Gold(I)-Catalyzed Ring Expansions of Unactivated Alkynylcyclopropanes to (E)-2-Alkylidene cyclobutanamines in the Presence of Sulfonamides

Siyu Ye and Zhi-Xiang Yu*

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

E-mail: yuzx@pku.edu.cn

Contents

1. General........................................................................................................................................S2
2. Experimental procedures and characterization data ....................................................................S3
   2.1 Synthesis of alkynylcyclopropanes ..................................................................................S3
   2.2 Synthesis of substituted cyclopropylacetylenes S5, S10, and S14.................................S9
   2.3 General procedure for the ring expansion reaction.....................................................S11
3. Effect of substituents on the cyclopropane rings ..................................................................S17
4. $^1$H and $^{13}$C-NMR spectra for new compounds .....................................................................S18
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. Tetrahydrofuran and toluene were distilled from sodium and benzophenone prior to use. 1,2-Dichloroethane was distilled from CaH₂ prior to use. 1,1,2,2-tetrachloroethane was dried over anhydrous K₂CO₃ and distilled prior to use. Dioxane (extra dry, water < 50 ppm) was commercially available and used as received. Synthetic reagents purchased from Acros and Alfa Aesar were used without further purification, unless otherwise indicated. Analytical TLC was performed with 0.25 mm silica gel G plates containing 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 column chromatography on silica gel and the purified compounds show a single spot by analytical TLC.

NMR spectra were measured on Varian Mercury Plus 300 (¹H at 300 MHz, ¹³C at 75 MHz) or Bruker ARX400 (¹H at 400 MHz, ¹³C at 100 MHz) nuclear magnetic resonance spectrometers. Data for ¹H-NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, dt = doublet of triplets, tt = triplet of triplets, 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, d₆-DMSO: 39.5 ppm). Infrared spectra were recorded on an AVATAR 330 Fourier transform spectrometer (FT-IR) with an OMNI sampler and are reported in wavenumbers (cm⁻¹). Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded on Waters micromass GCT (EI, 70 eV) and Bruker APEX IV (ESI) mass spectrometers.

Abbreviations:

THF = tetrahydrofuran
PE = petroleum ether
EA = ethyl acetate
DCE = 1,2-dichloroethane
TCE = 1,1,2,2-tetrachloroethane
DMPU = 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidone
PDC = pyridinium dichromate
m.p. = melting point
2. Experimental procedures and characterization data

2.1 Synthesis of alkynylcyclopropanes

Alkynylcyclopropanes 1a – 1o and 1v – 1x were prepared by following the reported Sonogashira cross-coupling procedures. And 1a, 1b, 1c, and 1e are known compounds. 1t and 1u are also known compounds, which were prepared by following the literature procedures.

General Sonogashira procedure for the preparation of aryl alkynylcyclopropanes: Pd(PPh3)4 (0.10 mmol) and CuI (0.20 mmol) were dissolved in 30 mL dry THF at room temperature under argon atmosphere. Then aryl iodide (10 mmol), (i-Pr)2NH (15 mmol), and cyclopropylacetylene (11 mmol) was added successively. The reaction was stirred at room temperature and a brown precipitate appeared. When TLC indicated the reaction was complete, the reaction mixture was filtered through a thin pad of neutral Al2O3. The filter cake was washed with Et2O and the combined filtrate was concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE) to afford the corresponding alkynylcyclopropane.

1-Chloro-4-cyclopropylethynylbenzene (1a):

\[
\begin{align*}
\text{Cl} &\text{C} &\text{H} &\text{C} &\text{H} \\
&\text{C} &\text{H} &\text{C} &\text{H} \\
\end{align*}
\]

colorless oil, 97% yield.

\(^1\)H NMR (400 MHz, CDCl3): \(\delta\) 7.29 (d, \(J = 8.9\) Hz, 2H), 7.23 (d, \(J = 8.9\) Hz, 2H), 1.43 (tt, \(J = 8.2\) and 5.1 Hz, 1H), 0.90 – 0.84 (m, 2H), 0.82 – 0.78 (m, 2H).

\(^1\)C NMR (100 MHz, CDCl3): \(\delta\) 133.3, 132.8, 128.4, 122.4, 94.5, 74.7, 8.6, 0.1.

FT-IR (neat): \(\nu\) 2925, 2234, 1490, 1362 cm\(^{-1}\).

MS (EI, 70 eV): \(m/z\) (%) 176 (M\(^+\), 74), 141 (100), 113 (14), 99 (2).


1-Cyclopropylethynyl-4-methylbenzene (1c):

\[
\begin{align*}
&\text{C} &\text{H} &\text{C} &\text{H} \\
&\text{C} &\text{H} &\text{C} &\text{H} \\
\end{align*}
\]

colorless oil, 99% yield.

\(^1\)H NMR (400 MHz, CDCl3): \(\delta\) 7.26 (d, \(J = 8.2\) Hz, 2H), 7.06 (d, \(J = 8.2\) Hz, 2H), 2.32 (s, 3H), 1.43 (tt, \(J = 8.2\) and 5.0 Hz, 1H), 0.87 – 0.81 (m, 2H), 0.80 – 0.76 (m, 2H).

\(^1\)C NMR (100 MHz, CDCl3): \(\delta\) 137.4, 131.5, 128.9, 120.8, 92.5, 75.8, 21.4, 8.5, 0.2.

FT-IR (neat): \(\nu\) 3010, 2234, 1511, 1452, 1363 cm\(^{-1}\).

MS (EI, 70 eV): \(m/z\) (%) 156 (M\(^+\), 100), 141 (86), 128 (31), 115 (41), 101 (2), 91 (2).


1-Cyclopropylethynylnaphthalene (1d):

\[
\begin{array}{c}
\text{\includegraphics[width=1cm]{naphthalene.png}}
\end{array}
\]

colorless oil, 79% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.30\) (d, \(J = 8.2\) Hz, 1H), \(7.81\) (d, \(J = 8.2\) Hz, 1H), \(7.75\) (d, \(J = 8.2\) Hz, 1H), \(7.60\) (dd, \(J = 7.1\) and 1.0 Hz, 1H), \(7.56 - 7.46\) (m, 2H), \(7.37\) (dd, \(J = 8.2\) and 7.1 Hz, 1H), \(1.59\) (tt, \(J = 8.2\) and 5.2 Hz, 1H), \(0.97 - 0.89\) (m, 4H).

\(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 133.5, 133.1, 130.0, 128.2, 127.8, 126.4, 126.2, 125.2, 121.6, 98.6, 73.7, 8.9, 0.5\).

FT-IR (neat): \(\nu 3059, 3009, 2224, 1585, 1506, 1398\) cm\(^{-1}\).

