C–C bond activation enabled by dyotropic rearrangement of Pd(IV) species

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General information
Reagents and solvents were purchased from commercial sources (Aldrich and Acros) and used without further purification. Flash column chromatography was performed using Silicycle P60 silica: 230-400 mesh (40-63 μm) silica. Reactions were monitored using Merck Kieselgel 60F254 aluminium plates. TLC was visualized by UV fluorescence (254 nm) then one of the following: KMnO₄, phosphomolybdic acid, ninhydrin, p-anisaldehyde, vanillin. NMR spectra were recorded on aBruker Avance III-400, Bruker Avance-400 or Bruker DPX-400 spectrometer at room temperature. Chemical shifts (δ) were reported in parts per million (ppm) relative to residual solvent peaks rounded to the nearest 0.01 for proton and 0.1 for carbon (ref: CHCl₃ [¹H: 7.26, ¹³C: 77.16]). Coupling constants (J) were reported in Hz to the nearest 0.1 Hz. Peak multiplicity was indicated as follows s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Attribution of peaks was done using the multiplicities and integrals of the peaks. The accurate masses were measured by the mass spectrometry service of the EPFL by ESI-TOF using a QTOF Ultima from Waters. Optical rotations were obtained with a Jasco P-2000 polarimeter (589 nm). Melting points were measured using a Stuart SMP30. Enantiomeric excesses were determined with a Thar SFC Investigator system using chiral stationary columns by comparing the samples with the appropriate racemic samples. IR spectra were recorded in a Jasco FT/IR-4100 spectrometer outfitted with a PIKE technology MIRacle™ ATR accessory as neat films compressed onto a Zinc Selenide window. The spectra were reported in cm⁻¹.
Table S1. Screening of directing groups.

Reaction conditions: 1 (0.1 mmol), boronic acid (0.2 mmol), Pd(OAc)$_2$ (10 mol%), ligand (12 mol%), Selectfluor (0.2 mmol), Na$_2$CO$_3$ (0.2 mmol), DCE (2 mL), 50 $^\circ$C, 4 h.
Table S2. Screening of chiral ligands.

Reaction Conditions: 1a (0.1 mmol), boronic acid (0.2 mmol), Pd(OAc)$_2$ (10 mol%), ligand (12 mol%), Selectfluor (0.2 mmol), Na$_2$CO$_3$ (0.2 mmol), DCE (2 mL), 50 °C, 4 h.
Table S3. Screening of Pd catalysts, solvents, oxidants, bases and additives.

| entry | Pd cat. | L   | solvent | oxidant   | base            | additive | yield | ee  |
|-------|---------|------|---------|-----------|-----------------|----------|-------|-----|
| 1     | Pd(OAc)₂ | L₃   | DCE     | Selectfluor | Na₂CO₃ (2 eq)   | /        | 42%   | 92% |
| 2     | Pd(TFA)₂ | L₃   | DCE     | Selectfluor | Na₂CO₃ (2 eq)   | /        | <5%   | ND  |
| 3     | PdCl₂    | L₃   | DCE     | Selectfluor | Na₂CO₃ (2 eq)   | /        | No reaction | ND  |
| 4     | PdCl₂(CH₃CN)₂ + AgBF₄ | L₃   | DCE     | Selectfluor | Na₂CO₃ (2 eq)   | /        | 20%   | ND  |
| 5     | Pd₂(dba)₃ | L₃   | DCE     | Selectfluor | Na₂CO₃ (2 eq)   | /        | 46%   | 93% |
| 6     | Pd(OAc)₂ | L₂   | DCE     | Selectfluor | Na₂CO₃ (2 eq)   | /        | 47%   | 92% |
| 7     | Pd(OAc)₂ | L₂   | DCE + H₂O | Selectfluor | Na₂CO₃ (2 eq)   | /        | No reaction | ND  |
| 8     | Pd(OAc)₂ | L₂   | CHCl₃   | Selectfluor | Na₂CO₃ (2 eq)   | /        | 20%   | ND  |
| 9     | Pd(OAc)₂ | L₂   | DCM     | Selectfluor | Na₂CO₃ (2 eq)   | /        | 20%   | ND  |
| 10    | Pd(OPiv)₂| L₂   | DCE     | Selectfluor | Na₂CO₃ (2 eq)   | /        | 58%   | 92% |
| 11    | Pd(OPiv)₂| L₂   | DCE     | NFPy      | Na₂CO₃ (2 eq)   | /        | No reaction | ND  |
| 12    | Pd(OPiv)₂| L₂   | DCE     | Selectfluor | Na₂CO₃ (3 eq) AdCO₂H (1 equiv) | 65% | 92% |
| 13    | Pd(OPiv)₂| L₂   | DCE     | Selectfluor | Na₂CO₃ (3 eq) PivOH (1 equiv) | 50% | ND  |
| 14    | Pd(AdCOO)₂ | L₂   | DCE     | Selectfluor | Na₂CO₃ (2 eq)   | /        | 50%   | ND  |
| 15    | Pd(AdCOO)₂ | L₂   | DCE     | Selectfluor | Na₂CO₃ (3 eq) AdCO₂H (1 equiv) | 70% | 92% |

Reaction conditions: 1a (0.1 mmol), boronic acid (0.2 mmol), Pd cat. (10 mol%), ligand (12 mol%), Selectfluor (0.2 mmol), solvent (2 mL), 50 °C, 4 h.
Figure S1. Detection of Pd(IV)-F species by HRMS

Chemical Formula: Pd
Exact Mass: 105.90
Molecular Weight: 106.42
m/z: 105.90 (100.0%), 107.90 (96.8%), 104.91 (81.7%), 109.91 (42.9%), 103.90 (40.8%), 101.91 (3.7%)

Full spectra

See next page for details.
HRMS (ESI/QTOF) m/z: [M] +
Calcd for C44H49FN3O3Pd + 792.2809; Found 792.2825.

Full spectra
See next page for details.

Chemical Formula: Pd
Exact Mass: 105.90
Molecular Weight: 106.42
m/z: 105.90 (100.0%), 107.90 (96.8%), 104.91 (81.7%), 109.91 (42.9%), 103.90 (40.8%), 101.91 (3.7%)
Figure S2. Control experiments of (±)-7a

Conditions: (±)-7a (0.05 mmol), Selectfluor (0.1 mmol), Na2CO3 (0.1 mmol), additives (0.1 mmol), DCE (1 mL), 50 °C, 16 h.
Preparation of cyclopentenes 1

Pyridine-oxazoline ligands were prepared according to the reported methods. Cyclopentenes 1a-1i were prepared according to the reported methods:

To a solution of S1 (1.0 equiv) in DMF (1.0 M) at 0 °C was added sodium hydride (60% oil dispersion, 2.5 equiv) and the resulting suspension was stirred at 0 °C for 10 min. Allyl bromide (2.5 equiv) was added, and the reaction mixture was stirred at rt for 30 min. Saturated sodium chloride was added and the reaction mixture was extracted with ethyl acetate. The organic layers were separated and concentrated in vacuo to give S2. The crude product was used directly for the next reaction.

To a solution of S2 (1.0 equiv) in dichloromethane (0.3 M) was added Grubbs’ I catalyst (0.05 equiv) and the resulting suspension was heated under reflux for 1 h. The solvent was removed in vacuo, and the crude product was purified by flash chromatography (10% ethyl acetate/90% hexane) to give S3.

To a solution of KOH (5.0 equiv) in ethanol (1.0 M) was added S3 (1.0 equiv) and the reaction mixture was heated at reflux for 2 h. The reaction mixture was cooled to rt and partially concentrated under reduced pressure. The residue was diluted with water and extracted twice with dichloromethane. The aqueous layer was acidified until pH = 1 with HCl (3 M) and extracted twice with dichloromethane. The combined organic extracts were dried (Na₂SO₄) and concentrated under reduced pressure to afford S4 which was used for the next step without further purification.

To a solution of S4 (1.0 equiv) in dichloromethane (0.3 M) was added dropwise oxalyl chloride (4.0 equiv) followed by 3 drops of DMF at 0 °C. The reaction mixture was stirred at rt for 1.5 h. The reaction mixture was then concentrated. The resulting acid chloride was redissolved in dichloromethane (0.3 M) and aniline (1.5 equiv) and triethylamine (2.0 equiv) were added. The resulting mixture was stirred at rt for 1.5 h. Whereupon diluted, it was washed twice with HCl (3 M), once with satd. NaHCO₃ solution, and once with brine. The organic extracts were dried (Na₂SO₄) and concentrated under reduced pressure. Flash chromatography on silica gel (hexanes:ethyl acetate 90:10) afforded 1a-1i.

Cyclopentene 1j was prepared according to the previously reported methods.
To a cooled (0 °C) solution of 3-cyclopentenecarboxylic acid (1.12 g, 10 mmol) in THF (8 mL) was slowly added LDA (14.7 mL, 1.5 M solution in THF, 22 mmol). The resultant mixture was stirred at that temperature for 1 h followed by a 1 h-stir at room temperature. The reaction mixture was then cooled to 0 °C and methyl iodide (2.84 g, 20 mmol) was added dropwise. The resultant mixture was slowly raised to room temperature and stirred for the total of 18 h. The mixture was quenched with dilute HCl (3M) and extracted with ethyl acetate (3 x 25 mL). The combined organic layers were dried (Na₂SO₄) and concentrated under reduced pressure to give 1-methyl-3-cyclopentenecarboxylic acid which was used for the next step without further purification.

To a solution of 1-methyl-3-cyclopentenecarboxylic acid (0.63 g, 5 mmol) in dichloromethane (0.3 M) was added dropwise oxalyl chloride (4.0 equiv) followed by 3 drops of DMF at 0 °C. The reaction mixture was stirred at rt for 1.5 h. The reaction mixture was then concentrated. The resulting acid chloride was redissolved in dichloromethane (0.3 M) and aniline (1.5 equiv) and triethylamine (2.0 equiv) were added. The resulting mixture was stirred at rt for 1.5 h. Whereupon diluted, it was washed twice with HCl (3 M), once with satd. NaHCO₃ solution, and once with brine. The organic extracts were dried (Na₂SO₄) and concentrated under reduced pressure. Flash chromatography on silica gel (hexanes:ethyl acetate 90:10) afforded 1j.

Cyclopentene 1k was prepared according to the following procedure:

To a solution of S5 (prepared according to the reported method from diethyl oxalate, 1.0 equiv) in DMF (1.0 M) at 0 °C was added sodium hydride (60% oil dispersion, 1.5 equiv) and the resulting suspension was stirred at 0 °C for 10 min. MeI (1.5 equiv) was added, and the reaction mixture was stirred at rt for 30 min. Saturated sodium chloride was added and the reaction mixture was extracted with ethyl acetate. The organic layer was separated and concentrated in vacuo to give S6. The crude product was used directly for the next reaction.

To a solution of S6 (1.0 equiv) in dichloromethane (0.3 M) was added Grubbs’ II catalyst (0.05 equiv) and the resulting suspension was heated under reflux for 1 h. The solvent was removed in vacuo, and the crude product was purified by flash chromatography (10% ethyl acetate/90%...
hexane) to give S7.

To a solution of KOH (5.0 equiv) in ethanol (1.0 M) was added S7 (1.0 equiv) and the reaction mixture was heated at reflux for 2 h. The reaction mixture was cooled to rt and partially concentrated under reduced pressure. The residue was diluted with water and extracted twice with dichloromethane. The aqueous layer was acidified until pH = 1 with HCl (3 M) and extracted twice with dichloromethane. The combined organic extracts were dried (Na₂SO₄) and concentrated under reduced pressure to afford S8 which was used for the next step without further purification.

To a solution of S8 (1.0 equiv) in dichloromethane (0.3 M) was added dropwise oxalyl chloride (4.0 equiv) followed by 3 drops of DMF at 0 °C. The reaction mixture was stirred at rt for 1.5 h. The reaction mixture was then concentrated. The resulting acid chloride was redissolved in dichloromethane (0.3 M) and aniline (1.5 equiv) and triethylamine (2.0 equiv) were added. The resulting mixture was stirred at rt for 1.5 h. Whereupon diluted, it was washed twice with HCl (3 M), once with satd. NaHCO₃ solution, and once with brine. The organic extracts were dried (Na₂SO₄) and concentrated under reduced pressure. Flash chromatography on silica gel (hexanes:ethyl acetate 90:10) afforded 1k.

Characterization of the cyclopentenes is listed below.

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\begin{array}{c}
\text{CONHPh} \\
\text{Ph}
\end{array}
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**N,1-diphenylcyclopent-3-ene-1-carboxamide (1a)**

Methyl 2-phenylacetate was used as the starting material. 0.61 g, 68% yield (four steps). White powder; m.p. 89-91 °C. IR (νmax, cm⁻¹) 3336 (w), 3057 (w), 1662 (s), 1597 (s), 1520 (s), 1496 (s), 1437 (s), 1313 (m), 1242 (m), 756 (s), 694 (s), 671 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.42-7.35 (m, 6H), 7.33-7.24 (m, 3H), 7.05 (t, J = 7.2 Hz, 1H), 6.87 (brs, 1H), 5.78 (s, 2H), 3.40 (d, J = 15.6 Hz, 2H), 2.89 (d, J = 15.6 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 174.5, 144.6, 138.2, 129.1, 128.9, 128.8, 127.3, 126.8, 124.2, 119.7, 59.3, 43.9; HRMS (nanochip-ESI/LTQ-Orbitrap) m/z: [M + H]⁺ Calcd for C₁₈H₁₈NO⁺ 264.1383; Found 264.1378.

