# Pd-Catalyzed Asymmetric Hydroalkylation of 1,3-Dienes: Access to Unnatural $\alpha$-Amino Acid Derivatives Containing Vicinal Quaternary and Tertiary Stereogenic Centers 

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## I. General Remarks

${ }^{1} \mathrm{H}$ NMR spectra were recorded on a Bruker 400 MHz spectrometer in $\mathrm{CDCl}_{3}$. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. ${ }^{13} \mathrm{C}$ NMR spectra were recorded on a Bruker 100 MHz spectrometer in $\mathrm{CDCl}_{3}$. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. ${ }^{19} \mathrm{~F}$ NMR spectra were recorded on a Bruker 376 MHz spectrometer in $\mathrm{CDCl}_{3}$. Chemical shifts are reported in ppm with the internal $\mathrm{CF}_{3} \mathrm{COOH}$ signal at 76.55 ppm . The data are reported as $(\mathrm{s}=$ single, $\mathrm{d}=$ double, $\mathrm{t}=$ triple, $\mathrm{q}=$ quarter, $\mathrm{m}=$ multiple or unresolved, brs = broad single, coupling constant(s) in Hz, integration). Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel-coated plates. Enantiomeric ratios were determined by chiral-phase HPLC analysis in comparison with authentic racemic materials. Substrates $\mathbf{1}$ and $\mathbf{2}$ were prepared according to the literature procedure. ${ }^{1,2}$ The absolute configuration of compound $\mathbf{7}$ was determined by comparing with the optical rotation of known chiral compound. ${ }^{3}$ The absolute configuration of others were assigned by analogy.

## II. General Procedure for Pd-Catalyzed Asymmetric Hydroalkylation of 1,3-

## Dienes with Azlactones

In an Ar-filled glovebox, to a vial equipped with a magnetic stirring rod was added successively: Pd-L7 catalyst ( $0.01 \mathrm{mmol}, 10 \mathrm{~mol} \%$ ), azalctone ( $0.15 \mathrm{mmol}, 1.5$ equiv.), $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ( 1 mL ), 1,3-diene ( $0.10 \mathrm{mmol}, 1.0$ equiv.), and lastly $\mathrm{Et}_{3} \mathrm{~N}(0.3 \mathrm{mmol}, 3.0$ equiv.). Then $\mathrm{HBF}_{4} \cdot \mathrm{Et}_{2} \mathrm{O}$ ( 0.01 mmol in 1 mL DCM) was added dropwise to the solution. Once starting material was consumed (monitored by TLC), the organic solvent was removed by rotary evaporation. The dr value was determined by ${ }^{1} \mathrm{H}$ NMR analysis of the crude mixture and the residue was purified by column chromatography to give the product. Procedure for the alcoholysis with MeOH : After the reaction of 1,3-diene with azlactone was completed, $\mathrm{MeOH}(1 \mathrm{~mL})$ and $\mathrm{K}_{2} \mathrm{CO}_{3}(0.5 \mathrm{mmol})$ were added, then
the mixture was stirred at room temperature for 2 h . The solvent was removed by vacuo, and the residue was purified by column chromatography on silica column.

## (R)-4-methyl-2-phenyl-4-((S,E)-4-phenylbut-3-en-2-yl)oxazol-5(4H)-one (3a):



Yield ( $92 \%$ ); 28.1 mg ; colorless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=20 / 1) ;[\alpha]^{28} \mathrm{D}=+119.8\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} N \mathrm{NR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.04(\mathrm{dd}, J=5.2,3.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.62-7.54(\mathrm{~m}, 1 \mathrm{H}), 7.53-$ $7.45(\mathrm{~m}, 2 \mathrm{H}), 7.44-7.36(\mathrm{~m}, 2 \mathrm{H}), 7.32(\mathrm{t}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.25-7.20(\mathrm{~m}, 1 \mathrm{H}), 6.54(\mathrm{~d}, J$ $=15.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.25(\mathrm{dd}, J=15.9,9.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.91-2.65(\mathrm{~m}, 1 \mathrm{H}), 1.50(\mathrm{~s}, 3 \mathrm{H}), 1.05$ $(\mathrm{d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 180.9,160.1,136.9,132.74,132.65$, 129.2, 128.8, 128.5, 128.0, 127.5, 126.3, 125.8, 72.4, 45.0, 22.6, 15.8. HRMS (ESI+) Calcd. For $\mathrm{C}_{20} \mathrm{H}_{20} \mathrm{NO}_{2}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 306.1489$, found: 306.1487. The product was analyzed by HPLC to determine the enantiomeric excess: 95\% ee (Chiralpak AD-H, $i$ propanol $/$ hexane $=2 / 98$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=220 \mathrm{~nm}$ ); $\mathrm{t}_{\mathrm{r}}=4.65$ and 5.15 min .

## (R)-4-ethyl-2-phenyl-4-((S,E)-4-phenylbut-3-en-2-yl)oxazol-5(4H)-one (3b):



Yield (85\%); 27.1 mg ; colorless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=20 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=+87.8\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ $\delta 8.06(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.59(\mathrm{t}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.50(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.40(\mathrm{~d}, J$ $=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.31(\mathrm{t}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.22(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.52(\mathrm{~d}, J=15.9 \mathrm{~Hz}$, $1 \mathrm{H}), 6.26(\mathrm{dd}, J=15.9,9.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.84(\mathrm{dq}, J=13.7,6.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.02(\mathrm{dq}, J=14.9$, $7.5 \mathrm{~Hz}, 1 \mathrm{H}), 1.90(\mathrm{dq}, J=14.6,7.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.04(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}), 0.80(\mathrm{t}, J=7.4$ $\mathrm{Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 180.5, 160.4, 136.9, 132.7, 132.3, 129.6, 128.8, 128.5, 128.0, 127.4, 126.3, 125.8, 77.2, 44.6, 29.3, 16.0, 8.1. HRMS (ESI+) Calcd. For
$\mathrm{C}_{21} \mathrm{H}_{22} \mathrm{NO}_{2}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 320.1645$, found: 320.1634 . The product was analyzed by HPLC to determine the enantiomeric excess: $>99 \%$ ee (Chiralpak ID, $i$-propanol/hexane $=$ $2 / 98$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ ); $\mathrm{t}_{\mathrm{r}}=4.24$ and 4.71 min .

## Methyl (2R,3S,E)-2-benzamido-2-benzyl-3-methyl-5-phenylpent-4-enoate (3c):



Yield (82\%); 33.8 mg ; colorless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=5 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=-40.6\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $7.62(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.45(\mathrm{t}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.36(\mathrm{t}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.31-7.25(\mathrm{~m}$, 4H), 7.21-7.18 (m, 4H), 7.14-7.07 (m, 2H), $6.86(\mathrm{~s}, 1 \mathrm{H}), 6.42(\mathrm{~d}, J=15.7 \mathrm{~Hz}, 1 \mathrm{H}), 6.17$ (dd, $J=15.7,9.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.90(\mathrm{~d}, J=13.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.87(\mathrm{~s}, 3 \mathrm{H}), 3.53(\mathrm{~d}, J=13.7 \mathrm{~Hz}$, $1 \mathrm{H}), 3.47(\mathrm{dd}, J=15.5,7.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.34(\mathrm{~d}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 172.7,167.2,137.0,136.6,135.4,132.0,131.4,130.6,130.0,128.6,128.5$, 128.2, 127.4, 126.8, 126.3, 67.9, 52.6, 42.4, 37.1, 16.0. HRMS (ESI+) Calcd. For $\mathrm{C}_{27} \mathrm{H}_{28} \mathrm{NO}_{3}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 414.2064$, found: 414.2055 . The product was analyzed by HPLC to determine the enantiomeric excess: $95 \%$ ee (Chiralpak AD-H, $i$-propanol/hexane $=$ $10 / 90$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}=13.55$ and 16.81 min .

## Methyl (2R,3S,E)-2-benzamido-2-isobutyl-3-methyl-5-phenylpent-4-enoate (3d):



Yield (80\%); 30.0 mg ; colorless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=5 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=-55.0\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 7.80-7.71 (m, 2H), 7.51-7.44 (m, 1H), 7.40 (dd, $J=15.1,8.0 \mathrm{~Hz}, 3 \mathrm{H}), 7.25(\mathrm{dd}, J=8.6$, $1.8 \mathrm{~Hz}, 3 \mathrm{H}), 7.24-7.15(\mathrm{~m}, 1 \mathrm{H}), 6.38(\mathrm{~d}, J=15.7 \mathrm{~Hz}, 1 \mathrm{H}), 6.02(\mathrm{dd}, J=15.7,9.1 \mathrm{~Hz}$,
$1 \mathrm{H}), 3.84$ (s, 3H), $3.51(\mathrm{dq}, J=14.2,7.0 \mathrm{~Hz}, 1 \mathrm{H}), 2.77(\mathrm{dd}, J=14.1,4.3 \mathrm{~Hz}, 1 \mathrm{H}), 1.96$ (dd, $J=14.1,8.9 \mathrm{~Hz}, 1 \mathrm{H}), 1.66-1.57(\mathrm{~m}, 1 \mathrm{H}), 1.21(\mathrm{~d}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}), 0.94(\mathrm{~d}, J=6.7$ $\mathrm{Hz}, 3 \mathrm{H}), 0.78(\mathrm{~d}, J=6.6 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 174.5,166.5,137.2$, 135.5, 131.7, 131.3, 130.8, 128.6, 128.4, 127.2, 126.8, 126.2, 67.0, 52.5, 43.5, 40.8, 25.0, 24.1, 21.9, 15.7. HRMS (ESI+) Calcd. For $\mathrm{C}_{24} \mathrm{H}_{30} \mathrm{NO}_{3}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 380.2220$, found: 320.2208. The product was analyzed by HPLC to determine the enantiomeric excess: $93 \%$ ee (Chiralpak AD-H, $i$-propanol/hexane $=10 / 90$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254$ $\mathrm{nm}) ; \mathrm{t}_{\mathrm{r}}=5.99$ and 7.04 min .

## Methyl (2R,3S,E)-2-allyl-2-benzamido-3-methyl-5-phenylpent-4-enoate (3e):



Yield (75\%); 27.2 mg ; colorless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=5 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=-49.0\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 7.76-7.69 (m, 2H), 7.50-7.44 (m, 1H), 7.41-7.36 (m, 2H), 7.35-7.32 (m, 2H), 7.31-7.26 $(\mathrm{m}, 2 \mathrm{H}), 7.24-7.18(\mathrm{~m}, 1 \mathrm{H}), 7.05(\mathrm{~s}, 1 \mathrm{H}), 6.47(\mathrm{~d}, J=15.7 \mathrm{~Hz}, 1 \mathrm{H}), 6.17(\mathrm{dd}, J=15.7$, $9.3 \mathrm{~Hz}, 1 \mathrm{H}), 5.67-5.63(\mathrm{~m}, 1 \mathrm{H}), 5.17-5.03(\mathrm{~m}, 2 \mathrm{H}), 3.84(\mathrm{~s}, 3 \mathrm{H}), 3.41(\mathrm{dd}, J=14.0,7.6$ $\mathrm{Hz}, 1 \mathrm{H}), 3.31(\mathrm{dq}, J=14.0,7.0 \mathrm{~Hz}, 1 \mathrm{H}), 2.95(\mathrm{dd}, J=14.0,7.0 \mathrm{~Hz}, 1 \mathrm{H}), 1.21(\mathrm{~d}, J=$ $7.0 \mathrm{~Hz}, 3 \mathrm{H}$ ); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 173.1, 166.6, 137.0, 135.1, 132.8, 132.0, 131.4, 130.7, 128.6, 128.5, 127.4, 126.8, 126.3, 119.0, 66.9, 52.7, 42.9, 36.2, 15.8. HRMS (ESI+) Calcd. For $\mathrm{C}_{23} \mathrm{H}_{26} \mathrm{NO}_{3}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 364.1907$, found: 364.1902. The product was analyzed by HPLC to determine the enantiomeric excess: $99 \%$ ee $($ Chiralpak IE, $i$-propanol $/$ hexane $=10 / 90$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}=29.77$ and 30.78 min .


Yield (54\%); 19.7 mg ; colorless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=5 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=-19.1\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 7.80 (d, $J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 7.49(\mathrm{t}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.43(\mathrm{t}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.35(\mathrm{~d}, J=$ $7.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.28(\mathrm{~d}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.22-7.16(\mathrm{~m}, 2 \mathrm{H}), 6.47(\mathrm{~d}, J=15.8 \mathrm{~Hz}, 1 \mathrm{H})$, $6.39(\mathrm{dd}, J=15.8,8.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.86(\mathrm{~s}, 3 \mathrm{H}), 3.83-3.74(\mathrm{~m}, 1 \mathrm{H}), 3.10-3.03(\mathrm{~m}, 1 \mathrm{H})$, $1.18(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 3 \mathrm{H}), 1.03(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 174.1$, $166.9,137.5,136.2,131.6,131.2,131.0,128.6,128.4,127.0,126.8,126.3,72.2,52.8$, 40.4, 31.2, 18.4, 18.1, 16.7. HRMS (ESI+) Calcd. For $\mathrm{C}_{23} \mathrm{H}_{28} \mathrm{NO}_{3}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 366.2064$, found: 366.2054 . The product was analyzed by HPLC to determine the enantiomeric excess: $97 \%$ ee (Chiralpak AD-H, $i$-propanol/hexane $=10 / 90$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda$ $=254 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}=6.60$ and 9.39 min .
(R)-4-methyl-4-((S,E)-4-phenylbut-3-en-2-yl)-2-(p-tolyl)oxazol-5(4H)-one (3g):


Yield (89\%); 28.4 mg ; white solid; mp 84-86 ${ }^{\circ} \mathrm{C}$; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=20 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=+78.5\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.92(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 2 \mathrm{H}), 7.40(\mathrm{~d}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.31(\mathrm{t}, J=8.4 \mathrm{~Hz}$, $4 \mathrm{H}), 7.23(\mathrm{t}, J=7.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.53(\mathrm{~d}, J=15.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.25(\mathrm{dd}, J=15.9,9.3 \mathrm{~Hz}, 1 \mathrm{H})$, 2.83-2.76 (m, 1H), $2.44(\mathrm{~s}, 3 \mathrm{H}), 1.49(\mathrm{~s}, 3 \mathrm{H}), 1.04(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 181.1,160.2,143.4,136.9,132.7,129.5,129.3,128.5,127.9,127.5$, 126.4, 123.0, 72.3, 45.1, 22.7, 21.7, 15.8. HRMS (ESI+) Calcd. For $\mathrm{C}_{21} \mathrm{H}_{22} \mathrm{NO}_{2}$ $\left([\mathrm{M}+\mathrm{H}]^{+}\right): 320.1645$, found: 320.1634. The product was analyzed by HPLC to determine the enantiomeric excess: $96 \%$ ee (Chiralpak AD-H, $i$-propanol/hexane $=3 / 97$,
flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}=4.86$ and 5.70 min .

