Supporting Information

Enantioselective organocatalytic intramolecular Morita-Baylis-Hillman (IMBH) reaction of dienones, and elaboration of the IMBH adducts to fluorenones

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General experimental methods: All the starting compounds and catalysts employed in this study were procured from Sigma-Aldrich and were used without further purification. For thin layer chromatography (TLC), silica aluminium foils with fluorescent indicator 254 nm (from Aldrich) were used and compounds were visualised by irradiation with UV light and/or by treatment with a solution of p-anisaldehyde (23 mL), conc. H₂SO₄ (35 mL), and acetic acid (10 mL) in ethanol (900 mL) followed by heating. Column chromatography was performed using SD Fine silica gel 100-200 mesh (approximately 15–20 g per 1 g of the crude product). Dry THF was obtained by distillation over sodium and stored over sodium wire. IR spectra were recorded on a Perkin-Elmer FT IR spectrometer as thin films or KBr pellet, as indicated, with v_{max} in inverse centimetres. Melting points were recorded on a digital melting point apparatus Stuart SMP30 and were uncorrected. ¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz Bruker Biospin Avance III FT-NMR spectrometer. NMR shifts are reported as delta (δ) units in parts per million (ppm) and coupling constants (J) are reported in Hertz (Hz). The following abbreviations are utilised to describe peak patterns when appropriate: br=broad, s=singlet, d=doublet, t=triplet, q=quartet and m=multiplet. Proton chemical shifts are given in δ relative to tetramethylsilane (δ 0.00 ppm) in CDCl₃ or in $(CD_3)_2SO$ (δ 2.50 ppm). Carbon chemical shifts are internally referenced to the deuterated solvent signals in CDCl₃ (δ 77.1 ppm) or in (CD₃)₂SO (δ 39.5 ppm). Single crystal X-ray analysis was carried on a Bruker AXS KAPPA APEX II system or Rigaku XtaLAB mini Xray diffractometer. High-resolution mass spectra were recorded on a Waters QTOF mass spectrometer. Optical rotations were recorded on Rudolph APIII/2W instrument. HPLC data was acquired from a Waters machine (model no 515).

General procedure-1: Synthesis of the dienones 1q and 1r.

The dienones 1q and 1r were synthesised as in the literature methods.¹ Directed α -alkylation of benzothiophene-3-carboxaldehydes **A** afforded the dienols **B** which upon IBX oxidation generated the dienones, Scheme 1S.



Scheme 1S. Synthesis of the dienones 1q and 1r.

Representative procedure for step-I (Scheme 1S): To a solution of *N*-methylpiperazine (NMP, 0.18 mL, 1.6 mmol) in THF (5 mL) at -78 °C was added *n*-BuLi (1.6 *M* in hexane, 1.0 mL, 1.6 mmol). After 15 min, benzothiophene-3-carboxaldehyde (200 mg, 1.2 mmol) was added and then the reaction mixture was stirred for an additional 30 min. A hexane solution of *n*-BuLi (2.0 mL, 3.2 mmol) was added and the mixture was stirred for an additional 15 min and then the mixture was warmed to -30 °C in 2 h. The solution was again cooled to -78 °C and a dienal C (1.5 mmol) was added drop wise over 5 min. The mixture was warmed to room temperature over 30 min. The reaction progress was monitored by TLC. Reaction mixture was quenched with saturated aqueous ammonium chloride solution and extracted with ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford dienol **B**.

Representative procedure for step-II (Scheme 1S): Alcohol **B** (1 mmol) was dissolved in ethyl acetate (10 mL), and IBX (1.5 mmol) was added. The resulting suspension was immersed in an oil bath set to 75 °C and stirred until alcohol **B** disappeared as monitored by TLC. The reaction was cooled to room temperature and filtered through Buchner funnel. The filter cake was washed with 3×2 mL of ethyl acetate. Organic extracts were combined and worked up using saturated sodium bicarbonate solution to remove excess iodobenzoic acid. The extract was dried over anhydrous sodium sulphate and concentrated under vacuum. The

¹ (a) S. Dhiman and S. S. V. Ramasastry, *Ind. J. Chem., Sect. A*, 2013, **52**, 1103; (b) R. P. Shirke and S. S. V. Ramasastry, *J. Org. Chem.*, 2015, **80**, 4893.

crude product was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford the dienone **1**.

General procedure-2: Synthesis of the dienones 1a-1p, 1s and 1t.

All these dienones were prepared as in Scheme 2S and 3S. For example, commercially available 2-bromobenzaldehydes C (when $R^1 = H$ and X = CH) were converted to 2-bromo benzyl alcohols E via a straightforward sodium borohydride reduction. *n*-Butyllithium mediated metal-halogen exchange followed by alkylation with an appropriate dienal C generated the diols F. IBX oxidation of the diols F led to the formation of the dienone-aldehydes **1a-1m** and **1p**, Scheme 2S. Similarly, **1n** and **1o** were prepared as in Scheme 3S, and the dienones **1s** and **1t** were prepared as described in Scheme 4S.



Scheme 2S. Synthesis of the dienones 1a-1m and 1p.



Scheme 3S. Synthesis of the dienones 1n and 1o.



Scheme 4S. Synthesis of the dienones 1s and 1t.

Representative procedure for step-I (Scheme 2S): An oven dried 25 mL RB flask was charged with 2-bromo benzaldehyde **D** (2.0 mmol), 10 mL dry MeOH and placed at 0 $^{\circ}$ C. Sodium borohydride (2.1 mmol) was added portion wise under nitrogen atmosphere and stirred at room temperature until **D** disappeared (monitored by TLC) and quenched by saturated aqueous ammonium chloride. Methanol was removed under vacuum and extracted using ethyl acetate. Organic extracts were combined, dried over anhydrous sodium sulphate. Solvent was distilled off under reduced pressure to afford crude bromoalcohol **E** and proceeded to the next step without further purification.

Representative procedure for step-II (Scheme 2S):² An oven dried 25 mL long neck RB flask was charged with bromoalcohol **E** (1.0 mmol), 5 mL dry THF and placed at -78 °C. *n*-BuLi (1.6 *M* in hexanes, 2.2 mmol) was added drop wise at same temperature and stirred for 2 hours. A dienal **C** (1.3 mmol) dissolved in 1 mL of dry THF, was added dropwise over 2 mins and stirred at room temperature for 30 mins. The reaction mixture was quenched with saturated aq. ammonium chloride solution and extracted using ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexanes/ethyl acetate as eluent to afford the diol **F**.

Representative procedure for step-III (Scheme 2S): The diol **F** were oxidised using IBX following the general procedure described for step II in Scheme 1S to afford dienones **1a-1p**, **1s** and **1t**.

² S. R. Flanagan, D. C. Harrowven and M. Bradely, *Tetrahedron*, 2002, **58**, 5989.

General procedure-3: Screening of reaction parameters

An oven dried 5 mL glass vial was charged with **1a** (30 mg, 0.15 mmol). An appropriate solvent (1 mL) and a catalyst (0.015 mmol) were introduced at room temperature under nitrogen atmosphere and stirring continued at appropriate temperature until **1a** disappeared as monitored by TLC. All the volatiles were removed under reduced pressure. The crude product was directly purified by silica gel flash chromatography using hexane/ethyl acetate as eluent, to afford **2a** as a pale yellow solid.



S.No	catalyst (10 mol%)	solvent	temp (°C)	time	% yield/(E/Z)
1	PPh ₃	Toluene	50	48 h	no reaction
2	PCy ₃	Toluene	rt	1 h	91 (4/1)
3	PCy ₃	DCE	rt	1 h	90 (4/1)
4	PMe ₃	Toluene	rt	15 min	95 (3/1)
5	PMe ₃	DCM	rt	15 min	92 (3/1)
6 ^{<i>a</i>}	DBU	DCM	rt	24 h	86 (5/1)
7 ^a	DABCO	DCM	45	24 h	81 (3/1)
8	PPh ₂ Et	Toluene	rt	30 min	89 (4/1)
9	PPh ₂ Et	DCM	rt	30 min	88 (4/1)
10 ^a	DMAP	Toluene	rt	24 h	85 (3/1)

^aYields are based on starting material recovery

General procedure-4: Evaluating the substrate scope (Table 1).

An oven dried 5 mL glass vial was charged with 1 (30 mg, 0.15 mmol). Toluene (1 mL) and PMe₃ (1 M solution in toluene, 0.1 mL, 0.015 mmol) were introduced at room temperature (rt) under nitrogen atmosphere and stirring continued at rt until 1 disappeared as monitored by TLC. All the volatiles were removed under reduced pressure. The crude product was purified by silica gel flash chromatography using hexane/ethyl acetate as eluent, to afford 2.





An oven dried 5 mL glass vial was charged with **1** (20 mg, 0.1 mmol) in 1,1,1,3,3,3hexafluoroisopropanol (HFIP, 0.5 mL), catalyst **9** was introduced at room temperature (rt) under nitrogen atmosphere and stirring continued at rt until **1** disappeared as monitored by TLC. Volatiles were removed under reduced pressure. The crude product was purified by silica gel flash chromatography using hexane/ethyl acetate as eluent, to afford **2**.

General Procedure-6: Synthesis of 3-substituted-4-acetylated-9-fluorenones 13.



Scheme 5S: Synthesis of fluorenones (13).

Representative procedure for step-I (Scheme 5S):¹ An oven dried 5 mL glass vial was charged with **2** (30 mg, 0.15 mmol) and acetylacetone (20 mg, 0.2 mmol) in dichloroethane (DCE, 1 mL) and bismuth(III)chloride (10 mol %) was introduced at room temperature (rt). Stirring continued at RT until **2** disappeared as monitored by TLC. Reaction mixture was quenched with water and extracted using dichloromethane. Volatiles were removed under reduced pressure. The crude product **12** was subjected to next step without further purification.

Representative procedure for step-II (Scheme 5S): An oven dried 5 mL glass vial was charged with **12** (0.1 mmol) in dimethylformamide (DMF, 1 mL) and potassium carbonate (0.11 mmol) was introduced at room temperature (rt) and stirring continued at 60 °C until **12** disappeared as monitored by TLC. The crude reaction mixture was purified by silica gel flash chromatography using hexanes/ethyl acetate as eluent, to afford **13**.

Spectroscopic data of the newly synthesised compounds during the present study

2-((2E,4E)-Hexa-2,4-dienoyl)benzaldehyde (1a).



This compound was prepared by following the general procedure-2 and isolated as pale yellow oil. $R_f = 0.4$ (Hexane/EtOAc = 4/1). IR (thin film, neat): v_{max}/cm^{-1} 3447, 2910, 1701, 1663, 1586, 1199, 1002, 770. ¹H NMR (400 MHz, CDCl₃): δ 10.12 (s, 1H), 7.97-

7.95 (m, 1H), 7.68-7.56 (m, 3H), 7.06 (dd, J = 15.3 and 10.8 Hz, 1H), 6.56 (d, J = 15.3 Hz, 1H), 6.31-6.18 (m, 2H), 1.88 (d, J = 6.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 194.6, 191.2, 147.6, 142.6, 142.0, 135.4, 133.2, 130.7, 130.2, 129.2, 128.3, 127.3, 19.0. HRMS (ESI): m/z calcd for C₁₃H₁₃O₂ (M+H): 201.0916. Found: 201.0905.

(E)-2-((E)-But-2-en-1-ylidene)-3-hydroxy-2,3-dihydro-1H-inden-1-one (2a).



This compound was isolated as pale yellow solid. Following the general procedure-3, 30 mg of **1a** afforded 28.5 mg of **2a** (95% yield). M.P = 117-119 °C. $R_f = 0.2$ (Hexane/EtOAc = 5/1). IR (thin film, neat): v_{max}/cm^{-1} 3382, 2910, 1687, 1632, 1030, 922, 754. ¹H NMR (400 MHz, CDCl₃): δ 7.76 (t, J = 7.6 Hz, 2H), 7.69 (dt, J =

7.6 and 1.2 Hz, 1H), 7.50-7.46 (m, 1H), 7.28-7.26 (m, 1H), 6.86-6.79 (m, 1H), 6.41 (sextet, 3.2 Hz, 1H), 5.73 (d, *J* = 9.6 Hz, 1H), 2.25 (d, *J* = 9.5 Hz, 1H), 2.00 (dd, *J*= 7.0 and 0.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 192.1, 151.0, 143.8, 138.0, 137.3, 136.3, 135.1, 129.6, 127.7, 125.9, 123.4, 69.0, 19.3. HRMS (ESI): *m/z* calcd for *m/z* calcd for C₁₃H₁₁O (M-OH): 183.0810. Found: 183.0821.

(S)-2-((E)-But-2-en-1-ylidene)-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (2a).



Following the general procedure-5, 25 mg of **1a** afforded 24 mg of **2a** (97% yield, E/Z = 4:1). **Optical rotation:** $[\alpha]^{23}{}_{\rm D} + 31.7$ (*c* 0.20, CHCl₃) for a sample with *ee* 97%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS Column (92:8 *n*-Hexane/2-Propanol, 0.8 mL/min, 254 nm, $\tau_{\rm maior} = 34.4$ min,

 $\tau_{\rm minor} = 39.7$ min).

2-((2E,4E)-5-Phenylpenta-2,4-dienoyl)benzaldehyde (1b).



