Supporting Information

for

Enantioselective N-heterocyclic carbene catalyzed synthesis of functionalized indenes

Changhe Zhang, David W. Lupton*

INDEX

I. General experimental	2
II. Chiral indene synthesis.	3
II-1. Preparation of α , β -unsaturated carboxylic acid fluorides	3
II-2. Preparation of trimethylsilyl enol ethers	7
II-3. Preparation of chiral indenes	7
II-4. Derivatization	16
III. X-ray crystal structures	18
IV. ¹ H, ¹³ C-NMR spectra and HPLC traces	19

I. General experimental

Proton (¹H) and carbon (¹³C) NMR spectra were recorded in deuterated solvents on Varian NMR spectrometers (400 MHz and 800 MHz) and calibrated to residual solvent peaks. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quatet, pent = pentet, sext = sextet, m = multiplet and br = broad. 2D correlation spectra were recorded on a Bruker DRX400 spectrometer. Infrared spectra (ν_{max}) were recorded on an Agilent Cary 630 FTIR Spectrometer. High resolution mass spectra (HRMS, ESI) were recorded on a Bruker BioApex 47e FTMS fitted with an Analytical electrospray source using NaI for accurate mass calibration. Analytical chiral HPLC was performed with a Perkin Elmer Series 225 HPLC or Agilent Series 1260 using Chiralpak AD-H or AS-H, Chiralcel OJ-H (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. or using RegisCellTM 5μm column (4.6 mm x 25 cm) obtained from Regis Technologies, Inc., with visualization at 254 nm or staining solutions of anisaldehyde or KMnO₄. Optical rotations were measured with a PolAAr 3005 polarimeter at 589nm.

Flash column chromatography was performed on silica gel (Davisil LC60A, 40-63 μ m silica media) using compressed air. Thin layer chromatography (TLC) was performed using aluminium-backed plates coated with 0.2 mm silica (Merck, DC-Platten, Kieselgel; 60 F254 plates). Eluted plates were visualized using a 254 nm UV lamp and/or by treatment with a suitable stain followed by heating. Concentration under reduced pressure was performed on a rotary evaporator with a water bath temperature of 40 °C, except for toluene where temperature was set to 60 °C.

The starting materials and reagents were purchased from Sigma-Aldrich or Oakwood and were used as supplied or, in the case of some liquids, distilled. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl and acetonitrile (CH₃CN) and dichloromethane (CH₂Cl₂) were dried by passing over activated alumina. Unless otherwise stated, all reactions were conducted in flame-dried glassware under a N_2 atmosphere. "Salt-free" generation of carbene catalyst was filtered through syringe filters (hydrophobic, $25 \text{mm} \times 0.2 \ \mu\text{m}$) purchased from Merck Pty. Ltd.

II. Chiral indene synthesis.

II-1. Preparation of α,β-unsaturated carboxylic acid fluorides

General procedure A (G-A):

General procedure B (G-B):

S2

R1
$$\frac{1}{1!}$$
OH

S1

CO₂t-Bu

TFA, DCM,
RT, 15 h

R1 $\frac{1}{1!}$
R

Pb(OAc)₄
THF, RT

S3

R1 $\frac{1}{1!}$
R

Pb(OAc)₄
THF, RT

R1 $\frac{1}{1!}$
R

DCM, RT

Ph₃P CO₂tBu
DCM, RT

DCM, RT

Ph₃P CO₂tBu
DCM, RT

THF, RT

R1 $\frac{1}{1!}$
R

S3

S4

O

O

TFA, DCM,
RT, 15 h

R1 $\frac{1}{1!}$
R

S5-b

S6

General procedure C (G-C):

Hydrozone S3 formation (in G-A and G-B)

Following reported synthesis¹: acylhydrazine **S2** (10 mmol) was added to a solution of the corresponding salicylaldehyde derivative **S1** (10 mmol) in EtOH (50 mL) and the mixture was heated to reflux. The reaction was monitored by TLC (2-16h). The mixture was cooled to room temperature, concentrated and washed with hexanes. The solid was recrystallized from MeOH, and dried *in vacuo*. The hydrazones **S3** were essentially pure and some of them existed as a mixture of E and E isomers.

2-Ketobenzaldehydes S4 from oxidation of hydrazones to (in G-A and G-B)

Following reported synthesis¹: $Pb(OAc)_4$ (2.44g, 5.5 mmol) was added in 3 portions to a stirring solution of hydrazone **S3** (5.0 mmol) in THF (25 mL). The mixture turned orange immediately with a mild evolution of N_2 gas. The mixture was stirred at room temperature for 2-3 h (monitored by TLC). The solid was filtered off by passing the mixture through a pad of celite and washed with Et_2O . The

^{1. (}a) Phan, D. H.; Kim, B.; Dong, V. M. J. Am. Chem. Soc. **2009**, 131, 15608; (b) Dethe, D. H.; Murhade, G. M. Chem. Commun. **2015**, 51, 10891.

combined filtrate was washed with saturated aqueous $NaHCO_3$ and then brine, dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified via flash column chromatography over silica gel (EtOAc/Hexanes as the eluents) and 2-ketobenzaldehyde **S4** were obtained.

Ethyl esters S5-a from HWE reaction (in G-A)

To a stirred suspension of NaH (60% in mineral oil, 1.1 equiv.) in anhydrous THF (0.05 M) was added slowly a solution of phosphonate (1.1 equiv.) in THF (0.1 M) at 0 $^{\circ}$ C. Upon completion of effervescence, a solution of the corresponding 2-ketobenzaldehyde S4 (1.0 equiv.) in THF (0.2 M) was added in one portion. The resultant mixture was stirred overnight at room temperature. The reaction mixture was quenched with saturated aqueous NH₄Cl solution. The aqueous layer was extracted with EtOAc (2 x 30 mL), and the combined organic layers were washed with brine, dried over MgSO₄, filtered and the solvent was removed under reduced pressure. Then residue was purified via flash column chromatography over silica gel with EtOAc/hexanes as the eluents and ethyl esters S5-a were obtained.

tert-Butyl esters S5-b from Wittig reaction (in G-B)

To a solution of 2-ketobenzaldyde S4 in DCM (0.1 M) was added a solution of *tert*-butyl ester phosphorus ylide in DCM (0.2 M) and the reaction was stirred for 2 h. The solvent was removed and residue was suspended in ether and the precipitations were removed by filtration and solid washed with ether. The combined filtrate was concentrated under reduced pressure and residue was purified by flash column chromatography over silica gel with EtOAc/hexanes as the eluents, affording the desired *tert*-butyl ester products S5-b.

o-Bromophenyl ketones S9 (G-C)

To a stirred solution of 2-bromobenzaldehyde **S7** (1 equiv.) in anhydrous THF (0.1 M) was added dropwise a solution of phenyl magnesium bromide (1.0 M in Et₂O, 1.5 equiv.) at 0 °C. The resultant mixture was stirred for 4 hours at room temperature, before being treated with saturated aqueous NH₄Cl solution. The aqueous layer was extracted with ether (2 x 30 mL), and the combined organic layers were washed with brine, dried over MgSO₄, filtered and evaporated under reduced pressure. The crude product **S8** was dissolved in DCM (0.1 M), celite was added, and the mixtrue was treated with PCC (1.5 equiv.) and stirred for 1–3 h. Upon completion (as monitored by TLC analysis), the reaction mixture was concentrated in reduced pressure, suspended in ether, filtered through a pad of celite and concentrated under reduced pressure. The crude residue was purified by column chromatography over silica (EtOAc/hexanes as the eluent) to afford the desired ketones **S9**.

Ethyl esters S5-a from Heck reactions (G-C)

To an oven-dried Schlenk tube under N_2 were added o-bromophenyl ketones $\mathbf{S9}$ (10.0 mmol), $Pd(OAc)_2$ (0.5 mmol, 5 mol%), Ph_3P (1.0 mmol, 10 mol%), Et_3N (30.0 mmol), and anhydrous toluene (25 mL), and this was followed by the addition of ethyl acrylate (30.0 mmol). The resulting mixture was stirred at 110 °C for 24 h. The reaction was cooled to room temperature, quenched by the addition of saturated aqueous NH_4Cl , followed by extraction with EtOAc (3 × 15 mL). The combined organic extracts were washed with brine and dried (Na_2SO_4). The filtrate was concentrated under reduced pressure and residue purified by column chromatography over silica gel, affording the desired ester products S5-a.

Acids S6 from hydrolysis of ethyl esters (in G-A and G-C)

To a solution of esters in EtOH (1 M) was added KOH (3 eq. dissolved in water, 3 M) at room temperature and refluxed for 2 hours. The mixture was cooled to room temperature and acidified to pH <1.0 with 2N HCl. The precipitations were collected and washed with water (3 x 30 mL). The solid was dried in air, affording the desired products **S6**. In some cases, the dried solid was recrystallized in EtOAc/hexanes.

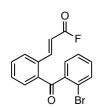
Acids S6 from *tert*-butyl esters S5b (in G-B)

Following reported synthesis²: Trifluoroacetic acid (18 mmol, 1.5 mL) was added in one portion to a solution of the ester **S5-b** (3 mmol, 1 equiv.) in dichloromethane (3 mL). The resultant dark brown solution was maintained at 23°C for 15 h. The solution was concentrated and the residual trifluoroacetic acid was removed by being suspended in ether (5 mL) and concentration in *vacuo*. This procedure was repeated twice. The beige solid was then washed with ether by filtration to afford the desired acids **S6**.

Preparation of α,β-unsaturated carboxylic acid fluorides 7 (in G-A, G-B and G-C)

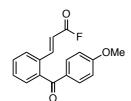
Following reported synthesis³: To a suspension of the appropriate α,β -unsaturated carboxylic acid **S6** (5 mmol) in CH₂Cl₂ (5 ml) at 0 °C was added diethylaminosulfur trifluoride (DAST, 0.73 ml, 5.5 mmol). After stirring at 0 °C for 15 minutes, the reaction was quenched by slow addition of NaHCO₃ (5 ml of a saturated aqueous solution) at 0 °C. Until no more gas release from the mixture, the mixture was extracted with CH₂Cl₂ (3 x 5 ml), the organic phase dried (Na₂SO₄), concentrated under reduced pressure. The crude product was purified via passing through a short column of celite (These electron-deficient acid fluorides are generally unstable to survive a column chromatography over silica gel). After removal of the solvent, the oily products were dried in *vacuo* to afford desired acid fluorides **7**. If not solidified, the oily products were re-dissolved in ether, concentrated and dried in *vacuo*. This process might be repeated for a few times until the products solidified except for **7e** and **7i**, which were sticky oil with any attempt.

(E)-3-(2-(2-bromobenzoyl)phenyl)acryloyl fluoride (7a)



Following the general procedure, the title compound was obtained as yellow solid (1.22g, 73% yield). MP 64-66 °C. IR v_{max} 2964, 1796, 1664, 1246, 1186, 1110, 928, 759, 738 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, J = 15.8 Hz, 1H), 7.70 (brd, J = 7.9, 1H), 7.66 – 7.59 (m, 2H), 7.51 – 7.36 (m, 5H), 6.31 (dd, J = 15.8, 8.7 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 197.0, 156.9 (d, J = 340.4 Hz), 150.6 (d, J = 5.4 Hz), 140.5, 137.7, 135.0, 133.9, 133.1, 132.6, 132.0, 130.8, 130.6, 128.8, 127.8, 127.8, 115.3 (d, J = 66.2 Hz).

