Cyano-Borrowing Reaction: Nickel-Catalyzed Direct Conversion of Cyanohydrins and Aldehydes/Ketones to β-Cyano Ketone

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I General information

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker 14A04336 (600 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). All high resolution mass spectra (HRMS) were obtained on a micrOTOF-Q II 10269 spectrometer. For thin layer chromatography (TLC), TLC plates were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine, or potassium permanganate solution followed by heating using a heat gun. Flash chromatography separations were performed on 300-400 mesh silica gel. The cyanohydrins are commercially available or synthesis via the known procedures$^1$.
II General Procedure for preparation of product from cyanohydrins

Method A: To a vial equipped with a dried stir bar was added aldehydes (0.2 mmol) ketone cyanohydrins (0.4 mmol) NiCl₂ (5 mol%), ligand L* (5 mol%), LiOH (0.6 mmol), 100 mg 4Å MS and anhydrous dioxane (1 mL) in the glovebox. The reaction mixture was taken outside the glovebox and allowed to stir at room temperature for 30 min. After then, the reaction mixture was allowed to stir at 100 °C for 18 hours. The crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography to give pure products.

Method B: To a vial equipped with a dried stir bar was added ketones (0.2 mmol) aldehyde cyanohydrins (0.4 mmol) NiCl₂ (5 mol%), ligand L* (5 mol%), LiOH (0.6 mmol), 100 mg 4Å MS and anhydrous dioxane (1 mL) in the glovebox. The reaction mixture was taken outside the glovebox and allowed to stir at room temperature for 30 min. After then, the reaction mixture was allowed to stir at 100 °C for 18 hours. The crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography to give pure products.

III Characterization of products

4-oxo-2,4-diphenylbutanenitrile (3aa)

The title compound was prepared according to the general procedure as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (Rf = 0.40 in hexane:ethyl acetate = 5:1) resulting in a white solid in 82% yield (method A), 83% yield (method B).

\(^1\)H NMR (600 MHz, CDCl₃) δ 7.91 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.1 Hz, 1H), 7.44 (m, 4H), 7.38 (t, J = 7.1 Hz, 2H), 7.32 (t, J = 7.1 Hz, 1H), 4.59-4.52 (m, 1H), 3.71 (dd, J = 17.9 Hz, 8.0 Hz, 1H), 3.50 (dd, J = 17.9 Hz, 5.7 Hz, 1H).
$^{13}$C NMR (151 MHz, CDCl$_3$) δ 194.66, 135.79, 135.36, 133.87, 129.28, 128.84, 128.38, 128.11, 127.51, 126.03, 44.49, 31.94.

4-(4-chlorophenyl)-4-oxo-2-phenylbutanenitrile (3ba)$^2$

The title compound was prepared according to the general procedure as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R$_f$ = 0.40 in hexane:ethyl acetate = 5:1) resulting in a white solid in 70% yield (method A) and 75% yield (method B).

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.78 (d, $J$ = 7.7 Hz, 2H), 7.39-7.29 (m, 6H), 7.27 (d, $J$ = 5.9 Hz, 1H), 4.47 (t, $J$ = 7.6 Hz, 1H), 3.62 (d, $J$ = 17.7 Hz, 7.6 Hz, 1H), 3.39 (d, $J$ = 17.2 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 193.49, 140.48, 135.13, 134.09, 130.36-128.85, 128.46, 127.46, 120.98, 44.48, 31.94.

4-(4-bromophenyl)-4-oxo-2-phenylbutanenitrile (3ca)$^2$

The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R$_f$ = 0.40 in hexane:ethyl acetate = 5:1) resulting in a white solid in 90% yield.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.70 (d, $J$ = 8.5 Hz, 2H), 7.52 (d, $J$ = 8.5 Hz, 2H), 7.36-7.29 (m, 4H), 7.26 (t, $J$ = 7.1 Hz, 1H), 4.46 (dd, $J$ = 7.7 Hz, 6.1 Hz, 1H), 3.60 (dd, $J$ = 17.9 Hz, 8.1 Hz, 1H), 3.38 (dd, $J$ = 17.9 Hz, 5.9 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 193.73, 135.11, 134.47, 132.19, 129.57, 129.33, 129.22, 128.47, 127.47, 120.47, 44.4, 31.93, 29.69.

4-(4-fluorophenyl)-4-oxo-2-phenylbutanenitrile (3da)$^3$

The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was
performed using hexanes and ethyl acetate (10:1) (Rf = 0.40 in hexane:ethyl acetate = 5:1) resulting in a white solid in 85% yield.

¹H NMR (600 MHz, CDCl₃) δ 7.60 (d, J = 4.5 Hz, 2H), 7.34 (d, J = 7.4 Hz, 2H), 7.30 (t, J = 7.4 Hz, 2H), 7.25 (t, J = 7.2 Hz, 1H), 7.19 (d, J = 12.7 Hz, 1H), 7.04 (t, J = 4.1 Hz, 1H), 4.47 (t, J = 7.0 Hz, 1H), 3.57 (dd, J = 17.3 Hz, 7.8 Hz, 1H), 3.36 (dd, J = 17.3 Hz, 6.3 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 187.42, 142.76, 135.06, 134.73, 132.56, 129.30, 128.40 (d, J = 13.7 Hz), 127.49, 120.37, 44.81, 31.99.

