Supporting Information

for

Annulative Morita-Baylis-Hillman reaction to synthesise chiral dibenzocycloheptanes

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General experimental methods: All the reagents, solvents and catalysts employed in this study were procured from Sigma-Aldrich and were used without further purification. For thin-layer chromatography (TLC), silica aluminum foils with fluorescent indicator 254 nm (from Aldrich) were used and compounds were visualized 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 60-120 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 pellets, as indicated, with v_{max} in inverse centimeters. Melting points were recorded on a digital melting point apparatus Stuart SMP30. ¹H NMR and ¹³C NMR spectra were recorded on a 400 and 500 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 utilized 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 (δ 7.26 ppm) or in (CD₃)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 Xray analysis was carried on a Rigaku XtaLAB mini 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 protocol for the synthesis of 2-bromoenones (3)

All the 2-bromoenones were synthesized according to the reported literature.¹



Scheme 1S: Synthesis of the 2-bromoenones 3

General protocol for the synthesis of 2-formyl boronic acids (4)

All the 2-formyl boronic acids were synthesized according to the reported literature.²



Scheme 2S: Synthesis of the 2-formyl boronic acids 4

General procedure-1: Synthesis of racemic biaryl enone-aldehydes (1)

All the biaryl enone-aldehydes were synthesized according to the reported literature.³

¹ a) Patel, K.; Mishra, U. K.; Mukhopadhyay, D.; Ramasastry, S. S. V. *Chem. Asian J.* **2019**, *14*, 4568. b) Diemer, V.; Berthelot, A.; Bayardon, J.; Jugé, S.; Leroux, F. R.; Colobert, F. J. Org. Chem. **2012**, *77*, 14, 6117.

 ² a) Adamczyk-Woźniak, A. A.; Ejsmont, K.; Gierczyk, B.; Kaczorowska, E.; Matuszewska, A.; Schroeder, G.; Sporzyński, A.; Zarychta, B. J. Organomet. Chem. 2015, 788, 36. b) Tseng, N. -W.; Lautens, M. J. Org. Chem. 2009, 74, 1809.

³ a) Mondal, A.; Hazra, R.; Grover, J.; Raghu, M.; Ramasastry, S. S. V. *ACS Catal.* **2018**, *8*, 2748. b) Xia, Y.; Qu, P.; Liu, Z.; Ge, R.; Xiao, Q.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 2543.

Condition A: when, R³ = aryl, het-aryl, ^cPr



Scheme 3S: Synthesis of the biaryl-enone aldehydes 1

General procedure-2: Synthesis of axially chiral biaryl enone-aldehydes (+/-)-1

The chiral biaryl enone-aldehydes (+/-)-1 were prepared by following a four-step protocol, as depicted in Scheme 4S. Biaryl aldehydes $(\pm)-7$ can be easily synthesized by the Suzuki-Miyaura cross-coupling reaction between aryl boronic acids and 2-bromo aryl aldehydes by following the literature report.⁴ Palladium-catalyzed asymmetric C–H olefination of $(\pm)-7$ delivered chiral biaryl enone-ester aldehydes (+/-)-8.⁵ The reaction of (+/-)-8 with ethylene glycol in the presence of a catalytic amount of PTSA afforded (+/-)-9. The ozonolysis reaction of (+/-)-9 afforded chiral biaryl aldehydes (+/-)-10, which upon treatment with MeMgBr and subsequent IBX oxidation delivered corresponding ketones (+/-)-11. The aldol condensation reaction of (+/-)-11 with appropriate aldehydes under basic condition and PTSA-catalyzed deprotection of the acetal functional group successfully delivered the desired axially chiral biaryl enone-aldehydes (+/-)-1.

⁴ Mamane, V.; Louerat, F.; Mohamed, J. I.; Fort, A. Y. *Tetrahedron* **2008**, *64*, 10699.

⁵ Yao, Q. -J.; Zhang, S.; Zhan B. -B.; Shi, B. -F. Angew. Chem., Int. Ed. 2017, 56, 6617.



Scheme 4S: Synthesis of chiral biaryl-enone aldehydes (+/-)-1

Representative procedure for step-I (Scheme 4S): To an oven-dried 25 mL Schlenk tube, biaryl aldehyde (\pm)-7 (1.0 eq), *n*-butyl acrylate (3.0 eq), Pd(OAc)₂ (0.1 eq), *L*-tert-Leucine (0.2 eq), *p*-benzoquinone (0.1 eq), HFIP (0.8 mL) and AcOH (0.2 mL) were taken and the tube was purged with O₂ gas then the reaction mixture was stirred for 48 h at 60 °C until the aldehyde (\pm)-7 disappeared as monitored by TLC. The resulting reaction mixture was quenched with aq. NaHCO₃ (~2-3 mL), filtered through a celite pad and concentrated in *vacuo*. Then it was extracted using ethyl acetate (2x5 mL). The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The product was purified by neutral alumina column chromatography using hexane/ethyl acetate (50:1) as eluent to afford (+/–)-8 (yield 70-80%).

Representative procedure for step-II (Scheme 4S): A 25 mL oven-dried RB flask was charged with chiral biaryl ester aldehyde (+/–)-8, ethylene glycol (1.2 eq), 10 mL toluene and PTSA (0.03 eq). The reaction flask was connected to the Dean-Stark apparatus and heated at 150 °C until aldehyde (+/–)-8 disappeared as monitored by TLC. The reaction mixture was cooled to room temperature and carefully quenched with triethylamine. The reaction mixture was concentrated under reduced pressure and then subsequently extracted with EtOAc (2x5 mL). The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The product was purified by silica gel column chromatography using hexane/ethyl acetate (10:1) as eluent to afford (+/–)-9 (yield 90-92%).

Representative procedure for step-III (Scheme 4S): To an oven-dried 25 mL long neck RB flask, (+/-)-9 was dissolved in DCM. Then the reaction flask was kept at -78 °C and charged with O₃ for 2-5 minutes (6.0-8.0 g/min flow rate) until the reaction mixture turned pale-blue. The excess amount of O₃ was removed from reaction mixture by purging N₂ through the reaction mixture. Then, PPh₃ (1.5 eq) was added at the room temperature (rt) and stirred at rt for 12-15 h until the color of the reaction mixture became pale-yellow. The resulting reaction mixture was quenched by water (~5-6 mL), filtered through a celite pad and extracted using DCM (2x6 mL). The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The product was purified by silica gel column chromatography using hexane/ethyl acetate (10:1) as eluent to afford chiral biaryl aldehyde (+/-)-10 (yield 85-90%).

Representative procedure for step-IV (Scheme 4S): An oven-dried 25 mL RB flask was charged with chiral biaryl aldehyde (+/–)-10 in 10 mL dry THF and placed at 0 °C under N₂ atmosphere. The methyl magnesium chloride (3.0 M in THF, 1.2 eq) was added dropwise at the same temperature and stirred for 1 h. Upon completion, the reaction mixture was quenched with water (~2-3 mL) and extracted with ethyl acetate (2x5 mL). The organic extracts were combined and dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was taken to the next step without further purification.

The crude product was dissolved in ethyl acetate, and IBX (1.2 eq) was added. The suspension was stirred at reflux condition until the alcohol disappeared as monitored by TLC. The mixture was filtered through celite pad. The residue was washed with ethyl acetate (2x6 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (5:1) as eluent to afford chiral biaryl ketone (+/–)-**11** (yield 70-78%).

Representative procedure for step-V (Scheme 4S): The chiral biaryl ketone (+/-)-11 and the corresponding aldehyde (1.0 eq) was dissolved in MeOH and KOH (1.0 eq) was introduced at -10 °C. The reaction mixture was stirred at the same temperature until the reactant (+/-)-11 disappeared as monitored by TLC. The reaction mixture was quenched with saturated aqueous NH₄Cl (~2-3 mL) solution and extracted with ethyl acetate (2x5 mL). The organic extracts were

combined, dried over anhydrous sodium sulphate and concentrated. The crude product was taken to the next step without further purification.

The crude product was dissolved in acetone (5 mL), and a catalytic amount of PTSA was added at room temperature. After completion of the reaction (monitored by TLC), the reaction was quenched with aqueous NaHCO₃ (~2-3 mL), and acetone was removed under reduced pressure. The aqueous layer was extracted with ethyl acetate (2x5 mL). The combined organic extracts were dried over anhydrous sodium sulphate and concentrated. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (5:1) as eluent to afford (+/–)-1 (yield 88-90%).

General procedure-3: PBu₃-Catalyzed synthesis of racemic and chiral 2



Scheme 5S: Synthesis of dibenzocycloheptenones 2 and (+/-)-2

An oven-dried 5 mL glass vial was charged with the racemic or chiral **1** (0.1 mmol), DMF (1.0 mL), and tributylphosphine (0.02 mmol) at room temperature and stirred until **1** disappeared as monitored by TLC. Then the reaction mixture was quenched with water (\sim 1-2 mL) and extracted using ethyl acetate (2x3 mL). The organic extracts were combined and dried over anhydrous sodium sulfate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate as an eluent to afford **2** or (+/–)-**2**.

Chiral Catalyst Screening: An exhaustive chiral catalyst screening was performed on the biaryl enone aldehyde (\pm) -1d under a variety of conditions. Some of the results are presented in Figure 1S.



Figure 1S: List of chiral catalysts screened

General procedure-4: Synthesis of chiral dibenzocycloheptenones (+/-)-2 catalyzed by 6



Scheme 6S: Synthesis of chiral dibenzocycloheptenones (+/-)-2

An oven-dried 5 mL glass vial was charged with (\pm) -1 (0.1 mmol), and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP, 0.5 mL), water (0.5 mmol), and the catalyst **6** (0.02 mmol) were introduced. The reaction mixture was then stirred at 50 °C for 5 days. Volatiles were removed under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford (+/-)-2.

Scale-up batch:

A scale-up reaction was done with **1a** on 1.01 mmol scale as depicted in Scheme 7S. The respective product **2a** was obtained in 85% yield in 7 h.



General procedure-5: Determination of relative stereochemistry of (+/–)-2 (Table 3)

A synthetic elaboration was done to determine the relative stereochemistry of the MBH products. (–)-2n was subjected to hydrogenation using Crabtree's catalyst to obtain (–)-2n'. Then alkylation of (–)-2n' by methyl iodide, delivered (+)-2n", whose X-ray diffraction analysis confirmed the structure of (–)-2n, Scheme 8S. The relative stereochemistry of the other products was assigned in analogy.



Scheme 8S: Determination of the relative stereochemistry of (-)-2n.

Spectroscopic data of all the new compounds synthesized during this study

2'-Cinnamoyl-[1,1'-biphenyl]-2-carbaldehyde (1a).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow oil. $R_f = 0.5$ (hexane/EtOAc = 5/1). IR (thin film, neat): v_{max}/cm^{-1} 3060, 3027, 1694, 1667, 1597, 1208, 757. ¹H NMR (400 MHz, CDCl₃): δ 9.96 (s, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.78-7.76 (m, 1H), 7.60-7.55 (m, 3H), 7.49-7.42 (m, 2H), 7.38-7.31 (m, 7H), 6.78 (d, *J* = 15.9 Hz, 1H). ¹³C NMR (100 MHz,

CDCl₃): δ 194.69, 191.62, 145.4, 143.9, 140.0, 137.1, 134.2, 134.0, 133.4, 131.7, 131.1, 130.7, 130.5, 128.9 (2C), 128.6, 128.37 (2C), 128.32, 128.2, 128.1, 125.8. **HRMS (ESI)**: *m*/*z* calcd for C₂₂H₁₆O₂Na (M+Na)⁺: 335.1048. Found: 335.1055.

2'-(3-(Naphthalen-1-yl)acryloyl)-[1,1'-biphenyl]-2-carbaldehyde (1b).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow oil. $R_f = 0.6$ (hexane/EtOAc = 5/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3079, 3059, 3042, 1694, 1662, 1597, 1252, 756. ¹H NMR (400 MHz, CDCl₃): δ 9.99 (s, 1H), 8.30 (d, J = 15.6 Hz, 1H), 8.06-8.01 (m, 2H), 7.87 (t, J = 7.4 Hz, 3H), 7.66-7.50 (m, 6H), 7.47-7.38 (m, 4H), 6.89 (d, J = 15.6 Hz, 1H). ¹³C

NMR (**100 MHz**, **CDCl**₃): δ 194.1, 191.5, 144.0, 141.8, 140.1, 137.2, 134.1, 133.6, 133.4, 131.8, 131.7, 131.5, 131.2, 130.9, 130.6, 128.7 (2C), 128.3 (2C), 128.1 (2C), 127.0, 126.3, 125.3, 125.2, 123.2. **HRMS** (**ESI**): *m*/*z* calculated for C₂₆H₁₈O₂Na (M+Na)⁺: 385.1204. Found: 385.1226.

2'-(3-(*m*-Tolyl)acryloyl)-[1,1'-biphenyl]-2-carbaldehyde (1c).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow oil. $R_f = 0.5$ (hexane/EtOAc = 5/1). **IR** (thin film, neat): v_{max}/cm^{-1} 3059, 3023, 2982, 2922, 1694, 1644, 1598, 1239, 770. ¹H NMR (400 MHz, CDCl₃): δ 9.96 (s, 1H), 8.00 (d, J = 7.7 Hz, 1H), 7.77 (d, J = 7.1 Hz, 1H), 7.62-7.56 (m, 3H), 7.48 (t, J = 7.5 Hz, 1H), 7.39-7.32 (m, 3H), 7.25-7.17 (m, 4H), 6.78

(d, *J* = 15.9 Hz, 1H), 2.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 194.6, 191.5, 145.6, 143.9, 140.1, 138.5, 137.1, 134.2, 134.1, 133.3, 131.7, 131.5, 131.0, 130.4, 129.0, 128.7, 128.5, 128.28, 128.23, 128.0, 125.8, 125.5, 21.2. HRMS (ESI): *m*/*z* calculated for C₂₃H₁₈O₂Na (M+Na)⁺: 349.1204. Found: 349.1212.

2'-(3-(4-Methoxyphenyl)acryloyl)-[1,1'-biphenyl]-2-carbaldehyde (1d).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow oil. $R_f = 0.3$ (hexane/EtOAc = 4/1). IR (thin film, neat): v_{max}/cm^{-1} 3064, 3016, 2933, 1692, 1636, 1595, 1255, 757. ¹H NMR (400 MHz, CDCl₃): δ 9.95 (s, 1H), 7.99 (dd, J = 7.7 and 1.0 Hz, 1H), 7.75-7.73 (m, 1H), 7.59-7.54 (m, 3H), 7.46 (t, J = 7.5 Hz, 1H), 7.38-7.29 (m, 5H),

6.85 (d, J = 8.7 Hz, 2H), 6.65 (d, J = 15.8 Hz, 1H), 3.82 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 194.7, 191.6, 161.8, 145.3, 144.0, 140.3, 137.0, 134.0, 133.3, 131.7, 131.0, 130.2, 130.1 (2C), 128.5, 128.2 (2C), 127.9, 126.9, 123.8, 114.3 (2C), 55.4. HRMS (ESI): m/z calculated for C₂₃H₁₉O₃ (M+H)⁺: 343.1334. Found: 343.1341.

2'-(3-(3-Fluorophenyl)acryloyl)-[1,1'-biphenyl]-2-carbaldehyde (1e).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow oil. $R_f = 0.4$ (hexane/EtOAc = 5/1). **IR** (thin film, neat): v_{max}/cm^{-1} 2925, 2855, 1697, 1657, 1596, 1079, 756. ¹H NMR (400 MHz, CDCl₃): δ 9.91 (s, 1H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.62-7.54 (m, 3H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.38-7.28 (m, 4H), 7.10-6.98 (m, 3H), 6.72 (d, *J* =

15.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 194.1, 191.5, 162.9 (d, J = 245.6 Hz, 1C), 143.7, 143.5 (d, J = 2.4 Hz, 1C), 139.7, 137.3, 136.6 (d, J = 7.7 Hz, 1C), 134.1, 133.4, 131.7, 131.0, 130.7, 130.4, 130.3 (d, J = 8.1 Hz, 1C), 128.6, 128.4, 128.3 (d, J = 2.6 Hz, 1C), 126.8, 124.3 (d, J = 2.7 Hz, 1C), 117.4 (d, J = 21.2 Hz, 1C), 114.3 (d, J = 21.7 Hz, 1C). ¹⁹F NMR (376.4 MHz, CDCl₃): δ –112.3. HRMS (ESI): m/z calculated for C₂₂H₁₆O₂F (M+H)⁺: 331.1134 Found: 331.1148.

