DOI: 10.1002/adsc.201100813

One-Pot Three-Component Click Reaction of Cyclic Sulfates and Cyclic Sulfamidates

Alicia Megia-Fernandez,[a] Mariano Ortega-Muñoz,[a] Fernando Hernandez-Mateo,[a] and Francisco Santoyo-Gonzalez[a,*]

[a] Química Orgánica, Instituto de Biotecnología, Facultad de Ciencias, Universidad de Granada, E-18071 Granada, Spain
Fax: (+34)-95-824-3186; phone: (+34)-95-824-808; e-mail: fsantoyo@ugr.es

Received: October 19, 2011; Revised: March 8, 2012; Published online: June 5, 2012

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201100813.

Abstract: A one-pot, three-component methodology involving tandem azidation and click copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) of cyclic sulfates or cyclic sulfamidates in the presence of sodium azides and alkynes is reported. The developed protocol takes also advantage of the concomitant use of microwave (MW) irradiation and heterogeneous catalysis. The protocol allows the fast and efficient preparation of (alkyl sulfate)- and (alkyl sulfamidate)-1*H*-1,2,3-triazoles in a simple manner.

Keywords: click chemistry; cyclic sulfamidates; cyclic sulfates; cycloadditions; multi-component reactions

Introduction

Multi-component reactions[1] (MCRs), where three or more starting materials react to afford a product that essentially contains all or most of the atoms of the reagents, have achieved great importance due to their broad scope since they are highly convergent processes that increase the molecular complexity in just one process. In this context the orthogonality of "click chemistry"[2] is an attractive feature that turns the Cu(I)-catalyzed version of the azide-alkyne cycloaddition (CuAAC)[3] – the most relevant example of the "click-chemistry" concept – into a suitable reaction for its implementation in a one-pot, multi-component process. The appealing characteristics of CuAAC (modularity, regioselectivity, mild reaction conditions, wide substrate scope, high yield and stability of the resulting triazole ring) have brought about the success of this powerful methodology in the last decade, with a growing number of applications found in many areas of modern chemistry including drug discovery, materials science or bioconjugation.[4]

Many efforts have been made over the last years in order to develop CuAAC-based MCRs. One of the major aims pursued in these approaches is to avoid the manipulation and isolation of organic azides since some of them, especially those having low molecular weights and those containing several azide functionalities, could be unstable and difficult to handle.[5] In this regard, Maksikova et al.[6] reported the first uncatalyzed one-pot synthesis of 1,2,3-triazoles from alkyl halides, alkynes and sodium azide. However, high temperatures and long times are required in this protocol leading to a mixture of the 1,4 and 1,5 regioisomers in low yields. After the discovery of the Cu(I) catalytic effect in azido-alkyne cycloadditions,[3a] this three-component methodology has turned out to be efficient and numerous examples have emerged in which organic azides are generated from different precursors and then trapped *in situ* by alkynes to obtain exclusively the corresponding 1,4-disubstituted 1,2,3-triazole. Aromatic and aliphatic halides are by far the most preferred azide precurors,[7] although other good leaving groups, such as the tosyl group, have also been employed.[8] Other alternatives for these multi-component click reactions include the use of boronic acids,[9] aromatic and aliphatic amines,[7q,10] epoxides,[11] aziridines,[12] diazonium salts,[7q] diaryliodonium salts[13] or 1,2-diaza-1,3-dienes[14] as azide precursors.

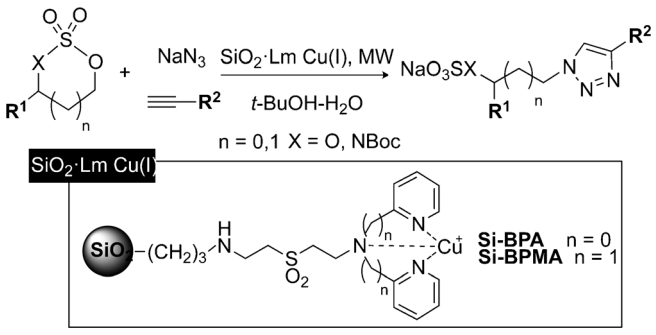
On the other hand, cyclic sulfates[15] and cyclic sulfamidates[15d,16] are versatile electrophilic synthons that have emerged as important intermediates in organic synthesis. They show a particularly enhanced reactivity toward nucleophilic reagents and their applications have gained importance since the development of efficient methods for their preparation. In particular, cyclic sulfates and sulfamidates are adequate precursors for accessing organic azides.[17,18] Examples in which this approach has been used for the

ulterior use of the isolated azides in click reactions have been described.[17h–j,18e] In addition, the ring opening of cyclic sulfates and sulfamidates possesses some attributes that perfectly fit the criteria required for click chemistry.[2] In spite of the fact that cyclic sulfates are usually regarded as synthetic equivalents of epoxides,[19] their implementation in CuAAC-based MCRs by combination with sodium azide and alkynes has not been reported. However, this approach is conceptually attractive and can be postulated as a powerful, safe and direct methodology for the synthesis of (alkylsulfate)-1*H*-1,2,3-triazoles by a tandem click–click process. The importance of these functionalized triazoles is illustrated in a recent report[20] that describes the synthesis of a Cu(I) tris(triazolylmethyl)-amine-based ligand containing a 1-ethyl sulfate fragment and its application as an excellent biocompatible water-soluble click catalyst that promotes the rapid cycloaddition reaction in living systems without apparent toxicity. In addition, sulfate monoester 1,2,3-triazoles can be regarded as valuable compounds as they can experience other interesting transformations through hydrolysis or nucleophilic substitution of the sulfate group.[15]

Herein, we describe a new and feasible procedure to obtain (alkyl sulfate)- and (alkyl sulfamidate)-1*H*-1,2,3-triazoles in a one-pot, three-component reaction through the *in situ* generation of organic azides by the opening of cyclic sulfates or sulfamidates with sodium azide and tandem CuAAC with an alkyne present in the reaction media (Scheme 1).