4-oxo-2-phenyl-4-(p-tolyl)butanenitrile (3ea)²

The title compound was prepared according to the general procedure as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (Rf = 0.40 in hexane:ethyl acetate = 5:1) resulting in a white solid in 72% yield (method A) and 77% yield (method B).

¹H NMR (600 MHz, CDCl₃) δ 7.74 (d, J = 7.1 Hz, 2H), 7.29 (m, 5H), 7.18 (d, J = 6.4 Hz, 2H), 4.48 (s, 1H), 3.61 (dd, J = 17.7 Hz, 7.8 Hz, 1H), 3.40 (dd, J = 17.7 Hz, 3.8 Hz, 1H), 2.33 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 194.22, 144.86, 135.45, 133.37, 129.50, 129.25, 128.33, 128.23, 127.50, 120.67, 44.38, 31.96, 21.66.

4-(4-methoxyphenyl)-4-oxo-2-phenylbutanenitrile (3fa)³

The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (Rf = 0.30 in hexane:ethyl acetate = 5:1) resulting in a white solid in 86% yield.

¹H NMR (600 MHz, CDCl₃) δ 7.83 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 7.4 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.26 (t, J = 7.2 Hz, 1H), 6.86 (d, J = 8.7 Hz, 2H), 4.50 (t, J = 6.9 Hz, 1H), 3.80 (s, 3H), 3.60 (dd, J = 17.6 Hz, 7.9 Hz, 1H), 3.38 (dd, J = 17.6 Hz, 6.0 Hz, 1H).
$^{13}$C NMR (151 MHz, CDCl$_3$) δ 193.03, 164.12, 135.49, 130.44, 129.23, 128.88, 128.30, 127.49, 120.72, 114.00, 55.53, 44.16, 32.01.

4-(2-chlorophenyl)-4-oxo-2-phenylbutanenitrile (3ga)$^4$

The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R$_f$ = 0.40 in hexane:ethyl acetate = 5:1) resulting in a white solid in 65% yield.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.40 (d, $J$ = 7.4 Hz, 1H), 7.35-7.28 (m, 6H), 7.28–7.22 (m, 2H), 4.46 (t, $J$ = 7.1 Hz, 1H), 3.63 (dd, $J$ = 17.9 Hz, 8.0 Hz, 1H), 3.46 (dd, $J$ = 17.9 Hz, 6.3 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 197.53, 137.67, 134.87, 132.67, 131.36, 130.77, 129.54, 129.28, 128.46, 127.51, 127.19, 120.23, 48.30, 32.26.

HRMS (ESI): m/z Calcd. for [C$_{17}$H$_{15}$NO, M+H]$^+$: 272.1046; Found: 272.1047.

4-oxo-2-phenyl-4-(o-tolyl)butanenitrile (3ha)

The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R$_f$ = 0.40 in hexane:ethyl acetate = 5:1) resulting in a white solid in 72% yield.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.48 (t, $J$ = 10.3 Hz, 1H), 7.31 (m, 5H), 7.25 (t, $J$ = 7.1 Hz, 1H), 7.16 (t, $J$ = 8.1 Hz, 2H), 4.46 (t, $J$ = 7.1 Hz, 1H), 3.55 (dd, $J$ = 17.6 Hz, 8.0 Hz, 1H), 3.36 (dd, $J$ = 17.6 Hz, 6.2 Hz, 1H), 2.41 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 198.02, 139.05, 136.20, 135.29, 132.32, 132.18, 129.26, 128.57, 128.37, 127.50, 125.87, 120.62, 46.86, 32.22, 21.39.

HRMS (ESI): m/z Calcd. for [C$_{17}$H$_{15}$NO, M+H]$^+$: 272.1046; Found: 272.1047.

4-(3-chlorophenyl)-4-oxo-2-phenylbutanenitrile (3ia)$^4$
The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (Rf = 0.40 in hexane:ethyl acetate = 5:1) resulting in a white solid in 65% yield.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.81 (s, 1H), 7.71 (d, $J = 7.3$ Hz, 1H), 7.48 (d, $J = 7.4$ Hz, 1H), 7.38–7.29 (m, 5H), 7.27 (d, $J = 5.9$ Hz, 1H), 4.46 (s, 1H), 3.62 (dd, $J = 17.6$ Hz, 7.4 Hz, 1H), 3.40 (dd, $J = 17.8$ Hz, 2.9 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 193.47, 137.24, 135.28, 135.05, 133.81, 130.18, 129.34, 128.50, 128.23, 127.47, 126.15, 120.34, 44.62, 31.90.

HRMS (ESI): m/z Calcd. for [$C_{17}H_{15}NO_2$, M+H]$^+$: 288.0995; Found: 288.1000.

4-(3-methoxyphenyl)-4-oxo-2-phenylbutanenitrile (3ja)

The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (Rf = 0.40 in hexane:ethyl acetate = 5:1) resulting in a white solid in 85% yield.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.40–7.24 (m, 8H), 7.04 (d, $J = 7.7$ Hz, 1H), 4.46 (t, $J = 6.7$ Hz, 1H), 3.75 (s, 3H), 3.62 (dd, $J = 17.9$ Hz, 8.0 Hz, 1H), 3.41 (dd, $J = 17.9$ Hz, 5.8 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 193.49, 159.02, 136.11, 134.31, 128.78, 128.25, 127.35, 126.47, 119.59 (d, $J = 9.4$ Hz), 119.36, 111.41, 54.47, 43.54, 30.97.

