Catalytic Insertion of Aldehydes into Dihalonitroacetophenones via Sequential Bond Scission-Aldol Reaction-Acyl Transfer

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1. Synthetic Procedures

NMR spectra were obtained at 400 MHz ($^1$H NMR) and 100 MHz ($^{13}$C NMR) using CDCl$_3$ as solvent. Chemical shifts are reported in ppm relative to TMS. Reaction products were purified by column chromatography on silica gel (particle size 32-63 μm) or neutral Al$_2$O$_3$ unless stated otherwise.

**Synthesis of dichloronitroacetophenone (1a)**

![Dichloronitroacetophenone](image)

Into an oven heated mortar and pestle, was added benzylnitromethane (1.15 g, 7.0 mmol) and N-chlorosuccinimide (2.06 g, 15.4 mmol) under nitrogen atmosphere. The mixture was ground until melted. After 15 hours, the viscous mixture was dissolved in approximately 10 mL of methanol. To this solution was added 50 mL of brine and it was then extracted with dichloromethane three times. The combined organic layers were dried over MgSO$_4$, and the solvent was removed under reduced pressure. Purification by flash chromatography (EtOAc:hexanes = 1:8) gave dichloronitroacetophenone 1a (1.31 g, 5.6 mmol) as a pale yellow oil in 80% yield. $^1$H NMR $\delta$ = 7.52 (dd, $J$ = 8.9, 7.6 Hz, 2H), 7.68 (dd, $J$ = 8.9, 1.2 Hz, 1H), 8.06 (dd, $J$ = 7.6, 1.2 Hz, 2H). $^{13}$C NMR $\delta$ = 108.3, 128.7, 129.0, 130.4, 135.2, 179.3. Anal. Calcd. for C$_8$H$_5$Cl$_2$NO$_3$: C, 41.06; H, 2.15; N, 5.99. Found: C, 41.19; H, 2.32; N, 5.85.

**Synthesis of difluoronitroacetophenone, (1b)$^1$**

![Difluoronitroacetophenone](image)

Benzoylnitromethane (1.15 g, 7.0 mmol), Selectfluor (5.46 g, 15.4 mmol) and potassium phosphate (1.56 g, 7.35 mmol) were dissolved in 15 mL of anhydrous acetonitrile. The mixture was stirred at room temperature for 2 days and the reaction was monitored by F NMR. After completion, the reaction mixture was centrifuged. The mother liquor was added to 50 mL of aqueous ammonium chloride, and the solution was extracted with diethyl ether twice. The combined organic layers were dried over MgSO$_4$, and the solvent was removed under reduced pressure. Purification by flash chromatography afforded 1b (1.05 g, 5.25 mmol) as a yellow oil in 75% yield. $^1$H NMR $\delta$ = 7.58 (dd, $J$ = 8.7, 7.1 Hz, 2H), 7.76 (dd, $J$ = 7.1, 1.3 Hz, 1H), 8.05 (dd, $J$ = 8.7, 1.3 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 129.5, 130.0 (t, $J$ = 2.6 Hz), 136.3, 179.0 (t, $J$ = 26.6 Hz).

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*S2*
General procedure for the synthesis of O-benzoyl α,α-dihalo-α-nitro alcohols 3
Lithium bromide (4.4 mg, 0.05 mmol), aldehyde (0.25 mmol) and 0.15 mL anhydrous ether solvent (varied as described below) were combined under nitrogen atmosphere. Dihalonitroacetophenone 1a or 1b (as described below) was then added. The mixture was stirred for 1 minute followed by the addition of N,N-diisopropylethylamine (6.4 mg, 8.7 μL). After the completion of the reaction, the mixture was directly purified by flash chromatography.

2,2-Dichloro-2-nitro-1-(4-nitrophenyl)ethyl benzoate (3a)

Following the general procedure described above, 4-nitrobenzaldehyde (38.0 mg, 0.25 mmol), 1a (70.2 mg, 0.30 mmol) and lithium bromide (4.4 mg, 0.05 mmol) were dissolved in 0.15 mL of tetrahydrofuran and N,N-diisopropylethylamine (8.7 μL, 0.05 mmol) was added. The reaction mixture was stirred for 1 day at room temperature. Chromatographic purification (EtOAc:hexanes = 1:20) gave 87.0 mg (0.23 mmol, 90%) of a white solid. \(^1\)H NMR \(\delta = 6.97\) (s, 1H), 7.51 (dd, \(J = 9.2, 6.6\) Hz, 2H), 7.67 (dd, \(J = 8.6, 6.6\) Hz, 1H), 7.83 (dd, \(J = 8.5, 1.2\) Hz, 2H), 8.03 (dd, \(J = 8.5, 1.2\) Hz, 2H), 8.29 (dd, \(J = 9.2, 8.6\) Hz, 2H). \(^1\)C NMR \(\delta = 78.3, 112.7, 123.6, 127.6, 128.9, 130.0, 130.0, 134.5, 138.3, 149.1, 163.3\). Anal. Calcd. for C\(_{15}\)H\(_{10}\)Cl\(_2\)N\(_2\)O\(_6\): C, 46.78; H, 2.62; N, 7.27. Found: C, 47.15; H, 2.83; N, 7.14.

