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Supporting Information

for

Rh(I)-Catalyzed Intramolecular [3+2] Cycloaddition of

trans-2-Allene-Vinylcyclopropanes

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1. General

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry 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. 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 followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds showed a single spot by analytical TLC.

Tetrahydrofuran, 1,2-dimethoxyethane and toluene were distilled from sodium and benzophenone prior to use. Dioxane, 1,2-dichloroethane and chlorobenzene (SuperDry, with molecular sieves) were purchased from J&K and used directly. Synthetic reagents were purchased from Acros, Aldrich, and Alfa Aesar and used without further purification, unless otherwise indicated.

NMR spectra were measured on Bruker ARX 400 (¹H at 400 MHz, ¹³C at 101 MHz) nuclear magnetic resonance spectrometers. ¹H-NMR spectra are reported relative to Me₄Si (0.00 ppm) or residual solvent signals (C₆D₆: 7.16 ppm). Data for ¹H-NMR spectra are reported as follows: chemical shift (ppm, s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dm = doublet of multiplet, ddd = doublet of doublet of doublet of doublets, tdd = triplet of doublet of doublets, 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: 77.0 ppm, C₆D₆: 128.0 ppm). ¹³C signals are analyzed as follows: (+) = CH3/CH, (-) = CH2, quaternary carbons and other carbons with no attached protons are not marked. The assignment resulted from DEPT-135 °. 2C or 3C in ¹³C-NMR represents the number of carbon atoms. Infrared spectra were recorded on Bruker Tensor 27 fourier transform infrared spectra were recorded on Bruker Tensor 27 fourier transform infrared spectra (HRMS) were recorded on Bruker Apex IV FTMS mass spectrometer (ESI) and ThermoFisher Q Exactive GC GC–MS mass spectrometer (EI).

Abbreviations:

Bs = p-bromobenzenesulfonyl	MS = molecular sieve
COD = 1,5-cyclooctadiene	Ms = methylsulfonyl
COE = cyclooctene	Ns = p-nitrobenzenesulfonyl
DCE = 1,2-dichloroethane	PDC = pyridinium dichromate
DCM = dichloromethane	PE = petroleum ether
DIAD = diisopropyl azodicarboxylate	TBS = t-butyldimethylsilyl
DMF = N,N-dimethylformamide	THF = tetrahydrofuran
DMSO = dimethyl sulphoxide	TLC = thin layer chromatography
EA = ethyl acetate	Ts = p-toluenesulfonyl

2. Synthesis of Substrates

Substrate (1a)



To a stirred solution of $V1a^1$ (196 mg, 2 mmol), tosylamide $A1a^2$ (553 mg, 2.2 mmol), and PPh₃ (1.05 g, 4 mmol) in anhydrous THF (10 mL) was added DIAD (810 mg, 4 mmol) at 0 °C under N₂. The mixture was then stirred for 5 h at room temperature. 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 product **1a** (417 mg, 63%).

1a: white solid, m.p. = 45–48 °C, TLC $R_{\rm f}$ = 0.68 (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 5.31 (ddd, J = 17.1, 10.2, 8.6 Hz, 1H), 4.99 (dd, J = 17.1, 1.6 Hz, 1H), 4.85 (dd, J = 10.2, 1.6 Hz, 1H), 4.76–4.65 (m, 1H), 3.96 (dd, J = 15.1, 6.7 Hz, 1H), 3.85 (dd, J = 15.1, 7.3 Hz, 1H), 3.25 (dd, J = 14.5, 6.5 Hz, 1H), 3.08 (dd, J = 14.5, 7.3 Hz, 1H), 2.41 (s, 3H), 1.65 (s, 3H), 1.65 (s, 3H), 1.32–1.24 (m, 1H), 1.01–0.92 (m, 1H), 0.65–0.60 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 203.3, 143.0, 140.3 (+), 137.8, 129.6 (+, 2C), 127.0 (+, 2C), 112.5 (-), 96.7, 84.4 (+), 49.5 (-), 46.7 (-), 21.7 (+), 21.5 (+), 20.4 (+), 20.3 (+), 18.8 (+), 12.4 (-). HRMS (ESI) calcd for C₁₉H₂₆NO₂S ([M+H]⁺): 332.1679. Found: 332.1685.

Substrate (1b)



To a stirred solution of **V1a** (196 mg, 2 mmol), tosylamide **A1b**³ (552 mg, 2 mmol), and PPh₃ (1.05 g, 4 mmol) in anhydrous THF (10 mL) was added DIAD (808 mg, 4 mmol) at 0 $^{\circ}$ C under N₂. The mixture was then stirred for 6 h at room temperature. 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 product **1b** (451 mg, 63%).

1b: light yellow oil, TLC $R_f = 0.81$ (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 5.31 (ddd, J = 17.1, 10.5, 8.5 Hz, 1H), 4.99 (dd, J = 17.1, 1.5 Hz, 1H), 4.96–4.90 (m, 1H), 4.85 (dd, J = 10.5, 1.5 Hz, 1H), 3.95 (dd, J = 15.0, 6.8 Hz, 1H), 3.88 (dd, J = 15.0, 7.2 Hz, 1H), 3.24 (dd, J = 14.5, 6.7 Hz, 1H), 3.12 (dd, J = 14.5, 7.2 Hz, 1H), 2.41 (s, 3H), 1.98–1.88 (m, 4H), 1.34–1.24 (m, 1H), 1.04–0.99 (m, 1H), 0.99–0.92 (m, 6H), 0.68–0.58 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 201.7, 143.0, 140.2 (+), 137.9, 129.6 (+, 2C), 127.1 (+, 2C), 112.5 (-), 109.7, 88.5 (+), 49.6 (-), 47.2 (-), 25.5 (-), 25.4 (-), 21.8 (+), 21.5 (+), 19.0 (+), 12.6 (-), 12.3 (+, 2C). HRMS (ESI) calcd for C₂₁H₃₀NO₂S ([M+H]⁺): 360.1992. Found: 360.1999.

Substrate (1c)



To a stirred solution of **V1a** (196 mg, 2 mmol), tosylamide $A1c^4$ (641 mg, 2.2 mmol), and PPh₃ (1.05 g, 4 mmol) in anhydrous THF (10 mL) was added DIAD (808 mg, 4 mmol) at 0 °C under N₂. The mixture was then stirred for 6 h at room temperature. 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 product **1c** (493 mg, 66%).

1c: colorless oil, TLC $R_f = 0.63$ (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 5.31 (ddd, J = 17.0, 10.2, 8.6 Hz, 1H), 5.00 (dd, J = 17.0, 1.5 Hz, 1H), 4.85 (dd, J = 10.2, 1.5 Hz, 1H), 4.75–4.66 (m, 1H), 3.97 (dd, J = 15.0, 6.7 Hz, 1H), 3.87 (dd, J = 15.0, 7.3 Hz, 1H), 3.26 (dd, J = 14.4, 6.5 Hz, 1H), 3.08 (dd, J = 14.4, 7.3 Hz, 1H), 2.41 (s, 3H), 2.09–2.01 (m, 4H), 1.59–1.47 (m, 6H), 1.32–1.23 (m, 1H), 1.01–0.91 (m, 1H), 0.66–0.58 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 200.1, 143.0, 140.3 (+), 138.0, 129.6 (+, 2C), 127.1 (+, 2C), 112.5 (-), 103.8, 84.2 (+), 49.4 (-), 46.9 (-), 31.3 (-), 31.2 (-), 27.2 (-), 27.1 (-), 25.9 (-), 21.7 (+), 21.5 (+), 18.8 (+), 12.4 (-). HRMS (ESI) calcd for C₂₂H₃₀NO₂S ([M+H]⁺): 372.1992. Found: 372.1984.

Substrate (1d)



To a stirred solution of **SA1d**⁵ (492 mg, 4 mmol), TsNHBoc (1.29 g, 4.76 mmol), and PPh₃ (2.08 g, 8 mmol) in anhydrous THF (20 mL) was added DIAD (1.60 g, 8 mmol) at 0 °C under N₂. The mixture was then stirred for 5 h at room temperature. 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 intermediate, which was used directly in the following step.