Results and Discussion

The utility of cyclic sulfates as azide precursors in CuAAC-based MCRs was first evaluated in a model reaction. 1,3-Propanediol cyclic sulfate (**1a**) and phenylacetylene (**3a**) were the substrates of choice (Table 1, entry 1). Equimolecular amounts of these reagents and sodium azide were merely dissolved in aqueous *t*-BuOH. With the aim to simplify the manipulation and the isolation procedure, a heterogeneous



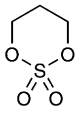
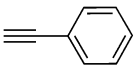
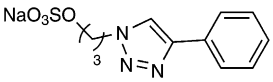
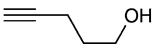
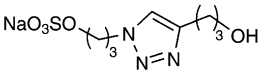
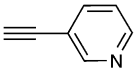
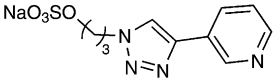
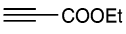
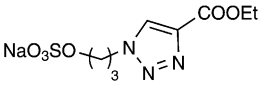
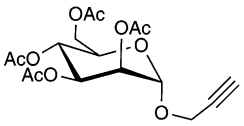
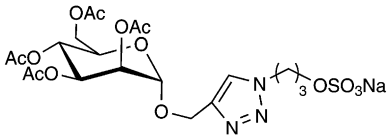
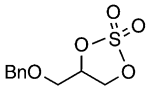
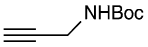
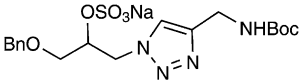
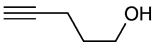
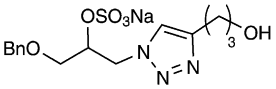
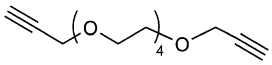
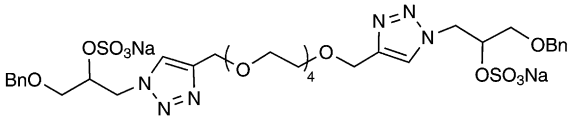
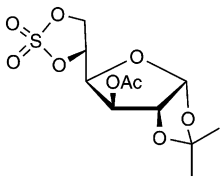
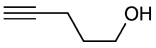
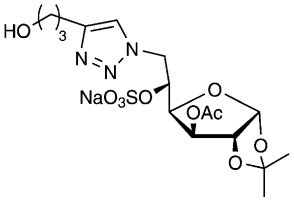
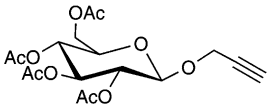
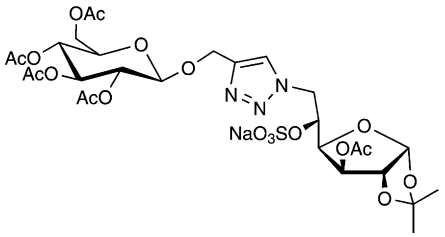
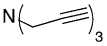
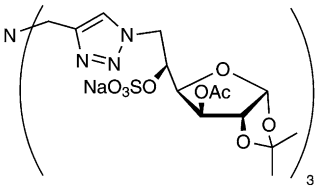
Scheme 1. CuAAC-based MCRs of cyclic sulfates or cyclic sulfamidates with alkynes and sodium azide.

click catalyst, namely Si-BPMA·Cu^+ or Si-BPA·Cu^+ (Scheme 1),[21] was used as source of Cu(I). These catalysts proved to be very robust and efficient heterogeneous click catalysts. They take advantage of the Cu(I) chelating capabilities of nitrogen-based ligands covalently immobilized on silica.[21] They were recently found to be very well suited for multiple CuAAC involving cyclodextrins.[22] The reaction was performed under MW irradiation. The utility of the MW assistance to improve and reduce the reaction time of cycloaddition reactions is well known.[23] In particular, the use of this technique in three-component reactions between alkyl halides, sodium azide and alkynes[7b] and azidation reactions has been reported.[24] As expected, the reaction was completed in a short reaction time (15 min). The corresponding 1,2,3-triazole **4a** was isolated as a pure compound in high yield (85%) by simple filtration of the catalyst and evaporation of the solvent without further purification. NMR spectroscopy confirmed that triazole was produced in a completely regioselective manner just like the ring-opening of cyclic sulfate, affording exclusively 1,4-disubstituted 1,2,3-triazoles after the azide attack at the least-hindered carbon of cyclic sulfate.

To investigate the scope of this one-pot, three-component methodology, **1a** as well as the 1,2 cyclic sulfates derived from glycerol **1b** and α-D-glucofuranose **1c** were reacted with different alkynes using identical reaction conditions and experimental procedure (Table 1). The alkynes were selected to offer a variety of different functional (primary aliphatic alcohols and esters) and protective groups (acetyl, benzyl ether, *tert*-butoxycarbonyl (Boc) or isopropylidene ketal). In all cases, the expected products (**4b–k**) were obtained in high to excellent yields in very short reaction times (10–20 min) (Table 1, entries 2–11). These results highlight the compatibility of this cascade process with a wide range of functionalities. Furthermore, the methodology allows the easy synthesis of glycoconjugates (entries 5, 9–11) and also the access to multivalent systems like compounds **4h** and **4k** (entries 8 and 11) when starting from the corresponding multialkyne derivatives of tetraethylene glycol or tripropargylamine, respectively, by the simultaneous formation of up to nine C–N bonds in a fully selective and efficient manner

Considering the similar reactivity between cyclic sulfates and sulfamidates we anticipate that these latter compounds should also undergo a tandem nucleophilic ring-opening and click reaction when combined with sodium azide and an alkyne. In fact, the ring opening of cyclic sulfamidates with sodium azide followed by one-pot propargylation and cycloaddition has been recently reported[18e] for the preparation of triazole-fused heterocycles. However, no antecedents were found involving cyclic sulfamidates in an MCR. In this extension of our study, the cyclic sulfamidates **2a** and **2b**

Table 1. One-pot three-component click reaction of cyclic sulfates.

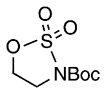
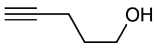
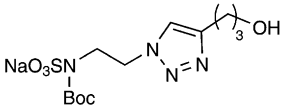
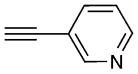
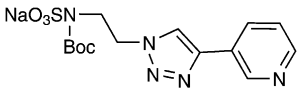
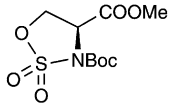
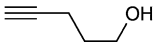
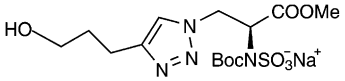
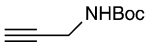
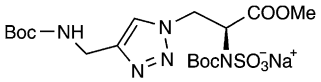
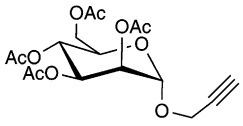
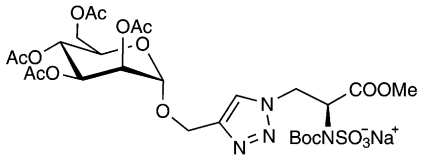
Entry	Cyclic sulfate	Alkyne	Product	Yield [%]
1	**1a** 	**3a** 	**4a** 	85
2		**3b** 	**4b** 	96
3		**3c** 	**4c** 	90
4		**3d** 	**4d** 	90
5		**3e** 	**4e** 	87
6	**1b** 	**3f** 	**4f** 	97
7		**3b** 	**4g** 	100
8		**3g** 	**4h** 	95
9	**1c** 	**3b** 	**4i** 	94
10		**3h** 	**4j** 	91
11		**3i** 	**4k** 	85

were prepared from aminoethanol and Boc-L-serine methyl ester, respectively. Both cyclic sulfamidates reacted under similar conditions as those described for cyclic sulfates in the presence of sodium azide and different alkynes giving an easy access to the (alkyl sulfamidate)-1*H*-1,2,3-triazoles **4l–4p** (Table 2).

