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Introducing deep eutectic solvents in enolate chemistry: synthesis of 1-arylpropan-2-ones under aerobic conditions†

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Alkoxide-mediated enolization of 1-arylpropan-2-ones and their fluorinated derivatives, followed by α-functionalization with nucleophilic addition and substitution reactions, has been accomplished in the environmentally friendly eutectic mixture choline chloride/urea, under aerobic conditions. The usefulness of this new protocol has also been exemplified through the synthesis of a small selection of building-block like molecules through Pd-catalyzed α-arylation reactions.

Since its introduction at the beginning of the 20th century, enolate chemistry has played a dominant role in synthetic organic chemistry for the generation of branched carbon backbones in a proximal position to carbonyl groups, which represent important skeletons present in complex molecules.[1] Enolates are ambident nucleophiles, with the metal being found either closer to the oxygen (as in the case of groups I, II, and III enolates) or closer to the carbon atom, and can adopt an astonishing array of self-assembled structures due to aggregation, depending on the nature of the cation and the solvent.[1a] Being the conjugate bases of enols, enolates can be prepared using a base, and with strong bases [*e.g.*, lithium diisopropyl amide (LDA), lithium tetramethylpiperidide (LTMP), lithium bis(trimethylsilyl)amide (LiHMDS)] the deprotonation is quantitative. As powerful nucleophiles, enolates can react with a variety of electrophiles including alkyl, allyl and benzyl halides, and carbonyl compounds, to cite just a few examples. In particular, the α-alkylation of arylpropan-2-one derivatives, *via* the corresponding enolates, has been extensively studied due to the importance of such branched skeletons in the functionalization of psychotropic phenethylamines, and in the preparation of several pharmacologically active compounds (Fig. 1).[2] Most of these reactions, however, are generally carried out in anhydrous, nonpolar and volatile organic compounds (VOCs) [*e.g.*, open chain or cyclic ethers, (chloro)hydrocarbons], under an inert atmosphere, and preferably at low temperature (up to −78 °C), using LDA and metal hydrides as bases.[3] The C-alkylation of arylpropan-2-one enolates has also been investigated in the absence of solvent, using KOH as the base,[4] in the presence of alkali hydroxides in biphasic mixtures,[5] with phase-transfer catalysts such as tetrabutylammonium bromide (TBAB) and tetrabutylammonium hydrogen sulfate,[6] or using calix[4]-arene TAC4M.[7]

Pioneering, independent contributions from our group and those of Hevia and García-Álvarez have shown that the use of polar organometallic compounds of s- and d-block elements is truly compatible with environmentally responsible, nature-inspired solvents [*e.g.*, glycerol, water, and deep eutectic solvents, (DESs)], even when working at room temperature (RT) and under aerobic conditions.[8] We have also focused recently on the use of DESs in metal-,[9] and biocatalyzed[10] transformations, and for the synthesis of heterocyclic compounds.[11] On the basis of these precedents, we became eager to explore the chemistry of enolates in DESs. Herein, we wish to report the first examples of generation of an enolate directly in a protic eutectic mixture under aerobic conditions,

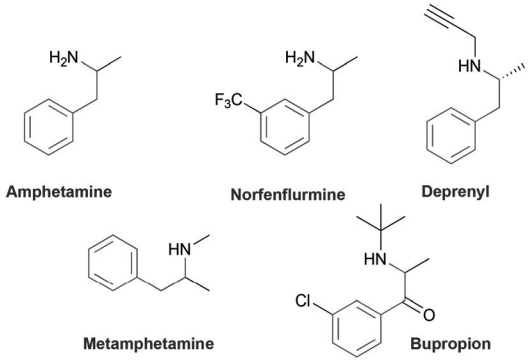

Fig. 1 Selected examples of pharmacologically active phenethylamine derivatives.

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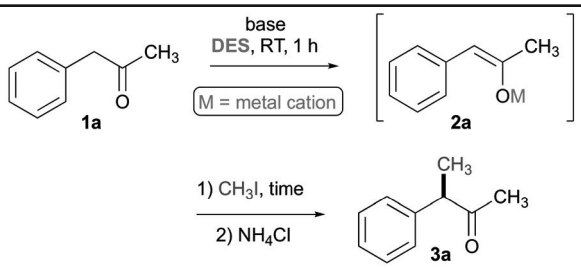
discussing its reactivity towards alkylation and addition reactions as well as in cross-coupling reactions.

