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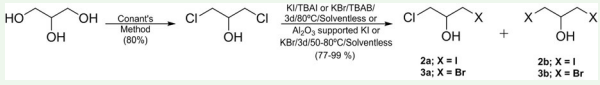
Green synthesis of glycerol 1,3-bromo- and iodohydrins under solvent-free conditions

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ABSTRACT

New eco-friendly conditions for Finkelstein reaction employing homogeneous media or alumina-supported reagents, both solventless, were utilized in the bromohydrins and iodohydrins synthesis from 1,3-dichlorohydrin (1,3-DCH), obtained from glycerol. Thus, the *trans*-halogenation of glycerol-1,3-dichlorohydrin (**1**) in homogeneous media, using NaI, NaBr salts and organic additives (TBAI, TBAB), led to the synthesis of four different glycerol halohydrins (**2a**, **2b**, **3a**, **3b**) in regular to excellent conversions (43–96%) and good selectivities to **3a** and **2b**. Already, the alumina-supported reagents such as KI, KBr, NaBr were used for glycerol-1,3-dichlorohydrin *trans*-halogenation, in the absence of solvent, producing halohydrin mixtures in high conversions (77–99%) and very good selectivity (82%) to 1,3-diiodo-2-propanol (**2b**).



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1. Introduction

Glycerol is the main co-product formed in 10% p/p in the process of producing biodiesel which consists of a base-catalyzed transesterification of triacylglycerides with methanol or ethanol (Scheme 1) (*1–5*).

The global crude glycerol production forecast for 2020 is 4 billion liters (*6*). This triol exhibits enormous applicability in the chemical, pharmaceutical, food, cosmetic industries. Furthermore, it has been used as a building block and solvent inorganic synthesis (*1–5*). Biologically it is used as source energy and carbon for many microorganisms, to produce various chemicals, as cryopreservation agent of different biological materials, as an osmoregulatory agent and also used in the production of bioplastics (*7, 8*).

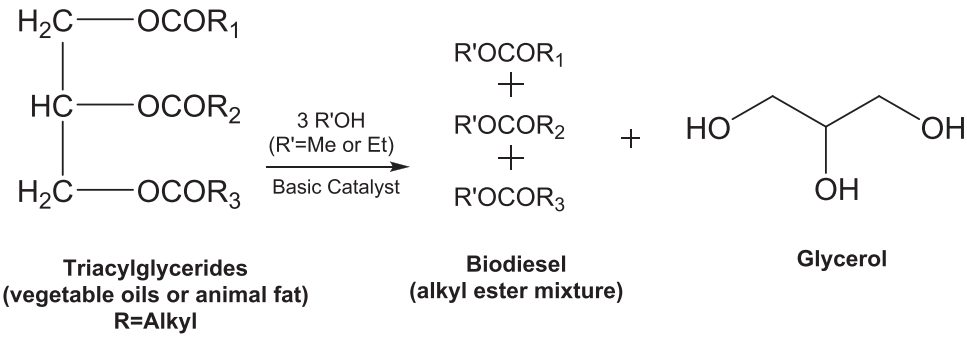
The dichlorohydrins (DCH's) are low-cost glycerol derivatives with important industrial applications, being used mainly for the manufacture of epoxy resins, acting as a substrate and solvent during the process. The 1,3-diclorohydrin (1,3-DCH) is largely obtained from propene; however, sustainable synthesis in one step from glycerol using HCl catalyzed by acetic acid and Cl_2 at high temperatures are already consolidated (*9–14*). On the other hand, the brominated and iodinated derivatives of glycerol are mainly applied as intermediates in fine chemistry, whereas they exhibit higher reactivity than DCHs. Despite the higher cost, brominated and iodinated intermediates considerably increase the rate in bimolecular nucleophilic substitution reaction (S_N2) when compared with the chlorinated intermediates, since the dissociation energy of the carbon-chloro bond is 83.7 kcal/mol, higher than 72.1 and 57.6 kcal/mol for C-bromine and C-iodine, respectively (*15, 16*).

