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Supporting Information

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Radical Alkylation of Organic Nitro Compounds via bis-Silyloxyenamines

Jin Young Lee, Young-Taek Hong and Sunggak Kim*

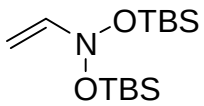
Center for Molecular Design & Synthesis and Department of Chemistry, School of Molecular Science (BK-21), Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea

General. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance-400 spectrometers. The chemical shifts in $CDCl_3$ or benzene-d_6 are reported in δ(ppm) relative to $CDCl_3$ or Me_4Si as an internal reference. Splitting patterns are designated as follows: s; singlet, d; doublet, t; triplet, q; quartet, s; sextet, m; multiplet, dt; double of triplet, ddt; double of double of triplet. IR spectra were measured on a BOMEM MB-100 Fourier Tansform spectrometer. 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. Flash chromatography was carried out on Merck silica 60 (230-400 mesh ASTM). Analytical thin-layer chromatography (TLC) was performed on E. Merck precoated silica gel 60 F_{254} plates. All reagents were purchased from Aldrich Co. All dry solvents were freshly distilled under nitrogen from the appropriate drying agent before use. The photochemical reactor was RAYONET purchased from the Southern New England Ultraviolet Company.

***N,N*-bis(*tert*-buthyldimethylsilyloxy)enamines 3a-h, 9; General Procedure:**

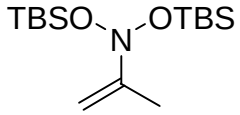
To a stirred solution of 2-nitropropane (**1b**) (89 mg, 1 mmol) in CH_2Cl_2 (2 mL) at 0 ^oC were added successively Et_3N (0.31 mL, 2.2 mmol) and TBSOTf (0.47 mL, 2 mmol). After being stirred for 2 h at 0 ^oC, the reaction mixture was diluted with petroleum ether (10 ml), quenched with aqueous NH_4Cl solution and washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude *N,N*-bis(*tert*-buthyldimethylsilyloxy)prop-1-en-2-amine compound (**3b**) was used for the radical reaction. In the case of the formation of **3f**, the reaction was carried out with **1f** at -78 ^oC.

***N,N*-bis(*tert*-butyldimethylsilyloxy)ethenamine (3a)**



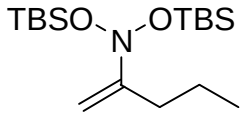
MW: $C_{14}H_{33}NO_2Si_2$ = 303.20; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.16 (s, 12H), 0.89 (s, 18H), 4.61 (d, J= 8 Hz, 1H), 4.95 (d, J= 15 Hz, 1H), 6.22 (dd, J= 15 Hz, 8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ -4.2 (C4), 17.8 (C2), 25.8 (C6), 102.2, 148.6.

***N,N*-bis(*tert*-butyldimethylsilyloxy)prop-1-en-2-amine (3b)**



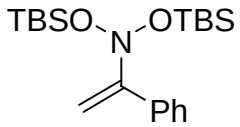
MW: $C_{15}H_{35}NO_2Si_2$ = 317.22; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.14 (s, 12H), 0.88 (s, 18H), 1.88 (d, J= 0.5 Hz, 3H), 4.51 (d, J= 0.5 Hz, 1H), 4.89 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ -4.3 (C4), 13.1, 17.9 (C2), 25.9 (C6), 104.4, 155.8.

***N,N*-bis(*tert*-butyldimethylsilyloxy)pent-1-en-2-amine (3c)**



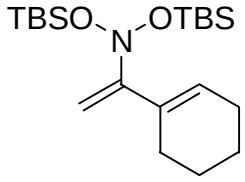
MW: $C_{17}H_{39}NO_2Si_2$ = 345.25; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.14 (s, 12H), 0.87 (s, 18H), 0.93 (t, J= 7.4 Hz, 3H), 1.47-1.56 (m, 2H), 2.26 (t, J= 7.5 Hz, 2H), 4.52 (s, 1H), 4.97 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ -4.2 (C4), 14.0, 17.9 (C2), 21.2, 25.9 (C6), 29.6, 102.5, 159.6.

***N,N*-bis(*tert*-butyldimethylsilyloxy)-1-phenylethenamine(3d)**



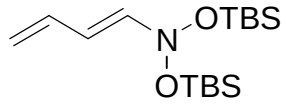
MW: $C_{20}H_{37}NO_2Si_2$ = 379.24; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.20 (s, 12H), 0.77 (s, 18H), 4.91 (s, 1H), 5.34 (s, 1H), 7.26-7.28 (m, 3H), 7.47-7.49 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ -4.0 (C4), 17.9 (C2), 25.7 (C6), 102.2, 127.7, 127.8, 127.9, 137.1, 159.0.

1-Cyclohexenyl-*N*,*N*-bis(*tert*-butyldimethylsilyloxy)ethenamine (3e)



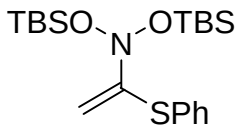
MW: $C_{20}H_{41}NO_2Si_2$ = 383.27; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.14 (s, 12H), 0.87 (s, 18H), 1.54-1.63 (m, 4H), 2.05-2.16 (m, 4H), 4.63 (s, 1H), 5.09 (s, 1H), 5.99(m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ -4.0 (C4), 17.9 (C2), 22.1, 22.7, 25.4, 25.9 (C6), 27.0, 99.0, 126.6, 133.3, 160.7.

(*E*)- *N*,*N*-bis(*tert*-butyldimethylsilyloxy)buta-1,3-dien-1-amine (3f)



MW: $C_{16}H_{35}NO_2Si_2$ = 329.22; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.16 (s, 12H), 0.90 (s, 18H), 5.09 (d, J= 10.2 Hz, 1H), 5.21 (d, J= 16.9 Hz, 1H), 6.02 (dd, J= 16.9 Hz, 10.2 Hz, 1H), 6.19-6.28 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ -4.2 (C4), 17.9 (C2), 25.9 (C6), 118, 120.4, 133.4, 144.9.

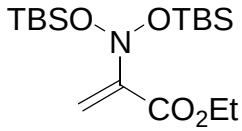
***N*,*N*-bis(*tert*-butyldimethylsilyloxy)-1-(phenylthio)ethenamine (3g)**



MW: $C_{20}H_{37}NO_2SSi_2$ = 411.21; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.19 (s, 12H), 0.92 (s, 18H), 4.65 (s, 1H), 5.40 (s, 1H), 7.26-7.32 (m, 3H), 7.51-7.54(m, 2H); **^{13}C NMR**

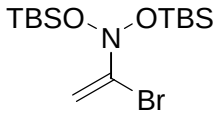
($CDCl_3$, 100 MHz) δ -4.2 (C4), 18.0 (C2), 25.8 (C6), 108.9, 127.6, 129.0, 133.4, 134.1, 159.3.