MS (EI, 70 eV): \(m/z\) (%) 192 (M\(^+\), 100), 165 (54), 163 (32), 152 (6), 149 (7), 115 (3).


1-Cyclopropylethynyl-4-methoxybenzene (1e):

\[
\begin{array}{c}
\text{\includegraphics[width=1cm]{methoxybenzene.png}}
\end{array}
\]

colorless oil, 91% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.31\) (d, \(J = 9.1\) Hz, 2H), \(6.79\) (d, \(J = 9.1\) Hz, 2H), \(3.79\) (s, 3H), \(1.43\) (tt, \(J = 8.2\) and 5.1 Hz, 1H), \(0.86 - 0.81\) (m, 2H), \(0.79 - 0.75\) (m, 2H).

\(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 159.0, 132.9, 116.0, 113.8, 91.7, 75.5, 55.2, 8.4, 0.1\).

FT-IR (neat): \(\nu 3008, 2837, 2233, 1606, 1509\) cm\(^{-1}\).

MS (EI, 70 eV): \(m/z\) (%) 172 (M\(^+\), 100), 157 (45), 141 (3), 128 (41), 127 (18), 115 (6), 101 (3).


1-Bromo-4-cyclopropylethynylbenzene (1f)

\[
\begin{array}{c}
\text{\includegraphics[width=1cm]{bromo.png}}
\end{array}
\]

colorless oil, 85% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.39\) (d, \(J = 8.8\) Hz, 2H), \(7.22\) (d, \(J = 8.8\) Hz, 2H), \(1.43\) (tt, \(J = 8.4\) and 5.1 Hz, 1H), \(0.90 - 0.83\) (m, 2H), \(0.82 - 0.78\) (m, 2H).

\(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 133.0, 131.4, 122.9, 121.5, 94.7, 74.8, 8.6, 0.1\).

FT-IR (neat): \(\nu 3014, 2234, 1485, 1393, 1361\) cm\(^{-1}\).

MS (EI, 70 eV): \(m/z\) (%) 220 (M\(^+\), 59), 141 (100), 115 (56), 113 (22), 87 (6).


Methyl 4-cyclopropylethynylbenzoate (1g):

\[
\begin{array}{c}
\text{\includegraphics[width=1cm]{methylbenzoate.png}}
\end{array}
\]

white solid, 99% yield, m.p.: 46 – 47 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.93\) (d, \(J = 8.5\) Hz, 2H), \(7.41\) (d, \(J = 8.5\) Hz, 2H), \(3.90\) (s, 3H),
1.47 (tt, $J = 8.3$ and 5.2 Hz, 1H), 0.92 – 0.86 (m, 2H), 0.85 – 0.81 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.6, 131.4, 129.3, 128.8, 128.7, 97.0, 52.1, 8.8, 0.2.

FT-IR (neat): $\nu$ 2950, 2232, 1720, 1605 cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) 200 (M$^+$, 69), 169 (100), 141 (19), 115 (22), 101 (2).

HRMS (EI) calcd for C$_{13}$H$_{12}$O$_2$: 200.0837. Found: 200.0840.

1-Cyclopropylethynyl-4-trifluoromethylbenzene (1h):

![Image](image)

colorless oil, 97% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.52 (d, $J = 8.5$ Hz, 2H), 7.45 (d, $J = 8.5$ Hz, 2H), 1.46 (tt, $J = 8.1$ and 5.2 Hz, 1H), 0.93 – 0.87 (m, 2H), 0.85 – 0.81 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 131.8, 129.1 (q, $J = 32.8$ Hz), 127.8, 125.1 (q, $J = 4.6$ Hz), 124.0 (q, $J = 270.9$ Hz), 96.3, 74.7, 8.7, 0.2.

FT-IR (neat): $\nu$ 2930, 2235, 1615, 1408, 1323 cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) 210 (M$^+$, 100), 191 (8), 182 (12), 141 (56), 115 (12).


4-Cyclopropylethynylbenzonitrile (1i):

![Image](image)

white solid, 99% yield, m.p.: 47 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.55 (d, $J = 8.4$ Hz, 2H), 7.43 (d, $J = 8.4$ Hz, 2H), 1.47 (tt, $J = 8.2$ and 5.0 Hz, 1H), 0.95 – 0.88 (m, 2H), 0.87 – 0.82 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 132.0, 131.8, 129.0, 118.6, 110.6, 98.7, 74.6, 8.8, 0.2.

FT-IR (neat): $\nu$ 3016, 2232, 2222, 1601, 1499 cm$^{-1}$.

HRMS (ESI) calcd for C$_{12}$H$_{10}$N [M+H$^+$]: 168.0808. Found: 168.0806.

1-Cyclopropylethynyl-4-nitrobenzene (1j):

![Image](image)

light yellow solid, 97% yield, m.p.: 56 – 57 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.14 (d, $J = 9.0$ Hz, 2H), 7.48 (d, $J = 9.0$ Hz, 2H), 1.49 (tt, $J = 8.3$ and 5.1 Hz, 1H), 0.97 – 0.92 (m, 2H), 0.89 – 0.84 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.4, 132.1, 131.1, 123.4, 99.9, 74.5, 9.0, 0.3.

FT-IR (neat): $\nu$ 3016, 2930, 2230, 2212, 1594, 1507 cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) 187 (M$^+$, 100), 171 (8), 157 (25), 141 (28), 139 (30), 128 (21), 115 (70).

HRMS (EI) calcd for C$_{11}$H$_9$NO$_2$: 187.0633. Found: 187.0636.
1-Chloro-2-cyclopropylethynylbenzene (1k):

![Chemical structure](image)

colorless oil, 99% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.41–7.39 (m, 1H), 7.36–7.34 (m, 1H), 7.20–7.13 (m, 2H), 1.51 (tt, $J = 8.2$ and 5.1 Hz, 1H), 0.93–0.88 (m, 2H), 0.87–0.83 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 135.7, 133.2, 129.1, 128.4, 126.3, 123.7, 99.2, 72.6, 8.9, 0.3.

FT-IR (neat): $\nu$ 3018, 2232, 1475, 1437 cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) 176 (M$^+$, 100), 141 (97), 115 (39), 113 (22), 99 (2).


1-Chloro-3-cyclopropylethynylbenzene (1l):

![Chemical structure](image)

colorless oil, 99% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.36–7.35 (m, 1H), 7.25–7.16 (m, 3H), 1.44 (tt, $J = 8.2$ and 5.2 Hz, 1H), 0.90–0.84 (m, 2H), 0.82–0.78 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 134.0, 131.5, 129.7, 129.4, 127.7, 125.7, 94.9, 74.5, 8.7, 0.1.

FT-IR (neat): $\nu$ 3011, 2228, 1593, 1560, 1475 cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) 176 (M$^+$, 79), 141 (100), 115 (31), 113 (12), 99 (2).