## (R)-2-(4-methoxyphenyl)-4-methyl-4-((S,E)-4-phenylbut-3-en-2-yl)oxazol-5(4H)one (3h):



Yield (90\%); 30.1 mg ; yellow oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=20 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=+75.1\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ $\delta 7.98(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.40(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.31(\mathrm{t}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.25-7.19$ (m, 1H), 6.99 (d, $J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.53(\mathrm{~d}, J=15.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.25(\mathrm{dd}, J=15.9,9.3 \mathrm{~Hz}$, $1 \mathrm{H}), 3.89$ (s, 3H), 2.79 (dq, $J=13.8,6.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.49$ (s, 3H), 1.04 (d, $J=6.8 \mathrm{~Hz}, 3 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 181.2,163.1,159.8,137.0,132.6,129.8,129.4,128.5$, 127.4, 126.3, 118.2, 114.2, 72.2, 55.5, 45.1, 22.8, 15.8. HRMS (ESI+) Calcd. For $\mathrm{C}_{21} \mathrm{H}_{22} \mathrm{NO}_{3}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 336.1594$, found: 336.1586 . The product was analyzed by HPLC to determine the enantiomeric excess: $98 \%$ ee (Chiralpak AD-H, $i$-propanol/hexane $=$ $2 / 98$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}=6.17$ and 6.96 min .

## ( $R$ )-2-(4-fluorophenyl)-4-methyl-4-((S,E)-4-phenylbut-3-en-2-yl)oxazol-5(4H)-one

 (3i):

Yield ( $87 \%$ ); 28.1 mg ; white solid; mp $74-76^{\circ} \mathrm{C}$; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=20 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=+69.9\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.04(\mathrm{ddd}, J=8.0,5.0,2.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.40(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.32(\mathrm{t}, J$ $=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.24-7.21(\mathrm{~m}, 1 \mathrm{H}), 7.20-7.14(\mathrm{~m}, 2 \mathrm{H}), 6.53(\mathrm{~d}, J=15.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.23$ (dd, $J=15.9,9.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.80(\mathrm{dq}, J=13.7,6.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.50(\mathrm{~s}, 3 \mathrm{H}), 1.05(\mathrm{~d}, J=6.8$
$\mathrm{Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 180.7,166.7,164.2,159.2,136.9,132.8,130.4$ $(\mathrm{d}, J=9.1 \mathrm{~Hz}), 129.1,128.5,127.5,126.3,122.1(\mathrm{~d}, J=3.1 \mathrm{~Hz}), 116.1(\mathrm{~d}, J=21.3 \mathrm{~Hz})$, 72.5, 45.0, 22.6, 15.8. ${ }^{19}$ F NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$-105.45; HRMS (ESI+) Calcd. For $\mathrm{C}_{20} \mathrm{H}_{19} \mathrm{FNO}_{2}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 324.1394$, found: 324.1381 . The product was analyzed by HPLC to determine the enantiomeric excess: $95 \%$ ee (Chiralpak AD-H, $i-$ propanol $/$ hexane $=1.5 / 98.5$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ ); $\mathrm{t}_{\mathrm{r}}=5.49$ and 6.20 min .

## (R)-2-(4-chlorophenyl)-4-methyl-4-((S,E)-4-phenylbut-3-en-2-yl)oxazol-5(4H)-

 one (3j):

Yield (80\%); 27.1 mg ; colourless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=20 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=+101.9\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ $\delta 7.97(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.47(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.40(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.32(\mathrm{t}, J$ $=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.23(\mathrm{~d}, J=7.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.53(\mathrm{~d}, J=15.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.22(\mathrm{dd}, J=15.9$, $9.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.80(\mathrm{dq}, J=13.7,6.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.50(\mathrm{~s}, 3 \mathrm{H}), 1.04(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\left.100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 180.5,159.3,139.0,136.8,132.9,129.3,129.2,129.0,128.5$, 127.5, 126.3, 124.3, 72.5, 45.0, 22.6, 15.8. HRMS (ESI+) Calcd. For $\mathrm{C}_{20} \mathrm{H}_{19} \mathrm{ClNO}_{2}$ $\left([\mathrm{M}+\mathrm{H}]^{+}\right): 340.1099$, found: 340.1104. The product was analyzed by HPLC to determine the enantiomeric excess: $95 \%$ ee (Chiralpak AD-H, $i$-propanol/hexane $=2 / 98$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}=5.11$ and 5.81 min .
(R)-4-methyl-4-((S,E)-4-phenylbut-3-en-2-yl)-2-(m-tolyl)oxazol-5(4H)-one (3k):


Yield (78\%); 24.9 mg ; colorless oil; (Flash column chromatography eluent, petroleum
ether/ethyl acetate $=20 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=+87.2\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ $\delta 7.88(\mathrm{~s}, 1 \mathrm{H}), 7.86-7.77(\mathrm{~m}, 1 \mathrm{H}), 7.40(\mathrm{t}, J=7.1 \mathrm{~Hz}, 4 \mathrm{H}), 7.32(\mathrm{t}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.22$ (d, $J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.54(\mathrm{~d}, J=15.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.25(\mathrm{dd}, J=15.9,9.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.81(\mathrm{dq}$, $J=13.8,6.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.43(\mathrm{~s}, 3 \mathrm{H}), 1.50(\mathrm{~s}, 3 \mathrm{H}), 1.05(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 181.0,160.3,138.7,136.9,133.5,132.7,129.3,128.7,128.5$, 128.4, 127.5, 126.4, 125.7, 125.2, 72.3, 45.1, 22.7, 21.3, 15.8. HRMS (ESI+) Calcd. For $\mathrm{C}_{21} \mathrm{H}_{22} \mathrm{NO}_{2}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 320.1645$, found: 320.1634 . The product was analyzed by HPLC to determine the enantiomeric excess: $95 \%$ ee (Chiralpak AD-H, $i-$ propanol $/$ hexane $=2 / 98$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ ); $\mathrm{t}_{\mathrm{r}}=4.14$ and 4.78 min .
( $\boldsymbol{R}$ )-2-(3-fluorophenyl)-4-methyl-4-((S, $\boldsymbol{E})$-4-phenylbut-3-en-2-yl)oxazol-5(4H)-one (31):


Yield (86\%); 27.7 mg ; colorless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=20 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=+63.8\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ $\delta 7.82(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.75(\mathrm{ddd}, J=9.2,2.3,1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.48(\mathrm{td}, J=8.0,5.6 \mathrm{~Hz}$, $1 \mathrm{H}), 7.40(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.35-7.26(\mathrm{~m}, 3 \mathrm{H}), 7.23(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.54(\mathrm{~d}, J=$ $15.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.23(\mathrm{dd}, J=15.9,9.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.81(\mathrm{dq}, J=13.7,6.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.50(\mathrm{~s}$, 3 H ), 1.05 (d, $J=6.8 \mathrm{~Hz}, 3 \mathrm{H}$ ); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 180.5,162.7$ (d, $J=246.1$ $\mathrm{Hz}), 159.1,136.8,132.9,130.5(\mathrm{~d}, ~ J=8.0 \mathrm{~Hz}), 129.0,128.5,127.9$ (d, $J=8.4 \mathrm{~Hz})$, $127.5,126.3,123.7(\mathrm{~d}, J=3.1 \mathrm{~Hz}), 119.7(\mathrm{~d}, J=21.3 \mathrm{~Hz}), 114.9(\mathrm{~d}, J=24.0 \mathrm{~Hz}), 72.6$, 45.0, 22.6, 15.8. ${ }^{19}$ F NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$-111.43; HRMS (ESI+) Calcd. For $\mathrm{C}_{20} \mathrm{H}_{19} \mathrm{FNO}_{2}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 324.1394$, found: 324.1388 . The product was analyzed by HPLC to determine the enantiomeric excess: $95 \%$ ee (Chiralpak AD-H, $i-$ propanol $/$ hexane $=3 / 97$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ ); $\mathrm{t}_{\mathrm{r}}=4.54$ and 4.95 min .
( $\boldsymbol{R}$ )-2-(2-fluorophenyl)-4-methyl-4-((S, $\boldsymbol{E}$ )-4-phenylbut-3-en-2-yl)oxazol-5(4H)-one (3m):


Yield (75\%); 24.2 mg ; colorless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=20 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=+78.6\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ $\delta 7.94-7.90(\mathrm{~m}, 1 \mathrm{H}), 7.61-7.50(\mathrm{~m}, 1 \mathrm{H}), 7.39(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.31(\mathrm{t}, J=7.6 \mathrm{~Hz}$, $3 \mathrm{H}), 7.25-7.19(\mathrm{~m}, 2 \mathrm{H}), 6.54(\mathrm{~d}, J=15.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.22(\mathrm{dd}, J=15.9,9.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.85-$ $2.81(\mathrm{~m}, 1 \mathrm{H}), 1.53(\mathrm{~s}, 3 \mathrm{H}), 1.09(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 180.3, 161.5 (d, $J=258.8 \mathrm{~Hz}), 157.0(\mathrm{~d}, J=5.3 \mathrm{~Hz}), 136.8,134.2(\mathrm{~d}, J=8.8 \mathrm{~Hz}), 132.9$, $130.6,128.9,128.4,127.5,126.3,124.3(\mathrm{~d}, J=3.8 \mathrm{~Hz}), 117.1(\mathrm{~d}, J=21.3 \mathrm{~Hz}), 114.4$ $(\mathrm{d}, J=10.0 \mathrm{~Hz}), 72.1,44.9,22.4,15.6 .{ }^{19} \mathrm{~F}$ NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta-108.51$; HRMS (ESI+) Calcd. For $\mathrm{C}_{20} \mathrm{H}_{19} \mathrm{FNO}_{2}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 324.1394$, found: 324.1383 . The product was analyzed by HPLC to determine the enantiomeric excess: 94\% ee (Chiralpak AD-H, $i-$ propanol $/$ hexane $=2 / 98$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}=5.20$ and 6.16 min .

## Methyl (2R,3S,E)-2-acetamido-3-methyl-2,5-diphenylpent-4-enoate (3n):



Yield (70\%); 23.6 mg ; colorless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=5 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=-3.6\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right){ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.47(\mathrm{dd}, J=5.3,3.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.37-7.31 (m, 2H), 7.31-7.27 $(\mathrm{m}, 5 \mathrm{H}), 7.24-7.19(\mathrm{~m}, 1 \mathrm{H}), 6.48-6.44(\mathrm{~m}, 2 \mathrm{H}), 6.03(\mathrm{dd}, J=15.9,8.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.77(\mathrm{~s}$, $3 \mathrm{H}), 3.80-3.67(\mathrm{~m}, 1 \mathrm{H}), 2.01(\mathrm{~s}, 3 \mathrm{H}), 1.15(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 172.2,169.1,137.8,137.1,131.8,130.3,128.5,128.0,127.6,127.4,127.2$, 126.3, 68.5, 52.7, 43.1, 23.8, 16.2. HRMS (ESI+) Calcd. For $\mathrm{C}_{21} \mathrm{H}_{24} \mathrm{NO}_{3}\left([\mathrm{M}+\mathrm{H}]^{+}\right)$:
338.1751, found: 338.1743. The product was analyzed by HPLC to determine the enantiomeric excess: 95\% ee (Chiralpak AS-H, $i$-propanol/hexane $=5 / 95$, flow rate 1.0 $\mathrm{mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}=17.76$ and 25.21 min .

## Methyl (2S,3S,E)-2-benzamido-3-methyl-2,5-diphenylpent-4-enoate (30) and

Methyl (2R,3S,E)-2-benzamido-3-methyl-2,5-diphenylpent-4-enoate (3o'):


Yield ( $85 \%$ ); $33.9 \mathrm{mg} ; \mathbf{3 0} \mathbf{3 0} \mathbf{3 o}^{\prime}=1.25: 1$, colourless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=5 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=-2.2\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ 8 7.81-7.76 (m, 2H), 7.58-7.48 (m, 3H), 7.47-7.41 (m, 2H), 7.39-7.26 (m, 7 H ), 7.24-7.17 (m, 1H), 6.57 (major) (d, $J=15.9 \mathrm{~Hz}, 0.55 \mathrm{H}$ ), 6.52 (minor) (d, $J=15.9$ $\mathrm{Hz}, 0.45 \mathrm{H}$ ), 6.14 (minor) (dd, $J=15.9,8.2 \mathrm{~Hz}, 0.45 \mathrm{H}), 6.02$ (major) (dd, $J=15.9,8.8$ $\mathrm{Hz}, 0.55 \mathrm{H}$ ), 3.81-3.76 (m, 1H), 3.80 (minor) ( $\mathrm{s}, 1.35 \mathrm{H}$ ), 3.77 (major) ( $\mathrm{s}, 1.65 \mathrm{H}$ ), 1.23 (minor) (d, $J=6.9 \mathrm{~Hz}, 1.35 \mathrm{H}$ ), 1.19 (major) (d, $J=6.9 \mathrm{~Hz}, 1.65 \mathrm{H}$ ). ${ }^{13} \mathrm{C} \mathrm{NMR}(100 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) \delta 172.5,172.3,166.3,166.0,137.8,137.1,136.9,136.5,134.6,134.4,132.1$, 132.0, 131.7, 131.6, 130.53, 130.50, 128.7, 128.6, 128.58, 128.5, 128.1, 128.0, 127.7, $127.63,127.58,127.4,127.2,126.98,126.96,126.3,68.6,68.4,53.0,52.9,43.7,43.4$, 16.5, 16.2. HRMS (ESI+) Calcd. For $\mathrm{C}_{26} \mathrm{H}_{26} \mathrm{NO}_{3}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 400.1907$, found: 400.1902. The product was analyzed by HPLC to determine the enantiomeric excess: $87 \%$ ee (major); $84 \%$ ee (minor) (Chiralpak AD-H, $i$-propanol/hexane $=10 / 90$, flow rate 1.0 $\mathrm{mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}($ major $)=15.98$ and $18.84 \mathrm{~min} ; \mathrm{t}_{\mathrm{r}}($ minor $)=24.36$ and 27.60 min.

