Supporting Information For:

**Enantioselective Friedel-Crafts Reaction of 4,7-dihydroindoles with \( \beta\)-CF\(_3\)-\( \beta\)-disubstituted Nitroalkenes**

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**General information:**

NMR spectra were recorded on 500 MHz spectrometers for \(^1\)H NMR and 125 MHz spectrometer for \(^{13}\)C NMR with deuterated chloroform (CDCl\(_3\)) as a solvent at 298 K. Chemical shifts are expressed in \(\delta\) ppm according to SiMe\(_4\) as an internal standard (\(\delta = 0\)) for \(^1\)H NMR, chloroform-\(d\) (\(\delta = 77.0\)) for \(^{13}\)C NMR. HRMS were obtained with a TOF MS spectrometer. Melting points were uncorrected. Anhydrous toluene and ether were freshly distilled over Na and benzophenone. Anhydrous DCE was freshly distilled over calcium hydride. Chiral bisoxazoline ligands L\(_1\)-L\(_6\)\(^1\) and L\(_7\)-L\(_8\)\(^2\) were synthesized according to the literatures. Substrates \(\beta\)-CF\(_3\)-\(\beta\)-disubstituted nitroalkenes 1\(_a\)-1\(_m\)\(^3\) and 4,7-dihydroindoles 2\(_a\),\(^4\) 2\(_b\),\(^5\) 2\(_c\),\(^6\) and

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were prepared according to the reported methods.

**Synthesis of substrate:**

6-fluoro-4,7-dihydro-1H-indole (2d):

![Structure of 6-fluoro-4,7-dihydro-1H-indole (2d)](image)

The solution of the 6-fluoro-indole (1 g, 7.4 mmol) in dry methanol (6 mL) was added to liquid ammonia (20 mL) under N₂. When the resulting solution was cooled to -40 °C, lithium metal (0.21 g, 29.6 mmol) was added in small pieces for 5–10 min. The resulting deep blue solution was stirred at the same temperature for 1h and then was allowed to warm to rt. After the excess ammonia had evaporated, saturated aq. NH₄Cl were carefully added to the mixture and extracted with Et₂O. The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/petroleum ether (1:20) to give the 6-fluoro-4,7-dihydro-1H-indole (2d) as a yellow liquid (0.57 g, 4.2 mmol, 56%). ¹H NMR (500 MHz, CDCl₃): δ 3.26-3.31 (m, 2H), 3.48 (t, J = 7.0 Hz, 2H), 5.51 (d, J = 18.0 Hz, 1H), 6.08 (s, 1H), 6.76 (s, 1H), 7.85 (s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 22.5 (d, J = 8.6 Hz), 25.2 (d, J = 31.0 Hz), 101.7 (d, J = 17.1 Hz), 106.7 (d, J = 0.9 Hz), 113.8 (d, J = 2.4 Hz), 117.6, 122.2 (d, J = 16.6 Hz), 156.7 (d, J = 246.9 Hz); HRMS m/z (EI⁺): Calculated for C₈H₈NF ([M]⁺): 137.0641, Found 137.0648.
General procedure for Friedel-Crafts reaction:

To a dried Schlenk tube were added Ni(ClO$_4$)$_2$·6H$_2$O (7.3 mg, 0.02 mmol) and ligand L7 (11.7 mg, 0.024 mmol) under N$_2$, 2.0 mL toluene was then added through syringe. The resulting mixture was stirred at 80 °C for 1h, after which the nitroalkene (0.2 mmol) and 4,7-dihydroindole (0.3 mmol) were added. The mixture was stirred at 80 °C until the reaction was completed (monitored by TLC). The solvent was then evaporated under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether (1:10–1:5) to afford the product.

2-(1,1,1-trifluoro-3-nitro-2-phenylpropan-2-yl)-4,7-dihydro-1H-indole (3aa):

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 94% yield, [α]$_D^{25}$ = + 38.2 (c 1.0, CH$_2$Cl$_2$), 91% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 85/15, 1.0 mL/min, 254 nm; t$_{minor}$ = 15.3 min, t$_{major}$ = 9.6 min]; $^1$H NMR (500 MHz, CDCl$_3$): δ 3.20-3.27 (m, 4H), 5.18 (d, $J$ = 13.0 Hz, 1H), 5.42 (d, $J$ = 13.5 Hz, 1H), 5.82-5.85 (m, 1H), 5.91-5.94 (m, 1H), 6.22 (d, $J$ = 1.5 Hz, 1H), 7.35-7.43 (m, 5H), 7.75 (s, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$): δ -68.6 (s, 3F); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 23.7, 24.6, 55.0 (q, $J$ = 25.9 Hz), 78.3, 108.8, 114.1, 122.5, 122.6, 125.4 (q, $J$ = 283.5 Hz), 125.7, 125.9, 128.5, 128.6, 129.0, 133.9; HRMS m/z (ESI+): Calculated for C$_{17}$H$_{16}$F$_3$N$_2$O$_2$ ([M+H]$^+$): 337.1164, Found 337.1151.
2-(1,1,1-trifluoro-3-nitro-2-\textit{m}-tolylpropan-2-yl)-4,7-dihydro-1H-indole (3ba):

