Electronic Supplementary Information

Iron/Zinc-Catalyzed Benzannulation Reaction of 2-(2-Oxo-alkyl)benzketones Leading to Naphthalene and Isoquinoline Derivatives
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## Contents

1. Condition optimization .......................................................................................................................3
2. General information ............................................................................................................................4
3. Experimental details ............................................................................................................................4
   3.1 General Procedure for the Preparation of 1 ..................................................................................4
   3.2 General Procedure for the Preparation of Product 3a-p .................................................................6
   3.3 General Procedure for the Preparation of Product 3s-v .................................................................11
   3.4 General Procedure for the Preparation of Product 3q .................................................................12
   3.5 General Procedure for the Preparation of Product 4a-h .................................................................12
   3.6 General Procedure for the Preparation of Product 4i-j .................................................................15
   3.7 General Procedure for the Preparation of Product 6 .................................................................15
   3.8 General Procedure for the Preparation of Product 7a-b .................................................................16
4. References ............................................................................................................................................17
5. Copies of $^1$H, $^{13}$C and $^{19}$F NMR Spectra ..................................................................................18
1. Condition optimization.

Table S1. Optimization of reaction conditions.[a]

<table>
<thead>
<tr>
<th>entry</th>
<th>Cat.</th>
<th>1a:2a</th>
<th>Solvent</th>
<th>T/°C</th>
<th>Yield[b]</th>
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<td>FeCl₃(5%)</td>
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<td>DCE</td>
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<td>trace</td>
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<td>2</td>
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<td>DCE</td>
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<td>56%</td>
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<td>DCE</td>
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<td>80%[c]</td>
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<td>NR</td>
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<td>11</td>
<td>TfOH(20%)</td>
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<td>12</td>
<td>TFA(20%)</td>
<td>1:2.0</td>
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<td>80-100</td>
<td>trace</td>
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</table>

[a] [1a] = 0.25 M.;
[b] The yields were determined by ¹H NMR;
[c] Isolated yield;
2. General information.

All reactions were carried out under an inert atmosphere of dry N\textsubscript{2} in Schlenk tube. \textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{19}F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for \textsuperscript{1}H; 100 MHz for \textsuperscript{13}C; 376 MHz for \textsuperscript{19}F). \textsuperscript{1}H NMR and \textsuperscript{13}C NMR chemical shifts were determined relative to internal standard TMS at \(\delta 0.0\). Chemical shifts (\(\delta\)) are reported in ppm, and coupling constants (\(J\)) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Infrared (IR) spectra were recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra were obtained using ESI mass spectrometer. Melting points were determined using a hot stage apparatus. All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. Aryne precursors\textsuperscript{[1]} and 2-(alkanoyl phenyl) ethyl ketones (1\textit{a}, 1\textit{n})\textsuperscript{[2a]} were prepared according to the method of reference.

3. Experimental details

3.1 General Procedure for the Preparation of 1

To the solution of \(\beta\)-diketone (0.3 mmol) and CsF (0.5 mmol) in anhydrous acetonitrile (2 mL), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.25 mmol) was added at room temperature under N\textsubscript{2}. The reaction mixture was stirred at 60 °C for 2 h and then quenched with saturated NH\textsubscript{4}Cl aqueous solution. The mixture was extracted with ethyl acetate. Combined organic layers were dried over anhydrous sodium sulfate, and evaporated. Crude products were purified by column chromatography (ethyl acetate/petroleum ether = 1:10) to afford the 2-(alkanoyl phenyl) ethyl ketones 1.

\textbf{2-(Acetethyl) acetoephene (1l).}[2a]

Yellow oil (22 mg, 50%); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta 7.84 (d, J = 7.7 \text{ Hz}, 1\text{H}), 7.47 (t, J = 7.4 \text{ Hz}, 1\text{H}), 7.39 (t, J = 7.6 \text{ Hz}, 1\text{H}), 7.18 (d, J = 7.4 \text{ Hz}, 1\text{H}), 4.03 (s, 2\text{H}), 2.58 (s, 3\text{H}), 2.29 (s, 3\text{H}); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta 205.7, 201.0, 136.6, 135.1, 133.0, 132.2, 130.2, 127.3, 49.5, 30.0, 28.6.\)

\textbf{2-(Acetylthethyl) propiophene (1m).}
Yellow oil (31 mg, 61%); ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 7.7 Hz, 1H), 7.44 (t, J = 7.3 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 7.5 Hz, 1H), 4.00 (s, 2H), 2.96 (q, J = 7.3 Hz, 2H), 2.59 (q, J = 7.3 Hz, 2H), 1.15 (t, J = 7.2 Hz, 3H), 1.08 (t, J = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 208.4, 204.3, 137.3, 134.8, 134.5, 132.8, 131.6, 129.0, 127.0, 48.1, 35.8, 33.8, 8.3, 7.72; IR (KBr) νmax 2927, 1800, 1735, 1705, 1682, 1465, 1376, 845, 771, 750, 732; HRMS (ESI) calcd. for C₁₃H₁₇O₂ [M+H]⁺: 205.1223, found 205.1227.

2-(Benzylophenyl)-1-phenylpropan-1-one (1o).[2b]

To the solution of 2-methyl-1,3-diphenylpropane-1,3-dione (0.25 mmol) and CsF (0.63 mmol) in anhydrous acetonitrile (2 mL), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.31 mmol) was added at room temperature under N₂. The reaction mixture was stirred at 80 °C for 4 h and then quenched with saturated NH₄Cl aqueous solution. The mixture was extracted with ethyl acetate. Combined organic layers were dried over anhydrous sodium sulfate, and evaporated. Crude products were purified by column chromatography (ethyl acetate/petroleum ether = 1:30) to afford 1o. Yellow oil (49 mg, 63%); ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 7.8 Hz, 2H), 7.83 (d, J = 7.8 Hz, 2H), 7.63 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H), 7.46-7.36 (m, 2H), 7.32-7.28 (m, 5H), 5.15 (q, J = 6.7 Hz, 1H), 1.50 (d, J = 6.7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 200.7, 198.3, 140.8, 137.7, 137.4, 136.3, 133.5, 132.7, 131.0, 130.5, 129.5, 129.4, 128.8, 128.5, 128.4, 128.3, 128.2, 125.9, 43.5, 19.5.

2-(Benzylophenyl) phenylpent-4-en-1-one (1r)

To the solution of 2-allyl-1,3-diphenylpropane-1,3-dione[3] (0.25 mmol) and CsF (0.63 mmol) in anhydrous acetonitrile (2 mL), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.31 mmol) was added at room temperature under N₂. The reaction mixture was stirred at 80 °C for 4 h and then quenched with saturated NH₄Cl aqueous solution. The mixture was extracted with ethyl acetate. Combined organic layers were dried over anhydrous sodium sulfate, and evaporated. Crude products were purified by column chromatography (ethyl acetate/petroleum ether = 1:30) to afford 1r. Yellow oil (42.2 mg, 64%); ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 7.9 Hz, 2H), 7.79 (d, J = 7.8 Hz, 2H), 7.73 (d, J = 7.9 Hz, 1H), 7.60 (t, J = 7.3 Hz, 1H), 7.50-7.22 (m, 8H), 5.69 (td, J = 17.0, 6.9 Hz, 1H), 5.23 (t, J = 7.1 Hz, 1H), 4.96-4.78 (m, 2H), 2.71 (ddt, J = 163.0, 13.9, 6.9 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 199.6, 198.3, 138.6, 137.8, 137.6, 136.5, 135.7, 133.3, 132.8, 131.1, 130.6, 129.8, 128.9, 128.6, 128.4, 128.3, 126.0, 117.0, 48.4, 38.4; IR (KBr) νmax 3063, 2925, 1736, 1683, 1590, 1579, 1447, 1316, 1267, 1211, 1180, 999, 845, 705; HRMS (ESI) calcd. for C₂₄H₂₁O₂ [M+H]⁺: 341.1536, found 341.1541.

