Supporting Information

for

Phosphine-Catalyzed Intramolecular Vinylogous Aldol Reaction of \( \alpha \)-Substituted Enones

Atanu Mondal, Bishnupada Satpathi and S. S. V. Ramasastry*

Organic synthesis and catalysis lab, Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Mohali, Sector 81, S A S Nagar, Manauli PO, Punjab 140 306, India
E-mail: ramsastry@iisermohali.ac.in

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**General experimental methods:** All the reagents, solvents and catalysts employed in this study were procured from Sigma-Aldrich and were used without further purification. For thin-layer chromatography (TLC), silica aluminum foils with fluorescent indicator 254 nm (from Aldrich) were used, and compounds were visualized by irradiation with UV light and/or by treatment with a solution of p-anisaldehyde (23 mL), conc. H$_2$SO$_4$ (35 mL), and acetic acid (10 mL) in ethanol (900 mL) followed by heating with a heat 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 was obtained by distillation over sodium and stored over sodium wire. IR spectra were recorded on a Perkin–Elmer FT IR spectrometer as thin films or KBr pellets, as indicated, with $\nu_{\text{max}}$ in inverse centimeters. Melting points were recorded on a digital melting point apparatus Stuart SMP30. $^1$H NMR and $^{13}$C NMR spectra were recorded on a 400 MHz Bruker Biospin Avance III FT-NMR spectrometer. NMR shifts are reported as delta ($\delta$) units in parts per million (ppm) and coupling constants ($J$) are reported in Hertz (Hz). The following abbreviations are utilized to describe peak patterns when appropriate: br=broad, s=singlet, d=doublet, t=triplet, q=quartet and m=multiplet. Proton chemical shifts are given in $\delta$ relative to tetramethylsilane ($\delta$ 0.00 ppm) in CDCl$_3$ ($\delta$ 7.26 ppm). Carbon chemical shifts are internally referenced to the deuterated solvent signals in CDCl$_3$ ($\delta$ 77.1 ppm). Single crystal X-ray analysis was carried on a Rigaku XtaLAB mini X-ray diffractometer. High resolution mass spectra were recorded on a Waters QTOF mass spectrometer. Optical rotations were recorded on Rudolph APIII/2W instrument.
General procedure-1: Synthesis of enone-aldehydes 1a-t.

All the α-substituted enone-aldehydes were synthesized according to the procedures described in the literature.¹

Synthesis of 1a-d, 1f-k, and 1n-q:


Synthesis of 1e and 1l:

Synthesis of 1m and 1r:
Synthesis of 1s:

\[
\begin{align*}
\text{Br} & \quad \text{(CH}_2\text{OH)}_2 (1.5 \text{ eq}) \quad \text{cat. } \text{p-TSA} \quad \text{toluene, reflux} \quad 94\% \\
\text{Br} & \quad \text{CHO} (1.2 \text{ eq}) \quad \text{n-BuLi (1.2 eq)} \quad \text{dry THF, } -78 \degree \text{C} \quad 78\% \\
\text{CHO} & \quad \text{IBX (1.2 eq.)} \quad \text{EtOAc, reflux} \quad 64\% \\
\text{CHO} & \quad \text{cat. } \text{p-TSA} \quad \text{acetone, rt} \quad 89\% \\
\end{align*}
\]

Scheme 1S: Synthesis of \(\alpha\)-substituted enone-aldehydes 1a-t.

Synthesis of 1t:

\[
\begin{align*}
\text{CHO} & \quad \text{CHO} (1.2 \text{ eq}) \quad \text{LNMP, n-BuLi} \quad -78\degree \text{C, dry THF} \quad 69\% \\
\text{CHO} & \quad \text{IBX (1.2 eq.)} \quad \text{EtOAc, reflux} \quad 65\% \\
\end{align*}
\]

General procedure-2: Synthesis of biaryl enone-aldehydes 5a-c.

All the \(\alpha\)-substituted biaryl enone-aldehydes were synthesized according to the reported literature.\(^2\)

\[
\begin{align*}
\text{Br} & \quad \text{CHO} (1.1 \text{ eq}) \quad \text{PrMgBr (1.1 eq)} \quad \text{dry THF:Et}_2\text{O (1:1 v/v)} \quad -78\degree \text{C, 3 h, 75-80\%} \\
\text{R}^1 & \quad \text{R}^2 \quad \text{R}^1 \quad \text{R}^2 \quad \text{IBX (1.2 eq.), EtOAc reflux, 70-72\%} \\
\end{align*}
\]

Scheme 2S: Synthesis of the \(\alpha\)-substituted biaryl enone-aldehydes 5a-c.

General procedure-3: Optimization of the reaction parameters for 2a.

![Scheme 3S: Optimization of the reaction parameters for 2a](image)

An oven dried 5 mL glass vial was charged with 1a (20 mg, 1.0 eq, 0.1 mmol). An appropriate solvent (1 mL), and a catalyst (0.2 eq, 0.02 mmol) were introduced at room temperature (rt) and stirring continued until 1a disappeared as monitored by TLC. The reaction mixture was quenched with aqueous NH₄Cl (~1-2 mL) and extracted using ethyl acetate (2x3 mL). All the volatiles were removed under reduced pressure. The crude product was directly purified by silica gel chromatography using hexane/ethyl acetate (5:1) as eluent, to afford 2a as colorless oil.

General procedure-4: Evaluating the substrate scope for 2.

![Scheme 4S: Synthesis of cyclopentannulated arenes and heteroarenes 2 via IVAR](image)

An oven-dried 5 mL glass vial was charged with 1 (1.0 eq, 0.1 mmol), DMF (1.0 mL), and tributylphosphine (0.2 eq, 0.02 mmol) at room temperature (or 60 °C using a heating mantle) and stirred until 1 disappeared as monitored by TLC. Then the reaction mixture was quenched with aqueous NH₄Cl (~1-2 mL) and extracted using ethyl acetate (2x3 mL). The organic extracts were combined and dried over anhydrous sodium sulfate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate as an eluent to afford 2.
General procedure-5: Optimization of the reaction parameters for 6a.

An oven dried 5 mL glass vial was charged with 5a (20 mg, 1.0 eq, 0.07 mmol). An appropriate solvent (1 mL), and a catalyst (0.2 eq, 0.015 mmol) were introduced at room temperature (rt) and stirring continued at an appropriate temperature for 5 days. The reaction mixture was quenched with aqueous NH₄Cl (~1-2 mL) and extracted using ethyl acetate (2x3 mL). All the volatiles were removed under reduced pressure. The crude product was directly purified by silica gel chromatography using hexane/ethyl acetate (5:1) as eluent, to afford 6a as pale-yellow oil.

<table>
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<tr>
<th>Sl. No.</th>
<th>Lewis base (20 mol%)</th>
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<th>temperature</th>
<th>Time (d)</th>
<th>Yield (%)</th>
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<tr>
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<td>PBu₃</td>
<td>DMF</td>
<td>rt</td>
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<tr>
<td>2</td>
<td>PBu₃</td>
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<tr>
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<td>rt</td>
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<tr>
<td>4</td>
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<td>rt</td>
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<tr>
<td>5</td>
<td>PBu₃</td>
<td>1,2-DME</td>
<td>rt</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
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<td>rt</td>
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<tr>
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<td>DBU</td>
<td>DMF</td>
<td>rt</td>
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<tr>
<td>9</td>
<td>DBU</td>
<td>DMF</td>
<td>100 °C</td>
<td>5</td>
<td>64</td>
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Table1S: Optimization of the reaction parameters for 6a

General procedure-6: Evaluating the substrate scope for 6.

Scheme 6S: Synthesis of dibenzocycloheptanones 6 via IVAR
An oven-dried 5 mL glass vial was charged with 5 (1.0 eq, 0.1 mmol), DMF (1.0 mL), and tributylphosphine or DBU (0.2 eq, 0.02 mmol) at 100 °C (using a heating mantle) and stirred for 5 days. Then the reaction mixture was quenched with aqueous NH₄Cl (~1-2 mL) and extracted using ethyl acetate (2x3 mL). The organic extracts were combined and dried over anhydrous sodium sulfate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (10:1) as an eluent to afford 6.

**General procedure-7: Elaboration of 2 to benzannulated nine-membered carbocycles 8a-e.**

![Scheme 7S](image)

**Representative procedure:** An oven-dried 25 mL RB flask was charged with 2 (1.0 eq) in 10 mL dry THF and placed at 0 °C under N₂ atmosphere. Then, vinyl magnesium chloride (1.6 M in THF, 2.2 eq) was added dropwise at the same temperature and stirred for 20 min. Upon completion, the reaction mixture was quenched with aqueous NH₄Cl (~2-3 mL) and extracted with ethyl acetate (2x5 mL). The organic extracts were combined and dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was taken to the next step without further purification.

The crude product was dissolved in 7 mL dry THF and placed at 0 °C under N₂ atmosphere. 18-crown-6 (1.0 eq) and KH (2.2 eq, 30 wt% dispersion in mineral oil) were added and stirred for 15-20 min at room temperature until the allylic tert-alcohol disappeared as monitored by TLC. The mixture was quenched with aqueous NH₄Cl (~2-3 mL) and extracted with ethyl acetate (2x5 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (10:1) as eluent to afford benzannulated nine-membered carbocycles 8a-e (yield 48-75%, over 2 steps).
General procedure-8: Elaboration of 2 to 1,3,5-trienes (9a), 1-yn-3,5-dienes (11), 1,3-dienes (13) and 3-methylene indanols (15).

Representative procedure: An oven-dried 25 mL RB flask was charged with 2a (1.0 eq) in 10 mL dry THF and placed at 0 °C under N₂ atmosphere. The RMgX or RLi (2.2 eq) was added dropwise at the same temperature and stirred until 2a disappeared as monitored by TLC. Upon completion, the reaction mixture was quenched with aqueous NH₄Cl (~2-3 mL) and extracted with ethyl acetate (2x5 mL). The organic extracts were combined and dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was taken to the next step without further purification.

The crude product was dissolved in 5 mL dry 1,2-DCE and p-TSA (0.1 eq) was added and stirred for 5 min until the allylic tert-alcohol disappeared as monitored by TLC. The mixture was quenched with aqueous NH₄Cl (~2-3 mL) and extracted with ethyl acetate (2x5 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (20:1) as eluent to afford 9a, 11, 13, and 15 (yield 64-84%, over 2 steps).


Representative procedure for step-I (Scheme 9S): An oven-dried 25 mL RB flask was charged with 2a or 2d (1.0 eq) in 10 mL dry DCM and placed at 0 °C under N₂ atmosphere.
Boron trifluoride etherate (5 eq), and triethylsilane (10 eq) were added at the same temperature and stirred for 8 h until 2 disappeared as monitored by TLC. Upon completion, the reaction mixture was quenched with aqueous NH₄Cl (~2-3 mL) and extracted with DCM (2x5 mL). The organic extracts were combined and dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (10:1) as an eluent to afford the deoxygenated product 16 or 17 respectively.

**Representative procedure for step-II (Scheme 9S):** The deoxygenated product 16 or 17 (1 eq) was then dissolved in 8 mL 1,4-dioxane:water (3:1). 2,6-lutidine (3 eq) and OsO₄ (0.025 eq) were added and stirred for 8 h. The mixture was quenched with aqueous NaHSO₃ (~2-3 mL) and extracted with ethyl acetate (2x5 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was taken to the next step without further purification.

The crude product was dissolved in 5 mL MeOH and placed at 0 °C. NaBH₄ (1.5 eq) was added at the same temperature and stirred for 15 min until the aldehyde was disappeared as monitored by TLC. The mixture was quenched with aqueous NH₄Cl (~2-3 mL) and extracted with ethyl acetate (2x5 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (5:1) as eluent to afford 18 or 19 respectively (yield 73-75%, over 2 steps).
Trapping of the phosphonium intermediate with MeOH

**Scheme 10S:** Trapping of the phosphonium intermediate with MeOH and plausible mechanism for the formation of 4a.
A plausible mechanism for the formation of 4a is presented in Scheme 10S based on the experimental evidence and related literature reports. The α-substituted enone-aldehyde 1a can undergo a cascade phospha-Michael addition/aldol reaction to generate the zwitterionic species 1a1. Next, in the presence of methanol, 1a1 can form the ion pair 1a2, and elimination of phosphine by the methoxide delivers 2a (path A). On the other hand, the zwitterionic species 1a1 upon reaction with 1a and MeOH generates the ion pair 1a3 and 1a3’ (path B). Subsequently, 1a3 converts to 4a by protonation and 1a3’ generates 2a via phosphine elimination. An alternative mechanism for 4a can also involve the displacement of phosphine by methoxide as depicted in 1a4 (path C).