A stirred solution of the above intermediate in DMSO (50 mL) was immersed in a preheated oil bath at 180 $^{\circ}$ C for 20 min. The mixture was cooled to rt and diluted with ether. The solution was washed 5 times with water, and dried over MgSO₄. After removing the solvent, the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 5:1) to afford tosylamide A1d (894 mg, 81%, 2 steps).

A1d: white solid, m.p. = 107–110 °C, TLC $R_{\rm f}$ = 0.34 (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 5.06–4.93 (m, 1H), 4.42 (t, J = 5.4 Hz, 1H), 3.56–3.51 (m, 2H), 2.43 (s, 3H), 2.34–2.25 (m, 4H), 1.70–1.61 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 196.4, 143.4, 137.1, 129.7 (+, 2C), 127.2 (+, 2C), 108.0, 88.1 (+), 42.2 (–), 31.3 (–), 26.9 (–), 21.5 (+). HRMS (ESI) calcd for C₁₅H₂₀NO₂S ([M+H]⁺): 278.1209. Found: 278.1208. To a stirred solution of **V1a** (149 mg, 1.5 mmol), tosylamide **A1d** (458 mg, 1.65 mmol), and PPh₃ (787 mg, 3 mmol) in anhydrous THF (7 mL) was added DIAD (607 mg, 3 mmol) at 0 °C under N₂. The mixture was then stirred for 16 h at room temperature. 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 product **1d** (347 mg, 64%).

1d: light yellow oil, TLC $R_f = 0.59$ (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 5.31 (ddd, J = 17.0, 10.3, 8.6 Hz, 1H), 4.99 (dd, J = 17.0, 1.2 Hz, 1H), 4.85 (dd, J = 10.3, 1.2 Hz, 1H), 4.83–4.75 (m, 1H), 3.98 (dd, J = 15.1, 6.7 Hz, 1H), 3.87 (dd, J = 15.1, 7.3 Hz, 1H), 3.24 (dd, J = 14.3, 6.5 Hz, 1H), 3.07 (dd, J = 14.3, 7.3 Hz, 1H), 2.41 (s, 3H), 2.36–2.25 (m, 4H), 1.71–1.60 (m, 4H), 1.31–1.24 (m, 1H), 1.01–0.92 (m, 1H), 0.65–0.58 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 198.7, 143.0, 140.3 (+), 137.9, 129.6 (+, 2C), 127.1 (+, 2C), 112.5 (-), 105.2, 86.8 (+), 49.5 (-), 46.8 (-), 31.2 (-), 31.1 (-), 27.0 (-, 2C), 21.7 (+), 21.5 (+), 18.9 (+), 12.4 (-). HRMS (ESI) calcd for C₂₁H₂₈NO₂S ([M+H]⁺): 358.1835. Found: 358.1833.

Substrate (1e)



To a stirred solution of **V1a** (150 mg, 1.5 mmol), PPh₃ (472 mg, 1.8 mmol) and imidazole (123 mg, 1.8 mmol) in anhydrous DCM (6 mL) was added I₂ (571 mg, 2.25 mmol) slowly and the resulting mixture was stirred for 1 hour in dark. Saturated aqueous $Na_2S_2O_3$ was added to quench the reaction. The layers were separated, and the aqueous layers were extracted with ether. The combined organic layer was dried over MgSO₄ and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE) and concentrated, which was used directly in the next step.

To a solution of A1e (311 mg, 1 mmol) in DMF (5 mL) was added NaH (60% purity, 72 mg, 1.80 mmol) and stirred at 0 °C for 10 min. Then a solution of the above iodide in DMF (5 mL) was added and the reaction mixture was allowed to slowly warm to rt and stirred for 2 h. Saturated aqueous NH₄Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over MgSO₄, and concentrated. After removing the solvent, the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1 then 10:1) to afford 1e (352 mg, 90%).

1e: light yellow oil, TLC $R_f = 0.59$ (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.74–7.69 (m, 2H), 7.34–7.26 (m, 6H), 7.24–7.19 (m, 1H), 5.29–5.18 (m, 2 H), 4.99–4.89 (m, 1H), 4.86–4.78 (m, 1H), 4.17–3.91 (m, 2H), 3.27 (dd, J = 14.4, 6.6 Hz, 1H), 3.12 (dd, J = 14.4, 7.3 Hz, 1H), 2.41 (s, 3H), 2.08–2.04 (m, 3H), 1.28–1.16 (m, 1H), 0.99–0.90 (m, 1H), 0.62–0.52 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 205.4, 143.1, 140.12 & 140.11 (+), 137.63 & 137.61, 136.3, 129.7 (+, 2C), 128.4 (+, 2C), 127.1 (+, 2C), 127.0 (+), 125.8 (+, 2C), 112.62 & 112.59 (-), 102.2, 88.8 & 88.7 (+), 50.0 & 49.9 (-), 46.3 & 46.2 (-), 21.8 & 21.7 (+), 21.5 (+), 18.85 & 18.79 (+), 17.0 & 16.9 (+), 12.43 & 12.41 (-).HRMS (ESI) calcd for C₂₄H₂₈NO₂S ([M+H]⁺): 394.1835. Found: 394.1840.

Substrate (1f)



To a stirred solution of **V1a** (100 mg, 1 mmol), tosylamide **A1f**³ (227 mg, 0.80 mmol), and PPh₃ (420 mg, 1.6 mmol) in anhydrous THF (5 mL) was added DIAD (325 mg, 1.6 mmol) at 0 °C under N₂. The mixture was then stirred overnight (16 h) at room temperature. 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 product **1f** (260 mg, 89%).

1f: light yellow oil, TLC $R_{\rm f} = 0.58$ (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 8.34 (d, J = 9.0 Hz, 2H), 8.01 (d, J = 9.0 Hz, 2H), 5.30 (ddd, J = 17.1, 10.2, 8.6 Hz, 1H), 5.01 (dd, J = 17.1, 1.1 Hz, 1H), 4.88 (dd, J = 10.2, 1.1 Hz, 1H), 4.75–4.69 (m, 1H), 4.01 (dd, J = 15.2, 6.6 Hz, 1H), 3.91 (dd, J = 15.2, 7.1 Hz, 1H), 3.33 (dd, J = 14.4, 6.4 Hz, 1H), 3.13 (dd, J = 14.4, 7.4 Hz, 1H), 1.66 (s, 3H), 1.65 (s, 3H), 1.35–1.25 (m, 1H), 1.00–0.90 (m, 1H), 0.69–0.62 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 203.5, 149.8, 146.9, 139.8 (+), 128.2 (+, 2C), 124.3 (+, 2C), 113.0 (-), 97.4, 83.9 (+), 49.8 (-), 46.9 (-), 21.9 (+), 20.3 (+), 20.2 (+), 18.7 (+), 12.4 (-). HRMS (ESI) calcd for C₁₈H₂₃N₂O₄S ([M+H]⁺): 363.1373. Found: 363.1379.

Substrate (1g)



To a stirred solution of **V1a** (98 mg, 1 mmol), tosylamide **A1g**³ (346 mg, 1.1 mmol), and PPh₃ (524 g, 2 mmol) in anhydrous THF (5 mL) was added DIAD (406 mg, 2 mmol) at 0 °C under N₂. The mixture was then stirred overnight (16 h) at room temperature. 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 product **1g** (272 mg, 68%).