Conclusion

In summary, a one-pot three-component methodology involving azidation of cyclic sulfates or sulfamidates by sodium azide in the presence of alkynes has been developed broadening the state-of-the-art of CuAAC-

Table 2. One-pot three-component click reaction of cyclic sulfamidates.

Entry	Cyclic sulfamidate	Alkyne	Product	Yield [%]
1	**2a** 	**3b** 	**4l** 	93
2		**3c** 	**4m** 	89
3	**2b** 	**3b** 	**4n** 	95
4		**3f** 	**4o** 	93
5		**3e** 	**4p** 	92

based MCRs allowing the synthesis of 1,4-disubstituted 1,2,3-triazoles. The reported protocol benefits from the simultaneous use of MW irradiation and heterogeneous catalysis that allow fast reaction times, avoid the need of any reducing agent or other additives commonly used in CuAAC click chemistry and any purification step. Other noteworthy features of this method are its atom economy, efficiency, absence of by-products, safety, user friendliness and simplicity that make this process attractive for the synthesis of screening libraries.

Experimental Section

General Remarks

Commercially available reagents, compounds **1a**, **3a–3d**, **3i** and solvents were used as purchased without further purification. Starting materials as cyclic sulfates **1b**,[25] **1c**,[26] cyclic sulfamidates **2a**,[27] **2b**[28] and alkynes **3e**,[29] **3f**,[30] **3g**[31] and **3h**[32] were prepared according to reported procedures in literature. TLCs were performed on Merck Silica Gel 60 F254 aluminium sheets. Reagents used for developing plates include potassium permanganate (1% w/v), ninhydrin (0.3% w/v) in ethanol and UV light when applicable. Flash column chromatography was performed on silica gel Merck (230–400 mesh, ASTM). Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. Optical rotations were recorded on a Perkin–Elmer 141 polarimeter at room temperature. IR spectra were recorded on a Satellite Mattson FTIR. ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Varian Direct Drive (300, 400 and 500 MHz) spectrometer. Chemical shifts are given in ppm and referenced to internal $CDCl_3$. *J* values are given in Hz. Electrospray ionization (ESI) mass spectra were recorded on an LCT Premier Spectrometer.

Typical Experimental Procedure

Cyclic sulfate or sulfamidate (1.0 mmol), sodium azide (1.0 mmol), the alkyne derivative (1.0 mmol) and catalyst Si-BPA·Cu^+ or Si-BPMA·Cu^+ (30 mg) were added to 4:1 *t*-BuOH-H_2O (10 mL). The reaction mixture was irradiated by MW at 60 °C. Progress of the reaction was followed by TLC until complete disappearance of the starting materials, normally less that 15 min. Filtration of the catalyst and evaporation of the solvent under vacuum afforded the pure 1,2,3-triazoles in the yields indicated in Table 1 and Table 2, without any chromatographic purification.

Analytical and Spectroscopic Data of the 1,2,3-Triazoles

Sodium 3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)propyl sulfate (4a): Compound **4a** was obtained as a syrup; yield: 259 mg (85%). IR (film): ν_{max} = 2924, 2853, 1655, 1461, 1250, 1206, 1074, 841 cm^{-1}; ^{1}H NMR (CD_3OD, 400 MHz): δ = 8.37 (s, 1H), 7.81 (d, 2H, *J* = 7.4 Hz), 7.42 (t, 2H, *J* = 7.6 Hz), 7.33 (t, 1H, *J* = 7.4 Hz), 4.60 (t, 2H, *J* = 6.9 Hz), 4.06 (t, 2H, *J* = 5.9 Hz), 2.31 (p, 2H, *J* = 6.4 Hz); ^{13}C NMR (CD_3OD, 100 MHz): δ = 148.9, 131.9, 130.1, 129.4, 126.8, 123.1, 65.6, 48.3, 31.2; HRMS (ESI): *m*/*z* = 284.0701, calcd. for $C_{11}H_{14}N_3O_4S$ $[M-Na+2H]^+$: 284.0705; HPLC purity: 92.85%.

Sodium 3-[4-(3-hydroxypropyl)-1*H*-1,2,3-triazol-1-yl]propyl sulfate (4b): Compound **4b** was obtained as a syrup; yield: 276 mg (96%). IR (film): ν_{max} = 3446, 2952, 1655, 1438, 1224, 1022, 946, 825 cm^{-1}; ^{1}H NMR (CD_3OD, 400 MHz): δ = 7.80 (s, 1H), 4.50 (t, 2H, *J* = 6.9 Hz), 4.00 (t, 2H, *J* = 5.9 Hz), 3.58 (t, 2H, *J* = 6.4 Hz), 2.76 (t, 2H, *J* = 7.6 Hz), 2.24 (p, 2H, *J* = 6.1 Hz), 1.87 (p, 2H, *J* = 6.5 Hz); ^{13}C NMR (CD_3OD,

100 MHz): δ = 148.8, 124.0, 65.6, 62.1, 48.0, 33.4, 31.3, 22.8; HR-MS (ESI): m/z = 266.0799, calcd. for $C_8H_{16}N_3O_5S$ $[M-Na+2H]^+$: 266.0811; HPLC purity: 100%.

