

Supporting Information

A high-performance chiral ^{19}F -labeled probe with an increased structural twisting

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General Methods and Materials

Material: All reactions were carried out under nitrogen using standard Schlenk techniques unless otherwise noted. All solvents were of ACS reagent grade or better unless otherwise noted. **Probe-1** and **probe-3** were synthesized according to literature procedures.^{1,2} Silica gel (60 μm) was purchased from SiliCycle Inc. All reagent-grade materials were purchased from commercial sources and used without further purification.

Infrared Spectroscopy: Infrared spectra were recorded on an HP5973 Fourier Transform Infrared Spectrometer (FT-IR).

Mass Spectrometry: High-resolution mass spectra (HRMS) were obtained at the SIOC Instrumentation Facility employing ESI or EI as the ionization technique.

NMR Spectroscopy: ^1H , ^{19}F , and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for products characterization were recorded by Agilent-400, Bruker Avance-400, or Bruker Avance-600 spectrometer, chemical shifts (δ) are reported in parts per million (ppm) and referenced with TMS or solvent residue for ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR, and CFCl_3 for ^{19}F NMR. The solutions used for analysis were prepared by mixing the probe and analyte in CDCl_3 . ^{19}F NMR spectra were recorded on a Bruker Avance neo 600 NMR spectrometer (565 MHz for ^{19}F nucleus) using a scan number of 64.

DFT Calculation: Structures of **probe-1** and **probe-2** were calculated using Spartan' 20,³ the $\omega\text{B97X-D}$ function and the 6-31G* & LANL2DZ>Kr basis set were used for structure optimization.

General procedure for NMR experiment:

Preparation of NMR Samples. For Figure 1, precise quantities of analytes were dissolved in deuterated chloroform (CDCl_3) to prepare stock solutions at the desired concentration (51 mM for **A₁-A₇**; 17 mM for **A₈-A₁₉**). Additionally, stock solutions of **probe-1** (8.5 mM, corresponding to 42 mg in 10 mL of CDCl_3) and **probe-2** (17 mM, equivalent to 75 mg in 10 mL of CDCl_3) were prepared. For the analysis involving **probe-1**, a mixture consisting of 200 μL of the **probe-1** solution (containing 0.8 mg of **probe-1**), 100 μL of the analyte solution (containing 0.2–1.1 mg of the analyte), and 100 μL of pure CDCl_3 was prepared and transferred to an NMR tube for ^{19}F NMR measurements. Similarly, for the experiments with **probe-2**, 200 μL of the **probe-2** solution (containing 1.5 mg of **probe-2**) and 200 μL of the analyte solution (containing between 0.5–1.0 mg of the analyte) were combined and placed into an NMR tube for ^1H -decoupled ^{19}F NMR spectroscopy.

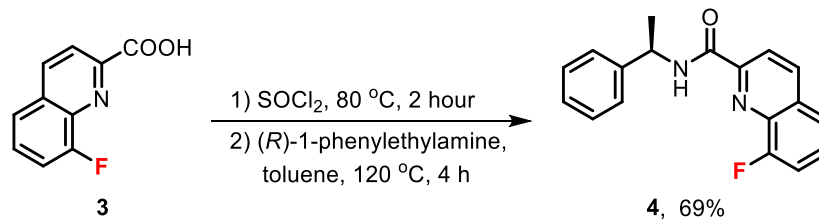
For the studies represented in Figure 3, approximately 1.5 mg of **probe-2** was mixed with the raw reaction mixture in CDCl_3 and then transferred into an NMR tube to conduct ^1H -decoupled ^{19}F NMR measurements.

NMR Measurements. For Figure 1, ^1H -decoupled ^{19}F NMR spectra were recorded on a Bruker Avance neo 600 NMR spectrometer (565 MHz for ^{19}F nucleus) at 298 K, using a default relaxation delay (D1) of 1 s and a scan number of 64. For Figures S2, ^1H -decoupled ^{19}F NMR spectra were recorded on a Bruker Avance neo 600 NMR spectrometer (565 MHz for ^1H -decoupled ^{19}F nucleus

at 298 K, using a default relaxation delay (D1) of 1 s and a scan number of 256. For Figure S3, S16, S19 and S20, ^1H -decoupled ^{19}F NMR spectra were recorded on a Bruker Avance neo 600 NMR spectrometer (565 MHz for ^1H -decoupled ^{19}F nucleus at 298 K, using a default relaxation delay (D1) of 1 s and a scan number of 32.

General Procedures for the Preparation of Fluorinated Ligands

a) amidation



b) C-H palladation

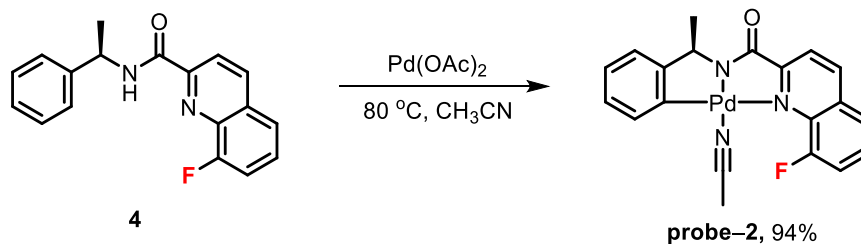
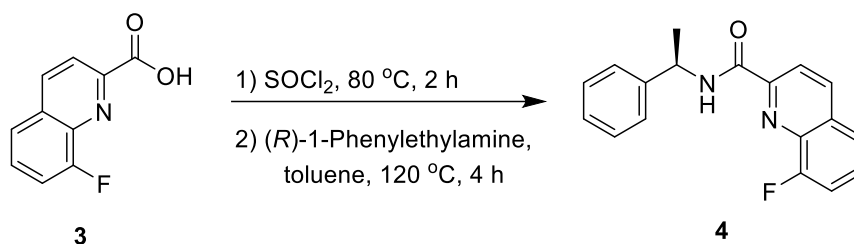


Figure S1. Synthetic Route for ^{19}F -labeled Cyclopalladium **Probe-2**

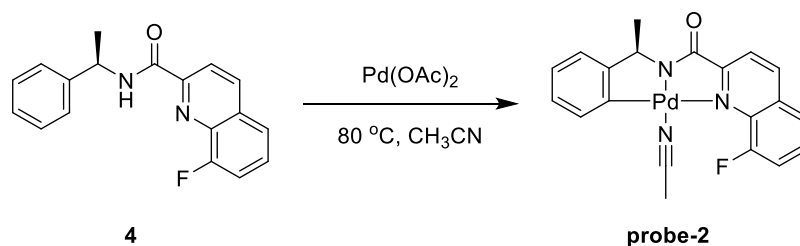


A solution of 8-Fluoro-2-quinolinecarboxylic acid (100 mg, 0.523 mmol, 1.0 equiv) in SOCl_2 (2 mL) was heated to 80 °C for 2 hours, and then SOCl_2 was removed by vacuum pumping, resulting in the precipitated of a white solid in the reaction vessel. To dissolve the white solid, 20 ml toluene was added in the reaction flask, and after 5 minutes, (*R*)-Phenylethylamine (127 mg, 1.05 mmol, 2 equiv) was introduced into the solution. The reaction mixture was stirred at 120 °C for 4 hours. The organic layer was then concentrated under reduced pressure. The resulting residue was subjected to purification through silica gel column chromatography (EtOAc/hexane = 1/4) to give ligand **4** as a white solid (103 mg, yield: 69%). M.P.: 130 – 132 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.54 (d, J = 8.5 Hz, 1H), 8.34 (q, J = 9.0, 7.3 Hz, 2H), 7.65 (d, J = 8.2 Hz, 1H), 7.54 (m, J = 7.9, 4.9 Hz, 1H), 7.48 – 7.40 (m, 3H), 7.35 (t, J = 7.7 Hz, 2H), 7.31 – 7.23 (t, 1H), 5.37 (m, J = 7.2 Hz, 1H), 1.68 (d, J = 6.8 Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -124.18 (dd, J = 10.7, 5.0 Hz). ^{13}C NMR (101 MHz, CDCl_3) δ 163.20, 158.07 (d, J = 258.9 Hz), 149.92, 143.25, 137.30 (d, J = 3.1 Hz), 136.86 (d, J = 12.4 Hz), 130.81 (d, J = 1.9 Hz), 128.72, 127.81 (d, J = 8.1 Hz), 127.36, 126.26, 123.39 (d, J = 4.8 Hz), 119.94, 114.12 (d, J = 18.6 Hz), 49.03, 22.15. IR (KBr): 3387, 3325, 3087, 3061, 3028, 2958, 2926, 2853, 1935, 1753, 1676, 1626, 1602, 1570, 1530, 1498, 1470, 1448, 1428, 1376, 1327, 1314, 1292, 1239, 1264, 1207, 1190, 1160, 1131, 1111, 1078, 1061, 1045, 1020, 993, 970, 927, 912, 893, 882, 860, 841, 816, 772, 740, 716, 698, 602, 590, 569, 558, 529, 500, 479 cm^{-1} .

HRMS (ESI): $\text{C}_{18}\text{H}_{16}\text{FN}_2\text{O}^+$ $[\text{M}+\text{H}]^+$ calc. 295.12412, found: 295.12363.

Procedures for the Preparation of probe-2



Ligand **4** (100 mg, 0.34 mmol, 1.0 equiv) was added to a solution of Pd(OAc)₂ (84 mg, 0.37 mmol, 1.1 equiv) in acetonitrile (15 mL). The resulting mixture was stirred at 80 °C for 4 h, and filtered through a 0.22 μm syringe filter. The filtrate was concentrated to give the crude product which was transferred to a filter funnel and washed extensively with water and hexane. The yellow powder was then dried under vacuum to give **probe-2** as a yellow solid (140 mg, yield: 94%). M.P.: 180 – 182 °C.

¹⁹F NMR (376 MHz, CDCl₃) δ -117.93 (dd, *J* = 11.5, 4.5 Hz). ¹H NMR (400 MHz, CDCl₃) δ 8.37 (s, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.52 (td, *J* = 8.0, 4.4 Hz, 1H), 7.47 – 7.37 (m, 1H), 7.05 (t, *J* = 8.1 Hz, 2H), 6.98 – 6.83 (m, 2H), 5.30 – 5.22 (m, 1H), 2.39 (s, 3H), 1.58 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.69, 161.63, 159.93, 156.08 (d, *J* = 258.6 Hz), 141.70, 139.20 (d, *J* = 2.9 Hz), 135.93 (d, *J* = 11.4 Hz), 133.11, 131.70, 127.06 (d, *J* = 7.8 Hz), 125.01, 124.43, 124.35 (d, *J* = 4.7 Hz), 122.53 (d, *J* = 15.4 Hz), 117.21, 115.16 (d, *J* = 19.9 Hz), 63.15, 23.45, 3.29. IR (KBr): 3048, 2962, 2922, 2855, 1732, 1689, 1616, 1556, 1507, 1456, 1433, 1389, 1373, 1308, 1253, 1199, 1167, 1123, 1084, 1053, 1023, 946, 919, 888, 854, 813, 748, 726, 660, 642, 626, 572, 244, 482, 447, 426, 403 cm⁻¹. HRMS (ESI): C₂₀H₁₇FN₃OPd⁺ [M+H]⁺ calc. 440.0385, found: 440.0393.

