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Copper-Catalyzed C-4 Carboxylation of 1-Naphthylamide Derivatives with CBr_4/MeOH

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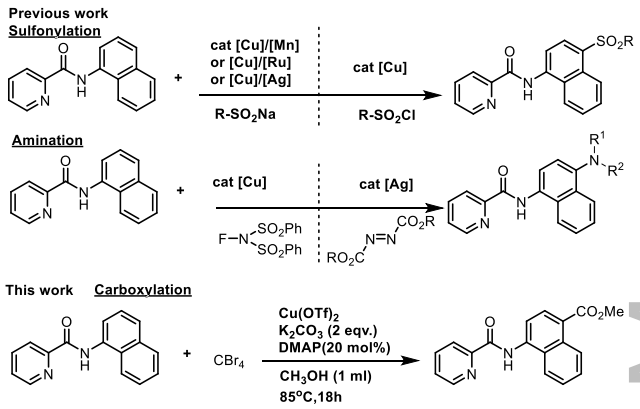
Abstract. A simple and practical Copper catalyzed C-4 carboxylation reaction of 1-naphthylamide derivatives using carbon tetra bromide and methanol is reported here. Picolinamide and its derivatives are used as a bidentate directing group for the distal C4-H functionalization. Various substituted naphthylamide derivatives, and anilides are employed for the carboxylation and proceeds in good yields under mild condition. From the outcome of experimental results, it is proposed that C4-H carboxylation reaction of 1-naphthylamides might proceed through a single electron transfer (SET) pathway

Keywords: Carboxylation; Copper-catalyzed; regioselective; 1-naphthaylamide; SET

Transition metal catalyzed direct C-H functionalization strategy is rapidly growing for the synthesis of valuable organic molecules.[1] In this active research area, the regioselective carboxylation of arenes and heteroarenes is one of the important organic transformation to install a C1 unit in the aromatic moiety.[2] Naphthalenes are privileged aromatic compounds that widely presents in numerous pharmaceuticals, agrochemicals and functional materials like organic semiconductor, or electroluminescent materials.[3] In this context, considerable efforts have been made for the synthesis of substituted naphthalene compounds *via* direct C-H functionalization.[4] Among them, regioselective functionalization of 1-nathylamine scaffolds using a bidentate chelation controlled strategy achieved significant progress in recent years. [5] Directing group assisted adjacent ortho (C-2) and peri (C-8) selective C-H functionalization is very common, as it is controlled by the cyclometalation strategy. [6] However, over the couple of years' a little progress has been achieved on para-(C-4) selective C-H functionalization which proceeds through bidentate chelation assisted single electron transfer pathway. In 2017, Manolikakes and co-workers[7] first reported the copper catalyzed remote para C-H sulfonylation of 1-naphthylamide framework using Daugulis[8] developed bidentate picolinamide (PA) as a directing group. Later, Weng and Lu et al. reported the copper catalyzed sulfonylation of 1-naphthylamide.[9] Ru/ Cu or Cu/Ag catalyzed C4-H sulfonylation[10] and silver catalyzed amination were reported by Wu and co-workers.[11] Recently, Yu et al. reported Cu catalyzed C-4 phosphorylation and trifluromethylation.[12] Most of the reports are on C-hetero atom bond forming reactions. Key steps for the remote functionalization is bidentate chelation controlled SET to the naphthalene ring to generate the reactive radical cation species, followed by the addition of nucleophile or radical. The regioselective carboxylation of naphthalene is a vital transformation and as it could be elaborated to important functional group like acid, ester and amides. Therefore, the development of a simple and practical method for carboxylation (C-C bond formation) at C4-position of naphthylamide is still remain a challenge and strongly desired.



Scheme 1. *para*-selective C-H functionalization of naphthalene

In this direction, CBr_4 was recognized as a masked carboxylating agent, was 1st reported by Khusnutdinovand co-workers for C2-carboxylation of benzofuran using an iron catalyst at 140 °C. Ruthenium catalyzed meta-carboxylation of 2-phenyl

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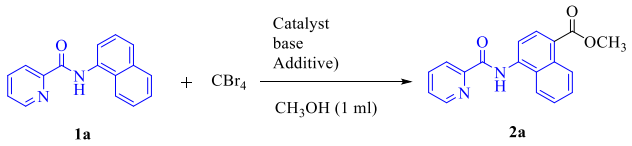
Table 1: Optimization of reaction condition [a]

