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Versatile palladium(II)-catalyzed Suzuki–Miyaura coupling in ethanol with a novel, stabilizing ligand

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ABSTRACT

Suzuki–Miyaura coupling reactions of arylboronic acids with aryl bromides were mediated by $PdCl_2$ and bdppmapy (*N*,*N*-bis-(diphenylphosphanylmethyl)-2-aminopyridine) that both stabilizes and solubilizes the catalyst in predominantly ethanol as a solvent. Excellent yields for a wide variety of substrates were obtained under relatively mild conditions in this 'green' solvent.

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1. Introduction

Numerous modifications have been made to the reaction conditions of the Suzuki–Miyaura cross-coupling reaction and the carbonylative Suzuki–Miyaura reaction since their discoveries in 1979[1] and 1993,[2] respectively. Diaryl compounds are widespread structural motifs in natural products and pharmacologically active compounds.[3] The Suzuki–Miyaura reactions have provided highly efficient routes to otherwise challenging C_{sp2}–C_{sp2} bond formation.[4] Recent advances in this chemistry include ligand-free and/or 'green' reaction conditions with water or alcohol solubilizing ligands.[5,6] These include bulky or electron rich phosphines,[7] nitrogen-donors,[8] *N*-heterocyclic carbenes,[9] and other ligands[10] capable of increasing the electron density at palladium and thereby accelerating the oxidative addition step in the catalytic cycle.[11] Among these ligands, phosphines are the best known and still widely used because of their superior stabilization of the catalytically active Pd(0).[12]

One disadvantage of palladium catalysts is their cost and the potential for toxic contamination of pharmaceutical products. Many groups have therefore investigated Pd composites that can be easily separated and/or ultra-low loadings of catalyst.[13] For instance, a tetraphosphine ligand, *N*,*N*,*N*′,*N*′-tetra(diphenylphosphinomethyl)-1,2-ethylenediamine (dppeda), was used in the coupling of aryl and heteroaryl bromides, which led to the yield of 98% with the $PdCl_2$ loading of 0.001 mol %.[13e] However, such a catalyst system sometimes involves ligands that are complicated and difficult to synthesize.[14]

The most frequently used solvents for these coupling reactions are acetone, toluene, THF, acetonitrile, and DMF,[15] which can be somewhat expensive, toxic, and difficult to recycle. Water-phase Suzuki–Miyaura reactions are an area of intensive investigation, but plagued with the low solubility of most substrates and catalysts.[10b,16–19]

Ethanol is an alternative renewable solvent, which is relatively cheap and nontoxic. Importantly, the range of organic substrates soluble in this solvent is much greater than those that are soluble in water. However, ethanol soluble palladium catalyst systems are not well studied.

P- and N-donor ligands bearing large groups are of interest because of their ability to stabilize transition metal catalysts.[6c] Additional N-donors in the ligand also accelerate certain reactions, even when there is no observable metal–nitrogen interaction in the pre-catalyst.[20] For example, a N-containing bis(phosphine) ligand displayed much higher activity in rhodium-catalyzed hydroformylation than did its all carbon analogue.[21] An amino-substituted *P*,*S*-phosphinite was also found to be more

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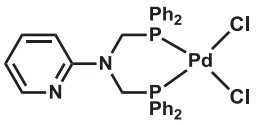
efficient in the palladium-catalyzed Heck reaction[22] and in a rhodium-catalyzed hydroformylation compared to the corresponding ligand without an amino group.[23]

A new complex [(bdppmapy)$PdCl_2$], constructed from $PdCl_2$ and a hybrid diphosphine-pyridine ligand bdppmapy (*N*,*N*-bis-(diphenylphosphanylmethyl)-2-aminopyridine) exhibits good catalytic performance in the decarboxylative C–C coupling of 4-piconic acid and aromatic bromides.[24] We herein report the extension of this investigation to the Suzuki–Miyaura cross-coupling reaction of arylboronic acids with aryl halides in predominantly ethanol as a solvent.



