Supporting Information

Palladium-Catalysed Mono-α-Alkenylation of Ketones with Alkenyl Tosylates

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1. General considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All arylation reactions were performed in resealable screw-capped Schlenk tube (approx. 20 mL volume) in the presence of Teflon-coated magnetic stirrer bar (4 mm × 10 mm). Tertiary butanol (t-BuOH) and CH$_3$CN was distilled under calcium hydride under reduced pressure. Toluene, Dioxane and tetrahydrofuran (THF) were distilled from sodium under nitrogen. LiOr-Bu, NaOr-Bu, and K$_3$PO$_4$ were purchased from Aldrich. LiOH•H$_2$O and Li$_2$CO$_3$ were purchased from Merck. Pd(dba)$_2$ and Pd(OAc)$_2$ were purchased from Strem. [PdCl(cinnamyl)]$_2$, PdCl$_2$(CH$_3$CN)$_2$, PdCl$_2$(allyl)$_2$ and Pd(cod)Cl$_2$ were purchased from Aldrich. CM-Phos and PhMezole-Phos were prepared according to reported literature procedures.\(^1\) BrettPhos, XPhos, SPhos, DavePhos, cataCXium A, NiXantPhos and SIMes-HBF$_4$ were purchased from Strem. DPPE, Mor-DalPhos and XantPhos were purchased from Aldrich. PPh$_3$ was purchased from Acros, Thin layer chromatography was performed on Merck precoated silica gel 60 F$_{254}$ plates. Silica gel (Merck, 70-230 and 230-400 mesh) was used for column chromatography. \(^1\)H NMR spectra were recorded on ADVANCE III (400 MHz). Spectra were referenced internally to the residual proton resonance in CDCl$_3$ (δ 7.26 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. \(^1\)C NMR spectra were referenced to CDCl$_3$ (δ 77.0 ppm, the middle peak). Coupling constants (\(J\)) were reported in Hertz (Hz).
2. Preparation of alkenyl tosylates substrates

Alkenyl tosylates 1a, 1e-1k were prepared from their corresponding species according to the literature method\textsuperscript{2-4} without modifications. Spectral data for the alkenyl tosylates 1a,\textsuperscript{2} 1e,\textsuperscript{2} 1f,\textsuperscript{2} 1g,\textsuperscript{3} 1h,\textsuperscript{3} 1i,\textsuperscript{4} 1j,\textsuperscript{2} and 1k\textsuperscript{2} showed good agreement with the literature data.

Alkenyl tosylate 1b-1d were synthesized from corresponding ketones according to the literature method. A round bottom flask was charged with ketone (20 mmol) and purged with nitrogen. NMP (40 ml) was added and was cooled to -15°C. Solid NaOtBu (22 mmol) was added and the solution was stirred at room temperature for 2h. The solution was cooled to -20 °C and p-toluencesulfonic anhydride (24 mmol) was added in a single portion. The reaction mixture was stirred at -20 °C to r.t. for overnight. The tan solution was combined MTBE (300ml) and washed with aq NaHCO\textsubscript{3} (200ml) and water. The organic phase was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired product.

\[
\text{R}^1\text{C} (20 \text{ mmol}) \rightarrow \text{Ts}_2\text{O (1.2 equiv)} \rightarrow \text{NaOtBu (1.1 equiv)} \rightarrow \text{R}^2\text{C} (100 \text{ mmol}) \rightarrow \text{Rs}^3\text{Ts}
\]

2-(Naphthalen-2-yl) cyclohex-1-en-1-yl 4-methylbenzenesulfonate (1b): White solid (71%
yield, eluent: Hexane/EA 20:1). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.82 – 7.74 (m, 1H), 7.61 (m, 2H), 7.51 – 7.44 (m, 2H), 7.29 (d, $J = 1.9$ Hz, 1H), 7.26 – 7.11 (m, 3H), 6.62 (d, $J = 8.1$ Hz, 2H), 2.67 (m, 2H), 2.44 (m, 2H), 2.12 (s, 3H), 1.92 – 1.84 (m, 2H), 1.83 – 1.74 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.0, 143.8, 135.6, 133.0, 132.9, 132.1, 128.7, 128.3, 127.8, 127.4, 127.3, 127.0, 126.7, 126.6, 125.7, 125.7, 30.5, 29.2, 23.0, 22.4, 21.4.