This compound was prepared by following the general procedure-2 and isolated as a pale yellow solid. M.P = 67-69 °C. $R_f = 0.5$ (Hexane/EtOAc = 3/1). IR (thin film, neat): v_{max}/cm^{-1} 3029, 2859, 1695, 1649, 1614, 1581, 1253, 1022, 775. ¹H NMR

(400 MHz, CDCl₃): δ 10.18 (s, 1H), 8.02 (d, *J* = 7.2 Hz, 1H), 7.71-7.64 (m, 3H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.41-7.35 (m, 3H), 7.31-7.25 (m, 1H), 7.01-6.99 (m, 2H), 6.80 (d, *J* = 7.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 194.3, 191.2, 147.1, 143.0, 141.9, 135.7, 135.5, 133.2, 130.9, 129.6, 129.3, 129.1, 128.9(2C), 128.3, 127.4(2C), 126.4. HRMS (ESI): *m/z* calcd for C₁₈H₁₅O₂ (M+H): 263.1072 Found: 263.1081.

(E)-3-Hydroxy-2-((E)-3-phenylallylidene)-2,3-dihydro-1*H*-inden-1-one (2b).



This compound was isolated as pale yellow solid. Following the general procedure-4, 50 mg of **1b** afforded 46 mg of **2b** (91% yield). M.P = 162-164 °C. $R_f = 0.3$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3395, 3064, 1691, 1614, 1293, 976, 765. ¹H NMR

(400 MHz, CDCl₃): δ 7.80-7.78 (m, 1H), 7.70-7.51 (m, 5H), 7.43-7.34 (m, 5H), 7.02 (dd, J = 15.2 and 3.2 Hz, 1H), 5.97 (d, J = 4.8 Hz, 1H), 2.86 (d, J = 4.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 192.2, 151.2, 144.1, 138.3, 137.9, 137.3, 136.0, 135.2, 129.6, 129.5, 128.9(2C), 127.7(2C), 125.9, 124.0, 123.4, 69.1. HRMS (ESI): m/z calcd for C₁₈H₁₃O (M-OH): 245.0966. Found: 245.0970.

2-((2E,4E)-5-(Naphthalen-2-yl)penta-2,4-dienoyl)benzaldehyde (1c).



This compound was prepared by following the general procedure-2 and isolated as pale yellow solid. M.P = 107-109 °C. R_f = 0.4 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** v_{max}/cm⁻¹ 3056, 1695, 1650, 1579, 1326,

1274, 1022, 748. ¹H NMR (400 MHz, CDCl₃): δ 10.20 (s, 1H), 8.02 (d, J = 7.5 Hz, 1H), 7.85-7.83 (m, 4H), 7.72-7.65 (m, 4H), 7.53-7.50 (m, 2H), 7.36-7.33 (m, 1H), 7.13-7.12 (m, 2H), 6.83 (d, J = 15.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 194.2, 191.3, 147.1, 143.1, 141.9, 135.6, 133.8, 133.4, 133.3, 133.2, 130.9, 129.4, 129.0, 128.8, 128.7, 128.43, 128.4, 127.8, 127.0, 126.8, 126.7, 123.3. HRMS (ESI): m/z calcd for C₂₂H₁₆NaO₂ (M+Na): 335.1048. Found: 335.1051.

(*E*)-3-Hydroxy-2-((*E*)-3-(naphthalen-2-yl)allylidene)-2,3-dihydro-1*H*-inden-1-one (2c).



This compound was isolated as pale yellow solid. Following the general procedure-4, 30 mg of 1c afforded 29 mg of 2c (95% yield). M.P = 169-171 °C. $R_f = 0.2$ (Hexane/EtOAc = 3/1). IR (thin film, neat): v_{max}/cm^{-1} 3660, 2937, 1697, 1604, 1072, 1022, 746. ¹H NMR (400 MHz, (CD₃)₂SO): δ 8.08 (s, 1H), 7.99-7.87 (m, 4H), 7.81-7.68 (m, 4H), 7.59-

7.54 (m, 3H), 7.54-7.37 (m, 2H), 6.18 (d, J = 8.4 Hz, 1H), 5.85 (d, J = 8.4 Hz, 1H). ¹³C NMR (100 MHz, (CD₃)₂SO): δ 192.0, 152.9, 142.8, 140.6, 138.0, 135.6, 135.3, 134.3, 133.7, 133.5, 129.7, 129.0, 128.8, 128.7, 128.1, 127.4, 127.2, 126.9, 125.7, 124.1, 123.0, 67.7. HRMS (ESI): m/z calcd for C₂₂H₁₅O (M-OH): 295.1123. Found: 295.1129.

(S)-3-Hydroxy-2-((E)-3-(naphthalen-2-yl)allylidene)-2,3-dihydro-1*H*-inden-1-one (2c). Following the general procedure-5, 20 mg of 1c afforded 19.4 mg of 2c (97% yield, E/Z = 5:1). Optical rotation: $[\alpha]^{23}_{D} + 78.9$ (c 0.08, DMSO) for a sample with *ee* 92%. The enantiomeric excess was determined by HPLC analysis

> using Daicel Chiralpak AS Column (88:12 *n*-Hexane/2-Propanol, 0.8 mL/min, 254 nm, $\tau_{maior} = 22.1$ min, $\tau_{minor} =$

30.2 min).

2-((2E,4E)-5-(3,4-Dimethoxyphenyl)penta-2,4-dienoyl)benzaldehyde (1d).



2c(E/Z = 5/1)

This compound was prepared by following the general procedure-2 and isolated as pale yellow oil. $R_f = 0.4$ (Hexane/EtOAc = 3/1). **IR (thin film, neat):** v_{max}/cm^{-1} 2956, 2925, 1712, 1654, 1463, 1378, 1267, 1023, 745.

¹H NMR (400 MHz, CDCl₃): δ 10.17 (s, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.68-7.62 (m, 3H), 7.30-7.23 (m, 1H), 7.05-7.02 (m, 2H), 6.90-6.85 (m, 3H), 6.75 (d, J = 14.9 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 194.2, 191.2, 150.6, 149.2, 147.6, 143.2, 142.1, 135.4, 133.2, 130.8, 129.2, 128.8, 128.3, 128.0, 124.5, 121.8, 111.1, 109.1, 56.0, 55.9. HRMS (ESI): m/z calcd for C₂₀H₁₉O₄ (M+H): 323.1283. Found: 323.1290.

(E)-2-((E)-3-(3,4-dimethoxyphenyl)allylidene)-3-hydroxy-2,3-dihydro-1H-inden-1-one



(2d). This compound was isolated as pale brown solid. Following the general procedure-4, 30 mg of 1d afforded 27 mg of 2d (90% yield). M.P = 144-146 °C. $R_f = 0.2$ (Hexane/EtOAc = 3/1). IR (thin film, neat): v_{max}/cm^{-1} 3456, 2932, 1694, 1608, 1517, 1269, 1023, 759. ¹H NMR (400 MHz, (CD₃)₂SO): δ 7.77-7.76 (m, 2H), 7.72 (d, J =7.6 Hz, 1H), 7.57-7.53 (m, 1H), 7.43 (dd, J = 15.4 and

12.1 Hz, 1H), 7.31-7.16 (m, 4H), 7.02 (d, J = 8.4 Hz, 1H), 6.11 (d, J = 8.0 Hz, 1H), 5.80 (d, J = 8.0 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H). ¹³**C NMR (100 MHz, (CD₃)₂SO):** δ 191.9, 152.8, 150.7, 149.4, 143.4, 139.2, 138.1, 135.8, 135.4, 129.6, 129.5, 126.8, 123.0, 122.9, 122.2, 112.2, 110.1, 67.7, 56.0, 55.9. **HRMS (ESI):** *m*/*z* calcd for C₂₀H₁₇O₃ (M-OH): 305.1178. Found: 305.1180.

(S)-2-((E)-3-(3,4-dimethoxyphenyl)allylidene)-3-hydroxy-2,3-dihydro-1H-inden-1-one



(2d). Following the general procedure-5, 20 mg of 1d afforded 17.5 mg of 2d (87% yield, E/Z = 5:1). Optical rotation: $[\alpha]^{23}_{D} + 135.8$ (*c* 0.18, CHCl₃) for a sample with *ee* 78%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AD Column (85:15 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, $\tau_{major} = 20.3 \text{ min}, \tau_{minor} = 29.1 \text{ min}$).

2-((2E,4E)-5-Phenylhexa-2,4-dienoyl)benzaldehyde (1e).



This compound was prepared by following the general procedure-2 and isolated as pale yellow oil. $R_f = 0.4$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3379, 3058, 1695, 1651, 1578, 1445, 1291, 1022, 761. ¹H NMR (400

MHz, CDCl₃): δ 10.22 (s, 1H), 8.02 (d, J = 7.3 Hz, 1H), 7.74-7.66 (m, 3H), 7.55-7.53 (m, 2H), 7.42-7.35 (m, 4H), 6.82 (d, J = 15.4 Hz, 1H), 6.73 (d, J = 7.5 Hz, 1H), 2.30 (s, 3H). ¹³C **NMR (100 MHz, CDCl₃):** δ 193.9, 191.4, 148.7, 142.7, 142.2, 141.6, 135.7, 133.1, 131.0, 129.2, 128.8, 128.6(2C), 128.4, 128.3, 126.0(2C), 125.2, 16.8. **HRMS (ESI):** *m/z* calcd for C₁₉H₁₇O₂ (M+H)⁺: 277.1229. Found: 277.1223.

(E)-3-Hydroxy-2-((E)-3-phenylbut-2-en-1-ylidene)-2,3-dihydro-1*H*-inden-1-one (2e).



This compound was isolated as pale yellow solid. Following the general procedure-4, 25 mg of 1e afforded 22 mg of 2e (87% yield). M.P = 158-160 °C. $R_f = 0.4$ (Hexane/EtOAc = 3/1). IR (thin film, neat): v_{max}/cm^{-1} 3416, 3006, 1681, 1610, 1275, 749. ¹H NMR (400 MHz, CDCl₃): δ 7.80-7.75 (m, 1H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.62-

7.60 (m, 2H), 7.50-7.37 (m, 6H), 7.29-7.25 (m, 1H), 5.83 (s, 1H), 2.48 (br s, 1H), 2.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 192.2, 151.0, 149.9, 141.9, 138.2, 138.0, 135.2, 132.8, 129.6, 128.8, 128.5(2C), 126.2(2C), 125.9, 123.5, 122.4, 69.1, 16.5. HRMS (ESI): *m/z* calcd for C₁₉H₁₅O (M-OH): 259.1123. Found: 259.1136.

(E)-2-(5,5-Diphenylpenta-2,4-dienoyl)benzaldehyde (1f).



This compound was prepared by following the general procedure-2 and isolated as pale yellow oil. $R_f = 0.4$ (Hexane/EtOAc = 4/1). IR (thin film, neat): v_{max}/cm^{-1} 3378, 3057, 2854, 1696, 1647, 1577, 1445, 1278, 1023, 772, 700. ¹H

NMR (400 MHz, CDCl₃): δ 10.15 (s, 1H), 7.95-7.93 (m, 1H), 7.64-7.58 (m, 2H), 7.40-7.17 (m, 12H), 6.93 (d, J = 11.2 Hz, 1H), 6.85 (dd, J = 15.2 and 0.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 194.1, 191.2, 153.8, 145.1, 142.0, 141.0, 138.2, 135.5, 133.1, 130.8, 130.4(2C), 129.6, 129.2, 129.1, 128.6, 128.5(2C), 128.4(2C), 128.3(2C), 125.5. HRMS (ESI): m/z calcd for C₂₄H₁₉O₂ (M+H): 339.1385. Found: 339.1392.

(E)-2-(3,3-Diphenylallylidene)-3-hydroxy-2,3-dihydro-1H-inden-1-one (2f).



This compound was isolated as pale yellow solid. Following the general procedure-4, 30 mg of **1f** afforded 28 mg of **2f** (93% yield). M.P = 162-164 °C. $R_f = 0.3$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3395, 3056, 1681, 1610, 1275, 749. ¹H NMR (400 MHz, CDCl₃): δ 7.80 (d, J = 6.5 Hz, 2H), 7.70-7.66 (m, 1H), 7.50-

7.34 (m, 11H), 7.28-7.25 (m, 2H), 5.88 (d, J = 7.2 Hz, 1H), 2.39 (d, J = 7.1 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 191.7, 154.2, 150.8, 141.5, 139.2, 138.3, 138.2, 135.1, 134.5, 130.6(2C), 129.6, 129.1, 128.6, 128.5(2C), 128.4(2C), 128.3 (2C), 125.9, 123.5, 122.9, 69.2. HRMS (ESI): m/z calcd for C₂₄H₁₇O (M-OH): 321.1279. Found: 321.1283.

(S)-2-(3,3-Diphenylallylidene)-3-hydroxy-2,3-dihydro-1H-inden-1-one (2f).



Following the general procedure-5, 25 mg of **1f** afforded 23 mg of **2f** (92% yield, E/Z = 6:1). **Optical rotation:** $[\alpha]^{23}{}_{\rm D}$ +20.5 (*c* 0.05, CHCl₃) for a sample with *ee* 97%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS Column (90:10 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, $\tau_{\rm major} = 44.5$

min, $\tau_{\text{minor}} = 20.7$ min).

5-Fluoro-2-((2*E*,4*E*)-hexa-2,4-dienoyl)benzaldehyde (1g).



