Supporting Information
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Amide Synthesis by Nucleophilic Attack of Vinyl Azides**
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1. General

$^1$H NMR (400 MHz) spectra were recorded on a Bruker Avance 400 spectrometer in CDCl$_3$ [using CDCl$_3$ (for $^1$H, $\delta = 7.26$) or DMSO-d$_6$ (for $^1$H, $\delta = 2.50$) as the internal standard]. $^{13}$C NMR (100 MHz) spectra on a Bruker Avance 400 spectrometer in CDCl$_3$ [using CDCl$_3$ (for $^{13}$C, $\delta = 77.0$) or DMSO-d$_6$ (for $^{13}$C, $\delta = 39.5$) as internal standard]. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of doublet of doublet, dt = doublet of triplet, sep = septet, m = multiplet, s br = single broad. IR spectra were recorded on a Shimazu IR Prestige-21 FT-IR Spectrometer either on NaCl plate or KBr plate. High-resolution mass spectra were obtained with a Q-Tof Premier LC HR mass spectrometer (Waters). X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractionmeter. Melting points were uncorrected and were recorded on a Buchi B-54 melting point apparatus. Flash column chromatography was performed using Merck silica gel 60 with distilled solvents. Aldehyde 4a, 4b, and alcohol 7a, 7c were purchased from Sigma-Aldrich Co., Inc.

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

2.1. Sodium azide (NaN$_3$)

Sodium azide is toxic ($LD_{50}$ oral = 27 mg/kg for rats) and can be absorbed through skin. Appropriate gloves are necessary when using it. It decomposes explosively upon heating to above 275 °C. Sodium azide is relatively safe especially in aqueous solution, unless acidified to form HN$_3$, which is volatile and highly toxic.

2.2. Organic azides

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, we keep in mind the following equation. It is noted that this equation takes into account all nitrogen atoms in the organic azide, not just those in the azido group.

$$\frac{N_C + N_O}{N_N} \geq 3 \quad (N: \text{number of the atom})$$
All organic azides prepared in this work are satisfied with the equation above except for 1a, 1i, and 1j and they are enough stable to be stored under –20 °C at least for 6 months. We have never experienced a safety problem with these materials.

3. **Synthesis of vinyl azides 1 (Scheme 4)**

**Typical procedure**

\[
\begin{array}{cccc}
\text{ICl, NaN}_3 & \text{CH}_3\text{CN-CH}_2\text{Cl}_2 & -20 ^\circ \text{C} & \text{Et}_2\text{O, 0 }^\circ \text{C} \\
\text{N}_3 & \text{N}_3
\end{array}
\]

This procedure was slightly modified from Hassner’s method.[3]

To a 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 CH\(_2\)Cl\(_2\) (60 mL) at –20 °C, and the mixture was stirred at the same temperature. After 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 stirred for 1 h. The reaction was quenched with saturated aqueous Na\(_2\)S\(_2\)O\(_3\), and the organic materials were extracted two times with Et\(_2\)O. The combined extracts were washed with brine and dried over MgSO\(_4\). After 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; 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\(_3\)) \(\delta\) 98.0, 125.6, 128.5, 129.1, 134.3, 145.1.
1-Azidocyclohept-1-ene (1i):

\[
\begin{array}{c}
\text{MeCN-CH}_2\text{Cl}_2 \\
-20^\circ \text{C}
\end{array}
\xrightarrow{\text{IN}_3 \text{ (1.1 equiv)}}
\begin{array}{c}
\text{t-BuOK} \\
(2.5 \text{ equiv})
\end{array}
\xrightarrow{\text{Et}_2\text{O}, 0^\circ \text{C}}
\begin{array}{c}
\text{N}_3 \\
\text{1i} \text{ 48%}
\end{array}
\]

Vinyl azide 1i was obtained in 48% yield as a pale yellow liquid from cycloheptene along with formation of 3-azidocyclohept-1-ene 1i' (18% yield). The synthetic procedure was the same as that of 1a except for 2.5 equiv of t-BuOK employed in the second step. Banert has also prepared vinyl azide 1i by the same procedure.\[4\] IR (NaCl) 2928, 2852, 2104, 1655, 1466, 1265 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.51-1.61 (4H, m), 1.71-1.77 (2H, m), 2.13-2.20 (4H, m), 5.48 (1H, t, \(J = 6.8\) Hz); \(^1^\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 25.6, 26.5, 27.1, 31.2, 31.5, 116.2, 141.0; ESIHRMS: Found: m/z 110.0967. Calcd for C\(_7\)H\(_{12}\)N: (M-N\(_2\)+H)\(^+\) 110.0970.

Vinyl azides 1b,\[^5\] 1c,\[^5\] 1d,\[^5\] 1e,\[^5\] 1f,\[^5\] 1g,\[^6\] 1h,\[^6\] 1j\[^7\] were known compounds and prepared according to the reported procedures.

4. BF\(_3\)•OEt\(_2\)-mediated reactions of vinyl azides 1 with N-Ts aldimines 2 (Table 1, entry 11; Schemes 5, 7-9)

4.1. Synthesis of N-Ts aldimine 2

Typical procedure:

\[
\text{Ph} \quad + \quad \text{TsNH}_2 \quad \xrightarrow{\text{BF}_3\cdot\text{OEt}_2 (10 \text{ mol%})} \quad \text{NTs}
\]

The suspension of benzaldehyde (2.28 mL, 22.4 mmol), TsNH\(_2\) (3.49 g, 20.4 mmol), BF\(_3\)•OEt\(_2\) (252 mL, 2.04 mmol) in benzene (50 mL) was heated to reflux using a Dean-Stark trap which was filled with benzene. The reaction mixture was refluxed and stirred until no more water can be separated with Dean-Stark trap. After cooling to room temperature, the mixture was evaporated to remove the solvent and then crystalized using ethyl acetate and hexane to give pure product 2a\[^8\] (4.01 g, 15.5 mmol) in 76% yield.
\(^1\)H NMR (400 Hz, CDCl\(_3\)): \(\delta\) 2.44 (3H, s), 7.35 (2H, d, \(J = 7.6\) Hz), 7.49 (2H, dd, \(J = 7.6, 7.6\) Hz), 7.62 (1H, t, \(J = 7.6\) Hz), 7.88-7.94 (4H, m), 9.03 (1H, s). \(^{13}\)C NMR (100 Hz, CDCl\(_3\)) \(\delta\) 21.6, 128.1, 129.1, 129.8, 131.3, 132.4, 134.9, 135.1, 144.6, 170.

\((E)-N\)-(3-Bromobenzylidene)-4-methylbenzenesulfonamide (2e):

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

83\% yield as a white solid from 3-bromobenzaldehyde and \(p\)-toluenesulfonamide.

mp 95-97 °C; IR (KBr) 3073, 1611, 1557, 1467, 1427, 1329, 1292, 1157 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.44 (3H, s), 7.34-7.38 (3H, m), 7.71 (1H, d, \(J = 8.0\) Hz), 7.81 (1H, dd, \(J = 0.8, 8.0\) Hz), 7.88 (2H, d, \(J = 8.0\) Hz), 8.08 (1H, d, \(J = 1.6\) Hz), 8.97 (1H, s); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 21.6, 123.2, 128.1, 129.8, 130.1, 130.6, 133.1, 134.2, 134.6, 137.5, 144.9, 168.4; ESIHRMS: Found: \(m/z\) 337.9853. Calcd for C\(_{14}\)H\(_{13}\)BrNO\(_2\): (M+H)\(^+\) 337.9850.