Multicomponent Detection via probe-2

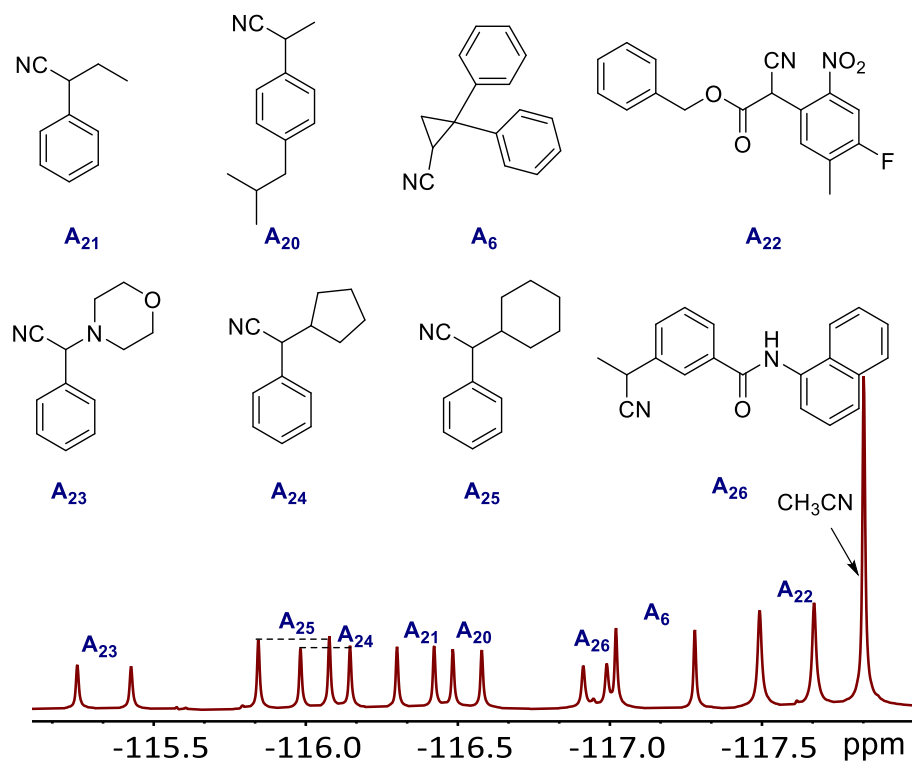


Figure S2. ¹H-decoupled ¹⁹F NMR spectra of mixtures of **probe-2** (ca. 3.5 mg), and 8 pairs of enantiomers (each ca. 0.8–4.5 mg) in CDCl₃. ¹H-decoupled ¹⁹F NMR spectra were recorded on a Bruker Avance neo 600 NMR spectrometer (565 MHz for ¹H-decoupled ¹⁹F nucleus) using a scan number of 256.

Evaluation of Enantiomeric Excess Values with Probe-2

a) ^{19}F NMR spectra for measurement of enantiocomposition

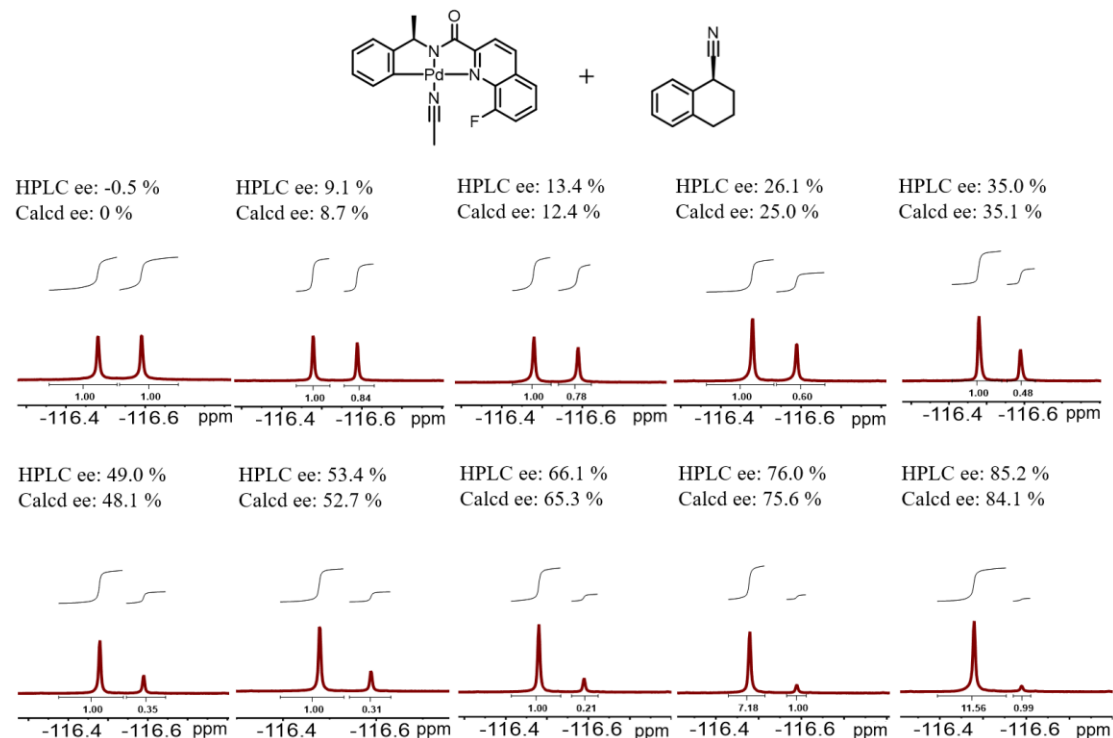


Figure S3. Evaluation of the *ee* values of enantioenriched 1,2,3,4-tetrahydronaphthalene-1-carbonitrile (**A**₇). ^1H -decoupled ^{19}F NMR spectrum of a mixture of **probe-2** (ca. 1.5 mg) and **A**₇ (ca. 2.4 mg) in CDCl_3 . ^{19}F NMR spectra were recorded on a Bruker AVANCE NEO 600 NMR spectrometer (565 MHz for the ^{19}F nucleus) using a scan number of 64.

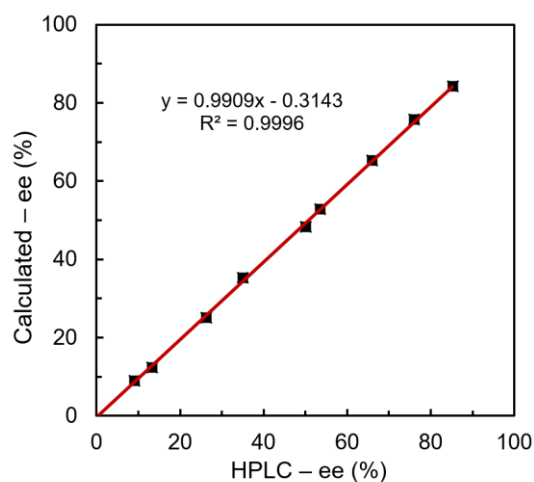
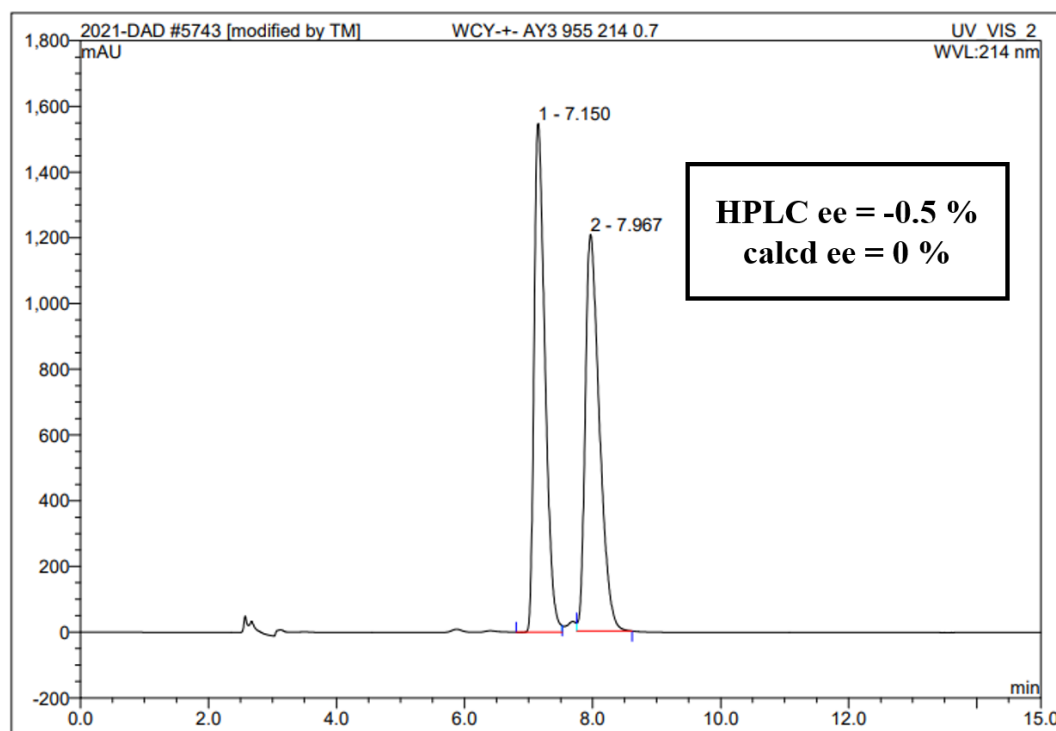


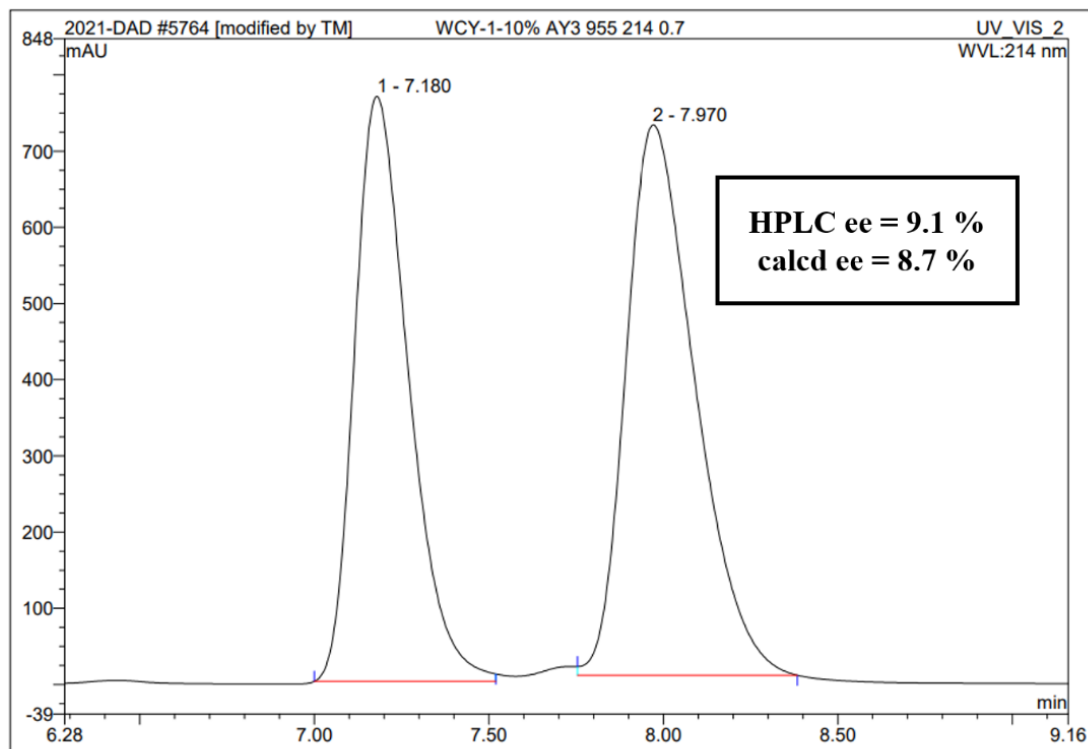
Figure S4. A plot depicting the linear relationship between measured ee using **probe-2** versus the actual ee. Measurements were taken in CDCl_3 using a mixture of **probe-2** (ca. 1.5 mg) and **A**₇ (ca. 1.0 mg).