This compound was prepared by following the general procedure-2 and isolated as a pale yellow solid. M.P = 100-102 $^{\circ}$ C. R_f = 0.4 (Hexane/EtOAc = 5/1). IR (thin film, neat): v_{max}/cm^{-1} 2956, 1691, 1658, 1588, 1341, 1257, 1000, 836. ¹H

NMR (400 MHz, CDCl₃): δ 10.14 (d, J = 2.8 Hz, 1H), 7.70-7.65 (m, 2H0, 7.35 (dt, J = 8.1 and 2.6 Hz, 1H), 7.20-7.13 (m, 1H), 6.61 (d, J = 15.2 Hz, 1H), 6.34-6.29 (m, 2H), 1.93 (d, J = 6.0 Hz, 3H). ¹³C **NMR (100 MHz, CDCl₃):** δ 192.5, 189.9, 163.2 (d, J = 260.3 Hz), 147.9, 143.1, 138.5 (d, J = 6.2 Hz), 138.1 (d, J = 3.7 Hz), 131.0 (d, J = 8.2 Hz), 130.2, 126.4, 119.8 (d, J = 22.1 Hz), 115.5 (d, J = 23.0 Hz), 19.0. ¹⁹F **NMR (376 MHz, CDCl₃):** δ -106.7. **HRMS (ESI):** m/z calcd for C₁₃H₁₂FO₂ (M+H): 219.0821. Found: 219.0821.

(E)-2-((E)-But-2-en-1-ylidene)-5-fluoro-3-hydroxy-2,3-dihydro-1H-inden-1-one (2g).



This compound was isolated as pale yellow solid. Following the general procedure-4, 30 mg of **1g** afforded 29 mg of **2g** (97% yield). M.P = 159-161 °C. R_f = 0.3 (Hexane/EtOAc = 5/1). **IR** (thin film, neat): v_{max}/cm^{-1} 3442, 2927, 1703, 1634, 1266, 1015, 750. ¹H NMR (400 MHz, CDCl₃): δ 7.75-7.72 (m, 1H), 7.42 (dd,

J = 8.1 and 1.9 Hz, 1H), 7.24 (dd, J = 11.2 and 2.4 Hz, 1H), 7.18-7.13 (m, 1H), 6.84-6.77 (m, 1H), 6.40 (sextet, J = 3.2 Hz, 1H), 5.60 (s, 1H), 2.42 (br s, 1H), 2.01 (dd, J = 6.8 and 1.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 190.6, 163.3 (d, J = 253.1 Hz), 144.3, 137.5, 135.9, 134.2, 127.5, 125.8 (d, J = 10.3 Hz), 117.6 (d, J = 32.0 Hz), 117.5, 112.8 (d, J = 25.3 Hz), 68.7, 19.4. ¹⁹F NMR (376 MHz, CDCl₃): δ -101.1. HRMS (ESI): m/z calcd for C₁₃H₁₀FO (M-OH): 201.0716. Found: 201.0722.

(S)-2-((E)-But-2-en-1-ylidene)-5-fluoro-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (2g).



Following the general procedure-5, 20 mg of **1g** afforded 18.5 mg of **2g** (93% yield, E/Z = 3:1). **Optical rotation:** $[\alpha]^{23}{}_{\rm D}$ +69.1 (*c* 0.12, CHCl₃) for a sample with *ee* 99%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak IC Column (95:5 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, $\tau_{\rm maior} =$

39.5 min, $\tau_{\rm minor} = 27.7$ min).

2-((2E,4E)-Hexa-2,4-dienoyl)-5-methoxybenzaldehyde (1h).



This compound was prepared by following the general procedure-2 and isolated as pale yellow solid. M.P = 82-85 $^{\circ}$ C. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3440, 2938, 1693, 1653, 1596, 1260, 1015, 750. ¹H

NMR (400 MHz, CDCl₃): δ 10.20 (s, 1H), 7.67 (d, J = 8.5 Hz, 1H), 7.45 (d, J = 2.4 Hz, 1H), 7.25-7.12 (m, 2H), 6.65 (d, J = 15.2 Hz, 1H), 6.33-6.27 (m, 2H), 3.92 (s, 3H), 1.91 (d, J = 6.0 Hz, 3H). ¹³C **NMR (100 MHz, CDCl₃):** δ 192.2, 191.6, 161.8, 146.7, 142.2, 138.6, 134.3, 130.8, 130.3, 126.1, 118.9, 112.3, 55.7, 18.9. **HRMS (ESI):** m/z calcd for C₁₄H₁₄NaO₃ (M+Na): 253.0841. Found: 253.0836.

(E)-2-((E)-But-2-en-1-ylidene)-3-hydroxy-5-methoxy-2,3-dihydro-1*H*-inden-1-one (2h).



This compound was isolated as pale yellow solid. Following the general procedure-4, 30 mg of **1h** afforded 27.6 mg of **2h** (92% yield). M.P = 129-131 °C. $R_f = 0.2$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3374, 2926, 1681, 1631, 1597, 1290, 1018, 759. ¹H NMR (400 MHz, CDCl₃): δ 7.69-

7.67 (m, 1H), 7.21-7.18 (m, 2H), 6.99-6.97 (m, 1H), 6.83-6.76 (m, 1H), 6.38-6.33 (m, 1H), 5.65 (s, 1H), 3.94 (s, 3H), 2.46 (br s, 1H), 1.98 (dd, J = 6.8 and 1.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 190.8, 165.5, 154.1, 143.0, 136.7, 136.2, 131.3, 127.6, 125.3, 117.5, 108.9, 68.9, 55.8, 19.3. HRMS (ESI): *m*/*z* calcd for C₁₄H₁₅O₃ (M+H): 231.1021. Found: 231.1009. (*S*)-2-((*E*)-But-2-en-1-ylidene)-3-hydroxy-5-methoxy-2,3-dihydro-1*H*-inden-1-one (2h).



Following the general procedure-5, 25 mg of **1h** afforded 23.5 mg of **2h** (94% yield, E/Z = 5:1). **Optical rotation:** $[\alpha]^{23}_{D}$ -2.7 (*c* 0.14, CHCl₃) for a sample with *ee* 94%. The enantiomeric excess was determined by HPLC analysis using Daicel

Chiralpak AS Column (90:10 *n*-Hexane/2-Propanol, 0.8 mL/min, 254 nm, $\tau_{\text{major}} = 18.2$ min, $\tau_{\text{minor}} = 16.2$ min).

5-Methoxy-2-((2E,4E)-5-phenylpenta-2,4-dienoyl)benzaldehyde (1i).



This compound was prepared by following the general procedure-2 and isolated as pale brown oil. $R_f = 0.4$ (Hexane/EtOAc = 4/1). IR (thin film, neat): v_{max} /cm⁻¹ 3027, 1692, 1653, 1596, 1579, 1350, 1237, 1016, 736. ¹H NMR

(400 MHz, CDCl₃): δ 10.25 (s, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.51-7.34 (m, 7H), 7.16 (dd, J = 8.4 and 2.7 Hz, 1H), 7.02 (d, J = 4.8 Hz, 1H), 7.00 (s, 1H), 6.89 (d, J = 15.2 Hz, 1H), 3.93 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 191.6, 162.0, 146.2, 142.7, 138.9, 138.8, 135.8, 134.2, 130.9, 129.5, 128.9(2C), 127.9, 127.4(2C), 126.5, 118.9, 112.5, 55.8. HRMS (ESI): m/z calcd for C₁₉H₁₇O₃ (M+H): 293.1178. Found: 293.1178.

(E)-3-Hydroxy-5-methoxy-2-((E)-3-phenylallylidene)-2,3-dihydro-1*H*-inden-1-one (2i).



This compound was isolated as pale yellow solid. Following the general procedure-4, 30 mg of **1i** afforded 27 mg of **2i** (90% yield). M.P = 170-172 °C. $R_f = 0.2$ (Hexane/EtOAc = 3/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3308, 2928, 1667, 1601, 1275, 1260, 1020, 749. ¹H NMR (400 MHz, (CD₃)₂SO): δ

7.68 (d, J = 8.3 Hz, 1H), 7.64-7.62 (m, 2H), 7.55 (dd, J = 16.0 and 12.0 Hz, 1H), 7.45-7.42 (m, 2H), 7.38-7.35 (m, 1H), 7.24-7.18 (m, 3H), 7.09 (dd, J = 8.0 and 2.4 Hz, 1H), 6.12 (d, J = 8.4 Hz, 1H), 5.73 (d, J = 8.2 Hz, 1H), 3.91 (s, 3H). ¹³C NMR (100 MHz, (CD₃)₂SO): δ 190.2, 165.5, 155.9, 141.9, 141.0, 136.7, 133.9, 131.3, 129.6, 129.4(2C), 127.8(2C), 125.2, 125.0, 117.4, 110.0, 67.7, 56.3. HRMS (ESI): m/z calcd for C₁₉H₁₅O₂ (M-OH): 275.1072. Found: 275.1085.

(S)-3-Hydroxy-5-methoxy-2-((E)-3-phenylallylidene)-2,3-dihydro-1*H*-inden-1-one (2i).



Following the general procedure-5, 18 mg of **1i** afforded 17 mg of **2i** (95% yield, E/Z = 4:1). **Optical rotation:** $[\alpha]^{23}_{D} + 125.2$ (*c* 0.10, CHCl₃) for a sample with *ee* 96%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H Column (80:10 *n*-Hexane/2-Propanol, 1.0

mL/min, 254 nm, $\tau_{major} = 28.7 \text{ min}$, $\tau_{minor} = 22.0 \text{ min}$).

(E)-2-(5,5-Diphenylpenta-2,4-dienoyl)-5-methoxybenzaldehyde (1j).



This compound was prepared by following the general procedure-2 and isolated as pale brown oil. $R_f = 0.4$ (Hexane/EtOAc = 3/1). IR (thin film, neat): v_{max}/cm^{-1} 3055, 1690, 1595, 1577, 1444, 1276, 1018, 765. ¹H NMR

(400 MHz, CDCl₃): δ 10.22 (s, 1H), 7.75-7.70 (m, 1H), 7.44-7.36 (m, 11H), 7.24-7.21 (m, 1H), 7.15-7.11 (m, 1H), 7.01-6.95 (m, 2H), 3.98 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 191.7, 191.5, 161.9, 153.4, 144.0, 141.2, 138.9, 138.4, 134.3, 130.8, 130.4(2C), 129.1, 128.7, 128.6, 128.5(2C), 128.4(2C), 128.3(2C), 125.7, 118.8, 112.3, 55.8. HRMS (ESI): *m/z* calcd for C₂₅H₂₁O₃ (M+H): 369.1491. Found: 369.1479.

(E)-2-(3,3-Diphenylallylidene)-3-hydroxy-5-methoxy-2,3-dihydro-1H-inden-1-one (2j).



This compound was isolated as pale yellow solid. Following the general procedure-4, 20 mg of **1j** afforded 18.5 mg of **2j** (92% yield). M.P = 191-193 °C. $R_f = 0.3$ (Hexane/EtOAc = 3/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3006, 2919, 1691, 1609, 1275, 1260, 750. ¹H NMR (400 MHz, (CD₃)₂SO): δ 7.63 (d,

J = 8.8 Hz, 1H), 7.54-7.50 (m, 4H), 7.43-7.35 (m, 5H), 7.25-7.23 (m, 3H), 7.07 (dd, J = 8.6 and 2.2 Hz, 1H), 6.96 (dd, J = 8.1 and 1.4 Hz, 1H), 6.15 (d, J = 8.0 Hz, 1H), 5.78 (d, J = 7.9 Hz, 1H), 3.91 (s, 3H). ¹³C NMR (100 MHz, (CD₃)₂SO): δ 190.1, 165.6, 156.0, 151.2, 141.9, 141.3, 138.5, 131.2, 130.7, 130.5(2C), 129.4, 129.1(2C), 129.0(2C), 128.9, 128.2(2C), 125.0, 123.7, 117.3, 169.9, 67.7, 56.3. HRMS (ESI): m/z calcd for C₂₅H₁₉O₂ (M-OH): 351.1385. Found: 351.1399.

(S)-2-(3,3-Diphenylallylidene)-3-hydroxy-5-methoxy-2,3-dihydro-1*H*-inden-1-one (2j).



Following the general procedure-5, 15 mg of **1j** afforded 13 mg of **2j** (88% yield, E/Z = 7:1). **Optical rotation:** $[\alpha]^{23}_{D}$ +20.2 (*c* 0.30, CHCl₃) for a sample with *ee* 97%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AD Column (94:6 *n*-Hexane/2-Propanol,

1.0 mL/min, 254 nm, $\tau_{\text{major}} = 39.8 \text{ min}$, $\tau_{\text{minor}} = 30.2 \text{ min}$).

2-((2E,4E)-Hexa-2,4-dienoyl)-4,5-dimethoxybenzaldehyde (1k).



This compound was prepared by following the general procedure-2 and isolated as a pale yellow solid. M.P = 127-129 °C. $R_f = 0.3$ (Hexane/EtOAc = 4/1). IR (thin film, neat): v_{max}/cm^{-1} 3006, 2851, 1672, 1588, 1519, 1355, 1283,

1118, 871, 736. ¹H NMR (400 MHz, CDCl₃): δ 10.05 (s, 1H), 7.50 (s, 1H), 7.15-7.08 (m, 1H), 7.03 (s, 1H), 6.54 (d, *J* = 15.2 Hz, 1H), 6.32-6.25 (m, 2H), 3.98 (s, 6H), 1.89 (d, *J* = 6.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 193.5, 189.8, 152.7, 150.7, 147.4, 142.7, 137.1, 130.2, 129.2, 127.5, 110.5, 109.5, 56.3, 56.2, 19.0. HRMS (ESI): *m/z* calcd for C₁₅H₁₆NaO₄ (M+H): 283.0946. Found: 283.0965.

