Supporting Information

For

Reactivity of alkynylzirconates towards allyl bromides: Selective Formation of β-allyl-zirconacyclopentadienes

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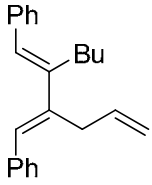
Experimental Sections

General. All manipulations were conducted in Schlenk tube and under nitrogen with a slightly positive pressure. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Tetrahydrofuran (THF) was refluxed and freshly distilled from dark purple solutions of sodium and benzophenone under nitrogen atmosphere. ^{1}H NMR and ^{13}C NMR spectra were recorded on JOEL 300 NMR spectrometer with TMS as internal standard. Mass spectra were obtained using a Bruker Esquire ion trap mass spectrometer in positive ion mode. Flash column chromatography was performed using silica gel (200-300 mesh).

Representative procedure for coupling of zirconate complexes with allyl bromide.

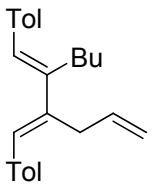
^{n}BuLi (3.0 mmol, 1.6 M solution in hexane) was added to a THF solution of phenylacetylene (2.0 mmol) at -78^{o}C and stirred for 1 h. Then Cp_2ZrCl_2 (1.0 mmol)

was added. The solution was stirred at -78°C for 1h and then another 12 h at room temperature. After cooling the reaction mixture to 0°C, allyl bromide (1.0 mmol) was added and stirred for 3 h. The reaction mixture was quenched with 2N HCl and extracted with ethyl ether. The organic extract was dried over $MgSO_4$. Removing the solvent and subsequent purification by column chromatography on silica gel (petroleum ether) afforded **4a** (201 mg, 67%) as colorless liquid. ^{1}H NMR (300MHz, $CDCl_3$, Me_4Si) δ 0.92 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 1.27-1.56 (m, 4H), 2.51 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 3.28 (d, $^3J_{HH}$ = 5.5 Hz, 2H), 5.10-5.18 (m, 2H), 5.92-6.05 (m, 1H), 6.70 (s, 1H), 6.82 (s, 1H), 7.21-7.37 (m, 10H); ^{13}C NMR (75MHz, $CDCl_3$, Me_4Si) δ 14.1 (CH_3), 23.0 (CH_2), 28.3 (CH_2), 31.5 (CH_2), 33.2 (CH_2), 116.1 (CH_2), 126.5 (CH), 126.8 (CH), 127.9 (CH), 128.2 (CH), 128.3 (CH), 128.5 (CH), 129.0 (CH), 136.8 (CH), 138.3 (C), 138.7 (C), 141.1 (C), 144.2 (C). HRMS calcd for $C_{23}H_{26}$ 302.2035, found 302.2031.



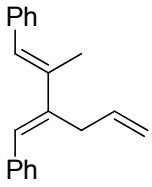
4a

Diene 4b: 64% isolated yield. ^{1}H NMR (300MHz, $CDCl_3$, Me_4Si) δ 0.88 (t, $^3J_{HH}$ = 7.5 Hz, 3H), 1.26-1.56 (m, 4H), 2.35 (s, 6H), 2.48 (t, $^3J_{HH}$ = 7.2 Hz, 2H), 3.25 (d, $^3J_{HH}$ = 5.5 Hz, 2H), 5.08-5.16 m, 2H), 5.89-6.00 (m, 1H), 6.63 (s, 1H), 6.75 (s, 1H), 7.14-7.25 (m, 8H); ^{13}C NMR (75MHz, $CDCl_3$, Me_4Si) δ 14.1 (CH_3), 21.1 (CH_3), 23.0 (CH_2), 28.3 (CH_2), 31.6 (CH_2), 33.2 (CH_2), 116.0 (CH_2), 127.6 (CH), 128.2 (CH), 129.0 (CH), 135.1 (C), 135.4 (C), 135.8 (C), 136.1 (C), 136.9 (CH), 140.5 (C), 143.6 (C). HRMS calcd for C25H30 330.2348, found 330.2345.



