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Zinc Homologation–Elimination Reaction of α-Sulfinyl Carbanions as a New Route to Olefins

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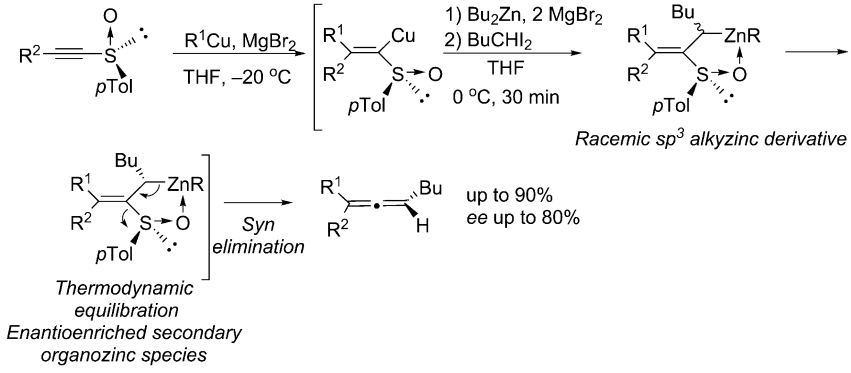
α-Lithiosulfinyl carbanions react either intermolecularly, after transmetalation into an organocopper derivative in an S_N2-type process, with zinc carbenoids, or intramolecularly by higher-order zincates through a tandem zinc homologation–β-elimination reaction into the corresponding alkenes. α,α- and α,β-Disubstituted alkenes can also be produced through these two methodologies.

Introduction

Enantiomerically pure sulfoxide moieties are very efficient chiral auxiliaries that are inducing important asymmetric transformations. Therefore, the past decades have witnessed an exponential use of these chiral auxiliaries in asymmetric synthesis, establishing the chiral sulfinyl group as one of the most efficient and versatile chiral controllers in carbon–carbon formations.[1] In this context, we recently reported that the chiral sulfinyl group plays multiple roles in asymmetric nucleophilic allylations[2] as chelating elements to slow down the metalotropic equilibrium, as activators and regiocontrol elements for the carbometalation reaction of the alkynyl moiety, as well as a chiral auxiliary for the creation of two new stereogenic centers, including the extremely challenging all-carbon quaternary stereocenters.[3] In such reaction, three new carbon–carbon bonds are created in a single-pot operation from common starting materials.[4] However, in most of the applications, sulfoxides are the only chiral synthetic tools and must be disposed of at the end of the sequence. In this context, we[5] and others[6,7] have recently reported the easy transformation of vinyl sulfoxides into organometallic species. This was found to be synthetically very interesting, as further functionalization easily increases the complexity of the carbon skeleton. In contrast, the thermal *syn*-β-elimination reaction between a hydrogen and a sulfoxide is a well-known process and has been found to be a powerful route to chiral alkenes.[8] Similarly, the reduction of sulfoxides[9] as well as the β-elimination reaction of sulfinyl radicals (estimated to be very fast process, ca 10^9 s^{-1}) for aryl sulfoxide borne by a Csp^3 center[10] or a Csp^2 center[11] was recently used in synthesis. Following the pioneering work of Posner,[12] we were recently interested in the formation of enantioenriched allene by the in situ combination of a carbometalation reaction



Scheme 1. Combined carbometalation–zinc homologation–*syn*-elimination sequence.

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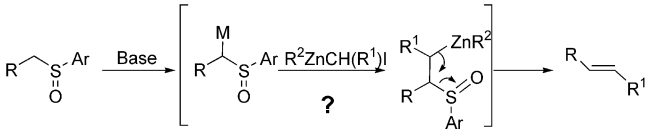
zinc homologation followed by a β-elimination reaction as described in Scheme 1.[13] Although the enantioselectivity of the reaction was only moderate, it implies an interesting "deracemization" of the sp^3 organometallic species before the β-elimination reaction.

The question of the fate of sp^3 α-sulfinyl carbanions for the tandem zinc homologation followed by β-elimination reactions as a new source of olefins was logically raised (Scheme 2).

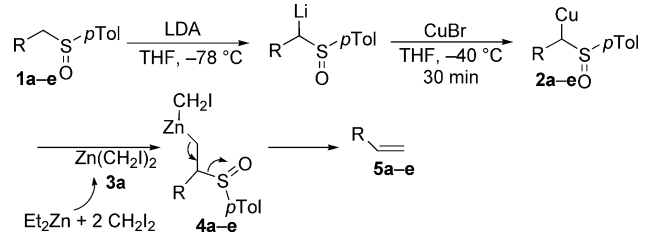


Scheme 2. α-Sulfinyl carbanions as a new source of alkenes.