We commenced our study with an exploration of the reaction parameters aimed at converting 1-phenylpropan-2-one (**1a**) into the corresponding α-methyl derivative (**3a**) *via* the enolate intermediate **2a** in three prototypical choline chloride (ChCl)-based eutectic mixtures, namely ChCl/glycerol (Gly) (1 : 2 mol mol^{-1}), ChCl/L-lactic acid (LA) (1 : 2 mol mol^{-1}), and ChCl/urea (1 : 2 mol mol^{-1}) (Table 1). When the reaction was performed in ChCl/urea at RT and under air, the addition of bases like LDA (THF solution) or Cs_2CO_3 (3 equiv.) to a solution of **1a** in the above eutectic mixture (1 h), followed by CH_3I (up to 16 h reaction time) and quenching of the mixture by an aqueous saturated solution of NH_4Cl, did not lead to any appreciable amount of the desired adduct **3a** (Table 1, entries 1, 2). The alternative use of NaOH (3 equiv.) or LiOH (3 equiv.) produced a similar higher yield (70–72%) of **3a** after 16 h (Table 1, entries 3, 4). Pleasingly, the employment of NaH (3 equiv.) as the base led to the isolation of **3a** in 93% yield, and an almost quantitative conversion (98%) was observed when using *t*-BuOK (3 equiv.) (Table 1, entries 5, 6). Under the latter conditions (Table 1, entry 6), the change of the eutectic mixture to ChCl/LA was ineffective, whereas in ChCl/Gly a conversion not higher than 20% of **3a** was obtained (Table 1, entries 7, 8). By reducing the equiv. of *t*-BuOK up to 2 in ChCl/urea, the conversion of **3a** dropped down to 42% yield (Table 1, entry 9). Notably, the effectiveness of this transformation was still maintained (**2a**: 96% yield) by shortening the reaction time up to 7 h, after the addition of CH_3I (Table 1, entries 10–14). On the other hand, on further screening of eutectic mixtures, the conversion of **1a** into **3a** was only moderate (32–36%) [ChCl/sorbitol (1 : 1 mol mol^{-1}); ChCl/isosorbide (1 : 2 mol mol^{-1})] (Table 1, entries 15, 16) or null [fructose/urea (3 : 2 w w^{-1}); menthol/L-lactic acid (LA) (1 : 2 mol mol^{-1}); Gly/L-proline (L-Pro) (1.1 mol mol^{-1})] (Table 1, entries 17–19]. Thus, the combination of ChCl with urea proved to be the best compromise between solubility and compatibility of DES components with the strong base used, with enolate formation being strongly disfavored in acidic DESs. The preparation of ketone **3a** by enolization of ketone **1a** with NaH, followed by a quenching reaction with MeI, was reported to take place in 80% yield when working in anhydrous THF (by distillation from sodium-benzophenone ketyl) and under a nitrogen atmosphere at 0 °C.[12] It is worth noting that by running the same reaction in air and in non-anhydrous THF led to no formation of **3a**.

Table 1 α-Methylation of 1-phenylpropan-2-one (**1a**) in different eutectic mixtures[a]

