A highly efficient thiourea catalyzed dehydrative nucleophilic substitution reaction of 3-substituted oxindoles with xanthydrols

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General: Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products were carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. $^1$H and $^{13}$C NMR spectra were obtained using a Bruker DPX-400 spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad.

All reactions were run under N$_2$ atmosphere. Anhydrous THF and toluene were prepared by distillation over sodium-benzophenone ketyl prior to use. Anhydrous acetone was distilled over anhydrous CaSO$_4$ and stored over MS 4Å. Anhydrous DMF was prepared by first distillation over anhydrous CaSO$_4$ and then from MS 4 Å. Anhydrous halogenated solvents and CH$_3$CN were prepared by first distillation over P$_2$O$_5$ and then from CaH$_2$. Anhydrous Ethyl acetate was prepared by first dried in anhydrous Na$_2$SO$_4$ and then distilled over P$_2$O$_5$ and stored over MS 4Å. Anhydrous CH$_3$NO$_2$ was prepared by first dried in anhydrous Na$_2$SO$_4$ and then distilled under reduced pressure. Oxindoles 1 were prepared according to literature report.$^1$ 9H-xanthen-9-ol (2a) and 9H-thioxanthen-9-ol (2b) were prepared through the reduction of corresponding ketone using NaBH$_4$.$^2$ In(OTf)$_3$ and CuCl were purchased individually from Strem chemicals and Aldrich. Thiourea catalysts A1–A4$^3a$, B1–B2$^3b$, C1–C2$^3c$ were prepared according to the literature methods.

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General procedure for the dehydrative nucleophilic substitution reaction of 3-substituted oxindoles with 9H-xanthen-9-ol (2a) and 9H-thioxanthen-9-ol (2b)

Under an atmosphere of N₂, to a flame-dried Schlenk tube were added A₁ (12.5 mg, 0.025 mmol, 0.1 eq), oxindole 1 (0.25 mmol, 1.0 eq), 2a or 2b (0.5 mmol, 2.0 eq) and 1.0 mL of anhydrous CH₃CN. The reaction mixture was heated to 50 °C and stirred till almost full conversion of 1 by TLC analysis. The solvent was removed under reduced pressure and the residue was subjected to column chromatography using petroleum ether/ethyl acetate as the eluent to afford the desired product 3.

Column chromatography afforded the desired product 3a in 81% yield as white solid. Mp 213-215 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.74-7.72 (m, 2H), 7.58-7.56 (m, 1H), 7.48 (s, 1H), 7.36-7.33 (m, 3H), 7.20-7.12 (m, 2H), 7.05-7.01 (m, 2H), 6.96-6.91 (m, 2H), 6.73-6.64 (m, 3H), 6.59-6.57 (m, 1H), 6.44-6.42 (m, 1H), 5.15 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 178.82, 153.54, 152.80, 140.62, 136.36, 129.97, 129.86, 128.73, 128.47, 128.45, 128.22, 128.18, 127.79, 127.66, 127.05, 122.74, 122.20, 121.49, 120.16, 119.82, 116.06, 115.72, 109.11, 63.24, 48.57; IR (neat): 2928, 1713, 1475, 1253, 878, 739, 696 cm⁻¹; HRMS (ESI): Exact mass calcd for C₂₇H₁₉NNaO₂ [M+Na]+: 412.1308, Found: 412.1305.

