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Authors: Ramakrishna Visannagari, Jhansi Rani Morla, and Dastagiri Reddy Nareddula

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FULL PAPER

A Zwitterionic Palladium(II) Complex as a Precatalyst for Neat Water Mediated Cross-Coupling Reactions of Heteroaryl, Benzyl and Aryl Acid Chlorides with Organoboron Reagents

V. Ramakrishna,[a] M. Jhansi Rani,[a] and N. Dastagiri Reddy*[a]

Abstract: The Suzuki-Miyaura cross coupling (SMC) reactions of several heteroaryl chlorides, benzyl chlorides and aryl acid chlorides with (hetero)arylboron reagents were investigated in the presence of $[Pd(HL1)(PPh_3)Cl_2]$ (**I**) as a catalyst and K_2CO_3 as a base in neat water. Synthesis of heterocycle-containing biaryls required the addition of 2 mol% of a phosphine ligand (PPh_3 or X-Phos). A combination of more than 115 substrates were screened and found that **I** was a versatile catalyst, which produced heterocycle-containing biaryls, diarylmethanes and benzophenones in moderate to excellent yields.

Introduction

The Suzuki-Miyaura coupling (SMC) is one of the most powerful tools in the organic synthesis and a widely preferred reaction in laboratory as well as in industry for the preparation of heterocycle-containing biaryls and diarylmethanes.[1] These moieties are frequently found in natural products, agrochemicals, pharmaceutically active compounds, fine chemicals and engineering materials such as conjugate polymers and liquid crystals, and also serve as ligand precursors in supramolecular chemistry.[2] In spite of the possibility of catalyst poisoning, which arises due to the ability of heteroatom strongly binding to the metal center,[3] the syntheses of (hetero)biaryls and heterocycle-containing diarylmethanes have been successfully carried out under the SMC conditions.[4] In most cases, an organic solvent or an aqueous-organic mixture has been used as a reaction medium. There is a plethora of catalyst systems, which work in neat water, known for aryl/benzyl bromide substrates.[5],[6] However, catalysts, which can effect coupling reactions for less reactive chloride analogues are less common.[7] Among them, only a handful of reports describe the coupling reactions of heteroaryl chlorides in neat water under SMC conditions.[8] When water is used as the reaction medium, the heteroatom present in the heterocycle is preferably engaged in hydrogen bonding thereby reducing the poisoning of the catalyst.[9] Therefore, the efficiency of the catalyst is expected to increase in water. However, due to poor solubility of catalysts, water has been discouraged as solvent. To overcome this problem, water soluble ligands such as double sulfonated fluorenyldicyclohexylphosphine[8d] and indenyldicyclohexylphosphine[8a] were used as ligands. In another strategy, the catalyst was used in conjunction with a phase transfer reagent like tetrabutylammonium bromide.[8b],[8c],[8e]

There is only one report, which describes the synthesis of diarylmethanes in neat water, known in the literature.[10] *N*-Methylimidazole coordinated (NHC)$PdCl_2$ [NHC–Pd(II)–Im] was employed as a catalyst for bringing about cross coupling reaction between benzyl chlorides and arylboronic acids. To the best of our knowledge, water mediated SMC reactions leading to the synthesis of heterocycle-containing diarylmethane units have not yet been reported. In the only example, which demonstrates the synthesis of diheteroarylmethanes, dioxane was used as the solvent.[11] Water as a solvent is not only economically viable but also environmental friendly. Moreover, the products, which are mostly insoluble in water, can easily be separated from the reaction mixture. Recently, we synthesized a zwitterionic complex **I** (Figure 1), which is found to be highly efficient in carrying out Suzuki-Miyaura coupling of (hetero)aryl bromides and benzyl bromides with organoboron reagents in neat water in the presence of K_2CO_3 as a base.[12] Heteroaryl/benzyl chlorides have the advantages over bromides and iodides of being cheaper, more stable and readily available. Hence, we investigated the efficiency of **I** in catalyzing the C–C bond coupling reactions of various combinations of (hetero)aryl/benzyl chlorides and (hetero)aryl-boronic acids/trifluroborates in neat water and the results are reported herein.

Apart from the aforementioned biaryl and diarylmethane derivatives, carbonyl building blocks such as unsymmetrical 1,2-diarylethanones, dienones, benzophenones and *β*-alkoxyimino carbonyl compounds can also be synthesized from the SMC reactions.[13] Ketones are used as starting materials for the preparation of oximes, acetals, carbazones, cyanohydrins, pinacols, *etc* and these compounds are frequently found in pharmaceuticals and fine chemicals.[14] The most common route for the synthesis of diarylketones is the reaction between a aryl halide and a organoboron reagent in presence of carbon monoxide.[15] This method suffers from the setback of handling toxic carbon monoxide. Recently, aryl amides and esters have been coupled with organoboron reagents eliminating the usage of carbon monoxide.[16] Research groups of Štěpnička and Bora reported coupling reactions between acid halides, which are cheaper than amides and esters, and organoboron reagents in biphasic medium.[17] So far there are no economically viable methods reported in neat water. Hence, we further examined the suitability of **I** as a catalyst in the SMC reactions of benzoyl chlorides with organoboronic acids in neat water.

[a] Prof. Dr. N. Dastagiri Reddy, V. Ramakrishna, M. Jhansi Rani
Department of Chemistry
Pondicherry University (A Central University)
Puducherry 605014, India
E-mail: ndreddy.che@pondiuni.edu.in

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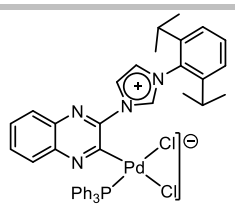


[Pd(HL1)(PPh$_3$)Cl$_2$], **I**

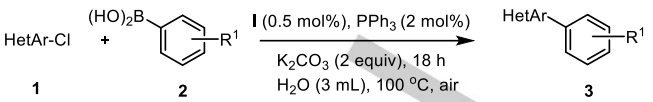
Figure 1. Zwitterionic Pd(II) complex **I**.

Results and Discussion

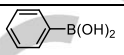
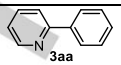
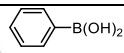
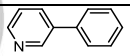
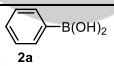
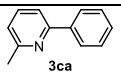
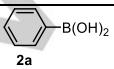
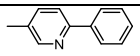
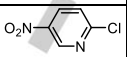
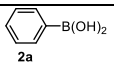
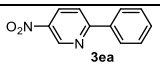
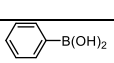
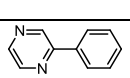
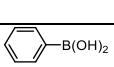
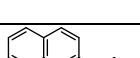
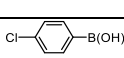
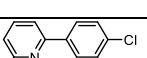
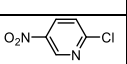
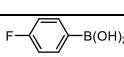
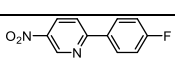
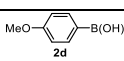
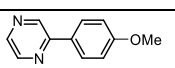
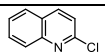
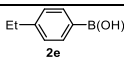
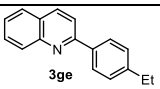
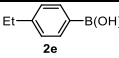
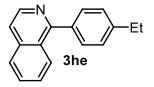
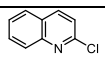
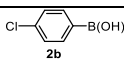
The zwitterionic Pd(II) complex **I** was prepared by following the method reported in our earlier communication.[12] Encouraged by the successful application of complex **I** in the synthesis of heterocycle-containing biaryls from (hetero)/aryl bromides and (hetero)/aryl boronic acids, investigations into the similar reactions of analogous chlorides were carried out. In a typical reaction, as we reported earlier, (hetero)/arly bromides reacted with (hetero)/aryl boronic acids in neat water at 70 °C in presence of 0.5 mol% of **I** and 2 equiv of K_2CO_3 to afford the corresponding cross-coupled products in excellent yields (>90%) within 3 h. In the present work, however, the reaction of 2-chloropyridine (**1a**) with phenylboronic acid (**2a**), under similar conditions, did not produce any coupled products in 3 h and even after 18 h at 100 °C, it gave the expected cross coupled product only in 40% yield. The formation of a good amount of palladium black, which was observed during the course of the reaction, indicated the decomposition of the complex. Phosphine ligands have been known to stabilize palladium thereby improving the longevity of the active center in the reaction medium.[18] Hence a 2 mol% of triphenylphosphine was added to the reaction mixture, which produced the cross coupled product 2-phenylpyridine (**3aa**) in excellent yield (92%). Once the reaction conditions were optimized, the catalyst was explored for its scope in catalyzing the reactions of various combinations of hetroaryl chlorides and arylboronic acids. Based on partners, the results are categorized into three sets *viz*. the reactions between i) heteroaryl chlorides and arylboronic acids (Table 1), ii) aryl chloride (4-chloroacetophenone) and heteroaryl boronic acids (Table 2), and iii) heteroaryl chlorides and heteroarylboronic acids (Tables 3 and 4).

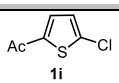
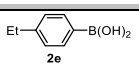
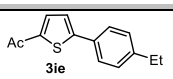
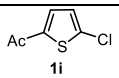
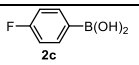
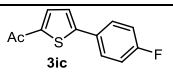
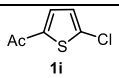
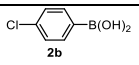
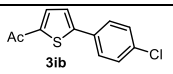
The cross-coupling of phenylboronic acid (**2a**) with a series of *N*-heteroaryl chlorides resulted in the desired *N*-heteroaryl-containing biaryls in good yields in 18 h (Table 1, entries 1–7). Similarly, the corresponding coupled products were obtained in excellent yields from various combinations of *N*-heteroaryl chlorides and arylboronic acids (Table 1, entries 8–13). Successful outcome of these reactions prompted us to explore the efficiency of **I** for *S*-heteroaryl chloride substrates. Carrying out coupling reactions on thiophene substrates is highly challenging as thiophene, which is generally used as a reagent in the poisoning test for Pd catalysts, has the great potential to poison the catalyst compared to *N*-heteroaryl substrates.[19] However, the SMC reactions of 2-acetyl-5-chlorothiophene (**1i**) afforded the desired products in excellent yields surprisingly within 3 h (Table 1, entries 14–17).

Table 1. Suzuki reactions of heteroaryl chlorides with simple arylboronic acids[a]



1 2 3

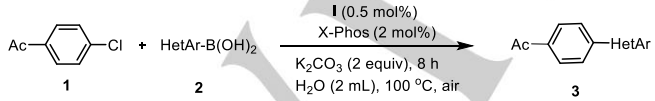
Entry	Heteroaryl chloride **1**	Boronic acid **2**	Product **3**	[b]Yield (%)
1	 **1a**	 **2a**	 **3aa**	92
2	 **1b**	 **2a**	 **3ba**	88
3	 **1c**	 **2a**	 **3ca**	92
4	 **1d**	 **2a**	 **3da**	88
5	 **1e**	 **2a**	 **3ea**	79
6	 **1f**	 **2a**	 **3fa**	90
7	 **1g**	 **2a**	 **3ga**	88
8	 **1c**	 **2b**	 **3cb**	92
9	 **1e**	 **2c**	 **3ec**	94
10	 **1f**	 **2d**	 **3fd**	93
11	 **1g**	 **2e**	 **3ge**	92
12	 **1h**	 **2e**	 **3he**	80
13	 **1g**	 **2b**	**3gb**	93
14[c]	**1i**	**2a**	**3ia**	95

15[c]	 1i	 2e	 3ie	87
16[c]	 1i	 2c	 3ic	92
17[c]	 1i	 2b	 3ib	88

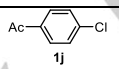
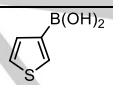
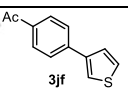
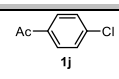
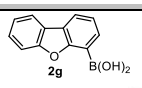
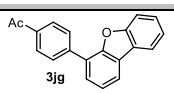
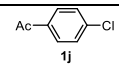
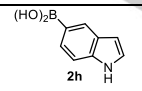
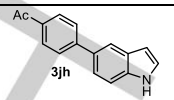
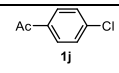
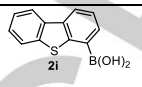
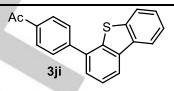
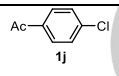
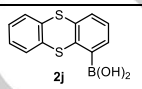
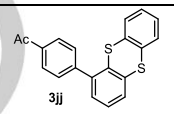
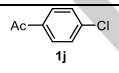
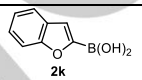
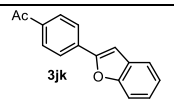
[a]Reaction conditions: heteroaryl chloride (1.00 mmol), boronic acids (1.20 mmol), K_2CO_3 (2.00 mmol), water (3 mL), [Pd] (0.5 mol%), PPh_3 (2 mol%), reaction time 18 h, in air. [b]Isolated yields after column chromatography. [c]Time 3 h.

While biaryls containing one heteroaryl moiety and one aryl moiety can be synthesized by a reaction between i) heteroaryl halides and arylboronic acids or ii) aryl halides and heteroarylboronic acids, the later method is yet to be reported in water. Hence, we investigated the coupling of 4-chloroacetophenone (**1j**) with various heteroarylboronic acids in neat water (Table 2). Initial attempts to synthesize these biaryls by employing 4-chloroacetophenone (**1j**) and 3-thiopheneboronic acid (**2f**) or 4-dibenzofuranboronic acid (**2g**) were unsuccessful and the reactions resulted in very low yields of the desired products (<10% in case of **2f** and 40% in case of **2g**). It has been demonstrated in the literature that sterically demanding and electronically rich phosphines enhance catalytic ability of Pd complexes.[20] Consequently, PPh_3 was replaced by 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (X-Phos). The yields were tremendously improved (Table 2, entries 1 and 2). Under these conditions, four different types of heteroarylboronic acids underwent coupling with 4-chloroacetophenone (**1j**) (Table 2, entries 3–6) and produced corresponding cross coupled products in moderate to good yields. The reactions of 3-thiopheneboronic acid (**2f**) and benzofuranboronic acid (**2k**) with 4-chloroacetophenone (**1j**) gave less yields presumably due to protodeboronation (Table 2, entries 1 and 6).[21] Hence, the heteroarylboronic acids were used in excess (1.5 equiv). Indole-5-boronic acid (Table 2, entry 3) also underwent coupling without requiring a protection to the N-H group.