Methyl (2R,3S,E)-2-benzamido-2,3-dimethyl-5-(p-tolyl)pent-4-enoate (4a):


Yield (82\%); 28.8 mg ; colourless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=5 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=-71.9\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 7.71 (d, $J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.47(\mathrm{t}, J=7.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.38(\mathrm{t}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.24(\mathrm{~s}, 2 \mathrm{H})$, 7.12 (d, $J=7.9 \mathrm{~Hz}, 2 \mathrm{H}$ ), 6.82 (s, 1H), 6.49 (d, $J=15.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.11$ (dd, $J=15.8,9.3$ $\mathrm{Hz}, 1 \mathrm{H}), 3.78$ (s, 3H), 2.99-2.92 (m, 1H), 2.33 (s, 3H), 1.79 (s, 3H), 1.21 (d, J=7.0 Hz, 3 H ) ${ }^{13}{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 173.3,166.7,137.5,134.6,134.0,132.3,131.5$, 129.3, 129.0, 128.6, 126.9, 126.2, 62.5, 52.4, 45.3, 21.2, 20.7, 15.7. HRMS (ESI+) Calcd. For $\mathrm{C}_{22} \mathrm{H}_{26} \mathrm{NO}_{3}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 352.1907$, found: 352.1899. The product was analyzed by HPLC to determine the enantiomeric excess: $92 \%$ ee (Chiralcel OD-H, $i$ propanol $/$ hexane $=10 / 90$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}=7.97$ and 8.58 min .

## Methyl (2R,3S,E)-2-benzamido-5-(4-methoxyphenyl)-2,3-dimethylpent-4-enoate

 (4b):

Yield (90\%); 33.0 mg ; white solid; mp 120-122 ${ }^{\circ} \mathrm{C}$; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=5 / 1) ;[\alpha]^{28} \mathrm{D}=-58.5\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.71(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.47(\mathrm{t}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.38(\mathrm{t}, J=7.5$ $\mathrm{Hz}, 2 \mathrm{H}), 7.30(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H}), 6.86-6.83(\mathrm{~m}, 3 \mathrm{H}), 6.47(\mathrm{~d}, J=15.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.02$ (dd, $J=15.7,9.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H}), 2.97-2.89(\mathrm{~m}, 1 \mathrm{H}), 1.79(\mathrm{~s}, 3 \mathrm{H})$, $1.21(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 173.3$, 166.7, 159.2, 134.6, $131.9,131.5,129.5,128.6,127.8,127.5,126.8,114.0,62.5,55.3,52.4,45.3,20.7,15.8$. HRMS (ESI+) Calcd. For $\mathrm{C}_{22} \mathrm{H}_{26} \mathrm{NO}_{4}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 368.1856$, found: 368.1848. The product was analyzed by HPLC to determine the enantiomeric excess: $97 \%$ ee
(Chiralpak AS-H, $i$-propanol/hexane $=10 / 90$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ ); $\mathrm{t}_{\mathrm{r}}=$ 10.66 and 20.45 min .

## Methyl (2R,3S,E)-2-benzamido-5-(4-fluorophenyl)-2,3-dimethylpent-4-enoate (4c):



Yield (82\%); 29.1 mg ; white solid; mp $94-96^{\circ} \mathrm{C}$; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=5 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=-57.6\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}(400 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) \delta$ 7.74-7.68(m, 2H), $7.47(\mathrm{dd}, J=8.4,6.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.38(\mathrm{t}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H})$, 7.34-7.28 (m, 2H), $6.99(\mathrm{t}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.87(\mathrm{~s}, 1 \mathrm{H}), 6.47(\mathrm{~d}, J=15.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.09$ $(\mathrm{dd}, J=15.8,9.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H}), 3.04-2.96(\mathrm{~m}, 1 \mathrm{H}), 1.80(\mathrm{~s}, 3 \mathrm{H}), 1.21(\mathrm{~d}, J=$ $7.0 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 173.4,166.7,162.2(\mathrm{~d}, J=245.3 \mathrm{~Hz}$ ), 134.6, 132.9, 131.5, 131.1, $129.9(\mathrm{~d}, J=2.1 \mathrm{~Hz}), 128.5,127.8(\mathrm{~d}, J=8.0 \mathrm{~Hz}), 126.8$, $115.4(\mathrm{~d}, J=21.5 \mathrm{~Hz}), 62.7,52.5,45.0,20.5,15.7 .{ }^{19} \mathrm{~F}$ NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 114.41; HRMS (ESI+) Calcd. For $\mathrm{C}_{21} \mathrm{H}_{23} \mathrm{FNO}_{3}\left([\mathrm{M}+\mathrm{H}]^{+}\right)$: 356.1656, found: 356.1648 . The product was analyzed by HPLC to determine the enantiomeric excess: $96 \%$ ee (Chiralpak ID-H, $i$-propanol/hexane $=10 / 90$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ ); $\mathrm{t}_{\mathrm{r}}=$ 16.29 and 19.33 min .

## Methyl (2R,3S,E)-2-benzamido-5-(4-chlorophenyl)-2,3-dimethylpent-4-enoate

 (4d):

Yield (71\%); 26.3 mg ; colorless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=5 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=-71.4\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 7.75-7.68 (m, 2H), 7.50-7.44 (m, 1H), 7.38 (dd, $J=10.4,4.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.27(\mathrm{~d}, J=2.1$

Hz, 4H), 6.86 (s, 1H), 6.45 (d, $J=15.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.15(\mathrm{dd}, J=15.8,9.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.79$ $(\mathrm{s}, 3 \mathrm{H}), 3.07-2.99(\mathrm{~m}, 1 \mathrm{H}), 1.80(\mathrm{~s}, 3 \mathrm{H}), 1.21(\mathrm{~d}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 173.4,166.7,135.3,134.6,133.2,131.6,131.0,130.9,128.7,128.6,127.5$, 126.8, 62.7, 52.5, 45.0, 20.5, 15.6. HRMS (ESI+) Calcd. For $\mathrm{C}_{21} \mathrm{H}_{23} \mathrm{ClNO}_{3}\left([\mathrm{M}+\mathrm{H}]^{+}\right)$: 372.1361, found: 356.1348 . The product was analyzed by HPLC to determine the enantiomeric excess: $96 \%$ ee (Chiralpak AS-H, $i$-propanol/hexane $=10 / 90$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}=7.73$ and 13.40 min .

## Methyl (2R,3S,E)-2-benzamido-5-(4-bromophenyl)-2,3-dimethylpent-4-enoate

 (4e):

Yield (62\%); 25.7 mg ; colorless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=5 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=-69.0\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 7.70 (dd, $J=8.4,7.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.50-7.45 (m, 1H), 7.40 (dd, $J=15.6,7.8 \mathrm{~Hz}, 4 \mathrm{H}), 7.21$ (d, $J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 6.86(\mathrm{~s}, 1 \mathrm{H}), 6.44(\mathrm{~d}, J=15.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.17(\mathrm{dd}, J=15.8,9.2 \mathrm{~Hz}$, $1 \mathrm{H}), 3.79(\mathrm{~s}, 3 \mathrm{H}), 3.03(\mathrm{dq}, J=14.0,7.0 \mathrm{~Hz}, 1 \mathrm{H}), 1.80(\mathrm{~s}, 3 \mathrm{H}), 1.21(\mathrm{~d}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H})$; ${ }^{13}{ }^{\text {C NMR }}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 173.4,166.7,135.7,134.6,131.63,131.56,131.1,131.0$, 128.6, 127.8, 126.8, 121.3, 62.7, 52.5, 44.9, 20.5, 15.6. HRMS (ESI+) Calcd. For $\mathrm{C}_{21} \mathrm{H}_{23} \mathrm{BrNO}_{3}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 416.0856$, found: 416.0849 . The product was analyzed by HPLC to determine the enantiomeric excess: 95\% ee (Chiralpak ID-H, ipropanol $/$ hexane $=10 / 90$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}=17.58$ and 19.11 min .

## Methyl (2R,3S, $\boldsymbol{E}$ )-2-benzamido-2,3-dimethyl-5-(o-tolyl)pent-4-enoate (4f):



Yield (50\%); 17.5 mg ; colorless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=5 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=-57.3\left(c 0.3, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 7.73 (d, $J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.47$ (t, $J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.42-7.34$ (m, 3H), 7.19-7.06 (m, 3H), $6.87(\mathrm{~s}, 1 \mathrm{H}), 6.71(\mathrm{~d}, J=15.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.01(\mathrm{dd}, J=15.6,9.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.79(\mathrm{~s}, 3 \mathrm{H})$, 3.08-3.00 (m, 1H), $2.28(\mathrm{~s}, 3 \mathrm{H}), 1.82(\mathrm{~s}, 3 \mathrm{H}), 1.24(\mathrm{~d}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 100 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 173.3,166.6,136.0,135.1,134.6,131.7,131.5,130.4,130.2,128.6$, 127.5, 126.8, 126.2, 126.0, 62.6, 52.5, 45.3, 20.6, 19.7, 15.8. HRMS (ESI+) Calcd. For $\mathrm{C}_{22} \mathrm{H}_{26} \mathrm{NO}_{3}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 352.1907$, found: 352.1898 . The product was analyzed by HPLC to determine the enantiomeric excess: $97 \%$ ee (Chiralcel OD-H, $i$-propanol/hexane $=$ $10 / 90$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ ); $\mathrm{t}_{\mathrm{r}}=9.36$ and 11.20 min .

## Methyl (2R,3S,E)-2-benzamido-5-(2-fluorophenyl)-2,3-dimethylpent-4-enoate

 (4g):

Yield (74\%); 26.2 mg ; white solid; mp $90-92^{\circ} \mathrm{C}$; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=5 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=-52.0\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $(400 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) \delta$ 7.76-7.71(m, 2H), 7.49-7.37 (m, 4H), $7.21(\mathrm{tdd}, J=7.2,5.2,1.7 \mathrm{~Hz}, 1 \mathrm{H})$, 7.11-6.99 (m, 2H), $6.85(\mathrm{~s}, 1 \mathrm{H}), 6.68(\mathrm{~d}, J=16.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.25(\mathrm{dd}, J=15.9,9.2 \mathrm{~Hz}$, $1 \mathrm{H}), 3.79(\mathrm{~s}, 3 \mathrm{H}), 3.06-2.98(\mathrm{~m}, 1 \mathrm{H}), 1.80(\mathrm{~s}, 3 \mathrm{H}), 1.23(\mathrm{~d}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 173.3,166.6,160.0(\mathrm{~d}, J=247.2 \mathrm{~Hz}), 134.6,132.9,131.5,128.6$, $127.4(\mathrm{~d}, J=3.6 \mathrm{~Hz}), 126.9,124.7(\mathrm{~d}, J=3.6 \mathrm{~Hz}), 124.2,115.6(\mathrm{~d}, J=21.9 \mathrm{~Hz}), 62.5$, 52.5, 45.5, 20.6, 15.5. ${ }^{19}$ F NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$-118.56; HRMS (ESI+) Calcd. For $\mathrm{C}_{21} \mathrm{H}_{23} \mathrm{FNO}_{3}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 356.1656$, found: 356.1648 . The product was analyzed by HPLC to determine the enantiomeric excess: $95 \%$ ee (Chiralpak AS-H, $i-$ propanol $/$ hexane $=10 / 90$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ ); $\mathrm{t}_{\mathrm{r}}=7.76$ and 17.78 min .

## Methyl (2R,3S,E)-2-benzamido-2,3-dimethyl-5-(m-tolyl)pent-4-enoate (4h):



4h
Yield (85\%); 29.8 mg ; colourless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=5 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=-66.8\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 7.72 (d, $J=7.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.47(\mathrm{t}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.38(\mathrm{t}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.23-7.11(\mathrm{~m}$, $3 \mathrm{H}), 7.06(\mathrm{~d}, J=7.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.83(\mathrm{~s}, 1 \mathrm{H}), 6.49(\mathrm{~d}, J=15.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.15(\mathrm{dd}, J=15.8$, $9.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.79(\mathrm{~s}, 3 \mathrm{H}), 3.01-2.93(\mathrm{~m}, 1 \mathrm{H}), 2.34(\mathrm{~s}, 3 \mathrm{H}), 1.80(\mathrm{~s}, 3 \mathrm{H}), 1.22(\mathrm{~d}, J=7.0$ $\mathrm{Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 173.3,166.7,138.1,136.7,134.6,132.6,131.5$, 129.8, 128.54, 128.46, 128.4, 127.0, 127.0, 123.5, 62.5, 52.4, 45.2, 21.4, 20.6, 15.7. HRMS (ESI+) Calcd. For $\mathrm{C}_{22} \mathrm{H}_{26} \mathrm{NO}_{3}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 352.1907$, found: 352.1897. The product was analyzed by HPLC to determine the enantiomeric excess: $96 \%$ ee (Chiralpak AD-H, $i$-propanol/hexane $=5 / 95$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ ); $\mathrm{t}_{\mathrm{r}}=$ 13.22 and 14.68 min.

