Supporting Information

Alkyl-Aryl Ketone Synthesis via Nickel-Catalyzed Reductive Coupling of Alkyl Halides with Aryl Acids and Anhydrides

Xiao Jia,\textsuperscript{a} Xinghua Zhang,\textsuperscript{b} Qun Qian,\textsuperscript{a} Hegui Gong\textsuperscript{b*}

\textsuperscript{a} Department of Chemistry, Shanghai University, 99 Shang-Da Road, Shanghai 200444, China
\textsuperscript{b} School of Chemical and Environmental Engineering, Shanghai Institute of Technology, 100 Hai-Quan Road, Shanghai 201418, China

hegui_gong@shu.edu.cn

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Experimental Section

Part 1. General Information

Experiments were conducted under a nitrogen atmosphere in oven-dried or flame-dried glassware with magnetic stirring, unless otherwise specified. For product purification by flash column chromatography, silica gel (300–400 mesh) and petroleum ether (bp 60–90 °C) were used. NMR spectra were measured on 500 MHz instruments at room temperature. Reference peaks for chloroform in $^1$H NMR and $^{13}$C NMR spectra were set at 7.26 ppm and 77.0 ppm, respectively. High-resolution mass spectra (HRMS) were obtained usingalon Spec 4.7 TESLA FTMS. Low resolution mass spectra were recorded on GCMS-QP2010 SE (SHIMADZU). Melting point was recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China).

The following chemicals were purchased and used as received: Zn (99.9%, powder), NiI$_2$ (99.5%, Alfa Aesar), Ni(cod)$_2$ (99%, Stream), NiCl$_2$(99.5%, Alfa Aesar), NiBr$_2$ (99.5%, Alfa Aesar), Ni(acac)$_2$ (99%, Alfa Aesar), Ni(ClO$_4$)$_2$·6H$_2$O (99.5%, Alfa Aesar), 2,2’-bipyridine (4a, Aldrich), 4,4’-Di-tert-butyl-2,2’-bipyridine (4b, Aldrich), 4,4’-dimethyl-2,2’-bipyridine (4c, Aldrich), 4,4’-dimethoxy-2,2’-bipyridine (4d, Aldrich), 1,10-phenanthroline (5a, Aldrich), 4,7-diphenyl-1,10-phenanthroline (5b, Aldrich), DMA (99.8%, Super Dry, with molecular sieves), DMF (99.8%, Super Dry, with molecular sieves), Dioxane (99.5%, Super Dry, with molecular sieves), THF (99.5%, Super Dry, with molecular sieves), CH$_3$CN (99.5%, Super Dry, with molecular sieves), MgCl$_2$ (99%, Alfa Aesar), TBAI (99%, Aladdin), Boc$_2$O (99%, Aladdin), 2-iodopropane (TCI), iodocyclohexane (TCI) 2,3,4,6-Tetra-O-acetyl-alpha-D glucopyranosyl bromide (98%, Aladdin), 2,3,4,6-Tetra-O-acetyl-alpha-D-galactopyranosyl bromide (93%, Aladdin), benzoic anhydride (Alfa Aesar). Ligands 3a, 3b, 3c, 5c, 6f, L-1, were synthesized according to the literature procedures. The anhydrides were prepared based on reported procedures.$^7$

Part 2. Details of Optimization of Glycosyl Bromides
A typical procedure for optimization reactions of glycosyl bromide with benzoic anhydride: To a flame-dried Schlenk tube equipped with a stir bar was loaded benzoic anhydride (51.0 mg, 0.225 mmol, 150%), followed by addition of zinc power (29.4 mg, 0.45 mmol, 300%), glycosyl bromide (61.7 mg, 0.15 mmol, 100%), MgCl₂ (28.6 mg, 0.3 mmol, 200%), ligand (0.018 mmol, 12%) and Ni sources (0.015 mmol, 10%). The tube was evacuated and refilled nitrogen (N₂) three times. Solvent (0.5 mL) was added via syringe. After the reaction mixture was allowed to stir for 12 hours under N₂ atmosphere at 25 ℃, the suspension was partitioned between Na₂CO₃ (saturated) and EtOAc. The organic phase was dried (over MgSO₄) and filtered. The mixture was concentrated under reduced pressure, and the residue was loaded onto a silica column. Flash column chromatography provided the product as oil or solid.

Table S1: Screening of catalysts

<table>
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<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Yield (%)</th>
<th>α/β</th>
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<tr>
<td>1</td>
<td>Ni(COD)₂</td>
<td>20</td>
<td>4.6/1</td>
</tr>
<tr>
<td>2</td>
<td>NiI₂</td>
<td>trace</td>
<td>2.85/1</td>
</tr>
<tr>
<td>3</td>
<td>NiBr₂</td>
<td>20</td>
<td>3.3/1</td>
</tr>
<tr>
<td>4</td>
<td>NiCl₂</td>
<td>trace</td>
<td>ND b</td>
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<tr>
<td>5</td>
<td>Ni(acac)₂</td>
<td>25</td>
<td>7/1</td>
</tr>
<tr>
<td>6</td>
<td>Ni(ClO₄)₂·6H₂O</td>
<td>22</td>
<td>5.5/1</td>
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<tr>
<td>7</td>
<td>NiBr₂·dimethoxyethane</td>
<td>21</td>
<td>5/1</td>
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<tr>
<td>8</td>
<td>none</td>
<td>ND b</td>
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</table>

a Determined by NMR using trimethyl(phenyl)silane as the internal standard. b Not detected.

Table S2: Screening of ligands
<table>
<thead>
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<th>Entry</th>
<th>Ligands</th>
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<td>4.7/1</td>
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<td>2</td>
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<tr>
<td>4</td>
<td>4c</td>
<td>29</td>
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<td>5</td>
<td>4d</td>
<td>28</td>
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<td>6</td>
<td>5a</td>
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<tr>
<td>8</td>
<td>L-1</td>
<td>21</td>
<td>4.9/1</td>
</tr>
<tr>
<td>9</td>
<td>tBu-Terpy</td>
<td>trace&lt;sup&gt;b&lt;/sup&gt;</td>
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<sup>a</sup> Determined by NMR using trimethyl(phenyl)silane as the internal standard. <sup>b</sup> Not detected.

**Table S3**: Screening of additives

<table>
<thead>
<tr>
<th>Entry</th>
<th>TBAI</th>
<th>Yield(%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>α/β</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>none&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>2</td>
<td>10</td>
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<td>3.9/1</td>
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<td>6</td>
<td>50</td>
<td>54</td>
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<sup>a</sup> Determined by NMR using trimethyl(phenyl)silane as the internal standard. <sup>b</sup> Not detected.

