Supporting Information

Palladium-catalyzed synthesis of indene-1-acetates via sequential double carbopalladation and aryloxycarbonylation

Fei Sun,[‡] Yiyi Zheng,[‡] Zhongyao Jiang, Mingxia Wu, Zeng Lv, Hongsen Ji, and Xin-Xing Wu* College of Chemistry and Chemical Engineering, Nantong University, Nantong 226019, P. R. China

Email: wuxinxng@163.com

[‡]F. S. and Y. Z. contributed equally.

Table of Contents

1. General considerations	S2
2. Preparation of substrates	S2
3. Experiment procedure	S2
4. Scale-up reaction	S2-S3
5. Synthetic transformations of 4a	S 3
6. Spectra data	S4-S22
7. Crystallographic data of 4aj	S23
8. Reference	S24
9. NMR spectra	S25-S78

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.⁶⁻⁸ Substrates **3** were synthesized according to the known literature.⁹

3. Experiment procedure



O-iodostyrenes **1** (0.2 mmol, 1.0 equiv), internal alkynes **2** (0.4 mmol, 2.0 equiv), formates **3** (0.6 mmol, 3.0 equiv), Pd(MeCN)₂Cl₂ (10 mol%), xphos (20 mol%), K₂CO₃ (0.6 mmol, 3.0 equiv) were added to a sealed tube, DME (1.0 mL) were added via syringe. The mixture was heated at 70 °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 **4** or **5**.

4. Scale-up reaction



1-iodo-2-(prop-1-en-2-yl)benzene **1a** (4.0 mmol, 976 mg, 1.0 equiv), 1,2-diphenylethyne **2a** (8.0 mmol, 1.424 g, 2.0 equiv), phenyl formate **3a** (12.0 mmol, 1.464 g, 3.0 equiv), Pd(MeCN)₂Cl₂ (10 mol%, 103.6 mg), xphos (20 mol%, 381.3 mg), K₂CO₃ (12.0 mmol, 1.656 mg, 3.0 equiv) were added to a sealed tube, DME (20.0 mL) were added via syringe. The mixture was heated at 70 °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** in 52% yield.

5. Synthetic transformations of 4a



N-butyl-2-(1-methyl-2,3-diphenyl-1H-inden-1-yl)acetamide (6) was synthesized according to the following procedure. To a solution of **4a** (0.2 mmol) in 1 mL ^{*n*}BuNH₂ was added La(OTf)₃ (6 mg, 5 mol%). The reaction mixture was stirred at 50 °C for 4 h. After cooling at room temperature, the mixture was extracted with ethyl acetate, dried with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified through silica gel chromatography (petroleum ether/EtOAc = 5:1) to give amide **6** with 79% yield.

N-benzyl-2-(1-methyl-2,3-diphenyl-1H-inden-1-yl)acetamide (**7**) was synthesized according to the following procedure. To a solution of **4a** (0.2 mmol) in 1 mL BnNH₂ was added La(OTf)₃ (6 mg, 5 mol%). The reaction mixture was stirred at 50 °C for 4 h. After cooling at room temperature, the mixture was extracted with ethyl acetate, dried with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified through silica gel chromatography (petroleum ether/EtOAc = 5:1) to give amide **7** with 84% yield.

2-(1-methyl-2,3-diphenyl-1H-inden-1-yl)ethan-1-ol (8) was synthesized according to the following procedure. To a solution of 4a (0.2 mmol, 84 mg) in THF (2.0 mL) was added LiAlH₄ (0.6 mmol, 22.8 mg, 3.0 equiv) at 0 °C under air. Then the reaction mixture was allowed to room temperature, and stirred for 1 h. The reaction mixture was filtered through Celite. The solvent in the filtrate was evaporated under reduced pressure, and the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1-5:1, v/v) to afford the pure product 8 with 91% yield.



phenyl 2-(*1-methyl-2,3-diphenyl-1H-inden-1-yl*)*acetate* (*4a*): 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 oil, 51 mg, 61% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.52-7.48 (m, 1H), 7.30 (dd, J = 6.3, 2.6 Hz, 1H), 7.27-7.12 (m, 14H), 7.03 (t, J = 7.5 Hz, 1H), 6.52-6.40 (m, 2H), 2.98 (q, J = 13.8 Hz, 2H), 1.50 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.1, 150.5, 150.1, 149.4, 143.7, 140.2, 136.1, 134.8, 130.4, 129.6, 129.4, 128.3, 128.2, 127.4, 127.3, 127.2, 125.80, 125.77, 122.7, 121.5, 121.0, 53.5, 41.7, 24.4. HRMS (ESI-TOF) calcd for C₃₀H₂₅O₂ [M+H]⁺ : 417.1849, found: 417.1854.



phenyl 2-(*1*,6-*dimethyl*-2,3-*diphenyl*-1*H*-*inden*-1-*yl*)*acetate* (**4b**): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $30:1\sim10:1$, v/v) affords the title compound as a yellow oil, 46 mg, 54% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, *J* = 1.5 Hz, 1H), 7.32-7.18 (m, 13H), 7.14-7.08 (m, 2H), 6.57 (dd, *J* = 8.0, 1.6 Hz, 2H), 3.08-2.97 (m, 2H), 2.43 (s, 3H), 1.56 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.2, 150.6, 149.7, 149.1, 141.1, 140.0, 136.2, 135.5, 135.0, 130.5, 129.6, 129.4, 128.2, 128.12, 128.05, 127.2, 127.1, 125.7, 123.6, 121.5, 120.7, 53.3, 41.8, 24.5, 21.8. HRMS (ESI-TOF) calcd for C₃₁H₂₇O₂ [M+H]⁺ : 431.2006, found: 431.2009.



phenyl 2-(6-*fluoro-1-methyl-2,3-diphenyl-1H-inden-1-yl)acetate* (**4***c*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $30:1 \sim 10:1$, v/v) affords the title compound as a yellow solid, Mp = 98-100 °C, 49 mg, 57% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.26 (m, 7H), 7.25-7.21 (m, 7H), 7.15-7.11 (m, 1H), 7.04-6.98 (m, 1H), 6.67-6.60 (m, 2H), 3.09-2.98 (m, 2H), 1.56 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.9, 162.1 (d, *J* = 245.7 Hz), 151.8 (d, *J* = 7.7 Hz), 150.4, 149.7 (d, *J* = 4.1 Hz), 139.5 (d, *J* = 2.3 Hz), 139.4, 135.8, 134.6,

130.4, 129.51, 129.47, 128.33, 128.25, 127.4, 127.3, 125.9, 121.7 (d, J = 8.4 Hz), 121.5, 114.0 (d, J = 22.5 Hz), 110.5 (d, J = 23.5 Hz), 53.4 (d, J = 2.1 Hz), 41.6, 24.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -116.43. HRMS (ESI-TOF) calcd for C₃₀H₂₄FO₂ [M+H]⁺ : 435.1755, found: 435.1755.



phenyl 2-(6-*chloro-1-methyl-2,3-diphenyl-1H-inden-1-yl)acetate* (*4d*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $30:1 \sim 10:1$, v/v) affords the title compound as a yellow oil, 45 mg, 50% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.55-7.54 (m, 1H), 7.27 (q, *J* = 7.2, 6.1 Hz, 8H), 7.22 (d, *J* = 8.0 Hz, 6H), 7.15-7.11 (m, 1H), 6.67-6.64 (m, 2H), 3.03 (q, *J* = 14.2 Hz, 2H), 1.56 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.8, 151.4, 150.40, 150.39, 142.2, 139.5, 135.6, 134.4, 131.7, 130.3, 129.5, 128.4, 128.3, 127.5, 127.4, 125.9, 123.2, 121.9, 121.5, 53.5, 41.5, 24.2. HRMS (ESI-TOF) calcd for C₃₀H₂₄ClO₂ [M+H]⁺ : 451.1459, found: 451.1466.