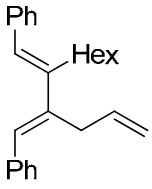
4b

Diene 4c: 71% isolated yield. ^{1}H NMR (300MHz, $CDCl_3$, Me_4Si) δ 2.12 (s, 3H), 3.33 (dt, $^{3}J_{HH}$ = 5.1 Hz, $^{4}J_{HH}$ = 2.0 Hz, 2H), 5.12-5.18 (m, 2H), 5.96-6.09 (m, 1H), 6.78 (s, 1H), 6.87 (s, 1H), 7.21-7.34 (m, 8H); ^{13}C NMR (75MHz, $CDCl_3$, Me_4Si) δ 16.2 (CH_3), 33.0 (CH_2), 116.1 (CH_2), 126.5 (CH), 126.8 (CH), 127.6 (CH), 128.2 (CH), 128.3 (CH), 128.6 (CH), 129.0 (CH), 129.5 (CH), 137.1 (C), 137.7 (C), 138.3 (C), 141.3 (C). GC-MS (*m/z*) : 260.



4c

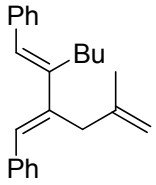
Diene 4d: 62% isolated yield. ^{1}H NMR (300MHz, $CDCl_3$, Me_4Si) δ 0.91 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H), 1.21-1.56 (m, 4H), 2.50 (t, $^{3}J_{HH}$ = 7.6 Hz, 2H), 3.29 (d, $^{3}J_{HH}$ = 5.5 Hz, 2H), 5.13-5.21 (m, 2H), 5.93-6.04 (m, 1H), 6.72 (s, 1H), 6.83 (s, 1H), 7.20-7.42 (m, 10H); ^{13}C NMR (75MHz, $CDCl_3$, Me_4Si) δ 14.2 (CH_3), 22.8 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 31.8 (CH_2), 33.2 (CH_2), 116.1 (CH_2), 126.6 (CH), 126.7 (CH), 127.9 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 128.9 (CH), 129.0 (CH), 136.8 (C), 138.2 (C), 138.8 (C), 141.1 (C), 144.2 (C). HRMS calcd for C25H30 330.2348, found 330.2344.



4d

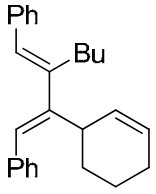
Diene 4e: 21% isolated yield. ^{1}H NMR (300MHz, $CDCl_3$, Me_4Si) δ 0.91 (t, $^{3}J_{HH}$ = 6.9

Hz, 3H), 1.30-1.59 (m, 4H), 1.80 (s, 3H), 2.49 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 3.15 (s, 2H), 4.82 (s, 1H), 4.88 (s, 1H), 6.67 (s, 1H), 6.88 (s, 1H), 7.21-7.39 (m, 10H); ^{13}C NMR (75MHz, $CDCl_3$, Me_4Si) δ 14.0 (CH_3), 23.0 (CH_2), 23.5 (CH_3), 28.1 (CH_2), 31.7 (CH_2), 37.1 (CH_2), 111.7 (CH_2), 126.4 (CH), 126.8 (CH), 127.8 (CH), 128.2 (CH), 128.3 (CH), 128.8 (CH), 129.0 (CH), 129.1 (CH), 138.3 (C), 138.8 (C), 140.7 (C), 144.0 (C), 144.2 (C). GC-MS (*m/z*) : 316.



4e

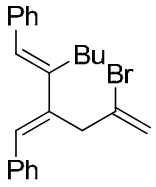
Diene 4f: 44% isolated yield. ^{1}H NMR (300MHz, $CDCl_3$, Me_4Si) δ 0.89 (t, $^3J_{HH}$ = 7.0 Hz, 3H), 1.22-1.58 (m, 6H), 1.69-1.81 (m, 2H), 1.98-2.04 (m, 2H), 2.48 (t, $^3J_{HH}$ = 7.4 Hz, 2H), 3.67 (m, 1H), 5.72-5.83 (m, 2H), 6.56 (s, 2H), 7.18-7.40 (m, 10H); ^{13}C NMR (75MHz, $CDCl_3$, Me_4Si) δ 14.1 (CH_3), 22.6 (CH_2), 22.9 (CH_2), 25.0 (CH_2), 28.4 (CH_2), 30.0 (CH_2), 31.2 (CH_2), 37.7 (CH), 126.3 (CH), 126.5 (CH), 127.5 (CH), 127.7 (CH), 128.2 (CH), 128.3 (CH), 128.4 (CH), 128.9 (CH), 129.1 (CH), 131.8 (CH), 138.2 (C), 138.5 (C), 146.7 (C), 148.9 (C). GC-MS (*m/z*) : 342.