Sodium 3-[4-(pyridin-3-yl)-1*H*-1,2,3-triazol-1-yl]propyl sulfate (4c): Compound **4c** was obtained as a syrup; yield: 275 mg (90%). IR (film): ν_{max} = 3269, 2961, 2858, 1694, 1646, 1535, 1452, 1065, 584 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz): δ = 9.02 (s, 1H), 8.53–8.50 (m, 2H), 8.26 (d, 1H, J = 7.9 Hz), 7.51 (dd, 1H, J = 7.5, 5.1 Hz), 4.63 (t, 2H, J = 6.8 Hz), 4.05 (t, 2H, J = 5.8 Hz), 2.32 (m, 2H); ^{13}C NMR (CD_3OD, 100 MHz): δ = 149.6, 147.4, 145.3, 135.1, 128.9, 125.7, 124.0, 65.5, 48.4, 31.2; HR-MS (ESI): m/z = 285.0645, calcd. for $C_{10}H_{13}N_4O_4S$ $[M-Na+2H]^+$: 285.0658; HPLC purity: 100%.

Sodium 3-[4-(ethoxycarbonyl)-1*H*-1,2,3-triazol-1-yl]propyl sulfate (4d): Compound **4d** was obtained as a syrup; yield: 271 mg (90%). IR (film): ν_{max} = 3260, 2966, 1716, 1649, 1539, 1221, 1024, 574 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz): δ = 8.59 (s, 1H), 4.62 (t, 2H, J = 6.9 Hz), 4.38 (q, 2H, J = 7.1 Hz), 4.03 (t, 2H, J = 5.9 Hz), 2.30 (m, 2H), 1.36 (t, 3H, J = 7.1 Hz); ^{13}C NMR (CD_3OD, 100 MHz): δ = 162.4, 140.6, 130.2, 65.5, 62.5, 43.6, 31.0, 14.7; HR-MS (ESI): m/z = 280.0600, calcd. for $C_8H_{14}N_3O_6S$ $[M-Na+2H]^+$: 280.0603; HPLC purity: 97.42%.

Sodium 3-[4-(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]propyl sulfate (4e): Compound **4e** was obtained as a syrup; 512 mg (87%); $[\alpha]_D$: +33.2° (*c* 1, MeOH). IR (film): ν_{max} = 3142, 2923, 1747, 1436, 1370, 1226, 1134, 1048, 942 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz): δ = 8.14 (s, 1H), 5.29–5.22 (m, 3H), 4.97 (s, 1H), 4.82 (m, 1H), 4.71 (d, 1H, J = 12.0 Hz), 4.57 (t, 2H, J = 6.9 Hz), 4.25 (dd, 1H, J = 12.3, 4.7 Hz), 4.13–4.05 (m, 2H), 4.03 (t, 2H, J = 5.9 Hz), 2.27 (p, 2H, J = 6.2 Hz), 2.12 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (CD_3OD, 100 MHz): δ = 171.1, 170.2, 170.1, 170.1, 123.8, 96.8, 69.3, 69.2, 68.6, 64.1, 62.1, 60.0, 46.8, 29.7, 19.3, 19.2, 19.2; HR-MS (ESI): m/z = 568.1422, calcd. for $C_{20}H_{30}N_3O_{14}S$ $[M-Na+2H]^+$: 568.1448; HPLC purity: 100%.

Sodium 1-(benzyloxy)-3-{4-[(*tert*-butoxycarbonylamino)-methyl]-1*H*-1,2,3-triazol-1-yl}propan-2-yl sulfate (4f): Compound **4f** was obtained as a syrup; yield: 450 mg (97%). IR (film): ν_{max} = 3433, 2976, 1703, 1523, 1366, 1253, 1169, 1029, 761 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ = 7.78 (s, 1H), 7.35–7.19 (m, 5H), 4.65 (dd, 1H, J = 15.1, 6.0 Hz), 4.65 (m, 2H), 4.56 (m, 2H), 4.45 (s, 2H), 4.16 (d, 2H, J = 5.3 Hz), 3.37 (m, 3H, 1H exchangeable with D_2O), 1.36 (s, 9H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 156.0, 145.7, 138.6, 128.7, 127.9, 127.9, 124.0, 78.3, 73.2, 72.8, 69.0, 50.3, 36.1, 28.7; HR-MS (ESI): m/z = 443.1595, calcd. for $C_{18}H_{27}N_4O_7S$ $[M-Na+2H]^+$: 443.1600; HPLC purity: 79.47%.

Sodium 1-(benzyloxy)-3-[4-(3-hydroxypropyl)-1*H*-1,2,3-triazol-1-yl)propan-2-yl sulfate (4g): Compound **4g** was obtained as a syrup; yield: 393 mg (100%). IR (film): ν_{max} = 3406, 2933, 1599, 1259, 1036 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ = 7.70 (s, 1H), 7.32 (m, 5H), 4.63–4.43 (m, 5H), 3.44–3.38 (m, 4H), 2.61 (t, 2H, J = 7.7 Hz), 1.71 (m, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 146.4, 138.2, 128.2, 127.5, 127.4, 122.7, 72.9, 72.4, 68.4, 68.7, 60.0, 49.9, 32.3, 21.6; HR-MS (ESI): m/z = 416.0864, calcd. for $C_{15}H_{20}N_3O_6Na_2S$ $[M+Na]^+$: 416.0868; HPLC purity: 87.24%.

Sodium 3,3′-[4,4′-(2,5,8,11,14-pentaoxapentadecane-1,15-diyl)bis(1*H*-1,2,3-triazole-4,1-diyl)]bis[1-(benzyloxy)propane-3,2-diyl] disulfate (4h): Compound **4h** was obtained as a syrup; yield: 870 mg (95%). IR (film): ν_{max} = 3467, 2872, 1654, 1455, 1235, 1098, 1028, 762 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ = 7.94 (s, 2H), 7.35–7.18 (m, 10H), 4.66 (dd, 2H, J = 15.4, 6.1 Hz), 4.61–4.53 (m, 4H), 4.50 (s, 4H), 4.46 (d, 4H, J = 3.8 Hz), 3.54–3.31 (several m, 20H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 143.6, 138.2, 128.2, 127.5, 127.4, 124.8, 72.7, 72.4, 69.7, 69.6, 68.9, 68.7, 63.5, 50.0; HR-MS (ESI): m/z = 911.2162, calcd. for $C_{34}H_{46}N_6O_{15}S_2Na_3$ $[M+Na]^+$: 911.2156; HPLC purity: 92.32%.

