N-Heterocyclic Carbene-Catalyzed Cyclocondensation of 2-Aryl Carboxylic Acids and Enones: Highly Enantioselective Synthesis of δ-Lactones

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Part I General Information

Unless otherwise indicated, all reactions were carried out under N₂ at -10 °C with magnetic stirring. Anhydrous THF and toluene were distilled from sodium and benzophenone. Anhydrous CH₂Cl₂ was distilled from CaH₂. Chiral triazolium salts A₁, A₂, B₁, B₂, enones were synthesized according to literatures. Column chromatography was performed on silica gel 200–300 mesh. All ¹H NMR, ¹³C NMR spectra were recorded on a Bruker-DMX 300 spectrometer or Bruker-DMX 400 spectrometer in CDCl₃, with tetramethylsilane as an internal standard and reported in parts per million (ppm, δ). ¹H NMR Spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br). Infrared spectra were recorded on a JASCO FT/IR-480 spectrophotometer and reported as wave number (cm⁻¹). Optical rotations were measured on Perkin Elmer/Model-343 digital polarimeter operating at the sodium D line with a 100 mm path cell, and are reported as follows: [α]D (concentration (g/100 mL), solvent).
Part II Experimental part

1. NHC-catalyzed [4+2] cyclocondensation of 2-aryl carboxylic acids and enones (Table 2)

To a solution of 2-arylacetic acids 1 (0.44 mmol, 2.2 equiv) in CH$_2$Cl$_2$ (2.0 ml) was added DIPEA (0.6 mmol, 77.4 mg, 3.0 equiv.) and pivaloyl chloride (0.44 mmol, 53 mg, 2.2 equiv.) at -10 ℃. After stirring at -10 ℃ for 30 minutes, to the reaction mixture was added NHC precursor A$_2$ (0.04 mmol, 17 mg, 0.2 equiv.), enones 2 (0.2 mmol) and another 2.0 equivalent of DIPEA (0.4 mmol, 51.6 mg). The reaction mixture was stirred at -10 ℃ until the full consumption of the enone (typically, 24-48 h). The reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent, typically 10:1-5:1) to furnish the corresponding cycloadduct 3.

Racemic samples for the chiral phase HPLC analysis were prepared using NHC precursor C under the same conditions but at room temperature with longer reaction time (typically 2-3 d). It should be noted that sometimes the trans-isomers of cycloadduct 3 were isolated as majority (cis/trans = 20:1 to 1:8) for the reaction possibly due to the epimerization of cis-3 to trans-3 at room temperature with longer reaction time.
(3S,4R)-ethyl 3-(2-methoxyphenyl)-2-oxo-6-phenyl-3,4-dihydro-2H-pyran-4-carboxylate

54.3 mg, 77% yield, cis/trans = 10:1, white solid, Rf = 0.4 (petroleum ether/ethyl acetate 5:1); [α]D 25 -148.4 (c 0.2, CH2Cl2), HPLC analysis: >99% ee (cis), 79% ee (trans) [Daicel CHIRALPACK OD-3 column, 20 °C, 254 nm hexane/i-PrOH = 90:10, 1.0 mL/min, 254 nm, 13.4 min (trans-minor), 16.2 min (trans-major), 18.0 min(cis-major), 19.9 min (cis-minor)]; 1H NMR (300 MHz, CDCl3) δ 7.72-7.68 (m, 2H), 7.57 (dd, J = 7.7, 1.3 Hz, 1H), 7.44 – 7.39 (m, 3H), 7.32 – 7.29 (m, 1H), 7.00 – 6.88 (m, 2H), 5.99 (d, J = 6.8 Hz, 1H), 4.69 (d, J = 6.2 Hz, 1H), 4.06 (q, J = 7.2 Hz, 2H), 3.84 (s, 3H), 3.67 (t, J = 6.5 Hz, 1H), 1.15 (t, J = 7.2 Hz, 3H). 13C NMR (75 MHz, CDCl3) δ 170.6, 167.6, 156.9, 152.6, 132.1, 130.2, 129.6, 129.2, 128.6, 125.0, 122.3, 120.7, 110.4, 99.0, 61.5, 55.6, 44.0, 39.3, 14.0. IR (KBr) 2919, 2849, 1775, 1732, 1646, 1600, 1495, 1180, 754; HRMS (ESI) calcd for C21H20O5Na [M+Na]+ 375.1203, found 375.1197.
(3S,4R)-ethyl 6-(4-fluorophenyl)-3-(2-methoxyphenyl)-2-oxo-3,4-dihydro-2H-pyran-4-carboxylate

49.9 mg, 67% yield; cis/trans = 10:1, colorless oil, R_f = 0.4 (petroleum ether/ethyl acetate 5:1); [α]_D^{25} -148.7 (c 0.2, CH₂Cl₂), HPLC analysis: 99% ee (cis), 62% ee (trans) [Daicel CHIRALPAK IA column, 20 °C, 254 nm, hexane/i-PrOH/MeOH = 80:10:10, 1.0 mL/min, 254 nm, 9.5 min (trans-major), 10.9 min (trans-minor), 12.0 min (cis-major)]; _1^H NMR (300 MHz, CDCl₃) δ 7.71-7.66 (m, 2H), 7.56 (dd, J = 7.7, 1.5 Hz, 1H), 7.32-7.26 (m, 1H), 7.11-7.06 (m, 2H), 6.99-6.88 (m, 2H), 5.92 (d, J = 6.8 Hz, 1H), 4.68 (d, J = 6.2 Hz, 1H), 4.06 (q, J = 7.1 Hz, 2H), 3.84 (s, 3H), 3.66 (t, J = 6.5 Hz, 1H), 1.14 (t, J = 7.1 Hz, 3H). _1^3C NMR (75 MHz, CDCl₃) δ 170.5, 166.8, 156.9, 151.2, 130.1, 129.2, 127.0, 126.9, 122.1, 120.6, 115.7, 115.4, 110.3, 98.6, 61.4, 55.5, 43.9, 39.2, 13.9. IR (KBr) 2921, 2848, 1733, 1633, 1509, 1246, 1180; HRMS (ESI) calcd for C₂₁H₁₉O₅FNa [M+Na]^+ 393.1109, found 393.1104.