b) HPLC Traces corresponding to the samples described in Figure S2



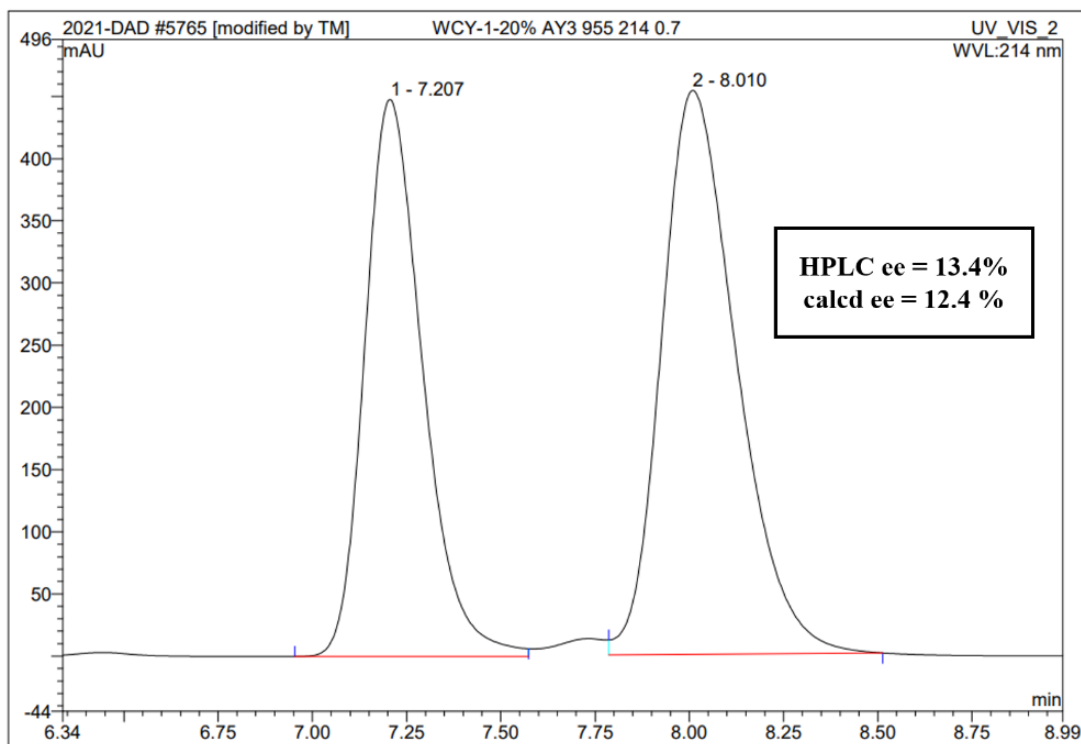
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.15	n.a.	1548.312	305.917	49.75	n.a.	BM *
2	7.97	n.a.	1207.441	309.037	50.25	n.a.	MB*
Total:			2755.753	614.954	100.00	0.000	

Figure S5. Evaluation of the *ee* values of enantioenriched 1,2,3,4-tetrahydronaphthalene-1-carbonitrile (**A₇**) via HPLC. HPLC analysis of Samples with different *ee* values: Chiralpak OJ-H column, hexane/isopropanol = 95/5; 0.7 mL/min; detected at 214 nm. Retention time (T_R) for *R* and *S* enantiomers are 7.15 min (minor) and 7.97 min (major), and peak areas of *S* and *R* enantiomers are 49.75 % and 50.25 % respectively. The *ee* value measured by HPLC is -0.5 %.



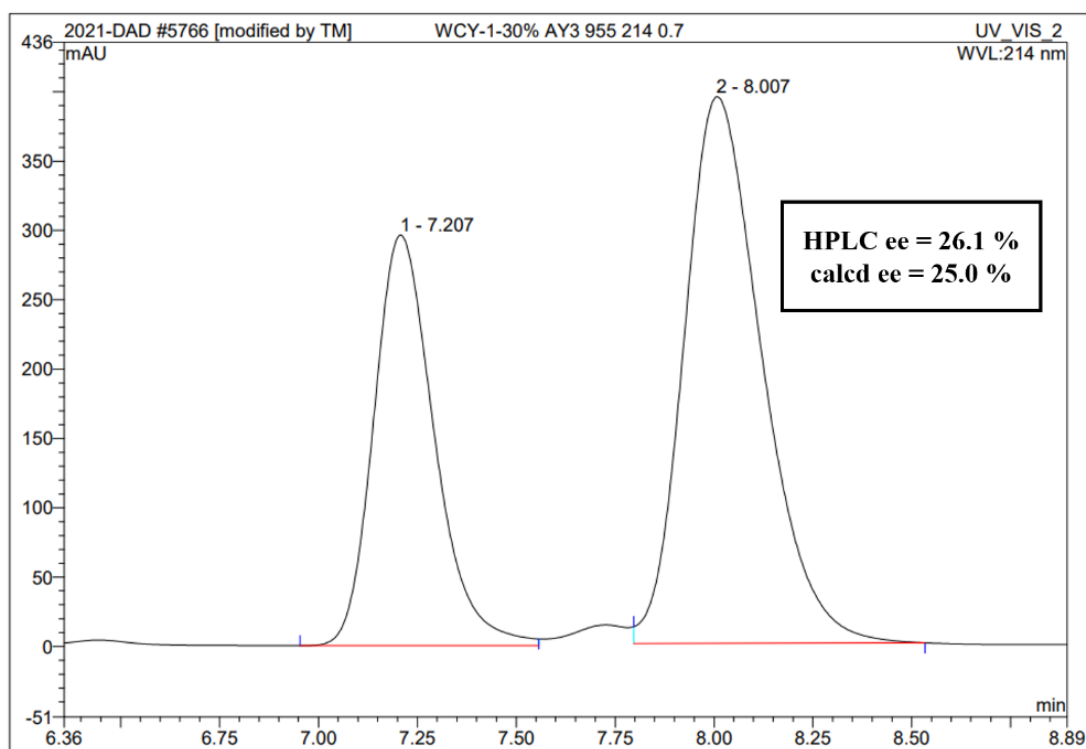
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.18	n.a.	767.984	137.988	45.44	n.a.	BM *
2	7.97	n.a.	722.592	165.703	54.56	n.a.	MB*
Total:			1490.576	303.691	100.00	0.000	

Figure S6. Evaluation of the *ee* values of enantioenriched 1,2,3,4-tetrahydronaphthalene-1-carbonitrile (**A₇**) via HPLC. HPLC analysis of Samples with different *ee* values: Chiralpak OJ-H column, hexane/isopropanol = 95/5; 0.7 mL/min; detected at 214 nm. Retention time (*T_R*) for *R* and *S* enantiomers are 7.18 min (minor) and 7.97 min (major), and peak areas of *R* and *S* enantiomers are 45.44 % and 54.56 % respectively. The *ee* value measured by HPLC is 9.1 %.



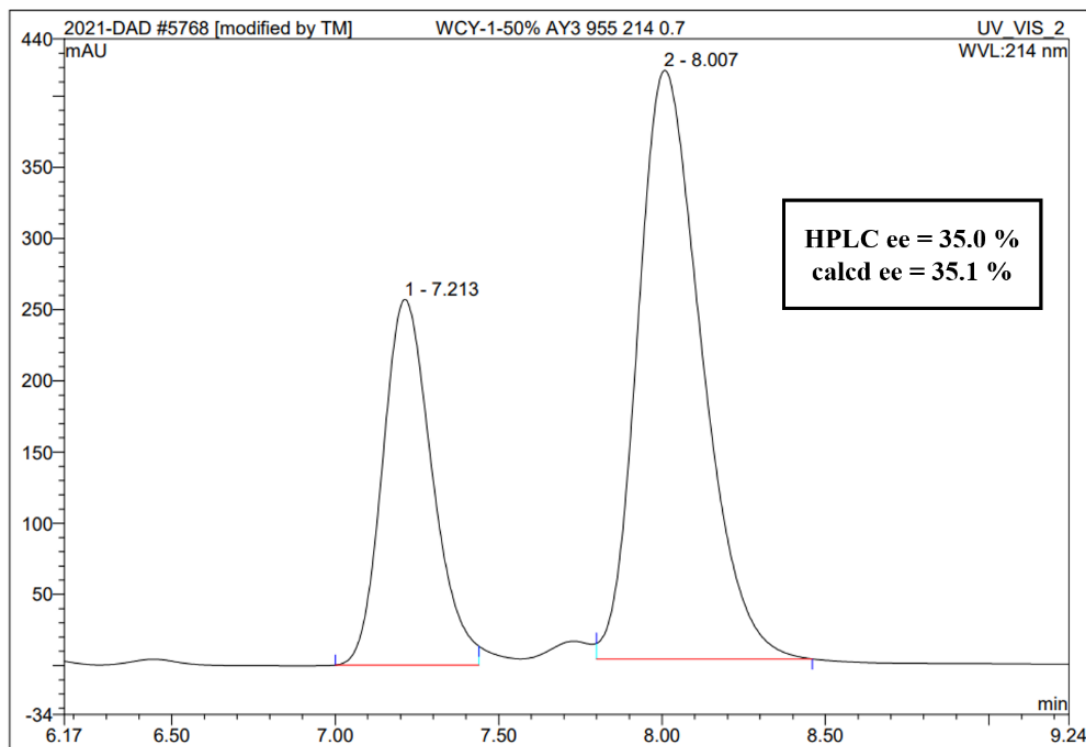
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.21	n.a.	447.918	79.737	43.31	n.a.	BM *
2	8.01	n.a.	453.432	104.353	56.69	n.a.	MB*
Total:			901.350	184.090	100.00	0.000	

Figure S7 Evaluation of the *ee* values of enantioenriched 1,2,3,4-tetrahydronaphthalene-1-carbonitrile (**A₇**) via HPLC. HPLC analysis of Samples with different *ee* values: Chiralpak OJ-H column, hexane/isopropanol = 95/5; 0.7 mL/min; detected at 214 nm. Retention time (T_R) for *R* and *S* enantiomers are 7.21 min (minor) and 8.01 min (major), and peak areas of *R* and *S* enantiomers are 43.31 % and 56.69 % respectively. The *ee* value measured by HPLC is 13.4 %.