Table 2. Suzuki reactions of 4-chloroacetophenone with various heteroarylboronic acids in water[a]



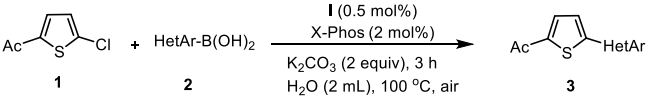
1 2 3

Entry	Aryl chloride **1**	Boronic acid **2**	Product **3**	[b]Yield (%)
1	 1j	 2f	 3jf	40
2	 1j	 2g	 3jg	82
3	 1j	 2h	 3jh	71
4	 1j	 2i	 3ji	72
5	 1j	 2j	 3jj	62
6	 1j	 2k	 3jk	51

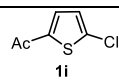
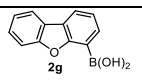
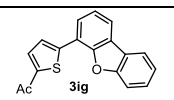
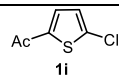
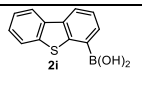
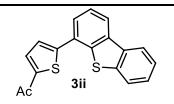
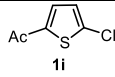
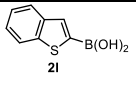
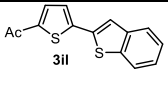
[a]Reaction conditions: 4-chloroacetophenone (0.50 mmol), boronic acid (0.75 mmol), K_2CO_3 (1.00 mmol), water (2 mL), [Pd] (0.5 mol%), X-Phos (2 mol%), reaction time 8 h, in air. [b]Isolated yields after column chromatography.

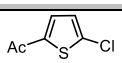
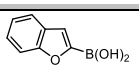
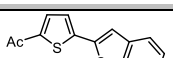
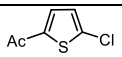
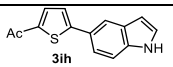
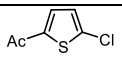
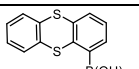
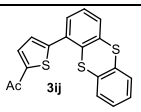
Table 3 lists the reactions of 2-acetyl-5-chlorothiophene (**1i**) with a series of heteroaryl boronic acids in the presence of **I**/X-Phos. The targeted molecules, heteroaryl-substituted thiophenes, are often found in drug candidates, conjugate polymers and functional materials.[22],[23] The heteroarylboronic acids such as 4-dibenzofuranboronic acid (**2g**), 4-dibenzothiopheneboronic acid (**2i**), 1-thianthrenylboronic acid (**2j**) and indole-5-boronic acid (**2h**) were effectively coupled with 2-acetyl-5-chlorothiophene (**1i**) to produce the heteroaryl-substituted thiophene products in good yields (Table 3, entries 1, 2, 5 and 6). It was observed that 2-benzofuranboronic acid (**2k**) and 2-benzothiopheneboronic acid (**2l**) afforded the cross coupled products in somewhat low yields (Table 3, entries 3 and 4).

Table 3. Suzuki reactions of various heteroarylboronic acids with 2-acetyl-5-chlorothiophene in water[a]



1 2 3

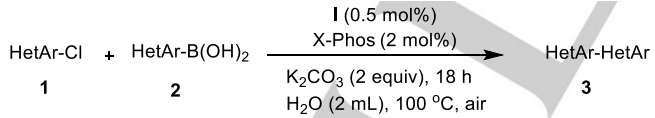
Entry	Heteroaryl chloride **1**	Boronic acid **2**	Product **3**	[b]Yield (%)
1	 1i	 2g	 3ig	72
2	 1i	 2i	 3ii	71
3	 1i	 2l	 3il	51

4	 1i	 2k	 3ik	48
5	 1i	 2h	 3ih	64
6	 1i	 2j	 3ij	62

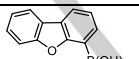
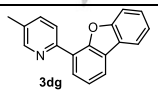
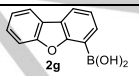
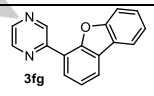
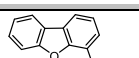
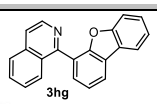
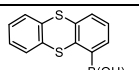
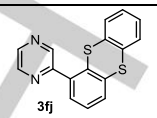
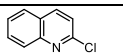
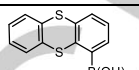
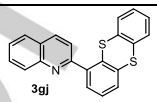
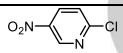
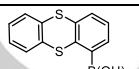
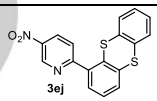
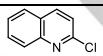
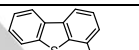
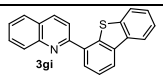
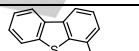
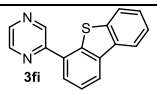
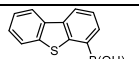
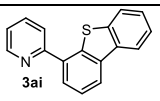
[a]Reaction conditions: 2-acetyl-5-chlorothiophene (0.50 mmol), boronic acid (0.75 mmol), K_2CO_3 (1.00 mmol), water (2 mL), [Pd] (0.5 mol%), X-Phos (2 mol%), reaction time 3 h, in air. [b]Isolated yields after column chromatography.

Heterobiaryl structures are present in drugs like Gleevec, an anticancer drug, PDE-IV inhibitor and bioactive natural products, such as diazonamide A, dragmacidin D and F.[24] To the best of our knowledge, there are no reports on Suzuki–Miyaura coupling of heteroaryl chlorides with heteroarylboron reagents in neat water present in the literature. In the present study, a total of nine heterobiaryls were synthesized using **I**/XPhos catalyst system in moderate to good yields (Table 4). These heterobiaryls are also used as supporting ligands in organometallic complexes of heavier transition metals.[25] The cross-coupling of six-membered *N*-heteroaryl chlorides such as 2-chloro-5-methylpyridine (**1d**), 2-chloropyrazine (**1f**) and 1-chloroisoquinoline (**1h**) with 4-dibenzofuranboronic acid (**2g**) were carried out successfully and the corresponding hetrobiaryls were obtained in good yields (Table 4, entries 1–3). Sulfur containing boronic acids 4-dibenzothiopheneboronic acid (**2i**) and 1-thianthrenylboronic acid (**2j**) also afforded coupled products with 2-chloro-5-nitropyridine (**1e**), 2-chloropyrazine (**1f**), 2-chloropyridine (**1a**) and 2-chloroquinoline (**1g**) in good yields (Table 4, entries 4–9). However, surprisingly, 2-benzofuranboronic acid, indole-5-boronic acid, 3-thiopheneboronic acid and 2-methoxy-5-pyridineboronic acid did not react with 2-chloropyridine (**1a**) under similar conditions.

Table 4. Suzuki reactions of *N*-heteroaryl chlorides with heteroarylboronic acids[a]



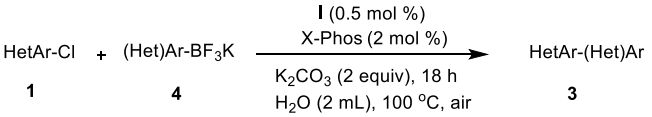
1 **2** **3**

Entry	Heteroaryl chloride **1**	Boronic acid **2**	Product **3**	[b]Yield (%)
1	 1d	 2g	 3dg	65
2	 1f	 2g	 3fg	75
3	 1h	 2g	 3hg	55
4	 1f	 2j	 3fj	60
5	 1g	 2j	 3gj	62
6	 1e	 2j	 3ej	65
7	 1g	 2i	 3gi	75
8	 1f	 2i	 3fi	78
9	 1a	 2i	 3ai	72

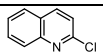
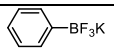
[a]Reaction conditions: heteroaryl chloride (0.50 mmol), boronic acid (0.75 mmol), K_2CO_3 (1.00 mmol), water (2 mL), [Pd] (0.5 mol%), X-Phos (2 mol%), reaction time 18 h, in air. [b]Isolated yields after column chromatography.

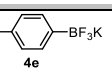
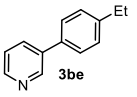
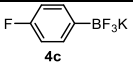
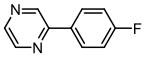
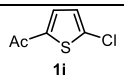
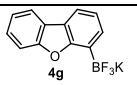
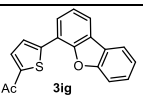
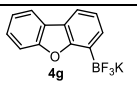
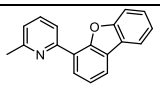
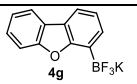
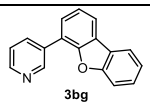
Potassium organotrifluoroborates are promising alternatives to organoboronic acids. The advantages of these salts are easy preparation, air/moisture stability, long shelf life at room temperature and no formation of cyclic dimers or trimers.[26] Hence, we explored the reactions of organotrifluoroborates with heteroaryl chlorides using **I/**X-Phos in water and the results are summarized in Table 5. 2-Chloropyrazine (**1f**), 2-chloroquinoline (**1g**) and 3-chloropyridine (**1b**) were successfully coupled with various potassium aryltrifluoroborates to afford the desired products in excellent yields (Table 5, entries 1–3). The **I/**X-Phos system in water was also found to be effective in bringing about the cross coupling reaction between potassium dibenzofuran-4-trifluoroborate (**4g**) and heteroaryl chlorides. The corresponding coupled products are furnished in Table 5 (entries 4–6).

Table 5. The couplings between potassium (hetero)aryltrifluoroborates and heteroaryl chlorides[a]



1 **4** **3**

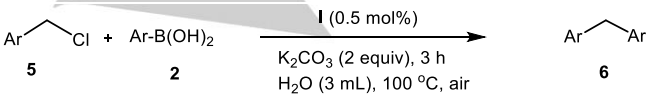
Entry	Heteroaryl chloride **1**	Trifluoroborate **4**	Product **3**	[b]Yield (%)
1	 1g	 4a	3ga	85

2	 1b	 4e	 3be	92
3	 1f	 4c	 3fc	93
4	 1i	 4g	 3ig	68[c]
5	 1c	 4g	 3cg	62
6	 1b	 4g	 3bg	61

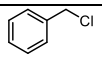
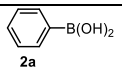
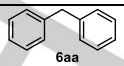
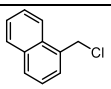
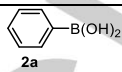
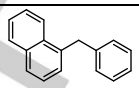
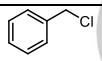
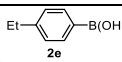
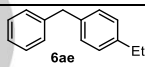
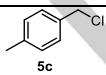
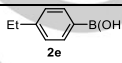
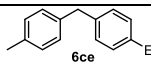
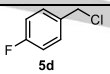
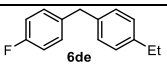
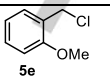
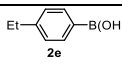
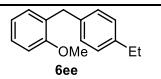
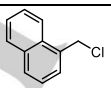
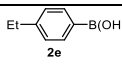
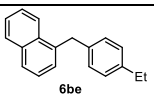
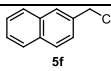
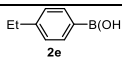
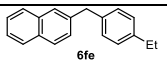
[a]Reaction conditions: heteroaryl chloride (0.50 mmol), potassium aryltrifluoroborate (0.75 mmol), K_2CO_3 (1.00 mmol), water (2 mL), [Pd] (0.5 mol%), X-Phos (2 mol%), reaction time 18 h, in air. [b]Isolated yields after column chromatography, [c]reaction time 3 h.

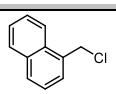
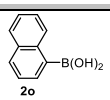
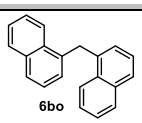
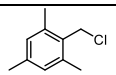
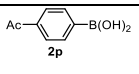
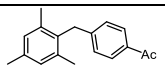
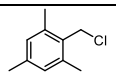
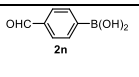
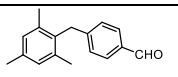
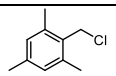
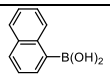
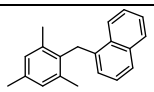
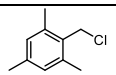
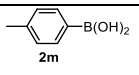
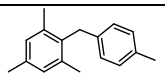
The versatility of the zwitterionic complex **I** in effecting the cross-coupling for a wide variety of aryl halides prompted us to investigate whether the noticed high activity was applicable to sp^3(C)−sp^2(C) cross-coupling reactions too. The SMC reactions of various combinations of benzyl chlorides (**5**) and arylboronic acids (**2**) were carried out in neat water using **I** as a catalyst and K_2CO_3 as a base at 100 °C. A facile sp^3(C)−sp^2(C) coupling occurred and diarylmethanes (**6**) were obtained in excellent yields within 3 h (Table 6). The coupling reactions of benzyl chloride (**5a**) and 1-chloromethylnaphthalene (**5b**) with phenylboronic acid (**2a**), which were conducted as probe reactions, afforded diphenylmethane (**6aa**) and 1-benzylnaphthalene (**6ba**) respectively in excellent yields (Table 6, entries 1 and 2). Similarly, the reactions of benzyl chlorides bearing functional groups such as methyl (−CH_3), fluoro (−F) and methoxy (−OCH_3), and 1/2-(chloromethyl)naphthalene with 4-ethylpheylboronic acid (**2e**) resulted in the cross-coupled products in good to excellent yields (Table 6, entries 3−8). 2-Methylbenzyl chloride (**5g**) reacted with phenylboronic acids possessing methyl (−CH_3), aldehyde (−CHO) and methoxy (−OCH_3) groups, and 1-naphthaleneboronic acid (**2o**) to give the corresponding cross-coupled products in excellent yields (Table 6, entries 9−12). Similarly, reactions of 1 and 2-(chloromethyl)naphthalenes (**5b** and **5f**) with 1-naphthaleneboronic acid (**2o**) and phenylboronic acids having fluorine and aldehyde functional groups resulted in the corresponding cross-coupled diarylmethanes in good yields (Table 6, entries 13−15). It is noteworthy that sterically encumbered *ortho* substituted 2-methoxybenzyl chloride (**5e**) and 2,4,6-trimethylbenzyl chloride (**5h**) also produced cross-coupled products in good yields (Table 6, entries 6 and 16−19).

