Supplementary Materials

New Multicomponent Approach for the Creation of Chiral Quaternary Centers in the Carbonyl Allylation Reactions

Genia Sklute and Ilan Marek*

The Mallat Family Laboratory of Organic Chemistry

Department of Chemistry, Institute of Catalysis Science and Technology and The Lise

Meitner-Minerva Center for Computational Quantum Chemistry.

Technion-Israel Institute of Technology, Haifa 32 000 Israel.

General: All reactions involving organometallic compounds were carried out under a positive pressure of Ar using standard techniques. THF and Et₂O were distilled over sodium benzophenone under argon atmosphere. Diethylzinc (1 M solution in hexane), dimethylzinc (2 M solution in toluene), dibutylzinc (1 M solution in heptane), butyllithium (1.6 M solution in hexane), methyllithium with lithium bromide (1.5 M solution in diethyl ether), *t*-butyllithium (1.7 M solution in hexane), zinc bromide, and copper (I) bromide were purchased from Aldrich Chemical Co INC and used without further purification. Grignard reagents were prepared and titrated before use.ⁱ Alkynyl sulfoxides were prepared according to literature procedure.ⁱⁱ NMR spectra were recorded in CDCl₃ solution at either 200, 300 or 500 MHz (¹H), and 50, 75 or 125 MHz (¹³C).

General procedure A

Preparation of homoallylic alcohols by treatment of the vinyl copper with bis(iodomethyl)zinc and aldehydes or imines (Scheme 8)

To a suspension of organocopper (3 mmol Grignard reagent and 3 mmol CuBr) in 13 mL of THF was added a solution of alkynyl sulfoxide (2 mmol) in 5 ml of THF at -70⁰C and

warmed to -30°C . Meanwhile, to a stirred solution of diethylzinc (1.0 M in hexane, 9 mmol) in 8 mL of THF was added diiodomethane (1.46 mL, 18 mmol) at -50°C . It was then warmed to -10°C during 30 minutes and kept at this temperature for 15 minutes. During this time, aldehyde or imine (1.2 mmol) was added to the vinyl copper solution at -30°C and warmed to -15°C for 15 minutes. The zinc carbenoid solution was then cooled again to -50°C and transferred through cannula to the solution of vinyl copper and kept at -15°C for 30 minutes. The reaction mixture was then quenched with a 2:1 aqueous $\text{NH}_4\text{Cl}:\text{NH}_4\text{OH}$ solution and extracted with ether and the organic phase is dried on MgSO_4 . The crude product was purified by filtering through silica gel using 3:1 hexane:ethyl acetate as eluent.

General procedure B

Cu-catalyzed reactions (Scheme 12)

To a solution of alkynyl *p*-tolylsulfoxide (0.8 mmol) in Et_2O (3 mL) and CuI (0.08 mmol, 10 mol%) at -50°C was added dropwise a solution of Et_2Zn (1.0 M in hexane, 2.4 mL, 2.4 mmol) and the mixture was slowly warmed to 0°C and stirred at this temperature till the disappearance of the starting material. The solution was cooled to -20°C and benzaldehyde (0.05 mL, 0.48 mmol) was added and stirred at this temperature for 20 min. Methylene iodide (0.13 mL, 1.6 mmol) was added and the solution was stirred overnight, quenched with $\text{NH}_4\text{Cl}:\text{NH}_4\text{OH}$ (2:1), extracted with ether and dried over Na_2SO_4 . The crude product was purified by column chromatography on silica gel using 3:1 hexane:ethyl acetate as eluent.

When the reaction was carried out in the presence of dimethylzinc, another equivalent of Et_2Zn was added to the reaction mixture before the addition of the aldehyde for the in situ generation of the zinc carbenoid.

General procedure C

***In-situ* formation of zinc carbenoid (Scheme 10)**

To a solution of CuI (0.266 g, 1.4 mmol) in THF (10 mL) was added dropwise the Grignard reagent (1.4 mmol) at -50°C and the solution was stirred at -30°C for 45 min (in

the case of methylmagnesium bromide the organocopper was formed at -5°C). The solution was cooled to -30°C and alkynyl *p*-tolylsulfoxide (0.8 mmol) in THF (3mL) was added and stirred at this temperature till the disappearance of the starting material. Aldehyde (1.6 mmol), methylene iodide (0.39 mL, 4.8 mmol), and Et_2Zn (1.0 M in hexane, 2.4 mL, 2.4 mmol) were added and the solution was stirred at -30°C till completion. After hydrolysis with $\text{NH}_4\text{Cl}:\text{NH}_4\text{OH}$ (2:1), the work-up was performed according to the general procedure A.

General procedure D

Multicomponent reaction (Scheme 11)

Alkynyl *p*-tolylsulfoxide (0.8 mmol) in THF (3 mL), aldehyde (1.6 mmol), methylene iodide (0.39 mL, 4.8 mmol), and Et_2Zn (1.0 M in hexane, 2.4 mL, 2.4 mmol) were added to a solution of organocopper (1.4 mmol) at -50°C . The solution was stirred at -30°C overnight. After hydrolysis with $\text{NH}_4\text{Cl}:\text{NH}_4\text{OH}$ (2:1), the treatment was performed as described for the general procedure A.

Spectral data of homoallylic alcohols

Benzenemethanol, α -[(1R)-1-ethyl-1-[1-[(S)-(4-methylphenyl)sulfinyl]ethenyl]pentyl] - , (α R) (21a): Prepared according to the general procedure C. Isolated in 78% yield (230 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.75 (t, $J = 7.2$ Hz, 3H), 0.89 (t, $J = 7.2$ Hz, 3H), 1.11-1.55 (m, 6H), 1.75 (dt, $J = 12.6$ Hz, $J = 4.8$ Hz, 1H), 2.03 (dt, $J = 13.8$ Hz, $J = 3.9$ Hz, 1H), 2.40 (s, 3H), 4.70 (s, 1H), 4.86 (d, $J = 1$ Hz, 1H), 5.49 (d, $J = 1$ Hz, 1H), 7.18-7.25 (5H, m), 7.28 (d, $J = 8.1$ Hz, 2H), 7.53 (d, $J = 8.1$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 8.3, 14.5, 21.9, 23.6, 26.0, 26.5, 31.2, 52.8, 78.8, 122.4, 127.4, 127.6, 127.7,

128.9, 130.3, 138.9, 141.5, 142.7, 156.8. HRMS (ESI, methanol) calcd for C₂₃H₃₁O₂S (MH⁺): 371.2059, Found: 371.2039.

Benzenemethanol, α -[(1S)-1-ethyl-1-[1-[(S)-(4-methylphenyl)sulfinyl]ethenyl]pentyl]-, (α R) (21b): Prepared according to the general procedure A. Isolated in 68% yield (200 mg). ¹H NMR (300 MHz, CDCl₃) δ 0.82 (t, J = 7.2 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H), 1.13-1.50 (m, 6H), 1.86 (sext, J = 6.9 Hz, 1H), 2.16 (sext, J = 6.9 Hz, 1H), 2.40 (s, 3H), 4.72 (s, 1H), 4.90 (d, J = 1.5 Hz, 1H), 5.48 (d, J = 1.2 Hz, 1H), 7.19-7.26 (5H, m), 7.30 (d, J = 7.8 Hz, 2H), 7.54 (d, J = 7.8 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 7.0, 13.0, 20.5, 22.2, 23.2, 24.3, 31.8, 51.4, 77.2, 121.3, 125.9, 126.2, 127.1, 127.5, 128.9, 137.5, 140.1, 141.2, 155.5.

