Supplementary Materials

α -Sulfinyl Carbanions as A new source of olefins

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General: All reactions involving organometallic compounds were carried out under a positive pressure of Argon using standard Schlenk techniques. THF, and diethyl ether were distilled over benzophenone/sodium under an argon atmosphere. Alkyl- and arylmagnesium halides were prepared and titrated with 2-buthanol (1M in toluene) using 2,2'-biquinoyl as indicator. CuBr was purchased from Aldrich and used without further purification. ^1H and ^{13}C NMR spectra were reported for CDCl_3 solution with external standard on Bruker NMR spectrometers.

All the starting materials **6a**, **6b**, **6c**, **6d**, **6e**, **12**, **20a**, **20b**, **20c** and **20d** were prepared from known procedures.¹

General procedure for the intermolecular homologation between α -sulfinyl organocopper and zinc carbenoid. Procedure A

To a prepared solution of LDA (2 mmol) in THF (10 mL), primary sulfoxide (2 mmol), dissolved in THF (2 mL), was added at -70°C . The reaction was allowed to warm to -40°C and stirred for additional 30 min. CuBr (2 mmol) was then added and the reaction was allowed to warm to room temperature for 30 min. Meantime, bis(iodomethyl)zinc carbenoid **3** (6 mmol) [prepared from the reaction of diethylzinc (6 mmol, 1 M solution in hexanes, 6 mL) and diiodomethane (12 mmol, 3.2 gr) in THF at -50°C] was then added in the reaction mixture in 10 mL of THF 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 three times with diethyl ether and the combined organic phases were washed with Na_2S solution, dried, filtrated, and then concentrated to give a yellow oily crude product. After chromatography (hexane as eluent), the colorless oily olefin was obtained.

General procedure for the intramolecular homologation between α -sulfinyl organolithium and zinc carbenoid. Procedure B

To a prepared solution of LDA (2 mmol) in THF (10 mL), primary sulfoxide (2 mmol), dissolved in THF (2 mL), was added at -70°C . The reaction was allowed to warm to -40°C and stirred for 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 **3** (2 mmol) [prepared from the reaction of diethylzinc (2 mmol, 1 M solution in hexanes, 2 mL) and diiodomethane (4 mmol, 1 gr) in THF at -50°C] was then added in the reaction mixture and the resulting yellow solution was allowed to warm to room temperature and was stirred for 1 h at room temperature. A saturated solution of NH_4Cl was then added and the phases were separated. The water phase was extracted three times with diethyl ether and the combined organic phases were dried over

Na₂SO₄, filtrated, and then concentrated to give a yellow oily crude product. After chromatography (hexane as eluent), the colorless oily olefin was obtained.

1-Tridecene 9a The reaction was performed according to the general procedure A from dodecyl *p*-tolylsulfoxide **6a** (617 mg, 2 mmol) and gave **9a** (281 mg, 77%). When the reaction was performed according to the general procedure B, dodecyl *p*-tolylsulfoxide **6a** (617 ml, 2 mmol) gave **9a** (255 mg, 70%). Spectroscopic analyses were compared with authentic sample² and with the spectral data available from The Aldrich Library of ¹³C and ¹H FT NMR spectra [Vol 1(1), 20B].³

4-Phenyl-1-butene 9b The reaction was performed according to the general procedure A from 3-phenyl 1-(*p*-tolylsulfinyl)-propane **6b** (516 mg, 2 mmol) and gave **9b** (0.169 mg, 65%) as colorless oil. Spectroscopic analyses were compared with authentic sample⁴ and with the spectral data available from The Aldrich Library of ¹³C and ¹H FT NMR spectra [Vol 1(2), 24C].⁵

Styrene 9c The reaction was performed according to the general procedure A from benzyl *p*-tolylsulfoxide **6c** (460 mg, 2 mmol) and gave **9c** (104 mg, 50%) as colorless oil. Spectroscopic analyses were compared with authentic sample⁶ and with the spectral data available from The Aldrich Library of ¹³C and ¹H FT NMR spectra [Vol 1(2), 23A].⁵