Ethyl 2-*N*,*N*-bis(*tert*-butyldimethylsilyloxyamino)acrylate (3h)



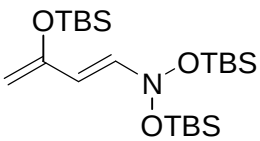
MW: $C_{17}H_{37}NO_4Si_2$ = 375.23; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.19 (s, 12H), 0.87 (s, 18H), 1.28 (t, J= 7.0 Hz, 3H), 4.19 (q, J= 7.0 Hz, 2H), 5.73 (s, 1H), 5.77 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ -4.1 (C4), 14.1, 17.9 (C2), 25.8 (C6), 60.8, 111.5, 151.7, 163.1.

1-bromo-*N*,*N*-bis(*tert*-butyldimethylsilyloxy)ethenamine (9)



MW: $C_{14}H_{32}BrNO_2Si_2$ = 381.12; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.18 (s, 12H), 0.89 (s, 18H), 5.24 (d, J=1.6 Hz, 1H), 5.69 (d, J= 1.6 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ -4.2 (C4), 17.9 (C2), 25.7 (C6), 112.3, 144.

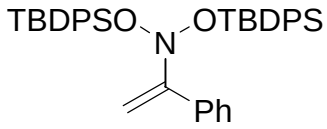
Compound 16



MW: $C_{22}H_{49}NO_3Si_3$ = 459.30; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.17 (s, 12H), 0.18 (s, 6H), 0.91 (s, 18H), 0.94 (s, 9H), 4.27 (s, 2H), 5.85 (d, J= 17.6 Hz, 1H), 6.49 (d, J= 17.6

Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ -4.6 (C2), -4.1 (C4), 17.9, 18.1 (C2), 25.7 (C3), 25.8 (C6), 95.8, 116.7, 142.8, 153.5.

***N,N*-bis(*tert*-butyldiphenylsilyloxy)-1-phenylethenamine(22)**



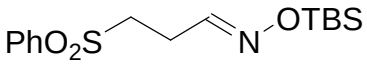
MW: $C_{40}H_{45}NO_2Si_2$ = 627.29; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.84 (s, 18H), 4.41 (s, 1H), 4.72 (s, 1H), 7.27-7.30 (m, 11H), 7.37-7.39 (m, 9H), 7.70-7.72 (m, 5H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 19.1 (C2), 26.8 (C6), 108.4, 126.9 (C2), 127.5 (C2), 127.6 (C2), 127.7 (C2), 128.6 (C2), 129.2 (C3), 129.6, 134.7 (C2), 135.0, 135.2, 136.6, 137.6, 156.9.

Radical reaction of 3b; Typical procedure:

A solution of iodomethyl phenylsulfone (56 mg, 0.2 mmol), **3b** (95 mg, 0.3 mmol), and hexamethylditin (65 mg, 0.2 mmol) in benzene (1 mL; 0.2 M in iodide) was degassed with nitrogen for 10 min, and the solution was then irradiated in a photochemical reactor (300 nm) for 9 h. The solvent was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography with EtOAc/hexane (1:5) as the eluant to give **6b** (49 mg, 71%) as a colorless oil. **MW:** $C_{16}H_{27}NO_3SSi$ = 341.14; E : Z = 5 : 1 (from ^{1}H NMR ratio); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ E: 0.04 (s, 6H), 0.79 (s, 9H), 1.85 (s, 3H), 2.61-2.66 (m, 2H), 3.22-3.26 (m, 2H), 7.53-7.57 (m, 2H), 7.62-7.64 (m, 1H), 7.87-7.90 (m, 2H); Z: 0.07 (s, 6H), 0.86 (s, 9H), 1.80 (s, 3H), 2.52-2.57 (m,

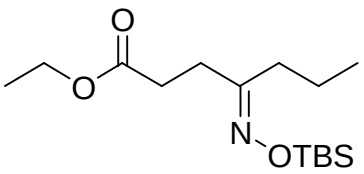
2H), 3.3-3.35 (m, 2H), 7.53-7.57 (m, 2H), 7.62-7.64 (m, 1H), 7.87-7.90 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ E: -5.3 (C2), 17.8, 20.2, 23.5, 25.9 (C3), 51.7, 128.1, 129.3, 133.8, 138.6, 157.4; **IR** (polymer) 784, 838, 1153, 1308, 1447, 1472, 1586, 1637, 2857, 2930, 2955 cm^{-1}; **HRMS** (M^+) calcd for $C_{16}H_{27}NO_3SSi$: 341.1481, found 341.1430.

(*E*)-3-(phenylsulfonyl)propanal *O*-*tert*-butyldimethylsilyl oxime (6a)



MW: $C_{15}H_{25}NO_3SSi$ = 327.13; E : Z = 1.1 : 1 (from ^{1}H NMR ratio); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ E: 0.09 (s, 6H), 0.87 (s, 9H), 2.57-2.62 (m, 2H), 3.24-3.33 (m, 2H), 7.48 (t, J= 4.8 Hz, 1H), 7.56-7.59 (m, 2H), 7.65-7.66 (m, 1H), 7.88-7.91 (m, 2H); Z: 0.09 (s, 6H), 0.85 (s, 9H), 2.70-2.74 (m, 2H), 3.24-3.33 (m, 2H), 6.86 (t, J= 5.3 Hz, 1H), 7.56-7.59 (m, 2H), 7.65-7.66 (m, 1H), 7.88-7.91 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ E: -5.4 (C2), 18.0, 23.6, 25.9 (C3), 52.4, 128.1, 129.4, 133.9, 138.5, 150.6; **IR** (polymer) 701, 924, 1148, 1319, 1428, 1589, 2857, 2932, 2960 cm^{-1}; **HRMS** (M^+) calcd for $C_{15}H_{25}NO_3SSi$ = 327.1324, found 327.1330.

