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Supporting Information

for

Phosphine-Promoted Intramolecular Rauhut-Currier/Wittig Reaction Cascade to Access (Hetero)arene-Fused Diquinanes

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General experimental methods

All the reagents, solvents and catalysts employed in this study were procured from Sigma-Aldrich, BLD pharma, TCI, Avra, GLR, and Spectrochem were used without further purification. For thin-layer chromatography (TLC), silica aluminium foils with fluorescent indicator 254 nm (from Merck) 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 (using a hot air gun). 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 and toluene were obtained by distillation over sodium and stored over sodium wire. Dry DCM was obtained by distillation over calcium hydride and stored on 4 Å molecular sieves. IR spectra were recorded on a Perkin-Elmer FT IR spectrometer as thin films or KBr pellets, as indicated, with vmax 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 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, quint=quintet, 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 (CD₃)₂SO (δ 39.5 ppm). Single crystal X-ray analysis was carried out on a Rigaku XtaLAB mini. High-resolution mass spectra were recorded on a Waters QTOF mass spectrometer.

General procedure-1: Synthesis of bis-enones 7a-7z and 7aa-7ab



Scheme 1S: Synthesis of bis-enones 7a-7z and 7aa-7ab

Representative procedure for step-I, II, and III: Compounds **D** were synthesized according to reported literature.¹

Representative procedure for step-IV: Enone-aldehyde **D** (1.0 equiv) was taken in an ovendried round bottom flask (RBF) and dissolved in DCM (10 mL). Then the Wittig salt (1.5 equiv) was introduced and the reaction mixture was stirred at room temperature until the reactant **D** disappeared (as monitored by TLC). The reaction mixture was quenched with saturated aqueous NH₄Cl solution (~5 mL) and extracted with DCM (2×5 mL). The organic extracts were combined, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (5:1 to 3:1) as eluent to obtain **7a-7z** and **7aa-7ab** (65-90% yield).

Synthesis of bis-enones 7ac and 7ad



Scheme 2S: Synthesis of aliphatic substrates 7ac and 7ad

¹ a) Satpathi, B.; Ramasastry, S. S. V. Angew. Chem. Int. Ed. **2016**, 55, 1777. b) Maurya, J. P.; Ramasastry, S. S. V. J. Org. Chem. **2021**, 86, 525-537.

Step I: Allyl alcohol F was synthesised by literature procedure.²

Step II: An oven-dried 25 mL RB flask was charged with **F** (350 mg, 1.07 mmol) and 5 mL DCM/H₂O (9:1). Then DDQ (365 mg, 1.61 mmol) was added to the reaction mixture at 0 °C and warmed to room temperature. Upon completion, the reaction mixture was quenched with aqueous NaHCO₃ (2-3 mL) and extracted with DCM (2×5 mL). The organic extracts were dried over Na₂SO₄ and concentrated under reduced pressure. The crude mixture product was purified by silica gel column chromatography by using ethyl acetate/hexane (9:1 to 8:2) as an eluent to obtain diol.

The diol (132 mg, 0.65 mmol) was dissolved in DMSO (3 mL) and IBX (2.2 equiv) was added. The reaction mixture was stirred at room temperature until the starting material disappeared (as monitored by TLC). The reaction was quenched by water (1-2 mL) and the precipitate was filtered by a Buchner funnel. The solution was treated with aqueous NaHCO₃ solution and extracted with EtOAc (2×3 mL). The organic extracts were dried over Na₂SO₄ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography by using ethyl acetate/hexane (9:1 to 8:2) as an eluent to afford **G**.

Step III&IV: The bis-enone **7ac** was synthesised by the literature procedure³ and **7ad** was synthesised by following the procedure described in Scheme 1S.



General procedure-2: Synthesis of bis-enones 10a-10d and 7ae

Scheme 3S: Synthesis of bis-enones 10a-10d

² Komine, K.; Lambert, K. M.; Savage, Q. R.; Cox, J. B.; Wood, J. L. *Chem. Sci.* **2020**, *11*, 9488–9493. ³ Yadav, V. K.; Ganesh Babu, K. *Tetrahedron* **2003**, *59*, 9111–9116.

Step-I: Compound I was synthesized according to reported literature.⁴

Step-II: Compound **I** (1.0 equiv, 10 mmol) was dissolved in dry THF (10 mL) under the nitrogen atmosphere at 0 °C and LiAlH₄ (1.1 equiv, 10.5 mmol) was added to it. The reaction mixture was stirred at room temperature for 4 h. After completion, the reaction was quenched with a slow addition of water and the white precipitate was filtered using the Buchner funnel and washed with EtOAc (2×5 mL). The organic extracts were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude allylic alcohols were used for the next step without further purification.

The allylic alcohol was dissolved in EtOAc (5 mL) and IBX (1.2 equiv, 12 mmol) was added. The reaction mixture was stirred at reflux temperature until the starting material disappeared (as monitored by TLC). The reaction was cooled at room temperature and filtered by a Buchner funnel. The solution was treated with aqueous NaHCO₃ solution and extracted with EtOAc (2×4 mL). The organic extracts were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (9:1 to 8:2) as eluent to afford J in 64% yield.

Representative procedure for step-III: To a solution of **J** (1.0 equiv, 7 mmol) in dry THF (10 mL) at 0 °C under nitrogen atmosphere, R¹Li or R¹MgX (1.2 equiv) was added dropwise over 3-5 min and the reaction mixture was stirred for an additional 45 min at the same temperature. Upon completion, the reaction mixture was quenched with saturated aqueous NH₄Cl solution and extracted with EtOAc (2×5 mL). The organic extracts were dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using hexanes/ethyl acetate (8:2 to 7:3) as eluent to afford alcohol **K** (85-90% yield).

Representative procedure for step-IV: To a solution of **K** (1.0 equiv, 5 mmol) in dry THF (10 mL) at -78 °C was added *n*-BuLi (2.5 M in hexane, 4.4 mL, 2.2 equiv, 11 mmol). After 1 h, enal (1.1 equiv, 5 mmol) was introduced at the same temperature. The reaction mixture was warmed to reflux temperature and continued stirring for an additional 4-5 h. Upon completion, the reaction was quenched with saturated aqueous NH₄Cl solution and extracted with EtOAc (2×5 mL). The organic extracts were dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (7:3 to 6:4) as eluent to afford the respective diol L (24-35% yield). **Representative procedure for step-V:** See the procedure described in Scheme 2S.

⁴ Narczyk, A.; Pieczykolan, M.; Stecko, S. Org. Biomol. Chem. **2018**, 16, 3921–3946.

Compound **7ae** was synthesized by following the protocol described for **10a-10d**, starting from **M**.⁵



Scheme 4S: Synthesis of bis-enone 7ae

General procedure-3: Optimization of reaction parameters for 8a



Scheme 5S: Optimization of reaction parameters for 8a

An oven-dried 5 mL glass vial was charged with 7a (40 mg, 0.11 mmol), then appropriate phosphine (1.2 equiv) and a solvent (1-2 mL) were added sequentially. The reactions were carried out at different temperatures until 7a disappeared (as monitored by TLC). After completion, the reaction mixture was quenched with aqueous NH₄Cl (\sim 2 mL) and extracted with EtOAc (2×3 mL). The organic extracts were combined, dried over anhydrous Na₂SO₄, and the solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (15:1 to 9:1) as eluent to afford 8a.

General procedure-4: Evaluating the substrate scope for 8 and 11



Scheme 6S: Synthesis of diquinanes and benzo-fused diquinanes 8 and 11

⁵ Bayrak, Ç.; Taslimi, P.; Gülçin, İ.; Menzek, A. Bioorg. Chem. 2017, 72, 359-366.

An oven-dried 5 mL glass vial was charged with 7 or 10 (1.0 equiv), 'BuOH (1-2 mL), and tributylphosphine (1.2 equiv) at room temperature. Then the reaction mixture was shifted to 70 °C and stirred at the same temperature for 1 h. Then the reaction mixture was quenched with aqueous NH₄Cl (~2 mL) and extracted with EtOAc (2×3 mL). The organic extracts were combined, dried over anhydrous Na₂SO₄, and the solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (10:1 to 8:2) as eluent to afford **8** (34-90% yield) or **11** (67-90% yield).

Synthetic elaborations

(a) Transformation of 8g to indacene derivative 15g



Scheme 7S: Synthesis of Indacene derivative 15g

Step I: See the procedure described in Scheme 2S.

Step II: Then primary alcohol (140 mg, 0.51 mmol) was taken in 5 mL RB flask and dissolved in dry THF. Then, 2-nitrophenylselenocyanate (352 mg, 1.55 mmol) and tributyphosphine (0.38 mL, 1.55 mmol) were added in a sequence and the resulting mixture was stirred at room temperature for 4 h (monitored by TLC). Then, NaHCO₃ (430 mg, 5.1 mmol) was added and stirred for another 5 min. After 5 min, H₂O₂ (1.3 mL, 30% in H₂O) was added and continued stirring for another 2 h. Upon complete conversion, the reaction mixture was quenched with aqueous NaHCO₃ (2-3 mL) and extracted with EtOAc (2x3 mL). The organic extracts were combined and dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude mixture product was purified by silica gel column chromatography by using ethyl acetate/hexane (10:1 to 5:1) as an eluent to afford 108 mg of **12g** (83% yield).

Step III: See the procedure described in Scheme 3S.

Step IV: The allylic alcohol **13g** (40 mg, 0.13 mmol) was dissolved in 2 mL dry THF and placed at 0 °C under N₂ atmosphere. 18-crown-6 (39 mg, 0.14 mmol, 1.1 equiv) and KH (22 mg, 0.16 mmol, 1.2 equiv, 30 wt% dispersion in mineral oil) were added and stirred for 15-20 min at room temperature until the allylic alcohol disappeared as monitored by TLC. The reaction mixture was quenched with aqueous NH₄Cl (2-3 mL) and extracted with EtOAc (2x5 mL). The combined organic layers were dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (10:1) as eluent to afford 22 mg of **14g** (54% yield).

Step V: The tertiary alcohol **14g** (22 mg, 0.07 mmol, 1 equiv) was dissolved in 1 mL toluene and *p*-TSA (2.5 mg, 0.014 mmol, 0.2 equiv) was added at room temperature. The reaction mixture was stirred for 5 h at the same temperature. After complete conversion, the reaction was quenched with saturated aq. NaHCO₃ (2 mL) and extracted with EtOAc (2x3 mL). The combined organic layers were dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by neutral alumina column chromatography using hexane as eluent to afford 15 mg of **15g** (72% yield).

(b) Elaboration of 8a to cyclic carbonate 17a



Scheme 8S: Synthesis of cyclic carbonate 17a

Step-I: An oven-dried 25 mL RBF was charged with **8a** (150 mg, 0.44 mmol) in 5 mL THF/H₂O (5/1). Then OsO₄ (4% in water, 150 μ L, 10 mol%) and NMO (130 mg, 1.11 mmol) were added and the reaction mixture was stirred at room temperature. Upon completion, the reaction mixture was quenched with aqueous NaHSO₃ (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 mixture product was purified by silica gel column chromatography by using ethyl acetate/hexane (5:1 to 8:2) as an eluent to afford 148 mg of **16a** (90% yield).

Step-II: An oven-dried 25 mL RB flask was charged with **16a** (70 mg, 0.189 mmol) and dissolved in dry DCM (3 mL) under N₂ atmosphere. Then carbonyl diimidazole (CDI) (61 mg, 0.37 mmol) and NEt₃ (52 μ L, 0.37 mmol) were introduced at room temperature and stirred the

resulting mixture for 6 h. After complete conversion, the reaction mixture was quenched with aqueous NH₄Cl (3 mL) and extracted with DCM (2×3 mL) The organic extracts were combined, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (5:1 to 8:2) as eluent to afford 65 mg of **17a** (86% yield).

(c) Conversion of 8g to different tetracyclic structures



Scheme 9S: Synthesis of different tetracyclic structures

Step-I: See Scheme 2S for step-I(i) and step-I(ii).

Step-I(iii): An oven-dried 25 mL RBF was charged with methyltriphenylphosphonium bromide (305 mg, 0.85 mmol, 1.5 equiv) in dry THF (5 mL) and the resultant solution was placed at 0 $^{\circ}$ C under N₂ atmosphere. Then KO/Bu (100 mL, 0.85 mmol, 1.5 equiv) was added and stirred at the same temperature for 1 h. After 1 h, the keto-aldehyde (160 mg, 0.57 mmol, 1 equiv) was added to the reaction mixture and continued stirring for another 1 h. After completion, the reaction mixture was quenched with aqueous NH₄Cl (2-3 mL) and extracted with EtOAc (2x5 mL). The organic extracts were combined and dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude mixture product was purified by silica gel column chromatography by using ethyl acetate/hexane (10:1 to 5:1) as an eluent to afford 140 mg of **19g** (89% yield).

Representative procedure for step-II: See Scheme 3S for step-II(i).

Step-II(ii): The crude product obtained after Grignard addition was dissolved in dry DCM under N₂ atmosphere. The Grubbs second generation catalyst (5 mol%) was introduced at the room temperature and reaction shifted to reflux temperature. Upon completion, the reaction mixture was quenched with aqueous NaHCO₃ (2-3 mL) and extracted with DCM (2x2 mL).

The organic extracts were combined and dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude mixture product was purified by silica gel column chromatography by using ethyl acetate/hexane (5:1 to 8:2) as an eluent to afford **20g-22g** in 82-88% yield.



(d) Synthesis of advanced intermediate 20ae for the synthesis of sativamide A

Scheme 10S: Synthesis of tetracyclic core of sativamide A

Step-I: See Scheme 6S.

Step-II & III: See Scheme 2S for step-II and step-III(i). For step-III(ii) see Scheme 9S.Step-IV & V: See Scheme 9S.

Crystal structure of 8m (CCDC 2325678): The structure of 8m was confirmed by singlecrystal X-ray diffraction analysis.

Crystallization procedure of 8m: In a 5 mL glass vial, 10 mg of **8m** was dissolved in MeOH (2 mL) and the solution was kept at room temperature for slow evaporation. After 3-5 days, suitable single crystals were obtained.



Figure 1: ORTEP diagram of 8m with 50% ellipsoidal probability.

Crystal Data for C₂₆H₂₂O₂ (M =366.44 g/mol): orthorhombic, space group P2₁2₁2₁ (no. 19), a = 10.3208(6) Å, b = 12.3275(7) Å, c = 16.0767(12) Å, V = 2045.4(2) Å³, Z = 4, T = 293(2) K, μ (Mo K α) = 0.074 mm-1, D*calc* = 1.190 g/cm3, 5365 reflections measured (5.14° $\leq 2\Theta \leq 50.1^{\circ}$), 3599 unique (Rint = 0.0187, Rsigma = 0.0257) which were used in all calculations. The final *R*1 was 0.0398 (>2sigma(I)) and *wR*2 was 0.1057 (all data).

Identification code	8m
Empirical formula	$C_{26}H_{22}O_2$
Formula weight	366.44
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	P212121
a/Å	10.3208(6)
b/Å	12.3275(7)
c/Å	16.0767(12)
α/°	90.00
<u>β</u> /°	90.00
γ/°	90.00
Volume/Å ³	2045.4(2)
Z	4
ρcalcg/cm ³	1.190
μ/mm ⁻¹	0.074
F(000)	776.0
Crystal size/mm ³	0.3 imes 0.2 imes 0.12
Radiation	Μο Κα (λ = 0.71073)
20 range for data collection/°	5.14 to 50.1
Index ranges	$-12 \le h \le 9, -7 \le k \le 14, -19 \le l \le 3$
Reflections collected	5365
Independent reflections	3599 [Rint = 0.0187, Rsigma = 0.0257]
Data/restraints/parameters	3599/0/341
Goodness-of-fit on F ²	1.063
Final R indexes [I>=2σ (I)]	R1 = 0.0398, wR2 = 0.0967
Final R indexes [all data]	R1 = 0.0476, wR2 = 0.1057
Largest diff. peak/hole / e Å ⁻³	0.10/-0.16
Flack parameter	0.3(15)

Table 1S: Crystal data and structure refinement for 8m

Crystal structure of 17a (CCDC 2327817): The structure of **17a** was confirmed by singlecrystal X-ray diffraction analysis.

Crystallization procedure of 17a: In a 5 mL glass vial, 10 mg of **17a** was dissolved in EtOH:DCM (5:1) in 2 mL and the solution was kept at room temperature for slow evaporation. After 2-3 days, suitable single crystals were obtained.



Figure 2: ORTEP diagram of 17a with 50% ellipsoidal probability.

Crystal Data for C₂₆H₂₀O₄ (M =396.42 g/mol): monoclinic, space group P2₁/c (no. 14), a = 8.5179(4) Å, b = 10.2457(5) Å, c = 23.2567(10) Å, $\beta = 93.088(4)^{\circ}$, V = 2026.71(16) Å³, Z = 4, T = 293(2) K, μ (Mo K α) = 0.087 mm⁻¹, D*calc* = 1.299 g/cm³, 31399 reflections measured (5.3° $\leq 2\Theta \leq 65.6^{\circ}$), 7201 unique (Rint = 0.0442, Rsigma = 0.0344) which were used in all calculations. The final *R*1 was 0.0620 (>2sigma(I)) and *wR*2 was 0.2108 (all data).

Identification code	17 a
Empirical formula	$C_{26}H_{20}O_4$
Formula weight	396.42
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	8.5179(4)
b/Å	10.2457(5)
c/Å	23.2567(10)
a/o	90.00
<u>β</u> /°	93.088(4)
γ/°	90.00
Volume/Å ³	2026.71(16)
Z	4
ρcalcg/cm ³	1.299
μ/mm-1	0.087
F(000)	832.0
Crystal size/mm ³	$0.25\times0.2\times0.19$
Radiation	Mo Kα (λ = 0.71073)
20 range for data collection/°	5.3 to 65.6
Index ranges	$-12 \le h \le 11, -14 \le k \le 14, -34 \le l \le 34$
Reflections collected	31399
Independent reflections	7201 [Rint = 0.0442, Rsigma = 0.0344]
Data/restraints/parameters	7201/36/271
Goodness-of-fit on F ²	1.040
Final R indexes [I>=2σ (I)]	R1 = 0.0620, wR2 = 0.1665
Final R indexes [all data]	R1 = 0.1014, wR2 = 0.2108
Largest diff. peak/hole / e Å ⁻³	0.29/-0.22

Table 2S: Crystal data and structure refinement for 17a

Spectral data of all the new compounds reported during this study (E)-2-Benzyl-1-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)prop-2-en-1-one (7a).



