Palladium-Catalyzed C(sp^2)-N Bond Cross-Coupling with Triarylphosphates

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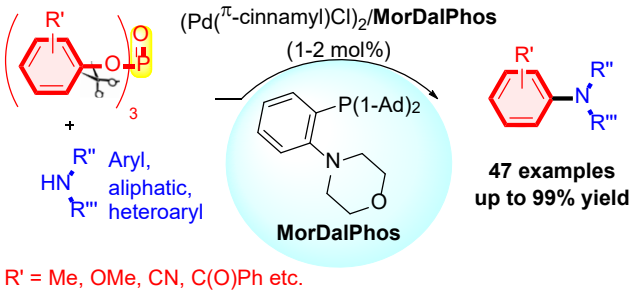


ABSTRACT. The first general palladium-catalyzed amination of aryl phosphates is described. The combination of MorDalPhos with [Pd(π-cinnamyl)Cl]$_2$ enables the amination of electron-rich, -neutral, and -poor aryl phosphates with a board range of aromatic, aliphatic, and heterocyclic amines. Common functional groups such as ether, keto, ester and nitrile show an excellent compatibility in this reaction condition. The solvent-free amination reactions are also successful in both of solid coupling partners. The gram-scale cross-coupling is achieved by this catalytic system.

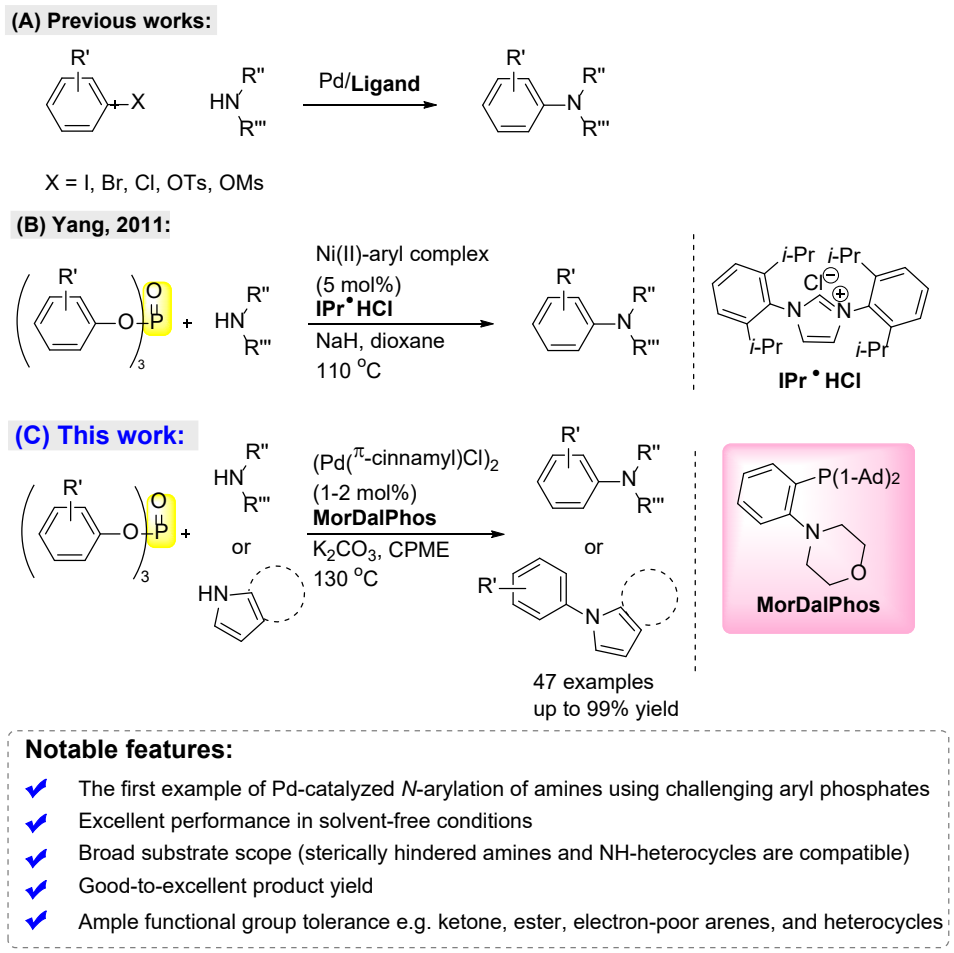
Introduction

Aryl amines constitute important building blocks in many natural products, pharmaceutically active molecules, organic materials, and useful catalysts.[1] Considering their importance and versatility, the development of efficient and diverse synthetic methods is highly desirable. Nucleophilic substitution,[2] addition to benzyne,[3] electrophilic nitration,[4] and reductive amination[5] are conventional routes for preparing these valuable products through C(sp^2)-N bond formation. In the past two decades, many transition metal catalysts have been shown to efficiently perform the coupling reaction of amines with aryl halides.[6] Since the first report of palladium-catalyzed *N*-arylation reactions,[7] the continual development of improved ligands/precatalysts, optimization studies, and mechanistic studies have resulted in remarkable growth in this aromatic C-N bond construction process.[8]

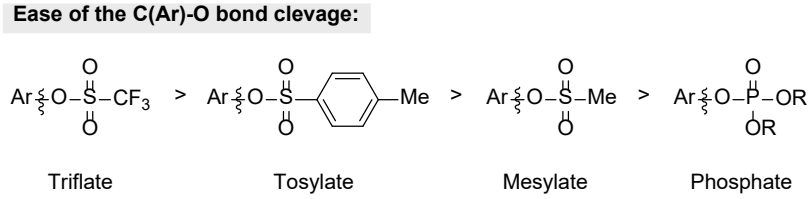
Aryl halides were commonly employed as electrophiles in amination because of their easy oxidative addition (Scheme 1A).[9] However, the halogenated compounds may not readily available in view of pharmaceutical chemistry. The additional steps are required to synthesize aryl halides from naturally occurring aromatic compounds. Indeed, aryl electrophiles generating from phenolic moieties are highly desirable due to their easy preparation, high stability towards air and moisture, low cost, and unique substitution pattern.[10] In recent years, aryl sulfonates, such as triflates, tosylates, and mesylates, have successfully utilized in palladium-catalyzed C(sp^2)-N bond forming reactions (Scheme 1A).[11] On the other hand, aryl phosphates also derived from phenols have similar advantages and are common biologically functional group. However, only one report by Yang has used the Ni(II) /NHC catalyst system to demonstrate the amination of aryl phosphate up-to-now (Scheme 1B).[12] To our best knowledge, palladium-catalyzed *N*-arylation of amines with aryl phosphates are not reported.

We believe that the application of aryl phosphate was obstructed by its inherently low reactivity towards palladium-catalyzed oxidative addition, and the competing hydrolysis under harsh conditions (Scheme 2).[10c] Taking the aforementioned points into account, palladium-catalyzed *N*-arylation of amines with aryl phosphates is deemed a challenge. To tackle this problematic issue, developing a general and active catalyst system is highly desirable. In the past decade, the development and selection of appropriate ligands have effectively tackled the electrophiles considered extremely difficult at that moment, such as aryl chlorides, tosylates and mesylates, which have been applied in amination reactions as well as other transformations.[13] The past decades have also seen the development of copper-catalyzed amination reactions.[14] As our research group's interest focused on phosphine ligands development[15] and challenging electrophiles exploration for cross-coupling reactions,[11a] we herein report the first palladium-catalyzed *N*-arylation of aromatic amines, aliphatic amines, and heterocyclic amines with aryl

phosphates, and even solvent-free reaction conditions (Scheme 1C).



Scheme 1. Palladium-catalyzed *N*-arylation of amines



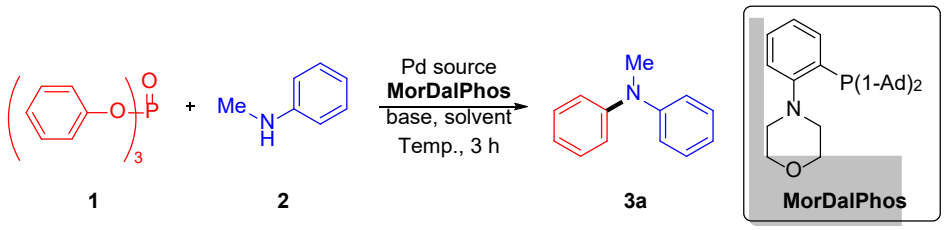
Scheme 2. A comparison on the difficulty of phenol derivatives in cross-coupling reactions

Results and Discussion

To initiate the study on unexplored aryl phosphates as the electrophile, we first focused on the intensive screening of the cutting-edge phosphine ligands, especially for those are commercially available and/or active towards C-O bond activation reactions. A total of 40 ligands with diverse scaffolds were attempted in this reaction. The selective results were described as follows (see Supporting Information, Table S1 for the full screening details). Classical phosphine ligands, such as

PPh_3, PCy_3, and dppf, were found inactive. Bidentate ligands, such as XantPhos, PCy_2-XantPhos, and dcype, which were found active towards C-O bond activation reactions, were also inactive towards amination of aryl phosphates reaction. The Beller group ligands, such as cataCXium®A and cataCXium®ABn, bear a more electron-rich ─PAd_2 group, but could not realize the conversion. Buchwald-type ligands were also screened. DavePhos and SPhos gave zero or trace amount product yield. XPhos and BrettPhos, which were highly active in aryl tosylates and mesylates reactions, also afforded trace amount of product yield. Indole (CM-Phos), benzimidazole (PhMezole-Phos), and carbazole (PhenCar-Phos) -based ligands all failed in this transformation. In addition, commercially available NHC-carbene ligand was tested and also inefficient in this context. Interestingly, MorDalPhos introduced by Stradiotto's group was found a unique ligand in this amination of aryl phosphate reaction. In the previous reports of Stradiotto's group, MorDalPhos also demonstrated good capability in the transformation of ammonia and other amines. [16] With the preliminary reaction condition, $Pd(OAc)_2$/MorDalPhos system catalyzed the amination reaction to give the corresponding product 58% yield. In contrast, PCy_2-MorDalPhos failed to provide the desired product. Coming up with the screening results, we believed that the electron richness and the steric effect provided by the MorDalPhos might fulfil the unique requirement of aryl phosphate activation.

