Stereoselective Preparation of Dienyl Zirconocene Complexes via a Tandem Allylic C-H bond Activation-Elimination Sequence

Nicka Chinkov, Swapan Majumdar and Ilan Marek*

Department of Chemistry and Institute of Catalysis Science and Technology, Technion-Israel Institute of Technology, Technion City, 32000 Haifa, Israel

Email: chilanm@tx.technion.ac.il

Supporting Information Available.

All reactions involving air- and moisture- sensitive compounds were carried out under argon atmosphere, using flamed flask and dry, oxygen-free solvents. Diethyl ether and tetrahydrofuran were distilled under argon from sodium benzophenone ketyl. HMPA was distilled under vacuum from CaH_2 . Allyl bromide, allyl chloride and methallyl chloride were distilled under argon from K_2CO_3 . *n*-BuLi was commercially obtained and titrated under argon atmosphere by 1M 2-*isobutanol* solution in toluene, using 1,10-phenantrolin as an indicator. All NMR spectra were recorded at room temperature with a Bruker-AG-200, Bruker-AG-400 and Bruker Avance-300 instruments. Chemical shifts are referenced to the residual proton or carbon resonance of the deuteriated solvent and are reported relative to $\text{Si}(\text{CH}_3)_4$.

1Z-Methoxy-2-pentyl-1,4-pentadiene (20a) To an ethereal solution (100 ml) of dibutylcuprate reagent, prepared from CuI (4.26 g, 25 mmol) and *n*-BuLi (36.76 ml, 50 mmol, 1.36 M solution in hexane) was added dropwise at -50°C , methoxyallene (2.8 g, 40 mmol) in 20 ml of Et_2O . The mixture was stirred at -40°C for 30 min, while the formation of the alkenylcuprate reagent was confirmed by GC analysis. The reaction mixture was cooled down to -65°C and allyl bromide (10.15 ml, 120 mmol) in THF (20 ml) was slowly added. After the addition, the temperature was allowed to reach -40°C and was maintained at this temperature for 1h. Hydrolysis was carried out by a saturated aqueous solution of $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}=2:1$. The mixture was then stirred 1h and then filtered through a pad of Celite, on a sintered glass funnel (the salts were washed several times with ether). The aqueous phase was extracted with ether (5x50 ml), the combined organic extracts and filtrates were washed with a saturated solution of NH_4Cl (until the blue color vanished), brine and dried over K_2CO_3 . Filtration and concentration under reduced pressure afforded an orange crude oil, which was then distilled on K $\ddot{u}$ gel-Rohr ($130^\circ\text{C}/30\text{ mmHg}$) to yield 6 g (89%) of **Z-20a**. ^1H NMR (200 MHz, CDCl_3) δ 0.85 (t, $J=6.97\text{Hz}$, 3H), 1.15-1.39 (m, 6H), 1.83 (t, $J=7.43\text{Hz}$, 2H), 2.76 (d, $J=6.58\text{Hz}$, 2H), 3.51 (s, 3H), 4.91-5.05 (m, 2H), 5.64-5.81 (m, 1H), 5.77 (s, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.2, 22.8, 28.1, 31.6, 31.7, 32.2, 59.4, 114.1, 118.2, 139.2, 142.5.

1E-Methoxy-2-pentyl-1,4-pentadiene (20a) The reaction was carried out according to the procedure described above, but in THF instead of Et_2O : CuI (457.1 mg, 2.4 mmol), *n*-BuLi (194 ml, 2.4 mmol), THF (15 ml), methoxyallene (140 mg, 2 mmol) in THF (5 ml), allyl bromide (0.3 ml, 3.5 mmol) in THF (2 ml). Purification by chromatography on silica gel (hexane/ $\text{EtOAc}=90:1$) yielded 0.2 g (60%) of **E-20a**. ^1H NMR (200 MHz, CDCl_3) δ 0.87 (t, $J=6.88\text{Hz}$, 3H), 1.15-1.41 (m, 6H), 2.01 (t, $J=7.78\text{Hz}$, 2H), 2.57 (d, $J=6.65\text{Hz}$, 2H), 3.51 (s, 3H), 4.94-5.06 (m, 2H), 5.65-5.79 (m, 1H), 5.74 (s, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 13.9, 22.5, 27.7, 31.3, 31.5, 31.6, 59.1, 114.5, 116.2, 136.6, 142.3.

1Z-Methoxy-2-pentyl-1,5-hexadiene (20b) The reaction was carried out according to the procedure described for **Z-20a** with 4-iodo-but-1-ene (1.27 g, 7 mmol) in THF (5 ml) as electrophile and freshly distilled HMPA (1.22 ml, 7 mmol). After classical treatment, the crude was purified by chromatography on basic alumina (hexane/ $\text{EtOAc}=100:1$) to yield 0.8 g (66%) of **20b** as pale yellow oil. ^1H NMR (200 MHz,

CDCl_3) δ 0.86 (t, $J=6.79\text{Hz}$, 3H), 1.24-1.39 (m, 6H), 1.83 (t, $J=7.27\text{Hz}$, 2H), 2.10 (s, 2H), 2.11 (s, 2H), 3.501 (s, 3H), 4.88-5.03 (m, 2H), 5.79-5.84 (m, 1H), 5.74 (s, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.2, 22.8, 26.6, 28.1, 31.6, 31.7, 32.2, 59.4, 114.1, 118.2, 139.2, 142.5.