Spectroscopic data of all the new compounds synthesized during this study

2-(2-Methylbut-2-enoyl)benzaldehyde (1a).
This compound was prepared by following the general procedure-1 and isolated as colorless oil; 200 mg of A4 (R₁ = Me, R₃ = H) afforded 139 mg of 1a (86% yield). R_f = 0.5 (hexane/EtOAc = 10/1). IR (thin film, neat): ν_max/cm⁻¹ 2973, 1773, 1700, 1647, 1570, 978, 749. ¹H NMR (400 MHz, CDCl₃): δ 9.93 (s, 1H), 7.93 (dd, J = 7.2 and 1.1 Hz, 1H), 7.63-7.55 (m, 2H), 7.35-7.33 (m, 1H), 6.25-6.20 (m, 1H), 1.99 (s, 3H), 1.83 (d, J = 6.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 198.6, 190.6, 144.5, 142.5, 134.6, 133.2, 129.9, 129.6, 128.2, 15.1, 11.0. HRMS (ESI): m/z calcd for C₁₂H₁₁O₂ (M-H⁺): 187.0759. Found: 187.0772.

2-(2-Phenylbut-2-enoyl)benzaldehyde (1b).
This compound was prepared by following the general procedure-1 and isolated as pale-yellow oil; 200 mg of A4 (R₁ = Ph, R₃ = H) afforded 153 mg of 1b (90% yield). R_f = 0.5 (hexane/EtOAc = 10/1). IR (thin film, neat): ν_max/cm⁻¹ 2925, 1699, 1660, 1596, 1244, 748. ¹H NMR (400 MHz, CDCl₃): δ 10.0 (s, 1H), 7.93 (d, J = 7.5 Hz, 1H), 7.66-7.57 (m, 2H), 7.49-7.42 (m, 3H), 7.36-7.35 (m, 3H), 6.54 (q, J = 6.2 Hz, 1H), 1.78 (d, J = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 197.4, 190.9, 145.0, 144.8, 142.1, 134.7, 134.5, 133.5, 131.0, 129.99, 129.94 (2C), 128.39, 128.2 (2C), 127.7, 16.1. HRMS (ESI): m/z calcd for C₁₇H₁₅O₂ (M+H)⁺: 251.1072. Found: 251.1053.

5-Fluoro-2-(2-methylbut-2-enoyl)benzaldehyde (1c).
This compound was prepared by following the general procedure-1 and isolated as pale-yellow oil; 200 mg of A4 (R₁ = Me, R₃ = H) afforded 148 mg of 1c (90% yield). R_f = 0.5 (hexane/EtOAc = 10/1). IR (thin film, neat): ν_max/cm⁻¹ 3062, 2926, 1701, 1641, 1603, 1490, 1268, 979. ¹H NMR (400 MHz, CDCl₃): δ 9.90 (s, 1H), 7.63 (d, J = 9.7 Hz, 1H), 7.42-7.39 (m, 1H), 7.33-7.28 (m, 1H), 6.31-6.26 (m, 1H), 1.99 (s, 3H), 1.86 (d, J = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 197.2, 189.2 (d, J = 1.3 Hz, 1C), 163.2 (d, J = 250.8 Hz, 1C), 145.2, 140.0, 138.7 (d, J = 3.5 Hz, 1C), 137.2 (d, J = 6.4 Hz, 1C), 130.8 (d, J = 7.7 Hz, 1C), 120.1 (d, J = 22.4 Hz, 1C), 115.6 (d, J = 22.4 Hz, 1C), 15.1, 11.1. ¹⁹F NMR (376.4 MHz,

5-Methoxy-2-(2-methylbut-2-enoyl)benzaldehyde (1d).
This compound was prepared by following the general procedure-1 and isolated as pale-yellow oil; 200 mg of A₄ (R¹ = Me, R³ = H) afforded 148 mg of 1d (89% yield). Rₜ = 0.3 (hexane/EtOAc = 5/1). IR (thin film, neat): ν_max/cm⁻¹ 2842, 1776, 1696, 1636, 1492, 749. ¹H NMR (400 MHz, CDCl₃): δ 9.93 (s, 1H), 7.43 (d, J = 2.6 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.09 (dd, J = 8.4 and 2.6 Hz, 1H), 6.33-6.27 (m, 1H), 3.88 (s, 3H), 1.97 (s, 3H), 1.84 (dd, J = 6.9 and 0.92 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 197.9, 190.5, 160.8, 144.2, 140.1, 137.0, 135.2, 130.7, 119.4, 112.3, 55.7, 15.1, 11.2. HRMS (ESI): m/z calcd for C₁₃H₁₅O₃ (M+H)^+: 219.1021. Found: 219.1041.

4,5-Dimethoxy-2-(2-methylbut-2-enoyl)benzaldehyde (1e).
This compound was prepared by following the general procedure-1 and isolated pale-brown oil; 200 mg of A₆ (R¹ = Me, R² = H) afforded 151 mg of 1e (75% yield). Rₜ = 0.3 (hexane/EtOAc = 5/1). IR (thin film, neat): ν_max/cm⁻¹ 2974, 1754, 1682, 1635, 1022, 784. ¹H NMR (400 MHz, CDCl₃): δ 9.80 (s, 1H), 7.44 (s, 1H), 6.83 (s, 1H), 6.34-6.29 (m, 1H), 3.96 (s, 3H), 3.94 (s, 3H), 1.98 (s, 3H), 1.85 (dd, J = 6.9 and 0.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 197.9, 189.0, 153.0, 150.0, 145.2, 140.6, 137.8, 128.4, 110.6, 109.5, 56.3, 56.2, 15.2, 11.2. HRMS (ESI): m/z calcd for C₁₄H₁₅O₄ (M+H)^+: 249.1127. Found: 249.1109.

2-(2-Methylpent-2-enoyl)benzaldehyde (1f).
This compound was prepared by following the general procedure-1 and isolated as colorless oil; 200 mg of A₄ (R¹ = Me, R³ = Me) afforded 139 mg of 1f (85% yield). Rₜ = 0.5 (hexane/EtOAc = 10/1). IR (thin film, neat): ν_max/cm⁻¹ 2961, 1701, 1593, 1570, 1285, 748. ¹H NMR (400 MHz, CDCl₃): δ 9.90 (s, 1H), 7.89 (d, J = 7.4 Hz, 1H), 7.60-7.52 (m, 2H), 7.32 (d, J = 7.2 Hz, 1H), 6.07 (t, J = 7.2 Hz, 1H), 2.23-2.16 (m, 2H), 1.94 (s, 3H), 0.91 (t, J = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 198.8, 190.6, 151.0, 142.4, 138.3,
134.7, 133.2, 129.9, 129.7, 128.3, 22.6, 12.7, 11.2. **HRMS (ESI):** m/z calcd for C_{13}H_{13}O_{2} (M–H)^+: 201.0915. Found: 201.0909.

5-Methoxy-2-(5-methyl-2-phenylhex-2-enoyl)benzaldehyde (1g).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow oil; 100 mg of A4 (R^1 = Ph, R^3 = Me;CH) afforded 74 mg of 1g (85% yield). R_f = 0.3 (hexane/EtOAc = 5:1). IR (thin film, neat): ν_{max}/cm^{-1} 2958, 1777, 1700, 1654, 1600, 1025, 748. ^1H NMR (400 MHz, CDCl_3): δ 10.12 (s, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 2.6 Hz, 1H), 7.42-7.39 (m, 2H), 7.35-7.34 (m, 1H), 7.26-7.24 (m, 2H), 7.13 (dd, J = 8.4 and 2.6 Hz, 1H), 6.49 (t, J = 7.5 Hz, 1H), 3.91 (s, 3H), 2.09 (t, J = 7.2 Hz, 2H), 1.69-1.64 (m, 1H), 0.84 (s, 3H), 0.82 (s, 3H). ^13C NMR (100 MHz, CDCl_3): δ 196.5, 190.6, 161.1, 148.3, 144.4, 137.5, 135.2, 134.9, 131.0, 129.7 (2C), 128.2 (2C), 127.6, 119.2, 113.1, 55.7, 38.7, 28.5, 22.4 (2C). **HRMS (ESI):** m/z calcd for C_{21}H_{23}O_{3} (M+H)^+: 323.1642. Found: 323.1628.

2-(2,4-Diphenylbut-2-enoyl)benzaldehyde (1h).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow oil; 80 mg of A4 (R^1 = Ph, R^3 = Ph) afforded 60 mg of 1h (85% yield). R_f = 0.5 (hexane/EtOAc = 10:1). IR (thin film, neat): ν_{max}/cm^{-1} 3058, 1695, 1597, 1449, 1283, 753. ^1H NMR (400 MHz, CDCl_3): δ 10.0 (s, 1H), 7.88-7.86 (m, 1H), 7.63-7.54 (m, 2H), 7.47-7.36 (m, 6H), 7.26-7.22 (m, 2H), 7.19-7.17 (m, 1H), 7.02-6.99 (m, 2H), 6.50 (t, J = 7.6 Hz, 1H), 3.47 (d, J = 7.6 Hz, 2H). **HRMS (ESI):** m/z calcd for C_{23}H_{17}O_{2} (M–H)^+: 325.1229. Found: 325.1225.

2-(2-Methyl-5-phenylpent-2-enoyl)benzaldehyde (1i).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow oil; 100 mg of A4 (R^1 = Me, R^3 = CH_{3}Ph) afforded 77 mg of 1i (89% yield). R_f = 0.5 (hexane/EtOAc = 10:1). IR (thin film, neat): ν_{max}/cm^{-1} 2927, 1775, 1700, 1656, 1600, 1203, 750. ^1H NMR (400 MHz, CDCl_3): δ 9.90 (s, 1H), 7.93-7.91 (m, 1H), 7.60-7.57 (m, 2H), 7.28-7.23 (m, 3H), 7.20-7.18 (m, 1H), 7.08-7.06 (m, 2H), 6.12-...
6.09 (m, 1H), 2.68-2.64 (m, 2H), 2.58-2.52 (m, 2H), 1.93 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 198.7, 190.5, 148.1, 142.4, 140.6, 139.4, 134.7, 133.2, 130.0, 129.7, 128.4 (2C), 128.3 (3C), 126.2, 34.4, 31.0, 11.3. HRMS (ESI): $m/z$ calcd for C$_{19}$H$_{19}$O$_2$ (M+H)$^+$: 279.1385. Found: 279.1364.

2-(2-Benzyl-5-phenylpent-2-enoyl)benzaldehyde (1j).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow oil; 100 mg of A4 (R$^1$ = CH$_2$Ph, R$^3$ = CH$_2$Ph) afforded 75 mg of 1j (85% yield). R$_f$ = 0.5 (hexane/EtOAc = 10/1). IR (thin film, neat): $\nu_{max}$/cm$^{-1}$ 3028, 2928, 1701, 1647, 1598, 1202, 745. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.85 (s, 1H), 7.92-7.90 (m, 1H), 7.56-7.54 (m, 2H), 7.27-7.21 (m, 5H), 7.19-7.16 (m, 4H), 7.02-7.00 (m, 2H), 6.30-6.26 (m, 1H), 3.81 (s, 2H), 2.63-2.61 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.9, 190.3, 149.9, 142.4, 142.3, 140.5, 139.3, 134.9, 133.1, 129.9, 129.6, 128.5 (4C), 128.4 (2C), 128.4 (3C), 126.3, 126.1, 34.4, 31.44, 31.4. HRMS (ESI): $m/z$ calcd for C$_{25}$H$_{23}$O$_2$ (M+H)$^+$: 355.1698. Found: 355.1681.

