Supplementary Information (SI) for Chemical Communications. This journal is © The Royal Society of Chemistry 2025

Supporting Information

Palladium-catalyzed intermolecular formal [3+2] cyclization/C-H alkylation of polyfluoroarenes

Zhongyao Jiang, Chenglin Liu, Mingxia Wu, Erhao Xu, and Xin-Xing Wu*

College of Chemistry and Chemical Engineering, Nantong University, Nantong 226019, P. R. China

Email: wuxinxng@163.com

Table of Contents

1. General Considerations	S2
2. Preparation of Substrates	S2
3. Optimization of the Reaction Conditions	S2-S3
4. Experiment Procedure	S3-S4
5. Scale-Up Reaction	S4
6. Synthetic Transformations	S4-S6
7. Spectra Data	S7-S26
8. Crystallographic Data of 4b	S27- S28
9. Reference	S29
10. NMR Spectra	S30-S128

1. General Considerations

All reactions were carried out under N₂ atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. Solvents were purified and dried according to standard methods prior to use. For product purification by flash column chromatography, silica gel (200~300 mesh) and light petroleum ether (bp. 60~90) are used. ¹H NMR spectra were recorded on a Bruker advance III 400 MHz in CDCl₃ and ¹³C{¹H} NMR spectra were recorded on 101 MHz in CDCl₃ using TMS as internal standard. Data for ¹H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, dd = doublet of doublet, dt = triplet of doublets, ddd = doublet of doublet of doublets, coupling constant (s) in Hz, integration). Data for ¹³C NMR is reported in terms of chemical shift (δ , ppm). High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II.

2. Preparation of Substrates

Substrates 1 were synthesized according to the known literature.¹⁻⁵ Substrates 2 were prepared from the coresponding ternal alkynes via Sonogashira coupling through the known literatures.⁶ Polyfluoroarenes 3 or oxanorbornadiene (5a) were obtained from commercial suppliers.

3. Optimization of the Reaction Conditions

Table S1: Optimization of Reaction Conditions of the intermolecular formal [3+2] cyclization/C-H alkylation of polyfluoroarenes^{*a*}

CH ₃	+ Ph Ph + F F Pd(TFA) ₂ (10 mol%) (10 mol%) F K_2CO_3 (2.0 equiv) Ag_2CO_3 (1.0 equiv) DME, 90 °C	F F F F CH ₃ Ph 4a
Entry	Variation from the standard conditions	$\operatorname{Yield}^{b}(\%)$
1	none	71
2	PdCl ₂ instead of Pd(TFA) ₂	45
3	[Pd(C ₃ H ₅)Cl] ₂ instead of Pd(TFA) ₂	62
4	PdCl ₂ (PPh ₃) ₂ instead of Pd(TFA) ₂	50
5	Sphos as ligand	58
6	$P(p-FC_6H_4)_3$ as ligand	22
7	PPh ₃ as ligand	17
8	dppb as ligand	39
9	PCy ₃ as ligand	0
10	^t BuOK instead of K ₂ CO ₃	36
11	KOAc instead of K ₂ CO ₃	20
12	toluene as solvent	47
13	dioxane as solvent	54
14	AgOAc instead of Ag ₂ CO ₃	<10
15	CuI instead of Ag ₂ CO ₃	<10
16	at 80 °C (or 100 °C)	57 (66)

^{*a*}Reaction conditions unless otherwise noted: **1a** (0.2 mmol), **2a** (0.4 mmol), **3a** (0.6 mmol), Pd(TFA)₂ (10 mol %), Qphos (10 mol %), K₂CO₃ (0.4 mmol), Ag₂CO₃ (0.2 mmol), DME (2.0 mL, 0.1 M), 90 °C, 16 h under a N₂ atmosphere. ^{*b*}Isolated yields.

CH3 + 1a	CO_2Me + F + GMe	PdCl ₂ (PCy ₃) ₂ (10 mol%) PCy ₃ HBF ₄ (20 mol%) Cs ₂ CO ₃ (x equiv) Ag ₂ CO ₃ (y equiv) DCE, 130 °C	Heo F F F CH ₃ 6a
Entry	Cs_2CO_3 (x equiv)	Ag ₂ CO ₃ (y equiv)	$\operatorname{Yield}^{b}(\%)$
1	1.0	1.0	15
2	1.0	2.0	21
3	2.0	1.0	23
4	2.0	2.0	36
5	2.0	3.0	40
6	3.0	2.0	51
7	3.0	3.0	48

Table S2: Screening the amount of base and Ag salt for [3+2] cyclization/C-H alkylation with ONBD^a

^{*a*}Reaction conditions unless otherwise noted: **1a** (0.2 mmol), **5a** (0.4 mmol), 1,2,4,5-tetrafluoro-3-methoxybenzene (0.4 mmol), $PdCl_2(PCy_3)_2$ (10 mol %), PCy_3HBF_4 (20 mol %), Cs_2CO_3 (x equiv), Ag_2CO_3 (y equiv), DCE (2.0 mL, 0.1 M), 130 °C, 16 h under a N₂ atmosphere. ^{*b*}Isolated yields.

The results of above screening revealed that adequate amounts of Cs_2CO_3 and Ag_2CO_3 may be beneficial for effectively increasing the concentration of polyfluoroarylsilver intermediate involved in the transmetallization process.

4. Experiment Procedure



O-iodostyrenes **1** (0.2 mmol, 1.0 equiv), internal alkynes **2** (0.4 mmol, 2.0 equiv), polyfluoroarenes **3** (0.6 mmol, 3.0 equiv), Pd(TFA)₂ (10 mol%), Qphos (10 mol%), K₂CO₃ (0.4 mmol, 2.0 equiv), Ag₂CO₃ (0.2 mmol, 1.0 equiv) were added to a sealed tube, DME (2.0 mL, 0.1 M) were added via syringe. The mixture was heated at 90 $\$ in an oil bath about for 16 h until completion (monitored by TLC). After cooling at room temperature, the reaction mixture was filtered through celite. The solvent in the filtrate was evaporated under reduced pressure. The residue was purified through silica gel chromatography to afford the products **4**.



O-iodostyrenes **1** (0.2 mmol, 1.0 equiv), oxanorbornadiene **5a** (0.4 mmol, 2.0 equiv), polyfluoroarenes **3** (0.4 mmol, 2.0 equiv), $PdCl_2(PCy_3)_2$ (10 mol%), PCy_3HBF_4 (20 mol%),

 Cs_2CO_3 (0.6 mmol, 3.0 equiv), Ag_2CO_3 (0.4 mmol, 2.0 equiv) were added to a sealed tube, DCE (2.0 mL, 0.1 M) were added via syringe. The mixture was heated at 130 °C in an oil bath about for 16 h until completion (monitored by TLC). After cooling at room temperature, the reaction mixture was filtered through celite. The solvent in the filtrate was evaporated under reduced pressure. The residue was purified through silica gel chromatography to afford the products **6**.

5. Scale-Up Reaction



1-iodo-2-(prop-1-en-2-yl)benzene **1a** (3.0 mmol, 1.0 equiv), 1,2-diphenylethyne **2a** (6.0 mmol, 2.0 equiv), 1,2,3,4,5-pentafluorobenzene **3a** (9.0 mmol, 3.0 equiv), Pd(TFA)₂ (10 mol%), Qphos (10 mol%), K₂CO₃ (6.0 mmol, 2.0 equiv), Ag₂CO₃ (3.0 mmol, 1.0 equiv) were added to a sealed tube, DME (30.0 mL) were added via syringe. The mixture was heated at 90 °C in an oil bath about for 12 h until completion (monitored by TLC). After cooling at room temperature, the reaction mixture was filtered through celite. The solvent in the filtrate was evaporated under reduced pressure. The residue was purified through silica gel chromatography to afford the products **4a** (0.79 g) in 57% yield.

6. Synthetic Transformations



Under nitrogen atmosphere, **4a** (92.4 mg, 0.2 mmol, 1.0 equiv), ^tBuOK (44.8 mg, 0.4 mmol), 18-crown-6 (26.4 mg, 0.1 mmol) and Et₂O (2 mL) were added to a Schlenk flask. The reaction mixture was stirred under 60 °C for 24 h. After the indicated time the reaction mixture was quenched with water and extracted with EA. The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄, and concentrated at the reduced pressure. The residue was purified by flash silica gel column chromatography to provide the pure product **7** (85% yield).



4a (92.4 mg, 0.2 mmol, 1.0 equiv) and NaOPh (69.6 mg, 0.6 mmol, 3.0 equiv) were suspended in

acetone (1 mL). The reaction mixture was stirred under 80 °C for 24 h. After the indicated time the reaction mixture was quenched with water and extracted with EA. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 , and concentrated at the reduced pressure. The residue was purified by flash silica gel column chromatography to provide analytical pure product **8** (92% yield).



NaO^tBu (21 mg, 0.22 mmol) in DMA (1 mL) was added to imidazole (13.6 mg, 0.2 mmol) in DMA (1 mL) and the mixture was cooled down to 0 $^{\circ}$ C. A solution of **4a** (92.4 mg, 0.2 mmol, 1.0 equiv) in DMA (1 mL) was added dropwise to the reaction. After 15 min stirring at 0 $^{\circ}$ C, the reaction was warmed up to rt. Water was added and the mixture was extracted with ethyl acetate. The organic phase was washed with water, treated with brine, dried over MgSO₄, and evaporated. The resultant residue was subjected to purification by column chromatography on silica gel to afford **9** (87% yield).



Under nitrogen atmosphere, **4a** (92.4 mg, 0.2 mmol, 1.0 equiv), indole (46.8 mg, 0.4 mmol, 2.0 equiv), NaOH (16 mg, 0.4 mmol) and DMF (2 mL) were added to a Schlenk flask. The reaction mixture was stirred under 40 $^{\circ}$ C for 24 h. After the indicated time the reaction mixture was quenched with water and extracted with EA. The combined organic phases were washed with brine, dried over anhydrous Na2SO4, and concentrated at the reduced pressure. The residue was purified by flash silica gel column chromatography to provide analytical pure product **10** (62% yield).



4w (0.2 mmol, 1.0 equiv), BnCl (0.4 mmol, 2.0 equiv), Pd(OAc)₂ (10 mol%), PPh₃ (20 mol%),

 Cs_2CO_3 (0.6 mmol, 3.0 equiv)were added to a sealed tube, toluene (2.0 mL, 0.1 M) were added via syringe. The mixture was heated at 140 °C in an oil bath about for 16 h until completion (monitored by TLC). After cooling at room temperature, the reaction mixture was filtered through celite. The solvent in the filtrate was evaporated under reduced pressure. The residue was purified through silica gel chromatography to afford the products **11** (78% yield).



4w (0.2 mmol, 1.0 equiv), 1-(thiophen-2-yl)ethan-1-one (0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (10 mol%), PPh₃ (20 mol%), Ag₂CO₃ (0.3 mmol, 1.5 equiv), HOAc (0.2 mmol, 1.0 equiv) were added to a sealed tube, DMF (2.0 mL) were added via syringe. The mixture was heated at 120 °C in an oil bath about for 24 h until completion (monitored by TLC). After cooling at room temperature, the reaction mixture was filtered through celite. The solvent in the filtrate was evaporated under reduced pressure. The residue was purified through silica gel chromatography to afford the products **12** (67% yield).

