Accepted Manuscript

TBHP/$R_4N^+X^-$ promoted hydroaroylation of dialkyl azodicarboxylates with methyl arenes, aldehydes, aryl methanols and arylmethyl chlorides

Mehdi Adib, Rahim Pashazadeh, Saideh Rajai-Daryasarei, Fatemeh Moradkhani, Mehdi Jahani, Seyed Jamal Addin Gohari

PII: S0040-4020(18)30571-4

DOI: 10.1016/j.tet.2018.05.038

Reference: TET 29545

To appear in: *Tetrahedron*

Received Date: 23 November 2017

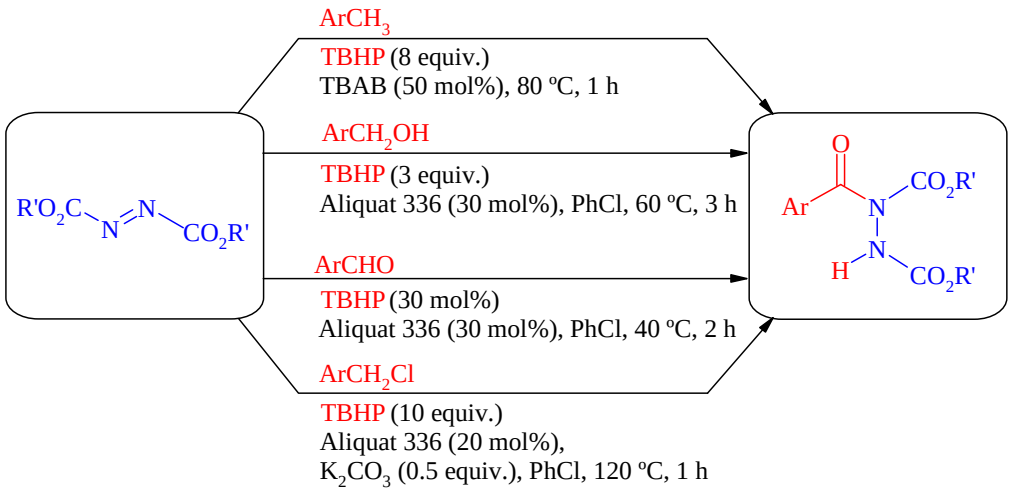
Revised Date: 10 May 2018

Accepted Date: 15 May 2018

Please cite this article as: Adib M, Pashazadeh R, Rajai-Daryasarei S, Moradkhani F, Jahani M, Gohari SJA, TBHP/$R_4N^+X^-$ promoted hydroaroylation of dialkyl azodicarboxylates with methyl arenes, aldehydes, aryl methanols and arylmethyl chlorides, *Tetrahedron* (2018), doi: 10.1016/j.tet.2018.05.038.

TBHP/$R_4N^+X^-$ promoted hydroaroylation of dialkyl azodicarboxylates with methyl arenes, aldehydes, aryl methanols and arylmethyl chlorides

Mehdi Adib, Rahim Pashazadeh, Saideh Rajai-Daryasarei, Fatemeh Moradkhani, Mehdi Jahani, Seyed Jamal Addin Gohari



TBHP/$R_4N^+X^-$ promoted hydroaroylation of dialkyl azodicarboxylates with methyl arenes, aldehydes, aryl methanols and arylmethyl chlorides

Mehdi Adib,[a,*] Rahim Pashazadeh,[a] Saideh Rajai-Daryasarei,[a] Fatemeh Moradkhani,[b] Mehdi Jahani,[a] Seyed Jamal Addin Gohari[c]

[a] *School of Chemistry, College of Science, University of Tehran, PO Box 14155-6455, Tehran, Iran*

[b] *Department of Medicinal Chemistry, Drug Design and Development Research Center, Faculty of Pharmacy, Tehran University of Medical Sciences, Tehran, Iran*

[c] *Department of Chemistry, Imam Hossein University, Tehran, Iran*

Abstract: Efficient TBHP/$R_4N^+X^-$ promoted hydroaroylations of dialkyl azo-1,2-dicarboxylates with methyl arenes, aldehydes, aryl methanols and arylmethyl chlorides are described. These oxidation/oxygenation and hydroaroylation processes were carried out by *tert*-butyl hydroperoxide as terminal oxidant/oxygen source, and were catalyzed by tetrabutylammonium bromide and tricaprylmethylammonium chloride as the driving force. During this investigation, all these hydroaroylating sources were found to be highly efficient reagents without the need of any transition-metal.

Keywords: *tert*-butyl hydroperoxide, tetrabutylammonium bromide, tricaprylmethylammonium chloride, methyl arenes, aldehydes, aryl methanols, arylmethyl chlorides, dialkyl azo-1,2-dicarboxylates, hydrazine imides.

[*]Corresponding author. Tel./fax: +98(21)66495291; E-mail: madib@khayam.ut.ac.ir

1. Introduction

C−H functionalization protocol is a rapidly expanding area in organic synthesis as it offers high impetus for developing novel, short and attractive methodologies for synthesizing a variety of complex organic molecules.[1] Moreover, due to their relatively inert nature, the functionalization and activation of C−H bonds plays a vital role in the development of more efficient and sustainable bond forming reactions. From an atom-economical and environmental point of view, the use of un-functionalized starting materials in the construction of C−C and C−heteroatom bonds is one of the major concerns for synthetic chemists.[2]

Methyl arenes,[3] alcohols[4] and arylmethyl halides[4c,5] have been recognized as cheap, simple, stable and easily available starting materials, which made them attractive substrates from both academic and industrial perspective in the synthesis of complex molecules.

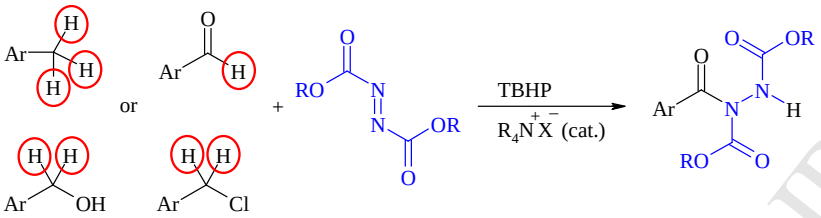
Remarkably, construction of various bonds and complex compounds using oxidant/$R_4N^+X^-$ system has emerged as an efficient and unique catalytic methodology which obviates the foregoing impediments of metal-catalyzed reactions.[6]

Dialkyl azodicarboxylates (DAADs) are excellent electrophiles due to the presence of two carboalkoxy groups and electrophilic π bond on the nitrogen atoms of the azo skeleton.[7] Thus, DAADs have been employed as nucleophile acceptors and coupling partners in various reactions such as *N*-arylation,[8] C−H derivatization at the *α*-position to heteroatoms,[9] electrophilic α-amination of carbonyl compounds,[10] ene-type reactions with olefins[11] and also reactions with zwitterionic intermediates.[12]

On the other hand, acylation of DAADs has also received considerable attention from the synthetic community.[13] In recent years, hydrazine imides have been prepared from aliphatic and aromatic aldehydes as hydroacylating agents. While the reaction can be performed under various conditions using metal catalyst such as Rh(II),[14] Cu(II),[15] and Zn(II),[16] aqueous media,[17] ionic liquid,[18] Lewis- and Brønsted-acid catalysis,[19] pyridine-catalysis under microwave irradiation,[20] photocatalytic method,[21a] decatungstate anion photocatalysis,[21b] graphite flakes as the carbocatalyst,[21c] and CoO-Fe_3O_4 as magnetic catalysis.[22]

As part of our continuing effort to develop efficient methods for the preparation of biologically active organic compounds from readily available precursors,[23] recently, we have been particularly interested in oxidant/$R_4N^+X^-$ catalytic systems and have focused our attention on the development of acylation-based novel transformations.[24]

Herein, we present highly efficient and transition metal-free hydroaroylations of DAADs with readily accessible hydroaroylating reagents *via* C(sp^3)−H and C(sp^2)−H oxidation functionalization strategies promoted by oxidant/$R_4N^+X^-$ leading to the corresponding hydrazine imides (Scheme 1).



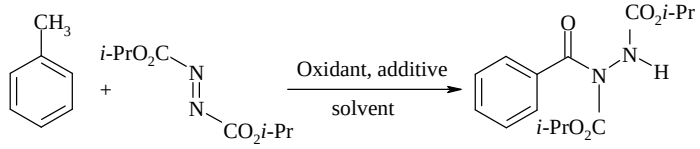
Scheme 1 Synthesis of hydrazine imides through hydroaroylation of dialkyl azodicarboxylate promoted by the TBHP/$R_4N^+X^-$ system.

2. Result and discussion

Initially, we selected toluene **1a** and DAAD **2a** as the model substrates to evaluate the most suitable conditions. In this optimization, various parameters such as the type as well as the quantity of oxidant and additive, solvents, and reaction temperature were examined (Table 1). The reaction between **1a** and **2a** was first started in the presence of *tert*-butyl hydroperoxide (TBHP, 6 equiv.) as oxidant and tetrabutylammonium bromide (TBAB, 30 mol%) as additive at ambient temperature for 1 h, however, no reaction was observed (entry 1). Carrying out the reaction at 50 and 80 °C, gave dialkyl hydrazine-1,2-dicarboxylate (DAHD, **3a**) in 28 and 55% yields, respectively (entries 2 and 3). In order to improve the reaction efficiency, reaction time increased to 2 h, but the yield of **3a** decreased to 35% (entry 4). By increasing the reaction time, the NH group of the formed hydrobenzoylated product may undergo further oxidation and functionalizion.[25] By increasing the amount of TBHP and TBAB the efficiency of the reaction improved (entries 5–7) and the best result was observed with 50 mol% of TBAB and 8.0 equiv of TBHP at 80 °C with which **3a** was obtained in 93% yield (entry 6). However, higher TBHP loading did not improve the formation of **3a** (entry 7). An excess amount of TBHP led to the formation of benzoic acid in the reaction mixture. Also, in several reports, increasing the amount of the oxidant has a negative effect on the yield of the product.[5,26] Other additives were also examined (entries 8–13). NBS, TBPB and Aliquat 336 gave **3a** in 10%, 75%, and 48% yields, respectively (entries 8–10) and KI as well as elemental iodine (I_2) were ineffective (entries 11 and 12). Notably, no product was detected by use of BPO, $K_2S_2O_8$, and H_2O_2 as oxidant

(entries 13–15). Moreover, the solvent screening studies indicated that no product was formed in solvents such as PhCl, CH_3CN, 1,4-dioxane and DMSO (entries 16–19). Furthermore, the reaction was carried out in the presence of different amounts of toluene (4, 6 and 10 mmol), which led to the formation of **3a** in 40%, 62%, and 79% yields, respectively (entries 20–22). In the absence of TBHP and TBAB, **3a** was not detected (entries 23 and 24), which suggested that both TBHP and TBAB played a crucial role in this reaction. Carrying out the reaction at 100 °C and 120 °C, **3a** was obtained in 93% and 90% yields, respectively, after 30 minutes (entries 25 and 26). According to the above results, the optimal conditions for synthesis of DAHD **3a** were determined as: DAAD **2a** (0.4 mmol), toluene (8 mmol,), TBHP (8 equiv.), 50 mol% of TBAB, at 80 °C for 1 h (entry 6).