2-(2-Benzyl-5-phenylpent-2-enoyl)-5-fluorobenzaldehyde (1k).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow oil; 100 mg of A4 (R$^1$ = CH$_2$Ph, R$^3$ = CH$_2$Ph) afforded 77 mg of 1k (86% yield). R$_f$ = 0.5 (hexane/EtOAc = 10/1). IR (thin film, neat): $\nu_{max}$/cm$^{-1}$ 3028, 1697, 1653, 1601, 1415, 742. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.83 (d, $J$ = 2.4 Hz, 1H), 7.64 (dd, $J$ = 8.4 and 2.1 Hz, 1H), 7.31-7.28 (m, 4H), 7.27-7.23 (m, 4H), 7.17-7.15 (m, 2H), 7.08-7.06 (m, 2H), 6.34-6.30 (m, 1H), 3.83 (s, 2H), 2.72-2.71 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.5, 189.1, 163.3 (d, $J$ = 250.0 Hz, 1C), 149.9, 142.4, 140.3, 139.0, 138.4 (d, $J$ = 3.5 Hz, 1C), 137.6 (d, $J$ = 6.3 Hz, 1C), 131.0 (d, $J$ = 7.5 Hz, 1C), 128.61 (2C), 128.6 (3C), 128.3 (4C), 126.3 (d, $J$ = 14.8 Hz, 1C), 119.9 (d, $J$ = 21.9 Hz, 1C), 115.4 (d, $J$ = 22.4 Hz, 1C), 34.4, 31.5, 31.3. $^{19}$F NMR (376.4 MHz, CDCl$_3$): $\delta$ -108.3. HRMS (ESI): $m/z$ calcd for C$_{25}$H$_{23}$O$_2$FNa (M+Na)$^+$: 396.1457. Found: 396.1424.
4,5-Dimethoxy-2-(2-methyl-5-phenylpent-2-enoyl)benzaldehyde (1l).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow oil; 200 mg of A6 (R<sub>1</sub> = Me, R<sub>2</sub> = CH<sub>2</sub>Ph) afforded 193 mg of 1l (70% yield). R<sub>f</sub> = 0.3 (hexane/EtOAc = 5/1). IR (thin film, neat): v<sub>max</sub>/cm<sup>-1</sup> 2937, 1762, 1685, 1636, 1589, 1019, 749. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.80 (s, 1H), 7.47 (s, 1H), 7.29-7.28 (m, 2H), 7.22-7.21 (m, 1H), 7.12-7.10 (m, 2H), 6.78 (s, 1H), 6.26-6.22 (m, 1H), 4.00 (s, 3H), 3.91 (s, 3H), 2.73-2.70 (m, 2H), 2.63-2.57 (m, 2H), 1.96 (d, J = 1.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 197.9, 189.0, 152.9, 150.0, 148.9, 140.5, 139.9, 137.6, 128.5 (3C), 128.2 (2C), 126.3, 110.6, 109.6, 56.3, 56.2, 34.3, 31.0, 11.5. HRMS (ESI): m/z calcd for C<sub>21</sub>H<sub>22</sub>O<sub>4</sub> (M+Na)<sup>+</sup>: 361.1415. Found: 361.1433.

1-(2-Benzyl-5-phenylpent-2-enoyl)-2-naphthaldehyde (1m).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow oil; 100 mg of A9 (R<sub>1</sub> = CH<sub>2</sub>Ph, R<sub>2</sub> = CH<sub>2</sub>Ph) afforded 77 mg of 1m (78% yield). R<sub>f</sub> = 0.5 (hexane/EtOAc = 10/1). IR (thin film, neat): v<sub>max</sub>/cm<sup>-1</sup> 3028, 2929, 1694, 1661, 1598, 1197, 744. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.92 (s, 1H), 7.99 (s, 2H), 7.94 (d, J = 8.2 Hz, 1H), 7.67-7.63 (m, 1H), 7.51-7.45 (m, 2H), 7.36-7.33 (m, 2H), 7.29-7.27 (m, 3H), 7.19-7.17 (m, 3H), 6.90-6.87 (m, 2H), 7.31 (t, J = 7.0 Hz, 1H), 3.93 (s, 2H), 2.69-2.64 (m, 2H), 2.58-2.55 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 199.1, 190.1, 151.4, 143.7, 143.4, 140.1, 139.1, 135.9, 130.7, 130.5, 129.4, 129.1, 128.6 (6C), 128.4, 128.3, 128.2, 127.6, 126.7, 126.3, 126.2, 122.9, 34.3, 31.7, 31.1. HRMS (ESI): m/z calcd for C<sub>29</sub>H<sub>25</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 405.1855. Found: 405.1841.

2-(2-Methyl-3-phenylbut-2-enoyl)benzaldehyde (1n).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow oil; 100 mg of A4 (R<sub>1</sub> = Me, R<sub>2</sub> = Ph, R<sub>3</sub> = H) afforded 73 mg of 1n (85% yield). R<sub>f</sub> = 0.5 (hexane/EtOAc = 5/1). IR (thin film, neat): v<sub>max</sub>/cm<sup>-1</sup> 2916, 1765, 1696, 1593, 1376, 1072, 750. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 10.05 (s, 1H), 7.59-7.57 (m, 1H), 7.37-7.34 (m, 1H), 7.30-7.28 (m, 2H), 7.00-6.95 (m, 3H), 6.93-6.90 (m, 2H), 2.23 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 201.0, 191.6, 145.2, 142.8, 142.7, 135.1, 134.7, 132.0, 130.7, 128.8, 128.2 (2C), 115.2, 75.0.
128.0 (2C), 127.7, 127.6, 21.9, 17.5. **HRMS (ESI):** $m/z$ calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2\text{Na}$ (M+Na)$^+$: 287.1048. Found: 287.1028.

5-Methoxy-2-(2-methyl-3-phenylbut-2-enoyl)benzaldehyde (1o).
This compound was prepared by following the general procedure-1 and isolated as pale-yellow oil; 100 mg of A4 ($R^1 = \text{Me}, R^2 = \text{Ph}, R^3 = \text{H}$) afforded 76 mg of 1o (87% yield). $R_f = 0.5$ (hexane/EtOAc = 5/1). **IR (thin film, neat):** $\nu_{\text{max}}/\text{cm}^{-1}$ 2823, 1697, 1597, 1494, 1028, 764. **$^1\text{H NMR}$ (400 MHz, CDCl$_3$):** $\delta$ 10.47 (s, 1H), 7.84 (d, $J = 8.5$ Hz, 1H), 7.45-7.39 (m, 4H), 7.07 (d, $J = 2.6$ Hz, 1H), 6.98-6.96 (m, 2H), 3.92 (s, 3H), 2.19 (s, 3H), 1.94 (s, 3H). **$^{13}\text{C NMR}$ (100 MHz, CDCl$_3$):** $\delta$ 200.3, 192.1, 162.8, 143.0, 142.1, 140.2, 138.0, 134.8, 132.8, 131.6, 128.4 (2C), 127.5 (2C), 118.7, 112.9, 55.8, 22.8, 18.3. **HRMS (ESI):** $m/z$ calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2\text{Na}$ (M$^+$Na)$^+$: 317.1154. Found: 317.1154.

2-((1R,5S)-6,6-Dimethylbicyclo[3.1.1]hept-2-ene-2-carbonyl)benzaldehyde (1p).
This compound was prepared by following the general procedure-1 and isolated as pale-yellow oil; 200 mg of A4 (6,6-Dimethylbicyclo[3.1.1]hept-2-ene) afforded 146 mg of 1p (86% yield). $R_f = 0.5$ (hexane/EtOAc = 10/1). **IR (thin film, neat):** $\nu_{\text{max}}/\text{cm}^{-1}$ 2978, 1772, 1700, 1648, 1369, 749. **Optical rotation:** $[\alpha]_D^{25} -62.3$ (c 0.1, CH$_2$Cl$_2$). **$^1\text{H NMR}$ (400 MHz, CDCl$_3$):** $\delta$ 9.99 (s, 1H), 7.96 (d, $J = 8.8$ Hz, 1H), 7.65-7.57 (m, 2H), 7.42 (d, $J = 8.6$ Hz, 1H), 6.27-6.25 (m, 1H), 3.17 (t, $J = 5.4$ Hz, 1H), 2.59-2.54 (m, 1H), 2.47-2.43 (m, 2H), 2.17 (brs, 1H), 1.39 (s, 3H), 1.16 (d, $J = 9.2$ Hz, 1H), 0.83 (s, 3H). **$^{13}\text{C NMR}$ (100 MHz, CDCl$_3$):** $\delta$ 195.2, 190.5, 150.7, 143.7, 142.2, 134.8, 133.1, 129.8, 129.4, 128.3, 140.2, 39.8, 37.6, 32.9, 31.1, 25.7, 20.9. **HRMS (ESI):** $m/z$ calcd for $\text{C}_{17}\text{H}_{19}\text{O}_2$ (M+H)$^+$: 255.1385. Found: 255.1376.

(S)-2-(4-(Prop-1-en-2-yl)cyclohex-1-ene-1-carbonyl)benzaldehyde (1q).
This compound was prepared by following the general procedure-1 and isolated as pale-yellow oil; 200 mg of A4 (4-(Prop-1-en-2-yl)cyclohex-1-ene) afforded 153 mg of 1q (90% yield). $R_f = 0.5$ (hexane/EtOAc = 10/1). **IR (thin film, neat):** $\nu_{\text{max}}/\text{cm}^{-1}$ 2965, 1773, 1700, 1642, 823, 749. **Optical rotation:** $[\alpha]_D^{25} -91.4$ (c 0.1, CH$_2$Cl$_2$). **$^1\text{H NMR}$ (400 MHz, CDCl$_3$):** $\delta$ 9.95 (s, 1H), 7.94-7.92 (m, 1H), 7.64-7.56 (m, 2H), 7.38-7.36 (m, 1H), 6.39-
6.38 (m, 1H), 4.76 (brs, 1H), 4.71 (brs, 1H), 2.76-2.71 (m, 1H), 2.42-2.08 (m, 4H), 2.00-1.94 (m, 1H), 1.74 (s, 3H), 1.57-1.47 (m, 1H). 13C NMR (100 MHz, CDCl3): δ 197.7, 190.6, 148.5, 145.9, 142.3, 140.6, 134.7, 133.3, 129.9, 129.8, 128.2, 109.4, 40.1, 31.6, 26.7, 23.4, 20.6. HRMS (ESI): m/z calcd for C17H19O2 (M+H)+: 255.1385. Found: 255.1387.

4-(2-Methylbut-2-enoyl)-2H-chromene-3-carbaldehyde (1r).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow oil; 100 mg of A9 (R1 = Me, R2 = H) afforded 59 mg of 1r (60% yield). Rf = 0.5 (hexane/EtOAc = 5/1). IR (thin film, neat): νmax/cm−1 3028, 1718, 1665, 1602, 1482, 769. 1H NMR (400 MHz, CDCl3): δ 9.51 (s, 1H), 7.33-7.28 (m, 1H), 6.97-6.89 (m, 3H), 6.81-6.76 (m, 1H), 5.00 (brs, 2H), 1.96 (s, 3H), 1.89 (d, J = 6.9 Hz, 3H). 13C NMR (100 MHz, CDCl3): δ 196.0, 187.6, 155.5, 149.8, 147.8, 139.9, 133.5, 127.0, 126.9, 122.2, 120.1, 117.1, 62.3, 15.5, 10.2. HRMS (ESI): m/z calcd for C15H13O3 (M−H): 241.0865. Found: 241.0878.

3-(2-Methylbut-2-enoyl)benzo[b]thiophene-2-carbaldehyde (1s).

This compound was prepared by following the general procedure-1 and isolated as pale-brown oil; 100 mg of A13 afforded 75 mg of 1s (89% yield). Rf = 0.5 (hexane/EtOAc = 5/1). IR (thin film, neat): νmax/cm−1 3057, 2925, 1673, 1513, 1203, 1104, 735. 1H NMR (400 MHz, CDCl3): δ 9.97 (s, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 6.56 (q, J = 7.0 Hz, 1H), 2.08 (s, 3H), 1.89 (d, J = 6.9 Hz, 3H). 13C NMR (100 MHz, CDCl3): δ 193.4, 183.9, 147.3, 147.8, 139.9, 133.5, 127.0, 126.9, 122.2, 120.1, 117.1, 62.3, 15.5, 10.2. HRMS (ESI): m/z calcd for C14H11O2S (M−H): 243.0480. Found: 243.0494.

