Supporting Information for

Asymmetric Construction of Fluorinated Imidazolidines via 
Cu(I)-Catalyzed $exob^\prime$-Selective 1,3-Dipolar Cycloaddition of 
Azomethine Ylides with Fluorinated Imines

Qing-Hua Li, Liang Wei, Xuan Chen and Chun-Jiang Wang*

Table of Contents

I. General Remarks........................................................................................................S2
II. Ligand Screening for Asymmetric 1,3-Dipolar Cycloaddition of Azomethine 
    Ylides with Fluorinated Imines...........................................................................S2-S3
III. General Procedure for the Synthesis of Racemic Cycloadducts............................S3
IV. General Procedure for Asymmetric 1,3-Dipolar Cycloaddition of Azomethine 
    Ylides with Fluorinated Imines..........................................................................S4-22
V. Synthetic Transformtions.......................................................................................S22-24
VI. Linear Effect for the 1,3-DC of Trifluoromethylated Imine 1a with Imino Ester 
    2a Catalyzed by Cu(I)/($S,R_p$)-PPFOMe Complex.............................................S24-25
VII. Proposed Transition States of the $exob^\prime$-Selectivity for Asymmetric 1,3-Dipolar 
    Cycloaddition of Imino Esters with Fluorinated Imines.................................S25-26
VIII. References...........................................................................................................S26
IX. $^1$H NMR and $^{13}$C NMR Spectra......................................................................S27-94
X. HPLC Chromatograms.........................................................................................S95-S162
I. General Remarks

$^1$H NMR spectra were recorded on a VARIAN Mercury 300 MHz or Bruker 400 MHz spectrometer in CDCl$_3$. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data are reported as (s = single, d = double, t = triple, q = quartet, m = multiple or unresolved, and brs = broad single). $^{13}$C NMR spectra were recorded on a Bruker 100 MHz or 75 MHz spectrometer in CDCl$_3$ or DMSO-$d_6$. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. Commercially available reagents were used without further purification. All reactions were monitored by TLC with silica gel-coated plates. Diastereomeric ratios were determined from crude $^1$H NMR or HPLC analysis. Enantiomeric ratios were determined by HPLC, using a chiralpak AD-H column, a chiralpak AS-H column or a chiralcel OD-H column with hexane and $i$-PrOH as solvents, or determined by GC using $\beta$-dex 325 column. Chiral ligand ($S,R_p$)-PPFOMe and Fluorinated imines was prepared according to the literature procedure.$^{1,2}$ The racemic adducts were obtained by using AgOAc/PPh$_3$ as the catalyst. The absolute configuration of (2$R$,4$R$,5$R$)-3s was determined unequivocally according to the X-ray diffraction analysis, and those of other adducts were deduced on the basis of these results.

II. Ligand Screening for Asymmetric 1,3-Dipolar Cycloaddition of Azomethine Ylides with Fluorinated Imines

![Screened chiral ligands.](image)
**Table 1.** Optimization for catalytic asymmetric 1,3-dipolar cycloaddition of imino ester 2a with trifluoromethylated imine 1a

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*a All reactions were carried out with 0.35 mmol of 2a and 0.23 mmol of 1a in 2 mL of solvent. *CuBF4 = Cu(CH3CN)4BF4. *C Isolated yield. *dr was determined by the crude 1H NMR and HPLC analysis. *ee was determined by chiral HPLC analysis. *CuBF4 is 3 mol % and L5 is 6.6 mol %. *f 1 mol % catalyst loading.

III. General Procedure for the Synthesis of Racemic Cycloadducts.

Under argon atmosphere, PPh3 (6.6 mg, 0.025 mmol) and AgOAc (3.8 mg, 0.023 mmol) were dissolved in 2 mL of DCM, and stirred at room temperature for about 0.5 h. Then, imine substrate (0.35 mmol), Et3N (0.03 mmol) and fluorinated imines (0.23 mmol) were added sequentially. Once starting material was consumed (monitored by TLC), the organic solvent was removed and the residue was purified by column chromatography to give the cycloaddition product, which was used as the racemic sample for the HPLC analysis.
IV. General Procedure for Asymmetric 1,3-Dipolar Cycloaddition of Azomethine Ylides with Fluorinated Imines.

Under argon atmosphere, \((S,R_p)-\text{PPFOMe (L5)}\) (3.3 mg, 0.0077 mmol) and \(\text{Cu(CH}_3\text{CN)}_4\text{BF}_4\) (2.2 mg, 0.007 mmol) were dissolved in 2 mL of ether, and stirred at room temperature for about 0.5 h. After imine substrate (0.35 mmol) was added, the mixture was dropped to -20 °C. Then, fluorinated imines (0.23 mmol) and \(\text{Et}_3\text{N}\) (0.03 mmol) was added sequentially. Once starting material was consumed (monitored by TLC), the mixture was filtered through celite and the filtrate was concentrated to dryness. The residue was purified by column chromatography to give the corresponding cycloaddition product, which was then directly analyzed by HPLC analysis to determine the enantiomeric excess.

\[(3a)\]

\((2R,4R,5R)-\text{methyl 2-(4-chlorophenyl)-1-(4-methoxyphenyl)-5-(trifluoromethyl) imidazolidine-4-carboxylate}\)

The title compound was prepared according to the general procedure as described above in 95% yield; \([\alpha]^{25}_{D} = -44.2 (c 0.97, \text{CHCl}_3); {^1}\text{H NMR (CDCl}_3, \text{TMS, 300 MHz)}\)

\(\delta 7.49 (d, J = 8.1 \text{ Hz}, 2\text{H}), 7.35 (d, J = 8.1 \text{ Hz}, 2\text{H}), 6.76 (d, J = 8.4 \text{ Hz}, 2\text{H}), 6.67(d, J = 8.4 \text{ Hz}, 2\text{H}), 5.40 (s, 1\text{H}), 4.62 (q, J = 6.6 \text{ Hz}, 1\text{H}), 4.32 (s, 1\text{H}), 3.79 (s, 3\text{H}), 3.72 (s, 3\text{H}), 2.66 (brs, 1\text{H}); {^{13}}\text{C NMR (CDCl}_3, \text{TMS, 100 MHz)}\)

\(\delta 170.4, 154.0, 139.5, 137.5, 134.7, 129.2, 128.1, 125.8 (q, J = 280.6 \text{ Hz}), 117.2, 114.5, 81.2, 65.5 (q, J = 30.6 \text{ Hz}), 60.5, 55.4, 53.0; \text{IR (KBr)} \nu 3340, 2953, 2845, 1742, 1513, 1450, 1346, 1260, 1175, 1134, 1036, 931, 815, 680, 590 \text{ cm}^{-1}\). 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 mL/min, \(\lambda = 220 \text{ nm}\)); \(t_r = 9.49 \text{ and } 11.47 \text{ min}\).
(2\textit{R},4\textit{R},5\textit{R})-methyl 2-(3-chlorophenyl)-1-(4-methoxyphenyl)-5-(trifluoromethyl) imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 85% yield. \([\alpha]_{25}^{\text{D}} = -42.0\ (c\ 0.29,\ \text{CHCl}_3)\); \(^1\text{H}\) NMR (CDCl\(_3\), TMS, 400 MHz) \(\delta\) 7.54 (s, 1H), 7.44-7.42 (m, 1H), 7.32-7.31 (m, 2H), 6.77 (d, \(J = 9.2\) Hz, 2H), 6.69 (d, \(J = 9.2\) Hz, 2H), 5.40 (s, 1H), 4.61 (q, \(J = 6.8\) Hz, 1H), 4.31 (s, 1H), 3.79 (s, 3H), 3.72 (s, 3H); \(^{13}\text{C}\) NMR (CDCl\(_3\), TMS, 100 MHz) \(\delta\) 170.4, 154.1, 141.1, 139.5, 134.8, 130.3, 129.1, 126.9, 125.7 (q, \(J = 280.8\) Hz), 124.8, 117.3, 114.6, 81.3, 65.6 (q, \(J = 30.6\) Hz), 60.5, 55.4, 53.0; IR (KBr) \(\nu\) 3318, 2948, 2920, 2815, 1750, 1517, 1395, 1251, 1138, 1036, 950, 759, 590 cm\(^{-1}\). HRMS: calcd. for C\(_{19}\)H\(_{18}\)ClF\(_3\)N\(_2\)O\(_3\) + H\(^+\): 415.1031, found: 415.1037. 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 mL/min, \(\lambda = 220\) nm); \(t_r\) = 7.81 and 11.19 min.