2-Chloro-4-cyclopropylethynyl-1-methylbenzene (1m):

![Chemical structure](image)

colorless oil, 99% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.35 (d, $J = 1.9$ Hz, 1H), 7.15 (dd, $J = 8.0$ and 1.9 Hz, 1H), 7.09 (d, $J = 8.0$ Hz, 1H), 2.33 (s, 3H), 1.42 (tt, $J = 8.3$ and 5.0 Hz, 1H), 0.88–0.82 (m, 2H), 0.81–0.77 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 135.5, 134.0, 131.9, 130.6, 129.7, 122.9, 93.9, 74.5, 19.9, 8.6, 0.1.

FT-IR (neat): $\nu$ 3012, 2922, 2233, 1548, 1495 cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) 190 (M$^+$, 100), 175 (10), 155 (75), 127 (20), 115 (10), 101 (3).

HRMS (EI) calcd for C$_{12}$H$_{11}$Cl: 190.0549. Found: 190.0551.

4-Bromo-1-cyclopropylethynyl-2-methylbenzene (1n):

![Chemical structure](image)

colorless oil, 98% yield.
\( ^1 \text{H NMR (400 MHz, CDCl}_3\): } \delta 7.31 \text{ (s, 1H), 7.21 (d, } J = 8.3 \text{ Hz, 1H), 7.18 (d, } J = 8.3 \text{ Hz, 1H), 2.35 (s, 3H), 1.47 (tt, } J = 8.2 \text{ and } 5.1 \text{ Hz, 1H), 0.91−0.83 (m, 2H), 0.81−0.77 (m, 2H).} \\
\( ^{13} \text{C NMR (100 MHz, CDCl}_3\): } \delta 142.0, 133.0, 132.2, 128.6, 122.7, 121.2, 98.7, 73.6, 20.5, 8.8, 0.3. \\
\text{FT-IR (neat): } \nu 3009, 2916, 2231, 1587, 1479 \text{ cm}^{-1}. \\
\text{MS (EI, 70 eV): } m/z (\%) 234 (M\textsuperscript{+}, 100), 206 (13), 193 (28), 155 (26), 153 (50), 127 (38), 115 (18), 101 (4), 77 (7). \\
\text{HRMS (EI) calcd for C}_{12}\text{H}_{11}\text{Br: 234.0044. Found: 234.0042.} \\

\text{Methyl 3-chloro-5-cyclopropylethynylbenzoate (1o):} \\

\[
\begin{array}{c}
\text{Cl} \\
\text{MeOC} \\
\end{array}
\]

colorless oil, 99% yield.
\( ^1 \text{H NMR (400 MHz, CDCl}_3\): } \delta 7.90 \text{ (t, } J = 1.5 \text{ Hz, 1H), 7.88 (t, } J = 1.5 \text{ Hz, 1H), 7.51 (t, } J = 1.5 \text{ Hz, 1H), 3.91 (s, 3H), 1.45 (tt, } J = 8.3 \text{ and } 5.1 \text{ Hz, 1H), 0.93−0.86 (m, 2H), 0.84−0.80 (m, 2H).} \\
\( ^{13} \text{C NMR (100 MHz, CDCl}_3\): } \delta 165.3, 135.4, 134.2, 131.7, 130.8, 128.4, 126.0, 96.1, 73.7, 52.4, 8.7, 0.1. \\
\text{FT-IR (neat): } \nu 3013, 2952, 2227, 1728, 1595, 1571, 1439 \text{ cm}^{-1}. \\
\text{HRMS (ESI) calcd for C}_{13}\text{H}_{12}\text{ClO}_2 [M+H\textsuperscript{+}]: 235.0520. Found: 235.0520.} \\

\text{Oct-1-ynylcyclopropane (1p):} \\

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\]

To a solution of cyclopropylacetylene (606 mg, 9.2 mmol) in 10 mL dry THF was added n-BuLi (1.6 M hexane solution, 5.6 mL, 9 mmol) at −78 °C. And then the mixture was warmed to room temperature by removal of the cooling bath. After stirred for 1 h, the solution was cooled to −78 °C again, and DMPU (1.15 g, 9 mmol) and 1-iodohexane (1.27 g, 6 mmol) were added. The resulting mixture was warmed to room temperature and stirred for 3 h. The mixture was quenched with saturated aqueous NH\textsubscript{4}Cl and extracted with Et\textsubscript{2}O. The combined organic phase was washed with water and brine and dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. The solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluted with hexane) to afford 1p as a colorless oil (599 mg, 66%).
\( ^1 \text{H NMR (300 MHz, CDCl}_3\): } \delta 2.11 \text{ (td, } J = 7.0 \text{ and } 1.9 \text{ Hz, 2H), 1.50−1.16 (m, 9H), 0.89 (t, } J = 6.9 \text{ Hz, 3H), 0.73−0.65 (m, 2H), 0.62−0.57 (m, 2H).} \\
\( ^{13} \text{C NMR (75.5 MHz, CDCl}_3\): } \delta 83.1, 75.8, 31.4, 29.1, 28.5, 22.5, 18.7, 14.0, 7.9, -0.5. \\
\text{FT-IR (neat): } \nu 3013, 2956, 2930, 2858, 1467, 1360 \text{ cm}^{-1}. \\
\text{MS (EI, 70 eV): } m/z (\%) 150 (M\textsuperscript{+}, 6), 121 (17), 107 (20), 93 (30), 79 (100). \\
\text{HRMS (EI) calcd for C}_{11}\text{H}_{18}: 150.1409. Found: 150.1411.}
(±)-(1S,2S)-2-butylocyclopropyl]ethynylbenzene (1v):

\[
\begin{align*}
\text{colorless oil, 99% yield.} \\
^1H \text{ NMR (400 MHz, CDCl}_3\text{): } & \delta 7.37–7.35 (m, 2H), 7.26–7.23 (m, 3H), 1.45–1.31 (m, 5H), \\
& 1.27–1.12 (m, 3H), 0.95–0.90 (m, 1H), 0.91 (t, J = 7.1 Hz, 3H), 0.65 (ddd, J = 7.9, 5.9, and 4.4 Hz, 1H). \\
^{13}C \text{ NMR (100 MHz, CDCl}_3\text{): } & \delta 131.5, 128.1, 127.3, 124.1, 93.4, 75.9, 33.4, 31.3, 22.9, 22.4, 15.8, \\
& 14.1, 7.2. \\
\text{FT-IR (neat): } & \nu 2957, 2926, 2857, 2226, 1598, 1491, 1442 \text{ cm}^{-1}. \\
\text{MS (EI, 70 eV): } & m/z (\%) 198 (M^+, 36), 155 (19), 141 (35), 128 (100), 115 (21). \\
\text{HRMS (EI) calcd for C}_{15}H_{18}: 198.1409. Found: 198.1412.
\end{align*}
\]