Benzenemethanol, α -[(1R)-1-methyl-1-[1-[(S)-(4-methylphenyl)sulfinyl]ethenyl]pentyl]-, (α R) (21c): Prepared according to the general procedure C. Isolated in 66% (186 mg). ¹H NMR (300 MHz, CDCl₃) δ 0.71 (t, J = 6.9 Hz, 3H), 0.95 (s, 3H), 0.93-1.06 (m, 4H), 1.14 (dt, J = 13.2 Hz, J = 4.2 Hz, 1H), 1.61 (dt, J = 12.5 Hz, J = 3.6 Hz, 1H), 2.37 (s, 3H), 4.85 (s, 1H), 5.60 (s, 1H), 5.92 (s, 1H), 7.20-7.25 (m, 5H), 7.27 (d, J = 6.6 Hz, 2H), 7.54 (d, J = 6.6 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 13.0, 17.5, 20.4, 21.9, 25.1, 35.6, 48.9, 78.5, 120.1, 125.3, 126.3, 126.4, 127.5, 128.8, 138.2, 139.6, 141.0, 157.9. HRMS (ESI, methanol) calcd for C₂₂H₂₉O₂S (MH⁺): 357.1883 Found: 357.1875.

Benzenemethanol, α -[(1R)-1-ethyl-1-methyl-2-[(S)-(4-methylphenyl)sulfinyl]-2-propenyl]-(α R) (21d): Prepared according to the general procedure A. Isolated in 66% yield (173 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.57 (t, $J = 7.5$ Hz, 3H), 0.93 (s, 3H), 1.21 (sext, $J = 7.5$ Hz, 1H), 1.77 (sext, $J = 7.5$ Hz, 1H), 2.39 (s, 3H), 4.87 (s, 1H), 5.63 (d, $J = 1.5$ Hz, 1H), 5.89 (d, $J = 1.2$ Hz, 1H), 7.24-7.32 (m, 7H), 7.54 (d, $J = 6.3$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 7.1, 16.4, 20.4, 28.1, 49.6, 78.6, 121.0, 125.1, 126.3, 126.4, 127.5, 128.9, 137.9, 139.5, 140.8, 157.9. HRMS (ESI, methanol) calcd for $\text{C}_{20}\text{H}_{25}\text{O}_2\text{S}$ (MH^+): 329.1582, Found: 329.1570.

Benzenemethanol, α -[(1S)-1-ethyl-2-[(S)-(4-methylphenyl)sulfinyl]-2-propenyl]-, (α S) (21e): Prepared according to the general procedure A. Isolated in 78% yield (194mg). ^1H NMR (200 MHz, CDCl_3) δ (t, $J =$ Hz, 3H), 1.37-1.50 (m, 2H), 2.13-2.23 (m, 1H), 3.06 (s, 1H), 4.42 (d, $J = 5.0$ Hz, 1H), 5.58 (s, 1H), 6.16 (s, 1H), 7.13-7.31 (m, 5H), 7.39-7.60 (m, 5H). ^{13}C NMR (50 MHz, CDCl_3) δ 10.6, 20.8, 48.0, 76.2, 116.8, 125.9, 126.3, 127.5, 127.6, 128.1, 129.0, 131.4, 142.1, 154.6.

Benzenesulfonamide, N-[(1R,2R)-2-ethyl-2-[1-[(S)-(4-methylphenyl)sulfinyl]ethenyl]-1-phenylhexyl]-4-methyl (21f): Prepared according to the general procedure A. Isolated in 72% yield (300mg). ^1H NMR (300 MHz, CDCl_3) δ 0.79 (t, $J = 7.2$ Hz, 3H), 0.90 (t, $J = 7.2$ Hz, 3H), 1.18-1.44 (m, 6H), 2.05 (q, $J = 7.5$ Hz, 2H), 2.23 (s, 3H), 2.40 (s, 3H), 4.49 (d, $J = 9.9$ Hz, 1H), 4.70 (s, 1H), 5.20 (s, 1H), 6.87-7.64 (m, 13H). ^{13}C NMR (75 MHz, CDCl_3) δ 8.3, 14.6, 21.7, 21.9, 23.5, 26.0, 27.7, 31.3, 51.5, 62.7, 125.2, 127.1, 127.2, 127.3, 129.2, 129.7, 130.4, 137.2, 137.7, 139.0, 142.3, 142.8, 156.5. HRMS (ESI, methanol) calcd for $\text{C}_{30}\text{H}_{38}\text{NO}_3\text{S}_2$ (MH^+): 524.2288, Found: 524.2312.

Benzenesulfonamide, N-[(1R,2S)-2-ethyl-2-[1-[(S)-(4-methylphenyl)sulfinyl]ethenyl]-1-phenylhexyl]-4-methyl (21g): Prepared according to the general procedure A. Isolated in 70% yield (293 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.75 (t, $J = 6.9$ Hz, 3H), 0.87 (t, $J = 7.2$ Hz, 3H), 1.05-1.16 (m, 6H), 2.05 (q, $J = 7.2$ Hz, 2H), 2.14 (s, 3H), 2.33 (s, 3H), 4.45 (d, $J = 10.2$ Hz, 1H), 4.64 (d, $J = 1.5$ Hz, 1H), 5.10 (d, $J = 0.9$ Hz, 1H), 6.77-7.53 (m, 13H). ^{13}C NMR (75 MHz, CDCl_3) δ 6.9, 13.0, 20.3, 20.5, 22.1, 23.5, 24.6, 32.9, 50.1, 61.3, 124.0, 125.7, 126.2, 126.4, 127.7, 128.3, 129.0, 135.8, 136.1, 137.5, 140.8, 141.4, 155.2.

5-Decanol, 6-ethyl-6-[1-[(S)-(4-methylphenyl)sulfinyl]ethenyl]-, (5R, 6R) (21h): Prepared according to the general procedure A. Isolated in 60% yield (168 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.37 (t, $J = 7.2$ Hz, 3H), 0.74-0.80 (m, 6H), 1.09-1.24 (m, 14H),

1.15-1.53 (m, 14H), 2.30 (s, 3H), 3.34 (d, $J = 9$ Hz, 1H), 5.71 (s, 1H), 6.25 (s, 1H), 7.18 (d, $J = 8.1$ Hz, 2H), 7.41 (d, $J = 8.1$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 6.6, 13.0, 13.2, 20.3, 21.7, 22.35, 23.1, 24.3, 28.2, 28.7, 31.0, 31.8, 52.9, 76.5, 122.7, 124.1, 128.7, 138.7, 140.1, 156.9.

