

Insights on Bimetallic Micellar Nanocatalysis for Buchwald-Hartwig Aminations

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Supplementary Material

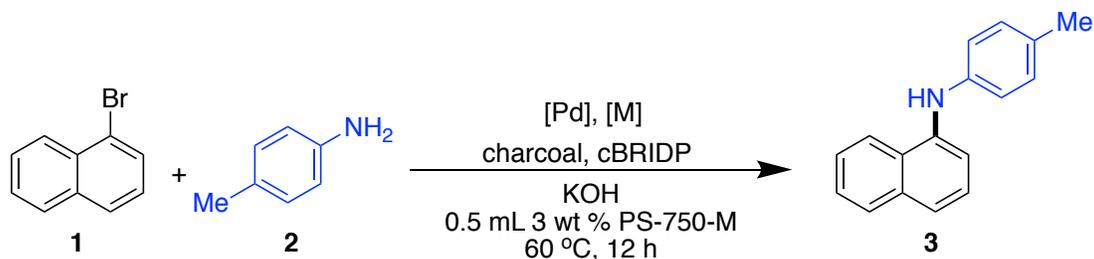
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1. GENERAL EXPERIMENTAL DETAILS

All manipulations were carried out under argon atmosphere unless otherwise noted. TLC plates (UV 254 indicator, glass backed, thickness 200 μ m) and silica gel (standard grade, 230 – 400 mesh) were purchased from Merck. Diethyl ether, THF, ethyl acetate, methylene chloride, and hexanes were purchased from Fisher Scientific. Methyl *tert*-butyl ether was purchased from Sigma-Aldrich. Et₃N and *i*-Pr₂NEt were distilled and stored under argon. KOH, K₃PO₄, and K₂CO₃ were purchased from Fisher Scientific and used as such without any further purification. MeMgBr and Fe₂O₃ was purchased from Sigma Aldrich. Ligands were either purchased from Strem Chemicals, Sigma-Aldrich or gifted by Novartis Pharmaceuticals. Palladium(II) acetate and tetrakis(acetonitrile)copper(I) hexafluorophosphate was purchased from Strem Chemicals and used as such without further purification. Pure NMR solvents were purchased from Cambridge Isotopes Laboratories. (Hetero)aryl amines and (hetero)aryl bromides were purchased from Sigma-Aldrich, Combi-Block, Alfa Aesar, and Oakwood chemicals. The coupling reactions were performed in 4 mL close-cap microwave vials under argon atmosphere. The charcoal was purchased from Acros with a brand name NORIT®. Microwave vials were purchased from VWR International and Biotage. Reaction vials were also recycled and reused. Bulk aqueous solution of surfactant PS-750-M was prepared in HPLC grade water and thoroughly purged with argon before use. Melting points were determined using a MEL-TEMP II melting point apparatus with samples in Kimble Kimex 51 capillaries (1.5-1.8 x 90 mm). Unless otherwise mentioned, all NMR spectra were recorded at 25 °C on Varian Unity INOVA (400, 500 and 700 MHz) spectrometers. Reported chemical shifts are referenced to residual solvent peaks. HRMS spectra were obtained on a Thermo Electron MAT 95XP mass spectrometer using either electron ionization (EI) or chemical ionization (CI).

2. REACTION OPTIMIZATION

Table S1. Optimal Pd/M ratio



entry	[Pd]	[M]	cBRIDP (mol %)	3 (%) ^a
1	1 mol % Pd(OAc) ₂	-	1	62
2	0.5 mol % Pd(OAc) ₂	-	0.5	16
3	1 mol % Pd(OAc)₂	2 mol % Cu(CH ₃ CN) ₄ PF ₆	3	85
4	0.5 mol % Pd(OAc) ₂	2 mol % Cu(CH ₃ CN) ₄ PF ₆	2.5	61
5	-	2 mol % Cu(CH ₃ CN) ₄ PF ₆	2	0
6	1 mol % Pd(OAc) ₂	1 mol % Cu(CH ₃ CN) ₄ PF ₆	2	72
7	-	2 mol % Ni(OAc) ₂	2	0
8	1 mol % Pd(OAc) ₂	2 mol % Ni(OAc) ₂	3	traces
9	-	2 mol % CoCl ₂ ·6H ₂ O ^b	-	0
10	1 mol % [(π-cinnamyl)PdCl] ₂	-	1	26
11	1 mol % [(π-cinnamyl)PdCl] ₂ ^c	-	1	traces
12	1 mol % [(π-crotyl)PdCl] ₂	-	1	traces
13	1 mol % [(π-crotyl)PdCl] ₂ ^c	-	1	29
14	1 mol % Pd(OAc) ₂ ^c	5 mol % FeCl ₃	1	8
15	1 mol % Pd(OAc) ₂ ^d	-	1	71

Conditions. **1** (0.25 mmol), **2** (0.3 mmol), [Pd], [M], charcoal (*ca.* 1.0 equiv. based on 12 amu), cBRIDP, KOH (1 mmol), 3 wt % PS-750-M (0.5 mL), 60 °C, 12 h.

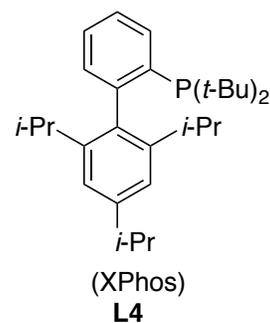
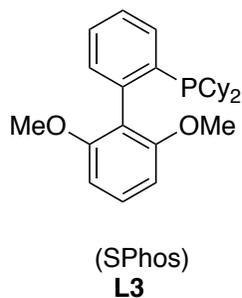
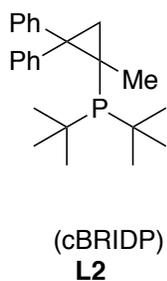
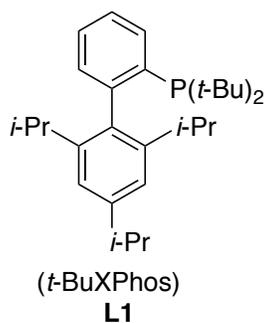
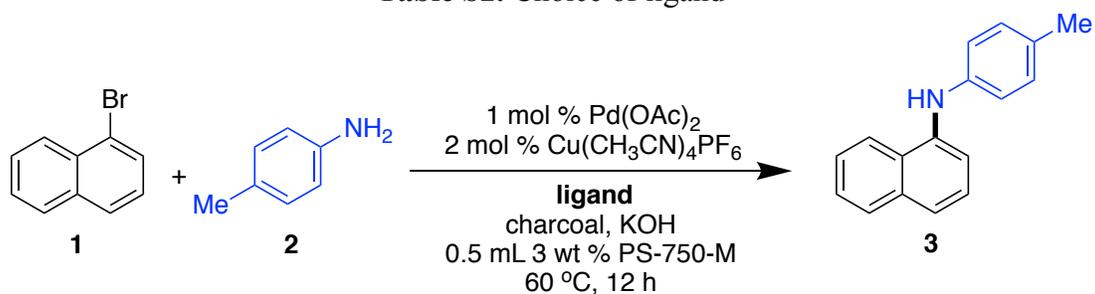
^aYields based on GCMS.

^b(2 mol%) 1*E*,1'*E*-1,1'-(pyridine-2,6-diyl)bis(*N*-(2,6-diisopropylphenyl)ethan-1-imine) was used as ligand.

^cMeMgBr (2 mol%) was used to generate nanoparticles (no charcoal support was used).

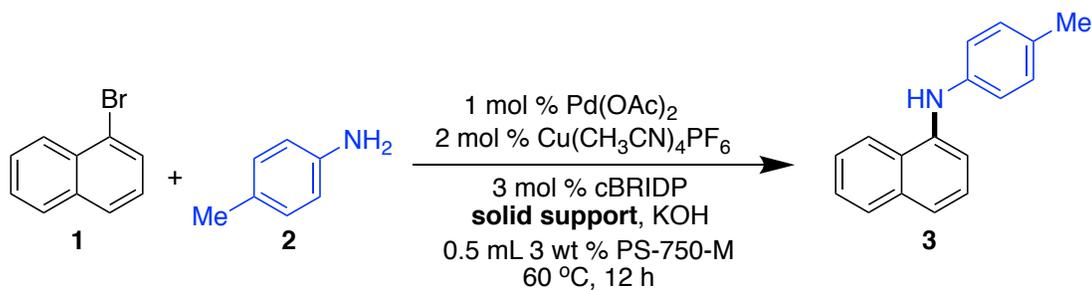
^dKOH(0.75 mmol) was used instead of 1.0 mmol.

Table S2. Choice of ligand



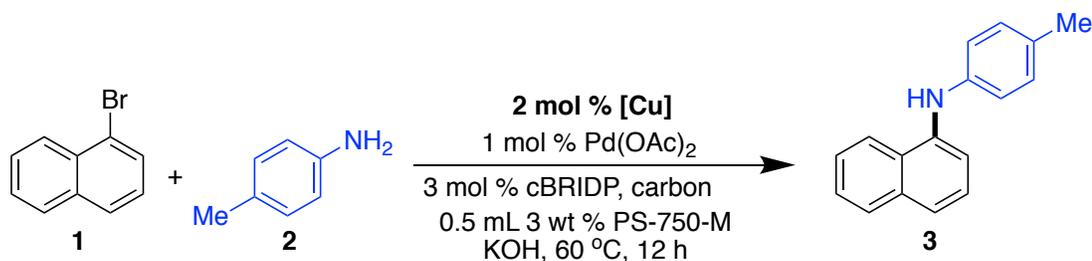
entry	ligand	3 (%) ^a
1	L1	20
2	L2	85
3	L3	12
4	L4	<7

Conditions: **1** (0.25 mmol), **2** (0.3 mmol), Pd(OAc)₂ (1 mol %), Cu(CH₃CN)₄PF₆ (2 mol %), charcoal (ca. 1.0 equiv. based on 12 amu), ligand (3 mol %), KOH (1 mmol), 3 wt % PS-750-M (0.5 mL), 60 °C, 12 h. ^aYields based on GCMS.

Table S3. Solid support other than carbon

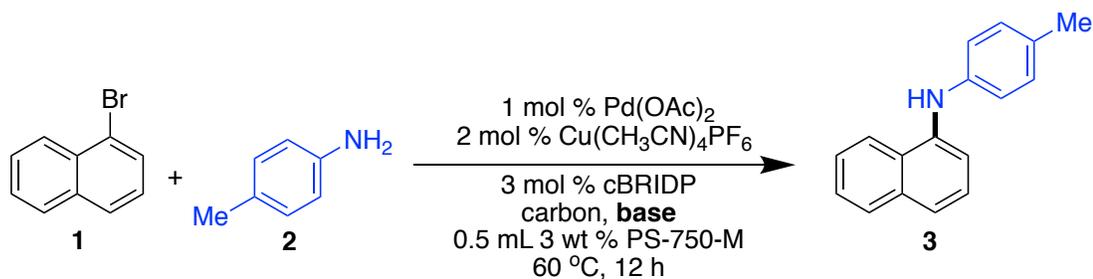
entry	solid support (1.0 equiv)	3 (%) ^a
1	chitin	59
2	Fe ₂ O ₃	17
3	chitosan	46
3	carbon	85

Conditions: **1** (0.25 mmol), **2** (0.3 mmol), Pd(OAc)₂ (1 mol %), Cu(CH₃CN)₄PF₆ (2 mol %), solid support, cBRIDP (3 mol %), KOH (1 mmol), 3 wt % PS-750-M (0.5 mL), 60 °C, 12 h. ^aYields based on GCMS.

Table S4. Nature of copper source

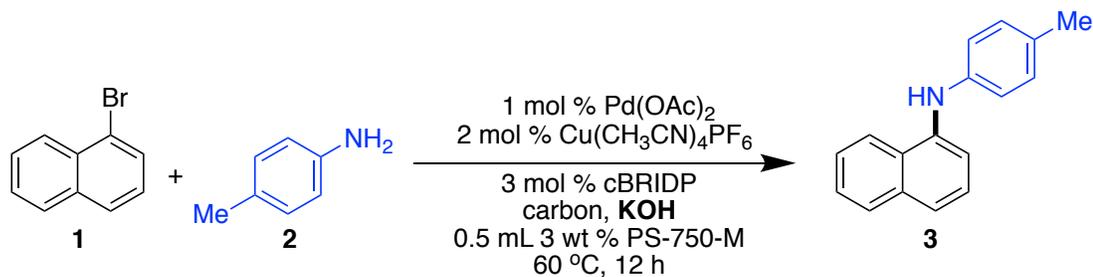
entry	[Cu] (mol %)	3 (%) ^a
1	CuI	77
2	CuCl	47
3	Cu(OTf) ₂	19
4	Cu(MeCN)₄PF₆	85

Conditions: **1** (0.25 mmol), **2** (0.3 mmol), Pd(OAc)₂ (1 mol %), [Cu] (2 mol %), charcoal (*ca.* 1.0 equiv. based on 12 amu), cBRIDP (3 mol %), KOH (1.0 mmol), 3 wt % PS-750-M (0.5 mL), 12 h. ^aYields based on GCMS.

Table S5. Choice of base

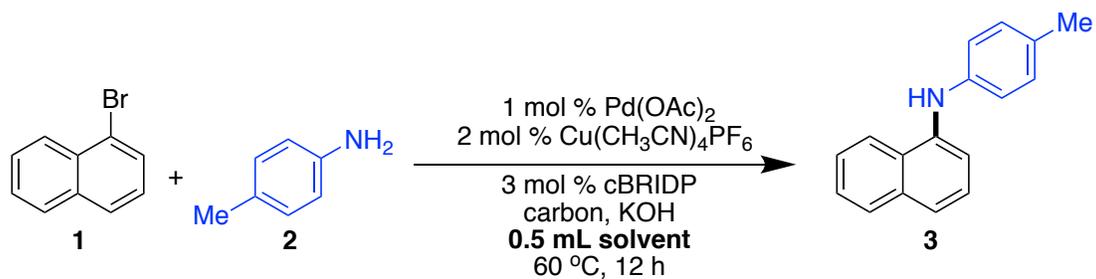
entry	base (4.0 equiv.)	3 (%) ^a
1	K ₂ CO ₃	70
2	K₃PO₄•H₂O	80
4	<i>i</i> -PrNEt ₂	24
5	Et ₃ N	40
6	KOH	85

Conditions: **1** (0.25 mmol), **2** (0.3 mmol), Pd(OAc)₂ (1 mol %), Cu(CH₃CN)₄PF₆ (2 mol %), charcoal (ca. 1.0 equiv. based on 12 amu), cBRIDP (3 mol %), base (1.0 mmol), 3 wt % PS-750-M (0.5 mL), 60 °C, 12 h. ^aYields based on GCMS.

Table S6. Optimal equivalents of base

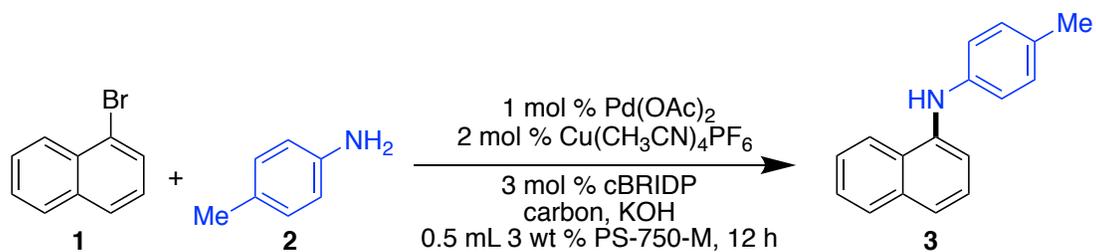
entry	KOH (equiv.)	3 (%) ^a
1	1.0	72
2	2.0	80
3	3.0	95
4	4.0	85

Conditions: **1** (0.25 mmol), **2** (0.3 mmol), Pd(OAc)₂ (1 mol %), Cu(CH₃CN)₄PF₆ (2 mol %), charcoal (ca. 1.0 equiv. based on 12 amu), cBRIDP (3 mol %), KOH, 3 wt % PS-750-M (0.5 mL), 12 h. ^aYields based on GCMS.

Table S7. Reaction solvent

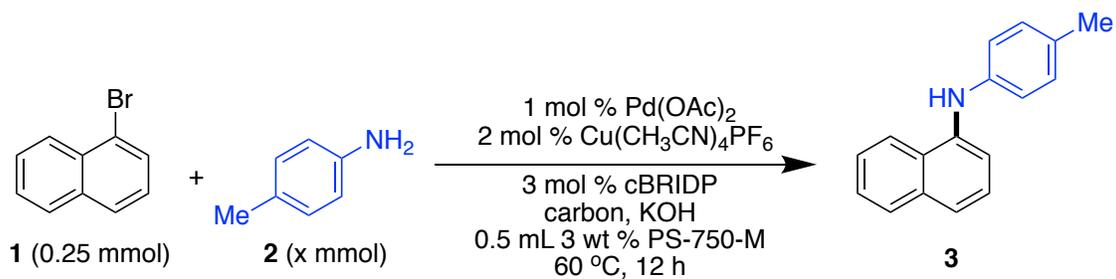
entry	Solvent (0.5 mL)	3 (%) ^a
1	water	20
2	THF	78
3	3 wt % aq. PS-750-M	95
4	3 wt % aq. TPGS-750-M	80
5	3 wt% aq. SPGS-550-M	78

Conditions: **1** (0.25 mmol), **2** (0.3 mmol), Pd(OAc)₂ (1 mol %), Cu(CH₃CN)₄PF₆ (2 mol %), charcoal (ca. 1.0 equiv. based on 12 amu), cBRIDP (3 mol %), KOH (3.0 equiv.), 0.5 mL solvent, 60 °C, 12 h. ^aYields based on GCMS.

