Supplementary Material (ESI) for Chemical Communications

A Novel Approach for the Direct Conversion of Alkylsulfonyl Derivatives into Alkylcarbonyl Derivatives via Tin-Free Radical Carbonylation

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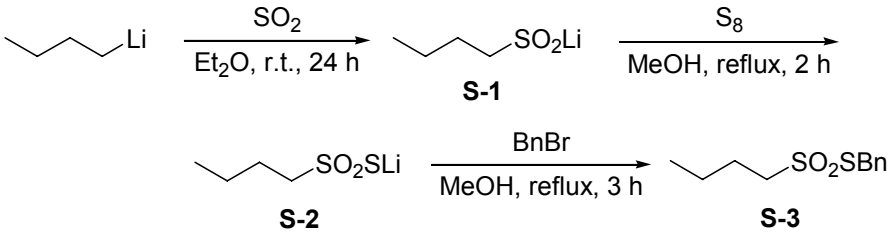
General. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance-400 spectrometers and Bruker Avance-300 spectrometers. The chemical shifts in $CDCl_3$ in δ (ppm) relative to $CDCl_3$ or Me_4Si as an internal reference. Splitting patterns are designated as follows: br; broad, s; singlet, d; doublet, t; triplet, q; quartet, m; multiplet, dt; double of triplet, td; triple of doublet, dd; double of doublet, dis; distorted. IR spectra were measured on a VECTOR-33 Fourier Transform 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 F254 plates. All reagents were purchased from Aldrich Co. and TCI Co. All dry solvents were freshly distilled under nitrogen from the appropriate drying agent before use.

Typical procedure for the preparation of *S*-benzyl alkylthiosulfonates from alkyllithiums: *S*-benzyl butane-1-sulfonothioate (S-3)[1,2]



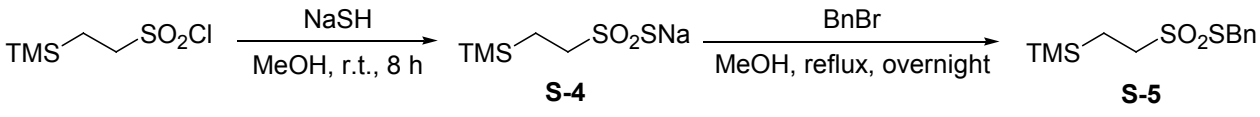
S-1 **S-2** **S-3**

Sulfur dioxide (4.4 ml, 100 mmol) was condensed in a dry flask at -78 °C, and 16 ml of cold Et_2O was added. A 2.5 M hexane solution of *n*-BuLi (4.0 ml, 10 mmol) was added to the solution dropwise over 10 min. The reaction mixture was stirred for 30 min at -78 °C, and then was allowed to warm up to room temperature for 24 h. All volatile materials were removed under reduced pressure to give lithium butane-1-sulfinate (**S-1**) (1.27 g, 99%). MW: $C_4H_9LiO_2S$ = 128.12; ^{1}H NMR (D_2O, 300 MHz) δ 0.78 (t, *J* = 7.2 Hz, 3H), 1.26-1.46 (m, 4H), 2.24 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (D_2O, 75 MHz) δ 13.1, 21.6, 23.8, 60.6.

A mixture of lithium butane-1-sulfinate (**S-1**) (1.27 g, 9.9 mmol) and sulfur (3.17 g, 9.9 mmol) in MeOH (60 ml) was heated under reflux for 2 h. Removal of solvent gave crude lithium butane-1-sulfonothioate (**S-2**) (1.59 g, 100%). MW: $C_4H_9LiO_2S_2$ = 160.18; ^{1}H NMR (D_2O, 400 MHz) δ 0.76 (t, *J* = 7.4 Hz, 3H), 1.23-1.41 (m, 4H), 2.22 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (D_2O, 100 MHz) δ 13.5, 22.0, 24.2, 61.0.