(2\textit{R},4\textit{R},5\textit{R})-methyl 2-(2-chlorophenyl)-1-(4-methoxyphenyl)-5-(trifluoromethyl) imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 80% yield. \([\alpha]_{25}^{\text{D}} = +15.1\ (c\ 1.37,\ \text{CHCl}_3)\); \(^1\text{H}\) NMR (CDCl\(_3\), TMS, 300 MHz) \(\delta\) 7.62-7.60 (m, 1H), 7.45-7.42 (m, 1H), 7.31-7.23 (m, 2H), 6.76 (d, \(J = 9.0\) Hz, 2H), 6.63 (d, \(J = 9.0\) Hz, 2H), 5.85 (s, 1H), 4.60 (q, \(J = 6.9\) Hz, 1H), 4.32 (s, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 2.78 (brs, 1H); \(^{13}\text{C}\) NMR (CDCl\(_3\), TMS, 100 MHz) \(\delta\) 170.6, 153.8, 139.4, 136.3, 133.5, 130.0, 129.9, 127.7, 127.4, 125.7 (q, \(J = 280.9\) Hz), 116.6, 114.6, 78.0, 65.4 (q, \(J = 30.9\) Hz), 60.4, 55.4, 53.0; IR (KBr) \(\nu\) 3319, 2910, 2834,
1744, 1510, 1390, 1252, 1157, 1143, 1030, 955, 750, 591 cm\(^{-1}\). The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralpak AS-H, \(i\)-propanol/hexane = 10/90, flow rate 1.0 mL/min, \(\lambda = 220\) nm); \(t_r = 7.58\) and 8.47 min.

(3d)

\((2R,4R,5R)\)-methyl 2-(4-bromophenyl)-1-(4-methoxyphenyl)-5-(trifluoromethyl) imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 94% yield. \([\alpha]^{25}_{D} = -56.2\) (c 0.96, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), TMS, 400 MHz) \(\delta\) 7.51 (d, \(J = 8.4\) Hz, 2H), 7.42 (d, \(J = 8.4\) Hz, 2H), 6.76 (d, \(J = 9.2\) Hz, 2H), 6.67 (d, \(J = 9.2\) Hz, 2H), 5.39 (s, 1H), 4.61 (q, \(J = 6.8\) Hz, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 2.66 (brs, 1H); \(^{13}\)C NMR (CDCl\(_3\), TMS, 100 MHz) \(\delta\) 170.4, 154.0, 139.5, 138.0, 132.1, 128.4, 125.7 (q, \(J = 280.7\) Hz), 122.8, 117.2, 114.6, 81.2, 65.6 (q, \(J = 30.6\) Hz), 60.5, 55.4, 53.0; IR (KBr) \(\nu\) 3340, 2950, 2840, 1714, 1522, 1460, 1251, 1134, 1050, 928, 816, 746, 588 cm\(^{-1}\). 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 mL/min, \(\lambda = 220\) nm); \(t_r = 10.01\) and 12.77 min.

(3e)

\((2R,4R,5R)\)-methyl 1-(4-methoxyphenyl)-2-phenyl-5-(trifluoromethyl)imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 90% yield. \([\alpha]^{25}_{D} = -35.6\) (c 1.35, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), TMS, 400 MHz) \(\delta\) 7.54 (d, \(J = 7.2\) Hz, 2H), 7.40-7.33 (m, 3H), 6.75 (d, \(J = 9.2\) Hz, 2H), 6.69 (d, \(J =
9.2 Hz, 2H), 5.43 (s, 1H), 4.63 (q, J = 7.2 Hz, 1H), 4.32 (s, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 2.69 (brs, 1H); $^{13}$C NMR (CDCl$_3$, TMS, 100 MHz) δ 170.5, 153.7, 139.8, 139.0, 129.0, 128.9, 126.6, 125.9 (q, J = 280.8 Hz), 116.9, 114.5, 81.8, 65.5 (q, J = 30.6 Hz), 60.6, 55.5, 53.0; IR (KBr) ν 3365, 2950, 2847, 1750, 1514, 1422, 1366, 1240, 1138, 1036, 930, 701, 620 cm$^{-1}$. 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 mL/min, λ = 220 nm); t$_r$ = 7.85 and 11.61 min.

(3f)

(2R,4R,5R)-methyl 1-(4-methoxyphenyl)-2-(p-tolyl)-5-(trifluoromethyl)imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 91% yield. [α]$^2_\text{D}$ = -49.6 (c 1.37, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 400 MHz) δ 7.43 (d, J = 7.6 Hz, 2H), 7.18 (d, J = 7.6 Hz, 2H), 6.75 (d, J = 9.2 Hz, 2H), 6.69 (d, J = 9.2 Hz, 2H), 5.40 (s, 1H), 4.63 (q, J = 6.8 Hz, 1H), 4.31 (s, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 2.69 (brs, 1H), 2.34 (s, 3H); $^{13}$C NMR (CDCl$_3$, TMS, 100 MHz) δ 170.5, 153.6, 139.9, 138.7, 136.0, 129.6, 126.5, 125.9 (q, J = 280.9 Hz), 116.8, 114.5, 81.6, 65.4 (q, J = 30.5 Hz), 60.6, 55.4, 52.9, 21.1; IR (KBr) ν 3318, 2930, 2847, 1742, 1513, 1450, 1379, 1138, 1039, 960, 817, 755, 590 cm$^{-1}$. 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 mL/min, λ = 220 nm); t$_r$ = 8.03 and 9.95 min.

(3g)

(2R,4R,5R)-methyl 1-(4-methoxyphenyl)-2-(m-tolyl)-5-(trifluoromethyl)imidazolidine-4-carboxylate
The title compound was prepared according to the general procedure as described above in 85% yield. [α]$_D^{25}$ = -38.9 (c 0.85, CHCl$_3$); H NMR (CDCl$_3$, TMS, 400 MHz) δ 7.35-7.33 (m, 2H), 7.28-7.24 (m, 1H), 7.16 (d, $J$ = 7.6 Hz, 1H), 6.76 (d, $J$ = 9.2 Hz, 2H), 6.69 (d, $J$ = 9.2 Hz, 2H), 5.38 (s, 1H), 4.64 (q, $J$ = 6.8 Hz, 1H), 4.31 (s, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 2.35 (s, 3H); $^{13}$C NMR (CDCl$_3$, TMS, 100 MHz) δ 170.5, 153.6, 139.9, 138.9, 138.6, 129.6, 128.9, 127.3, 125.9 (q, $J$ = 283.7 Hz), 123.5, 116.8, 114.5, 81.8, 65.4 (q, $J$ = 30.5 Hz), 60.6, 55.4, 52.9, 21.4; IR (KBr) ν 3345, 2930, 2832, 1747, 1513, 1364, 1217, 1168, 1137, 1040, 961, 812, 756, 588 cm$^{-1}$. HRMS: calcd. for C$_{20}$H$_{21}$F$_3$N$_2$O$_3$ + H$: 395.1577, found: 395.1579. The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak AS-H, $i$-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 220 nm); $t_r$ = 7.00 and 10.68 min.

![Molecule Image]

(3h)

(2R,4R,5R)-methyl 1-(4-methoxyphenyl)-2-(o-tolyl)-5-(trifluoromethyl)imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 82% yield. [α]$_D^{25}$ = -48.1 (c 1.35, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 400 MHz) δ 7.54-7.52 (m, 1H), 7.33-7.23 (m, 2H), 7.18-7.17 (m, 1H), 6.75 (d, $J$ = 9.2 Hz, 2H), 6.59 (d, $J$ = 9.2 Hz, 2H), 5.59 (s, 1H), 4.59 (q, $J$ = 6.8 Hz, 1H), 4.32 (s, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 2.57 (s, 3H), 2.53 (brs, 1H); $^{13}$C NMR (CDCl$_3$, TMS, 100 MHz) δ 170.5, 153.7, 139.9, 138.7, 136.0, 129.6, 126.5, 125.9 (q, $J$ = 280.9 Hz), 116.8, 114.5, 81.6, 65.4 (q, $J$ = 30.5 Hz), 60.6, 55.5, 53.0, 21.2; IR (KBr) ν 3319, 2948, 2926, 1742, 1513, 1449, 1381, 1208, 1165, 1135, 1039, 931, 817, 750, 589 cm$^{-1}$. HRMS: calcd. for C$_{20}$H$_{21}$F$_3$N$_2$O$_3$ + H$: 395.1577, found: 395.1579. 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 mL/min, λ = 220 nm); $t_r$ = 8.03 and 9.93 min.
(2R,4R,5R)-methyl 1,2-bis(4-methoxyphenyl)-5-(trifluoromethyl)imidazoline-4-carboxylate

The title compound was prepared according to the general procedure as described above in 88% yield. $[\alpha]_{D}^{25} = -50.6$ (c 1.56, CHCl$_3$); $^{1}$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 7.46 (d, $J = 8.8$ Hz, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 6.75 (d, $J = 9.2$ Hz, 2H), 6.69 (d, $J = 9.2$ Hz, 2H), 5.37 (s, 1H), 4.62 (q, $J = 7.6$ Hz, 1H), 4.31 (s, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 2.65 (brs, 1H); $^{13}$C NMR (CDCl$_3$, TMS, 100 MHz) $\delta$ 170.5, 159.9, 153.7, 139.9, 131.0, 127.9, 125.9 (q, $J = 280.8$ Hz), 117.0, 114.5, 114.2, 81.4, 65.4 (q, $J = 30.5$ Hz), 60.5, 55.4, 55.2, 52.9; IR (KBr) $\nu$ 3380, 2960, 2831, 1742, 1513, 1451, 1383, 1249, 1169, 1135, 1036, 931, 840, 690, 593 cm$^{-1}$. The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee (Chiralpak AS-H, $\pi$-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda$ = 220 nm); $t_R = 12.73$ and 16.73 min.