1-(3-*O*-Acetyl-6-deoxy-1,2-O-isopropyliden-5-*O*-sulfo-α-D-glucofuranos-6-yl)-4-(3-hydroxypropyl)-1*H*-1,2,3-triazole sodium salt (4i): Compound **4i** was obtained as a syrup; yield: 445 mg (94%); $[\alpha]_D$: −36.5° (*c* 1, MeOH). IR (film): ν_{max} = 3471, 2932, 1739, 1639, 1376, 1244, 1067, 1017, 753 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz): δ = 7.84 (s, 1H), 5.89 (d, 1H, J = 3.5 Hz), 5.12 (d, 1H, J = 2.8 Hz), 5.01 (dd, 1H, J = 14.5, 3.1 Hz), 4.79 (m, 1H), 4.69 (dd, 1H, J = 14.5, 2.9 Hz), 4.49 (d, 1H, J = 3.5 Hz), 3.89 (dd, 1H, J = 9.0, 2.8 Hz), 3.57 (t, 2H, J = 5.3 Hz), 2.75 (t, 2H, J = 7.6 Hz), 2.07 (s, 3H), 1.87 (q, 2H, J = 6.8 Hz), 1.36 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (CD_3OD, 100 MHz): δ = 172.0, 113.9, 106.7, 84.4, 77.9, 76.6, 73.5, 62.1, 51.6, 33.4, 27.3, 26.8, 22.9, 21.1; HR-MS (ESI): m/z = 450.1176, calcd. for $C_{16}H_{25}N_3O_{10}S$ $[M-Na]^-$: 450.1182; HPLC purity: 91.37%.

1-(3-*O*-Acetyl-6-deoxy-1,2-*O*-isopropyliden-5-*O*-sulfo-α-D-glucofuranos-6-yl)-4-(2′,3′,4′, 6′-tetra-*O*-acetyl-β-D-glucopyranosyloxymethyl)-1*H*-1,2,3-triazole sodium salt (4j): Compound **4j** was obtained as a syrup; yield: 705 mg (91%); $[\alpha]_D$: −27.8° (*c* 1, MeOH); IR (film): ν_{max} = 2934, 1752, 1374, 1224, 1162, 1046, 749 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz): δ = 8.08 (s, 1H), 5.89 (d, 1H, J = 3.6 Hz), 5.18 (t, 1H, J = 9.4 Hz), 5.11 (d, 1H, J = 2.9 Hz), 5.04 (dd, 1H, J = 14.5, 3.1 Hz), 4.99 (t, 1H, J = 9.7 Hz), 4.88–4.71 (m, 6H), 4.50 (d, 1H, J = 3.6 Hz), 4.28 (dd, 1H, J = 12.4, 4.4 Hz), 4.14 (dd, 1H, J = 12.4, 2.3 Hz), 3.92 (dd, 1H, J = 8.9, 2.9 Hz), 3.89 (m, 1H), 2.08 (s, 3H), 2.05 (s, 3H), 1.98 (s, 3H), 1.95 (s, 3H), 1.92 (s, 3H), 1.38 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (CD_3OD, 100 MHz): δ = 172.6, 172.3, 171.9, 171.6, 113.9, 106.7, 103.2, 84.5, 78.2, 76.7, 76.5, 74.6, 73.6, 73.2, 72.9, 70.3, 63.4, 63.3, 51.8, 27.3, 26.8, 21.1, 20.9, 20.8, 20.8; HR-MS (ESI): m/z = 752.1827, calcd. for $C_{28}H_{38}N_3O_{19}S$ $[M-Na]^-$: 752.1820; HPLC purity: 89.14%.

***N*,*N*,*N*-Tris-[(1-(3-*O*-Acetyl-6-deoxy-1,2-*O*-isopropyliden-5-*O*-sulfo-α-D-glucofuranos-6-yl)-1*H*-1,2,3-triazol-4-yl)methyl]amine sodium salt (4k):** Compound **4k** was obtained as a syrup; yield: 1103 mg (85%); $[\alpha]_D$: −38.7° (*c* 1, MeOH). IR (film): ν_{max} = 3145, 2985, 2925, 2850, 1738, 1638, 1375, 1239, 1015, 751 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz): δ = 8.07 (s, 3H), 5.91 (d, 3H, J = 3.1 Hz), 5.14 (s, 3H), 5.04 (d, 3H, J = 15.4 Hz), 4.88 (m, 3H), 4.73 (dd, 3H, J = 13.8, 3.7 Hz), 4.53 (d, 3H, J = 3.4 Hz), 4.03 (dd, 3H, J = 8.1, 2.0 Hz), 3.82 (s, 6H), 2.09 (s, 9H), 1.36 (s, 9H), 1.27 (s, 9H); ^{13}C NMR (CD_3OD, 125 MHz): δ = 172.0, 145.1, 127.7, 113.8, 106.6, 84.4, 78.6, 76.8, 73.7, 52.2, 49.2, 27.3, 26.7, 21; HR-MS (ESI): m/z = 1299.2307, calcd. for $C_{42}H_{58}N_{10}O_{27}S_3Na_3$ $[M+H]^+$: 1299.2328; m/z = 1277.2560, calcd. for $C_{42}H_{59}N_{10}O_{27}S_3Na_2$ $[M-Na+2H]^+$: 1277.2509; m/z = 1255.2726, calcd. for $C_{42}H_{60}N_{10}O_{27}S_3Na$ $[M-2Na+3H]^+$: 1255.2689; m/z = 1233.2874, calcd. for $C_{42}H_{61}N_{10}O_{27}S_3$ $[M-3Na+4H]^+$: 1233.2870; HPLC purity: 97.96%.

Sodium *tert*-butoxycarbonyl{2-[4-(3-hydroxypropyl)-1*H*-1,2,3-triazol-1-yl]ethyl}sulfamate (4l): Compound **4l** was ob-

tained as a syrup; yield: 345 mg (93%). IR (film): ν_{max} = 3355, 3142, 2928, 1698, 1522, 1366, 1251, 1169, 1067, 1011, 764 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ = 7.72 (s, 1H), 4.44 (t, 3H, J = 5.6 Hz), 3.83 (t, 2H, J = 6.0 Hz), 3.43 (q, 2H, J = 5.9 Hz), 2.60 (t, 2H, J = 7.7 Hz), 1.75–1.68 (m, 2H), 1.25 (s, 9H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 152.5, 122.4, 79.1, 60.0, 48.7, 46.5, 32.2, 27.7, 21.7; HR-MS (ESI): m/z = 349.1187, calcd. for $C_{12}H_{21}N_4O_6S$ $[M-Na]^-$: 349.1182.

