Supporting information

Facile nucleophilic substitution of sulfonyl oxime ethers: An easy access to oxime ethers, carbonyl compounds and amines

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1. Instrument and Measurement

Analytical thin layer chromatography (TLC) was performed on pre-coated glass plates with Kieselgel 60 F254 (0.2 mm, Merck). Flash column chromatography was carried out on Kieselgel 60 (230-400 mesh ASTM, Merck). Proton nuclear magnetic resonance spectroscopy (\(^1\)H NMR) was recorded on Bruker Fourier Transform AC 300 (300MHz) or Bruker Fourier Transform AM 400 (400MHz) spectrometers. The following abbreviations were used to describe peak patterns when appropriate: s = singlet, bs = broad singlet, d = doublet, bd = broad doublet, dd = doublet of doublet, t = triplet, q = quartet, m = multiplet. Coupling constant, \(J\), was reported in Hertz unit (Hz). Carbon -13 nuclear magnetic resonance spectroscopy (\(^{13}\)C NMR) was recorded on Bruker Fourier Transform AC 300 (75MHz) or Bruker Fourier Transform AM 400 (100MHz) and was fully decoupled by broad-band decoupling. High resolution mass spectra were obtained on a VG AUTOSPEC Ultma GC/MS system using direct insertion probe (DIP) and electron impact (EI) (70 eV) method.

2. Materials

All the commercially available reagent grade chemicals were obtained from Sigma-Aldrich, Fluka, and Tokyo Kasei Chemical company and generally used without further purifications. If necessary, distillation or recrystallization was done before use. Tetrahydrofuran was distilled from sodium-benzophenone system under nitrogen. \(N,N\)-Dimethylformamide was distilled from CaH\(_2\). Solvents including ethyl acetate (EA) and \(n\)-hexane for column chromatography were technical grade and distilled before use.
3. Experimental procedure and spectral data

Preparation of 3-Phenyl-1-(phenylsulfonyl)propan-1-one O-Benzyl Oxime (4)

\[
\begin{align*}
\text{Ph} & \quad \text{N} \quad \text{O} \quad \text{Bn} \\
\text{Ph} & \quad \text{N} \quad \text{Cl} \\
\text{Ph} & \quad \text{N} \quad \text{O} \quad \text{Bn}
\end{align*}
\]

The solution of oxime ether A (5.96 g, 25 mmol) and N-chlorosuccinimide (4.31 g, 32.3 mmol) in N, N-dimethylformamide (20 mL) was heated at 40 °C for 3 h. The mixture was diluted with diethyl ether, washed with brine several times. The organic phase was dried over anhydrous MgSO₄, filtered, and evaporated. The residue was purified by silica gel column chromatography using ethyl acetate : n-hexane = 1 : 20 as eluent to give 6a (6.7g, 98%).

\[
\begin{align*}
\text{Ph} & \quad \text{N} \quad \text{O} \quad \text{Bn} \\
\text{Ph} & \quad \text{N} \quad \text{Cl} \\
\text{Ph} & \quad \text{N} \quad \text{O} \quad \text{Bn}
\end{align*}
\]

1H NMR (CDCl₃, 400MHz) δ 2.75~2.80 (m, 2H), 2.92~2.96 (m, 2H), 5.13 (s, 2H), 7.16~7.36 (m, 10H); 13C NMR (CDCl₃, 100MHz) δ 32.8, 38.8, 76.7, 126.5, 128.2, 128.3, 128.6, 128.7, 137.0, 139.2, 140.0;

HRMS(ESI): (M+H)^+ calcd for C₁₆H₁₆NO: 274.1008, found 274.0999

To a slurry of sodium hydride (1.47 g, 36.8 mol) in THF (80 mL) was added benzenethiol (2.5 mL, 24.5 mmol) at 0 °C. The mixture was warmed up to room temperature and stirred for 30 min. The solution of 6a (6.7 g, 24.5 mmol) in THF (10 mL) was added to the sodium thiophenoxide solution at 0 °C. The mixture was stirred for 4 h at room temperature and diluted with diethyl ether. The organic phase was washed with aqueous NH₄Cl solution and brine. The
organic phase was dried over anhydrous MgSO₄, filtered, and evaporated. The residue was purified by passing through a short column of silica gel using ethyl acetate : \textit{n}-hexane = 1 : 10 as eluent to give \textbf{6b} (7.9g, 93%).

