Nickel-catalyzed Enantioselective α-Heteroarylation of Ketones via Siteselective C–F bond Activation to Construct All-Carbon Quaternary Stereocenters

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Supporting Information Placeholder

Table of Contents

1.	General information	2
2.	Procedure for the synthesis of fluoropyridine derivatives	;
3.	Optimization of reaction conditions and general procedural for the asymmetry	ic
	heteroarylationS	8
4.	Characterization of products	2
5.	Gram-scale reaction and synthetic applications	
	S30	
6.	Control	
	experiments	
7.	X-Ray crystallographic analysis	8
8.	Reference	9
9.	BDE (Bond dissociation energy) of C _{Ar} -F bond	10
10.	NMR spectrum	5
11.	HPLC	
	spectrum	

1. General information

NMR Spectra were recorded on a Bruker DPX-500 (400) spectrometer at 500 MHz or 400 MHz for ¹H NMR, 376 MHz for ¹⁹F NMR and 100 MHz or 125 MHz for ¹³C NMR in CDCl₃ with tetramethylsilane (TMS) or the residual deuterated solvent peaks as internal standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Flash column chromatograph was carried out using 200-300 mesh silica gel at medium pressure. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer. ESI-HRMS data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source. Optical rotation was obtained on a Rudolph Research Analytical (Atopol I). HPLC analysis was performed on Agilent 1260 series, UV detection monitored at 254 nm, using a Chiralcel AS-H, OJ-3, IA, IB, IC, ID , OD-H or AD-H column with hexane and *i*-PrOH as the eluent. Related HPLC analysis of **3as to 3az, 3nj** and other materials that needs improvement are were performed on Waters e2695. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under argon. Anhydrous toluene and dioxane were distilled from sodium benzophenone prior to use.

2. Procedure for the synthesis of fluoropyridine derivatives

The fluoropyridine derivatives $2b'^1$, $2s^2$, $2c^3$, $2k'^3$, $2a'^4$, $2d'^5$, $2c'^6$, $2h'^6$ were prepared according to the reported procedure. Other non-specified fluoropyridines were bought from manufacturers.

$$F + alkyl-OH + THF, RT, 24 h$$

Sodium hydride (60% NaH, 696 mg, 17.4 mmol) was slowly added to a mixture of aliphatic alcohols (17.4 mmol) in dry tetrahydrofuran (25 ml THF) at 0 °C and stirred for 30 mins. Then 2,6-difluoropyridine (2 g, 17.4 mmol) was added dropwise to the mixture and stirred for 24 h at room temperature, the reaction was quenched with water (20 ml). Then the mixture was evaporated under vacuum and the crude product was extracted with ethyl acetate (\times 2) and washed with saturated brine. The combined organic phase was dried over anhydrous sodium sulfate (Na₂SO₄) and evaporated to dryness. The crude product was purified by silica gel chromatography (eluent: Petroleum ether (PE), Rf: about 0.2 to 0.4) to afford product **2b**, **2c**, **2b'**, **2e'**.⁷

The mixture of 2,6-difluoropyridine (2 g, 17.4 mmol), potassium carbonate (2.88 g, 20.88 mmol, 1.2 equiv.) and phenol derivatives (19.1 mmol, 1.1 equiv) were added to DMF or 1,4-dioxane (25 ml) and stirred at 70 °C for 24 or 48 h. Then the mixture was evaporated under vacuum and the crude product was extracted with ethyl acetate (×2) and washed with saturated brine. The combined organic phase was dried over anhydrous Na₂SO₄ and evaporated to dryness. The crude product was purified by silica gel chromatography (eluent: PE, Rf: about 0.2 to 0.4) to afford product 2d, 2e, 2f, 2g, 2g', 2t', 2u', 2v'.⁸

$$F = N = Br + aryl = B(OH)_2 = \frac{1\% Pd(PPh_3)_4}{K_2CO_3, DME:H_2O} = aryl = N = F$$

A round bottom flask was charged with K_2CO_3 (3.0 equiv) and water (1 mL) at room temperature. The mixture was stirred until a clear solution was obtained (about 2 minutes). Dimethoxyethane (DME) (15 mL) was added and the mixture was sparged with argon for 15 minutes. Phenylboronic acid (1.05 equiv) and 2-bromo-6-fluoropyridine (1 g, 5.72 mmol) were added to the mixture, followed by Pd (PPh₃)₄ (1 mol%). The reaction mixture was sparged again with argon for 5 minutes. Then the reaction mixture was heated to 85° C under an atmosphere of argon for 16 hours. The reaction mixture was cooled and directly concentrated. Water was added to the residue and the mixture was extracted with ethyl acetate (EA). The combined organic phase was dried with anhydrous Na₂SO₄ and concentrated. The crude product was purified by silica gel chromatography to afford product 2j, 2p, 2q, 2k, 2l, 2m, 2n, 2o, 2y (PE, Rf: about 0.2 to 0.4).⁹

2-(Benzyloxy)-6-fluoropyridine (2b)

¹H NMR (500 MHz, CDCl₃): δ 7.53 (q, J = 8.1 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.32 (dd, J = 8.3, 6.4 Hz, 2H), 7.29 – 7.24 (m, 1H), 6.60 (dd, J = 8.1, 1.7 Hz, 1H), 6.40 (dd, J = 7.8, 2.5 Hz, 1H), 5.30 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 162.7 (d, J = 13.6 Hz), 162.2 (d, J = 240.5 Hz), 142.7 (d, J = 8.0 Hz), 136.6, 128.5, 128.1, 128.0, 107.4 (d, J = 5.1 Hz), 100.1 (d, J = 35.4 Hz), 68.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -70.27.

t-Butyl (*R*)-2-(((6-fluoropyridin-2-yl)oxy)methyl)morpholine-4-carboxylate (2c)



¹H NMR (500 MHz, CDCl₃): δ 7.65 (q, *J* = 8.1 Hz, 1H), 6.72 – 6.61 (m, 1H), 6.48 (dd, *J* = 7.7, 2.4 Hz, 1H), 4.41 – 4.25 (m, 2H), 4.06 – 3.71 (m, 4H), 3.58 (td, *J* = 11.7, 2.8 Hz, 1H), 3.07 – 2.70 (m, 2H), 1.47 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 162.44 (d, *J* = 13.4 Hz), 154.76, 142.73 (d, *J* = 7.9 Hz), 107.46 (d, *J* = 5.2 Hz), 100.41 (d, *J* = 35.1 Hz), 80.23, 77.24, 73.61, 66.72, 66.58, 28.38. ¹⁹F NMR (376 MHz, CDCl₃) δ -70.27. 2-(6-Fluoropyridin-2-yl)acetonitrile (2b')



¹H NMR (500 MHz, CDCl₃): δ 7.90 (q, *J* = 8.0 Hz, 1H), 7.41 – 7.29 (m, 1H), 6.95 (dd, *J* = 8.3, 2.8 Hz, 1H), 3.94 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 163.01 (d, *J* = 241.5 Hz), 149.18 (d, *J* = 13.6 Hz), 142.63 (d, *J* = 7.8 Hz), 119.85 (d, *J* = 4.2 Hz), 116.54, 109.09 (d, *J* = 36.1 Hz), 25.85. ¹⁹F NMR (376 MHz, CDCl₃) δ - 67.05.

2-Fluoro-6-(4-fluorophenoxy) pyridine (2e)



¹H NMR (500 MHz, CDCl₃): δ 7.73 (q, *J* = 8.0 Hz, 1H), 7.13 – 7.03 (m, 4H), 6.71 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.58 (dd, *J* = 8.0, 2.7 Hz, 1H). ¹³C NMR: (125 MHz, CDCl₃) δ 162.4 (d, *J* = 13.6 Hz), 162.1 (d, *J* = 242.8 Hz), 159.8 (d, *J* = 243.4 Hz), 149.2 (d, *J* = 2.7 Hz), 143.6 (d, *J* = 7.9 Hz), 122.8 (d, *J* = 8.4 Hz), 116.3 (d, *J* = 23.3 Hz), 107.3 (d, *J* = 5.1 Hz), 102.6 (d, *J* = 35.4 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -68.07, -117.79.

2-([1,1'-Biphenyl]-4-yloxy)-6-fluoropyridine (2f)



¹H NMR (500 MHz, CDCl₃): δ 7.77 (q, J = 8.0 Hz, 1H), 7.64 – 7.57 (m, 4H), 7.47 – 7.43 (m, 2H), 7.38 – 7.33 (m, 1H), 7.24 – 7.20 (m, 2H), 6.77 (dd, J = 7.9, 1.5 Hz, 1H), 6.63 (dd, J = 7.9, 2.7 Hz, 1H). ¹³C NMR: (125 MHz, CDCl₃) δ 162.4 (d, J = 13.6 Hz), 162.1 (d, J = 242.8 Hz), 159.8 (d, J = 243.4 Hz), 149.2 (d, J = 2.7 Hz), 143.6 (d, J = 7.9 Hz), 122.8 (d, J = 8.4 Hz), 116.3 (d, J = 23.3 Hz), 107.3 (d, J = 5.1 Hz), 102.6 (d, J = 35.4 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -67.83.

4-((6-Fluoropyridin-2-yl)oxy)aniline (2g)



¹H NMR (500 MHz, CDCl₃): δ 7.69 (q, J = 8.0 Hz, 1H), 7.00 – 6.89 (m, 2H), 6.74 – 6.66 (m, 2H), 6.62 (dd, J = 8.0, 1.7 Hz, 1H), 6.55 (dd, J = 7.9, 2.7 Hz, 1H), 3.47 (br, 2H). ¹³C NMR: (125 MHz, CDCl₃) δ . 163.5 (d, J = 13.8 Hz), 162.3 (d, J = 241.9 Hz), 145.6, 144.0, 143.4 (d, J = 7.9 Hz), 122.31 116.2, 106.6 (d, J = 5.1 Hz), 102.0 (d, J = 35.5 Hz).

2-Fluoro-6-(p-tolyloxy)pyridine (2g')



¹H NMR (500 MHz, CDCl₃): δ 7.73 (q, J = 8.0 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.08 – 7.04 (m, 2H), 6.69 (dd, J = 8.0, 1.6 Hz, 1H), 6.61 (dd, J = 8.0, 2.5 Hz, 1H), 2.39 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -68.20.

2-Fluoro-6-(4-(trifluoromethyl)phenoxy)pyridine (2n')



¹H NMR (500 MHz, CDCl₃): δ 7.81 (q, *J* = 7.9 Hz, 1H), 7.69 – 7.63 (m, 2H), 7.26 – 7.22 (m, 2H), 6.83 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.67 (dd, *J* = 7.9, 2.6 Hz, 1H).

2-Fluoro-6-(4-methoxyphenoxy)pyridine (2o')



¹H NMR (400 MHz, CDCl₃): δ 7.71 (q, J = 7.9 Hz, 1H), 7.10 – 7.03 (m, 2H), 6.97 – 6.86 (m, 2H), 6.66 (dd, J = 7.9, 1.6 Hz, 1H), 6.57 (dd, J = 7.9, 2.6 Hz, 1H), 3.82 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.1(d, J = 13.8 Hz), 162.2 (d, J = 242.4 Hz), 156.9, 146.9, 143.3 (d, J = 8.0 Hz), 122.3, 114.8, 106.8 (d, J = 5.1 Hz), 102.1 (d, J = 35.6 Hz), 55.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -67.96.

2-Fluoro-6-thiophen-2-ylpyridine (2m)



¹H NMR (500 MHz, CDCl₃): δ 8.03 – 7.94 (m, 2H), 7.78 (q, J = 8.0 Hz, 1H), 7.53 (dd, J = 7.6, 2.5 Hz, 1H), 7.29 – 7.22 (m, 2H), 6.83 (dd, J = 8.2, 3.0 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 163.44 (d, J = 238.8 Hz), 154.68 (d, J = 13.4 Hz), 150.27 (d, J = 1.9 Hz), 141.91 (d, J = 7.7 Hz), 136.12, 128.45, 121.00, 120.56 (q, J= 257.5 Hz), 117.25 (d, J = 3.9 Hz), 108.12 (d, J = 37.5 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -57.88, -66.54.

2-Fluoro-6-(naphthalen-2-yl)pyridine (2p)



¹H NMR (500 MHz, CDCl₃): δ 8.52 (d, J = 2.2 Hz, 1H), 8.11 (dd, J = 8.6, 1.9 Hz, 1H), 7.98 – 7.83 (m, 4H), 7.76 (dd, J = 7.6, 2.6 Hz, 1H), 7.52 (dt, J = 6.4, 3.6 Hz, 2H), 6.89 (dd, J = 7.9, 3.1 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 163.6 (d, J = 238.4 Hz), 156.3 (d, J = 13.5 Hz), 141.9 (d, J = 7.7 Hz), 134.9, 134.0, 133.5, 129.0, 128.7, 127.8, 127.0, 126.8, 126.6, 124.3, 117.7 (d, J = 4.1 Hz), 107.9 (d, J = 37.7 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -66.51.

2-Fluoro-6-thiophen-2-ylpyridine (2q)



¹H NMR (500 MHz, CDCl₃): δ 7.78 – 7.66 (m, 1H), 7.66 – 7.56 (m, 1H), 7.50 – 7.41 (m, 1H), 7.41 – 7.36 (m, 1H), 7.12 – 7.03 (m, 1H), 6.73 (dt, *J* = 8.3, 2.4 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 163.06 (d, *J* = 239.3 Hz), 151.41 (d, *J* = 14.1 Hz), 142.88, 141.69 (d, *J* = 8.0 Hz), 128.24, 128.22, 125.79, 115.92 (d, *J* = 4.1 Hz), 107.20 (d, *J* = 37.2 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -66.92.

