Green synthesis of haloformates from olefins using formic acid as reactant, protonic acid and solvent

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1. General Information

All of the commercial available substrates which were employed without further purification were obtained from Aladdin Regent Co., Ltd, Alfa Aesar (China) Chemical Co., Ltd, Macklin (Shanghai) Biochemical Co., Ltd and Shanghai LingFeng Chemical Reagent Co., Ltd. The crude reaction mixture was analyzed on a GC2000 / MSS6100 GC-MS system. The crude products were purified by column chromatography on silica gel. $^1$H-NMR spectra were recorded on a BRUKER 500 MHz and $^{13}$C-NMR spectra were recorded with 126 MHz (CDCl$_3$ or DMSO-$d_6$ as solvent, TMS as internal standard). Date are consisted of chemical shift ($\delta$), multiplicity, coupling constant (J) in hertz (Hz). Melting points were measured on a X-4 melting point detector (Beijing Tech Instrument Co. Ltd) and uncorrected. Agilent LC-QTOF-MS high resolution mass spectrometer was used for high-resolution mass spectra.
2. General Procedure for ZnAl-BrO₃-LDHs

Bromate intercalated ZnAl-layered double hydroxides were synthesized by the coprecipitation method according to the procedures described in literature\(^1\). The reaction was conducted in a 500 mL four-necks-flask with a mechanical stirrer. Two dropping funnel, a reflux condenser and 8.35 g KBrO₃ (AR, 0.05 mol) were formulated as 100 mL solution in flask. Then 200 mL aqueous solution dissolving Al(NO₃)₃·6H₂O (18.75 g, 0.05 mol) and Zn(NO₃)₂·9H₂O (29.75 g, 0.10 mol), 200 mL NaOH (12.00 g ,0.30 mol) solution were added within 1 h with temperature at 30 ℃ and pH ± 0.2. The mixture was stirred constantly at 30 ℃ for 1 h and then crystallized at 70 ℃ for 24 h. The crude product was filtered and washed with deionized water repeatedly until the solution pH at 7. The wet solid was dried at 60 ℃ for 18 h, and the product was recorded as ZnAl-BrO₃-LDHs.

3. General Procedure for haloformates

3.1 The synthesis of bromoformates

Substrate (2 mmol), KBr (1.6 mmol), formic acid (10 mL) were added to 50 mL three-necked flask and KBr was absolutely dissolved in the mixture with proper stir at room temperature. After ZnAl-BrO₃-LDHs (0.8g) was added to the mixture, the reaction system stirred at 40 ℃ in water bath with reflux condensation until the substrate completely disappeared (monitored by TLC). The molecule bromine was treated with sodium bisulfite solution right away. The solid phase ZnAl-BrO₃-LDHs was removed by centrifugation. Furthermore, dichloromethane (3×5 mL) used for washing the ZnAl-BrO₃-LDHs was merged into the liquid mixture after centrifugation, then the products were extracted into organic phase with dichloromethane (3×10 mL) and H₂O (30 mL). The organic phase was dried by sodium sulfate and concentrated in vacuum. The crude product was purified by column chromatography on silica gel with 1:5-1:20 ethyl acetate-hexane developer (volume ratio) and the pure products were identified by means of \(^1\)H NMR and \(^{13}\)C NMR spectroscopy.

3.2 The synthesis of iodoformates
Substrate (2 mmol), KI (2.2 mmol), formic acid (10 mL) were added to 50 mL three-necked flask and KI was absolutely dissolved in the mixture with proper stir at room temperature. After ZnAl-BrO₃⁻-LDHs (0.8g) was added to the mixture, the reaction system was stirred at 25 °C in water bath with reflux condensation until the substrate completely disappeared (monitored by TLC). The molecule iodine was treated with sodium bisulfite solution right away. The solid phase ZnAl-BrO₃⁻-LDHs was removed by centrifugation. Furthermore, dichloromethane (3×5 mL) used for washing the ZnAl-BrO₃⁻-LDHs was merged into the liquid mixture after centrifugation, then the products were extracted with into organic phase dichloromethane (3×10 mL) and H₂O (30 mL). The organic phase was dried by sodium sulfate and concentrated in vacuum. The crude product was purified by column chromatography on silica gel with 1:5-1:20 ethyl acetate-hexane developer (volume ratio) and the pure products were identified by means of ¹H NMR and ¹³C NMR spectroscopy.

