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PAPER

Aerobic oxidative acylation of nitroarenes with arylacetic esters under mild conditions: Facile access to diarylketones

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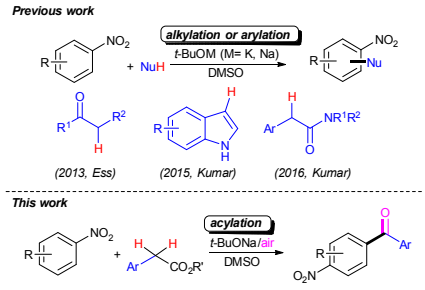
A facile and regioselective base-mediated aerobic oxidative acylation of nitroarenes to access diarylketones under mild conditions has been developed. It features the use of bench-stable and readily available arylacetates as acyl surrogates, and the absence of transition-metals and synthetic oxidants. This protocol involves a cascade CDC/oxidative decarboxylation process.

Introduction

The cross-dehydrogenative coupling (CDC) reaction is of fundamental importance in organic synthetic community, which readily enables the efficient construction of C-based chemical bonds, especially C-C bonds.[1] Due to the superior sustainability and environmental compatibility, significant progress in the CDC chemistry has flourished mostly in the last decade.[2] These reactions can undergo catalytically using transition-metals (TMs) such as copper[3] or iron salts[4] combined with synthetic oxidants or elemental oxygen. Nevertheless, one of the challenging difficulties encountered in practical industrial applications is to efficiently remove trace amounts of transition-metal residues from coupled products, especially pharmaceuticals. Accordingly, tremendous efforts have been devoted to developing novel TM-free CDC reactions,[5] but aerobic CDC reactions without TM catalysts are still very limited.[5c-k] Most of them relates to the acid-catalysed aerobic C-C bond-forming reactions centring on the benzylic sp^3 C-H bonds in xanthenes,[5e] acridines,[5e] tetrahydroisoquinolines[5e, 5f] and glycine derivatives[5g] in the absence of metal catalysts. Very recently, the TM-free aerobic CDC reactions have been disclosed to accomplish the C-C bond formation of nitroarenes sp^2 C-H bonds mediated by bases such as tertiary butoxides.[5h-j] In 2013, the group of Ess reported a *t*-BuONa-mediated TM-free aerobic CDC alkylation of nitroarenes with ketones, allowing regiospecific synthesis of momo-α-arylated ketones under open-to-air conditions (scheme 1).[5h] Later, Kumar et al has developed a *t*-BuOK-mediated TM-free aerobic CDC indolylation of nitroarenes with indoles in an open flask, enabling the facile access to β-(2/4-nitroaryl)-indoles under mild conditions (scheme 1).[5i] Following this work, they have further presented the synthesis of unsymmetrical diaryl acetamides through TM-free CDC reactions of nitroarenes sp^2 C-H and amides sp^3 C-H bonds (scheme 1).[5j] However, there seem few reports concerning the direct CDC version of nitroarenes with arylacetates under TM-free and aerobic conditions.[6]

The incorporation of an acyl substituent into arenes is of central importance in organic transformations due to the extensive applications of arylketones in synthesis, materials and pharmaceuticals.[7] Thus the numerous methods have been developed.[7a, 8] Remarkably, the direct acylative functionalization of electron-deficient arenes including nitroarenes is a great challenge. To our knowledge, the direct and efficient acylation reactions of electron-deficient nitroarenes sp^2 C-H bonds without any directing group have not been reported. Continuing our effort of *t*-BuONa-mediated TM-free autoxidative carbonylation of diarylmethylenes,[9] herein, we present a TM-free aerobic formal acylation reaction of simple nitroarenes with readily available and bench-stable arylacetic esters under very mild conditions through a cascade CDC/oxidative decarboxylation process (scheme 1).



Scheme 1 Previous and current studies.