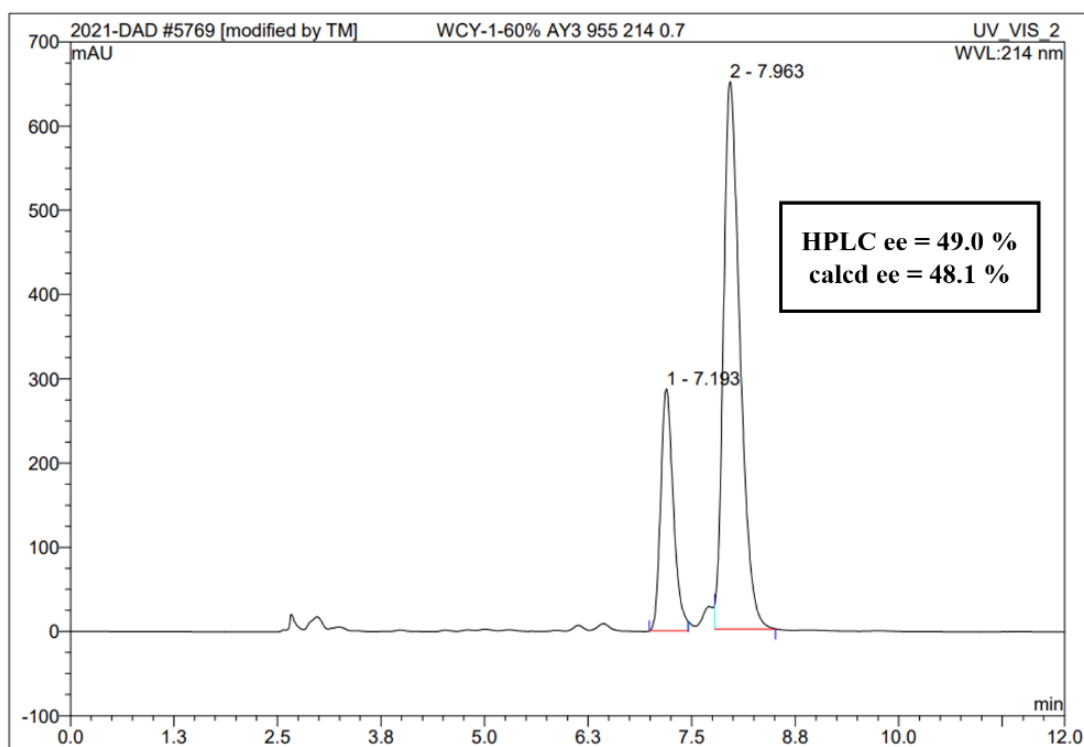
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.21	n.a.	296.129	52.547	36.93	n.a.	BM *
2	8.01	n.a.	394.325	89.729	63.07	n.a.	MB*
Total:			690.454	142.277	100.00	0.000	

Figure S8. Evaluation of the *ee* values of enantioenriched 1,2,3,4-tetrahydronaphthalene-1-carbonitrile (**A₇**) via HPLC. HPLC analysis of Samples with different *ee* values: Chiralpak OJ-H column, hexane/isopropanol = 95/5; 0.7 mL/min; detected at 214 nm. Retention time (*T_R*) for *R* and *S* enantiomers are 7.21 min (minor) and 8.01 min (major), and peak areas of *R* and *S* enantiomers are 36.93 % and 63.07 % respectively. The *ee* value measured by HPLC is 26.1 %.



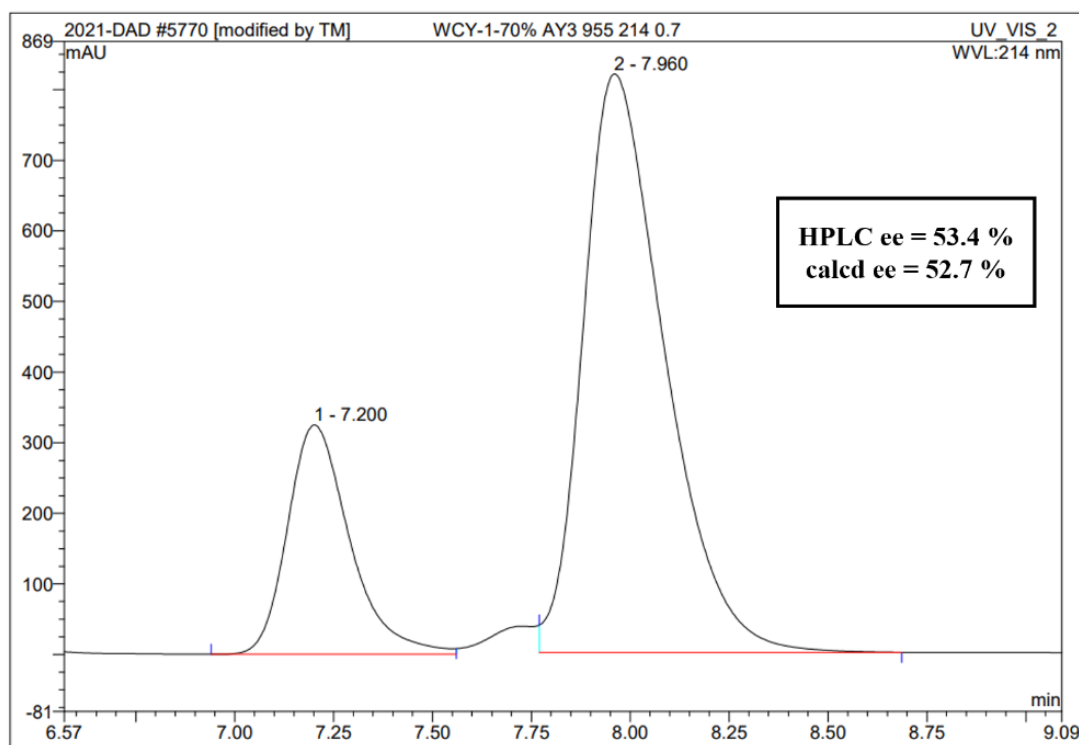
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.21	n.a.	256.880	44.931	32.48	n.a.	BM *
2	8.01	n.a.	413.394	93.403	67.52	n.a.	MB*
Total:			670.275	138.334	100.00	0.000	

Figure S9. Evaluation of the *ee* values of enantioenriched 1,2,3,4-tetrahydronaphthalene-1-carbonitrile (**A₇**) via HPLC. HPLC analysis of Samples with different *ee* values: Chiralpak OJ-H column, hexane/isopropanol = 95/5; 0.7 mL/min; detected at 214 nm. Retention time (T_R) for *R* and *S* enantiomers are 7.21 min (minor) and 8.01 min (major), and peak areas of *R* and *S* enantiomers are 32.48 % and 67.52 % respectively. The *ee* value measured by HPLC is 35.0 %.



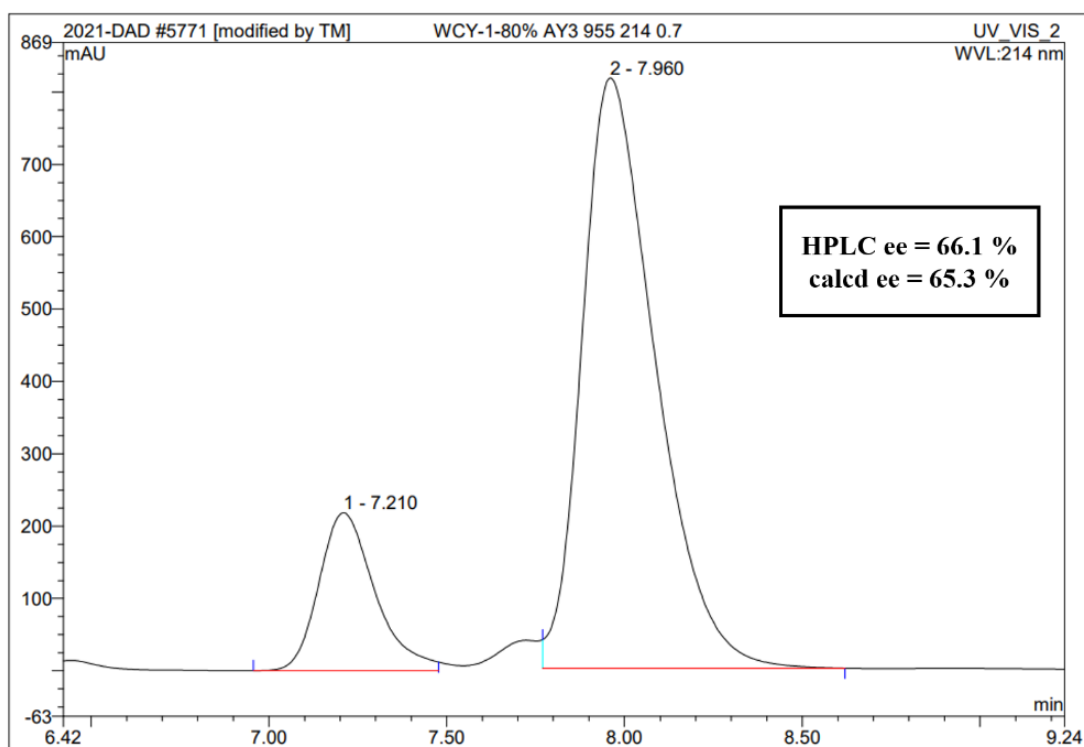
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.19	n.a.	287.270	51.039	25.26	n.a.	BM *
2	7.96	n.a.	649.612	151.009	74.74	n.a.	MB*
Total:			936.882	202.048	100.00	0.000	

Figure S10. Evaluation of the *ee* values of enantioenriched 1,2,3,4-tetrahydronaphthalene-1-carbonitrile (**A₇**) via HPLC. HPLC analysis of Samples with different *ee* values: Chiralpak OJ-H column, hexane/isopropanol = 95/5; 0.7 mL/min; detected at 214 nm. Retention time (T_R) for *R* and *S* enantiomers are 7.19 min (minor) and 7.96 min (major), and peak areas of *R* and *S* enantiomers are 25.26 % and 74.74 % respectively. The *ee* value measured by HPLC is 49.0 %.



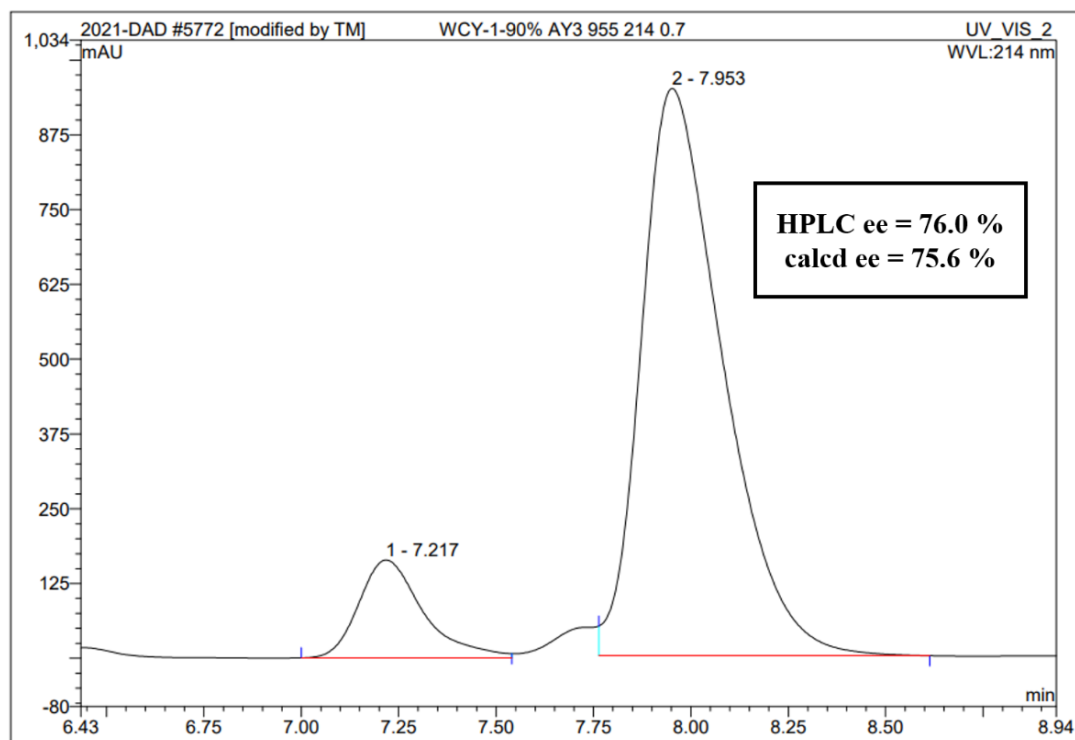
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.20	n.a.	324.873	59.497	23.29	n.a.	BM *
2	7.96	n.a.	819.410	195.914	76.71	n.a.	MB*
Total:			1144.284	255.411	100.00	0.000	

Figure S11. Evaluation of the *ee* values of enantioenriched 1,2,3,4-tetrahydronaphthalene-1-carbonitrile (**A₇**) via HPLC. HPLC analysis of Samples with different *ee* values: Chiralpak OJ-H column, hexane/isopropanol = 95/5; 0.7 mL/min; detected at 214 nm. Retention time (T_R) for *R* and *S* enantiomers are 7.20 min (minor) and 7.96 min (major), and peak areas of *R* and *S* enantiomers are 23.29 % and 76.71 % respectively. The *ee* value measured by HPLC is 53.4 %.