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\begin{array}{c}
\text{CONHPh} \\
\text{OMe}
\end{array}
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**1-(4-methoxyphenyl)-N-phenylcyclopent-3-ene-1-carboxamide (1b)**
Methyl 2-(4-methoxyphenyl)acetate was used as the starting material. 1.25 g, 65% yield (four steps). White powder: m.p. 92-94 °C. IR (neat): 3318, 3060, 2935, 1669, 1599, 1510, 1438, 1311, 1244, 1184, 1034, 833, 752, 692 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.36 (m, 2H), 7.33-7.23 (m, 4H), 7.08-7.03 (m, 1H), 6.94-6.88 (m, 3H), 5.77 (s, 2H), 3.82 (s, 3H), 3.41-3.33 (m, 2H), 2.89-2.81 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 174.0, 158.8, 138.3, 136.5, 129.0, 128.8, 128.0, 124.1, 119.6, 114.4, 58.7, 55.4, 44.1; HRMS (ESI/QTOF) m/z: [M + H]+ Calcd for C₁₉H₂₀NO₂⁺ 294.1489; Found 294.1488.

1-(4-bromophenyl)-N-phenylcyclopent-3-ene-1-carboxamide (1c)
Methyl 2-(4-bromophenyl)acetate was used as the starting material. 0.51 g, 73% yield (four steps). White powder: m.p. 142-144 °C. IR (neat): 3314, 3061, 2929, 1660, 1598, 1523, 1494, 1436, 1316, 1246, 1009, 754 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 7.20-7.10 (m, 4H), 7.01-6.93 (m, 1H), 6.92 (br s, 1H), 5.66 (s, 2H), 3.26 (d, J = 16.1 Hz, 2H), 2.70 (d, J = 16.1 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 173.8, 143.7, 138.0, 132.0, 129.0, 128.8, 128.5, 124.4, 121.2, 119.9, 58.9, 43.8; HRMS (ESI/QTOF) m/z: [M + H]+ Calcd for C₁₈H₁₇BrNO⁺ 342.0489; Found 342.0489.

1-(4-chlorophenyl)-N-phenylcyclopent-3-ene-1-carboxamide (1d)
Methyl 2-(4-chlorophenyl)acetate was used as the starting material. 0.774 g, 69% yield (four steps). White powder: m.p. 140-142 °C. IR (neat): 3305, 3059, 1658, 1600, 1539, 1494, 1436, 1318, 1246, 829, 758, 691 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.44-7.26 (m, 8H), 7.12-7.08 (m, 1H), 6.98 (s, 1H), 5.80 (s, 2H), 3.40 (d, J = 14.4 Hz, 2H), 2.84 (d, J = 14.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 174.0, 143.2, 138.0, 133.2, 129.1, 129.0, 128.8, 128.2, 124.4, 119.8, 58.9, 43.9; HRMS (ESI/QTOF) m/z: [M + H]+ Calcd for C₁₈H₁₇ClNO⁺ 298.0993; Found 298.0993.

N-phenyl-1-(m-tolyl)cyclopent-3-ene-1-carboxamide (1e)
Methyl 2-\textit{m}-tolylacetate was used as the starting material. 1.21 g, 67\% yield (four steps). White powder: m.p. 92-94 °C. IR (neat): 3322, 3054, 1665, 1599, 1524, 1438, 1315, 1244, 752, 692 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.46 (d, \(J = 8.0\) Hz, 2H), 7.36-7.24 (m, 5H), 7.19-7.10 (m, 3H), 5.83 (s, 2H), 3.46 (d, \(J = 15.2\) Hz, 2H), 2.95 (d, \(J = 15.2\) Hz, 2H), 2.43 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 174.6, 144.4, 138.6, 138.2, 128.8, 128.78, 128.70, 128.0, 127.4, 124.0, 123.6, 119.6, 59.1, 43.7, 21.6; HRMS (ESI/QTOF) m/z: [M + H]\(^{+}\) Calcd for C\(_{19}\)H\(_{20}\)NO\(^+\) 278.1539; Found 278.1541.

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\text{CONHPh}
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1-(4-fluorophenyl)-\textit{N}-phenylcyclopent-3-ene-1-carboxamide (1f)

Methyl 2-(4-fluorophenyl)acetate was used as the starting material. 1.24 g, 70\% yield (four steps). White powder: m.p. 119-121 °C. IR (neat): 3318, 3056, 1657, 1599, 1506, 1435, 1317, 1233, 1161, 837, 754, 694 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.44-7.36 (m, 4H), 7.33-7.26 (m, 2H), 7.13-6.97 (m, 4H), 5.80 (s, 2H), 3.41 (d, \(J = 15.2\) Hz, 2H), 2.86 (d, \(J = 15.2\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 174.3, 161.9 (d, \(J = 246.5\) Hz), 140.4, 138.1, 129.0, 128.8, 128.4 (d, \(J = 7.9\) Hz), 124.3, 119.8 (d, \(J = 3.2\) Hz), 115.8 (d, \(J = 21.3\) Hz), 58.8, 44.0; \(^{19}\)F NMR (377 MHz, CDCl\(_3\)): -115.31; HRMS (QTOF) m/z: [M + H]\(^{+}\) Calcd for C\(_{18}\)H\(_{17}\)FNO\(^+\) 282.1289; Found 282.1292.

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\text{CONHPh}
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\textit{N}-(4-chlorophenyl)-1-phenylcyclopent-3-ene-1-carboxamide (1g)

Methyl 2-phenylacetate was used as the starting material. 0.616 g, 64\% yield (four steps). White powder: m.p. 116-118 °C. IR (neat): 3322, 3062, 1661, 1595, 1494, 1395, 1302, 1240, 1093, 827, 700 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42-7.28 (m, 7H), 7.21 (d, \(J = 8.8\) Hz, 2H), 6.89 (s, 1H), 5.78 (s, 2H), 3.38 (d, \(J = 15.2\) Hz, 2H), 2.89 (d, \(J = 15.2\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 174.9, 144.4, 136.8, 129.22, 129.18, 129.0, 128.8, 127.5, 126.8, 121.0, 59.3, 44.0; HRMS (ESI/QTOF) m/z: [M + H]\(^{+}\) Calcd for C\(_{18}\)H\(_{17}\)ClNO\(^+\) 298.0993; Found 298.1001.
methyl 4-(1-phenylcyclopent-3-ene-1-carboxamido)benzoate (1h)

Methyl 2-phenylacetate was used as the starting material. 0.24 g, 58% yield (four steps). White powder: m.p. 152-154°C. IR (neat): 3338, 2947, 1718, 1694, 1595, 1518, 1280, 1248, 1175, 1111, 702 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 8.8 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H), 7.42-7.36 (m, 4H), 7.07 (s, 1H), 5.79 (s, 2H), 3.87 (s, 3H), 3.39 (d, J = 14.8 Hz, 2H), 2.90 (d, J = 14.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 174.8, 166.7, 144.1, 142.4, 130.8, 129.2, 128.8, 127.6, 126.8, 125.5, 118.7, 59.5, 52.1, 43.9; HRMS (ESI/QTOF) m/z: [M + H]+ Calcd for C₂₀H₂₀NO₃+ 322.1438; Found 322.1436.

1-phenyl-N-(o-tolyl)cyclopent-3-ene-1-carboxamide (1i)

Methyl 2-phenylacetate was used as the starting material. 1.12 g, 69% yield (four steps). White powder: m.p. 137-139°C. IR (νmax, cm⁻¹) 3306, 3058, 1647, 1504, 1452, 1252, 1196, 750, 696; ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.0 Hz, 1H), 7.46-7.36 (m, 4H), 7.34-7.28 (m, 1H), 7.06 (d, J = 7.2 Hz, 1H), 7.01-6.97 (m, 1H), 6.82 (s, 1H), 5.81 (s, 2H), 3.42 (d, J = 14.8 Hz, 2H), 2.95 (d, J = 14.8 Hz, 2H), 1.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 174.6, 144.7, 136.1, 130.4, 129.0, 128.9, 128.0, 127.5, 127.2, 126.9, 124.7, 122.0, 59.4, 43.9, 17.2; HRMS (ESI/QTOF) m/z: [M + H]+ Calcd for C₁₉H₂₀NO+ 278.1539; Found 278.1544.

1-methyl-N-phenylcyclopent-3-ene-1-carboxamide (1j)

3-cyclopenteneacrylic acid was used as the starting material. 0.85 g, 74% yield (two steps). White powder: m.p. 94-96 °C. IR (νmax, cm⁻¹) 3309 (m), 1655 (s), 1599 (s), 1535 (s), 1500 (m), 1437 (s), 1321 (m), 1240 (m), 758 (s), 673 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.55 – 7.46 (m, 2H), 7.39 – 7.27 (m, 3H), 7.09 (m, 1H), 5.74 (s, 2H), 3.02 – 2.89 (m, 2H), 2.42 – 2.30 (m, 2H), 1.41 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 176.7, 138.3, 129.3, 129.1, 124.2, 120.0, 49.0, 45.3, 26.2; HRMS (nanochip-ESI/LTQ-Orbitrap) m/z: [M + H]+ Calcd for C₁₃H₁₆NO⁺ 202.1226; Found 202.1224.
**1-methoxy-N-phenylcyclopent-3-ene-1-carboxamide (1k)**

Diethyl oxalate was used as the starting material. 1.06 g, 24% yield (four steps). White powder: m.p. 96-98 °C. IR (neat): 3383, 2935, 1679, 1599, 1520, 1440, 1309, 1081, 756, 690 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.65 (s, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.35-7.30 (m, 2H), 7.13-7.09 (m, 1H), 5.73 (s, 2H), 3.28 (s, 3H), 3.07 (d, J = 16.8 Hz, 2H), 2.61 (d, J = 16.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 173.0, 137.7, 128.8, 127.9, 124.1, 119.5, 87.1, 51.5, 41.8; HRMS (ESI/QTOF) m/z: [M + Na]^+ Calcd for C₁₃H₁₅NNaO₂^+ 240.0995; Found 240.1002.

**General procedure for fluoroarylation of cyclopentenes:**

A vial was charged with Pd(AdCOO)₂ (4.6 mg, 0.01 mmol, 10 mol%), L₂ (4.4 mg, 0.012 mmol, 12 mol%), and DCE (1.0 mL). The mixture was stirred at rt for 30-40 min. Then cyclopentene 1 (0.1 mmol), arylboronic acid (0.2 mmol), Selectfluor (70.9 mg, 0.2 mmol), sodium carbonate (31.8 mg, 0.3 mmol), 1-adamantanecarboxylic acid (18.0 mg, 0.1 mmol) and DCE (1 mL) were added. The reaction mixture was stirred at 50 °C under argon for 4-8 h. Then, the mixture was diluted with EtOAc, filtered over a plug of silica gel (washed with 20 mL EtOAc), and the filtrate was washed with saturated aqueous solution of sodium carbonate (20 mL × 2). The organic phase was dried over Na₂SO₄, and the products were purified by flash chromatography or preparative TLC (10% ethyl acetate/90% hexane).

27.4 mg, 70% yield. White powder, m.p. 101-103 °C. [α]D⁺ 25 +62.4 (c 1.0, CHCl₃), 92% ee, determined by SFC (IB column, 5% MeOH in supercritical CO₂ as eluent, 4.0 mL/min; major enantiomer 9.0 min, minor enantiomer 8.1 min); IR (neat): 3355, 3070, 2164, 2006, 1683, 1601, 1537, 1442, 1259, 752, 695 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, J = 6.4 Hz, 1H), 7.27-7.04 (m, 10H), 6.99 (t, J = 7.6 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 6.88 (s, 1H), 6.72 (d, J = 8.0 Hz, 1H), 3.86-3.75 (m, 5H), 2.97 (dt, J = 14.1, 8.6 Hz, 1H), 2.91-2.80 (m, 1H), 2.36 (ddd, J = 21.8, 14.1, 7.0 Hz, 1H), 2.24-2.18 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 169.0 (d, J = 23.8 Hz), 160.0, 148.0, 137.3, 136.4, 129.8, 128.9, 128.5, 128.2, 127.6, 125.0, 120.8, 119.5, 113.4, 111.4, 106.6 (d, J = 199.4 Hz), 55.4, 54.3 (d, J = 21.1 Hz), 43.4 (d, J = 20.4 Hz), 41.4 (d, J =
$5.0 \text{ Hz}, 37.4 \text{ (d, } J = 6.8 \text{ Hz); }^{19}\text{F NMR (377 MHz, CDCl}_3\text{): } -149.0; \text{ HRMS (ESI/QTOF) } m/z: [M + H]^+ \text{ Calcd for C}_{25}\text{H}_{25}\text{FNO}_2^+ 390.1864; \text{ Found 390.1862.}$

![Image 2b](image2b.png)

24.7 mg, 66% yield. White powder, m.p. 135-137 °C. $[\alpha]_D^{25} +20.4 \text{ (c 1.3, CHCl}_3\text{), 83% ee, determined by SFC (IB column, 2% MeOH in supercritical CO}_2\text{ as eluent, 4.0 mL/min; major enantiomer 12.1 min, minor enantiomer 11.3 min); IR (neat): 3433, 3032, 2929, 1691, 1602, 1529, 1446, 1308, 1241, 1033, 695 cm}^{-1}; ^1\text{H NMR (400 MHz, CDCl}_3\text{) } \delta 7.51 \text{ (d, } J = 6.8 \text{ Hz, 1H), 7.27-7.05 \text{ (m, 13H), 7.02-6.96 \text{ (m, 2H), 2.97 \text{ (dt, } J = 14.1, 8.7 \text{ Hz, 1H), 2.90-2.80 \text{ (m, 1H), 2.41-2.27 \text{ (m, 4H), 2.23-2.15 \text{ (m, 1H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{) } \delta 169.1 \text{ (d, } J = 23.8 \text{ Hz), 143.3, 137.4, 136.4, 135.9, 129.5, 128.9, 128.5, 128.2, 127.6, 127.1, 125.0, 120.8, 106.7 \text{ (d, } J = 199.3 \text{ Hz), 54.3 \text{ (d, } J = 21.1 \text{ Hz), 43.5 \text{ (d, } J = 20.3 \text{ Hz), 41.0 \text{ (d, } J = 4.7 \text{ Hz), 37.6 \text{ (d, } J = 6.7 \text{ Hz), 21.1; } ^{19}\text{F NMR (377 MHz, CDCl}_3\text{): } -148.8; \text{ HRMS (ESI/QTOF) } m/z: [M + Na]^+ \text{ Calcd for C}_{25}\text{H}_{24}\text{FNNaO}^+ 396.1734; \text{ Found 396.1733.}$

