SUPPLEMENTAL MATERIAL

Fe-mediated S-S bond cleavage and its application in the synthesis of α -arylthio carbonyl compounds

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EXPERIMENTAL

In a round bottomed flask, activated iron dust (168 mg, 3.0 mmol) was added to a solution of α -bromo carbonyl compounds (1.0 mmol) and diaryl disulfides (0.5 mmol) in DMF (3.0 mL). The reaction mixture was stirred at room temperature under N₂ atmosphere for 15 hours. Then ethyl acetate (20 mL) was added, stirred and filtered. To filter liquor, the water (15 mL) was added and the mixture was extracted with ethyl acetate (15 mL×3). The combined organic phase was washed with water (20 mL×2) and dried over anhydrous Na₂SO₄, and concentrated under vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether:ethyl acetate =30:1)

Compound 3a: PhSCH₂COOEt: ^[S1] Oil; ¹H NMR (CDCl₃, 400 MHz): 7.41 (d, *J* = 7.6 Hz, 2H, ArH), 7.30 (t, *J* = 7.4 Hz, 2H, ArH), 7.22 (t, *J* = 7.4 Hz, 1H, ArH), 4.16 (q, *J* = 7.2 Hz, 2H, CH₂CH₃), 3.63 (s, 2H, SCH₂), 1.22 (t, *J* = 7.2 Hz, 3H, CH₂CH₃); ¹³C NMR (CDCl₃, 100 MHz): 169.7 (C=O), 134.9 (C₆H₅), 130.0 (C₆H₅), 129.0 (C₆H₅), 126.9 (C₆H₅), 61.5 (OCH₂CH₃), 36.7 (SCH₂), 14.0 (OCH₂CH₃).

Compound 3b: PhCH₂SCH₂COOEt: ^[S1] Oil; ¹H NMR: (CDCl₃, 400 MHz) 7.30-7.34 (m, 4H, ArH),

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7.22-7.27 (m, 1H, ArH), 4.18 (q, $J = 7.2$ Hz, 2H, CH₂CH₃), 3.83 (s, 2H, SCH₂CO), 3.06 (s, 2H, PhCH₂), 1.29 (t, $J = 7.2$ Hz, 3H, CH₂CH₃); ¹³C NMR (CDCl₃, 100 MHz): 165.6 (C=O), 132.4 (C₆H₅), 124.4 (C₆H₅), 123.8 (C₆H₅), 122.5 (C₆H₅), 56.5 (OCH₂CH₃), 31.5 (SCH₂COOEt), 27.5 (PhCH₂), 9.4 (OCH₂CH₃).

Compound 3c: *p*-CH₃C₆H₄SCH₂COOEt: ^[S1] Oil; ¹H NMR (CDCl₃, 400 MHz): 7.33 (d, $J = 8.0$ Hz, 2H, ArH), 7.10 (d, $J = 7.6$ Hz, 2H, ArH), 4.15 (q, $J = 6.8$ Hz, 2H, CH₂CH₃), 3.57 (s, 2H, SCH₂), 2.31 (s, 3H, *p*-CH₃C₆H₄), 1.22 (t, $J = 7.0$ Hz, 3H, CH₂CH₃); ¹³C NMR (CDCl₃, 100 MHz): 169.9 (C=O), 137.3 (C₆H₄), 131.2 (C₆H₄), 130.9 (C₆H₄), 129.8 (C₆H₄), 61.5 (OCH₂CH₃), 36.4 (SCH₂), 21.3 (*p*-CH₃C₆H₄), 14.1 (OCH₂CH₃).

Compound 3d: *p*-CH₃OC₆H₄SCH₂COOEt: ^[S1] Oil; ¹H NMR: (CDCl₃, 400 MHz): 7.40-7.44 (m, 2H, ArH), 6.82-6.86 (m, 2H, ArH), 4.14 (q, $J = 7.2$ Hz, 2H, OCH₂CH₃), 3.79 (s, 3H, *p*-CH₃OC₆H₄), 3.50 (s, 2H, SCH₂), 1.21 (t, $J = 7.2$ Hz, 3H, CH₂CH₃); ¹³C NMR (CDCl₃, 100 MHz): 169.9 (C=O), 159.6 (C₆H₄), 134.2 (C₆H₄), 124.9 (C₆H₄), 114.6 (C₆H₄), 61.3 (OCH₂CH₃), 55.3 (*p*-OCH₃C₆H₄), 38.6 (SCH₂), 14.1 (OCH₂CH₃).