1g: white solid, m.p. = 37–40 °C, TLC $R_{\rm f}$ = 0.66 (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, *J* = 8.7 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 5.31 (ddd, *J* = 17.0, 10.2, 8.6 Hz, 1H), 5.00 (dd, *J* = 17.0, 1.5 Hz, 1H), 4.87 (dd, *J* = 10.2, 1.5 Hz, 1H), 4.76–4.68 (m, 1H), 3.96 (dd, *J* = 15.1, 6.6 Hz, 1H), 3.86 (dd, *J* = 15.1, 7.2 Hz, 1H), 3.26 (dd, *J* = 14.4, 6.5 Hz, 1H), 3.09 (dd, *J* = 14.4, 7.4 Hz, 1H), 1.66 (s, 3H), 1.65 (s, 3H), 1.33–1.24 (m, 1H), 1.00–0.92 (m, 1H), 0.67–0.61 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 203.4, 140.1, 140.0 (+), 132.3 (+, 2C), 128.6 (+, 2C), 127.2, 112.7 (−), 97.0, 84.2 (+), 49.6 (−), 46.7 (−), 21.8 (+), 20.3 (+), 20.2 (+), 18.8 (+), 12.4 (−). HRMS (ESI) calcd for C₁₈H₂₃BrNO₂S ([M+H]⁺): 396.0627. Found: 396.0626.

Substrate (1h)



To a stirred solution of **V1a** (196 mg, 2 mmol), tosylamide **A1h**³ (522 mg, 2.2 mmol), and PPh₃ (1.05 g, 4 mmol) in anhydrous THF (10 mL) was added DIAD (808 mg, 4 mmol) at 0 $^{\circ}$ C under N₂. The mixture was then stirred for 6 h at room temperature. 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 product **1h** (441 mg, 69%).

1h: light yellow oil, TLC $R_{\rm f} = 0.66$ (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.85–7.79 (m, 2H), 7.58–7.46 (m, 3H), 5.31 (ddd, J = 17.1, 10.2, 8.5 Hz, 1H), 4.99 (dd, J = 17.1, 1.2 Hz, 1H), 4.85 (dd, J = 10.2, 1.2 Hz, 1H), 4.76–4.66 (m, 1H), 3.98 (dd, J = 15.1, 6.7 Hz, 1H), 3.87 (dd, J = 15.1, 7.3 Hz, 1H), 3.27 (dd, J = 14.4, 6.5 Hz, 1H), 3.10 (dd, J = 14.4, 7.3 Hz, 1H), 1.65 (s, 3H), 1.64 (s, 3H), 1.33–1.24 (m, 1H), 1.00–0.91 (m, 1H), 0.66–0.60 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 203.3, 140.9, 140.2 (+), 132.3 (+), 129.0 (+, 2C), 127.0 (+, 2C), 112.6 (-), 96.8, 84.4 (+), 49.6 (-), 46.7 (-), 21.7 (+), 20.4 (+), 20.3 (+), 18.8 (+), 12.4 (-). HRMS (ESI) calcd for C₁₈H₂₄NO₂S ([M+H]⁺): 318.1522. Found: 318.1522.

Substrate (1i)



To a stirred solution of V1a (150 mg, 1.5 mmol) in anhydrous THF (7 mL) was added *n*-BuLi (1.6 M, 1.2 mL, 1.92 mmol) at -78 °C under N₂. The mixture was then stirred for 15 min at -78 °C and MsCl (206 mg, 1.8 mmol) was added. After 5 min, LiBr (651 mg, 7.5 mmol) was added and the mixture was stirred for another 20 min at -78 °C. The solution of bromide product was used in the next step directly.

To a stirred solution of A1i³ (212 mg, 1 mmol) in DMF (5 mL) was added NaH (80 mg, 60% purity, 2 mmol) at 0 $^{\circ}$ C under N₂. After 30 min, the above THF solution of bromide was added at -78 $^{\circ}$ C and the reaction mixture was stirred for 20 h at 60 $^{\circ}$ C. After the completion of this transformation, saturated aqueous NH₄Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over MgSO₄, and concentrated. After removing the solvent, the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford 1i (102 mg, 35%).

1i: yellow oil, TLC $R_f = 0.63$ (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 5.33 (ddd, J = 17.0, 10.2, 8.7 Hz, 1H), 5.00 (dd, J = 17.0, 1.2 Hz, 1H), 4.84 (dd, J = 10.2, 1.4 Hz, 1H), 4.78–4.70 (m, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 2.75–2.60 (m, 2H), 2.00 (dd, J = 14.4, 6.5 Hz, 1H), 1.91 (dd, J = 14.4, 7.3 Hz, 1H), 1.67–1.64 (m, 6H), 1.21–1.12 (m, 1H), 0.72–0.63 (m, 1H), 0.61–0.48 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 203.8, 171.6, 171.5, 141.1 (+), 111.9 (–), 95.2, 82.8 (+), 57.8,

52.4 (+, 2C), 36.0 (-), 32.8 (-), 22.2 (+), 20.5 (+), 20.4 (+), 15.8 (+), 13.2 (-). HRMS (ESI) calcd for C₁₇H₂₅O₄ ([M+H]⁺): 293.1747. Found: 293.1742.

Substrate (1j)



To a stirred solution of $V1j^6$ (174 mg, 1 mmol), tosylamide A1a (278 mg, 1.1 mmol), and PPh₃ (524 g, 2 mmol) in anhydrous THF (5 mL) was added DIAD (405 mg, 2 mmol) at 0 °C under N₂. The mixture was then stirred overnight (16 h) at room temperature. 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 product 1j (163 mg, 40%).

1*j*: colorless oil, TLC $R_f = 0.60$ (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.73–7.68 (m, 2H), 7.29–7.25 (m, 6H), 7.21–7.15 (m, 1H), 6.36 (d, J = 15.8 Hz, 1H), 5.67 (dd, J = 15.8, 8.7 Hz, 1H), 4.78–4.70 (m, 1H), 3.97 (dd, J = 15.0, 6.7 Hz, 1H), 3.88 (dd, J = 15.0, 7.3 Hz, 1H), 3.33 (dd, J = 14.4, 6.3 Hz, 1H), 3.10 (dd, J = 14.4, 7.5 Hz, 1H), 2.39 (s, 3H), 1.69–1.64 (m, 6H), 1.46–1.39 (m, 1H), 1.11–1.03 (m, 1H), 0.77–0.69 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 203.4, 143.0, 137.9, 137.4, 132.4 (+), 129.6 (+, 2C), 128.5 (+, 2C), 128.2 (+), 127.1 (+, 2C), 126.8 (+), 125.6 (+, 2C), 96.7, 84.5 (+), 49.6 (-), 46.8 (-), 21.6 (+), 21.5 (+), 20.4 (+), 20.3 (+), 19.3 (+), 12.9 (-). HRMS (ESI) calcd for C₂₅H₃₀NO₂S ([M+H]⁺): 408.1992. Found: 408.1992.

Substrate (1k)



To a stirred solution of $V1k^7$ (126 mg, 1 mmol), tosylamide A1a (280 mg, 1.1 mmol), and PPh₃ (527 mg, 2 mmol) in anhydrous THF (5 mL) was added DIAD (404 mg, 2 mmol) at 0 °C under N₂. The mixture was then stirred for 11 h at room temperature. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1 then 20:1) to afford product 1k (199 mg, 55%).

1k: colorless oil, TLC $R_f = 0.60$ (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.3 Hz, 2H), 5.45 (dt, J = 15.2, 6.4 Hz, 1H), 4.92 (dd, J = 15.2, 8.3 Hz, 1H), 4.75–4.67 (m, 1H), 3.96 (dd, J = 15.0, 6.7 Hz, 1H), 3.86 (dd, J = 15.0, 7.3 Hz, 1H), 3.22 (dd, J = 14.3, 6.6 Hz, 1H), 3.07 (dd, J = 14.3, 7.2 Hz, 1H), 2.41 (s, 3H), 2.02–1.91 (m, 2H), 1.66–1.63 (m, 6H), 1.23–1.15 (m, 1H), 0.94 (t, J = 7.4 Hz, 3H), 0.91–0.85 (m, 1H), 0.58–0.51 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 203.3, 142.9, 137.9, 130.8 (+), 130.6 (+), 129.6 (+, 2C), 127.1 (+, 2C), 96.6, 84.5 (+), 49.7 (-), 46.7 (-), 25.4 (-), 21.5 (+), 20.6 (+), 20.4 (+), 20.3 (+), 18.5 (+), 13.8 (+), 12.1 (-). HRMS (ESI) calcd for C₂₁H₃₀NO₂S ([M+H]⁺): 360.1992. Found: 360.1990.