(2R,4R,5R)-methyl 2-(2-methoxyphenyl)-1-(4-methoxyphenyl)-5-(trifluoromethyl)imidazoline-4-carboxylate

The title compound was prepared according to the general procedure as described above in 76% yield. $[\alpha]_{D}^{25} = +4.7$ (c 0.58, CHCl$_3$); $^{1}$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 7.49 (d, $J = 7.6$ Hz, 1H), 7.33-7.31 (m, 1H), 6.95-6.93 (m, 2H), 6.75 (d, $J = 8.8$ Hz, 2H), 6.65 (d, $J = 8.8$ Hz, 2H), 5.84 (s, 1H), 4.59 (q, $J = 6.8$ Hz, 1H), 4.32 (s, 1H), 3.94 (s, 3H), 3.78 (s, 3H), 3.71 (s, 3H); $^{13}$C NMR (CDCl$_3$, TMS, 100 MHz) $\delta$ 170.7, 157.2, 153.5, 139.9, 129.8, 126.8, 126.6, 125.8 (q, $J = 280.9$ Hz), 121.1, 116.5, 114.4, 110.5, 75.6, 65.2 (q, $J = 30.7$ Hz), 60.5, 55.6, 55.4, 52.9; IR (KBr) $\nu$ 3340, 2956, 2928, 1741,
1513, 1446, 1388, 1252, 1202, 1176, 1134, 931, 1036, 817, 699, 585 cm\(^{-1}\). 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 mL/min, \(\lambda = 220\) nm); \(t_r = 10.27\) and 15.63 min.

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(3k)
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\((2R,4R,5R)\)-methyl 1-(4-methoxyphenyl)-2-(naphthalen-1-yl)-5-(trifluoromethyl) imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 85% yield. \([\alpha]^{25}_D = -58.4\) (c 1.42, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), TMS, 400 MHz) \(\delta\) 8.47 (d, \(J = 8.8\) Hz, 1H), 7.91 (d, \(J = 8.0\) Hz, 1H), 7.85 (d, \(J = 8.4\) Hz, 1H), 7.74 (d, \(J = 7.6\) Hz, 1H), 7.63-7.61 (m, 1H), 7.57-7.55 (m, 1H), 7.44-7.41 (m, 1H), 6.72 (d, \(J = 9.2\) Hz, 2H), 6.62 (d, \(J = 9.2\) Hz, 2H), 6.20 (s, 1H), 4.68 (q, \(J = 6.8\) Hz, 1H), 4.38 (s, 1H), 3.83 (s, 3H), 3.69 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), TMS, 100 MHz) \(\delta\) 170.6, 153.4, 139.8, 133.9, 133.5, 130.9, 129.2, 128.5, 126.6, 125.90, 125.86 (q, \(J = 281.0\) Hz), 125.8, 124.0, 123.3, 116.2, 114.5, 78.8, 65.3 (q, \(J = 30.7\) Hz), 60.5, 55.4, 52.9; IR (KBr) \(\nu\) 3328, 2956, 1743, 1515, 1425, 1250, 1134, 1037, 929, 817, 763, 669, 588 cm\(^{-1}\). HRMS: calcd. for C\(_{23}\)H\(_{21}\)F\(_3\)N\(_2\)O\(_3\) + H\(^+\): 431.1577, found: 431.1576. The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak AS-H, \(i\)-propanol/hexane = 10/90, flow rate 1.0 mL/min, \(\lambda = 220\) nm); \(t_r = 7.29\) and 8.59 min.

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(3l)
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\((2R,4R,5R)\)-methyl 1-(4-methoxyphenyl)-2-(naphthalen-2-yl)-5-(trifluoromethyl)
imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 76% yield. $[\alpha]_{D}^{25} = -68.1$ (c 1.03, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 400 MHz) δ 8.00 (s, 1H), 7.89-7.83 (m, 3H), 7.68-7.66 (m, 1H), 7.50-7.48 (m, 2H), 6.74 (s, 4H), 5.59 (s, 1H), 4.70 (q, $J = 6.8$ Hz, 1H), 4.36 (s, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 2.78 (brs, 1H); $^{13}$C NMR (CDCl$_3$, TMS, 100 MHz) δ 170.5, 153.8, 139.8, 136.4, 133.6, 133.3, 128.9, 128.2, 127.7, 126.4, 126.3, 126.2, 125.9 (q, $J = 280.9$ Hz), 124.0, 117.1, 114.5, 82.0, 65.5 (q, $J = 30.5$ Hz), 60.6, 55.4, 53.0; IR (KBr) ν 3324, 2956, 1743, 1513, 1425, 1250, 1134, 1037, 953, 815, 765, 677, 588 cm$^{-1}$. 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 mL/min, $\lambda = 220$ nm); $t_r = 10.63$ and 16.58 min.

(3m)

(2R,4R,5R)-methyl 2-(furan-2-yl)-1-(4-methoxyphenyl)-5-(trifluoromethyl)imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 85% yield. $[\alpha]_{D}^{25} = +36.3$ (c 1.29, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 300 MHz) δ 7.42 (s, 1H), 6.80 (s, 4H), 6.42 (d, $J = 2.7$ Hz, 1H), 6.34 (s, 1H), 5.49 (s, 1H), 4.51 (q, $J = 6.6$ Hz, 1H), 4.33 (s, 1H), 3.78 (s, 3H), 3.74 (s, 3H); $^{13}$C NMR (CDCl$_3$, TMS, 100 MHz) δ 170.6, 154.5, 152.1, 142.9, 139.6, 125.5 (q, $J = 280.5$ Hz), 118.1, 114.6, 110.6, 108.5, 75.9, 65.1 (q, $J = 30.8$ Hz), 60.5, 55.5, 53.0; IR (KBr) ν 3318, 2956, 2840, 1745, 1513, 1455, 1250, 1134, 1037, 955, 815, 765, 650 cm$^{-1}$. 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 mL/min, $\lambda = 220$ nm); $t_r = 10.17$ and 21.37 min.
(3n)

\((2R,4R,5R)\)-methyl 1-(4-methoxyphenyl)-2-(thiophen-2-yl)-5-(trifluoromethyl) imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 80% yield. \([ \alpha ]^{25}_D = -52.7 \ \text{(c 0.87, CHCl}_3)\); \(^1\)H NMR (CDCl\(_3\), TMS, 400 MHz) \( \delta \) 7.29-7.27 (m, 1H), 7.22-7.21 (m, 1H), 6.99-6.97 (m, 1H), 6.84 (d, \( J = 9.2 \) Hz, 2H), 6.78 (d, \( J = 9.2 \) Hz, 2H), 5.69 (s, 1H), 4.52 (q, \( J = 6.8 \) Hz, 1H), 4.33 (s, 1H), 3.79 (s, 3H), 3.73 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), TMS, 100 MHz) \( \delta \) 170.5, 154.4, 143.5, 139.6, 127.0, 125.94, 125.90, 125.6 (q, \( J = 280.5 \) Hz), 118.1, 114.5, 77.9, 65.8 (q, \( J = 30.7 \) Hz), 60.5, 55.4, 52.9; IR (KBr) v 3318, 2950, 2844, 1743, 1513, 1460, 1250, 1134, 1038, 935, 822, 721, 529 cm\(^{-1}\). 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 mL/min, \( \lambda = 220 \) nm); \( t_r \) = 9.15 and 14.01 min.

(3o)

\((2R,4R,5R)\)-ethyl 1-(4-methoxyphenyl)-2-phenyl-5-(trifluoromethyl)imidazole-4-carboxylate

The title compound was prepared according to the general procedure as described above in 80% yield. \([ \alpha ]^{25}_D = -21.6 \ \text{(c 1.52, CHCl}_3)\); \(^1\)H NMR (CDCl\(_3\), TMS, 400 MHz) \( \delta \) 7.55 (d, \( J = 6.4 \) Hz, 2H), 7.40-7.34 (m, 3H), 6.75 (d, \( J = 9.2 \) Hz, 2H), 6.69 (d, \( J = 9.2 \) Hz, 2H), 5.44 (s, 1H), 4.60 (q, \( J = 7.2 \) Hz, 1H), 4.29 (s, 1H), 4.23 (q, \( J = 7.2 \) Hz, 2H), 3.71 (s, 3H), 1.25 (t, \( J = 7.2 \) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), TMS, 100 MHz) \( \delta \) 170.0, 153.8, 140.0, 139.1, 128.94, 128.86, 126.7, 125.9 (q, \( J = 280.8 \) Hz), 117.0, 114.5, 81.9, 65.6 (q, \( J = 30.5 \) Hz), 62.0, 60.8, 55.5, 14.0; IR (KBr) v 3362, 2951, 2844, 1743, 1513, 1460, 1250, 1134, 1038, 935, 822, 721, 529 cm\(^{-1}\). HRMS: calcd. for \( \text{C}_{20}\text{H}_{21}\text{F}_3\text{N}_2\text{O}_3 + \text{H}^+ \): 395.1577, found: 395.1569. 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 mL/min, λ = 220 nm); t<sub>r</sub> = 6.90 and 10.26 min.

