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Catalytic *O*- to *N*-Alkyl Migratory Rearrangement: Transition Metal-Free Direct and Tandem Routes to *N*-Alkylated Pyridones and Benzothiazolones

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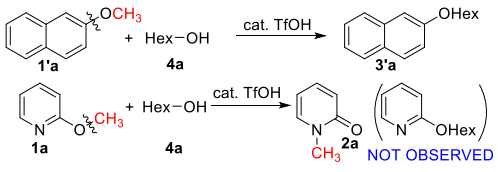
Abstract. The present study reports the synthesis of *N*-alkylated pyridones and benzothiazolones *via O*- to *N*-alkyl group migration under transition metal-free TfOH-catalyzed reaction conditions for the first time, to the best of our knowledge. Primary as well as secondary alkyl groups smoothly migrate under the present reaction conditions. Moreover, a minor modification of the protocol used in this study is found to be applicable for an entirely new tandem synthesis of 2-alkoxy-*N*-heterocycles from the simplest starting materials in a solvent-free reaction conditions. Density Functional Theory (DFT) calculation identifies the energy species associated with the rearrangement, whereas, mechanistic experiments explore the role of the catalyst as the alkyl group transfer mediator.

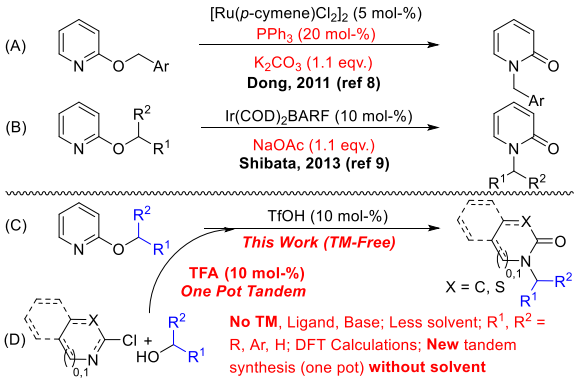
Keywords: Benzothiazolones; Metal-free; Pyridones; Rearrangement; Tandem; DFT

Introduction

Catalysis without using transition metals is emerging as a widely applicable and sustainable alternative owing to the increasing awareness of environmental aspects and limited resources of many transition metals, particularly in pharmaceutical industries, where a very low limit for heavy metal impurities are allowed in the drugs produced.[1a] This has recently been acknowledged by AstraZeneca, and it has been documented that some precious metal resources will be exhausted in 30 years.[1b] One of the major interests of our research group is the development of transition metal-free catalytic methods of aryl C–O bond cleavages of phenols and its simplest derivatives, such as, aryl methyl ethers.[2] Previous studies on nucleophilic *ipso*-substitution of aryl methyl ethers,[2b] showed a different reactivity when



Scheme 1. The new reactivity of 2-methoxypyridine.



Scheme 2. Catalytic synthesis of *N*-substituted-2-alkylation due to the aromaticity of pyridine pyridones.

2-methoxypyridine (**1a**) was used as an electrophile (Scheme 1). Aromatic electrophile, such as 2-methoxynaphthalene (**1'a**), when treated with an *O*-centered nucleophile, such as, 1-hexanol (**4a**), generated the expected *ipso*-substitution product **3'a**. However, hetero aromatic electrophile, such as 2-

10.1002/adsc.201800664

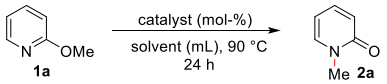
methoxypyridine (**1a**) generated a completely different product 1-methylpyridin-2(1*H*)-one (**2a**), whereas no *ipso*-substitution product was observed. This interesting result prompted us to explore the reaction further owing to the prominence of *N*-alkylated pyridones in natural products[3] and medicinal targets.[4]

Literature survey revealed the lack of general and efficient methods of synthesizing *N*-alkylated pyridones.[5] Alkylations of ambivalent aromatic imidates often suffer from competitions between *O*- and *N*-alkylation because of the aromaticity of the pyridine ring.[6] By comparison, *O*- to *N*-alkyl migratory rearrangement of *O*-alkyl pyridines are more practical due to have relatively easier access to the starting materials *via* nucleophilic aromatic substitution reactions. Stoichiometric version of such reaction was reported by Anderson and co-workers where, the *O*- to *N*-alkyl migration was promoted by LiI;[7] whereas, only two catalytic versions are available using heavy transition metal catalysts, such as, Ru by Dong (Scheme 2A)[8] and Ir, by Shibata (Scheme 2B).[9] These catalytic methods were remarkable on this area but urged for consequential synthetic advancement for addressing concerns such as use of heavy metals, ligands, and stoichiometric amounts of bases/additives. Inspired by this, and in agreement with our interest to develop transition metal-free catalytic transformations, we herein report the first transition metal-free catalytic strategy to achieve *O*- to *N*- alkyl migratory rearrangements in a very small amount of solvent (Scheme 2C). Density Functional Theory (DFT) calculation has been performed, which identifies the lower energy species associated with the catalytic cycle while revealing the role of the catalyst. As an important and practical application, a minor modification of the protocol is found to work for an entirely new tandem synthesis of *N*-alkylated pyridones and benzothiazolones, directly from the simplest starting materials, such as 2-chloropyridine or 2-chlorobenzothiazole, and alcohols (Scheme 2D), without using any organic solvent.

Results and Discussion

The simplest substrate, 2-methoxypyridine (**1a**), was used to optimize the reaction parameters (Table 1). The reaction temperature and time were fixed at 90 °C and 24 h after an initial screening. Different commercially available Brønsted acid catalysts, such as *para*-toluenesulfonic acid monohydrate (*p*-TSA·H_2O), methanesulfonic acid (CH_3SO_3H), trifluoromethanesulfonic acid (TfOH), phosphinic acid (H_3PO_2), and phosphorous acid (H_3PO_3) were tested in 0.5 mL dry 1,2-dichloroethane (DCE) solvent (table 1, entries 1–5). TfOH was found to be the best catalyst in DCE. Changing the solvent made the reaction sluggish, whereas, reducing the amount of solvent to 0.3 mL largely increased the conversion

