DOI: 10.1002/ejoc.201403288

Radical Titanocene Promoted Coupling of Epoxides and Vinyl Sulfones

Alfonso Fernández-Mateos,*[a] Soledad Encinas-Madrazo,[a] Pablo Herrero-Teijón,[a] and Rosa Rubio González[a]

Keywords: Synthetic methods / Radicals / Titanium / Cross-coupling / Epoxides / Vinyl sulfones

A radical coupling reaction of diverse vinyl sulfones and epoxides was mediated by Cp_2TiCl (Cp = cyclopentadienyl) to provide a straightforward synthetic pathway to hydroxy sulfones. The reaction was successfully achieved by using either an excess or a catalytic amount of the Ti^{III} reagent. The scope of the reaction was studied for several different functionalized and substituted epoxides and vinyl sulfones.

Introduction

One of the first examples described for a radical addition to a vinyl sulfone was published by G. A. Russell's group in 1984.[1] In this paper, alkyl radicals were obtained by the homolytic cleavage of organomercury compounds, RHgX, and those radicals underwent an addition to the C=C bond of a vinyl sulfone, which formed a new radical that proceeded through a sulfone elimination. Many methods to carry out a radical addition to different kinds of vinyl sulfones have been subsequently described.[2] In these papers, different alternatives to generate the radical are reported. The more recent ones focus on a substitution to Russell's mercury-based approach by using greener alternatives such as silanes[2f,2g] or boranes.[2h,2l]

Radicals that are generated by the homolytic cleavage of epoxides with Cp_2TiCl (Cp = cyclopentadienyl) have scarcely been used in intermolecular addition reactions. Nujent and RajanBabu introduced this method[3] for the radical addition to acrylates and vinyl ketones.[4] Shortly after, the catalytic coupling of epoxides and acrylates induced by Ti^{III} was described by Gänsauer's group,[5] who also described the addition to vinyl ketones, acrylonitriles, and acrylic amide derivatives in further publications.[6] However, no attention has been paid to vinyl sulfones.

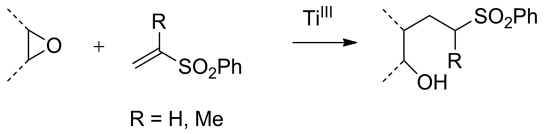
Vinyl sulfones are exceptional radical acceptors, and sulfones are versatile functional groups that can be transformed into other groups through straightforward reactions. These reasons motivated the study of the intermolecular coupling between epoxides and vinyl sulfones, which is promoted by titanocene chloride.

[a] Departamento de Química Orgánica, Facultad de CC Químicas, Universidad de Salamanca,
Plaza de los Caídos 1–5, 37008 Salamanca, Spain
E-mail: afmateos@usal.es
www.usal.es

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201403288.

Results and Discussion

The intermolecular reaction between epoxides and vinyl sulfones was mediated by titanocene chloride to provide hydroxy sulfones in good yields (see Scheme 1). An exhaustive study was carried out to evaluate the scope of this reaction.



Scheme 1. Coupling of epoxides with sulfones that is mediated by titanocene.

The coupling of cyclohexene oxide (**1**) and phenyl vinyl sulfone (**6**; see Figure 1) was first examined by increasing the number of equivalents of **6**. Then, the influence of the order of the addition (i.e., titanocene to a mixture of epoxide and sulfone or vice versa) was studied. All reactions were performed with an excess amount of Ti^{III} (2.2 equiv.), and the results are summarized in Table 1.

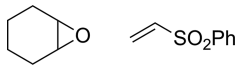


Figure 1. Sulfone and epoxide used in preliminary studies.

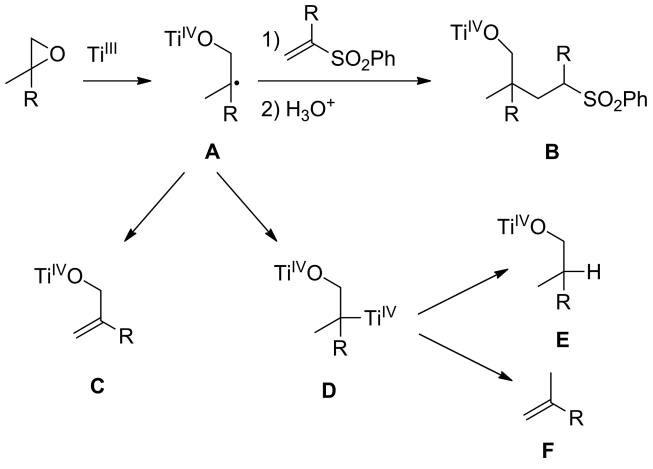
The yields increased with the number of equivalents of vinyl sulfone **6**, and the reaction that used 10.0 equiv. of **6** afforded the highest yield. However, as all of the reactions provided the products in good yield, a moderate excess amount of sulfone (2.0 or 5.0 equiv.) was employed in further experiments to ease the experimental work. As far as we observed, the order of addition had no effect on the yield.

All possible reaction pathways are depicted in Scheme 2. The initial step of the coupling reaction is the well-known

Table 1. Preliminary studies.

Entry	**1** [equiv.]	**6** [equiv.]	Addition method[a]	Products	Yield [%]
1	1	1	A	**1a/1b** (60:40)	51
2	1	2	B	**1a/1b** (62:38)	53
3	1	5	A	**1a/1b** (67:33)	58
4	1	5	B	**1a/1b** (56:44)	60
5	1	10	B	**1a/1b** (58:42)	68

[a] Addition method A: a tetrahydrofuran (THF) solution of Ti^{III} was added to a THF solution of the epoxide and sulfone. Addition method B: a THF solution of the epoxide and sulfone was added to a THF solution of Ti^{III}.



Scheme 2. Possible reaction pathways.

titanocene-mediated ring-opening of epoxides, which regioselectively affords the more substituted β-alkoxy radical **A**. This initial radical undergoes a further reaction with the corresponding vinyl sulfone to afford a new radical, which after reduction and hydrolysis provides coupling product **B**. β-Alkoxy radical **A** could follow alternative pathways, which are also depicted in Scheme 2. Thus, when R = Me, **A** could undergo a hydrogen abstraction by using another equivalent of Cp_2TiCl to afford **C**. A different option would be the direct coupling with Cp_2TiCl when R = H to give **D**, and either the further elimination of $(Cp_2TiO)_2$ would afford **E** or a hydrolysis by hydrogen interchange would give **F**. As a result, in cases when R = H and addition method B is used with an excess amount of Ti^{III}, the coupling product will only be obtained if the addition to the vinyl sulfone is faster than that to Ti^{III}. However, coupling product **B** is the only product observed in the experiments so far described.

In a next step, a series of oxiranes and two different vinyl sulfones were studied. To evaluate the scope of the reaction, a selection of cyclic and acyclic epoxides with different substitution patterns were selected. The epoxides, sulfones, and coupling products are depicted in Figure 2, and the reaction conditions and results are summarized in Table 2.

