OL Organic Letters

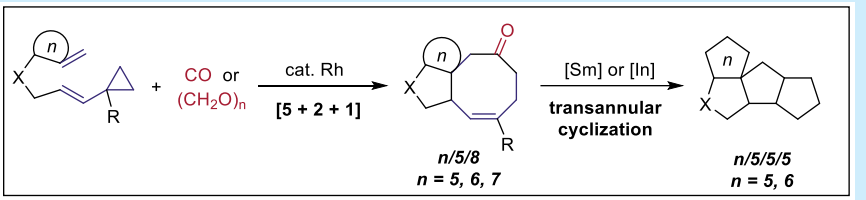
pubs.acs.org/OrgLett Letter

# Synthesis of Polycyclic *n*/5/8 and *n*/5/5/5 Skeletons Using Rhodium-Catalyzed [5 + 2 + 1] Cycloaddition of Exocyclic-ene-vinylcyclopropanes and Carbon Monoxide

Lu-Ning Wang,[†] Zhiqiang Huang,[†] and Zhi-Xiang Yu*

Cite This: *Org. Lett.* 2023, 25, 1732−1736 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information




**ABSTRACT:** A rhodium-catalyzed [5 + 2 + 1] reaction of exocyclic-ene-vinylcyclopropanes (exo-ene-VCPs) and CO has been realized to access challenging tricyclic *n*/5/8 skeletons (*n* = 5, 6, 7), some of which are found in natural products. This reaction can be used to build tetracyclic *n*/5/5/5 skeletons (*n* = 5, 6), which are also found in natural products. In addition, 0.2 atm CO can be replaced by $(CH_2O)_n$ as the CO surrogate to achieve the [5 + 2 + 1] reaction with similar efficiency.



Eight-membered carbocycles are found in many natural products, many of which have significant biological activities (Figure 1a and b).[1] The synthesis of eight-membered carbocycles is still posing challenges, and many leading chemists have been developing new methods and strategies for accessing this skeleton.[2] Among these reported reactions, transition-metal-catalyzed cycloadditions using various synthons provide many efficient ways to build target skeletons. For example, we once developed a rhodium-catalyzed [5 + 2 + 1] reaction of ene-vinylcyclopropanes (ene-VCPs) and CO (Scheme 1a, atom labeling of the substrates is also shown here).[3a,b] We applied this reaction to the synthesis of eight-membered ring containing natural products, such as (±)-asterisca-3(15),6-diene[3c] and (+)-asteriscanolide.[3d,e] Recently, we wondered whether this [5 + 2 + 1] reaction can be used to synthesize angular tricycles containing eight-membered carbocycles using substrates of exocyclic ene-vinylcyclopropanes (exo-ene-VCPs), which have their $C_8$ and $C_a$ atoms fused by a ring (Scheme 1b). We felt excited by this idea because the target tricyclic skeletons from this [5 + 2 + 1] reaction, if successful, are found in natural products such as hyphenrones D and pepluanol B shown in Figure 1b.[4]

Previously, we developed strategies to combine the [5 + 2 + 1] reaction with other transannular reactions such as aldol, ene, and radical coupling to access 5/5/5 tricyclic skeletons (Scheme 1a).[5] Some natural products synthesized by this strategy are shown in Figure 1c.[5] If the above-mentioned idea of the synthesis of angular tricycles containing eight-membered carbocycles can be accomplished using exocyclic ene-vinylcyclopropanes, we then envisioned that the cycloadducts from the [5 + 2 + 1] reactions could also be converted to 5/5/5/5 and 6/5/5/5 tetracyclic skeletons (Scheme 1b), some of which are found in natural products shown in Figure 1d.[6] Importantly, these natural products have significant biological activities (listed also in Figure 1d) and have attracted intensive attention from many leading total synthetic chemists.[7] Therefore, the synthesis of these multicyclic rings by the present strategy would provide new and step-economic ways to access related natural products and analogues, which could then be beneficial for future drug discovery. We were happy to realize the above two formidable goals, which are communicated here.