2-(2-Methylbut-2-enoyl)furan-3-carbaldehyde (1t).

This compound was prepared by following the general procedure-1 and isolated as pale-yellow oil; 100 mg of A15 afforded 64 mg of 1t (65% yield). Rf = 0.5 (hexane/EtOAc = 5/1). IR (thin film, neat): νmax/cm−1 3113, 2929, 1684, 1628, 1570, 785, 761. 1H NMR (400 MHz, CDCl3): δ 10.28 (s, 1H), 7.45 (s, 1H), 6.89-6.85 (m, 2H), 1.91-1.89 (m, 6H). 13C NMR (100 MHz,
CDCl$_3$): $\delta$ 187.0, 184.7, 155.4, 144.2, 143.2, 137.1, 130.9, 109.6, 15.1, 11.7. HRMS (ESI): $m/z$ calcd for C$_{10}$H$_{11}$O$_3$ (M+H)$^+$: 179.0708. Found: 179.0699.

3-Hydroxy-2-methyl-2-vinyl-2,3-dihydro-1H-inden-1-one (2a).
This compound was isolated as colorless viscous oil. Following the general procedure-4, 40 mg of 1a afforded 36.4 mg of 2a (91% yield). $R_f = 0.3$ (hexane/EtOAc = 5/1). IR (thin film, neat): $\nu_{\text{max}}$/cm$^{-1}$ 3432, 2977, 1707, 1631, 1465, 797. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.77 (d, $J = 3.8$ Hz, 1H), 7.73-7.70 (m, 2H), 7.50-7.48 (m, 1H), 5.84-5.76 (m, 1H), 5.32 (d, $J = 10.7$ Hz, 1H), 5.25-5.23 (m, 1H), 4.97 (s, 1H), 2.37 (brs, 1H), 1.44 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 205.6, 152.7, 139.3, 135.5, 135.0, 129.5, 125.8, 123.9, 118.3, 78.2, 58.5, 19.5.

HRMS (ESI): $m/z$ calcd for C$_{12}$H$_{11}$O$_2$ (M-H)$^+$: 187.0759. Found: 187.0740.

3-Hydroxy-2-phenyl-2-vinyl-2,3-dihydro-1H-inden-1-one (2b).
This compound was isolated as pale-yellow viscous oil. Following the general procedure-4, 40 mg of 1b afforded 36.0 mg of 2b (90% yield). $R_f = 0.3$ (hexane/EtOAc = 5/1). IR (thin film, neat): $\nu_{\text{max}}$/cm$^{-1}$ 3427, 3025, 1714, 1604, 1495, 1186, 701. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.83 (d, $J = 7.6$ Hz, 1H), 7.73-7.71 (m, 2H), 7.53-7.49 (m, 1H), 7.44-7.43 (m, 2H), 7.35-7.31 (m, 2H), 7.27-7.26 (m, 1H), 6.24-6.17 (m, 1H), 5.53 (d, $J = 7.9$ Hz, 1H), 5.43 (d, $J = 10.7$ Hz, 1H), 5.14 (d, $J = 17.6$ Hz, 1H), 2.62 (d, $J = 8.2$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 202.1, 152.5, 140.5, 135.74, 135.70, 135.4, 129.6, 128.6 (2C), 127.7 (2C), 127.2, 125.6, 124.1, 120.5, 78.7, 66.2. HRMS (ESI): $m/z$ calcd for C$_{17}$H$_{15}$O$_2$ (M-H)$^+$: 251.1072. Found: 251.1049.

5-Fluoro-3-hydroxy-2-methyl-2-vinyl-2,3-dihydro-1H-inden-1-one (2c).
This compound was isolated as pale-yellow oil. Following the general procedure-4, 40 mg of 1c afforded 32.0 mg of 2c (80% yield). $R_f = 0.3$ (hexane/EtOAc = 5/1). IR (thin film, neat): $\nu_{\text{max}}$/cm$^{-1}$ 3432, 2972, 1709, 1605, 1097, 924, 763. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.79-7.76 (m, 1H), 7.36 (dd, $J = 8.0$ and 2.0 Hz, 1H), 7.17 (td, $J = 8.6$ and 2.0 Hz, 1H), 5.77 (m, 1H), 5.33 (d, $J = 10.8$ Hz, 1H), 5.21 (d, $J = 17.5$ Hz, 1H), 4.94 (s, 1H), 2.48 (brs, 1H), 1.44 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 202.8, 167.6 (d, $J = 256.3$ Hz, 1C), 155.8 (d, $J = 9.3$ Hz, 1C), 135.9, 131.2 (d, $J = 1.6$ Hz, 1C), 126.4 (d, $J = 10.1$ Hz, 1C), 118.5, 117.7
(d, J = 23.8 Hz, 1C), 112.6 (d, J = 22.5 Hz, 1C), 77.7 (d, J = 1.5 Hz, 1C), 58.9, 19.4. \(^{19}\text{F NMR (376.4 MHz, CDCl}_3\)): \(\delta\) -100.8. \(\text{HRMS (ESI)}\): \(m/z\) calcd for C\(_{12}\)H\(_{12}\)O\(_2\)F (M+H): 207.0821. Found: 207.0814.

3-Hydroxy-5-methoxy-2-methyl-2-vinyl-2,3-dihydro-1H-inden-1-one (2d).

This compound was isolated as colorless solid. Following the general procedure-4, 40 mg of \(1\text{d}\) afforded 36.8 mg of \(2\text{d}\) (92% yield). \(R_f = 0.3\) (hexane/EtOAc = 5/1). \(\text{M. P.} = 92-94^\circ\text{C. IR (thin film, neat): }\nu_{\text{max}}/\text{cm}^{-1} 3411, 2974, 1700, 1598, 1369, 749.\) \(^{1}\text{H NMR (400 MHz, CDCl}_3\)): \(\delta\) 7.72 (d, \(J = 8.5\) Hz, 1H), 7.16 (d, \(J = 2.1\) Hz, 1H), 7.02 (dd, \(J = 8.5\) and 2.2 Hz, 1H), 5.84-5.77 (m, 1H), 5.33 (d, \(J = 10.7\) Hz, 1H), 5.22 (d, \(J = 17.6\) Hz, 1H), 4.93 (d, \(J = 7.0\) Hz, 1H), 3.92 (s, 3H), 2.43 (brs, 1H), 1.45 (s, 3H).

\(^{13}\text{C NMR (100 MHz, CDCl}_3\)): \(\delta\) 202.8, 166.0, 155.8, 136.5, 128.0, 125.7, 118.2, 117.7, 108.5, 78.1, 58.6, 19.5. \(\text{HRMS (ESI)}\): \(m/z\) calcd for C\(_{13}\)H\(_{15}\)O\(_3\) (M+H): 219.1021. Found: 219.1013.

3-Hydroxy-5,6-dimethoxy-2-methyl-2-vinyl-2,3-dihydro-1H-inden-1-one (2e).

This compound was isolated as pale-yellow oil. Following the general procedure-4, 40 mg of \(1\text{e}\) afforded 32.8 mg of \(2\text{e}\) (82% yield). \(R_f = 0.3\) (hexane/EtOAc = 5/1).

\(\text{IR (thin film, neat): }\nu_{\text{max}}/\text{cm}^{-1} 3452, 2967, 1689, 1592, 1500, 1028, 772.\) \(^{1}\text{H NMR (400 MHz, CDCl}_3\)): \(\delta\) 7.14 (s, 1H), 7.10 (s, 1H), 5.81-5.74 (m, 1H), 5.26 (dd, \(J = 10.7\) and 0.68 Hz, 1H), 5.16 (dd, \(J = 17.5\) and 0.7 Hz, 1H), 4.86 (s, 1H), 3.94 (s, 3H), 3.87 (s, 3H), 2.60 (brs, 1H), 1.37 (s, 3H). \(^{13}\text{C NMR (100 MHz, CDCl}_3\)): \(\delta\) 203.4, 156.1, 150.8, 148.1, 136.9, 127.7, 117.8, 106.6, 104.1, 78.0, 58.2, 56.3, 56.2, 19.8. \(\text{HRMS (ESI)}\): \(m/z\) calcd for C\(_{14}\)H\(_{17}\)O\(_4\) (M+H): 249.1127. Found: 249.1123.

3-Hydroxy-2-methyl-2-(prop-1-en-1-yl)-2,3-dihydro-1H-inden-1-one (2f).

This compound was isolated as colorless viscous oil. Following the general procedure-4, 40 mg of \(1\text{f}\) afforded 35.6 mg of \(2\text{f}\) (89% yield). \(R_f = 0.3\) (hexane/EtOAc = 5/1).

\(\text{IR (thin film, neat): }\nu_{\text{max}}/\text{cm}^{-1} 3422, 2925, 1704, 1605, 1466, 1279, 728.\) \(^{1}\text{H NMR (400 MHz, CDCl}_3\)): \(\delta\) 7.78 (d, \(J = 7.6\) Hz, 1H), 7.75-7.68 (m, 2H), 7.52-7.48 (m, 1H), 5.68-5.59 (m, 1H), 5.43-5.38 (m, 1H), 4.93 (d, \(J = 6.8\) Hz, 1H), 2.39 (brs, 1H), 1.71-1.69 (m, 3H), 1.44 (s, 3H). \(^{13}\text{C
NMR (100 MHz, CDCl₃): δ 205.2, 152.9, 135.4, 135.0, 129.7, 129.3, 128.8, 125.7, 123.8, 78.2, 57.9, 20.0, 18.5. HRMS (ESI): m/z calcd for C₁₃H₁₅O₂ (M+H)⁺: 203.1072. Found: 203.1049.

3-Hydroxy-5-methoxy-2-[(4-methylpent-1-en-1-yl)-2-phenyl-2,3-dihydro-1H-inden-1-one (2g).

This compound was isolated as pale-yellow oil. Following the general procedure-4, 40 mg of 1g afforded 35.2 mg of 2g (88% yield). Rᶠ = 0.3 (hexane/EtOAc = 5/1). IR (thin film, neat): νmax/cm⁻¹ 3447, 3085, 2965, 1701, 1599, 1490, 749.1H NMR (400 MHz, CDCl₃): δ 7.78 (d, J = 8.5 Hz, 1H), 7.47-7.45 (m, 2H), 7.37-7.34 (m, 2H), 7.30-7.25 (m, 2H), 7.21-7.19 (m, 1H), 7.04 (dd, J = 8.3 and 2.0 Hz, 1H), 5.77 (dd, J = 16.0 and 1.0 Hz, 1H), 5.61-5.55 (m, 1H), 5.44 (d, J = 8.2 Hz, 1H), 3.95 (s, 3H), 2.38-2.31 (m, 1H), 1.00 (d, J = 6.7 Hz, 3H), 0.96 (d, J = 6.7 Hz, 3H).13C NMR (100 MHz, CDCl₃): δ 200.7, 166.0, 155.7, 144.0, 141.7, 128.9, 128.4 (2C), 127.7 (2C), 126.9, 125.9, 124.6, 117.7, 108.4, 78.4, 65.2, 55.8, 31.6, 22.27, 22.25. HRMS (ESI): m/z calcd for C₂₁H₂₁O₃ (M–H)⁺: 321.1501. Found: 321.1501.

3-Hydroxy-2-phenyl-2-(styryl)-2,3-dihydro-1H-inden-1-one (2h).