This compound was prepared by following the general procedure-1 and isolated as pale-yellow solid. 300 mg of **D** (Ar = C_6H_4 , R¹ = CH_2Ph , R² = Ph) afforded 300 mg of 7a (71% yield). $R_f = 0.6$ (hexane/EtOAc = 8/2). M.P = 96-98 °C. IR (thin film, neat): v_{max}/cm^{-1} 3060, 2925, 1654, 1608, 1457, 1217, 985, 757. ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, J = 7.4Hz, 2H), 7.81–7.74 (m, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.6 Hz, 3H), 7.41 – 7.37 (m,

2H), 7.33 – 7.13 (m, 6H), 5.80 (s, 1H), 5.67 (s, 1H), 3.78 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 198.5, 190.3, 149.1, 142.1, 140.1, 138.4, 137.8, 134.0, 132.9, 131.3, 130.4, 129.31, 129.30 (2C), 128.8, 128.67 (4C), 128.61 (2C), 127.3, 126.4, 124.8, 36.9. HRMS (ESI): m/z calcd for C₂₅H₂₀NaO₂ (M+Na)⁺: 375.1361. Found: 375.1370.

8a-Benzyl-2-phenyl-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8a).



This compound was prepared by following the general procedure-4 and isolated as pale-yellow liquid. 30 mg of 7a afforded 25 mg of 8a (87% yield). $R_f = 0.6$ (hexane/EtOAc = 19/1). IR (thin film, neat): v_{max}/cm^{-1} 3027, 2912, 1704, 1602, 1494, 1279, 962, 750. ¹H NMR (400 MHz, **CDCl₃**): δ 7.72 (d, J = 7.8 Hz, 1H), 7.58 (t, J = 7.2 Hz, 1H), 7.44 (d, J =

7.6 Hz, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.31 – 7.21 (m, 5H), 7.19 – 7.11 (m, 5H), 6.10 (s, 1H), 3.79 (d, J = 9.3 Hz, 1H), 3.21 (s, 2H), 2.97 (ddd, J = 16.4, 9.5, 2.4 Hz, 1H), 2.72 (d, J = 16.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 207.0, 157.1, 142.7, 137.9, 135.3, 135.2, 135.2, 129.9 (2C), 128.3 (2C), 128.1 (2C), 127.9, 127.8, 127.3, 126.3, 125.9, 125.8 (2C), 124.1, 70.4, 44.9, 39.6, 39.0. **HRMS (ESI):** *m/z* calcd for C₂₅H₂₁O (M+H)⁺: 337.1592. Found: 337.1599.

(E)-3-(2-Methacryloylphenyl)-1-phenylprop-2-en-1-one (7b).



This compound was prepared by following the general procedure-1 and isolated as pale-yellow liquid. 350 mg of **D** (Ar = C_6H_4 , R¹ = Me, R² = Ph) afforded 290 mg of 7b (60% yield). $R_f = 0.5$ (hexane/EtOAc = 8/2). IR (thin film, neat): v_{max}/cm⁻¹ 3062, 2932, 1662, 1603, 1276, 1076, 743. ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, J = 8.3 Hz, 2H), 7.78 – 7.72 (m, 2H), 7.58 –

7.54 (m, 1H), 7.50 – 7.46 (m, 3H), 7.44 – 7.35 (m, 3H), 6.01 (s, 1H), 5.58 (s, 1H), 2.05 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 199.4, 190.4, 145.2, 142.1, 140.4, 137.8, 133.7, 132.8, 131.2, 130.1, 129.3, 128.64 (2C), 128.61 (2C), 128.5, 127.2, 124.6, 17.3. **HRMS (ESI)**: *m/z* calcd for C₁₉H₁₆NaO₂ (M+Na)⁺: 299.1048. Found: 299.1048.

(E)-2-Methylene-1-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)butan-1-one (7c).



This compound was prepared by following the general procedure-1 and isolated as pale-yellow liquid. 150 mg of **D** (Ar = C₆H₄, R¹ = Et, R² = Ph) afforded 160 mg of **7c** (69% yield). R_f = 0.5 (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max}/cm^{-1} 3061, 2969, 1659, 1603, 1475, 1213, 976, 662. ¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, *J* = 7.0 Hz, 2H), 7.79 – 7.74 (m, 2H),

7.58 – 7.55 (m, 1H), 7.51 – 7.46 (m, 3H), 7.42 (t, J = 7.4 Hz, 1H), 7.39 – 7.35 (m, 2H), 5.96 (s, 1H), 5.59 (s, 1H), 2.48 (q, J = 7.4 Hz, 2H), 1.13 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 199.3, 190.5, 151.1, 142.2, 140.7, 137.8, 133.7, 132.8, 130.2, 129.3 (2C), 128.6 (5C), 127.1, 124.6, 23.7, 12.4. HRMS (ESI): m/z calcd for C₂₀H₁₈NaO₂ (M+Na)⁺: 313.1204. Found: 313.1207.

(E)-2-Methylene-1-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)-5-phenylpentan-1-one (7d).



This compound was prepared by following the general procedure-1 and isolated as pale-yellow liquid. 110 mg of **D** (Ar = C₆H₄, R¹ = C₃H₆Ph, R² = Ph) afforded 120 mg of **7d** (79% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3060, 2929, 1659, 1604, 1450, 1214, 977, 748. ¹H NMR (400 MHz, CDCl₃):

δ 7.96 – 7.94 (m, 2H), 7.78 – 7.74 (m, 2H), 7.57 – 7.51 (m, 1H), 7.49 – 7.40 (m, 4H), 7.38 – 7.33 (m, 2H), 7.30 – 7.25 (m, 2H), 7.20 – 7.16 (m, 3H), 5.97 (s, 1H), 5.61 (s, 1H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.50 (t, *J* = 7.4 Hz, 2H), 1.88 – 1.80 (m, 2H). ¹³**C NMR (100 MHz, CDCl₃):** δ 199.1, 190.5, 149.4, 142.2, 142.0, 140.5, 137.8, 133.9, 132.8, 130.5, 130.3, 129.3, 128.69, 128.65 (2C), 128.6 (2C), 128.5 (2C), 128.3 (2C), 127.2, 125.8, 124.8, 35.7, 30.4, 29.9. **HRMS (ESI):** *m/z* calcd for C₂₇H₂₄NaO₂ (M+Na)⁺: 403.1674. Found: 403.1681.

(*E*)-2-((Benzyloxy)methyl)-1-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)prop-2-en-1-one (7e).



This compound was prepared by following the general procedure-1 and isolated as pale-yellow liquid. 220 mg of **D** (Ar = C₆H₄, R¹ = CH₂OBn, R² = Ph) afforded 200 mg of **7e** (66% yield). R_f = 0.5 (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max}/cm^{-1} 3061, 2922, 1659, 1605, 1476, 1277, 981, 758. ¹H NMR (400 MHz, CDCl₃): δ 7.98 – 7.95 (m, 2H), 7.81 – 7.77 (m, 2H), 7.57 – 7.51 (m, 2H), 7.49 – 7.43 (m, 3H), 7.41 –

7.39 (m, 2H), 7.37 – 7.34 (m, 4H), 7.30 – 7.26 (m, 2H), 6.32 (s, 1H), 5.79 (s, 1H), 4.61 (s, 2H), 4.42 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 198.0, 190.4, 145.9, 142.0, 139.7, 137.9, 137.8, 134.0, 132.9, 130.6, 129.3, 128.8, 128.6 (2C), 128.6 (3C), 128.4 (2C), 127.7, 127.7 (2C), 127.4, 125.0, 73.1, 67.9. HRMS (ESI): *m/z* calcd for C₂₆H₂₃O₃ (M+H)⁺: 383.1647. Found: 383.1649.

(E)-4-(Benzyloxy)-2-methylene-1-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)butan-1-one

(7f). This compound was prepared by following the general procedure-1 and isolated as pale-



yellow liquid. 130 mg of **D** (Ar = C₆H₄, R¹ = C₂H₄OBn, R² = Ph) afforded 150 mg of **7f** (85% yield). R_f = 0.5 (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max}/cm^{-1} 3060, 2862, 1657, 1605, 1475, 1275, 978, 734. ¹H NMR (400 MHz, CDCl₃): δ 7.97 – 7.95 (m, 2H), 7.81 – 7.76 (m, 2H), 7.57 – 7.53 (m, 1H), 7.50 – 7.44 (m, 3H), 7.41 – 7.35

(m, 3H), 7.31 - 7.30 (m, 4H), 7.27 - 7.22 (m, 1H), 6.08 (s, 1H), 5.66 (s, 1H), 4.51 (s, 2H), 3.68 (t, J = 6.3 Hz, 2H), 2.79 (t, J = 6.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 198.9, 190.5, 146.5, 142.2, 140.2, 138.3, 137.8, 134.0, 132.8, 131.9, 130.4, 129.3, 129.0, 128.67 (2C), 128.65 (2C), 128.3 (2C), 127.7 (2C), 127.5, 127.2, 124.7, 72.8, 68.5, 31.3. HRMS (ESI): m/z calcd for C₂₇H₂₄NaO₃ (M+Na)⁺: 419.1623. Found: 419.1614.

(E)-4-((4-Methoxybenzyl)oxy)-2-methylene-1-(2-(3-oxo-3-phenylprop-1-en-1-

yl)phenyl)butan-1-one (7g).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow



liquid. 370 mg of **D** (Ar = C₆H₄, R¹ = C₂H₄OPMB, R² = Ph) afforded 410 mg of **7g** (84% yield). R_f = 0.4 (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max}/cm^{-1} 3031, 2856, 1705, 1606, 1463, 1246, 821. ¹H NMR (400 MHz, CDCl₃): δ 7.98 – 7.96 (m, 2H), 7.81 – 7.76 (m, 2H), 7.57 – 7.54 (m, 1H), 7.48 (q, *J* = 7.7 Hz, 3H),

7.41 – 7.34 (m, 3H), 7.23 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 6.07 (s, 1H), 5.65 (s,

1H), 4.43 (s, 2H), 3.76 (s, 3H), 3.65 (t, J = 6.4 Hz, 2H), 2.77 (t, J = 6.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 198.9, 190.4, 159.1, 146.6, 142.2, 140.2, 137.8, 134.0, 132.8, 131.8, 130.4, 130.4, 129.39 (2C), 129.30, 129.0, 128.6 (4C), 127.2, 124.7, 113.7 (2C), 72.5, 68.1, 55.2, 31.2. HRMS (ESI): m/z calcd for C₂₈H₂₆NaO₄ (M+Na)⁺: 449.1729. Found: 449.1716.

(E)-2-Benzyl-1-(3-fluoro-2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)prop-2-en-1-one (7h)

This compound was prepared by following the general procedure-1 and isolated as pale-yellow



semi-solid. 150 mg of **D** (Ar = 3-FC₆H₃, R¹ = CH₂Ph, R² = Ph) afforded 140 mg of **7h**(67% yield). R_f = 0.7 (hexane/EtOAc = 8/2). **IR (thin film, neat)**: v_{max}/cm^{-1} 3062, 2931, 1664, 1600, 1494, 1280, 1074, 698. ¹H **NMR (400 MHz, CDCl₃)**: δ 7.97 – 7.95 (m, 2H), 7.66 – 7.54 (m, 2H), 7.50 – 7.47 (m, 3H), 7.38 – 7.33 (m, 1H), 7.26 – 7.24 (m, 2H), 7.22 –

7.14 (m, 4H), 7.09 (dd, J = 7.5, 0.9 Hz, 1H), 5.81 (s, 1H), 5.68 (s, 1H), 3.76 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 197.6 (d, J = 2.6 Hz, 1C), 189.9, 161.4 (d, J = 253.6 Hz, 1C), 148.9, 142.2 (d, J = 1.8 Hz, 1C), 138.1, 137.6, 135.1, 133.0, 131.9, 130.3 (d, J = 9.1 Hz, 1C), 129.2 (2C), 128.7 (2C), 128.66 (2C), 128.62 (2C), 128.5, 126.4, 124.1 (d, J = 3.7 Hz, 1C), 121.9 (d, J = 12.4 Hz, 1C), 117.7 (d, J = 22.9 Hz, 1C), 36.7. ¹⁹F NMR (376.4 MHz, CDCl₃): δ –110.09. HRMS (ESI): m/z calcd for C₂₅H₁₉FNaO₂ (M+Na)⁺: 393.1267. Found: 393.1273.

(*E*)-2-Benzyl-1-(3-fluoro-2-(3-(3-methoxyphenyl)-3-oxoprop-1-en-1-yl)phenyl)prop-2-en-1-one (7i).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow



liquid. 100 mg of **D** (Ar = 3-FC₆H₃, R¹ = CH₂Ph, R² = 3-OMeC₆H₄) afforded 120 mg of **7i** (89% yield). R_f = 0.4 (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max}/cm^{-1} 3062, 2939, 1663, 1593, 1452, 1256, 1026, 738. ¹H NMR (400 MHz, **CDCl₃):** δ 7.63 (d, *J* = 15.9 Hz, 1H), 7.54 – 7.47 (m, 3H), 7.41 – 7.33 (m, 2H), 7.26 – 7.16 (m, 6H), 7.15 – 7.11 (m, 1H), 7.08 (d,

J = 7.6 Hz, 1H), 5.81 (s, 1H), 5.68 (s, 1H), 3.87 (s, 3H), 3.76 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 197.6 (d, J = 2.5 Hz, 1C), 189.7, 161.3 (d, J = 253.8 Hz, 1C), 159.9, 148.9, 142.2 (d, J = 1.8 Hz, 1C), 139.0, 138.1, 135.1, 131.9, 130.3 (d, J = 9.3 Hz, 1C), 129.6, 129.2 (2C), 128.7, 128.6 (2C), 126.4, 124.1 (d, J = 3.5 Hz, 1C), 121.9 (d, J = 12.5 Hz, 1C), 121.2, 119.7,

117.6 (d, J = 23.0 Hz, 1C), 112.8, 55.4, 36.7. ¹⁹F NMR (376.4 MHz, CDCl₃): δ –110.07. HRMS (ESI): m/z calcd for C₂₆H₂₁FNaO₃ (M+Na)⁺: 423.1372. Found: 423.1374.

(*E*)-2-Benzyl-1-(2-methyl-6-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)prop-2-en-1-one (7j). This compound was prepared by following the general procedure-1 and isolated as white



crystalline solid. 150 mg of **D** (Ar = 2-MeC₆H₃, R¹ = CH₂Ph, R² = Ph) afforded 130 mg of **7j** (62% yield). R_f = 0.5 (hexane/EtOAc = 9/1). M.P = 124-126 °C. **IR (thin film, neat):** v_{max} /cm⁻¹ 3028, 2922, 1660, 1597, 1448, 1221, 978, 765. ¹H NMR (400 MHz, CDCl₃): δ 7.95 – 7.93 (m, 2H), 7.60 – 7.56 (m, 3H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.31 (m, 2H),

7.29 – 7.26 (m, 2H), 7.22 –7.16 (m, 4H), 5.77 (s, 1H), 5.66 (s, 1H), 3.77 (s, 2H), 2.10 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 200.6, 190.1, 149.4, 141.7, 140.5, 138.4, 137.9, 135.3, 132.9, 132.5, 131.97, 131.92, 129.3 (2C), 129.0, 128.6 (2C), 128.59 (2C), 128.56 (2C), 126.4, 124.6, 124.1, 36.0, 19.1. HRMS (ESI): *m*/*z* calcd for C₂₆H₂₂NaO₂ (M+Na)⁺: 389.1517. Found: 389.1519.

(*E*)-1-(2,4-Dimethoxy-6-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)-2-methylprop-2-en-1one (7k).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow



solid. 220 mg of **D** (Ar = 2,4-(OMe)₂C₆H₂, R¹ = Me, R² = Ph) afforded 215 mg of **7k** (68% yield). R_f = 0.4 (hexane/EtOAc = 8/2). M.P = 146-148 °C. **IR (thin film, neat):** v_{max}/cm^{-1} 3063, 2941, 1650, 1601, 1452, 1283, 974, 783. ¹H NMR (400 MHz, CDCl₃): δ 7.93 (d, J = 7.7 Hz, 2H), 7.57 – 7.54 (m, 1H), 7.50 – 7.44 (m, 3H), 7.33 (d, J

= 15.6 Hz, 1H), 6.82 (d, *J* = 1.84 Hz, 1H), 6.52 (s, 1H), 5.92 (s, 1H), 5.60 (s, 1H), 3.88 (s, 3H), 3.74 (s, 3H), 2.02 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 198.8, 190.4, 161.1, 158.2, 146.0, 141.5, 137.7, 134.7, 132.9, 129.7, 128.6 (2C), 128.5 (2C), 125.0, 123.6, 102.5, 100.3, 55.9, 55.5, 16.7. HRMS (ESI): *m/z* calcd for C₂₁H₂₁O₄ (M+H)⁺: 337.1440. Found: 337.1445.

(E)-3-(1-Methacryloylnaphthalen-2-yl)-1-phenylprop-2-en-1-one (7l).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow



solid. 150 mg of **D** (Ar = Naphthyl, R¹ = Me, R² = Ph) afforded 160 mg of **7l** (73% yield). R_f = 0.7 (hexane/EtOAc = 8/2). M.P = 106-108 °C. **IR** (thin film, neat): v_{max}/cm^{-1} 3060, 2956, 1657, 1599, 1448, 1217, 737. ¹H NMR (400 MHz, CDCl₃): δ 7.99 – 7.97 (m, 2H), 7.91 – 7.82 (m, 3H), 7.71 (d, *J* = 15.5 Hz, 1H), 7.60 – 7.56 (m, 2H), 7.54 – 7.45 (m, 5H),

6.04 (s, 1H), 5.55 (s, 1H), 2.16 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 201.2, 190.2, 146.1, 141.3, 139.7, 137.8, 133.8, 132.9, 132.4, 130.8, 129.5, 129.4, 128.67 (2C), 128.60 (2C), 128.2, 127.5, 127.4, 126.0, 124.5, 122.6, 16.7. HRMS (ESI): *m/z* calcd for C₂₃H₁₈NaO₂ (M+Na)⁺: 349.1204. Found: 349.1209.