Column chromatography afforded the desired product 3b in 76% yield as white solid. Mp 252-253 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.71-7.69 (m, 2H), 7.57-7.55 (m, 1H), 7.38-7.31 (m, 4H), 7.23-7.19 (m, 1H), 7.10-7.05 (m, 2H), 6.95-6.92 (m, 1H), 6.88-6.83 (m, 1H), 6.77-6.69 (m, 2H), 6.52-6.49 (m, 1H), 6.42-6.36 (m, 2H), 5.15 (s, 1H); ¹³C NMR (100 MHz, DMSO-d₆): δ = 177.54, 158.17, 155.83, 153.05, 152.28, 138.34, 136.27, 130.02, 129.82, 128.91, 128.73, 128.65, 128.54, 128.33, 128.21, 127.69, 122.86, 122.40, 119.86, 119.79, 115.81, 115.64, 115.04, 114.81, 114.53, 114.27, 109.82,
Column chromatography afforded the product 3c in 83% yield as white solid. Mp 234-236 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.66-7.64\) (m, 2H), 7.55-7.53 (m, 2H), 7.45-7.44 (m, 1H), 7.40-7.36 (m, 3H), 7.24-7.22 (m, 1H), 7.14-7.06 (m, 2H), 6.97-6.93 (m, 1H), 6.82-6.80 (m, 1H), 6.74-6.70 (m, 1H), 6.59-6.58 (m, 1H), 6.41-6.39 (m, 1H), 5.14 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 177.18, 153.54, 152.59, 139.42, 135.12, 133.21, 129.78, 129.74, 128.98, 128.96, 128.46, 128.35, 128.12, 123.03, 122.45, 119.30, 118.93, 116.14, 116.09, 114.35, 102.37, 65.10, 49.10\); IR (neat): 3190, 1708, 1455, 1253, 898, 757, 699, 632 cm\(^{-1}\); HRMS (ESI): Exact mass calcd for C\(_{27}\)H\(_{17}\)Br\(_2\)NNaO\(_2\) [M+Na]+: 567.9518, Found: 567.9501.

Column chromatography afforded the desired product 3d in 80% yield as yellow solid. Mp 190-192 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.96\) (s, 1H), 7.75-7.73 (m, 2H), 7.55-7.53 (m, 1H), 7.34-7.29 (m, 3H), 7.21-7.17 (m, 1H), 7.00-6.97 (m, 2H), 6.83-6.77 (m, 2H), 6.71-6.68 (m, 2H), 6.43-6.41 (m, 1H), 6.20 (s, 1H), 5.12 (s, 1H), 2.22 (s, 3H), 2.00 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 179.41, 153.73, 152.71, 137.05, 136.69, 130.66, 130.00, 129.84, 129.82, 128.83, 128.38, 128.06, 128.00, 127.49, 126.60, 125.94, 122.53, 122.01, 120.24, 119.71, 117.84, 115.76, 115.61, 63.76, 48.63, 21.14, 16.14\); IR (neat): 2974, 2893, 1695, 1477, 1255, 1089, 1049, 880, 750, 696, 644 cm\(^{-1}\); HRMS (ESI): Exact mass calcd for C\(_{29}\)H\(_{23}\)NNaO\(_2\) [M+Na]+: 440.1621, Found: 440.1608.

Column chromatography afforded the desired product 3e in 89% yield as white solid. Mp 226-228 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.73-7.70\) (m, 2H), 7.56-7.54 (m, 1H), 7.24-7.12 (m, 3H), 7.08-7.01 (m, 4H), 6.96-6.93 (m, 2H), 6.76-6.72 (m, 2H), 6.65-6.63 (m, 1H), 6.58-6.56 (m, 1H), 6.42-6.40 (m, 1H), 5.08 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 178.87, 163.54, 161.09, 153.53, 152.75, 140.61, 132.21, 132.18, 130.51, 130.43, 129.90, 129.74, 128.61, 128.29, 127.62, 126.95, 122.75, 122.30, 121.65, 119.93, 119.62, 116.17, 115.79, 115.10, 114.89, 109.26, 62.63, 48.78; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta = -114.75\); IR (neat): 3300, 1713, 1476, 1256, 812, 743, 679 cm\(^{-1}\); HRMS (ESI): Exact mass calcd for C\(_{27}\)H\(_{18}\)FNNaO\(_2\) [M+Na]+: 430.1214, Found: 430.1203.
Column chromatography afforded the desired product 3f in 75% yield as white solid. Mp 218-220 °C; ^1H NMR (400 MHz, CDCl3): δ = 7.62-7.60 (m, 2H), 7.54-7.52 (m, 2H), 7.47-7.45 (m, 2H), 7.24-7.20 (m, 1H), 7.17-7.13 (m, 1H), 7.07-7.03 (m, 2H), 6.96-6.88 (m, 2H), 6.79-6.71 (m, 2H), 6.63-6.58 (m, 2H), 6.46-6.44 (m, 1H), 5.08 (s, 1H); ^13C NMR (100 MHz, CDCl3): δ = 178.49, 153.52, 152.46, 140.59, 135.57, 131.26, 130.49, 129.87, 129.74, 128.70, 128.66, 128.35, 127.59, 126.60, 122.76, 122.43, 122.04, 121.70, 119.84, 119.47, 116.21, 115.80, 109.31, 62.87, 48.59; IR (neat): 3290, 1706, 1474, 1250, 1098, 816, 767, 673 cm^-1; HRMS (ESI): Exact mass calcd for C_{27}H_{18}BrNNaO_{2} [M+Na]^+: 490.0413, Found: 490.0404.