![NMR spectrum of 6b](image)

\textbf{1H NMR} (CDCl₃, 400MHz) δ 2.35~2.40 (m, 2H), 2.64~2.68 (m, 2H), 5.21 (s, 2H), 6.74~6.79 (d, \textit{J} = 7.8 Hz, 2H), 7.11~7.18 (m, 3H), 7.32~7.44 (m, 8H), 7.46~7.58 (d, \textit{J} = 7.8 Hz, 2H); \textbf{13C NMR} (CDCl₃, 100MHz) δ 34.1, 34.6, 76.4, 126.2, 127.9, 128.0, 128.1, 128.4, 128.5, 129.3, 129.5, 129.8, 136.5, 137.9, 140.9, 154.6; HRMS(ESI): (M+H)⁺ calcd for C₂₂H₂₁NOS: 348.1416, found 348.1422

Sodium bicarbonate (2.77 g, 33 mmol) and \textit{m}-chloroperoxybenzoic acid (4.93 g, 22 mmol) were added to the solution of \textbf{6b} (3.47 g, 10 mmol) in methylene chloride (100 mL) at 0 °C. After being stirred at room temperature for 6 h, the mixture was diluted with methylene chloride and washed with aqueous sodium thiosulfate solution. The organic phase was washed with aqueous sodium bicarbonate solution several times and washed with brine. The combined organic phase was dried over anhydrous MgSO₄, filtered, and evaporated. The residue was purified by silica gel column chromatography using ethyl acetate : \textit{n}-hexane (1 : 5) as eluent to give \textbf{4} (3.41g, 90%).

![NMR spectrum of 4](image)

\textbf{1H NMR} (CDCl₃, 400MHz) δ 2.98~3.04 (m, 4H), 4.97 (s, 2H), 6.92 (d, \textit{J} = 7.4 Hz, 2H), 7.16-7.27 (m, 8H), 7.35 (t, \textit{J} = 7.8 Hz, 2H), 7.56 (t, \textit{J} = 7.8 Hz, 2H), 7.75 (d, \textit{J} = 7.4 Hz, 2H); \textbf{13C NMR} (CDCl₃, 100MHz) δ 32.5, 33.4, 78.2, 126.5, 128.4, 128.6, 128.8, 128.85, 129.0, 133.9, 135.9, 140.3,
Typical procedure of nucleophilic substitution reactions of 3-phenyl-1-(phenylsulfonyl) propan-1-one O-benzyl oxime (4)

Reaction of 4 with n-butyllithium; Preparation of 1-phenylheptan-3-one O-benzyl oxime (5a)

To the solution of 4 (75.9 mg, 0.2 mmol) in THF (2 ml) was added 2.5M n-butyllithium solution in hexane (0.096 ml, 0.24 mmol) at -78 °C. After being stirred for 3 h at -78 °C, the reaction mixture was diluted with ethyl acetate and quenched with saturated aqueous ammonium chloride solution. The organic layer was separated and the aqueous layer was further extracted with ethyl acetate. The combined organic layer was dried over anhydrous magnesium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate : n-hexane 1 : 15 as eluent to give 5a (54 mg, 91%).

\( ^1H \text{ NMR} (\text{CDCl}_3, 400 \text{ MHz}) \delta 0.88\sim0.93 (\text{m, 3H}), 1.29\sim1.32 (\text{m, 2H}), 1.46\sim1.48 (\text{m, 2H}), 2.12 (t, J = 7.9 \text{ Hz}, 1\text{H}), 2.37 (t, J = 8.0 \text{ Hz}, 1\text{H}), 2.50 (t, J = 7.9 \text{ Hz}), 2.63 (t, J = 8.0 \text{ Hz}, 1\text{H}), 2.80\sim2.84 (\text{m, 2H}), 5.10 (d, J = 3.7 \text{ Hz}, 2\text{H}), 7.16\sim7.38 (\text{m, 10H}); ^{13}C \text{ NMR} (\text{CDCl}_3, 100 \text{ MHz}) \delta 13.8, 22.4, 22.8, 27.9, 28.3, 28.5, 30.4, 31.8, 32.7, 34.2, 35.9, 75.3, 75.4, 125.9, 126.0, 127.4, 127.5, 127.8, 127.9, 128.19, 128.2, 128.25, 128.3, 128.4, 138.3, 138.4, 141.4, 141.5, 161.0, 161.2; \text{HRMS (M+)} \text{calcd for C}_{20}\text{H}_{25}\text{NO: 295.1936, found 295.1940
Reaction of 4 with sodium methoxide; Preparation of methyl N-benzyloxy-3-phenylpropanimidate (5i)