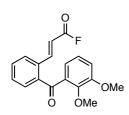
(E)-3-(2-(4-methoxybenzoyl)phenyl)acryloyl fluoride (7b)



Following the general procedure G-A, the title compound was obtained as pale yellow solid (1.29g, 91% yield). MP 91-93 °C. IR $v_{\rm max}$ 2847 (week), 1792, 1594, 1509, 1257, 1195, 1173, 930, 839, 759, 737 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, J = 15.9 Hz, 1H), 7.82 – 7.68 (m, 1H), 7.77 (AA'BB' J = 8.9 Hz, 2H), 7.60 – 7.48 (m, 2H), 7.49 – 7.40 (m, 1H), 6.94 (AA'BB', J = 8.9 Hz, 2H), 6.31 (dd, J = 15.9, 7.8 Hz, 1H), 3.87 (s, 3H). ¹³C NMR (101 MHz,

CDCl₃) δ 195.5, 164.6, 156.8 (d, J = 339.7 Hz), 149.0 (d, J = 5.5 Hz), 140.9, 133.1, 132.6, 130.9, 130.8, 130.3, 129.5, 127.8, 114.7 (d, J = 66.9 Hz), 114.3, 55.9. HRMS (ESI) m/z: Found (M–HF+H)⁺ $C_{17}H_{13}O_3^+$ 265.0862, requires 265.0859.

(E)-3-(2-(2,3-dimethoxybenzoyl)phenyl)acryloyl fluoride (7c)



Following the general procedure, the title compound was obtained as white solid (1.23g, 78% yield). m.p. 96-98 °C. IR v_{max} 2942, 1798, 1649, 1475, 1315, 1263, 1193, 1064, 1003, 954, 829, 761, 742 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, J = 15.8 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.58 – 7.50 (m, 1H), 7.47 – 7.42 (m, 2H), 7.25 – 6.94 (m, 3H), 6.31 (dd, J = 15.8, 8.5 Hz, 1H), 3.88 (s, 3H), 3.55 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.3, 157.0 (d, J = 340.1 Hz), 153.3, 150.4 (d, J = 5.2 Hz), 148.3, 140.8, 134.2, 133.4, 131.9, 130.7,

² Myers, A. G.; Glatthar, R.; Hammond, M.; Harrington, P. M.; Kuo, E. Y.; Liang, J.; Schaus, S. E.; Wu, Y.; Xiang, J.-N. *J. Am. Chem. Soc.* **2002**, *124*, 5380.

³ (a) Bappert, E.; Muller, P.; Fu, G. C. *Chem. Commun.* **2006**, 2604; (b) Levens, A.; Zhang, C.; Candish, L.; Forsyth, C. M.; Lupton, D. W. *Org. Lett.* **2015**, *17*, 5332; (c) Levens, A.; Ametovski, A.; Lupton, D. W. *Angew. Chem. Int. Ed.* **2016**, *55*, 16136.

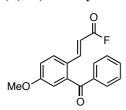
130.7, 128.1, 124.5, 121.6, 116.3, 114.9 (d, J = 66.1 Hz), 61.6, 56.3. HRMS (ESI) m/z: Found (M–HF+H)⁺ $C_{18}H_{15}O_4$ 295.0967, requires 295.0965.

(E)-3-(2-(2-chlorobenzoyl)-4-methoxyphenyl)acryloyl fluoride (7d)

Following the general procedure G-A, the title compound was obtained deep red solid (1.04g, 65% yield). MP 76-78 °C. IR v_{max} 2842, 1794, 1594, 1295, 1258, 1214, 1096, 1035, 958, 758 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, J = 15.8 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.52 – 7.42 (m, 3H), 7.41 – 7.36 (m, 1H), 7.13 – 7.08 (m, 1H), 6.93 (d, J = 2.6 Hz, 1H), 6.22 (dd, J = 15.8, 8.6 Hz, 1H), 3.81 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 196.1, 161.7, 157.3 (d, J = 339.0 Hz), 149.4 (d, J = 5.2 Hz), 140.5, 138.3, 132.9, 132.7, 131.0, 130.9,

130.2, 127.3, 126.5, 117.7, 117.1, 113.0 (d, J = 65.9 Hz), 56.0.

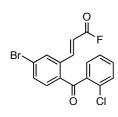
(E)-3-(2-benzoyl-4-methoxyphenyl)acryloyl fluoride (7e)



Following the general procedure G-C, the title compound was obtained as pale yellow sticky oil (1.0g, 70% yield). IR v_{max} 2841, 2362, 1788, 1657, 1592, 1489, 1278, 1213, 1086, 1031, 957, 820, 715 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, J = 15.7 Hz, 1H), 7.82 – 7.79 (m, 2H), 7.74 (d, J = 8.8 Hz, 1H), 7.68 – 7.58 (m, 1H), 7.54 – 7.43 (m, 2H), 7.12 – 7.06 (m, 1H), 6.94 (d, J = 2.7 Hz, 1H), 6.20 (dd, J = 15.7, 7.8 Hz, 1H), 3.84 (s, 3H). ¹³C NMR (101

MHz, CDCl₃) δ 196.7, 161.7, 157.2 (d, J = 338.2 Hz), 148.2 (d, J = 5.6 Hz), 142.2, 137.1, 134.3, 130.6, 129.6, 129.0, 124.9, 117.0, 114.7, 112.0 (d, J = 67.0 Hz), 56.0. HRMS (ESI) m/z: Found (M–HF+H)⁺ $C_{18}H_{15}O_4^+$ 265.0861, requires 265.0859.

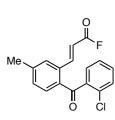
(E)-3-(5-bromo-2-(2-chlorobenzoyl)phenyl)acryloyl fluoride (7f)



Following the general procedure G-A, the title compound was obtained as yellow solid (1.16g, 63% yield). MP 94.5-96 °C. IR $v_{\rm max}$ 2360, 1802, 1669, 1632, 1296, 1192, 1104, 939, 746 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, J = 15.8 Hz, 1H), 7.82 (d, J = 1.9 Hz, 1H), 7.60 (dd, J = 8.3, 1.9 Hz, 1H), 7.55 – 7.37 (m, 4H), 7.32 (d, J = 8.3 Hz, 1H), 6.30 (dd, J = 15.8, 8.2 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 195.4, 156.4 (d, J = 342.3 Hz), 148.9 (d, J = 5.1 Hz), 138.2, 136.9, 136.5, 133.7, 133.0(1), 132.9(5), 132.5, 131.8, 130.9, 130.7,

127.9, 127.5, 116.6 (d, J = 66.3 Hz).

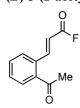
(E)-3-(2-(2-chlorobenzoyl)-5-methylphenyl)acryloyl fluoride (7g)



Following the general procedure G-A, the title compound was obtained as deep red solid (757mg, 50% yield). MP 62-64 °C. IR $v_{\rm max}$ 1786, 1658, 1288, 1194, 1053, 961, 826, 763, 738 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, J = 15.8 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.54 – 7.43 (m, 3H), 7.43 – 7.35 (m, 2H), 7.23 (s, 1H), 6.27 (dd, J = 15.8, 8.7 Hz, 1H), 2.37 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 196.5, 157.1 (d, J = 341.0 Hz), 150.2 (d, J = 5.4 Hz), 141.7, 138.7, 138.6, 133.6, 132.7, 132.6, 132.0, 131.8, 130.9, 130.8, 128.6, 127.3, 114.4 (d, J

= 66.1 Hz), 21.7. HRMS (ESI) m/z: Found (M–HF+H)⁺ $C_{17}H_{12}ClO_2$ ⁺ 283.0524, requires 283.0520.

(E)-3-(2-acetylphenyl)acryloyl fluoride (7h)



Following the general procedure G-B, the title compound was obtained as white solid (586mg, 61% yield). MP 89-91 °C. IR v_{max} 3075, 1795, 1671, 1626, 1259, 1195, 1097, 973, 840, 755 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.38 (d, J = 15.8 Hz, 1H), 8.03 – 7.83 (m, 1H), 7.72 – 7.50 (m, 3H), 6.20 (dd, J = 15.8, 8.6 Hz, 1H), 2.65 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 200.4, 157.0 (d, J = 340.2 Hz), 151.8 (d, J = 5.3 Hz), 138.3, 134.2, 132.7, 131.0, 130.1, 129.0, 114.9 (d, J = 66.3 Hz), 29.1. HRMS (ESI)

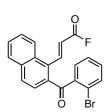
m/z: Found (M–HF+H)⁺ C₁₁H₉O₂⁺ 173.0598, requires 173.0597.

(E)-3-(2-isobutyrylphenyl)acryloyl fluoride (7i)

Following the general procedure G-B, except that it was purified by distillation (130 °C, 1.5 mBar), the title compound was obtained as pale yellow oil (750 mg, 68% yield). IR v_{max} 2973, 1796, 1680, 1626, 1214, 1190, 1102, 975, 760 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, J = 15.8 Hz, 1H), 7.74 – 7.70 (m, 1H), 7.65 – 7.62 (m, 1H), 7.59 – 7.51 (m, 2H), 6.24 (dd, J = 15.8, 8.2 Hz, 1H), 3.42 (sept, J = 6.9 Hz, 1H), 1.21 (d, J = 6.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 207.6, 157.0 (d, J = 339.9 Hz), 151.0 (d, J = 5.4 Hz), 139.3, 133.9, 132.0, 131.0, 128.8, 128.6, 114.8 (d, J =

66.4), 38.6, 18.9. HRMS (ESI) m/z: Found (M-HF+H)⁺ $C_{13}H_{13}O_2^+$ 201.0911, requires 201.0910.

(E)-3-(2-(2-bromobenzoyl)naphthalen-1-yl)acryloyl fluoride (7j)



Following the general procedure G-B, the title compound was obtained as yellow solid (1.32g, 69% yield). MP 97-99 °C. IR v_{max} 3060, 1803, 1669, 1633, 1289, 1241, 1203, 1110, 757 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.38 (d, J = 16.1 Hz, 1H), 8.13 – 8.06 (m, 1H), 7.97 – 7.87 (m, 2H), 7.73 – 7.56 (m, 4H), 7.47 – 7.32 (m, 3H), 6.12 (dd, J = 16.1, 7.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 197.2, 156.1 (d, J = 342.0), 150.2 (d, J = 5.8 Hz), 140.8, 135.4, 134.9, 134.2, 134.1, 132.7, 130.9, 130.8, 130.0, 129.0, 128.9, 128.3, 127.9, 126.6, 126.4, 121.0, 120.6

(d, J = 66.3 Hz). HRMS (ESI) m/z: Found (M-HF+OH) $^{\circ}$ C₂₀H₁₂BrO₃ $^{\circ}$ 378.9972, requires 378.9975.

II-2. Preparation of trimethylsilyl enol ethers

Following reported synthesis⁴, the trimethylsilyl enol ethers **8** were prepared from the corresponding ketones **S12**: To a 100 mL flask was loaded a mixture of ketone **S10** (25 mmol) and sodium iodide (4.5 g, 30 mmol) under nitrogen, and dry acetonitrile (30 mL). The resulting solution was stirred for 5 min at room temperature, and triethylamine (4.2 mL, 30 mmol) was added, followed by chlorotrimethylsilane (3.82 mL, 30 mmol). The reaction mixture was then stirred at 40 °C overnight. After cooled to room temperature, the reaction was quenched with cold pentane (50 mL) and ice water (50 mL). The organic phase was separated, and the aqueous layer was extracted with pentane (30 mL). The combined organics were washed with brine and then dried over anhydrous MgSO₄. The solvent was removed first in *vacuo* by rotatory evaporator, and the residue was distilled under reduced pressure to provide pure silyl enol ethers **8**.