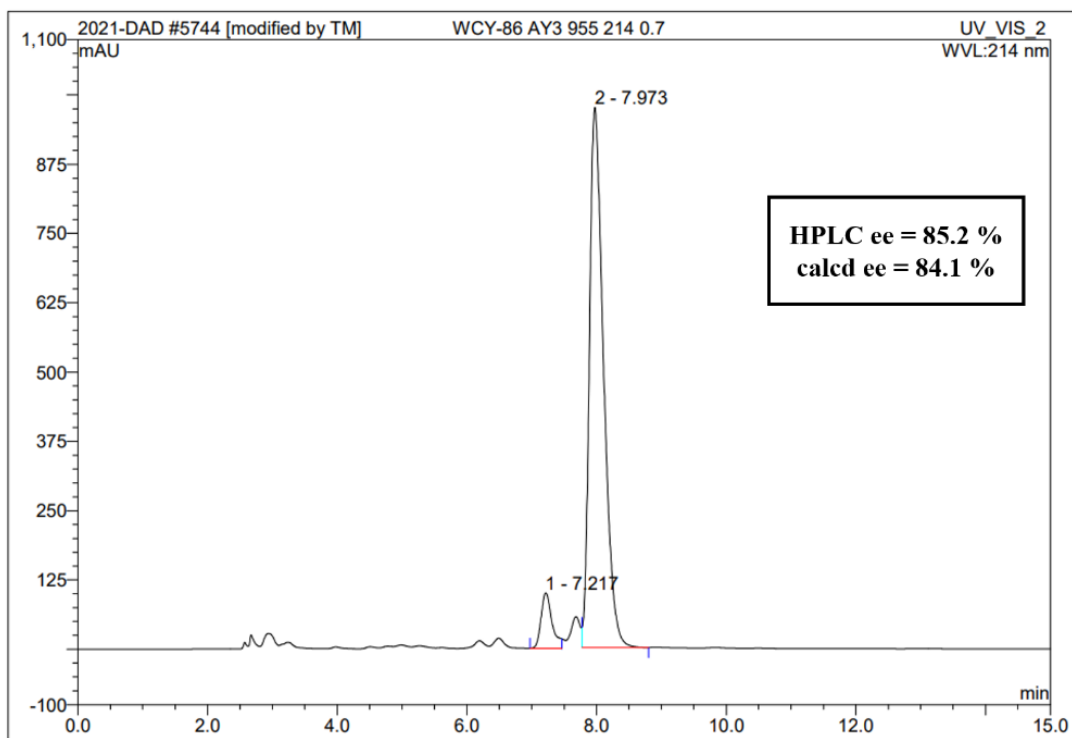
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.21	n.a.	218.361	39.806	16.96	n.a.	BM *
2	7.96	n.a.	815.846	194.966	83.04	n.a.	MB*
Total:			1034.208	234.772	100.00	0.000	

Figure S12. Evaluation of the *ee* values of enantioenriched 1,2,3,4-tetrahydronaphthalene-1-carbonitrile (**A₇**) via HPLC. HPLC analysis of Samples with different *ee* values: Chiralpak OJ-H column, hexane/isopropanol = 95/5; 0.7 mL/min; detected at 214 nm. Retention time (*T_R*) for *R* and *S* enantiomers are 7.21 min (minor) and 7.96 min (major), and peak areas of *R* and *S* enantiomers are 16.96 % and 83.04 % respectively. The *ee* value measured by HPLC is 66.1 %.



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.22	n.a.	164.007	31.312	12.01	n.a.	BM *
2	7.95	n.a.	948.379	229.398	87.99	n.a.	MB*
Total:			1112.386	260.709	100.00	0.000	

Figure S13. Evaluation of the *ee* values of enantioenriched 1,2,3,4-tetrahydronaphthalene-1-carbonitrile (**A₇**) via HPLC. HPLC analysis of Samples with different *ee* values: Chiralpak OJ–H column, hexane/isopropanol = 95/5; 0.7 mL/min; detected at 214 nm. Retention time (T_R) for *R* and *S* enantiomers are 7.22 min (minor) and 7.95 min (major), and peak areas of *R* and *S* enantiomers are 12.01 % and 87.99 % respectively. The *ee* value measured by HPLC is 76.0 %.



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.22	n.a.	99.892	19.571	7.39	n.a.	BM *
2	7.97	n.a.	974.365	245.215	92.61	n.a.	MB*
Total:			1074.257	264.786	100.00	0.000	

Figure S14. Evaluation of the *ee* values of enantioenriched 1,2,3,4-tetrahydronaphthalene-1-carbonitrile (**A₇**) via HPLC. HPLC analysis of Samples with different *ee* values: Chiralpak OJ–H column, hexane/isopropanol = 95/5; 0.7 mL/min; detected at 214 nm. Retention time (T_R) for *R* and *S* enantiomers are 7.22 min (minor) and 7.97 min (major), and peak areas of *R* and *S* enantiomers are 7.39 % and 92.61 % respectively. The *ee* value measured by HPLC is 85.2 %.

Differentiation of Chiral Amines Using Probe-2

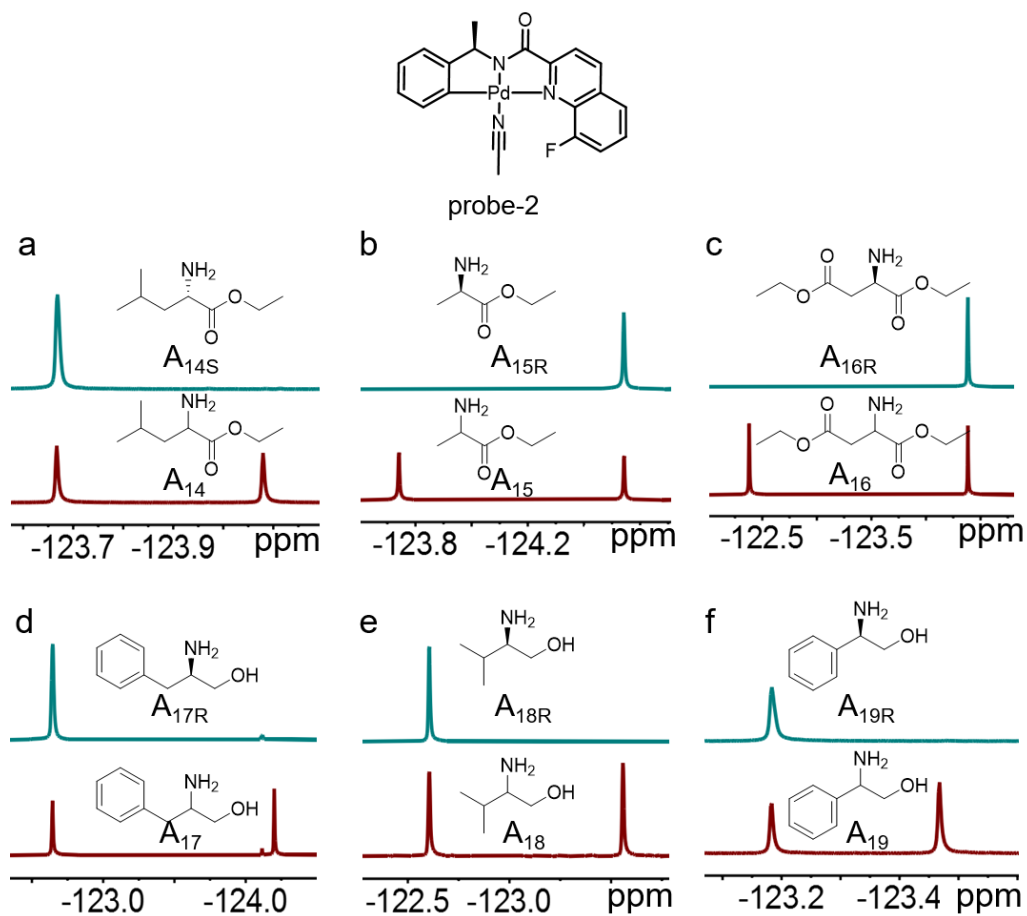


Figure S15. Detection of racemic amine using **probe-2** (a-f). ^1H -decoupled ^{19}F NMR spectra of mixtures of **probe-2** (1.5 mg), various racemic analytes and enantiopure (0.3–0.6 mg) in CDCl_3 ; The red chromatogram represents the racemic analyte, the green chromatogram represents the analyte in the single configuration. Spectra were recorded on a Bruker Avance-600 NMR spectrometer using a scan number of 64.

Evaluation of Enantiomeric Excess Values of Crude Reaction Product

Under a nitrogen atmosphere, an oven-dried 25 mL Schlenk tube was charged with $\text{Cu}(\text{acac})_2$ (7.6 mg, 0.029 mmol, 10 mol%), chiral ligand **L1/L2** (0.043 mmol, 15 mol%) and 1.0 mL of solvent (DMF was used in conditions using ligand **L1**, and acetone was used for conditions using ligand **L2**). After stirring at room temperature for 5 minutes, the 2-(4-isobutylphenyl)propanoic acid (60 mg, 0.29 mmol), $\text{PhI}=\text{O}$ (128 mg, 0.58 mmol, 2.0 equiv), $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ (76 mg, 0.44 mmol, 1.5 equiv), TMSCN (57 mg, 0.58 mmol, 2.0 equiv), and 4 mL of solvent were added and the resulting solution was stirred at 30 °C in oil bath for 15 h. Taking 0.5 mL of the reaction solution, extracted with $\text{EtOAc}/\text{H}_2\text{O}$, removing the solvent under vacuum, and then mixing it with 1.5 mg of the **probe-3** in 0.5 mL of CDCl_3 . The solution was filtered through a syringe filter (0.22 μm) before ^{19}F NMR analysis. The spectra were recorded on a Bruker Avance-600 NMR neo spectrometer (32 scans). Enantiomeric excess values determined based on the integrations of the ^{19}F NMR signals corresponding to the enantiomers.