![Image 2c](image2c.png)

27.9 mg, 68% yield. Yellow oil. $[\alpha]_D^{25} +49.3 \text{ (c 2.03, CHCl}_3\text{), 90% ee, determined by SFC (IB column, 3% MeOH in supercritical CO}_2\text{ as eluent, 4.0 mL/min; major enantiomer 9.9 min, minor enantiomer 8.9 min); IR (neat): 2907, 2854, 1693, 1600, 1533, 1444, 1290, 1134, 843, 752, 693 cm}^{-1}; ^1\text{H NMR (400 MHz, CDCl}_3\text{) } \delta 7.56 \text{ (d, } J = 6.8 \text{ Hz, 1H), 7.30-7.05 \text{ (m, 10H), 6.72-6.68 \text{ (m, 2H), 6.49 \text{ (dt, } J = 10.4, 2.4 \text{ Hz, 1H), 3.89-3.76 \text{ (m, 5H), 3.03 \text{ (dt, } J = 14.2, 8.8 \text{ Hz, 1H), 2.90 \text{ (dt, } J = 9.7, 12.4 \text{ Hz, 1H), 2.38 \text{ (ddd, } J = 21.6, 14.2, 7.0 \text{ Hz, 1H), 2.25 \text{ (ddd, } J = 12.6, 8.5, 3.5 \text{ Hz, 1H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{) } \delta 168.9 \text{ (d, } J = 23.5 \text{ Hz), 164.0 \text{ (d, } J = 243.4 \text{ Hz), 161.1 \text{ (d, } J = 11.3 \text{ Hz), 149.5 \text{ (d, } J = 8.9 \text{ Hz), 137.0, 136.3, 128.9, 128.5, 128.2, 127.7, 125.1, 120.8, 109.3 \text{ (d, } J = 2.5 \text{ Hz), 106.4 \text{ (d, } J = 199.8 \text{ Hz), 106.2 \text{ (d, } J = 21.6 \text{ Hz), 99.3 \text{ (d, } J = 24.9 \text{ Hz), 55.7, 54.3 \text{ (d, } J = 21.0 \text{ Hz), 43.1 \text{ (d, } J = 21.0 \text{ Hz), 41.4 \text{ (dd, } J = 4.9, 2.0 \text{ Hz), 37.2 \text{ (d, } J = 6.8 \text{ Hz); } ^{19}\text{F NMR (377 MHz, CDCl}_3\text{): } -111.5, -149.0; \text{ HRMS (ESI/QTOF) } m/z:}$
[M + Na]$^+$ Calcd for C$_{25}$H$_{23}$F$_2$NNaO$_2$ $^+$ 430.1589; Found 430.1592.

27.0 mg, 65% yield. White powder, m.p. 112-114 °C. [$\alpha$]$^25$ +57.6 ($c$ 1.4, CHCl$_3$), 93% ee, determined by SFC (IB column, 3% MeOH in supercritical CO$_2$ as eluent, 4.0 mL/min; major enantiomer 10.8 min, minor enantiomer 9.1 min); IR (neat): 3439, 2957, 1693, 1602, 1507, 1444, 1027, 1241, 750, 695 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51 (d, $J$ = 7.2 Hz, 1H), 7.32 (d, $J$ = 8.4 Hz, 2H), 7.28-7.24 (m, 4H), 7.20-7.05 (m, 7H), 7.02-6.97 (m, 1H), 3.87-3.76 (m, 2H), 2.97 (dt, $J$ = 14.1, 8.7 Hz, 1H), 2.85 (dt, $J$ = 9.5, 12.8 Hz, 1H), 2.37 (ddd, $J$ = 21.9, 14.2, 7.1 Hz, 1H), 2.21 (ddd, $J$ = 12.6, 8.5, 3.5 Hz, 1H), 1.26 (m, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.1 (d, $J$ = 23.9 Hz), 149.2, 143.2, 137.4, 136.4, 128.9, 128.4, 128.2, 127.6, 126.9, 125.7, 125.0, 120.8, 106.6 (d, $J$ = 199.2 Hz), 54.3 (d, $J$ = 21.1 Hz), 43.4 (d, $J$ = 20.0 Hz), 40.9 (d, $J$ = 4.5 Hz), 37.5 (d, $J$ = 6.8 Hz), 34.6, 31.5; $^{19}$F NMR (377 MHz, CDCl$_3$): -148.9; HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcd for C$_{28}$H$_{31}$FNO $^+$ 416.2384; Found 416.2387.

22.0 mg, 61% yield. White powder, m.p. 114-116 °C. [$\alpha$]$^25$ +81.8 ($c$ 1.0, CHCl$_3$), 90% ee, determined by SFC (IC column, 3% MeOH in supercritical CO$_2$ as eluent, 4.0 mL/min; major enantiomer 8.6 min, minor enantiomer 7.3 min); IR (neat): 3421, 3032, 2943, 1691, 1598, 1531, 1496, 1442, 1310, 1241, 1029, 756, 697 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51 (d, $J$ = 6.4 Hz, 1H), 7.36-7.24 (m, 6H), 7.21-7.05 (m, 8H), 7.02-6.97 (m, 1H), 3.88-3.75 (m, 2H), 2.98 (dt, $J$ = 14.1, 8.3 Hz, 1H), 2.87 (dt, $J$ = 9.7, 12.7 Hz, 1H), 2.37 (ddd, $J$ = 21.8, 14.1, 7.1 Hz, 1H), 2.21 (ddd, $J$ = 12.5, 8.4, 3.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.1 (d, $J$ = 24.0 Hz), 146.3, 137.3, 136.4, 128.9, 128.8, 128.5, 128.2, 127.6, 126.4, 125.0, 120.8, 106.7 (d, $J$ = 199.2 Hz), 54.3 (d, $J$ = 21.0 Hz), 43.5 (d, $J$ = 20.3 Hz), 41.4 (d, $J$ = 5.0 Hz), 37.5 (d, $J$ = 6.9 Hz), 21.1; $^{19}$F NMR (377 MHz, CDCl$_3$): -149.0; HRMS (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for C$_{28}$H$_{31}$FNO $^+$ 382.1578; Found 382.1586.
29.6 mg, 72% yield. White powder, m.p. 125-127 °C. [α]_D^20 +74.0 (c 1.1, CHCl₃), 92% ee, determined by SFC (IC column, 10% MeOH in supercritical CO₂ as eluent, 4.0 mL/min; major enantiomer 8.6 min, minor enantiomer 6.8 min); IR (neat): 3423, 3061, 2927, 1685, 1600, 1531, 1444, 1023, 750, 695 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.79-7.73 (m, 4H), 7.52 (d, J = 6.8 Hz, 1H), 7.47-7.34 (m, 3H), 7.29-7.26 (m, 2H), 7.20-7.06 (m, 7H), 6.99 (t, J = 7.2 Hz, 1H), 4.00-3.93 (m, 1H), 3.86 (ddd, J = 24.3, 12.0, 8.6 Hz, 1H), 3.05 (dt, J = 14.2, 8.7 Hz, 1H), 2.93 (dt, J = 9.6, 12.8 Hz, 1H), 2.49 (ddd, J = 24.3, 12.0, 8.6 Hz, 1H), 2.31 (ddd, J = 12.5, 8.5, 3.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 169.0 (d, J = 23.8 Hz), 146.3, 138.4, 137.3, 136.4, 128.9, 128.7, 128.4, 128.2, 128.0, 127.6, 127.1, 125.0, 124.1, 120.8, 106.7 (d, J = 199.0 Hz), 54.3 (d, J = 21.1 Hz), 43.5 (d, J = 20.0 Hz), 41.3 (d, J = 4.7 Hz), 37.4 (d, J = 6.9 Hz), 21.7; ¹⁹F NMR (377 MHz, CDCl₃): -148.9; HRMS (ESI/QTOF) m/z: [M + Na]^+ Calcd for C₂₈H₂₄FNNaO⁺ 432.1734; Found 432.1737.

27.1 mg, 72% yield. White powder, m.p. 83-85 °C. [α]_D^25 +76.0 (c 1.7, CHCl₃), 92% ee, determined by SFC (IC column, 3% MeOH in supercritical CO₂ as eluent, 4.0 mL/min; major enantiomer 8.9 min, minor enantiomer 7.3 min); IR (neat): 3433, 3038, 2947, 1681, 1602, 1533, 1446, 1312, 1244, 1033, 754, 693 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, J = 6.8 Hz, 1H), 7.25 (d, J = 7.2 Hz, 2H), 7.20-7.05 (m, 10H), 7.00-6.96 (m, 2H), 3.87-3.72 (m, 2H), 2.95 (dt, J = 14.1, 8.5 Hz, 1H), 2.85 (dt, J = 9.5, 12.7 Hz, 1H), 2.36 (ddd, J = 21.9, 14.1, 7.3 Hz, 1H), 2.30 (s, 3H), 2.20 (ddd, J = 12.6, 8.5, 3.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 169.0 (d, J = 23.8 Hz), 146.3, 138.4, 137.3, 136.4, 128.9, 128.7, 128.4, 128.2, 128.0, 127.6, 127.1, 125.0, 124.1, 120.8, 106.7 (d, J = 199.0 Hz), 54.3 (d, J = 21.1 Hz), 43.5 (d, J = 20.0 Hz), 41.3 (d, J = 4.7 Hz), 37.4 (d, J = 6.9 Hz), 21.7; ¹⁹F NMR (377 MHz, CDCl₃): -148.9; HRMS (ESI/QTOF) m/z: [M + H]^+ Calcd for C₂₅H₂₅FNO⁺ 374.1915; Found 374.1912.
31.9 mg, 76% yield. White powder, m.p. 122-124 °C. [α]D^25 +35.3 (c 1.1, CHCl₃), 91% ee, determined by SFC (IB column, 5% MeOH in supercritical CO₂ as eluent, 4.0 mL/min; major enantiomer 9.0 min, minor enantiomer 8.4 min); IR (neat): 3243, 1723, 1689, 1608, 1533, 1442, 1294, 1205, 1110, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, J = 7.2 Hz, 1H), 7.25 (d, J = 7.2 Hz, 2H), 7.18-7.05 (m, 7H), 6.49 (d, J = 2.0 Hz, 2H), 6.28 (t, J = 2.0 Hz, 1H), 3.86-3.69 (m, 2H), 2.95 (dt, J = 14.1, 8.7 Hz, 1H), 2.83 (dt, J = 9.6, 12.7 Hz, 1H), 2.36 (ddd, J = 21.8, 14.2, 7.1 Hz, 1H), 2.22 (ddd, J = 12.6, 8.5, 3.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 169.0 (d, J = 23.4 Hz), 161.1, 148.8, 137.3, 136.4, 128.9, 128.5, 128.2, 127.6, 125.0, 120.8, 106.6 (d, J = 199.0 Hz), 105.0, 98.0, 55.5, 54.3 (d, J = 21.0 Hz), 43.3 (d, J = 20.3 Hz), 41.7 (d, J = 4.5 Hz), 37.3 (d, J = 6.6 Hz); ¹⁹F NMR (377 MHz, CDCl₃): -148.9; HRMS (ESI/QTOF) m/z: [M + H]^+ Calcd for C₂₆H₂₇FNO₃⁺ 420.1969; Found 420.1977.

31.2 mg, 75% yield. Colorless oil. [α]D^25 +61.5 (c 0.8, CHCl₃), 87% ee, determined by SFC (IB column, 5% MeOH in supercritical CO₂ as eluent, 4.0 mL/min; major enantiomer 9.8 min, minor enantiomer 9.1 min); IR (neat): 3243, 1723, 1689, 1608, 1533, 1442, 1294, 1205, 1110, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.02 (s, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 7.6 Hz, 2H), 7.36 (t, J = 8.0 Hz, 1H), 7.26 (d, J = 7.6 Hz, 2H), 7.21-7.06 (m, 7H), 7.00 (t, J = 7.2 Hz, 1H), 3.91-3.75 (m, 2H), 3.86 (s, 3H), 3.00 (dt, J = 14.1, 8.6 Hz, 1H), 2.88 (dt, J = 9.8, 12.5 Hz, 1H), 2.38 (ddd, J = 21.7, 14.1, 7.4 Hz, 1H), 2.24 (ddd, J = 12.8, 8.6, 3.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 168.8 (d, J = 23.7 Hz), 167.3, 146.6, 137.3, 136.3, 132.0, 130.7, 129.0, 128.8, 128.5, 128.20, 128.17, 127.74, 127.68, 125.1, 120.8, 106.5 (d, J = 199.7 Hz), 54.3 (d, J = 20.9 Hz), 52.3, 43.4 (d, J = 20.4 Hz), 41.2 (d, J = 4.9 Hz), 37.3 (d, J = 6.6 Hz); ¹⁹F NMR (377 MHz, CDCl₃): -148.9; HRMS (ESI/QTOF) m/z: [M + H]^+ Calcd for C₂₆H₂₇FNO₃⁺ 418.1813; Found 418.1818.
22.8 mg, 52% yield. White powder, m.p. 103-105 °C. [α]$_D^{25}$ +66.5 (c 0.9, CHCl$_3$), 83% ee, determined by SFC (IC column, 5% MeOH in supercritical CO$_2$ as eluent, 4.0 mL/min; major enantiomer 8.8 min, minor enantiomer 6.8 min); IR (neat): 3427, 3062, 1687, 1601, 1532, 1444, 1246, 1024, 750, 692 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 (d, $J$ = 7.1 Hz, 1H), 7.47-7.45 (m, 1H), 7.31-7.28 (m, 1H), 7.26-7.22 (m, 3H), 7.20-7.10 (m, 6H), 7.07-7.04 (m, 2H), 7.01-6.97 (m, 1H), 3.83-3.71 (m, 2H), 2.96 (dt, $J$ = 14.1, 8.6 Hz, 1H), 2.85 (dt, $J$ = 9.6, 13.2 Hz, 1H), 2.31 (ddd, $J$ = 21.6, 14.1, 7.2 Hz, 1H), 2.18 (ddd, $J$ = 12.8, 8.6, 3.7 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.8 (d, $J$ = 23.5 Hz), 148.6, 137.0, 136.3, 130.35, 130.28, 129.6, 128.9, 128.5, 128.2, 127.7, 125.9, 125.1, 122.9, 120.8, 106.4 (d, $J$ = 199.8 Hz), 54.3 (d, $J$ = 21.1 Hz), 43.3 (d, $J$ = 20.5 Hz), 41.1 (d, $J$ = 4.8 Hz), 37.2 (d, $J$ = 6.7 Hz); $^{19}$F NMR (377 MHz, CDCl$_3$): -149.0; HRMS (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for C$_{24}$H$_{21}$BrFNNaO$^+$ 460.0683; Found 460.0694.