Table 1. Optimization of the reaction conditions for the hydrobenzoylation of **2a** with toluene **1a**[a]



1a **2a** **3a**

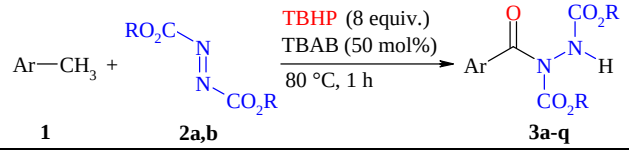
Entry	Oxidant (equiv.)[b]	Additive (mol%)[b]	Solvent	Temp. (°C)	Yield (%)[c]
1	TBHP[d] (6)	TBAB[e] (30)	$PhCH_3$	r.t.	NR[f]
2	TBHP (6)	TBAB (30)	$PhCH_3$	50	28
3	TBHP (6)	TBAB (30)	$PhCH_3$	80	55
4[g]	TBHP (6)	TBAB (30)	$PhCH_3$	80	35
5	TBHP (8)	TBAB (30)	$PhCH_3$	80	52
6	**TBHP (8)**	**TBAB (50)**	**$PhCH_3$**	**80**	**93**
7	TBHP (10)	TBAB (50)	$PhCH_3$	80	82
8	TBHP (8)	NBS[h] (50)	$PhCH_3$	80	10
9	TBHP (8)	TBPB[i] (50)	$PhCH_3$	80	75
10	TBHP (8)	Aliquat 336[j] (50)	$PhCH_3$	80	48
11	TBHP (8)	KI (50)	$PhCH_3$	80	NR
12	TBHP (8)	I_2 (50)	$PhCH_3$	80	NR
13	BPO[k] (8)	TBAB (50)	$PhCH_3$	80	NR
14	$K_2S_2O_8$ (8)	TBAB (50)	$PhCH_3$	80	NR
15	H_2O_2[l] (8)	TBAB (50)	$PhCH_3$	80	NR
16[m]	TBHP (8)	TBAB (50)	PhCl	80	NR
17	TBHP (8)	TBAB (50)	CH_3CN	80	NR
18	TBHP (8)	TBAB (50)	Dioxane	80	NR
19	TBHP (8)	TBAB (50)	DMSO	80	NR
20[n]	TBHP (8)	TBAB (50)	$PhCH_3$	80	40
21[o]	TBHP (8)	TBAB (50)	$PhCH_3$	80	62
22[p]	TBHP (8)	TBAB (50)	$PhCH_3$	80	79
23	–	TBAB (50)	$PhCH_3$	80	NR
24	TBHP (8)	–	$PhCH_3$	80	NR
25[q]	TBHP (8)	TBAB (50)	$PhCH_3$	100	93
26[q]	TBHP (8)	TBAB (50)	$PhCH_3$	120	90

[a]Reaction conditions: **1a** (8 mmol), **2a** (0.4 mmol) for 1 h. [b]In respect to **2a**. [c]Isolated yields. [d]70 wt% *t*-BuOOH in H_2O. [e]Tetrabutylammonium bromide. [f]NR = no reaction. [g]Reaction time of 2 h. [h]*N*-Bromosuccinimide. [i]Tetrabutylphosphonium bromide. [j]Methyltrioctylammonium chloride. [k]Benzoyl peroxide. [l]30wt% H_2O_2 in H_2O. [m]Entries 17–20: 0.5 mL solvent. [n]**1a** (4 mmol). [o]**1a** (6 mmol). [p]**1a** (10 mmol). [q]Reaction time of 30 min.

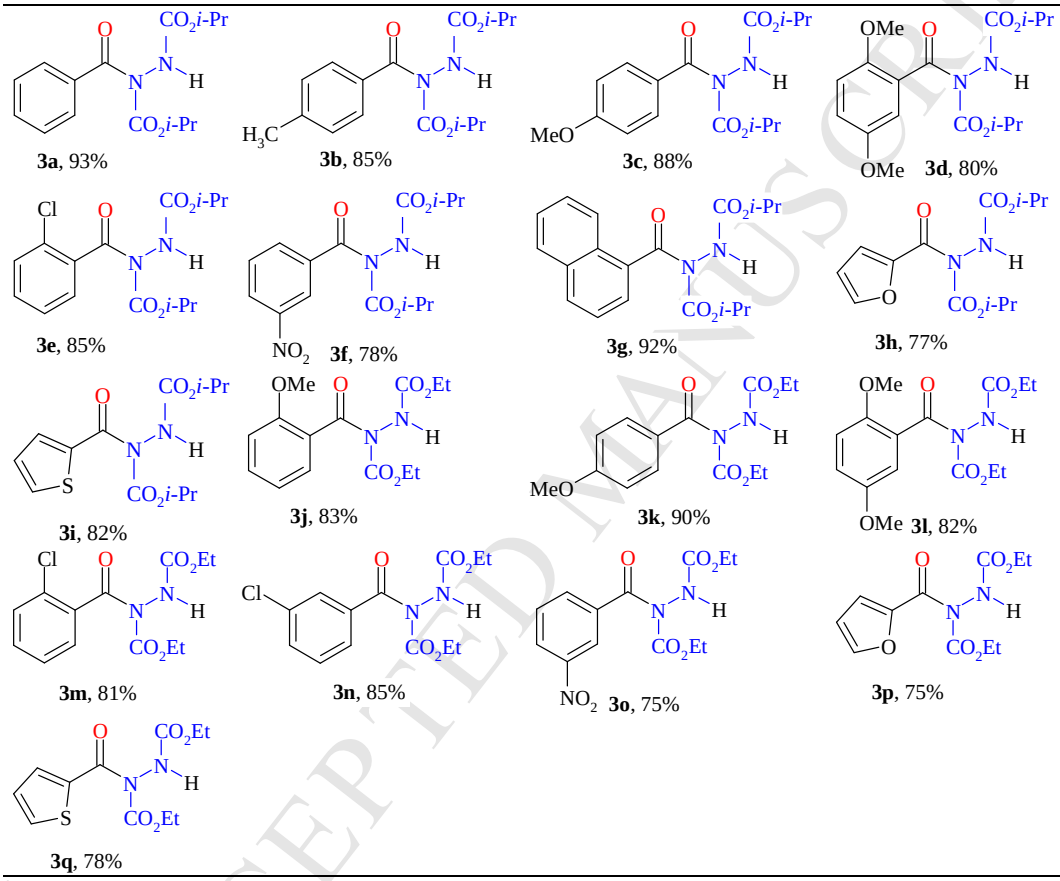
With the optimal conditions in hand, various methyl arenes **1** and DAADs **2a**,**b** were used and the corresponding DAHDs **3a**–**q** were obtained in 75–93% yields. The results are summarized in Table 2. The reaction of methyl arenes with neutral and electron-donating substituents such as (one or more) Me and OMe at the *meta*-, *ortho*- and *para*-positions of the aryl ring with DAADs **2a**,**b** afforded the corresponding DAHDs **3a**–**d** and **3j**–**l** in 80–93% yields. Also, strong electron-withdrawing nitro group on *meta*-position of the methyl arene decreased the yield of the corresponding

products **3f** and **3o**, whereas chloro substituent gave **3e**, **3m** and **3n** in 75–85% yields. The reaction was also carried out by use of methyl heteroarenes with furan and thiophene rings and methyl naphthalene, which afforded the corresponding products **3g–i**, **3p** and **3q** in 75–92% yields.

Table 2. Substrate scope for the synthesis of DAHDs **3a-r** by use of methyl arenes **1**[a,b]



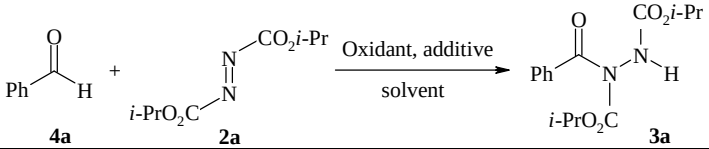
1 **2a,b** **3a-q**



[a]Reaction conditions: DAADs (**2**, 0.4 mmol), methyl arenes (**1**, 8 mmol), TBHP (3.2 mmol), TBAB (50 mol%) for 1 h. [b]Isolated yields.

Encouraged by the above results, we extended the scope of this reaction with aldehydes as aroylating sources. Thus, the optimal conditions for the reaction between DAADs **2** and aldehydes **4** leading to **3** were determined: aldehyde 2 equiv. (in respect to **2**), Aliquat 336 (30 mol%) and TBHP (30 mol%.) in chlorobenzene at 40 °C for 2 h (entry 5, Table 3).

Table 3. Condition screening for the conversion of DAAD **2a** to DAHD **3a** by use of benzaldehyde **4a**[a]



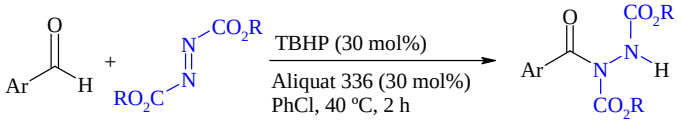
4a **2a** **3a**

Entry	Oxidant (mol%)[b]	Additive (mol%)[b]	Solvent	Temp (ºC)	Yield (%)[c]
1	TBHP[d] (0.2)	–	PhCl	18	NR[e]
2	TBHP (0.2)	Aliquat 336 (15)	PhCl	18	NR
3	TBHP (0.2)	Aliquat 336 (15)	PhCl	40	40
4	TBHP (0.3)	Aliquat 336 (15)	PhCl	40	65
5	**TBHP (0.3)**	**Aliquat 336 (30)**	**PhCl**	**40**	**90**
6	TBHP (0.5)	Aliquat 336 (30)	PhCl	40	82
7	TBHP (1.0)	Aliquat 336 (30)	PhCl	40	80
8	TBHP (0.3)	Aliquat 336 (40)	PhCl	40	90
9	TBHP (0.3)	Aliquat 336 (30)	PhCl	50	88
10	TBHP (0.3)	Aliquat 336 (30)	PhCl	70	78
11	TBHP (0.3)	TBPB[f] (30)	PhCl	40	65
12	TBHP (0.3)	TBAB[g] (30)	PhCl	40	65
13	TBHP (0.3)	TBAI[h]	PhCl	40	NR
14	TBHP (0.3)	KI (30)	PhCl	40	NR
15	TBHP (0.3)	I_2 (30)	PhCl	40	NR
16	$K_2S_2O_8$ (0.3)	Aliquat 336 (30)	PhCl	40	25
17	BPO[i] (0.3)	Aliquat 336 (30)	PhCl	40	50
18	$(NH_4)_2S_2O_8$ (0.3)	Aliquat 336 (30)	PhCl	40	20
19	H_2O_2[j] (0.3)	Aliquat 336 (30)	PhCl	40	10
20	TBHP (0.3)	Aliquat 336 (30)	DCE	40	60
21	TBHP (0.3)	Aliquat 336 (30)	$PhCH_3$	40	30
22	TBHP (0.3)	Aliquat 336 (30)	DMSO	40	NR
23	TBHP (0.3)	Aliquat 336 (30)	H_2O	40	10
24	TBHP (0.3)	Aliquat 336 (30)	THF	40	trace
25	TBHP (0.3)	Aliquat 336 (30)	DMSO:H_2O (1:1)	40	10
26	TBHP (0.3)	Aliquat 336 (30)	CH_2Cl_2	40	60
27	TBHP (0.3)	Aliquat 336 (30)	CH_3CN	40	Trace
28	TBHP (0.3)	Aliquat 336 (30)	EtOAc	40	20
29	–	Aliquat 336 (30)	PhCl	40	NR
30	TBHP (0.3)	–	PhCl	40	35
31[k]	TBHP (0.3)	Aliquat 336 (30)	PhCl	40	75
32[l]	TBHP (0.3)	Aliquat 336 (30)	PhCl	40	70

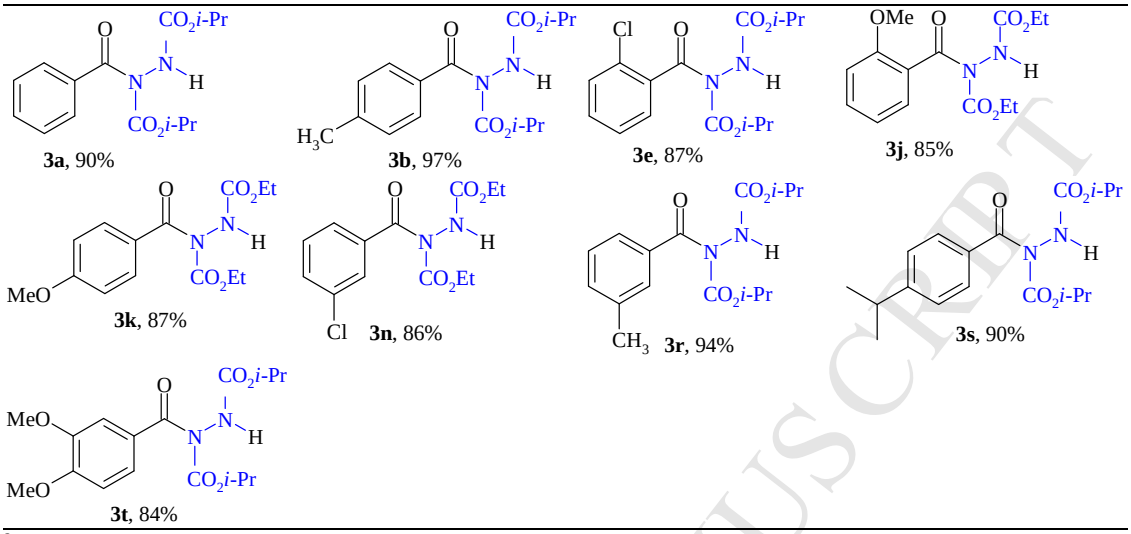
[a]Reaction conditions: **1a** (1.0 mmol), **2a** (0.5 mmol), solvent (1 mL) for 2 h. [b]In respect to **2a**. [c]Isolated yields. [d]70 wt% *t*-BuOOH in H_2O. [e]NR = no reaction. [f]Tetrabutylphosphonium bromide. [g]Tetrabutylammonium bromide. [h]Tetrabutyla mmonium iodide. [i]Benzoyl peroxide. [j]30 wt% H_2O_2 in H_2O. [k]Ratio **1a**:**2a** (1:1). [l]Ratio **1a**:**2a** (3:1).

