

Electronic Supplementary Material (ESI) for Nanoscale.  
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## Electronic Supplementary Information for

### Consecutive One-Pot Alkyne Semihydrogenation/Alkene Dioxygenation Reactions by Pt(II)/Cu(II) Single-Chain Nanoparticles in Green Solvent

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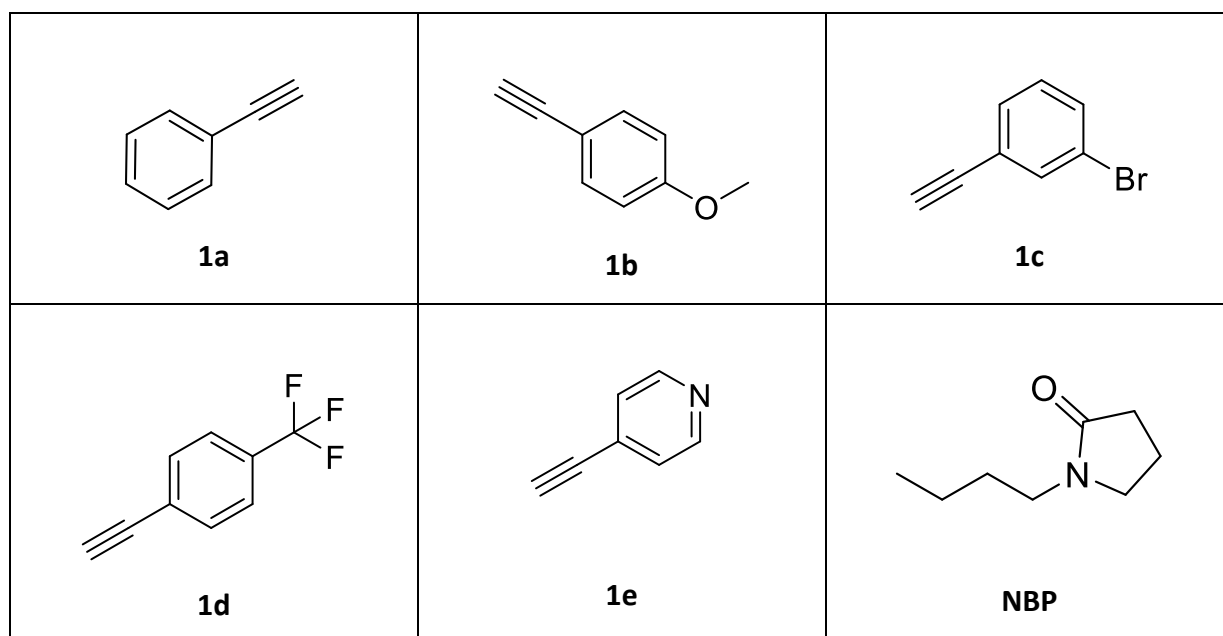
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## 1. Materials

Methyl methacrylate (MMA) (99%), (2-acetoacetoxy)ethyl methacrylate (AEMA) (95%), 2,2'-azo(2-methylpropionitrile) (AIBN) ( $\geq 98\%$ ), *p*-carboxybenzenesulfonazide (*p*-CBSA) (97%), triethylamine ( $\text{Et}_3\text{N}$ ) ( $>99\%$ ), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) (anhydrous,  $\geq 99.8\%$ ), ethyl acetate ( $\text{EtOAc}$ ) (anhydrous, 99.8%), diethyl ether ( $\text{Et}_2\text{O}$ ) (ACS reagent, anhydrous,  $>99.0\%$ ), deuterated chloroform ( $\text{CDCl}_3$ ) (99.96 atom % D, containing 0.03% (v/v) tetramethylsilane), *N,N*-dimethylformamide (DMF) ( $\geq 99.9\%$ ), *n*-hexane (Hex) ( $>95\%$ ), *N*-butylpyrrolidinone (NBP) ( $\geq 99.5\%$ ), (1,5-cyclooctadiene)platinum(II) dichloride ( $\text{Pt}(\text{COD})\text{Cl}_2$ ), copper (II) acetate ( $\text{Cu}(\text{OAc})_2$ ) (98%), magnesium sulphate ( $\text{Mg}_2\text{SO}_4$ ) (anhydrous,  $\geq 99.5\%$ ), phenylacetylene (**1a**) (98%) were purchased from Sigma-Aldrich and used, unless specified, as received. 2-Cyanoprop-2-yl-dithiobenzoate (CPDB) ( $\geq 97\%$ ) was purchased from Strem Chemicals. Methanol (MeOH) (synthesis grade) and THF (HPLC grade) were purchased from Scharlab. 1-Ethynyl-4-methoxybenzene (**1b**) ( $>98.0\%$  by GC), 3-bromophenylacetylene (**1c**) ( $>98.0\%$  by GC), 4-ethynylbenzotrifluoride (**1d**) ( $>98.0\%$  by GC), 4-Pyridylacetylene (**1e**) ( $>98.0\%$  by GC) were purchased from TCI Chemicals. *N*-Hydroxyphthalimide (NHPI) (98%) was purchased from BLDPharm. Purified water was obtained from a Thermo Scientific apparatus (Barnstead TII Pure Water System). AIBN was recrystallized from methanol. MMA was purified by distillation before use. AEMA was purified by passing through alumina.