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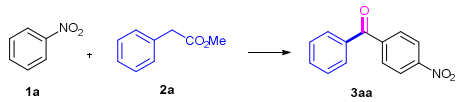
Results and discussion

Table 1 Optimization of the oxidative acylation conditions[a]



1a 2a 3aa

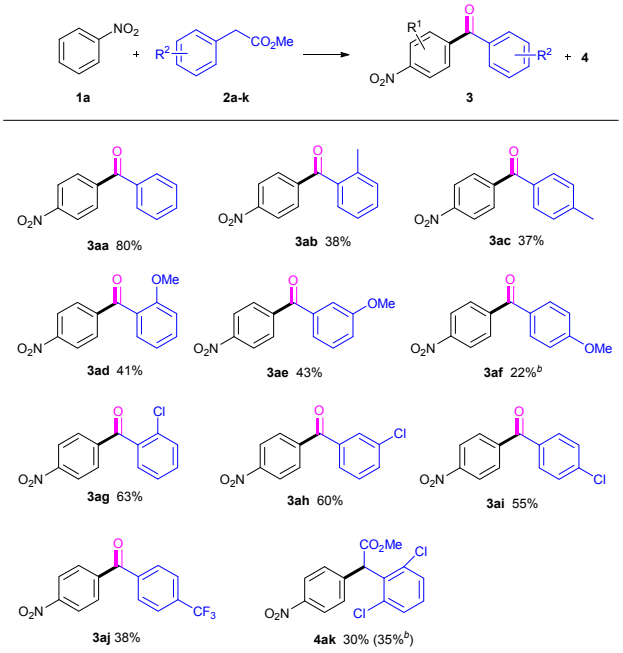
Entry	Base	Solvent	Time (h)	T (°C)	Yield[b] (%)
1	NaO^{t}Bu	DMSO	12	25	70
2	NaO^{t}Bu	DMSO	12	15	65
3	NaO^{t}Bu	DMSO	12	10	50
4	NaO^{t}Bu	DMSO	8	35	77
5	NaO^{t}Bu	DMSO	3	45	80
6	NaO^{t}Bu	DMSO	3	60	56
7	K_2CO_3	DMSO	8	45	N.R.
8	KO^{t}Bu	DMSO	3	45	75
9	NaH	DMSO	3	45	65
10	KOH	DMSO	3	45	20
11	NaOH	DMSO	3	45	50
12	DBU	DMSO	8	45	N.R.
13	NaO^{t}Bu	CH_3CN	3	45	25
14	NaO^{t}Bu	DMF	3	45	35
15	NaO^{t}Bu	CH_3OH	8	45	N.R.
16	NaO^{t}Bu	CH_2Cl_2	3	45	10
17	NaO^{t}Bu	THF	8	45	40
18	NaO^{t}Bu	EtOAc	3	45	10
19[c]	NaO^{t}Bu	DMSO	3	45	65
20[d]	NaO^{t}Bu	DMSO	3	45	76

[a] Reaction was performed using **1a** (0.4 mmol), **2a** (0.2 mmol), base (0.4 mmol), dry solvent (0.5 mL) in open flask unless otherwise stated. [b] Isolated yield. [c] DMSO was not dried. [d] Under O_2 balloon. N.R. = No reaction.

Our initial investigation on this acylation chemistry commenced by the treatment of nitrobenzene **1a** with methyl phenylacetate **2a** using the strong base NaO^{t}Bu (2.0 equiv) in dry DMSO under open air atmosphere at room temperature (entry 1, Table 1). Delightedly, the acylation product 4-nitro-diphenylketone **3aa** was formed regioselectively and isolated in 70% yield, with a concomitant normal CDC product 2-arylated phenylacetic ester. Decreasing the reaction temperatures diminished the yields of **3aa**, while elevating the temperatures significantly increased those of **3aa** (entries 2, 3 *vs* 4, 5, Table 1). However, the higher temperature of 60 °C gave rise to the dramatic fall in the yield (entry 6, Table 1). Therefore, the reaction at 45 °C was preferred, wherein the ketone **3aa** was isolated in 80% yield. The other inorganic bases such as K_2CO_3, KO^{t}Bu, NaH, KOH, and NaOH were screened (entries 7-11, Table 1). It was found that the strong bases delivered better yields, while the weak base K_2CO_3 could not initiate the reaction with the materials recovered. Likewise, the organic base DBU was ineffective for this chemistry (entry 12, Table 1). Typically, DMSO has been used as best solvent in base-mediated autoxidative reactions reported previously.[5h-j, 9] Nevertheless, the other solvents were further considered, including CH_3CN, DMF, CH_3OH, CH_2Cl_2, THF, and EtOAc (entries 13-18, Table 1). The results showed that all the aforementioned solvents furnished worse efficiencies than DMSO. Noteworthy, the protic solvent CH_3OH afforded no product, due to its strong acidity disfavoring the formation of **2a** carbanion (entry 15, Table 1). Similarly, a trace amount of water in the undried DMSO imposed an adverse effect on the reaction yield (entry 19, Table 1). Additionally, performing the reaction under O_2 balloon instead of open air didn't improve the yield of the desired ketone **2a** (entry 20, Table 1). After the further optimization with respect to the equivalents of base, nitrobenzene and the concentration (please see ESI), the optimum acylation conditions were established: NaO^{t}Bu (2.0 equiv)-mediated acylation of **1a** (2.0 equiv) with **2a** (0.2 mmol) in dry DMSO (0.5 ml) in open flask at 45 °C, providing **3aa** in the isolated 80% yield.