Column chromatography afforded the desired product 3g in 86% yield as white solid. Mp 223-224 °C; ^1H NMR (400 MHz, CDCl3): δ = 7.59-7.55 (m, 3H), 7.26 (s, 1H), 7.22-7.11 (m, 4H), 7.03-7.01 (m, 2H), 6.94-6.88 (m, 2H), 6.74-6.70 (m, 2H), 6.62-6.56 (m, 2H), 6.50-6.48 (m, 1H), 5.13 (s, 1H), 2.35 (s, 3H); ^13C NMR (100 MHz, CDCl3): δ = 179.38, 153.53, 152.77, 140.80, 137.30, 133.31, 130.07, 129.82, 128.86, 128.56, 128.38, 128.34, 128.14, 127.63, 127.31, 122.68, 122.19, 121.39, 120.30, 119.87, 115.99, 115.65, 109.19, 63.14, 48.24, 21.03; IR (neat): 3300, 1707, 1454, 1251, 1099, 1020, 812, 744, 698, 630 cm^-1; MS (ESI): 426 [M+Na]^+; HRMS (ESI): Exact mass calcd for C_{28}H_{21}NNaO_{2} [M+Na]^+: 426.1448, Found: 426.1465.

Column chromatography afforded the desired product 3h in 91% yield as white solid. Mp 193-194 °C; ^1H NMR (400 MHz, CDCl3): 8.02 (s, 1H), 7.89-7.87 (m, 2H), 7.61-7.59 (m, 2H), 7.54-7.52 (m, 1H), 7.24-7.16 (m, 2H), 7.06-6.96 (m, 3H), 6.88-6.84 (m, 1H), 6.74-6.62 (m, 4H), 6.40-6.38 (m, 1H), 5.15 (s, 1H); ^13C NMR (100 MHz, CDCl3): 178.39, 153.58, 152.83, 140.68, 140.59, 129.72, 129.21, 128.91, 128.81, 128.47, 127.68, 126.43, 125.07 (q, J = 4.0 Hz), 122.82, 122.47, 121.88, 119.71, 119.36, 116.37, 115.90, 109.49, 63.30, 48.85; ^19F NMR (376 MHz, CDCl3): δ = -62.49; IR (neat): 3360, 2975,1702, 1455, 1323, 1251, 1049, 974, 881, 748 cm^-1; HRMS (EI): Exact mass calcd for C_{28}H_{18}F_{3}NNaO_{2} [M+Na]^+: 480.1182, Found: 480.1177.
Column chromatography afforded the desired product 3i in 65% yield as white solid. Mp 180-182 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.51-7.50 (m, 2H), 7.30-7.28 (m, 1H), 7.26-7.24 (m, 1H), 7.15-7.04 (m, 4H), 6.98-6.90 (m, 3H), 6.84-6.80 (m, 1H), 6.75-6.72 (m, 2H), 6.59-6.56 (m, 2H), 4.94 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 178.34, 153.48, 152.71, 140.42, 140.17, 129.73, 129.67, 128.79, 128.66, 128.35, 128.05, 127.52, 126.53, 126.46, 125.81, 122.77, 122.38, 121.86, 119.84, 119.46, 115.99, 115.75, 109.19, 61.11, 50.29; IR (neat): 2892, 1698, 1618, 1475, 1255, 747, 714, 653 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{25}$H$_{17}$NNaO$_2$S [M+Na]$^+$: 418.0872, Found: 418.0853.

