Electronic Supplementary Information

Stereoselective Synthesis of \((Z)\)-\(\alpha\)-Halo-\(\alpha,\beta\)-Unsaturated Esters, and Amides from Aldehydes and Trihaloesters or Amides Promoted by Manganese

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GENERAL
Reactions requiring an inert atmosphere were conducted under dry nitrogen, and the glassware was oven dried (120 °C). THF was distilled from sodium/benzophenone ketyl immediately prior to use. All reagents were purchased in the higher quality available and were used without further purification. Flash column chromatography was carried out on silica gel 230-400 mesh. Compounds were visualized on analytical thin layer chromatograms (TLC) by UV light (254 nm). $^1$H NMR spectra were recorded at 200, 300 or 400 MHz. $^{13}$C NMR spectra and DEPT experiments were determined at 50 or 75 MHz. Chemical shifts are given in ppm relative to tetramethylsilane (TMS), which is used as an internal standard, and coupling constants ($J$) are reported in Hz. The diastereoisomeric ratios were obtained using $^1$H-NMR analysis and GC-MS of crude products. GC-MS and HRMS were measured at 70 eV or using FAB conditions. When HRMS could not be measured on molecular ion the HRMS of a significant fragment is given. Only the most important IR absorptions (cm$^{-1}$) and the molecular ions and/or base peaks in MS are given.

Preparation of highly active Manganese (Mn*): A mixture of lithium (26 mmol) and 2-phenylpyridine (4 mmol) in THF (20 mL) under a nitrogen atmosphere was stirred for 1h. In a separate flask a solution of the Li$_2$MnCl$_4$ complex was prepared by stirring a suspension of anhydrous MnCl$_2$ (13 mmol) and LiCl (26 mmol) in THF (20 mL) for 30 min. Then, this yellow solution was added at room temperature with a syringe to the 2-phenylpyridine/lithium solution previously prepared and was stirred, under a nitrogen atmosphere at room temperature for 3 h. The black slurry was allowed to stir at room temperature for 3 h.

General procedure for the synthesis of α,β−unsaturated compounds 3 or 5:
The slurry of Mn* (2.5 mmol, 8.5 mL) in THF was added to a stirred solution of the trihaloester or amide (0.6 mmol) 2, or 4, respectively and the corresponding aldehyde (0.5 mmol) 1 in THF (2 mL) under inert atmosphere. The mixture was heated at reflux for 5 h before it was quenched with HCl 3 M. The organic material was extracted with diethyl ether (3 x 20 mL), the combined organic extracts were washed sequentially with HCl 3 M (2 x 10 mL), saturated NaHCO$_3$ (2 x 20 mL), and water (2 x 20 mL) and dried over Na$_2$SO$_4$. Solvents were removed in vacuo. Purification by flash column chromatography on silica gel (compounds 3: hexane/ EtOAc 10/1; compounds 5: hexane/ EtOAc 3/1) provided pure compounds 3 and 5.

General procedure for the synthesis of ketones 9:
The requisite organolithium compound (3.0 mmol) was added dropwise to the morpholine amide 5c (1.0 mmol) in THF (4 mL) at –78°C. After stirring for 30 min the reaction was quenched with an aqueous saturated solution of NH$_4$Cl (10 mL), followed by extraction with diethyl ether (3 x 10 mL). Usual workup provided crude products 9, which were purified by flash column chromatography on silica gel (hexane: EtOAc 10:1).
Ethyl (Z)-2-Chloro-5-methylhex-2-enoate (3a): Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 6.98 (t, $J = 7.3$ Hz, 1 H), 4.17 (q, $J = 7.2$ Hz, 2 H), 2.15 (t, $J = 7.3$ Hz, 2 H), 1.72 (hp, $J = 6.7$ Hz, 1 H), 1.23 (t, $J = 7.2$ Hz, 3 H), 0.85 (d, $J = 6.6$ Hz, 6 H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 162.5 (C), 141.3 (CH), 124.9 (C), 62.1 (CH$_2$), 38.3 (CH$_2$), 27.8 (CH), 22.4 (2 x CH$_3$), 14.1 (CH$_3$); MS (70 eV, EI) $m/z$ (%) 190 [M$^+$, 6], 243 (91), 169 (39), 131 (48), 69 (100); HRMS (70 eV) calc. for C$_9$H$_{15}$ClO$_2$ 190.0761, found 190.0786; IR (neat): 3422, 1654, 1265 cm$^{-1}$; $R_f$ = 0.5 (Hexane: EtOAc 10:1).