(±)-(1S,2S)-2-phenylocyclopropyl]ethynylbenzene (1w):

\[
\begin{align*}
\text{colorless oil, 79% yield.} \\
^1H \text{ NMR (400 MHz, CDCl}_3\text{): } & \delta 7.41–7.39 (m, 2H), 7.29–7.25 (m, 5H), 7.22–7.16 (m, 1H), \\
& 7.12–7.10 (m, 2H), 3.36 (ddd, J = 8.9, 6.2, and 4.4 Hz, 1H), 1.70 (ddd, J = 8.4, 5.3, and 4.4 Hz, 1H), \\
& 1.41 (ddd, J = 8.9, 5.3, and 4.4 Hz, 1H), 1.33 (ddd, J = 8.4, 6.2, and 4.4 Hz, 1H). \\
^{13}C \text{ NMR (100 MHz, CDCl}_3\text{): } & \delta 140.7, 131.6, 128.4, 128.2, 127.6, 126.2, 125.9, 123.7, 91.9, 77.03, \\
& 26.6, 18.0, 12.1. \\
\text{FT-IR (neat): } & \nu 3028, 2226, 1598, 1491, 1458, 1441 \text{ cm}^{-1}. \\
\text{MS (EI, 70 eV): } & m/z (\%) 218 (M^+, 62), 217 (61), 203 (38), 202 (100), 141 (13), 115 (12). \\
\text{HRMS (EI) calcd for C}_{17}H_{14}: 218.1096. Found: 218.1099.
\end{align*}
\]

(1R,6S,7r)-7-(phenylethynyl)bicyclo[4.1.0]heptane (1x):

\[
\begin{align*}
\text{white solid, 93% yield, m.p.: 33–35 °C.} \\
^1H \text{ NMR (400 MHz, CDCl}_3\text{): } & \delta 7.36–7.34 (m, 2H), 7.29–7.21 (m, 3H), 1.96–1.87 (m, 2H), \\
& 1.78–1.71 (m, 2H), 1.37–1.35 (m, 2H), 1.31–1.21 (m, 2H), 1.19–1.13 (m, 3H). \\
^{13}C \text{ NMR (100 MHz, CDCl}_3\text{): } & \delta 131.5, 128.1, 127.2, 124.1, 93.6, 76.4, 22.9, 21.8, 21.0, 12.4. \\
\text{FT-IR (neat): } & \nu 2926, 2856, 2223, 1598, 1490, 1447 \text{ cm}^{-1}. \\
\text{MS (EI, 70 eV): } & m/z (\%) 196 (M^+, 90), 167 (100), 153 (48), 141 (53), 128 (95), 115 (66), 91 (27). \\
\text{HRMS (EI) calcd for C}_{15}H_{16}: 196.1252. Found: 196.1255.
\end{align*}
\]
2.2 Synthesis of substituted cyclopropylacetylenes S5, S10, and S14

\[
\begin{align*}
R = \text{Ph} & \quad \text{S6} \\
R = \text{t-Bu} & \quad \text{S1}
\end{align*}
\]

To a solution of ZnEt₂ (1 M hexane solution, 26 mL, 26 mmol) in 100 mL dry CH₂Cl₂ at \(-10 \, ^{\circ}C\) was added dropwise CH₂I₂ (13.0 g, 49 mmol). The resulting solution was stirred at that temperature for 15 min and a white precipitate was formed. Then the alcohol S₁ (2.37 g, 20.7 mmol) and Ti(O(i-Pr))₄ (0.35 g, 1.2 mmol) were added successively. The reaction mixture was warmed to room temperature and stirred over night. The reaction was quenched with saturated aqueous NH₄Cl and extracted with Et₂O. The combined organic phase was washed with brine and dried over anhydrous Na₂SO₄. The solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/AE = 4:1) to afford alcohol S₂ as a colorless oil (2.15 g, 81%).

\[\text{S₂: } \delta \text{ NMR (400 MHz, CDCl₃): } 3.48-3.40 (m, 2H), 1.41-1.20 (m, 7H), 0.89 (t, J = 7.0 Hz, 3H), 0.86-0.80 (m, 1H), 0.63-0.56 (m, 1H), 0.38-0.28 (m, 2H).\]

\[\text{S₂: } \delta \text{ C NMR (100 MHz, CDCl₃): } 67.3, 33.3, 31.8, 22.5, 21.2, 17.2, 14.1, 9.9.\]

To a solution of S₂ (2.15 g, 16.8 mmol) in 60 mL CH₂Cl₂ was added PDC powder (12.6 g, 33.6 mmol). The reaction mixture was stirred at room temperature over night, diluted with 100 mL PE, and stirred for another 1 h. The resulting mixture was filtered through a pad of neutral Al₂O₃, and the filter cake was washed with Et₂O. The combined filtrate was concentrated to afford the crude aldehyde S₃. To a solution of PPh₃ (16.8 g, 64 mmol) in 30 mL CH₂Cl₂ was added a solution of CBr₄ (10.6 g, 32 mmol) in 20 mL CH₂Cl₂ at \(0 \, ^{\circ}C\) under argon. After stirred for 10 min, the crude aldehyde S₃ was added. The resulting mixture was stirred for 30 min at room temperature and diluted with 100 mL PE. The precipitate was removed by filtration through a pad of neutral Al₂O₃ and washed with PE. The combined filtrate was concentrated and purified by flash column chromatography on silica gel (eluted with PE) to afford compound S₄ as a colorless oil (3.28 g, 69%).

\[\text{S₄: } \delta \text{ NMR (400 MHz, CDCl₃): } 5.80 (d, J = 9.4 Hz, 1H), 1.41-1.24 (m, 8H), 0.90 (t, J = 6.9 Hz, 3H), 0.71-0.65 (m, 2H).\]

\[\text{S₄: } \delta \text{ C NMR (100 MHz, CDCl₃): } 142.0, 84.5, 33.2, 31.4, 22.7, 22.4, 21.1, 14.06, 14.04.\]

To a solution of S₄ (3.28 g, 11.6 mmol) in 15 mL dry Et₂O was added \(n\)-BuLi (1.6 M hexane solution, 15 mL, 24 mmol) at \(-78 \, ^{\circ}C\). The reaction mixture was allowed to stir at \(-78 \, ^{\circ}C\) for 1 h and at room temperature for 4 h, and then quenched with water and extracted with Et₂O. The combined organic phase was washed with brine and dried over anhydrous Na₂SO₄. The solvent was evaporated. The crude product was purified by flash column chromatography on silica gel.
(eluted with pentane) to afford alkyne S5 as a colorless oil (0.93 mg, 65%).