\((E)-4\)-Methyl-\(N\)-((1-(phenylsulfonyl)-1H-indol-3-yl)methylene)benzenesulfonamide (2f):

\[
\begin{array}{c}
\text{H} \\
\text{N} \\
\text{SO}_2\text{Ph}
\end{array}
\]

67\% as a white solid from 1-tosylindole-3-carboxaldehyde\(^{[9]}\) and \(p\)-toluenesulfonamide; mp 191-193 °C; IR (KBr) 3074, 1624, 1581, 1449, 1364, 1314, 1290, 1153, 1092 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.41 (3H, s), 7.31-7.34 (3H, m), 7.40 (1H, d, \(J = 1.2, 7.2, 7.2\) Hz), 7.50 (2H, dd, \(J = 7.6, 8.0\) Hz), 7.60 (1H, t, \(J = 7.2, 7.6\) Hz), 7.89 (2H, d, \(J = 8.0\) Hz), 7.94-7.96 (3H, m), 8.24-8.26 (2H, m), 9.14 (1H, s); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 21.6, 113.2, 117.5, 123.3, 125.1, 126.4, 126.6, 127.1, 127.9, 129.72, 129.74, 134.8, 135.4, 135.5, 137.0, 137.1, 144.3, 162.8; ESIHRMS: Found: \(m/z\) 439.0782. Calcd for C\(_{22}\)H\(_{19}\)N\(_2\)O\(_4\)S\(_2\): (M+H)\(^+\) 439.0786.

\((E)-4\)-methyl-\(N\)-((\(E\))-3-phenylallylidene)benzenesulfonamide (2h):

\[\text{SI-5}\]
67% as a white solid from trans-cinnamaldehyde and \( p \)-toluenesulfonamide; mp 120-122 °C; IR (KBr) 3078, 1597, 1446, 1391, 1354, 1316, 1238, 1151 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 2.43 (3H, s), 6.98 (1H, dd, \( J = 9.6, 16.0 \) Hz), 7.34 (2H, d, \( J = 8.0 \) Hz), 7.48 (1H, d, \( J = 16.0 \) Hz), 7.54-7.57 (2H, m), 7.86 (2H, d, \( J = 8.0 \) Hz), 8.77 (1H, d, \( J = 8.0 \) Hz); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 21.6, 124.7, 127.9, 128.6, 129.2, 129.8, 131.6, 134.1, 135.4, 144.5, 153.8, 170.8; ESIHRMS: Found: \( m/z \) 286.0890. Calcd for C\(_{16}\)H\(_{16}\)N\(_2\)O\(_2\)S: (M\(^{+}\)H\(^{+}\)) 286.0902.

Imines \( 2b,^{[10]} \) \( 2c,^{[9]} \) \( 2d,^{[11]} \) \( 2g,^{[12]} \) \( 2i^{[13]} \) were known compounds and prepared according to the reported procedures.

4.2. Amide synthesis

Typical procedure:

\[
\begin{align*}
\text{N}_2^+ &\rightarrow \text{N}^- \\
\text{Ph} &\overset{\text{1a}}{\text{N}} \text{Ts} \\
\text{Ph} &\overset{\text{2a}}{\text{H}} \\
\text{H} &\overset{\text{BF}_3\cdot\text{OEt}_2 (2 \text{ equiv})}{\text{N}} \text{Ts} \\
\text{H}_2\text{O} &\overset{\text{2 equiv}}{\text{H})} \\
\text{CH}_2\text{Cl}_2, -40 ^\circ \text{C} &\rightarrow \text{Ph} \overset{\text{3aa}}{\text{N}} \overset{\text{H}}{\text{N}} \text{Ts}
\end{align*}
\]

To a solution of \( N \)-Ts benzaldimine \( 2a \) (83.0 mg, 0.320 mmol), \( \text{BF}_3\cdot\text{OEt}_2 \) (79.0 \( \mu \)L, 0.640 mmol) and \( \text{H}_2\text{O} \) (11.5 \( \mu \)L, 0.640 mmol) in \( \text{CH}_2\text{Cl}_2 \) (1.5 mL) was added a solution of vinyl azide \( 1a \) (69.7 mg, 0.480 mmol) in \( \text{CH}_2\text{Cl}_2 \) (1.5 mL) by a syring pump for 5 h at -40 °C. The reaction mixture was stirred at the same temperature until TLC showed the disappearance of \( 2a \). Then the reaction was quenched with saturated NaHCO\(_3\) (aq) and warmed to room temperature. The resulting mixture was extracted three times with EtOAc. The combined organic extracts were washed with brine, dried over MgSO\(_4\) and concentrated. Recrystallization of the crude material from hexane/ethyl acetate gave \( \beta \)-amino amide \( 3aa \) (100.0 mg, 0.253 mmol, 79% yield) as a colorless crystal. The residue was further purified by flash column chromatography (silica gel; hexane : ethyl acetate = 1 : 1) afforded \( 3aa \) (20.0 mg, 0.051 mmol, 16% yield) as a white solid. The combined yield of \( 3aa \) is 95%.

3-(4-Methylphenylsulfonylamido)-N,3-diphenylpropanamide (3aa):
CCDC 983123; mp 193-195 °C; IR (KBr) 3335, 3308, 3053, 2960, 1657, 1597, 1518, 1499, 1445, 1346, 1151 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 2.27 (3H, s), 2.62 (1H, dd, J = 7.2, 14.8 Hz), 2.71 (1H, dd, J = 8.0, 14.8 Hz), 4.77 (1H, ddd, J = 7.2, 8.0, 8.8 Hz), 7.00 (1H, t, J = 7.2 Hz), 7.10-7.19 (7H, m), 7.24 (2H, dd, J = 7.6, 8.4 Hz), 7.42 (2H, d, J = 8.0 Hz), 7.48 (2H, d, J = 8.0 Hz), 8.30 (1H, d, J = 8.8 Hz), 9.78 (1H, s); ¹³C NMR (100 MHz, DMSO-d₆) δ 20.9, 44.3, 54.6, 119.1, 123.1, 126.3, 126.6, 126.9, 128.0, 128.6, 129.1, 138.6, 138.9, 141.2, 142.0, 167.5; ESIHRMS: Found: m/z 395.1432. Calcd for C₂₂H₂₃N₂O₃S: (M+H)⁺ 395.1429.

(Z)-Methyl 3-(4-methylphenylsulfonamido)-N,3-diphenylpropanimide (3aa’):

This compound was obtained when MeOH was used as the additive instead of H₂O.