7. Spectra Data



1-methyl-1-((perfluorophenyl)methyl)-2,3-diphenyl-1H-indene (*4a*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale yellow solid, Mp = 123-125 °C, 66 mg, 71% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.12 (m, 13H), 6.87 (d, *J* = 7.5 Hz, 1H), 3.14 (dd, *J* = 13.6, 1.9 Hz, 1H), 2.93 (dd, *J* = 13.7, 1.9 Hz, 1H), 1.56 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.9, 149.6, 145.5 (dm, *J* = 246.9 Hz), 143.0, 139.9 (dm, *J* = 239.8 Hz), 139.8, 137.3 (dm, *J* = 235.3 Hz), 136.2, 134.9, 130.1, 129.6, 128.4, 128.3, 127.3 (t, *J* = 3.8 Hz), 125.5, 122.2, 121.0, 112.3 (td, *J* = 18.6, 3.1 Hz), 55.0, 31.3, 22.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -138.3 (m, 2F), -156.3 (t, *J* = 21.0 Hz, 1F), -162.8 (m, 2F). HRMS (ESI-TOF) calcd for C₂₉H₂₀F₅ [M+H]⁺ : 463.1480, found: 463.1486.



1,6-dimethyl-1-((perfluorophenyl)methyl)-2,3-diphenyl-1H-indene (**4b**): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow solid, Mp = 93-95 °C, 72 mg, 76% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.18 (m, 11H), 7.06 (d, J = 7.7 Hz, 1H), 6.68 (s, 1H), 3.13 (dd, J = 13.5, 2.1 Hz, 1H), 2.93 (dt, J = 13.6, 1.9 Hz, 1H), 2.33 (s, 3H), 1.55 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 149.9, 149.8, 145.6 (dm, J = 248.9 Hz), 140.4, 139.9 (dm, J = 234.3 Hz), 139.6, 137.4 (dm, J = 251.4 Hz), 136.3, 135.3, 135.1, 130.2, 129.6, 128.3, 128.2, 127.9, 127.2 (t, J = 2.1 Hz), 123.1, 120.7, 112.4 (td, J = 19.2, 3.3 Hz), 54.8, 31.4, 22.0, 21.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -138.4 (m, 2F), -156.5 (t, J = 21.0 Hz, 1F), -163.2 (td, J = 22.6, 8.0 Hz, 2F). HRMS (ESI-TOF) calcd for C₃₀H₂₂F₅ [M+H]⁺ : 477.1636, found: 477.1636.



6-fluoro-1-methyl-1-((perfluorophenyl)methyl)-2,3-diphenyl-1H-indene (4c): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title

compound as a yellow solid, Mp = 117-119 °C, 64 mg, 67% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.21 (m, 11H), 6.95 (td, J = 8.8, 2.4 Hz, 1H), 6.60 (dd, J = 8.8, 2.3 Hz, 1H), 3.13 (d, J = 13.7 Hz, 1H), 2.93 (d, J = 13.7 Hz, 1H), 1.56 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 161.7 (d, J = 245.8 Hz), 151.9 (d, J = 7.7 Hz), 150.5 (d, J = 4.1 Hz), 145.5 (dm, J = 248.2 Hz), 140.0 (dm, J = 242.6 Hz), 139.0, 138.9 (d, J = 2.3 Hz), 137.3 (dm, J = 254.3 Hz), 135.9, 134.6, 130.1, 129.5, 128.4, 128.3, 127.5 (d, J = 2.3 Hz), 121.8 (d, J = 8.6 Hz), 114.1 (d, J = 32.6 Hz), 111.8 (td, J = 18.9, 5.3 Hz), 110.0 (d, J = 23.6 Hz), 54.9, 31.2, 22.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -116.6 (s, 1F), -138.4 (m, 2F), -155.7 (t, J = 21.0 Hz, 1F), -162.5 (m, 2F). HRMS (ESI-TOF) calcd for C₂₉H₁₉F₆ [M+H]⁺ : 481.1385, found: 481.1388.



6-*chloro-1-methyl-1-((perfluorophenyl)methyl)-2,3-diphenyl-1H-indene* (*4d*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale yellow solid, Mp = 145-147 °C, 63 mg, 63% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.18 (m, 12H), 6.84 (s, 1H), 3.18-3.08 (m, 1H), 2.93 (dd, *J* = 13.6, 2.1 Hz, 1H), 1.56 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 151.4, 151.1, 145.6 (dm, *J* = 246.6 Hz), 141.5, 140.0 (dm, *J* = 253.5 Hz), 139.0, 137.5 (dm, *J* = 253.5 Hz), 135.4, 134.4, 131.5, 130.0, 129.5, 128.5, 128.3, 127.6, 127.4, 111.8 (td, *J* = 18.7, 3.2 Hz), 55.0, 31.2, 21.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -138.5 (m, 2F), -155.6 (t, *J* = 21.0 Hz, 1F), -162.5 (m, 2F). HRMS (ESI-TOF) calcd for C₂₉H₁₉ClF₅ [M+H]⁺ : 497.1090, found: 497.1088.



1-methyl-1-((perfluorophenyl)methyl)-2,3-diphenyl-6-(trifluoromethyl)-1H-indene (4*e*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~50:1, v/v) affords the title compound as a pale yellow solid, Mp = 144-145 °C, 57 mg, 54% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.32-7.22 (m, 10H), 7.04 (s, 1H), 3.18 (d, *J* = 13.7 Hz, 1H), 2.99-2.85 (m, 1H), 1.59 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 153.8, 149.9, 146.5, 145.6 (dm, *J* = 255.1 Hz), 140.2 (dm, *J* = 251.4 Hz), 139.1, 137.5 (dm, *J* = 248.1 Hz), 135.4, 134.1, 129.9, 129.5, 128.6, 128.4 (q, *J* = 2.7 Hz), 127.8, 127.7 (t, *J* = 2.6 Hz), 124.7 (q, *J* = 5.5 Hz), 123.3 (q, *J* = 271.5 Hz), 121.0, 119.2 (q, *J* = 4.4 Hz), 111.8 (td, *J* = 17.3, 4.6 Hz), 55.2, 31.2, 21.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -61.8 (m, 3F), -138.7 (dt, *J* = 22.6, 13.0 Hz, 2F), -155.5 (m, 1F), -162.4 (td, *J* = 22.8, 22.0, 8.8 Hz, 2F). HRMS (ESI-TOF) calcd for C₃₀H₁₉F₈ [M+H]⁺: 531.1354, found: 531.1357.



5-*fluoro-1-methyl-1-((perfluorophenyl)methyl)-2,3-diphenyl-1H-indene* (*4f*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale yellow solid, Mp = 122-124 °C, 62 mg, 65% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.26 (m, 10H), 7.00 (dd, J = 9.2, 2.4 Hz, 1H), 6.88-6.76 (m, 2H), 3.18-3.06 (m, 1H), 2.97-2.86 (m, 1H), 1.55 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 162.9 (d, J = 244.3 Hz), 152.8, 145.5 (dm, J = 247.0 Hz), 145.1 (d, J = 8.6 Hz), 144.9 (d, J = 2.4 Hz), 139.1 (d, J = 3.1 Hz), 137.4 (dm, J = 253.8 Hz), 135.8, 134.3, 130.6, 130.0, 129.4, 128.5, 128.3, 127.6 (t, J = 1.8 Hz), 123.0 (d, J = 9.0 Hz), 112.0 (d, J = 22.9 Hz), 108.3 (t, J = 23.9 Hz), 54.6, 31.3, 22.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -115.3 (s, 1F), -138.4 (m, 2F), -155.9 (t, J = 20.9 Hz, 1F), -162.5 (td, J = 22.6, 8.0 Hz, 2F). HRMS (ESI-TOF) calcd for C₂₉H₁₉F₆ [M+H]⁺ : 481.1385, found: 481.1393.



1,4-dimethyl-1-((perfluorophenyl)methyl)-2,3-diphenyl-1H-indene (*4g*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a colorless solid, Mp = 107-109 °C, 49 mg, 51% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.26 (m, 2H), 7.23-7.14 (m, 7H), 7.06-6.95 (m, 3H), 6.64 (d, *J* = 7.3 Hz, 1H), 3.09 (dd, *J* = 13.5, 2.3 Hz, 1H), 2.85 (dd, *J* = 13.6, 2.4 Hz, 1H), 1.86 (s, 3H), 1.52 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 152.3, 149.8, 145.6 (dm, *J* = 246.4 Hz), 141.4, 140.6, 140.0 (dm, *J* = 251.3 Hz), 137.6, 137.5 (dm, *J* = 252.2 Hz), 135.9, 132.3, 130.5, 130.1, 130.0, 129.7, 128.0, 127.9, 127.8, 127.1, 127.0, 125.4, 112.5 (td, *J* = 18.3, 4.1 Hz), 54.2, 31.2, 22.0 (t, *J* = 2.1 Hz), 20.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -138.3 (m, 2F), -156.4 (t, *J* = 20.8 Hz, 1F), -162.8 (dd, *J* = 21.6, 14.6 Hz, 2F). HRMS (ESI-TOF) calcd for C₃₀H₂₂F₅ [M+H]⁺ : 477.1636, found: 477.1639.



1-ethyl-1-((perfluorophenyl)methyl)-2,3-diphenyl-1H-indene (4h): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title

compound as a viscous oil, 73 mg, 77% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.13 (m, 13H), 6.87 (d, *J* = 7.4 Hz, 1H), 3.14 (d, *J* = 13.7 Hz, 1H), 3.01 (d, *J* = 13.7 Hz, 1H), 2.35 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.08 (dq, *J* = 14.3, 7.3 Hz, 1H), 0.55 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 147.7, 147.6, 145.6 (dm, *J* = 251.7 Hz), 144.3, 141.9, 139.7 (dm, *J* = 243.3 Hz), 137.4 (dm, *J* = 251.9 Hz), 136.2, 135.2, 129.9, 129.7, 128.4, 128.2, 127.3, 127.2 (d, *J* = 3.6 Hz), 125.6, 122.0, 120.9, 112.2 (td, *J* = 19.1, 4.4 Hz), 59.87, 31.31, 28.15, 8.47. ¹⁹F NMR (376 MHz, CDCl₃) δ -137.8 (m, 2F), -156.5 (t, *J* = 21.1 Hz, 1F), -163.0 (td, *J* = 22.9, 8.0 Hz, 2F). HRMS (ESI-TOF) calcd for C₃₀H₂₂F₅ [M+H]⁺ : 477.1636, found: 477.1637.



1-ethyl-5-methoxy-1-((perfluorophenyl)methyl)-2,3-diphenyl-1H-indene (**4i**): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~50:1, v/v) affords the title compound as a pale red solid, Mp = 106-108 °C, 71 mg, 70% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.24-7.12 (m, 10H), 6.74 (d, *J* = 2.2 Hz, 1H), 6.72-6.58 (m, 2H), 3.68 (s, 3H), 3.02 (d, *J* = 13.7 Hz, 1H), 2.94-2.85 (m, 1H), 2.24 (dq, *J* = 14.3, 7.2 Hz, 1H), 1.94 (m, 1H), 0.47 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 159.4, 148.9, 145.7, 145.6 (dm, *J* = 237.5 Hz), 141.7, 139.9 (dm, *J* = 251.2 Hz), 139.8, 136.2, 135.2, 129.8, 129.7, 128.5, 128.2, 127.4, 127.3, 122.5, 112.4 (td, *J* = 17.3, 3.9 Hz), 111.0, 106.7, 59.2, 55.5, 31.4, 28.3, 8.5. ¹⁹F NMR (376 MHz, CDCl₃) δ -137.9 (m, 2F), -156.6 (t, *J* = 21.0 Hz, 1F), -163.07 (td, *J* = 22.9, 8.0 Hz, 2F). HRMS (ESI-TOF) calcd for C₃₁H₂₄OF₅ [M+H]⁺ : 507.1742, found: 507.1740.