Table S8. Optimal reaction temperature

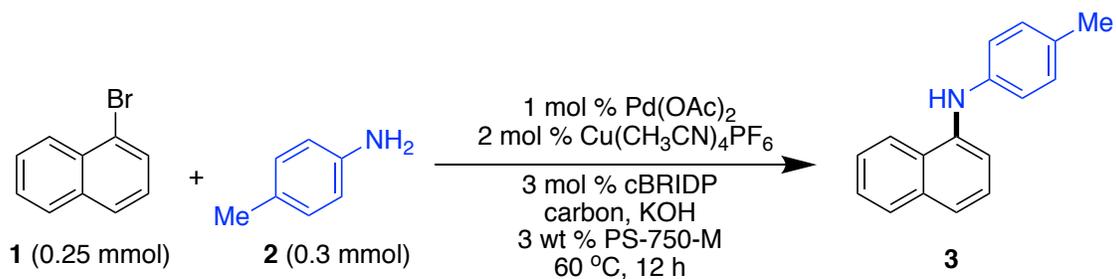
entry	temperature (°C)	3 (%) ^a
1	rt	12
2	45	48
3	60	95
4	80	71

Conditions: **1** (0.25 mmol), **2** (0.3 mmol), Pd(OAc)₂ (1 mol %), Cu(CH₃CN)₄PF₆ (2 mol %), charcoal (ca. 1.0 equiv. based on 12 amu), cBRIDP (3 mol %), KOH (3.0 equiv.), 3 wt % PS-750-M in H₂O (0.5 mL), 12 h. ^aYields based on GCMS.

Table S9. Optimal stoichiometry of coupling partners

entry	2 (equiv.)	3 (%) ^a
1	1.05	87
2	1.2	95
3	2.0	83
4	3.0	72
5	4.0	41

Conditions: **1** (0.25 mmol), **2**, Pd(OAc)₂ (1 mol %), Cu(CH₃CN)₄PF₆ (2 mol %), charcoal (ca. 1.0 equiv. based on 12 amu), cBRIDP (3 mol %), KOH (3.0 equiv.), 0.5 mL 3 wt % aq. PS-750-M, 60 °C, 12 h. ^aYields based on GCMS.

Table S10. Optimal global concentration

entry	conc. (M)	3 (%) ^a
1	0.25	79
2	0.5	95
3	1.0	81
4	2.0	30

Conditions: **1** (0.25 mmol), **2** (0.3 mmol), Pd(OAc)₂ (1 mol %), Cu(CH₃CN)₄PF₆ (2 mol %), charcoal (ca. 1.0 equiv. based on 12 amu), cBRIDP (3 mol %), KOH (3.0 equiv.), 3 wt % aq. PS-750-M, 60 °C, 12 h. ^aYields based on GCMS.

3. SYNTHESIS AND ISOLATION OF NANOCATALYST

In an oven-dried 4 mL reaction vial containing a PTFE-coated stir bar, Pd(OAc)₂ (6.7 mg, 0.028 mmol), *tetrakis*(acetonitrile)copper(I) hexafluorophosphate (22 mg, 0.057 mmol), and cBRIDP (31.7 mg, 0.084 mmol) were added. Reaction vial was closed with a rubber septum. Reaction vials was evacuated and then back-filled with argon. This process of evacuation and backfilling with argon was repeated for three times. 1.0 mL dry THF was added to the reaction mixture. Reaction mixture was gently heated with a heat gun (*ca.* 70 °C) for a minute. During heating, reaction mixture color was changed from yellow to reddish-brown. Using pre-heated oil bath, reaction mixture was further heated at 60 °C for 15 min. Reaction mixture was allowed to cool to rt. Reaction vial was opened under argon atmosphere and activated charcoal (30 mg) was added to it. Reaction vial was closed with a rubber septum, and the mixture was further stirred for 30 minutes at 60 °C. Finally, volatiles were removed under reduced pressure and resulting solid material was dried under vacuum for an hour. The resulting solid (yield 92 mg) was used as such as a catalyst. The catalyst is stable under air and can be stored under ambient conditions for months.

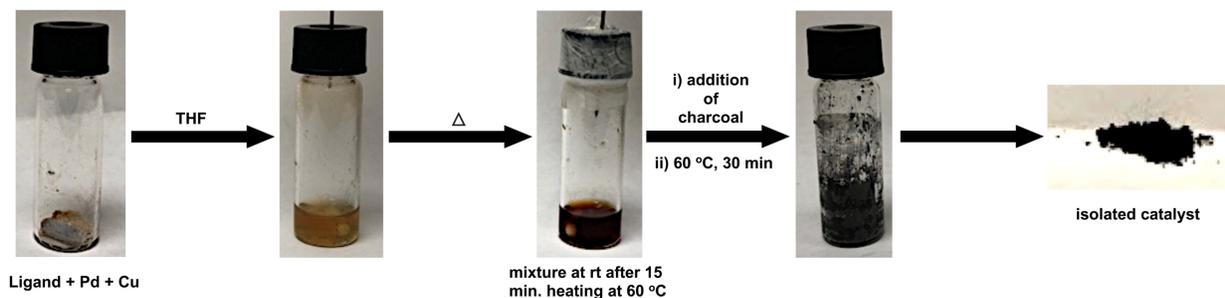
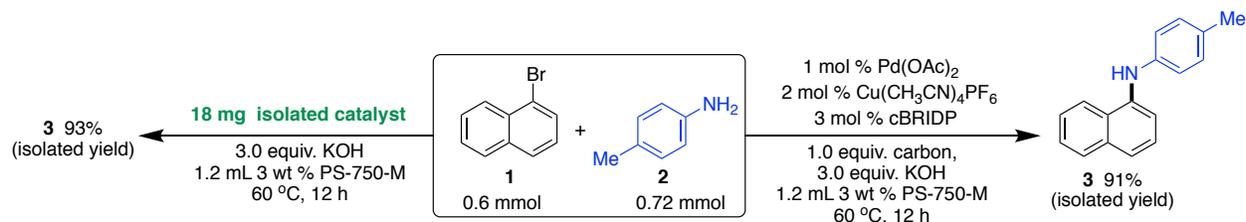


Figure S1. Nanocatalyst preparation and isolation.

4. CATALYTIC ACTIVITY – ISOLATED NANOCATALYST *VERSUS* IN-SITU FORMED



Scheme S1. Catalytic activity - isolated nanocatalyst v/s in-situ generated catalyst.

4.1. Amination with the isolated catalyst. 1-Bromonaphthalene (124 mg, 0.6 mmol), *p*-toluidine (77 mg, 0.72 mmol), nanocatalyst (18 mg), and KOH (100 mg, 1.8 mmol) were added into a 4 mL oven-dried reaction vial containing PTFE-coated stirrer bar (Scheme S1 – left side). Reaction vial was evacuated and back-filled with argon for three times. 1.2 mL aqueous solution of PS-750-M was added to the reaction mixture. Reaction mixture was purged with argon for 2 minutes and then stirred for 12 h at 60 °C.

After complete consumption of starting material as monitored by TLC, reaction mixture was allowed to cool to rt. MTBE (0.5 mL) was added to the reaction mixture and mixture was stirred for a minute at rt. Stirring was stopped and organic layer was allowed to separate. Organic layer was withdrawn with the aid of syringe needle. This extraction process was repeated for an additional time. Combined organic layers were dried over anhydrous sodium sulfate. Volatiles were removed under reduce pressure to obtain crude product. Crude product was purified by flash chromatography over silica gel using EtOAc/hexanes as eluent ($R_f = 0.4$, 9:1 hexanes/EtOAc). Pure product was obtained as viscous oil, yield 130 mg (93%). Similar result is obtained up on using 6-month-old catalyst.

4.2. Amination with in-situ formed catalyst. Pd(OAc)₂ (1.34 mg, 0.006 mmol), *tetrakis*(acetonitrile)copper(I) hexafluorophosphate (4.4 mg, 0.012 mmol), and cBRIDP (6.4 mg, 0.018 mmol) were transferred into a 4 mL oven-dried reaction vial containing PTFE-coated stirrer bar (Scheme S1 – right side). Reaction vessel was evacuated and back-filled with argon for three times. 0.3 mL dry THF was added to the reaction vial and mixture was gently heated with a heat gun to obtain dark red color mixture. Reaction mixture was heated at 60 °C for additional 15 min. Reaction mixture was allowed to cool to rt. Charcoal powder was added to the reaction mixture, which was then heated at 60 °C for 15 min. Reaction mixture was allowed to cool to rt. THF was

removed under vacuum. To the resulting mixture, 1-boromonaphthalene (124 mg, 0.6 mmol), *p*-toluidine (77 mg, 0.72 mmol), and KOH (100 mg, 1.8 mmol) were sequentially added under positive argon pressure. 1.2 mL aqueous solution of PS-750-M was then added to the reaction mixture. Reaction mixture was purged with argon for 2 min. Reaction mixture was stirred at 60 °C for 12 h.

After complete consumption of starting material as monitored by TLC, reaction mixture was allowed to cool to rt. MTBE (0.5 mL) was added to the reaction mixture, and mixture was stirred for a minute at rt. Stirring was stopped and organic layer was allowed to separate. Organic layer was withdrawn with the aid of syringe needle. This extraction process was repeated for an additional time. Combined organic layer was dried over anhydrous sodium sulfate and volatiles were removed under reduce pressure to obtain crude product. Crude product was purified by flash chromatography over silica gel using EtOAc/hexanes as eluent ($R_f = 0.4$, 9:1 hexanes/EtOAc). Pure product was obtained as viscous oil, yield 127 mg (91%).

5. OPTIMIZED PROCEDURE FOR CATALYTIC COUPLINGS

5.1. With the isolated catalyst. Hetero/aryl bromide (0.3 mmol), Aryl/alkyl amine (0.36 mmol), charcoal immobilized nanocatalyst (9.0 mg), and KOH (50.4 mg, 0.9 mmol) were added into the 4 mL oven-dried reaction vial containing PTFE-coated stirrer-bar. Reaction vial was closed with a rubber septum. Reaction mixture was evacuated and back-filled with argon for three times. 0.6 mL aqueous solution of 3 wt % PS-750-M was added to the reaction mixture. Reaction mixture was purged with argon for 2 min. Reaction vial was heated at 60 °C.

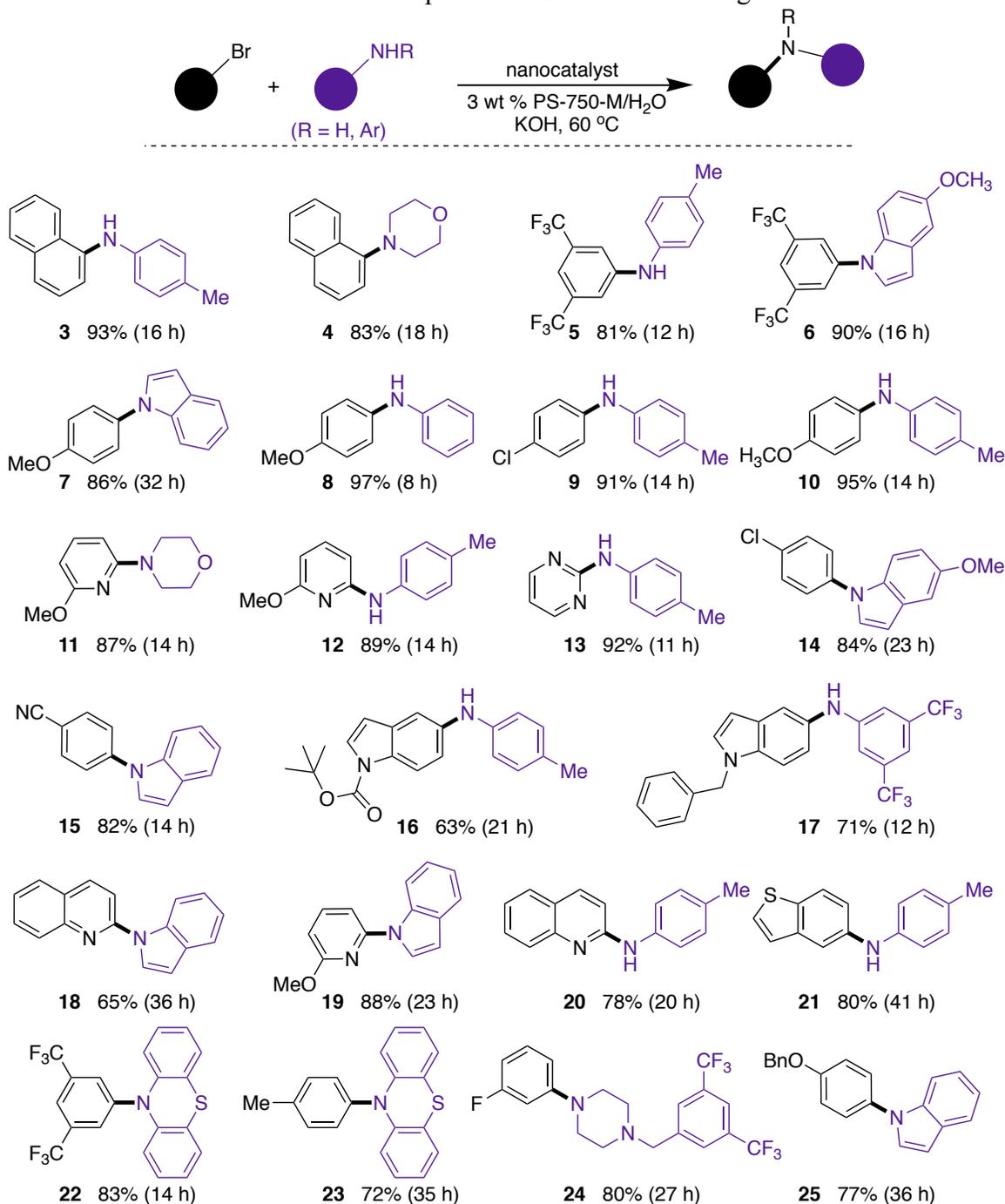
After the complete consumption of starting material as monitored by TLC and GCMS, the mixture was cooled to room temperature. Septum was removed and 0.5 mL MTBE or EtOAc was added to the reaction mixture, which was then stirred for a minute at rt. Stirring was stopped and organic layer was allowed to separate from aqueous layer. Organic layer was removed with the help of pipette. This extraction process was repeated for additional time. Combined organic layer was dried over anhydrous sodium sulfate and volatiles were removed under reduced pressure to obtain crude product. Crude product was further purified by flash chromatography over silica gel using EtOAc and Hexanes as eluent.

5.2. With *in-situ* formed catalyst. In a 4 mL oven-dried reaction vial equipped with PTFE coated magnetic stirrer bar, Pd(OAc)₂ (0.003 mmol, 100 μL from a 0.03 M stock solution in THF), tetrakis(acetonitrile)copper(I) hexafluorophosphate (2.2 mg, 0.006 mmol), and cBRIDP (3.2 mg, 0.009 mmol) were added under inert atmosphere. Reaction vial was closed with a rubber septum. Reaction mixture was gently heated with a heat gun to obtain dark red color mixture. Reaction mixture was heated at 60 °C for additional 15 min. Reaction mixture was allowed to cool to rt. Under inert atmosphere, charcoal (3.0 mg) powder was added to the reaction mixture. Reaction mixture was again heated at 60 °C for 15 min to generate active nanocatalyst. THF was evacuated from the catalyst at rt, Aryl(heteroaryl) bromide (0.3 mmol), aryl(alkyl) amine (0.36 mmol), and KOH (50.4 mg, 0.9 mmol) were added to the reaction mixture. Reaction vessel was closed with a rubber septum. Reaction vessel was evacuated and backfilled with argon for three times. To this mixture, 0.6 mL aqueous solution of 3 wt % PS-750-M was added. Reaction mixture was purged with argon for 2 min. Reaction mixture was heated at 60 °C.

After the complete consumption of starting material as monitored by TLC and GCMS, the mixture was cooled to room temperature. 0.5 mL MTBE or EtOAc was added to the reaction mixture and mixture was stirred for a minute at rt. Stirring was stopped and two layers were allowed to separate. Organic layer was withdrawn with the help of pipette. This extraction process was repeated for an additional time. Combined organic layers were dried over anhydrous sodium sulfate and volatiles were removed under reduced pressure to obtain crude product. Crude product was further purified by flash chromatography over silica gel using EtOAc/hexanes as eluent.

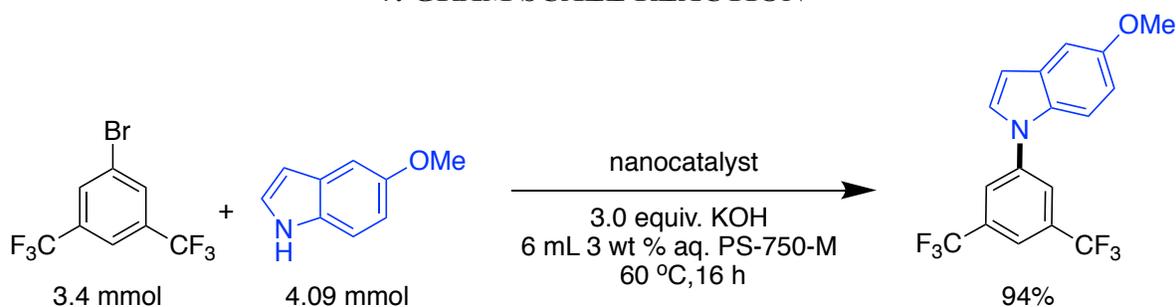
6. SUBSTRATE SCOPE

Table S11. Substrate scope for the Buchwald-Hartwig amination



Conditions: ArBr (0.3 mmol), aryl amine (0.36 mmol), nanocatalyst (9 mg, 1 mol % based on Pd), KOH (0.9 mmol, 3.0 equiv), 3 wt % PS-750-M in H₂O (0.6 mL), 60 °C. All yields are isolated.

