

## Supporting Information

# N-Heterocyclic Carbene-based Porous Polymer Macroligand for the Ni-catalyzed C-H Arylation of Benzothiophenes

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## 1. Materials and methods

### 1.1 Materials

4-vinylbenzyl chloride (90%), 1-methylimidazole (99%), Nickel(II) chloride ethylene glycol dimethyl ether complex ( $\text{NiCl}_2:\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$ , 98%), divinylbenzene (DVB, 80%), 1,1'-azobis(cyclohexanecarbonitrile) (ACHN, 98%), thianaphthene (98%), lithium bis(trimethylsilyl)amide (LiHMDS, 97%), potassium bis(trimethylsilyl)amide (KHMDS, 95%), sodium bis(trimethylsilyl)amide (NaHMDS, 95%), magnesium bis(hexamethyldisilazide) ( $\text{Mg}(\text{HMDS})_2$ , 95%), lithium tert-butoxide ( $\text{LiO}^t\text{Bu}$ , 97%), potassium tert-butoxide ( $\text{KO}^t\text{Bu}$ ,  $\geq 98\%$ ), potassium carbonate ( $\text{K}_2\text{CO}_3$ ,  $\geq 99\%$ ), cesium carbonate ( $\text{Cs}_2\text{CO}_3$ , 99%), chlorobenzene (99.8%), bromobenzene (99.5%), anisole (anhydrous, 99.7%), iodobenzene (98%), dodecane (anhydrous,  $\geq 99\%$ ), acetonitrile (anhydrous, 99.8%), tetrahydrofuran (THF) (anhydrous,  $\geq 99.9\%$ ), 1,4-dioxane (anhydrous, 99.8%), 2-methyltetrahydrofuran (anhydrous,  $\geq 99\%$ ), toluene (anhydrous, 99.8%), were purchased from Sigma-Aldrich.

TCI: phenyl *p*-toluenesulfonate (99%)

All the chemicals were used without any further purification.

### 1.2 Methods

The solid-state NMR spectra were recorded at room temperature on a Bruker AVANCE III 500 WB spectrometer (11.7 T,  $^{13}\text{C}$  at 125.73 MHz spectral frequency) which is equipped with a 2.5 mm MAS (magic angle spinning) probe with 12.5KHz spinning rate.

ICP-OES analyses were carried out using an Activa instrument from Jobin Yvon.

Nitrogen physisorption experiments of all solids were performed at 77 K using a BELSORP-mini II. Prior to measurements the samples were degassed at 80°C overnight.

IR spectra were recorded using a Nicolet Magna IR 550 FT-IR spectrometer (Thermo Fisher Scientific) in diffuse reflection (resolution 2  $\text{cm}^{-1}$ , 64 scans, Praying Mantis Diffuse Reflection Accessory, Harrick Scientific).

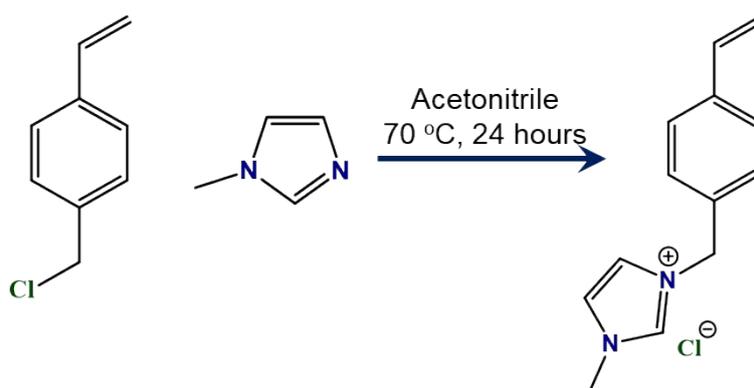
Thermogravimetry analyses were performed on a TGA/DSC 1 STARE System (Mettler Toledo) with a 10 K/min ramp under synthetic air.

Gas Chromatography (GC) FID analysis was conducted on an Agilent Technologies 7890A instrument equipped with a HP-5 column (30 m  $\times$  0.320 mm  $\times$  0.25  $\mu\text{m}$ , Agilent).

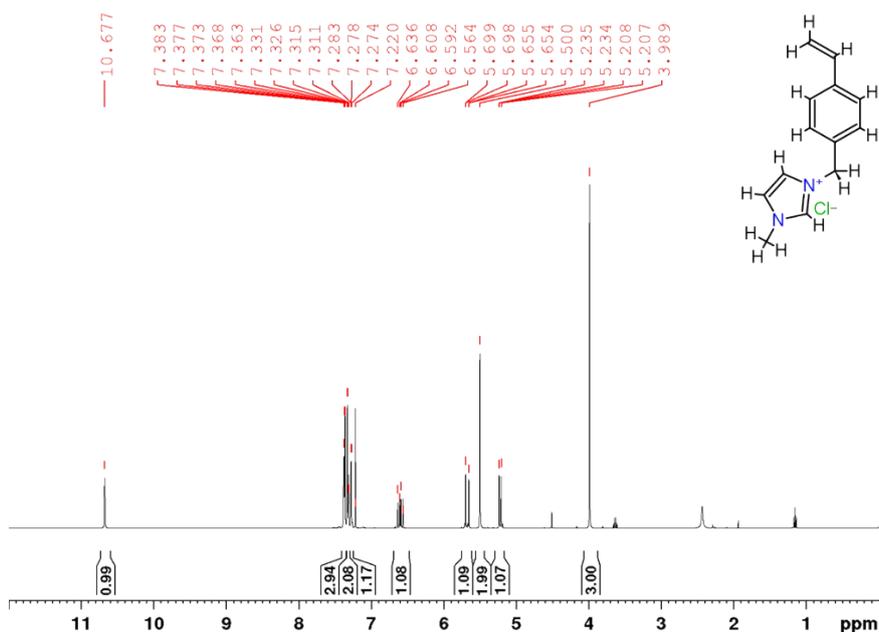
## 2. Catalysts synthesis and characterizations

### 2.1 Synthesis of the imidazolium functionalized vinyl monomer (1-methyl-3-(4-vinylbenzyl)-1H-imidazol-3-ium chloride)

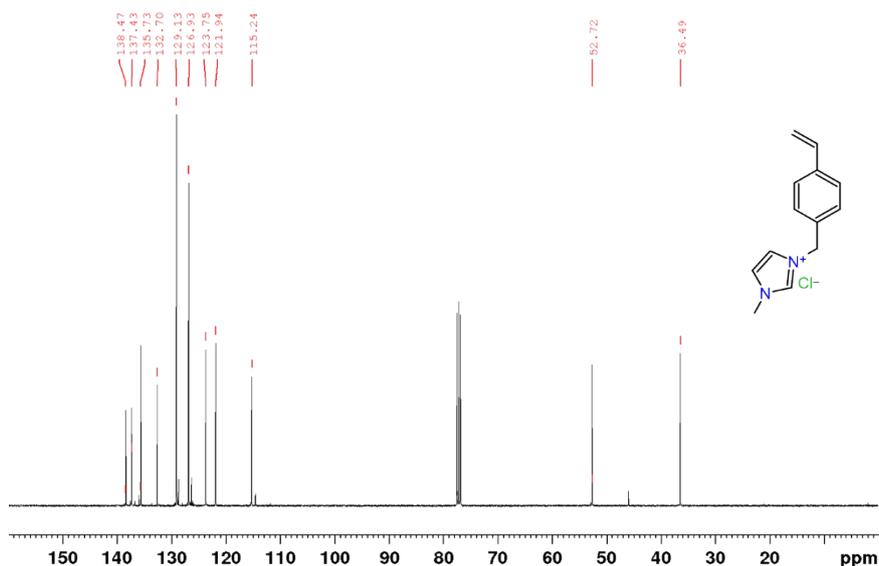
Synthesis of the monomer has been carried out following a reported protocol with minor modification.<sup>1</sup> In a 100 ml round bottom flask 5 g of 4-vinylbenzyl chloride (4.6 ml, 0.033mol) were dissolved in 15 ml of acetonitrile. Then 3.25 g of 1-methylimidazole (2.15 ml, 0.04 mol) was added and was allowed to stir at 70 °C for 24 hours. After completion of the reaction the solvent was evaporated under reduced pressure. Thus, obtained gummy product was washed three times with diethyl ether to remove excess reactants. Furthermore, the gummy product was dried under vacuum at room temperature for 3 hours.



