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One-Pot Synthesis of Carbamoyl Azides via Palladium-Catalysed Azidocarbonylation of Haloarenes Using *N*-Formylsaccharin as a CO Surrogate

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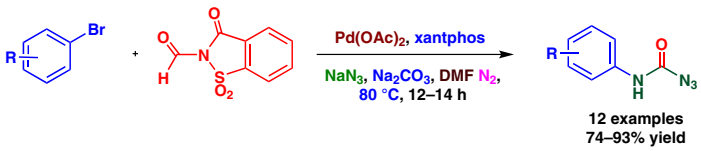

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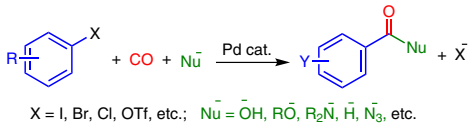
Abstract A highly efficient one-pot synthesis of carbamoyl azides from haloarenes and sodium azide has been developed. The protocol involves palladium-catalysed azidocarbonylation of haloarenes utilizing *N*-formylsaccharin as a CO source to form acyl azides, which undergo in situ Curtius rearrangement to afford the desired carbamoyl azides. *N*-Formylsaccharin is an easy-to-handle solid alternative to CO gas.

Key words aromatic halides, sodium azide, *N*-formylsaccharin, catalysis, CO surrogates, carbamoyl azides

Metal-catalysed carbonylation reactions have undoubtedly changed the landscape of organic synthesis both in academia and in industry,[1] owing to their great flexibility for the design of innovative, yet practical tactics for multistep bond formation and bond cleavage in a minimum number of synthetic steps. Notably, they have been employed for the synthesis of various pharmaceuticals, agrochemicals and their intermediates.[1] In 1974, Heck and Schoenberg reported[2] their seminal work on palladium-catalysed carbonylation of haloarenes with carbon monoxide, which demonstrated its great synthetic potential and impact in the field of palladium catalysis. Recently, this reaction has emerged as one of the most powerful tools for the synthesis of various carbonyl-containing aromatic compounds of academic and industrial importance such as carboxylic acids, esters, amides, aldehydes, and azides (Scheme 1).[1d,h,i,2c,3]

In general, carbonylation reactions employ CO gas as one of the reagents, which is highly toxic, odourless, inflammable, difficult to transport in bulk, and must be handled with special care. In order to overcome the disadvantages of using gaseous carbon monoxide, CO-free carbonylation reactions have been the target of extensive research over the last three decades.[1c,g,h,3c,4] Consequently, several CO surrogates have been developed,[5–9] which include alcohols,[5] formic acid,[6] formates,[7] formaldehyde,[8] biomass,[5b] and carbon dioxide.[9] Recently, Manabe and co-workers reported *N*-formylsaccharin as an efficient and advantageous CO source for palladium-catalysed reductive carbonylation of aryl halides[1g] and fluorocarbonylation of aryl and alkenyl halides.[1h] It has also been very recently used by Fleischer et al. as a CO surrogate in alkoxycarbonylation of alkenes.[1b] *N*-Formylsaccharin is a superior alternative to other available CO surrogates for palladium-catalysed carbonylation reactions, due to its low cost, ready availability, stability to storage, ease of handling, and high reactivity.



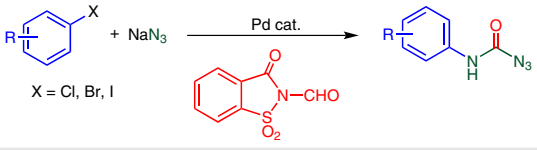
Scheme 1 Palladium-catalysed carbonylative synthesis of aromatic compounds