5-(2-Benzoylphenyl)-6-oxo-6-phenylhexanenitrile 1s

Thick oil (57 mg, 52%); ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, J = 7.8 Hz, 2H), 7.81 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.4 Hz,
1H), 7.51 (d, J = 7.7 Hz, 2H), 7.40 (dd, J = 15.9, 7.2 Hz, 4H), 7.28 (dd, J = 11.7, 7.6 Hz, 3H), 5.14 (dd, J = 7.7, 6.2 Hz, 1H), 2.40 – 2.28 (m, 3H), 2.05 – 1.94 (m, 1H), 1.83 – 1.71 (m, 1H), 1.65 – 1.57 (m, 1H); 13C NMR (100 MHz, CDCl3) δ 199.3, 198.2, 138.5, 137.6, 133.6, 133.0, 131.4, 130.5, 130.1, 128.7, 128.6, 128.5, 128.4, 126.3, 119.4, 47.7, 33.1, 23.6, 17.1; IR (KBr) νmax 3063, 2937, 1677, 1587, 1446, 1277, 761, 700; HRMS (ESI) calcd. for C25H21NNaO2 [M+Na]+: 390.1465, found 390.1466.  

2-(2-(2-Benzoylphenyl)-3-oxo-3-phenylpropyl)benzonitrile 1t

Yellow solid (62.2 mg, 50%, m.p. = 119-120 °C): 1H NMR (400 MHz, CDCl3) δ 8.05 (d, J = 7.3 Hz, 2H), 7.55 (dd, J = 7.9, 6.6 Hz, 4H), 7.47 – 7.36 (m, 5H), 7.27 (dd, J = 14.3, 7.0 Hz, 4H), 7.22 – 7.14 (m, 2H), 7.01 (td, J = 7.6, 1.2 Hz, 1H), 5.80 (t, J = 7.4 Hz, 1H), 3.73 (dd, J = 14.2, 7.1 Hz, 1H), 3.35 (dd, J = 14.2, 7.7 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 198.8, 197.5, 143.0, 137.8, 137.4, 136.9, 136.1, 133.1, 133.0, 132.6, 132.3, 131.6, 130.4, 129.9, 129.2, 128.4, 128.2, 126.7, 126.3, 117.8, 113.2, 48.9, 38.4; IR (KBr) νmax 3064, 1667, 1589, 1446, 1256, 931, 762, 700; HRMS (ESI) calcd. for C29H21NNaO2 [M+Na]+: 438.1465, found 438.1471.

3.2 General Procedure for the Preparation of Product 3a-p

To a DCE (1 mL) solution of 1 (0.25 mmol) in Schlenk tube with a magnetic bar was added FeCl3 (10 mol%) and arylethyne (2 eq.) under N2. The reaction mixture was stirred at 80-100 °C, followed by TLC. After the substrates were completely consumed, then the solvent was evaporated under vacuum, and the mixture was purified by chromatography (SiO2) with eluent of petroleum ether, the products were obtained.

1,3-Diphenylnaphthalene (3a).[a]

Yellow solid (61.6 mg, 88%): 1H NMR δ 8.10 (s, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 8.6 Hz, 1H), 7.80 (d, J = 7.1 Hz, 2H), 7.76 (d, J = 1.8 Hz, 1H), 7.62-7.44 (m, 9H), 7.41 (t, J = 7.4 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 140.9, 140.8, 140.7, 138.0, 134.2, 130.9, 130.1, 128.8, 128.6, 128.3, 127.4, 127.3, 126.7, 126.2, 126.1, 125.9, 125.4.

1-Phenyl-3-(p-tolyl) naphthalene (3b).

Thick oil (53.7 mg, 73%): 1H NMR (400 MHz, CDCl3) δ 8.10 (s, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 8.6 Hz, 1H), 7.80 (d, J = 7.1 Hz, 2H), 7.76 (d, J = 1.8 Hz, 1H), 7.60-7.52 (m, 5H), 7.49 (d, J = 7.1 Hz, 1H), 7.46 (d, J = 7.3 Hz, 1H), 7.32 (d, J = 7.9 Hz, 2H), 2.45 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 140.8, 138.0, 137.9, 137.2, 134.2, 130.8, 130.1, 129.6, 128.5, 128.3, 127.3, 127.2, 126.6, 126.1, 125.9, 125.8, 125.0; IR (KBr) νmax 3054, 3028, 2922, 2856, 1598, 1492, 1446, 1395, 1186, 1113, 1027, 968, 889, 785, 752, 702; HRMS (ESI) calcd. for C23H19 [M+H]+: 295.1481, found 295.1482.
1-Phenyl-3-(m-tolyl) naphthalene (3c).

Thick oil (63.2 mg, 86%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.09 (s, 1H), 7.99 (d, $J = 8.2$ Hz, 1H), 7.94 (d, $J = 8.4$ Hz, 1H), 7.75 (s, 1H), 7.60 (d, $J = 9.6$ Hz, 4H), 7.55 (t, $J = 7.4$ Hz, 3H), 7.51-7.37 (m, 3H), 7.23 (d, $J = 7.5$ Hz, 1H), 2.48 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.9, 140.8, 138.4, 138.1, 134.2, 130.8, 130.1, 128.8, 128.3, 128.2, 127.3, 126.7, 126.2, 126.0, 125.9, 125.3, 124.5, 21.5; IR (KBr) $\nu_{\text{max}}$ 3053, 2922, 1700, 1599, 1491, 1400, 1304, 1282, 1264, 1094, 972, 882, 785, 766, 751; HRMS (ESI) calcd. for C$_{23}$H$_{19}$ [M+H]$^+$: 295.1481, found 295.1480.

3-(4-Methoxyphenyl)-1-phenylnaphthalene (3d),[4a]

To a DCE (1 mL) solution of 1a (0.25 mmol) in Schlenk tube with a magnetic bar was added ZnCl$_2$ (10 mol%) and ethynyl-4-methoxybenzene (2eq.) under N$_2$. The reaction mixture was stirred at 100 °C, followed by TLC. After the substrates were completely consumed, then the solvent was evaporated under vacuum, and the mixture was purified by chromatography (SiO$_2$) with eluent of petroleum ether, the product was obtained. Thick oil (64.3 mg, 83%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.03 (s, 1H), 7.96 (d, $J = 8.2$ Hz, 1H), 7.92 (d, $J = 8.4$ Hz, 1H), 7.72 (d, $J = 7.2$ Hz, 3H), 7.59-7.47 (m, 6H), 7.45-7.40 (m, 1H), 7.04 (d, $J = 7.9$ Hz, 2H), 3.89 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.3, 140.8, 137.6, 134.2, 133.4, 130.6, 130.4, 130.1, 128.4, 128.3, 127.3, 126.5, 126.1, 125.9, 125.8, 124.6, 114.3, 55.4.