$^1$H NMR (300 MHz)

\[ \text{O} \]
\[ \text{Cl} \]
\[ \text{3a} \]

$^{13}$C NMR (75 MHz)
**Ethyl (Z)-2-Chloro-3-cyclohexylacrylate (3b):** Colourless oil. $^1$H NMR (300 MHz, CDCl$_3$):
\[ \begin{align*}
\delta & \ 6.78 \ (d, \ J = 9.3 \ Hz, \ 1 \ H), \ 4.15 \ (q, \ J = 7.2 \ Hz, \ 2 \ H), \ 2.58-2.48 \ (m, \ 1 \ H), \ 1.65-1.52 \ (m, \ 5 \ H), \\
& \ 1.25-1.07 \ (m, \ 5 \ H), \ 1.24 \ (t, \ J = 7.2 \ Hz, \ 3 \ H) ; \ ^{13}$C NMR (75 MHz, CDCl$_3$): \[ \delta \ 162.8 \ (C), \ 146.7 \ (CH), \ 122.8 \ (C), \ 62.1 \ (CH$_2$), \ 38.5 \ (CH), \ 30.8 \ (2 \times \ CH$_2$), \ 25.7 \ (CH$_2$), \ 25.3 \ (2 \times \ CH$_2$), \ 14.1 \ (CH$_3$) ; \\
\end{align*} \]
MS (70 eV, EI) $m/z$ (%) 216 [M$,^+$, 52], 135 (100), 106 (37), 82 (33); HRMS (70 eV) calc. for C$_{11}$H$_{17}$ClO$_2$ 216.0917, found 216.0911; IR (neat): 3425, 1643, 1469, 749 cm$^{-1}$; $R_f$ = 0.5 (Hexane: EtOAc 10:1).

$^1$H NMR (300 MHz)

$^{13}$C NMR (75 MHz)
**isoPropyl (Z)-2-Chlorodec-2-enoate (3c):** ¹H NMR (400 MHz, CDCl₃): δ 7.00 (t, J = 7.3 Hz, 1 H), 5.06 (hp, J = 6.1 Hz, 1 H), 2.30 (q, J = 7.4 Hz, 2 H), 1.46-1.43 (m, 2 H), 1.28-1.21 (m, 14 H), 0.84 (t, J = 6.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 161.8 (C), 141.7 (CH), 124.9 (C), 69.6 (CH), 31.5 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 28.8 (CH₂), 27.5 (CH₂), 22.4 (CH₂), 21.5 (2 x CH₃), 13.9 (CH₃); MS (70 eV, EI) m/z (%) 264 [M⁺, 2], 187 (50), 107 (100), 69 (40); HRMS (70 eV) calc. for C₁₃H₂₃ClO₂ [M⁺] 246.1387, found 246.1382; IR (neat): 1736, 1632, 1467, 1108 cm⁻¹; Rᵣ = 0.43 (Hexane: EtOAc 20:1).

\[ \text{Cl} \quad \text{O} \quad \text{3c} \]

¹H NMR (400 MHz)