Column chromatography afforded the desired product 3j in 82% yield as white solid. Mp 253-255 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.16-8.14 (m, 1H), 7.95-7.93 (m, 1H), 7.88-7.86 (m, 1H), 7.75-7.73 (m, 2H), 7.66 (s, 1H), 7.58-7.57 (m, 1H), 7.52-7.44 (m, 2H), 7.32-7.30 (m, 1H), 7.21-7.17 (m, 1H), 7.08-7.02 (m, 2H), 6.92-6.89 (m, 1H), 6.79-6.77 (m, 1H), 6.69 (s, 1H), 6.60-6.57 (m, 1H), 6.51-6.49 (m, 1H), 6.42-6.41 (m, 1H), 5.30 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta$ = 177.05, 153.21, 152.39, 141.49, 133.95, 132.37, 132.16, 131.32, 130.12, 129.63, 129.57, 129.41, 128.94, 128.63, 128.22, 127.76, 127.41, 127.22, 126.53, 126.34, 122.90, 122.43, 119.90, 119.66, 115.77, 115.72, 112.75, 111.00, 63.37, 46.48; IR (neat): 3218, 1716, 1476, 1256, 814, 751, 691 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{31}$H$_{20}$BrNNaO$_2$ [M+Na]$^+$: 540.0570, Found: 540.0558.

Column chromatography afforded the desired product 3k in 65% yield as white solid. Mp 265-266 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.50-7.48 (m, 1H), 7.42-7.36 (m, 2H), 7.23-7.18 (m, 2H), 7.07-7.01 (m, 2H), 6.97-6.85 (m, 6H), 6.78-6.72 (m, 4H), 6.24-6.22 (m, 1H ), 4.64 (s, 1H), 3.43 (AB, $J$ = 12.4 Hz, 1H), 3.07 (AB, $J$ = 12.8 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 179.62, 153.86, 152.77, 140.44, 135.51, 131.08, 130.02, 129.28, 128.84, 128.39, 128.03, 127.49, 126.25, 125.10, 122.83, 122.79, 121.62, 120.85, 120.62, 116.82, 115.73, 108.49, 61.06, 46.82, 41.25; IR (neat): 3304, 2972, 1716, 1476, 1256, 814, 751, 691 cm$^{-1}$; MS (ESI): 426 [M+Na]$^+$; HRMS (ESI): Exact mass calcd for C$_{28}$H$_{21}$NNaO$_2$ [M+Na]$^+$: 426.1465, Found: 426.1452.
Column chromatography afforded the desired product $3i$ in 85% yield as white solid. Mp 240-242 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.66 (s, 1H), 7.40-7.29 (m, 3H), 7.19-7.17 (m, 3H), 7.09-7.01 (m, 1H), 6.93-6.89 (m, 1H), 6.79-6.77 (m, 1H), 6.57 (s, 1H), 6.44-6.42 (m, 1H), 4.38 (s, 1H), 1.41 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 181.59, 153.69, 152.63, 139.06, 133.30, 130.73, 129.03, 128.98, 128.23, 127.69, 122.79, 122.73, 120.47, 119.96, 116.65, 116.00, 114.68, 110.23, 55.04, 46.56, 21.06; IR (neat): 3252, 2966, 1713, 1668, 1476, 1253, 1097, 815, 765, 695, 612 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{22}$H$_{16}$BrNNaO$_2$ [M+Na]$^+$: 428.0257, Found: 428.0248.