![Chemical Structure](image)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 95% yield, $[\alpha]_D^{27} = +26.0$ (c 1.0, CH$_2$Cl$_2$), 85% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 85/15, 1.0 mL/min, 254 nm; $t_{\text{minor}} = 15.7$ min, $t_{\text{major}} = 7.2$ min]; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.37 (s, 3H), 3.20-3.26 (m, 4H), 5.16 (d, $J = 13.5$ Hz, 1H), 5.40 (d, $J = 13.0$ Hz, 1H), 5.82-5.85 (m, 1H), 5.91-5.95 (m, 1H), 6.21 (d, $J = 1.0$ Hz, 1H), 7.15 (d, $J = 8.0$ Hz, 1H), 7.17 (s, 1H), 7.22 (d, $J = 7.5$ Hz, 1H), 7.29 (t, $J = 8.0$ Hz, 1H), 7.74 (s, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -68.6 (s, 3F); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 21.6, 23.8, 24.6, 54.9 (q, $J = 25.8$ Hz), 78.4, 108.6, 114.1, 122.5, 122.8, 125.4 (q, $J = 283.9$ Hz), 125.71, 125.74, 125.8, 128.5, 129.0, 129.8, 133.7, 138.4; HRMS m/z (EI+): calculated for C$_{18}$H$_{17}$N$_2$O$_2$F$_3$ ([M$^+$]): 350.1242, found 350.1249.
2-(1,1,1-trifluoro-3-nitro-2-p-tolylpropan-2-yl)-4,7-dihydro-1H-indole (3ca):

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 92% yield, $[\alpha]_D^{27} = +30.5$ (c 1.0, CH$_2$Cl$_2$), 88% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 85/15, 1.0 mL/min, 254 nm; t$_{minor} = 15.3$ min, t$_{major} = 8.4$ min]; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.38 (s, 3H), 3.20-3.26 (m, 4H), 5.15 (d, $J = 13.0$ Hz, 1H), 5.39 (d, $J = 13.0$ Hz, 1H), 5.81-5.84 (m, 1H), 5.90-5.94 (m, 1H), 6.20 (d, $J = 1.5$ Hz, 1H), 7.21 (d, $J = 8.5$ Hz, 2H), 7.24 (d, $J = 8.5$ Hz, 2H), 7.74 (s, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -68.9 (s,
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 21.0, 23.8, 24.7, 54.8 (q, $J = 25.9$ Hz), 78.4, 108.7, 114.2, 122.6, 122.9, 125.5 (q, $J = 283.4$ Hz), 125.7, 125.8, 128.5, 129.4, 130.8, 139.1; HRMS $m/z$ (EI+): Calculated for C$_{18}$H$_{17}$N$_2$O$_2$F$_3$ ([M$^+$]): 350.1242, Found 350.1265.
The document contains a chromatogram with two peaks labeled as Rac and Opt. The retention times and areas are listed in the table below:

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The peaks are identified as Rac and Opt with corresponding retention times and areas.
2-(1,1,1-trifluoro-2-(4-methoxyphenyl)-3-nitropropan-2-yl)-4,7-dihydro-1H-indole (3da):

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); Yellow oil, 90% yield, $[\alpha]_D^{27} = +30.6$ (c 1.0, CH$_2$Cl$_2$), 88% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 85/15, 1.0 mL/min, 254 nm; $t_{\text{minor}} = 21.9$ min, $t_{\text{major}} = 12.4$ min]; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.20-3.25 (m, 4H), 3.84 (s, 3H), 5.14 (d, $J = 13.0$ Hz, 1H), 5.37 (d, $J = 13.5$ Hz, 1H), 5.83 (d, $J = 10.0$ Hz, 1H), 5.93 (d, $J = 10.5$ Hz, 1H), 6.20 (d, $J = 1.0$ Hz, 1H), 6.91 (dt, $J = 2.5$, 9.0 Hz, 2H), 7.28 (d, $J = 9.0$ Hz, 2H), 7.76 (s, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -69.1 (s, 3F); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 23.8, 24.6, 54.5 (q, $J = 25.9$ Hz), 55.2, 78.4, 108.6, 114.0, 114.1, 122.5, 122.9, 125.4, 125.5 (q, $J = 283.4$ Hz), 125.73, 125.78, 129.9, 159.9; HRMS m/z (EI+): Calculated for C$_{18}$H$_{17}$N$_2$O$_3$F$_3$ ([M]$^+$): 366.1191, Found 366.1211.
2-(2-(3,5-dimethylphenyl)-1,1,1-trifluoro-3-nitropropan-2-yl)-4,7-dihydro-1H-indole (3ea):