Table 6. Suzuki-Miyaura sp^3(C)−sp^2(C) cross coupling of benzyl chlorides with arylboronic acids in neat water[a]



5 2 6

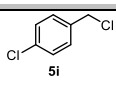
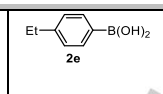
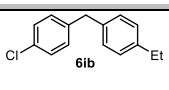
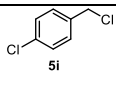
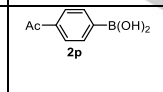
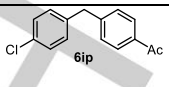
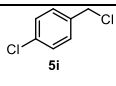
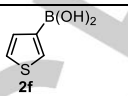
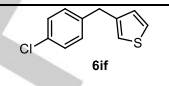
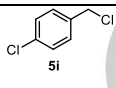
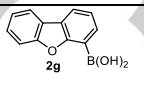
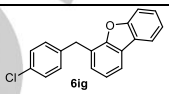
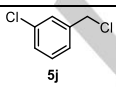
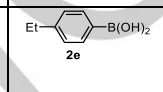
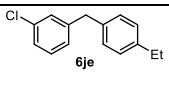
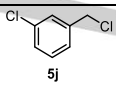
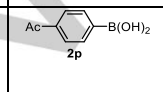
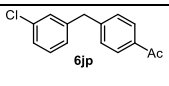
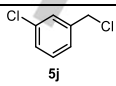
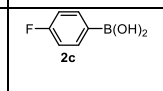
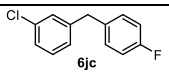
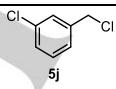
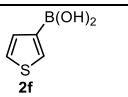
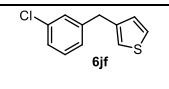
Entry	Benzyl chloride **5**	Boronic acid **2**	Methylene linked diaryl **6**	[b]Yield (%)
1	 5a	 2a	 6aa	95
2	 5b	 2a	 6ba	92
3	 5a	 2e	 6ae	86
4	 5c	 2e	 6ce	88
5	 5d	 2e	 6de	75
6	 5e	 2e	 6ee	77
7	 5b	 2e	 6be	86
8	 5f	 2e	 6fe	88
9	5g	2m	6gm	78
10	5g	2n	6gn	87
11	5g	2d	6gd	92
12	5g	2o	6go	85
13	5f	2c	6fc	83
14	5f	2n	6fn	82

15	 **5b**	 **2o**	 **6bo**	92
16	 **5h**	 **2p**	 **6hp**	81
17	 **5h**	 **2n**	 **6hn**	78
18	 **5h**	 **2o**	 **6ho**	88
19	 **5h**	 **2m**	 **6hm**	86

[a]Reaction conditions: benzyl chloride (1.00 mmol), boronic acid (1.20 mmol), K_2CO_3 (2.00 mmol), water (3 mL), [Pd] (0.5 mol%), reaction time 3 h, in air. [b]Isolated yields after column chromatography.

The Suzuki-Miyaura reaction of equimolar mixtures of chlorobenzyl chlorides, which contain chlorine atoms on both sp^3 and sp^2 carbons, and arylboronic acids resulted in selective cross-coupling at sp^3 carbon with high yields. The reactions of 4/3-chlorobenzyl chloride (**5i** and **5j**) with arylboronic acids, including two heteroarylboronic acids, progressed smoothly under the optimized reaction conditions and afforded exclusively the corresponding diarylmethanes in excellent yields (Table 7, entries 1−8). The chlorine atom on the aromatic ring remained intact even when excess of boronic acid was used under the reaction conditions. Chemoselectivity favoring benzylic chloride over aryl chloride in the SMC reactions is quite common and is frequently reported in the literature.[27] Interestingly, even when Cl is replaced by Br on the aromatic ring, preference for benzylic chloride was observed. When 4-bromobenzyl chloride (**5k**) was treated with one equiv of phenylboronic acid (**2a**), a mixture containing 40% of diarylmethane (with Br intact), 40% of arylbiarylmethane (double cross-coupled product), 10% of biaryl (with Cl intact) and 10% of **5k** was obtained (from ^{1}H NMR spectra). However, arylbiarylmethanes were the sole products when two equiv of arylboronic acids were used (Table 7, entries 9−12).

Table 7. Suzuki coupling reactions of chloro/bromo-benzyl chlorides[a]

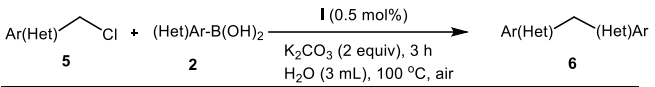
Entry	Benzyl chloride **5**	Boronic acid **2**	Methylene linked diaryl **6**	[b]Yield (%)
1	 **5i**	 **2e**	 **6ib**	95
2	 **5i**	 **2p**	 **6ip**	92
3	 **5i**	 **2f**	 **6if**	93
4	 **5i**	 **2g**	 **6ig**	72
5	 **5j**	 **2e**	 **6je**	90
6	 **5j**	 **2p**	 **6jp**	88
7	 **5j**	 **2c**	 **6jc**	85
8	 **5j**	 **2f**	 **6jf**	86
9[c]	**5k**	**2a**	**6ka**	88
10[c]	**5k**	**2e**	**6ke**	78
11[c]	**5k**	**2f**	**6kf**	87
12[c]	**5l**	**2a**	**6la**	92

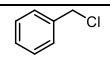
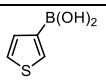
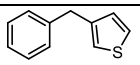
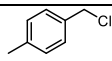
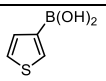
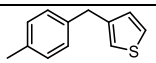
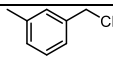
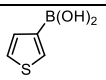
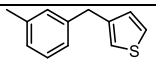
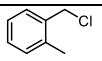
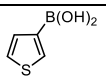
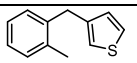
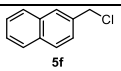
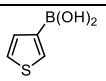
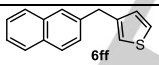
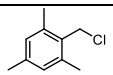
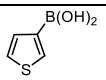
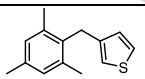
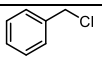
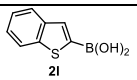
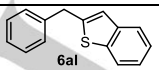
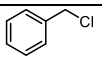
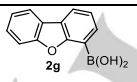
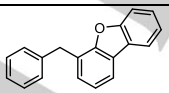
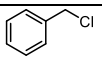
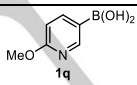
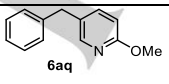
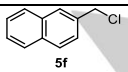
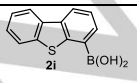
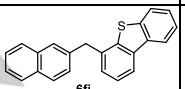
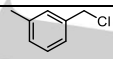
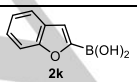
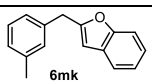
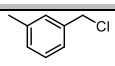
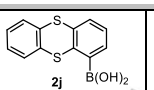
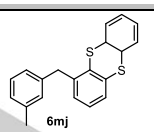
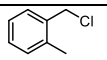
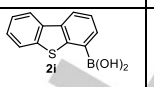
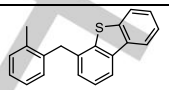
[a]Reaction conditions: benzyl chloride (1.00 mmol), boronic acid (1.20 mmol), K_2CO_3 (2.00 mmol), water (3 mL), [Pd] (0.5 mol%), reaction time 3 h, in air. [b]Isolated yields after column chromatography, [c]Benzyl chloride (0.50 mmol).

A thorough literature search revealed the synthesis of heteroaryl containing diarylmethanes had been limited only to three examples and these routes require organic or biphasic media.[28] Hence, the reactions of a few benzyl chlorides with heteroarylboronic acids were conducted in neat water under the optimized conditions and the results are listed in Table 8. A total of seven heteroarylboronic acids were tested with various benzyl chlorides as coupling partners. Initial runs using 3-thiopheneboronic acid (**2f**) and eight different benzyl chlorides containing various substituents resulted in the desired products in excellent yields (Table 8, entries 1−6). The cross-coupling of

benzyl chlorides with heteroarylboronic acids bearing benzothiophene, benzofuran, dibenzofuran, dibenzothiophene, thianthrene and pyridine moieties also afforded benzylated heteroarenes in good yields (Table 8, entries 7−15). The catalyst was also able to bring about the cross coupling reaction between 2-chloro-5-(chloromethyl)pyridine (**1i**) and (hetero)arylboronic acids leading to the formation heteroaryl containing diarylmethane derivatives including a diheteroarylmethane (Table 8, entries 16−19).

Table 8. Synthesis of heteroaryl-containing diarylmethanes in neat water[a]



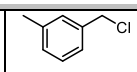
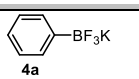
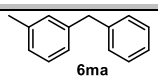
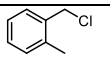
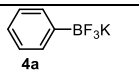
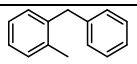
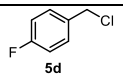
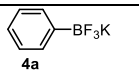
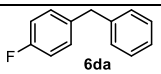
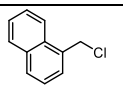
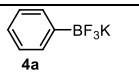
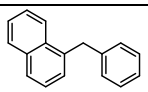
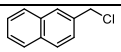
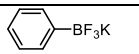
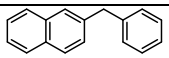
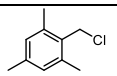
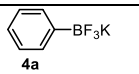
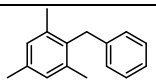
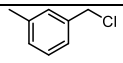
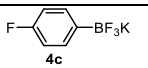
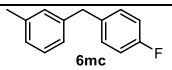
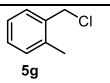
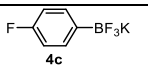
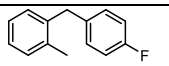
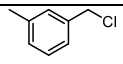
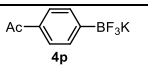
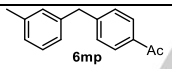
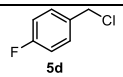
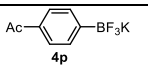
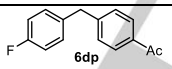
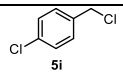
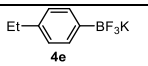
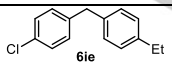
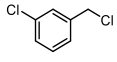
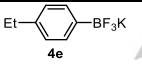
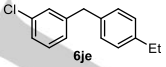
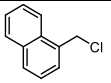
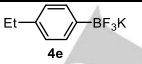
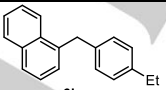
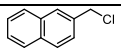
Entry	Benzyl chloride **5**	Boronic acid **2**	Methylene linked diaryl **6**	[b]Yield (%)
1	 **5a**	 **2f**	 **6af**	95
2	 **5c**	 **2f**	 **6cf**	90
3	 **5m**	 **2f**	 **6mf**	89
4	 **5g**	 **2f**	 **6gf**	88
5	 **5f**	 **2f**	 **6ff**	86
6	 **5h**	 **2f**	 **6hf**	88
7[c]	 **5a**	 **2l**	 **6al**	78
8[c]	 **5a**	 **2g**	 **6ag**	87
9[c]	 **5a**	 **1q**	 **6aq**	91
10[c]	 **5f**	 **2i**	 **6fi**	71
11[c]	 **5m**	 **2k**	 **6mk**	77
12[c]	 **5m**	 **2j**	 **6mj**	65
13[c]	 **5g**	 **2i**	 **6gi**	78
14[c]	**5h**	**2g**	**6hg**	76
15[c]	**5h**	**2k**	**6hk**	51
16	**5n**	**2a**	**6na**	87
17	**5n**	**2o**	**6no**	85
18[d]	**5n**	**2f**	**6nf**	65

[a]Reaction conditions: benzyl chloride (1.00 mmol), boronic acid (1.20 mmol), K_2CO_3 (2.00 mmol), water (3 mL), [Pd] (0.5 mol%), reaction time 3 h, in air. [b]Isolated yields after column chromatography, [c]boronic acid (1.50 mmol), [d]PPh_3 (2 mol%).

The sp^3(C)−sp^2(C) cross coupling reactions have also been carried out between potassium aryltrifluoroborates and benzyl chlorides in the presence of **I**, which revealed that the catalyst was also highly efficient in catalyzing these reactions. All the substrates employed in the study produced the cross coupled products in excellent yields within 3 h. In total, 18 combinations of the reagents were employed and the results are listed in Table 9.

Table 9. Suzuki Muyara coupling reaction of benzyl chlorides with potassium aryltrifluoroborates[a]

Entry	Benzyl chloride **5**	Trifluoroborate **4**	Methylene linked diaryl **6**	[b]Yield (%)
1	**5a**	**4a**	**6aa**	95
2	**5c**	**4a**	**6ca**	90

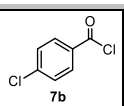
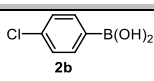
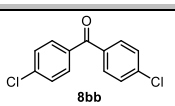
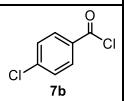
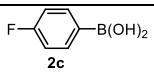
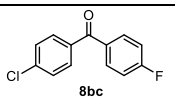
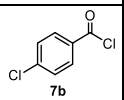
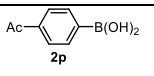
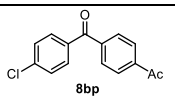
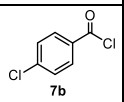
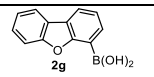
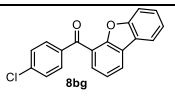
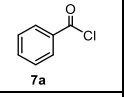
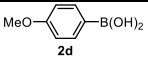
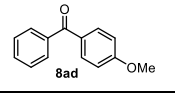
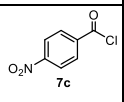
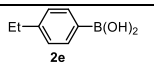
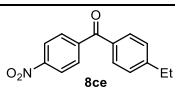
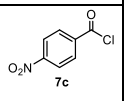
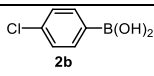
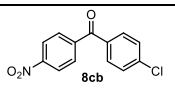
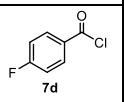
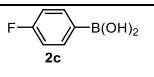
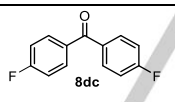
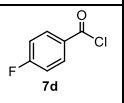
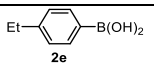
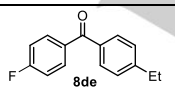
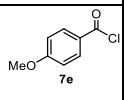
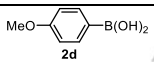
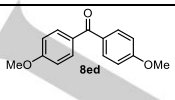
3	 5m	 4a	 6ma	91
4	 5g	 4a	 6ga	88
5	 5d	 4a	 6da	85
6	 5b	 4a	 6ba	87
7	 5f	 4a	 6fa	86
8	 5h	 4a	 6ha	88
9	 5m	 4c	 6mc	78
10	 5g	 4c	 6gc	76
11	 5m	 4p	 6mp	72
12[c]	 5d	 4p	 6dp	71
13	 5i	 4e	 6ie	88
14	 5j	 4e	 6je	86
15	 5b	 4e	 6be	82
16	 5f	4e	6fe	85
17	5h	4p	6hp	70
18	5h	4m	6hm	78

[a]Reaction conditions: benzyl chloride (1.00 mmol), organoboron reagent (1.20 mmol), K_2CO_3 (2.00 mmol), water (3 mL), [Pd] (0.5 mol%), reaction time 3 h, in air. [b]Isolated yields after column chromatography.

Further, the catalyst **I** was examined for producing benzophenones (**8**) from benzoyl chlorides (**7**) and arylboronic acids (**2**) in neat water at room temperature (Table 10). The model coupling reactions were done between phenylboronic acid and the acid chlorides benzoyl chloride (**7a)** and 4-chlorobenzoyl chloride (**7b**) (Table 10, entries 1 and 2), which produced the corresponding biaryl ketones in excellent yields. Under similar conditions, **7b** underwent coupling with several boronic acids, including 4-dibenzofuranboronic acid (**2g**) (Table 10, entries 3−9). Further, the reaction protocol was successfully applied in the preparation of various unsymmetrical benzophenones in good to excellent yields from their corresponding partners (Table 10, entries 10−15). In case of 4-nitrobenzoyl chloride (**7c**), heating was required due to its poor solubility in water (Table 10, entries 11 and 12). As the acid chlorides are susceptible to hydrolysis in water they were used in slight excess (1.2 equiv).

