Electronic Supplementary Information for

N-Heterocyclic Carbene-Catalyzed Annulation of α-Cyano-1,4-Diketones with Ynals

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Abstract Herein, we disclose the first stereoselective annulation reaction between α-cyano-1,4-diketones and ynals, mediated by catalytic amounts of a triazolium salt precatalyst and co-catalytic amounts of a weak carboxylate base. The title transformation proceeds smoothly under mild reaction conditions and generates three contiguous stereogenic centers, one of which is a quaternary acetal carbon. This reaction tolerates a wide variety of electronically distinct substituents on both reaction partners, and affords privileged bicyclic scaffolds in 61-90% isolated yields and with up to 20:1 diastereomeric preference.
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General

$^1$H, $^{13}$C, $^{19}$F and $^{31}$P NMR spectra were recorded on a Bruker ($^1$H, 300 MHz), a Bruker ($^1$H, 400 MHz), or a Bruker ($^1$H, 500 MHz) spectrometers, using deuterated solvents CDCl$_3$, CD$_2$Cl$_2$ or C$_6$D$_6$. Chemical shifts (δ) are reported in ppm downfield from Me$_4$Si by using the residual solvent peak as an internal standard. Scalar coupling constants (J) are reported in hertz (Hz). All reactions were carried out in heat-gun dried glassware equipped with magnetic stirrer bars under an inert atmosphere of dry nitrogen or argon. $^1$H NMR, TLC or GC-MS control of the crude reaction mixtures was routinely performed to ensure complete conversions of the starting material. 3 Å and 4 Å molecular sieves were powdered and heated under high vacuum at 260 °C during overnight prior to use. DMF was distilled over CaH$_2$ and stored over activated 4 Å molecular sieves. 1,2-Dichloroethane, 1-chlorobenzene and chloroform were distilled over P$_2$O$_5$ and stored over activated 4 Å molecular sieves. MeOH and EtOH were distilled over CaH$_2$ under argon, and stored over activated 4 Å molecular sieves. N,N-Diisopropylethylamine and 1,1,1,3,3,3-hexamethyldisilazane were distilled over CaH$_2$ and stored over activated 4 Å molecular sieves. Acrylonitrile, 1-fluorobenzene and hexafluorobenzene were distilled over P$_2$O$_5$ and stored over activated 4 Å molecular sieves. Benzene and 1,4-dioxane were distilled over Na/benzophenone under argon, and stored over activated 4 Å molecular sieves. Toluene, THF, Et$_2$O, CH$_2$Cl$_2$ and CH$_3$CN were dried by passage through a column of activated alumina, under nitrogen.
atmosphere. KHMDS and KOt-Bu were sublimed under high vacuum prior to use. NaH (60% w/w suspension in mineral oils) was washed with anhydrous n-hexane prior to use. Neutralized silica gel was prepared by suspending silica gel in EtOAc containing Et3N (1 mL / 50 g of silica gel) followed by concentration of the solvents and drying under high vacuum for overnight. Imidazolium salts A and B were prepared according to known literature procedures. Triazolium salts E and H were purchased from Sigma-Aldrich. All other chemical reagents were purchased from commercial suppliers and used as such without further purification. Electrospray-ionization high-resolution mass (ESI-HRMS) spectra were recorded on a QSTAR Pulsar (AB/MDS Sciex) apparatus. Electron-impact high-resolution mass (EI-HRMS) spectra were recorded on a DFS-Thermofischer instrument. Chiral separations were carried out on a Waters SFC apparatus using OD-3 column. Temperature = 30 °C. Methanol gradient: 10% → 1% / min → 25%. X-ray data were measured using Cu radiation on a SuperNova Dual source equipped with an Atlas detector.

Synthesis of Substrates

General Procedure A: Synthesis of Ynals (6a-b, 6d-g, 6j-k)

\[
\begin{align*}
\text{R} &= \text{Br} \\
\text{O} &= \text{H} \\
\text{CBr}_4, \text{Ph}_3\text{P} &\rightarrow \text{R} \quad \text{Br} \quad \text{Br} \\
\text{CBr}_4, \text{Ph}_3\text{P} &\rightarrow \text{R} \quad \text{Br} \quad \text{Br} \\
\text{1) n-BuLi, THF, -40 °C} \quad &\rightarrow \text{R} \quad \text{Br} \quad \text{Br} \\
\text{2) DMF, -40 °C to rt} \quad &\rightarrow \text{R} \quad \text{Br} \quad \text{Br} \\
\text{3) KH}_2\text{PO}_4 \text{aq.} \quad &\rightarrow \text{R} \quad \text{Br} \quad \text{Br}
\end{align*}
\]

A well-stirred solution of alkyne (1.0 equiv.) in anhydrous THF (0.4 M) was cooled down to -40 °C. n-BuLi (1.6 M solution in hexanes, 1.1 equiv.) was then added dropwise via syringe. The solution was stirred at -40 °C for 15 min, and anhydrous DMF (2.0 equiv.) was added in one portion. The mixture was allowed to slowly reach ambient temperature. After stirring for further 1 h, the reaction mixture was poured into a vigorously stirred mixture of NaH2PO4 and tert-butyl methyl ether. The layers were separated and the aqueous layer was extracted with tert-butyl methyl ether. The combined organic layers were washed with brine, dried over anhydrous Na2SO4, filtered and concentrated under reduced pressure. The crude oil was purified by flash chromatography on silica gel using n-hexane/EtOAc as eluent.

General Procedure B: Synthesis of Ynals (6c, 6h-i)

\[
\begin{align*}
\text{R} &= \text{Br} \\
\text{O} &= \text{H} \\
\text{CBr}_4, \text{Ph}_3\text{P} &\rightarrow \text{R} \quad \text{Br} \quad \text{Br} \\
\text{CBr}_4, \text{Ph}_3\text{P} &\rightarrow \text{R} \quad \text{Br} \quad \text{Br} \\
\text{1) n-BuLi (2.0 equiv.)} \quad &\rightarrow \text{R} \quad \text{Br} \quad \text{Br} \\
\text{2) DMF, -40 °C to rt} \quad &\rightarrow \text{R} \quad \text{Br} \quad \text{Br} \\
\text{3) KH}_2\text{PO}_4 \text{aq.} \quad &\rightarrow \text{R} \quad \text{Br} \quad \text{Br}
\end{align*}
\]

First Step To a solution of aldehyde (1.0 equiv.) and CBr4 (1.05 equiv.) in anhydrous CH2Cl2 (0.45 M) cooled down to 0 °C (ice/water bath) was added Ph3P (2.1 equiv.) as a solid in small portions. The resultant yellow reaction mixture was then stirred at ambient temperature for 4 h. Solvent was removed in vacuo, and the residue was dissolved in n-hexane. Triphenylphosphine oxide was filtered off by suction. The filtrate was concentrated under
reduced pressure, and the crude gem-dibromide was purified by flash chromatography on silica gel using n-hexane/EtOAc as eluent.

**Second Step** A well-stirred solution of gem-dibromide (1.0 equiv.) in anhydrous THF (0.4 M) was cooled down to -40 °C. n-BuLi (1.6 M solution in hexanes, 2.05 equiv.) was then added dropwise via syringe. The solution was stirred at -40 °C for 15 min, and anhydrous DMF (2.0 equiv.) was added in one portion. The mixture was allowed to slowly reach ambient temperature. After stirring for further 1 h, the reaction mixture was poured into a vigorously stirred mixture of NaH₂PO₄ and tert-butyl methyl ether. The layers were separated and the aqueous layer was extracted with tert-butyl methyl ether. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude oil was purified by flash chromatography on silica gel using n-hexane/EtOAc as eluent.

**General Procedure C: Synthesis of Symmetrical α-Cyano-1,4-Diketones (7a-h, 7p)**

First Step (Conditions a) A mixture of arylaldehyde (1.0 equiv.) and KCN (2.0 equiv.) in absolute DMSO (1.4 M) was stirred at ambient temperature under an argon atmosphere in an ultrasound bath for 30 min. The resultant orange mixture was then diluted with water and extracted three times with methyl tert-butyl ether. The combined organic layers were washed two times with water, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude benzoin was purified by flash chromatography on silica gel using n-hexane/EtOAc as eluent.

First Step (Conditions b) Thiamine hydrochloride (5 mol%) was dissolved in absolute EtOH (3.0 M), and Et₃N (30 mol%) and arylaldehyde (1.0 equiv.) were added sequentially. The resultant mixture was stirred at ambient temperature, under an inert atmosphere. The solution presented a light-yellow color, turning to dark-orange in 25 min. The reaction progress was followed by TLC on silica gel (n-Hex/EtOAc 4:1). After 24 h of stirring, the product started to precipitate. The mixture was stirred for a further 48 h, and then diluted with ethyl acetate, and 5% (v/v) aqueous HCl was added. The layers were separated, and the aqueous layer was extracted twice with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The crude benzoin was purified by flash chromatography on silica gel using n-hexane/EtOAc as eluent.

Second Step A well-stirred solution of benzoin (1.0 equiv.), NH₄NO₃ (1.25 equiv.), and Cu(OAc)₂•H₂O (1.0 mol%) in AcOH/water (4:1 v/v, 1.0 M) was heated at reflux under open-air conditions for 90 min. Upon cooling down to ambient temperature, the desired benzil crystallized out of the reaction mixture. The resultant light-yellow crystals were recovered by...
vacuum filtration, washed abundantly with water, and recrystallized from boiling ethanol or boiling benzene.

**Third Step** To a cooled (0 °C, ice/water bath) solution of benzil (1.0 equiv.), anhydrous acrylonitrile (1.2 equiv.) and Me₂SiCN (0.5 equiv.) in anhydrous THF (0.18 M) was added (n-Bu)₄NF (1 M solution in THF, 0.5 equiv.) dropwise via syringe. The resultant deep-orange solution was stirred at ambient temperature under an inert atmosphere for 2 h. The mixture was then poured into water, the organic solvent was removed in vacuo, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel using n-hexane/EtOAc as eluent.

**General Procedure D: Synthesis of Unsymmetrical α-Cyano-1,4-Diketones (7i–n, 7q)**

\[
\begin{align*}
\text{Ar}^1\text{O} - \text{CN} & + \text{Ar}^2\text{O} - \text{Br} & \xrightarrow{\text{K₂CO₃, EtOH, rt}} & \text{Ar}^1\text{O} - \text{CN} - \text{Ar}^2
\end{align*}
\]

To a well-stirred solution of 2-bromoacetophenone (1.5 equiv.) and benzoylacetonitrile (1.0 equiv.) in anhydrous EtOH (0.25 M), was added anhydrous K₂CO₃ (2.5 equiv.) as a solid in one portion. The resulting light-orange mixture was stirred at ambient temperature for 12 h. After the reaction was over (monitoring by TLC on silica gel, n-Hex/EtOAc 4:1), 10% (v/v) aqueous HCl (40 mL) was added to quench the reaction, and organic solvents were concentrated under reduced pressure. The residue was extracted twice with ethyl acetate. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and liberated of solvents in vacuo. The obtained crude product was purified by flash chromatography on silica gel using n-hexane/EtOAc as eluent.

**General Procedure E: Synthesis of a Symmetrical Alkyl α-Cyano-1,4-Diketone (7o)**

\[
\begin{align*}
\text{MeO} \xrightarrow{\text{NaOMe, MeOH, rt}} & \text{Na}^{+} \xrightarrow{\text{H₂O, reflux}} & \xrightarrow{\text{KOH, MeOH/water}} \\
\text{MeO} - \text{CO₂Et} & + \text{MeO} - \text{CN} & \text{MeO} - \text{CN}
\end{align*}
\]
3-Phenylpropionaldehyde (6a)  

According to General Procedure A 1-phenylacetylene (2.20 mL, 20 mmol, 1.0 equiv.), n-BuLi (1.6 M solution in hexanes, 14.0 mL, 22 mmol, 1.1 equiv.), anhydrous THF (50 mL), followed by DMF (3.10 mL, 40 mmol, 2.0 equiv.). The crude oil was purified by flash chromatography on silica gel (n-hexane → n-hexane/EtO 99:1). Light-yellow oil. Isolated yield 71% (1.85 g, 14.2 mmol). R_f (silica gel, c-Hex/EtOAc 95:5) 0.53. ¹H NMR (400 MHz, CDCl_3): δ 9.43 (1H, s, CH=O), 7.61 (2H, d, J 7.0, ortho-C^H), 7.41 (2H, t, J 7.7, meta-C^H) ppm. ¹³F NMR (376 MHz, CD_2Cl_2): δ -106.2 (1F, s, C^2F) ppm.

3-(4-Fluorophenyl)propionaldehyde (6b)  

According to General Procedure A 1-ethynyl-4-fluorobenzene (1.0 g, 8.33 mmol, 1.0 equiv.), n-BuLi (1.6 M solution in hexanes, 5.47 mL, 8.75 mmol, 1.05 equiv.), anhydrous THF (25 mL), followed by DMF (1.30 mL, 16.7 mmol, 2.0 equiv.). The crude residue was purified by flash chromatography on silica gel (n-hexane/EtO 95:5), affording a white crystalline solid. Isolated yield 86% (1.06 g, 7.16 mmol). R_f (silica gel, c-Hex/EtOAc 4:1) 0.45. ¹H NMR (400 MHz, CD_2Cl_2): δ 9.40 (1H, s, CH=O), 7.62-7.67 (2H, m, C^αH), 7.14 (2H, t, J 8.7, J_2 1.9, C^γH) ppm. ¹³F NMR (376 MHz, CD_2Cl_2): δ -106.2 (1F, s, C^2F) ppm.

1-Chloro-4-(2,2-dibromovinyl)benzene  

According to General Procedure B 4-chlorobenzaldehyde (2.0 g, 14.2 mmol, 1.0 equiv.), CBr_4 (4.94 g, 14.9 mmol, 1.05 equiv.), Ph_3P (7.82 g, 29.8 mmol, 2.1 equiv.), anhydrous CH_2Cl_2 (30 mL). The crude residue was purified by flash chromatography on silica gel (n-hexane). Colorless oil. Isolated yield 87% (3.68 g, 12.4 mmol). R_f (silica gel, c-Hex/EtO 99:1) 0.70. ¹H NMR (400 MHz, CD_2Cl_2): δ 7.49-7.52 (2H, AA'XX' d, J 8.6, C^αH), 7.48 (1H, s, C=CH), 7.34-7.38 (2H, AA'XX' d, J 8.6, C^αH) ppm.

3-(4-Chlorophenyl)propionaldehyde (6c)  

According to General Procedure B 1-chloro-4-(2,2-dibromovinyl)benzene (3.12 g, 10.5 mmol, 1.0 equiv.), n-BuLi (1.6 M solution in hexanes, 13.5 mL, 21.5 mmol, 2.05 equiv.), anhydrous THF (35 mL), followed by DMF (1.67 mL, 21.5 mmol, 2.05 equiv.). The crude residue was purified by flash chromatography on silica gel (n-hexane/EtO 95:5 → 9:1), affording a white crystalline solid (recrystallized from benzene). Isolated yield 71% (1.22 g, 7.41 mmol). R_f (silica gel, c-Hex/EtOAc 98:2) 0.63. ¹H NMR (400 MHz, CD_2Cl_2): δ 9.40 (1H,
s, aldehydic CH=O), 7.56-7.58 (2H, AA’XX’ d, J 8.6, C'\nH), 7.41-7.43 (2H, AA’XX’ d, J 8.6, C'\nH) ppm. $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ 177.1 (aldehydic CH=O), 138.1 (ipso(Cl)-Cq), 135.0 (CH), 129.8 (CH), 118.5 (para(Cl)-Cq), 93.5 (alkyne Cq), 89.3 (alkyne Cq) ppm.

3-(\(\rho\)-Tolyl)propiolaldehyde (6d)

![Chemical Structure](image)

Chemical Formula: C$_{10}$H$_8$O  
Molecular Weight: 144.17

According to General Procedure A 4-ethynyltoluene (1.01 mL, 8.00 mmol, 1.0 equiv.), n-BuLi (1.6 M solution in hexanes, 5.25 mL, 8.40 mmol, 1.05 equiv.), anhydrous THF (20 mL), followed by DMF (1.25 mL, 16.0 mmol, 2.0 equiv.). The crude residue was purified by flash chromatography on silica gel (n-hexane $\rightarrow$ n-hexane/EtOAc 99:1), affording a light-orange oil. Isolated yield 97% (1.12 g, 7.77 mmol). $R_f$ (silica gel, c-Hex/EtOAc 4:1) 0.69. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 9.40 (1H, s, CH=O), 7.52 (2H, AA’XX’ d, J 8.2, ortho-C'\nH), 7.24 (2H, AA’XX’ d, J 7.9, meta-C’\nH), 2.40 (3H, s, CH$_3$) ppm. $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ 177.3 (aldehyde CH=O), 143.0 (Cq), 133.8 (CH), 130.1 (CH), 116.8 (Cq), 95.8 (Cq), 88.8 (Cq), 22.1 (CH$_3$) ppm.

3-(4-Methoxyphenyl)propiolaldehyde (6e)

![Chemical Structure](image)

Chemical Formula: C$_{10}$H$_8$O$_2$  
Molecular Weight: 160.17

According to General Procedure A 4-ethynylanisole (1.0 g, 7.57 mmol, 1.0 equiv.), n-BuLi (1.6 M solution in hexanes, 5.0 mL, 7.95 mmol, 1.05 equiv.), anhydrous THF (20 mL), followed by DMF (1.17 mL, 15.1 mmol, 2.0 equiv.). The crude residue was purified by flash chromatography on silica gel (n-hexane/EtOAc 98:2), affording a white crystalline solid. Isolated yield 91% (1.10 g, 6.87 mmol). $R_f$ (silica gel, c-Hex/EtOAc 4:1) 0.53. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 9.38 (1H, s, CH=O), 7.58 (2H, AA’XX’ d, J 8.8, ortho-C’\nH), 6.93 (2H, AA’XX’ d, J 8.8, meta-C’\nH), 3.85 (3H, s, O-CH$_3$) ppm.

3-(2-Methoxyphenyl)propiolaldehyde (6f)

![Chemical Structure](image)

Chemical Formula: C$_{10}$H$_8$O$_2$  
Molecular Weight: 160.17

According to General Procedure A 2-ethynylanisole (1.0 g, 7.57 mmol, 1.0 equiv.), n-BuLi (1.6 M solution in hexanes, 5.0 mL, 7.95 mmol, 1.05 equiv.), anhydrous THF (20 mL), followed by DMF (1.17 mL, 15.1 mmol, 2.0 equiv.). The crude residue was purified by flash chromatography on silica gel (n-hexane/EtO$_2$ 98:2), affording a colorless oil. Isolated yield 88% (1.07 g, 6.68 mmol). $R_f$ (silica gel, c-Hex/EtOAc 4:1) 0.59. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 9.43 (1H, d, J 1.2, CH=O), 7.55 (1H, d, J 7.5, C'\nH), 7.48 (1H, t, J 8.2, C'\nH), 6.98 (2H, t, J 8.6, C'\nH), 3.92 (3H, d, J 1.0, O-CH$_3$) ppm. $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ 177.3 (aldehyde CH=O), 162.5 (O-Cq), 135.7 (CH), 133.8 (CH), 121.3 (CH), 111.7 (CH), 109.1 (Cq), 93.1 (Cq), 92.5 (Cq), 56.5 (O-CH$_3$) ppm.
3-(3-Chlorophenyl)propiolaldehyde (6g)

According to General Procedure A 3-chloro-1-ethynylbenzene (1.0 g, 7.32 mmol, 1.0 equiv), n-BuLi (1.6 M solution in hexanes, 4.81 mL, 7.69 mmol, 1.05 equiv.), anhydrous THF (20 mL), followed by DMF (1.14 mL, 14.6 mmol, 2.0 equiv.). The crude residue was purified by flash chromatography on silica gel (n-hexane/EtOAc 99:1), affording a colorless oil. Isolated yield 65% (780 mg, 4.74 mmol). \( R_f \) (silica gel, c-Hex/EtOAc 4:1) 0.62. \( ^1H \) NMR (400 MHz, CDCl\(_2\)): \( \delta \) 9.41 (1H, s, \( \text{C} = \text{O} \)), 7.61 (1H, t, \( J = 1.8 \), \( \text{C}^\text{ar} \)), 7.49-7.54 (2H, m, \( \text{C}^\text{ar} \)), 7.38 (1H, t, \( J = 7.8 \), \( \text{C}^\text{ar} \)) ppm.