Sodium *tert*-butoxycarbonyl{2-[4-(pyridin-3-yl)-1*H*-1,2,3-triazol-1-yl]ethyl}sulfamate (4m): Compound **4m** was obtained as a syrup; yield: 348 mg (89%). IR (film): ν_{max} = 2971, 2925, 1701, 1340, 1252, 1151, 1048 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz): δ = 9.07 (s, 1H), 8.57 (s, 1H), 8.46 (s, 1H), 8.27 (d, 1H, J = 7.9 Hz), 7.55 (s, 1H), 4.55 (t, 2H, J = 5.8 Hz), 3.58 (t, 2H, J = 5.7 Hz), 1.36 (s, 9H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 156.9, 148.1, 145.8, 144.0, 133.5, 122.3, 79.1, 50.1, 40.1, 27.3; HR-MS (ESI): m/z = 392.1019, calcd. for $C_{14}H_{19}N_5O_5SNa$ $[M+H]^+$: 392.1005; HPLC purity: 98.09%.

Sodium (*S*)-*tert*-butoxycarbonyl{3-[4-(3-hydroxypropyl)-1*H*-1,2,3-triazol-1-yl]-1-methoxy-1-oxopropan-2-yl}sulfamate (4n): Compound **4n** was obtained as a syrup; yield: 408 mg (95%); $[\alpha]_D$: −43.7° (*c* 1, MeOH); IR (film): ν_{max} = 3422, 2953, 1741, 1710, 1438, 1370, 1251, 1051 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ = 7.79 (s, 1H), 5.12 (dd, 1H, J = 8.5, 4.4 Hz), 4.91 (dd, 1H, J = 14.1, 4.3 Hz), 4.65 (dd, 1H, J = 14.1, 8.9 Hz), 3.60 (s, 3H), 3.40 (t, 2H, J = 6.3 Hz), 2.56 (t, 2H, J = 7.5 Hz), 1.68 (p, 2H, J = 6.7 Hz), 1.23 (s, 9H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 170.1, 155.1, 146.6, 122.5, 78.7, 59.9, 53.6, 52.2, 49.2, 32.2, 28.0, 21.6; HR-MS (ESI): m/z = 407.1224, calcd. for $C_{14}H_{23}N_4O_8S$ $[M-Na]^-$: 407.1237; HPLC purity: 100%.

Sodium (*S*)-*tert*-butoxycarbonyl(3-{4-[(*tert*-butoxycarbonylamino)methyl]-1*H*-1,2,3-triazol-1-yl}-1-methoxy-1-oxopropan-2-yl)sulfamate (4o): Compound **4o** was obtained as a syrup; yield: 0.46 g (93%); $[\alpha]_D$: −43.1° (*c* 1, MeOH); IR (film): ν_{max} = 3379, 2977, 1741, 1702, 1249, 1049 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ = 7.86 (s, 1H), 7.18 (t, 1H, J = 5.7 Hz, interchangeable with D_2O), 5.12 (dd, 1H, J = 7.7, 4.6 Hz), 4.94 (dd, 1H, J = 13.9, 4.8 Hz), 4.63 (dd, 1H, J = 13.8, 8.0 Hz), 4.09 (d, 2H, J = 5.6 Hz), 3.59 (s, 3H), 1.36 (s, 9H), 1.24 (s, 9H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 169.6, 155.4, 123.6, 80.0, 58.7, 51.8, 49.9, 35.6, 28.2, 27.7; HR-MS (ESI): m/z = 478.1603, calcd. for $C_{17}H_{28}N_5O_9S$ $[M-Na]^-$: 478.1608; HPLC purity: 94.96%.

Sodium (*S*)-*tert*-butoxycarbonyl{1-methoxy-1-oxo-3-[4-(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]}sulfamate (4p): Compound **4p** was obtained as a syrup; yield: 0.67 g (92%); $[\alpha]_D$: −3.3° (*c* 1, MeOH). IR (film): ν_{max} = 2926, 1749, 1437, 1370, 1230, 1048 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ = 8.10 (s, 1H), 5.18 (dd, 1H, J = 8.6, 4.5 Hz), 5.13–4.99 (m, 4H), 4.96 (dd, 1H, J = 14.2, 4.6 Hz), 4.72 (dd, 1H, J = 14.1, 8.8 Hz), 4.64 (d, 1H, J = 12.0 Hz), 4.56 (d, 1H, J = 12.0 Hz), 4.15 (dd, 1H, J = 12.2, 5.0 Hz), 4.07–3.95 (m, 2H), 3.61 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.90 (s, 3H), 1.24 (s, 9H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 170.1, 169.6, 169.6, 169.4, 155.1, 142.3, 125.3, 95.9, 78.8, 68.6, 68.6, 68.0, 65.3, 61.8, 59.8, 53.6, 52.3, 49.5, 28.0, 20.6, 20.5, 20.4, 20.4; HR-MS (ESI): m/z = 709.1851, calcd. for $C_{26}H_{37}N_4O_{17}S$ $[M-Na]^-$: 709.1874.

Supporting Information

^1H- and ^{13}C NMR spectra of the obtained 1,2,3-triazoles **4a–p** are available in the Supporting Information.

Acknowledgements

The authors acknowledge Direccion General de Investigacion Cientifica y Tecnica (DGICYT) (CTQ2008-01754) and Junta de Andalucia (P07-FQM-02899) for financial support. A.M.-F. thanks University of Granada for a research grant (Programa Puente). The authors also want to thank the reviewers for their advice.

References

[1] a) L Weber, *Drug Discovery Today* **2002**, *7*, 143–147; b) H. Bienaymé, C. Hulme, G. Oddon, P. Schmitt, *Chem. Eur. J.* **2000**, *6*, 3321–3329; c) D. J. Ramón, M. Yus, *Angew. Chem.* **2005**, *117*, 1628–1661; *Angew. Chem. Int. Ed.* **2005**, *44*, 1602–1634; d) B. Jiang, T. Rajale, W. Wever, S.-J. Tu, G. Li, *Chem. Asian J.* **2010**, *5*, 2318–2335.

[2] H. C. Kolb, M. G. Finn, M. G.; K. B. Sharpless, *Angew. Chem.* **2001**, *113*, 2056–2075; *Angew. Chem. Int. Ed.* **2001**, *40*, 2004–2021.