Substrate (11)



To a solution of DME (1.17 g, 13 mmol) in DCM (50 mL) was added $ZnEt_2$ (1 M, 20 mL) and $CH_3CHI_2^8$ (11.11g, 39 mmol) successively at 0 °C under N₂. The mixture was then stirred for 30 min at 0 °C and a solution of **SV11**⁹ (2.63g, 13 mmol) in DCM (50 mL) was added. After 16 h, saturated aqueous NH₄Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was dried over Na₂SO₄, and concentrated. The crude product was purified by flash column chromatography (eluted with PE/EA 5:1) to afford cyclopropane product (1.46 g, 49%).

The cyclopropane product (1.46 g, 6.34 mmol) was dissolved in DCM (30 mL), then PDC (2.38 g, 6.34 mmol) and 4 Å MS (1.5 g) were added successively. The resulting mixture was stirred for 2 h at rt. After the accomplishment of the oxidation reaction, the mixture was filtered and the filtrate was concentrated. The crude aldehyde product was purified by flash column chromatography (eluted with PE/EA 20:1) and used in the next step directly.

To a mixture of methyltriphenylphosphonium bromide (4.98 g, 13.9 mmol) and *t*-BuOK (1.42 g, 12.68 mmol) in round bottle was added THF (20 mL) under an argon atmosphere at 0 °C, and the resulting solution was stirred for 30 min at 0 °C. Then a solution of the crude aldehyde product in THF (20 mL) was added dropwise at 0 °C, and the resulting mixture was stirred for 1 h at room temperature. After that, saturated aqueous NH₄Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over MgSO₄, and concentrated. The crude product was purified by flash column chromatography (eluted with PE) to afford **V11** (868 mg, 60% for two steps, d.r. = 1.4:1).

V1I: colorless oil, TLC $R_f = 0.76$ (PE/EA, 10:1). ¹H NMR (400 MHz, CDCl₃): δ 5.56 (ddd, J = 17.1, 10.1, 9.1 Hz, 1H), 5.44 (ddd, J = 17.0, 10.3, 9.1 Hz, 1.4H), 5.09 (dd, J = 17.1, 1.8 Hz, 1H), 5.02–4.95 (m, 1H+1.4H), 4.82 (dd, J = 10.3, 1.6 Hz, 1.4H), 3.83 (dd, J = 11.0, 5.9 Hz, 1.4H), 3.63 (dd, J = 10.9, 5.7 Hz, 1H), 3.55–3.47 (m, 1H+1.4H), 1.41–1.33 (m, 1H), 1.17–1.09 (m, 1.4H), 1.12 (d, J = 5.8 Hz, 3×1.4H), 1.07 (d, J = 6.2 Hz, 3H), 1.02–0.93 (m, 1H+2×1.4H), 0.90 (s, 9×1.4H), 0.89 (s, 9H), 0.86–0.81 (m, 1H), 0.06 (s, 3×1.4H), 0.06 (s, 3×1.4H), 0.04 (s, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 141.4 & 137.4 (+), 114.1 & 111.3 (–), 65.7 & 62.2 (–), 29.9 & 28.4 (+), 27.5 & 25.1 (+), 25.97 & 25.95 (+, 3C), 19.4 & 17.8 (+), 18.35 & 18.34, 13.2 & 12.4 (+), -5.10 & -5.19 & -5.12 (+, 2C, -5.10 & -5.19 belong to one isomer and -5.12 belongs to another). HRMS (EI) calcd for C₉H₁₇OSi ([M-C(CH₃)₃]⁺): 169.1043. Found: 169.1042.

V11 (860 mg, 3.8 mmol) was dissolved in THF (8 mL) and Et_3N 3HF (702 mg, 4.35 mmol) was added. The resulting solution was stirred for 15 h at rt. After removing the solvent, the crude

product was purified by flash column chromatography on silica gel (eluted with PE/Et_2O 3:1 then 1:1) to afford alcohol (373 mg, 88%).

To a stirred solution of the above alcohol (112 mg, 1 mmol), tosylamide **A1a** (276 mg, 1.1 mmol), and PPh₃ (523 mg, 2 mmol) in anhydrous THF (5 mL) was added DIAD (406 mg, 2 mmol) at 0 $^{\circ}$ C under N₂. The mixture was then stirred for 5 h at room temperature. 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 product **11** (219 mg, 63%, d.r. = 1.4:1).

11: light yellow oil, TLC $R_{\rm f} = 0.78$ (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.74–7.66 (m, 2H+2×1.4H), 7.31–7.26 (m, 2H+2×1.4H), 5.47 (ddd, J = 17.1, 10.2, 8.9 Hz, 1H), 5.33 (ddd, J = 17.1, 10.3, 8.0 Hz, 1.4H), 5.04 (dd, J = 17.1, 1.5 Hz, 1H), 4.98 (dd, J = 10.2, 1.5 Hz, 1H), 4.93 (dd, J = 17.1, 1.5 Hz, 1.4H), 4.82 (dd, J = 10.3, 1.5 Hz, 1.4H), 4.75–4.61 (m, 1H+1.4H), 4.02–3.78 (m, 2H+2×1.4H), 3.52 (dd, J = 14.3, 4.7 Hz, 1.4H), 3.22 (dd, J = 14.3, 6.9 Hz, 1H), 3.17–3.05 (m, 1H+1.4H), 2.41 (s, 3H+3×1.4H), 1.69–1.60 (m, 6H+6×1.4H), 1.35–1.28 (m, 1H), 1.14–1.04 (m, 3×1.4H), 1.01 (d, J = 6.3 Hz, 3H), 0.99–0.85 (m, 1H+3×1.4H), 0.77–0.69 (m, 1H). ¹³C NMR (101 MHz, CDCl₃): δ 203.22 & 203.18, 142.9, 140.7 & 136.4 (+), 137.90 & 137.89, 129.61 & 129.60 (+, 2C), 127.09 & 127.06 (+, 2C), 114.8 & 111.9 (-), 96.63 & 96.59, 84.5 (+), 49.5 & 46.3 (-), 46.6 & 44.9 (-), 29.8 (+), 26.6 & 25.7 (+), 23.2 & 21.5 (+), 20.44 & 20.36 (+), 20.29 & 20.26 (+), 19.0 & 18.9 (+), 12.9 & 12.6 (+). HRMS (ESI) calcd for C₂₀H₂₈NO₂S ([M+H]⁺): 346.1835. Found: 346.1834.

3 [3+2] Cycloaddition



General procedure: To a mixture of Rh(CO)(PMe₃)₂Cl¹⁰ (3.2 mg, 0.01 mmol, 5 mol%) and AgOTf (2.6 mg, 0.01 mmol, 5 mol%) was added DCE (2 mL) and stirred at room temperature under argon for 5 min. A solution of substrate **1** (0.2 mmol) in DCE (2 mL) was added at room temperature, and the resulting solution was immersed into an oil bath and was stirred at 80 °C. After 20 h or 18 h, the reaction mixture was cooled to room temperature and concentrated. The crude product was purified by flash column chromatography on silica gel to afford the corresponding [3+2] cycloadduct **2**.

Product (2a)



Reaction time: 20 h. Eluted with PE/EA 20:1

Run 1: 67.5 mg **1a** was converted to 49.8 mg **2a**, yield 74%. Run 2: 66.7 mg **1a** was converted to 48.1 mg **2a**, yield 72%. So the average yield of two runs was 73%.