Compound 3e: *p*-ClC₆H₄SCH₂COOEt: ^[S1] Oil; ¹H NMR: (CDCl₃, 400 MHz): 7.33-7.37 (m, 2H, ArH), 7.26-7.28 (m, 2H, ArH); 4.17 (q, $J = 6.8$ Hz, 2H, CH₂CH₃), 3.60 (s, 2H, SCH₂), 1.23 (t, $J = 7.2$ Hz, 3H, CH₂CH₃); ¹³C NMR (CDCl₃, 100 MHz): 169.4 (C=O), 133.4 (C₆H₄), 133.1 (C₆H₄), 131.4 (C₆H₄), 129.1 (C₆H₄), 61.6 (OCH₂CH₃), 36.8 (SCH₂), 14.1 (OCH₂CH₃).

Compound 3f: PhSCH(Me)COOMe: ^[S2] Oil; ¹H NMR: (CDCl₃, 400 MHz) 7.44-7.45 (m, 2H, ArH), 7.25-7.31 (m, 3H, ArH), 3.80 (q, $J = 5.6$ Hz, 1H, CHCH₃), 3.67 (s, 3H, OCH₃), 1.48 (d, $J = 5.2$ Hz, 3H, SCHCH₃); ¹³C NMR (CDCl₃, 100 MHz): 173.1 (C=O), 133.1 (C₆H₅), 133.0 (C₆H₅), 128.9 (C₆H₅), 128.0 (C₆H₅), 52.2 (SCHCH₃), 45.2 (OCH₃), 17.4 (SCHCH₃).

Compound 3g: $p\text{-CH}_3\text{C}_6\text{H}_4\text{SCH}(\text{Me})\text{COOMe}$:^[S2] Oil; ^1H NMR (CDCl_3 , 400 MHz): 7.34 (d, $J = 8.4$ Hz, 2H, ArH), 7.11 (d, $J = 8.0$ Hz, 2H, ArH), 3.72 (q, $J = 7.2$ Hz, 1H, SCHCH₃), 3.66 (s, 3H, OCH₃), 2.33 (s, 3H, $p\text{-CH}_3\text{C}_6\text{H}_4$), 1.45 (d, $J = 7.2$ Hz, 3H, SCHCH₃); ^{13}C NMR (CDCl_3 , 100 MHz): 173.1 ($\text{C}=\text{O}$), 138.5 (C_6H_4), 133.9 (C_6H_4), 129.7 (C_6H_4), 129.0 (C_6H_4), 52.2 (OCH₃), 45.5 (SCHCH₃), 21.1 ($p\text{-CH}_3\text{C}_6\text{H}_4$), 17.3 (SCHCH₃).

Compound 3h: $p\text{-ClC}_6\text{H}_4\text{SCH}(\text{Me})\text{COOMe}$:^[S3] Oil; ^1H NMR (CDCl_3 , 400 MHz): 7.38 (d, $J = 8.4$ Hz, 2H, ArH), 7.28 (d, $J = 8.4$ Hz, 2H, ArH), 3.75 (q, $J = 7.2$ Hz, 1H, SCHCH₃), 3.67 (s, 2H, OCH₃), 1.47 (d, $J = 7.2$ Hz, 3H, SCHCH₃); ^{13}C NMR (CDCl_3 , 100 MHz): 172.8 ($\text{C}=\text{O}$), 134.5 (C_6H_4), 131.4 (C_6H_4), 129.7 (C_6H_4), 129.1 (C_6H_4), 52.3 (SCHCH₃), 45.2 (OCH₃), 17.3 (SCHCH₃).

Compound 3i: $\text{PhSCH}_2\text{COMe}$:^[S4] Oil; ^1H NMR: (CDCl_3 , 400 MHz): 7.32-7.35 (m, 2H, ArH), 7.29 (t, $J = 7.6$ Hz, 2H, ArH), 7.19-7.23 (m, 1H, ArH), 3.67 (s, 2H, SCH₂), 2.28 (s, 3H, COCH₃); ^{13}C NMR (CDCl_3 , 100 MHz): 203.6 ($\text{C}=\text{O}$), 134.6 (C_6H_5), 129.5 (C_6H_5), 129.1 (C_6H_5), 126.9 (C_6H_5), 44.6 (SCH₂), 28.0 (COCH₃).

Compound 3j: $p\text{-CH}_3\text{C}_6\text{H}_4\text{SCH}_2\text{COMe}$:^[S1] Oil; ^1H NMR (CDCl_3 , 400 MHz): 7.25 (d, $J = 8.0$ Hz, 2H, ArH), 7.09 (d, $J = 8.0$ Hz, 2H, ArH), 3.60 (s, 2H, SCH₂), 2.30 (s, 3H, $p\text{-CH}_3\text{C}_6\text{H}_4$), 2.25 (s, 3H, COCH₃); ^{13}C NMR (CDCl_3 , 100 MHz): 203.6 ($\text{C}=\text{O}$), 137.2 (C_6H_4), 130.8 (C_6H_4), 130.4 (C_6H_4), 129.9 (C_6H_4), 45.3 (SCH₂), 28.0 (COCH₃), 21.0 ($p\text{-CH}_3\text{C}_6\text{H}_4$).