18.4 mg, 43% yield. White solid, m.p = 111 – 113 °C. [α]$_D^{25}$ +88.6 (c 0.40, DCM), 92% ee. SFC: IB column, 3.0% MeOH in supercritical CO$_2$ as eluent, 4 mL/min. tR = 6.4 min (minor), 8.0 min (major). IR (ν$_{max}$, cm$^{-1}$) 2362 (m), 1687 (m), 1529 (s), 1327 (s), 1120 (s), 752 (s), 669 (s). $^1$H NMR (400 MHz, Chloroform-d) δ 7.64 (d, $J$ = 8.1 Hz, 2H), 7.58 (d, $J$ = 7.1 Hz, 1H), 7.52 (d, $J$ = 8.1 Hz, 2H), 7.37 – 7.31 (m, 2H), 7.31 – 7.19 (m, 5H), 7.18 – 7.13 (m, 2H), 7.12 – 7.06 (m, 1H), 4.00 – 3.91 (m, 1H), 3.87 (ddd, $J$ = 24.3, 12.0, 8.5 Hz, 1H), 3.10 (dt, $J$ = 14.2, 8.7 Hz, 1H), 2.98 (ddd, $J$ = 13.4, 12.1, 9.6 Hz, 1H), 2.44 (ddd, $J$ = 21.6, 14.2, 7.1 Hz, 1H), 2.30 (ddd, $J$ = 13.0, 8.6, 3.8 Hz, 1H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 168.8 (d, $J$ = 23.8 Hz), 150.3 (d, $J$ = 1.5 Hz), 136.9, 136.3, 129.0, 128.8 (q, $J$ = 32.3 Hz), 128.6, 128.2, 127.8, 127.6 (d, $J$ = 0.6 Hz), 125.8 (q, $J$ = 3.8 Hz), 125.2, 124.4 (q, $J$ = 272.9 Hz), 120.9, 106.4 (d, $J$ = 201.0 Hz), 54.3 (d, $J$ = 21.3 Hz), 43.2 (d, $J$ = 20.6 Hz), 41.3 (d, $J$ = 4.8 Hz), 37.3 (d, $J$ = 6.7 Hz). $^{19}$F NMR (377 MHz, Chloroform-d) δ -62.35, -149.05. HRMS (ESI/QTOF) m/z: [M +
H]+ Calcd for C_{25}H_{22}F_2NO^+ 428.1632; Found 428.1625.

25.3 mg, 63% yield. White solid, m.p = 130 – 132 °C. [α]^{25}_D +76.3 (c 1.15, DCM), 88% ee. Chiral HPLC: Chiralpak IA, hexane:iPrOH = 80:20, 1.0 mL/min, 254 nm; tR = 13.3 min (major), 16.8 min (minor). IR (ν_{max}, cm^{-1}) 3354 (w), 2933 (w), 1680 (s), 1603 (s), 1442 (m), 1269 (m), 748 (w), 696 (m). 1H NMR (400 MHz, Chloroform-d) δ 7.92 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 7.1 Hz, 1H), 7.44 (d, J = 8.1 Hz, 2H), 7.25 – 7.12 (m, 5H), 7.09 (d, J = 7.6 Hz, 2H), 7.03 (t, J = 7.4 Hz, 1H), 3.94 – 3.75 (m, 2H), 3.03 (dt, J = 14.1, 8.7 Hz, 1H), 2.92 (td, J = 12.7, 9.6 Hz, 1H), 2.56 (s, 3H), 2.39 (ddd, J = 21.6, 14.1, 7.1 Hz, 1H), 2.24 (ddd, J = 12.8, 8.5, 3.7 Hz, 1H). 13C NMR (101 MHz, Chloroform-d) δ 197.8, 168.8 (d, J = 23.8 Hz), 151.8, 136.9, 136.3, 135.6, 128.99, 128.96, 128.5, 128.2, 127.8, 127.4, 125.1, 120.9, 106.4 (d, J = 200.9 Hz), 54.3 (d, J = 21.2 Hz), 43.2 (d, J = 20.8 Hz), 41.5 (d, J = 4.9 Hz), 37.2 (d, J = 6.8 Hz), 26.8. 19F NMR (377 MHz, Chloroform-d) δ -149.07.

HRMS (ESI/QTOF) m/z: [M + Na]^+ Calcd for C_{26}H_{24}FNNaO_2^+ 424.1683; Found 424.1682.

23.0 mg, 51% yield. Colorless oil. [α]^{25}_D +70.3 (c 0.30, DCM), 89% ee. SFC: OD-H column, 30.0% MeOH in supercritical CO_2 as eluent, 4 mL/min. tR = 6.1 min (minor), 8.0 min (major). IR (ν_{max}, cm^{-1}) 2914 (m), 2156 (s), 1757 (s), 1253 (s), 1249 (s), 1051 (m), 1011 (m), 760 (m), 719 (s). 1H NMR (400 MHz, Chloroform-d) δ 7.93 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 7.2 Hz, 1H), 7.58 (dd, J = 7.9, 1.4 Hz, 1H), 7.50 (s, 1H), 7.33 – 7.23 (m, 6H), 7.23 – 7.18 (m, 2H), 7.15 – 7.10 (m, 1H), 5.35 (s, 2H), 4.07 – 3.96 (m, 1H), 3.85 (ddd, J = 23.7, 12.0, 8.7 Hz, 1H), 3.10 (dt, J = 14.3, 8.6 Hz, 1H), 2.98 (ddd, J = 13.5, 12.0, 9.7 Hz, 1H), 2.46 (ddd, J = 21.6, 14.3, 7.4 Hz, 1H), 2.32 (ddd, J = 13.0, 8.6, 3.8 Hz, 1H). 13C NMR (101 MHz, Chloroform-d) δ 170.9, 168.5 (d, J = 23.6 Hz), 153.1, 147.6, 136.1, 135.3, 133.7, 129.6, 129.1, 128.7, 128.5, 126.3, 125.4, 124.4, 120.8, 120.7, 106.1 (d, J = 201.7 Hz), 69.7, 53.8 (d, J = 21.4 Hz), 43.5 (d, J = 21.0 Hz), 41.8 (d, J = 4.9 Hz), 37.7 (d, J = 6.8 Hz). 19F NMR (377 MHz, Chloroform-d) δ -149.28. HRMS (ESI/QTOF) m/z: [M + H]^+ Calcd for C_{26}H_{22}ClFNO_3^+ 450.1267; Found 450.1265.
26.5 mg, 62% yield. White powder, m.p. 93-95 °C. [α]$^\text{D}_{25}$ +29.4 (c 2.8, CHCl$_3$), 93% ee, determined by SFC (IB column, 3% MeOH in supercritical CO$_2$ as eluent, 4.0 mL/min; major enantiomer 20.7 min, minor enantiomer 19.5 min); IR (neat): 2909, 2852, 1695, 1594, 1523, 1492, 1454, 1401, 1250, 1290, 1092, 697 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.55 (d, $J = 7.2$ Hz, 1H), 7.30-7.14 (m, 8H), 7.09-7.05 (m, 2H), 6.98 (d, $J = 7.6$ Hz, 1H), 6.95-6.93 (m, 1H), 6.78 (dd, $J = 8.4, 2.4$ Hz, 1H), 3.92-3.78 (m, 2H), 3.83 (s, 3H), 3.03 (dt, $J = 14.2, 8.8$ Hz, 1H), 2.89 (dt, $J = 9.4, 13.0$ Hz, 1H), 2.43 (ddd, $J = 21.8, 14.2, 7.0$ Hz, 1H), 2.27 (ddd, $J = 12.6, 8.5, 3.5$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.1 (d, $J = 24.0$ Hz), 160.0, 147.8, 137.1, 134.9, 130.1, 129.8, 129.0, 128.5, 128.1, 127.7, 122.0, 119.5, 113.4, 111.3, 106.7 (d, $J = 199.2$ Hz), 55.3, 54.3 (d, $J = 20.7$ Hz), 43.2 (d, $J = 20.3$ Hz), 41.4 (d, $J = 4.6$ Hz), 37.2 (d, $J = 6.7$ Hz); $^{19}$F NMR (377 MHz, CDCl$_3$): -149.1; HRMS (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for C$_{25}$H$_{23}$ClFNNaO$_2$: 446.1294; Found 446.1281.

26.6 mg, 59% yield. White powder, m.p. 73-75 °C. [α]$^\text{D}_{25}$ +67.3 (c 2.16, CHCl$_3$), 93% ee, determined by SFC (IB column, 5% MeOH in supercritical CO$_2$ as eluent, 4.0 mL/min; major enantiomer 17.6 min, minor enantiomer 16.2 min); IR (neat): 2907, 2853, 1718, 1696, 1601, 1524, 1409, 1282, 1250, 1177, 1109, 770, 698 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.83 (d, $J = 8.8$ Hz, 2H), 7.64 (d, $J = 7.2$ Hz, 1H), 7.24-7.06 (m, 8H), 6.92 (d, $J = 7.6$ Hz, 1H), 6.87 (s, 1H), 6.72 (dd, $J = 8.4, 2.0$ Hz, 1H), 3.87-3.75 (m, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 2.97 (dt, $J = 14.2, 8.8$ Hz, 1H), 2.83 (dt, $J = 9.6, 12.8$ Hz, 1H), 2.37 (ddd, $J = 21.8, 14.2, 7.0$ Hz, 1H), 2.22 (ddd, $J = 12.4, 8.4, 3.3$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.2 (d, $J = 24.0$ Hz), 160.6, 160.0, 147.8, 140.6, 137.0, 130.7, 129.8, 128.5, 128.1, 127.7, 126.3, 119.53, 119.47, 113.3, 111.4, 106.7 (d, $J = 199.7$ Hz), 55.3, 54.4 (d, $J = 20.9$ Hz), 52.1, 43.2 (d, $J = 20.4$ Hz), 41.4 (d, $J = 4.6$ Hz), 37.2 (d, $J = 6.7$ Hz); $^{19}$F NMR (377 MHz, CDCl$_3$): -149.1; HRMS (ESI/QTOF)
m/z: [M + H]⁺ Calcd for C_{27}H_{27}FNO₄⁺ 448.1919; Found 448.1924.

20.1 mg, 50% yield. Yellow oil. [α]_{D}^{25} +41.5 (c 1.4, CHCl₃), 74% ee, determined by SFC (IB column, 5% MeOH in supercritical CO₂ as eluent, 4.0 mL/min; major enantiomer 8.3 min, minor enantiomer 7.7 min); IR (neat): 3447, 2949, 1693, 1590, 1527, 1496, 1456, 1256, 1043, 701 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 7.2 Hz, 1H), 7.31-7.14 (m, 7H), 7.09-6.90 (m, 5H), 6.74 (dd, J = 8.0, 2.4 Hz, 1H), 3.90-3.76 (m, 2H), 3.78 (s, 3H), 3.01 (dt, J = 14.1, 8.4 Hz, 1H), 2.89 (dt, J = 9.5, 12.9 Hz, 1H), 2.41 (ddd, J = 21.7, 14.1, 7.1 Hz, 1H), 2.22 (ddd, J = 12.5, 8.5, 3.4 Hz, 1H), 1.82 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.0 (d, J = 23.8 Hz), 159.9, 148.1, 137.3, 134.3, 130.4, 129.8, 129.7, 128.5, 127.6, 126.6, 125.6, 123.3, 119.5, 113.3, 111.3, 106.8 (d, J = 199.1 Hz), 55.3, 54.2 (d, J = 20.9 Hz), 43.5 (d, J = 20.4 Hz), 41.3 (d, J = 5.0 Hz), 37.3 (d, J = 6.9 Hz), 17.2; ¹⁹F NMR (377 MHz, CDCl₃): -149.0; HRMS (ESI/QTOF) m/z: [M + Na]⁺ Calcd for C_{26}H_{26}FNaO₂⁺ 426.1840; Found 426.1840.

