An Enyne Cycloisomerization/[5+1] Reaction Sequence to Synthesize Tetrahydroisoquinolinones from Enyne-Enes and CO

Zhe Zhuang, Chen-Long Li, Yu Xiang, Yu-Hao Wang, and Zhi-Xiang Yu*

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

E-mail: yuzx@pku.edu.cn

Contents

I. General Information Page S2

II. Preparation of Substrates Page S4

III. Reaction Condition Screening Page S15

IV. General Procedure and Experimental Details of Au(I)-Catalyzed Cycloisomerization Page S17

V. General Procedure and Experimental Details of Rh(I)-Catalyzed [5+1] Cycloaddition Page S25

VI. General Procedure and Experimental Details of Rh(I)-Catalyzed Rearrangement of VCPs Page S32

VII. General Procedure of One-pot Cycloisomerization/[5+1] Reaction Sequence Page S37

VIII. General Procedure of One-pot Cycloisomerization/Rearrangement Sequence Page S39

IX. General Procedure of Pauson-Khand Cycloaddition Page S40

X. General Procedure of Synthetic Transformation Page S41

XI. References Page S44

XII. NMR Spectra Page S45
I. General Information

Air and moisture sensitive reactions were carried out in oven and flame-dried glassware sealed with rubber septa under a positive pressure of dry nitrogen or argon. Similarly, sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. DCE was superdry (water ≤ 30 ppm), which could be purchased from J&K. Synthetic reagents were purchased from J&K and Acros, and used without further purification, unless otherwise indicated.

Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with phosphomolybdic acid stain or KMnO₄ stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds show a single spot by analytical TLC.

NMR spectra were measured on Bruker ARX 400 (¹H at 400 MHz, ¹³C at 100 MHz) and Bruker AVANCE III (¹H at 500 MHz, ¹³C at 125 MHz) nuclear magnetic resonance spectrometers. Data for ¹H NMR spectra are reported as follows: chemical shift (ppm, referenced to residual solvent peak (CDCl₃ = δ 7.26 ppm, CD₂Cl₂ = δ 5.32 ppm; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, dm = doublet of multiplet, m = multiplet), coupling constant (Hz), and integration. Data for ¹³C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak (CDCl₃ = δ 77.16 ppm, CD₂Cl₂ = δ 53.84 ppm). Infrared spectra were recorded on a Mettler-Toledo ReactIR iC10 system with a SiComp probe and are reported in wavenumbers (cm⁻¹).

High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI or EI) with an FT-ICR analyzer.

Abbreviations:
Ar = argon
Bn = benzyl
Boc = t-butoxycarbonyl
DCE = 1,2-dichloroethane
DCM = dichloromethane
DIAD = diisopropyl azodicarboxylate
DIBAL-H = diisobutyl aluminium hydride
DIPA = diisopropylamine
DMF = N,N-dimethylformamide
dppp = 1,3-bis(diphenylphosphino) propane
EA = ethyl acetate
IPr = 1,3-bis(2,6-diisopropylphenyl) imidazole-2-ylidine
JohnPhos = 2-(di-t-butylphosphino)biphenyl
MS = molecular sieve
N₂ = nitrogen
o-Ns = o-nitrobenzenesulfonyl
PE = petroleum ether
rt = room temperature
TBS = t-butyldimethylsilyl
Tf = trifluoromethanesulfonyl  
THF = tetrahydrofuran  
TLC = thin layer chromatography  
TMS = trimethylsilyl  
Ts = p-toluenesulfonyl
II. Preparation of Substrates

To a suspension of NaH (239.7 mg, 6.0 mmol, 60%) in DMF (20 mL) was added S1 (704.4 mg, 3.0 mmol) at 0 °C. After stirred for 15 min, a solution of allyl bromide (0.51 mL, 6.0 mmol) in DMF (10 mL) was added at 0 °C and the reaction mixture was stirred at the same temperature. The reaction was monitored by TLC and stirred for 1.5 h. Upon completion, saturated NH₄Cl solution was added to quench the reaction. The resulting mixture was extracted with ether (3×150 mL), and the combined organic phase was washed with brine, then dried over Na₂SO₄, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford 1a (804.7 mg, 98%).

Colorless oil, TLC Rf = 0.54 (EA/PE = 1/5). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 5.80 – 5.67 (m, 1H), 5.56 – 5.43 (m, 1H), 5.40 – 5.19 (m, 4H), 4.19 (d, J = 1.5 Hz, 2H), 3.80 (d, J = 6.4 Hz, 2H), 2.40 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 143.5, 136.1, 132.2, 129.6, 127.9, 127.4, 120.0, 116.4, 84.4, 82.6, 49.3, 36.7, 21.6. IR (neat): 2923, 1349, 1162, 1092 cm⁻¹. HRMS (ESI): calcd. for C₁₅H₁₈NO₂S ([M+H]⁺): 276.1053, found 276.1049.

CuI (15.2 mg, 0.08 mmol) and Pd(PPh₃)₄ (34.8 mg, 0.03 mmol) were dissolved in DIPA (1.6 mL). 2-bromoprop-1-ene (483.2 mg, 4.0 mmol) was added to the resulting solution at 0 °C. After stirred for 5 min, S2 (497.2 mg, 2.0 mmol) in DIPA (3.2 mL) and THF (2.0 mL) was added to the solution at 0 °C. The reaction was gradually allowed to warm to room temperature overnight. The reaction was monitored by TLC and stirred for 16 h. Upon completion, 2M HCl solution (15 ml) was added to quench the reaction. The resulting mixture was extracted with ether (3×20 mL), and the combined organic phase was washed with brine, then dried over Na₂SO₄, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford 1b (183.6 mg, 32%).

Yellow oil, TLC Rf = 0.50 (EA/PE = 1/5). ¹H NMR (500 MHz, CDCl₃) δ 7.74 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 5.76 (ddt, J = 16.9, 10.1, 6.4 Hz, 1H), 5.29 (dd, J = 16.9, 1.3 Hz, 1H), 5.23 (dd, J = 10.1, 1.3 Hz, 1H), 5.12 – 5.08 (m, 1H), 4.97 (s, 1H), 4.20 (s, 2H), 3.81 (d, J = 6.4 Hz, 2H), 2.40 (s, 3H), 1.66 – 1.62 (m, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 143.5, 136.2, 132.2, 129.6, 127.9, 126.1, 122.1, 119.9, 87.0, 80.9, 49.3, 36.7, 23.1, 21.6. IR (neat): 2955, 2922, 1351, 1163.
1093 cm\(^{-1}\). HRMS (ESI): calcd. for C\(_{16}H_{19}NaNO_2S ([M+Na]^+): 312.1029, found 312.1037.

CuI (15.2 mg, 0.08 mmol) and Pd(PPh\(_3\))\(_4\) (34.9 mg, 0.03 mmol) were dissolved in DIPA (1.6 mL). 1-bromoprop-1-ene (cis- and trans- mixture, 487.1 mg, 4.0 mmol) was added to the resulting solution at 0 °C. After stirred for 5 min, S\(_2\) (498.9 mg, 2.0 mmol) in DIPA (3.2 mL) and THF (2.0 mL) was added to the solution at 0 °C. The reaction was gradually allowed to warm to room temperature overnight. The reaction was monitored by TLC and stirred for 16 h. Upon completion, 2M HCl solution (15 mL) was added to quench the reaction. The resulting mixture was extracted with ether (3 × 20 mL), and the combined organic phase was washed with brine, then dried over Na\(_2\)SO\(_4\), then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford 1c (203.3 mg, Z/E = 1/3.5, 35%).

Light yellow oil, TLC \(R_f = 0.53\) (EA/PE = 1/5). (Z)-1c: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, \(J = 8.3\) Hz, 2H), 7.29 (d, \(J = 8.3\) Hz, 2H), 5.91 – 5.69 (m, 2H), 5.32 – 5.17 (m, 3H), 4.17 (d, \(J = 1.3\) Hz, 2H), 3.80 (d, \(J = 6.5\) Hz, 2H), 2.42 (s, 3H), 1.71 (dd, \(J = 6.8, 1.7\) Hz, 3H). (E)-1c: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, \(J = 8.3\) Hz, 2H × 3.5), 7.27 (d, \(J = 8.3\) Hz, 2H × 3.5), 5.91 – 5.69 (m, 2H × 3.5), 5.32 – 5.17 (m, 3H × 3.5), 4.25 (d, \(J = 1.6\) Hz, 2H × 3.5), 3.83 (d, \(J = 6.4\) Hz, 2H × 3.5), 2.40 (s, 3H × 3.5), 1.62 (dd, \(J = 6.8, 1.6\) Hz, 3H × 3.5). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.5, 143.4, 140.3, 138.9, 136.2, 136.1, 132.2, 129.5, 127.94, 127.87, 119.91, 119.88, 109.9, 109.3, 86.4, 84.4, 82.4, 80.0, 49.20, 49.19, 36.9, 36.8, 21.6, 18.7, 15.9. IR (neat): 1440, 1348, 1161, 1119, 1092, 1056 cm\(^{-1}\). HRMS (ESI): calcd. for C\(_{16}H_{19}NaNO_2S ([M+Na]^+): 312.1029, found 312.1033.

CuI (15.2 mg, 0.08 mmol) and Pd(PPh\(_3\))\(_4\) (35.0 mg, 0.03 mmol) were dissolved in DIPA (2 mL). Bromoethene (4.0 mL, 1.0 M in THF) was added to the resulting solution at 0 °C. After stirred for 5 min, S\(_3\) (524.6 mg, 2.0 mmol) in DIPA (8 mL) and THF (2 mL) was added to the solution at 0 °C. The reaction was gradually allowed to warm to room temperature overnight. The reaction was monitored by TLC and stirred for 12 h. Upon completion, 2M HCl solution (30 mL) was added to quench the reaction. The resulting mixture was extracted with ether (3 × 15 mL), and the combined organic phase was washed with brine, then dried over Na\(_2\)SO\(_4\), then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford 1d (483.4 mg, 84%).
Light yellow oil, TLC $R_f = 0.65$ (EA/PE = 1/5). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J = 8.2$ Hz, 2H), 7.28 (d, $J = 8.2$ Hz, 2H), 5.47 (ddt, $J = 17.3$, 11.2, 1.7 Hz, 1H), 5.34 (dd, $J = 11.2$, 2.2 Hz, 1H), 5.28 (dd, $J = 17.3$, 2.2 Hz, 1H), 5.02 – 4.93 (m, 2H), 4.15 (d, $J = 1.8$ Hz, 2H), 3.71 (s, 2H), 2.41 (s, 3H), 1.77 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 143.5, 139.5, 136.2, 129.5, 128.0, 127.2, 116.4, 115.5, 84.1, 82.3, 52.8, 36.4, 21.6, 19.8. IR (neat): 2924, 1350, 1163, 1097 cm$^{-1}$. HRMS (ESI): calcd. for C$_{16}$H$_{20}$NO$_2$S ([M+H]$^+$): 290.1209, found 290.1214.

To a solution of $\mathbf{1h}$ (526.1 mg, 1.51 mmol) (for the synthesis of $\mathbf{1h}$, see below) in toluene (15 mL) was added DIBAL-H (3.8 mL, 1.0 M in hexane, 3.8 mmol) under Ar at 0 °C. The reaction was gradually allowed to warm to room temperature, monitored by TLC, and stirred for 2 h. Upon completion, the reaction mixture was added saturated potassium sodium tartrate solution (30 mL) and stirred for further 30 min. The resulting mixture was extracted with ether (3×30 mL), and the combined organic phase was washed with brine, then dried over Na$_2$SO$_4$, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 3:1) to afford $\mathbf{1f}$ (346.5 mg, 75%).

Colorless oil, TLC $R_f = 0.49$ (EA/PE = 1/2). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J = 8.2$ Hz, 2H), 7.29 (d, $J = 8.2$ Hz, 2H), 5.50 (ddt, $J = 17.2$, 11.2, 1.8 Hz, 1H), 5.37 (dd, $J = 11.2$, 2.4 Hz, 1H), 5.32 (dd, $J = 17.2$, 2.4 Hz, 1H), 5.23 (s, 1H), 5.10 (s, 1H), 4.18 (s, 4H), 3.83 (s, 2H), 2.41 (s, 3H), 2.30 – 2.11 (br. s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.8, 142.8, 135.7, 129.6, 128.0, 127.6, 116.3, 115.9, 84.6, 82.4, 63.5, 48.8, 36.7, 21.7. IR (neat): 2953, 2921, 1461, 1349, 1162, 1095 cm$^{-1}$. HRMS (ESI): calcd. for C$_{16}$H$_{20}$NO$_3$S ([M+H]$^+$): 306.1158, found 306.1161.

To a stirred solution of $\mathbf{S1}^1$ (282.3 mg, 1.2 mmol) and PPh$_3$ (475.2 mg, 1.8 mmol) in THF (11 mL) was added DIAD (365.6 mg, 1.8 mmol) at 0 °C. After stirring for 5 min, the solution was added $\mathbf{S4}^5$
(270.7 mg, 1.3 mmol) in THF (5 mL). The reaction was gradually allowed to warm to room temperature, monitored by TLC, and stirred for 3 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford \( \text{Ig} \) (466.2 mg, 93%).

Colorless oil, TLC \( R_t = 0.70 \) (EA/PE = 1/5). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.74 (d, \( J = 8.1 \) Hz, 2H), 7.28 (d, \( J = 8.1 \) Hz, 2H), 5.47 (dd, \( J = 17.2, 11.2 \) Hz, 1H), 5.38 – 5.22 (m, 3H), 5.11 (s, 1H), 4.17 (s, 2H), 4.15 (s, 2H), 3.78 (s, 2H), 2.41 (s, 3H), 0.91 (s, 9H), 0.07 (s, 6H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 143.5, 142.3, 141.9, 129.5, 128.9, 127.3, 116.4, 114.2, 84.6, 82.4, 63.7, 49.0, 36.6, 26.0, 21.6, 18.5, -5.3. IR (neat): 2953, 2928, 2856, 1463, 1351, 1257, 1094 cm\(^{-1}\). HRMS (ESI): calcd. for \( \text{C}_{22}\text{H}_{34}\text{NO}_3\text{SSi} \) ([M+H]\(^+\)): 420.2023, found 420.2030.

To a stirred solution of \( \text{S1} \) (934.5 mg, 3.97 mmol), PPh\(_3\) (1.5630 g, 5.96 mmol) in THF (39 mL) was added DIAD (1.2023 g, 5.95 mmol) at 0 °C. After stirring for 5 min, the solution was added \( \text{S5} \) (621.8 mg, 4.78 mmol) in THF (13 mL). The reaction was gradually allowed to warm to room temperature, monitored by TLC, and stirred for 3 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford \( \text{1h} \) (1.1513 g, 83%).