The transformation of alkyl sulfones into olefins is a well-known reaction,[14] and it has been successfully used in natural product syntheses[15] but usually requires unstable lithium or magnesium carbenoids (generated at low temperature).[16] The use of thermally stable zinc carbenoids[17] combined with the well-known and rich chemistry of sulfoxides led us to examine this reaction in detail. Moreover, the in situ formation of zinc sulfenates (leaving group) may find interesting synthetic applications.[18]

Results and Discussion

Our first experiments were performed by treatment of alkyl sulfoxides **1a**,**e** with one equivalent of LDA at low temperature, followed by a transmetalation reaction to give the corresponding α-sulfinyl copper species **2a**–**e**. Then, by addition of zinc carbenoid **3a**, easily prepared by the addition of Et_2Zn (1 equiv.) to CH_2I_2 (2 equiv.),[19] the intermolecular zinc homologated adducts **4a**–**e** are in situ formed, followed by a β-elimination reaction to give monosubstituted olefins **5a**–**e** in good overall yields as described in Scheme 3 and Table 1.



Scheme 3. General route to the preparation of terminal olefins.

As can be seen from analysis of Table 1, alkyl sulfoxides **1a** (R = n-$C_{11}H_{23}$) and **1b** [R = $Ph(CH_2)_2$] lead to the corresponding alkenes **5a** and **5b** in good isolated yields (Table 1, entries 1 and 2, respectively). When benzyl sulfoxide **1c** (R = Ph) was used as starting material, styrene **5c** was obtained only in moderate yield (Table 1, entry 3) due to the volatile nature of the final product. Various substituted styrenyl derivatives were also prepared in good yields by this simple strategy (Table 1, entries 4 and 5). Dimethyl sulfoxide

Table 1. Preparation of 1-alkenes from α-sulfinyl copper and zinc carbenoid species.

Entry[a]	R	Yield [%][b] (product)
1 (**1a**)	n-$C_{11}H_{23}$	77 (**5a**)
2 (**1b**)	$Ph(CH_2)_2$	70 (**5b**)
3 (**1c**)	Ph	50 (**5c**)
4 (**1d**)	pTol	65 (**5d**)
5 (**1e**)	pMeOC_6H_4	67 (**5e**)

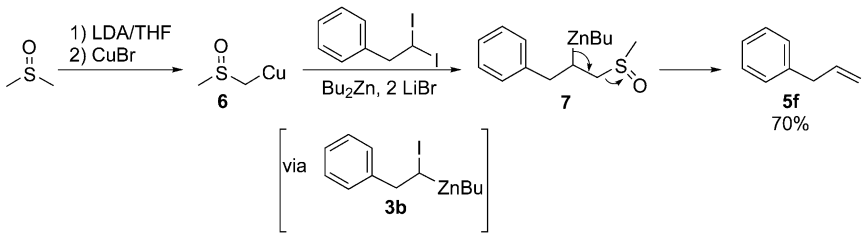
[a] See experimental part. [b] Isolated yield after column chromatography.

(DMSO) can also be used in this reaction as a source of terminal olefins as described in Scheme 4. In such a case, dimsyl copper **6** (obtained after metalation and transmetalation of DMSO) was treated with the in situ prepared secondary zinc carbenoid **3b** (formed by treatment of 1,1-bisiodoalkane[20] with Bu_2Zn, 2 LiBr)[21] to give the zinc homologated product **7**, which spontaneously undergoes a β-elimination reaction to lead to the corresponding allylbenzene **5f** in 70% isolated yield. This particular example illustrates the mild experimental condition used for this transformation, as no conjugated alkene (β-methyl styrene) was detected.

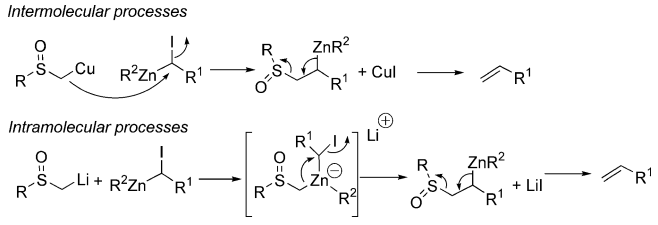
The first step, namely the metalation followed by the transmetalation reactions into the organocopper species occurs quantitatively to provide the corresponding dimsyl copper species **6** in quantitative yield as originally described in Scheme 4. Then, Bu_2Zn and $RCHI_2$ are all added to the reaction mixture at –20 °C. As the transmetalation from alkylcopper to alkylzinc is a slow process at –20 °C, the reaction between R_2Zn and $RCHI_2$ occurs first to lead to the in situ formation of the secondary zinc carbenoid **3b**.[21] This carbenoid readily homologates alkylcopper **6** (although not demonstrated, it may be through a S_N2-type mechanism)[22] into species **7**, which undergoes spontaneous β-elimination to give the expected alkene in good yield (intermolecular processes, Scheme 5). The β-elimination could proceed either by a *syn* or *anti* process.