Methyl (2R,3S, $\boldsymbol{E}$ )-2-benzamido-5-(3-fluorophenyl)-2,3-dimethylpent-4-enoate (4i):


Yield (84\%); 29.8 mg ; colourless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=5 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=-65.8\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 7.76-7.67 (m, 2H), 7.51-7.44 (m, 1H), 7.39 (t, $J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.29-7.22(\mathrm{~m}, 1 \mathrm{H}), 7.11$ $(\mathrm{d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.05(\mathrm{dd}, J=10.1,2.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.92(\mathrm{td}, J=8.3,2.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.86$ (s, 1H), 6.47 (d, $J=15.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.18(\mathrm{dd}, J=15.8,9.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.80(\mathrm{~s}, 3 \mathrm{H}), 3.09-$ $3.02(\mathrm{~m}, 1 \mathrm{H}), 1.80(\mathrm{~s}, 3 \mathrm{H}), 1.22(\mathrm{~d}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 173.4, 166.7, $163.0(\mathrm{~d}, J=243.9 \mathrm{~Hz}), 139.1(\mathrm{~d}, J=7.7 \mathrm{~Hz}), 134.6,131.6(\mathrm{~d}, J=8.0$ $\mathrm{Hz}), 131.2(\mathrm{~d}, J=2.5 \mathrm{~Hz}), 130.0(\mathrm{~d}, J=8.4 \mathrm{~Hz}), 128.6,126.8,122.1(\mathrm{~d}, J=2.7 \mathrm{~Hz})$, $114.3(\mathrm{~d}, J=21.4 \mathrm{~Hz}), 112.7(\mathrm{~d}, J=21.6 \mathrm{~Hz}), 62.7,52.6,44.8,20.5,15.6 .{ }^{19} \mathrm{~F}$ NMR
( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$-113.45; HRMS (ESI+) Calcd. For $\mathrm{C}_{21} \mathrm{H}_{23} \mathrm{FNO}_{3}\left([\mathrm{M}+\mathrm{H}]^{+}\right)$: 356.1656, found: 356.1645 . The product was analyzed by HPLC to determine the enantiomeric excess: $94 \%$ ee (Chiralpak AS-H, $i$-propanol/hexane $=10 / 90$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}=7.87$ and 13.54 min .

## Methyl (2R,3S,E)-2-benzamido-5-(furan-2-yl)-2,3-dimethylpent-4-enoate (4j):



Yield (86\%); 28.1 mg ; yellow oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=5 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=-82.8\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 7.77-7.69 (m, 2H), 7.53-7.44 (m, 1H), 7.40 (t, $J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.33(\mathrm{~d}, J=1.3 \mathrm{~Hz}, 1 \mathrm{H})$, $6.81(\mathrm{~s}, 1 \mathrm{H}), 6.36-6.29(\mathrm{~m}, 2 \mathrm{H}), 6.20(\mathrm{~d}, J=3.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.10(\mathrm{dd}, J=15.8,9.1 \mathrm{~Hz}$, $1 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H}), 3.02-2.98(\mathrm{~m}, 1 \mathrm{H}), 1.78(\mathrm{~s}, 3 \mathrm{H}), 1.21(\mathrm{~d}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 173.3,166.7,152.1,141.9,134.7,131.4,128.5,128.4,126.8$, 120.7, 111.1, 107.6, 62.7, 52.4, 44.5, 20.5, 15.6. HRMS (ESI+) Calcd. For $\mathrm{C}_{19} \mathrm{H}_{22} \mathrm{NO}_{4}$ $\left([\mathrm{M}+\mathrm{H}]^{+}\right): 328.1534$, found: 328.1543 . The product was analyzed by HPLC to determine the enantiomeric excess: $97 \%$ ee (Chiralpak AS-H, $i$-propanol/hexane $=$ $10 / 90$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}=10.00$ and 21.11 min .

## Methyl (2R,3S,E)-2-benzamido-5-cyclohexyl-2,3-dimethylpent-4-enoate (4k):



4k
Yield (55\%); 28.1 mg ; colourless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=5 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=-15.2\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 7.75 (d, $J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.50(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.42(\mathrm{t}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 6.76(\mathrm{~s}, 1 \mathrm{H})$, $5.55(\mathrm{dd}, J=15.4,7.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.35(\mathrm{dd}, J=15.5,9.1 \mathrm{~Hz}, 1 \mathrm{H}), 3.75(\mathrm{~s}, 3 \mathrm{H}), 2.66-2.59$
$(\mathrm{m}, 1 \mathrm{H}), 2.04-1.85(\mathrm{~m}, 1 \mathrm{H}), 1.73(\mathrm{~s}, 3 \mathrm{H}), 1.73-1.63(\mathrm{~m}, 8 \mathrm{H}), 1.30-1.03(\mathrm{~m}, 8 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 173.1,166.5,140.1,134.6,131.5,128.5,127.6,126.9,61.9$, 52.2, 45.3, 40.7, 33.1, 33.0, 26.0, 25.9, 20.6, 15.7. HRMS (ESI+) Calcd. For $\mathrm{C}_{21} \mathrm{H}_{30} \mathrm{NO}_{3}$ $\left([\mathrm{M}+\mathrm{H}]^{+}\right): 344.2220$, found: 344.2212. The product was analyzed by HPLC to determine the enantiomeric excess: 86\% ee (Chiralpak ID, $i$-propanol/hexane $=10 / 90$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=230 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}=11.25$ and 19.41 min .

Methyl (2R,3S,E)-2-benzamido-2,3-dimethyl-7-phenylhept-4-enoate (41):


Yield (78\%); 28.4 mg ; colourless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=5 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=-13.1\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 7.76-7.69 (m, 2H), 7.50 (t, $J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.42(\mathrm{t}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.29-7.22(\mathrm{~m}, 2 \mathrm{H})$, 7.16 (dd, $J=12.7,7.2 \mathrm{~Hz}, 3 \mathrm{H}), 6.72(\mathrm{~s}, 1 \mathrm{H}), 5.67-5.60(\mathrm{~m}, 1 \mathrm{H}), 5.43(\mathrm{dd}, J=15.3,9.1$ $\mathrm{Hz}, 1 \mathrm{H}), 3.74(\mathrm{~s}, 3 \mathrm{H}), 2.75-2.62(\mathrm{~m}, 3 \mathrm{H}), 2.38-2.35(\mathrm{~m}, 2 \mathrm{H}), 1.71(\mathrm{~s}, 3 \mathrm{H}), 1.08(\mathrm{~d}, \mathrm{~J}=$ $7.0 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 173.2, 166.6, 141.5, 134.6, 132.9, 131.5, $130.8,128.5,128.33,128.29,126.8,125.9,62.0,52.2,45.0,35.8,34.2,20.6,15.7$. HRMS (ESI+) Calcd. For $\mathrm{C}_{23} \mathrm{H}_{28} \mathrm{NO}_{3}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 366.2064$, found: 366.2055. The product was analyzed by HPLC to determine the enantiomeric excess: $93 \%$ ee (Chiralpak AD-H, $i$-propanol/hexane $=10 / 90$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=210 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}=$ 7.99 and 9.27 min .

## Methyl $\quad(S, E)$-4-( $(R)$-4-methyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)pent-2enoate (4m):



Yield (82\%); 23.5 mg ; colourless oil; (Flash column chromatography eluent, petroleum
ether/ethyl acetate $=10 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=+79.6\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ $\delta 8.04-8.01(\mathrm{~m}, 2 \mathrm{H}), 7.59-7.55(\mathrm{~m}, 1 \mathrm{H}), 7.53-7.46(\mathrm{~m}, 2 \mathrm{H}), 7.02(\mathrm{dd}, J=15.7,9.4 \mathrm{~Hz}$, $1 \mathrm{H}), 5.98$ (dd, $J=15.7,0.7 \mathrm{~Hz}, 1 \mathrm{H}$ ), 3.76 (s, 3H), 2.83-2.77 (m, 1H), 1.47 (s, 3H), 1.01 $(\mathrm{d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 180.2,166.4,160.5,147.4,132.8$, 128.8, 128.0, 125.6, 123.6, 71.6, 51.6, 43.8, 22.6, 15.0. HRMS (ESI+) Calcd. For $\mathrm{C}_{16} \mathrm{H}_{18} \mathrm{NO}_{4}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 288.1230$, found: 288.1222. The product was analyzed by HPLC to determine the enantiomeric excess: $87 \%$ ee (Chiralpak AS-H, $i$-propanol/hexane $=$ $10 / 90$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}=5.64$ and 6.08 min .

## III. Synthetic Transformations

## (1). Scale-up reaction



In an Ar-filled glovebox, to a vial equipped with a magnetic stirring rod was added successively: Pd-L7 catalyst ( $0.2 \mathrm{mmol}, 357 \mathrm{mg}, 10 \mathrm{~mol} \%$ ), 1a ( $3 \mathrm{mmol}, 525 \mathrm{mg}, 1.5$ equiv.), $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL}), \mathbf{2 a}\left(2 \mathrm{mmol}, 260 \mathrm{mg}, 1.0\right.$ equiv.), and lastly $\mathrm{Et}_{3} \mathrm{~N}(6 \mathrm{mmol}$, $606 \mathrm{mg}, 3.0$ equiv.). Then $\mathrm{HBF}_{4} \cdot \mathrm{Et}_{2} \mathrm{O}(0.2 \mathrm{mmol}, 32.4 \mathrm{mg}$ in 10 mL DCM) was added dropwise to the solution. Once starting material was consumed (monitored by TLC), the organic solvent was removed by rotary evaporation. The dr value was determined by ${ }^{1} \mathrm{H}$ NMR analysis of the crude mixture and the residue was purified by column chromatography (petroleum ether/ethyl acetate $=10 / 1$ ) to give the product as a colorless oil ( $573 \mathrm{mg}, 94 \%$ ). The product was analyzed by HPLC to determine the enantiomeric excess: 94\% ee (Chiralpak AD-H, $i$-propanol $/$ hexane $=2 / 98$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=$ $220 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}=4.65$ and 5.15 min .

## (2). Reduction of $\mathbf{3 a}{ }^{\mathbf{4}}$



To a solution of $\mathbf{3 a}(0.2 \mathrm{mmol}, 61 \mathrm{mg})$ in THF $(1 \mathrm{~mL})$ was added $\mathrm{NaBH}_{4}(2 \mathrm{mmol}$, 10 equiv.) at $0^{\circ} \mathrm{C}$. Then, $\mathrm{H}_{2} \mathrm{O}(1 \mathrm{~mL})$ was added at the same temperature. The reaction mixture was allowed to stir at rt for 4 h . The solvent was removed by vacuo, and the residue was purified by column chromatography on silica column.

[^0]Yield (99\%); 61.8 mg ; white solid; mp $110-112{ }^{\circ} \mathrm{C}$; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=1 / 1) ;[\alpha]^{28} \mathrm{D}=-75.3\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.72(\mathrm{dd}, J=5.2,3.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.53-7.47(\mathrm{~m}, 1 \mathrm{H}), 7.45-7.35(\mathrm{~m}$, 4 H ), 7.31 (dd, $J=10.3,4.7 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.23 (ddd, $J=7.2,3.8,1.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), 6.58 (d, $J=$ $16.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.35-6.28(\mathrm{~m}, 2 \mathrm{H}), 5.11(\mathrm{~s}, 1 \mathrm{H}), 3.89(\mathrm{~d}, J=11.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.77(\mathrm{~d}, J=$ $11.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.30-3.23(\mathrm{~m}, 1 \mathrm{H}), 1.30(\mathrm{~s}, 3 \mathrm{H}), 1.19(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 3 \mathrm{H}),{ }^{13} \mathrm{C}$ NMR ( 100 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 168.5,137.2,134.7,131.72,131.67,130.6,128.7,128.5,127.4,126.8$, 126.2, 68.4, 61.8, 40.5, 19.6, 14.0. HRMS (ESI+) Calcd. For $\mathrm{C}_{20} \mathrm{H}_{24} \mathrm{NO}_{2}\left([\mathrm{M}+\mathrm{H}]^{+}\right)$: 310.1802, found: 310.1796 . The product was analyzed by HPLC to determine the enantiomeric excess: 94\% ee (Chiralpak ID, $i$-propanol/hexane $=5 / 95$, flow rate 1.0 $\mathrm{mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}=47.03$ and 52.64 min .

## (3) RCM reaction of $3 e^{5}$



A solution of $\mathbf{3 e}(0.1 \mathrm{mmol}, 36.3 \mathrm{mg})$ and Grubbs-II catalyst ( $0.01 \mathrm{mmol}, 8.49 \mathrm{mg}$ )
in DCM ( 2 mL ) was refluxed in oil bath under nitrogen for 12 h . The solvent was removed by vacuo, and the residue was purified by column chromatography on silica column.

## Methyl (1R,2S)-1-benzamido-2-methylcyclopent-3-ene-1-carboxylate (6):



6
Yield (70\%); 18.1 mg ; colourless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=3 / 1) ;[\alpha]^{28}{ }_{\mathrm{D}}=-16.3\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 7.80-7.75 (m, 2H), 7.54-7.49 (m, 1H), 7.47-7.40 (m, 2H), 6.66 (s, 1H), 5.70-5.63 (m, 2 H ), 3.75 ( $\mathrm{s}, 3 \mathrm{H}$ ), 3.47-3.34 (m, 1H), 3.29-3.24 (m, 1H), 2.83-2.77 (m, 1H), 1.15 (d, J $=7.3 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 174.0,167.2,134.0,131.7,128.6,127.0$, 126.9, 66.8, 52.7, 46.7, 43.6, 14.1. HRMS (ESI+) Calcd. For $\mathrm{C}_{15} \mathrm{H}_{18} \mathrm{NO}_{3}\left([\mathrm{M}+\mathrm{H}]^{+}\right)$: 260.1281, found: 260.1272. The product was analyzed by HPLC to determine the enantiomeric excess: $99 \%$ ee (Chiralpak AD-H, $i$-propanol/hexane $=10 / 90$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=220 \mathrm{~nm}) ; \mathrm{t}_{\mathrm{r}}=11.82$ and 15.03 min .
(4) Alcoholysis of 3a

$\mathrm{MeOH}(1 \mathrm{~mL})$ and $\mathrm{K}_{2} \mathrm{CO}_{3}(0.5 \mathrm{mmol})$ were added to the solution of $\mathbf{3 a}(0.1 \mathrm{mmol}$, 30.5 mg ), then the mixture was stirred at room temperature for 2 h . The solvent was removed by vacuo, and the residue was purified by column chromatography on silica column.


