Tetrahedron Letters 56 (2015) 1378–1382

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Convenient and rapid strategies towards 6-(hetero)aryl pyridylmethylamines: first catalytic issues

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ARTICLE INFO

Article history:
Received 12 December 2014
Revised 23 January 2015
Accepted 28 January 2015
Available online 4 February 2015

Keywords:
Pyridylmethylamine
Microwave-assisted synthesis
Heterocyclic chemistry
Naphthol oxidative coupling
Binaphthyl platform

ABSTRACT

The convenient preparation of new pyridylmethylamines is described using a short two step sequence. The first step involved the straightforward microwave-assisted construction of 6-aryl and 6-heteroaryl pyridine scaffolds bearing carboxaldehyde and nitrile fragments. The pendant arm comprising a second nitrogen atom by mean of amine and oxazoline moieties is installed in the second step. Finally, a first entry towards catalytic activity is given. In this context, modification of the ligand pattern and steric crowding around the central pyridine ring is examined and led to modest to fair ee's in the construction of binaphthyl substrates.

Introduction

2-(Aminomethyl) pyridines represent a useful family of ligands known as ampy, pyme or pma depending on the literature source. This family of ligands revealed recently efficient in the field of transition metal complexation and homogeneous catalysis.[1–4] Structural modifications have already been done on the pma scaffold expanding the scope of the catalytic transformations potentially promoted by these ligands. Rigid pyridylpiperidines in which the second nitrogen atom is included within the piperidine ring were successfully applied to Suzuki coupling.[5] Installation of an aryl group in position 6 of the pma motif resulted in a further generation of pma-based ligands.[6] Such 6-arylpyridylmethyleamine in combination with group IV metals such as Os, Ru, Pd, Ir or Pt, catalyse olefin polymerization,[7] hydride transfer,[8,9] and allylation reactions[6] for example. Among these ligands, 6-phenyl or 6-(*para*tolyl)pyridinemethylamines are of considerable interest since they have been able to generate stable pincer-type catalyst precursors.[6,10] Accesses to 6-arylpyridylmethylamines have been reported either from aryl pyridines and further installation of the methylamine fragment through multistep sequences[11] or from arylation of bromopyridinecarboxaldehydes[7] followed by reductive amination.[8] If phenyl, tolyl and naphthyl substituted pyridylmethylamine are the most common members of the 6-arylpyridylmethylamine family, the installation of heteroaromatics fragments including furyl, thienyl and pyridyl remains challenging. There is a strong interest of the scientific community for this family of compounds and thus a steady demand for convenient and rapid strategies towards 6-aryl but also 6-heteroaryl pyridylmethylamines. As part of a research programme devoted to the synthesis, characterization and reactivity studies of pyridinemethylamine-based catalytic systems, we draw particular attention on the installation of various aryl and heteroaryl groups in position 6 of the pma system. We reported herein on a two step preparation procedure of new pma derivatives as highlighted in Figure 1.

The construction of the 6-aryl and 6-heteroaryl pyridine scaffold bearing carboxaldehyde and nitrile fragments is envisioned through microwave-assisted coupling reactions.

The construction of pendant arms comprising amine or oxazoline moieties from precursors such as carboxaldehyde and nitrile groups is next described. Finally, a first set of catalytic transformations is given.

We first focused on the synthesis of 6-arylpyridine-2-carboxaldehydes and -carbonitriles. In order to obtain aryl or heteroaryl pyridines in the most practical way, we decided to examine the Suzuki coupling between commercially available aryl boronic acids and 6-bromopyridine-2-carboxaldehyde under microwave activation. Indeed, microwave-assisted organic chemistry has grown in the last decades as a valuable and versatile tool for organic chemists.[12] It was thus of high benefits for us to increase reaction yields of key materials within this study, reduce reaction times and avoid undesirable side reactions that may occur in cross-coupling reactions under conventional heating methods (vide infra). After a