To our delight, aldehydes with neutral and electron-donating groups such as 3-Me, 4-Me, 4-*i*Pr and 3,4-$(OMe)_2$ or electron-withdrawing groups including 2-Cl and 3-Cl were converted to the desired DAHDs in excellent yields (Table 4).

Table 4. Hydroaroylation of DAADs **2** with aldehydes **4** promoted by the TBHP/Aliquat 336 system[a,b]



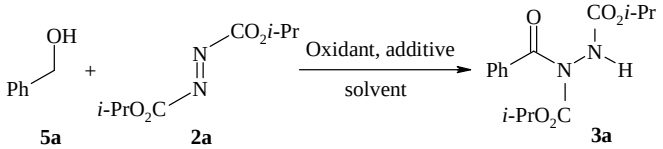
4 **2a,b** **3**



[a]Reaction conditions: DAADs (**2**, 0.5 mmol), aldehyde (**4**, 1.0 mmol), TBHP (30 mol%), Aliquat 336 (30 mol%), in PhCl (1 mL). [b]Isolated yields.

Next, we were stimulated to examine other approaches for the construction of DAHDs. The high efficiency of the hydroaroylation reaction with the azodicarboxylate component prompted us to explore the possibility of employing simple aryl methanols as hydroaroylating agents. A slightly different optimum reaction conditions relative to the aldehydes were obtained. The optimal conditions for the conversion of DAADs **2** to DAHDs **3** by use of aryl methanols **5** as hydroaroylating agents include: aryl methanol (2 equiv. in respect to **2**), TBHP (3 equiv.), 30 mol% of Aliquat 336, in chlrorobenzene at 60 °C for 3 h (entry 6, Table 5) which afforded the corresponding DAHDs **3** in 77–90% yields (Table 6).

Table 5. Condition screening for the hydrobenzoylation of **2a** with benzyl alcohol **5a**[a]

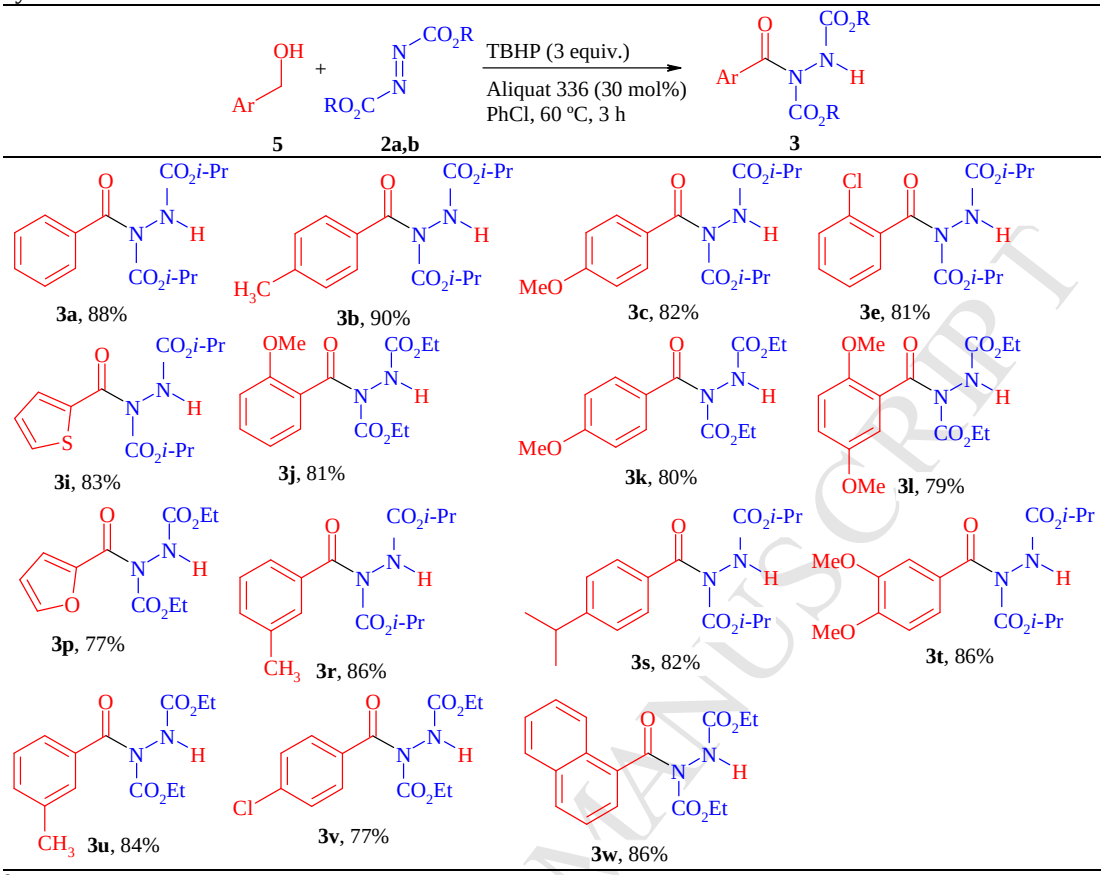


5a **2a** **3a**

Entry	Oxidant (equiv.)[b]	Additive (mol%)[b]	Solvent	Temp. (°C)	Yield (%)[c]
1	TBHP[d] (1)	–	PhCl	25	NR[e]
2	TBHP (1)	Aliquat 336 (15)	PhCl	25	NR
3	TBHP (1)	Aliquat 336 (15)	PhCl	60	35
4	TBHP (2)	Aliquat 336 (15)	PhCl	60	68
5	TBHP (3)	Aliquat 336 (15)	PhCl	60	80
6	**TBHP (3)**	**Aliquat 336 (30)**	**PhCl**	**60**	**88**
7	TBHP (4)	Aliquat 336 (30)	PhCl	60	78
8	TBHP (3)	Aliquat 336 (40)	PhCl	60	88
9	TBHP (3)	Aliquat 336 (30)	PhCl	80	81
10	TBHP (3)	Aliquat 336 (30)	PhCl	100	74
11	TBHP (3)	TBPB[f] (30)	PhCl	60	60
12	TBHP (3)	TBAB[g] (30)	PhCl	60	60
13	TBHP (3)	TBAI[h]	PhCl	60	NR
14	TBHP (3)	KI (30)	PhCl	60	NR
15	TBHP (3)	I_2 (30)	PhCl	60	NR
16	$K_2S_2O_8$ (3)	Aliquat 336 (30)	PhCl	60	NR
17	BPO[i] (3)	Aliquat 336 (30)	PhCl	60	40
18	$(NH_4)_2S_2O_8$ (3)	Aliquat 336 (30)	PhCl	60	NR
19	H_2O_2[j] (3)	Aliquat 336 (30)	PhCl	60	NR
20	TBHP (3)	Aliquat 336 (30)	DCE	60	72
21	TBHP (3)	Aliquat 336 (30)	$PhCH_3$	60	25
22	TBHP (3)	Aliquat 336 (30)	DMSO	60	NR
23	TBHP (3)	Aliquat 336 (30)	H_2O	60	NR
24	TBHP (3)	Aliquat 336 (30)	THF	60	NR
25	TBHP (3)	Aliquat 336 (30)	DMSO:H_2O (1:1)	60	NR
26	TBHP (3)	Aliquat 336 (30)	CH_2Cl_2	60	NR
27	TBHP (3)	Aliquat 336 (30)	CH_3CN	60	55
28	TBHP (3)	Aliquat 336 (30)	EtOAc	60	NR
29	–	Aliquat 336 (30)	PhCl	60	NR
30	TBHP (3)	–	PhCl	60	NR
31[k]	TBHP (3)	Aliquat 336 (30)	PhCl	60	53
32[l]	TBHP (3)	Aliquat 336 (30)	PhCl	60	66

[a]Reaction conditions: **1a** (1.0 mmol), **2a** (0.5 mmol), solvent (1 mL) for 3 h. [b]In respect to **2a**. [c]Isolated yields. [d]70 wt% *t*-BuOOH in H_2O. [e]NR = no reaction. [f]Tetrabutylphosphonium bromide. [g]Tetrabutylammonium bromide. [h]Tetrabutylammonium iodide. [i]Benzoyl peroxide. [j]30 wt% H_2O_2 in H_2O. [k]Ratio **1a**:**2a** (1:1). [l]Ratio **1a**:**2a** (3:1).

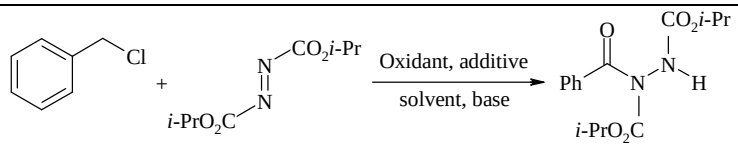
Table 6. Hydroaroylation of DAADs **2** with aryl methanols **5** promoted by the TBHP/Aliquat 336 system[a,b]



[a]Reaction conditions: DAADs (**2**, 0.5 mmol), aryl methanol (**5**, 1.0 mmol), TBHP (1.5 mmol), Aliquat 336 (30 mol%), in PhCl (1 mL).
[b]Isolated yields.

To develop a more general and useful method, we subsequently turned our attention to investigate the hydroaroylation reaction between arylmethyl chlorides **6** and DAADs **2** under the TBHP/Aliquat 336 optimized conditions (entry 4, Table 7). This hydroaroylation methodology is correspondingly compatible with various substituted arylmethyl chlorides providing DAHDs **3** in 67–83% yields (Table 8).

