Supporting Information

General Remarks

Most of chemicals were purchased from Sigma-Aldrich, Strem, Acros, TCI or Alfa Aesar and used as such unless stated otherwise. Solvents (Anhydrous and under inert atmosphere) were collected from The Solvent purification system by M BRAUN and used under standard schlenk technique. NMR spectra were recorded on Bruker Avance 300 and Bruker ARX 400 spectrometers. Chemical shifts (ppm) are given relative to solvent: references for CDCl$_3$ were 7.26 ppm (1H NMR) and 77.00 ppm (13C NMR). Multiplets were assigned as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet) dd (doublet of doublet), m (multiplet) and br. s (broad singlet).

GC-yields were calculated using hexadecane as internal standard. All measurements were carried out at room temperature unless otherwise stated. Electron impact (EI) mass spectra were recorded on AMD 402 mass spectrometer (70 eV). High resolution mass spectra (HRMS) were recorded on Agilent 6210. The data are given as mass units per charge (m/z). Gas chromatography analysis was performed on an Agilent HP-7890A instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 µm film thickness) using argon as carrier gas. The products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063-0.2 mm, 70-230 mesh (Merck).

General Procedure

A: A 4 mL screw-cap vial was charged with CuBr(Me$_2$S) (5.1 mg, 5 mol%), 4,4′,4″-tri-tert-butyl-2,2′:6′,2″-terpyridine (20 mg, 10 mol%), di(1-adamantyl)-n-butylphosphine (8.96 mg, 5mol%), acetonitrile (3 mL) and an oven-dried stirring bar. The vial was closed by Teflon septum and phenolic cap and connected with atmosphere with a needle. After 3-phenyl-1-propanol (0.5 mmol) and DTBP (2 mmol) were injected by syringe, the vial was fixed in an alloy plate and put into Paar 4560 series autoclave (300 mL) under argon atmosphere. At room temperature, the autoclave is flushed with 20 bar of ethene and 40 bar of carbon monoxide was charged. The autoclave was placed on a heating plate equipped with magnetic stirring and an aluminum block. The reaction is allowed to be heated under 120 °C for 12 hours. Afterwards, the autoclave is cooled to room temperature and the pressure was carefully released. After removal of solvent under reduced pressure, pure product was obtained by column chromatography on silica gel (eluent: pentane/ethyl acetate = 50-10:1).

B: A 4 mL screw-cap vial was charged with CuBr(Me$_2$S) (5.1 mg, 5 mol%), 4,4′,4″-tri-tert-butyl-2,2′:6′,2″-terpyridine (20 mg, 10 mol%), di(1-adamantyl)-n-butylphosphine (8.96 mg, 5mol%), acetonitrile (3 mL) and an oven-dried stirring bar. The vial was closed by Teflon septum and phenolic cap and connected with atmosphere with a needle. After 1-hexene (2 mmol), 3-phenyl-1-propanol (0.5 mmol) and DTBP (2 mmol) were injected by syringe, the vial was fixed in an alloy plate and put into Paar 4560 series autoclave (300 mL) under argon atmosphere. At room temperature, the autoclave is flushed with carbon monoxide for three times and 40 bar of carbon monoxide was charged. The autoclave was placed on a heating plate equipped with magnetic stirring and an aluminum block. The reaction is allowed to be heated under 110 °C for 12 hours. Afterwards, the autoclave is cooled to room temperature and the pressure was carefully released. After removal of solvent under reduced pressure, pure product was obtained by column chromatography on silica gel (eluent: pentane/ethyl acetate = 50-30:1).
Mechanistic studies

Reaction in the presence of TEMPO

A 4 mL screw-cap vial was charged with CuBr(Me_S) (5.1 mg, 5 mol%), 4,4',4''-tri-tert-butyl-2,2',6,2"-terpyridine (20 mg, 10 mol%), di(1-adamantyl)-n-butylphosphine (8.96 mg, 5 mol%), Tempo (156 mg, 2 equiv), acetonitrile (3 mL) and an oven-dried stirring bar. The vial was closed by Teflon septum and phenolic cap and connected with atmosphere with a needle. After 3-phenyl-1-propanol (0.5 mmol) and DTBP (2 mmol) were injected by syringe, the vial was fixed in an alloy plate and put into Paar 4560 series autoclave (300 mL) under argon atmosphere. At room temperature, the autoclave is flushed with 20 bar of ethane and 40 bar of carbon monoxide was charged. The autoclave was placed on a heating plate equipped with magnetic stirring and an aluminum block. The reaction is allowed to be heated under 120 °C for 12 hours. Afterwards, the autoclave is cooled to room temperature and the pressure was carefully released.

Synthesis of piperidin-2-one\(^1\)

A 4 mL screw-cap vial was charged with PtO\(_2\) (5.6 mg, 10 mol%). The vial was closed by Teflon septum and phenolic cap and connected with atmosphere with a needle. The vial is flushed with carbon monoxide for three times than 3-Phenylpropyl 4-cyanobutanoate (0.25 mmol), MeOH (3 mL) were injected by syringe, the vial was fixed in an alloy plate and put into Paar 4560 series autoclave (300 mL) under argon atmosphere. At room temperature, the autoclave is flushed with H\(_2\) for three times and 5 bar of H\(_2\) was charged. The autoclave was placed on a heating plate equipped with magnetic stirring and an aluminum block. The reaction is allowed to be heated under 25 °C for 72 hours. Afterwards, the pressure was carefully released. After removal of solvent under reduced pressure, pure product was obtained by column chromatography on silica gel (MeOH/CH\(_2\)Cl\(_2\) = 1:10).

Synthesis of estrone derivative

A 4 mL screw-cap vial was charged with Pd(OAc)\(_2\) (2.24 mg, 2 mol%), di(1-adamantyl)-n-butylphosphine (10.74 mg, 6 mol%), estrone (135 mg, 0.5 mmol), 1-4dioxane (2 mL) and an oven-dried stirring bar. The vial was closed by Teflon septum and phenolic cap and connected with atmosphere with a needle. After 2-bromobenzyl 2-(2-cyanoethyl)octanoate (0.5 mmol), and Et\(_3\)N (1 mmol) were injected by syringe, the vial was fixed in an alloy plate and put into Paar 4560 series autoclave (300 mL) under argon atmosphere. At room temperature, the autoclave is flushed with carbon monoxide for three times and 5 bar of carbon monoxide was charged. The autoclave was placed on a heating plate equipped with magnetic stirring and an aluminum block. The reaction is allowed to be heated under 100 °C for 16 hours. Afterwards, the autoclave is cooled to room temperature and the pressure was carefully released. After removal of solvent under reduced pressure, pure product was obtained by column chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1).
Analytic Data of Products

3-Phenylpropyl 4-cyanobutanoate

\[
\text{NC} \quad \text{O} \quad \text{O} \\
\text{H NMR (300 MHz, Chloroform-}d) \delta 7.28 – 7.05 (m, 5H), 4.05 (t, J = 6.5 Hz, 2H), 2.62 (dd, J = 8.5, 6.8 Hz, 2H), 2.40 (dt, J = 8.2, 7.1 Hz, 2H), 1.98 – 1.85 (m, 4H), 1.45 – 1.31 (m, 2H).
\]
\[\text{13C NMR (75 MHz, CDCl}_3) \delta 171.98, 141.02, 128.48, 128.38, 126.08, 118.98, 64.22, 32.34, 32.20, 30.09, 20.75, 16.57.\]
\[\text{GC-MS (EI, 70ev): m/z(%) = 231(M+, 1), 119(6), 118(85), 117(100), 96(15), 91(59), 78(11), 77(12), 68(15), 65(17), 41(29), 39(13).}\]
\[\text{HRMS(ESI): calcd. for [C}_{14}\text{H}_{17}\text{NO}_2^+\text{Na}^+]: 254.12593, \text{found: 254.11524.}\]