1Z-Methoxy-2-pentyl-1,6-heptadiene (20c) The reaction was carried out according to the procedure described for **20b** with 5-iodo-pent-1-ene (1.03 g, 5.26 mmol) in THF (5 ml) as electrophile and triethylphosphite (1.35 ml, 7.89 mmol) and HMPA (0.92 ml, 5.26 mmol). After classical treatment, the crude was purified by chromatography on silica gel (hexane/EtOAc=100:1) to yield 790 mg (80%) of **20c**. ^1H NMR (200 MHz, CDCl_3) δ 0.86 (t, $J=6.94\text{Hz}$, 3H), 1.15-1.34 (m, 6H), 1.42 (q, $J=7.89\text{Hz}$, 2H), 1.82 (t, $J=7.23\text{Hz}$, 2H), 1.96-2.07 (m, 2H), 3.49 (s, 3H), 4.89-5.02 (m, 2H), 5.73 (s, 1H), 5.75-5.89 (s, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.2, 22.5, 26.4, 27.1, 27.9, 31.4, 31.5, 33.7, 59.2, 114.1, 118.4, 139.1, 142.1.

1E-Methoxy-2-(7-octene)-heptene (20d) The reaction was carried out according to the procedure described for **20b** with 8-iodo-oct-1-ene (0.88 ml, 5.23 mmol) in THF (5 ml) as electrophile and triethylphosphite (1.34 ml, 7.85 mmol) and HMPA (1.83 ml, 10.46 mmol). After classical treatment, the crude was purified by chromatography on silica gel (hexane/EtOAc=100:1) to yield 786 mg (66%) of **20d**. ^1H NMR (200 MHz, CDCl_3) δ 0.86 (t, $J=7.04\text{Hz}$, 3H), 1.27 (m, 14H), 1.81 (t, $J=7.17\text{Hz}$, 2H), 1.96-2.07 (m, 4H), 3.49 (s, 3H), 4.87-5.00 (m, 2H), 5.71 (s, 1H), 5.71-5.86 (m, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.0, 22.5, 26.7, 27.7, 27.9, 28.9, 29.0, 29.4, 31.4, 31.6, 33.8, 59.2, 114.1, 118.9, 139.3, 141.9.

1Z-Methoxy-2-pentyl-(1,4E)-hexadiene (20e) and 1Z-Methoxy-3-methyl-2-pentyl-(1,4)-pentadiene (20h) The reaction was carried out according to the procedure described for **Z-20a** with crotyl bromide (3.1 ml, 3 mmol) in Et_2O (8 ml) as electrophile. Classical purification afforded a mixture of two isomers **20e** and **20h** in a 6:1 ratio respectively (2.2 g). Purification by chromatography on silica gel (hexane/EtOAc=100:1) lead to 1.045 g of pure **20e** and 66 mg of pure **20h** (the balance being the mixture of the two products). **20e** ^1H NMR (200 MHz, CDCl_3) δ 0.85 (t, $J=7.15\text{Hz}$, 3H), 1.17-1.38 (m, 6H), 1.6 (d, $J=4.81$, 3H), 1.82 (t, $J=7.36\text{Hz}$, 2H), 2.68 (d, $J=5.18\text{Hz}$, 2H), 3.51 (s, 3H), 5.26-5.48 (m, 2H), 5.73 (s, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.0, 22.5, 27.7, 30.3, 31.2, 31.5, 31.8, 59.2, 115.0, 125.2, 138.2, 141.9. **20h** ^1H NMR (200 MHz, CDCl_3) δ 0.86 (t, $J=6.77\text{Hz}$, 3H), 1.079 (d, $J=6.92\text{Hz}$, 3H), 1.25 (m, 6H), 1.8 (t, $J=7.72\text{Hz}$, 2H), 3.33 (m, 1H), 3.51 (s, 3H), 4.86-5.00 (m, 2H), 5.69 (s, 1H), 5.8-5.79 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.03, 17.7, 22.5, 28.8, 29.3, 31.8, 36.4, 59.3, 112.1, 121.3, 142.1, 142.6.

1E-Methoxy-2-(7-tetradecene)-heptene (20f) The reaction was carried out according to the procedure described for **20b** with 14-bromo-tetradec-7-ene (1.12 g, 4.07 mmol) in THF (3 ml) as electrophile and triethylphosphite (1.04 ml, 6.10 mmol) and freshly distilled HMPA (0.71 ml, 4.07 mmol). After classical treatment, the crude was purified by chromatography on silica gel (hexane/EtOAc=250:1) to yield 590 mg (45%) of **20f**. ^1H NMR (200 MHz, CDCl_3) δ 0.86 (t, $J=6.67\text{Hz}$, 6H), 1.25 (m, 22H), 1.78-2.00 (m, 8H), 3.49 (s, 3H), 5.26-5.36 (m, 2H), 5.71 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.7, 15.8, 23.2, 27.3, 28.3, 28.5, 29.4, 29.7, 30.1, 30.2, 30.3, 32, 32.2, 32.4, 33.2, 59.7, 119.4, 130.9, 131.0, 142.4.

1Z-Methoxy-2-pentyl-4-methyl-(1,4)-pentadiene (20g) The reaction was carried out according to the procedure described for **Z-20a** with methallyl chloride (0.86 g, 9.5 mmol) in Et_2O (2 ml) as electrophile. After classical treatment, the crude was purified by chromatography on silica gel (hexane/EtOAc=80:1) to yield 700 mg (82%) of **20g**. ^1H NMR (200 MHz, CDCl_3) δ 0.86 (t, $J=6.4\text{Hz}$, 3H), 1.18-1.36 (m, 6H), 2.75 (s, 2H), 3.51 (s, 3H), 4.67 (d, $J=4.4\text{Hz}$, 2H), 5.83 (s, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.0, 22.0, 27.7, 31.0, 31.5, 35.4, 59.2, 110.5, 116.1, 142.9, 144.0.

