

Cover page for Supporting Information

Manuscript Title:

Zirconocene-Mediated Ligand-Switched Selective Cleavage of Active and Inert Carbon-Carbon Bonds in Allylcyclopropanes

Authors:

Chao Wang, Liang Deng, Jun Yan, Hailin Wang, Qian Luo, Wen-Xiong Zhang, and Zhenfeng Xi*

Affiliations:

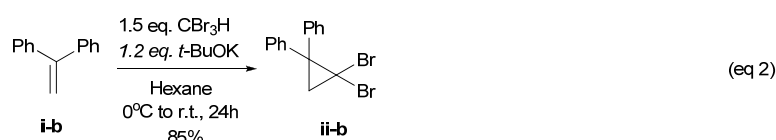
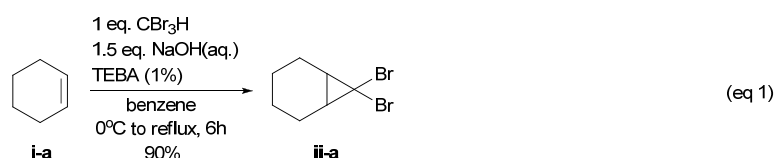
Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

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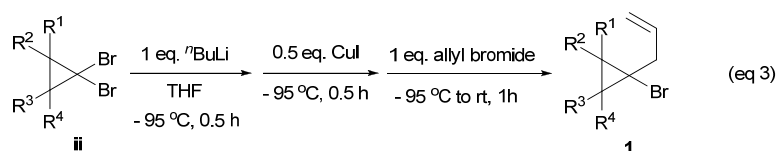
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1) Experimental Details and Characterization Data

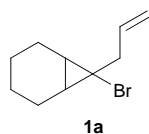
General Methods. All reactions were conducted under a slightly positive pressure of dry, prepurified nitrogen using standard Schlenk line techniques when appropriate. Unless otherwise noted, all starting materials were commercially available and were used without further purification. THF and toluene were refluxed and distilled from sodium/benzophenone ketyl under a nitrogen atmosphere. 1,1-Dibromocyclopropanes **ii** are easily prepared from corresponding alkenes **i** according to the literature, as showed in eq 1^a and 2^b. ¹H and ¹³C NMR spectra were recorded in CDCl₃ solution at 300 and 75 MHz respectively.



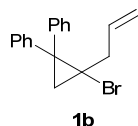
Synthesis of 1-allyl-1-bromocyclopropane **1**²



As showed in eq 3, to a solution of 1,1-dibromocyclopropane **ii** (10 mmol) in 30 ml THF was added *n*-BuLi (10 mmol, 2.89M in hexane) at -95 °C. The reaction mixture was stirred at -95 °C for 0.5 h and then was added CuI (10 mmol). The above mixture was kept at the same temperature for another 0.5 h and Allylbromide (10 mmol) was added thereafter. The reaction completed within one hour and was quenched with HCl (3N). The aqueous layer was extracted with hexanes and the combined organic layer was washed successively with saturated NaHCO₃ and brine. Solvent was removed under reduced pressure and the residue was purified by chromatography to give product **1**.



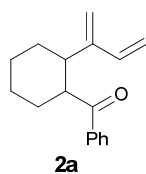
1a: Colorless liquid, isolated yield 77% (1.68 g); ^1H NMR (300 MHz, CDCl_3 , Me_4Si , 25 $^\circ\text{C}$): δ = 1.15-1.30 (m, 4H, CH_2), 1.51-1.61 (m, 4H, CH_2), 1.86-1.93 (m, 2H, CH), 2.61 (d, J = 6.3 Hz, 2H, CH_2), 5.17-5.23 (m, 2H, CH), 5.90-6.04 (m, 1H, CH) ; ^{13}C NMR (75 MHz, CDCl_3 , Me_4Si , 25 $^\circ\text{C}$): δ = 18.57 (2 CH_2), 21.35 (2 CH_2), 23.03 (2 CH), 37.69 (1 CH_2), 42.02 (1 quat C), 117.02 (1 CH_2), 135.10 (1 CH); HRMS(EI) calcd. for $\text{C}_{10}\text{H}_{15}^{79}\text{Br}$: 136.1252, found 136.1246.