## 2. Techniques

$^1\text{H}$  nuclear magnetic resonance (NMR) spectra were obtained at room temperature (r.t.) using a Bruker spectrometer operating at 400 MHz with  $\text{CDCl}_3$  as the solvent. Size exclusion chromatography (SEC) data were acquired using a PL-GPC 50 instrument from Agilent Technologies, which integrates differential refractive index (DRI) and multi-angle light scattering (MALS) detectors. DMF containing 0.1% of LiBr with a flow of 1.0 mL/min was used as an eluent. A PLgel MIXED, 7.5 x 50 mm, 10  $\mu\text{m}$ , guard column, and a PLgel 500 Å, 7.5 x 300 mm, 5  $\mu\text{m}$ , or a PL PolarGel-M, 7.5 x 300 mm, 8  $\mu\text{m}$ , HPLC columns were used. The molecular weights of the different samples were determined using a  $\text{dn}/\text{dc}$  value of 0.0608. SEC data were analysed using Wyatt's ASTRA Software (version 8.1). Dynamic light scattering (DLS) measurements were carried out at r.t. on a Malvern Zetasizer Nano ZS apparatus. Metal content in the single-chain nanoparticles was determined by inductively coupled plasma-mass spectrometry (ICP-MS). Fourier transform infrared (IR) spectra were recorded at r.t. on a JASCO 3600 FTIR spectrometer. Elemental analysis (EA) were performed in a Euro EA3000 elemental analyzer (CHNS).

## 3. Methods

### *Synthesis of P0.*

In a typical procedure, MMA (3 mL, 28.2 mmol), AEMA (2.63 mL, 15.58 mmol), CPDB (22.2 mg, 0.1 mmol) and AIBN (16.5 mg, 1 mmol) were dissolved in EtOAc (10.45 mL). The solution was degassed by bubbling  $\text{N}_2$  for 15 min. The copolymerization reaction was carried at 65 °C for 24 h. After isolation of the resulting copolymer **P0** by precipitation in MeOH, it was dried under dynamic vacuum until constant weight. Yield: 94.0%.  $\beta$ -ketoester content ( $^1\text{H}$  NMR): 30 mol%.  $M_w(\text{SEC}) = 73.6$  kDa,  $D(\text{SEC}) = 1.17$ .

### *Synthesis of P1.*

The synthesis of **P1** was conducted under light-protected conditions. The process involved dissolving 300 mg (0.47 mmol) of **P0** in 10 mL of  $\text{CH}_2\text{Cl}_2$  at r.t. Next, *p*-CBSA (12.25 mg, 0.35 eq.) and  $\text{Et}_3\text{N}$  (0.4 mL, 2.87 mmol) were added to the solution, which was then stirred for 24 h

protected from light. Upon completion of the reaction, the resulting solution was concentrated and precipitated in MeOH, and the functionalized copolymer, **P1**, was dried in a vacuum oven in the absence of light. Yield: 76%.  $\alpha$ -diazo- $\beta$ -ketoester content (EA): 19 mol%.  $M_w$  (SEC) = 75.3 kDa,  $\bar{D}$  (SEC) = 1.15,  $R_h$  (DLS) = 12.5 nm.

#### *Synthesis of P1-SCNPs (as a control).*

The synthesis of **P1-SCNPs** from **P1** was achieved *via* irradiation with ultraviolet light. 15 mg (0.07 mmol) of **P1** were dissolved in 15 mL of DMF and the solution was exposed to UV light irradiation (365 nm) for 1 h. Subsequently, the reaction was quenched by the addition of liquid nitrogen. The resulting **P1-SCNPs** were precipitated with diethyl ether and dried under dynamic vacuum. Yield: 92%.  $M_w$  (SEC) = 75.6 kDa,  $\bar{D}$  (SEC) = 1.11,  $R_h$  (DLS) = 10.0 nm.

