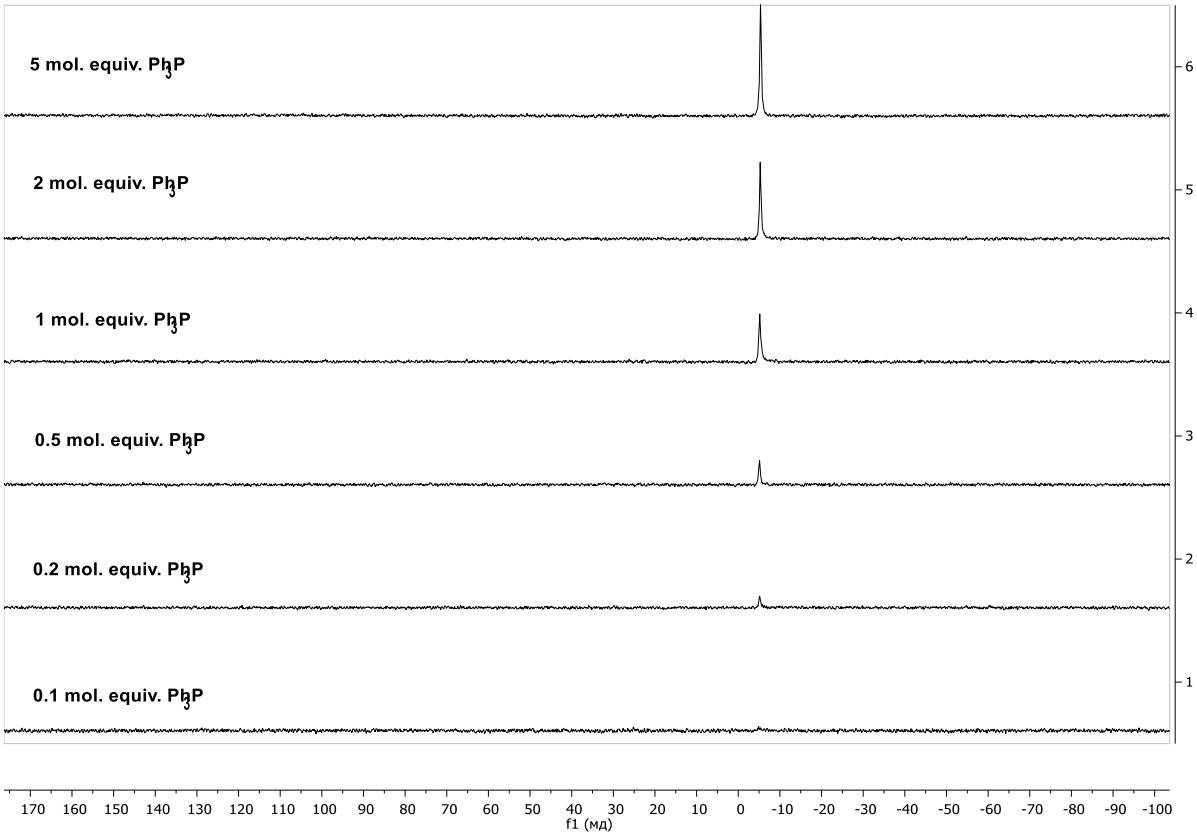


**Figure S7.** $^{31}$P NMR (400 MHz) spectrum of **2** titrated with $PPh_3$ in $CD_2Cl_2$.

**Table S1.** Crystal data and structure refinements for complexes **3-4**

| Compound | **3** | **4** |
|---|---|---|
| Empirical formula | $C_{62}H_{68}Br_6N_{10}Ni_3P_2$ | $C_{46}H_{59}Br_4N_8Ni_2O_{1.50}P$ |
| Formula weight | 1670.67 | 1215.96 |
| Temperature, K | 100(2) | 100(2) |
| Crystal system | Triclinic | Monoclinic |
| Space group | P-1 | $P2_1/n$ |
| *a*, Å | 9.6743(19) | 14.695(3) |
| *b*, Å | 10.044(2) | 10.158(2) |
| *c*, Å | 20.289(4) | 35.371(7) |
| $\alpha$, deg. | 79.47(3) | 90 |
| $\beta$, deg. | 76.24(3) | 91.65(3) |
| $\gamma$, deg. | 64.55(3) | 90 |
| *V*, Å$^3$ | 1721.8(7) | 5277.7(18) |
| *Z* | 1 | 4 |
| $D_{calc}$, g/cm$^3$ | 1.611 | 1.530 |
| Absorption coefficient, $\mu$ | 3.208 | 5.177 |
| *F*(000) | 834 | 2456 |
| Crystal size, mm | 0.20 x 0.10 x 0.02 | 0.12 x 0.07 x 0.02 |