2-(2,2-dibromovinyl)furan

According to General Procedure B 2-furaldehyde (828 \( \mu \)L, 10.0 mmol, 1.0 equiv.), CBr\(_4\) (4.97 g, 15.0 mmol, 1.5 equiv.), Ph\(_3\)P (7.87 g, 30.0 mmol, 3.0 equiv.), anhydrous CH\(_2\)Cl\(_2\) (25 mL). The crude residue was purified by flash chromatography on silica gel (n-hexane). Light-yellow oil. Isolated yield 79% (2.0 g, 7.94 mmol). \( R_f \) (silica gel, c-Hex/EtOAc 9:1) 0.81. \( ^1H \) NMR (400 MHz, CDCl\(_2\)): \( \delta \) 7.47 (1H, d, \( J = 1.7 \), \( \text{C}^\text{ar} \)), 7.43 (1H, s, \( \text{C} = \text{C} \)), 6.96 (1H, d, \( J = 3.5 \), \( \text{C}^\text{ar} \)), 6.49 (1H, dd, \( J_1 = 3.5 \), \( J_2 = 1.8 \), \( \text{C}^\text{ar} \)) ppm.

3-(furan-2-yl)propiolaldehyde (6h)

According to General Procedure B 2-(2,2-dibromovinyl)furan (2.0 g, 7.94 mmol, 1.0 equiv.), n-BuLi (1.6 M solution in hexanes, 9.93 mL, 15.9 mmol, 2.05 equiv.), anhydrous THF (25 mL), followed by DMF (1.24 mL, 15.9 mmol, 2.05 equiv.). The crude residue was purified by flash chromatography on silica gel (n-hexane/EtOAc 98:2), affording a light-brown oil. Isolated yield 90% (860 mg, 7.16 mmol). \( R_f \) (silica gel, c-Hex/EtOAc 9:1) 0.39. \( ^1H \) NMR (400 MHz, CDCl\(_2\)): \( \delta \) 9.39 (1H, s, aldehydic \( \text{C} = \text{O} \)), 7.61 (1H, d, \( J = 1.7 \), \( \text{C}^\text{ar} \)), 7.07 (1H, d, \( J = 3.6 \), \( \text{C}^\text{ar} \)), 6.55 (1H, dd, \( J_1 = 3.6 \), \( J_2 = 1.8 \), \( \text{C}^\text{ar} \)) ppm. \( ^13C \) NMR (100 MHz, CDCl\(_2\)): \( \delta \) 176.1 (aldehydic \( \text{CH} = \text{O} \)), 148.0 (O-CH), 134.8 (O-Cq), 123.3 (CH), 112.7 (CH), 94.5 (alkyne Cq), 85.0 (alkyne Cq) ppm.

5-(2,2-dibromovinyl)benzo[1,3]dioxole

According to General Procedure B piperonal (1.50 g, 10.0 mmol, 1.0 equiv.), CBr\(_4\) (4.97 g, 15.0 mmol, 1.5 equiv.), Ph\(_3\)P (7.87 g, 30.0 mmol, 3.0 equiv.), anhydrous CH\(_2\)Cl\(_2\) (25 mL). The crude residue was purified by flash chromatography on silica gel (n-hexane/Et\(_2\)O 95:5 → 9:1). Colorless oil. Isolated yield
64% (1.95 g, 6.37 mmol). Rf (silica gel, c-Hex/EtOAc 9:1) 0.54. 1H NMR (400 MHz, CD2Cl2): δ 7.41 (1H, s, C=CH), 7.19 (1H, d, J 1.7, C=H), 6.97 (1H, dd, J 8.1, J 2 1.7, C=H), 6.81 (1H, d, J 8.1, C=H), 5.99 (2H, s, O-CH2-O) ppm.

3-(benzo[1,3]dioxol-5-yl)propiolaldehyde (6i)

According to General Procedure B 5-(2,2-dibromovinyl)benzo[1,3]dioxole (1.90 g, 6.21 mmol, 1.0 equiv.), n-BuLi (1.6 M solution in hexanes, 8.0 mL, 12.7 mmol, 2.05 equiv.), anhydrous THF (25 mL), followed by DMF (1.0 mL, 12.7 mmol, 2.05 equiv.). The crude residue was purified by flash chromatography on silica gel (n-hexane/EtOAc 95:5), affording a light-yellow crystalline solid. Isolated yield 93% (1.01 g, 5.80 mmol). Rf (silica gel, c-Hex/EtOAc 9:1) 0.28. 1H NMR (400 MHz, CD2Cl2): δ 9.36 (1H, s, aldehydic CH=O), 7.21 (1H, dd, J 8.1, J 2 1.4, C=H), 7.03 (1H, d, J 1.3, C=H), 6.85 (1H, d, J 8.0, C=H), 6.05 (2H, s, acetal O-CH2-O) ppm. 13C NMR (100 MHz, CD2Cl2): δ 177.1 (aldehydic CH=O), 151.3 (O-Cq), 148.5 (O-Cq), 130.0 (CH), 113.0 (CH), 112.8 (Cq), 109.4 (CH), 102.8 (acetal O-CH2-O), 96.0 (alkyne Cq), 88.3 (alkyne Cq) ppm.

3-Cyclopropylpropiolaldehyde (6j)

According to General Procedure A 1-cyclopropylacetylene (2.0 mL, 23.6 mmol, 1.0 equiv.), n-BuLi (1.6 M solution in hexanes, 15.5 mL, 24.8 mmol, 1.05 equiv.), anhydrous THF (35 mL), followed by DMF (3.67 mL, 47.2 mmol, 2.0 equiv.). The crude residue was purified by flash chromatography on silica gel (eluting with n-pentane), affording a colorless oil. Isolated yield 92% (2.04 g, 21.7 mmol). Rf (silica gel, c-Hex/EtOAc 9:1) 0.62. 1H NMR (400 MHz, CD2Cl2): δ 9.10 (1H, d, J 1.2, CH=O), 1.43-1.50 (1H, m, cyclopropyl CH), 1.00-1.06 (2H, m, cyclopropyl CH2), 0.92-0.99 (2H, m, cyclopropyl CH2) ppm. 13C NMR (100 MHz, CD2Cl2): δ 177.3 (aldehyde CH=O), 104.0 (Cq), 78.0 (Cq), 10.5 (CH2), 0.24 (CH) ppm.

Oct-2-ynal (6k)

According to General Procedure A 1-heptyne (1.58 mL, 12.0 mmol, 1.0 equiv.), n-BuLi (1.6 M solution in hexanes, 7.88 mL, 12.6 mmol, 1.05 equiv.), anhydrous THF (20mL), followed by DMF (1.87 mL, 24.0 mmol, 2.0 equiv.). The crude residue was purified by flash chromatography on silica gel (eluting with n-hexane), affording a colorless oil. Isolated yield 97% (1.45 g, 11.6 mmol). Rf (silica gel, c-Hex/ EtOAc 9:1) 0.75. 1H NMR (400 MHz, CD2Cl2): δ 9.16 (1H, s, CH=O), 2.42 (2H, t, J 7.1, propargylic CH2), 1.60 (2H, quin., J 7.0, CH2), 1.26-1.43 (4H, m, CH2), 0.91 (3H, t, J 7.1, CH3) ppm. 13C NMR (100 MHz, CD2Cl2): δ 177.8 (aldehyde CH=O), 99.7 (Cq), 82.0 (Cq), 31.5 (CH2), 27.9 (CH2), 22.7 (CH2), 19.5 (CH2), 14.2 (CH3) ppm.
2-Benzoyl-4-oxo-4-phenylbutanenitrile (7a)

According to General Procedure C benzil (1.0 g, 4.76 mmol, 1.0 equiv.), anhydrous acrylonitrile (347 µl, 5.23 mmol, 1.1 equiv.), Me$_3$SiCN (319 µl, 2.38 mmol, 0.5 equiv.), anhydrous THF (25 ml), followed by (n-Bu)$_3$NF (1 M solution in THF, 2.38 ml, 2.38 mmol, 0.5 equiv.). The crude residue was purified by flash chromatography on silica gel (c-hexane/EtOAc 98:2 → 95:5 → 9:1), affording a colorless oil that crystallized slowly upon standing in the refrigerator. Isolated yield 32% (400 mg, 1.52 mmol). R$_f$ (silica gel, c-Hex/EtOAc 4:1) 0.28. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.09 (2H, dd, J, 8.6, J$_2$ 1.4, ortho-$C^\equivN$), 7.99 (2H, dd, J, 8.5, J$_2$ 1.4, ortho-$C^\equivN$), 7.48-7.70 (6H, m, C$^awH$), 5.05 (1H, dd, J, 8.9, J$_2$ 4.4, CH-CN), 4.10 (1H, dd, J, 18.0, J$_2$ 8.9, diastereotopic CH$_2$), 3.56 (1H, dd, J, 18.0, J$_2$ 4.4, diastereotopic CH$_2$) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 194.8 (ketone Cq), 189.1 (ketone Cq), 135.4 (Cq), 134.8 (CH), 134.2 (CH), 134.1 (Cq), 129.23 (CH), 129.15 (CH), 129.0 (CH), 128.4 (CH), 117.1 (C≡N), 37.7 (CH$_2$), 33.3 (CH) ppm.

1,2-Bis(4-fluorophenyl)-2-hydroxyethanone

According to General Procedure C 4-fluorobenzaldehyde (1.76 g, 14.2 mmol, 1.0 equiv.), KCN (1.85 g, 28.4 mmol, 2.0 equiv.) in absolute DMSO (20 ml). The crude residue was purified by flash chromatography on silica gel (c-hexane/EtOAc 98:2 → 95:5 → 9:1) to afford a white crystalline solid. Isolated yield 81% (1.43 g, 5.76 mmol). R$_f$ (silica gel, c-Hex/EtOAc 4:1) 0.16. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.90-7.95 (2H, m, C$^awH$), 7.27-7.32 (2H, m, C$^awH$), 7.00-7.11 (4H, m, C$^awH$), 5.89 (1H, d, J 5.8, α-carbonyl CH), 4.51 (1H, d, J 5.9, OH) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -102.5 (1F, s, C$^awF$), -112.6 (1F, s, C$^awF$) ppm.

1,2-Bis(4-fluorophenyl)ethane-1,2-dione

According to General Procedure C 1,2-bis(4-fluorophenyl)-2-hydroxyethanone (1.41 g, 5.68 mmol, 1.0 equiv.), NH$_4$NO$_3$ (568 mg, 7.10 mmol, 1.25 equiv.), and Cu(OAc)$_2$•H$_2$O (11 mg, 0.057 mmol, 1.0 mol%) in AcOH/water (5.0 ml, 4:1 v/v). Purified by recrystallization from boiling ethanol. Pale-yellow needles. Isolated yield 86% (1.19 g, 4.83 mmol). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.99-8.05 (4H, m, C$^awH$), 7.17-7.23 (4H, m, C$^awH$) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -100.9 (1F, s, C$^awF$) ppm.
According to General Procedure C 1,2-bis(4-fluorophenyl)ethane-1,2-dione (1.09 g, 4.43 mmol, 1.0 equiv.), anhydrous acrylonitrile (353 µL, 5.32 mmol, 1.2 equiv.), Me$_3$SiCN (297 µL, 2.22 mmol, 0.5 equiv.), anhydrous THF (24 mL), followed by (n-Bu)$_4$NF (1 M solution in THF, 2.22 mL, 2.22 mmol, 0.5 equiv.). The crude residue was purified by flash chromatography on silica gel (c-hexane/EtOAc 98:2 → 95:5), affording a light-yellow oil that crystallized slowly upon standing in the fridge. Isolated yield 26% (345 mg, 1.15 mmol). R$_f$ (silica gel, c-Hex/EtOAc 4:1) 0.31. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.14 (2H, dd, J$_1$ 8.4, J$_2$ 5.4, Car H), 8.03 (2H, dd, J$_1$ 8.4, J$_2$ 5.5, Car H), 7.16-7.26 (4H, m, Car H), 4.99 (1H, dd, J$_1$ 9.1, J$_2$ 4.0, CH-CN), 4.08 (1H, dd, J$_1$ 17.9, J$_2$ 9.2, diastereotopic CH$_2$), 3.52 (1H, dd, J$_1$ 17.9, J$_2$ 4.0, diastereotopic CH$_2$) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -101.5 (1F, s, Car F), -102.9 (1F, s, Car F) ppm.

According to General Procedure C 4-chlorobenzaldehyde (2.0 g, 14.2 mmol, 1.0 equiv.), KCN (1.85 g, 28.4 mmol, 2.0 equiv.) in absolute DMSO (20 mL). The crude residue was purified by flash chromatography on silica gel (c-hexane/EtOAc 98:2 → 95:5 → 9:1) to afford a white crystalline solid. Isolated yield 78% (1.56 g, 5.54 mmol). R$_f$ (silica gel, c-Hex/EtOAc 4:1) 0.23. $^1$H NMR (400 MHz, CDCl$_3$): δ 6.80-6.84 (2H, m, Car H), 6.37-6.41 (2H, m, Car H), 6.29-6.32 (2H, m, Car H), 6.23-6.26 (2H, m, Car H), 4.88 (1H, d, J 5.9, α-carbonyl CH), 3.49 (1H, d, J 5.9, OH) ppm.

According to General Procedure C 1,2-bis(4-chlorophenyl)ethane-1,2-dione (1.40 g, 4.98 mmol, 1.0 equiv.), NH$_4$NO$_3$ (498 mg, 6.22 mmol, 1.25 equiv.), and Cu(OAc)$_2$•H$_2$O (10 mg, 0.05 mmol, 1.0 mol%) in AcOH/water (5.0 mL, 4:1 v/v). The crude residue was recrystallized from boiling benzene. Pale-yellow needles. Isolated yield 81% (1.12 g, 4.02 mmol). R$_f$ (silica gel, c-Hex/EtOAc 4:1) 0.55. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.90-7.93 (4H, m, Car H, AA’XX’ spin-system), 7.48-7.52 (4H, m, Car’H, AA’XX’ spin-system) ppm.
2-(4-Chlorobenzoyl)-4-(4-chlorophenyl)-4-oxobutanenitrile (7c)

According to General Procedure C

1,2-bis(4-chlorophenyl)ethane-1,2-dione (1.10 g, 3.94 mmol, 1.0 equiv.), anhydrous acrylonitrile (315 µL, 4.73 mmol, 1.2 equiv.), Me₃SiCN (264 µL, 1.97 mmol, 0.5 equiv.), anhydrous THF (20 mL), followed by (n-Bu)₃NF (1 M solution in THF, 1.97 mL, 1.97 mmol, 0.5 equiv.).

The crude residue was purified by flash chromatography on silica gel (c-hexane/THF 92:8 → 95:5), affording a light-yellow powder. Isolated yield 23% (305 mg, 0.92 mmol).

Rᵣ (silica gel, c-Hex/THF 4:1) 0.33. ¹H NMR (400 MHz, CDCl₃): δ 8.03 (2H, d, J 8.7, C'₂H), 7.93 (2H, d, J 8.7, C'₃H), 7.54 (2H, d, J 8.6, C'₄H), 7.49 (2H, d, J 8.6, C'₅H), 4.97 (1H, dd, J₁ 9.2, J₂ 4.1, CH-CN), 4.07 (1H, dd, J₁ 18.0, J₂ 9.2, diastereotopic CH₂), 3.52 (1H, dd, J₁ 18.0, J₂ 4.1, diastereotopic CH₂) ppm.

1,2-Bis(4-bromophenyl)-2-hydroxyethanone

According to General Procedure C

4-bromobenzaldehyde (2.15 g, 11.6 mmol, 1.0 equiv.), thiamine hydrochloride (196 mg, 0.58 mmol, 5 mol%), Et₃N (490 µL, 3.48 mmol, 30 mol%), absolute EtOH (3.5 mL). The crude residue was triturated from cold methanol, affording a white crystalline solid. Isolated yield 38% (2.27 g, 10.2 mmol).

Rᵣ (silica gel, c-Hex/THF 4:1) 0.31. ¹H NMR (400 MHz, CDCl₃): δ 7.74 (2H, AA’XX’ d, J 8.6, C’₂H), 7.55 (2H, AA’XX’ d, J 8.6, C’₃H), 7.46 (2H, AA’XX’ d, J 8.4, C’₄H), 7.18 (2H, AA’XX’ d, J 8.4, C’₅H), 5.86 (1H, brs, J 4.6, α-carbonyl CH), 4.49 (1H, brs, J 4.6, OH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 197.8 (ketone Cq), 137.8 (Cq), 132.6 (CH), 132.4 (CH), 132.0 (Cq), 130.6 (CH), 129.7 (Cq), 129.5 (CH), 123.1 (Cq), 75.7 (CH-O) ppm.

1,2-Bis(4-bromophenyl)ethane-1,2-dione

According to General Procedure C

1,2-bis(4-bromophenyl)-2-hydroxyethanone (2.10 g, 5.68 mmol, 1.0 equiv.), NH₄NO₃ (568 mg, 7.10 mmol, 1.25 equiv.), and Cu(OAc)₂·H₂O (12 mg, 0.06 mmol, 1.0 mol%) in AcOH/water (6.0 mL, 4:1 v/v). The crude residue was recrystallized from boiling benzene. Pale-yellow needles. Isolated yield 95% (938 mg, 4.22 mmol).

Rᵣ (silica gel, c-Hex/THF 4:1) 0.65. ¹H NMR (400 MHz, CDCl₃): δ 7.83 (4H, AA’XX’ d, J 8.5, C’₂H), 7.67 (4H, AA’XX’ d, J 8.5, C’₃H) ppm.
According to General Procedure C 1,2-bis(4-bromophenyl)ethane-1,2-dione (1.56 g, 4.24 mmol, 1.0 equiv.), anhydrous acetonitrile (338 µL, 5.09 mmol, 1.2 equiv.), Me$_3$SiCN (284 µL, 2.12 mmol, 0.5 equiv.), anhydrous THF (25 mL), followed by (n-Bu)$_2$NF (1 M solution in THF, 2.12 mL, 2.12 mmol, 0.5 equiv.). The crude residue was purified by flash chromatography on silica gel (n-hexane/EtOAc 98:2 → 95:5 → 9:1), affording a light-yellow powder. Isolated yield 26% (464 mg, 1.10 mmol). R$_f$ (silica gel, c-Hex/EtOAc 4:1) 0.44. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ 7.93-7.97 (2H, AA'XX' d, J 8.6, C$^a$H), 7.84-7.87 (2H, AA'XX' d, J 8.6, C$^a$H), 7.66-7.69 (2H, AA'XX' d, J 8.6, C$^a$H), 7.60 (2H, AA'XX' d, J 8.6, C$^a$H), 4.96 (1H, dd, J$_1$ 18.1, J$_2$ 8.6, diastereotopic CH$_2$), 3.58 (1H, dd, J$_1$ 18.1, J$_2$ 4.6, diastereotopic CH$_2$) ppm. $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): δ 194.4 (ketone Cq), 189.0 (ketone Cq), 134.6 (Cq), 133.4 (Cq), 133.0 (CH), 132.8 (CH), 130.9 (CH), 130.6 (Cq), 130.3 (CH), 129.8 (Cq), 117.2 (C≡N), 38.2 (CH$_2$), 33.9 (CH) ppm.

2-Hydroxy-1,2-di-p-tolylethane

According to General Procedure C p-tolualdehyde (1.68 mL, 14.2 mmol, 1.0 equiv.), KCN (1.85 g, 28.4 mmol, 2.0 equiv.) in absolute DMSO (20 mL). The crude residue was purified by flash chromatography on silica gel (c-hexane/EtOAc 99:1 → 95:5) to afford a white crystalline solid. Isolated yield 56% (939 mg, 3.91 mmol). R$_f$ (silica gel, c-Hex/EtOAc 4:1) 0.42. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.82 (2H, d, J 8.2, ortho-C$^a$H), 7.17-7.22 (4H, m, C$^a$H), 7.12 (2H, d, J 7.9, C$^a$H), 5.89 (1H, d, J 5.8, α-carbonyl CH), 4.54 (1H, d, J 5.8, OH), 2.35 (3H, s, CH$_3$), 2.29 (3H, s, CH$_3$) ppm.

