ORGANOMETALLICS

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Article

Silver(I)-Catalyzed Stereochemical Isomerization of Cyclopropanols

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Cite This: *Organometallics* 2025, 44, 520−528

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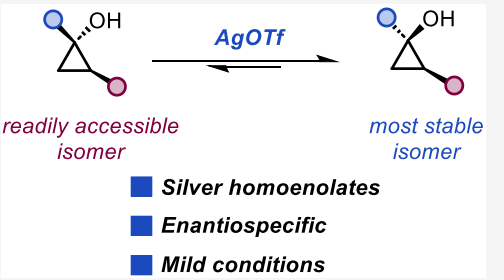
ABSTRACT: Isomerization of cyclopropane-containing molecules offers a direct pathway to access all of their diastereoisomers. Current catalytic methods, however, are largely confined to isomerization of carbonyl- and vinyl-substituted cyclopropanes. We report a catalytic isomerization of cyclopropanols, which converts readily accessible *cis*-1,2-disubstituted cyclopropanols into their more stable, yet often less accessible, *trans*-isomers. This enables a straightforward access to both diastereoisomers of these small-ring molecules. Mechanistic studies indicate the catalytic reactivity of silver homoenolates.



INTRODUCTION

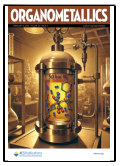
Isomerization of cyclopropane-containing molecules intrigued chemists for several decades. While the isomerization of cyclopropanes under pyrolysis serves as an excellent model system for studying the homolytic activation of C−C σ−bonds,[1] catalyst-controlled isomerizations of cyclopropanes under mild conditions are much less developed.[2] Recently, metal catalysis has gained significant momentum in this area. In 2020, Knowles and Houk demonstrated that the coordination of a redox-active Lewis acid to cyclopropyl ketones lowers the barrier of the cyclopropane's C−C σ−bond homolytic cleavage, enabling isomerization at 80 °C (Scheme 1a, [*M*] = Ru).[3] A fundamentally different strategy was later developed by Gilmour and Neugebauer. The photochemical activation of a chiral Al-salen catalyst in the presence of cyclopropyl ketones enabled *cis-trans* interconversion and importantly deracemization of these compounds.[4] The isomerization of vinyl cyclopropanes requires a different approach (Scheme 1b). In 2017, Echavarren demonstrated a gold(I)-catalyzed isomerization involving allylic carbocations.[5] Subsequently, two reports described suitable gold(III)[6] and rhodium(II) catalysts.[7] Very recently, Schoenebeck disclosed a mechanistically distinct strategy employing Ni(I) metalloradicals for the dynamic stereomutation of vinylcyclopropanes,[8] which represents a rare example of cyclopropanes' isomerization without racemization. Although a few catalytic isomerization strategies have been developed, their application is limited to specific substrates and conditions. These strategies do not translate to other classes of cyclopropane-containing molecules due to differences in their electronic and steric properties. For example, cyclopropanols, which are important structural motif in biologically active compounds[9] and valuable synthetic building blocks,[10] feature distinct reactivity.[11] They undergo facile ring opening under acidic,[12] basic[13] and oxidative[14] conditions even at low temperatures. With metals, they form metal homoenolates, which participate in a range of reactions as nucleophiles[15] and electrophiles (Scheme 1c).[16]

The metal homoenolates are in equilibrium with cyclopropoxides, however, catalytic isomerization of cyclopropanols are scarce. A notable example involves isomerization mediated by Ti(IV) and a Lewis acid under the Kulinkovich reaction conditions.[17] Although a catalytic example was reported, it is limited to a single, relatively unstable compound. Moreover, few reports have demonstrated the isomerization of cyclopropoxides during cyclopropanation with organozinc reagents,[18] and in processes delivering products with decreased ring strain.[19] To date, however, the factors determining stereochemical (*cis*−*trans* interconversion) and structural (formation of the corresponding carbonyl compounds) isomerization are not well understood, and a general platform for the stereochemical isomerization of cyclopropanols remains not developed. We seek to address these questions employing the metal homoenolates. Herein, we demonstrate a catalytic stereochemical isomerization of cyclopropanols employing the largely undeveloped chemistry of silver homoenolates.

RESULTS AND DISCUSSION

To study the stereochemical isomerization we selected *cis*-1,2-disubstituted cyclopropanol **1a** as a model substrate, which is readily accessible via the Kulinkovich reaction with excellent selectivity.[20] Notably, stereoselective preparation of the *trans*-1,2-disubstituted cyclopropanols requires a different strategy,[21] such as addition of Grignard reagents to, generated in situ,

Received: October 10, 2024
Revised: December 19, 2024
Accepted: January 9, 2025
Published: January 16, 2025



https://doi.org/10.1021/acs.organomet.4c00432
Organometallics 2025, 44, 520−528

Scheme 1. Metal Catalyzed Isomerization of Cyclopropane-Containing Molecules

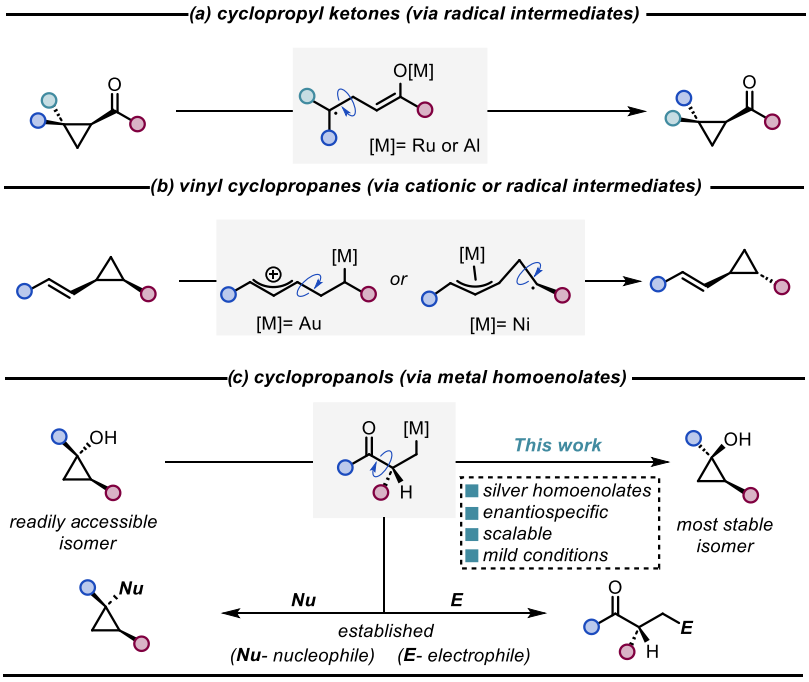
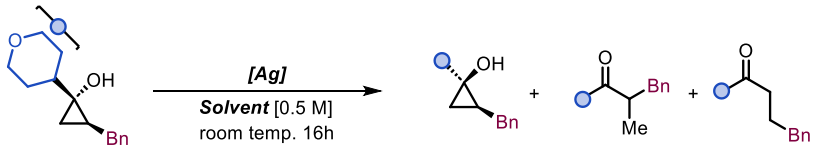


Table 1. Optimization Studies[a]