| Theta range for data collection | 3.235 to 35.998 | 3.349 to 30.981 |
| Index ranges | -11<=h<=11,-12<=k<=12,-24<=l<=24 | -18<=h<=17,-13<=k<=12,-43<=l<=44 |
| Reflections collected | 18142 | 40148 |
| Independent reflections, $R_{int}$ | 6152 [R(int) = 0.0996] | 11204 [R(int) = 0.1058] |
| Reflections observed with $I > 2\sigma(I)$ | 3867 | 7873 |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents |
| Data / restraints/ parameters | 6152 / 0 / 382 | 11204 / 10 / 595 |
| Goodness-of-fit on $F^2$ | 0.808 | 1.020 |
| $R_1$ [$I > 2\sigma(I)$] | 0.1139 | 0.0766 |
| $wR_2$ [all data] | 0.2933 | 0.1971 |
| Extinction coefficient | 0.0104(10) | 0.0056(3) |
| $T_{min}$ / $T_{max}$ | 0.6 / 0.93 | 0.570 / 0.9 |

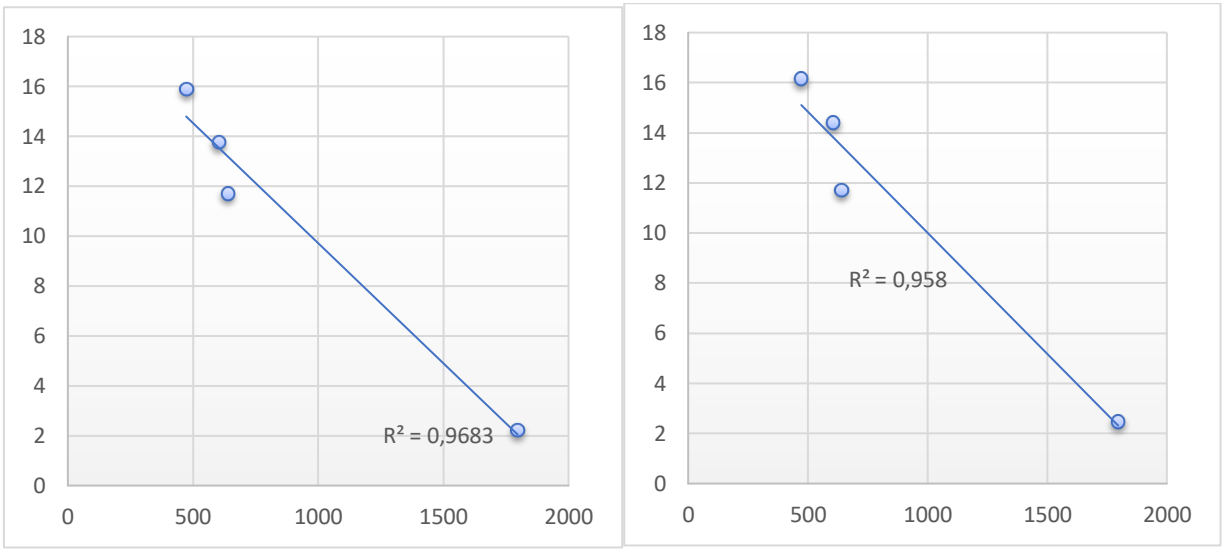


**Figure S8**. Dependencies of 1-butene (A) and α-olefin (B) shares on activity of **2**/$Et_2AlCl$ 150 with different amounts of $Ph_3P$.