Although this reaction proceeds nicely, an excess amount of zinc carbenoid (classically 3 equiv.) was needed to reach good chemical yields. Therefore, to improve our methodology and to only use stoichiometric amounts of reagents, we decided to investigate the intramolecular reaction between α-sulfinyllithium derivatives and zinc carbenoid by a 1,2-zincate rearrangement (intramolecular processes, Scheme 5).[23] In such an intramolecular rearrangement, the organolithium species reacts with the zinc atom to form first a zincate species and then, one of the ligands on the zinc migrates to the carbon center bearing the leaving group to lead to the rearranged product.[24]

Accordingly, dodecyl p-tolyl sulfoxide (**1a**) was first metalated with LDA and then added to bis(iodomethyl)zinc carbenoid **3a**, in a 1 to 1 ratio, to form the corresponding zincate **8**. However, even after a few hours at room temperature, no rearrangement was observed (path A, Scheme 6). Either zincate **8** is not reactive enough to undergo the expected 1,2-metalate rearrangement or the in situ generated $HN(iPr)_2$ protonates organozincate **8** (two possible different



Scheme 4. DMSO as a source of alkene.

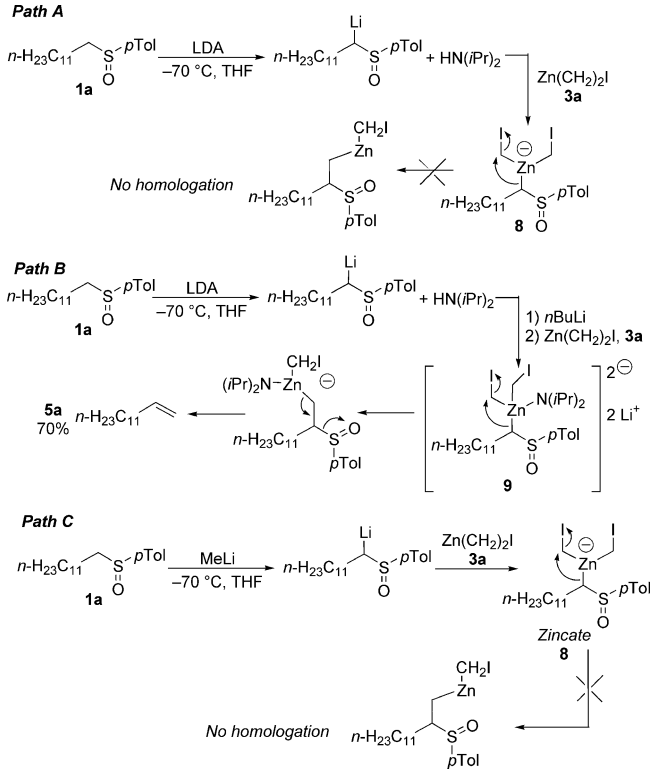


Scheme 5. Two possible mechanistic pathways.

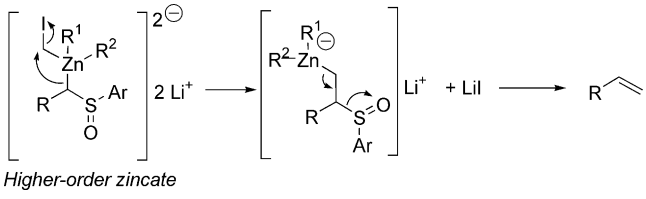
carbon–carbon bonds can be protonated). Therefore, to solve these potential problems, once the alkyl sulfoxide was deprotonated to give the α-sulfinyl carbanion and $HN(iPr)_2$, one more equivalent of *n*BuLi was added to regenerate LDA (path B, Scheme 6). Then, zinc carbenoid **3a** was added to the reaction mixture and after 1 h at room temperature, we were pleased to observe the formation of alkene **5a** in 70% isolated yield as described in Scheme 6, path B. Following this positive result, we wanted to further underline the effect of regenerated LDA, and more precisely, to see if the formally higher-order zincate **9** (we use the term higher-order zincate when four groups are formally attached to the zinc atom)[25] was necessary to promote the rearrangement. Although alternative mechanisms could be proposed, such as the S_N2 substitution on the carbon–iodine bond of the zincate generated from LDA and zinc carbenoid **3a**, we proposed that the formation of higher-order zincate should be faster.[26] As we have already reported that higher-order nucleophilic species are needed to perform anionic rearrangements,[27] we tested this hypothesis by performing the same experiment with MeLi as deprotonating agent. When sulfoxide **1a** was metalated with MeLi, the corresponding α-sulfinyl carbanion was obtained and after addition of zinc carbenoid **3a** at –70 °C, intermediate zincate **8** was obtained (path C, Scheme 6). However, even after a few hours at room temperature, neither homologated nor alkene species was detected (Path C, Scheme 6).