4'-(Tert-butyl)-3, 4, 5, 6-tetrahydro-[1, 1'-biphenyl]-2-yl 4-methylbenzenesulfonate (1c): Colorless oil (82% yield, eluent: Hexane/EA 20:1). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.33 – 7.28 (m, 2H), 7.18 – 7.11 (m, 2H), 7.00 (d, $J = 8.0$ Hz, 2H), 6.95 – 6.84 (m, 2H), 2.61 (m, 2H), 2.37 (s, 3H), 2.31 (m, 2H), 1.86 – 1.77 (m, 2H), 1.77 – 1.68 (m, 2H), 1.33 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.5, 143.8, 143.0, 135.1, 133.1, 129.0, 128.4, 127.8, 127.7, 124.5, 34.4, 31.4, 30.5, 28.9, 23.1, 22.5, 21.6.

3', 5'-Bis (trifluoromethyl)-3, 4, 5, 6-tetrahydro-[1, 1'-biphenyl]-2-yl 4-methylbenzenesulfonate (1d): Colorless oil (69% yield, eluent: Hexane/EA 20:1). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.58 (s, 1H), 7.47 (d, $J = 1.6$ Hz, 2H), 7.39 – 7.31 (m, 2H), 7.02 (d, $J = 8.1$ Hz, 2H), 2.64 (m, 2H), 2.40 – 2.29 (m, 5H), 1.84 (m, 2H), 1.77 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 145.8, 144.9, 140.3, 133.0, 131.0 (d, $J_{C-F} = 33$ Hz), 129.3, 128.3, 128.3, 127.5, 125.6, 123.1 (d, $J_{C-F} = 271$ Hz), 120.4, 30.1, 29.1, 22.7, 22.1, 21.3.
3. General procedures for ligand and reaction condition screenings

General procedure for screening: A Schlenk tube equipped with a Teflon-coated stir bar was carefully evacuated and backfilled with nitrogen for three cycles. Pd source (0.0125 mmol) and ligand with corresponding ratio in 5 mL DCM (1.00 mol% Pd per 1.00 mL stock solution) was then prepared under N\textsubscript{2} with stirring until all of the solids are dissolved (usually within 1 min). The corresponding volume of stock solution was then immediately added to the Schlenk tube by syringe (In case of 0.25 mol% Pd, additional 0.25 mL of DCM was added). The palladium complex solution was stirred and placed in a preheated oil bath (40 °C) for 2 minutes. The solvent was then evaporated under high vacuum. Alkenyl tosylates (0.375 mmol) and base (0.375 mmol) were loaded into the tube, and the system was further evacuated and filled with nitrogen for three cycles. Solvent (0.5 mL) and subsequently 2-Acetonaphthone (0.25 mmol) were added with stirring (250 rpm) at room temperature. After that, the tube was further stirred (1000 rpm) at room temperature for 5 minutes. The tube was then placed into a preheated oil bath (100 °C) and stirred for 24 h. Ethyl acetate (~3 mL), dodecane (57 μL, internal standard), water (~2 mL) were added. The organic layer was separated and the aqueous layer was washed with ethyl acetate. The combined organic layer was concentrated under reduced pressure. The organic layer was subjected to GC analysis. The GC yield was previously calibrated by authentic sample/dodecane calibration curve.

Table S1. Screening of solvent\textsuperscript{a}

<table>
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<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>t-BuOH</td>
<td>87</td>
</tr>
<tr>
<td>2</td>
<td>toluene</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>dioxane</td>
<td>67</td>
</tr>
<tr>
<td>4</td>
<td>DMF</td>
<td>58</td>
</tr>
<tr>
<td>5</td>
<td>THF</td>
<td>66</td>
</tr>
<tr>
<td>6</td>
<td>CH\textsubscript{3}CN</td>
<td>24</td>
</tr>
<tr>
<td>7</td>
<td>i-PrOH</td>
<td>trace</td>
</tr>
<tr>
<td>8</td>
<td>MeOH</td>
<td>trace</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction conditions: Alkenyl tosylates (0.375 mmol), LiOt-Bu (0.375 mmol), ketone (0.25 mmol), solvent (0.5 mL), Pd/XPhos = 1:4 at 100 °C for 20 h under N\textsubscript{2}; Calibrated GC yields were reported using dodecane as the internal standard.
Table S2. Screening of Pd source<sup>a</sup>