3-(2-Fluorophenyl)-1-phenylnaphthalene (3e).

Thick oil (57.4 mg, 77%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.09 (s, 1H), 7.99 (t, $J = 7.9$ Hz, 2H), 7.70 (s, 1H), 7.66-7.46 (m, 8H), 7.43-7.34 (m, 1H), 7.30-7.21 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.0 (d, $J_{CF} = 248.0$ Hz), 140.5 (d, $J_{CF} = 10.1$ Hz), 133.9, 132.8, 131.1 (d, $J_{CF} = 3.4$ Hz), 131.0, 130.1, 129.1 (d, $J_{CF} = 8.3$ Hz), 129.0, 128.8, 128.6, 128.3, 128.0 (d, $J_{CF} = 2.7$ Hz), 127.7 (d, $J_{CF} = 3.1$ Hz), 127.4, 126.4, 126.2, 125.9, 124.4 (d, $J_{CF} = 3.6$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -117.5; IR (KBr) $\nu_{\text{max}}$ 3056, 2961, 2924, 2853, 1701, 1579, 1455, 1389, 1237, 1153, 969, 857, 757; HRMS (ESI) calcd. for C$_{22}$H$_{15}$FNa [M+Na]$^+$: 321.1050, found 321.1048.

3-(3-Fluorophenyl)-1-phenylnaphthalene (3f).
Yellow solid (61.6 mg, 88%, m.p. 73-74 °C): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.07 (s, 1H), 7.98 (d, \(J = 8.2\) Hz, 1H), 7.94 (d, \(J = 8.5\) Hz, 1H), 7.70 (s, 1H), 7.58-7.52 (m, 6H), 7.49-7.42 (m, 4H), 7.09 (td, \(J = 8.4, 1.0\) Hz, 1H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.3 (d, \(J_{C-F} = 245.7\) Hz), 143.2 (d, \(J_{C-F} = 7.6\) Hz), 141.1, 140.5, 136.7, 135.1, 131.1, 130.3 (d, \(J_{C-F} = 8.4\) Hz), 130.0, 128.6, 128.3, 127.5, 126.3 (d, \(J_{C-F} = 9.5\) Hz), 125.9, 125.5, 123.0 (d, \(J_{C-F} = 2.7\) Hz), 114.3 (d, \(J_{C-F} = 6.5\) Hz), 114.1 (d, \(J_{C-F} = 5.6\) Hz); \(^1^9\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -112.9; IR (KBr) \(\nu_{max}\) 3054, 2920, 1700, 1630, 1544, 1400, 1372, 1180, 1136, 1026, 899, 786, 755, 702; HRMS (ESI) calcd. for C\(_{22}\)H\(_{15}\)FNa [M+Na] \(^+\): 321.1050, found 321.1051.

3-(4-Chlorophenyl)-1-phenylnaphthalene (3g).\(^{[4b]}\)

Thick oil (70.8 mg, 90%): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.04 (s, 1H), 7.97 (d, \(J = 8.1\) Hz, 1H), 7.93 (d, \(J = 8.4\) Hz, 1H), 7.70 (s, 1H), 7.68 (d, \(J = 2.6\) Hz, 2H), 7.58-7.51 (m, 5H), 7.49-7.44 (m, 4H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 141.1, 140.5, 136.7, 134.1, 133.6, 131.0, 130.0, 129.0, 128.6, 128.5, 128.3, 127.5, 126.4, 126.3, 126.2, 125.9, 125.3.

3-(3,5-Bis(trifluoromethyl) phenyl)-1-phenylnaphthalene (3h).

Yellow solid (31.2 mg, 30%, m.p. 128-129 °C): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.18 (s, 2H), 8.10 (s, 1H), 8.01 (d, \(J = 8.1\) Hz, 1H), 7.93 (d, \(J = 8.4\) Hz, 1H), 7.68 (d, \(J = 2.6\) Hz, 2H), 7.58-7.51 (m, 5H), 7.49-7.44 (m, 4H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.1, 141.8, 140.1, 134.9, 134.0, 132.2 (q, \(J_{C-F} = 33.2\) Hz), 131.5, 130.0, 128.8, 128.5, 127.7, 127.4 (d, \(J_{C-F} = 3.6\) Hz), 127.1, 126.8, 126.1 (d, \(J_{C-F} = 2.9\) Hz), 125.7, 124.2 (q, \(J_{C-F} = 268.1\) Hz) 121.0 (m); \(^1^9\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -62.8; IR (KBr) \(\nu_{max}\) 3054, 3028, 2925, 1702, 1543, 1400, 1371, 1337, 1179, 1026, 900, 845, 754; HRMS (ESI) calcd. for C\(_{24}\)H\(_{14}\)F\(_6\) [M+H] \(^+\): 417.1072, found 417.1070.

3-Hexyl-1-phenylnaphthalene (3i).

Thick oil (61.2 mg, 85%): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.88 (t, \(J = 9.1\) Hz, 2H), 7.66 (s, 1H), 7.56-7.43 (m, 6H), 7.39 (t, \(J = 7.1\) Hz, 1H), 7.33 (d, \(J = 1.4\) Hz, 1H), 2.83 (t, \(J = 8\) Hz, 2H), 1.85-1.69 (m, 2H), 1.50-1.31 (m, 6H), 0.93 (t, \(J = 6.9\) Hz, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 140.9, 140.1, 140.0, 134.1, 130.2, 130.1, 128.6, 128.2, 127.8, 127.1, 126.0, 125.8, 125.7, 125.1, 36.1, 31.8, 31.3, 29.1, 22.6, 14.1; IR (KBr) \(\nu_{max}\) 3056, 2955, 2927, 2855, 1701, 1625, 1574, 1493, 1393, 1073, 1030, 878, 784, 749; HRMS (ESI) calcd. for C\(_{22}\)H\(_{25}\) [M+H] \(^+\): 289.1951, found 289.1951.

3-Cyclopropyl-1-phenylnaphthalene (3j).
Thick oil (34.2 mg, 56%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88-7.82 (m, 2H), 7.58 (s, 1H), 7.53-7.44 (m, 6H), 7.37 (t, $J$ = 7.6 Hz, 1H), 7.18 (s, 1H), 2.19-2.05 (m, 1H), 1.07 (q, $J$ = 5.4 Hz, 2H), 0.88 (q, $J$ = 5.2 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.0, 140.9, 140.2, 134.0, 130.1, 130.0, 128.2, 127.6, 127.2, 125.9, 125.8, 125.7, 125.0, 123.4, 15.6, 9.2; IR (KBr) $\nu_{\text{max}}$ 3056, 2923, 2852, 1701, 1650, 1558, 1541, 1508, 1492, 1459, 1398, 1213, 869, 750; HRMS (ESI) calcd. for C$_{19}$H$_{17}$ [M+H]$^+$: 245.1325, found 244.1230.