To the solution of 4 (76 mg, 0.2 mmol) in THF (2 ml) was added sodium methoxide (22 mg, 0.4 mmol) at 0 °C. After being stirred for 3 h at 0 °C, the reaction mixture was diluted with ethyl acetate and quenched with saturated aqueous ammonium chloride solution. The organic layer was separated and the aqueous layer was further extracted with ethyl acetate. The combined organic layer was dried over anhydrous magnesium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate : n-hexane 1 : 15 as eluent to give 5i (50 mg, 93%).

\[ \text{1H NMR (CDCl}_3, \text{ 400 MHz) } \delta 2.68-2.72 (m, 2H), 2.81-2.85 (m, 2H), 3.64 (s, 3H), 4.92 (s, 2H), 7.16-7.35 (m, 10H); \text{13C NMR (CDCl}_3, \text{ 100 MHz) } \delta 29.30, 31.2, 54.0, 75.7, 126.0, 127.6, 128.2, 128.26, 128.29, 128.3, 138.0, 141.0, 164.8; \text{HRMS (M+) calcd for C}_{17}H_{19}NO_2: 269.1416, found 269.1414} \]

Preparation of bis-methylsulfonyl methanone O-benzyl oxime (8)

[Diagram of the reaction]

Carbon disulfide (9 mL, 150 mmol) and iodomethane (9.4 mL, 150 mmol) were added to
the solution of O-benzyl hydorxyamine hydrochloride (4.8 g, 30 mmol) in methylene chloride (100 mL) at 0 °C. Triethylamine (21 mL, 150 mmol) was added to the mixture and the mixture was stirred at 0 °C for 30 min. After being stirred at room temperature for 3 h, the mixture was quenched with aqueous NH₄Cl solution and diluted with methylene chloride. The combined organic phase was dried over anhydrous MgSO₄, filtered and evaporated. The residue was purified by silica gel column chromatography with ethyl acetate: n-hexane = 1 : 20 as eluent to give 7 (4.80 g, 70%).

\[ ^1H\text{ NMR (CDCl}_3, 400\text{MHz)} \delta 2.40 \ (s, \ 3\text{H}), \ 2.41 \ (s, \ 3\text{H}), \ 5.15 \ (s, \ 2\text{H}), \ 7.25-7.39 \ (m, \ 5\text{H}); \ ^{13}\text{C NMR (CDCl}_3, 100\text{MHz)} \delta 13.7, \ 15.4, \ 76.7, \ 127.9, \ 128.3, \ 128.5, \ 138.0, \ 1523.1; \ HRMS(ESI): (M+H)^+ \text{ calcd for C}_{10}\text{H}_{13}\text{NOS}_2: 228.0511, \text{ found 228.0517}\]

Aqueous hydrogen peroxide (35 wt.%, 8.7 mL, 100 mmol) was added to the solution of 7 (4.8 g, 21 mmol) in acetic acid (25 mL). After being stirred at reflux for 5 h, the mixture was quenched with aqueous sodium thiosulfate solution and extracted with methylene chloride three times. After the organic phase was washed with aqueous sodium bicarbonate solution and brine, the combined organic phase was dried over anhydrous MgSO₄, filtered, and evaporated. The residue was purified by silica gel column chromatography with ethyl acetate : n-hexane = 1 : 2 as eluent to give bis-methylsulfonyl methanone O-benzyl oxime (8) (5.50 g, 90%).