(±) **1a** (±) **1b** (±) **1c** **1d**

entry	[Ag] (mol %)	solvent	**1a** (%)	**1b** (%)	**1c** (%)	**1d** (%)
1	$AgNO_3$ (10)	PhMe	80	4	12	0
2	$AgN(Tf)_2$ (10)	PhMe	34	3	27	18
3	$AgOC(O)CF_3$ (10)	PhMe	2	17	45	20
4	AgOTf (10)	PhMe	58	13	18	11
5	AgOTf (10)	DCM	16	45	23	16
6	AgOTf (10)	DMF	32	15	20	23
7	AgOTf (10)	MeOH	28	72	0	0
8	AgOTf (10)	i-PrOH	23	77	0	0
9	AgOTf (5)	*i*-PrOH	38	62	0	0
10[b]	AgOTf (5)	*i*-PrOH	**23**	77	**0**	**0**
11[b]		*i*-PrOH	100	0	0	0

[a]Conditions: 0.1 mmol 1a, 5-10 μmol [Ag] in solvent (200 μl) at r.t. for 16 h; yields determined by ^{1}H NMR spectroscopy with trichloroethylene as a standard. [b]in *i*-PrOH (100 μl).

cyclopropanones[21a] or reactions involving zinc carbenoids.[21b,c] We hypothesized that a thermodynamically driven stereochemical isomerization process would convert **1a** to its, presumably more stable, *trans* analog **1b**. This would enable accessing both diastereoisomers of 1,2-disubstituted cyclopropanols employing a unified strategy for constructing the cyclopropanol core. We performed density functional theory (DFT) computations to determine the relative Gibbs energies of **1a** and **1b**, which indicated a slight thermochemical bias favoring the *trans*-disubstituted isomer **1b**. For other cyclopropanols, the computed trends in substrate-product stability indicate a greater thermodynamic preference for the products (vide infra). Next, we subjected **1a** to the reaction with several metal catalysts with proven ability to form metal homoenolates including Cu, Fe, Mn, Co and Pd salts. Surprisingly, no stereochemical isomerization was observed (see Supporting Information for details). We found, however, that silver(I) salts act as promising catalysts. Performing reaction in the presence of silver nitrate, bis(trifluoromethanesulfonyl)imide, trifluoroacetate and triflate as catalysts in toluene delivered **1b** in low yields along with the structural isomerization products, ketones **1c** and **1d** (Table 1, entry 1−4). Switching the solvent to DCM significantly improved the process, delivering **1b** as a major product in 45% yield (entry 5). In DMF, structural isomerization was the predominant reaction pathway (entry 6), however, using methanol as the solvent delivered **1b** in 72%

https://doi.org/10.1021/acs.organomet.4c00432
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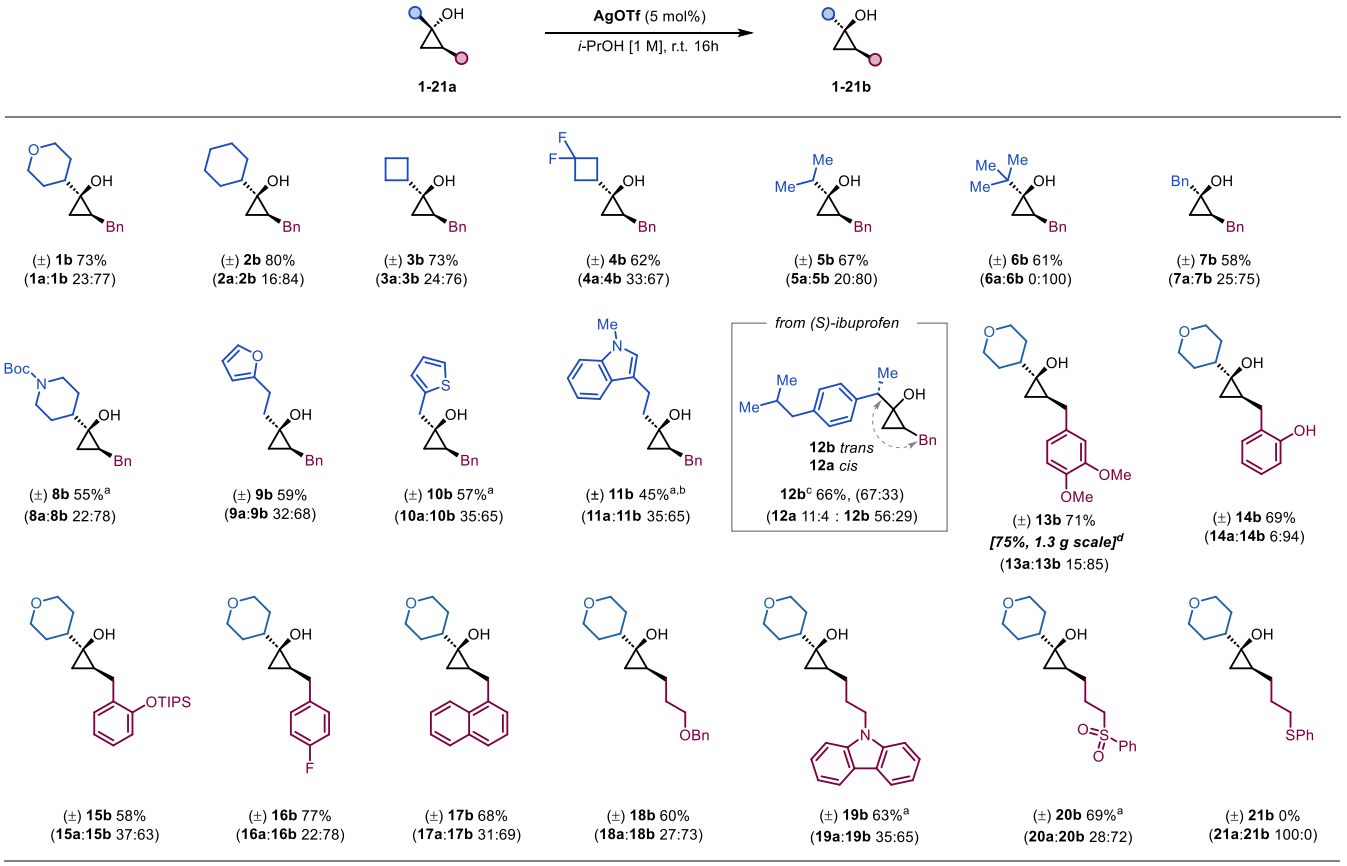
Scheme 2. Substrates Scope of Silver-Catalyzed Stereochemical Isomerization of Cyclopropanols[a]



[a]Reactions were performed at 0.4 mmol scale. Isolated yields of isomerized products are provided. Provided within the parentheses are d.r. of the reaction determined by 1H NMR integration of the unpurified product. [a]10 mol % of AgOTf was used, [b]reaction performed at 0.15 mmol scale, [c]cis-disubstituted 12a had a d.r. of 70:30, [d]5.9 mmol scale.

yield, with the remaining mass balance being the *cis*-disubstituted isomer **1a** (entry 7). The yield was further improved using isopropanol as a solvent giving **1b** in 77% yield (entry 8). Moreover, increasing the reaction concentration enabled reducing the catalyst loading to 5 mol % without compromising its efficiency (entry 10). No isomerization occurred in the absence of the catalyst (entry 11).