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 90% yield, $[\alpha]_D^{27} = +37.2$ (c 0.5, CH$_2$Cl$_2$), 84% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 93/7, 1.0 mL/min, 254 nm; $t_{\text{minor}} = 16.6$ min, $t_{\text{major}} = 8.2$ min]; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.33 (s, 6H), 3.21-3.27 (m, 4H), 5.15 (d, $J = 13.0$ Hz, 1H), 5.39 (d, $J = 13.0$ Hz, 1H), 5.82-5.86 (m, 1H), 5.92-5.95 (m, 1H), 6.20 (d, $J = 1.5$ Hz, 1H), 6.96 (s, 2H), 7.05 (s,
1H), 7.73 (s, 1H); 19F NMR (376 MHz, CDCl3): δ -68.5 (s, 3F); 13C NMR (125 MHz, CDCl3): δ 21.4, 23.8, 24.6, 54.8 (q, J = 25.8 Hz), 78.4, 108.5, 114.1, 122.5, 122.9, 125.4 (q, J = 283.5 Hz), 125.6, 125.7, 126.2 (d, J = 1.4 Hz), 130.7, 133.6, 138.2; HRMS m/z (EI+): Calculated for C_{19}H_{19}N_{2}O_{2}F_{3} ([M]+): 364.1399, Found 364.1402.

\[
\text{HN}\text{F}_3\text{CNO}_2
\]

\[
\text{HN}\text{F}_3\text{CNO}_2
\]
Retention Time | Height     | Area         | % Area
---|-----------|--------------|------
1 | 8.270     | 321657       | 9111087 | 91.89
2 | 16.646    | 15281        | 804641  | 8.11
2-(2-(4-chlorophenyl)-1,1,1-trifluoro-3-nitropropan-2-yl)-4,7-dihydro-1H-indole (3fa):

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 89% yield, \([\alpha]_D^{27} = +36.5\) (c 1.0, CH₂Cl₂), 81% ee [Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 85/15, 1.0 mL/min, 254 nm; \(t_{\text{minor}} = 14.4\) min, \(t_{\text{major}} = 18.0\) min]; \(^1\)H NMR (500 MHz, CDCl₃): \(\delta\) 3.20-3.27 (m, 4H), 5.15 (d, \(J = 13.0\) Hz, 1H), 5.39 (d, \(J = 13.0\) Hz, 1H), 5.82-5.86 (m, 1H), 5.91-5.94 (m, 1H), 6.20 (d, \(J = 1.5\) Hz, 1H), 7.30 (d, \(J = 8.5\) Hz, 2H), 7.38 (dt, \(J = 2.5, 9.5\) Hz, 2H), 7.75 (s, 1H); \(^{19}\)F NMR (376 MHz, CDCl₃): \(\delta\) -68.9 (s, 3F); \(^{13}\)C NMR (125 MHz, CDCl₃): \(\delta\) 23.8, 24.6, 54.7 (q, \(J = 26.0\)), 78.2, 109.1, 114.3, 122.2, 122.5, 125.3 (q, \(J = 283.6\)), 125.7, 126.2, 128.9, 130.0, 132.4, 135.4; HRMS \(m/z\) (EI+): Calculated for C₁₇H₁₄N₂O₂F₃Cl ([M⁺]): 370.0696, Found 370.0718.
2-(1,1,1-trifluoro-2-(3-fluorophenyl)-3-nitropropan-2-yl)-4,7-dihydro-1H-indole (3ga):