phenyl 2-(1-*methyl*-2,3-*diphenyl*-6-(*trifluoromethyl*)-1H-*inden*-1-*yl*)*acetate* (4e): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1 - 10:1, v/v) affords the title compound as a pale red oil, 49 mg, 51% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, J = 1.6 Hz, 1H), 7.59 (dd, J = 8.1, 1.6 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 4.7 Hz, 5H), 7.25-7.21 (m, 7H), 7.15-7.11 (m, 1H), 6.60 (dd, J = 7.8, 1.6 Hz, 2H), 3.15 (d, J = 14.4 Hz, 1H), 3.04 (d, J = 14.3 Hz, 1H), 1.60 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.7, 153.0, 150.3, 150.1, 147.3, 139.6, 135.4, 134.1, 130.1, 129.50, 129.49, 128.4 (d, J = 7.7 Hz), 127.7, 127.5, 125.9, 124.9 (d, J = 4.0 Hz), 121.4, 121.0, 119.5 (d, J = 3.9 Hz), 53.6, 41.3, 24.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -61.32. HRMS (ESI-TOF) calcd for C₃₁H₂₄F₃O₂ [M+H]⁺ : 485.1723, found: 485.1731.



phenyl 2-(1-ethyl-5-methoxy-2,3-diphenyl-1H-inden-1-yl)acetate (4f): Purification by column

chromatography on silica gel (petroleum ether/ethyl acetate = $20:1 \sim 10:1$, v/v) affords the title compound as a pale yellow viscous oil, 53 mg, 58% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, J = 8.1 Hz, 1H), 7.23-7.11 (m, 12H), 7.05-6.99 (m, 1H), 6.83 (d, J = 2.4 Hz, 1H), 6.77 (dd, J = 8.2, 2.5 Hz, 1H), 6.53-6.47 (m, 2H), 3.71 (s, 3H), 2.97 (s, 2H), 1.98 (q, J = 7.2 Hz, 2H), 0.58 (t, J = 7.2 Hz, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.1, 159.6, 150.5, 148.5, 146.4, 139.5, 136.2, 130.1, 129.7, 129.4, 128.3, 128.2, 127.3, 127.2, 125.7, 123.1, 121.5, 111.2, 106.8, 57.4, 55.6, 41.7, 30.3, 8.2. HRMS (ESI-TOF) calcd for C₃₂H₂₉O₃ [M+H]⁺ : 461.2111, found: 461.2112.



phenyl 2-(5-*chloro-1-methyl-2,3-diphenyl-1H-inden-1-yl)acetate* (**4***g*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $30:1\sim10:1$, v/v) affords the title compound as a pale brown oil, 43 mg, 48% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 1.7 Hz, 1H), 7.30-7.21 (m, 13H), 7.16-7.12 (m, 1H), 6.64-6.59 (m, 2H), 3.04 (q, *J* = 14.1 Hz, 2H), 1.56 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.9, 151.7, 147.7, 145.6, 135.6, 134.1, 133.4, 130.2, 129.5, 129.5, 128.36, 128.35, 127.6, 127.5, 125.9, 125.6, 123.7, 121.4, 121.2, 53.2, 41.45, 24.3. HRMS (ESI-TOF) calcd for C₃₀H₂₄ClO₂ [M+H]⁺ : 451.1459, found: 451.1459.



phenyl 2-(5-*fluoro-1-methyl-2,3-diphenyl-1H-inden-1-yl)acetate* (**4***h*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1~10:1, v/v) affords the title compound as a yellow oil, 48 mg, 55% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.49 (dd, J = 8.2, 5.0 Hz, 1H), 7.31-7.20 (m, 12H), 7.15-7.11 (m, 1H), 7.06 (dd, J = 9.2, 2.5 Hz, 1H), 6.99 (ddd, J = 9.2, 8.2, 2.5 Hz, 1H), 6.63-6.58 (m, 2H), 3.09-2.99 (m, 2H), 1.56 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.0, 163.0 (d, J = 244.3 Hz), 152.1, 150.4, 145.8 (d, J = 8.8 Hz), 144.7 (d, J = 2.5 Hz), 139.5 (d, J = 2.9 Hz), 135.7, 134.3, 130.2, 129.5, 129.4, 128.34, 128.31, 127.5, 127.4, 125.9, 123.6 (d, J = 9.1 Hz), 121.4, 112.2 (d, J = 22.9 Hz), 108.3 (d, J = 23.7 Hz), 53.0, 41.6, 24.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -115.31. HRMS (ESI-TOF) calcd for C₃₀H₂₄FO₂ [M+H]⁺ : 435.1755, found: 435.1758.



phenyl 2-(*1*,4-*dimethyl*-2,3-*diphenyl*-1*H*-*inden*-1-*yl*)*acetate* (4*i*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $30:1 \sim 10:1$, v/v) affords the title compound as a yellow solid, Mp = 88-90 °C, 51 mg, 60% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 7.4 Hz, 1H), 7.27-7.10 (m, 14H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.59-6.52 (m, 2H), 3.00 (q, *J* = 13.8 Hz, 2H), 1.87 (s, 3H), 1.54 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.1, 151.1, 150.6, 149.5, 137.7, 135.9, 132.1, 130.4, 130.3, 130.2, 129.5, 129.4, 127.9, 127.8, 127.7, 127.0, 126.8, 125.8, 125.6, 121.6, 120.4, 52.8, 41.7, 24.4, 20.2. HRMS (ESI-TOF) calcd for C₃₁H₂₇O₂ [M+H]⁺: 431.2006, found: 431.2006.



phenyl 2-(*1-ethyl-2,3-diphenyl-1H-inden-1-yl)acetate* (**4***j*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $30:1 \sim 10:1$, v/v) affords the title compound as a yellow solid, Mp = 89-91 °C, 43 mg, 50% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.49 (dd, J = 5.6, 2.9 Hz, 1H), 7.37-7.34 (m, 1H), 7.33-7.29 (m, 4H), 7.26-7.17 (m, 10H), 7.11-7.06 (m, 1H), 6.50 (dd, J = 7.5, 1.7 Hz, 2H), 3.08 (d, J = 2.9 Hz, 2H), 2.09 (m, 2H), 0.65 (t, J = 7.3 Hz, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.0, 150.5, 147.5, 147.2, 145.1, 142.3, 136.2, 135.1, 130.2, 129.7, 129.4, 128.3, 128.2, 127.3, 127.3, 127.1, 125.8, 125.7, 122.6, 121.5, 120.8, 58.1, 41.6, 30.2, 8.2. HRMS (ESI-TOF) calcd for C₃₁H₂₇O₂ [M+H]⁺ : 431.2006, found: 431.2014.



phenyl 2-(*1-butyl-2,3-diphenyl-1H-inden-1-yl)acetate* (**4***k*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $30:1 \sim 10:1$, v/v) affords the title compound as a yellow viscous oil, 44 mg, 48% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.52-7.49 (m, 1H), 7.37-7.34 (m, 1H), 7.32-7.27 (m, 5H), 7.24-7.17 (m, 9H), 7.09 (d, J = 7.4 Hz, 1H), 6.50 (dd, J = 7.8, 1.8 Hz, 2H), 3.11-3.03 (m, 2H), 2.07-2.01 (m, 2H), 1.22 (dd, J = 6.9, 4.7 Hz, 4H), 0.80 (d, J = 7.0 Hz, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.0, 150.5, 147.9, 147.6, 144.8, 142.0, 136.2, 130.2, 129.7, 129.3, 128.3, 128.2, 127.26, 127.25, 127.1, 125.73, 125.69, 122.6, 121.5,

120.8, 57.6, 41.8, 37.1, 25.6, 22.9, 14.1. HRMS (ESI-TOF) calcd for $C_{33}H_{31}O_2 [M+H]^+$: 459.2319, found: 459.2322.



phenyl 2-(*1-methyl-2,3-di-p-tolyl-1H-inden-1-yl*)*acetate* (*4l*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1~10:1, v/v) affords the title compound as a pale brown oil, 40 mg, 45% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.57-7.53 (m, 1H), 7.39-7.35 (m, 1H), 7.32-7.27 (m, 2H), 7.21 (m, 4H), 7.15-7.07 (m, 5H), 7.03 (d, J = 7.8 Hz, 2H), 6.53 (dd, J = 7.8, 1.7 Hz, 2H), 3.13-2.93 (m, 2H), 2.30 (d, J = 14.3 Hz, 6H), 1.56 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.2, 150.5, 149.8, 149.5, 144.0, 136.8, 136.6, 133.1, 132.0, 130.2, 129.5, 129.4, 129.0, 128.9, 127.3, 125.7, 125.6, 122.7, 121.5, 120.9, 53.4, 41.8, 24.4, 21.4. HRMS (ESI-TOF) calcd for C₃₂H₂₉O₂ [M+H]⁺ : 445.2162, found: 445.2163.