**Scheme S1.** Schematic representation for synthesis of the imidazolium functionalized vinyl monomer.



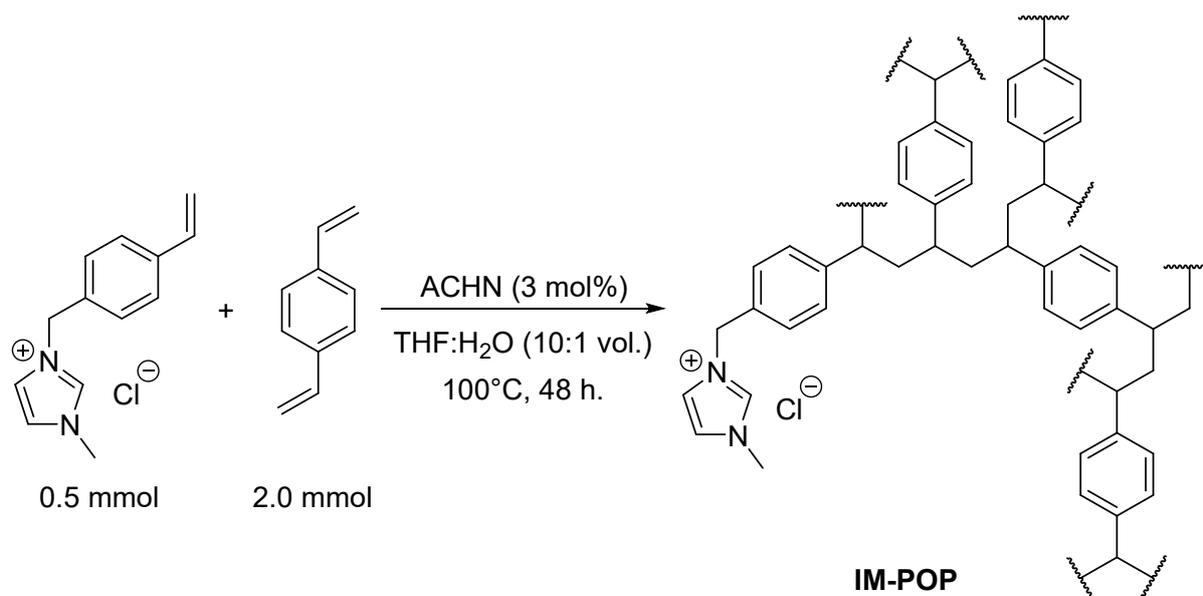
**Figure S1.** <sup>1</sup>H-NMR spectra of 1-methyl-3-(4-vinylbenzyl)-1H-imidazol-3-ium chloride.



**Figure S2.** <sup>13</sup>C-NMR spectra of 1-methyl-3-(4-vinylbenzyl)-1H-imidazol-3-ium chloride.

## 2.2 Synthesis of the N-heterocyclic porous organic polymer (IM-POP)

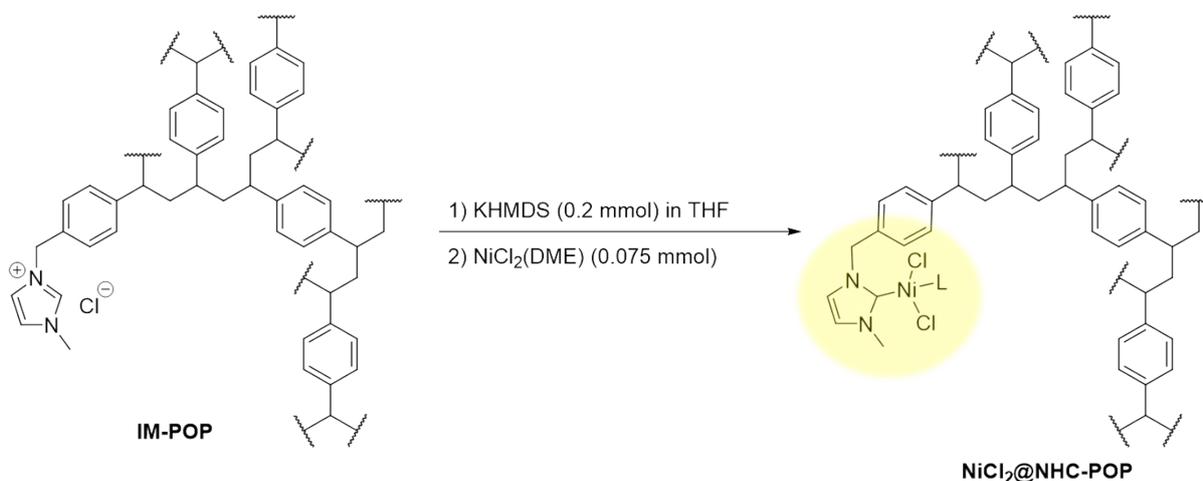
Synthesis of the N-heterocyclic porous organic polymer (**IM-POP**) has been carried out via solvothermal process. In a glass vial 117.5 mg 1-methyl-3-(4-vinylbenzyl)-1H-imidazol-3-ium chloride (0.50 mmol) was dissolved in 6.6 ml of a deaerated THF-H<sub>2</sub>O mixture (10:1, *V:V*). To the solution 356 μL (325.5 mg, 2.0 mmol) divinylbenzene (DVB) (80%, passed through a column of basic Al<sub>2</sub>O<sub>3</sub>) and 19.3 mg (79 μmol) 1,1'-Azobis(cyclohexanecarbonitrile) (ACHN) were added. The reaction mixture was stirred for 30 mins, and bubbled with Ar. Then it was transferred into a Teflon lined stainless-steel autoclave and was sealed properly. The sealed autoclave containing the reaction mixture was allowed to heat at 100 °C for 48 h in an oven. After completion of the reaction the autoclave was cooled to room temperature, the polymer (monolith) was transferred into a Soxhlet thimble and purified by Soxhlet extraction using THF for 24 h. The white solid was dried at 80 °C under vacuum overnight. (Yield: 350 mg of **IM-POP**)



**Scheme S2.** Schematic representation for synthesis of **IM-POP**.

### 2.3 Synthesis of the Ni-infiltrated N-heterocyclic carbene porous organic polymer (**NiCl<sub>2</sub>@NHC-POP**)

Synthesis of the Ni-loaded N-heterocyclic carbene porous organic polymer (**NiCl<sub>2</sub>@NHC-POP**) has been done via deprotonation imidazolium proton followed by infiltration of Ni. In a 15 ml glass vial 100 mg of desolvated **IM-POP** and 40 mg of potassium bis(trimethylsilyl)amide (KHMDs) (0.2 mmol) were taken under Ar atmosphere. 8 ml of anhydrous tetrahydrofuran (THF) was added to the vial and was allowed to stir at room temperature for 30 minutes. Then a solution of Ni(II) chloride ethylene glycol dimethyl ether (**NiCl<sub>2</sub>·glyme**) complex (16.5 mg, 0.075 mmol) was added slowly to the reaction mixture. The mixture was allowed to stir at room temperature for 16 hours under Ar atmosphere. After completion of the reaction, the light green colored solid was separated by centrifugation and was washed thoroughly with MeOH (4 ml, 3 times). Thus, the pale green colored solid was dried under vacuum at 80 °C overnight. (Yield: 80 mg of **NiCl<sub>2</sub>@NHC-POP**)