\[ ^1H\text{ NMR (CDCl}_3, 400\text{MHz)} \delta 3.21 \ (s, \ 3\text{H}), \ 3.30 \ (s, \ 3\text{H}), \ 5.50 \ (s, \ 2\text{H}), \ 7.25-7.39 \ (m, \ 5\text{H}); \ ^{13}\text{C NMR (CDCl}_3, 100\text{MHz)} \delta 13.7, \ 15.4, \ 76.7, \ 127.9, \ 128.3, \ 128.5, \ 138.0, \ 1523.1; \ HRMS(ESI): (M+H)^+ \text{ calcd for C}_{10}\text{H}_{13}\text{NOS}_2: 228.0511, \text{ found 228.0517}\]
7.38~7.41 (m, 5H); $^{13}$C NMR (CDCl$_3$, 100MHz) $\delta$ 43.4, 44.8, 82.1, 129.1, 129.2, 129.7, 134.1, 152.2; HRMS (M+) calcd for C$_{15}$H$_{15}$NO$_3$S: 289.0773, found 289.0777.

**Typical procedure for nucleophilic substitution of 8.**

**Preparation of N-(Benzyloxy)(methylsulfonyl)methanimidoyl cyanide (13)**

To the solution of 8 (58.3 mg, 0.2 mmol) in THF (1 ml), potassium cyanide (15.6 mg, 0.24 mmol) was added and further stirred for 2 h at room temperature. The reaction mixture was diluted with ethyl acetate and quenched by the addition of saturated aqueous ammonium chloride solution. The phases were separated and the aqueous layer was further extracted with ethyl acetate. The combined organic layer was dried over MgSO$_4$, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate : n-hexane 1 : 2 as eluent to give 13 (42.9 mg, 90%).

\[
\text{N} \quad \text{OBn}
\]

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 3.16 (s, 3H), 5.47 (s, 2H), 7.36~7.41 (m, 5H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 41.8, 81.7, 105.0, 128.9, 129.1, 129.5, 133.5, 134.1; HRMS (M+) calcd for C$_{10}$H$_{10}$N$_2$O$_3$S: 238.0412, found 238.0414.

**Preparation of 1-(Methylsulfonyl)-3-phenylprop-2-yn-1-one O-benzyl oxime (10g)**

To the solution of phenylacetylene (0.033 ml, 0.3 mmol) in THF (2 ml) was added 2.5 M butyllithium solution in hexane (0.12 ml, 0.3 mmol) at -78 °C. After being stirred for 10 min, the solution of 7 (58.3 mg, 0.2 mmol) in THF (1 ml) was added by cannula at -78 °C. After
being stirred at -78 °C for 4 h, the reaction mixture was diluted with ethyl acetate and quenched with saturated aqueous ammonium chloride solution. The phases were separated and the aqueous layer was further extracted with ethyl acetate. The combined organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using ethyl acetate : n-hexane 1 : 4 as eluent to give 10g (47 mg, 72%).

\[ \text{1H NMR (CDCl}_3, \ 400 \text{ MHz)} \delta 3.14 \ (s, 3H), \ 5.36 \ (s, 2H), \ 7.33-7.42 \ (m, 8H), \ 7.55-7.57 \ (m, 2H); \text{13C NMR (CDCl}_3, \ 100 \text{ MHz)} \delta 40.7, \ 73.5, \ 79.2, \ 107.1, \ 120.1, \ 128.5, \ 128.57, \ 128.59, \ 128.6, \ 130.6, \ 132.5, \ 135.6, \ 143.3; \text{HRMS (M+)} \text{ calcd for } C_{17}H_{15}NO_3S: 313.0773, \text{ found 313.0773} \]

**Additional Spectral data**

**1,3-Diphenylpropan-1-one O-benzyl oxime (5b)**

\[ \text{1H NMR (CDCl}_3, \ 400 \text{ MHz)} \delta 2.88-2.92 \ (m, 2H), \ 3.09-3.13 \ (m, 2H), \ 5.28 \ (s, 2H), \ 7.21-7.44 \ (m, 13H), \ 7.63-7.65 \ (m, 2H); \text{13C NMR (CDCl}_3, \ 100 \text{ MHz)} \delta 28.9, \ 32.4, \ 76.2, \ 126.0, \ 126.3, \ 127.7, \ 128.0, \ 128.3, \ 128.35, \ 128.4, \ 129.0, \ 135.6, \ 138.1, \ 141.4, \ 158.1; \text{HRMS (M+)} \text{ calcd for } C_{22}H_{21}NO: 315.1623, \text{ found 315.1624} \]