**Table S4**: Solvent screening
Table S4: Catalysts and Solvent screening

<table>
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<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>Solvent (0.5 mL)</th>
<th>Yield(%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>α/β</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni(acac)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN/DMF (4/1)</td>
<td>68</td>
<td>3.2/1</td>
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<tr>
<td>2</td>
<td>Ni(COD)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN/DMF (4/1)</td>
<td>35</td>
<td>3.9/1</td>
</tr>
<tr>
<td>3</td>
<td>Ni(ClO&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;·6H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN/DMF (4/1)</td>
<td>78</td>
<td>3.1/1</td>
</tr>
<tr>
<td>4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Ni(ClO&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;·6H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN/DMF (4/1)</td>
<td>83&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.7/1</td>
</tr>
<tr>
<td>5</td>
<td>Ni(ClO&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;·6H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN/DMF (9/1, 1 mL)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>90</td>
<td>2.7/1</td>
</tr>
</tbody>
</table>

<sup>a</sup> Determined by NMR using trimethyl(phenyl)silane as the internal standard.  
<sup>b</sup> Not detected.  
<sup>c</sup> 20°C.

**General procedure A for ketone synthesis via reductive coupling of alkyl bromides with aryl acids:** To a flame-dried Schlenk tube equipped with a stir bar was loaded aryl acids (0.225 mmol, 150%), followed by addition of zinc power (29.4 mg, 0.45 mmol, 300%), alkyl bromides (0.150 mmol, 100%), MgCl$_2$ (35.7 mg, 0.380 mmol, 250%), 4,4'-di-tert-butyl-2,2'-bipyridine (2.8 mg, 0.011 mmol, 7%) and Ni(acac)$_2$ (1.9 mg, 0.015 mmol, 5%). The tube was evacuated and refilled nitrogen (N$_2$) three times. Boc$_2$O (98.2 mg, 0.45 mmol) and CH$_3$CN/DMF (1:4, 1 mL) was then added via syringe. After the reaction mixture was stirred for 12 hours under N$_2$ atmosphere at 25 °C, it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM. Flash column chromatography provided the product as a solid or oil.

**General procedure B for ketone synthesis via reductive coupling of alkyl iodides with aryl acids:** To a flame-dried Schlenk tube equipped with a stir bar was loaded aryl acids (0.45 mmol), followed by addition of zinc power (58.8 mg, 0.9 mmol, 300%), MgCl$_2$ (57.2 mg, 0.6 mmol, 200%), 2,2'-bipyridine (5.6 mg, 0.036 mmol, 12%) and Ni(ClO$_4$)$_2$·6H$_2$O (11 mg, 0.030 mmol, 10%). The tube was evacuated and refilled nitrogen (N$_2$) three times. Boc$_2$O (196.4 mg, 0.9 mmol, 300%), alkyl iodides (0.3 mmol, 100%) and CH$_3$CN/DMF (4:1, 1 mL) was added via syringe. After the reaction mixture was stirred for 12 hours under N$_2$ atmosphere at 25 °C, it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM. Flash column chromatography provided the product as a solid or oil.

**General procedure C for ketone synthesis via reductive coupling of glycosyl bromides with aryl anhydrides:** To a flame-dried Schlenk tube equipped with a stir bar was loaded aryl anhydrides (0.45 mmol, 150%), followed by addition of zinc power (58.8 mg, 0.9 mmol, 300%), TBAI (22.2 mg, 0.06 mmol, 20%), glycosyl bromides (0.300 mmol, 100%), MgCl$_2$ (57.2 mg, 0.6 mmol), 2,2'-bipyridine (5.6 mg, 0.036 mmol, 12%) and Ni(ClO$_4$)$_2$·6H$_2$O (11 mg, 0.030 mmol, 10%). The tube was evacuated and refilled nitrogen (N$_2$) three times. CH$_3$CN/DMF (9:1, 1 mL) was added via syringe. After the reaction mixture was stirred for 12 hours under N$_2$ atmosphere at 25 °C, the suspension was washed with Na$_2$CO$_3$ (saturated) and extracted by EtOAc. The organic phase was dried (over MgSO$_4$) and filtered. The mixture was concentrated under reduced pressure, and the residue was
loaded onto a silica column. Flash column chromatography provided the product as a solid or oil.

**Phenyl(1-tosylpiperidin-4-yl)methanone (2a).**

According to the general procedure A, the title compound was obtained in (45.3 mg, 0.132 mmol) 88% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO$_2$: 20% ethyl acetate in petroleum ether)."}

**{(4-(tert-Butyl)phenyl)(1-tosylpiperidin-4-yl)methanone (2b).**

According to the general procedure A, this compound was obtained in (50.3 mg, 0.126 mmol) 84% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO$_2$: 20% ethyl acetate in petroleum ether)."}

**{(4-Butylphenyl)(1-tosylpiperidin-4-yl)methanone (2c).**

According to the general procedure A, this compound was obtained in (46.1 mg, 0.116 mmol) 77% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO$_2$: 20% ethyl acetate in petroleum ether). ¹H NMR (500 MHz, CDCl$_3$): $\delta$ 7.76 (d, $J = 8.2$ Hz, 2H), 7.65 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 7.9$ Hz, 2H), 7.22 (d, $J = 8.3$ Hz, 2H), 3.76 (dt, $J = 12.2$, 4.3 Hz, 2H), 3.20–3.14 (m, 1H), 2.65–2.62 (t, $J = 7.8$ Hz, 2H), 2.51 (td, $J = 11.4$, 3.4 Hz, 2H), 2.44 (s, 3H), 1.94–1.83 (m, 4H), 1.61–1.55 (m, 2H), 1.33 (h, $J = 7.4$ Hz, 2H), 0.91 (t, $J = 7.4$ Hz, 3H). ¹³C NMR (125 MHz, CDCl$_3$): 201.0, 149.0, 143.5, 133.14, 133.08, 129.6, 128.7, 128.3, 127.7, 45.6, 42.1, 35.6, 33.1, 27.9, 22.2, 21.5, 13.8. HRMS (ESI): calcd for C$_{23}$H$_{29}$NO$_3$S $[M]$ + 399.1868, found 399.1868. m.p. 119–120 °C.

**{(4-Chlorophenyl)(1-tosylpiperidin-4-yl)methanone (2d).**

According to the general procedure A, this compound was obtained in (39.6 mg, 0.105 mmol) 70% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO$_2$: 20% ethyl acetate in petroleum ether)."
(4-Fluorophenyl)(1-tosylpiperidin-4-yl)methanone (2e).