![Chemical structure]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pd (mol%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>71</td>
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<tr>
<td>2</td>
<td>Pd(TFA)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td>Pd(dba)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>81</td>
</tr>
<tr>
<td>4</td>
<td>Pd&lt;sub&gt;2&lt;/sub&gt;(dba)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>71</td>
</tr>
<tr>
<td>5</td>
<td>PdCl&lt;sub&gt;2&lt;/sub&gt;(cod)</td>
<td>70</td>
</tr>
<tr>
<td>6</td>
<td>[PdCl(cinnamyl)]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>60</td>
</tr>
<tr>
<td>7</td>
<td>PdCl&lt;sub&gt;2&lt;/sub&gt;(allyl)&lt;sub&gt;2&lt;/sub&gt;</td>
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<tr>
<td>8</td>
<td>PdCl&lt;sub&gt;2&lt;/sub&gt;(CH&lt;sub&gt;3&lt;/sub&gt;CN)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>69</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: Alkenyl tosylates (0.375 mmol), LiOt-Bu (0.375 mmol), ketone (0.25 mmol), t-BuOH (0.5 mL), Pd/XPhos = 1:4 at 100 °C for 20 h under N<sub>2</sub>; Calibrated GC yields were reported using dodecane as the internal standard.

Table S3. Optimization of metal-to-ligand ratio<sup>a</sup>

![Chemical structure]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pd: XPhos</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:1</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>1:2</td>
<td>81</td>
</tr>
<tr>
<td>3</td>
<td>1:3</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>1:4</td>
<td>81</td>
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</tbody>
</table>

<sup>a</sup>Reaction conditions: Alkenyl tosylates (0.375 mmol), LiOt-Bu (0.375 mmol), ketone (0.25 mmol), t-BuOH (0.5 mL), Pd(dba)<sub>2</sub> (0.06 mmol) at 100 °C for 20 h under N<sub>2</sub>; Calibrated GC yields were reported using dodecane as the internal standard.
4. General procedures for alkelyation of ketones

**General procedure for α-alkenylation of aryl ketones with alkenyl tosylates:** A Schlenk tube equipped with a Teflon-coated stir bar was carefully evacuated and backfilled with nitrogen for three cycles. Pd source (14.4 mg, 0.025 mmol) and L2 (24 mg, 0.05 mmol) in 5 mL DCM (1.00 mol% Pd per 1.00 mL stock solution) was then prepared under N2 until all of the solids are dissolved (usually within 1 min). The corresponding volume of stock solution was then immediately added to the Schlenk tube by syringe (In case of 0.25 mol% Pd, additional 0.25 mL of DCM was added). The palladium complex solution was stirred and placed in a preheated oil bath (40 °C) for 2 minutes. The solvent was then evaporated under high vacuum. Alkenyl tosylates (0.75 mmol) and LiO-tBu (0.75 mmol) or LiOH·H2O (0.75 mmol) were loaded into the tube, and the system was further evacuated and flushed with nitrogen for three cycles. t-BuOH (1 mL) and subsequently aryl ketone (0.5 mmol) were added with stirring (250 rpm) at room temperature. After that, the tube was further stirred (1000 rpm) at room temperature for 5 minutes. The tube was then placed into a preheated oil bath (100 °C) and stirred for 24 h. Ethyl acetate (~3 mL), water (~2 mL) were added. The organic layer was separated and the aqueous layer was washed with ethyl acetate. The combined organic layer was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired product.

**General procedure for α-alkenylation of aliphatic ketones with alkenyl tosylates:** A Schlenk tube equipped with a Teflon-coated stir bar was carefully evacuated and backfilled with nitrogen for three cycles. Pd source (7.2 mg, 0.0125 mmol) and L1 (12 mg, 0.025 mmol) in 5 mL DCM (1.00 mol% Pd per 1.00 mL stock solution) was then prepared under N2 until all of the solids are dissolved (usually within 1 min). The corresponding volume of stock solution was then immediately added to the Schlenk tube by syringe (In case of 0.25 mol% Pd, additional 0.25 mL of DCM was added). The palladium complex solution was stirred and placed in a preheated oil bath (40 °C) for 2 minutes. The solvent was then evaporated under high vacuum. Alkenyl tosylates (0.25 mmol) and LiO-tBu (0.375 mmol) were loaded into the tube, and the system was further evacuated and flushed with nitrogen for three cycles. t-BuOH (0.5 mL) and subsequently aliphatic ketone (2.5 mmol) were added with stirring (250 rpm) at room temperature. After that, the tube was further stirred (1000 rpm) at room temperature for 5 minutes. The tube was then placed into a preheated oil bath (100 °C) and stirred for 24 h. Ethyl acetate (~3 mL), water (~2 mL) were added.
The organic layer was separated and the aqueous layer was washed with ethyl acetate. The combined organic layer was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired product.