This compound was isolated as pale-yellow oil. Following the general procedure-4, 40 mg of 1h afforded 34.0 mg of 2h (85% yield). Rᶠ = 0.3 (hexane/EtOAc = 5/1). IR (thin film, neat): νmax/cm⁻¹ 3441, 3056, 2924, 1704, 1603, 1495, 1285, 743.1H NMR (400 MHz, CDCl₃): δ 7.86 (d, J = 7.6 Hz, 1H), 7.76-7.69 (m, 2H), 7.53-7.50 (m, 1H), 7.47-7.45 (m, 2H), 7.36-7.31 (m, 4H), 7.29-7.26 (m, 1H), 7.25-7.19 (m, 3H), 6.62 (d, J = 16.4 Hz, 1H), 6.50 (d, J = 16.4 Hz, 1H), 5.57 (d, J = 7.0 Hz, 1H), 2.59 (d, J = 8.4 Hz, 1H).13C NMR (100 MHz, CDCl₃): δ 202.0, 152.4, 141.2, 136.5, 135.7, 135.5, 135.1, 129.7, 128.7 (2C), 128.5 (2C), 127.99, 127.94 (2C), 127.2, 126.9, 126.5 (2C), 125.6, 124.2, 79.2, 65.8. HRMS (ESI): m/z calcd for C₂₃H₁₉O₂ (M+H)⁺: 327.1385. Found: 327.1373.
3-Hydroxy-2-methyl-2-(3-phenylprop-1-en-1-yl)-2,3-dihydro-1H-inden-1-one (2i).

This compound was isolated as pale-yellow oil. Following the general procedure-4, 40 mg of 1i afforded 35.2 mg of 2i (88% yield). R<sub>f</sub> = 0.3 (hexane/EtOAc = 5/1). IR (thin film, neat): ν<sub>max</sub>/cm<sup>-1</sup> 3450, 2929, 1767, 1709, 1605, 1287, 747. ¹H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.80 (d, J = 7.6 Hz, 1H), 7.76-7.70 (m, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.30-7.27 (m, 2H), 7.22-7.18 (m, 1H), 7.15-7.13 (m, 2H), 5.85-5.78 (m, 1H), 5.53 (d, J = 15.8 Hz, 1H), 4.97 (d, J = 6.8 Hz, 2H), 2.17 (brs, 1H), 1.47 (s, 3H). ¹³C NMR (100 MHz, CDCl<sub>3</sub>): δ 204.9, 152.7, 139.7, 135.4, 135.0, 133.3, 129.4, 129.2, 128.5 (2C), 128.4 (2C), 126.2, 125.8, 123.9, 78.3, 57.8, 39.2, 20.3. HRMS (ESI): m/z calcd for C<sub>19</sub>H<sub>17</sub>O<sub>2</sub> (M−H)<sup>+</sup>: 277.1228. Found: 277.1205.

2-Benzyl-3-hydroxy-2-(3-phenylprop-1-en-1-yl)-2,3-dihydro-1H-inden-1-one (2j).

This compound was isolated as pale-brown oil. Following the general procedure-4, 40 mg of 1j afforded 34.8 mg of 2j (87% yield). R<sub>f</sub> = 0.3 (hexane/EtOAc = 5/1). IR (thin film, neat): ν<sub>max</sub>/cm<sup>-1</sup> 3431, 3029, 2929, 1707, 1604, 1286, 1066, 700. ¹H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.74 (d, J = 7.6 Hz, 1H), 7.62-7.61 (m, 2H), 7.44-7.40 (m, 1H), 7.27-7.24 (m, 2H), 7.21-7.14 (m, 6H), 7.09 (d, J = 8.4 Hz, 2H), 5.85-5.78 (m, 1H), 5.62-5.58 (m, 1H), 5.19 (s, 1H), 3.36-3.33 (m, 3H), 3.13 (d, J = 13.6 Hz, 1H), 1.95 (brs, 1H). ¹³C NMR (100 MHz, CDCl<sub>3</sub>): δ 203.5, 153.0, 139.6, 137.2, 135.35, 135.33, 133.5, 130.4 (2C), 129.1, 129.0, 128.51 (2C), 128.50 (2C), 128.4 (2C), 126.7, 126.2, 125.4, 123.6, 73.9, 62.2, 40.2, 39.4. HRMS (ESI): m/z calcd for C<sub>25</sub>H<sub>23</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 355.1698. Found: 355.1684.

2-Benzyl-5-fluoro-3-hydroxy-2-(3-phenylprop-1-en-1-yl)-2,3-dihydro-1H-inden-1-one (2k).

This compound was isolated as pale-yellow oil. Following the general procedure-4, 40 mg of 1k afforded 29.2 mg of 2k (73% yield). R<sub>f</sub> = 0.3 (hexane/EtOAc = 5/1). IR (thin film, neat): ν<sub>max</sub>/cm<sup>-1</sup> 3455, 3029, 1713, 1611, 1331, 751. ¹H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.78 (dd, J = 8.5 and 3.3 Hz, 1H), 7.31-7.28 (m, 3H), 7.26-7.19 (m, 6H), 7.15-7.10 (m, 3H), 5.92-5.84 (m, 1H), 5.67 (d, J = 16.0 Hz, 1H), 5.20 (d, J = 7.0 Hz, 1H), 3.42-3.37 (m, 3H), 3.17 (d, J = 13.6 Hz, 1H), 2.38 (d, J = 7.6 Hz, 1H). ¹³C NMR
(100 MHz, CDCl₃): δ 201.9, 167.6 (d, J = 256.1 Hz, 1C), 156.2 (d, J = 9.4 Hz, 1C), 139.6, 137.1, 133.6, 131.6 (d, J = 1.9 Hz, 1C), 130.4 (2C), 128.7, 128.56 (4C), 128.52 (2C), 126.8, 126.2, 126.1 (d, J = 10.1 Hz, 1C), 117.4 (d, J = 23.8 Hz, 1C), 112.4 (d, J = 22.5 Hz, 1C), 73.4, 62.6, 40.1, 39.4. ¹⁹F NMR (376.4 MHz, CDCl₃): δ -100.8. HRMS (ESI): m/z calcd for C₂₅H₂₂O₂F (M+H)⁺: 373.1604. Found: 373.1592.

3-Hydroxy-5,6-dimethoxy-2-methyl-2-(3-phenylprop-1-en-1-yl)-2,3-dihydro-1H-inden-1-one (2l).

This compound was isolated as pale-yellow oil. Following the general procedure-4, 40 mg of 1l afforded 32.8 mg of 2l (82% yield). Rᵣ = 0.3 (hexane/EtOAc = 5/1). IR (thin film, neat): νmax/cm⁻¹ 3415, 2836, 1700, 1592, 1368, 750. ¹H NMR (400 MHz, CDCl₃): δ 7.28-7.24 (m, 2H), 7.19-7.18 (m, 2H), 7.14-7.13 (m, 3H), 5.81-5.74 (m, 1H), 5.50 (d, J = 15.8 Hz, 1H), 4.86 (s, 1H), 3.99 (s, 3H), 3.92 (s, 3H), 3.38 (d, J = 6.8 Hz, 2H), 2.17 (brs, 1H), 1.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 203.6, 156.0, 150.9, 147.9, 139.8, 133.1, 129.9, 128.5 (2C), 128.4 (2C), 127.8, 126.2, 106.6, 104.1, 78.1, 57.5, 56.4, 56.2, 39.2, 20.5. HRMS (ESI): m/z calcd for C₂₁H₂₂O₄Na (M+Na)⁺: 361.1433. Found: 361.1415.

2-Benzyl-3-hydroxy-2-(3-phenylprop-1-en-1-yl)-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-one (2m).

This compound was isolated as pale-yellow oil. Following the general procedure-4, 40 mg of 1m afforded 33.2 mg of 2m (83% yield). Rᵣ = 0.3 (hexane/EtOAc = 5/1). IR (thin film, neat): νmax/cm⁻¹ 3053, 1693, 1576, 1515, 1449, 1078, 701. ¹H NMR (400 MHz, CDCl₃): δ 9.12 (d, J = 8.3 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.71-7.65 (m, 2H), 7.59-7.55 (m, 1H), 7.26-7.13 (m, 8H), 7.09-7.08 (m, 2H), 5.92-5.84 (m, 1H), 5.65 (d, J = 15.9 Hz, 1H), 5.26 (s, 1H), 3.42 (d, J = 13.6 Hz, 1H), 3.33 (d, J = 6.7 Hz, 2H), 3.19 (d, J = 13.6 Hz, 1H), 2.10 (brs, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 203.7, 155.4, 139.7, 137.4, 136.4, 133.5, 133.4, 130.4 (2C), 129.8, 129.7, 129.2, 128.7, 128.5 (4C), 128.4 (2C), 128.3, 127.1, 126.6, 126.1, 124.8, 122.1, 73.7, 62.6, 40.3, 39.4. HRMS (ESI): m/z calcd for C₂₉H₂₃O₂ (M+H)⁺: 405.1855. Found: 405.1866.
3-Hydroxy-2-methyl-2-(1-phenylvinyl)-2,3-dihydro-1H-inden-1-one (2n).

This compound was isolated as pale-yellow oil. Following the general procedure-4, 40 mg of 1n afforded 23.2 mg of 2n (58% yield). Rf = 0.3 (hexane/EtOAc = 5/1). IR (thin film, neat): v_{max}/cm^{-1} 3448, 2923, 2914, 1605, 1285, 892, 703. ^1H NMR (400 MHz, CDCl₃): δ 7.83 (d, J = 7.6 Hz, 1H), 7.69-7.63 (m, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.21-7.19 (m, 3H), 7.14-7.12 (m, 2H), 5.47-5.44 (m, 2H), 5.29 (s, 1H), 2.28 (brs, 1H), 1.36 (s, 3H). ^13C NMR (100 MHz, CDCl₃): δ 205.7, 152.8, 149.7, 141.3, 135.4, 134.6, 129.3, 128.3 (2C), 127.7 (2C), 127.3, 125.7, 124.0, 118.2, 76.7, 60.5, 19.0. HRMS (ESI): m/z calcd for C_{18}H_{16}O_{2}Na (M+Na)^+: 287.1048. Found: 287.1039.

3-Hydroxy-5-methoxy-2-methyl-2-(1-phenylvinyl)-2,3-dihydro-1H-inden-1-one (2o).

This compound was isolated as pale-yellow oil. Following the general procedure-4, 40 mg of 1o afforded 24.8 mg of 2o (62% yield). Rf = 0.3 (hexane/EtOAc = 5/1). IR (thin film, neat): v_{max}/cm^{-1} 3470, 2925, 1706, 1599, 1565, 1443, 1026, 703. ^1H NMR (400 MHz, CDCl₃): δ 7.76 (d, J = 8.5 Hz, 1H), 7.34-7.27 (m, 1H), 7.20-7.18 (m, 2H), 7.15-7.12 (m, 2H), 7.05 (d, J = 2.0 Hz, 1H), 6.99 (dd, J = 8.6 and 2.4 Hz, 1H), 5.45 (s, 1H), 5.42 (s, 1H), 5.22 (s, 1H), 3.86 (s, 3H), 2.42 (brs, 1H), 1.35 (s, 3H). ^13C NMR (100 MHz, CDCl₃): δ 203.8, 165.9, 155.9, 149.9, 141.4, 128.4, 128.2 (2C), 127.79 (2C), 127.77, 127.3, 125.8, 118.1, 117.6, 108.4, 75.5, 60.6, 19.0. HRMS (ESI): m/z calcd for C_{19}H_{17}O_{3} (M–H)^−: 293.1178. Found: 293.1175.

(2R,5R)-1'-Hydroxy-6,6-dimethylspiro[bicyclo[3.1.1]heptane-2,2'-inden]-3-en-3'(1'H)-one (2p).

This compound was isolated as pale-yellow oil. Following the general procedure-4, 40 mg of 1p afforded 34.8 mg of 2p (87% yield). Rf = 0.3 (hexane/EtOAc = 5/1). IR (thin film, neat): v_{max}/cm^{-1} 3447, 2983, 1701, 1605, 1465, 1154, 764. Optical rotation: [α]_D^{25} +110.0 (c 0.1, CHCl₃). ^1H NMR (400 MHz, CDCl₃): δ 7.72 (m, 1H), 7.68-7.66 (m, 2H), 7.50-7.46 (m, 1H), 6.68-6.63 (m, 1H), 5.72-5.70 (m, 1H), 5.12 (s, 1H), 2.30-2.21 (m, 3H), 2.18-2.16 (m, 1H), 1.90-1.83 (m, 1H), 1.34 (s, 3H), 1.19 (s, 3H). ^13C NMR (100 MHz, CDCl₃): δ...
HRMS (ESI): m/z calcd for C_{17}H_{19}O_{2} (M+H)^+: 255.1385. Found: 255.1367.