24.3 mg, 58% yield. White solid, m.p = 129 – 131 °C. [α]_{D}^{25} +79.5 (c 1.10, DCM), 88% ee. SFC: IB column, 10.0% MeOH in supercritical CO₂ as eluent, 4 mL/min. tR = 7.7 min (minor), 8.4 min (major). IR (ν_{max}, cm⁻¹) 2360 (s), 2164 (m), 1689 (s), 1525 (s), 1284 (s), 1011 (s). ¹H NMR (400 MHz, Chloroform-d) δ 7.70 – 7.64 (m, 2H), 7.54 (d, J = 7.0 Hz, 1H), 7.50 (d, J = 8.2 Hz, 2H), 7.32 – 7.17 (m, 7H), 7.11 – 7.05 (m, 2H), 3.98 – 3.89 (m, 1H), 3.83 (ddd, J = 24.3, 12.2, 8.7 Hz, 1H), 3.08 (dt, J = 14.3, 8.8 Hz, 1H), 2.95 (ddd, J = 13.4, 12.1, 9.6 Hz, 1H), 2.41 (ddd, J = 21.5, 14.2, 7.1 Hz, 1H), 2.27 (ddd, J = 13.0, 8.5, 3.7 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-d) δ 168.7 (d, J = 23.9 Hz), 151.5, 136.6, 134.8, 132.7, 130.3, 129.0, 128.6, 128.1, 128.0, 127.9, 122.0, 119.0, 110.5, 106.3 (d, J = 201.1 Hz), 54.3 (d, J = 21.2 Hz), 42.9 (d, J = 21.0 Hz), 41.6 (d, J = 4.8 Hz), 37.0 (d, J = 6.9 Hz). ¹⁹F NMR (377 MHz, Chloroform-d) δ -149.34. HRMS (APCI/QTOF) m/z: [M + H]⁺ Calcd for C_{26}H_{26}ClFNO₂⁺ 419.1321; Found 419.1318.
27.5 mg, 63% yield. White solid, m.p = 112 – 114 °C. [α]$^{25 \circ}$D +82.6 (c 1.20, DCM), 90% ee.

SFC: IC column, 10.0% MeOH in supercritical CO2 as eluent, 4 mL/min. tR = 11.8 min (minor), 13.1 min (major). IR (νmax, cm$^{-1}$) 3332 (w), 2357 (m), 2158 (m), 1680 (s), 1597 (m), 1525 (s), 1402 (m), 1269 (s), 827 (m), 758 (m).

1H NMR (400 MHz, Chloroform-d) δ 7.95 – 7.90 (m, 2H), 7.53 (d, J = 7.1 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.28 – 7.23 (m, 2H), 7.23 – 7.19 (m, 2H), 7.18 – 7.12 (m, 3H), 7.06 – 7.02 (m, 2H), 3.93 – 3.75 (m, 2H), 3.03 (dt, J = 14.2, 8.8 Hz, 1H), 2.90 (ddd, J = 13.3, 12.1, 9.6 Hz, 1H), 2.57 (s, 3H), 2.40 (ddd, J = 21.6, 14.2, 7.0 Hz, 1H), 2.24 (ddd, J = 12.8, 8.5, 3.7 Hz, 1H).

13C NMR (101 MHz, Chloroform-d) δ 197.7, 168.8 (d, J = 24.0 Hz), 151.5, 136.7, 135.5, 134.7, 130.1, 128.9, 128.4, 128.0, 127.7, 127.3, 121.9, 106.4 (d, J = 201.0 Hz), 54.2 (d, J = 21.1 Hz), 42.9 (d, J = 20.8 Hz), 41.3 (d, J = 4.7 Hz), 37.0 (d, J = 6.8 Hz), 26.6. 19F NMR (377 MHz, Chloroform-d): δ -149.21.

HRMS (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for C$_{26}$H$_{23}$ClFNNaO$_2$ 458.1294; Found 458.1305.

19.3 mg, 45% yield. Colorless oil. [α]$^{25 \circ}$D +52.0 (c 1.2, CHCl$_3$), 93% ee, determined by SFC (AD-H column, 20% MeOH in supercritical CO2 as eluent, 4.0 mL/min; major enantiomer 10.6 min, minor enantiomer 23.4 min); IR (neat): 3429, 2949, 1689, 1602, 1513, 1444, 1241, 1181, 1037, 693 cm$^{-1}$; 1H NMR (400 MHz, CDCl$_3$) δ 7.65 (d, J = 7.2 Hz, 1H), 7.35-7.22 (m, 7H), 7.12 (t, J = 7.2 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 7.00 (s, 1H), 6.83 (m, 3H), 3.93-3.83 (m, 2H), 3.87 (s, 3H), 3.75 (s, 3H), 3.07 (dt, J = 14.1, 8.7 Hz, 1H), 2.92 (dt, J = 9.6, 12.8 Hz, 1H), 2.46 (ddd, J = 21.7, 14.2, 7.1 Hz, 1H), 2.30 (ddd, J = 12.6, 8.5, 3.5 Hz, 1H); 13C NMR (100 MHz, CDCl$_3$) δ 169.1 (d, J = 23.8 Hz), 159.9, 159.0, 148.1, 136.5, 129.7, 129.2, 128.9, 124.9, 120.7, 119.5, 113.8, 113.3, 111.3, 106.6 (d, J = 198.7 Hz), 55.33, 55.31, 53.7 (d, J = 21.1 Hz), 43.3 (d, J = 20.4 Hz), 41.3 (d, J = 4.8 Hz), 37.7 (d, J = 6.8 Hz); 19F NMR (377 MHz, CDCl$_3$): -149.3; HRMS (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for C$_{26}$H$_{26}$FNNaO$_3$ 442.1789; Found 442.1795.
28.3 mg, 70% yield. White powder, m.p. 125-127 °C. [α]_D ^25 +75.5 (c 0.9, CHCl₃), 85% ee, determined by SFC (IB column, 5% MeOH in supercritical CO₂ as eluent, 4.0 mL/min; major enantiomer 8.3 min, minor enantiomer 7.4 min); IR (neat): 3042, 2947, 1691, 1597, 1526, 1438, 1250, 1034, 752, 692 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 6.8 Hz, 1H), 7.23-7.13 (m, 3H), 7.09-7.01 (m, 1H), 6.93-6.90 (m, 2H), 6.89-6.86 (m, 1H), 6.70 (dd, J = 8.0, 2.4 Hz, 1H), 3.81-3.69 (m, 2H), 3.75 (s, 3H), 2.96 (dt, J = 14.0, 8.4 Hz, 1H), 2.82 (dt, J = 9.7, 12.8 Hz, 1H), 2.34 (dd, J = 21.7, 14.1, 7.2 Hz, 1H), 2.23-2.15 (m, 1H), 2.16 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.0 (d, J = 23.8 Hz), 159.9, 148.1, 138.0, 137.2, 136.4, 129.8, 128.89, 128.87, 128.3, 125.3, 125.0, 120.8, 119.5, 113.3, 111.3, 106.6 (d, J = 199.3 Hz), 55.4, 54.4 (d, J = 21.0 Hz), 43.4 (d, J = 20.3 Hz), 41.4 (d, J = 5.1 Hz), 37.4 (d, J = 6.7 Hz), 21.5; ¹⁹F NMR (377 MHz, CDCl₃): -149.5; HRMS (ESI/QTOF) m/z: [M + Na]^+ Calcd for C₂₆H₂₆FNNaO₂⁺ 426.1840; Found 426.1836.

26.0 mg, 56% yield. Colorless oil. [α]_D ^25 +55.7 (c 1.7, CHCl₃), 89% ee, determined by SFC (IC column, 10% MeOH in supercritical CO₂ as eluent, 4.0 mL/min; major enantiomer 6.2 min, minor enantiomer 5.0 min); IR (neat): 3413, 2947, 1681, 1600, 1527, 1492, 1442, 1250, 1041, 754, 689 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, J = 7.2 Hz, 1H), 7.29 (d, J = 8.4 Hz, 2H), 7.24-7.16 (m, 3H), 7.13-7.09 (m, 4H), 7.02 (t, J = 7.2 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 6.87-6.85 (m, 1H), 6.71 (dd, J = 8.4, 2.4 Hz, 1H), 3.80-3.67 (m, 2H), 3.76 (s, 3H), 2.94 (dt, J = 14.3, 8.9 Hz, 1H), 2.80 (dt, J = 9.5, 12.8 Hz, 1H), 2.37 (dd, J = 21.9, 14.2, 7.0 Hz, 1H), 2.20 (dd, J = 12.5, 8.5, 3.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 168.8 (d, J = 23.7 Hz), 160.0, 147.7, 136.2, 131.5, 130.0, 129.8, 129.1, 125.2, 121.5, 120.7, 119.5, 113.4, 111.4, 106.4 (d, J = 200.0
Hz), 55.4, 53.7 (d, J = 21.2 Hz), 43.4 (d, J = 20.5 Hz), 41.3 (d, J = 4.9 Hz), 37.7 (d, J = 6.6 Hz); \(^{19}\)F NMR (377 MHz, CDCl\(_3\)): -148.8; HRMS (ESI/QTOF) m/z: [M + Na]\(^+\) Calcd for C\(_{25}\)H\(_{23}\)BrFNNaO\(_2\)\(^+\) 490.0788; Found 490.0782.

20.9 mg, 49% yield. Colorless oil. \([\alpha]\)\(^{25}\)\(_D\) +64.4 (c 1.1, CHCl\(_3\)), 90% ee, determined by SFC (IC column, 10% MeOH in supercritical CO\(_2\) as eluent, 4.0 mL/min; major enantiomer 5.3 min, minor enantiomer 4.5 min); IR (neat): 3245, 2949, 1685, 1601, 1530, 1498, 1444, 1248, 1095, 1032, 833, 748, 694 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.57 (d, \(J = 7.2\) Hz, 1H), 7.23-7.09 (m, 9H), 6.90 (d, \(J = 7.6\) Hz, 1H), 6.86 (t, \(J = 2.1\) Hz, 1H), 6.71 (dd, \(J = 8.4, 2.4\) Hz, 1H), 3.75 (s, 3H), 2.80 (dt, \(J = 14.3, 8.9\) Hz, 1H), 2.19 (ddd, \(J = 12.6, 8.5, 3.5\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 160.0, 147.7, 136.2, 135.8, 133.4, 129.8, 129.6, 129.0, 128.6, 125.2, 120.7, 119.5, 113.4, 111.4, 106.4 (d, \(J = 199.8\) Hz), 55.3, 53.7 (d, \(J = 21.2\) Hz), 43.4 (d, \(J = 20.5\) Hz), 41.3 (d, \(J = 4.7\) Hz), 37.7 (d, \(J = 6.7\) Hz); \(^{19}\)F NMR (377 MHz, CDCl\(_3\)): -148.8; HRMS (ESI/QTOF) m/z: [M + Na]\(^+\) Calcd for C\(_{25}\)H\(_{23}\)ClFNNaO\(_2\)\(^+\) 446.1294; Found 446.1295.

24.2 mg, 52% yield. White solid, m.p = 125 – 127 °C. \([\alpha]\)\(^{25}\)\(_D\) +71.5 (c 1.10, DCM), 90% ee. SFC: IC column, 10.0% MeOH in supercritical CO\(_2\) as eluent, 4 mL/min. tR = 7.3 min (minor), 9.2 min (major). IR (\(\nu_{\text{max}}, \text{cm}^{-1}\)) 3330 (w), 2979 (w), 2360 (w), 2158 (m), 1711 (s), 1601 (m), 1531 (s), 1442 (m), 1277 (s), 1107 (s), 1018 (m), 831 (m). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.04 – 7.99 (m, 2H), 7.63 (d, \(J = 7.3\) Hz, 1H), 7.45 – 7.40 (m, 2H), 7.27 – 7.13 (m, 8H), 7.10 – 7.05 (m, 1H), 4.36 (q, \(J = 7.2\) Hz, 2H), 3.93 – 3.85 (m, 1H), 3.79 (ddd, \(J = 24.1, 12.3, 8.8\) Hz, 1H), 3.02 (dt, \(J = 14.3, 8.8\) Hz, 1H), 2.89 (ddd, \(J = 13.3, 12.1, 9.6\) Hz, 1H), 2.42 (ddd, \(J = 21.7, 14.2, 7.0\) Hz, 1H), 2.25 (ddd, \(J = 13.3, 8.5, 3.7\) Hz, 1H), 1.37 (t, \(J = 7.1\) Hz, 3H).
$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 168.7 (d, $J = 23.8$ Hz), 166.6, 151.1, 136.2, 135.6, 133.5, 130.2, 129.6, 129.1, 128.9, 128.6, 127.2, 125.3, 120.8, 106.3 (d, $J = 201.4$ Hz), 61.1, 53.7 (d, $J = 21.3$ Hz), 43.3 (d, $J = 20.8$ Hz), 41.4 (d, $J = 4.8$ Hz), 37.6 (d, $J = 6.6$ Hz), 14.5. $^{19}$F NMR (377 MHz, Chloroform-$d$) δ -148.99. HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcd for C$_{27}$H$_{26}$ClFNO$_3$+ 466.1580; Found 466.1586.

15.5 mg, 38% yield. Colorless oil. $[\alpha]_D^{25}$ +61.8 (c 1.1, CHCl$_3$), 91% ee, determined by SFC (IC column, 10% MeOH in supercritical CO$_2$ as eluent, 4.0 mL/min; major enantiomer 3.7 min, minor enantiomer 3.1 min); IR (neat): 3427, 2947, 1687, 1595, 1536, 1512, 1440, 1232, 1159, 1038, 837, 754, 694 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.58 (d, $J = 7.2$ Hz, 1H), 7.26-7.12 (m, 7H), 7.04 (t, $J = 7.6$ Hz, 1H), 6.95-6.85 (m, 4H), 6.74 (dd, $J = 8.0$, 2.0 Hz, 1H), 3.86-3.73 (m, 2H), 3.79 (s, 3H), 2.95 (dt, $J = 14.2$, 8.8 Hz, 1H), 2.81 (dt, $J = 9.4$, 12.8 Hz, 1H), 2.37 (ddd, $J = 21.8$, 14.2, 6.9 Hz, 1H), 2.19 (ddd, $J = 12.5$, 8.4, 3.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.9 (d, $J = 23.7$ Hz), 162.3 (d, $J = 244.2$ Hz), 160.0, 147.8, 136.3, 133.0 (d, $J = 3.2$ Hz), 129.81, 129.79 (d, $J = 7.8$ Hz), 129.0, 125.1, 120.7, 119.5, 115.3 (d, $J = 21.0$ Hz), 113.4, 111.4, 106.5 (d, $J = 200.0$ Hz), 55.4, 53.6 (d, $J = 21.2$ Hz), 43.3 (d, $J = 20.6$ Hz), 41.3 (d, $J = 4.9$ Hz), 37.8 (d, $J = 6.7$ Hz); $^{19}$F NMR (377 MHz, CDCl$_3$): -115.2, -149.0; HRMS (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for C$_{25}$H$_{23}$F$_2$NNaO$_2$+ 430.1589; Found 430.1586.