4f

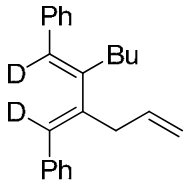
Diene 4g: 32% isolated yield. ^{1}H NMR (300MHz, $CDCl_3$, Me_4Si) δ 0.92 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 1.32-1.57 (m, 4H), 2.50 (m, 2H), 3.64 (s, 2H), 5.60 (s, 1H), 5.74 (s, 1H), 6.72 (s, 1H), 6.94 (s, 1H), 7.25-7.39 (m, 10H); ^{13}C NMR (75MHz, $CDCl_3$, Me_4Si) δ 14.0 (CH_3), 23.0 (CH_2), 28.0 (CH_2), 31.6 (CH_2), 41.6 (CH_2), 117.9 (CH_2), 126.7 (CH),

127.3 (CH), 128.0 (CH), 128.3 (CH), 128.4 (CH), 128.7 (CH), 128.8 (CH), 129.0 (CH), 131.7 (C), 137.4 (C), 138.3 (C), 138.7 (C), 142.8 (C). GC-MS (*m/z*) : 380, 382.



4g

Diene **5a**: 60% isolated yield with 98% D incorporation. ^{1}H NMR (300MHz, $CDCl_3$, Me_4Si) δ 0.90 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H), 1.26-1.56 (m, 4H), 2.50 (t, $^{3}J_{HH}$ = 7.5 Hz, 2H), 3.26 (d, $^{3}J_{HH}$ = 5.5 Hz, 2H), 5.10-5.18 (m, 2H), 5.92-6.05 (m, 1H), , 7.21-7.37 (m, 10H); ^{13}C NMR (75MHz, $CDCl_3$, Me_4Si) δ 14.1 (CH_3), 23.0 (CH_2), 28.3 (CH_2), 31.5 (CH_2), 33.2 (CH_2), 116.1 (CH_2), 126.5 (CH), 126.8 (CH), 127.9 (J_{DC} = 13.6 Hz), 128.2 (CH), 128.3 (CH), 128.5 (J_{DC} = 12.2 Hz), 129.0 (CH), 136.8 (CH), 138.13 (C), 138.5 (C), 141.1 (C), 144.0 (C). GC-MS (*m/z*) : 304.

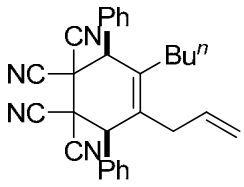


5a

D-A reaction of diene 4a with TCNE:

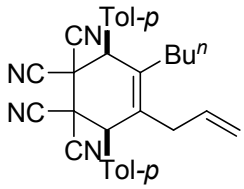
4a was treated with TCNE in THF at room temperature for 12 h, the TCNE-adduct **8a** was obtainedin 82% isolated yield. ^{1}H NMR (300MHz, $CDCl_3$, Me_4Si) δ 0.83 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H), 1.20-1.50 (m, 4H), 1.79-1.88 (m, 1H), 2.47-2.59 (m, 2H), 3.28-3.35 (m, 1H), 4.39 (s, 2H), 4.96 (d, $^{3}J_{HH}$ = 17.2 Hz, 1H), 5.15 (d, $^{3}J_{HH}$ = 10.0 Hz, 1H), 5.60-5.73 (m, 1H), 7.47-7.54 (m, 10H); ^{13}C NMR (75MHz, $CDCl_3$, Me_4Si) δ 13.8 (CH_3), 22.8 (CH_2), 30.4 (CH_2), 31.6 (CH_2), 35.7 (CH_2), 43.7 (C), 43.7 (C), 49.6 (CH), 50.4 (CH), 109.8 (C), 112.2 (C), 112.3 (C), 118.8 (CH_2), 129.1 (CH), 129.2 (CH),

129.5 (C), 130.3 (CH), 130.3 (CH), 131.5 (C), 131.7 (C), 133.4 (CH), 133.7 (CH).