phenyl 2-(2,3-*bis*(4-(*tert-butyl*)*phenyl*)-1-*methyl*-1*H*-*inden*-1-*yl*)*acetate* (4*m*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1~10:1, v/v) affords the title compound as a brown solid, Mp = 130-132 °C, 67 mg, 63% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.57-7.53 (m, 1H), 7.42-7.39 (m, 1H), 7.32-7.28 (m, 4H), 7.25-7.21 (m, 5H), 7.21-7.15 (m, 3H), 7.13-7.08 (m, 1H), 6.58-6.52 (m, 2H), 3.08-2.94 (m, 2H), 1.57 (s, 3H), 1.30 (s, 9H), 1.27 (s, 9H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.3, 149.8, 149.7, 149.6, 144.0, 133.1, 131.9, 130.0, 129.4, 129.2, 127.3, 125.7, 125.5, 125.04, 124.97, 122.6, 121.6, 121.1, 53.5, 41.8, 34.6, 31.5, 31.4, 24.4. HRMS (ESI-TOF) calcd for $C_{38}H_{41}O_2$ [M+H]⁺ : 529.3101, found: 529.3102.



phenyl 2-(2,3-bis(4-methoxyphenyl)-1-methyl-1H-inden-1-yl)acetate (**4n**): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $30:1 \sim 10:1$, v/v) affords the title compound as a brown viscous oil, 54 mg, 57% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.57-7.52 (m, 1H), 7.37 (dd, J = 7.1, 1.7 Hz, 1H), 7.29 (ddd, J = 6.1, 3.8, 1.5 Hz, 2H), 7.26-7.23 (m, 2H), 7.17 (dt, J = 8.6, 3.1 Hz, 4H), 7.09 (d, J = 7.5 Hz, 1H), 6.82 (d, J = 8.7 Hz, 2H), 6.76 (d, J = 6.9 Hz, 2H), 6.55-6.49 (m, 2H), 3.75 (s, 3H), 3.72 (s, 3H), 3.03 (q, J = 13.6 Hz, 2H), 1.55 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.2, 158.7, 158.5, 149.4, 149.1, 139.4, 131.5, 130.8, 129.6, 129.3, 128.4, 127.3, 125.7, 125.6, 122.6, 121.5, 120.8, 115.4, 113.7, 113.6, 55.18, 55.17, 53.4, 41.8, 24.4. HRMS (ESI-TOF) calcd for C₃₂H₂₉O₄ [M+H]⁺ : 477.2060, found: 477.2060.



phenyl 2-(2,3-*bis*(4-*fluorophenyl*)-1-*methyl*-1*H*-*inden*-1-*yl*)*acetate* (**4***o*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $30:1 \sim 10:1$, v/v) affords the title compound as a yellow oil, 49 mg, 54% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.52-7.47 (m, 1H), 7.28-7.18 (m, 5H), 7.15-7.07 (m, 4H), 7.02 (t, J = 7.4 Hz, 1H), 6.90 (t, J = 8.5 Hz, 2H), 6.83 (t, J = 8.6 Hz, 2H), 6.39 (d, J = 7.8 Hz, 2H), 3.01 (d, J = 13.6 Hz, 1H), 2.90 (d, J = 13.6 Hz, 1H), 1.46 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.9, 162.1 (dd, J = 247.7, 25.6 Hz), 150.4, 149.1 (d, J = 3.0 Hz), 143.4, 139.8, 132.1 (d, J = 8.1 Hz), 131.7 (d, J = 3.4 Hz), 131.2 (d, J = 8.0 Hz), 130.6 (d, J = 3.2 Hz), 129.4, 127.6, 126.1, 125.9, 122.8, 121.4, 120.8, 115.5, 115.4, 115.3, 115.2, 53.5, 41.7, 24.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -114.49, -114.52. HRMS (ESI-TOF) calcd for $C_{30}H_{23}F_2O_2$ [M+H]⁺: 453.1661, found: 453.1666.



phenyl 2-(1-methyl-2,3-bis(4-(trifluoromethyl)phenyl)-1H-inden-1-yl)acetate (**4***p*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1~10:1, v/v) affords the title compound as a brown solid, Mp = 120-122 °C, 49 mg, 44% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.64-7.56 (m, 3H), 7.48 (dd, J = 14.4, 8.0 Hz, 4H), 7.39-7.35 (m, 2H), 7.34-7.30 (m, 3H), 7.25-7.19 (m, 2H), 7.12 (t, J = 7.5 Hz, 1H), 6.46 (dd, J = 7.9, 1.6 Hz, 2H), 3.14 (d, J = 13.7 Hz, 1H), 3.00 (d, J = 13.7 Hz, 1H), 1.58 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.8, 150.3, 149.6, 149.1, 142.8, 140.2, 139.5, 138.1 (d, J = 1.7 Hz), 130.7, 129.8, 129.7 (dd, J = 32.9, 23.2 Hz), 129.5, 127.8, 126.6, 126.0, 125.5 (t, J = 3.4 Hz), 122.9, 121.4, 121.0, 54.0, 41.7, 24.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.53 (d, J = 5.4 Hz). HRMS (ESI-TOF) calcd for C₃₂H₂₃F₆O₂ [M+H]⁺ : 553.1597, found: 553.1599.



phenyl 2-(2,3-*bis*(3-*methoxyphenyl*)-1-*methyl*-1*H*-*inden*-1-*yl*)*acetate* (**4***q*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a yellow viscous oil, 55 mg, 58% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.50-7.44 (m, 1H), 7.34-7.30 (m, 1H), 7.25-7.19 (m, 2H), 7.11 (q, *J* = 3.7 Hz, 2H), 7.07-6.99 (m, 2H), 6.85-6.81 (m, 2H), 6.79-6.76 (m, 1H), 6.72-6.68 (m, 2H), 6.64 (td, *J* = 6.2, 4.9, 1.9 Hz, 2H), 6.43 (dd, *J* = 7.9, 1.6 Hz, 2H), 3.58 (s, 3H), 3.49 (s, 3H), 2.98 (d, *J* = 3.4 Hz, 2H), 1.48 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.1, 159.4, 159.3, 150.4, 149.9, 149.3, 143.5, 140.0, 137.4, 136.1, 129.6, 129.4, 129.24, 129.17, 127.4, 125.84, 125.76, 122.7, 122.0, 121.4, 121.0, 116.0, 115.4, 114.5, 113.4, 112.9, 55.2, 55.1, 53.5, 41.7, 24.5. HRMS (ESI-TOF) calcd for $C_{32}H_{29}O_4$ [M+H]⁺ : 477.2060, found: 477.2062.



phenyl 2-(2,3-*bis*(3-*fluorophenyl*)-1-*methyl*-1*H*-*inden*-1-*yl*)*acetate* (**4***r*): 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, 41 mg, 46% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.58 (ddd, *J* = 4.6, 3.1, 1.7 Hz, 1H), 7.35 (q, *J* = 2.6 Hz, 3H), 7.28-7.16 (m, 4H), 7.14-7.06 (m, 3H), 7.01-6.87 (m, 4H), 6.49 (dd, *J* = 8.1, 1.6 Hz, 2H), 3.11 (d, *J* = 13.8 Hz, 1H), 3.01 (d, *J* = 13.8 Hz, 1H), 1.55 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.8, 162.9 (dd, *J* = 247.1, 4.1 Hz), 150.4, 149.3 (d, *J* = 2.0 Hz), 149.1, 143.0, 139.8 (d, *J* = 2.1 Hz), 137.9 (d, *J* = 8.1 Hz), 136.7 (d, *J* = 8.0 Hz), 129.9 (t, *J* = 8.9 Hz), 129.5, 127.7, 126.3, 126.2 (d, *J* = 3.0 Hz), 125.9, 125.3 (d, *J* = 3.0 Hz), 122.8, 121.4, 121.0, 117.2 (d, *J* = 21.5 Hz), 116.3 (d, *J* = 21.8 Hz), 114.5 (d, *J* = 20.9 Hz), 53.7, 41.6, 24.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -112.80, -113.22. HRMS (ESI-TOF) calcd for C₃₀H₂₃F₂O₂ [M+H]⁺ : 453.1661, found: 453.1670.