(*E*)-2-Benzyl-1-(4-methoxy-2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)prop-2-en-1-one (7m).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow



solid. 250 mg of **D** (Ar = 4-OMeC₆H₃, R¹ = CH₂Ph, R² = Ph) afforded 250 mg of **7m** (73% yield). R_f = 0.4 (hexane/EtOAc = 8/2). M.P = 111-113 °C. **IR (thin film, neat):** v_{max}/cm^{-1} 3059, 2929, 1646, 1598, 1424, 1229, 735. ¹H NMR (400 MHz, CDCl₃): δ 8.00 – 7.97 (m, 2H), 7.87 (d, *J* = 15.6 Hz, 1H), 7.58 – 7.54 (m,

1H), 7.50 - 7.46 (m, 2H), 7.35 (d, J = 8.5 Hz, 1H), 7.31 - 7.24 (m, 3H), 7.23 - 7.16 (m, 4H), 6.89 (dd, J = 8.5 Hz, 2.5 Hz, 1H), 5.74 (s, 1H), 5.64 (s, 1H), 3.87 (s, 3H), 3.76 (s, 2H). ¹³C **NMR (100 MHz, CDCl₃):** δ 197.6, 190.7, 161.3, 149.3, 143.0, 138.5, 137.8, 137.0, 132.8, 132.2, 131.7, 129.2 (2C), 128.7 (2C), 128.6 (3C), 128.5 (2C), 126.3, 125.1, 114.2, 112.8, 55.6, 37.6. **HRMS (ESI):** m/z calcd for C₂₆H₂₂NaO₃ (M+Na)⁺: 405.1467. Found: 405.1459.

(*E*)-2-Benzyl-1-(2-(3-oxo-3-phenylprop-1-en-1-yl)naphthalen-1-yl)prop-2-en-1-one (7n). This compound was prepared by following the general procedure-1 and isolated as pale-yellow



solid. 220 mg of **D** (Ar = Naphthyl, $R^1 = CH_2Ph$, $R^2 = Ph$) afforded 210 mg of **7n** (71% yield). $R_f = 0.7$ (hexane/EtOAc = 8/2). M.P = 108-110 °C. **IR (thin film, neat):** v_{max}/cm^{-1} 3060, 2912, 1658, 1600, 1449, 1297, 970, 772. ¹H NMR (400 MHz, CDCl₃): δ 8.00 – 7.98 (m, 2H), 7.89 – 7.74 (m, 4H), 7.60 – 7.56 (m, 1H), 7.53 – 7.47 (m, 4H), 7.39 – 7.38 (m, 2H), 7.34 – 7.28 (m, 4H), 7.24 – 7.20 (m, 1H), 5.82 (s, 1H), 5.64 (s, 1H), 3.89 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 200.4, 190.1, 149.8, 141.2, 139.3, 138.3, 137.9, 133.8, 133.0, 132.9, 130.8, 129.6, 129.5, 129.4 (2C), 128.7 (2C), 128.66 (2C), 128.63 (2C), 128.2, 127.5, 127.4, 126.5, 125.8, 124.7, 122.6, 36.2. HRMS (ESI): *m/z* calcd for C₂₉H₂₂NaO₂ (M+Na)⁺: 425.1517. Found: 425.1517.

(*E*)-2-Benzyl-1-(2-(3-(4-chlorophenyl)-3-oxoprop-1-en-1-yl)naphthalen-1-yl)prop-2-en-1-one (70).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow



crystalline solid. 140 mg of **D** (Ar = Naphthyl, R¹ = CH₂Ph, R² = 4-ClC₆H₄) afforded 155 mg of **7o** (84% yield). R_f = 0.7 (hexane/EtOAc = 8/2). M.P = 145-147 °C. **IR (thin film, neat):** v_{max}/cm^{-1} 3061, 2953, 1657, 1588, 1483, 1266, 987, 1232, 733. ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.34 (d, *J* = 8.8 Hz, 1H), 8.22 (d, *J* = 8.6 Hz, 2H), 8.12 - 8.08 (m, 2H), 8.03 (d, *J* = 8.1 Hz, 1H),

7.67 (d, J = 8.6 Hz, 2H), 7.62 – 7.56 (m, 2H), 7.47 – 7.43 (m, 1H), 7.38 – 7.34 (m, 4H), 7.29 – 7.24 (m, 2H), 6.10 (s, 1H), 5.60 (s, 1H), 3.89 (s, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 200.5, 188.1, 149.5, 140.2, 139.6, 139.0, 138.8, 136.3, 134.4, 133.9, 131.0 (2C), 130.4, 129.9, 129.44 (4C), 129.41, 128.9 (2C), 128.8, 128.2, 127.9, 126.8, 125.7, 124.5, 123.6, 36.0. HRMS (ESI): *m*/*z* calcd for C₂₉H₂₂ClO₂ (M+H)⁺: 437.1308. Found: 437.1318.

3-(2-(2-Benzylacryloyl)phenyl)acrylaldehyde (7p).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow



liquid. 100 mg of **D** (Ar = C₆H₄, R¹ = CH₂Ph, R² = H) afforded 80 mg of **7p** (72% yield). R_f = 0.5 (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max}/cm^{-1} 3062, 2929, 1676, 1494, 1212, 980, 829. ¹H NMR (400 MHz, **CDCl₃):** δ 9.42 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.35 – 7.21 (m, 7H), 6.58 (dd, *J* = 15.9, 7.7 Hz, 1H), 5.96 (s, 1H), 5.65 (s, 1H), 3.81 (s, 2H). ¹³C NMR (100

MHz, CDCl₃): δ 198.3, 193.8, 149.4, 149.2, 139.6, 138.5, 132.9, 130.7, 130.3, 130.0, 129.4, 129.1 (2C), 128.9, 128.6 (2C), 127.1, 126.6, 37.3. **HRMS (ESI)**: *m/z* calcd for C₁₉H₁₇O₂ (M+H)⁺: 277.1229. Found: 277.1216.

(E)-4-(2-(2-Benzylacryloyl)phenyl)but-3-en-2-one (7q).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow



liquid. 100 mg of **D** (Ar = C₆H₄, R¹ = CH₂Ph, R² = Me) afforded 110 mg of **7q** (94% yield). R_f = 0.7 (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max}/cm^{-1} 3062, 2925, 1665, 1611, 1493, 1253, 955, 754. ¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, J = 8.0 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.39 (td, J = 7.5, 0.9 Hz, 1H), 7.34 – 7.26 (m, 5H), 7.24 – 7.20 (m, 1H), 6.56 (d, J

= 16.2 Hz, 1H), 5.91 (s, 1H), 5.67 (s, 1H), 3.80 (s, 2H), 2.23 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 198.54, 198.51, 149.1, 140.7, 139.5, 138.5, 133.6, 131.2, 130.6, 129.6, 129.3, 129.1 (2C), 128.9, 128.6 (2C), 127.0, 126.5, 37.2, 27.0. HRMS (ESI): *m/z* calcd for C₂₀H₁₈NaO₂ (M+Na)⁺: 313.1204. Found: 313.1207.

(E)-2-Benzyl-1-(2-(3-oxo-3-(p-tolyl)prop-1-en-1-yl)phenyl)prop-2-en-1-one (7r).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow



liquid. 200 mg of **D** (Ar = C₆H₄, R¹ = CH₂Ph, R² = *p*-Tolyl) afforded 195 mg of **7r** (66% yield). R_f = 0.6 (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max}/cm^{-1} 3060, 2923, 1659, 1605, 1325, 1275, 980, 734. ¹H **NMR (400 MHz, CDCl₃):** δ 7.89 (d, *J* = 7.9 Hz, 2H), 7.80 – 7.74 (m, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.32 (d, *J* = 4.8 Hz,

1H), 7.30 – 7.26 (m, 4H), 7.24 – 7.16 (m, 3H), 5.79 (s, 1H), 5.66 (s, 1H), 3.78 (s, 2H), 2.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 198.6, 189.8, 149.2, 143.7, 141.6, 140.0, 138.5, 135.3, 134.2, 131.2, 130.3, 129.36 (2C), 129.30 (2C), 129.1, 128.8 (2C), 128.7, 128.5 (2C), 127.3, 126.4, 124.9, 36.9, 21.7. HRMS (ESI): *m*/*z* calcd for C₂₆H₂₃O₂ (M+H)⁺: 367.1698. Found: 367.1689.

$(E) \hbox{-} 2-Benzyl \hbox{-} 1-(2-(3-(4-chlorophenyl)) \hbox{-} 3-oxoprop \hbox{-} 1-en \hbox{-} 1-yl) phenyl) prop \hbox{-} 2-en \hbox{-} 1-one (7s).$

This compound was prepared by following the general procedure-1 and isolated as pale-yellow



liquid. 200 mg of **D** (Ar = C₆H₄, R¹ = CH₂Ph, R² = 4-ClC₆H₄) afforded 180 mg of **7s** (58% yield). R_f = 0.7 (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max} /cm⁻¹ 3063, 2926, 2856, 1707, 1652, 1457, 1212, 921, 740.¹H NMR (400 MHz, DMSO-*d*₆): δ 8.22 (d, *J* = 7.8 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 15.4 Hz, 1H), 7.67 –

7.60 (m, 4H), 7.55 – 7.51 (m, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.26 – 7.19

(m, 3H), 6.03 (s, 1H), 5.65 (s, 1H), 3.76 (s, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 198.6, 188.3, 148.7, 141.3, 140.4, 139.1, 138.7, 136.4, 133.3, 132.6, 131.0, 130.9 (2C), 130.3, 129.4 (2C), 129.2 (2C), 128.9 (3C), 127.9, 126.7, 124.1, 36.7. HRMS (ESI): *m/z* calcd for C₂₅H₁₉ClNaO₂ (M+Na)⁺: 409.0971. Found: 409.0968.

(*E*)-2-Benzyl-1-(2-(3-(3-methoxyphenyl)-3-oxoprop-1-en-1-yl)phenyl)prop-2-en-1-one (7t).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow



solid. 220 mg of **D** (Ar = C₆H₄, R¹ = CH₂Ph, R² = 3-OMeC₆H₄) afforded 216 mg of **7t** (64% yield). R_f = 0.5 (hexane/EtOAc = 8/2). M.P = 79-81 °C. **IR (thin film, neat):** v_{max} /cm⁻¹ 3027, 2945, 1657, 1588, 1458, 1271, 1029, 980, 758. ¹H NMR (400 MHz, CDCl₃): δ 7.84 - 7.77 (m, 2H), 7.59 - 7.49 (m, 3H), 7.42 (t, *J* = 7.6 Hz,

2H), 7.38 – 7.30 (m, 4H), 7.28 – 7.20 (m, 3H), 7.16 – 7.12 (m, 1H), 5.83 (s, 1H), 5.70 (s, 1H), 3.90 (s, 3H), 3.81 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 198.5, 190.2, 159.9, 149.1, 142.1, 140.1, 139.2, 138.4, 134.1, 131.2, 130.4, 129.6, 129.3, 129.2 (2C), 128.8, 128.6 (2C), 127.3, 126.4, 124.9, 121.2, 119.5, 112.9, 55.5, 37.0. HRMS (ESI): *m/z* calcd for C₂₆H₂₃O₃ (M+H)⁺: 383.1647. Found: 383.1662.

(E)-2-Benzyl-1-(2-(3-(3-fluorophenyl)-3-oxoprop-1-en-1-yl)phenyl)prop-2-en-1-one (7u).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow



liquid. 200 mg of **D** (Ar = C₆H₄, R¹ = CH₂Ph, R² = 3-FC₆H₄) afforded 205 mg of **7u** (69% yield). R_f = 0.7 (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max} /cm⁻¹ 3064, 2922, 1662, 1584, 1440, 1244, 921, 736. ¹H NMR (400 MHz, CDCl₃): δ 7.81 (d, *J* = 15.6 Hz, 1H), 7.76 – 7.73 (m, 2H), 7.67 – 7.64 (m, 1H), 7.51 – 7.45 (m, 2H), 7.43 – 7.39

(m, 1H), 7.34 – 7.30 (m, 2H), 7.28 – 7.27 (m, 2H), 7.25 – 7.16 (m, 4H), 5.82 (s, 1H), 5.68 (s, 1H), 3.78 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 198.4, 189.0, 162.8 (d, *J* = 246.4 Hz, 1C), 149.1, 142.9, 140.1, 139.9 (d, *J* = 6.2 Hz, 1C), 138.4, 133.9, 131.3, 130.5, 130.3 (d, *J* = 7.6 Hz, 1C), 129.5, 129.2 (2C), 128.9, 128.6 (2C), 127.3, 126.4, 124.25 (d, *J* = 2.9 Hz, 1C), 124.29, 119.9 (d, *J* = 21.3 Hz, 1C), 115.4 (d, *J* = 22.2 Hz, 1C), 37.0. ¹⁹F NMR (376.4 MHz, CDCl₃): δ –111.67. HRMS (ESI): *m/z* calcd for C₂₅H₁₉FNaO₂ (M+Na)⁺: 393.1267. Found: 393.1276.

(*E*)-2-Benzyl-1-(2-(3-(3,4-dimethoxyphenyl)-3-oxoprop-1-en-1-yl)phenyl)prop-2-en-1one (7v).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow



liquid. 170 mg of **D** (Ar = C₆H₄, R¹ = CH₂Ph, R² = 3,4-(OMe)₂C₆H₃) afforded 160 mg of 7v (57% yield). R_f = 0.4 (hexane/EtOAc = 6/4). **IR (thin film, neat):** $v_{max}/cm^{-1} 3062, 2937,$ 1657, 1595, 1457, 1267, 983, 763. ¹H NMR (400 MHz, CDCl₃): δ 7.79 - 7.74 (m, 2H), 7.64 - 7.58 (m, 2H), 7.48 (t, *J* = 7.4 Hz,

1H), 7.40 – 7.36 (m, 2H), 7.34 – 7.30 (m, 2H), 7.27 – 7.26 (m, 1H), 7.23 – 7.18 (m, 3H), 6.91 (d, J = 8.3 Hz, 1H), 5.80 (s, 1H), 5.68 (s, 1H), 3.97 (s, 3H), 3.95 (s, 3H), 3.78 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 198.6, 188.6, 153.2, 149.1, 149.1, 141.2, 139.9, 138.4, 134.3, 131.2, 130.9, 130.4, 129.2 (2C), 129.1, 128.7, 128.5 (2C), 127.3, 126.4, 124.7, 123.2, 110.8, 110.0, 56.1, 56.0, 36.9. HRMS (ESI): m/z calcd for C₂₇H₂₄NaO₄ (M+Na)⁺: 435.1572. Found: 435.1584.

(E)-2-Benzyl-1-(2-(3-(furan-2-yl)-3-oxoprop-1-en-1-yl)phenyl)prop-2-en-1-one (7w).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow



solid. 250 mg of **D** (Ar = C₆H₄, R¹ = CH₂Ph, R² = 2-Furyl) afforded 150 mg of **7w** (43% yield). R_f = 0.4 (hexane/EtOAc = 8/2). M.P = 134-136 °C. **IR (thin film, neat):** v_{max}/cm^{-1} 3098, 2894, 1647, 1603, 1460, 1276, 926, 817. ¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, *J* = 15.7 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.63 (s, 1H), 7.47 (t, *J* = 8.6 Hz, 1H), 7.39 (t, *J* = 7.5

Hz, 1H), 7.33 – 7.28 (m, 4H), 7.26 – 7.21 (m, 4H), 6.58 – 6.56 (m, 1H), 5.80 (s, 1H), 5.66 (s, 1H), 3.80 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 198.5, 177.6, 153.4, 149.1, 146.7, 141.1, 140.1, 138.4, 133.8, 131.3, 130.3, 129.38, 129.32 (2C), 128.7, 128.6 (2C), 127.3, 126.41, 123.9, 117.9, 112.6, 36.9. HRMS (ESI): *m*/*z* calcd for C₂₃H₁₈NaO₃ (M+Na)⁺: 365.1154. Found: 365.1133.

(*E*)-2-Benzyl-1-(2-(3-oxo-3-(thiophen-2-yl)prop-1-en-1-yl)phenyl)prop-2-en-1-one (7x).



This compound was prepared by following the general procedure-1 and isolated as pale-yellow liquid. 150 mg of **D** (Ar = C₆H₄, R¹ = CH₂Ph, R² = 2-thiophenyl) afforded 127 mg of **7x** (59% yield). R_f = 0.5 (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max}/cm^{-1} 3055, 2887, 1650, 1600, 1461, 1255, 916, 815. ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, *J* = 15.5 Hz, 1H), 7.78 (d, *J* = 3.8 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.63 –

7.62 (m, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.31 – 7.22 (m, 6H), 7.19 – 7.11 (m, 2H), 5.79 (s, 1H), 5.65 (s, 1H), 3.78 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 198.5, 181.8, 149.1, 145.2, 141.2, 140.1, 138.4, 134.2, 133.8, 132.28, 132.26, 131.4, 130.4, 129.4, 129.3 (2C), 128.6 (2C), 128.4, 127.3, 126.4, 124.4, 37.0. HRMS (ESI): m/z calcd for C₂₃H₁₈NaO₂S (M+Na)⁺: 381.0925. Found: 381.0904.

(E)-1-(3-Fluorophenyl)-3-(2-methacryloyl-3,4,5-trimethoxyphenyl)prop-2-en-1-one (7y).