3. Optimization of reaction conditions and general procedural for the asymmetric

heteroarylation

Optimization of reaction conditions

Table S1. Exploring the influence of chiral ligands ^a



	Entry	ligand	Yield (%) ^b	ee (%) °	
-	1	L1	39	68	
	2	L2	21	65	
	3	L3	NR	_	
	4	L4	12	75	
	5	L5	17	-74	
	6	L6	67	-84	
	7	L7	42	92	
	8	L8	11	62	

8

9	L9	21	86
10	L10	7	-47

^a Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), Ni(cod)₂ (10 mol %), ligand (11 mol %), NaO'Bu (0.15 mmol), toluene (1.0 mL), 120°C, 24 h. ^b Yield of **3** determined by ¹H NMR using dibromomethane as internal standard. ^c Determined by chiral HPLC

Me N → OMe

0		MeO N F	Ni(cod) ₂ (10 mol %) (S)-Ph-Garphos [™] (11 mol %)
Me	+		Base, toluene, 120°C, 24 h,
1a		2a	
-	-		

Table S2. Exploring the influence of base ^a

	2a		3aa
Entry	Base	Yield (%) ^b	<i>ee</i> (%) °
1	NaHMDS	trace	25
2	LiO'Bu	17	86
3	KO'Bu	34	63
4	NaOMe	trace	91
5	LiOMe	trace	90
6	KOMe	trace	89
7	NaOEt	trace	60
8	K ₃ PO ₄	trace	94
9	DABCO	NR	-
10	NaOH	trace	67

^a Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), Ni(cod)₂ (10 mol %), (S)-Ph-GarphosTM (11 mol %), Base (0.15 mmol), toluene (1.0 mL), 120°C, 24 h. ^b Yield of **3aa** determined by ¹H NMR using dibromomethane internal standard. ^c Determined by chiral HPLC.

Table S3. The influence of temperature^a

1:	Me +	MeO N F 2a	Ni(cod) ₂ (10 mol %) (S)-Ph-Garphos [™] (11 mol %) NaO ^t Bu (1.5 equiv) toluene, T , 24 h,	O Me 3aa
•	Entry	T (°C)	Yield (%) ^b	ee (%) °
-	1	110	trace	-
	2	120	42	92

^a Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), Ni(cod)₂ (10 mol %), (S)-Ph-GarphosTM (11 mol %), NaO'Bu (0.15 mmol), toluene (1.0 mL), T, 24 h. ^b Yield of **3aa** determined by ¹H NMR using dibromomethane as internal standard. ^c Determined by chiral HPLC.

Table S4. Exploring the influence of solvent and concentration ratio of substrates^a

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O Me 1a	+ MeO N F 2a	Ni(cod) ₂ (10 mol %) (<i>S</i>)-Ph-Garphos [™] (11 mol %) NaO ^{<i>t</i>} Bu (1.5 equiv) solvent, 120 °C , 24 h,	Me 3aa
Entry	solvent	Yield (%) ^b	ee (%) °
1	toluene	42	92
2	m-Xylene	27	93
3	DMF	25	10
4	Benzotrifluoride	7	racemic
5	anisole	44	97
6	ethylbenzene	NR	-
7	mesitylene	NR	-
8	<i>p</i> -difluorobenzene	NR	-
9	<i>p</i> -xylene	NR	-
10	1,4-dioxane	84	90
11 ^d	anisole	78(77 °)	97
12 ^d	1,4-dioxane	85	91

^a Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), Ni(cod)₂ (10 mol %), (S)-Ph-GarphosTM (11 mol %), NaO'Bu (1.5 equiv), solvent (1.0 mL), 120°C, 24 h. ^b Yield of **3aa** determined by ¹H NMR using dibromomethane internal standard. ^c Determined by chiral HPLC. ^d **1a** (0.2 mmol), **2a** (0.1 mmol), NaO'Bu (0.11 mmol). ^d Isolated yield.

General procedural for the asymmetric heteroarylation

A flame-dried sealed pressure-resistant tube (10 mL) equipped with a magnetic stir bar (10 mm \times 5 mm, egg shaped) was evacuated and filled Ar for three times before being transferred into a glovebox. Ni(cod)₂ (0.01 mmol, 10 mol %), (*S*)-Ph-GarPhos (0.011 mmol, 11 mol%) and dry 1,4-dioxane (1 mL) was added to the tube stiring for 10 min. NaO'Bu (0.15 mmol, 1.5 equiv), indanone derivatives (0.1 mmol, 1 equiv) and heteroaryl fluorides (0.15 mmol, 1.5 equiv) were added in succession. The reaction tube was capped and taken out of the glovebox. The reaction was stirred at 120°C for 24 h. After cooling the reaction mixture to ambient temperature, the mixture was concentrated and directly purified by purified by silica gel chromatography using PE/EA (silica gel, 100:1 to 30:1) to afford the product.



Scheme S1. Weak or non-reactive substrate. Reaction conditions: 1 (0.2 mmol), 2 (0.1 mmol), Ni(cod)₂ (10 mol %), (S)-Ph-Garphos[™], NaO'Bu (0.11 mmol) (0.11 mmol), anisole (1.0 mL), 120 °C, 24 h, Isolated yield, ee was determined by chiral HPLC.

4. Characterization of products

(S)-2-(6-Methoxypyridin-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (3aa)

Light yellow oil (19.5 mg, 77% yield, 97% *ee*). ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, J = 7.7 Hz, 1H), 7.64 - 7.56 (m, 1H), 7.56 - 7.45 (m, 2H), 7.42 - 7.34 (m, 1H), 7.06 - 6.98 (m, 1H), 6.60 - 6.51 (m, 1H), 4.01 (d, J = 17.1 Hz, 1H), 3.70 (s, 3H), 3.14 (d, J = 17.1 Hz, 1H), 1.66 (s, 3H). ¹³C NMR: (100 MHz, CDCl₃) 208.5, 163.2, 160.0, 153.8, 139.2, 135.7, 135.0, 127.5, 126.4, 124.7, 113.4, 108.7, 55.9, 53.1, 42.7, 23.5. [α]²⁹_D = -32.2 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel AS-H (0.46 cm x 25 cm), Hexanes / IPA = 92 / 8, 1.0 mL/min, $\lambda = 254$ nm, t_r (minor) = 4.9 min, t_r (major) = 5.6 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₆H₁₆NO₂, 254.1181; found 254.1172.

(S)-2-(6-(Benzyloxy) pyridin-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (3ab)



Colorless oil (16.5 mg, 50% yield, 71% *ee*). ¹H NMR (400 MHz, CDCl₃): δ 7.84 – 7.75 (m, 1H), 7.67 – 7.60 (m, 1H), 7.56 – 7.47 (m, 2H), 7.43 – 7.38 (m, 1H), 7.31 – 7.21 (m, 5H), 7.05 – 7.00 (m, 1H), 6.65 – 6.59 (m, 1H), 5.24 – 5.03 (m, 2H), 3.88 (d, *J* = 17.1 Hz, 1H), 3.11 (d, *J* = 17.1 Hz, 1H), 1.65 (s, 3H). ¹³C NMR: (100 MHz, CDCl₃) 208.5, 162.6, 160.0, 153.9, 139.3, 137.8, 135.7, 135.0, 128.4, 128.2, 127.7, 127.5, 126.4, 124.8, 113.5, 109.3, 67.2, 55.8, 42.9, 23.3. [α]²⁹_D = -11.4 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel ID (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t_r (minor) = 10.0 min, t_r (major) = 12.4 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₂H₂₀NO₂, 330.1494; found 330.1485. *t*-butyl (*R*)-2-(((6-((*S*)-2-Methyl-1-oxo-2,3-dihydro-1*H*-inden-2-yl) pyridin-2-yl) oxy) methyl) morpholine-4-carboxylate (3ac)



Colorless oil (21.0 mg, 48% yield, 92% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 7.82 – 7.73 (m, 1H), 7.65 – 7.58 (m, 1H), 7.55 – 7.47 (m, 2H), 7.43 – 7.34 (m, 1H), 7.08 – 6.98 (m, 1H), 6.61 (d, *J* = 8.2 Hz, 1H), 4.20 – 3.87 (m, 6H), 3.68 – 3.59 (m, 1H), 3.54 – 3.45 (m, 1H), 3.14 (d, *J* = 17.0 Hz, 1H), 2.94 (s, 1H), 2.66 (s, 1H), 1.65 (s, 3H), 1.46 (d, *J* = 2.6 Hz, 9H). ¹³C NMR: (125 MHz, CDCl₃) 208.4, 162.4, 159.9, 159.8, 154.9, 139.4, 135.7, 135.1, 135.1, 127.6, 126.4, 126.4, 124.8, 113.8, 109.3, 80.2, 73.8, 66.7, 65.8, 55.9, 42.8, 28.5, 23.4. [α]²⁷_D = -85.9 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel IC (0.46 cm x 25 cm), Hexanes / IPA = 80 / 20, 1.0 mL/min, λ = 254 nm, t_r (minor) = 14.1 min, t_r (major) = 16.2 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₅H₃₁N₂O₅, 439.2233; found 439.2223.

(S)-2-Methyl-2-(6-phenoxypyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3ad)



Colorless oil (22.1 mg, 70% yield, 98% *ee*). ¹H NMR (400 MHz, CDCl₃): δ 7.79 – 7.68 (m, 1H), 7.68 – 7.51 (m, 2H), 7.43 – 7.32 (m, 2H), 7.31 – 7.16 (m, 3H), 7.16 – 7.07 (m, 1H), 7.07 – 6.96 (m, 2H), 6.69 – 6.61 (m, 1H), 3.91 (d, *J* = 17.2 Hz, 1H), 3.05 (d, *J* = 17.2 Hz, 1H), 1.63 (s, 3H). ¹³C NMR: (100 MHz, CDCl₃) 208.2, 162.8, 160.7, 154.1, 153.7, 140.0, 135.4, 135.1, 129.4, 127.4, 126.5, 124.7, 124.3, 121.2, 115.6, 108.9, 55.8, 42.1, 24.1. [α]²⁹_D = 0.2 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel AS-H (0.46 cm x 25 cm), Hexanes / IPA = 92 / 8, 1.0 mL/min, λ = 254 nm, t_r (minor) = 6.3 min, t_r (major) = 7.4 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₁H₁₈NO₂, 316.1338; found 316.1229.

(S)-2-(6-(4-Fluorophenoxy) pyridin-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (3ae)

Light yellow oil (18.3 mg, 55% yield, 94% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 7.73 – 7.68 (m, 1H), 7.62 (t, J = 7.9 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.39 – 7.33 (m, 2H), 7.18 (d, J = 7.5 Hz, 1H), 6.95 – 6.83 (m, 4H), 6.67 (d, J = 8.2 Hz, 1H), 3.78 (d, J = 17.0 Hz, 1H), 3.02 (d, J = 17.0 Hz, 1H), 1.61 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃) 208.2, 162.7, 160.7, 159.4 (d, J = 242.1 Hz), 153.8, 149.7 (d, J = 2.9 Hz), 140.1, 135.4, 135.1, 127.4, 126.4, 124.7, 122.8 (d, J = 8.4 Hz), 115.8 (d, J = 23.2 Hz), 115.3, 108.8, 55.7, 42.3, 23.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -119.25. [α]²⁹_D = 19.7 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel AS-H (0.46 cm x 25 cm), Hexanes / IPA = 92 / 8, 1.0 mL/min, $\lambda = 254$ nm, t_r (minor) = 6.4 min, t_r (major) = 7.7 min. HRMS (ESI) *m*/*z*: [M+H]⁺ calcd for C₂₁H₁₇NFO₂, 334.1243; found 334.1235. **(***S***)-2-(6-([1,1'-Biphenyl]-4-yloxy) pyridin-2-yl)-2-methyl-2,3-dihydro-1H-inden-1-one (3af)**



Colorless oil (27.8 mg, 71% yield, 98% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 7.77 – 7.69 (m, 1H), 7.67 – 7.61 (m, 1H), 7.59 – 7.55 (m, 2H), 7.54 – 7.49 (m,1H), 7.49 – 7.43 (m, 4H), 7.38 – 7.30 (m, 3H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.11 – 7.03 (m, 2H), 6.72 (d, *J* = 8.1 Hz, 1H), 3.91 (d, *J* = 17.1 Hz, 1H), 3.06 (d, *J* = 17.1 Hz, 1H), 1.64 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃) 208.2, 162.7, 160.8, 153.8, 153.6, 140.7, 140.1, 137.2, 135.4, 135.0, 128.9, 1280, 127.4, 127.2, 127.1, 126.5, 124.7, 121.5, 115.6, 109.0, 55.8, 42.3, 23.8. [α]²⁹_D = -29.4 (c 2.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel AS-H (0.46 cm x 25 cm), Hexanes / IPA = 92 / 8, 1.0 mL/min, λ = 254 nm, t_r (minor) = 7.8 min, t_r (major) = 9.7 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₇H₂₂NO₂, 392.1651; found 392.1639.

(S)-2-(6-(4-Aminophenoxy) pyridin-2-yl)-2-methyl-2,3-dihydro-1H-inden-1-one (3ag)

Light yellow oil (7.6 mg, 23% yield, 91% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 7.75 (d, J = 7.5 Hz, 1H), 7.63 – 7.53 (m, 2H), 7.44 – 7.39 (m, 1H), 7.39 – 7.34 (m, 1H), 7.15 (d, J = 7.5 Hz, 1H), 6.89 – 6.77 (m, 2H), 6.65 – 6.57 (m, 2H), 6.55 (d, J = 8.2 Hz, 1H), 3.97 (d, J = 17.2 Hz, 1H), 3.07 (d, J = 17.2 Hz, 1H), 1.63 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃) 208.4, 163.7, 160.7, 153.7, 146.3, 143.1, 139.9, 135.4, 135.0, 127.4, 126.6, 124.7, 122.4, 116.0, 115.1, 108.0, 55.8, 42.2, 24.3. [α]²⁷_D = -44.6 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel ID (0.46 cm x 25 cm), Hexanes / IPA = 60 / 40, 0.8 mL/min, $\lambda = 210$ nm, t_r (minor) = 8.0 min, t_r (major) = 10.7 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₁H₁₉N₂O₂, 331.1447; found 331.1435.

(S)-2-(6-(Diphenylphosphaneyl) pyridin-2-yl)-2-methyl-2,3-dihydro-1H-inden-1-one (3ah)



Yellow oil (19.1 mg, 47% yield, 90% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 7.76 – 7.70 (m, 1H), 7.61 – 7.56 (m, 1H), 7.55 – 7.49 (m, 1H), 7.46 – 7.41 (m, 1H), 7.41 – 7.19 (m, 12H), 7.09 – 7.00 (m, 1H), 4.06 (d, *J* = 17.1 Hz, 1H), 3.03 (d, *J* = 17.1 Hz, 1H), 1.65 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃) δ 208.4, 162.2, 162.1, 154.0, 136.3, 136.3, 135.3, 135.1, 134.5, 134.4, 134.3, 134.2, 134.1, 129.0, 128.8, 128.5, 128.4, 128.4, 128.3, 127.4, 126.7, 126.6, 126.5, 124.7, 119.8, 56.3, 41.8, 24.5. ³¹P NMR (202 MHz, CDCl₃) δ -3.75. [α]²⁹_D = 102.9 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel IC (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t_r (minor) = 9.4 min, t_r (major) = 12.3 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₇H₂₃NOP, 408.1517; found 408.1509.