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http://dx.doi.org/10.1016/j.tetlet.2015.01.182
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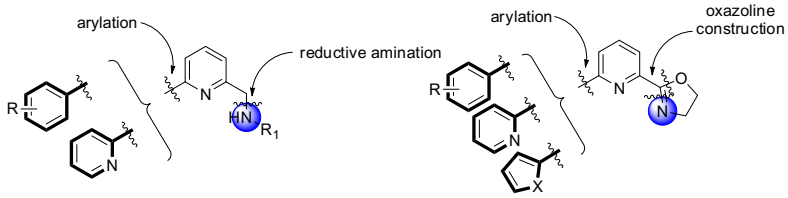


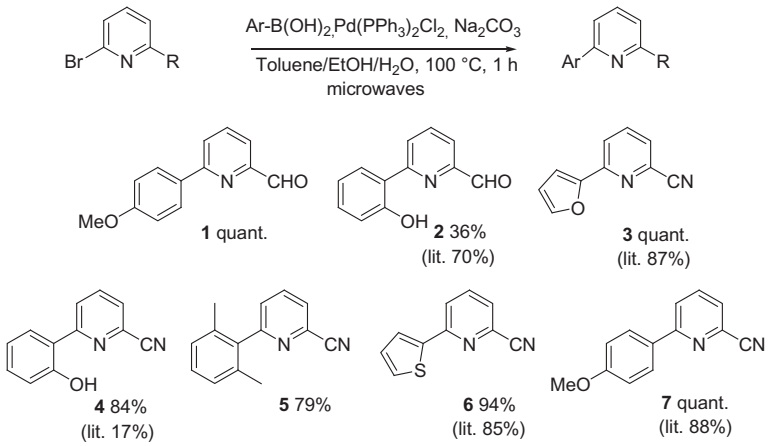
Figure 1. General strategy towards 6-(hetero)aryl pyridylmethylamines.

screening of Pd catalyst (Pd_2dba_3/$AsPh_3$, Na_2PdCl_4/BINAP, $Pd(PPh_3)_2Cl_2$/$FeCl_3$, $Pd(PPh_3)_2Cl_2$, $Pd(PPh_3)_2Cl_2$/CuI) base (Na_2CO_3, K_2CO_3) and solvent (THF, DME, dioxane, toluene/EtOH/H_2O), $Pd(PPh_3)_2Cl_2$, Na_2CO_3 in toluene/EtOH/H_2O represented the best catalytic compromise. One hour under microwave irradiation at 100 °C revealed optimal conditions to prepare 6-arylpyridine-2-carboxaldehydes **1** and **2**. The latter microwave assisted conditions (quantitative, 100 °C, 1 h) compares favorably with thermal conditions (74%, 100 °C, 16 h) for the preparation of compound **1** used the model compound. Interestingly, identical conditions were also successfully applied to the preparation of the corresponding carbonitriles **3**–**7** in comfortable yields ranging from 79% to quantitative (Scheme 1). Our results deserve additional comments: as it can be seen from yields obtained for **1** and **7**, introduction of *para*methoxyphenyl is equally efficient regardless of the carboxaldehyde or nitrile groups lying in position 2. The introduction of heterocycles such as thiophene and furan in compounds **3** and **6**, respectively, was realized with similar efficiency. Installation of aryl groups that exhibit increased steric crowding is also possible giving access to compounds **2**, **4** and **5**. If **4** and **5** could be obtained in good yields, **2** was isolated in a modest 36% yield mainly due to a tedious purification step. Noteworthy, yields obtained for isolated products in our study compare fairly to already reported methods (see Supplementary material and yields mentioned in brackets).[13]