2,2-Dichloro-1-(4-chlorophenyl)-2-nitroethyl benzoate (3b)

Following the general procedure described above, 4-chlorobenzaldehyde (35.1 mg, 0.25 mmol), 1a (70.2 mg, 0.30 mmol) and lithium bromide (4.4 mg, 0.05 mmol) were dissolved in 0.15 mL of diisopropyl ether-tetrahydrofuran (2:1) and N,N-diisopropylethylamine (8.7 μL, 0.05 mmol) was added. The reaction mixture was stirred for 2 days at room temperature. Chromatographic purification (EtOAc:hexanes = 1:50) gave 88.2 mg (0.23 mmol, 94%) of a yellow solid. \(^1\)H NMR \(\delta = 6.88\) (s, 1H), 7.40 (d, \(J = 8.6\) Hz, 2H), 7.49 (dd, \(J = 8.3, 7.8\) Hz, 2H), 7.57 (d, \(J = 8.6\) Hz, 2H), 7.65 (d, \(J = 7.8, 1.4\) Hz, 1H), 8.04 (dd, \(J = 8.3, 1.4\) Hz, 2H). \(^1\)C NMR \(\delta = 78.7, 113.5, 128.0, 128.8, 128.8, 130.0, 130.0, 130.2, 134.2, 136.6, 163.4\). Anal. Calcd. for C\(_{15}\)H\(_{10}\)Cl\(_3\)N\(_2\)O\(_4\): C, 48.10; H, 2.69; N, 3.74. Found: C, 48.28; H, 2.81; N, 3.82.
2,2-Dichloro-2-nitro-1-phenylethyl benzoate (3c)

Following the general procedure described above, benzaldehyde (53.0 mg, 0.50 mmol), 1a (176.0 mg, 0.75 mmol) and lithium bromide (8.8 mg, 0.10 mmol) were dissolved in 0.30 mL of diethyl ether-tetrahydrofuran (2:1) and N,N-diisopropylethylamine (17.6 μL, 0.10 mmol) was added. The reaction mixture was stirred for 2 days at room temperature. Chromatographic purification (EtOAc:hexanes = 1:50) gave 165.0 mg (0.48 mmol, 98%) of a white solid. $^1$H NMR $\delta = 6.92$ (s, 1H), 7.39 – 7.46 (m, 3H), 7.49 (dd, $J = 7.8$, 7.8 Hz, 2H), 7.60 – 7.66 (m, 3H), 8.07 (dd, $J = 8.1$, 1.5 Hz, 2H). $^{13}$C NMR $\delta = 79.3$, 113.9, 128.3, 128.4, 128.7, 128.9, 130.0, 130.3, 131.5, 134.0, 163.5. Anal. Calcd. for C$_{15}$H$_{11}$Cl$_2$NO$_4$: C, 52.97; H, 3.26; N, 4.12. Found: C, 53.04; H, 3.37; N, 4.18.

2,2-Dichloro-1-(2-naphthyl)-2-nitroethyl benzoate (3d)

Following the general procedure described above, 2-naphthaldehyde (39.0 mg, 0.25 mmol), 1a (103.3 mg, 0.45 mmol) and lithium bromide (4.4 mg, 0.05 mmol) were dissolved in 0.15 mL of tert-butyl methyl ether and N,N-diisopropylethylamine (8.7 μL, 0.05 mmol) was added. The reaction mixture was stirred for 2 days at room temperature. Chromatographic purification (dichloromethane:hexanes = 1:5) gave 97.4 mg (0.25 mmol, 99%) of a white solid. $^1$H NMR $\delta = 7.09$ (s, 1H), 7.47 – 7.57 (m, 4H), 7.49 (dd, $J = 7.8$, 7.8 Hz, 2H), 7.60 – 7.66 (m, 3H), 8.07 (dd, $J = 8.1$, 1.5 Hz, 2H). $^{13}$C NMR $\delta = 79.5$, 114.0, 125.2, 126.7, 127.3, 127.7, 128.3, 128.4, 128.7, 128.8, 129.4, 130.0, 132.6, 134.0, 134.1, 163.6. Anal. Calcd. for C$_{19}$H$_{13}$Cl$_2$NO$_4$: C, 58.48; H, 3.36; N, 3.59. Found: C, 58.64; H, 3.62; N, 3.56.

2,2-Dichloro-1-(4-cyanophenyl)-2-nitroethyl benzoate (3e)
Following the general procedure described above, 4-cyanobenzaldehyde (32.8 mg, 0.25 mmol), \textbf{1a} (77.0 mg, 0.33 mmol) and lithium bromide (4.4 mg, 0.05 mmol) were dissolved in 0.15 mL of diisopropyl ether-tetrahydrofuran (2:1) and \textit{N,N}-diisopropylethylamine (8.7 μL, 0.05 mmol) was added. The reaction mixture was stirred for 1 day at room temperature. Chromatographic purification (EtOAc:hexanes = 1:15) gave 87.5 mg (0.24 mmol, 96%) of a white solid. $^1$H NMR $\delta$ = 6.92 (s, 1H), 7.50 (dd, $J = 9.2$, 8.3 Hz, 2H), 7.66 (dd, $J = 9.2$, 1.4 Hz, 1H), 7.76 (dd, $J = 14.3$, 8.6 Hz, 4H), 8.03 (dd, $J = 8.3$, 1.4 Hz, 2H). $^{13}$C NMR $\delta$ = 78.5, 110.0, 112.8, 114.4, 117.9, 127.6, 128.9, 129.7, 129.9, 130.0, 132.2, 134.5, 136.5, 163.3. Anal. Calcd. for C$_{16}$H$_{10}$Cl$_2$N$_2$O$_4$: C, 52.63; H, 2.76; N, 7.67. Found: C, 53.04; H, 3.02; N, 7.58.