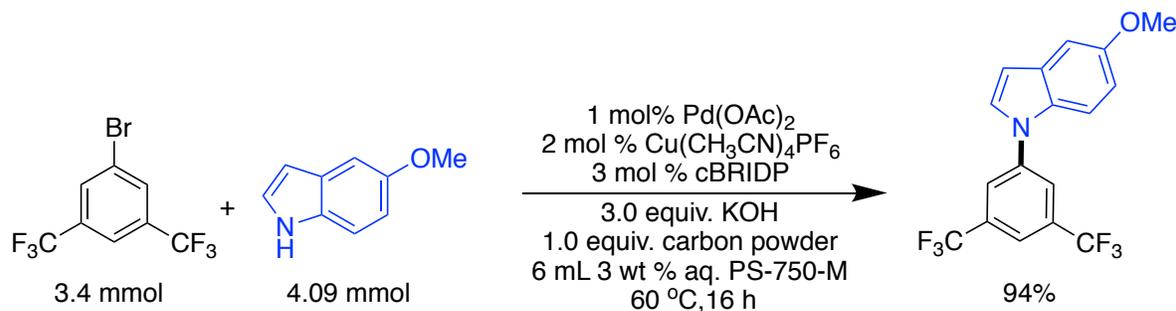
7. GRAM SCALE REACTION



Scheme S2. Gram scale reaction.

5-Methoxy-1H-indole (0.6 g, 4.09 mmol), nanocatalyst (110 mg), and KOH (0.57g, 10.2 mmol) were added into the 25 mL oven-dried reaction vial containing PTFE-coated stirrer bar. Reaction vial was evacuated and backfilled with argon for three times. 1-Bromo-3,5-bis(trifluoromethyl)benzene (0.58 mL, 3.4 mmol) and 6 mL aqueous solution of PS-750-M were added to the reaction vial. Reaction mixture was purged with argon for 5 minutes and then stirred at 60 °C for 16 h (Scheme S2). After complete consumption of starting material as monitored by TLC and GCMS, reaction flask was allowed to cool to rt. 3 mL of EtOAc was added to the reaction mixture without opening the septa. Reaction mixture was then stirred for 2 min at rt. Stirring was stopped and organic layers was allowed to separate out from an aqueous layer. Organic layer was taken out with the use of 3 mL syringe needle. Same extraction procedure was repeated for an additional time. Combined organic layers were dried over anhydrous sodium sulfate. Volatiles were removed under reduced pressure to obtain crude product. Crude product was purified by flash chromatography over silica gel using hexanes/ethyl acetate as eluent (R_f 0.4, 4: 1 hexanes/ethyl acetate), yield 95% (1.16 g).

8. RECYCLABILITY AT GRAM SCALE

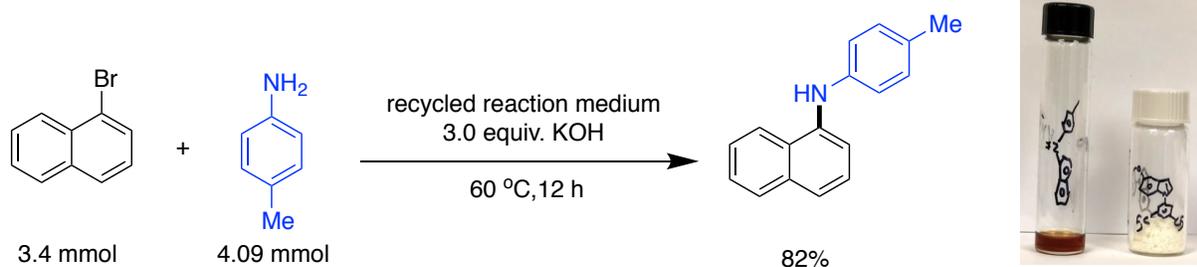


Scheme S3. Initial reaction: Recyclability of nanocatalyst at a gram scale reaction.

To a 25 mL oven-dried round-bottomed flask containing a PTFE-coated stir bar, Pd(OAc)₂ (7.65 mg, 1 mol%), tetrakis(acetonitrile)copper(I) hexafluorophosphate (25.4 mg, 2 mol %), and cBRIDP (36.0 mg, 3 mol%) were added. Reaction flask was closed with a rubber septum and mixture was evacuated and back-filled with argon for three times. Via syringe, dry THF (1.0 mL) was added to the reaction mixture and gently heated with heat gun, which caused immediate color change of a reaction mixture from yellow to reddish-brown. Mixture was further heated at 60°C for 15 min. Reaction mixture was allowed to cool to rt. The reaction vial was opened and activated charcoal (41 mg) was added to it. Reaction flask was closed with a rubber septum and mixture was stirred at 60°C for 15 min. THF was evaporated under reduced pressure and 6 mL aqueous solution of 3 wt % PS-750-M was added to the mixture. Reaction mixture was stirred for 5 min. Under argon atmosphere, 1-bromo-3,5-bis(trifluoromethyl)benzene (0.58 mL, 3.4 mmol), 5-methoxy-1H-indole (0.6 g, 4.09 mmol), and KOH (0.57 g, 10.2 mmol) were sequentially added to reaction mixture. Reaction flask was closed with a rubber septum and mixture was purged with argon for 5 min. Reaction mixture was stirred at 60 °C for 16 h (Scheme S3).

After complete consumption of starting material as monitored by TLC and GCMS, reaction flask was allowed to cool to rt. 3 mL of MTBE was added to the reaction mixture without opening the septum. Reaction mixture was then stirred for 2 min. Stirring was stopped and organic layers was allowed to separate out from an aqueous layer. Organic layer was taken out with the use of 3 mL syringe needle. Same extraction procedure was repeated for an additional time. *Aqueous layer containing the catalyst was retained for a recycling test at gram scale reaction.* Combined organic layers were dried over anhydrous sodium sulfate. Volatiles were removed under reduced pressure

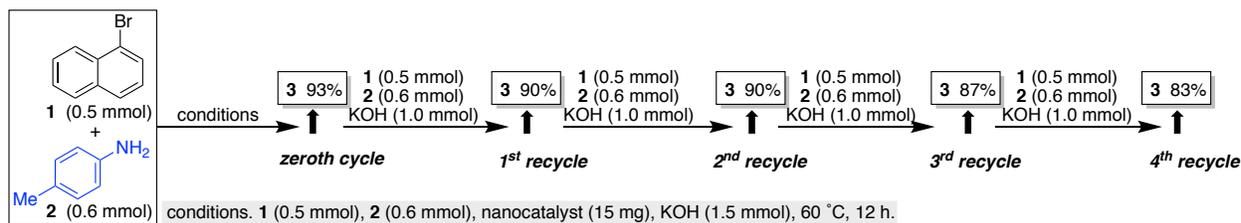
to obtain crude product. Crude product was purified by flash chromatography over silica gel using hexanes/ethyl acetate as eluent (R_f 0.4, 4:1 hexanes/ethyl acetate), white solid, yield 94% (1.14 g). To the remaining aqueous reaction medium containing the catalyst, 1 mL 3 wt % aqueous solution PS-750-M was added. Resulting solution was reused for another gram-scale reaction with different coupling partners as described below (Scheme S4).



Scheme S4. Recyclability of nanocatalyst at a gram scale reaction.

An above aqueous mixture retaining the catalyst was purged with an argon for 10 min. The solution was further charged with 1-bromonaphthalene (0.47 mL, 3.4 mmol), *p*-toluidine (0.48 g, 4.09 mmol) and KOH (0.57 g, 10.2 mmol) under positive argon pressure. Reaction flask was closed with a rubber septum and mixture was allowed to stir at 60 °C for 12 h. After complete consumption of starting material as monitored by TLC and GCMS, reaction flask was allowed to cool to rt. 3 mL of MTBE was added to the reaction mixture without opening the septa. Reaction mixture was then stirred for 2 min. Stirring was stopped and organic layer was allowed to separate out from an aqueous layer. Organic layer was taken out with the use of 3 mL syringe needle. Same extraction procedure was repeated for an additional time. Combined organic layers were dried over anhydrous sodium sulfate. Volatiles were removed under reduced pressure to obtain crude product. Crude product was purified by flash chromatography over silica gel using hexanes/ethyl acetate as eluent (R_f 0.4, 9:1 hexanes:ethyl acetate), viscous oil, yield 82% (650 mg).

9. E FACTOR AND RECYCLE STUDY



$$\text{E Factor} = \frac{\text{amount of waste}}{\text{amount of product}} = \frac{\text{MTBE used in each cycle (mg)} + \text{waste in each cycle (mg)}}{\text{total amount of product (mg)}}$$

$$= \frac{572 + 578 + 580 + 577 + 572 \text{ (in mg)}}{108 + 105 + 103 + 101 + 97 \text{ (in mg)}} = 2879/514 = 5.6$$

E Factor = 5.6

Scheme S5. Recycle study and E factor calculation.

Caution. (i) Argon purged MTBE must be used; (ii) after each cycle, the catalyst containing reaction medium must be purged with argon; (iii) for improved extraction, use warm MTBE.

Zeroth cycle: In a 4.0 mL flame-dried microwave reaction vial containing a PTFE-coated magnetic stir bar, *p*-toluidine (64 mg, 0.6 mmol), KOH (84 mg, 1.5 mmol) nanocatalyst (15 mg) were added. The reaction vial was closed with a rubber septum. Mixture was evacuated and back-filled with argon and this process was repeated for three times. Under the positive pressure of argon, 1-bromonaphthalene (70 μ L, 0.5 mmol) was added to the reaction mixture. Under inert atmosphere, freshly degassed 1.0 mL aqueous solution of 3 wt % PS-750-M was added to the reaction mixture. Reaction mixture was purged with argon for next two minutes. The rubber septum was wrapped with black electrical tape and parafilm. Reaction mixture was stirred at 60 °C for 12 h.

After complete consumption of 1-bromonaphthalene as indicated by TLC and GCMS, the mixture was cooled to room temperature. Then, 0.3 mL warm MTBE was added to the mixture, which was then stirred for 2 minutes at rt. Stirring was stopped and organic layer was allowed to separate. An organic layer was removed using a syringe. This extraction procedure was repeated for one more time (total 0.6 mL MTBE). The aqueous portion was kept for 1st recycle study. The combined organic layers were dried over anhydrous sodium sulfate. Volatiles were removed under reduced pressure to obtain crude product, which was further purified by a flash chromatography over silica gel using hexanes/ethyl acetate as eluent (1:9), R_f 0.4. Pure product was obtained as dark brown

viscous oil, yield 108 mg (93%) (The eluent used in the flash column chromatography was saved for reuse in the next cycle, also see Scheme S5).

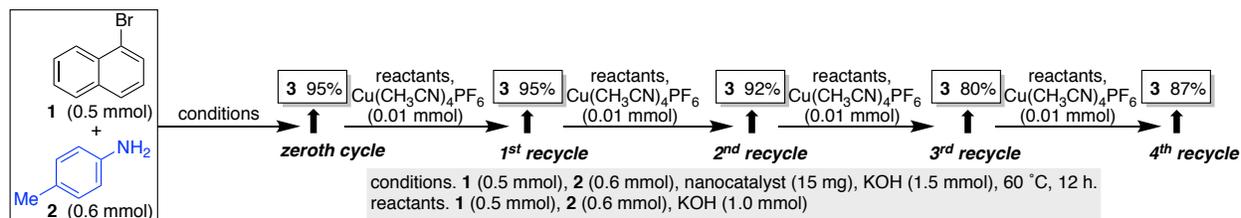
1st recycle: The aqueous solution obtained from the above reaction was purged with argon for 10 minutes prior to reuse. To this well purged aqueous solution, *p*-toluidine (64 mg, 0.6 mmol), KOH (56 mg, 1.0 mmol) and 1-bromonaphthalene (70 μ L, 0.5 mmol) were sequentially added under the positive argon pressure. Reaction vial was closed with a rubber septum. Septum was sealed with a PTFE tape and black electrical tape. The reaction mixture was stirred at 60 °C for 12 h. After complete consumption of 1-bromonaphthalene as monitored by GCMS, similar extraction and purification procedures were applied as in zeroth cycle. Pure product was obtained as brown oil, yield 105 mg (90%). The aqueous part was retained for the 2nd recycle.

iii) 2nd recycle: The 2nd recycle was also achieved following similar procedures as described above; yield 103 mg (89%).

iv) 3rd recycle: The 3rd recycle was also achieved following similar procedures as described above; yield 101 mg (87%).

v) 4th recycle: The 4th recycle was also achieved following similar procedures as described above; yield 97 mg (83%).

10. EFFECT OF ADDITIONAL $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ ADDITION ON RECYCLABILITY



Scheme S6. Effect of additional $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ on recyclability study and E factor calculation.

Caution. (i) Argon-purged MTBE must be used; (ii) after each cycle, the catalyst containing reaction medium must be purged with argon; (iii) for improved extraction, use warm MTBE.

Zeroth cycle: In a 4.0 mL flame-dried microwave reaction vial containing a PTFE-coated magnetic stir bar, *p*-toluidine (64 mg, 0.6 mmol), KOH (84 mg, 1.5 mmol), and nanocatalyst (15 mg) were added. The reaction vial was closed with a rubber septum. Mixture was evacuated and back-filled with argon and this process was repeated for three times. Under the positive pressure of argon, 1-bromonaphthalene (70 μL , 0.5 mmol) was added to the reaction mixture. Under inert atmosphere, freshly degassed 1.0 mL aqueous solution of 3 wt % PS-750-M was added to the reaction mixture. Reaction mixture was purged with argon for next two minutes. The rubber septum was wrapped with black electrical tape and parafilm. Reaction mixture was stirred at 60 °C for 12 h.

After 12 h, 0.3 mL warm MTBE was added to the mixture, which was then stirred for 2 minutes at rt. Stirring was stopped and organic layer was allowed to separate. An organic layer was removed using a syringe. This extraction procedure was repeated for one more time (total 0.6 mL MTBE). After the extraction, the septum was opened and 4.5 mg of $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ was added under an argon atmosphere. This aqueous portion was kept for 1st recycle study (also see Scheme S6). The combined organic layers were analyzed using GCMS and TLC. GCMS analysis indicated 95% of product.

1st recycle: The aqueous solution obtained from the above reaction was purged with argon for 10 minutes prior to reuse. To this well purged aqueous solution, *p*-toluidine (64 mg, 0.6 mmol), KOH (56 mg, 1.0 mmol), and 1-bromonaphthalene (70 μL , 0.5 mmol) were sequentially added under the positive argon pressure. Reaction vial was closed with a rubber septum. Septum was sealed

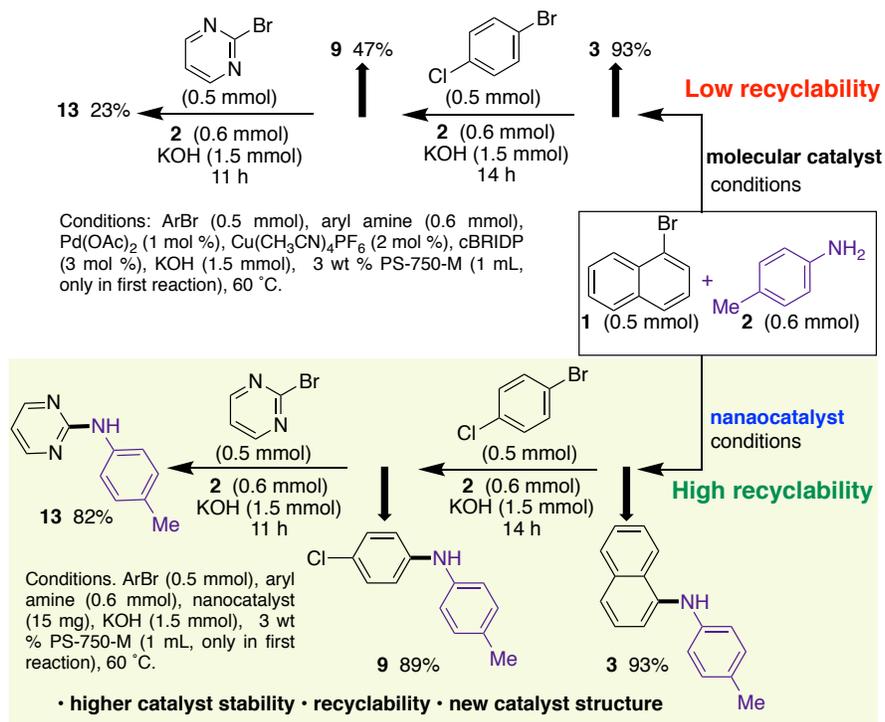
with a PTFE tape and black electrical tape. The reaction mixture was stirred at 60 °C for 12 h. Similar extraction and $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ addition procedures were repeated as in zeroth cycle. GCMS analysis indicated 95% of product.

iii) 2nd recycle: The 2nd recycle was also achieved following similar procedures as described above; conversion 92%.

iv) 3rd recycle: The 3rd recycle was also achieved following similar procedures as described above; conversion 90%.

v) 4th recycle: The 4th recycle was also achieved following similar procedures as described above; conversion 87%.

