Supporting Information for:

Redox Control in Palladium Catalyzed Norbornene and Alkyne Polymerization

Wenping Zou, Wenmin Pang, Changle Chen*

CAS Key Laboratory of Soft Matter Chemistry, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, 230026, China

*To whom correspondence should be addressed. Telephone: +86-551-63601495. Email: changle@ustc.edu.cn

Content

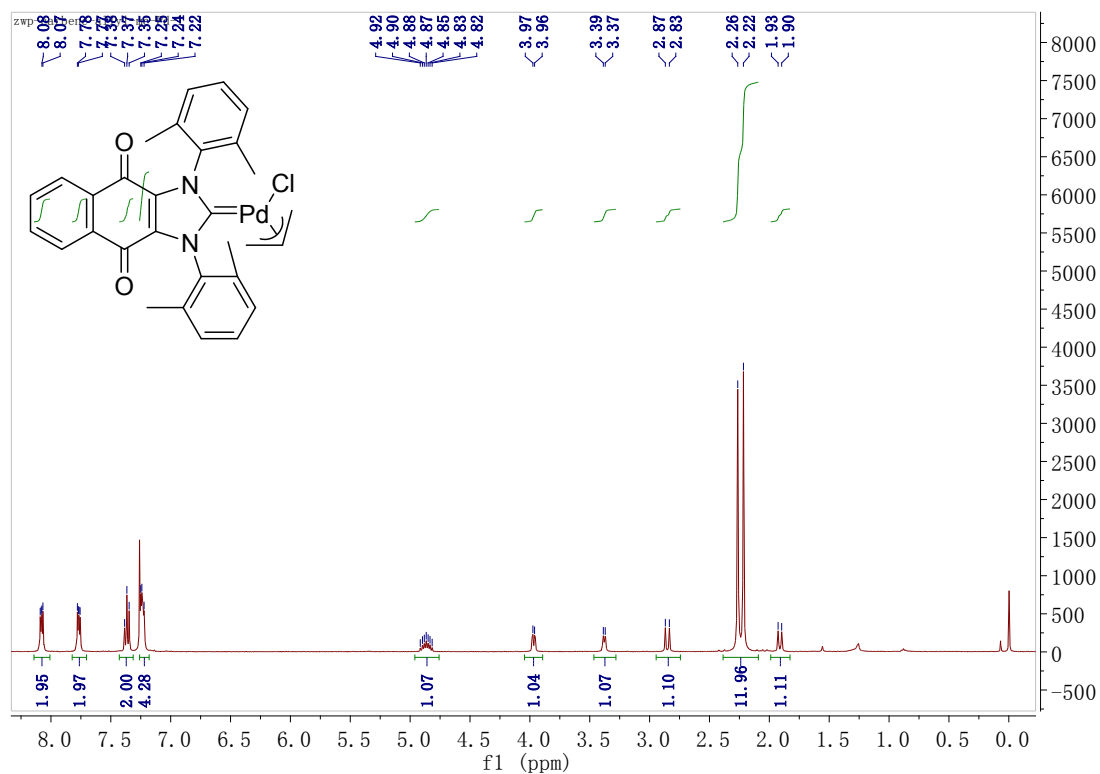## 1. NMR, electrochemical characterizations of Pd-Me complex.

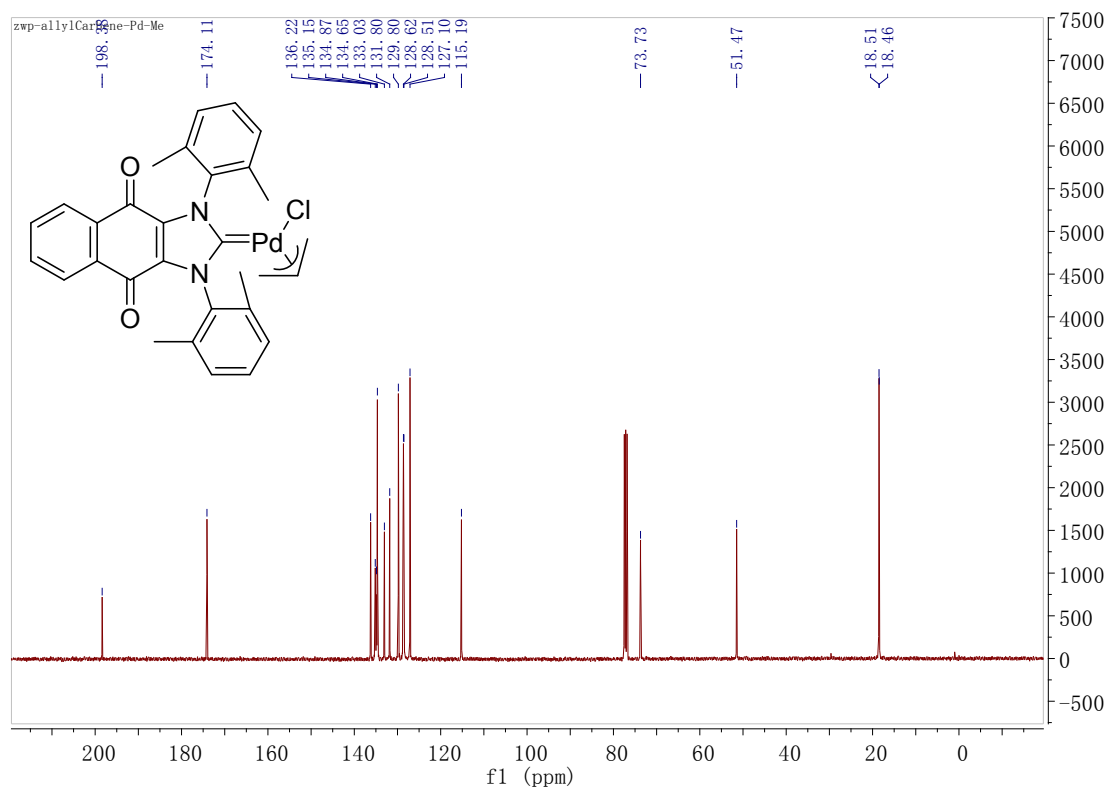**Figure S1.** ^{1}H NMR spectrum of **Pd-Me** in CDCl$_3$.

Figure S2. ^{13}C NMR spectrum of **Pd-Me** in CDCl$_3$.

Electrochemistry Cyclic voltametry measurements were performed on 0.01 mmol compound in 5 mL CH_2Cl_2 solution (0.002 M) with supporting electrolyte 0.2 M $[^nBu_4N]^+[PF_6]^-$, using Ag/AgCl as the reference electrode, along with platinum working and auxiliary electrodes, and a scan rate of 100 mV/s. The results of the electrochemical investigations are shown in Table S1. The $Ep_{1/2}$ of $CoCp_2$ is -1.334V has been reported previously.[1]

compound	Ep^A/ V	Ep^C/ V	$Ep_{1/2}$/ V
Pd-Me	-0.465	-0.732	-0.599
Pd-^iPr	-0.530	-0.725	-0.628

Table S1. Electrochemical studies.