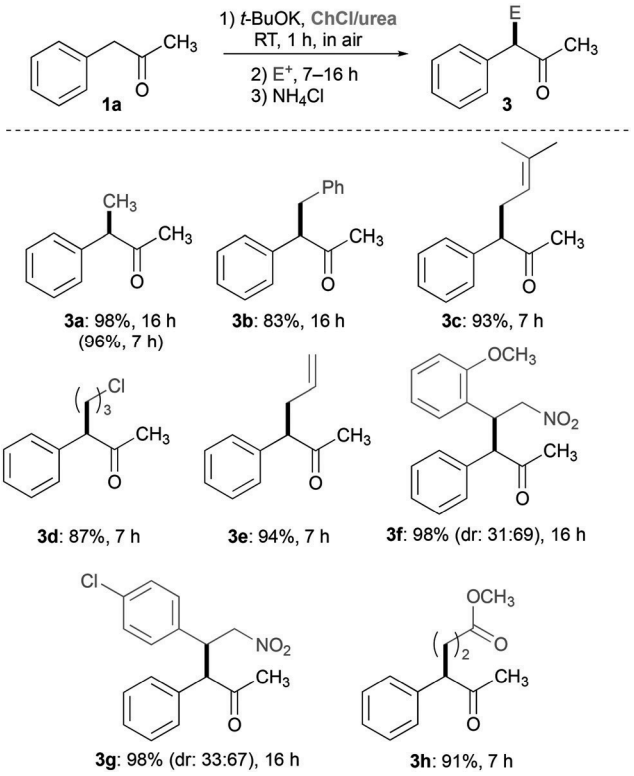


Entry	DES	Base (equiv.)	Time (h)	Conversion[b] (%)
1	ChCl/urea	LDA/THF (3)	16	NR[c]
2	ChCl/urea	Cs_2CO_3 (3)	16	4
3	ChCl/urea	NaOH (3)	16	70[d]
4	ChCl/urea	LiOH (3)	16	72[d]
5	ChCl/urea	NaH (3)	16	93[d]
6	ChCl/urea	*t*-BuOK (3)	16	98[d]
7	ChCl/LA	*t*-BuOK (3)	16	NR[c]
8	ChCl/Gly	*t*-BuOK (3)	16	20
9	ChCl/urea	*t*-BuOK (2)	16	42
10	ChCl/urea	*t*-BuOK (3)	1	62
11	ChCl/urea	*t*-BuOK (3)	2	88[d]
12	ChCl/urea	*t*-BuOK (3)	4	90[d]
13	ChCl/urea	*t*-BuOK (3)	6	92[d]
14	ChCl/urea	*t*-BuOK (3)	7	96[d]
15	ChCl/sorbitol	*t*-BuOK (3)	7	32
16	ChCl/isosorbide	*t*-BuOK (3)	7	36
17	Fructose/urea	*t*-BuOK (3)	7	NR[c]
18	Menthol/LA	*t*-BuOK (3)	7	NR[c]
19	Gly/L-Pro	*t*-BuOK (3)	7	NR[c]

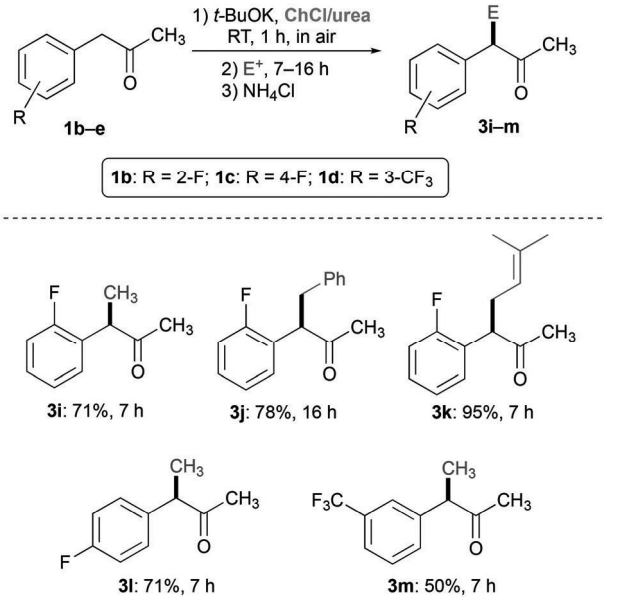
[a] Reaction conditions: **1a** (0.75 mmol), DES [ChCl/Gly (1 : 2 mol mol^{-1}); ChCl/urea (1 : 2 mol mol^{-1}); ChCl/LA (1 : 2 mol mol^{-1}); fructose/urea (3 : 2 w w^{-1}); ChCl/isosorbide (1 : 2 mol mol^{-1}); ChCl/sorbitol (1 : 2 mol mol^{-1}); menthol/LA (1 : 2 mol mol^{-1}); Gly/L-Pro (1 : 1 mol mol^{-1})] (2 g), RT, in air. [b] Determined by GC. [c] NR: no reaction; substrate **1a** was quantitatively recovered. [d] Yield of isolated product by column chromatography.

With these optimized conditions in place, we sought to capitalize on this process by exploring the scope of the reaction with a variety of electrophiles (Scheme 1). With regard to **1a**, high yields (83–94%) of the desired alkylated, allylated and benzylated products **3b–e** were obtained when benzyl bromide, allyl bromide or 1-chloro-3-bromopropane participated in the process. Nitrostyrenes bearing both electron-donating and electron-withdrawing substituents as well as methyl acrylate all underwent nucleophilic addition reactions smoothly, thereby affording products **3f–h** in 91–98% yield. The reaction with benzaldehyde gave a complex mixture of cross-condensation/dehydration products, and thus it was not investigated further, whereas less electrophilic partners like ketones (acetone), amides (dimethylformamide), nitrones, and malonates proved to be totally unreactive, under these conditions, towards the putative enolate intermediate **2a**.