8.8 mg, 27% yield. Colorless oil. $[\alpha]_D^{25}$ -9.4 (c 0.48, CHCl$_3$), 95% ee, determined by SFC (OJ-H column, 5% MeOH in supercritical CO$_2$ as eluent, 4.0 mL/min; major enantiomer 15.3 min, minor enantiomer 12.1 min); IR (neat): 2931, 2855 1689, 1601, 1531, 1442, 1426, 758, 695 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.13 (d, $J = 7.6$ Hz, 1H), 7.59 (d, $J = 7.6$ Hz, 2H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.25 (t, $J = 8.0$ Hz, 1H), 7.16 (t, $J = 7.6$ Hz, 1H), 6.91 (d, $J = 7.6$ Hz, 1H), 6.87

8.8 mg, 27% yield. Colorless oil. $[\alpha]_D^{25}$ -9.4 (c 0.48, CHCl$_3$), 95% ee, determined by SFC (OJ-H column, 5% MeOH in supercritical CO$_2$ as eluent, 4.0 mL/min; major enantiomer 15.3 min, minor enantiomer 12.1 min); IR (neat): 2931, 2855 1689, 1601, 1531, 1442, 1426, 758, 695 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.13 (d, $J = 7.6$ Hz, 1H), 7.59 (d, $J = 7.6$ Hz, 2H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.25 (t, $J = 8.0$ Hz, 1H), 7.16 (t, $J = 7.6$ Hz, 1H), 6.91 (d, $J = 7.6$ Hz, 1H), 6.87
(s, 1H), 6.77 (dd, J = 7.6, 2.0 Hz, 1H), 3.82 (s, 3H), 3.60 (quintet, J = 8.6 Hz, 1H), 3.02 (dd, J = 22.2, 14.8, 9.6 Hz, 1H), 2.65 (d sextet, J = 22.3, 7.2 Hz, 1H), 2.30-2.16 (m, 2H), 2.09 (dd, J = 12.9, 8.3, 6.2 Hz, 1H), 1.11 (d, J = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.0 (d, J = 22.9 Hz), 159.9, 147.6, 137.1, 129.6, 129.3, 124.9, 120.1, 119.7, 113.3, 111.4, 107.5 (d, J = 191.5 Hz), 55.3, 44.4 (d, J = 22.6 Hz), 43.2 (d, J = 21.1 Hz), 41.9 (d, J = 1.6 Hz), 41.6 (d, J = 3.1 Hz), 15.2 (d, J = 4.5 Hz); $^{19}$F NMR (377 MHz, CDCl$_3$): -144.0; HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcd for C$_{20}$H$_{23}$FNO$_2$+ 328.1707; Found 328.1705.

9.0 mg, 26% yield. Colorless oil. $[\alpha]_D^{25}$ -4.9 (c 1.0, CHCl$_3$), 80% ee, determined by SFC (IC column, 10% MeOH in supercritical CO$_2$ as eluent, 4.0 mL/min; major enantiomer 4.2 min, minor enantiomer 5.2 min); IR (neat): 3334, 2943, 2838, 1693, 1600, 1535, 1440, 1254, 1108, 1045, 756, 695 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.17 (d, J = 6.0 Hz, 1H), 7.62 (d, J = 7.6 Hz, 2H), 7.39-7.33 (m, 2H), 7.28-7.23 (m, 1H), 7.18-7.13 (m, 1H), 6.89 (d, J = 7.6 Hz, 1H), 6.84 (s, 1H), 6.78 (dd, J = 8.0, 1.6 Hz, 1H), 4.20 (dt, J = 17.2, 6.4 Hz, 1H), 3.82 (s, 3H), 3.71 (quintet, J = 8.4 Hz, 1H), 3.41 (s, 3H), 2.99 (dd, J = 23.9, 14.8, 9.2 Hz, 1H), 2.44 (dd, J = 13.9, 8.7, 5.8 Hz, 1H), 2.27-2.09 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.5 (d, J = 22.3 Hz), 160.0, 146.8, 137.2, 129.8, 129.2, 124.8, 120.1, 119.5, 113.3, 111.6, 105.1 (d, J = 194.1 Hz), 87.8 (d, J = 27.5 Hz), 58.3, 55.3, 41.6 (d, J = 20.7 Hz), 40.9 (d, J = 2.9 Hz), 37.8 (d, J = 4.3 Hz); $^{19}$F NMR (377 MHz, CDCl$_3$): -150.3; HRMS (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for C$_{20}$H$_{22}$FNNaO$_3$+ 366.1476; Found 366.1474.

7.7 mg, 18% yield. Yellow oil. $[\alpha]_D^{25}$ +41.8 (c 1.4, CHCl$_3$), 90% ee, determined by SFC (OJ-H column, 15% MeOH in supercritical CO$_2$ as eluent, 4.0 mL/min; major enantiomer 13.4 min, minor enantiomer 11.4 min); IR (neat): 3340, 2945, 1661, 1603, 1510, 1442, 1254, 1030, 754, 692 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.49-7.43 (m, 4H), 7.33-7.27 (m, 3H), 7.17 (s, 1H), 7.13-7.08 (m, 1H), 7.03-6.96 (m, 4H), 6.81 (dd, J = 8.4, 2.4 Hz, 1H), 5.74 (dt, J = 52.4, 4.4 Hz,
$13$ C NMR (100 MHz, CDCl$_3$) $\delta$ 170.4 (d, $J = 2.3$ Hz), 159.9, 159.3, 146.2, 137.9, 131.6 (d, $J = 5.1$ Hz), 129.7, 129.0, 127.7, 124.5, 120.1, 119.9, 114.8, 113.3, 112.0, 99.0 (d, $J = 2.3$ Hz), 62.9 (d, $J = 19.0$ Hz), 55.5, 55.3, 41.9, 40.0 (d, $J = 2.3$ Hz), 39.2 (d, $J = 2.3$ Hz); $19$ F NMR (377 MHz, CDCl$_3$): $-176.2$; HRMS (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for C$_{26}$H$_{26}$FNNaO$_3$ $+ 442.1789$; Found 442.1798.

14.7 mg, 45% yield. Colorless oil. $[\alpha]_{D}^{25} +59.2$ (c 0.34, CHCl$_3$), 95% ee, determined by SFC (IA column, 10% MeOH in supercritical CO$_2$ as eluent, 4.0 mL/min; major enantiomer 6.1 min, minor enantiomer 11.3 min); IR (neat): 3349, 2969, 1664, 1601, 1537, 1436, 1316, 1265, 1018, 669 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 - 7.51 (m, 2H), 7.49 (d, $J = 5.6$ Hz, 1H), 7.32 (t, $J = 8.0$ Hz, 2H), 7.25 (t, $J = 8.0$ Hz, 1H), 6.93 (d, $J = 8.0$ Hz, 1H), 6.89 (t, $J = 2.1$ Hz, 1H), 6.77 (dd, $J = 8.0$, 2.0 Hz, 1H), 5.11 (dd, $J = 53.2$, 4.4 Hz, 1H), 3.81 (s, 3H), 3.14-3.07 (m, 1H), 2.69 (dd, $J = 38.9$, 15.8, 10.7, 4.7 Hz, 1H), 2.44 (t, $J = 11.2$ Hz, 1H), 2.26 (dd, $J = 11.4$, 7.8 Hz, 1H), 2.18 (dd, $J = 32.0$, 15.9, 6.1 Hz, 1H), 1.37 (s, 3H); $^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.8, 160.0, 146.8, 137.8, 129.8, 129.1, 124.6, 120.3, 119.9, 113.4, 111.8, 100.7 (d, $J = 176.6$ Hz), 56.5 (d, $J = 18.9$ Hz), 55.4, 42.7, 41.2, 39.4 (d, $J = 22.2$ Hz), 21.4 (d, $J = 6.6$ Hz); $^{19}$F NMR (377 MHz, CDCl$_3$): -168.1; HRMS (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for C$_{20}$H$_{22}$FNNaO$_3$ $+ 350.1527$; Found 350.1532.

10.0 mg, 29% yield. Colorless oil. $[\alpha]_{D}^{25} +4.6$ (c 1.0, CHCl$_3$), 90% ee, determined by SFC (IA column, 15% MeOH in supercritical CO$_2$ as eluent, 4.0 mL/min; major enantiomer 3.6 min, minor enantiomer 7.7 min); IR (neat): 3383, 2945, 2834, 1683, 1599, 1526, 1444, 1264, 1091, 1046, 758, 698 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.28 (s, 1H), 7.63-7.61 (m, 2H), 7.38-7.33 (m, 2H), 7.28-7.23 (m, 1H), 7.16-7.12 (m, 1H), 6.96 (d, $J = 7.6$ Hz, 1H), 6.91 (t, $J = 2.1$ Hz,
1H), 6.79 (dd, J = 8.0, 2.0 Hz, 1H), 4.95 (dd, J = 52.4, 6.2, 4.7, 1.3 Hz, 1H), 3.82 (s, 3H), 3.38 (s, 3H), 3.23-3.13 (m, 1H), 2.76 (dd, J = 14.7, 12.0, 2.9 Hz, 1H), 2.72-2.61 (m, 1H), 2.45 (dd, J = 14.7, 7.0 Hz, 1H), 2.18-2.03 (m, 1H); 13C NMR (100 MHz, CDCl3) δ 167.9 (d, J = 1.9 Hz), 160.0, 145.1, 137.6, 129.7, 129.2, 124.7, 119.9, 119.8, 113.2, 112.1, 98.8 (d, J = 185.9 Hz), 90.7 (d, J = 23.3 Hz), 55.3, 52.6 (d, J = 1.0 Hz), 40.0 (d, J = 3.5 Hz), 39.6 (d, J = 20.7 Hz), 34.7; 19F NMR (377 MHz, CDCl3): -179.4; HRMS (ESI/QTOF) m/z: [M + H]+ Calcd for C20H23FNO3+ 344.1656; Found 344.1658.

**General procedure for the synthesis of (±)-7a and (±)-7b**

A 50 mL round-bottomed flask was charged with Pd(OAc)2 (225 mg, 1.0 mmol, 1.0 equiv), L1 (268 mg, 1.0 mmol, 1.0 equiv), cyclopentene 1a (263 mg, 1.0 mmol, 1.0 equiv), corresponding arylboronic acid (2.0 mmol, 2.0 equiv), sodium carbonate (212 mg, 2.0 mmol, 2.0 equiv) and DCE (20 mL). The mixture was stirred at rt under argon for 12 h. Then, the mixture was diluted with DCM (20 mL), filtered over a plug of silica gel (washed with DCM). The solvent was removed under vacuum. The residue was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (2 : 1 to 1 : 1 to 1 : 2) to afford the desired Pd(II) species (±)-7 in good yield.

66% yield, yellow solid. 1H NMR (400 MHz, Chloroform-d) δ 8.71 (d, J = 6.0 Hz, 1H), 8.02 – 7.96 (m, 3H), 7.91 – 7.84 (m, 3H), 7.56 (dd, J = 5.9, 2.1 Hz, 1H), 7.50 – 7.44 (m, 4H), 7.33 – 7.25 (m, 4H), 7.15 (tt, J = 7.3, 1.3 Hz, 1H), 7.10 (td, J = 7.2, 1.3 Hz, 1H), 6.98 (dd, J = 5.8, 1.9 Hz, 1H), 6.50 (d, J = 5.8 Hz, 1H), 3.42 – 3.25 (m, 1H), 2.98 (dd, J = 13.8, 10.3 Hz, 1H), 2.71 – 2.59 (m, 3H), 2.57 (s, 3H), 2.28 (q, J = 11.7 Hz, 1H), 1.44 (s, 9H), 1.33 (s, 9H). 13C NMR (101 MHz, Chloroform-d) δ 198.2, 187.1, 162.9, 162.7, 156.2, 153.6, 151.9, 149.7, 149.6, 149.4, 148.8, 134.9, 128.5, 128.2, 127.9, 127.7, 127.2, 125.3, 123.7, 123.6, 122.9, 119.0, 117.8, 65.3, 50.2, 46.9, 45.8, 44.6, 35.6, 35.3, 30.4, 30.4, 26.7. IR (νmax, cm⁻¹) 2960 (m), 2359 (s), 2324 (m), 2175 (m), 2152 (m), 1942 (m), 1795 (m), 1676 (m), 1604 (s), 1570 (m), 1547 (m), 3532 (m), 3441 (m).
1487 (m), 1410 (m), 1360 (m), 1267 (m), 1011 (m), 957 (m), 881 (m), 843 (m), 717 (s), 681 (m), 665 (s). HRMS (ESI/QTOF) m/z: [M + H]+ Calcd for C_{44}H_{48}N_{3}O_{2}Pd+ 756.2797; Found 756.2805.

83% yield, yellow solid, CCDC 2024253, crystallized from DCM/EtOAc/CH_{3}CN.

{\text{1H NMR (400 MHz, Chloroform-}d{\text{)}} \delta 8.69 (d, J = 6.0 Hz, 1H), 7.98 – 7.92 (m, 3H), 7.86 (d, J = 1.9 Hz, 1H), 7.52 (dd, J = 5.9, 2.0 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.33 – 7.22 (m, 4H), 7.17 – 7.06 (m, 2H), 6.97 (dd, J = 5.8, 1.9 Hz, 1H), 6.55 (d, J = 2.3 Hz, 2H), 6.46 (d, J = 5.9 Hz, 1H), 6.28 (t, J = 2.3 Hz, 1H), 3.75 (s, 6H), 3.31 – 3.18 (m, 1H), 2.86 (dd, J = 13.7, 10.9 Hz, 1H), 2.72 – 2.61 (m, 2H), 2.61 – 2.51 (m, 1H), 2.27 (q, J = 11.9 Hz, 1H), 1.42 (s, 9H), 1.32 (s, 9H).