1-Octen-4-ol, 3-ethyl-3-methyl-2-[(S)-(4-methylphenyl)sulfinyl]-, (3R, 4R) (21i): Prepared according to the general procedure A. Isolated in 58% yield (142 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.62 (t, $J = 7.4$ Hz, 3H), 0.82 (t, $J = 7.2$ Hz, 3H), 0.93 (s, 3H), 1.16-1.38 (m, 6H), 1.41 (sext, $J = 7.4$ Hz, 1H), 1.67 (sext, $J = 7.4$ Hz, 1H), 2.33 (s, 3H), 2.95 (broad, 1H), 3.50 (d, $J = 9.5$ Hz, 1H), 5.61 (d, $J = 1.2$ Hz, 1H), 5.73 (d, $J = 1.2$ Hz, 1H), 7.19 (d, $J = 8.2$ Hz, 2H), 7.45 (d, $J = 8.2$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 7.2, 13.1, 17.6, 20.5, 21.7, 27.8, 28.2, 30.2, 48.7, 75.7, 119.8, 125.3, 128.8, 138.9, 140.7, 158.9.

Benzenemethanol, α -[(1R)-1-ethyl-1-[1-[(S)-(4-methylphenyl)sulfinyl]ethenyl]heptyl]-, (α R) (21j): Prepared according to general procedure C. Isolated in 81% yield (257 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.70 (t, $J = 7.2$ Hz, 3H), 0.83 (t, $J = 7.2$ Hz, 3H), 1.15-1.30 (m, 9H), 1.49 (sext, $J = 7.2$ Hz, 1H), 1.69 (dt, $J = 12.3$ Hz, $J = 3.2$ Hz, 1H), 1.98 (dt, $J = 12.8$ Hz, $J = 4.2$ Hz, 1H), 2.35 (s, 3H), 4.25 (d, $J = 6.9$ Hz, 1H), 4.65 (d, $J = 5.7$ Hz, 1H), 4.83 (d, $J = 1.5$ Hz, 1H), 5.46 (d, $J = 1.5$ Hz, 1H), 7.10-7.20 (5H, m), 7.25 (d, $J = 8.1$ Hz, 2H), 7.50 (d, $J = 8.1$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 6.9, 13.1, 20.5, 22.3, 25.1, 28.7, 28.8, 30.0, 30.8, 51.3, 77.4, 120.8, 125.9, 126.2, 126.2, 127.5,

128.9, 137.6, 140.1, 141.2, 155.3. HRMS (APCI, MeOH) calcd for $C_{25}H_{34}O_2SNa$ (MNa^+): 421.2177, Found: 421.2159.

Benzenemethanol, α -[(1R)-1-methyl-1-[1-[(S)-(4-methylphenyl)sulfinyl]ethenyl]heptyl]-, (α R) (21k): Prepared according to the general procedure C. Isolated in 78% yield (220 mg). 1H NMR (300 MHz, $CDCl_3$) δ 0.77 (t, $J = 7.2$ Hz, 3H), 0.92 (s, 3H), 0.99-1.19 (m, 8H), 1.64 (m, 2H), 2.36 (s, 3H), 4.85 (s, 1H), 5.59 (d, $J = 1.5$ Hz, 1H), 5.86 (d, $J = 1.5$ Hz, 1H), 7.19-7.28 (7H, m), 7.52 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.0, 17.2, 20.4, 21.6, 23.0, 28.6, 30.8, 35.8, 49.3, 78.7, 120.8, 125.1, 126.4, 127.4, 128.9, 137.7, 139.2, 141.0, 158.3.

Benzenemethanol, 4-chloro α -[(1R)-1-ethyl-1-[1-[(S)-(4-methylphenyl)sulfinyl]ethenyl]pentyl]-, (α R) (21l): Prepared according to the general procedure C. Isolated in 70% yield (225 mg). 1H NMR (300 MHz, $CDCl_3$) δ 0.69 (t, $J = 7.2$ Hz, 3H), 0.81 (t, $J = 7.2$ Hz, 3H), 1.18-1.51 (m, 6H), 1.72 (dt, $J = 11.8$ Hz, $J = 3.8$ Hz, 1H), 2.00 (dt, $J = 13.1$ Hz, $J = 3.5$ Hz, 1H), 2.34 (s, 3H), 4.59 (broad, 1H), 4.71 (d, $J = 5.3$ Hz, 1H), 4.79 (d, $J = 1.5$ Hz, 1H), 5.35 (d, $J = 1.5$ Hz, 1H), 7.09-7.15 (4H, m), 7.24 (d, $J = 8.2$ Hz, 2H), 7.45 (d, $J = 8.2$ Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 6.8, 13.0, 20.4, 22.1, 24.5, 25.1, 29.6, 51.4, 76.5, 121.3, 125.9, 126.2, 128.8, 128.9, 131.8, 136.6, 138.7, 141.4, 155.1. HRMS (APCI, methanol) calcd for $C_{23}H_{30}O_2SCl$ (MH^+): 405.1655, Found: 405.1624.

Benzenemethanol, α -[1, 1-dimethyl-2-[(S)-(4-methylphenyl)sulfinyl]-2-propenyl]-, (α R) (21m): Prepared according to the general procedure C. Isolated in 76% yield (191 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.85 (s, 3H), 1.00 (s, 3H), 2.35 (s, 3H), 3.68 (d, J = 3.6 Hz, 1H), 4.69 (d, J = 3.2 Hz, 1H), 5.74 (d, J = 1.2 Hz, 1H), 6.07 (d, J = 1.2 Hz, 1H), 7.22-7.26 (m, 7H), 7.50 (d, J = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 20.4, 21.2, 23.9, 44.7, 78.8, 118.9, 125.3, 126.5, 126.7, 127.2, 128.9, 139.1, 139.3, 140.9, 159.4. HRMS (APCI, methanol) calcd for $\text{C}_{19}\text{H}_{23}\text{O}_2\text{S}$ (MH^+): 315.1419, Found: 315.1410.

Benzoic acid, 4-[1-hydroxy-2,2-dimethyl-3-[(S)-(4-methylphenyl)sulfinyl]3-butenyl] (1S)-, methyl ester (21n): Prepared according to the general procedure C. Isolated in 60% (178 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.91 (s, 3H), 0.97 (s, 3H), 2.35 (s, 3H), 3.85 (s, 3H), 4.02 (s, 1H), 4.75 (s, 1H), 5.70 (d, J = 1.2 Hz, 1H), 5.97 (d, J = 1.2 Hz, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 7.87 (d, J = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 20.3, 21.2, 23.8, 44.7, 50.9, 78.3, 119.3, 125.2, 127.1, 127.6, 128.9, 128.1, 138.5, 140.9, 144.8, 158.8, 165.9. HRMS (APCI, methanol) calcd for $\text{C}_{21}\text{H}_{24}\text{O}_4\text{SNa}$ (MNa^+): 395.1293, Found: 395.1292.