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 92% yield, [α]D27 = + 33.6 (c 1.0, CH2Cl2), 85% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), n-hexane/i-ProOH = 85/15, 1.0 mL/min, 254 nm; tminor = 10.7 min, tmajor = 8.3 min]; 1H NMR (500 MHz, CDCl3): δ 3.21-3.26 (m, 4H), 5.16 (d, J = 13.0 Hz, 1H), 5.39 (d, J = 13.5 Hz, 1H), 5.82-5.86 (m, 1H), 5.91-5.95 (m, 1H), 6.21 (d, J = 2.0 Hz, 1H), 7.08 (d, J = 10.5 Hz, 1H), 7.12 (tdd, J = 1.0, 2.5, 8.5 Hz, 1H), 7.16 (dt, J = 1.0, 8.0 Hz, 1H), 7.38 (td, J = 6.0, 8.5 Hz, 1H),
7.78 (s, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -63.7 (s, 1F), -68.7 (d, $J = 3.8$ Hz, 3F); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 23.7, 24.5, 54.8 (q, $J = 26.5$ Hz), 78.1, 109.0, 114.3, 116.1, 116.3, 121.9, 122.4, 124.2, 125.2 (q, $J = 283.8$ Hz), 125.6, 126.3, 130.1 (d, $J = 8.0$ Hz), 136.4 (d, $J = 7.1$ Hz), 162.6 (d, $J = 245.8$ Hz); HRMS m/z (EI+): Calculated for C$_{17}$H$_{14}$N$_2$O$_2$F$_4$ ([M$^+$]): 354.0991, Found 354.0991.
### Retention Time Table

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2-(1,1,1-trifluoro-3-nitro-2-(4-(trifluoromethyl)phenyl)propan-2-yl)-4,7-dihydro-1H-indole (3ha):

\[
\text{\includegraphics[width=0.2\textwidth]{image.png}}
\]

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 88% yield, \([\alpha]_D^{27} = +30.0\) (c 0.5, CH\(_2\)Cl\(_2\)), 86% ee [Daicel Chiralcel OD-H column (25 cm \times 0.46 cm ID), \(n\)-hexane/i-PrOH = 85/15, 1.0 mL/min, 254 nm; \(t_{\text{minor}} = 15.6\) min, \(t_{\text{major}} = 12.5\) min]; \(^1\)H NMR (500 MHz, CDCl\(_3\)):

\[
\begin{align*}
\delta 3.21-3.26 & (m, 4H), \\
5.19 & (d, J = 13.5\ Hz, 1H), \\
5.45 & (d, J = 13.5\ Hz, 1H), \\
5.84 & (dd, J = 1.5, 11.5\ Hz, 1H), \\
5.93 & (dd, J = 1.5, 11.5\ Hz, 1H), \\
6.21 & (d, J = 1.5\ Hz, 1H), \\
7.50 & (d, J = 8.5\ Hz, 2H), \\
7.67 & (d, J = 8.5\ Hz, 2H), \\
7.75 & (s, 1H); \\
19\text{F} & \text{NMR (376 MHz, CDCl}_3); \ \delta -63.7\ (s, 3F), -68.7\ (s, 3F); \\
13\text{C} & \text{NMR (125 MHz, CDCl}_3); \ \delta 23.7, 24.5, 54.9\ (q, J = 25.8\ Hz), \\
78.0, 109.2, 114.4, 121.8, 122.4, 123.6 & (q, J = 270.6\ Hz), 125.1\ (q, J = 283.6\ Hz), \\
125.60 & (q, J = 3.6\ Hz), 125.64, 126.5, 129.1, 131.3 & (q, J = 32.8\ Hz), 138.0; \\
\text{HRMS} & m/z (\text{EI}^+) \text{ Calculated for C}_{18}H_{14}N_2O_2F_6 ([M]^+) : 404.0959, \text{ Found } 404.0981.
\end{align*}
\]
2-(1,1,1-trifluoro-3-nitro-2-(thiophen-3-yl)propan-2-yl)-4,7-dihydro-1H-indole (3ia):

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 86% yield, \([\alpha]_D^{27} = +31.3\) (c 1.0, CH$_2$Cl$_2$), 68% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 85/15, 1.0 mL/min, 254 nm; t$_\text{minor}$ = 13.5 min, t$_\text{major}$ = 9.5 min]; \(^1\)H NMR (500 MHz, CDCl$_3$): \(\delta\) 3.19-3.26 (m, 4H), 5.13 (d, \(J = 12.5\) Hz, 1H), 5.28 (d, \(J = 12.5\) Hz, 1H), 5.82-5.84 (m, 1H), 5.91-5.93 (m, 1H), 6.16 (d, \(J = 2.5\) Hz, 1H), 7.07 (d, \(J = 3.0\) Hz, 1H), 7.40 (d, \(J = 4.0\) Hz, 2H), 7.72 (s, 1H); \(^1^9\)F NMR (376 MHz, CDCl$_3$): \(\delta\) -70.2 (s, 3F); \(^{13}\)C NMR (125 MHz, CDCl$_3$): \(\delta\) 23.8, 24.6, 52.7 (q, \(J = 27.0\) Hz), 78.3, 108.3, 114.5, 122.1, 122.5, 125.2 (q, \(J = 283.0\) Hz), 125.7, 125.9, 126.0 (d, \(J = 1.9\) Hz), 126.3, 127.5,
133.6; HRMS $m/z$ (EI+): Calculated for $\text{C}_{15}\text{H}_{13}\text{N}_{2}\text{O}_{2}\text{F}_{3}\text{S}$ ([M]$^+$): 342.0650, Found 342.0658.
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2-(1,1,1-trifluoro-2-(naphthalen-2-yl)-3-nitropropan-2-yl)-4,7-dihydro-1H-indole (3ja):