Benzyl 4-cyanobutanoate

\[
\text{NC} \quad \text{O} \quad \text{O} \\
\text{H NMR (300 MHz, Chloroform-}d) \delta 7.43 – 7.30 (m, 5H), 5.14 (s, 2H), 2.54 (t, J = 7.1 Hz, 2H), 2.45 (t, J = 7.1 Hz, 2H), 2.10 – 1.90 (m, 2H).
\]
\[\text{13C NMR (75 MHz, CDCl}_3) \delta 171.79, 135.58, 128.65, 128.43, 128.30, 118.95, 66.65, 32.41, 20.77, 16.54.\]
\[\text{GC-MS (EI, 70ev): m/z(%) = 203(M+, 10), 109(10), 108(90), 105(14), 96(19), 91(100), 79(24), 77(32), 68(14), 65(32), 63(12), 51(17), 42(11), 41(44), 40(12), 39(28), 29(7).}\]
\[\text{HRMS(EI): calcd. for [C}_{12}\text{H}_{13}\text{NO}_2^+: 203.09452, \text{found: 203.09408.}\]

Ethyl 4-cyanobutanoate

\[
\text{NC} \quad \text{O} \\
\text{H NMR (300 MHz, Chloroform-}d) \delta 4.13 (q, J = 7.1 Hz, 2H), 2.45 (t, J = 7.1 Hz, 2H), 2.02 – 1.88 (m, 2H), 1.24 (t, J = 7.1 Hz, 2H), 2.02 – 1.88 (m, 2H).
\]
\[\text{GC-MS (EI, 70ev): m/z(%) = 141(M+, 5), 114(10), 96(100), 68(30), 41(40).}\]

Cyclopropylmethyl 4-cyanobutanoate

\[
\text{NC} \quad \text{O} \\
\text{H NMR (300 MHz, Chloroform-}d) \delta 3.92 (d, J = 7.3 Hz, 2H), 2.49 (dt, J = 12.4, 7.1 Hz, 4H), 2.09 – 1.90 (m, 2H), 1.19 – 1.02 (m, 1H), 0.63 – 0.52 (m, 2H), 0.35 – 0.20 (m, 2H).
\]
\[\text{13C NMR (75 MHz, CDCl}_3) \delta 172.08, 119.05, 69.64, 32.43, 20.81, 16.56, 9.74, 3.29.\]
\[\text{GC-MS (EI, 70ev): m/z(%) = 167(M+, 5), 139(10), 114(10), 96(100), 68(40), 55(45), 41(30).}\]

(Perfluorophenyl)methyl 4-cyanobutanoate

\[
\text{NC} \quad \text{O} \\
\text{H NMR (300 MHz, Chloroform-}d) \delta 5.23 (t, J = 1.6 Hz, 2H), 2.53 (t, J = 7.1 Hz, 2H), 2.47 (t, J = 7.1 Hz, 2H), 2.11 – 1.90 (m, 2H).
\]
\[\text{13C NMR (75 MHz, CDCl}_3) \delta 171.25, 118.77, 53.57, 31.99, 20.58, 16.50.\]
\[\text{19F NMR (282 MHz, Chloroform-}d) \delta -141.93 (dddd, J = 21.5, 8.0, 3.8, 2.0 Hz), -152.15 (tt, J = 20.7, 2.4 Hz), -161.10 – -161.65 (m).\]
GC-MS (EI, 70ev): m/z(%) = 293(M+,5), 265(10), 211(8), 197(10), 181(100), 161(15), 143(5), 131(8), 117(10), 96(50), 69(15), 41(10).

Allyl 4-cyanobutanoate

\[
\text{\begin{center} \includegraphics[width=0.2\textwidth]{allyl_cyanobutanoate} \end{center}}\]

\(^1\)H NMR (300 MHz, Chloroform-d) \(\delta\) 5.90 (ddt, \(J = 17.2, 10.4, 5.8\) Hz, 1H), 5.39 – 5.19 (m, 2H), 4.58 (dt, \(J = 5.8, 1.4\) Hz, 2H), 2.49 (dt, \(J = 17.3, 7.1\) Hz, 4H), 2.11 – 1.88 (m, 2H).
\(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 171.62, 131.82, 118.64, 65.45, 32.29, 20.73.
GC-MS (EI, 70ev): m/z(%) = 153(M+,5), 138(5), 125(3), 110(5), 96(100), 81(10), 68(40), 55(10), 41(10).

4-((Trifluoromethyl)thio)benzyl 4-cyanobutanoate

\[
\text{\begin{center} \includegraphics[width=0.2\textwidth]{trifluoromethyl_thio_benzyl_cyanobutanoate} \end{center}}\]

\(^1\)H NMR (300 MHz, Chloroform-d) \(\delta\) 7.72 – 7.58 (m, 2H), 7.45 – 7.33 (m, 2H), 5.16 (s, 2H), 2.57 (t, \(J = 7.1\) Hz, 2H), 2.46 (t, \(J = 7.0\) Hz, 2H), 2.12 – 1.91 (m, 2H).
\(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 171.64, 138.65, 136.52, 131.54, 128.96, 127.45, 124.40, 118.88, 65.59, 32.27, 20.66, 16.53.

2-Bromobenzyl 4-cyanobutanoate

\[
\text{\begin{center} \includegraphics[width=0.2\textwidth]{2_bromobenzyl_cyanobutanoate} \end{center}}\]

\(^1\)H NMR (300 MHz, Chloroform-d) \(\delta\) 7.59 (ddd, \(J = 8.0, 1.3, 0.4\) Hz, 1H), 7.43 – 7.37 (m, 1H), 7.33 (ddd, \(J = 7.3, 1.3\) Hz, 1H), 7.25 – 7.17 (m, 1H), 5.22 (s, 2H), 2.58 (t, \(J = 7.1\) Hz, 2H), 2.52 – 2.43 (m, 2H), 2.10 – 1.95 (m, 2H).
\(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 171.56, 134.88, 132.98, 130.17, 129.99, 127.60, 123.65, 118.92, 66.23, 32.33, 20.77, 16.57.
GC-MS (EI, 70ev): m/z(%) = 281(M+,5), 251(5), 235(5), 239(5), 202(100), 185(10), 168(40), 157(10), 143(3), 131(5), 107(90), 96(20), 89(40), 68(20), 55(15), 41(20).

3-Phenylpropyl 2-(2-cyanoethyl)hexanoate

\[
\text{\begin{center} \includegraphics[width=0.2\textwidth]{3_phenylpropyl_cyanohexanoate} \end{center}}\]

\(^1\)H NMR (300 MHz, Chloroform-d) \(\delta\) 7.28 – 7.03 (m, 5H), 4.04 (td, \(J = 6.5, 1.1\) Hz, 2H), 2.62 (dd, \(J = 8.6, 6.7\) Hz, 2H), 2.43 (dddd, \(J = 9.5, 8.1, 5.7, 4.7\) Hz, 1H), 2.36 – 2.16 (m, 2H), 1.97 – 1.82 (m, 3H), 1.79 – 1.67 (m, 1H), 1.64 – 1.51 (m, 1H), 1.50 – 1.35 (m, 1H), 1.30 – 1.14 (m, 4H), 0.82 (t, \(J = 6.9\) Hz, 3H).
\(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 174.71, 141.00, 128.50, 128.42, 128.39, 126.11, 119.13, 64.05, 44.20, 32.20, 31.78, 30.22, 29.18, 27.53, 22.52, 15.38, 13.90.
GC-MS (EI, 70ev): m/z(%) = 287(M+,1), 119(10), 118(100), 117(60), 91(54), 79(6), 77(7), 65(9), 55(11), 41(20), 29(8).
HRMS(ESI): calcd. for \([C_{18}H_{25}NO_2]^+\): 310.17775, found: 310.17807; calcd. for \([C_{18}H_{25}NO_2]^+\): 288.19581, found: 288.19569.