The synthesis of exo-ene-VCP substrates was quick, and details are given in the Supporting Information. The reaction conditions for the present [5 + 2 + 1] reaction (Scheme 2) include 10 mol % $[Rh(CO)_2Cl]_2$, 0.2 atm CO, and dioxane as the solvent (using our traditional condition of 5 mol % catalyst gave only 42% yield of **2a**, see the Supporting Information for details). We were happy to find that **1a** can undergo [5 + 2 + 1] cycloaddition, giving rise to the *cis*−*cis*-5/5/8 tricyclic product **2a** (confirmed by X-ray analysis) in a 49% yield with excellent diastereoselectivity. The stereochemistry can be rationalized by the irreversible alkene insertion step, as revealed by DFT calculations shown in the Supporting

**Received:** February 8, 2023
**Published:** March 7, 2023





https://doi.org/10.1021/acs.orglett.3c00402
*Org. Lett.* 2023, 25, 1732−1736

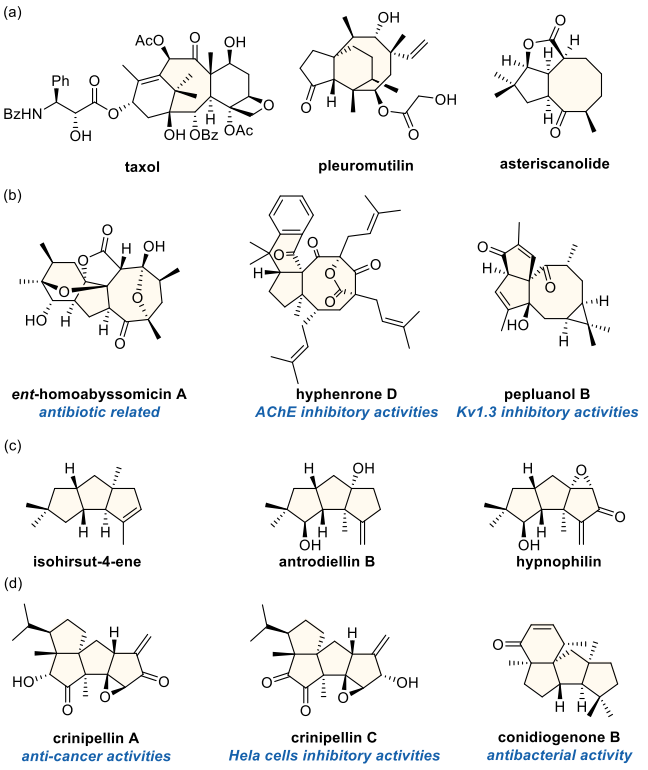
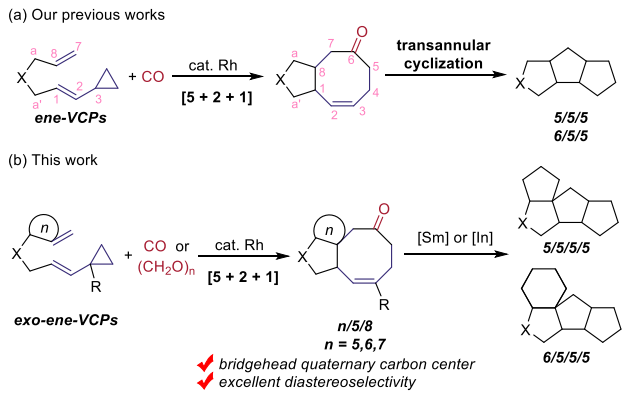



**Figure 1.** (a) Selected natural products featuring eight-membered carbocycles. (b) Examples of 6/5/8 and 5/5/8 embedded natural products. (c) Selected 5/5/5 natural products synthesized by a [5 + 2 + 1] reaction combined with transannular reactions. (d) Examples of 5/5/5/5 and 6/5/5/5 tetracyclic natural products.

