Supporting Information

Highly enantioselective Biginelli reaction catalyzed by SPINOL-phosphoric acids

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1. General Information

Unless otherwise noted, all reagents were purchased from commercial supplies and used without further purification. Solvents were used without dryness. $^1$H NMR spectra were recorded on 400 MHz spectrometer. The chemical shifts were reported relative to internal standard TMS (0) in CDCl$_3$ or 2.5 in DMSO-d$_6$. The following abbreviations were used to describe peak patterns where appropriate: br= broad, s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet. Coupling constants were reported in Hertz (Hz). $^{13}$C NMR spectra were recorded on 100 MHz spectrometer, referred to the internal solvent signals (77.0 for CDCl$_3$ or 40.0 for DMSO-d$_6$). Optical rotations were determined using a Perkin Elmer Model 341 polarimeter at 20 °C. The enantiomeric excesses (ee) were determined by chiral HPLC analysis on Daicel Chiralpak AS-H or AD-H columns.

2. General Procedure for the Enantioselective Biginelli Reaction

Under nitrogen atmosphere, aldehyde 2 (0.1 mmol), thiourea 3a (0.12 mmol) and catalyst (S)-1f (0.005 mmol) were dissolved in 1 mL xylene. After being stirred at room temperature for 2 hours, acetoacetate 4 (0.3 mmol) was added, and the resulting mixture was stirred at 50 °C for 3 days as monitored by TLC. Then the reaction was cooled to room temperature, diluted with ethyl acetate and added some silica gel. The organic solvents were removed under vacuum and the residue was purified by flash column chromatography on silica gel (ethyl acetate / petroleum ether = 1/4 – 1/2) to afford the corresponding DHPM product.

(S)-ethyl-6-methyl-4-(4-nitrophenyl)-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5a):

This product was obtained in 92% yield after chromatography and 94% ee as determined by HPLC [Daicel Chiralpak AS-H, n-hexane / i-propanol = 70 / 30, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 17.84 min, t (major) = 22.50 min]. $\left[\alpha\right]_{D}^{20} = +223.6^\circ$ (c = 0.6, EtOAc); $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 1.12 (t, $J = 6.8$ Hz, 3H), 2.33 (s, 3H), 4.03 (q, $J = 6.8$ Hz, 2H), 5.33 (d, $J = 3.6$ Hz, 1H), 7.51 (d, $J = 9.2$ Hz, 2H), 8.25 (d, $J = 8.8$ Hz, 2H), 9.76 (s, 1H), 10.49 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ 14.4, 17.7, 54.1, 60.2, 100.2, 124.4, 128.3, 146.4, 147.4, 150.8, 165.3, 175.0; MS (ESI) $m/z$ 320.1 ([M-H$^-$]).

(S)-ethyl-6-methyl-4-(3-nitrophenyl)-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5b):

This product was obtained in 86% yield after chromatography and 97% ee as determined by HPLC [Daicel Chiralpak AD-H, n-hexane / i-propanol = 80 / 20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 17.40 min, t (major) = 23.02 min]. $\left[\alpha\right]_{D}^{20} = +125.3^\circ$ (c = 0.44, EtOAc); $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$
1.12 (t, \( J = 6.4 \) Hz, 3H), 2.34 (s, 3H), 4.00-4.08 (m, 2H), 5.36 (d, \( J = 3.6 \) Hz, 1H), 7.69-7.72 (m, 2H), 8.10 (s, 1H), 8.16-8.19 (m, 1H), 9.77 (d, \( J = 1.6 \) Hz, 1H), 10.51 (s, 1H); \(^{13}\)C NMR (100 MHz, DMSO-d\(_6\)) \( \delta \) 14.4, 17.7, 54.0, 60.2, 100.3, 121.6, 123.2, 130.9, 133.5, 146.0, 146.5, 148.3, 165.3, 175.0; MS (ESI) \( m/z \) 320.1 ([M-H]⁻).