Methyl 2-(2-cyanoethyl)hexanoate

\[
\text{\begin{center} \includegraphics[width=0.2\textwidth]{methyl_cyanohexanoate} \end{center}}\]
H NMR (400 MHz, Chloroform-d) δ 3.70 (s, 3H), 2.51 (ddddd, J = 9.7, 8.0, 5.8, 4.6 Hz, 1H), 2.45 – 2.25 (m, 2H), 1.98 (ddddd, J = 13.7, 9.6, 7.4, 6.2 Hz, 1H), 1.81 (ddt, J = 13.8, 7.8, 4.6 Hz, 1H), 1.71 – 1.59 (m, 1H), 1.54 – 1.44 (m, 1H), 1.33 – 1.23 (m, 4H), 0.88 (t, J = 7.0 Hz, 3H).

13C NMR (75 MHz, CDCl3) δ 175.18, 119.10, 51.81, 44.09, 31.75, 29.15, 27.50, 22.48, 15.38, 13.85.

GC-MS (EI, 70ev): m/z(%) =183(M+,1), 152(100), 113(14), 84(20), 73(10), 69(10), 57(25), 55(62), 53(11), 43(85), 42(17), 41(67), 29(58).


Hexyl 2-(2-cyanoethyl)hexanoate

1H NMR (300 MHz, Chloroform-d) δ 4.08 (td, J = 6.7, 2.2 Hz, 2H), 2.56 – 2.40 (m, 1H), 2.39 – 2.23 (m, 2H), 1.96 (ddddd, J = 13.6, 9.5, 7.4, 6.2 Hz, 1H), 1.78 (dtd, J = 13.7, 7.9, 4.7 Hz, 1H), 1.69 – 1.15 (m, 14H), 0.98 – 0.76 (m, 6H).

13C NMR (75 MHz, CDCl3) δ 174.74, 119.10, 64.81, 44.21, 31.76, 31.36, 29.13, 28.55, 27.56, 25.56, 22.47, 17.34, 13.95, 13.82.

GC-MS (EI, 70ev): m/z(%) =253(M+,1), 152(56), 134(36), 113(11), 85(23), 84(20), 83(15), 73(10), 69(10), 56(31), 55(62), 53(11), 43(82), 41(80), 29(69).

Octyl 2-(2-cyanoethyl)hexanoate

1H NMR (300 MHz, Chloroform-d) δ 4.09 (td, J = 6.7, 2.4 Hz, 2H), 2.55 – 2.43 (m, 1H), 2.42 – 2.26 (m, 2H), 1.99 (ddddd, J = 13.7, 9.6, 7.4, 6.2 Hz, 1H), 1.89 – 1.74 (m, 1H), 1.71 – 1.17 (m, 18H), 0.88 (td, J = 7.0, 3.3 Hz, 6H).

13C NMR (75 MHz, CDCl3) δ 174.79, 119.14, 64.86, 44.22, 31.78, 31.76, 29.70, 29.16, 29.14, 28.60, 27.55, 25.91, 22.63, 22.49, 17.34, 13.95, 13.86.

GC-MS (EI, 70ev): m/z(%) = 281(M+,1), 252(5), 238(7), 224(10), 210(4), 166(20), 152(100), 96(16), 84(34), 57(20), 56(31), 55(54), 41(80), 29(40).

Benzyl 2-(2-cyanoethyl)hexanoate

1H NMR (300 MHz, Chloroform-d) δ 7.33 – 7.22 (m, 5H), 5.08 (d, J = 0.7 Hz, 2H), 2.48 (ddddd, J = 9.5, 8.0, 5.8, 4.7 Hz, 1H), 2.37 – 2.11 (m, 2H), 1.92 (ddddd, J = 13.7, 9.6, 7.4, 6.2 Hz, 1H), 1.74 (ddt, J = 13.8, 7.9, 4.7 Hz, 1H), 1.65 – 1.52 (m, 1H), 1.51 – 1.39 (m, 1H), 1.24 – 1.14 (m, 4H), 0.79 (t, J = 7.0 Hz, 3H).

13C NMR (75 MHz, CDCl3) δ 174.52, 135.75, 128.62, 128.41, 128.32, 119.07, 66.52, 44.18, 31.72, 29.08, 27.57, 22.46, 15.30, 13.83.

GC-MS (EI, 70ev): m/z(%) = 259(M+,5), 231(5), 214(10), 108(28), 107(10), 92(10), 91(100), 65(13), 55(10), 41(16), 29(7).


4-Fluorobenzyl 2-(2-cyanoethyl)hexanoate

1H NMR (300 MHz, Chloroform-d) δ 7.43 – 7.29 (m, 2H), 7.13 – 6.94 (m, 2H), 5.27 – 5.02 (m, 2H), 2.54 (ddddd, J = 9.5, 8.0, 5.7, 4.7 Hz, 1H), 2.43 – 2.18 (m, 2H), 1.98 (ddddd, J = 13.6, 9.5, 7.2, 6.2 Hz, 1H), 1.81 (ddt, J = 13.8, 7.8, 4.8 Hz, 1H), 1.72 – 1.57 (m, 1H), 1.56 – 1.42 (m, 1H), 1.34 – 1.17 (m, 4H), 0.85 (t, J = 7.0 Hz, 3H).

13C NMR (75 MHz, Chloroform-d) δ 174.49, 162.72 (d, J = 247.3 Hz), 131.61 (d, J = 3.3 Hz), 130.39 (d, J = 8.3 Hz), 115.56 (d, J = 21.6 Hz), 65.78 , 44.12 , 31.71 , 29.05 , 27.50 , 22.44 , 15.31, 13.81.
3-(Trifluoromethyl)benzyl 2-(2-cyanoethyl)hexanoate

\[
\text{\textbf{1H NMR (300 MHz, Chloroform-}d\textbf{)}} \delta 7.67 – 7.44 (m, 4H), 5.28 – 5.10 (m, 5H), 2.59 (dddd, \textit{J} = 9.4, 9.4, 7.1, 6.3 Hz, 1H), 1.83 (dt, \textit{J} = 13.9, 7.8, 4.8 Hz, 1H), 1.70 – 1.45 (m, 2H), 1.36 – 1.19 (m, 4H), 0.85 (t, \textit{J} = 7.0 Hz, 3H).
\]

13C NMR (75 MHz, Chloroform-\textit{d}) \delta 174.39, 136.77, 131.47, 129.17, 125.02 (dd, \textit{J} = 24.1, 3.8 Hz, 1H), 118.95, 65.57, 44.09, 31.74, 29.06, 27.45, 22.43, 15.32, 13.75.

GC-MS (EI, 70ev): m/z(%) = 277(M+,1), 152(5), 109(100), 107(5), 41(13). HRMS(ESI): calcd. for \([\text{C}_{16}\text{H}_{20}\text{FNO}_2+\text{Na}]^+\): 300.13703, found: 300.13645.