This compound was prepared by following the general procedure-1 and isolated as dark-yellow liquid. 150 mg of **D** (Ar = 3,4,5-(OMe)₃C₆H, R¹ = Me, R² = 3-FC₆H₄) afforded 145 mg of **7y** (66% yield). R_f = 0.4 (hexane/EtOAc = 7/3). **IR (thin film, neat):** v_{max}/cm^{-1} 3071, 2939, 1722, 1661, 1485, 1292, 1127, 822. ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, *J* = 7.7 Hz,

1H), 7.60 (d, J = 9.3 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.29 – 7.24 (m, 1H), 7.20 (d, J = 15.5 Hz, 1H), 7.01 (s, 1H), 6.00 (s, 1H), 5.61 (s, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 3.82 (s, 3H), 2.05 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 197.9, 189.1, 162.7 (d, J = 246.4 Hz, 1C), 154.1, 150.7, 146.3, 143.9, 141.9, 139.9 (d, J = 6.2 Hz, 1C), 130.3 (d, J = 7.5 Hz, 1C), 130.0, 129.2, 127.8, 124.2 (d, J = 2.9 Hz, 1C), 123.4, 119.8 (d, J = 21.4 Hz, 1C), 115.3 (d, J = 22.2 Hz, 1C), 105.5, 61.6, 60.9, 56.2, 16.7. ¹⁹F NMR (376.4 MHz, CDCl₃): δ –111.74. HRMS (ESI): m/z calcd for C₂₂H₂₁NaFO₅ (M+Na)⁺: 407.1271. Found: 407.1254.

(*E*)-1-(2-(3-(3-Methoxyphenyl)-3-oxoprop-1-en-1-yl)phenyl)-2-methylenebutan-1-one (7z).



This compound was prepared by following the general procedure-1 and isolated as pale-yellow liquid. 300 mg of **D** (Ar = C_6H_4 , $R^1 = Et$, $R^2 = 3$ -OMe C_6H_4) afforded 285 mg of 7z (55% yield). $R_f = 0.4$ (hexane/EtOAc = 8/2). IR (thin film, neat): v_{max}/cm^{-1} 3067, 2967, 1657, 1587, 1430, 1254, 976, 758. ¹H NMR (400 MHz, CDCl₃): δ 7.78 – 7.75 (m, 2H), 7.55 – 7.53

(m, 1H), 7.51 - 7.47 (m, 2H), 7.44 - 7.40 (m, 1H), 7.38 - 7.33 (m, 3H), 7.11 (dd, J = 8.2 Hz, 2.6 Hz, 1H), 5.96 (s, 1H), 5.59 (s, 1H), 3.86 (s, 3H), 2.49 (q, J = 7.4 Hz, 2H), 1.14 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 199.3, 190.2, 159.8, 151.0, 142.2, 140.6, 139.2, 133.7, 130.2, 129.5, 129.44, 129.40, 128.6, 127.1, 124.6, 121.1, 119.4, 112.8, 55.4, 23.7, 12.4. HRMS (ESI): m/z calcd for C₂₁H₂₀NaO₃ (M+Na)⁺: 343.1310. Found: 343.1315.

(*E*)-1-(2-(3-(3-Fluorophenyl)-3-oxoprop-1-en-1-yl)phenyl)-2-methylenebutan-1-one (7aa).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow



liquid. 300 mg of **D** (Ar = C₆H₄, R¹ = Et, R² = 3-FC₆H₄) afforded 250 mg of **7aa** (50% yield). R_f = 0.6 (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max}/cm^{-1} 3071, 2970, 1657, 1584, 1440, 1244, 976, 759. ¹H NMR (400 MHz, CDCl₃): δ 7.81 – 7.74 (m, 3H), 7.66 – 7.64 (m, 1H), 7.52 – 7.42 (m, 3H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.33 (d, *J* = 15.7 Hz, 1H), 7.28 – 7.24 (m, 1H), 5.98 (s, 1H), 5.60 (s, 1H), 2.49 (q, *J* =

7.4 Hz, 2H), 1.14 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 199.2, 189.1, 162.8 (d, J = 246.3 Hz, 1C), 151.0, 142.9, 140.7, 139.9 (d, J = 6.2 Hz, 1C), 133.5, 130.3 (d, J = 7.5 Hz, 1H), 130.3, 129.5, 129.4, 128.7, 127.1, 124.3 (d, J = 2.9 Hz, 1C), 124.0, 119.8 (d, J = 21.3 Hz, 1C), 115.3 (d, J = 22.2 Hz, 1C), 23.7, 12.4. ¹⁹F NMR (376.4 MHz, CDCl₃): δ –111.70. HRMS (ESI): m/z calcd for C₂₀H₁₇FNaO₂ (M+Na)⁺: 331.1110. Found: 331.1119.

(*E*)-2-Benzyl-1-(2-(3-oxo-3-phenylprop-1-en-1-yl)benzo[*b*]thiophen-3-yl)prop-2-en-1-one (7ab). This compound was prepared by following the general procedure-1 and isolated as pale-



yellow solid. 280 mg of **D** (Ar = Thianaphthene, $R^1 = CH_2Ph$, $R^2 = Ph$) afforded 310 mg of **7ab** (83% yield). $R_f = 0.5$ (hexane/EtOAc = 9/1). M.P = 114-116 °C. **IR (thin film, neat):** v_{max}/cm^{-1} 2924, 1737, 1653, 1457, 1205, 758. ¹H NMR (400 MHz, CDCl₃): δ 7.99 – 7.97 (m, 2H), 7.90 (dd, J = 15.3, 1.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.60 – 7.48 (m, 4H), 7.40 – 7.38 (m, 1H), 7.36 – 7.28 (m, 6H), 7.24 – 7.20 (m, 1H), 5.88 (s, 1H), 5.84 (s, 1H), 3.86 (s, 2H). ¹³**C NMR (100 MHz, CDCl₃):** δ 193.8, 189.2, 149.9, 140.5, 138.7, 138.7, 138.6, 138.2, 137.6, 135.2, 133.1, 131.7, 129.4 (2C), 128.7 (2C), 128.7 (2C), 128.5 (2C), 127.0, 126.5, 125.4, 125.1, 124.1, 122.2, 37.0. **HRMS (ESI):** m/z calcd for C₂₇H₂₀NaO₂S (M+Na)⁺: 431.1082. Found: 431.1095.

(E)-8-Benzylnona-3,8-diene-2,7-dione (7ac).



This compound was prepared by following the procedure described in Scheme 2S and isolated as colourless liquid. 100 mg of **G** afforded 50 mg of **7ac** (42% yield). $R_f = 0.4$ (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max}/cm^{-1} 3028, 2923, 1671, 1626, 1508, 1430, 1361, 1254, 1076, 975, 700. ¹H NMR (400 MHz, CDCl₃): δ 7.31 – 7.28 (m, 2H), 7.23 – 7.21 (m, 1H), 7.19 – 7.17 (m, 2H) 6.83 – 6.75 (m, 1H), 6.10 (s, 1H), 6.06 (d, J = 15.9 Hz, 1H), 5.69 (s, 1H),

3.62 (s, 2H), 2.89 (t, *J* = 7.1 Hz, 2H), 2.53 (qd, *J* = 6.9, 1.6 Hz, 2H), 2.23 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 199.3, 198.5, 148.0, 146.6, 138.8, 131.7, 129.0 (2C), 128.4 (2C), 126.3, 125.7, 37.1, 35.9, 26.9, 26.6. HRMS (ESI): *m*/*z* calcd for C₁₆H₁₈NaO₂ (M+Na)⁺: 265.1204. Found: 265.1198.

(E)-7-Benzyl-1-phenylocta-2,7-diene-1,6-dione (7ad).



This compound was prepared by following the procedure described in Scheme 2S and isolated as colourless liquid. 40 mg of **G** afforded 40 mg of **7ad** (65% yield). $R_f = 0.6$ (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max}/cm^{-1} 3028, 2926, 1669, 1619, 1578, 1448, 1285, 1076, 694. ¹H NMR (400 MHz, CDCl₃): δ 7.90 – 7.88 (m, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.25 (m, 2H), 7.20 – 7.15 (m, 3H), 7.04 – 6.96 (m, 1H), 6.87 (d, *J* = 15.4 Hz,

1H), 6.10 (s, 1H), 5.66 (s, 1H), 3.61 (s, 2H), 2.91 (t, J = 7.1 Hz, 2H), 2.62 (q, J = 6.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 199.3, 190.7, 148.1, 147.8, 138.9, 137.7, 132.7, 129.0 (2C), 128.57 (2C), 128.56 (2C), 128.4 (2C), 126.6, 126.3, 125.7, 37.1, 36.0, 27.0. HRMS (ESI): m/zcalcd for C₂₁H₂₀NaO₂ (M+Na)⁺: 337.1361. Found: 337.1352.

(*E*)-4-(4,5-Dimethoxy-2-(4-((4-methoxybenzyl)oxy)-2-methylenebutanoyl)phenyl)but-3en-2-one (7ae).



This compound was prepared by following the general procedure-2 and isolated as pale-yellow solid. 280 mg of N $(Ar = 4,5-(OMe)_2CH_2, R^1 = C_2H_4OPMB, R^2 = Me)$ afforded 310 mg of 7ae (83% yield). $R_f = 0.3$ (hexane/EtOAc = 6/4). M.P = 114-116 °C. IR (thin film, neat): v_{max}/cm^{-1} 3000, 2854, 1734, 1654, 1562, 1357, 1246, 818. ¹H NMR (400

MHz, CDCl₃): δ 7.66 (d, J = 16.2 Hz, 1H), 7.22 (d, J = 8.6 Hz, 2H), 7.14 (s, 1H), 6.95 (s, 1H), 6.84 (d, J = 8.5 Hz, 2H), 6.52 (d, J = 16.2 Hz, 1H), 6.03 (s, 1H), 5.64 (s, 1H), 4.45 (s, 2H), 3.95 (s, 3H), 3.789 (s, 3H), 3.783 (s, 3H), 3.70 (t, J = 6.2 Hz, 2H), 2.81 (t, J = 6.2 Hz, 2H), 2.31 (s, 3H). ¹³C **NMR (100 MHz, CDCl₃):** δ 198.8, 198.1, 159.1, 150.8, 149.7, 147.1, 141.4, 132.9, 130.2, 130.1, 129.2 (2C), 127.9, 127.4, 113.7 (2C), 112.6, 108.6, 72.5, 68.0, 56.1, 56.0, 55.2, 31.8, 26.7. **HRMS (ESI):** m/z calcd for C₂₅H₂₈NaO₆ (M+Na)⁺: 447.1784. Found: 447.1784.

(Z)-3-(2-Methacryloylphenyl)-1-phenylbut-2-en-1-one (10a).



This compound was prepared by following the general procedure-2 and isolated as pale-yellow liquid. 200 mg of L ($R^1 = Ph$, $R^2 = Me$) afforded 150 mg of **10a** (72% yield). $R_f = 0.4$ (hexane/EtOAc = 9/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3051, 2760, 1687, 1655, 1448, 1261, 823. ¹H **NMR (400 MHz, DMSO-***d*₆): δ 7.90 (d, J = 6.7 Hz, 2H), 7.69 – 7.50 (m, 6H), 7.46 (d, J = 7.4 Hz, 1H), 6.77 (q, J = 1.3 Hz, 1H), 6.05 (s, 1H), 5.49 (s, 1H), 2.41 (d, J = 1.3 Hz, 3H), 1.88 (s, 3H). ¹³C **NMR (100 MHz, DMSO-***d*₆): δ 199.9, 190.4, 155.7,

145.2, 143.2, 138.6, 138.3, 133.4, 130.7, 129.70, 129.2 (2C), 128.7, 128.5, 128.4, 128.3 (2C), 124.8, 21.3, 17.5. **HRMS (ESI):** *m/z* calcd for C₂₀H₁₈NaO₂(M+Na)⁺: 313.1204. Found: 313.1176.

(Z)-3-(2-(2-Benzylacryloyl)phenyl)-1-phenylbut-2-en-1-one (10b).



This compound was prepared by following the general procedure-2 and isolated as pale-yellow liquid. 220 mg of L ($R^1 = Ph$, $R^2 = CH_2Ph$) afforded 170 mg of **10b** (74% yield). $R_f = 0.6$ (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max}/cm^{-1} 3061, 2853, 1689, 1659, 1494, 1283, 757. ¹H **NMR (400 MHz, CDCl_3):** δ 7.74 – 7.72 (m, 2H), 7.40 (tt, J = 7.3 Hz, 1.1 Hz, 1H), 7.36 – 7.29 (m, 3H), 7.26 – 7.24 (m, 1H), 7.20 – 7.13 (m, 3H), 7.11 – 7.07 (m, 2H), 7.04 – 7.02 (m, 2H), 6.75 (q, J = 1.3 Hz, 1H), 5.72 (s, 1H), 5.57 (s, 1H), 3.54

(s, 2H), 2.18 (d, *J* = 1.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 198.4, 190.1, 155.4, 147.5, 141.8, 138.8, 138.3, 137.1, 132.4, 131.0, 130.4, 129.17 (2C), 129.12, 128.4 (2C), 128.38 (2C), 128.35 (2C), 127.7, 126.3, 126.2, 122.9, 37.2, 28.2. HRMS (ESI): *m/z* calcd for C₂₆H₂₃O₂(M+H)⁺: 367.1698. Found: 367.1687.

4-(2-(2-Benzylacryloyl)phenyl)pent-3-en-2-one (10c).



This compound was prepared by following the general procedure-2 and isolated as pale-yellow liquid. 300 mg of L ($R^1 = Me$, $R^2 = CH_2Ph$) afforded 250 mg of **10c** (80% yield). $R_f = 0.5$ (hexane/EtOAc = 8/2). **IR** (**thin film, neat**): v_{max}/cm^{-1} 3063, 2915, 1686, 1658, 1430, 1210, 983, 832. ¹H NMR (400 MHz, CDCl₃): δ 7.47 – 7.41 (m, 1H), 7.37 – 7.36 (m, 2H), 7.31 – 7.26 (m, 3H), 7.22 – 7.17 (m, 3H), 6.03 (q, *J* = 1.3 Hz, 1H),

5.64 (s, 1H), 5.53 (s, 1H), 3.67 (s, 2H), 2.36 (d, *J* = 1.3 Hz, 3H), 2.12 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 199.2, 198.1, 154.5, 149.4, 143.3, 138.3, 137.9, 130.2, 129.3 (2C), 129.1, 128.6, 128.6 (2C), 127.8, 127.7, 127.6, 126.4, 37.1, 32.0, 21.0. HRMS (ESI): *m/z* calcd for C₂₁H₁₉O₂(M-H)⁺: 303.1385. Found: 303.1367.

(E)-1-(Benzo[b]thiophen-2-yl)-3-(2-(2-benzylacryloyl)phenyl)but-2-en-1-one (10d).



This compound was prepared by following the general procedure-2 and isolated as pale-yellow liquid. 170mg of L (Ar = C₆H₄, R¹ = CH₂Ph, R² = 2-Thianaphthene) afforded 310 mg of 10d (83% yield). R_f = 0.5 (hexane/EtOAc = 8/2). IR (thin film, neat): v_{max}/cm^{-1} 3060, 2939, 1643, 1596, 1454, 1173, 823. ¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, *J* = 9.0 Hz, 2H), 7.80 (s, 1H), 7.52 – 7.48

(m, 1H), 7.45 - 7.35 (m, 5H), 7.19 - 7.13 (m, 2H), 7.10 - 7.04 (m, 3H), 6.75 (q, J = 1.2 Hz, 1H), 5.63 (s, 1H), 5.56 (s, 1H), 3.63 (s, 2H), 2.52 (d, J = 1.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 199.6, 184.0, 156.7, 149.8, 146.4, 143.3, 142.6, 139.4, 138.2, 138.0, 130.2, 129.24 (2C), 129.20, 128.57, 128.54 (3C), 128.1, 127.7, 127.3, 126.3, 126.1, 124.9, 124.0, 122.9, 37.1, 21.3. HRMS (ESI): m/z calcd for C₂₈H₂₂NaO₂S (M+Na)⁺: 445.1238. Found: 445.1225.

8a-Methyl-2-phenyl-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8b).

This compound was prepared by following the general procedure-4 and isolated as white solid.



30 mg of **7b** afforded 15 mg of **8b** (53% yield). $R_f = 0.7$ (hexane/EtOAc = 19/1). M.P = 76-78 °C. **IR (thin film, neat):** v_{max}/cm^{-1} 3028, 2922, 1712, 1651, 1508, 1286, 979, 755. ¹H NMR (400 MHz, CDCl₃): δ 7.74 (d, J = 7.6 Hz, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.40 – 7.36 (m, 3H), 7.29 – 7.19 (m, 3H), 6.04 (s, 1H), 3.66 (d, J = 9.6

Hz, 1H), 3.52 (ddd, *J* = 16.3, 9.7, 2.3 Hz, 1H), 2.89 (d, *J* = 16.4 Hz, 1H), 1.48 (s, 3H). ¹³C **NMR (100 MHz, CDCl₃):** δ 207.7, 157.0, 141.1, 135.3 (2C), 135.1, 128.5, 128.3 (2C), 127.9, 127.8, 126.0, 125.8 (2C), 124.3, 65.0, 48.7, 38.9, 20.2. **HRMS (ESI):** *m/z* calcd for C₁₉H₁₇O (M+H)⁺: 261.1279. Found: 261.1277.

8a-Ethyl-2-phenyl-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8c).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



liquid. 40 mg of 7c afforded 24 mg of 8c (63% yield). $R_f = 0.6$ (hexane/EtOAc = 19/1). IR (thin film, neat): v_{max}/cm^{-1} 3057, 2962, 1704, 1603, 1493, 1279, 992, 793. ¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, J = 7.6 Hz, 1H), 7.62 (t, J = 7.4 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.38 – 7.35 (m, 3H), 7.29 – 7.19 (m, 3H), 6.00 (s, 1H), 3.77 (d, J = 9.4

Hz, 1H), 3.47 (ddd, J = 16.5, 9.8, 2.2 Hz, 1H), 2.87 (d, J = 16.5 Hz, 1H), 1.98 – 1.86 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 207.7, 157.5, 141.8, 135.7, 135.3, 135.2, 128.3 (2C), 127.8 (2C), 127.3, 126.0, 125.8 (2C), 124.1, 70.1, 45.5, 39.4, 26.9, 9.4. HRMS (ESI): m/z calcd for C₂₀H₁₉O (M+H)⁺: 275.1436. Found: 275.1433.