(3S,4R)-ethyl 6-(4-chlorophenyl)-3-(2-methoxyphenyl)-2-oxo-3,4-dihydro-2H-pyran-4-carboxylate

3ab

3ac
46.8 mg, 61% yield; cis/trans = 10:1, colorless oil, Rf = 0.3 (petroleum ether/ethyl acetate 5:1); [α]D<sup>25</sup> = -184.1 (c 0.2, CH<sub>2</sub>Cl<sub>2</sub>), HPLC analysis: 99% ee (cis), 71% ee (trans) [Daicel CHIRALPAK IA-H column, 20 °C, 254 nm, hexane/i-PrOH/MeOH = 80:10:10, 1.0 mL /min, 254 nm, 9.9 min (trans-major), 11.0 min (trans-minor), 13.6 min (cis-major), 32.6 min (cis-minor)]; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.65-7.60 (m, 2H), 7.55 (dd, J = 7.7, 1.2 Hz, 1H), 7.39 – 7.36 (m, 2H), 7.32 – 7.27 (m, 1H), 6.99 – 6.88 (m, 2H), 5.97 (d, J = 6.8 Hz, 1H), 4.68 (d, J = 6.1 Hz, 1H), 4.06 (q, J = 7.1 Hz, 2H), 3.84 (s, 3H), 3.67 (t, J = 6.5 Hz, 1H), 1.15 (t, J = 7.2 Hz, 3H).<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 170.2, 166.8, 156.5, 151.2, 135.3, 130.5, 130.0, 129.2, 128.8, 126.2, 122.0, 120.6, 110.2, 99.3, 61.6, 55.5, 43.9, 39.1, 13.9. IR (KBr) 2922, 2850, 1779, 1732, 1647, 1602, 1494, 1180, 754; HRMS (ESI) calcd for C<sub>21</sub>H<sub>19</sub>O<sub>5</sub>ClNa [M+Na]<sup>+</sup> 409.0813, found 409.0807.

(3S,4R)-ethyl 6-(4-bromophenyl)-3-(2-methoxyphenyl)-2-oxo-3,4-dihydro-2H-pyran-4-carboxylate

47.7 mg, 55% yield; cis/trans = 7:1, colorless oil, Rf = 0.4 (petroleum ether/ethyl acetate 5:1); [α]D<sup>25</sup> = -17.4 (c 0.5, CH<sub>2</sub>Cl<sub>2</sub>), HPLC analysis: >99% ee (cis), 75% ee (trans) [Daicel CHIRALPAK IA column, 20 °C, 254 nm, hexane/i-PrOH/MeOH = 80:10:10, 1.0 mL /min, 254 nm, 10.8 min (trans-major), 11.8 min (trans-minor), 15.2
min (cis-major)]. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.59-7.51 (m, 5H), 7.32 – 7.26 (m, 1H), 6.99 – 6.88 (m, 2H), 5.99 (d, $J$ = 6.8 Hz, 1H), 4.68 (d, $J$ = 6.2 Hz, 1H), 4.06 (q, $J$ = 7.1 Hz, 2H), 3.84 (s, 3H), 3.66 (t, $J$ = 6.5 Hz, 1H), 1.14 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.2, 166.8, 156.9, 151.6, 131.7, 131.1, 130.1, 129.2, 126.4, 123.6, 121.9, 120.6, 110.3, 99.3, 61.5, 55.5, 43.9, 39.2, 13.8. IR (KBr) 2928, 1776, 1732, 1646, 1489, 1248, 1176, 754; HRMS (ESI) calcd for C$_{21}$H$_{19}$O$_5$BrNa $[M+Na]^+$ 453.0308, found 453.0300.

![Chemical structure](image)

(35,4R)-ethyl 3-(2-methoxyphenyl)-2-oxo-6-(p-tolyl)-3,4-dihydro-2H-pyran-4-carboxylate

40.5 mg, 55% yield; cis/trans = 6:1, colorless oil, $R_t = 0.4$ (petroleum ether/ethyl acetate 5:1); $[\alpha]_D^{25} -8.0$ (c 0.1, CH$_2$Cl$_2$), HPLC analysis: >99% ee (cis), 78% ee (trans) [Daicel CHIRALPAK IA column, 20 °C, 254 nm, hexane/i-PrOH /MeOH = 90:5:5, 1.0 mL /min, 254 nm, 13.2 min (trans-major), 14.7 min (trans-minor), 19.2 min (cis-major)]. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.60-7.55 (m, 3H), 7.31 – 7.19 (m, 3H), 6.99 – 6.88 (m, 2H), 5.93 (d, $J$ = 6.8 Hz, 1H), 4.68 (d, $J$ = 6.2 Hz, 1H), 4.05 (q, $J$ = 7.1 Hz, 2H), 3.84 (s, 3H), 3.65 (t, $J$ = 6.5 Hz, 1H), 2.38 (s, 3H), 1.15 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.5, 167.2, 156.5, 152.3, 139.3, 129.9, 129.0, 124.6, 122.0, 120.6, 110.4, 98.0, 61.5, 55.5, 43.9, 39.3, 21.3, 14.0. IR (KBr) 2920, 2849, 1733, 1651, 1606, 1495, 1180, 755; HRMS (ESI) calcd for C$_{22}$H$_{22}$O$_5$Na