In consideration of the fact that the introduction of fluorinated substituents in organic skeletons is known to dramatically change their physicochemical and pharmacokinetic properties,[13] as well as to improve drug delivery,[14] we next turned our attention to the synthesis of some fluorinated arylpropanone derivatives.[15] To our delight, the alkylation (CH_3I), allylation (1,1-dimethylallyl bromide), and benzylation (benzyl bromide) of a series of arylpropanones, decorated with a fluorine atom or a CF_3 group at the *ortho*-, *meta*-, or *para*-position of the aryl ring (**1b–1d**), proceeded uneventfully in ChCl/urea, under our standard reaction conditions, thereby leading to products **3i–m** in 50–95% yield (Scheme 2).



Scheme 1 *t*-BuOK-Mediated deprotonation of 1-phenylpropan-2-one (**1a**) and α-functionalization with electrophiles in ChCl/urea (dr = diastereomeric ratio; separable mixture of diastereomers).

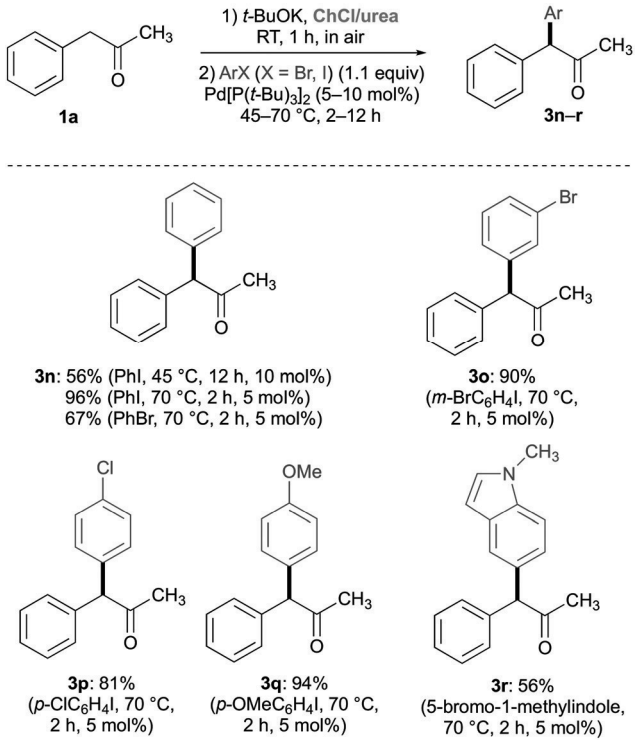


Scheme 2 *t*-BuOK-Mediated deprotonation of fluorinated 1-arylpropan-2-one derivatives (**1b–d**) and α-functionalization with electrophiles in ChCl/urea.

To further explore the utility of this new protocol, we investigated the synthesis of branched arylpropanone derivatives in DESs by means of Pd-catalyzed C–C bond-forming processes, which have become a powerful tool in the synthesis of both natural products and active pharmaceutical ingredients (APIs).[16] α-Arylation of ketones, by coupling enolates with aryl halides, has always been challenging to conduct, with preformed zinc or tin enolates and stoichiometric amounts of nickel complexes being typically used. β-Hydrogen elimination reactions were also found to seriously compete with reduction eliminations *en route* to the desired coupling products. Another hurdle is that alkali metal enolates are typically generated at low temperatures, whereas cross-coupling reactions usually take place at elevated temperatures.[17] Thus, various strategies have been developed for the α-arylation of carbonyl compounds to limit the aforementioned shortcomings. These include (a) photoinduced S_N1 (ref. 18*a*) or $S_{RN}1$ (ref. 18*b*) reactions, (b) polarity inversion of *N*-alkoxyenamines,[19] and (c) a three-component aminoarylation of alkynes followed by hydrolysis of *in situ* generated enamines.[20] As for enolate chemistry, the most effective catalysts found so far are based on palladium complexes containing sterically hindered, electron-rich phosphines or *N*-heterocyclic carbene ligands, whereas mechanistic studied disclosed the formation of unsaturated and catalytically active [PdL] species undergoing a fast oxidative addition with aryl halides, as the rate-limiting step, with the reductive elimination reaction from an arylpalladium enolate intermediate being most probably responsible for the C–C bond formation in the product.[4,21] α-Arylation of arylketones has also been recently enabled by working in aqueous micellar conditions in the presence of a designer surfactant and a lipophilic base.[22]