2'-Cinnamoyl-4',5'-dimethoxy-[1,1'-biphenyl]-2-carbaldehyde (1f).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow oil. $R_f = 0.3$ (hexane/EtOAc = 3/1). IR (thin film, neat): $v_{max}/cm^{-1} 3061$, 3001, 2970, 2933, 1693, 1658, 1596, 1232, 773. ¹H NMR (400 MHz, CDCl₃): δ 9.98 (s, 1H), 8.00 (d, J = 7.7 Hz, 1H), 7.60 (t, J = 7.4 Hz, 1H), 7.50-7.44 (m, 2H), 7.40-7.34 (m, 3H), 7.32-7.30 (m, 2H), 7.23-7.22 (m, 2H), 6.82 (s, 1H), 6.61 (d, J = 15.7 Hz, 1H), 4.02 (s, 3H), 3.96 (s, 3H). ¹³C NMR (100

MHz, **CDCl**₃): δ 192.6, 191.5, 150.8, 148.7, 144.2, 143.7, 134.5, 134.3, 133.5, 132.8, 131.4, 130.9, 130.4, 128.7 (2C), 128.3, 128.2 (2C), 128.0, 125.6, 114.1, 111.9, 56.2 (2C). **HRMS (ESI)**: *m/z* calculated for C₂₄H₂₀O₄Na (M+Na)⁺: 395.1259. Found: 395.1274.

4',5'-Dimethoxy-2'-(3-(naphthalen-1-yl)acryloyl)-[1,1'-biphenyl]-2-carbaldehyde (1g).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow oil. $R_f = 0.3$ (hexane/EtOAc = 3/1). IR (thin film, neat): v_{max}/cm^{-1} 3004, 2962, 2940, 2849, 1694, 1652, 1597, 1572, 1351, 1235, 1022, 732. ¹H NMR (400 MHz, CDCl₃): δ 10.01 (s, 1H), 8.31 (d, J = 15.5 Hz, 1H), 8.06-8.02 (m, 2H), 7.86-7.84 (m, 2H), 7.63 (td, J = 7.4 and 1.2 Hz, 1H), 7.56-7.50 (m, 3H), 7.46 (s, 1H), 7.42 (d, J = 7.5 Hz, 1H), 7.37 (t, J = 7.6

Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 6.84 (s, 1H), 6.72 (d, *J* = 15.4 Hz, 1H), 4.04 (s, 3H), 3.97 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 192.3, 191.5, 150.9, 148.7, 144.3, 140.4, 134.4, 133.6 (2C), 132.9, 131.8, 131.5 (2C), 131.1, 130.7, 128.7, 128.3, 128.0 (2C), 126.9, 126.2, 125.2, 125.0, 123.3, 114.2, 111.9, 56.28, 56.27. HRMS (ESI): *m*/*z* calcd for C₂₈H₂₂O₄Na (M+Na)⁺: 445.1416. Found: 445.1398.

4',5'-Dimethoxy-2'-(3-(p-tolyl)acryloyl)-[1,1'-biphenyl]-2-carbaldehyde (1h).



This compound was prepared by following the general procedure-1 (condition A) and isolated as pale-yellow oil. $R_f = 0.3$ (hexane/EtOAc = 3/1). **IR (thin film, neat):** $v_{max}/cm^{-1} 3004$, 2970, 2940, 2852, 1693, 1658, 1597, 1567, 1390, 1235, 1022, 814, 733. ¹H NMR (400 MHz, CDCl₃): δ 9.98 (s, 1H), 7.99 (d,

J = 7.7 Hz, 1H), 7.59 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.41-7.35 (m, 3H), 7.14-7.09 (m, 4H), 6.82 (s, 1H), 6.56 (d, J = 15.7 Hz, 1H), 4.02 (s, 3H), 3.95 (s, 3H), 2.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 192.7, 191.5, 150.7, 148.7, 144.3, 143.9, 141.0, 134.3, 133.4, 132.9, 131.7, 131.3, 130.8, 129.5 (2C), 128.3, 128.2 (2C), 127.9, 124.7, 114.1, 111.8, 56.2 (2C), 21.4. HRMS (ESI): m/z calcd for C₂₅H₂₂O₄Na (M+Na)⁺: 409.1416. Found: 409.1444.

4',5'-Dimethoxy-2'-(3-(thiophen-2-yl)acryloyl)-[1,1'-biphenyl]-2-carbaldehyde (1i).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow oil. $R_f = 0.4$ (hexane/EtOAc = 3/1). IR (thin film, neat): v_{max}/cm^{-1} 3012, 2962, 2936, 2845, 1693, 1651, 1596, 1515, 1391, 1235, 1021, 776. ¹H NMR (400 MHz, CDCl₃): δ 8.01 (d, J = 7.8 Hz, 1H), 7.61 (td, J = 7.5 and 1.1 Hz, 2H), 7.54 (d, J = 15.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.38-7.35 (m, 2H), 7.31-7.28 (m, 1H), 7.11(d, J = 3.4 Hz, 1H), 7.00-6.97 (m, 1H),

6.81 (s, 1H), 6.37 (d, *J* = 15.4 Hz, 1H), 4.02 (s, 3H), 3.95 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 191.8, 191.5, 150.8, 148.7, 144.1, 140.0, 135.8, 134.3, 133.5, 132.8, 131.7, 131.3, 131.0, 128.8, 128.4, 128.2, 128.0, 124.5, 114.1, 111.8, 56.2 (2C). HRMS (ESI): *m*/*z* calcd for C₂₂H₁₈O₄SNa (M+Na)⁺: 401.0823. Found: 401.0817.

2'-(3-(3-Fluorophenyl)acryloyl)-4',5'-dimethoxy-[1,1'-biphenyl]-2-carbaldehyde (1j).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow oil. $R_f = 0.4$ (hexane/EtOAc = 3/1). **IR** (thin film, neat): v_{max} /cm⁻¹ 3061, 3004, 2970, 2940, 1693, 1661, 1596, 1516, 1267, 1021, 733. ¹H NMR (400 MHz, CDCl₃): δ 9.93 (s, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.39 (s, 2H), 7.35 (d, *J* = 15.2 Hz, 1H), 7.27-7.22 (m,

1H), 7.03-6.97 (m, 2H), 6.84-6.82 (m, 2H), 6.54 (d, J = 15.7 Hz, 1H), 4.01 (s, 3H), 3.95 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 192.0, 191.4, 162.8 (d, J = 245.4 Hz, 1C), 151.0, 148.8, 144.1, 141.9 (d, J = 2.4 Hz, 1C), 136.8 (d, J = 7.5 Hz, 1C), 134.4, 133.6, 132.5, 131.3, 131.1, 130.3 (d, J = 8.2 Hz, 1C), 128.5, 128.1, 126.6, 124.3 (d, J = 2.7 Hz, 1C), 117.2 (d, J = 21.2 Hz, 1C), 114.2, 114.0, 111.8, 56.2 (2C). ¹⁹F NMR (376.4 MHz, CDCl₃): δ –112.5. HRMS (ESI): m/z calcd for C₂₄H₁₉FO₄Na (M+Na)⁺: 413.1165. Found: 413.1146.

4',5'-Dimethoxy-2'-(3-(4-methoxyphenyl)acryloyl)-[1,1'-biphenyl]-2-carbaldehyde (1k).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow oil. $R_f = 0.3$ (hexane/EtOAc = 3/1). IR (thin film, neat): v_{max}/cm^{-1} 2936, 2846, 1692, 1595, 1570, 1350, 1152, 1023, 770. ¹H NMR (500 MHz, CDCl₃): δ 9.93 (s, 1H), 7.94 (d, J = 7.7 Hz, 1H), 7.54 (td, J = 7.5 and 1.2 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.35-7.32 (m, 3H), 7.15-7.13 (m, 2H), 6.78-6.76 (m, 3H), 6.44 (d, J = 15.7 Hz, 1H), 3.97

(s, 3H), 3.90 (s, 3H), 3.78 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 192.7, 191.6, 161.5, 150.6, 148.7, 144.3, 143.7, 134.3, 133.4, 133.1, 131.3, 130.7, 129.9 (2C), 128.2, 127.8, 127.1, 123.5, 114.2 (2C), 114.1, 111.8, 56.2 (2C), 55.3. HRMS (ESI): *m*/*z* calcd for C₂₅H₂₃O₅ (M+H)⁺: 403.1545. Found: 403.1564.

2-(2-Cinnamoylnaphthalen-1-yl)benzaldehyde (11).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow oil. $R_f = 0.5$ (hexane/EtOAc = 5/1). IR (thin film, neat): v_{max}/cm^{-1} 3061, 3023, 1701, 1642, 1596, 1217, 766. ¹H NMR (400 MHz, CDCl₃): δ 9.67 (s, 1H), 8.07 (d, J = 7.7 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.64-7.51 (m, 3H), 7.47-7.38 (m, 2H), 7.36-7.33

(m, 7H), 6.78 (d, *J* = 16.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 195.7, 191.4, 145.7, 141.1, 137.6, 135.4, 134.6, 134.2, 133.9, 133.6, 132.9, 131.8, 130.7, 128.9 (2C), 128.78, 128.73, 128.4 (2C), 128.3, 127.7, 127.56, 127.54, 126.8, 126.4, 124.3. HRMS (ESI): *m*/*z* calculated for C₂₆H₁₉O₂ (M+H)⁺: 363.1385. Found: 363.1398.

(Ra)-2-(2-Cinnamoylnaphthalen-1-yl)benzaldehyde (-)-11.



This compound was prepared by following the general procedure-2 and isolated as pale-yellow oil. **Optical rotation:** $[\alpha]_D^{25} - 31.0$ (*c* 0.13, CHCl₃) for a sample with *ee* 97%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak OD-H Column (90:10 *n*-Hexane/2-Propanol, 0.8 mL/min, 254 nm, $\tau_{major} = 23.6 \text{ min}, \tau_{minor} = 21.5 \text{ min}$).

2-(2-(3-(Naphthalen-1-yl)acryloyl)naphthalen-1-yl)benzaldehyde (1m).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow oil. $R_f = 0.5$ (hexane/EtOAc = 5/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3066, 2852, 1659, 1649, 1596, 1348, 1198, 797, 764. ¹H NMR (400 MHz, CDCl₃): δ 9.69 (s, 1H), 8.24 (d, J = 15.7 Hz, 1H), 8.00 (dd, J = 7.6 and 0.9 Hz, 1H), 8.06 (d, J = 8.5 Hz, 1H), 7.99-7.96 (m, 2H), 7.87-7.82 (m, 3H), 7.66-7.60 (m,

1H), 7.59-7.52 (m, 2H), 7.51-7.47 (m, 3H), 7.46-7.37 (m, 4H), 6.90 (d, J = 15.7 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 195.2, 191.4, 142.2, 141.2, 137.7, 135.5, 134.8, 134.0, 133.69, 133.67, 132.9, 131.9, 131.59, 131.53, 131.0, 128.8 (3C), 128.6, 128.3, 127.8, 127.6, 127.5, 127.0, 126.9, 126.3, 125.3, 125.2, 124.4, 123.2. HRMS (ESI): m/z calculated for C₃₀H₂₀O₂Na (M+Na)⁺: 435.1361. Found: 435.1371.

(Ra)-2-(2-(3-(Naphthalen-1-yl)acryloyl)naphthalen-1-yl)benzaldehyde ((-)-1m).



This compound was prepared by following the general procedure-2 and isolated as pale-yellow oil. **Optical rotation:** $[\alpha]_D^{25}$ –52.0 (*c* 0.27, CHCl₃) for a sample with *ee* 99%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak OD-H Column (90:10 *n*-Hexane/2-Propanol, 0.8 mL/min, 348 nm, $\tau_{major} = 32.9$ min, $\tau_{minor} = 28.6$ min).

2-(2-(3-(*p*-Tolyl)acryloyl)naphthalen-1-yl)benzaldehyde (1n).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow oil. $R_f = 0.5$ (hexane/EtOAc = 5/1). IR (thin film, neat): v_{max}/cm^{-1} 3027, 2923, 2848, 1694, 1644, 1596, 1568, 1337, 1051, 753. ¹H NMR (400 MHz, CDCl₃): δ 9.67 (s, 1H), 8.08-8.01 (m, 2H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.62-7.53 (m, 3H), 7.46-7.38 (m, 2H), 7.34-7.29

(m, 2H), 7.26-7.24 (m, 2H), 7.14-7.12 (m, 2H), 6.74 (d, J = 16.0 Hz, 1H), 2.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 195.7, 191.4, 145.9, 141.3, 141.2, 137.8, 135.4, 134.4, 133.9, 133.6, 132.9, 131.8, 131.5, 129.6 (2C), 128.7, 128.6, 128.4 (2C), 128.3, 127.7, 127.5, 127.4, 126.8, 125.5, 124.4, 21.5. HRMS (ESI): m/z calcd for C₂₇H₂₀O₂Na (M+Na)⁺: 399.1361. Found: 399.1351.

(*Ra*)-2-(2-(3-(*p*-Tolyl)acryloyl)naphthalen-1-yl)benzaldehyde ((–)-1n).



This compound was prepared by following the general procedure-2 and isolated as pale-yellow oil. **Optical rotation:** $[\alpha]_D^{25}$ –41.8 (*c* 0.27, CHCl₃) for a sample with *ee* 96%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak OD-H Column (94:6 *n*-Hexane/2-Propanol, 0.5 mL/min, 219 nm, $\tau_{major} = 43.1 \text{ min}, \tau_{minor} = 37.9 \text{ min}$).

2-(2-(3-(4-Methoxyphenyl)acryloyl)naphthalen-1-yl)benzaldehyde (10).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow viscous oil. $R_f = 0.3$ (hexane/EtOAc = 4/1). IR (thin film, neat): v_{max}/cm^{-1} 3008, 2966, 2936, 2841, 1694, 1634, 1597, 1572, 1337, 1251, 1028, 735. ¹H NMR (400 MHz, CDCl₃): δ 9.69 (s, 1H), 8.09 (d, J = 7.8 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H),

7.76 (d, J = 8.4 Hz, 1H), 7.67-7.54 (m, 3H), 7.47 (t, J = 8.1 Hz, 1H), 7.42-7.28 (m, 5H), 6.87 (d, J = 8.3 Hz, 2H), 6.69 (d, J = 15.9 Hz, 1H), 3.84 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 195.7, 191.5, 161.8, 145.7, 141.2, 137.9, 135.3, 134.3, 133.8, 133.6, 132.9, 131.8, 130.2 (2C), 128.68, 128.65, 128.3, 127.6, 127.4, 127.3, 136.9, 126.8, 124.4, 124.3, 114.4 (2C), 55.4. HRMS (ESI): m/z calcd for C₂₇H₂₀O₃Na (M+Na)⁺: 415.1310. Found: 415.1295.

(*Ra*)-2-(2-(3-(4-Methoxyphenyl)acryloyl)naphthalen-1-yl)benzaldehyde ((–)-10).



This compound was prepared by following the general procedure-2 and isolated as pale-yellow oil. **Optical rotation:** $[\alpha]_D^{25}$ –49.1 (*c* 0.37, CHCl₃) for a sample with *ee* 95%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak OD-H Column (90:10 *n*-Hexane/2-Propanol, 0.8 mL/min, 219 nm, $\tau_{major} = 32.8$ min,

 $\tau_{\text{minor}} = 28.2 \text{ min}$).