A solution of lithium butane-1-sulfonothioate (**S-2**) (1.59 g, 9.9 mmol) and benzyl bromide (1.69 g, 9.9 mmol) in MeOH (50 ml) was refluxed for 3 h. After removal of solvent under reduced pressure, the mixture was diluted with CH_2Cl_2 (100 ml), washed with brine (100 ml), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using ethyl acetate and *n*-hexane (1:10) as eluant to give *S*-benzyl butane-1-sulfonothioate (**S-3**) (1.28 g, 53%). MW: $C_{11}H_{16}O_2S_2$ = 244.37; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.80 (t, *J* = 7.3, 3H), 1.20-1.27 (m, 2H), 1.67-1.71 (m, 2H), 2.82-2.86 (m, 2H), 4.31 (s, 2H), 7.28-7.37 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.3, 21.0, 25.2, 40.5, 62.7, 128.1, 129.0, 129.1, 135.3; IR (polymer) 2962, 1496, 1454, 1325, 1127, 701 cm^{-1}; HRMS (M^+) calcd for $C_{11}H_{16}O_2S_2$: 244.0592, found 244.0596.

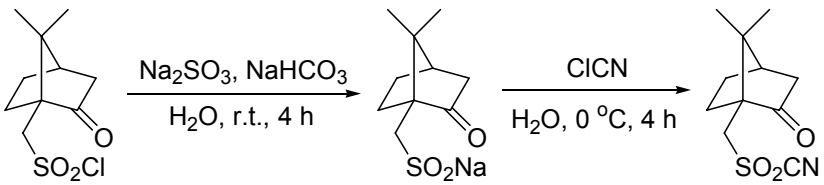
Typical procedure for the preparation of *S*-benzyl alkylthiosulfonates from alkylsulfonyl chlorides: *S*-benzyl 2-(trimethylsilyl)ethanesulfonothioate (S-5)[3]



A mixture of 2-(trimethylsilyl)ethanesulfonyl chloride (1.0 g, 5 mmol) and sodium hydrosulfide (1.4 g, 25 mmol) in MeOH (10 ml) was stirred at room temperature for 8 h. The solvent was evaporated under reduced pressure, and the excess sodium hydrosulfide was removed by passing through a short column of silica gel using acetone and methanol as eluant to give sodium 2-(trimethylsilyl)ethanesulfinate (**S-4**) (1.10 g, 100%). MW: $C_5H_{13}NaO_2S_2Si$ = 220.36; ^{1}H NMR (D_2O, 400 MHz) δ -0.07 (s, 9H), 0.94-0.98 (m, 2H), 3.07-3.21 (m, 2H); ^{13}C NMR (D_2O, 100 MHz) δ -3.0, 11.5, 62.1

A solution of crude sodium 2-(trimethylsilyl)ethanesulfinate (**S-4**) (1.10 g, 5.0 mmol) and benzyl bromide (1.28 g, 7.5 mmol) in MeOH (10 ml) was refluxed overnight. After removal of solvent under reduced pressure, the mixture was diluted with CH_2Cl_2 (50 ml), washed with brine (50 ml), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using ethyl acetate and *n*-hexane (1:20) as eluant to give *S*-benzyl 2-(trimethylsilyl)ethanesulfonothioate (**S-5**) (1.15 g, 80%). MW: $C_{12}H_{20}O_2S_2Si$ = 288.50; ^{1}H NMR ($CDCl_3$, 400 MHz) δ -0.11 (t, *J* = 3.4, 9H), 0.91-0.96 (m, 2H), 2.71-2.75 (m, 2H), 4.30 (s, 2H), 7.28-7.37 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -2.1, 10.4, 40.5, 60.2, 128.2, 129.0, 129.1, 135.8; IR (polymer) 2951, 1454, 1417, 1314, 1249, 1124, 699 cm^{-1}; HRMS (M^+) calcd for $C_{12}H_{20}O_2S_2Si$: 288.0674, found 288.0644.