We next evaluated the scope of silver-catalyzed stereochemical isomerization with respect to diversely substituted cyclopropanols at the C1 position (Scheme 2). Substrates bearing alkyl substituents, including cyclohexyl, cyclobutyl, and 3,3-difluorocyclobutyl groups, delivered products **2**−**4b** in yields ranging from 62 to 80%. Noncyclic alkyl substituents, such as isopropyl and benzyl groups, were also tolerated, allowing the formation of products **5b** and **7b** with yields of 67 and 58%, respectively. Notably, the *cis*-disubstituted cyclopropanol **6a** bearing a *tert*-butyl group converted to its corresponding *trans*-disubstituted diastereoisomer **6b** with perfect selectivity. The diminished isolated yield of 60% is a consequence of its moderate stability. We also investigated substrates with heteroatom containing substituents. For instance, cyclopropanol **8b** bearing Boc-protected piperidine was formed in 55% yield, while the thiophene and *N*-methylindole containing substrates **10a** and **11a** converted to their corresponding *trans* isomers **10b** and **11b** in yields of 57 and 45% respectively. These cases required increasing a catalyst loading to 10 mol %. The cyclopropanol **9b** bearing furane substituent was formed in 59% yield. We also prepared a cyclopropanol derivative of (S)-ibuprofen **12a** as a 70:30 mixture of diastereomers having *cis* arrangement of the alkyl substituents and subjected it to the isomerization conditions. The corresponding **12b** was isolated in 66% yield as a 67:33 mixture of *trans*-disubstituted diastereoisomers.

We then investigated the scope with respect to the substituents on cyclopropanol's C2 position. Electron-rich 3,4-dimethoxybenzyl groups and electron-poor 4-fluorobenzyl groups were well tolerated, delivering the cyclopropanols **13b** and **16b** in yields of 71 and 77%, respectively. The isomerization was also effective when employing cyclopropanol **14a** bearing a phenol moiety (69% yield) and a bulky triisopropylsilyl-protected phenol **15a** (58% yield). The cyclopropanol **17b** containing a naphthalen-1-ylmethyl group was isolated in 68% yield, while substrate **18a** bearing an alkyl chain converted to its trans isomer **18b** in 60% yield. Notably, the reaction tolerates carbazole and sulfone moieties, delivering the products **19b** and **20b** in yields of 63 and 69%, respectively, using 10 mol % of a catalyst. Substrate containing a thioether group **21a**, however, did not engage in a productive pathway. Notably, probing the stereochemical isomerization at 5.9 mmol scale yielded 1.3 g of **13b**, indicated comparable efficiency at 15-fold scale-up.

After establishing the synthetic potential of the stereochemical isomerization, we turned our attention to mechanistic investigations, seeking to explain the nature of this process. To

https://doi.org/10.1021/acs.organomet.4c00432
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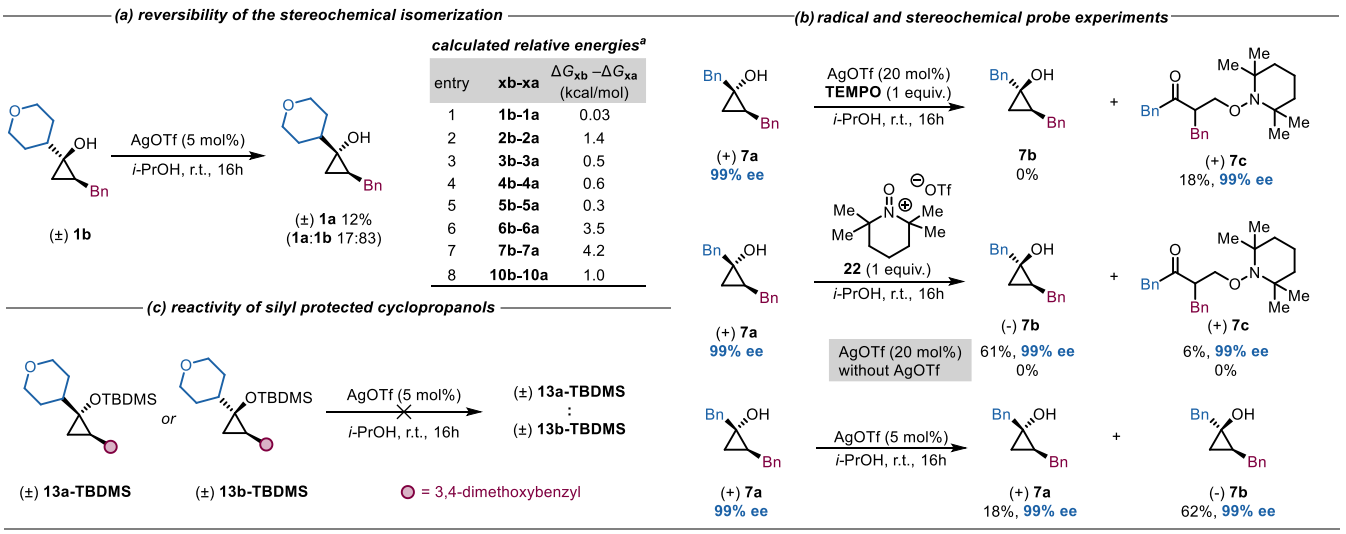
Scheme 3. Mechanistic Studies



[a]Level of theory: CAM-B3LYP/6-311 + g(2d,p), [SMD = 2-propanol]

test whether the reaction is reversible, we subjected *trans*-disubstituted cyclopropanol **1b** to standard reaction conditions. The resulting **1a**:**1b** mixture of 17:83 indicates the reversibility of the stereochemical isomerization (Scheme 3a). This ratio is similar to the 77:23 ratio obtained from the pure isomer **1a**. Moreover, DFT calculations of the relative Gibbs energies (ΔG) for a representative set of diastereomers indicate a thermochemical preference for the formation of *trans*-1,2-disubstituted cyclopropanols (Scheme 3a). Next, we investigated the role of the silver catalyst. There are only two reports suggesting the formation of silver homoenolates from siloxycyclopropanes using stoichiometric amounts of silver salts.[22] Notably, numerous silver catalyzed ring opening functionalizations of cyclopropanols take place under oxidative conditions via a radical mechanism.[23] To evaluate the feasibility of the radical pathway, we performed the reaction in the presence of TEMPO using 20 mol % of the catalyst (Scheme 3b). The isomerization was suppressed and we isolated the TEMPO adduct **7c** in 18% yield. Interestingly, the regioselectivity of this process suggests the involvement of metal homoenolates rather than the opening of the cyclopropanol ring via a radical mechanism. Moreover, **7c** was formed without an erosion of the enantiomeric excess (99% ee) when using enantiomerically pure cyclopropanol **7a**. Being intrigued by this result we hypothesized that TEMPO undergoes oxidation or disproportionation in the presence of AgOTf to form $TEMPO^+$,[24] which subsequently react with silver homoenolate or cyclopropanol. We subjected then oxoammonium triflate **22** to the reaction conditions with and without AgOTf. Enantiopure **7c** formed only in the presence of AgOTf, which suggests the involvement of silver homoenolate, however the detailed mechanism remains to be elucidated. Although TEMPO suppressed the reaction, these experiment suggests that the radical mechanism is unlikely. Next, we subjected the enantiopure **7a** to the standard reaction conditions. In this case both **7a** and **7b** were isolated in enantiopure forms. The absolute configurations of (+)**7a** and (−)**7b** were determined by comparison of computational and experimental circular dichroism spectroscopy[25] (see Supporting Information for details) revealing epimerization at the stereogenic center bearing the alcohol group. These observations further supports the formation of silver homoenolates. We also subjected TBDMS (*tert*-butyl(dimethyl)silyl) protected cyclopropanols to the standard reaction conditions (Scheme 3c). The lack of reactivity demonstrates the importance of alcohol moiety for the stereochemical isomerization.