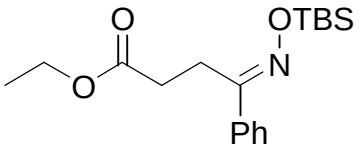
(*E*)-ethyl 4-(*tert*-butyldimethylsilyloxyimino)heptanoate (6c)



MW: $C_{15}H_{31}NO_3Si$ = 301.20; E : Z = 1.4 : 1 (from ^{1}H NMR ratio); **^{1}H NMR** ($CDCl_3$,

400 MHz) δ E: 0.08 (s, 6H), 0.89 (s, 9H), 0.88 (t, J= 7.0 Hz, 3H), 1.23 (t, J= 7.1 Hz, 3H), 1.48-1.50 (m, 2H), 2.27-2.31 (m, 2H), 2.48-2.58 (m, 4H), 4.11 (q, J= 7.1 Hz, 2H); Z: 0.11 (s, 6H), 0.90(s, 9H), 1.22 (t, J= 7.0 Hz, 3H), 1.23 (t, J= 7.1 Hz, 3H), 1.48-1.50 (m, 2H), 2.14-2.17 (m, 2H), 2.48-2.58 (m, 4H), 4.09 (q, J= 7.1 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ E: -5.3 (C2), 14.1 (C2), 18.0, 19.2, 26.0 (C3), 30.1, 30.4, 30.5, 60.3, 162.5, 173.1; **IR** (polymer) 804, 1031, 1096, 1260, 1374, 1464, 1740, 2931, 2961 cm^{-1}; **HRMS** (M^+) calcd for $C_{15}H_{31}NO_3Si$: 301.2073, found 301.2065.

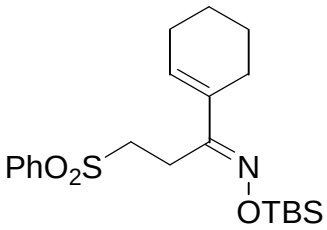
(*E*)-ethyl 4-(*tert*-butyldimethylsilyloxyimino)-4-phenylbutanoate (6d)



MW: $C_{18}H_{29}NO_3Si$ = 335.19; E : Z = 2.5 : 1 (from ^{1}H NMR ratio); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ E: 0.20 (s, 6H), 0.96 (s, 9H), 1.20 (t, J= 7.1 Hz, 3H), 2.52-2.56 (m, 2H), 3.05-3.09 (m, 2H), 4.09 (q, J= 7.1 Hz, 2H), 7.32-7.36 (m, 2H), 7.42-7.44 (m, 1H), 7.63-7.66 (m, 2H); Z: 0.11 (s, 6H), 0.86 (s, 9H), 1.23 (t, J= 7.1 Hz, 3H), 2.59-2.61 (m, 2H), 2.82-2.85 (m, 2H), 4.09 (q, J= 7.1 Hz, 2H), 7.32-7.36 (m, 2H), 7.42-7.44 (m, 1H), 7.63-7.66 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ E: -5.1 (C2), 14.1, 18.1, 22.0, 26.1 (C3), 30.9, 60.5, 126.2, 128.4, 129.1, 135.5, 160.7, 172.7; **IR** (polymer) 694, 933, 1181, 1257, 1556, 1599, 1737, 2930, 2957 cm^{-1}; **HRMS** (M^+) calcd for $C_{18}H_{29}NO_3Si$: 335.1917,

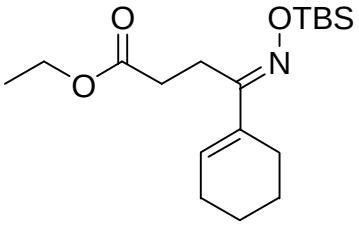
found 335.1906.

(*E*)-1-cyclohexenyl-3-(phenylsulfonyl)propan-1-one *O*-*tert*-butyldimethylsilyl oxime (6e)



MW: $C_{21}H_{33}NO_3SSi$ = 407.19; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.03 (s, 6H), 0.80 (s, 9H), 1.54-1.58 (m, 4H), 2.11-2.16 (m, 4H), 2.79-2.84 (m, 2H), 3.17-3.21 (m, 2H), 6.01-6.03 (m, 1H), 7.52-7.56 (m, 2H), 7.62-7.64 (m, 1H), 7.88-7.90 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ -5.3 (C2), 17.9, 18.3, 21.9, 22.2, 24.3, 25.6, 25.9 (C3), 52.6, 128.1, 129.2, 129.7, 133.5, 133.6, 138.6, 158.9; **IR** (polymer) 688, 784, 1152, 1253, 1307, 1586, 1637, 2857, 2931 cm^{-1}; **HRMS** (M^+) calcd for $C_{21}H_{33}NO_3SSi$: 407.1950, found 407.1928.

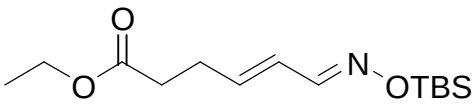
(*E*)-ethyl 4-(*tert*-butyldimethylsilyloxyimino)-4-cyclohexenylbutanoate (6f)



MW: $C_{18}H_{33}NO_3Si$ = 339.22; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.13 (s, 6H), 0.91 (s, 9H), 1.23 (t, J= 7.1 Hz, 3H), 1.56-1.62 (m, 4H), 2.14-2.24 (m, 4H), 2.39-2.43 (m, 2H), 2.76-2.81 (m, 2H), 4.10 (q, J= 7.1 Hz, 2H), 6.13-6.15 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ –5.2 (C2), 14.2, 18.1, 19.8, 22.1, 22.4, 24.4, 26.0, 26.1 (C3), 31.4, 60.4, 129.1, 133.9,

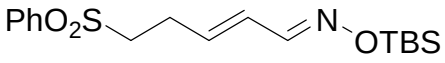
161.9, 173.0; **IR** (polymer) 784, 839, 925, 1181, 1250, 1462, 1638, 1739, 2858, 2932 cm^{-1}; **HRMS** (M^+) calcd for $C_{18}H_{33}NO_3Si$: 339.2230, found 339.2243.

(4*E*,6*E*)-ethyl 6-(*tert*-butyldimethylsilyloxyimino)hex-4-enoate (6g)



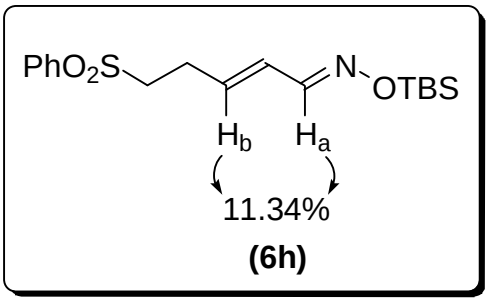
MW: $C_{14}H_{27}NO_3Si$ = 285.17; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.15 (s, 6H), 0.89 (s, 9H), 1.23 (t, J= 7.1 Hz, 3H), 2.39-2.47 (m, 4H), 4.11 (q, J= 7.1 Hz, 2H), 5.97 (dt, J= 15.7 Hz, 6.5 Hz, 1H), 6.19 (ddt, J= 15.7 Hz, 9.7 Hz, 1.5 Hz, 1H), 7,76 (d, J= 9,7 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ -5.7 (C2), 13.7, 17.6, 25.5 (C3), 27.4, 32.7, 60.0, 124.9, 138.7, 154.4, 172.1; **IR** (polymer) 788, 839, 949, 1259, 1654, 1739, 2859, 2932, 2960 cm^{-1}; **HRMS** (M^+) calcd for $C_{14}H_{27}NO_3Si$: 285.1760, found 285.1750.