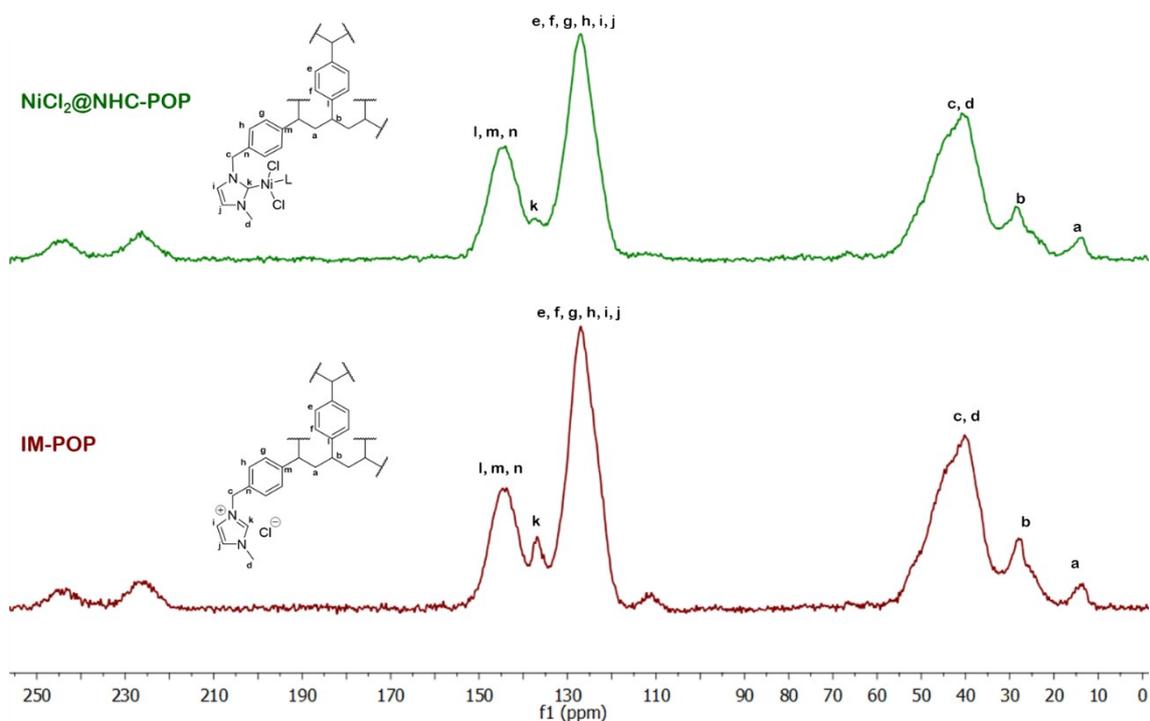


**Scheme S3.** Schematic representation for synthesis of **NiCl<sub>2</sub>@NHC-POP**.

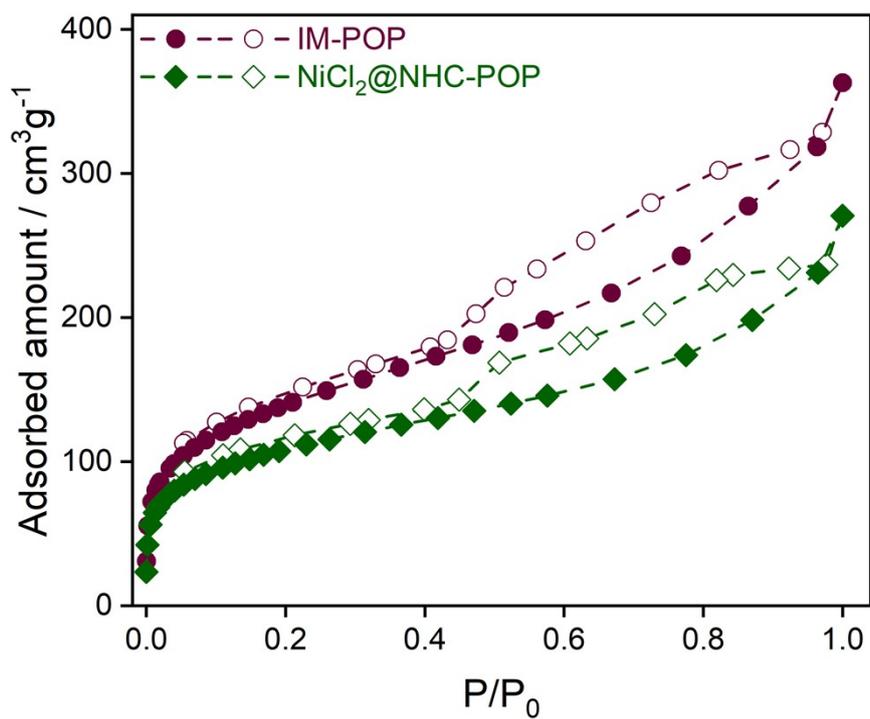
## 2.4 Synthesis of the Ni-infiltrated divinylbenzene porous organic polymer (Ni@DVB-POP)

The divinyl POP (**DVB-POP**) was synthesized in a similar way to **IM-POP**, except styrene has been used here instead of imidazolium monomer used in **IM-POP**. 356  $\mu\text{L}$  (325.5 mg, 2.0 mmol) of divinylbenzene (80%) and 58  $\mu\text{L}$  (52 mg, 0.5 mmol) of styrene (passed through a column of basic  $\text{Al}_2\text{O}_3$ ) were taken in a glass vial and 20.1 mg (0.084 mmol) of ACHN were added. This mixture was dissolved in 6.6 ml of a deaerated THF- $\text{H}_2\text{O}$  mixture (10:1) under Ar. The solution was stirred for 30 min at room temperature. Afterwards, the solution was transferred into a teflon lined stainless-steel autoclave. The autoclave was sealed and placed in a preheated oven at 100  $^\circ\text{C}$  for 48 h. After the completion of the reaction, the autoclave was cooled to room temperature. The obtained polymer (white monolith) was transferred into a Soxhlet thimble and purified by Soxhlet extraction using THF for overnight. The white solid was dried at 80  $^\circ\text{C}$  under vacuum.

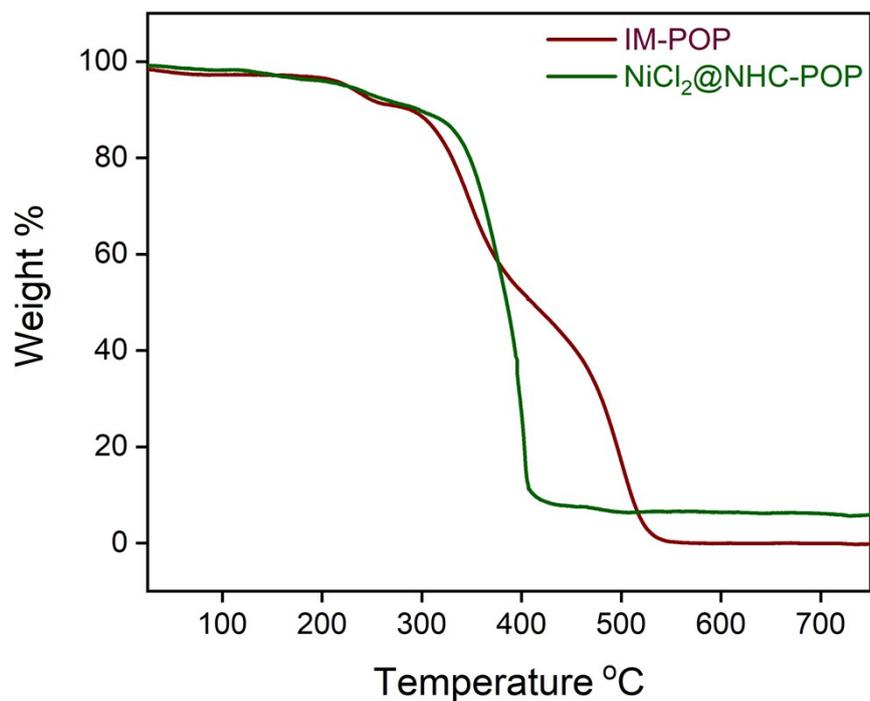
Then the Ni-infiltration in **DVB-POP** was carried out by following the similar protocol of  $\text{NiCl}_2$ @NHC-POP synthesis. 100 mg of desolvated DVB-POP and 40 mg of potassium bis(trimethylsilyl)amide (KHMDs, 0.2 mmol) were placed in a 15 ml glass vial under Ar atmosphere. To the mixture 8 ml of anhydrous THF was added and allowed to stir for 30 minutes at room temperature. After 30 minutes, a solution of  $\text{NiCl}_2$ ·glyme (16.5 mg, 0.075 mmol) was added slowly. The reaction mixture was stirred for 16 hours at room temperature under Ar atmosphere. After 16 hours the solid was separated by centrifugation and was washed with MeOH (4 ml, 3 times). The solid was dried under vacuum at 80  $^\circ\text{C}$  overnight. (Yield: 70 mg of  $\text{NiCl}_2$ @DVB-POP).



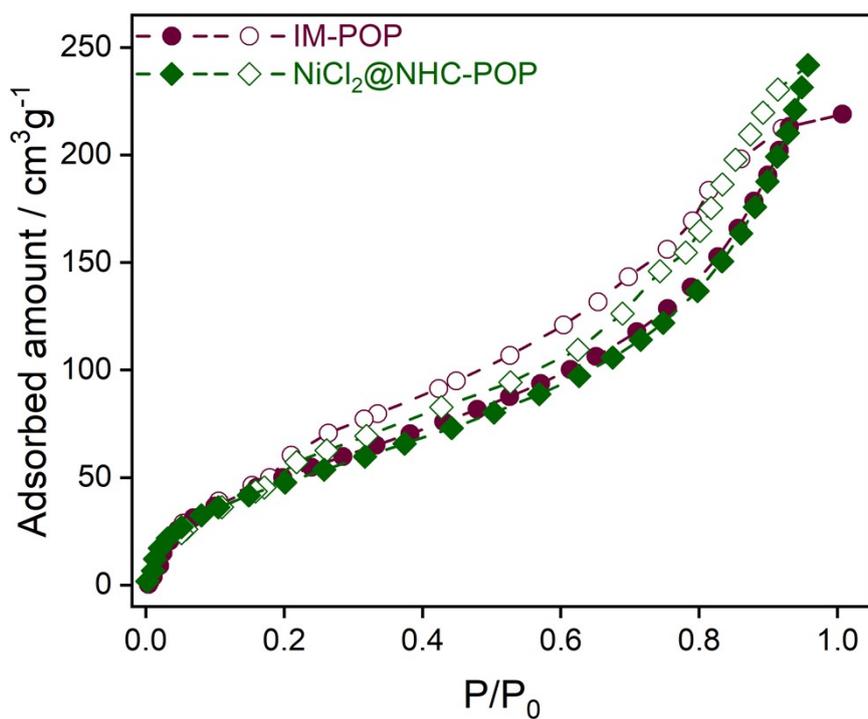
**Figure S3.** Solid state  $^{13}\text{C}$ -NMR of **IM-POP** (burgundy) and  $\text{NiCl}_2$ @NHC-POP (green).