2-Methyl-1,3-diphenynaphthalene (3k).

![2-Methyl-1,3-diphenynaphthalene](image)

Thick oil (52.9 mg, 72%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J$ = 8.1 Hz, 1H), 7.76 (s, 1H), 7.52 (t, $J$ = 7.3 Hz, 2H), 7.48-7.31 (m, 11H), 2.09 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.4, 141.1, 140.4, 139.1, 132.3, 131.6, 130.2, 129.5, 128.5, 128.1, 127.7, 127.0, 126.9, 126.3, 125.7, 125.2, 19.2; IR (KBr) $\nu_{\text{max}}$ 3056, 2957, 2921, 2852, 1737, 1599, 1490, 1376, 1186, 1075, 967, 854, 788; HRMS (ESI) calcd. for C$_{23}$H$_{19}$ [M+H]$^+$: 295.1481, found 295.1481.

1-Methyl-3-phenylnaphthalene (3l).

Yellow solid (28.9 mg, 53%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07-8.03 (m, 1H), 7.96-7.91 (m, 2H), 7.76 (d, $J$ = 7.3 Hz, 1H), 7.64 (s, 1H), 7.57-7.49 (m, 4H), 7.41 (t, $J$ = 7.4 Hz, 1H), 2.80 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.2, 138.2, 134.8, 133.9, 131.8, 128.8, 128.7, 127.4, 127.2, 126.3, 126.0, 125.8, 124.2, 124.0, 19.5.

1-Ethyl-3-phenylnaphthalene (3m).

Thick oil (23.2 mg, 40%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.17-8.13 (m, 1H), 8.01-7.93 (m, 2H), 7.84-7.78 (m, 2H), 7.71 (s, 1H), 7.63-7.53 (m, 4H), 7.45 (t, $J$ = 7.4 Hz, 1H), 3.26 (q, $J$ = 7.5 Hz, 2H), 1.52 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.4, 140.8, 138.3, 134.2, 131.0, 129.1, 128.8, 127.4, 127.2, 125.8, 125.7, 124.7, 124.3, 123.6, 26.1, 15.1.

5,7-Diphenyl-2,3-dihydro-1H-cyclopenta[b]naphthalene (3n).

![5,7-Diphenyl-2,3-dihydro-1H-cyclopenta[b]naphthalene](image)

Thick oil (59.2 mg, 74%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (s, 1H), 7.82-7.74 (m, 3H), 7.72 (s, 1H), 7.64 (s, 1H), 7.61-7.44 (m, 7H), 7.38 (t, $J$ = 7.4 Hz, 1H), 3.05 (dt, $J$ = 36.3, 7.2 Hz, 4H), 2.15 (p, $J$ = 7.3 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.0, 143.7, 141.3, 141.2, 140.3, 136.9, 133.7, 130.3, 130.1, 128.8, 128.2, 127.3, 127.2, 125.8, 125.1, 122.8, 120.1, 32.9, 32.6, 26.1; IR (KBr) $\nu_{\text{max}}$ 3055, 3030, 2953, 2841, 1747, 1599, 1480, 1389, 1265, 1075, 888, 762; HRMS (ESI) calcd. for C$_{25}$H$_{21}$ [M+H]$^+$: 321.1638, found 321.1640.
1-Methyl-2,4-diphenynaphthalene (3o).\[4e\]

White solid (45.6 mg, 62%): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.20 (d, \(J = 8.4\) Hz, 1H), 7.99 (d, \(J = 8.4\) Hz, 1H), 7.61 (t, \(J = 7.6\) Hz, 1H), 7.56-7.29 (m, 12H), 2.69 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 142.5, 140.7, 138.6, 138.1, 133.3, 130.9, 130.3, 130.2, 129.8, 129.3, 128.2, 128.1, 127.1, 126.8, 126.6, 126.1, 125.5, 124.8, 16.4.

1,3-Dimethyl-2,4-diphenynaphthalene (3p).\[4f\]

Yellowish crystal (53.9 mg, 70%): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.10 (d, \(J = 8.4\) Hz, 1H), 7.54-7.35 (m, 10H), 7.32 (d, \(J = 7.8\) Hz, 2H), 7.26 (d, \(J = 6.7\) Hz, 1H), 2.44 (s, 3H), 1.86 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 142.3, 140.6, 140.3, 136.8, 132.3, 132.2, 130.4, 129.4, 128.4, 126.9, 126.8, 125.3, 125.1, 124.3, 19.9, 16.8.

1-Allyl-2,4-diphenynaphthalene (3r).

Thick oil (48 mg, 60%): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.17 (d, \(J = 8.4\) Hz, 1H), 7.99 (d, \(J = 8.4\) Hz, 1H), 7.51-7.39 (m, 10H), 6.26-6.05 (m, 1H), 5.13 (d, \(J = 10.2\) Hz, 1H), 4.95 (d, \(J = 17.2\) Hz, 1H), 3.84 (d, \(J = 3.3\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 142.5, 140.7, 138.6, 138.1, 133.3, 130.9, 130.3, 130.2, 129.8, 129.3, 128.2, 128.1, 127.1, 126.8, 126.6, 126.1, 125.5, 124.8, 16.4; IR (KBr) \(\nu_{\text{max}}\) 3058, 2922, 1774, 1718, 1686, 1637, 1559, 1510, 1263, 1032, 912, 760, 701; HRMS (ESI) calcd. for C\(_{25}\)H\(_{21}\) [M+H]\(^+\): 321.1638, found 321.1634.

4-Allyl-1,3-diphenyl-1H-isochromen-1-ol (1r').

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, \(J = 7.2\) Hz, 2H), 7.62 (d, \(J = 6.9\) Hz, 1H), 7.49-7.33 (m, 8H), 7.16 (t, \(J = 7.5\) Hz, 1H), 6.91 (d, \(J = 7.7\) Hz, 1H), 6.17-6.04 (m, 1H), 5.19 (d, \(J = 12.3\) Hz, 2H), 3.46 (s, 1H), 3.39 (d, \(J = 3.3\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.2, 141.8, 137.1, 135.3, 132.8, 130.9, 128.9, 128.7, 128.6, 128.0, 127.2, 126.6, 125.8, 122.9, 116.4, 108.7, 99.3, 31.7; IR (KBr) \(\nu_{\text{max}}\) 3449, 3059, 2923, 1754, 1718, 1680, 1633, 1550, 1521, 1260, 1037, 910, 758, 698; HRMS (ESI) calcd. for C\(_{24}\)H\(_{20}\)O\(_2\) [M+H]\(^+\): 341.1536, found 341.1532.
3.3 General Procedure for the Preparation of Product 3s-v

To a DCE (1 mL) solution of 1 (0.25 mmol) in Schlenk tube with a magnetic bar was added FeCl\(_3\) (10 mol%), TFA (20%) and aldehyde/ketone (2 eq.) under N\(_2\). The reaction mixture was stirred at 100 °C, followed by TLC. After the substrates were completely consumed, then the solvent was evaporated under vacuum, and the mixture was purified by chromatography (SiO\(_2\)) with eluent of petroleum ether, the products were obtained.