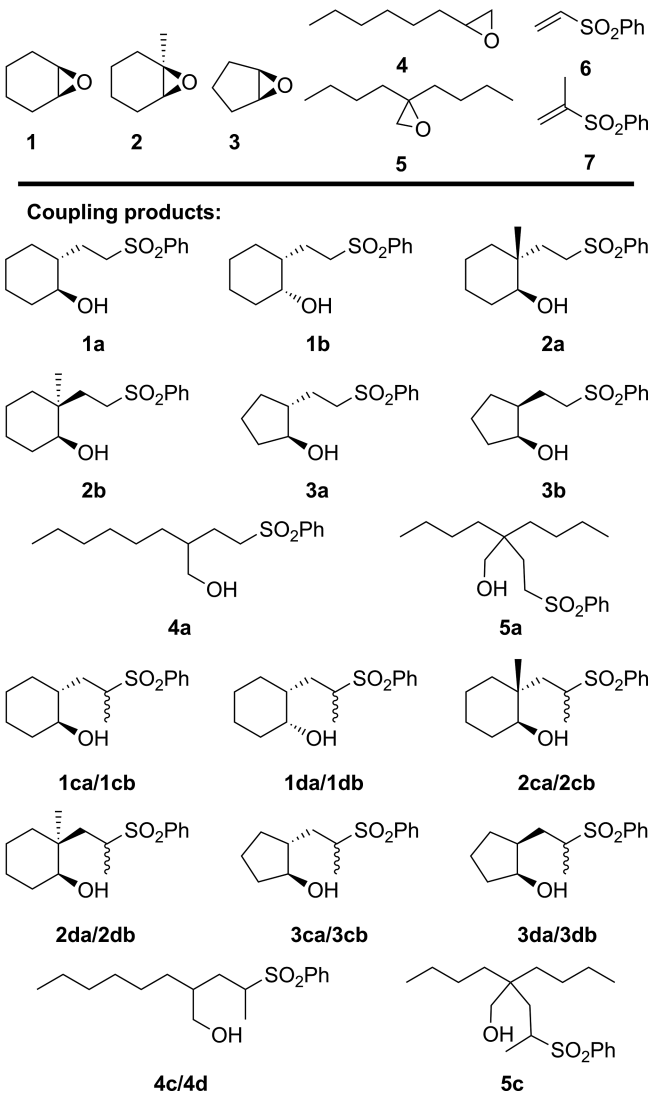


Figure 2. Epoxides, sulfones, and coupling products.

Table 2. Coupling reactions with an excess amount of Cp_2TiCl.

Entry	Epoxide	Sulfone	Addition method[a]	Product(s)	Yield [%]
1	1	6	A	**1a/1b** (67:33)	58
2	2	6	A	**2a/2b** (72:28)	77
3	3	6	A	**3a/3b** (88:12)	68
4	4	6	B	**4a**	69
5	5	6	B	**5a**	72
6	1	7	B	**1ca/1cb** (67:33)	40
7	2	7	B	**2ca/2cb** (85:15)	63
8	3	7	A	**3ca/3cb** (85:15)	54
9	4	7	B	**4c**, **4d**	29
10	5	7	A	**5c**	31

[a] Addition method A: a THF solution of Ti^{III} was added to a THF solution of the epoxide and sulfone. Addition method B: a THF solution of the epoxide and sulfone was added to a THF solution of Ti^{III}.

All reactions afforded the products in good yields. Nevertheless, better results were obtained by using the sterically less hindered sulfone **6**. In all cases, the cyclic epoxides afforded coupling compounds as a mixture of *cis*/*trans* diastereoisomers with the *trans* hydroxy sulfone as the major isolated product. This result is in agreement with previous intermolecular additions of cyclohexyl radicals to activated alkenes[5c] and nitriles,[7] in which the reaction took place preferentially at the less hindered site to give the *trans* product. The coupling reactions with the highest diastereoselectivity took place between sulfones **6** and **7** and cyclopentene oxide (**3**), respectively.

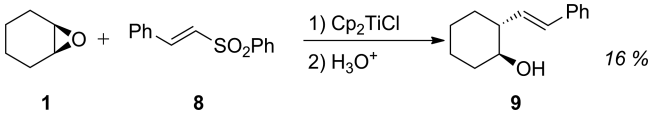
The coupling reactions were also performed with a catalytic amount of Cp_2TiCl (0.2 equiv.), according to the method described by Oltra and co-workers.[8] The results are summarized in Table 3.

Table 3. Coupling reactions with a catalytic amount of Cp_2TiCl.

Entry	Epoxide	Sulfone	Product(s)	Yield [%]
1	1	6	**1a/1b** (55:45)	43
2	2	6	**2a/2b** (75:25)	61
3	3	6	**3a/3b** (85:15)	41
4	4	6	**4a**	32
5	5	6	**5a**	49
6	1	7	**1ca/1cb** (70:30)	30
7	2	7	**2ca/2cb** (78:22)	48
8	3	7	**3ca/3cb** (95:5)	40
9	4	7	**4c**, **4d**	41
10	5	7	**5c**	54

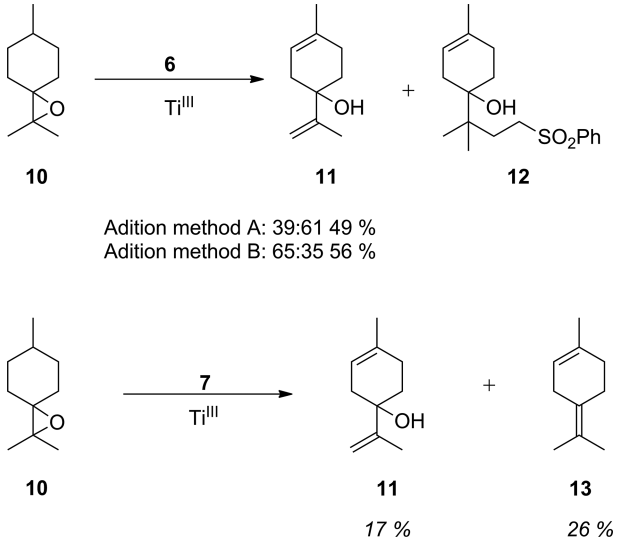
Under catalytic conditions, all of the coupling reactions took place successfully, but slightly lower yields were obtained compared with those obtained by using an excess amount of Cp_2TiCl. The stereochemical outcomes were also similar to those obtained by using 2.2 equiv. of Cp_2TiCl. The *trans* product was the major isolated product, and the highest stereoselectivity was obtained by the reactions of sulfones **6** and **7** with epoxide **3**.