(S)-2-Methyl-2-(6-methylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3ai)



Colorless oil (12.8 mg, 54% yield, 83% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 7.79 (d, J = 7.6 Hz, 1H), 7.61 (td, J = 7.5, 1.3 Hz, 1H), 7.58 – 7.45 (m, 2H), 7.38 (t, J = 7.5 Hz, 1H), 7.30 (d, J = 7.9 Hz, 1H), 6.97 (d, J = 7.6 Hz, 1H), 4.18 (d, J = 17.2 Hz, 1H), 3.16 (d, J = 17.2 Hz, 1H), 2.45 (s, 3H), 1.66 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃) δ 208.9, 161.4, 157. 8, 153.7, 136.7, 135.5, 135.1, 127.5, 126.6, 124.7, 121.3, 118.0, 56.0, 42.2, 24.9, 24.7. [α]²⁹_D = 12.9 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel AS-H (0.46 cm x 25 cm), Hexanes / IPA = 92 / 8, 1.0 mL/min, λ = 254 nm, t_r (minor) = 4.9 min, t_r (major) = 5.7 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₆H₁₆NO, 238.1232; found 238.1224.

(S)-2-Methyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3aj)



Yellow oil (27.2 mg, 91% yield, 98% *ee*). ¹H NMR (400 MHz, CDCl₃): δ 7.97 – 7.89 (m, 2H), 7.83 – 7.78 (m, 1H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.67 – 7.51 (m, 3H), 7.47 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.44 – 7.31 (m, 4H), 4.32 (d, *J* = 17.2 Hz, 1H), 3.21 (d, *J* = 17.2 Hz, 1H), 1.75 (s, 3H). ¹³C NMR: (100 MHz, CDCl₃) 208.6, 161.7, 156.0, 153.8, 139.4, 137.4, 135.6, 135.1, 129.0, 128.7, 127.5, 126.9, 126.6, 124.8, 119.6, 118.2, 56.4, 42.1, 24.7. [α]²⁹_D = -65.0 (c 2.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel IB (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t_r (minor) = 6.7 min, t_r (major) = 7.5 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₁H₁₈NO, 300.1388; found 300.1379.

(S)-2-Methyl-2-(6-(p-tolyl) pyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3ak)



Light yellow oil (31.0 mg, 99% yield, 97% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 7.86 – 7.75 (m, 3H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.59 – 7.51 (m, 2H), 7.47 – 7.42 (m, 1H), 7.42 – 7.37 (m, 1H), 7.21 (d, J = 8.0 Hz, 2H), 4.32 (d, J = 17.1 Hz, 1H), 3.21 (d, J = 17.1 Hz, 1H), 2.37 (s, 3H), 1.75 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃) 208.7, 161.6, 156.0, 153.9, 138.9, 137.3, 136.7, 135.6, 135.1, 129.4, 127.5, 126.8, 126.6, 124.8, 119.2, 117.9, 56.4, 42.1, 24.6, 21.4. [α]²⁹_D = -75.5 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel IB (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, $\lambda = 254$ nm, t_r (minor) = 6.2 min, t_r (major) = 6.7 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₂H₂₀NO, 314.1545; found 314.1536.

(S)-2-(6-(4-Methoxyphenyl) pyridin-2-yl)-2-methyl-2,3-dihydro-1H-inden-1-one (3al)



Light yellow oil (28.6 mg, 87% yield, 96% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 7.93 – 7.83 (m, 2H), 7.80 (d, J = 7.7 Hz, 1H), 7.70 – 7.59 (m, 2H), 7.53 (t, J = 7.6 Hz, 2H), 7.40 (d, J = 7.6 Hz, 2H), 6.98 – 6.87 (m, 2H), 4.30 (d, J = 17.1 Hz, 1H), 3.83 (s, 3H), 3.20 (d, J = 17.1 Hz, 1H), 1.74 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃) 208.7, 161.6, 160.5, 155.7, 153.9, 137.3, 135.6, 135.1, 132.1, 128.2, 127.5, 126.6, 124.8, 118.8, 117.4, 114.0, 56.3, 55.5, 42.2, 24.6. [α]²⁹_D = -84.0 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel IB (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, $\lambda = 254$ nm, t_r (minor) = 8.8 min, t_r (major) = 10.4 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₂H₂₀NO₂, 330.1494; found 330.1485.

(S)-2-Methyl-2-(6-(4-(trifluoromethoxy)phenyl)pyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3am)



Light yellow oil (24.9 mg, 65% yield, 94% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 7.97 – 7.92 (m, 2H), 7.83 – 7.78 (m, 1H), 7.76 – 7.70 (m, 1H), 7.69 – 7.62 (m, 1H), 7.60 – 7.52 (m, 2H), 7.52 – 7.46 (m, 1H), 7.44 – 7.37 (m, 1H), 7.26 – 7.21 (m, 2H), 4.26 (d, *J* = 17.1 Hz, 1H), 3.22 (d, *J* = 17.1 Hz, 1H), 1.75 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃) 208.5, 162.0, 154.6, 153.7, 149.9, 138.0, 137.6, 135.5, 135.2, 128.4, 127.6, 126.6, 124.8, 121.0, 120.6 (q, *J* = 257.2 Hz), 119.9, 118.2, 56.3, 42.2, 24.5. ¹⁹F NMR (376 MHz, CDCl₃) δ -57.54. [α]²⁹_D = -166.9 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel IB (0.46 cm x 25 cm),

Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 270 nm, t_r (minor) = 6.0 min, t_r (major) = 6.4 min. HRMS (ESI) m/z: [M+H]⁺ calcd for C₂₂H₂₀NO₂, 384.1211; found 384.1203.

(S)-2-Methyl-2-(6-(4-(trifluoromethyl)phenyl)pyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3an)



Yellow oil (34.1 mg, 93% yield, 98% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 8.07 – 7.98 (m, 2H), 7.81 (d, J = 7.7 Hz, 1H), 7.75 (t, J = 7.9 Hz, 1H), 7.68 – 7.59 (m, 4H), 7.59 – 7.51 (m, 2H), 7.41 (t, J = 7.4 Hz, 1H), 4.26 (d, J = 17.1 Hz, 1H), 3.23 (d, J = 17.1 Hz, 1H), 1.76 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃): 208.4, 162.2, 154.4, 153.7, 142.6, 137.7, 135.5, 135.3, 130.7 (q, J = 32.5 Hz), 127.6, 127.2, 126.6, 125.6 (q, J = 3.8 Hz), 124.8, 124.3 (q, J = 272.0 Hz), 120.5, 118.6, 77.4, 77.2, 76.9, 56.3, 42.2, 24.5. ¹⁹F NMR (376 MHz, CDCl₃): δ -62.57. [α]²⁹_D = -44.6 (c 2.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel IB (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, $\lambda = 254$ nm, t_r (minor) = 12.3 min, t_r (major) = 12.7 min. HRMS (ESI) *m*/*z*: [M+H]⁺ calcd for C₂₂H₁₇F₃NO, 368.1262; found 368.1255.

(S)-4-(6-(2-Methyl-1-oxo-2,3-dihydro-1*H*-inden-2-yl)pyridin-2-yl)benzonitrile (3ao)



Colorless oil (19.8 mg, 82% yield, 91% *ee*). ¹H NMR (400 MHz, CDCl₃): δ 8.07 – 7.97 (m, 2H), 7.83 – 7.73 (m, 2H), 7.71 – 7.59 (m, 4H), 7.58 – 7.51 (m, 2H), 7.45 – 7.38 (m, 1H), 4.23 (d, *J* = 17.2 Hz, 1H), 3.23 (d, *J* = 17.2 Hz, 1H), 1.75 (s, 3H). ¹³C NMR: (100 MHz, CDCl₃): 208.2, 162.4, 153.7, 153.6, 143.4, 137.8, 135.4, 135.3, 132.5, 127.7, 127.4, 126.6, 124.9, 120. 9, 119.0, 118.8, 112.3, 56.3, 42.2, 24.5. [α]²⁹_D = -87.4 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel ID (0.46 cm x 25 cm), Hexanes / IPA = 60 /40, 1.0 mL/min, λ = 270 nm, t_r (minor) = 8.0 min, t_r (major) = 10.7 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₂H₁₇N₂O, 325.1341; found 325.1332.

(S)-2-Methyl-2-(6-(naphthalen-2-yl) pyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3ap)



Yellow transparent crystal (32.5 mg, 93% yield, 98% *ee*). M.p. 122.3-123.5°C. ¹H NMR (500 MHz, CDCl₃): δ 8.42 – 8.30 (m, 1H), 8.12 – 8.05 (m, 1H), 7.91 – 7.81 (m, 4H), 7.79 – 7.72 (m, 2H), 7.71 – 7.63 (m, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.46 (m, 3H), 7.42 (t, *J* = 7.4 Hz, 1H), 4.35 (d, *J* = 17.2 Hz, 1H), 3.26 (d, *J* = 17.1 Hz, 1H), 1.80 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃) 208.7, 161.8, 155.8, 153.9, 137.5, 136.7, 135.6, 135.1, 133.7, 133.5, 128.8, 128.3, 127.7, 127.5, 126.6, 126.5, 126.3, 126.2, 124.8, 124.7, 119.5, 118.5, 56.4, 42.3, 24.5. [α]²⁹_D = -44.6 (c 2.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel IB (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t_r (minor) = 8.1 min, t_r (major) = 10.0 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₅H₂₀NO, 350.1545; found 350.1537.

(S)-2-Methyl-2-(6-(thiophen-2-yl)pyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3aq)



Light yellow oil (19.8 mg, 65% yield, 87% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 7.82 – 7.76 (m, 1H), 7.68 – 7.59 (m, 2H), 7.57 – 7.52 (m, 1H), 7.52 – 7.45 (m, 2H), 7.42 – 7.36 (m, 2H), 7.30 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.04 (dd, *J* = 5.1, 3.7 Hz, 1H), 4.29 (d, *J* = 17.1 Hz, 1H), 3.18 (d, *J* = 17.1 Hz, 1H), 1.72 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃) 208.4, 161.6, 153.9, 151.5, 145.5, 137.4, 135.5, 135.2, 128.0, 127.6, 127.5, 126.6, 124.8, 124.4, 119.3, 116.6, 56.2, 41.9, 24.6. [α]²⁹_D = -105.03 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel IB (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t_r (minor) = 7.3 min, t_r (major) = 9.6 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₉H₁₆NOS, 306.0953; found 306.0945.

(S)-2-Methyl-2-(pyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3ar)



Light yellow oil (17.6 mg, 79% yield, 81% *ee*). ¹H NMR (400 MHz, CDCl₃): δ 8.55 – 8.46 (m, 1H), 7.80 (d, J = 7.7 Hz, 1H), 7.70 – 7.59 (m, 2H), 7.55 – 7.48 (m, 2H), 7.43 – 7.36 (m, 1H), 7.16 – 7.10 (m, 1H), 4.10 (d, J = 17.2 Hz, 1H), 3.20 (d, J = 17.2 Hz, 1H), 1.69 (s, 3H). ¹³C NMR: (100 MHz, CDCl₃) δ 208.6, 162.4, 153.5, 149.3, 136.7, 135.4, 135.3, 127.7, 126.7, 124.9, 121.9, 121.2, 55.9, 42.5, 24.6. [α]²⁹_D = -111.0 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel AS-H (0.46 cm x 25 cm), Hexanes / IPA = 92 / 8, 1.0 mL/min, λ = 254 nm, t_r (minor) = 6.4 min, t_r (major) = 7.5 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₅H₁₄NO, 224.1075; found 224.1066.

(S)-2-(4-Fluoropyridin-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (3as)



Colorless oil (10. 1 mg, 42% yield, 90% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 8.51 – 8.42 (m, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.68 – 7.60 (m, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.34 – 7.28 (m, 1H), 6.92 – 6.86 (m, 1H), 4.08 (d, *J* = 17.2 Hz, 1H), 3.20 (d, *J* = 17.2 Hz, 1H), 1.67 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃) δ 207.8, 169.2 (d, *J* = 262.0 Hz), 165.9 (d, *J* = 6.5 Hz), 153.4, 151.5 (d, *J* = 7.2 Hz), 135.5, 135.1, 127.8, 126.7, 125.0, 109.9 (d, *J* = 16.4 Hz), 109.4 (d, *J* = 17.6 Hz), 55.8 (d, *J* = 2.8 Hz), 42.3, 24.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -102.01. [α]²⁹_D = 31.0 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel AS-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t_r (minor) = 6.1 min, t_r (major) = 7.1 min. HRMS (ESI) *m*/z: [M+H]⁺ calcd for C₁₅H₁₃FNO, 242.0981; found 242.0973. **(***S***)-2-(5-fluoropyridin-2-yl)-2-methyl-2,3-dihydro-1H-inden-1-one (3at)**



Colorless oil (15.9 mg, 66% yield, 94% *ee*). ¹H NMR (400 MHz, CDCl₃): δ 8.34 (d, J = 2.9 Hz, 1H), 7.86 – 7.72 (m, 1H), 7.70 – 7.68 (m, 1H), 7.59 – 7.47 (m, 2H), 7.46 – 7.32 (m, 2H), 4.07 (d, J = 17.2 Hz, 1H), 3.19 (d, J = 17.3 Hz, 1H), 1.67 (s, 3H). ¹³C NMR: (100 MHz, CDCl₃) δ 208.2, 159.7, 158.1, 157.2, 153.3, 137.3, 137.1, 135.4, 135.1, 127.8, 126.7, 124.9, 123.4, 123.2, 122.1, 122.1, 55.4, 42.3, 25.0. [α]²⁵_D = -0.26 (c 0.5, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel ASH (0.46 cm x 25 cm), Hexanes / IPA = 92 / 8, 1.0 mL/min, λ = 254 nm, t_r (major) = 5.7 min, t_r (minor) = 6.5 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₅H₁₂FNO, 242.0981; found 242.0976.