(3S,4R)-ethyl 3-(2-methoxyphenyl)-6-(4-methoxyphenyl)-2-oxo-3,4-dihydro-2H-pyran-4-carboxylate

61.1 mg, 80% yield; cis/trans = 10:1, colorless oil, $R_f = 0.2$ (petroleum ether/ethyl acetate 5:1); $[\alpha]_D^{25} -1.2$ (c 0.3, CH$_2$Cl$_2$), HPLC analysis: >99% ee (cis), 30% ee (trans)
[Daicel CHIRALPAK IA column, 20 °C, 254 nm, hexane/ i-PrOH/MeOH = 80:10:10, 1.0 mL /min, 254 nm, 13.0 min (trans-major), 15.0 min (trans-minor), 17.4 min (cis-major)]; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.65-7.62 (m, 2H), 7.57 (dd, $J = 7.7$, 1.2 Hz, 1H), 7.31 – 7.26 (m, 1H), 6.99 – 6.87 (m, 4H), 5.85 (d, $J = 6.8$ Hz, 1H), 4.67 (d, $J = 6.1$ Hz, 1H), 4.05 (q, $J = 7.1$ Hz, 2H), 3.84 (s, 6H), 3.64 (t, $J = 6.5$ Hz, 1H), 1.15 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.5, 167.2, 160.5, 156.5, 152.2, 129.9, 128.6, 126.3, 124.3, 122.3, 120.3, 113.7, 110.1, 96.7, 61.2, 55.5, 55.2, 43.6, 38.9, 13.6. IR (KBr) 2924, 2850, 1733, 1601, 1495, 1260, 1172, 757; HRMS (ESI) calcd for C$_{22}$H$_{22}$O$_6$Na [M+Na]$^+$ 405.1309, found 405.1304.

(3S,4R)-ethyl 6-(2-chlorophenyl)-3-(2-methoxyphenyl)-2-oxo-3,4-dihydro-2H-py
ran-4-carboxylate

48.9 mg, 63% yield; cis/trans = 6:1, colorless oil, Rf = 0.4 (petroleum ether/ethyl acetate 5:1); [α]D25 -65.4 (c 0.5, CH2Cl2), HPLC analysis: 98% ee (cis), 72% ee (trans) [Daicel CHIRALPAK IA column, 20 °C, 254 nm, hexane/ i-PrOH /MeOH = 90:5:5, 1.0 mL /min, 254 nm, 12.3 min (trans-major), 14.2 min (cis-major), 15.8 min (trans-minor), 18.0 min (cis-minor)]; 1H NMR (300 MHz, CDCl3) δ 7.60-7.53 (m, 2H), 7.45-7.42 (m, 1H), 7.35 – 7.26 (m, 3H), 7.00 – 6.89 (m, 2H), 5.88 (d, J = 6.7 Hz, 1H), 4.73 (d, J = 6.2 Hz, 1H), 4.09 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 3.68 (t, J = 6.5 Hz, 1H), 1.18 (t, J = 7.1 Hz, 3H). 13C NMR (75 MHz, CDCl3) 170.2, 167.2, 156.9, 150.5, 132.6, 131.9, 130.5, 130.4, 130.3, 130.1, 129.1, 126.8, 122.1, 120.6, 110.2, 104.9, 61.2, 55.2, 43.9, 38.9, 13.6. IR (KBr) 2923, 2849, 1732, 1673, 1600, 1495, 1260, 1173, 755; HRMS (ESI) calcd for C21H19O5ClNa [M+Na]+ 409.0813, found 409.0807.

(3S,4R)-ethyl 3-(2-methoxyphenyl)-6-(naphthalen-2-yl)-2-oxo-3,4-dihydro-2H-pyran-4-carboxylate

26.1 mg, 33% yield; cis/trans = 3:1, white solid, Rf = 0.4 (petroleum ether/ethyl acetate 5:1); [α]D25 -170.9 (c 0.1, CH2Cl2), HPLC analysis: >99% ee (cis), 88% ee (trans) [Daicel CHIRALPAK IA-H column, 20 °C, 254 nm, hexane/i-PrOH = 80:20, 1.0 mL /min, 254 nm, 11.3 min (trans-major), 14.0 min (trans-minor), 17.9 min.
(cis-major)]; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.21-8.18 (m, 1H), 7.84-7.77 (m, 4H), 7.65-7.62 (m, 1H), 7.53 (d, $J = 7.8$ Hz, 1H), 7.46-7.43 (m, 2H), 7.25-7.19 (m, 1H), 6.93-6.83 (m, 2H), 6.07 (d, $J = 6.8$ Hz, 1H), 4.67 (d, $J = 6.2$ Hz, 1H), 4.08 (q, $J = 7.1$ Hz, 2H), 3.85 (s, 3H), 3.73 (t, $J = 6.4$ Hz, 1H), 1.17 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.2, 167.2, 156.5, 152.3, 133.6, 133.1, 130.1, 129.2, 129.0, 128.8, 128.3, 127.6, 126.9, 126.7, 124.7, 122.0, 120.6, 109.6, 99.4, 61.1, 55.2, 43.9, 38.9, 13.6. IR (KBr) 2920, 2849, 1732, 1722, 1180, 1129, 753; HRMS (ESI) calcd for C$_{25}$H$_{22}$O$_5$Na [M+Na]$^+$ 425.1359, found 425.1354.