Yellow oil, TLC \( R_t = 0.42 \) (EA/PE = 1/5). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.76 (d, \( J = 8.2 \) Hz, 2H), 7.29 (d, \( J = 8.2 \) Hz, 2H), 6.39 (d, \( J = 1.0 \) Hz, 1H), 5.93 (d, \( J = 1.0 \) Hz, 1H), 5.56 – 5.42 (m, 1H), 5.39 – 5.28 (m, 2H), 4.62 – 4.18 (m, 4H), 4.07 (s, 2H), 2.41 (s, 3H), 1.31 (t, \( J = 7.1 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 165.9, 143.7, 136.0, 135.3, 129.6, 127.9, 127.6, 127.4, 116.3, 84.6, 82.6, 61.2, 47.0, 37.8, 21.6, 14.3. IR (neat): 2956, 2924, 2852, 1721, 1352, 1163, 1094 cm\(^{-1}\). HRMS (ESI): calcd. for \( \text{C}_{18}\text{H}_{22}\text{NO}_4\text{S} \) ([M+H]\(^+\)): 348.1264, found 348.1271.

To a stirred solution of \( \text{S1} \) (285.9 mg, 1.22 mmol), PPh\(_3\) (479.1 mg, 1.83 mmol) in THF (12 mL) was added DIAD (369.4 mg, 1.83 mmol) at 0 °C. After stirring for 5 min, the solution was added \( \text{S6} \) (195.8 mg, 1.46 mmol) in THF (4 mL). The reaction was gradually allowed to warm to room
temperature, monitored by TLC, and stirred for 2 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford 1i (405.4 mg, 95%).

Light yellow solid, TLC Rf = 0.58 (EA/PE = 1/5), m.p. = 113-116 °C. 1H NMR (400 MHz, CDCl3) δ 7.79 – 7.73 (m, 2H), 7.57 – 7.52 (m, 2H), 7.38 – 7.29 (m, 5H), 5.58 (s, 1H), 5.52 – 5.42 (m, 1H), 5.38 – 5.24 (m, 3H), 4.24 (s, 2H), 4.09 (d, J = 1.7 Hz, 2H), 2.42 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 143.6, 141.5, 137.8, 135.6, 129.5, 128.6, 128.3, 128.1, 127.3, 126.5, 117.3, 116.3, 84.8, 82.3, 50.3, 36.4, 21.6. IR (neat): 2917, 2849, 1462, 1350, 1162, 1094 cm⁻¹. HRMS (ESI): calcd. for C21H22NO2S ([M+H]⁺): 352.1366, found 352.1365.

To a stirred solution of SeO2 (7.70 g, 69.0 mmol) in DCM (30 mL) was added tBuOOH (8.90 g, 69.0 mmol, 70% solution in H2O) at 0 °C. After stirring for 10 min, the solution was added S7 (6.75 g, 46.0 mmol) in DCM (30 mL) at 0 °C. After stirred for 1.5 h, the reaction was quenched by saturated NaHCO3 (100 mL) at 0 °C. The reaction mixture was extracted with DCM (3×100 mL) and the combined organic phase was dried over Na2SO4 and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 4:1) to afford S8 (2.94 g, 48%). S8 is a known substrate.

To a stirred solution of S1 (235.8 mg, 1.0 mmol) and PPh3 (394.1 mg, 1.5 mmol) in THF (10 mL) was added DIAD (305.4 mg, 1.5 mmol) at 0 °C. After stirring for 5 min, the solution was added S8 (172.4 mg, 1.0 mmol) in THF (4 mL). The reaction was gradually allowed to warm to room temperature, monitored by TLC, and stirred for 3 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford 1j (262.2 mg, 69%).
Light yellow solid, TLC $R_f = 0.40$ (EA/PE = 1/5), m.p. = 162-163 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J = 8.2$ Hz, 2H), 7.54 – 7.48 (m, 2H), 7.30 (d, $J = 8.2$ Hz, 2H), 6.91 – 6.86 (m, 2H), 5.50 (s, 1H), 5.48 – 5.41 (m, 1H), 5.35 (dd, $J = 11.2$, 2.5 Hz, 1H), 5.26 (dd, $J = 17.2$, 2.5 Hz, 1H), 5.22 (d, $J = 0.8$ Hz, 1H), 4.21 (s, 2H), 4.07 (d, $J = 1.5$ Hz, 2H), 3.82 (s, 3H), 2.42 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.7, 143.6, 140.6, 135.6, 130.1, 129.5, 128.2, 127.7, 127.3, 116.4, 115.7, 113.9, 84.7, 82.3, 55.4, 36.3, 21.6. IR (neat): 2955, 2922, 1515, 1349, 1253, 1185, 1163, 1091 cm$^{-1}$. HRMS (ESI): calcd. for C$_{22}$H$_{24}$NO$_3$S ([M+H]$^+$): 382.1471, found 382.1480.

To a stirred solution of SeO$_2$ (735.2 mg, 6.6 mmol) in DCM (4 mL) was added tBuOOH (856.4 mg, 6.7 mmol, 70% solution in H$_2$O) at 0 º C. After stirring for 10 min, the solution was added S9 (602.5 mg, 4.4 mmol) in DCM (4 mL) at 0 º C. After stirred for 3 h at room temperature, the reaction was quenched by saturated NaHCO$_3$ at 0 º C. The reaction mixture was extracted with DCM (3×10 mL) and the combined organic phase was washed with saturated Na$_2$SO$_3$, saturated NaHCO$_3$ and brine, then dried over Na$_2$SO$_4$, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 10:1) to afford S10 (270.1 mg, 40%). S10 is a known substrate.

To a stirred solution of S1 (378.0 mg, 1.61 mmol) and PPh$_3$ (633.2 mg, 2.41 mmol) in THF (16 mL) was added DIAD (489.3 mg, 2.42 mmol) at 0 º C. After stirring for 5 min, the solution was added S10 (270.1 mg, 1.77 mmol) in THF (5 mL). The reaction was gradually allowed to warm to room temperature, monitored by TLC, and stirred for 7 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford 1k (521.7 mg, 88%).

White solid, TLC $R_f = 0.60$ (EA/PE = 1/5), m.p. = 97-98 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J = 8.3$ Hz, 2H), 7.60 – 7.47 (m, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.10 – 6.95 (m, 2H), 5.52 (s, 1H), 5.51 – 5.40 (m, 1H), 5.39 – 5.32 (m, 1H), 5.32 – 5.22 (m, 2H), 4.21 (s, 2H), 4.07 (d, $J = 1.4$ Hz, 2H), 2.42 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.9 (d, $J = 247.6$ Hz), 143.7, 140.5, 135.6, 133.8 (d, $J = 3.2$ Hz), 129.6, 128.3 (d, $J = 8.1$ Hz), 128.5, 127.7, 117.3, 116.3, 115.5 (d, $J = 21.5$ Hz), 84.9, 82.2, 50.5, 36.4, 21.7. IR (neat): 2955, 2924, 2852, 1351, 1164, 1093 cm$^{-1}$. HRMS (ESI): calcd. for C$_{21}$H$_{21}$FNO$_3$S ([M+H]$^+$): 370.1272, found 370.1275.
To a stirred solution of SeO$_2$ (1.5016 g, 13.5 mmol) in DCM (8 mL) was added tBuOOH (1.7453 g, 13.6 mmol, 70% solution in H$_2$O) at 0 ºC. After stirring for 10 min, the solution was added S$_{11}$ (1.5179 g, 9.02 mmol) in DCM (8 mL) at 0 ºC. After stirred for 2 h at room temperature, the reaction was quenched by saturated NaHCO$_3$ (30 mL) at 0 ºC. The reaction mixture was extracted with DCM (3×20 mL) and the combined organic phase was washed with saturated Na$_2$SO$_3$, saturated NaHCO$_3$ and brine, then dried over Na$_2$SO$_4$, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 10:1) to afford S$_{12}$ (751.0 mg, 45%). S$_{12}$ is a known substrate.

To a stirred solution of S$_1$ (447.6 mg, 1.90 mmol) and PPh$_3$ (748.5 mg, 2.85 mmol) in THF (18 mL) was added DIAD (575.1 mg, 2.84 mmol) at 0 ºC. After stirring for 5 min, the solution was added S$_{12}$ (386.3 mg, 2.10 mmol) in THF (7 mL). The reaction was gradually allowed to warm to room temperature, monitored by TLC, and stirred for 3 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford 11 (729.9 mg, 96%).

Light yellow solid, TLC $R_f$ = 0.46 (EA/PE = 1/5), m.p. = 146-149 ºC. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.03 (s, 1H), 7.93 – 7.72 (m, 5H), 7.66 (d, $J$ = 8.6 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.29 (d, $J$ = 8.0 Hz, 2H), 5.72 (s, 1H), 5.57 – 5.25 (m, 4H), 4.36 (s, 2H), 4.12 (s, 2H), 2.42 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.6, 141.5, 135.8, 135.1, 133.5, 133.3, 129.6, 128.7, 128.18, 128.15, 127.6, 127.4, 126.36, 126.35, 125.8, 124.5, 117.8, 116.4, 84.8, 82.5, 50.5, 36.6, 21.7. IR (neat): 2959, 2928, 2856, 1163, 1092 cm$^{-1}$. HRMS (ESI): calcd. for C$_{29}$H$_{24}$NO$_2$S ([M+H]$^+$): 402.1522, found 402.1525.
To a stirred solution of SeO₂ (3.3131 g, 29.9 mmol) in DCM (12 mL) was added iBuOOH (3.8445 g, 29.9 mmol, 70% solution in H₂O) at 0 ºC. After stirring for 10 min, the solution was added S₁₁ (2.4706 g, 19.9 mmol) in DCM (12 mL) at 0 ºC. After stirred for 1 h, the reaction was quenched by saturated NaHCO₃ (40 mL) at 0 ºC. The reaction mixture was extracted with DCM (3 × 20 mL) and the combined organic phase was washed with saturated Na₂SO₃, saturated NaHCO₃ and brine, then dried over Na₂SO₄, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 10:1) to afford S₁₄ (408.7 mg, 15%). S₁₄ is a known substrate.

To a stirred solution of S₁ (492.1 mg, 2.09 mmol) and PPh₃ (822.9 mg, 3.14 mmol) in THF (20 mL) was added DIAD (635.0 mg, 3.14 mmol) at 0 ºC. After stirring for 5 min, the solution was added S₁₄ (352.4 mg, 2.51 mmol) in THF (7 mL). The reaction was gradually allowed to warm to room temperature, monitored by TLC, and stirred for 5 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford 1m (711.4 mg, 95%).

White solid, TLC Rf = 0.51 (EA/PE = 1/5), m.p. = 68-69 ºC. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 3.5 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 5.1 Hz, 1H), 7.05 – 6.97 (m, 1H), 5.59 (s, 1H), 5.46 (dd, J = 17.2, 11.2 Hz, 1H), 5.35 (dd, J = 11.2, 2.3 Hz, 1H), 5.26 (dd, J = 17.2, 2.3 Hz, 1H), 5.19 (s, 1H), 4.18 (s, 4H), 2.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.7, 141.6, 135.6, 135.2, 129.6, 128.2, 128.0, 127.4, 125.7, 125.0, 116.3, 115.9, 85.0, 82.2, 50.6, 36.5, 21.7. IR (neat): 2952, 2922, 2854, 1351, 1094 cm⁻¹. HRMS (ESI): calcd. for C₁₉H₂₀N₂O₂S₂ ([M+H]⁺): 358.0930, found 358.0939.

To a suspension of NaH (30.2 mg, 0.76 mmol, 60%) in DMF (1.0 mL) was added S₁₅ (58.8 mg, 0.25 mmol) in DMF (1.5 mL) at 0 ºC. After stirred for 30 min, a solution of 1-bromobut-2-yne (60 uL, 0.67 mmol) was added at 0 ºC and the reaction mixture was allowed to warm to room
temperature. The reaction was monitored by TLC and stirred for 2 h. Upon completion, saturated NH₄Cl (2 mL) was added to quench the reaction. The resulting mixture was extracted with ether (3×10 mL) and the combined organic phase was washed with saturated NaCl, dried over Na₂SO₄, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford 1o (56.4 mg, 79%).

Colorless oil, TLC Rf = 0.49 (EA/PE = 1/5). ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 6.35 (dd, J = 17.7, 11.1 Hz, 1H), 5.62 (d, J = 17.7 Hz, 1H), 5.23 (s, 1H), 5.22 (s, 1H), 4.06 – 3.96 (m, 2H), 3.95 (s, 2H), 2.43 (s, 3H), 1.52 – 1.42 (m, 3H).

CuI (30.6 mg, 0.16 mmol) and Pd(PPh₃)₄ (69.2 mg, 0.06 mmol) were dissolved in Et₂NH (2.0 mL). S16 (783.0 mg, 4.0 mmol) in THF (6.0 mL) and bromoethene (8.0 mL, 1.0 M in THF) was added to the solution at 0 ºC. The reaction was gradually allowed to warm to room temperature, and was continued for another 13 h (TLC indicated that the reaction was completed). The reaction solution was then added to water (50 mL) at 0 ºC. The resulting mixture was extracted with ether (3×30 mL), and the combined organic phase was washed with brine, dried over Na₂SO₄, filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford 1p (775.0 mg, 87%).

Light yellow oil, TLC Rf = 0.53 (EA/PE = 1/10). ¹H NMR (400 MHz, CD₂Cl₂) δ 5.85 – 5.74 (m, 2H), 5.61 (dd, J = 17.6, 2.2 Hz, 1H), 5.47 (dd, J = 11.1, 2.2 Hz, 1H), 5.20 – 5.12 (m, 2H), 4.12 (s, 2H), 3.91 (d, J = 5.7 Hz, 2H), 1.44 (s, 9H). ¹³C NMR (100 MHz, CD₂Cl₂) δ 155.1, 134.0, 127.3, 117.2, 116.9, 86.3, 82.0, 80.3, 48.9, 36.4, 28.4. IR (neat): 2978, 2923, 1699, 1453, 1404, 1366, 1246, 1170, 1144, 920 cm⁻¹. HRMS (ESI): calcd. for C₁₆H₁₉NaNO₂S ([M+Na⁺]: 312.1029, found 312.1026.

S16 (190.6 mg, 0.86 mmol) was dissolved in DCM (1.5 mL), then CF₃COOH (0.25 mL, 3.4 mmol) was added to the solution at 0 ºC. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 2 h. Upon completion, the reaction was quenched by saturated NaHCO₃ (10 mL). The resulting mixture was extracted with DCM (3×5 mL), and the
combined organic phase was washed with brine, dried over Na₂SO₄, filtered and concentrated. The crude product was used in the next step directly. The crude product was dissolved in CH₃CN (4.0 mL), then K₂CO₃ (238.1 mg, 1.7 mmol) and BnBr (0.12 mL, 1.0 mmol) were added to the solution at room temperature. The reaction was monitored by TLC and stirred for 3 h at room temperature. Upon completion, the solution was added to water (40 mL). The resulting mixture was extracted with ether (3×20 mL), and the combined organic phase was washed with brine, dried over Na₂SO₄, filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford 1q (115.8 mg, 64%).

Colorless oil, TLC Rₜ = 0.68 (EA/PE = 1/5). ¹H NMR (400 MHz, CD₂Cl₂) δ 7.38 – 7.29 (m, 4H), 7.29 – 7.21 (m, 1H), 5.97 – 5.80 (m, 2H), 5.64 (dd, J = 17.5, 2.1 Hz, 1H), 5.47 (dd, J = 11.1, 2.1 Hz, 1H), 5.28 (dd, J = 17.2, 1.6 Hz, 1H), 5.17 (d, J = 10.1 Hz, 1H), 3.64 (s, 2H), 3.40 (d, J = 1.0 Hz, 2H), 3.18 (d, J = 6.3 Hz, 2H). ¹³C NMR (100 MHz, CD₂Cl₂) δ 139.4, 136.3, 129.4, 128.6, 127.4, 126.8, 117.9, 117.5, 85.7, 84.5, 57.7, 57.0, 42.4. IR (neat): 3065, 3029, 2920, 2815, 1643, 1606, 1452, 1424, 1327, 1147, 973, 921 cm⁻¹. HRMS (ESI): calcd. for C₁₅H₁₈N ([M+H]⁺): 212.1434, found 212.1434.