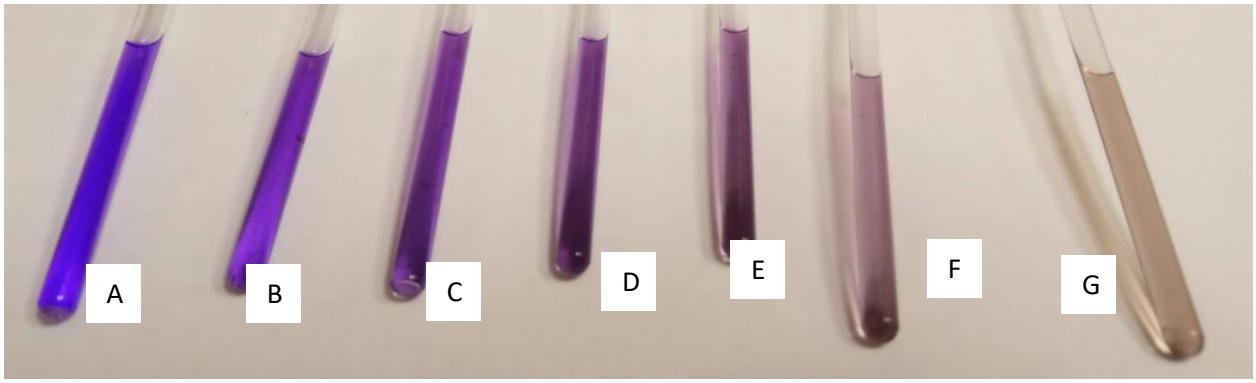


**Figure S9.** Change of complex **2** solution colors in $CD_2Cl_2$ with the addition of $Ph_3P$: (A) – pure complex, (B) – **2** + 0,1 mol. equiv. of $Ph_3P$, (C) – **2** + 0,2 mol. equiv. of $Ph_3P$, (D) – **2** + 0,5 mol. equiv. of $Ph_3P$, (E) – **2** + 1 mol. equiv. of $Ph_3P$, (F) – **2** + 2 mol. equiv. of $Ph_3P$, (G) – **2** + 5 mol. equiv. of $Ph_3P$.