2-(2-(3-(Thiophen-2-yl)acryloyl)naphthalen-1-yl)benzaldehyde (1p).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow solid. $R_f = 0.5$ (hexane/EtOAc = 5/1). M.P. = 197-199 °C. **IR (thin film, neat):** v_{max}/cm^{-1} 3060, 2925, 2850, 2749, 1697, 1651, 1594, 1583, 1270, 1073, 732. ¹H NMR (400 MHz, CDCl₃): δ 9.69 (s, 1H), 8.11 (d, J = 7.7 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.67 (t, J = 7.4

Hz, 1H), 7.62-7.56 (m, 2H), 7.52-7.46 (m, 2H), 7.42-7.35 (m, 3H), 7.17 (d, J = 3.0 Hz, 1H), 7.03 (t, J = 4.8 Hz, 1H), 6.60 (d, J = 15.6 Hz, 1H). ¹³**C** NMR (100 MHz, CDCl₃): δ 194.8, 191.4, 141.1, 139.7, 137.68, 137.62, 135.4, 134.6, 134.0, 133.7, 132.9, 132.1, 131.8, 129.3, 128.8, 128.7, 128.34, 128.30, 127.8, 127.5 (2C), 126.8, 125.1, 124.4. HRMS (ESI): m/z calcd for C₂₄H₁₆O₂SNa (M+Na)⁺: 391.0768. Found: 391.0770.

(Ra)-2-(2-(3-(Thiophen-2-yl)acryloyl)naphthalen-1-yl)benzaldehyde ((-)-1p).



This compound was prepared by following the general procedure-2 and isolated as pale-yellow semi-solid. **Optical rotation:** $[\alpha]_D^{25}$ -60.4 (*c* 0.27, CHCl₃) for a sample with *ee* 96%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak OD-H Column (90:10 *n*-Hexane/2-Propanol, 0.8 mL/min, 254 nm, $\tau_{major} = 24.1 \text{ min}, \tau_{minor} = 22.0 \text{ min}$).

2-(2-(3-(3-Fluorophenyl)acryloyl)naphthalen-1-yl)benzaldehyde (1q).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow semi-solid. $R_f = 0.5$ (hexane/EtOAc = 5/1). IR (thin film, neat): v_{max}/cm^{-1} 3065, 2955, 2928, 2852, 1697, 1650, 1598, 1582, 1242, 971, 765. ¹H NMR (400 MHz, CDCl₃): δ 9.69 (s, 1H), 8.10 (dd, J = 7.7 and 0.9 Hz, 1H), 8.06 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 8.5 Hz, 1H), 7.67 (td, J = 7.5

and 1.2 Hz, 1H), 7.64-7.56 (m, 2H), 7.48 (td, J = 7.0 and 1.0 Hz, 1H), 7.42 (d, J = 8.5 Hz, 1H), 6.78 (d, J = 16.6 Hz, 1H), 7.37 (d, J = 7.4 Hz, 1H), 7.34-7.29 (m, 2H), 7.14 (d, J = 7.6 Hz, 1H), 7.09-7.04 (m, 2H), 6.78 (d, J = 15.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 195.1, 191.3, 162.9 (d, J = 245.5 Hz, 1C), 143.8, 141.0, 137.3, 136 (d, J = 7.6 Hz, 1C), 135.4, 134.8, 134.0, 133.6, 132.8, 131.9, 130.4 (d, J = 8.1 Hz, 1C), 128.8 (d, J = 4.9 Hz, 2C), 128.3, 127.9, 127.5 (d, J = 6.4 Hz, 1C), 127.3, 126.9, 124.4 (d, J = 2.6 Hz, 1C), 124.3 (2C), 117.5 (d, J = 21.2 Hz, 1C), 114.4 (d, J = 21.8 Hz, 1C). ¹⁹F NMR (376.4 MHz, CDCl₃): δ -112.3. HRMS (ESI): m/z calcd for C₂₆H₁₇FO₂Na (M+Na)⁺: 403.1110. Found: 403.1127.

(*Ra*)-2-(2-(3-(3-Fluorophenyl)acryloyl)naphthalen-1-yl)benzaldehyde ((–)-1q).



This compound was prepared by following the general procedure-2 and isolated as pale-yellow oil. **Optical rotation:** $[\alpha]_D^{25}$ -85.4 (*c* 0.05, CH₂Cl₂) for a sample with *ee* 96%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak OD-H Column (90:10 *n*-Hexane/2-Propanol, 1.0 mL/min, 220 nm, $\tau_{major} = 18.5$ min, $\tau_{minor} = 16.8$ min).

2-(2-(3-(2-Bromophenyl)acryloyl)naphthalen-1-yl)benzaldehyde (1r).

This compound was prepared by following the general procedure-2 (by using DL-tert-leucine as



catalyst) and isolated as pale-yellow oil. $R_f = 0.6$ (hexane/EtOAc = 5/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3056, 2934, 1697, 1657, 1602, 1467, 1267, 738. ¹H NMR (400 MHz, CDCl₃): δ 9.65 (s, 1H), 8.09 (d, *J* = 7.7 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.77-7.70 (m, 2H), 7.64-7.54 (m, 4H), 7.45 (t, *J* =

8.1 Hz, 1H), 7.40-7.35 (m, 3H), 7.28-7.24 (m, 1H), 7.19 (t, J = 8.1 Hz, 1H), 6.71 (d, J = 16.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 195.4, 191.4, 144.0, 141.1, 137.3, 135.4, 134.7, 134.3, 134.0, 133.6, 133.4, 132.9, 131.9, 131.5, 129.0, 128.78, 128.71, 128.3, 127.7, 127.70, 127.6, 127.5 (2C), 126.9, 125.8, 124.4. HRMS (ESI): m/z calculated for C₂₆H₁₇BrO₂Na (M+Na)⁺: 463.0310. Found: 463.0317.

(*Ra*)-2-(2-(3-(2-Bromophenyl)acryloyl)naphthalen-1-yl)benzaldehyde ((–)-1r).



This compound was prepared by following the general procedure-2 and isolated as pale-yellow oil. **Optical rotation:** $[\alpha]_D^{25} - 31.0$ (*c* 0.09, CHCl₃) for a sample with *ee* 98%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak IA Column (90:10 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major}

 $= 15.1 \text{ min}, \tau_{\text{minor}} = 12.9 \text{ min}).$

2-(2-(3-Cyclopropylacryloyl)naphthalen-1-yl)benzaldehyde (1s).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow oil. $R_f = 0.4$ (hexane/EtOAc = 10/1). **IR (thin film, neat):** v_{max}/cm^{-1} 2956, 2924, 1695, 1642, 1596, 1377, 1195, 762. **¹H NMR (400 MHz, CDCl₃):** δ 9.58 (s, 1H), 8.08 (dd, *J* = 7.6 and 1.3 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.67-7.61 (m, 2H), 7.59-7.53 (m, 2H), 7.45-7.40 (m, 1H), 7.36-7.34 (m, m)

1H), 7.29 (dd, *J* = 7.5 and 1.0 Hz, 1H), 6.27 (d, *J* = 15.4 Hz, 1H), 6.11-6.04 (m, 1H), 1.48-1.42 (m, 1H), 0.94-0.90 (m, 2H), 0.54-0.50 (m, 2H). ¹³**C NMR (100 MHz, CDCl₃):** δ 195.3, 191.5, 157.1, 141.3, 137.7, 135.2, 134.0, 133.7, 133.5, 132.9, 131.9, 128.59, 128.52, 128.2, 127.7, 127.47, 127.43, 127.2, 126.7, 124.2, 15.1, 9.57, 9.53. **HRMS (ESI):** *m*/*z* calculated for C₂₃H₁₉O₂ (M+H)⁺: 327.1385. Found: 327.1383.

2'-Cinnamoyl-6'-methyl-[1,1'-biphenyl]-2-carbaldehyde (1t).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow semi-solid. $R_f = 0.6$ (hexane/EtOAc = 5/1). **IR** (thin film, neat): v_{max}/cm^{-1} 3064, 3034, 2971, 1694, 1644, 1596, 1229, 763. ¹H NMR (400 MHz, CDCl₃): δ 9.84 (s, 1H), 8.00 (d, J = 7.7 Hz, 1H), 7.59-7.52 (m, 2H), 7.48-7.44 (m, 3H), 7.42-7.40 (m, 2H), 7.37-7.33 (m, 4H), 7.21 (d, J = 7.6 Hz, 1H), 6.81 (d, J =

16.0 Hz, 1H), 2.08 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 195.5, 191.8, 145.7, 142.5, 140.1, 137.6, 136.3, 134.36, 134.31, 133.7, 132.2, 130.74, 130.72, 128.9 (2C), 128.4 (2C), 128.2, 127.99, 127.92, 126.3, 125.6, 20.6. HRMS (ESI): *m*/*z* calculated for C₂₃H₁₈O₂Na (M+Na)⁺: 349.1204. Found: 349.1213.

(*Ra*)-2'-Cinnamoyl-6'-methyl-[1,1'-biphenyl]-2-carbaldehyde ((–)-1t).



This compound was prepared by following the general procedure-2 and isolated as pale-yellow semi-solid. **Optical rotation:** $[\alpha]_D^{25}$ -69.0 (*c* 0.09, CH₂Cl₂) for a sample with *ee* 88%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak IA Column (95:5 *n*-Hexane/2-Propanol, 1.0 mL/min, 295 nm, $\tau_{major} = 20.9$ min, $\tau_{minor} = 18.3$ min).

2'-Methyl-6'-(3-(p-tolyl)acryloyl)-[1,1'-biphenyl]-2-carbaldehyde (1u).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow oil. $R_f = 0.5$ (hexane/EtOAc = 5/1). IR (thin film, neat): v_{max}/cm^{-1} 2956, 2855, 1694, 1648, 1596, 1452, 987, 758. ¹H NMR (400 MHz, CDCl₃): δ 9.80 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.54 (td, *J* = 7.4 and 0.8 Hz, 1H), 7.49-7.47 (m, 1H), 7.45-7.41 (m, 3H), 7.30-7.27 (m, 3H), 7.17 (d,

J = 7.5 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 6.72 (d, J = 16.0 Hz, 1H), 2.34 (s, 3H), 2.05 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 195.6, 191.8, 145.9, 142.6, 141.3, 140.3, 137.6, 136.2, 134.3, 133.7, 132.0, 131.5, 130.7, 129.6 (2C), 128.4 (2C), 128.2, 127.9, 127.8, 125.54, 125.53, 21.5, 20.6. HRMS (ESI): m/z calculated for C₂₄H₂₁O₂ (M+H)⁺: 341.1542. Found: 341.1557.

(*Ra*)-2'-Methyl-6'-(3-(*p*-tolyl)acryloyl)-[1,1'-biphenyl]-2-carbaldehyde ((–)-1u).



This compound was prepared by following the general procedure-2 and isolated as pale-yellow oil. **Optical rotation:** $[\alpha]_D^{25}$ –115.2 (*c* 0.11, CH₂Cl₂) for a sample with *ee* 92%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak IA Column (95:5 *n*-Hexane/2-Propanol, 1.0 mL/min, 302 nm, $\tau_{major} = 21.9$ min,

 $\tau_{\text{minor}} = 17.9 \text{ min}$).

2'-(3-(4-Methoxyphenyl)acryloyl)-6'-methyl-[1,1'-biphenyl]-2-carbaldehyde (1v).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow oil. $R_f = 0.5$ (hexane/EtOAc = 5/1). **IR** (thin film, neat): v_{max}/cm^{-1} 2956, 2843, 1694, 1596, 1570, 1254, 829, 759. ¹H NMR (400 MHz, CDCl₃): δ 9.80 (s, 1H), 7.96 (dd, J = 7.7 and 0.9 Hz, 1H), 7.55 (td, J = 7.4 and 1.2 Hz, 1H), 7.49-7.46 (m, 1H), 7.43-7.42 (m, 3H),

7.34 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 16.0 Hz, 1H), 7.18 (d, J = 7.4 Hz, 1H), 6.85 (d, J = 8.7 Hz, 2H), 6.64 (d, J = 15.9 Hz, 1H), 3.82 (s, 3H), 2.05 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 195.6, 191.8, 161.7, 145.7, 142.6, 140.4, 137.5, 136.1, 134.3, 133.7, 131.9, 130.7, 130.1 (2C), 128.1, 127.9, 127.8, 127.0, 125.4, 124.3, 114.3 (2C), 55.4, 20.6. HRMS (ESI): m/z calculated for C₂₄H₂₀O₃Na (M+Na)⁺: 379.1310. Found: 379.1295.

(*Ra*)-2'-(3-(4-Methoxyphenyl)acryloyl)-6'-methyl-[1,1'-biphenyl]-2-carbaldehyde ((–)-1v).



This compound was prepared by following the general procedure-2 and isolated as pale-yellow oil. **Optical rotation:** $[\alpha]_D^{25} -113.8$ (*c* 0.07, CH₂Cl₂) for a sample with *ee* 92%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak IA Column (95:5 *n*-Hexane/2-Propanol, 1.0 mL/min, 328 nm, $\tau_{major} = 36.9$ min,

 $\tau_{\text{minor}} = 29.9 \text{ min}$).

Methyl-4-(2-formylnaphthalen-1-yl)-3-(3-(p-tolyl)acryloyl)benzoate (1w).

This compound was prepared by following the general procedure-2 (by using DL-tert-leucine as



catalyst) and isolated as pale-yellow oil. $R_f = 0.5$ (hexane/EtOAc = 5/1). **IR (thin film, neat):** v_{max}/cm^{-1} 2956, 2923, 1726, 1693, 1596, 1437, 1298, 976, 766. ¹H NMR (400 MHz, CDCl₃): δ 9.86 (s, 1H), 8.53 (d, J = 1.32 Hz, 1H), 8.32 (dd, J = 7.9 and 1.5 Hz, 1H), 8.03 (d, J = 8.6 Hz, 1H), 7.92-7.88 (m, 2H), 7.59-7.53 (m, 2H), 7.48-7.45 (m, 2H), 7.30 (d, J

= 15.8 Hz, 1H), 7.08 (s, 4H), 6.72 (d, J = 15.8 Hz, 1H), 4.02 (s, 3H), 2.32 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 192.3, 191.4, 166.0, 145.9, 143.2, 141.5, 141.4, 139.5, 135.9, 132.6, 131.9, 131.34, 131.30 (2C), 130.6, 129.5 (2C), 129.54, 129.1, 128.8, 128.5, 128.4 (2C), 127.3, 126.9, 123.3, 122.4, 52.6, 21.5. HRMS (ESI): m/z calculated for C₂₉H₂₃O₄ (M+H)⁺: 435.1596. Found: 435.1589.

2'-(Hex-2-enoyl)-[1,1'-biphenyl]-2-carbaldehyde (1x).

This compound was prepared by following the general procedure-1 (condition B) and isolated as



pale-yellow oil. $R_f = 0.7$ (hexane/EtOAc = 10/1). **IR (thin film, neat):** v_{max}/cm^{-1} 2872, 1694, 1652, 1619, 1293, 981, 757. ¹**H NMR (400 MHz, CDCl_3):** δ 9.87 (s, 1H), 7.98 (dd, *J* = 7.6 and 0.7 Hz, 1H), 7.61 (dd, *J* = 7.0 and 1.3 Hz, 1H), 7.58-7.45 (m, 4H), 7.31 (dd, *J* = 7.6 and 1.6 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 6.64-

6.57 (m, 1H), 6.11 (d, J = 15.7 Hz, 1H), 2.06-2.00 (m, 2H), 1.35-1.25 (m, 2H), 0.80 (t, J = 7.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 195.4, 191.5, 151.2, 144.0, 140.0, 136.7, 133.9, 133.3, 131.6, 131.0, 130.2, 130.1, 128.4, 128.19, 128.12, 127.8, 34.5, 21.1, 13.6. HRMS (ESI): m/z calculated for C₁₉H₁₈O₂Na (M+Na)⁺: 301.1204. Found: 301.1232.

2'-(3-Methylbut-2-enoyl)-[1,1'-biphenyl]-2-carbaldehyde (1y).