(3p)

(2R,4R,5R)-benzyl 1-(4-methoxyphenyl)-2-phenyl-5-(trifluoromethyl)imidazolinedine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 88% yield. [α]<sup>25</sup><sub>D</sub> = -12.7 (c 0.93, CHCl₃); <sup>1</sup>H NMR (CDCl₃, TMS, 300 MHz) δ 7.54-7.52 (m, 2H), 7.37-7.22 (m, 8H), 6.73 (d, J = 9.0 Hz, 2H), 6.64 (d, J = 9.0 Hz, 2H), 5.44 (s, 1H), 5.19 (s, 2H), 4.58 (q, J = 6.9 Hz, 1H), 4.34 (s, 1H), 3.72 (s, 3H), 2.68 (brs, 1H); <sup>13</sup>C NMR (CDCl₃, TMS, 100 MHz) δ 169.8, 153.8, 139.9, 139.0, 134.9, 128.93, 128.87, 128.6, 128.4, 128.1, 126.7, 125.8 (q, J = 281.0 Hz), 117.0, 114.5, 82.0, 67.5, 65.6 (q, J = 30.5 Hz), 60.9, 55.5; IR (KBr) v 3318, 2951, 2844, 1755, 1510, 1442, 1360, 1228, 1123, 1035, 933, 825, 690 cm⁻¹. HRMS: calcd. for C<sub>25</sub>H<sub>23</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub> + H⁺: 457.1734, found: 457.1738. 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 mL/min, λ = 220 nm); t<sub>r</sub> = 9.33 and 16.08 min.

(3q)

(2R,4R,5R)-tert-butyl 1-(4-methoxyphenyl)-2-phenyl-5-(trifluoromethyl)imidazolinedine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 84% yield. [α]<sup>25</sup><sub>D</sub> = -22.3 (c 0.61, CHCl₃); <sup>1</sup>H NMR (CDCl₃, TMS, 400 MHz) δ 7.54 (d, J = 6.8 Hz, 2H), 7.39-7.33 (m, 3H), 6.75 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 8.8 Hz, 2H), 5.46 (s, 1H), 4.50 (q, J = 6.8 Hz, 1H), 4.18 (s, 1H), 3.71 (s, 3H), 2.63
(brs, 3H), 1.40 (s, 9H); $^{13}$C NMR (CDCl$_3$, TMS, 100 MHz) $\delta$ 169.2, 153.6, 140.3, 139.3, 128.9, 128.8, 126.7, 125.9 (q, $J = 281.0$ Hz), 116.7, 114.5, 82.7, 82.1, 65.8 (q, $J = 30.4$ Hz), 61.6, 55.5, 27.8; IR (KBr) $\nu$ 3320, 2955, 2844, 1755, 1510, 1442, 1360, 1228, 1123, 1035, 933, 825, 690 cm$^{-1}$. HRMS: calcd. for C$_{22}$H$_{25}$F$_3$N$_2$O$_3$ + H$^+$: 423.1890, found: 423.1905. The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak AD-H, $i$-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 220$ nm); $t_r = 5.56$ and 6.30 min.

(3r)

$(2R,4R,5R)$-methyl 5-(chlorodifluoromethyl)-2-(4-chlorophenyl)-1-(4-methoxyphenyl)imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 76% yield; $[\alpha]^{25}_D = -46.4$ (c 0.80, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 7.50 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.4$ Hz, 2H), 6.76 (d, $J = 9.2$ Hz, 2H), 6.72 (d, $J = 9.2$ Hz, 2H), 5.40 (s, 1H), 4.72 (dd, $J_1 = 5.2$ Hz, $J_2 = 13.6$ Hz, 1H), 4.37 (s, 1H), 3.80 (s, 3H), 3.72 (s, 3H); $^{13}$C NMR (CDCl$_3$, TMS, 100 MHz) $\delta$ 170.6, 154.4, 139.6, 137.4, 134.6, 129.9 (t, $J = 295.7$ Hz), 129.1, 128.3, 118.3, 114.5, 82.3, 71.2 (t, $J = 24.2$ Hz), 61.6, 55.4, 53.0; IR (KBr) $\nu$ 3340, 2951, 2927, 2844, 1744, 1710, 1595, 1513, 1445, 1360, 1160, 1131, 1040, 929, 815, 752, 669 cm$^{-1}$. HRMS: calcd. for C$_{19}$H$_{18}$Cl$_2$F$_2$N$_2$O$_3$ + H$^+$: 431.0735, found: 431.0743. 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 mL/min, $\lambda = 220$ nm); $t_r = 9.47$ and 12.17 min.

(3s)

$(2R,4R,5R)$-methyl 5-(bromodifluoromethyl)-1-(4-methoxyphenyl)-2-(naphtha-
alen-2-yl)imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 93% yield. \([\alpha]_{D}^{25} = -31.9 \ (c \ 1.81, \ CHCl_3); {^1}H \text{ NMR (CDCl}_3, \text{TMS, 400 MHz}) \delta 8.02 (s, 1H), 7.88-7.81 (m, 3H), 7.71 (dd, \(J_1 = 1.2 \text{ Hz, } J_2 = 8.4 \text{ Hz, } 1H\)), 7.51-7.46 (m, 2H), 6.78 (d, \(J = 9.2 \text{ Hz, } 2H\)), 6.73 (d, \(J = 9.2 \text{ Hz, } 2H\)), 5.58 (s, 1H), 4.84 (dd, \(J_1 = 4.4 \text{ Hz, } J_2 = 15.6 \text{ Hz, } 1H\)), 4.44 (s, 1H), 3.83 (s, 3H), 3.69 (s, 3H); \(13^C \text{ NMR (CDCl}_3, \text{TMS, 100 MHz}) \delta 170.6, 154.2, 139.8, 136.3, 133.6, 133.2, 128.8, 128.2, 127.7, 126.39, 126.3, 126.3, 124.5 (t, \(J = 309.8 \text{ Hz, } 1H\)), 124.2, 118.2, 114.4, 83.3, 72.7 (t, \(J = 21.3 \text{ Hz}\)), 62.0, 55.4, 53.0; IR (KBr) \nu 3347, 2957, 2927, 2855, 1742, 1513, 1450, 1220, 1178, 1038, 83.3, 72.7 (t, \(J = 21.3 \text{ Hz}\)), 62.0, 55.4, 53.0; IR (KBr) \nu 3347, 2957, 2927, 2855, 1742, 1513, 1450, 1220, 1178, 1038, 929, 756, 669, 590 cm\(^{-1}\). HRMS: calcd. for C\(_{23}\)H\(_{21}\)BrF\(_2\)N\(_2\)O\(_3\) + H\(^+\): 491.0776, found: 491.0769. 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 mL/min, \(\lambda = 220 \text{ nm}\)); \(t_r = 13.75 \text{ and } 17.03 \text{ min}\).

(2\(R\),4\(R\),5\(R\))-methyl 2-(4-chlorophenyl)-1-(4-methoxyphenyl)-5-(perfluoroethyl)-imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 80% yield; \([\alpha]_{D}^{25} = -63.2 \ (c \ 1.10, \ CHCl_3); {^1}H \text{ NMR (CDCl}_3, \text{TMS, 400 MHz}) \delta 7.49 (d, \(J = 8.4 \text{ Hz, } 2H\)), 7.35 (d, \(J = 8.4 \text{ Hz, } 2H\)), 6.75 (d, \(J = 9.2 \text{ Hz, } 2H\)), 6.66 (d, \(J = 9.2 \text{ Hz, } 2H\)), 5.32 (s, 1H), 4.76 (dd, \(J_1 = 7.6 \text{ Hz, } J_2 = 19.2 \text{ Hz, } 1H\)), 4.41 (s, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 2.65 (brs, 1H); \(13^C \text{ NMR (CDCl}_3, \text{TMS, 100 MHz}) \delta 170.5, 154.4, 139.7, 137.7, 134.7, 129.2, 128.2, 118.4, 114.6, 82.0, 63.9 (m), 60.6, 55.4, 53.1; IR (KBr) \nu 3347, 2953, 2940, 1744, 1711, 1595, 1513, 1424, 1361, 1176, 1132, 1040, 929, 815, 752, 669, 626 cm\(^{-1}\). HRMS: calcd. for C\(_{20}\)H\(_{18}\)ClF\(_3\)N\(_2\)O\(_3\) + H\(^+\): 465.0999, found: 465.1008. 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 mL/min, =
220 nm); t_r = 6.54 and 8.30 min.