Column chromatography afforded the desired product $3m$ in 79% yield as white solid. Mp 206-208 °C; $^1$H NMR (400 MHz, CDCl$_3$): 7.81-7.79 (m, 2H), 7.68-7.66 (m, 1H), 7.37-7.31 (m, 3H), 7.26 (s, 1H), 7.22-7.00 (m, 6H), 6.88-6.85 (m, 2H), 6.66-6.59 (m, 3H), 5.32 (s, 1H); $^{13}$C NMR (100 MHz,): $\delta$ = 178.34, 141.13, 136.67, 134.90, 133.12, 132.35, 131.04, 130.44, 129.67, 129.51, 128.84, 128.53, 128.09, 127.48, 127.17, 127.04, 126.82, 125.76, 125.61, 125.57, 125.16, 121.30, 109.11, 63.25, 56.16; IR (neat): 2924, 1693, 1469, 1208, 1038, 789, 734, 695, 632 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{27}$H$_{19}$NNaOS [M+Na]$^+$: 428.1080, Found: 428.1072.

Column chromatography afforded the desired product $3n$ in 63% yield as white solid. Mp 215-216 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.57-7.55 (m, 1H), 7.45-7.42 (m, 1H), 7.40-7.33 (m, 4H), 7.07-7.02 (m, 3H), 6.99-6.90 (m, 5H), 6.83-6.76 (m, 4H), 6.26-6.24 (m, 1H), 4.77 (s, 1H), 3.47 (AB, $J$ = 12.8 Hz, 1H), 3.09 (AB, $J$ = 12.8 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 179.55, 140.69, 135.51, 134.90, 133.04, 132.33, 131.49, 130.73, 130.63, 130.17, 128.21, 128.08, 127.52, 127.39, 127.17, 126.86, 126.70, 126.19, 125.80, 125.74, 125.69, 121.23, 108.40, 61.05, 54.32, 41.61; IR (neat): 2924, 1698, 1468, 1037, 909, 748, 697, 651 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{28}$H$_{21}$NNaOS[M+Na]$^+$: 442.1236, Found: 442.1230.

Column chromatography afforded the desired product $3o$ in 79% yield as white solid. Mp 214-215 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.43-7.42 (m, 2H), 7.38-7.31 (m, 4H), 7.22-7.20 (m, 1H), 7.08-7.05 (m, 3H), 6.71-6.70 (m, 1H), 6.45-6.43 (m, 1H), 4.50 (s, 1H), 1.41 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$):
δ = 181.11, 139.08, 134.68, 133.40, 132.83, 132.10, 131.12, 130.74, 130.57, 130.06, 129.28, 127.70, 127.05, 125.93, 125.78, 125.75, 114.62, 109.99, 55.08, 54.07, 21.77; IR (neat): 3341, 2924, 1708, 1469, 1377, 1278, 1048, 880, 746, 616 cm⁻¹; HRMS (EI): Exact mass calcd for C₂₂H₁₆BrNNaOS [M+Na]⁺: 444.0028, Found: 444.0026.

The catalytic asymmetric version of 1a with 2a catalyzed by chiral (thio)urea catalysts

To a 5.0 mL vial were successively added chiral (thio)urea (0.005 mmol, 0.1 eq), 1a (10.5 mg, 0.05 mmol), 2a (19.8 mg, 0.1 mmol, 2.0 eq) and 0.5 mL of anhydrous CH₂Cl₂. The mixture was stirred at room temperature. Generally, the reaction proceeded very slowly and 1a could not be consumed even after 48 h. The ee value of the product 3a was determined by HPLC analysis of a sample taken from the reaction mixture. Unfortunately, since almost no enantioselectivity was observed when several widely used chiral ureas were examined, so we did not check the yield of 3a.
The high resolution mass data for the complex of 1a and A₅

Shanghai Mass Spectrometry Center
Shanghai Institute of Organic Chemistry
Chinese Academy of Sciences
High Resolution MS Data Report

Instrument

Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS

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