This compound was prepared by following the general procedure-1 (condition B) and isolated as



pale-yellow oil. $R_f = 0.6$ (hexane/EtOAc = 10/1). IR (thin film, neat): v_{max}/cm^{-1} 2923, 1694, 1661, 1614, 1447, 1251, 757. ¹H NMR (400 MHz, CDCl₃): δ 9.86 (s, 1H), 7.99 (d, J = 7.1 Hz, 1H), 7.71-7.69 (m, 1H), 7.58 (t, J = 7.2 Hz, 1H), 7.52-7.46 (m, 3H), 7.30-7.27 (m, 2H), 6.06 (s, 1H), 1.97 (s, 3H), 1.70 (s, 3H). ¹³C NMR (100 MHz, CDCl₃):

δ 194.3, 191.6, 156.6, 144.6, 141.7, 136.7, 134.0, 133.3, 131.5, 131.0, 130.2, 128.3, 128.2, 128.0, 127.5, 124.5, 27.6, 20.8. **HRMS (ESI):** *m*/*z* calculated for C₁₈H₁₆O₂Na (M+Na)⁺: 287.1048. Found: 287.1080.

3-(2-Cinnamoylphenyl)benzo[b]thiophene-2-carbaldehyde (1z).

This compound was prepared by following the general procedure-1 (condition A) and isolated as



pale-yellow oil. $R_f = 0.5$ (hexane/EtOAc = 5/1). IR (thin film, neat): v_{max}/cm^{-1} 2924, 2853, 1715, 1667, 1604, 1209, 758. ¹H NMR (400 MHz, CDCl₃): δ 9.82 (s, 1H), 7.89-7.84 (m, 2H), 7.70-7.67 (m, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 6.9 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.31-7.27 (m, 2H), 7.24-7.21 (m, 2H), 7.10-7.08 (m, 2H), 6.65 (d, *J* = 15.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 193.6, 185.0, 145.5,

144.8, 141.6, 141.3, 139.7, 139.5, 134.1, 131.7, 131.2, 131.1, 130.6, 129.4, 129.2, 128.7 (2C), 128.4, 128.2 (2C), 125.5, 125.1, 124.7, 123.3. **HRMS (ESI):** *m*/*z* calculated for C₂₄H₁₆O₂SNa (M+Na)⁺: 391.0769. Found: 391.0762.

6-Benzylidene-7-hydroxy-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (major isomer) (2a).

This compound was isolated as pale-yellow oil. Following the general procedure-3, 40 mg of 1a



afforded 34 mg of **2a** (85% yield). $R_f = 0.4$ (hexane/EtOAc = 5/1). **IR** (**thin film, neat**): v_{max}/cm^{-1} 3434, 3061, 3023, 2960, 1660, 1597, 743. ¹H **NMR (400 MHz, CDCl_3):** δ 7.92 (s, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.65-7.61 (m, 1H), 7.56-7.42 (m, 9H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 5.92 (d, *J* = 3.4 Hz, 1H), 2.13 (d, *J* = 4.6 Hz, 1H). ¹³C **NMR**

(**100 MHz, CDCl₃**): δ 192.8, 141.7, 139.9, 139.1, 138.9, 138.1, 137.2, 134.9, 132.4, 131.2, 129.9,

129.49, 129.43 (3C), 129.0, 128.6 (3C), 128.4, 128.1, 71.5. **HRMS (ESI):** *m*/*z* calculated for C₂₂H₁₆O₂Na (M+Na)⁺: 335.1048. Found: 335.1058.

6-Benzylidene-7-hydroxy-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (major isomer)

((-)-2a).



Following the general procedure-4, 25 mg of (±)-1a afforded 5.0 mg of (–)-2a (20% yield). **Optical rotation:** $[\alpha]_D^{25}$ –36.7 (*c* 0.05, CHCl₃) for a sample with *ee* 76%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak IB Column (96:04 *n*-Hexane/2-Propanol, 1.0 mL/min, 244 nm, $\tau_{major} = 79.0$ min, $\tau_{minor} = 32.2$ min).

7-Hydroxy-6-(naphthalen-1-ylmethylene)-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (major isomer) (2b).

This compound was isolated as pale-yellow solid. Following the general procedure-3, 40 mg of 1b



afforded 32.4 mg of **2b** (81% yield). M.P. = 92-95 °C. $R_f = 0.4$ (hexane/EtOAc = 5/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3441, 3060, 2925, 1660, 1596, 742. ¹H NMR (400 MHz, CDCl₃): δ 8.39 (s, 1H), 7.93-7.91 (m, 3H), 7.64 (t, *J* = 7.0 Hz, 1H), 7.58-7.48 (m, 7H), 7.45-7.35 (m, 2H), 7.25 (s, 1H), 7.01 (d, *J* = 7.3 Hz, 1H), 5.75 (s, 1H), 2.04 (brs, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 192.3, 143.4, 139.0,

138.97, 138.93, 138.4, 137.2, 133.5, 132.5 (2C), 131.6, 131.2, 130.1, 129.66, 129.63, 129.35, 129.31, 128.5, 128.4, 128.1, 126.7, 126.58, 126.53, 125.2, 125.1, 72.0. **HRMS (ESI):** m/z calculated for C₂₆H₁₈O₂Na (M+Na)⁺: 385.1204. Found: 385.1221.

7-Hydroxy-6-(3-methylbenzylidene)-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (major isomer) (2c).

This compound was isolated as pale-yellow oil. Following the general procedure-3, 40 mg of 1c



afforded 35.6 mg of **2c** (89% yield). $R_f = 0.4$ (hexane/EtOAc = 5/1). **IR** (**thin film, neat**): v_{max}/cm^{-1} 3443, 3064, 3027, 2982, 2960, 1658, 1597, 741. ¹H NMR (400 MHz, CDCl₃): δ 7.89 (s, 1H), 7.82 (dd, J = 7.7 and 1.0 Hz, 1H), 7.62 (td, J = 7.7 and 1.4 Hz, 1H), 7.54-7.41 (m, 4H), 7.37-7.20 (m, 6H), 5.93 (d, J = 5.3 Hz, 1H), 2.42 (s, 3H), 2.12 (d, J = 5.4 Hz, 1H). ¹³C NMR (100

MHz, CDCl₃): δ 192.8, 141.6, 140.1, 139.2, 139.0, 138.3, 138.1, 137.2, 134.9, 132.4, 131.1, 130.0, 129.9, 129.8, 129.5, 129.3, 128.5, 128.4, 128.1, 127.9, 126.4, 71.5, 21.4. **HRMS (ESI):** *m/z* calculated for C₂₃H₁₈O₂Na (M+Na)⁺: 349.1204. Found: 349.1227.

7-Hydroxy-6-(4-methoxybenzylidene)-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (major isomer) (2d).

This compound was isolated as pale-yellow viscous oil. Following the general procedure-3, 35 mg



of 1d afforded 26.6 mg of 2d (76% yield). $R_f = 0.3$ (hexane/EtOAc = 4/1). IR (thin film, neat): v_{max}/cm^{-1} 3440, 3061, 2960, 2930, 1654, 1597, 742. ¹H NMR (400 MHz, CDCl₃): δ 7.86 (s, 1H), 7.80 (d, J = 7.5 Hz, 1H), 7.62 (t, J = 7.8 Hz, 1H), 7.54-7.41 (m, 6H), 7.32-7.22 (m, 2H), 6.99 (d, J = 8.5 Hz, 2H), 5.98 (d, J = 4.6 Hz, 1H), 3.87 (s, 3H), 2.14 (d, J = 4.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 193.0, 160.5, 140.2, 139.9, 139.4, 139.1, 137.9,

137.19, 137.15, 132.2, 131.5 (2C), 131.1, 129.8, 129.37, 129.33, 128.4, 128.1, 127.1, 114.2 (2C), 71.7, 55.3. **HRMS (ESI):** *m*/*z* calculated for C₂₃H₁₈O₃Na (M+Na)⁺: 365.1154. Found: 365.1163.

7-Hydroxy-6-(4-methoxybenzylidene)-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (major isomer) ((–)-2d).



Following the general procedure-4, 20 mg of (±)-1d afforded 3.6 mg of (–)-2d (18% yield). **Optical rotation:** $[\alpha]_D^{25}$ –34.9 (*c* 0.02, CH₂Cl₂) for a sample with *ee* 78%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak IB Column (90:10 *n*-Hexane/2-Propanol, 1.0 mL/min, 330 nm, $\tau_{major} = 56.6$ min, $\tau_{minor} = 22.6$ min).

6-(3-Fluorobenzylidene)-7-hydroxy-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (major isomer) (2e).

This compound was isolated as pale-yellow viscous oil. Following the general procedure-3, 30 mg



of **1e** afforded 21.6 mg of **2e** (72% yield). $R_f = 0.4$ (hexane/EtOAc = 5/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3428, 3069, 2930, 1692, 1657, 1446, 1077, 757, 738. ¹H NMR (400 MHz, CDCl₃): δ 7.82-7.80 (m, 2H), 7.63 (td, J = 7.7 and 1.4 Hz, 1H), 7.54-7.49 (m, 2H), 7.47-7.40 (m, 3H), 7.32 (td, J = 7.5 and 1.2 Hz, 1H), 7.25-7.23 (m, 1H), 7.19-7.17 (m, 2H), 7.12 (td, J = 8.4 and 2.3 Hz, 1H), 5.85 (d,

J = 5.0 Hz, 1H), 2.14 (d, J = 5.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 192.6, 162.7 (d, J = 245.7 Hz, 1C), 142.5, 138.9, 138.5, 138.1, 137.2 (d, J = 4.8 Hz, 1C), 137.0, 132.5, 131.2, 130.3 (d, J = 8.3 Hz, 1C), 130.0, 129.5 (2C), 128.5, 128.2, 127.9 (d, J = 2.5 Hz, 1C), 125.1 (d, J = 2.9 Hz, 1C), 116.2, 116.0, 115.8, 71.5. ¹⁹F NMR (376.4 MHz, CDCl₃): δ –112.1. HRMS (ESI): m/z calcd for C₂₂H₁₅FO₂Na (M+Na)⁺: 353.0954. Found: 353.0965.

6-Benzylidene-7-hydroxy-2,3-dimethoxy-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (major isomer) (2f).

This compound was isolated as pale-yellow viscous oil. Following the general procedure-3, 30 mg



of **1f** afforded 26.1 mg of **2f** (87% yield). $R_f = 0.2$ (hexane/EtOAc = 4/1). **IR** (**thin film, neat**): v_{max}/cm^{-1} 3479, 3076, 3064, 2956, 2932, 1651, 1586, 1268, 760. ¹H NMR (**400 MHz, (CD₃)₂SO**): δ 7.65-7.63 (m, 2H), 7.54-7.52 (m, 3H), 7.46-7.40 (m, 3H), 7.34-7.25 (m, 3H), 7.19 (brs, 1H), 7.04 (s, 1H), 5.81 (s, 1H), 3.94 (s, 3H), 3.87 (s, 3H). ¹³C NMR (**100 MHz, (CD₃)₂SO**): δ 191.2, 152.3, 148.2, 143.1, 140.0,

137.7, 135.4, 131.5, 131.4, 131.3, 130.1, 129.9, 129.8, 129.3, 129.1 (2C), 128.8, 128.3 (2C), 112.77, 112.73, 70.2, 56.1, 56.0. **HRMS (ESI):** *m*/*z* calculated for C₂₄H₂₀O₄Na (M+Na)⁺: 395.1259. Found: 395.1273.

7-Hydroxy-2,3-dimethoxy-6-(naphthalen-1-ylmethylene)-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (major isomer) (2g).

This compound was isolated as pale-yellow oil. Following the general procedure-3, 50 mg of 1g



afforded 40.5 mg of **2g** (81% yield). $R_f = 0.2$ (hexane/EtOAc = 4/1). **IR** (**thin film, neat**): v_{max}/cm^{-1} 3493, 3058, 2962, 2929, 1651, 1588, 1517, 1395, 1269, 1021, 784. ¹H NMR (**400 MHz, CDCl_3**): δ 8.35 (s, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.2 Hz, 1H), 7.55-7.48 (m, 5H), 7.46-7.39 (m, 3H), 7.22 (t, J = 7.2 Hz, 1H), 6.99 (s, 1H), 5.73 (s, 1H), 4.01 (s, 3H), 3.99 (s, 3H), 2.31 (brs, 1H). ¹³C NMR (100 MHz,

CDCl₃): δ 190.4, 152.5, 148.7, 143.4, 138.7, 133.4, 132.7, 132.6, 131.6, 131.1, 130.8, 129.2, 129.1, 128.7, 128.5, 128.1, 126.7, 126.5 (3C), 125.1 (3C), 112.8, 112.2, 72.1, 56.16, 56.10. **HRMS** (**ESI**): *m*/*z* calcd for C₂₈H₂₃O₄ (M+H)⁺: 423.1596. Found: 423.1578.

7-Hydroxy-2,3-dimethoxy-6-(4-methylbenzylidene)-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (major isomer) (2h).



This compound was isolated as pale-yellow oil. Following the general procedure-3, 40 mg of **1h** afforded 33.2 mg of **2h** (83% yield). $R_f = 0.2$ (hexane/EtOAc = 4/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3495, 3005, 2956, 2926, 1651, 1601, 1585, 1356, 1268, 1022, 782. **¹H NMR (400 MHz, CDCl_3):** δ 7.86 (s, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.42-7.35 (m, 5H), 7.29-7.27 (m, 1H), 7.24-7.19 (m, 2H), 6.97 (s, 1H), 5.94 (s, 1H), 3.98 (s, 3H), 3.96 (s, 3H), 2.41 (s, 3H), 2.05 (s, 1H). **¹³C NMR (100 MHz, CDCl_3):** δ

CDCl₃): δ 191.1, 152.3, 148.7, 141.2, 139.2, 138.8, 137.1, 132.4, 132.1, 131.4, 130.8, 129.9, 129.5 (2C), 129.3 (2C), 129.1, 128.6, 128.1, 112.7, 112.1, 71.6, 56.1, 56.0, 21.4. **HRMS (ESI)**: *m*/*z* calcd for C₂₅H₂₃O₄ (M+H)⁺: 387.1596. Found: 387.1579.

7-Hydroxy-2,3-dimethoxy-6-(thiophen-2-ylmethylene)-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (major isomer) (2i).

This compound was isolated as pale-yellow oil. Following the general procedure-3, 35 mg of 1i



afforded 29.7 mg of **2i** (85% yield). $R_f = 0.2$ (hexane/EtOAc = 4/1). **IR** (**thin film, neat**): v_{max}/cm^{-1} 3429, 3012, 2966, 2849, 1640, 1601, 1557, 1354, 1269, 1021, 731. ¹H NMR (**400 MHz, CDCl**₃): δ 7.69 (d, J = 7.0 Hz, 1H), 7.57 (s, 1H), 7.51 (s, 1H), 7.48-7.44 (m, 3H), 7.41-7.35 (m, 2H). 7.09-7.07 (m, 1H), 6.95 (s, 1H), 5.69 (s, 1H), 3.99 (s, 3H), 3.98 (s, 3H), 2.64 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 190.4, 152.3, 148.7, 140.6, 138.4,

138.0, 134.7, 132.4, 131.9, 130.8, 129.14, 129.13, 128.4 (2C), 127.6, 126.8 (2C), 112.2, 111.7, 77.2, 56.16, 56.14. **HRMS (ESI):** *m/z* calcd for C₂₂H₁₉O₄S (M+H)⁺: 379.1004. Found: 379.1016.

6-(3-Fluorobenzylidene)-7-hydroxy-2,3-dimethoxy-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (major isomer) (2j).