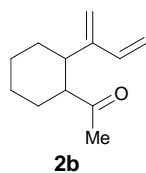
1b :Colorless liquid, isolated yield 61% (1.91 g); ^1H NMR (300 MHz, CDCl_3 , Me_4Si , 25 $^\circ\text{C}$): δ = 1.89 (dd, J = 6.6 Hz, 2H, CH_2), 2.48 (AB-d, J_{AB} = 15.1 Hz, J_d = 9.0 Hz, 2H, CH_2), 5.04 (d, J = 16.8 Hz, 1H, CH_2), 5.14 (d, J = 10.2 Hz, 1H, CH_2), 5.90-6.04 (m, 1H, CH), 7.13-7.51 (m, 10H, CH) ; ^{13}C NMR (75 MHz, CDCl_3 , Me_4Si , 25 $^\circ\text{C}$): δ = 27.35 (1 CH_2), 42.96 (1 quat C), 44.67 (1 CH_2), 45.37 (1 quat C), 117.55 (1 CH_2), 126.72 (1 CH), 126.83 (1 CH), 128.09 (2 CH), 128.58 (2 CH), 129.19 (2 CH), 129.78 (2 CH), 135.21 (1 CH), 141.44 (1 quat C), 143.92 (1 quat C).

Synthesis of butadiene derivatives **2** via $\text{Cp}_2\text{Zr}^n\text{Bu}_2$ and CuCl -mediated cascade reaction of **1a** with RCOCl

To a solution of $\text{Cp}_2\text{Zr}^n\text{Bu}_2$ (1 mmol, generated in situ by Cp_2ZrCl_2 and $^n\text{BuLi}$ [1.6 M in Hexanes] according to the literature.³) in 5ml THF was added 7-allyl-7-bromobicyclo[4.1.0.]heptane **1a** (1 mmol) at -78 $^\circ\text{C}$. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. CuCl (1.1 mmol) and RCOCl (1.1 mmol) was then added at 0 $^\circ\text{C}$. The reaction mixture was again warmed up to room temperature and stirred for 2 h before quenched with HCl (3N). The aqueous layer was extracted with ether and the combined organic layer was washed successively with saturated NaHCO_3 and brine. Solvent was removed under reduced pressure and the residue was purified by chromatography to give the title product **2**.



2a: Colorless liquid, isolated yield 40% (96 mg); ^1H NMR (300 MHz, CDCl_3 , Me_4Si , 25 $^\circ\text{C}$): δ = 1.34-1.95 (m, 7H, CH_2), 2.43 (dq, J_d = 13.0 Hz, J_q = 3.9 Hz, 1H, CH_2), 2.71 (dt, J_d = 12.0 Hz, J_t = 3.6 Hz, 1H, CH), 3.98-4.00 (m, 1H, CH), 4.98-5.06 (m, 3H, CH), 5.26 (d, J = 17.7 Hz, 1H, CH), 6.22 (dd, J_1 = 17.7 Hz, J_2 = 10.8 Hz, 1H, CH), 7.33-7.49 (m, 3H, CH), 7.76-7.80 (m, 2H, CH) ; ^{13}C NMR (75 MHz, CDCl_3 , Me_4Si , 25 $^\circ\text{C}$): δ = 21.43 (1 CH_2), 26.13 (1 CH_2), 26.22 (1 CH_2), 28.77 (1 CH_2), 40.28 (1 CH), 42.66 (1 CH), 112.34 (1 CH_2), 116.83 (1 CH_2), 127.98 (2 CH), 128.33 (2 CH), 132.25 (1 CH), 138.56 (1 quat C), 139.47 (1 CH), 147.81 (1 quat C), 203.49 (C=O); HRMS(EI) calcd. for $\text{C}_{17}\text{H}_{20}\text{O}$: 240.1514, found 240.1510.