5. Characterization data for coupling products

1-(Naphthalen-2-yl)-2-(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)ethan-1-one (3a): isolated yield 90%; colorless oil; Hexane:EA=100:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.06 (s, 1H), 7.83 – 7.76 (m, 1H), 7.68 (t, $J$ = 6.3 Hz, 3H), 7.39 (m, 2H), 7.20 (t, $J$ = 7.3 Hz, 2H), 7.10 (t, $J$ = 8.2 Hz, 3H), 3.61 (s, 2H), 2.23 (s, 2H), 2.04 (s, 2H), 1.62 (s, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 198.9, 143.6, 136.6, 135.4, 134.1, 132.3, 129.8, 129.4, 128.2, 128.1, 127.6, 127.3, 126.5, 123.9, 44.6, 32.2, 29.7, 23.1, 22.8. HRMS: (EI+) m/z calcd. for C$_{24}$H$_{22}$O : 326.1671, found 326.1655.

2-(3,4,5,6-Tetrahydro-[1,1'-biphenyl]-2-yl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (3b): isolated yield 72%; colorless oil; Hexane:DCM=50:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.87 (d, $J$ = 8.1 Hz, 2H), 7.65 (d, $J$ = 8.1 Hz, 2H), 7.32 (t, $J$ = 7.4 Hz, 2H), 7.25 (t, $J$ = 7.2 Hz, 1H), 7.16 (d, $J$ = 7.4 Hz, 2H), 3.63 (s, 2H), 2.36 (s, 2H), 2.14 (s, 2H), 1.77 (s, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 198.1, 143.4, 139.6, 137.3, 134.1 (q, $J$ = 33 Hz), 128.4, 128.3, 128.2, 127.9, 126.6, 125.4 (q, $J$ = 3.8 Hz), 123.6 (q, $J$ = 271 Hz), 44.9, 32.3, 29.8, 23.1, 22.8. $^{19}$F NMR (377 MHz, CDCl$_3$) δ -63.11. HRMS: (ESI+) m/z calcd. for C$_{21}$H$_{19}$F$_3$OH$^+$ : 345.1461, found 291.1456.
1-(4-Methoxyphenyl)-2-(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)ethan-1-one (3c): isolated yield 65%; colorless oil; Hexane:EA=20:1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 (d, $J = 8.8$ Hz, 2H), 7.20 (m, 2H), 7.15 – 7.04 (m, 3H), 6.76 (d, $J = 8.8$ Hz, 2H), 3.75 (d, $J = 6.8$ Hz, 3H), 3.46 (s, 2H), 2.25 (s, 2H), 2.03 (s, 2H), 1.65 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 197.6, 163.2, 143.7, 136.4, 130.4, 130.1, 128.2, 128.1, 127.6, 126.4, 113.5, 55.4, 44.2, 32.2, 29.8, 23.2, 22.8. HRMS: (EI+) m/z calcd. for C$_{21}$H$_{22}$O$_2$: 306.1620, found 306.1614.

![Image of the compound](image)

1-Phenyl-2-(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)propan-1-one (3d): isolated yield 84%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.68 (d, $J = 7.4$ Hz, 2H), 7.50 (t, $J = 7.4$ Hz, 1H), 7.47 – 7.39 (m, 2H), 7.35 (m, 3H), 7.25 (d, $J = 7.1$ Hz, 2H), 4.23 (q, $J = 6.7$ Hz, 1H), 2.34 (m, 1H), 2.20 (m, 2H), 1.78 – 1.67 (m, 2H), 1.59 (m, 3H), 1.33 (d, $J = 6.7$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 202.3, 143.8, 136.8, 135.7, 132.8, 132.5, 128.4, 128.2, 128.1, 126.7, 45.6, 32.8, 24.4, 23.0, 22.8, 15.7. HRMS: (ESI+) m/z calcd. for C$_{21}$H$_{23}$OH$^+$: 291.1743, found 291.1755

![Image of the compound](image)