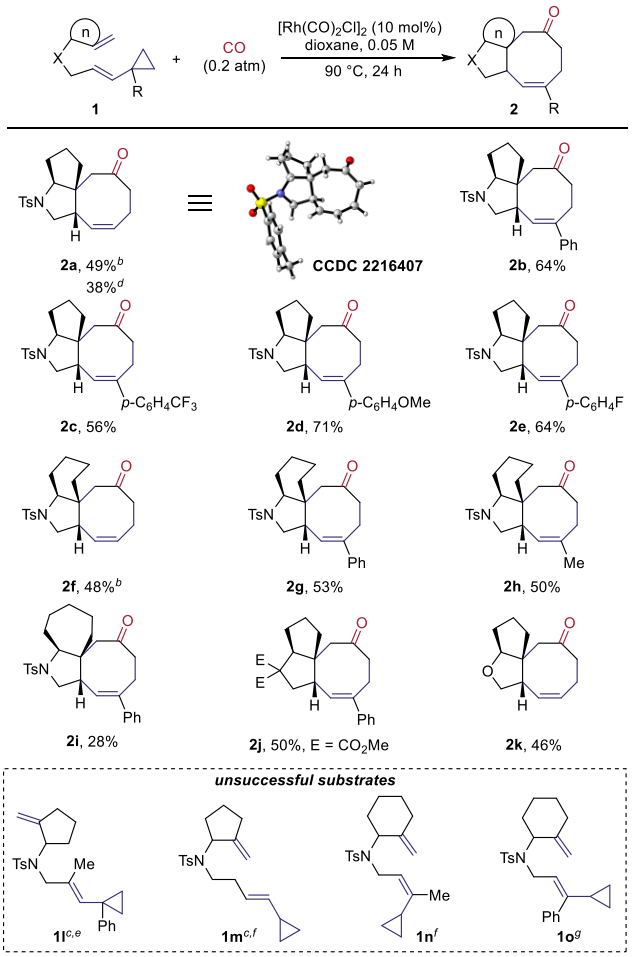
## Scheme 1. [5 + 2 + 1] Reaction and Its Application




Information. Then phenyl-substituted substrate **1b** was tested, showing that the corresponding tricyclic product **2b** was obtained in a 64% yield. To our delight, electron-withdrawing and electron-donating phenyl groups in the substrates were tolerated, delivering [5 + 2 + 1] products **2c**–**e** in moderate yields (56–71%).

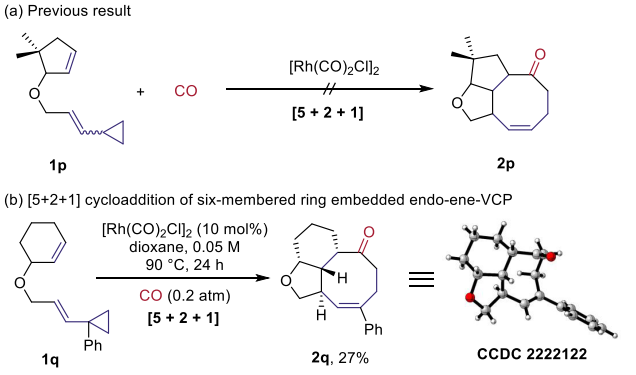
To our excitement, substrate **1f**, the phenyl-substituted substrate **1g**, and the methyl-substituted substrate **1h** can all undergo [5 + 2 + 1] reactions, generating respectively *cis*–*cis*-6/5/8 tricyclic products **2f**, **2g**, and **2h** in moderate yields with excellent diastereoselectivities (48%, 53%, and 50%). The structure of **2f** was also confirmed by X-ray analysis of its derivative (see the Supporting Information for details). It is important to underline that the seven-membered ring-embedded substrate **1i** was also suitable for the [5 + 2 + 1] reaction, and the rare 7/5/8 tricyclic product **2i** was obtained in a 28% yield. Finally, we evaluated substrates with different tethers, observing that substrates with *gem*-diester and ether tethers can successfully deliver the tricyclic products **2j** and **2k** in moderate yields (50% and 46%, respectively). Unfortu-

## Scheme 2. Substrate Scope of the [5 + 2 + 1] Reaction[a]




[a]All reactions used 10 mol % $[Rh(CO)_2Cl]_2$ in 0.05 M dioxane under 0.2 atm CO and 0.8 atm $N_2$ at 90 °C for 24 h unless otherwise specified, substrates were on the 0.07–0.68 mmol scale, and the reported yields represent an average of the yields of the isolated products from two runs. [b]Confirmed by X-ray analysis. [c]*Z*/*E* mixture. [d]1 mmol scale with 5 mol % $[Rh(CO)_2Cl]_2$. [e]Partially decomposed at 150 °C in *p*-xylene. [f]A mixture was obtained at 150 °C in *p*-xylene. [g]An undetermined byproduct was obtained at 120 °C in *p*-xylene.