2a: white solid, m.p. = 99–102 °C, TLC $R_{\rm f}$ = 0.59 (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 5.65 (ddd, J = 17.0, 10.2, 6.3 Hz, 1H), 4.90 (m, 1H), 4.83 (m, 1H), 3.53–3.43 (m, 1H), 3.34–3.25 (m, 1H), 3.24–3.14 (m, 2H), 3.14–3.05 (m, 1H), 2.95 (dd, J = 9.5, 7.3 Hz, 1H), 2.71–2.58 (m, 1H), 2.44 (s, 3H), 1.69 (dd, J = 12.5, 6.9 Hz, 1H), 1.62 (s, 3H), 1.58 (s, 3H), 1.56–1.48 (m, 1H). ¹³C NMR (101 MHz, CDCl₃): δ 143.3, 139.7 (+), 138.1, 133.2, 129.5 (+, 2C), 127.6 (+, 2C), 127.4, 112.9 (–), 52.8 (–), 52.2 (–), 47.1 (+), 45.8 (+), 41.7 (+), 36.8 (–), 22.0 (+), 21.5 (+), 21.0 (+). HRMS (ESI) calcd for C₁₉H₂₆NO₂S ([M+H]⁺): 332.1679. Found: 332.1670.

Product (2b)



Reaction time: 20 h. Eluted with PE/EA 20:1

Run 1: 72.5 mg **1b** was converted to 54.3 mg **2b**, yield 75%. Run 2: 72.6 mg **1b** was converted to 51.5 mg **2b**, yield 71%. So the average yield of two runs was 73%.

2b: white solid, m.p. = 89–92 °C, TLC $R_f = 0.69$ (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 5.68 (ddd, J = 16.6, 10.2, 6.1 Hz, 1H), 4.93–4.80 (m, 2H), 3.59–3.49 (m, 1H), 3.35–3.27 (m, 1H), 3.23–3.17 (m, 2H), 3.15–3.04 (m, 1H),

2.90 (dd, J = 9.5, 7.7 Hz, 1H), 2.68–2.56 (m, 1H), 2.44 (s, 3H), 2.04–1.88 (m, 4H), 1.66 (dd, J = 12.5, 6.8 Hz, 1H), 1.55–1.44 (m, 1H), 0.95 (t, J = 7.5 Hz, 3H), 0.90 (t, J = 7.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 143.3, 140.4 (+), 139.2, 137.1, 133.4, 129.6 (+, 2C), 127.6 (+, 2C), 113.0 (-), 53.1 (-), 52.0 (-), 46.5 (+), 45.4 (+), 41.5 (+), 36.6 (-), 25.3 (-), 24.1 (-), 21.5 (+), 12.9 (+), 12.5 (+). HRMS (ESI) calcd for C₂₁H₃₀NO₂S ([M+H]⁺): 360.1992. Found: 360.2002.

Product (2c)



Reaction time: 20 h. Eluted with PE/EA 20:1

Run 1: 75.0 mg **1c** was converted to 55.0 mg **2c**, yield 73%. Run 2: 75.4 mg **1c** was converted to 55.4 mg **2c**, yield 73%. So the average yield of two runs was 73%.

2c: white solid, m.p. = 128–131 °C, TLC $R_{\rm f}$ = 0.59 (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 5.68 (ddd, J = 16.4, 10.2, 5.9 Hz, 1H), 4.95– 4.80 (m, 2H), 3.52–3.42 (m, 1H), 3.39–3.30 (m, 1H), 3.25–3.18 (m, 1H), 3.18–3.06 (m, 2H), 2.93 (dd, J = 9.5, 7.3 Hz, 1H), 2.66–2.56 (m, 1H), 2.44 (s, 3H), 2.08–1.93 (m, 4H), 1.69 (dd, J = 12.5, 6.9 Hz, 1H), 1.56–1.38 (m, 7H). ¹³C NMR (101 MHz, CDCl₃): δ 143.3, 140.5 (+), 135.5, 134.8, 133.3, 129.6 (+, 2C), 127.7 (+, 2C), 112.8 (–), 53.1 (–), 52.1 (–), 46.2 (+), 45.1 (+), 41.5 (+), 36.5 (–), 32.8 (–), 31.7 (–), 28.0 (–), 27.6 (–), 26.5 (–), 21.5 (+). HRMS (ESI) calcd for C₂₂H₃₀NO₂S ([M+H]⁺): 372.1992. Found: 372.1982.

Product (2d)



Reaction time: 20 h. Eluted with PE/EA 20:1

Run 1: 71.1 mg **1d** was converted to 42.2 mg **2d**, yield 59%. Run 2: 72.3 mg **1d** was converted to 46.1 mg **2d**, yield 64%. So the average yield of two runs was 62%.

2d: white solid, m.p. = 129–132 °C, TLC $R_f = 0.40$ (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 5.62 (ddd, J = 17.1, 10.2, 7.1 Hz, 1H), 4.91– 4.81 (m, 2H), 3.47–3.39 (m, 1H), 3.22–3.11 (m, 3H), 3.08–2.96 (m, 2H), 2.74–2.64 (m, 1H), 2.44 (s, 3H), 2.20–2.02 (m, 4H), 1.76–1.53 (m, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 143.3, 138.9 (+), 138.7, 134.6, 133.1, 129.5 (+, 2C), 127.7 (+, 2C), 112.8 (+), 52.4 (–), 52.3 (–), 48.5 (+), 46.6 (+), 41.9 (+), 37.3 (–), 31.8 (–), 30.7 (–), 26.7 (–), 26.6 (–), 21.5 (+). HRMS (ESI) calcd for C₂₁H₂₈NO₂S ([M+H]⁺): 358.1835. Found: 358.1835.

Product (2e)



Reaction time: 20 h. Eluted with PE/EA 20:1 Run 1: 79.2 mg 1e was converted to 55.8 mg 2e-Z and 2e-E, yield 70%. Run 2: 78.9 mg 1e was converted to 51.7 mg 2e-Z and 2e-E, yield 66%. So the average yield of two runs was 68%. 2e-Z:2e-E = 1.2:1.

Compound 2e-Z and 2e-E were inseparable.

2e-Z and **2e-E**: colorless oil, TLC $R_f = 0.39$ (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.74 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2×1.2H), 7.38–7.21 (m, 5H+4×1.2H), 7.21–7.16 (m, 1.2H), 7.14–7.05 (2H+2×1.2H), 5.76 (ddd, J = 17.1, 10.2, 6.1 Hz, 1.2H), 5.48 (ddd, J = 16.8, 10.2, 6.2 Hz, 1H), 5.07–4.98 (m, 2×1.2H), 4.73 (m, 1H), 4.58 (m, 1H), 3.60–3.51 (m, 1H), 3.50–3.42 (m, 1.2H), 3.31–3.25 (m, 2H), 3.25–3.21 (m, 1H), 3.21–3.14 (m, 2H), 3.14–3.09 (m, 2×1.2H), 3.09–3.01 (m, 1.2H), 2.86–2.78 (m, 1.2H), 2.77–2.67 (m, 1H+1.2H), 2.67–2.58 (m, 1.2H), 2.46 (s, 3H), 2.42 (s, 3×1.2H), 1.95 (s, 3H), 1.90 (s, 3×1.2H), 1.77–1.64 (m, 1H+1.2H), 1.63–1.55 (m, 1H+1.2H). ¹³C NMR (101 MHz, CDCl₃): δ 144.2 (**2e-Z**), 143.6, 143.4, 143.1 (**2e-Z**), 142.0, 140.8 (**2e-Z**), 140.0 (+), 139.2 (+, **2e-Z**), 133.6 (**2e-Z**), 133.3 (**2e-Z**), 132.9, 132.6, 129.6 (+, 2C), 129.4 (+, 2C, **2e-Z**), 128.4 (+, 2C, **2e-Z**), 127.9 (+, 2C), 127.7 (+, 2C), 127.6 (+, 2C), 127.5 (+, 4C, **2e-Z**), 126.5 (+,**2e-Z**), 126.3 (+), 113.4 (-, **2e-Z**), 113.1 (-), 53.0 (-), 52.6 (-, **2e-Z**), 52.2 (-), 52.1 (-, **2e-Z**), 47.4 (+, **2e-Z**), 47.2 (+), 46.0 (+), 45.8 (+, **2e-Z**), 41.8 (+, **2e-Z**), 41.4 (+), 36.6 (-), 36.4 (-, **2e-Z**), 22.9 (+), 22.0 (+, **2e-Z**), 21.5 (+), 21.5 (+, **2e-Z**). HRMS (ESI) calcd for C₂₄H₂₈NO₂S ([M+H]⁺): 394.1835. Found: 394.1824.