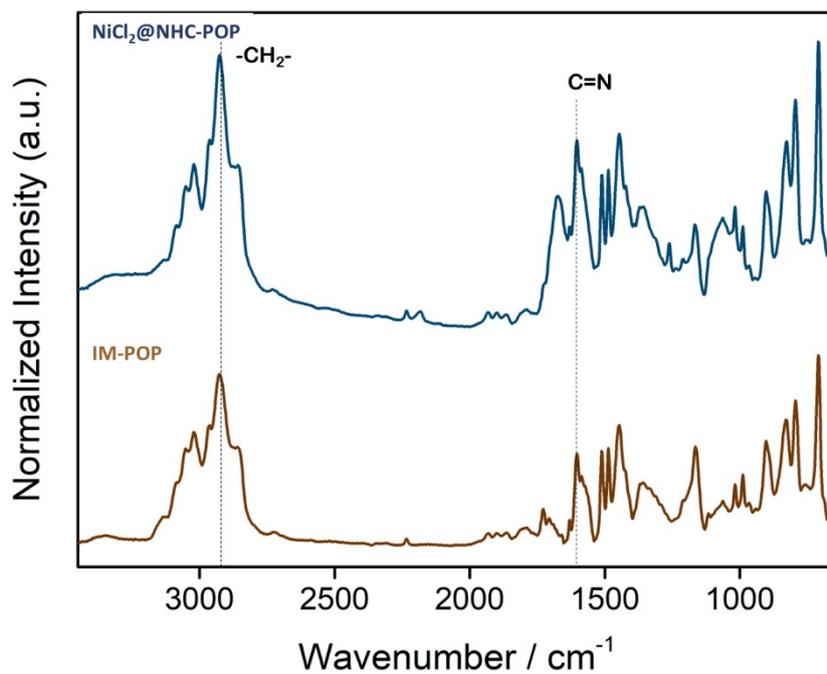
**Figure S4.** Low temperature (77 K) N<sub>2</sub> adsorption profile of **IM-POP** (burgundy) and **NiCl<sub>2</sub>@NHC-POP** (green).



**Figure S5.** Thermo-gravimetric analysis (TGA) of as-synthesized **IM-POP** (burgundy) and **NiCl<sub>2</sub>@NHC-POP** (green).



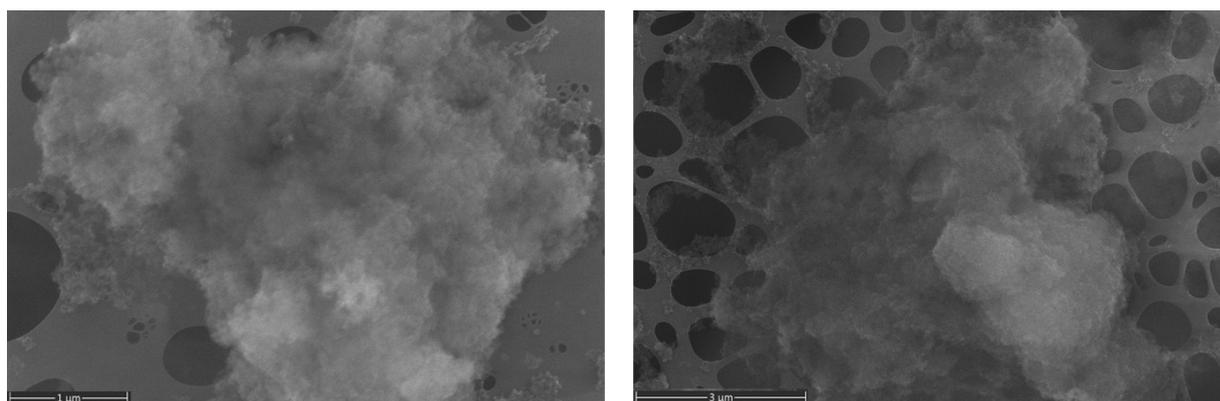
**Figure S6.** Toluene vapor adsorption profile of **IM-POP** (burgundy) and **NiCl<sub>2</sub>@NHC-POP** (green) at 298 K.



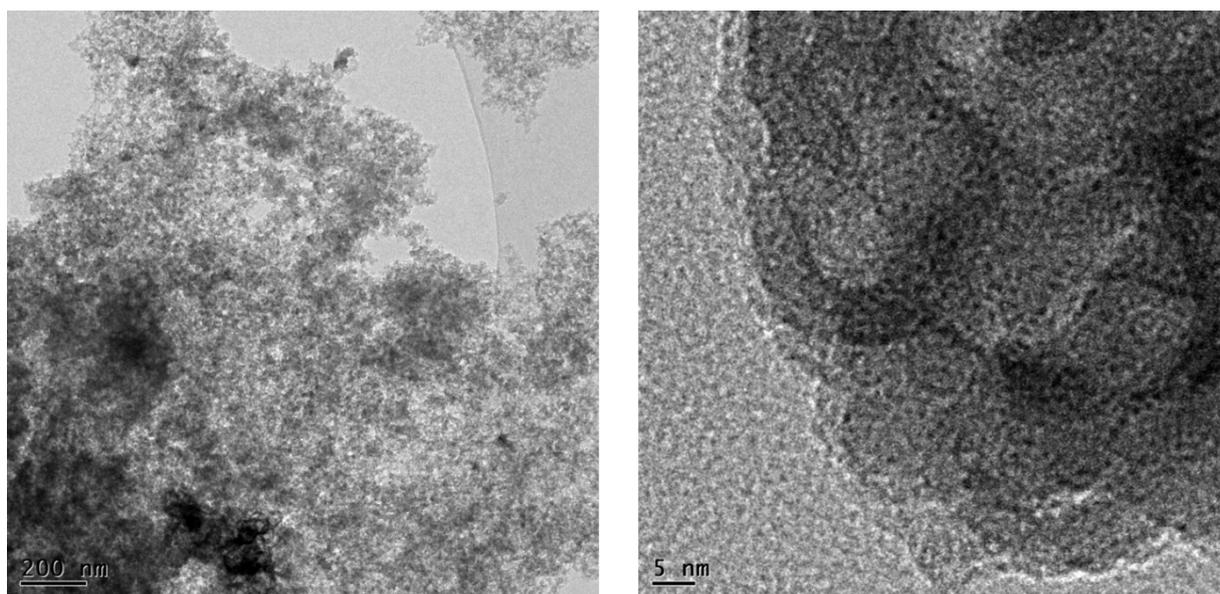
**Figure S7.** FT-IR spectra of **IM-POP** (burgundy) and **NiCl<sub>2</sub>@NHC-POP** (green).

**Table S1.** Summary of elemental analyses of **IM-POP** and **NiCl<sub>2</sub>@NHC-POP**

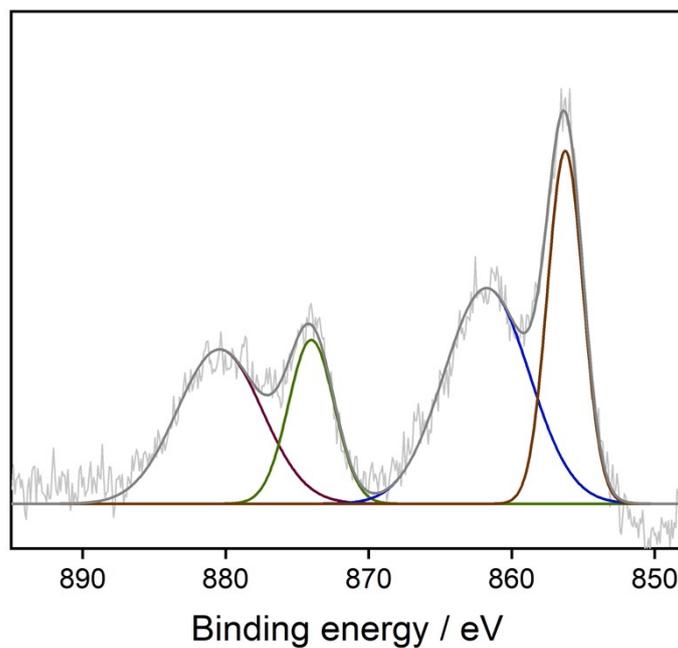
<b>Compounds</b>	<b>% C</b>	<b>% H</b>	<b>% N</b>
<b>IM-POP</b>	81.1	7.5	2.8
<b>NiCl<sub>2</sub>@NHC-POP</b>	76.1	7.3	2.5



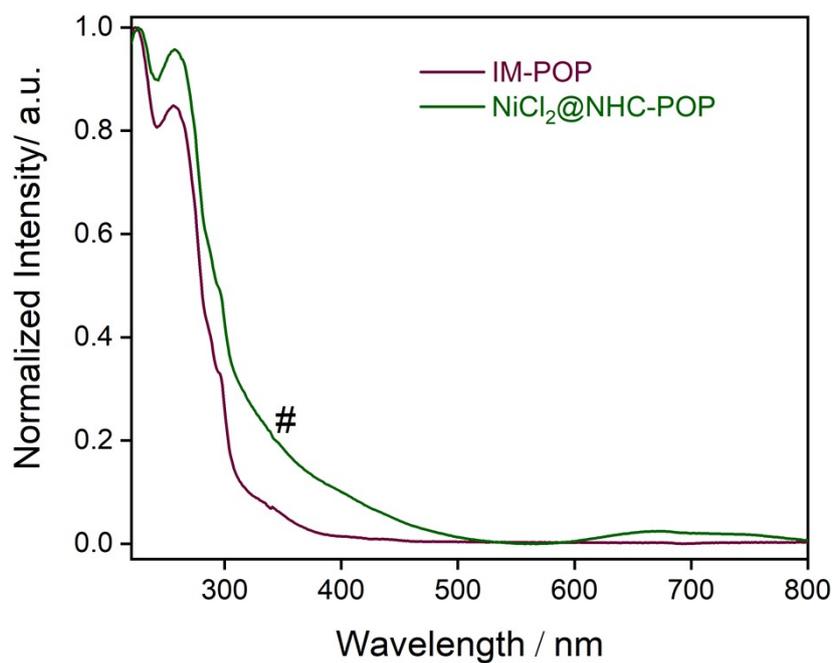
**Figure S8.** SEM images of **NiCl<sub>2</sub>@NHC-POP**.