HRMS (ESI): m/z Calcd. for [C$_{17}$H$_{15}$NO$_2$, M+H]$^+$: 288.0995; Found: 288.1000.

4-(naphthalen-2-yl)-4-oxo-2-phenylbutanenitrile (3ka)

The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (Rf = 0.40 in hexane:ethyl acetate = 5:1) resulting in a white solid in 53% yield.

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.32 (s, 1H), 7.90 (d, $J = 8.6$ Hz, 1H), 7.84 (d, $J = 8.2$ Hz, 1H), 7.79 (dd, $J = 11.8$, 8.6 Hz, 2H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 1H), 7.39 (d, $J = 7.4$ Hz, 2H), 7.32 (t, $J = 7.6$ Hz, 2H), 7.26 (t, $J = 7.4$ Hz, 1H), 4.54
(dd, $J = 7.7$ Hz, $6.2$ Hz, 1H), 3.77 (dd, $J = 17.7$ Hz, $8.0$ Hz, 1H), 3.56 (dd, $J = 17.7$ Hz, $6.0$ Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 194.56, 135.90, 135.40, 133.12, 132.42, 130.03, 129.61, 129.31, 128.94, 128.79, 128.40, 127.86, 127.55, 127.08, 123.50, 120.67, 44.59, 32.07.

4-oxo-2-phenyl-4-(thiophen-2-yl)butanenitrile (3la)$^2$

The title compound was prepared according to the general procedure as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) ($R_f = 0.40$ in hexane:ethyl acetate = 5:1) resulting in a white solid in 82% yield (method A), 80% yield (method B).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.60 (t, $J = 3.9$ Hz, 2H), 7.34 (d, $J = 7.3$ Hz, 2H), 7.30 (t, $J = 7.5$ Hz, 2H), 7.25 (t, $J = 7.2$ Hz, 1H), 7.07–7.02 (m, 1H), 4.47 (t, $J = 7.0$ Hz, 1H), 3.56 (dd, $J = 17.3$ Hz, 7.8 Hz, 1H), 3.36 (dd, $J = 17.3$ Hz, 6.3 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 197.44, 166.20, 140.29, 133.93, 129.82, 128.18, 52.40, 26.80.

HRMS (ESI): m/z Calcd. for [C$_{12}$H$_{13}$NO, M+H]$^+$: 210.0889; Found: 210.0892.

4-cyclopropyl-4-oxo-2-phenylbutanenitrile (3na)
The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (RF = 0.40 in hexane:ethyl acetate = 5:1) resulting in a white solid in 57% yield.

1H NMR (600 MHz, CDCl3) δ 7.33-7.24 (m, 5H), 4.30 (dd, J = 7.9 Hz, 6.2 Hz, 1H), 3.24 (dd, J = 17.7 Hz, 7.9 Hz, 1H), 3.02 (dd, J = 17.7 Hz, 6.1 Hz, 1H), 1.81 (tt, J = 7.8 Hz, 4.5 Hz, 1H), 1.05 (m, 1H), 0.98 (m, 1H), 0.86 (m, 2H).

13C NMR (151 MHz, CDCl3) δ 205.24, 135.23, 129.19, 128.28, 127.35, 120.44, 48.47, 31.73, 20.77, 11.43, 11.32.

HRMS (ESI): m/z Calcd. for [C13H13NO, M+H]+: 222.0889; Found: 222.0890.

2-(4-fluorophenyl)-4-oxo-4-phenylbutanenitrile (3ab)

The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (RF = 0.30 in hexane:ethyl acetate = 5:1) resulting in a white solid in 83% yield.

1H NMR (600 MHz, CDCl3) δ 7.84 (d, J = 7.4 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.8 Hz, 2H), 7.34 (dd, J = 8.6 Hz, 5.1 Hz, 2H), 7.00 (t, J = 8.6 Hz, 2H), 4.49 (t, J = 6.9 Hz, 1H), 3.63 (dd, J = 17.9 Hz, 7.4 Hz, 1H), 3.43 (dd, J = 17.9 Hz, 6.4 Hz, 1H).

13C NMR (151 MHz, CDCl3) δ 194.44, 163.37, 161.73, 135.68, 133.97, 131.12 (d, J = 3.2 Hz), 129.34 (d, J = 8.3 Hz), 128.87, 128.09, 44.43, 31.22.

2-(4-chlorophenyl)-4-oxo-4-phenylbutanenitrile (3ac)

The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (RF = 0.40 in hexane:ethyl acetate = 5:1) resulting in a white solid in 77% yield.

1H NMR (600 MHz, CDCl3) δ 7.84 (dd, J = 8.3, 1.1 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.8 Hz, 2H), 7.33–7.26 (m, 4H), 4.49 (t, J = 6.9 Hz, 1H), 3.63 (dd, J = 17.9 Hz, 7.4 Hz, 1H), 3.43 (dd, J = 17.9 Hz, 6.4 Hz, 1H).
C NMR (151 MHz, CDCl$_3$) δ 194.32, 135.62, 134.47, 134.01, 133.82, 129.45, 128.96, 128.88, 128.09, 44.27, 31.34.

