Supporting Information

A Controllable Synthesis of Homoallyl Ketones and/or Multiply Substituted Cyclopentadienes by Direct Insertion of Aryl Cyanides to Zirconacyclopentenes

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General Methods. All reactions were carried out using standard Schlenk techniques under nitrogen. THF was distilled from sodium/benzophenone. All commercial reagents were used without further purification. Zirconocene dichloride, ethylmagnesium bromide

(1.0M solution in THF) and alkynes were used as purchased. Zirconacyclopentenenes **1**¹ and zirconacyclopentanes **4a-b**, **4c** and **4d** were prepared according to the previously published procedures.² Benzoyl cyanide was used as purchased, other acyl cyanides were prepared by the published method.³ ¹H and ¹³C NMR spectra were recorded at 300 and 75.4 MHz, respectively, in CDCl₃ (containing 1% TMS) solutions. GC yields were determined using suitable hydrocarbons as internal standards.

(4E)-4-Butyl-1-(4-chlorophenyl)non-4-en-1-one (2e) GC yield: 81%. Column chromatography on silica gel (ethyl acetate / petroleum ether 1:30) afford 220mg (72%) product as a light yellow liquid. ¹H NMR (CDCl₃, Me₄Si) δ 0.86-0.93 (m, 6H), 1.26-1.39 (m, 8H), 1.98-2.07 (m, 4H), 2.39 (t, *J* = 7.5Hz, 2H), 3.00 (d, *J* = 6.3 Hz, 1H), 3.03 (d, *J* = 7.5 Hz, 1H), 5.14 (t, *J* = 7.2Hz, 1H), 7.41 (d, *J* = 8.4Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H). ¹³C NMR (CDCl₃) δ 13.9, 14.0, 22.3, 22.7, 27.4, 30.0, 30.6, 31.1, 32.2, 37.6, 125.5, 128.8, 129.4, 135.3, 137.8, 139.2, 198.9. IR (neat) 2959, 1931, 1688, 1599, 1450, 1204, 743 cm⁻¹; HRMS (MALDI/DHB) calcd. for C₁₉H₂₇ClO 306.1750, found 307.1837 [M+H]⁺.

(4Z)-5-Bromo-4-butyl-1-phenylnon-4-en-1-one (2i) GC yield: 95%. Column chromatography on silica gel (ethyl acetate / petroleum ether 1:30) afford 310mg (86%) product as a light yellow liquid. ¹H NMR (CDCl₃, Me₄Si) δ 0.91 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H), 1.26-1.45 (m, 6H), 1.50-1.60 (m, 2H), 2.11-2.16 (m, 2H), 2.49 (t, *J* = 7.5Hz,

2H), 2.58-2.64 (m, 2H), 3.09 (d, $J=8.1$ Hz, 1H), 3.11 (d, $J=10.2$ Hz, 1H), 7.41-7.47 (m, 2H), 7.51-7.57 (m, 1H), 7.97-8.00 (m, 2H). ^{13}C NMR (CDCl_3) δ 13.8, 13.9, 21.8, 22.6, 30.7, 30.9, 31.5, 32.5, 36.4, 37.0, 124.9, 128.0, 128.4, 132.9, 136.6, 137.1, 199.6. HRMS (MALDI/DHB) calcd. for $\text{C}_{19}\text{H}_{27}\text{BrO}$ 350.1245, found 351.1329 $[\text{M}+\text{H}]^+$.

(4Z)-4-Butyl-5-chloro-1-phenylnon-4-en-1-one (2j) GC yield: 80%. Column chromatography on silica gel (ethyl acetate / petroleum ether 1:30) afford 220mg (72%) product as a light yellow liquid. ^1H NMR (CDCl_3 , Me_4Si) δ 0.85-0.93 (m, 6H), 1.27-1.43 (m, 6H), 1.47-1.57 (m, 2H), 2.07-2.12 (m, 2H), 2.35 (t, $J = 7.5\text{Hz}$, 2H), 2.55-2.61 (m, 2H), 3.04-3.09 (m, 2H), 7.38-7.43 (m, 2H), 7.48-7.53 (m, 1H), 7.94-7.96 (m, 2H). ^{13}C NMR (CDCl_3) δ 13.7, 13.8, 21.8, 22.5, 28.3, 30.0, 30.6, 32.2, 34.7, 36.4, 127.9, 128.0, 130.8, 132.7, 134.3, 136.6, 199.4. HRMS (MALDI/DHB) calcd. for $\text{C}_{19}\text{H}_{27}\text{ClO}$ 306.1750, found 307.1832 $[\text{M}+\text{H}]^+$.