2-Methoxybenzyl 2-(2-cyanoethyl)hexanoate

\[
\text{\textbf{1H NMR (300 MHz, Chloroform-}d\textbf{)}} \delta 7.33 (td, \textit{J} = 7.5, 1.6 Hz, 2H), 7.02 – 6.84 (m, 2H), 5.18 (s, 2H), 3.85 (s, 3H), 2.64 – 2.47 (m, 1H), 2.45 – 2.20 (m, 2H), 1.99 (dddd, \textit{J} = 13.8, 9.6, 7.7, 6.0 Hz, 1H), 1.89 – 1.76 (m, 1H), 1.74 – 1.61 (m, 1H), 1.56 – 1.43 (m, 1H), 1.35 – 1.23 (m, 4H), 0.92 – 0.82 (m, 3H).
\]

13C NMR (75 MHz, CDCl\textit{d}) \delta 174.59, 157.67, 130.13, 129.92, 123.91, 120.42, 119.21, 110.47, 62.28, 55.37, 44.31, 31.75, 29.10, 27.75, 22.50, 15.20, 13.85.

GC-MS (EI, 70ev): m/z(%) = 327(M+,1), 159(100), 152(30), 124(31), 109(20), 82(8), 55(19), 41(27), 39(11), 29(16). HRMS(ESI): calcd. for \([\text{C}_{17}\text{H}_{20}\text{FNO}_3+\text{Na}]^+\): 350.13383, found: 350.13328.

4-Bromobenzyl 2-(2-cyanoethyl)hexanoate

\[
\text{\textbf{1H NMR (300 MHz, Chloroform-}d\textbf{)}} \delta 7.50 – 7.34 (m, 2H), 7.18 – 7.13 (m, 2H), 5.02 (d, \textit{J} = 1.7 Hz, 2H), 2.49 (dddd, \textit{J} = 9.5, 8.0, 5.8, 4.8 Hz, 1H), 2.38 – 2.16 (m, 2H), 1.92 (dddd, \textit{J} = 13.6, 9.5, 7.2, 6.2 Hz, 1H), 1.82 – 1.69 (m, 1H), 1.66 – 1.53 (m, 1H), 1.49 – 1.36 (m, 1H), 1.18 (dddd, \textit{J} = 14.6, 10.6, 8.5, 6.7, 2.7 Hz, 4H), 0.79 (t, \textit{J} = 7.0 Hz, 3H).
\]

13C NMR (75 MHz, CDCl\textit{d}) \delta 174.43, 134.72, 131.80, 121.70, 119.13, 65.72, 44.09, 31.71, 29.06, 27.46, 22.45, 15.34, 13.82.

GC-MS (EI, 70ev): m/z(%) = 337(M+,5), 311(11), 185(17), 171(100), 170(12), 169(98), 152(15), 124(23), 91(10), 90(55), 89(51), 82(11), 63(19), 55(33), 43(16), 41(47), 39(19), 29(26), 55(10), 41(16), 29(7).

HRMS(ESI): calcd. for \([\text{C}_{16}\text{H}_{20}\text{BrNO}_2+\text{Na}]^+\): 360.05696, found: 360.05631, calcd. for \([\text{C}_{16}\text{H}_{20}\text{BrNO}_2+\text{Na}]^+\): 362.05507, found: 362.05431.

2-(Thiophen-2-yl)ethyl 2-(2-cyanoethyl)hexanoate

\[
\text{\textbf{1H NMR (300 MHz, Chloroform-}d\textbf{)}} \delta 7.21 (ddd, \textit{J} = 4.9, 3.0, 0.4 Hz, 1H), 6.97 (ddt, \textit{J} = 3.0, 1.4, 0.9 Hz, 1H), 6.91 (ddt, \textit{J} = 4.9, 1.4, 0.4 Hz, 1H), 4.28 (dd, \textit{J} = 6.7, 1.4 Hz, 2H), 3.02 – 2.86 (m, 2H), 2.41 (dddd, \textit{J} = 9.6, 8.1, 5.8, 4.6 Hz, 1H), 2.29 – 2.06 (m, 2H), 1.85 (dddd, \textit{J} = 13.6, 9.6, 7.4, 6.0 Hz, 1H), 1.77 – 1.66 (m, 1H), 1.60 – 1.50 (m, 1H), 1.44 – 1.33 (m, 1H), 1.28 – 1.07 (m, 4H), 0.80 (t, \textit{J} = 7.0 Hz, 3H).
\]

13C NMR (75 MHz, CDCl\textit{d}) \delta 174.59, 137.82, 128.07, 125.82, 121.70, 119.13, 64.36, 44.22, 31.74, 29.59, 29.10, 27.55, 22.49, 15.22, 13.85.
4-Phenylbutyl 2-(2-cyanoethyl)hexanoate

$\text{H NMR (300 MHz, Chloroform-}d\text{)} \delta 7.24 - 7.17 (m, 2H), 7.15 - 7.05 (m, 3H), 4.04 (tdd, J = 6.2, 3.0, 1.8 Hz, 2H), 2.57 (ddt, J = 6.5, 4.0, 2.3 Hz, 2H), 2.49 - 2.35 (m, 1H), 2.34 (s, 3H), 1.90 (dddd, J = 13.6, 9.5, 7.3, 6.2 Hz, 1H), 1.79 - 1.66 (m, 5H), 1.65 - 1.50 (m, 5H), 1.47 - 1.33 (m, 1H), 1.31 - 1.09 (m, 4H), 0.81 (t, J = 6.9 Hz, 3H).

$\text{13C NMR (75 MHz, CDCl}_3\text{)} \delta 174.75, 141.90, 128.38, 125.90, 119.12, 64.56, 44.21, 35.41, 31.76, 29.16, 28.22, 27.74, 27.54, 22.50, 15.36, 13.87.

GC-MS (EI, 70ev): m/z(%) = 301(M+,1), 152(7), 132(10), 117(15), 107(100), 91(80), 79(10), 65(12), 55(18).


Allyl 2-(2-cyanoethyl)hexanoate

$\text{H NMR (300 MHz, Chloroform-}d\text{)} \delta 5.91 (ddt, J = 17.2, 10.4, 5.8 Hz, 1H), 5.38 - 5.20 (m, 2H), 4.60 (dt, J = 5.8, 1.4 Hz, 2H), 2.53 (dddd, J = 9.5, 8.0, 5.9, 4.7 Hz, 1H), 2.43 - 2.26 (m, 2H), 1.99 (dddd, J = 13.7, 9.5, 7.4, 6.2 Hz, 1H), 1.82 (dd, J = 13.8, 7.9, 4.7 Hz, 1H), 1.71 - 1.59 (m, 1H), 1.57 - 1.46 (m, 1H), 1.35 - 1.22 (m, 4H), 0.88 (t, J = 6.9 Hz, 3H).

$\text{13C NMR (75 MHz, CDCl}_3\text{)} \delta 174.36, 131.88, 119.10, 118.71, 65.31, 44.14, 31.71, 29.10, 27.51, 22.47, 15.35.

GC-MS (EI, 70ev): m/z(%) = 209(M+,1), 166(5), 124(100), 107(20), 94(10), 85(26), 84(34), 73(13), 69(30), 57(14), 56(34), 55(55), 43(100), 41(80), 29(40).

Hexyl 2-(2-cyanoethyl)octanoate

$\text{H NMR (300 MHz, Chloroform-}d\text{)} \delta 4.10 (td, J = 6.7, 2.5 Hz, 2H), 2.56 - 2.43 (m, 1H), 2.42 - 2.26 (m, 2H), 1.99 (dddd, J = 13.7, 9.5, 7.4, 6.2 Hz, 1H), 1.82 (dd, J = 13.8, 7.9, 4.7 Hz, 1H), 1.70 - 1.20 (m, 18H), 0.96 - 0.81 (m, 6H).