1-(4-Methoxyphenyl)-2-(2-(naphthalen-2-yl)cyclohex-1-en-1-yl)ethan-1-one (3e): isolated yield 72%; white solid; Hexane:EA=20:1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 – 7.70 (m, 5H), 7.62 (s, 1H), 7.48 – 7.40 (m, 2H), 7.33 (m, 1H), 6.80 (d, $J = 8.8$ Hz, 2H), 3.82 (s, 3H), 3.62 (d, $J = 12.0$ Hz, 2H), 2.44 (s, 2H), 2.16 (d, $J = 22.5$ Hz, 2H), 1.89 – 1.75 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 197.5, 163.2, 141.1, 136.3, 133.4, 132.2, 130.3, 130.1, 128.1, 127.8, 127.7, 127.5, 126.8, 126.5, 125.9, 125.5, 113.4, 55.3, 44.3, 32.3, 29.9, 23.3, 22.9. HRMS: (ESI+) m/z calcd. for C$_{25}$H$_{24}$O$_2$H$^+$: 357.1849, found 357.1850
2-(3',5'-Bis(trifluoromethyl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)-1-(4-methoxyphenyl)ethan-1-one (3f): isolated yield 69%; colorless oil; Hexane:DCM=20:1; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.81 – 7.73 (m, 2H), 7.71 (s, 1H), 7.64 (s, 2H), 6.92 – 6.81 (m, 2H), 3.85 (s, 3H), 3.47 (s, 2H), 2.35 (d, \(J = 5.4\) Hz, 2H), 2.17 (m, 2H), 1.80 (d, \(J = 6.1\) Hz, 4H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 196.7, 163.5, 145.7, 134.0, 131.5 (q, \(J = 33\) Hz ), 130.7, 130.2, 129.9, 128.4, 123.3 (q, \(J = 271\) Hz ) 120.4, 113.6, 55.4, 43.7, 32.0, 30.3, 22.9, 22.6. \(^{19}\)F NMR (377 MHz, CDCl\(_3\)) \(\delta\) -62.88. HRMS: (ESI+) m/z calcd. for C\(_{23}\)H\(_{20}\)F\(_6\)O\(_2\)H\(^+\): 443.1440, found 443.1433

2-(4'-(Tert-butyl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)-1-(m-tolyl)ethan-1-one (3g): isolated yield 85%; colorless oil; Hexane:DCM=10:1; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.59 – 7.35 (m, 2H), 7.25 – 7.15 (m, 4H), 7.01 (d, \(J = 8.2\) Hz, 2H), 3.52 (s, 2H), 2.26 (d, \(J = 12.0\) Hz, 5H), 2.02 (s, 2H), 1.69 – 1.60 (m, 4H), 1.22 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 199.5, 149.2, 140.5, 138.1, 137.1, 136.4, 133.5, 128.7, 128.2, 127.7, 127.1, 125.4, 125.1, 44.8, 34.4, 32.3, 31.4, 29.8, 23.3, 22.9, 21.3. HRMS: (ESI+) m/z calcd. for C\(_{25}\)H\(_{30}\)OH\(^+\): 347.2369, found 347.2365

1-(Pyridin-3-yl)-2-(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)ethan-1-one (3h): isolated yield 85%; colorless oil; Hexane:EA=8:1; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.86 (d, \(J = 1.4\) Hz, 1H), 8.64 (m, 1H), 7.96 (m, 1H), 7.24 (m, 3H), 7.13 (m, 1H), 7.09 – 7.02 (m, 2H), 3.51
(s, 2H), 2.25 (s, 2H), 2.03 (s, 2H), 1.71 – 1.62 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 197.8, 152.9, 149.4, 143.3, 137.5, 135.5, 132.2, 128.3, 127.9, 126.7, 126.4, 123.5, 44.9, 32.3, 29.8, 23.1, 22.8. HRMS: (EI+) m/z calcd. for C$_{19}$H$_{19}$NO : 277.1467, found 277.1472.

2-(3,4,5,6-Tetrahydro-[1,1′-biphenyl]-2-yl)-1-(thiophen-3-yl)ethan-1-one (3i): isolated yield 65%; colorless oil; Hexane: EA=50:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.68 (d, $J$ = 2.8 Hz, 1H), 7.35 (d, $J$ = 5.1 Hz, 1H), 7.21 (t, $J$ = 7.4 Hz, 2H), 7.17 – 7.11 (m, 2H), 7.07 (d, $J$ = 7.4 Hz, 2H), 3.42 (s, 2H), 2.25 (d, $J$ = 5.3 Hz, 2H), 2.05 (d, $J$ = 4.7 Hz, 2H), 1.66 (dt, $J$ = 7.8, 4.4 Hz, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 193.3, 143.6, 142.2, 136.7, 131.9, 128.2, 128.1, 127.2, 127.0, 126.5, 125.9, 45.7, 32.3, 29.8, 23.2, 22.8. HRMS: (EI+) m/z calcd. for C$_{18}$H$_{18}$SO : 282.1078, found 282.1075.