Carbamoyl azides are important synthetic intermediates in organic and biological chemistry.[10] This is mainly because they undergo various fundamental functional group transformations, such as conversion into amines, urea derivatives, and urethanes.[11] The synthesis of biotin carried out by Deroose and De Clercq is an important illustration of the synthetic applications of carbamoyl azides.[12] Most commonly, carbamoyl azides are synthesized from acyl azides, via a Curtius rearrangement.[11a,b,13] The general strategies for the synthesis of acyl azides involve reaction of activated acid derivatives such as carboxylic acids, acyl chlorides, anhydrides and acylbenzotriazoles.[14] They have also been prepared by azidation of aldehydes[15] with stoichiometric oxidants. Grushin and co-workers have prepared acyl azides by palladium-catalysed azidocarbonylation, a novel Heck-type carbonylation reaction, employing

haloarenes, NaN_3, and CO gas.[1d,i] Recently, TBAI-catalysed C–H azidation of aldehydes with TBA-N_3 has been reported by Saito et al.[16] We have also developed a visible light induced azidation of the aldehydic C–H with carbon tetrabromide and NaN_3 for the synthesis of acyl azides.[17] However, most of these methods are associated with one or more limitations such as use of sensitive substrates, toxic and explosive reagents, forcing reaction conditions or stoichiometric amounts of oxidants and may result in low yields.

There are several reports on the one-pot synthesis of carbamoyl azides starting from functionalized substrates such as ketones,[18a] primary alcohols,[18b] aldehydes,[15b] and amines.[18c] To the best of our knowledge, carbamoyl azides have never been prepared directly from haloarenes in a one-pot procedure. However, acyl azides have been prepared from haloarenes (vide supra) but the method employs CO gas.[1d,i] In view of the above points and in the course of our continued research on the development of efficient metal-catalysed organic syntheses,[19] we have devised a convenient one-pot palladium-catalysed synthesis of carbamoyl azides via azidocarbonylation of halorenes employing *N*-formylsaccharin as a solid alternative to the CO gas (Scheme 2).

To test our strategy and optimize the reaction conditions, a series of control experiments was performed using bromobenzene (**1a**) as a substrate, NaN_3 as an azidating agent, and *N*-formylsaccharin (**2**) as the CO surrogate to afford the desired product **3a**, and the results are summarised in Table 1.