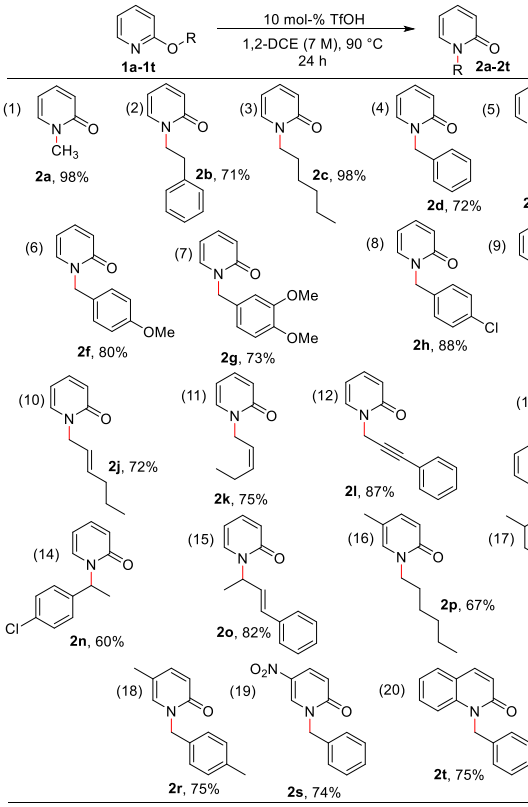
Table 1. Optimization of reaction parameters.[a]



entry	Catalyst (mol-%)	Solvent (mL)	Conversion[b]
1	*p*-TSA·H_2O (20)	DCE (0.5)	20%
2	CH_3SO_3H (20)	DCE (0.5)	22%
3	TfOH (20)	DCE (0.5)	50%
4	H_3PO_2 (20)	DCE (0.5)	5%
5	H_3PO_3 (20)	DCE (0.5)	0%
6	TfOH (20)	DMF (0.5)	35%
7	TfOH (20)	THF (0.5)	41%
8	TfOH (20)	$PhCH_3$ (0.5)	43%
9	TfOH (20)	H_2O (0.5)	15%
10	TfOH (20)	DCE (0.3)	83%
11	TfOH (20)	DCE (0.15)	85%
12	**TfOH (10)**	**DCE (0.15)**	**>99% (98%)[c]**
13	TfOH (5)	DCE (0.15)	76%
14	TfOH (10)	Neat	52%[d]
15	no catalyst	DCE (0.15)	0%

[a] 1.0 mmol **1a** and catalyst in solvent, heated at 90 °C for 24 h. [b] NMR conversion w. r. t. **1a**. [c] Isolated yield in the parenthesis. [d] Isolated yield.

Table 2. Substrate scope towards *N*-alkylated pyridones and quinolone.[a]

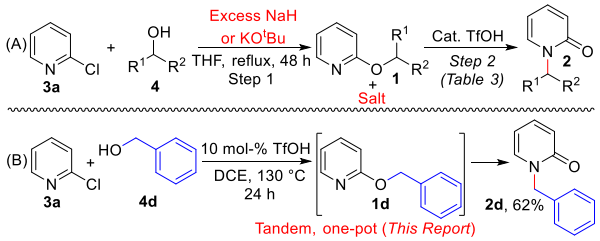


[a] 1.0 mmol **1**, 10 mol-% TfOH in 0.15 mL DCE (~7 M conc.), heated at 90 °C for 24 h. Yields refer to pure and isolated products.

10.1002/adsc.201800664

of **2a** from 50% to 83% (table 1, entries 3 and 10). Finally, the best result was obtained using 10 mol-% TfOH in only 0.15 mL DCE (~7 M conc.), which generated the product **2a** in 98% isolated yield (table 1, entry 12).

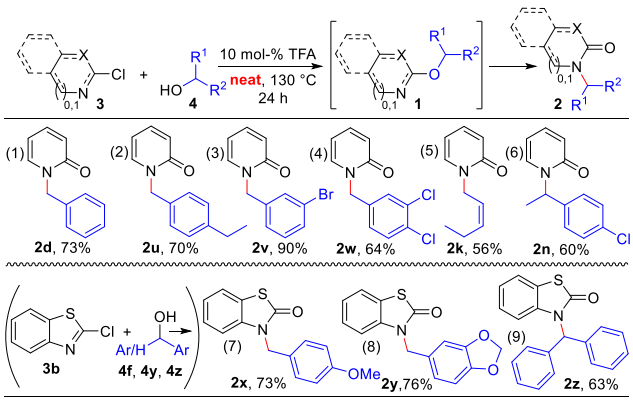
The optimized reaction conditions were applied to a variety of 2-alkoxypyridine derivatives (Table 2). Primary aliphatic groups at the R-position of the substrates underwent the rearrangement reaction smoothly to generate the *N*-alkylpyridone derivatives in high yields (entries 1–3). The desired rearrangement was observed for the substrate having benzyl group at the R position (entry 4). Electronically different substituents at different aromatic positions of the benzyl group also tolerated the reaction conditions and generated the products in good to excellent yields (entries 5–8). Similarly, excellent yield of the product was obtained when R was a 2-naphthyl group (entry 9). The rearrangement occurred for the substrate having *O*-allylic and propargylic substituents (entries 10–12), where the stereochemistry around the double bond was retained in case of *cis*- and *trans*- allylic systems (entries 10–11).[10] Unlike the reported Ru-catalyzed method,[8] the present protocol worked successfully for substrates having more challenging secondary benzyl and allylic substituents at the R position (entries 13–15). Presence of methyl and nitro substituents at the pyridine ring did not interfere with the rearrangement process and the desired products were generated in 67–75% yields (entries 16–19). Moreover, 2-(benzyloxy)quinoline took part in the reaction producing the *N*-benzyl-2-quinolone (**2t**) in 75% yield (entry 20).



Scheme 3. Traditional *vs.* tandem one pot synthesis of *N*-alkylated pyridones.

Except substrate **1a** (commercially available), all the remaining substrates (**1b**–**1t**) were prepared *via* reported[8,11] nucleophilic substitution reaction of the corresponding chloro-pyridine derivatives with alcohols. Excess amounts of alcohols and bases were necessary for this traditional synthetic process. The reaction time was 48 h, and the work-up and purification procedures were tedious and generated stoichiometric amounts of salts as by-products (Scheme 3A). Interestingly, when 2-chloropyridine (**3a**) and benzyl alcohol (**4d**) were exposed under the present catalytic reaction conditions, it generated the same product **2d** with an overall yield of 62% at 130 °C (Scheme 3B). Controlled experiments and GS-MS analysis of the crude reaction mixture

Table 3. Solvent-free tandem synthesis of *N*-alkylated pyridones and benzothiazolones.[a]



[a] 1.0 mmol **3**, 1.5 mmol **4**, 10 mol % TFA, 130 °C for 24 h.