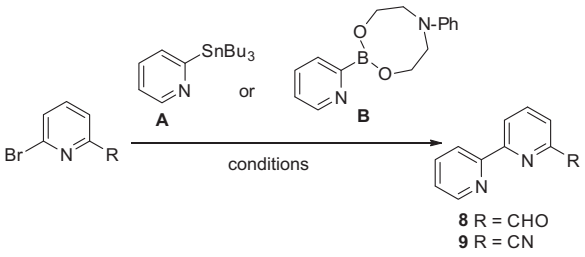
We next moved to the construction of the 2,2′-bipyridine analogues **8** and **9**. 2,2′-Bipyridines represent a family of versatile building blocks in the fields of analytical, photo-, supra-, nano-, macromolecular chemistry and catalysis.[14] Suzuki- and Stille-type reactions have been developed in order to build up the 2,2-bipyridine scaffold. Although elegant efforts in the Suzuki pathway have been done to overcome severe drawbacks such as prevalent protodeborylation, dimerization and relative low transmetalation steps, the preparation of unsymmetrical 2,2-bipyridines by coupling reactions is still considered challenging. To circumvent these drawbacks, ligands such as phosphite and phosphine oxide as well as alternate boron-based coupling partners[15] were recently shown effective. Still coupling was also recently applied to the preparation of symmetrical bipyridines and furyl- or thienyl-pyridine, but revealed hampered by substantial amounts of homocoupling side product in the case of unsymmetrical bipyridines.[16] In this context again, microwave-assisted synthesis was expected to reduce the aforementioned hurdles and drawbacks. We thus began to examine both Stille- and Suzuki-type couplings as described in Scheme 2 and Table 1. It is worth noting that both reaction conditions, times and temperatures deeply influenced the reaction issues. Indeed, at 120 °C for 60 min (entry 1) the use of 5% $Pd(PPh_3)_2Cl_2$ in combination with 10% CuI did not afford any expected coupling products albeit the starting material was fully consumed. Noteworthy debromation and/or homocoupling side reactions take place under these conditions.

In contrast at higher temperatures for shorter reaction times (entry 2), we were able to isolate bipyridine **8** in 18% yield. Other solvents were next tested but THF and NMP revealed less effective than dioxane. Similarly, the use of $Pd(PPh_3)_2Cl_2$ and CuI was found superior to other catalyst and mandatory to optimal conversions respectively. Best results could be obtained at 180 °C for 15 min (entry 3) whereas prolonged reaction times led to a significant amount of degradation products and a concomitant decrease of the isolated yield.

Although yields remained modest, our conditions provide a good compromise between efficiency and a relative easy purification as crude products were only poorly contaminated by side products. In addition, bipyridine **9** could also be obtained in a high 79% yield under similar conditions. Yields are similar to those observed recently by Duan[7] and Lützen[17] but our results compare favourably in term of reaction times. Attempts to increase yields were next done under Suzuki-type coupling conditions. The use of *N*-phenyldiethanolamino-2-pyridylboronate (see ESI) instead of a more classical 2-pyridylnucleophile was next examined. Again high temperature and short reaction times proved efficient providing an access to bipyridine **8** in a fair 57% yield under microwave activation (entry 7). K_2CO_3 as the base, dioxane/water 1:0.1 as



Scheme 1. 6-(Hetero)aryl-carboxaldehydes and carbonitriles **1**–**7**.



Scheme 2. Synthesis of bipyridine-carboxaldehyde **8** and carbonitrile **9**.

the solvent and a temperature of 150 °C for 15 min represented the best compromise obtained that has to be compared with higher reaction temperatures (entry 6) or other catalytic system such as $PddppfCl_2$. Experiments were run at a 90 mg scale of the starting bromopyridine derivative. Attempts to scale up were however hampered by the presence of larger amounts of side products and thus more tedious purification steps affording lower yields of expected targets.

We next focused on the preparation of new 6-arylpyridylmethylamines. Carboxaldehydes **1**, **2** and **8** reacted smoothly with α-(*R*)-methylbenzylamine or α-(*R*)-methylnaphthylamine to afford the intermediate imines which were in situ reduced using $NaBH_4$ in methanol to afford the corresponding pma **10**–**14** in high yields (Scheme 3).[18]

We further examined the preparation of oxazolines starting from nitriles **3**–**7** and **9**. Based on a previous study,[19] we were able to efficiently transform nitriles into the corresponding oxazolines using solvent free microwave activation and 1.2 equiv of (*R*)-phenylglycinol. After 2 h at 130 °C, oxazolines **15**–**19** were isolated in high yields regardless of the aromatic or heterocycle installed in position 6 of the central pyridine ring (Scheme 4).