Therefore, the 1,2-zincate rearrangement occurs only when a higher-order zincate is formed as a reactive intermediate (similarly to the 1,2-cuprate rearrangement, where an extra anionic charge is needed on the metal to promote the reaction)[17b,27] as described in Scheme 7. Interestingly, the added negative charge on the zinc atom by addition of $LiN(iPr)_2$ plays also the role of a dummy ligand (nontransferable group).

This new 1,2-metalate rearrangement was generalized to different primary alkyl sulfoxide derivatives (Table 2) and this improved procedure (with a 1:1 ratio between starting



Scheme 6. 1,2-Metalate rearrangement.



Scheme 7. Mechanistic hypothesis for 1,2-zincate rearrangement.

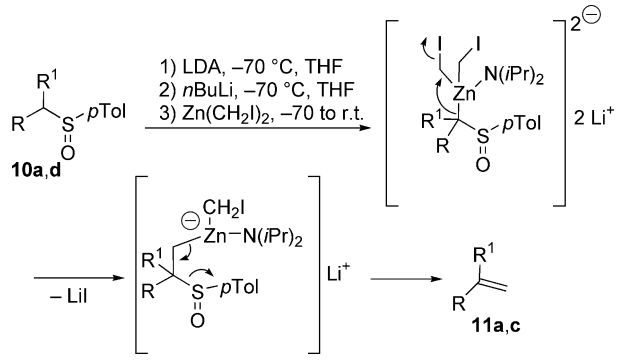
material and zinc carbenoid) led to identical yields as compared to the one described previously (Scheme 3 and Table 1, intermolecular homologation, where the sulfoxide/zinc carbenoid ratio was 1:3).[28] Then, we turned our attention to the preparation of 1,1-disubstituted olefins by reaction of secondary alkyl sulfoxides **10a**,**d** and zinc carbenoid **3a**. Our first attempt was performed by the intermolecular homologation reaction. However, this olefination reaction does not proceed in satisfactory yield when tertiary α-sulfinyl organocopper is used (only 30% yield of the final 1,1-disubstituted olefin was obtained).

Table 2. Preparation of 1-alkenes by 1,2-metalate rearrangement.

Entry[a]	R	Yield [%][b] (product)
1 (**1a**)	*n*-$C_{11}H_{23}$	70 (**5a**)
2 (**1b**)	$Ph(CH_2)_2$	60 (**5b**)
3 (**1c**)	Ph	50 (**5c**)
4 (**1d**)	*p*Tol	65 (**5d**)
5 (**1e**)	*p*$MeOC_6H_4$	65 (**5e**)

[a] See Experimental Section. [b] Isolated yield after column chromatography.

The main reason is that such a quaternary α-sulfinyl organocopper species was found to be thermally unstable, and even without addition of zinc carbenoid, this organocopper species undergoes fast degradation when the temperature reaches –40 °C. Therefore, the intramolecular 1,2-metalate rearrangement was tested as described in Scheme 8 and Table 3.



Scheme 8. Preparation of 1,1-disubstituted alkenes.

Table 3. Preparation of 1,1-disubstituted alkenes from disubstituted alkyl sulfoxides.

Entry[a]	R	R^1	Yield [%][b]
1 (**10a**)	*n*-$C_{11}H_{23}$	*n*-C_4H_9	66 (**11a**)
2 (**10b**)	*n*-$C_{11}H_{23}$	$CH_2CH{=}CH_2$	65 (**11b**)
3 (**10c**)	Ph	*n*-C_4H_9	68 (**11c**)
4 (**10d**)	Ph	$CH_2CH{=}CH_2$	67 (**11d**)

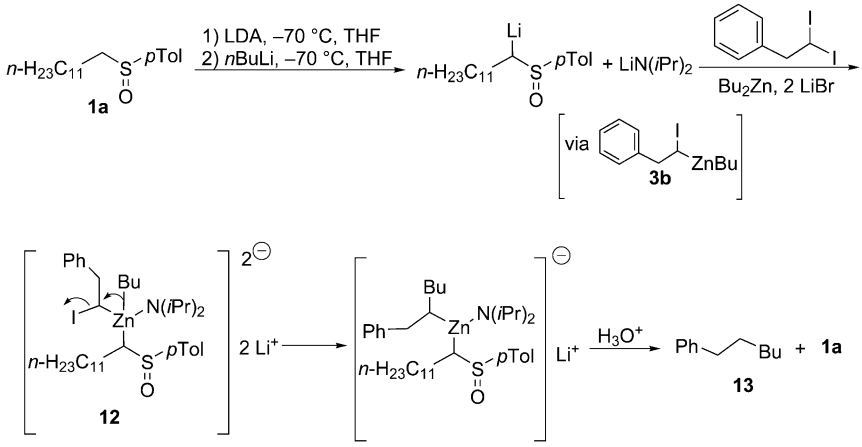
[a] See Experimental Section. [b] Isolated yield after column chromatography.