**1,5-Diphenylpent-1-yn-3-one O-benzyl oxime (5c)**

\[ \text{1H NMR (CDCl}_3, \ 400 \text{ MHz)} \delta 2.69-2.73 \ (m, 2H), \ 2.96-3.00 \ (m, 2H), \ 5.20 \ (s, 1H), \ 7.18-7.38 \ (m, 13H), \ 7.49-7.52 \ (m, 2H); \text{13C} \]
**NMR** (CDCl₃, 100 MHz) δ 33.4, 36.3, 76.4, 80.8, 100.2, 122.0, 126.3, 127.8, 127.9, 128.5, 128.58, 128.6, 128.7, 129.6, 132.3, 138.0, 140.0, 141.8; HRMS (M+) calcd for C₂₄H₂₁NO: 339.1623, found 339.1617

**3-(Benzoyloxyimino)-N,N-dimethyl-5-phenylpent-anamide (5d)**

**1H NMR** (CDCl₃, 400 MHz) δ 2.59–2.63 (m, 2H), 2.82 (s, 3H), 2.88 (s, 3H), 2.88–2.92 (m, 2H), 3.40 (s, 2H), 5.09 (s, 2H), 7.17–7.34 (m, 10H); **13C NMR** (CDCl₃, 100 MHz) δ 32.4, 34.3, 35.7, 36.1, 75.9, 126.1, 128.0, 128.4, 128.5, 128.7, 137.9, 141.5, 154.6, 168.4; HRMS (M+) calcd for C₂₀H₂₄N₂O₂: 324.1838, found 324.1837

**t-Butyl 3-(benzoyloxyimino)-5-phenylpentanoate (5e)**

1.41 (s, 9H), 2.56–2.60 (m, 2H), 2.85–2.89 (m, 2H), 3.27 (s, 2H), 5.10 (s, 2H), 7.17–7.34 (m, 10H); **13C NMR** (CDCl₃, 100 MHz) δ 28.1, 32.5, 36.4, 36.9, 75.8, 81.4, 126.2, 127.8, 128.0, 128.4, 128.5, 128.6, 138.2, 141.4, 153.9, 168.2; HRMS (M+) calcd for C₂₂H₂₇NO₃: 353.1991, found 353.1993

**Diethyl 1-(benzoyloxyimino)-3-phenylpropylphosphon-ate (5f)**

**1H NMR** (CDCl₃, 400 MHz) δ 1.24–1.29 (t, J = 7.1 Hz 6H), 2.70–2.77 (m, 2H), 2.87–2.91 (m, 2H), 4.01–4.15 (m, 4H), 5.21 (s, 2H), 7.16–7.20 (m, 3H), 7.24–7.38 (m, 7H); **13C NMR** (CDCl₃, 100 MHz) δ 16.4 (d, J$_{cp}$ = 6.7 Hz), 33.5, 35.2, 35.4, 62.6 (d, J$_{cp}$ = 5.8 Hz), 126.2, 128.1, 128.3, 128.5, 128.7, 137.2, 141.1, 151.7, 153.2; HRMS (M+) calcd for C₂₀H₂₆NO₄P: 375.1599, found 375.1596
N-(Benzyloxy)-3-phenylpropanimidoxy cyanide (5g)

\[ \text{1H NMR (CDCl}_3, 400 \text{ MHz)} \delta 2.71\text{~}2.81\text{(m, 2H)}, \ 2.88\text{~}2.95 \text{(m, 2H)}, \ 5.20 \text{ (d, } J = 3.8 \text{ Hz, 2H)}, \ 7.15\text{~}7.36 \text{(m, 10H)}; \ \text{13C NMR (CDCl}_3, 100\text{MHz)} \delta 29.6, 31.3, 32.3, 33.7, 77.8, 78.4, 110.3, 114.4, 126.6, 126.7, 128.1, 128.2, 128.3, 128.4, 128.47, 128.5, 128.57, 128.6, 131.8, 135.7, 136.1, 138.4, 138.9, 139.04; \ \text{HRMS (M+)} \text{ calcd for C}_{17}\text{H}_{16}\text{N}_2\text{O: 264.1263, found 264.1262} \]