1,2-Di-p-tolylethane-1,2-dione

According to General Procedure C 2-hydroxy-1,2-di-p-tolylethane (932 mg, 3.88 mmol, 1.0 equiv.), NH$_4$NO$_3$ (388 mg, 4.85 mmol, 1.25 equiv.), and Cu(OAc)$_2$•H$_2$O (8 mg, 0.04 mmol, 1.0 mol%) in AcOH/water (5.0 mL, 4:1 v/v). The crude residue was recrystallized from boiling ethanol. Pale-yellow needles. Isolated yield 94% (866 mg, 3.63 mmol). R$_f$ (silica gel, c-Hex/EtOAc 4:1) 0.66. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.86 (4H, d, J 8.2, ortho-C$^a$H), 7.30 (4H, d, J 8.2, meta-C$^a$H), 2.43 (6H, s, CH$_3$) ppm.
2-(4-Methylbenzoyl)-4-oxo-4-(p-tolyl)butanenitrile (7e)  

![Chemical Structure](image)

According to General Procedure C 1,2-di-p-tolyldiethane-1,2-dione (866 mg, 3.63 mmol, 1.0 equiv.), anhydrous acrylonitrile (289 μL, 4.36 mmol, 1.2 equiv.), Me3SiCN (244 μL, 1.82 mmol, 0.5 equiv.), anhydrous THF (20 mL), followed by (n-Bu)3NF (1 M solution in THF, 1.82 mL, 1.82 mmol, 0.5 equiv.). The crude residue was purified by flash chromatography on silica gel (n-hexane/EtOAc 98:2 → 95:5), affording a white crystalline solid. Recrystallized from boiling benzene. Isolated yield 27% (272 mg, 0.95 mmol). Rf (silica gel, c-Hex/EtOAc 4:1) 0.40. 1H NMR (500 MHz, CDCl3): δ 7.89 (2H, d, J 8.3, CαH), 7.79 (2H, d, J 8.2, Cα′H), 7.24 (2H, d, J 8.2, CαH′), 7.20 (2H, d, J 8.2, Cα′H′), 4.93 (1H, dd, J1 8.8, J2 4.5, CH-CN), 3.95 (1H, dd, J1 17.9, J2 8.8, diastereotopic CH2), 2.35 (3H, s, CH3), 2.33 (3H, s, CH3) ppm. 13C NMR (125 MHz, CDCl3): δ 194.4 (ketone Cq), 188.7 (ketone Cq), 152.3 (Cq), 133.1 (Cq), 131.7 (Cq), 129.9 (CH), 129.7 (CH), 129.3 (CH), 128.52 (CH), 128.47 (CH), 117.4 (C≡N), 37.6 (CH2), 33.2 (CH), 21.97 (CH3), 21.89 (CH3) ppm.

2-Hydroxy-1,2-bis(4-(trifluoromethyl)phenyl)ethanone  

![Chemical Structure](image)

According to General Procedure C 4-(trifluoromethyl)benzaldehyde (1.95 mL, 14.2 mmol, 1.0 equiv.), KCN (1.85 g, 28.4 mmol, 2.0 equiv.) in absolute DMSO (25 mL). The crude residue was purified by flash chromatography on silica gel (c-hexane/EtOAc 98:2 → 95:5 → 9:1) to afford a white crystalline solid. Recrystallized yield 56% (316 mg, 3.96 mmol). Rf (silica gel, c-Hex/EtOAc 4:1) 0.13. 1H NMR (400 MHz, CDCl3): δ 8.01 (2H, d, J 8.2, CαH), 7.70 (2H, d, J 8.2, Cα′H), 7.60 (2H, d, J 8.1, Cα′H′), 7.46 (2H, d, J 8.0, CαH′), 6.02 (1H, d, J 4.7, α-carbonyl CH), 4.50 (1H, d, J 5.4, OH) ppm. 19F NMR (376 MHz, CDCl3): δ -62.8 (3F, s, CF3), -63.4 (3F, s, CF3) ppm.

1,2-Bis(4-(trifluoromethyl)phenyl)ethane-1,2-dione  

![Chemical Structure](image)

According to General Procedure C 2-hydroxy-1,2-bis(4-(trifluoromethyl)phenyl)ethanone (1.10 g, 3.16 mmol, 1.0 equiv.), NH4NO3 (316 mg, 3.95 mmol, 1.25 equiv.), and Cu(OAc)2·H2O (6 mg, 0.03 mmol, 1.0 mol%) in AcOH/water (5.0 mL, 4:1 v/v). The crude residue was recrystallized from boiling benzene. Yellow needles. Isolated yield 94% (1.03 g, 2.97 mmol). Rf (silica gel, c-Hex/EtOAc 4:1) 0.78. 1H NMR (400 MHz, CDCl3): δ 8.12 (4H, d, J 8.1, CαH, AA′BB′ spin-system), 7.81 (4H, d, J 8.2, Cα″H, AA′BB′ spin-system) ppm. 19F NMR (376 MHz, CDCl3): δ -63.4 (3F, s, CF3) ppm.
4-Oxo-2-(4-(trifluoromethyl)benzoyl)-4-(4-(trifluoromethyl)phenyl)butanenitrile (7f)

According to General Procedure C 1,2-bis(4-(trifluoromethyl)phenyl)ethane-1,2-dione (1.03 g, 2.97 mmol, 1.0 equiv.), anhydrous acetonitrile (236 μL, 3.56 mmol, 1.2 equiv.), Me₃SiCN (200 μL, 1.49 mmol, 0.5 equiv.), anhydrous THF (20 mL), followed by (n-Bu)₂NF (1 M solution in THF, 1.49 mL, 1.49 mmol, 0.5 equiv.). The crude residue was purified by flash chromatography on silica gel (c-hexane/EtOAc 95:5 → 9:1), affording a light-yellow oil that crystallized slowly upon standing in the fridge. This solid was recrystallized from benzene/n-hexane. Light-yellow crystalline solid. Isolated yield 27% (318 mg, 0.79 mmol). R₇ (silica gel, c-Hex/EtOAc 4:1) 0.25. ¹H NMR (400 MHz, CD₂Cl₂): δ 8.22 (2H, d, J 8.2, C₅H₆), 8.12 (2H, d, J 8.2, C₅H₆), 7.86 (2H, d, J 8.4, C₅H₆), 7.81 (2H, d, J 8.4, C₅H₆), 5.03 (1H, dd, J 9.3, J 3.9, CH-CN), 4.11 (1H, dd, J 18.1, J 9.3, diastereotopic CH₂), 3.69 (1H, dt, J 18.1, J 1.1, C₅H₆), 3.56 (1H, dd, J 18.1, J 3.9, diastereotopic CH₂) ppm. ¹³C NMR (376 MHz, CD₂Cl₂): δ 194.6 (ketone Cq), 189.2 (ketone Cq), 138.5 (Cq), 137.4 (Cq), 136.1 (q, J₁C 32, Cq-CF₃), 135.6 (q, J₁C 33, Cq-CF₃), 130.0 (CH), 129.2 (CH), 126.8 (q, J₁C 4, CH), 126.5 (q, J₁C 4, CH), 116.8 (C≡N), 38.5 (CH₂), 34.4 (CH) ppm.

1,2-Bis(3-chlorophenyl)-2-hydroxyethanone

According to General Procedure C 3-chlorobenzaldehyde (3.17 mL, 28.0 mmol, 1.0 equiv.), thiamine hydrochloride (472 mg, 1.40 mmol, 5 mol%), Et₃N (1.18 mL, 8.40 mmol, 30 mol%), absolute EtOH (9.0 mL). The crude residue was purified by flash chromatography on silica gel (n-hexane/EtOAc 95:5 → 9:1), affording a white crystalline solid. Isolated yield 31% (1.23 g, 4.38 mmol). R₇ (silica gel, c-Hex/EtOAc 4:1) 0.35. ¹H NMR (400 MHz, CD₂Cl₂): δ 8.09 (1H, t, J 1.8, C₅H₆), 8.00 (1H, dt, J 7.8, J 1.3, C₅H₆), 7.90 (1H, t, J 1.8, C₅H₆), 7.76 (1H, J 8, 7.8, J 1.4, J 1.1, C₅H₆), 7.62 (1H, dd, J 8, J 2, J 2, J 3, 1.1, C₅H₆), 7.54 (1H, dd, J 8, J 2, J 3, 1.0, C₅H₆), 7.46 (1H, t, J 7, J 7.9, C₅H₆), 7.38 (1H, t, J 8, C₅H₆), 6.03 (1H, s, α-carbonyl CH), 4.37 (1H, brs, OH) ppm.

1,2-Bis(3-chlorophenyl)ethane-1,2-dione

According to General Procedure C 1,2-bis(3-chlorophenyl)-2-hydroxyethanone (1.23 g, 4.38 mmol, 1.0 equiv.), NH₄NO₃ (439 mg, 5.48 mmol, 1.25 equiv.), and Cu(OAc)₂·H₂O (8.7 mg, 0.04 mmol, 1.0 mol%) in AcOH/water (5.0 mL, 4:1 v/v). The crude residue was recrystallized from boiling ethanol. Pale-yellow needles. Isolated yield 47% (580 mg, 2.08 mmol). R₇ (silica gel, c-Hex/EtOAc 4:1) 0.63. ¹H NMR (400 MHz, CDCl₃): δ 7.97 (2H, t, J 1.8, C₅H₆), 7.84 (2H, dt, J 7.8, J 1.2, C₅H₆), 7.65 (2H, dd, J 8, J 2, J 8, J 2, 1.0, C₅H₆), 7.47 (2H, t, J 7, J 7.9, C₅H₆) ppm.
2-(3-Chlorobenzoyl)-4-(3-chlorophenyl)-4-oxobutanenitrile (7g)

According to General Procedure C, 1,2-bis(3-chlorophenyl)ethane-1,2-dione (574 mg, 2.06 mmol, 1.0 equiv.), anhydrous acrylonitrile (164 µL, 2.47 mmol, 1.2 equiv.), Me$_2$SiCN (138 µL, 1.03 mmol, 0.5 equiv.), anhydrous THF (13 mL), followed by (n-Bu)$_2$NF (1 M solution in THF, 1.03 mL, 1.03 mmol, 0.5 equiv.). The crude residue was purified by flash chromatography on silica gel (n-hexane/EtOAc 98:2 → 95:5), affording a light-yellow thick oil. Isolated yield 25% (173 mg, 0.52 mmol). R$_f$ (silica gel, c-Hex/EtOAc 4:1) 0.45. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 8.05 (1H, brs, C$^a$/H), 7.95-8.00 (2H, m, C$^a$/H), 7.89 (1H, d, J 7.8, C$^a$/H), 7.69 (1H, dt, J 1.8, J 8.0, C$^a$/H), 7.63 (1H, dt, J 8.0, J 2.0, C$^a$/H), 7.55 (1H, t, J 7.8, C$^a$/H), 7.49 (1H, t, J 7.9, C$^a$/H), 4.97 (1H, dd, J 8.6, J 4.6, CH-CN), 4.02 (1H, dd, J 18.1, J 2.6, diastereotopic CH$_2$), 3.60 (1H, dd, J 18.2, J 4.6, diastereotopic CH$_2$) ppm.

1,2-Bis(3-bromophenyl)-2-hydroxyethanone

According to General Procedure C, 3-bromobenzaldehyde (2.15 g, 11.6 mmol, 1.0 equiv.), thiamine hydrochloride (196 mg, 0.58 mmol, 5 mol%), Et$_3$N (490 µL, 3.48 mmol, 30 mol%), absolute EtOH (3.8 mL). The crude residue was purified by flash chromatography on silica gel (n-hexane/EtOAc 95:5 → 9:1). White crystalline solid. Isolated yield 84% (1.81 g, 4.86 mmol). R$_f$ (silica gel, c-Hex/EtOAc 4:1) 0.28. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.06 (1H, t, J 1.8, C$^a$/H), 7.77 (1H, dt, J 1.6, J 1.4, C$^a$/H), 7.67 (1H, dt, J 1.4, J 1.2, C$^a$/H), 7.47 (1H, t, J 1.8, C$^a$/H), 7.42 (1H, dt, J 1.7, J 2.2, J 1.2, C$^a$/H), 7.19-7.32 (3H, m, C$^a$/H), 5.86 (1H, s, a-carbonyl CH), 4.50 (1H, brs, OH) ppm.

1,2-Bis(3-bromophenyl)ethane-1,2-dione

According to General Procedure C, 1,2-bis(3-bromophenyl)-2-hydroxyethanone (1.80 g, 4.86 mmol, 1.0 equiv.), NH$_4$NO$_3$ (486 mg, 6.08 mmol, 1.25 equiv.), and Cu(OAc)$_2$•H$_2$O (10 mg, 0.05 mmol, 1.0 mol%) in AcOH/water (5.0 mL, 4:1 v/v). The crude residue was recrystallized from boiling ethanol. Pale-yellow needles. Isolated yield 94% (1.68 g, 4.56 mmol). R$_f$ (silica gel, c-Hex/EtOAc 4:1) 0.66. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.12 (2H, t, J 1.8, C$^a$/H), 7.88 (2H, d, J 7.8, C$^a$/H), 7.81 (2H, d, J 8.1, C$^a$/H), 7.41 (2H, t, J 7.9, C$^a$/H) ppm.
2-(3-Bromobenzoyl)-4-(3-bromophenyl)-4-oxobutanenitrile (7h)

According to General Procedure C, 1,2-bis(3-bromophenyl)ethane-1,2-dione (1.66 g, 4.51 mmol, 1.0 equiv.), anhydrous acrylonitrile (389 µL, 5.86 mmol, 1.3 equiv.), Me$_3$SiCN (303 µL, 2.26 mmol, 0.5 equiv.), and anhydrous THF (28 mL) followed by (n-Bu)$_3$NF (1 M solution in THF, 2.26 mL, 2.26 mmol, 0.5 equiv.). The crude residue was purified by flash chromatography on silica gel (n-hexane/EtOAc 98:2 → 95:5 → 9:1), affording a light-yellow crystalline solid. Isolated yield 26% (464 mg, 1.10 mmol). R$_f$ (silica gel, c-Hex/EtOAc 4:1) 0.44. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.20 (1H, t, J 1.8, C$^a$H), 8.12 (1H, t, J 1.8, C$^a$H), 8.03 (1H, dq, J 7.8, J 2.1, C$^a$H), 7.93 (1H, dq, J 7.8, J 1.1, C$^a$H), 7.82 (1H, dq, J 8.0, J 0.9, C$^a$H), 7.79 (1H, dq, J 8.0, J 0.9, C$^a$H), 7.49 (1H, t, J 7.9, C$^a$H), 7.43 (1H, t, J 7.8, C$^a$H), 4.96 (1H, dd, J 8.6, J 2.4, CH-CN), 4.02 (1H, dd, J 18.2, J 8.6, diastereotopic CH$_2$), 3.60 (1H, dd, J 18.2, J 2.4, diastereotopic CH$_2$) ppm.

1,2-Bis(2-fluorophenyl)-2-hydroxyethanone

According to General Procedure C, 2-fluorobenzaldehyde (1.50 mL, 14.0 mmol, 1.0 equiv.), KCN (1.80 g, 28.0 mmol, 2.0 equiv.) in absolute DMSO (20 mL). The crude residue was purified by flash chromatography on silica gel (n-hexane/EtOAc 98:2 → 95:5), affording a white crystalline solid. Isolated yield 76% (1.32 g, 5.32 mmol). R$_f$ (silica gel, c-Hex/EtOAc 4:1) 0.19. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.87 (1H, td, J 7.2, J 1.8, C$^a$H), 7.45-7.51 (1H, m, C$^a$H), 7.18-7.27 (3H, m, C$^a$H), 7.07 (1H, td, J 7.6, J 2.7, C$^a$H), 6.97-7.04 (2H, m, C$^a$H), 6.08 (1H, td, J 2.3, α-carbonyl CH), 4.45 (1H, brs, OH) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -107.9 (1F, d, J$^{F-F}$ 8.7, C$^{aF}$), -117.6 (1F, d, J$^{F-F}$ 8.3, C$^{aF}$) ppm.

1,2-Bis(2-fluorophenyl)ethane-1,2-dione

According to General Procedure C, 1,2-bis(2-fluorophenyl)-2-hydroxyethanone (1.32 g, 5.32 mmol, 1.0 equiv.), NH$_4$NO$_3$ (532 mg, 6.65 mmol, 1.25 equiv.), and Cu(OAc)$_2$·H$_2$O (10 mg, 0.05 mmol, 1.0 mol%) in AcOH/water (5.0 mL, 4:1 v/v). The crude residue was recrystallized from boiling ethanol. White powder. Isolated yield 42% (548 mg, 2.23 mmol). R$_f$ (silica gel, c-Hex/EtOAc 4:1) 0.59. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.08 (2H, td, J 8.4, J 2.7, C$^a$H), 7.63-7.68 (2H, m, C$^a$H), 7.35 (2H, td, J 7.8, J 2.0, C$^a$H), 7.15 (2H, td, J 10.2, J 0.5, C$^a$H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -108.3 (1F, s, C$^{aF}$) ppm.
2-(2-Fluorobenzoyl)-4-(2-fluorophenyl)-4-oxobutanenitrile (7p)

According to General Procedure C, 1,2-bis(2-fluorophenyl)ethane-1,2-dione (1.66 g, 4.51 mmol, 1.0 equiv.), anhydrous acrylonitrile (389 μL, 5.86 mmol, 1.3 equiv.), Me₂SiCN (303 μL, 2.26 mmol, 0.5 equiv.), and anhydrous THF (28 mL), followed by (n-Bu)₂NF (1 M solution in THF, 2.26 mL, 2.26 mmol, 0.5 equiv.). The crude residue was purified by flash chromatography on silica gel (n-hexane/EtOAc 95:5), affording a colorless oil. Isolated yield 37% (260 mg, 0.87 mmol). Rᵣ (silica gel, c-Hex/EtOAc 4:1) 0.28.¹H NMR (400 MHz, CD₂Cl₂): δ 7.91 (2H, td, J₁ 7.8, J₂ 1.4, C₆H), 7.59-7.71 (2H, m, C₁₅H), 7.35 (1H, td, J₁ 8.0, J₂ 1.0, C₆H), 7.20-7.31 (3H, m, C₁₅H), 4.89 (1H, ddd, J₁ 7.8, J₂ 5.0, J₃ 0.4, CH-CN), 3.96 (1H, ddd, J₁ 18.7, J₂ 7.8, J₃ 3.0, J₄ 1.4, diastereotopic CH₂), 3.64 (1H, ddd, J₁ 18.7, J₂ 4.8, J₃ 3.2, diastereotopic CH₂) ppm.¹⁹F NMR (376 MHz, CD₂Cl₂): δ -108.8 (1F, s, C₆F), -109.6 (1F, s, C₆F) ppm.¹³C NMR (100 MHz, CD₂Cl₂): δ 193.2 (d, Jₖ-F 4.0, ketone Cₖ), 188.5 (d, Jₖ-F 3.5, ketone Cₖ), 163.0 (d, Jₖ-F 254, ipso(F)-Cₖ), 162.3 (d, Jₖ-F 253, ipso(F)-Cₖ), 136.8 (d, Jₖ-F 9.0, meta(F)-CH), 136.4 (d, Jₖ-F 9.2, meta(F)-CH), 131.9 (d, Jₖ-F 1.6, para(F)-CH), 131.2 (d, Jₖ-F 1.9, para(F)-CH), 125.7 (d, Jₖ-F 3.4, meta(F)-CH), 125.4 (d, Jₖ-F 3.4, meta(F)-CH), 124.4 (d, Jₖ-F 12, ortho(F)-Cₖ), 123.7 (d, Jₖ-F 12, ortho(F)-Cₖ), 117.6 (d, Jₖ-F 6.6, ortho(F)-CH), 117.4 (d, Jₖ-F 6.6, ortho(F)-CH), 117.1 (C=N), 42.8 (d, Jₖ-F 9.6, CH₂), 38.9 (dd, J₁-Cₖ 7.5, J₂-Cₖ 2.5, CH) ppm.

2-(4-Fluorobenzoyl)-4-oxo-4-phenylbutanenitrile (7i)

According to General Procedure D, 2-bromoacetophenone (916 mg, 4.60 mmol, 1.5 equiv.), 4-fluorobenzoylacetonitrile (500 mg, 3.06 mmol, 1.0 equiv.), anhydrous K₂CO₃ (1.06 g, 7.65 mmol, 2.5 equiv.), absolute EtOH (18 mL). The obtained crude product was purified by flash chromatography on silica gel (c-hexane/EtOAc 98:2 → 95:5), affording a light-orange crystalline solid. Isolated yield 56% (480 mg, 1.70 mmol). Rᵣ (silica gel, c-Hex/EtOAc 4:1) 0.30.¹H NMR (400 MHz, CDCl₃): δ 8.12-8.16 (2H, AA’XX’ m, ortho(F)-C₆H), 7.99 (2H, dd, J₁ 8.3, J₂ 1.2, meta(F)-C₆H), 7.64 (1H, tt, J₁ 6.2, J₂ 1.2, C₆H), 7.52 (2H, t, J 8.0, C₆H), 7.24 (2H, t, J 8.7, C₆H), 5.01 (1H, dd, J₁ 9.1, J₂ 4.1, CH-CN), 4.12 (1H, dd, J₁ 18.0, J₂ 9.2, diastereotopic CH₂), 3.56 (1H, dd, J₁ 18.0, J₂ 4.1, diastereotopic CH₂) ppm.¹⁹F NMR (376 MHz, CDCl₃): δ -101.7 (1F, s, C₆F) ppm.¹³C NMR (100 MHz, CDCl₃): δ 194.8 (ketone Cₖ), 187.5 (ketone Cₖ), 166.8 (d, Jₖ-F 256, ipso(F)-Cₖ), 135.4 (Cₖ), 134.3 (CH), 132.0 (d, Jₖ-F 9, meta(F)-CH), 130.6 (d, Jₖ-F 3, para(F)-Cₖ), 129.1 (CH), 128.4 (CH), 117.0 (C=N), 116.6 (d, Jₖ-F 22, ortho(F)-CH), 37.7 (CH₂), 33.2 (CH) ppm.
crude product was purified by flash chromatography on silica gel (n-hexane/EtOAc 95:5 → 92:8), affording a light-orange crystalline solid. Isolated yield 40% (345 mg, 1.24 mmol). Rf (silica gel, c-Hex/EtOAc 4:1) 0.36. \(^1\)H NMR (400 MHz, CD$_2$Cl$_2$): δ 7.97-8.01 (4H, m, C$_n$H$_n$), 7.65 (1H, t, J 7.4, J$_1$ 1.9, C$_{ar}$H$_1$), 7.52 (2H, t, J 7.9, C$_{ar}$H$_2$), 7.38 (2H, d, J 8.0, C$_{ar}$H$_2$), 5.02 (1H, dd, J 8.4, J$_2$ 4.9, CH-CN), 4.03 (1H, dd, J 18.1, J$_2$ 8.4, diastereotopic CH$_2$), 3.60 (1H, dd, J 18.1, J$_2$ 4.9, diastereotopic CH$_2$), 2.46 (3H, s, CH$_3$) ppm. \(^1^3\)C NMR (100 MHz, CD$_2$Cl$_2$): δ 195.3 (ketone Cq), 189.4 (ketone Cq), 146.7 (Cq), 136.0 (Cq), 134.5 (CH), 132.1 (Cq), 130.3 (CH), 129.6 (CH), 129.4 (CH), 128.7 (CH), 117.8 (C≡N), 38.3 (CH$_2$), 33.9 (CH), 22.1 (CH$_2$) ppm.