¹³C NMR (100 MHz)
Ethyl (Z)-2-Bromodec-2-enoate (3d): Pale yellow oil. \( ^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 7.29 (t, \( J = 7.1 \) Hz, 1 H), 4.28 (q, \( J = 7.1 \) Hz, 2 H), 2.37-2.29 (apparent q, \( J = 7.0 \) Hz, 4 H), 1.53-1.20 (m, 11 H), 0.89 (t, \( J = 6.8 \) Hz, 3 H); \( ^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta \) 162.5 (C), 146.2 (CH), 116.2 (C), 62.2 (CH\(_2\)), 32.0 (CH\(_2\)), 31.6 (CH\(_2\)), 29.6 (CH\(_2\)), 29.2 (CH\(_2\)), 28.9 (CH\(_2\)), 27.4 (CH\(_2\)), 22.5 (CH\(_3\)), 13.9 (CH\(_3\)); MS (70 eV, EI) \( m/z \) (%) 126 [\( M^+ \)], 103 (74), 85 (100), 69 (98); HRMS (70 eV) calc. for C\(_{12}\)H\(_{21}\)BrO\(_2\) 276.0725, found 276.0728; IR (neat): 3503, 2927, 1732, 1466, 1258 cm\(^{-1}\); \( R_f \) = 0.54 (Cyclohexane: EtOAc 5:1).

\( ^1\)H NMR (300 MHz)

\( ^{13}\)C NMR (75 MHz)
Ethyl (Z)-2-Fluoro-4-methylhex-2-enoate (3e): Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 5.95 (dd, $J = 33.6$, 10.3 Hz, 1 H), 4.29 (q, $J = 7.3$ Hz, 2 H), 2.71-2.61 (m, 1 H), 1.52-1.20 (m, 2 H), 1.35 (t, $J = 7.1$ Hz, 3 H), 1.06 (d, $J = 6.8$ Hz, 3 H), 0.90 (t, $J = 7.3$ Hz, 3 H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 161.9 (d, $J = 26.2$ Hz, C), 149.1 (d, $J = 253.1$ Hz, C), 126.0 (d, $J = 9.8$ Hz, CH), 61.4 (CH$_2$), 31.3 (CH), 29.3 (CH$_2$), 19.7 (CH$_3$), 14.1 (CH$_3$), 11.7 (CH$_3$); HRMS (70 eV) calc. for C$_9$H$_{15}$FO$_2$ 174.1056, found 174.1055; IR (neat): 2960, 1730, 1465, 1215 cm$^{-1}$; $R_f = 0.52$ (Hexane: EtOAc 10:1).

$^1$H NMR (300 MHz)

$^{13}$C NMR (75 MHz)
(Z)-2-Chloro-\(N,N\)-diethyl-5-methylhex-2-enamide (5a):  Pale orange oil.  \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 5.94 (t, \(J = 7.1\) Hz, 1 H), 3.37 (q, \(J = 7.1\) Hz, 4 H), 2.15 (apparent t, \(J = 7.0\) Hz, 2 H), 1.75 (hp, \(J = 6.5\) Hz, 1 H), 1.15 (t, \(J = 7.1\) Hz, 6 H), 0.92 (d, \(J = 6.5\) Hz, 6 H); \(^1\)\(^3\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 165.7 (C), 129.7 (CH), 125.0 (C), 42.7 (CH\(_2\)), 38.8 (CH\(_2\)), 36.6 (CH), 27.6 (CH\(_2\)), 22.2 (2 x CH\(_3\)), 13.9 (CH\(_3\)), 12.2 (CH\(_3\)); MS (70 eV, EI) m/z (%) 217 \([M^+\, 19]\), 182 (48), 160 (58), 145 (42), 69 (100); HRMS (70 eV) calc. for C\(_{11}\)H\(_{20}\)ClNO 217.1233, found 217.1201; IR (neat): 3501, 2958, 1641, 1461 cm\(^{-1}\); \(R_f\) = 0.40 (Hexane: EtOAc 3:1).