According to the general procedure A, this compound was obtained in (41.7 mg, 0.116 mmol) 77% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO₂: 20% ethyl acetate in petroleum ether).

(1-Tosylpiperidin-4-yl)(4-trifluoromethyl)phenyl)methanone

According to the general procedure A, this compound was obtained in (21.6 mg, 0.053 mmol) 35% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO₂: 20% ethyl acetate in petroleum ether).

1H NMR (500 MHz, CDCl₃): δ7.94 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 3.77 (dt, J = 12.0, 3.4 Hz, 2H), 3.20-3.14 (m, 1H), 2.52 (td, J = 11.6, 3.1 Hz, 2H), 2.45 (s, 3H), 1.98–1.81 (m, 4H). 13C NMR (125 MHz, CDCl₃): δ200.4, 143.7, 138.3, 134.8, 134.5, 134.3, 134.0, 129.7, 125.82, 125.80, 125.77, 125.74, 124.5, 122.3, 120.2, 45.4, 42.6, 27.6, 21.5. HRMS (ESI): calcd for C₂₀H₁₉F₃NO₃S [M]+ 411.1116, found 411.1091.

Methyl 4-(1-tosylpiperidin-4-carbonyl)benzoate (2g)

According to the general procedure A, this compound was obtained in (24.1 mg, 0.06 mmol) 40% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO₂: 20% ethyl acetate in petroleum ether). 1H NMR (500 MHz, CDCl₃): δ8.07 (d, J = 8.5 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 3.92 (s, 3H), 3.78–3.74 (m, 2H), 3.24-3.18 (m, 1H), 2.51 (td, J = 11.5, 3.1 Hz, 2H), 2.44 (s, 3H), 1.98–1.86 (m, 4H), 1.36 (s, 1H). 13C NMR (125 MHz, CDCl₃): δ201.0, 166.1, 143.7, 138.9, 134.0, 133.0, 130.0, 129.7, 128.0, 127.7. HRMS (ESI): calcd for C₂₁H₂₃NO₅S [M]+ 401.1297, found 401.1263. m.p. 173-174 °C.

(4-Methoxyphenyl)(1-tosylpiperidin-4-yl)methanone (2h).

According to the general procedure A, this compound was obtained in (44.8 mg, 0.12 mmol) 80% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO₂: 20% ethyl acetate in petroleum ether).
According to the general procedure A, this compound was obtained in (44.8 mg, 0.12 mmol) 80% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO$_2$: 20% ethyl acetate in petroleum ether).$^8$

(3-Methoxyphenyl)(1-tosylpiperidin-4-yl)methanone (2i).

According to the general procedure A, this compound was obtained in 53% yield (29.7 mg, 0.080 mmol) as a white solid. Purification of the crude material was performed by column chromatography (SiO$_2$: 20% ethyl acetate in petroleum ether).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.65 (d, $J = 8.0$ Hz, 2H), 7.46 (dd, $J = 7.7$, 1.8 Hz, 1H), 7.44-7.41 (m, 1H), 7.32 (d, $J = 8.0$ Hz, 2H), 6.98 (t, $J = 7.6$ Hz, 1H), 6.91 (d, $J = 8.4$ Hz, 1H), 3.82 (s, 3H), 3.67 (dt, $J = 11.9$, 4.1 Hz, 2H), 3.12-3.18 (m, 1H), 2.49 (td, $J = 11.4$, 2.9 Hz, 2H), 2.44 (s, 3H), 1.93 (dd, $J = 13.5$, 3.9 Hz, 2H), 1.80-1.72 (m, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 204.4, 157.5, 143.4, 133.4, 133.1, 130.1, 129.6, 127.9, 127.7, 120.9, 111.3, 55.5, 46.7, 45.7, 27.3, 21.5. HRMS (ESI): calcd for C$_{20}$H$_{23}$NO$_4$S [M]+ 373.1348, found 373.1344. m.p. 111–112 °C.

(1-Tosylpiperidin-4-yl)(3,4,5-trimethoxyphenyl)methanone (2k).

According to the general procedure A, this compound was obtained in 58% yield (37.7 mg, 0.087 mmol) as a white solid. Purification of the crude material was performed by column chromatography (SiO$_2$: 30% ethyl acetate in petroleum ether).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.85 (dd, $J = 8.3$, 3.3 Hz, 2H), 7.33–7.20

(4-(4-butylbenzoyl)piperidin-1-yl)(2-methoxyphenyl)-methanone (8)

According to the general procedure A, this compound was obtained in (45.5 mg, 0.12 mmol) 80% yield as colorless oil. Purification of the crude material was performed by column chromatography (SiO$_2$: 30% ethyl acetate in petroleum ether).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.85 (dd, $J = 8.3$, 3.3 Hz, 2H), 7.33–7.20
(m, 4H), 6.96 (m, 1H), 6.89 (d, \( J = 8.3 \) Hz, 1H), 4.79–4.71 (m, 1H), 3.82 (d, \( J = 2.5 \) Hz, 3H), 3.58 (dd, \( J = 13.9, 3.8 \) Hz, 1H), 3.52–3.44 (m, 1H), 3.18–2.97 (m, 2H), 2.64 (t, \( J = 7.8 \) Hz, 2H), 1.98 (m, 1H), 1.85–1.69 (m, 3H), 1.62–1.59 (m, 2H), 1.36–1.31 (m, 2H), 0.91 (t, \( J = 7.4 \) Hz, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 201.4, 201.3, 167.7, 167.6, 155.24, 155.16, 148.88, 148.85, 133.2, 130.22, 130.17, 128.7, 128.3, 127.7, 127.6, 125.9, 125.8, 120.8, 120.7, 110.8, 110.7, 55.5, 55.4, 46.6, 46.0, 43.2, 43.1, 41.11, 41.10, 35.5, 33.1, 28.63, 28.57, 28.52, 28.46 22.2, 13.8.

HRMS (ESI): calcd for C\(_{24}\)H\(_{29}\)NO\(_3\) [M]\(^+\) 379.2147, found 379.2147.