2-(4-Methoxybenzoyl)-4-oxo-4-phenylbutanenitrile (7k)

According to General Procedure D 2-bromoacetoephone (852 mg, 4.28 mmol, 1.5 equiv.), 4-methoxybenzoylacetonitrile (500 mg, 2.85 mmol, 1.0 equiv.), anhydrous K$_2$CO$_3$ (985 mg, 7.13 mmol, 2.5 equiv.), absolute EtOH (18 mL). The obtained crude product was purified by flash chromatography on silica gel (n-hexane/EtOAc 95:5 → 85:15), affording a light-yellow crystalline solid. Isolated yield 41% (340 mg, 1.16 mmol). Rf (silica gel, c-Hex/EtOAc 4:1) 0.21. \(^1\)H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.07 (2H, AA’XX’ d, J 9.0, C$_{ar}$H$_2$), 8.00 (2H, d, J 7.2, C$_{ar}$H$_1$), 7.65 (1H, t, J 7.4, J$_1$ 1.2, C$_{ar}$H$_1$), 7.52 (2H, t, J 7.5, C$_{ar}$H$_2$), 7.05 (2H, AA’XX’ d, J 9.0, C$_{ar}$H$_2$), 5.01 (1H, dd, J$_1$ 8.4, J$_2$ 4.8, CH-CN), 4.02 (1H, dd, J$_1$ 18.0, J$_2$ 8.4, diastereotopic CH$_2$), 3.91 (3H, s, O-CH$_3$), 3.58 (1H, dd, J$_1$ 18.0, J$_2$ 4.8, diastereotopic CH$_2$) ppm. \(^1^3\)C NMR (100 MHz, CD$_2$Cl$_2$): δ 195.4 (ketone Cq), 188.0 (ketone Cq), 165.4 (Cq-OMe), 136.0 (Cq), 134.5 (CH), 131.9 (CH), 129.4 (CH), 128.7 (CH), 127.4 (Cq), 118.0 (C≡N), 114.9 (CH), 56.3 (O-CH$_3$), 38.3 (CH$_2$), 33.6 (CH) ppm.

2-Benzoyl-4-(4-fluorophenyl)-4-oxobutanenitrile (7l)

According to General Procedure D 2-bromo-4-1-fluoroacetoephone (897 mg, 4.13 mmol, 1.2 equiv.), benzoylacetonitrile (500 mg, 3.44 mmol, 1.0 equiv.), anhydrous K$_2$CO$_3$ (1.19 g, 8.60 mmol, 2.5 equiv.), absolute EtOH (18 mL). The obtained crude product was purified by flash chromatography on silica gel (n-hexane/EtOAc 95:5), affording a light-yellow crystalline solid. Isolated yield 58% (564 mg, 2.01 mmol). Rf (silica gel, c-Hex/EtOAc 4:1) 0.31. \(^1\)H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.08 (2H, d, J 7.2, C$_{ar}$H$_1$), 8.01-8.06 (2H, AA’XX’ m, meta(F)-C$_{ar}$H$_2$), 7.72 (1H, t, J 7.4, J$_1$ 1.8, C$_{ar}$H$_1$), 7.59 (2H, t, J 8.1, C$_{ar}$H$_2$), 7.18-7.23 (2H, AA’XX’ m, ortho(F)-C$_{ar}$H$_2$), 5.03 (1H, dd, J$_1$ 8.5, J$_2$ 4.8, CH-CN), 4.02 (1H, dd, J$_1$ 18.0, J$_2$ 8.5, diastereotopic CH$_2$), 3.59 (1H, dd, J$_1$ 18.0, J$_2$ 4.8, diastereotopic CH$_2$) ppm. \(^1^9\)F NMR (376 MHz, CD$_2$Cl$_2$): δ -104.3 (1F, s, C$_{ar}$F) ppm. \(^1^3\)C NMR (100 MHz, CD$_2$Cl$_2$): δ 193.8 (ketone Cq), 189.8 (ketone Cq), 166.8 (d, J$_{C-F}$ 254, ipso(F)-Cq), 135.3 (CH), 134.6 (Cq), 132.5 (d, J$_{C-F}$ 3, para(F)-Cq), 131.6 (d, J$_{C-F}$ 10, meta(F)-CH), 129.7 (CH), 129.5 (CH), 117.5 (C≡N), 116.6 (d, J$_{C-F}$ 22, ortho(F)-CH), 38.2 (CH$_2$), 34.0 (CH) ppm.
2-Benzoyl-4-oxo-4-(p-tolyl)butanenitrile (7m)

According to General Procedure D 2-bromo-4'-methylacetophenone (880 mg, 4.13 mmol, 1.2 equiv.), benzoylacetonitrile (500 mg, 3.44 mmol, 1.0 equiv.), anhydrous K$_2$CO$_3$ (1.19 g, 8.60 mmol, 2.5 equiv.), absolute EtOH (18 mL). The obtained crude product was purified by flash chromatography on silica gel (n-hexane/EtOAc 98:2 → 95:5), affording a pale-yellow crystalline solid. Isolated yield 61% (585 mg, 2.11 mmol). $R_f$ (silica gel, c-Hex/EtOAc 4:1) 0.35. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.07-8.09 (2H, AA'XX' d, J 8.1, C'"H), 7.89 (2H, d, J 8.3, C'"H), 7.71 (1H, tt, J 7.5, J 2 1.3, C'"H), 7.58 (2H, t, J 8.0, C'"H), 7.32 (2H, d, J 8.2, C'"H), 5.04 (1H, dd, J 1, J 18.0, J 2 8.4, diastereotopic $CH_2$), 3.60 (1H, dd, J 18.0, J 2 4.9, diastereotopic $CH_2$), 2.43 (3H, s, $CH_3$) ppm. $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): δ 194.8 (ketone $C_q$), 190.0 (ketone $C_q$), 145.8 ($C_q$), 135.2 (CH), 134.7 ($C_q$), 133.5 ($C_q$), 130.0 (CH), 129.6 (CH), 129.4 (CH), 128.8 (CH), 117.7 (C=N), 38.3 (CH$_2$), 34.0 (CH), 22.0 (CH$_3$) ppm.

2-Benzoyl-4-(4-methoxyphenyl)-4-oxobutanenitrile (7n)

According to General Procedure D 2-bromo-4'-methoxyacetophenone (946 mg, 4.13 mmol, 1.2 equiv.), benzoylacetonitrile (500 mg, 3.44 mmol, 1.0 equiv.), anhydrous K$_2$CO$_3$ (1.19 g, 8.60 mmol, 2.5 equiv.), absolute EtOH (18 mL). The obtained crude product was purified by flash chromatography on silica gel (n-hexane/EtOAc 98:2 → 95:1), affording a pale-yellow crystalline solid. Isolated yield 72% (726 mg, 2.48 mmol). $R_f$ (silica gel, c-Hex/EtOAc 4:1) 0.27. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.08 (2H, dd, J 1, J 8.3, J 2 1.1, C'"H), 7.95-7.99 (2H, AA'XX' d, J 9.0, C'"H), 7.71 (1H, tt, J 7.4, J 2 1.2, C'"H), 7.58 (2H, t, J 8.1, C'"H), 6.97-7.00 (2H, AA'XX' d, J 9.0, C'"H), 5.04 (1H, dd, J 1, J 8.4, J 2 4.9, CH-CN), 3.98 (1H, dd, J 1, J 17.9, J 2 8.4, diastereotopic $CH_2$), 3.88 (3H, s, O-$CH_3$), 3.57 (1H, dd, J 1, J 17.9, J 2 4.9, diastereotopic $CH_2$) ppm. $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): δ 193.5 (ketone $C_q$), 190.1 (ketone $C_q$), 164.8 (O-$C_q$), 135.1 (CH), 134.7 ($C_q$), 131.0 (CH), 129.6 (CH), 129.4 (CH), 128.9 ($C_q$), 117.7 (C=N), 114.5 (CH), 56.2 (O-$CH_3$), 38.1 (CH$_2$), 34.0 (CH) ppm.

2-Benzoyl-4-(2-chlorophenyl)-4-oxobutanenitrile (7q)

According to General Procedure D 2-bromo-2'-chloroacetophenone (1.0 g, 4.28 mmol, 1.0 equiv.), benzoylacetonitrile (622 mg, 4.28 mmol, 1.0 equiv.), anhydrous K$_2$CO$_3$ (1.48 g, 10.7 mmol, 2.5 equiv.), absolute EtOH (20 mL). The obtained crude product was purified by flash chromatography on silica gel (n-hexane/EtOAc 98:2 → 95:5), affording a pale-yellow crystalline solid. Isolated yield 84% (1.07 g, 3.60 mmol). $R_f$ (silica gel, c-Hex/EtOAc 4:1) 0.28. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.09 (2H, AA'XX' dd, J 1, J 7.2, J 2 1.4, C'"H), 7.72 (1H, tt, J 7.4, J 2 1.2, C'"H), 7.67 (1H, d, J 7.6, C'"H), 7.59 (2H, t, J
8.0, C\textsuperscript{\textalpha\textbeta\textgamma}H), 7.48-7.50 (2H, m, C\textsuperscript{\textalpha\textbeta\textgamma}H), 7.39-7.44 (1H, m, C\textsuperscript{\textalpha\textbeta\textgamma}H), 5.03 (1H, dd, J\textsubscript{1} 8.5, J\textsubscript{2} 4.8, CH-CN), 3.97 (1H, dd, J\textsubscript{1} 18.2, J\textsubscript{2} 8.5, diastereotopic CH\textsubscript{2}), 3.62 (1H, dd, J\textsubscript{1} 18.2, J\textsubscript{2} 4.8, diastereotopic CH\textsubscript{2}) ppm. \textsuperscript{13}C NMR (100 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \( \delta \) 197.6 (ketone C\textsubscript{q}), 189.7 (ketone C\textsubscript{q}), 137.5 (Cl-C\textsubscript{q}), 135.3 (CH), 134.6 (C\textsubscript{s}), 133.5 (CH), 132.1 (C\textsubscript{q}), 131.5 (CH), 130.4 (CH), 129.7 (CH), 129.5 (CH), 127.8 (CH), 117.3 (C=N), 41.9 (CH\textsubscript{2}), 34.6 (CH) ppm.

**Sodium 1-cyanoprop-1-en-2-olate**

To a cooled (0 °C, ice/water bath) solution of 5-methylisoxazole (2.0 mL, 24.6 mmol, 1.0 equiv.) in anhydrous CH\textsubscript{2}Cl\textsubscript{2} (30 mL), was added NaOMe (5.4 M solution in MeOH, 4.6 mL, 24.6 mmol, 1.0 equiv.). The resultant colorless solution was stirred at ambient temperature for 12 h. Solvents were removed in vacuo, and the crude residue was purified by trituration from anhydrous diethyl ether. White powder. Isolated yield 97% (2.51 g, 23.9 mmol). \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): \( \delta \) 3.15 (1H, s, CH=C), 2.96 (1H, s, CH=C), 1.71 (3H, s, CH\textsubscript{3}), 1.50 (3H, s, CH\textsubscript{3}) ppm.

**Ethyl 4-acetyl-5-amino-2-methylfuran-3-carboxylate**

A solution of the sodium enolate of cyanoacetone (2.0 g, 19.0 mmol, 1.0 equiv.) and ethyl 2-chloroacetoacetate (19.0 mmol, 1.0 equiv.) in water (20 mL) was heated at reflux for 90 min. The brownish precipitate which formed on cooling was collected by vacuum filtration. The crude product was purified by recrystallization from boiling EtOH to afford a white crystalline solid. Isolated yield 77% (3.10 g, 14.6 mmol). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 6.30 (2H, brs, NH\textsubscript{2}), 4.32 (2H, q, J 7.1, O-CH\textsubscript{2}), 2.36 (6H, s, 2 x CH\textsubscript{3}), 1.36 (3H, t, J 7.1, CH\textsubscript{3}) ppm.

**2-Acetyl-4-oxopentanenitrile (7o)**

A solution prepared from aminofuran (3.0 g, 14.2 mmol, 1.0 equiv.), anhydrous KOH (6.0 g, 107 mmol, 7.5), MeOH (40 mL) and water (10 mL) was heated at reflux for 4 h. After cooling down to ambient temperature, the solution was acidified with 3 N aqueous HCl, and organic solvents were concentrated under reduced pressure. The residue was extracted three times with methyl tert-butyl ether. The combined organic layers were washed with brine, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated in vacuo. The crude residue was purified by flash chromatography on silica gel (n-hexane/EtOAc 9:1 → 4:1). Colorless oil. Isolated yield 54% (1.06 g, 7.63 mmol). R\textsubscript{f} (silica gel, c-Hex/EtOAc 3:2) 0.36. \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \( \delta \) 3.81 (1H, dd, J\textsubscript{1} 6.7, J\textsubscript{2} 4.9, CH-CN), 3.16 (1H, dd, J\textsubscript{1} 18.3, J\textsubscript{2} 6.7, diastereotopic CH\textsubscript{2}), 2.98 (1H, dd, J\textsubscript{1} 18.3, J\textsubscript{2} 4.9, diastereotopic CH\textsubscript{2}), 2.45 (3H, s, CH\textsubscript{3}), 2.20 (3H, s, CH\textsubscript{3}) ppm. \textsuperscript{13}C NMR (100 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \( \delta \) 203.7 (ketone C\textsubscript{q}), 197.9 (ketone C\textsubscript{q}), 117.7 (C=N), 42.0 (CH\textsubscript{2}), 38.6 (CH), 29.7 (CH\textsubscript{3}), 29.1 (CH\textsubscript{3}) ppm.
Synthesis of Precatalysts

**5-methoxy-3,4-dihydro-2H-pyrrole**

To a well-stirred solution of pyrrolidin-2-one (309 µL, 4.01 mmol, 1.0 equiv.) in anhydrous CH$_2$Cl$_2$ (20 mL) was added trimethyloxonium tetrafluoroborate (651 mg, 4.41 mmol, 1.1 equiv.) in one portion, and the colorless mixture was stirred at ambient temperature for 16 h, and then diluted with anhydrous diethyl ether. The solution was cooled to 0 °C (ice/water bath) and cold saturated aqueous NaHCO$_3$ (30 mL) was slowly added. The layers were separated and the organic layer was washed once with cold saturated aqueous NaHCO$_3$. The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure to afford a colorless liquid.

Isolated yield 83% (328 mg, 3.31 mmol).

R$_f$ (silica gel, c-Hex/EtOAc 4:1) 0.11. $^1$H NMR (400 MHz, CDCl$_3$): δ 3.80 (3H, s, O-CH$_3$), 3.66 (2H, t, J 7.0, CH$_2$), 2.45 (2H, t, J 8.1, CH$_2$), 2.03 (2H, quin., J 8.0, CH$_2$) ppm.

**2-Mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium chloride (G)**

To a flame-dried sealed flask charged with a solution of 5-methoxy-3,4-dihydro-2H-pyrrole (201 mg, 2.03 mmol, 1.01 equiv.) in anhydrous MeOH (5.0 mL) was added mesitylhydrazine hydrochloride (375 mg, 2.01 mmol, 1.0 equiv.) as a solid in one portion. The flask was sealed under an atmosphere of nitrogen and the mixture was heated at 50 °C for 1 h (during this time it had become deep red in color). The solution was cooled to ambient temperature and concentrated in vacuo. The resulting oil was azeotroped twice with toluene to afford a crude brown solid, which was subsequently triturated several times with anhydrous diethyl ether to afford the hydrazinium chloride (430 mg, 1.70 mmol) as a white powder (85% yield). This was suspended in anhydrous chlorobenzene (1.7 mL, 17.0 mmol, 10 equiv.), and triethyl orthoformate (2.8 mL, 17.0 mmol, 10 equiv.) and anhydrous 4 M HCl in 1,4-dioxane (425 µL, 1.70 mmol, 1.0 equiv.) were added. The mixture was heated at 120 °C for 1 h. The tan solution was cooled to ambient temperature and concentrated in vacuo. The resulting oil was recrystallized from boiling toluene to
give, after drying under high vacuum at 100 °C, the title compound as a beige amorphous solid. Isolated yield 44% (199 mg, 0.75 mmol). \(^1\H NMR\) (400 MHz, CD\(_3\)CN): \(\delta\) 10.61 (1H, s, iminium CH=\(\text{N}^+\)), 7.11 (2H, s, MesH), 4.46 (2H, t, J 7.4, CH\(_2\)), 3.16 (2H, t, J 7.5, CH\(_2\)), 2.81 (2H, \(\text{J}\) 7.8, CH\(_2\)), 2.36 (3H, s, para-MesCH\(_3\)), 2.09 (6H, s, ortho-MesCH\(_3\)) ppm. \(^{13}\C NMR\) (100 MHz, CD\(_3\)CN): \(\delta\) 164.5 (Cq), 142.9 (Cq), 142.8 (CH), 136.3 (Cq), 133.1 (Cq), 130.4 (CH), 48.4 (CH\(_2\)), 27.4 (CH\(_2\)), 22.6 (CH\(_2\)), 21.2 (CH\(_3\)), 17.6 (CH\(_3\)) ppm.

**2-Mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (F)**

A one-necked, round-bottomed flask was charged with 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium chloride (196 mg, 0.74 mmol, 1.0 equiv.) and NaBF\(_4\) (245 mg, 2.23 mmol, 3.0 equiv.). Anhydrous CH\(_2\)Cl\(_2\) (3.0 mL) was then introduced followed by a few drops of absolute acetone. The resultant heterogeneous mixture was vigorously stirred at ambient temperature. After 2 h, the mixture was diluted with water and the layers were separated. The aqueous layer was extracted twice with methylene chloride. The combined organic layers were washed with water, dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated under reduced pressure. The resultant thick oil was triturated three times from anhydrous diethyl ether, affording the title triazolium salt as a beige solid. Isolated yield 99% (230 mg, 0.73 mmol). \(^1\H NMR\) (400 MHz, CD\(_3\)CN): \(\delta\) 9.28 (1H, s, iminium CH=\(\text{N}^+\)), 7.12 (2H, s, MesH), 4.42 (2H, t, J 7.4, CH\(_2\)), 3.18 (2H, t, J 7.5, CH\(_2\)), 2.82 (2H, \(\text{J}\) 7.4, CH\(_2\)), 2.36 (3H, s, para-MesCH\(_3\)), 2.06 (6H, s, ortho-MesCH\(_3\)) ppm. \(^{19}\F NMR\) (376 MHz, CD\(_3\)CN): \(\delta\) -151.74 (1F, s, \(^{10}\text{BF}_4\)), -151.79 (4F, s, \(^{11}\text{BF}_4\)) ppm.