1-methyl-1-((perfluorophenyl)methyl)-2,3-di-p-tolyl-1H-indene (**4***j*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow solid, Mp = 131-133 °C, 68 mg, 69% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.31-7.29 (m, 1H), 7.23-7.06 (m, 10H), 6.85 (d, *J* = 7.4 Hz, 1H), 3.13 (dt, *J* = 13.6, 1.7 Hz, 1H), 2.91 (dd, *J* = 13.6, 1.8 Hz, 1H), 2.32 (s, 6H), 1.54 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.5, 149.6, 145.5 (dm, *J* = 248.5 Hz), 143.3, 139.9 (dm, *J* = 259.1 Hz), 137.3 (dm, *J* = 254.0 Hz), 136.9 (d, *J* = 4.4 Hz), 130.0, 129.5, 129.1, 129.0, 127.3, 125.3, 122.1, 121.0, 112.4 (td, *J* = 17.3, 3.9 Hz), 54.9, 31.4, 22.0, 21.42, 21.35. ¹⁹F NMR (376 MHz, CDCl₃) δ -138.3 (m, 2F), -156.5 (t, *J* = 20.9 Hz, 1F), -163.0 (td, *J* = 22.6, 7.9 Hz, 2F). HRMS (ESI-TOF) calcd for C₃₁H₂₄F₅ [M+H]⁺:



2,3-bis(4-(tert-butyl)phenyl)-1-methyl-1-((perfluorophenyl)methyl)-1H-indene (**4k**): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a colorless solid, Mp = 141-143 °C, 89 mg, 77% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.21 (m, 8H), 7.18-7.11 (m, 3H), 6.92 (d, *J* = 7.4 Hz, 1H), 3.14 (d, *J* = 13.8 Hz, 1H), 2.99 (dt, *J* = 13.6, 1.9 Hz, 1H), 1.58 (s, 3H), 1.30 (d, *J* = 3.7 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 150.2, 150.0, 149.93, 149.91, 145.6 (dm, *J* = 250.4 Hz), 143.4, 139.9 (dm, *J* = 254.3 Hz), 139.3, 137.2 (dm, *J* = 248.8 Hz), 133.2, 132.1, 129.7, 129.3, 127.2, 125.3, 125.2, 124.9, 122.0, 121.1, 112.5 (td, *J* = 18.3, 3.2 Hz), 55.0, 34.7, 34.6, 31.5, 31.4, 22.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -138.2 (m, 2F), -156.7 (t, *J* = 21.0 Hz, 1F), -163.1 (td, *J* = 22.7, 7.9 Hz, 2F). HRMS (ESI-TOF) calcd for C₃₇H₃₆F₅ [M+H]⁺ : 575.2732, found: 575.2737.



1-methyl-2,3-bis(*4-fluorophenyl*)-*1-*((*perfluorophenyl*)*methyl*)-*1H-indene* (*4l*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale yellow solid, Mp = 146-148 °C, 52 mg, 52% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.16 (m, 7H), 7.07-6.96 (m, 4H), 6.89 (d, *J* = 7.4 Hz, 1H), 3.12 (d, *J* = 13.6 Hz, 1H), 2.90 (d, *J* = 13.6 Hz, 1H), 1.55 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 163.4 (d, *J* = 8.9 Hz), 160.9 (d, *J* = 8.4 Hz), 150.0, 149.4, 145.6 (dm, *J* = 248.2 Hz), 142.6, 140.0 (dm, *J* = 258.8 Hz), 139.2, 137.4 (dm, *J* = 243.1 Hz), 131.9 (d, *J* = 3.5 Hz), 131.8 (d, *J* = 8.0 Hz), 131.3 (d, *J* = 8.1 Hz), 130.6 (d, *J* = 3.4 Hz), 127.5, 125.8, 122.3, 120.9, 115.5 (dd, *J* = 21.4, 5.5 Hz),112.1 (td, *J* = 19.0, 3.4 Hz), 55.0, 31.2, 22.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -114.3 (d, *J* = 12.5 Hz, 2F), -138.5 (m, 2F), -156.0 (t, *J* = 20.9 Hz, 1F), -162.7 (dd, *J* = 21.2, 14.8 Hz, 2F). HRMS (ESI-TOF) calcd for C₂₉H₁₈F₇ [M+H]⁺: 499.1291, found: 499.1290.



1-methyl-2,3-bis(3-fluorophenyl)-1-((perfluorophenyl)methyl)-1H-indene (4m): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow solid, Mp = 110-112 °C, 59 mg, 59% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.27 (dq, *J* = 10.5, 3.9, 2.9 Hz, 4H), 7.19 (td, *J* = 6.9, 6.4, 2.3 Hz, 1H), 7.06-6.93 (m, 6H), 6.89 (d, *J* = 7.5 Hz, 1H), 3.20-3.10 (m, 1H), 2.92 (dt, *J* = 13.6, 1.9 Hz, 1H), 1.56 (d, *J* = 2.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 164.0 (d, *J* = 16.7 Hz), 161.5 (d, *J* = 17.0 Hz), 150.1 (d, *J* = 1.9 Hz), 149.4, 145.5 (dm, *J* = 246.0 Hz), 142.2, 140.0 (dm, *J* = 240.4 Hz), 139.4 (d, *J* = 2.1 Hz), 138.0 (d, *J* = 7.8 Hz), 136.7 (d, *J* = 8.0 Hz), 137.4 (dm, *J* = 258.0 Hz), 130.0 (dd, *J* = 13.6, 8.5 Hz), 127.6, 126.1, 126.0 (d, *J* = 2.9 Hz), 125.3 (dm, *J* = 2.9 Hz), 122.3, 121.1, 116.8 (d, *J* = 21.6 Hz), 116.4 (d, *J* = 22.0 Hz, CDCl₃) δ -112.8 (s, 1F), -112.9 (s, 1F), -138.4 (m, 2F), -155.9 (t, *J* = 19.9 Hz, 1F), -162.5 (m, 2F). HRMS (ESI-TOF) calcd for C₂₉H₁₈F₇ [M+H]⁺ : 499.1291, found: 499.1297.



1-methyl-2,3-bis(3-methoxyphenyl)-1-((perfluorophenyl)methyl)-1H-indene (*4n*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~30:1, v/v) affords the title compound as a pale yellow solid, Mp = 117-119 °C, 70 mg, 67% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, *J* = 7.5 Hz, 1H), 7.17-7.03 (m, 4H), 6.85-6.68 (m, 7H), 3.57 (s, 6H), 3.08 (d, *J* = 13.6 Hz, 1H), 2.84 (d, *J* = 13.7 Hz, 1H), 1.48 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 159.5, 159.3, 150.7, 149.5, 145.5 (dm, *J* = 248.2 Hz), 142.8, 139.8 (dm, *J* = 254.0 Hz), 137.5, 137.3 (dm, *J* = 237.6 Hz), 136.2, 129.4, 129.2, 127.4, 125.6, 122.4, 122.2, 122.0, 121.1, 115.9, 114.7, 113.4, 112.7, 112.3 (td, *J* = 19.3, 3.6 Hz), 55.2 (d, *J* = 2.3 Hz), 55.0, 31.3, 22.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -138.3 (dd, *J* = 23.1, 8.0 Hz, 2F), -156.3 (t, *J* = 21.0 Hz, 1F), -162.8 (td, *J* = 22.8, 8.0 Hz, 2F). HRMS (ESI-TOF) calcd for C₃₁H₂₄O₂F₅ [M+H]⁺ : 523.1691, found: 523.1687.



2,3-bis(3-chlorophenyl)-1-methyl-1-((perfluorophenyl)methyl)-1H-indene (**4o**): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale red solid, Mp = 105-107 °C, 74 mg, 70% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.17 (m, 9H), 7.13-7.05 (m, 2H), 6.88 (d, *J* = 7.5 Hz, 1H), 3.12 (d, *J* = 13.6 Hz, 1H), 2.91 (d, *J* = 13.6 Hz, 1H), 1.55 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.1, 149.4, 145.5 (dm, *J* = 248.3 Hz), 142.1, 139.9 (dm, *J* = 253.8 Hz), 139.4, 137.6, 137.4 (dm, *J* = 240.1 Hz), 136.3, 134.4, 134.3, 129.9, 129.70, 129.66, 129.4, 128.5, 127.9 (d, *J* = 1.6 Hz), 127.6, 126.1, 122.3, 121.1, 111.9 (td, *J* = 18.8, 4.1 Hz), 55.2, 31.1, 22.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -138.4 (m, 2F), -155.8 (t, *J* = 21.0 Hz, 1F), -162.5 (td, *J* = 22.7, 8.1 Hz, 2F). HRMS (ESI-TOF) calcd for C₂₉H₁₈F₅Cl₂ [M+H]⁺ : 531.0700, found: 531.0703.



1-methyl-2,3-bis(methoxymethyl)-1-((perfluorophenyl)methyl)-1H-indene (*4p*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~30:1, v/v) affords the title compound as a viscous oil, 55 mg, 69% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, *J* = 7.3 Hz, 1H), 7.23-7.08 (m, 3H), 4.53-4.32 (m, 4H), 3.39 (s, 3H), 3.35-3.30 (m, 1H), 3.28 (s, 3H), 2.97 (d, *J* = 13.7 Hz, 1H), 1.47 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 149.0, 147.1, 145.3 (dm, *J* = 246.5 Hz), 142.1, 139.5 (dm, *J* = 254.4 Hz), 138.2, 137.1 (dm, *J* = 252.8 Hz), 127.4, 125.6, 122.1 (t, *J* = 2.0 Hz), 120.6, 111.8 (td, *J* = 19.3, 3.8 Hz), 66.0, 58.4, 57.9, 54.4, 30.6, 22.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -139.3 (m, 2F), -156.5 (t, *J* = 21.0 Hz, 1F), -163.2 (m, 2F). HRMS (ESI-TOF) calcd for C₂₁H₂₀F₅O₂ [M+H]⁺ : 399.1378, found: 399.1380.



2,3-diethyl-1-methyl-1-((perfluorophenyl)methyl)-1H-indene (4q): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title

compound as a pale yellow solid, Mp = 98-100 °C, 44 mg, 60% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.19-7.12 (m, 2H), 7.10-6.91 (m, 2H), 3.17 (dd, *J* = 13.3, 1.7 Hz, 1H), 2.95 (dt, *J* = 13.4, 1.7 Hz, 1H), 2.62-2.26 (m, 4H), 1.43 (s, 3H), 1.12 (t, *J* = 7.6 Hz, 3H), 1.03 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 149.4, 148.6, 145.1 (dm, *J* = 257.0 Hz), 144.0, 139.4 (dm, *J* = 243.8 Hz), 138.6, 136.9 (dm, *J* = 246.8 Hz), 127.0, 124.0, 122.1 (d, *J* = 2.2 Hz), 118.2, 111.9 (td, *J* = 17.5, 3.7 Hz), 54.3, 31.1, 22.2, 18.6 (t, *J* = 3.3 Hz), 18.5, 15.2, 13.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -139.0 (m, 2F), -157.4 (t, *J* = 21.1 Hz, 1F), -163.9 (m, 2F). HRMS (ESI-TOF) calcd for C₂₁H₂₀F₅ [M+H]⁺ : 367.1480, found: 367.1481.