By using the conditions developed for the intramolecular 1,2-zincate rearrangement, α,α-disubstituted olefins **11** were obtained in good overall yields in an easy and straightforward manner from the corresponding tertiary α-sulfinyllithium species. It should be emphasized that the reaction does not require an excess of reagents and that the mild conditions used for this transformation leads to sensitive nonconjugated dienes such as **11b** and **11d**.

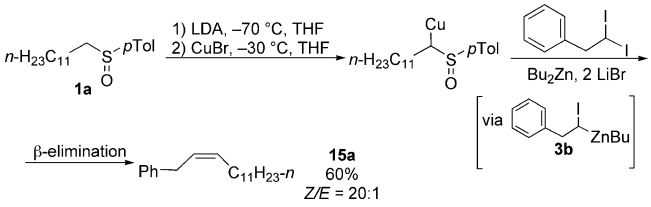
Finally, we investigated the formation of 1,2-disubstituted alkenes by the reaction of primary alkyl sulfoxides and secondary zinc carbenoids. When secondary carbenoid **3b** was added to α-sulfinyllithium species for the 1,2-intramolecular rearrangement, we did not observe the expected alkene but rather the formation of hexylbenzene **13** (Scheme 9). This result can be rationalized by a reaction between the in situ formed secondary zinc carbenoid **3b** and the lithiated sulfoxide to give the corresponding higher-order zincate **12**. In this particular case, a competition exists between the butyl and sulfinyl groups for the rearrangement. As a butyl group is a better migrating group, only the product resulting from its migration is obtained.

To succeed in the preparation of 1,2-disubstituted olefins from sulfinyl species, the intermolecular reaction was therefore tested. After metalation with LDA and transmetalation with CuBr, the corresponding α-sulfinyl copper species was treated at room temperature with the in situ prepared secondary zinc carbenoid **3b** as described in Scheme 10. Under such conditions, the zinc homologation–elimination occurred to give alkene **15a** in 60% isolated yield with a *Z*/*E* ratio of 20:1 (Scheme 10).

The observed stereoselectivity of the reaction (formation of the *Z*-isomer as major isomer) is rather puzzling and deeper mechanistic investigations are needed to clarify this stereochemical outcome. Indeed, intramolecular chelation[29] between the zinc organometallic species and the oxygen of the sulfoxide to lead to the most stable intermediate having an *anti* relationship between the benzyl and the alkyl (*n*-$C_{11}H_{23}$) groups, through a thermodynamic equilibration reaction,[30] followed by a β-elimination reaction could rationalize the stereochemistry, but the discrepancies in the *E*/*Z* ratio requires more study. Several additional ex-



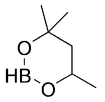
Scheme 9. Unsuccessful attempt to prepare 1,2-disubstituted alkenes.



Scheme 10. Preparation of 1,2-disubstituted alkenes by intermolecular reaction.

amples were performed as reported in Table 4. In entry 3, the stereochemistry is reversed (*Z*/*E* = 1:2) and could be rationalized by isomerization of *Z*-styrenyl adduct **15d**.[31]

Table 4. Preparation of 1,2-disubstituted alkenes.



MPBH (**1**)

PinBH (**2**)

Entry[a]	R	R^1	*Z*/*E* ratio[b]	Yield [%][c]
1 (**1a**)	*n*-$C_{11}H_{23}$	$PhCH_2$	20:1	60 (**15a**)
2 (**1b**)	$Ph(CH_2)_2$	$PhCH_2$	3:1	62 (**15b**)
3 (**1c**)	Ph	$PhCH_2$	1:2	51 (**15c**)
4 (**1f**)	*i*Pr	$PhCH_2$	12:1	40 (**15d**)

[a] See Experimental Section. [b] Determined from the NMR spectrum of the crude reaction mixture. [c] Isolated yield after column chromatography.

Conclusions

We have disclosed an easy and straightforward preparation of substituted alkenes from various alkyl sulfoxides either by an S_N2 process (intermolecular homologation followed by β-elimination) or by a 1,2-metalate rearrangement (intramolecular homologation followed by β-elimination). In the latter case, the formation of a higher-order zincate is necessary for the reaction to proceed.