[3] a) C. W. Tornøe, C. Christensen, M. Meldal, *Peptidotriazoles: copper(I)-catalyzed 1,3-dipolar cycloadditions on solid-phase*, in: *Peptides: The Wave of the Future*, (Eds.: M. Lebl, R. A. Houghten), San Diego, American Peptide Society and Kluwer Academic Publishers, **2001**, pp 263–264; b) C. W. Tornøe, C. Christensen, M. Meldal, *J. Org. Chem.* **2002**, *67*, 3057–3064; c) V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem.* **2002**, *114*, 2708–2711; *Angew. Chem. Int. Ed.* **2002**, *41*, 2596–2599.

[4] a) M. Meldal, C. W. Tornøe, *Chem. Rev.* **2008**, *108*, 2952–3015; b) J. E. Moses, A. D. Moorhouse, *Chem. Soc. Rev.* **2007**, *36*, 1249–1262; c) J.-F. Lutz, Z. Zarafshani, *Adv. Drug Delivery Rev.* **2008**, *60*, 958–970; d) N. K. Devaraj, J. P. Collman, *QSAR Comb. Sci.* **2007**, *26*, 1253–1260; e) W. H. Binder, R. Sachsenhofer, *Macromol. Rapid Commun.* **2008**, *29*, 952–981.

[5] a) E. F. V Scriven, K. Turnbull, *Chem. Rev.* **1988**, *88*, 297–368; b) S. Bräse, C. Gil, K. Knepper, V. Zimmermann, *Angew. Chem.* **2005**, *117*, 5320–5374; *Angew. Chem. Int. Ed.* **2005**, *44*, 5188–5240.

[6] A. V. Maksikova, E. S. Serebryakova, L. G. Tikhonova, L. I. Vereshchagin, *Chem. Heterocycl. Compd.* **1980**, *16*, 1284–1285.

[7] a) A. K. Feldman, B. Colasson, V. V. Fokin, *Org. Lett.* **2004**, *6*, 3897–3899; b) P. Appukkuttan, W. Dehaen, V. V. Fokin, E. van der Eycken, *Org. Lett.* **2004**, *6*, 4223–4225; c) K. Kacprzak, *Synlett* **2005**, 943–946; d) J. Andersen, S. Bolvig, X. Liang, *Synlett* **2005**, 2941–2947; e) S. Chittaboina, F. Xie, Q. Wang, *Tetrahedron Lett.* **2005**, *46*, 2331–2336; f) Y.-B. Zhao, Z.-Y. Yan, Y.-M. Liang, *Tetrahedron Lett.* **2006**, *47*, 1545–1549; g) M. L. Kantam, V. S. Jaya, B. Sreedhar, M. Rao, B. M. Chou-

dary, *J. Mol. Catal. A: Chemical* **2006**, *256*, 273–277; h) B. Sreedhar, P. S. Reddy, *Synth. Commun.* **2007**, *37*, 805 −812; i) B. Saha, S. Sharma, D. Sawant, B. Kundu, *Synlett* **2007**, 1591–1594; j) T. Miao, L. Wang, *Synthesis* **2008**, 363–368; k) H. Sharghi, R. Khalifeh, M. M. . Doroodmand, *Adv. Synth. Catal.* **2009**, *351*, 207–218; l) V. Bénéteau, A. Olmos, T. Boningari, J. Sommer, P. Pale, *Tetrahedron Lett.* **2010**, *51*, 3673–3677; m) T. Shamim, S. Paul, *Catal. Lett.* **2010**, *136*, 260–265; n) J. Yan, L. Wang, *Synthesis* **2010**, 447–452; o) K. A. Dururgkar, R. G. Gonnade, C. V. Ramana, *Tetrahedron* **2009**, *65*, 3974–3979; p) A. R. Bogdan, N. W. Sach, *Adv. Synth. Catal.* **2009**, *351*, 849–854; q) F. Alonso, Y. Moglie, G. Radivoy, M. Yus, *Org. Biomol. Chem.* **2011**, *9*, 6385–6395.

[8] D. Kumar, V. B. Reddy, R. S. Varma, *Tetrahedron Lett.* **2009**, *50*, 2065–2068.

[9] C.-Z. Tao, X. Cui, J. Li, A.-X. Liu, L. Liu, Q.-X. Guo, *Tetrahedron Lett.* **2007**, *48*, 3525–3529.

[10] a) H. S. G. Beckmann, V. Wittmann, *Org. Lett.* **2007**, *9*, 1–4; b) K. Barral, A. D. Moorhouse, J. E. Moses, *Org. Lett.* **2007**, *9*, 1809–1811; c) A. D. Moorhouse, J. E. Moses, *Synlett* **2008**, 2089–2092; d) N. M. Smith, M. J. Greaves, R. Jewell, M. W. D. Perry, M. J. Stocks, J. P. Stonehouse, *Synlett* **2009**, 1391–1394; e) C.-T. Lee, S. Huang, B. H. Lipshutz, *Adv. Synth. Catal.* **2009**, *351*, 3139–3142; f) J. R. Suarez, B. Trastoy, M. E. Perez-Ojeda, R. Marín-Barrios, J. L. Chiara, *Adv. Synth. Catal.* **2010**, *352*, 2515–2520.

[11] a) J. S. Yadav, B. V. S. Reddy, G. M. Reddy, D. N. Chary, *Tetrahedron Lett.* **2007**, *48*, 8773–8776; b) K. R. Reddy, C U. Maheswari, K. Rajgopal, M. L. Kantam, *Synth. Commun.* **2008**, *38*, 2158–2167; c) H. Sharghi, M. H. Beyzavi, A. Safavi, M. M. Doroodmand, R. Khalifeh, *Adv. Synth. Catal.* **2009**, *351*, 2391–2410; d) T. Boringari, A. Olmos, B. M. Reddy, J. Sommer, P. Pale, *Eur. J. Org. Chem.* **2010**, 6338–6347; e) H. Sharghi, M. Hosseini-Sarvari, F. Moeini, R. Khalifeh, A. S. Beni, *Helv. Chim. Acta* **2010**, *93*, 435–449; f) L. S. Campbell-Verduyn, W. Szymanski, C. P. Postema, R. A. Dierckx, P. H. Elsinga, D. B. Janssen, B. L. Feringa, *Chem. Commun.* **2010**, *46*, 898–900; g) F. Alonso, Y. Moglie, G. Radivoy, M. Yus, *J. Org. Chem.* **2011**, *76*, 8394–8405.

[12] G. Kumaraswamy, K. Ankamma, A. Pitchaiah, *J. Org. Chem.* **2007**, *72*, 9822–9825.

[13] D. Kumar, V. B. Reddy, *Synthesis* **2010**, 1687–1691.