[(bdppmapy)$PdCl_2$]

2. Results and discussion

The coupling of 4′-bromoacetophenone (1 mmol) and 4-methoxyphenylboronic acid (1.5 mmol) was chosen as a model reaction. Because the amount of the catalyst loading was quite low (ranging 0.001–0.01 mol %) in this work, which related to the weighing of less than 0.067 mg, [(bdppmapy)$PdCl_2$] was used as a 0.01 M DMF solution to prevent large deviation (the solubility of [(bdppmapy)$PdCl_2$] is lower in ethanol and its 0.01 M ethanol solution could not be prepared). As we reported previously,[24] the solution of [(bdppmapy)$PdCl_2$] in DMF was the same as that made in situ from mixing $PdCl_2$ with equimolar bdppmapy in DMF. All reactions were performed by using 1–10 μL of such a $PdCl_2$/bdppmapy DMF solution and 4 mL of ethanol. The positive-ion ESI mass spectrum of this palladium/bdppmapy complex in DMF (2 μL) in ethanol (4 mL) was examined and provided an insight into its solution behavior (Fig. 1). A significant signal at m/z=716.08 could be assigned to the [(bdppmapy)Pd·DMF·CH_3CH_2O]$^+$ cation (Fig. 1). The detection of this cation implied that the ligand and Pd^{2+} were coordinated and stable in solution. Similar cations were observed in the corresponding ESI investigation of the more commonly used triphenylphosphine or diphosphines *N*,*N*-bis((diphenylphosphanyl)methyl)aniline (bdppma),[25] 1,1′-bis(diphenylphosphino) methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe) or 1,3-bis(diphenylphosphino)propane (dppp) (Fig. S1–S5, Suppl ementary data).

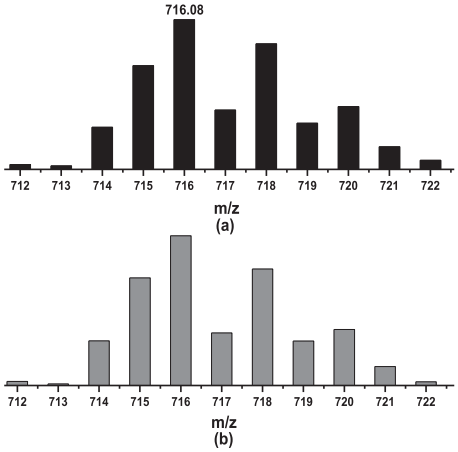
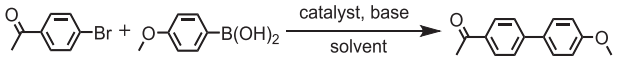


Fig. 1. The positive-ion ESI mass spectrum (top) and the calculated isotope pattern (below) of the [(bdppmapy)Pd·DMF·CH_3CH_2O]$^+$ in the catalyst system.

We initially evaluated the importance of different ligands (Table 1). Without ligand, the yield after 1.5 h was low relatively (13%, Table 1, entry 1). The utilization of bidentate ligands led to higher yields (Table 1, entries 4–6) than with monodentate triphenylphosphine and the backbone structure of the phosphines influenced the reaction rate (Table 1, entry 3). The highest yield was obtained with bdppmapy (Table 1, entry 2). Because the role of the pyridyl group in bdppmapy is unknown, a controlled experiment using its phenyl analogue, *N*,*N*-bis((diphenylphosphanyl)methyl) aniline (bdppma),[25] was performed. The yield (Table 1, entry 7) was the same as that using bdppmapy, implying that the pyridyl group in bdppmapy worked in the same manner as the phenyl group in bdppma, and could not coordinate to the Pd(II) center during the catalysis. Both groups only exhibited the steric hindrance effect, which is beneficial to the catalysis of the coupling reactions.[26]

