



Cite this: *RSC Adv.*, 2019, 9, 9468

Received 21st January 2019
Accepted 14th March 2019

DOI: 10.1039/c9ra00523d

rsc.li/rsc-advances

Synthesis of D-glyco-alkynone derivatives via carbonylative Sonogashira reaction†

Mariana P. Darbem,^a C. Henrique A. Esteves,^a Isadora M. de Oliveira,^b Joel S. Reis,^a Daniel C. Pimenta^c and Hélio A. Stefani ^{*a}

A carbonylative Sonogashira coupling approach to the synthesis of glyco-alkynones is described. Eighteen examples were obtained in moderate to nearly quantitative yields under mild conditions employing Mo(CO)₆ as a safe carbon monoxide source. Functionalization of the alkynyl moiety *via* cycloaddition with organic azides provided six examples of glyco-triazoles.

Introduction

Alkynones are attractive motifs in organic chemistry involved in the synthesis of medicinally valuable heteroaromatic compounds.¹ These molecules are also important intermediates in the synthesis of natural products² and as part of biologically active molecules (Fig. 1).³

Consequently, a rich variety of methodologies targeting their synthesis has been reported, some of which involve the addition of borylated terminal alkynes to acyl chlorides,⁴ the addition of hypervalent alkynyl iodides to aldehydes *via* C–C bond cleavage, metal-catalyzed C–H bond activation of aldehydes⁵ or the oxidation of propargylic alcohols.⁶ While impressive, these methodologies present some drawbacks, such as excessive generation of chemical waste, instability of some of the substrates required and poor functional group tolerance. The

Pd-catalyzed carbonylative Sonogashira coupling, on the other hand, offers a route to alkynones that is mild, atom-economical and functional-group-tolerant.⁷ Attracted by these features, we decided to explore the construction of glyco-alkynones relying on this reaction as part of our ongoing research interest in the synthesis of functionalized glycals.⁸

In a previous report,^{8a} we explored the synthesis of amido-glucals and glucal esters *via* the carbonylative coupling reaction of 2-iodo-D-glucal. Herein, we describe the synthesis of glyco-alkynones *via* carbonylative Sonogashira coupling reaction, expanding the spectrum of reactions involving this important substrate (Scheme 1).

Taking advantage of the alkynyl group readily installed by this reaction, we also explored the synthesis of glyco-substituted triazoles *via* click chemistry. This approach has been of pivotal importance for carbohydrate chemistry as a tool to efficiently connect a sugar moiety to a molecule of interest *via* a triazole linker, improving the hydrophilicity, bioavailability and chemical profile of these fragments.⁹ Moreover, the biological activity demonstrated by several alkynone derivatives (*e.g.* triazoles) make new routes to these structures synthetically relevant (Fig. 2).¹⁰

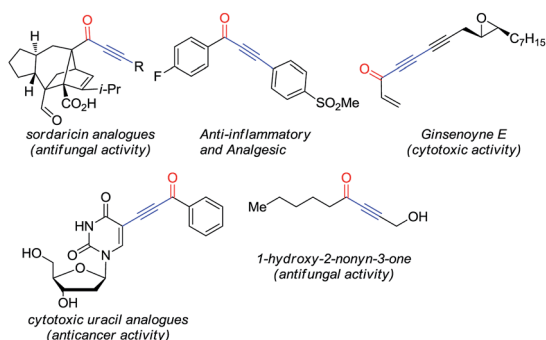


Fig. 1 Alkynones in biologically active compounds.

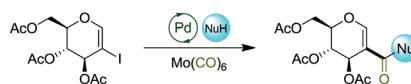
^aFaculdade de Ciências Farmacêuticas, Universidade de São Paulo, São Paulo, SP, Brazil. E-mail: hstefani@usp.br; Tel: +55 11 3091-3654

^bInstituto de Química, Universidade de São Paulo, São Paulo, SP, Brazil

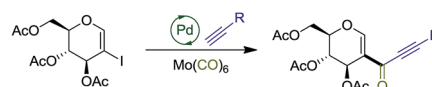
^cInstituto Butantã, São Paulo, SP, Brazil

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ra00523d

Previous results:



This work:



- Key features:
- High-yielding route to novel glucal-alkynones
 - broad functional group tolerance
 - 1 equiv. of Mo(CO)₆ required
 - Alkynone moiety available for further functionalization

Scheme 1 2-Iodoglucal carbonylative coupling reactions.



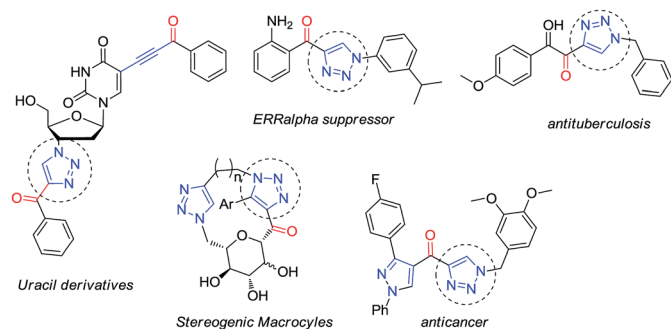
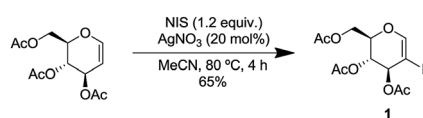


Fig. 2 Examples of biologically active triazolico-alkynes.



Scheme 2 Synthesis of 2-iodo-tri-O-acetyl-D-glucal.

Results and discussion

We commenced our study by synthesizing 2-iodo-tri-O-acetyl-D-glucal (**1**) from tri-O-acetyl-D-glucal, *N*-iodosuccinimide (NIS) and AgNO₃ (Scheme 2).¹¹

With substrate **1** in hand, we next screened the reaction conditions for the carbonylation of 2-iodo-tri-O-acetyl-D-

glucal (**1**) with Mo(CO)₆ and 4-ethynyltoluene. Reactions were followed by TLC to ensure full conversion of the starting material **1** (Table 1).

We started by screening the effect of the catalyst on the reaction outcome. PdCl₂, Pd(PhCN)₂Cl₂, and Pd(Prol)₂ (Table 1, entries 1, 2 and 4, respectively) led to the formation of alkyne **3a** in moderate yields. Catalysts containing ligands that are at the same time electron-rich and sterically demanding, such as xantphos and PEPPSI,¹² delivered alkyne **3a** in good to nearly quantitative yield (Table 1, entries 3, 5 and 6), with the combination PdCl₂/xantphos being the best. In order to seek other high-yielding set of conditions, the effect of the base was next examined. Organic and inorganic bases such as DIPEA, DBU, NaOAc and K₂CO₃ gave **3a** in lower yields, with inorganic K₂CO₃ delivering the desired product in only 25%. Different solvents were also screened, however, only poor to modest yields of **3a** were obtained.