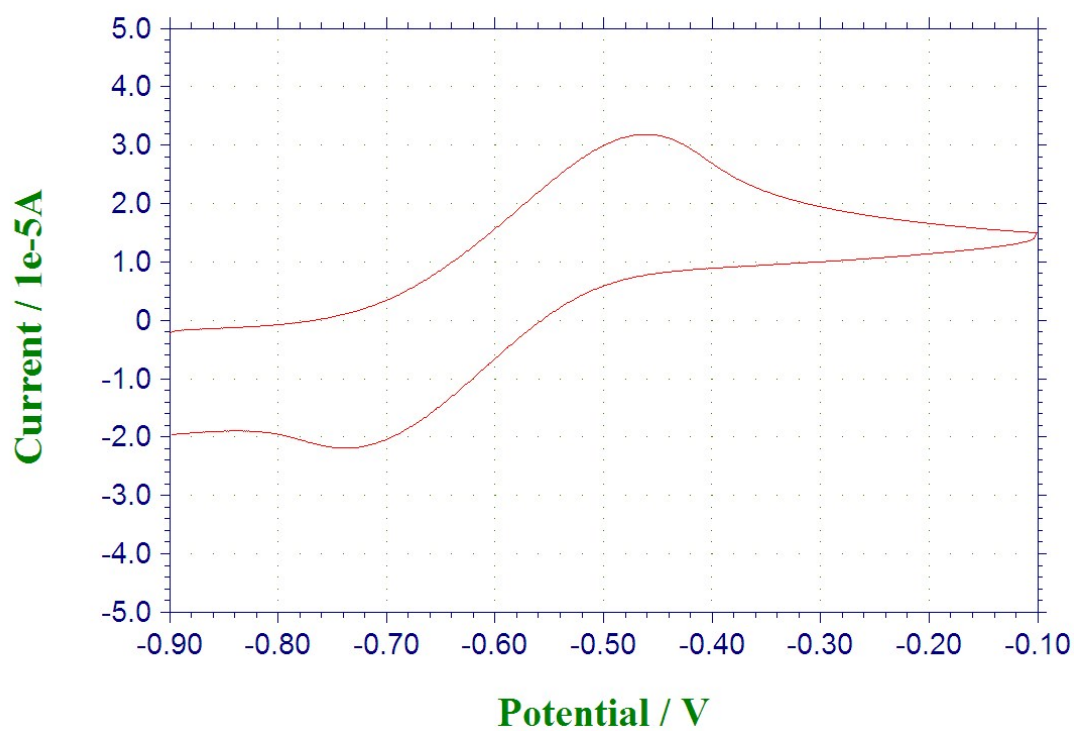(1) Sun, H.; Xue, F.; Nelson, A. P.; Redepenning, J.; DiMagno, S. G. *Inorg. Chem.* **2003**, 42, 4507– 4509.

Figure S3. Cyclic Voltamogram of **Pd-Me**.
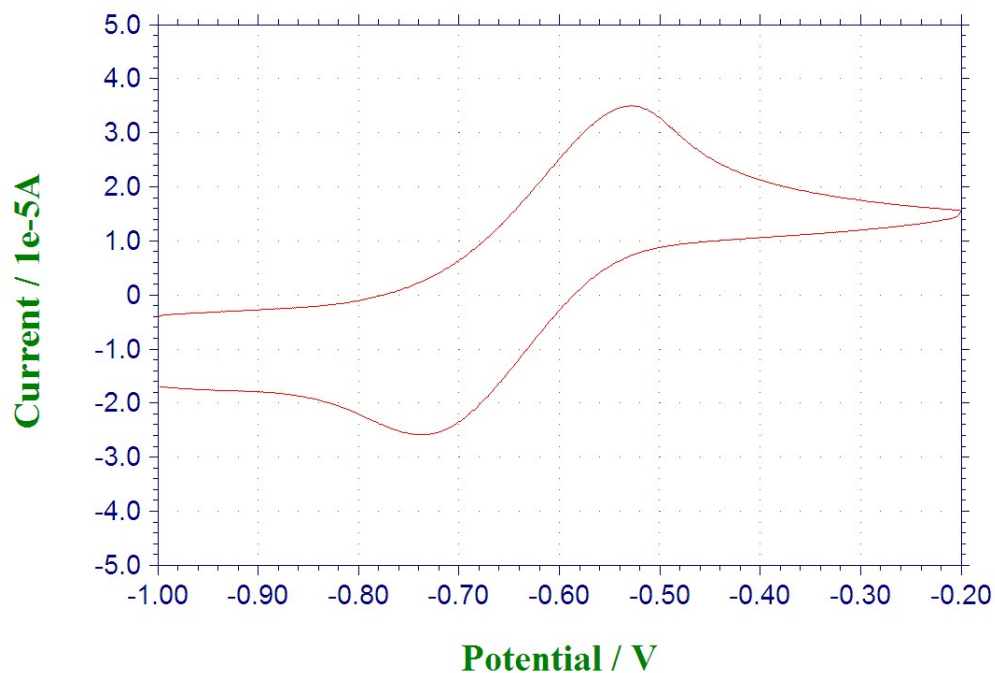
Figure S4. Cyclic Voltamogram of **Pd-^{i}Pr**.