We then investigated the lower limit of the catalyst loading (Table 2). The electron-poor substrate 4′-bromoacetophenone was almost completely converted into the desired product using 0.01 mol % $PdCl_2$ and 0.01 mol % bdppmapy for 0.5 h at 78 °C (Table 2, entry 1). When the catalyst loading was decreased to 0.005 mol %, 4′-bromoacetophenone could not be detected after 1 h (Table 2, entry 2). A yield of 99% was still achieved in the presence of 0.002 mol % catalyst after 1.5 h (Table 2, entry 3), but only 82% yield was observed after 1 h (Table 2, entry 4). Finally, a high yield was obtained with a catalyst loading as low as 0.001 mol % if the reaction time was prolonged to 4 h (Table 2, entry 5). These results indicated that the catalyst system has good longevity, which is attributed to the effective stabilization of the active palladium species by this bidentate phosphine. This lower catalyst loading was the same as the literature value using a tetraphosphine ligand (dppeda).[13e] However, the latter reaction reached 98% yield but was performed in dioxane in a longer time (20 h) and at a higher temperature (90 °C).

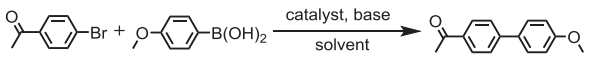
Table 1
The effect of different phosphine ligands on the Suzuki–Miyaura cross-coupling reaction



Entry	Ligand	Yield (%)
1	No ligand	13
2	bdppmapy	99
3	PPh_3	79
4	dppm	85
5	dppe	80
6	dppp	82
7	bdppma	99

Reaction conditions: 4′-bromoacetophenone 1 mmol, 4-methoxyphenylbor-onic acid 1.5 mmol, K_3PO_4 3 mmol, ethanol 4 mL, L/$PdCl_2$=1:1 (entries 2–7), catalyst 0.002 mol % Pd, 1.5 h, 78 °C, analyzed by GC, average of two runs.

Table 2
The effect of time and $PdCl_2$ loadings on the Suzuki–Miyaura cross-coupling reaction



Entry	Pd loading (mol %)	Time (h)	Yield (%)
1	0.01	0.5	99
2	0.005	1	99
3	0.002	1.5	99
4	0.002	1	82
5	0.001	4	99

Reaction conditions: 4′-bromoacetophenone 1 mmol, 4-methoxyphenylbor-onic acid 1.5 mmol, K_3PO_4 3 mmol, ethanol 4 mL, L/$PdCl_2$=1:1, 78 °C, analyzed by GC, average of two runs.

Next, we investigated the influence of solvents, bases, and temperatures on this coupling reaction (Table 3). The reactions were performed in some common solvents (4 mL) in the presence of the palladium–bisphosphine bdppmapy catalyst (0.01 mol %), combined in a small quantity of DMF, and with a base (3 mmol) at different temperatures for 2 h under a N_2 atmosphere. Only 15% of product 1-(4′-methoxy-[1,1′-biphenyl]-4-yl)ethan-1-one was obtained with water as solvent and K_3PO_4 as base at 100 °C (Table 3, entry 1). Ethanol and K_3PO_4, however, proved to be both efficient and an environmentally friendly combination (Table 3, entry 5). This catalytic reaction could adopt EtOH/H_2O as a mixed solvent system. The yield could reach 99% when the ratio of EtOH/H_2O was 1:2 (entries 9–12). However, it fell to 37% when the ratio of EtOH/H_2O was 1:4 (entry 13). The reaction did depend on the temperature as the yield decreased to 94% and 3% as the reaction was carried out at 60 °C and 40 °C, respectively (entries 14 and 15). Thus, we decided to choose ethanol as the optimized solvent taking into account the solubility of different substrates and the refluxing temperature.

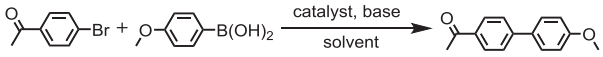
With optimal reaction conditions in hand, we turned our attention to the range of potential substrates. Unsurprisingly, aryl bromides were better substrates than an aryl fluoride or chloride (Table 4, entries 12 and 25, respectively) and an activating group at the *para*-position of the aryl bromide was the highest yielding (Table 4, entry 1). In contrast, reaction with the same group at the more hindered *ortho*-position leads to a significantly lower yield (Table 4, entry 5). These coupling conditions were tolerant of a wide range of functionality in the aryl halide (Table 4, entries 6–13) and arylboronic acid (Table 4, entries 14–24).

