Supporting Information
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Supporting Information

Table of Contents

1. General S2
2. The safety issues for handling of azido compounds S2
3. Synthesis of vinyl azides 1 S3
4. Synthesis of Donor-Acceptor cyclopropanes S4
5. [3+2]-Annulation of Donor-Acceptor cyclopropanes with vinyl azides (Table 1 and Scheme 2) S16
6. Derivatization of azidocyclopentane 6aa (Scheme 3) S31
7. Derivatization of azidocyclopentane 9aa (Scheme 4) S34
8. [3+2]-Annulation of chiral cyclopropane 2a with vinyl azide 1a S37

Appendix: $^1$H and $^{13}$C NMR spectra for new compounds S41
1. General

$^1$H NMR spectra were recorded on a Bruker Avance 400 MHz, or 500 MHz spectrometer in CDCl$_3$ [using TMS (for $^1$H, δ = 0.00) as internal standard] or C$_6$D$_6$ [using C$_6$D$_6$ (for $^1$H, δ = 7.16) as internal standard]. $^{13}$C NMR spectra were recorded on a Bruker Avance 400 MHz, or 500 MHz spectrometer in CDCl$_3$ [using CDCl$_3$ (for $^{13}$C, δ = 77.00) as internal standard]. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad. High-resolution mass spectra were obtained with a Waters Q-Tof Premier mass spectrometer. Melting points are uncorrected and were recorded on a MPA 100 OptiMelt Automated Melting Point System. X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractionmeter. Optical rotations were measured on an Anton Paar MCP 200 polarimeter. Enantiomeric excesses (ee) were determined by HPLC analysis on Shimadzu HPLC with Daicel chiral columns. Flash chromatography was performed using Merck silica gel 60 with distilled solvents. CH$_2$Cl$_2$ was distilled over CaH$_2$. MeNO$_2$ was distilled over MgSO$_4$. Sc(OTf)$_3$ (99%, CAS Number 144026-79-9) was purchased from Sigma-Aldrich and used as received.

2. The safety issues for handling of azido compounds$^{[1,2]}$

2.1. Sodium azide (NaN$_3$): Caution: Sodium azide can be absorbed through skin and is toxic (LD$_{50}$ oral = 27 mg/kg for rats). Wearing gloves are required when handling it. Sodium azide decomposes explosively upon heating to above 275 ºC. It is relatively safe especially in aqueous solution, unless acidified to form HN$_3$, which is volatile and highly toxic.

2.2. Organic azides: Caution: Organic azides are potentially explosive substances that can decompose with the slight input of energy from external sources (heat, light, pressure, etc). When designing the organic azides used for the project, please keep in mind the following equation.

$$\frac{N_C + N_O}{N_N} \geq 3$$

It should be noted that this equation takes into account all nitrogen atoms in the organic azide molecule, not just those in

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the azido group. All organic azides prepared in this work are enough stable to be stored under -20 °C at least for half a year. We have never experienced a safety problem with these compounds.

3. Synthesis of vinyl azides 1

Typical procedure A: synthesis of 1a

This procedure was slightly modified from the Hassner’s method.\(^3\)

To a stirred suspension of NaN\(_3\) (7.15 g, 110 mmol) in acetonitrile (30 mL) was added dropwise a solution of iodine monochloride (8.07 g, 49.7 mmol in 60 mL CH\(_2\)Cl\(_2\)) at -20 °C, and the mixture was stirred at the same temperature for 30 min. A solution of styrene (5.0 mL, 43.6 mmol) in CH\(_2\)Cl\(_2\) (20 mL) was added slowly, and the mixture was kept stirring for 1 h. The reaction was quenched with saturated aqueous Na\(_2\)S\(_2\)O\(_3\), and the reaction mixture was extracted twice with Et\(_2\)O. The combined extracts were washed with brine and dried over MgSO\(_4\). After filtration and evaporation of solvents, the resulting crude materials were used immediately for the next step without any further purification.

To a solution of the obtained compounds above in Et\(_2\)O (100 mL) was added t-BuOK (5.92 g, 52.3 mmol) at 0 °C, and the mixture was stirred for 1.5 h at the same temperature. The reaction mixture was filtered through celite and the solvent was removed in vacuo. The resulting crude materials were purified by flash column chromatography (silica gel; 100% hexane) to give vinyl azide 1a (5.38 g, 37.1 mmol, 85% yield from styrene) as a pale yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.98 (1H, d, \(J = 2.4\) Hz), 5.45 (1H, d, \(J = 2.4\) Hz), 7.37-7.40 (3H, m), 7.57-7.59 (2H, m); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 145.1, 134.3, 129.1, 128.5, 125.6, 98.0.

Vinyl azides 1b-1e\(^4\) were known compounds and prepared according to the reported procedures.

\[
\begin{align*}
1b: R &= 4-\text{MeC}_6\text{H}_4  \\
1c: R &= 2\text{-naphthyl}  \\
1d: R &= 4-\text{BrC}_6\text{H}_4  \\
1e: R &= \text{CH}_2\text{CH}_2\text{Ph}
\end{align*}
\]

4. Synthesis of Donor-Acceptor cyclopropanes

4.1. Synthesis of S1

To a solution of malonic acid (8.33 g, 80.0 mmol) and (2,6-dimethylphenyl)methanol\(^5\) (21.7 g, 160 mmol) in MeCN (190 mL) was added DCC (36.7 g, 178 mmol) at 0 °C. A precipitate of dicyclohexyl urea was formed immediately and the mixture was stirred at 23 °C for 2 h. The resulting suspension was filtered and the filter cake was washed with acetonitrile. The combined solution was evaporated to give the crude product. The crude material was purified by flash column chromatography (silica gel; hexane : ethyl acetate = 20 : 1) to give S1 (26.8 g, 78.8 mmol) in 98% yield as a white solid.

**bis(2,6-dimethylbenzyl) malonate (S1)**

mp. 64-65 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.31 (12H, s), 3.41 (2H, s), 5.23 (4H, s), 7.03 (4H, d, \(J = 7.6\) Hz), 7.15 (2H, t, \(J = 7.6\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 19.5, 41.4, 62.2, 128.3, 128.9, 131.2, 138.4, 166.6.

ESIHRMS: Found: m/z 341.1754. Calcd for C\(_{21}\)H\(_{25}\)O\(_4\): (M+H)\(^+\) 341.1753.


4.2. Typical procedure B: synthesis of alkene S2a

To a solution of benzaldehyde (2.2 mL, 21.6 mmol) and S1 (5.79 g, 17.0 mmol) in benzene (34 mL) was added AcOH (200 µL, 3.40 mmol) and piperidine (340 µL, 3.40 mmol) at 23 °C. The reaction was stirred under reflux conditions for 12 h until the starting materials were consumed. The mixture was then cooled down to 23 °C and evaporated to remove the solvent. The crude material was purified by recrystallization (hexane : ethyl acetate = 2 : 1) to give S2a (5.25 g, 12.2 mmol) in 72% yield as a white solid.

**bis(2,6-dimethylbenzyl) 2-benzylidenemalonate (S2a)**

mp. 130-131 °C.; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.14 (6H, s), 2.37 (6H, s), 5.27 (2H, s), 5.34 (2H, s), 6.96 (2H, d, \(J = 7.6\) Hz), 7.05 (2H, d, \(J = 7.6\) Hz), 7.10 (1H, t, \(J = 7.6\) Hz), 7.16 (1H, t, \(J = 7.6\) Hz), 7.26-7.30 (2H, m), 7.33-7.38 (3H, m), 7.71 (1H, s); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 19.2, 19.6, 62.39, 62.44, 126.0, 128.2, 128.3, 128.8, 128.9, 129.3, 130.5, 130.9, 131.4, 132.8, 138.47, 138.49, 142.6, 164.1, 166.8.


**bis(2,6-dimethylbenzyl) 2-(4-methoxybenzylidene)malonate (S2b)**

76% yield by procedure B from S1 and \(p\)-anisaldehyde; White solid; mp: 150-151 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.18 (6H, s), 2.36 (6H, s), 3.81 (3H, s), 5.29 (2H, s), 5.32 (2H, s), 6.78 (2H, d, \(J = 8.4\) Hz), 6.97 (2H, d, \(J = 7.6\) Hz), 7.04 (2H, d, \(J = 7.2\) Hz), 7.09 (2H, d, \(J = 8.4\) Hz).
Hz), 7.09-7.18 (2H, m), 7.32 (2H, d, \( J = 8.8 \) Hz), 7.64 (1H, s); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 19.4, 19.7, 55.4, 62.2, 62.4, 114.3, 123.2, 125.4, 128.26, 128.29, 128.8, 128.9, 131.0, 131.5, 131.6, 138.5, 138.6, 142.2, 161.6, 164.5, 167.3.; ESIHRMS: Found: m/z 459.2174. Calcd for C\(_{29}\)H\(_{31}\)O\(_5\): (M+H\(^+\)) 459.2171.

**bis(2,6-dimethylbenzyl) 2-(2-methylbenzylidene)malonate (S2c)**

92% yield by procedure B from S1 and o-tolualdehyde;

Pale yellow solid; mp: 90-91 °C.; \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 2.06 (6H, s), 2.32 (3H, s), 2.38 (6H, s), 5.15 (2H, s), 5.35 (2H, s), 6.93 (2H, d, \( J = 7.6 \) Hz), 7.02-7.11 (4H, m), 7.14-7.17 (2H, m), 7.21 (1H, d, \( J = 7.6 \) Hz), 7.27 (1H, d, \( J = 7.6 \) Hz), 7.95 (1H, s); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 19.1, 19.7, 19.9, 62.2, 62.4, 126.1, 127.4, 127.6, 128.2, 128.3, 128.79, 128.82, 130.1, 130.4, 131.0, 131.5, 132.5, 137.7, 138.46, 138.51, 142.0, 164.0, 166.5.; ESIHRMS: Found: m/z 465.2037. Calcd for C\(_{29}\)H\(_{30}\)O\(_4\)Na: (M+Na\(^+\)) 465.2042.

**bis(2,6-dimethylbenzyl) 2-(naphthalen-2-ylmethylene)malonate (S2d)**

81% yield by procedure B from S1 and 2-naphthaldehyde; Yellow solid; mp: 150-151 °C.; \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 2.11 (6H, s), 2.39 (6H, s), 5.31 (2H, s), 5.36 (2H, s), 6.92 (2H, d, \( J = 7.6 \) Hz), 7.05-7.10 (m, 3H), 7.17 (1H, t, \( J = 7.6 \) Hz), 7.43 (1H, d, \( J = 8.8 \) Hz), 7.46-7.54 (2H, m), 7.70-7.80 (3H, m), 7.86 (1H, s), 7.89 (1H, s); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 19.3, 19.7, 62.5, 62.6, 125.1, 125.9, 126.7, 127.7, 128.2, 128.3, 128.6, 128.75, 128.84, 128.9, 130.4, 130.87, 130.89, 131.5, 133.0, 134.1, 138.5, 142.7, 164.2, 167.0.

ESIHRMS: Found: m/z 479.2220. Calcd for C\(_{32}\)H\(_{31}\)O\(_4\): (M+H\(^+\)) 479.2222.
**bis(2,6-dimethylbenzyl) 2-(thiophen-2-ylmethylene)malonate (S2e)**

![Chemical structure](attachment:image)

80% yield by procedure B from S1 and 2-thiophenecarboxaldehyde; White solid; mp: 88-89 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.21 (6H, s), 2.32 (6H, s), 5.29 (2H, s), 5.35 (2H, s), 6.97 (2H, d, $J = 7.2$ Hz), 7.02-7.04 (m, 3H), 7.09-7.18 (2H, m), 7.30 (1H ,d, $J = 3.2$ Hz), 7.49 (1H, d, $J = 4.8$ Hz), 7.82 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 19.4, 19.6, 62.4, 62.7, 122.1, 127.9, 128.25, 128.31, 128.8, 128.9, 131.0, 131.4, 131.6, 134.3, 135.1, 136.0, 138.5, 138.6, 164.4, 166.5.