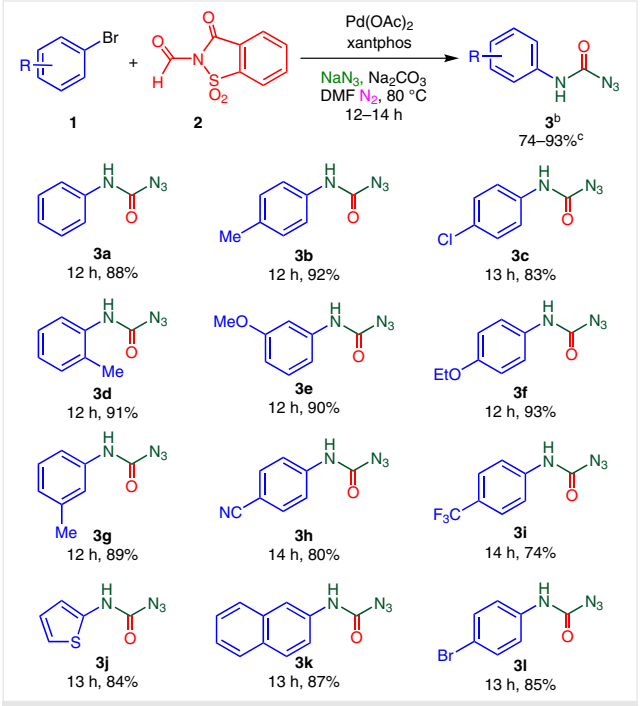


Scheme 2 Synthesis of carbamoyl azides from haloarenes

Initially, the desired product **3a** was not obtained, when the reaction was conducted at room temperature for 18 hours (Table 1, entry 1). However, when the reaction was performed at 70 °C, the desired product **3a** was obtained in 64% yield (Table 1, entry 2) and the optimum yield was obtained at 80 °C (Table 1, entries 3 and 4). Then, we optimised the reaction conditions with respect to various ligands such as xantphos, DPEphos, PPh_3, DPPM, DPPP, and DPPE. Xantphos was the best ligand in terms of time and yield (Table 1, entry 3 vs. entries 6–10). A decrease in the loading of xantphos ligand from 5 to 3 mol% resulted in lower yield of the product (Table 1, entry 3 vs. entry 11), and, on increasing the amount of xantphos ligand from 5 to 10 mol%, there was no effect on the yield of the product (Table 1, entry 1 vs. entry 12). Next, we tested several palladium catalysts such as $Pd(OAc)_2$, $PdCl_2$, $Pd(acac)_2$, and $Pd(TFA)_2$. $Pd(OAc)_2$ was the best catalyst in terms of time and yield (Table 1, entry 3 vs. entries 13–15). The optimum amount of $Pd(OAc)_2$ was 2 mol%, the yield decreasing with less catalyst but remaining unchanged on using 3 mol% (Table 1, entry 3 vs. entries 16 and 17).

With these optimized conditions, we screened several bases, viz. Na_2CO_3, K_2CO_3, Cs_2CO_3, DABCO, and Et_3N. Na_2CO_3 worked most efficiently in terms of yield (Table 1, entry 3 vs. entries 18–21). The best yield (88%) of **3a** was obtained with 2.5 equivalents of *N*-formylsaccharin (**2**) as the CO surrogate (Table 1, entry 3). Then, we examined solvents and found that among DMF, MeCN, CH_2Cl_2, THF, and toluene, DMF was the best (Table 1, entry 3 vs. entries 22–25). Consequently, the synthesis of **3a** was conducted under the optimized reaction conditions with **1a** (1 mmol), NaN_3 (3 mmol), Na_2CO_3 (2.5 mmol), $Pd(OAc)_2$ (2 mol%), xantphos (5 mol%) and *N*-formylsaccharin (**2**, 2.5 mmol) in DMF at 80 °C under stirring to afford 88% yield of the desired product (Table 1, entry 3).

Encouraged by the above studies, we investigated the substrate scope under the optimized reaction conditions and results are summarised in Scheme 3. The reaction of aromatic halides **1** bearing either an electron-donating or -withdrawing substituent generally afforded carbamoyl azides in good to excellent yields (74–93%). However, aromatic halides with an electron-donating group afforded slightly higher yields (Scheme 3, compounds **3b** and **3d**–**3g**) as compared to those bearing an electron-withdrawing

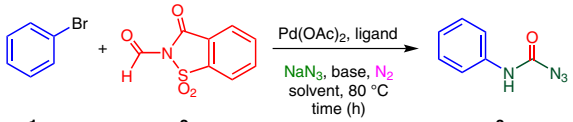


Scheme 3 Substrate scope for the synthesis of carbamoyl azides from aldehydes. [a] For experimental procedure; see ref. 21. [b] All compounds are known and were characterized by comparison of their spectroscopic data with those reported in the literature.[15a,b,18a,22] [c] Yield of isolated pure compounds **3**.

group (Scheme 3, compounds **3c**, **3h**, **3i**, and **3l**). Various functionalities, such as Me, OMe, OEt, CN, CF_3, Br, and Cl were well tolerated, giving carbamoyl azides **3** in good to excellent yields and high purity. The azidation protocol is also compatible with heterocyclic and bicyclic haloarenes (Scheme 3, compounds **3j** and **3k**).

On the basis of the above observations and literature precedents,[1d,g,h,i,20] a plausible mechanism for the formation of carbamoyl azides **3** is depicted in Scheme 4. According to the previously reported mechanism, palladium acetate is reduced to Pd^0 catalyst,[20] which undergoes oxidative addition with the aromatic halide to generate aromatic palladium halide **4**. *N*-Formylsaccharin (**2**) is decomposed to CO with Na_2CO_3, which reacts with aromatic palladium halide **4** and forms acylpalladium species **5**. The reaction of **5** with sodium azide gives acyl azide **7**, which undergoes in situ Curtius rearrangement to afford the desired carbamoyl azide **3**.