**Figure S9.** TEM images of **NiCl<sub>2</sub>@NHC-POP**.



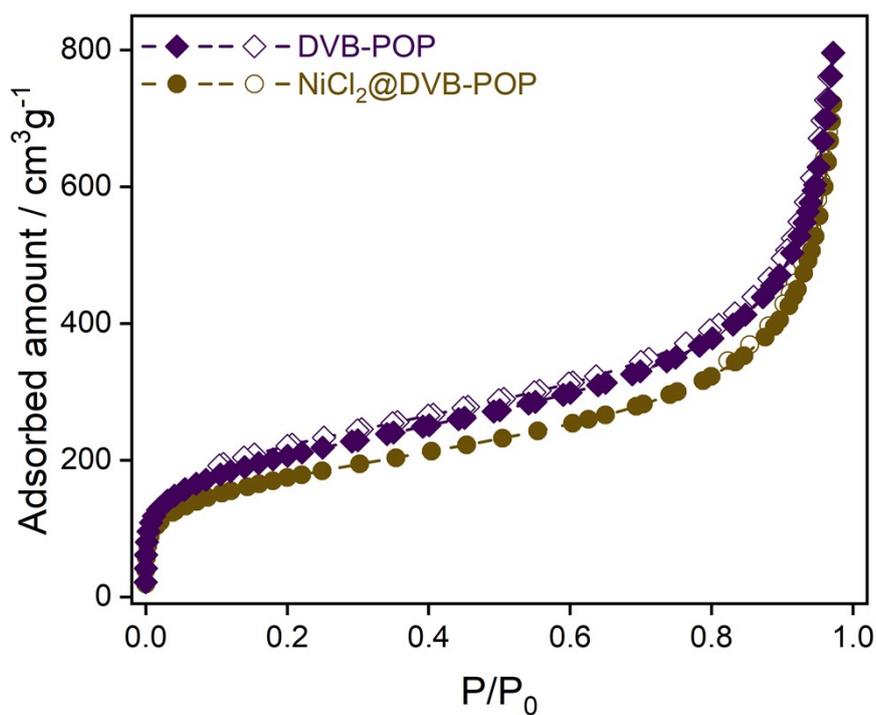
**Figure S10.** X-ray photoelectron spectroscopy (XPS) spectra of NiCl<sub>2</sub>@NHC-POP.



**Figure S11.** Solid state UV-visible spectra of IM-POP (burgundy) and NiCl<sub>2</sub>@NHC-POP (green). [# signal appears from changing the lamp at 340 nm.]

**Table S2.** Summary of Ni wt% and their corresponding BET surface area (single point analysis at 0.3  $p/p_0$ ) and total pore volume (determined at 0.97  $p/p_0$ ) of **IM-POP**, **NiCl<sub>2</sub>@NHC-POP**, **DVB-POP** and **NiCl<sub>2</sub>@DVB-POP**

Compounds	Wt% of Ni	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_{\text{tot}}$ (cm <sup>3</sup> /g)
IM-POP	-	510	0.54
NiCl <sub>2</sub> @NHC-POP	2.80	390	0.40
DVB-POP	-	738	1.23
NiCl <sub>2</sub> @DVB-POP	0.15	630	1.12

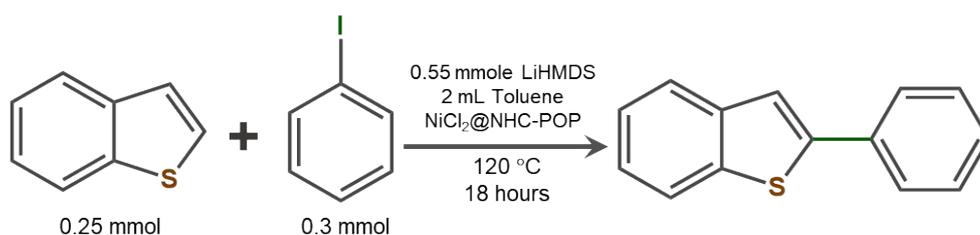


**Figure S12.** Low temperature (77 K) N<sub>2</sub> adsorption profiles of **DVB-POP** (purple) and **NiCl<sub>2</sub>@DVB-POP** (dark yellow).

### 3. Heterogeneous catalysis protocols

#### 3.1. Condition screening for catalysis

**3.1.1. Catalyst screening:** In a glovebox, 33.6 mg of benzothiophene (0.25 mmol, 1 equiv), 92 mg of LiHMDS (0.55 mmol, 2.2 equiv), and 5 mg of activated  $\text{NiCl}_2\text{@NHC-POP}$  catalyst were added to a flame-dried Schlenk tube equipped with a magnetic stirring bar. Then the flask was sealed with a silicon septum and transferred out of the glovebox. To the Schlenk tube 2 ml of dry toluene were injected through the septum and then mixed well. After mixing 34  $\mu\text{l}$  of iodobenzene (0.3 mmol, 1.2 equiv) and dodecane (40  $\mu\text{l}$ , 0.174 mmol) were injected through the septum. Here, dodecane was used as an internal standard for GC-FID analysis after the reaction. After addition of all reactands, the reaction mixture was allowed to heat at 120  $^\circ\text{C}$  with stirring at 500 rpm for 18 hours. After 18 hours, the mixture was quenched with 2 ml of methanol (MeOH), and the solid catalyst was separated by centrifugation. The solid was washed thoroughly with MeOH (3 x 3ml). The combined organic solution (toluene + MeOH from washing) was analyzed with GC-FID to calculate the yield by comparing the amount of product formed with amount of internal standard in the reaction.



**Scheme S4.** Schematic representation of catalytic C-H arylation reaction of benzothiophene.

**3.1.2. Base:** In a similar way as mentioned above, to a flame-dried Schlenk tube along with a magnetic stirring bar benzothiophene 33.6 mg (0.25 mmol, 1equiv), 5 mg of activated  $\text{NiCl}_2\text{@NHC-POP}$  and 0.55 mmol of respective base (LiHMDS, KHMDS, NaHMDS,  $\text{Mg}(\text{HMDS})_2$ ,  $^t\text{BuO-Li}$ ,  $^t\text{BuO-K}$ ,  $\text{K}_2\text{CO}_3$  or  $\text{Cs}_2\text{CO}_3$ ) were added inside a glovebox. The flask was transferred out of the glovebox after sealing it with a silicon septum, and then dry toluene (2 ml) was injected and mixed well. Afterwards, iodobenzene (34  $\mu\text{l}$ , 0.3 mmol, 1.2 equiv) and dodecane (40  $\mu\text{l}$ , 0.174 mmol) as an internal standard for GC-FID analysis were injected into the reaction mixture through the septum. Then, the reaction was heated at 120  $^\circ\text{C}$  and stirred at 500 rpm for 18 hours. After 18 hours, the reaction mixture was quenched with 2 ml of MeOH, and the solid catalyst was separated by centrifugation. Then the solid catalyst was washed with MeOH (3 x 3ml). The combined organic solution (toluene + MeOH from washing) was analyzed with GC-FID and the yield of the product was determined respectively.

**3.1.3. Solvent & temperature:** 33.6 mg of benzothiophene (0.25 mmol, 1 equiv), 92 mg of LiHMDS (0.55 mmol, 2.2 equiv) and 5 mg of activated **NiCl<sub>2</sub>@NHC-POP** were weighed into a flame-dried Schlenk tube equipped with a magnetic stirring bar inside glovebox. The reactor was sealed with a silicon septum and taken out of the glovebox. Then to the reaction mixture, 2 ml of respective dry solvent (toluene, THF, 1,4-dioxane or 2-methyl-THF) were added and mixed well. Then 34  $\mu$ l of iodobenzene (0.3 mmol, 1.2 equiv) and 40  $\mu$ l of dodecane (0.174 mmol; as an internal standard for GC-FID analysis) were injected into the reaction mixture through the septum. The reaction mixture was then stirred at 500 rpm and heated at a given temperature (30 °C, 60 °C, 90 °C or 120 °C) for 18 hours. After completion of the time, the mixture was quenched with 2 ml of MeOH, and the solid catalyst was separated by centrifugation. The obtained solid was washed thoroughly with MeOH (3 x 3ml). The combined organic solution (toluene + MeOH from washing) was analyzed with GC-FID to calculate the yield by comparing the amount of product formed with amount of internal standard in the reaction.

**3.1.4. Electrophile screening:** 33.6 mg of benzothiophene (0.25 mmol, 1 equiv), 92 mg of LiHMDS (0.55 mmol, 2.2 equiv) and 5 mg of activated **NiCl<sub>2</sub>@NHC-POP** were weighed into a flame-dried Schlenk tube equipped with a magnetic stirring bar inside glovebox. The reactor was sealed with a silicon septum and taken out of the glovebox. Then to the reaction mixture, 2 ml of dry toluene were added and mixed well. Then 0.3 mmol phenyl halide or phenol derivative (1.2 equiv) and 40  $\mu$ l of dodecane (0.174 mmol; as an internal standard for GC-FID analysis) were injected into the reaction mixture through the septum. The reaction mixture was then stirred at 500 rpm and heated at 120 °C for 18 hours. After completion of the time, the mixture was quenched with 2 ml of MeOH, and the solid catalyst was separated by centrifugation. the obtained solid was washed thoroughly with MeOH (3 x 3ml). The combined organic solution (toluene + MeOH from washing) was analyzed with GC-FID to calculate the yield by comparing the amount of product formed with amount of internal standard in the reaction.