In nature, iodohydrins and bromohydrins were found in the essential oils of marine algae of the genus *Asparagopsis taxiformis*, *A. armata* and *Falkenbergia rufolanosa* (*17, 18*). Synthetically, 1,3-dibromohydrins are normally produced from the corresponding epibromohydrin (*19*) or from the halogenation of propene (*20*) or yet from the treatment of glycerol with bromhidric acid (HBr) or bromine (Br_2), in the presence of red phosphorous, at high temperatures (*21, 22*). The glycerol bromohydrins can be also obtained from different substrates, via nucleophilic substitution in various solvents and moderate yields (*23–25*).

On the other hand, attempts to synthesize the glycerol iodohydrins in a single step, by treating the glycerol with excess hydriodic acid, result in the synthesis of isopropyl iodide, due to the exhaustive iodination of glycerol

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Scheme 1. Biodiesel and glycerol production via triacylglyceride transesterification with methanol or ethanol, under base catalysis.

(*26*). Consequently, some glycerol monoiodohydrins are generally obtained through the mildest Finkelstein reaction with different electrophilic species (*27–33*). Specifically, in the case of 1,3-diiodohydrin, there is a few reports in the literature to the production of this important synthon, which employs the homogeneous medium, in the presence of solvent.

In contrast to the glycerol chloro- and bromohydrins, the glycerol iodohydrins have been applied in various pharmaceutical preparations because for their antiseptic, mucolytic and fungicide properties (*34*, *35*). Some glycerol iodohydrins were used in the synthesis of cardiolipins (*36*, *37*), as key intermediates of a promising class of drugs in treating type 2 diabetes (*19*, *38*), and applied in organic synthesis as a building block to produce other chemicals (*39*, *40*).

The Finkelstein reaction is widely used in organic synthesis (*41–50*). It consists in the displacement of a leaving group under a C-sp^3 (Cl, Br, I, OTs, OMs, etc.) by the action of a metallic halogenated nucleophile mainly acetone as solvent, where the new organic or inorganic metallic salt is insoluble (*51*, *52*). Although the reaction has been considered to evolve via a mechanism S_N2, it is an equilibrium process. Kinetic studies ratify that the reversibility of the reaction is not observed during transhalogenation due to the difference in the solubility between the salts involved in the process (*53*, *54*). For example, NaI is highly soluble in acetone and when this is reacted with an alkyl chloride the NaCl formed is insoluble in acetone and precipitate, thus there is the equilibrium displacement in favour of the desired products (Le Châtelier's principle) (*55*).

In our continuing interest in adding value to glycerol-surpluses originated from biodiesel using sustainable and eco-friendly (*8*, *9*) routes, now we desire to describe the development of green processes for obtaining bromohydrins and iodohydrins from glycerol–biodiesel. Thus, the reactivity of metal halides in the presence or absence of additives (tetrabutylammonium bromide (TBAB)) and tetrabutylammonium iodide (TBAI) with glycerol-1,3-dichlorohydrin **1**, in homogeneous medium solventless was investigated. Furthermore, the reactivity of **1**, with different alumina-supported metal halides, in solvent-free conditions was also studied.

2. Results and discussion

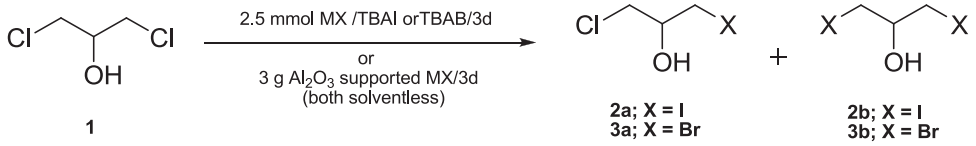
Our studies were begun, investigating the obtainment of bromo- and glycerol iodohydrins from **1**, using the Finkelstein reaction in free solvent conditions (Table 1). Glycerol-1,3-dichlorohydrin **1** was synthesized in multigrams via Conant´s methodology (*56*, *57*).