4. Analytical Data of Products of bromoformates

2-Bromo-1-phenylethyl formate (2a)

\[
\text{O} \\
\text{H} \\
\text{O} \\
\text{H} \\
\text{Br}
\]

Yield 91%. Colourless oil. ¹H NMR (500 MHz, CDCl₃) δ 8.17 (s, 1H), 7.42 – 7.38 (m, 5H), 6.12 (dd, J = 8.3, 4.5 Hz, 1H), 3.71 (dd, J = 11.0, 8.4 Hz, 1H), 3.64 (dd, J = 11.0, 4.5 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 159.62, 136.99, 129.08, 128.79, 74.69, 33.70.

2-Bromo-1-(naphthalen-2-yl)ethyl formate (2b)

\[
\text{O} \\
\text{H} \\
\text{O} \\
\text{H} \\
\text{Br}
\]

Yield: 89%. White solid. ¹H NMR (500 MHz, CDCl₃) δ 8.23 (s, 1H), 7.87 (dd, J = 10.2, 3.9 Hz, 4H), 7.54 (dd, J = 6.2, 3.3 Hz, 2H), 7.48 (dd, J = 8.5, 1.7 Hz, 1H), 6.29 (dd, J = 8.3, 4.5 Hz, 1H), 3.80 (dd, J = 11.0, 8.3 Hz, 1H), 3.72 (dd, J = 11.0, 4.6 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ
159.72, 134.30, 133.51, 133.05, 128.85, 127.80, 126.78, 126.68, 126.40, 123.65, 74.92, 33.67. HRMS (ESI, m/s): Calculated for C$_{15}$H$_{13}$BrO$_2$ (M+H)$^+$ 277.9942, found 277.9940.

2-Bromo-1-(4-tert-butylphenyl)ethyl formate (2c)

\[
\begin{align*}
\text{Yield: } & 88\%. \\
\text{White solid. } & ^1\text{H NMR (500 MHz, CDCl}_3\text{)} \\ & \delta 8.17 (s, 1H), 7.43 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 6.11 (dd, J = 8.5, 4.2 Hz, 1H), 3.74 – 3.68 (m, 1H), 3.63 (dd, J = 11.0, 4.2 Hz, 1H), 1.34 (s, 9H). \\
\text{HRMS (ESI, m/s): Calculated for } & C_{15}H_{13}BrO_2 (M+H)^+ 284.0412, \text{ found 284.0414.}
\end{align*}
\]

2-Bromo-1-(4-chlorophenyl)ethyl formate (2d)$^3$

\[
\begin{align*}
\text{Yield: } & 85\%. \\
\text{White solid. } & ^1\text{H NMR (500 MHz, CDCl}_3\text{)} \\ & \delta 8.15 (s, 1H), 7.39 – 7.37 (m, 2H), 7.34 – 7.32 (m, 2H), 6.07 (dd, J = 7.8, 4.9 Hz, 1H), 3.67 (dd, J = 11.0, 7.9 Hz, 1H), 3.60 (dd, J = 11.2, 5.1 Hz, 1H). \\
\text{HRMS (ESI, m/s): Calculated for } & C_{13}H_{17}BrClO_2 (M+H)^+ 262.9474, \text{ found 262.9472.}
\end{align*}
\]

2-Bromo-1-(4-bromophenyl)ethyl formate (2e)$^4$

\[
\begin{align*}
\text{Yield: } & 84\%. \\
\text{White solid. } & ^1\text{H NMR (500 MHz, CDCl}_3\text{)} \\ & \delta 8.15 (s, 1H), 7.55 – 7.52 (m, 2H), 7.28 – 7.26 (m, 2H), 6.05 (dd, J = 7.8, 4.9 Hz, 1H), 3.67 (dd, J = 11.0, 7.9 Hz, 1H), 3.60 (dd, J = 11.2, 5.1 Hz, 1H). \\
\text{HRMS (ESI, m/s): Calculated for } & C_{9}H_{8}Br_2O_2 (M+H)^+ 308.9770, \text{ found 308.9773.}
\end{align*}
\]

2-Bromo-1-(4-acetoxylphenyl)ethyl formate (2f)
Yield 86%. Colourless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.15 (s, 1H), 7.42 – 7.39 (m, 2H), 7.14 – 7.12 (m, 2H), 6.11 (dd, $J = 8.3$, 4.5 Hz, 1H), 3.68 (dd, $J = 11.0$, 8.4 Hz, 1H), 3.61 (dd, $J = 11.0$, 4.5 Hz, 1H), 2.31 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 169.16, 159.52, 151.09, 134.49, 127.84, 122.00, 74.04, 33.51, 21.07. HRMS (ESI, m/s): Calculated for C$_{11}$H$_{11}$BrO$_4$ (M+H)$^+$ 286.9919, found 286.9917.