With the optimized reaction conditions in hand, we set out to study the scope of the methyl arylacetic esters used in this TM-free base-mediated autoxidative acylation reaction, and the results are listed in Table 2. In general, all the methyl arylacetates except **2k** tested smoothly underwent the oxidative acylation to give their corresponding ketones **3** in moderate to good yields when nitrobenzene **1a** was used as reaction partner (**3aa**-**3aj**). The introduction of the substituent to the benzene ring of the arylacetate **2** remarkably resulted in the efficiency loss (**3ab**-**3aj**). Moreover, the electron-donating groups (-Me, -OMe) seemed to more disfavor the acylation occurrence than the electron-withdrawing one (-Cl). However, the group CF_3 delivered only 38% yield (**3aj**). The steric effects of the substituents on the reaction were observed. Surprisingly, the steric hindrance of the group accelerated this oxidative acylation to some extent. For example, the groups such as -Me, -OMe and -Cl, at the *ortho*-position resulted in the higher yields than at the *para*-position. It should be pointed out that **2f** led to the formation of complex system under standard conditions, and yielded and isolated the acylation product **3af** (22%) at 0 °C. Besides, methyl 2,6-dichlorophenylacetate **2k**

Table 2 Oxidative acylation of different 2-arylacetates with nitrobenzene[a]



[a] Conditions: nitrobenzene **1a** (0.4 mmol), arylacetates **2** (0.2 mmol), *t*-BuONa (0.4 mmol), dry DMSO (0.5 mL), 45 °C for 3 h in open-to-air flask. [b] Performed at 0 °C for 2 h. Isolated yields.

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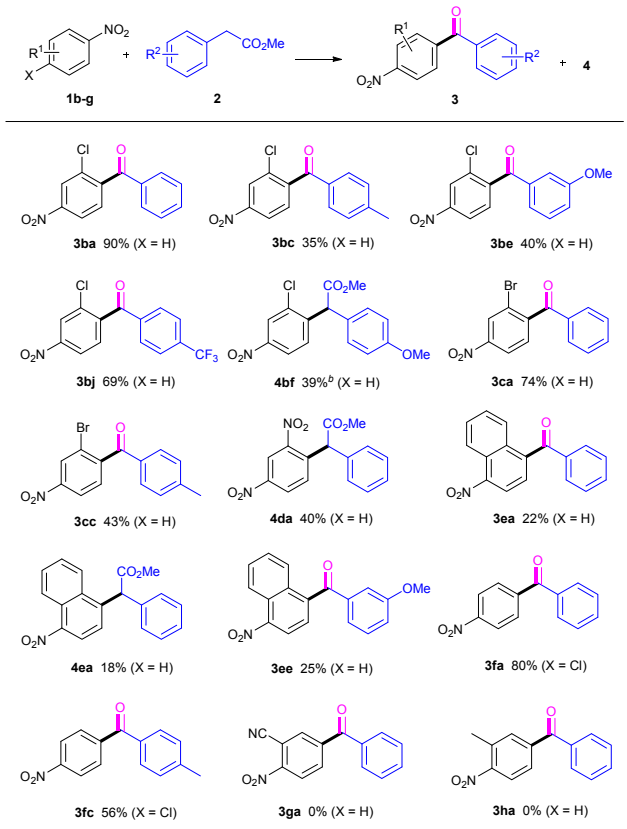
generated only the CDC ester **4ak**, whether at 45°C (30% yield) or at 0 °C (35% yield). This may be due to the difficulties in the formation of **4ak** carbanion by the hindered base NaO^{t}Bu, and in the autoxidative transformation with molecular O_2.