S5: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.78 (d, $J = 2.0$ Hz, 1H), 1.43−1.16 (m, 6H), 1.12−1.04 (m, 1H), 0.97−0.92 (m, 1H), 0.90 (t, $J = 7.2$ Hz, 3H), 0.86−0.82 (m, 1H), 0.56 (ddd, $J = 8.3$, 5.9, and 4.3 Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 87.6, 63.5, 33.3, 31.2, 22.5, 22.4, 15.2, 14.1, 6.1.

S6 was converted to S10 following the procedures for the preparation of S5. Compounds S7, S9, and S10 are known compounds.$^3$

S7: colorless oil, 86% yield.
S9: colorless oil, 62% yield.
S10: colorless oil, 77% yield.

**S11**

Alcohol S11 is a known compound$^4$ and was prepared by following the literature procedures. S11 was converted to S14 following the procedures for the preparation of S5.

S13: colorless oil, a 5.6 : 1 mixture of two inseparable diastereomers, 61% yield.

$^1$H NMR (400 MHz, CDCl$_3$): (major isomer) $\delta$ 5.80 (d, $J = 9.4$ Hz, 1H), 1.92−1.84 (m, 2H), 1.74−1.67 (m, 2H), 1.30−1.18 (m, 5H), 1.12−1.09 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): (major isomer) $\delta$ 142.6, 83.8, 28.1, 23.0, 21.2, 20.0.

S14: colorless oil, the major isomer obtained by flash column chromatography on silica gel (eluted with pentane), 59% yield. No attempt was taken to get the minor isomer from the reaction mixture.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.93−1.84 (m, 2H), 1.82 (d, $J = 2.0$ Hz, 1H), 1.73−1.67 (m, 2H), 1.29−1.20 (m, 4H), 1.16−1.07 (m, 2H), 0.94 (td, $J = 4.6$ and 2.0 Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 88.0, 63.8, 22.8, 21.2, 20.9, 11.3.

---


S10
2.3 General procedure for the ring expansion reaction

AuPPh₃Cl (12 mg, 0.025 mmol, 5 mol %) and AgOTf (6 mg, 0.025 mmol, 5 mol %) were mixed in 1 mL dry DCE (or TCE) under argon atmosphere. The mixture was stirred at room temperature (or 80 °C, TCE as solvent) for 30 min with sufficient precipitation of AgCl, and then was added to a solution of alkynylcyclopropane derivative (0.5 mmol) and sulfonamide (0.6 mmol) in 4 mL dry DCE (or TCE). The resulting mixture was heated at the indicated temperature. When TLC indicated the disappearance of the alkynylcyclopropane derivative, the reaction mixture was cooled to room temperature and purified by flash column chromatography on silica gel (eluted with PE to PE/EA = 7:1) to afford the corresponding alkylidenecyclobutyl sulfonamide product. All the products were assigned to have an E-olefinic configuration by compared to product 3h, which was determined by X-ray crystallographic analysis.

(E)-N-[2-(4-Chlorobenzylidene)cyclobutyl]-4-methylbenzenesulfonamide (3a):

![Chemical structure image]

white solid (76% yield, DCE as solvent, 80 °C, 14 h), m.p.: 145 − 146 °C.

1H NMR (400 MHz, CDCl₃): δ 7.81 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.6 Hz, 2H), 7.03 (d, J = 8.6 Hz, 2H), 6.05 − 6.03 (m, 1H), 5.13 (d, J = 9.7 Hz, 1H), 4.63 − 4.54 (m, 1H), 2.68 − 2.62 (m, 2H), 2.43 (s, 3H), 2.33 − 2.25 (m, 1H), 1.84 − 1.74 (m, 1H).

13C NMR (100 MHz, CDCl₃): δ 144.7, 143.6, 138.1, 134.7, 132.4, 129.8, 128.8, 128.5, 127.0, 120.3, 54.5, 29.8, 27.0, 21.5.

FT-IR (neat): ν 3277, 2925, 1598, 1491, 1329 cm⁻¹.


(E)-N-(2-Benzylidenecyclobutyl)-4-methylbenzenesulfonamide (3b):

![Chemical structure image]

white solid (63% yield, DCE as solvent, 80 °C, 6 h), m.p.: 141 − 142 °C.

1H NMR (400 MHz, CDCl₃): δ 7.81 (d, J = 8.2 Hz, 2H), 7.32 − 7.26 (m, 4H), 7.18 (t, J = 7.2 Hz, 1H), 7.11 (d, J = 7.0 Hz, 2H), 6.06 − 6.04 (m, 1H), 5.09 (d, J = 10.2 Hz, 1H), 4.64 − 4.56 (m, 1H), 2.70 − 2.65 (m, 2H), 2.42 (s, 3H), 2.32 − 2.24 (m, 1H), 1.82 − 1.73 (m, 1H).

13C NMR (100 MHz, CDCl₃): δ 143.9, 143.5, 138.2, 136.2, 129.8, 128.4, 127.7, 127.0, 126.9, 121.4, 54.6, 30.0, 27.1, 21.5.

FT-IR (neat): ν 3273, 2923, 1598, 1492, 1334 cm⁻¹.


(E)-4-Methyl-N-[2-(4-methylbenzylidene)cyclobutyl]benzenesulfonamide (3c):

![Chemical structure image]
white solid (46% yield, DCE as solvent, 80 °C, 20 h), m.p.: 144 − 145 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.81 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.1$ Hz, 2H), 7.08 (d, $J = 7.8$ Hz, 2H), 7.01 (d, $J = 7.8$ Hz, 2H), 6.01 − 5.99 (m, 1H), 5.02 (d, $J = 10.1$ Hz, 1H), 4.63 − 4.55 (m, 1H), 2.69 − 2.64 (m, 2H), 2.42 (s, 3H), 2.31 (s, 3H), 2.33 − 2.24 (m, 1H), 1.81 − 1.71 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.5, 142.7, 138.2, 136.6, 133.4, 129.7, 129.1, 127.6, 127.0, 121.2, 54.5, 29.9, 27.1, 21.4, 21.1.

FT-IR (neat): $\nu$ 3288, 2916, 2849, 1667, 1598, 1438 cm$^{-1}$.

HRMS (ESI) calcd for C$_{19}$H$_{21}$NNaO$_2$S [M+Na$^+$]: 350.1185. Found: 350.1181.