(2,3-Dihydro-1H-inden-2-yl)(phenyl)methanone (9). According to the general procedure A, this compound was obtained in (27.7 mg, 0.125 mmol) 83% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO\(_2\): 10% ethyl acetate in petroleum ether).\(^8\)

Phenyl(1-tosylpyrrolidin-3-yl)methanone (10)

According to the general procedure A, this compound was obtained in (34.5 mg, 0.105 mmol) 70% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO\(_2\): 20% ethyl acetate in petroleum ether). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.88–7.84 (m, 2H), 7.75–7.70 (m, 2H), 7.60–7.56 (m, 1H), 7.50–7.45 (m, 2H), 7.33 (d, \( J = 8.2 \) Hz, 2H), 3.93 (p, \( J = 7.7 \) Hz, 1H), 3.71 (dd, \( J = 10.1, 8.0 \) Hz, 1H), 3.47 (ddd, \( J = 9.8, 7.6, 6.4 \) Hz, 1H), 3.38 (dd, \( J = 10.1, 7.3 \) Hz, 1H), 3.25 (ddd, \( J = 9.9, 8.1, 6.0 \) Hz, 1H), 2.45 (s, 3H), 2.22–2.05 (m, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 198.1, 143.6, 135.5, 133.6, 133.2, 129.7, 128.8, 128.3, 127.7, 50.0, 47.5, 45.0, 28.5, 21.5. HRMS (ESI): calcd for C\(_{18}\)H\(_{19}\)NO\(_3\)S [M]\(^+\) 329.1086, found 329.1079. m.p. 109–110 \(^\circ\)C.

3-Methyl-4-oxo-4-phenylbutyl 4-methoxybenzoate (11)

According to the general procedure A, this compound was obtained in (29.5 mg, 0.0945 mmol) 63% yield as colorless oil. Purification of the crude material was performed by column chromatography (SiO\(_2\): 20% ethyl acetate in petroleum ether). \(^8\)

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8 These are references to specific procedures and compounds, likely found in a previous section or document.
4-Methyl-6-(3-methyl-4-oxo-4-phenylbutoxy)-2H-chromen-2-one (12)

According to the general procedure A, this compound was obtained in (23.2 mg, 0.069 mmol) 46% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO$_2$: 20% ethyl acetate in petroleum ether). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$7.98–7.97 (m, 2H), 7.57–7.53 (m, 1H), 7.47–7.43 (m, 3H), 6.77 (dd, $J = 6.3$, 2.5 Hz, 2H), 6.73 (d, $J = 2.4$ Hz, 1H), 6.10 (q, $J = 1.2$ Hz, 1H), 4.09 (ddd, $J = 9.5$, 6.8, 5.4 Hz, 1H), 4.02 (ddd, $J = 9.5$, 6.9, 5.3 Hz, 1H), 3.83–3.76 (m, 1H), 2.36 (d, $J = 1.3$ Hz, 1H), 1.96 (ddt, $J = 14.3$, 6.9, 5.6 Hz, 1H), 1.28 (d, $J = 7.0$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$203.4, 161.7, 161.2, 155.1, 152.4, 136.2, 133.0, 128.6, 128.2, 125.4, 113.5, 112.1, 111.9, 101.5, 66.2, 37.1, 32.5, 18.6, 17.8. HRMS (ESI): calcd for C$_{21}$H$_{20}$O$_4$ [M$^+$] 336.1362, found 336.1335. m.p. 127–128°C.

2-(4-(4-(tert-Butyl)phenyl)-3-methyl-4-oxobutyl)isoindoline-1,3-dione (13)

According to the general procedure A, this compound was obtained in (21.8 mg, 0.06 mmol) 40% yield as a colorless oil. Purification of the crude material was performed by column chromatography (SiO$_2$: 20% ethyl acetate in petroleum ether).$^8$

2-Methyl-1,3-diphenylpropan-1-one(1a)henyl(1-tosylpyrrolidin-3-yl)methanone (14)

According to the general procedure A, this compound was obtained in (24.9 mg, 0.111 mmol) 74% yield as a colorless oil. Purification of the crude material was performed by column chromatography (SiO$_2$: 5% ethyl acetate in petroleum ether).$^8$

4-((1H-Indol-1-yl)-2-methyl-1-phenylbutan-1-one (15)

According to the general procedure A, this compound was obtained in (45.7 mg, 0.165 mmol) 55% yield as a colorless oil. Purification of the crude material was performed by column chromatography (SiO$_2$: 10% ethyl acetate in petroleum ether). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$7.81–7.76 (m, 2H), 7.67 (d, $J = 7.65$Hz, 1H), 7.56–7.53 (m, 1H), 7.42–7.39 (t, $J = 7.74$, 2H), 7.32 (d, $J = 8.2$ Hz, 1H), 7.18 (dt, $J = 8.1$, 7.0, 1.2Hz, 1H), 7.12 (dt, $J = 7.9$, 7.0, 1.0Hz, 1H),
7.03 (d, \( J = 3.1 \text{ Hz} \), 1H), 6.51 (d, \( J = 3.1 \text{ Hz} \), 1H), 4.26–4.13 (m, 2H), 3.36–3.29 (m, 1H), 2.50–2.43 (m, 1H), 2.00–1.92 (m, 1H), 1.24 (d, \( J =7.1 \text{ Hz} \), 3H). \(^{13}\text{C NMR (125 MHz, CDCl}_3\)): \( \delta \) 203.1, 135.84, 135.80, 133.0, 128.60, 128.57, 128.2, 127.8, 121.5, 120.9, 119.3, 109.4, 101.2, 44.1, 37.6, 33.4, 17.8. HRMS (ESI): calcld for \( \text{C}_{19}\text{H}_{19}\text{NO}\) \([\text{M}]+\) 277.1467, found 277.1455.

(2-(tert-Butyldimethylsilyloxy)cyclopentyl)(4-tert-butylphenyl)methanone (16).

According to the general procedure A, this compound was obtained in (52.4 mg, 0.146 mmol) 97% yield as a colorless oil. Purification of the crude material was performed by column chromatography (SiO\(_2\): 3% ethyl acetate in petroleum ether).\(^8\)

(1-((tert-Butyldimethylsilyloxy)-2,3-dihydro-1H-inden-2-yl)(phenyl)methanone (17).

According to the general procedure A, this compound was obtained in (45.5 mg, 0.129 mmol) 86% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO\(_2\): 5% ethyl acetate in petroleum ether).\(^8\)

(4-tert-Butylphenyl)(cyclohexyl)methanone (18).

According to the general procedure B, this compound was obtained in (32.3 mg, 0.132 mmol) 88% yield as a colorless oil. Purification of the crude material was performed by column chromatography (SiO\(_2\): 3% ethyl acetate in petroleum ether).\(^8\)

1-(4-tert-Butylphenyl)-2-methylpropan-1-one (19).