\(^1\)H NMR (300 MHz)

\(^{13}\)C NMR (100 MHz)
(Z)-2-Chloro-3-cyclohexyl-N,N-diethylacrylamide (5b): Orange oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.78 (d, $J$ = 8.8 Hz, 1 H), 3.39-3.35 (m, 4 H), 2.59-2.51 (m, 1 H), 1.77-1.66 (m, 5 H), 1.36-1.20 (m, 5 H), 1.18 (t, $J$ = 6.9 Hz, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.8 (C), 135.6 (CH), 122.6 (C), 42.9 (CH$_2$), 39.0 (CH$_2$), 31.1 (2 x CH$_2$), 25.5 (3 x CH$_2$), 25.3 (CH), 13.9 (CH$_3$), 12.3 (CH$_3$); MS (70 eV, EI) $m/z$ (%) 243 [$M^+$, 47], 208 (100), 162 (25), 160 (60); HRMS (70 eV) calc. for C$_{13}$H$_{22}$ClNO 243.1390, found 243.1394; IR (neat): 3445, 2927, 1642, 1448 cm$^{-1}$; $R_f$ = 0.35 (Hexane: EtOAc 3:1).

$^1$H NMR (400 MHz)

$^{13}$C NMR (100 MHz)
**(Z)-4-[(1-Chloronon-1-en-1-yl)carbonyl]morpholine (5c)**: Colourless oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 6.07 (t, $J = 7.1$ Hz, 1 H), 3.71-3.68 (m, 4 H), 3.61-3.50 (m, 4 H), 2.27 (q, $J = 7.2$ Hz, 2 H), 1.48-1.42 (m, 2 H), 1.31-1.27 (m, 8 H), 0.88 (t, $J = 7.1$ Hz, 3 H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 165.2 (C), 133.5 (CH), 124.4 (C), 66.6 (CH$_2$), 60.3 (CH$_2$), 31.6 (CH$_2$), 29.5 (CH$_2$), 29.1 (CH$_2$), 28.9 (CH$_2$), 28.1 (CH$_2$), 27.8 (CH$_2$), 22.5 (CH$_2$), 20.9 (CH$_2$), 14.1 (CH$_3$); MS (70 eV, EI) $m/z$ (%) 273 [M$^+$, 24], 238 (84), 174 (100), 86 (82); HRMS (70 eV) calc. for C$_{14}$H$_{24}$ClNO$_2$ 273.1496, found 273.1495; IR (neat): 3441, 2924, 1644, 1456, 1117 cm$^{-1}$; $R_f = 0.22$ (Hexane: EtOAc 3:1).

$^1$H NMR (300 MHz)

![$^1$H NMR spectrum](image)

$^{13}$C NMR (75 MHz)

![$^{13}$C NMR spectrum](image)
**(Z)-2-Chloro-N,N-diethyl-3-(4-methoxyphenyl)acrylamide (5d):** Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.68 (d, $J = 8.8$ Hz, 2 H), 6.92 (d, $J = 8.8$ Hz, 2 H), 6.78 (s, 1 H), 3.84 (s, 3 H), 3.46 (q, $J = 7.1$ Hz, 4 H), 1.23 (t, $J = 7.1$ Hz, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.2 (C), 159.0 (C), 130.8 (2 x CH), 127.2 (CH), 125.1 (C), 121.0 (C), 113.2 (2 x CH), 55.2 (CH$_3$), 42.9 (CH$_2$), 38.9 (CH$_2$), 13.8 (CH$_3$), 12.2 (CH$_3$); MS (70 eV, EI) $m/z$ (%) 267 [$M^+$, < 1], 269 (35), 135 (82), 195 (100); HRMS (70 eV) calc. for C$_{14}$H$_{18}$ClNO$_2$ 267.1026, found 267.1030; IR (neat): 3055, 1643, 1265, 746 cm$^{-1}$; $R_f = 0.25$ (Hexane: EtOAc 3:1).