1Z-Methoxy-2-pentyl-4-phenyl-(1,4)-pentadiene (20i) The reaction was carried out according to the procedure described for **Z-20a-Z** with (1-chloromethyl-vinyl)-benzene¹ (1.08 g, 7.1 mmol) as electrophile. After classical treatment, the crude was purified by chromatography on silica gel (hexane/EtOAc=100:1) to yield 902 mg (55%) of **20i**. ^1H NMR (200 MHz, CDCl_3) δ 0.85 (t, $J=6.24\text{Hz}$, 3H), 1.19-1.35 (m, 6H), 1.76 (t, $J=6.59\text{Hz}$, 2H), 3.27 (s, 2H), 3.52 (s, 3H), 5.06 (s, 1H), 5.34 (s, 1H), 5.79 (s, 1H), 7.21-7.33 (m, 3H), 7.43-7.48 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.0, 22.5, 27.7, 30.8, 31.5, 32.6, 59.2, 113.0, 115.8, 126.1, 127.2, 127.9, 141.1, 142.8, 145.9.

1Z-Methoxy-(3,3)-bisdeuterio-2-pentyl-(1,5)-octadiene (20j) The reaction was carried out according to the procedure described for **20b** with 1-iodo-(1,1)-bisdeutero-hex-3-*trans*-ene (1.48 g, 7 mmol) as electrophile and freshly distilled HMPA (1.22 ml, 7 mmol). After classical treatment, the crude was purified

by chromatography on basic alumina (hexane) to yield 294 mg of **20j**. ^1H NMR (200 MHz, CDCl_3) δ 0.89- 1.00 (m, 6H), 1.17-1.38 (m, 6H), 1.82 (t, $J=7.36\text{Hz}$, 2H), 1.9-2.05 (m, 4H), 3.51 (s, 3H), 5.35-5.45 (m, 2H), 5.69 (s, 1H).

1-Pentyl-2E-methoxy-(1,4)-pentadiene (40) The reaction was carried out according to the procedure described for **Z-20a** on methoxy-hexa-1,2,5- triene as starting material² (110mg, 1 mmol) in Et_2O (5 ml). Purification by column chromatography on basic alumina (hexane as eluent) afforded 118 mg (70%) of **40** (*Z/E* ratio 10:1). ^1H NMR (200 MHz, CDCl_3) δ 0.86 (t, $J=6.63\text{Hz}$, 3H), 1.24-1.42 (m, 6H), 1.93 (m, 2H), 2.85 (d, $J=6.1\text{ Hz}$, 2H), 3.46 (s, 3H), 4.39 (t, $J=7.34\text{Hz}$, 1H), 5.02 (m, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.0, 22.5, 26.4, 30.6, 31.4, 34.9, 54.1, 97.6, 115.3, 136.0, 156.9.

General Procedure for the tandem allylic C-H bond activation-elimination sequence mediated by zirconocene Bu_2ZrCp_2 (13) A solution of *n*-BuLi in hexane (2.4 eq) was added dropwise to a stirred solution of bis(cyclopentadienyl)zirconium dichloride (1.2 eq) in dry THF at -78°C under inert atmosphere. The temperature was slowly allowed to reach -50°C and the substrate (1 eq), diluted in 5 ml of THF was added dropwise, keeping the temperature below -50°C . When the addition was finished, the cooling bath was removed and the reaction mixture was warmed as fast as possible to room temperature (the delay in warming the reaction mixture may cause the formation of side products). It was then heated to $+50^\circ\text{C}$ for 15 min (when the experiment is performed in Et_2O or toluene, the reaction mixture is heated to $+34^\circ\text{C}$ or $+65^\circ\text{C}$, respectively), and the metalated diene is ready for further use, or, alternatively, can be hydrolyzed by 1N HCl after cooling down the reaction mixture to room temperature. The layers were separated and the aqueous phase was extracted twice with ether. The combined organic extracts were washed successively with sodium bicarbonate saturated solution, brine and dried over MgSO_4 . The obtained residue is finally purified by column chromatography on silica gel.

2-Pentyl-1,3-trans-pentadiene (24) The previously described procedure was carried out on **Z-20a**. The purification of the crude residue afforded the desired diene in 80% yield. ^1H NMR (200 MHz, CDCl_3) δ 0.87 (m, 3H), 1.22-1.49 (m, 6H), 1.73 (d, $J=6.08\text{Hz}$, 3H), 2.15 (t, $J=7.96\text{Hz}$, 2H), 4.80 (s, 1H), 4.83 (s, 1H), 5.71 (dq, $J=6.58, 15.72\text{Hz}$, 1H), 6.01 (d, $J=15.77\text{Hz}$, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 13.3, 17.5, 21.9, 27.4, 31.2, 31.6, 111.9, 123.9, 132.8, 145.9. Anal. Calcd for $\text{C}_{10}\text{H}_{18}$: C, 86.87; H, 13.12 Found: C, 87.10 H, 13.67.