Product (2f)



Reaction time: 20 h. Eluted with PE/EA 20:1

Run 1: 72.2 mg **1f** was converted to 57.5 mg **2f**, yield 80%. Run 2: 72.4 mg **1f** was converted to 58.4 mg **2f**, yield 81%. So the average yield of two runs was 80%.

2f: white solid, m.p. = 154–156 °C, TLC $R_{\rm f}$ = 0.47 (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 8.39 (d, J = 8.7 Hz, 2H), 8.01 (d, J = 8.7 Hz, 2H), 5.65 (ddd, J = 17.1, 10.1, 6.2 Hz, 1H), 4.92 (m, 1H), 4.84 (m, 1H), 3.60–3.51 (m, 1H), 3.35–3.28 (m, 1H), 3.28–3.19 (m, 2H), 3.19–3.12 (m, 1H), 2.99 (dd, J = 9.5, 7.5 Hz, 1H), 2.75–2.65 (m, 1H), 1.72 (dd, J = 12.5, 6.9 Hz, 1H), 1.64 (s, 3H), 1.58 (s, 3H), 1.53–1.45 (m, 1H). ¹³C NMR (101 MHz, CDCl₃): δ 150.1, 142.5, 139.3 (+), 137.5, 128.6 (+, 2C), 128.0, 124.3 (+, 2C), 113.3 (–), 52.8 (–), 52.2 (–), 47.0 (–), 45.8 (–), 41.8 (–), 36.8 (–), 22.0 (–), 21.0 (–). HRMS (ESI) calcd for C₁₈H₂₃N₂O₄S ([M+H]⁺): 363.1373. Found: 363.1375.

Product (2g)



Reaction time: 18 h. Eluted with PE/EA 20:1

Run 1: 78.7 mg **1g** was converted to 61.2 mg **2g**, yield 78%. Run 2: 79.2 mg **1g** was converted to 59.7 mg **2g**, yield 75%. So the average yield of two runs was 76%.

2g: white solid, m.p. = 120–122 °C, TLC $R_{\rm f}$ = 0.58 (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.72–7.62 (m, 4H), 5.65 (ddd, J = 17.1, 10.1, 6.3 Hz, 1H), 4.91 (m, 1H), 4.85 (m, 1H), 3.52–3.44 (m, 1H), 3.35–3.26 (m, 1H), 3.26–3.08 (m, 3H), 2.95 (dd, J = 9.5, 7.3 Hz, 1H), 2.73–2.61 (m, 1H), 1.71 (dd, J = 12.5, 7.0 Hz, 1H), 1.63 (s, 3H), 1.58 (s, 3H), 1.55–1.48 (m, 1H). ¹³C NMR (101 MHz, CDCl₃): δ 139.5 (+), 137.9, 135.4, 132.3 (+, 2C), 129.1 (+, 2C), 127.7, 127.6, 113.1 (–), 52.8 (–), 52.2 (–), 47.1 (+), 45.8 (+), 41.8 (+), 36.8 (–), 22.0 (+), 21.0 (+). HRMS (ESI) calcd for C₁₈H₂₃BrNO₂S ([M+H]⁺): 396.0627. Found: 396.0625.

Product (2h)



Reaction time: 20 h. Eluted with PE/EA 20:1

Run 1: 64.7 mg **1h** was converted to 48.5 mg **2h**, yield 75%. Run 2: 63.2 mg **1h** was converted to 48.7 mg **2h**, yield 77%. So the average yield of two runs was 76%.

2h: white solid, m.p. = 84–87 °C, TLC $R_{\rm f}$ = 0.53 (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.86–7.79 (m, 2H), 7.64–7.50 (m, 3H), 5.65 (ddd, J = 17.0, 10.1, 6.3 Hz, 1H), 4.90 (m, 1H), 4.83 (m, 1H), 3.55–3.45 (m, 1H), 3.34–3.25 (m, 1H), 3.25–3.16 (m, 2H), 3.16–3.06 (m, 1H), 2.96 (dd, J = 9.5, 7.3 Hz, 1H), 2.70–2.59 (m, 1H), 1.69 (dd, J = 12.5, 6.9 Hz, 1H), 1.63 (s, 3H), 1.58 (s, 3H), 1.54–1.45 (m, 1H). ¹³C NMR (101 MHz, CDCl₃): δ 139.6 (+), 138.0, 136.3, 132.6 (+), 128.9 (+, 2C), 127.6 (+, 2C), 127.5, 113.0 (–), 52.8 (–), 52.2 (–), 47.1 (+), 45.8 (+), 41.8 (+), 36.8 (–), 22.0 (+), 21.0 (+). HRMS (ESI) calcd for C₁₈H₂₄NO₂S ([M+H]⁺): 318.1522. Found: 318.1516.

Product (2l)



Reaction time: 20 h. Eluted with PE/EA 20:1

Run 1: 69.9 mg **11** was converted to 49.6 mg **21**, yield 71%. Run 2: 69.8 mg **11** was converted to 51.6 mg **21**, yield 74%. So the average yield of two runs was 72%. d.r. = 1.4:1.

The two isomers were inseparable and the configuration of them was not determined.

21: colorless oil, TLC $R_f = 0.66$ (PE/EA, 5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.75–7.66 (m, 2H+2×1.4H), 7.36–7.28 (m, 2H+2×1.4H), 5.62–5.44 (m, 1H+1.4H), 5.00–4.83 (m, 2H+2×1.4H), 3.61–3.52 (m, 1.4H), 3.52–3.44 (m, 1H), 3.29–3.21 (m, 1H+1.4H), 3.21–3.08 (m, 3H+1.4H),

3.08–2.92 (m, 1H+2×1.4H), 2.74–2.64 (m, 2×1.4H), 2.44 (s, 3H), 2.43 (s, 3×1.4H), 2.23–2.14 (m, 1H), 1.79–1.69 (m, 1H+1.4H), 1.62–1.49 (m, 6H+6×1.4H), 0.90–0.76 (m, 3H+3×1.4H). ¹³C NMR (101 MHz, CDCl₃): δ 143.3, 143.2 (major isomer), 141.1 (+, major isomer), 138.5 (major isomer), 138.1, 135.8 (+), 133.4 (major isomer), 133.1, 129.5 (+, 2C), 129.4 (+, 2C, major isomer), 128.0(major isomer), 127.60 (+, 2C), 127.59 (+, 2C, major isomer), 127.4, 114.8 (-), 113.8 (-, major isomer), 54.6 (-, major isomer), 54.4 (+, major isomer), 53.0 (-), 52.7 (+), 50.7 (-), 48.8 (+), 48.4 (-, major isomer), 46.1 (+, major isomer), 45.9 (+, major isomer), 45.7 (+), 41.3 (+, major isomer), 40.8 (+), 22.5 (+, major isomer), 21.9 (+), 21.48 (+), 21.47 (+, major isomer), 21.1 (+, major isomer), 20.7 (+), 14.6 (+, major isomer), 14.3 (+). HRMS (ESI) calcd for C₂₀H₂₈NO₂S ([M+H]⁺): 346.1835. Found: 346.1846.