2-Phenyl-8a-(3-phenylpropyl)-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8d).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



solid. 32 mg of **7d** afforded 19 mg of **8d** (62% yield). $R_f = 0.6$ (hexane/EtOAc = 19/1). M.P = 115-117 °C. **IR** (thin film, neat): v_{max}/cm^{-1} 3027, 2852, 1706, 1603, 1452, 1281, 963, 751. ¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, J = 7.6 Hz, 1H), 7.61 (td, J = 7.7, 1.1 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.38 – 7.34 (m, 3H), 7.28 – 7.18 (m, 5H),

7.16 – 7.13 (m, 3H), 6.00 (s, 1H), 3.75 (d, J = 8.6 Hz, 1H), 3.45 (ddd, J = 16.5, 9.8, 2.4 Hz, 1H), 2.85 (dt, J = 16.5, 1.6 Hz, 1H), 2.63 (t, J = 7.6 Hz, 2H), 2.01 – 1.88 (m, 2H), 1.73 – 1.54 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 207.6, 157.4, 142.1, 141.7, 135.5, 135.3, 135.2,

128.44 (2C), 128.40 (2C), 128.3 (2C), 127.9, 127.8, 127.2, 126.0, 125.8 (3C), 124.2, 69.4, 45.9, 39.4, 36.4, 33.9, 27.3. **HRMS (ESI):** *m/z* calcd for C₂₇H₂₄NaO (M+Na)⁺: 387.1725. Found: 387.1725.

8a-((Benzyloxy)methyl)-2-phenyl-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8e).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



liquid. 49 mg of **7e** afforded 21 mg of **8e** (46% yield). $R_f = 0.5$ (hexane/EtOAc = 19/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3057, 2855, 1708, 1604, 1494, 1283, 958, 750. ¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, J = 7.6 Hz, 1H), 7.64 – 7.61 (m, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.39 –

7.35 (m, 3H), 7.31 – 7.19 (m, 8H), 5.93 (s, 1H), 4.55 (d, $J_{AB} = 12.3$ Hz, 1H), 4.50 (d, $J_{AB} = 12.3$ Hz, 1H), 4.10 – 4.06 (m, 2H), 3.65 (d, J = 9.2 Hz, 1H), 3.51 (ddd, J = 16.5, 9.8, 2.4 Hz, 1H), 2.90 (d, J = 16.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 205.7, 157.8, 143.7, 138.2, 135.6, 135.3, 135.1, 128.4 (2C), 128.3 (2C), 128.0, 127.8, 127.57 (2C), 127.55, 126.0, 125.8 (2C), 124.2, 123.7, 73.4, 71.1, 70.5, 44.4, 39.0. HRMS (ESI): m/z calcd for C₂₆H₂₃O₂ (M+H)⁺: 367.1698. Found: 367.1694.

8a-(2-(Benzyloxy)ethyl)-2-phenyl-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8f).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



liquid. 40 mg of **7f** afforded 25 mg of **8f** (65% yield). $R_f = 0.4$ (hexane/EtOAc = 19/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3030, 2916, 1706, 1604, 1455, 1219, 963, 750. ¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, J = 7.6 Hz, 1H), 7.63 (td, J = 7.6, 1.1 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.39 – 7.35 (m, 3H), 7.30 – 7.20 (m, 6H), 7.14 – 7.12 (m, 2H), 5.99

(s, 1H), 4.41 - 4.34 (m, 2H), 3.99 (d, J = 9.2 Hz, 1H), 3.60 (t, J = 6.3 Hz, 2H), 3.47 (ddd, J = 16.5, 9.8, 2.4 Hz, 1H), 2.83 (d, J = 16.4, 1.4 Hz, 1H), 2.27 - 2.23 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 207.2, 157.7, 142.3, 138.2, 135.3, 135.2 (2C), 128.3 (2C), 128.2 (2C), 127.9, 127.7, 127.5 (2C), 127.4, 126.8, 126.0, 125.8 (2C), 124.2, 73.2, 68.0, 67.6, 46.4, 39.3, 33.6. HRMS (ESI): m/z calcd for $C_{27}H_{25}O_2$ (M+H)⁺: 403.1674. Found: 403.1663.

8a-(2-((4-Methoxybenzyl)oxy)ethyl)-2-phenyl-3a,8a-dihydrocyclopenta[*a*]inden-8(3*H*)one (8g). This compound was prepared by following the general procedure-4 and isolated as pale-yellow



liquid. 50 mg of **7g** afforded 38 mg of **8g** (78% yield). $R_f = 0.4$ (hexane/EtOAc = 9/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3052, 2854, 1705, 1606, 1463, 1279, 896, 735. ¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, J = 7.6 Hz, 1H), 7.60 – 7.60 (m, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.38 – 7.35 (m, 3H), 7.29 – 7.19 (m, 3H), 7.05 (d, J = 8.5 Hz, 2H), 6.75 (d,

J = 8.6 Hz, 2H), 5.98 (s, 1H), 4.32 (d, $J_{AB} = 11.4$ Hz, 1H), 4.28 (d, $J_{AB} = 11.4$ Hz, 1H), 3.97 (d, J = 9.2 Hz, 1H), 3.76 (s, 3H), 3.56 (t, J = 6.2 Hz, 2H), 3.45 (ddd, J = 16.4, 9.7, 2.3 Hz, 1H), 2.82 (d, J = 16.4 Hz, 1H), 2.27 – 2.18 (m, 2H). ¹³**C** NMR (100 MHz, CDCl₃): δ 207.2, 159.0, 157.8, 142.2, 135.32, 135.30, 135.2, 130.3, 129.2 (2C), 128.3 (2C), 127.8, 127.7, 126.9, 126.0, 125.8 (2C), 124.2, 113.6 (2C), 72.8, 68.0, 67.3, 55.2, 46.4, 39.3, 33.6. HRMS (ESI): *m/z* calcd for C₂₈H₂₆NaO₃ (M+Na)⁺: 433.1780. Found: 433.1764.

8a-Benzyl-4-fluoro-2-phenyl-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8h).

This compound was prepared by following the general procedure-4 and isolated as white solid.



30 mg of **7h** afforded 26 mg of **8h** (90% yield). $R_f = 0.5$ (hexane/EtOAc = 20/1). M.P = 118-120 °C. **IR (thin film, neat):** v_{max}/cm^{-1} 3029, 2852, 1714, 1616, 1479, 1265, 914, 752. ¹H NMR (400 MHz, CDCl₃): δ 7.53 (d, J = 7.4 Hz, 1H), 7.36 – 7.31 (m, 3H), 7.28 – 7.21 (m, 4H), 7.20 – 7.12

(m, 5H), 6.08 (s, 1H), 3.92 (d, J = 7.5 Hz, 1H), 3.23 (d, $J_{AB} = 13.7$ Hz, 1H), 3.18 (d, $J_{AB} = 13.7$ Hz, 1H), 2.99 (ddd, J = 16.9, 9.6, 2.5 Hz, 1H), 2.84 (d, J = 16.7 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 205.7 (d, J = 2.7 Hz, 1C), 160.1 (d, J = 248.9 Hz, 1C), 143.0, 142.2 (d, J = 17.2 Hz, 1C), 138.2 (d, J = 14.7 Hz, 1C), 137.5, 135.0, 129.9 (2C), 129.89, 129.82, 128.4 (2C), 128.2 (2C), 128.0, 126.4 (d, J = 4.3 Hz, 1C), 125.9 (2C), 121.5 (d, J = 20.0 Hz, 1C), 120.0 (d, J = 3.8 Hz, 1C), 70.6, 41.8, 39.6, 37.6. ¹⁹F NMR (376.4 MHz, CDCl₃): δ –118.94. HRMS (ESI): m/z calcd for C₂₅H₁₉FNaO (M+Na)⁺: 377.1318. Found: 377.1315.

8a-Benzyl-4-fluoro-2-(3-methoxyphenyl)-3a,8a-dihydrocyclopenta[*a*]inden-8(3*H*)-one (8i).

This compound was prepared by following the general procedure-4 and isolated as white solid. 40 mg of **7i** afforded 32 mg of **8i** (83% yield). $R_f = 0.4$ (hexane/EtOAc = 19/1). M.P = 125-127 °C. **IR (thin film, neat):** v_{max}/cm^{-1} 3029, 2848, 1711, 1601, 1478, 1264, 1045, 758. ¹H NMR



(400 MHz, CDCl₃): δ 7.53 (d, J = 7.4 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.24 – 7.13 (m, 7H), 6.91 (d, J = 7.7 Hz, 1H), 6.84 (s, 1H), 6.77 (dd, J = 8.1, 2.1 Hz, 1H), 6.07 (s, 1H), 3.91 (d, J = 8.6 Hz, 1H), 3.77 (s, 3H), 3.22 (d, J_{AB} = 12.3 Hz, 1H), 3.18 (d, J_{AB} = 12.3 Hz, 1H), 2.98 (ddd, J = 16.9, 9.6, 2.3 Hz, 1H), 2.82

(d, J = 16.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 205.7 (d, J = 2.6 Hz, 1C), 160.1 (d, J = 249.0 Hz, 1C), 159.5, 142.9, 142.2 (d, J = 17.1 Hz, 1C), 138.2 (d, J = 4.6 Hz, 1C), 137.4, 136.4, 129.9 (2C), 129.8, 129.3, 128.2 (2C), 126.8, 126.5, 121.5 (d, J = 20.1 Hz, 1C), 120.0 (d, J = 3.7 Hz, 1C), 118.4, 113.6, 111.4, 70.5, 55.2, 41.8, 39.6, 37.6. ¹⁹F NMR (376.4 MHz, CDCl₃): δ –118.91. HRMS (ESI): m/z calcd for C₂₆H₂₁FO₂ (M)⁺: 384.1526. Found: 384.1505.

8a-Benzyl-7-methyl-2-phenyl-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8j).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



solid. 30 mg of **7j** afforded 22 mg of **8j** (76% yield). $R_f = 0.6$ (hexane/EtOAc = 19/1). M.P = 121-123 °C. **IR (thin film, neat):** v_{max}/cm^{-1} 3028, 2922, 1702, 1594, 1494, 1260, 937, 757. ¹H NMR (400 MHz, CDCl₃): δ 7.41 (t, J = 7.5 Hz, 1H), 7.31 – 7.29 (m, 2H), 7.26 – 7.22 (m, 3H), 7.21 – 7.16 (m, 5H), 7.15 – 7.11 (m, 1H), 7.07 (d,

J = 7.3 Hz, 1H), 6.10 (s, 1H), 3.73 (d, J = 9.0 Hz, 1H), 3.18 (q, J = 13.6 Hz, 2H), 2.90 (ddd, J = 16.4, 9.4, 2.4 Hz, 1H), 2.69 (d, J = 16.4 Hz, 1H), 2.64 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 207.9, 158.0, 142.6, 139.2, 138.1, 135.3, 134.4, 132.7, 129.9 (2C), 129.6, 128.3 (2C), 128.0 (2C), 127.8, 127.7, 126.2, 125.8 (2C), 123.2, 70.2, 44.4, 39.8, 39.3, 18.4. HRMS (ESI): m/z calcd for C₂₆H₂₃O (M+H)⁺: 351.1749. Found: 351.1740.

5,7-Dimethoxy-8a-methyl-2-phenyl-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8k).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



solid. 50 mg of **7k** afforded 24 mg of **8k** (55% yield). $R_f = 0.4$ (hexane/EtOAc = 8/2). M.P = 103-105 °C. **IR (thin film, neat):** v_{max}/cm^{-1} 3053, 2844, 1692, 1587, 1458, 1215, 968, 755. ¹H NMR (400 MHz, CDCl₃): δ 7.37 – 7.35 (m, 2H), 7.29 – 7.25 (m, 2H), 7.22

- 7.18 (m, 1H), 6.55 (s, 1H), 6.30 (s, 1H), 6.09 (s, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.55 – 3.43 (m, 2H), 2.86 (d, *J* = 15.8 Hz, 1H), 1.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 204.1, 167.4, 162.2, 159.7, 140.4, 135.5, 129.3, 128.3 (2C), 127.6, 125.7 (2C), 117.1, 101.2, 97.7, 65.3,

55.79, 55.76, 48.6, 39.0, 20.5. **HRMS (ESI):** m/z calcd for C₂₁H₂₁O₃ (M+H)⁺: 321.1491. Found: 321.1508.

9a-Methyl-8-phenyl-7,9a-dihydropentaleno[2,1-a]naphthalen-10(6bH)-one (8l).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



solid. 30 mg of **7l** afforded 20 mg of **8l** (70% yield). $R_f = 0.5$ (hexane/EtOAc = 19/1). M.P = 129-131 °C. **IR (thin film, neat):** v_{max}/cm^{-1} 2957, 2869, 1695, 1461, 1150, 968. ¹H NMR (400 MHz, CDCl₃): δ 9.16 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.86

(d, J = 8.1 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.59 – 7.51 (m, 2H), 7.37 – 7.35 (m, 2H), 7.27 – 7.17 (m, 3H), 6.13 (s, 1H), 3.74 (dd, J = 10.0, 2.1 Hz, 1H), 3.54 (ddd, J = 16.5, 10.0, 2.3 Hz, 1H), 2.93 (dt, J = 16.5, 2.0 Hz, 1H), 1.54 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 208.5, 159.4, 140.6, 136.4, 135.3, 133.0, 129.6, 129.05, 129.01, 128.8, 128.3 (2C), 128.1, 127.8, 126.6, 125.7 (2C), 124.1, 123.2, 65.2, 48.7, 38.2, 20.4. HRMS (ESI): m/z calcd for C₂₃H₁₈NaO (M+Na)⁺: 333.1255. Found: 333.1253.

8a-Benzyl-5-methoxy-2-phenyl-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8m).

This compound was prepared by following the general procedure-4 and isolated as white solid.



30 mg of **7m** afforded 22 mg of **8m** (76% yield). $R_f = 0.5$ (hexane/EtOAc = 9/1). M.P = 124-126 °C. **IR** (thin film, neat): v_{max}/cm^{-1} 3028, 2921, 1697, 1596, 1447, 1252, 971, 752. ¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, J = 8.1 Hz, 1H), 7.32 – 7.30 (m, 2H),

7.27 – 7.23 (m, 2H), 7.22 – 7.20 (m, 1H), 7.18 – 7.16 (m, 4H), 7.15 – 7.11 (m, 1H), 6.88 – 6.86 (m, 2H), 6.13 (s, 1H), 3.84 (s, 3H), 3.74 (d, J = 9.2 Hz, 1H), 3.21 (d, $J_{AB} = 13.6$ Hz, 1H), 3.16 (d, $J_{AB} = 13.6$ Hz, 1H), 2.95 (ddd, J = 16.4, 9.6, 2.4 Hz, 1H), 2.71 (d, J = 16.4 Hz, 1H). ¹³C **NMR (100 MHz, CDCl₃):** δ 205.3, 165.8, 160.1, 142.2, 138.0, 135.3, 129.9 (2C), 128.5, 128.3 (2C), 128.0 (2C), 127.8, 127.7, 126.2, 125.9, 125.8 (2C), 115.6, 109.2, 70.7, 55.6, 44.9, 39.7, 38.9. **HRMS (ESI):** m/z calcd for C₂₆H₂₂NaO₂ (M+Na)⁺: 389.1517. Found: 389.1518.

9a-Benzyl-8-phenyl-7,9a-dihydropentaleno[2,1-a]naphthalen-10(6bH)-one (8n).

This compound was prepared by following the general procedure-4 and isolated as white solid.



40 mg of **7n** afforded 27 mg of **8n** (70% yield). $R_f = 0.7$ (hexane/EtOAc = 19/1). M.P = 136-138 °C. **IR** (thin film, neat): v_{max}/cm^{-1} 3028, 2849, 1691, 1626, 1439, 1210, 933, 757. ¹H NMR (400 MHz, CDCl₃): δ 9.18 (d, J = 8.3 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.66 (t, J = 8.1 Hz, 1H), 7.54 – 7.48

(m, 2H), 7.31 - 7.29 (m, 2H), 7.25 - 7.15 (m, 7H), 7.14 - 7.10 (m, 1H), 6.20 (s, 1H), 3.87 (dd, J = 9.7, 1.6 Hz, 1H), 3.30 (d, $J_{AB} = 13.7$ Hz, 1H), 3.25 (d, $J_{AB} = 13.7$ Hz, 1H), 3.01 (ddd, J = 16.5, 9.8, 2.4 Hz, 1H), 2.78 (d, J = 16.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 207.7, 159.6, 142.1, 138.1, 136.4, 135.3, 132.9, 129.9 (2C), 129.5, 129.1, 129.0, 128.3 (2C), 128.1 (3C), 127.9, 127.8, 126.6, 126.2, 125.8 (2C), 124.2, 123.2, 70.6, 45.0, 39.8, 38.3. HRMS (ESI): m/z calcd for C₂₉H₂₂NaO (M+Na)⁺: 409.1568. Found: 409.1566.

9a-Benzyl-8-(4-chlorophenyl)-7,9a-dihydropentaleno[2,1-*a*]naphthalen-10(6*bH*)-one (80).

This compound was prepared by following the general procedure-4 and isolated as white solid.



40 mg of **70** afforded 24 mg of **80** (62% yield). R_f = 0.7 (hexane/EtOAc = 19/1). M.P = 121-123 °C. **IR (thin film, neat):** v_{max}/cm⁻¹ 3029, 2849, 1691, 1626, 1492, 1265, 931, 736. ¹H NMR (400 MHz, CDCl₃): δ 9.17 (d, *J* = 8.3 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.69

- 7.65 (m, 1H), 7.55 - 7.48 (m, 2H), 7.22 - 7.10 (m, 9H), 6.18 (s, 1H), 3.88 (dd, J = 9.8, 1.8 Hz, 1H), 3.27 (s, 2H), 2.96 (ddd, J = 16.5, 9.8, 2.4 Hz, 1H), 2.73 (dt, J = 16.4, 1.6 Hz, 1H). ¹³C **NMR (100 MHz, CDCl₃):** δ 207.4, 159.5, 141.0, 138.0, 136.5, 133.8, 133.5, 132.9, 129.9 (2C), 129.5, 129.1, 129.0, 128.6, 128.4 (2C), 128.18, 128.15 (2C), 127.0 (2C), 126.7, 126.3, 124.1, 123.1, 70.6, 45.0, 39.8, 38.3. **HRMS (ESI):** m/z calcd for C₂₉H₂₁ClNaO (M+Na)⁺: 443.1179. Found: 443.1187.