With the optimized reaction conditions in hand, we set out to investigate the generality of this reaction (Scheme 3).

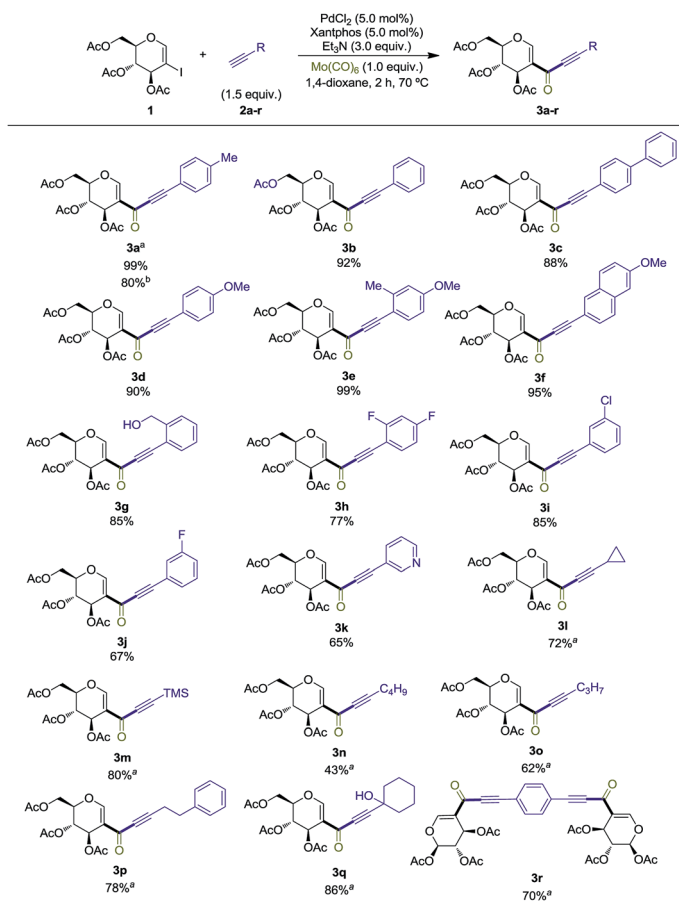
Terminal alkynes bearing electron-neutral and electron-donating groups delivered the desired alkyne in good to excellent yields (**3a–g**). Electron-withdrawing groups such as the difluorinated moiety present in **2h** and *meta*-chloro substituted **2i** gave **3h** and **3i** in good yields, while *meta*-fluorinated **2j** gave **3j** in 67%. Incorporation of a hetero-aromatic substituent was also tolerated, and alkyne **3k** was obtained in 65% yield. Pleasingly, both cyclopropyl and TMS groups proved to be stable under the reaction

Table 1 Screening of reaction conditions

Entry ^a	Catalyst/ligand	Base (3.0 equivi.)	Solvent	Reaction time (h)	Yield (%)
Effect of catalyst					
1	PdCl ₂	Et ₃ N	1,4-Dioxane	12	66
2	Pd(PhCN) ₂ Cl ₂	Et ₃ N	1,4-Dioxane	12	58
3	Pd(PhCN) ₂ Cl ₂ /xantphos	Et ₃ N	1,4-Dioxane	12	73
4	Pd(Prol) ₂	Et ₃ N	1,4-Dioxane	12	63
5	PEPPSI-IPr	Et ₃ N	1,4-Dioxane	12	75
6	PdCl ₂ /xantphos	Et ₃ N	1,4-Dioxane	2	99
Effects of base					
7	PdCl ₂ /xantphos	DIPEA	1,4-Dioxane	16	55
8	PdCl ₂ /xantphos	DBU	1,4-Dioxane	16	43
9	PdCl ₂ /xantphos	NaOAc	1,4-Dioxane	16	32
10	PdCl ₂ /xantphos	K ₂ CO ₃	1,4-Dioxane	16	25
Effect of solvent					
11	PdCl ₂ /xantphos	Et ₃ N	Toluene	16	55
12	PdCl ₂ /xantphos	Et ₃ N	THF	16	43
13	PdCl ₂ /xantphos	Et ₃ N	DMF	16	32
14	PdCl ₂ /xantphos	Et ₃ N	MeCN	16	25

^a Reaction condition: **1** (0.2 mmol), catalyst (5 mol%), ligand (5 mol%), 4-ethynyltoluene (1.5 equivi.), base (3.0 equivi.), solvent (3 mL).





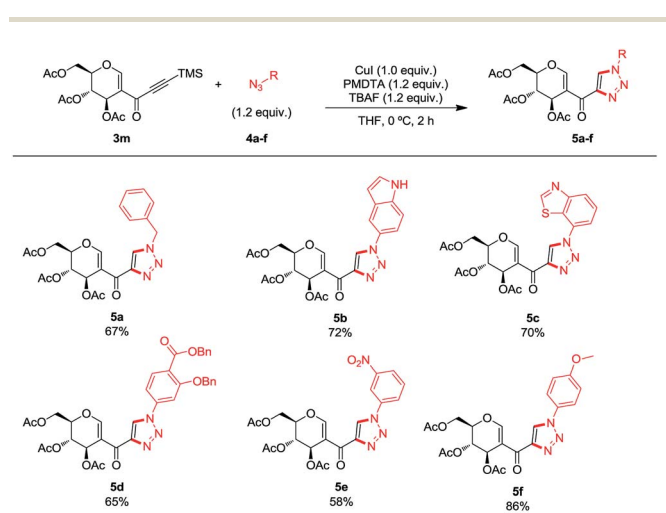
Reaction conditions: **1** (0.2 mmol), terminal alkyne (1.5 equiv.), PdCl₂ (5.0 mol%), Xantphos (5.0 mol%), Et₃N (3.0 equiv.), Mo(CO)₆ (1.0 equiv.), 1,4-dioxane, 2 h, 70 °C. ^a Reaction time: 4 h. ^b gram-scale reaction.

Scheme 3 Sonogashira carbonylative coupling reaction of 2-iodo-D-glucal and terminal alkynes.

conditions, with products **3l** and **3m** being isolated in 72% and 80%, respectively, both leaving useful handles for further functionalization (see Scheme 4).¹³ Incorporation of terminal alkynes bearing alkyl moieties provided mixed results, with **2n** and **2o** delivering alkynones in moderate yields, while **2p** and **2q**, bearing a tertiary alcohol, provided **3p** and **3q** in good yields. 1,4-Diethynylbenzene **2r** was subjected to the reaction conditions, giving the symmetrical alkynone **3r** in 70%. Finally, the reaction with **2a** was repeated on a gram scale, providing **3a** in 80% isolated yield (Scheme 4).