1-methyl-1-((perfluorophenyl)methyl)-2,3-dipropyl-1H-indene (*4r*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a colorless oil, 43 mg, 55% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.16-7.11 (m, 2H), 7.08-7.01 (m, 2H), 3.18 (dt, *J* = 13.3, 1.6 Hz, 1H), 2.95 (dt, *J* = 13.3, 1.7 Hz, 1H), 2.55-2.22 (m, 4H), 1.54-1.39 (m, 7H), 1.03 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 148.53, 148.48, 145.2 (dm, *J* = 246.9 Hz), 144.5, 139.5 (dm, *J* = 238.9 Hz), 137.6, 137.0 (dm, *J* = 250.8 Hz), 127.0, 124.0, 122.1 (t, *J* = 2.2 Hz), 118.4, 112.0 (td, *J* = 18.0, 3.1 Hz), 54.4, 31.1, 28.4 (d, *J* = 2.9 Hz), 27.7, 24.0, 22.4, 22.0, 15.2, 14.5. ¹⁹F NMR (376 MHz, CDCl₃) δ -138.9 (m, 2F), -157.4 (t, *J* = 21.0 Hz, 1F), -163.8 (m, 2F). HRMS (ESI-TOF) calcd for C₂₃H₂₄F₅ [M+H]⁺: 395.1793, found: 395.1797.



2,3-dibutyl-1-methyl-1-((perfluorophenyl)methyl)-1H-indene (4s): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil, 49 mg, 58% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.15 (ddd, J = 12.0, 6.7, 1.4 Hz, 2H), 7.10-7.00 (m, 2H), 3.18 (dt, J = 13.2, 1.7 Hz, 1H), 2.96 (dt, J = 13.4, 1.7 Hz, 1H), 2.54-2.21 (m, 4H), 1.47-1.25 (m, 11H), 0.99-0.89 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 148.5, 148.4, 145.3 (dm, J = 252.1 Hz), 144.4, 139.3 (dm, J = 239.0 Hz), 137.6, 136.7 (dm, J = 251.3 Hz), 127.0, 123.9, 122.1 (t, J = 2.2 Hz), 118.3, 112.0 (td, J = 18.7, 3.6 Hz), 54.4, 32.9, 31.2, 31.0, 25.8 (t, J = 3.0 Hz), 25.4, 23.8, 23.2, 22.5, 14.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -138.9 (m, 2F), -157.4 (t, J = 20.9 Hz, 1F), -163.8 (dd, J = 21.2, 15.0 Hz, 2F). HRMS (ESI-TOF) calcd for

 $C_{25}H_{28}F_5 [M+H]^+$: 423.2106, found: 423.2101.



1,2-dimethyl-1-((perfluorophenyl)methyl)-3-phenyl-1H-indene (*4t*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale yellow oil, 50 mg, 63% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (dd, *J* = 7.8, 6.2 Hz, 2H), 7.38-7.28 (m, 5H), 7.11 (td, *J* = 7.5, 6.9, 2.3 Hz, 1H), 6.71 (d, *J* = 7.4 Hz, 1H), 3.02 (m, 1H), 2.70 (dt, *J* = 13.5, 2.0 Hz, 1H), 2.00 (s, 3H), 1.44 (t, *J* = 1.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.0, 149.3, 145.4 (dm, *J* = 246.4 Hz), 144.1, 139.6 (dm, *J* = 238.4 Hz), 137.2 (dm, *J* = 250.8 Hz), 136.3, 134.4, 129.7, 129.0, 128.5, 128.4, 127.4, 127.2, 125.2, 121.7, 119.5, 54.4, 31.0, 21.5, 11.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -138.6 (m, 2F), -156.6 (t, *J* = 21.1 Hz, 2F), -162.9 (m, 2F). HRMS (ESI-TOF) calcd for C₂₄H₁₈F₅ [M+H]⁺ : 401.1323, found: 401.1325.



2-*ethyl-1-methyl-1-((perfluorophenyl)methyl)-3-phenyl-1H-indene* (*4u*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale yellow oil, 61 mg, 74% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (t, *J* = 7.3 Hz, 2H), 7.37 (dd, *J* = 10.8, 7.4 Hz, 2H), 7.31-7.26 (m, 3H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.5 Hz, 1H), 3.01 (dt, *J* = 13.4, 1.9 Hz, 1H), 2.71 (dd, *J* = 13.9, 2.1 Hz, 1H), 2.41 (qd, *J* = 7.6, 1.6 Hz, 2H), 1.40 (d, *J* = 1.9 Hz, 3H), 1.13 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 149.8, 149.7, 145.6 (dm, *J* = 253.4 Hz), 143.1, 140.4, 140.1 (dm, *J* = 249.9 Hz), 137.3 (dm, *J* = 252.3 Hz), 136.4, 129.8, 128.8, 128.7, 128.5, 127.5, 127.2, 125.1, 122.0, 119.9, 112.7 (td, *J* = 18.0, 4.4 Hz), 54.3, 30.9, 21.6, 19.2, 14.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -138.5 (m, 2F), -156.6 (t, *J* = 21.0 Hz, 1F), -162.9 (m, 2F). HRMS (ESI-TOF) calcd for C₂₅H₂₀F₅ [M+H]⁺ : 415.1480, found: 415.1488.



2-butyl-1-methyl-1-((perfluorophenyl)methyl)-3-phenyl-1H-indene (4v): Purification by column

chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale yellow oil, 51 mg, 58% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (dd, *J* = 8.0, 6.4 Hz, 2H), 7.39-7.33 (m, 2H), 7.31-7.24 (m, 3H), 7.11-7.06 (m, 1H), 6.70 (d, *J* = 7.5 Hz, 1H), 3.00 (dt, *J* = 13.6, 1.9 Hz, 1H), 2.69 (dt, *J* = 13.6, 2.0 Hz, 1H), 2.39 (t, *J* = 7.8 Hz, 2H), 1.56-1.49 (m, 2H), 1.40 (d, *J* = 1.9 Hz, 3H), 1.32-1.21 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.4, 149.6, 145.5 (dm, *J* = 251.2 Hz), 143.4, 139.9 (dm, *J* = 251.2 Hz), 139.0, 137.3 (dm, *J* = 255.7 Hz), 136.4, 129.9, 128.8, 128.6, 128.4, 127.5, 127.2, 125.0, 122.0, 120.1, 112.7 (td, *J* = 19.4, 3.7 Hz), 54.4, 31.3, 31.0, 25.7, 22.9, 21.6, 14.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -138.5 (m, 2F), -156.7 (t, *J* = 20.9 Hz, 1F), -162.9 (m, 2F). HRMS (ESI-TOF) calcd for C₂₇H₂₄F₅ [M+H]⁺ : 443.1793, found: 443.1799.



1-methyl-2,3-diphenyl-1-(2,3,5,6-tetrafluorobenzyl)-1H-indene (*4w*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale red solid, Mp = 109-111 $^{\circ}$ C, 55 mg, 62% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.25-7.13 (m, 12H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.85-6.73 (m, 2H), 3.09 (dd, *J* = 13.3, 2.2 Hz, 1H), 2.91-2.80 (m, 1H), 1.48 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 151.2, 149.7, 145.7 (dm, *J* = 247.8 Hz), 145.2 (dm, *J* = 242.3 Hz), 143.0, 139.6, 136.2, 134.9, 130.2, 129.7, 128.3, 128.2, 127.31, 127.25, 125.5, 122.3, 120.9, 118.4 (t, *J* = 18.2 Hz), 104.4 (t, *J* = 22.6 Hz), 55.1, 31.8 (d, *J* = 2.1 Hz), 22.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -139.0 (dd, *J* = 22.5, 12.8 Hz, 2F), -139.9 (dd, *J* = 22.6, 12.8 Hz, 2F). HRMS (ESI-TOF) calcd for C₂₉H₂₁F₄ [M+H]⁺ : 445.1574, found: 445.1577.



1-methyl-2,3-diphenyl-1-(2,3,4,6-tetrafluorobenzyl)-1H-indene (**4***x*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale yellow solid, Mp = 129-131 °C, 49 mg, 55% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.21 (m, 12H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.65 (tdd, *J* = 9.2, 5.9, 2.3 Hz, 1H), 3.10 (d, *J* = 13.6 Hz, 1H), 2.85 (d, *J* = 13.6 Hz, 1H), 1.54 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 156.0 (dm, *J* = 246.7 Hz), 151.4, 150.4 (dm, *J* = 255.6 Hz), 149.2 (dm, *J* = 254.7 Hz), 143.0, 139.4, 137.1 (dm, *J* = 244.9 Hz), 136.3, 135.0, 130.2, 129.7, 128.3 (d, *J* = 8.7 Hz), 127.3 (d, *J* = 3.9 Hz), 127.2, 125.3, 122.4, 120.9, 112.2 (td, *J* = 22.4, 4.6 Hz), 100.3 (m), 55.1, 31.1, 21.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -113.7 (d, *J* = 10.9 Hz, 1F), -131.0 (dd, *J* = 21.7, 5.3 Hz, 1F), -134.5 (dd, *J* = 21.5, 5.2 Hz, 1F), -165.5 (td, *J* = 21.4, 10.9 Hz, 1F). HRMS (ESI-TOF) calcd

for $C_{29}H_{21}F_4[M+H]^+$: 445.1574, found: 445.1575.



1-methyl-2,3-diphenyl-1-(2,3,5,6-tetrafluoro-4-methoxybenzyl)-1H-indene (**4***y*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~50:1, v/v) affords the title compound as a pale yellow solid, Mp = 114-116 °C, 66 mg, 70% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.22 (m, 12H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 4.04 (s, 3H), 3.10 (d, *J* = 13.4 Hz, 1H), 2.87 (d, *J* = 13.4 Hz, 1H), 1.56 (d, *J* = 2.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 151.3, 149.9, 145.8 (dm, *J* = 246.2 Hz), 143.0, 140.8 (dm, *J* = 256.5 Hz), 139.5, 136.3, 135.0, 130.2, 129.7, 128.3, 128.2, 127.2 (t, *J* = 3.1 Hz), 125.4, 122.4, 120.9, 110.6 (t, *J* = 18.9 Hz), 62.3, 55.1, 31.2, 21.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -140.2 (m, 2F), -158.7 (m, 2F). HRMS (ESI-TOF) calcd for C₃₀H₂₃OF₄ [M+H]⁺ : 475.1680, found: 475.1681.



l-(2,4,5-*trifluoro-3*-((*1-methyl-2,3-diphenyl-1H-inden-1-yl)methyl*)*phenyl*)*ethan-1-one* (4z): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~30:1, v/v) affords the title compound as a pale yellow solid, Mp = 121-123 °C, 59 mg, 63% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.52 (dt, J = 9.5, 4.8 Hz, 1H), 7.29-7.17 (m, 12H), 7.05 (d, J = 7.4 Hz, 1H), 6.74 (d, J = 7.5 Hz, 1H), 3.12 (d, J = 13.4 Hz, 1H), 2.87 (d, J = 13.2 Hz, 1H), 2.41 (d, J = 5.7 Hz, 3H), 1.51 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 194.0, 157.1 (dm, J = 264.7 Hz), 152.4 (dm, J = 246.8 Hz), 151.3, 149.7, 147.2 (dm, J = 247.9 Hz), 143.1, 139.6, 136.2, 134.9, 130.2, 129.6, 128.33, 128.26, 127.4, 127.3, 125.3, 122.4, 121.4 (td, J = 17.9, 4.0 Hz), 121.0, 117.9 (dd, J = 24.0, 17.0 Hz), 115.9 (qd, J = 18.8, 2.5 Hz), 55.1, 31.7, 31.6 (t, J = 8.6 Hz), 21.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -109.2 (dd, J = 16.3, 8.2 Hz, 1F), -124.2 (dd, J = 22.5, 8.2 Hz, 1F), -140.8 (dd, J = 22.4, 16.1 Hz, 1F). HRMS (ESI-TOF) calcd for C₃₁H₂₄OF₃ [M+H]⁺ : 469.1774, found: 469.1777.