**3.1.5. Kinetics and hot filtration test:** Kinetics study has been carried out for this catalytic conversion in a set of experiments, where all the reaction mixtures contain approximately same amount of the components and were started to heat at the same time. Approximately 33.6 mg of benzothiophene (0.25 mmol, 1 equiv), 92 mg of LiHMDS (0.55 mmol, 2.2 equiv) and 5 mg of activated **NiCl<sub>2</sub>@NHC-POP** were weighed into respective flame-dried Schlenk tubes equipped with magnetic stirring bar inside glovebox. Then those reactors were sealed with silicon septa and taken out of the glovebox. Then to the reactors, 2 ml of dry toluene were added and mixed well. Then 34  $\mu$ l of iodobenzene (0.3 mmol, 1.2 equiv) and 40  $\mu$ l of dodecane (0.174 mmol; as an internal standard for GC-FID analysis) were injected into each reaction mixture through the septum. Respective reaction mixtures were then stirred at 500 rpm and heated at 120 °C. After different time intervals (2 h, 3 h, 4 h, 6 h, 18 h and 24 h) one of the reactions was taken out and quenched with 2 ml of MeOH, and the solid catalyst was separated by centrifugation. The obtained solid was washed thoroughly with MeOH (3 x 3ml). The combined organic solution (toluene + MeOH from washing) was analyzed with

GC-FID to calculate the yield by comparing the amount of product formed with amount of internal standard in the reaction.

The hot filtration test was performed in a similar way. In this case, one reaction set was used, and after 4 hours the reaction mixture was transferred to another Schlenk tube under the Ar atmosphere by filtering through a cannula. Then the reaction was allowed to continue until 24 hours, and upon completion of the reaction, it was quenched with MeOH. The yield after 4 hours and 24 hours were quantified from GC-FID analysis.

### 3.1.6. Homogeneous catalysis:

**Preparation of 1:1 Ni-NHC Complex:** In a 30 ml glass vial 60 mg of KHMDS (0.3 mmol) was weighed inside a glovebox and then the vial was transferred out of it. 2.5 ml of anhydrous toluene were added to the vial to dissolve the base. To the reaction mixture 5 ml of a solution of 1-methyl-3-(4-vinylbenzyl)-1*H*-imidazol-3-ium chloride (70.5 mg, 0.3 mmol) in anhydrous toluene were added and stirred at room temperature for 30 min under an Ar atmosphere. Then a solution of NiCl<sub>2</sub>·glyme (65.9 mg, 0.3 mmol) was added slowly to the reaction mixture and continued to stir at room temperature for 2 hours to produce the 1:1 Ni-NHC complex.

**Preparation of 1:2 Ni-NHC Complex:** In a similar way the 1:2 Ni-NHC was also prepared, where, in a 30 ml glass vial 120 mg of KHMDS (0.6 mmol) was taken inside a glovebox and then the vial was transferred out of it. 2.5 ml of anhydrous toluene were added to the vial to dissolve the base. To the reaction mixture 5 ml of a solution of 1-methyl-3-(4-vinylbenzyl)-1*H*-imidazol-3-ium chloride (141 mg, 0.6 mmol) in anhydrous toluene were added and stirred at room temperature for 30 min under an Ar atmosphere. Then a solution of NiCl<sub>2</sub>·glyme (65.9 mg, 0.3 mmol) was added slowly to the reaction mixture and continued to stir at room temperature for 2 hours to produce the 1:2 Ni-NHC complex.

In a flame-dried Schlenk tube equipped with a magnetic stirring bar, 33.6 mg of benzothiophene (0.25 mmol, 1 equiv) and 92 mg of LiHMDS (0.55 mmol, 2.2 equiv) were weighed and then the Schlenk tube was sealed and transferred out of the glovebox. Then to the reactors, 2 ml of dry toluene were added and mixed well. Furthermore, 34  $\mu$ l of iodobenzene (0.3 mmol, 1.2 equiv) and 40  $\mu$ l of dodecane (0.174 mmol as an internal standard for GC-FID analysis) were injected into each reaction mixture through the septum. Finally, to the reaction mixture 100  $\mu$ l of the aforementioned homogeneous catalyst (1.2 mol% of Ni) was added and stirred at 120 °C and 500 rpm for 18 hours. After 18 hours, the mixture was quenched with 2 ml of MeOH, and was analyzed with GC-FID to calculate the yield by comparing the amount of product formed with amount of internal standard in the reaction.

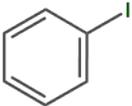
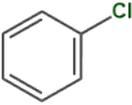
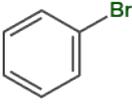
**3.1.7. Recyclability of the catalyst:** Inside a glovebox, 67.2 mg of benzothiophene (0.5 mmol, 1 equiv), 184 mg of LiHMDS (1.1 mmol, 2.2 equiv), and 10 mg of activated NiCl<sub>2</sub>@NHC-POP catalyst were added to a flame-dried Schlenk tube, which was equipped with a magnetic stirring bar. The flask was sealed with a silicon septum and transferred out of the glovebox. To the Schlenk tube 4 ml of dry toluene, 68  $\mu$ l of iodobenzene (0.6 mmol,

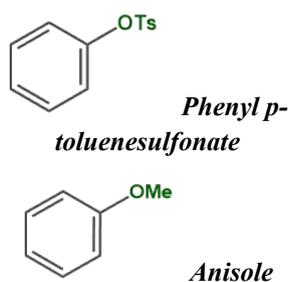
1.2 equiv) and dodecane (40  $\mu$ l, 0.174 mmol) were injected through the septum and then mixed well. The reaction mixture was allowed to heat at 120  $^{\circ}$ C with stirring at 500 rpm for 18 hours. After the time duration, the mixture was quenched with 4 ml of MeOH, and the solid catalyst was separated by centrifugation. The solid was washed thoroughly with MeOH (3 x 3ml). The combined organic solution (toluene + MeOH from washing) was analyzed with GC-FID to calculate the yield by it with amount of internal standard in the reaction. Thus, obtained solid catalyst was dried in an oven and reused for the next cycle in a similar way.

**Table S3.** Summary of catalytic activity with  $\text{NiCl}_2\text{@NHC-POP}$  catalyst with different bases under otherwise standard conditions

<i>Base</i>	<i>% of yield</i>	<i>TON</i>
<i>LiHMDS</i>	69	75
<i>NaHMDS</i>	5	5.5
<i>KHMDS</i>	No activity	-
<i>Mg(HMDS)<sub>2</sub></i>	No activity	-
<i><sup>t</sup>BuO-Li</i>	No activity	-
<i><sup>t</sup>BuO-K</i>	No activity	-
<i>K<sub>2</sub>CO<sub>3</sub></i>	No activity	-
<i>Cs<sub>2</sub>CO<sub>3</sub></i>	No activity	-

**Table S4.** Summary of catalytic activity with  $\text{NiCl}_2\text{@NHC-POP}$  with different electrophile under otherwise standard conditions

<i>Electrophile</i>	<i>% of yield</i>	<i>TON</i>
 <i>Iodobenzene</i>	69	75
 <i>Chlorobenzene</i>	No activity	-
 <i>Bromobenzene</i>	10	11



No activity -

No activity -

**Table S5.** Summary of catalytic activity with  $\text{NiCl}_2\text{@NHC-POP}$  at different temperatures under otherwise standard conditions

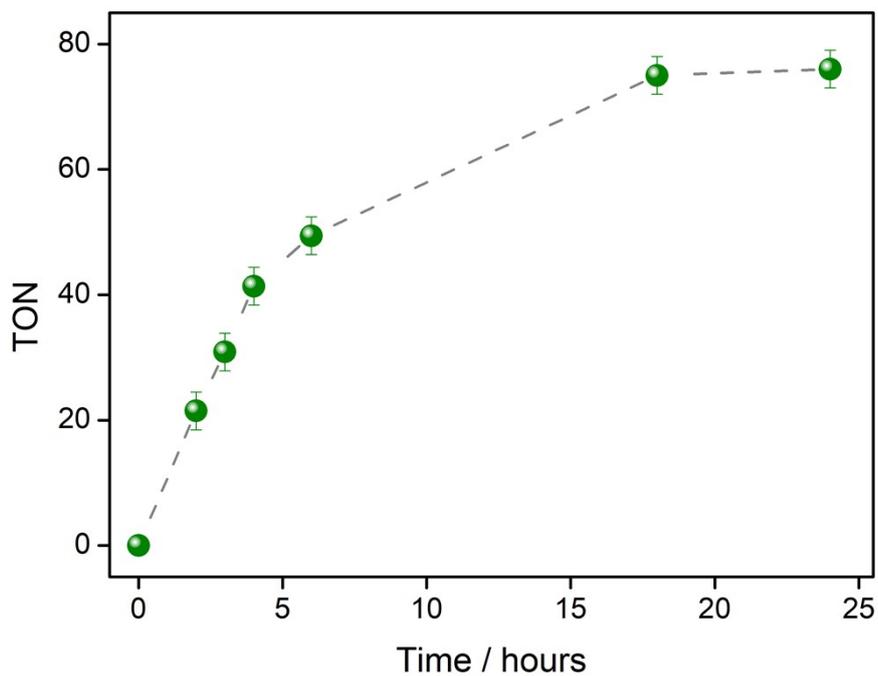
<i>Temperature (°C)</i>	<i>% of yield</i>	<i>TON</i>
<b>30</b>	No activity	-
<b>60</b>	No activity	-
<b>90</b>	13	14
<b>120</b>	69	75