Typical procedure for the preparation of alkylsulfonyl cyanides : (+)-camphor-10-sulfonyl cyanide (6)[4]

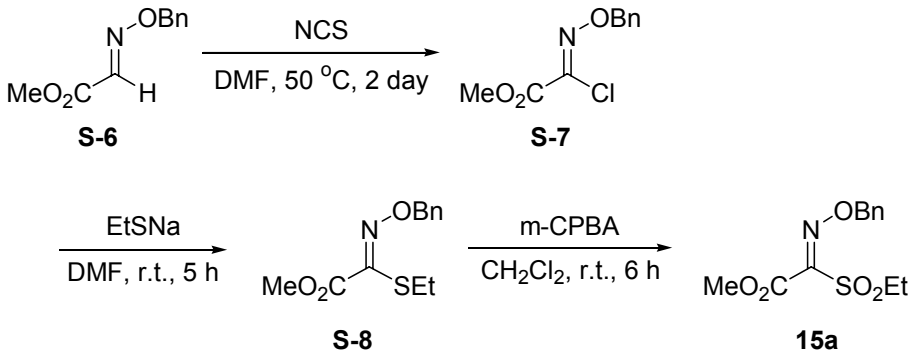


6

An aqueous mixture of (+)-camphor-10-sulfonyl chloride (1.25 g, 5 mmol), Na_2SO_3 (630 mg, 5 mmol), and $NaHCO_3$ (840 mg, 10 mmol) in H_2O (10 ml) was stirred at room temperature for 4h. After the reaction mixture was washed with Et_2O (10 ml x 2), ClCN (615 mg, 10 mmol)[5] was added to the aqueous mixture in one portion and the resulting mixture was then stirred at 0 °C for 4h. The mixture

was extracted with CH_2Cl_2 (20 ml), and the organic extracts were washed with brine (10 ml x 2), dried over $MgSO_4$, filtered, and concentrated to give an analytically pure (+)-camphor-10-sulfonyl cyanide (**6**) (1.07 g, 89%). MW: $C_{11}H_{15}NO_3S$ = 241.31; ^{1}H NMR (C_6D_6, 400 MHz) δ 0.24 (s, 3H), 0.39 (s, 3H), 0.72-0.77 (m, 1H), 1.29-1.35 (m, 3H), 1.49-1.59 (m, 1H), 1.71-1.84 (m, 2H), 2.67 (d, *J* = 15.4 Hz, 1H), 3.40 (d, *J* = 15.4 Hz, 1H); ^{13}C NMR (C_6D_6, 100 MHz) δ 18.8, 19.0, 25.4, 26.7, 41.8, 42.6, 47.9, 57.6, 59.1, 114.6, 211.4; IR (polymer) 2977, 2186, 1736, 1648, 1372, 1182 cm^{-1}; HRMS (M^+-CN) calcd for $C_{10}H_{15}O_3S$: 215.0742, found 215.0740.

Typical procedure for the preparation of alkylsulfonyl oxime ethers: Methyl 2-(benzyloxyimino)-2-(ethylsulfonyl)acetate (15a)



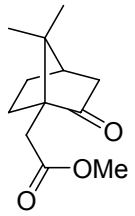
A solution of methyl 2-(benzyloxyimino)acetate (1.36 g, 7 mmol),[6] and *N*-chlorosuccinimide (2.82 g, 21 mmol) in DMF (15 ml) was stirred at 50 ^{O}C for 2 days. The mixture was diluted with Et_2O (60 ml), washed with brine (30 ml x 2), dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel using ethyl acetate and *n*-hexane (1:10) as eluant to give methyl 2-(benzyloxyimino)-2-chloroacetate (**S-7**) (1.55 g, 97 %). MW : $C_{10}H_{10}ClNO_3$ = 227.64; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.89 (s, 3H), 5.36 (s, 2H), 7.35-7.39 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 53.9, 78.8, 128.5, 128.6, 128.6, 130.9, 135.4, 159.0.