1p (216.3 mg, 0.98 mmol) was added to the solution at 0 °C. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 2 h. Upon completion, the reaction was quenched by saturated NaHCO₃ (10 mL). The resulting mixture was extracted with DCM (3×10 mL), and the combined organic phase was washed with brine, dried over Na₂SO₄, filtered and concentrated. The crude product was used in the next step directly. The crude product was dissolved in DCM (5.0 mL), then pyridine (0.16 mL, 2.0 mmol) and o-NsCl (326.0 mg, 1.5 mmol) were added to the solution at room temperature. The reaction was monitored by TLC and stirred for 3 h at room temperature. Upon completion, the solution was added to water (10 mL). The resulting mixture was extracted with DCM (3×10 mL), and the combined organic phase was washed with brine, dried over Na₂SO₄, filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 5:1) to afford 1r (119.9 mg, 40%).

Yellow oil, TLC Rₜ = 0.21 (EA/PE = 1/5). ¹H NMR (400 MHz, CDCl₃) δ 8.11 – 8.03 (m, 1H), 7.73 – 7.60 (m, 3H), 5.79 – 5.67 (m, 1H), 5.65 – 5.55 (m, 1H), 5.49 – 5.39 (m, 2H), 5.31 (dd, J = 17.1, 1.0 Hz, 1H), 5.26 (dd, J = 10.1, 1.0 Hz, 1H), 4.25 (d, J = 1.3 Hz, 2H), 4.02 (d, J = 6.4 Hz, 2H). ¹³C
NMR (100 MHz, CDCl₃) δ 148.3, 133.8, 133.0, 131.8, 131.7, 131.2, 128.0, 124.2, 120.4, 116.2, 84.4, 82.6, 49.7, 36.8. IR (neat): 3032, 3000, 2933, 1553, 1445, 1368, 1173, 1132, 1074, 936, 911 cm⁻¹. HRMS (ESI): calcd. for C₁₄H₁₅N₂O₄S ([M+H]⁺): 307.0747, found 307.0745.
III. Reaction Condition Screening

Table S1: Optimization of Au(I)-Catalyzed Cycloisomerization

<table>
<thead>
<tr>
<th>entry</th>
<th>cat.</th>
<th>x</th>
<th>solvent</th>
<th>yield (%)</th>
<th>conv. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Au(PPh₃)SbF₆</td>
<td>10</td>
<td>DCE</td>
<td>trace</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>Au(IPr)SbF₆</td>
<td>10</td>
<td>DCE</td>
<td>21</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>Au(L)SbF₆ᵈ</td>
<td>10</td>
<td>DCE</td>
<td>trace</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>Au(JohnPhos)SbF₆</td>
<td>10</td>
<td>DCE</td>
<td>52</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>Au(JohnPhos)OTf</td>
<td>10</td>
<td>DCE</td>
<td>56</td>
<td>96</td>
</tr>
<tr>
<td>6</td>
<td>Au(JohnPhos)NTf₂</td>
<td>10</td>
<td>DCE</td>
<td>52</td>
<td>97</td>
</tr>
<tr>
<td>7</td>
<td>Au(JohnPhos)SbF₆</td>
<td>10</td>
<td>DCM</td>
<td>43</td>
<td>97</td>
</tr>
<tr>
<td>8</td>
<td>Au(JohnPhos)SbF₆</td>
<td>10</td>
<td>THF</td>
<td>56</td>
<td>96</td>
</tr>
<tr>
<td>9</td>
<td>Au(JohnPhos)SbF₆</td>
<td>10</td>
<td>toluene</td>
<td>26</td>
<td>48</td>
</tr>
<tr>
<td>10</td>
<td>Au(JohnPhos)SbF₆</td>
<td>10</td>
<td>CH₃CN</td>
<td>N.R.</td>
<td>--</td>
</tr>
<tr>
<td>11</td>
<td>Au(JohnPhos)SbF₆</td>
<td>5</td>
<td>DCE</td>
<td>69</td>
<td>94</td>
</tr>
<tr>
<td>12</td>
<td>Au(JohnPhos)MeCNSbF₆ᵉ</td>
<td>5</td>
<td>DCE</td>
<td>56</td>
<td>92</td>
</tr>
</tbody>
</table>

α Conditions: 0.1 mmol 1a, x mol % cat., solvent (0.05 M), 30 ºC, 12 h. b Isolated yield. c Based on recovered starting material. d L = tris(2,4-di-i-butylphenyl)phosphate. e Commercially available Echavarren’s catalyst.

We also tested the Au(I)-catalyzed cycloisomerization using Boc, Bn, and o-Ns as the N-protecting groups (substrates 1p, 1q and 1r), finding that no cyclopropanation took place (see Part IV).

Table S2: Optimization of Au(I)-Catalyzed Cycloisomerization of 1h

<table>
<thead>
<tr>
<th>entry</th>
<th>x</th>
<th>time (h)</th>
<th>yield (%)</th>
<th>conv. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>14</td>
<td>42</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>14</td>
<td>46</td>
<td>100</td>
</tr>
</tbody>
</table>

α Conditions: 0.1 mmol 1h, x mol % cat., solvent (0.05 M), 30 ºC. b Isolated yield. c Based on recovered starting material.
**Table S3:** Optimization of Rh(I)-Catalyzed [5+1] Cycloaddition

<table>
<thead>
<tr>
<th>entry&lt;sup&gt;a&lt;/sup&gt;</th>
<th>x</th>
<th>Mole ratio of dppp to Rh</th>
<th>time (h)</th>
<th>yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>1.2</td>
<td>16</td>
<td>61</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>1.0</td>
<td>16</td>
<td>78</td>
</tr>
<tr>
<td>3&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.2</td>
<td>1.0</td>
<td>16</td>
<td>58</td>
</tr>
<tr>
<td>4</td>
<td>0.1</td>
<td>1.0</td>
<td>16</td>
<td>39</td>
</tr>
<tr>
<td>5</td>
<td>1.0</td>
<td>1.0</td>
<td>12</td>
<td>74</td>
</tr>
</tbody>
</table>

<sup>a</sup> Conditions: 0.1 mmol 2i, 10 mol % Rh(dppp)SbF<sub>6</sub>, DCE (0.05 M), 0.08 g 4Å MS, x atm CO, 90 °C. <sup>b</sup> Isolated yield. <sup>c</sup> Without 4Å MS.

**Table S4:** Test of CO Pressure on affecting the [5+1] Cycloaddition

<table>
<thead>
<tr>
<th>entry&lt;sup&gt;a&lt;/sup&gt;</th>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;3&lt;/sup&gt;</th>
<th>x</th>
<th>time (h)</th>
<th>yield 3 (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>yield 4 (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>conv. (%)&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me</td>
<td>H</td>
<td>0.2</td>
<td>12</td>
<td>56</td>
<td>29</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>Me</td>
<td>H</td>
<td>0.5</td>
<td>24</td>
<td>32</td>
<td>14</td>
<td>47</td>
</tr>
<tr>
<td>3</td>
<td>H</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;OH</td>
<td>0.2</td>
<td>3</td>
<td>40</td>
<td>36</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>H</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;OH</td>
<td>0.5</td>
<td>24</td>
<td>trace</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>5</td>
<td>H</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;Et</td>
<td>0.2</td>
<td>1</td>
<td>26</td>
<td>62</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>H</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;Et</td>
<td>0.5</td>
<td>24</td>
<td>trace</td>
<td>0</td>
<td>24</td>
</tr>
</tbody>
</table>

<sup>a</sup> Conditions: 0.1 mmol 2, 10 mol % Rh(dppp)SbF<sub>6</sub>, DCE (0.05 M), 0.08 g 4Å MS, x atm CO, 90 °C. <sup>b</sup> Isolated yield. <sup>c</sup> Based on recovered starting material.

**Table S5:** Optimization of Rh(I)-Catalyzed Rearrangement of VCPs

<table>
<thead>
<tr>
<th>entry&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Mole ratio of dppp to Rh</th>
<th>time (h)</th>
<th>yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.2</td>
<td>1</td>
<td>84</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>1</td>
<td>80</td>
</tr>
</tbody>
</table>

<sup>a</sup> Conditions: 0.1 mmol 2i, 10 mol % Rh(dppp)SbF<sub>6</sub>, DCE (0.05 M), 0.08g 4Å MS, 90 °C. <sup>b</sup> Isolated yield.
IV. General Procedure and Experimental Details of Au(I)-Catalyzed Cycloisomerization

General procedure A: (5 mol % catalyst)
Preparation of solution of cationic Au(I) catalyst: Anhydrous DCE (2.0 mL) was added to a mixture of Au(JohnPhos)Cl (2.6 mg, 4.9 μmol) and AgSbF₆ (2.1 mg, 6.1 μmol) under argon. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed AgCl precipitated. The supernatant was used in Au(I)-catalyzed cycloisomerization reactions as the catalyst precursor.

General procedure of Au(I)-catalyzed cycloisomerization: Under argon, the above Au(I)⁺ solution (2.0 mL) was added to a flame-dried glassware containing 1 (0.1 mmol) at 30 °C. The reaction was monitored by TLC. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel to afford 2.

General procedure B: (10 mol % catalyst)
Preparation of solution of cationic Au(I) catalyst: Anhydrous DCE (2.0 mL) was added to a mixture of Au(JohnPhos)Cl (5.3 mg, 10.0 μmol) and AgSbF₆ (4.1 mg, 11.9 μmol) under argon. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed AgCl precipitated. The supernatant was used in Au(I)-catalyzed cycloisomerization reactions as the catalyst precursor.

General procedure of Au(I)-catalyzed cycloisomerization: Under argon, the above Au(I)⁺ solution (2.0 mL) was added to a flame-dried glassware containing 1 (0.1 mmol) at 30 °C. The reaction was monitored by TLC. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel to afford 2.

Run 1: Following general procedure A, 27.4 mg 1a was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 18.6 mg 2a was obtained in 68% yield and 1.1 mg 1a was recovered.

Run 2: Following general procedure A, 27.9 mg 1a was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 19.5 mg 2a was obtained in 70% yield and 2.1 mg 1a was recovered.

Average yield: 69%.

Colorless oil, TLC Rf = 0.34 (EA/PE = 1/10). ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 6.41 (d, J = 8.3 Hz, 1H), 5.46 (d, J = 8.3 Hz, 1H), 5.43 (dd, J = 17.3, 10.6 Hz, 1H), 4.99 (d, J = 17.3 Hz, 1H), 4.93 (d, J = 10.6 Hz, 1H), 3.97 (d, J = 11.6 Hz, 1H), 3.03 (dd, J = 11.6, 2.7 Hz, 1H), 2.42 (s, 3H), 1.62 – 1.51 (m, 1H), 0.97 (dd, J = 8.6, 4.5 Hz, 1H), 0.85 – 0.78 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 143.9, 141.8, 134.9, 129.9, 127.2, 121.4, 111.5, 111.4, 40.6, 27.7, 22.8, 21.7, 19.7. IR (neat): 2921, 1630, 1349, 1166, 1113, 1090, 1002 cm⁻¹. HRMS (ESI): calcd. for C₁₅H₁₈NO₂S ([M+H]⁺): 276.1053, found 276.1051.
Run 1: Following general procedure A, 28.2 mg 1b was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 20.9 mg 2b was obtained in 74% yield and 2.5 mg 1b was recovered.

Run 2: Following general procedure A, 28.4 mg 1b was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 21.5 mg 2b was obtained in 76% yield and 2.8 mg 1b was recovered.

Average yield: 75%.

Colorless oil, TLC Rf = 0.37 (EA/PE = 1/10). 1H NMR (400 MHz, CDCl3) δ 7.66 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 6.39 (d, J = 8.3 Hz, 1H), 5.35 (d, J = 8.3 Hz, 1H), 4.77 – 4.74 (m, 1H), 4.73 – 4.69 (m, 1H), 3.92 (d, J = 11.7 Hz, 1H), 3.05 (dd, d, J = 11.7, 2.7 Hz, 1H), 2.43 (s, 3H), 1.66 (s, 3H), 1.60 – 1.55 (m, 1H), 1.05 (dd, J = 8.8, 4.5 Hz, 1H), 0.64 – 0.56 (m, 1H). 13C NMR (100 MHz, CDCl3) δ 146.3, 143.9, 135.1, 129.9, 127.2, 121.1, 113.7, 110.6, 40.8, 25.8, 23.2, 21.7, 20.6, 20.2. IR (neat): 2922, 1729, 1349, 1271, 1168, 1110, 1089, 1076, 1004 cm⁻¹. HRMS (ESI): calcd. for C16H20NO2S ([M+H]⁺): 290.1209, found 290.1212.

Run 1: Following general procedure A, 28.4 mg 1c was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 24.8 mg 2c was obtained in 87% yield, Z/E = 1/3.5.

Run 2: Following general procedure A, 29.6 mg 1c was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 26.5 mg 2c was obtained in 90% yield, Z/E = 1/3.5.

Average yield: 88%, Z/E = 1/3.5.

Colorless oil, TLC Rf = 0.41 (EA/PE = 1/10). (Z)-2c: 1H NMR (400 MHz, CDCl3) δ 7.64 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.41 – 6.33 (m, 1H), 5.54 – 5.34 (m, 2H), 5.10 (dd, J = 15.4, 1.0 Hz, 1H), 3.89 (d, J = 11.5 Hz, 1H), 3.03 (dd, d, J = 11.5, 2.6 Hz, 1H), 2.42 (s, 3H), 1.65 – 1.61 (m, 3H), 1.54 – 1.46 (m, 1H), 0.89 (dd, J = 8.6, 4.5 Hz, 1H), 0.74 – 0.68 (m, 1H). (E)-2c: 1H NMR (400 MHz, CDCl3) δ 7.65 (d, J = 8.2 Hz, 2H × 3.5), 7.31 (d, J = 8.2 Hz, 2H × 3.5), 6.33 – 6.29 (m, 1H × 3.5), 5.54 – 5.34 (m, 2H × 3.5), 5.29 (d, J = 8.1 Hz, 1H × 3.5), 3.91 (d, J = 11.7 Hz, 1H × 3.5), 3.11 (dd, J = 11.7, 2.5 Hz, 1H × 3.5), 2.42 (s, 3H × 3.5), 1.65 – 1.61 (m, 3H × 3.5), 1.54 – 1.46 (m, 1H × 3.5), 0.83 (dd, J = 8.6, 4.3 Hz, 1H × 3.5), 0.74 – 0.68 (m, 1H × 3.5). 13C NMR (100 MHz, CDCl3) δ 143.9, 143.8, 135.0, 134.8, 134.4, 132.7, 129.9, 128.8, 127.2, 127.1, 122.8, 121.0, 119.9, 116.0, 112.6, 40.8, 40.7, 27.3, 27.0, 22.43, 22.35, 21.67, 21.65, 18.7, 17.9, 16.5, 14.3. IR (neat): 1637, 1348, 1274, 1167, 1113, 1091, 1043, 1006 cm⁻¹. HRMS (ESI): calcd. for C16H18NaNO2S ([M+Na]⁺): 312.1029, found 312.1033.
Run 1: Following general procedure A, 29.4 mg 1d was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 27.1 mg 2d was obtained in 92% yield.
Run 2: Following general procedure A, 29.0 mg 1d was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 26.8 mg 2d was obtained in 92% yield.
Average yield: 92%.