The coupling reactions with β-alkyl-substituted sulfones did not provide any satisfactory results. Slightly better results were obtained when the β-aryl sulfone **8** was employed (see Scheme 3). The reaction of cyclohexene oxide (**1**) and styryl sulfone **8** in the presence of 2.2 equiv. of titanocene provided coupling product **9** in 16% as the best yield. The phenyl ring that is attached to the double bond of the sulfone directed the addition of the alkoxy radical to the α-position of the sulfone, and the resulting radical evolved by the elimination of the sulfone group. This behavior is in accordance with former results for radical additions to this sulfone.[1a] Throughout this part of the study, there was evidence of slower kinetics for the coupling reactions that involved aryl and alkyl sulfones, and therefore the use of these β-substituted acceptors were abandoned.



Scheme 3. Titanocene-mediated coupling reaction of epoxide **1** and aryl sulfone **8**.

To evaluate the effects of steric hindrance, the coupling reactions of sulfones **6** and **7** with epoxide **10** were then investigated. The results in Scheme 4 show that steric hindrance disfavored the coupling reaction and favored the side reactions that are shown in Scheme 2.



Scheme 4. Study of influence of steric hindrance.

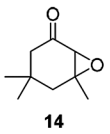
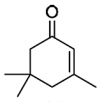
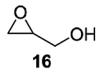
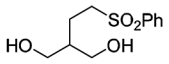
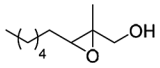
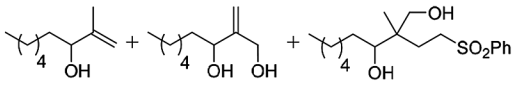
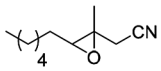
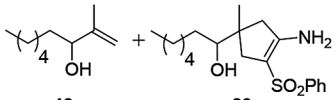
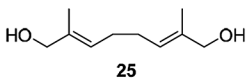
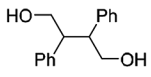
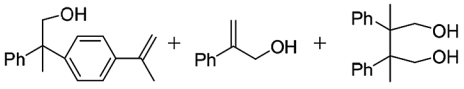
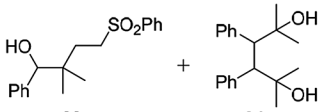
To finalize the study, reactions were carried out with a new series of functionalized epoxides to evaluate to what extent side reactions could compete with the coupling reaction. The epoxides, products, and yields are summarized in Table 4. All reactions were carried out with an excess amount of Cp_2TiCl.

The coupling attempt with isophorone oxide (**14**) and sulfone **6** was unsuccessful, as only deoxygenation product **15** was isolated. From this result, we concluded that the stabilized radical that formed immediately after the homolytic ring-opening of the epoxide is trapped faster by the Ti^{III} species than by the sulfone.

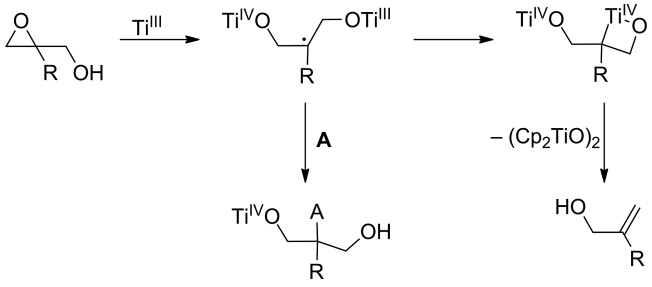
The behavior of 2,3-epoxy alcohols in the presence of Cp_2TiCl has been studied previously.[9] As reported, in the absence of H-atom donors, these epoxides can undergo a reaction with titanocene to give the corresponding allylic alcohols regioselectively through a Ti^{IV} four-membered cyclic intermediate (see Scheme 5). However, in the presence of some H-atom donors such as 1,4-cyclohexadiene,[3,10] acrylates,[4] acrylonitrile,[4] and nitriles,[11] the trapping of the radical intermediate has been described, and the coupling products have been obtained. In these cases, the acceptor trapping is faster than the dehydroxylation step.

In our experiments, epoxy alcohols **16** and **18** in the presence of sulfone **6** provided the corresponding coupling products **17** and **21a/21b**. Despite the number of times that the coupling reaction between **16** and **6** was carefully repeated, a yield better than 6% could not be achieved. We believe that this is, because both **17** and the corresponding dehydration product obtained from **16**, (i.e., 1,3-propane-

Table 4. Cp_2TiCl-mediated coupling reactions with functionalized epoxides.

	Epoxide	Sulfone	Product(s)	Yield [%]
1	 **14**	**6**[a]	 **15**	82
2	 **16**	**6**[b]	 **17**	6
3	 **18**	**6**[a]	 **19** **20** **21a/b** 5:10:85	62
4	 **22**	**6**[a]	 **19** **23** 60:40	56
5	 **24**	**6**[b]	 **25**	99
6	 **26**	**6**[b]	 **27a/b**	27
7	 **28**	**6**[b]	 **29** **30** **31** 17:20:36	54
8	 **32**	**6**[b]	 **33** **34** 22:78	80

[a] Addition method B. [b] Addition method A.



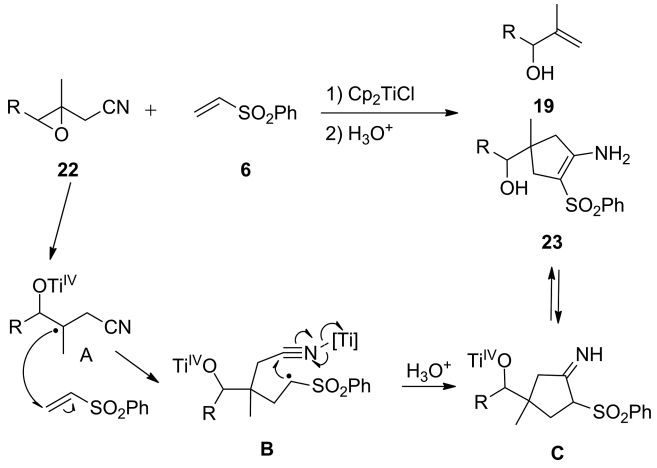
Scheme 5. Mechanistic development of 2,3-epoxy alcohols in the presence of Cp_2TiCl.

diol) are both very small polar molecules. They are water-soluble and, thus, are unfortunately lost during the extraction process.

In the reaction performed with epoxide **18**, coupling products **21a/21b** were isolated along with dehydroxylation and dehydrogenation products **19** and **20**. The ratio of the products shows that the addition reaction of the initial tertiary radical to vinyl sulfone **6** is faster than either its dehydroxylation or dehydrogenation reaction.

Similar products were obtained by the titanocene-mediated coupling of **22** and **6** (see Table 4, Entry 4). The major product, allylic alcohol **19**, was formed by elimination of the CN group, and the minor product (i.e., sulfone amine

23) was obtained by addition of the tertiary radical to **6** according to the mechanism depicted in Scheme 6. The ratio of the products suggests that the elimination of CN is faster than the addition process, which led us to conclude that for these functionalized epoxides, the CN group is a better leaving group than the OH group.