1-Iodo-2-pentyl-1Z,3E-pentadiene (25) The previously described procedure was carried out on **Z-20a**. After classical work-up, crude **25** was obtained as reddish oil. Due to the high sensitivity to light, heat and acidic conditions, the crude product was quickly purified by florisil (pentane as eluent) to afford **25** in 75% yield. ^1H NMR (200 MHz, C_6D_6) δ 0.81 (m, 3H), 1.02-1.21 (m, 6H), 1.47 (dd, $J=1.19, 6.64\text{Hz}$, 3H), 2.01 (t, $J=7.78\text{Hz}$, 2H), 5.5-5.71 (m, 1H), 5.75 (s, 1H), 6.42 (d, $J=15.8\text{Hz}$, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.0, 18.5, 22.6, 28.4, 31.5, 35.0, 76.7, 129.8, 132.3, 145.9.

1-Bromo-2-pentyl-1Z,3E-pentadiene (26) The previously described procedure was carried out on **Z-20a**. After classical work-up, crude **26** was obtained. Due to the high sensitivity of the product, a fast isomerization occurs to give a mixture of geometrical isomers in 60% yield. ^1H NMR (300 MHz, CDCl_3) of the *Z*-product: δ 0.88 (t, $J=6.6\text{Hz}$, 3H), 1.23-1.4 (m, 6H), 1.8 (dd, $J=1.8, 6.6\text{Hz}$, 3H), 2.19 (t, $J=6.9\text{Hz}$, 2H), 5.85-5.9 (m, 2H), 6.43 (d, $J=15.6\text{Hz}$, 1H).

1-Chloro-2-pentyl-1Z,3E-pentadiene (27) The previously described procedure was carried out on **Z-20a**. After classical work-up and silica gel purification, pure **27** was obtained in 60% yield. ^1H NMR (300 MHz, CDCl_3) δ 0.88 (t, $J=6.6\text{Hz}$, 3H), 1.23-1.43 (m, 6H), 1.82 (dd, $J=1.8, 6.6\text{Hz}$, 3H), 2.19 (t, $J=6.9\text{Hz}$, 2H), 5.79 (s, 1H), 5.9 (m, 1H), 6.5 (d, $J=15.6\text{Hz}$, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.0, 18.7, 22.4, 28.3, 31.7, 32.1, 113.1, 125.8, 128.5, 138.4.

5-Pentyl-1,4Z,6E-octatriene (28) The previously described procedure was carried out on **Z-20a**. When the formation of the dienyl zirconium derivative **23a** was complete and confirmed by GC analysis, freshly distilled allyl chloride (0.12 ml, 1.5 mmol), CuCl (9.9 mg, 0.1 mmol) and LiCl (85 mg, 2 mmol) were added at 0°C . The solution was then heated to $+60^\circ\text{C}$ and stirred at this temperature for 1 h. Quenching the reaction by addition of an aqueous mixture of $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ (2:1) was performed at room temperature and after classical work-up, the crude was purified by column chromatography on silica gel (hexane) to afford **28** as a unique isomer in 70 % yield. When the same experiment was performed on **E-20a**, a single

isomer of the same geometry has been formed in 72% of yield. ¹H NMR (200 MHz, CDCl₃) δ 0.87 (t, *J*=6.78Hz, 3H), 1.24- 1.52 (m, 6H), 1.76 (d, *J*=6.744Hz, 3H), 2.14 (t, *J*=7.92Hz, 2H), 2.88 (t, *J*=6.83Hz, 2H), 4.93-5.05 (m, 2H), 5.21 (t, *J*=7.5Hz, 1H), 5.62-5.84 (m, 2H), 6.24 (d, *J*=15.7Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 14.0, 18.6, 22.5, 28.7, 31.6, 31.9, 34.2, 114.5, 124.0, 125.1, 127.4, 134.6, 137.3.

5-pentyl-1,4Z,6E-nonatriene (29) The previously described procedure was carried out on **20b** as described for the formation of **28**. Purification by column chromatography on silica gel (hexane) give **29** as a unique isomer in 70% yield. When the same experiment was performed on **20e**, **29** is also formed as a single geometrical isomer in 80% of yield. ¹H NMR (200 MHz, CDCl₃) δ 0.87 (t, *J*=6.7Hz, 3H), 1.01 (t, *J*=7.46Hz, 3H), 1.24-1.50 (m, 6H), 2.05-2.18 (m, 2H), 2.88 (t, *J*=6.73Hz, 2H), 4.92-5.07 (m, 2H), 5.23 (t, *J*=7.48Hz, 1H), 5.65-5.82 (m, 2H), 6.22 (d, *J*=15.7Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 13.8, 14.0, 22.5, 26.3, 28.6, 31.6, 31.9, 34.2, 114.5, 124.3, 125.0, 132.3, 137.3, 137.5.

5-Pentyl-1,4Z,6E-decatriene (30) The previously described procedure was carried out on **20c** as described for the formation of **28**. Purification by column chromatography on silica gel (hexane) give **30** in 71% yield. ¹H NMR (200 MHz, CDCl₃) δ 0.83-0.92 (m, 6H), 1.23-1.52 (m, 8H), 2.03-2.18 (m, 4H), 2.88 (t, *J*=6.86Hz, 2H), 4.93-5.05 (m, 2H), 5.22 (t, *J*=7.48Hz, 1H), 5.61-5.9 (m, 2H), 6.21(d, *J*=15.7Hz, 1H); ¹³C (200 MHz, CDCl₃) δ 14.0, 14.3, 22.5, 22.7, 28.6, 31.6, 31.8, 34.2, 35.4, 114.5, 124.2, 126.1, 130.6, 137.3, 137.5.