(E)-2-((E)-But-2-en-1-ylidene)-3-hydroxy-5,6-dimethoxy-2,3-dihydro-1H-inden-1-one

(2k).



This compound was isolated as Pale yellow solid. Following the general procedure-4, 25 mg of **1k** afforded 23 mg of **2k** (91% yield). M.P = 147-149 °C. $R_f = 0.2$ (Hexane/EtOAc = 3/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3374, 2931, 1682, 1591,

1306, 1100, 760. ¹H NMR (400 MHz, CDCl₃): δ 7.17 (s, 1H), 7.05 (d, J = 12.1 Hz, 1H), 7.02 (s, 1H), 6.84-6.77 (m, 1H), 6.34-6.29 (m, 1H), 5.60 (s, 1H), 4.02 (s, 3H), 3.89 (s, 3H), 2.55 (br s, 1H), 1.98 (dd, J = 6.8 and 0.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 191.3, 155.6, 150.8, 146.4, 142.7, 136.8, 135.6, 131.3, 127.7, 106.7, 103.8, 68.8, 56.4, 56.1, 19.2. HRMS (ESI): m/z calcd for C₁₅H₁₅O₃ (M-OH): 243.1021. Found: 243.1035.

(S)-2-((E)-But-2-en-1-ylidene)-3-hydroxy-5,6-dimethoxy-2,3-dihydro-1H-inden-1-one



(2k). Following the general procedure-5, 25 mg of 1k afforded 23 mg of 2k (93% yield, E/Z = 4:1). Optical rotation: $[\alpha]^{23}_{D}$ - 49.6 (*c* 0.15, CHCl₃) for a sample with *ee* 93%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AD Column (88:12 *n*-Hexane/2-Propanol,

0.7 mL/min, 254 nm, $\tau_{\text{major}} = 20.8 \text{ min}$, $\tau_{\text{minor}} = 25.6 \text{ min}$).

2-((2E,4Z)-4-(Chroman-4-ylidene)but-2-enoyl)benzaldehyde (11).



This compound was prepared by following the general procedure-2 and isolated as pale brown oil. $R_f = 0.4$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** v_{max}/cm^{-1} 2925,

1694, 1646, 1578, 1481, 1276, 750. ¹H NMR (400 MHz, CDCl₃): δ 10.22 (s, 1H), 8.01 (d, J = 7.2 Hz, 1H), 7.71-7.64 (m, 5H), 7.28-7.26 (m, 1H), 6.98-6.95 (m, 1H), 6.92-6.87 (m, 2H), 6.84 (d, J = 15.2 Hz, 1H), 4.27 (t, J = 6.0 Hz, 2H), 2.90 (t, J = 6.1 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 193.4, 191.4, 156.0, 142.2, 141.4, 141.2, 135.7, 133.2, 131.2, 131.0, 129.2, 128.3, 128.1, 124.4, 121.5, 121.2, 118.8, 118.0, 65.6, 26.5. HRMS (ESI): m/z calcd for C₂₀H₁₇O₃ (M+H): 305.1178. Found: 305.1163.

(*E*)-2-((*Z*)-2-(Chroman-4-ylidene)ethylidene)-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (21).



This compound was isolated as Pale brown solid. Following the general procedure-4, 25 mg of 1l afforded 22 mg of 2l (89% yield). M.P = 166-168 °C. $R_f = 0.3$ (Hexane/EtOAc = 4/1). IR (thin film, neat): v_{max}/cm^{-1} 3400, 3002, 1683, 1609, 1260, 750. ¹H NMR (400 MHz, CDCl₃): δ 7.82-7.78 (m, 3H), 7.72-7.63

(m, 2H), 7.49 (t, J = 8.0 Hz, 1H), 7.43-7.40 (m, 1H), 7.28-7.24 (m, 1H), 6.97 (dt, J = 6.9 and 1.2 Hz, 1H), 6.90 (dd, J = 8.0 and 1.1 Hz, 1H), 5.85 (s, 1H), 4.27 (t, J = 6.0 Hz, 2H), 3.01-2.97 (m, 2H), 2.62 (br s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 192.0, 156.0, 151.1, 142.0, 138.1, 137.9, 135.1, 131.6, 131.2, 129.6, 125.9, 124.9, 123.5, 121.9, 121.2, 117.9, 116.2, 69.1, 65.7, 26.3. HRMS (ESI): m/z calcd for C₂₀H₁₅O₂ (M-OH): 287.1072. Found: 287.1099.

(2E,4E)-1-(2-Benzoylphenyl)hexa-2,4-dien-1-one (1m).



This compound was prepared by following the general procedure-2 and isolated as pale brown oil. $R_f = 0.5$ (Hexane/EtOAc = 4/1). IR (thin film, neat): max/cm⁻¹ 3451, 3061, 2930, 1664, 1587, 1448, 1284, 704. ¹H NMR (400 MHz, CDCl₃): δ 7.79-7.77 (m, 3H), 7.61-7.56 (m, 2H), 7.55-7.48 (m, 2H), 7.44-7.40 (m, 2H), 7.16-7.10

(m, 1H), 6.56 (d, J = 15.1 Hz, 1H), 6.24-6.17 (m, 2H), 1.86 (d, J = 6.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 197.4, 192.5, 146.5, 141.7, 140.6, 139.3, 137.2, 132.9, 131.0, 130.3, 129.9, 129.6(2C), 128.7, 128.6, 128.3(2C), 125.1, 18.9. HRMS (ESI): m/z calcd for $C_{19}H_{17}O_2$ (M+H): 277.1229. Found: 277.1244.

(E)-2-((E)-But-2-en-1-ylidene)-3-hydroxy-3-phenyl-2,3-dihydro-1H-inden-1-one (2m).



This compound was isolated as pale yellow sticky oil. Following the general procedure-4, 25 mg of **1m** afforded 23 mg of **2m** (92% yield). $R_f = 0.2$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** max/cm⁻¹ 3413, 2929, 1687, 1624, 1288, 982, 699. ¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, J = 8.4 Hz, 1H), 7.65 (dt, J = 11.6 and 1.2 Hz,

1H), 7.50 (dt, J = 7.7 and 0.9 Hz, 1H), 7.37-7.33 (m, 3H), 7.31-7.27 (m, 2H), 7.21-7.17 (m, 1H), 7.04 (d, J = 10.6 Hz, 1H), 6.56 (s, 1H), 6.36-6.29 (m, 2H), 1.72 (d, J = 5.8 Hz, 3H). ¹³C **NMR (100 MHz, CDCl₃):** δ 192.7, 157.3, 145.9, 143.1, 142.2, 136.4, 136.0, 134.6, 129.4, 128.6(2C), 127.8, 127.0, 125.7, 125.5(2C), 122.9, 77.6, 19.5. **HRMS (ESI):** *m/z* calcd for C₁₉H₁₅O (M-OH): 259.1123. Found: 259.1143.

1-((2E,4E)-Hexa-2,4-dienoyl)-2-naphthaldehyde (1n).



This compound was prepared by following the general procedure-2 and isolated as pale brown solid. M.P = 85-87 °C. $R_f = 0.4$ (Hexane/EtOAc = 4/1). IR (thin film, neat): v_{max}/cm^{-1} 3016, 1697, 1275, 1260, 764, 750. ¹H NMR (400 MHz,

CDCl₃): δ 10.17 (s, 1H), 8.05-7.94 (m, 3H), 7.85 (d, J = 8.8 Hz, 1H), 7.69-7.65 (m, 1H), 7.60-7.56 (m, 1H), 6.79-6.72 (m, 1H), 6.60 (d, J = 15.6 Hz, 1H), 6.31-6.28 (m, 1H), 6.09-6.03 (m, 1H), 1.85 (d, J = 6.8 Hz, 3H). ¹³**C NMR (100 MHz, CDCl₃):** δ 198.2, 190.4, 149.0, 143.3, 139.4, 136.1, 130.7, 130.4, 130.2, 129.9, 129.7, 129.3, 128.4, 127.8, 126.7, 123.0, 19.0. **HRMS (ESI):** *m/z* calcd for C₁₇H₁₄O₂ (M+H)⁺: 251.1072. Found: 251.1053.

(E)-2-((E)-But-2-en-1-ylidene)-3-hydroxy-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-



one (2n).This compound was isolated as pale yellow solid. Following the general procedure-4, 30 mg of 1n afforded 27 mg of 2n (90% yield). M.P = 196-198 °C. $R_f = 0.2$ (Hexane/EtOAc = 4/1). IR (thin film, neat): v_{max}/cm^{-1} 3365, 2926, 1693, 1608, 1517, 1441, 1176, 834, 760. ¹H NMR (400 MHz, (CD₃)₂SO): δ

9.13 (d, J = 8.4 Hz, 1H), 8.31 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.77-7.73 (m, 1H), 7.68-7.64 (m, 1H), 7.11 (d, J = 11.9 Hz, 1H), 6.86-6.79 (m, 1H), 6.45-6.40 (m, 1H), 5.99 (d, J = 8.4 Hz, 1H), 5.71 (d, J = 8.3 Hz, 1H), 1.94 (dd, J = 6.8 and 1.1 Hz, 3H). ¹³C NMR (100 MHz, (CD₃)₂SO): δ 193.0, 155.2, 141.9, 138.3, 136.5, 134.2,

133.5, 131.7, 129.5, 129.1, 128.6, 128.5, 127.6, 124.3, 123.7, 67.5, 19.5. HRMS (ESI): m/z calcd for C₁₇H₁₄O₂ (M+H)⁺: 251.1072. Found: 251.1089.

(S)-2-((E)-But-2-en-1-ylidene)-3-hydroxy-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-



one (2n). Following the general procedure-5, 20 mg of 1n afforded 18.6 mg of 2n (93% yield, E/Z = 5:1). Optical rotation: $[\alpha]^{23}_{D}$ +44.9 (*c* 0.08, CHCl₃) for a sample with *ee* 99%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H Column (90:10 *n*-Hexane/2-Propanol, 1.0

mL/min, 254 nm, $\tau_{\text{major}} = 19.6 \text{ min}$, $\tau_{\text{minor}} = 13.7 \text{ min}$).

(E)-1-(5,5-Diphenylpenta-2,4-dienoyl)-2-naphthaldehyde (10).



This compound was prepared by following the general procedure-2 and isolated as pale yellow solid. M.P = 122-124 $^{\circ}$ C. R_f = 0.4 (Hexane/EtOAc = 3/1). IR (thin film, neat): v_{max}/cm^{-1} 3007, 1695, 1641, 1604, 1275, 1260, 749. ¹H NMR

(400 MHz, CDCl₃): δ 10.17 (s, 1H), 7.93-7.89 (m, 3H), 7.69-7.61 (m, 2H), 7.36-7.19 (m, 7H), 7.07 (t, J = 7.6 Hz, 2H), 6.92-6.84 (m, 5H). ¹³C NMR (100 MHz, CDCl₃): δ 197.9, 190.5, 154.3, 147.2, 147.1, 143.5, 140.8, 137.8, 136.0, 132.5, 130.4, 130.3, 129.7, 129.6, 129.3, 129.2(2C), 128.4(2C), 128.3(2C), 127.9, 127.6(2C), 126.7, 125.2, 122.9. HRMS (ESI): m/z calcd for C₂₈H₂₁O₂ (M+H): 389.1542. Found: 389.1546.

(*E*)-2-(3,3-Diphenylallylidene)-3-hydroxy-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1one (20).



This compound was isolated as pale yellow solid. Following the general procedure-4, 35 mg of **1o** afforded 31 mg of **2o** (89% yield). M.P = 147-149 °C. $R_f = 0.2$ (Hexane/EtOAc = 4/1). IR (thin film, neat): v_{max}/cm^{-1} 3418, 3056, 1681, 1609, 1275, 1173, 749. ¹H NMR (400 MHz, CDCl₃): δ 9.19-9.17 (m, 1H), 8.14-

8.10 (m, 1H), 7.93-7.89 (m, 1H), 7.83-7.78 (m, 1H), 7.71-7.57 (m, 2H), 7.54-7.21 (m, 12H), 5.91 (s, 1H), 2.40 (br s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 192.5, 153.5, 152.73, 152.71, 141.5, 139.5, 138.3, 136.4, 139.5, 136.4, 133.1, 130.6(2C), 129.1, 129.0, 128.9, 128.5(2C), 128.4(4C), 128.3, 127.4, 125.0, 122.9, 122.4, 69.0. HRMS (ESI): *m*/*z* calcd for C₂₈H₁₉O (M–OH): 371.1436. Found: 371.1453.

(S)-2-(3,3-Diphenylallylidene)-3-hydroxy-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-



one (20). Following the general procedure-5, 24 mg of 10 afforded 23 mg of 20 (95% yield, E/Z = 7:1). Optical rotation: $[\alpha]^{23}_{D} +114.7$ (*c* 0.18, CHCl₃) for a sample with *ee* 89%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H Column (95:5 *n*-Hexane/2-Propanol, 1.0

mL/min, 254 nm, $\tau_{\text{major}} = 59.6 \text{ min}$, $\tau_{\text{minor}} = 37.8 \text{ min}$).

2-((2*E*,4*E*)-Hexa-2,4-dienoyl)nicotinaldehyde (1p).