(S)-ethyl-6-methyl-4-(2-nitrophenyl)-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5c):

![Chemical Structure](structure1.png)

This product was obtained in 81% yield after chromatography and 99% ee as determined by HPLC [Daicel Chiralpak AD-H, \( n \)-hexane / \( i \)-propanol = 90 / 10, 1.0 mL/min, \( \lambda = 254 \) nm, t (major) = 19.68 min, t (minor) = 29.28 min. \([\alpha]_D^{20} = +304.8^\circ\) (c = 0.34, EtOAc); \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \( \delta \) 0.94 (t, \( J = 6.8 \) Hz, 3H), 2.32 (s, 3H), 3.84-3.92 (m, 2H), 5.97 (d, \( J = 2.4 \) Hz, 1H), 7.52-7.57 (m, 2H), 7.76 (t, \( J = 7.6 \) Hz, 1H), 7.94 (d, \( J = 8.0 \) Hz, 1H), 9.58 (s, 1H), 10.46 (s, 1H); \(^{13}\)C NMR (100 MHz, DMSO-d\(_6\)) \( \delta \) 14.4, 17.7, 54.1, 60.2, 124.4, 128.3, 146.4, 147.4, 150.8, 165.3, 175.0; MS (ESI) \( m/z \) 320.1 ([M-H]⁻).

(S)-ethyl-6-methyl-4-(4-bromophenyl)-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5d):

![Chemical Structure](structure2.png)

This product was obtained in 92% yield after chromatography and 99% ee as determined by HPLC [Daicel Chiralpak AD-H, \( n \)-hexane / \( i \)-propanol = 80 / 20, 1.0 mL/min, \( \lambda = 254 \) nm, t (major) = 12.04 min, t (minor) = 9.07 min. \([\alpha]_D^{20} = +137.4^\circ\) (c = 0.66, EtOAc); \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \( \delta \) 1.10 (t, \( J = 6.8 \) Hz, 3H), 2.30 (s, 3H), 4.01 (q, \( J = 7.2 \) Hz, 2H), 5.16 (d, \( J = 3.2 \) Hz, 1H), 7.18 (d, \( J = 8.4 \) Hz, 2H), 7.56 (d, \( J = 8.4 \) Hz, 2H), 9.68 (d, \( J = 1.6 \) Hz, 1H), 10.40 (s, 1H); \(^{13}\)C NMR (100 MHz, DMSO-d\(_6\)) \( \delta \) 14.5, 17.7, 54.0, 60.2, 100.7, 121.3, 129.2, 134.3, 145.9, 165.5, 174.8; MS (ESI) \( m/z \) 355.0 ([M+H]⁺).

(S)-ethyl-6-methyl-4-(3-bromophenyl)-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5e):

![Chemical Structure](structure3.png)

This product was obtained in 82% yield after chromatography and 92% ee as determined by HPLC [Daicel Chiralpak AS-H, \( n \)-hexane / \( i \)-propanol = 70 / 30, 1.0 mL/min, \( \lambda = 254 \) nm, t (major) = 15.85 min. \([\alpha]_D^{20} = +105.0^\circ\) (c = 0.48, EtOAc); \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \( \delta \) 1.11 (t, \( J = 6.8 \) Hz, 3H), 2.30 (s, 3H), 3.98-4.07 (m, 2H), 5.18 (d, \( J = 3.2 \) Hz, 1H), 7.22 (d, \( J = 8.0 \) Hz, 1H), 7.32-7.38 (m, 2H), 7.49 (d, \( J = 8.0 \) Hz, 1H), 9.67 (s, 1H), 10.40 (s, 1H); \(^{13}\)C NMR (100 MHz, DMSO-d\(_6\)) \( \delta \) 14.5, 17.7, 54.0, 60.2, 100.7, 121.3, 129.2, 134.3, 145.9, 165.5, 174.8; MS (ESI) \( m/z \) 355.0 ([M+H]⁺).
DMSO-d$_6$ δ 14.4, 17.7, 54.0, 60.1, 100.6, 122.1, 125.8, 129.7, 131.0, 131.4, 146.0, 146.5, 165.4, 174.8; MS (ESI) m/z 354.9 ([M+H$^+$]).