1-Phenylnaphthalene (3s).\(^{[4a]}\)

\[
\text{Ph} \quad \text{Ph}
\]

White solid (33.7 mg, 66%): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.94 (d, \(J = 8.2 \text{ Hz}, 1\)H), 7.89 (d, \(J = 8.2 \text{ Hz}, 1\)H), 7.57-7.50 (m, 6H), 7.47-7.45 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 140.8, 140.2, 133.8, 131.6, 130.1, 128.2, 127.6, 127.2, 126.9, 126.0, 125.7, 125.4.

1,2-Diphenylnaphthalene (3t).\(^{[4b]}\)

\[
\text{Ph} \quad \text{Ph}
\]

White solid (57.4 mg, 82%): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.02-7.94 (m, 2H), 7.75 (d, \(J = 8.5 \text{ Hz}, 1\)H), 7.65 (d, \(J = 8.5 \text{ Hz}, 1\)H), 7.55 (t, \(J = 7.3 \text{ Hz}, 1\)H), 7.46 (t, \(J = 7.6 \text{ Hz}, 1\)H), 7.38-7.33 (m, 3H), 7.30-7.20 (m, 7H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 142.0, 139.0, 138.3, 137.6, 132.8, 132.7, 131.4, 130.1, 128.3, 127.9, 127.7, 126.8, 126.7, 126.2, 126.1, 125.7.

2-Ethyl-1-phenylnaphthalene (3u).\(^{[4c]}\)

\[
\text{Ph}
\]

Thick oil (38.3 mg, 66%): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.88 (d, \(J = 4 \text{ Hz}, 1\)H), 7.86 (d, \(J = 3.2 \text{ Hz}, 1\)H), 7.57-7.31 (m, 9H), 2.59 (q, \(J = 7.5 \text{ Hz}, 2\)H), 1.17 (t, \(J = 7.5 \text{ Hz}, 3\)H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 139.5, 139.3, 137.5, 133.1, 131.9, 130.3, 128.2, 127.7, 127.6, 127.1, 127.0, 126.4, 125.7, 124.8, 127.0, 16.0.

1-Methyl-4-phenylnaphthalene (3v).\(^{[4d]}\)

\[
\text{Ph}
\]

Thick oil (30 mg, 55%): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.08 (d, \(J = 8.4 \text{ Hz}, 1\)H), 7.93 (d, \(J = 8.4 \text{ Hz}, 1\)H), 7.59-7.46 (m, 6H), 7.45-7.31 (m, 3H), 2.76 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 141.0, 138.7, 133.8, 132.8, 131.7, 130.2, 128.2, 127.1, 126.7, 126.6, 126.2, 125.6, 124.4, 19.6.
3.4 General Procedure for the Preparation of Product 3q

To a DCE (5 mL) solution of 1 (4.5 eq.) in Schlenk tube with a magnetic bar was added FeCl$_3$ (20 mol%) and 1,3,5-triethynylbenzene (0.27 mmol) under N$_2$. The reaction mixture was stirred at 100 °C, followed by TLC. After the substrates were completely consumed, and was then quenched with distilled water. The mixture was extracted with dichloromethane. Combined organic layers were dried over anhydrous sodium sulfate, and evaporated. Crude products were purified by column chromatography (dichloromethane/petroleum ether = 1:4), the product was obtained.

1,3,5-Tris(4-phenylnaphthalen-2-yl)benzene (3q).

![Image of 1,3,5-Tris(4-phenylnaphthalen-2-yl)benzene (3q).]

White solid (135 mg, 73%, m.p. >350 °C): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.24 (s, 3H), 8.13 (s, 3H), 8.03 (d, $J$ = 8.1 Hz, 3H), 7.94 (d, $J$ = 8.4 Hz, 3H), 7.87 (d, $J$ = 1.4 Hz, 3H), 7.64-7.41 (m, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.4, 141.2, 140.6, 137.9, 134.2, 131.1, 130.2, 128.7, 128.4, 127.4, 126.7, 126.3, 126.2, 126.0, 125.9, 125.8; IR (KBr) $\nu$$_{max}$ 3030, 2954, 2921, 2850, 1796, 1718, 1651, 1522, 1438, 1219, 964, 842, 700; HRMS (ESI) calcd. for C$_{54}$H$_{37}$ [M+H]$^+$: 685.2890, found 685.2887.

3.5 General Procedure for the Preparation of Product 4a-h

To a DCE (1 mL) solution of 1 (0.25 mmol) in Schlenk tube with a magnetic bar was added ZnCl$_2$ (10 mol%) and styrene derivatives (2 eq.) under N$_2$. The reaction mixture was stirred at 100 °C, followed by TLC. After the substrates were completely consumed, the solvent was evaporated under vacuum, and the mixture was purified by chromatography (SiO$_2$) with eluent of ethyl acetate/petroleum ether = 1:30, the products were obtained.

(Trans)-(2,4-diphenyl-1,2-dihyronaphthalen-1-yl) (phenyl) methanone (4a).$^{[5]}$

![Image of (Trans)-(2,4-diphenyl-1,2-dihyronaphthalen-1-yl) (phenyl) methanone (4a).]

Thick oil (89 mg, $dr$ = 76:24, 92%). The relative chemistry of product 4a was determined by comparing the NMR data with those in the literature (Org. Lett. 2017, 19, 2470–2473), $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J$ = 7.3 Hz, 2H), 7.45 – 7.39 (m, 2H), 7.29 (7.35 – 7.24, 7H), 7.19 – 6.97 (m, 8H), 6.82 (d, $J$ = 7.3 Hz, 1H), 5.93 (d, $J$ = 4.1 Hz, 1H), 5.02 (d, $J$ = 9.2 Hz, 1H), 4.23 (dd, $J$ = 9.2, 4.1 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.3, 142.6, 139.9, 139.7, 137.5, 134.8, 133.6, 133.0, 129.6, 128.8, 128.7, 128.4, 128.3, 128.2, 128.1, 127.8, 127.4, 127.3, 126.9, 126.0, 53.8, 44.2. (Trans)-phenyl (4-phenyl-2-(p-tolyl)-1,2-dihyronaphthalen-1-yl) methanone (4b).
Thick oil (76 mg, \( dr = 74:26, 76\% \)): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.97 (d, \( J = 7.4 \text{ Hz}, 2\)H), 7.59-7.55 (m, 1H), 7.53-7.35 (m, 7H), 7.24-7.11 (m, 4H), 7.05 (d, \( J = 7.7 \text{ Hz}, 2\)H), 6.95 (d, \( J = 7.4 \text{ Hz}, 2\)H), 6.04 (d, \( J = 4.2 \text{ Hz}, 1\)H), 5.12 (d, \( J = 8.8 \text{ Hz}, 1\)H), 4.32 (dd, \( J = 8.8, 4.1 \text{ Hz}, 1\)H), 2.28 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 201.1, 140.0, 139.6, 139.5, 137.4, 136.5, 134.9, 133.6, 133.0, 129.8, 129.3, 128.8, 128.5, 128.3, 128.0, 127.9, 127.8, 127.4, 127.3, 125.9, 53.9, 43.8, 21.0; IR (KBr) \( \nu_{\text{max}} \) 3057, 3026, 2922, 1681, 1513, 1487, 1342, 1270, 1110, 1025, 998, 941, 910, 816, 768; HRMS (ESI) calcd. for C\(_{30}\)H\(_{24}\)NO\(_3\)Na [M+Na] \(^{+}\): 423.1719, found 423.1727.