#### *Synthesis of Pt(II)-SCNPs.*

The synthesis of **Pt(II)-SCNPs** from **P1** was achieved *via* irradiation with ultraviolet light. Specifically, 15 mg (0.07 mmol) of **P1** and 1.96 mg (0.00525 mmol) Pt(COD)Cl<sub>2</sub> were dissolved in 15 mL of DMF and the solution was exposed to UV light irradiation (365 nm) for 1 h. Subsequently, the reaction was quenched by the addition of liquid nitrogen. The resulting Pt(II)-SCNPs were precipitated with diethyl ether and dried under dynamic vacuum. Yield: 86%. Pt(II) content (ICP-MS): 0.13 mol%.  $M_w$  (SEC) = 78.4 kDa,  $\bar{D}$  (SEC) = 1.15,  $R_h$  (DLS) = 9.9 nm.

#### *Synthesis of Pt(II)/Cu(II)-SCNPs.*

**P1** (15 mg, 0.07 mmol) and Pt(COD)Cl<sub>2</sub> (1.96 mg, 0.00525 mmol) were dissolved in 15 mL of DMF and the solution was exposed to UV light irradiation (365 nm) for 1 h. The reaction was promptly quenched by the addition of liquid nitrogen. A concentrated solution of Cu(OAc)<sub>2</sub> in DMF (0.954 mg, 0.00525 mmol of Cu) was then added dropwise and the reaction mixture was stirred for 24 h. The resulting Pt(II)/Cu(II)-SCNPs were precipitated with diethyl ether and dried under dynamic vacuum. Yield: 79%. Pt(II) content (ICP-MS): 0.14 mol%. Cu(II) content (ICP-MS): 0.43 mol%.  $M_w$  (SEC) = 81.6 kDa,  $\bar{D}$  (SEC) = 1.18,  $R_h$  (DLS) = 8.6 nm.

*Synthesis of Cu(II)-SCNPs (as a control).*

**P1-SCNPs** (15 mg, 0.07 mmol) was dissolved in DMF (15 ml) at r.t. A solution of Cu(OAc)<sub>2</sub> in DMF (0.954 mg, 0.00525 mmol) was then added dropwise, and the reaction mixture was stirred for 24 h. The resulting **Cu(II)-SCNPs** were precipitated with diethyl ether and dried under dynamic vacuum. Yield: 95%. Cu(II) content (ICP-MS): 0.41 mol%.  $M_w$  (SEC) = 77.1 kDa,  $D$  (SEC) = 1.21,  $R_h$  (DLS) = 10.0 nm.

*General procedure for the consecutive one-pot alkyne semihydrogenation / alkene dioxygenation reactions catalysed by Pt(II)/Cu(II)-SCNPs in NBP at r.t.*

In a 10 mL round bottomed, oven-dried flask, which was previously equipped of magnetic stir bar, 2 mL of **Pt(II)/Cu(II)-SCNPs** solution in NBP ([polymer] = 1 mg mL<sup>-1</sup>) were added, followed by 0.07 mmol of the alkyne compound (**1a-1e**) and the system was sealed with rubber septum. The solution was then degassed by purging argon flow for 5 min. After displacement of atmospheric oxygen, the flask was equipped of a security elastic balloon to ensure both no extra-pressure in the system and, simultaneously, to reduce volatility of solvents and substrates. A low-pressure molecular hydrogen flow was then bubbled in the reaction mixture at r.t. at definite interval of times (10 min bubbling each 20 min until reaction completion). The progress of the reaction was monitored by thin layer chromatography (TLC) using EtOAc and Hex as eluents. After the semihydrogenation reaction was complete, 13.68 mg (0.084 mmol) of *N*-hydroxyphthalimide was added to the solution at r.t. and under air (open flask). The progress of the reaction was monitored by TLC using EtOAc and *n*-hexane as eluents. After reaction completion, 10 mL of water was added to the solution. The resultant mixture was extracted with EtOAc (3 x 5 mL) and successively washed with water (3 x 5 mL). The organic solution was dried over anhydrous Mg<sub>2</sub>SO<sub>4</sub>, filtered and evaporated to give a residue that was purified on silica gel column chromatography using Hex and EtOAc as eluents to afford the corresponding  $\beta$ -Keto-*N*-alkoxyphthalimide product (**3a-3e**).