phenyl 2-(2,3-*bis*(3-*chlorophenyl*)-1-*methyl*-1*H*-*inden*-1-*yl*)*acetate* (**4***s*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $30:1\sim10:1$, v/v) affords the title compound as a pale brown viscous oil, 43 mg, 44% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.60-7.55 (m, 1H), 7.39-7.32 (m, 4H), 7.26-7.09 (m, 9H), 7.05 (m, 1H), 6.53-6.43 (m, 2H), 3.11 (d, J = 13.8 Hz, 1H), 3.00 (d, J = 13.8 Hz, 1H), 1.55 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.8, 150.3, 149.2, 149.0, 139.8, 137.5, 136.3, 134.3, 134.1, 130.0, 129.71, 129.68, 129.5, 129.3, 128.8, 127.89, 127.87, 127.69, 127.67, 126.3, 125.9, 122.8, 121.4, 121.0, 53.7, 41.6, 24.4. HRMS (ESI-TOF) calcd for C₃₀H₂₃Cl₂O₂ [M+H]⁺: 485.1070, found: 485.1071.



phenyl 2-(2,3-*diethyl-1-methyl-1H-inden-1-yl)acetate* (4*t*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $30:1 \sim 10:1$, v/v) affords the title compound as a brown oil, 44 mg, 68% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.31 (m, 1H), 7.19 (d, J = 5.9 Hz, 2H), 7.15-7.08 (m, 3H), 7.03-6.98 (m, 1H), 6.52-6.45 (m, 2H), 2.95 (d, J = 13.2 Hz, 1H), 2.77 (d, J = 13.1 Hz, 1H), 2.41 (m, 3H), 2.28 (dd, J = 14.6, 7.3 Hz, 1H), 1.34 (s, 3H), 1.11 (t, J = 7.7 Hz, 3H), 1.05 (t, J = 7.6 Hz, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.1, 150.5, 149.5, 149.1, 144.3, 138.7, 129.2, 127.1, 125.6, 124.5, 122.1, 121.5, 118.7, 52.4, 42.2, 23.8, 18.8, 18.5, 14.8, 13.7. HRMS (ESI-TOF) calcd for C₂₂H₂₅O₂ [M+H]⁺ : 321.1849, found: 321.1853.



phenyl 2-(1-*methyl*-2,3-*dipropyl*-1*H*-*inden*-1-*yl*)*acetate* (**4***u*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1~10:1, v/v) affords the title compound as a brown oil, 47 mg, 67% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, J = 7.3 Hz, 1H), 7.19-7.10 (m, 5H), 7.02 (dt, J = 7.3, 1.2 Hz, 1H), 6.49 (dd, J = 7.7, 1.5 Hz, 2H), 2.97 (d, J = 13.3 Hz, 1H), 2.77 (d, J = 13.3 Hz, 1H), 2.41-2.37 (m, 2H), 2.35-2.29 (m, 1H), 2.24 (dt, J = 8.3, 6.6 Hz, 1H), 1.54-1.46 (m, 4H), 1.35 (s, 3H), 0.95 (t, J = 7.3 Hz, 3H), 0.87 (t, J = 7.3 Hz, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.2, 150.5, 149.6, 148.4, 144.6, 137.3, 129.3, 127.0, 125.6, 124.5, 122.1, 121.5, 118.9, 52.4, 42.3, 28.2, 28.0, 24.0, 23.4, 22.2, 15.2, 14.6. HRMS (ESI-TOF) calcd for C₂₄H₂₉O₂ [M+H]⁺ : 349.2162, found: 349.2166.



phenyl 2-(2,3-*dibutyl-1-methyl-1H-inden-1-yl)acetate* (**4***v*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1~10:1, v/v) affords the title compound as a brown oil, 45 mg, 60% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, J = 7.3 Hz, 1H), 7.27-7.16 (m, 5H), 7.09 (t, J = 7.4 Hz, 1H), 6.56 (dd, J = 7.7, 1.6 Hz, 2H), 3.04 (d, J = 13.3 Hz, 1H), 2.84 (d, J = 13.3 Hz, 1H), 2.50-2.38 (m, 3H), 2.35-2.29 (m, 1H), 1.55-1.35 (m, 11H), 0.97 (t, J = 7.2 Hz, 3H), 0.88 (t, J = 7.3 Hz, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.1, 150.5, 149.6, 148.3, 144.6, 137.4, 129.2, 127.0, 125.6, 124.4, 122.0, 121.5, 118.9, 52.4, 42.3, 32.3, 31.1, 25.7, 25.6, 24.0, 23.8, 23.12, 14.1. HRMS (ESI-TOF) calcd for C₂₆H₃₃O₂ [M+H]⁺ : 377.2475, found: 377.2475.



phenyl 2-(2-*ethyl-1-methyl-3-phenyl-1H-inden-1-yl)acetate* (**4***w*): 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 oil, 31 mg, 42% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.53-7.50 (m, 1H), 7.43-7.34 (m, 7H), 7.27 (dd, J = 7.3, 1.5 Hz, 1H), 7.23-7.19 (m, 2H), 7.12-7.08 (m, 1H), 6.52-6.48 (m, 2H), 2.97 (d, J = 13.6 Hz, 1H), 2.84 (d, J = 13.6 Hz, 1H), 2.36 (m, 2H), 1.47 (s, 3H), 1.05 (t, J = 7.5 Hz, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.2, 150.5, 149.5, 148.3, 143.8, 141.0, 136.3, 130.1, 129.3, 128.4, 127.4, 127.3, 125.7, 125.3, 122.7, 121.5, 119.8, 53.0, 41.5, 24.1, 19.3, 14.0. HRMS (ESI-TOF) calcd for C₂₆H₂₅O₂ [M+H]⁺ : 369.1849, found: 369.1844.



p-tolyl-2-(1-methyl-2,3-diphenyl-1H-inden-1-yl)acetate (**4***x*): 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 brown solid, Mp = $98-99 \,$ °C, 43 mg, 50% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.58-7.55 (m, 1H), 7.38-7.35 (m, 1H), 7.33-7.28 (m, 5H), 7.26-7.17 (m, 7H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.41 (d, *J* = 8.4 Hz, 2H), 3.03 (q, *J* = 13.7 Hz, 2H), 2.25 (s, 3H), 1.57 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.3, 150.2, 149.4, 148.2, 143.7, 140.1, 136.1, 135.4, 134.9, 130.4, 129.9, 129.6, 128.2, 128.1, 127.4, 127.3, 127.1, 125.8, 122.8, 121.2, 120.9, 53.5, 41.7, 24.4, 20.9. HRMS (ESI-TOF) calcd for C₃₁H₂₇O₂ [M+H]⁺ : 431.2006, found: 431.2009.



4-methoxyphenyl 2-(1-methyl-2,3-diphenyl-1H-inden-1-yl)acetate (4y): 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 oil, 46 mg, 52% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.58-7.55 (m, 1H), 7.39-7.36 (m, 1H), 7.34-7.29 (m, 5H), 7.26-7.18 (m, 7H), 6.72 (d, J = 9.0 Hz, 2H), 6.44 (d, J

= 9.0 Hz, 2H), 3.70 (s, 3H), 3.09-2.98 (m, 2H), 1.56 (s, 3H). $^{13}C{^{1}H}$ NMR (101 MHz, CDCl₃) δ 169.5, 157.2, 150.2, 149.4, 143.9, 143.7, 136.1, 130.4, 129.6, 128.2, 128.1, 127.4, 127.3, 127.1, 125.8, 122.8, 122.2, 120.9, 114.4, 55.6, 53.5, 41.7, 24.4. HRMS (ESI-TOF) calcd for C₃₁H₂₇O₃ [M+H]⁺ : 447.1955, found: 447.1958.