2-(4-bromophenyl)-4-oxo-4-phenylbutanenitrile (3ad)$^2$

The title compound was prepared according to the general procedure as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R$_f$ = 0.40 in hexane:ethyl acetate = 5:1) resulting in a white solid in 73% yield (method A), 78% yield (method B).

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.83 (d, $J = 7.5$ Hz, 2H), 7.52 (t, $J = 7.3$ Hz, 1H), 7.43 (d, $J = 8.2$ Hz, 2H), 7.39 (t, $J = 7.6$ Hz, 2H), 7.24 (d, $J = 8.1$ Hz, 2H), 4.46 (t, $J = 6.8$ Hz, 1H), 3.62 (dd, $J = 17.9$ Hz, 7.4 Hz, 1H), 3.42 (dd, $J = 17.9$ Hz, 6.4 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 194.32, 135.62, 134.37, 134.00, 132.41, 129.28, 128.88, 128.09, 122.50, 120.15, 44.19, 31.42.

4-oxo-4-phenyl-2-(p-tolyl)butanenitrile (3ae)$^2$

The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R$_f$ = 0.40 in hexane:ethyl acetate = 5:1) resulting in a white solid in 66% yield.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.84 (d, $J = 7.6$ Hz, 2H), 7.50 (t, $J = 7.4$ Hz, 1H), 7.38 (t, $J = 7.7$ Hz, 2H), 7.23 (d, $J = 7.9$ Hz, 2H), 7.11 (d, $J = 7.8$ Hz, 2H), 4.48–4.39 (m, 1H), 3.62 (dd, $J = 17.9$ Hz, 7.9 Hz, 1H), 3.40 (dd, $J = 17.9$ Hz, 6.0 Hz, 1H), 2.26 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 194.74, 138.24, 135.84, 133.82, 132.41, 129.28, 128.82, 128.10, 127.36, 44.53, 31.56, 21.04.

2-(4-methoxyphenyl)-4-oxo-4-phenylbutanenitrile (3af)$^2$
The title compound was prepared according to the general procedure as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (Rf = 0.30 in hexanes:ethyl acetate = 5:1) resulting in a white solid in 76% yield (method A), 79% yield (method B).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 7.7$ Hz, 2H), 7.52 (t, $J = 7.2$ Hz, 1H), 7.39 (t, $J = 7.4$ Hz, 2H), 7.27 (d, $J = 7.4$ Hz, 2H), 6.83 (d, $J = 7.4$ Hz, 2H), 4.45 (t, $J = 6.7$ Hz, 1H), 3.73 (s, 3H), 3.62 (dd, $J = 17.8$ Hz, 7.6 Hz, 1H), 3.42 (dd, $J = 17.8$ Hz, 6.2 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 194.76, 159.59, 135.85, 133.82, 128.81, 128.66, 128.08, 127.24, 120.85, 114.65, 55.36, 44.56, 31.17.

2-(2-chlorophenyl)-4-oxo-4-phenylbutanenitrile (3ag)$^3$

The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (Rf = 0.40 in hexanes:ethyl acetate = 5:1) resulting in a white solid in 56% yield.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.87 (d, $J = 7.8$ Hz, 2H), 7.61 (d, $J = 7.5$ Hz, 1H), 7.53 (t, $J = 7.2$ Hz, 1H), 7.40 (t, $J = 7.5$ Hz, 2H), 7.36 (d, $J = 7.8$ Hz, 1H), 7.26 (dt, $J = 23.7$ Hz, 7.3 Hz, 2H), 4.85 (d, $J = 9.3$ Hz, 1H), 3.60 (dd, $J = 17.9$ Hz, 9.4 Hz, 1H), 3.46 (dd, $J = 17.9$ Hz, 4.0 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 194.41, 135.67, 133.89, 132.75, 130.31, 129.88, 129.49, 128.84, 128.12, 127.77, 119.65, 42.42, 30.07.

2-(2-bromophenyl)-4-oxo-4-phenylbutanenitrile (3ah)$^4$

The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (Rf = 0.40 in hexanes:ethyl acetate = 5:1) resulting in a white solid in 75% yield.
\[ ^1\text{H NMR} \ (600 \text{ MHz, CDCl}_3) \ \delta \ 7.87 \ (d, \ J = 7.3 \text{ Hz, } 2\text{H}), \ 7.62 \ (d, \ J = 7.7 \text{ Hz, } 1\text{H}), \ 7.53 \ (t, \ J = 8.4 \text{ Hz, } 2\text{H}), \ 7.40 \ (t, \ J = 7.4 \text{ Hz, } 2\text{H}), \ 7.33 \ (t, \ J = 7.5 \text{ Hz, } 1\text{H}), \ 7.16 \ (dd, \ J = 13.8 \text{ Hz, } 6.3 \text{ Hz, } 1\text{H}), \ 4.85 \ (dd, \ J = 9.2 \text{ Hz, } 3.6 \text{ Hz, } 1\text{H}), \ 3.58 \ (dd, \ J = 17.9 \text{ Hz, } 9.7 \text{ Hz, } 1\text{H}), \ 3.45 \ (dd, \ J = 17.9 \text{ Hz, } 3.1 \text{ Hz, } 1\text{H}). \]

\[ ^{13}\text{C NMR} \ (151 \text{ MHz, CDCl}_3) \ \delta \ 194.35, \ 135.66, \ 134.46, \ 133.89, \ 133.64, \ 130.08, \ 129.50, \ 128.84, \ 128.42, \ 128.13, \ 122.87, \ 119.72, \ 42.73, \ 32.49. \]