(1*E*,2*E*)-5-(phenylsulfonyl)pent-2-enal *O*-*tert*-butyldimethylsilyl oxime (6h)



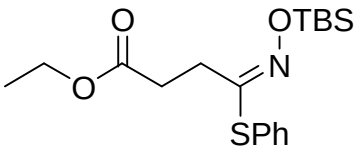
MW: $C_{17}H_{27}NO_3SSi$ = 353.14; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.12 (s, 6H), 0.90 (s, 9H), 2.56-2.60 (m, 2H), 3.15-3.19 (m, 2H), 5.84 (dt, J= 15.7 Hz, 6.4 Hz, 1H), 6.15 (ddt, J= 15.7 Hz, 9.7 Hz, 1.5 Hz, 1H), 7.54-7.58 (m, 2H), 7.63-7.65 (m, 1H), 7.70 (d, J= 9.7 Hz, 1H), 7.88-7.90 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ -5.3 (C2), 18.1, 25.6, 25.9 (C3), 54.9, 126.8, 128.0, 129.3, 133.8, 135.3, 138.8, 154.1; **IR** (polymer) 839, 948, 1149, 1307, 1447, 1650, 2857, 2930, 2956 cm^{-1}; **HRMS** (M^+) calcd for $C_{17}H_{27}NO_3SSi$:

353.1481, found 353.1489.



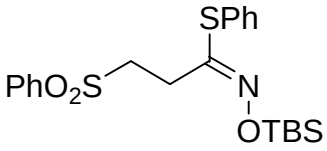
From the ^{1}H-^{1}H COSY NMR spectrum and decoupling technique, an NOE experiment of **6h** showed 11.34% NOE between H_b (5.84 ppm) and H_a (7.70 ppm), indicating that the stereochemistry of **6h** is *E*-form.

(*E*)-ethyl 4-(*tert*-butyldimethylsilyloxyimino)-4-(phenylthio)butanoate (6i)



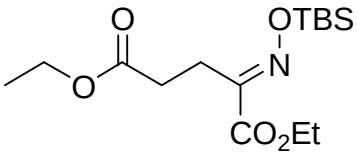
MW: $C_{18}H_{29}NO_3SSi$ = 367.16; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.16 (s, 6H), 0.95 (s, 9H), 1.18 (t, J= 7.1 Hz, 3H), 2.29 (m, 2H), 2.46 (m, 2H), 4.03 (q, J= 7.1 Hz, 2H), 7.34-7.38 (m, 3H), 7.53-7.56 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ -5.3 (C2), 14.1, 18.2, 26.0 (C3), 28.1, 30.7, 60.3, 129.2 (C2), 129.4, 136.2, 157.4, 172.2; **IR** (polymer) 839, 928, 1252, 1473, 1581, 1738, 2857, 2930, 2957 cm^{-1}; **HRMS** (M^+) calcd for $C_{18}H_{29}NO_3SSi$: 367.1637, found 367.1650.

(*E*)-phenyl *N*-*tert*-butyldimethylsilyloxy-3-(phenylsulfonyl)propanimidothioate (6j)



MW: $C_{21}H_{29}NO_3S_2Si$ = 435.13; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.15 (s, 6H), 0.92 (s, 9H), 2.29-2.33 (m, 2H), 3.21-3.25 (m, 2H), 7.30-7.33 (m, 2H), 7.39-7.47 (m, 5H), 7.60-7.62 (m, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ -5.2 (C2), 18.1, 25.9 (C3), 26.9, 52.9, 128.0, 128.4, 129.2, 129.4, 129.8, 133.6, 136.0, 138.2, 155.5; ; **IR** (polymer) 840, 1153, 1319, 1446, 1472, 1583, 2857, 2930, 2957 cm^{-1}; **HRMS** (M^+) calcd for $C_{21}H_{29}NO_3S_2Si$: 435.1358, found 435.1321.

(*E*)-diethyl 2-(*tert*-butyldimethylsilyloxyimino)pentanedioate (6k)

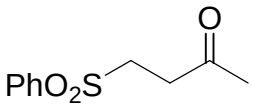


MW: $C_{15}H_{29}NO_5Si$ = 331.18; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.18 (s, 6H), 0.91 (s, 9H), 1.21 (t, J= 7.1 Hz, 3H), 1.30 (t, J= 7.1 Hz, 3H), 2.48-2.52 (m, 2H), 2.83-2.87 (m, 2H), 4.09 (q, J= 7.1 Hz, 2H), 4.25 (q, J= 7.1 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ -5.3 (C2), 14.1, 18.0, 20.9, 25.6, 25.8 (C3), 30.4, 60.5, 61.4, 155.8, 163.9, 172.3; **IR** (polymer) 798, 840, 1259, 1564, 1602, 1723, 1740, 2858, 2932, 2958 cm^{-1}; **HRMS** (M^+) calcd for $C_{15}H_{29}NO_5Si$: 331.1815, found 331.1863.

Acidic hydrolysis of oxime ether compounds; Typical procedure:

To a solution of **6a** (33 mg, 0.1 mmol) in 35% aqueous formaldehyde (1ml) and THF (2ml) was added several drops of 10% HCl at room temperature. After being stirred for 6 h at room temperature, the reaction mixture was diluted with diethyl ether (10ml), neutralized with aqueous $NaHCO_3$ and washed with brine (10ml). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was chromatographed on a silica gel column (ethyl acetate : *n*-hexane = 1:10) to give the product **7a** (17 mg, 86%) as a colorless oil. **MW:** $C_9H_{10}O_3S$ = 198.03; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.96 (t, J= 7.6 Hz, 2H), 3.39 (t, J= 7.6 Hz, 2H), 7.55-7.59 (m, 2H), 7.65-7.66 (m, 1H), 7.89-7.91 (m, 2H), 9.72 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 36.5, 49.0, 128.0, 129.4, 134.0, 139.0, 196.7; **IR** (polymer) 690, 801, 1088, 1151, 1307, 1415, 1727, 2856, 2961 cm^{-1}; **HRMS** (M^+) calcd for $C_9H_{10}O_3S$ = 198.0351, found 198.0354.