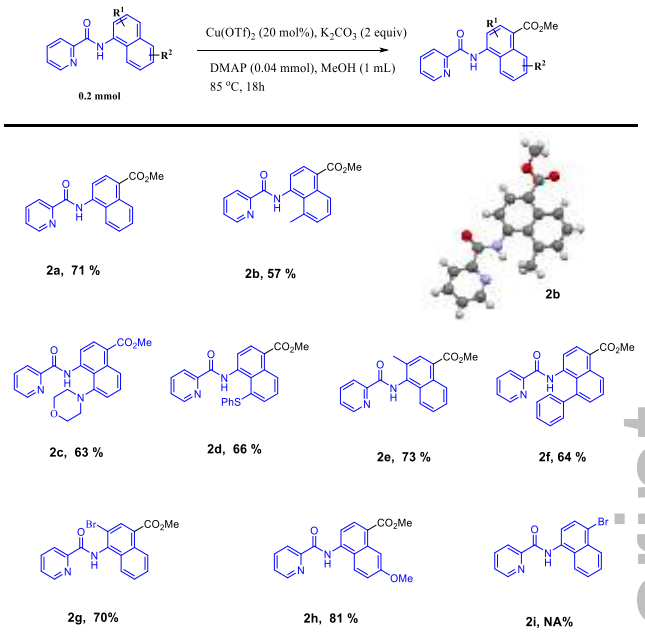


Entry	Catalyst (mol%)	Base	Additive	Yield (%)
1	$Cu(OTf)_2$ (10%)	K_2CO_3	-	36
2	$Cu(OTf)_2$ (20%)	K_2CO_3	-	63
3	$Cu(OTf)_2$ (30%)	K_2CO_3	-	63
4	$CuBr_2$	K_2CO_3	-	32[b]
5	$Cu(OAc)_2$	K_2CO_3	-	56
6	$Cu(OTf)_2$ (20%)	K_2CO_3	DMAP	71
7	$Cu(OTf)_2$ (20%)	Na_2CO_3	DMAP	64
8	$Cu(OTf)_2$ (20%)	K_3PO_4	DMAP	33
9	$Cu(OTf)_2$ (20%)	NaOAc	DMAP	35
10	$Cu(OTf)_2$ (20%)	iPr_2NH	DMAP	27
11	$Cu(OTf)_2$ (20%)	DABCO	DMAP	34
12	$Cu(OTf)_2$ (20%)	Et_3N	DMAP	41
13	$Cu(OTf)_2$ (20%)	-	DMAP	36
14	$Cu(OTf)_2$ (20%)	-	-	19
15	-	K_2CO_3	DMAP	nr
16	$Cu(OTf)_2$ (20%)	K_2CO_3	DMAP	20[c]
17	$Cu(OTf)_2$ (20%)	K_2CO_3	DMAP	27[d]

[a]1a (0.2 mmol), CBr_4 (3 equiv.), base (2 equiv.), additive (20 mol%) and MeOH (1ml) at 85°C, for 18h, otherwise mentioned in a sealed tube under inert atmosphere, isolated yields. [b]bromination product obtained ~20%; [c]air atmosphere; [d] at 65 °C;

pyridine and C2-carboxylations of indoles are independently reported by Greaney [13] and Bandini [14] group respectively. carboxylation of styrene using cooperative Eosin-Y as photocatalyst and cobalt iodide as catalyst with CBr_4 and DMSO was reported by Tang and co-workers. [15] In continuation of our work on regioselective C-H bond functionalization,[16] herein, we report a simple and practical strategy for the regioselective carboxylation of 1-naphthalene amide derivatives at C-4 position by exploring bidentate chelation controlled SET strategy using carbon tetra bromide as C1-source. We began our studies using N-(naphthalene-1-yl) picolinamide (1a) as a model substrate for the carboxylation of 1-naphthalne amide framework with CBr_4 and MeOH (2 mL). The results are summarized in Table 1. Initially $Cu(OTf)_2$ (10 mol%) was chosen as a catalyst, K_2CO_3 was used as a base, a modest yield (36%, Table 1, entry 1) of our desired *para*-selective carboxylated product was obtained. We realized that, increase of catalyst loading might be effective for this reaction, to our delight with 20 mol% catalyst loading 63% of desired product was obtained, further increase of catalyst loading to 30 mol% does not have any affect (62%, entry 3), Also, other copper salts were found less reactive (entries 4-5). Notably, addition of DMAP (20 mol%) as additive

Table 2: Substrate scope of 1-naphthylamides



1 (0.2 mmol), CBr_4 (3 equiv.), K_2CO_3 (2 equiv.), DMAP (20 mol%) and MeOH (1ml) at 85°C, for 18h, in a sealed tube under inert atmosphere.

increases the yield to 71% (entry 6).