Yield (95\%); 32.0 mg ; colorless oil; (Flash column chromatography eluent, petroleum ether/ethyl acetate $=5 / 1) ;[\alpha]^{28} \mathrm{D}=-65.4\left(c 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.71(\mathrm{dd}, J=5.2,3.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.48-7.43(\mathrm{~m}, 1 \mathrm{H}), 7.41-$ 7.33 (m, 4H), 7.33-7.28 (m, 2H), 7.26-7.20 (m, 1H), 6.86 (s, 1H), 6.52 (d, J=15.8 Hz, $1 \mathrm{H}), 6.17$ (dd, $J=15.8,9.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H}), 3.03-2.96(\mathrm{~m}, 1 \mathrm{H}), 1.80(\mathrm{~s}, 3 \mathrm{H}), 1.22$ $(\mathrm{d}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 173.3,166.7,136.7,134.6,132.4$, 131.5, 130.1, 128.52, 128.50, 127.6, 126.8, 126.3, 62.5, 52.4, 45.1, 20.5, 15.6. HRMS (ESI+) Calcd. For $\mathrm{C}_{21} \mathrm{H}_{24} \mathrm{NO}_{3}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 338.1751$, found: 338.1739 . The product was analyzed by HPLC to determine the enantiomeric excess: $94 \%$ ee (Chiralpak AS-H, $i$ propanol $/$ hexane $=10 / 90$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ ); $\mathrm{t}_{\mathrm{r}}=8.32$ and 17.15 min . The characterization data of compound $\mathbf{7}$ is in accordance with the reported data in the literature. ${ }^{3}$

## IV. Proposed Catalytic Cycle

Based on the experimental observations and literature results, ${ }^{6}$ a plausible reaction mechanism is proposed as follow. The chiral palladium complex A triggers the initial oxidative addition of Brønsted acid, affording hydrido-Pd(II) intermediate $\mathbf{B}$, which undergoes migration insertion with 2a to give a $\pi$-allyl-Pd complex $\mathbf{C}$. In the presence of $\mathrm{Et}_{3} \mathrm{~N}$, an intermolecular Tsuji-Trost allylation of intermediate $\mathbf{C}$ and azlactone proceeds to provide the final product 3a with exclusive regioselectivity and high diastereo-/enantioselectivity and to regenerate the chiral palladium complex $\mathbf{A}$, which was involved in the next catalytic cycle. The achieved high diastereoselectivity in this case can be ascribed to the substrate control, and similar phenomenon was also observed in previous Mo- or Ir-catalyzed asymmetric allylations of azlactones reported by Prof. Trost (J. Am. Chem. Soc. 2002, 124, 7256-7257) and Prof. Hartwig (J. Am. Chem. Soc. 2013, 135, 2068-2071), respectively. The stereochemical outcome of this
reaction could be rationalized by the proposed transition state. Admittedly, the detailed mechanism of those asymmetric allylation reactions and the current Pd-catalyzed asymmetric hydroalkylation need to be further investigated.



Scheme S1. Proposed catalytic cycle and rationale of the stereochemical outcome.

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## V. NMR and HPLC Spectra







3a



Data File E:\DATA \ZZP\ZZP-8-16\ZZP-8-16-1 2019-09-22 15-48-03\ZZP-8-162.D
Sample Name: ZZP-8-16-1


Additional Info : Peak(s) manually integrated
DAD1 B, Sig=254,4 Ref=off (E:IDATAIZZPIZZP-8-16IZZP-8-16-12019-09-22 15-48-031ZZP-8-162.D)
$\begin{aligned} &========================================================================= \\ & \text { Area Percent Report }\end{aligned}$


| Sorted By | $:$ | Signal |
| :--- | :---: | :---: |
| Multiplier | $:$ | 1.0000 |
| Dilution | $:$ | 1.0000 |
| Use Multiplier \& Dilution | Factor with | ISTDs |

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 4.665 | MF | 0.2380 | 3822.98901 | 267.72723 | 47.5827 |
| 2 | 5.110 | FM | 0.2662 | 4211.41797 | 263.68408 | 52.4173 |
| Total | $s$ : |  |  | 8034.40698 | 531.41132 |  |

Data File E:\DATA \ZZP\ZZP-6-1 \ZZP-6-1 2019-04-26 09-44-31\zzp-6-11.D
Sample Name: ZZP-6-1-1


Additional Info : Peak(s) manually integrated


Area Percent Report


| Sorted By | $:$ | Signal |
| :--- | :---: | :---: |
| Multiplier | $:$ | 1.0000 |
| Dilution | $:$ | 1.0000 |
| Use Multiplier \& Dilution | Factor with | ISTDs |

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime <br> [min] | Type | Width <br> [min] | Area [mAU*s] | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 4.653 |  | 0.2287 | 223.22818 | 16.26787 | 2.7089 |
| 2 | 5.154 | FM | 0.2705 | 8017.25293 | 494.06342 | 97.2911 |
| Totals |  |  |  | 8240.48111 | 510.33129 |  |

##  




Data File E:\DATA \ZZP\ZZP-6-10\ZZP-6-10) 2019-05-06 20-07-48\ZZP-6-105.D
Sample Name: ZZP-6-8

| Acq. Operator | : SYSTEM | Seq. Line : 6 |
| :---: | :---: | :---: |
| Acq. Instrument | : 1260 | Location : 72 |
| Injection Date | : 5/6/2019 8:51:25 PM | Inj : 1 |
|  |  | Inj Volume : $2.000 \mu \mathrm{l}$ |
| Acq. Method | $\begin{aligned} & \text { E: \DATA } \backslash Z Z P \backslash Z Z P-6-10 \backslash Z Z P-6-10) \\ & M \end{aligned}$ | 2019-05-06 20-07-48\ID-98-2, 2UL,1.0ML, 20MIN. |
| Last changed | 5/6/2019 8:57:31 PM by SYSTEM (modified after loading) |  |
| Analysis Method | E: \DATA \ZZP \ZZP-6-10\ZZP-6-10) <br> M (Sequence Method) | 2019-05-06 20-07-48\ID-98-2, 2UL,1.0ML, 20MIN. |
| Last changed | 9/10/2019 5:00:40 PM by SYSTEM (modified after loading) |  |

Additional Info : Peak(s) manually integrated


| Area Percent Report |  |
| :---: | :---: |
| Sorted By | Signal |
| Multiplier | 1.0000 |
| Dilution | 1.0000 |

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} \mathrm{~s}]} \end{gathered}$ | Height [mAU] | $\begin{gathered} \text { Area } \\ \text { \% } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 4.244 | MF | 0.1501 | 1198.40283 | 133.08110 | 49.6879 |
| 2 | 4.713 | FM | 0.2273 | 1213.45691 | 88.96022 | 50.3121 |
| Totals | $s$ : |  |  | 2411.85974 | 222.04132 |  |

Data File E:\DATA \ZZP\ZZP-6-10\ZZP-6-10) 2019-05-06 20-07-48\ZZP-6-106.D
Sample Name: ZZP-6-10


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} \mathrm{~s}]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 4.243 |  | 0.1559 | 4348.47412 | 464.82629 | 100.0000 |
| Tota | s : |  |  | 4348.47412 | 464.82629 |  |



Sample Name: ZZP-6-40-RAC


Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} \mathrm{~s}]} \end{gathered}$ | Height [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 13.963 | BB | 0.5869 | 2825.18457 | 71.52072 | 50.2184 |
| 2 | 17.367 | MM | 0.7934 | 2800.61499 | 58.83350 | 49.7816 |
| Totals |  |  |  | 5625.79956 | 130.35423 |  |

Data File E:\DATA \ZZP\ZZP-6-40\ZZP-6-40-GH 2019-05-25 15-21-09\ZZP-6-40-GH.D
Sample Name: ZZP-6-40-GH


Additional Info : Peak(s) manually integrated
DAD1 B, Sig=254,4 Ref=off (E:IDATAIZZPIZZP-6-40IZZP-6-40-GH 2019-05-25 15-21-09\ZZP-6-40-GH.D)


| $==================================$ |  |
| :--- | :--- | :--- |
|  | Area Percen |
| $====================================$ |  |

Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} \text { s }]} \end{gathered}$ | Height [mAU] | Area <br> \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 13.550 | PP | 0.5783 | 242.48613 | 6.98868 | 2.6410 |
| 2 | 16.808 | BB | 0.7094 | 8939.27051 | 188.44026 | 97.3590 |
| Total | s : |  |  | 9181.75664 | 195.42894 |  |



Data File E:\DATA \ZZP \ZZP-6-36\ZZP-6-36-RAC 2019-05-25 11-40-21 \ZZP-6-RAC.D
Sample Name: ZZP-6-26



Signal 1: DAD1 B, Sig=254,4 Ref=off


Data File E:\DATA\ZZP\ZZP-6-70\ZZP-6-70 2019-06-25 15-44-49\ZZP-6-701.D
Sample Name: ZZP-6-70



Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} * \mathrm{~s}]} \end{gathered}$ | Height [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 5.990 | BV | 0.3035 | 547.73846 | 27.60386 | 3.4401 |
| 2 | 7.040 | VBA | 0.3557 | 1.53745 e 4 | 655.31622 | 96.5599 |
| Totals | $s$ : |  |  | 1.59223 e 4 | 682.92008 |  |

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Data File E:\DATA\ZZP\ZZP-7-72\ZZP-7-79 2019-08-29 16-06-02\ZZP-7-793.D
Sample Name: ZZP-7-79-RAC


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} \mathrm{~s}]} \end{gathered}$ | Height <br> [mAU] | $\begin{gathered} \text { Area } \\ \text { \% } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 29.596 |  | 0.6188 | 1.40490 e 4 | 378.40958 | 47.9097 |
| 2 | 30.720 | FM | 0.6741 | 1.52749 e 4 | 377.65997 | 52.0903 |
| Total | : |  |  | 2.93239 e 4 | 756.06955 |  |

Data File E:\DATA\ZZP\ZZP-7-72\ZZP-7-79 2019-08-29 16-06-02\ZZP-7-794.D
Sample Name: ZZP-7-79


Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} \text { s }]} \end{gathered}$ | Height [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 29.773 | BV E | 0.4401 | 121.78240 | 3.98937 | 0.6101 |
| 2 | 30.779 | VB R | 0.5931 | 1.98406 e 4 | 504.22745 | 99.3899 |

Totals :
1.99624 e 4508.21681


Data File E:\DATA $\backslash Z Z P \backslash Z Z P-6-36 \backslash Z Z P-6-36-R A C \quad 2019-05-2511-40-21 \backslash Z Z P-6-R A C 1 . D$
Sample Name: ZZP-6-32



Signal 1: DAD1 B, Sig=254,4 Ref=off


Data File E:\DATA\ZZP\ZZP-6-38\ZZP-6-38 2019-05-25 12-34-20\ZZP-6-381.D
Sample Name: ZZP-6-38-2


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ {[\mathrm{min}]} \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} * \mathrm{~s}]} \end{gathered}$ | Height <br> [mAU] | $\begin{gathered} \text { Area } \\ \text { \% } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 6.600 | MM | 0.3588 | 5704.43311 | 264.95068 | 98.4146 |
| 2 | 9.387 | MP | 0.4124 | 91.89323 | 3.71346 | 1.5854 |
| Totals : |  |  |  | 5796.32634 | 268.66414 |  |



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Data File E:\DATA \ZZP\ZZP-6-31\ZZP-6-31 2019-05-18 21-00-00\ZZP-6-31.D
Sample Name: ZZP-6-31-2


Signal 1: DAD1 A, Sig=254,4 $\operatorname{Ref}=360,100$

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} \mathrm{~s}]} \end{gathered}$ | Height [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 4.795 | MF | 0.2472 | 1397.84070 | 94.22900 | 48.0597 |
| 2 | 5.583 | FM | 0.2987 | 1510.71204 | 84.30472 | 51.9403 |
| Totals |  |  |  | 2908.55273 | 178.53372 |  |

Data File E:\DATA \ZZP\ZZP-6-34\ZZP-6-34 2019-05-22 15-31-46\ZZP-6-341.D
Sample Name: ZZP-6-34-1


Signal 1: DAD1 A, Sig=254,4 Ref=360, 100

| Peak \# | RetTime [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}{ }^{*} \mathrm{~s}\right]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 4.855 | MM | 0.2279 | 13.45818 | $9.84306 \mathrm{e}-1$ | 1.8192 |
| 2 | 5.703 | BB | 0.2672 | 726.32715 | 41.10188 | 98.1808 |
| Total | s : |  |  | 739.78533 | 42.08619 |  |



Sample Name: ZZP-5-70-2

| Acq. Operator | : SYSTEM Seq. Line : |  |
| :---: | :---: | :---: |
| Acq. Instrument | : 1260 Location : | 61 |
| Injection Date | : 4/24/2019 4:14:29 PM Inj : | 1 |
|  | Inj Volume : | $2.000 \mu \mathrm{l}$ |
| Acq. Method | $\begin{aligned} & \text { E: \DATA } \mathrm{ZZZP} \backslash Z Z P-5-70 \backslash Z Z P-5-70-2 \text { 2019-04-24 } \\ & \text {.M } \end{aligned}$ | $15-37-28 \backslash A D-98-2,2 U L, 1.0 M L, 20 M I N$ |
| Last changed | 4/24/2019 4:21:57 PM by SYSTEM (modified after loading) |  |
| Analysis Method | E: \DATA $\backslash Z Z P \backslash Z Z P-5-70 \backslash Z Z P-5-70-2 ~ 2019-04-24 ~$ <br> .M (Sequence Method) | $15-37-28 \backslash A D-98-2,2 U L, 1.0 \mathrm{ML}, 20 \mathrm{MIN}$ |
| Last changed | 9/10/2019 7:24:10 PM by SYSTEM (modified after loading) |  |

Additional Info : Peak(s) manually integrated
DAD1 B, Sig=254,4 Ref=off (E:IDATAIZZPIZZP-5-701ZZP-5-70-2 2019-04-2415-37-281ZZP-5-70-2-RAC3.D)

| $=========================================================================$ |  |
| ---: | :--- |
|  | Area Percent Report |


| Sorted By | $:$ | Signal |
| :--- | :--- | :--- |
| Multiplier | $:$ | 1.0000 |
| Dilution | $:$ | 1.0000 |

Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime <br> [min] | Type | Width [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} \text { s }]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 6.210 | MM | 0.3084 | 1587.38989 | 85.77534 | 50.0083 |
| 2 | 7.002 | MM | 0.3404 | 1586.86047 | 77.69465 | 49.9917 |
| Total |  |  |  | 3174.25037 | 163.46999 |  |