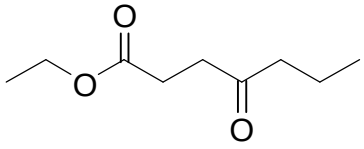
4-Benzenesulfonyl-butan-2-one (7b)



MW: $C_{10}H_{12}O_3S$ = 212.05; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.14 (s, 3H), 2.89 (t, J= 7.8 Hz, 2H), 3.34 (t, J= 7.8 Hz, 2H), 7.53-7.56 (m, 2H), 7.62-7.66 (m, 1H), 7.86-7.88 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 29.8, 35.8, 50.4, 127.9, 129.3, 133.8, 138.9, 203.6;

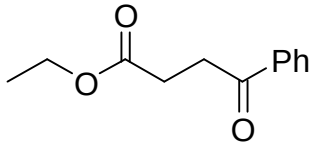
IR (polymer) 688, 738, 1145, 1267, 1305, 1716, 2990 cm^{-1}; **HRMS** (M^+) calcd for $C_{10}H_{12}O_3S$: 212.0507, found 212.0500.

4-Oxo-heptanoic acid ethyl ester (7c)



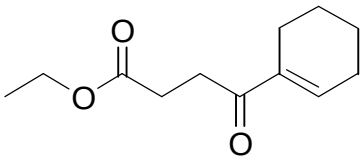
MW: $C_9H_{16}O_3$ = 172.10; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.89 (t, J= 7.4 Hz, 3H), 1.22 (t, J= 7.1 Hz, 3H), 1.58 (S, J= 7.4 Hz, 2H), 2.40 (t, J= 7.4 Hz, 2H), 2.55 (t, J= 6.7 Hz, 2H), 2.68 (t, J= 6.7 Hz, 2H), 4.10 (q, J= 7.1 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 13.7, 14.1, 17.2, 27.9, 37.0, 44.7, 60.5, 172.8, 209.0; **IR** (polymer) 1204, 1351, 1717, 1736, 2936, 2964 cm^{-1}; **HRMS** (M^+) calcd for $C_9H_{16}O_3$: 172.1099, found 172.1096.

4-Oxo-4-phenyl-butyric acid ethyl ester (7d)



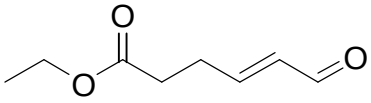
MW: $C_{12}H_{14}O_3$ = 206.09; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.24 (t, J= 7.1 Hz, 3H), 2.74 (t, J= 6.6 Hz, 2H), 3.29 (t, J= 6.6 Hz, 2H), 4.14 (q, J= 7.1 Hz, 2H), 7.42-7.46 (m, 2H), 7.53-7.56 (m, 1H), 7.95- 7.97 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 14.1, 28.2, 33.3, 60.6, 128.0, 128.5, 133.1, 136.6, 172.8, 198.1; **IR** (polymer) 692, 750, 1030, 1166, 1218, 1688, 1734, 2933, 2982 cm^{-1}; **HRMS** (M^+) calcd for $C_{12}H_{14}O_3$: 206.0943, found 206.0940.

4-Cyclohex-1-enyl-4-oxo-butyric acid ethyl ester (7e)



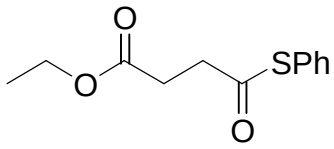
MW: $C_{12}H_{18}O_3$ = 210.12; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.23 (t, J= 7.2 Hz, 3H), 1.57-1.62 (m, 4H), 2.20-2.24 (m, 4H), 2.58 (t, J= 6.7 Hz, 2H), 2.94 (t, J= 6.7 Hz, 2H), 4.11 (q, J= 7.2 Hz, 2H), 6.92-6.94 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 14.1, 21.5, 21.8, 23.0, 26.0, 28.3, 31.7, 60.5, 138.9, 140.0, 173.2, 199.0; **IR** (polymer) 1027. 1164, 1211, 1349, 1669, 1736, 2934 cm^{-1}; **HRMS** (M^+) calcd for $C_{12}H_{18}O_3$: 210.1256, found 210.1257.

6-Oxo-hex-4-enoic acid ethyl ester (7f)



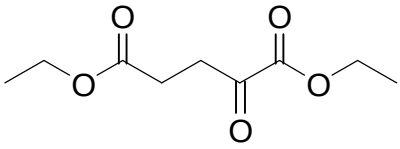
MW: $C_8H_{12}O_3$ = 156.07; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.24 (t, J= 7.1 Hz, 3H), 2.49-2.52 (m, 2H), 2.62-2.67 (m, 2H), 4.13 (q, J= 7.1 Hz, 2H), 6.11(dd, J= 15.7 Hz, 7.8 Hz, 1H), 6.84 (dt, J= 15.7 Hz, 6.4 Hz, 1H), 9.49 (d, J= 7.8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 1.41, 27.6, 32.1, 60.7, 133.3, 155.8, 172.0, 193.7; **IR** (polymer) 1031, 1196, 1258, 1350, 1691, 1732, 2984 cm^{-1}; **HRMS** (M^+) calcd for $C_8H_{12}O_3$: 156.0786, found 156.0737.

3-Phenylsulfanylcarbonyl-propionic acid ethyl ester (7g)



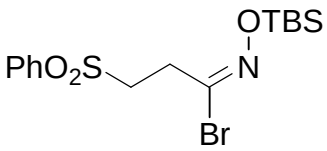
MW: $C_{12}H_{14}O_3S$ = 238.06; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.24 (t, J= 7.1 Hz, 3H), 2.65 (t, J= 6.9 Hz, 2H), 2.97 (t, J= 6.9 Hz, 2H), 4.13 (q, J= 7.1 Hz, 2H), 7.38-7.39 (m, 5H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 14.1, 29.2, 38.1, 60.8, 127.3, 129.2, 129.4, 134.5, 171.8, 196.1; **IR** (polymer) 690, 748, 1067, 1203, 1710, 1733, 2982 cm^{-1}; **HRMS** (M^+) calcd for $C_{12}H_{14}O_3S$: 238.0664, found 238.0659.

2-Oxo-pentanedioic acid diethyl ester (7h)



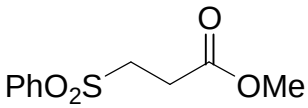
MW: $C_9H_{14}O_5$ = 202.08; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.23 (t, J= 7.1 Hz, 3H), 1.34 (t, J= 7.1Hz, 3H), 2.64 (t, J= 6.5 Hz, 2H), 3.13 (t, J= 6.5 Hz, 2H), 4.12 (q, J= 7.1 Hz, 2H), 4.31 (q, J= 7.1 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 13.9, 14.1, 27.6, 34.1, 60.9, 62.5, 160.5, 171.9, 192.6; **IR** (polymer) 1023, 1082, 1205, 1259, 1732, 2984 cm^{-1}; **HRMS** (M^+) calcd for $C_9H_{14}O_5$: 202.0841, found 202.0843.