*(Trans-)*(2-(4-bromophenyl)-4-phenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4c).

Thick oil (101 mg, \( dr = 64:36, 87\% \)): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.94 (d, \( J = 7.4 \text{ Hz}, 2\)H), 7.74 (d, \( J = 7.5 \text{ Hz}, 1\)H), 7.50-7.41 (m, 6H), 7.41-7.34 (m, 2H), 7.21-7.15 (m, 3H), 7.04 (d, \( J = 8.4 \text{ Hz}, 1\)H), 6.94 (d, \( J = 7.4 \text{ Hz}, 1\)H), 5.99 (d, \( J = 4.0 \text{ Hz}, 1\)H), 5.09 (d, \( J = 9.6 \text{ Hz}, 1\)H), 4.34 (dd, \( J = 9.8, 3.8 \text{ Hz}, 1\)H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 201.0, 141.8, 140.2, 139.7, 137.5, 134.7, 133.3, 131.7, 131.4, 130.6, 130.0, 129.1, 128.9, 128.8, 128.5, 128.4, 128.3, 128.0, 127.8, 127.7, 127.5, 126.2, 120.8, 53.7, 43.7; IR (KBr) \( \nu_{\text{max}} \) 3060, 2922, 1770, 1740, 1646, 1549, 1516, 1449, 1342, 1215, 1072, 940, 821, 770, 741, 698; HRMS (ESI) calcd. for C\(_{29}\)H\(_{21}\)BrO [M+H] \(^{+}\): 487.0668, found 487.0671.

*(Trans-)*(2-(4-chlorophenyl)-4-phenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4d).

Thick oil (95 mg, \( dr = 66:34, 90\% \)): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.94 (d, \( J = 7.6 \text{ Hz}, 2\)H), 7.75 (d, \( J = 7.6 \text{ Hz}, 1\)H), 7.58 (t, \( J = 7.3 \text{ Hz}, 1\)H), 7.52-7.39 (m, 7H), 7.40-7.33 (m, 1H), 7.29-7.09 (m, 5H), 6.95 (d, \( J = 7.4 \text{ Hz}, 1\)H), 6.01 (d, \( J = 3.9 \text{ Hz}, 1\)H), 5.10 (d, \( J = 9.6 \text{ Hz}, 1\)H), 4.36 (dd, \( J = 9.3, 4.1 \text{ Hz}, 1\)H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 201.0, 141.2, 140.1, 139.7, 137.4, 134.7, 133.2, 132.7, 132.6, 130.2, 129.5, 129.1, 128.9, 128.7, 128.4, 128.3, 128.2, 127.9, 127.7, 127.6, 127.4, 126.1, 53.7, 43.6; IR (KBr) \( \nu_{\text{max}} \) 3059, 3028, 2925, 1682, 1595, 1488, 1446, 1344, 1213, 1094, 1012, 769, 698; HRMS (ESI) calcd. for C\(_{29}\)H\(_{22}\)ClO [M+H] \(^{+}\): 421.1354, found 421.1354.

*(Trans-)*(2-(2,5-dimethylphenyl)-4-phenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4e).
Yellow solid (65 mg, \( dr = 79:21 \), 63\% m.p. 160-161 °C): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.92 (d, \( J = 7.4 \) Hz, 2H), 7.60-7.50 (m, 2H), 7.50-7.37 (m, 6H), 7.23-7.09 (m, 4H), 7.01-6.96 (m, 2H), 6.87 (d, \( J = 8.0 \) Hz, 1H), 6.00 (d, \( J = 3.5 \) Hz, 1H), 5.32 (d, \( J = 10.9 \) Hz, 1H), 4.63 (dd, \( J = 11.1, 3.4 \) Hz, 1H), 2.16 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 202.2, 140.5, 139.9, 139.0, 138.0, 135.4, 134.6, 134.5, 133.0, 132.7, 131.2, 130.6, 128.8, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.4, 127.3, 127.1, 126.0, 52.5, 40.1, 21.0, 19.4; IR (KBr) \( \nu \) \text{max} 3057, 3026, 2923, 2865, 1682, 1959, 1682, 1598, 1496, 1343, 1218, 1106, 997, 810, 770, 737; HRMS (ESI) calcd. for C\(_{31}\)H\(_{27}\)O [M+H]+: 415.2056, found 415.2056.

**(Trans-)(2-(3-bromophenyl)-4-phenyl-1,2-dihyronaphthalen-1-yl) (phenyl) methanone (4f).**

Thick oil (108 mg, \( dr = 67:33 \), 93\%):
\[ \begin{align*}
\text{1H NMR (400 MHz, CDCl}_3\text{)) } & \text{ } \delta \text{ } 7.95 \text{ (d, } J = 7.4 \text{ Hz, 2H), 7.72 (d, } J = 7.4 \text{ Hz, 1H), 7.58 (t, } J = 7.4 \text{ Hz, 1H), 7.51-7.41 \text{ (m, 7H), 7.30 (d, } J = 8.4 \text{ Hz, 1H), 7.08 (t, } J = 7.8 \text{ Hz, 1H), 6.01 (d, } J = 3.9 \text{ Hz, 1H), 5.13 (d, } J = 9.9 \text{ Hz, 1H), 4.35 (dd, } J = 9.9, 3.8 \text{ Hz, 1H); } \\
\text{13C NMR (100 MHz, CDCl}_3\text{)) } & \text{ } \delta \text{ } 201.1, 145.0, 140.2, 139.6, 137.5, 134.6, 133.4, 133.2, 131.2, 130.1, 130.0, 128.8, 128.4, 128.3, 128.2, 128.1, 128.0, 127.6, 127.4, 126.9, 126.1, 122.5, 53.6, 44.0; \text{ IR (KBr) } \nu \text{max } 3059, 3028, 2924, 1681, 1592, 1479, 1423, 1267, 1073, 997, 836, 771, 740, 696; \text{ HRMS (ESI) calcd. for C}_{29}H_{21}BrONa [M+Na]^+: 487.0668, found 487.0672.**