Table 7. Optimization of the reaction conditions for the formation of DAHD **3a** by use of benzyl chloride **6a**[a]

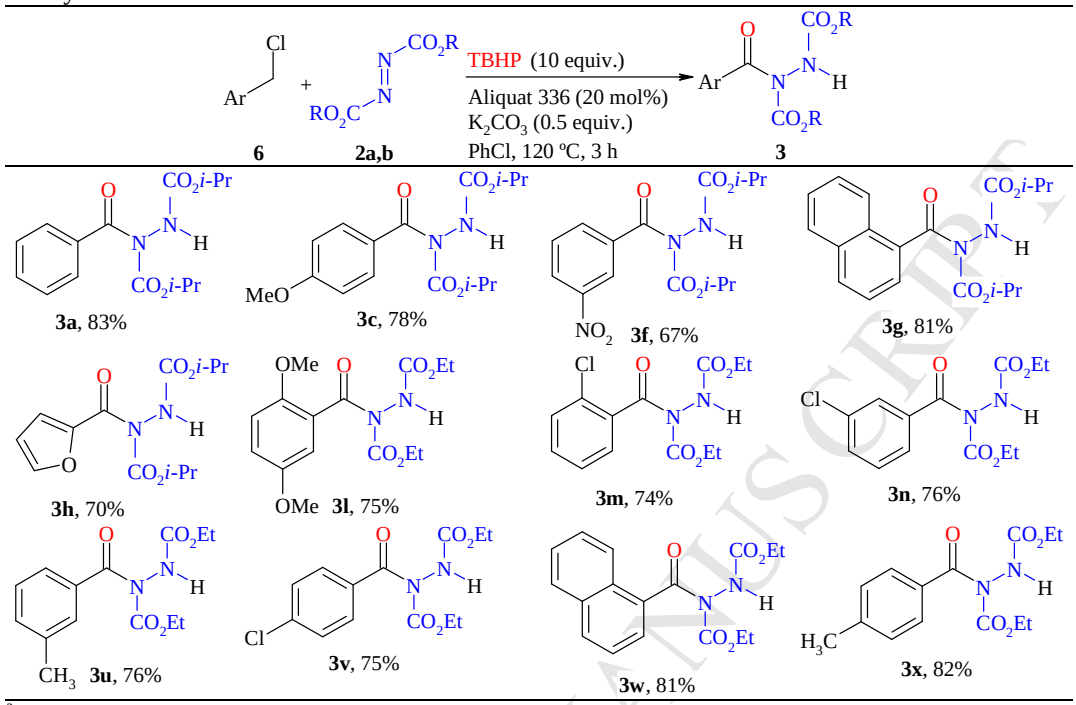


6a **2a** **3a**

Entry	Oxidant (equiv)[b]	Additive (mol%)[b]	Base (eq.)[b]	Solvent	T (°C)	Yield[c] %
1	TBHP[d] (10)	TBAB[e](20)	K_2CO_3 (0.5)	PhCl	120	NR[f]
2	TBHP (10)	TBPB[g](20)	K_2CO_3(0.5)	PhCl	120	NR
3	TBHP (10)	TBAI[h] (20)	K_2CO_3 (0.5)	PhCl	120	NR
4	**TBHP (10)**	**Aliquat 336[i] (20)**	**K_2CO_3 (0.5)**	**PhCl**	**120**	**83**
5	TBHP (10)	Aliquat 336 (20)	$KHCO_3$ (0.5)	PhCl	120	79
6	TBHP (10)	Aliquat 336 (20)	Na_2CO_3 (0.5)	PhCl	120	63
7	TBHP(10)	Aliquat 336 (20)	Cs_2CO_3 (0.5)	PhCl	120	55
8	TBHP (10)	Aliquat 336 (20)	K_2CO_3 (0.5)	DCE	120	30
9	TBHP (10)	Aliquat 336 (20)	K_2CO_3 (0.5)	DMF	120	NR
10	TBHP (10)	Aliquat 336 (20)	K_2CO_3 (0.5)	CH_3CN	120	NR
11	TBHP (10)	Aliquat 336 (20)	K_2CO_3 (0.5)	EtOH	120	NR
12	TBHP (10)	Aliquat 336 (20)	K_2CO_3 (0.5)	DMSO	120	NR
13	TBHP (5)	Aliquat 336 (20)	K_2CO_3 (0.5)	PhCl	120	11
14	H_2O_2[j] (10)	Aliquat 336 (20)	K_2CO_3 (0.5)	PhCl	120	trace
15	$K_2S_2O_8$ (10)	Aliquat 336 (20)	K_2CO_3 (0.5)	PhCl	120	NR
16[k]	TBHP (10)	Aliquat 336 (20)	K_2CO_3 (0.5)	PhCl	120	68
17	TBHP (10)	–	K_2CO_3 (0.5)	PhCl	120	20
18	TBHP (10)	Aliquat 336 (20)	–	PhCl	120	11
19[l]	TBHP (10)	Aliquat 336 (20)	K_2CO_3 (0.5)	PhCl	80	53
20[m]	TBHP (10)	Aliquat 336 (20)	K_2CO_3 (0.5)	PhCl	100	76

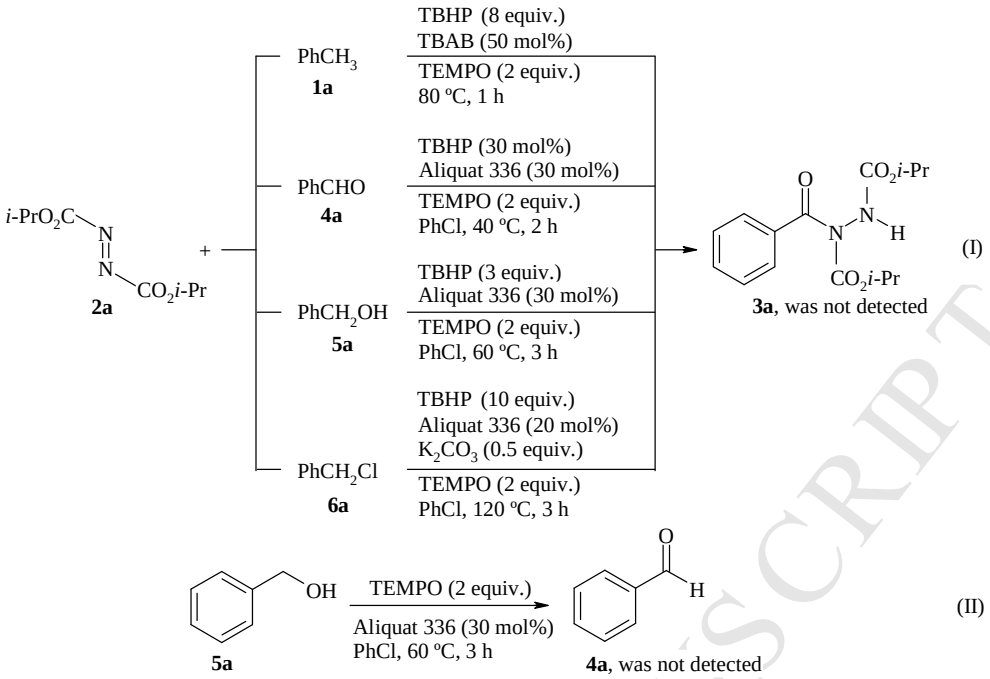
[a]Reaction conditions: **6a** (1.5 mmol), **2a** (0.3 mmol) for 3 h. [b]In respect to **2a**. [c]Isolated yields. [d]70 wt% *t*-BuOOH in H_2O. [e]Tetrabutylammonium bromide. [f]NR = No reaction. [g]Tetrabutylphosphonium bromide. [h]Tetrabutylammonium iodide. [i]Tricaprylmethylammonium chloride. [j]30wt% H_2O_2 in H_2O. [k]**6a** (0.9 mmol). [l]Reaction temperature of 80 °C. [m]Reaction temperature of 100 °C.

Table 8. Hydroaroylation of DAADs **2** with arylmethyl chlorides **6** promoted by the TBHP/Aliquat 336 system[a,b]



[a]Reaction conditions: DAADs (**2**, 0.3 mmol), arylmethyl chloride (**6**, 1.5 mmol), TBHP (3.0 mmol), Aliquat 336 (20 mol%), K_2CO_3 (0.15 mmol) in PhCl (1 mL).
[b]Isolated yields.

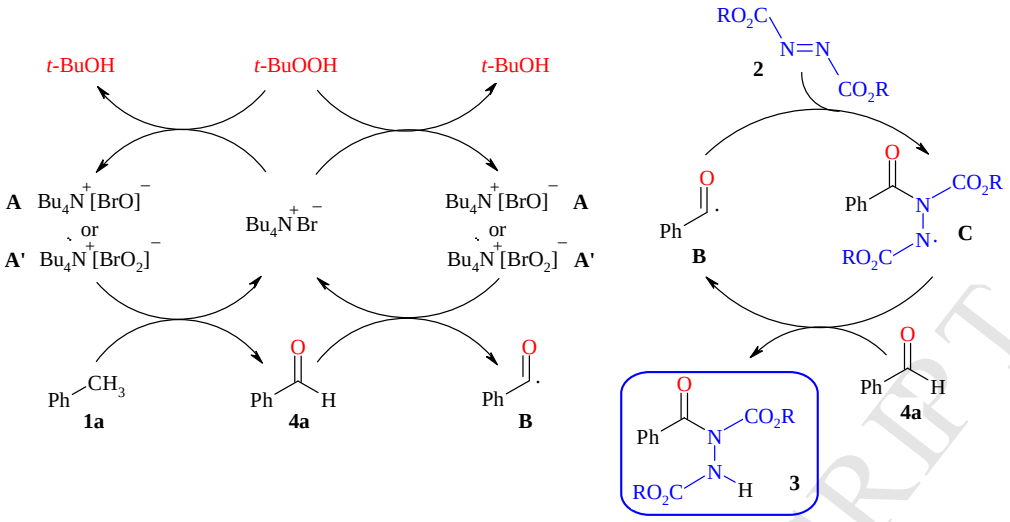
Under the optimized conditions (Tables 2, 4, 6 and 8), addition of the radical scavenger 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) to the reaction mixtures of the hydrobenzoylating reagents **1a**, **4a**, **5a** or **6a** with DAAD **2a**, hydrobenzoylated product **3a** was not detected (Eq. I). Torii and Anelli have reported that some TEMPO derivatives were converted to their *N*-oxoammonium salts in the presence of an oxidizing reagent ($NaBrO_2$ or NaOCl/KBr co-catalyst) in a pH 8.6 buffer (using aq. $NaHCO_3$ solution), which oxidized alcohols to the corresponding carbonyl compounds.[27] However, when benzyl alcohol **5a** was subjected to TEMPO and Aliquat 336 under the standard reaction conditions (Table 6) in the absence of TBHP, benzaldehyde **4a** was not observed. (Eq. II). Thus, to sum up, according to these results and the reported articles, the reactions probably occur *via* radical mechanisms (Scheme 2).[28]



Scheme 2 Control experiments

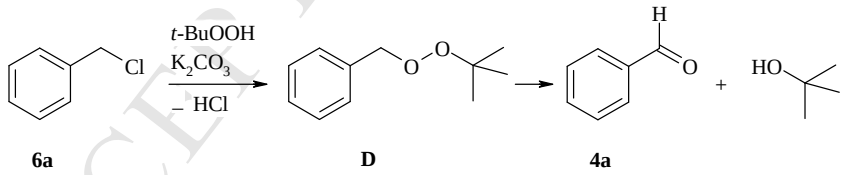
GC-Mass analyses of the reaction mixtures of toluene **1a**, benzyl alcohol **5a** and benzyl chloride **6a** under the related optimum conditions confirmed the presence of benzaldehyde in the mixtures. As another control experiment, the reactions of **1a**, **5a** and **6a** with TBHP/TBAB or -/Aliquat 336 in the absence of DAAD **2** were examined, all of which gave benzaldehyde confirming the formation of benzoyl radical through all these reactions.

On the bases of these experimental results, a tentative reaction mechanism is proposed in Scheme 3. Initially, tetrabutylammonium hypobromite (n-$Bu_4N^+[BrO]^-$) **A** or tetrabutylammonium bromite (n-$Bu_4N^+[BrO_2]^-$) **A′** species could be generated through the reaction between TBHP and TBAB.[6e,6h,6m,29] Then, toluene **1a** may be oxidized by **A** or **A′** to benzoyl radical **B** *via* benzaldehyde **4a**. Benzoyl radical **B** may be coupled with DAAD **2** to give hydrazine imide radical **C**. Finally, hydrogen abstraction of **C** from benzaldehyde **4a** produces DAHD **3** by returning benzoyl radical **B** to the reaction cycle.