**Table S6.** Summary of catalytic activity with  $\text{NiCl}_2\text{@NHC-POP}$  in different solvents under otherwise standard conditions

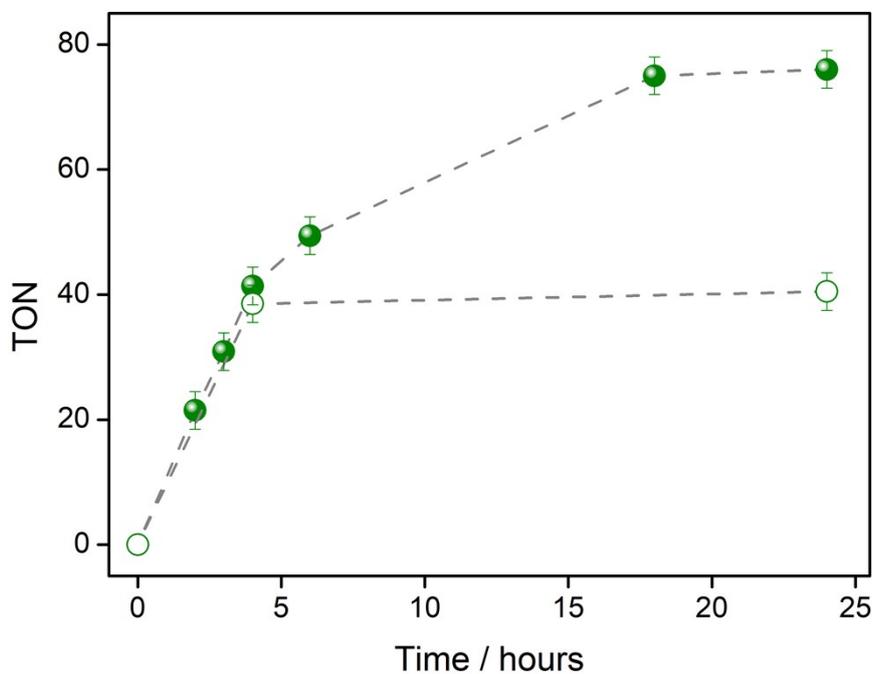
<i>Solvent</i>	<i>% of yield</i>	<i>TON</i>
<b>Toluene</b>	69	75
<b>1,4-dioxane</b>	No activity	-
<b>Methyl tetrahydrofuran</b>	No activity	-
<b>Tetrahydrofuran (THF)</b>	No activity	-

**Table S7.** Summary of blank test with **IM-POP**,  $\text{NiCl}_2\text{@NHC-POP}$  and  $\text{NiCl}_2\text{@DVB-POP}$  under otherwise standard conditions

<i>Compound</i>	<i>% of yield</i>	<i>TON</i>
<b><math>\text{NiCl}_2\text{@NHC-POP}</math></b>	69	75
<b>IM-POP</b>	No activity	-
<b><math>\text{NiCl}_2\text{@DVB-POP}</math></b>	No activity	-



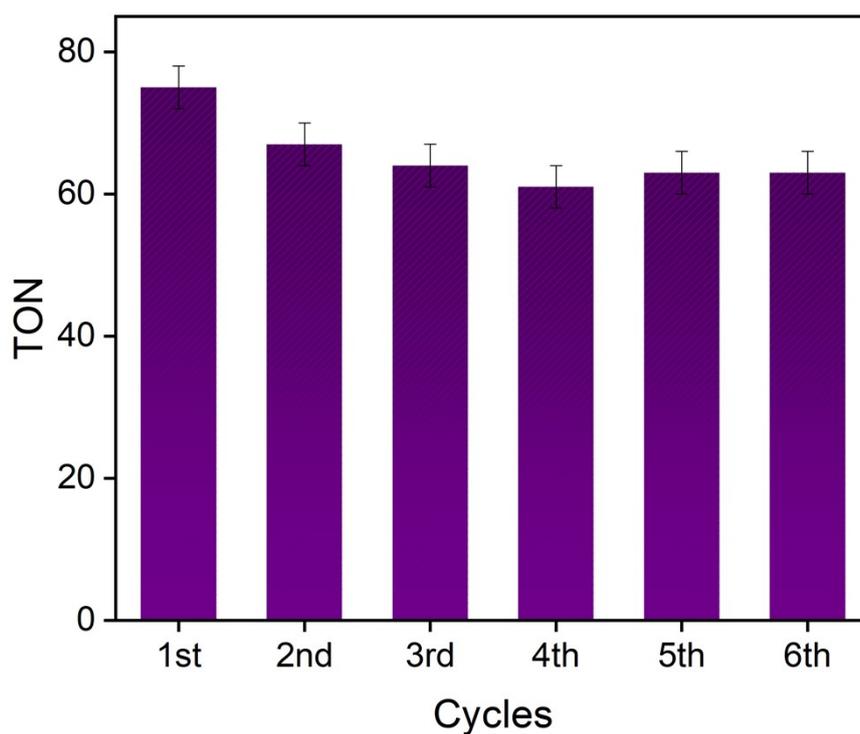
**Figure S13.** Kinetics of the C-H arylation of benzothiophene with  $\text{NiCl}_2\text{@NHC-POP}$  under standard conditions.



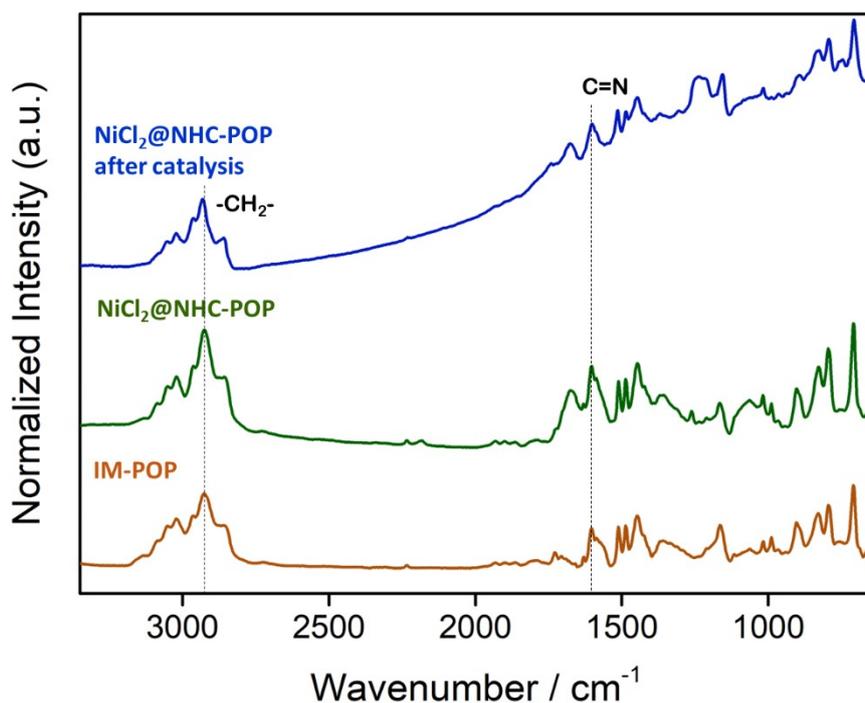
**Figure S14.** Comparison of the Kinetics (solid circles) and hot filtration (after 4 hours, empty circles) test of the C-H arylation of benzothiophene under standard conditions.