Table 1. Initial screening of palladium-catalyzed *N*-arylation of amine with aryl phosphate[a]



1 2 3a

Entry	Pd source (mol%)	base	solvent	yield (%)[b]
1	$Pd(OAc)_2$ (4)	NaO*t*-Bu	Dioxane	0%
2	$Pd(OAc)_2$ (4)	Cs_2CO_3	Dioxane	13%
3	$Pd(OAc)_2$ (4)	K_3PO_4	Dioxane	15%
4	$Pd(OAc)_2$ (4)	Na_2CO_3	Dioxane	12%
5	$Pd(OAc)_2$ (4)	CsF	Dioxane	20%
6	$Pd(OAc)_2$ (4)	K_2CO_3	Dioxane	59%
7	$Pd(OAc)_2$ (4)	K_2CO_3	DMF	24%
8	$Pd(OAc)_2$ (4)	K_2CO_3	*t*-BuOH	54%
9	$Pd(OAc)_2$ (4)	K_2CO_3	Toluene	45%
10	$Pd(OAc)_2$ (4)	K_2CO_3	CPME	77%
11	$Pd(TFA)_2$ (4)	K_2CO_3	Dioxane	59%
12	$PdCl_2(CH_3CN)_2$ (4)	K_2CO_3	Dioxane	67%
13	[Pd(π-cinnamyl)Cl]$_2$ (2)	K_2CO_3	Dioxane	70%
14	Pd_2dba_3 (2)	K_2CO_3	Dioxane	3%
15	[Pd(π-cinnamyl)Cl]$_2$ (2)	K_2CO_3	CPME	92%
16	[Pd(π-cinnamyl)Cl]$_2$ (2)	K_2CO_3	CPME	85%[b]
17	[Pd(π-cinnamyl)Cl]$_2$ (2)	K_2CO_3	CPME	78%[c]
18	[Pd(π-cinnamyl)Cl]$_2$ (1)	K_2CO_3	CPME	64%
19	[Pd(π-cinnamyl)Cl]$_2$ (1)	K_2CO_3	CPME	54%[d]
20	[Pd(π-cinnamyl)Cl]$_2$ (1)	K_2CO_3	CPME	85%[e]
21	[Pd(π-cinnamyl)Cl]$_2$ (1)	K_2CO_3	CPME	95% (90%)[e,f]

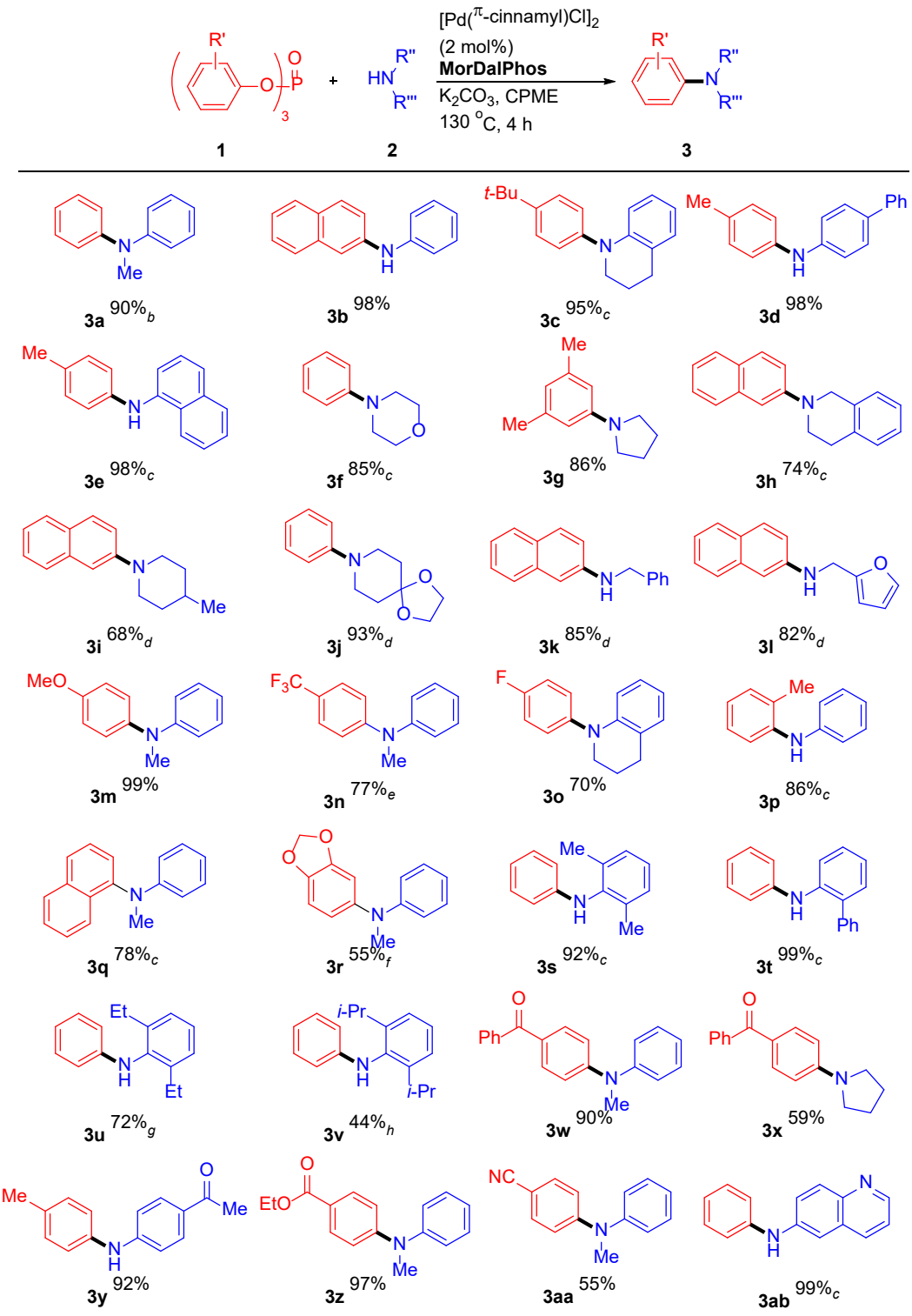
22	[Pd(π-cinnamyl)Cl]$_2$ (1)	K_2CO_3	CPME	39% [e,g]
23	[Pd(π-cinnamyl)Cl]$_2$ (2)	K_2CO_3	CPME	33%[h]

[a]Reaction conditions: aryl phosphate **1** (0.2 mmol), amine **2** (0.2 mmol), Pd source/MorDalPhos (mol% indicated), Pd:L = 1:2, base (0.6 mmol) and solvent (1 mL) were stirred at 130 °C for 3 h under N_2. Calibrated GC yields were reported by using dodecane as an internal standard and based on **1**. Isolated yield was shown in parentheses. [b]Pd:L = 1:1. [c]Pd:L = 1:3. [d]Arylphosphate (0.3 mmol) was used. [e]Amine (0.3 mmol) was used. [f]Reaction time: 4 h. [g]Reaction temperature: 120 °C. [h]Arylphosphate (0.066 mmol) was used and the reaction was conducted for 16 h.

Having identified the effective ligand, we next surveyed the reaction conditions for this catalysis (Table 1). Several common inorganic bases were tested. The triphenylphosphate was subjected to moderate or complete hydrolysis to the corresponding phenol if stronger bases such as NaO*t*-Bu, Cs_2CO_3 and K_3PO_4 were used in the reaction (Table 1, entries 1-3). However, if the bases were too weak such as Na_2CO_3 and CsF, the reaction was very slow and significant amount of starting triphenylphosphate was recovered (Table 1, entries 4-5). It was worthy to note that the best result was found to be mild inorganic base K_2CO_3 which allowed a better functional group tolerance in the subsequent substrate scope exploration (Table 1, entry 6). Then the screening of solvents and palladium sources were conducted in parallel. Highly polar solvent DMF and protic solvent *t*-BuOH accelerated the hydrolysis of triphenylphosphate while the amination reaction proceeded slowly in the relatively non-polar toluene (Table 1, entries 7-9). Ethereal solvents such as dioxane, THF, and CPME gave the better results, and CPME was the best solvent among them (Table 1, entries 10-11). On the other hand, a series of palladium source were screened (Table 1, entries 6, 11-14). The [Pd(π-cinnamyl)Cl]$_2$ was found to be the best palladium source in this reaction. Furthermore, the combination of [Pd(π-cinnamyl)Cl]$_2$ with CPME as solvent gave 92% yield of the desired product (Table 1, entry15). Either decreasing or increasing the metal to ligand ratio led to decrease in the product yield (Table 1, entries 15-17). We then attempted to reduce the catalyst loading from 2 mol% to 1 mol% of [Pd(π-cinnamyl)Cl]$_2$ (Table 1, entry 18). However, the desired product yield was decreased significantly. The effort was attempted to change the substrate ratio, increasing the use of *N*-methyl aniline to 1.5 equivalent significantly increased the product yield and 95% yield could be achieved by slightly prolonging the reaction time to 4 hours (Table 1, entries 19-21). However, the reaction rate was largely reduced, if the reaction temperature was reduced to 120 °C which might be resulted from the high activation barrier of the aryl phosphates (Table 1, entry 22). After reducing the use of triphenyl phosphate to 0.067 mmol, the product yield decreased to 33%. This result indicated that only one aryl

group was utilized in the reaction (Table 1, entry 23).