(4Z)-4,5-Dibutyl-1-(2-methoxyphenyl)octa-4,7-dien-1-one (2k) GC yield: 90%. Column chromatography on silica gel (ethyl acetate / petroleum ether 1:30) afford 215mg (70%) product as a light yellow liquid. ^1H NMR (CDCl_3 , Me_4Si) δ 0.89-0.93 (m, 6H), 1.29-1.40 (m, 8H), 1.97-2.07 (m, 4H), 2.35-2.41 (m, 2H), 2.78 (d, $J = 6.3\text{Hz}$, 2H), 2.97-3.03 (m, 2H), 3.86 (s, 3H), 4.92-5.01 (m, 2H), 5.70-5.79 (m, 1H), 6.92-6.99 (m, 2H), 7.42 (td, $J=7.7$, 1.8 Hz, 1H), 7.64 (dd, $J = 7.6$, 1.8Hz, 1H). ^{13}C NMR (CDCl_3) δ 13.9, 14.0, 22.8, 22.9, 26.5, 31.0, 31.3, 31.3, 31.3, 35.8, 43.0, 55.2, 111.2, 114.4, 120.4, 128.4, 130.0, 131.4, 133.0, 133.7, 137.0, 158.1, 202.7. IR (neat) 2958, 1675, 1598, 1486, 1245, 1026, 909 cm^{-1} ; HRMS

(MALDI/DHB) calcd. for $C_{23}H_{34}O_2$ 342.2559, found 343.2632 $[M+H]^+$.

3-[(1Z)-1-Butyl-2-(3'-oxo-3'-(p-tolylpropyl)hex-1-enyl)cyclohexanone (2m) Column chromatography on silica gel (ethyl acetate / petroleum ether 1:30) afford 200mg (52%) product as a light yellow liquid. 1H NMR ($CDCl_3$, Me_4Si) δ 0.92 (t, $J=6.6$ Hz, 3H), 0.93 (t, $J=6.6$ Hz, 3H), 1.24-1.35 (m, 8H), 1.57-1.69 (m, 3H), 1.95-2.44 (m, 14H), 2.84-2.96 (m, 3H), 7.24 (d, $J = 8.1$ Hz, 2H), 7.83 (d, $J = 7.8$ Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 13.7, 13.8, 21.3, 22.7, 23.2, 25.4, 25.5, 27.4, 30.1, 30.8, 31.5, 33.0, 37.9, 40.8, 41.6, 46.7, 127.9, 129.0, 133.5, 134.0, 135.8, 143.4, 199.2, 211.1. IR (neat) 2960, 1719, 1689, 1599, 1450, 1276 cm^{-1} ; HRMS (MALDI/DHB) calcd. for $C_{26}H_{38}O_2$ 382.2872, found 405.2769 $[M+Na]^+$.

(3b), GC yield: 80%. Column chromatography on silica gel (petroleum ether) afford 165mg (64%) product as a mixture of isomers in the ratio of 10:9:1. 1H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, $J=7.2$ Hz), 0.91 (t, $J = 6.9$ Hz), 0.95 (t, $J = 7.5$ Hz), 0.96 (t, $J = 7.2$ Hz), 1.28-1.66 (m), 2.10 (q, $J = 7.5$ Hz), 2.28-2.57 (m), 2.74-2.78 (m), 2.94 (s), 3.21 (s), 5.33-5.38 (m), 6.04 (s), 6.14 (s), 7.14-7.34 (m); ^{13}C NMR ($CDCl_3$) δ 13.8, 13.9, 14.0, 14.1, 22.8, 23.0, 23.1, 23.2, 25.3, 26.2, 26.3, 27.9, 30.7, 31.2, 31.5, 32.1, 34.3, 42.6, 117.6, 124.8, 125.8, 126.5, 127.4, 127.6, 128.0, 128.1, 128.2, 138.2, 138.8, 140.1, 140.2, 142.2, 143.0, 147.8, 149.3. HRMS (MALDI/DHB) calcd. for 254.2035, found 255.2107 $[M+H]^+$.