4. Crystallographic Data



CCDC 1562354

Table 1 Crystal data and structure refinement.

e e	
Identification code	exp_658
Empirical formula	$C_{19}H_{25}NO_2S$
Formula weight	331.46
Temperature/K	180.0(2)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	7.6052(4)
b/Å	13.0656(5)
c/Å	17.5426(9)
$\alpha/^{\circ}$	90
β/°	90
$\gamma^{\prime \circ}$	90
Volume/Å ³	1743.14(14)
Z	4
$\rho_{calc}g/cm^3$	1.263
μ/mm^{-1}	0.195
F(000)	712.0
Crystal size/mm ³	0.15 imes 0.1 imes 0.1
Radiation	MoK α ($\lambda = 0.71073$)
2Θ range for data collection/°	7.636 to 52.032
Index ranges	$-9 \le h \le 9, -16 \le k \le 16, -21 \le l \le 21$
Reflections collected	8514
Independent reflections	3190 [$R_{int} = 0.0315$, $R_{sigma} = 0.0398$]
Data/restraints/parameters	3190/0/211
Goodness-of-fit on F ²	1.031
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0309, wR_2 = 0.0796$
Final R indexes [all data]	$R_1 = 0.0323, wR_2 = 0.0806$
Largest diff. peak/hole / e Å ⁻³	0.15/-0.21
Flack parameter	0.19(4)
	S16

orthogonansed U _{IJ} tensor.							
Atom	x	У	Z.	U(eq)			
S 1	-1018.3(7)	4427.5(4)	6353.5(3)	27.94(15)			
O2	-1726(2)	4526.5(13)	7107.1(10)	35.1(4)			
01	-2052(2)	4728.1(13)	5709.4(11)	40.6(5)			
N1	770(2)	5118.3(14)	6333.4(11)	27.2(4)			
C14	15(3)	2550.9(17)	6863.5(12)	27.4(5)			
C16	440(3)	1071.5(17)	6053.2(13)	26.7(5)			
C13	-407(3)	3132.7(16)	6230.0(12)	25.5(5)			
C15	458(3)	1528.0(17)	6770.3(13)	28.2(5)			
C18	-367(3)	2704.0(17)	5503.7(13)	29.5(5)			
C10	4500(3)	6552.0(17)	7863.7(13)	26.6(5)			
C5	4083(3)	6551.0(15)	7127.7(12)	24.1(4)			
C6	3715(3)	5593.1(16)	6651.2(12)	26.2(4)			
C17	65(3)	1679.0(18)	5420.2(13)	30.1(5)			
C7	2132(3)	4938.2(16)	6920.0(13)	26.0(5)			
C4	3876(3)	7489.3(16)	6620.5(13)	29.9(5)			
C8	5598(4)	7844.8(19)	6269.9(15)	39.0(6)			
C11	4847(3)	7512.8(19)	8311.4(14)	34.2(5)			
C3	2610(4)	7109.8(18)	6000.3(14)	36.4(6)			
C19	786(4)	-61.7(17)	5967.1(15)	35.2(6)			
C12	4646(3)	5582(2)	8324.2(15)	36.0(5)			
C2	3173(4)	5997.2(19)	5853.9(14)	34.1(5)			
C1	1667(4)	5303.0(19)	5604.3(14)	37.8(6)			
C9	7143(4)	7433(2)	6352.3(18)	49.6(7)			

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Table 3 Anisotropic Displacement Parameters (Å²×10³). The Anisotropic displacement factor exponent takes the form: $-2\pi^{2}[h^{2}a^{*2}U_{11}+2hka^{*}b^{*}U_{12}+...]$.

	-		-		
U ₁₁	U_{22}	U ₃₃	U ₂₃	U ₁₃	U ₁₂
27.1(3)	24.9(2)	31.9(3)	-6.3(2)	-5.2(2)	2.3(2)
29.9(8)	34.4(9)	41.1(9)	-12.4(8)	5.6(7)	-0.6(7)
41.3(10)	31.8(9)	48.6(11)	-5.4(8)	-19.1(9)	5.7(8)
29.5(9)	24.8(8)	27.3(9)	-0.8(8)	-3.2(9)	-1.9(7)
30.1(12)	30.9(11)	21.1(10)	-2.6(9)	0.1(9)	-4.3(9)
26.1(11)	23.7(11)	30.3(11)	-1.5(9)	3.3(9)	-6.1(9)
25(1)	23.3(10)	28.4(11)	-2.9(9)	0.2(9)	-1.5(8)
	U ₁₁ 27.1(3) 29.9(8) 41.3(10) 29.5(9) 30.1(12) 26.1(11) 25(1)	U_{11} U_{22} 27.1(3)24.9(2)29.9(8)34.4(9)41.3(10)31.8(9)29.5(9)24.8(8)30.1(12)30.9(11)26.1(11)23.7(11)25(1)23.3(10)	U_{11} U_{22} U_{33} 27.1(3)24.9(2)31.9(3)29.9(8)34.4(9)41.1(9)41.3(10)31.8(9)48.6(11)29.5(9)24.8(8)27.3(9)30.1(12)30.9(11)21.1(10)26.1(11)23.7(11)30.3(11)25(1)23.3(10)28.4(11)	U_{11} U_{22} U_{33} U_{23} 27.1(3)24.9(2) $31.9(3)$ -6.3(2)29.9(8) $34.4(9)$ $41.1(9)$ -12.4(8)41.3(10) $31.8(9)$ $48.6(11)$ -5.4(8)29.5(9)24.8(8)27.3(9)-0.8(8)30.1(12)30.9(11)21.1(10)-2.6(9)26.1(11)23.7(11)30.3(11)-1.5(9)25(1)23.3(10)28.4(11)-2.9(9)	U_{11} U_{22} U_{33} U_{23} U_{13} 27.1(3)24.9(2) $31.9(3)$ $-6.3(2)$ $-5.2(2)$ 29.9(8) $34.4(9)$ $41.1(9)$ $-12.4(8)$ $5.6(7)$ 41.3(10) $31.8(9)$ $48.6(11)$ $-5.4(8)$ $-19.1(9)$ 29.5(9)24.8(8)27.3(9) $-0.8(8)$ $-3.2(9)$ 30.1(12)30.9(11)21.1(10) $-2.6(9)$ $0.1(9)$ 26.1(11)23.7(11) $30.3(11)$ $-1.5(9)$ $3.3(9)$ 25(1)23.3(10) $28.4(11)$ $-2.9(9)$ $0.2(9)$

C15	31.7(12)	27.9(10)	25.0(11)	3.6(9)	-1.9(9)	-6.3(9)
C18	38.6(12)	27.2(11)	22.6(10)	0.6(9)	-3.4(10)	-0.4(10)
C10	22.2(11)	25.4(10)	32.1(11)	1.3(9)	0.9(9)	0.7(9)
C5	23.6(10)	19.1(9)	29.7(10)	0.8(9)	3.3(9)	1.7(9)
C6	25.6(11)	21.7(9)	31.2(11)	-2.8(9)	2.4(9)	2.6(9)
C17	37.9(13)	28.0(11)	24.5(10)	-5.0(9)	1.4(10)	-1.9(10)
C7	27.8(11)	20.9(10)	29.4(11)	0.7(9)	-2.2(10)	0.5(9)
C4	37.9(12)	20.7(10)	31.1(10)	1.8(9)	1.1(11)	2.1(10)
C8	53.1(16)	27.8(11)	36.0(13)	3.5(11)	5.2(12)	-11.2(11)
C11	32.0(12)	34.7(12)	36.0(12)	-4.4(11)	-4.4(11)	0.7(10)
C3	47.4(15)	30.9(12)	30.8(12)	7(1)	-5.3(11)	-2.6(11)
C19	42.4(14)	24.7(11)	38.6(13)	-1.7(10)	-1.4(12)	-3.4(10)
C12	34.7(12)	35.1(12)	38.2(13)	9.3(11)	-7.0(11)	-1.4(11)
C2	43.5(14)	33.1(12)	25.7(11)	-2.7(10)	7.1(11)	-5.3(11)
C1	51.7(15)	36.2(13)	25.6(11)	-4.8(10)	2.5(12)	-8.6(12)
C9	42.6(15)	51.8(16)	54.4(17)	3.8(15)	11.8(15)	-12.5(13)

Table 4 Bond Lengths.