8a-Benzyl-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8p).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow solid. 40 mg of **7p** afforded 7 mg of **8p** (18% yield). $R_f = 0.6$ (hexane/EtOAc = 19/1). M.P = 81-83 °C. **IR (thin film, neat):** v_{max} /cm⁻¹ 2925, 1712, 1651, 1458, 1283, 762. ¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, J = 7.6 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.23



126.2, 125.9, 124.0, 70.2, 45.2, 39.4, 38.7. HRMS (ESI): *m/z* calcd for C₁₉H₁₆NaO (M+Na)⁺: 283.1099. Found: 283.1095.

8a-Benzyl-2-methyl-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8q).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



(hexane/EtOAc = 19/1). IR (thin film, neat): v_{max}/cm^{-1} 3031, 2913, 1709, 1605, 1328, 940, 702. ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, J = 7.6 Hz, 1H), 7.56 (td, J = 7.7, 1.0 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.21 -7.12 (m, 5H), 5.30 (s, 1H), 3.64 (d, J = 9.1 Hz, 1H), 3.10 (d, $J_{AB} = 13.6$ Hz, 1H), 3.06 (d, J_{AB} = 13.6 H =13.6 Hz, 1H), 2.50 (dd, J = 16.8, 9.5 Hz, 1H), 2.17 (d, J = 16.8 Hz, 1H), 1.56 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 207.9, 157.3, 141.7, 138.2, 135.4, 135.0, 130.0 (2C), 127.9 (2C), 127.6, 127.0, 126.1, 125.8, 123.9, 70.0, 45.8, 42.6, 39.5, 16.5. HRMS (ESI): m/z calcd for C₂₀H₁₈NaO (M+Na)⁺: 297.1255. Found: 297.1253.

8a-Benzyl-2-(p-tolyl)-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8r).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



liquid. 30 mg of 7r afforded 21 mg of 8r (72% yield). $R_f = 0.7$ (hexane/EtOAc = 19/1). IR (thin film, neat): v_{max}/cm^{-1} 3029, 2850, 1705, 1603, 1494, 1280, 937, 738. ¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, J = 7.6 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.43 (d, J = 7.6 Hz,

liquid. 25 mg of 7q afforded 14 mg of 8q (59% yield). $R_f = 0.7$

1H), 7.34 (t, J = 7.4 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.17 – 7.18 (m, 5H), 7.14 – 7.10 (m, 1H), 7.05 (d, J = 7.8 Hz, 2H), 6.04 (s, 1H), 3.77 (d, J = 9.3 Hz, 1H), 3.19 (s, 2H), 2.96 - 2.90 (m, 1H), 2.69 (d, J = 16.4 Hz, 1H), 2.29 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 207.1, 157.2, 142.6, 138.0, 137.7, 135.4, 135.2, 132.5, 129.9 (2C), 129.0 (2C), 128.0 (2C), 127.8, 126.4, 126.2, 125.9, 125.7 (2C), 124.1, 70.3, 45.0, 39.6, 39.1, 21.1. HRMS (ESI): m/z calcd for $C_{26}H_{23}O(M+H)^+$: 351.1749. Found: 351.1747.

8a-Benzyl-2-(4-chlorophenyl)-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8s).
This compound was prepared by following the general procedure-4 and isolated as white solid.



40 mg of **7s** afforded 31 mg of **8s** (80% yield). $R_f = 0.7$ (hexane/EtOAc = 19/1). M.P = 146-148 °C. **IR** (thin film, neat): v_{max} /cm⁻¹ 3030, 2849, 1707, 1651, 1493, 1281, 963, 757. ¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, J = 7.6 Hz, 1H), 7.58 (td, J= 7.6, 1.0 Hz, 1H), 7.43 (d, J = 7.7 Hz, 1H), 7.35 (t, J = 7.4 Hz,

1H), 7.22 (s, 4H), 7.19 – 7.13 (m, 5H), 6.08 (s, 1H), 3.80 (d, J = 9.2 Hz, 1H), 3.20 (s, 2H), 2.92 (ddd, J = 16.4, 9.5, 2.6 Hz, 1H), 2.67 (d, J = 16.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 206.7, 157.0, 141.6, 137.8, 135.39, 135.31, 133.7, 133.6, 129.9 (2C), 128.5 (2C), 128.1 (2C), 128.0, 127.9, 127.0 (2C), 126.3, 125.9, 124.2, 70.5, 45.0, 39.6, 39.0. HRMS (ESI): m/z calcd for C₂₅H₁₉ClNaO (M+Na)⁺: 393.1022. Found: 393.1012.

8a-Benzyl-2-(3-methoxyphenyl)-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8t).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



liquid. 29 mg of 7t afforded 21 mg of 8t (74% yield). $R_f = 0.5$ (hexane/EtOAc = 19/1). IR (thin film, neat): $v_{max}/cm^{-1} 3027$, 2852, 1706, 1603, 1494, 1281, 963, 751. ¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, J = 7.6 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.19 – 7.18

(m, 5H), 7.16 – 7.13 (m, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.83 (s, 1H), 6.77 – 6.74 (m, 1H), 6.10 (s, 1H), 3.78 (d, *J* = 8.6 Hz, 1H), 3.76 (s, 3H), 3.20 (s, 2H), 2.95 (ddd, *J* = 16.4, 9.5, 2.1 Hz, 1H), 2.70 (d, *J* = 16.4 Hz, 1H). ¹³**C NMR (100 MHz, CDCl₃):** δ 207.0, 159.5, 157.1, 142.6, 137.9, 136.7, 135.37, 135.30, 129.9 (2C), 129.3, 128.1 (2C), 127.8, 127.7, 126.3, 125.95, 124.1, 118.4, 113.4, 111.4, 70.4, 55.2, 44.9, 39.6, 39.1. **HRMS (ESI):** *m/z* calcd for C₂₆H₂₂NaO₂ (M+Na)⁺: 389.1517. Found: 389.1514.

8a-Benzyl-2-(3-fluorophenyl)-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8u).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



solid. 40 mg of **7u** afforded 29 mg of **8u** (75% yield). R_f = 0.6 (hexane/EtOAc = 19/1). M.P = 109-111 °C. **IR (thin film, neat):** v_{max}/cm⁻¹ 3064, 2849, 1706, 1605, 1491, 1222, 965, 755. ¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.58 (td, *J* = 7.6, 1.1 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.23

- 7.12 (m, 6H), 7.08 – 7.06 (m, 1H), 6.98 – 6.94 (m, 1H), 6.91 – 6.86 (m, 1H), 6.12 (s, 1H), 3.80 (d, J = 9.0 Hz, 1H), 3.20 (s, 2H), 2.93 (ddd, J = 16.4, 9.5, 2.4 Hz, 1H), 2.68 (dt, J = 16.4, 1.5 Hz, 1H). ¹³**C NMR (100 MHz, CDCl₃):** δ 206.7, 162.8, 157.0, 141.7 (d, J = 2.4 Hz, 1C), 137.7, 137.5 (d, J = 7.5 Hz, 1C), 135.4, 135.3, 129.9 (2C), 129.8 (d, J = 8.2 Hz, 1C), 128.7, 128.1 (2C), 128.0, 126.4, 125.9, 124.2, 121.5 (d, J = 2.8 Hz, 1C), 114.6 (d, J = 20.4 Hz, 1C), 112.7 (d, J = 21.8 Hz, 1C), 70.4, 44.9, 39.6, 39.0. ¹⁹**F NMR (376.4 MHz, CDCl₃):** δ –113.25. **HRMS (ESI):** m/z calcd for C₂₅H₂₀FO (M+H)⁺: 355.1498. Found: 355.1498.

8a-Benzyl-2-(3,4-dimethoxyphenyl)-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8v).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



solid. 19 mg of **7v** afforded 10 mg of **8v** (54% yield). $R_f = 0.3$ (hexane/EtOAc = 8/2). M.P = 106-108 °C. **IR** (thin film, neat): v_{max}/cm^{-1} 3058, 2838, 1704, 1602, 1461, 1262, 938, 757. ¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, J = 7.6 Hz, 1H), 7.56 (td, J = 8.0, 1.0 Hz, 1H), 7.43 (d, J = 8.3 Hz, 1H), 7.33 (t,

J = 7.4 Hz, 1H), 7.19 – 7.17 (m, 4H), 7.15 – 7.10 (m, 1H), 6.88 (d, J = 1.8 Hz, 1H), 6.81 (dd, J = 8.3, 1.9 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 5.99 (s, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.78 (d, J = 9.1 Hz, 1H), 3.24 (d, $J_{AB} = 13.6$ Hz, 1H), 3.18 (d, $J_{AB} = 13.6$ Hz, 1H), 2.97 (ddd, J = 16.3, 9.5, 2.4 Hz, 1H), 2.68 (d, J = 16.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 207.2, 157.2, 149.0, 148.7, 142.3, 138.0, 135.4, 135.2, 129.9 (2C), 128.3, 128.1 (2C), 127.8, 126.3, 125.9, 125.6, 124.1, 118.5, 110.7, 108.8, 70.3, 55.9, 55.8, 44.9, 39.6, 39.2. HRMS (ESI): *m/z* calcd for C₂₇H₂₅O₃ (M+H)⁺: 397.1804. Found: 397.1811.

8a-Benzyl-2-(furan-2-yl)-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8w).

This compound was prepared by following the general procedure-4 and isolated as brown



liquid. 50 mg of **7w** afforded 30 mg of **8w** (62% yield). $R_f = 0.7$ (hexane/EtOAc = 19/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3061, 2922, 1700, 1604, 1495, 1373, 1245, 846. ¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, J = 7.6 Hz, 1H), 7.56 (td, J = 7.5, 1.1 Hz, 1H), 7.41 (d, J = 8.4 Hz, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.29 (d, J = 1.4 Hz, 1H), 7.22

-7.16 (m, 4H), 7.15 - 7.11 (m, 1H), 6.29 (dd, J = 3.3, 1.8 Hz, 1H), 6.13 (d, J = 3.3 Hz, 1H), 5.99 (s, 1H), 3.76 (d, J = 9.0 Hz, 1H), 3.22 (d, $J_{AB} = 13.7$ Hz, 1H), 3.16 (d, $J_{AB} = 13.7$ Hz, 1H), 2.87 (ddd, J = 16.3, 9.4, 2.4 Hz, 1H), 2.62 (dt, J = 16.3, 1.5 Hz, 1H). 13 C NMR (100 MHz,

CDCl₃): δ 206.6, 156.8, 150.8, 142.3, 137.9, 135.3, 135.2, 132.8, 129.9 (2C), 128.1 (2C), 127.9, 126.3, 125.9, 125.8, 124.2, 111.0, 107.5, 70.4, 45.0, 39.5, 38.1. **HRMS (ESI):** *m/z* calcd for C₂₃H₁₉O₂ (M+H)⁺: 327.1385. Found: 327.1362.

8a-Benzyl-2-(thiophen-2-yl)-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8x).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



liquid. 50 mg of 7x afforded 23 mg of 8x (51% yield). $R_f = 0.7$ (hexane/EtOAc = 19/1). IR (thin film, neat): v_{max}/cm^{-1} 3065, 2919, 2849, 1705, 1602, 1462, 1326, 1213, 851. ¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, J = 7.6 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.42 (d, J = 7.7 Hz, 1H), 7.34 (t, J = 7.3 Hz, 1H), 7.21 – 7.12 (m, 6H), 6.89

(t, *J* = 3.8 Hz, 1H), 6.84 (d, *J* = 3.5 Hz, 1H), 5.94 (s, 1H), 3.77 (d, *J* = 9.2 Hz, 1H), 3.19 (s, 2H), 2.94 (ddd, *J* = 16.3, 9.5, 2.2 Hz, 1H), 2.70 (d, *J* = 16.3 Hz, 1H). ¹³**C NMR (100 MHz, CDCl₃):** δ 206.6, 156.8, 139.4, 137.8, 136.8, 135.3 (2C), 129.9 (2C), 128.1 (2C), 127.9, 127.2, 126.6, 126.3, 125.9, 125.0, 124.6, 124.2, 70.4, 45.1, 39.9, 39.6. **HRMS (ESI):** *m/z* calcd for C₂₃H₁₉OS (M+H)⁺: 343.1157. Found: 343.1133.

2-(3-Fluorophenyl)-5,6,7-trimethoxy-8a-methyl-3a,8a-dihydrocyclopenta[*a*]inden-8(*3H*)-one (8y).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



solid. 48 mg of **7y** afforded 25 mg of **8y** (54% yield). $R_f = 0.6$ (hexane/EtOAc = 7/3). M.P = 142-144 °C. **IR (thin film, neat):** v_{max} /cm⁻¹ 3067, 2866, 1697, 1481, 1149, 914, 819. ¹H **NMR (400 MHz, CDCl₃):** δ 7.25 - 7.21 (m, 1H), 7.17 - 7.13 (m, 1H), 7.06 - 7.03(m, 1H), 6.94 - 6.87 (m, 1H), 6.73

(s, 1H), 6.10 (s, 1H), 4.04 (s, 3H), 3.96 (s, 3H), 3.83 (s, 3H), 3.56 – 3.53 (m, 1H), 3.44 (ddd, J = 16.0, 9.7, 2.2 Hz, 1H), 2.83 (dt, J = 16.1, 1.48 Hz, 1H), 1.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 203.7, 162.8 (d, J = 243.6 Hz, 1C), 160.2, 154.9, 151.8, 141.1, 139.5 (d, J = 2.5 Hz, 1C), 137.6 (d, J = 7.5 Hz, 1C), 130.5, 129.8 (d, J = 7.5 Hz, 1C), 121.4 (d, J = 2.7 Hz, 1C), 120.6, 114.5 (d, J = 21.2 Hz, 1C), 112.6 (d, J = 21.8 Hz, 1C), 103.0, 65.5, 61.9, 61.4, 56.3, 48.2, 39.0, 20.4. ¹⁹F NMR (376.4 MHz, CDCl₃): δ –113.34. HRMS (ESI): *m*/*z* calcd for C₂₂H₂₁FNaO₄ (M+Na)⁺: 391.1322. Found: 391.1300.

8a-Ethyl-2-(3-methoxyphenyl)-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8z).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



solid. 40 mg of 7z afforded 23 mg of 8z (61% yield). M.P = 94-96 °C. $R_f = 0.4$ (hexane/EtOAc = 19/1). IR (thin film, neat): v_{max}/cm^{-1} 3068, 2852, 1705, 1606, 1488, 1275, 965, 778. ¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, J = 7.6 Hz, 1H), 7.63

(td, J = 7.7, 1.1 Hz, 1H), 7.55 – 7.53 (m, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.19 (t, J = 7.9 Hz, 1H), 6.97 (d, J = 7.8 Hz, 1H), 6.90 (t, J = 2.3 Hz, 1H), 6.77 (dd, J = 8.2, 2.4 Hz, 1H), 5.99 (s, 1H), 3.78 (s, 3H), 3.76 (d, J = 9.6 Hz, 1H), 3.46 (ddd, J = 16.5, 9.8, 2.4 Hz, 1H), 2.86 (dt, J = 16.5, 1.6 Hz, 1H), 1.93 (qd, J = 7.4, 3.1 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 207.7, 159.5, 157.5, 141.7, 136.7, 135.7, 135.2, 129.3, 127.8, 127.7, 126.0, 124.1, 118.4, 113.4, 111.3, 70.1, 55.2, 45.4, 39.5, 26.9, 9.4. HRMS (ESI): m/z calcd for C₂₁H₂₁O₂ (M+H)⁺: 305.1542. Found: 305.1546.

8a-Ethyl-2-(3-fluorophenyl)-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8aa).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



liquid. 40 mg of **7aa** afforded 24 mg of **8aa** (62% yield). $R_f = 0.7$ (hexane/EtOAc = 19/1). **IR** (thin film, neat): v_{max}/cm^{-1} 3068, 2852, 1705, 1606, 1488, 1275, 965, 738. ¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, J = 7.6 Hz, 1H), 7.64 (td, J = 8.0, 1.1 Hz, 1H),

7.54 (d, J = 8.4 Hz, 1H), 7.38 (t, J = 7.3 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.15 (dt, J = 7.8, 1.2 Hz, 1H), 7.06 – 7.02 (m, 1H), 6.93 – 6.88 (m, 1H), 6.02 (s, 1H), 3.78 (d, J = 9.6 Hz, 1H), 3.44 (ddd, J = 16.4, 9.8, 2.4 Hz, 1H), 2.85 (dt, J = 16.6, 1.7 Hz, 1H), 1.93 (qd, J = 7.5, 1.7 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H). ¹³**C NMR (100 MHz, CDCl₃):** δ 207.4, 162.8 (d, J = 243.8 Hz, 1C), 157.4, 140.8 (d, J = 2.3 Hz, 1C), 137.5 (d, J = 7.6 Hz, 1C), 135.6, 135.3, 129.8 (d, J = 8.2 Hz, 1C), 128.7, 127.9, 126.0, 124.2, 121.5 (d, J = 2.9 Hz, 1C), 114.5 (d, J = 21.1 Hz, 1C), 112.6 (d, J = 21.9 Hz, 1C), 70.1, 45.4, 39.4, 26.9, 9.4. ¹⁹**F NMR (376.4 MHz, CDCl₃):** δ –113.30. **HRMS (ESI):** m/z calcd for C₂₀H₁₈FO (M+H)⁺: 293.1342. Found: 293.1363.

9a-Benzyl-2-phenyl-3a,9a-dihydrobenzo[b]pentaleno[2,1-d]thiophen-9(3H)-one (8ab).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



solid. 30 mg of **7ab** afforded 10 mg of **8ab** (34% yield). $R_f = 0.7$ (hexane/EtOAc = 19/1). M.P = 138-140 °C. IR (thin film, neat): v_{max}/cm^{-1} 3058, 2849, 1693, 1494, 1268, 1054, 758. ¹H NMR (400 MHz, CDCl₃): δ 8.23 (d, J = 7.8 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H),

7.44 (td, J = 7.2, 1.0 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.29 – 7.23 (m, 3H), 7.21 – 7.12 (m, 5H), 6.24 (s, 1H), 3.99 (dd, J = 9.9, 2.3 Hz, 1H), 3.32 (d, $J_{AB} = 13.8$ Hz, 1H), 3.21 (d, $J_{AB} = 13.8$ Hz, 1H), 2.96 (ddd, J = 16.6, 10.0, 2.5 Hz, 1H), 2.79 (dt, J = 16.1, 1.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 198.9, 176.6, 144.1, 141.6, 137.6, 137.1, 135.1, 131.5, 129.8 (2C), 128.4 (2C), 128.2 (2C), 128.0, 127.2, 126.4, 125.9, 125.8 (2C), 125.6, 123.2, 123.2, 76.6, 44.1, 39.8, 38.1. HRMS (ESI): *m/z* calcd for C₂₇H₂₀SNaO (M+Na)⁺: 415.1133. Found: 415.1134.