$\text{13C NMR (75 MHz, CDCl}_3\text{)} \delta 174.80, 119.14, 64.87, 44.27, 32.11, 31.60, 31.39, 29.07, 28.59, 27.58, 26.96, 25.60, 22.55, 22.53, 15.38, 14.03, 13.98.

GC-MS (EI, 70ev): m/z(%) = 281(M+,1), 180(60), 153(5), 152(53), 138(6), 96(16), 94(15), 85(26), 84(34), 73(13), 69(30), 57(20), 56(31), 55(54), 43(100), 41(80), 29(40).

HRMS (ESI): calcd. for $[\text{C}_{17}\text{H}_{31}\text{NO}_2\text{S}+\text{Na}]^+$: 304.2247, found: 304.22531.

3-Phenylpropyl 2-(2-cyanoethyl)octanoate

$\text{H NMR (300 MHz, Chloroform-}d\text{)} \delta 7.26 - 7.17 (m, 2H), 7.16 - 7.06 (m, 3H), 4.05 (td, J = 6.5, 1.5 Hz, 2H), 2.62 (dd, J = 8.6, 6.7 Hz, 2H), 2.51 - 2.37 (m, 1H), 2.34 - 2.19 (m, 2H), 2.00 - 1.83 (m, 3H), 1.73 (td, J = 13.8, 7.9, 4.8 Hz, 1H), 1.63 - 1.52 (m, 1H), 1.48 - 1.35 (m, 1H), 1.21 (dd, J = 7.7, 3.2 Hz, 8H), 0.90 - 0.76 (m, 3H).

$\text{13C NMR (75 MHz, CDCl}_3\text{)} \delta 174.72, 140.98, 128.49, 128.38, 126.11, 119.12, 64.06, 44.23, 32.20, 32.10, 31.62, 30.21, 29.10, 27.53, 27.01, 22.57, 15.39, 14.06.

GC-MS (EI, 70ev): m/z(%) = 315(M+,1), 191(12), 118(100), 117(56), 91(58), 75(57), 65(7), 55(11), 41(18), 29(9).

HRMS (ESI): calcd. for $[\text{C}_{20}\text{H}_{30}\text{NO}_2\text{S}+\text{Na}]^+$: 338.20905, found: 338.20874.

3-Phenylpropyl 2-(2-cyanoethyl)nonanoate
¹H NMR (300 MHz, Chloroform-§) δ 7.30 – 7.02 (m, 5H), 4.05 (td, J = 6.6, 1.6 Hz, 2H), 2.62 (dd, J = 8.6, 6.7 Hz, 2H), 2.45 (ddddd, J = 9.5, 8.1, 5.7, 4.7 Hz, 1H), 2.34 – 2.19 (m, 2H), 1.97 – 1.85 (m, 3H), 1.73 (ddt, J = 13.8, 7.9, 4.8 Hz, 1H), 1.57 (dd, J = 13.7, 7.8, 5.8 Hz, 1H), 1.47 – 1.34 (m, 1H), 1.20 (dddd, J = 7.2, 4.1, 2.2 Hz, 10H), 0.87 – 0.69 (m, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 174.72, 140.97, 128.49, 128.38, 126.11, 119.11, 64.06, 44.23, 32.20, 32.10, 31.76, 30.21, 29.40, 29.09, 27.52, 27.05, 22.62, 15.39, 14.08.

GC-MS (EI, 70ev): m/z(%) = 329(M+, 1), 119(11), 118(100), 117(43), 91(48), 78(10), 65(6), 43(13), 41(20), 29(7).


3-Phenylpropyl 2-(2-cyanoethyl)dodecanoate

CN

1H NMR (300 MHz, Chloroform-§) δ 7.28 – 7.07 (m, 5H), 4.06 (td, J = 6.6, 1.7 Hz, 2H), 2.63 (dd, J = 8.6, 6.8 Hz, 2H), 2.51 – 2.39 (m, 1H), 2.36 – 2.19 (m, 2H), 1.91 (ddq, J = 13.0, 6.8, 4.0 Hz, 3H), 1.57 (d, J = 13.7, 7.8, 4.7 Hz, 1H), 1.49 – 1.35 (m, 1H), 1.20 (dt, J = 6.3, 3.7 Hz, 12H), 0.87 – 0.75 (m, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 174.73, 140.97, 128.49, 128.38, 126.11, 119.11, 64.07, 44.23, 32.20, 32.11, 31.83, 30.21, 29.44, 29.39, 27.52, 27.04, 22.65, 15.40, 14.10.

GC-MS (EI, 70ev): m/z(%) = 343(M+, 1), 118(100), 117(35), 103(5), 92(7), 91(49), 43(15), 41(22), 39(6), 29(8).


3-Phenylpropyl 2-(2-cyanoethyl)-4-methylpentanoate

CN

1H NMR (300 MHz, Chloroform-§) δ 7.32 – 6.97 (m, 5H), 4.05 (td, J = 6.6, 1.2 Hz, 2H), 2.63 (dd, J = 8.6, 6.8 Hz, 2H), 2.58 – 2.46 (m, 1H), 2.37 – 2.15 (m, 2H), 1.99 – 1.84 (m, 3H), 1.73 (ddt, J = 13.9, 7.9, 4.7 Hz, 1H), 1.64 – 1.50 (m, 1H), 1.49 – 1.35 (m, 1H), 1.20 (d, J = 10.8 Hz, 16H), 0.87 – 0.70 (m, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 174.73, 140.97, 128.49, 128.38, 126.11, 119.11, 64.07, 44.23, 32.20, 32.11, 31.90, 30.21, 29.59, 29.56, 29.44, 29.32, 27.52, 27.05, 22.69, 15.39, 14.12.

GC-MS (EI, 70ev): m/z(%) = 310(M+, 1), 159(3), 119(14), 118(100), 117(39), 91(45), 79(4), 65(5), 57(6), 43(19), 41(16), 29(7).

$^1$H NMR (300 MHz, Chloroform-$d$) δ 7.24 – 7.16 (m, 4H), 7.14 – 7.06 (m, 6H), 4.05 (t, $J = 6.6$ Hz, 2H), 2.62 (dd, $J = 8.6, 6.8$ Hz, 2H), 2.59 – 2.40 (m, 3H), 2.31 – 2.21 (m, 2H), 1.99 – 1.85 (m, 4H), 1.81 – 1.66 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 174.37, 140.95, 140.92, 128.64, 128.57, 128.56, 128.53, 128.42, 128.40, 126.27, 126.17, 119.04, 64.29, 43.84, 33.77, 33.36, 32.26, 30.23, 27.66, 15.34.

GC-MS (EI, 70ev): m/z(%) = 335(M+,1), 129(3), 119(12), 118(64), 117(29), 104(10), 103(5), 92(8), 91(100), 77(8), 65(15), 41(5).

HRMS(ESI): calcd. for [C$_{22}$H$_{25}$NO$_2$+Na$^+$]: 358.17775, found: 358.17762.

[1,1'-Biphenyl]-4-ylmethyl 2-(2-cyanoethyl)hexanoate

\[
\text{O} \quad \begin{array}{c}
\text{CN} \\
\text{Ph}
\end{array}
\]

$^1$H NMR (300 MHz, Chloroform-$d$) δ 7.61 – 7.19 (m, 9H), 5.10 (d, $J = 1.3$ Hz, 2H), 2.48 (dddd, $J = 9.5, 8.1, 5.7, 4.7$ Hz, 1H), 2.34 – 2.11 (m, 2H), 1.99 – 1.83 (m, 1H), 1.73 (ddt, $J = 13.8, 7.8, 4.8$ Hz, 1H), 1.65 – 1.51 (m, 1H), 1.49 – 1.34 (m, 1H), 1.24 – 1.10 (m, 4H), 0.77 (t, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 174.57, 141.38, 140.57, 134.76, 128.85, 128.83, 127.53, 127.37, 127.13, 119.12, 66.28, 44.22, 31.75, 29.11, 27.58, 22.50, 15.34, 13.88.