Experimental Section

General: Starting sulfoxides were prepared from literature procedures[32] and the NMR spectroscopic data were in full agreement with authentic samples: **1a**, 1-methyl-4-(dodecylsulfinyl)benzene, registry number 148017-75-8; **1b**, 1-methyl-4-[2-phenylethylsulfinyl]-benzene, registry number 120982-92-5; **1c**, 1-methyl-4-[(phenylmethyl)sulfinyl]benzene, registry number 10381-70-1; **1d**, 1-methyl-4-[(4-methylphenyl)methyl]sulfinylbenzene, registry number 95126-91-3; **1e**, 1-methoxy-{[(4-methylphenyl)sulfinyl]methyl}-benzene, registry number 180746-15-0; **1f**, 1-methyl-4-[(2-methylpropyl)sulfinyl]benzene, registry number 77919-66-5; **10a**, 1-[(1-butyldodecyl)sulfinyl-4-methyl]benzene, registry number 667447-30-5; **10c**, 1-methyl-4-[(1-phenylpentyl)sulfinyl]benzene, registry number 667447-32-7; **10d**, 1-methyl-4-[(1-phenyl-3-buten-1-yl)sulfinyl]benzene, registry number 667447-34-9.

General Procedure for the Intermolecular Homologation Reaction (α-Sulfinyl Organocopper and Zinc Carbenoid; Procedure A): To a prepared solution of LDA (2 mmol) in THF (10 mL) was added the primary alkyl sulfoxide (2 mmol) dissolved in THF (2 mL) at –70 °C. The reaction mixture was warmed to –40 °C and stirred for an additional 30 min. CuBr (2 mmol) was then added, and the reaction mixture was warmed to room temperature over 30 min. Bis(iodomethyl)zinc carbenoid **3a** (6 mmol), prepared from the reaction of diethylzinc (1 M in hexanes, 6 mL, 6 mmol) and diiodomethane (3.2 g, 12 mmol) in THF at –50 °C, was then added to the reaction mixture in THF (10 mL) at room temperature. The resulting black solution was allowed to stir for 1 h at room temperature. A mixture of NH_4OH (30%) and saturated NH_4Cl (1:2) was added and the phases were separated. The water phase was extracted with diethyl ether (3×), and the combined organic phase was washed with Na_2S solution, dried, filtered, and then concentrated to give a yellow crude product. After chromatography (hexane), the colorless olefins were obtained.

General Procedure for the Intramolecular Homologation (α-Sulfinyl Organolithium and Zinc Carbenoid; Procedure B): To a prepared solution of LDA (2 mmol) in THF (10 mL) was added the primary sulfoxide (2 mmol) dissolved in THF (2 mL) at –70 °C. The reaction was warmed to –40 °C and stirred for an additional 30 min. *n*BuLi (2 mmol) was added at –70 °C, and the reaction was allowed to stir for 10 min. Bis(iodomethyl)zinc carbenoid **3a** (2 mmol), prepared from the reaction of diethylzinc (1 M in hexanes, 2 mL, 2 mmol) and diiodomethane (1 g, 4 mmol) in THF at –50 °C, was then added to the reaction mixture, and the resulting yellow solution was warmed to room temperature and stirred for 1 h. A saturated solution of NH_4Cl was then added and the phases were separated. The water phase was extracted with diethyl ether (3×), and the combined organic phase was dried with Na_2SO_4, filtered, and then concentrated to give a yellow oily crude product. After chromatography (hexane), the colorless oily olefin was obtained.

General Procedure with DMSO (Procedure C): To a prepared solution of LDA (2 mmol) in THF (10 mL) was added DMSO (2 mmol) dissolved in THF (2 mL) at –70 °C. The reaction was warmed to 0 °C and stirred for an additional 30 min. CuBr (2 mmol) was then added at –40 °C, and the reaction mixture was warmed to room temperature. 1,1-Diiodoalkane (4 mmol) dissolved in THF (4 mL) was added at room temperature followed by dibutylzinc, prepared from *n*BuLi (1.5 M in hexane, 5.3 mL, 8 mmol) and zinc bromide (0.9 g, 4 mmol) in THF (10 mL) at –30 °C. The resulting black solution was stirred for 1 h at room temperature. A mixture of NH_4OH (30%) and saturated NH_4Cl (1:2) was added and the phases were separated. The water phase was extracted with diethyl ether (3×), and the combined organic phase was washed with Na_2S solution, dried, filtered, and then concentrated to give a yellow crude product. After chromatography (hexane), the colorless olefin was obtained.

General Procedure for the Preparation of 1,2 Disubstituted Olefins (General Procedure D): To a prepared solution of LDA (2 mmol) in THF (10 mL) was added the sulfoxide (2 mmol) dissolved in THF (2 mL) at –70 °C. The reaction was warmed to –60 °C and stirred for an additional 30 min. CuBr (2 mmol) was then added at –60 °C, and the reaction was warmed to room temperature. 1,1-Diiodoalkane (4 mmol) dissolved in THF (4 mL) was added at room temperature followed by dibutylzinc, prepared from *n*BuLi (1.5 M in hexane, 5.3 mL, 8 mmol) and zinc bromide (0.9 g, 4 mmol) in THF (10 mL) at –30 °C. The resulting black solution was stirred for 1 h at room temperature. A mixture of NH_4OH (30%) and saturated NH_4Cl (1:2) was added and the phases were

separated. The water phase was extracted with diethyl ether (3×), and the combined organic phase was washed with Na_2S solution, dried, filtered, and then concentrated to give a yellow crude product. After chromatography (hexane), the colorless olefin was obtained.