**2-(2-methoxyphenyl)-4-oxo-4-phenylbutanenitrile (3ai)**

The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (Rf = 0.30 in hexane:ethyl acetate = 5:1) resulting in a white solid in 90% yield.

\[ ^1\text{H NMR} \ (600 \text{ MHz, CDCl}_3) \ \delta \ 7.86 \ (d, \ J = 7.6 \text{ Hz, } 2\text{H}), \ 7.50 \ (t, \ J = 7.3 \text{ Hz, } 1\text{H}), \ 7.42 \ (d, \ J = 7.5 \text{ Hz, } 1\text{H}), \ 7.38 \ (t, \ J = 7.6 \text{ Hz, } 2\text{H}), \ 7.25 \ (t, \ J = 7.7 \text{ Hz, } 1\text{H}), \ 6.92 \ (t, \ J = 7.4 \text{ Hz, } 1\text{H}), \ 6.84 \ (d, \ J = 8.2 \text{ Hz, } 1\text{H}), \ 4.69 \ (dd, \ J = 8.9 \text{ Hz, } 4.7 \text{ Hz, } 1\text{H}), \ 3.78 \ (s, \ 3\text{H}), \ 3.57 \ (dd, \ J = 17.8 \text{ Hz, } 9.1 \text{ Hz, } 1\text{H}), \ 3.42 \ (dd, \ J = 17.8 \text{ Hz, } 4.6 \text{ Hz, } 1\text{H}). \]

\[ ^{13}\text{C NMR} \ (151 \text{ MHz, CDCl}_3) \ \delta \ 194.65, \ 156.31, \ 136.00, \ 133.65, \ 129.78, \ 128.95, \ 128.75, \ 128.09, \ 123.24, \ 121.11, \ 120.54, \ 111.10, \ 55.59, \ 42.19, \ 27.48. \]

**2-(3-methoxyphenyl)-4-oxo-4-phenylbutanenitrile (3aj)**

The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (Rf = 0.30 in hexane:ethyl acetate = 5:1) resulting in a white solid in 68% yield.

\[ ^1\text{H NMR} \ (600 \text{ MHz, CDCl}_3) \ \delta \ 7.84 \ (d, \ J = 7.6 \text{ Hz, } 2\text{H}), \ 7.51 \ (t, \ J = 7.3 \text{ Hz, } 1\text{H}), \ 7.38 \ (t, \ J = 7.7 \text{ Hz, } 2\text{H}), \ 7.22 \ (t, \ J = 7.9 \text{ Hz, } 1\text{H}), \ 6.92 \ (d, \ J = 7.5 \text{ Hz, } 1\text{H}), \ 6.88 \ (s, \ 1\text{H}), \ 6.78 \ (dd, \ J = 8.2 \text{ Hz, } 1.7 \text{ Hz, } 1\text{H}), \ 4.45 \ (dd, \ J = 7.8 \text{ Hz, } 6.0 \text{ Hz, } 1\text{H}), \ 3.73 \ (s, \ 3\text{H}), \ 3.64 \ (dd, \ J = 17.9 \text{ Hz, } 8.1 \text{ Hz, } 1\text{H}), \ 3.42 \ (dd, \ J = 17.9 \text{ Hz, } 5.8 \text{ Hz, } 1\text{H}). \]

\[ ^{13}\text{C NMR} \ (151 \text{ MHz, CDCl}_3) \ \delta \ 194.65, \ 160.23, \ 136.76, \ 135.78, \ 133.87, \ 130.35, \ 128.83, \ 128.11, \ 120.52, \ 119.64, \ 113.82, \ 113.35, \ 55.37, \ 44.47, \ 31.93. \]
2-(benzo[d][1,3]dioxol-5-yl)-4-oxo-4-phenylbutanenitrile (3ak)

The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (Rf = 0.30 in hexane:ethyl acetate = 5:1) resulting in a white solid in 70% yield.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.89–7.82 (m, 2H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.40 (t, $J = 7.8$ Hz, 2H), 6.84–6.79 (m, 2H), 6.72 (d, $J = 7.9$ Hz, 1H), 5.89 (s, 2H), 4.41 (t, $J = 6.9$ Hz, 1H), 3.60 (dd, $J = 17.8$ Hz, 7.6 Hz, 1H), 3.41 (dd, $J = 17.8$ Hz, 6.3 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 194.63, 148.35, 147.70, 135.76, 133.89, 128.84, 128.10, 121.02, 120.68, 108.77, 107.96, 101.46, 44.54, 31.59.