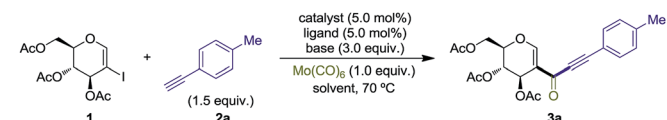
In order to demonstrate the usefulness of this methodology, we decided to explore the formation of 1,2,3-triazoles *via* click chemistry. An *in situ*-generated terminal alkyne provided the desired triazoles **5a-f** in the presence of organic azides, PMDTA and copper iodide (conditions found after a quick

screening).¹⁴ A variety of moieties were tolerated at the position 1 of the newly formed ring: a benzylic substituent (**5a**, 67%), heteroaromatic substituents (**5b**, 72% and **5c**, 70%) and



Reaction conditions: **3m** (0.25 mmol), CuI (1.0 equiv.), RN₃ (1.2 equiv.), PMDTA (1.2 equiv.), TBAF (1.2 equiv.), THF (3 mL), 0 °C for 2 h. PMDTA = *N,N,N',N',N''*-pentamethyldiethylenetriamine.

Scheme 5 Synthesis of D-glyco-1,2,3-triazoles.



Scheme 4 Gram-scale reaction.



unactivated (**5d**, 65% and **5e**, 58%) and activated aromatic rings (**5f**, 86%) (Scheme 5).

Conclusions

In conclusion, we have described a convenient palladium-catalyzed Sonogashira carbonylative coupling reaction for the synthesis of D-glyco-alkynones. This approach permitted the synthesis of 18 examples in moderate to nearly quantitative yields under mild conditions, employing Mo(CO)₆ as a safe carbon monoxide source. Further functionalization of a masked terminal alkynone allowed the synthesis of D-glyco-1,2,3-triazoles in moderate yields, demonstrating one of the potential applications of the alkynones described herein.

Experimental section

General considerations

The compounds were all identified by usual analytical methods: ¹H NMR, ¹³C NMR, IR, and HR-MS (ESI). ¹H and ¹³C NMR spectra were measured in CDCl₃, in a Bruker DPX-300 instrument. ¹H chemical shifts were reported in ppm referenced relative to TMS internal standard (0.00 ppm) or the residual chloroform peak (7.26 ppm). Abbreviations to denote the multiplicity of a particular signal are: m (multiplet), s (singlet), d (doublet), t (triplet) and dd (doublet of doublets). ¹³C chemical shift were reported in ppm relative to the CDCl₃ triplet (77.16 ppm). IR spectra were measured on an Agilent Technologies Cary 630 and were reported in wavenumbers (cm⁻¹). High-resolution mass spectra (HRMS) were recorded on a Shimadzu LCMS-TOF, using ESI with 50% solution of acetonitrile/H₂O and 0.1% formic acid as ionization method. Thin layer chromatography (TLC) was performed using silica gel UV₂₅₄ 0.20 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine or acidic vanillin solution. The solvents were purified by distillation or used without any purification in the case of HPLC-grade material. All other compounds were used as received.

General procedure for the synthesis of 3a-r

To a vial equipped with a magnetic stirrer bar and sealed with a rubber septum connected to a deflated balloon with a needle were added the tri-*O*-acetylated iodoglucal (0.2 mmol), 1,4-dioxane (3.0 mL), PdCl₂ (5 mol%), xantphos (5 mol%), Mo(CO)₆ (0.2 mmol, 1 equiv.), the alkyne (0.3 mmol, 1.5 equiv.) and Et₃N (0.6 mmol, 3 equiv.). The reaction mixture was vigorously stirred at 70 °C for 2 to 4 h. The resulting mixture was washed with water and extracted with ethyl acetate. The organic layers were then combined and evaporated. The crude products were purified by flash chromatography using hexane and ethyl acetate as eluent (7 : 3).

General procedure for the synthesis of 5a-f

To a vial (20 mL) equipped with a magnetic stirrer bar under a nitrogen atmosphere containing CuI (0.25 mmol, 1 equiv.), THF (4 mL), an organic azide (0.3 mmol, 1.2 equiv.) and **3m** (0.25 mmol, 1 equiv.) was added PMDETA (0.3 mmol, 1.2 equiv.)

and the reaction mixture was stirred at 0 °C for 2 h. After this period, the reaction mixture was diluted with ethyl acetate and washed with aqueous NaCl. The organic phase was collected, dried over MgSO₄, filtered and the solvent was evaporated under reduced pressure. Purification was performed using flash chromatography (ethyl acetate/hexane, 4 : 6).

Analytical data of compounds 3a-r/5a-f

Product **3a** was obtained as a yellow oil (83 mg, 0.20 mmol, 99%). ¹H NMR (300 MHz, CDCl₃): δ = 8.00 (s, 1H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 5.73 (dd, *J* = 3.1, 1.6 Hz, 1H), 5.15 (t, *J* = 3.0 Hz, 1H), 4.70–4.51 (m, 1H), 4.40 (dd, *J* = 12.1, 7.8 Hz, 1H), 4.14 (dd, *J* = 12.1, 4.4 Hz, 1H), 2.31 (s, 3H), 2.15–1.89 (m, 9H). ¹³C NMR (75 MHz, CDCl₃): δ = 174.5, 170.2, 169.4, 169.1, 160.7, 141.3, 132.8, 129.4, 116.7, 114.9, 91.4, 84.8, 75.6, 65.6, 61.2, 60.9, 21.6, 20.7, 20.6, 20.6. IR (ν, cm⁻¹) = 2877, 2112, 1685, 1564, 1177, 1328, 1197, 1154, 1143, 991. HRMS (ESI-TOF) calc. [C₂₂H₂₂O₈Na⁺] 437.1212, found 437.1212.

Product **3b** was obtained as a yellow oil (72 mg, 0.18 mmol, 92%). ¹H NMR (300 MHz, CDCl₃): δ = 8.08 (s, 1H), 7.65–7.55 (m, 2H), 7.49–7.34 (m, 3H), 5.82 (d, *J* = 1.8 Hz, 1H), 5.23 (t, *J* = 3.0 Hz, 1H), 4.74–4.60 (m, 1H), 4.48 (dd, *J* = 12.1, 7.8 Hz, 1H), 4.21 (dd, *J* = 12.1, 4.5 Hz, 1H), 2.18–2.01 (m, 9H). ¹³C NMR (75 MHz, CDCl₃): δ = 174.4, 170.2, 169.4, 169.1, 160.9, 132.8, 130.6, 128.6, 119.8, 114.9, 90.8, 84.9, 75.6, 65.6, 61.2, 60.9, 20.7, 20.6, 20.6. IR (ν, cm⁻¹) = 2959, 2864, 2127, 1682, 1566, 1324, 1266, 1175, 1151, 992. HRMS (ESI-TOF) calc. [C₂₁H₂₀O₈Na⁺] 423.1056, found 423.1051.