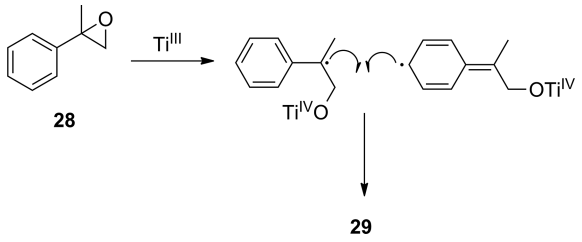


Scheme 6. Mechanism for the formation of **23**. R = C_6H_{13}.

Radicals that are formed by the reaction between vinyl epoxides and titanocene have been described to undergo three different reactions, that is, homocoupling,[11,12] deoxygenation,[9b,13] and reduction.[9b,13] Homocoupling has been observed under catalytic conditions[12] and seems to be a general route, whereas deoxygenation has been reported when terminal alkenes undergo a reaction with 2 equiv. of Cp_2TiCl.[9b,13] Reduction has been described to occur when internal alkenes are subjected to the same conditions.[9b,13] The reaction of vinyl epoxide **24** with phenyl vinyl sulfone (**6**) in the presence of titanocene quantitatively afforded homocoupling product **25** (see Table 4, Entry 5). This result is consistent with the previously reported studies that were conducted with acrylonitrile,[12] methyl acrylate,[12] and acetonitrile[11] as trapping agents and, therefore, confirms the allylic radical homocoupling as a very fast reaction.

To complete the study, a series of aryl epoxides were studied (see Table 4, Entries 6–8). The main benzyl radical formed from the homolytic regioselective ring-opening of aryl epoxides **26**, **28**, and **32** is less reactive than the allylic one and was expected to provide the coupling product. However, neither **26** nor **28** provided the corresponding coupling product when treated with **6** in the presence of titanocene chloride. Styrene oxide (**26**) afforded the homocoupling product, and epoxy arene **28** showed very similar behavior. No addition product was isolated, and the major product was homocoupling compound **31** along with **29** and **30**. The proposed mechanism for the formation of **29** is an asymmetric self-coupling of the initial benzyl radical, which can be explained by steric hindrance arguments (see Scheme 7).

Of the three examined aryl epoxides, only **32** provided the coupling product between the epoxide and vinyl sulfone **6**. From the obtained results, we can conclude that two different radicals are formed when **32** is treated with Cp_2TiCl, that is, the benzyl and the tertiary radical. The former one does not undergo a reaction with **6**, and thus only homocoupling product **34** is formed. However, the tertiary radical does undergo a reaction to yield hydroxy sulfone **33**. The ratio of the isolated products (22:78) favors **34**, which shows that the ring-opening of epoxide **32** to give the benzyl radical is faster than to give the tertiary radical.



Scheme 7. Mechanism for the formation of **29**.

Conclusions

The titanocene-promoted intermolecular coupling of epoxides and sulfones was successfully achieved to provide easy access to hydroxy sulfones from several different substituted epoxides and vinyl sulfones. A complete study was carried out by using either an excess or a catalytic amount of Cp_2TiCl in the reactions. All coupling products were afforded in good yields, which proved that the reaction was quite general but sensitive to steric hindrance factors. α-Functionalized epoxides were studied too. Interesting coupling results were realized when the epoxides were functionalized by a hydroxy or cyano group. In general, aryl epoxides and vinyl epoxides did not provide the addition product when treated with the vinyl sulfone as a result of the alternative faster radical homocoupling reaction.

Experimental Section

General Methods: IR spectra were recorded by using neat samples on NaCl plates, unless otherwise noted. The ^1H NMR spectroscopic data were recorded at either 200 or 400 MHz, and the ^{13}C NMR spectroscopic data were recorded at 50 or 100 MHz. The samples were dissolved in $CDCl_3$, and the chemical shifts were referenced to the solvent, except where otherwise indicated. Standard mass spectrometry data were acquired by using a GC–MS system in the EI mode with a maximum *m*/*z* range of 600. When required, all solvents and reagents were purified by standard techniques. Tetrahydrofuran was purified by distillation from sodium/benzophenone and then degassed before use. All reactions were conducted under a positive pressure of argon by using standard benchtop techniques for the handling of air-sensitive materials. Chromatographic separations were carried out under pressure on Merck silica gel 60 (0.040–0.063 mm) by using flash column techniques. Unless otherwise mentioned, the reported yields are for chromatographically pure isolated products.

Addition Method A: A mixture of Cp_2TiCl_2 (2.20 mmol) and Zn (6.60 mmol.) in strictly deoxygenated THF (11.0 mL) was stirred at room temperature until the red solution had turned green. In a

separate flask, the epoxide (1.00 mmol) and sulfone (1, 2, 5, or 10 mmol) were dissolved in strictly deoxygenated THF (10.0 mL). The green Ti^{III} solution was slowly added by cannula to the epoxide solution. After 30 min, an excess amount of saturated NaH_2PO_4 was added, and the mixture was stirred for 2 h. The mixture was filtered to remove the insoluble titanium salts. The filtrate was extracted with diethyl ether, and the organic layer was washed with H_2O and brine and then dried with anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified by flash chromatography.

Addition Method B: A mixture of Cp_2TiCl_2 (2.20 mmol) and Zn (6.60 mmol) in strictly deoxygenated THF (11.0 mL) was stirred at room temperature until the red solution had turned green. In a separate flask, the epoxide (1.00 mmol) and sulfone (1, 2, 5 or 10 mmol) were dissolved in strictly deoxygenated THF (10.0 mL). The epoxide solution was slowly added by cannula to the green Ti^{III} solution. After 1 h, an excess amount of saturated NaH_2PO_4 was added, and the mixture was stirred for 2 h. The mixture was filtered to remove the insoluble titanium salts. The filtrate was extracted with diethyl ether, and the organic layer was washed with H_2O and brine and then dried with anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified by flash chromatography.

Catalytic Procedure: A mixture of Cp_2TiCl_2 (0.20 mmol) and Zn (8.00 mmol) in strictly deoxygenated THF (8.0 mL) was stirred at room temperature until the red solution had turned green. In a separate flask, the epoxide (1.00 mmol), 2,4,6-collidine (8.00 mmol), and the sulfone (1, 2, 5 or 10 mmol) were dissolved in strictly deoxygenated THF (0.8 mL). In a separate flask, chlorotrimethylsilane (TMSCl, 2.5 mmol) was strictly deoxygenated. Next, the epoxide solution and the TMSCl were slowly added through different cannulas at the same time to the green Ti^{III} solution. After 8 h, an excess amount of HCl (2 M solution) was added, and the mixture was stirred for 30 min. The layers were separated, and the aqueous phase was extracted with diethyl ether. The organic layer was washed with H_2O and brine and then dried with anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified by flash chromatography.