GC-MS (EI, 70ev): m/z(%) = 335(M+,10), 184(10), 167(100), 165(30), 152(15), 124(6), 77(5), 55(9).

HRMS(ESI): calcd. for [C$_{22}$H$_{25}$NO$_2$+Na$^+$]: 358.17775, found: 358.17701.

2-(Phenylthio)ethyl 2-(2-cyanoethyl)hexanoate

\[
\text{O} \quad \begin{array}{c}
\text{CN} \\
\text{S}
\end{array}
\]

$^1$H NMR (300 MHz, Chloroform-$d$) δ 7.34 – 7.28 (m, 2H), 7.27 – 7.20 (m, 2H), 7.18 – 7.11 (m, 1H), 4.20 (t, $J = 6.7$ Hz, 2H), 3.08 (t, $J = 6.7$ Hz, 2H), 2.50 – 2.34 (m, 1H), 2.32 – 2.17 (m, 2H), 1.88 (dddd, $J = 13.9, 7.9, 4.7$ Hz, 1H), 1.61 – 1.48 (m, 1H), 1.46 – 1.34 (m, 1H), 1.31 – 1.10 (m, 4H), 0.90 – 0.74 (m, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 174.45, 134.97, 129.98, 129.12, 126.72, 119.11, 62.95, 44.15, 32.56, 31.65, 29.12, 27.44, 22.48, 15.37, 13.88.

GC-MS (EI, 70ev): m/z(%) = 305(M+,5), 253(5), 207(7), 152(10), 136(100), 109(20), 91(10), 65(8), 55(9).

HRMS(ESI): calcd. for [C$_{17}$H$_{23}$NO$_2$+H$^+$]: 306.15223, found: 306.15276.calcd. for[C$_{17}$H$_{23}$NO$_2$+Na$^+$]: 328.13417, found: 328.13381.

Naphthalen-1-ylmethyl 2-(2-cyanoethyl)hexanoate

\[
\text{O} \quad \begin{array}{c}
\text{CN} \\
\text{Ph}
\end{array}
\]

$^1$H NMR (300 MHz, Chloroform-$d$) δ 8.06 – 7.97 (m, 1H), 7.93 – 7.83 (m, 2H), 7.63 – 7.41 (m, 4H), 5.70 – 5.53 (m, 2H), 2.55 (dddd, $J = 9.5, 8.1, 5.7, 4.7$ Hz, 1H), 2.38 – 2.15 (m, 2H), 1.98 (dddd, $J = 13.8, 9.5, 7.3, 6.4$ Hz, 1H), 1.78 (ddt, $J = 13.8, 7.8, 4.7$ Hz, 1H), 1.70 – 1.55 (m, 1H), 1.54 – 1.40 (m, 1H), 1.28 – 1.14 (m, 4H), 0.88 – 0.72 (m, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 174.55, 133.77, 131.58, 131.21, 129.50, 128.81, 127.86, 126.63, 126.04, 125.26, 123.44, 119.06, 64.89, 44.30, 31.74, 29.05, 27.53, 22.44, 15.28, 13.77.

GC-MS (EI, 70ev): m/z(%) = 309(M+,15), 158(20), 141(100), 140(10), 139(12), 115(20), 102(5), 82(8), 55(10).

HRMS(ESI): calcd. for [C$_{20}$H$_{23}$NO$_2$+Na$^+$]: 332.1621, found: 332.16163.
4-((Trifluoromethyl)thio)benzyl 2-(2-cyanoethyl)hexanoate

\[
\text{\text{H NMR (300 MHz, Chloroform-}d\text{) } \delta 7.74 – 7.53 (m, 2H), 7.47 – 7.34 (m, 2H), 5.17 (d, } J = 2.4 \text{ Hz, 2H), 2.59 (ddd, } J = 9.4, 8.0, 5.8, 4.8 \text{ Hz, 1H), 2.46 – 2.22 (m, 2H), 2.01 (ddd, } J = 13.6, 9.4, 7.2, 6.4 \text{ Hz, 1H), 1.83 (dtt, } J = 13.9, 7.8, 4.8 \text{ Hz, 1H), 1.73 – 1.44 (m, 2H), 1.37 – 1.16 (m, 4H), 0.85 (t, } J = 7.0 \text{ Hz, 3H).}
\]

\[
\text{\text{13C NMR (75 MHz, CDCl}_3\text{) } \delta 174.39, 138.77, 136.49, 129.02, 118.94, 65.51, 44.08, 31.71, 29.06, 27.43, 22.43, 15.33, 13.78.}
\]

\[
\text{GC-MS (EI, 70eV): } m/z(\%) = 359(M^+, 10), 331(5), 207(10), 193(8), 192(100), 171(4), 152(20), 124(25), 122(50), 107(10), 82(15), 78(13), 69(10), 55(10).
\]

\[
\text{HRMS(ESI): calcd. for } [\text{C}_{17}\text{H}_{20}\text{F}_3\text{NO}_2\text{+Na }^+]^+: 382.10591, \text{ found: 382.10582.}
\]

4-Methoxybenzyl 2-(2-cyanoethyl)hexanoate

\[
\text{\text{H NMR (300 MHz, Chloroform-}d\text{) } \delta 7.29 – 7.14 (m, 2H), 6.87 – 6.72 (m, 2H), 5.00 (s, 2H), 3.73 (s, 3H), 2.50 – 2.36 (m, 1H), 2.33 – 2.10 (m, 2H), 1.89 (ddd, } J = 13.7, 9.5, 7.4, 6.2 \text{ Hz, 1H), 1.72 (dtt, } J = 13.8, 7.9, 4.7 \text{ Hz, 1H), 1.64 – 1.49 (m, 1H), 1.48 – 1.34 (m, 1H), 1.25 – 1.08 (m, 4H), 0.78 (t, } J = 6.9 \text{ Hz, 3H).}
\]

\[
\text{\text{13C NMR (75 MHz, CDCl}_3\text{) } \delta 174.56, 159.73, 130.16, 127.91, 119.11, 113.98, 66.30, 55.28, 44.20, 31.70, 29.06, 27.59, 22.46, 15.26, 13.82.}
\]

\[
\text{GC-MS (EI, 70eV): } m/z(\%) = 289(M^+, 10), 138(5), 137(7), 122(10), 121(100), 109(5), 105(4), 91(15), 78(20), 65(10), 55(15).
\]

\[
\text{HRMS(ESI): calcd. for } [\text{C}_{17}\text{H}_{23}\text{NO}_3\text{+Na }^+]^+: 312.15701, \text{ found: 312.15751.}
\]

2-Benzylbenzyl 2-(2-cyanoethyl)hexanoate

\[
\text{\text{H NMR (300 MHz, Chloroform-}d\text{) } \delta 7.32 – 7.27 (m, 1H), 7.26 – 7.14 (m, 4H), 7.14 – 7.07 (m, 2H), 7.02 (s, 2H), 4.00 (s, 2H), 2.43 – 2.30 (m, 1H), 2.24 – 2.04 (m, 2H), 1.82 (ddd, } J = 13.8, 9.3, 7.5, 6.2 \text{ Hz, 1H), 1.66 (dtt, } J = 13.9, 7.9, 4.8 \text{ Hz, 1H), 1.57 – 1.45 (m, 1H), 1.43 – 1.33 (m, 1H), 1.23 – 1.09 (m, 4H), 0.77 (t, } J = 7.0 \text{ Hz, 3H).}
\]

\[
\text{\text{13C NMR (75 MHz, CDCl}_3\text{) } \delta 174.47, 140.20, 139.44, 133.89, 130.79, 130.03, 128.91, 128.68, 128.64, 128.55, 126.80, 126.23, 119.10, 64.57, 44.16, 38.52, 31.64, 29.10, 27.45, 22.50, 15.25, 13.87.}
\]

\[
\text{HRMS(ESI): calcd. for } [\text{C}_{17}\text{H}_{24}\text{NO}_2\text{+Na }^+]^+: 342.2042, \text{ found: 372.259.}
\]