Product **3c** was obtained as a yellow oil (84 mg, 0.18 mmol, 88%). ¹H NMR (300 MHz, CDCl₃): δ = 8.10 (s, 1H), 7.74–7.53 (m, 6H), 7.49–7.36 (m, 3H), 5.93–5.79 (m, 1H), 5.24 (t, *J* = 3.1 Hz, 1H), 4.75–4.64 (m, 1H), 4.49 (dd, *J* = 12.0, 7.8 Hz, 1H), 4.22 (dd, *J* = 12.1, 4.5 Hz, 1H), 2.19–1.98 (m, 9H). ¹³C NMR (75 MHz, CDCl₃): δ = 174.4, 170.2, 169.4, 169.1, 160.8, 143.5, 139.7, 133.3, 128.9, 128.1, 127.3, 127.1, 118.5, 114.9, 90.9, 85.7, 75.7, 65.6, 61.2, 60.9, 20.7, 20.6, 20.6. IR (ν, cm⁻¹) = 2959, 2931, 2123, 1685, 1566, 1438, 1324, 1264, 1175, 1151, 991. HRMS (ESI-TOF) calc. [C₂₇H₂₄O₈Na⁺] 499.1363, found 499.1361.

Product **3d** was obtained as a yellow oil (78 mg, 0.18 mmol, 90%). ¹H NMR (300 MHz, CDCl₃): δ = 8.06 (s, 1H), 7.54 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.87–5.78 (m, 1H), 5.23 (t, *J* = 3.0 Hz, 1H), 4.72–4.62 (m, 1H), 4.47 (dd, *J* = 12.1, 7.9 Hz, 1H), 4.21 (dd, *J* = 12.2, 4.5 Hz, 1H), 3.84 (s, 3H), 2.19–1.99 (m, 9H). ¹³C NMR (75 MHz, CDCl₃): δ = 174.5, 170.2, 169.4, 169.1, 161.6, 160.3, 134.8, 114.7, 114.4, 111.6, 91.9, 84.8, 75.5, 65.7, 61.3, 60.9, 55.4, 20.7, 20.6, 20.6. IR (ν, cm⁻¹) = 2866, 2747, 2119, 1685, 1549, 1460, 1175, 1151, 1134, 991. HRMS (ESI-TOF) calc. [C₂₂H₂₂O₉Na⁺] 453.1156, found 453.1159.

Product **3e** was obtained as a yellow oil (88 mg, 0.19 mmol, 99%). ¹H NMR (300 MHz, CDCl₃): δ = 7.88 (s, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 6.61–6.47 (m, 2H), 5.67–5.59 (m, 1H), 5.05 (t, *J* = 3.4 Hz, 1H), 4.54–4.41 (m, 1H), 4.33–4.23 (m, 1H), 4.12–3.95 (m, 1H), 3.62 (s, 3H), 2.29 (s, 3H), 1.96–1.80 (m, 9H). ¹³C NMR (75 MHz, CDCl₃): δ = 174.5, 170.2, 169.4, 169.1, 161.5, 160.4, 144.1, 135.2, 115.4, 115.0, 111.8, 111.6, 90.8, 88.4, 75.6, 65.6, 61.2, 60.9, 55.3, 21.0, 20.7, 20.6, 20.5. IR (ν, cm⁻¹) = 2821, 2756, 2112, 1685,



1566, 1549, 1324, 1259, 1179, 1151, 992. HRMS (ESI-TOF) calc. $[\text{C}_{23}\text{H}_{24}\text{O}_9\text{Na}^+]$ 467.1313, found 453.1311.

Product **3f** was obtained as a yellow oil (91 mg, 0.19 mmol, 95%). ^1H NMR (300 MHz, CDCl_3): δ = 8.05 (s, 1H), 7.98 (s, 1H), 7.64 (m, 2H), 7.45 (d, J = 8.4 Hz, 1H), 7.11 (dd, J = 9.0, 2.4 Hz, 1H), 7.04 (d, J = 2.6 Hz, 1H), 5.85–5.70 (m, 1H), 5.28–5.06 (m, 1H), 4.64–4.56 (m, 1H), 4.52–4.35 (m, 1H), 4.24–4.11 (m, 1H), 3.85 (s, 3H), 2.19–1.96 (m, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ = 174.5, 170.2, 169.4, 169.2, 160.7, 159.3, 135.4, 133.9, 129.7, 128.9, 128.1, 127.2, 119.9, 114.9, 114.4, 105.9, 92.1, 85.0, 75.6, 65.7, 61.3, 61.0, 55.4, 20.7, 20.6, 20.6. IR (ν , cm^{-1}) = 2913, 2866, 2117, 1680, 1560, 1436, 1324, 1177, 1151, 991. HRMS (ESI-TOF) calc. $[\text{C}_{26}\text{H}_{24}\text{O}_9\text{Na}^+]$ 503.1313, found 503.1312.

Product **3g** was obtained as a yellow oil (73 mg, 0.17 mmol, 85%). ^1H NMR (300 MHz, CDCl_3): δ = 9.21 (s, 1H), 7.70 (s, 1H), 7.55–7.33 (m, 4H), 5.93 (s, 1H), 5.37 (s, 2H), 5.23 (t, J = 3.4 Hz, 1H), 4.60–4.52 (m, 1H), 4.47 (dd, J = 11.6, 7.7 Hz, 1H), 4.20 (dd, J = 11.8, 4.1 Hz, 1H), 2.12–2.03 (m, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ = 171.5, 170.3, 169.6, 169.3, 154.2, 144.0, 131.9, 130.9, 128.3, 128.0, 120.4, 114.5, 96.0, 90.3, 74.3, 73.9, 66.2, 62.5, 61.0, 20.7, 20.7, 20.6. IR (ν , cm^{-1}) = 2861, 2080, 1680, 1574, 1527, 1324, 1177, 1145, 981, 732. HRMS (ESI-TOF) calc. $[\text{C}_{22}\text{H}_{22}\text{O}_9\text{Na}^+]$ 453.1156, found 453.1156.

Product **3h** was obtained as a yellow oil (67 mg, 0.15 mmol, 77%). ^1H NMR (300 MHz, CDCl_3): δ = 7.93 (s, 1H), 7.45–7.30 (m, 1H), 6.80–6.68 (m, 2H), 5.63–5.56 (m, 1H), 5.05 (t, J = 2.8 Hz, 1H), 4.54–4.45 (m, 1H), 4.34–4.21 (m, 1H), 4.13–3.94 (m, 1H), 2.01–1.79 (m, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ = 173.9, 170.2, 169.3, 169.1, 164.4, 164.3 (dd, J = 253.5 Hz, J = 7.5 Hz), 161.6, 135.7, 135.6, 115.0, 112.3, 112.2 (dd, J = 22.2 Hz, 3.3 Hz), 105.2 (dd, J = 3.7 Hz), 104.7 (t, J = 24.7 Hz) 89.4, 75.7, 65.5, 61.0, 60.9, 20.7, 20.6. IR (ν , cm^{-1}) = 2976, 2136, 1685, 1560, 1456, 1326, 1175, 1151, 992, 937, 711. HRMS (ESI-TOF) calc. $[\text{C}_{21}\text{H}_{18}\text{F}_2\text{O}_8\text{Na}^+]$ 436.0862, found 436.0869.