Compound 1a: IR: $\tilde{\nu}$ = 3496, 2929, 2350, 1609, 1449, 1304, 1147 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.8–2.1 (m, 12 H), 3.22 (m, 3 H), 7.60 (m, 3 H), 7.91 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.9 (CH_2), 25.5 (CH_2), 26.3 (CH_2), 30.9 (CH_2), 36.3 (CH_2), 44.0 (CH), 54.7 (CH_2), 74.9 (CH), 128.3 (2CH), 129.5 (2 CH), 133.8 (CH), 139.4 (C) ppm. HRMS (ESI): calcd. for $C_{16}H_{26}O_3NaS$ 291.1025; found 291.1009.

Compound 1b: IR: $\tilde{\nu}$ = 3499, 3005, 2352, 1611, 1452, 1304, 1145 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.2–1.9 (m, 12 H), 3.16 (t, J = 8.4 Hz, 2 H), 3.82 (br. s 1 H), 7.58 (m, 3 H), 7.91 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.4 (CH_2), 25.0 (CH_2), 26.7 (CH_2), 33.2 (2 CH_2), 40.3 (CH), 54.5 (CH_2), 68.8 (CH), 128.2 (2 CH), 129.5 (2 CH), 133.8 (CH), 139.4 (C) ppm. HRMS (ESI): calcd. for $C_{16}H_{26}O_3NaS$ 291.1025; found 291.1009.

Compounds 2a† and 2b*: IR: $\tilde{\nu}$ = 3519, 3065, 2929, 2851, 1450, 1294, 1151, 1093 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.80† (s, 3 H), 0.85* (s, 3 H), 1.2–2.0 (m, 20 H), 2.48 (br. s, 2 H), 3.0–3.3 (m, 6 H), 7.55 (m, 6 H), 7.89 (m, 4 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.4† (CH_3), 21.1* (CH_2), 21.2† (CH_2), 23.1* (CH_2), 23.8* (CH_3), 24.5† (CH_2), 29.9* (CH_2), 30.0* (CH_2), 31.1† (CH_2), 33.8† (CH_2), 35.0* (CH_2), 36.1† (CH_2), 37.2* (C), 37.9† (C), 52.9* (CH_2), 52.4† (CH_2), 75.8† (CH), 75.9* (CH), 128.2 (4 CH), 129.5 (4 CH), 133.8 (2 CH), 139.4 (2 C) ppm. HRMS (ESI): calcd. for $C_{15}H_{22}O_3NaS$ 305.1182; found 305.1191.

Compound 3a: IR: $\tilde{\nu}$ = 3519, 3059, 2955, 2870, 1735, 1450, 1307, 1151, 1093 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.0–2.2 (m, 9 H), 2.2 (br. s, 1 H), 3.19 (m, 2 H), 3.73 (dd, J_1 = 5.6 Hz, J_2 = 11.4 Hz), 7.58 (m, 3 H), 7.88 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.7 (CH_2), 26.7 (CH_2), 30.1 (CH_2), 34.9 (CH_2), 46.6 (CH), 55.3 (CH_2), 78.9 (CH), 128.2 (2 CH), 129.5 (2 CH), 133.9 (CH), 139.3 (C) ppm. HRMS (ESI): calcd. for $C_{13}H_{18}O_3NaS$ 277.0869; found 277.0886.

Compound 3b: IR: $\tilde{\nu}$ = 3522, 3049, 2973, 2850, 1728, 1453, 1310, 1151, 1090 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.2–2.0 (m, 10 H), 3.18 (m, 2 H), 4.12 (br. s, 1 H), 7.59 (m, 3 H), 7.91 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.9 (CH_2), 22.7 (CH_2), 28.9 (CH_2), 35.4 (CH_2), 44.4 (CH), 55.6 (CH_2), 74.1 (CH), 128.3 (2 CH), 129.5 (2 CH), 133.8 (CH), 139.4 (C) ppm. HRMS (ESI): calcd. for $C_{13}H_{18}O_3NaS$ 277.0869; found 277.0886.

Compound 4a: IR: $\tilde{\nu}$ = 3487, 2929, 2851, 1729, 1450, 1307, 1145 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.85 (t, J = 6.6 Hz, 3 H), 1.21 (br. s, 10 H), 1.2–1.8 (m, 4 H), 3.17 (m, 2 H), 3.43 (dd, J_1 = 6.2 Hz, J_2 = 10.6 Hz, 1 H), 3.56 (dd, J_1 = 4.8 Hz, J_2 = 11.0 Hz, 1 H), 7.58 (m, 3 H), 7.90 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.3 (CH_3), 22.8 (CH_2), 24.4 (CH_2), 26.9 (CH_2), 29.7 (CH_2), 30.0 (CH_2), 31.9 (CH_2), 39.5 (CH), 54.4 (CH_2), 65.2 (CH_2), 128.3 (2 CH), 129.5 (2 CH), 133.9 (CH), 139.3 (C) ppm. HRMS (ESI): calcd. for $C_{16}H_{26}O_3NaS$ 321.1495; found 321.1486.

Compound 5a: IR: $\tilde{\nu}$ = 3526, 3065, 2935, 2870, 1735, 1456, 1307, 1151, 1093 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.84 (t, J = 7.4 Hz, 6 H), 1.0–1.2 (m, 12 H), 1.63 (m, 2 H), 3.10 (m, 2 H), 3.29 (br. s, 2 H), 7.60 (m, 3 H), 7.90 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.2 (2 CH_3), 23.6 (2 CH_2), 25.2 (2 CH_2), 27.2 (CH_2), 33.5 (2 CH_2), 39.6 (C), 51.9 (CH_2), 66.9 (CH_2), 128.3 (2 CH), 129.5 (2 CH), 133.9 (CH), 139.2 (C) ppm. HRMS (ESI): calcd. for $C_{18}H_{30}O_3NaS$ 349.1808; found 349.1811.

Compound 1ca: IR: $\tilde{\nu}$ = 3439, 3067, 2929, 1720, 1644, 1455, 1298, 1147, 1071 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.25 (d, J = 6.6 Hz, 3 H), 1.1–2.3 (m, 12 H), 3.17 (m, 1 H), 3.58 (m, 1 H), 7.58 (m, 3 H), 7.88 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1 (CH_3), 24.8 (CH_2), 25.7 (CH_2), 32.5 (CH_2), 35.1 (CH_2), 36.3 (CH_2), 42.3 (CH), 59.1 (CH), 76.3 (CH), 129.2 (2 CH), 129.3 (2 CH), 133.7 (CH), 137.4 (C) ppm. HRMS (ESI): calcd. for $C_{15}H_{22}O_3NaS$ 305.1182; found 305.1188.