Methyl (S)-6-(2-methyl-1-oxo-2,3-dihydro-1H-inden-2-yl)nicotinate (3au)

Me COOMe

Colorless oil (18.3 mg, 65% yield, 78% *ee*). ¹H NMR (400 MHz, CDCl₃): δ 9.09 (dd, J = 2.2, 0.9 Hz, 1H), 8.25 (dd, J = 8.3, 2.3 Hz, 1H), 7.84 – 7.76 (m, 1H), 7.69 – 7.58 (m, 2H), 7.56 – 7.48 (m, 1H), 7.48 – 7.36 (m, 1H), 4.11 (d, J = 17.3 Hz, 1H), 3.92 (s, 3H), 3.21 (d, J = 17.3 Hz, 1H), 1.71 (s, 3H). ¹³C NMR: (100 MHz, CDCl₃) δ 207.7, 166.7, 165.9, 153.3, 150.4, 137.8, 135.4, 135.1, 127.8, 126.7, 125.0, 124.2, 120.8, 56.2, 52.5, 42.3, 24.6. [α]²⁵_D = -0.13 (c 0.5, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel ASH (0.46 cm x 25 cm), Hexanes / IPA = 92 / 8, 1.0 mL/min, λ = 254 nm, t_r (major) = 11.2 min, t_r (minor) = 16.9 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₇H₁₆NO₃, 282.1130; found 282.1124.

(S)-6-(2-methyl-1-oxo-2,3-dihydro-1H-inden-2-yl)nicotinonitrile (3av)

Me CN

Colorless oil (8.6 mg, 35% yield, 37% *ee*). ¹H NMR (400 MHz, CDCl₃): δ 8.79 – 8.69 (m, 1H), 7.96 – 7.88 (m, 1H), 7.82 – 7.74 (m, 1H), 7.73 – 7.61 (m, 2H), 7.56 – 7.49 (m, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 4.10 (d, *J* = 17.3 Hz, 1H), 3.21 (d, *J* = 17.3 Hz, 1H), 1.70 (s, 3H). ¹³C NMR: (100 MHz, CDCl₃) δ 206.9, 166.6, 153.1, 151.8, 139. 8, 135.7, 134.8, 123.0, 126.7, 125.2, 121.4, 116.8, 108.0, 56.4, 41.9, 24.7. [α]²⁵_D = -0.09 (c 0.5, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel ASH (0.46 cm x 25 cm), Hexanes / IPA = 80 / 20, 1.0 mL/min, λ = 254 nm, t_r (major) = 10.7 min, t_r (minor) = 15.4 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₆H₁₃N₂O, 249.1028; found 249.1022.

(S) 2-methyl-2-(5-methylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3aw)



Colorless oil (5.7 mg, 24% yield, 81% *ee*). ¹H NMR (400 MHz, CDCl₃): δ 8.41 – 8.27 (m, 1H), 7.81 – 7.76 (m, 1H), 7.65 – 7.57 (m, 1H), 7.53 – 7.34 (m, 4H), 4.07 (d, *J* = 17.2 Hz, 1H), 3.18 (d, *J* = 17.5 Hz, 1H), 2.28 (s, 3H), 1.66 (s, 3H). ¹³C NMR: (100 MHz, CDCl₃) δ 208.8, 159.5, 153.5, 149.7, 137.2, 135.4, 135.2, 131.2, 127.6, 126.7, 124.9, 120.6, 55.6, 42.5, 24.6, 18.1. [α]²⁵_D = -0.09 (c 0.5, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel ASH (0.46 cm x 25 cm), Hexanes / IPA = 92 / 8, 1.0 mL/min, λ = 254 nm, t_r (major) = 5.8 min, t_r (minor) = 6.8 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₆H₁₆NO, 238.1232; found 238.1226.

(S)- 2-(5-methoxypyridin-2-yl)-2-methyl-2,3-dihydro-1H-inden-1-one (3ax)



Colorless oil (14.9 mg, 59% yield, 86% *ee*). ¹H NMR (400 MHz, CDCl₃): δ 8.20 (dd, *J* = 3.1, 0.7 Hz, 1H), 7.83 – 7.73 (m, 1H), 7.66 – 7.56 (m, 1H), 7.53 – 7.34 (m, 3H), 7.20 – 7.12 (m, 1H), 4.06 (d, *J* = 17.2 Hz, 1H), 3.81 (s, 3H), 3.17 (d, *J* = 17.2 Hz, 1H), 1.66 (s, 3H). ¹³C NMR: (100 MHz, CDCl₃) δ 208.8, 154.4, 154.2, 153.5, 136.7, 135.3, 135.2, 127.6, 126.7, 124.8, 121.3, 121.1, 55.7, 55.2, 42.5, 24.7. [α]²⁵_D = -0.23 (c 0.5, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel ASH (0.46 cm x 25 cm), Hexanes / IPA = 92 / 8, 1.0 mL/min, λ = 254 nm, t_r (major) = 8.7 min, t_r (minor) = 11.0 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₆H₁₆NO₂, 254.1181; found 254.1176.

(S)-2-methyl-2-(5-phenylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3ay)



Colorless oil (23.0 mg, 77% yield, 90% *ee*). ¹H NMR (400 MHz, CDCl₃): δ 8.79 – 8.67 (m, 1H), 7.90 – 7.78 (m, 2H), 7.66 – 7.58 (m, 2H), 7.57 – 7.50 (m, 3H), 7.49 – 7.33 (m, 4H), 4.15 (d, *J* = 17.3 Hz, 1H), 3.24 (d, *J* = 17.3 Hz, 1H), 1.74 (s, 3H). ¹³C NMR: (100 MHz, CDCl₃) δ 208.5, 161.2, 153.5, 147.7, 137.8, 135.4, 135.3, 135.1, 134.8, 129.2, 128.0, 127.7, 127.2, 126.7, 124.9, 121.0, 55.7, 42.5, 24.6. [α]²⁵_D = -0.34 (c 0.5, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel ASH (0.46 cm x 25 cm), Hexanes / IPA = 92 / 8, 1.0 mL/min, λ = 254 nm, t_r (major) = 7.6 min, t_r (minor) = 9.6 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₁H₁₈NO, 300.1388; found 300.1383.

(S)-2-Methyl-2-(pyrazin-2-yl)-2,3-dihydro-1H-inden-1-one (3az)



Light yellow solid (11.6 mg, 52% yield, 79% *ee*). M.p. 90.3-93.1°C. ¹H NMR (400 MHz, CDCl₃): δ 8.83 (s, 1H), 8.53 – 8.38 (m, 2H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.70 – 7.60 (m, 1H), 7.58 – 7.47 (m, 1H), 7.46 – 7.38 (m, 1H), 4.04 (d, *J* = 17.3 Hz, 1H), 3.22 (d, *J* = 17.3 Hz, 1H), 1.74 (s, 3H). ¹³C NMR: (100 MHz, CDCl₃) δ 207.3, 157.9, 153.1, 143.8, 143.3, 142.9, 135.6, 134.9, 128.0, 126.7, 125.1, 54.8, 41.9, 24.2. [α]²⁹_D = 153.7 (c 1.0, CHCl₃). ¹⁹F NMR (376 MHz, CDCl₃) δ -130.19.The enantiomeric excess was determined by Daicel Chiralcel IB (0.46 cm x 25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t_r (major) = 7.9 min, t_r (minor) = 8.7 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₄H₁₃N₂O, 225.1028; found 225.1020.

(S)-5-Fluoro-2-methyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3bj)



Light yellow solid (21.9 mg, 69% yield, 94% *ee*). M.p. 98.0-98.5°C. ¹H NMR (400 MHz, CDCl₃): δ 7.97 – 7.88 (m, 2H), 7.83 – 7.76 (m, 1H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.60 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.49 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.45 – 7.34 (m, 3H), 7.23 – 7.17 (m, 1H), 7.14 – 7.06 (m, 1H), 4.36 (d, *J* = 17.4 Hz, 1H), 3.17 (d, *J* = 17.4 Hz, 1H), 1.74 (s, 3H). ¹³C NMR: (100 MHz, CDCl₃): 206.7, 167.6 (d, *J* = 256.3 Hz), 161.3, 156.8 (d, *J* = 9.9 Hz), 156.0, 139.3, 137.5, 131.9 (d, *J* = 1.9 Hz), 129.0, 128.7, 127.1 (d, *J* = 10.5 Hz),126.9, 119.5, 118.4, 115.9 (d, *J* = 23.8 Hz), 113.2 (d, *J* = 22.2 Hz), 56.7, 41.8, 41.8, 24.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -102.64. [α]²⁹_D = -184.2 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel IB (0.46 cm x 25 cm), Hexanes / IPA = 97 / 3, 1.0 mL/min, λ = 254 nm, t_r (minor) = 8.2 min, t_r (major) = 9.2 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₁H₁₇FNO, 318.1294; found 318.1286.

(S)-5-Methoxy-2-methyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3cj)



Colorless oil (32.6 mg, 99% yield, 96% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 7.99 – 7.92 (m, 2H), 7.77 – 7.67 (m, 2H), 7.62 – 7.55 (m, 1H), 7.52 – 7.47 (m, 1H), 7.46 – 7.39 (m, 2H), 7.39 – 7.33 (m, 1H), 6.97 (d, *J* = 2.2 Hz, 1H), 6.94 – 6.90 (m, 1H), 4.29 (d, *J* = 17.2 Hz, 1H), 3.90 (s, 3H), 3.16 (d, *J* = 17.2 Hz, 1H), 1.74 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃): 206.8, 165.8, 161.9, 156.8, 155.9, 139.4, 137.4, 128.9, 128.7, 128.7, 126.9, 126.5, 119.6, 118.2, 115.7, 109.6, 56.5, 55.8, 42.0, 24.9. [α]²⁹_D = 4.7 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel IB (0.46 cm x 25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t_r (minor) = 7.6 min, t_r (major) = 8.3 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₂H₂₀NO₂, 330.1494; found 330.1484.

(S)-2,5-Dimethyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3dj)



Colorless oil (31.0 mg, 99% yield, 97% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 7.98 – 7.93 (m, 2H), 7.70 (dt, *J* = 7.8, 3.9 Hz, 2H), 7.59 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.47 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.39 – 7.32 (m, 2H), 7.21 (d, *J* = 7.8 Hz, 1H), 4.27 (d, *J* = 17.1 Hz, 1H), 3.16 (d, *J* = 17.1 Hz, 1H), 2.47 (s, 3H), 1.74 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃): 208.2, 161.9, 155.9, 154.3, 146.3, 139.4, 137.4, 133.3, 128.9, 128.8, 128.7, 126.9, 126.9, 124.6, 119.6, 118.2, 56.5, 41.9, 24.8, 22.3. [α]²⁹_D = -84.0 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel IB (0.46 cm x 25 cm), Hexanes / IPA = 97 / 3, 1.0 mL/min, λ = 254 nm, t_r (minor) = 6.5 min, t_r (major) = 7.0 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₃H₂₁NO₃, 314.1545; found 314.1536.

(S)-6-Fluoro-2-methyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3ej)



Light yellow oil (21.9 mg, 69% yield, 94% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 7.97 – 7.87 (m, 2H), 7.72 (t, J = 7.8 Hz, 1H), 7.60 (dd, J = 7.8, 0.9 Hz, 1H), 7.53 – 7.31 (m, 7H), 4.28 (d, J = 16.9 Hz, 1H), 3.16 (d, J = 16.9 Hz, 1H), 1.75 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃): 207.7 (d, J = 2.8 Hz), 162.5 (d, J = 247.5 Hz), 161.4, 156.1, 149.2 (d, J = 2.2 Hz), 139.3, 137.5, 137.3 (d, J = 7.2 Hz), 129.0, 128.7, 127.9 (d, J = 7.8 Hz), 126.9, 122.8 (d, J = 23.6 Hz), 119.4, 118.4, 110.4 (d, J = 21.8 Hz), 57.3, 41.5, 24.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -114.70. [α]²⁹_D = -196.8 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel IB (0.46 cm x 25 cm), Hexanes / IPA = 97 / 3, 1.0 mL/min, $\lambda = 254$ nm, t_r (minor) = 6.6 min, t_r (major) = 6.9 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₁H₁₇FNO, 318.1294; found 318.1286.

(S)-6-Methoxy-2-methyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3fj)



Colorless oil (32.2 mg, 98% yield, 98% *ee*). ¹H NMR (400 MHz, CDCl₃): δ 8.04 – 7.86 (m, 2H), 7.70 (t, J = 7.8 Hz, 1H), 7.64 – 7.55 (m, 1H), 7.48 – 7.33 (m, 5H), 7.26 – 7.20 (m, 2H), 4.19 (d, J = 16.9 Hz, 1H), 3.85 (s, 3H), 3.14 (d, J = 16.9 Hz, 1H), 1.75 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃): 208.7, 161.8, 159.6, 156.0, 146.7, 139.4, 137.4, 136.7, 129.0, 128.7, 127.3, 126.9, 124.6, 119.5, 118.2, 105.8, 57.2, 55.7, 41.6, 24.6. [α]²⁹_D = -121.0 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel AS-H (0.46 cm x 25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, $\lambda =$ 254 nm, t_r (minor) = 6.8 min, t_r (major) = 8.1 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₂H₂₀NO₂, 330.1494; found 330.1485.

(S)-5,6-Dimethoxy-2-methyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3gj)



White soild (30.5 mg, 85% yield, 96% *ee*). M.p. 127.9-128.9°C.¹H NMR (500 MHz, CDCl₃): δ 7.99 – 7.92 (m, 2H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.39 – 7.34 (m, 1H), 7.22 (s, 1H), 6.95 (s, 1H), 4.20 (d, *J* = 16.9 Hz, 1H), 4.00 (s, 3H), 3.92 (s, 3H), 3.12 (d, *J* = 16.9 Hz, 1H), 1.74 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃): 207.3, 162.0, 156.0, 155.9, 149.6, 149.2, 139.5, 137.4, 128.9, 128.7, 128.1, 126.9, 119.5, 118.2, 107.5, 105.1, 56.6, 56.4, 56.2, 42.0, 24.8. [α]²⁹_D = -112.1 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel AS-H (0.46 cm x 25 cm), Hexanes / IPA = 80 / 20, 1.0 mL/min, λ = 254 nm, t_r (minor) = 10.2 min, t_r (major) = 11.4 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₃H₂₁NO₃, 360.1600; found 360.1589.