Data File E:\DATA\ZZP\ZZP-5-69\ZZP-5-69 2019-04-24 19-09-24\ZZP-5-691.D
Sample Name: ZZP-5-69-2

| Acq. Operator | : SYSTEM | Seq. Line : | 2 |
| :---: | :---: | :---: | :---: |
| Acq. Instrument | : 1260 | Location | 62 |
| Injection Date | : 4/24/2019 7:25:11 PM | Inj : | 1 |

Acq. Method : E:\DATA \ZZP \ZZP-5-69\ZZP-5-69 2019-04-24 19-09-24\AD-98-2,2UL,1.0ML,20MIN.M Last changed : 4/24/2019 7:22:34 PM by SYSTEM
Analysis Method : E:\DATA \ZZP\ZZP-5-69\ZZP-5-69 2019-04-24 19-09-24\AD-98-2,2UL,1.0ML, 20MIN.M
(Sequence Method)
Last changed : 9/10/2019 7:30:12 PM by SYSTEM (modified after loading)
Additional Info : Peak(s) manually integrated
DAD1 B, Sig=254,4 Ref=off (E:IDATAIZZPIZZP-5-691ZZP-5-69 2019-04-2419-09-24ZZZP-5-691.D)
===========================================================================2,
Area Percent Report
==============================================================================2

| Sorted By | $:$ | Signal |
| :--- | :---: | :---: |
| Multiplier | $:$ | 1.0000 |
| Dilution | $:$ | 1.0000 |
| Use Multiplier \& Dilution | Factor with | ISTDs |

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 6.174 | BB | 0.2853 | 58.57859 | 2.74153 | 0.8707 |
| 2 | 6.960 | BB | 0.3119 | 6669.56201 | 319.02716 | 99.1293 |
| Totals |  |  |  | 6728.14060 | 321.76869 |  |


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Data File E:\DATA \ZZP\ZZP-6-2\ZZP-6-2-2 2019-04-25 10-33-32\ZZP-6-21.D
Sample Name: ZZP-6-2


Additional Info : Peak(s) manually integrated
DAD1 B, Sig=254,4 Ref=off (E:IDATAIZZPIZZP-6-2IZZP-6-2-2 2019-04-25 10-33-32IZZP-6-21.D)
DAD1 B, Sig=254,4 Ref=off (E:IDATAIZZPIZZP-6-2|ZZP-6-2-2 2019-04-25 10-33-321ZZP-6-21.D)

| $========================================================================$ |  |
| ---: | :--- |
|  | Area Percent Report |


| Sorted By | $:$ | Signal |
| :--- | :--- | :--- |
| Multiplier | $:$ | 1.0000 |
| Dilution | $:$ | 1.0000 |

Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} \mathrm{~s}]} \end{gathered}$ | Height [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 5.164 | BV | 0.2436 | 2987.37036 | 178.20671 | 49.2600 |
| 2 | 5.777 | VB | 0.2708 | 3077.12915 | 165.56377 | 50.7400 |
| Totals |  |  |  | 6064.49951 | 343.77048 |  |

Data File E:\DATA $Z Z Z P \backslash Z Z P-F \backslash Z Z P-F L$ 2019-11-09 19-49-25\ZZP-F6.D
Sample Name: ZZP-F-6

| Acq. Operator | : SYSTEM | Seq. Line | 7 |
| :---: | :---: | :---: | :---: |
| Acq. Instrument | : 1260 | Location | 46 |
| Injection Date | : 11/9/2019 8:56:04 PM | Inj | 1 |
|  |  | Inj Volume | . 000 |

 Last changed : 11/9/2019 7:49:25 PM by SYSTEM
Analysis Method : E:\DATA \ZZP \ZZP-F\ZZP-Fl 2019-11-09 19-49-25\AD-98.5-1.5,2UL,1.0ML, 10MIN.M
(Sequence Method)
Last changed : 11/20/2019 10:00:45 AM by SYSTEM (modified after loading)
Additional Info : Peak(s) manually integrated
Additional Info : Peak( s manually integrated
$==================================================================$
Area Percent Report
==============================================================================2

| Sorted By | $:$ | Signal |
| :--- | :---: | :---: |
| Multiplier | $:$ | 1.0000 |
| Dilution | $:$ | 1.0000 |
| Use Multiplier \& Dilution | Factor with | ISTDs |

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}^{*} \mathrm{~s}\right]} \end{gathered}$ | Height [mAU] | $\begin{gathered} \text { Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 5.491 |  | 0.1198 | 65.99379 | 8.20404 | 2.4674 |
| 2 | 6.199 | VB | 0.1353 | 2608.59082 | 289.15280 | 97.5326 |
| Totals |  |  |  | 2674.58461 | 297.35684 |  |

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Data File E:\DATA $\backslash Z Z P \backslash Z Z P-6-29 \backslash Z Z P-6-29$ 2019-05-17 14-58-01\SC-11-31-rearrangement.D
Sample Name: ZZP-6-29-1


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ {[\mathrm{min}]} \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} * \mathrm{~s}]} \end{gathered}$ | Height [mAU] | $\begin{gathered} \text { Area } \\ \text { \% } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 4.936 | BV | 0.2378 | 3362.96606 | 208.92862 | 49.5938 |
| 2 | 5.611 |  | 0.2687 | 3418.05737 | 189.29442 | 50.4062 |
| Totals : |  |  |  | 6781.02344 | 398.22304 |  |

Data File E:\DATA\ZZP\ZZP-CL\ZZP-CL 2019-11-09 16-16-11\ZZP-Cl6.D
Sample Name: zzp-cl-6

| Acq. Operator $:$ SYSTEM | Seq. Line : 7 |
| :--- | ---: | :--- |
| Acq. Instrument : 1260 | Location : 46 |
| Injection Date $: 11 / 9 / 20195: 04: 56 \mathrm{PM}$ | Inj : 1 |


Last changed : 11/9/2019 4:16:11 PM by SYSTEM
Analysis Method : E:\DATA \ZZP $\backslash Z Z P-C l \backslash z z p-c l ~ 2019-11-09 ~ 16-16-11 \backslash A D 98-2,2 U L, 1 M L, 7 M I N . M ~(~$
Sequence Method)
Last changed : 11/20/2019 9:55:31 AM by SYSTEM (modified after loading)
Additional Info : Peak(s) manually integrated
DAD1 B, Sig=254,4 Ref=off (E:IDATAIZZPIZZP-CLIZZP-CL 2019-11-09 16-16-11/ZZP-C16.D)
===========================================================================2
Area Percent Report
================================================================================2

| Sorted By | $:$ | Signal |
| :--- | :---: | :---: |
| Multiplier | $:$ | 1.0000 |
| Dilution | $:$ | 1.0000 |
| Use Multiplier \& Dilution | Factor with | ISTDs |

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width <br> [min] | Area [mAU*s] | Height [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 5.107 | MM | 0.1252 | 67.41597 | 8.97214 | 2.7347 |
| 2 | 5.812 | BB | 0.1273 | 2397.80884 | 287.62769 | 97.2653 |
| Totals |  |  |  | 2465.22481 | 296.59982 |  |


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Data File E:\DATA \ZZP \ZZP-6-11 \ZZP-6-11-1 2019-05-07 10-14-50\ZZP-6-11-11.D
Sample Name: ZZP-6-11-1

| Acq. Operator | : SYSTEM Seq. Line : |  |
| :---: | :---: | :---: |
| Acq. Instrument | 1260 Location | 63 |
| Injection Date | $:$ 5/7/2019 10:23:46 AM Inj | 1 |
|  | Inj Volume | $2.000 \mu \mathrm{l}$ |
| Acq. Method | $: E: \backslash D A T A \backslash Z Z P \backslash Z Z P-6-11 \backslash Z Z P-6-11-1 \quad 2019-05-07$ .M | 10-14-50\AD-98-2, 2UL , 1.0ML, 20MIN |
| Last changed | : 5/7/2019 10:32:24 AM by SYSTEM (modified after loading) |  |
| Analysis Method | : E:\DATA \ZZP \ZZP-6-11\ZZP-6-11-1 2019-05-07 .M (Sequence Method) | $10-14-50 \backslash A D-98-2,2 U L, 1.0 M L, 20 M I N$ |
| Last changed | : 9/10/2019 5:35:09 PM by SYSTEM (modified after loading) |  |

Additional Info : Peak(s) manually integrated
DAD1 B, Sig=254,4 Ref=off (E:IDATAIZZPIZZP-6-11IZZP-6-11-1 2019-05-07 10-14-50ZZP-6-11-11.D)



Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} \mathrm{~s}]} \end{gathered}$ | Height [mAU] | $\begin{gathered} \text { Area } \\ \text { \% } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 4.244 | MM | 0.2417 | 3122.70117 | 215.35159 | 50.0252 |
| 2 | 4.997 | VB | 0.2339 | 3119.55615 | 195.78053 | 49.9748 |
| Totals | $s$ : |  |  | 6242.25732 | 411.13213 |  |

Data File E:\DATA $\backslash Z Z P \backslash Z Z P-6-18 \backslash Z Z P-6-18$ 2019-05-11 15-11-08\CC-9-136-R1.D
Sample Name: ZZP-6-18-1


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}{ }^{*} \mathrm{~s}\right]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 4.143 | BB | 0.2460 | 110.51006 | 7.16107 | 2.3603 |
| 2 | 4.781 |  | 0.2288 | 4571.43604 | 291.73410 | 97.6397 |
| Total | s : |  |  | 4681.94610 | 298.89517 |  |




|  |  |  |  |  |  |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 10 | 1 | -10 | -20 | -30 | -40 | -50 | -60 | -70 | 1 |

Data File E:\DATA \ZZP\ZZP-6-25\ZZP-6-25-1-2 2019-05-14 17-49-34\XSM 201905143.D
Sample Name: ZZP-6-25-1


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak \# | RetTime [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} \mathrm{~s}]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 4.538 | MF | 0.2292 | 544.58289 | 39.59743 | 47.8651 |
| 2 | 4.943 |  | 0.2559 | 593.16199 | 38.62579 | 52.1349 |
| Total | s : |  |  | 1137.74487 | 78.22322 |  |

Data File E:\DATA\ZZP\ZZP-6-34\ZZP-6-34 2019-05-22 15-31-46\ZZP-6-342.D
Sample Name: ZZP-6-34-2

| Acq. Operator | : SYSTEM | Seq. Line | 3 |
| :---: | :---: | :---: | :---: |
| Acq. Instrument | : 1260 | Location | 62 |
| Injection Date | : 5/22/2019 3:48:44 PM | Inj | 1 |
|  |  | Inj Volume | . 000 |

Acq. Method : E:\DATA\ZZP\ZZP-6-34\ZZP-6-34 2019-05-22 15-31-46\AD-97-3,1UL,1ML,10MIM.M
Last changed : 5/22/2019 3:47:16 PM by SYSTEM
Analysis Method : E:\DATA \ZZP\ZZP-6-34\ZZP-6-34 2019-05-22 15-31-46\AD-97-3,1UL,1ML,10MIM.M (
Sequence Method)
Last changed : 9/10/2019 7:55:37 PM by SYSTEM (modified after loading)
Additional Info : Peak(s) manually integrated

$=====================================================================$
Area Percent Report
==============================================================================2

| Sorted By | $:$ | Signal |
| :--- | :---: | :---: |
| Multiplier | $:$ | 1.0000 |
| Dilution | $:$ | 1.0000 |
| Use Multiplier \& Dilution | Factor with | ISTDs |

Signal 1: DAD1 A, Sig=254,4 Ref=360,100







Data File E:\DATA \ZZP \ZZP-6-11 \ZZP-6-11-3 2019-05-07 10-49-34\ZZP-6-11-11.D
Sample Name: ZZP-6-11-3


Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | ```RetTime [min]``` | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}{ }^{*} \mathrm{~s}\right]} \end{gathered}$ | Height <br> [mAU] | $\begin{gathered} \text { Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 5.149 | MF | 0.2770 | 2008.51721 | 120.82961 | 49.0794 |
| 2 | 6.099 | FM | 0.3220 | 2083.86230 | 107.86211 | 50.9206 |
| Total | s : |  |  | 4092.37952 | 228.69172 |  |

Data File E:\DATA $\backslash Z Z P \backslash Z Z P-6-18 \backslash Z Z P-6-18$ 2019-05-11 15-11-08\CC-9-136-R2.D
Sample Name: ZZP-6-18-2

| =========================================================================== |  |
| :--- | ---: |
| Acq. Operator : SYSTEM | Seq. Line : 3 |
| Acq. Instrument : 1260 | Location : 62 |
| Injection Date : 5/11/2019 3:29:21 PM | Inj : 1 |

Acq. Method : E:\DATA \ZZP \ZZP-6-18\ZZP-6-18 2019-05-11 15-11-08\AD98-2,2UL,1ML,7MIN.M
Last changed : 5/11/2019 3:17:53 PM by SYSTEM
Analysis Method : E:\DATA\ZZP\ZZP-6-18\ZZP-6-18 2019-05-11 15-11-08\AD98-2, 2UL, 1ML,7MIN.M (
Sequence Method)
Last changed : 9/10/2019 5:40:04 PM by SYSTEM (modified after loading)


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}^{*} \mathrm{~s}\right]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 5.196 | BB | 0.2171 | 51.19048 | 3.44931 | 2.9350 |
| 2 | 6.159 |  | 0.2756 | 1692.94031 | 89.93631 | 97.0650 |
| Total | s : |  |  | 1744.13079 | 93.38562 |  |




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$3 n$



Data File E:\DATA\ZZP\ZZP-9-11\ZZP-9-12 2019-11-27 14-08-42\ZZP-9-111.D
Sample Name: ZZP-9-11


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}^{*} \mathrm{~s}\right]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 14.985 | BB | 0.6928 | 2325.13940 | 51.88815 | 27.5755 |
| 2 | 16.961 | BB | 0.8652 | 1658.62830 | 28.23995 | 19.6709 |
| 3 | 20.505 | BB | 1.0598 | 2575.21631 | 34.86258 | 30.5414 |
| 4 | 24.522 | BB | 1.0713 | 1872.90759 | 21.77895 | 22.2122 |

Data File E:\DATA\ZZP\ZZP-9-11\ZZP-9-12 2019-11-27 14-08-42\ZZP-9-112.D
Sample Name: ZZP-9-11-GH