As part of our ongoing research in metal-catalyzed transformations run in bio-based solvents, we recently set up direct Pd-catalyzed cross-coupling reactions between organolithiums or organozinc halides and (hetero)aryl halides, working in air under mild conditions, either in bulk water/NaCl or in eutectic mixtures, while using Pd catalysts containing bulky electron-rich ligands.[9c,f] Our investigation first focused on the $C(sp^3)$–$C(sp^2)$ cross-coupling between **1a** and PhI (1.1 equiv.), in ChCl/urea, and in the presence of *t*-BuOK as the base and $Pd[P(t\text{-}Bu)_3]_2$ as the catalyst, for the preparation of **3n** (Scheme 3). When the reaction was run at 45 °C in air using 10 mol% catalyst, adduct **3n** was isolated in 56% yield only after 12 h. By increasing the temperature to 70 °C and lowering the loading of the catalyst to 5 mol%, the yield of **3n** remarkably increased up to 96% after 2 h only. A lower yield of **3n** (67%) was instead obtained by switching to PhBr as the electrophilic partner. Reducing the loading of the catalyst up to 2 mol% caused a further decrease of the product yield.

Under the best experimental conditions of temperature and catalyst loading in ChCl/urea, both aryl iodides bearing electron-donating and electron-withdrawing groups successfully cross-coupled with **1a**, thereby furnishing products **3o–q** in excellent 81–94% yield. The brominated coupling module 5-bromo-1-methylindole cross-coupled with good reaction efficiency as well with **1a** to afford α-indolyl derivative **3r** in 56% yield (Scheme 3).



Scheme 3 α-Arylation of phenylacetone (**1a**) *via* Pd-catalyzed cross-coupling reactions with (hetero)aryl halides in ChCl/urea (yields of isolated compounds).

Conclusions

In summary, the environmentally benign eutectic mixture ChCl/urea (1 : 2) revealed to be an effective reaction medium for performing an alkoxide-mediated enolization of 1-arylpropan-2-ones and their fluorinated derivatives, and for promoting α-functionalization reactions by nucleophilic addition to conjugated systems and substitution reactions with alkyl, benzyl and allyl halides. These reactions proceed under remarkably mild conditions (room temperature) and in air, providing the desired products in up to 98% yield. Less electrophilic partners like ketones, nitrones, amides and malonates, however, proved to be unreactive under these conditions. Of note, regioselective Pd-catalyzed cross-coupling reactions between the potassium enolate of phenylacetone and (hetero)aryl halides proved to be also feasible under such aerobic conditions in ChCl/urea upon simple warming the reaction mixture to 70 °C and with a catalyst loading up to 5 mol%, thereby furnishing branched, α-arylated derivatives in 56–96% yield, irrespective of the electronic effects of substituents.

According to recent investigations,[8b,j] the chemistry of s-block elements, run in DESs under aerobic conditions, sometimes benefited from the presence of ethereal solvents (*e.g.*, cyclopentyl methyl ether) in the mixture. It is worth highlighting that the present protocol allows instead the formation and the functionalization of enolates in a neat eutectic mixture, thereby complementing the traditional approaches still adopted in enolate chemistry that generally make use of stronger bases, anhydrous VOCs or biphasic mixtures with phase transfer catalysts, inert atmospheres, and low temperatures (up to −78 °C). This opens the door towards other exciting opportunities to functionalize enolates in a more sustainable way, which are still unexploited in DESs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

1 (*a*) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1624; (*b*) D. Stolz and U. Kazmaier, *Metal Enolates as Synthons in Organic Chemistry*, Patai's Chemistry of Functional Groups, John Wiley & Sons, Ltd, 2010; (*c*) D. J. Hart and C. D. Ha, *Chem. Rev.*, 1989, **89**, 1447; (*d*) G. Wu and M. Huang, *Chem. Rev.*, 2006, **106**, 2596.