revealed that the reaction proceeded in a tandem fashion, where, TfOH promoted the aromatic nucleophilic substitution reaction to generate the intermediate **1d**, which was converted *in situ* to the product **2d**. To the best of our knowledge, this is the first report of tandem synthesis of *N*-alkylated pyridones from such simple precursors. A brief optimization of the tandem reaction conditions was performed where trifluoroacetic acid (TFA) worked the best instead of TfOH under a noteworthy solvent-free reaction conditions (Table 3). Different substituents at different positions of the benzyl ring of **4**, such as 4-Et, 3-Br, and 3,4-di-Cl, were compatible with the modified protocol furnishing the products **2u**–**2w** directly from 2-chloropyridine (**3a**) and alcohols (**4u**, **4v**, **3w**) in one pot (entries 2–4). Allylic alcohol **4k** (*Z*) reacted smoothly and generated the products **2k** (entry 5). More challenging 2° alcohol, such as **4n**, succeeded in following the tandem reaction sequences to generate the product **2n** in 60% yields (entry 6). Most importantly, when 2-chlorobenzothiazole (**3b**) was exposed to the tandem catalytic reaction conditions instead of 2-chloropyridine (**3a**), it reacted with 4-methoxybenzylic alcohol **4f** smoothly to generate the corresponding benzothiazolone derivative **2x** in 73% yield (entry 7). This is certainly a crucial result as the corresponding 2-alkoxy benzothiazole could not be synthesized as starting material (of Table 2) using reported nucleophilic substitution of 2-chlorobenzothiazole **3b**.[8,11] Piperonyl alcohol **4y**, as well as sterically and electronically more demanding diphenylmethanol **4z** also reacted with **3b**, furnishing the products **2y** and **2z** in 76% and 63% of the yields respectively (entry 8–9). It is important to mention that the core benzothiazolone motif has recently received attention for its anti HIV activity.[12] To the best of our knowledge, this is the first report of tandem synthesis of *N*-alkylated pyridones and benzothiazolones from such simples precursors.

To understand the mechanism of the TfOH catalyzed *O*- to *N*-alkyl rearrangement,[13] mechanistic investigation was performed by DFT

10.1002/adsc.201800664

Table 4. Proton Affinity (in kJ mol^{-1}) in gas-phase calculated at G4 theory.

entry	protonation reaction	proton affinity (PA) calculated	experimental
1	$TfO^- + H^+$	1250.28 (1063.72)[a]	1278.0 ± 9.2
2	**1a** + H^+ protonation at *O*-center	781.24 (968.33)[a]	–
3	**1a** + H^+ protonation at *N*-center	932.65 (1113.56)[a]	–

[a] PA including solvent effect within the parenthesis using a modified version of G4 theory.

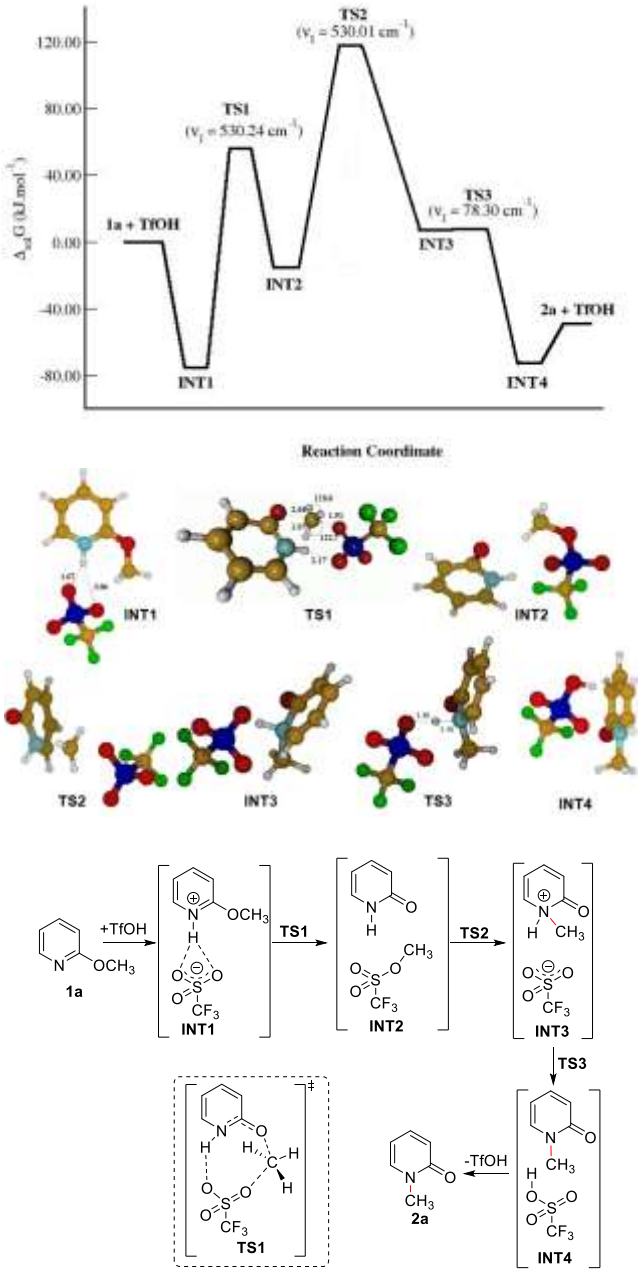


Figure 1. Energy profile (upper), optimized molecular structures (middle), and possible mechanism (lower) for TfOH catalysed conversion of **1a** to **2a**.

calculations. Formation of 1-methylpyridin-2(1*H*)-one (**2a**) from 2-methoxypyridine (**1a**) *via* TfOH catalyzed *O*- to *N*- methyl migratory rearrangement was chosen for computational modeling using the DFT B3LYP/6-311++G(3df,2p) method. The reaction mechanism was studied in 1,2-dichloroethane (DCE) solution using SMD method. The dispersion corrections were included using semiempirical atom pairwise interactions (DFT-D3).