II-3. Preparation of chiral indenes

Sub millimolar scale: To a flame-dried RBF charged with precatalyst **B1•**HBF₄ (4.2 mg, 0.01 mmol) and toluene (0.5 mL) was added KHMDS (0.02 mL, 0.01 mmol). The resulting solution was stirred at room temperature for 30 minutes before the solution was filtered through a 50 μm syringe filter in N₂. The filtrate was dried in a Schlenk under vacuum carefully for 30 min and the residue dissolved in 0.5 mL THF. The salt-free solution of NHC catalyst **B1** was then transferred via cannula to a solution of

4. Shen, H.; Li, J.; Liu, Q.; Pan, J.; Huang, R.; Xiong, Y. J. Org. Chem. 2015, 80, 7212.

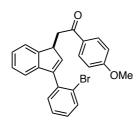
S-7

acid fluoride 7 (0.1 mmol) and trimethylsilyl enol ether 8 (0.12 mmol) in THF (0.5 mL) at 0 °C. The reaction was stirred at 0°C for 5 min and the ice-water bath was then removed. Upon completion (1-2 h), the resulting mixture was concentrated under reduced pressure and purified via column chromatography (EtOAc:hexanes, SiO₂) to afford indenes 6.

Millimolar scale (Synthesis of 6y): To a flame-dried RBF charged with precatalyst B1•HBF₄ (42 mg, 0.1 mmol) and toluene (5 mL) was added KHMDS (0.2 mL, 0.1 mmol). The resulting solution was stirred at room temperature for 30 minutes before the solution was filtered through a 50 μm syringe filter in N₂. The filtrate was dried in a Schlenk under vacuum carefully for 30 min and the residue dissolved in 5 mL of THF. The salt-free solution of NHC catalyst B1 was transferred via cannula to a solution of acid fluoride 7g (302 mg, 1 mmol) and ((1-(2-methoxyphenyl)vinyl)oxy)trimethylsilane 8 (222 mg, 1.2 mmol) in THF (5 mL) at 0 °C. The reaction was stirred at 0 °C for 5 min and the ice-water bath was then removed. Upon completion (2 h), the resulting mixture was concentrated under reduced pressure and purified via column chromatography (5% Acetone:hexanes, SiO₂) to afford a yellow oild which solidified to give indenes 6y (200 mg, 57% yield).

All racemic samples were obtained with achiral precatalyst IMes•HCl, except otherwise mentioned with precatalyst C•HBF₄. And filtration for generation of free NHC catalyst was not performed when racemic samples were prepared.

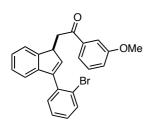
2-(3-(2-Bromophenyl)-1H-inden-1-yl)-1-(4-methoxyphenyl)ethan-1-one (6a)



Following general procedure, the title compound was obtained as colorless oil. 17.5 mg (42% yield). Rf 0.52 (7:3 v/v hexanes:EtOAc). HPLC AD-H 5µm, $\lambda = 254$ nm, hexane : i-PrOH = 95:5, 1.0 mL/min, fraction $t_r = 15.80$ (major) and 14.36 (minor); e.r. = 97:3. $[\alpha]_D^{25} = +9.0^\circ$ (c = 0.61, CHCl₃); IR v_{max} 2962, 1673, 1598, 1509, 1258, 1220, 1166, 1013, 800, 759 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.99 (AA'BB', J = 8.9 Hz, 2H), 7.73 – 7.64 (m, 1H), 7.53 – 7.48 (m, 1H), 7.41 – 7.35 (m, 2H), 7.30 – 7.20 (m, 3H), 7.17 –

7.12 (m, 1H), 6.95 (AA'BB', J = 8.9 Hz, 2H), 6.61 (d, J = 2.0 Hz, 1H), 4.33 (ddd, J = 8.6, 6.2, 2.0 Hz, 1H), 3.88 (s, 3H), 3.46 (dd, J = 17.1, 6.2 Hz, 1H), 3.17 (dd, J = 17.1, 8.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 197.5, 164.0, 147.5, 144.0, 143.8, 138.4, 137.1, 133.4, 131.3, 130.8, 130.3, 129.4, 127.6, 127.0, 125.6, 123.7, 123.4, 121.4, 114.1, 55.8, 45.5, 40.3. HRMS (ESI) m/z: Found (M+H)⁺ $C_{24}H_{20}^{79}BrO_{2}^{+}419.0634$, requires 419.0641.

(S)-2-(3-(2-bromophenyl)-1H-inden-1-yl)-1-(3-methoxyphenyl)ethan-1-one (6b)



Following general procedure, the title compound was obtained as colorless oil. 23 mg (55% yield). Rf 0.28 (95:5 v/v hexanes:EtOAc). HPLC AD-H 5µm, λ = 254 nm, hexane : i-PrOH = 92:8, 1.0 mL/min, fraction $t_{\rm r}$ = 9.76 (major) and 8.44 (minor); e.r. = 92:8. [α]_D²⁵ = +12.3° (c = 0.83, CHCl₃). IR v_{max} 2965, 1683, 1428, 1254, 1021, 737 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.63 (m, 1H), 7.60 – 7.53 (m, 2H), 7.54 – 7.46 (m, 1H), 7.42 – 7.32 (m, 3H), 7.32 – 7.20 (m, 3H), 7.17 – 7.08 (m, 2H), 6.61 (d, J = 2.0

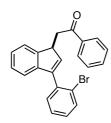
Hz, 1H), 4.33 (ddd, J = 8.6, 6.0, 2.0 Hz, 1H), 3.86 (s, 3H), 3.51 (dd, J = 17.5, 6.0 Hz, 1H), 3.21 (dd, J = 17.5, 8.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 198.8, 160.2, 147.4, 144.1, 144.0, 138.5, 138.1, 137.1, 133.4, 131.3, 130.0, 129.5, 127.6, 127.1, 125.7, 123.7, 123.4, 121.4, 121.2, 120.2, 112.7, 55.8, 45.3, 40.9. HRMS (ESI) m/z: Found (M+H)⁺ $C_{24}H_{20}^{79} BrO_{2}^{+} 419.0642$, requires 419.0641.

(S)-2-(3-(2-bromophenyl)-1H-inden-1-yl)-1-(2-methoxyphenyl)ethan-1-one (6c)

Following general procedure, the title compound was obtained as colorless oil. 18 mg (43% yield). Rf 0.22 (95:5 v/v hexanes:EtOAc). 5% Acetone in hexanes was used as the eluent for flash chromatography. HPLC AD-H 5µm, λ = 254 nm, hexane : i-PrOH = 99:1, 1.0 mL/min, fraction $t_{\rm r}$ = 12.49 (major) and 10.34 (minor); e.r. = 99:1. [α]_D²⁵ = +50.5° (c = 0.55, CHCl₃). IR v_{max} 2962, 2923, 1739, 1259, 1084, 1018, 794 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (dd, J = 7.8, 1.8 Hz, 1H), 7.72 – 7.63 (m, 1H), 7.57 – 7.43 (m, 2H), 7.42 – 7.32 (m,

2H), 7.30 - 7.20 (m, 3H), 7.19 - 7.11 (m, 1H), 7.07 - 7.01 (m, 1H), 6.99 - 6.94 (m, 1H), 6.62 (d, J = 2.0 Hz, 1H), 4.31 (ddd, J = 8.8, 6.0, 2.0 Hz, 1H), 3.87 (s, 3H), 3.55 (dd, J = 17.6, 6.0 Hz, 1H), 3.21 (dd, J = 17.6, 8.8 Hz, 1H). 13 C NMR (101 MHz, CDCl₃) δ 201.2, 159.1, 147.7, 144.1, 143.6, 138.7, 137.3, 134.1, 133.4, 131.4, 130.8, 129.4, 128.4, 127.6, 126.8, 125.5, 123.7, 123.5, 121.3, 121.1, 111.9, 55.8, 45.8, 45.7. HRMS (ESI) m/z: Found (M+H)⁺ $C_{24}H_{20}^{79}$ BrO₂⁺419.0647, requires 419.0641.

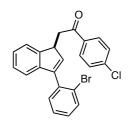
2-(3-(2-Bromophenyl)-1*H*-inden-1-yl)-1-phenylethan-1-one (6d)



Following general procedure, the title compound was obtained as pale yellow oil. 20 mg (51% yield). Rf 0.25 (9:1 v/v hexanes:EtOAc). HPLC AD-H 5 μ m, λ = 254 nm, hexane : i-PrOH = 97:3, 1.0 mL/min, fraction t_r = 12.31 min (major) and 9.67 min (minor); e.r. = 95:5. [α]_D²⁵ = +43.3° (c = 0.25, CHCl₃). IR v_{max} 2961, 1639, 1532, 1259, 1175, 1149, 1091, 1014, 795 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.21 – 7.93 (m, 2H), 7.71 – 7.65 (m, 1H), 7.63 – 7.55 (m, 1H), 7.53 – 7.45 (m, 3H), 7.40 – 7.35 (m, 2H), 7.31 – 7.20 (m, 3H), 7.17 – 7.13 (m, 1H), 6.62 (d, J =

2.0 Hz, 1H), 4.34 (ddd, J = 8.6, 6.2, 2.0 Hz, 1H), 3.52 (dd, J = 17.5, 6.2 Hz, 1H), 3.23 (dd, J = 17.5, 8.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 199.0, 147.4, 144.1, 144.0, 138.2, 137.2, 137.1, 133.6, 133.4, 131.3, 129.5, 129.0, 128.5, 127.6, 127.1, 125.7, 123.7, 123.5, 121.4, 45.3, 40.8. HRMS (ESI) m/z: Found (M+H)⁺C₂₃H₁₈⁷⁹BrO⁺ 389.0547, requires 389.0536.

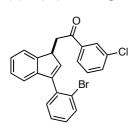
(S)-2-(3-(2-bromophenyl)-1H-inden-1-yl)-1-(4-chlorophenyl)ethan-1-one (6e)



Following general procedure, the title compound was obtained as pale yellow oil. 28 mg (66% yield). Rf 0.35 (95:5 v/v hexanes:EtOAc). HPLC AD-H 5µm, $\lambda = 254$ nm, hexane : i-PrOH = 95 : 5, 1.0 mL/min, fraction $t_r = 10.80$ (major) and 9.60 (minor); e.r. = 88:12. $[\alpha]_D^{25} = +16.9^{\circ}$ (c = 0.62, CHCl₃). IR ν_{max} 2921, 1685, 1588, 1400, 1259, 1090, 1007, 760 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ

7.84 (AA'BB', J = 8.6 Hz, 2H), 7.58 (brd, J = 8.0 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.34 (AA'BB', J = 8.6 Hz, 2H), 7.29 – 7.22 (m, 2H), 7.21 – 7.10 (m, 3H), 7.09 – 7.01 (m, 1H), 6.49 (d, J = 2.0 Hz, 1H), 4.21 (ddd, J = 8.4, 6.2, 2.0 Hz, 1H), 3.38 (dd, J = 17.5, 6.2 Hz, 1H), 3.08 (dd, J = 17.5, 8.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 197.8, 147.2, 144.1, 144.0, 140.1, 137.9, 137.0, 135.4, 133.4, 131.3, 129.9, 129.5, 129.3, 127.6, 127.1, 125.7, 123.6, 123.4, 121.5, 45.2, 40.7. HRMS (ESI) m/z: Found (M+H)⁺ $C_{23}H_{17}^{79}$ BrClO⁺ 423.0149, requires 423.0146.