Next, we replaced K_2CO_3 with other inorganic and organic bases, but inferior results were obtained (entries 7-12). Control experiments revealed that base is essential for this reaction (entries 13-14). The reaction does not proceed in absence of the catalyst (entry 15). When reaction was carried under air atmosphere resulted lower yield (entry 16), indicates the interference of oxygen in the reaction. In addition, performing the reaction at lower temperature, decreased the yield (entry 17).

Under the optimized reaction conditions (entry 6), we then explored the substrate scope of the various naphthaylamide derivatives, as shown in **Table 2**. The carboxylation with various substituents at the C2, C6 and C8 position of the naphthalene ring was first explored, C2-methyl substituent provided the desired carboxylated product in good yield (Table 2, 2b, 73%), the structure of the compound was confirmed by single crystallography.[17] Various electron -donating and –withdrawing substituent at C8 position of 1-naphthylamine had showed excellent compatibility and almost similar yields were obtained. Electron donating groups like methyl, piperidin-1-yl, -SPh, -Ph afforded good yields of desired carboxaylated product (entries 2c-2f). In the presence of bromo as electron withdrawing group, similar yield was observed (2g, 70%,). C6-methoxy substituted naphthylamide derivatives afforded the corresponding carboxylated product in high yields (2i, 81%). When the C4-position is blocked, no carboxylation was observed, as expected (2i).

Next, the role of the directing group in the carboxylation reaction was examined. Several

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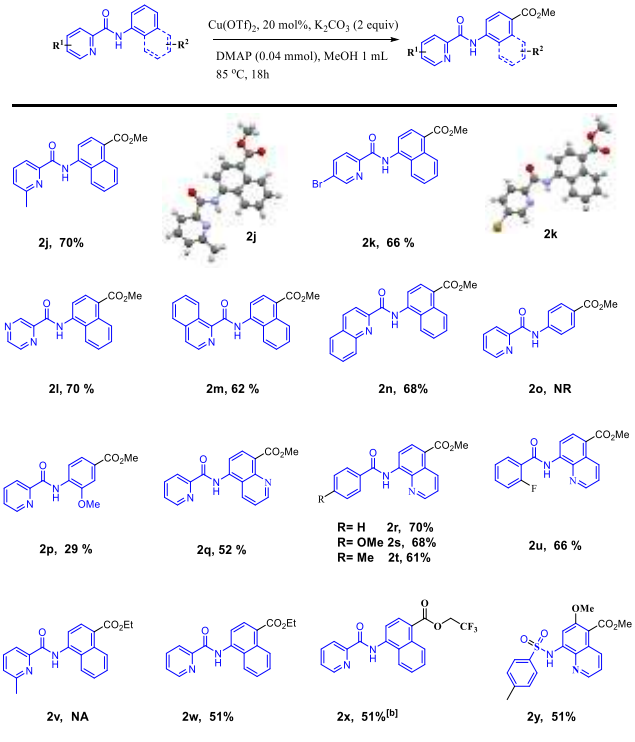
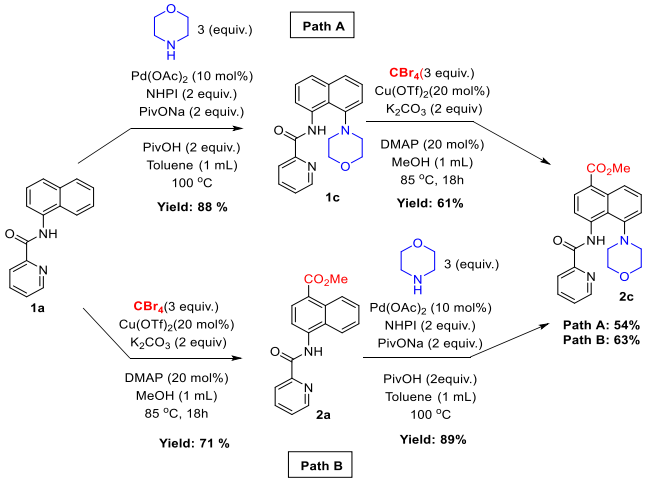
Table 3: Substrate scope for carboxylation reaction [a]