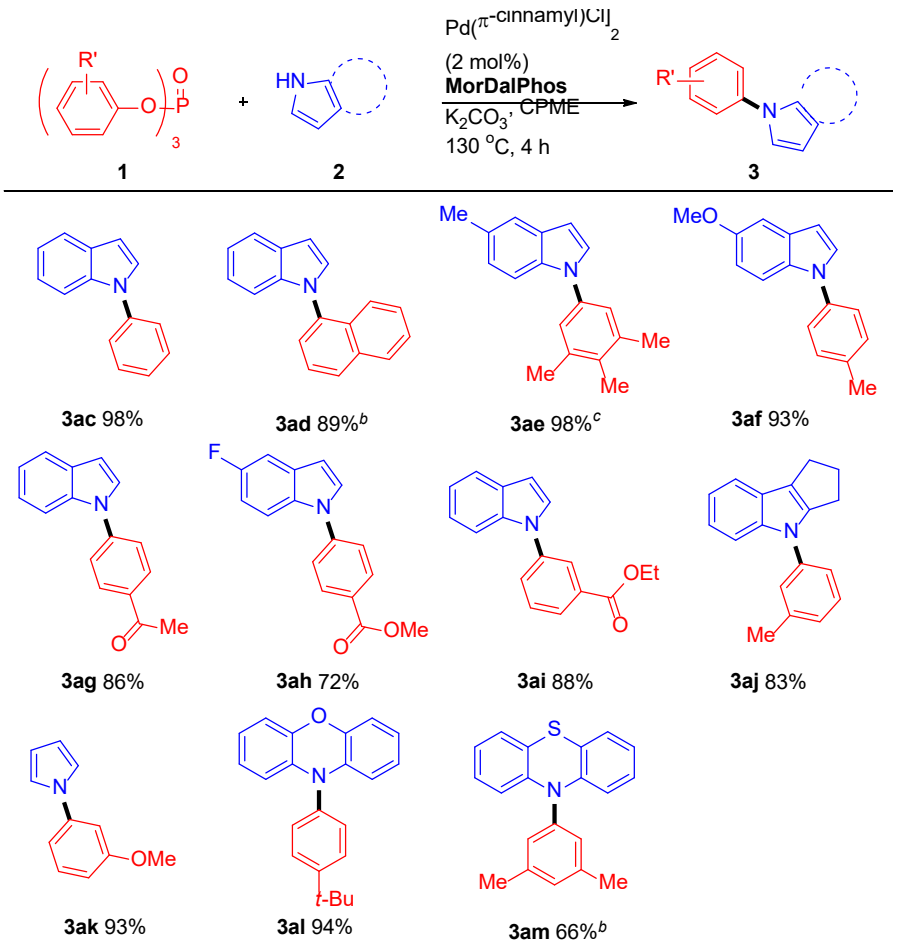
Table 2. Palladium-catalyzed *N*-arylation of aryl amines and aliphatic amines with aryl phosphates[a]



[a]Reaction conditions: aryl phosphate **1** (0.2 mmol), aryl amine **2** (0.3 mmol), [Pd(π-cinnamyl)Cl]$_2$ (2 mol%), MorDalPhos (8 mol%), K_2CO_3 (0.6 mmol), and CPME (1.0 mL) were stirred at 130 °C for 4 h

under N_2. Isolated yields were reported and based on **1**. [b][Pd(π-cinnamyl)Cl]$_2$ (1 mol%). [c]Reaction time: 16 h. [d]Reaction time: 18 h. [e]Reaction time: 3 h. [f]Reaction time: 6 h. [g]Reaction time: 36 h. [h]Reaction time 48 h.

Table 3. Palladium-catalyzed *N*-arylation of NH-heterocycles with aryl phosphates[a]



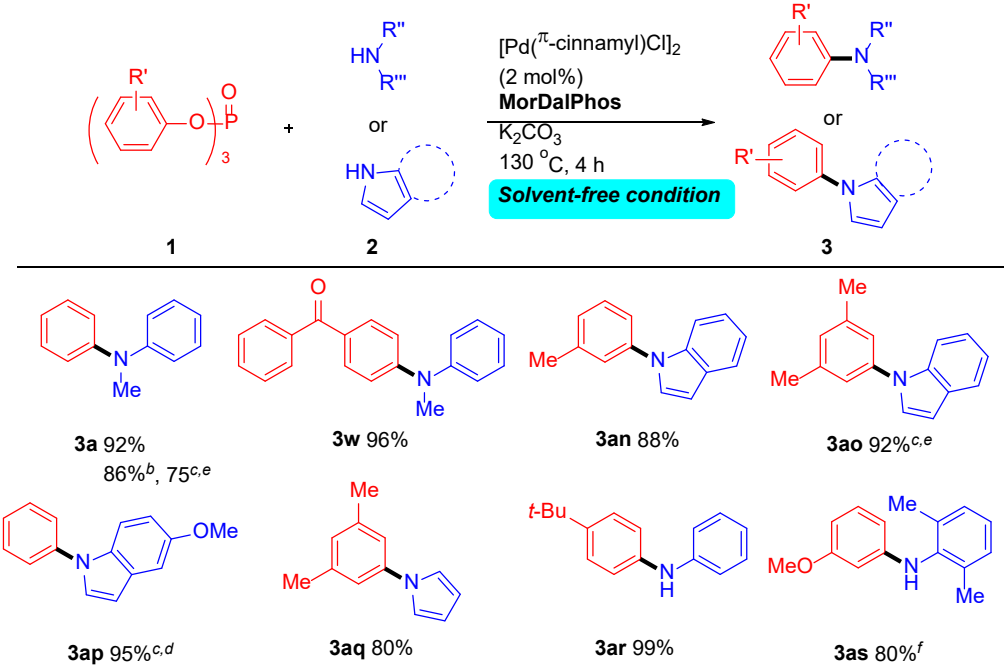
[a]Reaction conditions: aryl phosphate **1** (0.2 mmol), aryl amine **2** (0.3 mmol), [Pd(π-cinnamyl)Cl]$_2$ (2 mol%), MorDalPhos (8 mol%), K_2CO_3 (0.6 mmol), and CPME (1.0 mL) were stirred at 130 °C for 4 h under N_2. Isolated yields were reported and based on **1**. [b]Reaction time: 24 h. [c]Reaction time: 6 h.

Encouraged by the promising Pd/MorDalPhos system, we then turned our attention toward exploring the substrate scope. In general, unactivated arenes with aromatic amines were converted to the corresponding products in excellent yields (Table 2, **3a—3e**). Aliphatic primary, secondary cyclic, spirocyclic, and heterocyclic primary amines were effective coupling partners (Table 2, **3f—3l**). Deactivated tris(4-methoxyphenyl) phosphate was also transformed to the corresponding product in quantitative yield (Table 2, **3m**). The slightly lower yield was observed with the activated tris(4-(trifluoromethyl)phenyl) phosphate because the electron-deficient substrates might be more easily

subjected to the hydrolysis reaction (Table 2, **3n**). Sterically hindered aryl phosphates and anilines were generally feasible substrates under this reaction condition (Table 2, **3p, 3q,** and **3s—3u**). With extended reaction time, good-to-excellent yields were obtained. Highly sterically congested 2,6-diisopropylaniline was also a capable substrate (Table 2, **3v**). Furthermore, the functional groups ketone, ester, and nitrile were compatible under these reaction conditions (Table 2, **3w—3z, 3aa**). The relatively fast hydrolysis of tris(4-cyanophenyl) phosphate to the 4-cyanophenol accounted for the moderate yield of the desired product. It was noteworthy that heteroaryl amine was also a good substrate in this reaction condition to give the product quantitative yield (Table 2, **3ab**). Heterocyclic phosphate, for example, tri(pyridin-3-yl) phosphate, was attempted to couple with *N*-methylaniline. However, only trace amount of product yield was observed in GCMS spectrum due to the decomposition of tri(pyridin-3-yl) phosphate.

To further explore the wide-ranging effectiveness of the palladium system, aryl phosphates cross-coupling with a range of nitrogen heterocycles were also investigated (Table 3). Indole and substituted indoles were *N*-arylated smoothly in good-to-excellent yields (Table 3, **3ac—3aj**). Pyrrole, phenoxazine, and phenothiazine were also effective substrates (Table 3, **3ak—3am**). It was noteworthy that this was the first example of *N*-arylation of heterocyclic compounds with aryl phosphates.