(S)-2-Ethyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3hj)



Light yellow oil (26.3 mg, 84% yield, 96% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 8.03 – 7.93 (m, 2H), 7.76 (d, J = 7.8 Hz, 1H), 7.71 (t, J = 7.8 Hz, 1H), 7.66 – 7.54 (m, 4H), 7.46 – 7.40 (m, 2H), 7.40 – 7.34 (m, 2H), 4.51 (d, J = 17.4 Hz, 1H), 3.28 (d, J = 17.4 Hz, 1H), 2.36 – 2.23 (m, 1H), 2.23 – 2.07 (m, 1H), 0.87 (t, J = 7.4 Hz, 3H) ¹³C NMR: (125 MHz, CDCl₃): 208.3, 160.1, 155.7, 154.4, 139.5, 137.3, 136.3, 135.1, 128.9, 128.7,

127.4, 126.9, 126.5, 124.4, 120.3, 118.2, 61.0, 37.4, 31.8, 9.5. $[\alpha]^{29}_{D} = -78.7$ (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel IB (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, $\lambda = 254$ nm, t_r (minor) = 5.5 min, t_r (major) = 6.2 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₂H₂₀NO, 314.1545; found 314.1535.

(S)-2-Pentyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3ij)



Light yellow oil (20.6 mg, 58% yield, 96% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 8.01 – 7.93 (m, 2H), 7.75 (d, J = 7.8 Hz, 1H), 7.71 (t, J = 7.8 Hz, 1H), 7.66 – 7.53 (m, 4H), 7.45 – 7.32 (m, 4H), 4.54 (d, J = 17.4 Hz, 1H), 3.28 (d, J = 17.4 Hz, 1H), 2.29 – 2.18 (m, 1H), 2.12 – 1.99 (m, 1H), 1.30 – 1.15 (m, 6H), 0.88 – 0.76 (m, 3H). ¹³C NMR: (125 MHz, CDCl₃): 208.3, 160.2, 155.7, 154.4, 139.5, 137.3, 136.2, 135.1, 128.9, 128.7, 127.4, 126.9, 126.5, 124.5, 120.2, 118.2, 60.7, 39.0, 37.8, 32.4, 24.8, 22.6, 14.2. [α]²⁹_D = -39.8 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel IB (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, $\lambda = 210$ nm, t_r (minor) = 5.5 min, t_r (major) = 6.0 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₅H₂₆NO, 356.2014; found 356.2003.

(S)-2-Benzyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3jj)



Yellow oil (15.0 mg, 40% yield, 86% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 7.98 – 7.90 (m, 2H), 7.76 – 7.69 (m, 2H), 7.69 – 7.65 (m, 1H), 7.63 – 7.58 (m, 1H), 7.54 – 7.50 (m, 1H), 7.47 – 7.35 (m, 4H), 7.33 – 7.27 (m, 1H), 7.18 – 7.04 (m, 5H), 4.37 (d, *J* = 17.3 Hz, 1H), 3.62 (d, *J* = 13.8 Hz, 1H), 3.50 (d, *J* = 13.8 Hz, 1H), 3.39 (d, *J* = 17.3 Hz, 1H). ¹³C NMR: (125 MHz, CDCl₃): 207.6, 159.9, 155.9, 154.2, 139.4, 137.5, 137.4, 136.1, 135.1, 130.3, 129.0, 128.7, 128.2, 127.3, 126.9, 126.6, 126.3, 124.4, 120.4, 118.4, 61.6, 43.9, 36.8. [α]²⁹_D = -19.2 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm

x 25 cm), Hexanes / IPA = 95/ 5, 1.0 mL/min, λ = 210 nm, t_r (major) = 9.2 min, t_r (minor) = 12.7 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₇H₂₂NO, 376.1701; found 376.1692.

(S)-2-(4-Methylbenzyl)-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3kj)



Light yellow oil (22.6 mg, 58% yield, 89% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 7.97 – 7.89 (m, 2H), 7.75 – 7.65 (m, 3H), 7.63 – 7.57 (m, 1H), 7.55 – 7.50 (m, 1H), 7.46 – 7.35 (m, 4H), 7.33 – 7.27 (m, 1H), 6.94 (d, *J* = 1.5 Hz, 4H), 4.37 (d, *J* = 17.3 Hz, 1H), 3.58 (d, *J* = 13.9 Hz, 1H), 3.45 (d, *J* = 13.9 Hz, 1H), 3.38 (d, *J* = 17.3 Hz, 1H), 2.22 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃): 207.7, 160.0, 155.9, 154.3, 139.5, 137.4, 136.1, 136.0, 135.1, 134.4, 130.2, 129.0, 128.9, 128.7, 127.3, 126.9, 126.4, 124.4, 120.4, 118.4, 61.7, 43.5, 36.7, 21.1. [α]²⁹_D = -18.8 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 210 nm, t_r (major) = 8.0 min, t_r (minor) = 8.9 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₈H₂₄NO, 390.1858; found 390.1848.

(S)-2-(3-Methylbut-2-en-1-yl)-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3lj)



Light yellow oil (24.0 mg, 68% yield, 94% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 8.00 – 7.94 (m, 2H), 7.76 (d, J = 7.7 Hz, 1H), 7.74 – 7.67 (m, 1H), 7.64 – 7.57 (m, 3H), 7.54 (d, J = 7.7 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.40 – 7.33 (m, 2H), 5.08 – 4.94 (m, 1H), 4.43 (d, J = 17.3 Hz, 1H), 3.28 (d, J = 17.3 Hz, 1H), 3.02 – 2.90 (m, 1H), 2.87 – 2.76 (m, 1H), 1.61 (d, J = 1.3 Hz, 3H), 1.60 (d, J = 1.5 Hz, 3H). ¹³C NMR: (125 MHz, CDCl₃): 208.0, 160.1, 155.7, 154.5, 139.5, 137.3, 136.1, 135.1, 135.1, 128.9, 128.7, 127.3, 126.9, 126.5, 124.5, 120.3, 119.5, 118.2, 60.7, 37.5, 37.0, 26.0, 18.2. [α]²⁹_D = -4.2 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel AS-H (0.46 cm x 25 cm), Hexanes / IPA = 98/ 2, 1.0 mL/min, $\lambda = 254$

nm, t_r (minor) = 6.5 min, t_r (major) = 8.1 min. HRMS (ESI) m/z: [M+H]⁺ calcd for C₂₅H₂₄NO, 354.1858; found 354.1848.

(S)-2-(3-Methylbut-2-en-1-yl)-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3mj)



Light yellow oil (34.6 mg, 65% yield, 93% *ee*). ¹H NMR (500 MHz, CDCl₃): δ 8.00 – 7.94 (m, 2H), 7.70 – 7.65 (m, 2H), 7.58 – 7.54 (m, 1H), 7.48 – 7.33 (m, 4H), 7.30 – 7.20 (m, 4H), 7.14 (s, 1H), 6.96 (s, 1H), 4.59 (d, *J* = 17.0 Hz, 1H), 3.98 (s, 3H), 3.87 (s, 3H), 3.48 – 3.41 (m, 2H), 3.18 (d, *J* = 17.0 Hz, 1H), 2.84 – 2.74 (m, 2H), 2.37 – 2.31 (m, 1H), 2.01 – 1.94 (m, 1H), 1.88 – 1.77 (m, 2H), 1.66 – 1.60 (m, 1H), 1.40 – 1.32 (m, 3H). ¹³C NMR: (125 MHz, CDCl₃): 206.3, 159.9, 155.9, 155.4, 149.5, 149.5, 139.5, 137.4, 137.2, 129.5, 128.9, 128.7, 128.2, 128.1, 127.2, 126.8, 120.6, 118.2, 107.3, 104.9, 63.1, 60.6, 56.3, 56.1, 53.5, 45.2, 37.7, 33.3, 32.9. [α]²⁹_D = -35.7 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel IA (0.46 cm x 25 cm), Hexanes / IPA = 80 / 20, 1.0 mL/min, λ = 254 nm, t_r (minor) = 9.7 min, t_r (major) =

(S)-2-methyl-2-(6-phenylpyridin-2-yl)-3,4-dihydronaphthalen-1(2H)-one (3nj)

19.1 min. HRMS (ESI) m/z: [M+H]⁺ calcd for C₃₅H₃₇N₂O₃, 533.2804; found 533.2796.



Colorless oil (27.5 mg, 88% yield, 97% *ee*). ¹H NMR (400 MHz, CDCl₃): δ 8.21 – 8.13 (m, 1H), 7.99 – 7.91 (m, 2H), 7.66 – 7.54 (m, 2H), 7.49 – 7.28 (m, 5H), 7.17 – 7.04 (m, 2H), 3.09 – 2.78 (m, 3H), 2.35 – 2.19 (m, 1H), 1.63 (s, 3H). ¹³C NMR: (100 MHz, CDCl₃): 201.2, 161.6, 156.0, 144.1, 139.2, 137.4, 133.1, 133.1, 129.0, 128.8, 128.7, 127.9, 126.8, 126.5, 119.8, 118.0, 53.2, 35.8, 26.5, 25.7. [α]²⁵_D = 0.64 (c 0.5, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel IC (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t_r (minor) = 8.6 min, t_r (major) = 14.7 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₂H₂₀NO, 314.1545; found 314.1540.

5. Gram-scale reaction and synthetic applications

Gram-scale reaction



A flame-dried sealed pressure-resistant tube (50 mL) equipped with a magnetic stir bar (10 mm × 5 mm, egg shaped) was evacuated and filled Ar for three times before being transferred into a glovebox. Ni(cod)₂ (0.3 mmol, 10 mol %), (*S*)-Ph-GarPhos (0.33 mmol, 11 mol%) and dry 1,4-dioxane (20 mL) was added to the tube and stirred for 10 min. NaO'Bu (4.5 mmol, 1.5 equiv), indanone derivatives (3.0 mmol, 1 equiv) and heteroaryl fluorides (4.5 mmol, 1.5 equiv) were added in succession. The reaction tube was capped and taken out of the glovebox. The reaction was stirred at 120°C for 48 h. After cooling the reaction mixture to ambient temperature, the mixture was concentrated and directly purified by purified by silica gel chromatography using PE/EA (silica gel, 10:1) to afford the desired product **3ap** with 83% yields (0.865g). The enantiomeric excess was determined by Daicel Chiralcel IB (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t_r (minor) = 8.1 min, t_r (major) = 10.0 min.



A flame-dried sealed pressure-resistant tube (50 mL) equipped with a magnetic stir bar (10 mm \times 5 mm, egg shaped) was evacuated and filled Ar for three times before being transferred into a glovebox. Ni(cod)₂ (0.075 mmol, 2.5 mol %), (*S*)-Ph-GarPhos (0.0825 mmol, 2.75 mol%) and anisole (7.5 mL) was added to the tube and stirred for 30 min. NaO'Bu (3.3 mmol, 1.1 equiv), indanone derivatives (3.75 mmol, .1.25 equiv) and heteroaryl fluorides (3.0 mmol, 1.0 equiv) were added in succession. The reaction tube was capped and

taken out of the glovebox. The reaction was stirred at 120°C for 96 h. After cooling the reaction mixture to ambient temperature, the mixture was concentrated and directly purified by purified by silica gel chromatography using PE/EA (silica gel, 10:1) to afford the desired product **3ap** with 68% yields (0.7120 g). The enantiomeric excess was determined by Daicel Chiralcel IB (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, $\lambda = 254$ nm, t_r (minor) = 8.1 min, t_r (major) = 10.0 min.

Synthetic applications

(2S)-2-Methyl-2-(6-(naphthalen-2-yl) pyridin-2-yl)-2,3-dihydro-1H-inden-1-ol (4)



The solution of **3ap** (69.8 mg, 0.2 mmol) in THF (0.5 mL) was added MeOH (0.5 mL) and NaBH₄ (0.4 mmol) at 0°C under air. The reaction mixture was then stirred at room temperature for 2 h and quenched with 5 ml water. The reaction mixture was extracted with EA (3 x 2 mL). The combined organic phases were dried over with anhydrous Na₂SO₄, filtered, evaporated in vacuo and purified by flash chromatography (silica gel, PE/EA) to afford product **4** as white solid (69.5 mg, 99% yield, dr: 1.2: 1, major: 99% ee, minor: 99% ee). ¹H NMR (400 MHz, CDCl₃): δ 8.41 – 8.31 (m, 1H), 8.14 – 7.99 (m, 1H), 7.97 – 7.79 (m, 3H), 7.78 – 7.64 (m, 2H), 7.61 – 7.44 (m, 3H), 7.34 – 7.18 (m, 4H), 5.68 – 5.26 (d, 1H), 3.45 (dd, *J* = 15.3, 14.8 Hz, 1H), 3.08 (dd, *J* = 15.3, 14.8 Hz, 1H), 1.40 (d, 3H). ¹³C NMR: (100 MHz, CDCl₃): 167.9, 166.6, 156.4, 155.4, 144.5, 143.4, 141.6, 139.3, 138.3, 137.8, 136.8, 136.2, 133.8, 133.7, 133.5, 133.5, 128.8, 128.8, 128.7, 128.6, 128.2, 127.8, 127.8, 127.5, 127.0, 126.9, 126.7, 126.5, 126.5, 126.4, 126.4, 125.1, 125.1, 125.0, 124.7, 124.5, 123.8, 120.8, 118.8, 118.6, 118.3, 83.6, 81.6, 55.2, 53.1, 44.0, 41.5, 27.4, 22.5. [α]²⁹_D = -74.4 (c 3.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel IA (0.46 cm x 25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t_r-major (minor) = 10.5 min, t_r-minor (major) = 14.9 min, t_r-major (major) = 10.5 min, t_r-minor (major) = 14.9 min, t_r-major (major) = 10.5 min, t_r-minor (major) = 14.9 min, t_r-major (major) = 10.5 min, t_r-minor (major) = 14.9 min, t_r-major (major) = 10.5 min, t_r-minor (major) = 14.9 min, t_r-major (major) = 10.5 min, t_r-minor (major) = 14.9 min, t_r-major (major) = 10.5 min, t_r-minor (major) = 14.9 min, t_r-major (major) = 10.5 min, t_r-minor (major) = 14.9 min, t_r-major (major) = 10.5 min, t_r-minor (major) = 14.9 min, t_r-major (major) = 10.5 min, t_r-minor (major) = 14.9 min, t_r-major (major) = 10.5 min, t_r-minor (major) = 14.9 min, t_r-major (major) = 10.5 m

19.4 min, t_r - minor (minor) = 20.5 min. HRMS (ESI) m/z: [M+H]⁺ calcd for C₂₅H₂₂NO, 352.1701; found 352.1692.