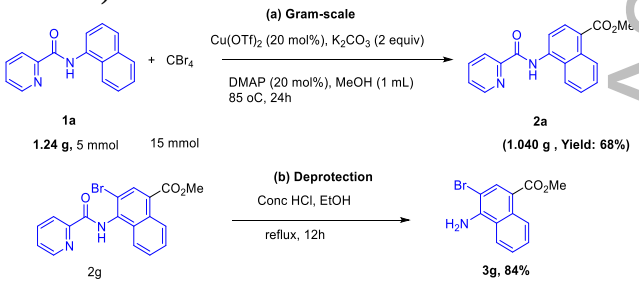
[a]1 (0.2 mmol), CBr_4 (3 equiv.), K_2CO_3 (2 equiv.), DMAP (20 mol%) and MeOH (1ml) at 85°C, for 18h, in a sealed tube under inert atmosphere; [b] 36h.

substituted and analogous amides of picolinamide were tested and the results are summarized in table 3. Under the optimal reaction condition, C3-methyl and C5-bromo substituted pyridine are well tolerated and desired carboxylated products were obtained in similar yield (Table 3, entries 2j-2k, 70 and 66 %). The structure of the carboxylated products were well characterized by single crystallography.[17] Interestingly, additional N atom in the pyridine ring, pyrazine also furnished good yield (entry 2l, 70%). Instead of pyridine when isoquinoline (1m) and quinoline carboxamide (1n) were tested, similar effectivity was observed (entries 2m and 2n). Next, we turned our attention for the carboxylation of other aromatic and heteroaromatic compounds (table 3). First, reaction with aniline derivatives were investigated, interestingly our developed carboxylation is sensitive to the benzene ring, with simple aniline moiety no carboxylated product was obtained (2o), whereas substrates bearing electron donating group (-OMe), carboxylation proceeds, furnished in low yields (2p, 29%), Furthermore, the carboxylation occurs smoothly with quinoline moiety, under the standard condition N-(quinolin-5-yl)picolinamide afforded the C8-carboxylated product in good yield (entry 2q, 52%). Interestingly, where 8-amino quinoline moiety act as a directing group, with various substituted benzamide moiety, reaction proceeds well, and the desired carboxylated products were obtained in good yields (entries 2r-2u). To further demonstrate the potential application of our developed methodology, we have



Scheme 2: Sequential C-H functionalization of 1-naphthaylamide moiety.

carried out the carboxylation with ethanol and 2,2,2-trifluoroethanol with the model substrate (1a) and afforded ethyl carboxylate (2v-2w) and fluorinated carboxylate (2x, 51%) in moderate yields, for the latter case (2x) elongated reaction time (36h) is required to complete the reaction. In this case after 18h, we have isolated the intermediate (orthoester, 3x) as a major product. To showcase the synthetic utilty of our developed methodology, we have regioselectivity carboxylated TSQ (6-Methoxy-8-p-Toluenesulfonamido-Quinoline, 1y), a common fluorescent sensor for cellular zinc.[18] Further, we have carried out the sequential C-H functionalization of 1-naphthayl amide moiety to synthesize various substituted naphthalene in a regioselective manner (Scheme 2). In path A, Pd catalyzed *peri*-selective amination [6d] was carried out in the 1st step, to get intermediate 1c, which was carboxylated by our newly developed methodology at C4 position. In path B, C-H functionalization sequence was reversed, initially carboxylation at C-4 position and next, amination was carried out, little higher overall yield was obtained in path B. The reaction can be easily scaled-up without affecting the yield, also selective deprotection of picolinamide with HCl afforded high yield, further showcased the synthetic utility of our methodology (scheme 3).