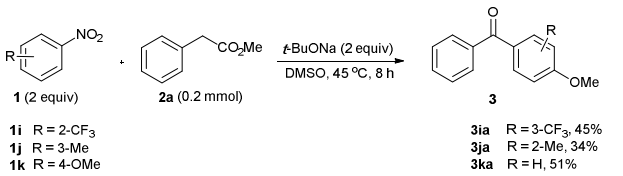
Next, we turned our attention to the nitroarene reaction partners, as shown in Table 3. 3-Chloro-4-nitrobenzene **1b** was found to produce its expected acylation products **3**. Its reaction with **2a** afforded the desired ketone **3ba** in 90% yield, and with **2j** delivered **3bj** in 69% yield. In two cases of **3ba** and **3bj**, the efficiencies are higher compared to those of **3aa** and **3aj**. With regard to **2f**, the CDC product **4bf** was obtained in 39% yield at 0 °C. Likewise, 3-bromo-4-nitrobenzene **1c** readily reacted with **2a** and **2c**, providing the expected ketones **3ca** and **3cc** in 74% and 43% yields, respectively. However, the reaction of 1,3-dinitrobenzene **1d** with **2a** gave only the CDC ester **4da** in 40% yield under standard conditions. 1-Nitronaphthalene **1e** is an effective coupling partner. Its reaction with **2a** generated our desired product **3ea**, along with the intermediate **4ea** unconverted even for the prolonged time, while with **2e** only the ketone **3ee** was isolated in 25% yield. When 4-chloronitrobenzene **1f** was used instead, no *ortho*-nitro ketones were detected. A competitive S_NAr/oxidative decarboxylative carbonylation reaction preferably occurred by the replacement of the Cl moiety instead of hydrogen atom, whereby the same products with those derived from **1a** were obtained in moderate to good yields (**3fa** & **3fc**). It is disappointed to find that 2-nitrobenzonitrile **1g** and 2-nitrotoluene **1h** are bad substrates. **1g** was almost fully converted, but no corresponding ketone detected. **1h** was recovered quantitatively after workup.

Surprisingly, when it came to 2-CF_3-nitrobenzene **1i**, the cascade oxidative reaction yielded an abnormal product **3ia** via the subsequent nucleophilic displacement of the nitro group by the -OMe group generated in the oxidative decarboxylation step (scheme 2, **1i**).[10] In the case of 3-nitrotoluene **1j**, the abnormal reaction occurred in the same manner, affording the 4-methoxylated ketone **3ja** in 34% yield (scheme 2, **1j**). More interestingly, the use of 4-nitroanisole **1k** gave rise to the 51% yield of a denitro-coupling product **3ka**, where the nitro group was formally displaced by an acyl group (scheme 2, **1k**).

Table 3 Oxidative acylation of 2-arylacetates with different nitroarenes [a]

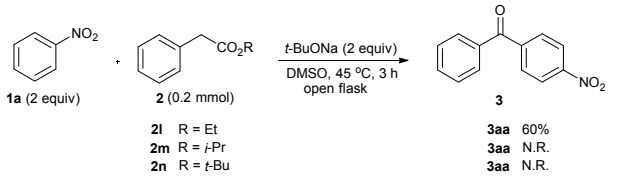


[a] Conditions: nitroarenes **1** (0.4 mmol), arylacetates **2** (0.2 mmol), *t*-BuONa (0.4 mmol), dry DMSO (0.5 mL), 45 °C for 3 h in open-to-air flask. [b] Performed at 0 °C for 2 h. Isolated yields.



Scheme 2 Exceptional examples related to the nitro displacement.