(5R)-1'-Hydroxy-5-(prop-1-en-2-yl)spiro[cyclohexane-1,2'-inden]-2-en-3'(1'H)-one (2q).
This compound was isolated as pale-yellow oil. Following the general procedure-4, 40 mg of 1q afforded 36.8 mg of 2q (92% yield). R_f = 0.3 (hexane/EtOAc = 5/1).
IR (thin film, neat): v_{max}/cm^{-1} 3430, 3020, 1706, 1605, 1465, 764, 749.
Optical rotation: [\alpha]_{D}^{25} = -36.3 (c 0.1, CH_{2}Cl_{2}).^1H NMR (400 MHz, CDCl_3): \delta 7.77-7.75 (m, 1H), 7.71-7.69 (m, 2H), 7.49-7.46 (m, 1H), 6.06 (dd, J = 10.2 and 3.4 Hz, 1H), 5.42-5.38 (m, 1H), 4.96 (s, 1H), 4.88-4.85 (m, 2H), 2.84-2.80 (m, 1H), 2.28 (brs, 1H), 1.93-1.87 (m, 1H), 1.79 (s, 3H), 1.74-1.70 (m, 1H).^13C NMR (100 MHz, CDCl_3): \delta 205.2, 152.6, 146.9, 136.8, 135.3, 134.8, 129.4, 125.8, 123.99, 123.93, 112.0, 78.0, 57.4, 41.8, 27.7, 23.8, 21.3. HRMS (ESI): m/z calcd for C_{17}H_{19}O_{2} (M+H)^+: 255.1385. Found: 255.1367.

3-Hydroxy-2-methyl-2-vinyl-2,3-dihydrocyclopenta[c]chromen-1(4H)-one (2r).
This compound was isolated as pale-yellow oil. Following the general procedure-4, 40 mg of 1r afforded 32.8 mg of 2r (82% yield). R_f = 0.3 (hexane/EtOAc = 5/1).
IR (thin film, neat): v_{max}/cm^{-1} 3450, 2931, 1719, 1607, 1570, 1261, 750.
^1H NMR (400 MHz, CDCl_3): \delta 8.01 (d, J = 7.6 Hz, 1H), 7.20 (t, J = 7.7 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 8.1 Hz, 1H), 5.86-5.79 (m, 1H), 5.39-5.28 (m, 3H), 5.24-5.13 (m, 1H), 4.56 (s, 1H), 2.1 (brs, 1H), 1.38 (s, 3H).^13C NMR (100 MHz, CDCl_3): \delta 202.2, 160.2, 152.9, 136.1, 130.9, 130.7, 125.0, 121.7, 118.6, 116.2, 115.9, 77.7, 65.6, 57.1, 19.8. HRMS (ESI): m/z calcd for C_{15}H_{13}O_{3} (M-H)^+: 241.0864. Found: 241.0863.

3-Hydroxy-2-methyl-2-vinyl-2,3-dihydro-1H-benzo[b]cyclopenta[d]thiophen-1-one (2s).
This compound was isolated as pale-yellow oil. Following the general procedure-4, 40 mg of 1s afforded 25.6 mg of 2s (64% yield). R_f = 0.3 (hexane/EtOAc = 5/1).
IR (thin film, neat): v_{max}/cm^{-1} 3420, 2963, 1689, 1631, 1561, 1267, 751. ^1H NMR (400 MHz, CDCl_3): \delta 8.24 (d, J = 7.4 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.49-7.43 (m, 2H), 5.96-5.89 (m, 1H), 5.40-5.28 (m, 2H), 5.15 (s, 1H), 2.64 (brs, 1H), 1.51 (s, 3H). ^13C NMR (100 MHz,
**2’-(2-Methylbut-2-enoyl)-[1,1’-biphenyl]-2-carbaldehyde (5a).**

This compound was prepared by following the general procedure-2 and isolated as colorless oil; 100 mg of A18 (R1 = Me, R2 = Me) afforded 72 mg of 5a (65% yield). Rf = 0.5 (hexane/EtOAc = 5/1). IR (thin film, neat): νmax/cm⁻¹: 2936, 1694, 1639, 1596, 1195, 737. **1H NMR (400 MHz, CDCl3):** δ 9.86 (s, 1H), 7.97 (dd, J = 7.7 and 1.1 Hz, 1H), 7.55-7.42 (m, 5H), 7.31-7.29 (m, 1H), 7.19 (d, J = 8.4 Hz, 1H), 6.25-6.19 (m, 1H), 1.65 (d, J = 6.9 Hz, 3H), 1.59 (s, 3H). **13C NMR (100 MHz, CDCl3):** δ 199.5, 191.6, 144.0, 143.3, 140.6, 139.4, 136.4, 133.6, 133.1, 131.2, 130.9, 129.1, 128.2, 128.0, 127.8, 127.6, 14.6, 10.8. **HRMS (ESI):** m/z calcd for C18H16O2Na (M+Na)⁺: 301.1204. Found: 301.1205.

**2’-(2-Methylpent-2-enoyl)-[1,1’-biphenyl]-2-carbaldehyde (5b).**

This compound was prepared by following the general procedure-2 and isolated as pale-yellow oil; 100 mg of A18 (R1 = Me, R2 = Et) afforded 79 mg of 5b (72% yield). Rf = 0.5 (hexane/EtOAc = 5/1). IR (thin film, neat): νmax/cm⁻¹: 2629, 1696, 1648, 1636, 1596, 1260, 757. **1H NMR (400 MHz, CDCl3):** δ 9.89 (s, 1H), 7.98 (d, J = 7.7 Hz, 1H), 7.56-7.44 (m, 5H), 7.32-7.29 (m, 1H), 7.21 (d, J = 7.6 Hz, 1H), 6.08 (t, J = 7.3 Hz, 1H), 2.08-2.00 (m, 2H), 1.60 (s, 3H), 0.84 (t, J = 7.5 Hz, 3H). **13C NMR (100 MHz, CDCl3):** δ 199.9, 191.6, 149.8, 144.0, 140.6, 137.8, 136.1, 133.6, 133.2, 131.3, 131.0, 129.1, 128.3, 128.0, 127.9, 127.6, 22.3, 12.8, 11.0. **HRMS (ESI):** m/z calcd for C19H18O2Na (M+Na)⁺: 301.1204. Found: 301.1205.
2′-(2-Phenylbut-2-enoyl)-[1,1′-biphenyl]-2-carbaldehyde (5c).

This compound was prepared by following the general procedure-2 and isolated as pale-yellow oil; 100 mg of A18 (R\textsuperscript{1} = Ph, R\textsuperscript{2} = Me) afforded 81 mg of 5c (75% yield). R\textsubscript{f} = 0.5 (hexane/EtOAc = 5/1). \textbf{IR (thin film, neat):} \nu\textsubscript{max}/\text{cm}^{-1} 3057, 2750, 1692, 1595, 756. \textbf{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})}: \delta 9.88 (s, 1H), 8.04 (dd, J = 7.5 and 1.4 Hz, 1H), 7.63-7.50 (m, 5H), 7.33-7.23 (m, 5H), 6.72-6.70 (m, 2H), 6.53 (q, J = 7.0 Hz, 1H), 1.59 (d, J = 7.1 Hz, 3H). \textbf{\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3})}: \delta 198.2, 191.5, 144.8, 144.6, 143.8, 140.7, 136.1, 134.2, 133.7, 133.4, 131.4, 131.3, 129.5, 129.4, 128.4, 128.3, 128.1, 128.0, 127.9, 127.5, 15.7. \textbf{HRMS (ESI):} m/z calcd for C\textsubscript{23}H\textsubscript{18}O\textsubscript{2}Na (M+Na)\textsuperscript{+}: 349.1204. Found: 349.1188.

7-Hydroxy-6-methyl-6-vinyl-6,7-dihydro-5H-dibenzo[a,c][7]annulen-5-one (6a).

This compound was isolated as pale-yellow oil. Following the general procedure-6, 40 mg of 5a afforded 12.0 mg of 6a (30% yield). R\textsubscript{f} = 0.3 (hexane/EtOAc = 5/1). \textbf{IR (thin film, neat):} \nu\textsubscript{max}/\text{cm}^{-1} 3578, 3282, 1650, 1050, 760. \textbf{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})}: \delta 7.66 (d, J = 8.3 Hz, 1H), 7.59-7.55 (m, 1H), 7.45-7.40 (m, 3H), 7.39-7.33 (m, 3H), 6.04-5.97 (m, 1H), 5.39 (d, J = 2.5 Hz, 1H), 5.36-5.35 (m, 2H), 2.04 (brs, 1H), 1.21 (s, 3H). \textbf{\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3})}: \delta 206.5, 139.7, 138.5, 137.5, 136.6, 135.5, 131.4, 128.9, 128.2, 128.1, 128.0 (2C), 127.8, 125.3, 117.5, 72.1, 65.6, 12.6. \textbf{HRMS (ESI):} m/z calcd for C\textsubscript{18}H\textsubscript{16}O\textsubscript{2}Na (M+Na)\textsuperscript{+}: 287.1048. Found: 287.1039.

7-Hydroxy-6-methyl-6-(prop-1-en-1-yl)-6,7-dihydro-5H-dibenzo[a,c][7]annulen-5-one (6b).

This compound was isolated as pale-yellow oil. Following the general procedure-6, 40 mg of 5b afforded 16.8 mg of 6b (42% yield). R\textsubscript{f} = 0.3 (hexane/EtOAc = 5/1). \textbf{IR (thin film, neat):} \nu\textsubscript{max}/\text{cm}^{-1} 3469, 2979, 1685, 1649, 1597, 748. \textbf{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})}: \delta 7.66 (d, J = 7.3 Hz, 1H), 7.58-7.55 (m, 1H), 7.45-7.33 (m, 6H), 5.86-5.77 (m, 1H), 5.39 (d, J = 2.5 Hz, 1H), 5.36-5.35 (m, 2H), 2.04 (brs, 1H), 1.77 (dd, J = 6.4 and 1.5 Hz, 3H), 1.17 (s, 3H). \textbf{\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3})}: \delta 206.9, 139.9, 137.5, 136.6, 135.5, 131.4, 128.9, 128.2, 128.1, 128.0 (2C), 127.8, 125.3, 117.5, 72.1, 65.6, 12.6. \textbf{HRMS (ESI):} m/z calcd for C\textsubscript{18}H\textsubscript{16}O\textsubscript{2}Na (M+Na)\textsuperscript{+}: 287.1048. Found: 287.1039.
128.8, 128.2, 128.04, 128.03 (2C), 128.01, 127.8, 125.3, 72.4, 64.9, 18.4, 12.9. HRMS (ESI): m/z calcd for C$_{19}$H$_{18}$O$_2$Na (M+Na)$^+$: 301.1204. Found: 301.1212.

11-Hydroxy-10-methyl-6,7,8,11-tetrahydro-5H-benzo[9]annulen-5-one (8a).

This compound was isolated as colorless oil. Following the general procedure-7, 30 mg of 2a afforded 25.8 mg of 8a (75% yield, over two steps). R$_f$ = 0.5 (hexane/EtOAc = 10/1). IR (thin film, neat): $\nu_{max}$/cm$^{-1}$ 3406, 2950, 1711, 1680, 1659, 1024, 764. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.43 (d, $J$ = 7.4 Hz, 1H), 7.35-7.27 (m, 2H), 7.01 (d, $J$ = 7.0 Hz, 1H), 5.62 (d, $J$ = 12.3 Hz, 1H), 4.91 (d, $J$ = 8.4 Hz, 1H), 2.56-2.40 (m, 3H), 2.32-2.21 (m, 3H), 2.11-2.06 (m, 1H), 1.38 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 212.8, 144.4, 140.8, 136.1, 130.6, 129.6, 128.1, 124.2, 79.3, 40.2, 30.5, 26.9, 15.4. HRMS (ESI): m/z calcd for C$_{19}$H$_{18}$O$_2$Na (M+Na)$^+$: 301.1204. Found: 301.1212.

11-Hydroxy-8,10-dimethyl-6,7,8,11-tetrahydro-5H-benzo[9]annulen-5-one (8b).