While the heteroaryl 2-bromopyridine was a reasonable substrate under these conditions (Table 4, entry 13), heteroaryl boronic acids were variable (Table 4, entries 20–23), with thiophen-2-ylboronic acid reacting very slowly (Table 4, entry 21). One-pot double arylation of *o*-, or *m*-, or *p*-dibromobenzene (Table 4, entries 26–28) with 4-methoxyphenylboronic acid proceeded in reasonable to good yields.

3. Conclusions

In summary, we have developed an efficient $PdCl_2$/bdppmapy catalytic system for the Suzuki–Miyaura coupling reaction of arylboronic acid with aryl bromides in predominantly ethanol as a solvent under moderate conditions. A wide range of substrates could be coupled with good to excellent yields, even over extended periods, under-scoring the stabilizing ability of this ligand.

Table 3
The effect of solvents, bases, and temperature on the Suzuki–Miyaura cross-coupling reaction



Entry	Solvent	Base	*T* (°C)	Yield (%)
1	H_2O	K_3PO_4	100	15
2	DMF	K_3PO_4	100	65
3	Dioxane	K_3PO_4	100	59
4	Toluene	K_3PO_4	100	99
5	Ethanol	K_3PO_4	78	99
6	Ethanol	KOH	78	72
7	Ethanol	K_2CO_3	78	85
8	Ethanol	NaOH	78	67
9	Ethanol/H_2O=4:1	K_3PO_4	78	99
10	Ethanol/H_2O=2:1	K_3PO_4	78	99
11	Ethanol/H_2O=1:1	K_3PO_4	78	99
12	Ethanol/H_2O=1:2	K_3PO_4	78	99
13	Ethanol/H_2O=1:4	K_3PO_4	78	37
14	Ethanol	K_3PO_4	60	94
15	Ethanol	K_3PO_4	40	3

Reaction conditions: 4′-bromoacetophenone 1 mmol, 4-methoxyphenylboro-nic acid 1.5 mmol, base 3 mmol, solvent 4 mL, L/$PdCl_2$=1:1, catalyst 0.01 mol % Pd, 2 h, analyzed by GC, average of two runs.

4. Experimental

4.1. General

All reactions were carried out under nitrogen atmosphere using standard Schlenk-techniques. Solvents were dried by conventional methods. The two ligands (bdppma and bdppmapy) were prepared according to the literature procedures.[25,27] All other reagents were used as received from commercial suppliers. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a Varian UNITYplus-300, 400 and 600 spectrometers. ^{1}H NMR and ^{13}C NMR chemical shifts were referenced to the solvent signal in $CDCl_3$ or DMSO-d_6. Electrospray ion mass spectra (ESI-MS) were performed on an Agilent 1200/6200 mass spectrometer. GC measurements were recorded on an Agilent 7820A Gas Chromatograph with an Agilent HP-5 chromatographic column and N_2 as mobile phase. The LC–MS were recorded in a Rapid Resolution HT-3 chromatographic column on an Agilent 1260 Infinity Liquid Chromatograph with 6120 Quadrupole Mass Spectrometer and MeCN as mobile phase.

4.2. General procedure for the Suzuki–Miyaura reaction

The ligand bdppmapy (4.9 mg, 0.01 mmol) and $PdCl_2$ (1.8 mg, 0.01 mmol) were added to a Schlenk tube containing a magnetic stirrer bar, and then degassed DMF (1 mL) was added. The mixture was stirred 3 h at room temperature. 4′-Bromoacetophenone (199 mg, 1 mmol), 4-methoxyphenylboronic acid (228 mg, 1.5 mmol), and K_3PO_4 (637 mg, 3 mmol) were added to another Schlenk tube with a magnetic stirrer bar. The dissolved mixture of bdppmapy/$PdCl_2$ (2 μL, 0.00002 mmol) was transferred to the Schlenk tube of reactants by syringe. Then, ethanol (4 mL) was added. The reaction mixture was heated at reflux for 1.5 h. At the end of the reaction, the solution was cooled to room temperature and water (5 mL) was added. The mixture solution was extracted with ethyl acetate (3×5 mL) and the organic layer was dried over magnesium sulfate. The dried solution was filtered and reduced to approx. 1–2 mL under vacuum, then purified with silica gel chromatography to give the corresponding product with an isolated yield. See Supplementary data for general experimental details, ESI-MS data of the catalysts, and characterization data for the catalytic products.