By the analysis of Table 1, it can be observed that **1** was converted in the mixture of glycerol iodohydrins **2a**+**2b** (77:23) in 43% yield by treatment with NaI (Entry 1). Initially, a yellowish homogeneous mixture was formed and with the evolution of time the mixture became brownish with the presence of NaCl precipitate. Interestingly, the 1,3-DCH acted as the solvent and reagent of the reaction, favouring an adequate sodium iodide dissociation. In this manner, as the reaction evolved the action of 1,3-DCH as the solvent decreased, leading to lowest NaI dissociation, which can explain the low conversion. In order to obtain better conversions, we decided to evaluate the use of TBAI as an additive that could promote greater ion iodide availability (Entry 2). Gratifyingly, the use of TBAI provided 1,3-DCH in 96% conversion as a iodohydrin mixture **2a**+**2b** (28:72).

The synthesis of **2a** and/or **2b** using KI as source iodide anion was also experienced in the absence of the solvent. However, low conversion of **2a**+**2b** was obtained (3% without TBAI addition and 11% with TBAI addition). We believe that the lower trend to the KI dissociation can explain the poor conversion observed.

The bromohydrin synthesis **3a**+**3b** was also tried using NaBr at 80°C (Entry 3). In this case, there was not a good conversion and selectivity to the desired bromohydrins, probably due to the lower nucleophilicity and dissociation constant of the sodium bromide despite the heating.

Table 1. Bromo- and iodohydrin synthesis from **1**, in homogeneous media or alumina-supported reagents, in solvent-free conditions.



Entry	M+X-	Temperature (°C)	Conversion (%)	Selectivity (%) Mono-	Di-
1	NaI	80	43[c]	77	23
2	NaI[a]	80	96[c]	28	72
3	NaBr[b]	80	47[c]	78	22
4	KI/Al_2O_3	Rt	5	100	0
5	KI/Al_2O_3	80	99	9	91
6[d]	KI/Al_2O_3	80	96	12	88
7[e]	KI/Al_2O_3	80	89	42	58
8	NaI/Al_2O_3	Rt	74	40	60
9	KBr/Al_2O_3	Rt	26	97	3
10	$NaBr/Al_2O_3$	Rt	48	93	7
11	KBr/Al_2O_3	50	55	100	0
12	$NaBr/Al_2O_3$	50	77	70	30

[a]Using 10% TBAI; [b]Using 10% TBAB; [c]Homogeneous medium. [d]Reaction performed for 2 days. [e]Reaction performed in 1 day.

Aiming to develop other eco-friendly route for the selective iodination of 1,3-DCH, we propose the use of metallic salts supported on alumina as a source of halogenation, in the absence of the solvent. In recent years, there is great interest in the support of metallic halides on alumina and its use in the production of biodiesel, due to the basic species present in this solid reagent. Xie (*58*) and Evangelista (*59*) independently have used KI/Al_2O_3 as an efficient basic catalyst for biodiesel production. X-ray diffraction measurements have evidenced the presence of K_3AlI_6 and K_2O in significant concentrations, in addition to residual KI, as an active species in this catalyst (*58*, *59*). We imagine that the presence of iodine in the species K_3AlI_6 could alternatively to react with the glycerol 1,3-DCH and provide the desired iodohydrins **2a** and **2b**, since only the use of KI salt solventless did not exhibit good conversion, as shown previously. Then, we employed KI/Al_2O_3 reagent, at room temperature for the production of **2a** and **2b**; however, a low conversion of **1** was observed (Entry 4). Thus, we chose to perform the iodination with the same reagent at higher temperature (Entry 5). Gratifyingly, 99% of consumption of **1** was observed, providing an iodohydrin mixture (**2a**:**2b**; 9:91). It is important to mention that when the same 1,3-DCH iodination was processed at 100°C, no product or reagent was obtained. On the other hand, the use of a shorter reaction time led to lower conversions and selectivity (Entries 6, 7). Besides, the use of 1.0 equivalent of KI/Al_2O_3 led to 90% conversion and **2a**:**2b**; 92:8 selectivity.

Similarly, when the classical halogenating agent used in Finkelstein reaction was supported on alumina (NaI/Al_2O_3) and reacted with **1** by 3 days, at room temperature, a regular conversion of **1** (76%) was observed with higher selectivity to **2b** (Entry 8). Aiming at a greater conversion and selectivity, we processed the reaction at 80°C, however, no mass of product or reagent was recuperated. Possibly, in this temperature there was the alkoxides formation promoted by the action of basic species, causing the impregnation of the substrates and product irreversibly in the reagent (NaI/Al_2O_3). A posterior study about the structural arrangement of this alumina-supported reagent will be necessary to rationalize the results obtained (*59*).