4-fluorophenyl 2-(1-methyl-2,3-diphenyl-1H-inden-1-yl)acetate (4z): 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, Mp = $95-97 \, \text{°C}$, 41mg, 47% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.57-7.54 (m, 1H), 7.39-7.36 (m, 1H), 7.31 (m, 5H), 7.27-7.19 (m, 7H), 6.88 (dd, J = 9.6, 7.6 Hz, 2H), 6.47-6.42 (m, 2H), 3.09-3.00 (m, 2H), 1.56 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.1, 160.2 (d, J = 244.9 Hz), 150.0, 149.3, 146.2 (d, J = 3.0 Hz), 143.7, 140.2, 136.0, 134.7, 130.4, 129.6, 128.2 (d, J = 9.1 Hz), 127.46, 127.35, 127.2, 125.8, 122.9, 122.8, 122.7, 121.0, 116.0 (d, J = 23.5 Hz), 53.5, 41.6, 24.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -117.16. HRMS (ESI-TOF) calcd for C₃₀H₂₄FO₂ [M+H]⁺ : 435.1755, found: 435.1757.



4-chlorophenyl 2-(1-methyl-2,3-diphenyl-1H-inden-1-yl)acetate (4aa): 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 = 109-111 °C, 52 mg, 58% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.56-7.53 (m, 1H), 7.39-7.36 (m, 1H), 7.31 (dt, J = 4.7, 2.0 Hz, 5H), 7.26-7.20 (m, 6H), 7.15 (d, J = 8.8 Hz, 3H), 6.42 (d, J = 8.8 Hz, 2H), 3.09-3.00 (m, 2H), 1.56 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.8, 149.9, 149.2, 148.9, 143.7, 135.9, 134.7, 131.1, 130.3, 129.5, 129.4, 128.3, 128.2, 127.5, 127.4, 127.2, 125.8, 122.9, 122.7, 121.0, 53.5, 41.7, 24.3. HRMS (ESI-TOF) calcd for C₃₀H₂₄ClO₂ [M+H]⁺: 451.1459, found: 451.1459.



m-tolyl 2-(*1-methyl-2,3-diphenyl-1H-inden-1-yl*)*acetate* (*4ab*): 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 oil, 45 mg, 53% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.59-7.56 (m, 1H), 7.39-7.36 (m, 1H), 7.32 (tq, J = 5.1, 2.2 Hz, 5H), 7.27-7.19 (m, 7H), 7.09 (t, J = 7.7 Hz, 1H), 6.91 (d, J = 7.6 Hz, 1H), 6.35-6.30 (m, 2H), 3.04 (q, J = 13.8 Hz, 2H), 2.22 (s, 3H), 1.57 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.2, 150.4, 150.1, 149.4, 143.8, 140.1, 139.5, 136.1, 134.8, 130.4, 129.6, 129.1, 128.3, 128.1, 127.4, 127.3, 127.1, 126.6, 125.8, 122.8, 122.1, 121.0, 118.4, 53.5, 41.7, 24.4, 21.3. HRMS (ESI-TOF) calcd for C₃₁H₂₇O₂ [M+H]⁺ : 431.2006, found: 431.2007.



3-methoxyphenyl 2-(*1-methyl-2,3-diphenyl-1H-inden-1-yl)acetate* (*4ac*): 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 oil, 45 mg, 51% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.49 (dd, *J* = 5.7, 3.0 Hz, 1H), 7.29 (dd, *J* = 5.5, 3.4 Hz, 1H), 7.23 (dt, *J* = 12.2, 7.7 Hz, 5H), 7.18-7.08 (m, 7H), 7.02 (t, *J* = 8.2 Hz, 1H), 6.57 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.11 (dd, *J* = 8.1, 2.1 Hz, 1H), 5.87 (t, *J* = 2.4 Hz, 1H), 3.53 (s, 3H), 3.02-2.92 (m, 2H), 1.48 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.0, 160.4, 151.4, 150.1, 149.3, 143.8, 136.0, 134.8, 130.4, 129.7, 129.6, 128.24, 128.15, 127.4, 127.3, 127.2, 125.8, 122.8, 120.9, 113.7, 112.1, 107.1, 55.5, 53.6, 41.7, 24.4. HRMS (ESI-TOF) calcd for C₃₁H₂₇O₃ [M+H]⁺: 447.1955, found: 447.1953.



3-fluorophenyl 2-(1-methyl-2,3-diphenyl-1H-inden-1-yl)acetate (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 oil, 54 mg, 62% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.49-7.46 (m, 1H), 7.32-7.29 (m, 1H), 7.27-7.21 (m, 5H), 7.19-7.06 (m, 8H), 6.74 (dt, J = 8.3, 2.5 Hz, 1H), 6.26-6.13 (m, 2H), 3.02-2.92 (m, 2H), 1.49 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.7, 162.8 (d, J = 248.3 Hz), 151.3 (d, J = 10.9 Hz), 149.9, 149.2, 143.7, 140.3, 136.0, 134.7, 130.4, 130.1 (d, J = 9.3 Hz), 129.6, 128.3, 128.2, 127.5, 127.4, 127.2, 125.8, 122.7, 121.0, 117.3 (d, J = 3.3 Hz), 112.8 (d, J = 21.1 Hz), 109.6 (d, J = 24.4 Hz), 53.5, 41.7, 24.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -115.92. HRMS (ESI-TOF) calcd for C₃₀H₂₄FO₂ [M+H]⁺ : 435.1755, found: 435.1760.



3-(*trifluoromethyl*)*phenyl* 2-(1-*methyl*-2,3-*diphenyl*-1*H*-*inden*-1-*yl*)*acetate* (4*ae*): 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, 37 mg, 38% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.58-7.55 (m, 1H), 7.42-7.22 (m, 15H), 6.68 (d, J = 6.5 Hz, 2H), 3.12-3.03 (m, 2H), 1.60 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.7, 150.5, 149.8, 149.2, 143.7, 140.4, 135.9, 134.7, 131.9 (d, J = 33.0 Hz), 130.4, 129.9, 129.5, 128.8, 128.3, 128.2, 127.6, 127.4, 127.2, 125.9, 125.2, 122.8, 122.6 (dd, J = 7.6, 3.8 Hz), 121.1, 119.0 (d, J = 7.7, 3.9 Hz), 53.6, 41.7, 24.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.66. HRMS (ESI-TOF) calcd for C₃₁H₂₄F₃O₂ [M+H]⁺ : 485.1723, found: 485.1726.



o-tolyl 2-(*1-methyl-2,3-diphenyl-1H-inden-1-yl)acetate* (*4af*): 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 oil, 48 mg, 56% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.60-7.56 (m, 1H), 7.39-7.34 (m, 2H), 7.31 (ddd, J = 8.7, 3.4, 1.9 Hz, 4H), 7.27-7.19 (m, 7H), 7.10-7.07 (m, 1H), 7.05-7.01 (m, 2H), 6.38-6.33 (m, 1H), 3.18-3.04 (m, 2H), 1.80 (s, 3H), 1.57 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.7, 150.1, 149.5, 143.9, 136.1, 134.9, 131.0, 130.4, 130.3, 129.6, 128.2, 128.2, 127.4, 127.3, 127.1, 126.9, 126.0, 125.8, 122.6, 121.7, 121.1, 53.4, 41.4, 24.8, 16.0. HRMS (ESI-TOF) calcd for C₃₁H₂₇O₂ [M+H]⁺ : 431.2006, found: 431.2006.



2-methoxyphenyl 2-(1-methyl-2,3-diphenyl-1H-inden-1-yl)acetate (**4ag**): 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 oil, 44 mg, 50% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.62-7.58 (m, 1H), 7.38-7.35 (m, 1H), 7.33-7.18 (m, 12H), 7.11-7.05 (m, 1H), 6.85 (dd, J = 8.3, 1.4 Hz, 1H), 6.76 (dt, J = 7.7, 1.4 Hz, 1H), 6.37 (dd, J = 7.9, 1.6 Hz, 1H), 3.68 (s, 3H), 3.17-2.98 (m, 2H), 1.57 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.5, 151.2, 149.6, 143.7, 139.9, 136.1, 134.9, 130.4, 129.6, 128.2, 128.1, 127.2, 127.1, 126.8, 125.7, 122.8, 122.7, 120.8, 120.7, 112.3, 55.7, 53.3, 41.2, 24.1. HRMS (ESI-TOF) calcd for C₃₁H₂₇O₃ [M+H]⁺: 447.1955, found: 447.1956.