Yield: 34%; viscous oil; IR (NaCl) 3367, 3053, 2980, 1674, 1597, 1489, 1435, 1329, 1265, 1161 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.36 (3H, s), 2.50 (1H, dd, J = 6.0, 14.4 Hz), 2.64 (1H, dd, J = 7.6, 14.4 Hz), 2.67 (3H, s), 4.61 (1H, ddd, J = 6.0, 7.6, 7.6 Hz), 5.38 (1H, d, J = 7.6 Hz), 6.32 (2H, d, J = 7.6 Hz), 6.87-6.90 (2H, m), 6.98 (1H, t, J = 7.2 Hz), 7.12-7.18 (7H, m), 7.56 (2H, d, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 21.5, 37.2, 53.3, 55.2, 120.8, 123.1, 126.2, 127.1, 127.7, 128.5, 129.0, 129.4, 137.4, 139.6, 143.2, 147.6, 159.3; ESIHRMS: Found: m/z 409.1579. Calcd for C₂₃H₂₅N₂O₃S: (M+H)⁺ 405.1586.

3-(4-Methylphenylsulfonamido)-N-phenyl-3-(o-tolyl)propanamide (3ab):
Yield: 66%; white solid, mp 148-151 °C; IR (KBr) 3252, 3055, 2983, 1657, 1599, 1543, 1491, 1447, 1319, 1165, 1170 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 2.23 (3H, s), 2.27 (3H, s), 2.65 (1H, dd, J = 6.8, 14.8 Hz), 2.72 (1H, dd, J = 8.0, 14.8 Hz), 5.04 (1H, ddd, J = 6.8, 8.0, 8.4 Hz), 6.94-7.03 (4H, m), 7.14 (2H, d, J = 8.0 Hz), 7.23 (2H, dd, J = 7.6, 8.4 Hz), 7.26-7.29 (1H, m), 7.42 (2H, d, J = 8.0 Hz), 7.47 (2H, d, J = 8.0 Hz), 8.23 (1H, d, J = 8.4 Hz), 9.78 (1H, s); ¹³C NMR (100 MHz, DMSO-d₆) δ 19.2, 21.3, 44.1, 50.6, 119.6, 123.6, 126.3, 126.6, 126.8, 127.2, 129.1, 129.5, 130.3, 135.1, 139.1, 139.3, 139.9, 142.5, 168.0; ESIHRMS: Found: m/z 409.1582. Calcd for C₂₃H₂₅N₂O₃S: (M+H)⁺ 409.1586.

3-(4-Methoxyphenyl)-3-(4-methylphenylsulfonamido)-N-phenylpropanamide (3ac):

Yield: 97%; white solid, mp 203-205 °C; IR (KBr) 3319, 3277, 3054, 2981, 1655, 1597, 1518, 1498, 1445, 1346, 1257, 1157 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 2.27 (3H, s), 2.67-2.69 (2H, m), 3.66 (3H, s), 4.67-4.73 (1H, m), 6.69 (2H, d, J = 8.4 Hz), 6.99 (1H, T, J = 7.2 Hz), 7.07-7.14 (4H, m), 7.23 (2H, dd, J = 7.6, 8.0 Hz), 7.45-7.47 (4H, m), 8.27 (1H, s br), 9.95 (1H, s br); ¹³C NMR (100 MHz, DMSO-d₆) δ 20.8, 44.2, 54.2, 55.0, 113.3, 119.0, 123.0, 126.3, 127.8, 128.5, 129.0, 133.2, 138.7, 139.0, 141.8, 158.2, 167.6; ESIHRMS: Found: m/z 425.1537. Calcd for C₂₃H₂₅N₂O₄S: (M+H)⁺ 425.1535.

3-(4-Chlorophenyl)-3-(4-methylphenylsulfonamido)-N-phenylpropanamide (3ad):

Yield: 88%; white solid, mp 147-150 °C; IR (KBr) 3374, 3163, 3059, 2981, 1662, 1602, 1547, 1499, 1445, 1369, 1152 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 2.29 (3H, s), 2.65 (1H, dd, J = 6.8, 14.4 Hz), 2.70 (1H, dd, J = 8.4, 14.4 Hz), 4.74 (1H, ddd, J = 6.8, 8.4, 8.8 Hz)), 7.00 (1H, t, J = 7.6 Hz), 7.13-7.26 (8H, m), 7.42-7.45 (4H, m), 8.36 (1H, d, J = 8.8 Hz), 9.82 (1H, s); ¹³C NMR (100 MHz, DMSO-d₆) δ 21.0, 44.0, 54.0, 119.1, 123.2, 126.3, 127.9, 128.6 (overlapped),
129.1, 131.6, 138.3, 138.8, 139.9, 142.2, 167.2; ESIHRMS: Found: m/z 429.1043. Calcd for C_{22}H_{22}ClN_{2}O_{3}: (M+H)^{+} 429.1040.

3-(3-Bromophenyl)-3-(4-methylphenylsulfonamido)-N-phenylpropanamide (3ae):

Yield: 69%; white solid, mp 178-181 °C; IR (KBr) 3347, 3123, 3026, 2926, 1670, 1601, 1549, 1499, 1443, 1339, 1152 cm\(^{-1}\); \(^{1}\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 2.28 (3H, s), 2.65 (1H, dd, \(J = 7.2, 14.8\) Hz), 2.71 (1H, dd, \(J = 8.0, 14.8\) Hz), 4.75 (1H, ddd, \(J = 7.2, 8.0, 8.8\) Hz), 7.01 (1H, t, \(J = 7.2\) Hz), 7.08-7.17 (4H, m), 7.23-7.29 (4H, m), 8.37 (1H, d, \(J = 8.8\) Hz), 9.83 (1H, s); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 20.9, 44.1, 54.1, 119.1, 121.4, 123.2, 125.8, 126.2, 128.6, 129.1, 129.4, 129.7, 130.1, 138.2, 138.7, 142.2, 143.4, 167.1; ESIHRMS: Found: m/z 473.0530. Calcd for C_{22}H_{22}BrN_{2}O_{3}: (M+H)^{+} 473.0535.

3-(4-Methylphenylsulfonamido)-N-phenyl-3-(1-(phenylsulfonyl)-1H-indol-3-yl)propanamide (3af):

Yield: 80%; white solid, dec. at 216 °C; IR (KBr) 3306, 3235, 3064, 2966, 1682, 1651, 1600, 1541, 1499, 1445, 1371, 1303, 1175 cm\(^{-1}\); \(^{1}\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 2.21 (3H, s), 2.69 (1H, dd, \(J = 6.8, 14.4\) Hz), 3.04 (1H, dd, \(J = 8.0, 14.4\) Hz), 4.99 (1H, ddd, \(J = 6.8, 8.0, 9.6\) Hz), 6.98 (2H, d, \(J = 8.4\) Hz), 7.04 (1H, dd, \(J = 7.2, 7.6\) Hz), 7.12 (1H, t, \(J = 7.6\) Hz), 7.24-7.30 (5H, m), 7.39 (1H, d, \(J = 8.0\) Hz), 7.45-7.49 (4H, m), 7.55 (1H, dd, \(J = 7.6, 7.6\) Hz), 7.74-7.76 (2H, m), 7.79 (2H, d, \(J = 7.6\) Hz), 8.28 (1H, d, \(J = 8.4\) Hz), 10.04 (1H, s); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 20.8, 41.9, 46.4, 112.7, 119.0, 120.0, 121.8, 123.0, 123.2, 124.1, 124.6, 126.2, 126.4, 128.62, 128.64, 128.9, 129.5, 134.0, 134.3, 136.9, 138.1, 138.8, 142.1, 167.4; ESIHRMS: Found: m/z 574.1495. Calcd for C_{30}H_{28}N_{3}O_{5}S_{2}: (M+H)^{+} 574.1470.
3-(Benzofuran-2-yl)-3-(4-methylphenylsulfonamido)-N-phenylpropanamide (3ag):