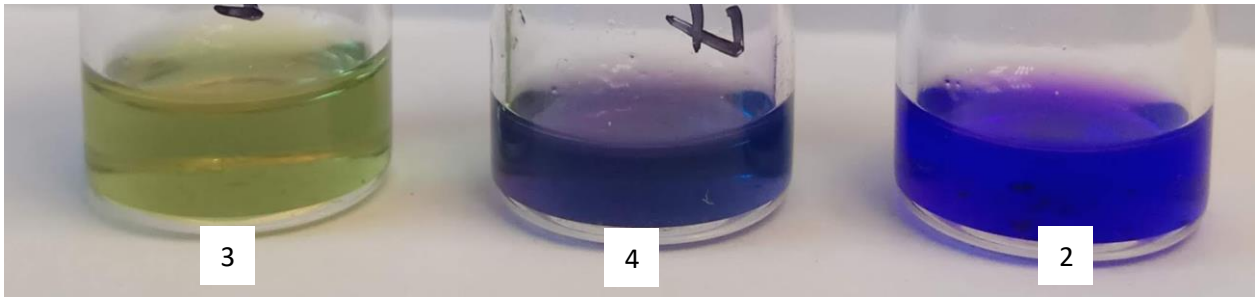


**Figure S10.** Colors of complexes **2-4** in $CH_2Cl_2$ solutions

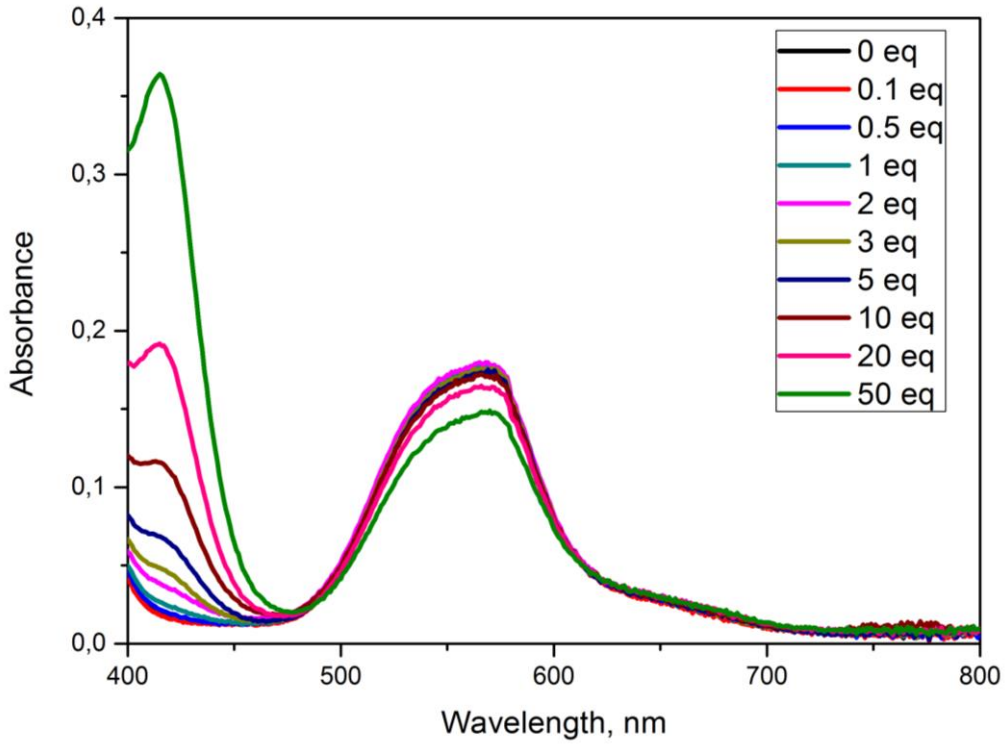


**Figure S11.** UV-Vis spectrum of complex **2** titrated with $Ph_3P$ in toluene.

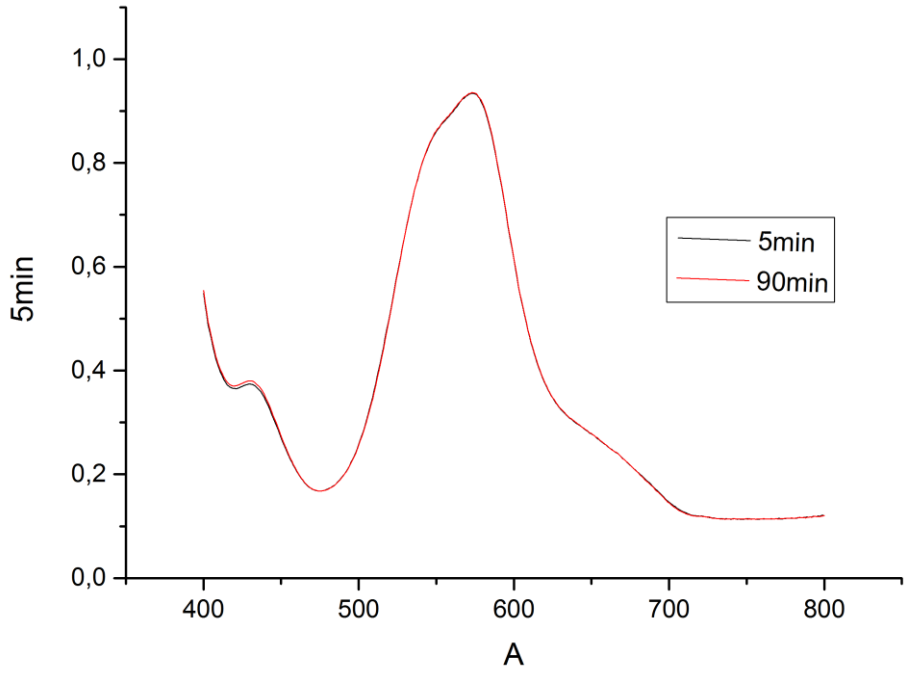


**Figure S12.** UV-Vis spectrum of complex **4** in $CH_2Cl_2$.

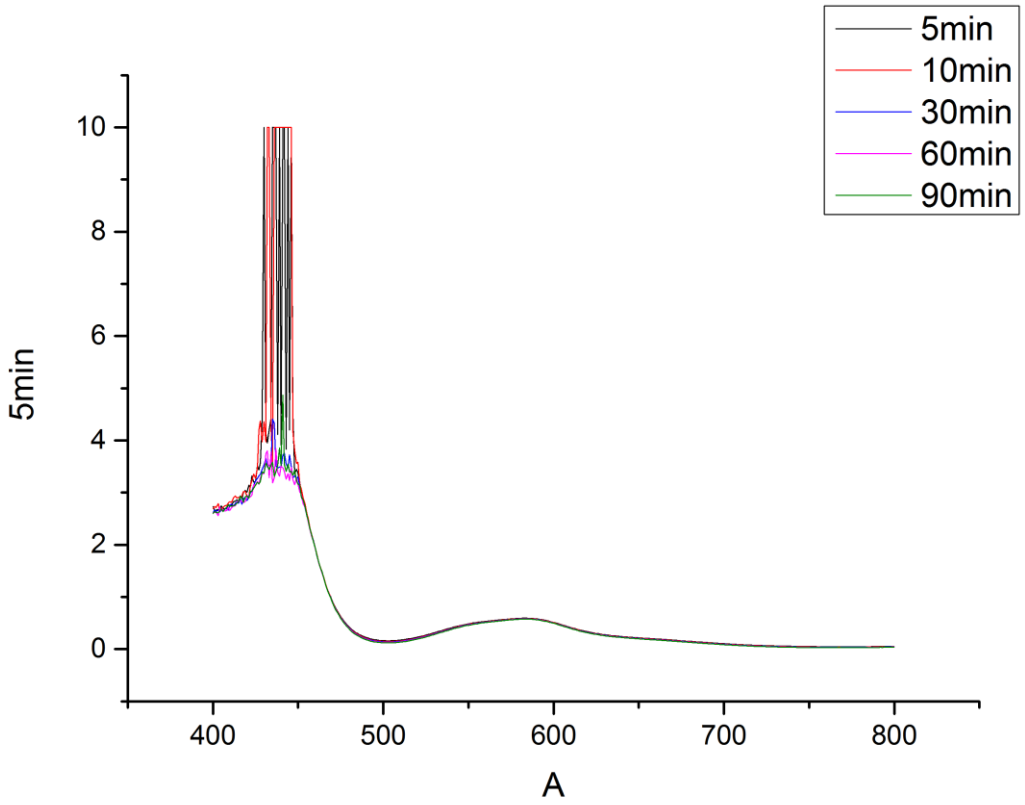