Benzoic acid, 4-[2-ethyl-1-hydroxy-2-methyl-3-[(S)-(4-methylphenyl)sulfinyl]3-butenyl] (1R, 2S)-,methyl ester (21o): Prepared according to the general procedure C. Isolated in 60% yield (185 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.55 (t, $J = 7.2$ Hz, 3H), 0.99 (s, 3H), 1.41 (m, 1H), 1.74 (m, 1H), 2.37 (s, 3H), 3.61 (broad, 1H), 3.88 (s, 3H), 4.60 (s, 1H), 5.42 (d, $J = 0.9$ Hz, 1H), 6.11 (d, $J = 0.9$ Hz, 1H), 7.25 (d, $J = 8.1$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 7.50 (d, $J = 8.1$ Hz, 2H), 7.94 (d, $J = 8.1$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 9.7, 20.8, 23.3, 29.9, 51.1, 53.9, 82.5, 122.5, 128.7, 130.2, 130.5, 131.8, 131.2, 141.0, 144.1, 147.4, 158.3, 168.8. HRMS (ESI, methanol) calcd for $\text{C}_{22}\text{H}_{26}\text{O}_4\text{SNa}$ (MNa⁺): 409.1468, Found: 409.146.

Ethanone, 1-[4-[(2S)-2-ethyl-2-methyl-(1R)-1-hydroxy-3-butenyl-3-[(S)-(4-methylphenyl)sulfinyl]phenyl] (21p): Prepared according to the general procedure C. Isolated in 60% yield (177 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.53 (t, $J = 7.2$ Hz, 3H), 0.97 (s, 3H), 1.41 (m, 1H), 1.75 (m, 1H), 2.36 (s, 3H), 2.55 (s, 3H), 3.79 (broad, 1H), 4.61 (s, 1H), 5.45 (s, 1H), 6.14 (s, 1H), 7.24 (d, $J = 8.1$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.48 (d, $J = 8.1$ Hz, 2H), 7.84 (d, $J = 8.1$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 6.9, 17.7, 25.6, 27.3, 29.3, 48.1, 79.7, 119.4, 125.9, 126.5, 127.6, 128.9, 135.3, 138.4, 141.3, 145.0, 155.5, 197.0. HRMS (ESI, methanol) calcd for $\text{C}_{22}\text{H}_{26}\text{O}_3\text{SNa}$ (MNa⁺): 393.1495, Found: 393.1509.

2-Thiophenmethanol, α -[(1R)-1-ethyl-1-[1-[(S)-(4-methylphenyl)sulfinyl]ethenyl]pentyl]-, (α S) (21q): Prepared according to the general procedure C. Isolated in 83% yield (250 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.78 (m, 6H), 1.08-1.27 (m, 4H), 1.52 (m, 2H), 1.77 (m, 2H), 2.34 (s, 3H), 4.88 (s, 1H), 5.23 (d, $J = 1.2$ Hz, 1H), 5.60 (d, $J = 1.5$ Hz, 1H), 6.87 (m, 2H), 7.12 (dd, $J = 1.2$ Hz, $J = 4.8$ Hz, 1H), 7.24 (d, $J = 8.1$ Hz, 2H), 7.50 (d, $J = 8.1$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 9.8, 15.9, 23.3, 24.9, 27.5, 28.1, 31.5, 32.9, 54.2, 76.8, 124.1, 126.2, 127.5, 127.9, 128.8, 131.7, 140.2, 144.1, 146.7, 158.8. HRMS (ESI, methanol) calcd for $\text{C}_{21}\text{H}_{28}\text{O}_2\text{S}_2\text{Na}$ (MNa^+) 399.1423, Found 399.1420.

2-Furanmethanol, α -[1, 1-dimethyl-2-[(S)-(4-methylphenyl)sulfinyl]-2-propenyl]-, (α S) (21r): Prepared according to the general procedure C. Isolated in 75% yield (182 mg). ^1H NMR (500 MHz, CDCl_3) δ 0.94 (s, 3H), 1.11 (s, 3H), 2.36 (s, 3H), 2.65 (s, 1H), 4.66 (s, 1H), 5.79 (d, $J = 1.0$ Hz, 1H), 6.06 (d, $J = 1.0$ Hz, 1H), 6.21 (d, $J = 3.5$ Hz, 1H), 6.28 (dd, $J = 1.5$ Hz, $J = 3.5$ Hz, 1H), 7.30 (d, $J = 8.1$ Hz, 2H), 7.35 (m, 1H), 7.54 (d, $J = 8.1$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 21.9, 23.0, 24.9, 46.5, 75.2, 108.5, 110.6, 120.6, 126.7, 130.4, 140.1, 142.0, 142.4, 154.5, 160.6. HRMS (ESI, methanol) calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3\text{SNa}$ (MNa^+): 327.1025, Found: 327.1016.

2-Furanmethanol, α -[(1R)-1-ethyl-1-[1-[(S)-(4-methylphenyl)sulfinyl]ethenyl]pentyl]-, (α S) (21s): Prepared according to the general procedure C. Isolated in 70% yield (201 mg). ^1H NMR (300 MHz, CDCl_3) 0.73-0.82 (m, 6H), 0.92-1.26 (m, 4H), 1.45-1.86 (m,

2H), 2.34 (s, 3H), 4.68 (s, 1H), 5.23 (d, $J = 1.5$ Hz, 1H), 5.50 (d, $J = 1.5$ Hz, 1H), 6.18 (d, $J = 3.0$ Hz, 1H), 6.22 (dd, $J = 1.8$ Hz, $J = 3.0$ Hz, 1H), 7.22-7.25 (m, 3H), 7.48 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 7.5, 13.6, 21.0, 22.6, 25.0, 25.3, 30.4, 51.8, 72.4, 107.3, 109.6, 120.5, 126.6, 129.4, 138.1, 140.7, 141.8, 154.7, 157.3. HRMS (ESI, methanol) calcd for $\text{C}_{21}\text{H}_{28}\text{O}_3\text{SNa}$ (MNa^+): 383.1651, Found: 383.1641.

Benzenemethanol, α -[1-buthyl-1-[1-[(S)-(4-methylphenyl)sulfinyl]ethenyl]pentyl]-, (αR) (21t): Prepared according to the general procedure D. Isolated in 84% yield (267 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.76-0.87 (m, 6H), 1.08-1.47 (m, 10H), 1.74 (dt, $J = 13.2$ Hz, $J = 4.0$ Hz, 1H), 1.98 (dt, $J = 13.2$ Hz, $J = 4.0$ Hz, 1H), 2.35 (s, 3H), 4.29 (broad, 1H), 4.66 (s, 1H), 4.85 (d, $J = 1.5$ Hz, 1H), 5.43 (d, $J = 1.5$ Hz, 1H), 7.16-7.21 (m, 5H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.50 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 12.9, 13.0, 20.4, 22.1, 22.1, 24.3, 24.6, 30.4, 32.4, 51.1, 77.5, 120.9, 125.8, 126.1, 126.1, 127.4, 128.8, 137.3, 140.1, 141.1, 155.6. HRMS (APCI, methanol) calcd for $\text{C}_{25}\text{H}_{34}\text{O}_2\text{SNa}$ (MNa^+): 421.2177, Found: 421.2170.