2. NMR study of the interconversion between the neutral and oxidized complexes.
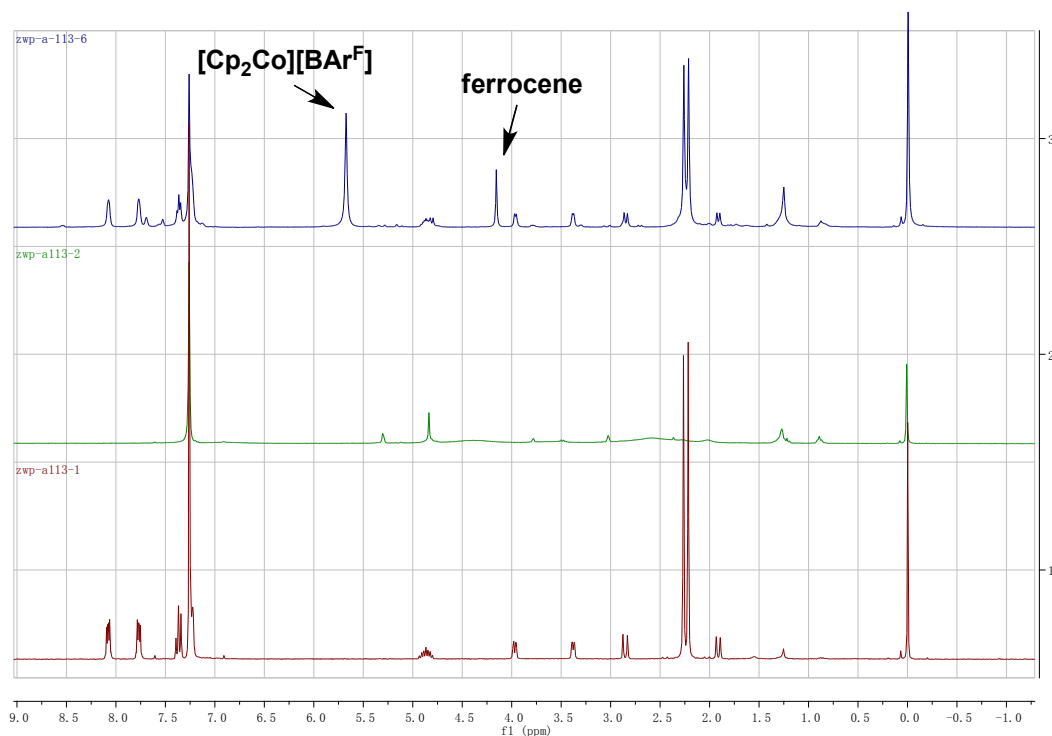

Figure S5. ^{1}**H NMR stack (CDCl$_3$) showing (a) complex Pd-Me; (b) complex Pd-Me + 1 equiv CoCp$_2$ (i.e. in situ formation of Pd-Me ^{red}); (c) mixture from spectrum (b) + 1 equiv FcBAr^F, showing the reformation of the resonances for complex Pd-Me.**

3. Table of Polymerization and In-situ switching polymerization of Norbornene, NB-OAc and 1-chloro-1-octyne.[a]

entry	Pd complex	Monomer	additive[b]	Time (min)	Yield[c] (%)	TOF[d]	Mn	PDI
1	**Pd-Me**	NB	NaBAr$_4$	2min	96	2880	-	-
2	**Pd-Me**	NB	NaBAr$_4$	5min	95	1140	-	-
3	**Pd-Me**	NB	none	2h	0	-	-	-
4	**[Pd-Me]**[-]	NB	NaBAr$_4$	2h	0	-	-	-
5	**[Pd-Me]**[-]	NB	none	2h	0	-	-	-
6	**[Pd-Me]**[- e]	NB	NaBAr$_4$	2min	95	2850	-	-
7	**[Pd-Me]**[- e]	NB	none	2h	0	-	-	-
8	**Pd-iPr**	NB	NaBAr$_4$	2min	80	2400	-	-
9	**Pd-iPr**	NB	NaBAr$_4$	5min	96	1152	-	-
10	**Pd-iPr**	NB	none	2h	0	-	-	-
11	**[Pd-iPr]**[-]	NB	NaBAr$_4$	2h	0	-	-	-
12	**[Pd-iPr]**[-]	NB	none	2h	0	-	-	-
13	**[Pd-iPr]**[- e]	NB	NaBAr$_4$	2min	83	2490	-	-
14	**[Pd-iPr]**[- e]	NB	NaBAr$_4$	5min	94	1128	-	-
15	**[Pd-iPr]**[- e]	NB	none	2h	0	-	-	-
16	**Pd-Me**	NB-OAc	NaBAr$_4$	1h	33	33	3870	1.29
17	**Pd-Me**	NB-OAc	NaBAr$_4$	4h	65	16	4010	1.31
18	**Pd-Me**	NB-OAc	NaBAr$_4$	9h	87	10	4221	1.30
19	**Pd-iPr**	NB-OAc	NaBAr$_4$	9h	22	2	3030	1.28
20	**Pd-Me**	1-chloro-octyne	NaBAr$_4$	1.5h	46	31	3950	1.25
21	**Pd-iPr**	1-chloro-octyne	NaBAr$_4$	0.5h	37	74	6530	1.26
22	**Pd-iPr**	1-chloro-octyne	NaBAr$_4$	1h	52	52	6680	1.35
23	**Pd-iPr**	1-chloro-octyne	NaBAr$_4$	1.5h	65	43	6820	1.23
24	**[Pd-iPr]**[-]	1-chloro-octyne	NaBAr$_4$	1.5h	trace	-	-	-

[a]Conditions: 10 μmol cat., 1.0 mmol monomer, NB and NB-OAc in 2 ml CHCl$_3$ at 25 °C, 1-chloro-1-octyne in 2 ml toluene at 60 °C, The molecular weight of polynorbornene was not determined due to the low solubility of the polymer product even in trichloro-benzene at 120

4. NMR monitoring experiments of NB-OAc and 1-chloro-1-octyne homopolymerization.
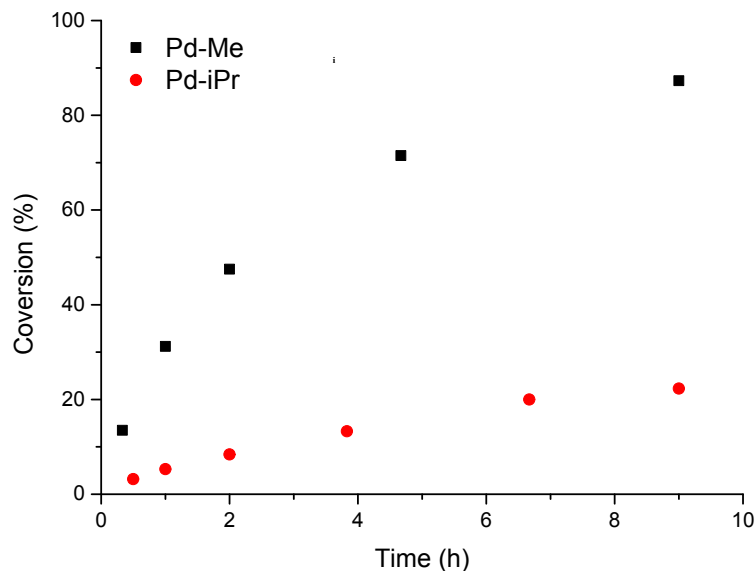