![3ba](image)

(3S,4R)-ethyl 2-oxo-3,6-diphenyl-3,4-dihydro-2H-pyran-4-carboxylate

56.6 mg, 88% yield; cis/trans = 1:1, white solid, $R_f = 0.4$ (petroleum ether/ethyl acetate 5:1); $[\alpha]_D^{25} -106.7$ (c 0.1, CH$_2$Cl$_2$). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.65-7.62 (m, 2H), 7.37-7.33 (m, 3H), 7.30-7.22 (m, 5H), 6.02 (d, $J = 5.3$ Hz, 1H), 4.17 (d, $J = 6.3$ Hz, 1H), 4.02 (q, $J = 7.1$ Hz, 2H), 3.77-3.74 (m, 1H), 1.07 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 171.0, 167.6, 151.5, 135.6, 131.8, 129.8, 129.1, 128.8, 128.7, 128.2, 125.0, 97.5, 62.0, 46.9, 45.4, 14.1. IR (KBr) 2920, 2849, 1774, 1732, 1181, 1130, 754; HRMS (ESI) calcd for C$_{20}$H$_{18}$O$_4$Na [M+Na]$^+$ 345.1079, found 345.1093.
(3S,4R)-ethyl 2-oxo-6-phenyl-3-(p-tolyl)-3,4-dihydro-2H-pyran-4-carboxylate

48.6 mg, 72% yield; cis/trans = 6:1, white solid, Rf = 0.3 (petroleum ether/ethyl acetate 5:1); [α]D25 -145.9 (c 0.1, CH2Cl2), HPLC analysis: 98% ee (cis), 48% ee (trans) [Daicel CHIRALPAK OD-H column, 20 °C, 254 nm, hexane/i-PrOH = 90:10, 1.0 mL /min, 254 nm, 17.3 min (cis-minor), 18.6 min (trans-major), 22.1 min (cis-major), 24.3 min (trans-minor)]; 1H NMR (300 MHz, CDCl3) δ 7.64-7.59 (m, 2H), 7.35-7.31 (m, 3H), 7.18-7.14 (m, 2H), 7.06 (t, J = 7.3 Hz, 2H), 6.00 (d, J = 5.3 Hz, 1H), 4.12 (d, J = 6.3 Hz, 1H), 4.02 (q, J = 7.1 Hz, 2H), 3.73 (t, J = 5.8 Hz, 1H), 2.24 (s, 3H), 1.08 (t, J = 7.1 Hz, 3H). 13C NMR (75 MHz, CDCl3) δ 169.9, 167.3, 151.9, 138.0, 131.8, 130.9, 129.6, 129.5 129.4, 128.8, 128.6, 127.9, 124.9, 98.5, 61.4, 46.3, 44.3, 21.0, 13.8. IR (KBr) 2919, 2849, 1769, 1732, 1719, 1632, 1180, 1131, 755; HRMS (ESI) calcd for C21H20O4Na [M+Na]+ 359.1254, found 359.1249.

(3S,4R)-ethyl 3-(4-methoxyphenyl)-2-oxo-6-phenyl-3,4-dihydro-2H-pyran-4-carboxylate
45.5 mg, 58% yield; cis/trans = 3:1, white solid, Rf = 0.4 (petroleum ether/ethyl acetate 5:1); [α]D25 -161.0 (c 0.1, CH2Cl2), HPLC analysis: >99% ee (cis), 48% ee (trans) [Daicel CHIRALPAK IA-H column, 20 °C, 254 nm, hexane/i-PrOH = 80:20, 1.0 mL /min, 254 nm, 14.5 min (trans-major), 18.8 min (trans-minor), 20.8 min (cis-major)]; 1H NMR (400 MHz, CDCl3) δ 7.64-7.58 (m, 2H), 7.36-7.33 (m, 4H), 7.21-7.19 (m, 1H), 6.81-6.77 (m, 2H), 6.00 (d, J = 5.3 Hz, 1H), 4.12 (d, J = 6.3 Hz, 1H), 4.02 (q, J = 7.2 Hz, 2H), 3.74-3.71 (m, 4H), 1.09 (t, J = 7.2 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 170.0, 167.0, 159.4, 151.7, 131.8, 130.1, 129.6, 129.3, 128.6, 125.9, 124.9, 114.4, 114.1, 98.4, 61.4, 54.7, 46.1, 44.4, 13.8. IR (KBr) 2918, 2849, 1732, 1646, 1180, 1132; HRMS (ESI) calcd for C21H20O5Na [M+Na]⁺ 375.1203, found 375.1198.

(3S,4R)-ethyl 3-(2,4-dimethoxyphenyl)-2-oxo-6-phenyl-3,4-dihydro-2H-pyran-4-carboxylate

41.3 mg, 54% yield; cis/trans = 6:1, colorless oil, Rf = 0.3 (petroleum ether/ethyl acetate 5:1); [α]D25 -177.0 (c 0.1, CH2Cl2), HPLC analysis: >99% ee (cis), 80% ee (trans) [Daicel CHIRALPAK AD-H column, 20 °C, 254 nm, hexane/i-PrOH = 60:40, 1.0 mL /min, 254 nm, 10.9 min (trans-major), 12.6 min (trans-minor), 18.2 min (cis-major), 41.0 min (cis-minor)]; 1H NMR (300 MHz, CDCl3) δ 7.71-7.66 (m, 2H), 7.48 (d, J = 8.5 Hz, 1H), 7.42 – 7.38 (m, 3H), 6.52 – 6.44 (m, 2H), 5.98 (d, J = 6.7 Hz, 1H), 4.14 (d, J = 6.7 Hz, 1H), 3.74-3.71 (m, 4H), 1.09 (t, J = 7.2 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 170.0, 167.0, 159.4, 151.7, 131.8, 130.1, 129.6, 129.3, 128.6, 125.9, 124.9, 114.4, 114.1, 98.4, 61.4, 54.7, 46.1, 44.4, 13.8. IR (KBr) 2918, 2849, 1732, 1646, 1180, 1132; HRMS (ESI) calcd for C21H20O5Na [M+Na]⁺ 375.1203, found 375.1198.
1H), 4.60 (d, J = 6.2 Hz, 1H), 4.06 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 3.80 (s, 3H), 3.64 (t, J = 6.5 Hz, 1H), 1.17 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 170.5, 167.5, 160.5, 157.5, 152.2, 132.0, 130.7, 129.5, 128.5, 124.9, 114.7, 104.2, 98.9, 98.2, 61.3, 55.5, 55.4, 43.9, 38.6, 13.6. IR (KBr) 2920, 2849, 1772, 1732, 1646, 1209, 752; HRMS (ESI) calcd for C$_{22}$H$_{22}$O$_6$Na [M+Na]$^+$ 405.1309, found 405.1303.