According to the general procedure B, this compound was obtained in (16.9 mg, 0.0825 mmol) 55% yield as a colorless oil. Purification of the crude material was performed by column chromatography (SiO\(_2\): 3% ethyl acetate in petroleum ether).\(^9\)

According to the general procedure C, this compound was obtained in (117.7 mg, 0.27 mmol) 90% yield and ratio of α to β (3.4:1) as a colorless oil. Purification of the crude material was performed by column chromatography (SiO₂; 30% ethyl acetate in petroleum ether). ¹H NMR (500 MHz, CDCl₃): δ7.94–7.92 (m, 2H), 7.59 (d, J = 6.4 Hz, 1H), 7.59 (t, J = 9.2 Hz, 1H), 5.87 (t, J = 9.4 Hz, 1H), 5.59 (d, J = 13.9, 3.9 Hz, 1H), 5.25 (dd, J = 9.8, 6.3 Hz, 1H), 5.06 (t, J = 9.2 Hz, 1H), 4.21–4.17 (m, 2H), 3.99 (dd, J = 13.9, 3.9 Hz, 1H), 2.01 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H), 1.78 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ195.9, 170.4, 170.4, 169.8, 169.8, 169.7, 169.4, 168.9, 168.9, 134.9, 134.9, 129.3, 129.3, 128.6, 77.7, 76.7, 74.2, 68.9, 68.2, 62.3, 20.6, 20.6, 20.6, 20.4. HRMS (ESI): calcd for C₂₁H₂₄O₁₀ [M]+ 436.1369, found 436.1369.

m.p. 127–128 °C.


¹H NMR (500 MHz, CDCl₃): δ7.90 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 5.93 (t, J = 9.4 Hz, 1H), 5.60 (d, J = 6.3 Hz, 1H), 5.29–5.24 (m, 1H), 5.09 (t, J = 9.3 Hz, 1H), 4.22–4.18 (m, 2H), 4.00 (dd, J = 13.8, 3.4 Hz, 1H), 2.03 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.80 (s, 3H), 1.33 (s, 9H). ¹³C NMR (125 MHz, CDCl₃): δ191.9, 170.5, 170.5, 169.7, 169.4, 168.9, 168.9, 134.9, 134.9, 129.3, 129.3, 128.6, 77.7, 76.7, 74.2, 68.9, 68.2, 62.3, 20.6, 20.6, 20.6, 20.4. HRMS (ESI): calcd for C₂₁H₂₄O₁₀ [M]+ 436.1369, found 436.1368. m.p. 127–128°C.


According to the general procedure C, this compound was obtained in (122.6 mg, 0.249 mmol) 83% yield and ratio of α to β (2.8:1) as a white solid. Purification of the crude material was performed by column chromatography (SiO₂; 30% ethyl acetate in petroleum ether). ¹H NMR (500 MHz, CDCl₃): δ7.90 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 5.93 (t, J = 9.4 Hz, 1H), 5.60 (d, J = 6.3 Hz, 1H), 5.29–5.24 (m, 1H), 5.09 (t, J = 9.3 Hz, 1H), 4.22–4.18 (m, 2H), 4.00 (dd, J = 13.8, 3.4 Hz, 1H), 2.03 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.80 (s, 3H), 1.33 (s, 9H). ¹³C NMR (125 MHz, CDCl₃): δ195.3, 170.5, 170.2, 169.9, 169.7, 158.0, 133.2, 128.7, 125.8, 71.9, 71.2, 70.4, 69.4, 68.5, 61.9, 35.2, 31.04, 30.95, 20.69, 20.61, 20.60, 20.4. HRMS (ESI): calcd for C₂₃H₃₂O₁₀ [M]+ 492.1995, found 492.1994. m.p. 139–140 °C.

\[ \text{H NMR (500 MHz, CDCl}_3\text{): } \delta 7.91 (d, J = 8.5, 2H), 7.48 (d, J = 8.4 Hz, 2H), 5.49 (t, J = 9.6 Hz, 1H), 5.35 (t, J = 9.4 Hz, 1H), 5.15 (t, J = 9.7 Hz, 1H), 4.73 (d, J = 9.9 Hz, 1H), 4.24 (dd, J = 12.3, 5.4 Hz, 1H), 4.14 (dd, J = 12.4, 2.4 Hz, 1H), 3.90 (ddd, J = 10.1, 5.5, 2.4 Hz, 2H), 2.06 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.82 (s, 3H), 1.33 (s, 9H).

13C NMR (125 MHz, CDCl\text{)}\text{): } \delta 191.3, 170.52, 170.47, 169.3, 168.9, 157.9, 132.3, 129.2, 125.5, 77.6, 76.6, 74.2, 68.9, 68.2, 62.2, 35.2, 31.0, 29.6, 20.66, 20.62, 20.56, 20.4. HRMS (ESI): calcd for C\text{25}H\text{32}O\text{10}[M]^{+} 492.1995, found 492.1993. m.p. 128-129 °C.


According to the general procedure C, this compound was obtained in (102.6 mg, 0.228 mmol) 76% yield and ratio of α to β (1.8:1) as a white solid. Purification of the crude material was performed by column chromatography (SiO\text{2}: 30% ethyl acetate in petroleum ether). \[ \text{H NMR (500 MHz, CDCl}_3\text{): } \delta 7.55 (d, J = 7.7 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 7.1 Hz, 2H), 5.75 (t, J = 6.7 Hz, 1H), 5.19 (dd, J = 9.8, 6.7 Hz, 1H), 5.09 (t, J = 9.4 Hz, 1H), 4.61 (ddd, J = 10.0, 4.8, 2.2 Hz, 1H), 4.25 (dd, J = 12.5, 4.8 Hz, 1H), 4.10 (dd, J = 12.5, 2.3 Hz, 1H), 2.51 (s, 3H), 2.05 (s, 6H), 2.02 (s, 3H), 1.63 (s, 3H).

13C NMR (125 MHz, CDCl\text{)}\text{): } \delta 201.1, 170.6, 169.82, 169.79, 135.2, 132.0, 128.5, 125.8, 72.8, 71.9, 70.1, 69.6, 68.3, 62.0, 20.8, 20.68, 20.62, 20.0. HRMS (ESI): calcd for C\text{22}H\text{25}O\text{9}[M]^{+} 450.1526, found 450.1526. m.p. 122–123 °C.


\[ \text{H NMR (500 MHz, CDCl}_3\text{): } \delta 7.70 (d, J = 7.7 Hz, 1H), 7.40 (t, J = 7.3 Hz, 1H), 7.27 (t, J = 9.4 Hz, 2H), 5.40 (t, J = 9.6 Hz, 1H), 5.31 (t, J = 9.4 Hz, 1H), 5.12 (t, J = 9.7 Hz, 1H), 4.70 (d, J = 9.8 Hz, 1H), 4.21 (dd, J = 12.3, 6.1 Hz, 1H), 4.12 (dd, J = 12.4, 2.4 Hz, 1H), 3.84 (ddd, J = 10.1, 5.5, 2.4 Hz, 2H), 2.45 (s, 3H), 2.03 (s, 6H), 2.00 (s, 3H), 1.75 (s, 3H). 13C NMR (125 MHz, CDCl\text{)}\text{): } \delta 194.9, 170.5, 170.4, 169.3, 168.9, 140.0, 135.2, 132.2, 132.1, 129.4, 125.4, 78.3, 76.4, 74.2, 69.1, 68.2, 62.2, 21.3, 20.63, 20.58, 20.53, 20.2. HRMS (ESI): calcd for C\text{22}H\text{25}O\text{9}[M]^{+} 450.1526, found 450.1526. m.p. 109-110 °C.

