TBHP-Mediated Oxidative Cross Coupling of Disulfides with Ethers through A C(sp³)-H Thiolation Process

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Supporting Information

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(A) Analytical data

2-(Phenylthio)tetrahydrofuran (3aa)¹

Light-yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 7.43 (d, *J* = 8.0 Hz, 2H), 7.15-7.24 (m, 3H), 5.57 (m, 1H), 3.93-3.98 (m, 1H), 3.87-3.91 (m, 1H), 2.28-2.32 (m, 1H), 1.87-1.97 (m, 2H), 1.79-1.83 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 135.7, 131.1, 128.8, 126.8, 87.1, 67.3, 32.6, 24.8; IR (KBr, cm⁻¹): 2971, 2923, 2869, 1476, 1434, 1040, 1018, 902, 736, 688; LRMS (EI, 70 eV) *m/z* (%): 180 (M⁺, 5), 71 (100).

2-(*p*-Tolylthio)tetrahydrofuran (3ba)²

Light-yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 7.33 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 8.1 Hz, 2H), 5.49 (m, 1H), 3.92-3.97 (m, 1H), 3.84-3.88 (m, 1H), 2.22-2.28 (m, 1H), 2.23 (s, 3H), 1.85-1.94 (m, 2H), 1.77-1.81 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 137.0, 131.8, 131.7, 129.6, 87.6, 67.2, 32.6, 24.8, 21.0; IR (KBr, cm⁻¹): 2975, 2867, 1492, 1456, 1241, 1045, 906, 806; LRMS (EI, 70 eV) *m/z* (%): 194 (M⁺, 5), 124 (8), 71 (100).

2-(4-Chlorophenylthio)tetrahydrofuran (3ca)³

Light-yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 7.36 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 5.52 (m, 1H), 3.87-3.96 (m, 2H), 2.28-2.31 (m, 1H), 1.79-1.96 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 134.2, 132.9, 132.4, 128.9, 87.2, 67.3, 32.6, 24.8; IR (KBr, cm⁻¹): 2975, 2949, 2866, 1475, 1095, 1045, 1011, 814; LRMS (EI, 70 eV) *m/z* (%): 214 (M⁺, 3), 71 (100).

2-(4-Bromophenylthio)tetrahydrofuran (3da)

Light-yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 7.33 (d, *J* = 8.7 Hz, 2H), 7.29 (t, *J* = 8.7 Hz, 2H), 5.53 (m, 1H), 3.87-3.96 (m, 2H), 2.27-2.31 (m, 1H), 1.79-1.95 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 134.9, 132.6, 131.8, 120.9, 87.1, 67.3, 32.6, 24.8; IR (KBr, cm⁻¹): 2952, 2920, 2862, 1473, 1093, 1045, 1007, 810; LRMS (EI, 70 eV) *m/z* (%): 260 (M⁺+2, 3), 258 (M⁺, 3), 71 (100); HRMS (ESI) for C₁₀H₁₁BrOS (M+H)⁺: calcd. 258.9787, found 258.9791.

Methyl 2-(tetrahydrofuran-2-ylthio)benzoate (3ea)

Light-yellow oil; ^1H NMR (500 MHz, CDCl_3) δ : 7.83 (d, $J = 7.8$ Hz, 1H), 7.78 (d, $J = 7.8$ Hz, 1H), 7.37 (t, $J = 8.5$ Hz, 1H), 7.11 (t, $J = 8.5$ Hz, 1H), 5.67 (m, 1H), 3.90-3.94 (m, 2H), 3.82 (s, 3H), 2.32-2.37 (m, 1H), 1.97-2.02 (m, 2H), 1.81-1.85 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ : 166.9, 140.9, 132.3, 130.8, 128.3, 128.1, 124.6, 84.5, 67.5, 52.0, 32.3, 25.0; IR (KBr, cm^{-1}): 2975, 2946, 2869, 1712, 1434, 1274, 1247, 1040, 742; LRMS (EI, 70 eV) m/z (%): 238 (M^+ , 2), 71 (100); HRMS (ESI) for $\text{C}_{12}\text{H}_{14}\text{O}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: calcd. 239.0736, found 339.0735.

5-Amino-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-(tetrahydrofuran-2-ylthio)-1H-pyrazole-3-carbonitrile (3fa)

White solid, mp 162.3-164.1 $^\circ\text{C}$ (uncorrected); ^1H NMR (500 MHz, $\text{C}_3\text{D}_6\text{O}$) δ : 8.09 (s, 2H), 5.99 (brs, 2H), 5.36 (m, 1H), 4.04-4.10 (m, 1H), 3.87-3.91 (m, 1H), 2.29-2.35 (m, 1H), 2.00-2.07 (m, 2H), 1.88-1.92 (m, 1H); ^{13}C NMR (125 MHz, $\text{C}_3\text{D}_6\text{O}$) δ : 152.8, 137.4, 137.2, 134.6 (q, $J = 33.9$ Hz, 1C), 133.4, 127.3 (q, $J = 1.2$ Hz, 2C), 125.5 (q, $J = 271.4$ Hz, 1C), 114.1, 93.4, 88.7, 68.3, 32.9, 25.4; IR (KBr, cm^{-1}): 3381, 3308, 2920, 2882, 2850, 1626, 1556, 1400, 1386, 1320, 1139, 1105, 1026, 887, 815; LRMS (EI, 70 eV) m/z (%): 422 (M^+ , 1), 352 (2), 255 (3), 71 (100); HRMS (ESI) for $\text{C}_{15}\text{H}_{11}\text{Cl}_2\text{F}_3\text{N}_4\text{OS}$ ($\text{M}+\text{H}$) $^+$: calcd. 423.0055, found 423.0061.