**Figure S13.** UV-Vis spectrum of complex **3** in $CH_2Cl_2$.

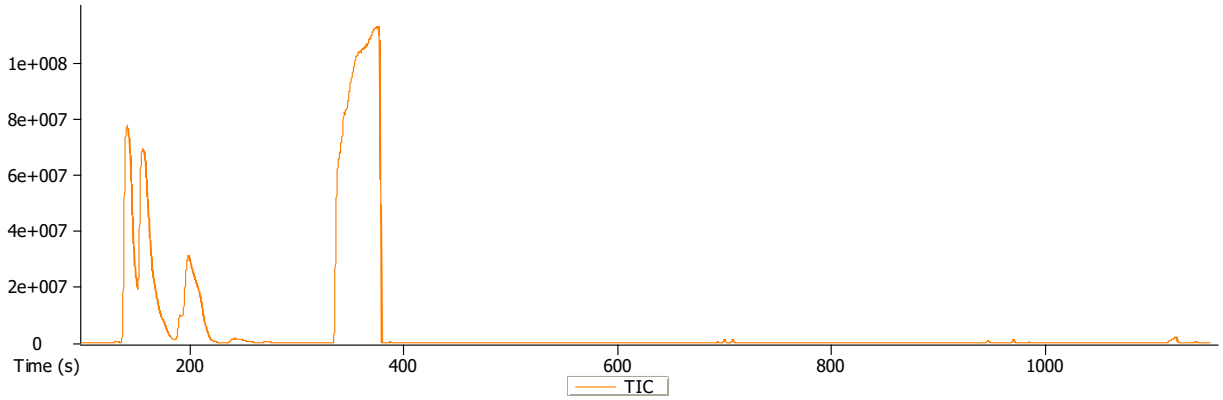


**Figure S14.** GC–MS total ion current chromatogram of run 4, Table 2, system **2**/$Et_2AlCl$ 150

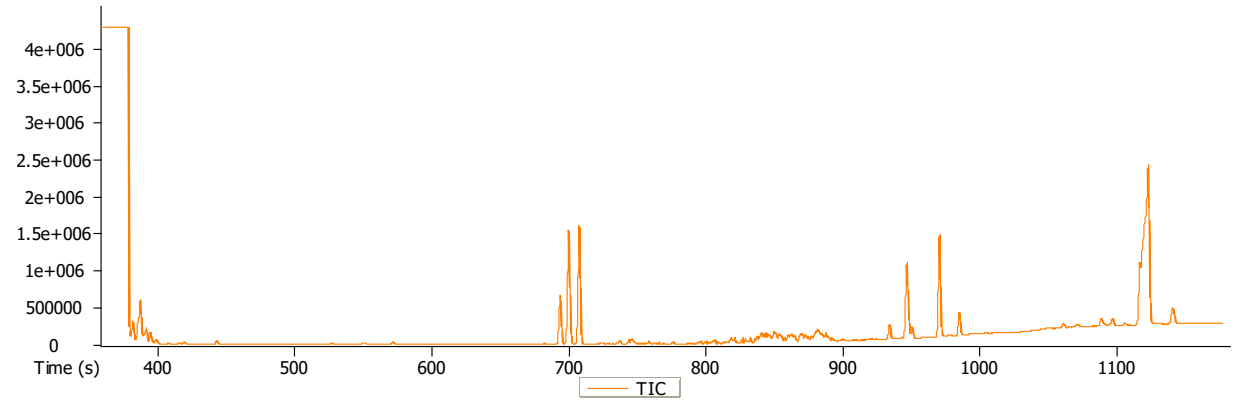


**Figure S15**. Part GC–MS total ion current chromatogram run 4, Table 2, system **2**/$Et_2AlCl$ 150

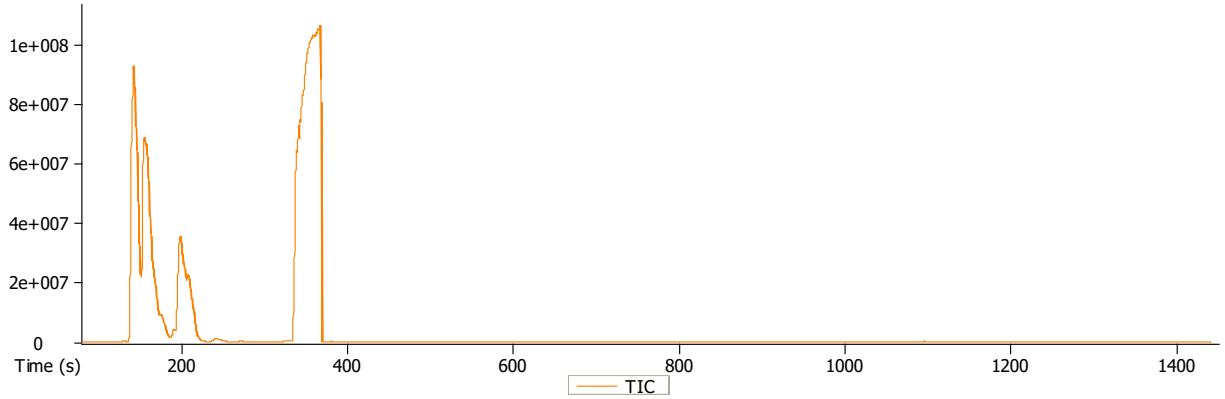