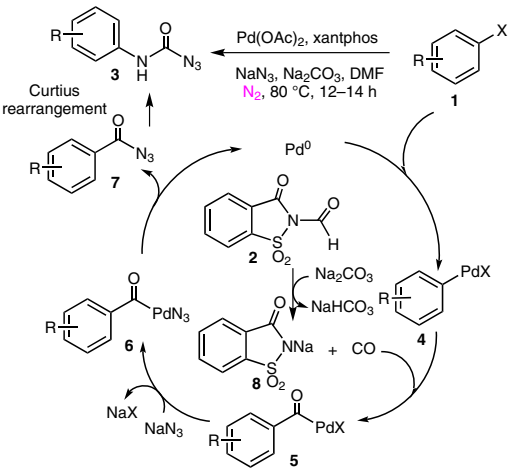
Table 1 Optimization of Reaction Conditions[a]



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

Entry	Ligand (mol%)	Catalyst (mol%)	Solvent	Base	Time (h)	Temp. (°C)	Yield (%)[b]
1	Xantphos	$Pd(OAc)_2$	DMF	Na_2CO_3	18	r.t.	n.d.
2	Xantphos	$Pd(OAc)_2$	DMF	Na_2CO_3	12	70	64
3	Xantphos	$Pd(OAc)_2$	DMF	Na_2CO_3	12	80	88
4	Xantphos	$Pd(OAc)_2$	DMF	Na_2CO_3	12	90	88
5	–	–	DMF	–	18	80	n.d.
6	DPEphos	$Pd(OAc)_2$	DMF	Na_2CO_3	18	80	74
7	PPh_3	$Pd(OAc)_2$	DMF	Na_2CO_3	18	80	49
8	DPPM	$Pd(OAc)_2$	DMF	Na_2CO_3	18	80	51
9	DPPP	$Pd(OAc)_2$	DMF	Na_2CO_3	18	80	56
10	DPPE	$Pd(OAc)_2$	DMF	Na_2CO_3	18	80	43
11	Xantphos	$Pd(OAc)_2$	DMF	Na_2CO_3	12	80	58[c]
12	Xantphos	$Pd(OAc)_2$	DMF	Na_2CO_3	12	80	88[d]
13	Xantphos	$PdCl_2$	DMF	Na_2CO_3	18	80	52
14	Xantphos	$Pd(acac)_2$	DMF	Na_2CO_3	18	80	57
15	Xantphos	$Pd(TFA)_2$	DMFF	Na_2CO_3	18	80	47
16	Xantphos	$Pd(OAc)_2$	DMF	Na_2CO_3	18	80	53[e]
17	Xantphos	$Pd(OAc)_2$	DMF	Na_2CO_3	18	80	88[f]
18	Xantphos	$Pd(OAc)_2$	DMF	K_2CO_3	12	80	81
19	Xantphos	$Pd(OAc)_2$	DMF	Cs_2CO_3	12	80	75
20	Xantphos	$Pd(OAc)_2$	DMF	Et_3N	12	80	60
21	Xantphos	$Pd(OAc)_2$	DMF	DABCO	12	80	52
22	Xantphos	$Pd(OAc)_2$	MeCN	Na_2CO_3	12	80	70
23	Xantphos	$Pd(OAc)_2$	CH_2Cl_2	Na_2CO_3	12	80	67
24	Xantphos	$Pd(OAc)_2$	THF	Na_2CO_3	12	80	61
25	Xantphos	$Pd(OAc)_2$	toluene	Na_2CO_3	12	80	58

[a] Reaction conditions: bromobenzene (**1a**, 1 mmol), *N*-formylsaccharin (**2**, 2.5 mmol), sodium azide (3 mmol), ligand (5 mol%), palladium catalyst (2 mol%), base (2.5 mmol), solvent (3 mL), N_2 atmosphere, at 70–90 °C for 12–18 h.
[b] Isolated yield of **3a**; n.d. = not detected.
[c] The amount of xantphos used was 3 mol%.
[d] The amount of xantphos used was 10 mol%.
[e] The amount of $Pd(OAc)_2$ used was 1 mol%.
[f] The amount of $Pd(OAc)_2$ used was 3 mol%.