2-(Trifluoromethyl)benzyl 2-(2-cyanoethyl)hexanoate

\[
\text{\text{H NMR (300 MHz, Chloroform-}d\text{) } \delta 7.69 (ddt, } J = 7.7, 1.3, 0.7 \text{ Hz, 1H), 7.62 – 7.51 (m, 2H), 7.49 – 7.41 (m, 1H), 5.35 – 5.22 (m, 2H), 2.58 (ddd, } J = 9.4, 8.0, 5.8, 4.7 \text{ Hz, 1H), 2.47 – 2.23 (m, 2H), 2.07 – 1.93 (m, 1H), 1.83 (dtt, } J = 13.9, 7.8, 4.7 \text{ Hz, 1H), 1.73 – 1.60 (m, 1H), 1.58 – 1.43 (m, 1H), 1.35 – 1.20 (m, 4H), 0.86 (t, } J = 6.9 \text{ Hz, 3H).}
\]
$^{13}$C NMR (75 MHz, Chloroform-$d$) δ 174.22, 133.77 (d, $J = 1.8$ Hz), 132.13 (d, $J = 1.2$ Hz), 130.52, 128.56, 126.68 – 125.67 (m), 122.30, 119.02, 63.06, 44.15, 31.62, 29.02, 27.42, 22.43, 15.28, 13.77.

GC-MS (EI, 70ev): m/z(%) = 327(M+,1), 307(8), 240(5), 199(8), 176(6), 159(100), 152(30), 140(10), 124(20), 119(10), 110(5), 109(20), 107(5), 98(5), 83(10), 82(12), 55(28).

HRMS(ESI): calcd. for [C$_{17}$H$_{20}$F$_3$NO$_2$ + Na$^+$]: 350.13383, found: 350.1335.

Benzy1 2-(2-cyanoethyl)-5-phenoxypentanoate

2-Bromobenzyl 2-(2-cyanoethyl)octanoate

Cyclopropylmethyl 2-(2-cyanoethyl)hexanoate

Benzy1 2-benzyl-4-cyanobutanoate

$^{1}$H NMR (300 MHz, Chloroform-$d$) δ 7.34 – 7.09 (m, 7H), 6.91 – 6.83 (m, 1H), 6.82 – 6.74 (m, 2H), 5.08 (s, 2H), 3.91 – 3.81 (m, 2H), 2.62 – 2.52 (m, 1H), 2.36 – 2.15 (m, 2H), 1.96 (dddd, $J = 13.7, 9.4, 7.3, 6.3$ Hz, 1H), 1.87 – 1.64 (m, 5H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 174.15, 158.79, 135.62, 129.47, 128.67, 128.48, 128.35, 120.77, 118.97, 114.47, 67.03, 66.71, 43.92, 28.63, 27.66, 26.76, 15.27.

GC-MS (EI, 70ev): m/z(%) = 337(M+,5), 224(20), 184(5), 152(8), 99(20), 91(100), 78(10), 65(15), 41(5).

2-Bromobenzyl 2-(2-cyanoethyl)octanoate

Cyclopropylmethyl 2-(2-cyanoethyl)hexanoate

$^{1}$H NMR (300 MHz, Chloroform-$d$) δ 7.58 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.41 (dd, $J = 7.6, 1.8$ Hz, 1H), 7.32 (td, $J = 7.5, 1.3$ Hz, 1H), 7.20 (ddd, $J = 7.9, 7.4, 1.8$ Hz, 1H), 5.21 (s, 2H), 2.58 (dddd, $J = 9.5, 8.0, 5.7, 4.7$ Hz, 1H), 2.46 – 2.23 (m, 2H), 2.01 (ddddd, $J = 13.7, 9.5, 7.4, 6.3$ Hz, 1H), 1.75 – 1.55 (m, 1H), 1.33 – 1.19 (m, 8H), 0.95 – 0.78 (m, 3H), 0.64 – 0.46 (m, 2H), 0.32 – 0.17 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 174.28, 134.97, 132.97, 130.45, 130.03, 127.58, 123.79, 119.08, 66.20, 44.25, 31.57, 29.04, 27.53, 26.91, 22.52, 15.36, 14.04.

Cyclopropylmethyl 2-(2-cyanoethyl)hexanoate

$^{1}$H NMR (300 MHz, Chloroform-$d$) δ 3.92 (dd, $J = 7.4, 1.0$ Hz, 2H), 2.57 – 2.42 (m, 1H), 2.41 – 2.24 (m, 2H), 1.97 (dddd, $J = 13.7, 9.6, 7.4, 6.2$ Hz, 1H), 1.80 (ddt, $J = 13.8, 7.9, 4.7$ Hz, 1H), 1.63 (dddt, $J = 9.7, 7.9, 6.2$ Hz, 1H), 1.56 – 1.42 (m, 1H), 1.28 (dddd, $J = 7.1, 6.0, 4.5, 2.7$ Hz, 4H), 1.17 – 1.02 (m, 1H), 0.92 – 0.78 (m, 3H), 0.64 – 0.46 (m, 2H), 0.32 – 0.17 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 174.79, 119.14, 69.38, 44.25, 31.76, 29.11, 27.62, 22.46, 15.31, 13.84, 9.88, 3.27.

GC-MS (EI, 70ev): m/z(%) = 223(M+,1), 194(5), 183(10), 167(8), 152(20), 141(10), 127(55), 124(80), 107(10), 95(10), 82(15), 55(100), 54(18), 41(20).

Benzy1 2-benzyl-4-cyanobutanoate

$^{1}$H NMR (300 MHz, Chloroform-$d$) δ 7.28 – 7.22 (m, 3H), 7.19 – 7.12 (m, 5H), 7.06 – 7.01 (m, 2H), 5.00 (s, 2H), 2.94 (dd, $J = 12.6, 6.7$ Hz, 1H), 2.84 – 2.65 (m, 2H), 2.33 – 2.11 (m, 2H), 1.99 – 1.84 (m, 1H), 1.74 (ddt, $J = 13.9, 7.9, 4.2$ Hz, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 173.76, 137.80, 135.48, 128.89, 128.67, 128.63, 128.42, 128.35, 126.84, 118.92, 66.72, 46.05, 38.16, 27.12, 15.30.

GC-MS (EI, 70ev): m/z(%) = 293(M+,20), 248(15), 215(10), 202(21), 180(20), 158(15), 118(30), 107(35), 91(100), 77(11), 65(17).

HRMS(ESI): calcd. for [C$_{19}$H$_{18}$NO$_2$ + Na$^+$]: 316.1308, found: 316.1308.
4-(2-oxooxazolidine-3-carbonyl)decanenitrile

\[\text{CN} \quad \text{O} \quad \text{N} \quad \text{O} \quad \text{O}\]

1H NMR (300 MHz, Chloroform-d) \(\delta\) 4.46 – 4.35 (m, 2H), 4.12 – 3.96 (m, 2H), 3.87 (dddd, \(J = 8.8, 7.1, 6.3, 4.5\) Hz, 1H), 2.37 (dd, \(J = 7.5, 7.0, 2.9\) Hz, 2H), 2.13 – 2.01 (m, 1H), 1.86 (dddd, \(J = 13.9, 8.0, 6.8, 4.5\) Hz, 1H), 1.77 – 1.62 (m, 1H), 1.50 – 1.39 (m, 1H), 1.25 (td, \(J = 5.8, 5.3, 3.4\) Hz, 8H), 1.05 – 0.73 (m, 3H).