Colorless oil, TLC R<sub>t</sub> = 0.43 (EA/PE = 1/10). ¹H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.66 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 6.37 (d, J = 8.1 Hz, 1H), 5.60 (dd, J = 17.2, 10.6 Hz, 1H), 5.39 (d, J = 8.1 Hz, 1H), 5.12 – 5.03 (m, 2H), 3.83 (d, J = 11.5 Hz, 1H), 2.69 (d, J = 11.5 Hz, 1H), 2.42 (s, 3H), 1.09 (s, 3H), 0.99 (d, J = 4.6 Hz, 1H), 0.83 (d, J = 4.6 Hz, 1H). ¹³C NMR (125 MHz, CDCl<sub>3</sub>) δ 143.9, 138.7, 135.1, 129.9, 127.2, 121.2, 114.9, 113.4, 46.5, 32.7, 27.0, 25.3, 21.7, 18.1. IR (neat): 2920, 1351, 1272, 1170, 1112, 1003 cm<sup>-1</sup>. HRMS (ESI): calcd. for C<sub>16</sub>H<sub>20</sub>NO<sub>2</sub>S ([M+H]<sup>+</sup>): 290.1209, found 290.1210.

Run 1: Following general procedure A, 29.7 mg 1e was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 29.5 mg 2e was obtained in 99% yield.
Run 2: Following general procedure A, 30.7 mg 1e was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 29.1 mg 2e was obtained in 95% yield.
Average yield: 97%.

2e is a known substrate<sup>4</sup>.

Run 1: Following general procedure A, 31.1 mg 1f was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 21.0 mg 2f was obtained in 68% yield.
Run 2: Following general procedure A, 30.7 mg 1f was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 21.8 mg 2f was obtained in 71% yield.
Average yield: 70%.

Colorless oil, TLC R<sub>t</sub> =0.41 (EA/PE = 1/2). ¹H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.67 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 6.43 (d, J = 8.2 Hz, 1H), 5.74 (dd, J = 17.4, 10.4 Hz, 1H), 5.36 (d, J = 8.2 Hz, 1H), 5.25 – 5.11 (m, 2H), 3.96 (d, J = 11.4 Hz, 1H), 3.72 (d, J = 12.2 Hz, 1H), 3.52 (d, J = 12.2 Hz, 1H), 3.10 (d, J = 11.4 Hz, 1H), 2.42 (s, 3H), 1.58 – 1.38 (br. s, 1H), 1.14 (d, J = 4.9 Hz, 1H), 1.06 (d, J = 4.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.1, 137.9, 134.8, 130.0, 127.3, 122.0, 116.7, 112.6, 65.5, 43.0, 38.6, 25.0, 24.7, 21.7. IR (neat): 2953, 2923, 2852, 1462, 1168, 1091, 1022 cm<sup>-1</sup>. HRMS (ESI): calcd. for C<sub>16</sub>H<sub>20</sub>NO<sub>2</sub>S ([M+H]<sup>+</sup>): 306.1158, found 306.116.
Run 2: Following general procedure A, 41.8 mg 1g was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 31.6 mg 2g was obtained in 76% yield. Average yield: 74%.

Colorless oil, TLC Rf = 0.50 (EA/PE = 1/10). 1H NMR (400 MHz, CDCl3) δ 7.66 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 6.40 (d, J = 8.2 Hz, 1H), 5.67 (dd, J = 17.0, 10.7 Hz, 1H), 5.34 (d, J = 8.2 Hz, 1H), 5.16 – 5.08 (m, 1H), 5.08 – 5.00 (m, 1H), 3.93 (d, J = 11.6 Hz, 1H), 3.55 (d, J = 10.9 Hz, 1H), 3.48 (d, J = 10.9 Hz, 1H), 2.98 (d, J = 11.6 Hz, 1H), 2.42 (s, 3H), 0.95 (d, J = 4.9 Hz, 1H), 0.89 (d, J = 4.9 Hz, 1H), 0.84 (s, 9H), -0.01 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 143.9, 137.8, 134.8, 129.9, 127.2, 121.5, 115.6, 113.5, 64.8, 43.4, 37.7, 25.9, 25.0, 24.2, 21.7, 18.3, -5.3. IR (neat): 2957, 2924, 2853, 1464, 1169, 1020 cm⁻¹. HRMS (ESI): calcd. for C22H34NO3SSi ([M+H]+): 420.2023, found 420.2033.

Run 1: Following general procedure A, 34.6 mg 1h was used, 14 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 14.8 mg 2h was obtained in 43% yield.

Run 2: Following general procedure A, 33.9 mg 1h was used, 14 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 13.8 mg 2h was obtained in 41% yield. Average yield: 42%.

Colorless oil, TLC Rf = 0.30 (EA/PE = 1/10). 1H NMR (400 MHz, CDCl3) δ 7.67 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 6.50 (d, J = 8.2 Hz, 1H), 5.74 (dd, J = 17.4, 10.7 Hz, 1H), 5.47 (d, J = 8.2 Hz, 1H), 5.17 (d, J = 17.4 Hz, 1H), 5.12 (d, J = 10.7 Hz, 1H), 4.18 – 4.07 (m, 2H), 4.02 (d, J = 12.2 Hz, 1H), 3.42 (d, J = 12.2 Hz, 1H), 2.43 (s, 3H), 1.81 (d, J = 4.9 Hz, 1H), 1.28 (d, J = 4.9 Hz, 1H), 1.22 (t, J = 7.1 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 169.2, 158.5, 146.2, 134.8, 129.9, 127.2, 123.6, 116.5, 112.2, 61.4, 42.1, 40.5, 28.8, 26.0, 21.7, 14.4. IR (neat): 2954, 2925, 1730, 1291, 1168, 1103 cm⁻¹. HRMS (ESI): calcd. for C18H22NO3S ([M+H]+): 348.1264, found 348.1271.

Run 1: Following general procedure A, 34.6 mg 1i was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 31.6 mg 2i was obtained in 91% yield.

Run 2: Following general procedure A, 35.5 mg 1i was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 33.7 mg 2i was obtained in 95% yield. Average yield: 93%.

Light yellow solid, TLC Rf = 0.39 (EA/PE = 1/10), m.p. = 229-230 °C. 1H NMR (400 MHz, CDCl3) δ 7.66 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.26 – 7.23 (m, 1H), 7.23 – 7.16 (m, 2H), 6.51 (d, J = 8.2 Hz, 1H), 5.66 (d, J = 8.2 Hz, 1H), 5.34 (d, J = 10.1, 2.6 Hz, 1H), 5.01 – 4.93 (m, 1H), 4.89 (dd, J = 10.4, 2.6 Hz, 1H), 4.02 (d, J = 11.7 Hz, 1H), 2.99 (d, J = 11.7 Hz, 1H), 2.44 (s, 3H), 1.52 (d, J = 4.8 Hz, 1H), 1.41 (dd, J = 4.8, 0.9 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 144.0, 139.9, 138.5, 135.0, 130.2, 130.0, 128.6, 127.5, 127.2, 122.0, 112.7, 112.4, 48.0,

Run 1: Following general procedure A, 38.4 mg \(1j\) was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 32.4 mg \(2j\) was obtained in 84% yield.

Run 2: Following general procedure A, 37.9 mg \(1j\) was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 33.4 mg \(2j\) was obtained in 88% yield.

Average yield: 86%.

Light yellow solid, TLC R\(_f\) = 0.28 (EA/PE = 1/10), m.p. = 197-198 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.65 (d, \(J = 8.2\) Hz, 2H), 7.32 (d, \(J = 8.2\) Hz, 2H), 7.15 – 7.08 (m, 2H), 6.87 – 6.74 (m, 2H), 6.49 (d, \(J = 8.2\) Hz, 1H), 5.64 (d, \(J = 8.2\) Hz, 1H), 5.04 (dd, \(J = 16.7, 2.3\) Hz, 1H), 5.00 – 4.92 (m, 1H), 4.90 (dd, \(J = 10.1, 2.3\) Hz, 1H), 3.99 (dd, \(J = 11.7, 0.7\) Hz, 1H), 2.93 (d, \(J = 11.7\) Hz, 1H), 2.43 (s, 3H), 1.50 (d, \(J = 4.8\) Hz, 1H), 1.36 (dd, \(J = 4.8, 1.0\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 158.9, 144.0, 141.0, 134.9, 131.2, 130.5, 130.0, 127.2, 121.9, 114.0, 112.4, 112.5, 55.4, 48.1, 41.8, 26.3, 25.8, 21.7. IR (neat): 2956, 2925, 2852, 1463, 1171, 1021 cm\(^{-1}\). HRMS (ESI): calcd. for C\(_{22}\)H\(_{24}\)NO\(_3\)S ([M+H]+): 382.1475, found 382.1475.

Run 1: Following general procedure A, 36.4 mg \(1k\) was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 30.4 mg \(2k\) was obtained in 84% yield.

Run 2: Following general procedure A, 36.9 mg \(1k\) was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 30.7 mg \(2k\) was obtained in 83% yield.

Average yield: 84%.

Light yellow solid, TLC R\(_f\) = 0.37 (EA/PE = 1/10), m.p. = 209-210 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.65 (d, \(J = 8.1\) Hz, 2H), 7.32 (d, \(J = 8.1\) Hz, 2H), 7.20 – 7.11 (m, 2H), 7.04 – 6.91 (m, 2H), 6.50 (d, \(J = 8.2\) Hz, 1H), 5.63 (d, \(J = 8.2\) Hz, 1H), 5.13 – 4.98 (m, 1H), 4.98 – 4.84 (m, 2H), 3.99 (d, \(J = 11.7\) Hz, 1H), 2.93 (d, \(J = 11.7\) Hz, 1H), 2.44 (s, 3H), 1.51 (d, \(J = 4.8\) Hz, 1H), 1.37 (d, \(J = 4.8\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.1 (d, \(J = 246.5\) Hz), 144.1, 139.7, 135.0, 134.3 (d, \(J = 3.2\) Hz), 131.8 (d, \(J = 8.1\) Hz), 130.0, 127.2, 122.1, 115.6 (d, \(J = 21.4\) Hz), 113.1, 112.3, 48.1, 41.6, 26.3, 25.8, 21.7. IR (neat): 2925, 2854, 1731, 1286, 1170 cm\(^{-1}\). HRMS (ESI): calcd. for C\(_{21}\)H\(_{19}\)FNO\(_2\)S ([M+H]+): 370.1272, found 370.1271.
Run 1: Following general procedure A, 40.8 mg 11 was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 34.4 mg 2i was obtained in 84% yield.
Run 2: Following general procedure A, 40.3 mg 11 was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 34.2 mg 2i was obtained in 85% yield.
Average yield: 84%.
White solid, TLC Rf = 0.33 (EA/PE = 1/10), m.p. = 223-225 °C. 1H NMR (400 MHz, CDCl3) δ 7.88–7.73 (m, 3H), 7.70 (s, 1H), 7.66 (d, J = 8.2 Hz, 2H), 7.51–7.43 (m, 2H), 7.32 (d, J = 8.2 Hz, 1H), 7.29 (dd, J = 8.5, 1.7 Hz, 1H), 6.55 (d, J = 8.3 Hz, 1H), 5.69 (d, J = 8.3 Hz, 1H), 5.09 (dd, J = 17.0, 1.5 Hz, 1H), 4.98 (dd, J = 17.0, 10.4 Hz, 1H), 4.88 (dd, d, J = 10.4, 1.5 Hz, 1H), 4.07 (dd, J = 11.7, 0.6 Hz, 1H), 3.09 (d, J = 11.7 Hz, 1H), 2.44 (s, 3H), 1.62 (d, J = 4.8 Hz, 1H), 1.57–1.53 (m, 1H).

13C NMR (100 MHz, CDCl3) δ 144.0, 139.8, 136.1, 134.9, 133.5, 132.7, 130.0, 129.1, 128.3, 128.0, 127.81, 127.77, 127.2, 126.4, 126.3, 122.1, 112.8, 112.2, 48.0, 42.4, 26.3, 25.9, 21.7. IR (neat): 2956, 2923, 2853, 1469, 1170 cm–1.

Run 1: Following general procedure A, 35.7 mg 1m was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 29.9 mg 2m was obtained in 84% yield.
Run 2: Following general procedure A, 35.9 mg 1m was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 31.0 mg 2m was obtained in 86% yield.
Average yield: 85%.
Light yellow solid, TLC Rf = 0.34 (EA/PE = 1/10), m.p. = 276-277 °C. 1H NMR (400 MHz, CDCl3) δ 7.67 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.16 (dd, J = 5.1, 1.1 Hz, 1H), 6.92 (dd, J = 5.1, 3.5 Hz, 1H), 6.84 (dd, J = 3.5, 1.1 Hz, 1H), 6.49 (d, J = 8.2 Hz, 1H), 5.59 (d, J = 8.2 Hz, 1H), 5.16 (dd, J = 17.3, 10.2 Hz, 1H), 5.07 (dd, J = 17.3, 1.5 Hz, 1H), 4.95 (dd, J = 10.2, 1.5 Hz, 1H), 4.11 (d, J = 11.6 Hz, 1H), 3.09 (d, J = 11.6 Hz, 1H), 2.44 (s, 3H), 1.56 (d, J = 5.1 Hz, 1H), 1.54 (d, J = 5.1 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 144.1, 142.0, 138.6, 134.9, 130.1, 127.2, 127.0, 126.8, 124.9, 122.1, 113.9, 112.1, 47.5, 37.7, 27.7, 27.0, 21.7. IR (neat): 2925, 1345, 1164, 1089 cm–1.

Following the reported procedure: 15: A solution of 2d (171.7 mg, 0.59 mmol) in DCM (12 mL) was cooled to -20 °C, and allyltrimethylsilane (560 μL, 3.5 mmol) and trifluoroacetic acid (180 μL, 2.4
mmol) were added to the solution. The reaction mixture was stirred at the same temperature for 2 h. The mixture was allowed to warm to room temperature and stirred for 2 h. Saturated NaHCO₃ solution (10 mL) was added, and the mixture was extracted with DCM (3×10 mL), and organic layer was washed with brine (10 mL), dried over Na₂SO₄, filtered, and concentrated. The reaction mixture was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford 2n (159.9 mg, dr > 20/1, 81%).