![Structural formula](image)

(3S,4R)-ethyl 3-(2,4-dimethoxyphenyl)-2-oxo-6-(p-tolyl)-3,4-dihydro-2H-pyran-4-carboxylate

52.7 mg, 66% yield; cis/trans = 20:1, colorless oil, R$_f$ = 0.3 (petroleum ether/ethyl acetate 5:1); [$\alpha$]$_D^{25}$ -119.8 (c 0.1, CH$_2$Cl$_2$), HPLC analysis: >99% ee for major cis-diastereoisomer [Daicel CHIRALPAK IA-H column, 20 °C, 254 nm, hexane/i-PrOH/MeOH = 60:20:20, 1.0 mL/min, 254 nm, 11.1 min (cis-major)], $^1$H NMR (300 MHz, CDCl$_3$) δ 7.50 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.5 Hz, 1H), 7.11 (d, J = 8.1 Hz, 2H), 6.43-6.35 (m, 2H), 5.84 (d, J = 6.7 Hz, 1H), 4.51 (d, J = 6.2 Hz, 1H), 3.98 (q, J = 7.2 Hz, 2H), 3.72 (s, 3H), 3.71 (s, 3H), 3.54 (t, J = 6.4 Hz, 1H), 2.29 (s, 3H), 1.08 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 170.8, 167.9, 160.2, 157.9, 152.2, 139.3, 130.7, 129.3, 129.2, 124.8, 114.7, 104.4, 98.3, 98.0, 61.3, 55.5, 55.4, 44.1, 38.9, 21.3, 14.0. IR (KBr) 2923, 2849, 1772, 1732, 1614, 1508, 1464, 1209; HRMS (ESI) calcd for C$_{23}$H$_{24}$O$_6$Na [M+Na]$^+$ 419.1465, found 419.1459.
(3S,4R)-ethyl 3-(2,4-dimethoxyphenyl)-6-(4-methoxyphenyl)-2-oxo-3,4-dihydro-2H-pyran-4-carboxylate

41.0 mg, 50% yield; cis/trans > 20:1, colorless oil, Rf = 0.2 (petroleum ether/ethyl acetate 5:1); [α]D25 -194.0 (c 0.1, CH2Cl2), HPLC analysis: 99% ee for major cis-diastereoisomer [Daicel CHIRALPAK IA column, 20 °C, 254 nm, hexane/i-PrOH/MeOH = 60:20:20, 1.0 mL /min, 254 nm, 12.4 min (cis-major)], 1H NMR (300 MHz, CDCl3) δ 7.63 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.5 Hz, 1H), 6.91 (d, J = 8.8 Hz, 2H), 6.52-6.44 (m, 2H), 5.84 (d, J = 6.7 Hz, 1H), 4.58 (d, J = 6.2 Hz, 1H), 4.06 (q, J = 7.1 Hz, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.63-3.59 (m, 1H), 1.17 (t, J = 7.1 Hz, 3H). 13C NMR (75 MHz, CDCl3) δ170.8, 168.0, 160.6, 160.5, 157.9, 152.3, 130.7, 126.4, 124.7, 114.8, 113.9, 104.4, 98.3, 97.0, 61.3, 55.5, 55.4, 44.0, 38.9, 14.0. IR (KBr) 2921, 2849, 1771, 1732, 1611, 1457, 1178, 1034, 836; HRMS (ESI) calcd for C23H24O7Na [M+Na]+ 435.1414, found 435.1407.

(3S,4R)-methyl 3-(2-methoxyphenyl)-2-oxo-6-phenyl-3,4-dihydro-2H-pyran-4-carboxylate

3ai
44.3 mg, 66% yield, cis/trans = 10:1, white solid, Rf = 0.4 (petroleum ether/ethyl acetate 5:1); [α]D\textsuperscript{25} -269.0 (c 0.1, CH\textsubscript{2}Cl\textsubscript{2}), HPLC analysis: >99% ee (cis), 88% ee (trans) [Daicel CHIRALPAK IA-H column, 20 °C, 254 nm hexane/i-PrOH/MeOH = 80:10:10, 1.0 mL/min, 254 nm, 10.4 min (trans-major), 11.4 min (trans-minor), 12.7 min(cis-major)]; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 0.72-0.69 (m, 2H), 0.53 (d, J = 7.7, 1.3 Hz, 1H), 0.74 - 0.76 (m, 1H), 0.72 (t, J = 7.8 Hz, 1H), 6.08 (t, J = 8.3 Hz, 1H), 5.98 (d, J = 6.8 Hz, 1H), 4.69 (d, J = 6.2 Hz, 1H), 3.84 (s, 3H), 3.70 (t, J = 6.5 Hz, 1H), 3.81 (s, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 170.9, 167.3, 156.8, 152.6, 132.0, 129.6, 129.2, 128.6, 124.9, 122.2, 110.3, 98.7, 55.5, 52.2, 43.9, 39.3. IR (KBr) 2919, 2848, 1773, 1697, 1651, 1495, 1244, 752; HRMS (ESI) calcd for C\textsubscript{20}H\textsubscript{18}O\textsubscript{5}Na [M+Na]\textsuperscript{+} 361.1043, found 361.1046.