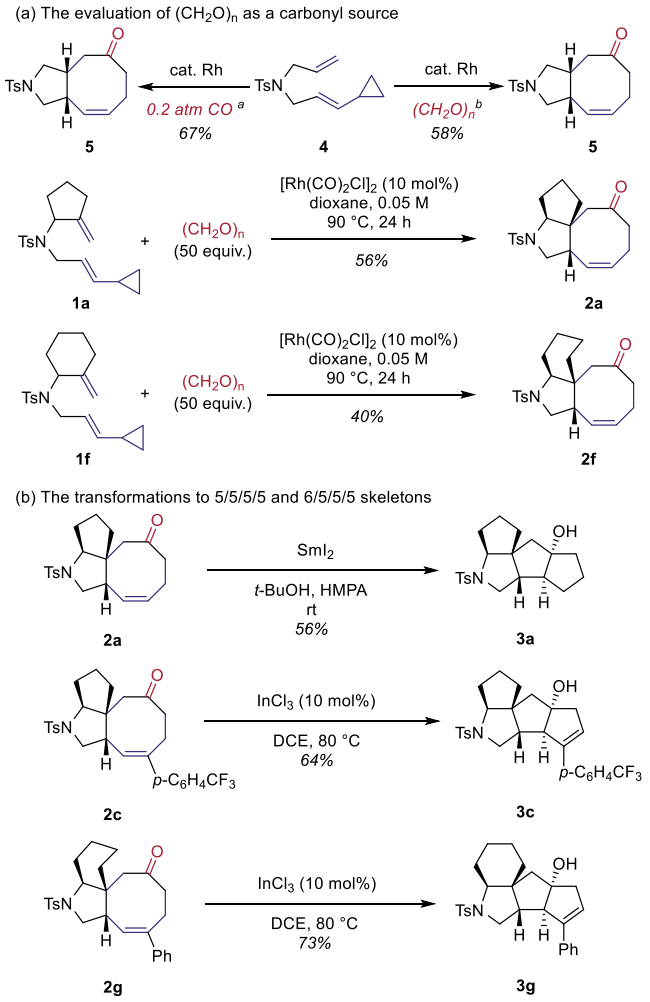
## Scheme 3. [5 + 2 + 1] Reaction of Endo-ene-VCPs and CO






https://doi.org/10.1021/acs.orglett.3c00402
Org. Lett. 2023, 25, 1732–1736

**Scheme 4. Evaluation of $(CH_2O)_n$ as a Carbonyl Source for the [5 + 2 + 1] Reaction and the Transformations of [5 + 2 + 1] Cycloadducts to 5/5/5/5 and 6/5/5/5 Compounds**




[a]The reaction used 6 mol % $[Rh(CO)_2Cl]_2$ in 0.05 M dioxane under 0.2 atm CO and 0.8 atm $N_2$ at 80 °C for 36 h. [b]The reaction used 6 mol % $[Rh(CO)_2Cl]_2$ in 0.05 M dioxane under an argon atmosphere at 80 °C for 36 h with 50 equiv of $(CH_2O)_n$.

nately, substrate **1l** with two substituents, a methyl group in the $C_1$ position and a phenyl group in the $C_3$ position of the VCP moiety, failed. The [5 + 2 + 1] reaction of substrate **1m** to synthesize the 5/6/8 product was not successful either. We were also disappointed by finding that neither substrate **1n** with a *cis* $C_1$═$C_2$ double bond in its VCP moiety nor substrate **1o** with a phenyl group in its $C_2$ position can participate in the [5 + 2 + 1] reactions (Scheme 2).