CONCLUSIONS

In summary, we reported a catalytic stereochemical isomerization of cyclopropanols. This study establishes the catalytic reactivity of silver homoenolates, enabling the conversion of readily available *cis*-1,2-disubstituted cyclopropanols into their less accessible *trans*-diastereomers. This provides access to both diastereomers employing a single strategy to construct the cyclopropanol core. Mechanistic studies indicate that the isomerization is enantiospecific and reversible, favoring the formation of the more stable product. Formation for of the silver homoenolates is supported by experimental investigations.

EXPERIMENTAL SECTION

General Procedure for the Silver-Catalyzed Stereochemical Isomerization of Cyclopropanols. A 4 mL vial was charged under air with substrate (0.4 mmol), *i*-PrOH (0.4 mL) and AgOTf (20−40 μmol). The mixture was stirred at r.t for 16 h covered by alumina foil. After that time, the reaction mixture was diluted with DCM and washed with saturated aqueous solution of $NaHCO_3$. The aqueous phase was washed with DCM (2 × 15 mL) and the combined organic phases were washed with brine, dried under Na_2SO_4 and the solvent was evaporated. The mixture was purified by flash column chromatography on silica gel.

(*trans*)-2-Benzyl-1-(tetrahydro-2*H*-pyran-4-yl)cyclopropan-1-ol (1b). Reaction time: 16 h. (cis)-2-benzyl-1-(tetrahydro-2H-pyran-4-yl)cyclopropan-1-ol **1a** (93 mg, 0.4 mmol), AgOTf (5.1 mg, 20 μmol) and *i*-PrOH (0.4 mL). The crude mixture was purified by column chromatography (10% EtOAc-pentane) to afford product as white solid in 73% yield (68 mg, 0.29 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.24 (m, 4H), 7.22−7.16 (m, 1H), 4.05−3.93 (m, 2H), 3.38−3.25 (m, 2H), 2.89−2.74 (m, 2H), 1.98 (brs, 1H), 1.68−1.50 (m, 3H), 1.48−1.41 (m, 1H), 1.23−1.13 (m, 1H), 1.04−0.95 (m, 1H), 0.71 (dd, J = 9.4, 5.6 Hz, 1H), 0.50 (t, J = 5.9 Hz, 1H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 128.5, 128.4, 126, 68.1, 68.1, 61.7, 43.3, 33.9, 28.6, 28.5, 24.5, 18 ppm. IR (ATR) 3369, 3058,

https://doi.org/10.1021/acs.organomet.4c00432
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3028, 3004, 2956, 2938, 2916, 2866, 2850, 1602, 1496, 1440, 1456, 1383, 1293, 1253, 1237, 1134, 1082, 985, 733, 696 cm^{-1}. HRMS (ESI): calcd for $[C_{15}H_20O_2 + Na]^+$, $[M + Na]^+$: 255.1361; found: 255.1358.

(*trans*)-2-Benzyl-1-cyclohexylcyclopropan-1-ol (2b). Reaction time: 16 h. (cis)-2-benzyl-1-cyclohexylcyclopropan-1-ol **2a** (92.1 mg, 0.4 mmol), AgOTf (5.1 mg, 20 μmol) and *i*-PrOH (0.4 mL). The crude mixture was purified by column chromatography (10% EtOAc-pentane) to afford product as amorphous white solid in 80% yield (74 mg, 0.32 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.25 (m, 4H), 7.23−7.15 (m, 1H), 2.87−2.75 (m, 2H), 1.83−1.72 (m, 3H), 1.70−1.55 (m, 3H), 1.31−1.09 (m, 5H), 1.00−0.92 (m, 1H), 0.90−0.80 (m, 1H), 0.68 (dd, J = 9.3, 5.4 Hz, 1H), 0.47 (t, J = 5.8 Hz, 1H) ppm.^{13}C NMR (101 MHz, $CDCl_3$ δ 142.6, 128.4, 125.8, 62.8, 46.3, 34.1, 28.8, 28.6, 26.5, 24.9, 18.4 ppm). IR (ATR) 3393, 3062, 3026, 2924, 2851, 1496, 1449, 1259, 1195, 1103, 1071, 1050, 979, 892, 849, 739, 699 cm^{-1}. HRMS (ESI): calcd for $[C_{16}H_{22}O + Na]^+$, $[M + Na]^+$: 253.1569; found: 253.1559.

(*trans*)-2-Benzyl-1-cyclobutylcyclopropan-1-ol (3b). Reaction time: 16 h. (cis)-2-benzyl-1-cyclobutylcyclopropan-1-ol **3a** (82 mg, 0.4 mmol), AgOTf (5.1 mg, 20 μmol) and *i*-PrOH (0.4 mL). The crude mixture was purified by column chromatography (10% EtOAc-pentane) to afford product as an oil in 73% yield (60 mg, 0.29 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.26 (m, 4H), 7.23−7.17 (m, 1H), 2.91−2.77 (m, 2H), 2.52−2.43 (m, 1H), 1.99−1.89 (m, 2H), 1.88−1.78 (m, 2H), 1.77−1.69 (m, 2H), 1.07−0.97 (m, 1H), 0.75 (dd, J = 9.3, 5.5 Hz, 1H), 0.49 (t, J = 5.9 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$ δ 142.5, 128.4, 128.2, 125.9, 60.5, 42.3, 33.7, 24.1, 24.1, 22.8, 17.8, 16.9 ppm). IR (ATR) 3375, 3063, 3026, 2926, 2853, 1496, 1450, 1246, 1105, 1071, 1030, 990, 893, 739, 698 cm^{-1}. HRMS (ESI): calcd for $[C_{14}H_{18}O + Na]^+$, $[M + Na]^+$: 225.1256; found: 225.1253.

(*trans*)-2-Benzyl-1-(3,3-difluorocyclobutyl)cyclopropan-1-ol (4b). Reaction time: 16 h. (cis)-2-benzyl-1-(3,3-difluorocyclobutyl)-cyclopropan-1-ol **4a** (95.3 mg, 0.4 mmol), AgOTf (10.3 mg, 40 μmol), *i*-PrOH (0.4 mL). The crude mixture was purified by column chromatography (10% EtOAc-pentane) to afford product as white solid in 62% yield (59 mg, 0.25 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.16 (m, 5H), 2.90 (dd, J = 15.0, 6.4 Hz, 1H), 2.79 (dd, J = 15.1, 8.1 Hz, 1H), 2.62−2.48 (m, 2H), 2.46−2.29 (m, 2H), 2.21−2.09 (m, 1H), 1.82 (s, 1H), 1.09−1.00 (m, 1H), 0.79 (dd, J = 9.5, 5.9 Hz, 1H), 0.58 (t, J = 6.2 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 128.6, 128.2, 126, 119.6, 58.9, 4, 33.6, 30.5, 23.8, 17.7 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −82.33, −82.84, −97.46, −97.97 ppm. IR (ATR) 3452, 3065, 3034, 3002, 2955, 2926, 2850, 2367, 2344, 1498, 1454, 1298, 1168, 1084, 1068, 1033, 898, 696 cm^{-1}. HRMS (ESI): calcd for $[C_{14}H_{16}F_2O + Na]^+$, $[M + Na]^+$: 261.1067; found: 261.1065.