Product **3i** was obtained as a yellow oil (74 mg, 0.17 mmol, 85%). ^1H NMR (300 MHz, CDCl_3): δ = 7.57 (s, 1H), 7.51–7.39 (m, 1H), 7.35 (d, J = 7.8 Hz, 2H), 5.85–5.75 (m, 1H), 5.23 (t, J = 3.0 Hz, 1H), 4.70–4.68 (m, 1H), 4.56–4.42 (m, 1H), 4.23 (d, J = 4.5 Hz, 1H), 2.22–1.92 (m, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ = 174.1, 170.2, 169.3, 169.1, 161.2, 134.5, 132.4, 130.9, 130.8, 129.9, 121.5, 114.9, 88.7, 85.5, 75.8, 65.5, 61.0, 60.9, 20.7, 20.6, 20.6. IR (ν , cm^{-1}) = 2975, 2130, 1682, 1562, 1426, 1365, 1266, 1173, 1151, 991. HRMS (ESI-TOF) calc. $[\text{C}_{21}\text{H}_{19}\text{ClO}_8\text{Na}^+]$ 457.0661, found 457.0660.

Product **3j** was obtained as a yellow oil (56 mg, 0.13 mmol, 67%). ^1H NMR (300 MHz, CDCl_3): δ = 8.07 (s, 1H), 7.43–7.37 (m, 2H), 7.32–7.23 (m, 1H), 7.24–7.07 (m, 1H), 5.88–5.78 (m, 1H), 5.23 (t, J = 3.0 Hz, 1H), 4.82–4.64 (m, 1H), 4.49 (dd, J = 12.1, 7.9 Hz, 1H), 4.21 (dd, J = 12.2, 4.5 Hz, 1H), 2.18–2.01 (m, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ = 174.1, 170.2, 169.3, 169.12, 162.53 (d, J = 246.7 Hz), 161.1, 130.4 (d, J = 8.5 Hz), 128.7 (d, J = 3.2 Hz), 121.6 (d, J = 9.3 Hz), 119.4 (d, J = 23.3 Hz), 118.1 (d, J = 21.2 Hz), 114.9, 88.9 (d, J = 3.4 Hz), 85.2, 75.8, 65.5, 61.0, 60.9, 20.7, 20.6, 20.5. IR (ν , cm^{-1}) = 2970, 2132, 1685, 1564, 1326, 1268, 1177, 1151, 1113, 985, 849. HRMS (ESI-TOF) calc. $[\text{C}_{21}\text{H}_{19}\text{FO}_8\text{Na}^+]$ 441.0956, found 441.0956.

Product **3k** was obtained as a yellow oil (52 mg, 0.13 mmol, 65%). ^1H NMR (300 MHz, CDCl_3): δ = 8.74 (s, 1H), 8.60 (d, J = 4.0 Hz, 1H), 8.01 (s, 1H), 7.87–7.73 (m, 1H), 7.28 (dd, J = 7.9, 5.0 Hz, 1H), 5.74 (s, 1H), 5.16 (s, 1H), 4.68–4.58 (m, 1H), 4.42 (dd, J = 12.2, 7.9 Hz, 1H), 4.13 (dd, J = 12.1, 4.5 Hz, 1H), 2.09–1.90 (m, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ = 173.9, 170.2, 169.3, 169.1, 161.3, 153.0, 150.6, 139.6, 123.2, 117.2, 114.9, 87.5, 86.8, 75.8, 65.5, 61.0, 60.8, 20.7, 20.6, 20.6. IR (ν , cm^{-1}) = 2859, 2119, 1680, 1566, 1326, 1181, 992. HRMS (ESI-TOF) calc. $[\text{C}_{20}\text{H}_{19}\text{NO}_8\text{Na}^+]$ 424.1003, found 444.1002.

Product **3l** was obtained as a yellow oil (53 mg, 0.14 mmol, 72%). ^1H NMR (300 MHz, CDCl_3): δ = 7.90 (s, 1H), 5.72 (s, 1H), 5.18 (s, 1H), 4.64–4.54 (m, 1H), 4.44 (dd, J = 12.1, 7.8 Hz, 1H), 4.19 (d, J = 4.5 Hz, 1H), 2.19–1.91 (m, 9H), 1.45–1.42 (m, 1H), 1.07–0.86 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3): δ = 174.8, 174.8, 170.5, 169.7, 169.5, 160.8, 115.1, 98.5, 75.8, 66.0, 61.5, 61.3, 21.0, 21.0, 20.9, 9.8, 9.8. IR (ν , cm^{-1}) = 2915, 2138, 1682, 1566, 1365, 1175, 1149, 991, 864. HRMS (ESI-TOF) calc. $[\text{C}_{18}\text{H}_{20}\text{O}_8\text{Na}^+]$ 387.1050, found 387.1051.

Product **3m** was obtained as a yellow oil (64 mg, 0.16 mmol, 80%). ^1H NMR (300 MHz, CDCl_3): δ = 7.82 (s, 1H), 5.60–5.48 (m, 1H), 5.02 (t, J = 3.1 Hz, 1H), 4.51–4.39 (m, 1H), 4.26 (dd, J = 12.2, 7.9 Hz, 1H), 4.01 (dd, J = 12.2, 4.5 Hz, 1H), 1.99–1.81 (m, 9H), 0.08 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ = 174.8, 170.9, 170.03, 169.8, 162.1, 115.6, 99.7, 98.6, 76.4, 66.3, 61.7, 61.7, 21.4, 21.3, 21.3, 0.0. IR (ν , cm^{-1}) = 2864, 2028, 1914, 1685, 1566, 1324, 1261, 1175, 1151, 987, 817. HRMS (ESI-TOF) calc. $[\text{C}_{18}\text{H}_{24}\text{O}_8\text{SiNa}^+]$ 419.1133, found 419.1135.

Product **3n** was obtained as a yellow oil (53 mg, 0.14 mmol, 70%). ^1H NMR (300 MHz, CDCl_3): δ = 7.95 (s, 1H), 5.73 (dd, J = 3.1, 1.7 Hz, 1H), 5.19 (t, J = 3.1 Hz, 1H), 4.69–4.58 (m, 1H), 4.45 (dd, J = 12.1, 7.8 Hz, 1H), 4.17 (dd, J = 12.1, 4.5 Hz, 1H), 2.39 (t, J = 7.0 Hz, 2H), 2.18–1.96 (m, 9H), 1.69–1.36 (m, 4H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ = 174.7, 170.2, 169.3, 169.1, 160.7, 114.9, 94.1, 77.0, 75.5, 65.6, 61.1, 60.9, 29.7, 22.0, 20.7, 20.6, 20.6, 18.6, 13.4. IR (ν , cm^{-1}) = 2838, 2862, 2147, 1685, 1566, 1365, 1324, 1175, 1149, 991, 864. HRMS (ESI-TOF) calc. $[\text{C}_{19}\text{H}_{24}\text{O}_8\text{Na}^+]$ 403.1363, found 403.1361.