(*E*)-*N*-(*tert*-butyldimethylsilyloxy)-3-(phenylsulfonyl)propanimidoyl bromide (10)



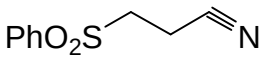
MW: $C_{15}H_{24}BrNO_3SSi$ = 405.04; E : Z = 4 : 1 (from ^{1}H NMR ratio); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ E: 0.15 (s, 6H), 0.90 (s, 9H), 2.97-3.01 (m, 2H), 3.40-3.44 (m, 2H), 7.56-7.59 (m, 2H), 7.65-7.69 (m, 1H), 7.89-7.92 (m, 2H); Z: 0.10 (s, 6H), 0.83 (s, 9H), 3.14-3.17 (m, 2H), 3.29-3.33 (m, 2H), 7.56-7.59 (m, 2H), 7.65-7.69 (m, 1H), 7.89-7.92 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ E: -5.2 (C2), 18.0, 25.7 (C3), 32.8, 53.1, 128.1, 129.4, 132.2, 134.0, 138.4; **IR** (polymer) 688, 791, 840, 1447, 1472, 1604, 2858, 2931, 2958 cm^{-1}; **HRMS** (M^+) calcd for $C_{15}H_{24}BrNO_3SSi$: 405.0430, found 405.0441.

3-Benzenesulfonyl-propionic acid methyl ester (11)



MW: $C_{10}H_{12}O_4S$ = 228.04; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.74 (t, J= 7.9 Hz, 2H), 3.41 (t, J= 7.9 Hz, 2H), 3.62 (s, 3H), 7.54-7.58 (m, 2H), 7.63-7.67 (m, 1H), 7.88-7.90 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 27.5, 51.4, 52.2, 128.1, 129.3, 133.9, 138.5, 170.3; **IR** (polymer) 691, 779, 1178, 1251, 1306, 1446, 1743 cm^{-1}; **HRMS** (M^+) calcd for $C_{10}H_{12}O_4S$: 228.0456, found 228.0456.

3-Benzenesulfonyl-propionitrile (12)



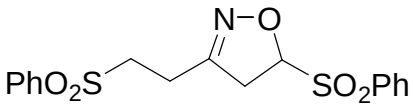
MW: $C_9H_9NO_2S$ = 195.03; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.78-2.81 (m, 2H), 3.35-3.38 (m, 2H), 7.59-7.61 (m, 2H), 7.69-7.71 (m, 1H), 7.90-7.92 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 11.9, 51.1, 115.8, 128.2, 129.7, 134.7, 137.5; **IR** (polymer) 695, 737, 1154, 1304, 1447, 1651, 2248, 2955, 3001 cm^{-1}; **HRMS** (M^+) calcd for $C_9H_9NO_2S$: 195.0354, found 195.0351.

1,3-Dipolar cycloaddtion of oxime ether 10; Typical procedure:

To a solution of **10** (40 mg, 0.1 mmol) in DMF (2ml) was added potassium fluoride (9 mg, 0.15 mmol) at room temperature. After being stirred for 30 min at room temperature, ethyl acrylate (13 μl, 0.12 mmol) was added to the reaction mixture at room temperature. After being stirred for 2 h at room temperature, the reaction mixture was diluted with diethyl ether (10ml), quenched with aqueous NH_4Cl solution and washed with water and brine (10ml). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was chromatographed on a silica gel column (ethyl acetate : *n*-hexane = 1:10) to give **14a** (25 mg, 81%) as a white solid. **MW:** $C_{14}H_{17}NO_5S$ = 311.08; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.25 (t, J= 7.1 Hz, 3H), 2.72-2.76 (m, 2H), 3.19 (d, J= 9.1 Hz, 2H), 3.41-3.45 (m, 2H), 4.20 (q, J= 7.1 Hz, 2H), 4.95 (t, J= 9.1 Hz, 1H), 7.55-7.58 (m, 2H), 7.64-7.66

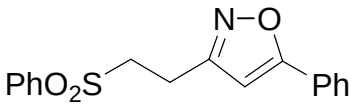
(m, 1H), 7.88-7.90 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 14.0, 21.2, 40.9, 52.3, 62.0, 77.4, 128.0, 129.4, 134.0, 138.4, 154.9, 169.8; **IR** (polymer) 690, 739, 1149, 1308, 1447, 1633, 1739, 2985 cm^{-1}; **HRMS** (M^+) calcd for $C_{14}H_{17}NO_5S$: 311.0827, found 311.0826.

5-Benzenesulfonyl-3-(2-benzenesulfonyl-ethyl)-4,5-dihydro-isoxazole (14b)



MW: $C_{17}H_{17}NO_5S_2$ = 379.05; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.69-2.75 (m, 2H), 3.29-3.34 (m, 2H), 3.42 (dd, J= 18.7 Hz, 10.6 Hz, 1H), 3.59 (dd, J= 18.7 Hz, 4.3 Hz, 1H), 5.36 (dd, J= 10.6 Hz, 4.3 Hz, 1H), 7.53-7.59 (m, 4H), 7.65-7.67 (m, 2H), 7.87-7.91 (m, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 20.9, 38.7, 52.1, 92.6, 128.0, 129.2, 129.5, 129.6, 134.1, 134.6, 135.0 138.3, 156.2; **IR** (polymer) 689, 735, 1085, 1148, 1308, 1478, 1584, 1633 cm^{-1}; **HRMS** (M^+) calcd for $C_{17}H_{17}NO_5S_2$: 379.0548, found 379.0544.

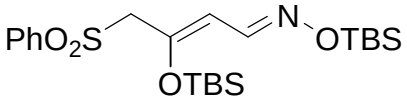
3-(2-Benzenesulfonyl-ethyl)-4-phenyl-isoxazole (14c)



MW: $C_{17}H_{15}NO_3S$ = 313.07; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.12-3.16 (m, 2H), 3.51-3.55 (m, 2H), 6.35 (s, 1H), 7.41-7.43 (m, 3H), 7.56-7.58 (m, 2H), 7.63-7.65 (m, 1H), 7.68-7.70 (m, 2H), 7.92-7.94 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 20.2, 53.9, 99.0,

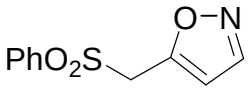
125.7, 127.0, 128.1, 128.9, 129.4, 130.3, 134.0, 138.6, 160.6, 170.4; **IR** (polymer) 691, 762, 1154, 1305, 1655 cm^{-1}; **HRMS** (M^+) calcd for $C_{17}H_{15}NO_3S$: 313.0773, found 313.0774.