(*trans*)-Benzyl-1-isopropylcyclopropan-1-ol (5b). Reaction time: 16 h. (cis)-benzyl-1-isopropylcyclopropan-1-ol **6a** (76.1 mg, 0.4 mmol), AgOTf (5.1 mg, 20 μmol) and *i*-PrOH (0.4 mL). The crude mixture was purified by column chromatography (10% EtOAc-pentane) to afford product as colorless oil in 67% yield (51 mg, 0.27 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.25 (m, 4H), 7.23−7.15 (m, 1H), 2.89−2.75 (m, 2H), 1.63 (s, 1H), 1.27−1.16 (m, 1H), 1.01 (d, J = 6.9 Hz, 3H), 0.99−0.93 (m, 1H), 0.92 (d, J = 6.8 Hz, 3H), 0.71−0.64 (m, 1H), 0.49 (t, J = 5.8 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 128.4, 128.4, 125.9, 63.3, 36.26, 34.1, 25.4, 18.8, 18.2, 18.1 ppm. IR (ATR) 3396, 3063, 3026, 2959, 2926, 2872, 2852, 1604, 1496, 1451, 1383, 1365, 1261, 1123, 1065, 992, 893, 740, 699 cm^{-1}. HRMS (ESI): calcd for $[C_{13}H_{18}O + Na]^+$, $[M + Na]^+$: 213.1255; found: 213.1248.

(*trans*)-2-Benzyl-1-(*tert*-butyl)cyclopropan-1-ol (6b). Reaction time: 16 h. (cis)-2-benzyl-1-(*tert*-butyl)cyclopropan-1-ol **7a** (81.7 mg, 0.4 mmol), AgOTf (5.1 mg, 20 μmol) and *i*-PrOH (0.4 mL). The crude mixture was purified by column chromatography (8% EtOAc-pentane) to afford product as colorless oil in 61% yield (50 mg, 0.24 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.26 (m, 4H), 7.23−7.16 (m, 1H), 2.90−2.76 (m, 2H), 1.74 (s, 1H), 1.24−1.15 (m, 1H), 0.88 (s, 9H), 0.87−0.83 (m, 1H), 0.38 (t, J = 6.0 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 128.5, 128.4, 125.9, 65.4, 34.2, 34.2, 26.2, 22, 16.2 ppm. IR (ATR) 3567, 3464, 3064, 3026, 2957, 2909, 2869, 1604, 1496, 1471, 1454, 1393, 1364, 1245, 1205, 1153, 1073, 1030, 990, 902, 795, 740, 699 cm^{-1}. HRMS (ESI): calcd for $[C_{14}H_{20}O+Na]^+$, $[M + Na]^+$: 227.1412; found: 227.1402.

(*trans*)-1,2-Dibenzylcyclopropan-1-ol (7b). Reaction time: 16 h. (cis)-1,2-dibenzylcyclopropan-1-ol **8a** (95.3 mg, 0.4 mmol), AgOTf (5.1 mg, 20 μmol) and *i*-PrOH (0.4 mL). The crude mixture was purified by column chromatography (10% EtOAc-pentane) to afford product as amorphous white solid in 69% yield (66 mg, 0.28 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.17 (m, 10H), 2.96 (d, J = 14.2 Hz, 1H), 2.88−2.80 (m, 3H), 1.85 (s, 1H), 1.24−1.14 (m, 1H), 0.89 (dd, J = 9.3, 5.6 Hz, 1H), 0.61 (t, J = 6.0 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 138.4, 129.5, 128.7, 128.5, 128.4, 126.7, 125.9, 59.3, 45.3, 33.9, 25.2, 18.6 ppm. IR (ATR) 3310, 3084, 3064, 3029, 2930, 2854, 2839, 1603, 1494, 1453, 1404, 1351, 1338, 1295, 1188, 1102, 1085, 1060, 1035, 1001, 893, 863, 750, 699 cm^{-1}. HRMS (ESI): calcd for $[C_{17}H_{18}O+Na]^+$, $[M + Na]^+$: 261.1256; found: 261.1253.

(*trans*)-2-Benzyl-1-(*N*-boc-piperidine)cyclopropan-1-ol (8b). Reaction time: 16 h. (cis)-2-benzyl-1-(*N-boc-piperidine*)cyclopropan-1-ol **8a** (133 mg, 0.4 mmol), AgOTf (10.3 mg, 40 μmol) and *i*-PrOH (0.4 mL). The crude mixture was purified by column chromatography (20% EtOAc-pentane) to afford product as colorless oil in 55% yield (73 mg, 0.22 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.23 (m, 4H), 7.21−7.15 (m, 1H), 4.34−3.90 (m, 2H), 2.87−2.73 (m, 2H), 2.67−2.47 (m, 2H), 2.14 (brs, 1H), 1.70−1.62 (m, 1H), 1.54−1.32 (m, 12H), 1.06−0.91 (m, 2H), 0.69 (dd, J = 9.4, 5.5 Hz, 1H), 0.50 (t, J = 5.9 Hz, 1H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 142.4, 128.5, 125.9, 79.5, 61.6, 44.7, 34, 28.6, 28.5, 27.8, 24.9, 18.4 ppm. IR (ATR) 3432, 2973, 2922, 2856, 2360, 2342, 1668, 1478, 1436, 1364, 1278, 1241, 1158, 1070, 1021, 892, 864, 765, 739, 699, 642, 610, 548, 499, 453 cm^{-1}. HRMS (ESI): calcd for $[C_{20}H_{29}NO_3 + Na]^+$, $[M + Na]^+$: 354.2045; found: 354.2038.

(*trans*)-2-Benzyl-1-(2-(furan-2-yl)ethyl)cyclopropan-1-ol (9b). Reaction time: 16 h. (cis)-2-benzyl-1-(2-(furan-2-yl)ethyl)-cyclopropan-1-ol **9a** (96.9 mg, 0.4 mmol), AgOTf (5.1 mg, 20 μmol) and *i*-PrOH (0.4 mL). The crude mixture was purified by column chromatography (10% EtOAc-pentane) to afford product as a colorless oil in 59% yield (57 mg, 0.23 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.23 (m, 5H), 7.22−7.16 (m, 1H), 6.29−6.24 (m, 1H), 5.98−5.93 (m, 1H), 2.85−2.76 (m, 4H), 1.95−1.83 (m, 2H), 1.82 (s, 1H), 0.99−0.90 (m, 1H), 0.67 (dd, J = 9.2, 5.5 Hz, 1H), 0.52 (t, J = 6.0 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 142.3, 141, 128.5, 128.3, 125.9, 110.3, 105.1, 58.6, 38.2, 34, 25.4, 24.6, 19.2 ppm. IR (ATR) 3398, 3114, 3063, 3026, 2996, 2917, 2851, 1599, 1507, 1496, 1453, 1259, 1149, 1119, 1071, 1029, 1005, 920, 884, 800, 730, 699 cm^{-1}. HRMS (ESI): calcd for $[C_{16}H_{18}O_2 + Na]^+$, $[M + Na]^+$: 265.1205; found: 265.1201.