Compound 1cb: ^1H NMR (400 MHz, $CDCl_3$): δ = 1.23 (d, J = 6.8 Hz, 3 H), 0.8–2.0 (m, 12 H), 3.20 (m, 2 H), 7.59 (m, 3 H), 7.87 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8 (CH_3), 24.6 (CH_2), 25.2 (CH_2), 29.7 (CH_2), 32.2 (CH_2), 35.7 (CH_2), 42.0 (CH), 57.8 (CH), 74.4 (CH), 129.0 (2 CH), 129.1 (2 CH), 133.5 (CH), 137.1 (C) ppm. HRMS (ESI): calcd. for $C_{15}H_{22}O_3NaS$ 305.1182; found 305.1188.

Compound 1da: ^1H NMR (200 MHz, $CDCl_3$): δ = 1.25 (d, 3 H), 1.1–2.0 (m, 12 H), 3.17 (m, 1 H), 3.76 (m, 1 H), 7.58 (m, 3 H), 7.88 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1 (CH_3), 20.8 (CH_2), 25.8 (CH_2), 27.9 (CH_2), 31.6 (CH_2), 32.9 (CH_2), 38.3 (CH), 58.0 (CH), 69.9 (CH), 129.2 (2 CH), 129.3 (2 CH), 133.7 (CH), 137.4 (C) ppm. HRMS (ESI): calcd. for $C_{15}H_{22}O_3NaS$ 305.1182; found 305.1188.

Compound 1db: ^1H NMR (200 MHz, $CDCl_3$): δ = 1.25 (d, 3 H), 1.1–2.0 (m, 12 H), 3.17 (m, 1 H), 3.74 (m, 1 H), 7.58 (m, 3 H), 7.88 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.9 (CH_3), 20.4 (CH_2), 24.4 (CH_2), 25.3 (CH_2), 31.3 (CH_2), 33.1 (CH_2), 38.6 (CH), 57.8 (CH), 67.1 (CH), 129.2 (2 CH), 129.3 (2 CH), 133.7 (CH), 137.4 (C) ppm. HRMS (ESI): calcd. for $C_{15}H_{22}O_3NaS$ 305.1182; found 305.1188.

Compounds 2ca, 2cb, 2da, and 2db: IR: $\tilde{\nu}$ = 3508, 3061, 2935, 1632, 1462, 1298, 1153, 1071 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.79 (s, 6 H), 0.86 (s, 6 H), 1.26 (m, 12 H), 1.1–1.7 (m, 32 H), 2.1–2.6 (m, 8 H), 2.99 (br. s, 4 H), 3.0–3.5 (m, 8 H), 7.56 (m, 12 H), 7.85 (m, 8 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, isomer **2ca**): δ = 17.9 (CH_3), 18.4 (CH_3), 21.3 (CH_2), 25.1 (CH_2), 30.0 (CH_2), 35.2 (CH_2), 39.2 (C), 39.7 (CH_2), 55.9 (CH), 73.1 (CH), 129.2 (2 CH), 129.4 (2 CH), 133.9 (CH), 137.1 (C) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, isomer **2cb**): δ = 16.1 (CH_3), 17.5 (CH_3), 21.2 (CH_2), 24.8 (CH_2), 31.1 (CH_2), 37.1 (CH_2), 38.6 (C), 41.2 (CH_2), 56.5 (CH), 76.1 (CH), 128.5 (2 CH), 130.2 (2 CH), 134.0 (CH), 137.6 (C) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, isomer **2da**): δ = 18.2 (CH_3), 21.3 (CH_2), 22.2 (CH_2), 22.8 (CH_3), 29.4 (CH_2), 35.5 (CH_2), 35.8 (CH_2), 38.1 (C), 56.3 (CH), 74.0 (CH), 128.3 (2 CH), 130.2 (2 CH), 133.3 (CH), 137.6 (C) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, isomer **2db**): δ = 17.0 (CH_3), 20.9 (CH_2), 23.1 (CH_2), 24.9 (CH_3), 30.1 (CH_2), 34.4 (CH_2), 35.5 (CH_2), 37.9 (C), 56.8 (CH), 76.7 (CH), 129.3 (2 CH), 129.5 (2 CH), 133.8 (CH), 137.5 (C) ppm. HRMS (ESI): calcd. for $C_{16}H_{24}O_3NaS$ 319.1338; found 319.1348.

Compound 3da (less polar *cis* isomer): IR: $\tilde{\nu}$ = 3487, 3059, 2942, 2877, 1722, 1450, 1300, 1151, 1086 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (d, J = 7.0 Hz, 3 H), 1.4–1.9 (m, 7 H), 2.21 (m, 1 H), 3.19 (m, 1 H), 4.10 (m, 1 H), 7.60 (m, 3 H), 7.89 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.5 (CH_3), 21.8 (CH_2), 29.0 (CH_2), 29.3 (CH_2), 34.8 (CH_2), 43.1 (CH), 59.1 (CH), 73.2 (CH), 129.1 (4 CH), 133.5 (CH), 137.1 (C) ppm. HRMS (ESI): calcd. for $C_{14}H_{20}O_3NaS$ 291.1025; found 291.1016.

Compounds 3db* and 3ca†: IR: $\tilde{\nu}$ = 3526, 3074, 2933, 2857, 1729, 1449, 1307, 1147, 1095 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.24* (d, J = 6.9 Hz, 3 H), 1.25† (d, J = 6.8 Hz, 3 H), 1.1–2.2 (m, 20 H), 3.10* (m, 1 H), 3.33† (m, 1 H), 3.73† (dd, J_1 = 6.0 Hz, J_2 = 12.2 Hz, 1 H), 4.09* (m, 1 H), 7.58 (m, 6 H), 7.85 (m, 4 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.3† (CH_3), 14.6* (CH_3), 21.8* (CH_2), 22.0† (CH_2), 28.3* (CH_2), 29.2* (CH_2), 31.5† (CH_2), 34.0† (CH_2), 35.1* (CH_2), 35.3* (CH_2), 42.6* (CH_2), 44.7† (CH), 59.1† (CH), 59.5* (CH), 75.0* (CH), 79.2† (CH), 129.2 (4 CH), 129.3 (4 CH), 133.8† (CH), 133.9* (CH), 137.3 (2 C) ppm. HRMS (ESI): calcd. for $C_{14}H_{20}O_3NaS$ 291.1025; found 291.1016.

Compound 3cb (more polar *trans* isomer): IR: $\tilde{\nu}$ = 3493, 3085, 2979, 2887, 1722, 1456, 1305, 1149, 1093 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (d, J = 6.9 Hz, 3 H), 1.0–1.9 (m, 9 H), 3.13 (m, 1 H), 3.79 (dd, J_1 = 5.7 Hz, J_2 = 11.8 Hz, 1 H), 7.60 (m, 3 H), 7.88 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.7 (CH_3), 21.3 (CH_2), 29.1 (CH_2), 33.1 (CH_2), 34.6 (CH_2), 44.78 (CH), 58.8 (CH), 79.1 (CH), 129.0 (4 CH), 133.6 (CH), 137.1 (C) ppm. HRMS (ESI): calcd. for $C_{14}H_{20}O_3NaS$ 291.1025; found 291.1016.