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 85% yield, $[\alpha]_D^{27} = +109.0$ (c 0.5, CH$_2$Cl$_2$), 82% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 85/15, 1.0 mL/min, 254 nm; t$_{\text{minor}}$ = 16.7 min, t$_{\text{major}}$ = 12.6 min]; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.16-3.21 (m, 2H), 3.25-3.29 (m, 2H), 5.26 (d, $J = 13.0$ Hz, 1H), 5.52 (d, $J = 13.5$ Hz, 1H), 5.82-5.84 (m, 1H), 5.92-5.95 (m, 1H), 6.25 (d, $J = 1.5$ Hz, 1H), 7.39 (d, $J = 8.5$ Hz, 1H), 7.54-7.59 (m, 2H), 7.70 (s, 1H), 7.86 (t, $J = 4.0$ Hz, 2H), 7.89 (d, $J = 16.5$ Hz, 2H); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -68.4 (s, 3F); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 23.8, 24.7, 55.2 (q, $J = 25.8$ Hz), 78.3, 108.7, 114.3, 122.6, 122.8, 125.4, 125.6 (q, $J = 283.8$ Hz), 125.7, 126.1, 126.8, 127.3, 127.5, 128.4, 128.5, 128.6, 131.0, 132.8, 133.0; HRMS m/z (EI+): Calculated for C$_{21}$H$_{17}$N$_2$O$_2$F$_3$ ([M]$^+$): 386.1242, Found 386.1249.
2-(1,1,1-trifluoro-2-(nitromethyl)-4-phenylbutan-2-yl)-4,7-dihydro-1H-indole (3ka):

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 84% yield, [α]D 27 = + 28.6 (c 1.0, CH2Cl2), 71% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 90/10, 1.0 mL/min, 254 nm; t_min = 8.9 min, t_major = 11.4min]; 1H NMR (500 MHz, CDCl3): δ 2.33-2.41 (m, 1H), 2.53-2.61 (m, 2H), 2.87-2.94 (m, 1H), 3.20-3.23 (m, 2H), 3.27-3.31 (m, 2H), 4.92 (d, J = 12.0 Hz, 1H), 5.07 (d, J = 12.0 Hz, 1H), 5.84-5.88 (m, 1H), 5.91-5.95 (m, 1H), 6.00 (d, J = 2.5 Hz, 1H), 7.24 (t, J = 7.5 Hz, 2H), 7.26 (dt, J = 2.0, 7.5 Hz, 1H), 7.33 (t, J = 7.5 Hz, 2H), 7.94 (s, 1H); 19F NMR (376 MHz, CDCl3): δ -72.2 (s, 3F); 13C NMR (125 MHz, CDCl3): δ 23.8, 24.6, 29.8, 32.9, 49.4 (q, J =
25.5 Hz), 75.5, 108.0, 114.4, 121.2, 122.4, 125.7, 126.0 (q, $J = 283.4$ Hz), 126.3, 126.5, 128.3, 128.7, 140.5; HRMS $m/z$ (EI+): Calculated for $C_{19}H_{19}N_2O_2F_3$ ([M$^+$]): 364.1399, Found 364.1419.
<table>
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2-(1,1,1-trifluoro-2-(nitromethyl)decan-2-yl)-4,7-dihydro-1H-indole (3la):