(1*E*,2*Z*)-3(*tert*-butyldimethylsilyloxy)-4-(phenylsulfonyl)but-2-enal *O*-*tert*-butyl-dimethylsilyl oxime (17)



MW: $C_{22}H_{39}NO_4SSi_2$ = 469.21; **^{1}H NMR** (C_6D_6, 400 MHz) δ -0.05 (s, 6H), 0.23 (s, 6H), 0.76 (s, 9H), 1.00 (s, 9H), 3.42 (s, 2H), 5.34 (d, J= 9.9 Hz, 1H), 6.83-6.87 (m, 2H), 6.91-6.94 (m, 1H), 7.72-7.74 (m, 2H), 8.31 (d, J= 9.9 Hz, 1H); **^{13}C NMR** (C_6D_6, 100 MHz) δ -5.0 (C2), -4.2 (C2), 18.2, 18.4, 25.5 (C3), 26.2 (C3), 63.8, 111.2, 128.8, 128.9, 133.4, 138.9, 146.7, 150.1; **IR** (polymer) 784, 839, 935, 1640, 2858, 2931, 2956 cm^{-1}; **HRMS** (M^+) calcd for $C_{22}H_{39}NO_4SSi_2$: 469.2138, found 469.2139.

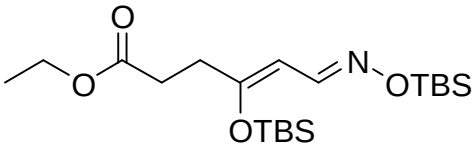
5-Benzenesulfonylmethyl-isoxazole (19)



MW: $C_{10}H_9NO_3S$ = 223.03; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 4.56 (s, 2H), 6.38 (s, 1H), 7.50-7.54 (m, 2H), 7.64-7.68 (m, 1H), 7.73-7.75 (m, 2H), 8.20 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 53.8, 105.3, 128.3, 129.4, 134.5, 137.5, 150.5, 159.6; **IR** (polymer) 688, 1154, 1324, 1448, 1469, 1643, 2855, 2929 cm^{-1}; **HRMS** (M^+) calcd for

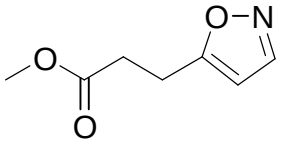
$C_{10}H_9NO_3S$: 223.0303, found 223.0307.

(4*Z*,6*E*)-ethyl-4-(*tert*-butyldimethylsilyloxy)-6-(*tert*-butyldimethylsilyloxyimino) hex-4-enoate (20)



MW: $C_{20}H_{41}NO_4Si_2$ = 415.25; E : Z = 1.78 : 1 (from ^{1}H NMR ratio); **^{1}H NMR** (C_6D_6, 400 MHz) δ E: -0.02 (s, 6H), 0.32 (s, 6H), 0.80 (s, 9H), 0.94 (t, J= 7.1 Hz, 3H), 1.08 (s, 9H), 2.22-2.29 (m, 4H), 3.91 (q, J= 7.1 Hz, 2H), 6.31 (d, J= 9.3 Hz, 1H), 7.85 (d, J= 9.3 Hz, 1H); Z: -0.01 (s, 6H), 0.28 (s, 6H), 0.82 (s, 9H), 0.91 (t, J= 7.1 Hz, 3H), 1.05 (s, 9H), 2.22-2.29 (m, 4H), 3.87 (q, J= 7.1 Hz, 2H), 5.54 (d, J= 10.2 Hz, 1H), 8.49 (d, J= 10.2 Hz, 1H); **^{13}C NMR** (C_6D_6, 100 MHz) δ E: -4.8 (C2), -4.1 (C2), 14.2, 18.2, 18.5, 25.6 (C3), 26.4 (C3), 31.4, 32.3, 60.3, 99.2, 147.4, 159.6, 171.5; **IR** (polymer) 839, 923, 1256, 1472, 1638, 1739, 2858, 2931, 2957 cm^{-1}; **HRMS** (M^+) calcd for $C_{20}H_{41}NO_4Si_2$: 415.2574, found 415.2571.

3-Isoxazol-5-yl-propionic acid methyl ester (21)



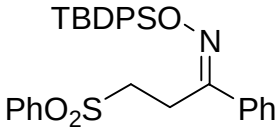
MW: $C_7H_9NO_3$ = 155.05; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.72 (t, J= 7.5 Hz, 2H), 3.10 (t, J= 7.5 Hz, 2H), 3.67 (s, 3H), 6.01 (s, 1H), 8.12 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz)

δ 21.9, 31.5, 51.9, 100.4, 150.2, 170.6, 172.1; **IR** (polymer) 867, 1199, 1299, 1689, 1732 cm^{-1}; **HRMS** (M^+) calcd for $C_7H_9NO_3$: 155.0582, found 155.0549.

Tin-Free Radical Alkylation of Organic Nitro Compounds; Typical procedure:

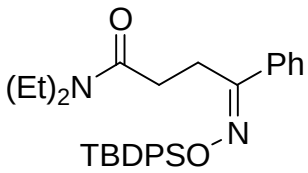
A solution of ethyl iodoacetate (45 mg, 0.2 mmol), **22** (188 mg, 0.3 mmol), and V-70 (12 mg, 0.04 mmol) in dichloromethane (1 mL; 0.2 M in iodide) was degassed with nitrogen for 10 min, and the solution was then stirred at 30 ^oC under nitrogen for 9 h. The solvent was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography with EtOAc/hexane (1:20) as the eluant to give **23** (82 mg, 83%). **MW:** $C_{28}H_{33}NO_3Si$ = 459.22; E : Z = 3.3 : 1 (from ^1H NMR ratio); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ E: 1.14 (s, 9H), 1.21 (t, J= 7.1 Hz, 3H), 2.66-2.70 (m, 2H), 3.23-3.27 (m, 2H), 4.11 (q, J= 7.1 Hz, 2H), 7.31-7.40 (m, 10H), 7.61-7.62 (m, 2H), 7.71-7.73 (m, 3H); Z: 1.00 (s, 9H), 1.21 (t, J= 7.1 Hz, 3H), 2.50-2.54 (m, 2H), 2.84-2.88 (m, 2H), 3.91 (q, J= 7.1 Hz, 2H), 7.31-7.40 (m, 10H), 7.61-7.62 (m, 2H), 7.71-7.73 (m, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ E: 14.1, 19.4, 22.2, 27.2 (C3), 31.0, 60.6, 126.4, 127.4, 127.5 (C2), 127.9, 128.4, 129.3, 129.6, 133.7, 135.1, 135.5 (C2), 161.5, 172.6; **IR** (polymer) 704, 744, 1114, 1528, 1566, 1690, 1732, 2859, 2934 cm^{-1}; **HRMS** (M^+) calcd for $C_{28}H_{33}NO_3Si$: 459.2230, found 459.2231.