3-Methyl-4,4-diphenyl-1-(p-tolyl)but-3-en-1-one (3j): isolated yield 73%; white solid; Hexane: EA=50:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.79 (d, $J$ = 8.1 Hz, 2H), 7.35 – 7.21 (m, 11H), 3.84 (s, 2H), 2.43 (s, 3H), 1.87 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 198.2, 143.8, 142.6, 142.5, 140.8, 134.4, 129.7, 129.3, 129.1, 128.8, 128.3, 128.2, 127.9, 126.7, 126.4, 45.9, 21.6, 20.7. HRMS: (EI+) m/z calcd. for C$_{24}$H$_{22}$O : 326.1671, found 326.1654.

2-(1,1-Diphenylprop-1-en-2-yl)-3,4-dihydronaphthalen-1(2H)-one (3k): isolated yield 60%; white solid; Hexane: EA=25:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.02 (d, $J$ = 7.5 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.24 (t, $J$ = 7.7 Hz, 3H), 7.21 – 7.12 (m, 9H), 3.55 (m, 1H), 2.91 – 2.82 (m, 2H), 2.42 – 2.26 (m, 1H), 2.14 – 2.01 (m, 1H), 1.69 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 198.4, 144.1, 142.8, 142.6, 141.2, 133.2, 132.9, 132.7, 129.7, 129.1, 128.6, 128.2, 127.9, 127.4, 126.6, 126.6, 126.4, 54.2, 29.5, 29.0, 16.8. HRMS: (EI+) m/z calcd. for
2-(3,4-Dihyronaphthalen-2-yl)-1-phenylpentan-1-one (3l): isolated yield 74%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.02 (d, $J = 7.6$ Hz, 2H), 7.53 (t, $J = 7.3$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 2H), 7.22 – 7.03 (m, 3H), 7.01 (d, $J = 7.2$ Hz, 1H), 6.43 (s, 1H), 4.21 (t, $J = 7.1$ Hz, 1H), 2.83 – 2.66 (m, 2H), 2.43 – 2.22 (m, 2H), 2.08 – 1.91 (m, 1H), 1.77 (m, 1H), 1.47 – 1.30 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 200.0, 139.2, 137.3, 134.7, 134.3, 132.8, 128.5, 128.4, 127.2, 126.8, 126.4, 126.3, 125.9, 54.8, 32.4, 28.1, 24.8, 20.9, 14.1. HRMS: (EI+) m/z calcd. for C$_{21}$H$_{22}$O : 290.1671, found 290.1654.

2-(Cyclohex-1-en-1-yl)-1,2-diphenylethan-1-one (3m): isolated yield 54%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.97 (d, $J = 7.6$ Hz, 2H), 7.54 (t, $J = 7.3$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.37 – 7.32 (m, 2H), 7.29 (m, 3H), 5.48 (s, 1H), 5.21 (s, 1H), 2.05 (d, $J = 3.9$ Hz, 4H), 1.66 – 1.58 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 198.6, 137.8, 137.3, 136.3, 132.7, 129.4, 128.6, 128.5, 128.4, 127.0, 126.3, 61.1, 28.6, 25.4, 23.0, 22.1. HRMS: (ESI+) m/z calcd. for C$_{20}$H$_{20}$OH$^+$ : 277.1587, found 277.1584.

1,2-Diphenyl-2-(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)ethan-1-one (3n): isolated yield 90%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.53 (d, $J = 7.8$ Hz, 2H), 7.34 (t, $J = 7.4$ Hz, 1H), 7.16 (m, 8H), 7.01 (m, 4H), 5.45 (s, 1H), 2.29 – 2.17 (m, 3H), 1.85 – 1.73 (m, 1H), 1.61 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 200.1, 143.7, 139.0, 137.3, 136.9, 132.6, 131.3, 129.0, 128.5, 128.4, 128.2, 128.0, 126.6, 126.5, 56.4, 33.0, 26.7, 23.0, 22.9. HRMS: (EI+) m/z calcd. for C$_{26}$H$_{24}$O : 352.1827, found 352.1828.
2-(4-(Tert-butyl)cyclohex-1-en-1-yl)-1-phenylpropan-1-one (3o): isolated yield 82%; colorless oil; Hexane:DCM=10:1; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.99 (dq, \(J = 7.1, 1.6\) Hz, 2H), 7.57 – 7.50 (m, 1H), 7.44 (m, 2H), 5.65 (m, 1H), 3.84 (m, 1H), 2.13 – 2.03 (m, 2H), 1.95 – 1.69 (m, 5H), 1.18 – 1.04 (m, 2H), 0.91 – 0.88 (m, 3H), 0.83 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 200.7, 200.6, 137.6, 137.5, 135.6, 135.4, 132.5, 132.5, 128.4, 128.4, 128.3, 126.2, 126.2, 77.3, 77.0, 76.7, 56.8, 56.4, 43.9, 43.8, 32.1, 27.7, 27.6, 27.1, 27.1, 24.3, 24.2, 23.6, 23.3, 12.3, 12.3. HRMS: (ESI+) m/z calcd. for C\(_{19}\)H\(_{28}\)OH\(^+\) : 285.2213, found 285.2209.