1-Tridecene (5a): The reaction was performed according to general procedure A from dodecyl *p*-tolyl sulfoxide (**1a**; 617.2 mg, 2 mmol) and gave **5a** (0.281 g, 77%). When the reaction was performed according to general procedure B, **1a** (617.2 mg, 2 mmol) gave **5a** (0.280 g, 70%; registry number 2437-56-1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.8–5.7 (m, 1 H), 5–4.8 (m, 2 H), 2.1–2.0 (m, 2 H), 1.3–1.1 (m, 18 H), 0.8 (t, J = 6.7 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.1, 114.5, 34.1, 32, 29.9, 29.8,29.7, 29.6, 29.5,29.4, 29.2, 22.8, 14 ppm.

But-3-enylbenzene (5b): The reaction was performed according to general procedure A from 3-phenyl 1-(*p*-tolylsulfinyl)propane (**1b**; 516.7 mg, 2 mmol) and gave **5b** (0.18 g, 70%; registry number 768-56-9) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.2–7.0 (m, 5 H), 5.8–5.7 (m, 1 H), 4.9–4.8 (m, 2 H), 2.6 (t, J = 7.5 Hz, 2 H), 2.4–2.2 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.4, 137.7, 128, 127.9, 128.8, 125.4, 114.5, 35.1 ppm.

Vinylbenzene (5c): The reaction was performed according to general procedure A from benzyl *p*-tolyl sulfoxide (**1c**; 460.6 mg, 2 mmol) and gave **5c** (0.104 g, 50%; registry number 100-42-5) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.3–7.1 (m, 5 H), 6.7 (dd, J = 17.6 Hz, J = 10.8 Hz, 1 H), 5.7 (d, J = 10.8 Hz, 1 H), 5.2 (d, J = 10.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.5, 128.5, 128, 126.1, 113.9 ppm.

1-Methyl-4-vinylbenzene (5d): The reaction was performed according to general procedure A from 4-methylbenzyl *p*-tolyl sulfoxide (**1d**; 488.7 mg, 2 mmol) and gave **5d** (0.153 g, 65%; registry number 622-97-9) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.3 (d, J = 8.1 Hz, 2 H), 7.1 (d, J = 8.1 Hz, 2 H), 6.6 (dd, J = 10.8 Hz, J = 10.8 Hz, 1 H), 5.7 (d, J = 17.7 Hz, 1 H), 5.1 (d, J = 11.1 Hz, 1 H), 2.3 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.9, 136.2, 135, 129.1, 126.1, 112.2, 21.8 ppm.

1-Methoxy-4-vinylbenzene (5e): The reaction was performed according to general procedure A from 4-methoxybenzyl *p*-tolyl sulfoxide (**1e**; 520.7 mg, 2 mmol) and gave **5e** (0.179 g, 67%; registry number 636-69-4) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.4 (d, J = 6.3 Hz, 2 H), 6.7 (d, J = 6.3 Hz, 2 H), 6.6–6.4 (m, 1 H), 5.5 (d, J = 18.6 Hz, 1 H), 5.0 (d, J = 9.9 Hz, 1 H), 3.7 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.9, 136, 131, 126.5, 114.1, 111.6, 55.1 ppm.

Allylbenzene (5f): The reaction was performed according to general procedure C with DMSO (0.14 mL, 2 mmol) and 1,1-diiodo-2-phenylethane (1.43 g, 4 mmol,) and gave **5f** (0.165 g, 70%; registry number 410095-78-2) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.3–7.1 (m, 5 H), 6.1–5.9 (m, 1 H), 5.1–5.0 (m, 2 H), 3.4 (t, 2 H) ppm.

11a: The reaction was performed according to general procedure B from (1-undecyl-1-butyl)-*p*-tolyl sulfoxide (**10a**; 729.4 mg, 2 mmol) and gave **11a** (0.314 g, 66%; registry number 667447-31-6) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.6 (s, 1 H), 4.6 (s, 1 H), 1.9 (t, 4 H), 1.5–1.2 (m, 22 H), 0.9 (t, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.9, 105.5, 38.2, 37.9, 32.5, 30.7, 30.4, 30.3, 30.0, 27.8, 23.5, 23.1, 14.1, 14.0 ppm.