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 88% yield, [α]D<sup>27</sup> = + 1.7 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>), 62% ee [Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 90/10, 1.0 mL/min, 254 nm; t<sub>minor</sub> = 36.3 min, t<sub>major</sub> = 29.7 min]; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.90 (t, J = 7.0 Hz, 3H), 1.28-1.41 (m, 11H), 1.51-1.58 (m, 1H), 2.03-2.09 (m, 1H), 2.18-2.24 (m, 1H), 3.17-3.21 (m, 2H), 3.26-3.29 (m, 2H), 4.81 (d, J = 12.0 Hz, 1H), 4.96 (d, J = 11.5 Hz, 1H), 5.82-5.86 (m, 1H), 5.89-5.91 (m, 1H), 5.92 (d, J = 3.0 Hz, 1H), 7.92 (s, 1H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -72.2 (s, 3F); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 14.0, 22.6, 23.3, 23.8, 24.6, 29.18, 29.19, 29.8, 30.7, 31.7, 49.4 (q, J = 25.3 Hz), 75.8, 107.7, 114.3, 121.8, 122.5, 125.7, 126.0, 126.1 (q, J = 283.5 Hz); HRMS m/z (EI+): Calculated for C<sub>19</sub>H<sub>27</sub>N<sub>2</sub>O<sub>2</sub>F<sub>3</sub> ([M]+): 372.2025, Found 372.2023.
5-methyl-2-(1,1,1-trifluoro-3-nitro-2-phenylpropan-2-yl)-4,7-dihydro-1H-indole (3ab):
25.8 Hz), 78.3, 108.5, 114.8, 117.0, 122.8, 125.4 (q, J = 283.6 Hz), 126.2, 128.5, 128.7, 129.0, 132.9, 133.9; HRMS m/z (EI+): Calculated for C₁₈H₁₇N₂O₂F₃ ([M]⁺): 350.1242, Found 350.1247.
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5-fluoro-2-(1,1,1-trifluoro-3-nitro-2-phenylpropan-2-yl)-4,7-dihydro-1H-indole (2ac):

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 87% yield, $[\alpha]_D^{27} = +43.0$ (c 0.5, CH$_2$Cl$_2$), 88% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 85/15, 1.0 mL/min, 254 nm; $t_{\text{minor}} = 14.7$ min, $t_{\text{major}} = 9.5$ min]; $^1$H NMR (500 MHz, CDCl$_3$): δ 3.25-3.29 (m, 2H), 3.39 (t, $J = 7.0$ Hz, 2H), 5.17 (d, $J = 13.5$ Hz, 1H), 5.36-5.43 (m, 2H), 6.24 (d, $J = 1.5$ Hz, 1H), 7.34-7.43 (m, 5H), 7.85 (s, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$): δ -68.9 (s, 3F), -105.9 to -106.0 (m, 1F); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 22.3 (d, $J = 9.0$ Hz), 25.3 (d, $J = 28.9$ Hz), 55.0 (q, $J = 25.8$ Hz), 78.2, 98.8 (d, $J = 20.6$ Hz), 108.8, 113.2 (d, $J = 14.1$ Hz), 123.9, 125.1, 125.3 (q, $J = 283.6$ Hz), 128.5, 128.7, 129.1, 133.6, 159.0 (d, $J = 249.6$ Hz); HRMS m/z (EI+): Calculated for C$_{17}$H$_{14}$N$_2$O$_2$F$_4$ ([M]+): 354.0991, Found 354.0999.
6-fluoro-2-(1,1,1-trifluoro-3-nitro-2-phenylpropan-2-yl)-4,7-dihydro-1H-indole (3ad):

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 89% yield, [α]D27 = +32.6 (c 0.5, CH2Cl2), 88% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 85/15, 1.0 mL/min, 254 nm; tminor = 18.5 min, tmajor = 8.9 min]; 1H NMR (500 MHz, CDCl3): δ 3.24-3.29 (m, 2H), 3.38-3.41 (m, 2H), 5.18 (d, J = 13.0 Hz, 1H), 5.41 (d, J = 13.5 Hz, 1H), 5.46-5.52 (m, 1H), 6.24 (d, J = 1.5 Hz, 1H), 7.34-7.44 (m, 5H), 7.85 (s, 1H); 19F NMR (376 MHz, CDCl3): δ -69.8 (s, 3F), -107.5 to -107.6 (m, 1F); 13C NMR (125 MHz, CDCl3): δ 22.3 (d, J = 8.5 Hz), 25.1 (d, J = 31.4 Hz), 55.0 (q, J = 25.9 Hz), 78.2, 101.5 (d, J = 17.2 Hz), 108.7, 114.1, 124.0, 124.1, 125.3 (q, J = 283.8 Hz), 128.5,
128.7, 129.1, 133.6, 156.3 (d, J = 247.5 Hz); HRMS m/z (EI+): Calculated for C₁₇H₁₄N₂O₂F₄ ([M]+): 354.0991, Found 354.0997.
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**General procedure for one-pot synthesis of 2-alkylated indoles 4:**

To a dried Schlenk tube were added Ni(ClO$_4$)$_2$·6H$_2$O (7.3 mg, 0.02 mmol) and ligand L7 (11.7 mg, 0.024 mmol) under N$_2$, 2.0 mL toluene was then added through syringe. The resulting mixture was stirred at 80 °C for 1h, after which the nitroalkene (0.2 mmol) and 4,7-dihydroindole (0.3 mmol) were added. The mixture was stirred at 80 °C until the reaction was completed (monitored by TLC). The reaction mixture was then cooled to room temperature and 10 mL CH$_2$Cl$_2$ and 3.0 equiv of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were added. The resulting mixture was stirred at room temperature for 2 h. The solvent was then evaporated and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether (1:5~1:3) to afford the 2-alkylated indole product.