To a slurry of NaH (200 mg, 5 mmol) in DMF (10 ml) was added ethanethiol (342 mg, 5.5 mmol) at 0 ^{O}C. After being stirred at 0 ^{O}C for 30 min, methyl 2-(benzyloxyimino)-2-chloroacetate (**S-7**) (1.25 g, 5.5 mmol) was added to the reaction mixture at 0 ^{O}C. After being stirred at room temperature for additional 5 h, the reaction mixture was treated with NH_4Cl (aq), diluted with Et_2O (50 ml), washed with brine (30

ml x 2), dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel using ethyl acetate and *n*-hexane (1:10) as eluant to give methyl 2-(benzyloxyimino)-2-(ethylthio)acetate (**S-8**) (1.24 g, 98 %). MW : $C_{12}H_{15}NO_3S$ = 253.32; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.24 (t, *J* = 7.4 Hz, 3H), 2.99 (q, *J* = 7.4 Hz, 2H), 3.85 (s, 3H), 5.27 (s, 2H), 7.26-7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.2, 25.8, 53.1, 77.8, 128.0, 128.1, 128.4, 136.5, 147.0, 161.3.

To a solution of methyl 2-(benzyloxyimino)-2-(ethylthio)acetate (**S-8**) (1.24 g, 4.9 mmol) in CH_2Cl_2 (25 ml) was added $NaHCO_3$ (1.23 g, 14.7 mmol), and m-CPBA (3.29 g, 14.7 mmol) at 0 ^{O}C successively. After being stirred at room temperature for 6 h, the reaction mixture was diluted with CH_2Cl_2 (25 ml), washed with 10 % $Na_2S_2O_3$ (aq, 50 ml), $NaHCO_3$ (aq, 50 ml), and brine (30 ml x 2), dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel using ethyl acetate and *n*-hexane (1:3) as eluant to give methyl 2-(benzyloxyimino)-2-(ethylsulfonyl)acetate (**15a**) (1.38 g, 99 %). MW: $C_{12}H_{15}NO_5S$ = 285.32; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.25 (t, *J* = 7.5 Hz, 3H), 3.27 (q, *J* = 7.5 Hz, 2H), 3.87 (s, 3H), 5.35 (s. 2H), 7.35-7.37 (m, 5H) ^{13}C NMR ($CDCl_3$, 100 MHz) δ 6.3, 51.0, 53.7, 80.2, 128.4, 128.7, 128.9, 134.6, 145.8, 159.0; IR (polymer) 2957, 1751, 1600, 1455, 1336, 1151, 997 cm^{-1}; HRMS (M^+) calcd for $C_{12}H_{15}NO_5S$: 285.0671, found 285.0664.

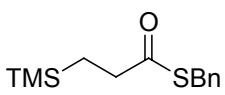
Typical procedure for direct conversion of alkyl sulfonyl cyanide 6 into methyl ester 7 via acyl cyanide : Dried heptane (20 ml), **6** (48 mg, 0.2 mmol), and V-40 (15 mg, 0.06 mmol) were placed in a 50 ml stainless steel autoclave. The autoclave was sealed, purged three times with 10 atm of CO, pressurized with 95 atm of CO, and then heated at 120 ^{o}C with stirring for 24 h. After excess CO was discharged at room temperature, the reaction mixture was poured into a 100 ml round-bottom flask, quenched with excess MeOH at room temperature for 4 h with stirring. After the solvent and MeOH were removed under reduced pressure, the residue was purified by a silica gel column chromatography using ethyl acetate and *n*-hexane (1:50) as eluant to give 3-(7,7-Dimethyl-2-oxo-bicyclo[2.2.1]hept-1-yl)-2-oxo-propionic acid methyl ester (**7**) (40 mg, 84%).



MW: $C_{12}H_{18}O_3$ = 210.27; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.85 (s, 3H), 0.93 (s, 3H), 1.32-1.37 (m, 1H), 1.69-1.75 (m, 1H), 1.83 (d, *J* = 18.3 Hz, 1H), 1.92-2.05 (m, 3H), 2.18 (d, *J* = 15.0 Hz, 1H), 2.28-2.36 (m, 1H), 2.46 (d, *J* = 15.0 Hz, 1H), 3.63 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.4, 19.8, 26.8, 26.9, 30.5, 42.7, 43.1, 47.2, 51.4, 58.9, 172.4, 216.4; IR (polymer) 2954, 1743, 1417, 1315, 1279, 1196, 1171 cm^{-1}; HRMS (M^+) calcd for $C_{12}H_{18}O_3$: 210.1256, found 210.1240