Besides, we changed the alkyl groups in phenylacetates used in this transformation, to scrutinize their effect on oxidative acylation efficiency (scheme 3). It was found that the ethyl ester **2l** led to the notably lower yield of **3aa** than the methyl version **2a**, and moreover the *iso*-propyl and *tert*-butyl variants (**2m** & **2n**) can't realize such acylation reaction under the standard conditions.



Scheme 3 The effect of the alkyl groups in phenylacetates (N.R.= No reaction).

To figure out the mechanism of this oxidative acylation chemistry, a variety of control experiments were carried out, as shown in scheme 4. From the experiments for reaction temperature optimization, we realized that the reaction probably underwent the CDC process and that the low reaction temperature may favour the formation of the CDC product without the further conversion to the acylation product. Thus, we strived to obtain **4aa** by performing the reaction at 0 °C wherein **4aa** was isolated in 30% yield. Then the CDC product **4aa** as precursor was fully converted under the standard conditions, and the ketone **3aa** isolated in 92% yield (scheme 4,

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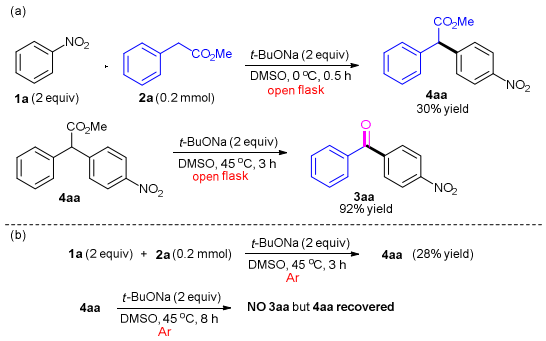
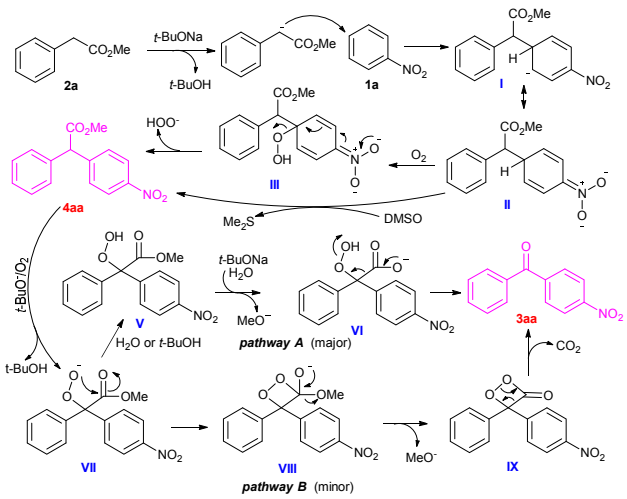


Scheme 4 Control experiments.

a). Furthermore, **4aa** was observed and isolated in 28% yield when the mixture of **1a** and **2a** were treated at 45 °C under argon atmosphere after five freeze-pump-thaw cycles (scheme 4, b). This suggests that DMSO could play a role as hydrogen acceptor in the CDC coupling step (please see SI, section 5). However, the reaction of **4aa** as precursor under argon afforded nothing even for the prolonged time (8 h), but **4aa** fully recovered after neutralization under argon. This indicates that the followed oxidative decarboxylation process necessitates the involvement of molecular oxygen (O_2). All these results confirmed our hypothesis that the first step of this chemistry involved a CDC reaction between nitroarenes and arylacetic esters and the second step implicated an aerobic oxidative decarboxylation mediated by base.

Based on our experimental observations and previous reports,[5h, 5i, 11] a tentative mechanism is proposed for this cascade oxidative acylation reaction (scheme 5). Firstly, **2a** is deprotonated by *t*-BuONa to generate a carbanion, which undergoes sequential nucleophilic addition to **1a**, O_2-mediated H-atom abstraction from **II**, radical combination and HOO^- dissociation to furnish a CDC product **4aa** with a concomitant hydroperoxide anion.[5h] In this stage (**II** to **4aa**), DMSO as an oxidant can't be ruled out. Secondly, the intermediate **4aa** is



Scheme 5 Proposed pathways for the cascade oxidative reaction.

oxidized into a peroxide anion **VII** in the presence of base and O_2. Then two possible pathways may exist in next transformation.[11a,11b] One possible route involves a sequential hydrolysis-decarboxylation-hydroperoxy bond cleavage process[11a,11b] (*pathway A*). This may explain why the reaction gave better yield under open air than under pure O_2. That may be because a trace amount of water from the environment helps promote the base-catalysed hydrolysis of **IV**. The minor competitive alternative implicates intramolecular ester exchange of **VII** to *in situ* generate a dioxetanone **IX**, and subsequent decarboxylation to the product **3aa**, along with peroxide cleavage[11a] (*pathway B*).