11. ROLE OF CHARCOAL



Scheme S7. Role of charcoal on catalyst recyclability

11.1. Nanoparticles on charcoal – highly recyclable nanocatalyst

(a) First reaction: In a 4.0 mL flame-dried microwave reaction vial containing a PTFE-coated magnetic stir bar was charged with *p*-toluidine (64 mg, 0.6 mmol), KOH (84 mg, 1.5 mmol) and charcoal-immobilized nanocatalyst (15 mg). The reaction vial was closed with a rubber septum. Mixture was evacuated and back-filled with argon and this process was repeated for three times. Under the positive pressure of argon, 1-bromonaphthalene (70 μ L, 0.5 mmol) was added to the vial. Under inert atmosphere, freshly degassed 1.0 mL aqueous solution of 3 wt % PS-750-M was added to the reaction mixture. Reaction mixture was purged with argon for next two minutes. Rubber septum was further wrapped with PTFE and black electrical tape. Reaction mixture was heated at 60 °C for 16 h.

After complete consumption of 1-bromonaphthalene as indicated by TLC and GCMS, reaction mixture was cooled to rt. Then, 0.5 mL warm MTBE was added to it and mixture was allowed to stir for 2 min at rt. Stirring was stopped and organic layer was allowed to separate. An organic layer was removed using a syringe. This extraction procedure was repeated for one more time

(total 1.0 mL of MTBE). The aqueous portion was kept for next recycling analysis. The combined extracts were dried over anhydrous sodium sulfate. Volatiles were removed under reduced pressure at room temperature to obtain crude product, which was further purified by a flash chromatography over silica gel using hexanes/ethyl acetate as eluent (1:9), R_f 0.4. Pure product was obtained as dark brown viscous oil, yield 108 mg (93%).

(b) Second reaction: The aqueous solution obtained from the above reaction was purged with argon for 10 minutes prior to reuse (also see Scheme S7). To this well purged aqueous solution, *p*-toluidine (64 mg, 0.6 mmol), 4-chlorobromobenzene (95.5 mg, 0.5 mmol), and KOH (84 mg, 1.5 mmol) were sequentially added under the positive argon pressure. Reaction vial was closed with a rubber septum. Septum was sealed with a PTFE tape and black electrical tape. The reaction mixture was stirred at 60 °C for 14 h. After complete consumption of starting material as monitored by GCMS, similar extraction procedures were applied as in the above reaction. Pure product was obtained as a white solid (96.5 mg, 89% yield) after flash column chromatography over silica gel using hexanes/ethyl acetate as eluent (19:1), R_f 0.3. The aqueous part was retained for the next reaction.

(c) Third reaction: The aqueous solution obtained from the above reaction was purged with argon for 10 minutes prior to reuse. To this well purged aqueous solution, *p*-toluidine (64 mg, 0.6 mmol) and 2-bromopyrimidine (95 mg, 0.5 mmol) and KOH (84 mg, 1.5 mmol) were sequentially added under the positive argon pressure. Reaction vial was closed with a rubber septum. Septum was sealed with a PTFE tape and black electrical tape. The reaction mixture was stirred at 60 °C for 11 h. After complete consumption of starting material as monitored by GCMS, similar extraction and purification procedures were applied as in the first cycle. Pure product was obtained as a white solid (76 mg, 82% yield) after flash column chromatography over silica gel using hexanes/ethyl acetate as eluent (5:1), R_f 0.4.

11.2. Nanoparticles without charcoal – low recyclability

(a) First reaction: In a 4 mL oven dried-reaction vial, 0.05 M (1 mL) stock solution of palladium(II) acetate was prepared in dry THF. In another oven-dried 4 mL reaction vial equipped with PTFE-coated stir bar, *tetrakis*(acetonitrile)copper(I) hexafluorophosphate (3.7 mg, 0.01 mmol) and cBRIDP (5.3 mg, 0.015 mmol) were added. The vessel was closed with a rubber septum

and under inert atmosphere, 0.1 mL of Pd(OAc)₂ from a stock solution was added to it. Mixture was gently heated with a heat gun to obtain dark red color mixture. Reaction mixture was heated at 60 °C for additional 15 min. After evaporating THF under vacuum, the vial was charged with *p*-toluidine (64 mg, 0.5 mmol) and KOH (84 mg, 1.5 mmol). The reaction vial was closed with a rubber septum. Mixture was evacuated and back-filled with argon and this process was repeated for three times. Under the positive pressure of argon, 1-bromonaphthalene (70 μL, 0.5 mmol) were then added. Freshly degassed 1.0 mL aqueous solution of 3 wt % PS-750-M was added to the reaction mixture. The mixture was purged with argon for next two minutes. Reaction mixture was stirred for 16 h at 60 °C.

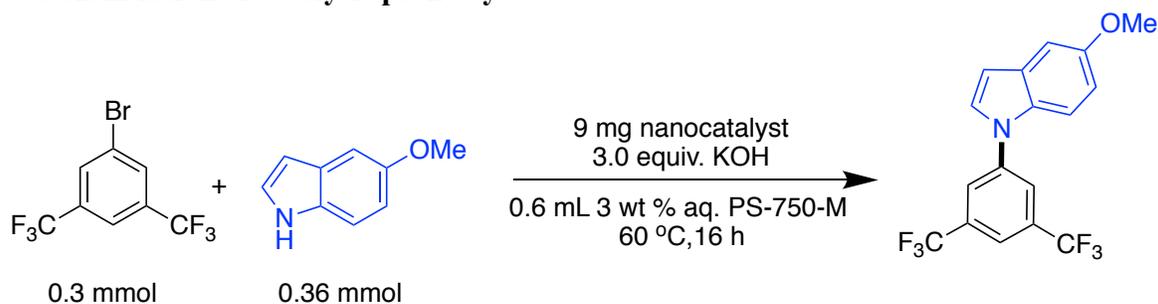
After complete consumption of 1-bromonaphthalene, as indicated by TLC and GCMS, the mixture was cooled to room temperature. 0.5 mL warm MTBE was added and mixture was stirred for 2 min at rt. Stirring was stopped and organic layer was allowed to separate. An organic layer was removed using a syringe. This extraction procedure was repeated for one more time (total 1.0 mL of MTBE). An aqueous portion was kept for second reaction. The combined extracts were dried over anhydrous sodium sulfate. Volatiles were removed under reduced pressure at rt to obtain crude product, which was further purified by a flash chromatography over silica gel using hexanes/ethyl acetate as eluent (1:9), *R_f* = 0.4. Pure product was obtained as dark brown viscous oil, yield 114 mg (98%).

(b) Second reaction: An aqueous solution obtained from the above reaction was purged with argon for 10 minutes prior to reuse. To this well purged aqueous solution, *p*-toluidine (64 mg, 0.6 mmol), 4-chlorobromobenzene (95.5 mg, 0.5 mmol), and KOH (84 mg, 1.5 mmol) were sequentially added under the positive argon pressure. Reaction vial was closed with a rubber septum. Septum was sealed with a PTFE tape and black electrical tape. The reaction mixture was stirred at 60 °C for 15 h. After 14 h, similar extraction procedures were applied as in the above reaction. Pure product was obtained as a white solid after flash column chromatography (hexanes/EtOAc, 19:1 *R_f* 0.3), yield 51 mg (47%). An aqueous part was retained for the next reaction.

(c) Third reaction: An aqueous solution obtained from the above reaction was purged with argon for 10 minutes prior to reuse. To this well purged aqueous solution, *p*-toluidine (64 mg, 0.6 mmol),

2-bromopyrimidine (95 mg, 0.5 mmol), and KOH (84 mg, 1.5 mmol) were sequentially added under the positive argon pressure. Reaction vial was closed with a rubber septum. Septum was sealed with a PTFE tape and black electrical tape. The reaction mixture was stirred at 60 °C for 21 h. After 11 h, similar extraction and purification procedures were applied as in the first cycle. Pure product was obtained as a white solid after flash column chromatography (hexanes:EtOAc, 5:1 R_f 0.4), yield 20 mg (22%).

11.3. Continuation of catalytic pathway

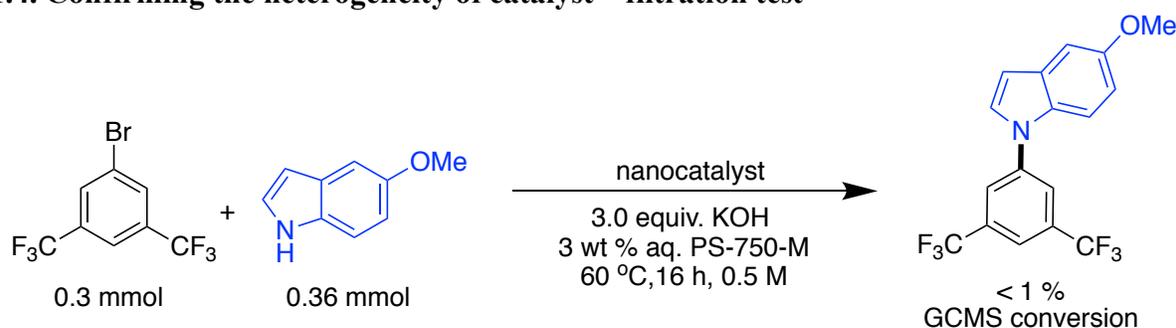


Scheme S8. Continuous reactions without isolation.

5-Methoxy-1H-indole (53 mg, 0.6 mmol), nanocatalyst (9 mg), and KOH (50.4 mg, 0.9 mmol) were added into the 4 mL oven-dried reaction vial containing PTFE-coated stirrer bar. Reaction vial was evacuated and back-filled with argon for three times. 1-Bromo-3,5-bis(trifluoromethyl)benzene (51 μ L, 0.3 mmol) and 0.6 mL aqueous solution of PS-750-M was added to the reaction mixture. Reaction mixture was purged with argon for 2 minutes and then stirred for 16 h at 60 °C (Scheme S8). After complete consumption of starting material as monitored by TLC, reaction mixture was allowed to cool to rt. Without isolating the product, another batch of reactants were introduced into the reaction mixture, i.e., 1-bromo-3,5-bis(trifluoromethyl)benzene (51 μ L, 0.3 mmol), 5-methoxy-1H-indole (53 mg, 0.6 mmol), and KOH (50.4 mg, 0.9 mmol). Reaction vial was evacuated and back-filled with argon. Reaction mixture was purged with argon for 2 minutes and then stirred for 16 h at 60 °C. Reaction progress monitoring using GCMS. After complete consumption of starting material, reaction mixture was allowed to cool to rt. Without isolating the product, another batch of reactants were introduced into the reaction mixture, i.e., 1-bromo-3,5-bis(trifluoromethyl)benzene (51 μ L, 0.3 mmol), 5-methoxy-1H-indole (53 mg, 0.6 mmol), and KOH (50.4 mg, 0.9 mmol). Reaction vial was

evacuated and back-filled with argon. Reaction mixture was purged with argon for 2 minutes and then stirred for 16 h at 60 °C. Reaction progress monitoring using GCMS. After complete consumption of starting material, reaction mixture was allowed to cool to rt. EtOAc (0.5 mL) was added to the reaction mixture and stirred for a minute at rt. Stirring was stopped and organic layer was allowed to separate. Organic layer was withdrawn with the aid of syringe needle. This extraction process was repeated for an additional time. Combined organic layers were dried over anhydrous sodium sulfate. Volatiles were removed under reduce pressure to obtain crude product. Crude product was purified by flash chromatography over silica gel using EtOAc/hexanes as eluent (R_f 0.4, 1:4 EtOAc/hexanes), yield 297.2 mg (92% over all isolated yield).

11.4. Confirming the heterogeneity of catalyst – filtration test



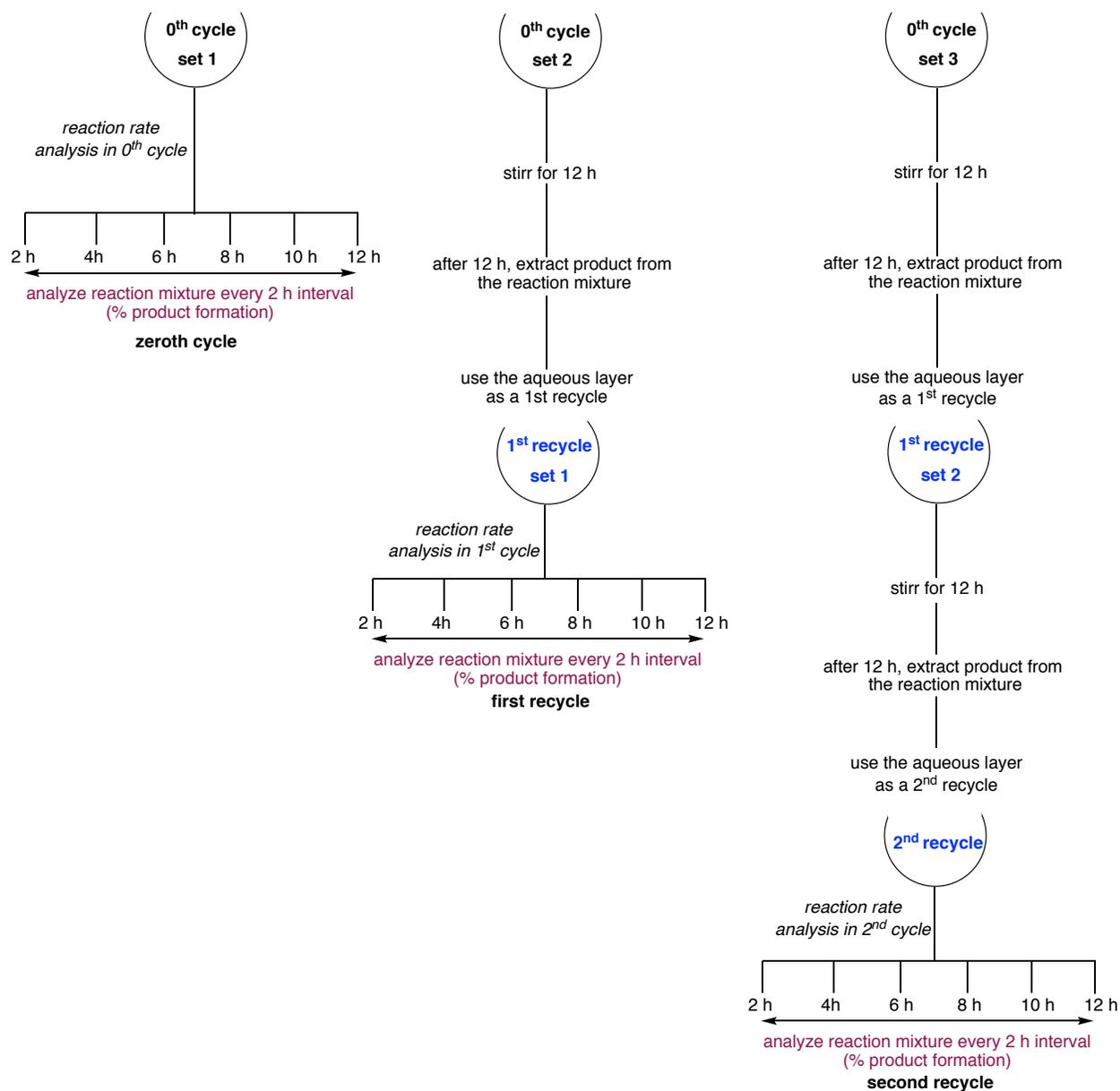
Scheme S9. Metal leaching study by filtration.

In a 4 mL oven-dried reaction vial containing PTFE-coated stirrer-bar was charged with nanocatalyst (9 mg). The reaction vial was closed with a rubber septum and evacuated and backfilled with argon three times. Later, 0.6 mL of 3 wt% aq. solution of PS-750-M was added, and the mixture was stirred for the next two hours at 60 °C. Later, the obtained turbid solution (small black particles) was filtered using glass fiber filter paper to another oven-dried 4 mL reaction vial which already contained PTFE-coated stirrer-bar, 5-methoxyindole (53 mg, 0.36 mmol), and KOH (50.4 mg, 0.9 mmol). The reaction vial was closed with a rubber septum and evacuated and backfilled with argon three times (cautions: appropriate technique must be used to avoid the entry of foams to the vacuum/argon line). Later, 3,5-bis(trifluoromethyl)benzyl bromide (51 μ L, 0.3 mmol) was added, and the septum was wrapped with parafilm. The reaction mixture was purged with argon for 2 min. The reaction vial was stirred for the next 16 h at 60 °C (Scheme S9). Later, the mixture was cooled to room temperature. The septum was removed and 0.5 mL EtOAc was added to the reaction mixture, which was then stirred for a minute at rt. Stirring was

stopped, and the organic layer was allowed to separate from the aqueous layer. The organic layer was removed with the help of a pipette. This extraction process was repeated for additional time. An aliquot from this organic layer was analyzed using GCMS and TLC (R_f 0.4, 4:1 Hex: EtOAc). GCMS indicated traces of product formation (<1%).

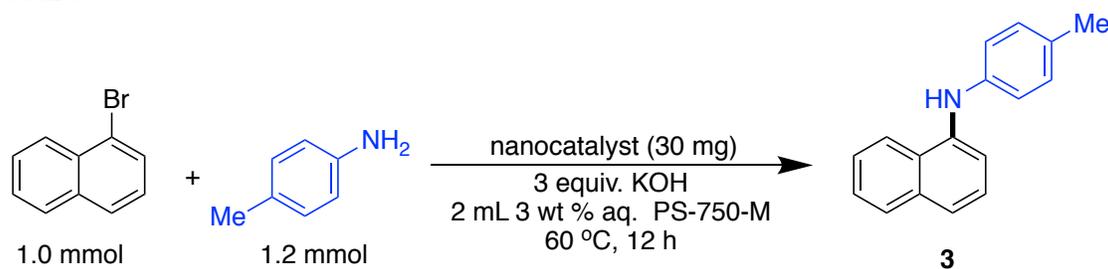
12. KINETIC STUDY ON RECYCLABILITY OF CATALYST

Outline of a plan for kinetic studies (see Scheme S10 below)



Scheme S10. Role of charcoal on catalyst recyclability

Procedure



Scheme S11. Kinetic study on recyclability of catalyst.