(*E*)-1-phenyl-3-(phenylsulfonyl)propan-1-one *O*-*tert*-butyldiphenylsilyl oxime



MW: $C_{31}H_{33}NO_3SSi$ = 527.19; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.05 (s, 9H), 3.29-3.32 (m, 2H), 3.38-3.41 (m, 2H), 7.31-7.40 (m, 8H), 7.50-7.52 (m, 5H), 7.61-7.63 (m, 5H), 7.89-7.91 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 19.3, 20.4, 27.0 (C3), 52.1, 126.1, 127.6 (C2), 127.7, 128.1, 128.6, 129.3, 129.7, 129.8, 133.1, 133.8, 134.0, 134.3, 135.3 (C2), 138.5, 158.6; **IR** (polymer) 700, 742, 934, 1116, 1154, 1308, 1591, 1651, 2860, 2934 cm^{-1}; **HRMS** (M^+) calcd for $C_{31}H_{33}NO_3SSi$: 527.1950, found 527.1904.

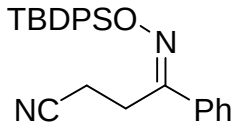
(*E*)-4-(*tert*-butyldiphenylsilyloxyimino)-*N*,*N*-diethyl-4-phenylbutanamide



MW: $C_{30}H_{38}N_2O_2Si$ = 486.27; E : Z = 3.66 : 1 (from ^{1}H NMR ratio); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ E: 0.99 (t, J= 7.1 Hz, 3H), 1.05 (t, J= 7.1 Hz, 3H), 1.14 (s, 9H), 2.60-2.65 (m, 2H), 3.16 (q, J= 7.1 Hz, 2H), 3.23-3.28 (m, 2H), 3.34 (q, J= 7.1 Hz, 2H), 7.30-7.39 (m, 10H), 7.67-7.73 (m, 5H); Z: 0.90 (t, J= 7.1 Hz, 3H), 0.99 (t, J= 7.1 Hz, 3H), 1.00 (s, 9H), 2.46-2.50 (m, 2H), 2.87-2.91 (m, 2H), 3.04 (q, J= 7.1 Hz, 2H), 3.23 (q, J= 7.1 Hz, 2H), 7.30-7.39 (m, 10H), 7.67-7.73 (m, 5H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ E: 13.0, 14.1, 19.5, 22.6, 27.2 (C3), 29.6, 40.1, 41.9, 126.4, 127.3, 127.5 (C2), 127.8, 128.0,

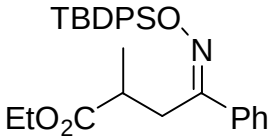
128.4, 129.3, 129.6, 133.7, 135.4 (C2), 162.5, 170.9; **IR** (polymer) 701, 936, 1116, 1429, 1623, 1645, 2860, 2936 cm^{-1}; **HRMS** (M^+) calcd for $C_{30}H_{38}N_2O_2Si$: 486.2703, found 486.2705.

(*E*)-4-(*tert*-butyldiphenylsilyloxyimino)-4-phenylbutanenitrile



MW: $C_{26}H_{28}N_2OSi$ = 412.19; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.16 (s, 9H), 2.71-2.75 (m, 2H), 3.26-3.30 (m, 2H), 7.35-7.42 (m, 9H), 7.58-7.60 (m, 2H), 7.69-7.71 (m, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 14.2, 19.4, 22.7, 27.2 (C3), 118.7, 126.3, 127.6 (C2), 128.7, 129.6, 129.8 (C2), 133.2, 134.2, 134.7, 135.3 (C2), 159.5; **IR** (polymer) 700, 937, 1115, 1428, 1589, 2249, 2857, 2932, 2958 cm^{-1}; **HRMS** (M^+) calcd for $C_{26}H_{28}N_2OSi$: 412.1971, found 412.1992.

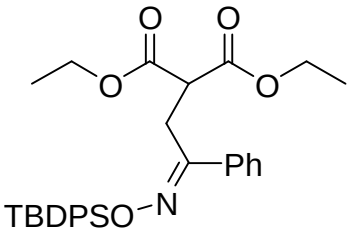
(*E*)-ethyl 4-(*tert*-butyldiphenylsilyloxyimino)-2-methyl-4-phenylbutanoate



MW: $C_{29}H_{35}NO_2Si$ = 473.23; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.00 (s, 9H), 1.07 (t, J= 7.1 Hz, 3H), 1.09 (d, J= 7.0 Hz, 3H), 2.56 (dd, J= 15.3 Hz, 6.9 Hz, 1H), 2.65-2.71 (m, 1H), 3.00 (dd, J= 15.3 Hz, 7.1 Hz, 1H), 3.72-3.80 (m, 1H), 3.87-3.95 (m, 1H), 7.31-7.41 (m, 9H), 7.51-7.53 (m, 2H), 7.60-7.65 (m, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 14.0,

16.9, 19.2, 26.9 (C3), 36.5, 38.7, 60.2, 127.4 (C2), 127.5, 127.8, 128.0, 128.7, 129.4, 133.6, 133.7, 133.8, 135.5 (C2), 160.1, 175.6; **IR** (polymer) 700, 741, 938, 1115, 1559, 1654, 1734, 2859, 2962 cm^{-1}; **HRMS** (M^+) calcd for $C_{29}H_{35}NO_2Si$: 473.2386, found 473.2363.

(*E*)-diethyl 2-(2-(*tert*-butyldiphenylsilyloxyimino)-2-phenylethyl)malonate



MW: $C_{31}H_{37}NO_5Si$ = 531.24; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.99 (s, 9H), 1.06 (t, J= 7.2 Hz, 3H), 1.09 (t, J= 7.1 Hz, 3H), 3.14 (d, J= 7.4 Hz, 2H), 3.77 (t, J= 7.4 Hz, 1H), 3.80-3.88 (m, 2H), 3.97-4.05 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 13.6 (C2), 18.9, 26.7 (C3), 34.0, 48.3, 61.0 (C2), 127.2 (C2), 127.4, 127.7, 127.8, 128.6, 129.2, 129.3, 133.4, 134.5, 135.2 (C2), 158.7, 168.5; **IR** (polymer) 700, 1114, 1428, 1590, 1733, 1748, 2857, 2932, 2959 cm^{-1}; **HRMS** (M^+) calcd for $C_{31}H_{37}NO_5Si$: 531.2441, found 531.2441.