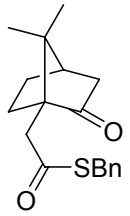
Typical procedure for direct conversion of alkyl sulfonyl oxime ether 15 into acylated oxime ether 16: Dried heptane (20 ml), **15a** (57 mg, 0.2 mmol), and V-40 (15 mg, 0.06 mmol) were placed in a 50 ml stainless steel autoclave. The autoclave was sealed, purged triple with 10 atm of CO, pressurized with 50 atm of CO, and then heated at 120 ^{o}C with stirring for 18 h. After excess CO was discharged at room temperature, the solvent was removed under reduced pressure. The residue was purified by a silica gel column chromatography using ethyl acetate and *n*-hexane (1:50) as eluant to give 2-Benzyloxyimino-3-oxo-pentanoic acid methyl ester (**16a**) (48 mg, 96%). MW: $C_{13}H_{15}NO_4$ = 249.26; major : minor = 4.13 : 1; ^{1}H NMR ($CDCl_3$, 400 MHz) major: δ 1.08 (t, *J* = 7.3 Hz, 3H), 2.76 (q, *J* = 7.3 Hz, 2H), 3.84 (s, 3H), 5.28 (s, 2H), 7.31-7.35 (m, 5H); minor: δ 1.09 (t, *J* = 7.3 Hz, 3H), 2.61 (q, *J* = 7.3 Hz, 2H), 3.84 (s, 3H), 5.27 (s, 2H), 7.31-7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) major: δ 7.5, 31.0, 52.6, 78.5, 128.2, 128.4, 128.5, 135.9, 149.6, 161.6, 195.7; minor: δ 6.6, 36.0, 53.0, 78.8, 128.3, 128.5, 128.6, 135.6, 150.2, 160.7, 199.7; IR (polymer) 2943, 1751, 1696, 1457, 1296, 1218, 1007, 700 cm^{-1}; HRMS (M^+) calcd for $C_{13}H_{15}NO_4$: 249.1001, found 249.0999

3-Trimethylsilanyl-thiopropionic acid *S*-benzyl ester



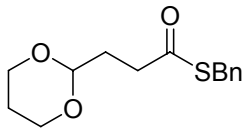
MW: $C_{13}H_{20}OSSi$ = 252.45; ^{1}H NMR ($CDCl_3$, 400 MHz) δ -0.03-0.00 (m, 9H), 0.86-0.90 (m, 2H), 2.49-2.53 (m, 2H), 4.10 (s, 2H), 7.22-7.28 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -1.8, 12.4, 33.2, 38.5, 127.2, 128.6, 128.8, 137.8, 200.3; IR (polymer) 2954, 1695, 1496, 1455, 1250, 1178, 862 cm^{-1}; HRMS (M^+) calcd for $C_{13}H_{20}OSSi$: 252.1004, found 252.1006

(7, 7-Dimethyl-2-oxo-bicyclo[2.2.1]hept-1-yl)-thioacetic acid *S*-benzyl ester



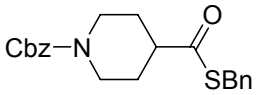
MW: $C_{18}H_{22}O_2S$ = 302.43; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.87 (s, 3H), 0.94 (s, 3H), 1.32-1.39 (m, 1H), 1.62-1.71 (m, 1H), 1.85 (d, *J* = 18.3 Hz, 1H), 1.91-1.99 (m, 1H), 2.02-2.12 (m, 2H), 2.30-2.37 (m, 1H), 2.45 (d, *J* = 15.2 Hz, 1H), 2.80 (d, *J* = 15.2 Hz, 1H), 4.10 (dd, *J* = 17.1, 18.3 Hz, 2H), 7.19-7.27 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.7, 19.9, 26.8, 26.9, 33.5, 39.5, 42.7, 43.1, 47.5, 60.1, 127.1, 128.5, 128.8, 137.5, 196.6, 216.2; IR (polymer) 2961, 1745, 1696, 1496, 1455, 1056, 750 cm^{-1}; HRMS (M^+) calcd for $C_{18}H_{22}O_2S$: 302.1340, found 302.1345