The above-described successes encouraged us to test whether endo-ene-VCP substrates (with the $C_a$, $C_7$, and $C_8$ in a ring) can also give the tricyclic products (Scheme 3). Actually, we tested this idea using **1p** in our previous synthesis of asteriscanolide.[3d,e] Unfortunately, this substrate did not succeed. Maybe the five-membered ring in this substrate is too compact and consequently alkene insertion of the $2\pi$ component in the [5 + 2 + 1] reaction could be difficult (Scheme 3a). We then speculated that a substrate with a six-membered ring could have easier alkene insertion and the corresponding [5 + 2 + 1] reaction would have the opportunity to occur. To our delight, the [5 + 2 + 1] reaction of **1q** did give the desired cycloadduct, even though the yield was 27% (Scheme 3b). We also computationally studied the stereochemistry of this [5 + 2 + 1] reaction, showing the diastereoselectivity is determined by the reductive elimination step, not the alkene insertion step (see the Supporting Information for details).

In the [5 + 2 + 1] reaction, we applied 0.2 atm CO, which can be easily prepared by mixing two gases of CO and $N_2$ in a 1:4 ratio. If 0.2 atm CO gas was not available, we recommend chemists use $(CH_2O)_n$ as the surrogate for the 1C synthon. This idea was inspired by the rhodium-catalyzed Pauson–Khand reaction using $(CH_2O)_n$ as the carbonyl source.[8] We were happy to find that, using 50 equiv of $CH_2O$, substrate **4** can undergo the [5 + 2 + 1] reaction to generate bicyclic product **5** in a 58% yield, which was 9% lower than that using 0.2 atm CO (Scheme 4a). For substrates **1a** and **1f**, similar yields (56% and 40% with $(CH_2O)_n$ vs 49% and 48% with CO, respectively) were obtained.

Finally, we demonstrated that the present tricyclic products can be converted into compounds with 5/5/5/5 and 6/5/5/5 skeletons (Scheme 4b). First, compound **2a** could undergo a $SmI_2$-mediated reductive coupling reaction to deliver the tetracyclic product **3a** in a 56% yield at room temperature. Compound **2c** catalyzed by 10 mol % $InCl_3$[5b] underwent an ene reaction to generate product **3c** in a 64% yield. Additionally, the 6/5/5/5 tetracyclic product **3g** was obtained in a 73% yield from the ene reaction of [5 + 2 + 1] cycloadduct **2g**.

In conclusion, the rhodium-catalyzed [5 + 2 + 1] cycloadditions of exocyclic-ene-vinylcyclopropanes with CO can successfully take place to access *cis*–*cis*-*n*/5/8 ($n$ = 5, 6, 7) tricyclic products. Importantly, these tricyclic products can in principle be converted into molecules with 5/5/5/5 or 6/5/5/5 tetracyclic skeletons, as demonstrated by three examples in this paper. In addition, cheap and convenient $(CH_2O)_n$ can act as an effective carbonyl source for the [5 + 2 + 1] reaction.

## ■ ASSOCIATED CONTENT

### Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.3c00402.

DFT study, experimental procedures, characterization data, and crystallographic data for new compounds (PDF)

### Accession Codes

CCDC 2216407–2216408 and 2222122 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

## ■ AUTHOR INFORMATION

### Corresponding Author

**Zhi-Xiang Yu** − *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;*



https://doi.org/10.1021/acs.orglett.3c00402
Org. Lett. 2023, 25, 1732−1736

orcid.org/0000-0003-0939-9727; Email: yuzx@pku.edu.cn

## Authors

**Lu-Ning Wang** − *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*

**Zhiqiang Huang** − *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*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.3c00402

## Author Contributions

†L.-N.W. and Z.H. contributed equally to this work.

## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21933003) and the High-Performance Computing Platform of Peking University. We thank Mr. Chen-Kai Fan at Peking University for his assistance in some synthetic experiments.

## ■ REFERENCES

(1) (a) Kavanagh, F.; Hervey, A.; Robbins, W. J. Antibiotic Substances From Basidiomycetes: VIII. *Pleurotus Multilus* (Fr.) Sacc. and *Pleurotus Passeckerianus* Pilat. *Proc. Natl. Acad. Sci. U. S. A.* **1951**, *37*, 570−574. (b) Wani, M. C.; Taylor, H. L.; Wall, M. E.; Coggon, P.; Mcphail, A. T. Plant Antitumor Agents. VI. Isolation and Structure of Taxol, a Novel Antileukemic and Antitumor Agent from *Taxus brevifolia*. *J. Am. Chem. Soc.* **1971**, *93*, 2325−2327. (c) Goethe, O.; Heuer, A.; Ma, X.; Wang, Z.; Herzon, S. B. Antibacterial Properties and Clinical Potential of Pleuromutilins. *Nat. Prod. Rep.* **2019**, *36*, 220−247.