2,6-dimethoxyphenyl 2-(1-methyl-2,3-diphenyl-1H-inden-1-yl)acetate (4ah): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 - 10:1, v/v) affords the title compound as a pale yellow oil, 39 mg, 41% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.67 (dd, J = 5.5, 3.1 Hz, 1H), 7.35 (dd, J = 5.6, 3.2 Hz, 1H), 7.30-7.18 (m, 12H), 7.05 (t, J = 8.4 Hz, 1H), 6.52 (d, J = 8.4 Hz, 2H), 3.67 (s, 6H), 3.18 (d, J = 15.0 Hz, 1H), 2.91 (d, J = 15.0 Hz, 1H), 1.61 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.5, 152.4, 150.7, 150.0, 136.2, 135.0, 130.4, 129.6, 128.2, 128.1, 127.2, 127.0, 126.2, 125.6, 122.9, 120.7, 104.8, 56.0, 52.9, 40.8, 23.7. HRMS (ESI-TOF) calcd for C₃₂H₂₉O₄ [M+H]⁺ : 477.2060, found: 477.2062.



benzo[d][1,3]dioxol-5-yl 2-(1-methyl-2,3-diphenyl-1H-inden-1-yl)acetate (4ai): Purification by

column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 - 10:1, v/v) affords the title compound as a pale yellow oil, 49 mg, 54% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.57-7.53 (m, 1H), 7.40-7.36 (m, 1H), 7.34-7.28 (m, 5H), 7.26-7.18 (m, 7H), 6.60 (d, J = 8.4 Hz, 1H), 5.99 (ddd, J = 8.4, 2.4, 1.1 Hz, 1H), 5.94 (t, J = 1.7 Hz, 1H), 5.86 (s, 2H), 3.08-2.97 (m, 2H), 1.56 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.4, 150.0, 149.3, 147.9, 145.3, 144.7, 143.7, 136.0, 134.8, 130.4, 129.6, 128.24, 128.15, 127.4, 127.3, 127.2, 125.8, 122.7, 121.0, 113.8, 107.9, 103.6, 101.6, 53.5, 41.6, 24.4. HRMS (ESI-TOF) calcd for C₃₁H₂₅O₄ [M+H]⁺ : 461.1747, found: 461.1749.



naphthalen-1-yl 2-(*1-methyl-2,3-diphenyl-1H-inden-1-yl*)*acetate* (*4aj*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $30:1 \sim 10:1$, v/v) affords the title compound as a yellow solid, Mp = 131-132 °C, 43 mg, 46% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.67-7.59 (m, 2H), 7.44-7.34 (m, 6H), 7.31-7.15 (m, 10H), 7.08 (d, *J* = 8.5 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 3.30 (d, *J* = 14.1 Hz, 1H), 3.19 (d, *J* = 14.1 Hz, 1H), 1.62 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.1, 150.1, 136.1, 134.8, 134.6, 130.5, 129.6, 128.3, 128.1, 127.9, 127.6, 127.3, 127.1, 126.4, 126.04, 125.98, 125.4, 122.7, 121.5, 121.2, 117.9, 53.5, 41.6, 24.9. HRMS (ESI-TOF) calcd for C₃₄H₂₇O₂ [M+H]⁺ : 467.2006, found: 467.2009.



4-isopropyl-2-methylphenyl 2-(2,3-bis(4-methoxyphenyl)-1-methyl-1H-inden-1-yl)acetate (5a): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $30:1\sim5:1$, v/v) affords the title compound as a pale yellow oil, 52 mg, 49% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.57 (dd, J = 6.6, 1.8 Hz, 1H), 7.38-7.36 (m, 1H), 7.32-7.26 (m, 4H), 7.17 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 7.8 Hz, 1H), 6.88 (dd, J = 7.8, 1.8 Hz, 1H), 6.85-6.81 (m, 2H), 6.78-6.73 (m, 2H), 6.09 (d, J = 1.8 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.14-3.02 (m, 2H), 2.71 (m, 1H), 1.77 (s, 3H), 1.55 (s, 3H), 1.10 (d, J = 6.9 Hz, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.8, 158.5, 149.5, 149.2, 148.0, 144.2, 131.6, 130.8, 130.7, 128.5, 127.4, 125.6, 124.2, 122.7, 120.8, 119.5, 113.7, 113.6, 55.2, 53.4, 41.6, 33.6, 24.9, 24.0, 23.9, 15.6. HRMS (ESI-TOF) calcd for C₃₆H₃₇O₄ [M+H]⁺ : 533.2686, found: 533.2688.



4-oxo-2-phenyl-4H-chromen-6-yl 2-(2,3-bis(4-methoxyphenyl)-1-methyl-1H-inden-1-yl)acetate (**5b**): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $10:1\sim5:1$, v/v) affords the title compound as a pale red oil, 77 mg, 62% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.91-7.85 (m, 2H), 7.59-7.49 (m, 5H), 7.43-7.32 (m, 4H), 7.26-7.22 (m, 2H), 7.21-7.14 (m, 2H), 6.89-6.83 (m, 2H), 6.78 (d, J = 8.9 Hz, 3H), 6.65 (dd, J = 9.0, 2.8 Hz, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 3.14-2.97 (m, 2H), 1.59 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 177.8, 169.0, 163.6, 158.8, 158.6, 153.7, 149.3, 148.9, 139.6, 131.8, 131.7, 131.5, 130.7, 129.2, 127.9, 127.5, 126.4, 125.7, 122.6, 120.9, 119.4, 117.6, 113.8, 113.7, 107.2, 55.3, 55.2, 53.4, 41.7, 24.4. HRMS (ESI-TOF) calcd for C₄₁H₃₃O₆ [M+H]⁺ : 621.2272, found: 621.2273.



4-(3-oxobutyl)phenyl 2-(2,3-bis(4-methoxyphenyl)-1-methyl-1H-inden-1-yl)acetate (5c): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $10:1\sim5:1$, v/v) affords the title compound as a pale red oil, 63 mg, 58% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.54 (dd, J = 7.0, 1.6 Hz, 1H), 7.39-7.36 (m, 1H), 7.29 (ddd, J = 6.5, 4.6, 1.5 Hz, 2H), 7.26-7.22 (m, 2H), 7.20-7.14 (m, 2H), 7.01 (d, J = 8.5 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 8.7 Hz,

2H), 6.42 (d, J = 8.5 Hz, 2H), 3.75 (d, J = 10.5 Hz, 6H), 3.02 (q, J = 13.6 Hz, 2H), 2.77 (d, J = 7.3 Hz, 2H), 2.67 (q, J = 6.5 Hz, 2H), 2.09 (s, 3H), 1.54 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 208.1, 169.3, 158.6, 158.4, 149.3, 149.1, 148.7, 138.4, 131.5, 130.7, 129.2, 128.3, 127.3, 127.2, 125.5, 122.6, 121.4, 120.7, 113.7, 113.6, 55.2, 55.1, 53.3, 45.1, 41.7, 30.1, 29.0, 24.4. HRMS (ESI-TOF) calcd for C₃₆H₃₅O₅ [M+H]⁺ : 547.2479, found: 547.2477.



(R)-2,8-dimethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl

2-(2,3-bis(4-methoxyphenyl)-1-methyl-1H-inden-1-yl)acetate (5d): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1~5:1, v/v) affords the title compound as a pale yellow oil, 69 mg, 44% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.56-7.52 (m, 1H), 7.39-7.35 (m, 1H), 7.33-7.28 (m, 2H), 7.26-7.23 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.3 Hz, 2H), 6.77 (d, *J* = 8.3 Hz, 2H), 6.07 (dt, *J* = 11.1, 3.1 Hz, 2H), 3.77 (d, *J* = 9.3 Hz, 6H), 3.05-2.90 (m, 2H), 2.57 (t, *J* = 5.9 Hz, 2H), 2.01 (s, 3H), 1.56-1.46 (m, 6H), 1.32-1.19 (m, 18H), 1.15-1.11 (m, 2H), 1.08-1.03 (m, 3H), 0.85 (dd, *J* = 10.6, 6.6 Hz, 12H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 170.0, 158.7, 158.5, 149.3, 131.6, 130.8, 128.5, 127.2, 125.6, 122.8, 121.1, 120.8, 120.7, 119.0, 113.7, 113.6, 76.1, 55.2, 53.4, 41.8, 40.3, 39.5, 37.6, 37.54, 37.53, 37.4, 32.9, 32.8, 28.1, 24.9, 24.6, 24.4, 24.4, 24.3, 22.9, 22.8, 22.4, 21.1, 19.9, 19.8, 16.2. HRMS (ESI-TOF) calcd for C₅₃H₆₉O₅ [M+H]⁺ : 785.5140, found: 785.5143.