Yield: 80%; white solid, mp 150-153 °C; IR (KBr) 3292, 3130, 3064, 2962, 1676, 1599, 1557, 1500, 1445, 1329, 1161 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 2.16 (3H, s), 2.79 (1H, dd, J = 6.8, 14.8 Hz), 2.97 (1H, dd, J = 8.0, 14.8 Hz), 4.99 (1H, ddd, J = 6.8, 8.0, 8.4 Hz), 6.56 (1H, s), 7.01 (1H, t, J = 7.2 Hz), 7.08 (2H, d, J = 8.0 Hz), 7.13-7.31 (5H, m), 7.46-7.49 (3H, m), 7.54 (2H, d, J = 8.4 Hz), 8.46 (1H, d, J = 8.4 Hz), 9.98 (1H, s); ¹³C NMR (100 MHz, DMSO-d₆) δ 21.3, 41.5, 48.9, 104.1, 111.3, 119.6, 121.5, 123.1, 123.7, 124.5, 126.7, 128.0, 129.1, 129.4, 138.8, 139.3, 142.6, 154.3, 156.3, 167.5; ESIHRMS: Found: m/z 435.1368. Calcd for C₂₄H₂₃N₂O₄S: (M+H)⁺ 435.1379.

(E)-3-(4-Methylphenylsulfonamido)-N,5-diphenylpent-4-enamide (3ah):

Yield: 53%; white solid, mp 128-130 °C; IR (KBr) 3387, 3267, 3063, 2960, 1659, 1597, 1520, 1495, 1445, 1350, 1315, 1155 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 2.22 (3H, s), 2.54-2.61 (2H, m), 4.27-4.35 (1H, m), 5.86 (1H, dd, J = 7.2, 16.0 Hz), 6.20 (1H, d, J = 16.0 Hz), 7.01 (1H, t, J = 7.6 Hz), 7.09-7.11 (2H, m), 7.17-7.27 (7H, m), 7.50 (2H, d, J = 8.0 Hz), 7.65 (2H, d, J = 8.0 Hz), 7.94 (1H, d, J = 8.4 Hz), 9.89 (1H, s); ¹³C NMR (100 MHz, DMSO-d₆) δ 20.8, 42.9, 52.9, 119.2, 123.2, 126.1, 126.6, 127.5, 128.4, 128.5, 128.7, 129.3, 130.1, 136.1, 138.8, 138.9, 142.3, 167.6; ESIHRMS: Found: m/z 421.1588. Calcd for C₂₄H₂₃N₂O₃S: (M+H)⁺ 421.1586.

3-Cyclohexyl-3-(4-methylphenylsulfonamido)-N-phenylpropanamide (3ai):

Yield: 36%; white solid, mp 197-199 °C; IR (KBr) 3321, 3180, 3122, 2926, 2853, 1674, 1603, 1549, 1501, 1489, 1443, 1331, 1147 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 0.98-1.04 (5H, m),
1.29-1.31 (1H, m), 1.48-1.65 (5H, m), 2.09 (1H, dd, J = 6.0, 14.8 Hz), 2.28 (3H, s), 2.42 (1H, dd, J = 7.6, 14.8 Hz), 3.54-3.60 (1H, m), 7.01 (1H, t, J = 7.6 Hz), 7.23-7.27 (4H, m), 7.45-7.50 (3H, m), 7.65 (2H, d, J = 8.0 Hz), 9.72 (1H, s); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 20.9, 25.7, 25.8, 25.9, 27.5, 28.6, 41.6, 54.9, 119.1, 123.0, 126.3, 128.5, 129.3, 139.0, 139.2, 142.0, 168.6; ESIHRMS: Found: m/z 401.1891. Calcd for C$_{22}$H$_{29}$N$_2$O$_3$S: (M+H)$^+$ 401.1899.

3-(4-Methylphenylsulfonamido)-3-phenyl-N-(p-tolyl)propanamide (3ba):

![Chemical structure](image)

Yield: 90%; white solid, mp 184-186 °C; IR (KBr) 3299, 3034, 2920, 1666, 1597, 1524, 1497, 1450, 1404, 1346, 1153 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 2.21 (3H, s), 2.27 (3H, s), 2.60 (1H, dd, J = 7.2, 14.8 Hz), 2.68 (1H, dd, J = 8.0, 14.8 Hz), 4.76 (1H, ddd, J = 7.2, 8.0, 8.8 Hz), 7.03 (2H, d, J = 8.4 Hz), 7.10-7.18 (7H, m), 7.30 (2H, d, J = 8.4 Hz), 7.48 (2H, d, J = 8.4 Hz), 8.30 (1H, d, J = 8.8 Hz), 9.70 (1H, s); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 20.4, 20.9, 44.2, 54.5, 119.1, 126.3, 126.6, 126.9, 127.9, 128.9, 129.1, 132.0, 136.3, 138.6, 141.1, 142.0, 167.1; ESIHRMS: Found: m/z 409.1580. Calcd for C$_{23}$H$_{25}$N$_2$O$_3$S: (M+H)$^+$ 409.1586.

3-(4-Methylphenylsulfonamido)-3-phenyl-N-(o-tolyl)propanamide (3ca):

![Chemical structure](image)

Yield: 56%; white solid, mp 180-183 °C; IR (KBr) 3298, 3142, 3034, 2920, 1670, 1587, 1535, 1485, 1458, 1346, 1150 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 1.89 (3H, s), 2.29 (3H, s), 2.61 (1H, dd, J = 6.4, 14.0 Hz), 2.76 (1H, dd, J = 8.8, 14.0 Hz), 4.73 (1H, ddd, J = 6.4, 8.8, 8.0 Hz), 7.00-7.51 (11H, m), 7.50 (2H, d, J = 8.0 Hz), 8.31 (1H, d, J = 8.0 Hz), 9.18 (1H, s); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 17.5, 20.9, 43.6, 54.9, 125.2, 125.7, 126.3, 126.8, 126.9, 127.9, 129.1 (overlapped), 130.1, 131.9, 135.9, 138.6, 140.8, 142.0, 167.4; ESIHRMS: Found: m/z 409.1581. Calcd for C$_{23}$H$_{25}$N$_2$O$_3$S: (M+H)$^+$ 409.1586.
3-(4-Methylphenylsulfonamido)-N-(naphthalen-2-yl)-3-phenylpropanamide (3da):

Yield: 67%; white solid, mp 133-136 °C; IR (KBr) 3233, 3146, 3034, 2933, 1667, 1585, 1557, 1494, 1470, 1361, 1304, 1161 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 2.21 (3H, s), 2.69 (1H, dd, J = 7.2, 14.4 Hz), 2.78 (1H, dd, J = 8.0, 14.4 Hz), 4.82 (1H, ddd, J = 7.2, 8.0, 8.8 Hz), 7.12-7.23 (7H, m), 7.36-7.50 (5H, m), 7.75-7.81 (3H, m), 8.14 (1H, d, J = 1.2 Hz), 8.34 (1H, d, J = 8.8 Hz), 10.01 (1H, s); ¹³C NMR (100 MHz, DMSO-d₆) δ 21.3, 44.8, 55.1, 115.6, 120.3, 125.0, 126.77, 126.85, 127.1, 127.4, 127.7, 127.9, 128.5, 128.7, 129.6, 130.2, 133.8, 135.9, 139.1, 141.7, 142.5, 168.2; ESIHRMS: Found: m/z 445.1591. Calcd for C₂₆H₂₅N₂O₃S: (M+H)⁺ 445.1586.