6a-Benzyl-5-methyl-3,3a,4,6a-tetrahydropentalen-1(2*H*)-one (8ac).

This compound was prepared by following the general procedure-4 and isolated as colourless



liquid. 37 mg of **7ac** afforded 15 mg of **8ac** (41% yield). $R_f = 0.5$ (hexane/EtOAc = 40/1). **IR (thin film, neat):** v_{max}/cm^{-1} 2957, 2930, 1732, 1622, 1495, 1454, 1159, 1030, 702. ¹H NMR (400 MHz, CDCl₃): δ 7.24 – 7.15 (m, 3H), 7.10 – 7.08 (m, 2H), 5.12 (s, 1H), 3.01 (d, J = 13.2 Hz, 1H),

2.69 – 2.64 (m, 2H), 2.30 – 2.23 (m, 2H), 1.96 – 1.87 (m, 2H), 1.82 – 1.77 (m, 1H), 1.66 (s, 3H) 1.46 – 1.41 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 220.7, 142.8, 137.9, 130.1 (2C), 127.9 (2C), 126.1 (2C), 68.5, 43.9, 42.3, 40.8, 38.3, 26.9, 16.5. HRMS (ESI): *m/z* calcd for C₁₆H₁₇O (M-H)⁺: 225.1279. Found: 225.1264.

6a-Benzyl-5-phenyl-3,3a,4,6a-tetrahydropentalen-1(2H)-one (8ad).

This compound was prepared by following the general procedure-4 and isolated as colourless



liquid. 40 mg of **7ad** afforded 20 mg of **8ad** (52% yield). $R_f = 0.5$ (hexane/EtOAc = 9/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3028, 2927, 1732, 1599, 1494, 1454, 1163, 1029, 754, 693. ¹H NMR (400 MHz, CDCl₃): δ 7.41 - 7.39 (m, 2H), 7.35 - 7.32 (m, 2H), 7.29 - 7.25 (m, 2H), 7.24 - 7.20

(m, 2H), 7.16 - 7.14 (m, 2H), 5.96 (s, 1H), 3.16 (d, J = 13.3 Hz, 1H), 2.87 - 2.75 (m, 3H), 2.46 (d, J = 15.9 Hz, 1H), 2.38 - 2.31 (m, 1H), 2.04 - 1.88 (m, 2H), 1.55 - 1.48 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 219.8, 143.8, 137.5, 135.5, 130.0 (2C), 128.4 (2C), 128.1 (2C), 127.8,

126.6, 126.3, 125.8 (2C), 69.0, 41.5, 40.9, 40.0, 38.4, 26.9. **HRMS (ESI):** m/z calcd for $C_{21}H_{21}O (M+H)^+$: 289.1592. Found: 289.1591.

4-Benzoyl-2-benzylcyclohept-4-en-1-one (9ad).

This compound was prepared by following the general procedure-4 and isolated as colourless



liquid. 40 mg of **7ad** afforded 7 mg of **9ad** (17% yield). $R_f = 0.3$ (hexane/EtOAc = 9/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3027, 2924, 2853, 1704, 1647, 1495, 1447, 1271, 701, 693. ¹H NMR (400 MHz, CDCl₃): δ 7.61 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.3 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.30 – 7.26 (m, 2H), 7.21 – 7.19 (m, 3H), 6.61 (t, J = 5.3 Hz, 1H), 3.21 – 3.05 (m, 2H), 2.96 (dd, J = 16.2, 3.1 Hz, 1H), 2.81 – 2.65 (m, 3H), 2.62 – 2.46 (m, 3H). ¹³C NMR (100 MHz, CDCl₃):

δ 212.5, 197.9, 143.6, 141.0, 139.2, 137.8, 131.8, 129.3, 129.2, 128.4, 128.2, 126.3, 53.1, 40.6, 37.0, 28.6, 25.3. **HRMS (ESI):** *m/z* calcd for C₂₁H₂₀NaO₂ (M+Na)⁺: 337.1361. Found: 337.1352.

3a,8a-Dimethyl-2-phenyl-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (11a).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



liquid. 30 mg of **10a** afforded 19 mg of **11a** (67% yield). $R_f = 0.7$ (hexane/EtOAc = 19/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3031, 2868, 1710, 1604, 1494, 1289, 863. ¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, J = 7.6 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.38 – 7.32 (m, 3H), 7.28 – 7.24 (m, 2H), 7.21 – 7.18 (m, 1H), 5.99 (s, 1H), 3.13 (s, 2H), 1.46 (s, 3H), 1.35 (s,

3H). ¹³C NMR (100 MHz, CDCl₃): δ 207.7, 162.2, 140.4, 135.2 (2C), 134.0, 130.0, 128.3 (2C), 127.8, 127.8, 125.6 (2C), 124.2, 124.0, 66.9, 50.9, 47.3, 24.5, 16.6. HRMS (ESI): *m/z* calcd for C₂₀H₁₉O (M+H)⁺: 275.1436. Found: 275.1431.

8a-Benzyl-3a-methyl-2-phenyl-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (11b).

This compound was prepared by following the general procedure-4 and isolated as white solid.



30 mg of **10b** afforded 26 mg of **11b** (90% yield). $R_f = 0.6$ (hexane/EtOAc = 19/1). M.P = 137-139 °C **IR** (thin film, neat): v_{max}/cm^{-1} 3029, 2842, 1705, 1602, 1494, 1284, 932, 749. ¹H NMR (400 MHz, **CDCl₃**): δ 7.73 (d, J = 7.6 Hz, 1H), 7.60 (td, J = 7.8, 1.1 Hz, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.31 – 7.26 (m, 4H), 7.24- 7.14

(m, 6H), 6.04 (s, 1H), 3.43 (d, J = 14.5 Hz, 1H), 3.08 - 3.01 (m, 2H), 2.87 (dd, J = 16.4, 2.4 Hz, 1H), 1.51 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 206.6, 162.2, 141.6, 138.3, 135.2, 135.2, 133.9, 130.6 (2C), 129.2, 128.3 (2C), 127.9, 127.8 (3C), 126.0, 125.7 (2C), 124.0, 124.0, 70.8, 52.2, 47.5, 37.1, 25.0. **HRMS (ESI):** *m/z* calcd for C₂₆H₂₃O (M+H)⁺: 351.1749. Found: 351.1742.

8a-Benzyl-2,3a-dimethyl-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (11c).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow

liquid. 40 mg of 10c afforded 28 mg of 11c (71% yield). $R_f = 0.5$



(hexane/EtOAc = 19/1). IR (thin film, neat): v_{max}/cm^{-1} 3062, 2870, 1706, 1602, 1495, 1218, 817. ¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, J = 7.6 Hz, 1H), 7.60 (td, J = 7.7, 1.2 Hz, 1H), 7.47 (d, J = 7.7 Hz, 1H), 7.36 (td, J = 7.6, 1.0 Hz, 1H), 7.28 – 7.21 (m, 4H), 7.19 – 7.15 (m, 1H), 5.24 (s, 1H), 3.29 (d, J = 14.6 Hz, 1H), 2.93 (d, J = 14.6 Hz, 1H), 2.52 – 2.38 (m, 2H), 1.55 (s, 3H), 1.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 207.4, 162.4, 140.6, 138.7, 135.0, 133.9, 130.6 (2C), 128.9, 127.7, 127.6 (2C), 125.8, 123.9, 123.8, 70.7, 53.0, 51.2, 36.8, 24.9, 16.6. HRMS (ESI): m/z calcd for C₂₁H₂₀NaO (M+Na)⁺: 311.1412. Found: 311.1411.

2-(Benzo[b]thiophen-2-yl)-8a-benzyl-3a-methyl-3a,8a dihydrocyclopenta[a]inden-8(3H)one (11d).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



liquid. 33 mg of 10d afforded 22 mg of 11d (69% yield). $R_f =$ 0.5 (hexane/EtOAc = 19/1). IR (thin film, neat): v_{max}/cm^{-1} 3061, 2843, 1708, 1603, 1558, 1433, 1205, 827. ¹H NMR (400 **MHz, CDCl₃**): δ 7.75 (d, J = 7.6 Hz, 1H), 7.70 – 7.68 (m, 1H),

7.64 - 7.60 (m, 2H), 7.55 (d, J = 7.9 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.31 - 7.29 (m, 2H), 7.26 - 7.14 (m, 5H), 6.99 (s, 1H), 6.00 (s, 1H), 3.46 (d, J = 14.6 Hz, 1H), 3.12 (d, J = 16.2 Hz, 1H), 3.02 (d, J = 14.6 Hz, 1H), 2.87 (dd, J = 16.1, 2.4 Hz, 1H), 1.53 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 8 205.9, 161.9, 139.8, 139.36, 139.31, 138.0, 136.4, 135.4, 133.8, 131.4, 130.6 (2C), 128.1, 127.9 (2C), 126.1, 124.8, 124.4, 124.1, 124.0, 123.5, 122.1, 121.4, 71.1, 52.6, 47.9, 37.0, 25.0. HRMS (ESI): *m/z* calcd for C₂₈H₂₃OS (M+H)⁺: 407.1470. Found: 407.1455.

8a-(2-Hydroxyethyl)-2-phenyl-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8gA').

This compound was prepared by following the procedure described in Scheme 7S and isolated



as colourless liquid. 250 mg of **8g** afforded 140 mg of **8gA'** (79% yield). $R_f = 0.4$ (hexane/EtOAc = 7/3). **IR (thin film, neat):** v_{max}/cm^{-1} 3419, 3054, 2921, 1700, 1603, 1493, 1280, 964, 748. ¹H NMR (400 MHz, **CDCl3**): δ 7.73 (d, J = 7.6 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.54 – 7.52 (d, J = 7.7 Hz, 1H), 7.39 – 7.36 (m, 3H), 7.29 – 7.20 (m, 3H), 6.08 (s, 1H),

3.90 – 3.83 (m, 2H), 3.78 – 3.72 (m, 1H), 3.52 (ddd, *J* = 16.5, 9.6, 2.4 Hz, 1H), 2.89 (d, *J* = 16.5 Hz, 1H), 2.59 (brs, 1H), 2.24 – 2.17 (m, 1H), 2.14 – 2.08 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 208.0, 157.4, 142.6, 135.6, 135.0, 128.4 (2C), 128.1, 128.0, 126.3, 125.9, 125.9 (3C), 124.4, 68.1, 60.0, 47.1, 39.0, 36.6. HRMS (ESI): *m/z* calcd for C₂₀H₁₈NaO₂ (M+Na)⁺: 313.1204. Found: 313.1179.

2-Phenyl-8a-vinyl-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (12g).

This compound was prepared by following the procedure described in Scheme 7S and isolated



as pale-yellow liquid. 140 mg of **8gA'** afforded 106 mg of **12g** (83% yield). $R_f = 0.4$ (hexane/EtOAc = 19/1). **IR (thin film, neat):** v_{max}/cm^{-1} 2954, 2852, 1712, 1604, 1449, 1280, 902, 754. ¹H NMR (400 MHz, **CDCl₃):** δ 7.75 (d, J = 7.6 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.54 (d, J = 7.6

Hz, 1H), 7.40 – 7.37 (m, 3H), 7.30 – 7.20 (m, 3H), 6.19 – 6.12 (m, 2H), 5.35 – 5.27 (m, 2H), 3.92 (d, J = 9.2 Hz, 1H), 3.52 (ddd, J = 16.5, 9.6, 2.4 Hz, 1H), 2.91 (dt, J = 16.5, 1.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 205.4, 156.9, 142.6, 137.1, 135.5, 135.1, 134.9, 128.4 (2C), 128.1 (2C), 125.9, 125.9 (2C), 125.6, 124.5, 116.2, 71.7, 47.6, 38.9. HRMS (ESI): m/z calcd for C₂₀H₁₆NaO (M+Na)⁺: 295.1099. Found: 295.1076.

2-Phenyl-8,8a-divinyl-3,3a,8,8a-tetrahydrocyclopenta[a]inden-8-ol (13g).

This compound was prepared by following the procedure described in Scheme 7S and isolated



as colourless liquid. 55 mg of **12g** afforded 58 mg of **13g** (95% yield). $R_f = 0.3$ (hexane/EtOAc = 10/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3397, 3047, 2909, 1599, 1494, 1361, 1232, 1057, 965, 767. ¹H NMR (400 **MHz, CDCl₃):** δ 7.43 – 7.41 (m, 2H), 7.29 – 7.18 (m, 7H), 6.30 (s, 1H),

6.21 – 6.14 (m, 1H), 5.98 – 5.91 (m, 1H), 5.17 – 5.02 (m, 4H), 3.69 (d, *J* = 7.2 Hz, 1H), 3.27 – 3.20 (m, 1H), 2.99 (d, *J* = 16.6 Hz, 1H), 2.30 – 2.28 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 145.4, 144.6, 142.09, 142.05, 139.2, 135.8, 128.5, 128.3 (2C), 127.7, 127.6, 126.6, 125.9 (2C),

124.3, 123.8, 113.7, 112.1, 87.4, 72.0, 49.0, 39.7. **HRMS (ESI):** *m/z* calcd for C₂₂H₁₉O (M-H)⁺: 299.1436. Found: 299.1421.

2-Phenyl-3b,4,5,6-tetrahydrobenzo[*e*]-as-indacen-6a(1*H*)-ol (14g).

This compound was prepared by following the procedure described in Scheme 7S and isolated



as dark brown liquid. 40 mg of **13g** afforded 22 mg of **14g** (54% yield). $R_f = 0.5$ (hexane/EtOAc = 7/3). **IR (thin film, neat):** v_{max}/cm^{-1} 3516, 3044, 2907, 1605, 1502, 1462, 1263, 1014, 959, 774. ¹H NMR (400 MHz, CDCl₃): δ 7.64 - 7.62 (m, 1H), 7.57 - 7.55 (m, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.28 - 7.25 (m, 2H), 7.23 - 7.18 (m, 2H), 6.88 (s, 1H), 3.78 - 3.65 (m, 2H), 3.05

(brs, 1H), 2.52 – 2.41 (m, 1H), 2.05 – 2.01 (m, 1H), 1.92 – 1.82 (m, 3H), 1.64 -1.59 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 145.9, 144.9, 139.8, 135.8, 134.6, 130.5, 128.7 (2C), 128.0, 127.5, 126.9, 126.4, 125.5, 124.9 (2C), 122.0, 82.6, 48.0, 42.7, 38.8, 31.2, 21.8. HRMS (ESI): *m/z* calcd for C₂₂H₁₉O (M-H)⁺: 299.1436. Found: 299.1414.

5-Phenyl-1,2,3,6-tetrahydrobenzo[*e*]-*as*-indacene (15g). (NMR data of 15g was compared with the reported part structure in the literature)⁶

This compound was prepared by following the procedure described in Scheme 7S and isolated



as pale-yellow solid. 22 mg of **14g** afforded 15 mg of **15g** (72% yield). $R_f = 0.5$ (hexane/EtOAc = 99/1). M.P = 146-148 °C. **IR (thin film, neat):** v_{max}/cm^{-1} 2953, 2924, 2852, 1456, 1263, 1023, 895, 735. ¹H NMR (400 MHz, CDCl₃): δ 7.99 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.75 – 7.71 (m, 2H), 7.45 – 7.39 (m, 4H), 7.34 (s, 1H), 7.29 (d, J = 7.3 Hz, 1H),

4.11 (s, 2H), 3.30 (t, J = 7.4 Hz, 2H), 3.23 (t, J = 7.3 Hz, 2H), 2.32 (quint, J = 7.5 Hz, 2H). ¹³C **NMR (100 MHz, CDCl₃):** δ 146.4, 139.9, 139.1, 138.0, 136.2, 135.1, 129.1, 128.7 (2C), 128.6, 127.3, 125.59, 125.55 (2C), 125.4, 125.1, 124.4, 123.9, 38.0, 32.0, 31.3, 24.6. **HRMS (ESI):** m/z calcd for C₂₂H₁₇ (M-H)⁺: 281.1330. Found: 281.1316.

8a-Benzyl-1,2-dihydroxy-2-phenyl-2,3,3a,8a-tetrahydrocyclopenta[*a*]inden-8(*1H*)-one (16a).

⁶ (a) Mahecha-Mahecha, C.; Lecornué, F.; Akinari, S.; Charote, T.; Gamba-Sánchez, D.; Ohwada, T.; Thibaudeau, S. *Org. Lett.* **2020**, *22*, 6267–6271. (b) Zhou, Q.; Li, S.; Zhang, Y.; Wang, J. *Angew. Chem. Int. Ed.* **2017**, *56*, 16013–16017.

This compound was prepared by following the procedure described in Scheme 8S and isolated



as colourless liquid. 150 mg of 8a afforded 148 mg of 16a (90% yield). $R_f = 0.3$ (hexane/EtOAc = 8/2). IR (thin film, neat): v_{max}/cm^{-1} 3443, 3059, 2938, 1687, 1604, 1464, 1265, 929, 782. ¹H NMR (400 MHz, **CDCl₃**): δ 7.66 (d, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.37 (d, J

= 7.6 Hz, 1H), 7.33 - 7.25 (m, 5H), 7.23 - 7.16 (m, 6H), 4.62 (d, $J_{AB} = 6.1$ Hz, 1H), 4.55 (d, J = 6.1 Hz, 1H), 3.69 (t, J = 5.7 Hz, 1H), 3.17 (d, $J_{AB} = 13.6$ Hz, 1H), 3.13 (d, $J_{AB} = 13.7$ Hz, 1H), 2.35 – 2.31 (m, 1H), 2.14 – 2.13 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 212.3, 158.5, 143.2, 136.5, 136.3, 135.5, 130.2 (2C), 128.39 (2C), 128.34 (2C), 127.6, 127.3, 126.9, 125.5, 125.3 (2C), 123.5, 83.8, 82.5, 59.7, 44.3, 42.0, 40.3. HRMS (ESI): m/z calcd for C₂₅H₂₂NaO₃ (M+Na)⁺: 393.1467. Found: 393.1467.