(2R,4R,5R)-methyl 2-(4-chlorophenyl)-1-(4-methoxyphenyl)-5-(perfluoropropyl) imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 80% yield; [α]_{25}^{25} = -66.6 (c 1.30, CHCl₃); ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.49 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 8.8 Hz, 2H), 6.66 (d, J = 8.8 Hz, 2H), 5.34 (s, 1H), 4.86 (dd, J₁ = 4.4 Hz, J₂ = 21.6 Hz, 1H), 4.41 (s, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 2.65 (brs, 1H); ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 170.5, 154.4, 139.8, 137.7, 134.7, 129.2, 128.2, 118.3, 117.6 (q, J = 283.7 Hz), 114.6, 81.5, 64.1 (m), 60.7, 55.4, 53.1; IR (KBr) ν 3341, 2940, 1740, 1513, 1476, 1425, 1377, 1262, 1175, 1015, 929, 783, 669 cm⁻¹. HRMS: calcd. for C₂₁H₁₈ClF₇N₂O₃ + H⁺: 515.0967, found: 515.0968. 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 mL/min, = 220 nm); t_r = 5.72 and 6.75 min.

(2R,4R,5R)-methyl 2-(4-chlorophenyl)-1-(4-methoxyphenyl)-5-(perfluorohexyl) imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 88% yield; [α]_{25}^{25} = -30.9 (c 1.02, CHCl₃); ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.49 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 8.8 Hz, 2H), 6.66 (d, J = 8.8 Hz, 2H), 5.35 (s, 1H), 4.88 (dd, J₁ = 4.0 Hz, J₂ = 22.4 Hz, 1H), 4.42 (s, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 2.65 (brs, 1H); ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 170.5,
154.3, 139.8, 137.7, 134.7, 129.2, 128.2, 118.2, 114.6, 81.5, 64.3 (m), 60.8, 55.4, 53.0;
IR (KBr) ν 3340, 2950, 2834, 1744, 1515, 1446, 1425, 1144, 1016, 929, 771, 669, cm⁻¹. HRMS: calcd. for C₂₄H₁₈ClF₁₃N₂O₃ + H⁺: 665.0871, found: 665.0861. The product was analyzed by HPLC to determine the enantiomeric excess: 98% ee (Chiralcel OD-H, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 220 nm); tᵣ = 4.21 and 4.77 min.

(5a)

(2R,4R,5R)-methyl 1-(4-methoxyphenyl)-2-propyl-5-(trifluoromethyl)imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 80% yield. d.r. = 10:1; [α]²⁵ D = -26.1 (c 0.42, CHCl₃); ¹H NMR (CDCl₃, TMS, 400 MHz) δ 6.94 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 4.47-4.46 (m, 1H), 4.26 (q, J = 7.2 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 1.85-1.82 (m, 1H), 1.44-1.40 (m, 3H), 0.94 (t, J = 6.8 Hz, 3H); ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 171.2, 155.1, 140.5, 125.6 (q, J = 280.0 Hz), 120.9, 114.6, 79.8, 67.2 (q, J = 30.0 Hz), 60.5, 55.5, 52.9, 36.8, 18.1, 14.1; IR (KBr) ν 3336, 2957, 2927, 2855, 1742, 1513, 1450, 1220, 1038, 929, 756, 669 cm⁻¹. HRMS: calcd. for C₁₆H₂₁F₃N₂O₃ + H⁺: 347.1577, found: 347.1584. The product was analyzed by HPLC to determine the enantiomeric excess: 89% ee (Chiralpak AS-H, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 220 nm); tᵣ = 5.14 and 6.13 min.

(5b)

(2R,4R,5R)-methyl 2-butyl-1-(4-methoxyphenyl)-5-(trifluoromethyl)imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described
above in 76% yield. d.r. > 20:1; \([\alpha]_{25}^{25} = -14.3\) (c 0.83, CHCl₃); \(^1\)H NMR (CDCl₃, TMS, 400 MHz) \(\delta 6.93\) (d, \(J = 9.2\) Hz, 2H), 6.85 (d, \(J = 9.2\) Hz, 2H), 4.46-4.45 (m, 1H), 4.26 (q, \(J = 7.2\) Hz, 1H), 4.21 (s, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 1.90-1.85 (m, 1H), 1.51-1.29 (m, 5H), 0.88 (t, \(J = 7.2\) Hz, 3H); \(^1^3\)C NMR (CDCl₃, TMS, 100 MHz) \(\delta 171.2, 155.1, 140.4, 125.9\) (q, \(J = 279.8\) Hz), 120.8, 114.7, 80.0, 67.1 (q, \(J = 29.9\) Hz), 60.5, 55.5, 52.9, 34.3, 26.9, 22.7, 14.0; IR (KBr) v 3368, 1736, 1516, 1448, 1425, 1210, 1044, 929, 705, 656 cm\(^{-1}\). HRMS: calcd. for C\(_{17}\)H\(_{23}\)F\(_3\)N\(_2\)O\(_3\) + H\(^+\): 361.1734, found: 361.1742. The product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (Chiralpak AD-H, i-propanol/hexane = 5/95, flow rate 1.0 mL/min, \(\lambda\) = 220 nm); \(t_r\) = 6.34 and 7.30 min.

(5c)

\((2R,4R,5R)\)-methyl 1-(4-methoxyphenyl)-2-pentyl-5-(trifluoromethyl)imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 85% yield. d.r. = 17:1; \([\alpha]_{25}^{25} = -19.0\) (c 0.55, CHCl₃); \(^1\)H NMR (CDCl₃, TMS, 400 MHz) \(\delta 6.93\) (d, \(J = 8.8\) Hz, 2H), 6.86 (d, \(J = 8.8\) Hz, 2H), 4.46-4.45 (m, 1H), 4.26 (q, \(J = 7.2\) Hz, 1H), 4.21 (s, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 1.87-1.85 (m, 1H), 1.51-1.29 (m, 7H), 0.88 (t, \(J = 6.8\) Hz, 3H); \(^1^3\)C NMR (CDCl₃, TMS, 100 MHz) \(\delta 171.2, 155.1, 140.4, 125.6\) (q, \(J = 281.6\) Hz), 120.8, 114.7, 80.0, 67.1 (q, \(J = 30.1\) Hz), 60.5, 55.5, 52.9, 34.6, 31.8, 24.5, 22.6, 14.0; IR (KBr) v 3335, 1756, 1512, 1469, 1255, 1032, 917, 740, 669 cm\(^{-1}\). HRMS: calcd. for C\(_{18}\)H\(_{25}\)F\(_3\)N\(_2\)O\(_3\) + H\(^+\): 375.1890, found: 375.1883. The product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (Chiralpak AD-H, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, \(\lambda\) = 220 nm); \(t_r\) = 5.34 and 5.88 min.
(2R,4R,5R)-methyl 5-(bromodifluoromethyl)-1-(4-methoxyphenyl)-2-propylimidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 80% yield. d.r. = 15:1; [α]$_{D}^{25}$ = -12.6 (c 0.27, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 400 MHz) δ 7.03 (d, $J$ = 8.8 Hz, 2H), 6.86 (d, $J$ = 8.8 Hz, 2H), 4.38-4.33 (m, 2H), 4.26 (s, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 1.86-1.80 (m, 1H), 1.48-1.45 (m, 2H), 1.32-1.30 (m, 3H), 0.88 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (CDCl$_3$, TMS, 100 MHz) δ 171.3, 156.0, 140.3, 125.3 (t, $J$ = 309.0 Hz), 123.5, 114.6, 81.8, 74.5 (t, $J$ = 20.3 Hz), 62.1, 55.5, 52.9, 34.1, 26.9, 22.8, 14.0; IR (KBr) ν 3317, 2957, 1740, 1515, 1477, 1425, 1250, 1023, 755, 670 cm$^{-1}$. HRMS: calcd. for C$_{17}$H$_{23}$BrF$_2$N$_2$O$_3$ + H$: 421.0933, found: 421.0935. The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak AD-H, i-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 220 nm); t$_r$ = 6.23 and 6.90 min.

(5e)

(2R,4R,5R)-methyl 5-(bromodifluoromethyl)-2-ethyl-1-(4-methoxyphenyl)imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 76% yield. d.r. = 10:1; [α]$_{D}^{25}$ = -20.7 (c 0.15, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 400 MHz) δ 7.03 (d, $J$ = 8.8 Hz, 2H), 6.86 (d, $J$ = 8.8 Hz, 2H), 4.38-4.33 (m, 2H), 4.26 (s, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 1.86-1.79 (m, 1H), 1.47-1.26 (m, 7H), 0.87 (t, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (CDCl$_3$, TMS, 100 MHz) δ 171.4, 156.0, 140.3, 123.5, 114.6, 81.9, 74.5 (t, $J$ = 20.6 Hz), 62.1, 55.5, 52.9, 34.4, 31.9, 24.5, 22.5, 14.0; IR (KBr) ν 2958, 2924, 1743, 1512, 1477, 1435, 1215, 1133, 1021, 935, 783, 670 cm$^{-1}$. HRMS: calcd. for C$_{18}$H$_{25}$BrF$_2$N$_2$O$_3$ + H$: 435.1089, found: 435.1076. The
product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (Chiralpak AD-H, $i$-propanol/hexane = 5/95, flow rate 1.0 mL/min, $\lambda = 220$ nm); $t_r = 6.08$ and 6.84 min.