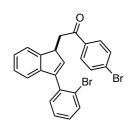
(S)-2-(3-(2-Bromophenyl)-1H-inden-1-yl)-1-(3-chlorophenyl)ethan-1-one (6f)



Following general procedure, the title compound was obtained as colorless oil. 27 mg (64% yield). Rf 0.35 (95:5 v/v hexanes:EtOAc). HPLC AD-H 5 μ m, λ = 254 nm, hexane : i-PrOH = 90 : 10, 1.0 mL/min, fraction t_r = 7.64 (major) and 6.72 (minor); e.r. = 87:13. IR v_{max} 2922, 1687, 1423, 1220, 1023, 741, 680Ncm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.99 (t, J = 1.9 Hz, 1H), 7.91 – 7.84 (m, 1H), 7.69 (dt, J = 8.0, 0.8 Hz, 1H), 7.56 (ddd, J = 8.0, 2.1, 1.1 Hz, 1H), 7.54 – 7.46 (m, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.31

-7.22 (m, 3H), 7.18 - 7.13 (m, 1H), 6.60 (d, J = 2.0 Hz, 1H), 4.32 (ddd, J = 8.4, 6.1, 2.0 Hz, 1H), 3.50 (dd, J = 17.6, 6.1 Hz, 1H), 3.20 (dd, J = 17.6, 8.4 Hz, 1H). 13 C NMR (101 MHz, CDCl₃) δ 197.7, 147.1, 144.2, 144.0, 138.6, 137.8, 137.0, 135.4, 133.6, 133.4, 131.3, 130.4, 129.5, 128.7, 127.6, 127.2, 126.6, 125.7, 123.6, 123.4, 121.5, 45.1, 40.9. HRMS (ESI) m/z: Found (M+H)⁺ $C_{23}H_{17}^{79}$ BrClO⁺ 423.0135, requires 423.0146.

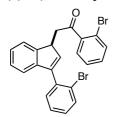
1-(4-bromophenyl)-2-(3-(2-bromophenyl)-1*H*-inden-1-yl)ethan-1-one (6g)



Following general procedure, the title compound was obtained as colorless oil. 25 mg (53% yield). Rf 0.45 (9:1 v/v hexanes:EtOAc). HPLC AD-H 5µm, λ = 254 nm, hexane : i-PrOH = 98:2, 1.0 mL/min, fraction $t_{\rm r}$ = 16.47 (major) and 14.35 (minor); e.r. = 92:8. [α]_D²⁵ = +17.3° (c = 0.58, CHCl₃). IR $\nu_{\rm max}$ 3061, 1686, 1585, 1397, 1221, 1006, 757 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.87 (AA'BB', J = 8.6 Hz, 2H), 7.71 – 7.66 (m, 1H), 7.62 (AA'BB', J = 8.6 Hz, 2H), 7.52 – 7.46 (m, 1H), 7.40 – 7.34 (m, 2H), 7.32 – 7.21 (m, 3H), 7.19 – 7.09 (m,

1H), 6.59 (d, J = 2.0 Hz, 1H), 4.31 (ddd, J = 8.6, 6.2, 2.0 Hz, 1H), 3.48 (dd, J = 17.5, 6.2 Hz, 1H), 3.18 (dd, J = 17.5, 8.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 197.7, 146.9, 143.9, 143.7, 137.6, 136.7, 135.5, 133.1, 132.0, 131.0, 129.7, 129.2, 128.6, 127.3, 126.8, 125.4, 123.3, 123.1, 121.2, 44.9, 40.4. HRMS (ESI) m/z: Found (M+H)⁺ $C_{23}H_{17}^{81}Br_2O^+$ 470.9600, requires 470.9600.

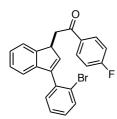
(S)-1-(2-Bromophenyl)-2-(3-(2-bromophenyl)-1H-inden-1-yl)ethan-1-one (6h)



Following general procedure, the title compound was obtained as colorless oil. 26 mg (58% yield). Racemic sample was obtained from achiral precatalyst C•HBF₄. Rf 0.25 (9:1 v/v hexanes:EtOAc). HPLC AD-H 5µm, λ = 254 nm, hexane : i-PrOH = 95:5, 1.0 mL/min, fraction t_r = 12.69 (major) and 10.15 (minor); e.r. = 90:10. $[\alpha]_D^{25}$ = +27.3° (c = 0.86, CHCl₃). IR v_{max} 2922, 2853, 1681, 1260, 1071, 1008, 799 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.67 (m, 1H),

7.65 – 7.60 (m, 1H), 7.54 – 7.50 (m, 1H), 7.43 (dd, J = 7.6, 1.8 Hz, 1H), 7.40 – 7.34 (m, 3H), 7.33 – 7.21 (m, 4H), 7.16 – 7.11 (m, 1H), 6.63 (d, J = 2.0 Hz, 1H), 4.30 (ddd, J = 8.6, 6.1, 2.0 Hz, 1H), 3.47 (dd, J = 17.7, 6.1 Hz, 1H), 3.19 (dd, J = 17.7, 8.6 Hz, 1H). 13 C NMR (101 MHz, CDCl₃) δ 202.9, 146.9, 144.1, 144.0, 141.7, 137.6, 137.0, 134.2, 133.4, 132.1, 131.3, 129.5, 129.0, 127.8, 127.6, 127.1, 125.7, 123.7, 123.5, 121.4, 119.2, 45.3, 44.6. HRMS (ESI) m/z: Found (M+H)⁺ C_{23} H₁₇⁷⁹Br ⁸¹BrO⁺ 468.9622, requires 468.9620.

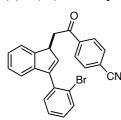
(S)-2-(3-(2-Bromophenyl)-1H-inden-1-yl)-1-(4-fluorophenyl)ethan-1-one (6i)



Following general procedure, the title compound was obtained as pale yellow oil. 21 mg (52% yield). Rf 0.43 (8:2 v/v hexanes:EtOAc). HPLC AD-H 5µm, λ = 254 nm, hexane : i-PrOH = 95:5, 1.0 mL/min, fraction t_r = 10.24 (major) and 8.87 (minor); e.r. = 94:6. [α]_D²⁵ = +81.8° (c = 0.15, CHCl₃). IR v_{max} 2924, 1685, 1596, 1226, 1155, 1025, 770, 741 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.09 – 7.91 (m, 2H), 7.69 – 7.64 (m, 1H), 7.54 – 7.45 (m, 1H), 7.41 – 7.33 (m, 2H), 7.32 – 7.19 (m, 3H), 7.19 – 7.06 (m, 3H), 6.59 (d, J = 2.0 Hz, 1H), 4.31 (ddd, J

= 8.6, 6.2, 2.0 Hz, 1H), 3.47 (dd, J = 17.4, 6.2 Hz, 1H), 3.18 (dd, J = 17.4, 8.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 197.4, 166.2 (d, J = 256.0 Hz), 147.2, 144.1, 144.0, 138.0, 137.0, 133.6 (d, J = 3.0 Hz), 133.4, 131.3, 131.2 (d, J = 9.4 Hz), 129.5, 127.6, 127.1, 125.7, 123.7, 123.4, 121.5, 116.1 (d, J = 22.0 Hz), 45.2, 40.7. HRMS (ESI) m/z: Found (M+H)⁺ $C_{23}H_{17}^{79}$ BrFO⁺ 407.0440, requires 407.0441.

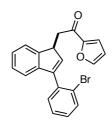
(S)-2-(3-(2-Bromophenyl)-1H-inden-1-yl)-1-(4-cyanophenyl)ethan-1-one (6j)



Following general procedure, the title compound was obtained as colorless oil. 27.5 mg (66% yield). Racemic sample was obtained from achiral precatalyst C•HBF₄. R*f* 0.20 (95:5 v/v hexanes:EtOAc). HPLC AS-H 5µm, λ = 254 nm, hexane : i-PrOH = 90 : 10, 1.0 mL/min, fraction t_r = 38.19 (major) and 37.74 (minor); e.r. = 77:23. IR v_{max} 2962, 1685, 1259, 1087, 1019, 795 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (AA'BB', J = 8.7 Hz, 2H), 7.78 (AA'BB', J = 8.7 Hz, 2H), 7.72 – 7.63 (m, 1H), 7.52 – 7.45 (m, 1H), 7.42 – 7.33 (m, 2H),

7.33 - 7.21 (m, 3H), 7.19 - 7.10 (m, 1H), 6.58 (d, J = 2.0 Hz, 1H), 4.31 (ddd, J = 8.4, 6.2, 2.0 Hz, 1H), 3.53 (dd, J = 17.7, 6.2 Hz, 1H), 3.23 (dd, J = 17.7, 8.4 Hz, 1H). 13 C NMR (101 MHz, CDCl₃) 8 197.7, 146.9, 144.4, 144.0, 140.0, 137.4, 136.8, 133.4, 132.9, 131.2, 129.6, 128.9, 127.6, 127.3, 125.8, 123.6, 123.4, 121.6, 118.2, 116.9, 45.0, 41.2. HRMS (ESI) m/z: Found (M+H)⁺ $C_{24}H_{17}^{79}$ BrNO⁺ 414.0426, requires 414.0488.

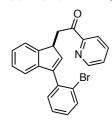
(S)-2-(3-(2-Bromophenyl)-1*H*-inden-1-yl)-1-(furan-2-yl)ethan-1-one (6k)



Following general procedure, the title compound was obtained as colorless oil. 22.7 mg (58% yield). Rf 0.18 (9:1 v/v hexanes:EtOAc). HPLC AD-H 5µm, λ = 254 nm, hexane : i-PrOH = 90:10, 1.0 mL/min, fraction $t_{\rm r}$ = 8.44 (major) and 7.44 (minor); e.r. = 92:8. [α]_D²⁵ = +52.5° (c = 0.93, CHCl₃). IR $\nu_{\rm max}$ 3061, 1671, 1566, 1465, 1021, 907, 758, 733 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.68 – 7.63 (m, 1H), 7.58 (dd, J = 1.7, 0.8 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.39 – 7.30 (m, 2H), 7.28 – 7.18 (m, 4H), 7.14 – 7.08 (m, 1H), 6.55 (d, J = 2.0 Hz, 1H), 6.53 (dd, J = 3.6,

1.7 Hz, 1H), 4.26 (ddd, J = 8.7, 6.5, 2.0 Hz, 1H), 3.34 (dd, J = 16.8, 6.5 Hz, 1H), 3.05 (dd, J = 16.8, 8.7 Hz, 1H). 13 C NMR (101 MHz, CDCl₃) δ 188.1, 152.9, 147.1, 147.0, 144.1, 144.0, 137.8, 137.0, 133.4, 131.3, 129.5, 127.6, 127.1, 125.7, 123.7, 123.4, 121.4, 117.8, 112.7, 45.1, 40.5. HRMS (ESI) m/z: Found (M+H)⁺ $C_{21}H_{16}^{6}$ BrO₂⁺ 379.0287, requires 379.0328; $C_{21}H_{16}^{8}$ BrO₂⁺ 381.0272, requires 381.0308

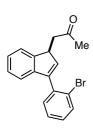
(S)-2-(3-(2-Bromophenyl)-1*H*-inden-1-yl)-1-(pyridin-2-yl)ethan-1-one (6l)



Following general procedure, the title compound was obtained as pale yellow oil. 23.3 mg (60% yield). Rf 0.18 (9:1 v/v hexanes:EtOAc). HPLC AD-H 5µm, λ = 254 nm, hexane : i-PrOH = 95:5, 1.0 mL/min, fraction $t_{\rm r}$ = 8.65 (major) and 7.06 (minor); e.r. = 93:7. [α]_D²⁵ = +74.2° (c = 0.79, CHCl₃). IR $v_{\rm max}$ 2921, 1692, 1260, 1091, 1044, 1022, 992, 799, 772, 674 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.69 – 8.64 (m, 1H), 8.14 (dt, J = 7.8, 1.1 Hz, 1H), 7.87 (td, J = 7.8, 1.7 Hz, 1H), 7.70 – 7.65 (m, 1H), 7.58 – 7.49 (m, 1H), 7.51 – 7.45 (m, 1H), 7.40 – 7.32 (m, 2H), 7.29

-7.20 (m, 3H), 7.16 - 7.11 (m, 1H), 6.63 (d, J = 2.0 Hz, 1H), 4.31 (ddd, J = 8.6, 6.2, 2.0 Hz, 1H), 3.83 (dd, J = 18.1, 6.2 Hz, 1H), 3.48 (dd, J = 18.1, 8.6 Hz, 1H). 13 C NMR (101 MHz, CDCl₃) δ 200.8, 153.6, 149.4, 147.5, 144.0, 143.9, 138.2, 137.3, 137.2, 133.4, 131.4, 129.4, 127.6, 127.5, 126.9, 125.5, 123.8, 123.5, 122.2, 121.3, 45.2, 40.1. HRMS (ESI) m/z: Found (M+H)⁺ $C_{22}H_{17}^{79}$ BrN⁺ 390.0484, requires 390.0488.