This compound was prepared by following the general procedure-2 and isolated as pale brown solid. M.P = 114-116 °C. $R_f = 0.4$ (Hexane/EtOAc = 3/1). IR (thin film, neat): v_{max}/cm^{-1} 3009, 1700, 1662, 1574, 1275, 997, 750. ¹H NMR (400 MHz, CDCl₃): δ

10.49 (s, 1H), 8.86-8.85 (m, 1H), 8.23 (d, J = 7.6 Hz, 1H), 7.60 (dd, J = 7.6 and 4.8 Hz, 1H), 7.55-7.49 (m, 1H), 7.33 (d, J = 15.6 Hz, 1H), 6.41-6.37 (m, 2H), 1.94 (d, J = 5.6 Hz, 3H). ¹³C **NMR (100 MHz, CDCl₃):** δ 191.2, 190.8, 156.0, 151.9, 147.0, 143.1, 136.3, 133.0, 130.8, 126.2, 123.5, 19.1. **HRMS (ESI):** m/z calcd for C₁₂H₁₂NO₂ (M+H): 202.0868. Found: 202.0881.

(E)-6-((E)-But-2-en-1-ylidene)-5-hydroxy-5H-cyclopenta[b]pyridin-7(6H)-one (2p).



This compound was isolated as Pale brown solid. Following the general procedure-4, 20 mg of **1p** afforded 17.5 mg of **2p** (87% yield). M.P = 123-125 °C. $R_f = 0.2$ (Hexane/EtOAc = 5/1). IR (thin film, neat): v_{max}/cm^{-1} 3417, 2834, 1659, 1651, 1025, 999, 764. ¹H NMR (400 MHz, (CD₃)₂SO): δ 8.81-8.80 (m, 1H), 8.21-8.19 (m,

1H), 7.68 (dd, J = 8.0 and 6.9 Hz, 1H), 7.20 (d, J = 7.0 Hz, 1H), 6.84-6.76 (m, 1H), 6.53-6.47 (m, 1H), 6.00 (d, J = 8.4 Hz, 1H), 5.67 (d, J = 8.1 Hz, 1H), 1.94 (d, J = 6.8 Hz, 3H). ¹³C NMR (100 MHz, (CD₃)₂SO): δ 191.5, 154.6, 152.2, 148.1, 144.0, 137.0, 136.8, 135.5, 128.6, 128.4, 65.9, 19.6. HRMS (ESI): m/z calcd for C₁₂H₁₀NO (M-OH): 184.0762. Found: 184.0756.

(S)-6-((E)-But-2-en-1-ylidene)-5-hydroxy-5H-cyclopenta[b]pyridin-7(6H)-one (2p).



Following the general procedure-5, 20 mg of **1p** afforded 17.7 mg of **2p** (88% yield, E/Z = 4:1). **Optical rotation:** $[\alpha]^{23}_{D} + 39.2$ (*c* 0.05,

DMSO) for a sample with *ee* 96%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS Column (87:13 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, $\tau_{\text{major}} = 9.2 \text{ min}, \tau_{\text{minor}} = 11.8 \text{ min}$).

2-((2E,4E)-Hexa-2,4-dienoyl)benzo[b]thiophene-3-carbaldehyde (1q).



This compound was prepared by following the general procedure-1 and isolated as a pale yellow solid. M.P = 122-124 °C. $R_f = 0.5$ (Hexane/EtOAc = 4/1). IR (thin film, neat): v_{max}/cm^{-1} 3442, 3002, 1671, 1655, 1592, 1499, 1000, 751. ¹H

NMR (400 MHz, CDCl₃): δ 10.65 (s, 1H), 8.80-8.78 (m, 1H), 7.92-7.90 (m, 1H), 7.58-7.54 (m, 2H), 7.53-7.47 (m, 1H), 6.70 (d, *J* = 14.8 Hz, 1H), 6.40-6.39 (m, 2H), 1.96 (d, *J* = 5.2 Hz, 3H). ¹³C **NMR (100 MHz, CDCl₃):** δ 188.0, 184.7, 150.7, 147.7, 144.3, 138.9, 136.6, 136.4, 130.2, 127.8, 126.9, 126.7, 125.4, 122.2, 19.1. **HRMS (ESI):** *m/z* calcd for C₁₅H₁₃O₂S (M+H): 257.0636. Found: 257.0654.

(E)-2-((E)-But-2-en-1-ylidene)-1-hydroxy-1H-benzo[b]cyclopenta[d]thiophen-3(2H)-one



(2q). This compound was isolated as pale yellow solid. Following the general procedure-4, 25 mg of 1q afforded 23 mg of 2q (93% yield). M.P = 127-129 °C. $R_f = 0.4$ (Hexane/EtOAc = 4/1). IR (thin film, neat): v_{max}/cm^{-1} 3467, 2925, 1690, 1633, 1270, 1019, 760. ¹H NMR (400 MHz, CDCl₃): δ 8.16-8.14 (m, 1H), 7.92-7.90

(m, 1H), 7.56-7.49 (m, 2H), 7.16 (d, J = 11.6 Hz, 1H), 6.85-6.78 (m, 1H), 6.36 (sextet, J = 7.2 Hz, 1H), 5.91 (d, J = 6.5 Hz, 1H), 2.35 (d, J = 6.4 Hz, 1H), 2.00 (dd, J = 6.9 and 1.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 185.4, 158.9, 148.1, 145.0, 143.2, 138.9, 135.3, 133.3, 128.3, 127.2, 125.5, 124.6, 124.3, 67.0, 19.3. HRMS (ESI): m/z calcd for C₁₅H₁₃O₂S (M+H)⁺: 257.0636. Found: 257.0644.

(S)-2-((E)-But-2-en-1-ylidene)-1-hydroxy-1H-benzo[b]cyclopenta[d]thiophen-3(2H)-one



(2q). Following the general procedure-5, 20 mg of 1q afforded 18.3 mg of 2q (91% yield, E/Z = 4:1). Optical rotation: $[\alpha]^{23}_{D}$ - 36.3 (*c* 0.11, CHCl₃) for a sample with *ee* 94%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS Column (98:2 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm,

 $\tau_{\rm major} = 13.2 \text{ min}, \tau_{\rm minor} = 23.9 \text{ min}).$

(2E,4E)-1-(3-Acetylbenzo[b]thiophen-2-yl)hexa-2,4-dien-1-one (1r).



This compound was prepared by following the general procedure-1 and isolated as pale yellow oil. $R_f = 0.4$ (Hexane/EtOAc = 4/1). IR (thin film, neat): max/cm⁻¹ 3444, 3064, 2918, 1699, 1652, 1585, 1510, 1140, 757. ¹H NMR (400 MHz, CDCl₃): δ 7.89 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 7.9 Hz,

1H), 7.52-7.47 (m, 3H), 6.67 (d, J = 14.8 Hz, 1H), 6.37-6.35 (m, 2H), 2.62 (s, 3H), 1.94 (d, J = 4.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 200.9, 184.0, 146.9, 143.5, 142.1, 140.5, 136.7, 130.2, 127.6, 125.8, 125.2, 124.5, 124.3, 122.7, 31.5, 19.1. HRMS (ESI): m/z calcd for C₁₆H₁₅O₂S (M+H): 271.0793. Found: 271.0793.

(E)-2-((E)-But-2-en-1-ylidene)-1-hydroxy-1-methyl-1H-benzo[b]cyclopenta[d]thiophen-



3(2*H***)-one (2r).** This compound was isolated as light yellow semi solid. Following the general procedure-4, 20 mg of **1r** afforded 17.8 mg of **2r** (89% yield). $R_f = 0.3$ (Hexane/EtOAc = 3/1). **IR** (thin film, neat): max/cm⁻¹ 3387, 2929, 1681, 1632, 1267, 1041, 735. ¹H NMR (400 MHz, CDCl₃): δ 8.18-8.15 (m, 1H), 7.93-7.90

(m, 1H), 7.53-7.49 (m, 2H), 7.03 (d, J = 12.0 Hz, 1H), 6.97-6.93 (m, 1H), 6.34-6.28 (m, 1H), 2.61 (br s, 1H), 2.00 (dd, J = 6.7 and 1.6 Hz, 3H), 1.96 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 185.1, 162.8, 148.3, 143.0, 142.8, 133.4, 132.2, 128.8, 127.2, 126.5, 125.3, 125.0, 124.4, 74.7, 26.1, 19.3. HRMS (ESI): m/z calcd for C₁₆H₁₅O₂S (M+H)⁺: 271.0793. Found: 271.0782.

4-((2*E*,4*E*)-Hexa-2,4-dienoyl)-2*H*-chromene-3-carbaldehyde (1s).



This compound was prepared by following the general procedure-2 and isolated as light brown oil. $R_f = 0.5$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** v_{max} /cm⁻¹ 3370, 3030, 2832, 2745, 1701, 1654, 1616, 1578, 1458, 1100, 752. ¹H

NMR (400 MHz, CDCl₃): δ 9.65 (s, 1H), 7.36-7.32 (m, 1H), 7.16-7.09 (m, 2H), 6.97-6.94 (m, 2H), 6.37 (d, J = 15.2 Hz, 1H), 6.31-6.29 (m, 2H), 5.03 (s, 2H), 1.91 (d, J = 5.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 194.2, 187.8, 155.8, 149.8, 149.7, 149.3, 144.6, 133.6, 130.0, 128.6, 127.0, 122.3, 119.4, 117.2, 62.4, 19.1. **HRMS (ESI):** m/z calcd for C₁₆H₁₅O₃(M+H): 255.1021. Found: 255.1036.

(E)-2-((E)-But-2-en-1-ylidene)-3-hydroxy-2,3-dihydrocyclopenta[c]chromen-1(4H)-one



(2s). This compound was isolated as pale brown solid. Following the general procedure-4, 20 mg of 1s afforded 19 mg of 2s (93% yield). M.P = 167-169 °C. $R_f = 0.3$ (Hexane/EtOAc = 5/1). IR (thin film, neat): v_{max}/cm^{-1} 2929, 1696, 1608, 1459, 1277, 1072, 1019, 757. ¹H NMR (400 MHz, CDCl₃): δ 8.16-8.12 (m, 1H),

7.24-7.20 (m, 1H), 7.05 (d, J = 11.6 Hz, 1H), 6.98-6.94 (m, 1H), 6.85 (dd, J = 8.0 and 0.8 Hz, 1H), 6.69-6.28 (m, 1H), 6.37-6.30 (m, 1H), 5.41-5.35 (m, 1H), 5.26 (s, 2H), 5.25-5.19 (m, 1H), 1.98 (dd, J = 6.8 and 1.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 190.3, 156.9, 153.0, 143.2, 134.5, 134.1, 133.9, 130.8, 127.0, 125.2, 121.7, 116.5, 115.9, 68.5, 65.2, 19.2. HRMS (ESI): m/z calcd for C₁₆H₁₅O₃ (M+H)⁺: 255.1021. Found: 255.1043.

(S)-2-((E)-But-2-en-1-ylidene)-3-hydroxy-2,3-dihydrocyclopenta[c]chromen-1(4H)-one



(2s). Following the general procedure-5, 22 mg of 1s afforded 21.3 mg of 2s (97% yield, E/Z = 6:1). Optical rotation: $[\alpha]^{23}_{D} + 3.1$ (*c* 0.05, CHCl₃) for a sample with *ee* 95%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H Column (95:5 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, $\tau_{major} =$

34.6 min, $\tau_{\rm minor} = 23.4$ min).

(E)-4-(5,5-Diphenylpenta-2,4-dienoyl)-2H-chromene-3-carbaldehyde (1t).



This compound was prepared by following the general procedure-2 and isolated as pale brown sticky oil. $R_f = 0.4$ (Hexane/EtOAc = 4/1). IR (thin film, neat): v_{max}/cm^{-1} 3058, 2855, 1759, 1672, 1602, 1445, 1275, 751. ¹H NMR (400

MHz, CDCl₃): δ 9.66 (s, 1H), 7.40-7.35 (m, 4H), 7.34-7.28 (m, 4H), 7.27-7.25 (m, 2H), 7.12 (dd, J = 8.0 and 1.6 Hz, 1H), 7.01-6.98 (m, 3H), 6.93 (dd, J = 8.0 and 0.8 Hz, 1H), 6.89 (d, J = 11.6 Hz, 1H), 6.61 (d, J = 15.2 Hz, 1H), 4.90 (s, 2H). ¹³C **NMR (100 MHz, CDCl₃):** δ 194.1, 187.8, 155.7, 155.5, 149.4, 148.1, 140.7, 137.8, 133.5, 130.5, 130.4(2C), 129.5, 128.9, 128.6(2C), 128.5(2C), 128.3(2C), 127.2, 126.9, 124.9, 122.1, 119.4, 117.1, 62.1. **HRMS (ESI):** m/z calcd for C₂₇H₂₁O₃ (M+H)⁺: 393.1491. Found: 393.1473.

(E)-2-(3,3-Diphenylallylidene)-3-hydroxy-2,3-dihydrocyclopenta[c]chromen-1(4H)-one



(2t). This compound was isolated as light yellow liquid. Following the general procedure-4, 25 mg of 1t afforded 24 mg of 2t (96% yield). $R_f = 0.3$ (Hexane/EtOAc = 3/1). IR (thin film, neat): v_{max}/cm^{-1} 3437, 2924, 1634, 1614, 1269, 760. ¹H NMR (400 MHz, CDCl₃): δ 8.11 (dd, J = 7.8 and 0.8 Hz,

1H),7.44-7.43 (m, 3H), 7.36-7.35 (m, 5H), 7.32-7.28 (m, 2H), 7.26-7.19 (m, 3H), 6.96-6.93 (m, 1H), 6.92-6.83 (m, 1H), 5.42-5.20 (m, 3H), 2.07 (br s, 1H) . ¹³C NMR (100 MHz, CDCl₃): δ 189.9, 156.7, 153.8, 153.0, 141.4, 138.1, 136.9, 134.1, 131.8, 130.6(2C), 129.0, 128.6, 128.4(6C), 125.2, 122.3, 121.7, 116.5, 115.9, 68.7, 65.2. HRMS (ESI): *m/z* calcd for C₂₇H₂₁O₃ (M+H)⁺: 393.1491. Found: 393.1474.