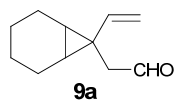


2b: Colorless liquid, isolated yield 45% (82 mg); ^1H NMR (300 MHz, CDCl_3 , Me_4Si , 25 $^\circ\text{C}$): δ = 1.25-2.13 (m, 8H, CH_2), 2.00 (s, 3H, CH_3), 2.66-2.72 (m, 1H, CH), 3.05 (q, J = 7.5 Hz, 1H, CH), 4.99-5.11 (m, 3H, CH), 5.27 (d, J = 17.7 Hz, 1H, CH), 6.31 (dd, J_1 = 17.7 Hz, J_2 = 10.8 Hz, 1H, CH) ; ^{13}C NMR (75 MHz, CDCl_3 , Me_4Si , 25 $^\circ\text{C}$): δ = 22.25 (1 CH_3), 25.27 (1 CH_2), 26.61 (1 CH_2), 27.29 (1 CH_2), 31.43 (1 CH_2), 39.33 (1 CH), 49.41 (1 CH), 112.78 (1 CH_2), 116.47 (1 CH_2), 139.15 (1 CH), 147.79 (1 quat C), 211.65 (C=O).

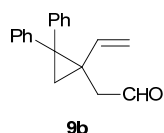
Synthesis of **9** via $\text{Cp}_2\text{Zr}^n\text{Bu}_2$ -mediated reaction of **1a** followed by carbonylation with CO

To a solution of $\text{Cp}_2\text{Zr}^n\text{Bu}_2$ (1 mmol, generated in situ by Cp_2ZrCl_2 and $n\text{-BuLi}$ [1.6 M in Hexanes] according to the literature.³) in 5ml THF was added 1-allyl-1-bromocyclopropane **1** (1 mmol) at -78 $^\circ\text{C}$. The reaction mixture was allowed to warm to room temperature and stirred for 2h. CO gas was slowly bubbled into the reaction mixture for 2h. HCl (3N) was added to stop the reaction and the aqueous layer was extracted with Ether. The combined organic layer was washed successively with saturated NaHCO_3 and brine. Solvent was removed under reduced pressure and

the residue was purified by chromatography to give the title product **9**.



9a: Colorless liquid, isolated yield 33% (54mg). ^1H NMR (300 MHz, CDCl_3 , Me_4Si , 25 $^\circ\text{C}$): δ = 1.12-1.44 (m, 8H, CH_2), 2.01 (t, J = 7.9 Hz, 2H, CH), 2.38 (d, J = 2.1 Hz, 2H, CH_2), 4.78 (d, J = 17.2 Hz, 1H, CH_2), 4.86 (d, J = 10.8 Hz, 1H, CH_2), 5.40 (dd, J_1 = 17.1 Hz, J_2 = 10.8 Hz, 1H, CH_2), 9.78 (t, J = 2.1 Hz, 1H, CH) ; ^{13}C NMR (75 MHz, CDCl_3 , Me_4Si , 25 $^\circ\text{C}$): δ = 19.30 (2 CH_2), 20.97 (2 CH), 21.85 (2 CH_2), 24.72 (1 quat C), 40.67 (1 CH_2), 109.93 (1 CH_2), 146.35 (1 CH), 203.49 (1 CH) ; HRMS(EI) calcd. for $\text{C}_{11}\text{H}_{16}\text{O}$: 164.1201, found 164.1197.

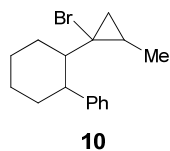


9b : Colorless crystals, isolated yield 21% (57 mg); ^1H NMR (300 MHz, CDCl_3 , Me_4Si , 25 $^\circ\text{C}$): δ = 1.78 (AB, J = 5.3 Hz, 2H, CH_2), 2.38 (AB-d, J_{AB} = 17.4 Hz, J_d = 3.3 Hz, 2H, CH_2), 4.92 (d, J = 17.4 Hz, 1H, CH_2), 4.98 (d, J = 10.8 Hz, 1H, CH_2), 5.36 (dd, J_1 = 17.4 Hz, J_2 = 10.8 Hz, 1H, CH_2), 7.13-7.45 (m, 10H, CH), 9.68-9.70 (m, 1H, CH) ; ^{13}C NMR (75 MHz, CDCl_3 , Me_4Si , 25 $^\circ\text{C}$): δ = 24.88 (1 CH_2), 29.03 (1 quat C), 42.66 (1 quat C), 46.82 (1 CH_2), 113.19 (1 CH), 126.51 (1 CH), 126.77 (1 CH), 128.34 (2 CH), 128.68 (2 CH), 129.37 (2 CH), 130.21 (2 CH), 141.49 (1 CH), 142.56 (1 quat C), 142.64 (1 quat C), 202.38 (1 CH) ; HRMS(EI) calcd. for $\text{C}_{19}\text{H}_{18}\text{O}$: 262.1358, found 262.1356.