**(Trans-)(2-(4-fluorophenyl)-4-phenyl-1,2-dihyronaphthalen-1-yl) (phenyl) methanone (4g).**

Thick oil (88 mg, \( dr = 74:26 \), 87\%):
\[ \begin{align*}
\text{1H NMR (400 MHz, CDCl}_3\text{)) } & \text{ } \delta \text{ } 7.94 \text{ (d, } J = 7.4 \text{ Hz, 2H), 7.71 \text{ (t, } J = 12.4 \text{ Hz, 1H), 7.48-7.40 \text{ (m, 7H), 7.20-7.13 \text{ (m, 4H), 6.96-6.90 \text{ (m, 2H), 6.02 (d, } J = 3.9 \text{ Hz, 1H), 5.11 (d, } J = 9.7 \text{ Hz, 1H), 4.37 (dd, } J = 9.8, 4.0 \text{ Hz, 1H); } \\
\text{13C NMR (100MHz, CDCl}_3\text{)) } & \text{ } \delta \text{ } 200.3, 161.7 (d, } J_{C-F} = 245.3 \text{ Hz), 139.8 (d, } J_{C-F} = 17.0 \text{ Hz, 138.4, 137.5, 134.7, 133.6, 133.2, 129.7 (d, } J_{C-F} = 7.9 \text{ Hz), 129.6, 128.8, 128.7 (d, } J_{C-F} = 3.7 \text{ Hz), 128.3 (d, } J_{C-F} = 3.2 \text{ Hz, 128.2, 127.9, 127.7, 127.5, 127.4, 126.0, 115.4 (d, } J_{C,F} = 21.3 \text{ Hz), 54.0, 43.6; 19F NMR (376 MHz, CDCl}_3\text{)) } \delta \text{ -115.7; IR (KBr) } \nu \text{max } 2060, 3030, 2924, 1680, 1600, 1508, 1418, 1270, 1161, 1073, 998, 909, 835, 737, 697; \text{ HRMS (ESI) calcd. for C}_{29}H_{22}FO [M+H]^+: 405.1649, found 405.1648.**

**(Trans-)(2-(2-chlorophenyl)-4-phenyl-1,2-dihyronaphthalen-1-yl) (phenyl) methanone (4h).**

Thick oil (99 mg, \( dr = 72:28 \), 94\%): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.95 (d, \( J = 7.6 \) Hz, 2H), 7.71 (t, \( J = 12.4 \) Hz, 1H), 7.48-7.40 (m, 7H), 7.24-7.18 (m, 2H), 7.13-7.02 (m, 4H), 6.93 (d, \( J = 7.3 \) Hz, 1H), 5.96 (d, \( J = 4.8 \) Hz, 1H), 5.15 (d, \( J = 6.6 \) Hz, 1H), 4.79 (t, \( J = 5.2 \) Hz, 1H); \(^1\)C NMR (100MHz, CDCl\(_3\)) \( \delta \) 200.3, 140.1, 139.8, 139.1, 137.3, 134.8, 133.4, 133.0, 132.7, 130.0, 129.6, 128.8, 128.6, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 127.4, 127.0, 126.2, 51.6, 39.8; IR (KBr) \( \nu \text{max } 3060, 3027, 2924,14 / 62
1682, 1596, 1477, 1444, 1395, 1269, 1209, 1041, 996, 910, 762, 698; HRMS (ESI) calcd. for C_{29}H_{22}ClO [M+H]^+: 421.1354, found 421.1354.

3.6 General Procedure for the Preparation of Product 4i-j

To a DCE (1 mL) solution of 1 (0.25 mmol) in Schlenk tube with a magnetic bar was added ZnCl₂ (10 mol%) and styrene derivatives (2 eq.) under N₂. The reaction mixture was stirred at 120 °C, followed by TLC. After the substrates were completely consumed, then the solvent was evaporated under vacuum, and the mixture was purified by chromatography (SiO₂) with eluent of ethyl acetate/petroleum ether = 1:30, the products were obtained.

(Trans)-1-methyl-2,4-diphenyl-1,2-dihydonaphthalen-1-yl) (phenyl) methanone (4i).

\[
\begin{align*}
\text{Thick oil (78 mg, } dr = 94:6, 78\%): & \quad \text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3) \delta 7.58 (d, J = 7.9 Hz, 2H), 7.53-7.42 (m, 4H), 7.38-7.33 (m, 5H), 7.28-7.17 (m, 6H), 6.98 (d, J = 7.0 Hz, 2H), 6.24 (d, J = 4.0 Hz, 1H), 4.87 (d, J = 4.0 Hz, 1H), 1.55 (s, 3H); \\
\text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3) \delta 205.6, 140.0, 139.8, 138.9, 138.6, 137.6, 133.6, 131.2, 130.6, 129.7, 129.5, 128.7, 128.3, 128.1, 128.0, 127.8, 127.5, 127.4, 127.2, 127.1, 126.2, 56.6, 48.5, 21.2; \\
\text{IR (KBr) } \nu_{\text{max}} 3061, 3026, 2927, 1677, 1593, 1488, 1448, 1228, 1079, 1036, 768, 702; \\
\text{HRMS (ESI) calcd. for C}_{30}H_{25}O [M+H]^+: 401.1900, found 401.1899.
\end{align*}
\]

(Trans)-1,3-dimethyl-2,4-diphenyl-1,2-dihydonaphthalen-1-yl) (phenyl) methanone (4j).

\[
\begin{align*}
\text{Thick oil (42.4 mg, } dr = 90:10, 41\%): & \quad \text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3) \delta 7.38-7.26 (m, 6H), 7.17-7.09 (m, 10H), 7.00 (dd, J = 7.8, 1.6 Hz, 1H), 6.62-6.57 (m, 1H), 4.17 (s, 1H), 1.66 (s, 3H), 1.50 (s, 3H); \\
\text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3) \delta 208.2, 139.7, 139.1, 139.0, 138.5, 137.2, 135.1, 134.5, 130.3, 129.8, 128.3, 128.0, 127.8, 127.5, 127.4, 127.3, 127.1, 126.8, 126.7, 125.4, 55.8, 54.9, 21.5, 20.3; \\
\text{IR (KBr) } \nu_{\text{max}} 3062, 3027, 2975, 2925, 2857, 1674, 1592, 1487, 1448, 1230, 1074, 962, 763, 704; \\
\text{HRMS (ESI) calcd. for C}_{31}H_{27}O [M+H]^+: 415.2056, found 415.2057.
\end{align*}
\]

3.7 General Procedure for the Preparation of Product 6

To a DCE (1 mL) solution of 1 (0.25 mmol) in Schlenk tube with a magnetic bar was added FeCl₃ (10 mol%) and N,N-dimethylaniline (2eq.) under N₂. The reaction mixture was stirred at 100 °C, followed by TLC. After the substrates were completely consumed, then the solvent was evaporated under vacuum, and the mixture was purified by chromatography (SiO₂) with eluent of petroleum ether, the product was obtained.

4-(1,3-Diphenyl-1H-isochromen-1-yl)-N,N-dimethylaniline (6).
Yellow solid (63.5 mg, 63%, m.p. 145-146 °C): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\ 7.84\) (d, \(J = 7.4\) Hz, 2H), 7.43-7.22 (m, 10H), 7.18 (d, \(J = 7.6\) Hz, 1H), 7.10 (d, \(J = 7.8\) Hz, 2H), 6.70 (d, \(J = 7.6\) Hz, 1H), 6.64 (d, \(J = 8.0\) Hz, 2H), 6.50 (s, 1H), 2.94 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 151.2, 149.8, 144.4, 134.6, 133.9, 131.9, 131.4, 129.4, 128.6, 128.2, 128.0, 127.5, 127.3, 125.9, 125.0, 123.9, 111.2, 101.4, 87.3, 40.4; IR (KBr) \(v_{\text{max}}\) 3085, 3027, 2923, 1681, 1592, 1486, 1446, 1343, 1213, 1104, 1008, 940, 822, 770, 739, 698; HRMS (ESI) calcd. for C\(_{29}\)H\(_{25}\)NONa [M+Na]: 426.1828, found 426.1836.