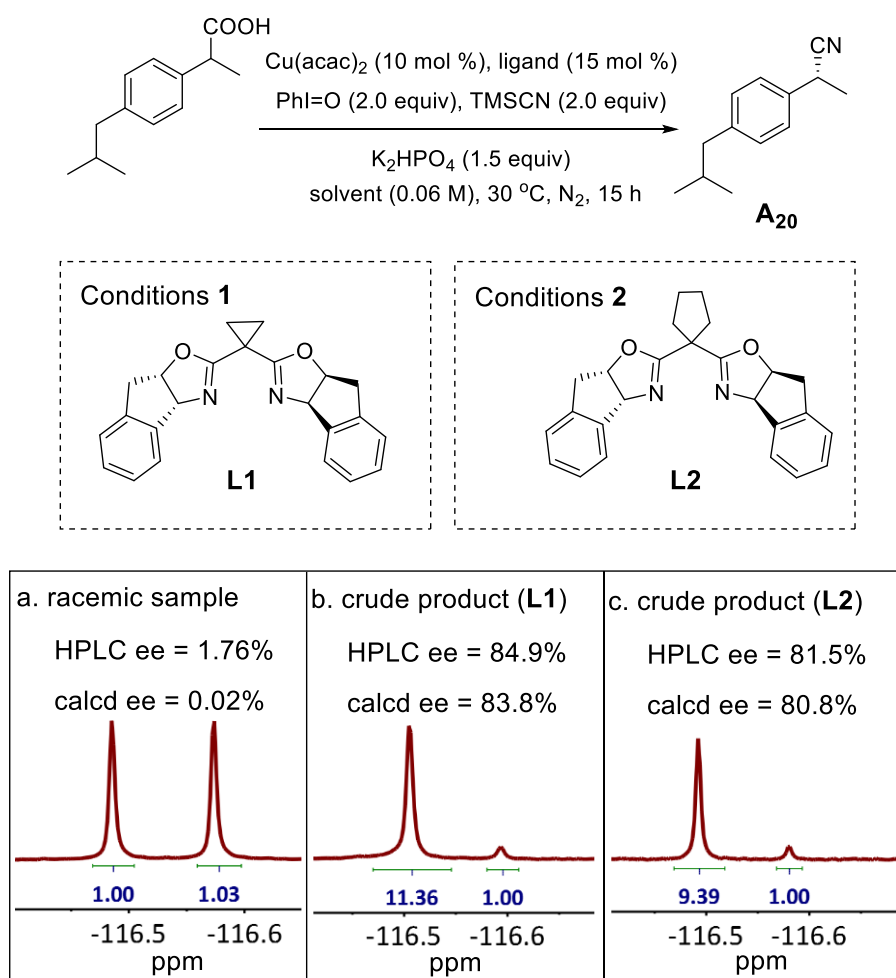
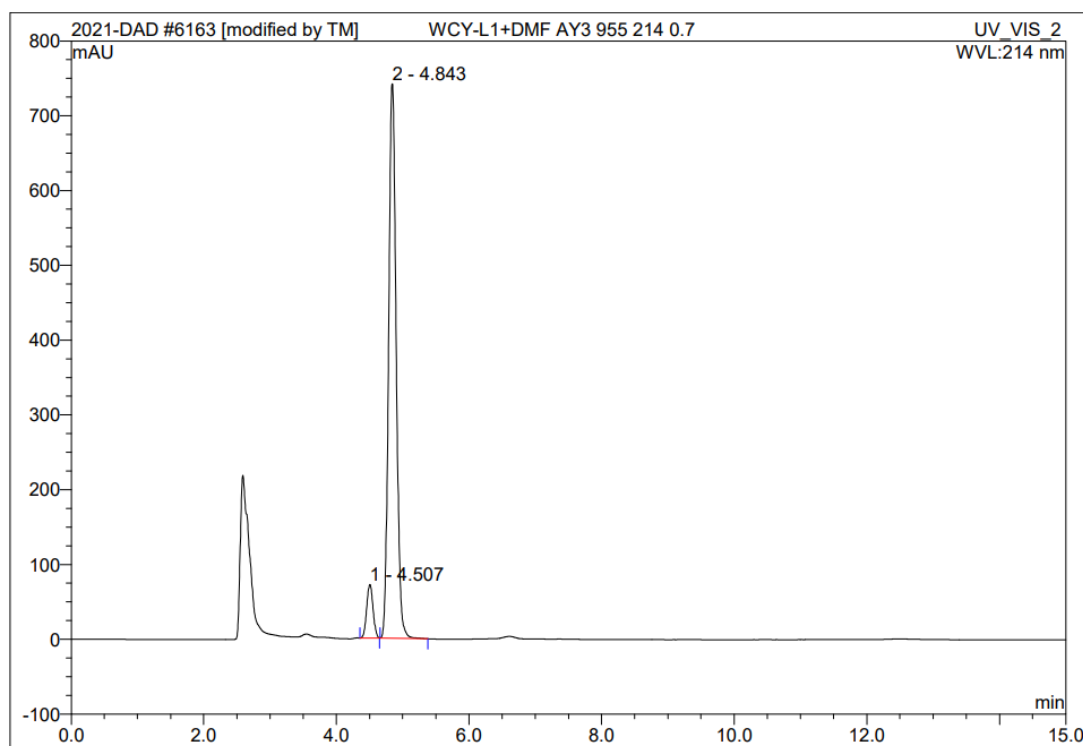
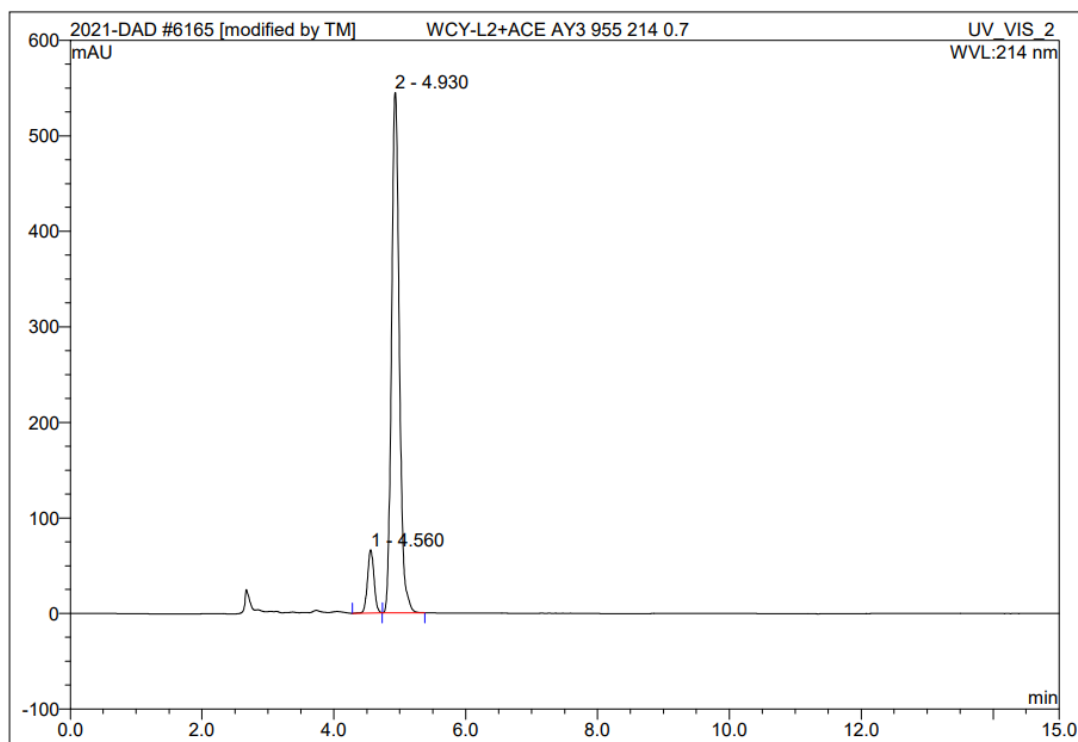


Figure S16. Evaluation of the enantioselectivity of an asymmetric cyanation reaction using **probe-2**. (a) ^1H -decoupled ^{19}F NMR spectrum of a mixture of **probe-2** (1.5 mg) and racemic **A**₂₀ (ca. 1.0 mg) in CDCl_3 . (b, c) ^1H -decoupled ^{19}F NMR spectra of mixtures of **probe-2** (1.5 mg) and crude reaction products obtained under different conditions (conditions 1: ligand **L1** was used with DMF serving as the solvent; conditions 2: ligand **L2** was used with acetone serving as the solvent).



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	4.51	n.a.	71.693	7.951	7.53	n.a.	BMB
2	4.84	n.a.	741.688	97.577	92.47	n.a.	BMB
Total:			813.381	105.528	100.00	0.000	

Figure S17. HPLC analysis of reaction mixture under the reaction conditions using ligand **L1** with DMF serving as the solvent. HPLC analysis of Samples with different *ee* values: Chiralpak OJ–H column, hexane/isopropanol = 95/5; 0.7 mL/min; detected at 214 nm. Retention time (T_R) for *S* and *R* enantiomers are 4.51 min (minor) and 4.84 min (major), and peak areas of *R* and *S* enantiomers are 92.47 % and 7.53 % respectively. The *ee* value measured by HPLC is 84.9 %.



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	4.56	n.a.	66.517	7.607	9.25	n.a.	BMB
2	4.93	n.a.	544.610	74.633	90.75	n.a.	BMB
Total:			611.127	82.240	100.00	0.000	

Figure S18. HPLC analysis of reaction mixture under the reaction conditions using ligand **L2** with acetone serving as the solvent. HPLC analysis of Samples with different *ee* values: Chiralpak OJ-H column, hexane/isopropanol = 95/5; 0.7 mL/min; detected at 214 nm. Retention time (T_R) for *S* and *R* enantiomers are 4.56 min (minor) and 4.93 min (major), and peak areas of *R* and *S* enantiomers are 90.75 % and 9.25 % respectively. The *ee* value measured by HPLC is 81.5 %.

Evaluation of Influence of the Presence of Ligand L1/L2 on Chiral Discrimination of Nitriles.

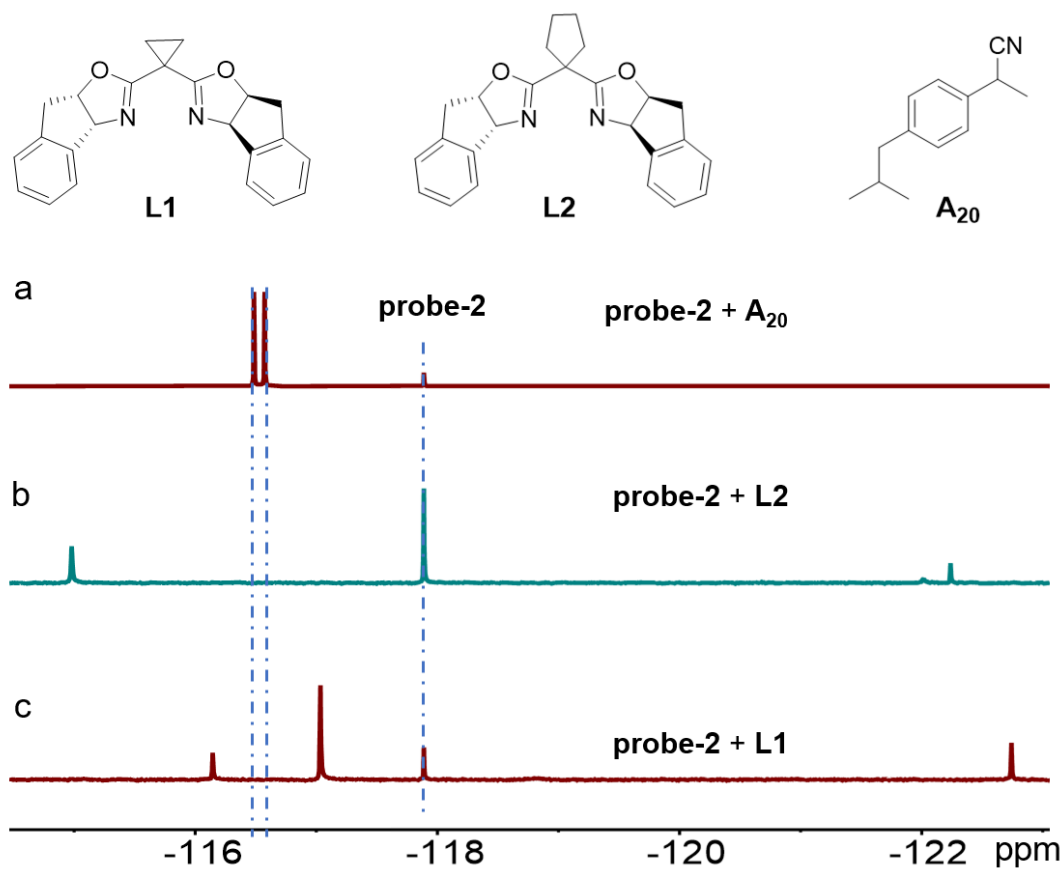


Figure S19. Evaluation of influence of the presence of ligand **L1/L2** on chiral discrimination of nitriles. (a) ¹H-decoupled ¹⁹F NMR spectrum of a mixture of **probe-2** (1.5 mg) and racemic **A₂₀** (ca. 1.0 mg) in CDCl₃. (b,c) ¹H-decoupled ¹⁹F NMR spectra of mixtures of **probe-2** (1.5 mg), **L1** or **L2** (0.6 mg) in CDCl₃.