In a 4.0 mL flame-dried microwave reaction vial containing a PTFE-coated magnetic stir bar, *p*-toluidine (128.4 mg, 1.2 mmol), KOH (168 mg, 3 mmol), and nanocatalyst (30 mg) were added. The reaction vial was closed with a rubber septum. The mixture was evacuated and backfilled with argon, and this process was repeated for three times. Under the positive pressure of argon, 1-bromonaphthalene (140 μ L, 1 mmol) was added to the reaction mixture. Under an inert atmosphere, a freshly degassed 2.0 mL aqueous solution of 3 wt % PS-750-M was added to the reaction mixture. The reaction mixture was purged with argon for the next two minutes. The rubber septum was wrapped with black electrical tape and parafilm. The reaction mixture was transferred to a preheated well plate at 60 °C and allowed to stir. After 2 h, under vigorous stirring conditions, an aliquot of 50 μ L (equivalent to 0.025 mmol) was withdrawn from the vial without disturbing any key reaction parameters (temperature and argon atmosphere). The aliquot was diluted with 1 mL EtOAc containing 0.87 μ L (0.25 equiv. to aliquot or 0.00625 mmol) of mesitylene [to ensure accuracy, a stock solution of 8.7 μ L mesitylene in 10 mL EtOAc was prepared and 1.0 mL from this solution was used each time to dilute the 50 μ L aliquot]. The diluted 1.0 mL mixture was passed through a silica pad to remove metal impurities, and organic layer was analyzed using GCMS. Following a same protocol, reaction mixture was analyzed for every 2 h interval until 12 h of reaction.

Following a plan for the kinetic studies as outlined on last page, a separate, undisturbed similar reaction set was kept for 12 h at 60 °C, later the mixture was treated with 0.3 mL warm MTBE, which was then stirred for 2 minutes at rt. Stirring was stopped and organic layer was allowed to separate. An organic layer was removed using a syringe. This extraction procedure was repeated for one more time (total 0.6 mL MTBE). The aqueous portion was kept for 1st recycle.

The aqueous solution obtained from the above was purged with argon for 10 minutes prior to reuse. To this well purged aqueous solution, *p*-toluidine (128 mg, 1.2 mmol), KOH (168 mg, 3 mmol),

and 1-bromonaphthalene (140 μL , 1 mmol) were sequentially added under the positive argon pressure. Reaction vial was closed with a rubber septum and sealed with a PTFE tape and black electrical tape. The reaction mixture was stirred at 60 $^{\circ}\text{C}$. After 2 h, under vigorous stirring conditions, an aliquot of 50 μL (equivalent to 0.025 mmol) was withdrawn from the vial without disturbing any key reaction parameters (temperature and argon atmosphere). The aliquot was diluted with 1.0 mL EtOAc containing 0.87 μL (0.25 equiv. to aliquot or 0.00625 mmol) of mesitylene [to ensure accuracy, a stock solution of 8.7 μL mesitylene in 10 mL EtOAc was prepared and 1 mL from this solution was used each time to dilute the 50 μL aliquot]. The diluted 1.0 mL mixture was passed through a silica pad to remove metal impurities and analyzed using GCMS. Following a same protocol, reaction mixture was analyzed for every 2 h interval until 12 h of reaction.

For the second recycle, a plan described in the outline was exactly followed. This aqueous solution was purged with argon for 10 minutes prior to reuse. To this well purged aqueous solution, *p*-toluidine (128 mg, 1.2 mmol), KOH (168 mg, 3 mmol) and 1-bromonaphthalene (140 μL , 1 mmol) were sequentially added under the positive argon pressure. Reaction vial was closed with a rubber septum and sealed with a PTFE tape and black electrical tape. The reaction mixture was stirred at 60 $^{\circ}\text{C}$. After 2 h, under vigorous stirring conditions, an aliquot of 50 μL (equivalent to 0.025 mmol) was withdrawn from the vial without disturbing any key reaction parameters (temperature and argon atmosphere). The aliquot was diluted with 1 mL EtOAc containing 0.87 μL (0.25 equiv. to aliquot or 0.00625 mmol) of mesitylene [to ensure accuracy, a stock solution of 8.7 μL mesitylene in 10 mL EtOAc was prepared and 1 mL from this solution was used each time to dilute the 50 μL aliquot]. The diluted 1.0 mL mixture was passed through a silica pad to remove metal impurities and analyzed using GCMS. Following a same protocol, reaction mixture was analyzed for every 2 h interval until 12 h of reaction.

Note-Following precautions must be taken to get consistent results (i) vigorous stirring must be ensured while withdrawing aliquots, this will guarantee homogeneity, (ii) argon purged MTBE must be used, (iii) after each cycle, the catalyst-containing reaction medium must be purged with argon.

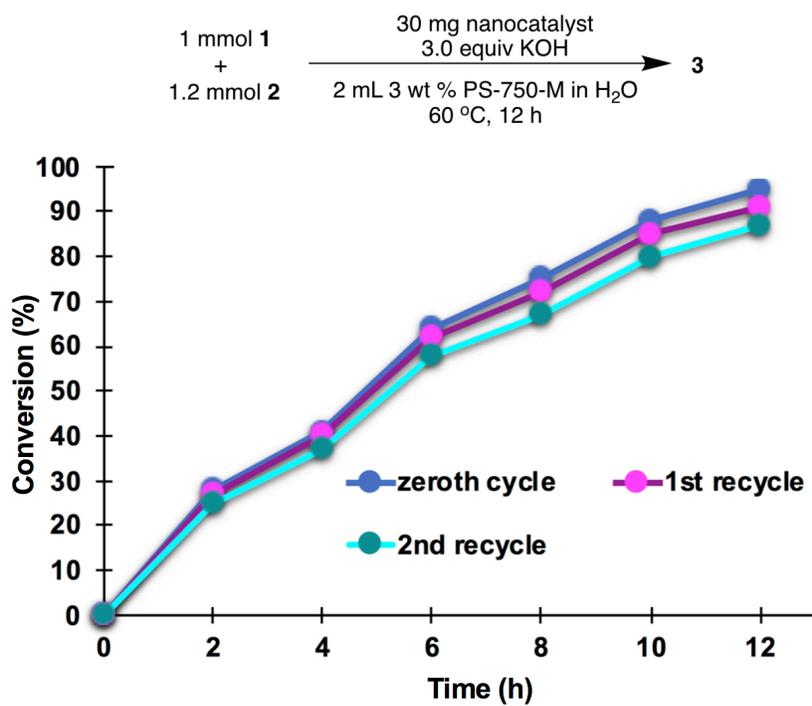
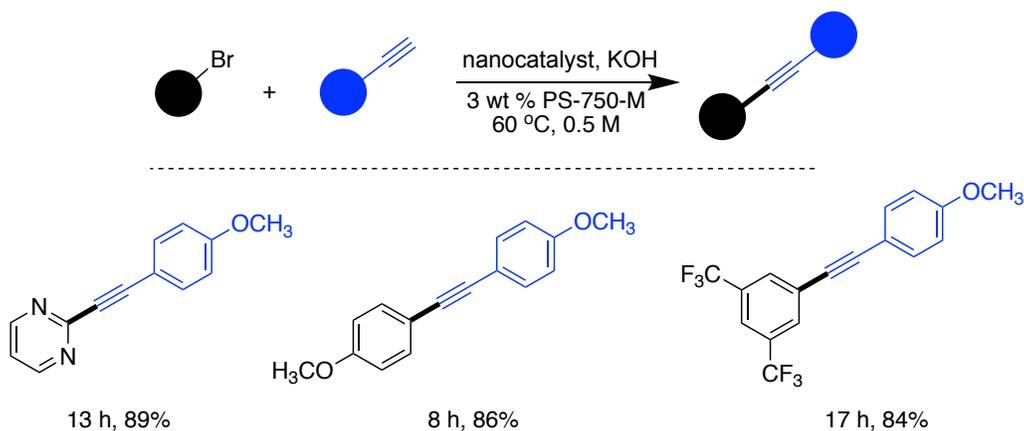


Figure S2. Kinetic studies as a valid assessment regarding the stability of catalyst.

13. SONOGASHIRA COUPLINGS USING NANOCATALYST

Hetero/aryl bromide (0.3 mmol), alkyne (0.36 mmol), nanocatalyst (9.0 mg), and KOH (50.4 mg, 0.9 mmol) were added into the 4 mL oven-dried reaction vial containing PTFE-coated stirrer-bar. Reaction vial was closed with a rubber septum. Vessel was quickly evacuated and back-filled with argon. To this mixture, 0.6 mL aqueous solution of 3 wt% PS-750-M was added. Reaction mixture was purged with argon for 2 min. Reaction mixture was stirred at 60 °C. After the complete consumption of starting material indicated by TLC and GCMS, the mixture was cooled to room temperature. 0.5 mL EtOAc was added and mixture was stirred for a minute at rt. Organic and aqueous layers were allowed to separate. An organic layer was withdrawn with pipette. This extraction process was repeated for an additional time. Combined organic layers were dried over anhydrous sodium sulfate. Volatiles were removed under reduced pressure to obtain the crude product (see Table S12). The crude mixture was further purified by flash chromatography over silica gel using EtOAc/hexanes as eluent.

Table S12. Substrate scope for the Sonogashira coupling using nanocatalyst

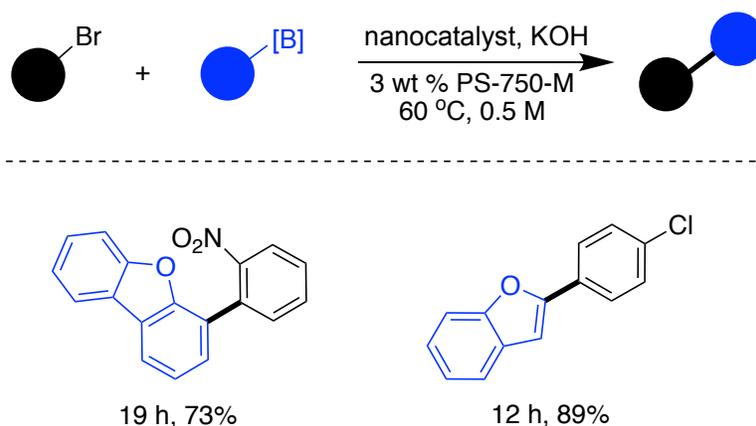


Conditions: hetero/aryl bromide (0.3 mmol), alkyne (0.36 mmol), Isolated charcoal nanocatalyst (9 mg), KOH (0.9 mmol), 0.6 mL 3 wt % aq. PS-750-M, 60 °C, 12 h, all yields are isolated.

14. SUZUKI-MIYAURA COUPLINGS USING NANOCATALYST

Hetero/aryl bromide (0.3 mmol), arylboronic acid/MIDA ester (0.36 mmol), nanocatalyst (9.0 mg), and KOH (50.4 mg, 0.9 mmol) were added into 4 mL oven-dried reaction vial containing PTFE-coated stirrer-bar. Reaction vial was closed with a rubber septum. Reaction vial was evacuated and backfilled with argon. To this mixture, 0.6 mL aqueous solution of 3 wt% PS-750-M was added. Reaction mixture was purged with argon for 2 min. Reaction mixture was stirred at 60 °C. After complete consumption of starting material as monitored by TLC and GCMS, mixture was cooled to rt. 0.5 mL EtOAc was added and mixture stirred for a minute at rt. Stirring was stopped and two layers were allowed to separate. An organic layer was taken out with use of pipetted. This extraction process was repeated for an additional time. Combined organic layers were dried over anhydrous sodium sulfate. Volatiles were removed under reduced pressure to obtain crude product, which was further purified by flash chromatography over silica gel using EtOAc/hexanes as eluent (see Table S13).

Table S13. Substrate scope for the Suzuki-Miyaura coupling using nanocatalyst



Conditions: hetero/aryl bromide (0.3 mmol), boronate ester/acid (0.36 mmol), Isolated charcoal nanocatalyst (9 mg), KOH (0.9 mmol), 0.6 mL 3 wt % aq. PS-750-M, 60 °C, all yields are isolated.

15. ICP–MS ANALYSIS OF A SAMPLE PRODUCT

Sample #: PLUMMSC1-009-EXP082-6

Test #: 1 Received: 04/24/2019 Completed: 04/25/2019

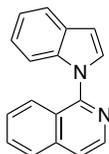
ICP-MS

Palladium: 1 ppm

Copper: <1 ppm

Services

ICP-MS



16. DLS EXPERIMENTS FOR PARTICLE SIZE DETERMINATION

16.1. DLS analysis at rt (also see Figure S3)

(a) **0.3 wt % PS-750-M in water.** Average particle size is *129.4 nm*.

(b) **Nanocatalyst in 0.3 wt % PS-750-M.** Nanocatalyst (1 mg) was dispersed in 10 mL 0.3 wt % aq. solution of PS-750-M. Resulting suspension was filtered to through a membrane filter (pore size 2 μm) and clean solution was analyzed for particle size distribution. Average particle size was *535.4 nm*.

(c) **1-Bromonaphthalene in 0.3 wt % PS-750-M.** 1-bromonaphthalene (7 μL) was dissolved in 10 mL 0.3 wt % aq. solution of PS-750-M. Resulting mixture was vigorously stirred for 30 min. and the mixture was filtered through a membrane filter (pore size 2 μm). A drop of THF was added to the solution. The obtained clean solution was analyzed for particle size distribution. Average particle size was *683.2 nm*.

(d) **1-Bromonaphthalene and nanocatalyst in 0.3 wt % PS-750-M.** To the nanocatalyst in 0.3 wt % PS-750-M sample prepared above, 1-bromonaphthalene (7 μL) was added. The solution was vigorously stirred 30 minutes and filtered through a membrane filter (pore size 2 μm). Cloudiness was removed by adding one drop of THF. A drop of THF was added to the solution. The obtained clean solution was analyzed for particle size distribution. Average particle size was *1220.4 nm*.

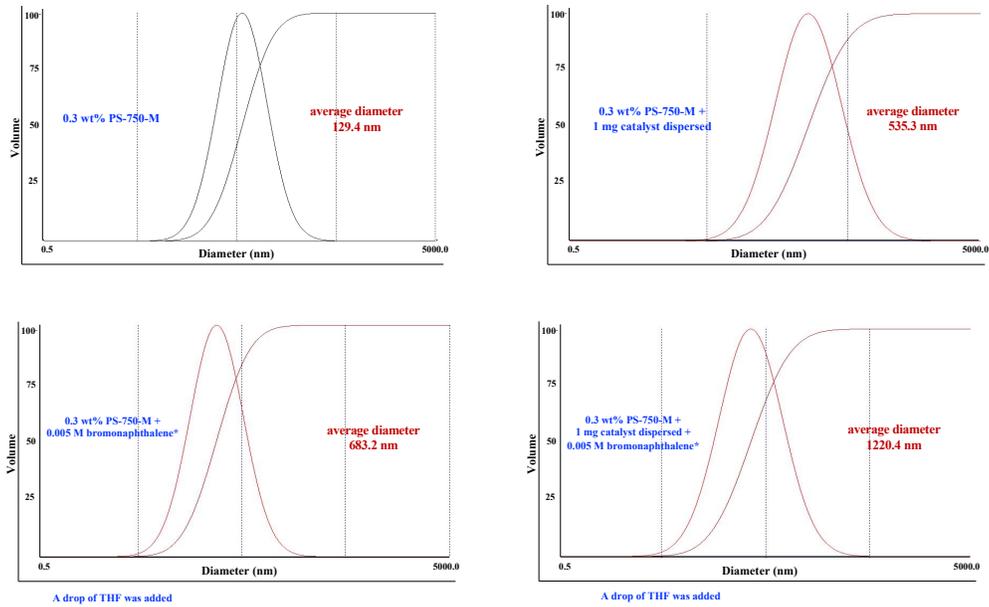


Figure S3. DLS studies at 25 °C.

16.2. DLS analysis at 60 °C (see Figure S4 below)

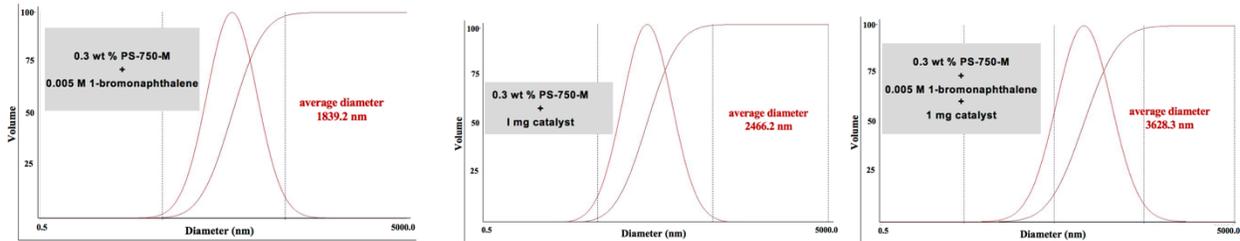


Figure S4. DLS studies at 60 °C.

17. DETALIED ANALYSIS OF NANOCATALYST

S17.1 Analysis by NMR spectroscopy

(a) Sample preparation. All samples described in Table S14 were heated at 60 °C under inert atmosphere for 15 minutes.