1-(3,4,5,6-Tetrahydro-[1,1'-biphenyl]-2-yl)propan-2-one (4a): isolated yield 72%; colorless oil; Hexane:DCM=10:1; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.23 (t, \(J = 7.4\) Hz, 2H), 7.16 (q, \(J = 7.4\) Hz, 1H), 7.05 – 7.00 (m, 2H), 2.93 (s, 2H), 2.22 (s, 2H), 1.97 (s, 2H), 1.91 (s, 3H), 1.65 (m, 4H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 207.8, 143.7, 137.0, 128.2, 127.9, 126.9, 126.4, 49.6, 32.3, 29.7, 29.4, 23.1, 22.8. HRMS: (EI+) m/z calcd. for C\(_{15}\)H\(_{18}\)O : 214.1358, found 214.1341.

1-(2-(Naphthalen-2-yl)cyclohex-1-en-1-yl)propan-2-one (4b): isolated yield 72%; colorless oil; Hexane:DCM=10:1; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.77 – 7.68 (m, 3H), 7.48 (s, 1H), 7.38 (m, 2H), 7.18 (m, 1H), 2.97 (s, 2H), 2.31 (s, 2H), 2.02 (s, 2H), 1.91 (s, 3H), 1.74 – 1.67 (m, 4H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 207.7, 141.1, 137.0, 133.4, 132.2, 127.9, 127.8, 127.6, 127.5, 126.7, 126.3, 126.0, 125.6, 49.6, 32.3, 29.8, 29.6, 23.2, 22.9. HRMS: (EI+) m/z calcd. for C\(_{19}\)H\(_{20}\)O : 264.1514, found 264.1484.
1-(4’-(Tert-butyl)-3,4,5,6-tetrahydro-[1,1’-biphenyl]-2-yl)propan-2-one (4c): isolated yield 70%; colorless oil; Hexane:DCM=10:1; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33 (d, \(J = 8.2\) Hz, 2H), 7.04 (d, \(J = 8.2\) Hz, 2H), 3.04 (s, 2H), 2.30 (s, 2H), 2.05 (s, 2H), 2.02 (s, 3H), 1.73 (m, 4H), 1.33 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 208.1, 149.2, 140.5, 136.9, 127.5, 126.8, 125.1, 49.7, 34.4, 32.3, 31.4, 29.8, 29.5, 23.2, 22.8. HRMS: (EI+) m/z calcd. for C\(_{19}\)H\(_{26}\)O : 270.1984, found 270.1990.

4-Methyl-5,5-diphenylpent-4-en-2-one (4d): isolated yield 62%; colorless oil; Hexane:DCM=10:1; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.20 (tt, \(J = 5.3, 2.5\) Hz, 4H), 7.16 – 7.08 (m, 4H), 7.07 – 6.98 (m, 2H), 3.17 (s, 2H), 2.00 (s, 3H), 1.72 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 207.1, 142.7, 142.2, 141.2, 129.5, 129.0, 128.2, 129.5, 128.0, 126.7, 126.5, 50.7, 29.7, 20.7. HRMS: (EI+) m/z calcd. for C\(_{18}\)H\(_{18}\)O : 250.1358, found 250.1366.

1-(2-(P-tolyl)cyclohept-1-en-1-yl)propan-2-one (4e): isolated yield 70%; colorless oil; Hexane:DCM=10:1; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.11 (d, \(J = 7.8\) Hz, 2H), 6.98 (d, \(J = 7.9\) Hz, 2H), 3.10 (s, 2H), 2.53 – 2.47 (m, 2H), 2.34 (s, 3H), 2.28 – 2.24 (m, 2H), 2.03 (s, 3H), 1.82 (m, 2H), 1.63 – 1.57 (m, 4H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 208.1, 142.8, 142.3, 135.8, 132.8, 128.9, 127.4, 51.6, 36.4, 34.1, 32.5, 29.6, 26.7, 26.0, 21.1. HRMS: (EI+) m/z calcd. for C\(_{17}\)H\(_{22}\)O : 242.1671, found 242.1668.
1-(6,7-Dihydro-5H-benzo[7]annulen-9-yl)propan-2-one (4f): isolated yield 50%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.27 – 7.20 (m, 3H), 7.16 – 7.12 (m, 1H), 6.28 (d, $J$ = 1.6 Hz, 1H), 2.98 (s, 2H), 2.76 (t, $J$ = 5.8 Hz, 2H), 2.30 (s, 3H), 1.80 – 1.75 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 198.7, 162.9, 143.0, 139.8, 129.0, 128.5, 126.9, 126.3, 124.9, 33.8, 32.1, 31.5, 26.9, 26.2. HRMS: (ESI+) m/z calcd. for C$_{14}$H$_{16}$OH$^+$ : 201.1474, found 201.1474.