**2-Phenyl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (C)**

To a stirred solution of pyrrolidin-2-one (210 µL, 2.72 mmol, 1.0 equiv.) in anhydrous CH\(_2\)Cl\(_2\) (10 mL) was added trimethylxonium tetrafluoroborate (414 mg, 2.80 mmol, 1.03 equiv.) in one portion, and the colorless mixture was stirred at ambient temperature for 18 h. Phenyldrazine (278 µL, 2.80 mmol, 1.03 equiv.) was then added in one portion via syringe and the resulting orange solution was stirred for a further 18 h at ambient temperature. The mixture was then concentrated in \textit{vacuo} and the resulting tan residue was triturated several times from diethyl ether, and then dried under high vacuum for several hours to give the hydrazone as an off-white solid. Anhydrous toluene (3.0 mL) followed by freshly distilled triethyl orthoformate (1.16 mL, 7.07 mmol, 2.6 equiv.) were then added and the mixture was refluxed for 48 h. Upon cooling down to ambient temperature, the mixture was concentrated in \textit{vacuo} and the resulting dark-orange residue was triturated several times from benzene/diethyl ether (1:1 v/v). The obtained light-tan solid was recrystallized from boiling benzene/acetonitrile. This was then heated under high vacuum at 110 °C for 18 h to remove residual water. Colorless crystalline solid. Isolated yield 57% over 3 steps (420 mg, 1.54 mmol). \(^1\H NMR\) (400 MHz, CD\(_3\)CN): \(\delta\) 9.65 (1H, s, iminium CH=\(\text{N}^+\)), 7.77 (2H, \(dd\), \(J_1\) 8.4, \(J_2\) 1.36, \(C^\text{N}H\)), 7.62-7.67 (3H,
m, C$^a$H), 4.41 (2H, t, J 7.3, CH$_2$), 3.19 (2H, t, J 7.5, CH$_2$), 2.81 (2H, quin., J 7.6, CH$_2$) ppm.  
$^{19}$F NMR (376 MHz, CD$_3$CN): δ -151.69 (1F, s, $^{10}$BF$_4$), -151.74 (4F, s, $^{11}$BF$_4$) ppm.

Benzyldihydrazine

To a well-stirred suspension of benzyldihydrazine monohydrochloride (1.5 g, 9.46 mmol, 1.0 equiv.) in absolute Et$_2$O (30 mL), cooled down to -10 °C, was slowly added 2 N aqueous NaOH (20 mL). The resulting biphasic mixture was stirred vigorously at that temperature for 1 h. The layers were separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with brine, filtered and concentrated in vacuo. The recovered colorless liquid was used immediately without further purification. Isolated yield 42% (486 mg, 3.98 mmol).

$^1$H NMR (400 MHz, CD$_6$D$_6$): δ 7.11-7.19 (5H, m, C$_6$H), 3.49 (2H, s, benzylic CH$_2$), 2.52 (3H, brs, NH) ppm.

2-Benzyl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (D)

A flame-dried Schlenk flask was charged with anhydrous pyrrolidin-2-one (309 µL, 4.01 mmol, 1.0 equiv.) and anhydrous CH$_2$Cl$_2$ (30 mL). Trimethyloxonium tetrafluoroborate (651 mg, 4.41 mmol, 1.1 equiv.) was then added in one portion, and the reaction mixture was stirred for 12 h at 23 °C. Freshly prepared benzyldihydrazine (539 mg, 4.41 mmol, 1.1 equiv.) was then added, and the mixture was stirred at ambient temperature for a further 12 h. The solvent was removed in vacuo, and the product was used without further purification. Triethyl orthoformate (24 mL) was then added and the mixture was stirred at 120 °C for 12 h. The excess orthoformate was removed in vacuo (80 °C, ca. 10$^{-1}$ mbar) to afford the crude product, which was purified by flash chromatography on silica gel (CH$_2$Cl$_2$ → CH$_2$Cl$_2$/MeOH 98:2). Thick light-orange oil. Isolated yield 66% (760 mg, 2.65 mmol). $^1$H NMR (400 MHz, CD$_2$CN): δ 9.25 (1H, s, iminium CH=N+), 7.43-7.44 (5H, m, C$^a$H), 5.49 (2H, s, benzylic CH$_2$), 4.28 (2H, t, J 7.3, CH$_2$), 3.04 (2H, t, J 7.5, CH$_2$), 2.71 (2H, quin., J 7.3, CH$_2$) ppm. $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$): δ -151.48 (1F, s, $^{10}$BF$_4$), -151.53 (4F, s, $^{11}$BF$_4$) ppm. $^{13}$C NMR (100 MHz, CD$_2$CN): δ 164.4 (Cq), 139.6 (iminium CH=N+), 134.0 (Cq), 130.2 (CH), 130.0 (CH), 129.9 (CH), 56.9 (CH$_2$), 48.2 (CH$_2$), 27.4 (CH$_2$), 22.4 (CH$_2$) ppm.

Annulation Products
General Procedure F: NHC-Catalyzed Annulation of α-Cyano-1,4-Diketones with Ynals

A flame-dried Schlenk tube was charged with triazolium salt F (9.5 mg, 0.03 mmol, 10 mol%) and activated powdered 4 Å molecular sieves (ca. 300 mg). The tube was then evacuated and back-filled with dry nitrogen. The ynal (1.05-1.2 equiv.) and the 1,4-diketone (0.30 mmol, 1.0 equiv.) were then added as solutions in anhydrous C₆H₆ (total volume: 3.0 mL). Finally, catalytic NaOBz (5.8 mg, 0.04 mmol, 13 mol%) was added to initiate the reaction. The mixture was then stirred and heated at 40 °C for 12 h, before being passed through a short plug of Celite, washed with methyl tert-butyl ether. The filtrate was concentrated in vacuo, followed by purification of the resultant residue by flash chromatography on neutralized silica gel, eluting with an adequate mixture of n-hexane/EtOAc.

Product (8a)

According to General Procedure F 2-benzoyl-4-oxo-4-phenylbutanenitrile (79 mg, 0.30 mmol, 1.0 equiv.), 3-phenylpropionaldehyde (47 mg, 0.36 mmol, 1.2 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOBz (5.8 mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C₆H₆ (total volume: 3.0 mL) for 14 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 98:2 → 95:5). Light-yellow amorphous solid, which can be recrystallized from boiling methanol to give colorless crystals of a single diastereomer. > 98% conversion (¹H NMR). Isolated yield 86% (102 mg, 0.26 mmol). Diastereomer ratio of the crude reaction mixture: 12:1 d.r. (¹H NMR). Can be improved to 14:1 after passage through a short column of neutralized silica gel. Isolated yield after recrystallization (single diastereomer) 67% (79 mg, 0.20 mmol). Rf (silica gel, c-Hex/EtOAc 4:1) 0.37. ¹H NMR (400 MHz, CD₂Cl₂): δ 8.07-8.09 (2H, m, ortho-C₆H₄), 7.52-7.61 (3H, m, C₆H₄), 7.24-7.39 (10H, m, C₆H₄), 4.12 (1H, dd, J₁ 3.0, J₂ 1.2, ring-junction CH₃), 3.74 (1H, q, J 4.7, benzyl CH₃), 3.03-3.09 (1H, ABX dd, J₁ 17.0, J₂ 5.0, diastereotopic CH₃), 2.97-3.02 (1H, ABKK ddd, J₁ 17.0, J₂ 4.8, J₃ 1.4, diastereotopic CH₂) ppm. ¹³C NMR (100 MHz, CD₂Cl₂): δ 168.5 (ester Cq), 165.3 (enol-ether Cq), 139.25 (Cq), 139.17 (Cq), 132.8 (CH), 130.0 (CH), 129.2 (CH), 129.1 (CH), 127.9 (CH), 127.6 (CH), 127.2 (CH), 126.3 (Cq), 124.6 (CH), 115.9 (nitrile Cq), 112.0 (enol-ether Cq), 83.3 (ketal Cq), 53.8 (CH), 40.1 (CH), 32.3 (CH₂) ppm. ESI-HRMS (positif) M = C₂₆H₁₉NO₃, expected (M+H)⁺ m/z 394.1437, observed (M+H)⁺ m/z 394.1432. Crystals suitable for X-ray diffraction analysis were grown by slow diffusion of n-hexane into a solution of the title compound in sec-butanol. Chiral SFC (AS column, AS10_1A): tr 7.08, 8.01 min.
Product (8b)

According to General Procedure F 2-(4-fluorobenzoyl)-4-(4-fluorophenyl)-4-oxobutane-2-nitrile (90 mg, 0.30 mmol, 1.0 equiv.), 3-phenylpropiolaldehyde (47 mg, 0.36 mmol, 1.2 equiv.), 2-mesityl-6,7-dihydro-5H-pyrylo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOBz (5.8 mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C₆H₆ (total volume: 3.0 mL) for 14 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 98:2 → 95:5). Light-yellow amorphous solid, which can be recrystallized from hot EtOH to give colorless crystals of a single diastereomer. > 98% conversion (1H NMR). Isolated yield 77% (99 mg, 0.23 mmol). Diastereomer ratio of the crude reaction mixture: 10:1 d.r. (1H NMR). Can be improved to 13:1 after passage through a short column of neutralized silica gel. Isolated yield after recrystallization (single diastereomer) 57% (72 mg, 0.17 mmol). 1H NMR (400 MHz, CD₂Cl₂): δ 8.08-8.12 (2H, AA’XX’ m, C’H), 7.21-7.38 (9H, m, C’H), 7.01-7.07 (2H, AA’XX’ m, C’H), 4.11 (1H, d, J 2.4, ring-junction CH), 3.76 (1H, q, J 4.5, benzylic CH), 3.04-3.09 (1H, ABX dd, J, 17.2, J₂ 4.9, diastereotopic CH₂), 2.99-3.03 (1H, ABXX dd, J₁ 17.2, J₂ 4.6, J₃ 1.2, diastereotopic CH₂) ppm. 13C NMR (100 MHz, CD₂Cl₂): δ 168.1 (ester Cq), 165.9 (d, JCF 173, ipso Cq-F), 164.6 (d, JCF 168, ipso Cq-F), 139.5 (Cq), 135.6 (d, JCF 3, Cq), 130.5 (d, JCF 9, CH), 129.7 (CH), 128.4 (CH), 127.5 (CH), 127.4 (d, JCF 9, CH), 123.2 (d, JCF 3, Cq), 116.9 (d, JCF 22, CH), 116.3 (d, JCF 22, CH), 115.8 (nitrite Cq), 112.3 (enol-ether Cq), 83.6 (d, JCF 2, ketal Cq), 54.4 (CH), 40.4 (CH), 32.3 (CH₂) ppm. El-HRMS M = C₃₀H₁₇F₂NO₃, expected m/z 429.1171, observed m/z 429.1168.

Product (8c)

According to General Procedure F 2-(4-chlorobenzoyl)-4-(4-chlorophenyl)-4-oxobutane-2-nitrile (100 mg, 0.30 mmol, 1.0 equiv.), 3-phenylpropiolaldehyde (47 mg, 0.36 mmol, 1.2 equiv.), 2-mesityl-6,7-dihydro-5H-pyrylo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOBz (5.8 mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C₆H₆ (total volume: 3.0 mL) for 14 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 98:2 → 95:5). Light-yellow amorphous solid, which can be recrystallized from hot i-PrOH to give colorless crystals of a single diastereomer. > 98% conversion (1H NMR). Isolated yield 77% (106 mg, 0.23 mmol). Diastereomer ratio of the crude reaction mixture: 9:1 d.r. (1H NMR). Can be improved to 12:1 after passage through a short column of neutralized silica gel. Isolated yield after recrystallization (single diastereomer) 54% (75 mg, 0.16 mmol). Rf (silica gel, c-Hex/EtOAc 4:1) 0.40. 1H NMR (400 MHz, CD₂Cl₂): δ 8.01-8.04 (2H, AA’XX’ d, J 8.7, C’H), 7.51-7.54 (2H, AA’XX’ d, J 8.7, C’H), 7.31-7.38 (5H, m, C’H), 7.20-7.24 (4H, m, C’H), 4.09 (1H, d, J 3.2, ring-junction CH), 3.76 (1H, q, J 4.6, benzylic CH), 3.04-3.09 (1H, ABX dd, J₁ 17.3, J₂ 4.9, diastereotopic CH₂), 2.99-3.03 (1H, ABXX dd, J₁ 17.3, J₂ 4.6, diastereotopic CH₂) ppm. 13C NMR (100 MHz, CD₂Cl₂): δ 167.9 (ester Cq),
Isolated yield after recrystallization (single diastereomer) 63% (79 mg, 0.19 mmol).

Can be improved to 17:1 after passage through a short column of neutralized silica gel.

(101 mg, 0.24 mmol) colorless crystals of a single diastereomer. > 98% conversion (1H NMR).

Product (8e)

According to General Procedure F 2-(4-bromobenzoyl)-4-(4-bromophenyl)-4-oxobutanenitrile (126 mg, 0.30 mmol, 1.0 equiv.), 3-phenylpropionaldehyde (47 mg, 0.36 mmol, 1.2 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOBr (5.8 mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C6H6 (total volume: 3.0 mL) for 14 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 99:1 → 98:2). Light-yellow waxy solid. > 98% conversion (1H NMR).

Isolated yield 84% (138 mg, 0.25 mmol). Diastereomer ratio of the crude reaction mixture: > 12:1 d.r. (1H NMR). Isolated yield of a single diastereomer (after purification by flash chromatography on silica gel) 62% (104 mg, 0.19 mmol). 1H NMR (500 MHz, C6D6): δ 7.59-7.61 (2H, AA’XX’ d, J 8.7, C’sH), 7.10-7.12 (2H, AA’XX’ d, J 8.6, C’arH), 7.05-7.07 (2H, AA’XX’ d, J 8.7, C’sH), 6.94-6.96 (3H, m, C’arH), 6.80-6.82 (2H, m, C’sH), 6.75-6.77 (2H, AA’XX’ d, J 8.6, C’arH), 3.55 (1H, dd, J1, 3.1, J2 1.2, ring-junction CH), 3.16 (1H, q, J 4.9, benzylic CH), 2.41-2.45 (1H, ABKX ddd, J1, 17.3, J2 4.7, J3 1.5, diastereotopic CH2), 2.35-2.40 (1H, ABX dd, J1 17.3, J2 5.1, diastereotopic CH2) ppm. 13C NMR (125 MHz, C6D6): δ 166.6 (ester Cq), 163.8 (enol-ether Cq), 139.2 (Cq), 138.6 (Cq), 132.6 (CH), 132.2 (CH), 129.2 (CH), 128.9 (CH), 128.4 (CH), 127.5 (CH), 127.2 (CH), 126.6 (CH), 125.3 (Cq), 124.3 (Cq), 115.3 (nitrile Cq), 111.7 (enol-ether Cq), 84.6 (ketol Cq), 53.9 (CH), 40.0 (CH), 31.4 (CH2) ppm. EI-HRMS M = C28H17Br2NO3, expected m/z 548.9570, observed m/z 548.9575.

Product (8d)

According to General Procedure F 2-(4-methylbenzoyl)-4-oxy-4-(p-tolyl)butanenitrile (87 mg, 0.30 mmol, 1.0 equiv.), 3-phenylpropionaldehyde (59 mg, 0.45 mmol, 1.5 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOBr (5.8 mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C6H6 (total volume: 3.0 mL) for 20 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 99:1 → 97:3). Light-yellow amorphous solid, which can be recrystallized from hot i-PrOH to give colorless crystals of a single diastereomer. > 98% conversion (1H NMR). Isolated yield 80% (101 mg, 0.24 mmol). Diastereomer ratio of the crude reaction mixture: 14:1 d.r. (1H NMR). Can be improved to 17:1 after passage through a short column of neutralized silica gel. Isolated yield after recrystallization (single diastereomer) 63% (79 mg, 0.19 mmol). 1H NMR...
(400 MHz, CD$_2$Cl$_2$): $\delta$ 7.96 (2H, AA'XX' d, J 8.3, C$^a$H), 7.16-7.38 (13H, m, C$^a$H), 4.09 (1H, dd, J 3.2, J 2.0, ring-junction CH), 3.71 (1H, q, J 4.9, benzylic CH), 2.99-3.05 (1H, ABX dd, J$_1$ 16.9, J$_2$ 5.0, diastereotopic CH$_2$), 2.92-2.98 (1H, ABKX ddd, J$_1$ 16.9, J$_2$ 5.0, J$_3$ 1.5, diastereotopic CH$_2$), 2.44 (3H, s, CH$_3$), 2.35 (3H, s, CH$_3$) ppm. $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ 168.5 (ester Cq), 165.9 (enol-ether Cq), 144.1 (Cq), 140.6 (Cq), 140.0 (Cq), 136.9 (Cq), 130.2 (CH), 130.0 (CH), 129.6 (CH), 128.2 (CH), 127.9 (CH), 127.6 (CH), 124.9 (CH), 124.2 (Cq), 116.3 (nitrile Cq), 112.7 (enol-ether Cq), 83.0 (ketal Cq), 54.2 (CH), 41.0 (CH), 33.0 (CH$_2$), 22.0 (CH$_3$), 21.4 (CH$_3$) ppm. ESI-HRMS $M = C_{26}H_{23}NO_3$, expected (M$^+$)$^+$ m/z 422.1750, observed (M$^+$)$^+$ m/z 422.1742.

**Product (8f)**

According to General Procedure F 4-oxo-2-(4-(trifluoromethyl)benzoyl)-4-(4-(trifluoromethyl)phenyl)butanenitrile (120 mg, 0.30 mmol, 1.0 equiv.), 3-phenylpropiolaldehyde (59 mg, 0.45 mmol, 1.5 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOBz (5.8 mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C$_6$H$_6$ (total volume: 3.0 mL) for 20 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 99:1 → 98:2).

Light-orange oil. Diastereomer ratio of the crude reaction mixture: > 20:1 d.r. ($^1$H NMR). Isolated yield 65% (103 mg, 0.20 mmol). $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ 7.78 (2H, d, J 8.2, C$^a$H), 7.20 (2H, d, J 8.3, C$^a$H), 7.14-7.16 (2H, m, C$^a$H), 6.95-6.97 (3H, m, C$^a$H), 6.93 (2H, d, J 8.3, C$^a$H), 6.81-6.83 (2H, dd, J$_1$ 7.3, J$_2$ 3.4, C$^a$H), 3.56 (1H, t, J 1.1, ring-junction CH), 3.20 (1H, q, J 4.7, benzylic CH), 2.47-2.51 (1H, ABKX ddd, J$_1$ 17.5, J$_2$ 4.4, J$_3$ 1.5, diastereotopic CH$_2$), 2.40-2.45 (1H, ABX dd, J$_1$ 17.5, J$_2$ 5.2, diastereotopic CH$_2$) ppm. $^{19}$F NMR (376 MHz, C$_6$D$_6$): $\delta$ -62.7 (3F, s, CF$_3$), -63.1 (3F, s, CF$_3$) ppm. $^{13}$C NMR (125 MHz, C$_6$D$_6$): $\delta$ 166.4 (ester Cq), 163.2 (enol-ether Cq), 142.9 (Cq), 138.8 (Cq), 133.8 (q, J$_{CF}$ 34, ipso Cq-CF$_3$), 131.9 (q, J$_{CF}$ 33, ipso Cq-CF$_3$), 129.3 (CH), 128.4 (CH), 128.0 (CH), 127.9 (CH), 127.1 (CH), 126.3 (q, J$_{CF}$ 4, CH), 126.0 (q, J$_{CF}$ 4, Cq), 114.8 (nitrile Cq), 111.5 (enol-ether Cq), 86.2 (ketal Cq), 54.0 (CH), 39.8 (CH), 31.1 (CH$_2$) ppm.

**Product (8g)**

According to General Procedure F 2-(3-chlorobenzoyl)-4-(3-chlorophenyl)-4-oxobutanenitrile (99 mg, 0.30 mmol, 1.0 equiv.), 3-phenylpropiolaldehyde (47 mg, 0.36 mmol, 1.2 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOAc (3.3 mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C$_6$H$_6$ (total volume: 3.0 mL) for 14 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 98:2 → 95:5).

Light-orange foam. > 98% conversion ($^1$H NMR). Isolated yield 75% (106 mg, 0.23 mmol). Diastereomer ratio of the crude reaction mixture: 9:1 d.r. ($^1$H NMR). Isolated yield of a single diastereomer (after purification by flash chromatography on silica gel) 47% (65 mg, 0.14
mmol). $^1$H NMR (500 MHz, C$_6$D$_6$): δ 8.07 (1H, t, J 1.9, C$_{2H}$), 7.77 (1H, ddd, J$_1$ 7.9, J$_2$ 1.4, J$_3$ 1.0, C$_{2H}$), 6.94-6.99 (4H, m, C$_{2H}$), 6.91 (1H, ddd, J$_1$ 8.1, J$_2$ 2.0, J$_3$ 1.0, C$_{2H}$), 6.79-6.83 (3H, m, C$_{2H}$), 6.67 (1H, t, J 8.0, C$_{2H}$), 6.59 (1H, t, J 8.0, C$_{2H}$), 3.55 (1H, dd, J$_1$ 2.6, J$_2$ 1.7, ring-junction CH), 3.17 (1H, q, J 4.6, benzylic CH), 2.43-2.47 (1H, ABX ddd, J$_1$ 17.5, J$_2$ 4.2, J$_3$ 1.6, diastereotopic CH$_2$), 2.36-2.40 (1H, ABX dd, J$_1$ 17.5, J$_2$ 5.2, diastereotopic CH$_2$) ppm. $^{13}$C NMR (125 MHz, C$_6$D$_6$): δ 166.5 (ester Cq), 163.1 (enol-ether Cq), 141.4 (Cq), 138.9 (Cq), 135.6 (Cq), 135.1 (Cq), 132.5 (CH), 130.6 (CH), 130.3 (CH), 130.0 (CH), 129.2 (CH), 128.6 (CH), 128.4 (CH), 128.18 (CH), 128.16 (CH), 128.0 (CH), 127.4 (CH), 127.1 (CH), 125.5 (CH), 125.4 (CH), 123.0 (CH), 115.0 (nitrile Cq), 111.5 (enol-ether Cq), 85.3 (ketal Cq), 54.0 (CH), 39.5 (CH), 30.9 (CH$_2$) ppm. EI-HRMS M = C$_{28}$H$_{17}$Br$_2$NO$_3$, expected m/z 461.0580, observed m/z 461.0585.