$(E)$-4-Methyl-N-[2-(naphthalen-1-ylmethylene)cyclobutyl]benzenesulfonamide (3d):

white solid (14% yield, TCE as solvent, 100 °C, 14 h), m.p. = 140 − 141 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.89 − 7.87 (m, 1H), 7.88 (d, $J = 8.4$ Hz, 2H), 7.82 − 7.79 (m, 1H), 7.70 (d, $J = 8.2$ Hz, 1H), 7.48 − 7.43 (m, 2H), 7.38 (t, $J = 7.6$ Hz, 1H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.26 (d, $J = 7.1$ Hz, 1H), 6.78 − 6.76 (m, 1H), 5.35 (d, $J = 10.2$ Hz, 1H), 4.74 − 4.66 (m, 1H), 2.70 − 2.61 (m, 1H), 2.56 − 2.48 (m, 1H), 2.38 (s, 3H), 2.32 − 2.24 (m, 1H), 1.81 − 1.71 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 145.8, 143.6, 138.2, 133.6, 132.3, 131.2, 129.8, 128.4, 127.4, 127.0, 125.9, 125.7, 125.2, 123.8, 117.7, 54.6, 29.8, 26.8, 21.5.

FT-IR (neat): $\nu$ 3276, 3047, 2948, 1598, 1433 cm$^{-1}$.

HRMS (ESI) calcd for C$_{22}$H$_{21}$NNaO$_2$S [M+Na$^+$]: 386.1185. Found: 386.1185.

(E)-N-[2-(4-Bromobenzylidene)cyclobutyl]-4-methylbenzenesulfonamide (3f):

white solid (66% yield, TCE as solvent, 100 °C, 7 h), m.p. = 143 − 144 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.80 (d, $J = 8.2$ Hz, 2H), 7.38 (d, $J = 8.6$ Hz, 2H), 7.30 (d, $J = 8.2$ Hz, 2H), 6.96 (d, $J = 8.6$ Hz, 2H), 6.03 − 6.01 (m, 1H), 5.23 (d, $J = 10.3$ Hz, 1H), 4.61 − 4.52 (m, 1H), 2.66 − 2.60 (m, 2H), 2.42 (s, 3H), 2.32 − 2.24 (m, 1H), 1.84 − 1.74 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.9, 143.5, 138.1, 135.1, 131.5, 129.7, 129.1, 127.0, 120.5, 120.3, 54.5, 29.7, 27.0, 21.5.

FT-IR (neat): $\nu$ 3210, 2924, 1491, 1434, 1236 cm$^{-1}$.

HRMS (ESI) calcd for C$_{18}$H$_{18}$BrNNaO$_2$S [M+Na$^+$]: 414.0134. Found: 414.0132.

(E)-Methyl 4-[2-(4-methylphenylsulfonamido)cyclobutylidene]methylbenzoate (3g):

white solid (77% yield, TCE as solvent, 100 °C, 7 h), m.p. = 157 − 158 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.92 (d, $J = 8.5$ Hz, 2H), 7.82 (d, $J = 8.2$ Hz, 2H), 7.31 (d, $J = 8.2$ Hz, 2H), 7.26 (d, $J = 8.2$ Hz, 2H), 7.18 (d, $J = 7.8$ Hz, 2H), 6.83 − 6.70 (m, 1H), 5.35 (d, $J = 10.3$ Hz, 1H), 4.61 − 4.52 (m, 1H), 2.66 − 2.60 (m, 2H), 2.42 (s, 3H), 2.32 − 2.24 (m, 1H), 1.84 − 1.74 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.9, 143.5, 138.1, 135.1, 131.5, 129.7, 129.1, 127.0, 120.5, 120.3, 54.5, 29.7, 27.0, 21.5.
Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 6.12—6.10 (m, 1H), 5.36 (d, J = 9.7 Hz, 1H), 4.65—4.57 (m, 1H), 3.89 (s, 3H), 2.73—2.66 (m, 2H), 2.42 (s, 3H), 2.34—2.26 (m, 1H), 1.87—1.77 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.8, 147.3, 143.6, 140.8, 138.1, 129.8, 129.7, 128.1, 127.4, 127.0, 120.6, 54.6, 52.0, 29.6, 27.3, 21.5.

FT-IR (neat): $\nu$ 3255, 2953, 1702, 1609, 1438 cm$^{-1}$.


(E)-4-Methyl-N-[2-(4-trifluoromethylbenzylidene)cyclobutyl]benzene sulfonamide (3h):

white solid (84% yield, TCE as solvent, 100 °C, 13 h), m.p. = 127—128 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.82 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 6.15—6.13 (m, 1H), 5.44 (d, J = 9.9 Hz, 1H), 4.65—4.56 (m, 1H), 2.73—2.65 (m, 2H), 2.41 (s, 3H), 2.33—2.25 (m, 1H), 1.87—1.78 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.1, 143.6, 139.7, 138.0, 129.7, 128.4 (q, $J$ = 32.4 Hz), 127.7, 127.0, 125.2 (q, $J$ = 4.6 Hz), 124.1 (q, $J$ = 272.1 Hz), 120.2, 54.5, 29.5, 27.1, 21.4.

FT-IR (neat): $\nu$ 3270, 2955, 1615, 1438, 1324 cm$^{-1}$.

HRMS (ESI) calcd for C$_{19}$H$_{18}$F$_3$NNaO$_2$S [M+Na$^+$]: 404.0903. Found: 404.0903.

(E)-N-[2-(4-Cyanobenzylidene)cyclobutyl]-4-methylbenzenesulfonamide (3i):

white solid (70% yield, TCE as solvent, 100 °C, 13 h), m.p. = 172—174 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.81 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 6.16—6.14 (m, 1H), 5.26 (d, J = 9.8 Hz, 1H), 4.66—4.58 (m, 1H), 2.75—2.65 (m, 2H), 2.44 (s, 3H), 2.36—2.28 (m, 1H), 1.88—1.78 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.8, 143.7, 140.8, 137.9, 132.2, 129.8, 128.0, 127.0, 120.1, 118.9, 109.9, 54.5, 29.6, 27.3, 21.5.

FT-IR (neat): $\nu$ 3270, 2952, 2225, 1604, 1437 cm$^{-1}$.

HRMS (ESI) calcd for C$_{19}$H$_{18}$N$_2$NaO$_2$S [M+Na$^+$]: 361.0981. Found: 361.0973.

(E)-4-Methyl-N-[2-(4-nitrobenzylidene)cyclobutyl]benzenesulfonamide (3j):

white solid (54% yield, TCE as solvent, 100 °C, 13 h), m.p. = 204—206 °C.

$^1$H NMR (400 MHz, d$_6$-DMSO): $\delta$ 8.31 (d, J = 7.8 Hz, 1H), 8.16 (d, J = 6.8 Hz, 2H), 7.75 (d, J = 6.8 Hz, 2H), 7.44—7.37 (m, 4H), 6.12 (s, 1H), 4.48 (br s, 1H), 2.79—2.69 (m, 1H), 2.69—2.58 (m, 1H), 2.40 (s, 3H), 2.11—2.02 (m, 1H), 1.82—1.71 (m, 1H).