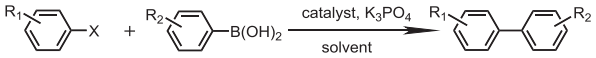
4.2.1. 1-(4′-Methoxy-[1,1′-biphenyl]-4-yl)ethanone.[28] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.00 (d, *J*=8.0 Hz, 2H), 7.64 (d, *J*=8.0 Hz, 2H), 7.58 (d, *J*=8.0 Hz, 2H), 7.00 (d, *J*=8.0 Hz, 2H), 3.86 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.7, 159.9, 145.4, 135.3, 132.3, 129.0, 128.4, 126.6, 114.4, 55.4, 26.7.

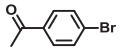
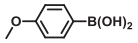
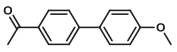
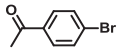
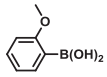
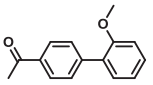
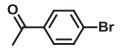
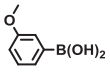
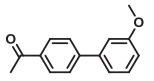
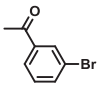
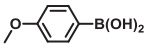
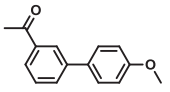
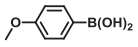
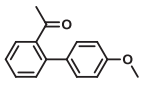
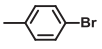
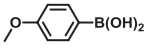
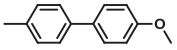
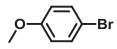
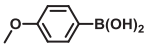
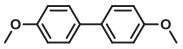
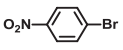
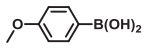
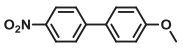
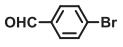
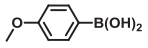
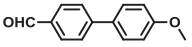
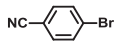
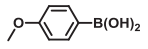
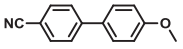
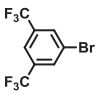
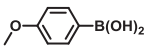
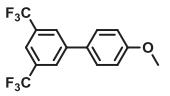
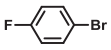
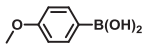
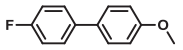
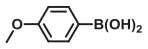
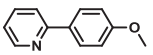
4.2.2. 1-(2′-Methoxy-[1,1′-biphenyl]-4-yl)ethanone.[29] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.00 (d, *J*=8.0 Hz, 2H), 7.63 (d, *J*=8.0 Hz, 2H), 7.38–7.32 (q, 2H), 7.07–6.99 (m, 2H), 3.82 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.9, 156.5, 143.6, 135.5, 130.7, 129.8, 129.5, 128.1, 121.0, 114.4, 55.6, 26.7.

4.2.3. 1-(3′-Methoxy-[1,1′-biphenyl]-4-yl)ethanone..[30] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.03 (d, *J*=8.0 Hz, 2H), 7.68 (d, *J*=8.0 Hz, 2H), 7.39 (t, *J*=8.0 Hz, 1H), 7.21 (d, *J*=8.0 Hz, 1H), 7.15 (s, 1H), 6.95 (d, *J*=8.0 Hz, 1H), 3.88 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.8, 160.0, 145.6, 141.4, 136.0, 130.0, 128.9, 127.3, 119.8, 113.5, 113.1, 55.4, 26.7.