N-Benzyl-N’-(benzyloxy)-3-phenylpropanimid amide (5h)

\[ \text{1H NMR (CDCl}_3, 400\text{MHz) } \delta 2.45\text{~}2.49 \text{(m, 2H)}, \ 2.85\text{~}2.9 \text{(m, 2H)}, \ 4.28\text{~}4.29 \text{(d, } J = 6.6 \text{ Hz, 2H)}, \ 5.01 \text{ (s, 2H)}, \ 5.57 \text{ (bs, 1H)}, \ 7.13\text{~}7.39 \text{(m, 15H); } \ \text{13C NMR (CDCl}_3, 100\text{MHz)} \delta 30.7, 33.5, 46.2, 75.4, 126.4, 126.9, 127.6, 127.9, 128.5, 128.54, 128.56, 128.6, 128.9, 138.5, 139.4, 141.2, 155.2; \ \text{HRMS (M+)} \text{ calcd for C}_{23}\text{H}_{24}\text{N}_2\text{O: 344.1889, found 344.1889} \]

Phenyl N-benzyloxy-3-phenylpropanimidothioate (5j)

\[ \text{1H NMR (CDCl}_3, 400\text{MHz) } \delta 2.35\text{~}2.40 \text{(m, 2H)}, \ 2.64\text{~}2.68 \text{(m, 2H)}, \ 5.21 \text{ (s, 2H)}, \ 6.74\text{~}6.79 \text{(d, } J = 7.8 \text{ Hz, 2H)}, \ 7.11\text{~}7.18 \text{(m, 3H)}, \ 7.32\text{~}7.44 \text{(m, 8H)}, \ 7.46\text{~}7.58 \text{(d, } J = 7.8 \text{ Hz, 2H); } \ \text{13C NMR (CDCl}_3, 100\text{MHz)} \delta 34.1, 34.6, 76.4, 126.2, 127.9, 128.0, 128.1, 128.4, 128.5, 129.3, 129.5, 129.8, 136.5, 137.9, 140.9, 154.6; \ \text{HRMS (M+)} \text{ calcd for C}_{22}\text{H}_{21}\text{NOS: 347.1344, found 347.1344} \]

3-(benzyloxyimino)-3-(methylsulfonyl)-1-phenylpropan-1-one (10b)
\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta 3.19\) (s, 3H), 4.41 (s, 2H), 5.26 (s, 2H), 7.65–7.27 (m, 8H), 7.93 (d, \(J = 8.3\) Hz, 2 H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta 35.4, 41.2, 78.7, 128.5, 128.7, 129.0, 134.1, 135.7, 135.8, 156.2, 191.7\); HRMS (M+) calcd for C\textsubscript{17}H\textsubscript{17}NO\textsubscript{4}S: 332.0957, found 332.0965

\[\text{Diethyl(benzyloxyimino)(methylsulfonyl)methylphosphonate (10c)}\]

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta 1.27\) (t, \(J = 7.1\) Hz, 6H), 3.14 (s, 3H), 4.15–4.24 (m, 4H), 5.36 (s, 2H), 7.36 (s, 5H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) \(\delta 16.3\) (d, \(J_{cp} = 6.7\) Hz), 41.7, 64.8 (d, \(J_{cp} = 5.7\) Hz), 80.3, 128.9, 129.1, 135.1, 153.3, 154.9; HRMS (M+) calcd for C\textsubscript{13}H\textsubscript{20}NO\textsubscript{6}PS: 349.0749, found 349.0745

\[\text{Ethyl 3-(benzyloxyimino)-3-(methylsulfonyl)-propano-ate (10d)}\]