Figure S6. Polymerization of 100 equivalents of NB-OAc in CDCl$_3$ at 25 °C starting from Pd-Me and Pd-^{i}Pr.
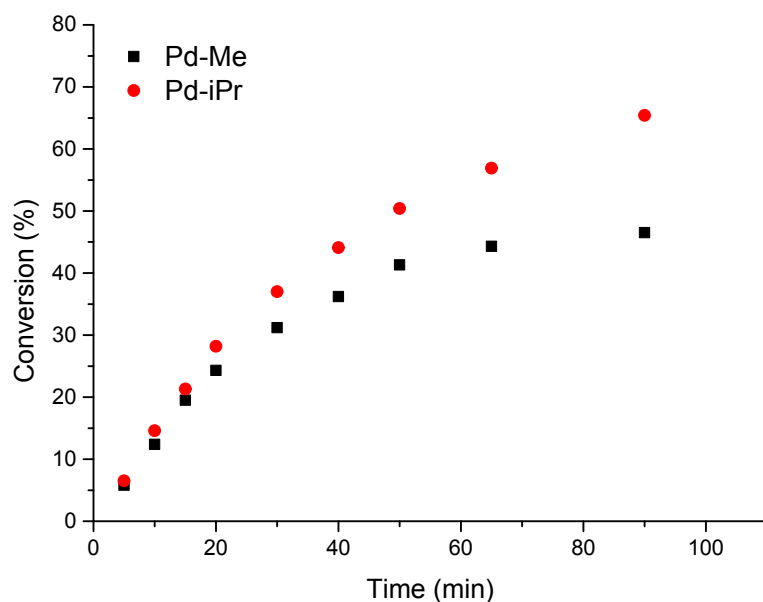

Figure S7. Polymerization of 100 equivalents of 1-chloro-1-octyne in d^8-toluene at 60 °C starting from Pd-Me and Pd-^{i}Pr.

5. In-situ switching experiment of NB-OAc homopolymerization.
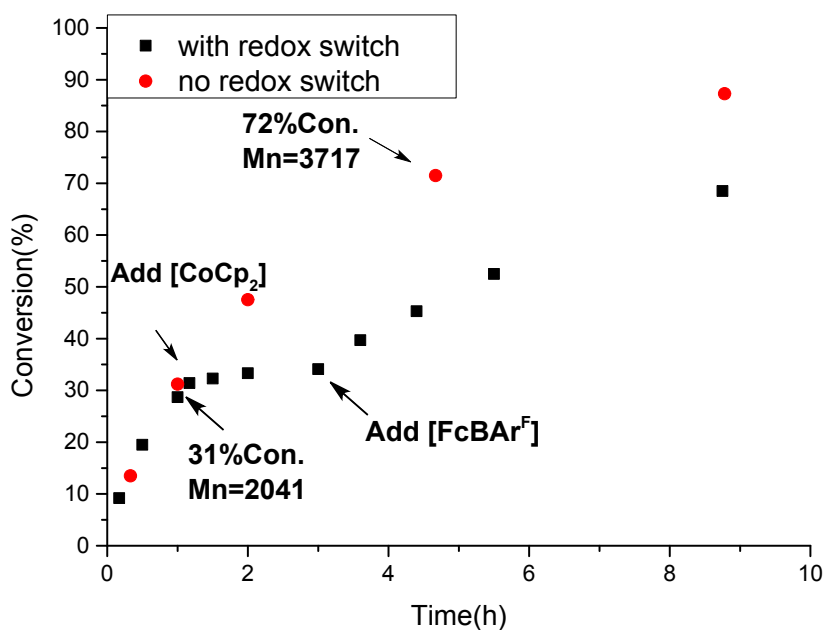
Figure S8. Polymerization of 50 equivalents of NB-OAc in CDCl₃ at 25 °C starting from Pd-Me.
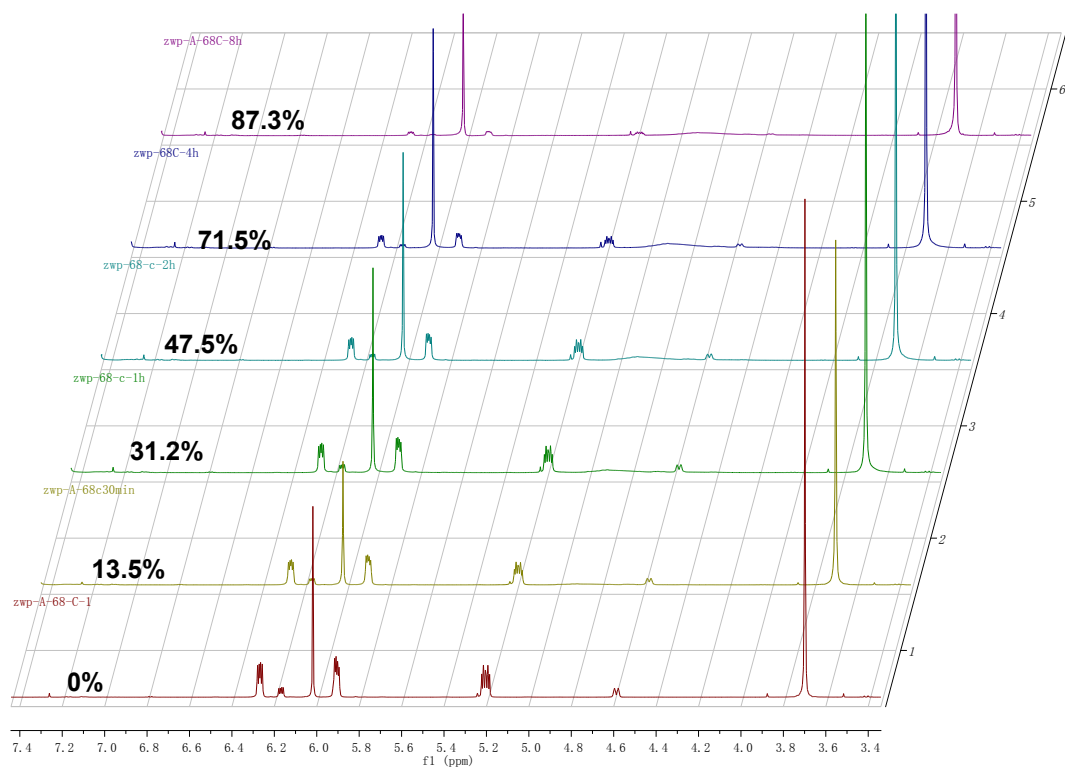