Reactions using KBr/Al_2O_3 and $NaBr/Al_2O_3$ and **1** were also investigated at room temperature (Entries 9 and 10). In this case, only a conversion of 26% and 48% to bromohydrins was observed, respectively. On the other hand, the use of 80°C led to recuperation of traces of a complex mixture of products to both bromination agents, probably, due to the action of the basic species present in the solid reagent. In view thereof, the use of a lower temperature (50°C) was experimented and as expected, a better conversion was observed (Entries 11 and 12).

3. Experimental section

3.1. General remarks

Tetrabutylammonium bromide (98%) and tetrabutylammonium iodide (98%) were purchased from Sigma-Aldrich™, Sodium Iodide P.A. (99%), potassium iodide (99%), potassium bromide (99.5%) and aluminium oxide basic were purchased from Merck. Sodium bromide P.A. (99.5%) was purchased from Vetec

Química Fina Ltda. All solvents were distilled prior to use. Gas chromatography analyses were performed every 30 min, using a GC-FID (Shimadzu GC-FID 2010 *Plus*; DB-5 (5%-Phenyl-methylpolysiloxane)-fused silica capillary column (30 m × 0.25 mm, film thickness 0.25 µm); carrier gas H_2 (1.0 mL min^{-1}); temperature: injector 290°C, column oven 50–290°C at 10°C min^{-1}, FID 290°C). The GC-MS analyses were conducted with a GC–MS Shimadzu QP500 instrument equipped with the same column used for the gas chromatograph. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian MR-400, at 400 and 100 MHz, respectively, using TMS as the internal reference.

3.2. Preparation of the alumina-supported reagents

The alumina-supported reagents were prepared by the incipient wet impregnation method, where 15.0 ml of the aqueous solution of KI, NaI, KBr or NaBr (35% p/v) was reacted with 5.0 g basic alumina oxide for 2 h under stirring and refluxing. After the mixture was dried in the oven for 16 h at 120°C, the solid reagent was calcined in a muffle at 500°C for 3 h, and after cooling, it was used as the reactant for the trans-halogenation reactions. It is important to mention that this reagent can be recycled and reused (*59*).

3.3. General procedure to iodohydrins 2a and 2b synthesis in the homogeneous medium

1,3-Dichloro-2-propanol **(1)** (1.0 mmol, 0.129 g, 0.1 mL) and metal iodide or tetrabutylammonium iodide (2.5 mmol) were added to a round bottom flask. Next, a Liebig condenser and a pressure equalizer were adapted to the system and the reaction medium was kept under strong magnetic stirring at 80°C for 3 days. After 24 h a brownish mixture with the presence of NaCl precipitate was formed. After the mixture was cooled into room temperature, the solid sodium chloride was filtered and washed with dichloromethane until it became white. Then, dichloromethane was removed, and the crude reaction was extracted with diethyl ether (3 × 40 mL) and the combined extracts were washed with the sodium thiosulfate-concentrated solution to remove the iodine. Next, the phase organic was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. When TBAI was used, this organic salt was removed by precipitation with dichloromethane and ethyl acetate (1:1) and removed by filtration.

1-Chloro-3-iodo-2-propanol (**2a**): ^{1}H NMR: δ = 2.44–2.45 (d, 1H;), 3.66–3.73 (m, 4H), 3.80–3.83 (m, 1H); ^{13}C NMR: δ = 9.37 (CH_2) 47.94 (CH_2) 70.41 (CH); MS (70 eV): *m/z* (%): 93 (80), 171 (80), 220 (60); Retention time was 5.4 min.

1,3-Diiodo-2-propanol (**2b**): ^{1}H NMR: δ = 2.36–2.37 (d, 1H), 3.36–3.43 (m, 4H), 3.52–3.57 (m, 1H). ^{13}C NMR: δ = 12.03 ($2CH_2$) 70.13 (CH); MS (70 eV): *m/z* (%): 185 (100), 312 (45); Retention time was 8.1 min.