Scheme 3: a) Gram Scale Synthesis b) deprotection of DG

To better understand the reaction profile we have monitored the reaction progress with time by HPLC (**Figure 1-a**). Interestingly, we have found the

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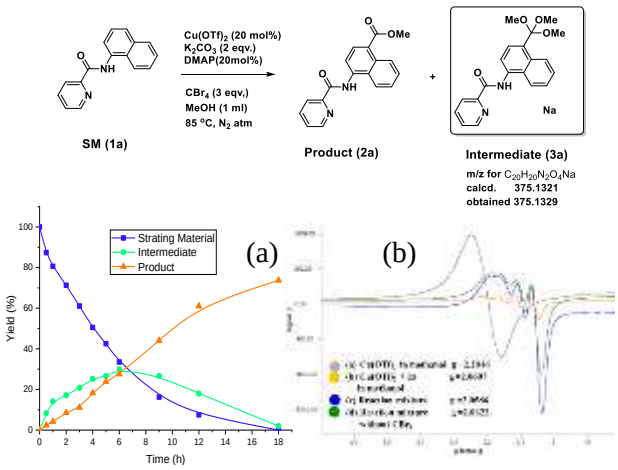
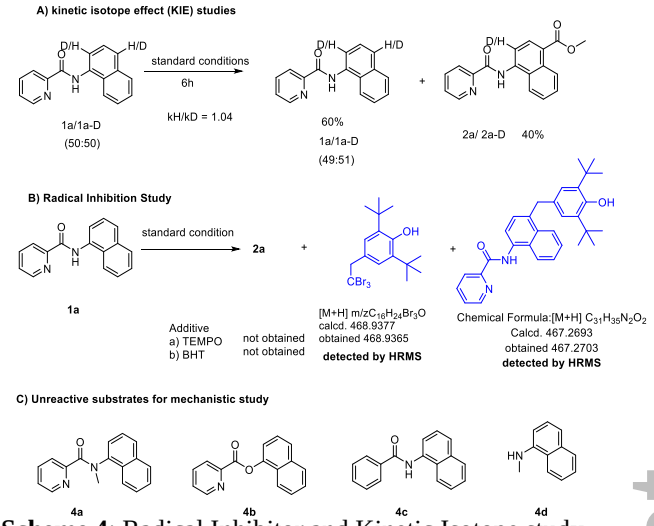


Figure 1: (a) Reaction kinetics; (b) EPR spectra

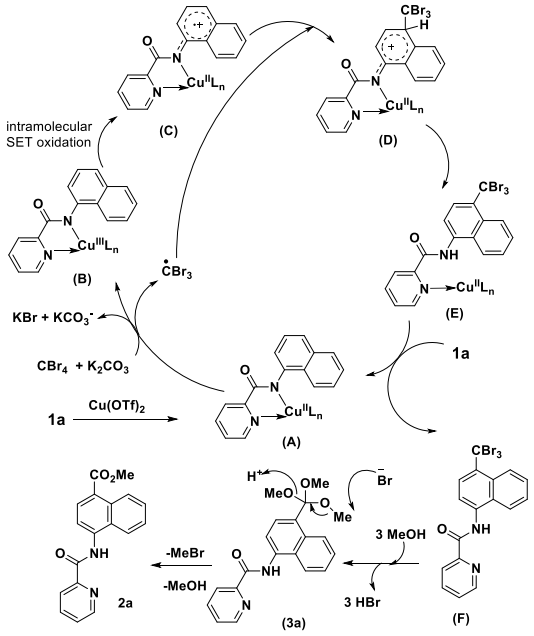


Scheme 4: Radical Inhibitor and Kinetic Isotope study

formation of an intermediate along with the desired product. However, in TLC monitoring we have not found any intermediate spot, may be it has the same Rf with the product. We have identified the intermediate (**3a**), tri-methoxy compound by HRMS analysis (see SI for details), which indiactes that the reaction proceed *via* complete methanolysis pathway with the formation of an ortho ester, (trimethoxymethyl)naphthalene (**3a**). From the reaction kinetics, it was observed that initial few hours (6h) reaction produces intermediate **3a** along with carboxylated product **2a**. The maximum formation of orthoester 3a was observed around 6h with ~70% conversion of starting material and, after that it essentially converted to the desired ester product **2a** (figure **1a**) within 18h. To investigate the reaction mechanism, we have carried out kinetic isotope effect (KIE) experiment. KIE was determined by the intermolecular competitive reaction of two isotopomeric substrates (1a and 1a-D, Scheme 4-A), and k_H/k_D =1.04 was obtained. Which indicates that C-H bond cleavage was not involved in the rate determining step.