**Table S8.** Summary of catalysis results (% yield and TON) and metal leaching obtained from ICP-OES for the recycling experiments with **NiCl<sub>2</sub>@NHC-POP** catalyst. (N.D.: not detectable)

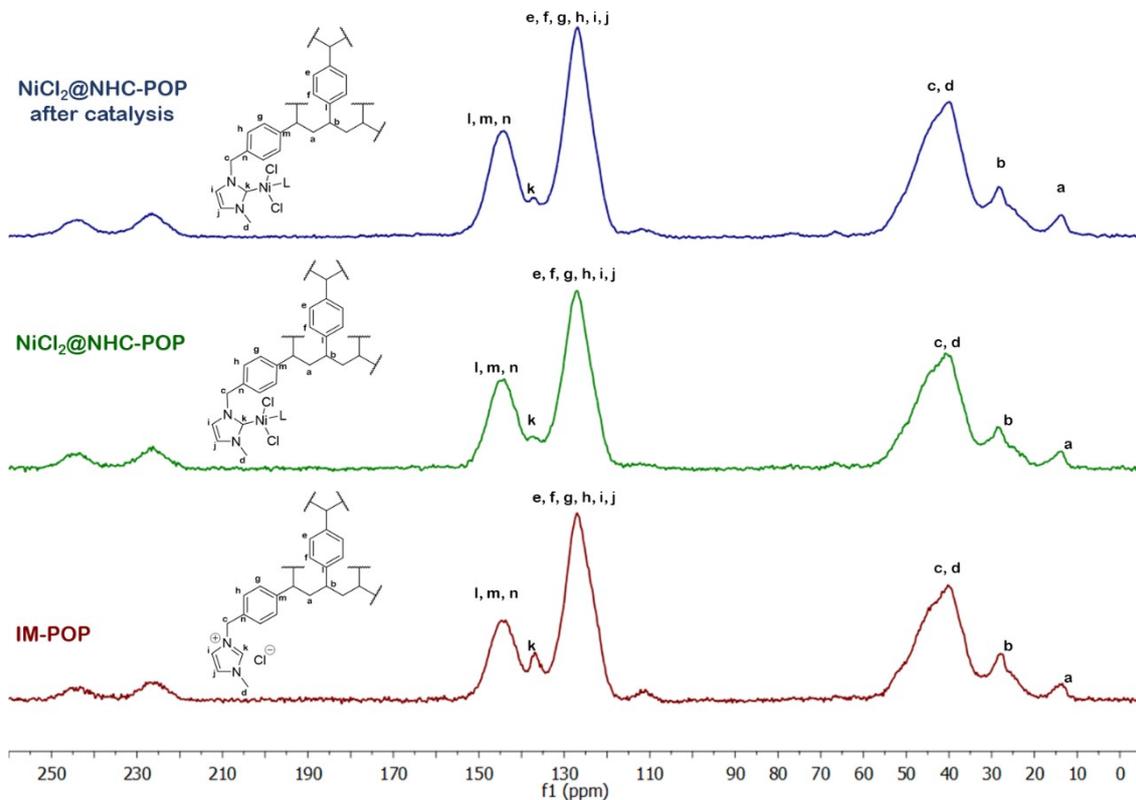
<i>Run</i>	<i>Yield (%)</i>	<i>TON per run</i>	<i>Cumulative TON</i>	<i>Leached Ni (mg)</i>	<i>Leached Ni as % of total amount</i>
<i>1st</i>	69	75	75	0.0248	9.0
<i>2nd</i>	56	67	142	0.0126	5.1
<i>3rd</i>	52	65	206	N.D.	-
<i>4th</i>	49	61	267	N.D.	-
<i>5th</i>	51	63	330	N.D.	-
<i>6th</i>	50	63	393	N.D.	-



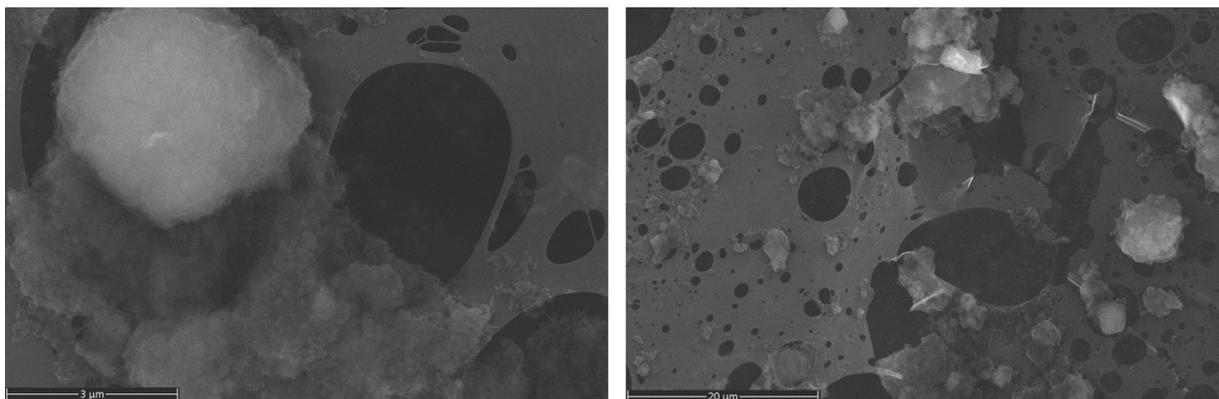
**Figure S15.** Recyclability of **NiCl<sub>2</sub>@NHC-POP** catalyst.



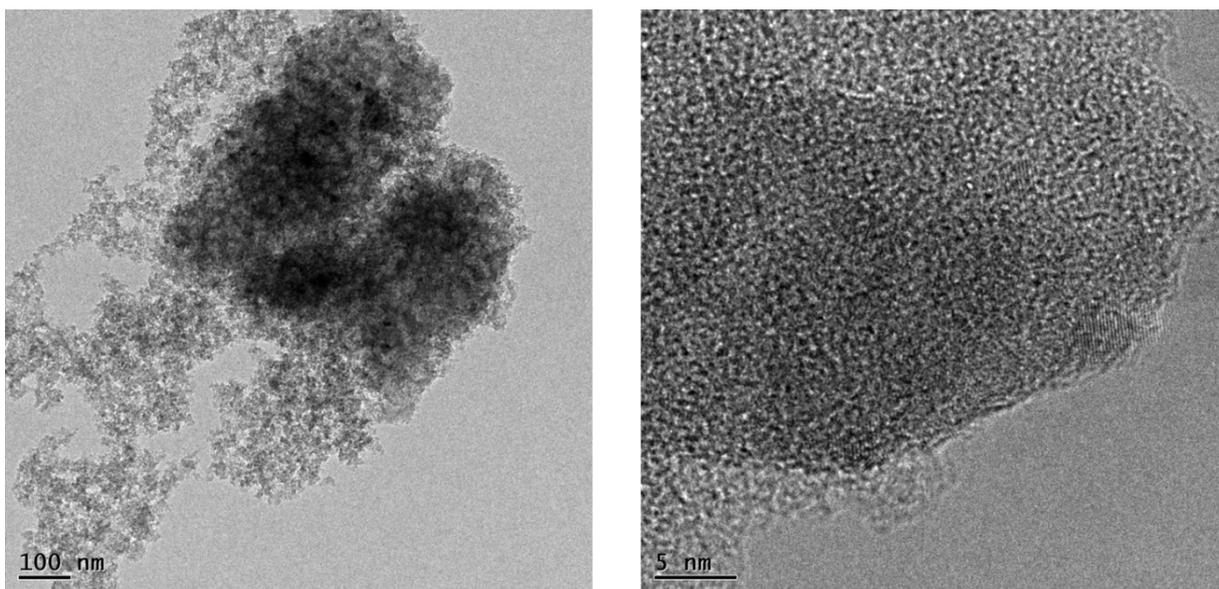
**Figure S16.** FT-IR spectra of IM-POP (burgundy), NiCl<sub>2</sub>@NHC-POP (green) and NiCl<sub>2</sub>@NHC-POP after catalysis (blue).



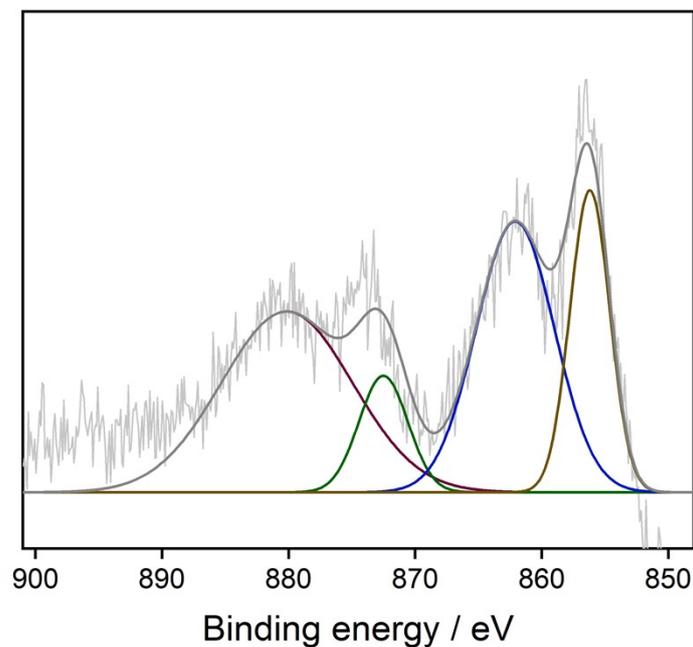
**Figure S17.** Solid state <sup>13</sup>C-NMR of IM-POP (burgundy), NiCl<sub>2</sub>@NHC-POP (green) and NiCl<sub>2</sub>@NHC-POP after catalysis (blue).



**Figure S18.** SEM images of NiCl<sub>2</sub>@NHC-POP after catalysis.



**Figure S19.** TEM images of NiCl<sub>2</sub>@NHC-POP after catalysis.



**Figure S20.** X-ray photoelectron spectroscopy (XPS) spectra of **NiCl<sub>2</sub>@NHC-POP** after catalysis.

## 9. References

- (1) Y. -S. Kim and S. -H. Choi, Synthesis of an Anion-Exchange Membrane Based on Imidazolium-Type Ionic Liquids for a Capacitive Energy Extraction Donnan Potential Device. *Mater. Chem. Sust. Energy*, **2014**, *136* (11), 4369–4381. <https://doi.org/10.1021/ja500330a>.