Additional Info : Peak(s) manually integrated

===========================================================================2
Area Percent Report
==============================================================================2

| Sorted By | $:$ | Signal |
| :--- | :---: | :---: |
| Multiplier | $:$ | 1.0000 |
| Dilution | $:$ | 1.0000 |
| Use Multiplier \& | Dilution | Factor with |
| ISTDs |  |  |

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width [min] | Area [mAU*s] | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 17.760 | BB | 0.9240 | 4010.64600 | 66.27621 | 97.6088 |
| 2 | 25.208 | PM | 1.2687 | 98.25127 | 1.29068 | 2.3912 |
| Total | s : |  |  | 4108.89726 | 67.56690 |  |



Data File E:\DATA \ZZP \ZZP-9-11\ZZP-9-11-3 2019-11-28 21-15-16\ZZP-9-11-31.D
Sample Name: ZZP-9-11-3


Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU*s}]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 15.832 | BB | 0.3935 | 1463.89966 | 57.41402 | 29.7159 |
| 2 | 18.567 | BB | 0.5035 | 1455.96118 | 44.28938 | 29.5548 |
| 3 | 24.147 | BB | 0.6228 | 1003.15607 | 24.65083 | 20.3632 |
| 4 | 27.348 | BB | 0.6895 | 1003.29791 | 21.07263 | 20.3661 |

Data File $E: \backslash D A T A \backslash Z Z P \backslash Z Z P-9-11 \backslash Z Z P-9-11-3$ 2019-11-28 21-15-16\ZZP-9-11-33.D
Sample Name: ZZP-9-11-3-GH


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime <br> [min] | Type | Width <br> [min] | Area [mAU*s] | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 15.976 | BB | 0.3922 | 2172.82910 | 85.00035 | 51.9735 |
| 2 | 18.835 | BB | 0.4452 | 150.99010 | 4.69492 | 3.6116 |
| 3 | 24.356 | BB | 0.4877 | 147.75714 | 3.63927 | 3.5343 |
| 4 | 27.597 | BB | 0.7201 | 1709.07373 | 35.85708 | 40.8806 |
| Total | $s$ : |  |  | 4180.65007 | 129.19162 |  |






Data File E:\DATA \ZZP \ZZP-6-41 \ZZP-6-41-1 2019-05-25 21-32-20\ZZP-6-41-12.D
Sample Name: ZZP-6-41-1

| Acq. Operator | : SYSTEM Seq. Line : |  |
| :---: | :---: | :---: |
| Acq. Instrument | : 1260 Location | 61 |
| Injection Date | : 5/25/2019 9:51:01 PM Inj | 1 |
|  | Inj Volume : | $2.000 \mu \mathrm{l}$ |
| Acq. Method | $: E: \backslash D A T A \backslash Z Z P \backslash Z Z P-6-41 \backslash Z Z P-6-41-1 \quad 2019-05-25$ M | 21-32-20\OD, 90-10, 2UL, 1ML, 30MIN. |
| Last changed | : 5/25/2019 10:00:44 PM by SYSTEM (modified after loading) |  |
| Analysis Method | : E:\DATA \ZZZP\ZZP-6-41\ZZP-6-41-1 2019-05-25 M (Sequence Method) | 21-32-20\OD, $90-10,2 U L, 1 M L, 30 M I N$. |
| Last changed | : 9/10/2019 8:05:14 PM by SYSTEM (modified after loading) |  |

Additional Info : Peak(s) manually integrated


| ==================================== |  |
| :--- | :--- | :--- |
|  | Area Percen |

Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} \mathrm{~s}]} \end{gathered}$ | Height [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 7.954 | MF | 0.4057 | 1883.46558 | 77.37347 | 49.0280 |
| 2 | 8.720 | FM | 0.4528 | 1958.14441 | 72.07433 | 50.9720 |
| Totals |  |  |  | 3841.60999 | 149.44780 |  |

Data File E:\DATA \ZZP\ZZP-6-42\ZZP-6-42-23 2019-05-27 20-36-24\ZZP-6-423.D
Sample Name: ZZP-6-42-3


Additional Info : Peak(s) manually integrated



| Sorted By | $:$ | Signal |
| :--- | :--- | :--- |
| Multiplier | $:$ | 1.0000 |
| Dilution | $:$ | 1.0000 |

Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU*s}]} \end{gathered}$ | Height [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 7.973 | MF | 0.4174 | 9402.24316 | 375.44598 | 95.9894 |
| 2 | 8.583 | FM | 0.3437 | 392.83899 | 19.04754 | 4.0106 |
| Totals | $s$ : |  |  | 9795.08215 | 394.49352 |  |



Data File E:\DATA \ZZP\ZZP-6-45\ZZP-6-45-35 2019-06-01 09-05-50\ZZP-6-451.D
Sample Name: ZZP-6-45-3



Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} * \mathrm{~s}]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 10.858 | BB | 0.8048 | 3301.74585 | 61.45637 | 49.9615 |
| 2 | 20.878 |  | 1.5570 | 3306.82788 | 28.89760 | 50.0385 |
| Tota | s : |  |  | 6608.57373 | 90.35397 |  |

Data File E:\DATA \ZZP \ZZP-6-46\ZZP-6-46-13 2019-06-03 10-49-44\ZZP-6-46-133.D
Sample Name: ZZP-6-46-3


Additional Info : Peak(s) manually integrated
(E:IDATAIZZPIZZP-6-46/ZZP-6-46-13 2019-06-0310-49-44/ZZP-6-46-133.D)


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU*s}]} \end{gathered}$ | Height <br> [mAU] | $\begin{gathered} \text { Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 10.664 | MM | 0.8517 | 65.96181 | 1.29073 | 1.5794 |
| 2 | 20.454 | MM | 1.7732 | 4110.40674 | 38.63438 | 98.4206 |
| Total | $s$ : |  |  | 4176.36855 | 39.92512 |  |








Data File E:\DATA \ZZP\ZZP-4BR\ZZP-4BR 2019-11-11 15-20-50\ZZP-4Br8.D
Sample Name: zzp-4f


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}^{*} \mathrm{~s}\right]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 16.383 | BB | 0.6005 | 1206.50049 | 30.30393 | 49.3635 |
| 2 | 19.331 | BB | 0.6441 | 1237.61365 | 28.75495 | 50.6365 |
| Total | s : |  |  | 2444.11414 | 59.05888 |  |

Data File E:\DATA \ZZP\ZZP-4Br\zzp-4br 2019-11-11 15-20-50\ZZP-4Br7.D
Sample Name: zzp-4f


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ {[\mathrm{min}]} \end{gathered}$ | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 16.293 | BB | 0.6243 | 9936.77637 | 245.43620 | 98.0621 |
| 2 | 19.328 | BB | 0.5430 | 196.37254 | 5.12484 | 1.9379 |
| Total | $s$ : |  |  | 1.01331 e 4 | 250.56104 |  |



Data File E:\DATA \ZZP\ZZP-6-45\ZZP-6-45-35 2019-06-01 09-05-50\ZZP-6-452.D
Sample Name: ZZP-6-45-4


Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak <br> RetTime <br> $\#$ | [min] |
| :---: | :---: | :---: | :---: | :---: | :---: |

Data File E:\DATA \ZZP \ZZP-6-59\ZZP-5-59-1 2019-06-19 09-01-25\ZZP-6-59-11.D
Sample Name: ZZP-5-59-1


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} \text { s }]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 7.726 | BB | 0.4821 | 216.48560 | 6.82393 | 1.8061 |
| 2 | 13.404 | BBA | 1.2058 | 1.17700 e 4 | 147.67722 | 98.1939 |
| Total | $s$ : |  |  | 1.19864 e 4 | 154.50114 |  |






Data File E:\DATA \ZZP\ZZP-4BR\ZZP-4BR-2 2019-11-11 18-46-59\ZZP-4Br.D
Sample Name: zzp-4Br


Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU*s}]} \end{gathered}$ | Height <br> [mAU] | $\begin{gathered} \text { Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 17.589 | BV | 0.6684 | 1963.27124 | 45.77510 | 48.8656 |
| 2 | 19.041 |  | 0.6693 | 2054.42603 | 45.80133 | 51.1344 |
| Total | $s$ : |  |  | 4017.69727 | 91.57644 |  |

Data File E:\DATA \ZZP-4BR\ZZP-4BR-3 2019-11-11 19-21-08\ZZP-4Br.D
Sample Name: zzp-4Br


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} * \mathrm{~s}]} \end{gathered}$ | Height [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 17.578 | MF | 0.7326 | 1.21459 e 4 | 276.32147 | 97.2736 |
| 2 | 19.110 | FM | 0.8253 | 340.42383 | 6.87504 | 2.7264 |
| Total | : |  |  | 1.24863e4 | 283.19652 |  |



Data File E:\DATA \ZZP\ZZP-6-41\ZZP-6-41-23-3 2019-05-28 19-39-55\ZZP-6-41-232.D
Sample Name: ZZP-6-41-3


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime <br> [min] | Type | Width <br> [min] | Area [mAU*s] | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 9.135 | BB | 0.4337 | 2272.83691 | 78.98444 | 50.4704 |
| 2 | 10.836 | BB | 0.5164 | 2230.47266 | 65.31155 | 49.5296 |
| Total | $s$ : |  |  | 4503.30957 | 144.29600 |  |


Sample Name: ZZP-6-42-1


Additional Info : Peak(s) manually integrated
DAD1 B, Sig=254,4 Ref=off (E:IDATAIZZPIZZP-6-41ZZZP-6-41-1-2 2019-05-2916-06-18/ZZP-6-414.D)

| $====================================$ |  |
| :--- | :--- | :--- |
|  | Area Percen |

Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} \mathrm{~s}]} \end{gathered}$ | Height [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 9.360 | BB | 0.4498 | 2123.67090 | 72.06597 | 98.7472 |
| 2 | 11.204 | MM | 0.5264 | 26.94297 | $8.53038 \mathrm{e}-1$ | 1.2528 |
| Total | $s$ : |  |  | 2150.61387 | 72.91901 |  |








Data File E:\DATA\ZZP\ZZP-6-47\ZZP-5-47 2019-06-04 16-47-05\ZZP-5-471.D
Sample Name: ZZP-6-47-1


Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU*s}]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 8.079 | BB | 0.8579 | 4156.84033 | 70.70460 | 50.0499 |
| 2 | 18.966 |  | 2.2232 | 4148.55811 | 31.10066 | 49.9501 |
| Total | s : |  |  | 8305.39844 | 101.80526 |  |

Data File E:\DATA\ZZP\ZZP-6-50\ZZP-6-50 2019-06-06 20-05-23\ZZP-6-501.D Sample Name: ZZP-6-50-1


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} * \mathrm{~s}]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 7.761 |  | 0.7743 | 89.62027 | 1.92902 | 2.6923 |
| 2 | 17.781 |  | 1.4826 | 3239.20337 | 26.98168 | 97.3077 |
| Total | $s$ : |  |  | 3328.82364 | 28.91070 |  |



Data File E:\DATA \ZZP\ZZP-6-42\ZZP-6-42-23 2019-05-27 20-36-24\ZZP-6-425.D
Sample Name: ZZP-6-41-2


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 13.721 |  | 0.5697 | 3910.41187 | 102.36488 | 49.1542 |
| 2 | 15.213 | VB | 0.6545 | 4044.98584 | 91.36078 | 50.8458 |
| Total | $s$ : |  |  | 7955.39771 | 193.72566 |  |

Data File E:\DATA \ZZP\ZZP-6-42\ZZP-6-42-23 2019-05-27 20-36-24\ZZP-6-424.D
Sample Name: ZZP-6-42-2


Additional Info : Peak(s) manually integrated



| Sorted By | $:$ | Signal |
| :--- | :--- | :--- |
| Multiplier | $:$ | 1.0000 |
| Dilution | $:$ | 1.0000 |

Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | Area $[\mathrm{mAU} * \mathrm{~s}]$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 13.223 | MF | 0.7540 | 4643.86768 | 102.64550 | 97.8793 |
| 2 | 14.678 | FM | 0.5768 | 100.61829 | 2.90725 | 2.1207 |
| Total | $s$ : |  |  | 4744.48597 | 105.55275 |  |


(2)


Data File E:\DATA\ZZP\ZZP-6-47\ZZP-5-47 2019-06-04 16-47-05\ZZP-5-472.D
Sample Name: ZZP-6-47-2

| Acq. Operator | : SYSTEM | Seq. Line : 3 |
| :---: | :---: | :---: |
| Acq. Instrument | : 1260 | Location : 54 |
| Injection Date | : 6/4/2019 5:25:15 PM | Inj : 1 |
|  |  | Inj Volume : $2.000 \mu \mathrm{l}$ |
| Acq. Method | : E: \DATA \ZZP\ZZP-5-47\ZZP-5-47 | 2019-06-04 16-47-05\AS, 90-10, 2UL, 1ML, 20MIN.M |
| Last changed | : 6/4/2019 5:21:19 PM by SYSTEM |  |
| Analysis Method | : E:\DATA\ZZP\ZZP-6-47\ZZP-5-47 (Sequence Method) | 2019-06-04 16-47-05\AS, 90-10, 2UL , 1ML, 20MIN.M |
| Last changed | : 9/24/2019 6:08:53 PM by SYSTEM |  |



Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}^{*} \mathrm{~s}\right]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 8.120 | BB | 0.7629 | 3462.03076 | 67.22150 | 49.4527 |
| 2 | 14.245 |  | 1.3475 | 3538.65649 | 38.10336 | 50.5473 |
| Total | s : |  |  | 7000.68726 | 105.32486 |  |

Data File E:\DATA \ZZP\ZZP-6-50\ZZP-6-50 2019-06-06 20-05-23\ZZP-6-502.D
Sample Name: ZZP-6-50-2


Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}{ }^{*} \mathrm{~s}\right]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 7.865 | MM | 0.7603 | 97.89665 | 2.14592 | 2.8456 |
| 2 | 13.537 | BB | 1.2137 | 3342.38647 | 40.21384 | 97.1544 |
| Total | $s$ : |  |  | 3440.28313 | 42.35976 |  |