Conclusions

In conclusion, we have demonstrated a facile TM-free base-mediated aerobic oxidative acylation of nitroarenes with bench-stable and readily available arylacetic acid esters under mild conditions. This approach allows for the facile and regioselective synthesis of 4-nitro-diarylketones, and obviates the use of harsh conditions, TMs and Lewis acids. This chemistry involves the *in situ* generation of 2-arylated arylacetic acid esters via the CDC reaction, followed by the aerobic oxidative decarboxylation mediated by base, and will supplement the classical Friedel-Crafts acylation chemistry. In view of its numerous advantages, it will provide an alternative and powerful tool to access ketones, particularly containing the nitro group in organic synthesis and pharmaceutical fields.

Experimental

General information

All solvents and reagents were purchased from the suppliers and used without further purification unless otherwise stated. Yields reported are for isolated yields unless otherwise stated. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded in $CDCl_3$ at room temperature on Bruker Avance III 400 spectrometer using TMS as the internal reference. MS spectra were performed on a Agilent 6890/5973 GC-MS (EI) or Waters UPLC_Xevo_TQD (ESI). Elemental analyses were measured on a Perkin Elmer 2400 series analyser. The melting point (m. p.) was determined using an open glass tube. TLC analyses were performed on silica gel plates and column chromatography was conducted over silica gel (mesh 200-300) at increased pressure.

General procedure for synthesis of diarylketones

To a predried 10 mL round-bottom flask were sequentially added phenylacetates **1** (0.2 mmol), nitroarenes **2** (0.4 mmol), dry DMSO (0.5 mL), and *t*-BuONa (0.4 mmol). The reaction system became dark purple on adding the base. The resulting mixture was stirred at 45°C for the specific time (normally 3 h). Then it was cooled to room temperature, to which added aqueous HCl (1 mol/L) to pH = 6-7, and the resulting mixture was extracted with ethyl acetate, dried over anhydrous Na_2SO_4, and concentrated with rotary evaporation. Then the resulting residue was subjected to column

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chromatography on silica gel using co-solvent (ethyl acetate/ petroleum ether=1/40, v/v) as eluent to give the corresponding diarylketones **3**. The representative ketones are listed here.

(4-Nitro-phenyl)-phenyl-methanone (3aa).[12] Yellow solid (36 mg, 80%), M. p. 132-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.6 Hz, 2H), 7.94 (d, *J* = 8.6 Hz, 2H), 7.80 (d, *J* = 7.7 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.8, 149.8, 142.9, 136.3, 133.5, 130.7 (2C), 130.1 (2C), 128.7 (2C), 123.6 (2C). MS (EI): m/z 227.1 $[M]^{+\bullet}$.

(4-Chlorophenyl)(4-nitrophenyl)methanone (3ai).[13] Yellow solid (29 mg, 55%), M. p. 103-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.3 Hz, 2H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 149.9, 142.5, 140.1, 134.6, 131.5 (2C), 130.6 (2C), 129.1 (2C), 123.7 (2C). MS (EI): m/z 261.0 $[M]^{+\bullet}$, 263.0.

(2-Chloro-4-nitrophenyl)(phenyl)methanone (3ba).[14] Yellow solid (46 mg, 90%), M. p. 93-94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$)δ193.3, 148.9, 144.5, 135.3, 134.6, 132.6, 130.0 (2C), 129.6, 129.0 (2C), 125.3, 121.9. MS (EI): m/z 261.0 $[M]^{+\bullet}$, 263.0.