#### 4. Additional Tables and Schemes

**Table S1.** Elemental analysis (EA) results of **P0** and **P1**

Sample	C (%)	H (%)	N (%)
<b>P0</b>	57.41	7.51	-
<b>P1</b>	55.62	6.65	4.16

**Table S2.** Inductively coupled plasma-mass spectrometry (ICP-MS) results of **Pt(II)-SCNPs**, **Cu(II)-SCNPs** and **Pt(II)/Cu(II)-SCNPs**

Sample	Pt(II) content ( $\mu\text{g}/\text{mg}$ )	Cu(II) content ( $\mu\text{g}/\text{mg}$ )
<b>Pt(II)-SCNPs</b>	9.29	-
<b>Cu(II)-SCNPs</b>	-	9.11
<b>Pt(II)/Cu(II)-SCNPs</b>	9.73	9.54

**Table S3.** Comparison of TON and TOF of **Pt(II)/Cu(II)-SCNPs** and previous results.

Catalyst	Reaction	Solvent <sup>a</sup>	T (°C)	t (h)	TON <sup>b</sup>	TOF <sup>c</sup> (h <sup>-1</sup> )	Ref.
Pt@mTiO <sub>2</sub>	<b>1a</b> → <b>2a</b>	14D	r.t.	7	80	11	1
Pt@CNTs	<b>1a</b> → <b>2a</b>	EtOH	50	1	127	127	2
Pt(COD)Cl <sub>2</sub>	<b>1a</b> → <b>2a</b>	DMF	r.t.	4	60	15	This work
<b>Pt(II)/Cu(II)SCNPs</b>	<b>1a</b> → <b>2a</b>	NBP	r.t.	4	679	170	This work
Cu(OAc) <sub>2</sub>	<b>2a</b> → <b>3a</b>	DMF	r.t.	9	6.5	0.7	3
[Cu(MeCN) <sub>4</sub> ]ClO <sub>4</sub>	<b>2a</b> → <b>3a</b>	MeCN	r.t.	12	17	1.4	4
<b>Pt(II)/Cu(II)SCNPs</b>	<b>2a</b> → <b>3a</b>	NBP	r.t.	7	186	27	This work

<sup>a</sup> 14D =1,4-Dioxane; EtOH = Ethanol; DMF = *N,N*-Dimethylformamide; NBP = *N*-Butyl pyrrolidone; MeCN = Acetonitrile.

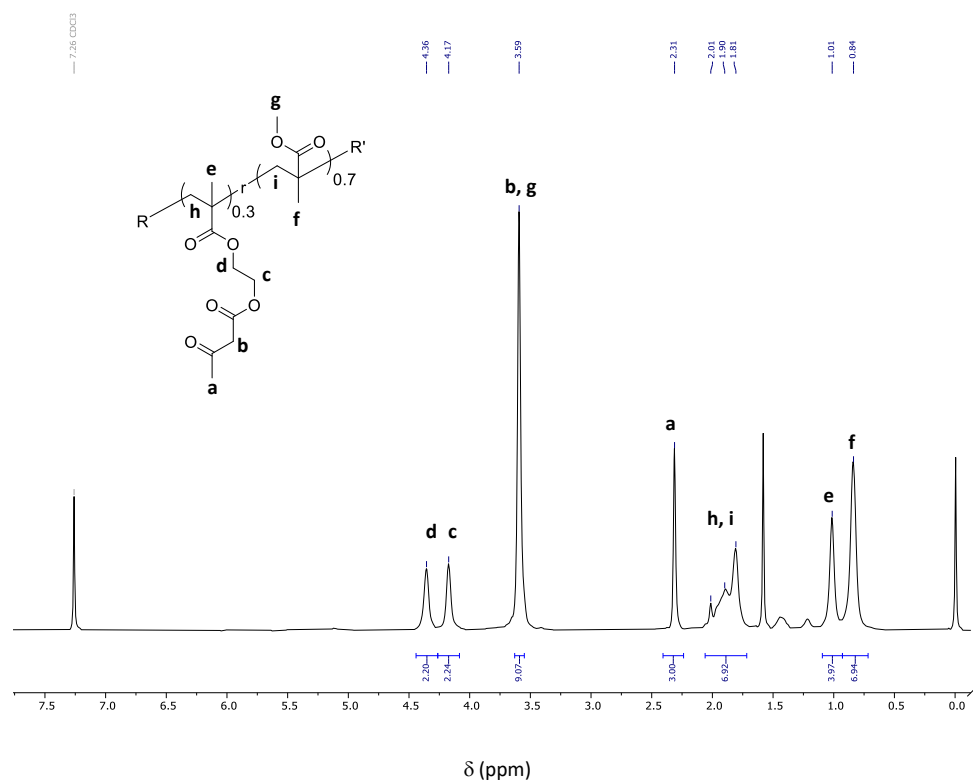
<sup>b</sup>TON = ( moles of product / moles of catalyst ).