4.2.4. 1-(4′-Methoxy-[1,1′-biphenyl]-3-yl)ethanone.[29] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.14 (t, *J*=2.0 Hz, 1H), 7.88 (d, *J*=8.0 Hz, 1H), 7.75 (d, *J*=8.0 Hz, 1H), 7.56 (d, *J*=8.0 Hz, 2H), 7.51 (t, *J*=8.0 Hz,

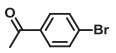
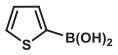
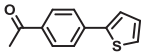
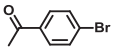
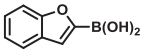
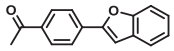
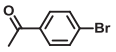
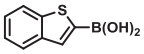
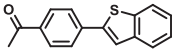
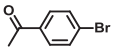
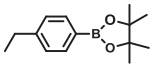
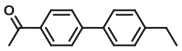
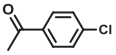
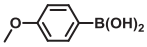
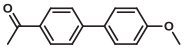
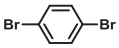
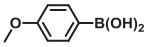
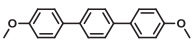
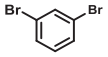
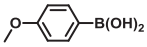
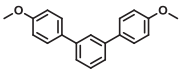
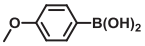
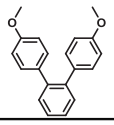
Table 4
Suzuki–Miyaura coupling of aryl halide with arylboronic acid



Entry	ArX	Ar′B(OH)$_2$	Product	Yield (%)
1				99
2				95
3				92
4				82
5				70
6				91
7				94
8				95
9				93
10				93
11				82
12				65
13				75
14				96
15				95
16				92
17				91
18				80
19				78
20[a]				90

(*continued on next page*)

Table 4 (*continued*)

Entry	ArX	$Ar'B(OH)_2$	Product	Yield (%)
21[a]				Trace
22[a]				93
23[a]				92
24[a]				nr
25[a]				32
26[a,b]				90
27[a,b]				73
28[a,b]				65

Reaction conditions: aryl halides 1 mmol, arylboronic acids 1.5 mmol, K_3PO_4 3 mmol, ethanol 4 mL, L/$PdCl_2$=1:1, catalyst 0.01 mol % $PdCl_2$, reflux, 1.5 h, isolated yield, average of two runs.

[a] Catalyst 0.1 mol % $PdCl_2$.

[b] Aryl halides 1 mmol, arylboronic acids 3 mmol, K_3PO_4 6 mmol, ethanol 8 mL.

1H), 7.00 (d, *J*=8.0 Hz, 2H), 3.86 (s, 3H), 2.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 198.2, 159.5, 141.3, 137.6, 131.3, 129.0, 128.2, 126.6, 126.4, 114.3, 55.4, 26.8.

4.2.5. 1-(4′-Methoxy-[1,1′-biphenyl]-2-yl)ethanone.[29] ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.53–7.47 (q, 2H), 7.38 (t, *J*=8.0 Hz, 2H), 7.27 (d, *J*=8.0 Hz, 2H), 6.96 (d, *J*=8.0 Hz, 2H), 3.85 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 205.3, 159.5, 140.9, 133.0, 130.6, 130.1, 130.0, 127.8, 127.0, 114.1, 55.3, 30.4.

4.2.6. 4-Methoxy-4′-methyl-1,1′-biphenyl.[28] ^1H NMR (400 MHz, DMSO-d_6, ppm): δ 7.57 (d, *J*=8.0 Hz, 2H), 7.50 (d, *J*=8.0 Hz, 2H), 7.23 (d, *J*=8.0 Hz, 2H), 7.00 (d, *J*=8.0 Hz, 2H), 3.79 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 158.6, 136.9, 135.8, 132.4, 129.4, 127.4, 125.9, 114.2, 55.1, 20.6.

4.2.7. 4,4′-Dimethoxy-1,1′-biphenyl.[28] ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.47 (d, *J*=8.0 Hz, 4H), 6.95 (d, *J*=8.0 Hz, 4H), 3.83 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 158.7, 133.5, 127.7, 114.2, 55.4.

4.2.8. 4-Methoxy-4′-nitro-1,1′-biphenyl.[28] ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.26 (d, *J*=8.0 Hz, 2H), 7.68 (d, *J*=8.0 Hz, 2H), 7.58 (d, *J*=8.0 Hz, 2H), 7.03–7.00 (d, *J*=12.0 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 160.5, 147.2, 146.6, 131.1, 128.6, 127.1, 124.2, 114.6, 55.5.