(S)-ethyl-6-methyl-4-(3-fluorophenyl)-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5f):

This product was obtained in 89% yield after chromatography and 94% ee as determined by HPLC [Daicel Chiralpak AD-H, n-hexane / i-propanol = 90 / 10, 0.6 mL/min, λ = 254 nm, t (major) = 32.42 min, t (minor) = 36.94 min]. [α]$_D^{20}$ = +86.5° (c = 0.47, EtOAc); $^1$H NMR (400 MHz, DMSO-d$_6$) δ 1.11 (t, $J$ = 5.2 Hz, 3H), 2.31 (s, 3H), 4.00-4.07 (m, 2H), 5.21 (d, $J$ = 2.8 Hz, 1H), 6.99 (d, $J$ = 7.6 Hz, 1H), 7.07-7.15 (m, 2H), 7.39-7.44 (m, 1H), 9.71 (s, 1H), 10.43 (s, 1H); 13C NMR (100 MHz, DMSO-d$_6$) δ 14.5, 17.7, 54.0, 60.2, 100.7, 113.6, 115.0, 122.9, 131.2, 146.1, 146.7, 162.6, 165.5, 174.9; MS (ESI) m/z 295.2 ([M+H$^+$]).

(S)-ethyl-6-methyl-4-(2-chlorophenyl)-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5g):

This product was obtained in 88% yield after chromatography and 97% ee as determined by HPLC [Daicel Chiralpak AS-H, n-hexane / i-propanol = 85 / 15, 1.0 mL/min, λ = 254 nm, t (major) = 21.62 min, t (minor) = 15.98 min]. [α]$_D^{20}$ = +59.5° (c = 0.6, EtOAc); $^1$H NMR (400 MHz, CDCl$_3$) δ 1.06 (t, $J$ = 6.8 Hz, 3H), 2.44 (s, 3H), 4.02 (q, $J$ = 7.6 Hz, 2H), 5.90 (d, $J$ = 2.8 Hz, 1H), 7.21-7.25 (m, 3H), 7.36-7.39 (m, 1H), 7.57 (s, 1H), 8.66 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.8, 17.8, 52.6, 60.3, 100.7, 127.6, 128.5, 129.6, 129.8, 132.6, 138.5, 144.6, 164.8, 174.1; MS (ESI) m/z 311.1 ([M+H$^+$]).

(S)-ethyl-6-methyl-2-thioxo-4-p-tolyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5h):

This product was obtained in 96% yield after chromatography and 91% ee as determined by HPLC [Daicel Chiralpak AS-H, n-hexane / i-propanol = 70 / 30, 1.0 mL/min, λ = 254 nm, t (minor) = 15.91 min]. [α]$_D^{20}$ = +77.6° (c = 0.71, MeOH); $^1$H NMR (400 MHz, CDCl$_3$) δ 1.17 (t, $J$ = 6.8 Hz, 3H), 2.31 (s, 3H), 2.34 (s, 3H), 4.05-4.11 (m, 2H), 5.34 (d, $J$ = 2.8 Hz, 1H), 7.10 (d, $J$ = 7.6 Hz, 2H), 7.17 (d, $J$ = 8.0 Hz, 2H), 7.86 (s, 1H), 8.50 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 14.0, 18.1, 21.1, 55.7, 60.3, 103.0, 126.6, 129.4, 138.0, 139.5, 142.8, 165.3, 174.1; MS (ESI) m/z 290.9 ([M+H$^+$]).
(S)-ethyl-4-(3-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5i):

![Chemical Structure]

This product was obtained in 90% yield after chromatography and 94% ee as determined by HPLC [Daicel Chiralpak AS-H, n-hexane / i-propanol = 70 / 30, 1.0 mL/min, λ = 254 nm, t (minor) = 13.97 min, t (major) = 19.77 min]. [α]D 20 = +71.7° (c = 0.38, MeOH); 1H NMR (400 MHz, CDCl3) δ 1.17 (t, J = 6.8 Hz, 3H), 2.35 (s, 3H), 3.77 (s, 3H), 4.06-4.14 (m, 2H), 5.36 (d, J = 3.2 Hz, 1H), 6.79-6.82 (m, 2H), 6.87 (d, J = 7.6 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.87 (s, 1H), 8.46 (s, 1H); 13C NMR (100 MHz, CDCl3) δ 14.1, 18.1, 55.2, 55.9, 60.3, 102.7, 112.7, 113.4, 118.9, 129.9, 143.0, 143.8, 159.9, 165.2, 174.3; MS (ESI) m/z 307.0 ([M+H]+).