<sup>c</sup>TOF = [ TON / t(h) ].

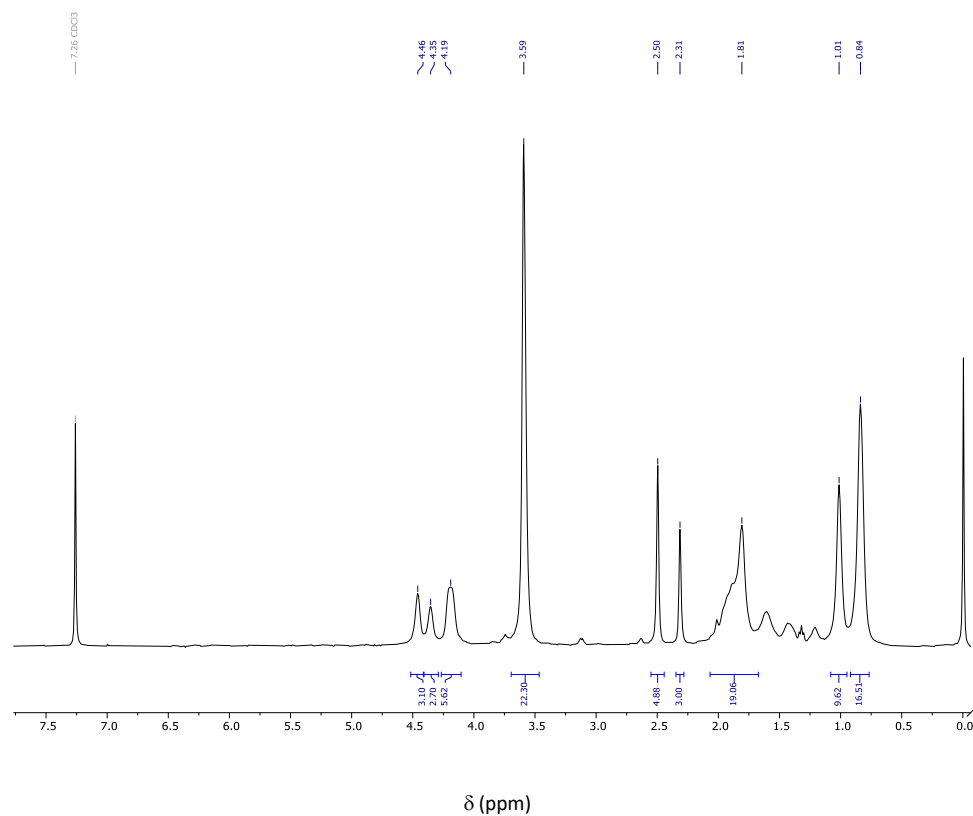




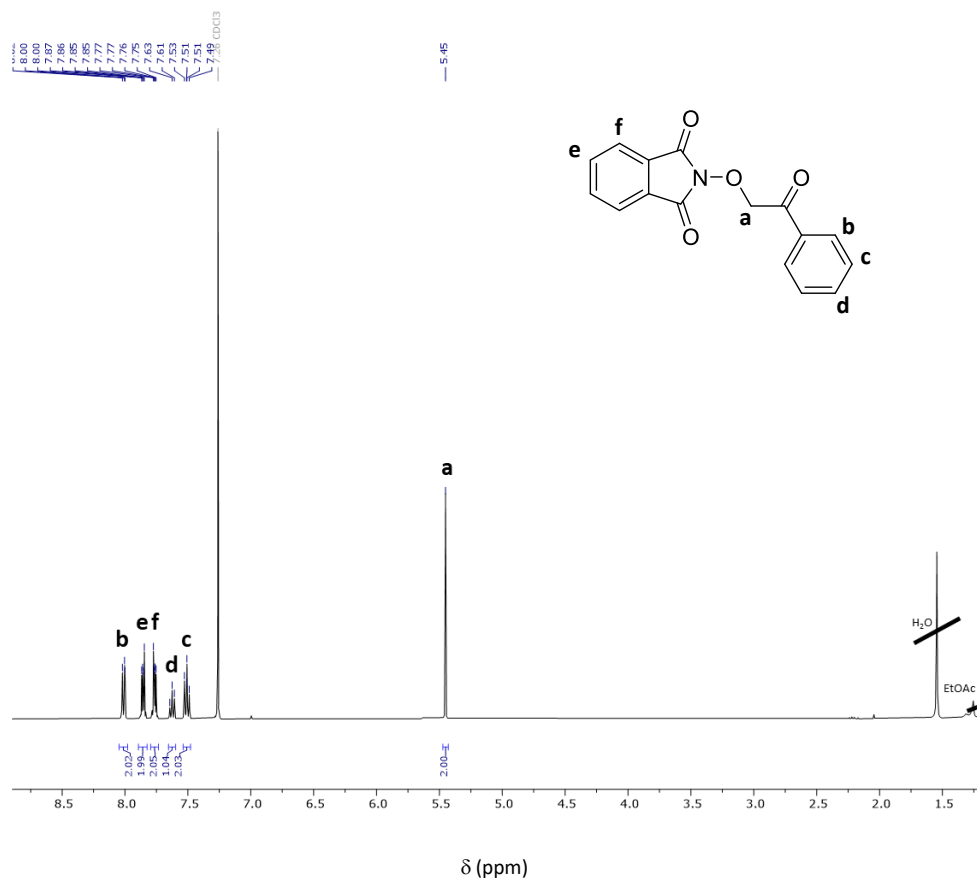