This compound was isolated as pale-yellow oil. Following the general procedure-3, 40 mg of 1j



afforded 34.4 mg of **2j** (86% yield). $R_f = 0.2$ (hexane/EtOAc = 4/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3436, 3065, 2966, 2936, 1583, 1651, 1518, 1357, 1267, 1022, 754. ¹H NMR (400 MHz, CDCl₃): δ 7.81 (s, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.45-7.42 (m, 3H), 7.31 (t, J = 7.4 Hz, 1H), 7.22-7.18 (m, 2H), 7.15-7.09 (m, 2H), 6.98 (s, 1H), 5.84 (s, 1H), 4.00 (s, 3H), 3.98 (s, 3H), 2.34 (brs, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 190.7,

162.7 (d, J = 245.3 Hz, 1C), 152.5, 148.7, 142.5, 138.3, 138.2, 137.3 (d, J = 7.8 Hz, 1C), 132.4, 131.0, 130.9, 130.3, 130.2, 129.3, 128.3, 125.0 (d, J = 2.8 Hz, 1C), 116.0 (d, J = 21.7 Hz, 1C), 115.8 (d, J = 21.0 Hz, 1C), 112.6 (2C), 112.1, 71.6, 56.17, 56.10. ¹⁹F NMR (376.4 MHz, CDCl₃): $\delta -112.2$. HRMS (ESI): m/z calcd for C₂₄H₂₀FO₄ (M+H)⁺: 391.1345. Found: 391.1328.

6-(3-Fluorobenzylidene)-7-hydroxy-2,3-dimethoxy-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (major isomer) ((+)-2j).



Following the general procedure-4, 50 mg of (±)-1j afforded 6.0 mg of (+)-2j (12% yield). **Optical rotation:** $[\alpha]_D^{25}$ +9.9 (*c* 0.05, CH₂Cl₂) for a sample with *ee* 67%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak IA Column (90:10 *n*-Hexane/2-Propanol, 1.0 mL/min, 260 nm, τ_{major} = 19.3 min, τ_{minor} = 16.3 min).

7-Hydroxy-2,3-dimethoxy-6-(4-methoxybenzylidene)-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (major isomer) (2k).



This compound was isolated as pale-yellow oil. Following the general procedure-3, 48 mg of **1k** afforded 41 mg of **2k** (85% yield). $R_f = 0.2$ (hexane/EtOAc = 3/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3423, 2927, 2849, 1651, 1602, 1566, 1355, 1165, 1024. ¹H NMR (**500 MHz, CDCl3**): δ 7.86 (s, 1H), 7.50-7.46 (m, 3H), 7.44-7.41 (m, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.23 (brs, 1H), 7.00-6.97 (m, 3H), 5.97 (s, 1H), 4.00 (s, 3H), 3.98 (s, 3H),

3.87 (s, 3H), 2.34 (brs, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 191.1, 160.4, 152.3, 148.7, 140.3, 140.0, 138.9, 132.3, 132.1, 131.4 (2C), 130.8, 129.1, 128.1, 127.3, 114.1 (3C), 113.2, 112.6, 112.0, 71.7, 56.1, 56.0, 55.4. HRMS (ESI): *m/z* calcd for C₂₅H₂₃O₅ (M+H)⁺: 403.1545. Found: 403.1560.

8-Benzylidene-9-hydroxy-8,9-dihydro-7*H*-benzo[6,7]cyclohepta[1,2-*a*]naphthalen-7-one (major isomer) (2l).

This compound was isolated as pale-yellow oil. Following the general procedure-3, 30 mg of 11



afforded 23.4 mg of **2l** (78% yield). $R_f = 0.3$ (hexane/EtOAc = 5/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3443, 3057, 3031, 2967, 2925, 1660, 1592, 763. **¹H NMR (400 MHz, CDCl₃):** δ 8.12 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.84 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.61-7.45 (m, 3H), 7.51-7.47 (m, 4H), 7.45-7.40 (m, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 1H), 5.89 (d, *J* = 6.3 Hz, 1H),

2.25 (d, J = 6.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 194.2, 142.7, 139.8, 139.5, 136.8, 136.4,

135.8, 134.7, 134.1, 134.0, 130.9, 129.6 (2C), 129.2, 128.7 (2C), 128.65, 128.62, 128.5, 128.4, 128.1, 127.7, 127.1, 126.9, 125.1, 71.6. **HRMS (ESI):** *m*/*z* calculated for C₂₆H₁₈O₂Na (M+Na)⁺: 385.1204. Found: 385.1219.

(9*S*)-8-Benzylidene-9-hydroxy-8,9-dihydro-7*H*-benzo[6,7]cyclohepta[1,2-*a*]naphthalen-7one (major isomer) ((–)-2l).



This compound was isolated as pale-yellow oil. Following the general procedure-3, 30 mg of (–)-1l afforded 25.5 mg of (–)-2l (85% yield). **Optical rotation:** $[\alpha]_D^{25}$ –48.9 (*c* 0.31, CHCl₃) for a sample with *ee* 96%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak IC Column (96:4 *n*-Hexane/2-Propanol, 0.5 mL/min, 254 nm, τ_{major} = 47.5 min, τ_{minor} = 43.5 min).

9-Hydroxy-8-(naphthalen-1-ylmethylene)-8,9-dihydro-7*H*-benzo[6,7]cyclohepta[1,2*a*]naphthalen-7-one (major isomer) (2m).

This compound was isolated as pale-yellow viscous oil. Following the general procedure-3, 30 mg



of **1m** afforded 24.6 mg of **2m** (82% yield). $R_f = 0.2$ (hexane/EtOAc = 4/1). **IR** (**thin film, neat**): v_{max}/cm^{-1} 3427, 2930, 2853, 1694, 1659, 1595, 1032, 762. ¹H NMR (400 MHz, CDCl₃): δ 8.38 (s, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.96-7.94 (m, 2H), 7.92-7.91 (m, 2H), 7.86 (d, J = 8.5 Hz, 1H), 7.62-7.59 (m, 2H), 7.58-7.56 (m, 2H), 7.54-7.52 (m, 2H), 7.51-7.48 (m, 1H),

7.44-7.43 (m, 1H), 7.41-7.31 (m, 1H), 7.28-7.24 (m, 1H), 7.04 (d, J = 7.6 Hz, 1H), 5.76 (s, 1H), 2.29 (brs, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 193.5, 144.2, 139.8, 138.1, 136.9, 136.7, 135.9, 134.2, 134.0, 133.5, 132.2, 131.8, 131.0, 129.5, 128.6 (2C), 128.5, 128.4, 128.3, 128.0, 127.7, 127.3, 126.86, 126.82, 126.7, 126.5, 125.4, 125.3, 125.0, 72.0. HRMS (ESI): m/z calculated for C₃₀H₂₀O₂Na (M+Na)⁺: 435.1361. Found: 435.1373.

(9*S*)-9-Hydroxy-8-(naphthalen-1-ylmethylene)-8,9-dihydro-7*H*-benzo[6,7]cyclohepta[1,2*a*]naphthalen-7-one (major isomer) ((+)-2m).



This compound was isolated as pale-yellow viscous oil. Following the general procedure-3, 30 mg of (–)-1m afforded 27.0 mg of (+)-2m (90% yield). **Optical rotation:** $[\alpha]_D^{25}$ +18.5 (*c* 0.21, CHCl₃) for a sample with *ee* 93%. 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, $\tau_{major} = 23.6 \text{ min}$, $\tau_{minor} = 13.4 \text{ min}$).

9-Hydroxy-8-(4-methylbenzylidene)-8,9-dihydro-7*H*-benzo[6,7]cyclohepta[1,2*a*]naphthalen-7-one (major isomer) (2n).

This compound was isolated as pale-yellow oil. Following the general procedure-3, 35 mg of 1n



afforded 31.1 mg of **2n** (89% yield). $R_f = 0.2$ (hexane/EtOAc = 4/1). **IR** (**thin film, neat**): v_{max}/cm^{-1} 3449, 3054, 2979, 2921, 1655, 1590, 1508, 1338, 1234, 1032, 757. ¹H NMR (400 MHz, CDCl₃): δ 8.12 (d, J = 8.4 Hz, 1H), 7.93-7.90 (m, 2H), 7.82 (s, 1H), 7.74 (d, J = 8.6 Hz, 1H), 7.59 (t, J = 7.1 Hz, 1H), 7.54-7.50 (m, 2H), 7.48-7.45 (m, 3H), 7.30-7.27 (m, 3H), 7.21 (d, J = 7.5

Hz, 1H), 5.92 (d, J = 6.6 Hz, 1H), 2.42 (s, 3H), 2.28 (d, J = 6.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 194.3, 142.1, 139.9, 139.7, 139.6, 137.0, 136.4, 135.7, 134.04, 134.0, 132.1, 131.7, 130.9, 130.2, 129.8 (2C), 129.5 (2C), 128.6, 128.4, 128.1, 127.6, 127.1, 126.8, 125.1, 71.7, 21.5. HRMS (ESI): m/z calcd for C₂₇H₂₁O₂ (M+H)⁺: 377.1541. Found: 377.1528.

(9*S*,13*b*)-9-hydroxy-8-(4-methylbenzylidene)-8,9-dihydro-7*H*-benzo[6,7]cyclohepta[1,2*a*]naphthalen-7-one (major isomer) ((–)-2n).



This compound was isolated as pale-yellow oil. Following the general procedure-3, 35 mg of (–)-1n afforded 30.1 mg of (–)-2n (86% yield). **Optical rotation:** $[\alpha]_D^{25}$ –37.4 (*c* 0.04, CHCl₃) for a sample with *ee* 95%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak IC Column (95:5 *n*-Hexane/2-Propanol, 1.0 mL/min, 270 nm, $\tau_{major} = 22.1 \text{ min}, \tau_{minor} = 26.3 \text{ min}$).

9-Hydroxy-8-(4-methoxybenzylidene)-8,9-dihydro-7*H*-benzo[6,7]cyclohepta[1,2*a*]naphthalen-7-one (major isomer) (20).

This compound was isolated as pale-yellow oil. Following the general procedure-3, 30 mg of 10



afforded 22.5 mg of **20** (75% yield). $R_f = 0.2$ (hexane/EtOAc = 3/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3438, 2924, 2854, 1651, 1604, 1509, 1338, 1247, 1033, 822. ¹H NMR (400 MHz, **CDCl3):** δ 8.12 (d, J = 8.4 Hz, 1H), 7.93-7.90 (m, 2H), 7.78 (s, 1H), 7.72 (d, J = 8.5 Hz, 1H), 7.61-7.54 (m, 3H), 7.52-7.48 (m, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H), 7.23 (d,

J = 7.4 Hz, 1H), 6.99 (d, J = 8.4 Hz, 2H), 5.93 (d, J = 5.3 Hz, 1H), 3.87 (s, 3H), 2.30 (d, J = 6.3 Hz, 1H). ¹³**C NMR (100 MHz, CDCl₃):** δ 194.4, 160.7, 141.2, 140.0, 139.5, 137.1, 136.2, 135.7, 133.9, 132.9, 131.7 (2C), 130.8, 128.68, 128.62, 128.4 (2C), 128.1, 127.6, 127.1, 126.9, 126.8, 125.1, 114.3 (2C), 71.8, 55.4. **HRMS (ESI):** m/z calcd for C₂₇H₂₁O₃ (M+H)⁺: 393.1490. Found: 393.1476.

(9*S*)-9-Hydroxy-8-(4-methoxybenzylidene)-8,9-dihydro-7*H*-benzo[6,7]cyclohepta[1,2*a*]naphthalen-7-one (major isomer) ((–)-20).



This compound was isolated as pale-yellow oil. Following the general procedure-3, 30 mg of (–)-10 afforded 24.6 mg of (–)-20 (82% yield). **Optical rotation:** $[\alpha]_D^{25}$ –70.7 (*c* 0.12, CHCl₃) for a sample with *ee* 96%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak IC Column (95:5 *n*-Hexane/2-Propanol, 1.0 mL/min, 268 nm, $\tau_{major} = 52.2 \text{ min}, \tau_{minor} = 43.5 \text{ min}$).

9-Hydroxy-8-(thiophen-2-ylmethylene)-8,9-dihydro-7*H*-benzo[6,7]cyclohepta[1,2*a*]naphthalen-7-one (major isomer) (2p). This compound was isolated as pale-yellow oil. Following the general procedure-3, 30 mg of 1p



afforded 21.0 mg of **2p** (70% yield). $R_f = 0.3$ (hexane/EtOAc = 4/1). M.P. = 136-137 °C. **IR** (**thin film, neat**): v_{max}/cm^{-1} 3436, 2960, 2935, 1650, 1601, 1584, 1356, 783. ¹H NMR (400 MHz, (**CD**₃)₂**SO**): δ 8.10-8.05 (m, 2H), 8.02 (d, J = 7.9 Hz, 1H), 7.99-7.95 (m, 1H), 7.81-7.78 (m, 3H), 7.69-7.67 (m, 1H), 7.65-7.60 (m, 1H), 7.57-7.54 (m, 1H), 7.52-7.46 (m, 2H), 7.44-7.39 (m, 1H), 7.22-

7.20 (m, 1H), 6.49 (d, *J* = 4.0 Hz, 1H), 5.62 (d, *J* = 3.1 Hz, 1H). ¹³**C NMR (100 MHz, (CD₃)₂SO):** δ 193.5, 143.3, 139.7, 138.2, 137.1, 136.8, 135.6, 134.5, 133.9, 132.6, 130.8, 130.2, 129.7, 129.0, 128.8, 128.7, 128.2, 127.9, 127.5, 127.1, 126.7, 125.6, 122.7, 70.0. **HRMS (ESI):** *m/z* calcd for C₂₄H₁₇O₂S (M+H)⁺: 369.0949. Found: 369.0934.

(9*S*)-9-Hydroxy-8-(thiophen-2-ylmethylene)-8,9-dihydro-7*H*-benzo[6,7]cyclohepta[1,2*a*]naphthalen-7-one (major isomer) ((–)-2p).



This compound was isolated as pale-yellow oil. Following the general procedure-3, 30 mg of (–)-1p afforded 25.2 mg of (–)-2p (84% yield). **Optical rotation:** $[\alpha]_D^{25}$ –34.3 (*c* 0.18, CHCl₃). *ee* of the sample cannot be determined as the isomers were not resolving in HPLC.

8-(3-Fluorobenzylidene)-9-hydroxy-8,9-dihydro-7*H*-benzo[6,7]cyclohepta[1,2*a*]naphthalen-7-one (major isomer) (2q).

This compound was isolated as pale-yellow oil. Following the general procedure-3, 35 mg of 1q



afforded 30.1 mg of **2q** (86% yield). $R_f = 0.3$ (hexane/EtOAc = 4/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3444, 2956, 1660, 1593, 1579, 1233, 1033, 760, 737. ¹H NMR (400 MHz, CDCl₃): δ 8.08 (d, J = 8.5 Hz, 1H), 7.89 (t, J = 8.0 Hz, 2H), 7.73-7.69 (m, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.48-7.44 (m, 2H), 7.42-7.38 (m, 2H), 7.34-7.27 (m, 2H), 7.24-7.21 (m, 2H), 7.17 (d, J =

7.4 Hz, 1H), 7.11 (t, J = 8.3 Hz, 1H), 5.81 (s, 1H), 2.42 (brs, 1H). ¹³C NMR (100 MHz, CDCl₃):

δ 194.1, 162.8 (d, J = 245.5 Hz, 1C), 143.5, 139.4, 137.8 (d, J = 1.9 Hz, 1C), 136.9, 136.8, 136.6 (d, J = 2.8 Hz, 1C), 135.8, 134.1, 133.5, 131.7, 130.8, 130.4 (d, J = 8.2 Hz, 1C), 128.66, 128.62, 128.4, 128.3, 127.7, 127.1, 126.9, 125.3 (d, J = 2.8 Hz, 1C), 125.1, 116.3 (d, J = 15.6 Hz, 1C), 116.1 (d, J = 14.8 Hz, 1C), 71.5. ¹⁹F NMR (376.4 MHz, CDCl₃): δ –112.0. HRMS (ESI): m/z calcd for C₂₆H₁₆FO₂ (M–H)⁺: 379.1134. Found: 379.1121.

(9*S*,13*bR*)-8-(3-Fluorobenzylidene)-9-hydroxy-8,9-dihydro-7*H*-benzo[6,7]cyclohepta[1,2*a*]naphthalen-7-one (major isomer) ((+)-2q).