Product **3o** was obtained as a yellow oil (45 mg, 0.12 mmol, 62%). ^1H NMR (300 MHz, CDCl_3): δ = 7.76 (s, 1H), 5.53 (dd, J = 3.1, 1.7 Hz, 1H), 4.99 (t, J = 3.1 Hz, 1H), 4.49–4.37 (m, 1H), 4.25 (dd, J = 12.1, 7.8 Hz, 1H), 3.97 (dd, J = 12.1, 4.5 Hz, 1H), 2.17 (t, J = 7.1 Hz, 2H), 1.94–1.81 (m, 9H), 1.44 (h, J = 7.2 Hz, 2H), 0.84 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ = 174.7, 170.2, 169.3, 169.1, 160.7, 114.9, 93.9, 77.8, 75.5, 65.6, 61.1, 60.9, 21.2, 20.8, 20.7, 20.6, 20.6, 13.5. IR (ν , cm^{-1}) = 2916, 2879, 1680, 1560, 1141989, 836, 724. HRMS (ESI-TOF) calc. $[\text{C}_{18}\text{H}_{22}\text{O}_8\text{Na}^+]$ 389.1207, found 403.1361.

Product **3p** was obtained as a yellow oil (67 mg, 0.15 mmol, 78%). ^1H NMR (300 MHz, CDCl_3): δ = 7.61 (s, 1H), 7.32–7.11 (m, 5H), 5.65–5.52 (m, 1H), 5.16–5.04 (m, 1H), 4.57–4.49 (m, 1H), 4.36 (dd, J = 11.8, 7.8 Hz, 1H), 4.07 (dd, J = 12.0, 4.5 Hz, 1H), 2.84 (t, J = 7.3 Hz, 2H), 2.63 (t, 2H), 2.05–1.94 (m, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ = 174.5, 170.2, 169.3, 169.1, 161.1, 139.5, 128.5, 128.3, 126.7, 114.9, 92.7, 78.3, 75.4, 65.6, 60.9, 60.8, 33.8, 21.0, 20.7, 20.6, 20.6. IR (ν , cm^{-1}) = 2926, 2840, 2149, 1685,



1566, 1324, 1261, 1175, 1151, 1017, 991, 678. HRMS (ESI-TOF) calc. $[\text{C}_{23}\text{H}_{24}\text{O}_8\text{Na}^+]$ 451.1363, found 451.1361.

Product **3q** was obtained as a yellow oil (73 mg, 0.17 mmol, 86%). ^1H NMR (300 MHz, CDCl_3): δ = 7.91 (s, 1H), 5.68 (d, J = 2.3 Hz, 1H), 5.12 (t, J = 3.0 Hz, 1H), 4.62–4.52 (m, 1H), 4.37 (dd, J = 12.2, 7.8 Hz, 1H), 4.12 (dd, J = 12.1, 4.4 Hz, 1H), 2.68 (s, 1H), 2.09–1.98 (m, 9H), 1.93–1.84 (m, 2H), 1.72–1.43 (m, 8H). ^{13}C NMR (75 MHz, CDCl_3): δ = 174.3, 170.2, 169.5, 169.1, 161.0, 114.7, 95.5, 79.9, 75.6, 65.5, 61.1, 60.9, 39.1, 39.1, 24.9, 22.9, 20.7, 20.6, 20.6. IR (ν , cm^{-1}) = 3363, 2840, 2766, 2136, 1691, 1568, 1326, 1182, 1156, 996. HRMS (ESI-TOF) calc. $[\text{C}_{21}\text{H}_{26}\text{O}_9\text{Na}^+]$ 445.1469, found 445.1467.

Product **3r** was obtained as a yellow oil (101 mg, 0.14 mmol, 70%). ^1H NMR (300 MHz, CDCl_3): δ = 8.07 (s, 2H), 7.61 (d, J = 2.6 Hz, 4H), 5.95–5.73 (m, 2H), 5.29–5.10 (m, 2H), 4.77–4.58 (m, 2H), 4.58–4.46 (m, 2H), 4.23 (dd, J = 9.7, 5.6 Hz, 2H), 2.25–1.97 (m, 18H). ^{13}C NMR (75 MHz, CDCl_3): δ = 174.0, 170.2, 169.3, 169.1, 161.2, 132.8, 122.0, 114.9, 89.0, 87.0, 75.8, 65.5, 61.0, 60.8, 20.7, 20.6, 20.6. IR (ν , cm^{-1}) = 2870, 2129, 1685, 1564, 1324, 1264, 1177, 1151, 989. HRMS (ESI-TOF) calc. $[\text{C}_{36}\text{H}_{34}\text{O}_{16}\text{Na}^+]$ 745.1739, found 745.1735.

Product **5a** was obtained as a yellow oil (61 mg, 0.13 mmol, 67%). ^1H NMR (300 MHz, CDCl_3): δ = 9.15 (s, 1H), 8.02 (s, 1H), 7.46–7.34 (m, 5H), 5.96–5.85 (m, 1H), 5.55 (d, J = 1.4 Hz, 1H), 5.30 (s, 2H), 4.64 (d, J = 5.3 Hz, 1H), 4.54–4.44 (m, 1H), 4.23 (dd, J = 12.2, 4.7 Hz, 1H), 2.19–2.05 (m, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ = 180.3, 169.3, 168.4, 168.2, 161.0, 132.6, 128.3, 128.1, 127.3, 126.5, 126.5, 111.5, 73.6, 64.9, 60.5, 60.1, 53.4, 19.7, 19.6, 19.6. IR (ν , cm^{-1}) = 3261, 2866, 2836, 1680, 1560, 1475, 1324, 1179, 1149, 989, 706. HRMS (ESI-TOF) calc. $[\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_8\text{Na}^+]$ 480.1377, found 480.1375.