(3c), GC yield: 90%. Column chromatography on silica gel (petroleum ether) afford 138mg (70%) product as a mixture of isomers in the ratio of 30:10:1. The characterization data is the same as the data of authentic sample prepared by the published method.⁴

(**3d**), GC yield: 97%. Recrystallization with diethyl ether afford 223mg (76%) The ^1H NMR data is the same as previous published one;⁵ ^{13}C NMR (CDCl_3) δ 43.3, 126.3, 126.7, 126.8, 127.7, 128.0, 128.1, 128.2, 129.9, 130.3, 136.5, 136.6, 136.9, 141.9, 142.5, 149.3.

(**3e**), GC yield: 89%. Column chromatography on silica gel (petroleum ether) afford 156mg (61%) product as a mixture of isomers in the ratio of 34:6:1. ^1H NMR (CDCl_3 , Me_4Si) δ 0.90-0.97 (m), 1.32-1.63 (m), 2.06-2.14 (m), 2.33 (s, 3H), 2.54-2.56 (m), 2.73-2.77 (m), 3.20(bs), 5.33 (t, $J = 7.2$ Hz, 1H), 6.01 (bs, 1H), 6.19 (s, 1H), 7.13 (d, $J = 8.7$ Hz, 2H), 7.22 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 13.9, 14.0, 14.1, 21.1, 21.1, 22.6, 22.8, 22.9, 23.1, 25.4, 26.2, 26.3, 27.9, 30.7, 31.2, 31.5, 31.9, 34.3, 42.6, 117.2, 124.5, 127.3, 127.6, 128.7, 128.8, 135.4, 135.9, 136.1, 139.3, 139.7, 142.4, 142.9, 147.9, 149.3. HRMS (MALDI/DHB) calcd. for $\text{C}_{20}\text{H}_{28}$ 268.2191, found 269.2264 $[\text{M}+\text{H}]^+$.

(**3i**), Column chromatography on silica gel (petroleum ether) afford 198mg (65%) product as a mixture of isomers in the ratio of 3:2:1. ^1H NMR (CDCl_3 , Me_4Si) δ 0.54 (t, $J = 7.2$ Hz), 0.63 (t, $J = 7.2$ Hz), 0.64 (t, $J = 7.2$ Hz), 0.98 (t, $J = 7.5$ Hz), 0.99 (t, $J = 7.5$ Hz), 1.04-1.11 (m), 1.25-1.70 (m), 2.02-2.20 (m), 2.38-2.46 (m), 2.68-2.70 (m), 3.08(bs), 3.24 (bs), 5.40 (t, $J = 7.2$ Hz, 1H), 6.13 (bs, 1H), 6.18 (bs, 1H), 7.22-7.44 (m), 7.70-7.82 (m); ^{13}C NMR (CDCl_3) δ 13.6, 13.7, 13.8, 14.1, 14.1, 14.2, 22.3, 22.6, 22.8, 22.9, 22.9, 23.0, 25.4, 25.6, 26.3, 26.8, 28.2, 28.4, 30.7, 30.8, 31.5, 31.8, 31.9, 32.9, 36.8, 42.4, 45.2, 117.3, 125.0, 125.2, 125.2, 125.4, 125.5, 125.5, 125.5, 125.6, 125.6, 125.8, 126.1, 126.3, 126.5, 126.6, 126.8, 127.0, 127.0, 128.0, 128.1, 128.2, 128.5, 131.4, 132.4, 132.5, 133.5, 133.6, 133.7,

136.5, 137.3, 137.6, 139.6, 140.8, 142.0, 142.1, 142.8, 144.3, 147.1, 147.6, 148.5. HRMS (MALDI/DHB) calcd. for $C_{23}H_{28}$ 304.2191, found 305.2264 $[M+H]^+$.