2-Pentyl-1,3E-decadiene (31) The previously described procedure for the preparation of **24** was carried out on **20d**. Purification by column chromatography on silica gel (hexane) yielded 70% of the desired product **31**. ¹H NMR (200 MHz, CDCl₃) δ 0.84-0.87 (m, 6H), 1.23-1.48 (m, 14H), 2.01-2.19 (m, 4H), 4.81 (s, 1H), 4.84 (s, 1H), 5.67 (dt, *J*=6.78, 15.75Hz, 1H), 5.98 (d, *J*=15.8Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 14.0, 22.5, 22.6, 28.0, 28.9, 29.4, 29.7, 31.7, 31.8, 32.3, 32.8, 112.7, 130.1, 132.0, 146.6.

2-Pentyl-1,3E-hexadecadiene (32) The previously described procedure was carried out on **20f** Purification by column chromatography on silica gel (hexane) yielded 61% of the desired product **32**. ¹H NMR (300 MHz, CDCl₃) δ 0.84-0.91 (m, 6H), 1.26-1.33 (m, 26H), 2.09 (m, 2H), 2.17 (t, *J*=6.6Hz, 1H), 4.85 (d, *J*=9.3Hz, 2H), 5.67 (dt, *J*=6.9, 15.75Hz, 1H), 6.01 (d, *J*=15.8Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 14.0, 22.5, 22.7, 28.1, 28.7, 29.25, 29.3, 29.5, 29.7, 31.9, 31.95, 32.3, 32.8, 112.7, 130.2, 132.1, 146.6.

2-Pentyl-3,5-bisdeutero-1,3E-octadiene (39) The previously described procedure was carried out on **20j**. Purification by column chromatography on silica gel (hexane) yielded 62% of **39**. An unidentified side product was formed as well. ¹H NMR (200 MHz, CDCl₃) δ 0.86 (m, 6H), 1.23-1.49 (m, 10H), 1.93-2.06 (m, 1H), 2.15 (t, *J*=7.88Hz, 2H), 4.82 (s, 1H), 4.84 (s, 1H), 5.62, (d, *J*=6.4Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 13.9, 14.0, 22.1, 22.7, 28.0, 29.7, 31.5, 31.8, 32.2 (t), 112.7, 129.9, 130.6(t), 146.5.

2E,4Z-decadiene (41) The previously described procedure was carried out on **40**. Purification by column chromatography on silica gel (hexane) yielded **40** in 75% yield. ¹H NMR (200 MHz, CDCl₃) δ 0.81-0.90 (m, 3H), 1.25-1.38 (m, 6H), 1.76 (d, *J*=6.44Hz, 3H), 2.13 (m, 2H), 5.28 (dt, *J*=7.43Hz, 1H), 5.65 (m, 1H), 5.93 (t, *J*=10.75Hz, 1H), 6.28 (m, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 14.09, 22.56, 22.7, 27.66, 29.37, 31.5, 31.95. Anal. Calcd for C₁₀H₁₈: C, 86.87; H, 13.12 Found: C, 87.02 H, 13.56.

(1-Benzyl-buta-1,3-diene-2-sulfonyl)-benzene (42a) A solution of *n*-BuLi (11.8 ml, 17.7 mmol) in hexanes was added dropwise to the stirred solution of allylphenyl sulfone (**3g**, 16.6 mmol) in THF (20 ml) at -78°C. After being stirred at -78°C for 30 min, a solution of benzaldehyde (1.8 gr, 16.9 mmol) in THF (5 ml) was added and the mixture was stirred for 1h at the above temperature. Acetic anhydride (7.5 ml) was then added and the reaction mixture was warmed to room temperature and kept for further two more hours. A solution of KOH (10g, 178 mmol) in water (10 ml) was added and stirred for additional 2 hours. The mixture was then diluted with water (50 ml) and CH₂Cl₂ (50 ml). After usual work-up and purification on silica gel (hexane/EtOAc = 9/1), white solid was obtained in 89% yield. ¹H NMR (CDCl₃, 200 MHz) δ 7.88-7.45 (m, 2H), 7.57-7.33 (m, 8H), 6.43-6.28 (dd, *J* = 18.3, 11.6 Hz, 1H), 5.88 (d, *J* = 18.2 Hz, 1H), 5.44 (d, *J* = 11.7Hz, 1H). ¹³C NMR (CDCl₃, 50 MHz) δ 139.93, 138.60, 138.20, 133.25, 133.08, 130.35, 129.92, 128.88, 128.58, 128.05, 126.40, 123.85.

(Nona-1,3-diene-3-sulfonyl)-benzene (42b) The same experimental procedure that of **42a** was used for the preparation of **42b**. *n*-BuLi (11.8 ml, 17.7 mmol, 1.50 M in hexane), allylphenyl sulfone (3.0g, 16.5 mmol), THF (20ml), valeraldehyde (1.80g, 16.9 mmol), acetic anhydride (7.5 ml), KOH (10g, 178 mmol) After classical treatment, the crude was purified by chromatography on silica gel [eluent: hexane-ethyl acetate (1:9)] to give the title compound **42b** as a mixture of two geometric isomers *trans/cis* 85/15 in 72% yield. ¹H NMR (CDCl₃, 200 MHz) (major) δ 7.80–7.73 (m, 2H), 7.56–7.37 (m, 3H), 6.96 (t, *J* = 7.6Hz, 1H), 6.26–6.11 (dd, *J* = 17.7, 11.5 Hz, 1H), 5.45 (d, *J* = 17.9Hz, 1H), 5.32 (d, *J* = 11.6Hz, 1H), 2.30–2.02 (m, 2H), 1.46–1.19 (m, 6H), 0.81 (bs, 3H); ¹³C NMR (CDCl₃, 50 MHz) δ 143.41, 142.92, 140.05, 132.84, 128.73, 127.64, 125.40, 122.84, 31.19, 28.37, 28.06, 22.14, 13.70.