2-(1,1,1-trifluoro-3-nitro-2-phenylpropan-2-yl)-1H-indole (4a):

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); White solid, 85% yield, [α]$_D^{27}$ = +22.5 (c 1.0, CH$_2$Cl$_2$), 91% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 85/15, 1.0 mL/min, 254 nm; t$_{minor}$ = 20.0 min, t$_{major}$ = 11.3 min]; $^1$H NMR (500 MHz, CDCl$_3$): δ 5.32 (d, $J$ = 13.5 Hz, 1H), 5.54 (d, $J$ = 13.5 Hz, 1H), 6.84 (s, 1H), 7.18 (td, $J$ = 1.0, 8.0 Hz, 1H), 7.26 (td, $J$ = 1.0, 8.0 Hz, 1H), 7.33 (t, $J$ = 8.5 Hz, 3H), 7.40-7.46 (m, 3H), 7.68 (d, $J$ = 8.0 Hz, 1H), 8.25 (s, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$): δ -68.4 (s, 3F); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 55.4 (q, $J$ = 26.0 Hz), 78.1, 104.9, 111.2, 120.6, 121.1, 123.4, 125.3 (q, $J$ = 283.8 Hz), 127.2, 128.6, 128.9, 129.5, 130.8, 133.0, 136.2; HRMS m/z (EI+): Calculated for C$_{17}$H$_{13}$N$_2$O$_2$F$_3$ ([M]+): 334.0929, Found 334.0941.
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S44
2-(2-(3,5-dimethylphenyl)-1,1,1-trifluoro-3-nitropropan-2-yl)-1H-indole (4b):

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); White solid, 86% yield, [α]D27 = +20.4 (c 0.5, CH2Cl2), 84% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{minor} = 13.5 min, t_{major} = 7.5 min]; 1H NMR (500 MHz, CDCl3): δ 2.31 (s, 6H), 5.29 (d, J = 13.5 Hz, 1H), 5.50 (d, J = 13.5 Hz, 1H), 6.82 (s, 1H), 6.93 (s, 2H), 7.07 (s, 1H), 7.18 (td, J = 1.0, 8.0 Hz, 1H), 7.26 (td, J = 1.0, 7.0 Hz, 1H), 7.34 (dd, J = 1.0, 8.0 Hz, 1H), 7.69 (d, J = 7.5 Hz, 1H), 8.24 (s, 1H); 13C NMR (125 MHz, CDCl3): δ 21.4, 55.2 (q, J = 25.9 Hz), 78.2, 104.6, 111.2, 120.4, 121.0, 123.2, 125.3 (q, J = 283.8 Hz), 126.20, 126.21, 127.2, 131.1, 132.7, 136.1, 138.5; HRMS m/z (EI+): Calculated for C19H17N2O2F3 ([M]+): 362.1242, Found 362.1234.
2-(1,1,1-trifluoro-2-(4-methoxyphenyl)-3-nitropropan-2-yl)-1H-indole (4c):

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v); White solid, 82% yield, $[\alpha]_D^{27} = +16.6$ (c 0.5, CH$_2$Cl$_2$), 88% ee [Daicel Chiralpak AS-H column (25 cm x 0.46 cm ID), n-hexane/i-PrOH = 80/20, 1.0 mL/min, 254 nm; $t_{\text{minor}} = 22.2$ min, $t_{\text{major}} = 14.7$ min]; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.84 (s, 3H), 5.28 (d, $J = 13.0$ Hz, 1H), 5.48 (d, $J = 13.0$ Hz, 1H), 6.83 (s, 1H), 6.91 (d, $J = 8.5$ Hz, 2H), 7.18 (t, $J = 7.5$ Hz, 1H), 7.23-7.27 (m, 3H), 7.34 (d, $J = 8.0$ Hz, 1H), 7.68 (d, $J = 8.0$ Hz, 1H), 8.26 (s, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -68.8 (s, 3F); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 54.9 (q, $J = 26.3$ Hz), 55.3, 78.2, 104.8, 111.1, 114.2,
120.5, 121.0, 123.3, 124.5, 125.3 (q, \(J = 283.9\) Hz), 127.2, 129.9, 131.0, 136.1, 160.2; HRMS \(m/z\) (EI+): Calculated for C_{18}H_{15}N_{2}O_{3}F_{3} ([M]+): 364.1035, Found 364.1039.
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2-(1,1,1-trifluoro-2-(3-fluorophenyl)-3-nitropropan-2-yl)-1H-indole (4d):