$^{13}$C NMR (100 MHz, d$_6$-DMSO): $\delta$ 151.7, 145.4, 143.1, 142.8, 138.9, 129.7, 128.1, 126.5, 123.9, 118.5, 54.2, 28.0, 27.1, 21.0.
FT-IR (neat): $\nu$ 3270, 2951, 2927, 1595, 1512 cm$^{-1}$.
HRMS (ESI) calcd for C$_{18}$H$_{18}$N$_2$NaO$_4$S [M+Na$^+$]: 381.0880. Found: 381.0873.

$(E)$-N-[2-(2-Chlorobenzylidene)cyclobutyl]-4-methylbenzenesulfonamide (3k):

white solid (75% yield, TCE as solvent, 100 °C, 7 h), m.p. = 134−135 °C.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.82 (d, $J = 8.2$ Hz, 2H), 7.30 (d, $J = 8.2$ Hz, 2H), 7.32−7.28 (m, 1H), 7.20−7.08 (m, 3H), 6.38−6.36 (m, 1H), 5.20 (d, $J = 10.4$ Hz, 1H), 4.67−4.59 (m, 1H), 2.69−2.51 (m, 2H), 2.41 (s, 3H), 2.34−2.26 (m, 1H), 1.85−1.75 (m, 1H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.6, 143.5, 138.1, 133.8, 133.0, 129.8, 129.6, 128.5, 127.9, 126.9, 126.4, 117.3, 54.6, 29.8, 26.8, 21.5.

FT-IR (neat): $\nu$ 3243, 2957, 2917, 2849, 1436, 1327 cm$^{-1}$.
HRMS (ESI) calcd for C$_{18}$H$_{18}$ClNNaO$_2$S [M+Na$^+$]: 370.0639. Found: 370.0637.

$(E)$-N-[2-(3-Chlorobenzylidene)cyclobutyl]-4-methylbenzenesulfonamide (3l):

white solid (88% yield, TCE as solvent, 100 °C, 7 h), m.p. = 105−106 °C.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.81 (d, $J = 8.2$ Hz, 2H), 7.32 (d, $J = 8.2$ Hz, 2H), 7.22−7.13 (m, 2H), 7.06 (s, 1H), 6.98 (d, $J = 7.7$ Hz, 1H), 6.00−5.98 (m, 1H), 5.15 (d, $J = 9.9$ Hz, 1H), 4.64−4.56 (m, 1H), 2.71−2.64 (m, 2H), 2.44 (s, 3H), 2.34−2.26 (m, 1H), 1.85−1.75 (m, 1H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 145.7, 143.6, 138.1, 138.0, 134.2, 129.8, 129.6, 127.5, 127.0, 126.8, 125.8, 120.2, 54.5, 29.7, 27.0, 21.5.

FT-IR (neat): $\nu$ 3267, 2949, 1593, 1563, 1434, 1332 cm$^{-1}$.
HRMS (ESI) calcd for C$_{18}$H$_{18}$ClNNaO$_2$S [M+Na$^+$]: 370.0639. Found: 370.0637.

$(E)$-N-[2-(3-Chloro-4-methylbenzylidene)cyclobutyl]-4-methylbenzenesulfonamide (3m):

white solid (87% yield, DCE as solvent, 100 °C, 36 h), m.p. = 119−120 °C.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.81 (d, $J = 8.2$ Hz, 2H), 7.31 (d, $J = 8.2$ Hz, 2H), 7.11 (d, $J = 7.9$ Hz, 1H), 7.05 (d, $J = 1.1$ Hz, 1H), 6.89 (dd, $J = 7.9$ and 1.1 Hz, 1H), 5.95−5.93 (m, 1H), 5.17 (d, $J = 9.7$ Hz, 1H), 4.62−4.54 (m, 1H), 2.68−2.63 (m, 2H), 2.43 (s, 3H), 2.32 (s, 3H), 2.31−2.24 (m, 1H), 1.84−1.69 (m, 1H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.5, 143.5, 138.1, 135.5, 134.4, 134.3, 130.8, 139.8, 127.9, 127.0, 125.8, 120.1, 54.5, 29.7, 27.0, 21.5, 19.7.

FT-IR (neat): $\nu$ 3274, 2989, 2949, 2919, 1598, 1553, 1495, 1438 cm$^{-1}$.
HRMS (ESI) calcd for C$_{19}$H$_{20}$ClNNaO$_2$S [M+Na$^+$]: 384.0796. Found: 384.0791.
(E)-N-[2-(4-Bromo-2-methylbenzylidene)cyclobutyl]-4-methylbenzenesulfonamide (3n):

![Chemical Structure](image)

white solid (59% yield, TCE as solvent, 100 °C, 13 h), m.p. = 140–141 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.82 (d, $J = 8.2$ Hz, 2H), 7.31 (d, $J = 8.2$ Hz, 2H), 7.26 (s, 1H), 7.22 (dd, $J = 8.2$ and 1.6 Hz, 1H), 6.96 (d, $J = 8.2$ Hz, 1H), 6.15–6.13 (m, 1H), 5.09 (d, $J = 10.1$ Hz, 1H), 4.65–4.56 (m, 1H), 2.66–2.47 (m, 2H), 2.42 (s, 3H), 2.32–2.24 (m, 1H), 2.14 (s, 3H), 1.80–1.71 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 145.1, 143.5, 138.1, 133.5, 132.9, 129.8, 128.66, 128.63, 126.9, 120.5, 117.7, 54.5, 29.7, 26.8, 21.5, 19.5.

FT-IR (neat): $\nu$ 3270, 2986, 2950, 2920, 1598, 1586, 1478, 1438 cm$^{-1}$.

HRMS (ESI) calcd for C$_{19}$H$_{20}$BrNNaO$_2$S [M+Na$^+$]: 428.0290. Found: 428.0293.

(E)-Methyl 3-chloro-5-[2-(4-methylphenylsulfonamido)cyclobutylidene]methylbenzoate (3o):

![Chemical Structure](image)

white solid (85% yield, TCE as solvent, 100 °C, 13 h), m.p. = 165–166 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.82 (d, $J = 8.2$ Hz, 2H), 7.31–7.79 (m, 1H), 7.63 (s, 1H), 7.33 (d, $J = 8.2$ Hz, 2H), 7.23–7.22 (m, 1H), 5.99–5.97 (m, 1H), 5.21 (d, $J = 10.3$ Hz, 1H), 4.65–4.57 (m, 1H), 3.91 (s, 3H), 2.75–2.68 (m, 2H), 2.45 (s, 3H), 2.38–2.29 (m, 1H), 1.89–1.79 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.8, 147.3, 143.7, 138.2, 138.1, 134.5, 131.8, 131.4, 129.8, 127.6, 127.0, 126.9, 119.5, 54.5, 52.5, 29.6, 27.0, 21.5.