Scheme 3 Proposed mechanism for the formation of DAHD **3** promoted by the TBHP/TBAB system

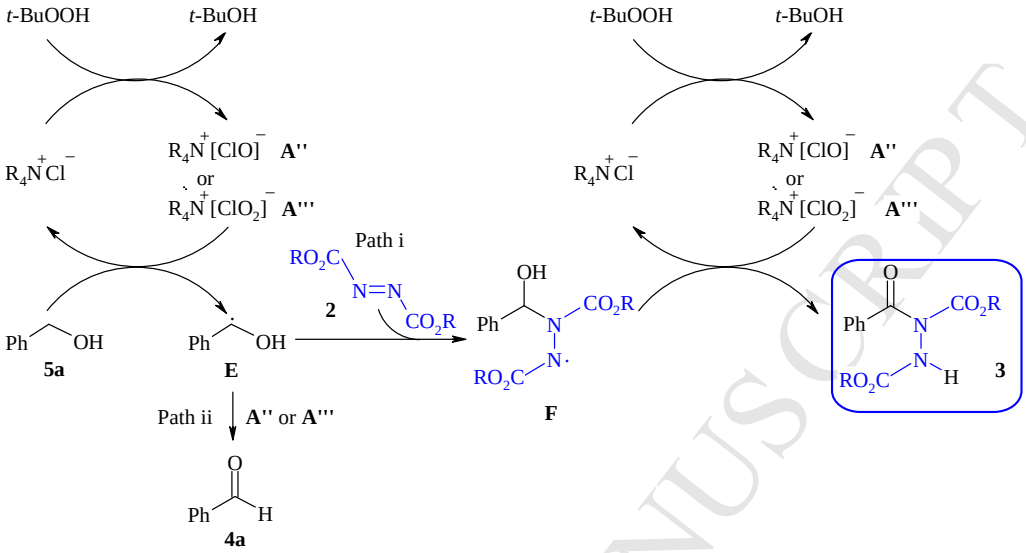
We also proposed a mechanism for the formation of benzaldehyde **4a** from benzyl chloride **6a** (Scheme 4). The reaction may be initiated by deprotonation of TBHP by K_2CO_3 followed by an SN_2 attack of the peroxide anion to the benzylic position of benzyl chloride **6a** to produce benzyl (*tert*-butyl) peroxide **D**. Peroxide **D** may be collapsed under the thermal reaction conditions to form benzaldehyde **4a** and *tert*-butanol.[30] The *in situ* generated benzaldehyde will form benzoyl radical **B**, which could hydroaroylate DAADs according to the outlined mechanism in Scheme 3.



Scheme 4 Suggested mechanism for the conversion of benzyl chloride **6a** to benzaldehyde **4a** promoted by the TBHP/K_2CO_3 system

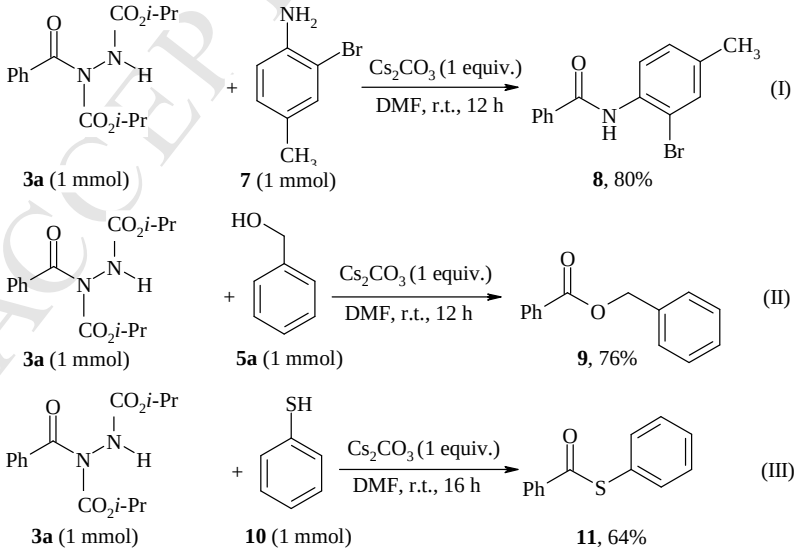
A plausible reaction mechanism has been provided with regard to aryl methanols, which may undergo a different process according to the literature (Scheme 5). Intermediate **E** may be generated *via* hydrogen abstraction from benzyl alcohol **5a** in the presence of $R_4N^+[ClO]^-$ **A″** or $R_4N^+[ClO_2]^-$ **A‴** species generated under the reaction conditions.[31] Next, radical addition of **E** to DAAD **2**, gives radical species **F** (Path i) followed by further oxidation under the reaction conditions which leads to the

formation of **3**. It is also possible that intermediate **E** undergo hydrogen abstraction under the reaction condition to produce benzaldehyde **4a**[32] (Path ii) which in turn can hydroaroylate DAADs according to the suggested mechanism in Scheme 3.



Scheme 5 Possible reaction mechanisms for the hydroaroylation of DAADs **2** with benzyl alcohol **5a** promoted by the TBHP/Aliquat 336 system

Providing the utility of the reaction products, hydrazine imide **3a** treated with 2-bromo-4-methyl aniline **7**, benzyl alcohol **5a** and thiophenol **10**, which afforded amide **8** (80%), benzyl benzoate **9** (76%) and thioester **11** (64%), respectively (Scheme 6, eqs. I, II and III).



Scheme 6 Using hydrazine imide **3a** for the preparation of amide **8**, ester **9** and thioester **11**

3. Conclusion

In conclusion, efficient methods leading to dialkyl hydrazine-1,2-dicarboxylates have been developed *via* TBHP/$R_4N^+X^-$ promoted C(sp^3)−H and C(sp^2)−H bond functionalization of ArX (X = CH_3, CH_2OH, CH_2Cl, CHO) with dialkyl azodicarboxylates. Stable and easily accessible methyl arenes, aryl methanols, arylmethyl chlorides and aldehydes were used as ideal hydroaroylation reagents, and TBHP was utilized as an effective oxidant and oxygen source to form the corresponding hydrazine imides. These methodologies showed high efficiency, short time, metal-free and mild reaction conditions, operational simplicity, and good to excellent yields.

4. Experimental

4.1. General

All chemicals were purchased from Merck (Germany) and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured ($CDCl_3$ solution) with Bruker DPX-250 (at 250.1 and 62.8 MHz, resp.) instrument. Chromatography columns were prepared from Merck silica gel 230–240 meshes.

4.2. General procedure for synthesis of diisopropyl 1-benzoylhydrazine-1,2-dicarboxylate (3a): To the mixture of diisopropyl azodicarboxylate **2a** (0.4 mmol, 0.08 g) in toluene **1a** (8 mmol, 0.74 g), *tert*-butylhydroperoxide (3.2 mmol, 0.42 g) and TBAB (0.2 mmol, 0.064 g) was added. The reaction mixture was stirred at 80 °C under air atmosphere in a sealed tube and the process of the reaction was monitored by TLC. Upon completion, the reaction mixture was transferred to a round-bottom flask. The solvent was then removed under vacuum and the residue was purified by silica gel chromatography, using a mixture of *n*-hexane/EtOAc (4:1) to afford the desired product **3a**.

*4.2.1. Diisopropyl 1-benzoylhydrazine-1,2-dicarboxylate (**3a**)*

Yield: 0.114 g (93%); colorless crystal; m.p. 119–121 °C, [lit.[21a] 115–117 °C]. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.07 (d, J = 6.0 Hz, 6H, $2CH_3$), 1.28 (d, J = 6.1 Hz, 6H, $2CH_3$), 4.9 (sept, J = 6.2 Hz, 1H, OCH), 5.0 (sept, J = 6.2 Hz, 1H, OCH), 7.15 (br s, 1H, NH**)**, 7.40 (t, J = 7.3 Hz, 2H, 2CH), 7.51 (t, J = 7.2 Hz, 1H, CH), 7.68 (d, J = 6.3 Hz, 2H, 2CH). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 21.1, 21.8, 70.5, 72.3, 128.0, 128.2, 131.7, 135.1, 152.8, 155.2, 171.1.

*4.2.2. Diisopropyl 1-(4-methylbenzoyl)hydrazine-1,2-dicarboxylate (**3b**)*

Yield: 0.109 g (85%); white solid; m.p. 106–108 °C [lit.[20] 105–107 °C]. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.10 (d, J = 5.7 Hz, 6H, $2CH_3$), 1.27 (d, J = 6.1 Hz, 6H, $2CH_3$), 2.38 (s, 3H, CH_3), 4.90 (sept, J = 6.2 Hz, 1H, OCH), 5.00 (sept, J = 6.2 Hz, 1H, OCH), 7.18 (s, 1H, NH**)**, 7.22 (s, 2H, 2CH), 7.59 (d, J = 6.6 Hz, 2H, 2CH). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 21.2, 21.5, 21.8, 70.4, 72.2, 128.3, 128.6, 132.0, 142.6, 153.0, 155.2, 171.1.

*4.2.3. Diisopropyl 1-(4-methoxybenzoyl)hydrazine-1,2-dicarboxylate (**3c**)*

Yield: 0.119 g (88%); white solid; m.p. 85–86 °C [lit.[21a] colorless oil]. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.11 (d, J = 5.6 Hz, 6H, $2CH_3$), 1.26 (d, J = 5.8 Hz, 6H, $2CH_3$), 3.83 (s, 3H, OCH_3), 4.85–5.03 (m, 2H, 2OCH), 6.89 (d, J = 8.5 Hz, 2H, 2CH), 7.27 (s, 1H, NH), 7.70 (d, J = 5.6 Hz, 2H, 2CH). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 21.3, 21.8, 55.3, 70.4, 72.1, 113.3, 130.9, 132.1, 153.1, 155.4, 162.8, 170.4.

*4.2.4. Diisopropyl 1-(2,5-dimethoxybenzoyl)hydrazine-1,2-dicarboxylate (**3d**)*

Yield: 0.118 g (80%); colorless oil. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.07 (d, J = 5.3 Hz, 6H, $2CH_3$), 1.21 (d, J = 6.2 Hz, 6H, $2CH_3$), 3.70 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 4.80–4.98 (m, 2H, 2OCH), 6.76 (d, J = 9.0 Hz, 1H, CH), 6.91 (dd, J = 7.5, 2.9 Hz, 1H, CH), 6.96 (s, 1H, NH), 7.28 (d, J = 2.0 Hz, 1H, CH). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 21.2, 21.7, 55.6, 56.0, 70.1, 72.0, 111.9, 113.6, 117.4, 125.7, 150.0, 152.1, 153.2, 155.0, 167.8. Anal. Calcd for $C_{17}H_{24}N_2O_7$ (368.39): C, 55.43; H, 6.57; N, 7.60. Found: C, 55.28; H, 6.45; N, 7.49%.

*4.2.5. Diisopropyl 1-(2-chlorobenzoyl)hydrazine-1,2-dicarboxylate (**3e**)*

Yield: 0.116 g (85%); white crystal; m.p. 119–120 °C. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.09 (s, 6H, $2CH_3$), 1.29 (d, J = 6.2 Hz, 6H, $2CH_3$), 4.86–5.07 (m, 2H, 2OCH), 7.02 (br s, 1H, NH), 7.33–7.48 (m, 4H, 4CH**)**. ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 21.1, 21.7, 70.6, 72.6, 126.5, 127.8, 129.2, 130.8, 131.2, 136.0, 151.5, 154.9, 168.4. Anal. Calcd for $C_{15}H_{19}ClN_2O_5$ (342.78): C, 52.56; H, 5.59; N, 8.17. Found: C, 52.43; H, 5.64; N, 8.04%.

*4.2.6. Diisopropyl 1-(3-nitrobenzoyl)hydrazine-1,2-dicarboxylate (**3f**)*

Yield: 0.110 g (78%); white crystsal; m.p. 116–118 °C [lit.[33] 114–116 °C]. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.15 (d, J = 5.9 Hz, 6H, $2CH_3$), 1.30 (d, J = 6.2 Hz, 6H, $2CH_3$), 4.88–5.06 (m, 2H, 2OCH), 7.21 (s, 1H, NH), 7.63 (t, J = 7.8 Hz, 1H, CH), 8.01 (d, J = 6.1, 1H, CH), 8.36 (d, J = 8.1, 1H, CH), 8.48 (s, 1H, CH). ^{13}C NMR (62.8

MHz, $CDCl_3$): δ 21.3, 21.8, 70.9, 73.0, 122.9, 126.0, 129.3, 133.6, 136.6, 147.6, 152.3, 155.0, 168.8.

*4.2.7. Diisopropyl 1-(1-naphthoyl)hydrazine-1,2-dicarboxylate (**3g**)*

Yield: 0.132 g (92%); white solid; m.p. 122–124 °C.[34] ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 0.68 (d, J = 5.2 Hz, 6H, $2CH_3$), 1.35 (d, J = 6.2 Hz, 6H, $2CH_3$), 4.69 (sept, J = 6.1 Hz, 1H, OCH), 5.09 (sept, J = 6.1 Hz, 1H, OCH), 7.21 (s, 1H, NH), 7.44–7.54 (m, 4H, 4CH), 7.66 (d, J = 5.8 Hz, 1H, CH), 7.86–7.95 (m, 2H, 2CH), 8.20 (d, J = 6.7 Hz, 1H, CH). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 20.7, 21.9, 70.6, 72.2, 124.5, 124.6, 126.3, 127.2, 128.1, 129.8, 130.4, 133.0, 134.0, 152.0, 155.3, 170.4. Anal. Calcd for $C_{19}H_{22}N_2O_5$ (358.39): C, 63.68; H, 6.19; N, 7.82. Found: C, 63.74; H, 6.01; N, 7.58%.