ESIHRMS: Found: m/z 435.1635. Calcd for C$_{26}$H$_{27}$O$_4$S: (M+H)$^+$ 435.1630.

**bis(2,6-dimethylbenzyl) (E)-2-(3-phenylallylidenemalonate (S2f)**

![Chemical structure](attachment:image)

81% yield by procedure B from S1 and trans-cinnamaldehyde; Yellow solid; mp: 116-117 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.31 (6H, s), 2.32 (6H, s), 5.28 (2H, s), 5.36 (2H, s), 6.97 (1H, d, $J = 15.6$ Hz), 7.03 (4H, d, $J = 7.2$ Hz), 7.09-7.19 (3H, m), 7.32-7.33 (5H, m), 7.52 (1H, d, $J = 11.6$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 19.5, 19.6, 61.9, 62.2, 123.2, 124.3, 127.8, 128.3, 128.4, 128.7, 128.82, 128.84, 129.9, 131.6, 131.7, 135.6, 138.49, 138.53, 144.9, 145.8, 164.8, 165.3.

ESIHRMS: Found: m/z 455.2224. Calcd for C$_{30}$H$_{31}$O$_4$: (M+H)$^+$ 455.2222.
4.3. Typical procedure C: synthesis of cyclopropane 2a-5

![Chemical structure of S2a and 5a]

To a stirred suspension of sodium hydride (709 mg, 17.7 mmol, 60% dispersion in mineral oil) in anhydrous DMF (23 mL) was added trimethylsulfoxonium iodide (3.85 g, 17.3 mmol) at 23 °C under a N₂ atmosphere. After stirring at 23 °C for 1 h, a solution of S2a (5.25 g, 12.2 mmol) in anhydrous DMF (93 mL) was added at 0 °C and the reaction mixture was stirred at 0 °C for 1 h. The solution was quenched with 1 M aqueous HCl solution and the organic materials were extracted thrice with Et₂O. The combined organic extracts were washed thrice with brine, dried over MgSO₄, filtered and concentrated in vacuo. The resulting crude material was purified by recrystallization (hexane : ethyl acetate = 2 : 1) to yield 5a (3.89 g, 8.78 mmol) in 72% yield as a white solid.

**bis(2,6-dimethylbenzyl) 2-phenylcyclopropane-1,1-dicarboxylate (5a)**

![Chemical structure of 5a]

mp: 118-119 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.73 (1H, dd, J = 5.2, 9.2 Hz), 1.87 (6H, s) 2.19 (1H, dd, J = 5.2, 8.0 Hz), 2.25 (6H, s), 3.20 (1H, t, J = 8.8 Hz), 4.63 (2H, d, J = 12.0 Hz), 4.88 (2H, d, J = 12.0 Hz), 5.22 (2H, s), 6.90 (2H, d, J = 7.6 Hz), 7.00...
(2H, d, J = 7.6 Hz), 7.08 (1H, t, J = 7.6 Hz), 7.12-7.16 (6H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 19.0, 19.3, 19.5, 32.6, 37.9, 62.0, 62.7, 127.4, 128.0, 128.2, 128.27, 128.29, 128.5, 128.7, 131.1, 131.3, 134.5, 138.4 (overlapped), 166.7, 170.0.

ESIHRMS: Found: m/z 443.2216. Calcd for C$_{29}$H$_{31}$O$_{4}$: (M+H)$^+$ 443.2222.

dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (2a)$^6$

75% yield by procedure C from dimethyl 2-benzylidene malonate$^7$.

$^1$H NMR (400 MHz, CDCl$_3$) δ 1.74 (1H, dd, J = 5.2, 9.2 Hz), 2.20 (1H, dd, J = 5.2, 8.0 Hz), 3.23 (1H, t, J = 8.8 Hz), 3.36 (3H, s), 3.79 (3H, s), 7.18-7.29 (5H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 19.1, 32.5, 37.2, 52.2, 52.8, 127.4, 128.1, 128.4, 134.5, 167.0, 170.2.

diisopropyl 2-phenylcyclopropane-1,1-dicarboxylate (3a)$^8$

85% yield by procedure C from diisopropyl 2-benzylidene malonate$^9$.

$^1$H NMR (500 MHz, CDCl$_3$) δ 0.68 (3H, d, J = 6.5 Hz), 1.05 (3H, d, J = 6.0 Hz), 1.26 (3H, d, J = 6.0 Hz), 1.28 (3H, d, J = 6.5 Hz), 1.64 (1H, dd, J = 5.0, 9.0 Hz), 2.12 (1H, dd, J = 5.5, 8.0 Hz), 3.18 (1H, t, J = 8.5 Hz), 4.72 (1H, septet, J = 6.5 Hz), 5.09 (1H, septet, J = 6.0 Hz), 7.19-7.26 (5H, m); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 18.3, 21.0, 21.2, 21.6, 21.7, 31.6, 37.8, 68.5, 69.1, 127.1, 128.0, 128.5, 134.7, 166.2, 169.5.

dibenzyl 2-phenylcyclopropane-1,1-dicarboxylate (4a)$^8$

27% yield by procedure C from dibenzyl 2-benzylidene malonate$^{10}$


$^1$H NMR (400 MHz, CDCl$_3$) δ 1.76 (1H, dd, $J = 5.2$, 9.2 Hz), 2.22 (1H, dd, $J = 5.2$, 8.4 Hz), 3.27 (1H, t, $J = 8.4$ Hz), 4.76 (2H, s), 5.15 (1H, d, $J = 12.4$ Hz), 5.26 (1H, d, $J = 12.4$ Hz), 6.93 (2H, d, $J = 6.8$ Hz), 7.17-7.25 (8H, m), 7.29-7.34 (5H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 19.2, 32.7, 37.5, 67.2, 67.3, 127.4, 127.9, 128.0, 128.1(6) (overlapped), 128.2(1), 128.3, 128.5 (overlapped), 134.4, 135.2, 135.4, 166.5, 169.6. 

bis(2,6-dimethylbenzyl) 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (5b)

70% yield by procedure C from S2b;
Pale yellow solid; mp: 115-116 °C.
$^1$H NMR (400 MHz, CDCl$_3$) δ 1.70 (1H, dd, $J = 5.2$, 9.2 Hz), 1.91 (6H, s) 2.14 (1H, dd, $J = 5.2$, 8.0 Hz), 2.26 (6H, s), 3.16 (1H, t, $J = 8.4$ Hz), 3.76 (3H, s), 4.69 (1H, d, $J = 12.0$ Hz), 4.88 (1H, d, $J = 12.0$ Hz), 5.22 (2H, s), 6.71 (2H, d, $J = 8.8$ Hz), 6.91 (2H, d, $J = 7.2$ Hz), 7.00 (2H, d, $J = 7.2$ Hz), 7.05-7.16 (4H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 19.0, 19.4, 19.5, 32.2, 37.6, 55.2, 61.9, 62.6, 113.6, 126.4, 128.0, 128.2, 128.5, 128.7, 129.4, 131.2, 131.4, 138.4 (overlapped), 158.9, 166.8, 170.0.
ESIHRMS: Found: m/z 473.2330. Calcd for C$_{30}$H$_{33}$O$_5$: (M+H)$^+$ 473.2328.

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bis(2,6-dimethylbenzyl) 2-(o-tolyl)cyclopropane-1,1-dicarboxylate (5c)

64% yield by procedure C from S2c; Pale yellow solid; mp: 111-112 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 1.71 (1H, dd, $J = 4.8, 9.2$ Hz), 1.90 (6H, s) 2.19 (3H, s), 2.27 (6H, s), 2.29-2.31 (1H, m), 3.13 (1H, t, $J = 8.8$ Hz), 4.70 (1H, d, $J = 12.0$ Hz), 4.78 (1H, d, $J = 12.0$ Hz), 5.23 (1H, d, $J = 12.0$ Hz), 5.28 (1H, d, $J = 12.0$ Hz), 6.90 (2H, d, $J = 7.6$ Hz), 6.96-7.16 (8H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 18.6, 19.0, 19.3, 19.4, 31.7, 36.6, 61.6, 62.5, 125.5, 127.0, 127.5, 128.0, 128.3, 128.4, 128.7, 129.8, 131.2, 131.4, 132.5, 138.4 (overlapped), 138.9, 166.6, 170.1.

ESIHRMS: Found: m/z 457.2384. Calcd for C$_{30}$H$_{33}$O$_4$: (M+H)$^+$ 457.2379.

bis(2,6-dimethylbenzyl) 2-(naphthalen-2-yl)cyclopropane-1,1-dicarboxylate (5d)

57% yield by procedure C from S2d; Pale yellow solid; mp: 93-94 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 1.68 (6H, s), 1.81 (1H, dd, $J = 5.2, 9.2$ Hz), 2.28 (6H, s), 2.33 (1H, dd, $J = 5.2, 8.0$ Hz), 3.35 (1H, t, $J = 8.4$ Hz), 4.56 (1H, d, $J = 11.6$ Hz), 4.79 (1H, d, $J = 11.6$ Hz), 5.25 (2H, s), 6.78 (2H, d, $J = 7.6$ Hz), 6.98-7.02 (3H, m), 7.15 (1H, t, $J = 7.6$ Hz), 7.24 (1H, m), 7.43-7.45 (2H, m), 7.59-7.64 (2H, m), 7.69-7.76 (2H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 18.7, 19.4, 19.5, 32.8, 38.0, 61.9,
62.7, 125.8, 126.1, 126.4, 127.0, 127.5, 127.76, 127.84 (overlapped), 128.3 (overlapped), 128.4, 128.7, 131.0, 131.3, 132.0, 132.7, 133.1, 138.2, 138.4, 166.7, 166.9.

ESIHRMS: Found: m/z 515.2194. Calcd for C_{33}H_{32}O_{4}Na: (M+Na)^+ 515.2198.

**bis(2,6-dimethylbenzyl) 2-(thiophen-2-yl)cyclopropane-1,1-dicarboxylate (5e)**

![Chemical structure](image)

33% yield by procedure C from S2e; White solid; mp: 106-107 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 1.81 (1H, dd, $J = 5.2$, 9.2 Hz), 1.97 (6H, s), 2.13 (1H, dd, $J = 5.2$, 7.6 Hz), 2.25 (6H, s), 3.28 (1H, t, $J = 8.4$ Hz), 4.77 (1H, d, $J = 11.6$ Hz), 4.97 (1H, d, $J = 12.0$ Hz), 5.21 (2H, s), 6.79 (1H, d, $J = 3.2$ Hz), 6.84-6.86 (1H, m), 6.93 (2H, d, $J = 7.6$ Hz), 7.00 (2H, d, $J = 7.6$ Hz), 7.08-7.16 (3H, m).$^{13}$C NMR (100 MHz, CDCl$_3$) δ 19.0, 19.5, 21.2, 27.4, 38.4, 62.2, 62.7, 124.8, 126.0, 126.7, 128.0, 128.3, 128.6, 128.7, 131.1, 131.2, 138.0, 138.4, 138.5, 166.4, 169.5.

ESIHRMS: Found: m/z 449.1788. Calcd for C$_{27}$H$_{29}$O$_{4}$S: (M+H)$^+$ 449.1787.

**bis(2,6-dimethylbenzyl) (E)-2-styrylcyclopropane-1,1-dicarboxylate (5f)**

![Chemical structure](image)

68% yield by procedure C from S2f; White solid; mp: 88-89 °C.
$^1$H NMR (400 MHz, CDCl$_3$) δ 1.68 (1H, dd, $J = 5.2$, 8.8 Hz), 1.84 (1H, dd, $J = 5.2$, 7.6 Hz), 2.05 (6H, s), 2.25 (6H, s), 2.73 (1H, dd, $J = 8.4$, 16.8 Hz), 5.08 (1H, d, $J = 12.0$ Hz), 5.12 (1H, d, $J = 12.0$ Hz), 5.17-5.23 (2H, m), 5.73 (1H, dd, $J = 8.8$, 16.0 Hz), 6.60 (1H, d, $J = 16.0$ Hz), 6.90 (2H, d, $J = 7.6$ Hz), 7.01 (2H, d, $J = 7.2$ Hz), 7.08 (1H, t, $J = 7.6$ Hz), 7.15 (1H, t, $J = 7.6$ Hz), 7.19-7.28 (5H, m).; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 19.2, 19.5, 21.5, 31.7, 36.4, 62.4, 62.6, 124.6, 126.1, 127.5, 128.1, 128.3, 128.4, 128.6, 128.7, 131.2, 131.3, 133.9, 136.5, 138.38, 128.41, 167.7, 169.7.