Product (8h)

According to General Procedure F 2-(3-bromobenzoyl)-4-(3-bromophenyl)-4-oxobutanenitrile (126 mg, 0.30 mmol, 1.0 equiv.), 3-phenylpropiolaldehyde (47 mg, 0.36 mmol, 1.2 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOBz (5.8 mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C$_6$H$_6$ (total volume: 3.0 mL) for 14 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 99:1 → 98:2).

Light-brown waxy solid. > 98% conversion ($^1$H NMR). Isolated yield 70% (116 mg, 0.21 mmol). Diastereomer ratio of the crude reaction mixture: 9:1 d.r. ($^1$H NMR). Isolated yield of a single diastereomer (after purification by flash chromatography on silica gel) 50% (83 mg, 0.15 mmol). $^1$H NMR (500 MHz, C$_6$D$_6$): δ 8.17 (1H, t, J 1.8, C$_{2H}$), 7.79 (1H, dq, J$_1$ 7.9, J$_2$ 0.9, C$_{2H}$), 7.30 (1H, t, J 1.9, C$_{2H}$), 7.14 (1H, dq, J$_1$ 8.1, J$_2$ 0.9, C$_{2H}$), 7.06 (1H, dq, J$_1$ 8.1, J$_2$ 0.9, C$_{2H}$), 6.93-6.97 (3H, m, C$_{2H}$), 6.85 (1H, dq, J$_1$ 7.9, J$_2$ 1.0, C$_{2H}$), 6.79-6.81 (2H, m, C$_{2H}$), 6.61 (1H, t, J 8.0, C$_{2H}$), 6.52 (1H, t, J 8.0, C$_{2H}$), 3.55 (1H, dd, J$_1$ 2.6, J$_2$ 1.6, ring-junction CH), 3.17 (1H, q, J 4.9, benzylic CH), 2.44-2.48 (1H, ABX ddd, J$_1$ 17.6, J$_2$ 4.2, J$_3$ 1.6, diastereotopic CH$_2$), 2.37-2.41 (1H, ABX dd, J$_1$ 17.5, J$_2$ 5.2, diastereotopic CH$_2$) ppm. $^{13}$C NMR (125 MHz, C$_6$D$_6$): δ 166.6 (ester Cq), 163.0 (enol-ether Cq), 141.6 (Cq), 138.9 (Cq), 135.5 (CH), 132.9 (CH), 130.8 (CH), 130.3 (CH), 129.2 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.0 (CH), 127.9 (CH), 127.1 (CH), 125.9 (CH), 123.5 (Cq), 123.4 (CH), 123.2 (Cq), 115.0 (nitrile Cq), 111.4 (enol-ether Cq), 85.3 (ketal Cq), 54.0 (CH), 39.5 (CH), 30.8 (CH$_2$) ppm. EI-HRMS M = C$_{28}$H$_{17}$Br$_2$NO$_3$, expected m/z 548.9570, observed m/z 548.9574.

Product (8i)

According to General Procedure F 2-(4-fluorobenzoyl)-4-oxo-4-phenylbutanenitrile (84 mg, 0.30 mmol, 1.0 equiv.), 3-phenylpropiolaldehyde (47 mg, 0.36 mmol, 1.2 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOBz (5.8 mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C$_6$H$_6$ (total volume: 3.0 mL) for
12 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 99:1 → 97:3). White amorphous solid. > 98% conversion (1H NMR). Isolated yield 80% (98 mg, 0.24 mmol). Diastereomer ratio of the crude reaction mixture: 12:1 d.r. (1H NMR). Isolated yield after purification by flash chromatography on silica gel (single diastereomer) 59% (74 mg, 0.18 mmol).1H NMR (500 MHz, CD2Cl2): δ 7.79-7.83 (2H, AA'XX' m, meta-F-C6H4), 7.14-7.16 (2H, m, C6H4), 6.95-6.98 (6H, m, C6H4), 6.85-6.87 (2H, m, C6H4), 6.58-6.63 (2H, AA'XX' m, ortho(F- C6H4)). 3.72 (1H, d, J 3.1, ring-junction CH), 3.19 (1H, q, J 5.0, benzylic CH), 2.45-2.49 (1H, ABXX ddd, J1 17.3, J2 5.1, J3 1.0, diastereotopic CH2), 2.40-2.44 (1H, ABX dd, J1 17.3, J2 5.1, diastereotopic CH2) ppm.13C NMR (125 MHz, CD2Cl2): δ 173.1 (ester Cq), 169.1 (Cq), 138.9 (Cq), 137.2 (Cq), 130.2 (d, JCF 8.8, meta CH-F), 129.8 (CH), 129.2 (CH), 129.0 (CH), 128.4 (CH), 127.84 (CH), 127.6 (CH), 127.3 (CH), 124.9 (CH), 123.1 (d, JCF 3.8, para Cq-F), 116.4 (d, JCF 21, ortho CH-F), 115.6 (nitrile Cq), 112.2 (enol ether Cq), 83.8 (d, JCF 1.3, ketal Cq), 54.1 (CH), 40.5 (CH), 32.0 (CH2) ppm. ESI-HRMS M = C26H18FNO3, expected (M+Na)+ m/z 434.1162, observed (M+Na)+ m/z 434.1159.

**Product (8j)**

According to General Procedure F 2-(4-methylbenzoyl)-4-oxo-4-phenylbutanenitrile (83 mg, 0.30 mmol, 1.0 equiv.), 3-phenylpropionaldehyde (47 mg, 0.36 mmol, 1.2 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOBz (5.8 mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C6D6 (total volume: 3.0 mL) for 12 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 99:1 → 97:3). White amorphous solid. > 98% conversion (1H NMR). Isolated yield 78% (95 mg, 0.23 mmol). Diastereomer ratio of the crude reaction mixture: 9:1 d.r. (1H NMR). Isolated yield after recrystallization from hot MeOH (single diastereomer) 57% (70 mg, 0.17 mmol).1H NMR (400 MHz, CD2Cl2): δ 7.98 (2H, d, J 8.3, C6H4), 7.25-7.39 (12H, m, C6H4), 4.09 (1H, d, J 1.6, ring-junction CH), 3.73 (1H, q, J 4.6, benzylic CH), 3.03-3.08 (1H, ABX dd), 17.0, J2 5.0, diastereotopic CH2), 2.96-3.01 (1H, ABX ddd, J1 17.0, J2 4.7, J3 3.1, diastereotopic CH2), 2.44 (3H, s, CH3) ppm.13C NMR (100 MHz, CD2Cl2): δ 168.5 (ester Cq), 165.9 (enol ether Cq), 144.2 (Cq), 139.9 (Cq), 139.8 (Cq), 130.3 (CH), 130.2 (CH), 129.6 (CH), 129.4 (CH), 128.3 (CH), 127.9 (CH), 127.6 (CH), 125.0 (CH), 124.1 (Cq), 116.2 (nitrile Cq), 112.5 (enol ether Cq), 83.0 (ketal Cq), 54.3 (CH), 40.8 (CH), 32.7 (CH2), 22.0 (CH3) ppm. ESI-HRMS M = C27H21NO3, expected (M+Na)+ m/z 430.1413, observed (M+Na)+ m/z 430.1410. Crystals suitable for X-ray diffraction analysis were grown by slow diffusion of n-hexane into a solution of the title compound in ethyl acetate.

**Product (8k)**

According to General Procedure F 2-(4-methoxybenzoyl)-4-oxo-4-phenylbutanenitrile (88 mg, 0.30 mmol, 1.0 equiv.), 3-phenylpropionaldehyde (47 mg, 0.36 mmol, 1.2 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOBz (5.8
mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C$_6$H$_6$ (total volume: 3.0 mL) for 12 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 98:2 → 95:5). White amorphous solid. 84% conversion ($^1$H NMR). Isolated yield 77% (98 mg, 0.23 mmol). Diastereomer ratio of the crude reaction mixture: > 13:1 d.r. ($^1$H NMR). Isolated yield after recrystallization from hot MeOH (single diastereomer) 60% (77 mg, 0.18 mmol). Colorless needles. $^1$H NMR (500 MHz, C$_6$D$_6$): δ 8.04-8.07 (2H, AA’XX’ d, J 8.9, C$_a^a$H), 7.20-7.22 (2H, m, C$_a^s$H), 6.94-6.98 (6H, m, C$_a^s$H), 6.88-6.90 (2H, m, C$_a^s$H), 6.57-6.60 (2H, AA’XX’ d, J 9.0, C$_a^s$H), 3.74 (1H, dd, J$_1$ 3.1, J$_2$ 1.4, ring-junction CH), 3.23 (1H, q, J 4.8, benzylic CH), 3.14 (3H, s, O-CH$_3$), 2.47-2.52 (1H, ABX dd, J$_1$ 17.1, J$_2$ 5.1, diastereotopic CH$_2$), 2.43-2.46 (1H, ABKX ddd, J$_1$ 17.1, J$_2$ 4.9, J$_3$ 1.5, diastereotopic CH$_2$) ppm. $^{13}$C NMR (125 MHz, C$_6$D$_6$): δ 167.4 (ester Cq), 165.0 (enol-ether Cq), 163.1 (O-C$_a^a$q), 140.2 (Cq), 139.8 (Cq), 129.7 (Cq), 129.6 (CH), 129.1 (CH), 129.0 (CH), 128.4 (CH), 128.2 (CH), 128.0 (CH), 127.6 (CH), 127.3 (CH), 124.9 (CH), 119.4 (Cq), 116.4 (nitrile Cq), 114.7 (CH), 112.1 (enol-ether Cq), 81.8 (ketal Cq), 55.0 (CH$_3$), 54.1 (CH), 40.7 (CH), 31.9 (CH$_2$) ppm. ESI-HRMS M = C$_{27}$H$_{21}$NO$_4$, expected (M+H)$^+$ m/z 424.1543, observed (M+H)$^+$ m/z 424.1548.

Product (8l)

According to General Procedure F 2-benzoyl-4-(4-fluorophenyl)-4-oxobutanenitrile (84 mg, 0.30 mmol, 1.0 equiv.), 3-phenylpropionaldehyde (47 mg, 0.36 mmol, 1.2 equiv.), 2-tolyl)butanenitrile (83 mg, 0.30 mmol, 1.0 equiv.), 3-fluorophenyl)acetophenone (47 mg, 0.36 mmol, 1.2 equiv.), and 4 Å molecular sieves were stirred and heated at 40 °C in C$_6$H$_6$ (total volume: 3.0 mL) for 12 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 99:1) for 12 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 98:2 → 95:5). White amorphous solid. 84% conversion ($^1$H NMR). Isolated yield after recrystallization from hot MeOH (single diastereomer) 72% (98 mg, 0.23 mmol). Diastereomer ratio of the crude reaction mixture: > 98% conversion ($^1$H NMR). Isolated yield 73% (91 mg, 0.22 mmol). Diastereomer ratio of the crude reaction mixture: 11:1 d.r. ($^1$H NMR). According to General Procedure F 2-benzoyl-4-oxo-4-(p-tolyl)butanenitrile (83 mg, 0.30 mmol, 1.0 equiv.), 3-phenylpropionaldehyde (47 mg, 0.36 mmol, 1.2 equiv.), 2-
mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOBz (5.8 mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C₆H₆ (total volume: 3.0 mL) for 12 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 10:1 → 98:2). Light-yellow amorphous solid. > 98% conversion (¹H NMR). Isolated yield 80% (96 mg, 0.24 mmol). Diastereomer ratio of the crude reaction mixture: > 20:1 d.r. (¹H NMR). Isolated yield after recrystallization from hot MeOH (single diastereomer) 57% (69 mg, 0.17 mmol). White powder. ¹H NMR (500 MHz, C₆D₆): δ 8.02-8.04 (2H, AA’XX’ d, J 7.8, C”H), 7.14 (2H, d, J 8.5, C”H), 6.97-7.02 (6H, m, C”H), 6.90-6.92 (2H, m, C”H), 6.79 (2H, d, J 8.1, C”H), 3.79 (1H, d, J 3.1, ring-junction CH), 3.22 (1H, q, J 5.0, benzyl CH), 2.46 (1H, A₂ d, J 5.1, diastereotopic CH₂), 1.95 (3H, s, CH₃) ppm. ¹³C NMR (125 MHz, C₆D₆): δ 167.4 (ester Cq), 165.0 (enol-ether Cq), 163.1 (O-C”q), 140.2 (Cq), 139.8 (Cq), 129.7 (CH), 129.6 (CH), 129.1 (CH), 129.0 (CH), 128.4 (CH), 128.2 (CH), 128.0 (CH), 127.6 (CH), 127.3 (CH), 124.9 (CH), 119.5 (Cq), 114.6 (nitrile Cq), 114.7 (CH), 112.1 (enol-ether Cq), 81.8 (ketal Cq), 55.0 (CH₃), 54.1 (CH), 40.7 (CH), 31.9 (CH₂) ppm. ESI-HRMS M = C₂₇H₂₁NO₃, expected (M+H)⁺ m/z 408.1594, observed (M+H)⁺ m/z 408.1583.

**Product (8n)**

According to General Procedure F 2-benzoyl-4-(4-methoxyphenyl)-4-oxobutanenitrile (88 mg, 0.30 mmol, 1.0 equiv.), 3-phenylpropionaldehyde (47 mg, 0.36 mmol, 1.2 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOBz (5.8 mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C₆H₆ (total volume: 3.0 mL) for 12 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 98:2 → 95:5). Light-orange foam. > 98% conversion (¹H NMR). Isolated yield 69% (89 mg, 0.21 mmol). Diastereomer ratio of the crude reaction mixture: > 20:1 d.r. (¹H NMR). Isolated yield after recrystallization from hot MeOH (single diastereomer) 54% (69 mg, 0.16 mmol). White powder. ¹H NMR (500 MHz, C₆D₆): δ 8.02 (2H, dd, J 7.6, J 1.5, C”H), 7.14-7.16 (2H, AA’XX’ m, C”H), 6.97-7.02 (6H, m, C”H), 6.91-6.93 (2H, m, C”H), 6.53-6.56 (2H, AA’XX’ d, J 8.9, C”H), 3.80 (1H, d, J 3.1, ring-junction CH), 3.23 (1H, q, J 5.1, benzyl CH), 3.17 (3H, s, O-CH₃), 2.46 (2H, d, J 5.0, diastereotopic CH₂) ppm. ¹³C NMR (125 MHz, C₆D₆): δ 167.3 (ester Cq), 164.9 (enol-ether Cq), 160.9 (O-C”q), 139.9 (Cq), 132.4 (CH), 132.1 (Cq), 129.20 (CH), 129.19 (CH), 128.4 (CH), 128.2 (CH), 128.0 (CH), 127.7 (CH), 127.6 (CH), 127.4 (CH), 127.1 (Cq), 126.5 (CH), 115.9 (nitrile Cq), 114.4 (CH), 112.4 (enol-ether Cq), 84.2 (ketal Cq), 54.8 (CH₃), 54.0 (CH), 40.7 (CH), 32.2 (CH₂) ppm. ESI-HRMS M = C₂₇H₂₁NO₃, expected (M+Na)⁺ m/z 446.1362, observed (M+Na)⁺ m/z 446.1356.

**Product (8o)**

According to General Procedure F 2-benzoyl-4-oxo-4-phenylbutanenitrile (79 mg, 0.30 mmol, 1.0 equiv.), 3-(4-fluorophenyl)propionaldehyde (53 mg, 0.36 mmol, 1.2 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOAc (3.3
mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C₆H₆ (total volume: 3.0 mL) for 12 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 98:2 → 95:5). White foam. 88% conversion (¹H NMR). Isolated yield 61% (75 mg, 0.18 mmol). Diastereomer ratio of the crude reaction mixture: > 11:1 d.r. (¹H NMR). Isolated yield after purification by flash chromatography on silica gel (single diastereomer) 54% (66 mg, 0.16 mmol).¹H NMR (400 MHz, C₆D₆): δ 8.01 (2H, dd, J₁ 7.5, J₂ 1.4, C₆H), 7.13-7.15 (2H, m, C₆H), 6.94-7.03 (6H, m, C₆H), 6.59-6.66 (4H, m, C₆H), 3.61 (1H, d, J 1.8, ring-junction CH), 3.10 (1H, q, J 4.6, benzylic CH), 2.40-2.45 (1H, ABX dd, J₁ 17.1, J₂ 5.0, diastereotopic CH₂), 2.32-2.38 (1H, ABX ddd, J₁ 17.1, J₂ 5.0, J₃ 1.2, diastereotopic CH₂) ppm.¹³C NMR (100 MHz, C₆D₆): δ 166.9 (ester Cq), 165.1 (enol-ether Cq), 162.3 (d, Jₑ₋ₓ 245, ipso(F)-Cq), 139.9 (Cq), 135.3 (d, Jₑ₋ₓ 3.4, para(F)-Cq), 132.5 (CH), 129.8 (CH), 129.3 (CH), 129.10 (d, Jₑ₋ₓ 8.0, meta(F)-CH), 129.07 (CH), 128.2 (CH), 127.9 (Cq), 127.6 (CH), 126.8 (Cq), 124.8 (CH), 116.0 (d, Jₑ₋ₓ 21.6, ortho(F)-CH), 115.7 (nitrile Cq), 112.1 (enol-ether Cq), 83.9 (ketal Cq), 54.2 (CH), 39.8 (CH), 32.0 (CH₂) ppm. ESI-HRMS M = C₂₆H₂₆FNO₃, expected (M+Na)+ m/z 434.1153, observed (M+Na)+ m/z 434.1153.

**Product (8p)**

According to General Procedure F 2-benzoyl-4-oxo-4-phenylbutanenitrile (79 mg, 0.30 mmol, 1.0 equiv.), 3-(4-chlorophenyl)propionaldehyde (54 mg, 0.33 mmol, 1.1 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOAc (3.7 mg, 0.045 mmol, 15 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C₆H₆ (total volume: 3.0 mL) for 14 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 98:2 → 95:5). Light-orange foam. 77% conversion (¹H NMR). Isolated yield 77% (99 mg, 0.23 mmol). Diastereomer ratio of the crude reaction mixture: 9:1 d.r. (¹H NMR). Isolated yield after purification by flash chromatography on silica gel (single diastereomer) 58% (73 mg, 0.17 mmol).¹H NMR (500 MHz, CD₂Cl₂): δ 8.07 (2H, dd, J₁ 7.1, J₂ 1.6, C₆H), 7.52-7.62 (3H, m, C₆H), 7.31-7.42 (7H, m, C₆H), 7.21 (2H, d, J 7.2, C₆H), 4.07 (1H, dd, J₁ 3.0, J₂ 1.5, ring-junction CH), 3.72 (1H, q, J 4.8, benzylic CH), 3.03-3.08 (1H, dd, J₁ 17.1, J₂ 5.0, diastereotopic CH₂), 2.94-3.00 (1H, ddd, J₁ 17.1, J₂ 4.8, J₃ 1.5, diastereotopic CH₂) ppm.¹³C NMR (125 MHz, CD₂Cl₂): δ 168.0 (ester Cq), 165.9 (enol-ether Cq), 139.6 (Cq), 138.4 (Cq), 134.2 (Cq), 133.2 (CH₃), 130.5 (CH), 129.8 (CH), 129.6 (CH), 129.5 (CH), 129.1 (CH), 128.0 (CH), 126.8 (Cq), 125.0 (CH), 115.9 (nitrile Cq), 112.5 (enol-ether Cq), 83.8 (ketal Cq), 54.3 (CH), 40.4 (CH), 32.7 (CH₂) ppm. ESI-HRMS M = C₂₆H₂₆FNO₃, expected (M+Na)+ m/z 450.0867, observed (M+Na)+ m/z 450.0869.