Next, we carried out the radical inhibition and capture experiment (Scheme 4-B) upon addition of the radical scavenger, TEMPO or BHT the reaction was completely inhibited, we have also identified the BHT trapped CBr_3 compound as well as BHT trapped **1a** in HRMS (see ESI for details). Which suggest that the reaction might undergo through a single electron transfer (SET) pathway. To get more information, EPR (electro paramagnetic resonance) experiments were carried out, showed in **Figure 1b**, (a) $Cu(OTf)_2$ in methanol solvent showed a EPR signal at g = 2.2016. (b) After addition of the substrate **1a** with catalyst in methanol, complex formation takes place, which clearly showed in EPR with a signal at g = 2.0607, and also (c) similar EPR signals with all the reagents (g = 2.0586) and (d) in absence of CBr_4 (g = 2.0622). moreover presence of Cu(II) species was clearly observed in all conditions. Several designed substrates (**4a-4d**) were synthesized and tested under the standard reaction condition to get some insight on the co-ordination of substrate with copper, but no caboxylated products were obtained. These results suggest that the presence of both pyridine nitrogen and amide nitrogen played key roles and N, N bidentate ligand might be crucial for carboxylation reaction. Also, it confirmed that reaction does not proceed through the classical aromatic electrophilic substitution pathway, otherwise, more electron rich substrate **4a** might afford better result compare to **1a**.

On the basis of above experimental outcome and in combination with previous reports, [9,10, 13] a plausible mechanism is presented as shown in Scheme 5. Initially, the coordination of **1a** with copper$^{(II)}$ triflate took place and led to a chelated intermediate **A**. Next, an intermolecular SET from Cu(II) complex to CBr_4 afforded CBr_3 radical and Cu(III) complex **B**. Then, the intermediate **B**, proceeds through an intramolecular SET oxidation pathway, generated aryl radical cation species **C**. Then the intermediate **D** was



Scheme 5: Plausible Reaction mechanism

generated by the radical combination between CBr_3 radical and intermediate **C**. The proton transfer process afforded intermediate **E**, and ligand exchange of which leads the regeneration of intermediate **A** to continue the catalytic cycle along with intermediate **F**, which upon methanolysis gave the desired product **2a**.

In summary, we have developed a simple copper catalyzed regioselective C4 carboxylation of 1-naphthylamine and other aromatic and heteroaromatic substrates, with CBr_4 and alcohol using picolinamide and analogous amide as directing group. The carboxylation showed wide substrate scope, good functional group tolerance and easy to scale up. Deprotection of directing group and functionalization of TSQ, fluorescent probe for Zn(II), and sequential C-H functionalization of 1-naphthayl amide moiety to poly substituted naphthalene showcased the applicability of our developed methodology. Control experiments, with trapping of radicals intermediates revealed that reaction proceeds through a single electron transfer (SET) pathway.

Experimental section

A mixture of Amide (**1a**) (49.6 mg, 0.2 mmol), CBr_4 (199 mg, 0.6 mmol, 3 eqv], $Cu(OTf)_2$ (14.5 mg, 20 mole%), K_2CO_3 (55.3 mg, 0.4 mmol) and DMAP (4.9 mg, 20 mole%) were taken in a carousel screw cap reaction tube equipped with a cross shape stirring bar. The reaction tube was evacuated and refill with nitrogen, 1 mL dry methanol was added over it and stirred at 85 °C for 12-18 h. Reaction was monitored by TLC. After completion the reaction, mixture was cooled to room temperature and filtered through a plug of celite, the filtrate was concentrated, and evaporated to dryness in rotary evaporator. The crude residue was purified by Flash column chromatography (Ethyl acetate: Hexane 5:95) to isolate methyl 4-(picolinamido)-1-naphthoate (43 mg, **2a**) in 71% yield.

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References

[1] Recent reviews a) L. McMurray, F. O'Hara, M. J. Gaunt, *Chem. Soc. Rev.* **2011**, *40*, 1885–1898. b) J. Yamaguchi, A. D. Yamaguchi, K. Itami, *Angew. Chem. Int. Ed.* **2012**, *51*, 8960–9009; c) T. Gensch, M. N. Hopkinson, F. Glorius, J. Wencel-Delord, *Chem. Soc. Rev.* **2016**, *45*, 2900–2936. d) J. Liu, G. Chen, Z. Tan, *Adv. Synth. Catal.* **2016**, *358*, 1174–119.