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-(4-methylbenzoyl)tetrahydro-2H-pyran-3,4,5-triyi

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triacetate (a-24).

According to the general procedure C, this compound was obtained in (112.1 mg, 0.249 mmol) 83% yield and ratio of α to β (3.2:1) as a colorless oil. Purification of the crude material was performed by column chromatography (SiO₂; 30% ethyl acetate in petroleum ether). ¹H NMR (500 MHz, CDCl₃): δ7.83 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 5.89 (t, J = 9.3 Hz, 1H), 5.57 (d, J = 6.3 Hz,) 1H, 5.24 (dd, J = 9.8, 6.4 Hz, 1H), 5.06 (t, J = 9.3 Hz, 1H), 4.21–4.15 (m, 2H), 4.00–3.96 (m, 1H), 2.39 (s, 3H), 2.00 (s, 3H) 1.97 (s, 3H), 1.79 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ195.3, 170.4, 170.1, 169.8, 169.6, 145.1, 133.2, 129.4, 128.8, 71.8, 71.0, 70.3, 69.3, 68.5, 61.8, 21.6, 20.6, 20.5, 20.4. HRMS (ESI): calcd for C₂₂H₂₆O₁₀ [M]+ 450.1526, found 450.1522.


¹H NMR (500 MHz, CDCl₃): δ7.87 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 5.48 (t, J = 9.6 Hz, 1H), 5.34 (t, J = 9.4 Hz, 1H), 5.15 (t, J = 9.7 Hz, 1H), 4.71 (d, J = 9.8 Hz, 1H), 4.23 (dd, J = 12.5, 5.7 Hz, 1H), 4.14 (dd, J = 12.3, 2.2 Hz, 1H), 3.89 (dd, J = 10.1, 5.5, 2.4 Hz, 2H), 2.41 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.83 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ191.4, 170.52, 170.45, 169.3, 168.9, 145.0, 132.4, 129.4, 129.3, 77.7, 76.6, 74.2, 68.9, 68.2, 62.2, 21.7, 20.68, 20.62, 20.56, 20.4. HRMS (ESI): calcd for C₂₂H₂₆O₁₀ [M]+ 450.1526, found 450.1523. m.p. 108–109 °C.


According to the general procedure C, this compound was obtained in (113.1 mg, 0.249 mmol) 83% yield and ratio of α to β (3.4:1) as a white solid. Purification of the crude material was performed by column chromatography. (SiO₂; 30% ethyl acetate in petroleum ether). ¹H NMR (500 MHz, CDCl₃): δ8.01–7.98 (m, 2H), 7.13(t, J = 8.6 Hz, 2H), 5.88 (t, J = 9.2 Hz, 1H), 5.54 (d, J = 6.3 Hz, 1H), 5.06 (t, J = 9.6, 6.2 Hz, 1H), 5.06 (t, J = 9.4 Hz, 1H), 4.18 (dd, J = 12.4, 4.9 Hz, 1H), 4.10 (dd, J = 9.9, 4.9, 2.2 Hz, 1H), 3.98 (dd, J = 12.4, 2.3 Hz, 1H), 2.03 (s, 6H), 1.97 (s, 3H), 1.83 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ194.0, 170.4, 170.1, 169.8, 169.6, 167.2, 165.1, 131.99, 131.97, 131.63, 131.55, 116.0, 115.9, 72.0, 71.3, 70.1, 69.3, 68.4, 61.8, 20.61, 20.58, 20.52, 20.4. HRMS (ESI): calcd for C₂₁H₁₉F₀ [M]+ 454.1275, found 454.1274. m.p. 88–89°C.
triacetate (β-25).

$^1$H NMR (500 MHz, CDCl$_3$): δ8.04–8.01 (m, 2H), 7.14 (t, $J = 8.6$ Hz, 2H), 5.47 (t, $J = 9.6$ Hz, 1H), 5.34 (t, $J = 9.4$ Hz, 1H), 5.15 (t, $J = 9.7$ Hz, 1H), 4.67 (d, $J = 9.9$ Hz, 1H), 4.23 (dd, $J = 12.5$, 5.4 Hz, 1H), 4.15 (dd, $J = 12.4$, 2.3 Hz, 1H), 3.90 (dd, $J = 10.1$, 5.6, 2.4 Hz, 2H), 2.07 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.87 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ190.4, 170.44, 170.40, 169.3, 168.9, 167.2, 165.1, 132.13, 132.06, 131.20, 131.17, 115.9, 115.7, 78.1, 76.7, 74.0, 68.8, 68.1, 62.2, 20.66, 20.60, 20.5, 20.4. HRMS (ESI): calcd for C$_{21}$H$_{23}$FO$_{10}$ [M]$^+$ 454.1275, found 454.1274. m.p. 128–129 °C.

$^{(2R,3R,4S,5R,6S)}$-2-(acetoxymethyl)-6-(3-methoxybenzoyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (α-26).

According to the general procedure C, this compound was obtained in (111.9 mg, 0.24 mmol) 80% yield and ratio of α to β (3.7:1). as a colorless oil. Purification of the crude material was performed by column chromatography (SiO$_2$: 30% ethyl acetate in petroleum ether). $^1$H NMR (500 MHz, CDCl$_3$): δ7.51 (d, $J = 7.8$ Hz, 1H), 7.47 (s, 1H), 7.38 (t, $J = 7.8$ Hz, 1H), 7.14 (dd, $J = 8.2$, 2.2 Hz, 1H) 5.89 (t, $J = 9.4$ Hz, 1H), 5.59 (d, $J = 6.4$ Hz, 1H), 5.29–5.24 (m, 1H), 5.07 (t, $J = 9.4$ Hz, 1H), 4.24–4.19 (m, 2H), 4.02 (dd, $J = 14.1$, 4.0 Hz, 1H), 3.84 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.80 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ195.8, 170.5, 170.1, 169.8, 169.6, 159.9, 137.0, 129.8, 121.3, 120.8, 112.5, 72.0, 71.3, 70.3, 69.3, 68.5, 61.9, 55.4, 20.7, 20.6, 20.4. HRMS (ESI): calcd for C$_{22}$H$_{26}$O$_{11}$ [M]$^+$ 466.1475, found 466.1474. m.p. 103–104 °C.