Comparison Between the Performance of Probe-2 and Probe-3 Both Labeled with a ^{19}F Atom.

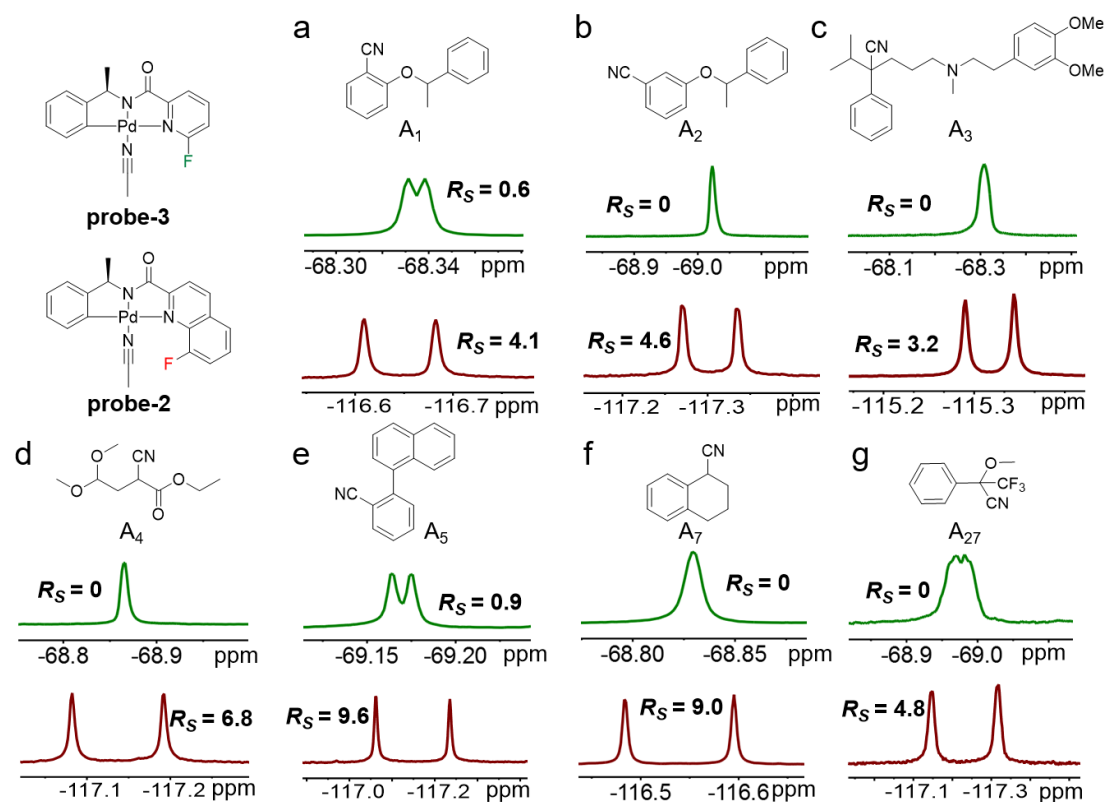


Figure S20. (a-g) $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of mixtures containing ^{19}F -labeled probes and various analytes dissolved in CDCl_3 . $^{19}\text{F}\{^1\text{H}\}$ NMR spectra associated with **probe-3** are presented in deep green and were obtained using **probe-3** (0.6 mg) and analytes (0.6–1.5 mg) in CDCl_3 , while those corresponding to **probe-2** are presented in dark red and were obtained using **probe-2** (1.5 mg) and analytes (0.6–1.5 mg) in CDCl_3 . All ^{19}F NMR measurements were conducted using a Bruker Avance Neo 600 MHz (565 MHz for the ^{19}F nucleus) NMR spectrometer, with each spectrum obtained from 32 scans.

Determination of the Degree of Twisting by DFT Calculations

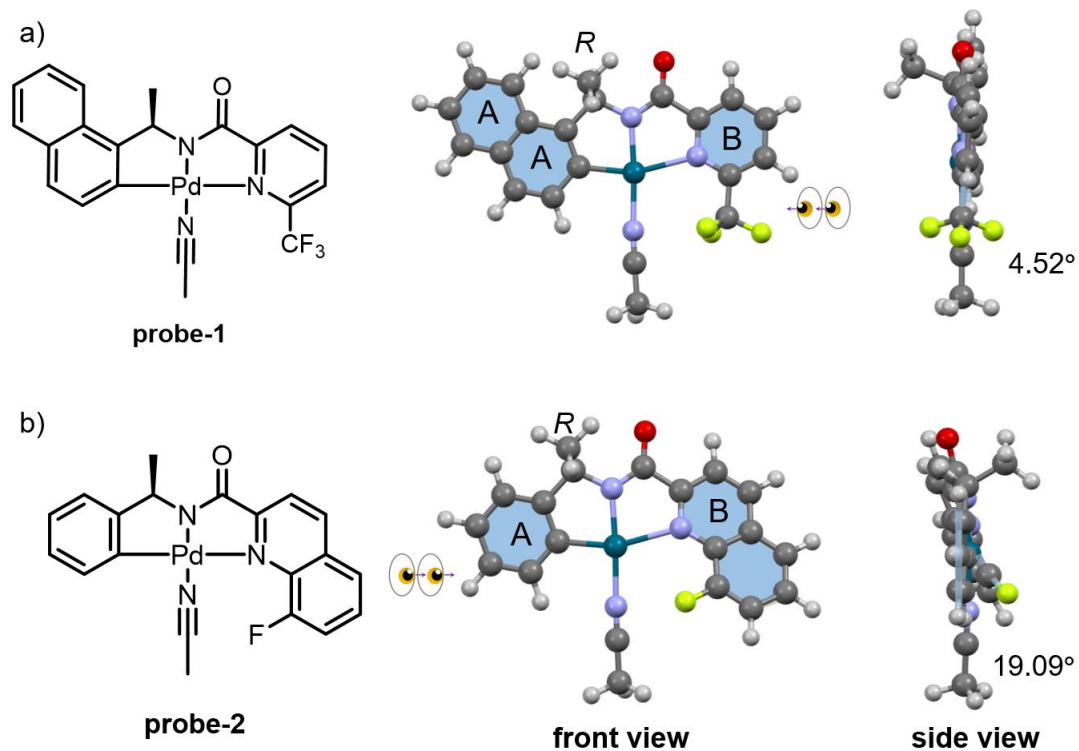


Figure S21. Optimized structures of **probe-2** or **probe-1** through DFT calculation.

probe-2

Pd	0.23803	-0.49931	0.27668
O	-1.77288	2.32063	2.41519
N	-0.44031	0.54737	1.80029
N	-0.36529	1.48481	-0.73806
N	0.81420	-1.74027	-1.27780
H	1.12143	-3.56412	0.51900
H	1.24320	-5.10589	2.43363
H	0.61481	-4.32607	4.70710
H	-2.65553	3.56111	0.55363
H	-2.79707	4.30598	-1.85622
H	-0.12652	-1.98841	5.04574
H	-1.34193	0.04257	3.61430
H	1.62660	0.77694	3.54480
H	0.70634	0.37309	5.01160
H	0.28787	1.82916	4.08025
H	1.37844	1.42437	-4.92535
H	-0.28004	3.10644	-5.75715
H	-1.90631	4.10956	-4.18140
H	0.55647	-3.66449	-3.76450

H	2.08189	-4.09216	-2.95118
H	2.01397	-2.67210	-4.02452
F	1.52530	0.57146	-2.52597
C	0.43044	-1.88606	1.68454
C	0.84727	-3.20496	1.50601
C	0.91692	-4.08065	2.58856
C	0.56689	-3.64465	3.86244
C	0.15101	-2.33087	4.05107
C	0.07954	-1.44669	2.97560
C	-0.34968	-0.01169	3.14501
C	-1.15478	1.64944	1.58394
C	-1.16744	2.08618	0.12668
C	-2.04614	3.13276	-0.23310
C	-2.10605	3.53083	-1.53617
C	-1.23466	2.94482	-2.48966
C	-0.34840	1.93654	-2.02599
C	0.63228	0.79463	4.00321
C	0.59952	1.43509	-2.95606
C	0.62461	1.83547	-4.26292
C	-0.30490	2.79512	-4.71814
C	-1.20787	3.34780	-3.84811
C	1.09167	-2.42049	-2.16375
C	1.45714	-3.26332	-3.29322