**Product (8q)**

According to General Procedure F 2-benzoyl-4-oxo-4-phenylbutanenitrile (79 mg, 0.30 mmol, 1.0 equiv.), 3-(4-methylphenyl)propionaldehyde (52 mg, 0.36 mmol, 1.2 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOBz (5.8
mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C₆H₆ (total volume: 3.0 mL) for 12 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 98:2 → 95:5). White foam. > 98% conversion (¹H NMR). Isolated yield 86% (105 mg, 0.26 mmol). Diastereomer ratio of the crude reaction mixture: > 10:1 d.r. (¹H NMR). Isolated yield after purification by flash chromatography on silica gel (single diastereomer) 67% (82 mg, 0.20 mmol).¹H NMR (400 MHz, C₆D₆): δ 8.01 (2H, dd, J₁, J₂, 1.4, C₆H₆), 7.21 (2H, dd, J₂, 7.9, J₂, 1.7, C₆H₆), 6.95-7.04 (6H, m, C₆H₆), 6.81-6.86 (4H, AA/BB′, m, C₆H₆), 3.78 (1H, d, J 2.9, ring-junction CH), 3.26 (1H, q, J 4.8, benzyl CH), 2.50 (2H, d, J 4.9, diastereotopic CH₂), 2.02 (3H, s, CH₃) ppm.¹³C NMR (100 MHz, C₆D₆): δ 167.3 (ester Cq), 164.9 (enol-ether Cq), 140.1 (Cq), 137.3 (Cq), 136.7 (Cq), 132.4 (CH), 129.9 (CH), 129.7 (CH), 129.2 (CH), 129.0 (CH), 127.6 (CH), 127.3 (CH), 126.9 (Cq), 124.9 (CH), 115.8 (nitrile Cq), 112.3 (enol-ether Cq), 84.3 (ketal Cq), 54.2 (CH), 40.3 (CH), 32.1 (CH₂), 20.9 (CH₃) ppm. ESI-HRMS M = C₂₇H₂₁NO₄, expected (M+H)+ m/z 408.1594, observed (M+H)+ m/z 408.1585.

Product (8r)

According to General Procedure F 2-benzoyl-4-oxo-4-phenylbutanenitrile (79 mg, 0.30 mmol, 1.0 equiv.), 3-(4-methoxyphenyl)propionaldehyde (51 mg, 0.32 mmol, 1.05 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOBz (5.8 mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C₆H₆ (total volume: 3.0 mL) for 12 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 98:2 → 95:5). Light-yellow foam. > 98% conversion (¹H NMR). Isolated yield 87% (110 mg, 0.26 mmol). Diastereomer ratio of the crude reaction mixture: 13:1 d.r. (¹H NMR). Isolated yield after purification by flash chromatography on silica gel (single diastereomer) 71% (89 mg, 0.21 mmol).¹H NMR (500 MHz, C₆D₆): δ 8.02 (2H, dd, J₁, 7.9, J₂, 1.4, C₆H₆), 7.21 (2H, dd, J₂, 7.3, J₂, 1.7, C₆H₆), 6.95-7.04 (6H, m, C₆H₆), 6.81-6.84 (2H, AA′XX′, d, J 8.6, C₆H₆), 6.58-6.61 (2H, AA′XX′, d, J 8.7, C₆H₆), 3.74 (1H, d, J 3.0, ring-junction CH), 3.25 (3H, s, O-CH₃), 3.23 (1H, q, J 4.8, benzyl CH), 2.49 (2H, d, J 4.9, diastereotopic CH₂) ppm.¹³C NMR (125 MHz, C₆D₆): δ 167.4 (ester Cq), 164.9 (enol-ether Cq), 159.4 (O-Cq), 140.2 (Cq), 132.4 (CH), 131.5 (Cq), 129.7 (CH), 129.2 (CH), 129.0 (CH), 128.44 (CH), 128.35 (CH), 128.2 (CH), 128.0 (CH), 127.6 (CH), 126.9 (Cq), 124.9 (CH), 115.8 (nitrile Cq), 114.6 (CH), 112.2 (enol-ether Cq), 84.2 (ketal Cq), 54.8 (O-CH₃), 54.3 (CH), 39.9 (CH), 32.2 (CH₂) ppm. ESI-HRMS M = C₂₇H₂₁NO₄, expected (M+Na)+ m/z 446.1362, observed (M+Na)+ m/z 446.1358. Chiral SFC (OD column, OD10_1A): tₙ 9.63, 10.51 min.
Product (8t)

According to General Procedure F 2-benzoyl-4-oxo-4-phenylbutanenitrile (79 mg, 0.30 mmol, 1.0 equiv.), 3-(2-methoxyphenyl)propionaldehyde (58 mg, 0.36 mmol, 1.2 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOAc (3.3 mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C₆H₆ (total volume: 3.0 mL) for 14 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 98:2 → 95:5). White crystalline solid. > 98% conversion (¹H NMR). Isolated yield 88% (111 mg, 0.26 mmol). Diastereomer ratio of the crude reaction mixture: > 7:1 d.r. (¹H NMR). Isolated yield after recrystallization from hot MeOH (single diastereomer) 71% (90 mg, 0.21 mmol). White crystalline solid.

Product (8s)

According to General Procedure F 2-benzoyl-4-oxo-4-phenylbutanenitrile (79 mg, 0.30 mmol, 1.0 equiv.), 3-(3-chlorophenyl)propionaldehyde (59 mg, 0.36 mmol, 1.2 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOBD (5.8 mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C₆H₆ (total volume: 3.0 mL) for 12 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 98:2 → 95:5). White foam. 85% conversion (¹H NMR). Isolated yield 59% (76 mg, 0.18 mmol). Diastereomer ratio of the crude reaction mixture: > 10:1 d.r. (¹H NMR). Isolated yield after purification by flash chromatography on silica gel (single diastereomer) 48% (62 mg, 0.14 mmol).¹H NMR (500 MHz, CD₂Cl₂): δ 8.08 (2H, d, J 7.3, C₆H₆), 7.60 (1H, tt, J₁ 7.4, J₂ 1.5, C₆H₆), 7.52-7.56 (2H, m, C₆H₆), 7.38-7.43 (3H, m, C₆H₆), 7.34-7.36 (2H, m, C₆H₆), 7.30-7.32 (2H, m, C₆H₆), 7.25 (1H, brs, C₆H₆), 7.17 (1H, tt, J₁ 6.4, J₂ 1.4, C₆H₆), 4.09 (1H, dd, J₁ 3.1, J₂ 1.6, ring-junction CH), 3.72 (1H, q, J 4.9, benzylic CH), 3.04-3.09 (1H, ABX dd, J₁ 17.2, J₂ 5.1, diastereotopic CH₂), 2.95-3.00 (1H, ABX dd, J₁ 17.2, J₂ 4.9, J₃ 1.6, diastereotopic CH₂) ppm.¹³C NMR (125 MHz, CD₂Cl₂): δ 167.8 (ester...
Cq), 166.0 (enol-ether Cq), 141.8 (Cl-Cq), 139.5 (Cq), 135.4 (Cq), 133.2 (CH), 131.0 (CH), 130.5 (CH), 129.6 (CH), 129.5 (CH), 128.5 (CH), 128.02 (CH), 128.00 (CH), 126.8 (Cq), 125.9 (CH), 125.0 (CH), 115.8 (nitrile Cq), 112.5 (enol-ether Cq), 83.7 (ketal Cq), 54.2 (CH), 40.6 (CH), 32.7 (CH₂) ppm. **ESI-HRMS** M = C₂₉H₁₈CINO₃, expected (M+H)⁺ m/z 428.1047, observed (M+H)⁺ m/z 428.1060.

**Product (8v)**

According to General Procedure F 2-benzoyl-4-oxo-4-phenylbutanenitrile (79 mg, 0.30 mmol, 1.0 equiv.), 3-(furan-2-y1)propiolaldehyde (43 mg, 0.36 mmol, 1.2 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOAc (3.7 mg, 0.045 mmol, 15 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C₅H₁₂ (total volume: 3.0 mL) for 14 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 99:1 → 95:5). White foam. > 98% conversion (¹H NMR). Isolated yield 77% (88 mg, 0.23 mmol). Diastereomer ratio of the crude reaction mixture: > 12:1 d.r. (¹H NMR). Isolated yield after purification by flash chromatography on silica gel (single diastereomer) 47% (54 mg, 0.14 mmol). **¹H NMR** (500 MHz, CD₂Cl₂): δ 8.11 (2H, d, J 7.3, CαH), 7.61 (1H, t, J 7.4, CαH), 7.54-7.57 (2H, m, CαH), 7.35-7.40 (4H, m, CαH), 7.21 (2H, dd, J = 8.3, J = 1.4, CαH), 6.38 (1H, dd, J = 3.3, J = 1.9, CαH), 6.24 (1H, d, J = 3.3, CαH), 4.18 (1H, t, J = 1.6, ring-junction CH), 3.79 (1H, brs, benzylic CH), 3.05-3.09 (1H, ABX ddd, J = 17.3, J = 3.5, J = 1.6, diastereotopic CH₂), 3.00-3.05 (1H, dd, J = 17.3, J = 4.8, diastereotopic CH₂) ppm. **¹³C NMR** (125 MHz, CD₂Cl₂): δ 167.8 (ester Cq), 166.3 (enol-ether Cq), 152.6 (O-Cq), 143.1 (O-CH), 139.8 (Cq), 133.2 (CH), 130.2 (CH), 129.6 (CH), 129.3 (CH), 128.0 (CH), 126.8 (Cq), 125.0 (CH), 115.8 (nitrile Cq), 112.6 (enol-ether Cq), 111.2 (CH), 107.7 (CH), 82.7 (ketal Cq), 52.0 (CH), 34.7 (CH), 30.1 (CH₂) ppm. **ESI-HRMS** M = C₂₉H₁₇NO₄, expected (M+H)⁺ m/z 384.1230, observed (M+H)⁺ m/z 384.1231.

**Product (8u)**

According to General Procedure F 2-benzoyl-4-oxo-4-phenylbutanenitrile (79 mg, 0.30 mmol, 1.0 equiv.), 3-(furan-2-y1)propiolaldehyde (43 mg, 0.36 mmol, 1.2 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOAc (3.7 mg, 0.045 mmol, 15 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C₅H₁₂ (total volume: 3.0 mL) for 14 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 99:1 → 95:5). White foam. > 98% conversion (¹H NMR). Isolated yield 82% (109 mg, 0.25 mmol). Diastereomer ratio of the crude reaction mixture: 8:1 d.r. (¹H NMR). Isolated yield after recrystallization from hot MeOH (single diastereomer) 63% (83 mg, 0.19 mmol). White crystalline solid. **¹H NMR** (400 MHz, CD₂Cl₂): δ 8.07 (2H, d, J 7.2, CαH), 7.50-7.61 (3H, m, CαH), 7.37-7.42 (5H, m, CαH), 6.78 (1H, d, J 8.6, CαH), 6.72 (1H, s, CαH), 6.71 (1H, d, J 8.6, CαH), 5.96 (2H, s, acetal O-
CH₂-O), 4.05 (1H, d, J 2.0, ring-junction CH), 3.64 (1H, q, J 4.9, benzylic CH), 2.98-3.04 (1H, dd, J₁ 17.0, J₂ 5.0, diastereotopic CH₂), 2.89-2.95 (1H, ddd, J₁ 17.0, J₂ 5.4, J₃ 1.2, diastereotopic CH₂) ppm. ¹³C NMR (100 MHz, CD₂Cl₂): δ 168.2 (ester Cq), 165.7 (enol-ether Cq), 148.9 (Cq), 147.7 (Cq), 139.7 (Cq), 133.5 (Cq), 133.1 (CH), 130.4 (CH), 129.5 (CH), 129.4 (CH), 127.9 (CH), 126.9 (Cq), 125.0 (CH), 120.8 (CH), 115.9 (nitrile Cq), 112.5 (enol-ether Cq), 109.0 (CH), 108.0 (CH), 102.1 (ketal CH₂), 84.0 (ketal Cq), 54.5 (CH), 40.7 (CH), 33.2 (CH₂) ppm. ESI-HRMS M = C₂₇H₁₉NO₅, expected (M+NH₄)⁺ m/z 455.1601, observed (M+NH₄)⁺ m/z 455.1604.

**Product (8w)**

According to General Procedure F 2-benzoyl-4-oxo-4-phenylbutanenitrile (79 mg, 0.30 mmol, 1.0 equiv.), 3-cyclopropylpropiolaldehyde (34 mg, 0.36 mmol, 1.2 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOAc (3.7 mg, 0.045 mmol, 15 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C₆H₆ (total volume: 3.0 mL) for 14 h. Purified by flash chromatography on neutralized silica gel (n-hexane → n-hexane/EtOAc 98:2). White foam. > 98% conversion (¹H NMR). Isolated yield 76% (82 mg, 0.23 mmol).

Diastereomer ratio of the crude reaction mixture: > 8:1 d.r. (¹H NMR). ¹H NMR (500 MHz, C₆D₆): δ 8.00 (2H, dd, J₁ 7.8, J₂ 1.5, C₆H), 7.38 (2H, d, J 9.7, C₆H), 7.06-7.10 (3H, m, C₆H), 6.98-7.02 (3H, m, C₆H), 3.43 (1H, s, ring-junction CH), 2.27 (2H, d, J 4.5, diastereotopic CH₂), 1.01-1.05 (1H, m, α-cyclopropyl CH), 0.46-0.53 (1H, m, cyclopropyl CH), 0.12 (1H, sept., J 4.6, cyclopropyl CH₂), 0.00 (1H, sept., J 5.3, cyclopropyl CH₂), -0.26 (1H, sept., J 4.9, cyclopropyl CH₂), -0.32 (1H, sept., J 4.8, cyclopropyl CH₂) ppm. ¹³C NMR (125 MHz, C₆D₆): δ 167.3 (ester Cq), 164.7 (enol-ether Cq), 140.6 (Cq), 132.4 (CH), 129.7 (CH), 129.2 (CH), 129.1 (CH), 128.4 (CH), 128.2 (CH), 128.0 (CH), 127.5 (CH), 126.9 (Cq), 124.8 (CH), 115.8 (nitrile Cq), 112.3 (enol-ether Cq), 83.7 (ketal Cq), 53.3 (CH), 41.6 (CH), 31.6 (CH₂), 14.6 (CH), 5.09 (CH₂), 4.79 (CH₂) ppm. ESI-HRMS M = C₂₃H₁₉NO₅, expected (M+H)⁺ m/z 358.1437, observed (M+H)⁺ m/z 358.1440.

**Product (8x)**

According to General Procedure F 2-(4-fluorobenzoyl)-4-oxo-4-phenylbutanenitrile (84 mg, 0.30 mmol, 1.0 equiv.), 3-(4-methoxyphenyl)propiolaldehyde (53 mg, 0.33 mmol, 1.1 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOBz (5.8 mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C₆H₆ (total volume: 3.0 mL) for 12 h. Purified by flash chromatography on neutralized silica gel (n-hexane/EtOAc 98:2 → 95:5). Light-yellow foam. > 98% conversion (¹H NMR). Isolated yield 90% (120 mg, 0.27 mmol). Diastereomer ratio of the crude reaction mixture: 12:1 d.r. (¹H NMR). Isolated yield after purification by flash chromatography on silica gel (single diastereomer) 60% (79 mg, 0.18 mmol). ¹H NMR (400 MHz, C₆D₆): δ 7.79-7.85 (2H, 37
AA'XX m, meta(F)-C\textsuperscript{\textalpha\textomega}H, 7.19-7.21 (2H, m, C\textsuperscript{\textomega}H), 6.95-6.98 (3H, m, C\textsuperscript{\textomega}H), 6.81 (2H, d, J 8.7, C\textsuperscript{\textomega}H), 6.61 (4H, t, J 9.2, C\textsuperscript{\textomega}H), 3.74 (1H, d, J 3.1, ring-junction CH), 3.25 (3H, s, O-CH\textsubscript{3}), 3.20 (1H, q, J 4.9, benzyl CH), 2.48 (2H, d, J 5.0, diastereotopic CH\textsubscript{2}) ppm. \textsuperscript{19}F NMR (376 MHz, C\textsubscript{6}D\textsubscript{6}): \( \delta -105.1 \) (1F, s, C\textsuperscript{\textomega}F) ppm. \textsuperscript{13}C NMR (100 MHz, C\textsubscript{6}D\textsubscript{6}): \( \delta 167.3 \) (ester C\textsubscript{q}), 165.0 (d, \( J^\text{CF} 253 \), ipso C\textsubscript{q}-F), 163.8 (enol-ether C\textsubscript{q}), 159.4 (O-C\textsubscript{q}), 140.0 (C\textsubscript{q}), 131.3 (C\textsubscript{q}), 130.1 (d, \( J^\text{CF} 9.0 \), meta CH-F), 129.8 (CH), 129.1 (CH), 128.4 (CH), 128.2 (CH), 127.9 (CH), 124.9 (CH), 123.1 (d, \( J^\text{CF} 3.4 \), para C\textsubscript{q}-F), 116.4 (d, \( J^\text{CF} 22 \), ortho CH-F), 115.7 (nitrile C\textsubscript{q}), 114.6 (CH), 112.3 (enol-ether C\textsubscript{q}), 83.8 (d, \( J^\text{CF} 1.4 \), ketal C\textsubscript{q}), 54.8 (O-CH\textsubscript{3}), 54.3 (CH), 39.9 (CH), 32.3 (CH\textsubscript{2}) ppm. \textsuperscript{EI}-HRMS \( m/z \) 317.1493, observed (M+H\textsuperscript{+}) \( m/z \) 317.1495.

**Product (8y)**

According to General Procedure F 2-acetyl-4-oxopentanenitrile (42 mg, 0.30 mmol, 1.0 equiv.), 3-(4-methoxyphenyl)propionaldehyde (51 mg, 0.32 mmol, 1.05 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOAc (3.5 mg, 0.045 mmol, 15 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C\textsubscript{6}H\textsubscript{6} (total volume: 3.0 mL) for 14 h. Purified by flash chromatography on neutralized silica gel (n-hexane/ EtOAc 9:1 → 95:5). Light-yellow foam. \approx 50% conversion (\textsuperscript{1}H NMR). Diastereomer ratio of the crude reaction mixture: 3:1 d.r. (\textsuperscript{1}H NMR). Isolated yield after purification by flash chromatography on silica gel (single diastereomer) 22% (20 mg, 0.07 mmol). \textsuperscript{1}H NMR (500 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \( \delta 7.13 \) (2H, AA'XX' d, J 8.7, C\textsuperscript{\textomega}H), 6.89 (2H, AA'XX' d, J 8.7, C\textsuperscript{\textomega}H), 3.79 (3H, s, O-CH\textsubscript{3}), 3.43-3.45 (1H, m, ring-junction CH), 3.40 (1H, q, J 4.7, benzyl CH), 2.77-2.81 (1H, ABX dd, J\textsubscript{1} 16.9, J\textsubscript{2} 5.0, diastereotopic CH\textsubscript{2}), 2.73-2.76 (1H, ABX ddd, J\textsubscript{1} 16.9, J\textsubscript{2} 3.7, J\textsubscript{3} 2.2, diastereotopic CH\textsubscript{2}), 2.13 (3H, d, J 1.7, CH\textsubscript{3}), 1.63 (3H, s, CH\textsubscript{3}) ppm. \textsuperscript{13}C NMR (125 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \( \delta 169.9 \) (ester C\textsubscript{q}), 168.4 (enol-ether C\textsubscript{q}), 159.6 (O-C\textsubscript{q}), 132.1 (C\textsubscript{q}), 128.6 (CH), 115.1 (nitrile C\textsubscript{q}), 114.9 (CH), 113.7 (enol-ether C\textsubscript{q}), 86.9 (ketal C\textsubscript{q}), 55.8 (O-CH\textsubscript{3}), 51.0 (CH), 39.8 (CH), 32.9 (CH\textsubscript{2}), 27.6 (CH\textsubscript{3}), 14.3 (CH\textsubscript{3}) ppm. \textsuperscript{ESI}-HRMS \( m/z \) 317.1495, observed (M+H\textsuperscript{+}) \( m/z \) 317.1493.