Table 4. Palladium-catalyzed *N*-arylation of amines with aryl phosphates in solvent-free condition[a]

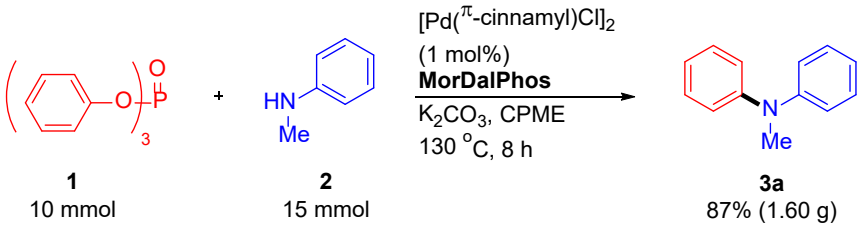


[a]Reaction conditions: aryl phosphate **1** (0.2 mmol), aryl amine **2** (1.0 mmol), [Pd(π-cinnamyl)Cl]$_2$ (2 mol%), MorDalPhos (8 mol%), and K_2CO_3 (0.6 mmol) were stirred at 130 °C for 4 h under N_2. Isolated yields were reported and based on **1**. [b]Amine (2.0 equiv.) was used. [c]Amine (1.5 equiv.) was used.

[d]Reaction time: 6 h. [e]Reaction time: 13 h. [f]Reaction time: 16 h.

Solvent-free reaction condition is an attractive operation, especially in the industrial application, where it can reduce solvent recovery costs and minimize organic waste. Herein, the amination of aryl phosphates could generally proceed under solvent-free reaction conditions with no obvious detrimental effects (Table 4). We also attempted to reduce amines use to prevent the generation of other organic waste forms. By reducing the amines to 1.5 equivalent, the product yields were still essentially the same (Table 4, **3a**, **3ao**, and **3ap**). It was noteworthy that both solid aryl phosphates and amines also worked well in this solventless condition (Table 4, **3ap**).

To test the feasibility of scaling up the current reaction condition, a gram-scale cross-coupling of triphenyl phosphate with *N*-methylaniline was conducted (Scheme 3). It afforded the desired coupling product in 87% yield.



Scheme 3. **Gram-scale cross-coupling reaction** (Reaction conditions: triphenyl phosphate **1** (10 mmol), *N*-methlyaniline **2** (15 mmol), [Pd(π-cinnamyl)Cl]$_2$ (1 mol%), MorDalPhos (4 mol%), K_2CO_3 (30 mmol) and CPME (50 mL) were stirred at 130 °C for 8 h under N_2. Isolated yield was reported.)

Conclusion

In summary, we demonstrated the first palladium-catalyzed *N*-H arylation of amines with aryl phosphates successfully. The reaction conditions exhibited good functional group tolerance and good reactivity towards a wide range of aryl, alkyl, and heterocyclic amines, even without solvent. The gram-scale cross-coupling was also feasible in this catalytic system. Further application of aryl phosphates in other coupling reactions and related mechanistic study is underway.

Experimental Section

General Information. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All Pd-catalyzed cross-coupling reactions were performed in resealable screw cap Schlenk tube (approx. 20 mL volume) in the presence of Teflon-coated magnetic stir bar (5 mm×10 mm). Solvents were distillated following the standard procedures under nitrogen.[17]

K_2CO_3, Na_2CO_3, Cs_2CO_3, K_3PO_4, CsF and NaO*t*-Bu were purchased from Dieckmann. Triphenyl phosphate was purchased from commercial suppliers and used directly. $Pd(OAc)_2$, $PdCl_2(CH_3CN)_2$, $[Pd(\pi\text{-cinamyl})Cl]_2$ and $Pd_2(dba)_3$ were purchased from Strem. $Pd(TFA)_2$ was purchased from Aldrich. Indolylphosphine ligand CM-Phos was prepared according to the reported literature.[15a] PhMezole-Phos was prepared according to the reported literature.[18] PPh_2-MorDalPhos and PCy_2-MorDalPhos were prepared according to the reported literature.[19] Known aryl phosphates (**1b-1t**) were synthesized according to the reported procedure.[20] Thin layer chromatography was performed on pre-coated silica gel 60 F_{254} plates. Silica gel (Merck, 70-230 and 230-400 mesh) was used for column chromatography. Melting points were recorded on an uncorrected Büchi Melting Point B-545 instrument. NMR spectra were recorded on a Brüker spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C, 376 MHz for ^{19}F and 162 MHz for ^{31}P). Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak). ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as the external standard and low field is positive. ^{31}P NMR spectra were referenced to 85% H_3PO_4 externally. Coupling constants (*J*) were reported in Hertz (Hz). Mass spectra (EI-MS and ES-MS) were recorded on a HP 5989B Mass Spectrometer. High-resolution mass spectra (HRMS) were obtained on a Brüker APEX 47e FTICR mass spectrometer (ESI-MS). GC-MS analysis was conducted on a HP 5973 GCD system using a HP5MS column (30 m × 0.25 mm). The products described in GC yield were accorded to the authentic samples/dodecane calibration standard from HP 6890 GC-FID system. All yields reported refer to isolated yield of compounds estimated to be greater than 95% purity as determined by capillary gas chromatography (GC) or ^1H NMR. Compounds described in the literature were characterized by comparison of their ^1H, ^{13}C and/or ^{19}F NMR spectra to the previously reported data. The procedures in this section are representative, and thus the yields may differ from those reported in tables.

General procedure for initial ligand screenings: A stock solution of $Pd(OAc)_2$ (0.08 mmol) in freshly distilled dioxane (10.0 mL) was first prepared under N_2. Ligands (16.0 mol% without specific notice), triphenyl phosphate (0.20 mmol), and K_2CO_3 (0.60 mmol) were added into an array of Schlenk tubes that charged with Teflon-coated magnetic stir bar (5 mm × 10 mm), and equipped with screw cap. The tubes were evacuated and flushed with nitrogen (3 cycles). The Schlenk tubes were then added with *N*-methyaniline (35.2 μL, 0.20 mmol) via syringe. The stock solutions (1.0 mL, 4.0 mol% Pd) were added by syringe to the array of Schlenk tubes respectively. The reaction mixture was stirred for 1 min at room temperature. The batch of Schlenk tubes were sealed and magnetically stirred in a preheated 130 °C oil bath for 3 h. The reactions were allowed to reach room temperature. Ethyl acetate (~8 mL), dodecane

(45.2 μL, internal standard) and water (~4 mL) were added. The organic layer was subjected to GC analysis. The GC yield was previously calibrated by authentic sample/dodecane calibration curve.

General procedure for reaction condition screening: An array of Schlenk tubes were charged with Teflon-coated magnetic stir bar (5 mm × 10 mm), Pd sources (each loading was indicated in the reaction condition screening Table 2), ligands (the Pd/Ligand ratio were indicated in Table 1), triphenyl phosphate (0.20 mmol), base (0.60 mmol) and then were evacuated and flushed with nitrogen (3 cycles). *N*-methyaniline (35.2 μL, 0.20 mmol) and the freshly distilled solvents (noted in Table 1) were added by syringes to the array of Schlenk tubes respectively. The reaction mixture was stirred for 1 min at room temperature. The batch of Schlenk tubes were sealed and magnetically stirred in a preheated oil bath for the indicated reaction temperature and time in Table 1. The reactions were allowed to reach room temperature. Ethyl acetate (~8 mL), dodecane (45.2 μL, internal standard) and water (~4 mL) were added. The organic layer was subjected to GC analysis. The GC yield was previously calibrated by authentic sample/dodecane calibration curve.

General procedure for palladium-catalyzed amination of aryl phosphates: Palladium(π-cinnamyl) chloride dimer (2.1 mg, 0.004 mmol), MorDalPhos (7.4 mg, 0.008 mmol), aryl phosphate (0.20 mmol, if solid), amine (0.30 mmol, if solid) and K_2CO_3 (83 mg, 0.60 mmol) were added to the Schlenk tube that charged with Teflon-coated magnetic stir bar (5 mm × 10 mm) and equipped with screw cap. The tube was carefully evacuated and flushed with nitrogen (3 cycles). Aryl phosphate (0.20 mmol, if liquid), amine (0.30 mmol, if liquid), and the freshly distilled CPME (1.0 mL) were added via syringes (exception for the solvent-free entries). The tube was sealed and magnetically stirred in a preheated 130 ^oC oil bath for the indicated time. After the completion of the reaction, the Schlenk tube was allowed to reach room temperature. Ethyl acetate (~8 mL) and water (~4 mL) were added. The organic layer was subjected to GC analysis. The organic layer was then separated and the aqueous layer was washed with ethyl acetate. The organic layers were combined and concentrated. The crude product was purified by column chromatography on silica gel (230-400 mesh) to afford the desired product.

General procedure for gram-scale cross-coupling reaction: Palladium(π-cinnamyl) chloride dimer (51.8 mg, 0.10 mmol), MorDalPhos (185.5 mg, 0.40 mmol), triphenyl phosphate (3.26 g, 10 mmol) and K_2CO_3 (4.15 g, 30 mmol) were added to the Schlenk flask (250 mL) that charged with Teflon-coated magnetic stir bar (8 mm × 30 mm) and equipped with screw cap. The flask was carefully evacuated and flushed with nitrogen (3 cycles). *N*-methyaniline (1.63 mL, 15 mmol) and the freshly distilled CPME (50 mL) were added via syringes. The flask was sealed and magnetically stirred in a preheated 130 ^oC oil bath for 8 h. After the completion of the reaction, the Schlenk flask was allowed to reach room temperature. Ethyl acetate and water were added. The organic layer was subjected to GC analysis. The

organic layer was then separated and the aqueous layer was extracted with ethyl acetate. The organic layers were combined and concentrated. The crude product was purified by column chromatography on silica gel (230-400 mesh) to afford the desired product.