Colorless oil, TLC Rf = 0.55 (EA/PE = 1/5). ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 5.66 (dd, J = 17.2, 10.6 Hz, 1H), 5.61 – 5.50 (m, 1H), 5.03 (dd, J = 10.6, 1.1 Hz, 1H), 5.02 – 4.98 (m, 1H), 4.97 – 4.95 (m, 1H), 4.93 (dd, J = 17.2, 1.1 Hz, 1H), 3.93 – 3.83 (m, 1H), 3.78 (d, J = 13.0 Hz, 1H), 2.88 (d, J = 13.0 Hz, 1H), 2.41 (s, 3H), 2.16 – 2.02 (m, 1H), 2.00 – 1.88 (m, 2H), 1.79 (dd, J = 14.5, 6.2 Hz, 1H), 1.02 (s, 3H), 0.64 (d, J = 4.9 Hz, 1H), 0.59 (d, J = 4.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 143.2, 142.1, 138.0, 134.9, 129.8, 127.1, 117.9, 113.6, 50.8, 44.7, 35.8, 30.8, 23.6, 22.4, 21.7, 21.5, 18.7. IR (neat): 2923, 2851, 1342, 1286, 1163, 1091, 1040 cm⁻¹. HRMS (ESI): calcd. for C₁₆H₂₆NO₂S ([M+H]+): 332.1679, found 332.1677.

Run 1: Following general procedure B, 27.1 mg 1o was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 19.9 mg 2o was obtained in 73% yield.
Run 2: Following general procedure B, 27.8 mg 1o was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 20.3 mg 2o was obtained in 73% yield.
Average yield: 73%.
Colorless oil, TLC Rf = 0.48 (EA/PE = 1/10). ¹H NMR (400 MHz, CD₂Cl₂) δ 7.64 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 6.32 – 6.27 (m, 1H), 5.72 (dd, J = 17.4, 10.8 Hz, 1H), 5.23 (d, J = 8.0 Hz, 1H), 5.13 (dd, J = 10.8, 1.1 Hz, 1H), 5.05 (dd, J = 17.4, 1.1 Hz, 1H), 3.84 (d, J = 11.3 Hz, 1H), 2.91 (d, J = 11.3 Hz, 1H), 2.42 (s, 3H), 1.08 (s, 3H), 0.90 (d, J = 4.6 Hz, 1H), 0.78 (d, J = 4.6 Hz, 1H). ¹³C NMR (100 MHz, CD₂Cl₂) δ 144.4, 137.3, 135.2, 130.2, 127.4, 121.1, 118.0, 115.6, 44.5, 36.9, 24.9, 21.7, 20.5, 19.2. IR (neat): 2929, 2854, 1353, 1351, 1168, 1127, 1097 cm⁻¹. HRMS (ESI): calcd. for C₁₆H₂₀NO₂S ([M+H]+): 290.1209, found 290.1209.

Run 1: Following general procedure A, 21.2 mg 1p was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 10:1), 5.2 mg point 1 was obtained in 33% yield and 7.3 mg point 2 was obtained in 46% yield.
Run 2: Following general procedure A, 22.1 mg \textbf{1p} was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 10:1), 4.8 mg \textbf{point 1} was obtained in 29% yield and 8.2 mg \textbf{point 2} was obtained in 50% yield.

Average yield: 31% \textbf{point 1}, 48% \textbf{point 2}.

Colorless oil, TLC $R_f = 0.17$ (EA/PE = 1/10). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.73 – 6.54 (m, 1H), 5.82 – 5.70 (m, 1H), 5.33 – 5.21 (m, 3H), 5.13 (d, $J = 17.1$ Hz, 1H), 5.03 (d, $J = 10.4$ Hz, 1H), 4.15 (d, $J = 0.7$ Hz, 2H), 3.94 – 3.90 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.2, 142.5, 131.3, 128.9, 119.9, 115.9, 104.3, 47.6, 46.6. IR (neat): 2919, 2849, 1789, 1689, 1646, 1478, 1438, 1413, 1305, 1258, 1056, 994, 972, 900 cm$^{-1}$. HRMS (ESI): calcd. for C$_9$H$_{12}$NO$_2$ ([M+H]$^+$): 166.0863, found 166.0861.

Colorless oil, TLC $R_f = 0.10$ (EA/PE = 1/10). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.04 (dd, $J = 17.2$, 11.0 Hz, 1H), 5.87 – 5.76 (m, 1H), 5.73 (d, $J = 17.2$ Hz, 1H), 5.30 – 5.20 (m, 3H), 5.05 (t, $J = 3.3$ Hz, 1H), 3.99 (d, $J = 6.0$ Hz, 2H), 3.86 (d, $J = 3.3$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.2, 147.9, 131.4, 128.0, 118.8, 116.3, 98.6, 51.3, 44.9. IR (neat): 2918, 1720, 1610, 1485, 1443, 1357, 1241, 1186, 1094, 991, 923 cm$^{-1}$. HRMS (ESI): calcd. for C$_9$H$_{12}$NO$_2$ ([M+H]$^+$): 166.0863, found 166.0860.

When \textbf{1q} was subjected to the Au(I)-catalyzed cycloisomerization, starting material was recovered (76%).

When \textbf{1r} was subjected to the Au(I)-catalyzed cycloisomerization, starting material was recovered (67%) and some unidentified products were also found (judged by TLC).
V. General Procedure and Experimental Details of Rh(I)-Catalyzed [5+1] Cycloaddition

General procedure C:

Preparation of solution of cationic Rh(I) catalyst: Anhydrous DCE (2.0 mL) was added to a mixture of [Rh(CO)\(_2\)Cl]\(_2\) (2.0 mg, 5.1 μmol), AgSbF\(_6\) (4.1 mg, 11.9 μmol), and dppp (4.1 mg, 9.9 μmol) under nitrogen. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed AgCl precipitated. The supernatant was used in Rh(I)-catalyzed [5+1] cycloaddition reactions as the catalyst precursor.

General procedure of Rh(I)-catalyzed [5+1] cycloaddition: Under nitrogen, the above Rh(I)\(^+\) solution (2.0 mL) was added to a flame-dried glassware containing 2 (0.1 mmol) and the newly activated 4 Å molecular sieves (0.08 g) at rt. Then the reaction mixture was bubbled with a mixed gas of CO/N\(_2\) (v/v = 1/4) for 10 min. The glassware was immersed into an oil bath at 90 º C and reacted under the atmosphere pressure of the mixed gas of CO/N\(_2\) (v/v = 1/4). The reaction was monitored by TLC. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel to afford 3.

(Attention: The present reaction is sensitive to solvent and very highly anhydrous DCE must be used. Molecular sieves also should be activated before the reaction. If the reaction system were not dry, VCP rearrangement products could be the major products.)

Run 1: Following general procedure C, 27.4 mg 2a was used, 20 h. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 19.8 mg 3a was obtained in 66% yield.

Run 2: Following general procedure C, 27.3 mg 2a was used, 20 h. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 19.4 mg 3a was obtained in 64% yield.

Average yield: 65%.

Colorless oil, TLC \(R_f = 0.37\) (EA/PE = 1/3). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.67 (d, \(J = 8.2\) Hz, 2H), 7.32 (d, \(J = 8.2\) Hz, 2H), 6.73 (d, \(J = 8.0\) Hz, 1H), 5.53 (t, \(J = 6.4\) Hz, 1H), 5.52–5.47 (m, 1H), 3.98–3.88 (m, 1H), 3.03 (d, \(J = 23.2\) Hz, 1H), 2.90 (d, \(J = 23.2\) Hz, 1H), 2.71–2.63 (m, 2H), 2.48 (dd, \(J = 14.3, 3.8\) Hz, 1H), 2.43 (s, 3H), 2.17–2.07 (m, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 207.2, 144.4, 134.9, 131.6, 130.2, 127.2, 125.7, 118.6, 109.6, 48.7, 42.3, 40.2, 33.8, 21.7. IR (neat): 2923, 1720, 1340, 1265, 1088 cm\(^{-1}\). HRMS (ESI): calcd. for C\(_{16}\)H\(_{18}\)NO\(_3\)S ([M+H\(^+\)]: 304.1002, found 304.1005.

Run 1: Following general procedure C, 26.9 mg 2b was used, 12 h. After flash column
chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 7.4 mg 4b was obtained in 28% yield and 16.9 mg 3b was obtained in 57% yield.

Run 2: Following general procedure C, 28.4 mg 2b was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 8.5 mg 4b was obtained in 30% yield and 17.0 mg 3b was obtained in 55% yield.

Average yield: 56% 3b, 29% 4b.

Colorless oil, TLC Rf = 0.34 (EA/PE = 1/3). 1H NMR (400 MHz, CDCl3) δ 7.67 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 6.74 (d, J = 8.3 Hz, 1H), 5.74 (d, J = 8.3 Hz, 1H), 3.94 − 3.83 (m, 1H), 2.96 (d, J = 22.4 Hz, 1H), 2.80 (d, J = 22.4 Hz, 1H), 2.68 − 2.55 (m, 2H), 2.51 − 2.44 (m, 1H), 2.42 (s, 3H), 2.13 − 2.01 (m, 1H), 1.72 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 207.4, 144.3, 134.7, 130.1, 127.1, 125.2, 125.1, 124.4, 106.2, 49.0, 46.1, 42.7, 34.3, 21.7, 17.9. IR (neat): 2921, 1718, 1663, 1340, 1163, 1090 cm⁻¹. HRMS (ESI): calcd. for C17H30NO3S ([M+H]+): 318.1158, found 318.1162.

Run 1: Following general procedure C, 27.9 mg 2c was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 12.1 mg 3c was obtained in 40% yield, dr = 1.4/1.

Run 2: Following general procedure C, 29.5 mg 2c was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 14.4 mg 3c was obtained in 44% yield, dr = 1.4/1.

Average yield: 42%, dr = 1.4/1.

Colorless oil, TLC Rf = 0.67 (EA/PE = 1/3). 1H NMR (400 MHz, CDCl3) δ 7.68 − 7.64 (m, 2.8H + 2H), 7.32 (d, J = 8.2 Hz, 2.8H + 2H), 6.76 − 6.70 (m, 1.4H + 1H), 5.55 − 5.47 (m, 1.4H + 1H), 5.43 − 5.37 (m, 1.4H + 1H), 3.95 − 3.86 (m, 1.4H + 1H), 3.08 − 3.01 (m, 1.4H), 2.92 − 2.80 (m, 1H), 2.73 − 2.61 (m, 2.8H + 2H), 2.47 − 2.45 (m, 1H), 2.43 (s, 4.2H + 3H), 2.40 − 2.36 (m, 1.4H), 2.27 − 2.20 (m, 1.4H), 2.16 − 2.09 (m, 1H), 1.18 (d, J = 7.4 Hz, 3H), 1.11 (d, J = 7.2 Hz, 4.2H). 13C NMR (100 MHz, CDCl3) δ 211.1, 208.6, 144.39, 144.38, 134.82, 134.78, 130.8, 130.5, 130.2, 127.2, 127.1, 125.9, 125.8, 125.2, 109.6, 109.3, 48.9, 48.6, 44.2, 43.6, 42.4, 39.7, 34.9, 33.9, 21.7, 19.3, 15.3. IR (neat): 1717, 1353, 1235, 1186, 1168, 1101, 1030, 1008 cm⁻¹. HRMS (ESI): calcd. for C17H19NaNO3S ([M+Na]+): 340.0978, found 340.0985.

Run 1: Following general procedure C, 29.2 mg 2d was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1 then 5:1), 4.8 mg 4d was obtained in 16% yield and 24.1 mg 3d was obtained in 75% yield.

Run 2: Following general procedure C, 28.8 mg 2d was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1 then 5:1), 2.4 mg 4d was obtained in 8% yield and 24.0 mg 3d was obtained in 76% yield.
Average yield: 76% 3d, 12 % 4d.
Yellow solid, TLC \( R_t = 0.39 \) (EA/PE = 1/3), m.p. = 141-143 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.69 (d, \( J = 8.2 \) Hz, 2H), 7.33 (d, \( J = 8.2 \) Hz, 2H), 6.73 (d, \( J = 8.1 \) Hz, 1H), 5.45 (d, \( J = 8.1 \) Hz, 1H), 5.41 (t, \( J = 3.9 \) Hz, 1H), 3.55 (d, \( J = 11.2 \) Hz, 1H), 3.02 (dd, \( J = 23.5, 3.9 \) Hz, 1H), 2.93 (dd, \( J = 23.5, 3.9 \) Hz, 1H), 2.68 (d, \( J = 11.2 \) Hz, 1H), 2.43 (s, 3H), 2.27 (s, 2H), 0.95 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 207.4, 144.4, 144.3, 136.3, 135.0, 130.1, 127.2, 124.8, 117.1, 107.8, 54.2, 49.8, 40.1, 37.1, 23.2, 21.7. IR (neat): 1717, 1350, 1163, 1097, 1046, 1007 cm\(^{-1}\). HRMS (ESI): calcd. for C\(_{17}\)H\(_{20}\)NO\(_2\)S ([M+H]\(^{+}\)): 318.1158, found 318.1167.

Run 1: Following general procedure C, 29.8 mg 2e was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1 then 5:1), 19.2 mg 4e was obtained in 64% yield and 11.2 mg 3e was obtained in 34% yield.

Run 2: Following general procedure C, 30.7 mg 2e was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1 then 5:1), 20.4 mg 4e was obtained in 66% yield and 11.0 mg 3e was obtained in 33% yield.

Average yield: 34% 3e, 65% 4e.

Colorless oil, TLC \( R_t = 0.41 \) (EA/PE = 1/3). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.69 (d, \( J = 8.2 \) Hz, 2H), 7.32 (d, \( J = 8.2 \) Hz, 2H), 6.74 (d, \( J = 8.3 \) Hz, 1H), 5.65 (d, \( J = 8.3 \) Hz, 1H), 3.52 (dd, \( J = 11.1, 1.1 \) Hz, 1H), 2.94 (d, \( J = 22.9 \) Hz, 1H), 2.85 (d, \( J = 22.9 \) Hz, 1H), 2.65 (d, \( J = 11.1 \) Hz, 1H), 2.42 (s, 3H), 2.24 (s, 2H), 1.70 (s, 3H), 0.90 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 207.6, 144.3, 134.9, 130.1, 129.0, 127.2, 124.3, 123.4, 104.4, 54.5, 50.2, 45.9, 37.5, 23.2, 21.7, 17.9. IR (neat): 2920, 2851, 1659, 1341, 1162, 1037 cm\(^{-1}\). HRMS (ESI): calcd. for C\(_{18}\)H\(_{22}\)NO\(_2\)S ([M+H]\(^{+}\)): 332.1315, found 332.1324.

Run 1: Following general procedure C, 28.4 mg 2f was used, 3 h. After flash column chromatography on silica gel (eluted with PE/EA 5:1 then 2:1), 11.3 mg 4f was obtained in 40% yield and 12.0 mg 3f was obtained in 39% yield.

Run 2: Following general procedure C, 32.9 mg 2f was used, 3 h. After flash column chromatography on silica gel (eluted with PE/EA 5:1 then 2:1), 10.8 mg 4f was obtained in 33% yield and 14.8 mg 3f was obtained in 41% yield.

Average yield: 40% 3f, 36% 4f.