FT-IR (neat): $\nu$ 3276, 2952, 1725, 1597, 1574, 1437 cm$^{-1}$.

HRMS (ESI) calcd for C$_{20}$H$_{20}$ClNNaO$_4$S [M+Na$^+$]: 428.0694. Found: 428.0691.

(E)-N-(2-Heptylidencyclobutyl)-4-methylbenzenesulfonamide (3p):

![Chemical Structure](image)

light brown oil (45% yield, DCE as solvent, 50 °C, 20 h).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.77 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 8.4$ Hz, 2H), 5.08–5.02 (m, 1H), 4.82 (d, $J = 9.8$ Hz, 1H), 4.41–4.34 (m, 1H), 2.43 (s, 3H), 2.41–2.33 (m, 1H), 2.27–2.09 (m, 2H), 1.84–1.79 (m, 2H), 1.65–1.56 (m, 1H), 1.31–1.25 (m, 8H), 0.88 (t, $J = 7.0$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.3, 140.6, 138.2, 129.6, 127.0, 121.9, 53.8, 31.7, 29.2, 28.74, 28.68, 27.5, 23.9, 22.6, 21.5, 14.0.

FT-IR (neat): $\nu$ 3267, 2955, 2926, 2854, 1599, 1437 cm$^{-1}$.

HRMS (ESI) calcd for C$_{18}$H$_{27}$NNaO$_2$S [M+Na$^+$]: 344.1655. Found: 344.1652.
\(\textbf{\((E)-N-[2-(4-Chlorobenzylidene)cyclobutyl]-N,4-dimethylbenzenesulfonamide (3r):}\)\\

![Diagram](image)

white solid (84% yield, DCE as solvent, 80 °C, 12 h), m.p. = 110—111 °C.

\[^1\text{H NMR (400 MHz, CDCl}_3\):} \delta 7.73 (d, \(J = 8.0 \text{ Hz}, 2\text{H}), 7.32 (d, J = 8.0 \text{ Hz}, 2\text{H}), 7.25 (d, \(J = 8.4 \text{ Hz}, 2\text{H}), 7.04 (d, J = 8.4 \text{ Hz}, 2\text{H}), 5.79—5.76 (m, 1\text{H}), 5.31 (t, J = 7.0 \text{ Hz}, 1\text{H}), 2.77 (s, 3\text{H}), 2.72—2.60 (m, 2\text{H}), 2.44 (s, 3\text{H}), 2.15—1.98 (m, 2\text{H}).

\[^{13}\text{C NMR (100 MHz, CDCl}_3\):} \delta 143.4, 142.3, 136.0, 134.8, 132.4, 129.7, 128.7, 128.6, 127.2, 121.3, 58.6, 29.2, 26.9, 23.3, 21.5.

FT-IR (neat): \(\nu \) 2957, 1597, 1491, 1338 cm\(^{-1}\).


\(\textbf{\((E)-N-[2-(4-Chlorobenzylidene)cyclobutyl]-4-nitrobenzenesulfonamide (3s):}\)\\

![Diagram](image)

white solid (47% yield, TCE as solvent, 100 °C, 14 h), m.p. = 161—162 °C.

\[^1\text{H NMR (400 MHz, CDCl}_3\):} \delta 8.33 (d, \(J = 9.0 \text{ Hz}, 2\text{H}), 8.09 (d, J = 9.0 \text{ Hz}, 2\text{H}), 7.25 (d, \(J = 8.5 \text{ Hz}, 2\text{H}), 7.06 (d, J = 8.5 \text{ Hz}, 2\text{H}), 6.17—6.15 (m, 1\text{H}), 5.15 (d, \(J = 9.3 \text{ Hz}, 1\text{H}), 4.68—4.60 (m, 1\text{H}), 2.75—2.69 (m, 2\text{H}), 2.42—2.34 (m, 1\text{H}), 1.91—1.82 (m, 1\text{H}).

\[^{13}\text{C NMR (100 MHz, CDCl}_3\):} \delta 150.3, 147.1, 143.7, 134.4, 133.0, 128.9, 128.8, 128.2, 124.4, 121.1, 54.7, 29.8, 27.2.

FT-IR (neat): \(\nu \) 3273, 3108, 2987, 1607, 1529, 1491 cm\(^{-1}\).

3. Effect of substituents on the cyclopropane rings

\[ 1t - 1x + TsNH_2 \xrightarrow{5 \text{ mol} \% \text{ AuPPh}_3\text{Cl}, 5 \text{ mol} \% \text{ AgOTf}} \]

<table>
<thead>
<tr>
<th>entry(^a)</th>
<th>substrate</th>
<th>solvent</th>
<th>temp (°C)</th>
<th>time (h)</th>
<th>yield (%)</th>
<th>conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="Ph=Me" alt="Me" /> (1t)</td>
<td>DCE</td>
<td>80</td>
<td>14</td>
<td>ND(^b)</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>(1t)</td>
<td>TCE</td>
<td>100</td>
<td>14</td>
<td>ND(^b)</td>
<td>&gt;99</td>
</tr>
<tr>
<td>3</td>
<td><img src="Ph" alt="Ph" /> (1u)</td>
<td>TCE</td>
<td>100</td>
<td>14</td>
<td>ND(^b)</td>
<td>&gt;99</td>
</tr>
<tr>
<td>4</td>
<td><img src="Ph=nBu" alt="nBu" /> (1v)</td>
<td>DCE</td>
<td>80</td>
<td>14</td>
<td>ND(^b)</td>
<td>&gt;99</td>
</tr>
<tr>
<td>5</td>
<td><img src="Ph" alt="Ph" /> (1w)</td>
<td>DCE</td>
<td>80</td>
<td>14</td>
<td>ND(^b)</td>
<td>&gt;99</td>
</tr>
<tr>
<td>6</td>
<td><img src="Ph" alt="Ph" /> (1x)</td>
<td>DCE</td>
<td>80</td>
<td>14</td>
<td>ND(^b)</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

\(^a\) Reaction condition: substrate (0.5 mmol), TsNH\(_2\) (0.6 mmol), catalyst (0.05 mmol), solvent (5 mL). \(^b\) ND = product not detected. Mixtures of unidentified products were obtained.
4. $^1$H and $^{13}$C-NMR spectra for new compounds

![Chemical structure and NMR spectra](image-url)
Br-\(\text{\scalebox{2}{\text{\textbullet}}\text{\scalebox{2}{\textbullet}}}\) If
S37
Cl

NTs

3r