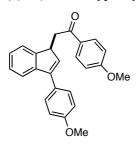
(S)-1-(3-(2-Bromophenyl)-1H-inden-1-yl)propan-2-one (6m)



Following general procedure, the title compound was obtained as pale yellow oil. 12 mg (37% yield). Rf 0.25 (9:1 v/v hexanes:EtOAc). HPLC AD-H 5 μ m, λ = 254 nm, hexane : i-PrOH = 98:2, 1.0 mL/min, fraction $t_{\rm r}$ = 9.56 (major) and 8.27 (minor); e.r. = 96:4. [α]_D²⁵ = +30.0° (c = 0.53, CHCl₃). IR $v_{\rm max}$ 3061, 1714, 1593, 1466, 1357, 1154, 1023, 756, 739 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.68 – 7.64 (m, 1H), 7.46 – 7.40 (m, 1H), 7.39 – 7.31 (m, 2H), 7.28 – 7.17 (m, 3H), 7.13 – 7.07 (m, 1H), 6.51 (d, J = 2.0 Hz, 1H), δ 4.10 (ddd, J = 8.3, 6.4, 2.0 Hz, 1H), 2.95 (dd, J = 17.5, 6.4 Hz,

1H), 2.69 (dd, J = 17.5, 8.3 Hz, 1H), 2.21 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 207.6, 147.1, 144.0(1), 143.9(6), 137.7, 137.0, 133.4, 131.3, 129.5, 127.6, 127.0, 125.7, 123.5, 123.4, 121.4, 45.4, 45.0, 30.7. HRMS (ESI) m/z: Found (M+H)⁺ $C_{18}H_{16}^{79}$ BrO⁺ 327.0373, requires 327.0379.

(S)-1-(4-Methoxyphenyl)-2-(3-(4-methoxyphenyl)-1H-inden-1-yl)ethan-1-one (6n)

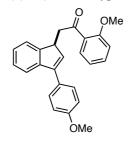


Following general procedure but with 5% acetone in hexanes as the eluent for flash column chromatography, the title compound was obtained as colorless oil. 17 mg (46% yield). Rf 0.11 (9:1 v/v hexanes:EtOAc). HPLC AD-H 5µm, λ = 254 nm, hexane : i-PrOH = 90:10, 1.0 mL/min, fraction $t_{\rm r}$ = 27.38 (major) and 20.85 (minor); e.r. = 91:9. [α]_D²⁵ = -3.24° (c = 0.50, CHCl₃). IR $v_{\rm max}$ 2924, 1711, 1673, 1599, 1509, 1256, 1002, 791 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (AA'BB', J = 8.8 Hz, 2H), 7.61 – 7.53 (m, 1H), 7.54 (AA'BB', J = 8.8 Hz, 2H), 7.51 – 7.48 (m, 1H), 7.36 – 7.29 (m,

1H), 7.28 - 7.21 (m, 1H), 6.98 (AA'BB', J = 8.8 Hz, 2H), 6.94 (AA'BB' J = 8.8 Hz, 2H), 6.57 (d, J = 2.2 Hz, 1H), 4.25 (ddd, J = 8.8, 6.0, 2.2 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.44 (dd, J = 17.2, 6.0 Hz, 1H), 3.11 (dd, J = 17.2, 8.8 Hz, 1H). 13 C NMR (101 MHz, CDCl₃) δ 197.7, 163.9, 159.6, 148.7, 144.0,

143.9, 135.2, 130.8, 130.3, 129.2, 128.6, 127.1, 125.5, 123.8, 120.9, 114.3, 114.1, 55.8, 55.7, 45.0, 40.6. HRMS (ESI) m/z: Found (M+H)⁺ $C_{25}H_{23}O_3^+$ 371.1649, requires 371.1642.

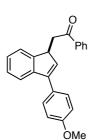
(S)-1-(2-Methoxyphenyl)-2-(3-(4-methoxyphenyl)-1H-inden-1-yl)ethan-1-one (60)



Following general procedure, the title compound was obtained as colorless oil. 14 mg (38% yield). Rf 0.18 (9:1 v/v hexanes:EtOAc). HPLC AD-H 5µm, λ = 254 nm, hexane : i-PrOH = 85:15, 1.0 mL/min, fraction $t_{\rm r}$ = 30.42 (major) and 13.32 (minor); e.r. = 97:3. [α]_D²⁵ = -39.0° (c = 0.48, CHCl₃). IR $v_{\rm max}$ 2932, 1668, 1596, 1508, 1459, 1244, 1176, 1022, 754 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.79 (m, 1H), 7.65 – 7.43 (m, 5H), 7.35 – 7.29 (m, 1H), 7.28 – 7.20 (m, 1H), 7.07 – 7.00 (m, 1H), 7.00 – 6.92 (m, 3H), 6.58 (d, J = 2.2 Hz, 1H), δ 4.23 (ddd, J = 8.8, 6.0, 2.2 Hz, 1H), 3.85(9) (s, 3H), 3.85(5) (s, 3H),

3.52 (dd, J = 17.6, 6.0 Hz, 1H), 3.16 (dd, J = 17.6, 8.8 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 201.3, 159.5, 159.1, 148.9, 143.9, 143.6, 135.5, 134.0, 130.8, 129.1, 128.7, 128.4, 126.9, 125.4, 123.8, 121.1, 120.8, 114.3, 111.9, 55.8, 55.7, 46.0, 45.3. HRMS (ESI) m/z: Found (M+H)⁺ C₂₅H₂₃O₃⁺ 371.1645, requires 371.1642. HRMS (ESI) m/z: Found (M+Na)⁺ C₂₅H₂₂NaO₃⁺ 393.1461, requires 393.1461.

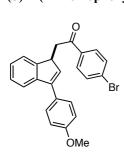
(S)-2-(3-(4-Methoxyphenyl)-1H-inden-1-yl)-1-phenylethan-1-one (6p)



Following general procedure, the title compound was obtained as colorless oil. 18 mg (53% yield). Rf 0.22 (9:1 v/v hexanes:EtOAc). HPLC AD-H 5µm, λ = 254 nm, hexane : i-PrOH = 90 : 10, 1.0 mL/min, fraction $t_{\rm r}$ = 19.90 (major) and 11.72 (minor); e.r. = 89:11. [α]_D²⁵ = +24.1° (c = 0.63, CHCl₃). IR $v_{\rm max}$ 2923, 1687, 1505, 1450, 1220, 1177, 1021, 1001, 816, 772, 746, 693 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.25 – 7.86 (m, 2H), 7.61 – 7.52 (m, 2H), 7.54 (AA'BB', J = 8.7 Hz, 2H), 7.48 (m, 3H), 7.36 – 7.31 (m, 1H), 7.25 (td, J = 7.4, 1.2 Hz, 1H), 6.99 (AA'BB', J = 8.7 Hz, 2H), 6.58 (d, J = 2.2 Hz, 1H), 4.26 (ddd, J = 8.8, 6.0, 2.2 Hz, 1H), 3.86 (s, 3H), 3.50

(dd, J = 17.4, 6.0 Hz, 1H), 3.17 (dd, J = 17.4, 8.8 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 199.2, 159.7, 148.6, 144.2, 143.9, 137.3, 134.9, 133.6, 129.2, 129.0, 128.6, 128.5, 127.1, 125.6, 123.8, 121.0, 114.4, 55.7, 44.8, 41.1. HRMS (ESI) m/z: Found (M+H)⁺ $C_{24}H_{21}O_2^{+3}41.1530$, requires 341.1536.

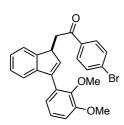
(S)-1-(4-Bromophenyl)-2-(3-(4-methoxyphenyl)-1H-inden-1-yl)ethan-1-one (6q)



Following general procedure, the title compound was obtained as pale yellow oil. 32 mg (77% yield). Rf 0.25 (9:1 v/v hexanes:EtOAc). HPLC AD-H 5µm, λ = 254 nm, hexane : i-PrOH = 95 : 5, 1.0 mL/min, fraction $t_{\rm r}$ = 32.11 (major) and 22.00 (minor); e.r. = 71:29. [α]_D²⁵ = -23.8° (c = 0.34, CHCl₃). IR v_{max} 2938, 1687, 1583, 1506, 1248, 1221, 1174, 1006, 824, 768, 742 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.85 (AA'BB', J = 8.6 Hz, 2H), 7.61 (AA'BB', J = 8.6 Hz, 2H), 7.57 (brd, J = 7.6 Hz, 1H), 7.53 (AA'BB', J = 8.8 Hz, 2H), 7.50 – 7.45 (m, 1H), 7.33 (ddd, J = 8.0, 7.6, 1.1 Hz, 1H), 7.29 – 7.21 (m, 1H), 6.98 (AA'BB', J = 8.8

Hz, 2H), 6.55 (d, J = 2.2 Hz, 1H), 4.23 (ddd, J = 8.6, 6.0, 2.2 Hz, 1H), 3.86 (s, 3H), 3.43 (dd, J = 17.5, 6.0 Hz, 1H), 3.12 (dd, J = 17.5, 8.6 Hz, 1H). 13 C NMR (101 MHz, CDCl₃) δ 198.1, 159.6, 148.3, 144.3, 143.8, 135.9, 134.6, 132.3, 132.2, 130.2, 130.0, 129.1, 128.8, 128.4, 127.2, 125.6, 123.8, 121.0, 114.3, 55.7, 44.6, 41.0. HRMS (ESI) m/z: Found (M+H)⁺ $C_{24}H_{20}^{79}$ BrO₂⁺ 419.0635, requires 419.0641.

1-(4-Bromophenyl)-2-(3-(2,3-dimethoxyphenyl)-1H-inden-1-yl)ethan-1-one (6r)



Following general procedure, the title compound was obtained as yellow solid. 32.5 mg (72% yield). Rf 0.29 (8:2 v/v hexanes:EtOAc). HPLC AD-H 5µm, λ = 254 nm, hexane: i-PrOH = 90: 10, 1.0 mL/min, fraction t_r = 19.75 (major) and 13.83 (minor); e.r. = 54:46. IR v_{max} 2932, 1683, 1583, 1470, 1268, 1221, 1069, 1004, 750 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (AA'BB', J = 8.6 Hz, 2H), 7.61 (AA'BB', J = 8.6 Hz, 2H), 7.50 – 7.44 (m, 1H), 7.39 – 7.31 (m, 1H), 7.31 – 7.20 (m, 2H), 7.14 – 7.08 (m, 1H), 7.00 – 6.92 (m, 2H), 6.63 (d, J = 2.1 Hz,

1H), 4.29 (ddd, J = 8.4, 6.2, 2.1 Hz, 1H), 3.92 (s, 3H), 3.63 (s, 3H), 3.46 (dd, J = 17.4, 6.2 Hz, 1H), 3.15 (dd, J = 17.4, 8.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 198.1, 153.4, 147.4, 147.3(7), 144.4,

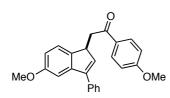
141.6, 137.2, 135.9, 132.3, 130.2, 130.0, 128.8, 127.1, 125.4, 124.2, 123.3, 122.7, 121.9, 112.3, 61.1, 56.3, 45.1, 40.9. HRMS (ESI) m/z: Found (M+H)⁺ $C_{25}H_{22}^{79}BrO_3^+$ 449.0745, requires 449.0747.