This compound was isolated as pale-yellow oil. Following the general procedure-3, 35 mg of (–)-1q afforded 31.5 mg of (+)-2q (90% yield). **Optical rotation:** $[\alpha]_D^{25}$ +03.5 (*c* 0.14, CHCl₃) for a sample with *ee* 95%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak IB Column (96:4 *n*-

Hexane/2-Propanol, 0.5 mL/min, 275 nm, $\tau_{major} = 57.2$ min, $\tau_{minor} = 38.7$ min).

8-(2-Bromobenzylidene)-9-hydroxy-8,9-dihydro-7*H*-benzo[6,7]cyclohepta[1,2-

a]naphthalen-7-one (major isomer) (2r).

This compound was isolated as pale-yellow semi-solid. Following the general procedure-3, 40 mg



of **1r** afforded 36 mg of **2r** (90% yield). $R_f = 0.5$ (hexane/EtOAc = 5/1). **IR** (**thin film, neat**): v_{max}/cm^{-1} 3254, 2360, 2255, 1653, 1538, 1418, 1048, 827, 765. ¹H NMR (**400 MHz, CDCl₃**): δ 8.08 (d, *J* = 8.5 Hz, 1H), 7.91 (m, 2H), 7.82 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.68-7.64 (m, 1H), 7.50-7.45 (m, 4H), 7.41-7.39 (m, 2H), 7.30-7.27 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 5.64 (s, 1H), 2.27 (brs,

1H). ¹³C NMR (100 MHz, CDCl₃): δ 193.3, 143.4. 139.3, 138.4, 136.9, 136.5, 135.9, 135.5, 134.2, 133.0, 130.9, 130.4, 130.3, 128.6, 128.5, 128.4, 128.3, 128.2, 127.7. 127.4, 127.2, 126.8, 125.3, 124.4, 121.9, 71.7. HRMS (ESI): *m/z* calculated for C₂₆H₁₈BrO₂ (M+H)⁺: 441.0490. Found: 441.0503.

(9*S*,13*bR*)-8-(2-Bromobenzylidene)-9-hydroxy-8,9-dihydro-7*H*-benzo[6,7]cyclohepta[1,2*a*]naphthalen-7-one (major isomer) ((+)-2r).



= 52.6 min).

8-(Cyclopropylmethylene)-7-hydroxy-7,8-dihydro-9H-benzo[6,7]cyclohepta[1,2-

a]naphthalen-9-one (major isomer) (2s).

This compound was isolated as pale-yellow oil. Following the general procedure-3, 30 mg of 1s



afforded 10 mg of 2s (33% yield). $R_f = 0.4$ (hexane/EtOAc = 10/1). **IR (thin film, neat):** v_{max}/cm⁻¹ 3422, 2956, 2854, 1693, 1656, 1591, 1377, 762. ¹H NMR (400 MHz, CDCl₃): δ 8.06 (d, J = 8.5 Hz, 1H), 7.91-7.86 (m, 2H), 7.73 (d, J = 8.5 Hz, 1H), 7.68 (d, J = 7.7 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.48-7.40 (m, 3H), 7.35-7.33 (m, 1H), 5.78 (dd, J = 11.0 and 1.2 Hz, 1H), 5.65 (s, 1H), 3.23-3.14 (m, 1H), 2.35

This compound was isolated as pale-yellow solid. Following the

general procedure-3, 35 mg of (-)-1r afforded 29.7 mg of (+)-2r

(85% yield). **Optical rotation:** $[\alpha]_D^{25}$ +34.6 (*c* 0.06, CHCl₃) for

a sample with ee > 99%. The enantiomeric excess was

determined by HPLC analysis using Daicel Chiralpak IB

Column (96:4 *n*-Hexane/2-Propanol, 0.5 mL/min, 273 nm, τ_{major}

(s, 1H), 1.05-1.00 (m, 2H), 0.63-0.61 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 194.5, 146.7, 141.9, 139.6, 137.3, 135.4, 134.5, 132.1, 131.2, 130.6, 128.7, 128.5, 128.3, 127.4, 127.3, 126.6, 126.2, 125.0, 121.3, 69.5, 12.7, 10.2, 10.0. HRMS (ESI): m/z calculated for C₂₃H₁₉O₂ (M+H)⁺: 327.1385. Found: 327.1409.

6-Benzylidene-7-hydroxy-1-methyl-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (major isomer) (2t).

This compound was isolated as brown viscous oil. Following the general procedure-3, 30 mg of



1t afforded 21.6 mg of 2t (72% yield). $R_f = 0.2$ (hexane/EtOAc = 4/1). IR (thin film, neat): v_{max}/cm^{-1} 3445, 3064, 3027, 2971, 2926, 1661, 1593, 748. ¹H NMR (400 MHz, CDCl₃): δ 7.76 (s, 1H), 7.53-7.41 (m, 7H), 7.37-7.34 (m, 3H), 7.25-7.20 (m, 1H), 7.10 (d, J = 7.5 Hz, 1H), 5.78 (s, 1H), 2.40 (s, 3H), 2.23 (brs, 1H). ¹³C NMR (100 **MHz**, **CDCl**₃): δ 194.6, 142.5, 140.7, 139.1, 138.8, 136.8, 135.8,
134.9, 134.7, 132.6, 129.6 (3C), 129.1, 128.7 (2C), 128.27, 128.25, 128.1, 128.0, 126.7, 71.6, 21.3. **HRMS (ESI):** *m/z* calculated for C₂₃H₁₈O₂Na (M+Na)⁺: 349.1204. Found: 349.1214.

(7*S*)-6-Benzylidene-7-hydroxy-1-methyl-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (major isomer) ((–)-2t).

This compound was isolated as brown viscous oil. Following the general procedure-3, 30 mg of



(-)-1t afforded 22.5 mg of (-)-2t (75% yield). Optical rotation: $[\alpha]_D^{25}$ -84.8 (*c* 0.10, CH₂Cl₂) for a sample with *ee* 83%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak OD-H Column (96:4 *n*-Hexane/2-Propanol, 1.0 mL/min, 298 nm, $\tau_{major} = 18.5$ min, $\tau_{minor} = 25.2$ min).

7-Hydroxy-1-methyl-6-(4-methylbenzylidene)-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5one (major isomer) (2u).

This compound was isolated as pale-yellow oil. Following the general procedure-3, 30 mg of 1u



afforded 25.2 mg of **2u** (84% yield). $R_f = 0.2$ (hexane/EtOAc = 4/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3450, 2956, 2858, 1695, 1662, 1595, 1263, 1029, 751. ¹H NMR (500 MHz, CDCl₃): δ 7.73 (s, 1H), 7.50-7.47 (m, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.36-7.32 (m, 3H), 7.27-7.25 (m, 2H), 7.23-7.20 (m, 1H), 7.11 (d, J = 7.5 Hz, 1H), 5.18 (s, 1H), 2.41 (s, 3H), 2.40 (s, 3H), 2.23 (brs, 1H). ¹³C

NMR (125 MHz, CDCl₃): δ 194.6, 141.9, 140.8, 139.5, 139.3, 138.9, 136.8, 135.8, 134.9, 134.5, 132.5, 131.7, 129.7 (2C), 129.5 (2C), 128.2, 128.19, 128.10, 128.0, 126.7, 71.6, 21.4, 21.2. HRMS (ESI): *m*/*z* calculated for C₂₄H₂₀O₂Na (M+Na)⁺: 363.1361. Found: 363.1375.

(7*S*)-7-Hydroxy-1-methyl-6-(4-methylbenzylidene)-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (major isomer) ((–)-2u).



This compound was isolated as pale-yellow oil. Following the general procedure-3, 30 mg of (–)-1u afforded 23.4 mg of (–)-2u (78% yield). **Optical rotation:** $[\alpha]_D^{25}$ –82.0 (*c* 0.09, CH₂Cl₂) for a sample with *ee* 86%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak IC Column (90:10 *n*-Hexane/2-Propanol, 1.0 mL/min, 237 nm, $\tau_{major} = 10.4$ min, $\tau_{minor} = 12.1$ min).

7-Hydroxy-6-(4-methoxybenzylidene)-1-methyl-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5one (major isomer) (2v).

This compound was isolated as pale-yellow oil. Following the general procedure-3, 30 mg of 1v



afforded 22.8 mg of **2v** (76% yield). $R_f = 0.2$ (hexane/EtOAc = 3/1). **IR** (**thin film, neat**): v_{max}/cm^{-1} 3450, 2927, 2855, 1663, 1592, 1510, 1032, 751. ¹H NMR (**500 MHz, CDCl**₃): δ 7.70 (s, 1H), 7.54-7.52 (m, 2H), 7.49 (d, J = 7.6 Hz, 1H), 7.47 (dd, J = 7.6 and 0.75 Hz, 1H), 7.36-7.33 (m, 3H), 7.23-7.20 (m, 1H), 7.13 (d, J = 7.2 Hz, 1H), 6.99 (d, J = 8.7 Hz, 2H), 5.82 (s, 1H), 3.87

(s, 3H), 2.41 (s, 3H), 2.25 (brs, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 194.7, 160.6, 140.99, 140.91, 139.4, 138.7, 136.6, 135.7, 134.9, 134.5, 132.7, 132.5, 131.6 (2C), 128.3, 128.1, 128.0, 126.9, 126.6, 114.3 (2C), 71.8, 55.4, 21.2. HRMS (ESI): *m*/*z* calculated for C₂₄H₂₁O₃ (M+H)⁺: 357.1491. Found: 357.1481.

(7S)-7-Hydroxy-6-(4-methoxybenzylidene)-1-methyl-6,7-dihydro-5H-

dibenzo[*a*,*c*][7]annulen-5-one (major isomer) ((–)-2v).



This compound was isolated as pale-yellow oil. Following the general procedure-3, 30 mg of (–)-1v afforded 22.2 mg of (–)-2v (74% yield). **Optical rotation:** $[\alpha]_D^{25}$ –37.9 (*c* 0.05, CH₂Cl₂) for a sample with *ee* 88%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak IA Column (90:10 *n*-Hexane/2-Propanol, 1.0 mL/min, 297 nm, $\tau_{major} = 26.7 \text{ min}, \tau_{minor} = 45.3 \text{ min}$).

Methyl-7-hydroxy-8-(4-methylbenzylidene)-9-oxo-8,9-dihydro-7*H*benzo[6,7]cyclohepta[1,2-*a*]naphthalene-11-carboxylate (major isomer) (2w).

This compound was isolated as pale-yellow oil. Following the general procedure-3, 20 mg of 1w



afforded 15 mg of **2w** (75% yield). $R_f = 0.4$ (hexane/EtOAc = 5/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3455, 2956, 2920, 1721, 1605, 1656, 1377, 1251, 1120. ¹H NMR (400 MHz, CDCl₃): δ 8.48 (d, J = 1.6Hz, 1H), 8.27 (dd, J = 8.0 and 1.7 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.86-7.81 (m, 3H), 7.68 (d, J = 8.0 Hz, 1H), 7.54-7.43 (m, 2H), 7.40-7.38 (m, 2H), 7.29-7.25 (m, 3H), 6.08 (s, 1H), 3.97 (s, 3H), 2.43 (s, 3H), 2.05 (brs, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 192.8, 166.2,

141.4, 140.8, 140.0, 139.9, 139.7, 136.7, 134.3, 133.0, 132.4, 132.1, 131.6, 131.2, 130.8, 129.8, 129.7, 129.6 (2C), 129.5 (2C), 128.4, 127.0, 126.4, 125.8, 125.6, 71.7, 52.4, 21.5. **HRMS (ESI):** *m/z* calculated for C₂₉H₂₂O₄Na (M+Na)⁺: 457.1416. Found: 457.1418.

6-Butylidene-7-hydroxy-6,7-dihydro-5*H***-dibenzo[***a***,***c***][7]annulen-5-one (major isomer) (2x). This compound was isolated as pale-yellow oil. Following the general procedure-3, 40 mg of 1x**



afforded 26.8 mg of **2x** (67% yield). $R_f = 0.5$ (hexane/EtOAc = 10/1). **IR** (**thin film, neat**): v_{max}/cm^{-1} 3441, 2961, 2872, 1661, 1605, 1447, 1228, 742. ¹H NMR (**400 MHz, CDCl**₃): δ 7.85 (dd, J = 7.7 and 0.84 Hz, 1H), 7.60 (td, J = 7.8 and 1.2 Hz, 1H), 7.52-7.49 (m, 2H), 7.46-7.40 (m, 2H), 7.35-7.34 (m, 2H), 6.91 (t, J = 7.7 Hz, 1H), 5.77 (d, J = 1.1 Hz, 1H), 2.50-2.37 (m, 2H), 2.08 (brs, 1H), 1.57-1.51 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 191.8, 143.3, 141.9, 139.5, 138.7, 138.3, 132.3, 131.07, 131.04, 130.1, 129.6, 129.0, 128.8, 128.4, 128.0, 71.3, 30.2, 22.0, 14.1. HRMS (ESI): *m/z* calculated for C₁₉H₁₇O₂ (M–H)⁺: 277.1229. Found: 277.1252.

7-Hydroxy-6-(propan-2-ylidene)-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (major isomer) (2y).

This compound was isolated as pale-yellow oil. Following the general procedure-3, 35 mg of 1y



afforded 10.5 mg of **2y** (30% yield). $R_f = 0.3$ (hexane/EtOAc = 10/1). **IR** (**thin film, neat**): v_{max}/cm^{-1} 3482, 2961, 2854, 1694, 1611, 1463, 1194, 756. ¹H NMR (400 MHz, CDCl₃): δ 7.94 (dd, J = 7.8 and 0.5 Hz, 1H), 7.59-7.52 (m, 3H), 7.46-7.40 (m, 2H), 7.36-7.31 (m, 2H), 5.77 (s, 1H), 2.31 (s, 4H), 2.06 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 193.2, 148.9, 140.0, 139.0,

138.8, 137.7, 136.9, 131.9, 130.8, 129.79, 129.72, 128.7, 128.2, 127.9, 126.8, 72.8, 24.8, 23.3. **HRMS (ESI):** *m*/*z* calculated for C₁₈H₁₆O₂Na (M+Na)⁺: 287.1048. Found: 287.1082.

6-Benzylidene-7-hydroxy-6,7-dihydro-5*H*-benzo[*b*]benzo[6,7]cyclohepta[1,2-*d*]thiophen-5one (major isomer) (2z).

This compound was isolated as pale-yellow oil. Following the general procedure-3, 45 mg of 1z



afforded 36 mg of 2z (80% yield). $R_f = 0.4$ (hexane/EtOAc = 5/1). IR (thin film, neat): v_{max}/cm^{-1} 3420, 2924, 2853, 1652, 1598, 1436, 1205, 772, 731. ¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, J = 7.1 Hz, 1H), 7.92-7.91 (m, 2H), 7.85 (d, J = 7.6 Hz, 1H), 7.78 (d, J = 7.4 Hz, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.52-7.45 (m, 5H), 7.42-7.39 (m, 3H), 6.02 (s, 1H), 2.39 (brs, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 192.8, 141.2,

140.1, 139.5, 139.0, 138.7, 134.5, 132.4, 131.8, 131.2, 129.8, 129.5 (2C), 129.2, 128.7 (2C), 128.6, 128.0, 127.9, 125.1, 125.0, 122.9 (2C), 64.7. **HRMS (ESI):** *m/z* calculated for C₂₄H₁₆O₂SNa (M+Na)⁺: 391.0769. Found: 391.0782.

(8*R*,9*R*)-9-Hydroxy-8-(4-methylbenzyl)-8,9-dihydro-7*H*-benzo[6,7]cyclohepta[1,2*a*]naphthalen-7-one (major isomer) ((–)-2n').