$^1$H NMR (400 MHz)

![$^1$H NMR](image)

$^{13}$C NMR (100 MHz)

![$^{13}$C NMR](image)
(Z)-2-Chloro-N,N-diisopropyl-3-(4-methoxyphenyl)acrylamide (5e): White solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.36 (d, \(J = 8.8\) Hz, 2 H), 6.90 (d, \(J = 8.8\) Hz, 2 H), 6.15 (s, 1 H), 3.80 (s, 3 H), 3.52 (hp, \(J = 6.6\) Hz, 1 H), 3.35 (hp, \(J = 6.6\) Hz, 1 H), 1.41 (d, \(J = 6.6\) Hz, 3 H), 1.30 (d, \(J = 6.6\) Hz, 3 H), 1.15 (d, \(J = 6.6\) Hz, 3 H), 0.72 (d, \(J = 6.6\) Hz, 3 H); \(^1\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 165.4 (C), 160.4 (C), 130.2 (2 x CH), 128.4 (CH), 125.0 (C), 114.4 (2 x CH), 113.7 (C), 63.0 (CH\(_3\)), 50.1 (CH), 46.1 (CH), 20.4 (CH\(_3\)), 20.0 (CH\(_3\)), 19.9 (CH\(_3\)), 19.6 (CH\(_3\)); MS (70 eV, EI) \(m/z\) (%) 195 \([M^+ - \text{Ni-Pr}_2, < 1]\), 155 (35), 135 (100), 128 (69), 86 (98); HRMS (70 eV) calc. for \([\text{C}_{16}\text{H}_{22}\text{ClNO}_2 - \text{Ni-Pr}_2]\) 195.0215, found 195.0222; IR (neat): 2975, 1639, 1607, 1258 cm\(^{-1}\); \(R_f = 0.49\) (Hexane: EtOAc 3:1).

\(^1\)H NMR (300 MHz)

\(^1\)C NMR (75 MHz)
(Z)-[1-Chloronon-1-en-1-yl]methyl ketone (9a): Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$): δ 6.84 (t, $J = 7.2$ Hz, 1 H), 2.31 (s, 3 H), 1.45-1.37 (m, 2 H), 1.95-1.09 (m, 10 H), 0.77 (t, $J = 7.2$ Hz, 3 H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 192.1 (C), 141.9 (CH), 133.6 (C), 31.6 (CH$_2$), 29.6 (CH$_2$), 29.2 (CH$_2$), 28.9 (CH$_2$), 27.7 (CH$_2$), 26.4 (CH$_2$), 22.5 (CH$_3$), 13.9 (CH$_3$); HRMS (70 eV) calc. for [C$_{11}$H$_{19}$ClO - Cl] 167.1436, found 167.1448; IR (neat): 3425, 1641, 1468, 1265 cm$^{-1}$; $R_f$ = 0.37 (Hexane: EtOAc 10:1).

$^1$H NMR (75 MHz)

$^{13}$C NMR (75 MHz)
(Z)-Butyl[1-chloronon-1-en-1-yl] ketone (9b): Pale yellow oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 6.83 (t, $J = 7.2$ Hz, 1 H), 2.62 (t, $J = 7.2$ Hz, 2 H), 2.26 (apparent q, $J = 7.3$ Hz, 2 H), 1.53-1.36 (m, 4 H), 1.28-1.16 (m, 10 H), 0.81 (t, $J = 7.3$ Hz, 3 H), 0.77 (t, $J = 7.0$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 194.7 (C), 140.7 (CH), 133.4 (C), 38.2 (CH$_2$), 31.6 (CH$_2$), 29.5 (CH$_2$), 29.2 (CH$_2$), 28.9 (CH$_2$), 27.7 (CH$_2$), 26.4 (CH$_2$), 22.5 (CH$_2$), 22.2 (CH$_2$), 14.0 (CH$_3$), 13.8 (CH$_3$); MS (70 eV, EI) $m/z$ (%) 244 [M$^+$, < 1], 145 (58), 85 (89), 57 (86), 41 (100); HRMS (70 eV) calc. for C$_{14}$H$_{25}$ClO 244.1594, found 244.1601; IR (neat): 3436, 1639, 1457, 1258 cm$^{-1}$; $R_f$ = 0.57 (Hexane: EtOAc 10:1).

$^1$H NMR (75 MHz)

\[\text{\includegraphics[width=0.5\textwidth]{9b}}\]

$^{13}$C NMR (100 MHz)