## 6. Additional Figures



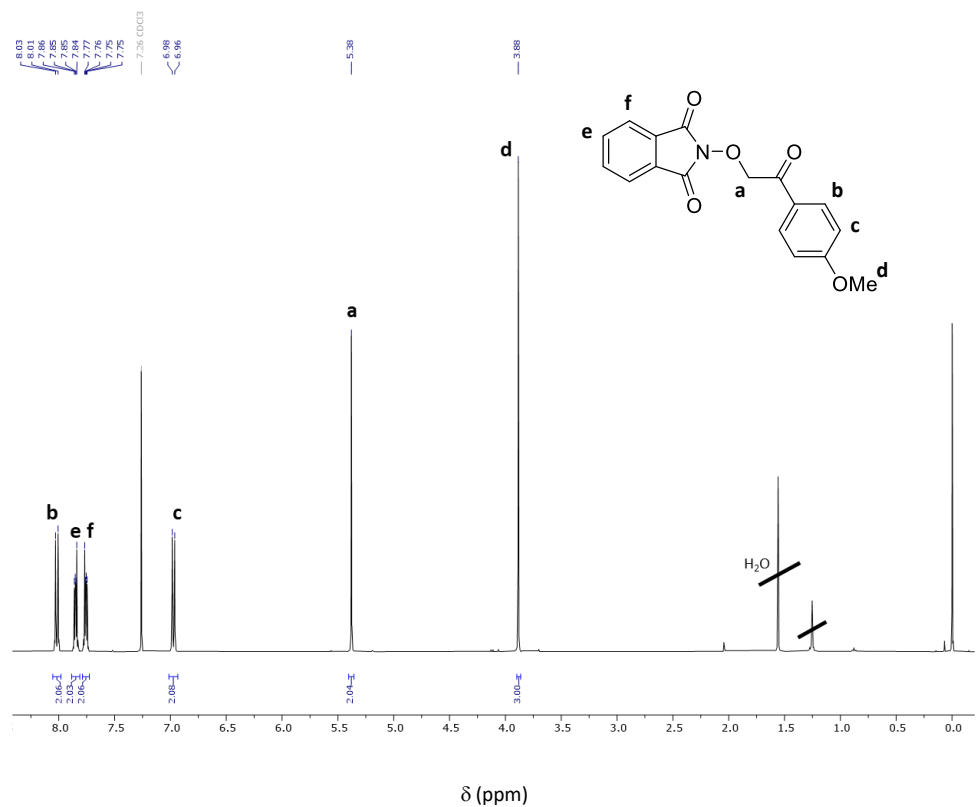
**Fig S1.** <sup>1</sup>H NMR spectrum of **PO** in CDCl<sub>3</sub>.