4.2.9. 4′-Methoxy-[1,1′-biphenyl]-4-carbaldehyde.[31] ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 10.03 (s, 1H), 7.92 (d, *J*=8.0 Hz, 2H), 7.71 (d, *J*=8.0 Hz, 2H), 7.59 (d, *J*=8.0 Hz, 2H), 7.01 (d, *J*=8.0 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 191.9, 160.1, 146.8, 134.7, 132.0, 130.3, 128.5, 127.0, 114.5, 55.4.

4.2.10. 4-Cyano-4′-methoxy-1,1′-biphenyl.[28] ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.70–7.62 (q, 4H), 7.55–7.52 (d, *J*=12.0 Hz, 2H), 7.00 (d, *J*=8.0 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 160.2, 145.2, 132.6, 131.5, 128.4, 127.1, 119.1, 114.5, 110.1, 55.4.

4.2.11. 4′-Methoxy-3,5-bis(trifluoromethyl)-1,1′-biphenyl.[32] ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.96 (s, 2H), 7.80 (s, 1H), 7.55 (d, *J*=8.0 Hz, 2H), 7.04–7.01 (d, *J*=12.0 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 160.3, 142.9, 131.9, 130.6, 128.4, 127.5, 126.7, 124.8, 122.1, 120.2, 119.4, 114.7, 55.4.

4.2.12. 4-Fluoro-4′-methoxy-1,1′-biphenyl.[29] ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.50–7.45 (q, 4H), 7.11–7.07 (t, 2H), 6.98–6.95 (d, *J*=12.0 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 163.3, 160.9, 159.1, 137.0, 132.8, 128.3, 128.2, 128.0, 115.6, 115.4, 114.2, 55.3.

4.2.13. 2-(4-Methoxyphenyl)pyridine.[28] ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.66 (d, *J*=4.0 Hz, 1H), 7.96 (d, *J*=12.0 Hz, 2H), 7.74 (t, *J*=8.0 Hz, 1H), 7.68 (d, *J*=8.0 Hz, 1H), 7.21–7.17 (m, 1H), 7.00 (d, *J*=12.0 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 160.6, 156.9, 149.2, 137.0, 131.6, 128.2, 121.5, 120.0, 114.2, 55.4.

4.2.14. 1-(4′-Methyl-[1,1′-biphenyl]-4-yl)ethan-1-one.[33] ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.01 (d, *J*=8.0 Hz, 2H), 7.67 (d, *J*=8.0 Hz, 2H), 7.53 (d, *J*=8.0 Hz, 2H), 7.28 (d, *J*=8.0 Hz, 2H), 2.63 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.8, 145.7, 138.2, 136.9, 135.5, 129.7, 128.9, 127.1, 126.9, 26.7, 21.2.

4.2.15. 1-([1,1′-Biphenyl]-4-yl)ethan-1-one.[29] ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.03 (d, *J*=8.0 Hz, 2H), 7.68 (d, *J*=8.0 Hz, 2H), 7.63–7.62 (d, *J*=4.0 Hz, 2H), 7.47 (d, *J*=8.0 Hz, 2H), 7.40 (t, *J*=8.0 Hz, 1H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.7, 145.7, 139.8, 135.8, 128.9, 128.2, 127.2, 26.6.

4.2.16. 1-(4′-Fluoro-[1,1′-biphenyl]-4-yl)ethan-1-one.[33] ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.04–8.01 (d, *J*=12.0 Hz, 2H), 7.63 (d,

J=8.0 Hz, 2H), 7.61–7.57 (q, 2H), 7.16 (t, *J*=8.0 Hz, 2H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.6, 164.2, 161.8, 144.7, 136.0, 135.9, 135.8, 129.0, 128.9, 127.1, 116.0, 115.8, 26.7.

4.2.17. 1-(4′-(Trifluoromethyl)-[1,1′-biphenyl]-4-yl)ethan-1-one.[10b] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.06 (d, *J*=8.0 Hz, 2H), 7.73 (s, 4H), 7.69 (d, *J*=8.0 Hz, 2H), 2.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.6, 144.2, 143.4, 136.6, 130.4, 130.1, 129.1, 127.6, 127.5, 126.0, 125.9, 125.8, 122.8, 26.7.