**Product (8δ)**

According to General Procedure F 2-benzoyl-4-(2-chlorophenyl)-4-oxobutanenitrile (89 mg, 0.30 mmol, 1.0 equiv.), 3-phenylpropionaldehyde (47 mg, 0.36 mmol, 1.2 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOAc (3.3 mg, 0.04 mmol, 13 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in C\textsubscript{6}H\textsubscript{6} (total volume: 3.0 mL) for 14 h. Purified by flash chromatography on neutralized silica gel (n-hexane/ EtOAc 98:2 → 95:5). Light-orange foam. 89% conversion (\textsuperscript{1}H NMR). Isolated yield 47% (60 mg, 0.14 mmol). Diastereomer ratio of the crude reaction mixture: < 5:2 d.r. (\textsuperscript{1}H NMR).
Product \((8\pi)\)

\[
\begin{align*}
\text{Me} & \quad \text{NC} \quad H \quad \text{O} \quad \text{Ph} \\
\end{align*}
\]

Chemical Formula: \(C_{25}H_{25}NO_3\)
Molecular Weight: 387.47

According to General Procedure F 2-benzoyl-4-oxo-4-phenylbutanenitrile (79 mg, 0.30 mmol, 1.0 equiv.), oct-2-ynal (47 mg, 0.36 mmol, 1.2 equiv.), 2-mesityl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (9.5 mg, 0.03 mmol, 10 mol%), NaOAc (3.7 mg, 0.045 mmol, 15 mol%), and 4 Å molecular sieves were stirred and heated at 40 °C in \(C_6H_6\) (total volume: 3.0 mL) for 14 h. Purified by flash chromatography on neutralized silica gel (\(n\)-hexane/EtOAc 98:2 → 95:5). Light-orange foam. 89% conversion \(^{1}H\) NMR. Isolated yield 47% (54 mg, 0.14 mmol). Diastereomer ratio of the crude reaction mixture: 7:1 d.r. \(^{1}H\) NMR. \(^{1}H\) NMR (400 MHz, \(C_6D_6\)): \(\delta\) 8.02 (2H, d, \(J\ 8.0\), Car H), 7.32-7.34 (2H, m, Car H), 6.98-7.04 (6H, m, Car H), 3.19 (1H, s, ring-junction C H), 2.25-2.31 (1H, dd, J1 16.8, J2 4.6, diastereotopic CH2), 2.12-2.17 (1H, dd, J1 16.8, J2 1.5, diastereotopic CH2), 1.91 (1H, brs, n-pentyl CH), 0.88-1.07 (6H, m, n-pentyl CH2), 0.80 (3H, t, J 7.2, n-pentyl CH2) ppm. \(^{13}C\) NMR (100 MHz, \(C_6D_6\)): \(\delta\) 167.2 (ester C q), 164.8 (enol-ether C q), 140.7 (Cq), 132.4 (CH), 129.6 (CH), 129.2 (CH), 129.1 (CH), 128.2 (CH), 127.8 (CH), 127.5 (CH), 126.9 (Cq), 124.8 (CH), 115.9 (nitrile Cq), 112.1 (enol-ether Cq), 83.8 (ketal Cq), 52.7 (CH), 35.5 (CH), 32.9 (CH2), 31.6 (CH2), 30.8 (CH2), 26.7 (CH2), 22.6 (CH2), 14.2 (CH3) ppm.

Optimization Studies

NHC-Catalyzed Annulation

A flame-dried Schlenk tube was charged with triazolium salt (8.2 mg, 0.03 mmol, 10 mol%) and activated powdered 4 Å molecular sieves. The tube was then evacuated and back-filled with dry nitrogen. The ynal (47 mg, 0.36 mmol, 1.2 equiv.) and the 1,4-diketone (0.30 mmol, 1.0 equiv.) were then added as solutions in anhydrous THF (total volume: 3.0 mL). Finally, a drop of DBU (5.9 mg, 0.039 mmol, 13 mol%) was added to initiate the reaction. The mixture was stirred at ambient temperature for 4 h, before being concentrated in vacuo and passed through a short plug of Celite, washed with methyl tert-butyl ether. Solvents were removed in vacuo, and the residue was purified by flash chromatography on neutralized silica gel (\(n\)-hexane/EtOAc 98:2 → 95:5).
A flame-dried Schlenk tube was charged with triazolium salt (7.9 mg, 0.03 mmol, 10 mol%) and activated powdered 4 Å molecular sieves. The tube was then evacuated and back-filled with dry nitrogen. The ynal (47 mg, 0.36 mmol, 1.2 equiv.) and the 1,4-diketone (0.30 mmol, 1.0 equiv.) were then added as solutions in anhydrous solvent (total volume: 3.0 mL). The mixture was then stirred and heated at 40 °C for the time stated (monitoring by TLC on silica gel plates, c-Hex/EtOAc 4:1), before being passed through a short plug of Celite, washed with methyl tert-butyl ether. The filtrate was concentrated in vacuo, followed by purification of the resultant residue by flash chromatography on neutralized silica gel (n-hexane/EtOAc 98:2 → 95:5).

A flame-dried Schlenk tube was charged with triazolium salt (9.5 mg, 0.03 mmol, 10 mol%) and activated powdered 4 Å molecular sieves. The tube was then evacuated and back-filled with dry nitrogen. The ynal (47 mg, 0.36 mmol, 1.2 equiv.) and the 1,4-diketone (0.30 mmol, 1.0 equiv.) were then added as solutions in anhydrous toluene/THF 2:1 (v/v) (total volume: 3.0 mL). Finally, catalytic base (0.04 mmol, 13 mol%) was added to initiate the reaction. The mixture was then stirred at a given temperature for the time stated (monitoring by TLC on silica gel plates, c-Hex/EtOAc 4:1), before being passed through a short plug of Celite, washed with methyl tert-butyl ether. The filtrate was concentrated in vacuo, followed by purification of the resultant residue by flash chromatography on neutralized silica gel (n-hexane/EtOAc 98:2 → 95:5).
NHC Precursor Screen

<table>
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<th>Entry</th>
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<th>Base</th>
<th>Conv. (%)</th>
<th>d.r.</th>
<th>Yield (%)</th>
<th>Yield major (%)</th>
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<td>2</td>
<td>B</td>
<td>Cs₂CO₃</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>3</td>
<td>C</td>
<td>Cs₂CO₃</td>
<td>73</td>
<td>7:2</td>
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<td>Cs₂CO₃</td>
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<td>9:5</td>
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<td>34</td>
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<tr>
<td>5</td>
<td>E</td>
<td>Cs₂CO₃</td>
<td>63</td>
<td>2:1</td>
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<tr>
<td>6</td>
<td>F</td>
<td>Cs₂CO₃</td>
<td>&gt; 98</td>
<td>9:1</td>
<td>80</td>
<td>53</td>
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<tr>
<td>7</td>
<td>G</td>
<td>none</td>
<td>&gt; 98</td>
<td>9:1</td>
<td>79</td>
<td>59</td>
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</table>

[a] Reaction conditions: 1,4-diketone (0.20 mmol, 1.0 equiv.), ynal (0.24 mmol, 1.2 equiv.), azolium salt A-G (0.02 mmol, 10 mol%), 4 Å molecular sieves (200 mg), and base (0.026 mmol, 13 mol%) in toluene (2.0 mL, 0.1 M) were stirred at 40 °C for 12 h; [b] Determined by ¹H NMR analysis of unpurified reaction mixtures; [c] Isolated yields after flash chromatography on silica gel; [d] Isolated yield of the major diastereomer after recrystallization.

Stoichiometry Screen

[Diagram of reaction]

<table>
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<tr>
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<th>d.r.</th>
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</thead>
<tbody>
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<td>10:1</td>
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<td>2</td>
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<td>58</td>
<td>10:1</td>
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<tr>
<td>3</td>
<td>1.2</td>
<td>62</td>
<td>10:1</td>
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[a] Reaction conditions: 1,4-diketone (0.30 mmol, 1.0 equiv.), ynal (0.36 mmol, 1.2 equiv.), triazolium salt (0.03 mmol, 10 mol%), 4 Å molecular sieves (300 mg), and anhydrous toluene (3.0 mL, 0.1 M) were stirred at 40 °C for 6 h; [b] Determined by ¹H NMR analysis of unpurified reaction mixtures.

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### Solvent Screen

<table>
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<tr>
<th>Entry&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Conv.&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>d.r.&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Yield&lt;sup&gt;c&lt;/sup&gt; (%)</th>
<th>Yield &lt;sup&gt;major&lt;sup&gt;d&lt;/sup&gt;&lt;/sup&gt; (%)</th>
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<td>n.d.&lt;sup&gt;e&lt;/sup&gt;</td>
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<td>-</td>
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<tr>
<td>8</td>
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<td>&gt; 98</td>
<td>9:1(14:1)</td>
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<td>9</td>
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<td>&gt; 98</td>
<td>7:1(9:1)</td>
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<tr>
<td>10</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;F</td>
<td>14</td>
<td>90</td>
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<tr>
<td>11</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;F&lt;sub&gt;6&lt;/sub&gt;</td>
<td>14</td>
<td>52</td>
<td>13:1(9:1)</td>
<td>80</td>
<td>53</td>
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</table>

[a] Reaction conditions: 1,4-diketone (0.30 mmol, 1.0 equiv.), ynal (0.36 mmol, 1.2 equiv.), triazolium salt (0.03 mmol, 10 mol%), 4 Å molecular sieves (300 mg), and solvent (3.0 mL, 0.1 M) were stirred at 40 °C for the time stated; [b] Determined by <sup>1</sup>H NMR analysis of unpurified reaction mixtures, the values in brackets refer to diastereomer ratios after flash chromatography on silica gel; [c] Isolated yields after flash chromatography on silica gel; [d] Isolated yield of the major diastereomer after recrystallization; [e] Only methyl cinnamate was recovered.

### Basic Additive Screen

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<thead>
<tr>
<th>Entry&lt;sup&gt;a&lt;/sup&gt;</th>
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<th>T (°C)</th>
<th>Time (h)</th>
<th>Conv.&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>d.r.&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Yield&lt;sup&gt;c&lt;/sup&gt; (%)</th>
<th>Yield &lt;sup&gt;major&lt;sup&gt;d&lt;/sup&gt;&lt;/sup&gt; (%)</th>
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<td>40</td>
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<td>&gt; 98</td>
<td>7:1(9:1)</td>
<td>80</td>
<td>53</td>
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</tbody>
</table>

[a] Reaction conditions: 1,4-diketone (0.30 mmol, 1.0 equiv.), ynal (0.36 mmol, 1.2 equiv.), triazolium salt (0.03 mmol, 10 mol%), 4 Å molecular sieves (300 mg), and base (0.04 mmol, 13 mol%) in toluene/THF 2:1 (v/v) (total volume: 3.0 mL, 0.1 M) were stirred at a given temperature for the time stated; [b] Determined by <sup>1</sup>H NMR analysis of unpurified reaction mixtures, the values in brackets refer to diastereomer ratios after flash chromatography on silica gel; [c] Isolated yields after flash chromatography on silica gel; [d] Isolated yield of the major diastereomer after recrystallization.
NMR Spectra: Compounds (8α-z, 8δ, 8π)

Example of Reaction Outcome

$^1$H NMR 400 MHz, CD$_2$Cl$_2$

13 mol% NaOBz
C$_6$H$_5$, 0.1 M
40 °C, 14 h

12:1 d.r.
Product (8a)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^1$H NMR 500 MHz, CD$_2$Cl$_2$
$^{13}$C NMR 125 MHz, CD$_2$Cl$_2$
Product (8b)

$^1$H NMR 400 MHz, CDCl$_3$
$^{19}$F NMR 376 MHz, CDCl$_3$
$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^{13}$C NMR 100 MHz, CD$_2$Cl$_2$
$^{19}$F NMR 376 MHz, CD$_2$Cl$_2$
Product (8c)

$^1$H NMR 400 MHz, CDCl$_3$
$^1$H NMR 400 MHz, CD$_2$Cl$_2$

$^{13}$C NMR 100 MHz, CD$_2$Cl$_2$
Product (8d)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^{13}\text{C NMR } 100 \text{ MHz, } \text{CD}_2\text{Cl}_2$
$^1$H NMR 500 MHz, C$_6$D$_6$
$^{13}$C NMR 125 MHz, C$_6$D$_6$
Product (8e)

$^1H$ NMR 500 MHz, CDCl$_3$
$^{13}$C NMR 125 MHz, CDCl$_3$
$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^{13}$C NMR 100 MHz, CD$_2$Cl$_2$
Product (8f)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^{19}$F NMR 376 MHz, CD$_2$Cl$_2$

$^{13}$C NMR 100 MHz, CD$_2$Cl$_2$
$^1$H NMR 500 MHz, C$_6$D$_6$
$^{19}$F NMR 376 MHz, C$_6$D$_6$
$^{13}$C NMR 125 MHz, C$_6$D$_6$
Product (8g)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^1$H NMR 500 MHz, C$_6$D$_6$

$^{13}$C NMR 125 MHz, C$_6$D$_6$
Product (8h)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^1$H NMR 500 MHz, C$_6$D$_6$
$^{13}$C NMR 125 MHz, C$_6$D$_6$
Product (8i)

$^1$H NMR 400 MHz, CDCl$_3$
$\text{C NMR 100 MHz, CDCl}_3$
$^1$H NMR 500 MHz, C$_6$D$_6$
$^{19}$F NMR 376 MHz, C₆D₆
$^{13}\text{C NMR} \ 125 \text{ MHz, C}_6\text{D}_6$
Product (8j)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^{13}$C NMR 100 MHz, CD$_2$Cl$_2$
$^1$H NMR 400 MHz, CD$_2$Cl$_2$
\( ^{13} \text{C NMR 100 MHz, CD}_2\text{Cl}_2 \)
Product (8k)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^{13}$C NMR 100 MHz, CD$_2$Cl$_2$

$^1$H NMR 500 MHz, C$_6$D$_6$
$^{13}$C NMR 125 MHz, C$_6$D$_6$
Product (8I)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
\[ ^{19}\text{F} \text{NMR 376 MHz, CD}_2\text{Cl}_2 \]

\[ ^{13}\text{C} \text{NMR 100 MHz, CD}_2\text{Cl}_2 \]
$^1$H NMR 500 MHz, C$_6$D$_6$
$^{19}$F NMR 376 MHz, C$_6$D$_6$
$^{13}$C NMR 125 MHz, C$_6$D$_6$
Product (8m)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$\text{C NMR 100 MHz, CD}_2\text{Cl}_2$

$\text{H NMR 500 MHz, C}_6\text{D}_6$
$^{13}$C NMR 125 MHz, C$_6$D$_6$
Product (8n)

^1H NMR 400 MHz, CD₂Cl₂

[Chemical structure image]
$^{13}$C NMR 100 MHz, CD$_2$Cl$_2$
$^{13}\text{C NMR 125 MHz, C}_6\text{D}_6$
Product (8o)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^1$H NMR 400 MHz, C$_6$D$_6$
$^{19}$F NMR 376 MHz, C$_6$D$_6$
$^{13}$C NMR 100 MHz, C$_6$D$_6$
Product (8p)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^{13}$C NMR 125 MHz, CD$_2$Cl$_2$
Product (8q)

\(^1\)H NMR 400 MHz, CD\(_2\)Cl\(_2\)

![NMR Spectrum Image]
$^{13}$C NMR 100 MHz, CD$_2$Cl$_2$

$^1$H NMR 400 MHz, C$_6$D$_6$
$^{13}$C NMR 100 MHz, C$_6$D$_6$
Product (8r)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^1$H NMR 500 MHz, C$_6$D$_6$
$^{13}$C NMR 125 MHz, C$_6$D$_6$
Product (8s)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^{13}$C NMR 100 MHz, CD$_2$Cl$_2$
$^{1}H$ NMR 400 MHz, CD$_2$Cl$_2$
Product (8t)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^{13}$C NMR 125 MHz, CD$_2$Cl$_2$
Product (8z)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^{19}$F NMR 376 MHz, CD$_2$Cl$_2$

$^{13}$C NMR 125 MHz, CD$_2$Cl$_2$
$^1$H NMR 500 MHz, CD$_2$Cl$_2$

< 4:1 d.r.
$^{19}$F NMR 376 MHz, CD$_2$Cl$_2$

> 98% conv.
< 3:1 d.r.

$^{13}$C NMR 125 MHz, CD$_2$Cl$_2$
Product (8δ)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^{13}$C NMR 100 MHz, CD$_2$Cl$_2$

$^1$H NMR 400 MHz, CD$_2$Cl$_2$

13 mol% NaOBz
C$_6$H$_6$ 0.1 M
40 °C, 14 h
\[ ^{13}\text{C NMR 100 MHz, CD}_2\text{Cl}_2 \]
Product ($8\pi$)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^{13}$C NMR 100 MHz, CD$_2$Cl$_2$

Me

$^{1}$H NMR 400 MHz, C$_6$D$_6$

Me

> 98% conv.
7:1 d.r.
Product (8u)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^{13}$C NMR 125 MHz, CD$_2$Cl$_2$
Product (8v)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^{13}$C NMR 100 MHz, CD$_2$Cl$_2$
$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^{13}$C NMR 100 MHz, CD$_2$Cl$_2$
Product (8w)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$
$^{13}$C NMR 100 MHz, CD$_2$Cl$_2$
$^{13}$C NMR 125 MHz, C$_6$D$_6$
Product (8x)

$^1$H NMR 400 MHz, C$_6$D$_6$
$^{19}$F NMR 376 MHz, C₆D₆
$^{13}$C NMR 100 MHz, C$_6$D$_6$
Product (8y)

$^1$H NMR 400 MHz, CD$_2$Cl$_2$

![NMR Spectrogram]

Formula: OCNMe

141
$^{13}$C NMR 100 MHz, CD$_2$Cl$_2$
$^{1}H$ NMR 500 MHz, CD$_2$Cl$_2$
$^{13}$C NMR 125 MHz, CD$_2$Cl$_2$
Chiral SFC Chromatograms and Optical Rotation: Compound (8r)

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<th>% Area</th>
<th>Height</th>
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<td>12.788</td>
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Crystal Structure Determination: Compound (8c)

X-ray data were measured using Cu radiation on a SuperNova Dual source equipped with an Atlas detector. The crystal was kept at 190 K during data collection. Refinement was made within the ShelXL [1] refinement package using Least Squares minimisation. Hydrogen atom positions were calculated geometrically and constrained to ride on the parent atom during the refinement.

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number:

CCDC 899807

**Crystal Data.** C_{26}H_{17}Cl_{2}NO_{3}, M = 462.31, monoclinic, a = 10.4926(3) Å, b = 6.9629(2) Å, c = 14.9608(4) Å, β = 99.944(2)°, U = 1076.60(5) Å³, T = 190 K; space group P2₁, Z = 2, μ(Cu Kα) = 2.956, 4299 reflections measured, 3029 unique (R_{int} = 0.0275) which were used in all calculations. The final R values (all data) were R₁ = 0.0381 and wR(F²) = 0. Flack parameter 0.38(2).


[^0] D +12° (c 2,2, acetone)
Abstract

Computing details


References

NOT FOUND

(alfrnew)

Crystal data

C_{26}H_{17}Cl_{2}NO_{3} F(000) = 476
M_r = 462.31 D_x = 1.426 Mg m^{-3}
Monoclinic, P2_1 Cu Kα radiation, λ = 1.5418 Å
a = 10.4926 (3) Å Cell parameters from 2700 reflections
b = 6.9629 (2) Å θ = 3.0–73.3°
c = 14.9608 (4) Å μ = 2.96 mm^{-1}
β = 99.944 (2)° T = 189 K
V = 1076.60 (5) Å³ Needle, Colourless
Z = 2 0.36 × 0.06 × 0.04 mm

Data collection

SuperNova, Dual, Cu at zero, Atlas diffractometer
Radiation source: SuperNova (Cu) X-ray Source
mirror 3029 independent reflections
Detector resolution: 10.4679 pixels mm^{-1}
θ scans
2839 reflections with I > 2σ(I)
R_{int} = 0.028
θ_{max} = 73.5°, θ_{min} = 3.0°
h = -11→12
Absorption correction: Multi-scan
Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

\[ k = -8 \rightarrow 5 \]
\[ T_{\text{min}} = 0.626, T_{\text{max}} = 1.000 \]
4299 measured reflections

Refinement

Refinement on \( F^2 \)
Least-squares matrix: Full

\[ R[F^2 > 2\sigma(F^2)] = 0.035 \]
\[ wR(F^2) = 0.092 \]
\[ S = 1.02 \]
3029 reflections
290 parameters
1 restraint

Primary atom site location: Structure-invariant direct methods
Secondary atom site location: Difference Fourier map
Hydrogen site location: Inferred from neighbouring sites

\[ w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 0.0827P] \]
where \( P = (F_o^2 + 2F_c^2)/3 \)

\[ (\Delta \sigma)_{\text{max}} < 0.001 \]
\[ \Delta \rho_{\text{max}} = 0.18 \text{ e Å}^{-3} \]
\[ \Delta \rho_{\text{min}} = -0.26 \text{ e Å}^{-3} \]

Flack parameter: 0.38 (2)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å\(^2\))

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<th>y</th>
<th>z</th>
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<th>( U_{eq}^*/U_{eq} )</th>
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Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of \( F^2 \) against ALL reflections. The weighted R-factor wR and goodness of fit S are based on \( F^2 \), conventional R-factors R are based on F, with F set to zero for negative \( F^2 \). The threshold expression of \( F^2 > 2\sigma(F^2) \) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on \( F^2 \) are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.
### Atomic displacement parameters (Å²)

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### Geometric parameters (Å, °)

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