(3j), Column chromatography on silica gel (diethyl ether/petroleum ether 1:10) afford 241mg (56%) product as a mixture of isomers in the ratio of 9:6:1. 1H NMR ($CDCl_3$, Me_4Si) δ 0.90-0.99 (m), 1.35-1.66 (m), 2.10 (q, $J = 7.2$ Hz), 2.31-2.59 (m), 2.78-2.82 (m), 2.97 (bs), 3.26 (bs), 5.36 (t, $J = 7.5$ Hz, 1H), 6.05 (bs, 1H), 6.20 (bs, 1H), 7.29-7.36 (m); ^{13}C NMR ($CDCl_3$) δ 13.8, 13.9, 14.0, 14.1, 22.8, 22.9, 23.0, 23.1, 25.3, 26.1, 26.2, 27.8, 30.7, 31.1, 31.5, 31.9, 34.2, 42.5, 118.2, 125.1, 128.3, 128.4, 128.4, 128.7, 128.7, 131.5, 132.2, 136.6, 137.2, 138.7, 140.7, 140.8, 143.7, 147.5, 149.3. HRMS (MALDI/DHB) calcd. for $C_{32}H_{46}$ 430.3600, found 431.3672 $[M+H]^+$.

3-Octylcyclopent-1-enylbenzene and 4-Octylcyclopent-1-enylbenzene (5). GC yield: 75%. Column chromatography on silica gel (petroleum ether) afford 165mg (65%) product as a mixture of isomers in the ratio of 1:1. 1H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, $J = 7.2$ Hz), 1.27-1.56 (m), 2.11-2.20 (m), 2.31-2.39 (m), 2.60-2.84 (m), 6.10 (bs, 1H), 6.13 (bs, 1H), 7.15-7.43 (m); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.7, 28.0, 28.4, 29.4, 29.7, 29.7, 29.9, 30.0, 30.3, 32.0, 32.6, 36.2, 36.7, 38.1, 39.6, 39.8, 46.3, 125.2, 125.4, 125.5, 126.7, 126.8, 128.2, 130.6, 136.7, 136.8, 141.5, 141.5. IR (neat) 2926, 1717, 1361, 1200, 753, 693 cm^{-1} ; HRMS (MALDI/DHB) calcd. for $C_{19}H_{28}$ 256.2191, found 257.2264 $[M+H]^+$.

1,2-Diphenylpentan-1-one (6). GC yield: 71%. Column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) afford 132mg (55%) product as a light yellow liquid.

The ^1H NMR data is the same as previous published one;⁶ ^{13}C NMR (CDCl_3) δ 14.1, 20.8, 36.1, 53.4, 126.9, 128.2, 128.5, 128.6, 128.8, 132.8, 136.9, 139.8, 200.1.

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X-ray single-crystal structure of 7c.

2c

2e

2f

2g

2h

2i

2j

21

3f

3g

3h

3i

3j

7b

Pulse Sequence: gHMOC
 Solvent: CDCl₃
 Ambient temperature
 File: gHMOC
 Mercury-30088 "0MC300"
 Relax delay 1.000 sec
 Acquisition time 21.38 sec
 Width 4807.7 Hz
 2D Width 15063.0 Hz
 32 repetitions
 2x 16 increments
 OBSERVE F1 300.13627850 MHz
 DECOUPLE C13 75.4488661 MHz
 Power 44 dB
 on during acquisition
 off during delay
 GARP on during delay
 DATA PROCESSING
 Gauss apodization 0.068 sec
 F1 DATA PROCESSING
 Gauss apodization 0.016 sec
 F1 F2 200.130000 MHz
 Total time 3 hr, 21 min, 38 sec

The 2D NMR spectra of **3g**:

Pulse Sequence: ghmhc
 Solvent: CDCl₃
 Acquisition Temperature: 300 K
 File: ghmhc
 Mercury-300BB "OMC300"
 Relax. delay 1.000 sec
 Acq. time 0.213 sec
 Width 1815.9 Hz
 2D Width 1815.9 Hz
 32 repetitions
 200 increments
 OBSERVE H1, 300.0279860 MHz
 USE PROCSH1
 Sine bell 0.007 sec
 F1 DATA PROCESSING
 Sine bell 0.006 sec
 FT size 2048 X 2048
 Total time 2 hr, 41 min, 7 sec

The 2D NMR spectra of **3g**: