Supplementary Information:

Highly Diastereoselective Friedel-Crafts reaction of Arenes with an N-tert-Butanesulfinylimino Ester: Efficient Synthesis of Optically Active α-Arylglycines

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1. General

Unless otherwise specified, all reactions were carried out in flame-dried glassware with magnetic stirring under an atmosphere of nitrogen. Solvents were dried and distilled by standard procedures. NMR spectra were recorded on a Varian spectrometer (300 MHz for $^1$H, and 100 MHz for $^{13}$C). Chemical shifts are reported in δ ppm referenced to an internal SiMe$_4$ standard for $^1$H NMR and chloroform-d (δ 77.16) for $^{13}$C NMR. HPLC was performed on a JASCO 2000 instrument by using Daicel AS-H, AD-H and AD-3 column with 2-propanol/hexane as the eluent at 214 nm.

2. General Procedure for In(OTf)$_3$-catalyzed Friedel-Crafts Reaction of Arenes 1 with N-tert-Butanesulfinylimino Ester 2.

\[
\begin{align*}
\text{Ar-H} + \text{O=S} \quad & \quad \text{In(OTf)$_3$ (30 mol%)} \\
\text{H} \quad \quad \text{COOEt} \quad & \quad \text{CH$_2$Cl$_2$, rt} \\
\text{N} \quad \quad \quad \quad & \quad 1-8h \\
\text{S} \quad \quad \quad \quad & \quad \text{EtO$_2$C} \\
\end{align*}
\]

Under nitrogen atmosphere, In(OTf)$_3$ (0.075 mmol, 30 mol%) was placed into a glass reaction vessel, glyoxylate imine 2 (0.25 mmol) in 2 mL of dry CH$_2$Cl$_2$ and arene 1 (0.375 mmol) were added successively. The mixture was stirred at room temperature and monitored by TLC. When the reaction was over, a saturated aq. NH$_4$Cl was added and the mixture was extracted with CH$_2$Cl$_2$ (10 mL×3). The combined organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated. The residue was purified by silica gel flash chromatography to afford the corresponding α-arylglycine product 3.


The diastereoselectivities of the α-arylglycine products were measured as enantiomeric excess for their acetate or N-sulfonylate derivatives after the removal or oxidation of the sulfinyl group by chiral HPLC analysis. α-Arylglycines 3e and 4 were converted to the corresponding N-sulfonylate, all others were converted to their acetate. The HPLC reference compound was a mixture of related products consisting of R and S enantiomers.
4. Characterization and HPLC of the Obtained Chiral α-Arylglycines

(R)-ethyl 2-(2,4-dimethoxyphenyl)-2(1(R))-1,1-dimethylethylsulfinamido)acetate (3a).

89% yield, yellow oil. $^1$H NMR (300 MHz, CDCl$_3$): δ 1.15 (s, 9H), 1.18 (t, 3H), 3.77 (s, 3H), 3.79 (s, 3H), 4.13-4.20 (m, 2H), 4.51 (d, $J =$ 4.2 Hz, 1H), 5.19 (d, $J =$ 4.2 Hz, 1H), 6.43-6.45 (m, 2H), 7.10 (d, $J =$ 9.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 14.14, 22.51, 55.39, 55.55, 55.82, 56.00, 61.85, 98.94, 104.22, 118.74, 130.12, 158.21, 161.03, 172.03; ESI-MS ($m/z$, %) 344 [M+H]$^+$; ESI-HRMS calcd for C$_{16}$H$_{25}$NNaO$_5$S [M+Na]$^+$ 366.1351, found 366.1351.

HPLC (acetate): 98% de. Chiracel AD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 90 / 10; flow = 0.7 mL / min; Retention time: 21.8 min (maj), 23.8 min.
(R)-ethyl 2-((R)-1,1-dimethylethylsulfinamido)-2-(2,4,6-trimethoxyphenyl)acetate (3b).

91% yield, colorless oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.10 (s, 9H), 1.17 (t, 3H), 3.77 (s, 6H), 3.80 (s, 3H), 4.09-4.22 (m, 2H), 4.58 (d, $J = 5.1$ Hz, 1H), 5.49 (d, $J = 5.1$ Hz, 1H), 6.09 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 14.27, 22.44, 51.35, 55.39, 55.76, 55.85, 61.59, 90.68, 107.92, 158.83, 161.38, 172.55; ESI-MS ($m/z$, %) 374 [M+H]$^+$; ESI-HRMS calcd for C$_{17}$H$_{27}$NNaO$_6$S [M+Na$^+$] 396.1457, found 396.1454.

HPLC (acetate): 97% de. Chiracel AD-3 Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 95 / 5; flow = 0.7 mL / min; Retention time: 58.2 min (maj), 63.9 min.
(R)-ethyl 2-(2,4-dimethoxy-6-methylphenyl)-2-((R)-1,1-dimethylethylsulfamido)acetate (3c).

84% yield, colorless oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.11 (s, 9H), 1.16 (t, 3H), 2.36 (s, 3H), 3.73 (s, 3H), 3.78 (s, 3H), 4.09-4.21 (m, 2H), 4.63 (d, $J = 3.0$ Hz, 1H), 5.33 (d, $J = 3.9$ Hz, 1H), 6.29 (d, $J = 5.7$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 14.24, 20.24, 22.50, 53.44, 55.26, 55.63, 55.71, 61.79, 96.58, 107.05, 117.52, 139.22, 158.74, 160.17, 172.34; ESI-MS (m/z, %) 358 [M+H$^+$]; ESI-HRMS calcd for C$_{17}$H$_{28}$NO$_5$S [M+H$^+$] 358.1688, found 358.1697.

HPLC (acetate): 95% de. Chiracel AD-H Column (250 mm); detected at 214 nm; n-hexane/i-propanol = 95/5; flow = 0.7 mL/min; Retention time: 28.0 min (maj), 31.3 min.
(R)-ethyl 2-(2-chloro-4,6-dimethoxyphenyl)-2-((R)-1,1-dimethylethylsulfinamido)acetate (3d).

80% yield, yellow oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.12 (s, 9H), 1.18 (t, 3H), 3.76 (s, 3H), 3.79 (s, 3H), 4.09-4.23 (m, 2H), 4.59 (d, $J = 4.2$ Hz, 1H), 5.60 (d, $J = 4.2$ Hz, 1H), 6.34 (d, $J = 2.1$ Hz, 1H), 6.52 (d, $J = 2.4$ Hz, 1H);
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 14.22, 22.44, 55.65, 55.91, 56.01, 62.07, 97.93, 106.12, 117.96, 135.60, 159.09, 160.55, 171.42; ESI-MS ($m/z$, %) 378 [M+H$^+$]; ESI-HRMS calcd for C$_{16}$H$_{24}$ClNNaO$_5$S [M+Na$^+$] 400.0961, found 400.0945.

HPLC (acetate): 98% de. Chiracel AD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 90 / 10; flow = 0.7 mL / min; Retention time: 18.6 min (maj), 21.8 min.
(R)-ethyl 2-((R)-1,1-dimethylethylsulfinamido)-2-(2,4,5-trimethoxyphenyl)acetate (3e).

86% yield, colorless oil. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 1.16 (s, 9H), 1.17 (t, 3H), 3.79 (s, 3H), 3.80 (s, 3H), 3.87 (s, 3H), 4.11-4.21 (m, 2H), 4.51 (d, \(J = 3.3\) Hz, 1H), 5.30 (d, \(J = 3.9\) Hz, 1H), 6.51 (s, 1H), 6.74 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 14.15, 22.56, 55.13, 55.85, 56.09, 56.57, 56.93, 61.97, 97.96, 112.45, 117.52, 143.19, 149.81, 151.89, 171.98; ESI-MS (m/z, %) 396 [M+Na]+; ESI-HRMS calcd for C\(_{17}\)H\(_{27}\)NNaO\(_6\)S [M+Na]+ 396.1457, found 396.1455.

HPLC (sulfonylate): 98% de. Chiralcel AD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 80 / 20; flow = 0.7 mL / min; Retention time: 30.2 min (maj), 40.4 min.
(R)-ethyl 2-((R)-1,1-dimethylsulfinamido)-2-(2-hydroxy-4,5-dimethoxyphenyl)acetate (3f).

72% yield, yellow oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.21 (t, 3H), 1.25 (s, 9H), 4.10-4.28 (m, 2H), 4.52 (d, $J = 1.5$ Hz, 1H), 5.21 (d, $J = 2.7$ Hz, 1H), 5.89 (s, 2H), 6.46 (s, 1H), 6.62 (s, 1H), 7.90 (br, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 14.16, 22.71, 55.87, 56.30, 62.49, 99.56, 101.35, 108.15, 113.68, 141.28, 148.77, 150.90, 171.63; ESI-MS (m/z, %) 344 [M+H$^+$].

HPLC (acetate): 93% de. Chiracel AD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 80 / 20; flow = 0.7 mL / min; Retention time: 13.8 min, 16.7 min (maj).
(R)-ethyl 2-((R)-1,1-dimethylethylsulfinamido)-2-(2,3,4-trimethoxyphenyl)acetate (3g).

60% yield, yellow oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.17 (s, 9H), 1.18 (t, 3H), 3.84 (s, 6H), 3.88 (s, 3H), 4.11-4.24 (m, 2H), 4.59 (d, $J = 3.9$ Hz, 1H), 5.18 (d, $J = 3.6$ Hz, 1H), 6.60 (d, $J = 8.4$ Hz, 1H), 6.91 (d, $J = 8.4$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 14.13, 22.61, 55.75, 55.84, 55.98, 60.77, 61.14, 62.06, 106.98, 123.75, 123.90, 142.15, 151.91, 154.07, 171.84; ESI-MS ($m/z$, %) 374 [M+H]$^+$; ESI-HRMS calcd for C$_{17}$H$_{27}$NNaO$_6$S [M+Na$^+$] 396.1457, found 396.1467.

HPLC (acetate): 70% de. Chiracel AD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 90 / 10; flow = 0.7 mL / min; Retention time: 21.6 min (maj), 27.8 min.
(R)-ethyl 2-((R)-1,1-dimethylethylsulfinamido)-2-(2,3,4-trimethoxy-6-methylphenyl)acetate (3h).

74% yield, yellow oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.15 (s, 9H), 1.18 (t, 3H), 2.34 (s, 3H), 3.79 (s, 3H), 3.83 (s, 3H), 3.85 (s, 3H), 4.08-4.22 (m, 2H), 4.73 (d, $J = 1.2$ Hz, 1H), 5.29 (d, $J = 2.7$ Hz, 1H), 6.46 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 14.22, 19.97, 22.61, 53.61, 55.76, 55.82, 60.70, 60.98, 61.99, 109.11, 122.28, 132.79, 139.91, 152.28, 153.17, 172.08; ESI-MS (m/z, %) 388 [M+H]$^+$; ESI-HRMS calcd for C$_{18}$H$_{30}$NO$_6$S [M+H]$^+$ 388.1794, found: 388.1791.

HPLC (acetate): 73% de. Chiracel AD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 95 / 5; flow = 0.7 mL / min; Retention time: 27.4 min (maj), 33.8 min.
(R)-ethyl 2-(2,4-dimethoxy-3-methylphenyl)-2-((R)-1,1-dimethylethylsulfamido)acetate (3i).

72% yield, yellow oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.16-1.18 (m, 12H), 2.15 (s, 3H), 3.77 (s, 3H), 3.81 (s, 3H), 4.09-4.23 (m, 2H), 4.59 (d, $J$ = 3.0 Hz, 1H), 5.27 (d, $J$ = 3.9 Hz, 1H), 6.60 (d, $J$ = 8.4 Hz, 1H), 7.06 (d, $J$ = 8.1 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 9.56, 14.15, 22.67, 55.09, 55.66, 55.84, 61.55, 62.10, 106.18, 119.99, 123.10, 126.58, 157.46, 159.03, 172.15; ESI-MS ($m/z$, %) 380 [M+Na]$^+$; ESI-HRMS calcd for C$_{17}$H$_{27}$NNaO$_5$S [M+Na]$^+$ 380.1508, found 380.1506.

HPLC (acetate): 79% de. Chiracel AS-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 90 / 10; flow = 0.7 mL / min; Retention time: 29.2 min, 35.4 min (maj).
(R)-ethyl 2-((R)-1,1-dimethylethysulfinamido)-2-(4-methoxynaphthalen-1-yl)acetate (3j).

66% yield, white solid. $^1$H NMR (300 MHz, CDCl₃): $\delta$ 1.10 (t, 3H), 1.13 (s, 9H), 4.01 (s, 3H), 4.08-4.21 (m, 2H), 4.66 (s, 1H), 5.50 (s, 1H), 6.76 (d, $J = 8.1$ Hz, 1H), 7.41 (d, $J = 8.4$ Hz, 1H), 7.47-7.51 (m, 2H), 7.98 (d, $J = 7.8$ Hz, 1H), 8.30 (d, $J = 7.8$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl₃): $\delta$ 14.08, 22.63, 55.63, 55.79, 59.32, 62.33, 102.97, 122.79, 123.90, 124.34, 125.33, 126.33, 126.95, 128.62, 131.90, 156.24, 172.41; ESI-MS (m/z, %) 364 [M+H]$^+$; ESI-HRMS calcd for C₁₉H₂₅NNaO₄S [M+Na$^+$] 386.1402, found 386.1411.

HPLC (acetate): >99% de. Chiracel AD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 90 / 10; flow = 0.7 mL / min; Retention time: 19.0 min (maj), 24.1 min.

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(R)-ethyl 2-[(R)-1,1-dimethylethylsulfinamido]-2-(1-methoxynaphthalen-2-yl)acetate (3j̲).

22% yield, white solid. ¹H NMR (300 MHz, CDCl₃): δ 1.13 (t, 3H), 1.21 (s, 9H), 4.00 (s, 3H), 4.07-4.21 (m, 2H), 5.73 (d, J = 3.9 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 7.47-7.61 (m, 3H), 8.18 (d, J = 8.4 Hz, 1H), 8.31 (d, J = 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 14.12, 22.65, 55.68, 56.46, 56.74, 61.88, 103.27, 122.85, 123.40, 125.06, 125.51, 126.11, 127.19, 127.46, 131.78, 156.21, 172.01; ESI-MS (m/z, %) 364 [M+H]; ESI-HRMS calcd for C₁₉H₂₅NNaO₄S [M+Na⁺] 386.1402, found 386.1390.

HPLC (acetate): >99% de. Chiracel AD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 90 / 10; flow = 0.7 mL / min; Retention time: 19.1 min, 23.9 min (maj).
(R)-ethyl 2-((R)-1,1-dimethylethylsulfinamido)-2-(2-methoxynaphthalen-1-yl)acetate (3k).

72% yield, white solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.06-1.10 (m, 12H), 3.98 (s, 3H), 4.11-4.18 (m, 2H), 4.76 (s, 1H), 6.10 (s, 1H), 7.28-7.36 (m, 2H), 7.46 (dd, $J$ = 8.4 Hz, 7.2 Hz, 1H), 7.78 (d, $J$ = 8.1 Hz, 1H), 7.84 (d, $J$ = 9.0 Hz, 1H), 7.93 (d, $J$ = 9.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 14.14, 22.51, 52.18, 55.69, 57.17, 62.12, 113.67, 118.42, 123.34, 123.76, 127.09, 128.75, 129.47, 130.90, 132.31, 155.83, 172.77; ESI-MS (m/z, %) 364 [M+H]$^+$; ESI-HRMS calc'd for C$_{19}$H$_{26}$NO$_4$S [M+H]$^+$ 364.1582, found: 364.1578.

HPLC (acetate): >99% de. Chiracel AD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 90 / 10; flow = 0.7 mL / min; Retention time: 19.3 min (maj), 22.6 min.

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(R)-ethyl 2-((R)-1,1-dimethylethylsulfinamido)-2-(4-hydroxynaphthalen-1-yl)acetate (3i).

74% yield, yellow solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.06 (t, 3H), 1.18 (s, 9H), 4.09-4.18 (m, 2H), 4.77 (d, $J = 2.1$ Hz, 1H), 5.49 (d, $J = 2.1$ Hz 1H), 6.78 (d, $J = 7.8$ Hz 1H), 7.32 (d, $J = 7.8$ Hz, 1H), 7.43-7.46 (m, 2H), 7.92-7.96 (m, 1H), 8.18 (s, 1H), 8.28-8.32 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 14.04, 22.74, 56.03, 59.76, 62.42, 107.83, 122.59, 123.16, 123.86, 124.93, 125.69, 126.80, 129.66, 132.14, 153.98, 172.40; ESI-MS (m/z, %) 350 [M+H]$^+$; ESI-HRMS calcd for C$_{18}$H$_{23}$NNaO$_4$S [M+Na]+ 372.1246, found 372.1244.

HPLC (acetate): 98% de. Chiracel AD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 90 / 10; flow = 0.7 mL / min; Retention time: 16.2 min (maj), 24.9 min.
(R)-ethyl 2-((R)-1,1-dimethylethylsulfinamido)-2-(1-hydroxynaphthalen-2-yl)acetate (31').

15% yield, yellow solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.19 (t, 3H), 1.28 (s, 9H), 4.11-4.29 (m, 2H), 4.59 (s, 1H), 5.36 (d, $J = 2.7$ Hz, 1H), 7.25 (d, $J = 8.4$ Hz, 1H), 7.39 (d, $J = 8.7$ Hz, 1H), 7.45-7.52 (m, 2H), 7.76-7.79 (m, 1H), 8.26-8.30 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 14.11, 22.68, 56.53, 57.25, 62.76, 114.46, 120.34, 122.67, 125.57, 126.79, 127.07, 127.51, 134.83, 151.71, 171.29; ESI-MS (m/z, %) 372 [M+Na$^+$]; ESI-HRMS calcd for C$_{18}$H$_{23}$NNaO$_4$S [M+Na$^+$] 372.1246, found 372.1253.

HPLC (acetate): 97% de. Chiracel AD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 90 / 10; flow = 0.7 mL / min; Retention time: 21.4 min, 24.7 min (maj).
(R)-ethyl 2-((R)-1,1-dimethylethylsulfinamido)-2-(2-hydroxynaphthalen-1-yl)acetate (3m).

70% yield, yellow solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.05 (t, 3H), 1.21 (s, 9H), 4.05-4.18 (m, 2H), 4.82 (s, 1H), 6.22 (s, 1H), 7.17 (d, $J = 8.7$ Hz, 1H), 7.26 (dd, $J = 6.6$ Hz, 8.4Hz, 1H), 7.39 (dd, $J = 8.4$ Hz, 7.2Hz, 1H), 7.67-7.74 (dd, $J = 8.7$ Hz, 8.4Hz, 2H), 7.80 (d, $J = 8.4$ Hz, 1H), 9.55 (br, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 14.07, 22.72, 52.00, 55.76, 62.32, 112.46, 118.40, 122.77, 122.90, 126.69, 128.74, 128.95, 130.81, 132.61, 155.18, 173.00; ESI-MS ($m/z$, %) 372 [M+Na]+; ESI-HRMS calcd for C$_{18}$H$_{23}$NNaO$_4$S [M+Na+] 372.1246, found 372.1246.

HPLC (acetate): 98% de. Chiracel AD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 95 / 5; flow = 0.7 mL / min; Retention time: 43.4 min (maj), 47.4 min.
(R)-ethyl 2-(2,7-dimethoxynaphthalen-1-yl)-2-((R)-1,1-dimethylethylsulfinamido)acetate (3n).

74% yield, white solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.05-1.24 (m, 12H), 3.86 (s, 3H), 3.95 (s, 3H), 4.10-4.17 (m, 2H), 4.71 (s, 1H), 6.06 (s, 1H), 6.96-7.00 (dd, $J = 1.5$ Hz, 8.7 Hz, 1H), 7.11 (d, $J = 8.7$ Hz, 1H), 7.25 (d, $J = 1.5$ Hz, 1H), 7.64 (d, $J = 9.3$ Hz, 1H), 7.738 (d, $J = 6.9$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 14.16, 14.29, 22.55, 52.14, 55.33, 55.57, 57.00, 62.09, 101.66, 110.87, 116.61, 124.82, 130.20, 130.53, 133.79, 156.50, 158.59, 172.88; ESI-MS (m/z, %) 416 [M+Na]$^+$; ESI-HRMS calcd for C$_{20}$H$_{27}$NNaO$_5$S [M+Na]$^+$ 416.1508, found 416.1516.

HPLC (acetate): 98% de. Chiracel AD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 90 / 10; flow = 0.7 mL / min; Retention time: 15.4 min (maj), 17.6 min.
(R)-ethyl 2-((R)-1,1-dimethylethylsulfinamido)-2-(5-methylfuran-2-yl)acetate (3o).

90% yield, colorless oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.22 (s, 9H), 1.25 (t, 3H), 2.25 (s, 3H), 4.19-4.28 (m, 2H), 4.41 (d, $J$ = 4.8 Hz, 1H), 5.03 (d, $J$ = 5.4 Hz, 1H), 5.91 (s, 1H), 6.18 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 13.07, 14.13, 22.57, 55.36, 56.23, 62.52, 106.53, 109.86, 147.66, 153.04, 169.70; ESI-MS ($m/z$, %) 310 [M+Na$^+$]; ESI-HRMS calcd for C$_{13}$H$_{21}$NNaO$_4$S [M+Na$^+$] 310.1089, found 310.1094.

HPLC (acetate): 90% de. Chiracel AD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 95 / 5; flow = 0.7 mL / min; Retention time: 20.8 min (maj), 26.1 min.
(R)-ethyl 2-(((R)-1,1-dimethylethylsulfinamido)-2-(5-methylthiophen-2-yl)acetate (3p).

74\% yield, colorless oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.26 (m, 12H), 2.44 (s, 3H), 4.18-4.28 (m, 2H), 4.57 (d, $J = 4.8$ Hz, 1H), 5.20 (d, $J = 4.8$ Hz, 1H), 6.60-6.61 (m, 1H), 6.84 (d, $J = 3.3$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 14.14, 15.54, 22.73, 56.35, 56.95, 62.60, 125.18, 126.38, 137.78, 140.82, 170.57; ESI-MS ($m/z$, %) 326 [M+Na]$^+$; ESI-HRMS calcd for C$_{13}$H$_{21}$NNaO$_3$S$_2$ [M+Na]$^+$ 326.0860, found 326.0862.

HPLC (acetate): 79\% de. Chiracel AD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 90 / 10; flow = 0.7 mL / min; Retention time: 29.4 min (maj), 33.6 min.
5. General procedure for the synthesis of the chiral Friedel-Crafts dialkylation product (4).

Under nitrogen atmosphere, In(OTf)$_3$ (0.25 mmol, 1 equiv) was placed into a glass reaction vessel, glyoxylate imine 2 (0.25 mmol) in 2 mL of dry CH$_2$Cl$_2$ and arene 1 (0.125 mmol) were added successively. The mixture was stirred at room temperature and monitored by TLC. When the reaction was over, a saturated aq. NH$_4$Cl was added and the mixture was extracted with CH$_2$Cl$_2$ (10 mL×3). The combined organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated. The residue was purified by silica gel flash chromatography to afford the corresponding product 4.

(2R,2'R,26R)-diethyl-2,2'-((4,6-dimethoxy-1,3-phenylene)bis((2-((R)-1,1-dimethylethylsulfinamido)acetate)) (4).

43% yield, colorless oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.14-1.20 (m, 24H), 3.85 (s, 6H), 4.08-4.21 (m, 4H), 4.51 (d, $J = 4.2$ Hz, 2H), 5.29 (d, $J = 4.2$ Hz, 2H), 6.44 (s, 1H), 7.07 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 14.17, 22.58, 55.00, 55.87, 55.90, 61.94, 95.56, 118.29, 129.81, 158.38, 171.73; ESI-MS ($m/z$, %) 549 [M+H]$^+$; ESI-HRMS calcd for C$_{24}$H$_{40}$N$_2$NaO$_8$S$_2$ [M+Na]$^+$ 571.2124, found 571.2133.

HPLC (sulfonylate): >99% de. Chiracel AD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 70 / 30; flow = 0.7 mL / min; Retention time: 17.4 min (maj), 23.7 min.
7. The synthesis and HPLC of \((R)-2-(\text{chloroamino})-2-(2,4-\text{dimethoxyphenyl})\text{acetic acid} ((R)-5)\).

To a round bottomed flask containing LiOH (37.8 mg, 0.9 mmol, 10 equiv) was added distilled H\(_2\)O (5.0 mL), and the resulting solution was cooled to 0 °C. A solution of 3a (30.0 mg, 0.09 mmol, 1.0 equiv) in dioxane (5.0 mL) was cannulated into the reaction flask. The resulting solution was stirred at 0 °C for 3 h. The reaction mixture was then concentrated to remove the dioxane, and the remaining material was diluted with distilled H\(_2\)O (3 mL) and EtOAc (3 mL) and placed in a separatory funnel. 1 N NaHSO\(_4\) (2 mL) was added and the aqueous layer was extracted with EtOAc (5×4 mL). The combined organic layers were dried over Na\(_2\)SO\(_4\), filtered, and concentrated under reduced pressure. The crude product was isolated with no further purification as a white solid. Subsequently, the crude product was treated with 5 mL solution of dry HCl in 1,4-dioxane at room temperature for 1 h. The reaction mixture was concentrated en vacuo, and the amine hydrochloride was precipitated with dry diethyl ether. The precipitate was collected by filtration and washed with diethyl ether to yield the \((R)-5\) (20 mg, 91% yield) as a white solid.

91% yield, white solid. \([\alpha]_{D}^{20} = -111.2\ (c\ 0.5, \text{MeOH});\) The absolute configuration was determined to be \((R)\) according to literature [lit\(^1\)[\(\alpha]_{D}^{22} = +106.6\ (c\ 1.0\ \text{MeOH})]. \(^1\)H NMR (300 MHz, CD\(_3\)OD): \(\delta\ 3.83\ (s, 3H), 3.88\ (s, 3H), 5.10\ (s, 1H), 6.58-6.61\ (dd, J = 2.4\ Hz, 8.4\ Hz, 1H), 6.64\ (d, J = 2.1\ Hz, 1H), 7.27\ (d, J = 8.4\ Hz, 1H);\) \(^13\)C NMR (100 MHz, CD\(_3\)OD): \(\delta\ 53.75, 56.06, 56.24, 99.73, 106.42, 114.21, 132.48, 159.90, 164.16, 171.17.\)

8. Copies of $^1$H and $^{13}$C NMR Spectra of Compounds 3a-p, 4 and (R)-5.