Table 10. The cross-coupling of acid chlorides with boronic acids in neat water[a]

Entry	Acid chloride **7**	Boronic acid **2**	Ketone **8**	[b]Yield (%)
1	7a	2a	8aa	95
2	7b	2a	8ba	92
3	7b	2e	8be	91
4	7b	2d	8bd	93
5	7b	2r	8br	77

6	 7b	 2b	 8bb	84
7	 7b	 2c	 8bc	83
8	 7b	 2p	 8bp	54
9	 7b	 2g	 8bg	71
10	 7a	 2d	 8ad	92
11	 7c	 2e	 8ce	82[c]
12	 7c	 2b	 8cb	78[c]
13	 7d	 2c	 8dc	88
14	 7d	 2e	 8de	82
15	 7e	 2d	 8ed	91

[a]Reaction conditions: acid chloride (1.20 mmol), boronic acid (1.10 mmol), K_2CO_3 (2.00 mmol), water (3 mL), [Pd] (0.5 mol%), reaction time 3 h, in air. [b]Isolated yields after column chromatography, [c]at 80 °C.

Conclusions

In summary, the zwitterionic Pd(II) complex **I** was found to be highly active in bringing about the cross coupling reactions between i) heteroaryl chlorides and arylboronic acids ii) 4-chloroacetophenone and heteroarylboronic acids and iii) heteroaryl chlorides and heteroarylboronic acids/trifluoroborates in neat water leading to the synthesis of heterocycle containing biaryls. Except in few cases, the desired products were obtained in good to excellent yields. It was observed that the efficiency of the catalyst increased in the presence of phosphine ligands such as PPh_3 and X-Phos. The **I**/K_2CO_3/water system was also successfully utilized in the preparation of heterocycle containing diarylmethanes and diarylketones from the corresponding benzyl/acid chlorides and organoboronic acids in excellent yields, and these reactions do not require the addition of phosphines (except in one case, where PPh_3 is required). This is the first time that a neat water mediated synthesis of biheteroaryls, heterocycle containing diarylmethanes and diarylketones from chloro substrates are reported. It is noteworthy that **I** is a unique catalyst, which catalyzes all the three types of aforesaid reactions. Though there are several advantages of using water as a solvent in SMC reactions, challenge of arresting protodeboronation in heteroboronic acids, which is reportedly enhanced by polar protic solvents,[29] is yet to be addressed. Currently, we are working towards developing catalyst systems, which can function at reduced temperatures thereby decreasing protodeboronation and homocoupling observed in some cases.

Experimental Section

General considerations: All manipulations were carried out under open atmosphere. [Pd(HL1)(PPh_3)Cl_2] (**I**) was prepared by following a method mentioned in our earlier communication.[12] Potassium (hetero)aryltrifluoroborates were prepared by following the literature procedures.[30] All commercially available chemicals including (hetero)aryl chlorides, benzyl chlorides, benzoyl chlorides and boronic acids were used as received. Analytical thin-layer chromatography was performed using pre-coated silica gel 60 F_{254} plates and UV light at 254 nm. ^{1}H and ^{13}C{^{1}H} spectra were recorded on a Bruker 400 MHz instrument and, ^{19}F spectra were recorded on a Bruker 500 MHz instrument. HR-MS were recorded on an Agilent 6540 UHD Q-TOF mass spectrometer. IR spectra were recorded on a Jasco 4100 FT-IR spectrometer.

General procedure for Suzuki–Miyaura cross-coupling reactions: To a 13 X 90 mm test tube with a stir bar were added boronic acid (0.75 - 1.2 mmol), K_2CO_3 (1 - 2 mmol), Pd catalyst (0.5 mol%), [preparation of heterocycle-containing biaryls required the addition of 2 mol% of PPh_3 or X-Phos], and aryl/benzyl/benzoyl chloride (0.5 - 1.2 mmol) in water (2 - 3 mL) and the resulting mixture was stirred in an oil bath at 100 °C under open atmosphere. The progress of the reaction was monitored by TLC and with ^{1}H NMR Spectroscopy. When there was no more significant conversion of aryl halide noticed, the reaction mixture was cooled to room temperature, mixed with water (5 mL) and extracted with diethyl ether (3 X 10 mL). The organic phase was dried with Na_2SO_4 and the solvent was removed using a rotary evaporator. The crude product was purified by column chromatography using a mixture of hexane/ethyl acetate as eluent on silica gel (230 - 400 mesh). The identity of the reported products was confirmed by comparing the NMR (^{1}H NMR) data with the reported in the literature and the new compounds were characterized by the NMR (^{1}H, ^{13}C & ^{19}F NMR) spectroscopy, IR and the ESI-MS.

Analytical data for heterobiaryls:

2-Phenylpyridine (3aa) (entry 1 of table 1)[31]: Yield: 92% (0.141 g); R_f = 0.33 (ethyl acetate/hexane 1:49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, 1H), 8.00 – 7.98 (m, 2H), 7.70 (m, 2H), 7.50 – 7.40 (m, 3H), 7.21 – 7.17 (m, 1H) ppm.

3-Phenylpyridine (3ba) (entry 2 of table 1)[31]: Yield: 88% (0.135 g); R_f = 0.32 (ethyl acetate/hexane 1:49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (s, 1H), 8.61 (s, 1H), 7.98 (d, 1H), 7.58 (d, 2H), 7.48 (m, 2H), 7.42 – 7.38 (m, 2H) ppm.

2-Methyl-6-phenylpyridine (3ca) (entry 3 of table 1)[31]: Yield: 92% (0.154 g); R_f = 0.33 (ethyl acetate/hexane 1:49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, 2H), 7.64 – 7.60 (m, 1H), 7.52 – 7.40 (m, 4H), 7.10 (d, 1H), 2.64 (s, 3H) ppm.

5-Methyl-2-phenylpyridine (3da) (entry 4 of table 1)[31]: Yield: 88% (0.148 g); R_f = 0.32 (ethyl acetate/hexane 1:49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H), 7.97 (m, 2H), 7.62 (d, 1H), 7.55 (dd, 1H), 7.46 (m, 2H), 7.41 – 7.37 (m, 1H), 2.36 (s, 3H) ppm.

5-Nitro-2-phenyl-pyridine (3ea) (entry 5 of table 1)[32]: Yield: 79% (0.158 g); R_f = 0.48 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.49 (s, 1H), 8.52 (dd, 1H), 8.08 (m, 2H), 7.91 (d, 1H), 7.52 (m, 3H) ppm.

2-Phenylpyrazine (3fa) (entry 6 of table 1)[33]: Yield: 90% (0.139 g); R_f = 0.42 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (d, 1H), 8.61 (s, 1H), 8.49 (d, 1H), 8.01 (d, 2H), 7.50 (m, 3H) ppm.

2-Phenylquinoline (3ga) (entry 7 of table 1 and entry 1 of table 5)[32]: Yield: 88% (0.179 g); R_f = 0.38 (ethyl acetate/hexane 1:49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 – 8.18 (m, 4H), 7.91 – 7.84 (m, 2H), 7.76 (m, 1H), 7.57 – 7.48 (m, 4H) ppm.

6-Methyl-2-(4-chlorophenyl)pyridine (3cb) (entry 8 of table 1)[34]: Yield: 92% (0.185 g); R_f = 0.45 (ethyl acetate/hexane 1:49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, 2H), 7.64 (t, 1H), 7.48 (d, 1H), 7.42 (d, 2H), 7.10 (d, 1H), 2.62 (s, 3H) ppm.

2-(4-Fluorophenyl)-5-nitropyridine (3ec) (entry 9 of table 1)[32]: Yield: 94% (0.203 g); R_f = 0.42 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.46 (s, 1H), 8.52 (dd, 1H), 8.11 – 8.08 (m, 2H), 7.86 (d, 1H), 7.23 – 7.18 (m, 2H) ppm.

2-(4-Methoxyphenyl)pyrazine (3fd) (entry 10 of table 1)[35]: Yield: 93% (0.172 g); R_f = 0.32 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (d, 1H), 8.57 (dd, 1H), 8.43 (d, 1H), 7.97 (d, 2H), 7.03 (d, 2H), 3.87 (s, 3H) ppm.

2-(4-Ethylphenyl)quinolone (3ge) (entry 11 of table 1): Obtained as a colorless oil; Yield: 92% (0.213 g); R_f = 0.36 (ethyl acetate/hexane 1:49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 – 8.09 (m, 4H), 7.87 – 7.70 (m, 2H), 7.73 (t, J = 7.2 Hz, 2H), 7.51 (m, 1H), 7.37 (d, 2H), 2.74 (q, J = 7.6 Hz, 2H), 1.30 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5, 148.4, 145.9, 137.3, 136.8, 129.8, 129.7, 128.5, 127.7, 127.6, 127.2, 126.2, 119.1, 28.8, 15.7 ppm; IR (KBr): 3059, 2958, 2924, 2867, 1594, 1493, 1428, 1315, 1051, 943, 817, 753, 676 cm^{-1}; HRMS (ESI): m/z calcd for $C_{17}H_{16}N$ $[M + H]^+$ 234.1282, found 234.1267.

1-(4-Ethylphenyl)isoquinoline (3he) (entry 12 of table 1): Obtained as a white solid; Yield: 80% (0.186 g); mp: 59 – 61 °C; R_f = 0.32 (ethyl acetate/hexane 1:49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, J = 6.0 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.69 – 7.61 (m, 4H), 7.52 (t, 1H), 7.36 (d, J = 8.4 Hz, 2H), 2.76 (q, J = 7.6 Hz, 2H), 1.32 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 144.9, 142.2, 137.0, 136.9, 131.0, 130.0, 128.0, 127.9, 127.2, 127.7, 126.9, 119.9, 28.9, 15.7 ppm; IR (KBr): 3049, 2964, 2930, 2871, 1617, 1552, 1455, 1383, 1355, 975, 828, 751, 678 cm^{-1}; HRMS (ESI): m/z calcd for $C_{17}H_{16}N$ $[M + H]^+$ 234.1282, found 234.1299.

2-(4-Chlorophenyl)quinolone (3gb) (entry 13 of table 1)[36]: Yield: 93% (0.221 g); R_f = 0.42 (ethyl acetate/hexane 1:49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 – 8.11 (m, 4H), 7.84 – 7.82 (m, 2H), 7.75 – 7.72 (m, 1H), 7.55 – 7.46 (m, 3H) ppm.

1-(5-Phenylthiophene-2-yl)ethanone (3ia) (entry 14 of table 1)[37]: Yield: 95% (0.190 g); R_f = 0.48 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 – 7.64 (m, 3H), 7.43 – 7.31 (m, 4H), 2.56 (s, 3H) ppm.

1-(5-(4-Ethylphenyl)thiophen-2-yl)ethanone (3ie) (entry 15 of table 1): Obtained as a white solid; Yield: 87% (0.199 g); mp: 101 – 103 °C; R_f = 0.35 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 4.0 Hz, 1H), 7.57 (d, J = 8.2 Hz, 2H), 7.26 (dd, J = 13.7, 6.1 Hz, 3H), 2.67 (q, J = 7.6 Hz, 2H), 2.55 (s, 3H), 1.26 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 153.2, 145.7, 142.7, 133.6, 130.9, 128.7, 126.4, 123.5, 28.8, 26.6, 15.5 ppm; IR (KBr): 2963, 2869, 1648, 1533, 1442, 1353, 1277, 1029, 919, 802 cm^{-1}; HRMS (ESI): m/z calcd for $C_{14}H_{15}OS$ $[M + H]^+$ 231.0843, found 231.0839.

1-(5-(4-Fluorophenyl)thiophene-2-yl)ethanone (3ic) (entry 16 of table 1)[37]: Yield: 92% (0.201 g); R_f = 0.44 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 – 7.59 (m, 3H), 7.25 – 7.08 (m, 3H), 2.56 (s, 3H) ppm.

1-(5-(4-Chlorophenyl)thiophene-2-yl)ethanone (3ib) (entry 17 of table 1)[37]: Yield: 88% (0.206 g); R_f = 0.42 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, 1H), 7.59 – 7.57 (m, 2H), 7.40 – 7.38 (m, 2H), 7.29 (d, 1H), 2.57 (s, 3H) ppm.

1-(4-(Thiophen-3-yl)phenyl)ethanone (3jf) (entry 1 of table 2)[38]: Yield: 40% (0.040 g); R_f = 0.33 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, 2H), 7.69 (d, 2H), 7.58 (dd, 1H), 7.43 (m, 2H), 2.62 (s, 3H) ppm.

4-(4'-Acetylphenyl)dibenzofuran (3jg) (entry 2 of table 2)[4h]: Yield: 82% (0.116 g); R_f = 0.31 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, 2H), 8.04 – 7.98 (m, 4H), 7.65 – 7.60 (m, 2H), 7.51 – 7.36 (m, 3H), 2.68 (s, 3H) ppm.

5-(4-Acetylphenyl)-1H-indole (3jh) (entry 3 of table 2)[39]: Yield: 71% (0.083 g); R_f = 0.35 (ethyl acetate/hexane 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1H), 8.03 (d, 2H), 7.91 (d, 1H), 7.74 (d, 2H), 7.47 (d, 2H), 7.25 (t, 1H), 6.62 (t, 1H), 2.64 (s, 3H) ppm.

1-(4-(Dibenzo[b,d]thiophen-4-yl)phenyl)ethan-1-one (3ji) (entry 4 of table 2): Obtained as a white solid; Yield: 72% (0.108 g); mp: 143 – 145 °C; R_f = 0.37 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 – 8.18 (m, 2H), 8.12 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8.5 Hz, 3H), 7.58 (t, J = 7.6 Hz, 1H), 7.53 – 7.46 (m, 3H), 2.69 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 145.4, 139.5, 138.5, 136.6, 135.9, 135.7, 129.1, 128.6, 127.2, 127.1, 125.3, 124.7, 122.8, 121.9, 121.3, 26.9 ppm; IR (KBr): 3044, 1676, 1597, 1438, 1357, 1257, 1106, 842, 798, 754 cm^{-1}; HRMS (ESI): m/z calcd for $C_{20}H_{15}OS$ $[M + H]^+$ 303.0843, found 303.0864.