(±)-erythro-2-Bromo-3-hydroxy-1-phenylpropyl formate (2g)$^i$

Yield: 73%. White solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.15 (s, 1H), 7.44 – 7.40 (m, 3H), 7.37 – 7.34 (m, 2H), 7.31 – 7.28 (m, 1H), 6.71 (d, $J = 15.9$ Hz, 1H), 6.31 (dt, $J = 15.9$, 6.5 Hz, 1H), 4.85 (d, $J = 6.5$ Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 160.73, 136.00, 134.80, 128.63, 128.21, 126.64, 122.37, 64.44. HRMS (ESI, m/s): Calculated for C$_{10}$H$_{11}$BrO$_3$ (M+H)$^+$ 258.9970, found 258.9968.

(±)-threo-2-Bromo-1,2-diphenylethyl formate (2h)$^i$

Yield: 90%. White solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.22 (s, 1H), 7.36 (d, $J = 7.9$ Hz, 4H), 7.22 (d, $J = 5.3$ Hz, 6H), 6.35 (d, $J = 4.6$ Hz, 1H), 5.24 (d, $J = 4.6$ Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 159.52, 137.34, 136.04, 128.66, 128.50, 128.34, 127.76, 127.38, 78.39, 55.94. HRMS (ESI, m/s): Calculated for C$_{15}$H$_{13}$BrO$_2$ (M+H)$^+$ 304.0099, found 304.0097.

(±)-erythro-2-bromo-3-(formyloxy)-3-(4-methylphenyl) propionic acid (2i)

Yield: 70%. White solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.20 (d, $J = 0.7$ Hz, 1H), 7.34 (d, $J = 8.1$ Hz,
2H), 7.22 (d, J = 7.9 Hz, 2H), 6.26 (d, J = 11.4 Hz, 1H), 5.82 (d, J = 11.4 Hz, 1H), 2.38 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 158.95, 139.62, 132.01, 129.28, 127.56, 78.01, 44.92, 21.30. HRMS (ESI, m/s): Calculated for C$_{11}$H$_{12}$BrO$_4$ (M+H)$^+$ 286.9919, found 286.9924.

(±)-erythro-Methyl-2-bromo-3-(formyloxy)-3-phenylpropanoate (2j)$^i$

Yield: 87%. White solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.72 (d, J = 16.0 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.43 – 7.37 (m, 4H), 6.46 (d, J = 16.0 Hz, 1H), 3.82 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 223.79, 167.37, 134.37, 130.26, 128.66, 128.04, 117.79, 51.64, 46.67. HRMS (ESI, m/s): Calculated for C$_{11}$H$_{12}$BrO$_4$ (M+H)$^+$ 286.9919, found 286.9916.

(±)-trans-2-Bromo-2,3-dihydro-1H–inden-1-ol formate (2k)$^3$

Yield: 88%. White solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.17 (s, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.32 (t, J = 5.9 Hz, 2H), 6.48 (d, J = 3.5 Hz, 1H), 4.58 – 4.54 (m, 1H), 3.75 (dd, J = 16.9, 6.7 Hz, 1H), 3.32 (dd, J = 16.9, 4.4 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 160.09, 141.23, 137.72, 129.89, 127.66, 125.83, 124.86, 83.54, 49.38, 41.39. HRMS (ESI, m/s): Calculated for C$_{10}$H$_{8}$BrNO$_2$ (M+H)$^+$ 239.9786, found 239.9788.