ESIHRMS: Found: m/z 491.2195. Calcd for C$_{31}$H$_{32}$O$_4$Na: (M+Na)$^+$ 491.2198.

4.4. Synthesis of cyclopropane 5g

![Cyclopropane 5g](image)

To a solution of N-vinyl-phthalimide (618 mg, 3.57 mmol) and bis[rhodium($\alpha$, $\alpha$, $\alpha'$,-$\alpha'$-tetramethyl-1,3-benzenedipropionic acid)] (5.90 mg, 0.00778 mmol) in anhydrous CH$_2$Cl$_2$ (8 mL) was added a solution of diazomalonate S3 (1.43 g, 3.92 mmol) (preparation method was shown below) in anhydrous CH$_2$Cl$_2$ (8 mL) dropwise at 0 °C under an Ar atmosphere. The reaction was allowed to warm to 23 °C and stirred for 20 h at 23 °C. The solvent was then removed in vacuo and the crude material was purified by recrystallization (ethyl acetate) to give 5g (666 mg, 1.30 mmol) in 33% yield as a white solid.
bis(2,6-dimethylbenzyl)
2-(1,3-dioxoisoiindolin-2-yl)cyclopropane-1,1-dicarboxylate (5g)

mp: 147-148 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 2.02 (1H, dd, $J = 6.4$, 8.4 Hz), 2.07 (6H, s), 2.25 (6H, s), 2.76-2.79 (1H, m), 3.69 (1H, dd, $J = 6.8$, 8.0 Hz), 4.93 (1H, d, $J = 12.0$ Hz), 5.04 (1H, d, $J = 12.0$ Hz), 5.25 (2H, s), 6.84 (2H, d, $J = 7.6$ Hz), 6.99-7.04 (3H, m), 7.14 (1H, t, $J = 7.6$ Hz), 7.66-7.73 (4H, m).; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 19.1, 19.4, 19.5, 33.4, 35.2, 62.4, 62.8, 123.3, 128.0, 128.2, 128.6, 128.7, 130.9, 131.1, 131.3, 134.1, 138.4, 138.5, 166.4, 167.6, 168.4.

ESIHRMS: Found: m/z 534.1898. Calcd for C$_{31}$H$_{29}$NO$_6$Na: (M+Na)$^+$ 534.1893.

The preparation of diazomalonate S3

To a stirred solution of 4-acetamidobenzenesulfonyl azide (1.49 g, 6.00 mmol) in MeCN (14 mL) was added triethylamine (977 mg, 6.00 mmol) and S1 (1.36 g, 4.00 mmol) in MeCN (7 mL). The reaction mixture was stirred at 23 °C for 22 h. The solvent was evaporated and the residue was filtered on cotton with acetonitrile. The crude mixture was concentrated in vacuo and filtered on cotton one more time with CH$_2$Cl$_2$. The resulting crude material was purified by flash column chromatography.
(hexane : ethyl acetate = 15 : 1) to yield S3 (1.43 g, 3.91 mmol) in 98\% yield as a white solid.

**bis(2,6-dimethylbenzyl) 2-diazomalonate (S3)**

![Chemical Structure](image)

mp: 98-99 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.35 (12H, s), 5.35 (4H, s), 7.01 (4H, d, $J = 7.6$ Hz), 7.14 (2H, t, $J = 7.6$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 19.6, 62.1, 128.3, 128.9, 131.4, 138.5, 161.0. (One carbon is not resolved.)

ESIHRMS: Found: m/z 389.1480. Calcd for C$_{21}$H$_{22}$N$_2$O$_4$Na: (M+Na)$^+$ 389.1477.
5. [3+2]-Annulation of Donor-Acceptor cyclopropanes with vinyl azides

5.1. Optimization of the Lewis acid in nitromethane

Table S1

<table>
<thead>
<tr>
<th>entry</th>
<th>Lewis acid</th>
<th>Time (h)</th>
<th>yield (%)(^{a})</th>
<th>dr (major:minor)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sc(OTf)(_3)</td>
<td>5</td>
<td>91(^{b})</td>
<td>57:43</td>
</tr>
<tr>
<td>2</td>
<td>ScCl(_3)·nH(_2)O</td>
<td>8</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>ScCl(_3)</td>
<td>25</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Yb(OTf)(_3)</td>
<td>25</td>
<td>43</td>
<td>53:47</td>
</tr>
<tr>
<td>5</td>
<td>Cu(OTf)(_2)</td>
<td>10</td>
<td>20</td>
<td>40:60</td>
</tr>
<tr>
<td>6</td>
<td>In(OTf)(_3)</td>
<td>25</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>Mg(OTf)(_2)</td>
<td>10</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>Bi(OTf)(_3)</td>
<td>33</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>Sn(OTf)(_2)</td>
<td>33</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>AgOTf</td>
<td>33</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^{a}\) Determined by \(^{1}\)H NMR using 1,1,2,2-tetrachloroethane. \(^{b}\) Isolated yield.

5.2. Typical procedure D: synthesis of 6aa (Table 1, run 1)

To a stirred solution of 2a (68.9 mg, 0.294 mmol) and vinyl azide 1a (88.3 mg, 0.608 mmol) in MeNO\(_2\) (1.0 mL) was added Sc(OTf)\(_3\) (15.0 mg, 0.0305 mmol) at 0 °C under a N\(_2\) atmosphere. The solution was allowed to warm to 23 °C and stirred until complete conversion (by monitoring by TLC). The mixture was quenched with saturated aqueous NaHCO\(_3\) and the organic materials were extracted thrice with CH\(_2\)Cl\(_2\). The combined extracts were washed with brine, dried over MgSO\(_4\), and concentrated \textit{in vacuo}. The resulting crude material was purified by flash column
chromatography (hexane : Et₂O =100:1 to 50:1) to yield 6aa (104.8 mg, 0.276 mmol) in 94 % yield as a mixture of diastereomer (major:minor = 53:47, which was determined by ¹H NMR analysis).

**dimethyl 2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (6aa)**

![Structure of dimethyl 2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (6aa)](image)

94% yield (major:minor = 53 : 47) by procedure D from 1a (0.60 mmol) and 2a (0.30 mmol); reaction time: 5 h.

White solid; mp: 139-140 °C.

¹H NMR (400 MHz, CDCl₃) δ 2.48 (1H × 0.82, dd, J = 9.2, 14.4 Hz), 2.55-2.63 (1H, m + 1H × 0.82, m), 2.79-2.93 (2H, m), 3.14-3.21 (1H, m + 1H × 0.82, m), 3.26 (1H×0.82, dd, J = 9.6, 14.4 Hz), 3.39 (3H×0.82, s), 3.58 (3H, s), 3.64-3.71 (1H, m + 1H×0.82, m), 3.78 (3H, s), 3.83 (3H×0.82, s), 7.21-7.46 (8H, m + 8H×0.82, m), 7.55 (2H, d, J = 7.6 Hz), 7.71 (2H×0.82, d, J = 8.0 Hz).  
ESIHRMS: Found: m/z 352.1552. Calcd for C₂₁H₂₂NO₄: (M-N₂+H)⁺ 352.1549.

Two diastereomers could be isolated partially by preparative TLC for characterization.

**dimethyl (2S*,4R*)-2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (6aa_major)** (major-6aa could be recrystallized from CH₂Cl₂/hexane as a colorless crystal: CCDC 1519381):

![X-ray of 6aa_major](image)

Colorless crystal; mp: 139-140 °C.

¹H NMR (400 MHz, CDCl₃) δ 2.57 (1H, dd, J = 6.4, 14.4 Hz), 2.79-2.93 (2H, m), 3.17 (1H, dd, J = 10.8, 14.4 Hz), 3.58 (3H, s), 3.61-3.70 (1H, m), 3.78 (3H, s), 7.23 (1H, t, J = 7.2 Hz), 7.32-7.41 (7H, m), 7.55 (2H, d, J = 7.6 Hz); ¹³C NMR (100 MHz,
CDCl$_3$ δ 39.8, 42.9, 46.8, 52.5, 52.6, 69.2, 78.4, 126.5, 127.4, 127.5, 128.1, 128.7, 128.1, 144.4, 169.5, 170.2.

dimethyl (2S*,4S*)-2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (6aa_minor):

\[
\begin{array}{c}
\text{Ph} \\
\text{CO}_2\text{Me} \\
\text{N}_3 \\
\text{CO}_2\text{Me} \\
\text{Ph}
\end{array}
\]

Colorless oil.
$^1$H NMR (400 MHz, CDCl$_3$) δ 2.48 (1H, dd, $J = 9.2$, 14.4 Hz), 2.60 (1H, dd, $J = 6.4$, 13.2 Hz), 3.14-3.21 (1H, m), 3.26 (1H, dd, $J = 9.6$, 14.4 Hz), 3.39 (3H, s), 3.64-3.74 (1H, m), 3.83 (3H, s), 7.24-7.28 (1H, m), 7.32-7.46 (7H, m), 7.71 (2H, d, $J = 8.0$ Hz);
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 40.9, 42.5, 45.2, 52.6, 68.4, 79.0, 126.7, 127.5, 128.0, 128.1, 128.5, 128.7, 136.9, 143.0, 169.3, 171.4.

diisopropyl 2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (7aa) (table 1, run 2):

81% yield (102.8 mg, 0.236 mmol) (major:minor = 77:23) by procedure D from 1a (0.605 mmol) and 3a (0.291 mmol), reaction time: 10 h.

White solid; mp: 84-85 °C.
$^1$H NMR (400 MHz, CDCl$_3$) δ 0.82 (3H×0.32, d, $J = 6.4$ Hz), 0.85 (3H, d, $J = 6.4$ Hz), 0.95 (3H×0.32, d, $J = 6.4$ Hz), 1.16 (3H, d, $J = 6.4$ Hz), 1.26 (3H, d, $J = 6.4$ Hz), 1.31 (3H×0.32, d, $J = 6.0$ Hz), 1.32 (3H, d, $J = 6.4$ Hz), 1.33 (3H×0.32, d, $J = 6.0$ Hz), 2.48 (1H×0.32, dd, $J = 9.2$, 14.4 Hz), 2.58-2.61 (1H×0.32, m), 2.65 (1H, dd, $J = 8.4$, 13.6 Hz), 2.81-2.94 (3H, m), 3.13-3.25 (3H×0.32, m), 3.46-3.55 (1H, m), 3.62-3.71 (1H×0.32, m), 4.71 (1H×0.32, septet, $J = 6.0$ Hz), 4.92 (1H, septet, $J = 6.4$ Hz), 5.11-5.20 (1H×0.32, m), 5.16 (1H, septet, $J = 6.4$ Hz), 7.21 (1H, t, $J = 7.2$ Hz), 7.27-7.54 (9H, m + 8H×0.32, m), 7.78 (2H×0.32, d, $J = 6.8$ Hz).