(S)-ethyl-4-(benzo[d][1,3]dioxol-5-yl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5j):

![Chemical Structure]

This product was obtained in 84% yield after chromatography and 94% ee as determined by HPLC [Daicel Chiralpak AS-H, n-hexane / i-propanol = 70 / 30, 1.0 mL/min, λ = 254 nm, t (minor) = 24.00 min, t (major) = 28.17 min]. [α]D 20 = +85.2° (c = 0.41, EtOAc); 1H NMR (400 MHz, DMSO-d6) δ 1.11 (t, J = 6.4 Hz, 3H), 2.29 (s, 3H), 4.02 (q, J = 6.8 Hz, 2H), 5.10 (d, J = 4.0 Hz, 1H), 6.00 (s, 2H), 6.67-6.73 (m, 2H), 6.87 (d, J = 8.0 Hz, 1H), 9.59 (d, J = 2.0 Hz, 1H), 10.31 (s, 1H); 13C NMR (100 MHz, DMSO-d6) δ 14.5, 17.6, 54.2, 60.1, 101.2, 101.6, 107.2, 108.6, 120.1, 138.0, 145.5, 147.2, 147.9, 165.6, 174.6; MS (ESI) m/z 321.0 ([M+H]+).

(S)-ethyl-6-methyl-4-(naphthalen-1-yl)-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5k):

![Chemical Structure]

This product was obtained in 98% yield after chromatography and 99% ee as determined by HPLC [Daicel Chiralpak AS-H, n-hexane / i-propanol = 70 / 30, 1.0 mL/min, λ = 254 nm, t (minor) = 18.99 min, t (major) = 27.21 min]. [α]D 20 = +0.6° (c = 0.44, EtOAc); 1H NMR (400 MHz, DMSO-d6) δ 0.82 (t, J = 6.8 Hz, 3H), 2.40 (s, 3H), 3.78-3.88 (m, 2H), 6.08 (d, J = 4.0 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 7.48-7.62 (m, 3H), 7.88 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 8.38 (d, J = 8.4 Hz, 1H), 9.65 (s, 1H), 10.38 (s, 1H); 13C NMR (100 MHz, DMSO-d6) δ 14.3, 17.6, 54.2, 60.1, 101.2, 101.6, 107.2, 108.6, 120.1, 138.0, 145.5, 147.2, 147.9, 165.6, 174.6; MS (ESI) m/z 327.0 ([M+H]+).
(R)-ethyl-4-(furan-2-yl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5l):

This product was obtained in 80% yield after chromatography and 90% ee as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/i-propanol = 80/20, 0.7 mL/min, λ = 254 nm, t (minor) = 14.71 min, t (major) = 18.09 min]. \([\alpha]D^{20} = -40.9^\circ (c = 0.6, \text{EtOAc})\); \(^1H\) NMR (400 MHz, DMSO-d\(_6\)) δ 1.14 (t, \(J = 5.6\) Hz, 3H), 2.28 (s, 3H), 4.03-4.06 (m, 2H), 5.24 (d, \(J = 2.0\) Hz, 1H), 6.14-6.15 (m, 1H), 6.38 (s, 1H), 7.59 (s, 1H), 9.66 (s, 1H), 10.42 (s, 1H); \(^13C\) NMR (100 MHz, DMSO-d\(_6\)) δ 14.6, 17.6, 48.2, 60.1, 98.7, 106.8, 111.0, 143.2, 146.5, 155.1, 175.4; MS (ESI) \(m/z\) 265.1 ([M-H]–).