(2R,4R,5R)-methyl 1-(4-methoxyphenyl)-2-phenethyl-5-(trifluoromethyl)imidazole-4-carboxylate

The title compound was prepared according to the general procedure as described above in 80% yield. d.r. > 20:1; $[\alpha]^{25}_D = -34.5$ (c 0.95, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 7.29-7.25 (m, 2H), 7.20-7.17 (m, 3H), 6.91 (d, $J = 9.2$ Hz, 2H), 6.83 (d, $J = 9.2$ Hz, 2H), 4.51-4.49 (m, 1H), 4.26 (q, $J = 7.2$ Hz, 1H), 4.23 (s, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 2.84-2.71 (m, 1H), 2.72-2.69 (m, 1H), 2.18-2.15 (m, 1H), 1.80-1.74 (m, 1H); $^{13}$C NMR (CDCl$_3$, TMS, 100 MHz) $\delta$ 171.2, 155.4, 141.3, 140.3, 128.4, 128.3, 126.0, 125.6 (q, $J = 279.9$ Hz), 121.4, 114.7, 79.6, 67.3 (q, $J = 30.1$ Hz), 60.6, 55.5, 52.9, 36.1, 31.0; IR (KBr) v 2956, 2840, 1743, 1603, 1512, 1480, 1439, 1214, 1133, 1036, 929, 783, 771, 669 cm$^{-1}$. HRMS: calcd. for C$_{21}$H$_{23}$F$_3$N$_2$O$_3$ + Na$: 431.1553$, found: 431.1568. The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak AD-H, $i$-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 220$ nm); $t_r = 7.77$ and 8.76 min.

(2R,4R,5R)-methyl 2-isopropyl-1-(4-methoxyphenyl)-5-(trifluoromethyl)imidazole-4-carboxylate

The title compound was prepared according to the general procedure as described above in 76% yield. d.r. > 20:1; $[\alpha]^{25}_D = -17.5$ (c 0.61, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 7.06 (d, $J = 9.2$ Hz, 2H), 6.85 (d, $J = 9.2$ Hz, 2H), 4.35 (d, $J = 3.6$...
Hz, 1H), 4.18-4.13 (m, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 1.94-1.89 (m, 1H), 0.99 (d, $J = 6.8$ Hz, 3H), 0.94 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, TMS, 100 MHz) $\delta$ 171.6, 156.1, 141.1, 125.7 ($q, J = 280.1$ Hz), 123.9, 114.6, 85.1, 68.6 ($q, J = 29.7$ Hz), 60.5, 55.5, 52.9, 29.7, 19.2, 14.6; IR (KBr) $\nu$ 3317, 2957, 2436, 1742, 1603, 1479, 1425, 1214, 1133, 1036, 929, 669 cm$^{-1}$. HRMS: calcd. for C$_{16}$H$_{21}$F$_3$N$_2$O$_3$ + H$^+$: 347.1577, found: 347.1585. The product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (Chiralpak AS-H, $i$-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda$ = 220 nm); $t_r$ = 4.79 and 5.33 min.

(5h)

(2R,4R,5R)-methyl 2-cyclohexyl-1-(4-methoxyphenyl)-5-(trifluoromethyl)imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 76% yield. d.r. > 20:1; $[\alpha]^{25}_D = -32.3$ (c 0.56, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 7.03 (d, $J = 8.8$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 4.35 (d, $J = 4.0$ Hz, 1H), 4.17-4.13 (m, 2H), 3.79 (s, 3H), 3.78 (s, 3H), 2.60 (brs, 1H), 1.92-1.89 (m, 1H), 1.79-1.65 (m, 5H), 1.19-1.12 (m, 4H), 0.95-0.92 (m, 1H); $^{13}$C NMR (CDCl$_3$, TMS, 100 MHz) $\delta$ 171.5, 155.8, 141.3, 125.6 ($q, J = 279.8$ Hz), 123.2, 114.5, 84.5, 68.3 ($q, J = 29.8$ Hz), 60.5, 55.4, 52.8, 40.2, 30.0, 26.6, 26.5, 26.1, 25.7; IR (KBr) $\nu$ 3317, 2957, 2434, 1740, 1601, 1469, 1423, 1210, 1131, 1034, 929, 669 cm$^{-1}$. HRMS: calcd. for C$_{19}$H$_{25}$F$_3$N$_2$O$_3$ + H$^+$: 387.1890, found: 387.1894. The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralpak AD-H, $i$-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda$ = 220 nm); $t_r$ = 5.43 and 6.32 min.
(2R,4R,5R)-methyl 2-isobutyl-1-(4-methoxyphenyl)-5-(trifluoromethyl)imidazolidine-4-carboxylate

The title compound was prepared according to the general procedure as described above in 85% yield. d.r. = 15:1; $[\alpha]_{D}^{25} = -37.3$ (c 1.12, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 6.92 (d, $J = 9.2$ Hz, 2H), 6.85 (d, $J = 9.2$ Hz, 2H), 4.56-4.54 (m, 1H), 4.24 (q, $J = 7.2$ Hz, 1H), 4.21 (s, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 1.84-1.71 (m, 2H), 1.35-1.33 (m, 1H), 0.98 (d, $J = 6.4$ Hz, 3H), 0.93 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, TMS, 100 MHz) $\delta$ 171.1, 154.9, 140.5, 125.6 (q, $J = 279.9$ Hz), 120.4, 114.6, 78.5, 67.0 (q, $J = 30.0$ Hz), 60.6, 55.5, 52.8, 44.3, 25.3, 23.7, 22.0; IR (KBr) $\nu$ 2955, 2434, 1741, 1608, 1468, 1421, 1210, 1135, 1037, 929, 668 cm$^{-1}$. HRMS: calcd. for C$_{17}$H$_{23}$F$_3$N$_2$O$_3$ + H$: 361.1734$, found: 361.1737. The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralpak AS-H, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 220$ nm); t$_R$ = 4.81 and 5.16 min.

V. Synthetic Transformtions.

Due to high volatility of (2R,3R)-2,3-diamino-4,4,4-trifluoro-butanooate, oxidative cleavage of the PMP group could be performed as below: Firstly, diamine 6 was obtained by acidic hydrolysis of the corresponding cycloadduct 3a in good yield. The diamine 6 was further transformed into cyclic urea 7 with triphosphoghen, then treatment with Ce(NH$_4$)$_2$(NO$_3$)$_6$ gave the derived amide 8 without loss of the diastereo-/enantiomeric excess.

3a (207 mg, 0.5 mmol) was dissolved in 3 mL of methanol at room temperature followed by the addition of TsOH·H$_2$O (380 mg, 2 mmol). The reaction mixture was
stirred until starting material was consumed (monitored by TLC) and neutralized the mixture by Na₂CO₃. Then the mixture was partitioned between ethyl acetate and water, then the organic layer was washed with brine, dried over MgSO₄, and concentrated in vacuo then the organic solvent was removed and the residue was purified by column chromatography to give compound 6 in 81% yield.

(2R,3R)-methyl 2-amino-4,4,4-trifluoro-3-((4-methoxyphenyl)amino)butanoate

\([\alpha]^{25}_D = -41.2 (c 0.73, \text{CHCl}_3); \) ¹H NMR (CDCl₃, TMS, 300 MHz) δ 6.76 (d, \(J = 8.7\) Hz, 2H), 6.66 (d, \(J = 8.7\) Hz, 2H), 4.54-4.51 (m, 1H), 4.43-4.36 (m, 1H), 4.12 (s, 1H), 3.73 (s, 3H), 3.59 (s, 3H), 1.78 (brs, 2H); ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 171.7, 153.1, 139.9, 125.6 (q, \(J = 283.1\) Hz), 116.0, 114.7, 58.4 (q, \(J = 27.9\) Hz), 55.6, 52.7, 52.6; IR (KBr) ν 3368, 2951, 1746, 1516, 1453, 1218, 1035, 929, 669 cm⁻¹. 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 mL/min, λ = 220 nm); \(t_r = 11.07\) and 20.46 min.

To a solution of 6 (100 mg, 0.34 mmol) and triethylamine (141 µL, 1.02 mmol) in dry CH₂Cl₂(15.0 mL) under nitrogen at 0 °C was added a solution of triphosgene (100 mg, 0.34 mmol) in dry CH₂Cl₂ dropwise. The reaction mixture was warmed to room temperature and stirred until the starting material was consumed completely as indicated by TLC. Then the reaction was quenched and purified by column chromatography to give the cyclic urea 7.