N-(4-Methoxyphenyl)-3-(4-methylphenylsulfonamido)-3-phenylpropanamide (3ea):

Yield: 69%; white solid, mp 184-186 °C; IR (KBr) 3321, 3120, 3034, 2920, 1654, 1601, 1514, 1494, 1456, 1342, 1238, 1151 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 2.28 (3H, s), 2.58 (1H, dd, J = 6.8, 14.4 Hz), 2.66 (1H, dd, J = 8.0, 14.4 Hz), 3.69 (3H, s), 4.76 (1H, ddd, J = 6.8, 8.0, 8.8 Hz), 6.81 (2H, dd, J = 8.8 Hz), 7.10-7.18 (7H, m), 7.32 (2H, d, J = 8.8 Hz), 7.48 (2H, d, J = 8.8 Hz), 7.29 (1H, d, J = 8.8 Hz), 9.64 (1H, s); ¹³C NMR (100 MHz, DMSO-d₆) δ 20.9, 44.1, 54.6, 55.1, 113.7, 120.6, 126.3, 126.6, 126.9, 127.9, 129.1, 132.0, 138.6, 141.2, 142.0, 155.1, 166.9; ESIHRMS: Found: m/z 425.1537. Calcd for C₂₃H₂₅N₂O₄S: (M+H)⁺ 425.1535.

N-(4-Bromophenyl)-3-(4-methylphenylsulfonamido)-3-phenylpropanamide (3fa):

Yield: 79%; white solid, mp 224-226 °C; IR (KBr) 3321, 3123, 3061, 2934, 1672, 1604, 1541, 1491, 1396, 1285, 1151 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 2.26 (3H, s), 2.64 (1H, dd, J = 7.2, 14.8 Hz), 2.70 (1H, dd, J = 8.0, 14.8 Hz), 4.77 (1H, ddd, J = 7.2, 8.0, 8.8 Hz), 7.12-7.18 (7H,
m), 7.39-7.48 (6H, m), 8.32 (1H, d, J = 8.8 Hz), 9.93 (1H, s); $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ 20.8, 44.3, 54.5, 114.7, 121.0, 126.2, 126.6, 126.9, 128.0, 129.1, 131.3, 138.2, 138.6, 141.1, 142.0, 167.6; ESIHRMS: Found: m/z 473.0528. Caled for C$_{22}$H$_{22}$$^{79}$BrN$_2$O$_3$: (M+H)$^+$ 473.0535.

3-(4-Methylphenylsulfonamido)-N-(3-nitrophenyl)-3-phenylpropanamide (3ga):

Yield: 90%; white solid, mp 237-239 °C; IR (KBr) 3327, 3126, 3034, 2920, 1680, 1597, 1475, 1433, 1354, 1285, 1150 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-d$_6$) δ 2.20 (3H, s), 2.74-2.76 (2H, m), 4.79-4.83 (1H, m), 7.08-7.24 (7H, m), 7.47 (2H, d, J = 8.4 Hz), 7.55 (1H, dd, J = 8.0, 8.4 Hz), 7.81-7.88 (2H, m), 8.47-8.51 (2H, m), 10.78 (1H, s br); $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ 20.8, 44.4, 54.7, 113.0, 117.5, 125.0, 126.2, 126.6, 126.9, 128.0, 129.0, 129.9, 138.7, 140.2, 141.6, 141.8, 147.8, 168.5; ESIHRMS: Found: m/z 440.1277. Caled for C$_{22}$H$_{22}$N$_3$O$_5$: (M+H)$^+$ 440.1280.

3-(4-Methylphenylsulfonamido)-3-phenyl-N-(3-phenylpropyl)propanamide (3ha):

Yield: 34%; white solid, mp 237-239 °C; IR (NaCl) 3374, 3053, 2985, 1645, 1599, 1494, 1454, 1422, 1265, 1157 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.60-1.68 (2H, m), 2.34 (3H, s), 2.42-2.52 (2H, m), 3.05-3.16 (2H, m), 4.64-4.68 (1H, m), 5.46 (1H, s br), 6.72 (1H, d, J = 6.8 Hz), 7.07-7.19 (10H, m), 7.23-7.26 (2H, m), 7.57 (2H, d, J = 8.4 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 21.4, 30.7, 33.0, 39.1, 42.6, 55.0, 126.0, 126.4, 127.1, 127.5, 128.3, 128.40, 128.41, 129.3, 137.5, 139.8, 141.2, 143.0, 170.0; ESIHRMS: Found: m/z 440.1277. Caled for C$_{22}$H$_{22}$N$_3$O$_5$: (M+H)$^+$ 440.1280.
4-Phenyl-2-(3-phenylpropyl)-1-tosyl-4,5-dihydro-1H-imidazole (6ha):

Yield: 34%; viscous pale yellow oil; IR (NaCl) 3053, 2985, 1651, 1599, 1494, 1452, 1422, 1356, 1265, 1161, 1096 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 2.00-2.07 (2H, m), 2.37 (3H, s), 2.66-2.74 (4H, m), 3.73 (1H, tdd, \(J = 1.2, 4.8, 15.2\) Hz), 4.12 (1H, tdd, \(J = 1.6, 10.4, 15.2\) Hz), 5.16 (1H, dd, \(J = 4.8, 10.4\) Hz), 7.13 (2H, d, \(J = 8.0\) Hz), 7.17-7.22 (5H, m), 7.25-7.31 (5H, m), 7.34 (2H, d, \(J = 8.4\) Hz); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 21.5, 23.7, 25.8, 28.5, 33.7, 34.1, 56.4, 60.4, 126.9, 127.3, 127.9, 128.6, 129.2, 135.4, 137.5, 143.1, 178.0; ESIHRMS: Found: \(m/z\) 440.1277. Calcd for C\(_{22}\)H\(_{22}\)N\(_3\)O\(_5\)S: (M+H\(^+\)) 440.1280.

4-Methyl-\(N\)-((\(S^*\))-((\(S^*\))-8-oxoazocan-2-yl)(phenyl)methyl)benzenesulfonamide (3ia):

An inseparable mixture of diastereomers (dr = 4.4 : 1) was isolated in 47% yield as white solid by flash column chromatography (silica gel; hexane : ethyl acetate = 2 : 8). Recrystallization from acetone/hexane gave a colorless crystal of the major isomer (shown above), the structure of which was secured by X-ray crystallography analysis.