Product **5b** was obtained as a yellow oil (69 mg, 0.14 mmol, 72%). ^1H NMR (300 MHz, CDCl_3): δ = 9.15 (s, 1H), 8.67 (s, 1H), 8.45 (s, 1H), 7.87 (s, 1H), 7.55–7.42 (m, 2H), 7.30 (d, J = 2.8 Hz, 1H), 6.68–6.52 (m, 1H), 5.97–5.84 (m, 1H), 5.23 (t, J = 2.9 Hz, 1H), 4.65–4.56 (m, 1H), 4.46 (m, 1H), 4.21 (m, 1H), 2.06–1.97 (m, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ = 181.5, 170.3, 169.5, 169.3, 162.0, 148.1, 135.90, 128.1, 126.7, 126.2, 126.2, 115.5, 113.5, 112.6, 112.1, 103.5, 74.7, 66.0, 61.6, 61.2, 20.8, 20.7, 20.6. IR (ν , cm^{-1}) = 2834, 2862, 2779, 1682, 1560, 1475, 1460, 1324, 1162, 1011, 989, 700. HRMS (ESI-TOF) calc. $[\text{C}_{23}\text{H}_{22}\text{N}_4\text{O}_8\text{Na}^+]$ 505.1330, found 505.1329.

Product **5c** was obtained as a yellow oil (70 mg, 0.14 mmol, 70%). ^1H NMR (300 MHz, CDCl_3): δ = 9.13 (s, 1H), 9.07 (s, 1H), 8.58 (s, 1H), 8.37 (t, 1H), 8.24 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.9 Hz, 1H), 5.93–5.89 (m, 1H), 5.24–5.22 (m, 1H), 4.64–4.57 (m, 1H), 4.47 (dd, J = 12.0, 7.8 Hz, 1H), 4.20 (dd, J = 12.0, 4.5 Hz, 1H), 2.08–1.94 (m, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ = 181.1, 170.3, 169.4, 169.2, 162.2, 162.1, 156.2, 148.6, 135.2, 126.0, 124.9, 120.0, 119.3, 115.1, 112.7, 74.8, 65.9, 61.5, 61.1, 20.8, 20.7, 20.6. IR (ν , cm^{-1}) = 2985, 2864, 2037, 1687, 1562, 1186, 1154, 994, 838, 855. HRMS (ESI-TOF) calc. $[\text{C}_{22}\text{H}_{20}\text{N}_4\text{O}_8\text{SNa}^+]$ 523.0894, found 523.0890.

Product **5d** was obtained as a yellow oil (89 mg, 0.13 mmol, 65%). ^1H NMR (300 MHz, CDCl_3): δ = 9.09 (s, 1H), 8.48 (s, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.49 (s, 1H), 7.40–7.21 (m, 11H), 6.28 (d, J = 3.5 Hz, 1H), 5.98–5.85 (m, 1H), 5.29 (s, 2H), 5.18 (s, 2H),

4.68–4.54 (m, 1H), 4.50–4.41 (m, 1H), 4.18 (dd, J = 12.1, 4.5 Hz, 1H), 2.10–1.92 (m, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ = 201.9, 180.2, 170.4, 169.8, 169.1, 164.9, 163.5, 159.3, 139.6, 135.6, 135.5, 133.7, 128.7, 128.5, 128.2, 128.2, 128.2, 127.2, 125.6, 121.5, 113.7, 112.7, 111.6, 105.9, 71.8, 71.1, 67.1, 65.3, 61.1, 60.5, 20.8, 20.6, 20.5. IR (ν , cm^{-1}) = 2967, 2931, 1687, 1559, 1195, 1169, 1046, 998. HRMS (ESI-TOF) calc. $[\text{C}_{36}\text{H}_{33}\text{N}_3\text{O}_{11}\text{Na}^+]$ 706.2007, found 706.2004.

Product **5e** was obtained as a yellow oil (57 mg, 0.12 mmol, 58%). ^1H NMR (300 MHz, CDCl_3): δ = 9.07 (s, 1H), 8.69–8.59 (m, 2H), 8.30 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 8.5 Hz, 1H), 7.74 (t, J = 8.1 Hz, 1H), 6.28 (d, J = 3.5 Hz, 1H), 5.92–5.83 (m, 1H), 4.66–4.57 (m, 1H), 4.52–4.41 (m, 1H), 4.19 (dd, J = 12.1, 4.5 Hz, 1H), 2.09–1.98 (m, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ = 180.1, 170.4, 169.8, 169.1, 163.6, 137.0, 131.2, 126.0, 125.7, 123.9, 115.8, 115.8, 113.7, 112.7, 74.9, 71.8, 61.5, 61.1, 20.7, 20.7, 20.6. IR (ν , cm^{-1}) = 2868, 1687, 1562, 1486, 1309, 1188, 1171, 994, 717. HRMS (ESI-TOF) calc. $[\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_{10}\text{Na}^+]$ 511.1072, found 511.1071.

Product **5f** was obtained as a yellow oil (81 mg, 0.17 mmol, 86%). ^1H NMR (300 MHz, CDCl_3): δ = 9.11 (s, 1H), 8.41 (s, 1H), 7.58 (d, J = 9.0 Hz, 2H), 6.98 (d, J = 8.9 Hz, 2H), 5.89 (t, 2H), 5.21 (t, J = 3.1 Hz, 1H), 4.64–4.55 (m, 1H), 4.44 (dd, J = 12.1, 7.7 Hz, 1H), 4.19 (dd, J = 12.0, 4.8 Hz, 3H), 2.08–1.94 (m, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ = 181.3, 170.3, 169.4, 169.2, 162.0, 160.3, 129.6, 127.8, 125.7, 122.3, 115.0, 112.6, 74.7, 65.9, 61.6, 61.1, 55.6, 20.7, 20.7, 20.6. IR (ν , cm^{-1}) = 2902, 2875, 1687, 1564, 1471, 1326, 1262, 1184, 1153, 998, 838. HRMS (ESI-TOF) calc. $[\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_9\text{Na}^+]$ 496.1327, found 496.1329.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank the São Paulo Research Foundation, FAPESP for financial support (grant 2017/24821-4) and fellowships to MPD (2016/24396-9), CHAE (2017/26673-2), IMO (2016/04289-3), JSR (2016/02392-1). They are also thankful for the financial support provided by The National Council for Scientific and Technological Development (CNPq) for the fellowship to HAS (306119/2014-5).

Notes and references

- (a) M. C. Bagley, J. W. Dale and J. Bower, *Synlett*, 2001, 7, 1149–1151; (b) C. G. Lee, K. Y. Lee, S. Lee and J. N. Kim, *Tetrahedron*, 2005, **61**, 8705–8710; (c) H. Liu, H. Jiang, M. Zhang, W. Yao, Q. Zhu and Z. Tang, *Tetrahedron Lett.*, 2008, **49**, 3805–3809; (d) J. D. Kirkham, S. J. Edeson, S. Strokes and J. P. Harrity, *Org. Lett.*, 2012, **14**, 5354–5357; (e) M. S. Mohamed Ahmed, K. Kobayashi and A. Mori, *Org. Lett.*, 2005, **7**, 4487–4489.
- (a) A. S. Karpov, E. Merkul, F. Rominger and T. J. Müller, *Angew. Chem., Int. Ed.*, 2005, **44**, 6951–6956; (b) K. T. Neumann, S. R. Laursen, A. T. Lindhardt, B. Bang-Andersen and T. Skrydstrup, *Org. Lett.*, 2014, **16**, 2216–