The reaction was assumed to begin with abstraction of the acidic proton (from TfOH) by the nucleophilic oxygen or nitrogen centers of **1a**. To understand the preference between these two centers, theoretical calculations of proton affinity (PA) was carried out (See SI for the electrostatic potential map EPM of **1a**). Table 4 shows the values of PAs for triflate anion (TfO^-), *O*- and *N*-centers of **1a**. The molecular systems were obtained at modified G4 theory[14] by including the solvent effects from the IEFPCM model. While in the gas phase, the TfO^- ion has a higher proton affinity (1250.28 kJ mol^{-1}) in the presence of DCE solvent, and the protonation is more preferable at the *N*-center of **1a** (1113.56 kJ mol^{-1}). Thus, the reaction was initiated by protonation at the *N*- center of **1a** by TfOH catalyst leading to the intermediate **INT1**, which was stable with respect to **1a** and TfOH by -80.90 kJ mol^{-1} (See Figure 1 for energy profile, optimized molecular structures, and possible mechanism). A methyl group transfer from the *O*-center of the substrate to the *O*-center of the catalyst occurred *via* the transition state **TS1**, where the planarity of the methyl group with partially positive sp^2-hybridized carbon center could be observed (56.07 kJ mol^{-1}).[15] After the transfer of the methyl group, an intermediate **INT2**, which was a van der Waals complex of TfOMe and the *N*-protonated-2-pyridone was formed. The methyl group transfer from TfOMe to the *N*-center of the pyridone occurred *via* **TS2** leading to **INT3** having a relative energy of 7.04 kJ mol^{-1}. Subsequently, a proton transfer from the *N*-center of pyridone to *O*-center of the catalyst occurred *via* the transition state **TS3**, which had a relative energy of 7.23 kJ mol^{-1}, leading to the intermediate **INT4**, at -66.27 kJ mol^{-1}. The energy difference between **INT3** and **TS3** was very small because of the involvement of an intramolecular proton transfer having an imaginary frequency value of 78.30 cm^{-1}. The product 1-methylpyridin-2(1*H*)-one (**2a**) was formed at the final step with regeneration of the catalyst. The overall process is exothermic having ΔG at 298.15 K (-50.32 kJ mol^{-1}).

To elucidate the mechanism of the reaction further, some experiments were conducted (Scheme 4). Complete conservation of deuterium at benzylic position of **2d-D** (90% D) was observed when **1d-D** (90% D) was treated with 40 mol-% TfOH (Scheme 4A).[16] Chirality was lost (mostly) when enantio-enriched **1m** (~84% ee) was exposed to the optimum reaction conditions to generate **2m** having ~10% ee

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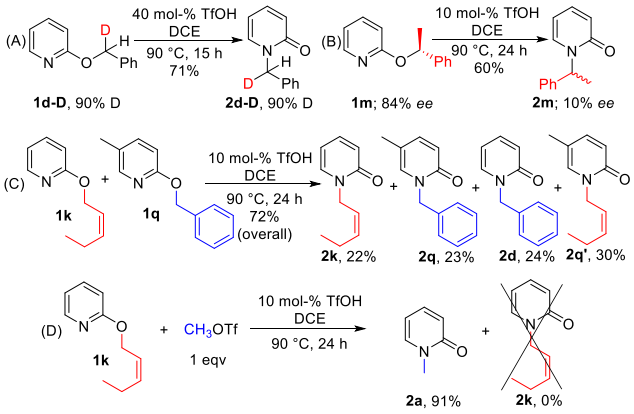
(Scheme 4B). The conservation of deuterium pointed towards a mechanism that did not involve C-H bond



Scheme 4. Experimental studies for mechanistic investigations.

cleavage, which was in agreement with the results obtained from theoretical calculations. However, the racemization experiment (Scheme 4B) suggested an S_N1-type mechanism from **INT2** to **INT3** in the case of the secondary benzylic group, probably owing to the stability of the carbocation intermediate. A crossover experiment was performed, where intermolecular *O*- to *N*-allyl and benzyl group migrations were observed when **1k** and **1q** together were exposed to the TfOH-catalyzed optimized reaction conditions, which generated a mixture of the products **2k**, **2q**, **2d**, **2q′** (Scheme 4C). Most importantly, the stereochemistry around the double bond was retained in the products **2k** and **2q′**. This observation ruled out the possibility of formation of carbocation for primary allylic group migration. Nonetheless, the observed crossover could be explained by anticipating the formation of an allyl triflet intermediate, which could have assisted the intermolecular allylic group transfer without the loss of olefin geometry. To support this hypothesis, another experiment was carried out using substrate **1k** in presence of excess (1 eqv) of methyl triflate (Scheme 4D). Exclusive formation of **2a** was observed under the optimized reaction conditions. This experiment clearly documented the ability of alkyl triflate to transfer alkyl groups under the present reaction conditions which is in agreement with the DFT calculations.

Conclusion

In summary, we have developed a transition metal-free catalytic protocol for the first time, to the best of our knowledge, for accessing *N*-alkylated pyridones and benzothiazolones *via* *O*- to *N*- alkyl group migration. Density Functional Theory (DFT) calculation and mechanistic experiments elucidate the role of the catalyst and the possible reaction mechanism *via* alkyl triflate intermediate. In addition, a minor modification of the protocol allows access to the products from the simplest precursors in an entirely new transition metal- and solvent-free tandem reaction conditions.

Experimental Section

General considerations: ^{1}H and ^{13}C NMR spectra were recorded with a 400 MHz spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CHCl_3$ (δ = 7.28 ppm) as an internal standard. All coupling constants are absolute values and are expressed in Hz. The description of the signals include: s = singlet, d = doublet, t = triplet, q = quadrate, m = multiplet, dd = doublet of doublets, dq = doublet of quadrate, ddd = doublet of doublet of doublets, td = triplet of doublet, and br. s. = broad singlet. ^{13}C NMR spectra were recorded as solutions in $CDCl_3$ with complete proton decoupling. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CDCl_3$ (δ = 77.16 ppm) as an internal standard. The molecular fragments in High Resolution Mass Spectra (HRMS) are quoted as the relation between mass and charge (*m*/*z*). The routine monitoring of reactions was performed with silica gel pre-coated Al plate, which was analyzed with iodine and/or uv light, ^{1}H NMR analysis, and GCMS analysis of the crude reaction mixture. All reactions were executed with oven-dried glassware under nitrogen atmosphere.

General procedure for TfOH catalyzed *O*- to *N*- alkyl migration to synthesize the *N*-alkylated pyridones (2a–2t) (Table 2 in the manuscript): Catalyst TfOH (15 mg, 10 mol-%), 2-alkoxypyridines **1a**–**1t** (1.0 mmol) and 1,2-dichloroethane solvent (0.15 mL) were taken in a 5 mL VWR reaction vial containing a small magnet without using inert atmosphere. The cap of the vial was closed and the reaction mixture was stirred at 90 °C for 24 h. After completion of the reaction (by TLC, GC or NMR), the crude was directly purified by silica-gel (230–400 mesh) column chromatography (flash) using ethyl acetate / hexane solution to afford the desired products **2a**–**1t**.

Experimental procedures and characterisation data of all products described in Scheme 3:

1-Methylpyridin-2(1*H*)-one (2a):[9] Catalyst TfOH (15 mg, 10 mol %) and 2-methoxypyridines **1a** (109 mg, 1.00 mmol) were treated following the general procedure to obtain **2a** as a brown oil (107 mg, 0.98 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.40 (s, 3 H), 6.03 (td, *J* = 6.66, 1.34 Hz, 1 H), 6.41 (dd, *J1* = *J2* = 9.78, 1.22 Hz, 1 H), 7.14–7.25 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.4, 105.8, 120.3, 138.3, 139.5, 162.9 ppm.