Tris(3,4,5-trimethylphenyl) phosphate

Tris(3,4,5-trimethylphenyl) phosphate was synthesized according to general procedure.[20] To 3,4,5-trimethylphenol (30.0 mmol) and NaH (100.0 mmol) in toluene (50 mL) was slowly added $POCl_3$ (11.0 mmol) at 0 °C under vigorous stirring. Then reaction mixture was stirred at room temperature for 3 h. A solution of NaOH (10.0 g) in water (30 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with toluene (5 × 50 mL). The combined organic layers were washed with saturated brine (3 × 15 mL), and dried over anhydrous Na_2SO_4. Solvent was removed under the reduced pressure, and the final product was recrystallized from methanol affording tris(3,4,5-trimethylphenyl) phosphate as a white solid 4.08 g (82%). m.p.= 114.8–115.3 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.12 (s, 3H), 2.25 (s, 6H), 6.89 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.8, 20.6, 118.9 (d, J = 5.2 Hz), 132.1, 137.9, 147.8 (d, J = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ -16.70; MS (EI): m/z (relative intensity) 452.3 (M^+, 100), 221.2 (14), 135.1 (13), 91.1 (14); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{34}O_4P$: 453.2189; Found 453.2181.

Triethyl 3,3',3''-(phosphoryltris(oxy))tribenzoate

Triethyl 3,3',3''-(phosphoryltris(oxy))tribenzoate was synthesized according to general procedure.[20] To ethyl 3-hydroxybenzoate (30.0 mmol) and Et_3N (100.0 mmol) in toluene (50 mL) was slowly added $POCl_3$ (11.0 mmol) at 0 °C under vigorous stirring. Then reaction mixture was stirred at room temperature for 3 h. A solution of NaOH (10.0 g) in water (30 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with toluene (5 × 50 mL). The combined organic layers were washed with saturated brine (3 × 15 mL), and dried over anhydrous Na_2SO_4. Solvent was removed under the reduced pressure, and the final product was recrystallized from methanol affording triethyl 3,3',3''-(phosphoryltris(oxy))tribenzoate as colorless viscous liquid 4.33 g (80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (t, J = 7.1 Hz, 3H), 4.35 (q, J = 7.1 Hz, 2H), 7.42–7.48 (m, 2H), 7.88–7.93 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.2, 61.4, 121.1 (d, J = 5.0 Hz), 124.4 (d, J = 4.6 Hz), 127.0, 130.0, 132.6, 150.1 (d, J = 7.3 Hz), 165.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ –17.91; MS (EI): *m/z* (relative intensity) 542.2 (M^+, 100), 497.2 (70), 351.1 (24), 212.1 (20), 121.0 (15); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{28}O_{10}P$: 543.1415, Found 543.1408.

***N*-methyl-*N*-phenylaniline (Table 2, compound 3a)**[21]

Yield: 90% (32.9 mg). Eluents (R_f = 0.4, Hexane/DCM = 20:1) was used for flash column

chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36 (s, 3H), 6.98–7.02 (m, 2H), 7.06–7.08 (m, 4H), 7.30–7.34 (m, 4H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 40.2, 120.4, 121.2, 129.2, 149.0; MS (EI): *m/z* (relative intensity) 183.1 (M^+, 100), 167.1 (27), 104.0 (13), 77.1 (19), 51.1 (7).

_N_-phenylnaphthalen-2-amine (Table 2, compound 3b)[22]

Yield: 98% (42.9 mg). Eluents (R_f = 0.25, Hexane/DCM = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (br, 1H), 7.00–7.04 (m, 1H), 7.18–7.20 (m, 2H), 7.23–7.26 (m, 1H), 7.32–7.37 (m, 3H), 7.42–7.46 (m, 2H), 7.67–7.69 (m, 1H), 7.76–7.79 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 111.6, 118.3, 120.0, 121.4, 123.5, 126.46, 126.5, 127.7, 129.2, 129.4, 134.6, 140.8, 142.9; MS (EI): *m/z* (relative intensity) 219.1 (M^+, 100), 191.1 (5), 116.1 (10), 108.6 (15).

1-(4-(*tert*-Butyl)phenyl)-1,2,3,4-tetrahydroquinoline (Table 2, compound 3c)[23]

Yield: 95% (50.4 mg). Eluents (R_f = 0.50, Hexane/DCM = 20:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 9H), 2.04–2.14 (m, 2H), 2.90 (t, *J* = 6.4 Hz, 2H), 3.66 (t, *J* = 5.6 Hz, 2H), 6.70–6.74 (m, 1H), 6.77–6.79 (m, 1H), 6.95–7.00 (m, 1H), 7.07–7.09 (m, 1H), 7.21–7.23 (m, 2H), 7.40–7.42 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 22.7, 27.8, 31.5, 34.4, 50.9, 115.4, 117.8, 124.1, 124.4, 126.2, 126.4, 129.3, 144.7, 145.6, 146.6; MS (EI): *m/z* (relative intensity) 265.1 (M^+, 55), 250.1 (100), 180.1 (10), 96.9 (8).

_N_-(*p*-tolyl)-[1,1'-biphenyl]-4-amine (Table 2, compound 3d)[24]

Yield: 98% (50.8 mg). Eluents (R_f = 0.40, Hexane/DCM = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 5.71 (br, 1H), 7.08–7.18 (m, 6H), 7.32–7.36 (m, 1H), 7.45–7.49 (m, 2H), 7.53–7.56 (m, 2H), 7.61–7.63 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 20.7, 116.8, 119.1, 126.4, 127.9, 128.7, 129.9, 131.1, 133.0, 140.0, 140.9, 143.3; MS (EI): *m/z* (relative intensity) 259.1 (M^+, 100), 243.1 (6), 152.0 (4), 115.0 (3), 77.1 (2).

_N_-(*p*-tolyl)naphthalen-1-amine (Table 2, compound 3e)[25]

Yield: 98% (45.7 mg). Eluents (R_f = 0.60, Hexane/DCM = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 5.92 (br, 1H), 7.00–7.03 (m, 2H), 7.15–7.17 (m, 2H), 7.35–7.37 (m, 1H), 7.41–7.46 (m, 1H), 7.50–7.59 (m, 3H), 7.91–7.93 (m, 1H), 8.06–8.08 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 20.6, 114.1, 118.4, 121.5, 122.0, 125.4, 125.98, 126.03, 127.0, 128.5, 129.8, 130.4, 134.6, 139.6, 141.7; MS (EI): *m/z* (relative intensity) 233.1 (M^+, 100), 217.1 (30), 127.0 (3), 115.3 (10), 77.0 (2).

4-Phenylmorpholine (Table 2, compound 3f)[21]

Yield: 85% (27.7 mg). Eluents (R_f = 0.30, Hexane/EA = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.16–3.18 (m, 4H), 3.86–3.89 (m, 4H), 6.88–6.94 (m, 3H), 7.27–7.30 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 49.3, 66.9, 115.7, 120.0, 129.1, 151.2; MS (EI): *m/z* (relative intensity) 163.1 (M^+, 85), 132.1 (7), 106.1 (100), 77.1 (19), 51.0 (6).

1-(3,5-Dimethylphenyl)pyrrolidine (Table 2, compound 3g)[26]

Yield: 86% (30.1 mg). Eluents (R_f = 0.8, Hexane/EA = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.99–2.02 (m, 4H), 2.31 (s, 6H), 3.28–3.31 (m, 4H), 6.25 (s, 2H), 6.37 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 21.7, 25.4, 47.6, 109.6, 117.5, 138.6, 148.1; MS (EI): *m/z* (relative intensity) 175.1 (M^+, 100), 132.1 (7), 119.1 (32), 105.1 (10), 77.0 (7).

2-(Naphthalen-2-yl)-1,2,3,4-tetrahydroisoquinoline (Table 2, compound 3h)[27]

Yield: 74% (38.3 mg). Eluents (R_f = 0.35, Hexane/DCM = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.06 (t, *J* = 5.7 Hz, 2H), 3.69 (t, *J* = 5.8 Hz, 2H), 4.53 (s, 2H), 7.19–7.23 (m, 5H), 7.27–7.31 (m, 1H), 7.36–7.39 (m, 1H), 7.40–7.44 (m, 1H), 7.71–7.78 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 29.2, 47.1, 51.0, 109.3, 118.7, 122.9, 126.1, 126.2, 126.4, 126.52, 126.55, 127.4, 128.0, 128.6, 128.8, 134.3, 134.7, 148.4; MS (EI): *m/z* (relative intensity) 259.1 (M^+, 100), 155.1 (23), 127.1 (24), 115.1 (10), 104.1 (25).

4-Methyl-1-(naphthalen-2-yl)piperidine (Table 2, compound 3i)[28]

Yield: 68% (30.6 mg). Eluents (R_f = 0.5, Hexane/EA = 4:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00–1.02 (m, 3H), 1.37–1.47 (m, 2H), 1.54–1.59 (m, 1H), 1.78–1.81 (m, 2H), 2.75–2.81 (m, 2H), 3.77–3.80 (m, 2H), 7.13–7.14 (m, 1H), 7.26–7.31 (m, 2H), 7.37–7.41 (m, 1H), 7.67–7.72 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 21.9, 30.8, 34.1, 50.3, 110.3, 120.1, 123.0, 126.1, 126.6, 127.3, 128.2, 128.5, 134.7, 149.8; MS (EI): *m/z* (relative intensity) 225.1 (M^+, 100), 182.1 (11), 155.1 (25), 127.1 (28), 115.1 (7).