2 (*a*) M. Suter and A. W. Weston, *J. Am. Chem. Soc.*, 1942, **64**, 533; (*b*) E. M. Schultz, J. B. Bicking, S. Mickey and F. S. Crossley, *J. Am. Chem. Soc.*, 1953, **75**, 1072; (*c*) P. Vitale, S. Tacconelli, M. G. Perrone, P. Malerba, L. Simone, A. Scilimati, A. Lavecchia, M. Dovizio, M. Marcantoni, A. Bruno and P. Patrignani, *J. Med. Chem.*, 2013, **56**, 4277; (*d*) M. G. Perrone, P. Vitale, A. Panella, C. G. Fortuna and A. Scilimati, *Eur. J. Med. Chem.*, 2015, **94**, 252; (*e*) M. G. Perrone, P. Malerba, M. J. Uddin, P. Vitale, A. Panella, B. C. Crews, C. K. Daniel, K. Ghebreselasie, M. Nickels, M. N. Tantawy, H. C. Manning, L. J. Marnett and A. Scilimati, *Eur. J. Med. Chem.*, 2014, **80**, 562; (*f*) M. Collins, *Drug Test. Anal.*, 2011, **3**, 404; (*g*) S. L. Hill and S. H. L. Thomas, *Clin. Toxicol.*, 2011, **49**, 705.

3 (*a*) P. Vitale and A. Scilimati, *Curr. Org. Chem.*, 2013, **17**, 1986; (*b*) L. Di Nunno, A. Scilimati and P. Vitale, *Tetrahedron*, 2002, **58**, 2659.

4 E. M. Schultz, J. B. Bicking, S. Mickey and F. S. Crossley, *J. Am. Chem. Soc.*, 1953, **75**, 1072.

5 (*a*) A. Aranda, A. Díaz, E. Díez-Barra, A. de la Hoz, A. Moreno and P. Sánchez-Verdú, *J. Chem. Soc., Perkin Trans. 1*, 1992, 2427; (*b*) N. Furukawa, K. Imaoka, H. Fujihara and S. Oae, *Chem. Lett.*, 1982, **11**, 1421.

6 C. Rodriguez, G. de Gonzalo, D. E. T. Pazmino, M. W. Fraaije and V. Gotor, *Tetrahedron: Asymmetry*, 2009, **20**, 1168.

7 S. Shimizu, T. Suzuki, S. Shirakawa, Y. Sasaki and C. Hirai, *Adv. Synth. Catal.*, 2002, **344**, 370.

8 For recent reviews and papers, see: (*a*) L. Cicco, M. J. Rodríguez-Álvarez, F. M. Perna, J. García-Álvarez and V. Capriati, *Green Chem.*, 2017, **19**, 3069; (*b*) J. García-Álvarez, E. Hevia and V. Capriati, *Chem. – Eur. J.*, 2018, **24**, 14854; (*c*) L. Cicco, A. Fombona-Pascual, A. Sánchez-Condado, G. A. Carriedo, F. M. Perna, V. Capriati, A. Presa Soto and J. García-Álvarez, *ChemSusChem*, 2020, **13**, 4967; (*d*) F. M. Perna, P. Vitale and V. Capriati, *Curr. Opin. Green Sustain. Chem.*, 2020, **21**, 27; (*e*) L. Cicco, A. Salomone, P. Vitale, N. Ríos-Lombardía, J. González-Sabín, J. García-Álvarez, F. M. Perna and V. Capriati, *ChemSusChem*, 2020, **13**, 3583; (*f*) M. Dell'Aera, F. M. Perna, P. Vitale, A. Altomare, A. Palmieri, L. C. H. Maddock, L. J. Bole, A. R. Kennedy, E. Hevia and V. Capriati, *Chem. – Eur. J.*, 2020, **26**, 8742; (*g*) F. M. Perna, P. Vitale and V. Capriati, *Curr. Opin. Green Sustain. Chem.*, 2021, **30**, 100487; (*h*) A. F. Quivelli, G. D'Addato, P. Vitale, J. García-Álvarez, F. M. Perna and V. Capriati, *Tetrahedron*, 2021, **81**, 131898; (*i*) L. Cicco, G. Dilauro, F. M. Perna, P. Vitale and V. Capriati, *Org. Biomol. Chem.*, 2021, **19**, 2558; (*j*) S. E. García-Garrido, A. P. Soto, E. Hevia and J. García-Álvarez, *Eur. J. Inorg. Chem.*, 2021, DOI: 10.1002/ejic.202100347.