Finally, we describe first entries towards the catalytic activity of new (hetero)arylpyridylmethylamines. In this context, we focused our attention to two catalytic transformations, naphthol oxidative and atroposelective Suzuki–Miyaura couplings, which have already been described within the pma series. Comparison with previously reported results obtained using ligands **23** and **24**, is given in Tables 2 and 3 (entries 1). To this end, pyridyloxazolines **21** and **22** were also prepared according to known procedures[19] and used in this study. Impacts of (i) the installation of (hetero)aryl groups at position 6 of the pyridine ring and/or (ii) the modification of the pendant arm towards a cyclic oxazoline was examined.

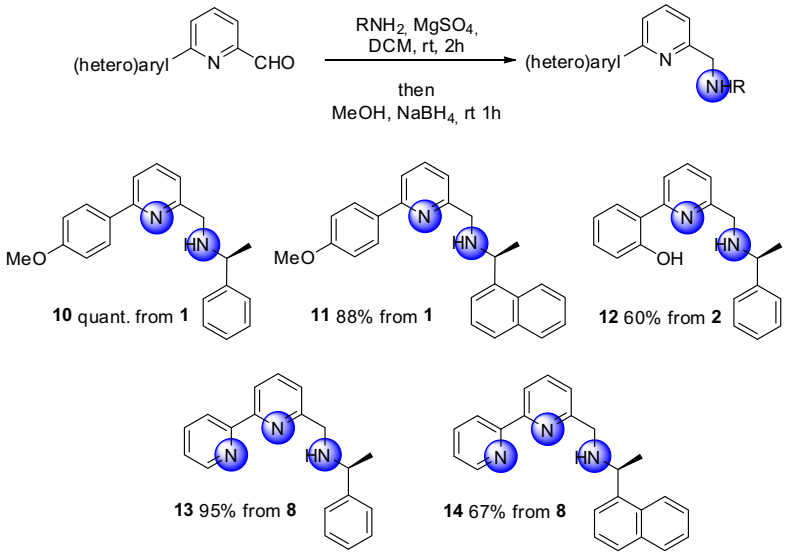
Oxidative naphthol coupling has been recently reported by us and others using iron or copper–amine complexes[20] including sparteine, proline-derived diamines, 1,5-diaza-*cis*-decalin, BINAM or even pma.[1] The catalytic systems were prepared in situ from CuI (5%) and pyridylmethylamines (5%) in dichloroethane (DCE). The experiments were performed under an oxygen atmosphere at temperatures and time indicated in Table 2 in agreement with a previous study.[1] As shown in Scheme 5 and Table 2 (entry 1), within the pma series, the use of ligand **24** gave 50% yield and 61% ee which represented the best results obtained.

An increase of steric crowding around the complexation site after installation of 4-MeOPh group in **10** and **11** as well as of π-deficient pyridyl substituent in **13** appears detrimental to the construction of the binaphthyl platform. At best, a poor 10% isolated yield of **20** could be reached (entry 4). Interestingly, moving from