8-Phenyl-1,4-dioxa-8-azaspiro[4.5]decane (Table 2, compound 3j)[29]

Yield: 93% (40.7 mg). Eluents (R_f = 0.4, Hexane/EA = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.84–1.87 (m, 4H), 3.32–3.35 (m, 4H), 3.40 (s, 4H), 6.83–6.86 (m, 1H), 6.95–6.97 (m, 2H), 7.24–7.28 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 34.5, 47.7, 64.3, 107.1, 116.6, 119.4, 129.1, 150.9; MS (EI): *m/z* (relative intensity) 219.1 (M^+, 100), 174.1 (24), 158.1 (19), 132.1 (50), 105.1 (78).

***N*-benzylnaphthalen-2-amine (Table 2, compound 3k)**[30]

Yield: 85% (39.6 mg). Eluents (R_f = 0.5, Hexane/EA = 9:1) was used for flash column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (s, 1H), 4.41 (s, 2H), 6.81–6.82 (m, 1H), 6.87–6.90 (m, 1H), 7.16–7.21 (m, 1H), 7.26–7.41 (m, 6H), 7.56–7.67 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 48.3, 104.6, 117.8, 122.0, 125.9, 126.3, 127.3, 127.53, 127.56, 127.59, 128.6, 128.9, 135.1, 139.1, 145.7; MS (EI): *m/z* (relative intensity) 233.2 (M^+, 100), 156.1 (13), 127.1 (13), 115.1 (21), 91.1 (50).

_N_-(furan-2-ylmethyl)naphthalen-2-amine (Table 2, compound 3l)[31]

Yield: 82% (36.6 mg). Eluents (R_f= 0.5, Hexane/EA = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21 (br, 1H), 4.44 (s, 2H), 6.30–6.37 (m, 2H), 6.92–6.95 (m, 2H), 7.23–7.27 (m, 1H), 7.39–7.42 (m, 2H), 7.65–7.70 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 41.4, 105.0, 107.1, 110.1, 117.9, 122.2, 126.0, 126.3, 127.6, 127.7, 128.9, 135.0, 142.0, 145.2, 152.4; MS (EI): *m/z* (relative intensity) 223.1 (M^+, 100), 194.2 (15), 127.1 (14), 115.1 (39), 81.1 (89).

4-Methoxy-_N_-methyl-_N_-phenylaniline (Table 2, compound 3m)[32]

Yield: 99% (42.2 mg). Eluents (R_f= 0.4, Hexane/EA = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.28 (s, 3H), 3.83 (s, 3H), 6.79–6.83 (m, 3H), 6.90–6.94 (m, 2H), 7.10–7.14 (m, 2H), 7.20–7.24 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 40.4, 55.5, 114.7, 115.7, 118.3, 126.2, 128.9, 142.2, 149.7, 156.2; MS (EI): *m/z* (relative intensity) 213.1 (M^+, 80), 198.1 (100), 154.1 (9), 129.0 (4), 77.0 (5).

_N_-methyl-_N_-phenyl-4-(trifluoromethyl)aniline (Table 2, compound 3n)[32]

Yield: 77% (38.7 mg). Eluents (R_f= 0.5, Hexane/EA = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36 (s, 3H), 6.86 (d, J = 8.5 Hz, 2H), 7.19–7.21 (m, 3H), 7.38–7.45 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 40.2, 114.8, 120.0 (q, J_{CF} = 32.7 Hz), 124.9 (q, J_{CF} = 268.2 Hz), 125.0, 125.3, 126.2 (q, J_{CF} = 3.7 Hz), 129.8, 147.8, 151.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.2; MS (EI): *m/z* (relative intensity) 251.2 (M^+, 100), 232.1 (9), 167.1 (13), 145.1 (11), 77.1 (10).

1-(4-Fluorophenyl)-1,2,3,4-tetrahydroquinoline (Table 2, compound3o)

Yield: 70% (31.8 mg). Eluents (R_f= 0.3, Hexane) was used for flash column chromatography to afford **3o** as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) 2.04–2.11 (m, 2H), 2.88 (t, J = 6.4 Hz, 2H), 3.59 (t, J = 5.6 Hz, 2H), 6.57–6.59 (m, 1H), 6.68–6.72 (m, 1H), 6.92–6.96 (m, 1H), 7.05–7.09 (m, 3H), 7.20–7.23 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 22.4, 27.7, 51.3, 114.8, 116.1 (d, J_{CF} = 22.1), 117.9, 123.7, 126.4, 127.2 (d, J_{CF} = 8.1 Hz), 129.3, 144.4 (d, J_{CF} = 2.9 Hz), 144.8, 159.5 (d, J_{CF} = 241.6); ^{19}F NMR (376 MHz, $CDCl_3$) δ –118.3; MS (EI): *m/z* (relative intensity) 227.1 (M^+, 100), 211.1 (9), 189.1 (12), 91.1 (7), 77.0 (7); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{15}FN$: 228.1183, Found 228.1181.

2-Methyl-*N*-phenylaniline (Table 2, compound 3p)[33]

Yield: 86% (31.5 mg). Eluents (R_f = 0.45, Hexane/EA = 19:1) was used for flash column chromatography. ^{1}H NMR (400MHz, $CDCl_3$) δ 2.29 (s, 3H), 5.41 (s, 1H), 6.93–7.01 (m, 4H), 7.17–7.20 (m, 1H), 7.24–7.26 (m, 1H), 7.28–7.32 (m, 3H); $^{13}C\{^1H\}$ NMR (100MHz, $CDCl_3$) δ 17.9, 117.4, 118.7, 120.4, 121.9, 126.7, 128.2, 129.3, 130.9, 141.1, 143.9; MS (EI): *m/z* (relative intensity) 183.1 (M^+, 100), 167.1 (28), 106.1 (19), 90.7 (11), 77.0 (10).

***N*-methyl-*N*-phenylnaphthalen-1-amine (Table 2, compound 3q)**[34]

Yield: 78% (36.4 mg). Eluents (R_f = 0.5, Hexane/DCM = 20:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.43 (s, 3H), 6.64–6.67 (m, 2H), 6.75–6.78 (m, 1H), 7.18–7.22 (m, 2H), 7.39–7.41 (m, 1H), 7.44–7.48 (m, 1H), 7.50–7.55 (m, 2H), 7.81–7.83 (m, 1H), 7.90–7.95 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 40.2, 113.5, 117.2, 123.8, 125.2, 126.2, 126.3, 126.4, 126.6, 128.4, 128.9, 131.3, 135.1, 145.3, 150.1; MS (EI): *m/z* (relative intensity) 233.1 (M^+, 100), 217.1 (34), 115.4 (8), 104.0 (5), 77.0 (5).

***N*-methyl-*N*-phenylbenzo[*d*][1,3]dioxol-5-amine (Table 2, compound 3r)**[34]

Yield: 55% (25.0 mg). Eluents (R_f= 0.5, Hexane/EA = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.28 (s, 3H), 5.99 (s, 2H), 6.62–6.64 (m, 1H), 6.68–6.69 (m, 1H), 6.80–6.87 (m, 4H), 7.23–7.27 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 40.6, 101.2, 106.1, 108.5, 116.5, 117.2, 118.9, 128.9, 143.7, 143.9, 148.2, 149.6; MS (EI): *m/z* (relative intensity) 227.1 (M^+, 100), 196.0 (10), 168.0 (18), 154.1 (18), 77.0 (14).

2,6-Dimethyl-*N*-phenylaniline (Table 2, compound 3s)[35]

Yield: 92% (36.3 mg). Eluents (R_f = 0.4, Hexane/DCM = 20:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 6H), 5.21 (s, 1H), 6.54–6.56 (m, 2H), 6.78–6.82 (m, 1H), 7.11–7.25 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 18.3, 113.5, 118.1, 125.7, 128.5, 129.2, 135.9, 138.2, 146.2; MS (EI): *m/z* (relative intensity) 197.1 (M^+, 100), 182.1 (34), 167.1 (12), 120.1 (13), 77.1 (7).

***N*-phenyl-[1,1'-biphenyl]-2-amine (Table 2, compound 3t)**[36]

Yield: 99% (48.5 mg). Eluents (R_f = 0.3, Hexane/DCM = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (s, 1H), 6.95–6.99 (m, 1H), 7.03–7.09 (m, 3H), 7.28–7.32 (m, 4H), 7.38–7.52 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 117.4, 118.1, 121.00, 121.01, 127.4, 128.2, 128.8, 129.26, 129.27, 130.8, 131.4, 139.0, 140.1, 143.3; MS (EI): *m/z* (relative intensity) 245.1 (M^+, 100), 167.1 (13), 152.0 (5), 115.0 (4), 77.1 (3).

2,6-Diethyl-*N*-phenylaniline (Table 2, compound 3u)[33]

Yield: 72% (32.4 mg). Eluents (R_f = 0.45, Hexane/EA = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, *J* = 7.5 Hz, 6H), 2.62 (q, *J* = 7.5 Hz, 4H), 6.50–6.53 (m, 2H), 6.73–6.78 (m, 1H), 7.15–7.24 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.7, 24.7, 113.2, 117.9, 126.5, 126.6, 129.2, 136.9, 142.3, 147.2; MS (EI): *m/z* (relative intensity) 225.1 (M^+, 85), 210.1 (100), 196.1 (12), 180.1 (65), 77.1 (9).