This compound was isolated as colorless solid. Following the general procedure-7, 30 mg of 2f afforded 16.3 mg of 8b (48% yield, over two steps). R$_f$ = 0.3 (hexane/EtOAc = 10/1). M. P. = 127-129 °C. IR (thin film, neat): $\nu_{max}$/cm$^{-1}$ 3424, 2955, 1681, 1455, 1420, 760. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.42 (d, $J$ = 7.0 Hz, 1H), 7.34-7.27 (m, 2H), 6.99 (d, $J$ = 7.0 Hz, 1H), 5.38 (d, $J$ = 11.3 Hz, 1H), 4.88 (d, $J$ = 6.4 Hz, 1H), 2.61-2.54 (m, 2H), 2.40-2.26 (m, 3H), 2.06-2.03 (m, 1H), 1.39 (s, 3H), 1.13 (d, $J$ = 6.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 213.2, 144.4, 140.4, 134.9, 134.4, 130.6, 128.6, 128.1, 124.1, 79.1, 40.4, 39.2, 33.7, 19.2, 16.0. HRMS (ESI): m/z calcd for C$_{15}$H$_{18}$O$_2$Na (M+Na)$^+$: 253.1204. Found: 253.1195.

2-Fluoro-11-hydroxy-10-methyl-6,7,8,11-tetrahydro-5H-benzo[9]annulen-5-one (8c).

This compound was isolated as yellow viscous oil. Following the general procedure-xx, 30 mg of 2c afforded 23.2 mg of 8c (68% yield, over two steps). R$_f$ = 0.3 (hexane/EtOAc = 10/1). IR (thin film, neat): $\nu_{max}$/cm$^{-1}$ 3423, 2934, 1681, 1604, 1583, 1232, 747. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.16 (d, $J$ = 8.8 Hz, 1H), 6.99-6.97 (m, 2H), 5.63-5.59 (m, 1H), 4.86 (d, $J$ = 7.8 Hz, 1H), 2.58-2.51 (m, 2H), 2.43-2.39 (m, 1H), 2.30-2.18 (m, 3H), 2.11-2.03 (m,
1H), 1.40 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 211.9, 162.06 (d, $J = 247.8$ Hz, 1C), 143.6 (d, $J = 6.2$ Hz, 1C), 140.5 (d, $J = 3.0$ Hz, 1C), 135.6, 130.0, 126.1 (d, $J = 7.8$ Hz, 1C), 117.7 (d, $J = 21.1$ Hz, 1C), 114.7 (d, $J = 21.0$ Hz, 1C), 78.8, 40.4, 30.4, 26.8, 15.3. $^{19}$F NMR (376.4 MHz, CDCl$_3$): δ –112.3. HRMS (ESI): $m/z$ calcd for C$_{14}$H$_{15}$FO$_2$Na (M+Na)$^+$: 257.0954. Found: 257.0951.


This compound was isolated as pale-yellow oil. Following the general procedure-7, 30 mg of 2d afforded 25.5 mg of 8d (75% yield, over two steps). $R_f = 0.3$ (hexane/EtOAc = 10/1). IR (thin film, neat): $\nu_{\text{max}}$/cm$^{-1}$ 3397, 2937, 1712, 1604, 1493, 1272, 742. $^1$H NMR (400 MHz, CDCl$_3$): δ 6.95–6.90 (m, 2H), 6.76 (dd, $J = 8.3$ and 2.4 Hz, 1H), 5.58–5.54 (m, 1H), 4.81 (brs, 1H), 3.80 (s, 3H), 2.74 (brs, 1H), 2.54–2.47 (m, 1H), 2.38–2.18 (m, 4H), 2.04 (brs, 1H), 1.37 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 213.1, 159.3, 142.7, 137.0, 136.0, 129.5, 125.5, 116.4, 112.5, 79.4, 55.4, 40.5, 30.5, 26.9, 15.4. HRMS (ESI): $m/z$ calcd for C$_{15}$H$_{18}$O$_3$Na (M+Na)$^+$: 269.1154. Found: 269.1132.

8,10-Dibenzyl-11-hydroxy-6,7,8,11-tetrahydro-5H-benzo[9]annulen-5-one (8e).

This compound was isolated as pale-yellow oil. Following the general procedure-7, 30 mg of 2j afforded 21.0 mg of 8e (65% yield, over two steps). $R_f = 0.3$ (hexane/EtOAc = 10/1). IR (thin film, neat): $\nu_{\text{max}}$/cm$^{-1}$ 3405, 2924, 1737, 1376, 1217, 758. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.38-7.27 (m, 6H), 7.23-7.21 (m, 2H), 7.13-7.04 (m, 4H), 6.51-6.49 (m, 2H), 5.65 (d, $J = 10.8$ Hz, 1H), 4.71 (d, $J = 5.3$ Hz, 1H), 3.54 (d, $J = 14.4$ Hz, 1H), 2.95-2.78 (m, 3H), 2.54-2.44 (m, 4H), 2.36 (d, $J = 14.4$ Hz, 1H), 2.22-2.17 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 212.8, 144.6, 140.9, 140.3, 139.4, 138.4, 133.4, 130.7, 129.0 (2C), 128.8, 128.5 (2C), 128.4 (2C), 128.3 (2C). 128.2, 126.2, 126.0, 124.3, 76.6, 42.5, 41.0, 40.8, 37.0, 35.2. HRMS (ESI): $m/z$ calcd for C$_{27}$H$_{26}$O$_2$Na (M+Na)$^+$: 405.1830. Found: 405.1831.

2-(4-Methylhexa-1,3,5-trien-3-yl)benzaldehyde (9a).

This compound was isolated as colorless oil. Following the general procedure-8, 40 mg of 2a afforded 26.9 mg of 9a (64% yield, over two steps). $R_f = 0.7$ (hexane/EtOAc = 20/1). IR (thin
film, neat): $\nu_{\text{max}}/\text{cm}^{-1}$ 2927, 1697, 1597, 1461, 1197, 771. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.81 (s, 1H), 7.99 (dd, $J = 7.8$ and 1.2 Hz, 1H), 7.6 (td, $J = 7.5$ and 1.4 Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 1H), 7.22-7.13 (m, 2H), 6.08-6.01 (m, 1H), 5.35 (d, $J = 17.2$ Hz, 1H), 5.24 (d, $J = 10.6$ Hz, 1H), 5.00 (d, $J = 10.9$ Hz, 1H), 4.54 (d, $J = 17.0$ Hz, 1H), 2.12 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 192.6, 143.3, 137.0, 136.4, 135.2, 135.0, 134.7, 133.9, 131.7, 127.8, 126.8, 119.5, 115.7, 13.0. HRMS (ESI): $m/z$ calcd for C$_{14}$H$_{13}$O (M-H)$^+$: 197.0966. Found: 197.0943.

2-(4-Methyl-1-phenylhexa-3,5-dien-1-yn-3-yl)benzaldehyde (11).

This compound was isolated as colorless oil. Following the general procedure-8, 40 mg of 2a afforded 42.2 mg of 11 (73% yield, over two steps). $R_f = 0.7$ (hexane/EtOAc = 20/1). IR (thin film, neat): $\nu_{\text{max}}/\text{cm}^{-1}$ 3062, 2917, 2190, 1694, 1644, 912, 754. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.2 (s, 1H), 7.99 (d, $J = 7.8$ Hz, 1H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.41-7.36 (m, 3H), 7.30-7.29 (m, 3H), 6.32-6.25 (m, 1H), 5.46 (dd, $J = 17.2$ and 0.8 Hz, 1H), 5.16 (d, $J = 10.8$ Hz, 1H), 2.37 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 192.0, 144.3, 142.2, 134.7, 134.2, 134.0, 131.3 (2C), 131.0, 128.5, 128.3 (2C), 128.2, 127.3, 123.1, 118.6, 117.8, 99.0, 90.1, 16.7. HRMS (ESI): $m/z$ calcd for C$_{20}$H$_{17}$O (M+H)$^+$: 273.1279. Found: 273.1263.

2-(2-Methyl-1-phenylbuta-1,3-dien-1-yl)benzaldehyde (13).

This compound was isolated as colorless oil. Following the general procedure-8, 40 mg of 2a afforded 36.9 mg of 13 (70% yield, over two steps). $R_f = 0.7$ (hexane/EtOAc = 20/1). IR (thin film, neat): $\nu_{\text{max}}/\text{cm}^{-1}$ 2923, 1695, 1595, 1433, 1060, 701. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.1 (s, 1H), 7.97 (d, $J = 7.7$ Hz, 1H), 7.60-7.56 (m, 1H), 7.43 (t, $J = 7.6$ Hz, 1H), 7.35-7.31 (m, 2H), 7.27-7.23 (m, 2H), 7.19-7.18 (m, 2H), 6.29-6.22 (m, 1H), 5.41 (d, $J = 17.2$ Hz, 1H), 5.12 (d, $J = 10.9$ Hz, 1H), 2.08 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 192.4, 145.9, 141.6, 137.0, 136.8, 135.2, 134.4, 133.8, 131.5, 129.7 (2C), 128.2 (2C), 127.6, 127.3, 127.1, 115.9, 15.6. HRMS (ESI): $m/z$ calcd for C$_{18}$H$_{17}$O (M+H)$^+$: 249.1279. Found: 249.1254.
2-Methyl-3-methylene-2-vinyl-2,3-dihydro-1H-inden-1-ol (15).

This compound was isolated as pale-yellow viscous oil. Following the general procedure-8, 40 mg of 2a afforded 33.2 mg of 15 (84% yield, over two steps). 

IR (thin film, neat): $\nu_{\text{max}}$/cm$^{-1}$ 3405, 3079, 2866, 1642, 1585, 1260, 728. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.52-7.50 (m, 1H), 7.46-7.44 (m, 1H), 7.33-7.31 (m, 2H), 5.97-5.90 (m, 1H), 5.59 (s, 1H), 5.25-5.21 (m, 2H), 4.99 (s, 1H), 4.79 (s, 1H), 1.92 (brs, 1H), 1.40 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.7, 144.3, 140.2, 139.0, 129.1, 128.8, 125.0, 121.1, 115.9, 104.9, 82.3, 54.5, 22.6.

HRMS (ESI): m/z calcd for C$_{13}$H$_{13}$O (M+H)$^+$: 185.0996. Found: 185.0938.

2-Methyl-2-vinyl-2,3-dihydro-1H-indene (16).

This compound was isolated as colorless viscous oil. Following the general procedure-9, 50 mg of 2a afforded 35.7 mg of 16 (85% yield). 

IR (thin film, neat): $\nu_{\text{max}}$/cm$^{-1}$ 2958, 2850, 1650, 1460, 1372, 910, 736. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.24-7.17 (m, 4H), 6.12 (dd, $J$ = 17.4 and 10.6 Hz, 1H), 5.10 (dd, $J$ = 17.3 and 1.2 Hz, 1H), 5.00 (dd, $J$ = 10.6 and 1.2 Hz, 1H), 3.04 (d, $J$ = 15.4 Hz, 2H), 2.78 (d, $J$ = 15.4 Hz, 2H), 1.26 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.0, 142.7 (2C), 126.2 (2C), 124.6 (2C), 110.5, 46.08, 46.03 (2C), 25.5. HRMS (ESI): m/z calcd for C$_{12}$H$_{13}$ (M–H)$^+$: 157.1017. Found: 157.0974.

5-Methoxy-2-methyl-2-vinyl-2,3-dihydro-1H-indene (17).

This compound was isolated as colorless viscous oil. Following the general procedure-9, 50 mg of 2d afforded 36.2 mg of 17 (84% yield). 

IR (thin film, neat): $\nu_{\text{max}}$/cm$^{-1}$ 2956, 2854, 1495, 1492, 1083, 600. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.09 (d, $J$ = 8.0 Hz, 1H), 6.78 (brs, 1H), 6.72 (dd, $J$ = 8.2 and 2.4 Hz, 1H), 6.09 (dd, $J$ = 17.4 and 10.6 Hz, 1H), 5.06 (dd, $J$ = 17.4 and 1.2 Hz, 1H), 4.97 (dd, $J$ = 10.6 and 1.2 Hz, 1H), 3.80 (s, 3H), 3.00-2.92 (m, 2H), 2.74-2.67 (m, 2H), 1.24 (s, 3H). 