13C NMR (101 MHz, Chloroform-}d{\text{)}} \delta 187.4, 162.8, 162.7, 160.7, 156.2, 153.6, 149.9, 149.8, 148.9, 148.2, 128.5, 128.3, 127.9, 127.2, 125.2, 123.6, 123.5, 122.9, 118.9, 117.8, 105.3, 98.4, 64.6, 55.5, 50.5, 46.6, 45.9, 44.1, 35.6, 35.4, 30.4, 30.4. IR (\nu_{\text{max}}, \text{cm}^{-1}) 2960 (m), 1601 (s), 1483 (s), 1462 (s), 1410 (s), 1361 (s), 1300 (s), 1252 (s), 1203 (s), 1149 (s), 1055 (s), 910 (s), 843 (s), 756 (s), 729 (s), 696 (s). HRMS (ESI/QTOF) m/z: [M + H]+ Calcd for C_{44}H_{50}N_{3}O_{3}Pd+ 774.2881; Found 774.2896.

**General procedure for the synthesis of 11:**

A vial was charged with Pd(OAc)_{2} (2.2 mg, 0.01 mmol, 10 mol%), L2 (4.4 mg, 0.012 mmol, 12 mol%), and DCE (1.0 mL). The mixture was stirred at rt for 20 min. The resulting solution was added to a mixture of alkynes 10 (0.13 mmol), alkene 2a (0.1 mmol), Selectfluor (53.0 mg, 0.15 mmol) and DCE (1.0 mL). The reaction mixture was stirred at 50 °C under argon for 12 h. After completion of the reaction (monitored by TLC), the mixture was filtered and the filtrate was concentrated under vacuum. The residue was purified by flash chromatography on silica gel, eluting with petroleum ether/ethyl acetate to afford compound 11.
22.0 mg, 35% yield. White foam. [α]$_D^{25}$ +11.5 (c 0.55, DCM), 76% ee, determined by SFC (IC column, 20% MeOH in supercritical CO$_2$ as eluent, 4.0 mL/min; major enantiomer 7.0 min, minor enantiomer 14.9 min). $^1$H NMR (400 MHz, Chloroform- $d$) δ 8.43 (d, $J = 8.2$ Hz, 1H), 7.83 (d, $J = 7.7$ Hz, 1H), 7.51 – 7.41 (m, 5H), 7.39 – 7.17 (m, 12H), 7.13 – 7.04 (m, 4H), 4.02 – 3.78 (m, 2H), 2.76 – 2.53 (m, 3H), 2.42 (m, 1H), 2.33 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 168.5 (d, $J = 23.7$ Hz), 144.6, 137.6, 137.1, 136.2, 135.8, 131.8, 131.2, 129.4, 129.1, 128.9, 128.8, 128.5, 128.2, 127.8, 127.7, 127.0, 125.4, 125.1, 124.9, 123.8, 120.9, 119.5, 116.5, 106.1 (d, $J = 201.0$ Hz), 54.8 (d, $J = 20.9$ Hz), 41.8 (d, $J = 19.7$ Hz), 34.8 (d, $J = 6.5$ Hz), 32.2 (d, $J = 6.7$ Hz), 21.7. IR ($v_{\text{max}}$, cm$^{-1}$) 2364 (m), 2153 (m), 1685 (m), 1602 (m), 1535 (m), 1483 (m), 1448 (m), 1373 (m), 1268 (m), 1177 (s), 1119 (m), 997 (m), 810 (m), 738 (s), 694 (s). $^{19}$F NMR (377 MHz, Chloroform-$d$) δ -150.65. HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcd for C$_{39}$H$_{34}$FN$_2$O$_3$S$^+$ 629.2269; Found 629.2272.

25.9 mg, 40% yield. Colorless oil. [α]$_D^{25}$ +14.7 (c 1.30, DCM), 83% ee, determined by SFC (IC column, 15% MeOH in supercritical CO$_2$ as eluent, 4.0 mL/min; major enantiomer 7.4 min, minor enantiomer 13.1 min). $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.18 (dd, $J = 10.5$, 2.4 Hz, 1H), 7.74 (dd, $J = 8.7$, 5.3 Hz, 1H), 7.53 – 7.40 (m, 4H), 7.36 – 7.31 (m, 2H), 7.28 – 7.19 (m, 8H), 7.17 – 7.04 (m, 6H), 3.97 – 3.65 (m, 2H), 2.73 – 2.45 (m, 3H), 2.43 – 2.37 (m, 1H), 2.35 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 168.4 (d, $J = 23.6$ Hz), 161.0 (d, $J = 241.6$ Hz), 144.9, 137.8 (d, $J = 12.4$ Hz), 137.2 (d, $J = 4.0$ Hz), 137.0, 136.2, 135.7, 131.8, 130.9, 129.5, 129.2, 128.9, 128.5, 128.2, 127.8, 127.7, 127.1, 125.1, 125.0, 124.9, 120.8, 120.1 (d, $J = 9.7$ Hz), 112.0 (d, $J = 23.8$ Hz), 106.1 (d, $J = 201.1$ Hz), 103.7 (d, $J = 28.8$ Hz), 54.8 (d, $J = 20.8$ Hz), 41.8 (d, $J = 19.8$ Hz), 34.9 (d, $J = 6.2$ Hz), 32.2 (d, $J = 6.6$ Hz), 21.7. IR ($v_{\text{max}}$, cm$^{-1}$) 2360 (m), 2158 (m), 1687 (m), 1599 (m), 1529 (m), 1481 (m), 1444 (m), 1371 (m), 1269 (m), 1174 (s), 1117 (m), 995 (m), 812 (m), 735 (s), 696 (s). $^{19}$F NMR (377 MHz, Chloroform-$d$) δ -116.05, -150.44. HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcd for C$_{39}$H$_{33}$F$_2$N$_2$O$_3$S$^+$ 647.2174; Found
30.7 mg, 44% yield. Pale yellow oil. $[\alpha]_{D}^{25} +9.4$ (c 1.40, DCM), 90% ee, determined by SFC (IC column, 20% MeOH in supercritical CO$_2$ as eluent, 4.0 mL/min; major enantiomer 2.8 min, minor enantiomer 3.5 min). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.54 (d, $J = 8.8$ Hz, 1H), 8.10 (s, 1H), 7.67 (d, $J = 8.9$ Hz, 1H), 7.54 – 7.50 (m, 2H), 7.45 (t, $J = 7.4$ Hz, 2H), 7.33 (d, $J = 7.9$ Hz, 2H), 7.26 (d, $J = 7.9$ Hz, 2H), 7.24 – 7.17 (m, 6H), 7.15 – 7.09 (m, 4H), 7.06 (t, $J = 7.3$ Hz, 1H), 3.99 – 3.89 (m, 1H), 3.67 (dt, $J = 21.1$, 10.1 Hz, 1H), 2.74 – 2.63 (m, 2H), 2.55 – 2.43 (m, 1H), 2.43 – 2.36 (m, 1H), 2.35 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 168.4 (d, $J = 23.7$ Hz), 145.2, 138.9, 138.5, 136.9, 136.2, 135.7, 131.9, 130.5, 129.7, 129.5, 129.0, 128.5, 128.2, 127.9, 127.7, 127.1, 126.0 (q, $J = 31.7$ Hz), 125.2, 125.1, 124.7 (q, $J = 272.1$ Hz), 121.6 (q, $J = 3.5$ Hz), 120.8, 116.7 (q, $J = 4.5$ Hz), 116.4, 106.1 (d, $J = 200.9$ Hz), 54.9 (d, $J = 21.0$ Hz), 41.8 (d, $J = 20.0$ Hz), 35.3 (d, $J = 6.0$ Hz), 32.1 (d, $J = 6.2$ Hz), 21.8. IR ($v_{\text{max}}$, cm$^{-1}$) 2360 (m), 1687 (m), 1599 (m), 1529 (m), 1444 (m), 1383 (m), 1317 (s), 1174 (s), 1120 (s), 816 (m), 737 (s), 696 (s). $^{19}$F NMR (377 MHz, Chloroform-$d$) $\delta$ -61.09, -150.15. HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcd for C$_{40}$H$_{33}$F$_4$N$_2$O$_3$S$^+$ 697.2143; Found 697.2137.

32.0 mg, 46% yield. Colorless oil. $[\alpha]_{D}^{25} +5.9$ (c 1.60, DCM), 86% ee, determined by SFC (IC column, 15% MeOH in supercritical CO$_2$ as eluent, 4.0 mL/min; major enantiomer 10.8 min, minor enantiomer 18.1 min). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.18 (d, $J = 9.0$ Hz, 1H), 7.84 (d, $J = 2.1$ Hz, 1H), 7.70 (dd, $J = 8.0$, 1.3 Hz, 1H), 7.62 (td, $J = 7.7$, 1.4 Hz, 1H), 7.50 (d, $J = 7.1$ Hz, 1H), 7.42 – 7.37 (m, 2H), 7.32 (td, $J = 7.8$, 1.4 Hz, 1H), 7.25 – 7.18 (m, 8H), 7.16 – 7.04 (m, 6H), 3.92 – 3.65 (m, 2H), 2.76 – 2.41 (m, 4H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 168.4 (d, $J = 23.6$ Hz), 147.5, 136.9, 136.7, 136.4, 136.2, 134.5, 133.1, 132.3, 132.0, 130.9, 129.7, 129.6, 129.0, 128.9, 128.5, 128.2, 128.1, 127.7, 125.5, 125.1, 124.9, 124.8, 120.9, 119.1, 117.4, 105.9 (d, $J = 201.4$ Hz), 54.7 (d, $J = 20.9$ Hz), 41.8 (d, $J = 19.8$ Hz), 34.7 (d, $J =
6.3 Hz), 32.1 (d, J = 6.6 Hz). IR (νmax, cm⁻¹) 2360 (m), 2021 (m), 1685 (m), 1539 (s), 1442 (s), 1365 (m), 1244 (m), 1176 (s), 1124 (m), 735 (s), 698 (s). 19F NMR (377 MHz, Chloroform-d) δ -150.66. HRMS (ESI/QTOF) m/z: [M + H]+ Calcd for C₃₈H₃₀ClF₅N₃O₅S 694.1573; Found 694.1584.

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Crystal data and copies of the NMR spectra

Crystal Data and Experimental of 2a (CCDC 1979593)

Experimental. Single clear pale colourless prism crystals of cj-1 were used as supplied. A suitable crystal with dimensions 0.57 × 0.11 × 0.09 mm³ was selected and mounted on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at a steady T = 140.00(10) K during data collection. The structure was solved with the ShelXT 2014/5 (Sheldrick, 2014) solution program using dual methods and by using Mercury 4.3.0 (CCDC, 2019) as the graphical interface. The model was refined with ShelXL-2018/3 (Sheldrick, 2018) using full matrix least squares minimisation on F².

Crystal Data.  C₂₅H₂₄FNO₂, M_r = 389.45, orthorhombic, Pca2₁ (No. 29), a = 11.42343(17) Å, b = 20.1518(3) Å, c = 8.70055(12) Å, α = β = γ = 90°, V = 2002.89(5) Å³, T = 140.00(10) K, Z = 4, Z' = 1, μ(Cu Kα) = 0.707, 13291 reflections measured, 3277 unique (R_int = 0.0225) which were used in all calculations. The final wR² was 0.0672 (all data) and R₁ was 0.0256 (I≥2 σ(I)).
| Property                      | Value                        |
|-------------------------------|------------------------------|
| **Compound**                  | cj-1                         |
| Formula                       | C_{25}H_{24}FNO_{2}           |
| $D_{calc}$/ g cm$^{-3}$       | 1.292                        |
| $\mu$/mm$^{-1}$               | 0.707                        |
| Formula Weight                | 389.45                       |
| Colour                        | clear pale colourless        |
| Shape                         | prism                        |
| Size/mm$^3$                   | 0.57$\times$0.11$\times$0.09 |
| $T$/K                         | 140.00(10)                   |
| Crystal System                | orthorhombic                 |
| Flack Parameter               | -0.04(7)                     |
| Hoof Parameter                | 0.01(7)                      |
| Space Group                   | $Pc\alpha_2_1$               |
| $a$/Å                         | 11.42343(17)                 |
| $b$/Å                         | 20.1518(3)                   |
| $c$/Å                         | 8.70055(12)                  |
| $\alpha$/$^\circ$            | 90                           |
| $\beta$/$^\circ$             | 90                           |
| $\gamma$/$^\circ$            | 90                           |
| $V$/Å$^3$                     | 2002.89(5)                   |
| $Z$                           | 4                            |
| $Z'$                          | 1                            |
| Wavelength/Å                  | 1.54184                      |
| Radiation type                | Cu $K\alpha$                |
| $\Theta_{min}$/$^\circ$       | 4.388                        |
| $\Theta_{max}$/$^\circ$       | 76.019                       |
| Measured Refl's.              | 13291                        |
| Indep't Refl's                | 3277                         |
| Refl's I$\geq$2 $\sigma$(I)  | 3185                         |
| $R_{int}$                     | 0.0225                       |
| Parameters                    | 268                          |
| Restraints                    | 1                            |
| Largest Peak                  | 0.179                        |
| Deepest Hole                  | -0.129                       |
| GooF                          | 1.015                        |
| $wR_2$ (all data)             | 0.0672                       |
| $wR_2$                        | 0.0663                       |
| $R_1$ (all data)              | 0.0267                       |
| $R_1$                         | 0.0256                       |
Crystal Data and Experimental for 2d (CCDC 1978762)

Experimental. Single clear intense colourless plate-shaped crystals of CJ-5_tw were obtained by recrystallisation from SOLVENT at TEMPERATURE. A suitable crystal of 0.87×0.18×0.07 mm3 was selected and mounted on a suitable support on a SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer. The crystal was kept at a steady T = 140.00(10) K during the data collection. The structure was solved with the ShelXT (Sheldrick, 2015) structure solution program using the dual solution method and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of ShelXL (Sheldrick, 2015) using full matrix least squares on |F|^2 minimisation.