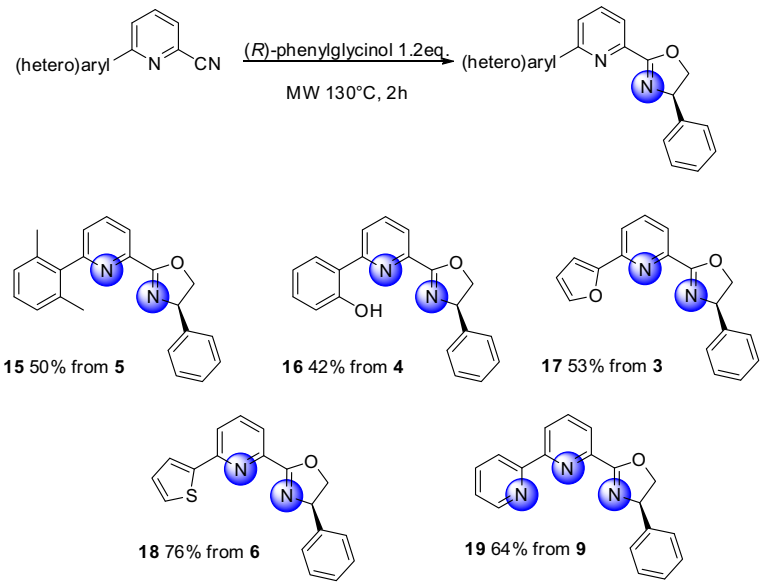
Table 1
Preparation of bipyridines **8** and **9**: comparison of Suzuki and Stille coupling reactions

Entry	Conditions	Temp (°C)/time (min)	Compound (yield %)
1	**A**, $Pd(PPh_3)_2Cl_2$ 5%, CuI 10%, dioxane	120/60 min	**8**(−)
2	**A**, $Pd(PPh_3)_2Cl_2$ 5%, CuI 10%, dioxane	180/10 min	**8**(18)
3	**A**, $Pd(PPh_3)_2Cl_2$ 5%, CuI 10%, dioxane	180/15 min	**8**(72)[a]
4	**A**, $Pd(PPh_3)_2Cl_2$ 5%, CuI 10%, dioxane	180/15 min	**9**(79)[b]
6	**B**, $Pd(PPh_3)_2Cl_2$ 10%, K_2CO_3 3 equiv, dioxane/H_2O	180/15 min	**8**(48)
7	**B**, $Pd(PPh_3)_2Cl_2$ 10%, K_2CO_3 3 equiv, dioxane/H_2O	150/15 min	**8**(57)

[a] Obtained in 70% yield by Lützen.[17]
[b] Obtained in 81% yield by Duan.[7]



Scheme 3. Synthesis of new pma derivatives.

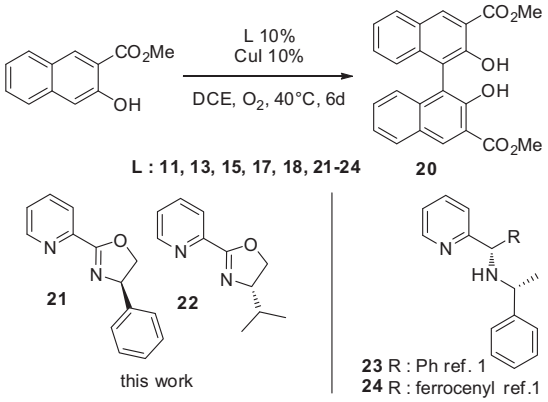


Scheme 4. Synthesis of pyridyl-oxazolines.

Table 2
Copper catalysed oxidative coupling

Entry	Ligand	Yield (%)	Ee (%)	Conf.
1	**24**	50	61[a]	(*S*)
2	**10**	—	—	—
3	**11**	—	—	—
4	**13**	10[b]	nd	—
5	**21**	35	75	(*R*)
6	**22**	25	43	(*S*)
7	**15**	—	-	—
8	**17**	42	rac.	—
9	**18**	Traces	nd	—

[a] See Ref. 1.
[b] Experiment run in four days.



Scheme 5. β-Naphthol oxidative coupling.