Scheme 4 A plausible mechanism for the formation of carbamoyl azides **3**

In conclusion, we have developed a novel and highly efficient one-pot palladium-catalysed synthesis of carbamoyl azides using a range of aromatic halides as substrates, *N*-formylsaccharin as the CO surrogate, and NaN_3 as an azidating agent. Importantly, the protocol offers a superior alternative to access carbamoyl azides, mainly because it utilizes a solid, easily accessible, and easy to handle *N*-formylsaccharin as the CO source in the present Heck-type carbamoylation reaction.

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References and Notes

(1) (a) Gu, L.; Jinb, C.; Liua, J. *Green Chem.* **2015**, *17*, 3733. (b) Gehrtz, P. H.; Hirschbeck, V.; Fleischer, I. *Chem. Commun.* **2015**, *51*, 12574. (c) Wu, L.; Liu, Q.; Jackstell, R.; Beller, M. *Angew. Chem. Int. Ed.* **2014**, *53*, 6310. (d) Miloserdov, F. M.; McMullin, C. L.; Belmonte, M. M.; Buchholz, J. B.; Bakhmutov, V. I.; Macgregor, S. A.; Grushin, V. V. *Organometallics* **2014**, *33*, 736. (e) Gadge, S. T.; Bhanage, B. M. *RSC Adv.* **2014**, *4*, 10367. (f) Dahl, K.; Schou, M.; Amini, N.; Halldin, C. *Eur. J. Org. Chem.* **2013**, 1228. (g) Ueda, T.; Konishi, H.; Manabe, K. *Angew. Chem. Int. Ed.* **2013**, *52*, 8611. (h) Ueda, T.; Konishi, H.; Manabe, K. *Org. Lett.* **2013**, *15*, 5370. (i) Miloserdov, F. M.; Grushin, V. V. *Angew. Chem. Int. Ed.* **2012**, *51*, 3668.

(2) (a) Schoenberg, A.; Bartoletti, I.; Heck, R. F. *J. Org. Chem.* **1974**, *39*, 3318. (b) Schoenberg, A.; Heck, R. F. *J. Org. Chem.* **1974**, *39*, 3327. (c) Schoenberg, A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 7761.

(3) (a) Wu, X.-F.; Neumann, H.; Beller, M. *Chem. Rev.* **2013**, *113*, 1. (b) Roy, S.; Roy, S.; Gribble, G. W. *Tetrahedron* **2012**, *68*, 9867. (c) Wu, X.-F.; Neumann, H.; Beller, M. *Chem. Soc. Rev.* **2011**, *40*, 4986. (d) Magano, J.; Dunetz, J. R. *Chem. Rev.* **2011**, *111*, 2177. (e) Grigg, R.; Mutton, S. P. *Tetrahedron* **2010**, *66*, 5515. (f) Brennführer, A.; Neumann, H.; Beller, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 4114. (g) Barnard, C. F. J. *Organometallics* **2008**, *27*, 5402. (h) Sergeev, A. G.; Spannenberg, A.; Beller, M. *J. Am. Chem. Soc.* **2008**, *130*, 15549. (i) Baillargeon, V. P.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 452. (j) Pri-Bar, I.; Buchman, O. *J. Org. Chem.* **1984**, *49*, 4009. (k) Baillargeon, V. P.; Stille, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 7175.

(4) Morimoto, T.; Kakiuchi, K. *Angew. Chem. Int. Ed.* **2004**, *43*, 5580.

(5) (a) Christensen, S. H.; Olsen, E. P. K.; Rosenbaum, J.; Madsen, R. *Org. Biomol. Chem.* **2015**, *13*, 938. (b) Verendel, J. J.; Nordlund, M.; Andersson, P. G. *ChemSusChem* **2013**, *6*, 426. (c) Jo, E.-A.; Lee, J.-H.; Jun, C.-H. *Chem. Commun.* **2008**, 5779.