Compound 3k: $p\text{-CH}_3\text{OC}_6\text{H}_4\text{SCH}_2\text{COMe}$:^[S5] Oil; ^1H NMR (CDCl_3 , 400 MHz): 7.35 (d, $J=8.8$ Hz, 2H, ArH), 6.84 (d, $J=8.8$ Hz, 2H, ArH), 3.79 (s, 3H, $p\text{-CH}_3\text{OC}_6\text{H}_4$), 3.54 (s, 2H, SCH₂), 2.26 (s, 3H, COCH₃); ^{13}C NMR (CDCl_3 , 100 MHz): 203.4 ($\text{C}=\text{O}$), 159.6 (C_6H_4), 133.6 (C_6H_4), 124.5 (C_6H_4), 114.8 (C_6H_4), 55.3 ($p\text{-CH}_3\text{OC}_6\text{H}_4$), 46.5 (SCH₂), 28.0 (COCH₃).

Compound 3l: $p\text{-ClC}_6\text{H}_4\text{SCH}_2\text{COMe}$:^[S6] Oil; ^1H NMR (CDCl_3 , 400 MHz): 7.26 (s, 4H, ArH), 3.64

(s, 2H, SCH₂), 2.27 (s, 3H, COCH₃); ¹³C NMR (CDCl₃, 100 MHz): 203.0 (C=O), 133.1 (C₆H₄), 133.0 (C₆H₄), 130.9 (C₆H₄), 129.3 (C₆H₄), 44.7 (SCH₂), 28.0 (COCH₃).

Compound 3m: PhSCH₂COPh: ^[S1] Yellow solid, Mp: 50-51 °C [Lit. 49-50 °C]; ¹H NMR (CDCl₃, 400 MHz): 7.99 (t, *J* = 8.4 Hz, 1H, ArH), 7.41-7.59 (m, 8H, ArH), 7.17 (s, 1H, ArH), 2.60 (s, 2H, SCH₂); ¹³C NMR (CDCl₃, 100 MHz) δ 191.7 (C=O), 132.5 (C₆H₅), 129.1 (C₆H₅), 128.6 (C₆H₅), 128.5 (C₆H₅), 128.5 (C₆H₅), 128.2 (C₆H₅), 126.4 (C₆H₅), 122.1 (C₆H₅), 18.8 (SCH₂).

Compound 3n: PhCH₂SCH₂COPh: ^[S7] Yellow solid, Mp: 89-90 °C [Lit. 90-92 °C]; ¹H NMR: (CDCl₃, 400 MHz): 7.93 (d, *J* = 7.6 Hz, 1H, ArH), 7.55-7.59 (m, 1H, ArH), 7.44-7.49 (m, 3H, ArH), 7.29-7.37 (m, 5H, ArH), 3.76 (s, 2H, SCH₂CO), 3.67 (s, 2H, PhCH₂); ¹³C NMR (CDCl₃, 100 MHz): 194.4 (C=O), 137.3(C₆H₅), 135.4 (C₆H₅), 133.3 (C₆H₅), 129.2 (C₆H₅), 128.7 (C₆H₅), 128.6 (C₆H₅), 128.5 (C₆H₅), 127.2 (C₆H₅), 36.1(PhCH₂), 35.8 (SCH₂CO).

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¹H NMR and ¹³C NMR spectra

¹H NMR of **3a** in CDCl₃

¹³C NMR of **3a** in CDCl₃

¹H NMR of **3b** in CDCl₃

¹³C NMR of **3b** in CDCl₃

¹H NMR of **3c** in CDCl₃

¹³C NMR of **3c** in CDCl₃

¹H NMR of **3d** in CDCl₃

¹³C NMR of **3d** in CDCl₃

¹H NMR of **3e** in CDCl₃

¹³C NMR of **3e** in CDCl₃

¹H NMR of **3f** in CDCl₃

¹³C NMR of **3f** in CDCl₃

¹H NMR of **3g** in CDCl₃

¹³C NMR of **3g** in CDCl₃

¹H NMR of **3h** in CDCl₃

¹³C NMR of **3h** in CDCl₃

¹H NMR of **3i** in CDCl₃

¹³C NMR of **3i** in CDCl₃

¹H NMR of **3j** in CDCl₃

¹³C NMR of **3j** in CDCl₃

¹H NMR of **3k** in CDCl₃

¹³C NMR of **3k** in CDCl₃

¹H NMR of **31** in CDCl₃

¹³C NMR of **31** in CDCl₃

¹H NMR of **3m** in CDCl₃

¹³C NMR of **3m** in CDCl₃

¹H NMR of **3n** in CDCl₃

¹³C NMR of **3n** in CDCl₃