\textbf{2,2-Dichloro-1-(3-fluorophenyl)-2-nitroethyl benzoate (3f)}

Following the general procedure described above, 3-fluorobenzaldehyde (31.0 mg, 0.25 mmol), \textbf{1a} (70.2 mg, 0.30 mmol) and lithium bromide (4.4 mg, 0.05 mmol) were dissolved in 0.15 mL of tert-butyl methyl ether and \textit{N,N}-diisopropylethylamine (8.7 μL, 0.05 mmol) was added. The reaction mixture was stirred for 2 days at room temperature. Chromatographic purification (EtOAc:hexanes = 1:45) gave 88.9 mg (0.25 mmol, 99%) of a pale yellow oil. $^1$H NMR $\delta$ = 7.04 (s, 1H), 7.29 (dd, $J = 7.9$, 2.4 Hz, 1H), 7.44 – 7.58 (m, 3H), 7.62 (dd, $J = 7.8$, 2.0 Hz, 2H), 7.76 (dd, $J = 7.5$, 1.9 Hz, 1H), 8.18 (d, $J = 7.8$, 1.9 Hz, 2H). $^{13}$C NMR $\delta$ = 78.5, 113.4, 115.9 (d, $J = 23.3$ Hz), 117.4 (d, $J = 21.0$ Hz), 124.8 (d, $J = 3.1$ Hz), 128.0, 128.8, 130.0, 130.1 (d, $J = 8.2$ Hz), 133.8 (d, $J = 7.6$ Hz), 134.2, 162.4 (d, $J = 247.6$ Hz), 163.4. Anal. Calcd. for C$_{15}$H$_{10}$Cl$_2$FNO$_4$: C, 50.30; H, 2.81; N, 3.91. Found: C, 50.36; H, 2.93; N, 4.01.

\textbf{1-(4-Acetylphenyl)-2,2-dichloro-2-nitroethyl benzoate (3g)}

Following the general procedure described above, 4-acetylbenzaldehyde (37.0 mg, 0.25 mmol), \textbf{1a} (70.2 mg, 0.30 mmol) and lithium bromide (4.4 mg, 0.05 mmol) were dissolved in 0.15 mL of diisopropyl ether-tetrahydrofuran (2:1) and \textit{N,N}-diisopropylethylamine (8.7 μL, 0.05 mmol) was added. The reaction mixture was stirred for 1 day at room temperature. Chromatographic purification (diethyl ether:hexanes = 1:4) gave 91.0 mg (0.24 mmol, 95%) of a white solid. $^1$H NMR $\delta$ = 2.61 (s, 3H), 6.94 (s, 1H), 7.49 (dd, $J = 8.3$, 7.4 Hz, 2H), 7.65 (dd, $J = 7.4$, 1.3 Hz, 1H), 7.73 (d, $J = 8.2$ Hz, 2H), 8.00 (d, $J = 8.2$ Hz, 2H), 8.04 (dd, $J = 8.3$, 1.3 Hz, 2H). $^{13}$C NMR $\delta$ = 26.6, 78.8, 113.2, 127.9, 128.3, 128.8, 129.2, 130.0, 134.2, 136.2, 138.5, 163.4, 197.1. Anal. Calcd. for C$_{17}$H$_{13}$Cl$_2$NO$_5$: C, 53.43; H, 3.43; N, 3.66. Found: C, 53.21; H, 3.52; N, 3.62.
2,2-Dichloro-2-nitro-1-(2-nitrophenyl)ethyl benzoate (3h)

\[
\begin{align*}
\text{Ph} & \quad \text{O} & \quad \text{Cl} \\
\text{O} & \quad \text{NO}_2 & \quad \text{Cl} \\
\text{O} & \quad \text{NO}_2 & \quad \text{Cl}
\end{align*}
\]

Following the general procedure described above, 2-nitrobenzaldehyde (38.0 mg, 0.25 mmol), 1a (87.7 mg, 0.37 mmol) and lithium bromide (4.4 mg, 0.05 mmol) were dissolved in 0.15 mL of diisopropyl ether-tetrahydrofuran (2:1) and N,N-diisopropylethylamine (8.7 μL, 0.05 mmol) was added. The reaction mixture was stirred for 2 day at room temperature. Chromatographic purification (EtOAc:hexanes = 1:20) gave 89.0 mg (0.22 mmol, 88%) of a white solid. \(^1\)H NMR δ = 7.49 (dd, J = 8.2, 7.9 Hz, 2H), 7.64 (dd, J = 7.9, 1.5 Hz, 2H), 7.70 (dd, J = 7.9, 1.5 Hz, 1H), 7.92 (dd, J = 7.9, 1.6 Hz, 1H), 8.04 (dd, J = 8.2, 1.6 Hz, 2H), 8.13 (dd, J = 8.2, 1.5 Hz, 1H), 8.23 (s, 1H). \(^{13}\)C NMR δ = 72.7, 113.0, 125.5, 126.8, 127.7, 128.8, 129.6, 130.0, 131.1, 133.3, 134.3, 149.2, 163.1. Anal. Calcd. for C\(_{15}\)H\(_{10}\)Cl\(_2\)N\(_2\)O\(_6\): C, 46.78; H, 2.62; N, 7.27. Found: C, 46.67; H, 2.83; N, 7.21.

2,2-Dichloro-2-nitro-1-(2-pyridyl)ethyl benzoate (3i)

\[
\begin{align*}
\text{N} & \quad \text{Ph} & \quad \text{O} \\
\text{Cl} & \quad \text{NO}_2 & \quad \text{Cl} \\
\text{Cl} & \quad \text{NO}_2 & \quad \text{Cl}
\end{align*}
\]

Following the general procedure described above, pyridine-2-carboxaldehyde (26.8 mg, 0.25 mmol), 1a (88.0 mg, 0.37 mmol) and lithium bromide (4.4 mg, 0.05 mmol) were dissolved in 0.15 mL of tert-butyl methyl ether and N,N-diisopropylethylamine (8.7 μL, 0.05 mmol) was added. The reaction mixture was stirred for 2 days at room temperature. Chromatographic purification (EtOAc:hexanes = 1:10) gave 86.1 mg (0.25 mmol, 99%) of a brown solid. \(^1\)H NMR δ = 7.06 (s, 1H), 7.34 (dd, J = 7.6, 4.9 Hz, 1H), 7.51 (dd, J = 9.5, 6.8 Hz, 2H), 7.57 (dd, J = 7.9, 1.0 Hz, 1H), 7.64 (dd, J = 9.3, 5.6 Hz, 1H), 7.75 (dd, J = 7.8, 1.8 Hz, 1H), 8.11 (dd, J = 8.3, 1.4 Hz, 2H), 8.64 (dd, J = 4.8, 1.7 Hz, 1H). \(^{13}\)C NMR δ = 79.4, 112.8, 122.9, 124.5, 128.1, 128.7, 130.1, 134.2, 136.8, 149.4, 151.9, 163.8. Anal. Calcd. for C\(_{14}\)H\(_{10}\)Cl\(_2\)N\(_2\)O\(_4\): C, 46.78; H, 2.62; N, 7.27. Found: C, 46.67; H, 2.83; N, 8.05.