(S,E)-2-(3,3-Diphenylallylidene)-3-hydroxy-2,3-dihydrocyclopenta[c]chromen-1(4H)-



one (2t). Following the general procedure-5, 20 mg of 1t afforded 18.3 mg of 2t (91% yield, E/Z = 6:1). Optical rotation: $[\alpha]^{23}{}_{D}$ +49.9 (*c* 0.10, CHCl₃) for a sample with *ee* 98%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H Column (93:7 *n*-Hexane/2-Propanol, 0.8

mL/min, 254 nm, $\tau_{major} = 35.7 \text{ min}$, $\tau_{minor} = 32.3 \text{ min}$).

2-((2E,4E)-Hexa-2,4-dienoyl)thiophene-3-carbaldehyde (1u).



This compound was prepared by following the general procedure-2 and isolated as pale yellow oil. $R_f = 0.5$ (Hexane/EtOAc = 4/1). IR (thin film, neat): v_{max}/cm^{-1} 2928, 1680, 1651, 1623, 1584, 1244, 1156, 732. ¹H NMR (400 MHz, CDCl₃): δ 10.50 (s, 1H), 7.65 (d, J

= 4.9 Hz, 1H), 7.50-7.47 (m, 2H), 6.68 (d, J = 14.8 Hz, 1H), 6.36-6.34 (m, 2H), 1.43 (d, J = 5.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 187.5, 182.8, 147.1, 146.6, 144.3, 143.5, 130.1, 129.2, 128.4, 124.6, 19.0. HRMS (ESI): m/z calcd for C₁₁H₁₁O₂S (M+H)⁺: 207.0480. Found: 207.0467.

(E)-5-((E)-But-2-en-1-ylidene)-4-hydroxy-4H-cyclopenta[b]thiophen-6(5H)-one (2u).



This compound was isolated as Pale yellow oil. Following the general procedure-3, 25 mg of 1u afforded 23.5 mg of 2u (94% yield). $R_f = 0.3$

(Hexane/EtOAc = 3/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3383, 2961, 2925, 1692, 1633, 1434, 1377, 1035, 732. ¹H NMR (400 MHz, CDCl₃): δ 7.89 (d, J = 4.8 Hz, 1H), 7.30 (d, J = 4.9 Hz, 1H), 7.09 (d, J = 12.0 Hz, 1H), 6.77-6.69 (m, 1H), 6.34-6.29 (m, 1H), 5.65 (s, 1H), 2.41 (br.s, 1H), 1.97 (dd, J = 8.0 and 1.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 184.1, 163.7, 144.6, 142.7, 140.0, 139.8, 135.4, 127.1, 123.3, 66.7, 19.2. HRMS (ESI): m/z calcd for C₁₁H₉OS (M-OH)⁺: 189.0374. Found: 189.0389.

(*R*,*E*)-5-((*E*)-But-2-en-1-ylidene)-4-hydroxy-4*H*-cyclopenta[*b*]thiophen-6(5*H*)-one (2u).



Following the general procedure-5, 20 mg of 1u afforded 19.4 mg of 2u (89% yield, E/Z = 5:1). Optical rotation: $[\alpha]^{23}{}_{\rm D}$ -6.6 (*c* 0.10, CHCl₃) for a sample with *ee* 92%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H Column (90:10 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, $\tau_{\rm major} = 22.1$ min,

 $\tau_{\rm minor} = 33.2 \text{ min}$).

2-((2E,4E)-3-Methyl-5-phenylpenta-2,4-dienoyl)benzaldehyde (1v).



This compound was prepared by following the general procedure-2 and isolated as pale yellow oil. $R_f = 0.4$ (Hexane/EtOAc = 4/1). IR (thin film, neat): v_{max}/cm^{-1} 2922, 1694, 1654, 1575, 1246, 968, 725. ¹H NMR (400 MHz, CDCl₃): δ 10.28 (s, 1H), 7.96 (d, J =

7.6 Hz, 1H), 7.74-7.72 (m, 1H), 7.68-7.52 (m, 4H), 7.41-7.28 (m, 3H), 7.14 (d, J = 16.0 Hz, 1H), 6.93 (d, J = 16.0 Hz, 1H), 6.78 (s, 1H), 2.52 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 192.8, 191.8, 153.9, 143.8, 136.7, 136.1, 135.8, 133.0, 132.0, 129.1, 128.9(2C), 128.8, 128.1, 127.3(2C), 125.9, 124.0, 14.7. HRMS (ESI): m/z calcd for C₁₉H₁₇O₂ (M+H)⁺: 277.1229. Found: 277.1216.

(E)-3-Hydroxy-2-((E)-4-phenylbut-3-en-2-ylidene)-2,3-dihydro-1*H*-inden-1-one (2v).



This compound was isolated as Pale yellow solid. Following the general procedure-3, 40 mg of 1v afforded 36.5 mg of 2v (91% yield). M.P = 127-129 °C. $R_f = 0.2$ (Hexane/EtOAc = 4/1). IR (thin film, neat): v_{max}/cm^{-1} 3400, 2924, 1668, 1605, 1579, 1336, 1094, 751. ¹H NMR (400 MHz, CDCl₃): δ 7.74-7.70 (m, 2H), 7.65-7.53

(m, 4H), 7.42-7.28 (m, 4H), 7.12 (d, J = 16.0 Hz, 1H), 5.8 (s, 1H), 2.92 (br.s, 2.50 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 193.7, 149.7, 149.3, 131.9, 137.6, 136.5, 135.3, 134.9, 129.2, 128.8(2C), 128.5, 127.6(2C), 125.8, 125.7, 123.2, 69.9, 13.3. **HRMS (ESI):** *m/z* calcd for C₁₉H₁₇O₂ (M+H)⁺: 277.1229. Found: 277.1215.

4-Acetyl-3-methyl-9H-fluoren-9-one (13a).



This compound was isolated as pale yellow solid. Following the general procedure-6, 30 mg of **2a** afforded 16 mg of **13a** (46% yield, over two steps). M.P = 150-152 °C. R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** v_{max}/cm^{-1} 2924, 2854, 1714, 1695, 1357, 1111, 752. ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, *J* = 7.3 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.46 (dt, *J* = 7.6 and 1.1 Hz, 1H), 7.35-7.28 (m, 2H), 7.71 (d, *J* = 7.6 Hz, 1H),

2.67 (s, 3H), 2.35 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 206.7, 192.5, 142.5, 139.8, 139.2, 137.2, 134.7, 134.6, 132.5, 130.9, 129.4, 124.6, 124.5, 122.1, 32.3, 19.3. HRMS (ESI): *m/z* calcd for C₁₆H₁₁O₂ (M-H)⁺: 235.0759. Found: 235.0750.

4-Acetyl-3-phenyl-9H-fluoren-9-one (13b).



This compound was isolated as pale yellow solid. Following the general procedure-6, 25 mg of **2b** afforded 12 mg of **13b** (43% yield, over two steps). M.P = 115-117 °C. R_f = 0.5 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** v_{max}/cm^{-1} 2993, 1715, 1698, 1606, 1576, 1412, 1275, 1259, 749. ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.73 (dd, *J* = 7.4 and 0.8 Hz, 1H), 7.48-7.41 (m, 7H), 7.36 (d, *J* = 7.6 Hz, 1H),

7.35 (dt, J = 7.6 and 1.3 Hz, 1H), 2.11 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 206.3, 192.5, 144.8, 142.8, 142.6, 139.7, 138.9, 136.5, 135.0, 134.5, 133.6, 130.7, 129.5, 128.9(2C), 128.8(2C), 128.7, 124.7, 124.5, 122.6, 32.0. HRMS (ESI): m/z calcd for C₂₁H₁₃O₂ (M-H)⁺: 297.0916. Found: 297.0903.

4-Acetyl-6-methoxy-3-methyl-9*H*-fluoren-9-one (13c).



This compound was isolated as pale yellow solid. Following the general procedure-6, 30 mg of **2h** afforded 15 mg of **13c** (44% yield). M.P = 116-117 °C. $R_f = 0.3$ (Hexane/EtOAc = 4/1). IR (thin film, neat): v_{max}/cm^{-1} 2928, 1704, 1688, 1612, 1584, 1363, 1228, 782. ¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, J = 8.2 Hz, 1H), 7.58

(d, J = 7.7 Hz, 1H), 7.17 (d, J = 7.7 Hz, 1H), 6.81 (d, J = 2.0 Hz, 1H), 6.77 (dd, J = 8.2 and

2.0 Hz, 1H), 3.89 (s, 3H), 2.67 (s, 3H), 2.37 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 206.5, 191.1, 165.2, 144.9, 139.2, 138.0, 137.2, 133.7, 131.1, 129.6, 126.5, 124.1, 112.5, 109.7, 55.8, 32.3, 19.2. HRMS (ESI): *m/z* calcd for C₁₇H₁₅O₃ (M+H)⁺: 267.1021. Found: 267.1009.

5-Acetyl-2,3-dimethoxy-6-methyl-9*H*-fluoren-9-one (13d).



This compound was isolated as pale yellow solid. Following the general procedure-6, 35 mg of **2k** afforded 16 mg of **13d** (43% yield). M.P = 178-180 °C. $R_f = 0.3$ (Hexane/EtOAc = 3/1). IR (thin film, neat): v_{max}/cm^{-1} 2926, 1704, 1681, 1609, 1480, 1276, 749. ¹H NMR (400 MHz, CDCl₃): δ 7.50 (d, J = 7.6 Hz, 1H), 7.23 (s, 1H), 7.07 (d, J = 7.6 Hz, 1H), 6.78 (s, 1H), 3.96 (s, 3H),

3.95 (s, 3H), 2.67 (s, 3H), 2.33 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 206.8, 191.8, 154.2, 149.8, 139.3, 138.8, 137.4, 136.1, 133.2, 129.9, 127.7, 124.0, 107.2, 105.3, 56.29, 56.28, 32.3, 19.3. HRMS (ESI): *m/z* calcd for C₁₈H₁₇O₄ (M+H)⁺: 297.1127. Found: 297.1123.

4-Acetyl-6-fluoro-3-methyl-9H-fluoren-9-one (13e).



This compound was isolated as off white solid. Following the general procedure-6, 25 mg of **2g** afforded 15 mg of **13e** (50% yield). M.P = 110-112 °C. $R_f = 0.3$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** v_{max}/cm^{-1} 2990, 1714, 1690, 1612, 1584, 1275, 1260, 750. ¹H NMR (400 MHz, CDCl₃): δ 7.70 (dd, J = 8.0 and 2.8 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.21 (7.7 Hz, 1H), 7.01-6.96 (m, 2H), 2.67 (s, 3H), 2.37 (s,

3H). ¹³C NMR (100 MHz, CDCl₃): δ 206.1, 190.7, 165.7 (d, J = 254.1 Hz), 145.4 (d, J = 9.7 Hz), 139.9, 137.53, 137.51, 132.9, 131.6, 130.6 (d, J = 2.5 Hz), 126.5 (d, J = 10.2 Hz), 124.5, 115.8 (d, J = 23.2 Hz), 110.4 (d, J = 25.0 Hz), 32.2, 19.3. ¹⁹F NMR (376 MHz, CDCl₃): δ - 101.9. HRMS (ESI): m/z calcd for C₁₆H₁₂FO₂ (M+H)⁺: 255.0821. Found: 255.0819.

7-Acetyl-8-methyl-11*H*-benzo[*a*]fluoren-11-one (13f).



This compound was isolated as pale yellow solid. Following the general procedure-6, 40 mg of **2n** afforded 22 mg of **13f** (48% yield). M.P = 162-164 °C. R_f = 0.4 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** v_{max}/cm^{-1} 2935, 1702, 1692, 1604, 1581, 1280, 1060, 761. ¹H **NMR (400 MHz, CDCl₃):** δ 9.02 (d, *J* = 8.5 Hz, 1H), 7.95 (*J* = 8.4 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.64-7.62 (m, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.49-7.46 (m, 1H), 7.41 (d, J = 8.1 Hz, 1H), 7.14 (d, J = 7.8 Hz, 1H), 2.71 (s, 3H), 2.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 206.8, 194.0, 144.3, 139.2, 138.6, 137.0, 135.8, 134.3, 132.9, 130.9, 130.2, 129.6, 128.3, 127.6, 126.8, 124.4, 123.9, 119.4, 32.6, 19.2. HRMS (ESI): *m/z* calcd for C₂₀H₁₅O₂ (M+H)⁺: 287.1072. Found: 287.1076.

Crystal structure of racemic 2a (CCDC 1520613): Structure of the racemic indanone **2a** was confirmed by single crystal X-ray diffraction analysis.