3.4. General procedure to bromohydrins 3a and 3b synthesis in the homogeneous medium

1,3-Dichloro-2-propanol (**1**) (1.0 mmol, 0.129 g, 0.1 mL) and metal bromide (2.5 mmol) were added to a round bottom flask. Next, a Liebig's condenser and a pressure equalizer were adapted to the system and the reaction medium was kept under strong magnetic stirring at 80°C for 3 days. After 24 h a brownish mixture was formed with the presence of metal chloride precipitate. After the mixture was cooled to room temperature, the metal chloride was filtered and washed with dichloromethane until it became white. Then, dichloromethane was removed under reduced pressure and the crude yellowish liquid consisted of a mixture of 1,3-dibromo-2-propanol (**3b**) and 1-chloro-3-bromo-2-propanol (**3a**), whose ratio was determined by the gas chromatography, see table.

1-Bromo-3-chloro-2-propanol (**3a**): ^{1}H NMR δ = 2.54 (s, 1H), 3.69–3.74 (m, 4H), 4.03–4.08 (m,1H); ^{13}C NMR δ = 35.56 (CH_2), 46.48 (CH_2), 70.45 (CH); MS (70 eV): *m/z* (%): 43 (90), 79 (80), 123 (90); Retention time was 3.2 min.

1,3-Dibromo-2-propanol (**3b**): ^{1}H NMR δ = 3.57–3.58 (d, 4 H), 4.03–4.08 (m,1H); ^{13}C NMR δ = 34.82 ($2CH_2$), 70.78 (CH); MS (70 eV): *m/z* (%): 43 (60), 123 (90); Retention time was 4.1 min.

3.5. General procedure to iodohydrins 2a and 2b synthesis using solid-supported reagents

1,3-Dichloro-2-propanol (**1**) (1.0 mmol, 0.129 g, 0.1 mL) and iodide potassium supported alumina or iodide sodium supported alumina (3.0 g) were added to a round bottom flask without magnetic stirring at 80°C for 3 days. After this period, dichloromethane (50 mL) was added to the reaction flask and the heterogeneous mixture was formed after strong magnetic stirring, aiming at the extraction of the iodohydrins mixture. After simple filtration, the brownish filtered obtained was worked up similarly to the reaction conducted in homogeneous medium.

3.6. General procedure to bromohydrins 3a and 3b synthesis using solid-supported reagents

1,3-Dichloro-2-propanol (**1**) (1.0 mmol, 0.129 g, 0.1 mL) and potassium bromide supported on alumina (KBr/

Al_2O_3) or bromide sodium-supported alumina (3.0 g) were added to a round bottom flask without magnetic stirring at 80°C for 3 days. After this period, dichloromethane (50 mL) was added to the reaction flask under strong magnetic stirring for the extraction of the bromohydrin mixture. After the solids were retired by simple filtration and the yellow organic phase was worked up similarly to the reaction processed in the homogeneous medium.

4. Conclusions

A green synthesis to glycerol bromohydrins (**3a**,**3b**) and glycerol iodohydrins (**2a**,**2b**) from bioglycerol was developed under solvent-free conditions. We report a cleaner method for the halohydrin synthesis (**2a,b** and **3a,b**), in high conversions and selectivities, employing reactions in homogeneous media or alumina-supported reagents, both solventless. To the best of our knowledge, this is the first time that KI supported on alumina, a reagent usually used as a basic catalyst in transesterification reactions (*58*, *59*), was employed as an efficient iodination agent in the solvent-free Finkelstein reaction.

Disclosure statement

No potential conflict of interest was reported by the authors.