[2] a) B. Yu, J.-N. Xie, C.-L. Zhong, W. Li, L.-N. He, *ACS Catal.* **2015**, *5*, 3940–3944. b) M. Börjesson, T. Moragas, D. Gallego, R. Martin, *ACS Catal*. **2016**, *6*, 6739–6749. c) S. E. Payer, H. Pollak, S. M. Glueck, K. Faber, *ACS Catal.* **2018**, *8*, 2438–2442. d) T. Mita, S. Ishii, Y. Higuchi, Y. Sato, *Org. Lett.* **2018**, *20*, 7603–7606. e) D. J. Charboneau, G. W. Brudvig, N. Hazari, H. M. C. Lant, A. K. Saydjari, *ACS Catal.* **2019**, *9*, 3228–3241. f) C. Ma, C.-Q. Zhao, X.-T. Xu, Z.-M. Li, X.-Y. Wang, K. Zhang, T.-S. Mei, *Org. Lett.* **2019**, *21*, 2464-2467. g) H. Jiang, Y. Zhang, W. Xiong, J. Cen, L. Wang, R. Cheng, C. Qi, W. Wu, *Org. Lett.* **2019**, *21*, 345–349.

[3] a) T. D. Thangadurai, C. J. Lee, S. H. Jeong, S. Yoon, Y. G. Seo, Y. I. Lee, *Microchem. J.* **2013**, *106*, 27–33. b) M. Jeleń, K. Pluta, K. Suwińska, B. Morak-Młodawska, M. Latocha, A. Shkurenko, *J. Mol. Struct.* **2015**, *1099*, 10–15. c) J. Chen, Y. Song, D. Bojadzic, A. Tamayo-Garcia, A. M. Landin, B. B. Blomberg, P. Buchwald, *J. Med. Chem.* **2017**, *60*, 8906–8922. d) T. Y. Zhang, Z. K. Yu, X. J. Jin, M. Y. Li, L. P. Sun, C. J. Zheng, H. R. Piao, *Bioorganic Med. Chem. Lett.* **2018**, *28*, 1657–1662. e) D. T. Tshitenge, D. Feineis, V. Mudogo, M. Kaiser, R. Brun, E. J. Seo, T. Efferth, G. Bringmann, *J. Nat. Prod.* **2018**, *81*, 918–933.

[4] For selected examples naphthalene derivatives C−H functionalization a) D. R. Stuart, M. Bertrand-Laperle, K. M. N. Burgess, K. Fagnou, *J. Am. Chem. Soc.***2008**, *130*, 16474−16475. b) D. Lee, S. Chang, *Chem. - Eur. J.* **2015**, *21*, 5364−5368. c) C. Wang, H. Chen, Z. Wang, J. Chen, . Huang, *Angew. Chem., Int. Ed*. **2012**, *51*, 7242−7245. d) J. Roane, O. Daugulis, *Org. Lett*. **2013**, *15*, 5842−5845. e) Q. Li, S. Y. Zhang, G. He, Z Ai, W. A. Nack, ,G. Chen, *Org. Lett.* **2014**, *16*, 1764−1767. f) S. Shi, C. Kuang, *J. Org. Chem.* **2014**, *79*, 6105−6112. g) M. Kondrashov, S. Raman, O. F. Wendt, *Chem. Commun*. **2015**, *51*, 911−913. h) F. M. Moghaddam, G. Tavakoli, B. Saeednia, P. Langer, B. J. Jafari, *J. Org. Chem.* **2016,** *81*, 3868−3876.

[5] For selected examples on the functionalization of 1-naphthylamide scaffolds a) L. Huang, Q. Li, C. Wang, C. Qi, *J. Org. Chem.* **2013**, *78*, 3030–3038. b) R. Odani, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2013**, *78*, 11045–11052. c) L. Huang, X. Sun, Q. Li, C. Qi, *J. Org. Chem.* **2014**, *79*, 6720–6725. d) J. Lan, H. Xie, X. Lu, Y. Deng, H. Jiang, W. Zeng, *Org. Lett.* **2017**, *19*, 4279–4282. e). H. Song, X. Liu, C. Wang, J. Qiao, W. Chu, Z. Sun, *Asian J. Org. Chem.* **2017**, *6*, 1693–1698. f) S. Roy, S. Pradhan, T. Punniyamurthy, *Chem. Commun.* **2018**, 3–6. g) G. You, K. Wang, X. Wang, G. Wang, J. Sun, G. Duan, C. Xia, *Org. Lett.* **2018**, *20*, 4005–4009. h) L. Huang, Q. Li, C. Wang, C. Qi, *J. Org. Chem.* **2013**, *78*, 3030–3038. i) S. Pradhan, P. B. De, T. Punniyamurthy, *J. Org. Chem.* **2017**, *82*, 4883–4890. j) L. Wang, M. Yang, X. Liu, H. Song, L. Han, W. Chu, Z. Sun, *Appl. Organomet. Chem.* **2016**, *30*, 680–683.