Crystal Data for C₁₃H₁₂O₂ (*M*=200.24 g/mol): triclinic, space group P-1 (no. 2), *a* = 7.8751(9) Å, *b* = 8.2320(4) Å, *c* = 8.8523(12) Å, *a* = 73.986(8)°, *β* = 73.564(11)°, *γ* = 83.983(8)°, *V* = 528.84(10) Å³, *Z* = 2, *T* = 298 K, μ (Mo K α) = 0.084 mm⁻¹, *Dcalc* = 1.2574 g/cm³, 11929 reflections measured (4.96° ≤ 2 Θ ≤ 65.5°), 3626 unique (*R*_{int} = 0.0618, R_{sigma} = 0.0428) which were used in all calculations. The final *R*₁ was 0.0969 (I>=2u(I)) and *wR*₂ was 0.2917 (all data).

Identification code	Racemic 2a
Empirical formula	$C_{13}H_{12}O_2$
Formula weight	200.24
Temperature/K	298
Crystal system	triclinic
Space group	P-1
a/Å	7.8751(9)
b/Å	8.2320(4)

Table 1: Crystal data and structure refinement for racemic 2a

c/Å	8.8523(12)
α/°	73.986(8)
β/°	73.564(11)
γ/°	83.983(8)
Volume/Å ³	528.84(10)
Z	2
$\rho_{calc}g/cm^3$	1.2574
μ/mm^{-1}	0.084
F(000)	212.1
Crystal size/mm ³	$0.25 \times 0.2 \times 0.14$
Radiation	Mo K α (λ = 0.71073)
2Θ range for data collection/°	4.96 to 65.5
Index ranges	$-11 \le h \le 10, -11 \le k \le 12, -12 \le l \le 13$
Reflections collected	11929
Independent reflections	$3626 [R_{int} = 0.0618, R_{sigma} = 0.0428]$
Data/restraints/parameters	3626/0/137
Goodness-of-fit on F ²	1.467
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0969, wR_2 = 0.2396$
Final R indexes [all data]	$R_1 = 0.1444, wR_2 = 0.2917$
Largest diff. peak/hole / e Å ⁻³	0.72/-0.35

Table 2: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	у	Z	U(eq)
O001	6489.9(19)	7938.7(19)	1949.2(16)	67.3(5)
O002	2431(2)	5482.5(18)	6815.7(18)	69.9(5)
C003	5107(3)	7023(2)	6204(2)	53.9(5)
C004	3686(3)	7263(2)	4112(2)	54.2(5)
C005	6154(3)	8021(2)	4790(2)	55.4(5)
C006	3576(2)	6465(2)	5852(2)	53.3(5)
C007	5327(3)	8328(2)	3368(2)	56.3(5)
C008	2483(3)	6998(2)	3406(2)	57.5(5)
C009	2413(3)	7727(3)	1744(3)	61.1(5)
C00A	1145(3)	7332(3)	1181(3)	63.2(5)
C00B	5564(3)	6618(3)	7674(3)	67.3(6)
C00C	7750(3)	8594(3)	4801(3)	67.7(6)
C00D	8210(3)	8167(3)	6260(3)	76.5(7)
COOE	7123(4)	7225(3)	7685(3)	76.0(7)
COOF	952(3)	8043(4)	-500(3)	76.7(7)

Table 3: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for bsme. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O001	67.6(9)	67.5(10)	61.0(9)	-9.4(7)	-10.6(7)	-11.3(7)

O002	70.5(10)	59.5(9)	73.3(10)	-16.9(7)	-9.7(7)	-10.9(7)
C003	60.7(10)	43.3(9)	59.9(10)	-1.0(7)	-18.8(8)	-14.1(8)
C004	57.6(10)	47.8(9)	58.6(10)	-0.2(8)	-16.6(8)	-15.1(8)
C005	57.3(10)	45.2(9)	65.8(11)	-3.6(8)	-17.5(9)	-15.7(8)
C006	56.4(10)	44.8(9)	58.7(11)	-4.0(7)	-13.7(8)	-14.0(8)
C007	62.7(11)	45.6(9)	58.9(11)	-9.5(8)	-17.2(9)	-6.9(8)
C008	55.2(10)	52.8(10)	66.0(12)	-5.3(8)	-15.7(9)	-16.9(9)
C009	58.8(11)	59.5(11)	66.7(12)	-5.4(8)	-18.4(9)	-15.9(9)
C00A	60.7(11)	63.3(12)	70.8(13)	-2.3(9)	-21.0(9)	-21.7(10)
C00B	80.2(14)	60.9(12)	61.9(12)	-1.1(10)	-24.7(11)	-12.0(9)
C00C	65.6(12)	62.1(12)	76.3(14)	-11.8(10)	-20.1(10)	-14.5(10)
C00D	74.2(14)	76.3(15)	89.5(16)	-8.8(11)	-35.0(12)	-22.3(12)
C00E	85.8(16)	72.6(15)	80.7(15)	-0.8(12)	-40.6(13)	-19.2(12)
C00F	76.2(15)	89.0(17)	74.2(14)	0.9(12)	-29.4(12)	-27.5(12)

Table 4: Bond Lengths for racemic 2a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O001	C007	1.425(3)	C005	C007	1.525(3)
O002	C006	1.238(2)	C005	C00C	1.391(3)
C003	C005	1.383(3)	C008	C009	1.442(3)
C003	C006	1.472(3)	C009	C00A	1.338(3)
C003	C00B	1.390(3)	C00A	C00F	1.486(3)
C004	C006	1.480(3)	C00B	C00E	1.377(3)
C004	C007	1.520(3)	C00C	C00D	1.382(3)
C004	C008	1.337(3)	C00D	C00E	1.383(4)

Table 5: Bond Angles for racemic 2a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C006	C003	C005	109.58(17)	C004	C006	C003	107.19(16)
C00B	C003	C005	121.9(2)	C004	C007	O001	114.40(16)
C00B	C003	C006	128.44(19)	C005	C007	O001	113.86(16)
C007	C004	C006	108.84(16)	C005	C007	C004	102.62(15)
C008	C004	C006	121.95(18)	C009	C008	C004	127.4(2)
C008	C004	C007	129.21(18)	C00A	C009	C008	121.4(2)
C007	C005	C003	111.61(17)	C00F	C00A	C009	125.1(2)
C00C	C005	C003	119.8(2)	C00E	C00B	C003	117.9(2)
C00C	C005	C007	128.54(18)	C00D	C00C	C005	117.9(2)
C003	C006	0002	126.68(17)	C00E	C00D	C00C	122.0(2)
C004	C006	0002	126.10(18)	C00D	C00E	C00B	120.4(2)

Table 6: Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for racemic 2a.

Atom	x	у	Ζ	U(eq)
H00C	8485(3)	9243(3)	3855(3)	81.2(7)

H00D	9281(3)	8525(3)	6285(3)	91.8(8)
HOOE	7447(4)	7000(3)	8656(3)	91.2(8)
H00B	4840(3)	5958(3)	8619(3)	80.8(7)
H001	6820(30)	6942(11)	2172(10)	100.9(7)
H007	4951(3)	9521(2)	3084(2)	67.5(6)
H008	1591(3)	6259(2)	4062(2)	69.0(6)
H009	3266(3)	8489(3)	1050(3)	73.3(6)
H00A	320(3)	6553(3)	1897(3)	75.9(7)
H00f	1895(17)	8800(20)	-1124(8)	115.1(10)
H00g	1000(30)	7141(4)	-1006(10)	115.1(10)
H00h	-165(13)	8650(20)	-456(3)	115.1(10)

Crystal structure of chiral 2j (CCDC 1520308): Structure of the chiral indanone 2j was confirmed by single crystal X-ray diffraction analysis. Absolute stereochemistry was realised to be (*S*).



Crystal Data for C₂₅H₂₀O₃ (*M* =368.42 g/mol): orthorhombic, space group P2₁2₁2₁ (no. 19), a = 10.1899(4) Å, b = 13.3377(5) Å, c = 14.4940(7) Å, V = 1969.88(14) Å³, Z = 8, T = 298 K, μ (Mo K α) = 0.081 mm⁻¹, *Dcalc* = 1.2422 g/cm³, 15325 reflections measured (5.62° $\leq 2\Theta \leq 65.52^{\circ}$), 6671 unique ($R_{int} = 0.0263$, $R_{sigma} = 0.0399$) which were used in all calculations. The final R_1 was 0.0593 (I>=2u(I)) and wR_2 was 0.1979 (all data).

Table 1: Crystal data and structure refinement for Chiral 2j

Identification code	Chiral 2j
Empirical formula	$C_{25}H_{20}O_3$
Formula weight	368.42
Temperature/K	298

Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	10.1899(4)
b/Å	13.3377(5)
c/Å	14.4940(7)
α/°	90
β/°	90
$\gamma/^{\circ}$	90
Volume/Å ³	1969.88(14)
Ζ	8
$\rho_{calc}g/cm^3$	1.2422
μ/mm^{-1}	0.081
F(000)	776.4
Crystal size/mm ³	0.2 imes 0.15 imes 0.12
Radiation	Mo K α (λ = 0.71073)
2Θ range for data collection/°	5.62 to 65.52
Index ranges	$-14 \le h \le 14, -16 \le k \le 19, -15 \le l \le 21$
Reflections collected	15325
Independent reflections	6671 [$R_{int} = 0.0263$, $R_{sigma} = 0.0399$]
Data/restraints/parameters	6671/0/254
Goodness-of-fit on F ²	1.053
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0593, wR_2 = 0.1576$
Final R indexes [all data]	$R_1 = 0.1099, wR_2 = 0.1979$
Largest diff. peak/hole / e Å ⁻³	0.28/-0.20
Flack parameter	-0.6(9)

Table 2: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for BS06OMediph. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	у	Z	U(eq)
O001	-5270.0(17)	-9422.2(12)	-3131.7(14)	71.4(5)
O002	-6061.1(16)	-6272.1(12)	-1904.2(13)	71.0(5)
O003	-1220.6(18)	-6755.7(13)	-683.1(14)	76.9(5)
C004	-4027.7(18)	-7214.5(15)	-2114.1(14)	48.2(4)
C005	-3937.0(19)	-8244.4(14)	-2271.1(14)	49.6(4)
C006	-3090(2)	-6727.5(16)	-1593.1(15)	54.8(5)
C007	-5060(2)	-8576.9(15)	-2825.9(14)	53.5(5)
C008	-5915.0(19)	-7689.5(15)	-2962.4(15)	52.1(5)
C009	-9242(2)	-6956.4(17)	-3781.7(15)	53.6(5)
COOA	-10059(2)	-6043.4(16)	-3685.7(15)	54.3(5)
C00B	-2075(2)	-7279.5(17)	-1207.6(15)	56.2(5)
C00C	-1981(2)	-8312.5(17)	-1365.4(17)	59.7(5)
COOD	-5244(2)	-6771.3(15)	-2551.7(16)	52.4(5)
C00E	-7104(2)	-7759.1(16)	-3355.1(16)	56.8(5)
COOF	-9878(2)	-7846.6(16)	-4197.6(14)	53.4(5)

COOG	-2902(2)	-8791.1(16)	-1902.4(16)	58.2(5)
С00Н	-8009(2)	-6933.9(17)	-3437.9(17)	59.1(5)
C00I	-11174(2)	-8073.9(18)	-3941.7(17)	62.2(6)
COOJ	-10774(2)	-5667.7(19)	-4416.8(17)	65.1(6)
C00K	-9248(2)	-8475.2(18)	-4820.5(16)	63.1(6)
COOL	-11550(3)	-4821(2)	-4311(2)	77.3(7)
C00M	-11789(3)	-8921(2)	-4278.6(19)	75.2(7)
COON	-10133(3)	-5542(2)	-2833.3(18)	69.6(6)
C00O	-11623(3)	-4351(2)	-3471(2)	84.8(8)
COOP	-11132(3)	-9551(2)	-4873(2)	83.2(8)
C00Q	-9876(3)	-9326(2)	-5141.5(19)	76.0(7)
COOR	-10912(3)	-4709(2)	-2748(2)	87.7(9)
COOS	-208(4)	-7278(2)	-209(3)	111.3(13)

Table 3:	Anisotropic	Displace	ement Par	ameters (Å ² ×	10 ³) for	BS06O	Mediph.	The
Anisotropi	c displac	ement	factor	exponent	takes	the	form:	-
$2\pi^2[h^2a^*U]$	11+2hka*b*U	J ₁₂ +].						

Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O 001	66.9(9)	52.5(8)	94.9(12)	-3.0(7)	-19.3(9)	-8.7(8)
O002	58.1(8)	59.1(9)	95.7(12)	9.7(8)	-7.5(9)	-14.5(9)
O003	73.6(11)	65.1(10)	92.0(12)	2.7(9)	-34.5(10)	-8.5(9)
C004	44.1(9)	48.6(9)	51.9(10)	-1.5(8)	-0.7(9)	3.9(8)
C005	46.9(9)	47.5(9)	54.4(11)	-1.6(8)	-0.5(9)	2.1(8)
C006	54(1)	46.4(10)	64.1(12)	-0.6(9)	-5.5(10)	1.2(9)
C007	53.8(10)	48.4(10)	58.2(11)	-1.8(9)	0.9(10)	0.8(9)
C008	44.9(9)	50.7(10)	60.7(12)	-3.4(8)	-3.4(9)	4.5(9)
C009	46.6(9)	60.2(12)	54.1(11)	-3.3(9)	-0.4(9)	4.5(9)
COOA	46.7(9)	52.6(10)	63.6(12)	-0.8(9)	-0.3(9)	0.1(10)
C00B	49.7(10)	58.6(12)	60.3(12)	-1.2(10)	-8.2(10)	1.9(10)
COOC	54.5(11)	58.6(12)	66.0(13)	6.2(10)	-10.5(11)	1.4(10)
COOD	48.1(9)	45.1(9)	63.9(12)	-1.2(8)	-5.5(10)	7.2(9)
C00E	50.1(10)	50.9(11)	69.3(13)	-4.3(9)	-3.4(10)	3.5(10)
COOF	49.9(10)	57.1(11)	53.4(10)	3.1(9)	-4.2(9)	2.7(9)
COOG	59.5(11)	48.4(10)	66.7(13)	5.4(9)	-5.4(11)	-0.4(10)
COOH	50.3(10)	54.9(11)	72.1(13)	-3.9(9)	-3.9(11)	2.9(10)
C00I	55.3(11)	64.0(12)	67.2(13)	-2(1)	-1.2(11)	-3.4(11)
COOJ	60.4(12)	69.7(14)	65.1(14)	0.9(11)	-3.5(11)	-2.1(11)
COOK	61.0(12)	68.5(14)	59.8(13)	11.9(11)	-2.9(11)	-3.1(11)
COOL	64.7(14)	68.0(14)	99(2)	9.0(12)	-4.4(14)	13.1(15)
COOM	67.7(15)	73.0(15)	84.8(16)	-15.6(13)	-5.0(14)	-4.7(14)
COON	64.6(13)	79.4(15)	64.7(13)	2.7(12)	-5.8(12)	-9.2(12)
C00O	63.2(14)	72.7(16)	118(2)	8.8(13)	6.8(16)	-12.2(17)
COOP	90(2)	68.7(15)	90.4(19)	-6.3(15)	-24.4(17)	-9.3(14)
C00Q	92.3(19)	69.1(14)	66.7(14)	17.0(14)	-15.7(14)	-14.3(12)
COOR	73.3(16)	90.7(19)	99(2)	6.7(15)	7.1(17)	-34.0(17)
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COOS	106(2)	89(2)	139(3)	8(2)	-74(2)	-10(2)

Table 4: Bond Lengths for chiral 2j

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O001	C007	1.230(3)	C00A	C00J	1.380(3)
O002	C00D	1.420(3)	C00A	C00N	1.407(3)
O003	C00B	1.351(3)	C00B	COOC	1.400(3)
O003	COOS	1.422(3)	C00C	C00G	1.376(3)
C004	C005	1.395(3)	C00E	C00H	1.441(3)
C004	C006	1.380(3)	C00F	C00I	1.405(3)
C004	C00D	1.512(3)	C00F	C00K	1.389(3)
C005	C007	1.467(3)	C00I	C00M	1.381(3)
C005	C00G	1.389(3)	C00J	C00L	1.387(4)
C006	C00B	1.387(3)	C00K	C00Q	1.383(3)
C007	C008	1.483(3)	C00L	C00O	1.371(4)
C008	C00D	1.524(3)	C00M	C00P	1.377(4)
C008	C00E	1.342(3)	C00N	C00R	1.370(4)
C009	C00A	1.482(3)	C00O	COOR	1.361(4)
C009	COOF	1.481(3)	COOP	COOQ	1.371(5)
C009	C00H	1.351(3)			

Table 5: Bond Angles for chiral 2j

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
COOS	O003	C00B	119.1(2)	C00C	C00B	C006	120.5(2)
C006	C004	C005	120.44(18)	C00G	C00C	C00B	120.1(2)
COOD	C004	C005	111.76(17)	C004	C00D	O002	112.74(18)
C00D	C004	C006	127.78(18)	C008	C00D	O002	111.82(16)
C007	C005	C004	109.59(18)	C008	C00D	C004	102.56(15)
C00G	C005	C004	120.28(19)	C00H	C00E	C008	124.1(2)
C00G	C005	C007	130.11(19)	C00I	C00F	C009	118.5(2)
C00B	C006	C004	119.13(19)	C00K	C00F	C009	123.12(19)
C005	C007	O001	127.6(2)	C00K	C00F	C00I	118.4(2)
C008	C007	O001	125.51(19)	C00C	C00G	C005	119.47(19)
C008	C007	C005	106.87(17)	C00E	C00H	C009	127.5(2)
C00D	C008	C007	109.00(16)	C00M	C00I	C00F	120.7(2)
C00E	C008	C007	122.1(2)	C00L	C00J	C00A	120.8(2)
C00E	C008	C00D	128.80(19)	C00Q	C00K	C00F	120.0(2)
COOF	C009	C00A	116.80(17)	C00O	C00L	C00J	120.1(3)
C00H	C009	C00A	118.0(2)	C00P	C00M	C00I	120.0(3)
C00H	C009	C00F	125.1(2)	COOR	C00N	C00A	119.7(3)
COOJ	C00A	C009	121.5(2)	COOR	C00O	C00L	119.6(3)
COON	C00A	C009	120.2(2)	C00Q	C00P	C00M	119.9(3)
COON	C00A	COOJ	118.2(2)	COOP	C00Q	COOK	121.0(3)
C006	C00B	0003	115.7(2)	C00O	COOR	COON	121.5(3)

C00C C	C00B	O003	123.8(2)

Atom	x	У	Z	U(eq)
H002	-5770(20)	-5708(10)	-1810(20)	106.4(7)
H006	-3139(2)	-6038.4(16)	-1501.7(15)	65.8(6)
H00C	-1294(2)	-8676.0(17)	-1106.9(17)	71.6(6)
H00D	-4993(2)	-6307.3(15)	-3045.4(16)	62.8(6)
HOOE	-7359(2)	-8378.5(16)	-3588.6(16)	68.1(6)
H00G	-2832(2)	-9474.9(16)	-2017.5(16)	69.8(6)
H00H	-7711(2)	-6314.5(17)	-3230.7(17)	70.9(6)
HOOI	-11623(2)	-7649.9(18)	-3541.5(17)	74.6(7)
H00J	-10735(2)	-5985.8(19)	-4987.1(17)	78.1(7)
H00K	-8405(2)	-8323.9(18)	-5021.8(16)	75.7(7)
HOOL	-12022(3)	-4572(2)	-4810(2)	92.7(9)
H00M	-12647(3)	-9065(2)	-4104.5(19)	90.2(8)
HOON	-9656(3)	-5774(2)	-2330.0(18)	83.5(7)
H00O	-12155(3)	-3791(2)	-3396(2)	101.7(10)
HOOP	-11539(3)	-10128(2)	-5091(2)	99.8(10)
H00Q	-9439(3)	-9752(2)	-5546.1(19)	91.2(9)
HOOR	-10955(3)	-4382(2)	-2182(2)	105.2(10)
H00a	399(17)	-7550(20)	-648(3)	167(2)
H00b	240(20)	-6823(6)	194(17)	167(2)
H00f	-585(4)	-7811(16)	148(18)	167(2)

Table 6: Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for chiral 2j

Efforts to gain evidence for 1,4- vs 1,6-addition of phosphines

In an attempt to prove 1,4- vs 1,6-addition of phosphine, we planned to synthesize the substrate **1b**, where the two double bonds (of the dienone moiety) are disposed *E* and *Z*, Scheme 1. In case of a 1,4-addition of phosphine (path a), the stereochemical integrity of the *Z*-configured double bond should remain unchanged, leading to the formation of *E*,*Z*-2b. But in case of a 1,6-addition (path b), the stereochemical information at the *Z*-configured double bond (of **1b**) should be lost and thus should lead to a thermodynamically preferred *E*,*E*-2b, Scheme 1.



Scheme 1

Accordingly, we have designed a synthetic route to access the E,Z-1b as in Scheme 2. The required E,Z-aldehyde A was obtained from phenylpropargyl aldehyde A1 via Wittig-Horner reaction, hydrogenation of A2 using Lindlar's catalyst, DIBAL-H reduction of the ester A3, and IBX oxidation sequence.









Further, *n*-butyllithium mediated alkylation, IBX oxidation, and acetal deprotection furnished the desired dienone **D** in 1:4 E/Z ratio (Scheme 3). IMBH reaction of **D** under the optimized conditions generated the indanone **E**. However, at this stage we were unable to extract the stereochemical information across the double bonds (see the ¹H-NMR of **E**). Thus, the indanone **E** was oxidized using tetrapropylammonium perruthenate (TPAP) to indanedione **F**. ¹H-NMR of indanedione **F** clearly indicated the presence of *E*-configured double bond. The data of **F** was also verified with the literature report.³



³ F. J. Chang, R. Gurubrahamam and K. Chen, Adv. Synth. Catal., 2017, 359, 1277.

SpinWorks 4: bs-07-275-mix





SpinWorks 4: bs-07-284



PPM 8 6 4 2 0

SpinWorks 4: BS-07-296



SpinWorks 4: BS-07-296

				7,455	7.0430	7.3441	7.2831
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Reported ¹H NMR of Compound F (F. J. Chang, R. Gurubrahamam and K. Chen, *Adv. Synth. Catal.*, 2017, **359**, 1277)



We also have performed the reaction of the dienone **D** (E/Z = 1:4) with the chiral catalyst **9**. ¹H-NMR of the diketone **F** also indicated the exclusive formation of the *E*-isomer.



SpinWorks 4: bs-07-283











A parallel approach has also been considered for the stereoselective synthesis of the required starting material, the dienone **D** (Scheme 4). Towards this, the enynone **I** was synthesized by following a similar synthetic sequence described in Scheme 3. The dienone **D** was achieved via the selective hydrogenation of **I** using the Lindlar's catalyst. Reaction of **D** with trimethyl phosphine produced the indanone **E**, but the stereochemical information across the double bonds could not be extracted. As described earlier, the indanone **E** was oxidised to indanedione **F** and the ¹H-NMR spectrum indicated the formation of only the *E*-isomer of **F**. The data of **F** was also verified with the literature report.¹



SpinWorks 4: BS-07-300









SpinWorks 4: bs-07-300



SpinWorks 4: bs-07-302



SpinWorks 4: bs-07-306



Reported ¹H NMR of Compound F (F. J. Chang, R. Gurubrahamam and K. Chen, *Adv. Synth. Catal.*, 2017, **359**, 1277)



We also have performed the reaction of the dienone **D** (E/Z = 1:3) with the chiral catalyst **9**. ¹H-NMR of the diketone **F** also indicated the exclusive formation of the *E*-isomer.



SpinWorks 3: bs-07-312



SpinWorks 3: bs-07-315

8.0125 8.4450 8.4748 8.5136	7.8246 7.8311 7.9913 7.9987 8.0044	7.7177 7.8096 7.8150 7.8185	7.4649 7.6650 7.7089 7.7106	7.2831 7.3533 7.3921 7.4476 7.4516 7.4503
		<u></u>		





Expansion of the aromatic region of F (below):



Copies of ¹H and ¹³C-NMR spectra of all the new compounds reported in this study

(Note: In general, in a ¹H NMR spectrum recorded in CDCl₃, a peak at around δ 1.6 refers to moisture in the solvent/sample and a peak at about δ 1.2 refers to oil/grease present in the sample. In a ¹³C NMR spectrum recorded in CDCl₃, a peak at about δ 29.7 usually represents oil/grease)







SpinWorks 4: BS 06 270 PROTON CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 26





10.189



76.726 77.043 77.361

SpinWorks 4: BS 06 270 C13CPD256 CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 26

.91.218 .94.305	44433052220222 735553099988344 7355530963349368 109752092948 101220929418 682044





SpinWorks 4: BS 06 281 PROTON CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 45













SpinWorks 4: BS 06 502 PROTON DMSO /opt/topspin3.5pl2/nmrdata nmrsu 27









SpinWorks 4: BS 06 355 PROTON CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 46 SpinWorks 4: bs-06-217



SpinWorks 4: BS-06-218-Re



SpinWorks 4: BS 06 200 PROTON CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 47





-106.738

SpinWorks 4: BS 06 200 F19CPD CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 47



SpinWorks 4: BS 06 185 PROTON CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 24



SpinWorks 4: bs-06-186








SpinWorks 4: BS 06 610 PROTON CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 35

10.226













3.918 ----





SpinWorks 4: BS 06 615 PROTON DMSO /opt/topspin3.5pl2/nmrdata nmrsu 43



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SpinWorks 4: BS-06-523







SpinWorks 4: BS-06-522-re











26.2984

SpinWorks 4: BS 06 197 PROTON CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 48







 $1.8602 \\ 1.8759$

SpinWorks 4: bs-07-70















SpinWorks 4: bs-06-620







SpinWorks 4: BS-06-667







1.957



SpinWorks 4: BS 06 223 RE PROTON CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 55 10.656 ----6.386 6.403 77.466 77.550 7.909 7.909 7.909 7.909 7.909 7.917

8.778 8.786 8.794 8.802

4

 \vee

SpinWorks 4: BS 06 228 PROTON CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 55



SpinWorks 4: BS-07-18



SpinWorks 4: BS-07-20-Re











PPM



 $1.902 \\ 1.913$

SpinWorks 4: BS 07 113 PROTON CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 14 SpinWorks 4: bs 07 120







SpinWorks 4: BS-06-640













SpinWorks 4: BS-05-111 PROTON CDCI3 /opt/topspin nmrsu 21



1.9277 1.9404



10.5771 -----









2.4189

1.9542 1.9582 1.9657 1.9695 1.9830 1.9869





SpinWorks 4: BS-07-160



SpinWorks 4: BS-07-163-mix



SpinWorks 4: BS-07-35



SpinWorks 4: PBS-07-38-Re



SpinWorks 4: bs 07 f1 PROTON CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 41



SpinWorks 4: bs 07 140



SpinWorks 4: bs-07-143





SpinWorks 4: BS 07 143 F19CPD CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 27



HPLC Spectra



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