1-(4-(Thianthren-1-yl)phenyl)ethan-1-one (3jj) (entry 5 of table 2): Obtained as a pale yellow solid; Yield: 62% (0.103 g); mp: 199 – 201 °C; R_f = 0.30 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 – 8.05 (m, 2H), 7.57 – 7.48 (m, 4H), 7.36 (dd, J = 7.6, 1.4 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.27 – 7.16 (m, 3H), 2.68 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 145.0, 141.5, 136.5, 136.3, 136.1, 135.6, 135.0, 129.9, 129.1, 129.0, 128.9, 128.7, 128.4, 128.1, 127.8, 127.4, 26.9 ppm; IR (KBr): 3059, 2998, 1675, 1599, 1444, 1385, 1350, 1263, 1108, 789, 747 cm^{-1}; HRMS (ESI): m/z calcd for $C_{20}H_{15}OS_2$ $[M + H]^+$ 335.0564, found 335.0597.

2-(4-Acetyl phenyl)benzo[b]furan (3jk) (entry 6 of table 2)[4h]: Yield: 51% (0.059 g); R_f = 0.32 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, 2H), 7.94 (d, 2H), 7.62 (d, 1H), 7.53 (d, 1H), 7.33 – 7.27 (m, 2H), 7.17 (s, 1H), 2.64 (s, 3H) ppm.

1-(5-(Dibenzo[b,d]furan-4-yl)thiophen-2-yl)ethan-1-one (3ig) (entry 1 of table 3 and entry 4 of table 5): Obtained as a yellow solid; Yield: 72% (0.104 g); mp: 132 – 134 °C; R_f = 0.26 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 – 7.89 (m, 3H), 7.79 – 7.74 (m, 2H), 7.67 (d, J = 8.2 Hz, 1H), 7.51 (t, J = 7.7 Hz, 1H), 7.39 (m, 2H), 2.62 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 156.3, 152.5, 147.0, 143.4, 133.4, 127.9, 127.1, 125.5, 125.4, 123.9, 123.4, 123.4, 121.2, 121.0, 118.5, 112.1, 26.8 ppm; IR (KBr): 3062, 1645, 1583, 1438, 1350, 1273, 1182, 1095, 835, 790, 747 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{13}O_2S$ $[M + H]^+$ 293.0636, found 293.0632.

1-(5-(Dibenzo[b,d]thiophen-4-yl)thiophen-2-yl)ethan-1-one (3ii) (entry 2 of table 3): Obtained as a white solid; Yield: 71% (0.108 g); mp: 100 – 102 °C; R_f = 0.29 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 – 8.17 (m, 2H), 7.91 – 7.87 (m, 1H), 7.77 (d, J = 4.0 Hz, 1H), 7.72 (dd, J = 7.5, 1.0 Hz, 1H), 7.65 (d, J = 3.9 Hz, 1H), 7.57 – 7.48 (m, 3H), 2.62 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 150.9, 143.8, 139.4, 137.9, 137.0, 135.4, 133.2, 128.9, 127.4, 126.9, 126.5, 125.2, 124.9, 122.8, 122.1, 122.0, 26.9 ppm; IR (KBr): 3051, 1651, 1482, 1434, 1390, 1276, 1018, 791, 755 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{13}OS_2$ $[M + H]^+$ 309.0407, found 309.0431.

2-(5-Acetylthiophen-2-yl)benzothiophene (3il) (entry 3 of table 3)[40]: Yield: 51% (0.065 g); R_f = 0.36 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.76 (m, 2H), 7.63 (d, 1H), 7.56 (s, 1H), 7.40 – 7.33 (m, 2H), 7.29 (d, 1H), 2.57 (s, 3H) ppm.

2-(5-Acetyl-2-thienyl)benzo[b]furan (3ik) (entry 4 of table 3)[41]: Yield: 48% (0.058 g); R_f = 0.38 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, 1H), 7.58 (d, 1H), 7.51 (d, 1H), 7.46 (d, 1H), 7.35 – 7.31 (m, 1H), 7.27 – 7.25 (m, 1H), 7.04 (s, 1H), 2.58 (s, 3H) ppm.

1-(5-(1H-indol-5-yl)thiophen-2-yl)ethan-1-one (3ih) (entry 5 of table 3): Obtained as a yellow solid; Yield: 64% (0.077 g); mp: 159 – 161 °C; R_f = 0.32 (ethyl acetate/hexane 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.96 (s, 1H), 7.67 (d, J = 4.0 Hz, 1H), 7.51 (dd, J = 8.5, 1.6 Hz, 1H), 7.42 (d, J = 8.5 Hz, 1H), 7.30 (d, J = 4.0 Hz, 1H), 7.26 (d, J = 3.7 Hz, 1H), 6.63 – 6.58 (m, 1H), 2.57 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 155.4, 141.9, 136.4, 133.9, 128.5, 125.7, 122.9, 121.1, 119.0, 111.8, 103.4, 26.6 ppm; IR (KBr): 3448, 3261, 2919, 1613, 1437, 1356, 1296, 1036, 792, 764 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{14}H_{12}NOS$ $[M + H]^+$ 242.0639, found 242.0625.

1-(5-(Thianthren-1-yl)thiophen-2-yl)ethan-1-one (3ij) (entry 6 of table 3): Obtained as a yellow solid; Yield: 62% (0.105 g); mp: 163 – 165 °C; R_f = 0.23 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 3.9 Hz, 1H), 7.54 (dd, J = 7.7, 1.3 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.45 – 7.42 (m, 1H), 7.39 (dd, J = 7.7, 1.4 Hz, 1H), 7.30 – 7.21 (m, 4H), 2.61 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0, 149.4, 144.8, 136.7, 136.2, 135.8, 135.4, 134.0, 132.5, 129.8, 129.7, 129.4, 129.1, 128.7, 128.2, 127.9, 127.4, 26.9 ppm; IR (KBr): 3075, 3049, 1650, 1466, 1426, 1387, 1276, 1030, 921, 794, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{13}OS_3$ $[M + H]^+$ 341.0128, found 341.0153.

2-(Dibenzo[b,d]furan-4-yl)-5-methylpyridine (3dg) (entry 1 of table 4): Obtained as a white solid; Yield: 65% (0.084 g); mp: 93 – 95 °C; R_f = 0.41 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (s, 1H), 8.30 (d, J = 8.1 Hz, 1H), 8.24 (dd, J = 7.7, 0.9 Hz, 1H), 7.99 (d, J = 7.6 Hz, 2H), 7.71 – 7.62 (m, 2H), 7.48 (t, J = 7.7 Hz, 2H), 7.38 (t, J = 7.5 Hz, 1H), 2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 153.7, 151.2, 150.4, 137.3, 132.2, 127.3, 127.8, 125.2, 124.5, 124.2, 123.9, 123.4, 123.0, 121.0, 120.8, 111.9, 18.5 ppm; IR (KBr): 2992, 2919, 1586, 1563, 1484, 1447, 1410, 1186, 837, 751 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{14}NO$ $[M + H]^+$ 260.1075, found 260.1063.

2-(Dibenzo[b,d]furan-4-yl)pyrazine (3fg) (entry 2 of table 4): Obtained as a white solid; Yield: 75% (0.092 g); mp: 133 – 135 °C; R_f = 0.23 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.74 (s, 1H), 8.73 (s, 1H), 8.58 (d, J = 2.1 Hz, 1H), 8.29 (d, J = 7.7 Hz, 1H), 8.02 (dd, J = 21.1, 7.5 Hz, 2H), 7.65 (d, J = 8.2 Hz, 1H), 7.50 (t, J = 7.7 Hz, 2H), 7.39 (t, J = 7.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 153.6, 149.9, 145.6, 144.5, 143.2, 127.7, 127.2, 125.5, 123.8, 123.6, 123.3, 122.4, 121.1, 120.9, 112.0 ppm; IR (KBr): 3031, 2963, 1462, 1454, 1417, 1189, 1069, 1014, 877, 793, 741 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{16}H_{11}N_2O$ $[M + H]^+$ 247.0871, found 247.0867.

1-(Dibenzo[b,d]furan-4-yl)isoquinoline (3hg) (entry 3 of table 4): Obtained as a yellow solid; Yield: 55% (0.081 g); mp: 135 – 137 °C; R_f = 0.13 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, J = 5.7 Hz, 1H), 8.11 (dd, J = 7.7, 1.1 Hz, 1H), 8.03 (d, J = 7.6 Hz, 1H), 7.95 (d, J = 8.3 Hz, 1H), 7.84 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 5.7 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.52 (dt, J = 15.5, 7.4 Hz, 2H), 7.43 – 7.35 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 156.4, 154.0, 142.6, 136.8, 130.4, 129.1, 127.8, 127.6, 127.4, 127.1, 125.0, 124.3, 124.2, 123.1, 123.0, 121.3, 120.9, 112.1 ppm; IR (KBr): 3050, 1657, 1582, 1495, 1447, 1405, 1184, 833, 804, 752 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{14}NO$ $[M + H]^+$ 296.1075, found 296.1071.

2-(Thianthren-1-yl)pyrazine (3fj) (entry 4 of table 4): Obtained as a pale yellow solid; Yield: 60% (0.088 g); mp: 93 – 95 °C; R_f = 0.15 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 8.76 (s, 1H), 8.63 (s, 1H), 7.62 (dd, J = 7.7, 1.3 Hz, 1H), 7.48 (dd, J = 7.6, 1.3 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.28 – 7.17 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7, 145.1, 143.7, 143.2, 137.7, 136.7, 136.6, 136.3, 135.7, 130.3, 129.1, 129.0, 128.7, 128.1, 127.8, 127.4 ppm; IR (KBr): 3048, 1553, 1472, 1445, 1405, 1376, 1143, 1012, 789, 747, 722 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{16}H_{11}N_2S_2$ $[M + H]^+$ 295.0363, found 295.0383.

2-(Thianthren-1-yl)quinolone (3gj) (entry 5 of table 4): Obtained as a pale yellow solid; Yield: 62% (0.106 g); mp: 139 – 141 °C; R_f = 0.38 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 8.57 (d, J = 5.9 Hz, 1H), 8.03 (d, J = 7.9 Hz, 1H), 7.98 – 7.84 (m, 2H), 7.76 (t, J = 7.5 Hz, 2H), 7.69 (d, J = 7.6 Hz, 1H), 7.51 (dd, J = 7.7, 1.0 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 7.4 Hz, 1H), 7.25 (d, J = 7.0 Hz, 2H), 7.19 (t, J = 7.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 147.6, 141.4, 136.7, 136.6, 136.5, 136.5, 135.9, 130.0, 129.8, 129.6, 129.1, 128.9, 128.6, 127.8, 127.7, 127.6, 127.2, 127.1, 127.0, 121.8 ppm; IR (KBr): 3044, 1591, 1499, 1444, 1423, 1395, 1142, 835, 781, 753, 723 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{14}NS_2$ $[M + H]^+$ 344.0567, found 344.0531.

5-Nitro-2-(thianthren-1-yl)pyridine (3ej) (entry 6 of table 4): Obtained as a yellow solid; Yield: 65% (0.109 g); mp: 109 – 111 °C; R_f = 0.30 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.62 (s, 1H), 8.64 (d, J = 7.0 Hz, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 7.7 Hz, 2H), 7.41 – 7.31 (m, 2H), 7.30 – 7.17 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 144.6, 143.1, 139.1, 136.7, 136.5, 135.5, 131.6, 130.7, 130.0, 129.1, 128.9, 128.8, 128.2, 127.8, 127.3, 124.3 ppm; IR (KBr): 3055, 1593, 1571, 1512, 1442, 1346, 1249, 856, 762, 745 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{17}H_{11}N_2O_2S_2$ $[M + H]^+$ 339.0262, found 339.0252.

2-(Dibenzo[b,d]thiophen-4-yl)quinolone (3gi) (entry 7 of table 4): Obtained as a white solid; Yield: 75% (0.116 g); mp: 129 – 131 °C; R_f = 0.58 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, J = 7.7 Hz, 1H), 8.33 – 8.27 (m, 2H), 8.25 – 8.22 (m, 1H), 8.19 (dd, J = 7.6, 0.9 Hz, 1H), 8.12 (d, J = 8.7 Hz, 1H), 8.00 – 7.97 (m, 1H), 7.89 – 7.85 (m, 1H), 7.81 (m, 1H), 7.65 (t, J = 7.7 Hz, 1H), 7.59 (m, 1H), 7.50 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 147.6, 142.8, 138.5, 137.6, 136.9, 134.8, 133.3, 130.0, 129.3, 127.6, 127.1, 126.9, 126.8, 125.7, 124.7, 124.2, 122.7, 122.6, 121.5, 118.7 ppm; IR (KBr): 3046, 1592, 1499, 1444, 1395,

1307, 1105, 835, 781, 753 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{14}NS$ $[M + H]^+$ 312.0846, found 312.0872.

2-(Dibenzo[b,d]thiophen-4-yl)pyrazine (3fi) (entry 8 of table 4): Obtained as a yellow solid; Yield: 78% (0.102 g); mp: 137 – 139 °C; R_f = 0.20 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.31 (d, J = 0.9 Hz, 1H), 8.85 (s, 1H), 8.57 (d, J = 2.4 Hz, 1H), 8.32 (d, J = 7.7 Hz, 1H), 8.26 – 8.18 (m, 1H), 8.10 (d, J = 7.5 Hz, 1H), 7.95 – 7.89 (m, 1H), 7.64 (t, J = 7.7 Hz, 1H), 7.52 – 7.44 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 143.0, 142.9, 142.6, 141.7, 137.9, 137.7, 134.7, 130.5, 127.2, 125.1, 124.8, 124.5, 123.2, 122.6, 121.6 ppm; IR (KBr): 3047, 1515, 1465, 1436, 1370, 1283, 1155, 1017, 798, 746 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{16}H_{11}N_2S$ $[M + H]^+$ 263.0643, found 263.0659.

2-(Dibenzo[b,d]thiophen-4-yl)pyridine (3ai) (entry 9 of table 4)[42]: Yield: 72% (0.094 g); R_f = 0.54 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (d, 1H), 8.26 (dd, 1H), 8.21 (m, 1H), 8.02 – 7.97 (m, 2H), 7.92 (m, 1H), 7.86 – 7.81 (m, 1H), 7.60 (t, 1H), 7.50 – 7.45 (m, 2H), 7.31 (m, 1H) ppm.

3-(4-Ethylphenyl)pyridine (3be) (entry 2 of table 5)[43]: Yield: 92% (0.084 g); R_f = 0.35 (ethyl acetate/hexane 1:49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (d, 1H), 8.58 (d, 1H), 7.98 (m, 1H), 7.52 – 7.49 (d, 2H), 7.47 – 7.43 (m, 1H), 7.33 – 7.30 (d, 2H), 2.74 – 2.68 (q, 2H), 1.30 – 1.26 (t, 3H) ppm.