(2S)-2-Methyl-2-(6-(naphthalen-2-yl)pyridin-2-yl)-1-phenyl-2,3-dihydro-1H-inden-1-ol (5)

The solution of **3ap** (69.8 mg, 0.2 mmol) in THF (1.0 mL) was added 220 µl phenylmagnesium bromide solution (PhMgBr, 1 M in THF, 0.22 mmol) at -78 °C. Then the reaction mixture was stirred at room temperature for 2 h and quenched with 1ml Saturated ammonium chloride solution. The reaction mixture was extracted with EA (3 x 2 mL). The combined organic phases were dried over with anhydrous Na₂SO₄, filtered, evaporated in vacuo and purified by flash chromatography (silica gel, PE/EA) to afford product **5** as corlorless oil (84.5 mg, 99% yield, dr: 12: 1, major: 96% ee). ¹H NMR (500 MHz, CDCl₃): δ 8.30 (d, *J* = 1.7 Hz, 1H), 8.03 – 7.90 (m, 4H), 7.59 – 7.50 (m, 5H), 7.45 – 7.42 (m, 1H), 7.37 – 7.34 (m, 2H), 7.02 – 6.91 (m, 6H), 4.10 – 3.90 (m, 2H), 3.18 (d, *J* = 15.2 Hz, 1H), 1.78 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃): 164.4, 155.2, 147.3, 144.2, 142.0, 136.9, 136.8, 133.7, 133.5, 128.8, 128.4, 128.2, 127.8, 127.4, 127.2, 126.6, 126.4, 126.3, 126.2, 125.0, 124.6, 124.4, 119.2, 118.0, 115.4, 89.2, 59.4, 41.7, 25.6. [α]²⁹_D = 188.9 (c 4.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel IB (0.46 cm x 25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 210 nm, t_r-major (major) = 5.8 min, t_r-major (minor) = 6.5 min, HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₃₁H₂₆NO, 428.2014; found 428.2007.

(R)-2-(2-Methyl-1-methylene-2,3-dihydro-1H-inden-2-yl)-6-(naphthalen-2-yl)pyridine (6)



Methyltriphenylphosphoniumbromide (PPh₃CH₃Br, 142.8 mg, 0.4 mmol) was dissolved in extra dry THF (1.5 mL) at RT. Then Potassium tert-butoxide ('BuOK, 44.8 mg, 0.4 mmol) was added and the mixture was stirred at RT for 5 min. Next, **3ap** (69.8 mg, 0.2 mmol) was dissolved with 1.5 mL extra dry THF and added to the mixture at 0°C. The reaction was stirred overnight at room temperature. Then, the reaction was evaporated in vacuo and purified by flash chromatography (silica gel, PE/EA) to afford product **6** as corlorless oil (68.0 mg, 98% yield, 99% ee). ¹H NMR (500 MHz, CDCl₃): δ 8.50 (d, *J* = 1.8 Hz, 1H), 8.26 (d, *J* = 1.8 Hz, 1H), 7.99 – 7.82 (m, 3H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.69 – 7.60 (m, 2H), 7.59 – 7.47 (m, 2H), 7.41 – 7.27 (m, 4H), 5.66 (s, 1H), 5.01 (s, 1H), 3.84 (d, *J* = 16.6 Hz, 1H), 3.20 (d, *J* = 16.6 Hz, 1H), 1.85 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃): 166.8, 158.7, 155.5, 144.1, 140.6, 137.2, 137.0, 133.8, 133.7, 129.0, 128.8, 128.4, 127.8, 126.8, 126.4, 126.3, 126.2, 125.4, 124.9, 121.2, 119.2, 117.7, 104.7, 53.5, 47.5, 30.3. [α]²⁹_D = -34.1 (c 1.0, CHCl₃). The enantiomeric excess was determined by Daicel Chiralcel ODH (0.46 cm x 25 cm), Hexanes / IPA = 99 / 1, 1.0 mL/min, λ = 254 nm, t_r (minor) = 7.4 min, t_r (major) = 7.8 min. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₆H₂₂N, 348.1752; found 348.1748.

(S)-2-Methyl-2-(6-(naphthalen-2-yl) pyridin-2-yl)-2,3-dihydro-1H-inden-1-one oxime (7)



The mixture of **3ap** (69.8 mg, 0.2 mmol), hydroxylamine hydrochloride (0.4 mmol) and pyridine (1.0 mmol) in ethanol (10 ml) was refluxed overnight. Then, the reaction was cooled to room temperature, added 2ml H₂O and 150 µL 10% NaOH solution, vigorous stirred and filtered. The residue was washed with water three times and evaporated in vacuo without further purity to give product **7** as light green solid (63.3 mg, 87% yield, Z/E = 1.6: 1). ¹H NMR (500 MHz, CDCl₃): δ 9.99 – 9.25 (br, 1H), 8.63 – 8.33 (m, 2H), 8.14 (t, *J* = 8.5 Hz, 1H), 7.91 – 7.77 (m, 3H), 7.62 – 7.39 (m, 4H), 7.34 – 7.13 (m, 4H), 4.10 – 3.50 (m, 1H), 3.19 (d, *J* = 16.7 Hz, 1H), 2.02 – 1.77 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃): 166.0, 164.6, 164.2, 155.8, 155.6, 149.7, 146.8, 146.0, 137.2, 137.2, 136.9, 136.3, 136.2, 133.7, 133.6, 133.2, 131.2, 130.6, 129.8, 128.8, 128.3,

128.2, 127.7, 127.3, 127.0, 126.4, 126.2, 125.4, 125.3, 124. 9, 124.8, 123.9, 122.0, 119.3, 119.0, 118.1, 118.0, 58.4, 52.4, 48.9, 45.8, 26.6, 22.7. $[\alpha]^{29}_{D} = -178.9$ (c 3.0, CHCl₃). HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₅H₂₁N₂O, 365.1654; found 365.1644.

2-Methoxy-6-((2-methyl-1*H*-inden-3-yl)oxy)pyridine (8)



Light yellow oil (4.3 mg, 17% yield). ¹H NMR (500 MHz, CDCl₃): δ 7.49 (t, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 7.0 Hz, 1H), 7.21 – 7.11 (m, 2H), 7.05 – 6.96 (m, 1H), 6.42 (d, *J* = 7.9 Hz, 1H), 6.31 (d, *J* = 7.8 Hz, 1H), 3.81 (s, 3H), 3.37 (s, 2H), 2.03 (s, 3H). ¹³C NMR: (125 MHz, CDCl₃): 163.6, 161.7, 146.8, 141.4, 140.7, 140.4, 127.7, 126.1, 124.5, 123.8, 118.2, 104.0, 100.0, 53.6, 39.0, 12.3. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₆H₁₆NO₂, 254.1181; found 254.1173.

6. Control experiments

Table S5. Exploring the influence of base ^a

0 1a	F、 -Me ⁺	N OMe 2a	additive, solvent	Me N 3aa	MeC + ~OMe	
Entry	1a (mmol)	2a (mmol)	Solvent	additive	3aa	8
1	0.1	0.1	1,4-dioxane	none	ND	ND
2	0.1	0.1	1,4-dioxane	10 mol% Ni(cod) ₂	ND	ND
3	0.1	0.1	1,4-dioxane	1.0 e.q ^t BuONa	14% yield	17% yield
4	0.2	0.1	anisole	1.1 e.q ^t BuONa	trace	trace
5	0.2	0.1	1,4-dioxane	1.1 e.q ^t BuONa	13% yield	14% yield
6	0.1	0.15	1,4-dioxane	1.5 e.q ^t BuONa	15% yield	19% yield

^a Reaction conditions: **1a**, **2a** and additive in 1.0 mL solvent, 120 °C, 24 h. Yield determined by ¹H NMR using dibromomethane internal standard.

Table S6. Exploring the transformation of O-arylation product^a



^a Reaction conditions: 0.1 mmol **8** with Ni(cod)₂ (10 mol %), L7 (11 mol %) and different additives in 1.0 mL 1,4dioxane, 120 °C, 24 h. Yield determined by ¹H NMR using dibromomethane internal standard.

Table S7. Study on existence of possible intermediates via ³¹P NMR and HRMS



For study on oxidative addition process was employed 32 mg (S)-Ph-GarPhos (0.05 mmol) in 0.5 ml Toluene-D₈. ³¹P NMR (202 MHz, Toluene-D₈) δ -12.19. Ni(cod)₂ (0.05 mmol) and 32 mg (S)-Ph-GarPhos (0.05
mmol) was stir at rt under glove box for 30 min, then transferred into the NMR tube under N₂ atmosphere. ³¹P NMR (202 MHz, Toluene-D₈) δ 33.32, -12.17. Ni(cod)₂ (0.05 mmol), 32 mg (S)-Ph-GarPhos (0.05 mmol) and 2-Fluoropyridine (0.5 mmol) was stir at rt in glove box for 12 h, then transferred into the NMR tube under N₂ atmosphere. ³¹P NMR (202 MHz, Toluene-D₈) δ 29.84, 26.43, -12.27, -13.59. After stir for 12h at RT, the mixture was transferred into a sealing tube and heated to 120 °C for 4h under N₂, then cool to rt and transferred into the NMR tube under N₂ atmosphere. ³¹P NMR (202 MHz, Toluene-D₈) δ 29.74, 27.67, 25.61, 15.39, -12.38, -13.67. After stir for 4 h at 120 °C, The mixture was detected by HRMS (ESI) *m/z*: [M-F]⁺ calcd for C₄₅H₄₀NNiO₄P₂, 778.1781; found 778.1679.

7. X-Ray crystallographic analysis

A. Crystal Data

Identification code	cxy1738_0m
Empirical formula	C25H19NO
Formula weight	349.41
Temperature/K	100
Crystal system	monoclinic
Space group	P21
a/Å	8.5649(3)
b/Å	10.4376(3)
c/Å	9.9968(3)
α /°	90
β /°	98.4180(10)
γ/°	90
Volume/Å3	884.06(5)
Z	2
ρ calcg/cm3	1.313
μ/ mm-1	0.619
F(000)	368.0
Crystal size/mm3	0.31 imes 0.25 imes 0.23
Radiation	CuK α ($\lambda = 1.54178$)
2Θ range for data collection/°	8.942 to 136.952
Index ranges	$-10 \leqslant h \leqslant 10, -12 \leqslant k \leqslant 11, -12 \leqslant l \leqslant 11$
Reflections collected	15418
Independent reflections	3227 [Rint = 0.0264, Rsigma = 0.0203]
Data/restraints/parameters	3227/1/246
Goodness-of-fit on F2	1.071
Final R indexes [I>= 2σ (I)]	R1 = 0.0251, wR2 = 0.0642
Final R indexes [all data]	R1 = 0.0253, wR2 = 0.0644
Largest diff. peak/hole / e Å-3	0.18/-0.14
Flack parameter	0.02(6)



Figure S1. X-Ray crystal structure of **3ap (CCDC 2156742)**

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9. BDE (Bond dissociation energy) of C_{Ar}-F bond

Density-functional theory (DFT) calculations were performed with Gaussian 16.¹ Geometry optimizations were performed with the ω B97X-D/6-31G(d) in gas phase.² Frequency calculations were performed at the same level of theory as for geometry optimization to characterize the stationary points as minima (no imaginary frequencies). Single-point energies were calculated with ω B97X-D/6-311++G(d,p) in gas phase. BDE (Bond dissociation energy) was calculated by the reaction enthalpy in gas phase.

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Energies	(performed w	th ωB97X-D/6-311++G(d,p)//ωB97X-D/6-31G(d))
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Structure	E_SPC	E	H_SPC
fluorobenzene	-331.46322	-331.373662	-331.363466
benzene radical	-231.529948	-231.474904	-231.436026
2-chloropyridine	-707.865944	-707.779052	-707.779313
pyridine radical	-247.573846	-247.514532	-247.491675
2-fluoropyridine	-347.506102	-347.412529	-347.418218
2-fluoro-6-methoxypyridine	-462.039964	-461.91437	-461.916263
2-methoxypyridine radical	-362.106992	-362.015722	-361.988973
Cl radical	-460.145539	-460.11662	-460.143179
F radical	-99.731408	-99.690741	-99.729048

BDE calculated (KJ/mol)

Structure	BDE (from ibond database) ³	BDE (calculated)
F	526	521
	379	379
F	/	519
F N OMe (2a)	/	521

Cartesian coordinates

fluorobenzene

С	-0.260367	-1.214064	-0.000008
С	1.131537	-1.205052	-0.000028
С	1.830186	0.000005	0.000025
С	1.131534	1.205052	-0.000006
С	-0.260378	1.214059	-0.000021
С	-0.930313	0.000003	0.000005
Н	-0.826024	-2.138642	-0.000027
Н	1.670605	-2.146996	0.000027
Н	2.914968	0.000015	0.000056
Н	1.670599	2.146996	0.000031
Н	-0.826038	2.138619	-0.000063
F	-2.273034	-0.000001	0.000019

benzene radical

С	1.223537	-0.769082	0.000000
С	1.210787	0.630599	0.000000
С	-0.000001	1.321228	0.000000
С	-1.210789	0.630595	0.000000
С	-1.223537	-0.769083	0.000000
С	0.000004	-1.397615	-0.000000
Н	2.159053	-1.320589	-0.000000
Η	2.150070	1.177156	-0.000003
Н	-0.000002	2.407026	-0.000002
Н	-2.150072	1.177152	-0.000000
Н	-2.159052	-1.320595	-0.000003

2-chloropyridine

С	-1.583051	1.176125	-0.000001
С	-2.231554	-0.056331	-0.000006
С	-1.453605	-1.206879	0.000001
С	0.470659	-0.015028	0.000002
С	-0.195582	1.209585	0.000005
Н	-2.149579	2.102263	-0.000003
Н	-3.313773	-0.125195	0.000003
Н	-1.914451	-2.191377	0.000005
Н	0.357334	2.141266	0.000008
N	-0.116527	-1.193873	0.000002
Cl	2.223233	-0.012628	-0.000002

pyridine radical

 $C \quad 1.032850 \quad 0.851310 \quad \text{-}0.000002$

С	-0.301382	1.269778	0.000004
С	-1.304501	0.311432	-0.000002
С	0.221676	-1.354515	0.000005
С	1.325499	-0.509216	-0.000002
Н	1.836041	1.583448	-0.000003
Н	-0.555379	2.324340	0.000004
Н	-2.356131	0.584942	-0.000005
Н	2.343451	-0.881550	-0.000000
Ν	-1.016119	-1.003416	-0.000002