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References

[1] Monteiro, M.R.; Kugelmeier, C.L.; Pinheiro, R.S.; Batalha, M.O.; César, A.S. *Renew. Sust. Energ. Rev.***2018,** *88*, 109–122.
[2] Bagnato, G.A.; Iulianelli, A.; Sanna, A.; Basile, A. *Membranes* **2017,** *7*, 17–31.
[3] Kong, P.S.; Aroua, M.K.; Wan Daud, W.M.A. *Renew. Sust. Energ. Rev.* **2016,** *63*, 533–555.
[4] Umpierre, A.P.; Machado, F. *Rev. Virtual Quim.* **2013**, *5*, 106–116.
[5] Pagliaro, M.; Rossi, M. *The Future of Glycerol*; RSC Publishing: Cambridge, 2010, pp. 1–25.
[6] Nomanbhay, S.; Hussein, R.; Ong, M.Y. *Green Chem. Lett. Rev.* **2018**, *11*, 135–157.
[7] Mota, C.J.A.; Pinto, B.P.; Lima, A.L. *Glycerol: A Versatile Renewable Feedstock for the Chemical Industry*, 1st ed.; Springer International Publishing: Zurich, 2017, pp. 110.
[8] Meireles, B.A.; Pereira, V.L.P. *J. Braz. Chem. Soc.* **2013,** *24*, 17–25.
[9] Nascimento, F.P.C.; Pereira, V.L.P. *BR 1020160159*, 2016
[10] Giomi, D.; Malavolti, M.; Piccolo, O.; Salvini, A.; Brandia, A. *RSC Adv.* **2014,** *4*, 46319–46326.
[11] Tesser, R.; Di Serio, M.; Vitiello, R.; Russo, V.; Ranieri, E.; Speranza, E.; Santacesaria, E. *Ind. Eng. Chem. Res.* **2012,** *51*, 8768–8776.
[12] Song, S.H.; Park, D.R.; Woo, S.Y.; Song, W.S.; Kwon, M.S.; Song, I.K. *J. Ind. Eng. Chem.* **2010,** *16*, 662–665.
[13] Luo, Z.H.; You, X.Z.; Li, H.R. *Ind. Eng. Chem. Res.* **2009,** *48*, 446–452.
[14] Lee, S.H.; Song, S.H.; Park, D.R.; Jung, J.C.; Song, J.H.; Woo, S.Y.; Song, W.S.; Kwon, M.S.; Song, I.K. *Catal. Commun.* **2008,** *10*, 160–164.
[15] Hamlin, T.A.; Swart, M.; Bickelhaupt, F.M. *ChemPhysChem* **2018,** *19*, 1315–1330
[16] Blanksby, S.J.; Ellison, G.B. *Acc. Chem. Res.* **2003,** *36*, 255–263.
[17] Wang, L.; Zhou, X.; Fredimoses, M.; Liao, S.; Liu, Y. *RSC Adv.* **2014**, *4*, 57350–57376.
[18] Gribble, G.W. *Environ. Sci. Pollut. Res.* **2000,** *7*, 37–49.
[19] Chen, J.; Jianga, C.S.; Ma, W.Q.; Gao, L.X.; Gong, J.X.; Li, J.Y.; Li, J.; Guo, Y.W. *Bioorg. Med. Chem. Lett.* **2013**, *23*, 5061–5065.
[20] Rosenau, T.; Potthast, A.; Kosma, P. *Tetrahedron* **2002,** *58*, 9809–9815.
[21] Braun, G. *Org. Synth.* **1934,** *14*, 42.
[22] Bouillaud, A.; Dargelos, M.; Borredon, M. *Aust. J. Chem.* **1994**, *47*, 2123.
[23] Camps, F.; Gasol, V.; Guerero, A. *Synthesis* **1987**, 511–512.