2,2-Dichloro-1-(2-furyl)-2-nitroethyl benzoate (3j)

\[
\begin{align*}
\text{Ph} & \quad \text{O} \\
\text{Cl} & \quad \text{NO}_2 & \quad \text{Cl} \\
\text{Cl} & \quad \text{NO}_2 & \quad \text{Cl}
\end{align*}
\]

Following the general procedure described above, 2-furaldehyde (24.0 mg, 0.25 mmol), 1a (88.0 mg, 0.37 mmol) and lithium bromide (4.4 mg, 0.05 mmol) were dissolved in 0.15 mL of tert-butyl methyl ether and N,N-diisopropylethylamine (8.7 μL, 0.05 mmol) was added. The reaction
mixture was stirred for 2 days at room temperature. Chromatographic purification (EtOAc:hexanes = 1:40) gave 75.0 mg (0.23 mmol, 91%) of a colorless oil. \(^1\)H NMR \(\delta = 6.44\) (dd, \(J = 3.4, 1.8\) Hz, 1H), \(6.72\) (dd, \(J = 3.4, 0.8\) Hz, 1H), \(7.43 - 7.53\) (m, 3H), \(7.63\) (d, \(J = 7.4, 1.4\) Hz, 1H), \(8.05\) (dd, \(J = 8.3, 1.4\) Hz, 2H). \(^{13}\)C NMR \(\delta = 73.6, 110.8, 111.9, 112.9, 128.0, 128.7, 130.1, 134.1, 144.4, 144.7, 163.5\). Anal. Calcd. for C\(_{13}\)H\(_9\)Cl\(_2\)NO\(_5\): C, 47.30; H, 2.75; N, 4.24. Found: C, 47.36; H, 2.78; N, 4.21.

**2,2-Dichloro-1-(4-methoxyphenyl)-2-nitroethyl benzoate (3k)**

\[
\begin{align*}
\text{MeO} & \quad \text{O} \\
\text{Cl} & \quad \text{NO}_2 \\
\text{Ph} & \quad \text{O} \\
\end{align*}
\]

Following the general procedure described above, 4-methoxybenzaldehyde (34.0 mg, 0.25 mmol), 1a (103.3 mg, 0.45 mmol) and lithium bromide (4.4 mg, 0.05 mmol) were dissolved in 0.15 mL of tert-butyl methyl ether and N,N-diisopropylethylamine (8.7 \(\mu\)L, 0.05 mmol) was added. The reaction mixture was stirred for 2 days at room temperature. Chromatographic purification (EtOAc:hexanes = 1:35) gave 54.9 mg (0.15 mmol, 59%) of a yellow oil. \(^1\)H NMR \(\delta = 3.81\) (s, 3H), \(6.86\) (s, 1H), \(6.92\) (d, \(J = 8.5\) Hz, 2H), \(7.48\) (dd, \(J = 7.7, 1.8\) Hz, 2H), \(7.54\) (d, \(J = 8.5\) Hz, 2H), \(7.61\) (dd, \(J = 7.3, 1.4\) Hz, 1H), \(8.05\) (dd, \(J = 8.3, 1.7\) Hz, 2H). \(^{13}\)C NMR \(\delta = 55.3, 79.1, 113.9, 114.1, 123.3, 128.4, 128.7, 130.0, 130.3, 134.0, 161.1, 163.5\). Anal. Calcd. for C\(_{16}\)H\(_{13}\)Cl\(_2\)NO\(_5\): C, 51.91; H, 3.54; N, 3.78. Found: C, 52.16; H, 3.51; N, 3.95.

**1,1-Dichloro-1-nitro-4-phenylbutan-2-yl benzoate (3l)**

\[
\begin{align*}
\text{Ph} & \quad \text{O} \\
\text{Cl} & \quad \text{NO}_2 \\
\text{O} & \quad \text{Cl} \\
\end{align*}
\]

Following the general procedure described above, 3-phenylpropanal (8.4 mg, 0.06 mmol), 1a (103.3 mg, 0.45 mmol) and lithium bromide (4.4 mg, 0.05 mmol) were dissolved in 0.15 mL of tert-butyl methyl ether and N,N-diisopropylethylamine (8.7 \(\mu\)L, 0.05 mmol) was added. The remaining 3-phenylpropanal (25.1 mg, 0.19 mmol) was added equally over 3 portions every 2 hours. The reaction mixture was stirred for 2 days at room temperature. Chromatographic purification (EtOAc:hexanes = 1:35) gave 85.7 mg (0.23 mmol, 92%) of a colorless oil. \(^1\)H NMR \(\delta = 2.28\) (m, 1H), \(2.39\) (m, 1H), \(2.79\) (t, \(J = 8.0\) Hz, 2H), \(6.18\) (dd, \(J = 9.7, 2.5\) Hz, 1H), \(7.16 - 7.24\) (m, 3H), \(7.28\) (dd, \(J = 8.7, 6.6\) Hz, 2H), \(7.49\) (dd, \(J = 7.2, 1.4\) Hz, 2H), \(7.64\) (dd, \(J = 8.4, 7.2\) Hz, 1H), \(8.04\) (dd, \(J = 8.4, 1.4\) Hz, 2H). \(^{13}\)C NMR \(\delta = 31.6, 32.6, 77.1, 113.8, 126.5, 128.2, 128.3, 128.6, 128.6, 130.1, 134.0, 139.8, 164.5\). Anal. Calcd. for C\(_{17}\)H\(_{15}\)Cl\(_2\)NO\(_4\): C, 55.45; H, 4.11; N, 3.80. Found: C, 55.59; H, 4.16; N, 3.82.
1,1-Dichloro-1-nitroheptan-2-yl benzoate (3m)

Following the general procedure described above, hexanal (12.5 mg, 0.12 mmol), 1a (198.9 mg, 0.85 mmol) and lithium bromide (8.8 mg, 0.10 mmol) were dissolved in 0.30 mL of tert-butyl methyl ether and N,N-diisopropylethylamine (17.6 μL, 0.10 mmol) was added. The remaining hexanal (37.6 mg, 0.38 mmol) was added equally over 3 portions every 2 hours. The reaction mixture was stirred for 2 days at room temperature. Chromatographic purification (EtOAc:hexanes = 1:100, neutral Al₂O₃ as stationary phase) gave 135.7 mg (0.41 mmol, 81%) of a colorless oil. 