13C NMR (75 MHz, CDCl3) \(\delta\) 175.21, 153.25, 119.20, 62.00, 42.75, 42.69, 32.22, 31.57, 29.17, 26.83, 22.53, 15.18, 14.02.

GC-MS (EI, 70ev): m/z(%) = 266(M+,1), 226(26), 195(18), 182(15), 170(11), 153(26), 142(80), 140(18), 122(10), 108(20), 100(10), 88(100), 69(20), 55(24), 41(21).

2-(2-cyanoethyl)-N-methyl-N-tosylhexanamide

\[\text{CN} \quad \text{O} \quad \text{N} \quad \text{S} \quad \text{O} \quad \text{O}\]

1H NMR (300 MHz, Chloroform-d) \(\delta\) 7.84 – 7.70 (m, 2H), 7.40 – 7.30 (m, 2H), 3.36 (s, 3H), 3.31 – 3.16 (m, 1H), 2.44 (dt, \(J = 0.4\) Hz, 3H), 2.31 – 2.07 (m, 2H), 1.97 (dd, \(J = 13.9, 8.4, 7.5\) Hz, 1H), 1.75 (dddd, \(J = 13.7, 8.0, 7.2, 5.1\) Hz, 1H), 1.61 – 1.46 (m, 1H), 1.44 – 1.31 (m, 1H), 1.22 – 1.08 (m, 2H), 1.06 – 0.93 (m, 2H), 0.78 (t, \(J = 7.2\) Hz, 3H).

13C NMR (75 MHz, CDCl3) \(\delta\) 175.52, 145.19, 136.58, 129.97, 127.48, 119.16, 43.88, 33.34, 32.33, 28.90, 27.60, 22.60, 21.62, 14.89, 13.79.

GC-MS (EI, 70ev): m/z(%) = 336(M+,1), 240(5), 216(6), 186(10), 166(15), 165(100), 154(25), 124(20), 122(10), 107(10), 91(50), 82(10), 65(18), 41(10).

2-Piperidinone

\[\text{H} \quad \text{N} \quad \text{O}\]

1H NMR (300 MHz, Chloroform-d) \(\delta\) 6.37 (s, 1H), 3.30 (dddd, \(J = 6.1, 4.2, 2.2, 0.9\) Hz, 2H), 2.39 – 2.31 (m, 2H), 1.86 – 1.70 (m, 4H).

13C NMR (75 MHz, CDCl3) \(\delta\) 172.46, 42.36, 31.51, 22.80, 22.28, 20.85.

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 2-(2-(2-cyanoethyl)octanoyl)benzoate

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

1H NMR (400 MHz, Chloroform-d) \(\delta\) 8.23 (dd, \(J = 7.9, 1.4\) Hz, 1H), 7.62 (td, \(J = 7.5, 1.4\) Hz, 1H), 7.58 – 7.52 (m, 1H), 7.48 (td, \(J = 7.6, 1.5\) Hz, 1H), 7.37 – 7.31 (m, 1H), 7.03 – 6.90 (m, 2H), 5.70 – 5.46 (m, 2H), 2.94 (dd, \(J = 8.3, 3.7\) Hz, 2H), 2.65 – 2.22 (m, 6H), 2.20 – 1.92 (m, 5H), 1.81 (td, \(J = 13.8, 8.0, 4.6\) Hz, 1H), 1.73 – 1.57 (m, 3H), 1.57 – 1.40 (m, 4H), 1.32 – 1.15 (m, 9H), 0.92 (s, 3H), 0.89 – 0.83 (m, 3H).

13C NMR (101 MHz, CDCl3) \(\delta\) 220.65, 174.12, 165.07, 148.42, 138.06, 137.54, 133.01, 131.36, 129.00, 128.15, 127.99, 126.42, 121.53, 119.07, 118.70, 64.70, 50.30, 47.83, 44.13, 44.05, 37.88, 35.74, 31.93, 31.44, 29.33, 28.93, 27.41, 26.81, 26.22, 25.66, 22.41, 21.48, 15.13, 13.94, 13.72.

LC-MS: calcd. for \([\text{C}_{37}\text{H}_{45}\text{NO}_{5}]^{+}\): 606, found \([\text{C}_{37}\text{H}_{45}\text{NO}_{5}]^{+}\): 606

HR-MS(EI): calcd. for \([\text{C}_{37}\text{H}_{45}\text{NO}_{5}]^{+}\): 583.32922, found: 583.32893
Reference


PROTON CDCl$_3$ (C:\Bruker\TopSpin3.5\spin) 1707 16

C13CPD CDCl$_3$ (C:\Bruker\TopSpin3.5\spin) 1707 16
Yahui Li  L-150-4a

PROTON CDCl3 (C:\Bruker\TopSpin3.5.pl6) 1705 10

C13CPD CDCl3 (C:\Bruker\TopSpin3.5.pl6) 1705 10
PROTON CDCl3 (C:\Bruker\TopSpin3.5pl6) 1706 22

\[ \text{Diagram image} \]

C13CPD CDCl3 (C:\Bruker\TopSpin3.5pl6) 1706 22

\[ \text{Diagram image} \]
PROTON CDC3 (C:/Bruker/TopSpin3.5/TopSpin1.1) 1706 19

C13CPD CDC3 (C:/Bruker/TopSpin3.5/TopSpin1.1) 1706 19
PROTON CDCl3 (C:\Bruker\TopSpin3.5\spks) 1706 20

1H NMR 620.1 Hz
Yahui Li L-162-1

O

N

O

C13CPD CDCl3 (C:\Bruker\TopSpin3.5\spks) 1706 20

1H NMR 620.1 Hz
Yahui Li L-162-1

O

N

O
PROTON CDCl3 (C:\Bruker\TopSpin3.5\pl6) 1707 12

\[ \text{f1 (ppm)} \]

\[ \text{Li/L-138-4} \]

\[ \text{C13CPD CDCl3 (C:\Bruker\TopSpin3.5\pl6) 1707 12} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{N} \]
PROTON CDCl₃ (C:\Bruker\TopSpin3.5pl6) 1706 23

Yahui Li  L-159-1

C₁₃CPD CDCl₃ (C:\Bruker\TopSpin3.5pl6) 1706 23
Yahui Li
L-168-5a

PROTON CDCl3 (C:\Bruker\TopSpin3.5.pl6) 1706.18

C13CPD CDCl3 (C:\Bruker\TopSpin3.5.pl6) 1706.18
Yahui Li  L-189-3

PROTON CDC13 (C:\Bruker\TopSpin3.5\pl6) 1707 16

C13CPD CDC13 (C:\Bruker\TopSpin3.5\pl6) 1707 16
PROTON CDCl₃ (C:\Bruker\TopSpin3.5\pl6) 1707 20

C₁₃CD₀ CDCl₃ (C:\Bruker\TopSpin3.5\pl6) 1707 20
PROTON CDCl3 (C:\Bruker\TopSpin3.5\pl6) 1707 3

C\13CPD CDCl3 (C:\Bruker\TopSpin3.5\pl6) 1707 3
PROTON CDC3 (C:\Bruker\TopSpin3.5\Spk) 1707 19

[Chemical structure image]

C13 CPD CDC3 (C:\Bruker\TopSpin3.5\Spk) 1707 19

[Chemical structure image]