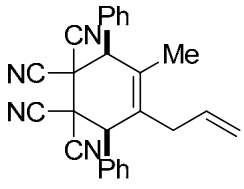
8a

Compound **8b**: 77% isolated yield. ^{1}H NMR (300MHz, $CDCl_3$, Me_4Si) δ 0.83 (t, $^3J_{HH}$ = 6.9 Hz, 3H), 1.20-1.45 (m, 4H), 1.78-1.87 (m, 1H), 2.39 (s, 6H), 2.51-2.59 (m, 2H), 3.27-3.31 (m, 1H), 4.33 (s, 2H), 4.96 (d, $^3J_{HH}$ = 16.9 Hz, 1H), 5.13 (d, $^3J_{HH}$ = 10.0 Hz, 1H), 5.58-5.72 (m, 1H), 7.25-7.39 (m, 8H); ^{13}C NMR (75MHz, $CDCl_3$, Me_4Si) δ 13.8 (CH_3), 21.4 (CH_3), 22.8 (CH_2), 30.4 (CH_2), 31.6 (CH_2), 35.6 (CH_2), 43.7 (C), 43.8 (C), 49.4 (CH), 50.2 (CH), 109.8 (C), 109.9 (C), 112.3 (C), 112.4 (C), 118.6 (CH_2), 129.5 (C), 129.8 (CH), 131.1 (CH), 133.5 (CH), 133.7 (C), 140.3 (C), 140.4 (C).



8b

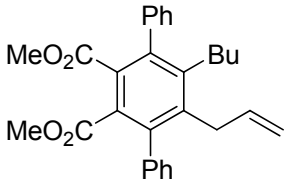
Compound **8c**: 74% isolated yield. ^{1}H NMR (300MHz, $CDCl_3$, Me_4Si) δ1.78 (s, 3H), 2.47-2.55 (m, 1H), 3.19-3.26 (m, 1H), 4.30 (s, 1H), 4.36 (s, 1H), 5.02 (d, $^3J_{HH}$ = 17.2 Hz, 1H), 5.14 (d, $^3J_{HH}$ = 10.0 Hz, 1H), 5.60-5.74 (m, 1H), 7.46-7.52 (m, 10H); ^{13}C NMR (75MHz, $CDCl_3$, Me_4Si) δ 18.8 (CH_3), 35.9 (CH_2), 43.7 (C), 43.8 (C), 49.6 (CH), 52.5 (CH), 109.4 (C), 110.1 (C), 112.2 (C), 112.3 (C), 118.0 (CH_2), 129.0 (CH), 129.3 (CH), 129.5 (C), 130.3 (CH), 131.3 (C), 131.9 (C), 132.2 (CH).



8c

Reaction of zirconacyclopentadiene with DMAD in the present of CuCl:

To the THF solution of zirconacyclopentadiene **6a**, 2 mmol CuCl was added in 0°C. Then 1 mmol DMAD was added, and the mixture was warmed up to room temperature and kept for 3 h. The reaction mixture was quenched with 2N HCl and extracted with ethyl ether. The organic extract was dried over $MgSO_4$. Removing the solvent and subsequent purification by column chromatography on silica gel afforded **4a** in 47 % yield. ^{1}H NMR (300MHz, $CDCl_3$, Me_4Si) δ 0.67 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 1.06-1.34 (m, 4H), 2.47 (t, $^3J_{HH}$ = 7.4 Hz, 2H), 3.29 (d, $^3J_{HH}$ = 5.1 Hz, 2H), 3.40 (s, 6H), 4.69 (d, $^3J_{HH}$ = 17.1 Hz, 1H), 4.95 (d, $^3J_{HH}$ = 10.0 Hz, 1H), 5.66-5.80 (m, 1H), 7.24-7.40 (m, 10H); ^{13}C NMR (75MHz, $CDCl_3$, Me_4Si) δ 13.5 (CH_3), 23.0 (CH_2), 30.1 (CH_2), 32.9 (CH_2), 34.4 (CH_2), 52.1 (CH_3), 115.9 (CH_2), 126.9 (CH), 127.0 (CH), 127.5 (CH), 128.0 (CH), 129.4 (CH), 129.6 (CH), 136.4 (CH), 138.5 (C), 138.9 (C), 139.0 (C), 140.0 (C), 140.5 (C), 143.4 (C), 168.7 (C), 168.8 (C). GC-MS (*m/z*) : 442.



6a