1-Phenethylpyridin-2(1*H*)-one (2b):[8] Catalyst TfOH (15 mg, 10 mol %) and 2-phenethoxypyridine **1b** (199 mg, 1.00 mmol) were treated following the general procedure to obtain **2b** as a white solid (141 mg, 0.71 mmol, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.08 (t, *J* = 7.04 Hz, 2 H), 4.16 (t, *J* = 7.34 Hz, 2 H), 6.01 (dd, *J1* = *J2* = 6.46 Hz, 1 H), 6.60 (d, *J* = 9.39 Hz, 1 H), 6.86–6.96 (m, 1 H), 7.16 (d, *J* = 7.04 Hz, 2 H), 7.21–7.36 (m, 4 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.1, 52.1, 105.6, 121.1, 126.8, 128.8, 129.1, 138.0, 138.1, 139.6, 162.7 ppm.

1-Hexylpyridin-2(1*H*)-one (2c):[17] Catalyst TfOH (15 mg, 10 mol %) and 2-(hexyloxy)pyridine **1c** (179 mg, 1.00 mmol) were treated following the general procedure to obtain **2c** as a brown liquid (175 mg, 0.98 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82–0.92 (m, 3 H), 1.25–1.38 (m, 6 H), 1.67–1.79 (m, 2 H), 3.91 (t, *J* = 7.46 Hz, 2 H), 6.14 (td, *J* = 6.60, 1.22 Hz, 1 H), 6.55 (d, *J* = 9.05 Hz, 1 H), 7.19–7.37 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.4, 26.3, 29.2, 31.4, 49.9, 105.7, 121.1, 137.5, 139.1, 162.6 ppm.

1-Benzylpyridin-2(1*H*)-one (2d):[9] Catalyst TfOH (15 mg, 10 mol %) and 2-(benzyloxy)pyridine **1d** (185 mg, 1.00 mmol) were treated following the general procedure to obtain **2d** as a brown oil (133 mg, 0.72 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.17 (s, 2 H), 6.17 (dd, *J1* = *J2* = 6.65 Hz, 1 H), 6.64 (d, *J* = 9.39 Hz, 1 H), 7.21–7.45 (m, 7 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.0, 106.4, 121.4, 128.1, 128.3, 129.0, 136.5, 137.4, 139.6, 162.9 ppm.

1-(4-Methylbenzyl)pyridin-2(1*H*)-one (2e):[9] Catalyst TfOH (15 mg, 10 mol %) and 2-((4-methylbenzyl)oxy)pyridine **1e** (199 mg, 1.00 mmol) were treated following the general procedure to obtain **2e** as a yellow oil (195 mg, 0.98 mmol, 98%). ^{1}H NMR (800 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 5.12 (s, 2 H), 6.14 (td, *J* = 6.75, 1.37 Hz, 1 H), 6.62 (dd, *J1* = *J2* = 9.00 Hz, 1 H), 7.16 (m, *J* = 7.83 Hz, 2 H), 7.21 (m, *J* = 8.22 Hz, 2 H), 7.26 (dd, *J* = 6.65, 1.57 Hz, 1 H), 7.31 (ddd, *J* = 9.00, 6.65, 1.96 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 51.7, 106.3, 121.3, 128.4, 129.7, 133.5, 137.2, 138.0, 139.4, 162.9 ppm.

1-(4-Methoxybenzyl)pyridin-2(1*H*)-one (2f):[9] Catalyst TfOH (15 mg, 10 mol %) and 2-((4-methoxybenzyl)oxy)pyridine **1f** (215 mg, 1.00 mmol) were treated following the general procedure to obtain **2f** as a brown oil (172 mg, 0.80 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.81 (s, 3 H), 5.10 (s, 2 H), 6.15 (dd, *J1* = *J2* = 6.48 Hz, 1 H), 6.62 (d, *J* = 9.29 Hz, 1 H), 6.89 (d, *J* = 8.56 Hz, 2 H), 7.25–7.35 (m, 4 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.6, 55.4, 106.3, 114.4, 121.3, 128.5, 129.9, 137.1, 139.5, 160.0, 162.9 ppm.

1-(3,4-Dimethoxybenzyl)pyridin-2(1*H*)-one (2g): Catalyst TfOH (15 mg, 10 mol %) and 2-((3,4-dimethoxybenzyl)oxy)pyridine **1g** (245 mg, 1.00 mmol) were treated following the general procedure to obtain **2g** as a brown oil (179 mg, 0.73 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.83–3.91 (m, 6 H), 5.08 (s, 2 H), 6.14 (td, *J* = 6.66, 1.35 Hz, 1 H), 6.54–6.67 (m, 1 H), 6.78–6.96 (m, 3 H), 7.19–7.40 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.7, 56.0 (2 C), 106.2, 111.3, 117.8, 120.9, 121.2, 129.0, 137.1, 139.4, 149.1, 149.5, 162.8 ppm; HRMS (ESI) calcd. for $C_{14}H_{16}NO_3$ $[M+H]^+$ *m/z* 246.1125 found *m/z* 246.1112.

1-(4-Chlorobenzyl)pyridin-2(1*H*)-one (2h):[9] Catalyst TfOH (15 mg, 10 mol %) and 2-((4-chlorobenzyl)oxy)pyridine **1h** (220 mg, 1.00 mmol) were treated following the general procedure to obtain **2h** as a white solid (194 mg, 0.88 mmol, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.09 (s, 2 H), 6.15 (td, *J* = 6.72, 1.22 Hz, 1 H), 6.59 (d, *J* = 9.29 Hz, 1 H), 7.17–7.39 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.6, 106.5, 121.5, 129.2, 129.6, 134.1, 135.0, 137.2, 139.7, 162.7 ppm.

1-(Naphthalen-2-ylmethyl)pyridin-2(1*H*)-one (2i):[9] Catalyst TfOH (15 mg, 10 mol %) and 2-(naphthalen-2-ylmethoxy)pyridine **1i** (235 mg, 1.00 mmol) were treated following the general procedure to obtain **2i** as a brown oil (212 mg, 0.90 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.32 (s, 2 H), 6.15 (dd, *J1* = *J2* = 6.60 Hz, 1 H), 6.67 (d, *J* = 9.05 Hz, 1 H), 7.25–7.39 (m, 2 H), 7.44 (dd, *J* = 8.31, 1.47 Hz, 1 H), 7.47–7.56 (m, 2 H,) 7.75 (s, 1 H), 7.78–7.89 (m, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.0, 106.4, 121.3, 126.0, 126.4, 126.5, 127.3, 127.9, 128.9, 133.0, 133.4, 133.9, 137.3, 139.6, 162.9 ppm.