Crystal Data. C28H30FNO, M_r = 415.53, monoclinic, P2 (No. 3), a = 17.7963(2) Å, b = 5.91762(9) Å, c = 21.2730(3) Å, β = 90.0080(12)°, α = γ = 90°, V = 2240.30(5) Å3, T = 140.00(10) K, Z = 4, Z' = 2, μ(CuKα) = 0.627, 8916 reflections measured, 8916 unique (R_int = .) which were used in all calculations. The final wR2 was 0.0720 (all data) and R_l was 0.0291 (1 > 2(I)).
Crystal data and structure refinement for compound 6s (CCDC 1978761).

Identification code          cj-4
Empirical formula           C_{26}H_{26}FNO_{3}
Formula weight              419.48
Temperature                 99.99(10) K
Wavelength                  1.54184 Å
Crystal system              Monoclinic
Space group                 C2/c
Unit cell dimensions        
    a = 31.734(2) Å  \quad \alpha = 90^\circ.
    b = 14.1296(13) Å  \quad \beta = 94.456(8)^\circ.
    c = 9.6377(8) Å    \quad \gamma = 90^\circ.
Volume                      4308.4(6) Å³
Z                            8
Density (calculated)        1.293 Mg/m³
Absorption coefficient      0.731 mm⁻¹
F(000)                      1776
Crystal size                0.376 x 0.031 x 0.017 mm³
\Theta range for data collection 3.426 to 75.345°.
Index ranges                -37 \leq h \leq 39, -16 \leq k \leq 17, -12 \leq l \leq 10
Reflections collected       15615
Independent reflections     4377 [R_{int} = 0.1324]
Completeness to \theta = 67.684° 100.0 %
Absorption correction       Gaussian
Max. and min. transmission  1.000 and 0.662
Refinement method           Full-matrix least-squares on F²
Data / restraints / parameters 4377 / 0 / 282
Goodness-of-fit on F²       0.965
Final R indices [I > 2\sigma(I)]\[R_1 = 0.0660, wR_2 = 0.1424\
R indices (all data)         \[R_1 = 0.1414, wR_2 = 0.1880\
Largest diff. peak and hole  0.290 and -0.270 e.Å⁻³
Crystal Data and Experimental for 7b (CCDC 2024253)

**Experimental.** Single colourless irregular crystals of _hwu-pd-35ome-inter_ were used as supplied. A suitable crystal with dimensions 0.31 × 0.19 × 0.10 mm³ was selected and mounted on a SuperNova, Dual, Cu at home/near, Atlas diffractometer. The crystal was kept at a steady T = 140.00(10) K during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2015) solution program using dual methods and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F².

**Crystal Data.** _C₃₄H₄₉N₃O₃Pd_, _Mᵣ_ = 774.26, trigonal, _R₃₃₃₃ (No. 148), a = 32.8315(3) Å, b = 32.8315(3) Å, c = 22.5355(3) Å, α = 90°, β = 90°, γ = 120°, _V_ = 21036.7(5) Å³, _T_ = 140.00(10) K, _Z_ = 18, _Z' = 1, μ(Cu Kα) = 3.476, 30084 reflections measured, 9131 unique (Rint = 0.0257) which were used in all calculations. The final _wR₂_ was 0.0922 (all data) and _R₁_ was 0.0340 (I=2σ(I)).
Structure Quality Indicators

| Reflections: | d min (Cu) | f(0) | R int | Completeness (CuKα) |
|-------------|------------|------|-------|---------------------|
|             | 0.81       | 46.1 | 2.57% | 100%                |

| Refinement: | Shift | Max Peak | Min Peak | Goof |
|-------------|-------|----------|----------|------|
|             | 0.005 | 0.8      | -0.6     | 1.026 |

A colourless irregular-shaped crystal with dimensions $0.31 \times 0.19 \times 0.10 \, \text{mm}^3$ was mounted.

Data were collected using a SuperNova, Dual, Cu at home/near, Atlas diffractometer operating at $T = 140.00(10) \, \text{K}$.

Data were measured using $\omega$ scans using Cu Kα radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.41.78a, 2020). The maximum resolution achieved was $\Theta = 72.636^\circ$ (0.81 Å).

The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.41.78a, 2020). The unit cell was refined using CrysAlisPro (Rigaku, V1.171.41.78a, 2020) on 20190 reflections, 67% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro (Rigaku, V1.171.41.78a, 2020). The final completeness is 99.90 % out to 72.636° in $\Theta$. A Gaussian absorption correction was performed using CrysAlisPro 1.171.41.78a (Rigaku Oxford Diffraction, 2020) Numerical absorption correction based on Gaussian integration over a multifaceted crystal model. Empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient $\mu$ of this material is 3.476 mm$^{-1}$ at this wavelength ($\lambda = 1.54184 \, \text{Å}$) and the minimum and maximum transmissions are 0.395 and 1.000.

The structure was solved and the space group $R-\overline{3}$ (# 148) determined by the ShelXT 2018/2 (Sheldrick, 2015) structure solution program using using dual methods and refined by full matrix least squares minimisation on $F^2$ using version 2018/3 of ShelXL 2018/3 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: $Z$ is 18 and $Z'$ is 1.

Citations

CrysAlisPro Software System, Rigaku Oxford Diffraction, (2020).

Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, Acta Cryst., (2015), A71, 3-8.

Sheldrick, G.M., Crystal structure refinement with ShelXL, Acta Cryst., (2015), C71, 3-8.

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, J. Appl. Cryst., (2009), 42, 339-341.
S85
$11c$
SFC chromatograms

Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|----------|---------|--------|--------|---------------|-------|------|-------------|----------|
| 50 methanol       | 6        | MeOH    | IB     | cJ-111-IB | 16A           | 30.9  | 4    | 5           | 150      |

Peak Information

| Peak No | % Area | Area    | Ret. Time | Height   | Cap. Factor |
|---------|--------|---------|-----------|----------|-------------|
| 1       | 49.9447 | 5203.8517 | 8.35 min  | 328.3574 | 0           |
| 2       | 50.0553 | 5215.3675 | 9.45 min  | 285.6455 | 0           |

Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|----------|---------|--------|--------|---------------|-------|------|-------------|----------|
| 50 methanol       | 10       | MeOH    | IB     | P4-IB  | 16C           | 29.9  | 4    | 5           | 150      |

Peak Information

| Peak No | % Area | Area    | Ret. Time | Height   | Cap. Factor |
|---------|--------|---------|-----------|----------|-------------|
| 1       | 4.0136 | 1605.7118 | 8.12 min  | 129.9368 | 8123.8833   |
| 2       | 95.9864 | 38424.7281 | 8.98 min  | 1245.597 | 8982.2      |
Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|----------|---------|--------|--------|---------------|-------|------|------------|----------|
| 2p methanol       | 15       | MeOH    | IB     | CJ-122-B | 16A           | 30.2  | 4    | 2          | 150      |

Peak Information

| Peak No | % Area | Area   | Ret. Time | Height | Cap. Factor |
|---------|--------|--------|-----------|--------|-------------|
| 1       | 47.2617| 10867.185| 11.43 min| 370.7296| 11432.1667  |
| 2       | 52.7383| 11903.264| 12.58 min| 349.8479| 12582.15    |

Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|----------|---------|--------|--------|---------------|-------|------|------------|----------|
| 2p methanol       | 15       | MeOH    | IB     | P14-B  | 16A           | 28.8  | 4    | 2          | 150      |

Peak Information

| Peak No | % Area | Area       | Ret. Time | Height    | Cap. Factor |
|---------|--------|------------|-----------|-----------|-------------|
| 1       | 8.0097 | 4286.268   | 11.27 min| 197.5106  | 11255.5     |
| 2       | 91.3903| 45497.968  | 12.11 min| 895.5019  | 12107.15    |
Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|---------|--------|--------|---------------|-------|------|------------|----------|
| sp methanol       | 5         | MeOH    | IB     | P198-BB| 16A           | 31.7  | 4    | 3          | 150      |

Peak Information

| Peak No | % Area | Area     | Ret. Time | Height | Cap. Factor |
|---------|--------|----------|-----------|--------|-------------|
| 1       | 3.2877 | 261.2921 | 9.06 min  | 20.0816| 9657.2      |
| 2       | 96.7123| 7686.2012| 10.81 min | 312.3994| 10807.1633  |

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Run Information

| Instrument Method | Inj. Vol. | Solvent | Column  | Sample  | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|---------|---------|---------|---------------|-------|------|------------|----------|
| 3p methanol       | 15        | MeOH    | IC      | P147.IC | 16A           | 29.8  | 4    | 3          | 150      |

Peak Information

| Peak No | % Area | Area  | Ret. Time | Height | Cap. Factor |
|---------|--------|-------|-----------|--------|-------------|
| 1       | 50.096 | 9402.393 | 7.43 min | 305.7775 | 7432.2333   |
| 2       | 49.904 | 9396.3517 | 8.77 min | 254.879 | 8765.5333   |

Run Information

| Instrument Method | Inj. Vol. | Solvent | Column  | Sample  | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|---------|---------|---------|---------------|-------|------|------------|----------|
| 3p methanol       | 5         | MeOH    | IC      | P194.IC | 16E           | 29.9  | 4    | 3          | 150      |

Peak Information

| Peak No | % Area | Area  | Ret. Time | Height | Cap. Factor |
|---------|--------|-------|-----------|--------|-------------|
| 1       | 3.8021 | 765.2672 | 7.72 min | 40.5644 | 7715.56     |
| 2       | 96.1979 | 19362.022 | 8.92 min | 639.0494 | 8915.5333   |
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| #  | RetTime | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|----|---------|------|-------------|--------------|--------------|--------|
| 1  | 13.179  | BB   | 0.3921      | 4906.05225   | 185.79102    | 50.3146|
| 2  | 16.629  | BB   | 0.4925      | 4844.70654   | 140.42215    | 49.6854|

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| #  | RetTime | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|----|---------|------|-------------|--------------|--------------|--------|
| 1  | 13.318  | BB   | 0.3904      | 6607.47656   | 249.97012    | 93.8230|
| 2  | 16.848  | BB   | 0.3689      | 435.01538    | 14.21828     | 6.1770 |
| Peak # | Ret. Time | Area     | Area %   |
|-------|-----------|----------|----------|
| 1     | 6.11 min  | 10497.4135 | 49.6742  |
| 2     | 8.18 min  | 10635.133  | 50.3258  |

Single Absorbance (230nm) Plot
Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|----------|---------|--------|--------|---------------|-------|------|------------|----------|
| 20µl methanol     | 10 µl    | MeOH    | AD-H   | np-140-AD | 16A           | 31.2  | 4    | 20         | 150      |

Peak Information

| Peak No | % Area | Area       | Ret. Time | Height     | Cap. Factor |
|---------|--------|------------|-----------|------------|-------------|
| 1       | 49.92% | 42304.355  | 10.61 min | 1123.9587  | 0           |
| 2       | 50.07% | 42428.038  | 22.65 min | 375.9199   | 0           |

Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|----------|---------|--------|--------|---------------|-------|------|------------|----------|
| 20µl methanol     | 10 µl    | MeOH    | AD-H   | np-13-AD | 16B           | 31.4  | 4    | 20         | 150      |

Peak Information

| Peak No | % Area | Area       | Ret. Time | Height     | Cap. Factor |
|---------|--------|------------|-----------|------------|-------------|
| 1       | 96.44% | 80145.941  | 10.58 min | 1982.795   | 0           |
| 2       | 3.56%  | 3141.5089  | 23.38 min | 42.9586    | 0           |
| Co-Solvent % | Total Flow | Column | Co-Solvent | Back Pressure |
|-------------|------------|--------|------------|---------------|
| 10          | 4          | IC     | MeOH       | 150           |

| Peak # | Ret. Time | Area   | Area %   |
|--------|-----------|--------|----------|
| 1      | 7.29 min  | 18166.0252 | 50.1744 |
| 2      | 9.24 min  | 19032.7539 | 49.8256 |

Single Absorbance (240nm) Plot

| Co-Solvent % | Total Flow | Column | Co-Solvent | Back Pressure |
|-------------|------------|--------|------------|---------------|
| 10          | 4          | IC     | MeOH       | 150           |

| Peak # | Ret. Time | Area   | Area %   |
|--------|-----------|--------|----------|
| 1      | 7.32 min  | 2023.267 | 4.9331  |
| 2      | 9.21 min  | 50553.1972 | 95.0699 |

Single Absorbance (240nm) Plot
### Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|---------|--------|--------|---------------|-------|------|-------------|----------|
| 10 µl methanol    | 10        | MeOH    | IC     | ci-332-ic | 16A          | 30.1  | 4    | 10          | 150      |

### Peak Information

| Peak No | % Area | Area     | Ret. Time | Height | Cap. Factor |
|---------|--------|----------|-----------|--------|-------------|
| 1       | 48.7797| 5093.276 | 4.91 min  | 433.0396| 0           |
| 2       | 51.22% | 5551.668 | 5.02 min  | 359.4958| 0           |

### Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|---------|--------|--------|---------------|-------|------|-------------|----------|
| 10 µl methanol    | 5         | MeOH    | IC     | ci-351-ic | 168          | 31.3  | 4    | 10          | 150      |

### Peak Information

| Peak No | % Area | Area     | Ret. Time | Height | Cap. Factor |
|---------|--------|----------|-----------|--------|-------------|
| 1       | 90.0376| 20560.155| 4.19 min  | 1375.7635| 0           |
| 2       | 9.9624 | 2321.3875| 5.24 min  | 128.0397 | 0           |