ESIHRMS: Found: m/z 408.2173. Calcd for C$_{25}$H$_{30}$NO$_4$: (M-N$_2$+H)$^+$ 408.2175.
The major isomer could be recrystallized from CH$_2$Cl$_2$/hexane as a colorless crystal.

diisopropyl $(2S^*,4R^*)$-2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (7aa_major):

Colorless crystal; mp: 84-85 °C (CCDC: 1519383).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.85 (3H, d, $J = 6.4$ Hz), 1.16 (3H, d, $J = 6.4$ Hz), 1.26 (3H, d, $J = 6.4$ Hz), 1.32 (3H, d, $J = 6.4$ Hz), 2.65 (1H, dd, $J = 8.4$, 13.6 Hz), 2.81-2.94 (3H, m), 3.46-3.55 (1H, m), 4.92 (1H, septet, $J = 6.4$ Hz), 5.16 (1H, septet, $J = 6.4$ Hz), 7.21 (1H, t, $J = 7.2$ Hz), 7.30-7.42 (7H, m), 7.53 (2H, d, $J = 7.6$ Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 20.9, 21.3, 21.4, 21.6, 39.7, 43.0, 48.0, 69.2, 69.4, 69.7, 78.0, 126.4, 127.2, 127.6, 127.8, 128.1, 128.6, 139.3, 144.4, 169.4, 169.6.

dibenzyl -2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (8aa) (table 1, run 3):

77% yield (120.4 mg, 0.226 mmol) (major:minor = 71:29) (as an inseparable major/minor-mixture) by procedure D from 1a (0.577 mmol) and 4a (0.293 mmol); reaction time: 10 h.

Pale yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.50 (1H×0.41, dd, $J = 8.8$, 14.4 Hz), 2.58 (1H, dd, $J = 6.4$, 14.0 Hz + 1H×0.41, m), 2.83-2.95 (2H, m), 3.07-3.21 (1H, dd, $J = 10.8$, 14.0 Hz + 1H×0.41, m), 3.31 (1H×0.41, dd, $J = 10.0$, 14.4 Hz), 3.56-3.71 (1H, m + 1H×0.41, m), 4.77 (2H×0.41, s), 4.96 (2H, s), 5.12-5.23 (2H, m + 2H×0.41, m), 6.94 (2H×0.41, d, $J = 7.2$ Hz), 6.98 (2H, d, $J = 6.8$ Hz), 7.23-7.40 (16H, m + 16H×0.41, m), 7.45 (2H, d, $J = 6.8$ Hz), 7.62 (2H×0.41, d, $J = 7.6$ Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) (for major-8aa) $\delta$ 39.8, 43.0, 47.2, 67.3, 67.5, 69.4, 78.4, 126.5, 127.5 (overlapped), 127.6,
128.1, 128.2, 128.3 (overlapped), 128.4 (overlapped), 128.5, 128.7, 134.7, 135.0, 138.0, 144.4, 169.0, 169.5.

ESIHRMS: Found: m/z 504.2172. Calcd for C_{33}H_{30}NO_{4}: (M-N_2+H)^+ 504.2175.

5.3. Typical procedure E: synthesis of 9aa (Table 1, run 7)

To a stirred solution of 5a (218 mg, 0.493 mmol) and vinyl azide 1a (144 mg, 0.993 mmol) in CH_{2}Cl_{2} (0.8 mL) and MeNO_{2} (0.2 mL) was added Sc(OTf)_{3} (37.6 mg, 0.0764 mmol) at 0 °C under an Ar atmosphere. The solution was stirred at 0 °C for 24 h and then quenched with saturated aqueous NaHCO_{3}. The mixture was extracted with CH_{2}Cl_{2} and the combined extracts were washed with brine, dried over MgSO_{4}, and concentrated in vacuo. The resulting crude material was purified by flash column chromatography (hexane : Et_{2}O = 100:1 to 90:1) to yield 9aa (275 mg, 0.468 mmol) in 95% yield as a mixture of diastereomer (major:minor = 88:12, which was determined by ^{1}H NMR analysis).

**bis(2,6-dimethylbenzyl)-2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (9aa)**

White solid; mp: 100-101 °C.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.02 (6H×0.14, s), 2.04 (6H, s), 2.15 (6H, s + 6H×0.14, s), 2.45-2.57 (2H×0.14, m + 1H, dd, $J = 6.8$, 14.0 Hz), 2.80-2.91 (2H, m), 3.03 (1H, dd, $J = 10.4$, 14.0 Hz), 3.13-3.20 (1H×0.14, m), 3.28 (1H×0.14, dd, $J = 10.0$, 14.0 Hz), 3.57-3.66 (1H, m + 1H×0.14, m), 4.85 (1H×0.14, d, $J = 12.0$ Hz), 4.93 (1H, d, $J = 12.0$ Hz), 5.08-5.14 (2H+1H×0.14, m), 5.29 (1H, d, $J = 12.0$ Hz), 5.34 (1H×0.14, d, $J = 12.0$ Hz), 6.92-7.38 (16H, m + 14H×0.14, m), 7.49 (2H×0.14, d, $J = 7.6$ Hz).

ESIHRMS: Found: m/z 560.2806. Calcd for C$_{37}$H$_{38}$NO$_4$: (M-N$_2$+H)$^+$ 560.2801.

The major isomer could be recrystallized from CH$_2$Cl$_2$/hexane as a colorless crystal.

**bis(2,6-dimethylbenzyl)**

**$(2S*,4R*)$-2-azido-2,4-diphenyleclopentane-1,1-dicarboxylate (9aa_major):**

Colorless crystal; mp: 100-101 °C (CCDC 1519478).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.04 (6H, s), 2.16 (6H, s), 2.52 (1H, dd, $J = 6.8$, 14.4 Hz), 2.79-2.91 (2H, m), 3.03 (1H, dd, $J = 10.4$, 14.4 Hz), 3.57-3.66 (1H, m), 4.94 (1H, d, $J = 12.0$ Hz), 5.08-5.14 (2H, m), 5.29 (1H, d, $J = 12.0$ Hz), 6.93 (2H, d, $J = 7.6$ Hz), 6.99 (2H, d, $J = 7.6$ Hz), 7.07-7.22 (6H, m), 7.27-7.31 (4H, m), 7.37 (2H, d, $J = 7.2$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 19.2, 19.3, 39.9, 43.2, 47.3, 62.2, 62.4, 69.8, 78.3, 126.4, 127.3, 127.4, 127.9, 128.09, 128.12 (overlapped), 128.2, 128.7, 128.8, 130.7, 131.1, 138.2, 138.4, 138.5, 144.4, 169.4, 170.1.
bis(2,6-dimethylbenzyl)

(2S*,4R*)-2-azido-4-phenyl-2-(p-tolyl)cyclopentane-1,1-dicarboxylate (9ba) (scheme 2)

82% yield (246 mg, 0.408 mmol) (major:minor = 86 : 14) (as an inseparable major/minor-mixture) by procedure E from 1b (0.993 mmol) and 5a (0.496 mmol) with Sc(OTf)₃ (0.101 mmol); reaction time: 24 h.

Pale yellow solid; mp: 114-115 °C.

^1H NMR (400 MHz, CDCl₃) δ 2.02 (6H×0.16, s), 2.04 (6H, s), 2.16 (6H, s), 2.18 (6H×0.16, s), 2.27 (3H×0.16, s), 2.29 (3H, s), 2.52 (1H, dd, J = 6.8, 14.4 Hz), 2.45-2.55 (2H×0.16, m), 2.77-2.89 (2H, m), 3.01 (1H, dd, J = 10.4, 14.4 Hz), 3.09-3.16 (1H×0.16, m), 3.25 (1H×0.16, dd, J = 10.0, 14.0 Hz), 3.56-3.65 (1H, m + 1H×0.16, m), 4.84 (1H×0.16, d, J = 12.0 Hz), 4.93 (1H, d, J = 12.0 Hz), 4.92-4.95 (1H×0.16, m), 5.08-5.13 (2H, m), 5.28 (1H, d, J = 12.0 Hz), 5.33 (1H×0.16, d, J = 12.4 Hz), 6.92-7.38 (15H, m + 15H×0.16, m); ^13C NMR (100 MHz, CDCl₃) (for major-9ba) δ 19.1, 19.3, 20.9, 39.9, 43.2, 47.2, 62.1, 62.4, 69.8, 78.2, 126.4, 127.2, 127.5, 128.07, 128.13, 128.3, 128.6, 128.7, 128.8, 130.7, 131.2, 135.1, 137.6, 138.4, 138.5, 144.5, 169.4, 170.1.

ESIHRMS: Found: m/z 574.2953. Calcd for C₅₈H₄₀N₂O₄: (M-N₂+H)⁺ 574.2957.
bis(2,6-dimethylbenzyl)

(2S*,4R*)-2-azido-2-(naphthalen-2-yl)-4-phenylcyclopentan-1,1-dicarboxylate (9ca) (scheme 2)

95% yield (297 mg, 0.466 mmol) \( (\text{major}:\text{minor} = 91:9) \) by procedure E from 1c (1.00 mmol) and 5a (0.491 mmol) with Sc(OTf)\(_3\) (0.102 mmol); reaction time: 26 h.

(Colorless crystal was obtained as a mixture of diastereomer in the same ratio from recrystallization in CH\(_2\)Cl\(_2\)/hexane, and the structure of 9ca\_major was secured by X-ray crystallographic analysis. mp: 123-124 °C.) (CCDC 1519384)

White solid; mp: 123-124 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \)

9.0 (6H \( \times \) 0.10, s), 1.87 (6H, s), 2.12 (6H, s), 2.17 (6H \( \times \) 0.10, s), 2.55 (1H \( \times \) 0.10, dd, \( J = 9.2, 14.4 \) Hz), 2.63 (1H, dd, \( J = 6.4, 14.0 \) Hz + 1H \( \times \) 0.10, m), 2.86-2.97 (2H, m), 3.21 (1H, dd, \( J = 10.4, 14.0 \) Hz), 3.28-3.37 (2H \( \times \) 0.10, m), 3.65-3.74 (1H, m + 1H \( \times \) 0.10, m), 4.71 (1H \( \times \) 0.10, d, \( J = 12.0 \) Hz), 4.86 (1H, d, \( J = 12.0 \) Hz + 1H \( \times \) 0.10, m), 5.08-5.13 (2H, m + 1H \( \times \) 0.10, m), 5.29 (1H, d, \( J = 12.0 \) Hz), 5.37 (1H \( \times \) 0.10, d, \( J = 12.0 \) Hz), 6.80-6.83 (2H, d, \( J = 7.6 \) Hz + 2H \( \times \) 0.10, m), 6.98-7.05 (3H, m + 3H \( \times \) 0.10, m), 7.14-7.64 (11H, m + 11H \( \times \) 0.10, m), 7.72-7.85 (1H, m + 1H \( \times \) 0.10, m), 7.87 (1H, s), 7.95 (1H \( \times \) 0.10, s); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (for \textit{major}-9ca) \( \delta \)

19.0, 19.3, 40.0, 43.3, 47.3, 62.2, 62.5, 70.0, 78.4, 125.1, 126.1, 126.5 (overlapped), 126.9, 127.2, 127.5, 127.8, 128.0, 128.2, 128.6, 128.69, 128.71, 128.8, 130.5, 131.1, 132.6, 132.7, 135.5, 138.3, 138.5, 144.5, 169.4, 170.1.

ESIHRMS: Found: m/z 610.2960. Calcd for C\(_{41}\)H\(_{40}\)NO\(_4\): (M-N\(_2\)+H)\(^+\) 610.2957.
bis(2,6-dimethylbenzyl) 
(2S*,4R*)-2-azido-2-(4-bromophenyl)-4-phenylcyclopentane-1,1-dicarboxylate 
(9da) (scheme 2) 

89% yield (294 mg, 0.442 mmol) \(\text{major:minor} = 90:10\) (as an inseparable \text{major}/\text{minor}-mixture) by procedure E from 1d (0.981 mmol) and 5a (0.494 mmol) with Sc(OTf)\(_3\) (0.102 mmol); reaction time: 32 h.
White solid; mp: 154-155 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.05 (6H×0.11, s), 2.09 (6H, s), 2.15 (6H, s), 2.18 (6H×0.11, s), 2.44-2.50 (1H, dd, \(J = 5.6, 14.0\) Hz + 2H×0.11, m), 2.78-2.88 (2H, m), 3.09-3.15 (1H, dd, \(J = 10.8, 14.0\) Hz + 1H×0.11, m), 3.28 (1H×0.11, dd, \(J = 10.4, 14.4\) Hz), 3.63-3.72 (1H, m + 1H×0.11, m), 4.89-5.09 (3H, m + 3H×0.11, m), 5.33 (1H, d, \(J = 11.6\) Hz), 5.38 (1H×0.11, d, \(J = 12.0\) Hz), 6.95-7.36 (15H, m + 15H×0.11, m).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (for \text{major-9da}) \(\delta\) 19.2, 19.3, 39.9, 43.0, 46.4, 62.1, 62.5, 69.8, 77.9, 122.2, 126.5, 127.4, 128.19, 128.21, 128.7, 128.88, 128.93, 129.4, 130.5, 131.0 (overlapped), 136.7, 138.3, 138.5, 144.3, 168.8, 169.7.