Colorless oil, TLC \( R_t = 0.15 \) (EA/PE = 1/2). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.69 (d, \( J = 8.1 \) Hz, 2H), 7.33 (d, \( J = 8.1 \) Hz, 2H), 6.70 (d, \( J = 8.0 \) Hz, 1H), 5.67 – 5.55 (m, 1H), 5.48 (d, \( J = 8.0 \) Hz, 1H), 3.85 (d, \( J = 11.6 \) Hz, 1H), 3.44 (d, \( J = 11.3 \) Hz, 1H), 3.32 (d, \( J = 11.3 \) Hz, 1H), 2.96 (s, 2H), 2.67 – 2.52 (m, 2H), 2.43 (s, 3H), 2.07 (d, \( J = 14.7 \) Hz, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 207.0, 144.6, 134.6, 131.9, 130.2, 127.2, 124.6, 120.5, 108.1, 64.5, 49.2, 45.1, 42.7, 40.1, 21.7. IR (neat): 2920,
Run 1: Following general procedure C, 41.5 mg 2g was used, 16 h. After flash column chromatography on silica gel (eluted with PE/EA 5:1), 37.1 mg 3g was obtained in 84% yield.

Run 2: Following general procedure C, 41.6 mg 2g was used, 16 h. After flash column chromatography on silica gel (eluted with PE/EA 5:1), 37.5 mg 3g was obtained in 84% yield.

Average yield: 84%.

Yellow solid, TLC $R_f = 0.56$ (EA/PE = 1/3), m.p. = 115-116 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.68 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 8.2$ Hz, 2H), 6.67 (d, $J = 8.1$ Hz, 1H), 5.59 (t, $J = 3.8$ Hz, 1H), 5.47 (d, $J = 8.1$ Hz, 1H), 3.80 (d, $J = 11.4$ Hz, 2H), 3.40 – 3.24 (m, 2H), 2.99 – 2.85 (m, 2H), 2.60 (d, $J = 11.4$ Hz, 1H), 2.52 (d, $J = 14.9$ Hz, 1H), 2.42 (s, 3H), 2.03 (d, $J = 14.9$ Hz, 1H), 0.82 (s, 9H), -0.05 (s, 3H), -0.06 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 206.3, 144.4, 134.7, 131.7, 130.1, 127.3, 124.3, 120.7, 108.2, 66.5, 49.8, 46.0, 42.6, 40.1, 26.0, 21.7, 18.5, -5.65, -5.70. IR (neat): 1718, 1344, 1253, 1167, 1091, 1043, 1005 cm$^{-1}$. HRMS (ESI): calcd. for C$_{17}$H$_{20}$NO$_4$S ([M+H]$^+$): 334.1108, found 334.1117.

Run 1: Following general procedure C, 32.5 mg 2h was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 10:1 then 3:1), 21.7 mg 4h was obtained in 67% yield and 8.3 mg 3h was obtained in 24% yield.

Run 2: Following general procedure C, 34.2 mg 2h was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 10:1 then 3:1), 19.2 mg 4h was obtained in 56% yield and 10.0 mg 3h was obtained in 27% yield.

Average yield: 26% 3h, 62% 4h.

Colorless oil, TLC $R_f = 0.22$ (EA/PE = 1/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 8.2$ Hz, 2H), 6.74 (d, $J = 8.2$ Hz, 1H), 5.73 (t, $J = 4.0$ Hz, 1H), 5.53 (d, $J = 8.2$ Hz, 1H), 4.32 (d, $J = 11.6$ Hz, 1H), 4.09 – 3.94 (m, 2H), 3.08 (dd, $J = 23.5$, 4.0 Hz, 1H), 3.00 (dd, $J = 23.5$, 4.0 Hz, 1H), 2.70 (d, $J = 11.6$ Hz, 1H), 2.69 (d, $J = 15.0$ Hz, 1H), 2.43 (s, 3H), 2.25 (d, $J = 15.0$ Hz, 1H), 1.16 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 204.9, 170.8, 144.4, 135.0, 130.2, 130.0, 127.3, 125.3, 121.4, 107.5, 62.2, 50.1, 47.5, 46.2, 39.7, 21.7, 14.0. IR (neat): 2924, 1727, 1346, 1252, 1164 cm$^{-1}$. HRMS (ESI): calcd. for C$_{19}$H$_{22}$NO$_5$S ([M+H]$^+$): 376.1213, found 376.1224.
Run 1: Following general procedure C, 35.0 mg 2i was used, 16 h. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 30.2 mg 3i was obtained in 80% yield.
Run 2: Following general procedure C, 35.1 mg 2i was used, 16 h. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 29.0 mg 3i was obtained in 77% yield. Average yield: 78%.
Light yellow solid, TLC Rf = 0.29 (EA/PE = 1/3), m.p. = 81-86 ºC. 1H NMR (400 MHz, CDCl3) δ 7.38 (d, J = 8.3 Hz, 2H), 7.17 – 7.10 (m, 5H), 7.10 – 7.04 (m, 2H), 6.71 (d, J = 8.1 Hz, 1H), 5.86 – 5.75 (m, 1H), 5.68 (d, J = 8.1 Hz, 1H), 4.22 (d, J = 11.8 Hz, 1H), 3.09 (d, J = 11.8 Hz, 1H), 2.99 (dd, J = 23.5, 4.8 Hz, 1H), 2.84 – 2.71 (m, 2H), 2.53 (d, J = 14.2 Hz, 1H), 2.38 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 206.4, 143.9, 139.1, 135.2, 134.6, 129.8 (CH2), 128.9 (CH), 127.4 (CH), 126.4 (CH), 126.0 (CH), 119.9 (CH), 108.5 (CH), 54.3 (CH2), 50.8 (CH2). 1H NMR (400 MHz, CDCl3) δ 7.37 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 6.74 (d, J = 8.0 Hz, 1H), 6.62 (d, J = 8.7 Hz, 2H), 5.81 – 5.75 (m, 1H), 5.68 (d, J = 8.0 Hz, 1H), 4.15 (d, J = 11.9 Hz, 1H), 3.74 (s, 3H), 3.10 (d, J = 11.9 Hz, 1H), 2.98 (dd, J = 23.5, 4.7 Hz, 1H), 2.84 – 2.68 (m, 2H), 2.52 (d, J = 14.0 Hz, 1H), 2.39 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 206.6, 158.8, 143.8, 135.5, 134.9, 130.9, 129.7, 127.5, 126.9, 125.9, 119.7, 114.2, 108.6, 55.2, 54.6, 50.8, 44.5, 40.1, 21.6. IR (neat): 1719, 1512, 1343, 1252, 1185, 1163 cm⁻¹. HRMS (ESI): calcd. for C22H21NNaO5S ([M+Na]⁺): 402.1240, found 402.1249.

Run 1: Following general procedure C, 38.3 mg 2j was used, 14 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 4.4 mg 4j was obtained in 11% yield and 32.1 mg 3j was obtained in 78% yield.
Run 2: Following general procedure C, 37.8 mg 2j was used, 14 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 4.0 mg 4j was obtained in 11% yield and 30.7 mg 3j was obtained in 76% yield. Average yield: 77% 3j, 11% 4j.

White solid, TLC Rf = 0.20 (EA/PE = 1/3), m.p. = 65-70 ºC. 1H NMR (400 MHz, CDCl3) δ 7.37 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 6.74 (d, J = 8.0 Hz, 1H), 6.62 (d, J = 8.7 Hz, 2H), 5.81 – 5.75 (m, 1H), 5.68 (d, J = 8.0 Hz, 1H), 4.15 (d, J = 11.9 Hz, 1H), 3.74 (s, 3H), 3.10 (d, J = 11.9 Hz, 1H), 2.98 (dd, J = 23.5, 4.7 Hz, 1H), 2.84 – 2.68 (m, 2H), 2.52 (d, J = 14.0 Hz, 1H), 2.39 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 206.6, 158.8, 143.8, 135.5, 134.9, 130.9, 129.7, 127.5, 126.9, 125.9, 119.7, 114.2, 108.6, 55.2, 54.6, 50.8, 44.5, 40.1, 21.6. IR (neat): 1719, 1512, 1343, 1252, 1185, 1163 cm⁻¹. HRMS (ESI): calcd. for C22H21NNaO5S ([M+Na]⁺): 432.1240, found 432.1249.

Run 1: Following general procedure C, 37.1 mg 2k was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 9.9 mg 4k was obtained in 27% yield and 28.0 mg 3k was obtained in 70% yield.
Run 2: Following general procedure C, 36.5 mg 2k was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 8.2 mg 4k was obtained in 22% yield and 27.7 mg 3k was obtained in 70% yield.
Average yield: 70% 3k, 24% 4k.

White solid, TLC $R_t = 0.27$ (EA/PE = 1/3), m.p. = 66-70 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 (d, $J = 8.2$ Hz, 2H), 7.14 (d, $J = 8.2$ Hz, 2H), 7.06 – 6.94 (m, 2H), 6.85 – 6.69 (m, 3H), 5.85 – 5.77 (m, 1H), 5.69 (d, $J = 8.0$ Hz, 1H), 4.13 (d, $J = 12.1$ Hz, 1H), 3.15 (d, $J = 12.1$ Hz, 1H), 3.00 (dd, $J = 23.5$, 4.7 Hz, 1H), 2.79 – 2.71 (m, 2H), 2.55 (d, $J = 14.1$ Hz, 1H), 2.40 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 206.0, 161.9 (d, $J = 244.9$ Hz), 143.9, 135.3, 134.7 (d, $J = 3.2$ Hz), 134.4, 129.7, 128.1 (d, $J = 8.3$ Hz), 126.7, 126.0, 120.0, 115.5 (d, $J = 21.4$ Hz), 108.2, 54.5, 50.5, 44.6, 40.0, 21.5. IR (neat): 1720, 1509, 1343, 1234, 1161, 1090 cm$^{-1}$. HRMS (ESI): calcd. for C$_{22}$H$_{30}$FN$_2$O$_5$S ([M+Na]$^+$): 420.1040, found 420.1056.

Run 1: Following general procedure C, 40.5 mg 2i was used, 14 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 9.6 mg 4i was obtained in 24% yield and 30.2 mg 3i was obtained in 70% yield.

Run 2: Following general procedure C, 40.8 mg 2i was used, 14 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 12.7 mg 4i was obtained in 31% yield and 28.7 mg 3i was obtained in 66% yield.

Average yield: 68% 3i, 28% 4i.

Light yellow solid, TLC $R_t = 0.24$ (EA/PE = 1/3), m.p. = 187-189 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 – 7.69 (m, 1H), 7.63 – 7.54 (m, 2H), 7.49 – 7.39 (m, 2H), 7.35 (d, $J = 1.4$ Hz, 1H), 7.19 (dd, $J = 8.6$, 2.0 Hz, 1H), 7.14 (d, $J = 8.2$ Hz, 2H), 6.81 (d, $J = 8.0$ Hz, 1H), 6.65 (d, $J = 8.2$ Hz, 2H), 5.97 – 5.86 (m, 1H), 5.80 (d, $J = 8.0$ Hz, 1H), 4.32 (d, $J = 12.3$ Hz, 1H), 3.31 (d, $J = 12.3$ Hz, 1H), 3.07 – 2.91 (m, 2H), 2.74 (dd, $J = 23.6$, 2.8 Hz, 1H), 2.62 (d, $J = 14.3$ Hz, 1H), 2.10 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 206.4, 143.5, 135.6, 135.5, 134.7, 133.2, 132.7, 129.3, 128.9, 128.2, 127.4, 126.4, 126.3, 126.2, 126.1, 126.0, 123.6, 120.2, 108.7, 54.8, 50.3, 45.2, 40.1, 21.5. IR (neat): 1720, 1345, 1163, 1107, 1090 cm$^{-1}$. HRMS (ESI): calcd. for C$_{22}$H$_{30}$FN$_2$O$_5$S ([M+H]$^+$): 430.1471, found 430.1474.

Run 1: Following general procedure C, 35.4 mg 2m was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 10.0 mg 4m was obtained in 28% yield and 22.5 mg 3m was obtained in 59% yield.

Run 2: Following general procedure C, 35.2 mg 2m was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 10.9 mg 4m was obtained in 31% yield and 20.7 mg 3m was obtained in 54% yield.

Average yield: 56% 3m, 30% 4m.

Colorless oil, TLC $R_t = 0.30$ (EA/PE = 1/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J = 8.2$ Hz, 2H), 7.21 (d, $J = 8.2$ Hz, 2H), 7.05 (dd, $J = 5.1$, 1.1 Hz, 1H), 6.80 – 6.70 (m, 2H), 6.69 (dd, $J = 3.6$, 1.1
Hz, 1H), 5.77 – 5.68 (m, 1H), 5.64 (d, J = 8.1 Hz, 1H), 4.13 (d, J = 11.7 Hz, 1H), 3.08 (d, J = 11.7 Hz, 1H), 3.06 – 2.96 (m, 1H), 2.91 (dd, J = 23.7, 3.0 Hz, 1H), 2.79 (d, J = 14.4 Hz, 1H), 2.56 (d, J = 14.4 Hz, 1H), 2.40 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 205.8, 144.5, 144.0, 135.2, 134.8, 129.9, 127.1, 127.0, 125.6, 125.09, 125.07, 119.6, 107.9, 54.9, 51.6, 43.0, 39.9, 21.7. IR (neat): 1721, 1344, 1263, 1161, 1091, 1018 cm⁻¹. HRMS (ESI): calcd. for C20H19NNaO3S2 ([M+Na]+): 408.0699, found 408.0710.
VI. General Procedure and Experimental Details of Rh(I)-Catalyzed Rearrangement of VCPs

**General procedure D:** (10 mol % catalyst)

**Preparation of solution of cationic Rh(I) catalyst:** Anhydrous DCE (2.0 mL) was added to a mixture of $[\text{Rh(CO)}_2\text{Cl}]_2$ (2.0 mg, 5.1 μmol), AgSbF$_6$ (4.1 mg, 11.9 μmol), and dppp (5.0 mg, 12.1 μmol) under nitrogen. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed AgCl precipitated. The supernatant was used in Rh(I)-catalyzed Rearrangement of VCPs as the catalyst precursor.

**General procedure of Rh(I)-catalyzed Rearrangement of VCPs:** Under nitrogen, the above Rh(I)$^+$ solution (2.0 mL) was added to a flame-dried glassware containing 2 (0.1 mmol) and the newly activated 4 Å molecular sieves (0.08 g) at rt. Then the glassware was immersed into an oil bath at 90 º C. The reaction was monitored by TLC. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel to afford 4.

**General procedure E:** (20 mol % catalyst)

**Preparation of solution of cationic Rh(I) catalyst:** Anhydrous DCE (2.0 mL) was added to a mixture of $[\text{Rh(CO)}_2\text{Cl}]_2$ (3.9 mg, 10.0 μmol), AgSbF$_6$ (8.2 mg, 23.9 μmol), and dppp (9.9 mg, 24.0 μmol) under nitrogen. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed AgCl precipitated. The supernatant was used in Rh(I)-catalyzed Rearrangement of VCPs as the catalyst precursor.

**General procedure of Rh(I)-catalyzed Rearrangement of VCPs:** Under nitrogen, the above Rh(I)$^+$ solution (2.0 mL) was added to a flame-dried glassware containing 2 (0.1 mmol) and the newly activated 4 Å molecular sieves (0.08 g) at rt. Then the glassware was immersed into an oil bath at 90 º C. The reaction was monitored by TLC. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel to afford 4.

**Run 1:** Following general procedure E, 27.6 mg 2b was used, 3 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 16.4 mg 4b was obtained in 59% yield.