2-(3-(2-Chlorophenyl)-5-methoxy-1H-inden-1-yl)-1-phenylethan-1-one (6s)

Following general procedure, the title compound was obtained as a colorless oil. 18 mg (48% yield). R*f* 0.38 (8:2 v/v hexanes:EtOAc). HPLC AD-H 5µm, λ = 254 nm, hexane : i-PrOH = 90:10, 1.0 mL/min, fraction $t_{\rm r}$ = 10.38 (major) and 9.67 (minor); e.r. = 90:10. [α]_D²⁵ = 46.2° (c = 4.33, CHCl₃). IR v_{max} 2963, 1599, 1476, 1259, 1082, 1025, 1007, 795, 755, 688 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.04 – 7.98 (m, 2H), 7.62 – 7.55 (m, 1H), 7.51 – 7.45 (m, 3H), 7.41 – 7.36 (m, 2H), 7.34 – 7.29 (m, 2H), 6.79 (dd, J = 8.2, 2.4 Hz, 1H), 6.72 (d, J

= 2.4 Hz, 1H), 6.66 (d, J = 2.0 Hz, 1H), 4.28 (ddd, J = 8.4, 6.4, 2.0 Hz, 1H), 3.78 (s, 3H), 3.47 (dd, J = 17.4, 6.4 Hz, 1H), 3.21 (dd, J = 17.4, 8.4 Hz, 1H). 13 C NMR (101 MHz, CDCl₃) δ 198.9, 159.4, 145.3, 142.0, 139.6, 139.4, 137.0, 134.7, 133.4, 133.3, 131.1, 130.0, 129.1, 128.8, 128.3, 126.3, 124.0, 111.2, 106.9, 55.7, 44.5, 40.8. HRMS (ESI) m/z: Found (M+H) $^+$ C₂₄H₂₀ClO $_2$ $^+$ 375.1149, requires 375.1146.

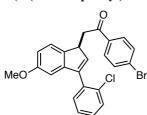
(S)-2-(5-methoxy-3-phenyl-1H-inden-1-yl)-1-(4-methoxyphenyl)ethan-1-one (6t)



Following general procedure, the title compound was obtained as a colorless oil. 16 mg (43% yield). Rf 0.23 (8:2 v/v hexanes:EtOAc). HPLC AS-H 5 μ m, λ = 254 nm, hexane : i-PrOH = 97:3, 1.0 mL/min, fraction $t_{\rm r}$ = 31.38 (major) and 34.58 (minor); e.r. = 91:9. $[\alpha]_{\rm D}^{25}$ = -35.8° (c = 0.55, CHCl₃). IR $v_{\rm max}$ 2962, 1670, 1596, 1255, 1222, 1169, 1025, 831, 700 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (AA'BB', J =

9.0 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.48 – 7.42 (m, 2H), 7.41 – 7.36 (m, 2H), 7.11 (d, J = 2.4 Hz, 1H), 6.94 (AA'BB', J = 9.0 Hz, 2H), 6.80 (dd, J = 8.2, 2.4, 1H), 6.65 (d, J = 2.1 Hz, 1H), 4.22 (ddd, J = 8.6, 6.4, 2.1 Hz, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 3.39 (dd, J = 17.1, 6.4 Hz, 1H), 3.11 (dd, J = 17.1, 8.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 197.7, 164.0, 159.6, 145.1, 144.4, 140.8, 137.7, 136.0, 130.9, 130.8, 130.4, 128.9, 128.0, 124.3, 114.2, 111.2, 107.1, 56.0, 55.8, 44.5, 40.7. HRMS (ESI) m/z: Found (M+H)⁺ C₂₅H₂₃O₃⁺ 371.1645, requires 371.1642.

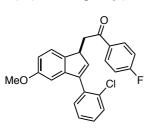
$\hbox{2-(3-(2-chlorophenyl)-5-methoxy-1$H-inden-1-yl)-1-(4-bromorophenyl)ethan-1-one (6u)}$



Following general procedure, the title compound was obtained as a colorless oil. 27 mg (59% yield). Rf 0.44 (8:2 v/v hexanes:EtOAc). HPLC RegisCellTM 5µm, $\lambda = 254$ nm, hexane : i-PrOH = 95 : 5, 1.0 mL/min, fraction $t_r = 8.84$ (major) and 9.84 (minor); e.r. = 84:16. $[\alpha]_D^{25} = -30.9^{\circ}$ (c = 0.20, CHCl₃). IR v_{max} 2921, 2852, 1686, 1584, 1461, 1376, 1259, 1009, 795 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (AA'BB', J = 8.6 Hz, 2H), 7.61 (AA'BB', J = 8.6 Hz, 2H), 7.53 – 7.45 (m, 1H), 7.44 –

7.35 (m, 2H), 7.36 – 7.27 (m, 2H), 6.79 (dd, J = 8.2, 2.4, 1H), 6.71 (d, J = 2.4 Hz, 1H), 6.62 (d, J = 2.0 Hz, 1H), 4.26 (ddd, J = 8.4, 6.4, 2.0, 1H), 3.77 (s, 3H), 3.42 (dd, J = 17.4, 6.4 Hz, 1H), 3.17 (dd, J = 17.4, 8.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 197.8, 159.4, 145.3, 142.2, 139.3, 135.6, 134.6, 133.3, 132.1, 132.0, 131.0, 130.0, 129.8, 129.1, 128.6, 126.8, 123.9, 111.2, 107.0, 55.7, 44.3, 40.8. HRMS (ESI) m/z: Found (M+H)⁺C₂₄H₁₉⁷⁹BrClO₂⁺453.0249, requires 453.0251.

2-(3-(2-Chlorophenyl)-5-methoxy-1*H*-inden-1-yl)-1-(4-fluorophenyl)ethan-1-one (6v)



Following general procedure, the title compound was obtained as a colorless oil. 26 mg (66% yield). Rf 0.42 (8:2 v/v hexanes:EtOAc). HPLC AD-H 5µm, λ = 254 nm, hexane : i-PrOH = 95 : 5, 1.0 mL/min, fraction $t_{\rm r}$ = 14.90 (major) and 13.94 (minor); e.r. = 83:17. [α]_D²⁵ = +54.6° (c = 0.86, CHCl₃). IR $\nu_{\rm max}$ 2934, 1684, 1594, 1476, 1216, 1154, 1031, 812, 749 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.07 – 7.97 (m, 2H), 7.52 – 7.45 (m, 1H), 7.41 – 7.35 (m, 2H), 7.35 – 7.29 (m, 2H), 7.18 – 7.09 (m,

2H), 6.79 (dd, J = 8.2, 2.2 Hz, 1H), 6.72 (d, J = 2.2 Hz, 1H), 6.63 (d, J = 1.6 Hz, 1H), 4.26 (ddd, J = 8.4, 6.4, 1.6 Hz, 1H), 3.78 (s, 3H), 3.43 (dd, J = 17.4, 6.4 Hz, 1H), 3.18 (dd, J = 17.4, 8.4 Hz, 1H). ¹³C

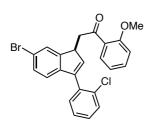
NMR (101 MHz, CDCl₃) δ 196.1, 164.8 (d, J = 256.0 Hz), 158.2, 144.2, 141.0, 138.2, 138.1, 133.5, 132.3 (d, J = 3.0 Hz), 132.1, 129.9, 129.8 (d, J = 9.4 Hz), 128.9, 128.0, 125.7, 122.8, 114.9 (d, J = 22.0 Hz), 114.7, 110.1, 105.8, 54.5, 43.3, 39.6. HRMS (ESI) m/z: Found (M+H)⁺ C₂₄H₁₉ClFO₂⁺ 393.1049, requires 393.1052.

(S)-2-(3-(2-Chlorophenyl)-5-methoxy-1H-inden-1-yl)-1-(2-methoxyphenyl)ethan-1-one (6w)

Following general procedure, the title compound was obtained as a colorless oil. 24 mg (59% yield). Rf 0.18 (9:1 v/v hexanes:EtOAc). HPLC AD-H 5 μ m, λ = 254 nm, hexane : i-PrOH = 90:10, 1.0 mL/min, fraction t_r = 17.42 (major) and 14.79 (minor); e.r. = 97:3. [α]_D²⁵ = +49.8° (c = 1.34, CHCl₃). IR v_{max} 2924, 1658, 1595, 1481, 1423, 1244, 1022, 756 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (dd, J = 7.8, 1.8 Hz, 1H), 7.54 – 7.40 (m, 2H), 7.40 – 7.31 (m, 2H), 7.33 – 7.23 (m, 2H), 7.00 (td, J

= 7.6, 1.0 Hz, 1H), 6.95 – 6.89 (m, 1H), 6.75 (dd, J = 8.2, 2.4 Hz, 1H), 6.68 (d, J = 2.4 Hz, 1H), 6.62 (d, J = 2.0 Hz, 1H), 4.21 (ddd, 8.6, 6.2, 2.0 Hz, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 3.46 (dd, J = 17.6, 6.2 Hz, 1H), 3.16 (dd, J = 17.6, 8.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 201.2, 159.4, 159.0, 145.5, 141.8, 140.3, 139.9, 135.0, 134.0, 133.5, 131.4, 130.8, 130.2, 129.2, 128.4, 127.0, 124.1, 121.1, 111.9, 111.3, 107.0, 55.9, 55.8, 46.0, 45.1. HRMS (ESI) m/z: Found (M+H)⁺ C₂₅H₂₂ClO₃⁺ 405.1253, requires 405.1252.

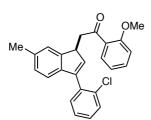
(S)-2-(6-Bromo-3-(2-chlorophenyl)-1H-inden-1-yl)-1-(2-methoxyphenyl)ethan-1-one (6x)



Following general procedure, the title compound was obtained as a pale yellow solid. 25 mg (55% yield). Rf 0.25 (9:1 v/v hexanes:EtOAc). Crystals for single crystal XRD were breed in iPrOH/hexane (v/v 50:50) solution by slow evaporation of the solvent and the absolute configuration was determined. HPLC AD-H 5 μ m, λ = 254 nm, hexane : i-PrOH = 90:10, 1.0 mL/min, fraction t_r = 14.73 (major) and 9.53 (minor); e.r. = 95:5. $[\alpha]_D^{25}$ = +112.7° (c = 0.78, CHCl₃). IR v_{max} 2922, 2852, 1665, 1596, 1462, 1435,

1244, 1019, 756 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (dd, J = 7.7, 1.8 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.54 – 7.44 (m, 2H), 7.40 – 7.35 (m, 2H), 7.34 – 7.29 (m, 2H), 7.07 – 6.95 (m, 3H), 6.61 (d, J = 2.0 Hz, 1H), 4.30 (ddd, J = 8.4, 6.2, 2.0 Hz, 1H), 3.89 (s, 3H), 3.49 (dd, J = 17.8, 6.2 Hz, 1H), 3.22 (dd, J = 17.8, 8.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 200.6, 159.1, 149.8, 143.0, 141.5, 139.2, 134.6, 134.2, 133.5, 131.3, 130.8, 130.2, 129.9, 129.4, 128.1, 127.1(2), 127.0(8), 122.5, 121.1, 119.7, 111.9, 55.9, 45.8, 45.4. HRMS (ESI) m/z: Found (M+H)⁺ $C_{24}H_{19}^{79}BrClO_2^+$ 453.0170, requires 453.0251; $C_{24}H_{19}^{81}BrClO_2^+$ 455.0175, requires 455.0231.

