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 (¹H 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 (¹³C 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 CaH₂. 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)

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 mixuture 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%).



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 NH_4Cl 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 : n-hexane = 1 : 10 as eluent to give **6b** (7.9g, 93%).



¹**H 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, J = 7.8 Hz, 2H), 7.11~7.18 (m, 3H), 7.32~7.44 (m, 8H), 7.46~7.58 (d, J = 7.8 Hz, 2H); ¹³**C 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 *m*-chloroperoxybenzoic acid (4.93 g, 22 mmol) were added to the solution of **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 : *n*-hexane (1 : 5) as eluent to give **4** (3.41g, 90%).



¹**H NMR** (CDCl₃, 400MHz) δ 2.98~3.04 (m, 4H), 4.97 (s, 2H), 6.92 (d, J = 7.4 Hz, 2H), 7.16-7.27 (m, 8H), 7.35 (t, J = 7.8 Hz, 2H), 7.56 (t, J = 7.8 Hz, 2H), 7.75 (d, J = 7.4 Hz, 2H); ¹³**C NMR** (CDCl₃,

100MHz) & 32.5, 33.4, 78.2, 126.5, 128.4, 128.6, 128.8, 128.85, 129.0, 133.9, 135.9, 140.3,

153.7; HRMS(ESI): $(M+H)^+$ calcd for C₂₂H₂₁NO₃S: 380.1328, found 380.1320

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 NMR (CDCl₃, 400 MHz) δ 0.88~0.93 (m, 3H), 1.29~1.32 (m, 2H),
1.46~1.48 (m, 2H), 2.12 (t, J = 7.9 Hz, 1H), 2.37 (t, J = 8.0 Hz, 1H),
2.50 (t, J = 7.9 Hz), 2.63 (t, J = 8.0 Hz, 1H), 2.80~2.84 (m, 2H), 5.10 (d,

J = 3.7 Hz, 2H), 7.16~7.38 (m, 10H); ¹³C NMR (CDCl₃, 100 MHz) δ 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; HRMS (M+) calcd for C₂₀H₂₅NO: 295.1936, found 295.1940

Reaction of 4 with sodium methoxide; Preparation of methyl *N*-benzyloxy-3phenylpropanimidate (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%).



¹H NMR (CDCl₃, 400 MHz) δ 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); ¹³C NMR (CDCl₃, 100 MHz) δ 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; HRMS (M+) calcd for C₁₇H₁₉NO₂: 269.1416, found 269.1414

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



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 NMR (CDCl₃, 400MHz) δ 2.40 (s, 3H), 2.41 (s, 3H), 5.15 (s, 2H), 7.25~7.39 (m, 5H); ¹³C NMR (CDCl₃, 100MHz) δ 13.7, 15.4, 76.7, 127.9, 128.3, 128.5, 138.0, 1523.1; HRMS(ESI): (M+H)⁺ calcd for C₁₀H₁₃NOS₂:

228.0511, 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 NMR (CDCl₃, 400MHz) δ 3.21 (s, 3H), 3.30 (s, 3H), 5.50 (s, 2H),

7.38~7.41 (m, 5H); ¹³C NMR (CDCl₃, 100MHz) δ 43.4, 44.8, 82.1, 129.1, 129.2, 129.7, 134.1, 152.2; HRMS (M+) calcd for C₁₅H₁₅NO₃S: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 MgSO₄, 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%).



¹H NMR (CDCl₃, 400 MHz) δ 3.16 (s, 3H), 5.47 (s, 2H), 7.36~7.41 (m, 5H); ¹³C NMR (CDCl₃, 100 MHz) δ 41.8, 81.7, 105.0, 128.9, 129.1, 129.5, 133.5, 134.1; HRMS (M+) calcd for C₁₀H₁₀N₂O₃S: 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%).



¹H NMR (CDCl₃, 400 MHz) δ 3.14 (s, 3H), 5.36 (s, 2H), 7.33~7.42 (m, 8H), 7.55~7.57 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 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; HRMS (M+) calcd for C₁₇H₁₅NO₃S: 313.0773, found 313.0773

Additional Spectral data



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

¹H NMR (CDCl₃, 400 MHz) δ 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); ¹³C NMR

(CDCl₃, 100 MHz) & 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; HRMS (M+) calcd for C₂₂H₂₁NO: 315.1623, found 315.1624



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

¹H NMR (CDCl₃, 400 MHz) δ 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); 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-(Benzyloxyimino)-*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, 37.6, 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-(benzyloxyimino)-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-(benzyloxyimino)-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-phenylpropanimidoyl cyanide (5g)

¹H NMR (CDCl₃, 400 MHz) δ 2.71~2.81(m, 2H), 2.88~2.95 (m, 2H), 5.20 (d, J = 3.8 Hz, 2H), 7.15~7.36 (m, 10H); ¹³C NMR (CDCl₃,