This compound was isolated as pale-yellow oil. Following the procedure-5, 50 mg of (-)-2n



afforded 43.2 mg of (-)-2n' (86% yield). $R_f = 0.5$ (hexane/EtOAc = 10/1). IR (thin film, neat): v_{max}/cm^{-1} 3466, 3056, 2856, 1680, 1513, 1256, 1070, 815, 760. ¹H NMR (500 MHz, CDCl₃): δ 8.03 (d, J = 10.6 Hz, 1H), 7.86 (d, J = 10.2 Hz, 1H), 7.81-7.77 (m, 2H), 7.55-7.52 (m, 1H), 7.47-7.41 (m, 2H), 7.35-7.23 (m, 3H), 7.17-7.10 (m, 2H), 7.03 (d, J = 9.6 Hz, 2H), 5.09 (d, J = 12.7 Hz, 1H), 3.30-3.24 (m, 1H), 3.13-3.04 (m, 2H), 2.25 (s, 3H), 2.20 (brs, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 207.0, 141.3, 137.4, 136.3, 135.2, 134.6, 135.2, 134.6, 134.5, 132.3, 132.0, 130.3, 129.4 (2C), 129.3 (2C), 128.9, 128.6, 128.4, 127.3, 127.1, 126.9, 126.7, 123.69, 123.6, 69.7, 67.7, 36.8, 21.1. Optical rotation: $[\alpha]_D^{25}$ –33.1 (*c* 0.10, CHCl₃). HRMS (ESI): *m*/*z* calculated for C₂₇H₂₂O₂Na (M+Na)⁺: 401.1517. Found: 401.1505.

(8*R*,9*S*)-9-Methoxy-8-methyl-8-(4-methylbenzyl)-8,9-dihydro-7*H*-benzo[6,7]cyclohepta[1,2*a*]naphthalen-7-one (major isomer) ((+)-2n").

This compound was isolated as white solid. Following the procedure-5, 40 mg of (-)-2n' afforded



36.5 mg of (+)-2n" (85% yield). $R_f = 0.7$ (hexane/EtOAc = 20/1). M.P. = 172-174 °C. IR (thin film, neat): v_{max}/cm^{-1} 2960, 2923, 2853, 1740, 1676, 1463, 1260, 1086, 800, 760. ¹H NMR (400 MHz, CDCl₃): δ 8.10 (d, J = 8.56 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.61-7.52 (m, 2H), 7.49-7.43 (m,

3H), 7.41-7.36 (m, 2H), 7.05-6.99 (m, 4H), 4.70 (s, 1H), 3.40 (s, 3H), 3.07 (s, 2H), 2.24 (s, 3H), 0.97 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 209.0, 137.5, 136.9, 136.0, 135.1, 134.4, 133.7, 133.4, 132.3, 130.3 (2C), 130.2, 128.7 (2C), 128.3, 128.0, 127.8, 127.2, 127.1, 126.8, 126.6, 125.9, 124.7, 80.3, 63.8, 57.5, 43.5, 21.1, 16.3. Optical rotation: [α]_D²⁵ +3.2 (*c* 0.39, CHCl₃). HRMS (ESI): *m*/*z* calculated for C₂₉H₂₇O₂ (M+H)⁺: 407.2011. Found: 407.2015.

Crystal structure of 2b (CCDC 1916664): The structure of **2b** was confirmed by single-crystal X-ray diffraction analysis.

Crystallization procedure of 2b: In a 5 mL glass vial, **2b** was dissolved in methanol (1 mL) and hexane (0.3 mL) and the solution were kept at room temperature for slow evaporation. After 2-3 days, suitable single crystals were obtained.



Figure 3S. ORTEP diagram of 2b with 50% ellipsoidal probability.

Crystal Data for C₂₆H₁₈O₂ (*M* =362.40 g/mol): monoclinic, space group P2₁/c (no. 14), *a* = 8.3826(15) Å, *b* = 12.595(2) Å, *c* = 17.554(3) Å, β = 95.527(16)°, *V* = 1844.8(6) Å³, *Z* = 4, *T* = 298.00(2) K, μ (MoK α) = 0.081 mm⁻¹, *Dcalc* = 1.305 g/cm³, 5990 reflections measured (5.676° ≤ 2 Θ ≤ 49.986°), 3233 unique (*R*_{int} = 0.0492, R_{sigma} = 0.0876) which were used in all calculations. The final *R*₁ was 0.0822 (I > 2 σ (I)) and *wR*₂ was 0.2842 (all data).

Identification code	2b
Empirical formula	$C_{26}H_{18}O_2$
Formula weight	362.40
Temperature/K	298.00(2)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	8.3826(15)
b/Å	12.595(2)
c/Å	17.554(3)
α/°	90
β/°	95.527(16)
γ/°	90
Volume/Å ³	1844.8(6)
Ζ	4
$\rho_{calc}g/cm^3$	1.305
μ/mm ⁻¹	0.081
F(000)	760.0
Crystal size/mm ³	0.3 imes 0.25 imes 0.25
Radiation	MoKα ($\lambda = 0.71073$)
20 range for data collection/°	5.676 to 49.986
Index ranges	$-9 \le h \le 6, -9 \le k \le 14, -20 \le l \le 20$
Reflections collected	5990
Independent reflections	3233 [$R_{int} = 0.0492$, $R_{sigma} = 0.0876$]
Data/restraints/parameters	3233/0/254
Goodness-of-fit on F ²	0.986
Final R indexes [I>=2σ (I)]	$R_1 = 0.0822, wR_2 = 0.2132$
Final R indexes [all data]	$R_1 = 0.1497, wR_2 = 0.2842$
Largest diff. peak/hole / e Å ⁻³	0.43/-0.28

 Table 2S: Crystal data and structure refinement for 2b

Crystal structure of (+)-2n" (**CCDC 2080392**): The structure of (+)-2n" was confirmed by single-crystal X-ray diffraction analysis.

Crystallization procedure of (+)-2n": In a 5 mL glass vial, (+)-2n" was dissolved in acetonitrile (1 mL) and *n*-pentane (0.3 mL) and the solution were kept at room temperature for slow evaporation. After 2-3 days, suitable single crystals were obtained.



Figure 4S. ORTEP diagram of (+)-2n" with 50% ellipsoidal probability.

Crystal Data for C₂₉H₂₆O₂ (M =406.50 g/mol): triclinic, space group P-1 (no. 2), a = 9.1696(5) Å, b = 10.6774(7) Å, c = 12.2477(7) Å, α = 87.619(5)°, β = 87.821(4)°, γ = 72.126(5)°, V = 1139.88(12) Å3, Z = 2, T = 298.0(2) K, μ (MoK α) = 0.073 mm-1, *Dcalc* = 1.184 g/cm3, 25197 reflections measured (5.132° ≤ 2 Θ ≤ 65.53°), 7910 unique (R_{int} = 0.0512, R_{sigma} = 0.0449) which were used in all calculations. The final R1 was 0.0799 (I > 2 σ (I)) and wR2 was 0.2854 (all data).

Identification code	(+)-2n"
Empirical formula	C ₂₉ H ₂₆ O ₂
Formula weight	406.50
Temperature/K	298.0(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.1696(5)
b/Å	10.6774(7)
c/Å	12.2477(7)
α/°	87.619(5)
β/°	87.821(4)
γ/°	72.126(5)
Volume/Å ³	1139.88(12)
Ζ	2
$\rho_{calc}g/cm^3$	1.184
μ/mm ⁻¹	0.073
F(000)	432.0
Crystal size/mm ³	0.4 imes 0.35 imes 0.3
Radiation	MoKα ($\lambda = 0.71073$)
20 range for data collection/°	5.132 to 65.53
Index ranges	$-13 \le h \le 12, -15 \le k \le 16, -18 \le l \le 18$
Reflections collected	25197
Independent reflections	7910 [$R_{int} = 0.0512$, $R_{sigma} = 0.0449$]
Data/restraints/parameters	7910/0/283
Goodness-of-fit on F ²	1.040
Final R indexes [I>=2σ (I)]	$R_1 = 0.0799, wR_2 = 0.2234$
Final R indexes [all data]	$R_1 = 0.1208, wR_2 = 0.2854$
Largest diff. peak/hole / e Å ⁻³	0.59/-0.23

 Table 3S: Crystal data and structure refinement for (+)-2n".

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























S52



S53





















S63



-112.3139 -----











S68







¹H NMR (400 MHz, CDCl₃)





S71



¹H NMR (400 MHz, CDCl₃)














¹⁹F NMR (376.4 MHz, CDCl₃)























¹H NMR (400 MHz, (CD₃)₂SO)





¹⁹F NMR (376.4 MHz, CDCl₃)





































	RT	Area	% Area	Height
1	29.468	26880244	49.76	391073
2	33.332	27135010	50.24	379377

Reported by User. System Report Method: Vishnu Report Method II 15925 Page: 1 of 2 Project Name: YR_01 Date Printed: 25-02-2020 23:39:51 Asia/Calcutta Empower 3 Vishnu SAMPLE INFORMATION Sample Name: AM-DS-115 DD-H 10% D-8 ML/minAcquired By: Sample Type: RF Internal Standard Sample Set Name System Acq. Method Set: Processing Method Channel Name: Vial: 1 Atanu Injection #: 2 am 05 115 Injection Volume: 10.00 ul 348.0nm Proc. Chnl. Descr.: Run Time: 120.0 Minutes PDA 348.0 nm Date Acquired: 13-12-2019 22:38:22 IST Date Processed: 25-02-2020 23:38:54 IST



	RT	Area	% Area	Height
1	28.690	242696	0.33	4396
2	32.929	73612289	99.67	990054

Reported by User: System Report Method: Vishnu Report Method II 15925 Page: 1 of 2

Project Name: YR_01 Date Printed: 25-02-2020 23:40:12 Asia/Calcutta





	RT	Area	% Area	Height
1	37.450	47839459	50.17	724039
2	43.606	47506260	49.83	531877

Reported by User: System Report Method: Vishnu Report Method II 15925 Page: 1 of 2

Project Name: YR_01 Date Printed: 19-07-2020 23:12:28 Asia/Calcutta




	RT	Area	% Area	Height
1	37.900	2051013	2.06	32185
2	43.126	97464242	97.94	1123534

Project Name: YR_01 Date Printed: 19-07-2020 23:13:38 Asia/Calcutta



S110

SOFTWARE			aireacha	Vish
	SAMPLE	INFORMATIC	N	
Sample Name:	AM-05-102-chiral-OD-H-10%	-0.8 Acquired By:	System	
Sample Type:	RF Internal Standard	Sample Set Name		
Vial:	1	Acq. Method Set:	Atanu	
njection #:	2	Processing Method	am 05 102 12	
njection Volume:	10.00 ul	Channel Name:	219.0nm	
Run Time:	120.0 Minutes	Proc. Chnl. Descr.:	PDA 219.0 nm	
Date Acquired:	22-11-2019 23:17:20 IST			
Date Processed:	19-07-2020 22:58:21 IST			



	RT	Area	% Area	Height
1	28.264	2037233	2.31	31588
2	32.829	86216407	97.69	1023232

Project Name: YR_01 Date Printed: 19-07-2020 23:01:30 Asia/Calcutta



Project Name: YR_01 Date Printed: 19-07-2020 22:47:34 Asia/Calcutta



	RT	Area	% Area	Height
1	22.019	2473870	2.13	53651
2	24.180	113711438	97.87	1628159

Project Name: YR_01 Date Printed: 19-07-2020 22:48:42 Asia/Calcutta





	RT	Area	% Area	Height
1	16.394	63684709	50.22	1666084
2	18.633	63128722	49.78	1145697

Project Name: YR_01 Date Printed: 02-03-2020 15:13:10 Asia/Calcutta



0.40-16.800 0.20 0.00 15.00 16.00 17.00 18.00 19.00 20.00 21.00 22.00 23.00 24.00 25.00 Minutes

	RT	Area	% Area	Height
1	16.800	1735071	2.00	41751
2	18.577	84932130	98.00	1641974

Reported by User: System Report Method: Vishnu Report Method II 15925 Page: 1 of 2 Project Name: YR_01 Date Printed: 02-03-2020 15:14:39 Asia/Calcutta

Empower" 3			Vishnu
	SAMPLE IN	NFORMATIO	O N
Sample Name: Sample Type: Vial: Injection #: Injection Volume: Run Time:	am-05-237-rac-IA-10%-1.0mL Standard 1 20.00 ul 120.0 Minutes	Acquired By: Sample Set Name Acq. Method Set: Processing Method Channel Name: Proc. Chnl. Descr.:	System Atanu am 05 237 rac IA 10% 1ml 283.0nm PDA 283.0 nm
Date Acquired: Date Processed:	13-08-2020 22:08:41 IST 13-08-2020 23:07:41 IST		



	RT	Area	% Area	Height
1	13.034	74444787	50.76	2553928
2	15.220	72211266	49.24	2247150

Project Name: YR_01 Date Printed: 13-08-2020 23:16:47 Asia/Calcutta

Empower 3 Vishnu				
	SAMPLE IN	IFORMATIC	D N	
Sample Name:	am-05-225-chiral-IA-10%-1.0mL	Acquired By:	System	
Sample Type:	Standard	Sample Set Name		
Vial:	1	Acq. Method Set:	Atanu	
Injection #:		Processing Method	am 05 225 chiral IA 10% 1 ml	
Injection Volume:	20.00 ul	Proc. Chnl. Descr.:	254.0nm	
Run Time:	120.0 Minutes		PDA 254.0 nm	
Date Acquired: Date Processed:	13-08-2020 22:47:32 IST 13-08-2020 23:14:08 IST			



	RT	Area	% Area	Height
1	12.937	602316	0.83	29683
2	15.129	71596811	99.17	2339172

Project Name: YR_01 Date Printed: 13-08-2020 23:15:42 Asia/Calcutta

	SAMPLE			
Alter alter and	JAMFLL			
Sample Name:	AM-05-149-rac-IA-5%-1mL	Acquired By:	System	
Sample Type:	RF Internal Standard	Sample Set Name	15.24	
Vial:	1	Acq. Method Set:	Atanu	
Injection #:	1	Processing Method	am 05 149 rep	
Injection Volume:	10.00 ul	Channel Name:	295.0nm	
Run Time:	120.0 Minutes	Proc. Chnl. Descr.:	PDA 295.0 nm	
Date Acquired:	23-01-2020 09:24:00 IST			
Date Processed:	25-02-2020 23:19:25 IST			



	RT	Area	% Area	Height
1	18.365	96450886	50.75	3008872
2	21.009	93604454	49.25	2706134

Project Name: YR_01 Date Printed: 25-02-2020 23:21:58 Asia/Calcutta





	RT	Area	% Area	Height
1	18.356	5136487	5.83	138193
2	20.904	82971567	94.17	2508189

Project Name: YR_01 Date Printed: 25-02-2020 23:21:11 Asia/Calcutta



S120



	RT	Area	% Area	Height
1	17.976	1499251	4.04	53346
2	21.975	35615536	95.96	1048986

Project Name: YR_01 Date Printed: 25-02-2020 23:03:34 Asia/Calcutta





	RT	Area	% Area	Height
1	30.118	23035609	49.91	489428
2	37.325	23115904	50.09	414415

Project Name: YR_01 Date Printed: 25-02-2020 23:01:30 Asia/Calcutta





č.	SAMPLE II	NFORMATI	O N
Sample Name:	AM-05-88-chiral-IC4%-0 5ml	Acquired By:	System
Sample Type:	RF Internal Standard	Sample Set Name	oyacin
Vial:	1	Acq. Method Set:	Atanu
Injection #:	2	Processing Method	am 05 88 chiral major
Injection Volume:	10.00 ul	Channel Name:	254 0nm
Run Time:	120.0 Minutes	Proc. Chnl. Descr.:	PDA 254.0 nm
Date Acquired:	04-11-2019 17:33:43 IST		
Date Processed:	21-01-2020 12:21:03 IST		



	RT	Area	% Area	Height
1	43.504	955179	1.96	8041
2	47.583	47747304	98.04	434357

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Reported by User: System Report Method: Vishnu Report Method II 15925 Page: 1 of 2