(1-Cyclohexyl-buta-1,3-diene-2-sulfonyl)-benzene (42c) The previously described procedure was carried out for the preparation of **42c** with cyclohexane carboxaldehyde. Combined yield: 70% *E*-**42c** ¹H NMR (CDCl₃, 200 MHz) δ 7.75–7.71 (d, *J* = 8.0Hz, 2H), 7.53–7.36 (m, 3H), 6.79 (d, *J* = 10 Hz, 1H), 6.26–6.12 (dd, *J* = 17.7, 11.6 Hz, 1H), 5.47 (d, *J* = 17.3 Hz, 1H), 5.29 (d, *J* = 11.6 Hz, 1H), 2.41 – 2.36 (m, 1H), 1.65–1.60 (m, 4H), 1.17 (bs, 6H); ¹³C NMR (CDCl₃, 50 MHz) δ 147.83, 140.13, 137.60, 132.87, 128.79, 127.65, 125.48, 122.60, 37.50, 31.80, 25.50, 25.10; *Z*-**42c** ¹H NMR (CDCl₃, 200 MHz) δ 7.81 (d, *J* = 7.0 Hz, 2H), 7.58–7.29 (m, 3H), 6.49–6.35 (dd, *J* = 17.0, 10.8 Hz, 1H), 6.06 (d, *J* = 10.8 Hz, 1H), 5.35 (d, *J* = 17.0 Hz, 1H), 5.10 (d, *J* = 10.9 Hz, 1H), 3.31–3.25 (m, 1H), 1.76–1.61 (m, 4H), 1.30–0.89 (m, 6H); ¹³C NMR (CDCl₃, 50 MHz) δ 148.05, 141.68, 138.42, 133.12, 131.71, 128.88, 127.04, 118.15, 37.49, 32.39, 25.91, 25.43.

(1-Benzyl-penta-1E-3E-diene-2-sulfonyl)-benzene (42d) The procedure described above was carried out for the preparation of **42d** with crotylphenyl sulfone and benzaldehyde. White solid was formed in 91%. ¹H NMR (CDCl₃, 200 MHz) δ 7.87–7.82 (m, 2H), 7.74 (s, 1H), 7.60–7.33 (m, 8H), 6.38–6.20 (m, 1H), 6.01 (d, *J* = 16.6 Hz, 1H), 1.80 (d, *J* = 7.8 Hz, 3H); ¹³C NMR (CDCl₃, 50 MHz) δ 140.22, 138.43, 136.85, 136.20, 133.72, 132.99, 130.28, 129.62, 128.86, 128.56, 128.04, 120.27, 19.06.

General Experimental Procedure for the preparation of 44-47 A solution of *n*-butyllithium in hexane (3.4 mmol) was added slowly to a solution of bis(cyclopentadienyl)zirconium dichloride (1.7 mmol) in dry THF (10ml) at –78°C. The solution was stirred for 30 min at –78°C and the vinylsulfone **42a-d** (1 mmol) was added at –78°C. The reaction mixture was allowed to warm to room temperature very rapidly and stirred for 2h for **42a** and overnight for **42b-d**. Then, the reaction mixture was quenched by a 1M HCl aqueous solution and diluted with ether (10ml). The layers were separated; the aqueous layer was extracted with ether (3 x 5ml). The combined organic layers were washed with aqueous NaHCO₃ (3x10ml), brine (3x10ml) and evaporated under vacuum to afford a crude residue, which was purified by column chromatography on silica gel using hexane as eluent.

Buta-1,3Z-dienyl-benzene (44) Yield: 73%; Major isomer ¹H NMR (200 MHz, CDCl₃) δ 7.41–7.17 (m, 5H), 6.97 (dt, *J* = 16.8, 11.4 Hz, 1H), 6.45 (d, *J* = 11.5 Hz, 1H), 6.25 (t, *J* = 11.4 Hz, 1H), 5.36 (d, *J* = 16.7 Hz, 1H), 5.22 (d, *J* = 10.1 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 137.36, 133.21, 130.79, 130.42, 129.01, 128.22, 127.04, 119.61.

Nona-1,3Z-diene (45) Yield: 52 %; ¹H NMR (200 MHz, CDCl₃) δ 6.72–6.53 (dt, *J* = 16.8, 10.5 Hz, 1H), 5.97 (t, *J* = 10.9 Hz, 1H), 5.50–5.37 (m, 1H), 5.14 (d, *J* = 16.8 Hz, 1H), 5.05 (d, *J* = 10.2 Hz, 1H), 2.21–2.07 (m, 2H), 1.43–1.23 (m, 6H), 0.89–0.83 (m, 3H); ¹³C NMR (50 MHz, CDCl₃) δ 133.10, 132.39, 129.13, 116.63, 31.45, 29.30, 27.72, 22.53, 14.02. Anal. Calcd for C₁₀H₁₀: C, 92.25; H, 7.77 Found: C, 92.73 H, 7.95

Buta-1,3Z-dienyl-cyclohexane (46) Yield: 71%; ¹H NMR (200 MHz, CDCl₃) δ 6.72–6.53 (m, 1H), 5.87 (t, *J* = 10.9 Hz, 1H), 5.28 (t, *J* = 9.8 Hz, 1H), 5.15 (d, *J* = 16.8 Hz, 1H), 5.04 (d, *J* = 9.3 Hz, 1H), 2.45 (m, 1H), 1.60 (m, 4H), 1.16 (m, 6H); ¹³C NMR (50 MHz, CDCl₃) δ 138.9, 132.6, 127.3, 115.1, 36.8, 33.2, 26.0, 25.8. Anal. Calcd for C₁₀H₁₆: C, 88.15; H, 11.84 Found: C, 88.62 H, 12.24

Transmetalation of vinyl zirconocene 44-47Zr into 44-47Cu. Isomerization of Metalated Dienes.