*4.2.8. Diisopropyl 1-(furan-2-carbonyl)hydrazine-1,2-dicarboxylate (**3h**)*

Yield: 0.092 g (77%); white solid; m.p. 94–95 °C. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.23 (d, J = 6.1 Hz, 12H, $4CH_3$), 4.93–5.06 (m, 2H, 2OCH), 6.51 (dd, J = 3.5, 1.6 Hz, 1H, CH), 7.12 (s, 1H, NH), 7.20 (d, J = 3.3 Hz, 1H, CH), 7.56 (s, 1H, CH). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 21.4, 21.7, 70.5, 72.4, 112.0, 119.2, 145.9, 152.5, 155.2, 159.2. Anal. Calcd for $C_{13}H_{18}N_2O_6$ (298.30): C, 52.35; H, 6.08; N, 9.39. Found: C, 52.33; H, 5.91; N, 9.12%.

*4.2.9. Diisopropyl 1-(thiophene-2-carbonyl)hydrazine-1,2-dicarboxylate (**3i**)*

Yield: 0.103 g (82%); pale yellow oil, [lit.[21a] orange oil]. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.01–1.11 (m, 12H, $4CH_3$), 4.74–4.88 (m, 2H, 2OCH), 6.90 (s, 1H, NH), 7.44 (d, J = 4.3 Hz, 1H, CH), 7.72 (d, J = 3.6 Hz, 1H, CH), 8.17 (s, 1H, CH). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 21.2, 21.6, 70.3, 72.2, 126.9, 133.6, 134.3, 135.4, 152.3, 155.6, 162.5.

*4.2.10. Diethyl 1-(2-methoxybenzoyl)hydrazine-1,2-dicarboxylate (**3j**)*

Yield: 0.103 g (83%); cream oil. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.01–1.20 (m, 6H, $2CH_3$), 3.74 (s, 3H, OCH_3), 4.06–4.14 (m, 4H, $2OCH_2$), 6.83 (d, J = 8.3 Hz, 1H, CH), 6.92 (d, J = 7.5 Hz, 1H, CH), 7.36 (m, 2H, 2CH), 7.55 (br s, 1H, NH). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 13.5, 14.2, 55.5, 62.2, 63.6, 110.5, 120.4, 128.7, 131.9, 134.4, 155.5, 155.9, 162.9, 168.1. Anal. Calcd for $C_{14}H_{18}N_2O_6$ (310.31): C, 54.19; H, 5.85; N, 9.03. Found: C, 54.00; H, 5.86; N, 8.86%.

*4.2.11. Diethyl 1-(4-methoxybenzoyl)hydrazine-1,2-dicarboxylate (**3k**)*

Yield: 0.111 g (90%); colorless oil, [lit.[19] colorless oil]. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.07 (t, J = 6.8 Hz, 3H, CH_3), 1.21 (t, J = 6.7 Hz, 3H, CH_3), 3.77 (s, 3H, OCH_3), 4.07–4.20 (m, 4H, $2OCH_2$), 6.84 (d, J = 8.7 Hz, 2H, 2CH), 7.65 (d, J = 8.0

Hz, 2H, 2CH), 7.80 (s, 1H, NH). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 13.7, 14.2, 55.3, 62.3, 63.7, 113.3, 130.9, 131.9, 153.7, 155.8, 162.8, 170.4.

*4.2.12. Diethyl 1-(2,5-dimethoxybenzoyl)hydrazine-1,2-dicarboxylate (**3l**)*

Yield: 0.112 g (82%); cream oil. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 0.94 (t, J = 6.2 Hz, 3H, CH_3), 1.09 (t, J = 7.1 Hz, 3H, CH_3), 3.58 and 3.60 (s, 6H, $2OCH_3$), 3.95–4.10 (m, 4H, $2CH_2$), 6.68 (d, J = 9 Hz, 1H, CH), 6.78 (d, J = 2.8 Hz, 1H, CH), 6.85 (d, J = 11.5 Hz, 1H, CH), 7.88 (s, 1H, NH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 13.4, 14.0, 55.4, 56.0, 62.0, 63.5, 111.9, 113.7, 117.2, 125.4, 150.0, 152.7, 153.1, 155.5, 167.7. Anal. Calcd for $C_{15}H_{20}N_2O_7$ (340.33): C, 52.94; H, 5.92; N, 8.23. Found: C, 52.82; H, 5.85; N, 8.05%.

*4.2.13. Diethyl 1-(2-chlorobenzoyl)hydrazine-1,2-dicarboxylate (**3m**)*

Yield: 0.102 g (81%); colorless oil, [lit.[19] colorless oil]. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.07 (t, J = 6.6 Hz, 3H, CH_3), 1.27 (t, J = 7.1 Hz, 3H, CH_3), 4.15 (q, J = 7.07 Hz, 2H, CH_2), 4.23 (q, J = 7.1 Hz, 2H, CH_2), 7.26–7.40 (m, 5H, 4CH and NH**)**. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 13.5, 14.2, 62.6, 64.1, 126.6, 127.8, 129.2, 130.9, 131.7, 135.6, 152.2, 155.3, 170.1.

*4.2.14. Diethyl 1-(3-chlorobenzoyl)hydrazine-1,2-dicarboxylate (**3n**)*

Yield: 0.107 g (85%); white solid; m.p. 83–85 °C. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.12 (t, J = 6.9 Hz, 3H, CH_3), 1.30 (t, J = 7.1 Hz, 3H, CH_3), 4.14–4.29 (m, 4H, $2OCH_2$), 7.28–7.65 (m, 5H, 4CH and NH). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 13.6, 14.2, 62.7, 64.1, 126.0, 127.9, 129.4, 131.8, 133.4, 134.1, 153.0, 155.5, 169.7. Anal. Calcd for $C_{13}H_{15}ClN_2O_5$ (314.73): C, 49.61; H, 4.80; N, 8.90. Found: C, 49.44; H, 4.63; N, 8.75%.

*4.2.15. Diethyl 1-(3-nitrobenzoyl)hydrazine-1,2-dicarboxylate (**3o**)*

Yield: 0.098 g (75%); white solid; m.p. 83–85 °C. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.17 (t, J = 7.0 Hz, 3H, CH_3), 1.31 (t, J = 7.0 Hz, 3H, CH_3), 4.20–4.32 (m, 4H, $2OCH_2$), 7.36 (s, 1H, NH), 7.64 (t, J = 7.9 Hz, 1H, CH), 7.99 (d, J = 6.7 Hz, 1H, CH), 8.37 (d, J = 8.1 Hz, 1H, CH) 8.49 (s, 1H, CH). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 13.7, 14.2, 62.9, 64.4, 122.9, 126.1, 129.3, 133.6, 136.3, 147.7, 152.9, 155.4, 170.8. Anal. Calcd for $C_{13}H_{15}N_3O_7$ (325.28): C, 48.00; H, 4.65; N, 12.92. Found: C, 47.88; H, 4.39; N, 12.84%.

*4.2.16. Diethyl 1-(furan-2-carbonyl)hydrazine-1,2-dicarboxylate (**3p**)*

Yield: 0.081 g (75%); pale yellow oil.[35] ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.10–1.26 (m, 6H, $2CH_3$), 4.07–4.24 (m, 4H, $2CH_2$), 6.46 (s, 1H, CH), 7.16 (d, J = 2.9 Hz, 1H,

CH), 7.51 (s, 1H, NH), 7.73 (s, 1H, CH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 13.8, 14.1, 62.4, 63.9, 112.0, 119.4, 146.0, 146.2, 153.1, 155.7, 158.9. Anal. Calcd for $C_{11}H_{14}N_2O_6$ (270.24): C, 48.89; H, 5.22; N, 10.37. Found: C, 48.73; H, 5.05; N, 10.08%.

*4.2.17. Diethyl 1-(thiophene-2-carbonyl)hydrazine-1,2-dicarboxylate (**3q**)*

Yield: 0.089 g (78%); colorless oil, [lit.[19] colorless oil]. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.24–1.29 (m, 6H, $2CH_3$), 4.21–4.33 (m, 4H, $2OCH_2$), 7.07 (d, J = 4.4 Hz, 1H, CH), 7.54 (s, 1H, NH), 7.59 (d, J = 4.9 Hz, 1H, CH), 7.87 (d, J = 3.7 Hz, 1H, CH). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 13.9, 14.2, 62.8, 64.2, 127.1, 133.6, 133.8, 135.6, 153.8, 155.8, 162.5.

*4.2.18. Diisopropyl 1-(3-methylbenzoyl)hydrazine-1,2-dicarboxylate (**3r**)*

Yield: 0.138 g (86%); colorless crystal; m.p. 101–103 °C [lit.[2] 102–104 °C]. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.07 (d, J = 5.8 Hz, 6H, $2CH_3$), 1.29 (d, J = 6.1 Hz, 6H, $2CH_3$), 2.37 (s, 3H, CH_3), 4.90 (sept, J = 6.2 Hz, 1H, OCH), 5.01 (sept, J = 6.2 Hz, 1H, OCH), 7.09 (s, 1H, NH), 7.30 (d, J = 6.2 Hz, 2H, 2CH), 7.49 (s, 2H, 2CH). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 21.1, 21.2, 21.8, 70.5, 72.2, 125.2, 127.9, 128.5, 132.5, 135.0, 137.8, 152.8, 155.2, 171.0.

*4.2.19. Diisopropyl 1-(4-isopropylbenzoyl)hydrazine-1,2-dicarboxylate (**3s**)*

Yield: 0.144 g (82%); white solid; m.p. 104–106 °C [lit.[20] 105–107 °C]. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 0.89 (d, J = 5.8 Hz, 6H, $2CH_3$), 1.07 (d, J = 6.8 Hz, 12H, $4CH_3$), 2.76 (sept, J = 6.8 Hz, 1H, CH), 4.73 (sept, J = 6.0 Hz, 1H, OCH), 4.84 (sept, J = 6.2 Hz, 1H, OCH), 7.08 (t, J = 8.1 Hz, 2H, 2CH), 7.47 (d, J = 7.6 Hz, 2H, 2CH), 8.23 (s, 1H, NH). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 20.9, 21.5, 23.4, 33.9, 69.8, 71.8, 125.8, 126.1, 128.3, 132.5, 152.9, 155.5, 171.0.

*4.2.20. Diisopropyl 1-(3,4-dimethoxybenzoyl)hydrazine-1,2-dicarboxylate (**3t**)*

Yield: 0.158 g (86%); white crystal; m.p. 110–112 °C. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.13 (d, J = 6.1 Hz, 6H, $2CH_3$), 1.26 (d, J = 6.1 Hz, 6H, $2CH_3$), 3.88 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 4.83–5.06 (m, 2H, 2OCH), 6.85 (d, J = 8.3 Hz, 1H, CH), 7.18 (s, 1H, CH), 7.28 (s, 1H, NH), 7.37 (d, J = 6.4 Hz, 1H, CH). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 21.3, 21.8, 55.8, 55.9, 70.3, 72.1, 109.9, 111.4, 122.9, 126.8, 148.4, 152.5, 153.2, 155.3, 170.6. Anal. Calcd for $C_{17}H_{24}N_2O_7$ (368.39): C, 55.43; H, 6.57; N, 7.60. Found: C, 55.14; H, 6.36; N, 7.45%.

*4.2.21. Diethyl 1-(3-methylbenzoyl)hydrazine-1,2-dicarboxylate (**3u**)*

Yield: 0.124 g (84%); white solid; m.p. 71–73 °C, [lit.[19] colorless oil]. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.08 (t, J = 7.0 Hz, 3H, CH_3), 1.30 (t, J = 7.1 Hz, 3H, CH_3), 2.38 (s, 3H, CH_3), 4.11–4.29 (m, 4H, $2OCH_2$), 7.21 (br s, 1H, NH), 7.31 (d, J = 7.2 Hz, 2H, 2CH), 7.50 (s, 2H, 2CH). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 13.6, 14.2, 21.1, 62.5, 63.8, 125.2, 127.9, 128.5, 132.7, 134.6, 137.9, 153.4, 155.5, 170.0.