(*E*)-1-(Hex-2-en-1-yl)pyridin-2(1*H*)-one (2j):[18] Catalyst TfOH (15 mg, 10 mol %) and (*E*)-2-(hex-2-en-1-yloxy)pyridine **1j** (177 mg, 1.00 mmol) were treated following the general procedure to obtain **2j** as a brown liquid (127 mg, 0.72 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81–0.93 (m, 3 H), 1.30–1.47 (m, 2 H), 1.96–2.08 (m, 2 H), 4.50 (d, *J* = 6.85 Hz, 2 H), 5.48–5.62 (m, 1 H), 5.62–5.76 (m, 1 H), 6.15 (dd, *J1* = *J2* = 7.34 Hz, 1 H), 6.56 (d, *J* = 8.80 Hz, 1 H), 7.20–7.37 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 22.1, 34.3, 50.5, 106.1, 121.0, 124.3, 136.0, 136.9, 139.3, 162.6 ppm.

(*Z*)-1-(Pent-2-en-1-yl)pyridin-2(1*H*)-one (2k): Catalyst TfOH (15 mg, 10 mol %) and (*Z*)-2-(hex-2-en-1-yloxy)pyridine **1k** (177 mg, 1.00 mmol) were treated following the general procedure to obtain **2k** as a brown liquid (133 mg, 0.75 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (t, *J* = 7.46 Hz, 3 H), 2.13–2.29 (m, 2 H), 4.56–4.68 (m, 2 H), 5.46 (dtt, *J* = 10.70, 7.12, 7.12, 1.59, 1.59 Hz, 1 H), 5.65–5.80 (m, 1 H), 6.16 (td, *J* = 6.66, 1.34 Hz, 1 H), 6.57 (d, *J* = 9.05 Hz, 1 H), 7.21–7.39 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 20.8, 45.2, 106.2, 120.9, 122.9, 136.7, 137.2, 139.3, 162.7 ppm; HRMS (ESI) calcd. for $C_{10}H_{14}NO$ $[M+H]^+$ *m/z* 164.1070 found *m/z* 164.1059.

1-(3-Phenylprop-2-yn-1-yl)pyridin-2(1*H*)-one (2l):[7b] Catalyst TfOH (15 mg, 10 mol %) and 2-((3-phenylprop-2-yn-1-yl)oxy)pyridine **1l** (209 mg, 1.00 mmol) were treated following the general procedure to obtain **2l** as a brown oil (182 mg, 0.87 mmol, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.97 (s, 2 H), 6.23 (td, *J* = 6.72, 1.22 Hz, 1 H), 6.51–6.64 (m, 1 H), 7.25–7.38 (m, 4 H), 7.40–7.52 (m, 2 H), 7.72 (dd, *J1* = *J2* = 6.97, 1.59 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.6, 82.1, 87.3, 106.5, 120.7, 122.1, 128.5, 129.1, 132.0, 136.0, 139.9, 162.3 ppm.

1-(1-Phenylethyl)pyridin-2(1*H*)-one (2m):[11] Catalyst TfOH (15 mg, 10 mol %) and 2-(1-phenylethoxy)pyridine **1m** (199 mg, 1.00 mmol) were treated following the general procedure to obtain **2m** as a brown oil (136 mg, 0.68 mmol, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.74 (d, *J* = 7.09 Hz, 3 H), 6.12 (dd, *J1* = *J2* = 6.60 Hz, 1 H), 6.48 (q, *J* = 6.85 Hz, 1 H), 6.63 (d, *J* = 9.05 Hz, 1 H), 7.11 (d, *J* = 5.62 Hz, 1 H), 7.23–7.44 (m, 7 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 52.5, 106.5, 120.8, 127.6, 128.1, 128.9, 134.4, 138.9, 140.3, 162.6 ppm.

1-(1-(4-Chlorophenyl)ethyl)pyridin-2(1*H*)-one (2n): Catalyst TfOH (15 mg, 10 mol %) and 2-(1-(4-chlorophenyl)ethoxy)pyridine **1n** (234 mg, 1.00 mmol) were treated following the general procedure to obtain **2n** as a white solid (140 mg, 0.60 mmol, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.72 (d, *J* = 7.09 Hz, 3 H), 6.14 (dd, *J1* = *J2* = 6.60 Hz, 1 H), 6.43 (q, *J* = 6.93 Hz, 1 H), 6.61 (d, *J* = 9.05 Hz, 1 H), 7.05–7.13 (m, 1 H), 7.21–7.31 (m, 3 H), 7.31–7.40 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 51.9, 106.7, 120.9, 128.9, 129.1, 134.0, 134.0, 138.9, 139.0, 162.5 ppm; HRMS (ESI) calcd. for $C_{13}H_{13}ClNO$ $[M+H]^+$ *m/z* 234.0680 found *m/z* 234.0669.

(*E*)-1-(4-phenylbut-3-en-2-yl)pyridin-2(1*H*)-one (2o): Catalyst TfOH (15 mg, 10 mol %) and (*E*)-2-((4-phenylbut-3-en-2-yl)oxy)pyridine **1o** (225 mg, 1.00 mmol) were treated following the general procedure to obtain **2o** as a brown oil (178 mg, 0.79 mmol, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.58 (d, *J* = 6.85 Hz, 3 H), 5.98 (ddd, *J* = 6.85, 5.01, 1.83 Hz, 1 H), 6.21 (td, *J* = 6.72, 1.47 Hz, 1 H), 6.32 (dd, *J* = 16.02, 5.01 Hz, 1 H), 6.59–6.69 (m, 2 H) 7.30–7.38 (m, 4 H), 7.39–7.43 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 51.2, 106.5, 121.0, 126.7, 128.3, 128.8, 129.0, 132.6, 134.2, 136.2, 139.1, 162.4 ppm. HRMS (ESI) calcd. for $C_{15}H_{16}NO$ $[M+H]^+$ *m/z* 226.1226 found *m/z* 226.1227.

1-Hexyl-5-methylpyridin-2(1*H*)-one (2p): Catalyst TfOH (15 mg, 10 mol %) and 2-(hexyloxy)-5-methylpyridine **1p** (193 mg, 1.00 mmol) were treated following the general procedure to obtain **2p** as a brown oil (129 mg, 0.67 mmol, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.36 Hz, 3 H), 1.26–1.34 (m, 6 H), 1.72 (t, *J* = 6.48 Hz, 2 H), 2.17 (s, 3 H), 3.88 (t, *J* = 7.46 Hz, 2 H), 5.96–6.08 (m, 1 H), 6.38 (s, 1 H), 7.14 (d, *J* = 6.85 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 21.3, 22.6, 26.4, 29.4, 31.6, 49.6, 108.6, 119.5, 136.6, 151.0, 162.8 ppm; HRMS (ESI) calcd. for $C_{12}H_{20}NO$ $[M+H]^+$ *m/z* 194.1539 found *m/z* 194.1528.