Table S14. Sample details for the NMR experiments

Sample ID	Constituents
Sample-A	2.8 mg cBRIDP in 0.5 mL dry dms _o -d ₆ under inert atmosphere
Sample-B	2.8 mg cBRIDP and 1.8 mg Pd(OAc) ₂ in 0.5 mL dry dms _o -d ₆
Sample-C	2.8 mg cBRIDP, 0.6 mg Pd(OAc) ₂ , and 1.98 mg Cu(CH ₃ CN) ₄ PF ₆ in 0.5 mL dry dms _o -d ₆
Sample-D	2.8 mg cBRIDP and 1.98 mg Cu(CH ₃ CN) ₄ PF ₆ in 0.5 mL dry dms _o -d ₆
Sample-E	2.8 mg cBRIDP, 0.6 mg Pd(OAc) ₂ , 1.98 mg Cu(CH ₃ CN) ₄ PF ₆ , and charcoal in 0.5 mL dry dms _o -d ₆

(b) NMR experiments. All experiments were carried out in Varian Innova 400 MHz NMR at 25 °C. DMSO (d₆) as NMR solvent and PPh₃ as internal standard were used in each experiment. From above stock solutions, 0.1 mL analyte was withdrawn and further diluted with 0.4 mL DMSO(d₆). Resulting sample was analyzed by NMR spectroscopy as illustrated in Figure S5.

(Note: The internal standard was prepared in a capillary tube by dissolving PPh₃ in DMSO(d₆) in a capillary tube, and tip of capillary tube was permanently sealed)

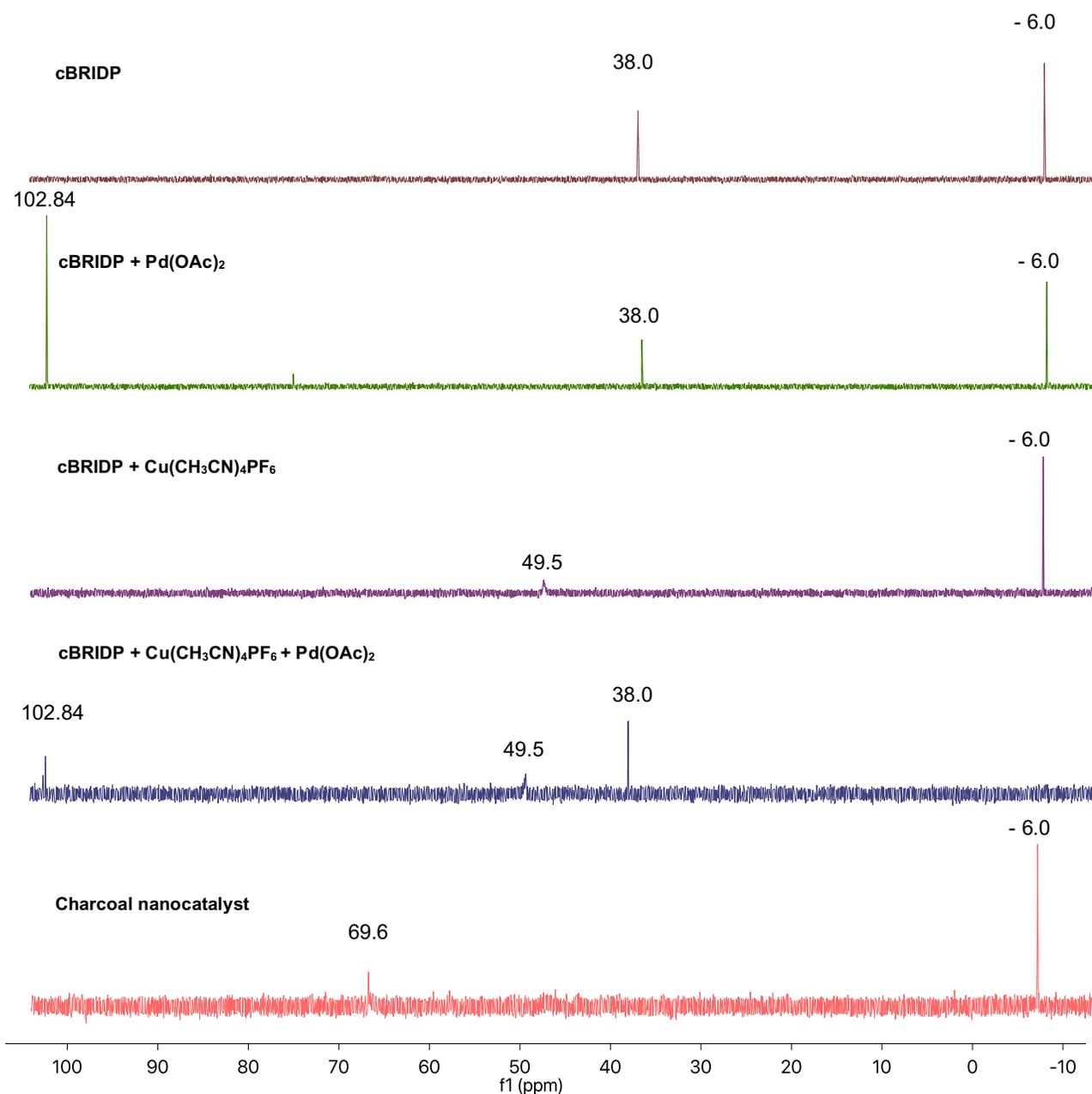


Figure S5. ^{31}P NMR studies on the catalyst.

- A signal at -6.0 ppm is from PPh_3 , an internal standard
- A peak at 38 ppm is from ^{31}P signal of cBRIDP
- A peak at 102.63 ppm is ^{31}P signal of cBRIDP bound Pd
- A peak at 49.5 ppm is ^{31}P signal of cBRIDP bound $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$
- A peak at 69.6 ppm is ^{31}P signal of metal-bound phosphine immobilized on charcoal surface. This is an active nanocatalyst

(c) Effect of Pd : Cu ratio on catalyst structure

(i) Sample preparation. All samples described in Table S15 were heated at 60 °C under inert atmosphere for 15 minutes.

Table S15. Sample details for the NMR experiments

Sample ID	Constituents
Sample-A	1.4 mg Pd(OAc) ₂ , 2.2 mg Cu(CH ₃ CN) ₄ PF ₆ , 3.2 mg cBRIDP, 3 mg charcoal in 0.5 mL dry THF (Pd : Cu : cBRIDP = 2 : 2 : 3)
Sample-B	1.4 mg Pd(OAc) ₂ , 1.1 mg Cu(CH ₃ CN) ₄ PF ₆ , 3.2 mg cBRIDP, 3 mg charcoal in 0.5 mL dry THF (Pd : Cu : cBRIDP = 2 : 1 : 3)
Sample-C	0.67 mg Pd(OAc) ₂ [*] , 3.3 mg Cu(CH ₃ CN) ₄ PF ₆ , 3.2 mg cBRIDP, 3 mg charcoal in 0.5 mL dry THF (Pd : Cu : cBRIDP = 1 : 3 : 3)

*stock solution method transfer

(ii) NMR experiments. All experiments were carried out in Varian Innova 400 MHz NMR at 25 °C. DMSO (d₆) as NMR solvent and PPh₃ as internal standard were used in each experiment. From above stock solutions, 0.1 mL analyte was withdrawn and further diluted with 0.4 mL DMSO(d₆). Resulting sample was analyzed by NMR spectroscopy as illustrated in Figure S6.

(Note: The internal standard was prepared in a capillary tube by dissolving PPh₃ in DMSO(d₆) in a capillary tube, and tip of capillary tube was permanently sealed)

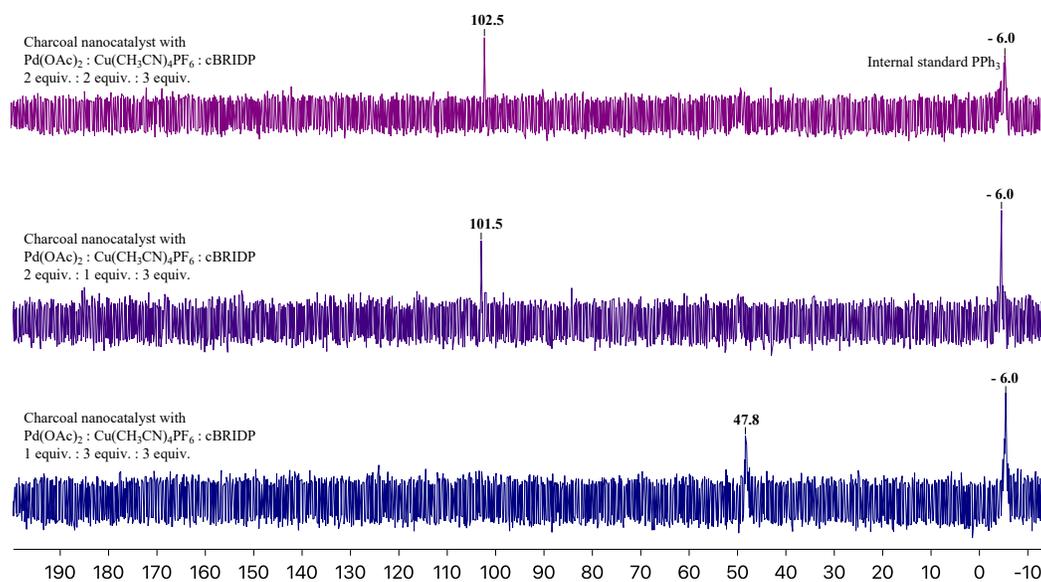


Figure S6. ³¹P NMR studies on the catalyst structure up varying the Pd/Cu ratio.

(d) Interaction of aniline with catalyst

(i) **Sample preparation.** Sample A, B & C described in Table S16 were heated at 60 °C under inert atmosphere for 1 h.

Table S16. Sample details for the NMR experiments

Sample ID	Constituents
Sample-A	9 mg charcoal nanocatalyst
Sample-B	10 mg <i>p</i> -toluidine, 9 mg charcoal nanocatalyst in 0.5 mL dry THF
Sample-C	1 mg <i>p</i> -toluidine, 9 mg charcoal nanocatalyst in 0.5 mL dry THF (Ar-NH ₂ : nanocatalyst = 1 : 1)

(ii) **NMR experiments.** All experiments were carried out in Varian Innova 400 MHz NMR at 25 °C. DMSO (d₆) as NMR solvent and PPh₃ as internal standard were used in each experiment. From above stock solutions, 0.2 mL analyte was withdrawn and further diluted with 0.4 mL DMSO(d₆). Resulting sample was analyzed by NMR spectroscopy as illustrated in Figure S7.

(Note: The internal standard was prepared in a capillary tube by dissolving PPh₃ in DMSO(d₆) in a capillary tube, and tip of capillary tube was permanently sealed)

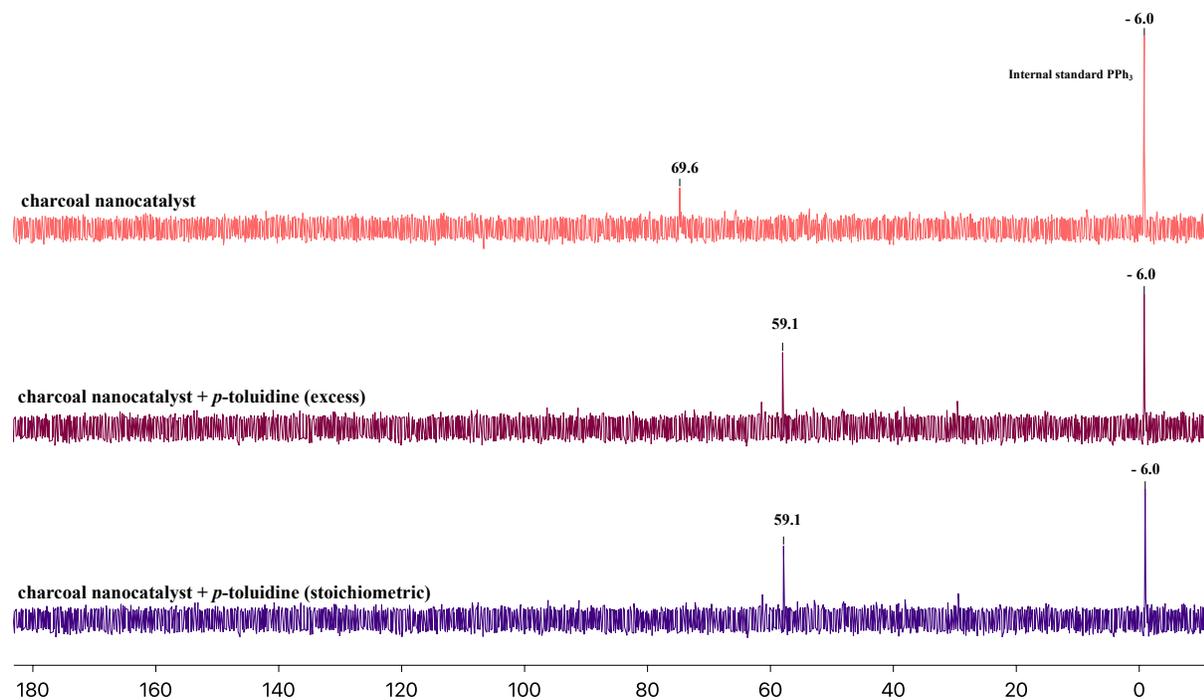


Figure S7. ³¹P NMR studies on the interaction of catalyst with *p*-toluidine.

(e) **Fresh versus recycled nanocatalyst.** Fresh and recycled catalyst was analyzed by ^{31}P NMR spectroscopy (Figure S8).

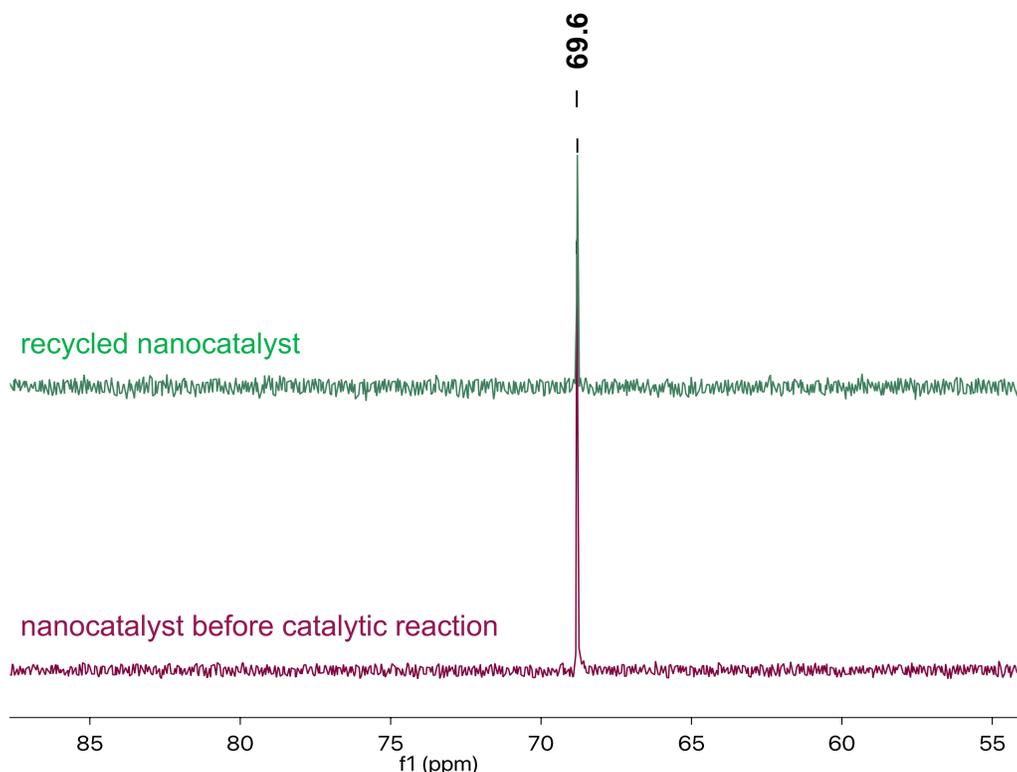


Figure S8. ^{31}P NMR studies on the stability of the recycled catalyst.

17.2. HRTEM analysis. In a 2 mL oven-dried reaction vial containing a PTFE-coated stir bar, palladium(II) acetate (6.7 mg, 0.028 mmol), *tetrakis*(acetonitrile)copper(I) hexafluorophosphate (22 mg, 0.057 mmol), and cBRIDP (31.7 mg, 0.084 mmol) were added. Reaction vial was closed with a cap containing PTFE septum cover. Reaction vials was evacuated and then backfilled with argon. This process of evacuation and backfilling with argon was repeated for three times. Via syringe, 1.0 mL dry THF was added to the reaction mixture. Reaction mixture was gently heated with a heat-gun for a minute. During heating, mixture color was changed from yellow to red. Using pre-heated oil bath, reaction mixture was further heated at 60°C for 15 min. Reaction mixture was allowed to cool to rt. Reaction vial was opened under argon atmosphere and activated charcoal (30 mg) was added to it. Reaction vial was closed with a cap and the mixture was further stirred at 60°C for 30 min. Finally, volatiles were removed under reduced pressure and resulting solid

material was dried under vacuum for overnight to obtain a free flowing nanopowder (92 mg). The resulting material was used analyzed by HRTEM (Figure S9).