After the formation of vinyl zirconocenes **44-47Zr**, anhydrous CuCl (1.8 mmol) and LiCl (3.6 mmol) were added to the reaction mixture and heated at 45°C for 1hr. Then, a mixture of 25% NH₃ and saturated aqueous solution of NH₄Cl (1:1) was added and stirred for 2h. The mixture was then filtered through celite

and washed with ether (50ml). After classical treatment, the crude product obtained was purified by column chromatography on silica gel with hexane as eluent to give the corresponding trans diene.

Buta-1,3E-dienyl-benzene (44) Yield: 73%; ^1H NMR (200 MHz, CDCl_3) δ 7.41-7.17 (m, 5H), 6.97 (dt, $J = 16.8, 11.4$ Hz, 1H), 6.45 (d, $J = 11.5$ Hz, 1H), 6.25 (t, $J = 11.4$ Hz, 1H), 5.36 (d, $J = 16.7$ Hz, 1H), 5.22 (d, $J = 10.1$ Hz, 1H). ^{13}C NMR (50 MHz, CDCl_3) δ 137.36, 133.21, 130.79, 130.42, 129.01, 128.22, 127.04, 119.61.

Nona-1,3E-diene (45) Yield: 48%; Major isomer ^1H NMR (200 MHz, CDCl_3) δ 6.16-6.38 (m, 1H), 5.96-6.089 (m, 1H), 5.61-5.75 (m, 1H), 5.10 (d, $J = 16.6$ Hz, 1H), 4.9 (d, $J = 9.77$ Hz, 1H), 1.19-2.10 (m, 2H), 1.23-1.40 (m, 4H), 0.86 (t, $J = 6.14$ Hz, 3H).

Buta-1,3E-dienyl-cyclohexane (46) Yield: 71%; Major isomer ^1H NMR (200 MHz, CDCl_3) δ 6.19-6.38 (m, 1H), 5.93-6.06 (m, 1H), 5.58-5.69 (dd, $J = 15.2, 6.78$ Hz, 1H), 5.11 (d, $J = 16.6$ Hz, 1H), 4.9 (d, $J = 10$ Hz, 1H).

Penta-2E,4E-dienyl-benzene (47) Yield: 60%; Major isomer ^1H NMR (200 MHz, CDCl_3) δ 7.46-7.14 (m, 5H), 6.75 (dd, $J = 15.6, 10.4$ Hz, 1H), 6.45 (d, $J = 15.6$ Hz, 1H), 6.2 (m, 1H), 5.8 (m, 1H), 1.8 (d, $J = 6.55$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 137.68, 131.86, 130.25, 129.73, 129.33, 128.51, 127.03, 126.10.

General procedure for the allylation reaction of 44-46Cu

E-(2-vinyl-penta-1,4-dienyl)-benzene (48) When the transmetalation step was over and **44-46Cu** was formed as described above, the reaction mixture was cooled down to 0°C and then freshly distilled allyl chloride (5 mmol, 3 fold excess) was added followed by heating at 45°C for 1h. The reaction mixture was then hydrolyzed with aqueous NH_4Cl and 25 % NH_3 solution (1:1). The mixture was filtered off through a celite pad on a sintered glass funnel, and after classical treatment, the residue was purified by column chromatography on silica gel with hexane as eluent to give the title product in 76% yield. ^1H NMR (200 MHz, CDCl_3) δ 7.37 (m, 5H), 6.62 (s, 1H), 6.55–6.41 (dd, $J = 17.4, 10.7$ Hz, 1H), 6.10 (m, 1H), 5.29 (d, $J = 17.4$ Hz, 1H), 5.15–5.07 (m, 3H), 3.22–3.18 (m, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 140.36, 137.45, 137.26, 135.95, 132.80, 128.77, 128.18, 126.94, 115.87, 113.70, 31.30. Anal. Calcd for $\text{C}_{13}\text{H}_{14}$: C, 91.70; H, 8.28 Found: C, 91.45 H, 8.66

E-(4-vinyl)-deca-1,4-diene (54) Yield: 60% (87 % is major isomer); ^1H NMR (200 MHz, CDCl_3) δ 6.35–6.21 (dd, $J = 17.5, 10.8$ Hz, 1H), 5.88–5.68 (m, 1H), 5.55 (t, $J = 7.4$ Hz, 1H), 5.13–4.88 (m, 4H), 2.99 (d, $J = 5.9$ Hz, 2H), 2.15–2.04 (m, 2H), 1.40–1.28 (m, 6H), 0.87 (t, $J = 6.4$ Hz, 3H).