(S)-ethyl-4-cyclohexyl-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5m):

This product was obtained in 40% yield after chromatography and 84% ee as determined by HPLC [Daicel Chiralpak AS-H, n-hexane/i-propanol = 85/15, 1.0 mL/min, λ = 254 nm, t (major) = 14.46 min, t (minor) = 18.62 min]. \([\alpha]D^{20} = +203.4^\circ (c = 0.54, \text{EtOAc})\); \(^1H\) NMR (400 MHz, CDCl\(_3\)) δ 0.97-1.02 (m, 1H), 1.12-1.19 (m, 4H), 1.29 (t, \(J = 6.8\) Hz, 3H), 1.50-1.75 (m, 6H), 2.34 (s, 3H), 4.16-4.24 (m, 3H), 8.07 (s, 1H), 8.58 (s, 1H); \(^13C\) NMR (100 MHz, CDCl\(_3\)) δ 14.2, 17.9, 25.8, 26.0, 26.1, 26.6, 28.5, 44.8, 57.0, 60.2, 101.6, 143.9, 165.8, 175.5; MS (ESI) \(m/z\) 283.1 ([M+H]+).

(S)-methyl-6-methyl-4-(3-nitrophenyl)-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5n):

This product was obtained in 94% yield after chromatography and 91% ee as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/i-propanol = 75/25, 1.0 mL/min, λ = 254 nm, t (minor) = 12.55 min, t (major) = 19.46 min]. \([\alpha]D^{20} = +100.3^\circ (c = 0.48, \text{EtOAc})\); \(^1H\) NMR (400 MHz, DMSO-d\(_6\)) δ 2.34 (s, 3H), 3.58 (s, 3H), 5.35 (d, \(J = 3.6\) Hz, 1H), 7.68-7.72 (m, 2H), 8.09 (s, 1H), 8.16-8.19 (m, 1H), 9.83 (s, 1H), 10.56 (s, 1H); \(^13C\) NMR (100 MHz, DMSO-d\(_6\)) δ 17.8, 51.8, 53.8, 100.1, 121.6, 123.3, 131.0, 133.5, 145.7, 146.8, 148.4, 165.9, 175.0; MS (ESI) \(m/z\) 306.1 ([M-H]–).

(S)-isopropyl-6-methyl-4-(3-nitrophenyl)-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5o):

This product was obtained in 94% yield after chromatography and 95% ee as determined by HPLC
[Daicel Chiralpak AD-H, n-hexane / i-propanol = 80 / 20, 1.0 mL/min, λ = 254 nm, t (minor) = 13.27 min, t (major) = 21.39 min]. \([\alpha]_D^{20} = +112.9^\circ \text{ (c = 0.5, EtOAc)}\); \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) 1.01 (d, \(J = 4.8\) Hz, 3H), 1.19 (d, \(J = 5.2\) Hz, 3H), 2.32 (s, 3H), 4.83-4.88 (m, 1H), 5.33 (d, \(J = 2.4\) Hz, 1H), 7.67-7.72 (m, 2H), 8.08 (s, 1H), 8.18 (d, \(J = 6.4\) Hz, 1H), 9.77 (s, 1H), 10.50 (s, 1H); \(^{13}\)C NMR (100 MHz, DMSO-d\(_6\)) \(\delta\) 17.7, 21.9, 22.1, 54.1, 67.6, 100.6, 121.7, 123.2, 130.9, 133.5, 146.2, 146.3, 148.2, 164.8, 175.0; MS (ESI) \(m/z\) 334.1 ([M-H]⁻).