2-(naphthalen-2-yl)-4-oxo-4-phenylbutanenitrile (3al)

The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (Rf = 0.50 in hexane:ethyl acetate = 5:1) resulting in a white solid in 58% yield.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.89–7.81 (m, 4H), 7.78 (d, $J = 8.3$ Hz, 1H), 7.71 (d, $J = 7.1$ Hz, 1H), 7.53–7.47 (m, 2H), 7.44 (m, 2H), 7.37 (t, $J = 7.8$ Hz, 2H), 5.24 (dd, $J =
9.7 Hz, 4.0 Hz, 1H), 3.79 (dd, J = 18.1 Hz, 9.7 Hz, 1H), 3.48 (dd, J = 18.1 Hz, 4.0 Hz, 1H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 194.91, 135.69, 134.17, 133.93, 130.81, 129.76, 129.47, 129.34, 128.85, 128.17, 127.29, 126.33, 125.93, 125.54, 122.02, 120.68, 43.74, 29.06.

**HRMS (ESI):** m/z Calcd. for \([C_{20}H_{15}NO, M+H]^+\): 308.1046; Found: 308.1048.

**2-(furan-2-yl)-4-oxo-4-phenylbutanenitrile (3an)**

The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R\(_f\) = 0.30 in hexane:ethyl acetate = 5:1) resulting in a white solid in 77% yield.

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.88 (dd, J = 8.3, 1.1 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.31 (d, J = 1.1 Hz, 1H), 6.31 (d, J = 3.3 Hz, 1H), 6.28 (dd, J = 3.2, 1.9 Hz, 1H), 4.60 (t, J = 6.9 Hz, 1H), 3.65-3.56 (m, 2H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 194.28, 146.94, 143.14, 135.61, 133.99, 128.88, 128.14, 118.36, 110.86, 108.24, 40.71, 26.02.

**4-oxo-4-phenyl-2-(thiophen-2-yl)butanenitrile (3ao)**

The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R\(_f\) = 0.30 in hexane:ethyl acetate = 5:1) resulting in a white solid in 67% yield (method A), 69% yield (method B).

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.90–7.86 (m, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.22–7.17 (m, 1H), 7.09 (d, J = 3.5 Hz, 1H), 6.91 (dd, J = 5.1 Hz, 3.6 Hz, 1H), 4.79 (t, J = 6.8 Hz, 1H), 3.69 (dd, J = 17.8 Hz, 7.3 Hz, 1H), 3.56 (dd, J = 17.8 Hz, 6.5 Hz, 1H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 194.26, 137.04, 135.63, 134.02, 128.89, 128.15, 127.18, 126.73, 125.90, 44.59, 27.27.

**2-(1H-indol-3-yl)-4-oxo-4-phenylbutanenitrile (3ap)**
The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (Rf = 0.30 in hexane:ethyl acetate = 5:1) resulting in a white solid in 51% yield.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.21 (s, 1H), 7.85 (d, $J = 7.5$ Hz, 2H), 7.62 (d, $J = 7.9$ Hz, 1H), 7.50 (t, $J = 7.4$ Hz, 1H), 7.38 (t, $J = 7.7$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 1H), 7.22 (d, $J = 2.0$ Hz, 1H), 7.18 (t, $J = 7.4$ Hz, 1H), 7.11 (t, $J = 7.5$ Hz, 1H), 4.77 (dd, $J = 7.9$, 5.9 Hz, 1H), 3.70 (dd, $J = 17.9$, 8.1 Hz, 1H), 3.60 (dd, $J = 17.9$, 5.7 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 195.31, 136.50, 135.88, 133.82, 128.81, 128.11, 125.00, 122.93, 122.89, 120.79, 120.39, 118.36, 111.77, 109.76, 42.94, 23.73.

HRMS (ESI): m/z Calcd. for [C$_{18}$H$_{14}$N$_2$O, M+H]$^+$: 297.0998; Found: 297.1003.

2-benzyl-4-oxo-4-phenylbutanenitrile (3aq)

The title compound was prepared according to the general procedure A as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (Rf = 0.50 in hexane:ethyl acetate = 5:1) resulting in a white solid in 64% yield.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.84 (dd, $J = 8.3$ Hz, 1.1 Hz, 2H), 7.53 (dd, $J = 10.6$ Hz, 4.3 Hz, 1H), 7.41 (t, $J = 7.8$ Hz, 2H), 7.29-7.24 (m, 2H), 7.21 (dd, $J = 7.1$ Hz, 5.0 Hz, 3H), 3.47 (dq, $J = 13.2$ Hz, 6.6 Hz, 1H), 3.28 (dd, $J = 17.9$ Hz, 6.5 Hz, 1H), 3.17 (dd, $J = 17.9$ Hz, 6.9 Hz, 1H), 2.94 (qd, $J = 13.7$ Hz, 7.0 Hz, 2H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 195.25, 136.50, 135.86, 133.82, 128.81, 128.11, 125.00, 122.49, 121.42, 39.79, 37.55, 28.21.

HRMS (ESI): m/z Calcd. for [C$_{18}$H$_{14}$NO, M+H]$^+$: 272.1046; Found: 272.1043.