**Run 2:** Following general procedure E, 28.2 mg 2b was used, 3 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 15.6 mg 4b was obtained in 55% yield.

Average yield: 57%.

Colorless oil, TLC $R_t = 0.38$ (EA/PE = 1/10). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.66 (d, $J = 8.2$ Hz, 2H), 7.29 (d, $J = 8.2$ Hz, 2H), 6.68 (d, $J = 8.0$ Hz, 1H), 5.63 (d, $J = 8.0$ Hz, 1H), 4.18 – 4.04 (m, 1H), 2.71 – 2.58 (m, 1H), 2.57 – 2.46 (m, 1H), 2.41 (s, 3H), 2.39 – 2.27 (m, 1H), 2.25 – 2.14 (m, 1H), 2.12 – 1.95 (m, 1H), 1.67 (s, 3H), 1.24 – 1.19 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.8, 135.3, 132.6, 129.9, 128.8, 127.1, 124.7, 104.1, 50.5, 42.2, 37.4, 28.1, 21.7, 13.8. IR (neat): 2925, 1595, 1351, 1271, 1238, 1167, 1092 cm$^{-1}$. HRMS (ESI): calcd. for C$_{16}$H$_{19}$NaNO$_2$S ($[\text{M+Na}^+]$): 312.1029, found 312.1030.

S32
Run 1: Following general procedure D, 29.9 mg 2d was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 26.1 mg 4d was obtained in 87% yield.
Run 2: Following general procedure D, 28.7 mg 2d was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 26.1 mg 4d was obtained in 91% yield.
Average yield: 89%.
Colorless oil, TLC Rf = 0.43 (EA/PE = 1/10). 1H NMR (400 MHz, CDCl3) δ 7.70 – 7.65 (dm, J = 8.0 Hz, 2H), 7.30 (d, J = 8.1 Hz, 1H), 5.52 (d, J = 8.1 Hz, 1H), 5.34 – 5.25 (m, 1H), 3.85 (d, J = 10.9 Hz, 1H), 2.64 (d, J = 10.9 Hz, 1H), 2.53 – 2.44 (m, 1H), 2.41 (s, 3H), 2.30 – 2.22 (m, 1H), 1.81 – 1.75 (m, 1H), 1.53 – 1.45 (m, 1H), 0.91 (s, 3H).
13C NMR (100 MHz, CDCl3) δ 143.9, 141.1, 135.4, 129.9, 127.1, 125.3, 120.9, 103.6, 55.7, 44.1, 37.3, 30.2, 21.7, 21.5. IR (neat): 2925, 2855, 1725, 1665, 1593, 1493, 1456, 1399, 1342, 1251, 1210, 1165, 1094, 1039, 978, 946 cm⁻¹. HRMS (ESI): calcd. for C16H20NO2S ([M+H]+): 290.1209, found 290.1212.

Run 1: Following general procedure D, 30.0 mg 2e was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 24.7 mg 4e was obtained in 82% yield.
Run 2: Following general procedure D, 29.7 mg 2e was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 24.8 mg 4e was obtained in 84% yield.
Average yield: 83%.
Colorless oil, TLC Rf = 0.45 (EA/PE = 1/10). 1H NMR (400 MHz, CDCl3) δ 7.67 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 6.67 (d, J = 8.1 Hz, 1H), 5.52 (d, J = 8.1 Hz, 1H), 3.81 (d, J = 10.8 Hz, 1H), 2.58 (d, J = 10.8 Hz, 1H), 2.54 – 2.45 (m, 1H), 2.40 (s, 3H), 2.17 – 2.08 (m, 1H), 1.75 – 1.69 (m, 1H), 1.64 (s, 3H), 1.48 – 1.39 (m, 1H), 0.87 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 143.8, 135.5, 133.4, 130.3, 129.8, 127.1, 123.9, 102.2, 55.9, 44.8, 36.2, 35.6, 21.6, 13.8. IR (neat): 2956, 2921, 2852, 1594, 1445, 1403, 1355, 1345, 1305, 1263, 1231, 1185, 1167, 1091, 1065, 1022, 1009, 962, 943 cm⁻¹. HRMS (ESI): calcd. for C17H22NO2S ([M+H]+): 304.1366, found 304.1364.

Run 1: Following general procedure D, 31.3 mg 2f was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 5:1), 27.8 mg 4f was obtained in 89% yield.
Run 2: Following general procedure D, 31.6 mg 2f was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 5:1), 26.4 mg 4f was obtained in 84% yield.
Average yield: 86%.
Colorless oil, TLC Rf = 0.48 (EA/PE = 1/2). 1H NMR (400 MHz, CDCl3) δ 7.71 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 6.70 (d, J = 8.1 Hz, 1H), 5.55 (d, J = 8.1 Hz, 1H), 5.51 – 5.42 (m, 1H), 3.85 (d, J = 10.9 Hz, 1H), 2.64 (d, J = 10.9 Hz, 1H), 2.53 – 2.44 (m, 1H), 2.41 (s, 3H), 2.30 – 2.22 (m, 1H), 1.81 – 1.75 (m, 1H), 1.53 – 1.45 (m, 1H), 0.91 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 143.9, 141.1, 135.4, 129.9, 127.1, 125.3, 120.9, 103.6, 55.7, 44.1, 37.3, 30.2, 21.7, 21.5. IR (neat): 2925, 2855, 1725, 1665, 1593, 1493, 1456, 1399, 1342, 1251, 1210, 1165, 1094, 1039, 978, 946 cm⁻¹. HRMS (ESI): calcd. for C17H22NO2S ([M+H]+): 304.1366, found 304.1364.
4.19 (d, J = 11.5 Hz, 1H), 3.38 (dd, J = 11.3, 1.5 Hz, 1H), 3.20 (d, J = 11.3 Hz, 1H), 2.59 (d, J = 11.5 Hz, 1H), 2.51 – 2.45 (m, 2H), 2.43 (s, 3H), 2.35 – 2.23 (m, 1H), 2.24 – 2.14 (m, 1H), 1.44 – 1.30 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.3, 136.9, 135.3, 130.0, 127.2, 125.3, 124.4, 103.8, 62.4, 50.20, 50.17, 32.0, 30.1, 21.7. IR (neat): 2924, 2855, 1345, 1165, 1101, 1034, 1020 cm$^{-1}$. HRMS (ESI): calcd. for C$_{16}$H$_{20}$NO$_3$S ([M+H$^+$]): 306.1158, found 306.1155.

Run 1: Following general procedure D, 41.9 mg 2g was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EtOAc 5:1), 37.2 mg 4g was obtained in 89% yield.
Run 2: Following general procedure D, 42.2 mg 2g was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EtOAc 5:1), 37.5 mg 4g was obtained in 89% yield.
Average yield: 89%.

White solid, TLC $R_f$ = 0.51 (EA/PE = 1/10), m.p. = 115-117 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.68 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 6.66 (d, J = 8.1 Hz, 1H), 5.50 (d, J = 8.1 Hz, 1H), 5.43 – 5.39 (m, 1H), 4.28 (d, J = 10.8 Hz, 1H), 3.35 (dd, J = 9.7, 1.3 Hz, 1H), 3.13 (d, J = 9.7 Hz, 1H), 2.49 (d, J = 10.8 Hz, 1H), 2.46 – 2.36 (m, 1H), 2.41 (s, 3H), 2.28 – 2.16 (m, 2H), 1.36 – 1.25 (m, 1H), 0.89 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.8, 137.0, 135.3, 129.9, 127.2, 125.6, 123.8, 103.6, 62.6, 50.5, 50.3, 32.4, 30.5, 26.0, 21.7, 18.4, -5.3, -5.5. IR (neat): 2954, 2928, 2856, 1638, 1590, 1462, 1397, 1364, 1351, 1276, 1249, 1198, 1169, 1104, 1086, 1021, 1013, 976, 938, 915 cm$^{-1}$. HRMS (ESI): calcd. for C$_{22}$H$_{34}$NO$_3$SSi ([M+H$^+$]): 420.2023, found 420.2037.

Run 1: Following general procedure D, 37.3 mg 2h was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EtOAc 10:1), 31.9 mg 4h was obtained in 86% yield.
Run 2: Following general procedure D, 34.5 mg 2h was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EtOAc 10:1), 28.2 mg 4h was obtained in 82% yield.
Average yield: 84%.

Colorless oil, TLC $R_f$ = 0.14 (EA/PE = 1/10). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.68 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 6.71 (d, J = 8.2 Hz, 1H), 5.67 – 5.46 (m, 2H), 4.58 (d, J = 11.2 Hz, 1H), 4.04 – 3.95 (m, 2H), 2.70 (d, J = 11.2 Hz, 1H), 2.58 – 2.46 (m, 1H), 2.42 (s, 3H), 2.38 – 2.32 (m, 1H), 2.27 (dd, J = 12.9, 6.9 Hz, 1H), 1.75 – 1.63 (m, 1H), 1.18 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.2, 144.0, 135.4, 135.2, 129.9, 127.2, 126.0, 125.7, 103.8, 61.3, 55.5, 52.1, 35.3, 31.2, 21.7, 14.2. IR (neat): 2926, 1727, 1346, 1236, 1164, 1021, 1007 cm$^{-1}$. HRMS (ESI): calcd. for C$_{18}$H$_{22}$NO$_3$S ([M+H$^+$]): 348.1264, found 348.1264.
Run 1: Following general procedure D, 35.7 mg 2i was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 31.1 mg 4i was obtained in 87% yield.
Run 2: Following general procedure D, 35.4 mg 2i was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 29.2 mg 4i was obtained in 82% yield.
Average yield: 84%.
White solid, TLC \(R_f = 0.54\) (EA/PE = 1/5), m.p. = 150-153 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.38 (d, \(J = 8.0\) Hz, 2H), 7.18 – 7.09 (m, 7H), 6.65 (d, \(J = 8.0\) Hz, 1H), 5.73 (d, \(J = 8.0\) Hz, 1H), 5.70 (s, 1H), 4.55 (d, \(J = 11.5\) Hz, 1H), 3.05 (d, \(J = 11.5\) Hz, 1H), 2.38 (s, 3H), 2.29 – 2.19 (m, 2H), 2.14 – 2.03 (m, 1H), 1.94 – 1.83 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.5, 142.5, 138.4, 135.5, 129.7, 128.2, 126.9, 126.6, 126.4, 124.6, 104.1, 55.3, 52.8, 40.1, 30.2, 21.6. IR (neat): 2922, 2849, 1641, 1592, 1511, 1457, 1398, 1284, 1177, 1139, 1124, 1107, 1032, 971 cm\(^{-1}\). HRMS (ESI): calcd. for C\(_{22}\)H\(_{24}\)NO\(_5\) ([M+H]\(^+\)): 352.1366, found 352.1365.

Run 1: Following general procedure D, 38.5 mg 2j was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 32.7 mg 4j was obtained in 85% yield.
Run 2: Following general procedure D, 37.7 mg 2j was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 33.5 mg 4j was obtained in 89% yield.
Average yield: 87%.
Colorless oil, TLC \(R_f = 0.24\) (EA/PE = 1/10). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37 (d, \(J = 8.2\) Hz, 2H), 7.11 (d, \(J = 8.2\) Hz, 2H), 7.02 (d, \(J = 8.7\) Hz, 2H), 6.66 (d, \(J = 8.0\) Hz, 1H), 6.64 (d, \(J = 8.7\) Hz, 2H), 5.72 (d, \(J = 8.0\) Hz, 1H), 4.47 (d, \(J = 8.0\) Hz, 1H), 3.76 (s, 3H), 3.05 (d, \(J = 11.6\) Hz, 1H), 2.38 (s, 3H), 2.27 – 2.18 (m, 2H), 2.08 – 2.01 (m, 1H), 1.89 – 1.80 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 158.2, 143.4, 138.6, 135.7, 134.4, 129.6, 127.7, 126.7, 126.3, 124.4, 113.5, 104.1, 55.6, 55.2, 52.1, 40.1, 30.1, 21.6. IR (neat): 2922, 2849, 1641, 1592, 1511, 1457, 1398, 1343, 1301, 1248, 1163, 1107, 1032, 1004, 971 cm\(^{-1}\). HRMS (ESI): calcd. for C\(_{22}\)H\(_{24}\)NO\(_5\) ([M+H]\(^+\)): 382.1471, found 382.1473.

Run 1: Following general procedure D, 36.9 mg 2k was used, 2 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 28.8 mg 4k was obtained in 78% yield.
Run 2: Following general procedure D, 34.9 mg 2k was used, 2 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 28.7 mg 4k was obtained in 82% yield.
Average yield: 80%.
Colorless oil, TLC \(R_f = 0.40\) (EA/PE = 1/10). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36 (d, \(J = 8.2\) Hz, 2H), 7.11 (d, \(J = 8.2\) Hz, 2H), 7.07 – 7.01 (m, 7H), 6.79 – 6.71 (m, 2H), 6.70 (d, \(J = 8.0\) Hz, 1H), 5.73 (d, \(J = 8.0\) Hz, 1H), 5.71 – 5.66 (m, 1H), 4.44 (d, \(J = 11.8\) Hz, 1H), 3.09 (d, \(J = 11.8\) Hz, 1H), 2.39 (s, 3H), 2.29 – 2.14 (m, 2H), 2.07 – 2.00 (m, 1H), 1.91 – 1.83 (m, 1H). \(^{13}\)C NMR (100 MHz,
CDCl$_3$ δ 161.6 (d, $J = 244.4$ Hz), 143.7, 138.3, 138.1 (d, $J = 3.0$ Hz), 135.7, 129.7, 128.3 (d, $J = 7.9$ Hz), 126.8, 126.5, 124.8, 114.8 (d, $J = 21.0$ Hz), 103.9, 55.6, 52.3, 40.1, 30.1, 21.5. IR (neat): 2924, 2849, 1641, 1590, 1508, 1455, 1397, 1343, 1305, 1227, 1186, 1162, 1112, 1094, 1005, 972 cm$^{-1}$. HRMS (ESI): calcd. for C$_{21}$H$_{21}$FNO$_2$S ([M+H]$^+$): 370.1272, found 370.1279.

Run 1: Following general procedure D, 40.4 mg 2l was used, 2 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 34.6 mg 4l was obtained in 86% yield.

Run 2: Following general procedure D, 39.9 mg 2l was used, 2 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 34.5 mg 4l was obtained in 86% yield.

Average yield: 86%.

White solid, TLC $R_f = 0.38$ (EA/PE = 1/10), m.p. = 63-66 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.76 – 7.72 (m, 1H), 7.64 – 7.60 (m, 1H), 7.56 (d, $J = 8.6$ Hz, 1H), 7.45 – 7.38 (m, 3H), 7.28 (dd, $J = 8.6, 1.9$ Hz, 1H), 7.15 (d, $J = 8.3$ Hz, 2H), 6.74 (d, $J = 8.0$ Hz, 1H), 6.65 (s, 1H), 6.63 (s, 1H), 5.86 (d, $J = 8.0$ Hz, 1H), 5.80 – 5.75 (m, 1H), 4.63 (d, $J = 12.1$ Hz, 1H), 3.27 (d, $J = 12.1$ Hz, 1H), 2.29 – 2.14 (m, 3H), 2.11 (s, 3H), 2.01 – 1.92 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.2, 139.9, 138.3, 135.7, 133.1, 132.4, 129.1, 128.1, 128.0, 127.3, 126.4, 125.8, 125.7, 125.6, 125.1, 125.0, 104.3, 55.9, 53.1, 40.0, 30.2, 21.5. IR (neat): 3091, 2924, 2850, 1915, 1692, 1639, 1594, 1502, 1493, 1454, 1398, 1345, 1303, 1255, 1201, 1165, 1108, 1005, 972 cm$^{-1}$. HRMS (EI): calcd. for C$_{25}$H$_{23}$NO$_2$S (M$^+$): 401.1444, found 401.1443.