4.2.18. 1-(4′-Nitro-[1,1′-biphenyl]-4-yl)ethan-1-one.[34] ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.35–8.32 (d, *J*=12.0 Hz, 2H), 8.10 (d, *J*=8.0 Hz, 2H), 8.04 (d, *J*=8.0 Hz, 2H), 7.93 (d, *J*=8.0 Hz, 2H), 2.65 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6, ppm): δ 198.0, 147.6, 145.7, 142.4, 137.2, 129.5, 128.0, 124.6, 27.3.

4.2.19. 1-(4-(Naphthalen-1-yl)phenyl)ethan-1-one.[35] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.09 (d, *J*=8.0 Hz, 2H), 7.92 (t, *J*=8.0 Hz, 2H), 7.84 (d, *J*=8.0 Hz, 1H), 7.61 (d, *J*=8.0 Hz, 2H), 7.56–7.50 (m, 2H), 7.47–7.42 (m, 2H), 2.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.9, 145.8, 139.0, 136.0, 133.8, 131.2, 130.3, 128.4, 128.3, 126.9, 126.4, 126.0, 125.6, 125.3, 26.7.

4.2.20. 1-(4-(Thiophen-3-yl)phenyl)ethan-1-one.[36] ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.10–8.08 (q, 1H), 8.00 (d, *J*=8.0 Hz, 2H), 7.89 (d, *J*=8.0 Hz, 2H), 7.71–7.69 (q, 1H), 7.68–7.66 (q, 1H), 2.60 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6, ppm): δ 197.7, 140.7, 139.8, 135.7, 129.4, 128.0, 126.7, 126.5, 123.6, 27.2.

4.2.21. 1-(4-(Benzofuran-2-yl)phenyl)ethan-1-one.[37] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.04–7.92 (q, 4H), 7.61 (d, *J*=8.0 Hz, 1H), 7.54 (d, *J*=8.0 Hz, 1H), 7.35–7.31 (t, *J*=8.0 Hz, 1H), 7.25–7.24 (d, *J*=4.0 Hz, 1H), 7.15 (s, 1H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.3, 155.2, 154.5, 136.5, 134.6, 128.9, 125.2, 124.8, 123.3, 121.3, 111.4, 103.7, 26.6.

4.2.22. 1-(4-(Benzo[b]thiophen-2-yl)phenyl)ethan-1-one.[38] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.01 (d, *J*=8.0 Hz, 2H), 7.86–7.78 (m, 4H), 7.66 (s, 1H), 7.38–7.35 (m, 2H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.3, 142.6, 140.5, 139.9, 138.7, 136.4, 129.1, 126.4, 125.0, 124.8, 122.4, 121.2, 26.6.

4.2.23. 4,4″-Dimethoxy-1,1′:4′,1″-terphenyl.[39] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.61 (s, 4H), 7.57 (d, *J*=8.0 Hz, 4H), 7.01–6.98 (d, *J*=12.0 Hz, 4H), 3.86 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 159.1, 139.1, 133.3, 128.0, 127.0, 114.2, 55.3.

4.2.24. 4,4″-Dimethoxy-1,1′:3′,1″-terphenyl.[39] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.72 (s, 1H), 7.58 (d, *J*=8.0 Hz, 4H), 7.50–7.46 (m, 3H), 7.69 (d, *J*=8.0 Hz, 4H), 3.86 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 159.2, 141.3, 133.8, 129.1, 128.2, 125.3, 125.1, 114.2, 55.4.

4.2.25. 4,4″-Dimethoxy-1,1′:2′,1″-terphenyl.[40] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.39–7.34 (m, 4H), 7.06 (d, *J*=8.0 Hz, 4H), 6.76 (d, *J*=8.0 Hz, 4H), 3.77 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 158.2, 140.0, 134.1, 130.9, 130.5, 127.1, 113.3, 55.1.

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Supplementary data

^{1}H and ^{13}C NMR spectra for the isolated products. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.04.052.

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