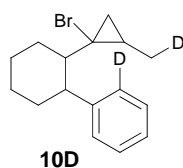
Synthesis of **10** via Cp_2ZrPh_2 -mediated reaction of **1a**

To a solution of Cp_2ZrPh_2 (1 mmol, generated in situ by Cp_2ZrCl_2 and PhLi [2.0 M in $n\text{Bu}_2\text{O}$] according to the literature.⁴) in 5ml toluene was added 7-allyl-7-bromobicyclo[4.1.0.]heptane **1a** (1 mmol) at 0 $^\circ\text{C}$. The reaction mixture was heated to 100 $^\circ\text{C}$ for 3h and then cooled down to 0 $^\circ\text{C}$ before quenched with with 3N HCl (for **10**) or $\text{DCI}/\text{D}_2\text{O}$ (for **10D**). The aqueous layer was extracted with Ether and the combined organic layer was washed successively with saturated

NaHCO₃ and brine. Solvent was removed under reduced pressure and the residue was purified by chromatography to give the title product **10**.



10: Colorless liquid, isolated yield 80% (234mg); ¹H NMR (300 MHz, CDCl₃, Me₄Si, 25 °C): δ = 0.74-1.64 (m, 1H, CH; 8H, CH₂), 1.38 (d, *J* = 7.0 Hz, 3H, CH₃), 1.86-2.04 (m, 1H, CH; 2H, CH₂), 3.35 (q, *J* = 7.2 Hz, 1H, CH), 7.16-7.31 (m, 5H, CH) ; ¹³C NMR (75 MHz, CDCl₃, Me₄Si, 25 °C): δ = 18.29 (1 CH₂), 19.33 (1 CH₂), 20.47 (1 CH₃), 21.35 (1 CH₂), 21.42 (1 CH₂), 23.41 (1 CH), 23.77 (1 CH), 38.92 (1 CH), 41.65 (1 CH₂), 44.25 (1 quat C), 126.15 (1 CH), 127.37 (2 CH), 128.33 (2 CH), 146.94 (1 quat C); HRMS(EI) calcd. for C₁₆H₂₁Br: 292.0825, found 292.0831.



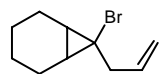
10D: Colorless liquid, isolated yield 75% (221mg); D > 98% ; ¹H NMR (300 MHz, CDCl₃, Me₄Si, 25 °C): δ = 0.57-1.57 (m, 1H, CH; 10H, CH₂), 1.77-1.97 (m, 1H, CH; 2H, CH₂), 3.22-3.31 (m, 1H, CH), 7.09-7.23 (m, 4H, CH) ; ¹³C NMR (75 MHz, CDCl₃, Me₄Si, 25 °C): δ = 18.25 (1 CH₂), 19.31 (1 CH₂), 20.12 (t, *J* = 19.2, 1 CD), 20.43 (1 CH₃), 21.33 (1 CH₂), 21.40 (1 CH₂), 23.36 (1 CH), 23.73 (1 CH), 38.83 (1 CH), 41.61 (1 CH₂), 44.26 (1 quat C), 126.12 (1 CH), 127.36 (1 CH and 1 quart. C), 128.30 (2 CH), 146.94 (1 quat C); HRMS(EI) calcd. for C₁₆H₁₉D₂Br: 294.0952, found 294.0953.

References

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3. S. L. Buchwald, B. T. Watson and J. C. Hoffman, *J. Am. Chem. Soc.*, 1986, **108**, 7411.

2) Copies of ^1H NMR and ^{13}C NMR spectra for all new compounds.



1a