Average yield: 84%.

Colorless oil, TLC $R_f = 0.30$ (EA/PE = 1/10). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.52 (d, $J = 8.2$ Hz, 2H), 7.21 (d, $J = 8.2$ Hz, 2H), 7.04 (dd, $J = 4.9, 1.3$ Hz, 1H), 6.79 – 6.72 (m, 2H), 6.67 (d, $J = 8.1$ Hz, 1H), 5.67 (d, $J = 8.1$ Hz, 1H), 5.64 – 5.59 (m, 1H), 4.48 (d, $J = 11.4$ Hz, 1H), 3.01 (d, $J = 11.4$ Hz, 1H), 2.54 – 2.45 (m, 1H), 2.40 (s, 3H), 2.34 – 2.27 (m, 1H), 2.20 – 2.13 (m, 1H), 1.92 – 1.82 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 147.7, 143.7, 139.1, 135.9, 129.8, 127.0, 126.7, 126.1, 124.0, 123.9, 123.6, 103.5, 55.6, 50.6, 40.5, 30.4, 21.7. IR (neat): 3091, 2924, 2850, 1641, 1592, 1493, 1454, 1398, 1345, 1303, 1255, 1201, 1165, 1108, 1005, 972 cm$^{-1}$. HRMS (ESI): calcd. for C$_{19}$H$_{20}$NO$_2$S$_2$ ([M+H]$^+$): 358.0930, found 358.0937.
VII. General Procedure of One-pot Cycloisomerization/[5+1] Reaction Sequence

Preparation of solution of cationic Au(I) catalyst: Anhydrous DCE (1.0 mL) was added to a mixture of Au(JohnPhos)Cl (2.6 mg, 4.9 μmol) and AgSbF$_6$ (2.1 mg, 6.1 μmol) under nitrogen. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed AgCl precipitated. The supernatant was used in Au(I)-catalyzed cycloisomerization reactions as the catalyst precursor.

Preparation of solution of cationic Rh(I) catalyst: Anhydrous DCE (1.0 mL) was added to a mixture of [Rh(CO)$_2$Cl]$_2$ (2.0 mg, 5.1 μmol), AgSbF$_6$ (4.1 mg, 11.9 μmol), and dppp (4.1 mg, 9.9 μmol) under nitrogen. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed AgCl precipitated. The supernatant was used in Rh(I)-catalyzed [5+1] cycloaddition reactions as the catalyst precursor.

One-pot Cycloisomerization/[5+1] Reaction Sequence: Under nitrogen, the above Au(I)$^+$ solution (1.0 mL) and Rh(I)$^+$ solution (1.0 mL) were added to a flame-dried glassware containing 1i (0.1 mmol) at 30 ºC. The reaction was monitored by TLC and stirred for 1 h. Upon completion, the newly activated 4 Å molecular sieves (0.08 g) were added to the reaction mixture, then the reaction mixture was bubbled with a mixed gas of CO/N$_2$ (v/v = 1/4) for 10 min. The glassware was immersed into an oil bath at 90 ºC and reacted under the atmosphere pressure of the mixed gas of CO/N$_2$ (v/v = 1/4). The reaction was monitored by TLC and stirred for 16 h. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel to afford 3i.

Run 1: Following procedure, 34.6 mg 1i was used. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 25.5 mg 3i was obtained in 68% yield.

Run 2: Following procedure, 35.0 mg 1i was used. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 27.2 mg 3i was obtained in 72% yield.

Average yield: 70%.

One-pot Cycloisomerization/[5+1] Reaction Sequence: Under nitrogen, the above Au(I)$^+$ solution (1.0 mL) was added to a flame-dried glassware containing 1i (0.1 mmol) at 30 ºC. The reaction was monitored by TLC and stirred for 1 h. Upon completion, the above Rh(I)$^+$ solution (1.0 mL) and the newly activated 4 Å molecular sieves (0.08 g) were added to the reaction mixture. Then the reaction mixture was bubbled with a mixed gas of CO/N$_2$ (v/v = 1/4) for 10 min. The glassware was immersed into an oil bath at 90 ºC and reacted under the atmosphere pressure of the mixed gas of CO/N$_2$ (v/v = 1/4). The reaction was monitored by TLC and stirred for 16 h. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel to afford 3i.

Run 1: Following procedure, 35.5 mg 1i was used. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 29.6 mg 3i was obtained in 77% yield.
Run 2: Following procedure, 34.9 mg 1i was used. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 27.4 mg 3i was obtained in 73% yield.
Average yield: 75%.
VIII. General Procedure of One-pot Cycloisomerization/Rearrangement Sequence

**Preparation of solution of cationic Au(I) catalyst:** Anhydrous DCE (1.0 mL) was added to a mixture of Au(JohnPhos)Cl (2.6 mg, 4.9 μmol) and AgSbF₆ (2.1 mg, 6.1 μmol) under nitrogen. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed AgCl precipitated. The supernatant was used in Au(I)-catalyzed cycloisomerization reactions as the catalyst precursor.

**Preparation of solution of cationic Rh(I) catalyst:** Anhydrous DCE (1.0 mL) was added to a mixture of [Rh(CO)₂Cl]₂ (2.0 mg, 5.1 μmol), AgSbF₆ (4.1 mg, 11.9 μmol), and dppp (5.0 mg, 12.1 μmol) under nitrogen. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed AgCl precipitated. The supernatant was used in Rh(I)-catalyzed [5+1] cycloaddition reactions as the catalyst precursor.

**One-pot Cycloisomerization/[5+1] Reaction Sequence:** Under nitrogen, the above Au(I)⁺ solution (1.0 mL) and Rh(I)⁺ solution (1.0 mL) were added to a flame-dried glassware containing 1i (0.1 mmol) at 30 °C. The reaction was stirred for 1 h (the cyclopropanation reaction was completed, as monitored by TLC). Then the newly activated 4 Å molecular sieves (0.08 g) were added to the reaction mixture and the glassware was immersed into an oil bath at 90 °C. The reaction was stirred for 1 h (the vinyl-cyclopropane isomerization reaction was completed, as monitored by TLC). The reaction mixture was directly purified by flash column chromatography on silica gel to afford 4i.

Run 1: Following procedure, 35.3 mg 1i was used. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 26.9 mg 4i was obtained in 76% yield.

Run 2: Following procedure, 34.9 mg 1i was used. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 26.1 mg 4i was obtained in 75% yield.

Average yield: 76%.
IX. General Procedure of Pauson-Khand Cycloaddition

Under argon, the solution of 1a (0.1 mmol) in DCE (2.0 mL) was added to a flame-dried glassware containing [Rh(CO)₂Cl]₂ (2.0 mg, 5.0 μmol) at rt. Then the reaction mixture was bubbled with a mixed gas of CO/N₂ (v/v = 1/4) for 10 min. The glassware was immersed into an oil bath at 90 ºC and reacted under the atmosphere pressure of the mixed gas of CO/N₂ (v/v = 1/4). The reaction was monitored by TLC and stirred for 12 h. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel to afford 5a.

Run 1: Following procedure, 28.2 mg 1a was used. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 26.6 mg 5a was obtained in 86% yield.

Run 2: Following procedure, 28.1 mg 1a was used. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 25.4 mg 5a was obtained in 82% yield.

Average yield: 84%.

Colorless oil, TLC Rf = 0.41 (EA/PE = 1/2). ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 6.29 (dd, J = 17.8, 11.3 Hz, 1H), 5.73 (d, J = 17.8 Hz, 1H), 5.44 (d, J = 11.3 Hz, 1H), 4.39 (d, J = 17.0 Hz, 1H), 4.10 – 3.96 (m, 2H), 3.20 – 2.98 (m, 1H), 2.64 (dd, J = 18.0, 6.5 Hz, 1H), 2.59 – 2.49 (m, 1H), 2.42 (s, 3H), 2.09 (dd, J = 18.0, 3.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 205.7, 171.5, 144.3, 134.0, 133.6, 130.1, 127.6, 124.9, 121.6, 52.4, 47.8, 42.1, 40.0, 21.7. IR (neat): 2923, 2853, 1711, 1344, 1306, 1289, 1261, 1120, 1161, 1092, 1047 cm⁻¹. HRMS (ESI): calcd. for C₁₆H₁₈NO₃S ([M+H]+): 304.1002, found 304.0997.
X. General Procedure of Synthetic Transformation

The solution of 3a (38.2 mg, 0.13 mmol) in EA (1.3 mL) was added to flame-dried glassware containing Pd/C (12.0 mg) at rt. Then the reaction mixture was bubbled with 1.0 atm H₂ (balloon) for 10 min. The glassware was immersed into an oil bath at 30 °C and reacted under the 1.0 atm H₂ (balloon). The reaction was monitored by TLC and stirred for 48 h. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel (eluted with PE/EA 3:1) to afford 6a (26.0 mg, 67%, dr = 1.6/1).

Colorless oil, TLC Rf = 0.40 (EA/PE = 1/1). ¹H NMR (400 MHz, CDCl₃) δ 7.67 – 7.56 (m, 3.2H + 2H), 7.35 – 7.28 (m, 3.2H + 2H), 3.87 (ddt, J = 11.6, 4.1, 2.0 Hz, 1.6H), 3.70 (ddd, J = 11.4, 3.8, 1.8 Hz, 1.6H), 3.56 – 3.42 (m, 1H), 3.13 (dd, J = 11.6, 4.4 Hz, 1H), 2.75 – 2.60 (m, 1.6H + 1H), 2.43 (s, 4.8H + 3H), 2.40 – 2.37 (m, 1.6H), 2.37 – 2.17 (m, 4.8H + 4H), 2.01 – 1.92 (m, 5H), 1.90 – 1.62 (m, 8H), 1.46 – 1.35 (m, 3.2H), 1.31 – 1.21 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 211.0, 209.0, 143.8, 133.3, 133.2, 129.83, 129.81, 127.72, 127.66, 51.7, 49.5, 46.5, 45.1, 44.6, 42.1, 41.2, 40.9, 39.4, 37.5, 37.1, 32.3, 32.0, 31.1, 29.0, 25.7, 21.6. IR (neat): 1715, 1340, 1306, 1174, 1092, 1014 cm⁻¹. HRMS (ESI): calcd. for C₁₆H₂₂NO₃S [(M+H)⁺]: 308.1315, found 308.1316.

The solution of 3i (47.2 mg, 0.12 mmol) in EA (1.2 mL) was added to flame-dried glassware containing Pd/C (14.0 mg) at rt. Then the reaction mixture was bubbled with 1.0 atm H₂ (balloon) for 10 min. The glassware was immersed into an oil bath at 30 °C and reacted under the 1.0 atm H₂ (balloon). The reaction was monitored by TLC and stirred for 48 h. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel (eluted with PE/EA 3:1) to afford 6i (31.6 mg, 66%, dr > 20/1).

Colorless oil, TLC Rf = 0.45 (EA/PE = 1/1). ¹H NMR (500 MHz, CDCl₃) δ 7.65 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 7.6 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.28 – 7.21 (m, 1H), 4.10 (d, J = 11.6 Hz, 1H), 4.09 – 4.04 (m, 1H), 2.80 (dd, J = 15.8, 1.3 Hz, 1H), 2.58 (dd, J = 16.9, 5.1 Hz, 1H), 2.50 (dd, J = 11.7, 3.1 Hz, 1H), 2.46 (s, 3H), 2.41 – 2.33 (m, 1H), 2.30 (d, J = 11.6 Hz, 1H), 002.18.
2.11 (d, J = 15.8 Hz, 1H), 1.89 – 1.78 (m, 1H), 1.78 – 1.71 (m, 1H), 1.71 – 1.66 (m, 1H), 1.66 – 1.59 (m, 1H), 1.59 – 1.51 (m, 1H). 13C NMR (125 MHz, CDCl3) δ 209.4, 143.8, 140.9, 132.6, 129.7, 129.1, 128.2, 127.8, 127.0, 57.9, 53.2, 47.0, 43.7, 43.1, 41.0, 27.0, 26.7, 21.5. IR (neat): 2959, 2925, 1468, 1106, 1033, 1021 cm−1. HRMS (ESI): calcd. for C22H26NO3S ([M+H]+): 384.1628, found 384.1629.

NMR analysis of 6i by the DEPT and 2D NMR.

Determination of the stereostructure of 6i by 2D NOESY.

Follow the reported procedure16, 17: To a solution of 6i (40.0 mg, 0.1 mmol) in THF (1 mL) was added KPPb2 (0.6 mL, 0.3 mmol, 0.5 M solution in THF) at 0 °C. The solution was stirred for 18 h at 30 °C. 1M HCl (0.5 mL) was added to the solution at 0 °C and the temperature was raised to rt. The resulting mixture was stirred for 30 min, added with saturated aqueous NaHCO3 (5 mL), extracted with DCM (3×10 mL), dried over Na2SO4, filtered, and concentrated. The crude amine was used without further purification. To the generated amine dissolved in THF (1 mL) was added...
K₂CO₃ (55.0 mg, 0.4 mmol) and allyl bromide (0.035 mL, 0.4 mmol). The solution was stirred at 30 °C for 12 h. Upon completion, the resulting mixture was quenched by water (10 mL) and extracted with ether (3×10 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 5:1) to afford 7i (11.4 mg, 42%, dr > 20:1).

Colorless oil, TLC Rf = 0.36 (EA/PE = 1/5). ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 7.7 Hz, 2H), 7.32 – 7.23 (m, 2H), 7.22 – 7.16 (m, 1H), 5.94 – 5.78 (m, 1H), 5.15 (d, J = 17.5 Hz, 1H), 5.10 (d, J = 10.2 Hz, 1H), 3.15 (d, J = 11.0 Hz, 2H), 3.06 (dd, J = 13.5, 5.7 Hz, 1H), 2.92 (dd, J = 13.5, 6.6 Hz, 1H), 2.76 (d, J = 16.0 Hz, 1H), 2.57 (dd, J = 17.1, 5.2 Hz, 1H), 2.39 (ddd, J = 17.1, 12.1, 7.7 Hz, 1H), 2.25 – 2.09 (m, 2H), 2.01 (d, J = 11.3 Hz, 1H), 1.84 – 1.54 (m, 4H), 1.52 – 1.42 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 211.6, 143.4, 135.6, 130.0, 127.7, 126.5, 117.5, 66.6, 61.8, 54.8, 54.3, 44.7, 43.8, 41.4, 28.2, 26.9. IR (neat): 2939, 2793, 1708, 1498, 1462, 1152 cm⁻¹. HRMS (ESI): calcd. for C₁₈H₂₄NO ([M+H]+): 270.1852, found 270.1849.
XI. References

XII. NMR Spectra
$\text{TsN}$

![Chemical Structure Image]
TsN

Me

1c
S69
2c