2-(4-Fluorophenyl)pyrazine (3fc) (entry 3 of table 5)[33]: Yield: 93% (0.080 g); R_f = 0.41 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (s, 1H), 8.68 (d, 1H), 8.52 (d, 1H), 8.03 (m, 2H), 7.21 (m, 2H) ppm.

2-(Dibenzo[b,d]furan-4-yl)-6-methylpyridine (3cg) (entry 5 of table 5): Obtained as a white solid; Yield: 62% (0.080 g); mp: 70 – 72 °C; R_f = 0.51 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (dd, J = 7.7, 1.1 Hz, 1H), 8.21 (d, J = 7.8 Hz, 1H), 8.00 (dd, J = 7.6, 1.2 Hz, 2H), 7.76 (t, J = 7.8 Hz, 1H), 7.64 (d, J = 8.2 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.38 (m, 1H), 7.17 (d, J = 7.7 Hz, 1H), 2.69 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 156.2, 153.8, 153.1, 136.9, 127.5, 127.3, 125.1, 124.7, 124.2, 123.4, 123.0, 122.2, 121.4, 121.1, 120.8, 111.9, 25.0 ppm; IR (KBr): 3048, 2918, 1575, 1490, 1444, 1388, 1260, 1187, 1106, 835, 781, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{14}NO$ $[M + H]^+$ 260.1075, found 260.1093.

3-(Dibenzo[b,d]furan-4-yl)pyridine (3bg) (entry 6 of table 5): Obtained as a colorless oil; Yield: 61% (0.074 g); R_f = 0.38 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.16 (d, J = 1.7 Hz, 1H), 8.66 (dd, J = 4.8, 1.6 Hz, 1H), 8.25 – 8.22 (m, 1H), 8.00 – 7.94 (m, 2H), 7.60 (dd, J = 7.7, 1.1 Hz, 2H), 7.50 – 7.43 (m, 3H), 7.37 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 153.4, 149.6, 148.8, 136.1, 132.3, 127.6, 126.6, 125.2, 124.0, 123.6, 123.5, 123.1, 122.3, 120.9, 120.7, 111.9 ppm; IR (KBr): 3053, 2955, 1567, 1450, 1426, 1395, 1189, 1128, 1009, 752, 710 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{17}H_{12}NO$ $[M + H]^+$ 246.0918, found 246.0902.

Analytical data for (hetero)diarylmethanes:

Diphenylmethane (6aa) (entry 1 of table 6 and entry 1 of table 9)[44]: Yield: 95% (0.159 g); R_f = 0.89 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 – 7.22 (m, 4H), 7.17 – 7.14 (m, 6H), 3.94 (s, 2H) ppm.

1-Benzylnaphthalene (6ba) (entry 2 of table 6 and entry 2 of table 9)[10]: Yield: 92% (0.200 g); R_f = 0.82 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 – 7.98 (m, 1H), 7.86 – 7.84 (m, 1H), 7.75 (d, 1H), 7.46 – 7.39 (m, 3H), 7.29 – 7.24 (m, 3H), 7.20 – 7.18 (m, 3H), 4.46 (s, 2H) ppm.

1-Benzyl-4-ethylbenzene (6ae) (entry 3 of table 6)[45]: Yield: 86% (0.168 g); R_f = 0.88 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (m, 2H), 7.31 – 7.24 (m, 3H), 7.21 (s, 4H), 4.04 (s, 2H), 2.71 (q, 2H), 1.32 (t, 3H) ppm.

1-Ethyl-4-(4-methylbenzyl)benzene (6ce) (entry 4 of table 6)[46]: Yield: 88% (0.185 g); R_f = 0.87 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (m, 8H), 3.94 (s, 2H), 2.63 (q, 2H), 2.34 (s, 3H), 1.24 (t, 3H) ppm.

1-Ethyl-4-(4-fluorobenzyl)benzene (6de) (entry 5 of table 6): Obtained as a colorless oil; Yield: 75% (0.160 g); R_f = 0.88 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 – 7.07 (m, 6H), 6.99 – 6.93 (m, 2H), 3.92 (s, 2H), 2.62 (q, J = 7.6 Hz, 2H), 1.22 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5 (d, $J_{C\text{-}F}$ = 242 Hz), 142.3, 138.3, 137.2 (d, $J_{C\text{-}F}$ = 4 Hz), 130.4 (d, $J_{C\text{-}F}$ = 8 Hz), 128.9, 128.1, 115.3 (d, $J_{C\text{-}F}$ = 21 Hz), 40.8, 28.6, 15.7 ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ -117.6 ppm; IR (KBr): 3019, 2965, 2929, 2871, 1603, 1508, 1456, 1224, 1157, 849, 815 cm^{-1}; HRMS data could not be obtained.

1-(4-Ethylbenzyl)-2-methoxybenzene (6ee) (entry 6 of table 6): Obtained as a colorless oil; Yield: 77% (0.174 g); R_f = 0.31 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 – 7.23 (m, 1H), 7.11 (d, 4H), 6.80 – 6.73 (m, 3H), 3.92 (s, 2H), 3.77 (s, 3H), 2.61 (q, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 143.1, 142.1, 138.2, 129.5, 129.0, 128.1, 121.5, 114.9, 111.4, 55.3, 41.7, 28.6, 15.7 ppm; IR (KBr): 3004, 2963, 2931, 2835, 1600, 1488, 1457, 1259, 1153, 1047, 779, 692 cm^{-1}; HRMS data could not be obtained.

1-(4-Ethylbenzyl)naphthalene (6be) (entry 7 of table 6 and entry 15 of table 9): Obtained as a colorless oil; Yield: 86% (0.211 g); R_f = 0.68 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 – 8.02 (m, 1H), 7.92 – 7.86 (m, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.52 – 7.42 (m, 3H), 7.33 (d, J = 7.0 Hz, 1H), 7.15 (d, J = 1.6 Hz, 4H), 4.46 (s, 2H), 2.64 (q, J = 7.5 Hz, 2H), 1.25 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 137.9, 137.0, 134.1, 132.3, 128.8, 128.8, 128.1, 127.4, 127.2, 126.1, 125.7, 125.7, 124.5, 38.8, 28.6, 15.7 ppm; IR (KBr): 3046, 2963, 2928, 2870, 1595, 1511, 1453, 1395, 1260, 1115, 778 cm^{-1}; HRMS data could not be obtained.

2-(4-Ethylbenzyl)naphthalene (6fe) (entry 8 of table 6 and entry 16 of table 9): Obtained as a colorless oil; Yield: 88% (0.216 g); R_f = 0.69 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 – 7.77 (m, 3H), 7.68 (s, 1H), 7.51 – 7.42 (m, 2H), 7.36 (dd, J = 8.4, 1.7 Hz, 1H), 7.21 – 7.15 (m, 4H), 4.15 (s, 2H), 2.66 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 139.0, 138.3, 133.8, 132.2, 129.1, 128.2, 128.1, 127.8, 127.8, 127.7, 127.2, 126.1, 125.4, 41.9, 28.6, 15.7 ppm; IR (KBr): 3051, 2964, 2927, 2869, 1603, 1510, 1435, 1367, 1178, 1118, 813, 723, 540 cm^{-1}; HRMS data could not be obtained.

1-Methyl-2-(4-methylbenzyl)benzene (6gm) (entry 9 of table 6)[46]: Yield: 78% (0.153 g); R_f = 0.89 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 – 7.14 (m, 3H), 7.10 – 7.07 (m, 3H), 7.01 (d, J = 7.0 Hz, 2H), 3.95 (s, 2H), 2.31 (s, 3H), 2.25 (s, 3H) ppm.

4-(2-Methylbenzyl)benzaldehyde (6gn) (entry 10 of table 6): Obtained as a white solid; Yield: 87% (0.182 g); mp: 129 – 131 ºC; R_f = 0.33 (ethyl acetate/hexane 1:49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H), 7.81 – 7.77 (m, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.18 (dd, J = 6.4, 3.3 Hz, 3H), 7.13 – 7.08 (m, 1H), 4.07 (s, 2H), 2.22 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 148.1, 137.8, 136.8, 134.8, 130.7, 130.2, 130.1, 129.5, 127.1, 126.4, 39.9, 19.8 ppm; IR (KBr): 3015, 2960, 2907, 1684, 1604, 1423, 1287, 1179, 926, 741cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{15}H_{15}O$ $[M + H]^+$ 211.1123, found 211.1135.

1-(4-Methoxybenzyl)-2-methylbenzene (6gd) (entry 11 of table 6)[47]: Yield: 92% (0.195 g); R_f = 0.32 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 – 7.10 (m, 4H), 7.05 (d, 2H), 6.83 (d, 2H), 3.93 (s, 2H), 3.79 (s, 3H), 2.25 (s, 3H) ppm.

1-(2-Methylbenzyl)naphthalene (6go) (entry 12 of table 6): Obtained as a colorless oil; Yield: 85% (0.197 g); R_f = 0.85 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (dd, J = 6.2, 3.5 Hz, 1H), 7.90 (dd, J = 6.0, 3.5 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.50 (dd, J = 6.3, 3.3 Hz, 2H), 7.41 – 7.36 (m, 1H), 7.25 (d, J = 6.1 Hz, 1H), 7.19 (t, J = 7.2 Hz, 1H), 7.13 – 7.04 (m, 2H), 6.93 (d, J = 7.5 Hz, 1H), 4.42 (s, 2H), 2.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 136.8, 136.2, 133.9, 132.4, 130.2, 129.8, 128.9, 127.0, 126.5, 126.5, 126.2, 126.1, 125.8, 125.7, 124.0, 36.3, 19.8 ppm; IR (KBr): 3048, 2916, 1597, 1490, 1457, 1394, 1258, 1160, 1105, 1016, 781, 741 cm^{-1}; HRMS data could not be obtained.

2-(4-Fluorobenzyl)naphthalene (6fc) (entry 13 of table 6)[48]: Yield: 83% (0.196 g); R_f = 0.82 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 – 7.71 (m, 3H), 7.60 (s, 1H), 7.52 – 7.42 (m, 2H), 7.29 (m, 1H), 7.21 – 7.17 (m, 2H), 7.01 – 6.97 (m, 2H), 4.12 (s, 2H) ppm.

4-(Naphthalen-1-ylmethyl)benzaldehyde (6fn) (entry 14 of table 6): Obtained as a colorless oil; Yield: 82% (0.201 g); R_f = 0.16 (ethyl acetate/hexane 1:49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.92 – 7.87 (m, 2H), 7.82 – 7.77 (m, 3H), 7.49 (m, 3H), 7.37 – 7.32 (m, 3H), 4.53 (s, 2H) ppm; ^{13}C NMR (100MHz, $CDCl_3$): δ 192.0, 148.2, 135.4, 134.8, 134.1, 132.1, 130.1, 129.4, 128.9, 127.8, 127.7, 126.3, 125.9, 125.7, 124.1, 39.4 ppm; IR (KBr): 3049, 2827, 2733, 1697, 1602, 1509, 1426, 1392, 1306, 1212, 1167, 841, 783 cm^{-1}; HRMS (ESI): m/z calcd for $C_{18}H_{15}O$ [M + H]$^+$ 247.1123, found 247.1094.

Di(naphthalen-1-yl)methane (6bo) (entry 15 of table 6)[49]: Yield: 92% (0.246 g); R_f = 0.83 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 – 8.04 (d, 2H), 7.93 (d, 2H), 7.79 (d, 2H), 7.55 – 7.48 (m, 4H), 7.36 (t, 2H), 7.10 (d, 2H), 4.91 (s, 2H) ppm.

1-(4-(2,4,6-Trimethylbenzyl)phenyl)ethan-1-one (6hp) (entry 16 of table 6 and entry 17 of table 9): Obtained as a white solid; Yield: 81% (0.204 g); mp: 79 – 81 °C; R_f = 0.30 (ethyl acetate/hexane 1:49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 – 7.81 (m, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.91 (s, 2H), 4.07 (s, 2H), 2.56 (s, 3H), 2.31 (s, 3H), 2.19 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 146.3, 137.1, 136.2, 135.2, 133.0, 129.1, 128.7, 128.1, 35.0, 26.6, 21.0, 20.2 ppm; IR (KBr): 2937, 2913, 2857, 1671, 1599, 1412, 1356, 1267, 960, 785 cm^{-1}; HRMS (ESI): m/z calcd for $C_{18}H_{21}O$ [M + H]$^+$ 253.1592, found 253.1609.

4-(2,4,6-Trimethylbenzyl)benzaldehyde (6hn) (entry 17 of table 6)[50]: Yield: 78% (0.185 g); R_f = 0.31 (ethyl acetate/hexane 1:49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (s, 1H), 7.76 (d, 2H), 7.17 (d, 2H), 6.92 (s, 2H), 4.09 (s, 2H), 2.30 (s, 3H), 2.19 (s, 6H) ppm.

1-(2,4,6-Trimethylbenzyl)naphthalene (6ho) (entry 18 of table 6): Obtained as a white solid; Yield: 88% (0.229 g); mp: 96 – 98 °C; R_f = 0.81 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.62 – 7.49 (m, 2H), 7.24 (dd, J = 10.7, 4.5 Hz, 1H), 6.95 (s, 2H), 6.69 – 6.63 (m, 1H), 4.40 (s, 2H), 2.34 (s, 3H), 2.16 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 136.0, 135.5, 133.8, 133.2, 132.4, 129.0, 129.0, 126.6, 126.0, 125.9, 125.7, 123.7, 123.3, 31.5, 21.1, 20.0 ppm; IR (KBr): 3045, 2913, 2856, 1591, 1481, 1445, 1393, 1375, 1253, 1159, 1025, 851, 789, 766 cm^{-1}; HRMS data could not be obtained.

1,3,5-Trimethyl-2-(4-methylbenzyl)benzene (6hm) (entry 19 of table 6 and entry 18 of table 9)[44]: Yield: 86% (0.192 g); R_f = 0.85 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, 2H), 7.03 – 6.93 (m, 4H), 4.06 (s, 2H), 2.38 (s, 6H), 2.29 (s, 6H) ppm.

1-Chloro-4-(4-ethylbenzyl)benzene (6ib) (entry 1 of table 7 and entry 13 of table 9): Obtained as a colorless oil; Yield: 95% (0.219 g); R_f = 0.84 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, J = 8.2 Hz, 2H), 7.09 (m, 6H), 3.89 (s, 2H), 2.61 (q, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3, 140.0, 137.9, 131.9, 130.4, 128.9, 128.7, 128.2, 41.0, 28.6, 15.7 ppm; IR (KBr): 3028, 2965, 2927, 1595, 1489, 1436, 1180, 1092, 1015, 802, 724 cm^{-1}; HRMS data could not be obtained.