ESIHRMS: Found: m/z 660.1723. Calcd for C\(_{37}\)H\(_{36}\)NO\(_4\)Na\(^{79}\)Br: (M-N\(_2\)+Na\(^+\)) 660.1725.
bis(2,6-dimethylbenzyl)

(2R*,4R*)-2-azido-2-phenethyl-4-phenylcyclopentane-1,1-dicarboxylate (9ea) (scheme 2)

73% yield (221 mg, 0.359 mmol) (major:minor = 71:29) (as an inseparable major/minor-mixture) by procedure E from 1e (1.00 mmol) and 5a (0.492 mmol) with Sc(OTf)₃ (0.154 mmol); reaction time: 38 h.

White solid; mp: 91-92 °C.

¹H NMR (400 MHz, C₆D₆) δ 2.00 (6H×0.41, s), 2.06 (6H, s), 2.12 (6H, s), 2.18 (6H×0.41, s), 2.16-2.90 (8H, m + 7H×0.41, m), 3.32-3.48 (1H, m + 2H×0.41, m), 4.78-4.99 (2H, m + 2H×0.41, m), 5.12 (1H, d, J = 12.0 Hz), 5.20-5.26 (1H, m + 2H×0.41, m), 6.73-7.16 (14H, m + 16H×0.41, m), 7.25 (2H, d, J = 7.6 Hz);¹³C NMR (100 MHz, CDCl₃) (for major-9ea) δ 19.4, 19.5, 31.2, 36.5, 40.0, 41.7, 43.4, 62.1, 62.4, 69.1, 75.5, 126.1, 126.5, 127.5, 128.2, 128.3, 128.4, 128.5, 128.6, 130.9, 131.3, 138.3 (overlapped), 138.5 (overlapped), 141.2, 144.5, 168.9, 169.7.

ESIHRMS: Found: m/z 588.3110. Calcd for C₃₉H₄₂NO₄: (M-N₂+H)⁺ 588.3114.

bis(2,6-dimethylbenzyl)(2S*,4R*)-2-azido-2-(4-bromophenyl)-4-(4-methoxyphen yl)cyclopentane-1,1-dicarboxylate (9db) (scheme 2)
94% yield (325 mg, 0.468 mmol) (\textit{major}:\textit{minor} = 86:14) (as an inseparable \textit{major}:\textit{minor}-mixture) by procedure E from \textbf{1d} (1.00 mmol) and \textbf{5b} (0.500 mmol) with Sc(OTf)$_3$ (0.0752 mmol).; reaction time: 6 h.

White solid; mp: 65-66 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.05 (6H×0.16, s), 2.09 (6H, s), 2.15 (6H, s), 2.18 (6H×0.16, s), 2.42 (1H, dd, $J = 6.0$, 14.4 Hz), 2.39-2.44 (2H×0.16, m), 2.79 (2H, d, $J = 9.2$ Hz), 3.07 (1H, dd, $J = 10.8$, 14.4 Hz), 3.04-3.11 (1H×0.16, m), 3.24 (1H×0.16, dd, $J = 10.0$, 13.6 Hz), 3.57-3.66 (1H, m + 1H×0.16, m), 3.78 (3H, s), 3.80 (3H×0.16, s), 4.89-5.09 (3H, m + 3H×0.16, m), 5.32-5.38 (1H, d, $J = 12.0$ Hz + 1H×0.16, m), 6.82-6.84 (2H, m + 2H×0.16, m), 6.95-7.32 (12H, m + 12H×0.16, m).; $^{13}$C NMR (100 MHz, CDCl$_3$) (for \textit{major}-\textbf{9db}) $\delta$ 19.2, 19.3, 39.1, 43.2, 46.6, 55.2, 62.1, 62.5, 69.8, 77.8, 114.1, 122.2, 128.2 (overlapped), 128.3, 128.87, 128.91, 129.3, 129.9, 130.5, 131.0, 136.3, 136.8, 138.3, 138.5, 158.2, 168.9, 169.7.

ESIHRMS: Found: m/z 668.2009. Calcd for C$_{38}$H$_{39}$NO$_5$Br: (M-N$_2$+H)$^+$ 668.2012.

\textbf{bis(2,6-dimethylbenzyl)}

(2$S^*$,4$R^*$)-2-azido-2-(4-bromophenyl)-4-(4-tolyl)cyclopentane-1,1-dicarboxylate (\textbf{9dc}) (scheme 2)

86% yield (293 mg, 0.430 mmol) (\textit{major}:\textit{minor} = 91:9) (as an inseparable \textit{major}:\textit{minor}-mixture) by procedure E from \textbf{1d} (1.01 mmol) and \textbf{5c} (0.500 mmol) with Sc(OTf)$_3$ (0.15 mmol).; reaction time: 24 h.

Pale yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.05 (6H×0.10, s), 2.10 (6H, s), 2.16 (6H, s), 2.19 (6H×0.10, s), 2.26-2.40 (4H, m + 5H×0.10, m), 2.71 (1H, dd, $J = 8.8$, 14.0 Hz), 2.84 (1H, dd, $J = 10.8$, 14.0 Hz), 3.14 (1H, dd, $J = 10.8$, 14.0 Hz), 3.08-3.29 (2H×0.10, m), 3.88-3.97 (1H, m + 1H×0.10, m), 4.88-5.11 (3H, m + 3H×0.10, m), 5.34 (1H, d, $J = 14.6$ Hz).
11.6 Hz), 5.38 (1H×0.10, d, J = 12.0 Hz), 6.96-7.23 (13H, m + 10H×0.10, m), 7.31-7.33 (3H×0.10, m), 7.42-7.46 (1H, m + 1H×0.10, m); 13C NMR (100 MHz, CDCl₃) (for major-9de) δ 19.2, 19.3, 19.9, 35.0, 41.8, 45.6, 62.1, 62.5, 69.8, 77.8, 122.2, 125.6, 126.3, 126.8, 128.18, 128.24, 128.9, 129.0, 129.5, 130.2, 130.6, 131.0, 131.1, 135.8, 136.6, 138.3, 138.5, 142.2, 168.8, 169.7.


bis(2,6-dimethylbenzyl)(2S*,4R*)-2-azido-2-(4-bromophenyl)-4-(naphthalen-2-yl)cyclopentane-1,1-dicarboxylate (9dd) (scheme 2)

89% yield (318 mg, 0.444 mmol) (major:minor = 88:12) by procedure E from 1d (1.00 mmol) and 5d (0.501 mmol) with Sc(OTf)₃ (0.0752 mmol); reaction time: 19 h. Pale yellow solid; mp: 175-176 °C. ¹H NMR (400 MHz, CDCl₃) δ 2.06 (6H×0.14, s), 2.10 (6H, s), 2.15 (6H, s), 2.19 (6H×0.14, s), 2.54-2.60 (1H, dd, J = 6.0, 14.4 Hz + 2H×0.14, m), 2.88 (1H, dd, J = 8.8, 14.0 Hz), 2.97 (1H, dd, J = 10.4, 14.0 Hz), 3.17-3.38 (1H, dd, J = 10.8, 14.4 Hz + 2H×0.14, m), 3.82-3.91 (1H, m + 1H×0.14, m), 4.90-5.11 (3H, m + 3H×0.14, m), 5.35 (1H, d, J = 11.6 Hz), 5.39 (1H×0.14, d, J = 11.6 Hz), 6.96-7.81 (17H, m + 17H×0.14, m); ESIHRMS: Found: m/z 738.1943. Calcd for C₄₁H₃₈N₃O₄Na⁷⁹Br: (M+Na)⁺ 738.1943.

The major isomer was isolated partially for characterization. major-9dd: ¹H NMR (400 MHz, CDCl₃) δ 2.10 (6H, s), 2.15 (6H, s), 2.19 (6H×0.14, s), 2.57 (1H, dd, J = 6.0, 14.4 Hz), 2.88 (1H, dd, J = 8.8, 14.0 Hz), 2.97 (1H, dd, J = 10.4, 14.0 Hz), 3.20 (1H, dd, J = 10.8, 14.4 Hz), 3.82-3.91 (1H, m), 5.01-5.11 (3H, m), 5.35 (1H, d, J = 11.6 Hz), 6.96-7.01 (4H, m), 7.11-7.25 (6H, m), 7.41-7.50 (3H, m), 7.71-7.81 (4H, m); ¹³C NMR (100 MHz, CDCl₃) δ 19.2, 19.3, 40.0, 42.8, 46.2, 62.1, 62.5, 69.8, 77.9, 89% yield (318 mg, 0.444 mmol) (major:minor = 88:12) by procedure E from 1d (1.00 mmol) and 5d (0.501 mmol) with Sc(OTf)₃ (0.0752 mmol); reaction time: 19 h. Pale yellow solid; mp: 175-176 °C. ¹H NMR (400 MHz, CDCl₃) δ 2.06 (6H×0.14, s), 2.10 (6H, s), 2.15 (6H, s), 2.19 (6H×0.14, s), 2.54-2.60 (1H, dd, J = 6.0, 14.4 Hz + 2H×0.14, m), 2.88 (1H, dd, J = 8.8, 14.0 Hz), 2.97 (1H, dd, J = 10.4, 14.0 Hz), 3.17-3.38 (1H, dd, J = 10.8, 14.4 Hz + 2H×0.14, m), 3.82-3.91 (1H, m + 1H×0.14, m), 4.90-5.11 (3H, m + 3H×0.14, m), 5.35 (1H, d, J = 11.6 Hz), 5.39 (1H×0.14, d, J = 11.6 Hz), 6.96-7.81 (17H, m + 17H×0.14, m); ESIHRMS: Found: m/z 738.1943. Calcd for C₄₁H₃₈N₃O₄Na⁷⁹Br: (M+Na)⁺ 738.1943.

The major isomer was isolated partially for characterization.

major-9dd: ¹H NMR (400 MHz, CDCl₃) δ 2.10 (6H, s), 2.15 (6H, s), 2.57 (1H, dd, J = 6.0, 14.4 Hz), 2.88 (1H, dd, J = 8.8, 14.0 Hz), 2.97 (1H, dd, J = 10.4, 14.0 Hz), 3.20 (1H, dd, J = 10.8, 14.4 Hz), 3.82-3.91 (1H, m), 5.01-5.11 (3H, m), 5.35 (1H, d, J = 11.6 Hz), 6.96-7.01 (4H, m), 7.11-7.25 (6H, m), 7.41-7.50 (3H, m), 7.71-7.81 (4H, m); ¹³C NMR (100 MHz, CDCl₃) δ 19.2, 19.3, 40.0, 42.8, 46.2, 62.1, 62.5, 69.8, 77.9, 89% yield (318 mg, 0.444 mmol) (major:minor = 88:12) by procedure E from 1d (1.00 mmol) and 5d (0.501 mmol) with Sc(OTf)₃ (0.0752 mmol); reaction time: 19 h. Pale yellow solid; mp: 175-176 °C. ¹H NMR (400 MHz, CDCl₃) δ 2.06 (6H×0.14, s), 2.10 (6H, s), 2.15 (6H, s), 2.19 (6H×0.14, s), 2.54-2.60 (1H, dd, J = 6.0, 14.4 Hz + 2H×0.14, m), 2.88 (1H, dd, J = 8.8, 14.0 Hz), 2.97 (1H, dd, J = 10.4, 14.0 Hz), 3.17-3.38 (1H, dd, J = 10.8, 14.4 Hz + 2H×0.14, m), 3.82-3.91 (1H, m + 1H×0.14, m), 4.90-5.11 (3H, m + 3H×0.14, m), 5.35 (1H, d, J = 11.6 Hz), 5.39 (1H×0.14, d, J = 11.6 Hz), 6.96-7.81 (17H, m + 17H×0.14, m); ESIHRMS: Found: m/z 738.1943. Calcd for C₄₁H₃₈N₃O₄Na⁷⁹Br: (M+Na)⁺ 738.1943.
bis(2,6-dimethylbenzyl)
(2S*,4R*)-2-azido-2-(4-bromophenyl)-4-(thiophen-2-yl)cyclopentane-1,1-dicarboxylate (9de) (scheme 2)

\[
\text{\begin{center}
\includegraphics[width=0.2\textwidth]{image}
\end{center}}
\]

92% yield (310 mg, 0.461 mmol) \((major:minor = 88:12)\) (as an inseparable \(major/minor\)-mixture) by procedure E from 1d (1.01 mmol) and 5e (0.501 mmol) with Sc(OTf)$_3$ (0.0752 mmol); reaction time: 4 h.
Pale yellow solid; mp: 146-147 °C.