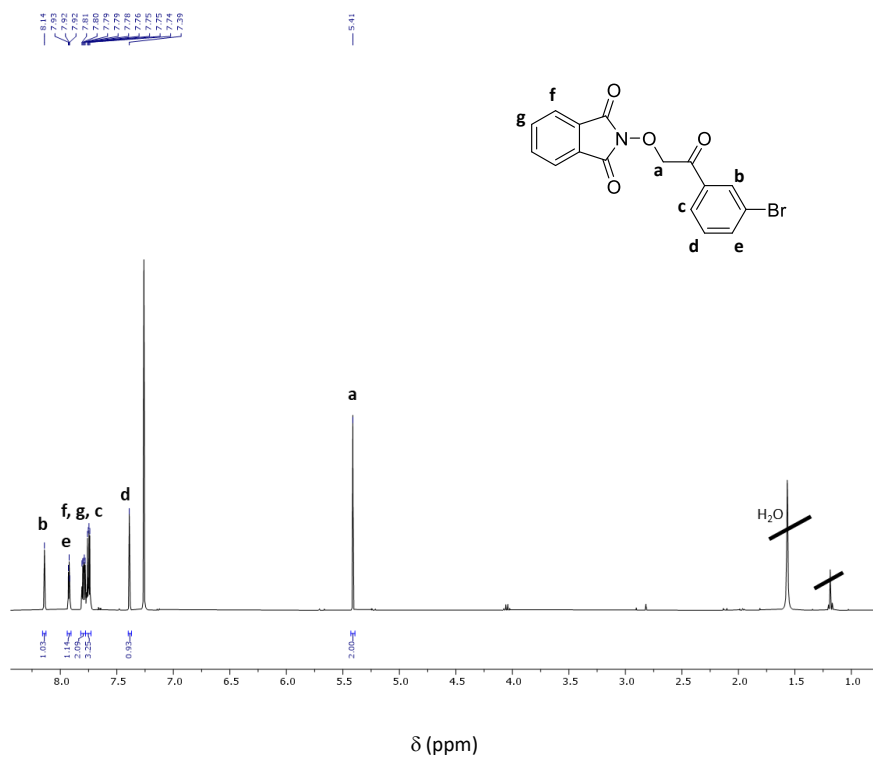
**Fig S2.** <sup>1</sup>H NMR spectrum of **P1** in CDCl<sub>3</sub>.



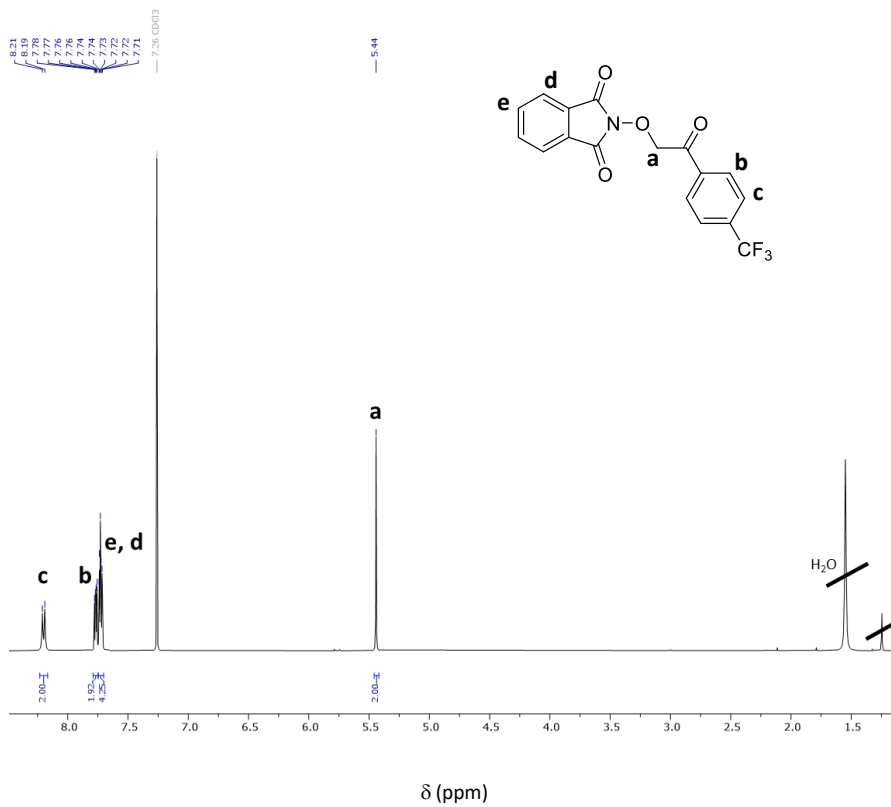
**Fig S3.** <sup>1</sup>H NMR spectrum of **3a** in CDCl<sub>3</sub>.