\((S)-methyl-4-(3,4-difluorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate\ (5p):

\[
\begin{array}{c}
\text{F} \\
\text{NH} \\
\text{S}
\end{array}
\]

This product was obtained in 90% yield after chromatography and 93% ee as determined by HPLC [Daicel Chiralpak AD-H, n-hexane / i-propanol = 90 / 10, 1.0 mL/min, λ = 254 nm, t (minor) = 21.90 min, t (major) = 28.21 min]. \([\alpha]_D^{20} = +60.9^\circ \text{ (c = 0.6, EtOAc)}\); \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) 2.32 (s, 3H), 3.58 (s, 3H), 5.21 (d, \(J = 3.2\) Hz, 1H), 7.07-7.10 (m, 1H), 7.20-7.25 (m, 1H), 7.40-7.47 (m, 1H), 9.73 (d, \(J = 1.6\) Hz, 1H), 10.47 (s, 1H); \(^{13}\)C NMR (100 MHz, DMSO-d\(_6\)) \(\delta\) 17.7, 51.6, 53.5, 100.3, 115.9, 118.2, 123.5, 141.4, 146.5, 149.6, 166.0, 174.9; MS (ESI) \(m/z\) 299.1 ([M+H]⁺).

3. Synthesis of dihydropyrimidinone 5q

\((S)-isopropyl-6-methyl-4-(3-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate\ (5q):

\[
\begin{array}{c}
\text{C} \\
\text{N} \\
\text{H}
\end{array}
\]

To a solution of \(5o\) (28.9 mg, 0.086 mmol) in ethyl acetate (1.6 mL) was added ammonia (0.7 mL) and 30% aqueous H\(_2\)O\(_2\) (0.7 mL). After stirred at 50 °C for 1 hour open to air, the reaction mixture was quenched with 1 mL water and extracted with ethyl acetate. The organic layer was dried over Na\(_2\)SO\(_4\), concentrated in vacuo, and the residue was purified by silica gel column chromatography (ethyl acetate / petroleum ether = 2/1). The product \(5q\) was obtained in 81% yield and 95% ee as determined by HPLC [Daicel Chiralpak AD-H, n-hexane / i-propanol = 80 / 20, 1.0 mL/min, λ = 254 nm, t (minor) = 9.30 min, t (major) = 13.19 min]. \([\alpha]_D^{20} = +90.8^\circ \text{ (c = 0.6, EtOAc)}\); \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) 1.00 (d, \(J = 6.4\) Hz, 3H), 1.19 (d, \(J = 6.4\) Hz, 3H), 2.30 (s, 3H), 4.81-4.88 (m, 1H), 5.32 (s, 1H), 7.66-7.74 (m, 2H), 7.91 (s, 1H), 8.11-8.16 (m, 2H), 9.37 (s, 1H); \(^{13}\)C NMR (100 MHz, DMSO-d\(_6\)) \(\delta\) 18.3, 21.9, 22.2, 54.2, 67.1, 99.1, 121.6, 122.7, 130.6, 133.5, 147.6, 148.2, 149.7, 152.3, 165.0; MS (ESI) \(m/z\) 317.9 ([M-H]⁻).
4. NMR spectra for compounds 5a-q
5. HPLC spectra for compounds 5a-q

94% ee. [Daicel Chiralpak AS-H, n-hexane / i-propanol = 70/30, 1.0 mL/min, λ = 254 nm]

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Totals: 2.75908e4 209.46260
97% ee. [Daicel Chiralpak AD-H, n-hexane / i-propanol = 80 / 20, 1.0 mL/min, $\lambda = 254$ nm]
99% ee. [Daicel Chiralpak AD-H, n-hexane / i-propanol = 90 / 10, 1.0 mL/min, $\lambda = 254$ nm]

**Figure 1:** Chromatogram showing the separation of compounds. The table below lists the peak retention times, widths, areas, heights, and percentages for the two peaks.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time [min]</th>
<th>Width [min]</th>
<th>Area [mAU]</th>
<th>Height [mAU]</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.981</td>
<td>0.6755</td>
<td>1.42570e4</td>
<td>319.13693</td>
<td>49.3004</td>
</tr>
<tr>
<td>2</td>
<td>30.768</td>
<td>1.0479</td>
<td>1.46616e4</td>
<td>208.03734</td>
<td>50.6996</td>
</tr>
</tbody>
</table>