$^{(2R,3R,4S,5R,6R)}$-2-(acetoxymethyl)-6-(3-methoxybenzoyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (β-26).

$^1$H NMR (500 MHz, CDCl$_3$): δ7.56 (d, $J = 7.6$ Hz, 1H), 7.5 (s, 1H), 7.38 (t, $J = 7.8$ Hz, 1H), 7.14 (dd, $J = 8.4$, 2.6 Hz, 1H), 5.49 (t, $J = 9.6$ Hz, 1H), 5.35 (t, $J = 9.4$ Hz, 1H), 5.15 (t, $J = 9.4$ Hz, 1H), 4.72 (d, $J = 9.8$ Hz, 1H), 4.22 (dd, $J = 12.4$, 5.6 Hz, 1H), 4.14 (dd, $J = 12.3$, 2.4 Hz, 1H), 3.91 (dd, $J = 10.0$, 5.6, 2.3 Hz, 1H), 3.84 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.86 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ191.6, 170.6, 170.5, 169.4, 168.9, 159.8, 136.1, 129.5, 121.8, 120.3, 113.7, 77.7, 76.7, 74.2, 68.9, 68.2, 62.2, 55.4, 20.63, 20.57, 20.4. HRMS (ESI): calcd for C$_{22}$H$_{26}$O$_{11}$ [M]$^+$ 466.1475, found 466.1474. m.p. 103-104 °C.

$^{(2R,3S,4S,5R,6S)}$-2-(Acetoxymethyl)-6-benzoyltetrahydro-2H-pyran-3,4,5-triyl triacetate (α-26).
According to the general procedure C, this compound was obtained in (109.9 mg, 0.252 mmol) 84% yield and ratio of α to β (4.5:1) as a white solid. Purification of the crude material was performed by column chromatography (SiO$_2$: 30% ethyl acetate in petroleum ether). $^1$H NMR (500 MHz, CDCl$_3$): δ7.91 (dd, $J = 8.6, 1.2$ Hz, 2H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.8$ Hz, 2H), 5.75 (dd, $J = 10.3, 3.4$ Hz, 1H), 5.68 (d, $J = 6.4$ Hz, 1H), 5.53–5.48 (m, 2H), 4.52 (dd, $J = 5.8, 1.7$ Hz, 1H), 4.07 (qd, $J = 11.5, 6.4$ Hz, 2H), 2.15 (s, 3H), 1.99 (s, 3H), 1.90 (s, 3H), 1.75 (s, 3H). 13C NMR (125 MHz, CDCl$_3$): δ196.5, 170.3, 170.0, 169.7, 136.1, 133.9, 128.7, 128.6, 71.2, 71.0, 67.9, 67.7, 66.8, 61.7, 20.63, 20.58, 20.5, 20.4. HRMS (ESI): calcd for C$_{21}$H$_{24}$O$_{10}$ [M]$^+$ 436.1369, found 436.1367.

Accordine to the general procedure C, this compound was obtained in (121.5 mg, 0.27 mmol) 90% yield and ratio of α to β (4.2:1). Colorless oil. Purification by column chromatography (SiO$_2$: 30% ethyl acetate in petroleum ether). $^1$H NMR (500 MHz, CDCl$_3$): δ7.80 (d, $J = 8.3$ Hz, 2H), 7.24 (d, $J = 8.1$ Hz, 2H), 5.75 (dd, $J = 10.4, 3.4$ Hz, 1H), 5.63 (d, $J = 6.4$ Hz, 1H), 5.51–5.45 (m, 2H), 4.50 (td, $J = 6.5, 1.8$ Hz, 1H), 4.08–4.00 (m, 2H), 2.39 (s, 3H), 2.13 (s, 3H), 1.97 (s, 3H), 1.89 (s, 3H), 1.75 (s, 3H). 13C NMR (125 MHz, CDCl$_3$): δ195.9, 170.29, 170.26, 170.0, 169.4, 144.9, 133.5, 129.4, 128.7, 71.2, 71.0, 67.9, 67.7, 66.8, 61.6, 21.6, 20.57, 20.52, 20.44, 20.39. HRMS (ESI): calcd for C$_{22}$H$_{26}$O$_{10}$ [M]$^+$ 450.1526, found 450.1525.

(2R,3S,4S,5R,6S)-2-(Acetoxymethyl)-6-(4-methylbenzoyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (α-28).

According to the general procedure C, this compound was obtained in (121.5 mg, 0.27 mmol) 90% yield and ratio of α to β (4.2:1). Colorless oil. Purification by column chromatography (SiO$_2$: 30% ethyl acetate in petroleum ether). $^1$H NMR (500 MHz, CDCl$_3$): δ7.58 (dd, $J = 7.7, 1.8$ Hz, 1H), 7.00 (t, $J = 7.5$ Hz, 1H), 6.93 (d, $J = 8.4$ Hz, 1H), 5.83 (d, $J = 6.6$ Hz, 1H), 5.59 (dd, $J = 10.1, 3.3$ Hz, 1H), 5.52–5.49 (m, 2H), 4.68 (td, $J = 6.5, 2.0$ Hz, 1H), 4.12–4.03 (m, 2H), 3.85 (s, 3H), 2.12 (s, 3H), 1.98 (s, 3H), 1.76 (s, 3H), 1.72 (s, 3H). 13C NMR (125 MHz, CDCl$_3$): δ195.9, 170.29, 170.26, 170.0, 169.6, 144.9, 133.5, 129.4, 128.7, 71.0, 70.9, 67.8, 67.7, 66.8, 61.6, 21.6, 20.57, 20.52, 20.44, 20.39. HRMS (ESI): calcd for C$_{22}$H$_{26}$O$_{11}$ [M]$^+$ 466.1526, found 466.1525.

(2R,3S,4S,5R,6S)-2-(Acetoxymethyl)-6-(2-methoxybenzoyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (α-29).