1-(4-((benzyloxy)methyl)-2,3,5,6-tetrafluorobenzyl)-1-methyl-2,3-diphenyl-1H-indene

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~50:1, v/v) affords the title compound as a pale yellow solid, Mp = 132-134 °C, 80 mg, 71% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.44-7.22 (m, 17H), 7.14 (td, *J* = 7.4, 1.2 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 4.63 (d, *J* = 1.9 Hz, 2H), 4.55 (s, 2H), 3.30-3.12 (m, 1H), 3.01-2.86 (m, 1H), 1.56 (d, *J* = 2.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 151.2, 149.7, 145.2 (dm, *J* = 254.6 Hz), 143.0, 139.6, 137.6, 136.2, 135.0, 130.2, 129.6, 128.6, 128.3, 128.2, 128.1, 128.0, 127.3, 127.2 (d, *J* = 1.7 Hz), 125.5, 122.4, 121.0, 117.9 (t, *J* = 18.2 Hz), 114.6 (t, *J* = 18.0 Hz), 72.9, 59.4, 55.1, 31.7, 21.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -139.21 (dd, *J* = 22.9, 13.2 Hz, 2F), -144.41 (dd, *J* = 23.0, 13.0 Hz, 2F). HRMS (ESI-TOF) calcd for C₃₇H₂₉OF₄ [M+H]⁺ : 565.2149, found: 565.2150.



tert-butyldimethyl((2,3,5,6-*tetrafluoro-4*-((*1-methyl-2,3-diphenyl-1H-inden-1-yl*)*methyl*)*benzyl*)*oxy*)*silane* (*4ab*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~30:1, v/v) affords the title compound as a pale yellow solid, Mp = 175-177 °C, 78 mg, 66% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.22-7.12 (m, 12H), 7.03 (ddd, *J* = 8.7, 6.8, 1.3 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 4.70-4.61 (m, 2H), 3.07 (dt, *J* = 13.5, 1.5 Hz, 1H), 2.86-2.77 (m, 1H), 1.58-1.46 (m, 3H), 0.80 (d, *J* = 1.1 Hz, 9H), 0.00 (d, *J* = 1.1 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 151.3, 149.7, 145.1 (dm, *J* = 251.2 Hz), 143.0, 139.5, 136.3, 135.0, 130.2, 129.7, 128.3, 128.2, 127.3, 127.2 (d, *J* = 1.5 Hz), 125.4, 122.4, 120.9, 117.3 (dd, *J* = 35.5, 25.0 Hz), 117.2 (d, *J* = 25.7 Hz), 55.1, 53.4, 31.6, 25.9, 21.9, 18.5, -5.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -139.7 (dd, *J* = 23.0, 12.9 Hz, 2F). HRMS (ESI-TOF) calcd for C₃₆H₃₇F₄OSi [M+H]⁺ : 589.2544, found: 589.2546.



2,3,5,6-tetrafluoro-4-((1-methyl-2,3-diphenyl-1H-inden-1-yl)methyl)pyridine (4ac): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $30:1\sim10:1$, v/v) affords the title compound as a pale yellow solid, Mp = $142-144 \, \degree$ C, 45 mg, 51% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.26-7.15 (m, 12H), 7.11 (td, J = 7.4, 1.4 Hz, 1H), 6.87 (d, J = 7.4 Hz, 1H), 3.23-3.12 (m, 1H), 3.07-2.94 (m, 1H), 1.55 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.2, 149.1, 143.5 (dm, J = 240.6 Hz), 142.9, 140.7 (dm, J = 239.9 Hz), 140.1, 135.8, 134.6, 132.1 (tm, J =16.9 Hz), 130.1, 129.6, 128.4, 128.3, 127.6 (t, J = 10.6 Hz), 125.8, 122.0, 121.2, 54.9, 32.6, 22.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -91.9 (m, 2F), -139.8 (m, 2F). HRMS (ESI-TOF) calcd for C₂₈H₂₀F₄N [M+H]⁺ : 446.1526, found: 446.1526.



2,3,5-trifluoro-4-((1-methyl-2,3-diphenyl-1H-inden-1-yl)methyl)pyridine (4ad): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1 - 10:1, v/v) affords the title compound as a pale yellow solid, Mp = $145-147 \, ^\circ$ C, 42 mg, 49% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.64 (t, J = 1.6 Hz, 1H), 7.24-7.15 (m, 12H), 7.10-7.06 (m, 1H), 6.82 (d, J = 7.5 Hz, 1H), 3.13 (d, J = 13.1 Hz, 1H), 2.93 (d, J = 13.0 Hz, 1H), 1.52 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 155.9 (dm, J = 252.0 Hz), 150.7, 149.2, 148.5 (dd, J = 235.2, 14.7 Hz), 143.9 (dd, J = 264.0, 32.9 Hz), 142.9, 139.9, 136.0, 134.7, 130.1, 129.6, 128.4, 128.3, 127.5, 127.4, 125.6, 122.2, 121.1, 54.9, 31.8 (d, J = 2.2 Hz), 22.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -90.3 (dd, J = 28.9, 26.0 Hz, 1F), -127.9 (dd, J = 28.7, 2.4 Hz, 1F), -135.5 (dd, J = 26.0, 2.4 Hz, 1F). HRMS (ESI-TOF) calcd for C₂₈H₂₁F₃N [M+H]⁺ : 428.1621, found: 428.1620.



1-methyl-2,3-diphenyl-1-(2,3,5,6-tetrafluoro-4-((1-methyl-2,3-diphenyl-1H-inden-1-yl)methyl)ben zyl)-1H-indene (*4ae*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $30:1 \sim 10:1$, v/v) affords the title compound as a pale yellow solid, 69 mg, 47% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.23-7.12 (m, 23H), 7.11-7.06 (m, 2H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.71 (dd, *J* = 18.6, 7.4 Hz, 2H), 3.08 (t, *J* = 13.5 Hz, 2H), 2.89 (t, *J* = 12.7 Hz, 2H), 1.40 (d, *J* = 5.1 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 151.3, 151.0, 149.7 (d, *J* = 2.5 Hz), 145.0 (dm, *J* = 257.7 Hz), 143.1 (d, *J* = 11.5 Hz), 139.6 (d, *J* = 14.1 Hz), 136.3 (d, *J* = 12.1 Hz), 135.0 (d, *J* = 11.2 Hz), 130.2, 129.7 (d, *J* = 10.6 Hz), 128.3 (d, *J* = 5.2 Hz), 120.7 (d, *J* = 3.7 Hz), 115.5 (m), 55.2 (d, *J* = 4.8 Hz), 31.5 (d, *J* = 19.4 Hz), 22.0 (d, *J* = 11.2 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -140.1 (d, *J* = 27.7 Hz, 4F). HRMS (ESI-TOF) calcd for C₅₂H₃₉F₄ [M+H]⁺ : 739.2982, found: 739.2988.



1-methyl-1-(2,3,5,6-tetrafluoro-4-methoxybenzyl)-1H-indene (6a): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $100:1 \sim 50:1$, v/v) affords the title compound as a pale yellow oil, 33 mg, 51% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (t, J = 4.7

Hz, 1H), 7.12 (d, J = 2.2 Hz, 3H), 6.52 (d, J = 5.5 Hz, 1H), 6.24 (dt, J = 5.3, 2.5 Hz, 1H), 3.92 (d, J = 1.3 Hz, 3H), 3.07 (dt, J = 13.5, 1.8 Hz, 1H), 2.90 (dt, J = 13.4, 1.8 Hz, 1H), 1.29 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.3, 145.4 (dm, J = 249.0 Hz), 144.0, 143.1, 140.6 (dm, J = 247.2 Hz), 136.7 (m), 129.5, 127.1, 125.2, 122.1, 121.3, 110.5 (t, J = 18.9 Hz), 62.2, 54.0, 30.8 (t, J = 1.7 Hz), 22.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -141.9 (m, 2F), -158.8 (m, 2F). HRMS (ESI-TOF) calcd for C₁₈H₁₅F₄O [M+H]⁺ : 323.1054, found: 323.1057.



1,6-dimethyl-1-(2,3,5,6-tetrafluoro-4-methoxybenzyl)-1H-indene (*6b*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~50:1, v/v) affords the title compound as a pale yellow oil, 38 mg, 57% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.20 (s, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 5.5 Hz, 1H), 6.24 (dd, *J* = 5.4, 2.7 Hz, 1H), 4.01 (t, *J* = 1.3 Hz, 3H), 3.14 (dt, *J* = 13.4, 1.6 Hz, 1H), 2.91 (dt, *J* = 13.4, 1.6 Hz, 1H), 2.40 (s, 3H), 1.34 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.8, 145.6 (dm, *J* = 241.9 Hz), 140.6 (dm, *J* = 249.8 Hz), 143.0 (t, *J* = 1.6 Hz), 140.7 (dm, *J* = 247.3 Hz), 140.4, 136.7 (m), 135.0, 129.2, 127.8, 123.0, 120.9, 110.7 (t, *J* = 19.1 Hz), 62.2 (dm, *J* = 3.6 Hz), 53.7, 30.9, 22.8, 21.7. ¹⁹F NMR (376 MHz, CDCl₃) δ -142.0 (m, 2F), -158.9 (m, 2F). HRMS (ESI-TOF) calcd for C₁₉H₁₇F₄O [M+H]⁺ : 337.1210, found: 337.1212.



5-chloro-1-methyl-1-(2,3,5,6-tetrafluoro-4-methoxybenzyl)-1H-indene (6c): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $100:1\sim30:1$, v/v) affords the title compound as a pale green oil, 38 mg, 53% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, J = 8.5 Hz, 1H), 7.20-7.12 (m, 2H), 6.53 (d, J = 5.5 Hz, 1H), 6.40 (dt, J = 5.3, 2.5 Hz, 1H), 4.01 (t, J = 1.4 Hz, 3H), 3.13 (dt, J = 13.5, 1.8 Hz, 1H), 3.06-2.96 (m, 1H), 1.36 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 148.5, 145.8, 145.4 (dm, J = 248.0 Hz), 144.8, 140.6 (dm, J = 243.7 Hz), 136.8 (m), 132.9, 128.7, 125.1, 123.1, 121.5, 110.0 (t, J = 19.1 Hz), 62.2, 53.9, 30.6 (t, J = 1.7 Hz), 23.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -142.0 (m, 2F), -158.6 (m, 2F). HRMS (ESI-TOF) calcd for C₁₈H₁₄OClF₄ [M+H]⁺ : 357.0664, found: 357.0665.



5-*fluoro-1-methyl-1-(2,3,5,6-tetrafluoro-4-methoxybenzyl)-1H-indene* (*6d*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1 - 50:1, v/v) affords the title compound as a pale yellow oil, 33 mg, 49% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.29 (dd, *J* = 9.0, 4.9 Hz, 1H), 6.87 (ddt, *J* = 9.3, 4.6, 2.4 Hz, 2H), 6.54 (d, *J* = 5.6 Hz, 1H), 6.41 (dt, *J* = 5.3, 2.5 Hz, 1H), 4.01 (t, *J* = 1.2 Hz, 3H), 3.13 (dt, *J* = 13.5, 1.8 Hz, 1H), 3.01 (dt, *J* = 13.6, 1.9 Hz, 1H), 1.37 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 162.6 (d, *J* = 243.5 Hz), 146.1 (t, *J* = 1.8 Hz), 145.5 (d, *J* = 2.5 Hz), 145.4 (dm, *J* = 245.9 Hz), 144.9 (dm, *J* = 9.1 Hz), 140.7 (dm, *J* = 247.5 Hz), 136.8 (m), 128.8 (d, *J* = 3.0 Hz), 122.9 (d, *J* = 9.3 Hz), 111.6 (d, *J* = 23.0 Hz), 110.1 (t, *J* = 18.9 Hz), 108.3 (d, *J* = 23.2 Hz), 62.2, 53.6, 30.8, 23.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -116.5 (s, 1F), -142.1 (m, 2F), -158.7 (m, 2F). HRMS (ESI-TOF) calcd for C₁₈H₁₄OF₅ [M+H]⁺ : 341.0959, found: 341.0957.