The \(^1\)H and \(^1\)C NMR described below are for the major isomer.

CCDC 983201; Decomposed at 110 °C; IR (NaCl) 3371, 3153, 1647, 1601, 1562, 1470, 1433, 1383, 1327, 1161 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 1.11-1.27 (3H, m), 1.57-1.92 (5H, m), 2.30 (3H, s), 2.31-2.42 (2H, m), 3.89-3.96 (1H, m), 4.53 (1H, dd, \(J = 4.0, 9.6\) Hz), 5.38 (1H, d, \(J = 11.2\) Hz), 6.04 (1H, d, \(J = 9.6\) Hz), 6.96 (2H, d, \(J = 8.0\) Hz), 7.04 (2H, d, \(J = 8.4\) Hz), 7.13-7.17 (3H, m), 7.48 (2H, d, \(J = 8.4\) Hz); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 21.4, 23.7, 25.8, 28.5, 33.7, 34.1, 56.4, 60.4, 126.9, 127.3, 127.9, 128.6, 129.2, 135.4, 137.5, 143.1, 178.0; ESIHRMS: Found: \(m/z\) 387.1744. Calcd for C\(_{21}\)H\(_{22}\)N\(_2\)O\(_3\)S: (M+H\(^+\)) 387.1742.
An inseparable mixture of diastereomers (dr = 6.3 : 1) was isolated in 54% yield as white solid by column chromatography (silica gel; hexane : ethyl acetate = 7 : 3). The major isomer (shown above) could be obtained as a colorless crystal by recrystallization from acetone/hexane and the structure was secured by X-ray crystallography analysis.

CCDC 982568; mp 168-170 °C; IR (NaCl) 2945, 1647, 1597, 1494, 1447, 1402, 1354, 1167, 979 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.14-1.28 (4H, m), 1.36-1.42 (1H, m), 1.46-1.58 (2H, m), 1.79-1.94 (2H, m), 1.97-2.03 (1H, m), 2.44 (3H, s), 2.52-2.58 (1H, m), 3.41 (1H, ddd, $J$ = 2.0, 7.2, 13.6 Hz), 4.32 (1H, dd, $J$ = 3.6, 8.4 Hz), 4.76 (1H, d, $J$ = 8.4 Hz), 7.06 (1H, s br), 7.24-7.33 (5H, m), 7.60-7.62 (3H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.0, 21.6, 25.9, 27.0, 29.8, 30.5, 31.8, 68.2, 70.5, 127.2, 127.3, 127.9, 128.0, 129.9, 133.0, 136.3, 144.7, 160.0; ESIHRMS: Found: m/z 383.1790. Calcd for C$_{22}$H$_{27}$N$_2$O$_2$S: (M+H)$^+$ 383.1793.
4.3. Discussion on diastereoselectivity for the reactions of cyclic vinyl azides 1i and 1j

The reactions of vinyl azides 1i and 1j with imine 2a proceeded in the diastereoselective manners. The structure of the major isomers 3ia and 6ja could be determined by X-ray crystallographic analyses (see above). Their structures suggested that the stereochemistry of the major isomers formed in these reaction is “syn”. This led to the one of the possibility on the reaction mechanism of the present nucleophilic addition of vinyl azides 1 to imines 2 that an acyclic transition state is involved as shown in Scheme S1. Further investigation on the reaction mechanism is currently underway.

Scheme S1.
5. BF$_3$·OEt$_2$-mediated reactions of vinyl azides 1 with aldehydes 4 (Scheme 6)

5.1. Optimization of reaction conditions for the reaction with benzaldehyde 4a

Table S1.

<table>
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<th>entry</th>
<th>additive</th>
<th>Yields of 5a $^{[a]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AcOH</td>
<td>9%</td>
</tr>
<tr>
<td>2</td>
<td>HFIP</td>
<td>30%</td>
</tr>
<tr>
<td>3</td>
<td>TMSOTf</td>
<td>20%</td>
</tr>
<tr>
<td>4</td>
<td>TMSCl</td>
<td>26%</td>
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</table>

$^{[a]}$ Isolated yields.

General procedure (Table S1, entry 2 as an example):

To a solution of benzaldehyde 4a (37.5 µL, 0.370 mmol), BF$_3$·OEt$_2$ (76.0 µL, 0.616 mmol) and hexafluoroisopropanol (63.9 mL, 0.616 mmol) in CH$_2$Cl$_2$ (1.5 mL). Then the solution of vinyl azide 1a (44.7 mg, 0.308 mmol) in CH$_2$Cl$_2$ (1.5 mL) was added to the reaction system by syring pump during 5 h under $-40$ °C. Reaction finished immediately after the addition and was quenched with saturated NaHCO$_3$ (aq) and then warmed to room temperature. The resulting mixture was extracted three times with EtOAc. The combined organic extracts were washed with brine, dried over MgSO$_4$ and concentrated. The reaction mixture was purified by flash column chromatography (silica gel; hexane : ethyl acetate = 1 : 1) afforded product 5a (23.0 mg, 0.095 mmol, 31% yield) as a white solid.

3-Hydroxy-N,N-diphenylpropanamide (5a): $^{[14]}$

$^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 2.58 (1H, dd, $J = 4.8$, 14.0 Hz), 2.67 (1H, dd, $J = 8.8$, 14.0 Hz), 5.07 (1H, ddd, $J = 4.4$, 4.8, 8.8 Hz), 5.46 (1H, d, $J = 4.4$ Hz), 7.02 (1H, dd, $J = 7.2$, 7.6 Hz),
7.22-7.40 (7H, m), 7.60 (2H, d, J = 7.6 Hz), 9.87 (1H, s); $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ 46.9, 69.7, 119.0, 123.0, 125.7, 126.9, 128.0, 128.6, 139.2, 145.3, 169.0.

5.2. Optimization of reaction conditions of the reaction with ethyl glyoxal 4b

Table S2.

<table>
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<tr>
<th>entry</th>
<th>additive</th>
<th>Yields of 5a$^{[b]}$</th>
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<tbody>
<tr>
<td>1</td>
<td>H$_2$O</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>AcOH</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>HFIP</td>
<td>31%</td>
</tr>
<tr>
<td>4</td>
<td>none</td>
<td>45%$^{[b]}$</td>
</tr>
<tr>
<td>5$^{[c]}$</td>
<td>none</td>
<td>39%</td>
</tr>
<tr>
<td>6$^{[d]}$</td>
<td>none</td>
<td>41%</td>
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</tbody>
</table>

[a] $^1$H NMR yields. [b] Isolated yields. [c] 4 equiv of 4b was employed. [d] 1 equiv of BF$_3$•OEt$_2$ was employed.