- 2219; (c) A. Linda, N. Patrik, W. Matyas, R. O. Luke and L. Mats, *J. Org. Chem.*, 2015, **80**, 1464–1471; (d) I. Muneaki and K. Yoshinori, *Eur. J. Org. Chem.*, 2007, 5180–5182; (e) Y. Tu, Z. Zhang, T. Wang, J. Ke and J. Zhao, *Org. Lett.*, 2017, **19**, 3466–3469; (f) J. D. Kirkham, S. J. Edeson, S. Stokes and J. P. A. Harrity, *Org. Lett.*, 2012, **14**, 5354–5357; (g) L. F. Tietze, R. R. Singidi, K. M. Gericke, H. Böckemeier and H. Laatsch, *Eur. J. Org. Chem.*, 2007, 5875–5878.
- 3 (a) N. G. Kundu, J. S. Mahanty, C. Chowdhury, S. K. Dasgupta, B. Das, C. P. Spears, J. Balzarini and E. De Clercq, *Eur. J. Med. Chem.*, 1999, **34**, 389–398; (b) C. A. Quesnelle, P. Gill, M. Dodier, D. S. Laurent, M. Serrano-Wu, A. Marinier, A. Martel, C. E. Mazzucco, T. M. Stickle, J. F. Barret, D. M. Vyas and B. N. Balasubramanian, *Bioorg. Med. Chem. Lett.*, 2003, **13**, 519–524; (c) D. V. Kuklev, A. J. Domb and V. M. Dembitsky, *Phytomedicine*, 2013, **20**, 1145–1159; (d) G. Prashant, J. T. Neelam and M. B. Bhalchandra, *ACS Omega*, 2019, **4**, 1560–1574.
- 4 C. Taylor and Y. Bolshan, *Org. Lett.*, 2014, **16**, 488–491.
- 5 W. Ai, Y. Wu, H. Tang, X. Yang, Y. Yang, Y. Li and B. Zhou, *Chem. Commun.*, 2015, **51**, 7871–7874.
- 6 Y. Maeda, N. Kakiuchi, S. Matsumura, T. Nishimura, T. Kawamura and S. Uemura, *J. Org. Chem.*, 2002, **67**, 6718–6724.
- 7 (a) K. T. Neumann, S. R. Laursen, A. T. Lindhardt, B. Bang-Andersen and T. Skrydstrup, *Org. Lett.*, 2014, **16**, 2216–2219; (b) X.-F. Wu, H. Neumann and M. Beller, *Chem.–Eur. J.*, 2010, **16**, 12104–12107; (c) A. Arcadi, S. Cacchi, F. Marinelli, P. Pace and G. Sanzi, *Synlett*, 1995, 823–824; (d) L. Delaude, A. M. Masdeu and H. Alper, *Synthesis*, 1994, **11**, 1149–1151.
- 8 (a) M. P. Darbem, K. S. Kanno, I. M. de Oliveira, C. H. A. Esteves, D. C. Pimenta and H. A. Stefani, *New J. Chem.*, 2019, **43**, 696–699; (b) A. Shamim, S. N. S. Vasconcelos, I. M. Oliveira, J. S. Reis, D. C. Pimenta, J. Zukerman-Schpector and H. A. Stefani, *Synthesis*, 2017, **49**, 5183–5196; (c) A. Shamim, F. B. Souza, S. N. S. Vasconcelos and H. A. Stefani, *Tetrahedron Lett.*, 2017, **58**, 884–888; (d) A. Shamim, C. S. Barbeiro, B. Ali and H. A. Stefani, *ChemistrySelect*, 2016, **1**, 5653–5659; (e) A. Shamim, S. N. S. Vasconcelos, B. Ali, L. S. Madureira, J. Zukerman-Schpector and H. A. Stefani, *Tetrahedron Lett.*, 2015, **56**, 5836–5842; (f) A. Shamim, F. B. Souza, G. H. G. Trossini, F. M. Gatti and H. A. Stefani, *Mol. Diversity*, 2015, **19**, 423–434; (g) A. S. Vieira, P. F. Fiorante, T. L. S. Hough, F. P. Ferreira, D. S. Ludtke and H. A. Stefani, *Org. Lett.*, 2008, **10**, 5215–5218.
- 9 For reviews see: (a) A. L. Garner, *Chem. Commun.*, 2018, **54**, 6531–6539; (b) V. Tiwari, B. B. Mishra, K. B. Mishra, N. Mishra, A. S. Singh and X. Chen, *Chem. Rev.*, 2016, **116**, 3086–3240; (c) P. Thirumurugan, D. Matosiuk and K. Jozwiak, *Chem. Rev.*, 2013, **113**, 4905–4979; (d) J. E. Moses and A. D. Moorhouse, *Chem. Soc. Rev.*, 2007, **36**, 1249–1262.
- 10 (a) A. Palasz and D. Ciez, *Eur. J. Med. Chem.*, 2015, **97**, 582–611; (b) A. Ajay, S. Sharma, M. P. Gupt, V. Bajpai, B. Kumar, M. P. Kaushik, R. Konwar, R. S. Ampapathi and R. P. Tripathi, *Org. Lett.*, 2012, **14**, 4306–4309; (c) J. Thomas, V. Goyvaerts, S. Liekens and W. Dehaen, *Chem.–Eur. J.*, 2016, **22**, 9966–9970.
- 11 S. Dharuman and Y. D. Vankar, *Org. Lett.*, 2014, **16**, 1172–1175.
- 12 N. Hadei, E. A. B. Kantchev, C. J. O'Brien and M. G. Organ, *Org. Lett.*, 2005, **7**, 3805–3807.
- 13 For reviews, see: (a) G. Fumagalli, S. Stanton and J. F. Bower, *Chem. Rev.*, 2017, **117**, 9404–9432; (b) M. A. Cavitt, L. H. Phun and S. France, *Chem. Soc. Rev.*, 2014, **43**, 804–818; (c) Z.-B. Zhu, Y. Wei and M. Shi, *Chem. Soc. Rev.*, 2011, **40**, 5534–5563; (d) M. Rubin, M. Rubina and V. Gevorgyan, *Chem. Rev.*, 2007, **107**, 3117–3179.
- 14 (a) H. A. Stefani, N. C. S. Silva, F. Manarin, D. S. Lüdtkke, J. Zukerman-Schpector, L. S. Madureira and E. R. T. Tiekink, *Tetrahedron Lett.*, 2012, **53**, 1742–1747; (b) H. A. Stefani, S. N. S. Vasconcelos, F. Manarin, D. M. Leal, F. B. Souza, L. S. Madureira, J. Zukerman-Schpector, M. N. Eberlin, M. N. Godoi and R. S. Galaverna, *Eur. J. Org. Chem.*, 2013, 3780–3785.