(6) (a) Mura, M. G.; Luca, L. D.; Giacomelli, G.; Porcheddu, A. *Adv. Synth. Catal.* **2012**, *354*, 3180. (b) Jiang, L.-B.; Li, R.; Li, H.-P.; Qi, X.; Wu, X.-F. *ChemCatChem* **2016**, *8*, 1788. (c) Qi, X.; Li, C.-L.; Jiang, L.-B.; Zhang, W.-Q.; Wu, X.-F. *Catal. Sci. Technol.* **2016**, *6*, 3099. (d) Qi, X.; Li, C.-L.; Wu, X.-F. *Chem. Eur. J.* **2016**, *22*, 5835. (e) Qi, X.; Jiang, L.-B.; Li, H.-P.; Wu, X.-F. *Chem. Eur. J.* **2015**, *21*, 17650. (f) Qi, X.; Jiang, L.-B.; Li, C.-L.; Li, R.; Wu, X.-F. *Chem. Asian J.* **2015**, *10*, 1870. (g) Li, W.; Wu, X.-F. *Adv. Synth. Catal.* **2015**, *357*, 3393. (h) Chen, J.; Natte, K.; Wu, X.-F. *Organomet. Chem.* **2016**, *803*, 9. (i) Chen, J.; Feng, J.-B.; Natte, K.; Wu, X.-F. *Chem. Eur. J.* **2015**, *21*, 16370. (j) Chen, J.; Natte, K.; Wu, X.-F. *Tetrahedron Lett.* **2015**, *56*, 6413. (k) Li, W.; Wu, X.-F. *J. Org. Chem.* **2014**, *79*, 10410.

(7) (a) Li, B.; Lee, S.; Shin, K.; Chang, S. *Org. Lett.* **2014**, *16*, 2010. (b) Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. *Org. Lett.* **2014**, *16*, 5960. (c) Kim, D.-S.; Park, W.-J.; Lee, C.-H.; Jun, C.-H. *J. Org. Chem.* **2014**, *79*, 12191. (d) Profir, I.; Beller, M.; Fleischer, I. *Org. Biomol. Chem.* **2014**, *12*, 6972. (e) Fleischer, I.; Jennerjahn, R.; Cozzula, D.; Jackstell, R.; Franke, R.; Beller, M. *ChemSusChem* **2013**, *6*, 417. (f) Konishi, H.; Ueda, T.; Muto, T.; Manabe, K. *Org. Lett.* **2012**, *14*, 4722.

(8) (a) Liu, Q.; Yuan, K.; Arockiam, P.-B.; Franke, R.; Doucet, H.; Jackstell, R.; Beller, M. *Angew. Chem. Int. Ed.* **2015**, *54*, 4493. (b) Kopfer, A.; Sam, B.; Breit, B.; Krische, M. *J. Chem. Sci.* **2013**, *4*, 1876. (c) Uhlemann, M.; Doerfelt, S.; Börner, A. *Tetrahedron Lett.* **2013**, *54*, 2209. (d) Cini, E.; Airiau, E.; Girard, N.; Mann, A.; Salvadori, J.; Taddei, M. *Synlett* **2011**, 199. (e) Makado, G.; Morimoto, T.; Sugimoto, Y.; Tsutsumi, K.; Kagawa, N.; Kakiuchi, K. *Adv. Synth. Catal.* **2010**, *352*, 299.

(9) (a) Wu, L.; Liu, Q.; Fleischer, I.; Jackstell, R.; Beller, M. *Nat. Commun.* **2014**, *5*, 3091. (b) Liu, Q.; Wu, L.; Fleischer, I.; Selent, D.; Franke, R.; Jackstell, R.; Beller, M. *Chem.-Eur. J.* **2014**, *20*, 6809. (c) Ostapowicz, T. G.; Schmitz, M.; Krystof, M.; Klankermayer, J.; Leitner, W. *Angew. Chem. Int. Ed.* **2013**, *52*, 12119. (d) Tsuchiya, K.; Huang, J.-D.; Tominaga, K.-I. *ACS Catal.* **2013**, *3*, 2865.

(10) (a) Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angew. Chem. Int. Ed.* **2005**, *44*, 5188. (b) Scriven, E. F. V.; Turnbull, K. *Chem. Rev.* **1988**, *88*, 297. (c) Lieber, E.; Minnis, R. L.; Rao, C. N. R. Jr. *Chem. Rev.* **1965**, *65*, 377.