1-(4-(4-Chlorobenzyl)phenyl)ethan-1-one (6ip) (entry 2 of table 7)[51]: Yield: 92% (0.225 g); R_f = 0.32 (ethyl acetate/hexane 1:49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, 2H), 7.28 – 7.22 (m, 4H), 7.10 (d, 2H), 3.99 (s, 2H), 2.57 (s, 3H) ppm.

3-(4-Chlorobenzyl)thiophene (6if) (entry 3 of table 7)[52]: Yield: 93% (0.194 g); R_f = 0.86 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.23 (m, 3H), 7.12 (d, 2H), 6.92 – 6.89 (m, 1H), 6.87 (dd, 1H), 3.94 (s, 2H) ppm.

4-(4-Chlorobenzyl)dibenzo[b,d]furan (6ig) (entry 4 of table 7): Obtained as a white solid; Yield: 72% (0.210 g); mp: 76 – 78 °C; R_f = 0.68 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 – 7.93 (m, 1H), 7.83 (dd, J = 7.6, 1.2 Hz, 1H), 7.59 (d, J = 8.2 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.35 (td, J = 7.6, 0.9 Hz, 1H), 7.30 – 7.24 (m, 5H), 7.22 – 7.18 (m, 1H), 4.31 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$):δ 156.2, 154.6, 138.6, 132.1, 130.4, 128.7, 127.7, 127.2, 124.7, 124.6, 124.3, 123.1, 122.9, 120.9, 119.0, 111.9, 35.2 ppm; IR (KBr): 3045, 3019, 2916, 1583, 1489, 1446, 1181, 1088, 825, 799, 744 cm^{-1}; HRMS data could not be obtained.

1-Chloro-3-(4-ethylbenzyl)benzene (6je) (entry 5 of table 7 and entry 14 of table 9): Obtained as a colorless oil; Yield: 90% (0.207 g); R_f = 0.86 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 – 7.07 (m, 8H), 3.93 (s, 2H), 2.64 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 142.4, 137.5, 134.3, 129.8, 129.1, 129.0, 128.2, 127.2, 126.4, 41.3, 28.6, 15.7 ppm; IR (KBr): 3053, 2965, 2928, 2870, 1594, 1511, 1433, 1195, 1117, 779, 688 cm^{-1}; HRMS data could not be obtained.

1-(4-(3-Chlorobenzyl)phenyl)ethan-1-one (6jp) (entry 6 of table 7): Obtained as a colorless oil; Yield: 88% (0.215 g); R_f = 0.31 (ethyl acetate/hexane 1:49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.23 (m, 2H), 7.19 (t, J = 1.8 Hz, 1H), 7.09 (m, 1H), 4.03 (s, 2H), 2.61 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 145.9, 142.2, 135.6, 134.5, 130.0, 129.2, 129.1, 128.9, 127.2, 126.8, 41.6, 26.7 ppm; IR (KBr): 3055, 2920, 1681, 1601, 1415, 1357, 1267, 779, 692 cm^{-1}; HRMS (ESI): m/z calcd for $C_{15}H_{14}ClO$ [M + H]$^+$ 245.0733, found 245.0703.

1-Chloro-3-(4-fluorobenzyl)benzene (6jc) (entry 7 of table 7): Obtained as a colorless oil; Yield: 85% (0.187 g); R_f = 0.85 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 – 7.20 (m, 2H), 7.16 – 7.12 (m, 3H), 7.07 – 7.04 (m, 1H), 7.01 – 6.97 (m, 2H), 3.93 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7 (d, $J_{C\text{-}F}$ = 243 Hz), 143.1, 136.0 (d, $J_{C\text{-}F}$ = 3 Hz), 134.5, 130.5 (d, $J_{C\text{-}F}$ = 8 Hz), 129.9, 129.1, 127.1, 126.6, 115.5 (d, $J_{C\text{-}F}$ = 21 Hz), 40.8 ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ -117.6 ppm; IR (KBr): 3043, 2919, 1600, 1508, 1432, 1224, 1158, 1091, 822, 785 cm^{-1}; HRMS data could not be obtained.

3-(3-Chlorobenzyl)thiophene (6jf) (entry 8 of table 7): Obtained as a colorless oil; Yield: 86% (0.179 g); R_f = 0.87 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.26 (m, 2H), 7.24 – 7.22 (m, 2H), 7.14 – 7.11 (m, 1H), 6.98 (m, 1H), 6.93 (d, J = 4.9Hz, 1H), 3.99 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 140.6, 134.4, 129.8, 129.0, 128.4, 127.1, 126.5, 126.0, 121.7, 36.3 ppm; IR (KBr): 3058, 2913, 1594, 1476, 1432, 1179, 1119, 1079, 772, 717, 688 cm^{-1}; HRMS data could not be obtained.

4-Benzyl-1,1'-biphenyl (6ka) (entry 9 of table 7)[10]: Yield: 88% (0.107 g); R_f = 0.61 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 – 7.54 (m, 2H), 7.51 (d, 2H), 7.41 (t, 2H), 7.27 (m, 8H), 4.02 (s, 2H) ppm.

4-Ethyl-4'-(4-ethylbenzyl)-1,1'-biphenyl (6ke) (entry 10 of table 7): Obtained as a white solid; Yield: 78% (0.117 g); mp: 66 – 68 °C; R_f = 0.6

(hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (dd, J = 8.2, 1.8 Hz, 4H), 7.27 – 7.22 (m, 4H), 7.14 (s, 4H), 3.98 (s, 2H), 2.65 (dq, J = 23.1, 7.6 Hz, 4H), 1.24 (dt, J = 17.8, 7.6 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 142.2, 140.3, 139.1, 138.6, 138.4, 129.4, 129.0, 128.4, 128.1, 127.2, 127.1, 41.3, 28.6, 28.6, 15.8, 15.7 ppm; IR (KBr): 3086, 3023, 2959, 2924, 2866, 1494, 1439, 1396, 1111, 1049, 836, 807, 778 cm^{-1}; HRMS data could not be obtained.

3-(4-(Thiophen-3-yl)benzyl)thiophene (6kf) (entry 11 of table 7): Obtained as a white solid; Yield: 87% (0.111 g); mp: 82 – 83 °C; R_f = 0.56 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 8.1 Hz, 2H), 7.41 (t, J = 2.1 Hz, 1H), 7.37 (d, J= 2.1 Hz, 2H), 7.27 – 7.21 (m, 3H), 6.96 – 6.91 (m, 2H), 4.00 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3, 141.5, 139.7, 134.0, 129.3, 128.6, 126.7, 126.4, 126.3, 125.8, 121.4, 120.1, 36.3 ppm; IR (KBr): 3094, 2879, 1499, 1426, 1206, 1083, 1015, 861, 829, 771, 701 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{15}H_{13}S_2$ $[M + H]^+$ 257.0458, found 257.0471.

2–Benzylbiphenyl (6la) (entry 12 of table 7)[10]: Yield: 92% (0.112 g); R_f = 0.61 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.11 (m, 12H), 6.97 (d, 2H), 3.95 (s, 2H) ppm.

3-Benzylthiophene (6af) (entry 1 of table 8)[11]: Yield: 95% (0.165 g); R_f = 0.89 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.19 (m, 6H), 6.91 – 6.90 (m, 2H), 3.97 (s, 2H) ppm.

3-(4-Methylbenzyl)thiophene (6cf) (entry 2 of table 8)[11]: Yield: 90% (0.169 g); R_f = 0.88 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (dd, 1H), 7.09 (s, 4H), 6.90 (dd, 2H), 3.93 (s, 2H), 2.32 (s, 3H) ppm.

3-(3-Methylbenzyl)thiophene (6mf) (entry 3 of table 8)[11]: Yield: 89% (0.167 g); R_f = 0.88 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 – 7.22 (m, 1H), 7.20 – 7.16 (m, 1H), 7.03 – 6.99 (m, 3H), 6.91 (m, 2H), 3.94 (s, 2H), 2.32 (s, 3H) ppm.

3-(2-Methylbenzyl)thiophene (6gf) (entry 4 of table 8)[11]: Yield: 88% (0.165 g); R_f = 0.86 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 – 7.23 (m, 1H), 7.17 – 7.12 (m, 4H), 6.89 (dd, 1H), 6.82 – 6.79 (m, 1H), 3.97 (s, 2H), 2.27 (s, 3H) ppm.

3-(Naphthalen-2-ylmethyl)thiophene (6ff) (entry 5 of table 8): Obtained as a Colorless oil; Yield: 86% (0.192 g); R_f = 0.67 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$):δ 7.82 – 7.73 (m, 3H), 7.63 (d, J = 0.5 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.33 (dd, J = 8.4, 1.7 Hz, 1H), 7.27 – 7.21 (m, 1H), 6.97 – 6.91 (m, 2H), 4.13 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 138.2, 133.7, 132.2, 128.6, 128.2, 127.8, 127.7, 127.6, 127.0, 126.1, 125.8, 125.5, 121.5, 36.8 ppm; IR (KBr): 3046, 2913, 2854, 1595, 1509, 1435, 1397, 1259, 1078, 829, 731 cm^{-1}; HRMS data could not be obtained.

3-(2,4,6-Trimethylbenzyl)thiophene (6hf) (entry 6 of table 8)[11]: Yield: 88% (0.190 g); R_f = 0.78 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (m, 1H), 6.88 – 6.86 (m, 3H), 6.63 (s, 1H), 3.95 (s, 2H), 2.28 (s, 3H), 2.24 (s, 6H) ppm.

2-Benzylbenzo[b]thiophene (6al) (entry 7 of table 8)[53]: Yield: 78% (0.174 g); R_f = 0.71 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 – 7.63 (d, 1H), 7.57 (d, 1H), 7.35 – 7.15 (m, 7H), 6.92 (s, 1H), 4.14 (s, 2H) ppm.

4-Benzyldibenzo[b,d]furan (6ag) (entry 8 of table 8)[11]: Yield: 87% (0.224 g); R_f = 0.68 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 – 7.90 (m, 1H), 7.79 (dd, 1H), 7.57 (m, 1H), 7.46 – 7.40 (m, 1H), 7.35 – 7.14 (m, 8H), 4.33 (s, 2H) ppm.

5-Benzyl-2-methoxypyridine (6aq) (entry 9 of table 8)[54]: Yield: 91% (0.181 g); R_f = 0.51 (ethyl acetate/hexane 1:49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (m, 1H), 7.36 (m,1H), 7.32 – 7.27 (m, 2H), 7.22– 7.15 (m, 3H), 6.67 (m, 1H), 3.92 (s, 3H), 3.90 (s, 2H) ppm.

4-(Naphthalen-2-ylmethyl)dibenzo[b,d]thiophene (6fi) (entry 10 of table 8): Obtained as a white solid; Yield: 71% (0.230 g); mp: 129 – 131 °C; R_f = 0.54 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 7.9 Hz, 1H), 7.88 (d, J = 7.5 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.55 – 7.38 (m, 6H), 7.30 – 7.22 (m, 2H), 7.10 (dd, J = 17.9, 7.4 Hz, 2H), 6.89 (d, J = 7.5 Hz, 1H), 4.68 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0, 136.6, 135.9, 135.6, 134.0, 132.2, 129.2, 129.0, 128.9, 128.8, 128.0, 127.8, 127.5, 127.4, 127.3, 127.1, 126.3, 125.8, 125.8, 124.2, 37.5 ppm; IR (KBr): 3050, 2920, 1553, 1441, 1400, 1163, 1109, 1021, 777, 752 cm^{-1}; HRMS data could not be obtained.

2-(3-Methylbenzyl)benzofuran (6mk) (entry 11 of table 8)[55]: Yield: 77% (0.171 g); R_f = 0.71 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.37 (m, 2H), 7.21 – 7.12 (m, 3H), 7.08 – 7.03 (m, 3H), 6.34 (s, 1H), 4.03 (s, 2H), 2.30 (s, 3H) ppm.

2-(3-Methylbenzyl)thianthrene (6mj) (entry 12 of table 8): Obtained as a colorless oil; Yield: 65% (0.209 g); R_f = 0.51 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.48 (m, 2H), 7.40 (d, J = 7.6 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.18 – 7.10 (m, 3H), 7.04 – 7.00 (m, 3H), 4.22 (s, 2H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 139.8, 138.2, 136.6, 136.0, 135.8, 135.7, 129.8, 129.3, 129.1, 128.7, 128.5, 127.9, 127.7, 127.5, 127.3, 127.1, 126.1, 40.4, 21.6 ppm; IR (KBr): 3052, 2919, 2856, 1606, 1559, 1445, 1408, 1251, 1113, 1034, 746 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{17}S_2$ $[M + H]^+$ 321.0771, found 321.0773.

4-(2-Methylbenzyl)dibenzo[b,d]thiophene (6gi) (entry 13 of table 8): Obtained as a white solid; Yield: 78% (0.224 g); mp: 74 – 76 °C; R_f = 0.62 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 – 8.15 (m, 1H), 8.05 (d, J = 7.8 Hz, 1H), 7.89 – 7.85 (m, 1H), 7.50 – 7.44 (m, 2H), 7.39 (t, J = 7.6 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.19 – 7.13 (m, 2H), 7.04 (dd, J = 7.3, 0.7 Hz, 1H), 4.23 (s, 2H), 2.29 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.4, 139.3, 137.2, 137.1, 136.2, 135.8, 134.9, 130.5, 130.1, 127.0, 126.8, 126.6, 126.2, 125.0, 124.5, 123.0, 121.9, 119.7, 38.5, 19.8 ppm; IR (KBr): 3057, 3014, 2915, 2877, 1576, 1439, 1396, 1305, 1250, 1043, 790, 749 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{17}S$ $[M + H]^+$ 289.1051, found 289.1023.

4-(2,4,6-Trimethylbenzyl)dibenzo[b,d]furan (6hg) (entry 14 of table 8): Obtained as a white solid; Yield: 76% (0.228 g); mp: 80 – 85 °C; R_f = 0.65 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 – 7.95 (m, 1H), 7.79 (d, J = 7.7 Hz, 1H), 7.66 (d, J = 8.2 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.37 (m, 1H), 7.16 (t, J = 7.6 Hz, 1H), 6.95 (s, 2H), 6.74 (dd, J = 7.5, 0.8 Hz, 1H), 4.38 (s, 2H), 2.34 (s, 3H), 2.25 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 154.8, 137.5, 136.0, 132.6, 129.1, 127.1, 125.6, 124.8, 124.3, 123.6, 123.0, 122.8, 120.9, 118.3, 111.9, 28.3, 21.1, 20.2 ppm; IR (KBr): 3059, 3027, 2911, 1587, 1494, 1450, 1422, 1325, 1185, 1078, 844, 753, 698 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{22}H_{20}ONa$ $[M + Na]^+$ 323.1411, found 323.1431.