2,6-Diisopropyl-*N*-phenylaniline (Table 2, compound 3v)[37]

Yield: 44% (22.3 mg). Eluents (R_f = 0.5, Hexane/EA = 19:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17–1.19 (m, 12H), 3.19–3.29 (m, 2H), 5.13 (br, 1H), 6.52 (d, *J* = 7.8 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 7.16–7.20 (m, 2H), 7.25–7.28 (m, 2H), 7.31–7.35 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 23.8, 28.2, 112.9, 117.6, 123.8, 127.2, 129.2, 135.1, 147.5, 148.1; MS (EI): *m/z* (relative intensity) 253.2 (M^+, 95), 238.1 (100), 196.1 (22), 180.1 (43).

(4-(Methyl(phenyl)amino)phenyl)(phenyl)methanone (Table 2, compound 3w)[38]

Yield: 90% (51.7 mg). Eluents (R_f = 0.5, Hexane/EA = 4:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.39 (s, 3H), 6.79–6.81 (m, 2H), 7.22–7.25 (m, 3H), 7.40–7.47 (m, 4H), 7.51–7.55 (m, 1H), 7.74–7.76 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 40.2, 113.4, 125.7, 126.1, 126.7, 128.0, 129.5, 129.9, 131.3, 132.3, 139.0, 147.2, 152.5, 195.1; MS (EI): *m/z* (relative intensity) 287.1 (M^+, 100), 210.1 (75), 167.1 (18), 105.0 (10), 77.1 (20).

Phenyl(4-(pyrrolidin-1-yl)phenyl)methanone (Table 2, compound 3x)[11b]

Yield: 59% (29.6 mg). Eluents (R_f = 0.45, Hexane/EA = 4:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.02–2.05 (m, 4H), 3.36–3.39 (m, 4H), 6.52–6.55 (m, 2H), 7.43–7.53 (m, 3H), 7.71–7.72 (m, 2H), 7.79–7.81 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 25.4, 47.5, 110.5, 124.1, 127.9, 129.4, 130.9, 132.9, 139.4, 150.8, 195.1; MS (EI): *m/z* (relative intensity) 251.1 (M^+, 100), 195.0 (8), 174.1 (51), 105.0 (14), 77.0 (18).

1-(4-(Phenylamino)phenyl)ethanone (Table 2, compound 3y)[39]

Yield: 92% (41.4 mg). Eluents (R_f = 0.45, Hexane/EA = 2:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 2.52 (s, 3H), 6.13 (br, 1H), 6.91–6.93 (m, 2H), 7.08–7.10 (m, 2H), 7.15–7.17 (m, 2H), 7.83–7.86 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 20.8, 26.1, 113.8, 121.4, 128.4, 130.0, 130.6, 133.3, 137.8, 149.1, 196.4; MS (EI): *m/z* (relative intensity) 225.1 (M^+, 70), 210.1 (100), 180.1 (11), 98.8 (4), 167.1 (19).

Ethyl 4-(methyl(phenyl)amino)benzoate (Table 2, compound 3z)[40]

Yield: 97% (49.5 mg). Eluents (R_f= 0.4, Hexane/EA = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, *J* = 7.2 Hz, 3H), 3.34 (s, 3H), 4.30 (q, *J* = 7.2 Hz, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 7.18–7.19 (m, 3H), 7.35–7.39 (m, 2H), 7.86 (d, *J* = 8.8 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.4, 40.2, 60.2, 113.8, 119.5, 125.2, 125.7, 129.7, 130.9, 147.5, 152.4, 166.7; MS (EI): *m/z* (relative intensity) 255.1 (M^+, 100), 227.1 (29), 210.1 (45), 180.1 (7), 167.1 (19).

4-(Methyl(phenyl)amino)benzonitrile (Table 2, compound 3aa)[34]

Yield: 55% (22.9 mg). Eluents (R_f= 0.6, Hexane/EA = 4:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.32 (s, 3H), 6.68–6.71 (m, 2H), 7.17–7.18 (m, 2H), 7.22–7,25 (m, 1H), 7.38–7.42 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 40.1, 99.2, 113.8, 120.3, 126.1, 126.4, 130.0, 133.2, 146.7, 151.9; MS (EI): *m/z* (relative intensity) 208.1 (M^+, 100), 192.1 (12), 102.0 (6), 77.0 (8).

***N*-phenylquinolin-6-amine (Table 2, compound 3ab)**[41]

Yield: 99% (43.6 mg). Eluents (R_f= 0.5, Hexane/EA = 2:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.21 (s, 1H), 7.01–7.05 (m, 1H), 7.19–7.21 (m, 2H), 7.28–7.36 (m, 4H), 7.40–7.41 (m, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 8.71 (dd, *J* = 4.2, 1.5 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 109.3, 119.0, 121.5, 122.1, 123.0, 129.45, 129.54, 130.5, 134.3, 141.7, 142.1, 144.2, 147.5; MS (EI): *m/z* (relative intensity) 220.1 (M^+, 100), 191.0 (6), 109.6 (12), 95.5 (6).

1-Phenyl-1*H*-indole (Table 3, compound 3ac)[42]

Yield: 98% (37.8 mg). Eluents (R_f= 0.4, Hexane) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77–6.78 (m, 1H), 7.24–7.33 (m, 2H), 7.40–7.45 (m, 2H), 7.58–7.59 (m, 4H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 7.5 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 103.5, 110.5, 120.3, 121.1, 122.3, 124.3, 126.4, 127.9, 129.3, 129.6, 135.8, 139.8; MS (EI): *m/z* (relative intensity) 193.1 (M^+, 100), 165.1 (22), 98.1 (10), 77.1 (4).

1-(Naphthalen-1-yl)-1*H*-indole (Table 3, compound 3ad)[43]

Yield: 89% (43.1 mg). Eluents (R_f= 0.5, Hexane/EA = 20:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81–6.82 (m, 1H), 7.07–7.09 (m, 1H), 7.15–7.22 (m, 2H), 7.39–7.45 (m, 2H), 7.49–7.51 (m, 1H), 7.55–7.64 (m, 3H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.99–8.01 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 102.9, 110.8, 120.1, 120.9, 122.1, 123.4, 125.1, 125.5, 126.6, 126.9, 128.2, 128.40, 128.43, 129.8, 130.5, 134.4, 136.0, 137.9; MS (EI): *m/z* (relative intensity) 242.1 (M^+, 100), 215.0 (6), 120.6 (12).

5-Methyl-1-(3,4,5-trimethylphenyl)-1*H*-indole (Table 3, compound 3ae)

Yield: 98% (48.8 mg). Eluents (R_f = 0.4, Hexane/DCM = 20:1) was used for flash column

chromatography to afford **3ae** as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 2.42 (s, 6H), 2.53 (s, 3H), 6.62 (d, *J* = 3.0 Hz, 1H), 7.08–7.10 (m, 1H), 7.20 (s, 2H), 7.32 (d, *J* = 3.1 Hz, 1H), 7.50–7.52 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 15.1, 20.7, 21.3, 102.4, 110.3, 120.6, 123.2, 123.6, 128.0, 129.2, 129.4, 133.2, 134.3, 137.0, 137.7; MS (EI): *m/z* (relative intensity) 249.1 (M^+, 100), 234.1 (15), 218.1 (7); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{20}N$: 250.1590, Found 250.1588.

5-Methoxy-1-(*p*-tolyl)-1*H*-indole (Table 3, compound 3af)[44]

Yield: 93% (44.1 mg). Eluents (R_f = 0.6, Hexane/EA = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H), 3.91 (s, 3H), 6.63 (d, *J* = 3.1 Hz, 1H), 6.92 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.18 (d, *J* = 2.3 Hz, 1H), 7.32–7.34 (m, 3H), 7.39–7.41 (m, 2H), 7.47 (d, *J* = 8.9 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 21.0, 55.8, 102.6, 102.8, 111.3, 112.4, 124.0, 128.4, 129.7, 130.1, 131.2, 136.1, 137.4, 154.4; MS (EI): *m/z* (relative intensity) 237.1 (M^+, 100), 221.1 (67), 194.1 (30), 152.0 (7), 118.6 (6).

1-(4-(1*H*-indol-1-yl)phenyl)ethanone (Table 3, compound 3ag)[45]

Yield: 86% (40.4 mg). Eluents (R_f = 0.35, Hexane/EA = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.64 (s, 3H), 6.72 (d, *J* = 3.2 Hz, 1H), 7.18–7.28 (m, 2H), 7.36 (d, *J* = 3.3 Hz, 1H), 7.58–7.60 (m, 2H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 8.09–8.11 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 26.5, 105.0, 110.5, 121.0, 121.4, 122.9, 123.2, 127.3, 129.8, 130.0, 134.4, 135.3, 143.7, 196.8; MS (EI): *m/z* (relative intensity) 235.1 (M^+, 100), 220.1 (58), 191.1 (48), 110.0 (7), 95.5 (9).

Methyl 4-(5-fluoro-1*H*-indol-1-yl)benzoate (Table 3, compound 3ah)

Yield: 72% (38.7 mg). Eluents (R_f = 0.2, Hexane/DCM = 19:1) was used for flash column chromatography to afford **3ah** as white solid. M.P.: 119.3-121.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (s, 3H), 6.68 (d, *J* = 3.2 Hz, 1H), 6.95-7.03 (m, 1H), 7.33 (dd, *J* = 9.1, 2.4 Hz, 1H), 7.40 (d, *J* = 3.3 Hz, 1H), 7.50–7.59 (m, 3H), 8.18–8.21 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 52.2, 104.6 (d, J_{CF} = 4.4 Hz), 106.2 (d, J_{CF} = 23.5 Hz), 111.1 (d, J_{CF} = 26.1 Hz), 111.3 (d, J_{CF} = 9.7 Hz), 123.1, 127.8, 128.9, 130.2 (d, J_{CF} = 10.0 Hz), 131.3, 132.0, 143.4, 158.3 (d, J_{CF} = 237.0 Hz), 166.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ –123.3; MS (EI): *m/z* (relative intensity) 269.1 (M^+, 100), 238.0 (37), 209.1 (32), 119.0 (7), 104.6 (8); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{13}FNO_2$: 270.0925, Found 270.0923.