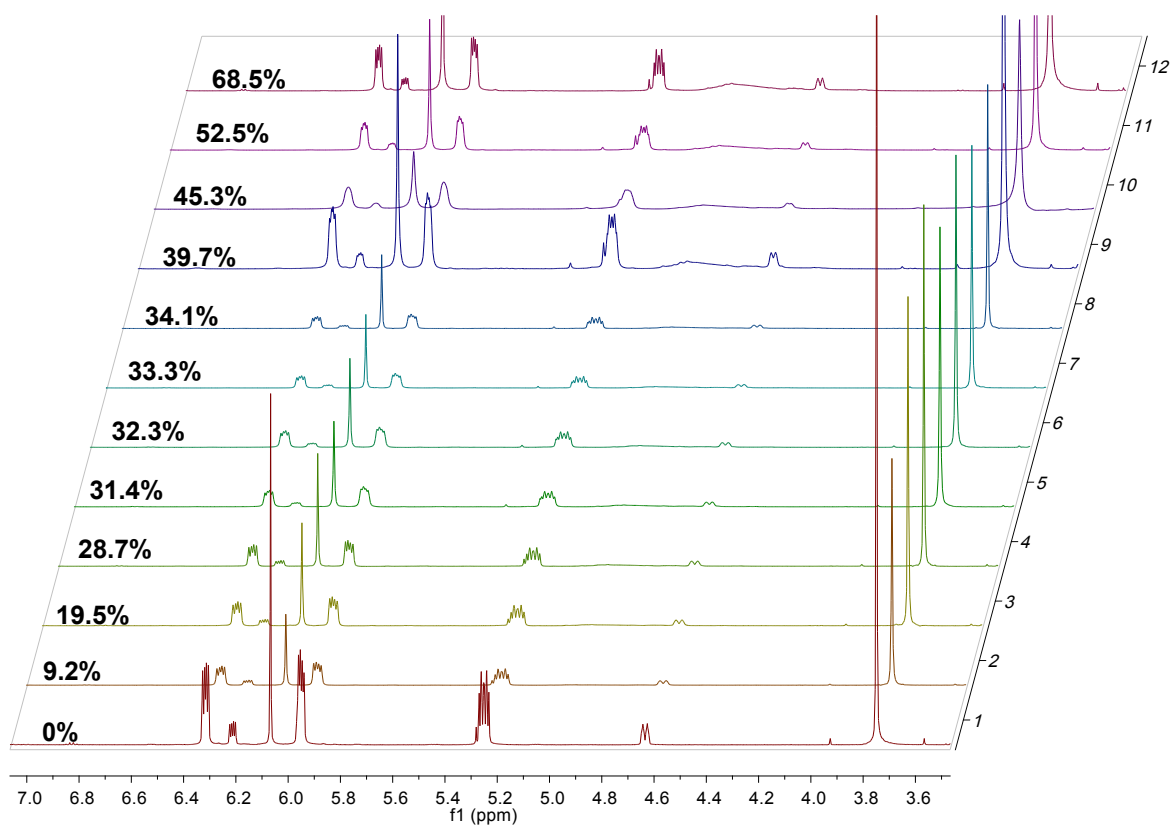**Figure S9. NMR monitoring experiments of NB-OAc homopolymerization using Pd-Me.**

Figure S10. In-situ switching experiment of NB-OAc homopolymerization using Pd-Me.

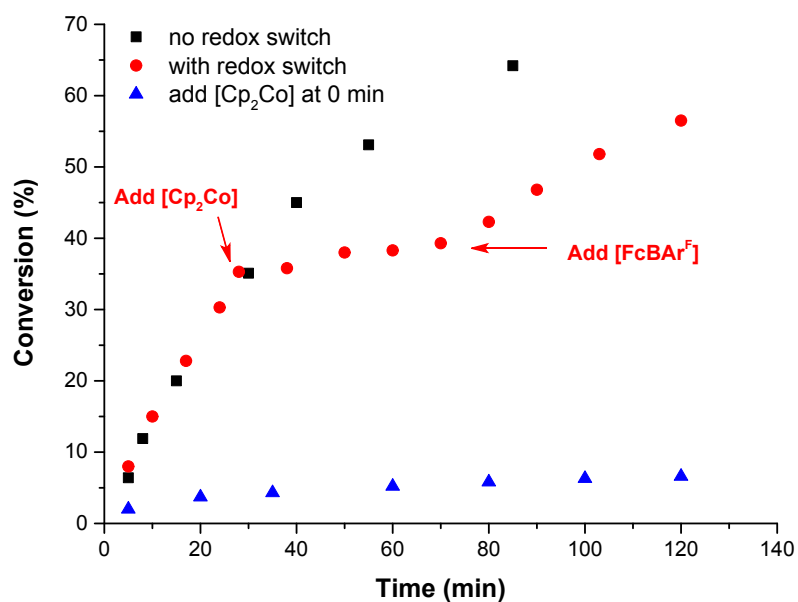## 6. In-situ switching experiment of 1-chloro-1-octyne homopolymerization.

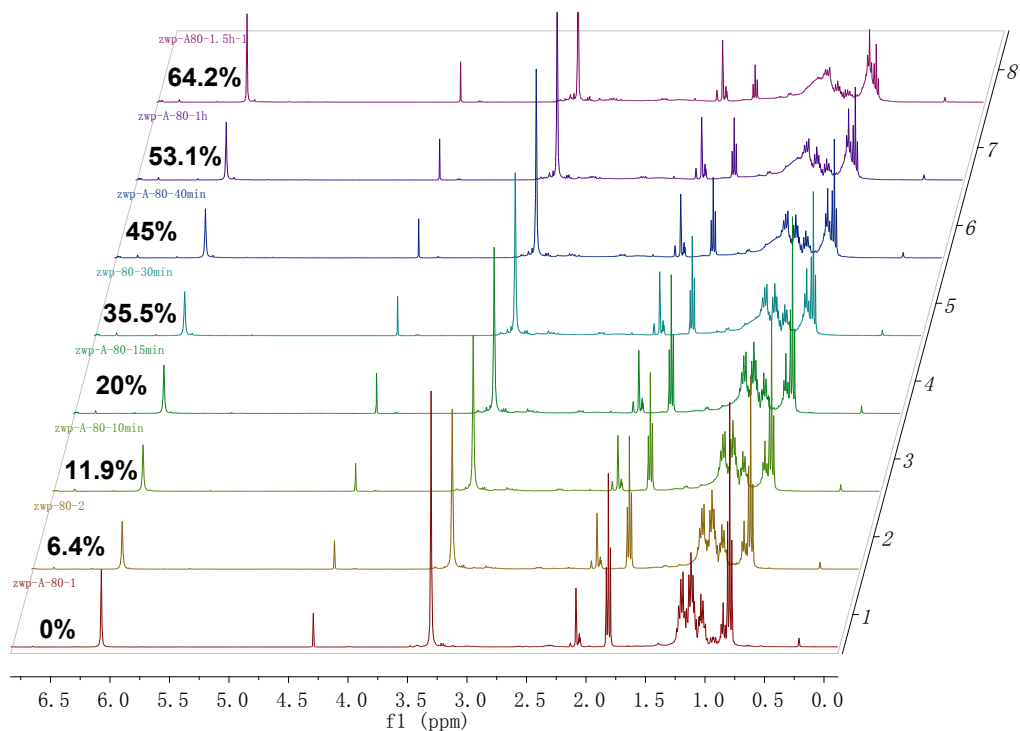**Figure S11.** Polymerization of 50 equivalents of 1-chloro-1-octyne in d^8-toluene at 60 °C starting from **Pd-^{i}Pr**.