(2) (a) Petasis, N. A.; Patane, M. A. The Synthesis of Carbocyclic Eight-Membered Rings. *Tetrahedron* **1992**, *48*, 5757−5821. (b) Mehta, G.; Singh, V. Progress in the Construction of Cyclooctanoid Systems: New Approaches and Applications to Natural Product Syntheses. *Chem. Rev.* **1999**, *99*, 881−930. (c) Yet, L. Metal-mediated synthesis of medium-sized rings. *Chem. Rev.* **2000**, *100*, 2963−3008. (d) Yu, Z.-X.; Wang, Y.; Wang, Y. Transition-Metal-Catalyzed Cycloadditions for the Synthesis of Eight-Membered Carbocycles. *Chem. - Asian J.* **2010**, *5*, 1072−1088. (e) Hu, Y.-J.; Li, L.-X.; Han, J.-C.; Min, L.; Li, C.-C. Recent Advances in the Total Synthesis of Natural Products Containing Eight-Membered Carbocycles (2009−2019). *Chem. Rev.* **2020**, *120*, 5910−5953. (f) Wang, L.-N.; Yu, Z.-X. Transition-Metal-Catalyzed Cycloadditions for the Synthesis of Eight-Membered Carbocycles: An Update from 2010 to 2020. *Youji Huaxue* **2020**, *40*, 3536−3558. (g) Inglesby, P. A.; Evans, P. A. Stereoselective Transition Metal-Catalysed Higher-Order Carbocyclisation Reactions. *Chem. Soc. Rev.* **2010**, *39*, 2791−2805. (h) Liu, L.; Du, L.; Li, B. Recent Advances in 8$\pi$ Electrocyclization Reactions. *Chem. Commun.* **2023**, *59*, 670−687.

(3) (a) Wang, Y.; Wang, J.; Su, J.; Huang, F.; Jiao, L.; Liang, Y.; Yang, D.; Zhang, S.; Wender, P. A.; Yu, Z.-X. A Computationally Designed Rh(I)-Catalyzed Two-Component [5 + 2 + 1] Cycloaddition of Ene-vinylcyclopropanes and CO for the Synthesis of Cyclooctenones. *J. Am. Chem. Soc.* **2007**, *129*, 10060−10061. (b) Wang, Y.; Liao, W.; Wang, Y.; Jiao, L.; Yu, Z.-X. Mechanism and Stereochemistry of Rhodium-Catalyzed [5 + 2 + 1] Cycloaddition of Ene-Vinylcyclopropanes and Carbon Monoxide Revealed by Visual Kinetic Analysis and Quantum Chemical Calculations. *J. Am. Chem. Soc.* **2022**, *144*, 2624−2636. (c) Fan, X.; Zhuo, L.-G.; Tu, Y. Q.; Yu, Z.-X. Formal Syntheses of (±)-Asterisca-3(15),6-diene and (±)-Pentalenene using Rh(I)-Catalyzed [(5 + 2) + 1] Cycloaddition. *Tetrahedron* **2009**, *65*, 4709−4713. (d) Liang, Y.; Jiang, X.; Yu, Z.-X. Enantioselective Total Synthesis of (+)-Asteriscanolide via Rh(I)-Catalyzed [(5 + 2) + 1] Reaction. *Chem. Commun.* **2011**, *47*, 6659−6661. (e) Liang, Y.; Jiang, X.; Fu, X.-F.; Ye, S.; Wang, T.; Yu, Z.-X. Total Synthesis of (+)-Asteriscanolide: Further Exploration of the Rhodium(I)-Catalyzed [(5 + 2) + 1] Reaction of Ene-Vinylcyclopropanes and CO. *Chem. - Asian J.* **2012**, *7*, 593−604.