Compounds 4c* and 4d†: IR: $\tilde{\nu}$ = 3490, 3105, 2895, 1731, 1449, 1315, 1139 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.87 (t, J = 6.2 Hz, 6 H), 1.24 (m, 26 H), 1.64 (m, 6 H), 1.93 (m, 2 H), 3.27 (m, 2 H), 3.52 (m, 4 H), 7.60 (m, 6 H), 7.88 (m, 4 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.3 (2 CH_3), 14.4* (CH_3), 14.5† (CH_3), 22.8 (2 CH_2), 26.5† (CH_2), 27.1* (CH_2), 29.7* (CH_2), 29.8† (CH_2), 30.3† (CH_2), 31.6† (CH_2), 31.7† (CH_2), 31.9* (2 CH_2), 32.3* (CH_2), 38.0 (2 CH), 58.2† (CH), 58.6* (CH), 65.4* (CH_2), 65.8† (CH_2), 129.3 (8 CH), 133.8 (2 CH), 137.4 (2 C) ppm. HRMS (ESI): calcd. for $C_{17}H_{28}O_3NaS$ 335.1651; found 335.1657.

Compound 5c: IR: $\tilde{\nu}$ = 3496, 3160, 2925, 2850, 1729, 1449, 1305, 1149 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (m, 6 H), 1.0–1.4 (m, 16 H), 2.22 (dd, J_1 = 5.2 Hz, J_2 = 12.6 Hz, 2 H), 3.18 (m, 1 H), 3.39 (m, 2 H), 7.59 (m, 3 H), 7.89 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.3 (2 CH_3), 17.8 (CH_3), 23.7 (2 CH_2), 25.1 (2 CH_2), 34.0 (2 CH_2), 34.1 (CH_2), 40.7 (C), 56.2 (CH), 66.4 (CH_2), 128.5 (2 CH), 129.4 (2 CH), 134.0 (CH), 138.7 (C) ppm. HRMS (ESI): calcd. for $C_{19}H_{32}O_3NaS$ 363.1964; found 363.1948.

Compound 9: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.2–1.9 (m, 8 H), 2.06 (m, 2 H), 3.33 (dt, J_1 = 4.4 Hz, J_2 = 9.6 Hz, 1 H), 6.07 (dd, J_1 = 8.8 Hz, J_2 = 15.8 Hz, 1 H), 6.53 (d, J = 15.8 Hz, 1 H), 7.32 (m, 5 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.0 (CH_2), 25.4 (CH_2), 31.7 (CH_2), 34.1 (CH_2), 50.9 (CH), 73.4 (CH), 126.4 (2 CH), 127.6 (CH), 128.8 (2 CH), 132.2 (CH), 132.3 (CH), 137.2 (C) ppm. HRMS (ESI): calcd. for $C_{14}H_{18}ONa$ 225.1249; found 225.1267.

Compound 12: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.84 (s, 3 H), 0.85 (s, 3 H), 1.64 (s, 3 H), 1.1–2.2 (m, 9 H), 3.25 (m, 2 H), 5.24 (br. s 1 H), 7.58 (m, 3 H), 7.89 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.9 (CH_3), 22.8 (CH_3), 23.4 (CH_3), 26.9 (CH_2), 27.7 (CH_2), 30.1 (CH_2), 33.1 (CH_2), 39.4 (C), 53.7 (CH_2), 74.2 (C), 118.4 (CH), 128.2 (2 CH), 129.5 (2 CH), 133.8 (CH), 134.3 (C), 139.4 (C) ppm. HRMS (ESI): calcd. for $C_{18}H_{26}O_3NaS$ 345.1495; found 345.1490.

Compound 17: IR: $\tilde{\nu}$ = 3408, 2923, 1720, 1650, 1449, 1298, 1147 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.8–2.1 (m, 5 H), 3.21 (t, J = 7.4 Hz, 2 H), 3.71 (m, 4 H), 7.62 (m, 3 H), 7.91 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.2 (CH_2), 41.0 (CH), 54.4 (CH_2), 64.9 (2 CH_2), 128.2 (2 CH), 129.6 (2 CH), 134.0 (2 CH), 139.2 (C) ppm. HRMS (ESI): calcd. for $C_{11}H_{16}O_4NaS$ 267.0661; found 267.0651.

Compound 21a (less polar isomer): IR: $\tilde{\nu}$ = 3461, 2929, 2851, 1443, 1307, 1158, 1093 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.74 (s, 3 H), 0.88 (m, 3 H), 1.27 (m, 10 H), 1.4–2.2 (m, 4 H), 3.0–3.6 (m, 6 H), 3.91 (m, 1 H), 7.60 (m, 3 H), 7.90 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.3 (CH_3), 19.4 (CH_3), 22.8 (CH_2), 24.1 (CH_2), 26.7 (CH_2), 29.4 (CH_2), 31.7 (CH_2), 32.0 (CH_2), 40.7 (C), 52.2 (CH_2), 70.1 (CH_2), 80.1 (CH), 128.2 (2 CH), 129.5 (2 CH), 133.9 (CH), 139.3 (C) ppm. HRMS (ESI): calcd. for $C_{18}H_{30}O_4NaS$ 365.1757; found 365.1754.

Compound 21b (more polar isomer): IR: $\tilde{\nu}$ = 3480, 2925, 2862, 1449, 1306, 1162, 1090 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.67 (s, 3 H), 0.85 (t, J = 6.6 Hz, 3 H), 1.24 (m, 10 H), 1.91 (m, 2 H), 2.94 (br. s, 2 H), 3.0–3.4 (m, 4 H), 3.67 (d, J = 11.4 Hz, 1 H), 7.59 (m, 3 H), 7.89 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.3 (CH_3), 18.2 (CH_3), 22.8 (CH_2), 26.9 (CH_2), 27.9 (CH_2), 29.5 (CH_2), 31.6 (CH_2), 32.0 (CH_2), 40.8 (C), 52.1 (CH_2), 68.0 (CH_2), 77.3 (CH), 128.2 (2 CH), 129.5 (2 CH), 133.9 (CH), 139.2 (C) ppm. HRMS (ESI): calcd. for $C_{18}H_{30}O_4NaS$ 365.1757; found 365.1754.