E-(4-vinyl)-penta-1,4-dienyl-cyclohexane (55) Yield: 71% (90 % is major isomer); ^1H NMR (200 MHz, CDCl_3) δ 6.32–6.18 (dd, $J = 17.5, 10.8$ Hz, 1H), 5.90–5.71 (m, 1H), 5.38 (d, $J = 9.6$ Hz, 1H), 5.13–4.89 (m, 4H), 2.98 (d, $J = 5.9$ Hz, 2H), 2.34–2.16 (m, 1H), 1.72–1.56 (m, 5H), 1.37–1.02 (m, 5H); ^{13}C NMR (50 MHz, CDCl_3) δ 140.38, 140.27, 136.55, 133.88, 114.80, 111.10, 37.27, 33.38, 33.00, 30.73, 26.00, 25.85.

3Z-bromo-4-phenyl-1,3-butadiene (49) When the transmetalation step was over and **44Cu** was formed as described above, the reaction mixture was cooled down to 0°C and then NBS (1.7 mmol, 1.7 eq.) was added. After classical treatment, the residue was purified by column chromatography on silica gel with hexane as eluent to give the title product in 58% yield. ^1H NMR (200 MHz, CDCl_3) δ 7.70 (d, $J = 6.9$ Hz, 2H), 7.41–7.25 (m, 3H), 6.97 (s, 1H), 6.56–6.43 (dd, $J = 16.2, 10.4$ Hz, 1H), 5.72 (d, $J = 16.2$ Hz, 1H), 5.33 (d, $J = 10.3$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 137.11, 135.57, 132.31, 129.55, 128.27, 128.15, 123.92, 119.02.

Z-(2-vinyl-oct-1-en-3-ynyl)-benzene (50) When the transmetalation step was over and **44Cu** was formed as described above, the reaction mixture was cooled down to room temperature and $\text{Pd}(\text{PPh}_3)_4$ (10%) and 1-iodohexyne (1mmol) was added. The mixture was heated to reflux at 68°C for 4 hrs. Then, after hydrolysis and classical treatment, the crude was purified by chromatography on silica gel (eluent: hexane) to afford the desired product in 61% yield. ^1H NMR (200 MHz, CDCl_3) δ 7.44-6.87 (m, 10H), 6.78–6.64 (dd, $J = 17.2, 10.4$ Hz, 1H), 6.56 (s, 1H), 5.13 (d, $J = 10.4$ Hz, 1H), 4.83 (d, $J = 17.3$ Hz, 1H),

2.83 (s, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 142.17, 142.03, 137.10, 134.00, 132.51, 131.60, 131.31, 130.30, 128.17, 127.06, 116.50, 21.23.

Z-(2-vinyl-oct-1-en-3-tolyl)-benzene (51) The same experimental procedure was used with *p*-iodotoluene and **Z-51** was obtained in 60% yield. ^1H NMR (200 MHz, CDCl_3) δ 7.89 (d, $J = 7.0$ Hz, 1H), 7.38–7.18 (m, 4H), 6.62 (s, 1H), 6.55–6.41 (dd, $J = 16.9, 10.1$ Hz, 1H), 5.71 (d, $J = 17.4$ Hz, 1H), 5.24 (d, $J = 10.0$ Hz, 1H), 2.51 (t, $J = 6.8$ Hz, 2H), 1.70–1.42 (m, 4H), 0.95 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 141.81, 138.73, 136.22, 128.90, 128.12, 128.03, 121.71, 119.04, 115.96, 30.69, 22.08, 19.48, 13.60.

E-(2-vinyl-hex-1-en-5-one)-benzene (52) The procedure described above was applied to **44Cu** and methyl vinyl ketone in the presence of TMSCl. Yield: 75%; ^1H NMR, (200 MHz, CDCl_3) δ 7.36–7.20 (m, 5H), 6.50 (s, 1H), 6.46–6.32 (dd, $J = 17.6, 10.8$ Hz, 1H), 5.24 (d, $J = 17.6$ Hz, 1H), 5.12 (d, $J = 10.8$ Hz, 1H), 2.77–2.57 (m, 4H), 2.11 (s, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 207.81, 140.05, 138.97, 137.77, 132.14, 128.54, 128.35, 126.92, 113.00, 42.67, 29.74, 20.66. Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{O}$: C, 83.95; H, 8.05 Found: C, 84.22 H, 8.62

3E-(1-benzylidene-allyl)-cyclohexanone (53) A premixed solution of cyclohexenone (0.18 ml, 1.8 mmol) and TMSCl (0.3 ml, 2 mmol) was added to the reaction mixture of **44Cu** in THF at 0°C . After 30 min, the cool bath was removed and the reaction mixture was stirred overnight at room temperature. After usual work-up, the purification by column chromatography on silica gel afforded **30** in 59% yield. ^1H NMR (200 MHz, CDCl_3) δ 7.35–7.13 (m, 5H), 6.64 (s, 1H), 6.50–6.36 (dd, $J = 17.2, 10.9$ Hz, 1H), 5.56–5.47 (dd, $J = 17.4, 1.3$ Hz, 1H), 5.18–5.13 (dd, $J = 10.8, 1.1$ Hz, 1H), 3.24–3.12 (m, 1H), 2.53 (t, $J = 14.0$ Hz, 1H), 2.35–2.24 (m, 3H), 2.11–2.01 (m, 1H), 1.84–1.78 (m, 2H), 1.68–1.62 (m, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 210.75, 142.19, 137.09, 136.02, 128.62, 128.36, 127.28, 126.92, 115.86, 46.33, 41.13, 39.20, 30.03, 25.37. Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}$: C, 84.91; H, 8.01 Found: C, 85.23 H, 8.44

References

¹ Duboudin, J.G.; Jousseau, B. *J. Organomet. Chem.* **1979**, 168, 1

² Clinet, J.C.; Linstrumelle, G. *Tetrahedron Lett.* **1978**, 1137