3.8 General Procedure for the Preparation of Product 7a-b

To a DCE (1 mL) solution of 1 (0.25 mmol) in Schlenk tube with a magnetic bar was added FeCl\(_3\) (10 mol%) under N\(_2\). The reaction mixture was stirred at 100 °C, followed by TLC. After the substrates were completely consumed, saturated potassium carbonate was added. The mixture was extracted with dichloromethane, combined organic layers were dried over anhydrous sodium sulfate, and evaporated., and the mixture was purified by chromatography (SiO\(_2\)) with eluent of ethyl acetate/petroleum ether = 1:30, the products were obtained.

5-phenyl-2,3-dihydro-1H-cyclopenta[c]isoquinoline 7a

Yellow solid (53.9 mg, 88%, m.p. = 80-81 °C): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.05 (d, \(J = 8.5\) Hz, 1H), 7.80 (d, \(J = 8.3\) Hz, 1H), 7.67 (dd, \(J = 9.9, 8.3\) Hz, 3H), 7.47 (ddd, \(J = 17.4, 14.9, 7.1\) Hz, 4H), 3.29 (t, \(J = 7.3\) Hz, 4H), 2.37 – 2.27 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 160.0, 156.9, 140.0, 134.3, 130.0, 129.9, 129.4, 128.4, 128.2, 125.6, 125.2, 123.6, 34.9, 29.1, 22.5; IR (KBr) \(v_{\text{max}}\) 3051, 2920, 1616, 1555, 1367, 1274, 1021, 756, 695; HRMS (ESI) calcd. for C\(_{18}\)H\(_{16}\)N [M+H]: 246.1277, found 246.1278.

5-phenyl-11H-indeno[1,2-c]isoquinoline 7b

Yellow solid (70.3 mg, 96%, m.p. = 160-161 °C): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.19 (d, \(J = 7.5\) Hz, 1H), 8.12 (d, \(J = 8.6\) Hz, 1H), 8.01 (d, \(J = 8.3\) Hz, 1H), 7.80 – 7.75 (m, 2H), 7.74 – 7.68 (m, 1H), 7.65 (d, \(J = 7.3\) Hz, 1H), 7.59 – 7.50 (m, 3H), 7.50 – 7.43 (m, 2H), 7.39 (td, \(J = 7.4, 1.2\) Hz, 1H), 4.17 (s, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 161.0, 153.3, 143.0, 142.3, 140.0, 134.4, 130.3, 129.0, 128.5, 128.3, 127.5, 127.1, 126.0, 125.6, 124.9, 123.5, 120.7, 33.3; IR (KBr) \(v_{\text{max}}\) 3058, 2924, 1710, 1615, 1560, 1381, 1343, 761, 698; HRMS (ESI) calcd. for C\(_{22}\)H\(_{16}\)N [M+H]: 294.1277, found 246.1283.
4. References


5. Copies of $^1$H, $^{13}$C and $^{19}$F NMR Spectra

2-(Acetymethyl) acetophenone (II).

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(Acetylethyl) propiophenone (1m).

\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3) \]

\[ \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3) \]
2-(Benzoylphenyl)-1-phenylpropan-1-one (1o).
5-(2-Benzoylphenyl)-6-oxo-6-phenylhexanenitrile 1s

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(2-(benzoylphenyl)-3-oxo-3-phenylpropyl)benzonitrile 1t

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

$^{13}$C NMR (100 MHz, CDCl$_3$) 1t
1,3-Diphenyl-naphthalene (3a)
1-Phenyl-3-(p-tolyl) naphthalene (3b).
1-Phenyl-3-(m-tolyl) naphthalene (3c).

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
3-(4-Methoxyphenyl)-1-phenynaphthalene (3d).

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
3-(2-Fluorophenyl)-1-phenylnaphthalene (3e).

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{19}$F NMR (376 MHz, CDCl3)
3-(3-Fluorophenyl)-1-phenynaphthalene (3f).

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{19}$F NMR (376 MHz, CDCl3)
3-(4-Chlorophenyl)-1-phenylnaphthalene (3g).

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
3-(3,5-Bis(trifluoromethyl)phenyl)-1-phenylnaphthalene (3h)

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

$^{13}C$ NMR (100 MHz, CDCl$_3$)
$^19$F NMR (376 MHz, CDCl3)
3-Hexyl-1-phenylnaphthalene (3i).

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-Cyclopropyl-1-phenylnaphthalene (3j).

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-Methyl-1,3-diphenylnaphthalene (3k).
1-Methyl-3-phenylnaphthalene (3l).

**H NMR (400 MHz, CDCl₃)**

1H NMR (400 MHz, CDCl₃)

**13C NMR (100 MHz, CDCl₃)**

13C NMR (100 MHz, CDCl₃)
1-Ethyl-3-phenyl napthalene (3m).
5,7-Diphenyl-2,3-dihydro-1H-cyclopenta[b]naphthalene (3n).

\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3) \]

\[ \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3) \]
1-Methyl-2,4-diphenynaphthalene (3o).
1,3-Dimethyl-2,4-diphenyl-naphthalene (3p).

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
1,3,5-Tris(4-phenyl)naphthalen-2-yl)benzene (3q).
1-Allyl-2,4-diphenynaphthalene (3r).
4-Allyl-1,3-diphenyl-1H-isochromen-1-ol (1r').

1-Phenynaphthalene (3s).
1,2-Diphenylnaphthalene (3t).
2-Ethyl-1-phenylnaphthalene (3u).
1-Methyl-4-phenynaphthalene (3v).
(2,4-Diphenyl-1,2-dihyronaphthalen-1-yl) (phenyl) methanone (4a).
Phenyl(4-phenyl-2-(p-tolyl)-1,2-dihydronaphthalen-1-yl) methanone (4b).
(2-(4-Bromophenyl)-4-phenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4c).
(2-(4-Chlorophenyl)-4-phenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4d).
(2-(2,5-Dimethylphenyl)-4-phenyl-1,2-dihyronaphthalen-1-yl) (phenyl) methanone (4e).
(2-(3-Bromophenyl)-4-phenyl-1,2-dihydropyanthalen-1-yl) (phenyl) methanone (4f).
(2-(4-Fluorophenyl)-4-phenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4g).
$^{19}$F NMR (376MHz, CDCl$_3$)
4g
(2-(2-Chlorophenyl)-4-phenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4h).
((1S,2S)-1-Methyl-2,4-diphenyl-1,2-dihyronaphthalen-1-yl) (phenyl) methanone (4i).
((1S,2R)-1,3-Dimethyl-2,4-diphenyl-1,2-dihyronaphthalen-1-yl) (phenyl) methanone (4j).

${}^1$H NMR (400 MHz, CDCl$_3$) 4j

${}^{13}$C NMR (100 MHz, CDCl$_3$) 4j
4-(1,3-Diphenyl-1H-isochromen-1-yl)-N,N-dimethylaniline (6).

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

5-phenyl-2,3-dihydro-1H-cyclopenta[c]isoquinoline 7a
5-phenyl-11H-indeno[1,2-c]isoquinoline 7b
^{1}H NMR (400 MHz, CDCl$_3$) $7b$

^{13}C NMR (100 MHz, CDCl$_3$) $7b$