2-(Benzylthio)tetrahydrofuran (3ga)⁴

Light-yellow oil; ^1H NMR (500 MHz, CDCl_3) δ : 7.22-7.28 (m, 4H), 7.14-7.18 (m, 1H), 5.14 (m, 1H), 3.84-3.91 (m, 2H), 3.81 (d, $J = 13.2$ Hz, 1H), 3.67 (t, $J = 13.2$ Hz, 1H), 2.08-2.14 (m, 1H), 1.91-1.94 (m, 1H), 1.70-1.78 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ : 138.6, 128.9, 128.4, 126.8, 83.0, 66.7, 35.0, 32.0, 24.8; IR (KBr, cm^{-1}): 2968, 2943, 2869, 1494, 1453, 1046, 907, 698; LRMS (EI, 70 eV) m/z (%): 194 (M^+ , 4), 71 (100).

2-(Phenylthio)-1,4-dioxane (3ab)⁵

Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ : 7.42-7.44 (m, 2H), 7.19-7.25 (m, 3H), 5.04 (m, 1H), 4.15 (m, 1H), 3.91 (d, $J = 11.7$ Hz, 1H), 3.58-3.67 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ : 133.9, 131.6,

128.9, 127.3, 83.2, 69.9, 66.5, 63.8; IR (KBr, cm^{-1}): 2962, 2917, 2850, 1479, 1437, 1121, 1082, 868, 740, 690; LRMS (EI, 70 eV) m/z (%): 196 (M^+ , 4), 86 (100).

2-(2-Methylfuran-3-ylthio)-1,4-dioxane (3hb)

Light-yellow oil; ^1H NMR (500 MHz, CDCl_3) δ : 7.21 (d, $J = 1.9$ Hz, 1H), 6.31 (d, $J = 1.9$ Hz, 1H), 4.68 (m, 1H), 4.06-4.07 (m, 1H), 3.82 (d, $J = 11.7$ Hz, 1H), 3.52-3.61 (m, 4H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ : 155.7, 140.5, 115.5, 107.4, 82.8, 69.7, 66.3, 64.4, 11.9; IR (KBr, cm^{-1}): 2962, 2917, 2850, 1511, 1447, 1111, 1085, 888, 868, 731; LRMS (EI, 70 eV) m/z (%): 200 (M^+ , 7), 114 (100), 86 (92); HRMS (EI) for $\text{C}_9\text{H}_{12}\text{O}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: calcd. 201.0580, found 236.0589.

((2-Methoxyethoxy)methyl)(phenyl)sulfane (3ac)⁶ and (1,2-dimethoxyethyl)(phenyl)sulfane (3ac')⁷

3ac/3ac' = 1:1; Light-yellow oil; ^1H NMR (500 MHz, CDCl_3) δ : 7.40-7.43 (m, 4H), 7.12-7.22 (m, 6H), 4.99 (s, 2H), 4.67 (m, 1H), 3.71 (m, 2H), 3.42-3.54 (m, 4H), 3.48 (s, 3H), 3.31 (s, 3H), 3.28 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ : 135.9, 133.8, 132.3, 130.1, 128.9, 128.8, 127.8, 126.6, 88.9, 76.4, 74.7, 71.5, 67.4, 59.0, 58.9, 56.3; IR (KBr, cm^{-1}): 2923, 2891, 2811, 1472, 1434, 1129, 1097, 1078, 1024, 739, 691.

(tert-Butoxymethyl)(phenyl)sulfane (3ad)⁸

Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ : 7.42 (d, $J = 8.1$ Hz, 2H), 7.19-7.23 (m, 2H), 7.12-7.15 (m, 1H), 4.83 (s, 2H), 1.18 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ : 136.6, 129.9, 128.7, 126.4, 75.3, 68.2, 27.8; IR (KBr, cm^{-1}): 2971, 2923, 2846, 1480, 1365, 1185, 1053, 1022, 738, 690; LRMS (EI, 70 eV) m/z (%): 196 (M^+ , 5), 110 (100).

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(c) Spectra

2-(phenylthio)tetrahydrofuran (3aa)

2-(phenylthio)tetrahydrofuran (3aa)

2-(p-tolylthio)tetrahydrofuran (3ba)

2-(p-tolylthio)tetrahydrofuran (3ba)

2-(4-chlorophenylthio)tetrahydrofuran (3ca)

2-(4-chlorophenylthio)tetrahydrofuran (3ca)

2-(4-bromophenylthio)tetrahydrofuran (3da)

2-(4-bromophenylthio)tetrahydrofuran (3da)

methyl 2-(tetrahydrofuran-2-ylthio)benzoate (3ea)

methyl 2-(tetrahydrofuran-2-ylthio)benzoate (3ea)

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5-amino-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-(tetrahydrofuran-2-ylthio)-1H-pyrazole-3-carbonitrile (3fa)

5-amino-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-(tetrahydrofuran-2-ylthio)-1H-pyrazole-3-carbonitrile (3fa)

2-(benzylthio)tetrahydrofuran (3ga)

2-(benzylthio)tetrahydrofuran (3ga)

2-(phenylthio)-1,4-dioxane (3ab)

2-(phenylthio)-1,4-dioxane (3ab)

2-(2-methylfuran-3-ylthio)-1,4-dioxane (3hb)

2-(2-methylfuran-3-ylthio)-1,4-dioxane (3hb)

((2-methoxyethoxy)methyl)(phenyl)sulfane (3ac) and (1,2-dimethoxyethyl)(phenyl)sulfane (3ac')

((2-methoxyethoxy)methyl)(phenyl)sulfane (3ac) and (1,2-dimethoxyethyl)(phenyl)sulfane (3ac')

(tert-butoxymethyl)(phenyl)sulfane (3da)

(tert-butoxymethyl)(phenyl)sulfane (3da)