Benzenemethanol, α -[(1S)-1-methyl-1-[1-[(S)-(4-methylphenyl)sulfinyl]ethenyl]pentyl]-, (αR) (21u): Prepared according to the general procedure D. Isolated in 74% yield (210 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.71 (t, $J = 6.9$ Hz, 3H), 0.82 (m, 2H), 0.89 (s, 3H), 1.00-1.11 (m, 2H), 1.30-1.40 (m, 1H), 1.67 (dt, $J = 12.6$ Hz, $J = 4.4$ Hz, 1H), 2.33 (s, 3H), 4.53 (s, 1H), 5.52 (s, 1H), 6.21 (s, 1H), 7.19-7.25 (m, 7H), 7.47 (d, $J =$

8.2 Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 13.3, 18.8, 20.8, 22.6, 25.1, 34.3, 47.9, 80.5, 119.2, 126.3, 126.9, 127.0, 127.6, 129.2, 139.3, 139.6, 141.4, 156.8. HRMS (ESI, methanol) calcd for $\text{C}_{22}\text{H}_{29}\text{O}_2\text{S}$ (MH^+): 357.1883, Found: 357.1875.

Benzenemethanol, α -[(1S)-1-ethyl-1-methyl-2-[(S)-(4-methylphenyl)sulfinyl]-2-propenyl]-(α R) (21v): Prepared according to the general procedure D. Isolated in 75% yield (196 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.49 (t, $J = 7.3$ Hz, 3H), 0.85 (s, 3H), 1.37 (sext, $J = 7.3$ Hz, 1H), 1.72 (sext, $J = 7.3$ Hz, 1H), 2.31 (s, 3H), 3.1 (broad, 1H), 4.48 (s, 1H), 5.48 (d, $J = 1.0$ Hz, 1H), 6.22 (d, $J = 1.0$ Hz, 1H), 7.16-7.25 (m, 7H), 7.44 (d, $J = 8.2$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 7.5, 18.0, 21.0, 27.7, 48.3, 80.8, 119.2, 126.6, 127.0, 127.1, 127.9, 129.4, 139.6, 139.9, 141.6, 156.2. HRMS (ESI, methanol) calcd for $\text{C}_{20}\text{H}_{25}\text{O}_2\text{S}$ (MH^+): 329.1570, Found: 329.1582.

Benzenemethanol, α -[(1R)-1-butyl-1-[1-[(S)-(4-methylphenyl)sulfinyl]ethenyl]heptyl]-, (α R) (21w): Prepared according to the general procedure B. Isolated in 57% yield (194 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.76-0.85 (m, 6H), 1.07-1.41 (m, 14H), 1.74 (dt, $J = 12.8$ Hz, $J = 4.2$ Hz, 1H), 1.94 (dt, $J = 12.8$ Hz, $J = 4.2$ Hz, 1H), 2.35 (s, 3H), 4.24 (d, $J = 6.0$ Hz, 1H), 4.66 (d, $J = 6.0$ Hz, 1H), 4.84 (d, $J = 1.0$ Hz, 1H), 5.42 (d, $J = 1.0$ Hz, 1H), 7.13-7.20 (5H, m), 7.24 (d, $J = 9.0$ Hz, 2H), 7.49 (d, $J = 9.0$ Hz, 2H).

Benzenemethanol, α -[(1R)-1-methyl-1-(methyl- d_3)-2-[(S)-(4-methylphenyl)sulfinyl]-2-propenyl]-, (α R) (21x): Prepared according to the general procedure B. Isolated in 82% yield (207 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.97 (s, 3H), 2.33 (s, 3H), 3.30 (d, $J = 3.3$ Hz, 1H), 4.71 (d, $J = 2.7$ Hz, 1H), 5.73 (d, $J = 1.2$ Hz, 1H), 6.02 (d, $J = 1.2$ Hz, 1H), 7.19-7.25 (m, 7H), 7.48 (d, $J = 8.1$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 21.8, 22.1, 46.1, 80.2, 120.6, 126.6, 127.8, 127.9, 128.5, 130.3, 140.2, 140.5, 142.2, 160.9.

Benzenemethanol, α -[(1S)-1-methyl-1-(methyl- ^{13}C)-2-[(S)-(4-methylphenyl)sulfinyl]-2-propenyl]-, (α R) (21y): Prepared according to the general procedure D. Isolated in 60% yield (151 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.92 (d, $J = 4.7$ Hz, 3H), 1.02 (d, $J = 127.6$ Hz, 3H), 2.38 (s, 3H), 3.37 (d, $J = 3.6$ Hz, 1H), 4.76 (d, $J = 3.4$ Hz, 1H), 5.77 (d, $J = 1.1$ Hz, 1H), 6.07 (d, $J = 1.1$ Hz, 1H), 7.25-7.34 (m, 7H), 7.53 (d, $J = 8.2$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 22.3, 23.4 (d, $J = 43.5$ Hz), 25.5, 64.1 (d, $J = 76.5$ Hz), 80.2, 120.5 (d, $J = 2.7$ Hz), 126.6, 127.9, 127.9, 128.5, 130.3, 140.3, 140.5, 142.2, 161.0. HRMS (ESI, methanol) calcd for $^{13}\text{CC}_{18}\text{H}_{22}\text{O}_2\text{SNa}$ (MNa $^{+}$): 338.1266, Found: 338.1278.

Sulfoxide-lithium exchange

Benzenemethanol, α -[(1S)-1-ethyl-1-[1-ethenyl]pentyl]-, (α S) (26a): To a solution of vinyl sulfoxide (0.7 mmol) in THF (4 mL), was added dropwise MeLi·LiBr (1.2 mmol) at -78°C and stirred at this temperature for 5 min. *t*-BuLi (1.7 mmol) was added dropwise and stirred below -60°C for 15min. The reaction was hydrolyzed with aqueous HCl (1M, 5 mL), extracted with ether and dried over Na_2SO_4 . Isolated in 82% yield (133 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.69 (t, $J = 7.5$ Hz, 3H), 0.89 (t, $J = 7.3$ Hz, 3H), 0.98-1.46 (m, 7H), 1.68 (dt, $J = 13.0$ Hz, $J = 4.4$ Hz, 1H), 4.52 (s, 1H), 5.00 (dd, $J = 17.7$ Hz, $J = 1.6$ Hz, 1H), 5.21 (dd, $J = 11.1$ Hz, $J = 1.6$ Hz, 1H), 5.61, (dd, $J = 17.7$ Hz, $J = 11.1$ Hz, 1H), 7.16-7.26 (m, 5H). ^{13}C NMR (125 MHz, CDCl_3) δ 8.0, 14.2, 23.6, 25.3, 25.4, 30.5, 47.3, 77.7, 116.0, 127.3, 127.4, 127.9, 141.5, 141.9. HRMS (ESI, methanol) calcd for $\text{C}_{16}\text{H}_{24}\text{ONa}$ (MNa $^{+}$): 255.1719, Found: 255.1727.

2-Furanmethanol, α -[1, 1-dimethyl-2-propenyl]-, (α S) (26r): Prepared according to the previous procedure. Isolated in 73% yield (84 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.95 (s, 3H), 1.01 (s, 3H), 4.35 (s, 1H), 5.01-5.09 (m, 2H), 5.86 (dd, $J = 17.4$ Hz, $J = 10.7$ Hz, 1H), 6.15 (d, $J = 3.2$ Hz, 1H), 6.27 (dd, $J = 3.2$ Hz, $J = 0.9$ Hz, 1H), 7.29 (d, $J = 0.9\text{Hz}$, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 24.0, 25.5, 43.9, 76.8, 109.2, 111.8, 115.7, 143.2, 146.1, 156.6.