1,4-dimethyl-1-(2,3,5,6-*tetrafluoro-4-methoxybenzyl*)-*1H-indene* (*6e*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~50:1, v/v) affords the title compound as a pale yellow oil, 43 mg, 64% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.20 (d, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 5.6 Hz, 1H), 6.31 (dt, *J* = 5.3, 2.5 Hz, 1H), 4.01 (d, *J* = 1.5 Hz, 3H), 3.14 (dt, *J* = 13.5, 1.8 Hz, 1H), 2.91 (dt, *J* = 13.5, 1.9 Hz, 1H), 2.36 (s, 3H), 1.33 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.5, 145.6 (dm, *J* = 242.6 Hz), 143.5 (d, *J* = 1.7 Hz), 141.7, 140.7 (dm, *J* = 247.0 Hz), 136.7 (m), 130.5, 128.3, 127.5, 125.4, 119.43, 110.7 (t, *J* = 18.9 Hz), 62.2, 54.1, 30.8 (t, *J* = 1.5 Hz), 22.8, 18.5. ¹⁹F NMR (376 MHz, CDCl₃) δ -141.9 (m, 2F), -158.8 (m, 2F).. HRMS (ESI-TOF) calcd for C₁₉H₁₇OF₄ [M+H]⁺ : 337.1210, found: 337.1211.



1-ethyl-1-(2,3,5,6-tetrafluoro-4-methoxybenzyl)-1H-indene (6f): Purification by column

chromatography on silica gel (petroleum ether/ethyl acetate = $100:1 \sim 50:1$, v/v) affords the title compound as a pale green oil, 34 mg, 50% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.33 (q, *J* = 4.2, 3.4 Hz, 1H), 7.22-7.14 (m, 3H), 6.63 (d, *J* = 5.6 Hz, 1H), 6.25 (dt, *J* = 5.4, 2.6 Hz, 1H), 3.98 (d, *J* = 1.3 Hz, 3H), 3.17 (dt, *J* = 13.5, 1.8 Hz, 1H), 3.04 (dt, *J* = 13.4, 1.8 Hz, 1H), 1.93 (qd, *J* = 7.2, 2.7 Hz, 2H), 0.54 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 148.3, 145.4 (dm, *J* = 244.4 Hz), 144.2, 142.0, 140.5 (dm, *J* = 247.2 Hz), 136.5 (m), 130.9, 127.0, 125.1, 122.3, 121.0, 110.4 (t, *J* = 18.9 Hz), 62.2 (dm, *J* = 3.6 Hz), 58.6, 30.2, 29.6, 8.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -141.7 (m, 2F), -159.1 (m, 2F). HRMS (ESI-TOF) calcd for C₁₉H₁₇OF₄ [M+H]⁺ : 337.1210, found: 337.1210.



1-ethyl-5-methoxy-1-(2,3,5,6-tetrafluoro-4-methoxybenzyl)-1H-indene (**6***g*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~30:1, v/v) affords the title compound as a yellow oil, 35 mg, 48% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.24-7.15 (m, 1H), 6.72 (dq, *J* = 5.1, 2.5 Hz, 2H), 6.57 (d, *J* = 5.6 Hz, 1H), 6.28 (dt, *J* = 5.5, 2.6 Hz, 1H), 3.98 (d, *J* = 1.3 Hz, 3H), 3.79 (s, 3H), 3.20-3.10 (m, 1H), 3.08-2.98 (m, 1H), 1.90 (q, *J* = 7.4 Hz, 2H), 0.55 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 159.2, 145.6, 145.4 (dm, *J* = 245.2 Hz), 143.3 (t, *J* = 1.6 Hz), 140.6 (dm, *J* = 246.8 Hz), 140.3, 136.5 (m), 130.7, 122.8, 110.5 (t, *J* = 18.9 Hz), 110.4, 106.8, 62.1, 57.9, 55.4, 30.3, 29.9, 8.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -141.7 (m, 2F), -159.1 (m, 2F). HRMS (ESI-TOF) calcd for C₂₀H₁₉O₂F₄ [M+H]⁺ : 367.1316, found: 367.1318.



1-methyl-1-((perfluorophenyl)methyl)-1H-indene (6h): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale yellow solid, Mp = 112-114 °C, 38 mg, 62% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.43-7.36 (m, 1H), 7.19 (t, *J* = 4.0 Hz, 3H), 6.59 (d, *J* = 5.6 Hz, 1H), 6.31 (dt, *J* = 5.4, 2.6 Hz, 1H), 3.18 (dt, *J* = 13.5, 2.0 Hz, 1H), 3.07 (dt, *J* = 13.4, 2.0 Hz, 1H), 1.40 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 149.8, 145.3 (dm, *J* = 246.2 Hz), 143.6 (t, *J* = 1.7 Hz), 143.0, 139.7 (dm, *J* = 253.4 Hz), 136.0 (m), 129.8, 127.3, 125.3, 122.1, 121.3, 112.0 (td, *J* = 20.2 Hz), 53.9, 30.8, 23.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -140.1 (m, 2F), -156.9 (t, *J* = 21.0 Hz, 1F), -163.0 (dd, *J* = 21.2, 14.8 Hz, 2F). HRMS (ESI-TOF) calcd for C₁₇H₁₂F₅ [M+H]⁺ : 311.0854, found: 311.0857.



1-methyl-1-(2,3,5,6-*tetrafluorobenzyl*)-*1H-indene* (*6i*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale green oil, 31 mg, 53% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.39 (t, *J* = 4.4 Hz, 1H), 7.20 (d, *J* = 3.1 Hz, 3H), 6.85 (m, 1H), 6.60 (d, *J* = 5.5 Hz, 1H), 6.33 (dt, *J* = 5.6, 2.6 Hz, 1H), 3.22 (m, 1H), 3.05 (m, 1H), 1.39 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.2, 145.7 (dm, *J* = 246.0 Hz), 145.0 (dm, *J* = 249.4 Hz), 143.9 (t, *J* = 1.6 Hz), 143.0, 129.5, 127.2, 125.3, 122.1, 121.3, 118.2 (t, *J* = 18.2 Hz), 104.2 (t, *J* = 22.6 Hz), 54.0, 31.4, 23.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -140.0 (m, 2F), -140.7 (m, 2F). HRMS (ESI-TOF) calcd for C₁₇H₁₃F₄ [M+H]⁺ : 293.0948, found: 293.0950.



2,4,5-trifluoro-3-((1-methyl-1H-inden-1-yl)methyl)benzonitrile (**6j**): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale green oil, 24 mg, 40% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.30 (m, 1H), 7.16-7.07 (m, 4H), 6.51 (d, *J* = 5.5 Hz, 1H), 6.24 (dt, *J* = 5.5, 2.7 Hz, 1H), 3.11 (qt, *J* = 13.3, 1.7 Hz, 2H), 1.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 158.5 (dm, *J* = 254.9 Hz), 152.6 (dm, *J* = 260.4 Hz), 149.3, 146.7 (dm, *J* = 250.4 Hz), 143.2, (t, *J* = 1.6 Hz), 142.9, 130.1, 128.9, 127.4, 125.4, 122.2, 121.3, 118.7 (dd, *J* = 20.8, 17.7 Hz), 118.3 (dt, *J* = 21.7, 2.1 Hz), 112.7, 96.5 (m), 54.0, 31.3, 23.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -108.1 (dd, *J* = 14.2, 7.5 Hz, 1F), -122.8 (dd, *J* = 22.1, 7.6 Hz, 1F), -138.7 (dd, *J* = 21.9, 14.3 Hz, 1F). HRMS (ESI-TOF) calcd for C₁₈H₁₃F₃N [M+H]⁺ : 300.0995, found: 300.0997.



tert-butyldimethyl((2,3,5,6-*tetrafluoro*-4-((1-*methyl*-1H-*inden*-1-*yl*)*methyl*)*benzyl*)*oxy*)*silane* (**6***k*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a pale yellow oil, 59 mg, 67% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.32 (m, 1H), 7.16-7.04 (m, 3H), 6.52 (d, *J* = 5.6 Hz, 1H), 6.26 (dt, *J* = 5.3, 2.5 Hz, 1H), 4.65 (t, *J* = 1.6 Hz, 2H), 3.14 (dt, *J* = 13.3, 1.8 Hz, 1H), 2.95 (dt, *J* = 13.2, 1.8 Hz, 1H), 1.31 (s, 3H), 0.81 (s,

9H), -0.00 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 150.3, 144.7 (dm, J = 247.2 Hz), 143.9, 143.0, 129.5, 127.2, 125.3, 122.1, 121.3, 117.0 (td, J = 17.8, 6.5 Hz), 54.0, 53.4 (t, J = 2.6 Hz), 31.3 (t, J = 1.9 Hz), 25.8 (d, J = 3.6 Hz), 22.9, 18.5, -5.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -141.3 (dd, J = 23.0, 13.1 Hz, 2F), -145.5 (dd, J = 22.8, 13.1 Hz, 2F). HRMS (ESI-TOF) calcd for C₂₄H₂₉OSiF₄ [M+H]⁺ : 437.1918, found: 437.1922.



1-methyl-1-(2,3,5,6-*tetrafluoro-4-((1-methyl-1H-inden-1-yl)methyl)benzyl)-1H-indene* (6*l*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1~10:1, v/v) affords the title compound as a pale yellow oil, 28 mg, 32% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.29 (dd, J = 8.9, 6.4 Hz, 2H), 7.22-7.13 (m, 6H), 6.56 (dd, J = 17.1, 5.6 Hz, 2H), 6.27 (d, J = 5.5 Hz, 2H), 3.10 (dd, J = 13.3, 6.9 Hz, 2H), 2.96 (dd, J = 13.2, 9.5 Hz, 2H), 1.33 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 150.2 (d, J = 34.0 Hz), 144.6 (dm, J = 249.7 Hz), 144.1 (d, J = 6.0 Hz), 143.0 (d, J = 3.3 Hz), 129.3 (d, J = 2.7 Hz), 127.1 (d, J = 4.3 Hz), 125.2, 122.1 (d, J = 7.0 Hz), 121.2 (d, J = 7.0 Hz), 115.2 (m), 54.0 (d, J = 2.4 Hz), 31.2, 22.7 (d, J = 4.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -141.9 (d, J = 18.5 Hz, 4F). HRMS (ESI-TOF) calcd for C₂₈H₂₃F₄ [M+H]⁺ : 435.1730, found: 435.1739.



1-(4-(tert-butoxy)-2,3,5,6-tetrafluorobenzyl)-1-methyl-2,3-diphenyl-1H-indene (7): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~50:1, v/v) affords the title compound as a pale yellow solid, Mp = 123-125 °C, 88 mg, 85% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.20 (m, 12H), 7.12 (td, *J* = 7.4, 1.3 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 3.14 (dt, *J* = 13.6, 1.6 Hz, 1H), 2.98 (dt, *J* = 13.5, 1.7 Hz, 1H), 1.58 (s, 3H), 1.35 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 151.1, 149.9, 145.6 (dm, *J* = 243.2 Hz), 143.3 (dm, *J* = 244.3 Hz), 143.1, 139.6, 136.3, 135.0, 132.5 (t, *J* = 13.8 Hz), 130.2, 129.6, 128.3, 128.2, 127.23 (d, *J* = 2.6 Hz), 127.17, 125.4, 122.3, 120.8, 112.2 (t, *J* = 18.8 Hz), 84.7, 55.2, 31.5, 28.4 (t, *J* = 1.8 Hz), 22.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -140.5 (m, 2F), -152.6 (m, 2F). HRMS (ESI-TOF) calcd for C₃₃H₂₉OF₄ [M+H]⁺ : 517.2149, found: 517.2151.