2-cyclohexyl-4-oxo-4-phenylbutanenitrile (3ar)

The title compound was prepared according to the general procedure as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (Rf = 0.50 in hexane:ethyl acetate = 5:1) resulting in a white solid in 83% yield (method A), 82% yield (method B).
\(^1\text{H NMR (600 MHz, CDCl}_3\) \(\delta\) 7.88 (d, \(J = 7.4\ \text{Hz, 2H}\)), 7.53 (t, \(J = 7.4\ \text{Hz, 1H}\)), 7.41 (t, \(J = 7.7\ \text{Hz, 2H}\)), 3.31 (td, \(J = 9.3\ \text{Hz, 3.3 Hz, 1H}\)), 3.17 (dt, \(J = 20.0\ \text{Hz, 5.7 Hz, 2H}\)), 1.82 (d, \(J = 6.3\ \text{Hz, 1H}\)), 1.72 (d, \(J = 10.5\ \text{Hz, 3H}\)), 1.62 (d, \(J = 11.2\ \text{Hz, 1H}\)), 1.52 (s, 1H), 1.25-1.06 (m, 5H).

\(^{13}\text{C NMR (151 MHz, CDCl}_3\) \(\delta\) 195.55, 136.07, 133.74, 128.82, 120.97, 38.97, 38.45, 32.55, 31.46, 29.20, 25.99, 25.86, 25.81.

2-(2-(methylthio)ethyl)-4-oxo-4-phenylbutanenitrile (3as)

The title compound was prepared according to the general procedure \textit{A} as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (\(R_f = 0.40\) in hexane:ethyl acetate = 5:1) resulting in a white solid in 32\% yield.

\(^1\text{H NMR (600 MHz, CDCl}_3\) \(\delta\) 7.88 (d, \(J = 7.3\ \text{Hz, 2H}\)), 7.55 (t, \(J = 7.4\ \text{Hz, 1H}\)), 7.43 (t, \(J = 7.8\ \text{Hz, 2H}\)), 3.50-3.42 (m, 1H), 3.38 (dd, \(J = 17.8\ \text{Hz, 6.4 Hz, 1H}\)), 3.23 (dd, \(J = 17.8\ \text{Hz, 6.9 Hz, 1H}\)), 2.71 (dt, \(J = 13.2\ \text{Hz, 6.6 Hz, 1H}\)), 2.61 (dt, \(J = 7.9\ \text{Hz, 6.3 Hz, 1H}\)), 2.08 (s, 3H), 1.95-1.87 (m, 2H).

\(^{13}\text{C NMR (151 MHz, CDCl}_3\) \(\delta\) 194.93, 135.87, 133.90, 128.88, 128.04, 121.23, 40.50, 31.43, 31.25, 25.43, 15.44.

\textbf{HRMS (ESI):} m/z Calcd. for [\text{C}_{13}\text{H}_{15}\text{NOS}, \text{M+H}]^+: 256.0767; Found: 256.0769.

3-methyl-4-oxo-2,4-diphenylbutanenitrile (8)

The title compound was prepared according to the general procedure \textit{A} as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (\(R_f = 0.30\) in hexane:ethyl acetate = 5:1) resulting in a white solid in 31\% yield (\textit{method A}), 25\% yield (\textit{method B}).

\(^1\text{H NMR (600 MHz, CDCl}_3\) \(\delta\) 7.99-7.84 (m, 2H), 7.50 (t, \(J = 7.4\ \text{Hz, 1H}\)), 7.40 (t, \(J = 7.8\ \text{Hz, 2H}\)), 7.35 (d, \(J = 7.2\ \text{Hz, 2H}\)), 7.29 (t, \(J = 7.6\ \text{Hz, 2H}\)), 7.22 (t, \(J = 7.3\ \text{Hz, 1H}\)), 4.93 (d, \(J = 8.0\ \text{Hz, 1H}\)), 3.83-3.65 (m, 1H), 1.00 (d, \(J = 7.2\ \text{Hz, 3H}\)).
2-((3S, 8R, 9S, 10R, 13S, 14S)-3-hydroxy-10,13-dimethyl-17-oxo-2, 3, 4, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17-tetradecahydro-1H-cyclopenta[a]phenanthren-16-yl)-2-phenylacetonitrile (10)

The title compound was prepared according to the general procedure B as described. Silica gel flash column chromatography was performed using hexanes and ethyl acetate (6:1) (Rf = 0.40 in hexane:ethyl acetate = 3:1) resulting in a white solid in 57% yield.

1H NMR (600 MHz, CDCl3) δ 7.50-7.43 (m, 2H), 7.36 (dt, J = 15.1 Hz, 5.0 Hz, 2H), 7.30 (d, J = 7.4 Hz, 1H), 5.35-5.28 (m, 1H), 3.51-3.43 (m, 1H), 2.83 (ddd, J = 15.8 Hz, 6.6 Hz, 1.9 Hz, 1H), 2.45-2.32 (m, 1H), 2.26 (dd, J = 5.2 Hz, 2.2 Hz, 1H), 2.20 (d, J = 2.7 Hz, 1H), 2.16-2.09 (m, 1H), 2.07-1.96 (m, 1H), 1.92 (ddd, J = 12.9 Hz, 4.3 Hz, 2.5 Hz, 1H), 1.84-1.69 (m, 3H), 1.69-1.58 (m, 3H), 1.54-1.40 (m, 3H), 1.37-1.25 (m, 3H), 1.00 (s, 3H), 0.92 (s, 3H).