2-(2,4,6-Trimethylbenzyl)benzofuran (6hk) (entry 15 of table 8): Obtained as a colorless oil; Yield: 51% (0.127 g); R_f = 0.68 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, J = 11.6, 4.6 Hz, 2H), 7.19 (m, 2H), 6.92 (s, 2H), 6.08 (d, J = 0.9 Hz, 1H), 4.10 (s, 2H), 2.34 (s, 6H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 155.0, 137.1, 136.4, 130.8, 129.1, 129.0, 123.3, 122.5, 120.3, 110.9, 102.6, 28.8, 21.1, 20.0 ppm; IR (KBr): 3006, 2919, 2861, 1588, 1451, 1253, 1163, 1136, 952, 853, 746 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{19}O$ $[M + H]^+$ 251.1436, found 251.1408.

5-Benzyl-2-chloropyridine (6na) (entry 16 of table 8)[11]: Yield: 87% (0.177 g); R_f = 0.56 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.41 (dd, 1H), 7.33 – 7.26 (m, 2H), 7.23 (dd, 2H), 7.14 (dd, 2H), 3.94 (s, 2H) ppm.

2-Chloro-5-(naphthalen-1-ylmethyl)pyridine (6no) (entry 17 of table 8): Obtained as a yellow oil; Yield: 85% (0.215 g); R_f = 0.32 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, J = 2.2 Hz, 1H), 7.90 – 7.84 (m, 2H), 7.79 (d, J = 8.3 Hz, 1H), 7.45 (m, 3H), 7.35 (dd, J = 8.2, 2.3 Hz, 1H), 7.27 (d, J = 7.0 Hz, 1H), 7.16 (d, J = 8.2 Hz, 1H), 4.39 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 149.4, 139.1, 135.2, 134.8, 134.1, 131.8, 129.0, 128.0, 127.5, 126.5, 126.0, 125.7, 124.2, 123.8, 35.6 ppm. IR (KBr): 3046, 2917, 1584, 1563, 1509, 1459, 1382, 1288, 1200, 1104, 1022, 814, 794 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{16}H_{13}ClN$ $[M + H]^+$ 254.0736, found 254.0757.

2-Chloro-5-(thiophen-3-ylmethyl)pyridine (6nf) (entry 18 of table 8)[11]: Yield: 65% (0.136 g); R_f = 0.36 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, 1H), 7.46 (dd, 1H), 7.28 (m, 1H), 7.24 (s, 1H), 6.97 – 6.91 (m, 1H), 6.87 (dd, 1H), 3.96 (s, 2H) ppm.

1-Benzyl-4-methylbenzene (6ca) (entry 2 of table 9)[10]: Yield: 90% (0.164 g); R_f = 0.89 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.29 (m, 2H), 7.24 – 7.20 (m, 3H), 7.12 (m, 4H), 3.98 (s, 2H), 2.35 (s, 3H) ppm.

1-Benzyl-3-methylbenzene (6ma) (entry 3 of table 9)[10]: Yield: 91% (0.165 g); R_f = 0.88 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.27 (m, 2H), 7.21 – 7.15 (m, 4H), 7.01 – 6.98 (m, 3H), 3.94 (s, 2H), 2.31 (s, 3H) ppm.

1-Benzyl-2-methylbenzene (6ga) (entry 4 of table 9)[10]: Yield: 88% (0.160 g); R_f = 0.88 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.09 (m, 9H), 3.98 (s, 2H), 2.24 (s, 3H) ppm.

1-Benzyl-4-fluorobenzene (6da) (entry 5 of table 9)[10]: Yield: 85% (0.158 g); R_f = 0.89 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 – 7.20 (m, 2H), 7.17 – 7.11 (m, 5H), 6.86 (t, 2H), 3.95 (s, 2H) ppm.

1-Benzylnaphthalene (6ba) (entry 6 of table 9)[56]: Yield: 87% (0.189 g); R_f = 0.82 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 – 7.98 (m, 1H), 7.88 – 7.86 (m, 1H), 7.78 (d, 1H), 7.49 – 7.41 (m, 3H), 7.31 – 7.26 (m, 3H), 7.22 – 7.20 (m, 3H), 4.47 (s, 2H) ppm.

2-Benzylnaphthalene (6fa) (entry 7 of table 9)[48]: Yield: 86% (0.187 g); R_f = 0.8 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 – 7.71 (m, 3H), 7.61 (s, 1H), 7.43 – 7.37 (m, 2H), 7.30 – 7.25 (m, 3H), 7.21 – 7.16 (m, 3H), 4.11 (s, 2H) ppm.

2-Benzyl-1,3,5-trimethylbenzene (6ha) (entry 8 of table 9)[44]: Yield: 88% (0.185 g); R_f = 0.84 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 – 7.15 (m, 3H), 7.00 (d, 2H), 6.88 (s, 2H), 4.01 (s, 2H), 2.28 (s, 3H), 2.20 (s, 6H) ppm.

1-(4-Fluorobenzyl)-3-methylbenzene (6mc) (entry 9 of table 9)[10]: Yield: 78% (0.156 g); R_f = 0.86 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 – 7.12 (m, 3H), 7.05 – 6.96 (m, 5H), 3.92 (s, 2H), 2.33 (s, 3H) ppm.

1-(4-Fluorobenzyl)-2-methylbenzene (6gc) (entry 10 of table 9)[47]: Yield: 76% (0.152 g); R_f = 0.87 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 – 7.14 (m, 3H), 7.08 – 7.04 (m, 3H), 6.94 (t, 2H), 3.96 (s, 2H), 2.23 (s, 3H) ppm.

1-(4-(3-Methylbenzyl)phenyl)ethan-1-one (6mp) (entry 11 of table 9)[51]: Yield: 72% (0.161 g); R_f = 0.25 (ethyl acetate/hexane 1:49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, 2H), 7.29 (d, 2H), 7.20 (t, 1H), 7.07 – 6.96 (m, 3H), 4.00 (s, 2H), 2.58 (s, 3H), 2.33 (s, 3H) ppm.

1-(4-(4-Fluorobenzyl)phenyl)ethan-1-one (6dp) (entry 12 of table 9)[57]: Yield: 71% (0.162 g); R_f = 0.28 (ethyl acetate/hexane 1:49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, 2H), 7.25 (d, 2H), 7.12 (dd, 2H), 6.98 (t, 2H), 4.00 (s, 2H), 2.57 (s, 3H) ppm.

Analytical data for ketones:

Benzophenone (8aa) (entry 1 of table 10)[58]: Yield: 95% (0.172 g); R_f = 0.68 (ethyl acetate/hexane 1:99); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.80 (m, 4H), 7.61 – 7.47 (m, 6H) ppm.

(4-Chlorophenyl)(phenyl)methanone (8ba) (entry 2 of table 10)[15d]: Yield: 92% (0.199 g); R_f = 0.71 (ethyl acetate/hexane 1:99); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 – 7.74 (m, 4H), 7.59 (m, 1H), 7.51 – 7.45 (m, 4H) ppm.

(4-Chlorophenyl)(4-ethylphenyl)methanone (8be) (entry 3 of table 10): Obtained as a white solid; Yield: 91% (0.222 g); mp: 87 – 89 °C; R_f = 0.61 (ethyl acetate/hexane 1:99); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 – 7.70 (m, 4H), 7.45 (d, 2H), 7.31 (d, 2H), 2.74 (q, 2H), 1.28 (t, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 149.9, 138.7, 136.4, 134.9, 131.5, 130.4, 128.7, 128.1, 29.1, 15.4 ppm; IR (KBr): 2970, 2928, 2859, 1645, 1608, 1403, 1280, 1144, 1086, 852, 753, 675 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{15}H_{14}ClO$ $[M + H]$+ 245.0733, found 245.0757.

(4-Chlorophenyl)(4-methoxyphenyl)methanone (8bd) (entry 4 of table 10)[59]: Yield: 93% (0.229 g); R_f = 0.38 (ethyl acetate/hexane 1:99); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, 2H), 7.71 (d, 2H), 7.45 (d, 2H), 6.97 (m, 2H), 3.90 (s, 3H) ppm.

(4-(tert-Butyl)phenyl)(4-chlorophenyl)methanone (8br) (entry 5 of table 10)[15c]: Yield: 77% (0.210 g); R_f = 0.68 (ethyl acetate/hexane 1:99); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, 4H), 7.50 (dd, 2H), 7.45 (d, 2H), 1.37 (s, 9H) ppm.

Bis(4-chlorophenyl)methanone (8bb) (entry 6 of table 10)[60]: Yield: 84% (0.210 g); R_f = 0.65 (ethyl acetate/hexane 1:99); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, 4H), 7.46 (m, 4H) ppm.

(4-Chlorophenyl)(4-fluorophenyl)methanone (8bc) (entry 7 of table 10)[61]: Yield: 83% (0.194 g); R_f = 0.63 (ethyl acetate/hexane 1:99); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.78 (m, 2H), 7.72 – 7.69 (m, 2H), 7.46 – 7.42 (m, 2H), 7.17 – 7.12 (m, 2H) ppm.

1-(4-(4-Chlorobenzoyl)phenyl)ethanone (8bp) (entry 8 of table 10)[62]: Yield: 54% (0.139 g); R_f = 0.58 (ethyl acetate/hexane 1:99); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, 2H), 8.06 (d, 2H), 7.51 (d, 2H), 7.33 (m, 2H), 2.63 (s, 3H) ppm.

(4-Chlorophenyl)(dibenzo[b,d]furan-4-yl)methanone (8bg) (entry 9 of table 10): Obtained as a white solid; Yield: 71% (0.217 g); mp: 123 – 125 °C; R_f = 0.38 (ethyl acetate/hexane 1:99); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (dd, J = 7.7, 1.0 Hz, 1H), 8.00 (d, J = 7.5 Hz, 1H), 7.85 (d, J = 8.5 Hz, 2H), 7.71 (dd, J = 7.6, 0.9 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.51 – 7.43 (m, 4H), 7.39 (dd, J = 11.4, 4.3 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.8, 156.5, 153.8, 139.7, 136.2, 131.7, 128.9, 128.7, 128.0, 125.8, 124.6, 123.4, 123.3, 122.9, 122.8, 120.8, 112.3 ppm; IR (KBr): 3041, 1657, 1587, 1485, 1412, 1289, 1187, 1089, 948, 848, 747 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{12}ClO_2$ $[M + H]^+$ 307.0525, found 307.0551.

(4-Methoxyphenyl)(phenyl)methanone (8ad) (entry 10 of table 10)[63]: Yield: 92% (0.195 g); R_f = 0.28 (ethyl acetate/hexane 1:99); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 – 7.82 (d, 2H), 7.75 (dd, 2H), 7.55 (m, 1H), 7.49 – 7.45 (m, 2H), 6.98 – 6.95 (d, 2H), 3.89 (s, 3H) ppm.

(4-Ethylphenyl)(4-nitrophenyl)methanone (8ce) (entry 11 of table 10): Obtained as a white solid; Yield: 82% (0.209 g); mp: 79 – 81 °C; R_f = 0.38 (ethyl acetate/hexane 1:99); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 – 7.92 (d, 2H), 7.91 – 7.90 (d, 2H), 7.75 – 7.72 (d, 2H), 7.35 – 7.33 (d, 2H), 2.78 – 2.72 (q, 2H), 1.33 – 1.25 (t, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.7, 150.9, 149.8, 143.5, 134.0, 130.7, 130.6, 128.4, 123.6, 29.2, 15.3 ppm; IR

(KBr): 3108, 2965, 2932, 2868, 1656, 1600, 1518, 1348, 1271, 1183, 927, 846, 707 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{15}H_{14}NO_3$ $[M + H]^+$ 256.0973, found 256.0999.

(4-Chlorophenyl)(4-nitrophenyl)methanone (8cb) (entry 12 of table 10)[64]: Yield: 78% (0.204 g); R_f = 0.31 (ethyl acetate/hexane 1:99); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, 2H), 7.91 (d, 2H), 7.75 (dd, 2H), 7.50 (dd, 2H) ppm.

Bis(4-fluorophenyl)methanone (8dc) (entry 13 of table 10)[61]: Yield: 88% (0.192 g); R_f = 0.63 (ethyl acetate/hexane 1:99); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (m, 4H), 7.19 – 7.15 (m, 4H) ppm.

(4-Ethylphenyl)(4-fluorophenyl)methanone (8de) (entry 14 of table 10)[65]: Yield: 82% (0.187 g); R_f = 0.72 (ethyl acetate/hexane 1:99); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (dd, 2H), 7.72 (d, 2H), 7.31 (d, 2H), 7.15 (t, 2H), 2.74 (q, 2H) 1.28 (t, 3H) ppm.

Bis(4-methoxyphenyl)methanone (8ed) (entry 15 of table 10)[66]: Yield: 91% (0.220 g); R_f = 0.16 (ethyl acetate/hexane 1:19); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, 4H), 6.96 (d, 4H), 3.89 (s, 6H) ppm.

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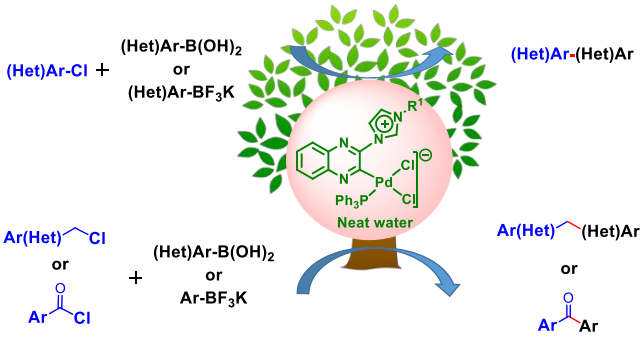

Cross coupling reactions*

V. Ramakrishna,[a] M. Jhansi Rani,[a] and N. Dastagiri Reddy[a]*

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A Zwitterionic Palladium(II) Complex as a Precatalyst for Neat Water Mediated Cross-Coupling Reactions of Heteroaryl, Benzyl and Aryl Acid Chlorides with Organoboron Reagents

A zwitterionic palladium(II) complex was found to be an efficient catalyst for catalyzing Suzuki-Miyaura cross coupling reactions of aryl and heteroaryl organoboron reagents with various heteroaryl chlorides, aryl- and heteroaryl-methyl chlorides, and aryl acid chlorides in neat water.

[a] Prof. Dr. N. Dastagiri Reddy, V. Ramakrishna, M. Jhansi Rani
Department of Chemistry
Pondicherry University (A Central University)