**1H NMR** δ = 0.87 (t, J = 7.0 Hz, 3H), 1.23 – 1.50 (m, 6H), 1.92 (m, 1H), 2.02 (m, 1H), 6.11 (dd, J = 9.7, 2.7 Hz, 1H), 7.47 (dd, J = 7.4, 1.4 Hz, 2H), 7.61 (dd, J = 8.8, 7.4 Hz, 1H), 8.03 (dd, J = 8.8, 1.4 Hz, 2H). 

**13C NMR** δ = 13.8, 22.2, 25.0, 30.6, 31.2, 77.4, 114.0, 128.3, 128.6, 130.0, 133.9, 164.5. Anal. Calcd. for C₁₄H₁₇Cl₂NO₄: C, 50.32; H, 5.13; N, 4.19. Found: C, 50.23; H, 5.31; N, 4.20.

2,2-Difluoro-1-(2-naphthyl)-2-nitroethyl benzoate (9a)

Following the general procedure described above, 2-naphthaldehyde (39.0 mg, 0.25 mmol), 1b (76.0 mg, 0.37 mmol) and lithium bromide (4.4 mg, 0.05 mmol) were dissolved in 0.15 mL of tert-butyl methyl ether and N,N-diisopropylethylamine (8.7 μL, 0.05 mmol) was added. The reaction mixture was stirred for 2 days at room temperature. Chromatographic purification (dichloromethane:hexanes = 1:5) gave 89.0 mg (0.25 mmol, 99%) of a yellow solid.

**1H NMR** δ = 6.91 (dd, J = 15.3, 6.0 Hz, 1H), 7.50 (dd, J = 5.8, 1.2 Hz, 2H), 7.49 – 7.60 (m, 2H), 7.64 (dd, J = 8.3, 1.3 Hz, 2H), 7.84 – 7.96 (m, 3H), 8.05 (m, 1H), 8.10 (dd, J = 8.3, 1.4 Hz, 2H). 

**13C NMR** δ = 72.7 (dd, J = 30.4, 22.1 Hz), 121.6 (dd, J = 294.7, 286.7 Hz), 124.2, 126.9, 126.9, 127.5, 127.8, 128.0, 128.4, 128.7, 128.8, 129.2, 130.1, 132.9, 134.2, 134.2, 134.2, 163.7. 

**19F NMR** δ = -97.9 (dd, J = 172.6, 15.3 Hz, 1F), -91.5 (dd, J = 172.4, 5.9 Hz, 1F). Anal. Calcd. for C₁₉H₁₃F₂NO₄: C, 63.87; H, 3.67; N, 3.92. Found: C, 63.94; H, 3.75; N, 3.95.

2,2-Difluoro-1-(3-methoxyphenyl)-2-nitroethyl benzoate (9b)
Following the general procedure described above, 3-methoxybenzaldehyde (34.0 mg, 0.25 mmol), 1b (76.0 mg, 0.37 mmol) and lithium bromide (4.4 mg, 0.05 mmol) were dissolved in 0.15 mL of tert-butyl methyl ether and N,N-diisopropylethylamine (8.7 μL, 0.05 mmol) was added. The reaction mixture was stirred for 2 days at room temperature. Chromatographic purification (dichloromethane:hexanes = 1:3) gave 74.3 mg (0.22 mmol, 88%) of a yellow oil. 1H NMR δ = 3.82 (s, 3H), 6.71 (dd, J = 15.2, 5.9 Hz, 1H), 6.99 (dd, J = 8.2, 1.1 Hz, 1H), 7.08 (s, 1H), 7.13 (dd, J = 7.7, 1.1 Hz 1H), 7.36 (dd, J = 8.2, 7.1 1H), 7.49 (dd, J = 7.4, 1.4 Hz, 2H), 7.63 (dd, J = 8.8, 7.4 Hz, 1H), 8.07 (dd, J = 8.8, 1.4 Hz, 2H). 13C NMR δ = 58.0, 75.0 (dd, J = 30.3, 22.4 Hz), 116.5, 118.6, 122.9, 124.1 (dd, J = 295.0, 287.2 Hz), 130.7, 131.4, 132.8, 132.9, 133.6, 136.9, 162.6, 166.3. 19F NMR δ = -98.1 (dd, J = 172.0, 15.3 Hz, 1F), -91.7 (dd, J = 172.3, 6.3 Hz, 1F). Anal. Calcd. for C16H13F2NO5: C, 56.98; H, 3.89; N, 4.15. Found: C, 57.13; H, 4.17; N, 4.23.