9 (*a*) G. Dilauro, S. M. García, D. Tagarelli, P. Vitale, F. M. Perna and V. Capriati, *ChemSusChem*, 2018, **11**, 3495; (*b*) A. F. Quivelli, P. Vitale, F. M. Perna and V. Capriati, *Front. Chem.*, 2019, **7**, 723; (*c*) G. Dilauro, A. F. Quivelli, P. Vitale, V. Capriati and F. M. Perna, *Angew. Chem., Int. Ed.*, 2019, **58**, 1799; (*d*) V. Pelliccioli, G. Dilauro, S. Grecchi, S. Arnaboldi, C. Graiff, F. M. Perna, P. Vitale, E. Licandro, A. Aliprandi, S. Cauteruccio and V. Capriati, *Eur. J. Org. Chem.*, 2020, 6981; (*e*) F. Messa, G. Dilauro, F. M. Perna, P. Vitale, V. Capriati and A. Salomone, *ChemCatChem*, 2020, **12**, 1979; (*f*) G. Dilauro, C. S. Azzolini, P. Vitale, A. Salomone, F. M. Perna and V. Capriati, *Angew. Chem., Int. Ed.*, 2021, **60**, 10632.

10 (*a*) L. Cicco, N. Ríos-Lombardía, M. J. Rodríguez-Álvarez, F. Morís, F. M. Perna, V. Capriati, J. García-Álvarez and J. González-Sabín, *Green Chem.*, 2018, **20**, 3468; (*b*) P. Vitale, F. Lavolpe, F. Valerio, M. Di Biase, F. M. Perna, E. Messina, G. Agrimi, I. Pisano and V. Capriati, *React. Chem. Eng.*, 2020, **5**, 859; (*c*) P. Vitale, V. M. Abbinante, F. M. Perna, A. Salomone, C. Cardellicchio and V. Capriati, *Adv. Synth. Catal.*, 2017, **359**, 1049.

11 (*a*) P. Vitale, L. Cicco, F. Messa, F. M. Perna, A. Salomone and V. Capriati, *Eur. J. Org. Chem.*, 2019, 5557; (*b*) P. Vitale, L. Cicco, I. Cellamare, F. M. Perna, A. Salomone and V. Capriati, *Beilstein J. Org. Chem.*, 2020, **16**, 1915.

12 P. Vitale, F. M. Perna, M. G. Perrone and A. Scilimati, *Tetrahedron: Asymmetry*, 2011, **22**, 1985.

13 (*a*) B. E. Smart, *J. Fluorine Chem.*, 2001, **109**, 3; (*b*) B. K. Park, N. R. Kitteringham and P. M. O'Neill, *Annu. Rev. Pharmacol. Toxicol.*, 2001, **41**, 443.

14 (*a*) F. M. D. Ismail and J. Fluorine, *Chem*, 2002, **118**, 27; (*b*) D. O'Hagan and D. B. Harper, *J. Fluorine Chem.*, 1999, **110**, 127.

15 Trifluoromethyl ketones have shown neuroprotective effects against low K(+)-induced apoptosis in cerebellar granule neurons; see: K. Sunaga, T. Tanaka, S. Tani and M. Kawase, *In Vivo*, 2002, **16**, 97.

16 S. T. Sivanandan, A. Shaji, I. Ibnusaud, C. C. C. J. Seechurn and T. J. Colacot, *Eur. J. Org. Chem.*, 2015, 38.

17 For an Account, see: D. A. Culkin and J. F. Hartwig, *Acc. Chem. Res.*, 2003, **36**, 234.

18 (*a*) A. Frabini, M. Fagnoni and A. Albini, *J. Org. Chem.*, 2003, **68**, 4886; (*b*) J. F. Gustavino and R. A. Rossi, *J. Org. Chem.*, 2012, **77**, 460.

19 T. Miyoshi, T. Miyakawa, M. Ueda and O. Miyata, *Angew. Chem., Int. Ed.*, 2011, **50**, 928.

20 J.-W. Park, B. Kang and V. M. Dong, *Angew. Chem., Int. Ed.*, 2018, **57**, 13598.

21 U. Christmann and R. Vilar, *Angew. Chem., Int. Ed.*, 2005, **44**, 366.

22 A. B. Wood, D. E. Roa, F. Gallou and B. H. Lipshutz, *Green Chem.*, 2021, **23**, 4858.