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); White solid, 85% yield, [α]$_D^{27}$ = + 18.2 (c 0.5, CH$_2$Cl$_2$), 85% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 85/15, 1.0 mL/min, 254 nm; $t_{\text{minor}}$ = 13.8 min, $t_{\text{major}}$ = 11.6 min]; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 5.30 (d, $J$ = 14.0 Hz, 1H), 5.50 (d, $J$ = 13.5 Hz, 1H), 6.84 (t, $J$ = 1.0 Hz, 1H), 7.06 (d, $J$ = 10.0 Hz, 1H), 7.13 (d, $J$ = 8.0 Hz, 1H), 7.16 (ddd, $J$ = 0.5, 2.5, 8.0 Hz, 1H), 7.20 (td, $J$ = 0.5, 7.0 Hz, 1H), 7.28 (td, $J$ = 1.0, 7.5 Hz, 1H), 7.36 (dd, $J$ = 1.0, 8.5 Hz, 1H), 7.40 (td, $J$ = 6.5, 8.5 Hz, 1H), 7.69 (d, $J$ = 8.0 Hz, 1H), 8.28 (s, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -68.3 (s, 3F), -111.01 to -111.07 (m, 1F); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 55.1 (q, $J$ = 25.0 Hz), 77.9, 105.1, 111.2, 116.1 (d, $J$ = 24.1 Hz), 116.6 (d, $J$ = 20.8 Hz), 120.7, 121.1, 123.6, 124.2, 125.0 (q, $J$ = 284.0 Hz), 127.0, 130.0, 130.4 (d, $J$ = 8.1 Hz), 135.3 (d, $J$ = 7.0 Hz), 136.2, 162.7 (d, $J$ = 246.4 Hz); HRMS m/z (EI+): Calculated for C$_{17}$H$_{12}$N$_2$O$_2$F$_4$ ([M$^+$]): 352.0835, Found 352.0833.
2-(1,1,1-trifluoro-3-nitro-2-(4-(trifluoromethyl)phenyl)propan-2-yl)-1H-indole (4e):

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); White solid, 80% yield, [α]$_D^{27}$ = +16.4 (c 0.5, CH$_2$Cl$_2$), 86% ee [Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 85/15, 1.0 mL/min, 254 nm; $t_{\text{minor}}$ = 46.4 min, $t_{\text{major}}$ = 24.0 min]; $^1$H NMR (500 MHz, CDCl$_3$): δ 5.33 (d, $J$ = 13.5 Hz, 1H), 5.56 (d, $J$ = 13.5 Hz, 1H), 6.85 (s, 1H), 7.20 (td, $J$ = 1.0, 7.0 Hz, 1H), 7.29 (td, $J$ = 1.0, 7.0 Hz, 1H), 7.36 (dd, $J$ = 1.0, 8.0 Hz, 1H), 7.47 (d, $J$ = 8.5, 2H), 7.69 (t, $J$ = 8.0 Hz, 3H), 8.26 (s, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$): δ -63.8 (s, 3F), -68.4 (s, 3F); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 55.3 (q, $J$ = 26.1 Hz), 77.7, 105.3, 111.3,
120.8, 121.2, 123.5 (q, $J = 270.8$ Hz), 123.8, 125.0 (q, $J = 284.3$ Hz), 125.8 (q, $J = 3.6$ Hz), 127.0, 129.2, 129.8, 131.7 (q, $J = 3.9$ Hz), 136.3, 137.0; HRMS $m/z$ (EI+):

Calculated for $\text{C}_{18}\text{H}_{12}\text{N}_{2}\text{O}_{2}\text{F}_{6} ([\text{M}]^{+})$: 402.0803, Found 402.0823.
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Determine the absolute configuration of product 4a:

The CD spectrum of product 4a and its analogous product (A) reported in our previous work (Ref. 11a, J. Am Chem. Soc. 2013, 135, 2983) were recorded on JASCO J-815 CD spectrometer. Based on the observed cotton effect of these two compounds at around 300 nm and the known R configuration for compound B, the absolute configuration of the present product 4a was assigned to be S.