(*trans*)-2-Benzyl-1-(thiophen-2-ylmethyl)cyclopropan-1-ol (10b). Reaction time: 16 h. (cis)-2-benzyl-1-(thiophen-2-ylmethyl)-cyclopropan-1-ol **10a** (97.7 mg, 0.4 mmol), AgOTf (10.3 mg, 40 μmol) and *i*-PrOH (0.4 mL). The crude mixture was purified by column chromatography (10% EtOAc-pentane) to afford product as colorless oil in 57% yield (56 mg, 0.29 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.15 (m, 6H), 6.98−6.94 (m, 1H), 6.90−6.86 (m, 1H), 3.13 (dd, J = 15.1, 0.9 Hz, 1H), 3.01 (dd, J = 15.2, 1.0 Hz, 1H), 2.92−2.76 (m, 2H), 2.07 (s, 1H), 1.24−1.15 (m, 1H), 0.91 (dd, J = 9.4, 5.7 Hz, 1H), 0.66 (t, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 140.6, 128.5, 128.4, 127, 126.1, 125.9, 124.3, 59.4, 39.9, 33.8, 25.5, 19 ppm. IR (ATR) 3420, 3063, 3025, 2995, 2916, 2849, 1603, 1495, 1453, 1438, 1271, 1240, 1179, 1127, 1072, 1028, 999, 919, 851, 822, 728, 698 cm^{-1}. HRMS (ESI): calcd for $[C_{15}H_{16}OS + Na]^+$, $[M + Na]^+$: 267.0820; found: 267.0813.

(*trans*)-1-(2-(1-Methyl-1*H*-indol-3-yl)ethyl)cyclopropan-1-ol (11b). Reaction time: 16 h. (cis)-1-(2-(1-methyl-1H-indol-3-yl)-ethyl)cyclopropan-1-ol **11a** (46 mg, 0.15 mmol), AgOTf (3.8 mg, 15 μmol) and *i*-PrOH (0.15 mL). The crude mixture was purified by column chromatography (10% EtOAc-pentane) to afford product as a yellow amorphous solid in 45% yield (21 mg, 0.068 mmol). ^{1}H NMR

https://doi.org/10.1021/acs.organomet.4c00432
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(400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.9 Hz, 1H), 7.33−7.25 (m, 5H), 7.24−7.17 (m, 2H), 7.12−7.06 (m, 1H), 6.73 (s, 1H), 3.70 (s, 3H), 2.92 (t, J = 7.8 Hz, 2H), 2.87−2.73 (m, 2H), 2.07−1.97 (m, 1H), 1.95−1.86 (m, 1H), 1.79 (s, 1H), 1.04−0.97 (m, 1H), 0.74 (dd, J = 9.2, 5.5 Hz, 1H), 0.54 (t, J = 5.9 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 137.1, 128.4, 128.3, 127. 7, 126, 125.8, 121.6, 119, 118.6, 114.7, 109.2, 59.4, 40, 33.9, 32.5, 25.2, 21.6, 19.1 ppm. IR (ATR) 3335, 3064, 3025, 2993, 2918, 2848, 2361, 2342, 1495, 1472, 1454, 1420, 1325, 1297, 1226, 1007, 739, 700 cm^{-1}. HRMS (ESI): calcd for $[C_{21}H_{23}NO + Na]^+$, $[M + Na]^+$: 328.1678; found: 328.1671.

(1*R*,2*S*)-2-Benzyl-1-((*S*)-1-(4-isobutylphenyl)ethyl)-cyclopropan-1-ol and (1*S*,2*R*)-2-Benzyl-1-((*S*)-1-(4-isobutylphenyl)ethyl)cyclopropan-1-ol (12b). Reaction time: 16 h. **12a** (123 mg, 0.4 mmol), AgOTf (5.1 mg, 20 μmol), *i*-PrOH (0.4 mL). The crude mixture was purified by column chromatography (5% EtOAc-pentane) to afford product as colorless oil in 66% yield, 67:33 *d.r.* (82 mg, 0.26 mmol). ^{1}H NMR (600 MHz, DMSO-D_6) (mixture of diastereomers, which could not be fully distinguished; signals are reported as seen) δ 7.27−7.20 (m, 1.8 H), 7.17−7.10 (m, 3.4H), 7.04 (p, J = 6.5 Hz, 3H), 6.98 (dt, J = 11.4, 8.2 Hz, 5.1H), 5.10 (s, 1H), 4.98 (s, 0.4H), 2.75 (dd, J = 14.6, 7.4 Hz, 0.4H), 2.64 (dd, J = 14.9, 7.7 Hz, 1H), 2.59−2.52 (m, 1.5H), 2.39−2.34 (m, 3H), 2.34−2.30 (m, 1H), 2.30−2.26 (m, 0.4H), 1.77 (dq, J = 13.7, 6.8 Hz, 1.5H), 1.28 (d, J = 7.1 Hz, 3H), 1.22 (d, J = 7.1 Hz, 1.8H), 0.87−0.93 (m, 1.2H), 0.86−0.80 (m, 9H), 0.65 (dd, J = 9.4, 5.2 Hz, 0.4H), 0.57 (dd, J = 9.4, 4.9 Hz, 1H), 0.33 (t, J = 5.5 Hz, 1H), 0.27 (t, J = 5.7 Hz, 0.4H) ppm. ^{13}C NMR (151 MHz, DMSO-D_6) (mixture of diastereomers, which could not be fully distinguished; signals are reported as seen) δ 143.1, 142.8, 142.3, 139.0, 138.9, 128.9, 128.8, 128.8, 128.7, 128.6, 128.3, 128.32, 126.0, 125.8, 61.7, 61.6, 47.0, 46.8, 44.9, 44.9, 34.0, 33.8, 30.2, 30.2, 25.7, 24.6, 22.8, 22.8, 18.9, 18.4, 17.9, 17.8 ppm. IR (ATR) 3566, 3447, 3062, 3025, 2954, 2924, 2868, 1716, 1454, 1247, 736, 699 cm^{-1}. HRMS (ESI): calcd for $[C_{22}H_{28}O + Na]^+$, $[M + Na]^+$: 331.2038; found: 331.2034.

(*trans*)-2-(3,4-Dimethoxybenzyl)-1-(tetrahydro-2H-pyran-4-yl)cyclopropan-1-ol (13b). Reaction time: 16 h. (cis)-2-(3,4-dimethoxybenzyl)-1-(tetrahydro-2H-pyran-4-yl)cyclopropan-1-ol **13a** (117 mg, 0.4 mmol), AgOTf (5.1 mg, 20 μmol) and *i*-PrOH (0.4 mL). The crude mixture was purified by column chromatography (20−30% EtOAc-pentane) to afford product as colorless oil in 71% yield (83 mg, 0.28 mmol). 5.9 mmol scale reaction: Reaction time: 16 h. (cis)-2-(3,4-dimethoxybenzyl)-1-(tetrahydro-2H-pyran-4-yl)-cyclopropan-1-ol **13a** (1.72g, 5.9 mmol), AgOTf (75.8 mg, 0.29 mmol) and *i*-PrOH (6 mL). The crude mixture was purified by column chromatography (20−30% EtOAc-pentane) to afford product as light yellow oil in 75% yield (1.3 g, 4.4 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85−6.75 (m, 3H), 4.05−3.93 (m, 2H), 3.86 (d, J = 5.5 Hz, 6H), 3.36−3.24 (m, 2H), 2.86−2.66 (m, 2H), 1.72 (s, 1H), 1.67−1.50 (m, 3H), 1.48−1.39 (m, 1H), 1.21−1.11 (m, 1H), 1.01−0.91 (m, 1H), 0.71 (dd, J = 9.4, 5.5 Hz, 1H), 0.48 (t, J = 5.9 Hz, 1H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 147.3, 135, 120, 111.8, 111.2, 68.1, 68.1, 61.7, 56, 55.9, 43.4, 33.6, 28.7, 28.5, 24.9, 18.1 ppm. IR (ATR) 3394, 3013, 2970, 2949, 2922, 2849, 2361, 2343, 1590, 1516, 1466, 1287, 1264, 1252, 1233, 1223, 1154, 1140, 1085, 1027, 757, 667 cm^{-1}. HRMS (ESI): calcd for $[C_{17}H_{24}O_4 + Na]^+$, $[M + Na]^+$: 315.1572; found: 315.1570.