2-Bromo-1-(pyridin-2-yl)ethyl formate (2l)$^i$

Yield: 87%. Claybank oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.28 (s, 1H), 7.68 (td, J = 7.7, 1.5 Hz, 1H), 7.40 (d, J = 7.9 Hz, 1H), 7.22 – 7.17 (m, 1H), 6.82 (dd, J = 17.6, 10.9 Hz, 1H), 6.14 (d, J = 17.6 Hz, 1H), 5.51 (d, J = 10.9 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 220.79, 194.03, 164.81, 155.19, 148.35, 137.34, 135.80, 122.72, 121.15, 119.16. HRMS (ESI, m/s): Calculated for C$_8$H$_8$BrNO$_2$ (M+H)$^+$ 229.9817, found 229.9815.
(±)-erythro-2-Bromo-3-hydroxy-1,1-dimethylpropyl formate (2m)

\[
\begin{align*}
\text{H} & \quad \text{O} \\
\text{Br} & \quad \text{OH} \\
\text{CH}_3 & \quad \text{C} \\
\text{H}_3 & \quad \text{C} \\
& \quad \text{O}
\end{align*}
\]

Yield: 89%. Claybank oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.10 (s, 1H), 7.96 (s, 1H), 4.66 – 4.60 (m, 2H), 4.42 (dt, $J = 11.5, 5.6$ Hz, 1H), 1.68 (d, $J = 3.7$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 160.18, 82.87, 64.30, 55.67, 24.83, 23.60. HRMS (ESI, m/s): Calculated for C$_6$H$_{11}$BrO$_3$ (M+H)$^+$ 210.9970, found 210.9972.

5. Analytical Data of Products of bromoformates

2-Iodo-1-phenylethyl formate (4a)$^2$

\[
\begin{align*}
\text{H} & \quad \text{O} \\
\text{H} & \quad \text{O} \\
\text{Br} & \quad \text{H}
\end{align*}
\]

Yield 86%. Colourless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.17 (d, $J = 7.1$ Hz, 1H), 7.41 – 7.37 (m, 5H), 6.02 (dd, $J = 7.7, 5.5$ Hz, 1H), 3.52 (qd, $J = 10.7, 6.7$ Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 159.56, 137.78, 128.99, 128.77, 126.44, 75.10, 6.87. HRMS (ESI, m/s): Calculated for C$_9$H$_9$IO$_2$ (M+H)$^+$ 275.9647, found 275.9646.

2-Iodo-1-(4-methylphenyl)ethyl formate (4b)$^5$

\[
\begin{align*}
\text{H} & \quad \text{O} \\
\text{H} & \quad \text{O} \\
\text{Br} & \quad \text{H}
\end{align*}
\]

Yield 88%. Colourless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.15 (s, 1H), 7.29 (d, $J = 8.1$ Hz, 2H), 7.22 (d, $J = 7.9$ Hz, 2H), 6.01 (dd, $J = 7.9, 5.2$ Hz, 1H), 3.52 (dt, $J = 10.7, 4.0$ Hz, 2H), 2.38 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 159.68, 139.00, 134.88, 129.50, 126.45, 75.16, 21.27, 7.01. HRMS (ESI, m/s): Calculated for C$_{10}$H$_{11}$IO$_2$ (M+H)$^+$ 289.9804, found 289.9803.

2-Iodo-1-(4-tert-butylphenyl)ethyl formate (4c)
Yield 90%. Colourless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.16 (s, 1H), 7.42 (d, $J$ = 8.4 Hz, 2H), 7.31 (d, $J$ = 8.3 Hz, 2H), 6.02 (dd, $J$ = 8.4, 5.0 Hz, 1H), 3.51 (qd, $J$ = 10.7, 6.7 Hz, 2H), 1.33 (s, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 159.71, 152.21, 133.98, 126.33, 125.74, 74.64, 34.65, 33.74, 31.23. HRMS (ESI, m/s): Calculated for C$_{13}$H$_{17}$IO$_2$ (M+H)$^+$ 332.0273, found 332.0371.

2-Iodo-1-(4-chlorophenyl)ethyl formate (4d)$^5$

Yield 82%. White solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.14 (s, 1H), 7.38 (dd, $J$ = 8.3, 1.4 Hz, 2H), 7.32 (d, $J$ = 8.5 Hz, 2H), 5.98 – 5.95 (m, 1H), 3.48 (qd, $J$ = 10.7, 6.7 Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 159.42, 136.25, 134.92, 129.02, 127.91, 74.32, 6.41. HRMS (ESI, m/s): Calculated for C$_9$H$_8$ClIO$_2$ (M+H)$^+$ 310.9336, found 310.9335.

2-Iodo-1-(4-bromophenyl)ethyl formate (4e)$^5$

Yield 87%. White solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.14 (s, 1H), 7.54 – 7.52 (m, 2H), 7.27 – 7.25 (m, 2H), 5.96 – 5.93 (m, 1H), 3.48 (qd, $J$ = 10.7, 6.5 Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 159.41, 136.76, 131.98, 128.19, 123.09, 74.36, 6.31. HRMS (ESI, m/s): Calculated for C$_9$H$_8$BrIO$_2$ (M+H)$^+$ 254.8831, found 254.8829.