(4R,5R)-methyl 1-(4-methoxyphenyl)-2-oxo-5-(trifluoromethyl)imidazolidine-4-carboxylate

\([\alpha]^{25}_D = +18.8 (c 0.16, \text{CHCl}_3); \) ¹H NMR (CDCl₃, TMS, 300 MHz) δ 7.24 (d, \(J = 9.0\) Hz, 2H), 6.92 (d, \(J = 9.0\) Hz, 2H), 5.85 (s, 1H), 4.91-4.88 (m, 1H), 4.33 (d, \(J = 2.4\) Hz,
1H), 3.89 (s, 3H), 3.81 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), TMS, 75 MHz) \(\delta\) 169.7, 158.9, 158.2, 129.3, 126.9, 123.8 (q, \(J = 281.5\) Hz), 114.3, 61.1 (q, \(J = 32.4\) Hz), 55.3, 53.3, 51.9; IR (KBr) \(\nu\) 2917, 2846, 2335, 1722, 1515, 1423, 1241, 1166 cm\(^{-1}\). HRMS: calcd. for C\(_{13}\)H\(_{13}\)F\(_3\)N\(_2\)O\(_4\) + H\(^+\): 319.0897, found: 319.0900. The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee (Chiralpak AD-H, \(i\)-propanol/hexane = 40/60, flow rate 1.0 mL/min, \(\lambda = 220\) nm); \(t_r = 14.87\) and 16.88 min.

To a solution of 7 (92 mg, 0.29 mmol) in dry acetonitrile (2.0 mL) was added dropwise a solution of CAN (477 mg, 0.87 mmol) in H\(_2\)O (1.0 mL) at 0 °C. The reaction was completed immediately and quenched by the addition of saturated NH\(_4\)Cl aqueous solution. The phases were separated and the aqueous phase was extracted with ethyl acetate. The combined organic phases were dried over sodium sulfate and concentrated under vacuum. The residue was purified by chromatography to give 8 as a white solid.

(4\(R\),5\(R\))-methyl 2-oxo-5-(trifluoromethyl)imidazolidine-4-carboxylate

[\(\alpha\)]\(^{25}\)\(_D\) = -35.0 (c 0.20, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), TMS, 300 MHz) \(\delta\) 6.92 (s, 1H), 6.41 (s, 1H), 4.46 (m, 1H), 4.33 (d, \(J = 3.2\) Hz, 1H), 3.85 (s, 3H); \(^{13}\)C NMR (DMSO-d\(_6\), TMS, 100 MHz) \(\delta\) 170.7, 161.1, 124.7 (q, \(J = 279.4\) Hz), 55.2 (q, \(J = 32.2\) Hz), 53.4, 52.9; IR (KBr) \(\nu\) 3243, 2922, 2360, 2341, 1724, 1443, 1240, 1176, 1145 cm\(^{-1}\). HRMS: calcd. for C\(_6\)H\(_7\)F\(_3\)N\(_2\)O\(_3\) + Na\(^+\): 235.0296, found: 235.0301. The product was analyzed by GC to determine the enantiomeric excess: 97% ee (\(\beta\)-dex 325 column, 30 m x 0.25 mm x 0.25 \(\mu\)m, column temperature: 170 °C, carrier gas: N\(_2\), 1 mL/min); \(t_r = 9.84\) and 14.29 min.

VI. Linear Effect for the 1,3-Dipolar Cycloaddition of Trifluoromethylated Imine 1a with Imino Ester 2a Catalyzed by Cu(CH\(_3\)CN\(_3\))BF\(_4\)(\(S,R_p\))-PPFOMe Complex.
Ee of \((S,R_p)-\text{L5}\) were determined by HPLC: Chiralpak AD-H, \(i\)-propanol/hexane = 1/99, flow rate 0.5 mL/min, \(\lambda = 254\) nm; \(t_r = 16.01\) and 21.18 min.

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VII. Proposed Transition States of the \(\text{exo'}\)-Selectivity for Asymmetric 1,3-Dipolar Cycloaddition of Imino Esters with Fluorinated Imines.

Scheme S1. Postulated catalytic cycle for Cu(I)-catalyzed asymmetric 1,3-DC of azomethine ylide with fluorinated imines.
Based on the relative and absolute configuration of (2R,4R,5R)-3s and previous studies, a plausible stepwise mechanism was proposed to rationalize the observed exo'-selectivity for this 1,3-DC. The in situ-formed azomethine ylide is coordinated to the Cu complex leading to the catalytically active species (A) based on the linear correlation results. Initial Mannich addition of the metalloazomethine ylide (A) to the Re face (C=N) of the fluorinated imine 1a through the gauche conformation generates the zwitterionic intermediate (B), which could be facilitated by the possible coordination interaction between the imino group of 1a and the Cu(I) center. After the Mannich reaction, the copper atom spontaneously switches from imino ester to NPMP for forming the six-membered chair-like species (C). Before the subsequent intramolecular cyclization, the C-N single bond must rotate into the species (D) hence the amino unit approaches the Re face of the imine moiety to give the exo'-diastereomer, in which the substituents at 2 and 4 position of imidazolidine ring are arranged at trans configuration. Nevertheless, the real catalytic mechanism still needs further investigation.

VIII. References.

IX. $^1$H NMR and $^{13}$C NMR Spectra.
**XII. HPLC Chromatograms**

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**End of Report**
Electronic Supplementary Material (ESI) for Chemical Communications

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Data File: D:\L08\DATA6\QR\LQH-7-12\LQH-7-12C 2012-01-29 14-26-59,075-3302L.D
Sample Name: LQH-7-12C

Area Percent Report

Signal 1: VH1 A, Wavelength=250 nm

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Totals : 5.7664e4 947.15192

End of Report **
**Data File D:\LC\DIONEX\LC\L0H-7-19\L0H-7-13 2012-03-29 22-03-21\064-000L.D**

**Sample Name:** L0K-7-130

**Acq. Operator:** LCN  **Seq. Line:** 3

**Injection Date:** 3/29/2012 10:59:22 PM  **Inj.:** 1

**Injection Volume:** 5 µL

**Acq. Method:** D:\LC\2012D\DIONEX\L0H-7-13\L0H-7-13 2012-03-29 22-03-21\AS5-20-90-10ML-20GH-10MIL.E

**Last Changed:** 3/29/2012 12:22:28 PM by PE

**Analysis Method:** D:\LC\DIONEX\LC\L0H-7-13\L0H-7-13 2012-03-29 22-03-21\064-000L.D\L0H-10-90-10ML-20GH-10MIL.WK

**Last changed:** 5/5/2012 4:24:36 PM by ligh

**Method Info:** AE5-90-50-2ML-24AM-20ML

---

**Area Percent Report**

---

**Sorted By:** Signal

**Multiplier:** 1.0000

**Baseline:** 1.0000

Use Multiplier & Baseline Factor with ISDs

**Signal 1: WAX1 A, Wavelength=220 mm**

<table>
<thead>
<tr>
<th>RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.632</td>
<td>0.045</td>
<td>1209.398</td>
<td>0.997</td>
</tr>
<tr>
<td>2</td>
<td>16.577</td>
<td>1.185</td>
<td>691.494</td>
<td>91.256</td>
</tr>
</tbody>
</table>

**Total:** 4137427 639.9227

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**Instruments: 1 5/5/2012 4:24:36 PM ligh**

Page 1 of 1
Area Percent Report

<table>
<thead>
<tr>
<th>Signal</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.347</td>
<td>0.243</td>
<td>1.678</td>
<td>0.656</td>
</tr>
<tr>
<td>2</td>
<td>14.532</td>
<td>0.000</td>
<td>1.668</td>
<td>0.000</td>
</tr>
<tr>
<td>Totals</td>
<td>3.347</td>
<td>0.243</td>
<td>0.656</td>
<td></td>
</tr>
</tbody>
</table>

End of Report
Area Percent Report

Signal 1: WAX1 A, Wavelength=280 nm

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU]</td>
<td>[mAU]</td>
</tr>
<tr>
<td>1</td>
<td>0.469</td>
<td>0.598</td>
<td>244.836</td>
<td>6.701</td>
</tr>
<tr>
<td>2</td>
<td>12.168</td>
<td>0.799</td>
<td>814.114</td>
<td>283.633</td>
</tr>
<tr>
<td>Totals</td>
<td></td>
<td></td>
<td>1.475</td>
<td>290.416</td>
</tr>
</tbody>
</table>

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

INSTRUMENT 1 9/30/2012 7:20:05 PM THL
Electronic Supplementary Material (ESI) for Chemical Communications
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Data File 3:ICLRCRQR1JLQ7-7-52LQ17-7-52 2012-04-16 17-26-24,076-0391,LD
Sample No: LQR-7-52B

==================================================================================================
Arq. Operation : LQR Seq. Line : 3
Injection Date : 4/16/2012 2:15:54 PM Inj V: 1
Inj Volume : 5 μl
Arq. Method : D:LLCR-IQRQR1JLQ7-7-52LQ17-7-52 2012-04-16 17-26-24,076-0391,LD
Last changed : 4/16/2012 2:16:37 PM by LQR
(modified after loading)
Analysis Method : D:LLCR-IQRQR1JLQ7-7-52LQ17-7-52 2012-04-16 17-26-24,076-0391,LD
Last changed : 5/5/2012 1:36:32 PM by LQR
(modified after loading)