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.6, 147.1, 144.2, 137.4, 125.1, 111.8, 110.5, 110.3, 55.3, 46.5, 46.2, 45.1, 25.5. HRMS (ESI): m/z calcd for C$_{13}$H$_{17}$O (M+H)$^+$: 189.1279. Found: 189.1257.
(2-Methyl-2,3-dihydro-1H-inden-2-yl)methanol (18). This compound was isolated as colorless oil. Following the general procedure-9, 35 mg of 16 afforded 26.1 mg of 18 (73% yield, over two steps). R_f = 0.5 (hexane/EtOAc = 10/1). IR (thin film, neat): ν_max/cm⁻¹ 3480, 2953, 1459, 1186, 1037, 795, 738. ¹H NMR (400 MHz, CDCl₃): δ 7.19-7.12 (m, 4H), 3.53 (s, 2H), 2.92 (d, J = 15.6 Hz, 2H), 2.67 (d, J = 15.6 Hz, 2H), 1.72 (brs, 1H), 1.18 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 142.5 (2C), 126.2 (2C), 124.8 (2C), 70.6, 44.9, 42.7 (2C), 24.0.

(5-Methoxy-2-methyl-2,3-dihydro-1H-inden-2-yl)methanol (19). This compound was isolated as pale-yellow viscous oil. Following the general procedure-9, 35 mg of 17 afforded 26.8 mg of 19 (75% yield, over two steps). R_f = 0.3 (hexane/EtOAc = 5/1). IR (thin film, neat): ν_max/cm⁻¹ 3497, 2938, 1684, 1601, 1342, 862, 765. ¹H NMR (400 MHz, CDCl₃): δ 7.06 (d, J = 8.1 Hz, 1H), 6.73 (s, 1H), 6.70-6.68 (m, 1H), 3.77 (s, 3H), 3.51 (s, 2H), 2.91-2.81 (m, 2H), 2.65-2.57 (m, 2H), 1.70 (brs, 1H), 1.17 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 158.6, 144.0, 134.4, 125.3, 112.1, 70.6, 54.4, 45.4, 43.0, 41.9, 24.0. HRMS (ESI): m/z calcd for C₁₂H₁₆O₂Na (M+Na)⁺: 215.1048. Found: 215.1023.

3-Hydroxy-2-(1-methoxyethyl)-2-methyl-2,3-dihydro-1H-inden-1-one (4a). This compound was isolated as colorless viscous oil. Following the general procedure-3, 30 mg of 1a afforded 11.5 mg of 4a (33% yield). R_f = 0.5 (hexane/EtOAc = 5/1). IR (thin film, neat): ν_max/cm⁻¹ 3472, 2926, 1710, 1606, 1282, 1053, 764. ¹H NMR (400 MHz, CDCl₃): δ 7.73-7.65 (m, 3H), 7.45 (t, J = 6.7 Hz, 1H), 4.92 (d, J = 9.0 Hz, 1H), 3.79-3.72 (m, 1H), 3.60 (d, J = 8.8 Hz, 1H), 3.22 (s, 3H), 1.30-1.29 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 206.2, 154.6, 135.9, 135.3, 129.0, 125.3, 123.0, 81.0, 79.6, 56.3, 55.8, 21.0, 12.8. HRMS (ESI): m/z calcd for C₁₃H₁₅O₃ (M–H)⁻: 219.1021. Found: 219.1042.

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3-Hydroxy-2-(methoxy(phenyl)methyl)-2-methyl-2,3-dihydro-1H-inden-1-one (4a’).

This compound was isolated as pale-yellow oil. Following the general procedure-3, 30 mg of 1a’ afforded 8.4 mg of 4a’ (25% yield). Rf = 0.5 (hexane/EtOAc = 5/1).

**IR (thin film, neat):** \( \nu_{\text{max}/\text{cm}^{-1}} \) 3469, 2925, 2824, 1711, 1606, 1454, 1095, 758. 
**\( ^1H \) NMR (400 MHz, CDCl\(_3\)):** \( \delta \) 7.76-7.72 (m, 2H), 7.70-7.66 (m, 1H), 7.47-7.44 (m, 1H), 7.41-7.32 (m, 4H), 7.25-7.23 (m, 1H), 4.98 (s, 1H), 4.60 (s, 1H), 3.39 (brs, 1H), 3.03 (s, 3H), 1.13 (s, 3H). 

**\( ^{13}C \) NMR (100 MHz, CDCl\(_3\)):** \( \delta \) 204.2, 154.2, 136.5, 135.4, 135.1, 129.0 (2C), 128.2, 127.6 (2C), 125.0, 122.9, 87.3, 79.5, 56.6, 56.3, 20.8. 

**HRMS (ESI):** \( m/z \) caled for \( C_{18}H_{18}O_3Na \) (M+Na\(^+\): 305.1154. Found: 305.1151.
Crystal structure of 2d (CCDC 2117421): The structure of 2d was confirmed by single-crystal X-ray diffraction analysis.

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

Figure 1S. ORTEP diagram of 2d with 50% ellipsoidal probability.

Crystal Data for C_{13}H_{14}O_{3} (M =218.24 g/mol): triclinic, space group P-1 (no. 2), a = 9.4694(4) Å, b = 10.7377(6) Å, c = 12.3519(5) Å, α = 108.725(4)°, β = 91.302(4)°, γ = 101.478(4)°, V = 1160.59(10) Å³, Z = 4, T = 298 K, μ(Mo Kα) = 0.088 mm⁻¹, Dcalc = 1.249 g/cm³, 9637 reflections measured (5.33° ≤ 2Θ ≤ 65.384°), 7377 unique (R_{int} = 0.0134, R_{sigma} = 0.0321) which were used in all calculations. The final R1 was 0.0627 (I > 2σ(I)) and wR2 was 0.2020 (all data).
Table 2S: Crystal data and structure refinement for 2d

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<td>7377 [R_{int} = 0.0134, R_{sigma} = 0.0321]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>7377/0/307</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.061</td>
</tr>
<tr>
<td>Final R indexes [I&gt;2σ (I)]</td>
<td>R₁ = 0.0627, wR₂ = 0.1745</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0852, wR₂ = 0.2020</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.27/-0.28</td>
</tr>
</tbody>
</table>
**Crystal structure of 8b (CCDC 2117423):** The structure of 8b was confirmed by single-crystal X-ray diffraction analysis.

**Crystallization procedure of 2d:** In a 5 mL glass vial, 8b was dissolved in ethyl acetate (1 mL) and hexane (0.3 mL) and the solution were kept at room temperature for slow evaporation. After 2-3 days, suitable single crystals were obtained.

![ORTEP diagram of 8b with 50% ellipsoidal probability.](image)

**Crystal Data** for C\textsubscript{15}H\textsubscript{18}O\textsubscript{2} (M =230.29g/mol): monoclinic, space group P2\textsubscript{1}/c, \(a = 8.1464(12)\) Å, \(b = 23.783(3)\) Å, \(c = 7.3403(12)\) Å, \(\alpha = 90^\circ\), \(\beta = 115.306(19)^\circ\), \(\gamma = 90^\circ\), \(V = 1285.7(4)\) Å\textsuperscript{3}, \(Z = 4\), \(T = 298\) K, \(\mu(\text{Mo }K\alpha) = 0.077\) mm\textsuperscript{-1}, \(D_{calc} = 1.190\) g/cm\textsuperscript{3}, 9637 reflections measured (5.33° ≤ 2\(\Theta\) ≤ 65.384°), 4213 unique (\(R_{int} = 0.0476\), \(R_{sigma} = 0.0821\)) which were used in all calculations. The final R1 was 0.0822 (I > 2\(\sigma(I)\)) and wR2 was 0.3262 (all data).
### Table 3S: Crystal data and structure refinement for 8b

<table>
<thead>
<tr>
<th>Identification code</th>
<th>8b</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C₁₅H₁₈O₂</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>230.29</td>
</tr>
<tr>
<td><strong>Temperature/K</strong></td>
<td>298.00(2)</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P2₁/c</td>
</tr>
<tr>
<td><strong>a/Å</strong></td>
<td>8.1464(12)</td>
</tr>
<tr>
<td><strong>b/Å</strong></td>
<td>23.783(3)</td>
</tr>
<tr>
<td><strong>c/Å</strong></td>
<td>7.3403(12)</td>
</tr>
<tr>
<td><strong>α/°</strong></td>
<td>90</td>
</tr>
<tr>
<td><strong>β/°</strong></td>
<td>115.306(19)</td>
</tr>
<tr>
<td><strong>γ/°</strong></td>
<td>90</td>
</tr>
<tr>
<td><strong>Volume/Å³</strong></td>
<td>1285.7(4)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
</tr>
<tr>
<td><strong>ρ.calc/g/cm³</strong></td>
<td>1.190</td>
</tr>
<tr>
<td><strong>μ/mm⁻¹</strong></td>
<td>0.077</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>496.0</td>
</tr>
<tr>
<td><strong>Crystal size/mm³</strong></td>
<td>0.3 × 0.3 × 0.25</td>
</tr>
<tr>
<td><strong>Radiation</strong></td>
<td>Mo Kα (λ = 0.71073)</td>
</tr>
<tr>
<td><strong>2Θ range for data collection/°</strong></td>
<td>5.532 to 65.568</td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
<td>-11 ≤ h ≤ 11, -33 ≤ k ≤ 15, -8 ≤ l ≤ 10</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>6778</td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>4213 [R(int) = 0.0476, R(sigma) = 0.0821]</td>
</tr>
<tr>
<td><strong>Data/restraints/parameters</strong></td>
<td>4213/0/158</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
<td>1.073</td>
</tr>
<tr>
<td><strong>Final R indexes [I&gt;=2σ (I)]</strong></td>
<td>R₁ = 0.0822, wR₂ = 0.2265</td>
</tr>
<tr>
<td><strong>Final R indexes [all data]</strong></td>
<td>R₁ = 0.1466, wR₂ = 0.3262</td>
</tr>
<tr>
<td><strong>Largest diff. peak/hole / e Å⁻³</strong></td>
<td>0.48/-0.32</td>
</tr>
</tbody>
</table>
Copies of $^1$H and $^{13}$C-NMR spectra of all the new compounds reported in this study:

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (400 MHz, CDCl$_3$)
$^{19}\text{F NMR (376.4 MHz, CDCl}_3)\}$

$^{1}\text{H NMR (400 MHz, CDCl}_3)\}$
$^{13}$C NMR (400 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (400 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (400 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (400 MHz, CDCl$_3$)
$^{19}$F NMR (376.4 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (400 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)

S52
$^{13}$C NMR (400 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (400 MHz, CDCl$_3$)

![Chemical Structure](image)

$^1$H NMR (400 MHz, CDCl$_3$)

![Chemical Structure](image)
$^{13}$C NMR (400 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (400 MHz, CDCl$_3$)

2a (11:1)

$^1$H NMR (400 MHz, CDCl$_3$)

2b (3:1)
$^{13}$C NMR (400 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (400 MHz, CDCl$_3$)

![Chemical Structure](image)

2c (10:1)

---

$^{19}$F NMR (376.4 MHz, CDCl$_3$)

![Chemical Structure](image)

2c (10:1)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (400 MHz, CDCl$_3$)

S63
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (400 MHz, CDCl$_3$)

S65
$^1$H NMR (400 MHz, CDCl$_3$)

$^1$C NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (400 MHz, CDCl$_3$)
$^{19}\text{F NMR (376.4 MHz, CDCl}_3\text{)}$

$^{1}\text{H NMR (400 MHz, CDCl}_3\text{)}$
$^{13}$C NMR (400 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (400 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (400 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)

2o (5:1)

2p (5:1)
$^{13}$C NMR (400 MHz, CDCl$_3$)

2q (4:1)

$^1$H NMR (400 MHz, CDCl$_3$)

2r (6:1)
$^{13}$C NMR (400 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (400 MHz, CDCl$_3$)

1H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (400 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (400 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (400 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
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$^{13}$C NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

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$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (400 MHz, CDCl$_3$)
\(^1\)H NMR (400 MHz, CDCl\(_3\))

\(^{13}\)C NMR (400 MHz, CDCl\(_3\))

S97
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (400 MHz, CDCl$_3$)