(S)-2-(3-(2-chlorophenyl)-6-methyl-1*H*-inden-1-yl)-1-(2-methoxyphenyl)ethan-1-one (6y)



Following general procedure but with 5% acetone in hexanes as the eluent for flash column chromatography, the title compound was obtained as pale yellow oil. 23 mg (59% yield). A 1 mmol reaction was also performed with 10% chiral catalyst and the title compound was obtained 200 mg (57%). Rf 0.30 (9:1 v/v hexanes:EtOAc). HPLC AS-H 5 μ m, λ = 254 nm, hexane : i-PrOH = 98:2, 1.0 mL/min, fraction t_r = 14.19 (major) and 11.96 (minor); e.r. = 98:2 (1 mmol scale reaction was

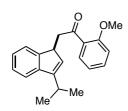
also 98:2 er). $[\alpha]_D^{25} = -113.7^{\circ}$ (c = 0.56, CHCl₃). IR v_{max} 2961, 1637, 1543, 1260, 1175, 1093, 1020, 797 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.79 (dd, J = 7.7, 1.8 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.39 – 7.33 (m, 2H), 7.32 – 7.26 (m, 2H), 7.07 – 6.96 (m, 2H), 6.95 – 6.91 (m, 2H), 6.60 (d, J = 2.0 Hz, 1H), 4.24 (ddd, J = 8.9, 6.0, 2.0 Hz, 1H), 3.84 (s, 3H), 3.50 (dd, J = 17.6, 6.0 Hz, 1H), 3.16 (dd, J = 17.6, 8.9 Hz, 1H), 2.33 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 201.2, 159.1, 144.9, 144.4, 141.8, 139.2, 136.6, 135.3, 134.0, 133.6, 131.4, 130.8, 130.1, 129.1, 128.4, 126.9, 126.3, 123.4, 121.8, 121.1, 111.9, 55.8, 45.9, 45.5, 21.8. HRMS (ESI) m/z: Found (M+H)⁺ C₂₅H₂₂ClO₂⁺ 389.1304, requires 389.1303.

1-(4-Methoxyphenyl)-2-(3-methyl-1H-inden-1-yl)ethan-1-one (6z)

Following general procedure, the title compound was obtained as colorless oil. 12.8 mg (46% yield). Rf 0.32 (9:1 v/v hexanes:EtOAc). HPLC OJ-H 5µm, λ = 254 nm, hexane : i-PrOH = 91:9, 1.0 mL/min, fraction $t_{\rm r}$ = 14.92 (major) and 13.19 (minor); e.r. = 91:9. [α]_D²⁵ = -78.5° (c = 0.30, CHCl₃). IR $v_{\rm max}$ 2914, 1673, 1598, 1509, 1258, 1166, 1015, 829, 759 cm⁻¹. ¹H NMR

(400 MHz, CDCl₃) δ 7.96 (AA'BB', J = 9.0 Hz, 2H), 7.44 – 7.39 (m, 1H), 7.34 – 7.30 (m, 2H), 7.24 – 7.16 (m, 1H), 6.93 (AA'BB', J = 9.0 Hz, 2H), 6.27 – 6.22 (m, 1H), 4.15 – 4.02 (m, 1H), 3.87 (s, 3H), 3.33 (dd, J = 17.0, 6.2 Hz, 1H), 2.99 (dd, J = 17.0, 8.8 Hz, 1H), 2.14 (t, J = 1.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.9, 163.9, 148.1, 145.8, 139.5, 134.3, 130.7, 130.4, 127.0, 125.2, 123.3, 119.4, 114.1, 55.8, 44.7, 40.6, 13.3. HRMS (ESI) m/z: Found (M+H)⁺ $C_{19}H_{19}O_2^{+}$ 279.1375, requires 279.1380.

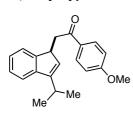
2-(3-Isopropyl-1*H*-inden-1-yl)-1-(2-methoxyphenyl)ethan-1-one (6za)



Following general procedure, the title compound was obtained as colorless oil. 16 mg (52% yield). Rf 0.32 (9:1 v/v hexanes:EtOAc). HPLC AD-H 5µm, λ = 254 nm, hexane : i-PrOH = 90:10, 1.0 mL/min, fraction $t_{\rm r}$ = 7.58 (major) and 6.77 (minor); e.r. = 98:2. [α]_D²⁵ = +187.5° (c = 0.69, CHCl₃). IR $v_{\rm max}$ 2963, 1666, 1594, 1454, 1244, 1164, 1003, 740 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (dd, J = 7.6, 1.8 Hz, 1H), 7.51 – 7.41 (m, 2H), 7.37 (d, J = 7.6 Hz, 1H),

7.32 – 7.27 (m, 1H), 7.23 – 7.15 (m, 1H), 7.08 – 7.00 (m, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.27 – 6.22 (s, 1H), 4.10 – 4.00 (m, 1H), 3.86 (s, 3H), 3.45 (dd, J = 17.5, 5.7 Hz, 1H), 3.03 (dd, J = 17.5, 9.1 Hz, 1H), 2.96 – 2.84 (m, 1H), 1.28 (s, 3H), 1.26 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 201.6, 159.0, 150.2, 148.8, 144.8, 133.9, 131.1, 130.8, 128.5, 126.7, 125.0, 123.5, 121.0, 119.8, 111.9, 55.8, 46.1, 44.8, 27.2, 22.2(0), 22.1(5). HRMS (ESI) m/z: Found (M+H)⁺ $C_{21}H_{23}O_{2}^{+}$ 307.1676, requires 307.1693.

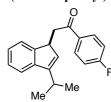
2-(3-isopropyl-1*H*-inden-1-yl)-1-(4-methoxyphenyl)ethan-1-one (6zb)



Following general procedure, the title compound was obtained as a colorless oil. 10.5 mg (34% yield). Rf 0.32 (9:1 v/v hexanes:EtOAc). HPLC OJ-H 5µm, $\lambda = 254$ nm, hexane : i-PrOH = 98:2, 1.0 mL/min, fraction $t_r = 15.37$ (major) and 22.15 (minor); e.r. = 94:6. $[\alpha]_D^{25} = +105.6^{\circ}$ (c = 0.72, CHCl₃). IR v_{max} 2961, 2924, 1677, 1600, 1260, 1169, 1016, 800 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (AA'BB', J = 9.0 Hz, 2H), 7.46 – 7.41 (m, 1H), 7.40 –

7.35 (m, 1H), 7.33 – 7.27 (m, 1H), 7.22 – 7.16 (m, 1H), 6.94 (AA'BB', J = 9.0 Hz, 2H), 6.24 (t, J = 1.7 Hz, 1H), 4.12 – 4.02 (m, 1H), 3.87 (s, 3H), 3.36 (dd, J = 17.1, 5.9 Hz, 1H), 2.98 (dd, J = 17.1, 9.0 Hz, 1H), 2.90 (m, 1H), 1.27 (d, J = 1.0 Hz, 3H), 1.25 (d, J = 1.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.9, 163.9, 150.6, 148.6, 144.8, 130.9, 130.8, 130.4, 126.9, 125.1, 123.5, 119.9, 114.1, 55.8, 44.5, 40.8, 27.2, 22.2, 22.1. HRMS (ESI) m/z: Found (M+H)⁺ C₂₁H₂₃O₂⁺307.1699, requires 307.1693.

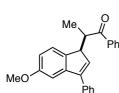
1-(4-Fluorophenyl)-2-(3-isopropyl-1*H*-inden-1-yl)ethan-1-one (6zc)



Following general procedure, the title compound was obtained as colorless oil. 17 mg (58% yield). Rf 0.25 (95:5 v/v hexanes:EtOAc). HPLC OJ-H 5 μ m, λ = 254 nm, hexane : i-PrOH = 98 : 2, 1.0 mL/min, fraction t_r = 7.44 (major) and 9.44 (minor); e.r. = 88:12. IR v_{max} 2961, 1685, 1595, 1227, 1155, 1008, 833, 771, 741 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.05 – 7.92 (m, 2H), 7.45 – 7.45 (m, 2H), 7.34 – 7.28 (m, 1H), 7.23 – 7.17 (m, 1H), 7.17 – 7.10 (m, 2H), 6.23

(brs, 1H), 4.11 - 4.01 (m, 1H), 3.38 (dd, J = 17.4, 5.9 Hz, 1H), 3.01 (dd, J = 17.4, 8.9 Hz, 1H), 2.95 - 2.82 (m, 1H), 1.27 (d, J = 2.0 Hz, 3H), 1.26 (d, J = 2.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.8, 166.1 (d, J = 2.0 Hz), 150.9, 148.3, 144.7, 133.72 (d, J = 3.0 Hz), 131.12 (d, J = 10.0 Hz), 130.5, 127.0, 125.2, 123.5, 120.0, 116.1(d, J = 22.2 Hz), 44.3, 41.1, 27.2, 22.2, 22.1. HRMS (ESI) m/z: Found (M+H)⁺ C₂₀H₂₀FO⁺ 295.1472, requires 295.1493.

2-(5-Methoxy-3-phenyl-1*H*-inden-1-yl)-1-phenylpropan-1-one (6zd)

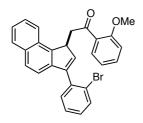


Following general procedure, the title compound was obtained as colorless oil. 15 mg (44% yield) as a mixture of diastereoisomers. d.r. 3:1. Rf 0.26 (9:1 v/v hexanes:EtOAc). HPLC AD-H 5 μ m, λ = 254 nm, hexane: i-PrOH = 90:10,

S-15

1.0 mL/min, fraction $t_r = 9.11$ (major) and 10.87 (minor); e.r. = 97:3 for major diastereoisomer (82:18 for minor diastereoisomer). IR v_{max} 2933, 1677, 1447, 1218, 970, 699 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) major: δ 8.08 – 8.01 (m, 2H), 7.64 – 7.58 (m, 2H), 7.54 – 7.49 (m, 2H), 7.49 – 7.42 (m, 3H), 7.41 – 7.38 (m, 1 H), 7.33 – 7.28 (m, 1H), 7.10 (d, J = 2.4 Hz, 1H), 6.75 (dd, J = 8.2, 2.4 Hz, 1H), 6.67 (d, J = 2.1 Hz, 1H), 4.06 – 4.01 (m, 1H), 3.86 (pent, J = 7.0 Hz, 1H), 3.81 (s, 3H), 1.11 (d, J = 7.0 Hz, 3H); minor: δ 7.99 – 7.94 (m, 2H), 7.65 – 7.35 (m, 9H), 7.08 (d, J = 2.4 Hz, 1H), 6.79 (dd, J = 8.3, 2.4 Hz, 1H), 6.47 (d, J = 2.1 Hz, 1H), 4.00 – 3.95 (m, 1H), 3.82 (s, 3H), 3.78 – 3.70 (m, 1H), 1.28 (d, J = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) major: δ 203.8, 159.6, 145.6, 145.5, 139.4, 136.8, 136.1, 135.3, 133.4, 129.1, 128.9, 128.8, 128.1, 128.0, 124.2, 111.1, 107.0, 55.9, 50.5, 43.6, 14.6. HRMS (ESI) m/z: Found (M+H)⁺ C₂₅H₂₃O₂⁺ 355.1685, requires 355.1693.