probe-1

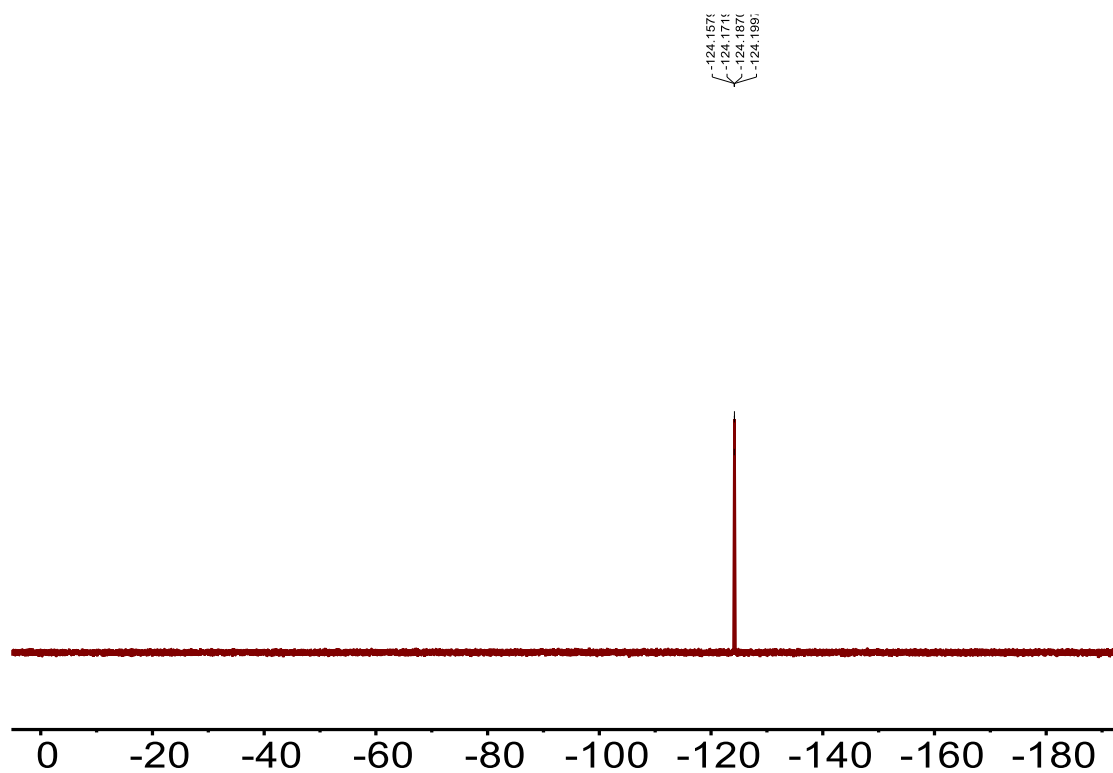
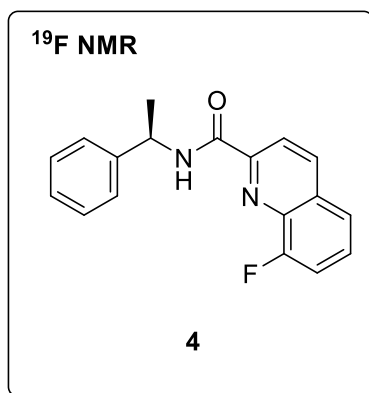
Pd	0.17206	-0.11406	-0.93792
O	3.14301	1.64095	1.26191
N	1.22111	0.57819	0.57650
N	2.11849	0.56419	-1.98812
N	-1.00830	-0.90534	-2.44162
H	-2.85918	-1.04291	-0.70344
H	-4.44343	-1.10537	1.16526
H	4.65899	2.16818	-0.51084
H	5.52696	2.16379	-2.89535
H	0.80162	1.37738	2.45765
H	1.37790	-1.60908	2.11549
H	1.03631	-0.83589	3.67556
H	2.49914	-0.38331	2.76795
H	4.11231	1.07474	-4.65324
H	-3.06240	-1.22185	-4.81393
H	-2.83051	-2.85348	-4.13480
H	-1.61172	-2.16524	-5.23861

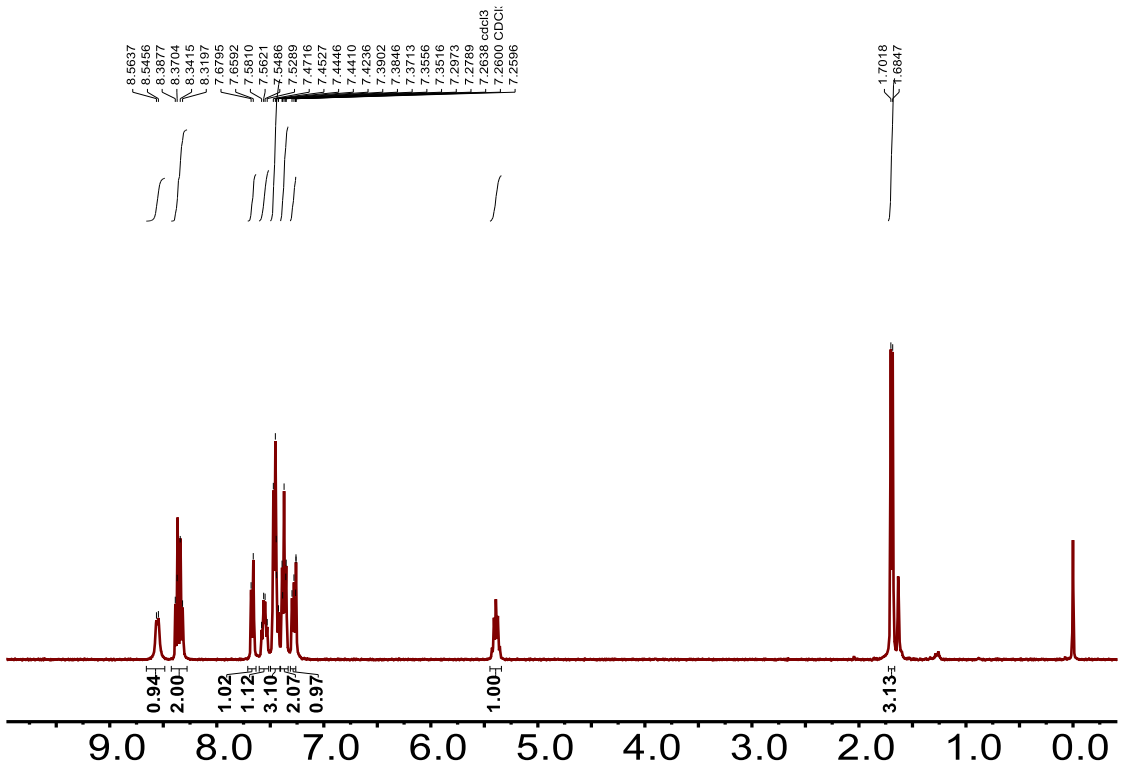
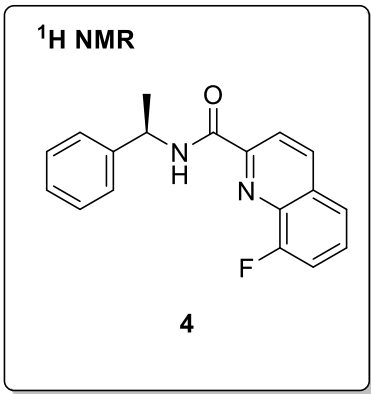
H	-4.96921	-0.69710	3.52617
H	-4.28776	0.06458	5.77480
H	-1.96158	0.87182	6.15800
H	-0.33753	0.88884	4.33459
F	2.28747	-0.11469	-5.48986
F	0.53271	0.55037	-4.42167
F	1.41916	-1.37257	-3.96430
C	-1.19513	-0.31533	0.48747
C	-2.53115	-0.73873	0.28470
C	-3.42095	-0.77069	1.32583
C	-3.03418	-0.35687	2.62540
C	-1.69646	0.07834	2.84409
C	-0.77579	0.06825	1.75178
C	0.67861	0.42594	1.92337
C	2.41093	1.14595	0.40012
C	2.88003	1.14152	-1.04511
C	4.11111	1.72654	-1.33499
C	4.57286	1.71547	-2.63800
C	3.79148	1.11302	-3.62044
C	2.57973	0.55533	-3.24513
C	1.44886	-0.67088	2.67580
C	-1.60504	-1.36194	-3.31375
C	1.69833	-0.10040	-4.28415
C	-2.32345	-1.93552	-4.44151
C	-3.95263	-0.35633	3.70811
C	-3.57543	0.06753	4.95503
C	-2.25451	0.52120	5.17262
C	-1.34283	0.52544	4.14857

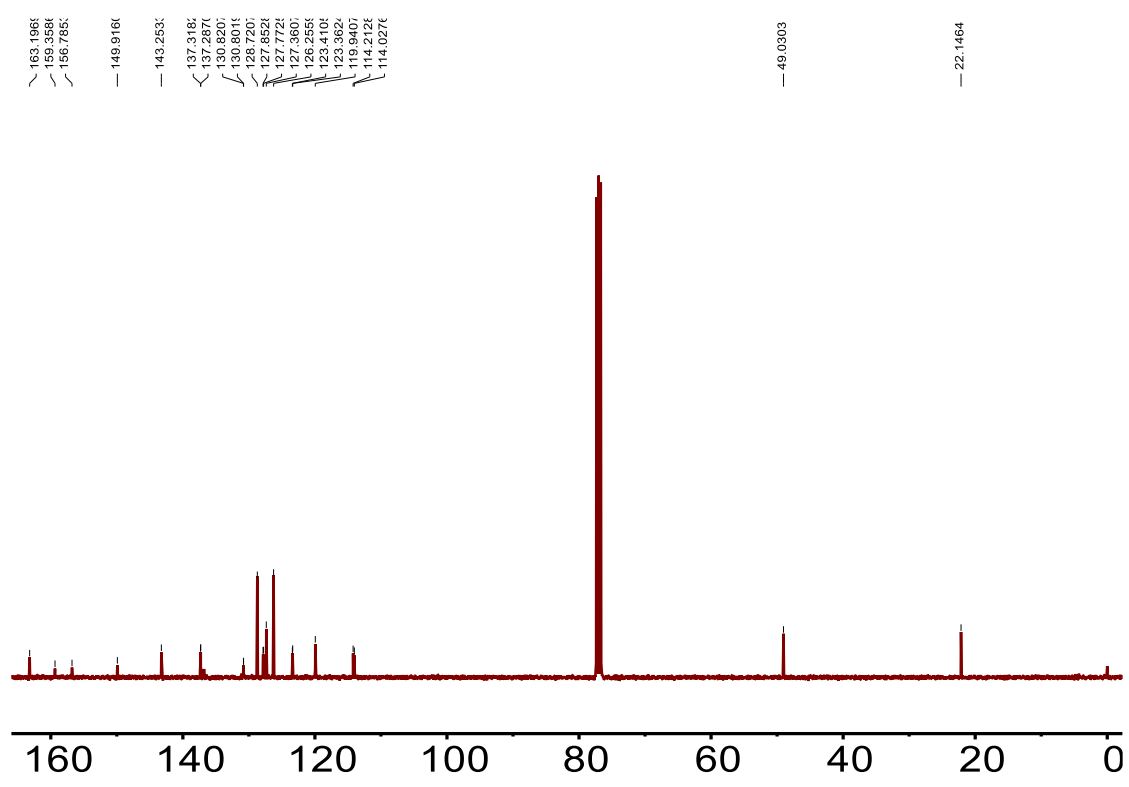
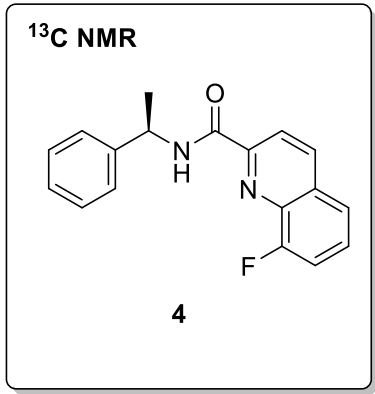
References

1. Gu, G.; Yue, Y.; Wang, C.; Zhang, W.; Wu, J.; Li, Y.; Zhao, Chiral Discrimination of Nitrile Compounds Using a ^{19}F -Labeled Palladium Probe. *Org. Lett.* **2023**, *25*, 4819–4824.
2. Gu, G.; Zhao, C.; Zhang, W.; Weng, J.; Xu, Z.; Wu, J.; Xie, Y.; He, X.; Zhao, Y. Chiral Discrimination of Acyclic Secondary Amines by ^{19}F NMR. *Anal. Chem.* **2024**, *96*, 730–736.
3. *Spartan' 20*, Wavefunction, Inc. Irvine, CA

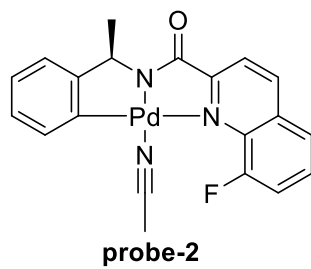
^1H , ^{19}F , and $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of All New Compounds







¹⁹F NMR



-117.9046
-117.9163
-117.9345
-117.9468