11b: The reaction was performed according to general procedure B from (1-undecyl-1-allyl)-*p*-tolyl sulfoxide (**10b**; 697.3 mg, 2 mmol) and gave **11b** (0.293 g, 65%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.8–5.6 (m, 1 H), 5.1–5.0 (m, 2 H), 4.7 (s, 1 H), 4.7 (s, 1 H), 2.8 (d, J = 6.9 Hz, 2 H), 2 (t, J = 7.2 Hz, 2 H), 1.4–1.3 (m, 2 H), 1.3–1.1 (m, 16 H), 0.9 (t, J = 6.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.6, 139.1, 138.6, 134.7, 130.3, 125.2, 118.2, 64.5, 32.3, 30.6, 29.9, 29.8, 29.7, 29.6, 27.7, 27.2, 23.03, 21.7, 14.4 ppm.

11c: The reaction was performed according to general procedure B from 1-phenyl-1-(*p*-tolylsulfinyl)-pentane sulfoxide (**10c**; 572.9 mL, 2 mmol) and gave **11c** (0.217 g, 68%; registry number 20826-80-6) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.3 (d, J = 6.9 Hz, 2 H), 7.2–7.0 (m, 2 H), 7.1 (d, J = 6.9 Hz, 1 H), 5.1 (d, J = 1.2 Hz, 1 H), 4.9 (d, J = 1.2 Hz, 1 H), 2.4 (t, J = 7.1 Hz, 2 H), 1.4–1.2 (m, 4 H), 0.8 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.1, 143.3, 141.9, 128.7, 128.6, 127.6, 126.5, 125.9, 112.3, 36.3, 35.4, 31.9, 31.6, 30.8, 22.9, 22.8, 14.4, 14.3 ppm.

15a: The reaction was performed according to general procedure D from dodecyl *p*-tolylsulfoxide (**1a**; 617.2 mg, 2 mmol) and gave olefin **15a** (0.2006 g, 60%; registry number 99464-25-2) as a colorless oil (mixture of isomers). Major isomer was Z (Z/E = 20:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.5–7.3 (m, 2 H), 7.3–7.2 (m, 3 H), 5.7–5.5 (m, 2 H), 3.5 (d, J = 6.5 Hz, 2 H), 3.4 (d, J = 6 Hz, 2 H), 2.2 (q, J = 7 Hz, 2 H), 1.4–1.2 (m, 18 H), 0.9 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.7, 131.7, 128.3, 128, 127.9, 125.5, 38.7, 33.1, 32.1, 31.5, 29.3, 29.2, 29, 28.8, 28.6, 26.9, 22.3, 13.7 ppm.

15b: The reaction was performed according to general procedure D from 3-phenyl 1-(*p*-tolylsulfinyl)propane (**1b**; 516.7 mg, 2 mmol) and gave olefin **15b** (0.274 g, 62%; registry number 69485-56-9) as a colorless oil (mixture of isomers). Major isomer was Z (Z/E = 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.4–7.3 (m, 4 H), 7.3–7.2 (m, 6 H), 5.8–5.7 (m, 2 H), 5.7–5.6 (m, 2 H), 3.5 (d, J = 5 Hz, 2 H), 3.4 (d, J = 6 Hz, 2 H), 2.8 (t, J = 7.5 Hz, 2 H), 2.4 (q, J = 6 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.8, 142.7, 132.9, 132.3, 130.2, 130.1, 127.8, 127.7, 127.6, 40.8, 37.8, 36.2, 35.3 ppm.

15c: The reaction was performed according to general procedure D from benzyl *p*-tolyl sulfoxide (**1c**; 460.7 mg, 2 mmol) and gave olefin **15c** (0.2 g, 51%; registry number 1138-83-6) as a colorless oil (mixture of isomers). Major isomer was E (Z/E = 1/2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.4–7.3 (m, 10 H), 6.4–6.3 (m, 2 H), 5.8 (q, J = 1.5 Hz, 2 H), 3.7 (d, J = 6.5 Hz, 2 H), 3.5 (d, J = 3.5 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.2, 139.6, 130.5, 129.2, 129, 128.5, 128.1, 127.9, 126.5, 125.6, 125.4, 38.8, 38.4 ppm.

15d: The reaction was performed according to general procedure D from isobutyl *p*-tolyl sulfoxide (**1f**; 392.7 mg, 2 mmol) and gave olefin **15d** (0.13 g, 40%; registry number 6016877-6) as a colorless oil (mixture of isomers). Major isomer was Z (Z/E = 12:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.4–7.3 (m, 2 H), 7.3–7.1 (m, 3 H), 5.6–5.5 (m, 2 H), 3.4 (d, J = 5 Hz, 2 H), 2.4–2.3 (m, 1 H), 1.1 (d, J = 7 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141, 130.3, 130.2, 130.1, 130, 129.9, 127.7, 127.5, 24.5, 16, 15.9 ppm.

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