[24] Feldmane, D.; Konstante, G.; Stonhys, V.; Shimanokaya, M. *US 1330125*, 1987.
[25] Kasireddy, K.; Ali, S.M.; Ahmad, M.U.; Choudhury, S.; Chien, P.Y.; Sheikh, S.; Ahmad, I. *Bioorg. Chem.* **2005,** *33*, 345–362.
[26] Bradbury, R.B. *Mikrochemie* **1951,** *74*, 2709–2712.
[27] Fairbourne, A.; Stephens, D.W. *J. Chem. Soc.* **1932**, *6*, 1973–1977.
[28] Glattfeld, J.W.E.; Klaas, R. *J. Chem. Soc.* **1933**, *55*, 1114–1119.
[29] Jones, A.R. *J. Label. Compd.* **1973,** *9*, 697–701.
[30] Hessel, L.W.; Lohuizen, V.; Verkade, P.E. *Rec.Trav. Chim.* **1954,** *73*, 842–848.
[31] Bevan, T.H.; Malkin, T.; Smith, D.B. *J. Chem. Soc.* **1955**, 1383–1384.
[32] Einhorn, C.; Luche, J.L. *J. Chem. Soc. Chem. Commun.* **1986**, 1368–1369.
[33] Sharghi, H.; Eskandari, M.M. *Tetrahedron* **2003,** *59*, 8509–8514.
[34] Narita, T.; Sato, T. *JP 62183304*, 1988.
[35] Sofia, R.D. *US 5723501*, 1998.
[36] Haas, G.H.; Van Deenen, L.M.M. *Recl. Trav. Chim.* **1963,** *82*, 1163–1172.
[37] Stamatov, S.D.; Satawinski, J. *Org. Biomol. Chem.* **2010,** *8*, 463.
[38] Guo, Y.; Shen, X.; Chen, J.; Gong, J.; Chen, L. *CN 104140412*, 2014.
[39] Quan, Z. *CN 103897167*, 2014.
[40] Zhang, L.; Cai, J.; Fang, Y.; Chen, Z. *CN 105111142*, 2015.
[41] Finkelstein, H. *Ber. Dtsch. Chem. Ger.* **1910,** *43*, 1528–1532.
[42] Lowe, P.T.; Cobb, S.L.; O'Hagan, D. *Org. Biomol. Chem.* **2019**, *17*, 7493–7496.
[43] Dong, C.; Nakamura, K.; Taniguchi, T.; Mita, S.; Kodama, S.; Kawaguchi, S.; Nomoto, A.; Ogawa, A.; Mizuno, T. *ACS Omega* **2018,** *3*, 9814–9821.
[44] Nguyen, A.T.H.; Nguyen, D.P.; Phan, N.T.K.; Lam, D.T.T.; Phan, N.T.S.; Truong, T.J. *Adv. Res.* **2018**, *10*, 9–13.
[45] Feng, X.; Zhang, H.; Lu, W.; Yamamoto, Y.; Almansour, A.I.; Natarajan Arumugam, N.; Kumarc, R.S.; Bao, M. *Synthesis* **2017,** *49*, 2727–2732.
[46] Nitelet, A.; Kairouz, V.; Lebel, H.; Charette, A.B.; Evano, G. *Synthesis* **2019,** *51*, 251–257.
[47] Pandit, P.; Gayen, K.S.; Khamarui, S.; Chatterjee, N.; Maiti, D.K. *Chem. Commun.* **2011**, *47*, 6933–6935.
[48] Song, S.; Huang, X.; Liang, Y.; Tang, C.; Lia, X.; Jiao, N. *Green Chem.* **2015**, *17*, 2727–2731.
[49] Dewkar, G.K.; Narina, S.V.; Sudalai, V. *Org. Lett.* **2003**, *5*, 4501–4504.
[50] Ai, L.; Wang, W.; Wei, J.; Li, Q.; Song, S.; Jiao, N. *Synlett* **2019,** *30*, 437–441.
[51] Liu, Y.; Xu, Y.; Jung, S.H.; Chae, J. *Synlett* **2012,** *23*, 2663–2666.
[52] Baughman, T.W.; Sworen, J.C.; Wagener, K.B. *Tetrahedron* **2004,** *60*, 10943–10948.
[53] Evano, G.; Nitelet, A.; Thilmany, P.; Dewez, D.F. *Front. Chem.* **2018,** *6*, 1–18.
[54] Smith, M.B. *March's Advanced Organic Chemistry*, 7th ed.; John Wiley and Sons: Hoboken, NJ, 2013, pp. 498–499.
[55] Pace, R.D.; Regmi, Y. *J. Chem. Educ.* **2006**, *83*, 1344–1348.
[56] Conant, J.B.; Quayle, O.R. *Org. Synth. Coll* **1941,** *1*, 292.
[57] Commercially available from Sigma-Aldrich.™
[58] Xie, W.; Li, H. *J. Mol. Catal. A: Chem.* **2006**, *255*, 1–9.
[59] Evangelista, J.P.C.; Gondim, A.D.; Souza, L.; Araujo, A.S. *Renew. Sust. Energy Rev* **2016,** *59*, 887–894.