(4-Nitronaphthalen-1-yl)(phenyl)methanone (3ea).[15] Yellow solid (12 mg, 22%). M. p. 85-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.8 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.76 (t, *J* = 7.8 Hz, 1H), 7.67 – 7.59 (m, 3H), 7.49 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 148.0, 142.7, 136.9, 134.3, 131.9, 130.4 (2C), 129.7, 128.9 (2C), 128.4, 126.2, 125.3, 124.3, 123.3, 122.2. MS (ESI): m/z 278.0 [M+1].

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

1. (a)Y. Qin, L. Zhu and S. Luo, *Chem. Rev.*, 2017, DOI: 10.1021/acs.chemrev.6b00657; (b)Y. Yang, J. Lan and J. You, *Chem. Rev.*, 2017, DOI: 10.1021/acs.chemrev.6b00567; (c)B. J. Li and Z. J. Shi, *Chem. Soc. Rev.*, 2012, **41**, 5588.
2. (a)C. Li and Z. Li, *Pure Appl. Chem.*, 2006, **78**, 935; (b)C. J. Li, *Acc. Chem. Res.*, 2009, **42**, 335; (c)C. J. Scheuermann, *Chem. Asian J*, 2010, **5**, 436; (d)B.-J. Li and Z.-J. Shi, *Chem. Soc. Rev.*, 2012, **41**, 5588; (e)S. A. Girard, T. Knauber and C.-J. Li, *Angew. Chem. Int. Ed.*, 2014, **53**, 74; (f)C. Liu, J. Yuan, M. Gao, S. Tang, W. Li, R. Shi and A. Lei, *Chem. Rev.*, 2015, **115**, 12138.
3. (a)H. Z. Zhi, S. P. M. Ung, Y. Liu, L. Zhao and C. J. Li, *Adv. Synth. Catal.*, 2016, **358**, 2553; (b)C. A. Correia and C. J. Li, *Adv. Synth. Catal.*, 2010, **352**, 1446; (c)O. Basle and C. J. Li, *Chem. Commun.*, 2009, 4124; (d)C. Zhang, X. L. Zong, L. R. Zhang and N. Jiao, *Org. Lett.*, 2012, **14**, 3280.
4. (a)Z. P. Li, L. Cao and C. J. Li, *Angew Chem. Int. Ed.*, 2007, **46**, 6505; (b)F. Jia and Z. Li, *Org. Chem. Front.*, 2014, **1**, 194; (c)T. Wang, W. Zhou, H. Yin, J. A. Ma and N. Jiao, *Angew Chem. Int. Ed.*, 2012, **51**, 10823.
5. (a)C.-L. Sun and Z.-J. Shi, *Chem. Rev.*, 2014, **114**, 9219; (b)P. Finkbeiner and B. J. Nachtsheim, *Synthesis*, 2013, **45**, 979; (c)Q. Lu, H. Yi and A. Lei, *Acta Chim. Sinica*, 2015, **73**, 1245; (d)K. Luo, Y. Z. Chen, L. X. Chen and L. Wu, *J. Org. Chem.*, 2016, **81**, 4682; (e)A. Pinter, A. Sud, D. Sureshkumar and M. Klussmann, *Angew Chem. Int. Ed.*, 2010, **49**, 5004; (f)H. Ueda, K. Yoshida and H. Tokuyama, *Org. Lett.*, 2014, **16**, 4194; (g)C. Huo, Y. Yuan, M. Wu, X. Jia, X. Wang, F. Chen and J. Tang, *Angew Chem. Int. Ed.*, 2014, **53**, 13544; (h)Q.-L. Xu, H. Gao, M. Yousufuddin, D. H. Ess and L. Kurti, *J. Am. Chem. Soc.*, 2013, **135**, 14048; (i)S. Kumar, V. Rathore, A. Verma, C. D. Prasad, A. Kumar, A. Yadav, S. Jana, M. Sattar, Meenakshi and S. Kumar, *Org. Lett.*, 2015, **17**, 82; (j)V. Rathore, M. Sattar, R. Kumar and S. Kumar, *J. Org. Chem.*, 2016, **81**, 9206; (k)S. Song, Y. Q. Zhang, A. Yeerlan, B. C. Zhu, J. Z. Liu and N. Jiao, *Angew Chem. Int. Ed.*, 2017, **56**, 2487; (l)P. M. Wang, F. Pu, K. Y. Liu, C. J. Li, Z. W. Liu, X. Y. Shi, J. Fan, M. Y. Yang and J. F. Wei, *Chem-Eur J.*, 2016, **22**, 6262.