Sample Name: ZZP-6-60-2


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} * \mathrm{~s}]} \end{gathered}$ | Height <br> [mAU] | $\begin{gathered} \text { Area } \\ \text { \% } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 10.178 | BB | 1.1312 | 2910.35864 | 37.42667 | 51.2927 |
| 2 | 21.766 | BB | 1.8478 | 2763.66260 | 17.56326 | 48.7073 |
| Totals : |  |  |  | 5674.02124 | 54.98993 |  |


Sample Name: ZZP-6-62

| Acq. Operator | SYSTEM Seq. Line : |  |
| :---: | :---: | :---: |
| Acq. Instrument | 1260 Location : | 82 |
| Injection Date | 6/22/2019 3:48:32 PM Inj : | 1 |
|  | Inj Volume : | $2.000 \mu \mathrm{l}$ |
| Acq. Method | : E:\DATA \ZZP \ZZP-6-62\ZZP-6-62-2 2019-06-22 M | $15-47-15 \backslash \mathrm{AS}, 90-10,2 \mathrm{UL}, 1 \mathrm{ML}, 20 \mathrm{MIN} .$ |
| Last changed | : 6/22/2019 3:47:37 PM by SYSTEM (modified after loading) |  |
| Analysis Method | : E:\DATA \ZZP \ZZP-6-62\ZZP-6-62-2 2019-06-22 M (Sequence Method) | $15-47-15 \backslash \mathrm{AS}, 90-10,2 \mathrm{UL}, 1 \mathrm{ML}, 20 \mathrm{MIN} .$ |
| Last changed | : 9/10/2019 9:16:52 PM by SYSTEM (modified after loading) |  |

Additional Info : Peak(s) manually integrated

$\begin{aligned} &======================================================================= \\ & \text { Area Percent Report }\end{aligned}$

| Sorted By | $:$ | Signal |
| :--- | :--- | :--- |
| Multiplier | $:$ | 1.0000 |
| Dilution | $:$ | 1.0000 |

Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} \mathrm{~s}]} \end{gathered}$ | Height <br> [mAU] | $\begin{gathered} \text { Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 10.003 | MP | 1.0187 | 90.11457 | 1.47428 | 1.3047 |
| 2 | 21.106 | BB | 2.0351 | 6816.76123 | 45.20910 | 98.6953 |
| Total | $s$ : |  |  | 6906.87580 | 46.68338 |  |



Data File E:\DATA \ZZP\ZZP-6-45\ZZP-6-45-13 2019-05-31 15-48-34\ZZP-6-458.D
Sample Name: ZZP-6-45-2


Additional Info : Peak(s) manually integrated



| Sorted By | $:$ | Signal |
| :--- | :--- | :--- |
| Multiplier | $:$ | 1.0000 |
| Dilution | $:$ | 1.0000 |

Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 D, Sig=230,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width [min] | Area $[\mathrm{mAU} * \mathrm{~s}]$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 11.293 | BB | 0.3389 | 2437.98535 | 110.72532 | 49.9757 |
| 2 | 19.346 | BB | 0.8447 | 2440.35522 | 44.71667 | 50.0243 |
| Total | $s$ : |  |  | 4878.34058 | 155.44199 |  |

Data File E:\DATA \ZZP \ZZP-6-46\ZZP-6-46-13 2019-06-03 10-49-44\ZZP-6-46-131.D
Sample Name: ZZP-6-46-1


Additional Info : Peak(s) manually integrated


| =================================== |  |  |
| :--- | :--- | :--- |
|  | Area Percent |  |
| ====================================== |  |  |
|  | $:$ | Signal |
| Sorted By | $:$ | 1.0000 |
| Multiplier | $:$ | 1.0000 |

Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 D, Sig=230,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} \mathrm{~s}]} \end{gathered}$ | Height [mAU] | $\begin{gathered} \text { Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 11.247 | BB | 0.3501 | 4394.93213 | 191.25177 | 93.1911 |
| 2 | 19.414 | BB | 0.7463 | 321.11188 | 6.28257 | 6.8089 |
| Total | $s$ : |  |  | 4716.04401 | 197.53434 |  |

$\stackrel{\stackrel{7}{7} \mathrm{~F}}{5}$


Data File E:\DATA \ZZP\ZZP-6-45\ZZP-6-45-13 2019-05-31 15-48-34\ZZP-6-451.D
Sample Name: ZZP-6-45-1


Additional Info : Peak(s) manually integrated



| Sorted By | $:$ | Signal |
| :--- | :---: | :---: |
| Multiplier | $:$ | 1.0000 |
| Dilution | $:$ | 1.0000 |

Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210,4 Ref=off

| Peak \# | RetTime [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} \mathrm{~s}]} \end{gathered}$ | Height [mAU] | $\begin{gathered} \text { Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 8.277 | BV | 0.3750 | 2930.12817 | 117.45807 | 50.8356 |
| 2 | 9.651 | VB | 0.4223 | 2833.80078 | 100.10265 | 49.1644 |
| Totals |  |  |  | 5763.92896 | 217.56072 |  |

Data File E:\DATA \ZZP\ZZP-6-53\ZZP-6-53 2019-06-12 19-00-55\ZZP-6-531.D
Sample Name: ZZP-6-53-2


Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ {[\mathrm{min}]} \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} \text { s }]} \end{gathered}$ | Height [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 7.991 | MF | 0.4139 | 9723.21973 | 391.51294 | 96.4628 |
| 2 | 9.274 | FM | 0.4375 | 356.54272 | 13.58161 | 3.5372 |



Data File E:\DATA \ZZP\ZZP-9-2\ZZP-9-2-GH 2019-11-19 19-12-35\ZZP-9-2-GH2.D
Sample Name: ZZP-9-2-RAC


Additional Info : Peak(s) manually integrated
DAD1 B, Sig=254,4 Ref=off (E:IDATAIZZPIZZP-9-2IZZP-9-2-GH 2019-11-19 19-12-35IZZP-9-2-GH2.D)

=============================================================================2
Area Percent Report

| Sorted By | $:$ | Signal |
| :--- | :---: | :--- |
| Multiplier | $:$ | 1.0000 |
| Dilution | $:$ | 1.0000 |
| Use Multiplier \& Dilution | Factor with | ISTDs |

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}^{*} \mathrm{~s}\right]} \end{gathered}$ | Height [mAU] | $\begin{gathered} \text { Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 5.470 | BV E | 0.0880 | 279.41269 | 47.92768 | 4.7455 |
| 2 | 5.631 | VB R | 0.1308 | 2650.54663 | 300.73383 | 45.0162 |
| 3 | 6.082 | BV R | 0.1416 | 2486.04419 | 269.43274 | 42.2223 |
| 4 | 6.518 | VB E | 0.1500 | 471.98459 | 48.30260 | 8.0161 |
| Total |  |  |  | 5887.98810 | 666.39684 |  |

Data File E:\DATA \ZZP\ZZP-9-2\ZZP-9-2-GH 2019-11-19 19-12-35\ZZP-9-2-GH1.D
Sample Name: ZZP-9-2-GH

| Acq. Operator | : SYSTEM | Seq. Line : | 2 |
| :---: | :---: | :---: | :---: |
| Acq. Instrument | : 1260 | Location | 56 |
| Injection Date | : 11/19/2019 7:24:46 PM | Inj | 2 |

Acq. Method : E:\DATA \ZZP \ZZP-9-2\ZZP-9-2-GH 2019-11-19 19-12-35
Last changed : 11/19/2019 7:12:35 PM by SYSTEM
Analysis Method : E:\DATA \ZZP\ZZP-9-2\ZZP-9-2-GH 2019-11-19 19-12-35\AS,90-10, 2UL,1ML,10MIN.M
(Sequence Method)
Last changed : 11/29/2019 9:34:42 AM by SYSTEM (modified after loading)
Additional Info : Peak(s) manually integrated
Additional Info : Peak(s) manually integrated
$==================================================================$
Area Percent Report
===============================================================================1

| Sorted By | $:$ | Signal |
| :--- | :---: | :---: |
| Multiplier | $:$ | 1.0000 |
| Dilution | $:$ | 1.0000 |
| Use Multiplier \& Dilution | Factor with | ISTDs |

Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}^{*} \mathrm{~s}\right]} \end{gathered}$ | Height [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 5.637 | BV | 0.1318 | 349.46179 | 40.05820 | 6.5368 |
| 2 | 6.084 |  | 0.1451 | 4996.57764 | 524.82355 | 93.4632 |
| Totals |  |  |  | 5346.03943 | 564.88175 |  |



Data File E:\DATA \ZZP \ZZP-8-3\ZZP-8-3-RAC-2 2019-09-04 17-10-56\ZZP-8-3-RAC3.D
Sample Name: zzp-8-3-rac

| Acq. Operator | : SYSTEM Seq. Line : 4 |
| :---: | :---: |
| Acq. Instrument | 1260 Location : 63 |
| Injection Date | : 9/4/2019 7:07:38 PM Inj : 1 |
|  | Inj Volume : $2.000 \mu \mathrm{l}$ |
| Acq. Method | : E:\DATA \ZZP\ZZP-8-3\ZZP-8-3-RAC-2 2019-09-04 17-10-56\ID,95-5,2UL,1ML, 20MIN .M |
| Last changed | 9/4/2019 7:08:05 PM by SYSTEM (modified after loading) |
| Analysis Method | : E:\DATA \ZZP\ZZP-8-3\ZZP-8-3-RAC-2 2019-09-04 17-10-56\ID, 95-5, 2UL, 1ML, 20MIN .M (Sequence Method) |
| Last changed | 9/10/2019 9:19:35 PM by SYSTEM (modified after loading) |

Additional Info : Peak(s) manually integrated
DAD1 B, Sig=254,4 Ref=off (E:IDATAIZZPIZZP-8-3IZZP-8-3-RAC-2019-09-0417-10-561ZZP-8-3-RAC3.D)


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width [min] | Area $\left[\mathrm{mAU}{ }^{*} \mathrm{~s}\right]$ | Height [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 46.017 | BB | 1.4743 | 1.04994 e 4 | 109.14314 | 49.9799 |
| 2 | 51.196 | BB | 1.6180 | 1.05079 e 4 | 94.88618 | 50.0201 |
| Total | $s$ : |  |  | 2.10073 e 4 | 204.02931 |  |

Data File E:\DATA
Sample Name: ZZP-8-3-GH


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} * \mathrm{~s}]} \end{gathered}$ | Height <br> [mAU] | $\begin{gathered} \text { Area } \\ \text { \% } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 47.027 | PM | 1.5874 | 4526.65625 | 47.52705 | 97.3833 |
| 2 | 52.644 | PM | 1.4867 | 121.63187 | 1.36354 | 2.6167 |
| Totals : |  |  |  | 4648.28812 | 48.89059 |  |



Data File E:\DATA \ZZP\ZZP-7-67\ZZP-7-67 2019-08-30 16-54-15\ZZP-7-671.D
Sample Name: ZZP-7-67


Use Multiplier \& Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=220,4 Ref=off

| Peak \# | RetTime [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} \mathrm{~s}]} \end{gathered}$ | Height [mAU] | $\begin{gathered} \text { Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 11.674 | PM | 0.4507 | 3036.45679 | 112.29697 | 48.5146 |
| 2 | 14.736 | BB | 0.5018 | 3222.39502 | 94.03548 | 51.4854 |
| Total | $s$ : |  |  | 6258.85181 | 206.33246 |  |

Data File E:\DATA \ZZP\ZZP-8-1\ZZP-8-1 2019-09-02 10-47-59\ZZP-8-11.D
Sample Name: ZZP-8-1


Signal 1: DAD1 A, Sig=220,4 Ref=off

| Peak \# | RetTime [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} * \mathrm{~s}]} \end{gathered}$ | Height <br> [mAU] | $\begin{gathered} \text { Area } \\ \text { \% } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 11.817 | MM | 0.5005 | 7022.30371 | 233.82272 | 99.5634 |
| 2 | 15.033 | MM | 0.3799 | 30.79710 | 1.35119 | 0.4366 |
| Totals : |  |  | 7053.10081 |  | 235.17392 |  |





Data File E:\DATA \ZZP \ZZP-8-16\ZZP-8-16-2 2019-09-22 16-15-31\ZZP-8-16-23.D
Sample Name: ZZP-8-16-2

| Acq. Operator | : SYSTEM Seq. Line : | 4 |
| :---: | :---: | :---: |
| Acq. Instrument | : 1260 Location | 4 |
| Injection Date | : 9/22/2019 4:41:28 PM Inj : | 1 |
|  | Inj Volume : | $2.000 \mu \mathrm{l}$ |
| Acq. Method | $\begin{aligned} & : ~ E: \backslash D A T A \backslash Z Z P \backslash Z Z P-8-16 \backslash Z Z P-8-16-2 \text { 2019-09-22 } \\ & \mathrm{M} \end{aligned}$ | 16-15-31\AS, 90-10, 2UL , 1ML, 20MIN. |
| Last changed | : 9/22/2019 5:02:24 PM by SYSTEM (modified after loading) |  |
| Analysis Method | : E:\DATA \ZZZP $\backslash Z Z P-8-16 \backslash Z Z P-8-16-2$ 2019-09-22 M (Sequence Method) | 16-15-31\AS, 90-10, 2UL , 1ML, 20MIN. |

Last changed : 9/22/2019 5:06:31 PM by SYSTEM


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 8.278 | BB | 0.8700 | 3980.96582 | 66.54219 | 49.7888 |
| 2 | 17.154 | BB | 1.4025 | 4014.73340 | 34.94067 | 50.2112 |
| Total | s : |  |  | 7995.69922 | 101.48286 |  |

Data File E:\DATA $\backslash Z Z P \backslash Z Z P-8-16 \backslash Z Z P-8-16-2$ 2019-09-22 16-15-31
Sample Name: ZZP-8-16-3


Signal 1: DAD1 B, Sig=254,4 Ref=off

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}^{*} \mathrm{~s}\right]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 8.324 | BB | 0.6487 | 222.15175 | 4.13547 | 3.0037 |
| 2 | 17.145 |  | 1.5344 | 7173.88672 | 62.25256 | 96.9963 |
| Total | s : |  |  | 7396.03847 | 66.38803 |  |


[^0]:    $\mathrm{N}-((2 R, 3 S, E)$-1-hydroxy-2,3-dimethyl-5-phenylpent-4-en-2-yl)benzamide (5):
    

    5