(*E*)-4-(3,5-dimethoxystyryl)phenyl 2-(2,3-bis(4-methoxyphenyl)-1-methyl-1H-inden-1-yl)acetate (**5e**): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $10:1\sim5:1$, v/v) affords the title compound as a pale yellow oil, 80 mg, 63% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.57-7.53 (m, 1H), 7.41-7.28 (m, 5H), 7.27-7.22 (m, 2H), 7.21-7.14 (m, 2H), 7.00-6.87 (m, 2H), 6.85-6.80 (m, 2H), 6.80-6.75 (m, 2H), 6.61 (d, *J* = 2.2 Hz, 2H), 6.57-6.43 (m, 2H), 6.37 (t, *J* = 2.2 Hz, 1H), 3.79 (s, 6H), 3.77 (s, 3H), 3.74 (s, 3H), 3.03 (q, *J* = 13.6 Hz, 2H),

1.55 (s, 3H). ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃) δ 169.1, 161.0, 158.7, 158.5, 150.0, 149.4, 149.1, 143.9, 139.3, 134.8, 131.5, 130.7, 128.8, 128.3, 128.3, 127.4, 127.33, 127.27, 125.6, 122.7, 121.7, 120.8, 113.7, 113.6, 104.6, 100.1, 55.4, 55.20, 55.18, 53.4, 41.8, 24.4. HRMS (ESI-TOF) calcd for $C_{42}H_{39}O_6$ [M+H]⁺ : 639.2741, found: 639.2745.



(8*S*,9*S*,12*R*,14*S*)-12-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phena nthren-3-yl 2-(2,3-bis(4-methoxyphenyl)-1-methyl-1H-inden-1-yl)acetate (5*f*): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1~5:1, v/v) affords the title compound as a brown oil, 79 mg, 61% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.55 (dd, J = 6.2, 2.1 Hz, 1H), 7.39-7.35 (m, 1H), 7.30 (m, 2H), 7.26-7.22 (m, 2H), 7.21-7.14 (m, 2H), 7.12 (d, J = 8.5 Hz, 1H), 6.87-6.80 (m, 2H), 6.77 (d, J = 8.4 Hz, 2H), 6.30 (dt, J = 8.5, 3.1 Hz, 1H), 6.22 (t, J = 2.8 Hz, 1H), 3.77 (d, J = 9.5 Hz, 6H), 3.13-2.89 (m, 2H), 2.84-2.67 (m, 2H), 2.48 (dd, J = 18.9, 8.6 Hz, 1H), 2.37-2.26 (m, 1H), 2.24-1.90 (m, 5H), 1.59-1.31 (m, 9H), 0.87 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.5, 158.7, 158.5, 149.5, 149.2, 148.4, 144.0, 139.4, 137.9, 137.2, 131.6, 130.8, 128.4, 127.31, 127.25, 126.3, 125.6, 122.7, 121.6, 120.7, 118.7, 113.7, 113.6, 55.21, 53.4, 50.4, 48.0, 44.2, 41.8, 38.0, 36.0, 31.6, 29.3, 26.4, 25.8, 24.4, 21.7, 13.9. HRMS (ESI-TOF) calcd for C₄₄H₄₅O₅ [M+H]⁺ : 653.3262, found: 653.3262.



N-butyl-2-(1-methyl-2,3-diphenyl-1H-inden-1-yl)acetamide (6): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $10:1 \sim 5:1$, v/v) affords the title compound as a pale yellow solid, Mp = $122-124 \, \text{°C}$, 62 mg, 79% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.48 (dd, J = 5.5, 3.1 Hz, 1H), 7.41 (dd, J = 5.5, 3.2 Hz, 1H), 7.35-7.18 (m, 12H), 4.92 (t, J = 5.7 Hz, 1H), 3.01 (dt, J = 13.1, 6.6 Hz, 1H), 2.94-2.72 (m, 3H), 1.42 (s, 3H), 1.11-0.90 (m, 4H), 0.69 (t, J = 7.0 Hz, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.9, 151.0, 150.2, 143.5, 139.7, 135.7, 134.6, 130.1, 129.5, 128.27, 128.25, 127.5, 127.31, 127.27, 126.1, 121.9, 121.3, 53.4,

44.2, 38.9, 31.3, 24.9, 19.8, 13.7. HRMS (ESI-TOF) calcd for $C_{28}H_{30}NO[M+H]^+$: 396.2322, found: 396.2323.



N-benzyl-2-(1-methyl-2,3-diphenyl-1H-inden-1-yl)acetamide (7): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $10:1\sim5:1$, v/v) affords the title compound as a colourless solid, Mp = 124-126 °C, 72 mg, 84% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.47-7.41 (m, 1H), 7.28-7.18 (m, 11H), 7.14-7.02 (m, 5H), 6.85-6.78 (m, 2H), 5.29 (s, 1H), 4.18 (dd, *J* = 14.6, 5.8 Hz, 1H), 4.05 (dd, *J* = 14.6, 5.3 Hz, 1H), 2.87 (q, *J* = 14.9 Hz, 2H), 1.44 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.8, 150.7, 150.0, 143.3, 139.9, 137.7, 135.7, 134.4, 130.1, 129.5, 128.5, 128.3, 128.2, 127.7, 127.5, 127.3, 127.2, 127.2, 126.2, 121.9, 121.5, 53.4, 44.0, 43.5, 25.0. HRMS (ESI-TOF) calcd for C₃₁H₂₈NO [M+H]⁺ : 430.2165, found: 430.2166.



2-(1-methyl-2,3-diphenyl-1H-inden-1-yl)ethan-1-ol (8): Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = $10:1\sim5:1$, v/v) affords the title compound as a pale yellow oil, 59 mg, 91% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.41 (dd, J = 5.5, 3.1 Hz, 1H), 7.36 (dd, J = 5.5, 3.2 Hz, 1H), 7.30-7.14 (m, 12H), 3.42 (dt, J = 10.8, 7.0 Hz, 1H), 3.21 (dt, J = 10.8, 7.1 Hz, 1H), 2.22 (t, J = 7.2 Hz, 2H), 1.44 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 151.0, 150.6, 143.4, 139.8, 136.3, 135.0, 129.8, 129.6, 128.28, 128.26, 127.2, 127.0, 125.8, 121.9, 121.0, 59.8, 53.9, 40.3, 24.9. HRMS (ESI-TOF) calcd for C₂₄H₂₃O [M+H]⁺ : 327.1743, found: 327.1743.

7. Crystallographic data of 4aj



Structure of 4aj CCDC: 2368290

Datablock:

Bond precision:	C-C = 0.0064 /	4	Wavelength = 0.71073		
Cell:	a = 24.585(4	4) b=9.4237(15) c=23.169(4)		
	alpha=990	beta=96.207(3)	gamma=90		
Temperature:	296 K				
	Calculated		Reported		
Volume	5336.4(15)		5336.3(15)		
Space group	C 2/c		C 2/c		
Hall group	-C 2yc		-C 2yc		
Moiety formula	2(C34 H26 O2	2), C H2 Cl2			
Sum formula	C69 H54 Cl2 O4	Ļ	C69 H54 Cl2 N0 O4		
Mr	1018.02		1018.02		
Dx,g cm-3	1.267		1.267		
Z	4		4		
Mu (mm-1)	0.173		0.173		
F000	2136.0		2136.0		
F000'	2138.03				
h,k,lmax	32,12,30		132,12,30		
Nref	6212		6068		
Tmin,Tmax					
Tmin'					
Correction method =	Not given				
Data completeness = 0.977		Theta (max	Theta (max) = 27.617		
R (reflections) = 0.0905(3549)		wR2 (reflect	wR2 (reflections) = 0.2357(6068)		
S = 1.170 Npar = 340					

8. Reference

- (1) Tripathi, C. B.; Mukherjee, S. Angew. Chem. Int. Ed. 2013, 52, 8450.
- (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.
- (7) Schmidt, B.; Berger, R.; Kelling, A.; Schilde, U. Chem. Eur. J. 2011, 17, 7032.
- (8) Lee, D.-H.; Kwon, Y.-J.; Jin, M.-J. Adv. Synth. Catal. 2011, 353, 3090.
- (9) Ueda, T.; Konishi, H.; Manabe, K. Org. Lett. 2012, 14, 5370.