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta 1.18\) (t, \(J = 7.1\) Hz, 3H), 3.11 (s, 3H), 4.11 (q, \(J = 7.1\) Hz, 2H), 5.27 (s, 2H), 7.31–7.35 (m, 5H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) \(\delta 14.1, 30.4, 41.2, 62.1, 77.6, 128.6, 128.7, 128.8, 135.8, 155.0, 166.5\); HRMS (M+) calcd for C\textsubscript{13}H\textsubscript{17}NO\textsubscript{5}S: 300.0906, found 300.0907

\[\text{Methanesulfonyl(thiophenyl)methanone O-benzyl oxime (10e)}\]

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta 3.11\) (s, 3H), 5.17 (s, 2H), 7.09–7.11 (m, 2H), 7.26–7.34 (m, 6H), 7.51–7.54 (m, 2H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) \(\delta 41.1, 78.9, 127.2, 128.6, 128.8, 129.3, 129.9, 134.1, 135.7\); HRMS(ESI) (M+H\textsuperscript{+}) calcd for C\textsubscript{13}H\textsubscript{15}NO\textsubscript{3}S\textsubscript{2}: 322.0570, found 322.0572

\[\text{Methyl N-benzyloxy(methylsulfonyl)methanimidate (10f)}\]
$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 3.08 (s, 3H), 4.22 (s, 3H), 5.10 (s, 2H), 7.33-7.38 (m, 5H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 41.0, 62.1, 78.4, 128.7, 128.72, 128.8, 128.8, 136.0, 152.2; HRMS (M+) calcd for C$_{10}$H$_{13}$NO$_4$S: 244.0644, found 244.0650

$N'$-(Benzyloxy)(methylsulfonyl)methanimidoyl azide (10g)

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 3.12 (s, 3H), 5.21 (s, 2H), 7.34~7.40 (m, 5H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 41.1, 79.2, 128.8, 128.9, 129.1, 135.3, 144.5; HRMS (M+) calcd for C$_9$H$_{10}$N$_4$O$_3$S: 254.0474, found 254.0472.

$N$-Benzy1-$N'$-(benzyloxy)(methylsulfonyl) methan-imidamide (11)

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 3.08 (s, 3H), 4.71 (d, $J$ = 6.4 Hz, 2H), 5.01 (s, 2H), 5.27 (s, 1H), 7.28-7.32 (m, 10H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 41.3, 48.1, 53.6, 127.8, 127.9, 128.3, 128.5, 128.6, 128.9, 136.9, 138.2, 151.0; HRMS (M+) calcd for C$_{16}$H$_{18}$N$_2$O$_3$S: 318.1038, found 318.1034

1,3-dibenzyl-2-(benzyloxy)guanidine (12)

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ 3.26 (s, 1H), 4.18~4.22 (m, 4 H), 4.89 (s, 2H), 5.42 (s, 1H), 7.24~7.37 (m, 15H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 45.8, 45.9, 75.7, 126.9, 127.3, 127.6, 127.8, 127.9, 128.4, 128.6, 128.9, 129.0, 138.5, 139.0, 139.3, 155.7; HRMS (M+) calcd for C$_{22}$H$_{23}$N$_3$O: 346.1919, found 346.1912.

$N$-(Benzyloxy)(methylsulfonyl)methanimidoyl cyanide (13)

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 3.16 (s, 3H), 5.47 (s, 2H), 7.36~7.41 (m,
$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 41.8, 81.7, 105.0, 128.9, 129.1, 129.5, 133.5, 134.1; HRMS (M+) calcd for C$_{10}$H$_{10}$N$_2$O$_3$S: 238.0412, found 238.0414

2-Benzylxoyiminopropionitrile (14)

$^1$H NMR (CDCl$_3$, 400MHz) major isomer: $\delta$ 2.08 (s, 3H), 5.26 (s, 2H), 7.36–7.38 (m, 5H); minor isomer: $\delta$ 2.14 (s, 3H), 5.23 (s, 2H), 7.36–7.38 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) major isomer: $\delta$ 15.2, 78.6, 115.5, 128.6, 128.8, 134.5, 136.0; minor isomer: 15.5, 77.9, 111.0, 128.4, 128.6, 128.8, 134.5, 136.3; HRMS(ESI) (M+H)$^+$ calcd for C$_{10}$H$_{10}$N$_2$O: 175.0870, found 175.0871