(4) (a) Abdalla, M. A.; Yadav, P. P.; Dittrich, B.; Schüffler, A.; Laatsch, H. ent-Homoabyssomicins A and B, Two New Spirotetronate Metabolites from Streptomyces sp. Ank 210. *Org. Lett.* **2011**, *13*, 2156−2159. (b) Yang, X. W.; Ding, Y.; Zhang, J. J.; Liu, X.; Yang, L. X.; Li, X. N.; Ferreira, D.; Walker, L. A.; Xu, G. New acylphloroglucinol derivatives with diverse architectures from Hypericum henryi. *Org. Lett.* **2014**, *16*, 2434−2437. (c) Wan, L.-S.; Nian, Y.; Ye, C.-J.; Shao, L.-D.; Peng, X.-R.; Geng, C.-A.; Zuo, Z.-L.; Li, X.-N.; Yang, J.; Zhou, M.; Qiu, M.-H. Three Minor Diterpenoids with Three Carbon Skeletons from Euphorbia peplus. *Org. Lett.* **2016**, *18*, 2166−2169.

(5) (a) Jiao, L.; Yuan, C.; Yu, Z.-X. Tandem Rh(I)-Catalyzed [(5 + 2) + 1] Cycloaddition/Aldol Reaction for the Construction of Linear Triquinane Skeleton: Total Syntheses of (±)-Hirsutene and (±)-1-Desoxyhypnophilin. *J. Am. Chem. Soc.* **2008**, *130*, 4421−4430. (b) Liu, J.; Zhou, Y.; Zhu, J.; Yu, Z.-X. Synthesizing Molecules with Linear Tricyclic 5/5/5 and 6/5/5 Skeletons via [5 + 2 + 1]/Ene Strategy. *Org. Lett.* **2021**, *23*, 7566−7570. (c) Liu, J.; Zhou, Y.; Yu, Z.-X. Six-Step Total Synthesis of Isohirsut-4-ene through [5 + 2 + 1] Cycloaddition and Transannular Epoxide−Alkene Cyclization. *Org. Lett.* **2022**, *24*, 1444−1447. (d) Wang, L.-N.; Huang, Z.; Yu, Z.-X. Antrodiellin B/Hypnophilin/Coriolin and Strained 5/5/5 and 5/6/4 Skeletons via [5+2+1]/Epoxidation/Transannular Radical Cyclization. *Cell Rep. Phys. Sci.* **2023**, 101302.

(6) For 5/5/5/5 tetracyclic natural products: (a) Kupka, J.; Anke, T.; Oberwinkler, F.; Schramm, G.; Steglich, W. Antibiotics from Basidiomycetes. VII. Crinipellin, a New Antibiotic from the Basidiomycetous Fungus Crinipellis Stipitaria (Fr.) Pat. *J. Antibiot.* **1979**, *32*, 130−135. (b) Anke, T.; Heim, J.; Knoch, F.; Mocek, U.; Steffan, B.; Steglich, W. Crinipellins, the First Natural Products with a Tetraquinane Skeleton. *Angew. Chem., Int. Ed.* **1985**, *24*, 709−711. (c) Li, Y.-Y.; Shen, Y.-M. Four Novel Diterpenoids from Crinipellis sp. 113. *Helv. Chim. Acta* **2010**, *93*, 2151−2157. For 6/5/5/5 tetracyclic natural products: (d) Roncal, T.; Cordobés, S.; Sterner, O.; Ugalde, U. Conidiation in Penicillium Cyclopium is Induced by Conidiogenone, an Endogenous Diterpene. *Eukaryotic Cell* **2002**, *1*, 823−829. (e) Rodríguez, I.; Rodríguez, A. D.; Zhao, H. Aberrarone: A Gorgonian-Derived Diterpene from Pseudopterogorgia Elisabethae. *J. Org. Chem.* **2009**, *74*, 7581−7584. (f) Niu, S.; Fan, Z.; Tang, X.; Liu, Q.; Shao, Z.; Liu, G.; Yang, X. W. Cyclopiane-type Diterpenes from the Deep-Sea-Derived Fungus Penicillium Commune MCCC 3A00940. *Tetrahedron Lett.* **2018**, *59*, 375−378. (g) Mitsuhashi, T.; Kikuchi, T.; Hoshino, S.; Ozeki, M.; Awakawa, T.; Shi, S. P.; Fujita, M.; Abe, I. Crystalline Sponge Method Enabled the Investigation of a Prenyltransferase-Terpene Synthase Chimeric Enzyme, Whose Product Exhibits Broadened NMR Signals. *Org. Lett.* **2018**, *20*, 5606−5609.