Project Name: YR_01 Date Printed: 21-01-2020 12:29:57 Asia/Calcutta





Project Name: YR_01 Date Printed: 21-07-2020 00:43:08 Asia/Calcutta

SOFTWARS				VISIII
	SAMPLE IN	FORMATIC	N	
Sample Name:	AM-05-118-IC-5%-1mI-ABnew	Acquired By:	System	
Sample Type:	RF Internal Standard	Sample Set Name		
Vial:	1	Acq. Method Set:	Atanu	
injection #:	3	Processing Method	am 05 118 lep	
Injection Volume:	10.00 ul	Channel Name:	254.0nm	
Run Time:	120.0 Minutes	Proc. Chnl. Descr.:	PDA 254.0 nm	
Date Acquired:	27-12-2019 20:05:16 IST			
Date Processed:	21-07-2020 00:40:30 IST			



	RT	Area	% Area	Height
1	13.435	752662	3.69	11675
2	23.668	19621112	96.31	170019

Project Name: YR_01 Date Printed: 21-07-2020 00:44:25 Asia/Calcutta

mpower [®] 3				Vish
	SAMPLE I	NFORMATIC	N	
Sample Name: Sample Type: Vial: Injection #: Injection Volume: Run Time:	SK-08-7A-rac-IC-5%-1mL-AM RF Internal Standard 1 1 10.00 ul 120.0 Minutes	Acquired By: Sample Set Name Acq. Method Set: Processing Method Channel Name: Proc. Chnl. Descr.:	System Atanu sk 08 7A am rac 270.0nm PDA 270.0 nm	
Date Acquired: Date Processed:	25-11-2019 11:38:27 IST 06-03-2020 17:28:38 IST			



	RT	Area	% Area	Height
1	22.154	10351524	50.27	216526
2	26.215	10240076	49.73	127051

Project Name: YR_01 Date Printed: 06-03-2020 17:30:48 Asia/Calcutta



Empower*3

Vishnu

	SAMPLE	INFORMATIO	N	
Sample Name: Sample Type: Vial: Injection #: Injection Volume: Run Time:	AM-05-94-chiral-IC-5%-1mL RF Internal Standard 1 2 10.00 ul 120.0 Minutes	Acquired By: Sample Set Name Acq. Method Set: Processing Methoc Channel Name: Proc. Chnl. Descr.:	System Atanu am 05 94 270.0nm PDA 270.0 nm	
Date Acquired: Date Processed:	25-11-2019 12:23:37 IST 06-03-2020 17:30:03 IST		, v	



	RT	Area	% Area	Height
1	22.138	12571982	97.58	273004
2	26.316	311595	2.42	4885

Reported by User: System Report Method: Vishnu Report Method II 15925 Page: 1 of 2 Project Name: YR_01 Date Printed: 06-03-2020 17:31:13 Asia/Calcutta

 $\alpha_{ij} = A$





	RT	Area	% Area	Height
1	43.298	7308124	50.53	65059
2	52.651	7153671	49.47	64531

Project Name: YR_01 Date Printed: 06-03-2020 17:36:15 Asia/Calcutta

mpower 3				Vish
	SAMPLE I	NFORMATIC	D N	
Sample Name: Sample Type: Vial: Injection #: Injection Volume: Run Time:	AM-05-103-chiral-IC-5%-1mL RF Internal Standard 1 2 10.00 ul 120.0 Minutes	Acquired By: Sample Set Name Acq. Method Set: Processing Method Channel Name: Proc. Chnl. Descr.:	System Atanu am 05 103 268.0nm@1 PDA 268.0 nm	
Date Acquired: Date Processed:	25-11-2019 16:34:24 IST 06-03-2020 17:34:36 IST			



	RT	Area	% Area	Height
1	43.589	556640	2.14	5953
2	52.292	25512166	97.86	225719

Project Name: YR_01 Date Printed: 06-03-2020 17:37:06 Asia/Calcutta

	SAMPLE	INFORMATIC	D N	
Sample Name:	am-05-114-rac-IB-4%-0.5 n	nL/min Acquired By:	System	
Sample Type:	Standard	Sample Set Name		
Vial:	1	Acq. Method Set:	Atanu	
Injection #:	1	Processing Method	am 05 114	
Injection Volume:	20.00 ul	Channel Name:	275.0nm	
Run Time:	120.0 Minutes	Proc. Chnl. Descr.:	PDA 275.0 nm	
Date Acquired:	22-08-2020 11:13:57 IST			
Date Processed:	22-08-2020 13:46:43 IST			



	RT	Area	% Area	Height
1	39.809	28756330	52.11	188009
2	58.910	26432217	47.89	130653

Project Name: YR_01 Date Printed: 22-08-2020 15:47:22 Asia/Calcutta

Empower*3				Vishnu
	SAMPLE	INFORMATIC	ЛС	-4
Sample Name: Sample Type:	am-05-107re-chi-IB-4%-0.5 Standard	Acquired By: Sample Set Name	System	
Vial: Injection #:	1	Acq. Method Set:	Atanu	
Injection Volume:	20.00 ul	Channel Name:	275.0nm	
Run Time:	120.0 Minutes	Proc. Chnl. Descr.:	PDA 275.0 nm	
Date Acquired: Date Processed:	22-08-2020 12:30:36 IST 22-08-2020 13:46:38 IST			



	RT	Area	% Area	Height
1	38.725	2679024	2.26	22831
2	57.226	116014688	97.74	735004

Project Name: YR_01 Date Printed: 22-08-2020 15:48:16 Asia/Calcutta

Empower"3				Vishnu
-	SAMPLE	INFORMATIC	N	
Sample Name: Sample Type: Vial: Injection #: Injection Volume: Run Time:	am-05-238-rac-IB-4%-0.5 m Standard 1 20.00 ul 120.0 Minutes	hL/minAcquired By: Sample Set Name Acq. Method Set: Processing Method Channel Name: Proc. Chnl. Descr.:	System Atanu am 05 238 1 273.0nm PDA 273.0 nm	
Date Acquired: Date Processed:	18-08-2020 19:53:50 IST 19-08-2020 01:17:31 IST			



	RT	Area	% Area	Height
1	48.827	107742882	51.02	1183185
2	55.297	103429193	48.98	392545

Project Name: YR_01 Date Printed: 19-08-2020 01:24:54 Asia/Calcutta



Vishnu

	SAMPLE	INFORMATIC	ΟN	
Sample Name: Sample Type: Vial: Injection #: Injection Volume: Run Time:	am-05-226-chira-IB-4%-0.5 Standard 1 3 20.00 ul 120.0 Minutes	Acquired By: Sample Set Name Acq. Method Set: Processing Method Channel Name: Proc. Chni. Descr.:	System Atanu am 05 226 1 273.0nm PDA 273.0 nm	
Date Acquired: Date Processed:	18-08-2020 22:44:22 IST 19-08-2020 01:19:19 IST			



	RT	Area	% Area	Height
1	52.657	88623071	100.00	645408

Reported by User. System Report Method: Vishnu Report Method II 17493 Page: 1 of 1

Project Name: YR_01 Date Printed: 19-08-2020 01:25:38 Asia/Calcutta



Vishnu

	SAMPLE IN	FORMATIC	O N	
Sample Name: Sample Type: Vial: Injection #: Injection Volume: Run Time:	am 05 153 rac OD-H 4% 1.0 Unknown 1 1 10.00 ul 120.0 Minutes	Acquired By: Sample Set Name Acq. Method Set: Processing Method Channel Name: Proc. Chnl. Descr.:	iiser Atanu 153 r 298.0nm PDA 298.0 nm	
Date Acquired: Date Processed:	11-05-2021 14:36:09 IST 11-05-2021 15:04:58 IST			



	RT	Area	% Area	Height
1	18.277	160505451	49.99	1291702
2	24.074	160541046	50.01	1793900

Reported by User: iiser mohali (iiser) Report Method: Vishnu Report Method II 19953 Page: 1 of 1 Project Name: YR_01 Date Printed: 11-05-2021 16:31:38 Asia/Calcutta

State and the second	Empower 3				Vishnu
		SAMPLE	NFORMATIC	D N	
	Sample Name: Sample Type: Vial: Injection #: Injection Volume: Run Time:	am 05 152 chi OD-H 4% 1.0 Unknown 1 2 10.00 ul 120.0 Minutes	Acquired By: Sample Set Name Acq. Method Set: Processing Method Channel Name: Proc. Chnl. Descr.:	iiser Atanu 152 c 298.0nm PDA 298.0 nm	
	Date Acquired: Date Processed:	11-05-2021 15:49:14 IST 11-05-2021 16:29:43 IST			



	RT	Area	% Area	Height
1	18.526	79166490	91.44	625678
2	25.292	7413954	8.56	98323

Reported by User: iiser mohali (iiser) Report Method: Vishnu Report Method II 19953 Page: 1 of 1

Project Name: YR_01 Date Printed: 11-05-2021 16:32:38 Asia/Calcutta

MINOW(21.15)				Vishnu
-	SAMPLE IN	IFORMATI	NC	
Sample Name: Sample Type: Vial: Injection #: Injection Volume: Run Time:	am-05-182-rac-IC-10%-1mI-rep Standard 1 20.00 ul 120.0 Minutes	Acquired By: Sample Set Name Acq. Method Set: Processing Methoc Channel Name: Proc. Chnl. Descr.:	System Atanu am 05 182 rep 237.0nm PDA 237.0 nm	
Date Acquired: Date Processed:	19-08-2020 16:16:59 IST 19-08-2020 17:04:18 IST			



12.228

2

9601198

49.26

220370

Reported by User: System Report Method: Vishnu Report Method II 17493 Page: 1 of 1

Project Name: YR_01 Date Printed: 19-08-2020 17:07:31 Asia/Calcutta

mpower 3				Vishni
	SAMPLE	INFORMATIC	N C	
Sample Name: Sample Type: Vial: Injection #: Injection Volume:	Standard 1 2 20.00 ul	Acquired By: Sample Set Name Acq. Method Set: Processing Method Channel Name:	System Atanu am 05 166B rep 237.0nm	
Run Time: Date Acquired: Date Processed:	120.0 Minutes 19-08-2020 16:41:49 IST 19-08-2020 17:05:41 IST	Proc. Chnl. Descr.:	PDA 237.0 nm	



	RT	Area	% Area	Height
1	10.408	39404479	93.18	980599
2	12.194	2883168	6.82	77817

Project Name: YR_01 Date Printed: 19-08-2020 17:08:53 Asia/Calcutta







	RT	Area	% Area	Height
1	26.755	54739032	93.93	969824
2	45.329	3536056	6.07	44907

Project Name: YR_01 Date Printed: 06-03-2020 17:03:43 Asia/Calcutta

mpower™3				Vishnu
	SAMPLE	INFORMATIC	D N	haran ara
Sample Name:	AM-06-12-rac-IB-4%-1ml	Acquired By:	iiser	
Sample Type:	Unknown	Sample Set Name	A 4	
Vial:	1	Acq. Method Set.	am 06 12 rac	
Injection #:	1	Channel Name:	244 0nm	
Injection volume:	20.00 UI	Brog Chal Deser :	PDA 244 0 nm	
Run Time:	120.0 Minutes	FIGC. Chill. Desch.	1 0/ 244.0 1111	
Date Acquired:	19-05-2021 16:51:01 IST			
Date Processed:	19-05-2021 18:33:32 IST			



	RT	Area	% Area	Height
1	31.624	43801066	50.01	616505
2	79.615	43789292	49.99	163021

Reported by User: iiser mohali (iiser) Report Method: Vishnu Report Method II 19989 Page: 1 of 1

Project Name: YR_01 Date Printed: 19-05-2021 20:13:28 Asia/Calcutta

				Vishnu
	SAMPLE	INFORMATIC	N C	1435 1-473 14
Sample Name:	AM-06-12-chiral-IB-4%-1ml	Acquired By:	iiser	
Sample Type:	Unknown	Sample Set Name		
Vial:	1	Acq. Method Set:	Atanu	
Injection #:	2	Processing Methoc	am 06 12 chiral	
Injection Volume:	20.00 ul	Channel Name:	244.0nm@1	
Run Time:	120.0 Minutes	Proc. Chnl. Descr.:	PDA 244.0 nm	
Date Acquired:	19-05-2021 18:32:56 IST			
Date Processed:	19-05-2021 20:10:41 IST			



	RT	Area	% Area	Height
1	32.299	6565086	12.24	99593
2	79.080	47057619	87.76	169795

Reported by User. iiser mohali (iiser) Report Method: Vishnu Report Method II 19989 Page: 1 of 1 Project Name: YR_01 Date Printed: 19-05-2021 20:15:18 Asia/Calcutta

	SAMPLE IN	IFORMATIC	D N	
Sample Name:	am 05 206 IB 10% 1.0 mL/min	Acquired By:	iiser	
Sample Type:	Unknown	Sample Set Name		
Vial:	1	Acq. Method Set:	Atanu	
njection #:	1	Processing Method	206	
njection Volume:	10.00 ul	Channel Name:	330.0nm	
Run Time:	120.0 Minutes	Proc. Chnl. Descr.:	PDA 330.0 nm	



	RT	Area	% Area	Height
1	21.780	85588443	50.51	1234001
2	56.515	83868210	49.49	333842

Reported by User: iiser mohali (iiser) Report Method: Vishnu Report Method II 19989 Page: 1 of 1 Project Name: YR_01 Date Printed: 17-05-2021 13:43:32 Asia/Calcutta
Empower*3				Vishnu
	SAMPLE IN	IFORMATIC	D N	
Sample Name: Sample Type: Vial: Injection #: Injection Volume: Run Time:	am 05 208 IB 10% 1.0 mL/min Unknown 1 2 10.00 ul 120.0 Minutes	Acquired By: Sample Set Name Acq. Method Set: Processing Methoc Channel Name: Proc. Chnl. Descr.:	iiser Atanu 208 330.0nm PDA 330.0 nm	
Date Acquired: Date Processed:	06-05-2021 20:07:06 IST 06-05-2021 21:23:13 IST			



	RT	Area	% Area	Height
1	22.652	8731343	10.87	140684
2	56.610	71584278	89.13	295777

Reported by User: iiser mohali (iiser) Report Method: Vishnu Report Method I[19989 Page: 1 of 1 Project Name: YR_01 Date Printed: 17-05-2021 14:35:11 Asia/Calcutte

Empower [®] 3				Vishnu
	SAMPLE	INFORMATIO	O N	
Sample Name: Sample Type: Vial: Injection #: Injection Volume: Run Time:	am 05 213R rac IA 10% 1.0 Unknown 1 1 10.00 ul 120.0 Minutes	Acquired By: Sample Set Name Acq. Method Set: Processing Methoc Channel Name: Proc. Chnl. Descr.:	iiser Atanu am 05 213 R 260.0nm PDA 260.0 nm	
Date Acquired: Date Processed:	12-05-2021 15:37:58 IST 12-05-2021 18:29:41 IST			



	RT	Area	% Area	Height
1	16.292	33447796	48.97	595525
2	19.362	34859075	51.03	504820

Reported by User: iiser mohali (iiser) Report Method: Vishnu Report Method II 19953 Page: 1 of 1

Project Name: YR_01 Date Printed: 12-05-2021 18:31:55 Asia/Calcutta

Empower" 3				Vishnu
	SAMPLE	INFORMATIC	O N	
Sample Name: Sample Type: Vial: Injection #: Injection Volume: Run Time:	am 05 213C chi IA 10% 1.0 Unknown 1 2 10.00 ul 120.0 Minutes	Acquired By: Sample Set Name Acq. Method Set: Processing Methoc Channel Name: Proc. Chnl. Descr.:	iiser Atanu am 05 213 C 260.0nm PDA 260.0 nm	
Date Acquired: Date Processed:	12-05-2021 17:00:05 IST 12-05-2021 18:29:19 IST			



	RT	Area	% Area	Height
1	16.311	992199	16.68	17351
2	19.379	4954592	83.32	70422

Reported by User: iiser mohali (iiser) Report Method: Vishnu Report Method II 19989 Page: 1 of 1

and methods and

Project Name: YR_01 Date Printed: 12-05-2021 18:32:25 Asia/Calcutta