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



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

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



 $^{13}\text{C}\{1\text{H}\}$ NMR (101 MHz, CDCl₃) Spectrum of **4b**

169.158	150,546 149,690 149,690 149,126 139,969 138,045 135,045 135,045 128,344 128,348 129,365 128,244 128,348 128,244 128,046 127,212 128,046 127,212 128,046 127,213 128,046 127,215 128,046 127,215 128,165 127,5736 127,5736 123,57376 123,5736 123,57577 123,57577 123,57577 123,575777 123,575777 123,5757777 123,5757777777777777777777777777777777777	77.478 77.161 76.843	53.281	41.794	24.470 21.753
1		\checkmark	1	1	11

N20240402-FC0000-WXX-PHOI-240.2.fid



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



S27

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



N20240329-FC0871-WXX-PHOI-2356.2.fid



10 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 **4d**



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



¹³C{1H} NMR (101 MHz, CDCl₃) Spectrum of **4e**

168.687	152.960 150.321 150.321 150.321 145.345 133.585 135.345 135.345 135.345 135.345 135.345 135.345 135.345 135.348 128.486 128.486 127.744 127.54	77.480 77.162 76.844	53.636	41.277	24.102
		\vee			

N20240329-FC0871-WXX-PHOI-235.2.fid



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



10 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 **4f**



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



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



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



10 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 **4i**



 $^{13}\text{C}\{1\text{H}\}$ NMR (101 MHz, CDCl₃) Spectrum of 4i

169.084	151.068 150.564 149.456 141.932 141.932 141.49 149.495 149.400 132.119 132.119 132.119 132.119 132.119 132.119 132.400 122.400 122.400 122.400 122.640 122.657 122.757 122.657 122.657 122.657 122.757 122.657 122.757 122.657 122.7577 122.7577 122.7577 122.7577 122.7577 122.7577 122.7577 122.7577 122.7577 122.7577 122.75777 122.75777 122.75777 122.757777 122.757777777777777777777777777777777777	76.843 52.786	41.721	24.438 20.179
1	\vee	· ۱	1	1.1

N20240402-FC0000-WXX-PHOI-239.2.fid










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



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



$^{13}\text{C}\{1\text{H}\}$ NMR (101 MHz, CDCl₃) Spectrum of **4**l



N20240319-FC0652-WXX-PHOI-215.1.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)







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

¹³C{1H} NMR (101 MHz, CDCl₃) Spectrum of **4n**

169.227	158.672 158.491	150,441 149,395 149,908 143,916 133,916 133,742 131,514 130,742 122,643 122,643 122,643 122,643 122,643 122,643 122,643 122,646 122,716 122,645 122,64	77.478 77.160 76.843	55.184 55.166 53.348	41.808	24.395
	\sim		\checkmark	42		

N20240319-FC0652-WXX-PHOI-216.1.fid





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



τι χργων

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



10 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 **4p**



 $^{13}C\{1H\}$ NMR (101 MHz, CDCl₃) Spectrum of 4p



N20240322-FC0744-WXX-PHOI-225.2.fid





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



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











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



N20240322-FC0668-WXX-PHOI-221.3.fid



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







110 100 90 f1 (ppm) -10 70 60 180 170







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

 $\begin{array}{c} 150.501\\ 149.564\\ 148.564\\ 148.564\\ 148.365\\ 148.365\\ 128.257\\ 128.255\\ 128.255\\ 128.256\\ 128.256\\ 128.256\\ 128.256\\ 128.256\\ 128.256\\ 128.436\\ 118.931\\ 118.931\\ 118.931\\ 118.931\\ 118.931\\ 128.439\\ 128.239\\ 28.237\\ 28.237\\ 28.237\\ 28.237\\ 28.237\\ 28.237\\ 15.296\\ 28.237\\ 28.236\\ 28.237\\ 28.236\\ 28.237\\ 28.236\\ 28.237\\ 28.236\\ 28.237\\ 28.236\\ 28.237\\ 28.236\\ 28.237\\ 28.236\\ 28.237\\ 28.236\\ 28.237\\ 28.236\\ 28.237\\ 28.236\\ 28.236\\ 28.237\\ 28.236\\ 28.237\\ 28.236\\ 28.256\\ 28.256\\ 28.256\\ 28.256\\ 28.256\\ 28.256\\ 28.256\\ 28.256\\$

N20240523-FC1891-WXX-PHOI-229.1.fid







N20240401-FC0907-WXX-PHOI-230.1.fid



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



S53





¹³C{1H} NMR (101 MHz, CDCl₃) Spectrum of 4x



N20240417-FC1191-WXX-PHBI-249.2.fid





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



¹³C{1H} NMR (101 MHz, CDCl₃) Spectrum of **4y**

169.497	157,178 150,147 150,147 149,384 143,722 143,020 134,823 130,402 134,823 130,402 134,823 130,402 134,823 130,402 128,235 128,235 128,235 127,295 127,395 127,295 127,205 127,29	77.477 77.160 76.842	55.612 53.525	41.656	24.353
1		\checkmark	17		1

N20240425-FC1383-WXX-PHOI-254.2.fid



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



S56

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



10 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 4aa



S58

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



$^{13}C\{1H\}$ NMR (101 MHz, CDCl₃) Spectrum of **4ab**

- 168.227 150.227 150.243 150.243 150.243 151.243 151.244 151.258 122.246 122.246 122.2771 122.655 122.655 122.655 122.655 122.655 122.655 122.655 122.655 122.655 122.771 122.655 122.771 122.655 122.771 122.655 122.771 122.655 122.771 122.655 122.771 122.655 122.771 122.655 122.771	77.477 77.160 76.843		— 41.706	— 24.377 — 21.313
--	----------------------------	--	----------	----------------------

N20240417-FC1191-WXX-PHBI-250.2.fid





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







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



10 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 4ae



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



10 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 **4af**







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



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



N20240506-FC1512-WXX-PHOI-266.2.fid









^1H NMR (400 MHz, CDCl₃) Spectrum of 5a







^1H NMR (400 MHz, CDCl₃) Spectrum of 5c



S72








1 H NMR (400 MHz, CDCl₃) Spectrum of **5**e

 $^{13}\text{C}\{1\text{H}\}$ NMR (101 MHz, CDCl₃) Spectrum of 5e

169.141	161.056 158.577 158.577 149.979 149.879 149.875 149.085 149.085 149.085 149.085 133.557 130.765 133.557 130.765 128.294 128.295 127.349 122.680 127.349 122.680 122.680 122.680 122.682 122.734 123.7444 124.744 124.7444 124.7444 124.7444 124.7444 124.7444 124.7444 124.744	55.471 55.231 55.214 53.401	41.870	24.411
	VVVIVII AND CONTRACTOR	\checkmark		

N20240930-FC3608- WXX-PHOI-302.1.fid







$^{13}\text{C}\{1\text{H}\}$ NMR (101 MHz, CDCl₃) Spectrum of $\mathbf{5f}$

169.522	158.670 158.487 149.165 149.165 149.165 143.352 143.352 137.259 137.229 137.229 137.229 137.229 137.229 137.229 137.229 137.229 137.229 137.229 137.229 137.526 125.566 125.566 125.564 125.564 125.564 125.564 125.564 125.564 125.564 125.564 125.564 125.564 125.556 125.564 125.556 125.55	77.477 77.160 76.843	55.213 50.441 44.160 44.160 33.953 38.006 38.006 33.953 33.953 31.775 26.365 26.365 31.662 31.7583 31.75833 31.75833 31.75833 31.75833 31.758333 31.758333 31.758331
1		\checkmark	

N20240705-FC2648-WXX-PHOI-306.1.fid



¹H NMR (400 MHz, CDCl₃) Spectrum of $\mathbf{6}$





S76











150.976 150.635 150.635 139.785 139.785 134.962 134.962 124.962 129.590 129.590 121.87 127.175 127.015 121.870 121.870 121.870 120.991 120.991	77.478 77.160 76.843	59.791 53.876	40.292	24.873
VIIIV	\checkmark		1	1

N20240627-FC2479-PHOI-294.1.fid