Atom	Length/Å	Atom	Atom	Length/Å
O2	1.4332(18)	C10	C5	1.330(3)
01	1.4314(18)	C10	C11	1.504(3)
N1	1.6328(19)	C10	C12	1.507(3)
C13	1.768(2)	C5	C6	1.531(3)
C7	1.479(3)	C5	C4	1.523(3)
C1	1.469(3)	C6	C7	1.551(3)
C13	1.384(3)	C6	C2	1.551(3)
C15	1.388(3)	C4	C8	1.519(4)
C15	1.392(3)	C4	C3	1.535(3)
C17	1.395(3)	C8	C9	1.301(4)
C19	1.511(3)	C3	C2	1.537(3)
C18	1.392(3)	C2	C1	1.525(4)
C17	1.387(3)			
	Atom O2 O1 N1 C13 C7 C1 C13 C15 C15 C15 C17 C19 C18 C17	AtomLength/ÅO21.4332(18)O11.4314(18)N11.6328(19)C131.768(2)C71.479(3)C11.469(3)C131.384(3)C151.388(3)C171.392(3)C191.511(3)C181.387(3)	AtomLength/ÅAtom $O2$ $1.4332(18)$ $C10$ $O1$ $1.4314(18)$ $C10$ $N1$ $1.6328(19)$ $C10$ $C13$ $1.768(2)$ $C5$ $C7$ $1.479(3)$ $C5$ $C1$ $1.469(3)$ $C6$ $C13$ $1.384(3)$ $C6$ $C15$ $1.388(3)$ $C4$ $C17$ $1.392(3)$ $C4$ $C17$ $1.395(3)$ $C8$ $C19$ $1.511(3)$ $C3$ $C18$ $1.392(3)$ $C2$ $C17$ $1.387(3)$ $C2$	AtomLength/ÅAtomAtom 02 $1.4332(18)$ $C10$ $C5$ 01 $1.4314(18)$ $C10$ $C11$ $N1$ $1.6328(19)$ $C10$ $C12$ $C13$ $1.768(2)$ $C5$ $C6$ $C7$ $1.479(3)$ $C5$ $C4$ $C1$ $1.469(3)$ $C6$ $C7$ $C13$ $1.384(3)$ $C6$ $C2$ $C15$ $1.388(3)$ $C4$ $C8$ $C17$ $1.392(3)$ $C8$ $C9$ $C19$ $1.511(3)$ $C3$ $C2$ $C18$ $1.392(3)$ $C2$ $C1$ $C17$ $1.387(3)$ $C2$ $C1$

Table 5 Bond Angles.

Atom Atom Atom Angle/°				Atom Atom Atom Angle/°				
O2	S 1	N1	106.42(10)	C5	C10	C12	122.5(2)	
O2	S 1	C13	107.34(10)	C11	C10	C12	114.1(2)	

01	S 1	O2	119.82(11)	C10	C5	C6	125.08(19)
01	S 1	N1	106.79(10)	C10	C5	C4	126.24(19)
01	S 1	C13	108.08(10)	C4	C5	C6	108.68(18)
N1	S 1	C13	107.89(10)	C5	C6	C7	115.27(18)
C7	N1	S 1	118.71(14)	C5	C6	C2	105.23(17)
C1	N1	S 1	119.74(15)	C7	C6	C2	104.79(18)
C1	N1	C7	107.88(18)	C18	C17	C16	120.9(2)
C13	C14	C15	119.4(2)	N1	C7	C6	104.14(17)
C15	C16	C17	118.5(2)	C5	C4	C3	102.63(18)
C15	C16	C19	120.5(2)	C8	C4	C5	113.2(2)
C17	C16	C19	120.9(2)	C8	C4	C3	110.64(19)
C14	C13	S 1	119.23(17)	C9	C8	C4	127.4(2)
C14	C13	C18	120.6(2)	C4	C3	C2	104.4(2)
C18	C13	S 1	120.19(17)	C3	C2	C6	104.21(18)
C14	C15	C16	121.1(2)	C1	C2	C6	104.85(19)
C17	C18	C13	119.4(2)	C1	C2	C3	113.7(2)
C5	C10	C11	123.4(2)	N1	C1	C2	101.31(18)

Table 6 Torsion Angles.

Α	B	С	D	Angle/°
S 1	N1	C7	C6	171.48(14)
S 1	N1	C1	C2	177.83(16)
S 1	C13	C18	C17	-178.08(19)
02	S 1	N1	C7	53.48(18)
02	S 1	N1	C1	-170.79(18)
02	S 1	C13	C14	-25.9(2)
02	S 1	C13	C18	153.56(19)
01	S 1	N1	C7	-177.44(16)
01	S 1	N1	C1	-41.7(2)
01	S 1	C13	C14	-156.40(19)
01	S 1	C13	C18	23.0(2)
N1	S 1	C13	C14	88.5(2)
N1	S 1	C13	C18	-92.1(2)
C14	C13	C18	C17	1.3(4)
C13	S 1	N1	C7	-61.46(18)
C13	S 1	N1	C1	74.27(19)
C13	C14	C15	C16	-1.7(4)
C13	C18	C17	C16	0.7(4)
C15	C14	C13	S 1	178.57(18)

Α	B	С	D	Angle/°
C5	C6	C2	C3	-20.1(2)
C5	C6	C2	C1	-139.9(2)
C5	C4	C8	C9	0.9(4)
C5	C4	C3	C2	-37.8(2)
C6	C5	C4	C8	-94.0(2)
C6	C5	C4	C3	25.3(2)
C6	C2	C1	N1	35.9(2)
C17	C16	C15	C14	3.7(4)
C7	N1	C1	C2	-42.2(2)
C7	C6	C2	C3	101.8(2)
C7	C6	C2	C1	-17.9(2)
C4	C5	C6	C7	-118.2(2)
C4	C5	C6	C2	-3.3(2)
C4	C3	C2	C6	36.2(2)
C4	C3	C2	C1	149.8(2)
C8	C4	C3	C2	83.3(2)
C11	C10	C5	C6	-179.9(2)
C11	C10	C5	C4	-0.4(4)
C3	C4	C8	C9	-113.6(3)

C15C14C13C18	-0.9(4)	C3	C2 C1	N1	-77.3(2)
C15C16C17C18	-3.2(4)	C19	C16C15	C14	-175.2(2)
C10C5 C6 C7	61.3(3)	C19	C16C17	C18	175.7(2)
C10C5 C6 C2	176.2(2)	C12	C10C5	C6	-0.5(4)
C10C5 C4 C8	86.5(3)	C12	C10C5	C4	178.9(2)
C10C5 C4 C3	-154.2(2)	C2	C6 C7	N1	-7.0(2)
C5 C6 C7 N1	108.2(2)	C1	N1 C7	C6	31.0(2)

Table 7 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³).

Atom	x	у	Z.	U(eq)
H14	2	2843	7347	33
H15	772	1141	7194	34
H18	-628	3101	5079	35
H6	4776	5170	6613	31
H17	105	1393	4935	36
H7A	2445	4219	6945	31
H7B	1726	5158	7418	31
H4	3335	8049	6909	36
H8	5540	8423	5961	47
H11A	4644	8099	7993	51
H11B	6046	7515	8484	51
H11C	4074	7538	8743	51
H3A	2722	7518	5541	44
H3B	1401	7141	6176	44
H19A	-311	-418	5913	53
H19B	1391	-310	6410	53
H19C	1498	-177	5523	53
H12A	3599	5492	8622	54
H12B	5645	5626	8657	54
H12C	4787	5009	7987	54
H2	4157	5964	5494	41
H1A	900	5643	5242	45
H1B	2099	4671	5383	45
H9A	7279	6854	6655	60
H9B	8113	7718	6109	60

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S27















S34



S35

















S42









S46





S48







S51















S58







S61