2-fluoropyridine

С	-1.141376	1.182586	-0.000001
С	-1.798732	-0.047806	-0.000005
С	-1.027822	-1.202166	0.000001
С	0.894494	-0.023590	0.000002
С	0.244796	1.208093	0.000004
Η	-1.703492	2.111423	-0.000003
Н	-2.881193	-0.109572	0.000008
Η	-1.496184	-2.183284	0.000005
Н	0.814765	2.129461	0.000008
Ν	0.310915	-1.197862	0.000001
F	2.229060	-0.029522	-0.000003

2-fluoro-6-methoxypyridine

-1.287636	1.669148	-0.000076
0.095883	1.672891	0.000025
0.744061	0.430079	0.000098
-1.215168	-0.687697	0.000017
-1.986197	0.460697	-0.000089
-1.832653	2.608021	-0.000129
0.678855	2.585357	0.000089
-3.067022	0.404458	-0.000164
0.101985	-0.732928	0.000093
-1.827553	-1.873197	0.000032
2.084004	0.436192	0.000130
2.738044	-0.826545	-0.000158
3.804027	-0.598026	-0.000239
2.472529	-1.405900	0.888619
2.472388	-1.405622	-0.889061
	-1.287636 0.095883 0.744061 -1.215168 -1.986197 -1.832653 0.678855 -3.067022 0.101985 -1.827553 2.084004 2.738044 3.804027 2.472529 2.472529 2.472388	-1.2876361.6691480.0958831.6728910.7440610.430079-1.215168-0.687697-1.9861970.460697-1.8326532.6080210.6788552.585357-3.0670220.4044580.101985-0.732928-1.827553-1.8731972.0840040.4361922.738044-0.8265453.804027-0.5980262.472529-1.4059002.472388-1.405622

2-methoxypyridine radical

С	-1.922731	0.822870	-0.000103
С	-0.602683	1.247238	0.000001

С	0.404287	0.273246	0.000064
С	-1.128684	-1.379021	0.000024
С	-2.228206	-0.544798	-0.000079
Η	-2.723337	1.557962	-0.000238
Η	-0.331532	2.296043	-0.000120
Η	-3.246699	-0.912660	-0.000134
Ν	0.119526	-1.031727	0.000226
0	1.679160	0.681756	0.000300
С	2.679139	-0.329053	-0.000283
Η	3.629643	0.204752	-0.000117
Η	2.597789	-0.960894	0.888887
Η	2.597456	-0.960059	-0.890005

Cl radical

Cl 0.000000	0.000000	0.000000	
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F radical

F 0.000000 0.000000 0.000000

10. NMR spectrum



(S)-2-(6-Methoxypyridin-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (3aa)



(S)-2-(6-(Benzyloxy)pyridin-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (3ab)



t-butyl (R)-2-(((6-((S)-2-Methyl-1-oxo-2,3-dihydro-1H-inden-2-yl) pyridin-2-yl)oxy)methyl)

morholine-4-carboxylate (3ac)



(S)-2-Methyl-2-(6-phenoxypyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3ad)



(S)-2-(6-(4-Fluorophenoxy)pyridin-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (3ae)



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(S)-2-(6-([1,1'-Biphenyl]-4-yloxy)pyridin-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (3af)



(S)-2-(6-(4-Aminophenoxy)pyridin-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (3ag)





(S)-2-(6-(Diphenylphosphaneyl)pyridin-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (3ah)





(S)-2-Methyl-2-(6-methylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3ai)



(S)-2-Methyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3aj)



(S)-2-Methyl-2-(6-(p-tolyl)pyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3ak)



(S)-2-(6-(4-Methoxyphenyl)pyridin-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (3al)



(S)-2-Methyl-2-(6-(4-(trifluoromethoxy)phenyl)pyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3am)





(S)-2-Methyl-2-(6-(4-(trifluoromethyl)phenyl)pyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3an)





(S)-4-(6-(2-Methyl-1-oxo-2,3-dihydro-1*H*-inden-2-yl)pyridin-2-yl)benzonitrile (3ao)



(S)-2-Methyl-2-(6-(naphthalen-2-yl)pyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3ap)



(S)-2-Methyl-2-(6-(thiophen-2-yl)pyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3aq)



(S)-2-Methyl-2-(pyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3ar)



(S)-2-(4-Fluoropyridin-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (3as)







(S)-2-(5-fluoropyridin-2-yl)-2-methyl-2,3-dihydro-1H-inden-1-one (3at)





Methyl (S)-6-(2-methyl-1-oxo-2,3-dihydro-1H-inden-2-yl)nicotinate (3au)



(S)-6-(2-methyl-1-oxo-2,3-dihydro-1H-inden-2-yl)nicotinonitrile (3av)



(S)-2-(5-fluoropyridin-2-yl)-2-methyl-2,3-dihydro-1H-inden-1-one (3aw)



(S)- 2-(5-methoxypyridin-2-yl)-2-methyl-2,3-dihydro-1H-inden-1-one (3ax)



(S)-2-methyl-2-(5-phenylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3ay)


(S)-2-(4-Fluoropyridin-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (3az)



(S)-5-Fluoro-2-methyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3bj)



<3.17 <3.14 -1.7425000 -20000 0 Me -15000 MeO -10000 -5000 5.0 4.5 4.0 f1 (ppm) 1.00H 3.00-= 2.08 1.03 1.03 2.04 1.00 0.99 1.01 1.01 6.5 6.0 5.5 3.5 3.0 9.5 9.0 8.5 8.0 7.0 2.5 2.0 1.5 1.0 0.0 -0.5 -1.0 7.5 0.5

(S)-5-Methoxy-2-methyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3cj)





(S)-2,5-Dimethyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3dj)





(S)-6-Fluoro-2-methyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3ej)





(S)-6-Methoxy-2-methyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3fj)



(S)-5,6-Dimethoxy-2-methyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3gj)



(S)-2-Ethyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3hj)



(S)-2-Pentyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3ij)



(S)-2-Benzyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3jj)



(S)-2-(4-Methylbenzyl)-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3kj)



(S)-2-(3-Methylbut-2-en-1-yl)-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3lj)



(S)-2-(3-Methylbut-2-en-1-yl)-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3mj)



(S)-2-methyl-2-(6-phenylpyridin-2-yl)-3,4-dihydronaphthalen-1(2H)-one (3nj)

80 70 60

90

30

40

20

10

0 -10

50

160 150 140 130 120 110 100 f1 (ppm)

210

200 190

180 170

-50



(2S)-2-Methyl-2-(6-(naphthalen-2-yl)pyridin-2-yl)-2,3-dihydro-1H-inden-1-ol (4)



(2S)-2-Methyl-2-(6-(naphthalen-2-yl)pyridin-2-yl)-1-phenyl-2,3-dihydro-1*H*-inden-1-ol (5)



(R)-2-(2-Methyl-1-methylene-2,3-dihydro-1H-inden-2-yl)-6-(naphthalen-2-yl)pyridine (6)



(S)-2-Methyl-2-(6-(naphthalen-2-yl)pyridin-2-yl)-2,3-dihydro-1H-inden-1-one oxime (7)



2-Methoxy-6-((2-methyl-1*H*-inden-3-yl)oxy)pyridine (8)

11. HPLC spectrum

(S)-2-(6-Methoxypyridin-2-yl)-2-methyl-2,3-dihydro-1H-inden-1-one (3aa)



(S)-2-(6-(Benzyloxy)pyridin-2-yl)-2-methyl-2,3-dihydro-1H-inden-1-one (3ab)



E	Name	Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		10.050	167714	14.54	14052	BB			Unknown	
2		12.448	985787	85.46	206306	BV		1	Unknown	

t-butyl (R)-2-(((6-((S)-2-Methyl-1-oxo-2,3-dihydro-1H-inden-2-yl)pyridin-2-yl)oxy)methyl)

morpholine-4-carboxylate (3ac)

Boc Ο Me



Peak RetTime Type Width Height Area Area # [min] 00 [min] [mAU*s] [mAU] 14.556 BB 0.4435 3685.80127 127.42435 50.6690 1 2 16.800 BB 0.5106 3588.46924 108.29905 49.3310 7274.27051 235.72340 Totals : DAD1 B, Sig=254,4 Ref=off (D:\ChemStation\data\gxd\gxd-A\gxd-A136-7-chiral-IC2021-05-2612-01-35.D) mAU -160 140 -120 100 80 60 14.083 40 20 0 14 15 16 17 13 18 19 Signal 2: DAD1 B, Sig=254,4 Ref=off Peak RetTime Type Width Height Area Area 00 # [min] [min] [mAU*s] [mAU] 14.083 BB 0.4232 254.85649 9.31612 4.2366 1

0.4918 5760.76367

Totals :

2

16.203 BB

6015.62016 190.10500

180.78888

95.7634

(S)-2-Methyl-2-(6-phenoxypyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3ad)

O Ме _{COPh}



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	010
1	6.316	FM	0.2353	4151.55420	294.12201	50.5260
2	7.341	MM	0.2639	4065.11816	256.75818	49.4740

Totals :

8216.67236 550.88019



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	olo
1	6.337	BV	0.1849	105.94891	8.77116	1.1391
2	7.380	MF	0.2648	9194.77344	578.81982	98.8609
Total	s:			9300.72235	587.59099	

(S)-2-(6-(4-Fluorophenoxy)pyridin-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (3ae)





RetTime	Туре	Width	Area	Height	Area
[min]		[min]	[mAU*s]	[mAU]	00
6.677	BV	0.2984	5462.82178	274.22858	49.6989
8.125	VB	0.2744	5529.01318	300.85895	50.3011
	RetTime [min] 6.677 8.125	RetTime Type [min] 6.677 BV 8.125 VB	RetTime Type Width [min] [min] 6.677 BV 0.2984 8.125 VB 0.2744	RetTime TypeWidthArea[min][min][mAU*s] 6.677 BV0.29846.677 BV0.29845462.821788.125 VB0.27445529.01318	RetTime Type Width Area Height [min] [min] [mAU*s] [mAU] 6.677 BV 0.2984 5462.82178 274.22858 8.125 VB 0.2744 5529.01318 300.85895



1.09918e4 575.08752



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak Re	etTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	00
			-		·	
1	6.399	BB	0.2354	31.49223	1.96058	3.1636
2	7.659	BB	0.2426	963.95435	59.62250	96.8364
Totals	:			995.44658	61.58308	

(S)-2-(6-([1,1'-Biphenyl]-4-yloxy)pyridin-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (3af)





Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	00
1	7.582	BV	0.3095	1.51630e4	726.57629	49.0767
2	9.355	VB	0.3483	1.57335e4	674.10547	50.9233

Totals :

3.08965e4 1400.68176



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	010
		-				
1	7.796	BB	0.3290	141.28993	6.36536	1.0518
2	9.661	MF	0.4051	1.32917e4	546.84534	98.9482
Total	s:			1.34330e4	553.21070	

(S)-2-(6-(4-Aminophenoxy)pyridin-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (3ag)





(S)-2-(6-(Diphenylphosphaneyl)pyridin-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (3ah)



Peak RetTime Type Width Height Area Area 00 # [min] [min] [mAU*s] [mAU] 9.509 BB 0.2261 2765.91748 187.55046 49.2840 1 0.3416 2846.28003 2 12.930 MF 138.86888 50.7160

Totals :

5612.19751 326.41934



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

Peak RetTime Type Width Area Height Area # [min] [min] [mAU*s] [mAU] 00 9.435 BB 0.2616 249.65086 14.30693 5.1451 1 12.336 BB 0.3223 4602.56738 221.61607 2 94.8549 Totals : 4852.21825 235.92301

(S)-2-Methyl-2-(6-methylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3ai)



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	00
1	4.915	BB	0.1488	3071.43213	306.85233	50.2167
2	5.782	BB	0.1774	3044.92480	258.53867	49.7833



6116.35693 565.39099



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	00
1	4.862	BB	0.1497	263.85211	26.60425	8.6070
2	5.657	BB	0.1735	2801.69580	244.92673	91.3930
Total	s:			3065.54791	271.53097	

(S)-2-Methyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3aj)





Peak RetTime Type Width Height Area Area [min] # [min] [mAU*s] [mAU] 00 6.579 MF 0.1419 1006.28082 118.17661 50.0037 1 2 7.394 MM 0.1589 1006.13074 105.52702 49.9963



2012.41156 223.70362



Signal 2: DAD1 B, Sig=254,4 Ref=off

Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	00
		-				
1	6.663	BB	0.1280	26.46866	3.14948	1.1149
2	7.487	BB	0.1456	2347.71362	245.46957	98.8851
Total	s:			2374.18228	248.61906	

(S)-2-Methyl-2-(6-(p-tolyl)pyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3ak)





Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	010
1	6.220	BV	0.1135	400.89880	53.46898	49.2298
2	6.738	MF	0.1364	413.44223	50.51876	50.7702



814.34103 103.98774



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	00
1	6.180	BB	0.1218	22.52283	2.80266	1.6324
2	6.709	BB	0.1309	1357.23352	156.88248	98.3676
Total	s:			1379.75635	159.68514	

(S)-2-(6-(4-Methoxyphenyl) pyridin-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (3al)





Signal 2: DAD1 B, Sig=254,4 Ref=off

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

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	00
1	8.877	BB	0.1745	1642.98352	142.49730	49.8866
2	10.563	BB	0.2091	1650.45435	119.52814	50.1134



3293.43787 262.02544



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

Peak RetTime Type		Width Area		Height	Area
#	[min]	[min]	[mAU*s]	[mAU]	010
1	8.824 BB	0.1965	53.68452	4.05393	1.7951
2	10.419 BB	0.2151	2936.87476	207.49667	98.2049
Total	s:		2990.55928	211.55060	

(S)-2-Methyl-2-(6-(4-(trifluoromethoxy)phenyl)pyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3am)







(S)-2-Methyl-2-(6-(4-(trifluoromethyl)phenyl)pyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3an)