Compound 23: IR: $\tilde{\nu}$ = 3451, 3060, 2934, 2855, 1735, 1461, 1260, 1150 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.87 (m, 6 H), 1.24 (m, 10 H), 2.01 (d, J = 13.2 Hz, 1 H), 2.12 (d, J = 16.4 Hz, 1 H), 2.39 (d, J = 13.2 Hz, 1 H), 2.70 (d, J = 16.3 Hz, 1 H), 3.29 (d, J = 9 Hz, 1 H), 7.53 (m, 3 H), 7.84 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.3 (CH_3), 22.0 (CH_3), 22.8 (CH_2), 26.8 (CH_2), 29.5 (CH_2), 32.0 (CH_2), 32.5 (CH_2), 40.7 (CH_2), 43.8 (C), 46.5 (CH_2), 78.3 (CH_2), 96.4 (C), 126.6 (2 CH), 129.1 (2 CH), 132.5 (CH), 142.5 (C), 156.2 (C) ppm. HRMS (ESI): calcd. for $C_{19}H_{28}O_4NaS$ 375.1600; found 375.1603.

Compound 33: IR: $\tilde{\nu}$ = 3500, 3065, 2929, 2864, 1722, 1450, 1300, 1151, 1093 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.82 (s, 3 H), 0.83 (s, 3 H), 1.74 (m, 2 H), 3.22 (m, 2 H), 4.37 (s, 1 H), 7.26 (m, 4 H), 7.59 (m), 7.90 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.9 (CH_3), 24.0 (CH_3), 31.4 (CH_2), 37.9 (C), 53.0 (CH_2), 81.2 (CH), 127.8 (2 CH), 127.9 (CH), 128.0 (2 CH), 128.3 (2 CH), 129.5 (2 CH), 133.8 (CH), 139.3 (C), 141.5 (C) ppm. HRMS (ESI): calcd. for $C_{18}H_{22}O_3NaS$ 341.1182; found 341.1172.

Acknowledgments

Financial support from the Junta de Castilla y León (SA200A12-1) is gratefully acknowledged. S. E. M. and P. H. T. would also like to thank the Spanish Ministry of Education and the University of Salamanca for the fellowships that allowed them to fulfill this work.

[1] a) G. A. Russell, H. Tashtoush, P. Ngoviwatchai, *J. Am. Chem. Soc.* **1984**, *106*, 4622–4623; b) G. A. Russell, P. Ngoviwatchai, *J. Org. Chem.* **1989**, *54*, 1836–1842.

[2] a) D. H. R. Barton, H. Togo, S. Z. Zard, *Tetrahedron Lett.* **1985**, *26*, 6349–6352; b) G. E. Keck, J. H. Byers, A. M. Tafesh, *J. Org. Chem.* **1989**, *53*, 1127–1128; c) J. R. McCarthy, D. P. Matthews, D. M. Stemerick, E. W. Huber, P. Bey, B. J. Lippert, R. D. Snyder, P. S. Sunkara, *J. Am. Chem. Soc.* **1991**, *113*, 7439–7440; d) B. Quiclet-Sire, S. Z. Zard, *J. Am. Chem. Soc.* **1996**, *118*, 1209–1210; e) F. Bertrand, B. Quiclet-Sire, S. Z. Zard, *Angew. Chem. Int. Ed.* **1999**, *38*, 1943–1946; *Angew. Chem.* **1999**, *111*, 2135; f) O. Yamazaki, H. Togo, S. Matsubayashi, M. Yokoyama, *Tetrahedron Lett.* **1998**, *39*, 1921–1924; g) O. Yamazaki, H. Togo, S. Matsubayashi, M. Yokoyama, *Tetrahedron* **1999**, *55*, 3735–3747; h) C. Ollivier, P. Renaud, *Angew. Chem. Int. Ed.* **2000**, *39*, 925–928; *Angew. Chem.* **2000**, *112*, 946; i) C. Cadot, J. Cossy, P. I. Dalko, *Chem. Commun.* **2000**, 1017–1018; j) D. H. Cho, D. O. Jang, *Tetrahedron Lett.* **2005**, *46*, 1799–1742; k) M. M. Zhao, C. Qu, J. E. Lynch, *J. Org. Chem.* **2005**, *70*, 6944–6947; l) A. P. Schaffner, V. Darmercy, P. Renaud, *Angew. Chem. Int. Ed.* **2006**, *45*, 5847–5849; *Angew. Chem.* **2006**, *118*, 5979.

[3] W. A. Nugent, T. V. RajanBabu, *J. Am. Chem. Soc.* **1988**, *110*, 8561–8562.

[4] T. V. RajanBabu, W. A. Nugent, *J. Am. Chem. Soc.* **1989**, *111*, 4525–4527.

[5] a) A. Gansäuer, M. Pierobon, H. Bluhm, *Angew. Chem. Int. Ed.* **1998**, *37*, 101–103; *Angew. Chem.* **1998**, *110*, 107; b) A. Gansäuer, H. Bluhm, M. Pierobon, *J. Am. Chem. Soc.* **1998**, *120*, 12849–12859; c) A. Gansäuer, H. Bluhm, B. Rinker, S. Narayan, M. Schick, T. Lauterbach, M. Pierobon, *Chem. Eur. J.* **2003**, *9*, 531–542.

[6] a) A. Gansäuer, H. Bluhm, *Chem. Commun.* **1998**, 2143–2144; b) A. Gansauer, T. Lauterbach, D. Geich-Gimbel, *Chem. Eur. J.* **2004**, *10*, 4983–4990.

[7] T. Shono, N. Kise, T. Fujimoto, N. Tominaga, H. Morita, *J. Org. Chem.* **1992**, *57*, 7175–7187.

[8] A. F. Barrero, A. Rosales, J. M. Cuerva, J. E. Oltra, *Org. Lett.* **2003**, *5*, 1935–1938.

[9] a) W. A. Nugent, T. V. RajanBabu, M. S. Beattie, *J. Am. Chem. Soc.* **1990**, *112*, 6408–6409; b) J. S. Yadav, T. Shekharam, V. R. Gadgil, *J. Chem. Soc., Chem. Commun.* **1990**, *11*, 843–845; c) A. Fernández-Mateos, S. Encinas Madrazo, P. Herrero Teijón, R. Rubio González, *Eur. J. Org. Chem.* **2010**, 856–861.

[10] a) T. K. Chakraborty, S. Das, *Tetrahedron Lett.* **2002**, *43*, 2313–2315; b) T. K. Chakraborty, S. Dutta, *J. Chem. Soc. Perkin Trans. 1* **1997**, 1257–1259.

[11] A. Fernández-Mateos, S. Encinas Madrazo, P. Herrero Teijón, R. Rubio González, *J. Org. Chem.* **2009**, *74*, 3913–3918.

[12] A. F. Barrero, J. F. Quílez del Moral, E. M. Sánchez, J. F. Arteaga, *Org. Lett.* **2006**, *8*, 669–672.

[13] J. S. Yadav, T. Shekharam, D. Srinivas, *Tetrahedron Lett.* **1992**, *33*, 7973–7976.

Received: October 1, 2014
Published Online: December 4, 2014