![3aj]

(3S,4R)-methyl 3-(2-methoxyphenyl)-2-oxo-6-(p-tolyl)-3,4-dihydro-2H-pyran-4-carboxylate

45.7 mg, 65% yield, cis/trans = 10:1, white solid, Rf = 0.4 (petroleum ether/ethyl acetate 5:1); [α]D\textsuperscript{25} -315.4 (c 0.1, CH\textsubscript{2}Cl\textsubscript{2}), HPLC analysis: >99% ee (cis), 70% ee (trans) [Daicel CHIRALPAK IA-H column, 20 °C, 254 nm hexane/i-PrOH/MeOH = 80:10:10, 1.0 mL/min, 254 nm, 10.8 min (trans-major), 11.3 min (trans-minor), 14.7 min(cis-major)]; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 0.75 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 7.8 Hz, 1H), 7.31 - 7.26 (m, 1H), 7.20 (d, J = 8.1 Hz, 2H), 6.98 (t, J = 7.6 Hz, 1H),
6.89 (d, $J = 8.3$ Hz, 1H), 5.92 (d, $J = 6.8$ Hz, 1H), 4.68 (d, $J = 6.2$ Hz, 1H), 3.84 (s, 3H), 3.68 (t, $J = 6.5$ Hz, 1H), 3.60 (s, 3H), 2.38 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.0, 167.5, 156.8, 152.7, 139.7, 130.0, 129.3, 129.2, 129.1, 124.9, 122.3, 120.7, 110.3, 97.8, 55.5, 52.2, 43.9, 39.3, 21.3. IR (KBr) 2920, 2845, 1775, 1738, 1646, 1602, 1495, 1170, 754; HRMS (ESI) calcd for C$_{21}$H$_{20}$O$_5$Na [M+Na]$^+$ 375.1198, found 375.1203.

(3$S$,4$R$)-ethyl 3-(2-methoxyphenyl)-6-methyl-2-oxo-3,4-dihydro-2H-pyran-4-carboxylate

23.6 mg, 27% yield, cis/trans > 20:1, white solid, $R_f = 0.3$ (petroleum ether/ethyl acetate 5:1); [α]$^\text{D}_{25}$ -433.2 (c 0.1, CH$_2$Cl$_2$), HPLC analysis: 97% ee (cis) [Daicel CHIRALPAK IA-H column, 20 °C, 254 nm hexane/i-PrOH/MeOH = 90:5:5, 1.0 mL/min, 254 nm, 9.2 min(cis-major), 10.6 min (cis-minor)]; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.51 (dd, $J = 7.7$, 1.4 Hz, 1H), 7.29-7.24 (m, 1H), 6.94 (t, $J = 7.6$ Hz, 1H), 6.87 (d, $J = 8.3$ Hz, 1H), 5.21 (dd, $J = 6.5$, 1.0 Hz, 1H), 4.55 (d, $J = 6.2$ Hz, 1H), 4.03 (q, $J = 7.1$ Hz, 2H), 3.83 (s, 3H), 3.42 (t, $J = 6.4$ Hz, 1H), 1.99 (s, 3H), 1.14 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) 171.0, 167.9, 156.8, 152.4, 130.1, 129.0, 122.4, 120.5, 110.2, 99.4, 61.2, 55.5, 43.6, 39.2, 19.0, 13.9. IR (KBr) 2919, 2849, 1775, 1732, 1602, 1495, 1245, 1180, 755; HRMS (ESI) calcd for C$_{16}$H$_{18}$O$_5$Na [M+Na]$^+$ 313.1044, found 313.1046.
2. X-Ray structure of 3aa (Figure S1)

The crystal suitable for X-ray analysis was prepared by slow evaporation of the solvent of the solution of 3aa in petroleum ether/ethyl acetate at room temperature (Figure 1). The 3S, 4R-configuration of the cycloadduct 3aa was determined by the X-ray analysis of its crystal with the Flack parameter of 0.05(7).

3. References


Part III NMR Spectra

cis/trans = 10:1
cis/trans = 7:1
cis/trans = 10:1
cis/trans = 6:1
cis/trans = 1:1
cis\textsubscript{trans} > 20:1

NAME: cjt-mkb-916
EXPER: 277
PROCOC: 1
DATE: 20141119
TIME: 18.30
INSTRUM: spect
PROCHD: 5 mm PARBO BB/
FILM: eg30
TD: 32768
SOLVENT: CDCl3
NS: 16
DS: 0
SNR: 8012.82 Hz
FIDRES: 0.240532 Hz
AQ: 2.0447731 sec
RG: 206.23
DN: 62.40 unsec
DE: 6.00 unsec
TE: 288.0 K
DI: 2.000000000 ssec
TD0: 1

---------- CHANNEL f1 ----------
SFO1: 400.2442716 MHz
MVC1: 1H
FS: 16.80 unsec
SI: 65536
SF: 400.2440095 MHz
MDW: EM
SBB: 0
LB: 0.30 Hz
GR: 0
AC: 1.00

---------- CHANNEL f2 ----------
SFO1: 100.56574916 MHz
MVC1: 1H
FS: 10.00 unsec
SI: 32768
SF: 100.64041280 MHz
MDW: EM
SBB: 0
LB: 1.00 Hz
GR: 2
PC: 1.40
Part IV HPLC Spectra

rac-3aa cis/trans = 1:4
3aa cis/trans = 10:1

Data file: C:\CHEM2\DATA\CJT\UU0512.D
Sample Name: cjt-mbh-680a

Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with :STDs

Signal: VWD1 A, Wavelength=254 nm

Peak RetTime Type Width Area Height Area percentages
# [min] [min] mAU * [mAU] %
--- --- --- --- --- ---
1 11.444 BB 0.387 664.00891 25.07204 10.6531
2 16.311 BB 0.4000 664.00891 25.07204 10.6531
3 17.985 BB 0.5524 5512.56354 51.60126 90.4414
Totals: 6233.01468 78.95546