1-(3,4-Dihydronaphthalen-1-yl)propan-2-one (4g): isolated yield 46%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.23 – 7.14 (m, 3H), 7.13 – 7.07 (m, 1H), 6.01 (t, $J$ = 4.6 Hz, 1H), 3.49 (s, 2H), 2.82 (t, $J$ = 8.1 Hz, 2H), 2.36 (m, 2H), 2.16 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 207.9, 136.3, 134.1, 131.0, 129.6, 127.7, 127.2, 126.6, 122.8, 49.1, 28.5, 28.0, 23.3. HRMS: (EI+) m/z calcd. for C$_{13}$H$_{14}$O : 186.1045, found 186.1055.

1-(2-Methyl-3,4-dihydronaphthalen-1-yl)propan-2-one (4h): isolated yield 46%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.24 – 7.09 (m, 3H), 7.06 (d, $J$ = 7.7 Hz, 1H), 3.60 (s, 2H), 2.78 (t, $J$ = 7.9 Hz, 2H), 2.33 (t, $J$ = 7.9 Hz, 2H), 2.13 (s, 3H), 1.96 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 207.8, 136.4, 135.6, 135.4, 127.3, 126.5, 126.1, 124.1, 122.4, 44.2, 30.6, 28.7, 28.2, 20.7. HRMS: (EI+) m/z calcd. for C$_{14}$H$_{16}$O : 200.1201, found 200.1190.
1-(3,4-Dihydonaphthalen-2-yl)propan-2-one (4i): isolated yield 47%; colorless oil; Hexane:DCM=10:1; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.19 – 7.10 (m, 3H), 7.02 (d, \(J = 6.8\) Hz, 1H), 6.36 (s, 1H), 3.30 (s, 2H), 2.85 (t, \(J = 8.1\) Hz, 2H), 2.29 (t, \(J = 8.1\) Hz, 2H), 2.22 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 206.5, 134.4, 134.4, 134.1, 127.3, 126.9, 126.6, 126.5, 125.8, 52.6, 29.2, 27.9, 27.3. HRMS: (EI+) m/z calcd. for C\(_{13}\)H\(_{14}\)O : 186.1045, found 186.1038.

2-(3,4-Dihydonaphthalen-2-yl)cyclohexan-1-one (4j): isolated yield 80%; colorless oil; Hexane:DCM=10:1; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.16 – 7.08 (m, 3H), 7.00 (d, \(J = 6.8\) Hz, 1H), 6.25 (s, 1H), 3.20 (m, 1H), 2.84 (m, 2H), 2.51 – 2.34 (m, 2H), 2.28 – 2.22 (m, 2H), 2.11 (m, 2H), 1.98 (m, 2H), 1.76 (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 210.6, 139.4, 135.1, 134.3, 127.1, 126.5, 126.3, 125.7, 124.3, 58.4, 42.2, 31.8, 28.0, 27.6, 26.4, 24.8. HRMS: (EI+) m/z calcd. for C\(_{16}\)H\(_{18}\)O : 226.1358, found 226.1341.

2-(3,4,5,6-Tetrahydro-[1,1'-biphenyl]-2-yl)pentan-3-one (4k): isolated yield 71%; colorless oil; Hexane:DCM=10:1; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.28 (t, \(J = 7.5\) Hz, 2H), 7.18 (m, 1H), 7.11 – 7.03 (m, 2H), 3.30 (q, \(J = 6.8\) Hz, 1H), 2.32 (m, 2H), 2.17 – 1.97 (m, 3H), 1.63 – 1.56 (m, 4H), 0.99 (d, \(J = 6.8\) Hz, 3H), 0.85 (t, \(J = 7.3\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 212.8, 144.1, 136.8, 132.4, 128.4, 127.9, 126.4, 49.9, 33.7, 32.8, 24.4, 23.2, 22.9, 13.7, 7.9. HRMS: (EI+) m/z calcd. for C\(_{17}\)H\(_{22}\)O : 242.1671, found 242.1668.
6. References


7. $^1$H and $^{13}$C NMR spectra
$3\text{l}$
$4f$
4k