2,2-Difluoro-1-(4-bromophenyl)-2-nitroethyl benzoate (9c)

Following the general procedure described above, 4-bromobenzaldehyde (46.0 mg, 0.25 mmol), 1b (60.0 mg, 0.3 mmol) and lithium bromide (4.4 mg, 0.05 mmol) were dissolved in 0.15 mL of diisopropyl ether and N,N-diisopropylethylamine (8.7 μL, 0.05 mmol) was added. The reaction mixture was stirred for 2 days at room temperature. Chromatographic purification (EtOAc:hexanes = 1:60) gave 95.5 mg (0.25 mmol, 99%) of a white solid. 1H NMR δ = 6.67 (dd, J = 15.1, 5.8 Hz, 1H), 7.42 (d, J = 8.4 Hz, 2H), 7.49 (dd, J = 7.8, 1.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.64 (dd, J = 7.8, 1.4 Hz, 1H), 8.04 (dd, J = 8.3, 1.4 Hz, 2H). 13C NMR δ = 71.9 (dd, J = 30.6, 22.4 Hz), 121.0 (dd, J = 294.5, 286.7 Hz), 125.2, 127.7, 128.6, 128.8, 129.6, 130.1, 132.4, 134.3, 163.5. 19F NMR δ = -98.3 (dd, J = 173.4, 15.1 Hz, 1F), -91.9 (dd, J = 173.4, 5.8 Hz, 1F). Anal. Calcd. for C15H10BrF2NO4: C, 46.66; H, 2.61; N, 3.63. Found: C, 46.87; H, 2.78; N, 3.77.

2,2-Difluoro-2-nitro-1-(4-nitrophenyl)ethyl benzoate (9d)

Following the general procedure described above, 4-nitrobenzaldehyde (38.0 mg, 0.25 mmol), 1b (60.0 mg, 0.3 mmol) and lithium bromide (4.4 mg, 0.05 mmol) were dissolved in 0.15 mL of diisopropyl ether and N,N-diisopropylethylamine (8.7 μL, 0.05 mmol) was added. The reaction mixture was stirred for 1 day at room temperature. Chromatographic purification (EtOAc:hexanes = 1:20) gave 83.1 mg (0.24 mmol, 94%) of a yellow solid. 1H NMR δ = 6.80 (dd, J = 15.0, 5.3 Hz, 1H), 7.51 (dd, J = 8.7, 7.8 Hz, 2H), 7.66 (dd, J = 7.8, 1.9 Hz, 1H), 7.75 (d,
$J = 8.6\text{ Hz, 2H}, 8.05 (d, J = 8.6\text{ Hz, 2H}), 8.31 (dd, J = 8.7, 1.9\text{ Hz, 2H})$. $^{13}\text{C NMR } \delta = 71.5 (dd, J = 30.8, 22.6 \text{ Hz}), 120.7 (dd, J = 294.7, 287.3 \text{ Hz}), 124.3, 127.3, 129.0, 129.1, 130.1, 134.7, 136.3, 149.4, 163.4$. $^{19}\text{F NMR } \delta = -98.0 (dd, J = 174.7, 15.0 \text{ Hz, 1F}), -91.3 (dd, J = 174.7, 5.3 \text{ Hz, 1F})$. Anal. Calcd. for C$_{13}$H$_{10}$F$_2$N$_2$O$_6$: C, 51.15; H, 2.86; N, 7.95. Found: C, 51.46; H, 2.94; N, 7.74.

2,2-Difluoro-1-(4-cyanophenyl)-2-nitroethyl benzoate (9e)

Following the general procedure described above, 4-cyanobenzaldehyde (98.0 mg, 0.75 mmol), 1b (181.0 mg, 0.90 mmol) and lithium bromide (13.2 mg, 0.15 mmol) were dissolved in 0.45 mL of diisopropyl ether-tetrahydrofuran (2:1) and N,N-diisopropylethylamine (26.1 μL, 0.15 mmol) was added. The reaction mixture was stirred for 1 day at room temperature. Chromatographic purification (EtOAc:hexanes = 1:15) gave 244.7 mg (0.73 mmol, 98%) of a white solid. $^1\text{H NMR } \delta = 6.75 (dd, J = 15.1, 5.3 \text{ Hz, 1H}), 7.50 (dd, J = 7.9, 7.7 \text{ Hz, 2H}), 7.63 – 7.71 (m, 3H), 7.76 (d, J = 8.2 \text{ Hz, 2H}), 8.04 (d, J = 7.9, 1.3 \text{ Hz, 2H})$. $^{13}\text{C NMR } \delta = 74.3 (dd, J = 30.9, 22.5 \text{ Hz}), 117.5, 120.4, 123.4 (dd, J = 294.9, 287.0 \text{ Hz}), 130.0, 131.4, 131.6, 132.8, 135.5, 137.2, 137.3, 166.1$. $^{19}\text{F NMR } \delta = -98.1 (dd, J = 174.6, 15.1 \text{ Hz, 1F}), -91.4 (dd, J = 174.4, 5.4 \text{ Hz, 1F})$. Anal. Calcd. for C$_{16}$H$_{10}$F$_2$N$_2$O$_4$: C, 57.84; H, 3.03; N, 8.43. Found: C, 57.85; H, 3.15; N, 8.32.

Denitration$^2$ of 3e to 7

To a solution of 3e (91.3 mg, 0.25 mmol), tributyltin hydride (101 μL, 0.37 mmol) in 5 mL of anhydrous toluene in a pressure vessel was added azobisisobutyronitrile (10.3 mg, 0.06 mmol). The vessel was then sealed and heated to 110 °C overnight. The mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (EtOAc:hexanes = 1:15, neutral Al$_2$O$_3$ as stationary phase) to give 7 (60.8 mg, 0.19 mmol) as a white solid in 76% yield. $^1\text{H NMR } \delta = 6.07 (d, J = 4.7 \text{ Hz, 1H}), 6.35 (d, J = 4.6 \text{ Hz, 1H}), 7.51 (dd, J = 8.3, 6.7 \text{ Hz, 2H}), 7.61 – 7.69 (m, 3H), 7.72 (d, J = 8.5 \text{ Hz, 2H}), 8.13 (dd, J = 8.3, 1.3 \text{ Hz, 2H})$. $^{13}\text{C NMR } \delta = 71.8, 77.5, 113.4, 118.1, 128.6, 128.7, 128.8, 129.9, 132.2, 134.0, 139.3, 164.6$. Anal. Calcd. for C$_{16}$H$_{11}$Cl$_2$NO$_2$: C, 60.02; H, 3.46; N, 4.37. Found: C, 60.36; H, 3.74; N, 4.34.
Allylation\(^2\) of 3e to 8

\[
\begin{align*}
\text{Ph} & \quad \text{O} \quad \text{CO} \\
\text{NC} & \quad \text{Cl} \quad \text{Cl} \\
\end{align*}
\]