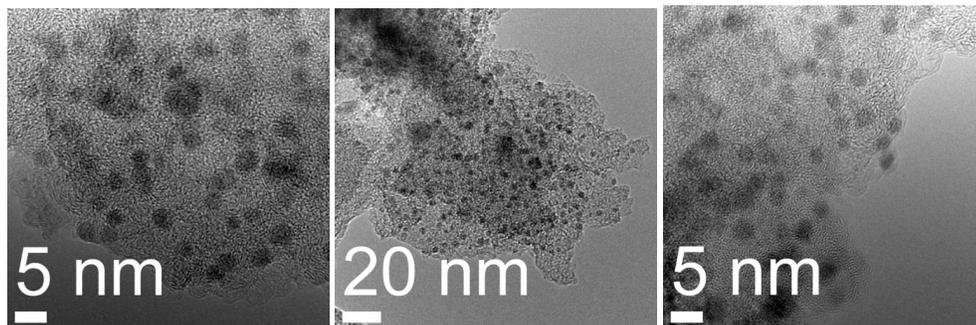


Figure S9. HRTEM images of nanocatalyst.

The average particle size was calculated from these images and histogram was obtained for the size distribution (Figure S10).

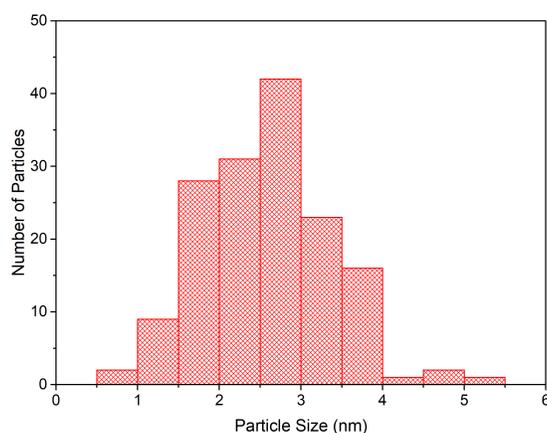


Figure S10. Particle size distribution of the nanocatalyst.

17.3. SEM analysis of surfactant bound nanocatalyst. 25 mg nanocatalyst was dissolved in 10 wt % aqueous PS-750-M (10 mL) and resulting material was analyzed by SEM (Figure S11).

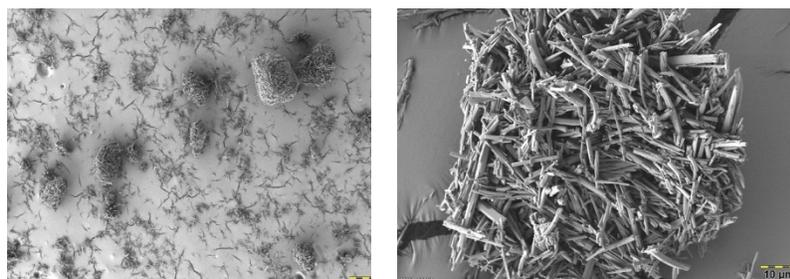


Figure S11. SEM analysis of the nanocatalyst.

17.4. TGA of nanocatalyst.

Sample prepared for HRTEM analysis in section 16.2 was used for TGA analysis (Figure S12).

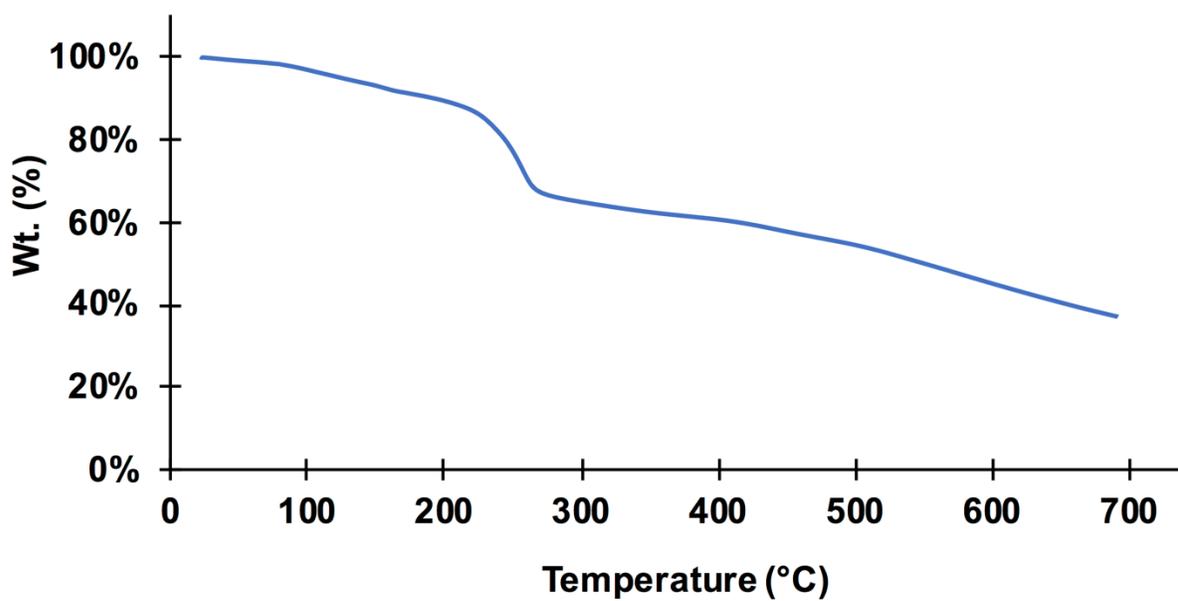


Figure S12. TGA analysis of the nanocatalyst.

17.5. XPS analysis of catalyst.

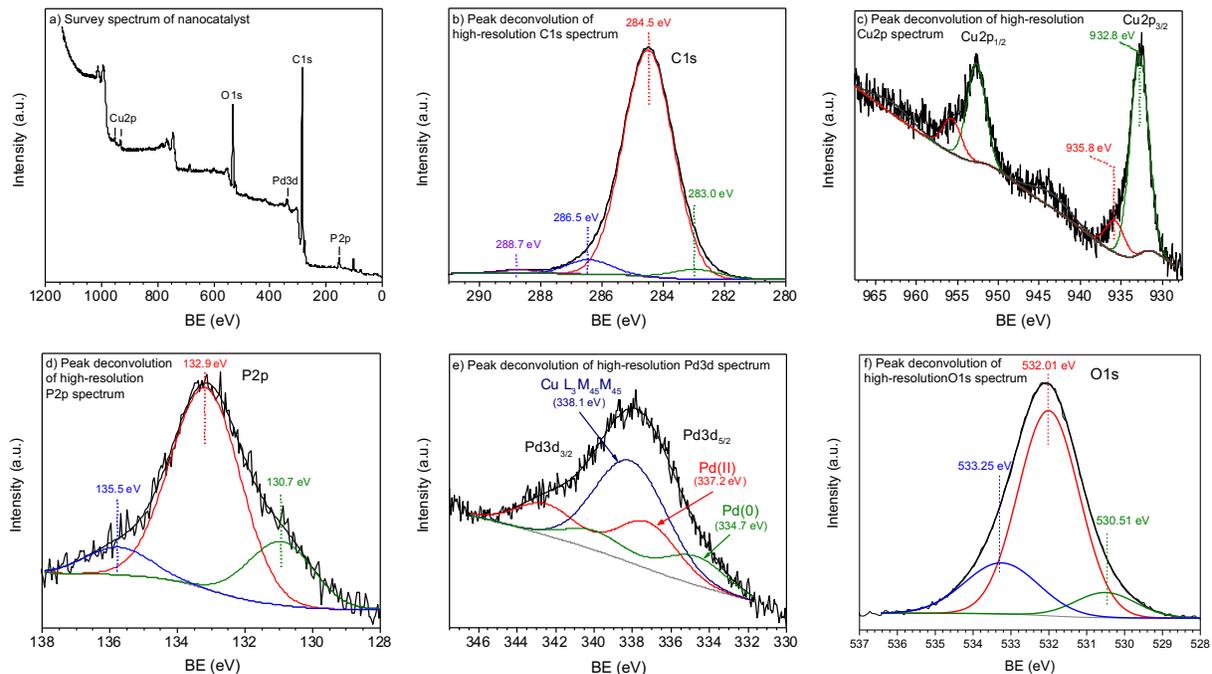


Figure S13. XPS analysis of the nanocatalyst, a) Survey spectrum of nanocatalyst, b) Peak deconvolution of high-resolution C1s spectrum, c) Peak deconvolution of high-resolution Cu2p spectrum, d) Peak deconvolution of high-resolution P2p spectrum, e) Peak deconvolution of high-resolution Pd3d spectrum, f) Peak deconvolution of high-resolution O1s spectrum.

Table S17. Details of XPS analysis.

ASF	XPS line	Area	% Atomic Composition
5.321	Cu2p	7552	0.5612315
5.356	Pd3d	1979	0.146109529
0.296	C1s	61425	82.05910394
0.486	P2p	712	0.579318024
0.711	O1s	29944.773	16.654237

X-ray photoelectron spectroscopy (XPS) measurements were conducted using a VG Scientific MultiLab 3000 ultra-high vacuum surface analysis system, operating at the base pressure in the 10^{-9} Torr range and equipped with dual-anode (Mg/Al) X-ray source and CLAM4 hemispherical electron energy analyzer. For this study, non-monochromatized Al $K\alpha$ X-ray beam ($h\nu \approx 1486.6$ eV) was used as the source. XPS spectra were collected at an electron emission angle of 54.7°

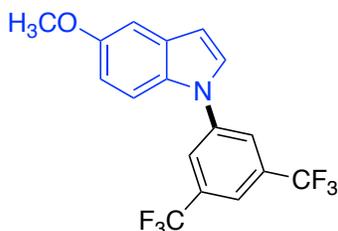
relative to the surface normal. A low-resolution survey spectrum from 1200 to 0 eV was collected using Pass energy of 100 eV to identify all elements. Additionally, high-resolution spectra of C1s, Pd3d, Cu2p, and O1s were collected at Pass energy of 20 eV, for the detailed binding energy (BE) analysis. The adventitious C1s, C-C peak at 284.5eV, was used for the BE calibration.

Fig. S13a shows the survey spectrum of nanocatalyst. Fig. S13b shows the deconvolution of high-resolution C1s spectrum. The spectrum confirmed the presence of Cu, O, Pd, C, and P. The peak deconvolution of the high-resolution spectrum of Cu2p (Fig. S13c) yields two species of Cu, one with the Cu2p_{3/2} peak at the BE of 932.8 eV and the other at 935.8 eV. These values correspond to the Cu(I) and Cu(II), respectively. Fig. S13d, presents the peak deconvolution of the high-resolution spectrum of P2p, which indicates three species of P, corresponding to the BE values of P2p peak equal 132.9 eV, 130.7 eV and 135.5 eV. The peak deconvolution of the high-resolution Pd3d spectrum (Fig. S13e) indicates multiple oxidation states. The obtained BE values of 337.2 eV and 334.7 eV represent Pd(O) and Pd(II) species, respectively. The peak deconvolution of the high-resolution spectrum of O1s (Fig. S13f) yields BE values, 533.5 eV, 532.01 and 530.51 eV which represent ethers/oxides.

The % atomic composition is described in Table S17.

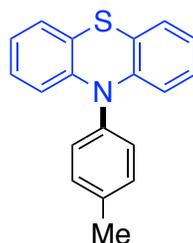
18. ANALYTICAL DATA

1-(3,5-Bis(trifluoromethyl)phenyl)-5-methoxy-1*H*-indole



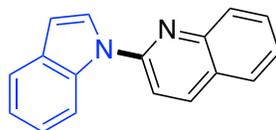
White solid, yield 96.8 mg (90%), mp = 79 °C, R_f 0.4 (4:1, hexanes/ethyl acetate). ^1H NMR (500 MHz, CDCl_3): δ 7.96 (s, 2H), 7.82 (s, 1H), 7.44 (d, J = 9.5 Hz, 1H), 7.33 (d, J = 3.5 Hz, 1H), 7.16 (d, J = 2.5 Hz, 1H), 6.95 (dd, J = 2.5 Hz, 9.5 Hz, 1H), 6.70 (dd, J = 0.5 Hz, 3Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 155.6, 141.7, 133.7(q, J = 26.97 Hz) 130.8, 130.8, 127.9, 123.7, 123.2 (q, J = 271 Hz), 119.6, 113.7, 111.0, 106.0, 103.7, 56.2; ^{19}F NMR (376 MHz, CDCl_3): -63.00 ppm. IR ν (cm^{-1}) 2933(m), 2200(w), 1406 (m). HRMS [$\text{C}_{17}\text{H}_{11}\text{F}_6\text{NO} + \text{H}^+$] calcd = 360.0818, found m/z = 360.0818.

10-(*p*-Tolyl)-10*H*-phenothiazine ¹



Yellow solid, yield 62.5 mg (72%), R_f 0.4 (4:1, hexanes/ethyl acetate). ^1H NMR (500 MHz, CDCl_3): δ 7.40 (d, J = 8.5 Hz, 2H), 7.28 (s, 1H), 6.99 (dd, J = 8 Hz, 2 Hz, 2H), 6.82-6.77 (m, 5H), 6.19(dd, J = 8 Hz, 1.5 Hz, 2H), 2.46 (s, 3H).

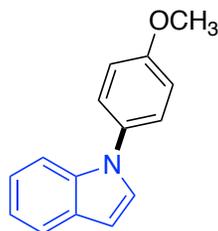
2-(1*H*-Indol-1-yl)quinoline ²



Yellow oil, yield 47.5 mg (65%), R_f 0.4 (3:2, hexanes/ethyl acetate). ^1H NMR (500 MHz, CDCl_3): δ 8.59 (d, J = 8.5 Hz, 1H), 8.27 (d, J = 9 Hz, 1H), 8.10 (d, J = 8.5 Hz, 1H), 7.85-7.81 (m, 2H),

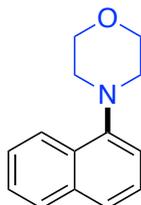
7.75 (t, $J = 7$ Hz, 1H), 7.70–7.66 (m, 2H), 7.52 (t, $J = 8.5$, 1H), 7.36 (t, $J = 7$ Hz, 1H), 7.24 (d, $J = 7$ Hz, 1H), 6.78 (d, $J = 3.5$ Hz, 1H).

1-(4-Methoxyphenyl)-1*H*-indole³



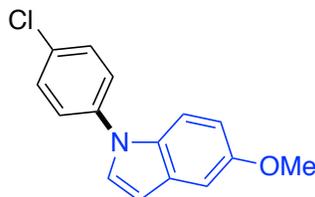
White solid, yield 57.5 mg (86%), R_f 0.4 (9:1, hexanes/ethyl acetate). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.68 (d, $J = 7.5$ Hz, 1H), 7.45 (d, $J = 8.5$ Hz, 1H), 7.41 (d, $J = 8.5$ Hz, 2H), 7.28 (d, $J = 3$ Hz, 1H), 7.2 (t, $J = 7$ Hz, 1H), 7.15 (t, $J = 7$ Hz, 1H), 7.04 (d, $J = 9$ Hz, 2H), 6.65 (d, $J = 3$ Hz, 1H), 3.88 (s, 3H).

4-(Naphthalen-1-yl)morpholine⁴



Yellow liquid, yield 53.0 mg (83%), R_f 0.4 (19:1, hexanes/ethyl acetate). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 8.22 (dd, $J = 2$ Hz, 7 Hz, 1H), 7.84 (dd, $J = 1$ Hz, 1H), 7.57 (d, $J = 8.5$ Hz, 1H), 7.50–7.45 (m, 2H), 7.43 (t, $J = 7.5$ Hz, 1H), 7.10 (d, $J = 8$ Hz, 1H), 3.99 (t, $J = 4.5$ Hz, 4H), 3.13 (t, $J = 4$ Hz, 4H).

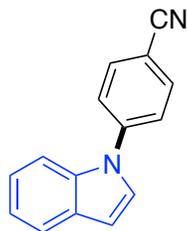
1-(4-Chlorophenyl)-5-methoxy-1*H*-indole⁵



Viscous oil, yield 65.0 mg (84%), R_f 0.3 (19:1, hexanes/ethyl acetate). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.54–7.37 (m, 5H), 7.27 (d, $J = 3.2$ Hz, 1H), 7.14 (d, $J = 2.4$ Hz, 1H), 6.89 (dd, $J = 2.4$

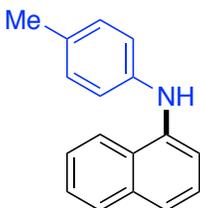
Hz, $J = 8.8$ Hz, 1H), 6.61(d, $J = 2.8$ Hz, 1H), 7.10 (d, $J = 8$ Hz, 1H), 3.99 (t, $J = 4.5$ Hz, 4H), 3.13 (t, $J = 4$ Hz, 4H), 3.98 (s, 3H).

4-(1*H*-Indol-1-yl)benzonitrile ⁶



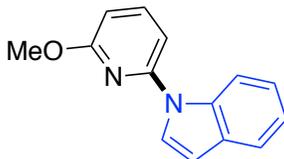
White solid, yield 52.1 mg (82%), R_f 0.3 (9:1, hexanes/ethyl acetate). ¹H NMR (500 MHz, CDCl₃): δ 7.81 (dd, $J = 1.5$ Hz, 6.5 Hz, 2H), 7.71 (d, $J = 8$ Hz, 1H), 7.64 (dd, $J = 2.5$ Hz, 7 Hz, 2H), 7.62 (d, $J = 8.5$ Hz, 1H), 7.35 (d, $J = 3$ Hz, 1H), 7.33–7.27 (m, 1H), 7.22–7.25 (m, 1H), 6.76 (d, $J = 3.5$ Hz, 1H).