(*trans*)-2-((2-Hydroxy-2-(tetrahydro-2*H*-pyran-4-yl)-cyclopropyl)methyl)phenol (14b). Reaction time: 16 h. (cis)-2-((2-hydroxy-2-(tetrahydro-2H-pyran-4-yl)cyclopropyl)methyl)phenol **14a** (99 mg, 0.4 mmol), AgOTf (5.1 mg, 20 μmol) and *i*-PrOH (0.4 mL). The crude mixture was purified by column chromatography (3% MeOH-DCM) to afford product as a yellow amorphous solid in 69% yield (68 mg, 0.27 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (brs, 1H), 7.17−7.07 (m, 2H), 6.88−6.78 (m, 2H), 4.81 (brs, 1H), 4.07−3.89 (m, 2H), 3.38−3.20 (m, 2H), 2.95−2.88 (m, 1H), 2.65−2.55 (m, 1H), 1.73−1.54 (m, 3H), 1.27−1.19 (m, 1H), 1.08−0.97 (m, 1H), 0.85−0.71 (m, 2H), 0.55 (t, J = 5.6 Hz, 1H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 130.7, 128, 127.9, 120.3, 116.4, 68.1, 61, 46.3, 43, 29.5, 28.3, 25.2, 17.9, 8.7 ppm. IR (ATR) 3266, 2952, 2851, 2692, 2360, 2342, 1705, 1594, 1489, 1457, 1387, 1363, 1240, 1088, 756, 732 cm^{-1}. HRMS (ESI): calcd for $[C_{15}H_{20}O_3 + Na]^+$, $[M + Na]^+$: 271.1310; found: 271.1306.

(*trans*)-1-(Tetrahydro-2*H*-pyran-4-yl)-2-(2-((triisopropylsilyl)oxy)benzyl)cyclopropan-1-ol (15b). Reaction time: 16 h. (cis)-1-(tetrahydro-2H-pyran-4-yl)-2-(2-((triisopropylsilyl)oxy)benzyl)cyclopropan-1-ol **15a** (162 mg, 0.4 mmol), AgOTf (5.1 mg, 20 μmol) and *i*-PrOH (0.4 mL). The crude mixture was purified by column chromatography (30% EtOAc-pentane) to afford product as an amorphous solid in 58% yield (94 mg, 0.23 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.19 (m, 1H), 7.10−7.03 (m, 1H), 6.93−6.87 (m, 1H), 6.84−6.80 (m, 1H), 4.03−3.89 (m, 2H), 3.36−3.21 (m, 2H), 2.89 (dd, J = 14.4, 5.7 Hz, 1H), 2.76 (dd, J = 14.4, 8.6 Hz, 1H), 2.37 (brs, 1H), 1.52−1.42 (m, 1H), 1.37−1.27 (m, 5H), 1.11 (dd, J = 11.2, 7.4 Hz, 18H), 1.02−0.96 (m, 1H), 0.91−0.82 (m, 2H), 0.67 (dd, J = 9.4, 5.5 Hz, 1H), 0.52 (dd, J = 6.4, 5.5 Hz, 1H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 132.6, 130.1, 127, 121.3, 118.4, 68.2, 68.1, 61.4, 43.4, 28.5, 28.5, 24.6, 18.1, 18, 13.2 ppm. IR (ATR) 3421, 2943, 2866, 2360, 2342, 1599, 1507, 1489, 1452, 1386, 1257, 1237, 1183, 1138, 1089, 996, 921, 882, 754, 680, 644 cm^{-1}. HRMS (ESI): calcd for $[C_{24}H_{40}O_3Si + Na]^+$, $[M + Na]^+$: 427.2645; found: 427.2640.

(*trans*)-2-(4-Fluorobenzyl)-1-(tetrahydro-2H-pyran-4-yl)-cyclopropan-1-ol (16b). Reaction time: 16 h. (tcis)-2-(4-fluorobenzyl)-1-(tetrahydro-2H-pyran-4-yl)cyclopropan-1-ol **16a** (100 mg, 0.4 mmol), AgOTf (5.1 mg, 20 μmol) and *i*-PrOH (0.68 mL), DCM (0.12 mL). The crude mixture was purified by column chromatography (20% EtOAc-pentane) to afford product as a colorless oil in 77% yield (77 mg, 0.31 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.18 (m, 2H), 7.00−6.92 (m, 2H), 4.04−3.94 (m, 2H), 3.36−3.25 (m, 2H), 2.85−2.70 (m, 2H), 1.70 (s, 1H), 1.66−1.48 (m, 3H), 1.45−1.37 (m, 1H), 1.21−1.12 (m, 1H), 1.00−0.89 (m, 1H), 0.72 (dd, J = 9.4, 5.6 Hz, 1H), 0.48 (t, J = 5.9 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 160.1, 138, 138, 129.8, 129.7, 115.2, 115, 68.1, 68.1, 61.6, 43.3, 33.1, 28.6, 28.5, 24.7, 18 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −117.64 ppm. IR (ATR) 3364, 2982, 2966, 2940, 2914, 2871, 2851, 2363, 2343, 1602, 1508, 1457, 1390, 1302, 1289, 1250, 1238, 1217, 1135, 1085, 1027, 999, 982, 907, 863, 838, 785, 757, 509 cm^{-1}. HRMS (ESI): calcd for $[C_{15}H_{19}FO_2 + Na]^+$, $[M + Na]^+$: 273.1267; found: 273.1261.

(*trans*)-2-(Naphthalen-1-ylmethyl)-1-(tetrahydro-2*H*-pyran-4-yl)cyclopropan-1-ol (17b). Reaction time: 16 h. (cis)-2-(naphthalen-1-ylmethyl)-1-(tetrahydro-2H-pyran-4-yl)cyclopropan-1-ol **17a** (114 mg, 0.4 mmol), AgOTf (5.1 mg, 20 μmol) and *i*-PrOH (0.4 mL). The crude mixture was purified by column chromatography (20% EtOAc-pentane) to afford product colorless oil in 68% yield (77 mg, 0.27 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14−8.09 (m, 1H), 7.87−7.83 (m, 1H), 7.75−7.70 (m, 1H), 7.54−7.39 (m, 4H), 4.03−3.92 (m, 2H), 3.35−3.23 (m, 4H), 1.94 (s, 1H), 1.63−1.48 (m, 3H), 1.44−1.38 (m, 1H), 1.25−1.10 (m, 2H), 0.78−0.72 (m, 1H), 0.56 (t, J = 5.9 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.44, 133.91, 132.09, 128.83, 126.74, 125.91, 125.73, 125.62, 125.34, 123.94, 68.13, 68.08, 61.96, 43.31, 30.58, 28.61, 28.48, 23.42, 18.14 ppm. IR (ATR) 3397, 2919, 2849, 2360, 2342, 1596, 1508, 1456, 1387, 1289, 1254, 1237, 1136, 1086, 1028, 981, 908, 789, 772, 728, 668, 556 cm^{-1}. HRMS (ESI): calcd for $[C_{19}H_{22}O_2 + Na]^+$, $[M + Na]^+$: 305.1518; found: 305.1510.