Benzenemethanol, α -[(1R)-1-ethyl-1-[1-[1-iodoethenyl]pentyl]]-, (α R) (29a): To a solution of vinyl sulfoxide (0.7 mmol) in THF (4 mL), was added dropwise MeLi·LiBr (1.2 mmol) at -78°C and stirred at this temperature for 5 min. *t*-BuLi (1.7 mmol) was added dropwise and stirred below -60°C for 15min. Iodine (3 mmol) was added to the reaction flask and the cooling bath was removed and stirred overnight. Na_2SO_3 was added and the mixture extracted with ether and dried over Na_2SO_4 . Isolated in 70% yield (175 mg). ^1H NMR (300 MHz, CDCl_3) δ 0.75 (t, $J = 7.4$ Hz, 3H), 0.81-0.90 (m, 3H), 1.20-1.57 (m, 7H), 1.70-1.83 (sext, $J = 7.2$ Hz, 1H), 4.78 (s, 1H), 6.00 (d, $J = 2.2$ Hz, 1H), 6.07 (d, $J = 2.2$ Hz, 1H), 7.19-7.28 (m, 3H), 7.33-7.36 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 8.2, 13.1, 22.5, 24.1, 25.6, 32.3, 52.2, 77.9, 122.3, 126.5, 126.6, 128.9, 139.6. HRMS (ESI, methanol) calcd for $\text{C}_{16}\text{H}_{23}\text{ONaI}$ (MNa^+): 381.0686, Found: 381.0696.

1H-15c

Current Data Parameters
NAME: 1H-15c
EXPNO: 37
PROCNO: 1

F2 - Acquisition Parameters
Date_: 20030509
Time: 14.17
INSTRUM: spect
PROBHD: 5 mm QNP 1H/1
PULPROG: zg
TD: 32768
SOLVENT: CDCl3
NS: 8
DS: 2
SWH: 6172.839 Hz
FIDRES: 0.180000 Hz
AQ: 2.6542500 sec
RG: 50.8
DM: 81.000 usec
DE: 6.00 usec
TE: 300.0 K
D1: 2.5000000 sec

===== CHANNEL f1 =====
NUC1: 1H
P1: 12.90 usec
PL1: 3.00 dB
SFO1: 300.1318534 MHz

F2 - Processing parameters
SI: 32768
SF: 300.1309132 MHz
WDW: no
SSB: 0
LB: 0.00 Hz
GB: 0
PC: 1.00

1D NMR plot parameters
CX: 20.00 cm
CY: 9.41 cm
FID: 8.500 spm
FI: 2251.10 Hz
F2P: -0.500 ppm
F2: -150.06 Hz
PRGCM: 0.45500 ppm/cm
ACQ: 130.95556 Hz/cm

1H-15e

Current Data Parameters
Name: 15e
Date: 20030209
Time: 16:35
INSTRUM: spect
PROBHD: 5 mm QNP 1H/1
PULPROG: zgpg30
TD: 65536
SOLVENT: Acetone
NS: 2099
DS: 2
SWH: 25140.140 Hz
F2: 125.761 MHz
AQ: 1.456276 sec
RG: 16384
DQ: 21.850 us
DE: 6.00 us
TE: 300.2 K
D1: 2.50000000 sec
d11: 0.03000000 sec

===== CHANNEL f1 =====
NUC1: 13C
P1: 11.20 usec
PL1: 3.00 dB
SFO1: 75.476315 MHz

===== CHANNEL f2 =====
CPDPRG2: waltz16
NUC2: 1H
P2: 100.00 usec
PL2: 120.00 dB
SFO2: 22.00 MHz
SFO: 300.1302130 MHz

F2 - Processing parameters
SI: 32768
SF: 75.4673853 MHz
WDW: EM
SSB: 0
GB: 0
PC: 1.40

10 MHz plot parameters
CX: 20.00 usec
CY: 10.18 usec
FID: 160.000.000
F1: 12074.85 Hz
F2: -10.000.000
F2: -75.468 MHz
FREQ: 0.52000.000 MHz
XDC: 640.47630.800 MHz

1H-21a

¹³C-21a

dept-21a

Current Data Parameters	
NAME	Gen14
EXPNO	5612
PROCNO	1

F2 - Acquisition Parameters	
Date_	20030622
Time	7.24
INSTRUM	gpcr1
PROBHD	5 mm gpcr 1H/13
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
RG	17145
DS	0
SWH	17965.631 Hz
FIDRES	0.248071 Hz
AQ	0.212000 sec
RG	30284
DS	27.800 sec
DE	6.00 sec
TE	300.2 K
DATFID	145.000000 sec
DS	2.000000 sec
DE	0.2014452 sec
DS	0.200000 sec
DE	0.200000 sec

===== CHANNEL f1 =====	
NUC1	13C
PC	12.00 sec
PL	0.00 dB
PL1	3.00 dB
PL2	15.470000 dB

===== CHANNEL f2 =====	
NUC2	1H
PC	12.00 sec
PL	0.00 dB
PL1	15.470000 dB
PL2	15.470000 dB
PL3	15.470000 dB
PL4	15.470000 dB

F2 - Processing parameters	
SI	32768
SF	25.477000 MHz
WDW	EM
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

F2 - Net size parameters	
EC	26.00 Hz
ET	6.00 Hz
ETP	120.000 Hz
ETI	1120.00 Hz
ETP	-5.000 Hz
ETI	-117.14 Hz
ETP	3.75000 Hz
ETI	504.87188 Hz

1H-21b

13C-21b

0.000
6.991
12.963
20.484
27.738
29.100
24.270
29.676
31.772

51.380

77.212
76.453
76.078
75.605

121.247
125.892
126.210
126.256
127.131
127.541
128.921
137.400
140.104
141.185
155.473

ppm

1H-21c

13C-21c

1H-21d

13C-21d

1H-21f

^{13}C -21f

8.295
14.530
21.679
21.891
23.495
26.031
27.674
31.304

51.489

62.659

77.854
77.430
77.007

125.159
127.056
127.144
127.347
129.160
129.394
130.190
137.570
138.966
142.253
142.827

156.197

1H-21g

13C-21g

0.000
6.912
12.902
13.141
20.272
20.491
22.050
23.482
24.250
24.520
26.275
28.673
29.888
32.422
50.104
61.272
75.000
76.032
76.456

123.226
124.004
125.265
125.670
125.700
125.726
125.943
126.242
126.350
127.712
130.320
132.001
135.824
136.070
136.256
137.472
140.017
143.385
155.148

¹³C-21h

1H-21i

S37

^{13}C -2*li*

1H-21j

SpinWorks 2.4: GS-248 13C dept

1H-21k

Current Data Parameters
 NAME Genia
 EXPNO 240
 PROCNO 2

F2 - Acquisition Parameters
 Date_ 20051230
 Time 16.30
 INSTRUM spect
 PROBHD 5 mm QNP 1H/2
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 6172.839 Hz
 FIDRES 0.188380 Hz
 AQ 2.6542580 sec
 RG 645.1
 DM 81.000 usec
 DE 6.00 usec
 TE 292.9 K
 D1 2.00000000 sec
 MCREST 0.00000000 sec
 MCWRRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 12.60 usec
 PL1 3.00 dB
 SF01 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300249 MHz
 WDW no
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 23.00 cm
 CY 20.43 cm
 F1P 8.500 ppm
 F1 2551.11 Hz
 F2P -0.500 ppm
 F2 -150.06 Hz
 PPMCM 0.39130 ppm/cm
 HZCM 117.44218 Hz/cm