1-methyl-2,3-diphenyl-1-(2,3,5,6-tetrafluoro-4-phenoxybenzyl)-1H-indene (8): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~50:1, v/v) affords the title compound as a colorless solid, Mp = 162-164 °C, 99 mg, 92% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.25-7.05 (m, 15H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 2H), 3.09 (d, *J* = 13.5 Hz, 1H), 2.95 (d, *J* = 13.5 Hz, 1H), 1.52 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.3, 150.8, 149.9, 145.8 (dm, *J* = 238.5 Hz), 143.1, 141.3 (dm, *J* = 250.8 Hz), 139.8, 136.2, 134.9, 131.8 (t, *J* = 13.1 Hz), 130.1, 129.7 (d, *J* = 26.0 Hz), 128.2 (d, *J* = 18.2 Hz), 127.3, 125.5, 123.7, 122.3, 120.9, 115.4, 113.5 (t, *J* = 18.6 Hz), 55.2, 31.6, 22.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -138.6 (m, 2F), -155.2 (m, 2F). HRMS (ESI-TOF) calcd for C₃₅H₂₅F₄O [M+H]⁺ : 537.1836, found: 537.1837.



I-(2,3,5,6-tetrafluoro-4-((*1*-methyl-2,3-diphenyl-1H-inden-1-yl)methyl)phenyl)-1H-imidazole (**9**): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~50:1, v/v) affords the title compound as a yellow solid, Mp = 125-127 °C, 89 mg, 87% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.64 (s, 1H), 7.27-7.06 (m, 15H), 6.89 (d, *J* = 7.4 Hz, 1H), 3.12 (d, *J* = 13.5 Hz, 1H), 3.01-2.90 (m, 1H), 1.54 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.5, 149.7, 145.7 (dm, *J* = 252.6 Hz), 142.9, 140.7 (dm, *J* = 248.8 Hz), 139.9, 137.7 (t, *J* = 3.2 Hz), 136.0, 134.7, 130.0, 129.5, 128.3, 128.2, 127.4, 127.3 (d, *J* = 3.6 Hz), 125.6, 122.0, 121.1, 120.0 (t, *J* = 2.3 Hz), 117.3 (t, *J* = 18.5 Hz), 115.3 (t, *J* = 13.4 Hz), 55.0, 31.7, 22.2, 1.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -136.7 (m, 2F), -149.7 (m, 2F). HRMS (ESI-TOF) calcd for C₃₂H₂₃N₂F₄ [M+H]⁺ : 511.1792, found: 511.1797.



1-(2,3,5,6-tetrafluoro-4-((1-methyl-2,3-diphenyl-1H-inden-1-yl)methyl)phenyl)-1H-indole (10): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~50:1,

v/v) affords the title compound as a pale brown solid, Mp = 129-131 °C, 69 mg, 62% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.39-7.16 (m, 16H), 7.04 (d, *J* = 7.6 Hz, 2H), 6.76 (d, *J* = 3.3 Hz, 1H), 3.26 (d, *J* = 13.4 Hz, 1H), 3.12 (d, *J* = 13.4 Hz, 1H), 1.68 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.7, 149.9, 145.9 (dm, *J* = 257.8 Hz), 143.1, 142.7 (dm, *J* = 252.6 Hz), 139.9, 136.4, 136.2, 134.9, 130.2, 129.7, 128.8, 128.4, 128.2, 127.4, 127.3, 125.6, 123.2, 122.2, 121.3 (d, *J* = 5.7 Hz), 121.1, 116.9 (t, *J* = 18.7 Hz), 110.5, 105.4, 55.3, 31.9, 22.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -137.7 (t, *J* = 31.0 Hz, 2F), -147.3 (d, *J* = 25.1 Hz, 2F). HRMS (ESI-TOF) calcd for C₃₇H₂₆F₄N [M+H]⁺ : 560.1996, found: 560.1989.



1-(4-benzyl-2,3,5,6-tetrafluorobenzyl)-1-methyl-2,3-diphenyl-1H-indene (11): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~50:1, v/v) affords the title compound as a colorless solid, Mp = 112-114 °C, 83 mg, 78% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.31-7.18 (m, 17H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 4.00 (s, 2H), 3.13 (d, *J* = 13.4 Hz, 1H), 2.92 (d, *J* = 13.4 Hz, 1H), 1.57 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 151.2, 149.9, 145.2 (dm, *J* = 248.4 Hz), 144.6 (dm, *J* = 249.4 Hz), 143.0, 139.5, 138.0, 136.3, 135.0, 130.1, 129.7, 128.8, 128.5, 128.3, 128.2, 127.2 (t, *J* = 3.2 Hz), 126.9, 125.4, 122.4, 120.9, 117.8 (t, *J* = 18.7 Hz), 115.6 (t, *J* = 18.4 Hz), 55.2, 31.6, 28.7, 22.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -139.5 (dd, *J* = 22.9, 12.5 Hz, 2F), -144.8 (dd, *J* = 22.9, 12.6 Hz, 2F). HRMS (ESI-TOF) calcd for $C_{36}H_{27}F_4$ [M+H]⁺: 535.2043, found: 535.2041.



1-(*5*-(2,3,5,6-tetrafluoro-4-((*1*-methyl-2,3-diphenyl-1H-inden-1-yl)methyl)phenyl)thiophen-2-yl)et han-1-one (*12*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~30:1, v/v) affords the title compound as a yellow solid, Mp = 131-133 °C, 76 mg, 67% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, J = 4.1 Hz, 1H), 7.49 (d, J = 4.0 Hz, 1H), 7.27-7.15 (m, 12H), 7.09 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 7.4 Hz, 1H), 3.13 (d, J = 13.4 Hz, 1H), 2.51 (d, J = 13.4 Hz, 1H), 2.52 (s, 3H), 1.53 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 190.9, 150.9, 149.7, 145.9 (dm, J = 244.8 Hz), 145.5, 143.6 (dm, J = 247.9 Hz), 142.9, 139.7, 136.2, 134.9, 132.1, 130.8 (t, J = 6.3 Hz), 130.1, 139.6, 128.3, 128.2, 127.3 (t, J = 2.3 Hz), 125.6, 122.3, 121.0, 117.7 (t, J = 18.7 Hz), 111.8 (t, J = 14.3 Hz), 55.2, 31.6, 27.1, 22.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -138.4 (q, J = 10.2 Hz, 2F), -140.2 (m, 2F). HRMS (ESI-TOF) calcd for C₃₅H₂₅F₄OS [M+H]⁺ : 569.1557, found: 569.1561.

8. Crystallographic Data of 4b



structure of 4b CCDC: 2413247

Datablock:

Bond precision:	C-C = 0.0056 A	١	Navelength = 0.71073
Cell:	a = 10.584(2)	b=13.468(3)	c=19.022(4)
	alpha=76.198(4)	beta=85.461(4)	gamma=77.856(4)
Temperature:	296 K		
	Calculated	Rep	orted
Volume	2573.1(9)	257	72.9(9)
Space group	р -1	р	-1
Hall group	-1 p	-1	р
Moiety formula	2(C30 H21F5), C20	C12	
Sum formula	C62 H42 C12 F10	С	62 H42 C12 F10
Mr	1047.86		1047.85
Dx,g cm-3	1.352	1.	353
Z	2	2	2
Mu (mm-1)	0.203		0.203
F000	1076.0		1076.0
F000'	1077.23		
h,k,lmax	12,16,22		12,16,22
Nref	9066		9013
Tmin,Tmax			
Tmin'			
Correction method =	Not given		
Data completeness =	= 0.994	Theta (max) = 24	.998
R (reflections) = 0.0	0863(6052)	wR2 (reflections	s) = 0.2554(9013)
S = 1.423		Npar = 671	

Datablock 20241105A_0m_a - ellipsoid plot



The product **4b** was recrystallized in dichloromethane, and the crystal structure of **4b** containing dichloromethane was confirmed by the X-ray crystallographic analysis. In addition, **4b** contains a quaternary carbon center and is racemic.

9. Reference

- (1) Li, J.; Chen, J.; Wang, L.; Shi, Y. Org. Lett. 2021, 23, 3646-3651.
- (2) Huang, Q.; Larock, R. C. J. Org. Chem. 2003, 68, 7342.
- (3) Yao, T.; Zhang, H.; Zhao, Y. Org. Lett. 2016, 18, 2532.
- (4) Emer, E.; Pfeifer, L.; Brown, J. M.; Gouverneur, V. Angew. Chem. Int. Ed. 2014, 53, 4181.
- (5) Lou, Z.; Zhang, S.; Chen, C.; Pang, X.; Li, M.; Wen, L. Adv. Synth. Catal. 2014, 356, 153.
- (6) Jia, X.; Petrone, D. A.; Lautens, M. Angew. Chem. Int. Ed. 2012, 51, 9870.





^{150 140 130 120} -10 110 100 f1 (ppm)

¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **4a**

|--|

N20240624-FC2401-WXX-YAO-F.2.fid



0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)

¹H NMR (400 MHz, CDCl₃) Spectrum of $\mathbf{4b}$



-1 110 100 fl (ppm)

19 F NMR (376 MHz, CDCl₃) Spectrum of **4b**



N20240415-FC1134-WXX-PHBI-311.2.fid



-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)

¹H NMR (400 MHz, CDCl₃) Spectrum of 4c



160 150 140 130 80 70 60 -10 110 100 f1 (ppm)

^{19}F NMR (376 MHz, CDCl₃) Spectrum of 4c



N20240423-FC1318-WXX-YAO-314.2.fid



-10 -20 -30 -40 -50 -60 -70 -80 -90 -10 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)

^1H NMR (400 MHz, CDCl₃) Spectrum of 4d


^{19}F NMR (376 MHz, CDCl₃) Spectrum of 4d



¹H NMR (400 MHz, CDCl₃) Spectrum of **4e**



150 140 130 120 110 100 f1 (ppm) -10

$^{19}\mathrm{F}\,\mathrm{NMR}$ (376 MHz, CDCl₃) Spectrum of $4\mathrm{e}$





¹H NMR (400 MHz, CDCl₃) Spectrum of 4f

^{19}F NMR (376 MHz, CDCl₃) Spectrum of **4f**







170 160 150 140 130 120 70 60 110 100 f1 (ppm) -10

^{19}F NMR (376 MHz, CDCl₃) Spectrum of 4g



N20240415-FC1134-WXX-PHBI-310.2.fid







150 140 130 110 100 f1 (ppm) -10

$^{19}\mathrm{F}\,\mathrm{NMR}$ (376 MHz, CDCl₃) Spectrum of 4h

N20240521-FC1834-WXX-YAO-316.2.fid









¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **4i**



N20240428-FC1429-WXX-YAO-317.3.fid







150 140 130 120 -10 110 100 f1 (ppm)

$^{19}\mathrm{F}\,\mathrm{NMR}$ (376 MHz, CDCl₃) Spectrum of 4j



¹H NMR (400 MHz, CDCl₃) Spectrum of **4**k



150 140 130 120 -10 110 100 f1 (ppm)

$^{19}\mathrm{F}\,\mathrm{NMR}$ (376 MHz, CDCl₃) Spectrum of 4k

165 187 227 248	595 651 707 707 002 002 080 080 119 140	
8 8 8 8 8		
<u> </u>	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	
\checkmark		