(7) For the total synthesis of 5/5/5/5 tetracyclic natural products: (a) Kotha, S.; Fatma, A. Synthetic Approaches to Natural and Unnatural Tetraquinanes. *Asian J. Org. Chem.* **2022**, *11*, e202100595. (b) Piers, E.; Renaud, J. Total Synthesis of the Tetraquinane Diterpenoid (±)-Crinipellin B. *J. Org. Chem.* **1993**, *58*, 11−13. (c) Piers, E.; Renaud, J.; Rettig, S. J. Tetraquinane Diterpenoids: Total Synthesis of (±)-Crinipellin B. *Synthesis* **1998**, *1998*, 590−602. (d) Wender, P. A.; Dore, T. M. A Formal Synthesis of Crinipellin B Based on the Arene-Alkene Meta-Photocycloaddition Reaction. *Tetrahedron Lett.* **1998**, *39*, 8589−8592. (e) Kang, T.; Song, S. B.; Kim, W.-Y.; Kim, B. G.; Lee, H.-Y. Total Synthesis of (−)-Crinipellin

A. *J. Am. Chem. Soc.* **2014**, *136*, 10274−10276. (f) Huang, Z.; Huang, J.; Qu, Y.; Zhang, W.; Gong, J.; Yang, Z. Total Syntheses of Crinipellins Enabled by Cobalt-Mediated and Palladium-Catalyzed Intramolecular Pauson−Khand Reactions. *Angew. Chem., Int. Ed.* **2018**, *57*, 8744−8748. (g) Zhao, Y.; Hu, J.; Chen, R.; Xiong, F.; Xie, H.; Ding, H. Divergent Total Syntheses of (−)-Crinipellins Facilitated by a HAT Initiated Dowd−Beckwith Rearrangement. *J. Am. Chem. Soc.* **2022**, *144*, 2495−2500. For the total synthesis of 6/5/5/5 tetracyclic natural products: (h) Jeon, H.; Winkler, J. D. Synthesis of Cyclohexane-Angularly-Fused Triquinanes. *Synthesis* **2021**, *53*, 475−488. (i) Hou, S.-H.; Tu, Y.-Q.; Wang, S.-H.; Xi, C.-C.; Zhang, F.-M.; Wang, S.-H.; Li, Y.-T.; Liu, L. Total Syntheses of the Tetracyclic Cyclopiane Diterpenes Conidiogenone, Conidiogenol, and Conidiogenone B. *Angew. Chem., Int. Ed.* **2016**, *55*, 4456−4460. (j) Xu, B.; Xun, W.; Su, S.; Zhai, H. Total Syntheses of (−)-Conidiogenone B, (−)-Conidiogenone, and (−)-Conidiogenol. *Angew. Chem., Int. Ed.* **2020**, *59*, 16475−16479. (k) Qu, Y.; Wang, Z.; Zhang, Z.; Zhang, W.; Huang, J.; Yang, Z. Asymmetric Total Synthesis of (+)-Waihoensene. *J. Am. Chem. Soc.* **2020**, *142*, 6511−6515. (l) Amberg, W. M.; Carreira, E. M. Enantioselective Total Synthesis of (+)-Aberrarone. *J. Am. Chem. Soc.* **2022**, *144*, 15475−15479. (m) Wang, Y.-P.; Fang, K.; Tu, Y.-Q.; Yin, J.-J.; Zhao, Q.; Ke, T. An Efficient Approach to Angular Tricyclic Molecular Architecture via Nazarov-Like Cyclization and Double Ring-Expansion Cascade. *Nat. Commun.* **2022**, *13*, 2335.

(8) Furusawa, T.; Morimoto, T.; Ikeda, K.; Tanimoto, H.; Nishiyama, Y.; Kakiuchi, K.; Jeong, N. Asymmetric Pauson−Khand-Type Reactions of 1,6-Enynes Using Formaldehyde as a Carbonyl Source by Cooperative Dual Rhodium Catalysis. *Tetrahedron* **2015**, *71*, 875−881.





https://doi.org/10.1021/acs.orglett.3c00402
*Org. Lett.* 2023, 25, 1732−1736