*** End of Report ***
rac-3ab cis/trans = 1:1
3ab cis/trans = 10:1

Data File C:\CHEMS\DATA\CJT\000791.D
Sample Name: cjtt-mbh-711

---

Area Percent Report
---

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm
Peak Ret Time Type Width Area Height Area [%] [%]
--- --- --- --- --- --- ---
1 9.497 VV 0.0215 2537.76218 175.07019 12.4061
2 10.880 VV 0.3268 601.44598 25.58925 2.9402
3 12.032 VV 0.2776 1.73166e+4 946.72989 84.6537
Totals : 2.04555e4 145.37543
---

*** End of report ***
**rac-3ac cis/trans = 2:1**

---

**Area Percent Report**

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

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Totals : 6.0974e4 2612.6578

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3ac cis/trans = 10:1
rac-3ad cis/trans = 2:1
cis/trans = 7:1

Data File C:\\CHEM321\DATA\CJT000841.D
Sample Name: CJT-MSH-753

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal : VWD1 A, Wavelength=254 nm

Peak RetTime Type Width Area Height Area
# [min] | [min] mAU* | mAU | %
---|---|---|---|
1 10.786 VV 0.2517 1.4824 744 893.8903 36.2099
2 11.820 VB 0.2697 2095.0632 118.7259 4.5320
3 15.245 VB 0.3967 2.9266 564 1083.2987 63.3609

Totals : 4.61843e4 2935.9207

*** End of Report ***
**rac-3ae cis/trans = 7:1**
$3ae \text{ cis/} \text{trans} = 6:1$

Data File: C:\CHEMS2\DATA\CJT\000759.D
Sample Name: cjt-mbh-653

Acq. Operator : cjt
Acq. Instrument : Instrument 1
Injection Date : 2014-10-22 14:18:38
Acq. Method : C:\CHEMS\1\METHODS\WQ20121205.M
Last changed : 2014-10-22 14:16:56 by cjt (modified after loading)
Analysis Method : C:\CHEMS\1\METHODS\WQ20121205.M
Last changed : 2014-10-25 14:06:06 by cjt (modified after loading)
Sample Info : IA-M N/1/MeOH=90/5/5 1.0 mL/min 254 nm

Area Percent Report

Signal 1: VWD1 A, Wavelength=254 nm

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Totals : 1.24092e6 \( \phi 6.62043 \)

*** End of Report ***
rac-3af cis/trans = 1:1
EtO₂C

3af cis/trans = 10:1

**Area Percent Report**

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Use Multiplier & Dilution Factor with ISSTDs

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*** End of Report ***

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Data File: C:\\CHEM32\DATA\CJT000808.D
Sample Name: cjtt-mbb-710

Acq. Operator: cjtt
Acq. Instrument: Instrument 1, Location: Via 1
Injection Date: 2014-10-29 20:51:45 (modified after loading)
Analysis Method: C:\\CHEM32\METHODS\W20121205.M
Last changed: 2014-10-29 22:23:03 by cjtt (modified after loading)
Sample Info: IA Hexane:I/MeOH=80:10:10 lmL/min 254 nm
rac-3ag cis/trans = 1:1
3ag cis/trans = 6:1

Data File C:\CNFLIB\DATA\CJT\G0813.D
Sample Name: CJT-MEN-698

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTs

Signal 1 : VWD1 A, Wavelength=254 nm

Peak RetTime Type Width Area Height Area %
# [min] [min] dU * [mAU] [mAU] [mAU]
1 12.323 W 0.2750 2.070 2908 130.54913 16.2452
2 14.334 W 0.3191 1.2197 164 584.46468 80.1924
3 15.779 W 0.3697 <0.46601 16.6590 2.6563
4 19.044 B 0.4308 137.93817 6.79090 0.9069

Totals : 1.52097e4 744.62462

End of Report
rac-3ah cis/trans = 3:1
3ah cis/trans = 3:1
rac-3ca
cis/trans = 1:2

---

**Data File:** C:\CHEM321\DATA\CJT\0000821.D
**Sample Name:** cjt-mbh-786xiao

---

**Area Percent Report**

**Signal**
**Multiplier** : 1.0000
**Dilution** : 1.0000

Use Multiplier & Dilution Factor with ISTDs

**Signal 1: VWD1 A, Wavelength=254 nm**

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<td>23.606</td>
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Totals : 2.53910e+4 10.81079

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***End of Report***
\[
3ca \\
cis/trans = 6:1
\]
rac-3da cis/trans=1:5
3da

cis/trans = 3:1
rac-3ea

cis/trans = 1:8
3ea cis/trans = 6:1
rac-3ee cis:trans = 1:1
cis:trans = 20:1

Area Percent Report

Signal 1: VWD A, Wavelength=254 nm

| Peak RetType | Width | Area | Height | Area
|-------------|-------|------|--------|------
| 1           | 0.229 | 11.08| 1328   | 1.0000
| 2           | 0.228 | 11.08| 1328   | 1.0000
| 3           | 0.232 | 11.08| 1328   | 1.0000

Totals: 1.56167e4 44.85680

*** End of Report ***
H₃CO \text{OCH₃} \quad \text{EtO₂C} \quad \text{CO} \quad \text{3ef cis:trans = 1:3}

Data File C:\\CHEM3\\DATA\\CJT000771.D
Sample Name: cjt-mbh-728xiacoxan

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Acq. Operator : CJT
Acq. Instrument : Instrument 1
Injection Date : 2014-10-25 9:06:50
Acq. Method : C:\\CHEMRD\\METHODS\\MQ20121205.W
(modified after loading)
Analysis Method : C:\\CHEMRD\\METHODS\\MQ20121205.W
Last changed : 2014-10-25 14:08:35 by cj
(modified after loading)
Sample Info : EA-H N/1/Organ=60:20120 1.0 mL/min 254 nm