1-Benzyl-5-methylpyridin-2(1*H*)-one (2q):[9] Catalyst TfOH (15 mg, 10 mol %) and 2-(benzyloxy)-5-methylpyridine **1q** (199 mg, 1.00 mmol) were treated following the general procedure to obtain **2q** as a brown oil (149 mg, 0.75 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18 (d, J = 0.98 Hz, 3 H), 5.13 (s, 2 H), 6.00 (dd, J = 6.97, 1.83 Hz, 1 H), 6.40–6.47 (m, 1 H), 7.15 (d, J = 7.09 Hz, 1 H), 7.25–7.41 (m, 5 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 51.5, 108.9, 119.7, 128.0, 129.0, 136.2, 136.8, 151.2, 162.8 ppm.

5-Methyl-1-(4-methylbenzyl)pyridin-2(1*H*)-one (2r): Catalyst TfOH (15 mg, 10 mol %) and 5-methyl-2-((4-methylbenzyl)oxy)pyridine **1r** (213 mg, 1.00 mmol) were treated following the general procedure to obtain **2r** as a white solid (160 mg, 0.75 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.14 (s, 3 H), 2.30 (s, 3 H), 5.00–5.09 (m, 2 H), 5.95 (dd, J = 6.97, 1.83 Hz, 1 H), 6.39 (s, 1 H), 7.08–7.14 (m, 3 H), 7.14–7.20 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 21.2, 51.2, 108.8, 119.5, 128.2, 129.6, 133.7, 136.1, 137.7, 151.0, 162.7 ppm; HRMS (ESI) calcd. for $C_{14}H_{16}NO$ $[M+H]^+$ *m/z* 214.1226 found *m/z* 214.1222; Melting point observed: 75–78 °C.

1-Benzyl-5-nitropyridin-2(1*H*)-one (2s):[19] Catalyst TfOH (15 mg, 10 mol %) and 2-(benzyloxy)-5-nitropyridine **1s** (230 mg, 1.00 mmol) were treated following the general procedure to obtain **2s** as a white solid (170 mg, 0.74 mmol, 74%). ^{1}H NMR (800 MHz, $CDCl_3$): δ = 5.20 (s, 2 H), 6.62 (d, J = 9.78 Hz, 1 H), 7.37 (d, J = 6.65 Hz, 2 H), 7.38–7.45 (m, 3 H), 8.09 (dd, J = 10.17, 3.13 Hz, 1 H), 8.60 (d, J = 2.74 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.3, 119.8, 128.6, 129.1, 129.4, 130.9, 133.2, 134.4, 139.1, 161.6 ppm.

1-Benzylquinolin-2(1*H*)-one (2t):[18] Catalyst TfOH (15 mg, 10 mol %) and 2-(benzyloxy)quinoline **1t** (235 mg, 1.00 mmol) were treated following the general procedure to obtain **2t** as a yellow oil (176 mg, 0.75 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.59 (br. s., 2 H), 6.83 (d, J = 9.54 Hz, 1 H), 7.16–7.36 (m, 7 H), 7.40–7.49 (m, 1 H), 7.59 (dd, J = 7.82, 1.47 Hz, 1 H), 7.77 (d, J = 9.54 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.1, 115.2, 121.1, 121.8, 122.4, 126.7, 127.4, 129.0, 129.0, 130.8, 136.5, 139.6, 139.7, 162.7 ppm.

General procedure for TFA catalyzed solvent free tandem synthesize of *N*-alkylated pyridones 2d, 2u, 2v, 2w, 2k, 2n and benzothiazolones 2x, 2y, 2z (Table 3 in the manuscript): Catalyst TFA (11 mg, 10 mol-%), 2-chloropyridine **3a** or 2-chlorobenzo[*d*]thiazole **3b** (1.0 mmol), and alcohol **4** (1.5 mmol) were taken in a 5 mL VWR reaction vial containing a small magnet without using inert atmosphere. The cap of the vial was closed and the reaction mixture was stirred at 130 °C for 24 h without any external solvents. After completion of the reaction (by TLC, GC or NMR), the crude was directly purified by silica-gel (230–400 mess) column chromatography (flash) using ethyl acetate / hexane solution to afford the desired products **2d**, **2u**, **2v**, **2w**, **2k**, **2n**, **2x**, **2y**, **2z**.

Experimental procedures and characterisation data of all products described in Scheme 5 (excluding characterization data for those compounds already given before):

1-Benzylpyridin-2(1*H*)-one (2d):[9] Catalyst TFA (11 mg, 10 mol %), and 2-chloropyridine **3a** (114 mg, 1.00 mmol), phenylmethanol (162 mg, 1.50 mmol) were treated following the general procedure to obtain **2d** as a brown oil (135 mg, 0.73 mmol, 73%).

1-(4-Ethylbenzyl)pyridin-2(1*H*)-one (2u): Catalyst TFA (11 mg, 10 mol %), and 2-chloropyridine **3a** (114 mg, 1.00 mmol), (4-ethylphenyl)methanol **4u** (204 mg, 1.50 mmol) were treated following the general procedure to obtain **2u** as a brown oil (146 mg, 0.70 mmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): 0.91 (t, J = 7.70 Hz, 3 H), 2.32 (q, J = 7.74 Hz, 2 H), 4.80 (s, 2 H), 5.82 (td, J = 6.72, 1.22 Hz, 1 H), 6.30 (d, J = 9.05 Hz, 1 H), 6.79–7.05 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.6, 28.6, 51.8, 106.3, 121.3, 128.4, 128.5, 133.7, 137.3, 139.4, 144.3, 162.9 ppm; $C_{14}H_{16}NO$ $[M+H]^+$ *m/z* 214.1226 found *m/z* 214.1225.

1-(3-Bromobenzyl)pyridin-2(1*H*)-one (2v):[20] Catalyst TFA (11 mg, 10 mol %), 2-chloropyridine **3a** (114 mg, 1.00 mmol) and (3-bromophenyl)methanol **4v** (281 mg, 1.50 mmol, 90%) were treated following the general procedure to obtain **2v** as a white solid (238 mg, 0.90 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.01 (s, 2 H), 6.08 (td, J = 6.72, 1.47 Hz, 1 H) 6.49–6.56 (m, 1 H), 7.07–7.20 (m, 3 H) 7.24 (ddd, J = 9.05, 6.72, 2.08 Hz, 1 H) 7.31–7.36 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.2, 106.3, 120.8, 122.5, 126.4, 130.2, 130.6, 130.8, 137.2, 138.5, 139.6, 162.2 ppm.