4-methylstyrene 9d The reaction was performed according to the general procedure A from 4-methyl-benzyl *p*-tolyl sulfoxide **6d** (488 mg, 2 mmol) and gave **9d** (145 mg, 60%) as colorless oil. Spectroscopic analyses were compared with authentic sample⁷ and with the spectral data available from The Aldrich Library of ¹³C and ¹H FT NMR spectra [FT-NMR 1(2), 27A].⁵

4-vinylnisole 9d The reaction was performed according to the general procedure A from 4-methoxy-benzyl *p*-tolyl sulfoxide **6e** (520 mg, 2 mmol) and gave **9e** (161 mg, 60%) as colorless oil. Spectroscopic analyses were compared with authentic sample⁷ and with the spectral data available from The Aldrich Library of ¹³C and ¹H FT NMR spectra [FT-NMR 1(2), 207C].⁵

Synthesis of allylbenzene from DMSO

To a prepared solution of LDA (2 mmol) in THF (10 mL), DMSO (0.14 mL, 2 mmol), dissolved in THF (2 mL), was added at -70 °C. The reaction was allowed to warm to 0 °C and stirred for additional 30 min. CuBr (2 mmol) was then added at -40 °C and the reaction was warmed to room temperature.

1,1-diiodo-2-phenylethane⁸ (1.43 gr, 4 mmol) dissolved in THF (4 mL) was added at room temperature followed by dibutylzinc [prepared from *n*-BuLi (8 mmol, 1.5 M solution in hexane, 5.3 mL) and zinc bromide (4 mmol, 0.9 gr) in THF (10 mL) at -30 °C]. The resulting black solution was allowed to stir for 1 h at room temperature. A mixture of NH₄OH (30%) and saturated NH₄Cl (1:2) was added and the phases were separated. The water phase was extracted three times with diethyl ether and the combined

organic phases were washed with Na₂S solution, dried, filtrated, and then concentrated to give a yellow oily crude product. After chromatography (hexane as eluent), **14** was obtained in 70% yield (0.165 gr). Spectroscopic analyses were compared with authentic sample.⁹

4-methylene-1-decene 23a The reaction was performed according to the general procedure B from (1-undecyl-1-allyl)-*p*-tolylsulfoxide **20a** (690 mg, 2 mmol) and gave **23a** (300 mg, 65%) as colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 5.8 (m, 1H), 5.1 (m, 2H), 4.7 (s, 1H), 4.7 (s, 1H), 2.8-2.7 (d, J = 6.9 Hz, 2H), 2 (t, J = 7.23 Hz, 2H), 1.4 (m, 2H), 1.3 (m, 16H), 0.9 (t, J = 6.24 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) : 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.

2-phenyl-1-hexene 23b The reaction was performed according to the general procedure B from 1-phenyl-1-(*p*-tolylsulfinyl)-pentane sulfoxide **20b** (570 mg, 2 mmol) and gave **23b** (220 mg, 68%) as colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.3 (d, J = 6.9 Hz, 2H), 7.2 (m, 2H), 7.1 (d, J = 6.9 Hz, 1H), 5.1 (d, J = 1.2 Hz, 1H), 4.9 (d, J = 1.2 Hz, 1H), 2.4-2.3 (t, J = 7.1 Hz, 2H), 1.4-1.2 (m, 4H), 0.8 (t, J = 7.3 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) 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

1-undecyl-1-butylethene 23c The reaction was performed according to the general procedure B from (1-undecyl-1-butyl)-*p*-tolylsulfoxide **20c** (730 mg, 2 mmol) and gave **23c** (320 mg, 66%) as colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 4.6 (s, 1H), 4.6 (s, 1H), 1.9 (t, 4H), 1.5-1.2 (m, 22H), 0.9 (t, 6H). ¹³C NMR (75 MHz, CDCl₃) 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.

2-phenyl-1,4-pentadiene 23d The reaction was performed according to the general procedure B from 1-phenyl-1-allyl)-*p*-tolylsulfoxide **20d** (541 ml, 2 mmol) and gave **23d** (200 mg, 67%) as colorless oil. Spectroscopic analyses were compared with authentic sample.¹⁰

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