3-[1, 3]Dioxan-2-yl-thiopropionic acid *S*-benzyl ester



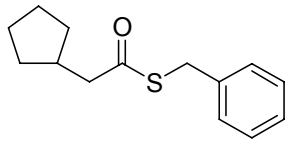
MW: $C_{14}H_{18}O_3S$ = 266.36; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.28-1.31 (m, 1H), 1.91-2.04 (m, 3H), 2.68 (t, *J* = 7.4 Hz, 2H), 3.68 -3.74 (td, *J* = 12.4, 2.3 Hz, 2H), 4.02-4.07 (dd, *J* = 10.9, 5.0 Hz, 2H), 4.10 (s, 2H), 4.55 (t, *J* = 4.9 Hz, 1H), 7.20-7.28 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.6, 30.4, 33.1, 37.9, 66.8, 100.5, 127.2, 128.5,128.8, 137.7, 198.2; IR (polymer) 2968, 2854, 1690, 1496, 1455, 1242, 1147, 1012, 705 cm^{-1}; HRMS (M^+) calcd for $C_{14}H_{18}O_3S$: 266.0977, found 266.0997

4-Benzylsulfanylcarbonyl-piperidine-1-carboxylic acid benzyl ester



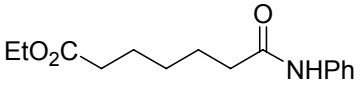
MW: $C_{21}H_{23}NO_3S$ = 369.48; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.63-1.73 (m, 2H), 1.87 (br, 2H), 2.60-2.67 (m, 1H), 2.83-2.89 (br, 2H), 4.22 (s, 2H), 4.12-4.15 (br, 2H), 5.11 (s, 2H), 7.22-7.35 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.4, 32.9, 43.2, 49.8, 67.1, 127.3, 127.8, 128.0, 128.4, 128.6, 128.7, 136.6, 137.3, 155.0, 200.5; IR (polymer) 2947, 2859, 1695, 1497, 1431, 1225, 968, 699 cm^{-1}; HRMS (M^+) calcd for $C_{21}H_{23}NO_3S$: 369.1399, found 369.1393

Cyclopentyl-thioacetic acid S-benzyl ester (**5**)



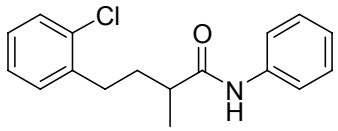
MW: $C_{14}H_{18}O$ = 202.29; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.11-1.20 (m, 2H), 1.48-1.63 (m, 4H), 1.76-1.84 (m, 2H), 2.23-2.31 (m, 1H), 2.56 (d, J = 7.4 Hz, 2H), 4.10 (s, 2H), 7.19-7.29 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.8, 32.3, 33.1, 37.1, 49.7, 127.1, 128.6, 128.7, 137.8, 198.4; IR (polymer) 2958, 1694, 1495, 1453, 972, 699 cm^{-1}; HRMS (M^+) calcd for $C_{14}H_{18}O$: 202.1358, found 234.1073

6-Phenylcarbamoyl-hexanoic acid ethyl ester (**11a**)



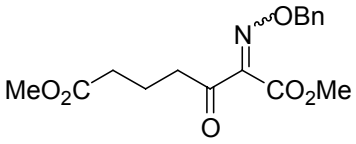
MW: $C_{15}H_{21}NO_3$ = 263.33; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.22 (t, *J* = 7.2 Hz, 3H), 1.34-1.58 (m, 2H), 1.60-1.74 (m, 4H), 2.26-2.34 (m, 4H), 4.09 (q, *J* = 7.1 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 7.25-7.29 (m, 2H), 7.5 (d, *J* = 7.9 Hz, 2H), 7.64 (br, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2, 24.4, 25.1, 28.5, 34.0, 37.2, 60.2, 119.8, 124.0, 128.8, 138.0, 171.3, 173.7; IR (polymer) 3319, 2941, 1734, 1669, 1601, 1541, 1444, 758 cm^{-1}; HRMS (M^+) calcd for $C_{15}H_{21}NO_3$: 263.1521, found 263.1521

4-(2-Chloro-phenyl)-2-methyl-N-phenyl-butyramide (**13**)