To a solution of 3e (91.3 mg, 0.25 mmol), allyltributylstannane (194 µL, 0.62 mmol) in 2 mL anhydrous toluene was added azobisisobutyronitrile (10.3 mg, 0.06 mmol). The vessel was then sealed and heated to 120 °C for 9 hours. During this time azobisisobutyronitrile (10.3 mg, 0.06 mmol) dissolved in 1 mL of toluene was added in two portions. The mixture was cooled to room temperature and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (EtOAc:hexanes = 1:15, neutral Al\(_2\)O\(_3\) as stationary phase) to give 8 (45.0 mg, 0.12 mmol) as a colorless oil in 70% yield. \(^1\)H NMR \(\delta = 3.08 (d, J = 7.0 \text{ Hz}, 2\text{H}), 5.21 (d, J = 17.1 \text{ Hz}, 1\text{H}), 5.33 (d, J = 10.2 \text{ Hz}, 1\text{H}), 6.04 (m, 1\text{H}), 6.28 (s, 1\text{H}), 7.51 (dd, J = 8.5, 6.5 \text{ Hz}, 2\text{H}), 7.61 - 7.70 (m, 3\text{H}), 7.75 (d, J = 8.1 \text{ Hz}, 2\text{H}), 8.13 (dd, J = 8.5, 1.2 \text{ Hz}, 2\text{H}).\)

\(^{13}\)C NMR \(\delta = 49.0, 79.3, 90.8, 113.2, 118.3, 121.5, 128.7, 128.7, 129.9, 130.0, 130.2, 131.6, 134.0, 139.6, 164.2.\) Anal. Calcd. for C\(_{19}\)H\(_{15}\)Cl\(_2\)NO\(_2\): C, 63.35; H, 4.20; N, 3.89. Found: C, 62.96; H, 4.45; N, 3.75.
2. Reaction Optimization

The optimization of the catalytic reaction involved screening of Lewis acids in the presence of DMAP, pyridine, lutidine, tertiary DABCO, Et3N, (i-Pr)2NEt, Cy2NEt and DBU as well as concentration, solvent, and counterion effects. Screening of several Lewis acids in the presence of DMAP, pyridine, lutidine, tertiary amines or DBU revealed that 4-nitrobenzaldehyde, 6a, is formed in up to 69% in the presence of 20 mol% of LiBr and diisopropylethylamine (Table, entries 1-9). Optimization of concentration, solvent, and counterion effects showed that the formal insertion of aldehyde 6a into dichloronitroacetophenone occurs quantitatively when catalytic amounts of LiBr and (i-Pr)2NEt are used in THF (entries 11-21). We also observed almost 100% conversion and no sign of side reactions with other aldehydes when homogeneous conditions were maintained, and we therefore based the selection of the ethereal solvent on the substrate solubility (compare entries 19-25).

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<th>Entry</th>
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General conditions: A solution of equimolar amounts of 1a and 6 (0.21 M) and 20 mol% of MX₂ and the additive was stirred for 24 h. aYields are based on NMR analysis. bIsolated yields. c0.42 M, d0.83 M, e1.67 M, f1.2 equiv. of 1a, g1.5 equiv. of 1a, h48 h.
3. Mechanistic Investigations
3.1. React FTIR Study

In a three-necked flask, 4-nitrobenzaldehyde (152 mg, 1.0 mmol) and lithium bromide (17.6 mg, 0.2 mmol) were dissolved in 1.2 mL of anhydrous THF under nitrogen at room temperature. After 10 minutes, dichloronitroacetophenone (234 mg, 1.0 mmol) was added to the stirred solution. After another 3 minutes, diisopropylethylamine (25.6 mg, 0.2 mmol) was added to start the reaction. The change in the IR absorption was measured under stirring (Figure 4).

React FTIR analysis of the C-C scission-nitroaldol-benzoyl transfer sequence.
3.2. NMR Studies

**NMR Analysis of the reaction between dichloronitroacetophenone and pyrrolidine**

The cleavage of dichloronitroacetophenone with pyrrolidine and the deprotonation of dichloronitromethane by Et$_3$N were investigated by $^1$H and $^{13}$C NMR spectroscopy (Figures 5 and 6). Addition of one equivalent of pyrrolidine to a solution of dichloronitroacetophenone in deuterated chloroform showed that smooth cleavage occurred yielding benzoyl pyrrolidine and dichloronitromethane having a proton NMR signal at 7.20 ppm and a carbon NMR signal at 92.9 ppm within a few minutes. The cleavage products were initially present in equimolar amounts. The dichloronitromethane/amide ratio, however, decreased over time which may be attributed to decomposition or loss due to evaporation of the nitro alkane. The cleavage was almost quantitative after 75 minutes. After 100 minutes, 2 equivalents of triethylamine were added. The $^1$H and $^{13}$C NMR signal for dichloronitromethane disappeared and characteristic peaks for triethylammonium were observed indicating quantitative deprotonation of CHCl$_2$NO$_2$. Meanwhile, a carbon NMR peak at 124.7 ppm appeared which may be correlated to the corresponding dichloronitronate (the sp$^2$-hybridized carbon in dichloronitronate is expected to be significantly downfield shifted compared to the sp$^3$-hybridized carbon in dichloronitromethane).
All $^1$H NMR spectra were recorded in CDCl$_3$. From bottom to top: Spectrum 1: Benzyldichloronitromethane (BDCNM). Spectrum 2: BDCNM + pyrrolidine after 5 minutes. Spectrum 3: BDCNM + pyrrolidine after 75 minutes. Spectrum 4: BDCNM + pyrrolidine after 100 minutes and upon addition of Et$_3$N. Spectrum 5: Benzoyl pyrrolidine reference.
All $^{13}$C NMR spectra were recorded in CDCl$_3$. From bottom to top: Spectrum 1: Benzoyldichloronitromethane (BDCNM). Spectrum 2: BDCNM + pyrrolidine after 75 minutes. Spectrum 3: BDCNM + pyrrolidine after 100 minutes and upon addition of Et$_3$N. Spectrum 4: Benzoyl pyrrolidine reference.