100MHz) δ 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; HRMS (M+) calcd for C₁₇H₁₆N₂O: 264.1263, found 264.1262



N-Benzyl-*N'*-(benzyloxy)-3-phenylpropanimid amide (5h)

¹**H NMR** (CDCl₃, 400MHz) δ 2.45~2.49 (m, 2H), 2.85~2.9 (m, 2H), 4.28~4.29 (d, J = 6.6 Hz, 2H), 5.01 (s, 2H), 5.57 (bs, 1H), 7.13~7.39

(m, 15H); ¹³C NMR (CDCl₃, 100MHz) δ 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; HRMS (M+) calcd for $C_{23}H_{24}N_2O$: 344.1889, found 344.1889



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

Ph SPh ¹**H** 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, J = 7.8 Hz, 2H), 7.11~7.18 (m, 3H), 7.32~7.44 (m, 8H), 7.46~7.58 (d, J = 7.8 Hz, 2H); 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 (M+) calcd for C₂₂H₂₁NOS: 347.1344, found 347.1344



3-(benxyloxyimino)-3-(methylsulfonyl)-1-phenylpropan-1-one (10b) ¹**H** NMR (CDCl₃, 400 MHz): δ 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); ¹³ C NMR (100 MHz, CDCl₃): δ 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 C₁₇H₁₇NO₄S: 332.0957, found 332.0965



Diethyl(benzyloxyimino)(methylsulfonyl)methylphosphonate (10c)
¹H NMR (CDCl₃, 400 MHz) δ 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); ¹³C NMR (CDCl₃, 100

MHz) δ 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 C₁₃H₂₀NO₆PS: 349.0749, found 349.0745



Ethyl 3-(benzyloxyimino)-3-(methylsulfonyl)-propano-ate (10d) ¹H NMR (CDCl₃, 400 MHz) δ 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); ¹³C

NMR (C₆D₆, 100 MHz) δ 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 C₁₃H₁₇NO₅S: 300.0906, found 300.0907



Methanesulfonyl(thiophenyl)methanone O-benzyl oxime (10e)

¹**H NMR** (CDCl₃, 400 MHz) δ 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); ¹³**C NMR** (CDCl₃, 100

MHz) δ 41.1, 78.9, 127.2, 128.6, 128.8, 129.3, 129.4, 134.1, 135.7; HRMS(ESI) (M+H)⁺ calcd for C₁₅H₁₅NO₃S₂: 322.0570, found 322.0572



Methyl N-benzyloxy(methylsulfonyl)methanimidate (10f)

¹**H** NMR (CDCl₃, 400 MHz) δ 3.08 (s, 3H), 4.22 (s, 3H), 5.10 (s, 2H), 7.33-7.38 (m, 5H); ¹³**C** NMR (CDCl₃, 100 MHz) δ 41.0, 62.1, 78.4, 128.7, 128.72, 128.8, 136.0, 152.2; HRMS (M+) calcd for C₁₀H₁₃NO₄S: 244.0644, found 244.0650



N'-(Benzyloxy)(methylsulfonyl)methanimidoyl azide (10g)
¹H NMR (CDCl₃, 400 MHz) δ 3.12 (s, 3H), 5.21 (s, 2H), 7.34~7.40 (m, 5H); ¹³C NMR (CDCl₃, 100 MHz) δ 41.1, 79.2, 128.8, 128.9, 129.1,

135.3, 144.5; HRMS (M+) calcd for C₉H₁₀N₄O₃S: 254.0474, found 254.0472.



N-Benzyl-*N'*-(benzyloxy)(methylsulfonyl) methan-imidamide (11)

¹**H NMR** (CDCl₃, 400 MHz) δ 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); ¹³C NMR (CDCl₃, 100 MHz) δ 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 C₁₆H₁₈N₂O₃S: 318.1038, found 318.1034



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

¹**H NMR** (CDCl₃, 400MHz): δ 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, CDCl₃): δ 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 C₂₂H₂₃N₃O: 346.1919, found 346.1912.



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

¹**H NMR** (CDCl₃, 400 MHz) δ 3.16 (s, 3H), 5.47 (s, 2H), 7.36~7.41 (m,

5H); ¹³C NMR (CDCl₃, 100 MHz) δ 41.8, 81.7, 105.0, 128.9, 129.1, 129.5, 133.5, 134.1; HRMS (M+) calcd for C₁₀H₁₀N₂O₃S: 238.0412, found 238.0414



2-Benzyloxyiminopropionitrile (14)

¹**H NMR** (CDCl₃, 400MHz) **major isomer**: δ 2.08 (s, 3H), 5.26 (s, 2H), 7.36~7.38 (m, 5H); **minor isomer**: δ 2.14 (s, 3H), 5.23 (s, 2H), 7.36~7.38 (m,

5H); ; ¹³ C NMR (100 MHz, CDCl₃) major isomer: δ 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 C₁₀H₁₀N₂O: 175.0870, found 175.0871











































































