3b-Benzyl-9a-phenyl-3b,8b,9,9a-tetrahydrobenzo[4,5]pentaleno[1,2-d][1,3]dioxole-2,4(3*aH*)-dione (17a).

This compound was prepared by following the procedure described in Scheme 8S and isolated



as colourless crystalline solid. 70 mg of 16a afforded 65 mg of 17a (86% yield). $R_f = 0.4$ (hexane/EtOAc = 8/2). M.P = 187-189 °C. IR (thin film, neat): v_{max}/cm^{-1} 3061, 1797, 1715, 1602, 1495, 1289, 1047, 756. ¹H NMR (400 MHz, CDCl₃): δ 7.82 (d, J = 7.6 Hz, 1H), 7.66 (t, J = 7.2 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.35 – 7.28 (m, 8H), 6.92 - 6.90 (m, 2H), 4.95 (s, 1H), 3.96 (d, J = 8.0 Hz, 1H), 3.54 (d, $J_{AB} = 13.9$ Hz, 1H), 3.19 $(d, J_{AB} = 13.9 \text{ Hz}, 1\text{H}), 2.96 (d, J = 15.5 \text{ Hz}, 1\text{H}), 2.63 (dd, J = 15.5, 8.2 \text{ Hz}, 1\text{H}).$ ¹³C NMR (100 MHz, CDCl₃): δ 201.7, 154.0, 152.4, 138.6, 136.3, 136.0, 135.8, 130.3 (2C), 129.1 (2C), 129.0 (3C), 128.9, 128.7, 127.4, 125.0, 124.4, 124.1, 95.7, 92.4, 65.9, 42.1, 38.6. HRMS (ESI): m/z calcd for C₂₆H₂₀NaO₄ (M+Na)⁺: 419.1259. Found: 419.1252.

8a-Allyl-2-phenyl-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (19g).

This compound was prepared by following the procedure described in Scheme 9S and isolated



as pale-yellow liquid. 150 mg of 8g afforded 60 mg of 19g (57% yield, after 3 steps). $R_f = 0.6$ (hexane/EtOAc = 8/2). IR (thin film, neat): v_{max}/cm^{-1} 3072, 2868, 1711, 1521, 1493, 1261, 858. ¹H NMR (400 MHz, **CDCl₃**): δ 7.73 (d, J = 7.6 Hz, 1H), 7.63 (td, J = 7.6, 1.0 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.40 - 7.36 (m, 3H), 7.30 - 7.120 (m, 3H), 6.03 (s,)

1H), 5.80 - 5.70 (m, 1H), 5.13 (dd, J = 16.9, 1.6 Hz, 1H), 5.03 (d, J = 11.9 Hz, 1H), 3.80 (d, J = 8.7 Hz, 1H), 3.44 (ddd, J = 16.5, 9.8, 2.4 Hz, 1H), 2.87 (dt, J = 16.5, 1.6 Hz, 1H), 2.71 - 2.59 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 206.9, 157.3, 142.3, 135.4, 135.3, 135.1, 134.1, 128.4 (2C), 127.95, 127.91, 126.7, 126.0, 125.8 (2C), 124.2, 118.1, 69.1, 45.3, 39.3, 38.5. HRMS (ESI): m/z calcd for C₂₁H₁₉O (M+H)⁺: 287.1436. Found: 287.1434.

2-phenyl-1,10b-dihydrodicyclopenta[*a*,*b*]inden-6a(4*H*)-ol (20g).

This compound was prepared by following the procedure described in Scheme 9S and isolated



as pale-yellow semi-solid. 45 mg of **19g** afforded 40 mg of **20g** (88% yield, over 2 steps). $R_f = 0.3$ (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max}/cm^{-1} 3397, 3047, 2841, 1599, 1494, 1264, 918, 725. ¹H NMR (400 MHz, CDCl₃): δ 7.45 – 7.39 (m, 3H), 7.30 – 7.19 (m, 6H), 6.22 (s, 1H),

5.96 – 5.88 (m, 2H), 3.48 – 3.39 (m, 2H), 2.93 (d, J = 14.9 Hz, 1H), 2.75 (d, $J_{AB} = 17.6$ Hz, 1H), 2.63 (d, J = 17.6 Hz, 1H), 2.07 (brs, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 146.8, 145.3, 142.5, 135.8, 134.7, 133.2, 128.5, 128.3 (2C), 127.7, 127.5, 127.0, 125.9 (2C), 124.4, 123.5, 96.3, 70.2, 54.1, 42.9, 40.4. HRMS (ESI): m/z calcd for C₂₁H₁₇ (M-OH)⁺: 269.1330. Found: 269.1329.

2-Phenyl-1,4,7,11b-tetrahydro-7a*H*-cyclopenta[*k*]fluoren-7a-ol (21g).

This compound was prepared by following the procedure described in Scheme 9S and isolated



as pale-yellow liquid. 33 mg of **19g** afforded 24 mg of **21g** (70% yield, over 2 steps). $R_f = 0.4$ (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max}/cm^{-1} 3400, 3039, 2839, 1598, 1494, 1264, 1036, 862. ¹H NMR (400 MHz, CDCl₃): δ 7.42 (d, J = 7.3 Hz, 2H), 7.35 – 7.33 (d, J = 8.8 Hz, 1H), 7.29 – 7.18 (m, 6H), 6.23 (s, 1H), 6.01 – 5.96 (m, 1H), 5.83 – 5.77

(m, 1H), 3.44 (d, J = 9.0 Hz, 1H), 3.34 (ddd, J = 16.0, 9.0, 2.1 Hz, 1H), 2.84 (d, J = 16.0 Hz, 1H), 2.70 – 2.64 (m, 1H), 2.59 – 2.53 (m, 1H), 2.47 – 2.41 (m, 1H), 2.32 – 2.27 (m, 1H), 1.97 (brs, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 148.5, 146.3, 141.5, 135.8, 129.2, 128.79, 128.73, 128.3 (2C), 127.6, 127.5, 127.3, 125.8 (2C), 124.1, 123.5, 85.0, 66.8, 52.4, 40.3, 38.3, 33.5. HRMS (ESI): m/z calcd for C₂₂H₁₉ (M-OH)⁺: 283.1487. Found: 283.1480.

21g' (minor): This compound was prepared by following the procedure described in Scheme



9S and isolated as pale-yellow liquid. 33 mg of **19g** afforded 5.5 mg of **21g'** (15% yield, over 2 steps). $R_f = 0.3$ (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max}/cm^{-1} 3415, 3038, 2842, 1595, 1490, 1270, 1055, 864. **¹H NMR (400 MHz, CDCl₃):** δ 7.34 – 7.32 (m, 3H), 7.30 – 7.25 (m, 2H), 7.25 – 7.19 (m, 3H), 7.17 – 7.14 (m, 1H), 6.06 (s, 1H), 5.95 – 5.85

(m, 2H), 3.58 (d, *J* = 6.6 Hz, 1H), 3.22 (ddd, *J* = 15.8, 6.7, 2.1 Hz, 1H), 2.96 – 2.87 (m, 3H), 2.79 – 2.73 (m, 1H), 2.24 – 2.19 (m, 1H), 1.86 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 147.8, 145.4, 140.1, 136.2, 132.0, 128.7, 128.2 (2C), 128.0, 127.3, 127.1, 125.6 (2C), 124.8, 124.4, 121.3, 80.7, 64.4, 47.9, 37.6, 34.1, 31.6. HRMS (ESI): *m*/*z* calcd for C₂₂H₂₀NaO (M+Na)⁺: 323.1412. Found: 323.1429.

2-Phenyl-1,7,8,12b-tetrahydrobenzo[*a*]cyclopenta[*c*]azulen-8a(4*H*)-ol (22g).

This compound was prepared by following the procedure described in Scheme 9S and isolated



as pale-yellow liquid. 31 mg of **19g** afforded 27 mg of **22g** (82% yield, over 2 steps). $R_f = 0.3$ (hexane/EtOAc = 9/1). **IR (thin film, neat):** v_{max}/cm^{-1} 3423, 3020, 2918, 2838, 1667, 1598, 1494, 1254, 862. ¹H **NMR (400 MHz, CDCl₃):** δ 7.42 - 7.39 (m, 2H), 7.29 - 7.24 (m, 6H), 7.21 - 7.18 (m, 1H), 6.30 (s, 1H), 5.60 - 5.53 (m, 2H), 3.76 (d, *J* = 8.2

Hz, 1H), 3.27 (ddd, *J* = 16.2, 8.4, 2.1 Hz, 1H), 2.91 – 2.82 (m, 2H), 2.54 – 2.48 (m, 1H), 2.27 – 2.06 (m, 4H), 1.73 – 1.61 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 146.8, 146.0, 140.4, 135.9, 131.0, 130.3, 128.7, 128.3 (2C), 127.6, 127.5, 126.3, 125.8 (2C), 124.3, 123.5, 86.8, 70.4, 49.5, 40.3, 37.7, 33.4, 25.9. HRMS (ESI): *m*/*z* calcd for C₂₃H₁₉ (M-OH)⁺: 297.1640. Found: 297.1640.

5,6-Dimethoxy-8a-(2-((4-methoxybenzyl)oxy)ethyl)-2-methyl-3a,8adihydrocyclopenta[a]inden-8(3*H*)-one (8ae).

This compound was prepared by following the general procedure-4 and isolated as pale-yellow



liquid. 50 mg of **7ae** afforded 22 mg of **8ae** (46% yield). $R_f = 0.5$ (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max}/cm^{-1} 3000, 2910, 1693, 1606, 1462, 1245, 1014, 820. ¹H NMR (400 MHz, **CDCl₃):** δ 7.12 – 7.09 (m, 3H), 6.85 (s, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.19 (s, 1H), 4.30 (s, 2H), 3.97 (s, 3H), 3.89 (s, 3H), 3.78 (s,

3H), 3.74 (dd, J = 9.6, 1.6 Hz, 1H), 3.50 (t, J = 6.3 Hz, 2H), 2.92 (dd, J = 17.5, 10.6 Hz, 1H), 2.25 (d, J = 16.8 Hz, 1H), 2.09 (t, J = 6.6 Hz, 2H), 1.64 (s, 3H). ¹³**C NMR (100 MHz, CDCl₃):** δ 206.9, 158.9, 155.7, 153.0, 149.5, 140.6, 130.4, 129.2 (2C), 127.8, 126.8, 113.6 (2C), 106.7, 104.3, 72.7, 68.0, 67.4, 56.2, 56.1, 55.2, 47.0, 42.5, 33.6, 16.6. **HRMS (ESI):** *m/z* calcd for C₂₅H₂₈NaO₅ (M+Na)⁺: 431.1834. Found: 431.1820.

8a-(2-Hydroxyethyl)-5,6-dimethoxy-2-methyl-3a,8a-dihydrocyclopenta[*a*]inden-8(3*H*)one (8aeA').

This compound was prepared by following the procedure described in Scheme 10S and



isolated as pale-red liquid. 180 mg of **8ae** afforded 100 mg of **8aeA'** (78% yield). $R_f = 0.3$ (hexane/EtOAc = 6/4). **IR** (thin film, **neat)**: v_{max}/cm^{-1} 3404, 2936, 1679, 1588, 1499, 1311, 1262, 1048, 757. ¹H NMR (400 MHz, CDCl₃): δ 7.10 (s, 1H), 6.85 (s, 1H), 5.31 (s, 1H), 3.96 (s, 3H), 3.87 (s, 3H), 3.79 – 3.75 (m, 1H), 3.70

- 3.66 (m, 1H), 3.60 (d, J = 9.4 Hz, 1H), 2.99 – 2.93 (m, 2H), 2.30 (d, J = 16.8 Hz, 1H), 2.07
- 2.01 (m, 1H), 1.96 – 1.89 (m, 1H), 1.63 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 207.7, 156.1, 152.8, 149.7, 141.2, 127.5, 126.3, 106.6, 104.5, 68.3, 59.9, 56.2, 56.1, 48.0, 42.1, 36.8, 16.7. HRMS (ESI): *m*/*z* calcd for C₁₇H₂₀NaO₄ (M+Na)⁺: 311.1259. Found: 311.1235.

8a-Allyl-5,6-dimethoxy-2-methyl-3a,8a-dihydrocyclopenta[a]inden-8(3H)-one (8aeB').

This compound was prepared by following the procedure described in Scheme 10S and



isolated as pale-yellow liquid. 67 mg of **8aeA**' afforded 52 mg of **8aeB**' (71% yield, after 2 steps). $R_f = 0.5$ (hexane/EtOAc = 8/2). **IR (thin film, neat):** v_{max}/cm^{-1} 2959, 2720, 1694, 1589, 1500, 1361, 1165, 913, 834. ¹H NMR (400 MHz, CDCl₃): δ 7.14 (s, 1H), 6.87 (s, 1H), 5.74 – 5.74 (m, 1H), 5.24 (s, 1H), 5.08 (d, J =

16.1 Hz, 1H), 4.99 (d, *J* = 10.1 Hz, 1H), 3.98 (s, 3H), 3.90 (s, 3H), 3.57 (d, *J* = 11.4 Hz, 1H), 2.94 – 2.87 (m, 1H), 2.51 (d, *J* = 7.2 Hz, 2H), 2.30 (d, *J* = 16.8 Hz, 1H), 1.65 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 206.8, 155.8, 152.7, 149.6, 140.7, 134.5, 127.9, 126.7, 117.5, 106.7, 104.4, 69.1, 56.2, 56.1, 45.9, 42.5, 38.6, 16.6. HRMS (ESI): *m/z* calcd for C₁₈H₂₁O₃ (M+H)⁺: 285.1491. Found: 285.1472.

8,9-Dimethoxy-2-methyl-1,10b-dihydrodicyclopenta[a,b]inden-6a(4H)-ol (20ae).

This compound was prepared by following the procedure described in Scheme 10S and



isolated as pale-yellow liquid. 52 mg of **8aeB**' afforded 42 mg of **20ae** (81% yield, over 2 steps). $R_f = 0.3$ (hexane/EtOAc = 6/4). IR (thin film, neat): v_{max}/cm^{-1} 3405, 3048, 2916, 1607, 1464, 1265, 1118, 735. ¹H NMR (400 MHz, CDCl₃): δ 6.90 (s, 1H), 6.68 (s,

1H), 5.89 (s, 2H), 5.34 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.28 (d, *J* = 8.4 Hz, 1H), 2.93 (dd, *J* = 16.4, 8.7 Hz, 1H), 2.63 – 2.52 (m, 2H), 2.36 (d, *J* = 16.4 Hz, 1H), 1.94 (brs, 1H), 1.73 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 149.7, 149.2, 141.4, 138.7, 136.9, 134.5, 132.9, 126.1, 106.9, 105.8, 95.9, 70.1, 56.0, 56.02, 55.07, 44.1, 43.0, 16.9. HRMS (ESI): *m*/*z* calcd for C₁₈H₁₉O₂ (M-OH)⁺: 267.1385. Found: 267.1387.

Copies of ¹H and ¹³C-NMR spectra of all new compounds reported in this study ¹H NMR (400 MHz, CDCl₃)









110 100 90 chemical shift (ppm)



S54





S56



110 100 90 chemical shift (ppm)



110 100 90 chemical shift (ppm)



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

¹⁹F NMR (376.4 MHz, CDCl₃)

JP-03-276.52.fid











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



S63

¹H NMR (400 MHz, CDCl₃)





S65





210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 chemical shift (ppm) ¹H NMR (400 MHz, DMSO-*d*₆)



¹H NMR (400 MHz, CDCl₃)





¹H NMR (400 MHz, CDCl₃)





S71





S72


JP-03-288-2.61.fid





¹³C NMR (100 MHz, CDCl₃)

















¹⁹F NMR (376.4 MHz, CDCl₃)

JP-03-351-1.21.fid



























S91















¹H NMR (400 MHz, CDCl₃)



¹⁹F NMR (376.4 MHz, CDCl₃)

JP-03-343-2.72.fid






































S113



¹⁹F NMR (376.4 MHz, CDCl₃)

JP-04-17.62.fid

























¹H NMR (400 MHz, CDCl₃)









110 100 90 chemical shift (ppm) ò -10





















¹H NMR (400 MHz, CDCl₃)







¹H NMR (400 MHz, CDCl₃) JP-04-48-1.10.fid ----7.1438 ----6.8773 ~ 3.9812 ~ 3.9013 ~ 3.503 ~ 3.503 ~ 3.503 ~ 3.503 ~ 2.8940 ~ 2.8940 ~ 2.87940 ~ 2.87940 ~ 2.87940 ~ 2.87940 ~ 2.87940 ~ 2.2777 ----0.0001 Ο -- 2.5237 5.7475 5.7264 5.7015 5.7015 5.6837 5.6837 5.6588 --5.1083 --5.0680 --5.0063 --4.9810 MeO Me Н MeÓ 8aeB' γ₩γ 2.9 2.04-5.7 5.5 5.4 5.3 5.2 chemical shift (ppm) 5.8 5.1 5.6 5.5 2.7 2.6 2.5 chemical shift (ppm) 5.0 2.8 2.4 2.3 i, i, ii ii يللله 111 1.01 2.04 1.17 1.18-1 1.00 년 1.01 년 1.07 년 3.11 ⊈ 3.24 ⊥ $1.01 \pm$ 3.11 - $1.12 \pm$ 1.03-4.5 4.0 3.5 chemical shift (ppm) 8.0 7.5 7.0 6.5 6.0 5.5 5.0 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ¹³C NMR (100 MHz, CDCl₃) JP-04-48-1.33.fid 56.2574 56.1294 ~45.9606 -42.5212 ~38.6355 0 II MeO Ме Ĥ MeO 8aeB' 110 100 90 chemical shift (ppm) 210 200 190 180 170 160 150 140 130 120 80 70 60 50 40 30 20 10 Ó -10