2-Iodo-1-(4-acetoxyphenyl)ethyl formate (4f)

Yield 85%. Colourless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.14 (s, 1H), 7.41–7.38 (m, 2H), 7.14–
7.11 (m, 2H), 6.01 (dd, \( J = 8.0, 5.2 \) Hz, 1H), 3.51 (dd, \( J = 10.7, 8.1 \) Hz, 1H), 3.47 (dd, \( J = 11.0, 5.4 \) Hz, 1H), 2.31 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 169.16, 159.48, 151.00, 135.26, 127.68, 121.97, 74.48, 21.10, 6.56. HRMS (ESI, m/s): Calculated for C\(_{11}\)H\(_{11}\)I\(_4\) (M+H\(^+\)) 334.9780, found 334.9783.

(±)-erythro-2-Iodo-3-hydroxy-1-phenylpropyl formate (4g)

Yield 76%. Colourless oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.15 (s, 1H), 7.42 (d, \( J = 7.3 \) Hz, 2H), 7.36 (t, \( J = 7.5 \) Hz, 2H), 7.30 (d, \( J = 7.2 \) Hz, 1H), 6.71 (d, \( J = 15.9 \) Hz, 1H), 6.31 (dt, \( J = 15.9, 6.5 \) Hz, 1H), 4.85 (d, \( J = 6.5 \) Hz, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 160.73, 136.01, 134.79, 128.62, 128.21, 126.64, 122.37, 77.29, 77.03, 76.78, 64.44. HRMS (ESI, m/s): Calculated for C\(_{10}\)H\(_{11}\)I\(_3\) (M+H\(^+\)) 305.9753, found 305.9758.

(±)-threo-2-Iodo-1,2-diphenylethyl formate (4h)

Yield 79%. White solid. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.18 (s, 1H), 7.25 (d, \( J = 3.2 \) Hz, 6H), 7.16 (s, 4H), 5.95 (d, \( J = 7.0 \) Hz, 1H), 4.97 (d, \( J = 7.0 \) Hz, 1H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 170.34, 160.18, 138.75, 136.19, 128.42, 128.24, 128.21, 127.33, 127.01, 79.94, 60.40. HRMS (ESI, m/s): Calculated for C\(_{15}\)H\(_{13}\)I\(_2\) (M+H\(^+\)) 351.9960, found 351.9963.

(±)-trans-2-Iodo-2,3-dihydro-1H–inden-1-ol formate (4i)

Yield 86%. Colourless oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.17 (s, 1H), 7.44 (d, \( J = 7.6 \) Hz, 1H), 7.39 (t, \( J = 7.4 \) Hz, 1H), 7.32 (t, \( J = 5.9 \) Hz, 2H), 6.47 (d, \( J = 3.5 \) Hz, 1H), 4.57 – 4.53 (m, 1H), 3.75 (dd, \( J = 16.9, 6.6 \) Hz, 1H), 3.32 (dd, \( J = 16.9, 4.4 \) Hz, 1H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 160.12, 141.25, 137.72, 129.91, 127.68, 125.85, 124.88, 83.55, 49.39, 41.40. HRMS (ESI, m/s): Calculated for C\(_{10}\)H\(_9\)I\(_2\) (M+H\(^+\)) 287.9647, found 287.9644.

(±)-erythro-2-Iodo-3-hydroxy-1,1-dimethylpropyl formate (4j)
Yield: 88%. Claybank oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.12 (s, 1H), 4.56 (ddd, $J = 12.2, 4.8, 0.9$ Hz, 1H), 4.49 (ddd, $J = 12.2, 8.0, 0.7$ Hz, 1H), 4.34 (dd, $J = 8.0, 4.8$ Hz, 1H), 2.41 (s, 1H), 1.47 (d, $J = 1.5$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 160.24, 71.68, 66.54, 45.26, 28.08, 27.73. HRMS (ESI, m/s): Calculated for C$_6$H$_{11}$IO$_3$ (M+H)$^+$ 258.9831, found 258.9827.

6. References

7. $^1$H NMR and $^{13}$C NMR Spectra of Products
8. $^1$H NMR and $^{13}$C NMR Spectra of 1, 2-Dibromophenylethane