(*trans*)-2-(3-(Benzyloxy)propyl)-1-(tetrahydro-2*H*-pyran-4-yl)cyclopropan-1-ol (18b). Reaction time: 16 h. (cis)-2-(3-(benzyloxy)propyl)-1-(tetrahydro-2H-pyran-4-yl)cyclopropan-1-ol **18a** (62.3 mg, 0.22 mmol), AgOTf (2.8 mg, 10 μmol) and *i*-PrOH (0.22 mL). The crude mixture was purified by column chromatography (50% EtOAc-pentane) to afford the product as a colorless oil in 60% yield (37 mg, 0.13 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.27 (m, 5H), 4.51 (s, 2H), 4.05−3.96 (m, 2H), 3.70−3.56 (m, 1H), 3.55−3.48 (m, 1H), 3.38−3.26 (m, 2H), 2.75 (s, 1H), 1.92−1.71 (m, 2H), 1.70−1.40 (m, 7H), 1.19−1.08 (m, 1H), 0.60−0.54 (m, 1H), 0.29 (t, J = 5.2 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.09, 128.58, 128.01, 127.88, 73.02, 69.61, 68.30, 68.18, 61.34, 43.49, 29.67, 28.82, 28.62, 24.08, 22.68, 17.47 ppm. IR (ATR) 3358, 2850, 2138,

https://doi.org/10.1021/acs.organomet.4c00432
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1637, 1454, 1364, 1237, 1135, 1088, 1027, 981 cm^{-1}. HRMS (ESI): calcd for $[C_{18}H_{26}O_3 + Na]^+$, $[M + Na]^+$: 313.1774; found: 313.1776.

(*trans*)-2-(3-(9*H*-Carbazol-9-yl)propyl)-1-(tetrahydro-2*H*-pyran-4-yl)cyclopropan-1-ol (19b). Reaction time: 16 h. (cis)-2-(3-(9H-carbazol-9-yl)propyl)-1-(tetrahydro-2H-pyran-4-yl)-cyclopropan-1-ol **20a** (140 mg, 0.4 mmol), AgOTf (10.3 mg, 40 μmol) and *i*-PrOH (0.4 mL). The crude mixture was purified by column chromatography (10% EtOAc-pentane) to afford product as an amorphous solid in 63% yield (88 mg, 0.25 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12−8.05 (m, 2H), 7.49−7.36 (m, 4H), 7.24−7.18 (m, 2H), 4.31 (t, J = 7.2 Hz, 2H), 4.01−3.91 (m, 2H), 3.32−3.22 (m, 2H), 2.00−1.88 (m, 2H), 1.71 (brs, 1H), 1.62−1.45 (m, 5H), 1.45−1.36 (m, 1H), 1.10−1.00 (m, 1H), 0.61−0.52 (m, 2H), 0.28−0.21 (m, 1H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 125.7, 122.9, 120.5, 118.9, 118.8, 108.8, 108.8, 68.1, 68.1, 61.5, 43.3, 43.1, 43.1, 29.5, 28.6, 28.5, 25.6, 23, 17.8 ppm. IR (ATR) 3404, 3051, 2935, 2849, 2362, 2343, 1596, 1484, 1464, 1452, 1385, 1347, 1326, 1291, 1236, 1153, 1134, 1120, 1087, 1014, 981, 750, 723 cm^{-1}. HRMS (ESI): calcd for $[C_{23}H_{27}NO_2 + Na]^+$, $[M + Na]^+$: 272.1940; found: 272.1935.

(*trans*)-2-(3-(Phenylsulfonyl)propyl)-1-(tetrahydro-2*H*-pyran-4-yl)cyclopropan-1-ol (20b). Reaction time: 16 h. (cis)-2-(3-(phenylsulfonyl)propyl)-1-(tetrahydro-2H-pyran-4-yl)-cyclopropan-1-ol **19a** (130 mg, 0.4 mmol), AgOTf (10.3 mg, 40 μmol) and *i*-PrOH (0.4 mL). The crude mixture was purified by column chromatography (30% EtOAc-pentane) to afford product as a colorless oil in 69% yield (89 mg, 0.27 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.87 (m, 2H), 7.71−7.62 (m, 1H), 7.62−7.54 (m, 2H), 4.06−3.95 (m, 2H), 3.37−3.27 (m, 2H), 3.19−3.11 (m, 2H), 2.02 (brs, 1H), 1.88−1.75 (m, 2H), 1.66−1.49 (m, 5H), 1.47−1.39 (m, 1H), 1.18−1.08 (m, 1H), 0.66−0.53 (m, 2H), 0.27 (t, J = 4.9 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 133.8, 129.4, 128.1, 128.1, 68.1, 68, 61.2, 56, 43.2, 28.6, 28.5, 26.3, 23.1, 22.5, 17.7 ppm. IR (ATR) 3503, 2922, 2851m 2360, 2342, 1447, 1305, 1146, 1087, 733 cm^{-1}. HRMS (ESI): calcd for $[C_{17}H_{24}O_4S + Na]^+$, $[M + Na]^+$: 347.1293; found: 347.1292.

Computational Studies. The geometry optimization of the transition states and local minima was performed using the Gaussian 09[26] suite of programs and the Cartesian coordinates preparation was made using the GaussView 6[27] visualization software. For thermodynamic stability computations and determination of ΔH and ΔG relationship between substrates and products the CAM-B3LYP/6-311 + g(2d,p) level of theory was used. The implicit solvation model based on electron density (SMD)[28] was used in all computations to reflect the molecular properties in 2-propanol environment (dielectric constant for 2-propanol: ε= 19.264). The ωB97XD/6-311 + g(2d,p) level of theory with SMD solvent model for acetonitrile (dielectric constant for acetonitrile: ε= 35.688) was used to compute ECD and ultraviolet−visible (UV−vis) spectra. The thermal and zero-point vibrational energy (ZPE) corrections have been used in the calculations and no geometry restrictions have been applied. Harmonic frequency analysis has been performed to localize the proper position of the ground state structures. For more details, please see SI.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.4c00432.

Experimental procedures; tabular data and spectral data; computational methods (PDF)

Cartesian coordinate (XYZ)

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⊥R.S. and S.G. contributed equally to this work. R.S., S.G, L.B., and Ł.W.: Investigation. K.B.: DFT studies. Ł.W.: Conceptualization, project administration, resources, supervision and writing—original draft.

Funding

The project is cofinanced by the Polish National Agency for Academic Exchange within Polish Returns Program (BPN/PPO/2021/1/00042/U/00001) and National Science Center, Poland (2022/01/1/ST4/00018).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The study was carried out using research infrastructure funded by the European Union in the framework of the Smart Growth Operational Program, Measure 4.2; grant no. POIR.04.02.00-00-D001/20, "ATOMIN 2.0 − Center for materials research on ATOMic scale for the INnovative economy. We express our thanks to the Wroclaw Center for Networking and Supercomputing (WCSS) and Interdisciplinary Center for Mathematical and Computational Modeling (ICM) in Warsaw (grant no. G50-2) for providing computer time and facilities. We gratefully acknowledge Polish high-performance computing infrastructure PLGrid (HPC Centers: ACK Cyfronet AGH) for providing computer facilities and support within computational grant no. PLG/2024/017834. We thank Katarzyna Pajor for help with ECD measurements.

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