N-(*p*-Tolyl)naphthalen-1-amine ⁷



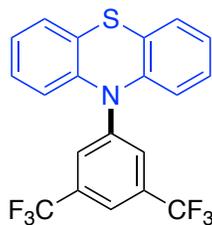
Pale yellow Oil, yield 64.1 mg (92%), R_f 0.4 (9:1, hexanes/ethyl acetate). ¹H NMR (500 MHz, CDCl₃): δ 8.02 (d, $J = 8$ Hz, 1H), 7.87 (d, $J = 9$ Hz, 1H), 7.53–7.46 (m, 3H), 7.38 (t, $J = 8$ Hz, 1H), 7.29 (d, $J = 7$ Hz, 1H), 7.10 (d, $J = 8.5$ Hz, 2H), 6.97 (d, $J = 8.5$, 2H), 2.33 (s, 3H).

1-(6-Methoxypyridin-2-yl)-1*H*-indole ⁸



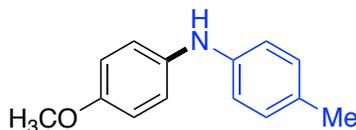
Colorless viscous oil, yield 59.2 mg (88%), R_f 0.3 (3:1, hexanes/ethyl acetate). ¹H NMR (400 MHz, CDCl₃): δ 7.92 (d, $J = 8.4$ Hz, 1H), 7.28–7.34 (m, 3H), 6.93 (t, $J = 7.2$ Hz, 1H), 6.85 (t, $J = 7.2$ Hz, 1H), 6.63 (d, $J = 7.6$ Hz, 1H), 6.33 (d, $J = 2.8$ Hz, 1H), 6.24 (d, $J = 8.4$ Hz, 4H), 3.67 (s, 3H).

10-(3,5-Bis(trifluoromethyl)phenyl)-10H-phenothiazine⁹



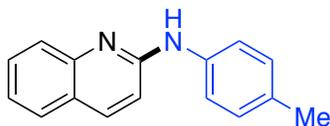
Yellow solid, yield 102.3 mg (83%), R_f 0.3 (9:1, hexanes/ethyl acetate). ^1H NMR (400 MHz, CDCl_3): δ 7.59 (s, 1H), 7.55 (s, 2H), 7.37 (dd, $J = 1.2$ Hz, 8 Hz, 2H), 7.25–7.12 (m, 2H), 7.16–7.12 (m, 2H), 6.96 (d, $J = 7.6$ Hz, 2H); ^{19}F NMR (376 MHz, CDCl_3) –62.99 ppm.

4-Methoxy-*N*-(*p*-tolyl)aniline¹⁰



White solid, yield 60.7 mg (95%), R_f 0.6 (4:1, hexanes/ethyl acetate). ^1H NMR (500 MHz, CDCl_3): δ 7.04–7.01 (m, 4H), 6.85–6.83 (m, 4H), 5.38 (s, 1H), 3.79 (s, 3H), 2.27 (s, 3H).

***N*-(*p*-Tolyl)quinolin-2-amine**¹¹



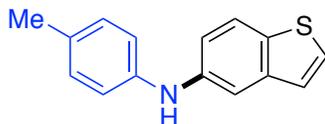
Off-white solid, yield 50.6 mg (72%), R_f 0.3 (4:1, hexanes/ethyl acetate). ^1H NMR (500 MHz, CDCl_3): δ 7.90 (d, $J = 8.5$ Hz, 1H), 7.75 (d, $J = 8.5$ Hz, 1H), 7.63 (d, $J = 8$ Hz, 1H), 7.59–7.56 (m, 1H), 7.41 (d, $J = 8.5$ Hz, 1H), 7.28 (d, $J = 8$ Hz, 1H), 7.18 (d, $J = 8.5$ Hz, 1H), 6.96 (d, $J = 9.5$ Hz, 1H), 2.36 (s, 3H).

***N*-(*p*-tolyl)pyrimidin-2-amine**¹²



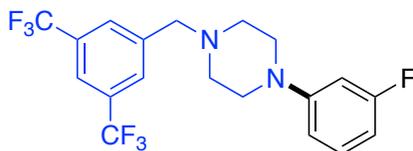
White solid, yield 50.6 mg (92%), R_f 0.3 (4:1, hexanes/ethyl acetate). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 8.39 (d, $J = 5$ Hz, 2H), 7.47 (d, $J = 8.5$ Hz, 2H), 7.14 (d, $J = 8.5$ Hz, 2H), 7.09 (s, 1H), 6.68 (t, $J = 5$ Hz, 1H), 2.32 (s, 3H).

***N*-(*p*-tolyl)benzo[*b*]thiophen-5-amine**



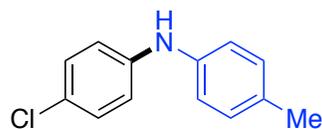
Yellow Oil, yield 57.4 mg (80%), R_f 0.3 (4:1, hexanes/ethyl acetate). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.67 (d, $J = 8.5$ Hz, 1H), 7.52 (s, 1H), 7.22 (dd, $J = 5.5$ Hz, 7 Hz, 2H), 7.12 (d, $J = 8$ Hz, 2), 7.03 (d, $J = 7.5$ Hz, 3H), 2.33 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 141.7, 141.0, 134.25, 131.59, 130.4, 124.6, 124.00, 123.8, 119.40, 117.1, 109.6, 21.2. IR ν (cm^{-1}) 348 (w), 2900(m), 1550(s). HRMS [$\text{C}_{15}\text{H}_{13}\text{NS} + \text{H}^+$] calcd = 240.0842, found $m/z = 240.0842$.

1-(3,5-Bis(trifluoromethyl)benzyl)-4-(3-fluorophenyl)piperazine



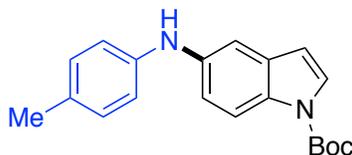
Viscous liquid, yield 86.3 mg (80%), R_f 0.3 (9:1, hexanes/ethyl acetate). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.84 (s, 2H), 7.79 (s, 1H), 7.27 (m, 1H), 6.67 (dd, $J = 1.5$ Hz, 8 Hz, 1H), 6.61–6.52 (m, 2H), 3.23 (t, $J = 5$, 4H), 2.62 (t, $J = 5$, 4H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 165.1, 141.4, 132.1, 131.9, 130.7 (q, $J = 26.8$), 130.4, 129.1, 121.61, 111.5, 106.4, 106.24, 103.2, 102.9, 62.2, 53.8, 49.0; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): -63.32, -11.32 ppm. IR ν (cm^{-1}) 1456 (m), 1245(s). HRMS [$\text{C}_{19}\text{H}_{17}\text{F}_7\text{N}_2 + \text{H}^+$] calcd = 407.1353, found $m/z = 407.1356$.

4-Chloro-*N*-(*p*-tolyl)aniline¹³



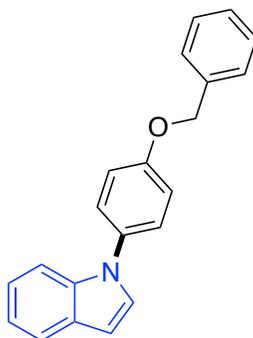
White solid, yield 59.5 mg (91%), R_f 0.3 (19:1, hexanes/ethyl acetate). ^1H NMR (500 MHz, CDCl_3): δ 7.17 (d, $J = 8.5$ Hz, 2H), 7.09 (d, $J = 8$ Hz, 2H), 6.97 (d, $J = 8.5$ Hz, 2H), 6.92 (d, $J = 8.5$ Hz, 2H), 2.31 (s, 3H).

***Tert*-butyl 5-(*p*-tolylamino)-1*H*-indole-1-carboxylate**



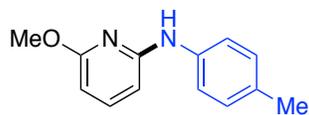
Light brown solid, yield 60.8 mg (63%), MP= 59 °C, R_f 0.3 (9:1, hexanes/ethyl acetate). ^1H NMR (500 MHz, CDCl_3): δ 8.02 (s, 1H), 7.55 (s, 1H), 7.25 (d, $J = 3$ Hz, 1H), 7.07 (d, $J = 8.5$ Hz, 2H), 7.03 (dd, $J = 2$ Hz, 9 Hz, 2H), 6.95 (d, $J = 8$ Hz, 2H), 6.45 (d, $J = 3.5$ Hz, 1H), 5.57 (s, 1H), 2.29 (s, 3H), 1.67 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3): δ 142.32, 132.28, 130.16, 126.78, 117.72, 117.46, 116.11, 110.33, 107.37, 28.56, 20.95. IR ν (cm^{-1}) 3512(broad), 1731(m), 1390 (m).

1-(4-(Benzyloxy)phenyl)-1*H*-indole



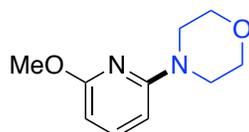
Brown liquid, yield 69 mg (77%), R_f 0.4 (9:1, hexanes/ethyl acetate). ^1H NMR (400 MHz, CDCl_3): δ 7.72 (d, $J = 7.6$ Hz, 1H), 7.50 (d, $J = 6.8$ Hz, 3H), 7.47–7.39 (m, 5H), 7.31 (d, $J = 3.2$ Hz, 1H), 7.24–7.19 (m, 2H), 7.13 (d, $J = 8.8$ Hz, 2H), 6.69 (d, $J = 3.2$ Hz, 1H), 5.16 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 157.7, 137.04, 136.59, 133.38, 129.28, 128.99, 128.56, 128.44, 127.81, 126.24, 122.5, 121.3, 120.4, 116.0, 110.7, 103.2, 70.7. IR ν (cm^{-1}) 3480 (w), 2900(m), 1550(s). HRMS [$\text{C}_{21}\text{H}_{17}\text{NO} + \text{H}^+$] calcd = 300.1383, found $m/z = 300.1384$

6-Methoxy-*N*-(*p*-tolyl)pyridin-2-amine



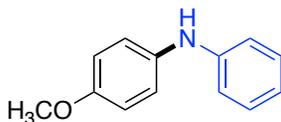
Colorless liquid, yield 67 mg (89%), R_f 0.2 (9:1, hexanes/ethyl acetate). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.28 (t, $J = 4\text{ Hz}$, 1H), 7.15 (d, $J = 8.4\text{ Hz}$, 2H), 7.29 (d, $J = 8\text{ Hz}$, 2H), 6.24 (d, $J = 8\text{ Hz}$, 2H), 6.07 (d, $J = 8\text{ Hz}$, 1H), 3.80 (s, 3H), 2.23 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 163.4, 155.1, 140.4, 138.2, 132.5, 130, 120.9, 100.0, 99.5, 53.6, 21.1. IR ν (cm^{-1}) 3490 (b), 2942(m), 1580 (w). HRMS [$\text{C}_{13}\text{H}_{15}\text{N}_2\text{O} + \text{H}^+$] calcd = 215.1179, found m/z = 215.1180.

4-(6-Methoxypyridin-2-yl)morpholine



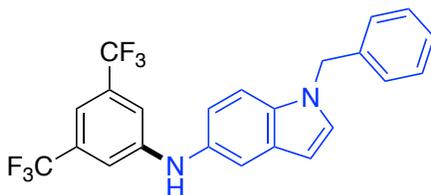
Colorless liquid, yield 61 mg (87%), R_f 0.3 (9:1, hexanes/ethyl acetate). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.41 (t, $J = 8\text{ Hz}$, 1H), 6.14 (d, $J = 8.4\text{ Hz}$, 1H), 6.12 (d, $J = 8.8\text{ Hz}$, 1H), 3.87 (s, 3H), 3.82 (t, $J = 5.2\text{ Hz}$, 4H), 3.48 (t, $J = 4.4\text{ Hz}$, 4H).

4-Methoxy-*N*-phenylaniline¹⁴



White Solid, yield 48 mg (97%), R_f 0.3 (9:1, hexanes/ethyl acetate). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.20-7.23 (m, 2H), 7.07-7.09 (m, 2H), 6.83-6.92 (m, 5H), 5.49 (bs, 1H), 3.80 (s, 3H).

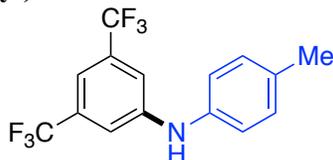
1-Benzyl-*N*-(3,5-bis(trifluoromethyl)phenyl)-1*H*-indol-5-amine



Waxy solid, yield 93 mg (71%), R_f 0.3 (9:1, hexanes/ethyl acetate). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.47 (s, 1H), 7.37-7.3 (m, 4H), 7.23-7.17 (m, 6H), 7.01 (d, $J = 8\text{ Hz}$, 1H), 6.55 (d, $J = 8\text{ Hz}$, 1H), 5.92 (s, 1H), 5.35 (s, 2H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 147.6, 136.9, 134.0, 132.24, 131.84

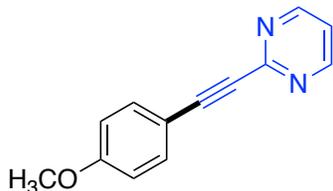
(q, $^2J = 23.5$ Hz) 129.2, 128.5, 127.7, 126.5, 123.2 (q, $^1J = 271.25$ Hz) 118.55, 115.58, 113.00, 110.89, 110.56, 101.34, 50.0; ^{19}F NMR (376 MHz, CDCl_3): -63.32 ppm. IR ν (cm^{-1}) 31400(s) 2900(m), 1550(s), 1470(w). HRMS [$\text{C}_{23}\text{H}_{17}\text{N}_2\text{F}_6 + \text{H}^+$] calcd = 435.1290, found $m/z = 435.1293$.

***N*-(*p*-Tolyl)-3,5-bis(trifluoromethyl)aniline**



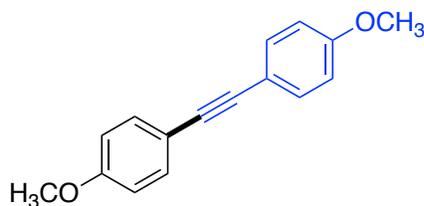
Yellow liquid, yield 77.6 mg (81%), R_f 0.3 (9:1, hexanes/ethyl acetate). ^1H NMR (400 MHz, CDCl_3): δ 7.35-7.32 (m, 3H), 7.25 (d, $J = 8$ Hz, 2H), 7.12 (d, $J = 8$ Hz, 2H), 5.92 (bs, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 146.1, 137.5, 134.0, 132.6 (q, $^2J = 33.5$ Hz), 130.4, 123.4 (q, $^2J = 271.1$ Hz), 121.5, 114.4, 112.3, 20.9; ^{19}F NMR (376 MHz, CDCl_3): -63.32 ppm. HRMS [$\text{C}_{15}\text{H}_{11}\text{NF}_6 + \text{H}$] calcd = 320.0823, found $m/z = 320.0816$.

2-((4-Methoxyphenyl)ethynyl)pyrimidine¹⁵



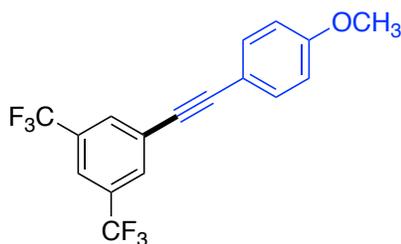
Off-white solid, yield 56 mg (89%), R_f 0.34 (4:1, hexanes/ethyl acetate). ^1H NMR (400 MHz, CDCl_3): δ 8.74 (d, $J = 5.2$ Hz, 2H), 7.62 (d, $J = 8$ Hz, 2H), 7.21 (t, $J = 4.8$ Hz, 1H), 6.9 (d, $J = 8$ Hz, 2H), 3.84 (s, 3H).

1,2-Bis(4-methoxyphenyl)ethyne¹⁶



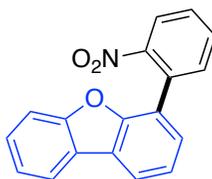
Off-white solid, yield 61 mg (86%), R_f 0.3 (Hexanes). ^1H NMR (400 MHz, CDCl_3): δ 7.46 (d, $J = 8$ Hz, 4H), 6.8 (d, $J = 8$ Hz, 4H), 3.82 (s, 6H).

1-((4-Methoxyphenyl)ethynyl)-3,5-bis(trifluoromethyl)benzene¹⁷



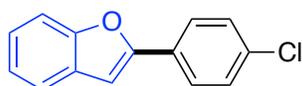
Off-white solid, yield 61 mg (87%), R_f 0.4 (Hexanes). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.93 (s, 2H), 7.78 (s, 1H), 7.5 (d, $J = 8$ Hz, 2H), 6.91 (d, $J = 8$ Hz, 2H), 3.84 (s, 3H); $^{19}\text{F NMR}$ (376 MHz, CDCl_3): -63.32.

4-(2-Nitrophenyl)dibenzo[*b,d*]furan¹⁸



Waxy liquid, yield 63.3 mg (73%), R_f 0.3 (4:1 hexanes:ethylacetate). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.9 (dd, $J = 7.2$ Hz, 1.2 Hz, 1H), 7.82–7.76 (m, 2H), 7.53 (td, $J = 6.4$, 1.2 Hz, 1H), 7.44–7.37 (m, 2H), 7.31–7.22 (m, 4H), 7.17–7.13 (m, 1H).

2-(4-Chlorophenyl)benzofuran¹⁹



Waxy liquid, yield 60.8 mg (89%), R_f 0.3 (9:1 hexanes:ethylacetate). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.04 (d, $J = 8$ Hz, 2H), 7.83 (d, $J = 8$ Hz, 1H), 7.77 (d, $J = 8$ Hz, 1H), 7.67 (d, $J = 8$ Hz, 2H), 7.56–7.47 (m, 3H).

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20. NMR SPECTRA