6. M. Makosza, K. Kamienska-Trela, M. Paszewski and M. Bechcicka, *Tetrahedron*, 2005, **61**, 11952.
7. (a)R. C. Larock, *Comprehensive organic transformations: a guide to functional group preparations*, Wiley-vch New York, 1999; (b)S.-B. Wu, C. Long and E. J. Kennelly, *Nat. Prod. Rep.*, 2014, **31**, 1158; (c)S. K. Vooturi, C. M. Cheung, M. J. Rybak and S. M. Firestine, *J. Med. Chem.*, 2009, **52**, 5020; (d)S. Y. Lee, T. Yasuda, Y. S. Yang, Q. Zhang and C. Adachi, *Angew Chem. Int. Ed.*, 2014, **53**, 6402; (e)J. S. Li, Y. Xue, Z. W. Li, W. D. Liu, C. H. Lu and P. X. Zhao, *Synlett*, 2013, **24**, 2003; (f)J. S. Li, F. F. Cai, Z. W. Li, W. D. Liu, J. Simpson, Y. Xue, H. L. Pang, P. M. Huang, Z. Cao and D. L. Li, *RSC Adv.*, 2014, **4**, 474.
8. (a)G. Sartori and R. Maggi, *Advances in Friedel-Crafts acylation reactions: catalytic and green processes*, CRC Press, 2009; (b)S. Sharma, N. Kumar Mishra, Y. Shin and I. Su Kim, *Curr. Org. Chem.*, 2016, **20**, 471; (c)X.-F. Wu, *Chem. –Eur. J.*, 2015, **21**, 12252; (d)C. Pan, X. Jia and J. Cheng, *Synthesis*, 2012, **44**, 677.
9. J.-S. Li, F. Yang, Q. Yang, Z.-W. Li, G.-Q. Chen, Y.-D. Da, P.-M. Huang, C. Chen, Y. Zhang and L.-Z. Huang, *Synlett*, 2017, **28**, 994.
10. (a)J. P. Idoux, M. L. Madenwald, B. S. Garcia, D. L. Chu and J. T. Gupton, *J. Org. Chem.*, 1985, **50**, 1876; (b)J. H. Gorvin and D. P. Whalley, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1364; (c)N. Kornblum, L. Cheng, R. C. Kerber, M. M. Kestner, B. N. Newton, H. W. Pinnick, R. G. Smith and P. A. Wade, *J. Org. Chem.*, 1976, **41**, 1560; (d)J. H. Gorvin, *Chem. Ind.*, 1967, 1525.
11. (a)Y. Sawaki and Y. Ogata, *J. Org. Chem.*, 1977, **42**, 40; (b)M. Avramoff and Y. Sprinzak, *J. Am. Chem. Soc.*, 1963, **85**, 1655.

DOI: 10.1039/C7OB02865B

12. S. Barroso, G. Blay, L. Cardona, I. Fernández, B. García, and J. R. Pedro, *J. Org. Chem.*, 2004, **69**, 6821.
13. M. Cai, J. Peng, W. Hao and G. Ding, *Green Chem*., 2011, **13**, 190.
14. J. Mahdi, H. Ankati, J. Gregory, B. Tenner and E. R. Biehl. *Tetrahedron Lett*., 2011, **52**, 2594.
15. M. Makosza and J. Winiarski, *J. Org*. *Chem*., 1984, **49**, 1494.

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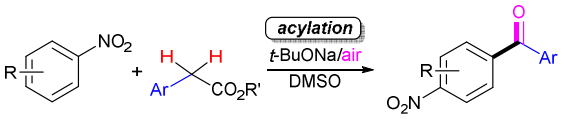

- *transition-metal-free*
- *aerobic oxidative*
- *chemical oxidants-free*
- *arylacetates as acyl surrogates*
- *cascade CDC/oxidative decarboxylation process*

A regioselective *t*-BuONa-mediated aerobic oxidative acylation of nitroarenes under mild conditions is developed through a cascade CDC/oxidative decarboxylation process.