$^1$H NMR (400 MHz, CDCl$_3$) \(\delta 2.04 (6H \times 0.13, s), 2.08 (6H, s), 2.10 (6H, s), 2.18 (6H \times 0.13, s), 2.45 (1H, dd, \(J = 4.4, 14.4\) Hz), 2.50-2.59 (2H \times 0.13, m), 2.83-2.94 (2H, m), 3.09-3.15 (1H \times 0.13, m), 3.29 (1H, dd, \(J = 10.8, 14.4\) Hz), 3.26-3.34 (1H \times 0.13, m), 3.91-3.98 (1H \times 0.13, m), 4.02-4.09 (1H, m), 4.85-5.06 (3H, m + 3H \times 0.13, m), 5.31 (1H, d, \(J = 11.6\) Hz), 5.37 (1H \times 0.13, d, \(J = 12.0\) Hz), 6.88-7.28 (13H, m + 13H \times 0.13, m).\)

$^{13}$C NMR (100 MHz, CDCl$_3$) (for \textit{major-9de}) \(\delta 19.3\) (overlapped), 35.0, 43.6, 46.1, 62.0, 62.7, 69.8, 77.7, 122.4, 123.7, 123.8, 126.9, 128.2, 128.3, 128.9, 129.0, 129.4, 130.5, 131.1, 135.9, 138.3, 138.5, 149.1, 168.4, 169.6.
ESIHRMS: Found: m/z 644.1465. Calcd for C$_{35}$H$_{35}$NO$_4$S$_7$Br: (M+H)$^+$ 644.1470.
bis(2,6-dimethylbenzyl)

\((2S^*,4R^*)\)-2-azido-2-phenyl-4-((E)-styrly)cyclopentane-1,1-dicarboxylate (9df)

(scheme 2)

\[
\begin{array}{c}
\text{Br} \\
\text{N} \\
\text{O} \\
\text{Ph} \\
\text{O} \\
\text{CO} \\
\text{CO}
\end{array}
\]

83% yield (289 mg, 0.417 mmol) \((major:minor = 90:10)\) by procedure E from \textbf{1d} (1.00 mmol) and \textbf{5f} (0.501 mmol) with Sc(OTf)\(_3\) (0.075 mmol).; reaction time: 4 h.

Pale yellow solid; mp: 147-148 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.06 (6H×0.11, s), 2.08 (6H, s), 2.12 (6H, s), 2.15 (6H×0.11, s), 2.22-2.37 (1H, dd, \(J = 4.0, 14.4\) Hz + 2H×0.11, m), 2.56 (1H, dd, \(J = 8.4, 14.4\) Hz), 2.71 (1H, dd, \(J = 8.8, 14.4\) Hz), 2.84-2.90 (1H×0.11, m), 2.99-3.12 (1H, dd, \(J = 10.8, 14.4\) Hz + 1H×0.11, m), 3.27-3.32 (1H, m + 1H×0.11, m), 4.87-5.06 (3H, m + 3H×0.11, m), 5.29-5.34 (1H, d, \(J = 11.6\) Hz + 1H×0.11, m), 6.22-6.32 (1H, dd, \(J = 8.4, 16.0\) Hz + 1H×0.11, m), 6.39 (1H, d, \(J = 16.0\) Hz), 6.47 (1H×0.11, d, \(J = 15.6\) Hz), 6.95-7.35 (15H, m + 15H×0.11, m).

ESIHRMS: Found: m/z 664.2065. Calcd for C\(_{39}\)H\(_{39}\)NO\(_7\)Br: (M-N\(_2\)+H)\(^+\) 664.2062.

The major isomer was isolated partially for characterization.

\textit{major-9df}: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.08 (6H, s), 2.12 (6H, s), 2.24 (1H, dd, \(J = 4.0, 14.4\) Hz), 2.56 (1H, dd, \(J = 8.4, 14.4\) Hz), 2.71 (1H, dd, \(J = 8.8, 14.4\) Hz), 3.09 (1H, dd, \(J = 10.8, 14.4\) Hz), 3.25-3.32 (1H, m), 4.93-5.06 (3H, m), 5.30 (1H, d, \(J = 11.6\) Hz), 6.24 (1H, dd, \(J = 8.4, 16.0\) Hz), 6.39 (1H, d, \(J = 16.0\) Hz), 6.96 (2H, d, \(J = 7.6\) Hz), 7.00 (2H, d, \(J = 7.6\) Hz), 7.10-7.21 (7H, m), 7.28-7.35 (4H, m); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 19.23, 19.25, 37.4, 41.1, 43.7, 61.9, 62.5, 69.6, 77.8, 122.2, 126.2, 127.3, 128.16, 128.22, 128.5, 128.8, 128.9, 129.3, 129.9, 130.5, 131.0, 131.1, 133.8, 136.2, 137.0, 138.3, 138.4, 168.7, 169.8.
bis(2,6-dimethylbenzyl)
(2S*,4R*)-2-azido-2-(4-bromophenyl)-4-(1,3-dioxisoindolin-2-yl)cyclopentane-1,1-dicarboxylate (9dg) (scheme 2)

**Scheme 2**

83% yield (307 mg, 0.417 mmol) (major:minor = 78:22) (as an inseparable major/minor-mixture) by procedure E from 1d (1.00 mmol) and 5g (0.501 mmol) with Sc(OTf)₃ (0.0752 mmol); reaction time: 6 h.

White solid; mp: 65-66 °C.

¹H NMR (400 MHz, CDCl₃) δ 2.08 (6H, s), 2.11 (6H, s), 2.25 (6H×0.28, s), 2.27 (6H×0.28, s), 2.59 (1H, dd, J = 8.0, 13.6 Hz), 2.85-2.91 (1H, dd, J = 5.6, 14.8 Hz + 1H×0.28, m), 3.12 (1H×0.28, d, J = 7.2 Hz), 3.20 (1H, dd, J = 11.6, 14.8 Hz), 3.31 (1H, dd, J = 11.6, 13.6 Hz), 3.40 (1H×0.28, dd, J = 10.4, 14.4 Hz), 3.78-3.84 (1H×0.28, m), 4.83 (1H, d, J = 11.6 Hz), 5.03-5.24 (2H, m + 4H×0.28, m), 5.36 (1H, d, J = 11.6 Hz), 5.43-5.52 (1H, m + 1H×0.28, m), 6.95-7.22 (10H, m + 10H×0.28, m), 7.72-7.77 (2H, m + 2H×0.28, m), 7.84-7.88 (2H, m + 2H×0.28, m). ᵃ¹³C NMR (100 MHz, CDCl₃) (for major-9dg) δ 19.2, 19.3, 38.0, 39.9, 45.9, 61.8, 62.8, 69.0, 76.4, 123.3, 128.1, 128.3, 128.8, 129.0, 129.8, 130.4, 130.9, 131.1, 131.8, 134.1, 134.3, 136.0, 138.3, 138.5, 167.6, 168.0, 169.2.

6. Derivatization of azidocyclopentane 6aa (Scheme 3)

6.1. Conversion of 6aa to cyclopentene 10

```
6aa
```

To a stirred solution of 6aa (major:minor = 53:47) (72.7 mg, 0.192 mmol) and water (50 µL, 2.78 mmol) in DMSO (2.2 mL) was added LiCl (30.4 mg, 0.717 mmol) at 130 °C under a N₂ atmosphere. After stirring at 130 °C for 29 hour, the mixture was diluted with water and the organic materials were extracted thrice with ethyl acetate. The combined organic extracts were washed with water and brine, dried over MgSO₄, filtered and concentrated in vacuo. The resulting crude material was purified by flash column chromatography (hexane:Et₂O = 80:1) to yield 10 (52.1 mg, 0.187 mmol) in 97% yield as a yellow oil.

**methyl 2,4-diphenylcyclopent-1-ene-1-carboxylate (10)**

```
Ph
Ph
\[\text{CO}_2\text{Me}\]
```

¹H NMR (400 MHz, CDCl₃) δ 2.96-3.08 (2H, m), 3.25-3.33 (2H, m), 3.59-3.68 (1H, m), 3.64 (3H, s), 7.20-7.40 (10H, m); ¹³C NMR (100 MHz, CDCl₃) δ 41.7, 42.9, 47.8, 51.2, 126.3, 126.8, 127.6, 127.79, 127.82, 128.2, 128.6, 136.4, 145.4, 152.4, 166.2.; ESIHRMS: Found: m/z 279.1383. Calcd for C₁₉H₁₉O₂: (M+H)⁺ 279.1385.

6.2. Conversion of 6aa to cyclopentene 11

```
6aa
```

To a stirred solution of 6aa (major:minor = 53:47) (76.4 mg, 0.201 mmol) in DCE (2 mL) was added TfOH (17.8 µL, 0.203 mmol) at 0 °C under a N₂ atmosphere. After stirring at 0 °C for 1 h, the mixture was quenched with saturated aqueous NaHCO₃ and the organic materials were extracted thrice with CH₂Cl₂. The combined extracts were washed with brine, dried over MgSO₄, and concentrated in vacuo. The resulting
crude material was purified by flash column chromatography (hexane:ethyl acetate = 20:1) to yield 11 (63.4 mg, 0.189 mmol) in 94% yield as a white solid.

dimethyl 2,4-diphenylcyclopent-2-ene-1,1-dicarboxylate (11)

\[
\begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array}
\quad
\begin{array}{c}
\text{CO}_2\text{Me} \\
\text{CO}_2\text{Me}
\end{array}
\]

mp: 64-65 °C.

\(^1\text{H NMR} (500 \text{ MHz, CDCl}_3) \delta 2.57 (1\text{H, dd, } J = 8.5, 13.5 \text{ Hz}), 3.24 (1\text{H, dd, } J = 7.5, 13.5 \text{ Hz}), 3.64 (3\text{H, s}), 3.78 (3\text{H, s}), 4.16-4.19 (1\text{H, m}), 6.36 (1\text{H, d, } J = 2.0 \text{ Hz}), 7.24-7.35 (8\text{H, m}), 7.48 (2\text{H, d, } J = 7.0 \text{ Hz}); \ ^{13}\text{C NMR} (125 \text{ MHz, CDCl}_3) \delta 46.0, 49.1, 52.5, 52.7, 67.9, 126.8, 127.3, 127.4, 127.6, 128.0, 128.6, 134.8, 136.6, 142.8, 143.5, 171.5, 171.6.