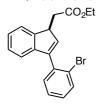
(S)-2-(3-(2-bromophenyl)-1H-cyclopenta[a]naphthalen-1-yl)-1-(2-methoxyphenyl)ethan-1-one (6ze)



Following general procedure, the title compound was obtained as a pale yellow solid. 34 mg (72% yield). Rf 0.25 (9:1 v/v hexanes:EtOAc). HPLC AD-H 5µm, λ = 254 nm, hexane : i-PrOH = 90:10, 1.0 mL/min, fraction $t_{\rm r}$ = 25.31 (major) and 12.67 (minor); e.r. = 60:40. [α]_D²⁵ = +19.1° (c = 1.93, CHCl₃). IR v_{max} 2968, 1669, 1596, 1434, 1242, 1022, 818, 751 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.85 – 7.72 (m, 2H), 7.67 – 7.65 (m, 1H), 7.54 – 7.47 (m, 1H), 7.47 –

7.27 (m, 5H), 7.25 – 7.18 (m, 1H), 7.05 – 6.96 (m, 1H), 6.90 (d, J = 8.4 Hz, 1H), 6.78 (d, J = 1.9 Hz, 1H), 4.63 (brd, J = 11.2 Hz, 1H), 4.05 (dd, J = 18.0, 3.3 Hz, 1H), 3.77 (s, 3H), 2.97 (dd, J = 18.0, 11.2 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 201.4, 159.0, 143.9, 143.0, 141.7, 139.3, 137.4, 134.0, 133.3, 132.4, 131.5, 130.8, 129.8, 129.6, 129.5, 128.4, 127.8, 127.7, 126.6, 124.9, 123.8, 123.6, 121.1, 120.7, 111.9, 55.8, 46.4, 45.4. HRMS (ESI) m/z: Found (M+Na)⁺ $C_{28}H_{21}^{79}$ BrNaO₂⁺ 491.0618, requires 491.0617.

Ethyl (S)-2-(3-(2-bromophenyl)-1H-inden-1-yl)acetate (12)



Following general procedure, the title compound was obtained as colorless oil with an unidentified impurity which could not be separated. 11 mg (31% yield). Rf 0.27 (95:5 v/v hexanes:EtOAc). HPLC AD-H 5 μ m, λ = 254 nm, hexane : i-PrOH = 95:5, 1.0 mL/min, fraction t_r = 6.10 (major) and 5.20 (minor); e.r. = 54:46. IR v_{max} 2979, 1730, 1464, 1369, 1214, 1152, 1024, 741 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.66 (m, 1H), 7.55 – 7.44 (m, 1H), 7.42 – 7.34 (m, 2H), 7.31 – 7.19 (m, 3H), 7.16

-7.10 (m, 1H), 6.56 (d, J = 2.0 Hz, 1H), 4.24 (qd, J = 7.2, 1.6 Hz, 2H), 4.05 (ddd, J = 9.0, 6.6, 2.0 Hz, 1H), 2.84 (dd, J = 15.9, 6.6 Hz, 1H), 2.53 (dd, J = 15.9, 9.0 Hz, 1H), 1.30 (t, J = 7.2 Hz, 3H). 13 C NMR (101 MHz, CDCl₃) δ 172.7, 146.6, 144.2, 144.0, 137.5, 137.0, 133.4, 131.3, 129.5, 127.6, 127.2, 125.7, 123.5, 123.4, 121.4, 61.1, 46.0, 36.6, 14.6. HRMS (ESI) m/z: Found (M+H)⁺ $C_{19}H_{18}^{79}BrO_{2}^{+3}$ 357.0465, requires 357.0485.

II-4. Derivatization

Reduction of indene to indane

2-((1R,3R)-3-(2-bromophenyl)-2,3-dihydro-1*H*-inden-1-yl)-1-(2-methoxyphenyl)-ethan-1-one (9c)

In a 10 mL RBF, indene (45 mg, 0.11 mol) was dissolved in MeOH (2 mL) and Pd/C (5%) was added. Then a septum was put on the RBF and then a balloon with $\rm H_2$ gas was plugged in with the needle tip emersed in the MeOH mixture. The reaction was stirred overnight, diluted with ether, and filtered. After removal of the solvent of the filtrate, the residue was purified by flash chromatography.

Colorless oil, 36 mg (80%) as a single diastereoisomer (confirmed by 2-D NMRs, see spectra). Rf 0.20 (9:1 v/v hexanes:EtOAc). HPLC RegisCellTM 5 μ m, λ = 254 nm, hexane : i-PrOH = 99:1, 1.0 mL/min, fraction t_r = 20.06 (major) and 21.33 (minor); e.r. = 95:5. [α]_D²⁵ = -38.9° (c = 0.79, CHCl₃). IR v_{max} 2941, 1669, 1596, 1433, 1242, 1022, 750, 700 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (dd, J = 7.7, 1.9 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.33 – 7.28 (m, 2H), 7.28 – 7.25 (m, 1H), 7.25 – 7.19 (m, 3H), 7.18 – 7.13 (m, 1H), 7.04 – 6.95 (m, 1H), 6.99 – 6.95 (m, 1H), 6.93 – 6.90 (m, 1H), 4.28 (dd, J = 10.6, 7.4 Hz, 1H), 3.89 (s, 3H), 3.86 – 3.75 (m, 1H), 3.69 (dd, J = 17.1, 4.9 Hz, 1H), 3.21 (dd, J = 17.1, 8.6 Hz, 1H), 2.87 (dt, J = 12.4, 7.4 Hz, 1H), 1.72 (dt, J = 12.4, 10.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 202.1, 158.8, 147.3, 147.2, 145.1, 133.8, 130.6, 128.9, 128.8, 128.7, 127.0(2), 126.9(6), 126.7, 125.2, 123.4, 121.1, 111.9, 55.8, 50.9, 49.8, 45.1, 40.0 (2 peaks missing or overlaped). HRMS (ESI) m/z: Found (M+H)⁺C₂₄H₂₂⁸¹BrO₂⁺ 423.0778, requires 423.0777.

2-((1aS,6R,6aS)-1a-(2-bromophenyl)-1a,6a-dihydro-6H-indeno[1,2-b]oxiren-6-yl)-1-(2-methoxyphenyl)ethan-1-one (10c)

To a 25-mL RBF were added sodium bicarbonate (29 mg, 0.35 mol), water (1.0 mL), acetone (1.0 mL), ethyl acetate (1.0 mL), and indene (16 mg, 0.07 mol) and were stirred vigorously. An aqueous Oxone solution (22 mg, water 1.0 mL) was added dropwise over 1 h at 20 to 25 °C. The reaction mixture was stirred for an additional 1 h. And another portion of oxone (11 mg) was added and the reaction was stirred for another 1 h. The organic layer was separated and washed with 20% (w/v) aqueous sodium chloride (5 mL) and then evaporated. The residue was purified by silica gel chromatograpy (silica gel). The desired product was obtained as colorless oil (72%), d.r. 2:1. HPLC AD-H 5 μ m, $\lambda = 254$ nm, hexane: i-PrOH = 95:5, 1.0 mL/min, fraction tr = 36.78 (major) and 38.46 (minor); e.r. = 99:1 (minor diastereoisomer: fraction tr = 20.14 (major) and 32.97 (minor)); e.r. = 97:3). $[\alpha]_D^{25} = +3.5^{\circ}$ (c = 0.74, CHCl₃). IR v_{max} 2924, 1657, 1594, 1482, 1432, 1246, 1022, 756, 741 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) major isomer: δ 7.80 (dd, J = 7.7, 1.8 Hz, 1H), 7.69 (dd, J = 7.7, 1.8 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.53 - 7.45 (m, 1H), 7.45 - 7.38 (m, 1H), 7.38 - 7.33 (m, 1H), 7.31 - 7.23 (m, 2H), 7.19 - 7.11(m, 1H), 7.07 - 7.01 (m, 2H), 6.98 - 6.95 (m, 1H), 4.15 (s, 1H), 4.14 - 4.06 (m, 1H), 3.86 (s, 3H), 3.60-3.45 (m, 2H); minor isomer: δ 7.85 (dd, J = 7.8, 1.8 Hz, 1H), 7.66 - 7.62 (m, 1H), 7.62 - 7.55 (m, 1H), 7.53 - 7.45 (m, 1H), 7.45 - 7.38 (m, 1H), 7.31 - 7.23 (m, 3H), 7.19 - 7.11 (m, 1H), 7.07 - 7.01(m, 2H), 7.00 - 6.98 (m, 1H), 4.39 (d, J = 2.9 Hz, 1H), 4.14 - 4.06 (m, 1H), 3.91 (s, 3H), 3.60 - 3.45(m, 2H). ¹³C NMR (101 MHz, CDCl₃) mixed: δ 200.9, 200.2, 159.3, 159.0, 147.2, 146.3, 142.8, 142.4, 135.4, 135.1, 134.2(1), 134.1(7), 132.8(4), 132.8(2), 131.0, 130.8, 130.6, 130.2(3), 130.1(8), 129.0, 128.9, 128.3, 128.1, 127.8, 127.6, 126.8(2), 126.7(6), 126.3, 125.5, 124.7, 124.6, 123.2, 121.2, 121.0, 111.9(7), 119.9(6), 70.3, 69.9, 69.5, 67.3, 55.9, 46.9, 45.1, 42.0, 41.2 (three peaks, one aliphatic and two aromatic, are missing or overlaped). HRMS (ESI) m/z: Found $(M+H)^+ C_{24} H_{20}^{79} BrO_3^+ 435.0586$, requires 435.0590; C₂₄H₂₀⁸¹BrO₃⁺437.0581, requires 437.0570.

III. X-ray crystal structures

Table S1. Crystal data and structure refinement

 $\begin{array}{ccc} \text{Identification code} & \text{shelx} \\ \text{Name} & \textbf{6x} \end{array}$

Empirical formula C24 H18 Br Cl O2

Formula weight 453.73 Temperature 123(2) K Wavelength 1.54184 A

Crystal system, space group Monoclinic, P2(1)

Unit cell dimensions a = 9.5385(4) A alpha = 90 deg.

b = 7.8621(3) A beta = 96.183(4) deg. c = 13.4830(7) A gamma = 90 deg.

Volume 1005.24(7) A^3 Z, Calculated density 2, 1.499 Mg/m^3 Absorption coefficient 4.657 mm^-1

F(000) 460

Crystal size $0.18 \times 0.04 \times 0.04 \text{ mm}$ Theta range for data collection 4.663 to 66.867 deg.

Limiting indices -11<=h<=11, -9<=k<=9, -16<=l<=15

Reflections collected / unique 10294 / 3565 [R(int) = 0.0381]

Completeness to theta = 66.867 99.7 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 1.00000 and 0.63383

Refinement method Full-matrix least-squares on F²

Data / restraints / parameters 3565 / 1 / 254

Goodness-of-fit on F² 1.029

Final R indices [I>2sigma(I)] R1 = 0.0268, wR2 = 0.0654 R indices (all data) R1 = 0.0279, wR2 = 0.0662

Absolute structure parameter -0.014(11) Extinction coefficient n/a

Largest diff. peak and hole 0.252 and -0.367 e.A^-3

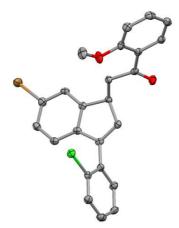


Figure S1. Molecular diagram of C₂₄H₁₈BrClO₂ with non-hydrogen atoms represented by 50% thermal ellipsoids.

IV. ¹H, ¹³C-NMR spectra and HPLC traces