1.188
1.147
1.122
1.106
1.011
0.998
0.924
0.796
0.773
0.749
0.005

2.644
2.362

7.535
7.507
7.282
7.267
7.263
7.256
7.244
7.237
7.221
7.214
7.198
7.194
7.193
4.853
5.867
5.862
5.592
5.588

2.29
11.55
4.14
5.96

3.31

1.03
1.01
1.00

2.23
6.09
1.27

Integral

SpinWorks 2.4: 13C-21k

SpinWorks 2.4: dept-21k

1H-211

Current Data Parameters
 NAME Genia
 EXPNO 289
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20051219
 Time 10.45
 INSTRUM spect
 PROBHD 5 mm QNP 1H/2
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 6172.839 Hz
 FIDRES 0.188380 Hz
 AQ 2.6542580 sec
 RG 28.5
 DW 81.000 usec
 DE 6.00 usec
 TE 294.2 K
 D1 2.5000000 sec
 MCREST 0.0000000 sec
 MCWRR 0.0150000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 12.90 usec
 PL1 3.00 dB
 SF01 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300249 MHz
 WDW no
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 23.00 cm
 CY 14.01 cm
 F1P 8.500 ppm
 F1 2551.11 Hz
 F2P -0.500 ppm
 F2 -150.06 Hz
 PPMCM 0.39130 ppm/cm
 HZCM 117.44218 Hz/cm

PPM

1H-21m

Current Data Parameters
 NAME Genia
 EXPNO 258
 PROCNO 2

F2 - Acquisition Parameters
 Date_ 20040712
 Time 20.15
 INSTRUM spect
 PROBHD 5 mm QNP 1H/1
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 6172.839 Hz
 FIDRES 0.188380 Hz
 AQ 2.6542580 sec
 RG 32
 DM 81.000 usec
 DE 6.00 usec
 TE 296.4 K
 D1 2.50000000 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 12.90 usec
 PL1 3.00 dB
 SF01 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300132 MHz
 WDW no
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 23.00 cm
 CY 10.75 cm
 F1P 8.500 ppm
 F1 2551.10 Hz
 F2P -0.500 ppm
 F2 -150.06 Hz
 PPMCM 0.39130 ppm/cm
 HZCM 117.44218 Hz/cm

SpinWorks 2.4: 13C-21m

¹H-2Dn

SpinWorks 2.4: 13C GS-301

1H-21o

Current Data Parameters
NAME Genia
EXPNO 313
PROCNO 3

F2 - Acquisition Parameters
Date_ 20041007
Time 15.55
INSTRUM spect
PROBHD 5 mm QNP 1H/2
PULPROG zg30
TD 32768
SOLVENT CDCl₃
NS 8
DS 2
SWH 6172.839 Hz
FIDRES 0.188360 Hz
AQ 2.6542580 sec
RG 203.2
DM 81.000 usec
DE 6.00 usec
TE 296.6 K
d11 2.00000000 sec
d1 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 12.60 usec
PL1 3.00 dB
SF01 300.1318534 MHz

===== CHANNEL f2 =====
CPDPRG2 off
NUC2
PCPD2 100.00 usec
PL2 120.00 dB
PL12 120.00 dB
SF02 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300126 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 9.15 cm
FAP 8.500 ppm
F1 2551.10 Hz
F2 -0.500 ppm
PPHMC 0.45000 ppm/cm
HZCM 135.05850 Hz/cm

¹H-21p

Current Data Parameters
NAME Genia
EXPNO 311
PROCNO 3

F2 - Acquisition Parameters

Date_ 20041008
Time 19.03
INSTRUM spect
PROBHD 5 mm QNP 1H/2
PULPROG zg30
TD 32768
SOLVENT CDCl₃
NS 8
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 90.5
DM 81.000 usec
DE 6.00 usec
TE 297.1 K
D1 2.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====

NUC1 1H
P1 12.60 usec
PL1 3.00 dB
SF01 300.1318534 MHz

F2 - Processing parameters

SI 32768
SF 300.1300126 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 20.00 cm
CY 7.77 cm
F1P 8.500 ppm
F1 2551.10 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PNUC 0.45000 ppm/cm
HZCM 135.05850 Hz/cm

Integral

SpinWorks 2.4: 13C GS-311

1H-21q

¹³C-21q

dept-21q

7.4
13.4
20.9
22.5
25.1
25.7
30.4

74.3

121.7
123.8
125.1
125.4
126.4
129.2

ppm

101

ppm

1H-21r

Current Data Parameters
 NAME Genia_500
 EXPNO 440
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20050622
 Time 21.31
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg
 TO 65536
 SOLVENT CDC13
 NS 10
 DS 0
 SWH 12019.230 Hz
 FIDRES 0.183399 Hz
 AQ 2.7263892 sec
 RG 14.3
 DW 41.600 usec
 DE 6.00 usec
 TE 296.5 K
 D1 3.00000000 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 12.10 usec
 PL1 0.00 dB
 SF01 500.1322608 MHz

F2 - Processing parameters
 SI 65536
 SF 500.1300103 MHz
 WDW no
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.00 cm
 CY 10.35 cm
 F1P 9.000 ppm
 F1 4501.17 Hz
 F2P -0.500 ppm
 F2 -250.07 Hz
 PPMCM 0.43182 ppm/cm
 HZCM 215.96523 Hz/cm

1.400
1.231
1.106
0.940

2.647
2.377
2.358

7.511
7.508
7.499
7.495
7.483
7.307
7.303
7.301
7.299
7.298
7.249
7.249
7.233
6.289
6.286
6.283
6.279
6.215
6.208
6.067
6.064
5.795
5.793
4.662

0.753
1.233
3.850
4.407

1.175
4.738

1.123

1.000
1.050
1.139
1.172

2.908
1.767
2.232

Integral

702

SpinWorks 2.4: 13C GS-440

1H-21s

Current Data Parameters
NAME Na'ama
EXPNO 9
PROCNO 5

F2 - Acquisition Parameters
Date_ 20050711
Time 14.49
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 24
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 645.1
DM 81.000 usec
DE 6.00 usec
TE 294.4 K
D1 2.00000000 sec
MCREST 0.00000000 sec
MCMRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 12.60 usec
PL1 3.00 dB
SF01 300.1318534 MHz

F2 - Processing parameters
S1 32768
SF 300.1300249 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 23.00 cm
CY 11.14 cm
F1P 8.500 ppm
F1 2551.11 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.39130 ppm/cm
HZCM 117.44218 Hz/cm

SpinWorks 2.4:

PPM 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0

1H-21t

Current Data Parameters
NAME Genia
EXPNO 543
PROCNO 2

F2 - Acquisition Parameters

Date_ 20051118
Time 18.41

INSTRUM spect

PROBHD 5 mm QNP 1H/2
PULPROG zg

TD 32768

SOLVENT CDCl3

NS 8

DS 0

SWH 6172.839 Hz

FIDRES 0.186380 Hz

AQ 2.6542580 sec

RG 45.3

DW 81.000 usec

DE 6.00 usec

TE 293.3 K

D1 2.5000000 sec

MCREST 0.0000000 sec

MCWRK 0.01500000 sec

===== CHANNEL f1 =====

NUC1 1H

P1 12.90 usec

PL1 3.00 dB

SFO1 300.1318534 MHz

F2 - Processing parameters

SI 32768

SF 300.1300249 MHz

WDW no

SSB 0

LB 0.00 Hz

GB 0

PC 1.00

1D NMR plot parameters

CX 23.00 cm

CY 11.22 cm

F1P 8.500 ppm

F1 2551.11 Hz

F2P -0.500 ppm

F2 -150.06 Hz

PPMCM 0.39130 ppm/cm

HZCM 117.44216 Hz/cm

ppm

0

1

2

3

4

5

6

7

8

S68

¹H-21u

SpinWorks 2.4: 13C-21u

168.89
168.89
168.89
168.89
168.89

132.29
132.29
132.29
132.29
132.29
132.29
132.29

77.00
77.00
77.00
77.00
77.00

50.17

31.24

20.00
20.00
20.00
20.00
20.00
20.00
20.00

SpinWorks 2.4: dept-21u

SpinWorks 2.4: dept-21v

1H-21w

Current Data Parameters
 NAME Genia
 EXPNO 95
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20030907
 Time 12.46
 INSTRUM spect
 PROBHD 5 mm QNP 1H/2
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 6172.839 Hz
 FIDRES 0.188380 Hz
 AQ 2.6542580 sec
 RG 114
 DW 81.000 usec
 DE 6.00 usec
 TE 292.7 K
 D1 2.00000000 sec
 MCREST 0.00000000 sec
 MCNRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 12.60 usec
 PL1 3.00 dB
 SF01 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300278 MHz
 WDW no
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 12.62 cm
 F1P 8.500 ppm
 F1 2551.11 Hz
 F2P -0.500 ppm
 F2 -150.06 Hz
 PPMCM 0.45000 ppm/cm
 HZCM 135.05850 Hz/cm

Deuterium NMR

13C-21x

21x: a) ^{13}C decoupled. b) ^{13}C - ^2H decoupled.

1H-21y

Current Data Parameters
 NAME Genia
 EXPNO 317
 PROCNO 3

F2 - Acquisition Parameters
 Date_ 20041008
 Time 19.12
 INSTRUM spect
 PROBHD 5 mm QNP 1H/2
 PULPROG zg
 TD 32768
 SOLVENT CDC13
 NS 8
 DS 2
 SWH 6172.839 Hz
 FIDRES 0.188360 Hz
 AQ 2.6542580 sec
 RG 80.6
 DW 81.000 usec
 DE 6.00 usec
 TE 297.1 K
 D1 2.5000000 sec
 MCREST 0.0000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 12.90 usec
 PL1 3.00 dB
 SF01 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300126 MHz
 WDW no
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 7.29 cm
 F1P 8.500 ppm
 F1 2551.10 Hz
 F2P -0.500 ppm
 F2 -150.06 Hz
 PPMCM 0.45000 ppm/cm
 HZCM 135.05850 Hz/cm

S81

1H-26a

Current Data Parameters
 NAME Genia
 EXPNO 376
 PROCNO 3

F2 - Acquisition Parameters
 Date_ 20050307
 Time 13.56
 INSTRUM spect
 PROBHD 5 mm QNP 1H/2
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 6172.839 Hz
 FIDRES 0.188380 Hz
 AQ 2.6542580 sec
 RG 406.4
 DW 81.000 usec
 DE 6.00 usec
 TE 295.8 K
 D1 2.00000000 sec
 MCREST 0.00000000 sec
 MCWRR 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 12.60 usec
 PL1 3.00 dB
 SF01 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300249 MHz
 WDW no
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 23.00 cm
 CY 11.25 cm
 F1P 8.500 ppm
 F1 2551.11 Hz
 F2P -0.500 ppm
 F2 -150.06 Hz
 PPMCM 0.39130 ppm/cm
 HZCM 117.44218 Hz/cm

ppm

7.260
7.249
7.240
7.233
7.226
7.216
7.205
7.201
7.198
7.188
7.185
7.177
5.654
5.617
5.594
5.558
5.233
5.228
5.196
5.191
5.006
5.001
4.947
4.942
4.520

100.000 MHz
200.000 MHz
400.000 MHz
800.000 MHz

100.000 MHz

100.000 MHz

100.000 MHz
100.000 MHz
100.000 MHz

100.000 MHz

PPM 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0

le :
 File : c:\group\genia\clean.run
 hod File : c:\group\philippe\chir.mth
 ple ID : Default Sample

ection Date: 21/06/05 11:55 Calculation Date: 29/06/05 09:44

rator : ADI Detector Type: 39XL (10 Volts)
 kstation: Bus Address : 44
 trument : GC3900r Sample Rate : 20.00 Hz
 nnel : Front = FID Run Time : 131.492 min

Star Chromatography Workstation Version 5.52 ** 00268-5b08-d91-23ec **

Mode : Analysis
 k Measurement: Peak Area
 ulation Type: Percent (Normalized Results)

Peak No.	Peak Name	Result (%)	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		99.9301	1.563	0.000	14451115	VP	1.7	
2		0.0671	92.321	0.000	9698	VV	0.0	
3		0.0029	93.119	0.000	414	VV	0.0	
Totals:		100.0001		0.000	14461227			

al Unidentified Counts : 14461227 counts

ected Peaks: 606 Rejected Peaks: 603 Identified Peaks: 0

tiplier: 1 Divisor: 1 Unidentified Peak Factor: 0

aseline Offset: -9 microVolts

lse (used): 1 microVolts - fixed value
 lse (monitored before this run): 32 microVolts

ual injection

1.23.5

ee = 924.

68S

1H-26r

SpinWorks 2.4: 13C-26r

PPM 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0

1H-29a

Current Data Parameters
 NAME Genia
 EXPNO 354
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20050126
 Time 0.33
 INSTRUM spect
 PROBD 5 mm QNP 1H/1
 PULPROG zg30
 TD 32768
 SOLVENT CDC13
 NS 8
 DS 2
 SWH 6172.839 Hz
 FIDRES 0.188380 Hz
 AQ 2.6542580 sec
 RG 57
 DW 81.000 usec
 DE 6.00 usec
 TE 296.3 K
 D1 2.00000000 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 12.60 usec
 PL1 3.00 dB
 SFO1 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300249 MHz
 WDW no
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 23.00 cm
 CY 7.82 cm
 F1P 8.000 ppm
 F1 2401.04 Hz
 F2P -0.500 ppm
 F2 -150.07 Hz
 PPMCM 0.36957 ppm/cm
 HZCM 110.91763 Hz/cm

-
- i. Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, 9, 165.
 - ii. Kosugi, H.; Kitaoka, M.; Tagami, K.; Takahashi, A.; Uda, H. *J. Org. Chem.* **1987**, 52, 1078.