N20240411-FC1080-WXX-YAO-306.2.fid



¹H NMR (400 MHz, CDCl₃) Spectrum of **4**l



160 150 140 130 120 70 60 210 200 110 100 f1 (ppm) -10

$^{19}\mathrm{F}\,\mathrm{NMR}$ (376 MHz, CDCl₃) Spectrum of **4**l



N20240322-FC0744-WXX-YAO-293.3.fid













210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)

$^{19}\mathrm{F}\,\mathrm{NMR}$ (376 MHz, CDCl₃) Spectrum of $4\mathrm{m}$



¹H NMR (400 MHz, CDCl₃) Spectrum of **4n**



70 60 170 160 150 140 130 120 -10 110 100 f1 (ppm)

$^{19}\mathrm{F}\,\mathrm{NMR}$ (376 MHz, CDCl₃) Spectrum of 4n

230	252	292	313	212	267	323	747	768	808	826	864	886	
œ	œ	ø	œ	ģ	ģ	ģ	N	<u>N</u>	<u>N</u>	N	<u>N</u>	<u>N</u>	
65	e,	()	e o	ų)	40	u)	e	e	e	e	e	e	
5	5	5	5	5	5	5	5	5	5	5	5	5	
- ÷.	- t.	- S.	- 11	÷.	- S.		÷.	- C.		- ÷.	- C.		
	~	2	~		_		~ ~		~ .	2	ے	_	
		~					_		_				

N20240709-FC2699-WXX-YAO-299.2.fid



¹H NMR (400 MHz, CDCl₃) Spectrum of 40



160 150 140 130 120 110 100 f1 (ppm) 70 60 -10

¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **40**

341 351 372 412 433 442	728 840 840 439 461 499 517 524 527 575
138.62	-155.155.155.155.155.155.155.155.155.155
	\lor

N20240402-FC0000-WXX-YAO-300.3.fid



¹H NMR (400 MHz, CDCl₃) Spectrum of **4p**



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

^{19}F NMR (376 MHz, CDCl₃) Spectrum of 4p



N20240407-FC0898-WXX-YAO-303.2.fid





1 H NMR (400 MHz, CDCl₃) Spectrum of **4**q

¹³C NMR (101 MHz, CDCl₃) Spectrum of **4**q

1445.365 1445.525 1445.527 1445.533 1445.533 1445.533 1445.533 1445.533 1445.533 1445.533 1445.633 1445.637 1435.667 1335.657 1335.757 1335.757 1335.757 1335.757 1335.757 1335.757 1335.757 1335.757 1335.757 1335.757 1335.757 1335.757 1335.757 1335.757 1355.7577 1355.7577 1355.7577 1355.7577 1355.75777 1355.75777 1355.757777 1355.75777777777777777777777777777777777	77.477 77.160 76.843	— 54.311	
---	----------------------------	----------	--

N20240712-FC2747-WXX-YAO-301.1.fid



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

^{19}F NMR (376 MHz, CDCl₃) Spectrum of 4q









^{19}F NMR (376 MHz, CDCl₃) Spectrum of 4r



N20240407-FC0898-WXX-YAO-302.2.fid







N20240407-FC0898-WXX-YAO-304.1.fid



-10 110 100 f1 (ppm)

¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **4s**

-138.815 -138.825 -138.828 -138.836 -138.891 -138.898 -157.426 -157.481 -157.481 -157.481 -157.481 -157.481 -157.481 -153.723

N20240407-FC0898-WXX-YAO-304.2.fid







210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)

$^{19}\mathrm{F}\,\mathrm{NMR}$ (376 MHz, CDCl₃) Spectrum of **4t**



N20250220-FC0335-YAO-500.2.fid



¹H NMR (400 MHz, CDCl₃) Spectrum of 4u



^{70 60} 150 140 130 120 110 100 f1 (ppm) -10

^{19}F NMR (376 MHz, CDCl₃) Spectrum of 4u



N20241213-FC4745-YAO-305-1.2.fid










13 C NMR (101 MHz, CDCl₃) Spectrum of 4v



N20250220-FC0335-YAO-501.1.fid



200 190 180 170 -10 110 100 f1 (ppm)



485 507 547 568	530 586 641 820 877 877 877
138. 138. 138. 138.	156. 156. 162.
- 1. 1. 1. 1 1 1.	- 11 11 11 11 11 11 11
\checkmark	$\neg \neg \lor$

N20250220-FC0335-YAO-501.2.fid









^{19}F NMR (376 MHz, CDCl₃) Spectrum of 4w



N20240315-FC0597-WXX-YAO-289.2.fid



¹H NMR (400 MHz, CDCl₃) Spectrum of 4x



150 140 130 110 100 f1 (ppm) -10

^{19}F NMR (376 MHz, CDCl₃) Spectrum of 4x



N20240507-FC1537-WXX-PHOI-330.3.fid



¹H NMR (400 MHz, CDCl₃) Spectrum of 4y



70 60 150 140 130 120 -10 110 100 f1 (ppm)

^{19}F NMR (376 MHz, CDCl₃) Spectrum of 4y



N20240428-FC1429-WXX-YAO-319.3.fid



¹H NMR (400 MHz, CDCl₃) Spectrum of 4z



^{70 60} 150 140 130 120 110 100 f1 (ppm) -10

^{19}F NMR (376 MHz, CDCl₃) Spectrum of 4z



N20240712-FC2747-WXX-YAO-332.2.fid







150 140 130 -10 110 100 f1 (ppm)

^{19}F NMR (376 MHz, CDCl₃) Spectrum of **4aa**



N20240724-FC2906-WXX-YAO-336.3.fid





¹H NMR (400 MHz, CDCl₃) Spectrum of **4ab**

150 140 130 120 -10 110 100 f1 (ppm)

$^{19}\mathrm{F}\,\mathrm{NMR}$ (376 MHz, CDCl_3) Spectrum of 4ab



¹H NMR (400 MHz, CDCl₃) Spectrum of 4ac



¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **4ac**



¹H NMR (400 MHz, CDCl₃) Spectrum of 4ad



150 140 130 120 70 60 110 100 f1 (ppm) -10

$^{19}\mathrm{F}\,\mathrm{NMR}$ (376 MHz, CDCl_3) Spectrum of 4ad





¹H NMR (400 MHz, CDCl₃) Spectrum of **4ae**





N20241126-FC0000-YAO-452.1.fid



150 140 130 120 -10 110 100 f1 (ppm)

$^{19}\mathrm{F}$ NMR (376 MHz, CDCl₃) Spectrum of **4ae**



N20241126-FC0000-YAO-452.2.fid



¹H NMR (400 MHz, CDCl₃) Spectrum of **6a**



¹³C NMR (101 MHz, CDCl₃) Spectrum of **6a**

150.338 446.759 446.759 446.759 446.759 446.759 446.759 444.6519 444.6519 444.277 444.1959 444.1959 444.1959 444.1959 444.1959 444.1959 444.1959 444.1959 444.1959 444.1959 444.1955 44555 44555 44555 445555 445555 44555555	77.479 77.161 76.844	62.165	53.984	30.794 30.777 30.759 22.852
	\checkmark			\vee 1

N20241111-FC4178-YAO-404.1.fid



150 140 130 120 110 100 f1 (ppm) -10

$^{19}\mathrm{F}$ NMR (376 MHz, CDCl₃) Spectrum of **6a**



N20241111-FC4178-YAO-404.2.fid



¹H NMR (400 MHz, CDCl₃) Spectrum of **6b**



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **6b**

-141.927 -141.927 -141.937 -141.933 -142.010 -142.010 -142.010 -158.864 -158.864 -158.864 -158.864 -158.960 -158.960

N20241024-FC3919-WXX-YAO-425.2.fid



¹H NMR (400 MHz, CDCl₃) Spectrum of **6c**



S96

¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **6c**

-141.996 -142.003 -142.003 -142.058 -142.058 -142.078 -158.558 -158.5

N20241101-FC4071-YAO-423.3.fid







^{80 70 60} 210 200 150 140 130 120 -10 110 100 f1 (ppm)

¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **6d**



N20241101-FC4071-YAO-424.3.fid



¹H NMR (400 MHz, CDCl₃) Spectrum of **6e**



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

$^{19}\mathrm{F}\,\mathrm{NMR}$ (376 MHz, CDCl₃) Spectrum of **6e**



N20241028-FC3950-YAO-428.2.fid





¹H NMR (400 MHz, CDCl₃) Spectrum of **6f**

80 70 60 210 200 150 140 130 120 -10 110 100 f1 (ppm)

$^{19}\mathrm{F}\,\mathrm{NMR}$ (376 MHz, CDCl₃) Spectrum of **6f**







210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)

$^{19}\mathrm{F}$ NMR (376 MHz, CDCl₃) Spectrum of **6g**





1 H NMR (400 MHz, CDCl₃) Spectrum of **6h**

¹³C NMR (101 MHz, CDCl₃) Spectrum of **6h**



N20241113-FC4232-YAO-F5.1.fid

10 0

-10

-20 -30 -40 -50



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)

¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **6h**



-80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)

-60 -70





160 150 140 130 120 110 100 f1 (ppm) 210 200 -10
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **6i**







¹H NMR (400 MHz, CDCl₃) Spectrum of **6j**

150 140 130 120 -10 110 100 f1 (ppm)

$^{19}\mathrm{F}\,\mathrm{NMR}$ (376 MHz, CDCl₃) Spectrum of 6j

-108.075 -108.095 -108.112 -108.132	-122.809 -122.848 -122.868	-138.650 -138.688 -138.708 -138.708 -138.746
--	----------------------------------	--

N20241101-FC4071-YAO-420.3.fid





¹H NMR (400 MHz, CDCl₃) Spectrum of 6k





N20241104-FC3568-YAO-430.1.fid



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

$^{19}\mathrm{F}\,\mathrm{NMR}$ (376 MHz, CDCl₃) Spectrum of 6k



N20241104-FC3568-YAO-430.2.fid







210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)

$^{19}\mathrm{F}\,\mathrm{NMR}$ (376 MHz, CDCl₃) Spectrum of **6**l



1 H NMR (400 MHz, CDCl₃) Spectrum of **7**





150 140 130 120 -10 210 200 70 60 110 100 f1 (ppm)

^{19}F NMR (376 MHz, CDCl₃) Spectrum of **7**





¹H NMR (400 MHz, CDCl₃) Spectrum of $\mathbf{8}$





160 150 140 130 120 -10 110 100 f1 (ppm)

$^{19}\mathrm{F}\,\mathrm{NMR}$ (376 MHz, CDCl₃) Spectrum of $\mathbf{8}$



N20241115-FC4274-YAO-451.2.fid



¹H NMR (400 MHz, CDCl₃) Spectrum of **9**



160 150 140 130 120 210 200 -10 110 100 f1 (ppm)

^{19}F NMR (376 MHz, CDCl₃) Spectrum of $\boldsymbol{9}$





¹H NMR (400 MHz, CDCl₃) Spectrum of 10



150 140 130 120 110 100 f1 (ppm) -10

19 F NMR (376 MHz, CDCl₃) Spectrum of **10**



N20241125-FC4425-YAO-453-1.2.fid

10



¹H NMR (400 MHz, CDCl₃) Spectrum of **11**





150 140 130 -10 110 100 f1 (ppm)

$^{19}\mathrm{F}\,\mathrm{NMR}$ (376 MHz, CDCl₃) Spectrum of **11**



¹H NMR (400 MHz, CDCl₃) Spectrum of 12



150 140 130 110 100 f1 (ppm) -10

$^{19}\mathrm{F}$ NMR (376 MHz, CDCl₃) Spectrum of **12**



N20240729-FC2961-WXX-YAO-337.3.fid



¹H NMR (400 MHz, CDCl₃) Spectrum of by-product **6'**