Ethyl 3-(1*H*-indol-1-yl)benzoate (Table 3, compound 3ai)[46]

Yield: 88% (46.7 mg). Eluents (R_f = 0.55, Hexane/EA = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (t, *J* = 7.2 Hz, 3H), 4.47 (q, *J* = 7.2 Hz, 2H), 6.77 (d, *J* = 3.1 Hz, 1H), 7.23–7.32 (m, 2H), 7.41–7.42 (m, 1H), 7.60–7.65 (m, 2H), 7.74–7.68 (m, 2H), 8.09 (d, *J* = 7.7 Hz, 1H), 8.24–8.25 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.3, 61.3, 104.1, 110.2, 120.6, 121.2,

122.6, 125.1, 127.3, 127.7, 128.3, 129.4, 129.6, 132.1, 135.7, 139.9, 165.8; MS (EI): *m/z* (relative intensity) 265.1 (M^+, 100), 237.1 (57), 220.1 (7), 191.1 (27), 165.1 (8).

4-(*m*-Tolyl)-1,2,3,4-tetrahydrocyclopenta[*b*]indole (Table 3, compound 3aj)

Yield: 83% (41.0 mg). Eluents (R_f = 0.4, Hexane/DCM = 19:1) was used for flash column chromatography to afford **3aj** as white solid. M.P.: 102.9–103.0 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49 (s, 3H), 2.59–2.64 (m, 2H), 2.94–2.99 (m, 4H), 7.18–7.21 (m, 3H), 7.29–7.32 (m, 2H), 7.41–7.45 (m, 1H), 7.50–7.52 (m, 1H), 7.55–7.57 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 21.4, 24.6, 26.2, 28.3, 110.8, 118.6, 120.0, 120.2, 120.7, 121.8, 124.9, 125.4, 126.9, 129.2, 138.9, 139.3, 140.9, 145.7; MS (EI): *m/z* (relative intensity) 247.1 (M^+, 100), 232.1 (19), 217.1 (11), 204.1 (6). HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{18}H_{18}N$: 248.1434, found 248.1431.

1-(3-Methoxyphenyl)-1*H*-pyrrole (Table 3, compound 3ak)[47]

Yield: 93% (32.2 mg). Eluents (R_f= 0.4, Hexane/EA = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.36–6.37 (m, 2H), 6.80–6.82 (m, 1H), 6.95–6.97 (m, 1H), 7.00–7.02 (m, 1H), 7.10–7.12 (m, 2H), 7.34 (t, *J* = 8.2 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 55.4, 106.7, 110.3, 110.8, 112.8, 119.3, 130.3, 141.9, 160.5; MS (EI): *m/z* (relative intensity) 173.1 (M^+, 100), 144.1 (15), 130.1 (26), 103.0 (18), 77.0 (18).

10-(4-(*tert*-Butyl)phenyl)-10*H*-phenoxazine (Table 3, compound 3al)[48]

Yield: 94% (59.3 mg). Eluents (R_f = 0.5, Hexane/DCM = 19:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (s, 9H), 5.97 (dd, *J* = 7.6, 1.4 Hz, 2H), 6.63–6.72 (m, 6H), 7.26–7.29 (m, 2H), 7.61–7.63 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 31.4, 34.8, 113.2, 115.2, 121.0, 123.2, 127.9, 130.0, 134.6, 136.0, 143.9, 151.4; MS (EI): *m/z* (relative intensity) 315.2 (M^+, 100), 300.1 (45), 285.1 (14), 182.1 (39), 136.1 (9).

10-(3,5-Dimethylphenyl)-10*H*-phenothiazine (Table 3, compound 3am)[11e]

Yield: 66% (40.0 mg). Eluents (R_f= 0.8, Hexane/EA = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 6H), 6.26 (dd, *J* = 8.0, 0.7 Hz, 2H), 6.79–6.88 (m, 4H), 7.00–7.03 (m, 4H), 7.11–7.14 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 21.3, 115.8, 119.8, 122.2, 126.5, 126.7, 128.3, 129.8, 140.5, 140.6, 144.3; MS (EI): *m/z* (relative intensity) 303.1 (M^+, 100), 287.0 (5), 271.1 (15), 254.1 (6), 198.0 (19).

1-(*m*-Tolyl)-1*H*-indole (Table 4, compound 3an)[49]

Yield: 88% (36.4 mg). Eluents (R_f= 0.6, Hexane/EA = 20:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (s, 3H), 6.71 (d, *J* = 3.0 Hz, 1H), 7.18–7.28 (m, 3H), 7.33–7.36 (m, 3H), 7.40–7.44 (m, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 21.4, 103.3, 110.6, 120.2, 121.0, 121.4, 122.2, 125.0, 127.2, 127.9, 129.2, 129.3, 135.8, 139.6,

139.7; MS (EI): *m/z* (relative intensity) 207.1 (M^+, 100), 191.0 (6), 165.0 (7), 102.4 (6), 89.0 (6).

1-(3,5-Dimethylphenyl)-1*H*-indole (Table 4, compound 3ao)[44]

Yield: 92% (40.7 mg). Eluents (R_f = 0.5, Hexane/DCM = 19:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 6H), 6.74 (d, *J* = 3.1 Hz, 1H), 7.07 (s, 1H), 7.20–7.32 (m, 4H), 7.39 (d, *J* = 3.2 Hz, 1H), 7.64–7.66 (m, 1H), 7.75–7.77 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 21.3, 103.1, 110.6, 120.1, 121.0, 122.06, 122.1, 128.0, 128.1, 129.2, 135.9, 139.3, 139.7; MS (EI): *m/z* (relative intensity) 221.1 (M^+, 100), 204.1 (12), 178.1 (7), 102.2 (6), 89.1 (6).

5-Methoxy-1-phenyl-1*H*-indole (Table 4, compound 3ap)[45]

Yield: 95% (42.4 mg). Eluents (R_f= 0.5, Hexane/EA = 9:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 3H), 6.65 (d, *J* = 3.1 Hz, 1H), 6.93 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.19 (d, *J* = 2.4 Hz, 1H), 7.34–7.39 (m, 2H), 7.50–7.53 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 55.8, 102.6, 103.2, 111.3, 112.4, 124.0, 126.2, 128.3, 129.6, 129.8, 131.0, 139.9, 154.5; MS (EI): *m/z* (relative intensity) 223.1 (M^+, 100), 208.1 (71), 180.1 (43), 152.1 (16), 77.1 (9).

1-(3,5-Dimethylphenyl)-1*H*-pyrrole (Table 4, compound 3aq)[50]

Yield: 80% (27.3 mg). Eluents (R_f = 0.5, Hexane/DCM = 20:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 6H), 6.36–6.37 (m, 2H), 6.92 (s, 1H), 7.05 (s, 2H), 7.10–7.11 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 21.4, 110.0, 118.5, 119.4, 127.3, 139.3, 140.7; MS (EI): *m/z* (relative intensity) 171.1 (M^+, 100), 156.0 (23), 129.0 (22), 77.1 (11), 51.0 (4).

4-(*tert*-Butyl)-*N*-phenylaniline (Table 4, compound 3ar)[24]

Yield: 99% (44.6 mg). Eluents (R_f = 0.5, Hexane/DCM = 20:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (s, 9H), 5.67 (s, 1H), 6.93–6.97 (m, 1H), 7.08–7.10 (m, 4H), 7.26–7.37 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 31.4, 34.1, 117.1, 118.1, 120.4, 126.1, 129.3, 140.3, 143.7, 144.1; MS (EI): *m/z* (relative intensity) 225.1 (M^+, 38), 210.1 (100), 195.1 (7), 180.0 (6), 167.0 (6).

***N*-(3-methoxyphenyl)-2,6-dimethylaniline (Table 4, compound 3as)**[51]

Yield: 80% (36.3 mg). Eluents (R_f = 0.3, Hexane/DCM = 20:1) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (s, 6H), 3.73 (s, 3H), 5.18 (br, 1H), 6.03–6.05 (m, 1H), 6.15 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.32 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.05–7.12 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 18.3, 55.0, 99.5, 103.1, 106.6, 125.9, 128.5, 129.9, 136.1, 138.0, 147.8, 160.8; MS (EI): *m/z* (relative intensity) 227.1 (M^+, 100), 212.1 (43), 196.1 (13), 120.1 (7), 77.1 (5).

***N*-methyl-*N*-phenylaniline (Scheme 3, compound 3a)**[21]

Yield: 87% (1.60 g). Eluents (R_f= 0.4, Hexane/DCM = 20:1) was used for flash column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.34 (s, 3H), 6.96–7.00 (m, 2H), 7.04–7.06 (m, 4H), 7.28–7.32 (m, 4H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 40.2, 120.4, 121.2, 129.2, 149.0; MS (EI): *m/z* (relative intensity) 183.1 (M^+, 100), 167.1 (45), 104.0 (20), 77.1 (25), 51.0 (9).

Supporting Information Available: Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, ^{31}P NMR and HRMS spectra of synthesized compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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