[6] for papers on C8 functionalizations of 1-naphthylamide derivatives see a) S. Rej, N. Chatani, *ACS Catal*. **2018**, *8*, 6699-6706; b) X. Li, X. Gong, M. Zhao, G. Song, J. Deng, X. Li, *Org. Lett*, **2011**, *13*, 5808-5811. c) R. Shang, L. Ilies, E. Nakamura, *J. Am. Chem. Soc***. 2015**, *137*, 7660-7663. d) Z. Li, S. Sun, H. Qiao, F. Yang, Y. Zhu, J. Kang, Y. Wu, Y. Wu, *Org. Lett*. **2016**, *18*, 4594-4597 and references cited therein. For C-2 functionalization e) O. Dauglis, V. G. Zaitsav, *Angew. Chem. Int. Ed.* **2005**, *44*, 4046- 4048.

[7] S. Liang, M. Bolte, G. Manolikakes, *Chem. - A Eur. J.* **2017**, *23*, 96–100.
[8] V. G. Zaitsev, D. Shabashov, O. Daugulis, *J. Am. Chem. Soc.* **2005**, *127*, 13154–13155.
[9] J.-M. Li, Y.-H. Wang, Y. Yu, R.-B. Wu, J. Weng, G. Lu, *ACS Catal.* **2017**, *7*, 2661–2667
[10] P. Bai, S. Sun, Z. Li, H. Qiao, X. Su, F. Yang, Y. Wu, Y. Wu, *J. Org. Chem.* **2017**, *82*, 12119–12127.
[11] H. Zhu, S. Sun, H. Qiao, F. Yang, J. Kang, Y. Y. Wu, Y. Y. Wu, *Org. Lett.* **2018**, *20*, 620–623.
[12] C. Jing, X. Chen, K. Sun, Y. Yang, T. Chen, Y. Liu, L. Qu, Y. Zhao, B. Yu, *Org. Lett.* **2019**, *21*, 486–489.
[13] H. L. Barlow, C. J. Teskey, M. F. Greaney, *Org. Lett.* **2017**, *19*, 6662–6665
[14] Q.-Q. Yang, M. Marchini, W.-J. Xiao, P. Ceroni, M. Bandini, *Chem. - A Eur. J.* **2015**, *21*, 18052–18056.
[15] C. X. Song, P. Chen, Y. Tang, *RSC Adv.* **2017**, *7*, 11233–11243.
[16] a) C. Sen, S. C. Ghosh *Adv. Synth. Catal*. **2018**, *360*, 905 –910; b) H. Singh, C. Sen, T. Sahoo, S. C. Ghosh. *Eur. J. Org. Chem*. **2018**, 4748-4753; c) H. Singh, T. Sahoo, C. Sen, S. M. Galani, S. C. Ghosh *Catal. Sci. Technol*., **2019**, *9*, 1691-1698; d) C. Sen, T. Sahoo, S. C. Ghosh, *ChemistrySelect* **2017**, *2*, 2745 – 2749.
[17] CCDC 1888191 (**2b**), CCDC 1888193 (**2j**) and CCDC 1888189 (**2k**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Centre via www.ccdc.cam.ac.uk/data_request/cif.
[18] a) J. W. Meeusen, H. Tomasiewicz, A. Nowakowski, D. H. Petering, *Inorg. Chem*. 2011, *50*, 7563; b) C. J. Fahrni, T. V. O'Halloran, *J. Am. Chem. Soc*. 1999,*121*, 11448–11458.

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Copper-Catalyzed C-4 Carboxylation of 1-Naphthylamide Derivatives with CBr_4/MeOH

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