ESIHRMS: Found: m/z 337.1444. Calcd for C\textsubscript{21}H\textsubscript{21}O\textsubscript{4}: (M+H)\textsuperscript{+} 337.1440.
6.3. Conversion of 6aa to tetrahydropyridines 12 and 13

To a stirred solution of 6aa (major:minor = 53:47) (76.1 mg, 0.201 mmol) in DCE (2 mL) was added SnCl₄ (28.5 µL, 0.244 mmol) at 23 °C under a N₂ atmosphere. After stirring at 23 °C for 14 h, the reaction was allowed to warm to 60 °C for complete conversion of 6aa. After stirring at 60 °C for 2 h, the mixture was cooled down to 0 °C and quenched with saturated aqueous NaHCO₃. The organic materials were extracted thrice with CH₂Cl₂ and the combined extracts were washed with brine, dried over MgSO₄, and concentrated in vacuo. The resulting crude material was purified by flash column chromatography (hexane:ethyl acetate = 50:1 to 10:1) to yield 12 (27.3 mg, 0.0777 mmol) in 39% yield as a sticky yellow oil and 13 (20.3 mg, 0.0692 mmol) in 34% yield as a yellow oil.

**dimethyl 2,5-diphenyl-5,6-dihydropyridine-3,3(4H)-dicarboxylate (12)**

![Diagram of 12]

$^1$H NMR (500 MHz, CDCl₃) δ 2.52-2.58 (1H, m), 2.77-2.80 (1H, m), 2.84-2.91 (1H, m), 3.48 (3H, s), 3.79 (1H, dd, J = 11.0, 19.0 Hz), 3.88 (3H, s), 4.38 (1H, dd, J = 4.5, 19.0 Hz), 7.25-7.29 (3H, m), 7.33-7.38 (5H, m), 7.64-7.66 (2H, m); $^{13}$C NMR (125 MHz, CDCl₃) δ 35.5, 35.8, 52.8, 53.2, 57.2, 61.0, 126.9, 127.0, 127.6, 127.9, 128.8, 129.2, 139.1, 142.1, 160.4, 169.8, 170.0.

ESIHRMS: Found: m/z 352.1551. Calcd for C₂₁H₂₂NO₄: (M+H)$^+$ 352.1549.

**methyl 2,5-diphenyl-1,4,5,6-tetrahydropyridine-3-carboxylate (13)**

![Diagram of 13]

$^1$H NMR (500 MHz, CDCl₃) δ 2.74 (1H, dd, J = 8.0, 14.5 Hz), 2.96 (1H, dd, J = 8.5, 17.0 Hz), 3.03 (1H, dd, J = 8.5, 14.5 Hz), 3.21 (1H, dd, J = 8.5, 17.0 Hz), 3.44-3.51 (1H, m), 3.75 (3H, s), 7.03-7.06 (3H, m), 7.21 (1H, t, J = 7.0 Hz), 7.25-7.32 (6H, m),
9.60 (1H, s br.); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 36.7, 41.4, 41.6, 50.5, 96.3, 121.0, 123.4, 126.3, 126.9, 128.5, 129.2, 140.3, 145.1, 159.1, 168.6.

ESIHRMS: Found: m/z 294.1495. Calcd for C$_{19}$H$_{20}$NO$_2$: (M+H)$^+$ 294.1494.

7. Derivatization of azidocyclopentane 9aa (Scheme 4)

7.1. Conversion of 9aa to triazole 14

To a stirred solution of 9aa (major:minor = 90:10) (117.6 mg, 0.200 mmol), phenyl acetylene (130 µL, 1.18 mmol) and copper(I) 2-Thiophenecarboxylate (19.1 mg, 0.100 mmol) in anhydrous DMF (2.5 mL) was added i-Pr$_2$NEt (140 µL, 0.804 mmol) at 23 °C under a N$_2$ atmosphere. After stirring at 80 °C for 50 h, the reaction was cooled down to 23 °C and quenched with pH 9 aqueous ammonium buffer. The organic materials were extracted thrice with ethyl acetate and the combined extracts were washed thrice with brine, dried over MgSO$_4$, and concentrated in vacuo. The resulting crude material was purified by flash column chromatography (hexane:ethyl acetate = 5:1) to yield 14 (135 mg, 0.195 mmol) in 98% yield as a mixture of diastereomer (major:minor = 90:10, which was determined by $^1$H NMR analysis).
bis(2,6-dimethylbenzyl)

(2\textsuperscript{S*},4\textsuperscript{R*})-2,4-diphenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)cyclopentane-1,1-dicarboxylate (14)

White solid; mp: 105-106 °C.

\( ^1 \text{H NMR} \) (400 MHz, CDCl\textsubscript{3}) \( \delta \) 1.90 (6H, s), 2.01 (6H × 0.11, s), 2.05 (6H × 0.11, s), 2.16 (6H, s), 2.55–2.68 (1H, m + 1H × 0.11, m), 2.84 (1H × 0.11, dd, \( J = 7.6, \) 14.0 Hz), 2.96 (1H, dd, \( J = 8.0, \) 13.6 Hz), 3.35–3.48 (2H, m), 3.54–3.74 (3H × 0.11, m), 4.15–4.21 (1H, m), 4.81–4.86 (2H, m + 1H × 0.11, m), 4.92 (1H × 0.11, d, \( J = 12.0 \) Hz), 5.04–5.11 (1H, m + 2H × 0.11, m), 5.40 (1H, d, \( J = 11.6 \) Hz), 6.85–7.32 (21H, m + 17H × 0.11, m), 7.58 (2H × 0.11, m), 7.71 (2H × 0.11, m), 7.83–7.94 (1H, s + 1H × 0.11, m), \( ^{13} \text{C NMR} \) (100 MHz, CDCl\textsubscript{3}) \( \delta \) 18.7, 19.4, 39.7, 43.6, 49.3, 62.8, 63.2, 69.5, 78.4, 122.0, 125.2, 125.5, 126.7, 127.7, 127.8, 128.0, 128.3, 128.4, 128.51, 128.52, 128.7, 129.0, 129.1, 130.3, 130.4, 130.5, 138.67, 138.70, 142.6, 143.3, 147.6, 170.2, 170.3.

ESIHRMS: Found: m/z 712.3147. Calcd for C\textsubscript{45}H\textsubscript{43}N\textsubscript{3}O\textsubscript{4}Na: (M+Na\textsuperscript{+}) 712.3151.

7.2. Conversion of 9aa to acetamide 15

To a stirred solution of 9aa (major:minor = 90:10) (59.1 mg, 0.101 mmol) in THF (1 mL) and water (50 µL) was added PMe\textsubscript{3} (200 µL, 0.200 mmol, 1.0 M in THF) at 0 °C under a N\textsubscript{2} atmosphere. The solution was stirred at 0 °C for 2 h and then diluted with
water. The organic materials was extracted with CH$_2$Cl$_2$ and the combined extracts were washed with brine, dried over MgSO$_4$, and concentrated under reduced pressure. The resulting crude material was used immediately for the next step.

To a stirred solution of crude material obtained above in anhydrous pyridine (1.2 mL) was added acetic anhydride (20 µL, 0.212 mmol) at 0 °C. After stirring at 0 °C for 2 h, the solution was stirred at 23 °C for 1 h. The solvent was then removed under reduced pressure. The resulting crude product was purified immediately by flash column chromatography (hexane:ethyl acetate = 10:1) to yield 15 (30.0 mg, 0.0497 mmol) in 49% yield as a single isomer.

**bis(2,6-dimethylbenzyl)**

(2S*,4R*)-2-acetamido-2,4-diphenylcyclopentane-1,1-dicarboxylate (15)

![Chemical Structure](image)

pale yellow oil;

$^1$H NMR (500 MHz, CDCl$_3$) δ 1.96 (3H, s), 2.10 (6H, s), 2.13 (6H, s), 2.67 (1H, dd, $J$ = 10.5, 14.0 Hz), 2.81 (1H, dd, $J$ = 6.5, 14.5 Hz), 2.92 (1H, dd, $J$ = 8.5, 14.0 Hz), 3.13 (1H, dd, $J$ = 11.0, 14.0 Hz), 3.69-3.77 (1H, m), 5.04 (2H, d, $J$ = 12.0 Hz), 5.13 (1H, d, $J$ = 12.0 Hz), 5.23 (1H, d, $J$ = 12.0 Hz), 6.96-6.97 (4H, m), 7.07-7.27 (12H, m), 9.25 (1H, s br.);

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 19.3 (overlapped), 20.8, 39.7, 42.7, 45.7, 61.9, 62.3, 69.1, 83.4, 126.3, 127.1, 127.2, 127.5, 127.9, 128.1, 128.2, 128.5, 128.79, 128.83, 130.9, 131.3, 138.3, 138.4, 139.7, 144.6, 169.7, 170.4, 172.2.

ESIHRMS: Found: m/z 604.3058. Calcd for C$_{39}$H$_{42}$NO$_5$: (M+H)$^+$ 604.3063.
8. [3+2]-Annulation of chiral cyclopropane 2a with vinyl azide 1a

8.1. Synthesis of chiral cyclopropane 2a

\[
\begin{align*}
\text{Ph} & \quad \text{CO}_2\text{Me} \\
\text{CO}_2\text{Me} & \quad \text{Ph}
\end{align*}
\]

The enantiopure (S)-2a was prepared according to a literature procedure. The ee of the product was measured by HPLC (Daicel Chiralpak IC column), i-PrOH/hexane = 1/99, flow 2.0 mL/min, 254 nm, \(t_1 = 9.3\) min (minor), \(t_2 = 11.5\) min (major); \([\alpha]_D^{20} = -166^\circ\) (c = 1.37, CHCl₃), lit: \(-101^\circ\) (c = 1.52, CHCl₃) for 99% ee (S).

**Chiral HPLC chart of racemic 2a:**

![Chiral HPLC chart of racemic 2a](image1)

**Chiral HPLC chart of (S)-2a:**

![Chiral HPLC chart of (S)-2a](image2)

---


8.2. [3+2]-Annulation of enantiopure cyclopropane 2a with vinyl azide 1a

To a stirred solution of (S)-2a (114 mg, 0.488 mmol) and vinyl azide 1a (143 mg, 0.984 mmol) in CH₂Cl₂ (0.8 mL) and MeNO₂ (0.2 mL) was added Sc(OTf)₃ (37.4 mg, 0.0760 mmol) at 0 °C under an Ar atmosphere. The solution was stirred at 0 °C for 23 h and then quenched with saturated aqueous NaHCO₃. The mixture was extracted with CH₂Cl₂ and the combined extracts were washed with brine, dried over MgSO₄, and concentrated in vacuo. The resulting crude material was purified by flash column chromatography (hexane : Et₂O = 120:1 to 90:1) to yield 6aa (112 mg, 0.294 mmol) in 59% yield as a mixture of diastereomer (major:minor = 62:38, which was determined by ¹H NMR analysis) with 34% recovery of 2a (39.4 mg, 0.168 mmol). Two diastereomers could be isolated partially by preparative TLC for characterization.

The ee of major-6aa was measured by HPLC (Daicel Chiralpak IA column), i-PrOH/hexane = 1/99, flow 1.0 mL/min, 254 nm, \( t_1 = 7.8 \text{ min (major)}, t_2 = 9.0 \text{ min (minor)}; [\alpha]_D^{20} = +23.8^\circ (c = 1.16, \text{CHCl}_3) \) for 86% ee.