General procedure (Table S2, entry 4 as an example):

To a solution of ethyl glyoxal 4b (110.1 mg, 50% solution in toluene, 0.540 mmol), BF$_3$•OEt$_2$ (76.5 µL, 0.540 mmol) in CH$_2$Cl$_2$ (1.5 mL) was added a solution of vinyl azide 1a (39.1 mg, 0.270 mmol) in CH$_2$Cl$_2$ (1.5 mL) by a syring pump over 5 h at -40 °C. Reaction finished immediately after addition and was quenched with saturated NaHCO$_3$ (aq) and then warmed to room temperature. The resulting mixture was extracted three times with EtOAc. The combined organic extracts were washed with brine, dried over MgSO$_4$ and concentrated. The reaction mixture was purified by flash column chromatography (silica gel; hexane : ethyl acetate = 3 : 2) afforded product 5b (28.7 mg, 0.121 mmol, 45% yield) as a white solid.

Ethyl 2-hydroxy-4-oxo-4-(phenylamino)butanoate (5b):
mp 68-70 °C; IR (KBr) 3300, 3197, 3142, 2982, 1746, 1678, 1606, 1557, 1499, 1406, 1335, 1180 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.28 (3H, t, $J = 7.2$ Hz), 2.79 (1H, dd, $J = 7.2, 15.6$ Hz), 2.89 (1H, dd, $J = 4.0, 15.6$ Hz), 3.86-3.87 (1H, m), 4.26 (2H, q, $J = 7.2$ Hz), 4.55-4.57 (1H, m), 7.09 (1H, t, $J = 7.6$ Hz), 7.29 (2H, dd, $J = 7.6, 7.6$ Hz), 7.49 (2H, d, $J = 7.6$ Hz), 8.12 (1H, s br); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.1, 41.1, 62.2, 67.7, 120.1, 124.5, 128.9, 137.5, 168.2, 173.4; ESIHRMS: Found: $m/z$ 238.1082. Calcd for C$_{12}$H$_{16}$NO$_4$: (M+H)$^+$ 238.1079.

6. BF$_3$•OEt$_2$-mediated reactions of vinyl azides 1 with alcohols 7 (Scheme 10)

6.1 Synthesis of alcohols 7b

To the solution of 1-(phenylsulfonyl)-1H-indole-3-carbaldehyde$^{[15]}$ (1.790 g, 6.30 mmol) in THF (15 mL) was added 3.0 M PhMgCl solution in diethyl ether (2.31 mL, 6.93 mmol) dropwise at -78°C. After the addition was complete, the reaction mixture was stirred at -78°C for 2 h and at room temperature for another 1 h. Then the reaction mixture was quenched with saturated NH$_4$Cl solution, the aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with brine, dried over MgSO$_4$ and concentrated. The residue was then purified by flash column chromatography (silica gel; hexane: ethyl acetate = 75 : 25) afforded 7b (2.05 g, 5.64 mmol) in 89% yield as a white solid.

Phenyl(1-(phenylsulfonyl)-1H-indol-3-yl)methanol (7b):

White solid, mp 106-109 °C; IR (KBr) 3532, 3057, 2960, 1602, 1581, 1492, 1449, 1356, 1258, 1175 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.44 (1H, s br), 5.95 (1H, s), 7.11 (1H, t, $J = 7.6$ Hz),

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7.22-7.39 (9H, m), 7.44-7.49 (2H, m), 7.83 (2H, d, $J = 8.0 \text{ Hz}$), 7.94 (1H, d, $J = 8.4 \text{ Hz}$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 70.3, 113.6, 120.6, 123.3, 123.8, 124.9, 125.8, 126.6, 126.7, 128.1, 128.6, 128.9, 129.2, 133.8, 135.6, 138.0, 141.9; ESIHRMS: Found: $m/z$ 386.0829. Calcd for C$_{21}$H$_{17}$NOSNa: (M+Na$^+$) 386.0827.

Alcohol 7d$^{[16]}$ was known compound and prepared according to the reported procedure.

### 6.2. Amide synthesis

**Typical procedure:**

To a solution of diphenylmethanol 7a (99.9 mg, 0.543 mmol), BF$_3$·OEt$_2$ (89.3 µL, 0.723 mmol) and in CH$_2$Cl$_2$ (1.5 mL) was added a solution of vinyl azide 1a (52.5 mg, 0.362 mmol) in CH$_2$Cl$_2$ (1.5 mL) by a syring pump over 5 h at -40 °C. Reaction finished immediately after addition and was quenched with saturated NaHCO$_3$ (aq) and then warmed to room temperature. The resulting mixture was extracted three times with EtOAc. The combined organic extracts were washed with brine, dried over MgSO$_4$ and concentrated. Recrystallization of the crude material from hexane/ethyl acetate gave amide 8a (50.0 mg, 0.166 mmol, 46% yield) as a white solid. The residue was further purified by flash column chromatography (silica gel; hexane : ethyl acetate = 7 : 3) afforded product 8a (21.0 mg, 0.070 mmol, 19% yield) as a white solid. The combined yield of product 8a is 65%.

$N,N,3,3$-triphenylpropanamide (8a):

Dec. at 170 °C; IR (KBr) 3246, 3032, 2930, 1659, 1595, 1553, 1491, 1445, 1350, 1155 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.07 (2H, $d$, $J = 7.6 \text{ Hz}$), 4.64 (1H, $t$, $J = 7.6 \text{ Hz}$), 6.92 (1H, s br), 7.04-7.07 (1H, m), 7.18-7.35 (14H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 44.4, 47.4, 120.0, 124.3,
126.7, 127.7, 128.7, 128.9, 137.5, 143.5, 169.3; ESIHRMS: Found: m/z 302.1541. Caled for C_{21}H_{20}NO: (M+H)^+ 302.1545.

\(N,3\)-diphenyl-3-(1-(phenylsulfonyl)-1H-indol-3-yl)propanamide (8b):

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\text{Yield: 83%; white solid, mp 193-195 °C; IR (KBr) 3235, 3038, 2934, 1636, 1591, 1545, 1495, 1447, 1368, 1298, 1175, 1134 cm}^{-1}; \text{ } ^1H \text{ NMR (400 MHz, CDCl}_3\text{) } \delta 2.97 (1H, dd, J = 8.0, 14.4 Hz), 3.16 (1H, dd, J = 7.2, 14.4 Hz), 4.79 (1H, dd, J = 7.2, 8.0 Hz), 7.04 (1H, s br), 7.07-7.12 (2H, m), 7.18-7.33 (13H, m), 7.46 (1H, dd, J = 7.6, 7.6 Hz), 7.57 (1H, s), 7.77 (2H, d, J = 7.6 Hz), 7.94 (1H, d, J = 8.8 Hz); ^{13}C \text{ NMR (100 MHz, CDCl}_3\text{) } \delta 39.3, 44.1, 113.7, 120.0, 120.4, 122.7, 123.4, 125.0, 125.7, 126.6, 127.0, 124.4, 127.6, 128.7, 128.9, 129.2, 130.2, 133.8, 135.6, 137.6, 137.7, 141.8, 169.0; \text{ ESIHRMS: Found: m/z 481.1583. Caled for C}_{29}H_{25}N_2O_3S: (M+H)^+ 481.1586.}