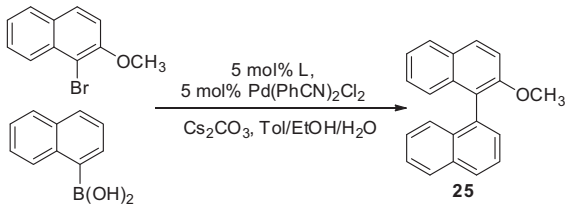
Table 3
Suzuki coupling

Entry	Ligand	Conv. (%)	Yield (%)	Ee (%)	Conf.
1	**23**	Quant.	70	40[a]	(*S*)
2	**10**	60	19	10	
3	**11**	40	30	8	[b]
4	**13**	34	21	7	[b]
5	**21**	84	34	21	(*R*)
6	**17**	62	14	10	(*S*)
7	**19**	15	—	—	—

[a] See Ref. 1.
[b] Not determined.

acyclic pendant arm to cyclic oxazoline as in **21** and **22** revealed beneficial in this transformation (entries 5, 6). Albeit in modest yields, binaphthol **20** could be obtained in 75 and 43% ee, respectively. Unfortunately, installation of aromatic groups at position 6 of the pyridine-oxazoline **21** led to a severe decrease of conversion and selectivity. Indeed, installation of the 2,6-diMePh group at the central pyridine led to any conversion (entry 7). The presence of heterocycles instead of phenyl rings was next examined. In this context π-excessive furan **17** and thiophene **18** were further tested. Interestingly, best isolated yield (42%) was obtained with the less coordinating heterocycle furan (entry 8). In the latter case binol **20** was obtained in a racemic form. Disappointingly, moving to the more coordinating thiophene **18** led only to traces of the target (entry 9). This first set of experiments seems to indicate that a further rigidification of the ligand platform induces an increase of steric crowding around the metal centre which becomes detrimental to the targeted transformation. A similar trend is observed whether the pendant arm nitrogen atom is embedded into a rigid oxazoline heterocycle or not.

Atroposelective Suzuki–Miyaura coupling was next examined. If Cammidge and Buchwald[21] paved the way to such catalytic transformation some years ago, this research area remains challenging. Indeed, 2-MeObinaphthyl **25** is commonly used as the benchmark target to the evaluation of catalytic systems. Several groups reached appealing compromise between high ee and comfortable yields.[22] Based on a similar strategy, ligands **10**, **11**, **13** were compared to previously results obtained within the pma series. As shown in Scheme 6 and Table 3 (entry 1) reference ligand **23**, which displays an acyclic pendant arm, afforded 70% yield and 40% ee. Neither bidentate **10** and **11** nor tridentate **13** ligands allowed an increase of both yields and ee's (entries 2–4). Modest conversions and isolated yields were obtained together with ee's ranging from 7 to 10%. An increase of conversion, yield and ee to 84%, 34% and 21%, respectively was observed when oxazoline **21** was used. Further substitution of ligand **21** by a furan or a pyridine



Scheme 6. Atroposelective palladium catalysed coupling.

ring was finally examined. The use of ligand **17** led to a clear decrease of both yield and ee to 14% and 10%, respectively. Catalytic combination using bipyridine **19** afforded poor conversion. Results obtained in the Suzuki–Miyaura coupling are deeply impacted by an increase of steric crowding and of rigidification of the ligand.

In summary, we succeeded in the convenient microwave-assisted synthesis of a series of arylpyridines bearing valuable carboxaldehyde and carbonitrile fragments. Both functionalized groups have been efficiently transformed into amines and oxazolines affording a broad panel of (hetero)arylpyridylmethylamines. First lines of catalytic activity of these new ligands have been described in the atroposelective Suzuki–Miyaura and naphthol oxidative couplings. The influence of additional substituents installed at position 6 of the central pyridine and of the nature, cyclic or acyclic, of the ligand pendant arm considerably impact conversion. Modification of the ligand pattern led to modest to fair ee's in the construction of binaphthyl substrates.

Acknowledgments

The authors are grateful to the French Research Ministry, CNRS – France, the University of Versailles Saint Quentin-en-Yvelines and ANR – France (ANR-11-BS07-030-01) for the financial support and grant (AR).

Supplementary data

Supplementary data (experimental details as well as characterization data and copies of NMR spectra, HPLC and MW profiles) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.01.182.

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