(11) (a) Oliveri-Mandala, E.; Noto, F. *Gazz. Chim. Ital.* **1913**, *43*, 514. (b) Oliveri-Mandala, E.; Calderaro, E. *Gazz. Chim. Ital.* **1913**, *43*, 538. (c) Lipschitz, W. L. *J. Am. Chem. Soc.* **1944**, *66*, 658. (d) Scott, F. L.; Koczarski, A. *Reilly J.* **1952**, *170*, 922. (e) Curtius, T.; Schmidt, F. *J. Prakt. Chem.* **1923**, *213*, 177. (f) Curtius, T.; Burkhardt, A. *J. Prakt. Chem.* **1898**, *116*, 205.

(12) Deroose, F. D.; De Clercq, P. *J. Org. Chem.* **1995**, *60*, 321.
(13) Curtius, T. *J. Prakt. Chem.* **1894**, *50*, 275.
(14) (a) Bräse, S.; Banert, K. *Organic Azides: Syntheses and Applications*; Wiley: Chichester, **2010**. (b) Katritzky, A. R.; Widyan, K.; Kirichenko, K. *J. Org. Chem.* **2007**, *72*, 5802. (c) Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angew. Chem. Int. Ed.* **2005**, *44*, 5188. (d) Bandgar, B. P.; Pandit, S. S. *Tetrahedron Lett.* **2002**, *43*, 3413. (e) Gumaste, V. K.; Bhawal, B. M.; Deshmukh, A. R. *Tetrahedron Lett.* **2002**, *43*, 1345. (f) Shao, H.; Colucci, M.; Tong, S.; Zhang, H.; Castelhano, A. L. *Tetrahedron Lett.* **1998**, *39*, 7235. (g) Froeyen, P. *Phosphorous Sulfur Silicon Relat. Elem.* **1994**, *89*, 57. (h) Canone, P.; Akssira, M.; Dahouh, A.; Kashmi, H.; Boumzebra, M. *Heterocycles* **1993**, *36*, 1305. (i) Arrieta, A.; Aizpurua, J. M.; Palomo, C. *Tetrahedron Lett.* **1984**, *25*, 3365. (j) Koyashi, S.; Kamiyama, K.; Iimori, T.; Ohno, M. *Tetrahedron Lett.* **1984**, *25*, 2557. (k) Lago, J. M.; Arrieta, A.; Palomo, C. *Synth. Commun.* **1983**, *13*, 289.
(15) (a) Sarkar, S. D.; Studer, A. *Org. Lett.* **2010**, *12*, 1992. (b) Li, X.-Q.; Zhao, X.-F.; Zhang, C. *Synthesis* **2008**, 2589. (c) Arota, N. D.; Akamanchi, K. G. *Tetrahedron Lett.* **2007**, *48*, 5661. (d) Bose, D. S.; Reddy, A. V. N. *Tetrahedron Lett.* **2003**, *44*, 3543. (e) Lee, J. G.; Kwak, K. H. *Tetrahedron Lett.* **1992**, *33*, 3165. (f) Reddy, P. S.; Yadagiri, P.; Lumin, S.; Falck, J. R.; Shin, D.-S. *Synth. Commun.* **1988**, *18*, 545. (g) Elmorsy, S. S. *Tetrahedron Lett.* **1995**, *36*, 1341.
(16) Shinomoto, Y.; Yoshimura, A.; Shimizu, H.; Yamazaki, M.; Zhdankin, V. V.; Saito, A. *Org. Lett.* **2015**, *17*, 5212.
(17) Yadav, V. K.; Srivastava, V. P.; Yadav, L. D. S. *Tetrahedron Lett.* **2016**, *57*, 2502.
(18) (a) Feng, P.; Sun, X.; Su, Y.; Li, X.; Zhang, L.-H.; Shi, X.; Jiao, N. *Org. Lett.* **2014**, *16*, 3388. (b) Li, X.-Q.; Wang, W.-K.; Zhanga, C. *Adv. Synth. Catal.* **2009**, *351*, 2342. (c) García-Egido, E.; Fernández-Suárez, M.; Muñoz, L. *J. Org. Chem.* **2008**, *73*, 2909.