*4.2.22. Diethyl 1-(4-chlorobenzoyl)hydrazine-1,2-dicarboxylate (**3v**)*

Yield: 0.121 g (77%); white solid; m.p. 83–85 °C. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.12 (t, J = 6.9 Hz, 3H, CH_3), 1.28 (t, J = 7.0 Hz, 3H, CH_3), 4.16 (q, J = 7.0 Hz, 2H, CH_2), 4.23 (q, J = 7.1 Hz, 2H, CH_2), 7.37 (s, 1H, NH), 7.40 (s, 2H, 2CH), 7.62 (d, J = 7.7 Hz, 2H, 2CH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 13.7, 14.2, 62.6, 64.0, 128.3, 129.5, 132.9, 138.2, 153.2, 155.6, 170.1. Anal. Calcd for $C_{13}H_{15}ClN_2O_5$ (314.73): C, 49.61; H, 4.80; N, 8.90. Found: C, 49.53; H, 4.66; N, 8.68%.

*4.2.23. Diethyl 1-(1-naphthoyl)hydrazine-1,2-dicarboxylate (**3w**)*

Yield: 0.142 g (86%); white solid; m.p. 88–90 °C.[34] ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 0.73 (t, J = 6.2 Hz, 3H, CH_3), 1.34 (t, J = 7.0 Hz, 3H, CH_3), 3.93 (q, J = 6.5 Hz, 2H, OCH_2), 4.32 (q, J = 7.0 Hz, 2H, OCH_2), 7.35 (s, 1H, NH), 7.44–7.65 (m, 4H, 4CH), 7.86–7.96 (m, 2H, 2CH), 8.20 (d, J = 6.4 Hz, 1H, CH). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 13.2, 14.3, 62.7, 63.8, 124.5, 124.8, 126.3, 127.3, 128.2, 129.7, 130.6, 133.0, 133.5, 152.6, 155.6, 170.3. Anal. Calcd for $C_{17}H_{18}N_2O_5$ (330.34): C, 61.81; H, 5.49; N, 8.48. Found: C, 61.67; H, 5.26; N, 8.37%.

*4.2.24. Diethyl 1-(4-methylbenzoyl)hydrazine-1,2-dicarboxylate (**3x**)*

Yield: 0.072 g (82%); white solid; m.p. 67–69 °C. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.11 (t, J = 7.0 Hz, 3H, CH_3), 1.29 (t, J = 7.0 Hz, 3H, CH_3), 2.40 (s, 3H, CH_3), 4.17 (q, J = 7.1 Hz, 2H, OCH_2), 4.24 (q, J = 7.1 Hz, 2H, OCH_2), 7.22 (d, J = 7.9 Hz, 2H, 2CH), 7.28 (s, 1H, NH), 7.61 (d, J = 7.4 Hz, 2H, 2CH). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 13.7, 14.2, 21.5, 62.5, 63.8, 128.4, 128.7, 131.6, 142.8, 153.5, 155.6, 170.9. Anal. Calcd for $C_{14}H_{18}N_2O_5$ (294.31): C, 57.14; H, 6.16; N, 9.52. Found: C, 56.91; H, 6.89; N, 9.35%.

Acknowledgement

This research was supported by the Research Council of University of Tehran.

References:

1. (a) Goldberga, K. I.; Goldman, A. S. Activation and Functionalization of C−H Bonds (ACS Symposium), Oxford University Press, Oxford, **2004**; (b) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507–514; (c) Godula, K.; Sames, D. *Science* **2006**, *312*, 67–72; (d) Bergman, R. G. *Nature* **2007**, *446*, 391–393; (e) Yeung C. S.; Dong, V. M. *Chem. Rev*. **2011**, *111*, 1215–1292; (f) Liu, C.; Zhang, H.; Shi, W.; Lei, A. *Chem. Rev*. **2011**, *111*, 1780–1824; (g) Bugaut, X.; Glorius, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 7479–7481; (h) Wendlandt, A. E.; Suess, A. M.; Stahl, S. S. *Angew. Chem., Int. Ed*. **2011**, *50*, 11062–11087; (i) Yamaguchi, J.; Itami, K.; Yamaguchi, A. D. *Angew. Chem., Int. Ed*. **2012**, *51*, 8960–9009; (j) Gutekunst, W. R.; Baran, P. S. *Chem. Soc. Rev*. **2011**, *40*, 1976–1991; (k) Wencel-Delord, J.; Dröge, T.; Liu, F.; Glorius, F. *Chem. Soc. Rev*. **2011**, *40*, 4740–4761; (l) Jazzar, R.; Hitce, J.; Renaudat, A.; Sofack-Kreutzer, J.; Baudoin, O. *Chem. Eur. J*. **2010**, *16*, 2654–2672; (m) Crabtree, R. H. *Chem. Rev*. **2010**, *110*, 575; (n) Kakiuchi, F.; Chatani, N. *Adv. Synth. Catal*. **2003**, *345*, 1077–1101; (o) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res*. **2001**, *34*, 633–639; (p) Dyker, G. *Angew. Chem., Int. Ed*. **1999**, *38*, 1698–1712.

2. (a) Dyker, G. Handbook of C−H Transformations: Applications in Organic Synthesis, Wiley-VCH, Weinheim, **2005**; (b) Yu, J. Q.; Shi, Z. J. C−H Activation, Springer, Berlin, Germany, **2010**; (c) Lewis, J. C. Bergman, R. G.; Ellman, J. A. *Acc. Chem. Res.* **2008**, *41*, 1013–1025; (d) Chen, X.; Engle, K. M.; Wang, D. H.; Yu, J. Q. *Angew. Chem., Int. Ed*. **2009**, *48*, 5094–5115; (e) Sun, C. L.; Li, B. J.; Shi, Z. J. *Chem. Commun*. **2010**, *46*, 677–685; (f) Gunay, A.; Theopold, K. H. *Chem. Rev*. **2010**, *110*, 1060–1081; (g) Lyons, T. W.; Sanford, M. S. *Chem. Rev*. **2010**, *110*, 1147–1169; (h) Sun, C. L.; Li, B. J.; Shi, Z. J. *Chem. Rev*. **2011**, *111*, 1293–1314; (i) Ackermann, L. *Chem. Rev*. **2011**, *111*, 1315–1345; (j) Lie, B. J.; Shi, Z. J. *Chem. Soc. Rev*. **2012**, *41*, 5588–5598.

3. (a) Piou, T.; Neuville, L.; Zhu, J. *Angew. Chem., Int. Ed*. **2012**, *51*, 11561–11565; (b) Zhou, S. L.; Guo, L. N.; Wang, S.; Duan, X. H. *Chem. Commun*. **2014**, *50*, 3589–3591; (c) Curto, J. M.; Kozlowski, M. C. *J. Am. Chem. Soc*. **2015**, *137*, 18–21; (d); Lin, Y.; Zhu, L.; Lan, Y.; Rao, Y. *Chem. Eur. J*. **2015**, *21*, 14937–14942; (e) Guo, L. N.; Wang, S.; Duan, X. H.; Zhou, S. L. *Chem. Commun*. **2015**, *51*, 4803–4806.

4. (a) Nordstrøm, L. U.; Vogt, H.; Madsen, R. *J. Am. Chem. Soc.* **2008**, *130*, 17672–17673; (b) Xiao, F.; Shuai, Q.; Zhao, F.; Basle, O.; Deng, G.; Li, C. J. *Org. Lett*.

2011, *13*, 1614–1617; (c) Xiao, F.; Liu, Y.; Tang, C.; Deng, G. J. *Org. Lett.* **2012**, *14*, 984–987; (d) Fu, Z.; Lee, J.; Kang, B.; Hong, S. H. *Org. Lett.* **2012**, *14*, 6028–6031; (e) Kang, B.; Fu, Z.; Hong, S. H. *J. Am. Chem. Soc.* **2013**, *135*, 11704–11707; (f) Wang, N.; Zou, X.; Ma, J.; Li, F. *Chem. Commun.* **2014**, *50*, 8303–8305.

5. Laha, J. K.; Jethava, K. P.; Patel, S. *Org. Lett.* **2015**, *17*, 5890–5893.
6. (a) Yu, Y.; Jiao, L.; Wang, J.; Wang, H.; Yu, C.; Hao, E.; Boens, N. *Chem. Commun.* **2017**, *53*, 581–584; (b) Hao, W.-J.; Du, Y.; Wang, D.; Jiang, B.; Gao, Q.; Tu, S.-J.; Li, G. *Org. Lett.* **2016**, *18*, 1884–1887; (c) Wong, Y. C.; Tseng, C. T.; Kao, T. T.; Yeh, Y. C.; Shia, K. S. *Org. Lett*. **2012**, *14*, 6024–6027; (d) Nobuta, T.; Fujiya, A.; Yamaguchi, T.; Tada, N.; Miura, T.; Itoh, A. *RSC Adv*. **2013**, *3*, 10189–10192; (e) Mai, W. P.; Song, G.; Yuan, J. W.; Yang, L. R.; Sun, G. C.; Xiao, Y. M.; Mao, P.; Qu, L. B. *RSC Adv*. **2013**, *3*, 3869–3872; (f) Xie, J.; Jiang, H.; Cheng, Y.; Zhu, C. *Chem. Commun*. **2012**, *48*, 979–981; (g) Froehr, T.; Sindlinger, C. P.; Kloeckner, U.; Finkbeiner, P.; Nachtsheim, B. J. *Org. Lett*. **2011**, *13*, 3754–3757; (h) Uyanik, M.; Okamoto, H.; Yasui, T.; Ishihara, K. *Science* **2010**, *328*, 1376–1379; (i) Uyanik, M.; Suzuki, D.; Yasui, T.; Ishihara, K. *Angew. Chem., Int. Ed*. **2011**, *50*, 5331–5334; (j) Shi, E.; Shao, Y.; Chen, S.; Hu, H.; Liu, Z.; Zhang, J.; Wan, X. *Org. Lett*. **2012**, *14*, 3384–3387; (k) Chen, J.; Jiang, Y.;Yu, J. T.; Cheng, J. *J. Org. Chem*. **2016**, *81*, 271–275; (l) Li, X.; Xu, X.; Hu, P.; Xiao, X.; Zhou, C. *J. Org. Chem*. **2013**, *78*, 7343–7348; (m) Feng, J.; Liang, S.; Chen, S. Y.; Zhang, J.; Fu, S. S.; Yu, X. Q. *Adv. Synth. Catal*. **2012**, *354*, 1287–1292.
7. (a) Hegedus, L. S. *Angew. Chem., Int. Ed*. **1988**, *27*, 1113–1126; (b) Nair, V.; Menon, R. S.; Sreekanth, A. R.; Abhilash, N.; Biju, A. T. *Acc. Chem. Res*. **2006**, *39*, 520–530.
8. (a) Demers, J. P.; Klaubert, D. H. *Tetrahedron Lett*. **1987**, *28*, 4933–4934; (b) Katritzky, A. R.; Wu, J.; Verin, S. V. *Synthesis* **1995**, *26*, 651–653; (c) Zaltsgendler, I.; Leblanc, Y.; Bernstein, M. A. *Tetrahedron Lett*. **1993**, *34*, 2441–2444; (d) Uemura, T.; Chatani, N. *J. Org. Chem*. **2005**, *70*, 8631–8634; (e) Gu, L.; Neo, S.; Zhang, Y. *Org. Lett*. **2011**, *13*, 1872–1874; (f) Yavari, I.; Ghazanfarpour-Darjani, M.; Ahmadian, S.; Solgi, Y. *Synlett* **2011**, *22*, 1745–1747; (g) Yavari, I.; Ghazanfarpour-Darjani, M.; Bayat, M. Malekafzali, A. *Synlett* **2015**, *26*, 942–944; (h) Khalaj, M.; Ghazanfarpour-Darjani, M. *RSC Adv*. **2015**, *5*, 80698–80701.

9. (a) Schenck, G. O.; Formanek, H. *Angew. Chem*. **1958**, *70*, 505; (b) Askani, R. *Chem. Ber*. **1965**, *98*, 2551–2555; (c) Denis, A.; Renou, C. *Tetrahedron Lett*. **2002**, *43*, 4171–4174.