According to the general procedure C, this compound was obtained in (90.9 mg, 0.195 mmol) 65% yield and ratio of α to β (4.5:1) as a colorless oil. Purification of the crude material was performed by column chromatography (SiO$_2$: 30% ethyl acetate in petroleum ether). $^1$H NMR (500 MHz, CDCl$_3$): δ7.58 (dd, $J = 7.7, 1.8$ Hz, 1H), 7.47 (ddd, $J = 8.9, 7.4, 1.8$ Hz, 1H), 7.00 (t, $J = 7.5$ Hz, 1H), 6.93 (d, $J = 8.4$ Hz, 1H), 5.83 (d, $J = 6.6$ Hz, 1H), 5.59 (dd, $J = 10.1, 3.3$ Hz, 1H), 5.52–5.49 (m, 2H), 4.68 (td, $J = 6.5, 2.0$ Hz, 1H), 4.12–4.03 (m, 2H), 3.85 (s, 3H), 2.12 (s, 3H), 1.98 (s, 3H), 1.76 (s, 3H), 1.72 (s, 3H). 13C NMR (125 MHz, CDCl$_3$): δ195.9, 170.4, 170.0, 169.9, 169.7, 158.2, 134.3, 130.6, 127.6, 121.0, 111.5, 74.0, 70.8, 68.1, 67.9, 66.6, 61.7, 55.6, 20.64, 20.60, 20.58, 20.3. HRMS (ESI): calcd for C$_{22}$H$_{26}$O$_{11}$ [M]$^+$ 466.1475, found 466.1472.
According to the general procedure C, this compound was obtained in (104.9 mg, 0.225 mmol) 75% yield and ratio of α to β (3.6:1) as a white solid. Purification of the crude material was performed by column chromatography (SiO$_2$: 30% ethyl acetate in petroleum ether). $^1$H NMR (500 MHz, CDCl$_3$): δ7.92–7.90 (m, 2H), 6.93–6.91 (m, 2H), 5.79 (dd, $J = 10.4$, 3.4 Hz, 1H), 5.62 (d, $J = 6.4$ Hz, 1H), 5.50 (dd, $J = 3.4$, 1.5 Hz, 1H), 5.46 (dd, $J = 10.1$, 6.3 Hz, 1H), 4.50 (td, $J = 6.4$, 1.7 Hz, 1H), 4.08–4.00 (m, 2H), 3.85 (s, 3H), 2.13 (s, 3H), 1.98 (s, 3H), 1.90 (s, 3H), 1.79 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): δ194.5, 170.4, 170.3, 170.0, 132.2, 131.1, 128.9, 113.9, 70.8, 67.9, 67.7, 66.9, 61.7, 55.5, 20.6, 20.55, 20.50, 20.48. HRMS (ESI): calcd for C$_{22}$H$_{26}$O$_{11}$ [M]$^+$ 466.1475, found 466.1477.

m.p. 145–146 °C

According to the general procedure C, this compound was obtained in (110.4 mg, 0.243 mmol) 81% yield and ratio of α to β (5.8:1) as a white solid. Purification of the crude material was performed by column chromatography (SiO$_2$: 30% ethyl acetate in petroleum ether). $^1$H NMR (500 MHz, CDCl$_3$): δ8.02–8.00 (m, 2H), 6.95–6.93 (m, 2H), 5.67 (t, $J = 10.0$ Hz, 1H), 5.50 (d, $J = 3.3$ Hz, 1H), 5.19 (dd, $J = 10.1$, 3.4 Hz, 1H), 4.63 (d, $J = 9.8$ Hz, 1H), 4.16–4.08 (m, 2H), 3.88 (s, 3H), 2.19 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.86 (s, 3H), $^{13}$C NMR (125 MHz, CDCl$_3$): δ194.5, 170.4, 170.3, 170.0, 169.7, 164.1, 132.2, 131.1, 129.0, 113.9, 70.9, 67.9, 67.8, 66.9, 61.7, 55.5, 20.6, 20.55, 20.51, 20.48. HRMS (ESI): calcd for C$_{22}$H$_{26}$O$_{11}$ [M]$^+$ 466.1475, found 466.1474.

According to the general procedure C, this compound was obtained in (104.9 mg, 0.225 mmol) 75% yield and ratio of α to β (3.6:1) as a white solid. Purification of the crude material was performed by column chromatography (SiO$_2$: 30% ethyl acetate in petroleum ether). $^1$H NMR (500 MHz, CDCl$_3$): δ7.98–7.95 (m, 2H), 6.95–6.93 (m, 2H), 5.50 (d, $J = 3.4$ Hz, 1H), 5.46 (dd, $J = 10.1$, 6.3 Hz, 1H), 4.50 (td, $J = 6.4$, 1.7 Hz, 1H), 4.08–4.00 (m, 2H), 3.85 (s, 3H), 2.13 (s, 3H), 1.98 (s, 3H), 1.90 (s, 3H), 1.79 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): δ194.5, 170.4, 170.3, 170.0, 169.7, 164.1, 132.2, 131.1, 128.9, 113.9, 70.8, 67.9, 67.7, 66.9, 61.7, 55.5, 20.6, 20.55, 20.50, 20.48. HRMS (ESI): calcd for C$_{22}$H$_{26}$O$_{11}$ [M]$^+$ 466.1475, found 466.1477.

(2R,3S,4S,5R,6S)-2-(Acetoxymethyl)-6-(4-methoxybenzoyl)tetrahydro-2H-pyran-3,4,5-triy1 triacetate ($\alpha$-30).
HRMS (ESI): calcd for C_{21}H_{23}FO_{10} [M]+ 454.1275, found 454.1271. m.p. 107–108 °C.


Following the general procedure C except that Ni(ClO_{4})_{2} (20 mol%), 4b (20 mol%) and furan-2-carbonyl chloride (150 mol%) were used.

Purification of the crude material was performed by column chromatography (SiO_{2}: 30% ethyl acetate in petroleum ether). The yield of the title compound was estimated to be 25% (for α product only) due to inseparable impurities using trimethyl(phenyl)silane as the internal standard. For the same reason, the ratio of α to β was not determined. \(^1^H\) NMR (500 MHz, Chloroform-\(d\)) for the α anomer: \(\delta\) 7.65 (s, 1H), 7.31 (d, \(J = 14.0\) Hz, 1H), 6.58(s, 1H), 5.79 (t, \(J = 9.2\) Hz, 1H), 5.42 (d, \(J = 6.6\) Hz, 1H), 5.30 (t, \(J = 8.0\) Hz, 1H), 5.09 (t, \(J = 9.3\) Hz, 1H), 4.57-4.55 (m, 1H), 4.27 (dd, \(J = 25.9, 9.0\) Hz, 1H), 4.22 (dd, \(J = 4.6\) Hz, 1H), 4.08 (d, \(J = 12.6\) Hz, 1H), 2.10 (s, 3H), 2.04 (s, 3H),2.02(s, 3H), 1.83 (s, 3H), 1.25 (s, 3H).

References


Spectral Data for New Compounds
(α: β = 3.4:1)
\[ \alpha: \beta = 4.5:1 \]
\[ \alpha : \beta = 3.6:1 \]
$\alpha: \beta = 5.8:1$