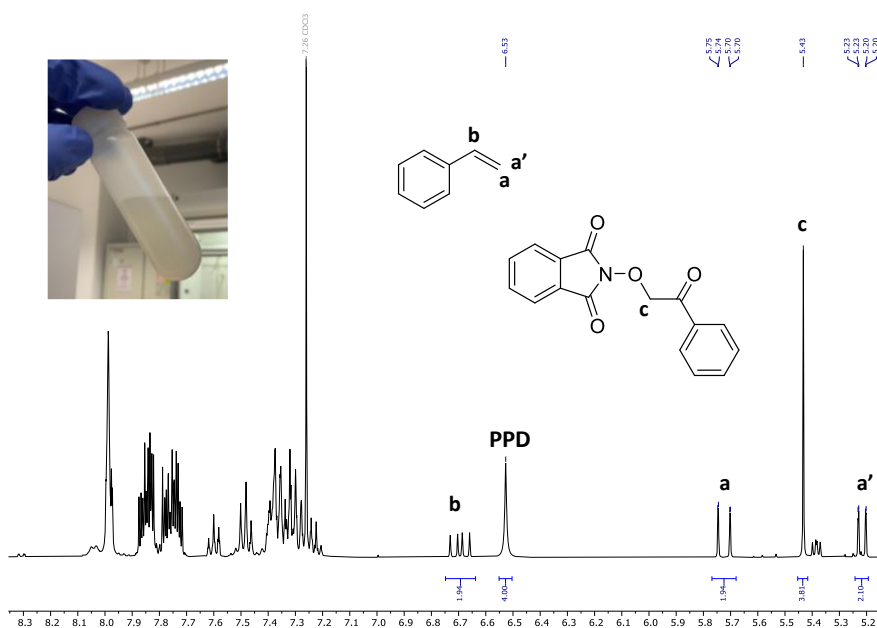
**Fig S4.** <sup>1</sup>H NMR spectrum of **3b** in CDCl<sub>3</sub>.



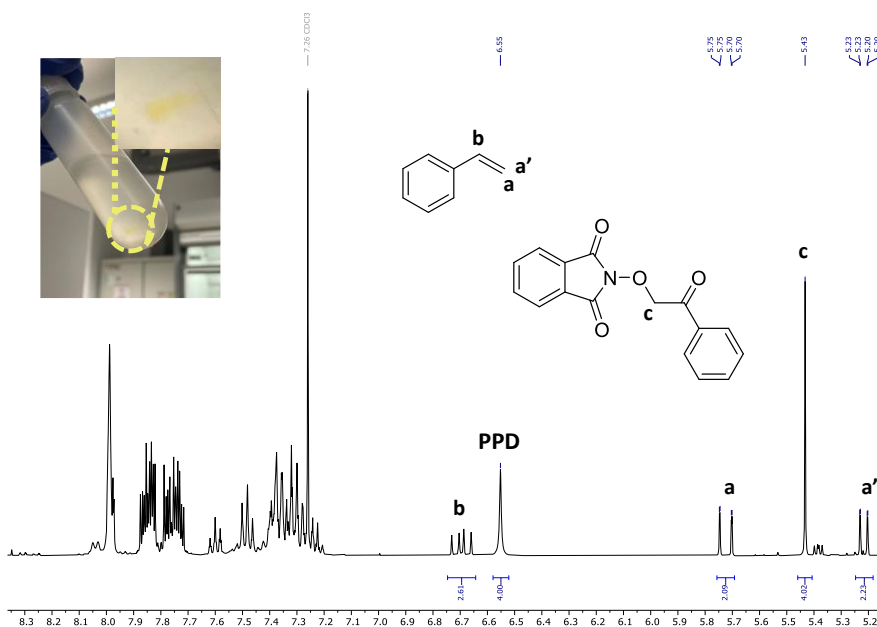
**Fig S5.** <sup>1</sup>H NMR spectrum of **3c** in CDCl<sub>3</sub>.



**Fig S6.** <sup>1</sup>H NMR spectrum of **3d** in CDCl<sub>3</sub>.



**Fig S7.** Results from leaching experiments: <sup>1</sup>H NMR spectrum of **1a** synthesized with Pt(II)/Cu(II)-SCNPs after 3h of reaction time (**yield: 33.6 %**). Solvent: CDCl<sub>3</sub>. Internal standard: *p*-phenylenediamine, PPD.



**Fig S8.** Results from leaching experiments: <sup>1</sup>H NMR spectrum of **1a** synthesized with Pt(II)/Cu(II)-SCNPs by removing the catalyst after 3h of reaction time and allowing the reaction to proceed additionally for 4h without Pt(II)/Cu(II)-SCNPs (**yield: 35.5 %**). Solvent: CDCl<sub>3</sub>. Internal standard: PPD.

## 7. References

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