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Signal 2: DAD1 B, Sig=254,4 Ref=off
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]	[min]		[mAU*s]	[mAU]	00
1	12.262	BV	0.1968	6763.39551	530.22046	49.8155
2	12.726	VB	0.2061	6813.49268	509.13394	50.1845
Total	s:			1.35769e4	1039.35440	



Peak	ak RetTime Type		Width	Area	Height	Area
#	[min]	[min]		[mAU*s]	[mAU]	olo
						I
1	12.265	BV E	0.1719	29.12238	2.57535	0.7564
2	12.715	VB R	0.2158	3820.89111	272.20615	99.2436
Total	ls :			3850.01349	274.78150	

(S)-4-(6-(2-Methyl-1-oxo-2,3-dihydro-1*H*-inden-2-yl)pyridin-2-yl)benzonitrile (3ao)





E	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µ∨)	Int Type	Amount	Units	Peak Type	Peak Codes
1		8.035	2527834	49.79	166201	BV			Unknown	
2		10.725	2549189	50.21	119534	VB			Unknown	



e	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		8.040	170798	4.37	11495	VB			Unknown	
2		10.703	3733175	95.63	177367	BB			Unknown	

(S)-2-Methyl-2-(6-(naphthalen-2-yl)pyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3ap)



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

Peak RetTime Type Width Height Area Area 00 # [min] [min] [mAU*s] [mAU] ----|-----|-----|-----| 8.096 BB 0.1615 2331.03271 220.28400 1 49.4676 2 10.087 BB 0.2094 2381.20703 170.02510 50.5324

Totals :

4712.23975 390.30910



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

Peak	eak RetTime Type		Area	Height	Area
#	[min]	[min]	[mAU*s]	[mAU]	00
	-			-	
1	8.123 B	BB 0.165	90.89558	8.29588	1.1410
2	10.016 B	BB 0.219	4 7875.12012	2 535.91010	98.8590
Total	s:		7966.01570	544.20597	

(S)-2-Methyl-2-(6-(thiophen-2-yl)pyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3aq)




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

Peak	RetTime T	ype Wid	th Are	ea Hei	lght Area	
#	[min]	[mi:	n] [mAU*	[m7]	4U] %	
	-					-
1	7.265 B	B 0.1	409 15.9)1391 1.	.73604 6.433	6
2	9.633 B	B 0.1	823 231.4	4313 19.	,52280 93.566	4
Total	s:		247.3	35704 21.	.25884	

(S)-2-Methyl-2-(pyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3ar)



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	00
1	6.744	BB	0.2151	3123.30957	218.08815	49.7657
2	8.071	BBA	0.2435	3152.71924	194.11169	50.2343
Total	s:			6276.02881	412.19984	



Peak F	RetTime T	ype	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	olo
-	-					
1	6.383 B	BV	0.1974	1766.98157	134.42104	8.0165
2	7.502 V	'B	0.2375	2.02747e4	1275.17188	91.9835
Totals	5 :			2.20417e4	1409.59291	

(S)-2-(4-Fluoropyridin-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (3as)



6.60 6.70 6.80 6.90

7.00 7.10 7.20 7.30 7.40 7.50 7.60 7.70 7.80 7.50 8.00 8.10 8.20 8.30 8.40

5.10 5.20 5.30 5.40 5.50 5.40 5.70 5.80 5.90 6.00 6.10 6.20 6.30 6.40 6.50

E	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		6.128	604285	5.19	51561	BB			Unknown	1 () () () () () () () () () (
2		7.463	11047472	94.81	749678	BB			Unknown	

(S)-2-(5-fluoropyridin-2-yl)-2-methyl-2,3-dihydro-1H-inden-1-one (3at)





13	Name	Retention Time (min)	Area (µV*sec)	<mark>% Are</mark> a	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		5.640	17597486	49.95	1536086	bV			Unknown	
2		6.439	17636041	50.05	1379708	Vb			Unknown	



E	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		5.689	37420715	97.56	2825802	vv			Unknown	
2		6.527	935240	2.44	71806	Vb			Unknown	

Methyl (S)-6-(2-methyl-1-oxo-2,3-dihydro-1H-inden-2-yl)nicotinate (3au)

Q Me СООМе



(S)-6-(2-methyl-1-oxo-2,3-dihydro-1H-inden-2-yl)nicotinonitrile (3av)





Ē	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		10.423	3101456	50.39	135766	VB			Unknown	
2		15.034	3053991	49.61	88858	BB			Unknown	



E	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		10.665	9590536	68.36	405355	BB			Unknown	
2		15.425	4438476	31.64	123608	BB			Unknown	

(S) 2-methyl-2-(5-methylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3aw)





13	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		5.758	9547475	50.01	763217	BV			Unknown	
2		6.674	9543423	49.99	660852	VB			Unknown	



(S)- 2-(5-methoxypyridin-2-yl)-2-methyl-2,3-dihydro-1H-inden-1-one (3ax)

1	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	<mark>Uni</mark> ts	Peak Type	Peak Codes
1		8.716	999160	50.39	52282	BB	2		Unknown	
2		11.057	983760	49.61	42080	BB			Unknown	



E	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		8.692	4602836	94.15	252957	BB			Unknown	
2		<mark>11.037</mark>	286250	5.85	14095	Bb			Unknown	

(S)-2-methyl-2-(5-phenylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3ay)

0 Me Ph



E	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		7.614	47228781	49.71	2705078	vv			Unknown	
2		9.561	47781406	50.29	2149407	VB			Unknown	



E	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		7.616	30396682	94.98	1808292	BV			Unknown	
2	· · · ·	9.594	1608069	5.02	75849	VB			Unknown	

(S)-2-Methyl-2-(pyrazin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3az)





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

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	00
1	7.805	BV	0.1654	4119.54395	371.37781	49.7867
2	8.653	VB	0.1771	4154.84131	348.49011	50.2133

8274.38525 719.86792



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

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	00
1	7.870	BB	0.1720	785.12885	68.38147	89.1686
2	8.747	BB	0.1839	95.37012	7.84107	10.8314
Total	s:			880.49896	76.22254	



(S)-5-Fluoro-2-methyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3bj)

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	00
1	7.584	VB R	0.1576	3993.69653	381.55051	50.1625
2	8.748	BBA	0.1985	3967.81982	299.54883	49.8375



7961.51636 681.09933



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	00
		-				
1	8.157	BB	0.1794	26.43185	2.24362	1.7122
2	9.210	BB	0.1967	1517.28845	115.89758	98.2878
Total	s:			1543.72030	118.14120	

(S)-5-Methoxy-2-methyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3cj)



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	00
1	7.695	BV	0.1497	2966.65015	299.22369	48.1542
2	8.370	VB	0.1638	3194.08325	291.59235	51.8458



6160.73340 590.81604



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak R	etTime Type	Width	Area	Height	Area
#	[min]	[min]	[mAU*s]	[mAU]	00
-					
1	7.610 MM	0.1938	5.72441	4.92230e-1	2.1961
2	8.271 BB	0.1689	254.93965	22.71818	97.8039
Totals	:		260.66407	23.21041	







Peak R	etTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	00
-						
1	6.480	BV E	0.2079	308.00690	23.04514	1.3176
2	7.012	VB R	0.2572	2.30680e4	1469.01599	98.6824
Totals	:			2.33760e4	1492.06113	

(S)-6-Fluoro-2-methyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3ej)



119

Peak RetTime Type Width Height Area Area 00 # [min] [min] [mAU*s] [mAU] 6.462 BV 0.1185 739.16156 95.31671 1 49.4419 755.84796 6.795 VB 2 0.1276 90.36465 50.5581

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Totals :
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1495.00952 185.68136



Signal 2: DAD1 B, Sig=254,4 Ref=off

Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	00
1	6.590	BV E	0.1333	11.57730	1.33330	3.0295
2	6.947	VB R	0.1371	370.57101	41.12797	96.9705
Total	s:			382.14832	42.46127	

(S)-6-Methoxy-2-methyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3fj)



120

Peak RetTime Type Width Height Area Area 00 # [min] [min] [mAU*s] [mAU] ----!-----!----!-----!-----!-----! 6.821 BB 0.2187 1151.40369 78.69646 49.7414 1 2 8.171 BBA 0.2783 1163.37805 62.74682 50.2586



2314.78174 141.44328



Signal 2: DAD1 B, Sig=254,4 Ref=off

Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak R	etTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	00
-		-				
1	6.793	BB	0.2238	578.56732	38.39893	1.2694
2	8.093	BBA	0.3292	4.49993e4	2041.42151	98.7306
Totals	:			4.55778e4	2079.82043	

(S)-5,6-Dimethoxy-2-methyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1H-inden-1-one (3gj)



Peak RetTime Type Width Height Area Area # 00 [min] [min] [mAU*s] [mAU] 1 10.254 BV 0.4136 3818.44409 136.83629 49.2807 11.465 VB 0.5292 3929.90967 2 110.41638 50.7193 Totals : 7748.35376 247.25267 DAD1 B, Sig=254,4 Ref=off (D:\ChemStation\data\gxd\gxd-A\gxd-A\gxd-A169-5-chiral-AS-H2021-06-1513-44-04.D) mAU 250 200 150 100 10.249 50 0 10 12 13 14 11 mir

Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	00
1	10.249	BV E	0.4030	206.90015	7.61542	2.1337
2	11.385	VB R	0.5129	9490.00586	276.14899	97.8663
Total	ls :			9696.90601	283.76441	

Totals :



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak RetTime Type Width Height Area Area 00 # [min] [min] [mAU*s] [mAU] ----|-----|-----|-----| 5.531 VB 0.1004 2043.91663 312.20636 49.6049 1 2 6.209 BB 0.1123 2076.47192 280.77417 50.3951



4120.38855 592.98053



Signal 2: DAD1 B, Sig=254,4 Ref=off

Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak H	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	00
-		-				
1	5.438	BB	0.1110	8.62617	1.15735	2.1237
2	6.099	BB	0.1203	397.56201	50.24480	97.8763
Totals	5 :			406.18819	51.40214	

(S)-2-Pentyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3ij)





(S)-2-Benzyl-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3jj)



E	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		9.194	24719124	49.61	1502577	BV			Unknown	
2		12.627	25106996	50.39	1065585	VB			Unknown	



E	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		9.230	27958613	93.08	1689639	BB			Unknown	
2		12.735	2078262	6.92	90609	BB			Unknown	

(S)-2-(4-Methylbenzyl)-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3kj)





E	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		8.031	20506961	94.37	1382537	BV			Unknown	
2		8.868	1222570	5.63	67203	VB			Unknown	

7.00 7.50 8.00 8.50 9.00 9.50 10.00 10.50 11.00

13.00 13.50 14.00 14.50

11.50 12.00 12.50

(S)-2-(3-Methylbut-2-en-1-yl)-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3lj)



1.00

1.50 2.00

0.50

2.50

3.00 3.50 4.00 4.50 5.00 5.50 6.00 6.50



E	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		6.534	10201643	50.65	625024	bv			Unknown	
2		8.169	9939222	49.35	444309	vv			Unknown	
1.20- 1.10- 1.00- 0.50- 0.70- 0.50- 0.40- 0.30- 0.20-							(11)8			
0.10	Δ			Δ		•				Δ
6.00	6.10 6.20	6.30 6.40 6.50 6.60 6	70 6.80 6.90 7.00	7.10 7.20 7.30	7.40 7.50 7.60	7.70 7.80 7.90 Minutes	ado alio alio	8.30 8.40 8.	50 8.80 8.70 8.80 8.90 9	00 9.10 9.20 9.30 9.40

E	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		6.516	874052	3.02	47924	bB			Unknown	
2		8.111	28102742	96.98	1193638	Vb			Unknown	

(S)-2-(3-Methylbut-2-en-1-yl)-2-(6-phenylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (3mj)





Peak RetTime Type Width Area Height Area # 00 [min] [min] [mAU*s] [mAU] 9.563 BB 0.5967 1.45413e4 347.10962 50.0761 1 2 19.010 BB 0.8443 1.44971e4 255.37648 49.9239



2.90383e4 602.48610



Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak	RetTime Type	Width	Area	Height	Area
#	[min]	[min]	[mAU*s]	[mAU]	00
1	9.725 BB	0.7460	277.43982	4.99529	3.3527
2	19.115 BB	0.8877	7997.72998	133.35741	96.6473
Total	ls :		8275.16980	138.35270	

(S)-2-methyl-2-(6-phenylpyridin-2-yl)-3,4-dihydronaphthalen-1(2H)-one (3nj)



E	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		8.598	18988496	49.95	1267747	VB			Unknown	
2		14.184	19026794	50.05	562907	BB			Unknown	



E	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		8.635	16948574	98.46	1105794	BV		22 	Unknown	2 () () ()
2	· · · · ·	14.675	265572	1.54	7718	BB			Unknown	

(2S)-2-Methyl-2-(6-(naphthalen-2-yl)pyridin-2-yl)-2,3-dihydro-1*H*-inden-1-ol (4)



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

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	olo
		-				
1	10.637	BB	0.2843	1.58784e4	833.23743	26.5509
2	15.045	BB	0.4036	1.39944e4	520.69348	23.4006
3	19.596	BV	0.5234	1.55026e4	450.58401	25.9225
4	20.711	VB	0.5533	1.44283e4	388.51685	24.1260
Total	s:			5.98037e4	2193.03177	



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

Peak RetT:	ime Type	Width	Area	Height	Area
# [mi]	n]	[min]	[mAU*s]	[mAU]	00
1 10.	532 BB	0.2751	47.65583	2.58524	0.2454
2 14.	907 BB	0.3984	8859.19629	335.13831	45.6234
3 19.3	397 MF	0.5765	1.04601e4	302.42783	53.8680
4 20.5	528 FM	0.2973	51.09517	2.86405	0.2631
Totals :			1.94181e4	643.01542	







E	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		5.799	10755429	49.24	1401545	bV			Unknown	
2		6.463	11085257	50.76	1258041	Vb			Unknown	



129

E	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		5.847	9205800	97.98	1202844	vv			Unknown	
2		6.515	189746	2.02	21723	VB			Unknown	

(R)-2-(2-Methyl-1-methylene-2,3-dihydro-1H-inden-2-yl)-6-(naphthalen-2-yl)pyridine (6)



E	Name	Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		7.369	8912264	48.17	685849	BV	1		Unknown	
2		7.840	9591017	51.83	639017	Vb			Unknown	



13	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		7.368	1216	0.35	129	bb			Unknown	
2		7.839	347750	99.65	24532	Bb			Unknown	

130