**NMR Analysis of the reaction between dichloronitroacetophenone and triethylamine**

The cleavage of dichloronitroacetophenone with triethylamine and the conversion of dichloronitronate with MeOH to methyl benzoate were investigated by $^1$H and $^{13}$C NMR spectroscopy (Figures 7 and 8). Mixing of dichloronitroacetophenone and triethylamine did not show any spectroscopic change even after 20 minutes, indicating that the equilibrium of the C-C bond scission lies far on the side of the starting materials. Spontaneous formation of methyl
benzoate and dichloronitronate (carbon NMR peak at 124.7 ppm) was observed upon addition of methanol. This suggests that small amounts of the free dichloronitronate are present and sufficient to start the reaction. For comparison, we mixed dichloronitroacetophenone with methanol. We found no sign of reaction in the absence of triethylamine.

All $^1$H NMR spectra were recorded in CDCl$_3$. From bottom to top: Spectrum 1: Benzoxyldichloronitromethane (BDCNM) and methanol (for comparison). Spectrum 2: BDCNM + Et$_3$N after 5 minutes. Spectrum 3: BDCNM + Et$_3$N after 20 minutes. Spectrum 4: BDCNM + Et$_3$N after 20 minutes and upon addition of methanol. Spectrum 5: Methyl benzoate reference.
All $^{13}$C NMR spectra were recorded in CDCl$_3$. From bottom to top: Spectrum 1: BDCNM + Et$_3$N after 5 minutes. Spectrum 2: BDCNM + Et$_3$N after 20 minutes. Spectrum 3: BDCNM + Et$_3$N after 20 minutes and upon addition of methanol. Spectrum 4: Methyl benzoate reference.
4. NMR Spectra

Dichloronitroacetophenone (1a)
Difluoronitroacetophenone (1b)
2,2-Dichloro-2-nitro-1-(4-nitrophenyl)ethyl benzoate (3a)
2,2-Dichloro-1-(4-chlorophenyl)-2-nitroethyl benzoate (3b)
2,2-Dichloro-2-nitro-1-phenylethyl benzoate (3c)
2,2-Dichloro-1-(2-naphthyl)-2-nitroethyl benzoate (3d)
2,2-Dichloro-1-(4-cyanophenyl)-2-nitroethyl benzoate (3e)
2,2-Dichloro-1-(3-fluorophenyl)-2-nitroethyl benzoate (3f)
1-(4-Acetylphenyl)-2,2-dichloro-2-nitroethyl benzoate (3g)
2,2-Dichloro-2-nitro-1-(2-nitrophenyl)ethyl benzoate (3h)
2,2-Dichloro-2-nitro-1-(2-pyridyl)ethyl benzoate (3i)
2,2-Dichloro-1-(2-furanyl)-2-nitroethyl benzoate (3j)
2,2-Dichloro-1-(4-methoxyphenyl)-2-nitroethyl benzoate (3k)
1,1-Dichloro-1-nitro-4-phenylbutan-2-yl benzoate (3l)
1,1-Dichloro-1-nitroheptan-2-yl benzoate (3m)
2,2-Difluoro-1-(2-naphthyl)-2-nitroethyl benzoate (9a)
2,2-Difluoro-1-(3-methoxyphenyl)-2-nitroethyl benzoate (9b)
2,2-Difluoro-1-(4-bromophenyl)-2-nitroethyl benzoate (9c)
2,2-Difluoro-2-nitro-1-(4-nitrophenyl)ethyl benzoate (9d)
2,2-Difluoro-1-(4-cyanophenyl)-2-nitroethyl benzoate (9e)
2,2-Dichloro-1-(4-cyanophenyl)ethyl benzoate (7)
2,2-Dichloro-1-(4-cyanophenyl)pent-4-en-1-yl benzoate (8)
5. Crystallography

2,2-Difluoro-2-nitro-1-(2-nitrophenyl)ethyl benzoate
A single crystal was obtained by slow evaporation of a solution of the product in a mixture of diisopropyl ether and THF. Single crystal X-ray analysis was performed at 100 K using a Siemens platform diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were integrated and corrected using the APEX 2 program. The structures were solved by direct methods and refined with full-matrix least square analysis using SHELX-14-7 software. Non-hydrogen atoms were refined with anisotropic displacement parameter. Crystal data: C₁₅H₁₀Cl₂N₂O₆, M = 385.15, colorless prism, 0.12 x 0.07 x 0.03 mm³, triclinic, space group P-1, a = 6.9802(7), b = 7.0738(7), c = 17.9149(18) Å. V = 804.58 Å³, Z = 1.

2,2-Difluoro-2-nitro-1-(4-nitrophenyl)ethyl benzoate
A single crystal was obtained by solvent layering of the product in a solution of chloroform and hexanes as a co-solvent. Single crystal X-ray analysis was performed at 100 K using a Siemens platform diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were integrated and corrected using the APEX 2 program. The structures were solved by intrinsic phasing and refined with full-matrix least square analysis using SHELX-14-7 software. Non-hydrogen atoms were refined with anisotropic displacement parameter. Crystal data:
C_{15}H_{10}Cl_{2}N_{2}O_{6}, M = 385.15, colorless needle, 0.13 x 0.03 x 0.01 mm$^3$, orthorhombic, space group $Pna2_1$, a = 7.0035(5), b = 37.401(3), c = 6.0429(4) Å. V = 1582.86(19) Å$^3$, Z = 4.

6. References