[14] O. A. Attanasi, G. Favi, P. Filippone, F. Mantellini, G. Moscatelli, F. R. Perrulli, *Org. Lett.* **2010**, *12*, 468–471.

[15] a) B. B. Lohray, *Synthesis* **1992**, 1035–1052; b) H. S. Byun, L. L. He, R. Bittman, *Tetrahedron* **2000**, *56*, 7051–7091; c) B. B. Lohray, V. Bhushan, *Adv. Heterocycl. Chem.* **1997**, *68*, 89–180; d) A. Megia-Fernandez, J. Morales-Sanfrutos, F. Hernandez-Mateo, F. Santoyo-Gonzalez, *Curr. Org. Chem.* **2011**, *15*, 401–432.

[16] R. E. Melendez, W. D. Lubell, *Tetrahedron* **2003**, *59*, 2581–2616.

[17] a) B. B. Lohray, Y. Gao, K. B. Sharpless, *Tetrahedron Lett.* **1989**, *30*, 2623–2626; b) K. P. A. M. Van, W. Filemon, G. H. Veeneman, M. G. A. Van, B. J. H. Van, *J. Carbohydr. Chem.* **1992**, *11*, 837–848; c) J. G. Steinmann, J. H. Phillips, W. J. Sanders, L. L. Kiessling, *Org. Lett.* **2001**, *3*, 3557–3559; d) A. Avenoza, J. H. Busto, F. Corzana, J. I. García, J. M. Peregrina, *J. Org. Chem.* **2003**, *68*, 4506–4513; e) D. D. Dhavale, S. D. Markad, N. S. Karanjule, J. P. Reddy, *J. Org. Chem.* **2004**, *69*, 4760–4766; f) P. Gupta, S. V. Naidu, P. Kumar, *Tetrahedron Lett.* **2004**, *45*, 9641–9643; g) O. Andriuzzi, C. Gravier-Pelletier, G. Bertho, T. Prange', Y. Le Merrer, *Beilstein J. Org. Chem.* **2005**, *1*; h) V. F. V. Prazeres, L. Castedo, C. González-Bello, *Eur. J. Org. Chem.* **2008**, 3991–4003; i) K. Koroniak, G. Haufe, *Synthesis* **2010**, 498,504; j) J. Lalot, T. Tite, A. Wadouachi, D. Postel, A. Nguyen Van Nhien, *Tetrahedron* **2011**, *67*, 6006–6017.

[18] a) J. E. Baldwin, A. C. Spivey, C. J. Schofield, *Tetrahedron: Asymmetry* **1990**, *1*, 881–884; b) M. Atfani, L. Wei, W. D. Lubell, *Org. Lett.* **2001**, *3*, 2965–2968; c) J. J. Posakony, T. J. Tewson, *Synthesis* **2002**, 859–864; d) A. Avenoza, J. H. Busto, F. Corzana, G. Jimenez-Oses, J. M. Peregrina, *Chem. Commun.* **2004**, 980–981; e) V. Sai-Sudhir, N. Y. Phani-Kumar, R. B. Nasir Baig, S. Chandrasekaran, *J. Org. Chem.* **2009**, *74*, 7588–7591.

[19] Y. Gao, K. B. Sharpless, *J. Am. Chem. Soc.* **1988**, *110*, 7538–7539.

[20] D. Soriano del Amo, W. Wang, H. Jiang, C. Besanceney, A. C. Yan, M. Levy, Y. Liu, F. L. Marlow, P. Wu, *J. Am. Chem. Soc.* **2010**, *132*, 16893–16899.

[21] A. Megia-Fernandez, M. Ortega-Muñoz, J. Lopez-Jaramillo, F. Hernandez-Mateo, F. Santoyo-Gonzalez, *Adv. Synth. Catal.* **2010**, *352*, 3306–3320.

[22] A. Mendez-Ardoy, N. Guilloteau, C. Di Giorgio, P. Vierling, F. Santoyo-Gonzalez, C. Ortiz-Mellet, J. M. García-Fernandez, *J. Org. Chem.* **2011**, *76*, 5882–5894.

[23] a) F. Langa, P. de La Cruz, A. de La Hoz, A. Diaz-Ortiz, E. Diez-Barra, *Contemp. Org. Synth.* **1997**, *4*, 373–386; b) P. Lidström, J. Tierney, B. Wathey, J. Westman, *Tetrahedron* **2001**, *57*, 9225–9283; c) P. Appukkuttan, V. P. Mehta, E. V. van Der Eycken, *Chem. Soc. Rev.* **2010**, *39*, 1467–1477; d) F. Perez-Balderas, M. Ortega-Muñoz, J. Morales-Sanfrutos, F. Hernandez-Mateo, F. G. Calvo-Flores, J. A. Calvo-Asin, J. Isac-Garcia, F. Santoyo-Gonzalez, *Org. Lett.* **2003**, *5*, 1951–1954.

[24] S. H. Park, *Bull. Korean Chem. Soc.* **2003**, *24*, 253–255.

[25] K. Wasek, J. Kedzia, H. Krawczyk, J. Wojciechowski, W. M. Wolf, *Arkivoc* **2010**, *9*, 146–154.

[26] F. G. Calvo-Flores, P. García-Mendoza, F. Hernández-Mateo, J. Isac-García, F. Santoyo-González, *J. Org. Chem.* **1997**, *62*, 3944–3961.

[27] S. J. Kim, H. B. Park, J. S. Lee, N. H. Jo, K. H. Yoo, D. Baek, B.-W. Kang, J.-H. Cho, C.-H. Oh, *Eur. J. Med. Chem.* **2007**, *42*, 1176–1183.

[28] R. B. Nasir Baig, R. N. Chandrakala, V. Sai Sudhir, S. J. Chandrasekaran, *J. Org. Chem.* **2010**, *75*, 2910–2921.

[29] R. J. Kaufman, R. S. Sidhu, *J. Org. Chem.* **1982**, *47*, 4941–4947.

[30] D. L. Boger, C. M. Tarby, P. L. Myers, L. H. Caporale, *J. Am. Chem. Soc.* **1996**, *118*, 2109–2110.

[31] L. A. Canalle, S. S. van Berkel, L. T. de Haan, J. C. M. van Hest, *Adv. Funct. Mater.* **2009**, *19*, 3464–3470.

[32] T. N. Hoheisel, H. Frauenrath, *Org. Lett.* **2008**, *10*, 4525–4528.