(19) (a) Yadav, V. K.; Srivastava, V. P.; Yadav, L. D. S. *Synlett* **2016**, *27*, 427. (b) Keshari, T.; Kapoor, R.; Yadav, L. D. S. *Eur. J. Org. Chem.* **2016**, 2695. (c) Yadav, A. K.; Yadav, L. D. S. *Tetrahedron Lett.* **2016**, *56*, 686. (d) Yadav, A. K.; Yadav, L. D. S. *Synlett* **2015**, *26*, 1026. (e) Yadav, A. K.; Yadav, L. D. S. *Org. Biomol. Chem.* **2015**, *13*, 2606. (f) Yadav, A. K.; Srivastava, V. P.; Yadav, L. D. S. *RSC Adv.* **2014**, *4*, 24498. (g) Srivastava, V. P.; Yadav, A. K.; Yadav, L. D. S. *Tetrahedron Lett.* **2014**, *55*, 1788. (h) Srivastava, V. P.; Yadav, L. D. S. *Synlett* **2013**, *24*, 2758.
(20) (a) Amatore, C.; Jutand, A.; Khalil, F. *ARKIVOC* **2006**, *(iv)*, 38. (b) Amatore, C.; Jutand, A.; M'Barki, M. A. *Organometallics* **1992**, *11*, 3009.
(21) **General Procedure for the One-Pot Synthesis of Carbamoyl Azides 3**: A mixture of haloarene **1** (1 mmol), sodium azide (3 mmol), Na_2CO_3 (2.5 mmol), $Pd(OAc)_2$ (2 mol%), xantphos (5 mol%), *N*-formylsaccharin (**2**, 2.5 mmol), and DMF (3 mL) was stirred at 80 °C for 12–14 h under a nitrogen atmosphere (Scheme 3). After confirming the complete conversion of aldehyde into the corresponding carbamoyl azide (TLC), H_2O (5 mL) was added and the mixture was extracted with EtOAc (3 × 5 mL). The combined organic phase was dried over anhyd Na_2SO_4, filtered and evaporated under reduced pressure. The resulting crude product was purified by silica gel chromatography using a mixture of hexane–EtOAc (4:1) as eluent to afford an analytically pure sample of product **3**. All the compounds **3** are known and were characterized by comparison of their spectroscopic data with those reported in the literature (see refs. 15a, 18a and 21). Characterization data of selected compounds **3** are given below:
Compound 3a (refs 18a and 15b): white solid; mp 84–86 °C (ref. 15b: 86–87 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 7.9 Hz, 2 H), 7.32–7.36 (m, 2 H), 7.10 (t, *J* = 7.3 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.08, 136.76, 129.25, 124.54, 119.38. HRMS (EI): *m*/*z* calcd for $C_7H_6N_4O$: 162.0542; found: 162.0544.
Compound 3c (refs 18a and 22): colourless solid; mp 103–104 °C (ref. 6: 103–105 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.7 Hz, 2 H), 7.32 (d, *J* = 8.7 Hz, 2 H), 6.89 (br s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.16, 135.34, 129.86, 129.29, 120.47. HRMS (EI): *m*/*z* calcd for $C_7H_5ClN_4O$: 196.0152; found: 196.0156.
Compound 3e (ref 15b): white solid; mp 96–97 °C (ref. 15b: 95–96 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20–7.22 (m, 2 H), 6.87–6.88 (m, 1 H), 6.85 (br s, 1 H), 6.68–6.78 (m, 1 H), 3.82 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.27, 154.13, 138.13, 129.78, 111.58, 110.31, 105.33, 55.29. HRMS (EI): *m*/*z* calcd for $C_8H_8N_4O_2$: 192.0647; found: 192.0644.
(22) Brandt, J. C.; Wirth, T. *Beilstein J. Org. Chem.* **2009**, *5*, No. 30.