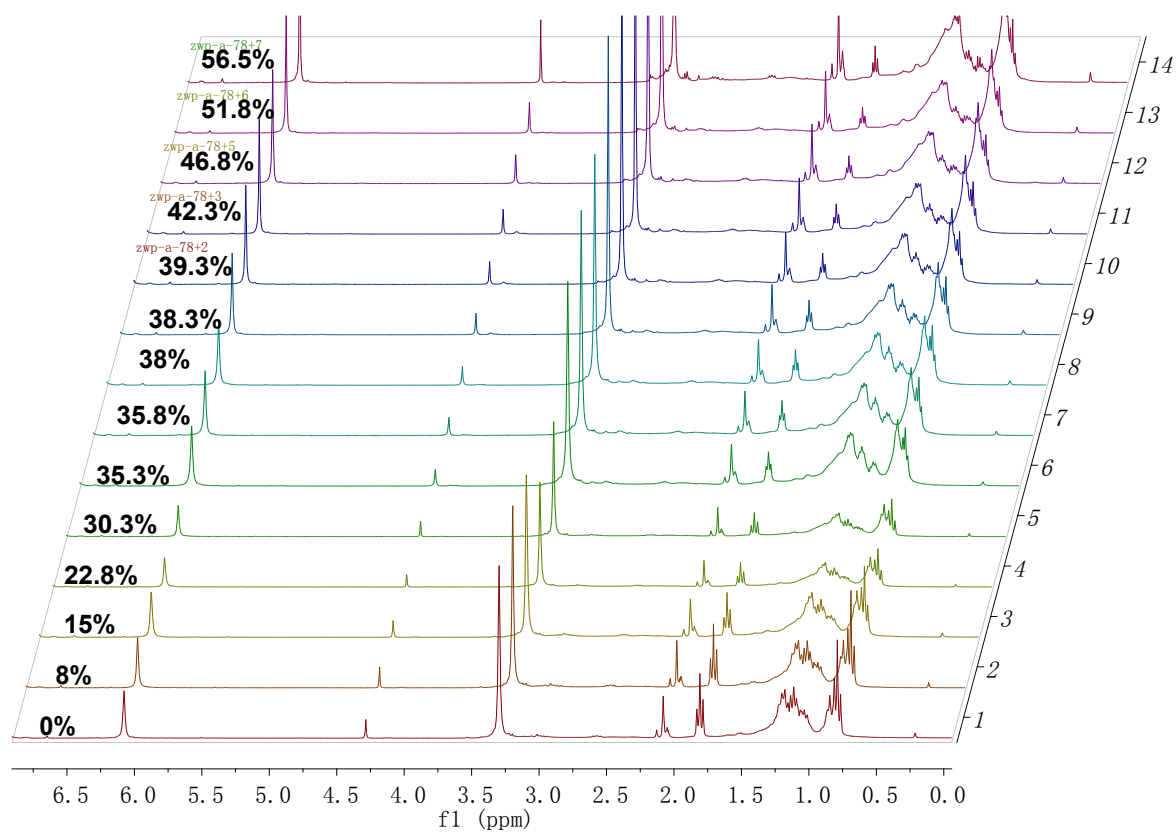**Figure S12. NMR monitoring experiments of 1-chloro-1-octyne homopolymerization using Pd-^{i}Pr.**

Figure S13. In-situ switching experiments of 1-chloro-1-octyne homopolymerization using Pd-^{i}Pr.

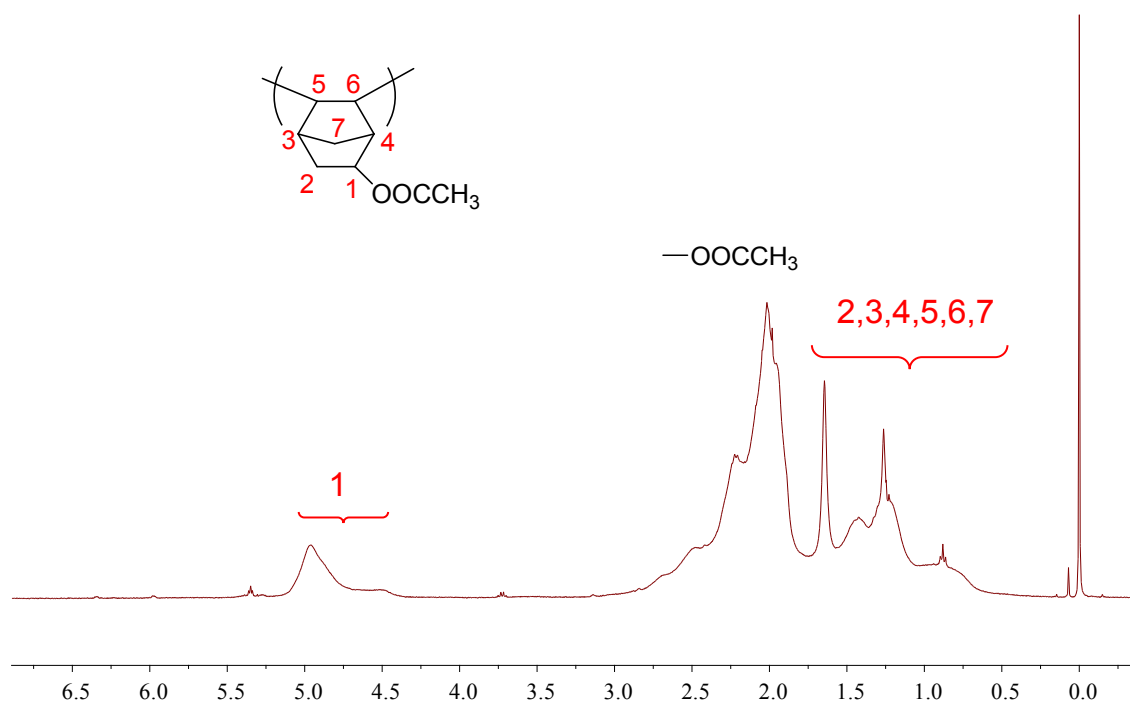## 7. ^{1}H and ^{13}C NMR spectra of the polymers