The ee of minor-6aa was measured by HPLC (Daicel Chiralpak IA column), i-PrOH/hexane = 2/98, flow 1.0 mL/min, 254 nm, \( t_1 = 6.3 \text{ min (minor)}, t_2 = 7.2 \text{ min (major)}; [\alpha]_D^{20} = +4.44^\circ (c = 0.990, \text{CHCl}_3) \) for 93% ee.
HPLC chart of the racemic one:

![HPLC chart of the racemic one](image)

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HPLC chart of the chiral one:

![HPLC chart of the chiral one](image)

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HPLC chart of the racemic one:

![HPLC chart of the racemic one]

HPLC chart of the chiral one:

![HPLC chart of the chiral one]
bis(2,6-dimethylbenzyl) malonate (S1) (400 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) malonate (S1) (100 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) 2-benzylidene malonate (S2a) (400 MHz, CDCl3)

ppm (t1)

S43
bis(2,6-dimethylbenzyl) 2-benzylidenemalonate (S2a) (100 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) 2-(4-methoxybenzylidene)malonate (S2b) (400 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) 2-(4-methoxybenzylidene)malonate (S2b) (100 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) 2-(2-methylbenzylidene)malonate (S2c) (400 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) 2-(2-methylbenzylidene)malonate (S2c) (100 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) 2-(naphthalen-2-ylmethylene)malonate (S2d) (400 MHz, CDCl$_3$)
bis(2,6-dimethylbenzyl) 2-(naphthalen-2-ylmethylene)malonate (S2d) (100 MHz, CDCl₃)

bis(2,6-dimethylbenzyl) 2-(thiophen-2-ylmethylene)malonate (S2e) (400 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) 2-(thiophen-2-ylmethylene)malonate (S2e) (100 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) (E)-2-(3-phenylallylidene)malonate (S2f) (400 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) (E)-2-(3-phenylallylidene)malonate (S2f) (100 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) 2-phenylcyclopropane-1,1-dicarboxylate (5a) (400 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) 2-phenylcyclopropane-1,1-dicarboxylate (5a) (100 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (5b) (400 MHz, CDCl3)
bis(2,6-dimethylbenzyl) 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (5b) (100 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) 2-(o-tolyl)cyclopropane-1,1-dicarboxylate (5c) (400 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) 2-(o-toly)cyclopropane-1,1-dicarboxylate (5c) (100 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) 2-(naphthalen-2-yl)cyclopropane-1,1-dicarboxylate (5d) (400 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) 2-(naphthalen-2-yl)cyclopropane-1,1-dicarboxylate (5d) (100 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) 2-(thiophen-2-yl)cyclopropane-1,1-dicarboxylate (5e) (400 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) 2-(thiophen-2-yl)cyclopropane-1,1-dicarboxylate (5e) (100 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) \((E)\)-2-styrylcyclopropane-1,1-dicarboxylate (5f) (400 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) (E)-2-styrylcyclopropane-1,1-dicarboxylate (5f) (100 MHz, CDCl$_3$)
bis(2,6-dimethylbenzyl) 2-(1,3-dioxoisooindolin-2-yl)cyclopropane-1,1-dicarboxylate (5g) (400 MHz, CDCl$_3$)
bis(2,6-dimethylbenzyl) 2-(1,3-dioxoisindolin-2-yl)cyclopropane-1,1-dicarboxylate (5g) (100 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) 2-diazomalonate (S3) (400 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) 2-diazomalonate (S3) (100 MHz, CDCl₃)
dimethyl 2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (6aa) (400 MHz, CDCl₃)

\[
\begin{array}{ccccccccccccccccccccccc}
0.820 & 2.000 & 1.820 & 1.820 & 2.440 & 2.960 & 2.960 & 2.430 & 0.820 & 1.820 & 1.610 & 1.990 & 15.000 & 3.000 & 2.500 & 2.000 & 1.500 & 1.000 & 0.500 & 0.000 \\
\end{array}
\]
dimethyl (2$S^*$,4$R^*$)-2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (6aa major) (400 MHz, CDCl$_3$)
dimethyl (2\textit{S},4\textit{R})-2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (\textbf{6aa\_major}) (100 MHz, CDCl$_3$)
**dimethyl (2S\(^\ast\),4S\(^\ast\))-2-azido-2,4-diphenylcyclo pentane-1,1-dicarboxylate (6aa\_minor)** (400 MHz, CDCl\(_3\))

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**Diagram:**

- **Structure:** dimethyl (2S\(^\ast\),4S\(^\ast\))-2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate
- **Chemical Shifts:** ppm values indicating the positions of the protons in the molecule.

**Note:** The diagram shows the chemical structure and the corresponding ppm values for various protons in the molecule.
dimethyl (2S*,4S*)-2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (6aa_minor) (100 MHz, CDCl₃)
diisopropyl-2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (7aa) (400 MHz, CDCl₃)

major:minor = 77:23
diisopropyl (2$S^*$,4$R^*$)-2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (7aa\_major) (400 MHz, CDCl$_3$)
diisopropyl (2S*,4R*)-2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (7aa_major) (100 MHz, CDCl₃)
dibenzyl-2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (8aa) (400 MHz, CDCl₃)
dibenzyl-2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (8aa) (100 MHz, CDCl$_3$)

major:minor = 71:29
bis(2,6-dimethylbenzyl)-2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (9aa) (400 MHz, CDCl$_3$)

major:minor = 88:12
bis(2,6-dimethylbenzyl) (2S*,4R*)-2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (9aa_major) (400 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) (2S*,4R*)-2-azido-2,4-diphenylcyclopentane-1,1-dicarboxylate (9aa_major) (100 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) (2S*,4R*)-2-azido-4-phenyl-2-(p-tolyl)cyclopentane-1,1-dicarboxylate (9ba) (400 MHz, CDCl₃)

major:minor = 86:14
bis(2,6-dimethylbenzyl) \((2S\*,4R\*)\)-2-azido-4-phenyl-2-(p-tolyl)cyclopentane-1,1-dicarboxylate (9ba) \((100\,\text{MHz, CDCl}_3)\)

major:\text{minor} = 86:14
bis(2,6-dimethylbenzyl) (2S*,4R*)-2-azido-2-(naphthalen-2-yl)-4-phenylcyclopentane-1,1-dicarboxylate (9ca) (400 MHz, CDCl₃)

major:minor = 91:9
bis(2,6-dimethylbenzyl) \((2S^*,4R^*)\)-2-azido-2-(naphthalen-2-yl)-4-phenylcyclopentane-1,1-dicarboxylate (9ca) (100 MHz, CDCl₃)

major:minor = 91:9
bis(2,6-dimethylbenzyl) (2S*,4R*)-2-azido-2-(4-bromophenyl)-4-phenylcyclopentane-1,1-dicarboxylate (9da) (400 MHz, CDCl₃)

**major**

**major + minor**

major:minor = 90:10
bis(2,6-dimethylbenzyl) (2$S^*$,4$R^*$)-2-azido-2-(4-bromophenyl)-4-phenylcyclopentane-1,1-dicarboxylate (9da) (100 MHz, CDCl$_3$)

major:minor = 90:10
bis(2,6-dimethylbenzyl) \((2R^*,4R^*)\)-2-azido-2-phenethyl-4-phenylcyclopentane-1,1-dicarboxylate (9ea) (400 MHz, \text{C}_6\text{D}_6)
bis(2,6-dimethylbenzyl) (2\textsuperscript{R*},4\textsuperscript{R*})-2-azido-2-phenethyl-4-phenylcyclopentane-1,1-dicarboxylate (9ea) (100 MHz, CDCl\textsubscript{3})

**TLC:**

- Major:minor = 71:29
bis(2,6-dimethylbenzyl)(2S*,4R*)-2-azido-2-(4-bromophenyl)-4-(4-methoxyphenyl)cyclopentane-1,1-dicarboxylate (9db) (400 MHz, CDCl₃)

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major:minor = 86:14
bis(2,6-dimethylbenzyl)(2S*,4R*)-2-azido-2-(4-bromophenyl)-4-(4-methoxyphenyl)cyclopentane-1,1-dicarboxylate (9db) (100 MHz, CDCl₃)


major:minor = 86:14
bis(2,6-dimethylbenzyl) (2S*,4R*)-2-azido-2-(4-bromophenyl)-4-(o-tolyl)cyclopentane-1,1-dicarboxylate (9dc) (400 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) (2S*,4R*)-2-azido-2-(4-bromophenyl)-4-(o-tolyl)cyclopentane-1,1-dicarboxylate (9dc) (100 MHz, CDCl₃)

major:minor = 91:9
S96

bis(2,6-dimethylbenzyl)-2-azido-2-(4-bromophenyl)-4-(naphthalen-2-yl)cyclopentane-1,1-dicarboxylate (9dd) (400 MHz, CDCl₃)

ppm (t1)

ppm (t1)

major

minor

major:minor = 88:12
bis(2,6-dimethylbenzyl)(2S*,4R*)-2-azido-2-(4-bromophenyl)-4-(naphthalen-2-yl)cyclopentane-1,1-dicarboxylate (9dd major) (400 MHz, CDCl3)
bis(2,6-dimethylbenzyl)(2S*,4R*)-2-azido-2-(4-bromophenyl)-4-(naphthalen-2-yl)cyclopentane-1,1-dicarboxylate (9dd_major) (100 MHz, CDCl₃)

ppm (t1)
bis(2,6-dimethylbenzyl) (2S*,4R*)-2-azido-2-(4-bromophenyl)-4-(thiophen-2-yl)cyclopentane-1,1-dicarboxylate (9de) (400 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) (2S*,4R*)-2-azido-2-(4-bromophenyl)-4-(thiophen-2-yl)cyclopentane-1,1-dicarboxylate (9de) (100 MHz, CDCl₃)

major:minor = 88:12
bis(2,6-dimethylbenzyl)-2-azido-2-phenyl-4-((E)-styryl)cyclopentane-1,1-dicarboxylate (9df) (400 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) (2S*,4R*)-2-azido-2-phenyl-4-((E)-styrly)cyclopentane-1,1-dicarboxylate (9df_major) (400 MHz, CDCl$_3$)

ppm (t1)

S102
bis(2,6-dimethylbenzyl) (2S*,4R*)-2-azido-2-phenyl-4-((E)-styryl)cyclopentane-1,1-dicarboxylate (9df_major) (100 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) (2S*,4R*)-2-azido-2-(4-bromophenyl)-4-(1,3-dioxoisindolin-2-yl)cyclopentane-1,1-dicarboxylate (9dg) (400 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) (2S*,4R*)-2-azido-2-(4-bromophenyl)-4-(1,3-dioxiisoindolin-2-yl)cyclopentane-1,1-dicarboxylate (9dg) (100 MHz, CDCl3)

**Diagram:**
- Major:Minor = 78:22
methyl 2,4-diphenylcyclopent-1-ene-1-carboxylate (10) (400 MHz, CDCl₃)
methyl 2,4-diphenylcyclopent-1-ene-1-carboxylate (10) (100 MHz, CDCl₃)
dimethyl 2,4-diphenycyclopent-2-ene-1,1-dicarboxylate (11) (500 MHz, CDCl₃)
dimethyl 2,4-diphenylcyclopent-2-ene-1,1-dicarboxylate (11) (125 MHz, CDCl$_3$)

![Chemical Structure](image)
dimethyl 2,5-diphenyl-5,6-dihydropyridine-3,3(4H)-dicarboxylate (12) (500 MHz, CDCl₃)
dimethyl 2,5-diphenyl-5,6-dihydropyridine-3,3(4H)-dicarboxylate (12) (125 MHz, CDCl₃)

ppm (t1)

- 169.997
- 169.795
- 160.383
- 142.100
- 139.106
- 129.198
- 128.800
- 128.800
- 127.877
- 127.635
- 127.043
- 126.943
- 61.003
- 57.176
- 53.179
- 52.835
- 35.804
- 35.457

S111
methyl 2,5-diphenyl-1,4,5,6-tetrahydropyridine-3-carboxylate (13) (500 MHz, CDCl$_3$)
methyl 2,5-diphenyl-1,4,5,6-tetrahydropyridine-3-carboxylate (13) (125 MHz, CDCl$_3$)
bis(2,6-dimethylbenzyl) (2S*,4R*)-2,4-diphenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)cyclopentane-1,1-dicarboxylate (14) (400 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) (2$S^*$$R^*$)-2,4-diphenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)cyclopentane-1,1-dicarboxylate (14) (100 MHz, CDCl$_3$)

[Chemical structure image]

major:minor = 90:10
bis(2,6-dimethylbenzyl) (2S*,4R*)-2-acetamido-2,4-diphenylcyclopentane-1,1-dicarboxylate (15) (500 MHz, CDCl₃)
bis(2,6-dimethylbenzyl) (2S*,4R*)-2-acetamido-2,4-diphenylcyclopentane-1,1-dicarboxylate (15) (125 MHz, CDCl$_3$)

$\text{ppm (t1)}$