**Figure S16.** GC–MS total ion current chromatogram of run 5, Table 2, system **2**/$Et_2AlCl$ 150/$Ph_3P$ 1

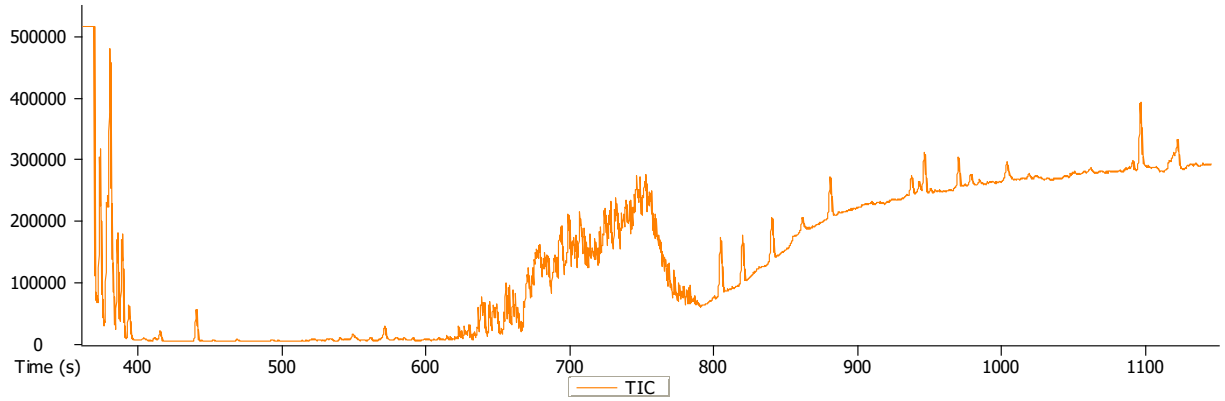


**Figure S17.** Part GC–MS total ion current chromatogram of run 5, Table 2, system **2**/$Et_2AlCl$ 150/$Ph_3P$ 1

**Table S2.** Composition of oligomer mixtures.

| **Isomers** | **2/$Et_2AlCl$ 150**<br>**Run 4** | **2/$Et_2AlCl$ 150/$Ph_3P$ 1**<br>**Run 5** |
|---|---|---|
| **Butenes** | 0,530 | 0,563 |
| **Hexenes** | 0,450 | 0,435 |
| **Octenes** | 0,002 | 0,002 |
| **Benzene + C5**[a] | 0,006 | - |
| **Benzene + C9**[a] | 0,004 | - |
| **Benzene + C13**[a] | 0,008 | - |

[a] C[number] - indicates number of carbon atoms in alkyl branches, attached to benzene