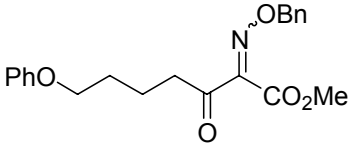
MW: $C_{17}H_{18}ClNO$ = 287.78; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.28 (d, *J* = 6.9 Hz, 3H), 1.76-1.83 (m, 1H), 2.02-2.12 (m, 1H), 2.34-2.39 (m, 1H), 2.79 (dis, t, 2H), 7.09-7.21 (m, 5H), 7.28-7.32 (m, 3H), 7.52 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.1, 31.3, 34.1, 42.1, 119.9, 124.5, 126.9, 127.5, 129.0, 129.5, 130.4, 133.9, 137.9, 139.2, 174.3; IR (polymer) 3303, 2934, 1662, 1601, 1540, 1442, 753 cm^{-1}; HRMS (M^+) calcd for $C_{17}H_{18}ClNO$: 287.1077, found 287.1073

2-Benzyloxyimino-3-oxo-heptanedioic acid dimethyl ester (**16b**)



MW: $C_{16}H_{19}NO_6$ = 321.33; major : minor = 2.54 : 1; ^{1}H NMR ($CDCl_3$, 400 MHz) major: δ 1.88-1.95 (m, 2H), 2.34 (t, *J* = 7.3 Hz, 2H), 2.81 (t, *J* = 7.2 Hz, 2H), 3.64 (s, 3H), 3.84 (s, 3H), 5.28 (s, 2H), 7.31-7.37 (m, 5H); minor: δ 1.89-1.97 (m, 2H), 2.31 (t, *J* = 7.3 Hz, 2H), 2.67 (t, *J* = 7.0 Hz, 2H), 3.62 (s, 3H), 3.84 (s, 3H), 5.26 (s, 2H), 7.29-7.36 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) major: δ18.7, 32.9, 36.6, 51.2, 52.6, 78.7, 128.2, 128.5, 128.6, 135.8, 149.7, 161.5, 173.4, 194.3; minor: δ 17.8, 32.6, 41.5, 51.5, 53.1, 78.9, 128.4, 128.6, 128.6, 135.5, 150.0, 160.6, 173.3, 198.3; IR (polymer) 2955, 1748, 1695, 1456, 1302, 1213, 1000, 700 cm^{-1}; HRMS (M^+) calcd for $C_{16}H_{19}NO_6$: 321.1212, found 321.1218

2-Benzyloxyimino-3-oxo-7-phenoxy-heptanoic acid methyl ester (**16c**)



MW: $C_{21}H_{23}NO_5$ = 369.41; major : minor = 2.96 : 1; ^{1}H NMR ($CDCl_3$, 400 MHz) major: δ 1.78-1.81 (m, 4H), 2.82-2.85 (m, 2H), 3.85 (s, 3H), 3.92-3.95 (m, 2H), 5.29 (s, 2H), 6.85-6.94 (m, 3H), 7.24-7.28 (m, 2H), 7.32-7.36 (m,5H); minor: δ 1.73-1.81 (m, 4H), 2.67 (dis, t, 2H), 3.84 (s, 3H), 3.87 (dis, t, 2H), 5.27

(s, 2H), 6.83-6.93 (m, 3H), 7.23-7.25 (m, 2H), 7.27-7.32 (m,5H); ^{13}C NMR ($CDCl_3$, 100 MHz) major: δ 20.4, 28.5, 37.1, 52.6, 67.2, 78.5, 114.4, 120.6, 128.2, 128.5, 128.5, 129.4, 135.8, 149.8, 158.9, 161.6, 194.9; minor: δ 19.2, 28.4, 42.1, 53.1, 67.1, 78.9, 114.4, 120.6, 128.4, 129.6, 129.4, 135.5, 150.2, 158.9, 160.7, 198.8; IR (polymer) 2953, 1748, 1694, 1601, 1498, 1245, 1000, 755, 694 cm^{-1}; HRMS (M^+) calcd for $C_{21}H_{23}NO_5$: 369.1576, found 369.1575

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