1-(3,4-Dichlorobenzyl)pyridin-2(1*H*)-one (2w): Catalyst TFA (11 mg, 10 mol %), 2-chloropyridine **3a** (114 mg, 1.00 mmol) and (3,4-dichlorophenyl)methanol **4w** (281 mg, 1.50 mmol) were treated following the general procedure obtain **2w** as a white solid (163 mg, 0.64 mmol, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.26 (s, 2 H), 6.21 (td, J = 6.72, 1.47 Hz, 1 H), 6.63 (d, J = 9.05 Hz, 1 H), 7.03–7.12 (m, 1 H), 7.17 (dd, $J1$ = $J2$ = 7.83 Hz, 1 H), 7.32 (dd, J = 6.85, 1.47 Hz, 1 H) 7.34–7.47 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.4, 106.5, 121.4, 127.9, 130.0, 131.6, 133.5, 136.0, 137.6, 140.0, 162.6 ppm; HRMS (ESI) calcd. for $C_{12}H_{10}Cl_2NO$ $[M+H]^+$ *m/z* 254.0134 found *m/z* 254.0131; Melting point observed: 89–92 °C.

(*Z*)-1-(Pent-2-en-1-yl)pyridin-2(1*H*)-one (2k): Catalyst TFA (11 mg, 10 mol %), 2-chloropyridine **3a** (114 mg, 1.00 mmol) and (*Z*)-pent-2-en-1-ol **4k** (129 mg, 1.50 mmol) were treated following the general procedure to obtain **2k** as a brown liquid (163 mg, 0.56 mmol, 56%).

1-(1-(4-Chlorophenyl)ethyl)pyridin-2(1*H*)-one (2n): Catalyst TFA (11 mg, 10 mol %), 2-chloropyridine **3a** (114 mg, 1.00 mmol) and 1-(4-chlorophenyl)ethan-1-ol (**4n**) (236 mg, 1.50 mmol) were treated following the general procedure to obtain **2n** as a white solid (140 mg, 0.60 mmol, 60%).

3-(4-Methoxybenzyl)benzo[*d*]thiazol-2(3*H*)-one (2x): Catalyst TFA (11 mg, 10 mol %), 2-chlorobenzo[*d*]thiazole **3b** (170 mg, 1.00 mmol) and (4-methoxyphenyl)methanol (**4f**) (207 mg, 1.50 mmol) were treated following the general procedure to obtain **2x** as a white solid (198 mg, 0.73 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 3 H), 5.11 (s, 2 H), 6.84–6.90 (m, 2 H), 7.02 (d, J = 8.07 Hz, 1 H), 7.11–7.18 (m, 1 H), 7.21–7.31 (m, 3 H), 7.44 (dd, J = 7.70, 0.86 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.8, 55.3, 111.3, 114.3, 122.6, 122.7, 123.2, 126.4, 127.3, 128.7, 137.0, 159.3, 170.3 ppm; HRMS (ESI) calcd. for $C_{15}H_{14}NO_2S$ $[M+H]^+$ *m/z* 272.0740 found *m/z* 272.0737; Melting point observed: 65–67 °C.

3-(Benzo[*d*][1,3]dioxol-5-ylmethyl)benzo[*d*]thiazol-2(3*H*)-one (2y): Catalyst TFA (11 mg, 10 mol %), 2-chlorobenzo[*d*]thiazole **3b** (170 mg, 1.00 mmol) and benzo[*d*][1,3]dioxol-5-ylmethanol (**4y**) (228 mg, 1.50 mmol) were treated following the general procedure to obtain **2y** as a white solid (217 mg, 0.76 mmol, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.07 (s, 2 H), 5.94 (s, 2 H), 6.74–6.79 (m, 1 H), 6.79–6.85 (m, 2 H), 6.98–7.04 (m, 1 H), 7.12–7.18 (m, 1 H), 7.22–7.28 (m, 1 H), 7.41–7.46 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.1, 101.3, 107.9, 108.6, 111.4, 120.9, 122.8, 123.4, 126.5, 129.1, 137.1, 147.5, 148.3, 170.4 ppm. HRMS (ESI) calcd. for $C_{15}H_{12}NO_3S$ $[M+H]^+$ *m/z* 286.0532 found *m/z* 286.0536; Melting point observed: 91–94 °C.

3-Benzhydrylbenzo[*d*]thiazol-2(3*H*)-one (2z): Catalyst TFA (11 mg, 10 mol %), 2-chlorobenzo[*d*]thiazole **3b** (170 mg, 1.00 mmol) and diphenylmethanol (**4z**) (276 mg, 1.50

mmol) were treated following the general procedure to obtain **2z** as a white solid (200 mg, 0.63 mmol, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.78 (dd, *J* = 8.19, 0.86 Hz, 1 H), 7.04 (td, *J* = 7.83, 1.47 Hz, 1 H), 7.10 (td, *J* = 7.64, 1.34 Hz, 1 H), 7.29–7.41 (m, 11 H), 7.42–7.48 (m, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.0, 114.0, 122.5, 122.6, 123.0, 125.8, 128.1, 128.5, 128.8, 136.8, 137.0, 170.6 ppm; HRMS (ESI) calcd. for $C_{20}H_{16}NOS$ $[M+H]^+$ *m/z* 318.0947 found *m/z* 318.0943; Melting point observed: 162–163 °C.

Computational methods: Electronic and molecular structures of compounds originated from the Brønsted acid catalyzed *O*- to *N*-alkyl migratory rearrangement of 2-methoxypyridine were investigated through theoretical calculation. The calculations were performed using DFT employing the hybrid exchange-correlation functional (B3LYP). Geometry optimizations and evaluation of harmonic frequencies were performed at the B3LYP/6-311++G(2d,p) level of theory. The optimized structures were confirmed to be minima by vibrational frequency analysis. The single point energy calculations were carried out at B3LYP/6-311++G(3df,2p) level on corresponding optimized geometries. The solvent effects (of 1, 2-dichloroethane, DCE) were included using the SMD solvation model. The dispersion corrections were included using semi empirical atom pair wise interactions. DFT-D3 method developed by Grimme *et al* was employed because this methodology has been shown to give quite accurate thermo chemistry for both covalently bonded systems and systems containing dispersion forces.[21] All computations were performed using the Gaussian 09, Revision D.01[22] and Gamess 2014, Version R1[23] quantum chemistry packages.

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FULL PAPER

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Adv. Synth. Catal. **Year**, *Volume*, Page – Page

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