10. (a) Bøgevig, A.; Juhl, K.; Kumaragurubaran, N.; Zhuang, W.; Jørgensen, K. A. *Angew. Chem., Int. Ed*. **2002**, *41*, 1790–1793; (b) List, B. *J. Am. Chem. Soc*. **2002**, *124*, 5656–5657; (c) Chowdari, N. S.; Barbas III, C. F. *Org. Lett*. **2005**, *7*, 867–870; (d) Mashiko, T.; Hara, K.; Tanaka, D.; Fujiwara, Y.; Kumagai, N.; Shibasaki, M. *J. Am. Chem. Soc*. **2007**, *129*, 11342–11343; (e) Desmarchelier, A.; Yalgin, H.; Coeffard, V.; Moreau, X.; Greck, C. *Tetrahedron Lett*. **2011**, *52*, 4430–4432; (f) Theodorou, A.; Papadopoulos, G. N.; Kokotos, C. G. *Tetrahedron* **2013**, *69*, 5438–5443.

11. (a) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl*. **1969**, *8*, 556–577; (b) Stephenson, L. M.; Mattern, D. L. *J. Org. Chem*. **1976**, *41*, 3614–3619; (c) Grigg, R.; Kemp, J. *J. Chem. Soc. Chem. Commun*. **1977**, 125–126; (d) Dang, H. S.; Davies, A. G. *J. Chem. Soc. Perkin Trans. 2* **1991**, 721–734; (e) Leblanc, Y.; Zamboni, R.; Bernstein, M. A. *J. Org. Chem*. **1991**, *56*, 1971–1972; (f) Brimble, M. A.; Heathcock, C. H. *J. Org. Chem*. **1993**, *58*, 5261–5263; (g) Kinart, W. J. *J. Chem. Res. (S)* **1994**, 486–487; (h) Sarkar, T. K.; Ghorai, B. K.; Das, S. K.; Grangopadhyay, P.; Subba Rao, P. S. V. *Tetrahedron Lett*. **1996**, *37*, 6607–6610; (i) Aly, A. A.; Ehrhardt, S.; Hopf, H.; Dix, I.; Jones, P. G. *Eur. J. Org. Chem*. **2006**, 335–350; (j) Biswas, A.; Sharma, B. K.; Willett, J. L.; Erhan, S. Z.; Cheng, H. N. *Green Chem*. **2008**, *10*, 298–303.

12. (a) Brunn, E.; Huisgen, R. *Angew. Chem., Int. Ed. Engl*. **1969**, *8*, 513–515; (b) Nair, V.; Biju, A. T.; Mohanan, K.; Suresh, E. *Org. Lett*. **2006**, *8*, 2213–2216; (c) Otte, R. D.; Sakata, T.; Guzei, I. A.; Lee, D. *Org. Lett*. **2005**, *7*, 495–498; (d) Nair, V.; Biju, A. T.; Abhilash, K. G.; Menon, R. S.; Suresh, E. *Org. Lett*. **2005**, *7*, 2121–2123; (e) Nair, V.; Biju, A. T.; Vinod, A. U.; Suresh, E. *Org. Lett*. **2005**, *7*, 5139–5142.

13. (a) Shamsabadi, A.; Chudasama, V. *Org. Biomol. Chem.* **2017**, *15*, 17–33; (b) Maruani, A.; Lee, M. T. W.; Watkins, G.; Akhbar, A. R.; Baggs, H.; Shamsabadi, A.; Richards, D. A.; Chudasama, V. *RSC Adv.* **2016**, *6*, 3372–3376; (c) Chudasama, V.; Akhbar, A. R.; Bahou, K. A.; Fitzmaurice, R. J.; Caddick, S. *Org. Biomol. Chem.* **2013**, *11*, 7301–7317.

14. Lee, D.; Otte, R. D. *J. Org. Chem*. **2004**, *69*, 3569–3571.

15. (a) Qin, Y.; Peng, Q.; Song, J.; Zhou, D. *Tetrahedron Lett*. **2011**, *52*, 5880–5883; (b) Inamdar, S. M.; More, V. K.; Mandal, S. K. *Chem. Lett*. **2012**, *41*, 1484–1486.
16. Qin, Y.; Zhou, D.; Li, M. *Lett. Org. Chem*. **2012**, *9*, 267–272.
17. (a) Zhang, Q.; Parker, E.; Headley, A. D.; Ni, B. *Synlett* **2010**, *16*, 2453–2456; (b) Chudasama, V.; Ahern, J. M.; Dhokia, D. V.; Fitzmaurice, R. J.; Caddick, S. *Chem. Commun*. **2011**, *47*, 3269–3271.
18. Ni, B.; Zhang, Q.; Garre, S.; Headley, A. D. *Adv. Synth. Catal*. **2009**, *351*, 875–880.
19. Zang, H. B.; Wang, Y.; Gu, Y.; Xu, P. F. *RSC Adv*. **2014**, *4*, 27796–27799.
20. Mariappan, A.; Rajaguru, K.; Muthusubramanian, S.; Bhuvanesh, N. *Tetrahedron Lett*. **2015**, *56*, 338–341.
21. (a) Kokotos, C. G.; Limnios, D.; Papadopoulos, G. N. *Chem. Eur. J*. **2014**, *20*, 13811–13814; (b) Ryu, I.; Tani, A.; Fukuyama, T.; Ravelli, D.; Montanaro, S.; Fagnoni, M. *Org. Lett.* **2013**, 15, 2554–2557; (c) Koutoulogenis, G. S.; Kokotou, M. G.; Voutyritsa, E.; Limnios, D.; Kokotos, C. G. *Org. Lett*. **2017**, *19*, 1760–1763.
22. Pérez, J. M.; Ramón, D. J. *Adv. Synth. Catal*. **2014**, *356*, 3039–3047.
23. (a) Adib, M.; Ayashi, N.; Heidari, F.; Mirzaei, P. *Synlett* **2016**, *27*, 1738–1742; (b) Adib, M.; Sheikhi, E.; Yazzaf, R.; Bijanzadeh, H. R.; Mirzaei P. *Tetrahedron Lett.* **2016**, *57*, 841–844; (c) Adib, M.; Yasaei, Z.; Mirzaei P. *Synlett* **2016**, *27*, 383–386; (d) Adib, M.; Zainali, M.; Kim, I. *Synlett* **2016**, *27*, 1844–1847; (e) Adib, M.; Janatian Ghazvini, H.; Soheilizad, M.; Saeedi, S.; Tajbakhsh, M.; Amanlou, M. *Helv. Chim. Acta* **2015**, *98*, 1079–1086; (f) Adib, M.; Soheilizad, M.; Rajai-Daryasarei, S.; Mirzaei, P. *Synlett* **2015**, *26*, 1101–1105; (g) Sayahi, M. H.; Adib, M.; Hamooleh, Z.; Zhu, L. G.; Amanlou, M. *Helv. Chim. Acta* **2015**, *98*, 1231–1239.
24. (a) Adib, M.; Pashazadeh, R.; Rajai-Daryasarei, S.; Kabiri, R.; Gohari, S. J. A. *Synlett* **2016**, *27*, 2241–2245; (b) Adib, M.; Pashazadeh, R.; Rajai-Daryasarei, S.; Mirzaei, P.; Gohari, S. J. A. *Tetrahedron Lett.* **2016**, *57*, 3071–3074; (c) Adib, M.; Rajai-Daryasarei, S.; Pashazadeh, R.; Tajik, M.; Mirzaei, P. *Tetrahedron Lett.* **2016**, *57*, 3701–3705; (d) Adib, M.; Pashazadeh, R.; Rajai-Daryasarei, S.; Kabiri, R.; Jahani, M. *RSC Adv.* **2016**, *6*, 110656–110660; (e) Adib, M.; Pashazadeh, R.; Gohari, S. J. A.; Shahsavari, F. *Synlett* **2017**, 28, 1481–1485; (f) Adib, M.; Pashazadeh, R. *Synlett* **2017**, in press, DOI: 10.1055/s-0036-1590905.

25. There are several similar reports in which increasing the reaction time has a negative effect on the yield of the product, for example see: Wang, P.; Rao, H.; Hua, R.; Li, C.-J. *Org. Lett*. **2012**, *14*, 902–905; Sankari Devi, E.; Alanthadka, A.; Tamilselvi, A.; Nagarajan, S.; Sridharan, V.; Maheswari, C. U. *Org. Biomol. Chem.* **2016**, *14*, 8228–8231; Yuan, J. W.; Yang, L. R.; Mao, P.; Qu, L. B. *Org. Chem. Front.* **2017**, *4*, 545–554.
26. Majji, G.; Rajamanickam, S.; Khatun, N.; Santra, S. K.; Patel, B. K. *J. Org. Chem.* **2015**, *80*, 3440–3446; Ma, D.; Chen, W.; Hu, G.; Zhang, Y.; Gao, Y.; Yin, Y.; Zhao, Y. *Green Chem.* **2016**, *18*, 3522–3526; Gao, P.; Wang, J.; Bai, Z. J.; Shen, L.; Yan, Y. Y.; Yang, D. S.; Fan, M. J.; Guan, Z. H. *Org. Lett*. **2016**, *18*, 6074–6077.
27. Anelli, P. L.; Biffi, C.; Montanari, F.; Quici, S. *J. Org. Chem.* **1987**, *52*, 2559–2562; Inokuchi, T.; Matsumoto, S.; Nishiyama, T.; Torii, S. *J. Org. Chem.* **1990**, *55*, 462–466.
28. There are several reports in which using TEMPO has proved the radical mechanism, for example see: Hua, J.; Guo, S.; Yang, Z.; Fang, Z.; Guo, K. *Org. Process Res. Dev*. **2017**, *21*, 1633–1637; Siddaraju, Y.; Prabhu, K. R. *Tetrahedron* **2016**, *72*, 959–967; Zhang, H.; Dong, D. Q.; Hao, S. H.; Wang, Z. L. *RSC Adv.* **2016**, *6*, 8465–8468; Gu, J.; Fang, Z.; Yang, Y.; Yang, Z.; Wan, L.; Li, X.; Wei, P.; Guo, K. *RSC Adv*. **2016**, *6*, 89413–89416; Ali, W.; Behera, A.; Guin, S.; Patel, B. K. *J. Org. Chem*. **2015**, *80*, 5625–5632; Liu, W.; Li, Y.; Liu, K.; Li, Z. *J. Am. Chem. Soc*. **2011**, *133*, 10756–10759.
29. (a) Zhu, C.; Wei, Y. *ChemSusChem*. **2011**, *4*, 1082–1086; (b) Rajamanickam, S.; Majji, G.; Santra, S. K.; Patel, B. K. *Org. Lett*. **2015**, *17*, 5586–5589.
30. Campbell, T. W.; Coppinger, G. M. *J. Am. Chem. Soc*. **1951**, *73*, 1788–1789; Behera, A.; Ali, W.; Guin, S.; Khatun, N.; Mohanta, P. R.; Patel, B. K. *RSC Adv.* **2015**, *5*, 33334–33338; Zhang, G.; Sun, S.; Yang, F.; Zhang, Q.; Kang, J.; Wu, Y.; Wu, Y. *Adv. Synth. Catal*. **2015**, *357*, 443–450.
31. Xie, Z.; Cai, Y.; Hu, H.; Lin, C.; Jiang, J.; Chen, Z.; Wang, L.; Pan, Y. *Org. Lett.* **2013**, *15*, 4600–4603.
32. Gadilohar, B. L.; Kumbhar, H. S.; Shankarling, G. S. *New J. Chem.* **2015**, *39*, 4647–4657.
33. Akhbar, A. R.; Chudasama, V.; Fitzmaurice, R. J.; Powell, L.; Caddick, S. *Chem. Commun*. **2014**, *50*, 743–746.

34. Sugimoto, O.; Arakaki, T.; Kamio, H.; Tanji, K. I. *Chem. Commun.* **2014**, *50*, 7314–7317.

35. Zaballos-García, E.; González-Rosende, M. E.; Jorda-Gregori, J. M.; Sepúlveda-Arques, J.; Jennings, W. B.; O'Leary, D.; Twomey, S. *Tetrahedron* **1997**, *53*, 9313–9322.