\(N,3,3,3\)-tetraphenylpropanamide (8e):

\[
\text{Yield: 60%; white solid, dec. at 198 °C; IR (KBr) 3252, 3057, 2960, 1668, 1597, 1545, 1497, 1445, 1368, 1250 cm}^{-1}; \text{ } ^1H \text{ NMR (400 MHz, CDCl}_3\text{) } \delta 3.76 (2H, s), 6.43 (1H, s br), 7.02-7.04 (3H, m), 7.20 (2H, dd, J = 7.6, 8.0 Hz), 7.27-7.39 (15H, m); ^{13}C \text{ NMR (100 MHz, CDCl}_3\text{) } \delta 50.2, 56.5, 119.7, 124.0, 126.8, 128.4, 128.7, 129.3, 137.5, 146.0, 168.8; \text{ ESIHRMS: Found: m/z 378.1861. Caled for C}_{28}H_{24}NO: (M+H)^+ 378.1858.}

(E)-\(N,3,5\)-triphenylpent-4-enamide (8d):

\[
\text{SI-21}
\]
Yield: 53%; white solid, mp 101-104 °C; IR (KBr) 3306, 3028, 2964, 1649, 1599, 1545, 1494, 1443, 1343, 1260 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.77 (1H, dd, J = 8.0, 14.4 Hz), 2.85 (1H, dd, J = 7.2, 14.4 Hz), 4.10 (1H, ddd, J = 6.8, 7.2, 8.0 Hz), 6.35-6.46 (2H, m), 6.91 (1H, s br), 7.03 (1H, t, J = 7.2 Hz), 7.14-7.33 (14 H, m); ¹³C NMR (100 MHz, CDCl₃) δ 44.4, 45.4, 120.1, 124.4, 126.3, 127.0, 127.4, 127.6, 128.5, 128.9 (overlapped), 130.5, 132.0, 137.0, 137.5, 142.7, 169.2; ESI-HRMS: Found: m/z 328.1697. Caled for C₂₃H₂₂NO: (M+H)⁺ 328.1701.

7. References

$^1$H NMR spectrum of 1 (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 1i (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 2e (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 2e (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 2f (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 2f (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 2h (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 2h (100 MHz, CDCl$_3$)
H NMR spectrum of 3aa (400 MHz, DMSO-d$_6$)

$^1$H NMR spectrum of 3aa (400 MHz, DMSO-d$_6$)
$^{13}$C NMR spectrum of 3aa (100 MHz, DMSO-$d_6$)
$^1$H NMR spectrum of 3aa' (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3aa' (100 MHz, CDCl$_3$)

Ph₃C=NOH₃ 

ppm (t1) 200 150 100 50 0
$^1$H NMR spectrum of 3ab (100 MHz, DMSO-$d_6$)
$^{13}$C NMR spectrum of 3ab (100 MHz, DMSO-d$_6$)
$^1$H NMR spectrum of 3ac (400 MHz, DMSO-d$_6$)
$^{13}$C NMR spectrum of 3ac (100 MHz, DMSO-d$_6$)
$^1$H NMR spectrum of 3ad (400 MHz, DMSO-d$_6$)
$^{13}$C NMR spectrum of 3ad (100 MHz, DMSO-d$_6$)
$^1$H NMR spectrum of 3ae (400 MHz, DMSO-$d_6$)
$^{13}$C NMR spectrum of 3ae (100 MHz, DMSO-d$_6$)

Ph

H

N

O

H

N

Ts

Br

ppm (t1)
\(^1\)H NMR spectrum of 3af (400 MHz, DMSO-\(d_6\))

Ph

H N

N

Ts

N

Ph\(\text{O}_2\)S

ppm (t1)

6.971

5.006

4.997

4.984

4.976

4.961

3.319

3.065

3.041

3.029

3.005

2.716

2.702

2.680

2.666

2.506

2.501

2.497

2.205

-0.00000
$^{13}$C NMR spectrum of 3af (100 MHz, DMSO-d$_6$)
The extracted text from the image is: "$^1$H NMR spectrum of 3ag (400 MHz, DMSO-d$_6$)

ppm (t1)

0.05.0 10.0

$^{13}$C NMR spectrum of 3ag (100 MHz, DMSO-$d_6$)
$^1$H NMR spectrum of 3ah (400 MHz, DMSO-d$_6$)
$^{13}$C NMR spectrum of 3ah (100 MHz, DMSO-$d_6$)

![NMR spectrum image]

Chemical shifts (ppm):
- 167.692
- 142.326
- 138.871
- 138.793
- 136.115
- 130.134
- 129.323
- 128.686
- 128.545
- 128.385
- 127.463
- 126.697
- 126.052
- 123.176
- 120.229
- 52.856
- 42.885
- 40.130
- 39.921
- 39.713
- 39.504
- 39.295
- 39.087
- 38.878
- 20.787

Structural formula:

Ph\text{N}H\text{O}H\text{N}$\text{Ts}$

Ph
$^1$H NMR spectrum of 3ai (400 MHz, DMSO-d$_6$)

 Ph

\[ \text{H NMR spectrum of 3ai (400 MHz, DMSO-d}_6\text{)} \]
$^{13}$C NMR spectrum of 3ai (100 MHz, DMSO-d$_6$)
$^1$H NMR spectrum of 3ba (400 MHz, DMSO-d$_6$)
$^{13}$C NMR spectrum of 3ba (100 MHz, DMSO-$d_6$)
$^1$H NMR spectrum of 3ca (400 MHz, DMSO-$d_6$)

![NMR spectrum diagram]

- H NMR spectrum of 3ca (400 MHz, DMSO-$d_6$)

![Structural formula diagram]
$^{13}$C NMR spectrum of 3ca (100 MHz, DMSO-$d_6$)
$^1$H NMR spectrum of 3da (400 MHz, DMSO-d$_6$)
$^{13}$C NMR spectrum of 3da (100 MHz, DMSO-$d_6$)

![Chemical structure and NMR spectrum](image-url)
$^1$H NMR spectrum of 3ea (400 MHz, DMSO-$_d_6$)
$^{13}$C NMR spectrum of 3ea (100 MHz, DMSO-$d_6$)
$^1$H NMR spectrum of 3fa (400 MHz, DMSO-d$_6$)
$^{13}$C NMR spectrum of 3fa (100 MHz, DMSO-$d_6$)

![NMR spectrum diagram]
$^1$H NMR spectrum of 3ga (400 MHz, DMSO-d$_6$)
$^{13}$C NMR spectrum of 3ga (100 MHz, DMSO-$d_6$)
$^1$H NMR spectrum of 3ha (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3ha (100 MHz, CDCl$_3$)

![13C NMR spectrum of 3ha](image)
$^1$H NMR spectrum of 6ha (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of **6ha** (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3ia (400 MHz, CDCl$_3$)
$^1$H NMR spectrum of diastereoisomers 3ia (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3ia (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 6ja (400 MHz, CDCl$_3$)
$^1$H NMR spectrum of diasteroisomers 6Ja (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 6ja (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 5b (400 MHz, CDCl$_3$)

Ph$_2$NH$_2$COOEt
$^{13}$C NMR spectrum of 5b (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 7b (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 7b (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 8a (400 MHz, CDCl$_3$)
$^1$C NMR spectrum of 8a (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 8b (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 8b (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 8c (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 8c (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 8d (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 8d (100 MHz, CDCl$_3$)