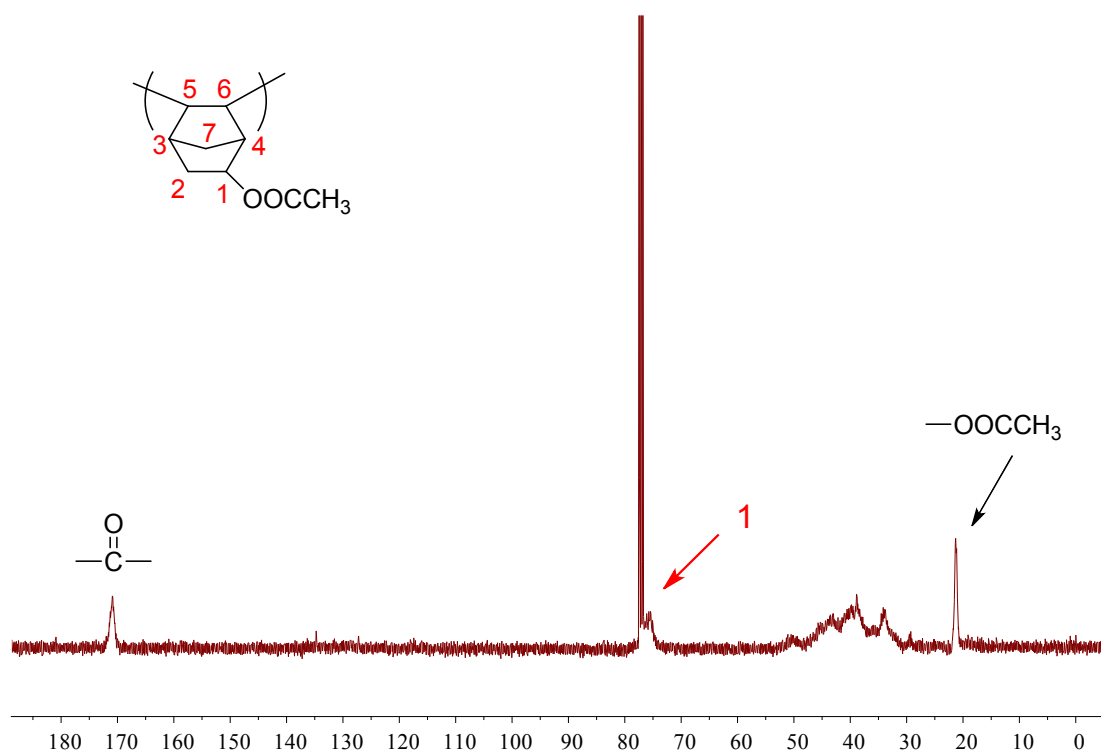Figure S14. ^{1}H NMR spectrum of Poly(NB-OAc) (table 1, entry 5).

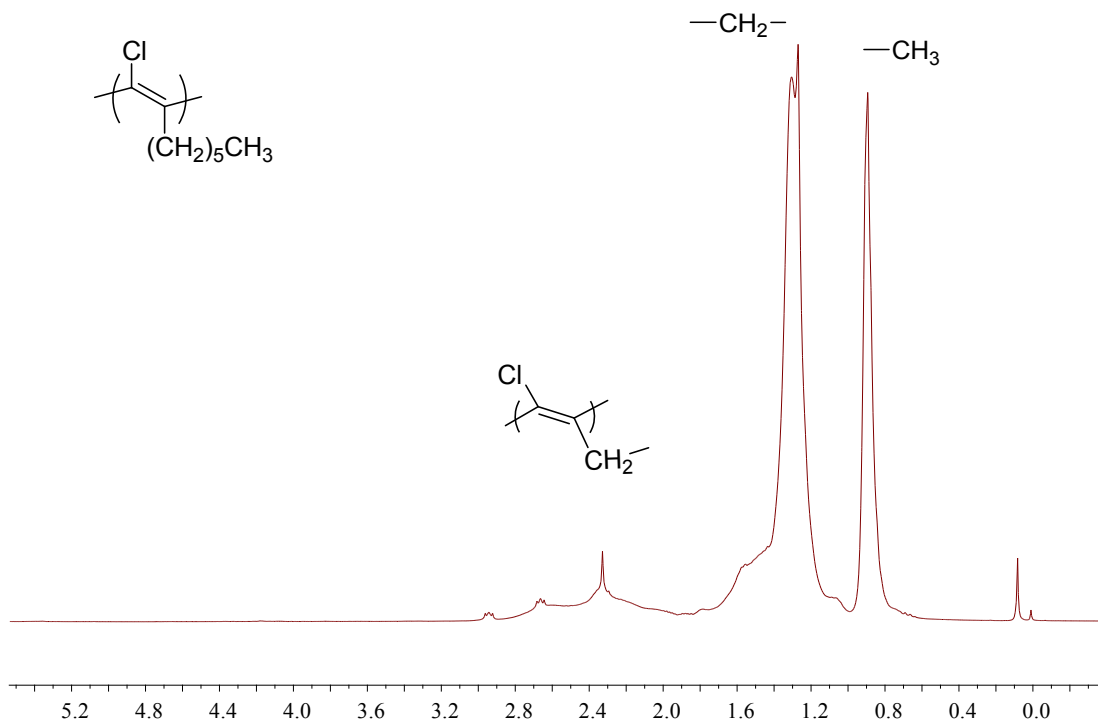Figure S15. ^{13}C NMR spectrum of Poly(NB-OAc) (table 1, entry 5).

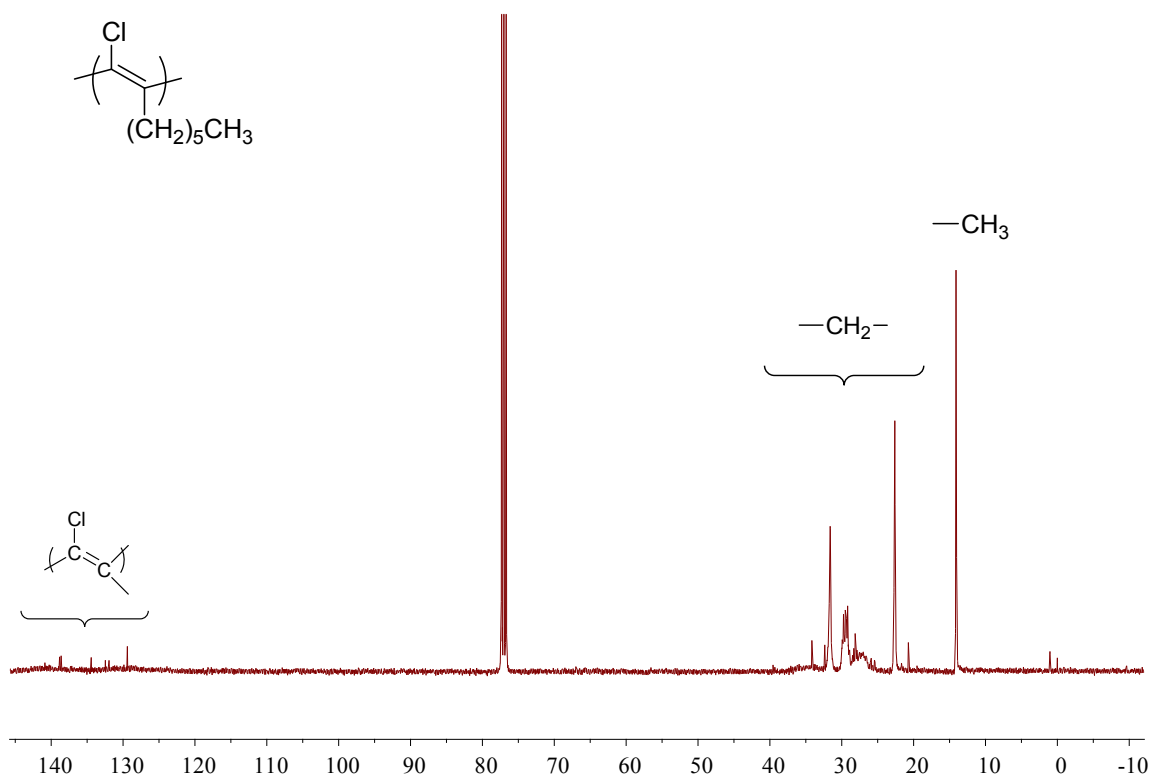**Figure S16. ¹H NMR spectrum of Poly(1-chloro-1-octyne) (table 1, entry 8).**

Figure S17. ¹³C NMR spectrum of Poly(1-chloro-1-octyne) (table 1, entry 8).