13C NMR (151 MHz, CDCl3) δ 209.61, 141.19, 135.99, 135.65, 133.08, 130.32, 128.68, 120.83, 71.62, 50.38, 49.92, 47.34, 42.25, 37.16, 36.75, 31.62, 31.60, 31.23, 30.95, 29.37, 20.44, 19.47, 14.23.

IV Procedure of gram scale reaction

To a vial equipped with a dried stir bar was added o-Anisaldehyde (5 mmol) aceto-phenone cyanohydrin (10 mmol) NiCl2 (5 mol%), ligand L (5 mol%), LiOH (300 mol%), 300 mg 4Å MS and anhydrous dioxane (10 mL) in the glovebox. The reaction mixture was taken outside the glovebox and allowed to stir at room temperature for 30 min. After then, the reaction mixture was allowed to stir at 100 °C for 18 hours. The crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography to give pure product 1.12 g, 85% yield.
V The mechanism study.

To a vial equipped with a dried stir bar was added Chalcone 11 (0.2 mmol), p-Tolu-aldehyde (0.2 mmol), acetophenone cyanohydrin (0.4 mmol), NiCl\(_2\) (5 mol%), ligand L (5 mol%), LiOH (0.6 mmol), 100 mg 4Å MS and anhydrous dioxane (1 mL) in the glovebox. The reaction mixture was taken outside the glovebox and allowed to stir at room temperature for 30 min. After then, the reaction mixture was allowed to stir at 100 °C for 18 hours. The crude reaction mixture was concentrated under reduced pressure and given \(^1\)H NMR. We got the corresponding products 3aa and 3ae with the ratio of 1.05:1, which shows that the cyano group from the cleavage of C-CN bond of cyanohydrin was a free anion in this nickel-catalyzed protocol and has the same opportunity to conjugated addition to each chalcone.
To a vial equipped with a dried stir bar was added Chalcone 11 (0.2 mmol), acetophenone cyanohydrin (0.4 mmol), under standard conditions in the glovebox. The reaction mixture was taken outside the glovebox and allowed to stir at room temperature for 30 min. After then, the reaction mixture was allowed to stir at 100 °C for 18 hours. The crude reaction mixture was concentrated under reduced pressure and given 1H NMR. We got the corresponding products 3aa with 89% yield, and the hydrogen-borrowing product 12 was not observed, showing that cleavage the C-CN bond is more easy than the C-H bond in cyanohydrins.

In order to observe the role of nickel in this cyano borrowing reaction, the 31P NMR and HIMS were tested. As it shown below, the peak of the mixture of NiCl₂ and "Bu-PAd₂ in 31P NMR spectrum is 24.04 ppm, but after the addition of acetophenone cyanohydrin 1a, the 31P was remove to 51.34 ppm and 68.76 ppm, which means that the nickel was interacted with the cyanohydrins. Additionally, HIMS was tested under the standard procedure A, we found the fragment of [("BuPAd₂)₂Ni(CN)(1a)]. All these results could
prove that the coordination of CN toward Ni.

The $^{31}$P NMR of the mixture of NiCl$_2$ and $^t$BuPAd$_2$.

The $^{31}$P NMR of the mixture of NiCl$_2$, $^t$BuPAd$_2$ and acetophenone cyanohydrin 1a.
The HIMS of the reaction mixture under standard condition.

In order to understand the role of nickel catalyst in mechanism, we have tested every step of the reaction in the presence and absence of the nickel catalyst in 1 h and 18 h, respectively, as it shows in figure 1. We found that the nickel catalyst improves the conjugate 1,4-addition of the cyano group to chalcone.

The control experiments with other Lewis acid catalyst, such as Ti(O-i-Pr)₄ was tested, and got 35% Yield. The Brønsted acid catalyst, such as benzoic acid (PhCO₂H) was used in this cyano-borrowing reaction, 23% Yield was obtained. These control experiments shown that the acid could improve the reaction, but nickel catalyst was the optimal choose. All these control experiments shows that the Lewis acid was the role playing for nickel complex, and the oxidation number of Ni does not change through the cyano borrowing process.
LiOH is very important in this nickel-catalyzed cyano borrowing process, and the reaction with different equivalents of LiOH were tested, the results were listed as below. The transformation did not work while catalytic amounts was tested, and trace desired product was obtained with one equivalent LiOH. But the desired product 3 was obtained in 64% yield while two equivalent of LiOH was introduced to the cyano borrowing reaction, and 85% yield was achieved under the standard reaction conditions.

| Entry | LiOH (eq.) | Yield (%) |
|-------|-----------|-----------|
| 1     | 0.2       | NR        |
| 2     | 0.5       | NR        |
| 3     | 1.0       | Trace     |
| 4     | 2.0       | 64        |
| 5     | 3.0       | 85        |

In addition, LiOH was very important in this transformation, not just work as the base for the Aldol condensation, but also important in the “Borrowing” and “Returning”. As it shows below, the nickel catalyzed cyano borrowing reaction has no activity at the absence of LiOH. Low conversion was achieved for the decyanoation of the cyanohydrins and no Micheal addition was occurred without the addition of LiOH. Overall, lithium hydroxide is the key additive for the transformation.
VI References

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VII NMR of products

3aa

3aa