----------------------------------------------------------------------

Area Percent Report

========================================================================

Signal 1: VWD A, Wavelength=254 nm

| Peak RetTime Type Width Area Height Area |
|---|---|---|---|---|
| 1  | 3.856  | VV    | 0.2406 | 4286.5454 | 77.4,3735 | 35.0512 |
| 2  | 11.169  | VY    | 0.3204 | 6271.3255 | 199.4901 | 34.5236 |
| 3  | 11.323  | VY    | 0.3109 | 8462.6734 | 91.4324 | 18.0660 |
| 4  | 35.915  | VY    | 1.0594 | 1829.3843 | 24.8736 | 14.9592 |

Totals : 1.12230564 591.86682

========================================================================

*** End of Report ***
3ef cis:trans >20:1

Data File: C:\CHEM32\1\DATA\CP\0005753.D
Sample Name: cjt-sbh-728

Acq. Operator: cjt
Acq. Instrument: Instrument 1
Injection Date: 2014-10-25 10:31:53
Acq. Method: C:\CHEM32\1\METHODS\WQ20121205.M
(modified after load.ng)
Analysis Method: C:\CHEM32\1\METHODS\WQ20121205.M
Last changed: 2014-10-25 14:08:35 by cjt
(modified after load.ng)
Sample Info: TH-M H2/MeOH=60:20:0 1.0 mL/min 254 nm

---

Signal 1: VWD 1 A, Wavelength=254 nm

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Totals: 7181.74414 139.11667

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*** End of Report ***
rac-3ai cis:trans = 1.5:1

Data File C:\CHEM32\DATA\Cjt\000008\D
Sample Name: Cjt-nbh-924XIAOXUAN

Acq. Operator: cjt
Acq. Instrument: Instrument 1
Location: Vial 1
Injection Date: 2014-11-21 19:51:14
Acq. Method: C:\\CHEM32\METHODS\WAC20121205.X
Last changed: 2014-11-21 19:41:42 by cjt
(modified after loading)
Analysis Method: C:\\CHEM32\METHODS\WAC20121205.X
Last changed: 2014-11-22 19:08:07 by cjt
(modified after loading)
Sample Info: IA El:MeOH=80:10:10 1.0mL/min 254 nm

---

Area Percent Report

Sort By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WAC1 A, Wavelength=254 nm

Peak RetTime Type Width Area Height Area
# [min] [min] [nAU] [%] [nAU] [%]
1 10.345 VV 0.2667 1531.7611 88.1711 21.1899
2 11.291 VB 0.2590 1464.8302 97.3104 20.2640
3 12.642 BB 0.2869 2129.0373 114.4901 29.4633
4 37.711 BB 1.1951 2102.3147 58.3857 29.0828
Totals: 7228.72974 315.35549

---

*** End of Report ***
3ai cis:trans = 10:1
rac-3aj cis:trans = 4:1
$3_{aj} \text{ cis:trans} = 10:1$

Data File C:\CHEM32\DATA\cjt000981.D  
Sample Name: cjt-mbh-920

Acq. Operator : cjt  
Acq. Instrument : Instrument 1  
Location : Via. 1

Injection Date : 2014-11-21 17:03:10  
Acq. Method : C:\CHEM32\METHODS\WQ20121205.M  
Last changed : 2014-11-21 16:11:05 by cjt  
(modified after loading)

Analysis Method : C:\CHEM32\METHODS\WQ20121205.M  
Last changed : 2014-11-21 16:02:100 by ctk  
(modified after loading)

Sample Info : IA E:IME08=09:10:11 1.0mL/min 254 nm

---

Area Percent Report

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000

Use Multiplier & Dilution Factor with 3STDs

Signal 1: VWD A, Wavelength=254 nm

| Peak RetTime Type Width Area Height Area  
<table>
<thead>
<tr>
<th>#</th>
<th>[min]</th>
<th>[min]</th>
<th>mAU</th>
<th>%</th>
<th>mAU</th>
<th>%</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.72%</td>
<td>VV</td>
<td>0.2996</td>
<td>896.06521</td>
<td>46.09442</td>
<td>10.627</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>11.32%</td>
<td>VB</td>
<td>0.2992</td>
<td>159.64058</td>
<td>7.71015</td>
<td>1.0222</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>14.73%</td>
<td>VB</td>
<td>0.3427</td>
<td>7381.79752</td>
<td>333.52679</td>
<td>87.5501</td>
<td></td>
</tr>
<tr>
<td>Totals</td>
<td>8431.41029</td>
<td>397.33636</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*** End of Report ***
**rac-3ak** cis:trans > 20:1
3ak cis:trans > 20:1

Data File C:\CHEM2\DATA\CJT\000856.D
Sample Name: cjt-mbh-916

Acq. Operator : cjt
Acq. Instrument : Instrument 1
Injection Date : 2014-11-21 21:31:20
Acq. Method : C:\CHEM2\METHODS\WP20121205.M
Last changed : 2014-11-21 21:29:16 by cjt (modified after loading)
Analysis Method : C:\CHEM2\METHODS\WP20121205.M
Last changed : 2014-11-32 18:56:47 by ckt (modified after loading)
Sample Info : IA:R6e08=90±5:5 1.0mL/min 214 nm

---

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
See Multiplier & Dilution Factor with MTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type Width Area Height Area
# [min] [mm] [AU] [AU] [%]
1 9.160 VV 0.2467 2560.23730 163.57327 98.2915
2 10.550 VV 0.3333 44.50246 1.928577 1.7085

Totals : 2604.73976 165.590195

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*** End of Report ***