**Totals:**

2.89186e4 mAU

**Figure 2:** Chromatogram showing the separation of another set of compounds. The table below lists the peak retention times, widths, areas, heights, and percentages for the two peaks.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time [min]</th>
<th>Width [min]</th>
<th>Area [mAU]</th>
<th>Height [mAU]</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.683</td>
<td>0.6870</td>
<td>3.79402e4</td>
<td>831.03552</td>
<td>99.4516</td>
</tr>
<tr>
<td>2</td>
<td>29.284</td>
<td>0.8822</td>
<td>209.19762</td>
<td>3.23646</td>
<td>0.5484</td>
</tr>
</tbody>
</table>

**Totals:**

3.81494e4 mAU
90% ee. [Daicel Chiralpak AD-H, n-hexane/\(i\)-propanol = 80/20, 1.0 mL/min, \(\lambda = 254\) nm]
92% ee. [Daicel Chiralpak AS-H, n-hexane / i-propanol = 70 / 30, 1.0 mL/min, $\lambda = 254$ nm]
94% ee. [Daicel Chiralpak AD-H, n-hexane / i-propanol = 90 / 10, 0.6 mL/min, λ = 254 nm]
97% ee. [Daicel Chiralpak AS-H, n-hexane / i-propanol = 85 / 15, 1.0 mL/min, λ = 254 nm]

Peak RetTime Type Width Area Height Area %
--- | ------ | ------ | ------------ | ------ | ------ | ------ | ------ | ------ |
1 15.298 BB 1.0028 1.24863e4 192.86852 50.1391
2 21.535 BB 1.4852 1.24170e4 117.87386 49.8609

Totals: 2.49033e4 310.74237
91% ee. [Daicel Chiralpak AS-H, n-hexane / i-propanol = 70 / 30, 1.0 mL/min, λ = 254 nm]
94% ee. [Daicel Chiralpak AS-H, n-hexane / i-propanol = 70 / 30, 1.0 mL/min, λ = 254 nm]
94% ee. [Daicel Chiralpak AS-H, n-hexane / i-propanol = 70 / 30, 1.0 mL/min, λ = 254 nm]
99% ee. [Daicel Chiralpak AS-H, \(n\)-hexane / \(i\)-propanol = 70 / 30, 1.0 mL/min, \(\lambda = 254\) nm]
90% ee. [Daicel Chiralpak AD-H, \( n \)-hexane / \( i \)-propanol = 80 / 20, 0.7 mL/min, \( \lambda = 254 \) nm]
84% ee. [Daicel Chiralpak AS-H, n-hexane / i-propanol = 85 / 15, 1.0 mL/min, λ = 254 nm]

**Peak RetTime Type Width Area Height Area %**

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.358</td>
<td>BB</td>
<td>1.0205</td>
<td>1.07209e4</td>
<td>162.72295</td>
<td>50.0956</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>17.920</td>
<td>BB</td>
<td>1.2667</td>
<td>1.06799e4</td>
<td>126.22408</td>
<td>49.9044</td>
<td></td>
</tr>
</tbody>
</table>

Totals: 2.14008e4 288.94703

**Peak RetTime Type Width Area Height Area %**

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.464</td>
<td>BB</td>
<td>1.1070</td>
<td>8649.51465</td>
<td>120.68172</td>
<td>91.9475</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>19.623</td>
<td>BB</td>
<td>1.1215</td>
<td>757.50275</td>
<td>9.75460</td>
<td>8.0525</td>
<td></td>
</tr>
</tbody>
</table>

Totals: 9407.01740 130.43632
91% ee. [Daicel Chiralpak AD-H, n-hexane / i-propanol = 75 / 25, 1.0 mL/min, λ = 254 nm]
95% ee. [Daicel Chiralpak AD-H, n-hexane / i-propanol = 80 / 20, 1.0 mL/min, λ = 254 nm]
93% ee. [Daicel Chiralpak AD-H, \( n \)-hexane / \( i \)-propanol = 90 / 10, 1.0 mL/min, \( \lambda \) = 254 nm]
95% ee. [Daicel Chiralpak AD-H, n-hexane / i-propanol = 80 / 20, 1.0 mL/min, \( \lambda = 254 \text{ nm} \)]