Area Percent Report

---

Signal at Wavelength: 250 nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>13.740 Br</td>
<td>1.241</td>
<td>3222.03198</td>
<td>109.82844</td>
</tr>
<tr>
<td>2</td>
<td>13.030 V</td>
<td>1.240</td>
<td>1248.30533</td>
<td>4047.0273</td>
</tr>
</tbody>
</table>

Totals: 1.29688s 1401.42817

---

End of Report

Instrument: LQR-7-52B 4:36:08 PM

Page 1 of 1
Area Percent Report

Sorted by: Signal
Multiplier: 1.0000
Baseline: 1.0000

Use Multiplier & Baseline Factor with ISDBs

Signal 1: Wavelength=220 mm

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.539</td>
<td>0.3816</td>
<td>166.4786</td>
<td>6.99069</td>
<td>1.3637</td>
</tr>
<tr>
<td>2</td>
<td>8.304</td>
<td>0.6017</td>
<td>10.023266</td>
<td>275.83178</td>
<td>99.3883</td>
</tr>
</tbody>
</table>

Total: 1.035308e+4 286.84246

xxv End of Report xxx
Data File: D:\COMAR\LQM-5-104\LQM-5-104_2012-03-03_10-27-07_007-0201.D
Sample File: LQM-5-104

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

Area Percent Report

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

Settled By: Signal
Multiplier: 1.0000

Dilution: 1.0000

Use Multiplier & Dilution Factor with ISTDs

Signal 1: 260 A, Wavelength=260 nm

Peak RetTime Type Width Area Height Area %
# [min] [min] [mAU] [mAU] [mAU] %
--- | --- | --- | --- | --- | ---
1 | 6.00 | 0.4179 | 1.0010 | 0.0034 | 141.7563 | 0.0034
2 | 6.704 | 0.3973 | 0.3000 | 0.0034 | 376.0499 | 0.0034
Totals: 1921.0263

*** End of Report ***
Data File: D:\LC\DATA\LCR\LQK8-107\LQK8-107-00H 2012-09-01 00-30-57,092-0201.D
Sample Name: LQK8-107-00H

Injection Date: 9/1/2012 9:21:40 AM
Inj: 1

Last Changed: 9/1/2012 9:21:30 AM by LQK

Analysis Method: D:\LC\DATA\LCR\LQK8-107\LQK8-107-00H 2012-09-01 00-30-57,092-0201.D (modified after loading)

Signal 1: Wavelength=220 nm (modified after loading)
Peak RetTime Type Width Area Height Area
[sec] [min] [min] [mAU] [mAU] [mAU] [mAU]
1 4.38 [MIN] 0.183 [MIN] 1.47639e6 1300 53047 499439
2 4.747 [MIN] 0.269G 1.48229e6 1300 38440 501391

Totals: 2.95827e6 2340 94287

End of Report

INSTRUMENT 1 9/4/2012 1:01:04 PM LQK

Page 1 of 1
**Electronic Supplementary Material (ESI) for Chemical Communications**

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**Data File:** 201205201137-005-0061.D

**Sample Date:** 2012-05-20 11:37:00

**Sample Name:** IQM-7-110

**Injection Date:** 5/18/2012 1:50:19 PM

**Injection Volume:** 5 µl

**Inj:** 1

**Acq. Method:** D:	LC DAD<style> .highlight { color: black; background-color: white; } </style> YL\YL-2-60 YL-2-64 2012-05-20 11:37-48.665-665.1 HOD H (AST-20-90-10ML-200W-100mR, 20)

**Last Changed:** 6/17/2011 8:50:19 AM by rsl

**Analysis Method:** D:	LC DAD YL\YL-2-60 YL-2-64 2012-05-20 11:37-48.665-665.1 HOD H (AST-20-90-10ML-200W-100mR, 20)

**Last changed:** 6/16/2012 3:57:51 PM by YDC

**modified after loading**

---

**Area Percent Report**

---

**Sorted By:** Signal

**Multiplier:** 1.0000

**Dilution:** 1.0000

**Use Multiplier & Dilution factor with Instrument**

**Signal 1: UV at λ, Wavelength=210 nm**

<table>
<thead>
<tr>
<th>Peak Number</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Max</td>
<td>0.2482</td>
<td>22.6527</td>
<td>1.4984</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Max</td>
<td>0.5213</td>
<td>338.5591</td>
<td>94.5085</td>
<td></td>
</tr>
</tbody>
</table>

**Totals:**

538.5591, 373.38192

---

**End of Report**

---

**Instrument 1:** 6/26/2012 8:57:39 PM YDC

---

S140
Electronic Supplementary Material (ESI) for Chemical Communications

Data File 5:\CHEMISTRY\(QZ4-LQ4-0-55)\(QZ4-8-55C 2012-07-05 09-16-50, 074-020L.D
Sample Name: QZ4-8-55C

Section: Area Percent Report

Signal 1: Vmax, Wavelength-210 nm

Peak Retime Type Width Area Height Area
# [min] [min] [nm] [nm] [%] [nm] [%]
--- --- --- --- --- --- ---
1 5.94E MF 0.28E9 2393.5626 138.47216 50.1718
2 6.71E MF 0.31E1 2367.6386 126.03162 49.5092

Totals: 6781.69132 264.59374

*** End of Report ***

Instruments 1 7/24/2012 6:12:13 PM 1gh

Page 1 of 1
**Area Percent Report**

**Sorted By**: Signal
**Multiplier** : 1.0000
** Dilution** : 1.0000

Use Multiplier & Dilution Factor with IS70c

**Signal 1**: Violet A, Wavelength=250 nm

<table>
<thead>
<tr>
<th>Peak #</th>
<th>RetTime Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.711 IV</td>
<td>0.2359</td>
<td>176.97564</td>
<td>8.44886</td>
<td>4.0093</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>8.757 VM</td>
<td>0.3183</td>
<td>691.11279</td>
<td>188.87128</td>
<td>91.9138</td>
<td></td>
</tr>
<tr>
<td>Totals</td>
<td>419.09943</td>
<td>197.2504</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**End of Report**

**Instrument**: 6/26/2012 3:16:19 PM YDC
Electronic Supplementary Material (ESI) for Chemical Communications

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Data File: D:\LQM\LQM-7-73\LQM-7-73 2012-05-05 06-35-24,094-0291,0D
Sample File: LQM-7-73

*********************************************************
:
Seq. Line: 2
:
Injection Date: 5/7/2012 09:47:17 AM
:
Inj. Volume: 5 µL
:
Acq. Method: D:\LQM\LQM-7-73\LQM-7-73 2012-05-05 06-35-24,094-0291,0D

Last Changed: 5/7/2012 09:47:17 AM by LQM

Analysis Method: D:\LQM\LQM-7-73\LQM-7-73 2012-05-05 06-35-24,094-0291,0D

Last changed: 5/7/2012 11:13:04 PM by FK

[Graph of UV/Vis spectrum]

**End of Report**
### Report

**Area Percent Report**

**Sorted By**: Signal  
**Multiplier**: [ ]  
**Dilution**: [ ]  

**Signal**: 6  
**Wavelength**: 220 nm

**Peak Profile Type**  |  **Width**  |  **Area**  |  **Height**  |  **Area %**
---|---|---|---|---
1 | 1.0100 min | 0.6823 | 32.48374 | 0.975849 | 1.6170

**Totals**: 21086.37089  
22.42973

---

**End of Report**
Area Percent Report

Sorted by:  Signal
Multiplier:  1.0000
Division:  1.0000
Use Multiplier & Division factor with ISIDs

Signal 1: VN1 A, Wavelength=220 nm

<table>
<thead>
<tr>
<th>Peak #</th>
<th>Ret Time</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.190</td>
<td>0.628</td>
<td>235</td>
<td>63.010</td>
<td>40.163</td>
</tr>
<tr>
<td>2</td>
<td>15.287</td>
<td>0.713</td>
<td>180</td>
<td>49.154</td>
<td>32.967</td>
</tr>
<tr>
<td>Total</td>
<td>1.14928e4</td>
<td></td>
<td>291</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**End of Report**

INSTRUMENT 1 2/28/2013 5:30:10 PM FK
Area Percent Report

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<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.866 min</td>
<td>1</td>
<td>0.144</td>
<td>50.153</td>
<td>739.819</td>
<td>41.254</td>
</tr>
</tbody>
</table>

Total: 1661.54844 87.77185
**Area Percent Report**

<table>
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<tr>
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<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Height</th>
<th>Area</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.841</td>
<td>C1</td>
<td>0.140</td>
<td>0.0175</td>
<td>0.014</td>
<td>3.36</td>
</tr>
<tr>
<td>2</td>
<td>14.193</td>
<td>C1</td>
<td>0.137</td>
<td>0.0175</td>
<td>0.014</td>
<td>3.36</td>
</tr>
</tbody>
</table>

**Total** |

|        | 0.62 | 16.45%

---

**End of Report**

---

**Instrument** 2 2/20/2013 10:24:38 PM LOH