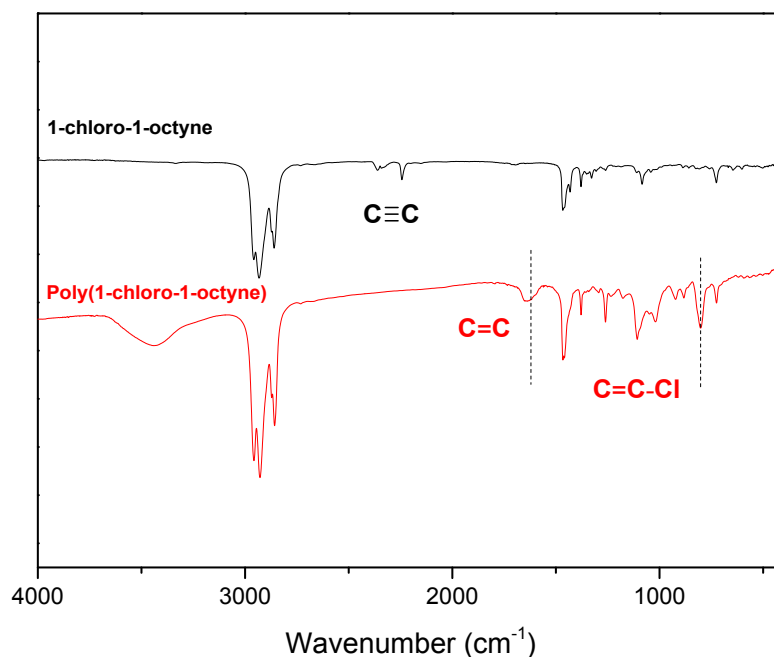## 8. IR spectra of Poly(1-chloro-1-octyne)

Figure S18. IR spectra of Poly(1-chloro-1-octyne) (table 1, entry 8).

9. X-Ray Crystallography of complex Pd-Me.

Experimental for Pd-Me

Single crystals of $C_{30}H_{27}ClN_2O_2Pd$ **[zwp-412]** were **[yellow]**. A suitable crystal was selected and **amounted** on a **Xcalibur, Sapphire3, Gemini ultra** diffractometer. The crystal was kept at 291(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

Crystal structure determination of [zwp-412]

Crystal Data for $C_{30}H_{27}ClN_2O_2Pd$ (M =589.38 g/mol): monoclinic, space group C2/c (no. 15), a = 38.488(3) Å, b = 7.7754(6) Å, c = 17.7580(9) Å, β = 93.993(6)°, V = 5301.3(6) Å^3, Z = 8, T = 292(2) K, μ(MoKα) = 0.831 mm^{-1}, $Dcalc$ = 1.477 g/cm^3, 15250 reflections measured (7.006° $\leq 2\Theta \leq$ 58.456°), 6088 unique (R_{int} = 0.0414, R_{sigma} = 0.0589) which were used in all calculations. The final R_1 was 0.0492 (I > 2σ(I)) and wR_2 was 0.1667 (all data).

Refinement model description

Number of restraints - 13, number of constraints - unknown.
Details:
N/A

This report has been created with Olex2, compiled on 2016.09.09 svn.r3337 for OlexSys. Please <u>let us know</u> if there are any errors or if you would like to have additional features.
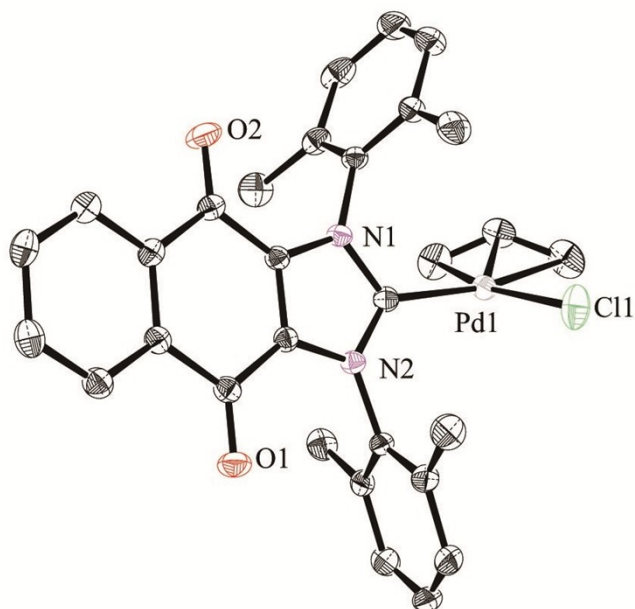

Figure S19. Molecular structure of **Pd-Me.**

Table S2. Crystal data and structure refinement for Pd-Me.

Identification code	zwp-412
Empirical formula	$C_{30}H_{27}ClN_2O_2Pd$
Formula weight	589.38
Temperature/K	292(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	38.488(3)
b/Å	7.7754(6)
c/Å	17.7580(9)
α /°	90
β /°	93.993(6)
γ /°	90
Volume/Å^3	5301.3(6)
Z	8
ρ $_{calc}$g/cm^3	1.477
μ /mm^{-1}	0.831
F(000)	2400.0
Crystal size/mm^3	0.350 × 0.320 × 0.280

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.006 to 58.456
Index ranges	$-52 \leq h \leq 48$, $-6 \leq k \leq 10$, $-23 \leq l \leq 22$
Reflections collected	15250
Independent reflections	6088 [R_{int} = 0.0414, R_{sigma} = 0.0589]
Data/restraints/parameters	6088/13/333
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ(I)]	R_1 = 0.0492, wR_2 = 0.1258
Final R indexes [all data]	R_1 = 0.0843, wR_2 = 0.1667
Largest diff. peak/hole / e Å^{-3}	0.72/-0.84

References

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. G. M. Sheldrick, SHELXL 97, Programs for structure refinement, Universität Göttingen, 1997.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.