Supporting Information

P(V) Intermediates-mediated E1cb Elimination for the Synthesis of Glycals

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1. Report synthesis of glycals from its first discovery in 1913 up to the present.

Protocols for the preparation of glycals were limited as shown in Fig. S1. Actually, since the Fischer-Zach method was first developed in 1913, which treated the air-sensitive peracetylated glycosyl bromide with much excess zinc in acetic acid to afford the corresponding glycals, it is still the most widely adopted approach for the preparation of glycals to date.[1] To obviate the requirement of excess zinc and acetic acid, numerous synthetic methods have been explored, such as Li/NH$_3$,[2] Cr(II)/EDA,[3] (CP$_2$TiCl)$_2$,[4] Zn/CuSO$_4$,[5] Zn/PEG-H$_2$O,[6] and etc. However, no substantial improvement was achieved. Therefore, nearly all disadvantages of the Fischer-Zach method remained, including expensive and excess metallic reagents, complicated operations. In addition, it is worth mentioning that the Fischer-Zach method was not suitable for furanoid glycals, which will further eliminate to give furans. Although some other methodologies for the synthesis of glycals have also been developed, which applied thiophenyl glycoside,[7] glycosyl sulfones,[8] and glycosyl sulfoxides,[9] as starting materials. These protocols seemingly showed some more serious drawbacks, such as the multistep preparation of the appropriate precursor and poor generality. In an attempt to compensate the deficiencies, an electrochemical strategy was also developed recently.[10] However, it requires using the toxic mercury cathode, complex divided electrochemical cell, and...
strongly acidic conditions. Therefore, it is highly worthwhile to conceive an innovative and green methodology to synthesize glycals with improved flexibility, efficiency, generality, and practicality.

2. Table S1. Optimization of reaction conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Base</th>
<th>Time</th>
<th>Temperture</th>
<th>3a (yield, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>THF</td>
<td>K$_2$CO$_3$</td>
<td>2 h</td>
<td>80 °C</td>
<td>23</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>K$_2$CO$_3$</td>
<td>2 h</td>
<td>80 °C</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>CH$_3$CN</td>
<td>K$_2$CO$_3$</td>
<td>2 h</td>
<td>80 °C</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>DCM</td>
<td>K$_2$CO$_3$</td>
<td>2 h</td>
<td>80 °C</td>
<td>69</td>
</tr>
<tr>
<td>5</td>
<td>DCM</td>
<td>K$_2$CO$_3$</td>
<td>4 h</td>
<td>80 °C</td>
<td>75</td>
</tr>
<tr>
<td>6</td>
<td>DCM</td>
<td>K$_2$CO$_3$</td>
<td>4 h</td>
<td>60 °C</td>
<td>76</td>
</tr>
<tr>
<td>7</td>
<td>DCM</td>
<td>NaOH (3 M)</td>
<td>1 h</td>
<td>60 °C</td>
<td>68</td>
</tr>
<tr>
<td>8</td>
<td>DCM</td>
<td>NaOH (3 M)</td>
<td>0.5 h</td>
<td>25 °C</td>
<td>76</td>
</tr>
<tr>
<td>9</td>
<td>DCM</td>
<td>NaOH (2 M)</td>
<td>1 h</td>
<td>25 °C</td>
<td>88</td>
</tr>
<tr>
<td>10</td>
<td>DCM</td>
<td>NaOH (1 M)</td>
<td>2 h</td>
<td>25 °C</td>
<td>94</td>
</tr>
<tr>
<td>11$^b$</td>
<td>DCM</td>
<td>NaOH (1 M)</td>
<td>2 h</td>
<td>25 °C</td>
<td>60</td>
</tr>
</tbody>
</table>

$^a$Reaction condictions: 1a (1 mmol), Ph$_3$P (1.2 mmol) and TMSOTf (1.1 mmol) in solvent (3.0 ml) at rt for 0.5-4 h, and then base and H$_2$O (1.0 ml) were added at rt. Total isolated yield for two steps.

$^b$TMSOTf was replaced with BF$_3$.

3. Conventional Preparation Route for 1D-glycals and Our Synthestic Method.
A: Previous route:

B: Our process:

Scheme S1. Previous reported preparation method and our direct one-pot two-step strategy for 1D-glucose derivatives.

Multistep reactions (at least 7 steps for D-3f, 8 steps for D-3f) were required for the synthesis of triacetyl or tribenzyl protected 1-D-glucose in previous report (as shown in Scheme S1A).\textsuperscript{[12]} Several protections/deprotections as additional processes are necessary due to the incompatibility of protecting group to halogen/lithium-exchange or reductive elimination reaction. However, only two steps are required even in one-pot system from the commercial substrates to 1-deuterium-glycals by our developed P(V) intermediates-mediated elimination as shown in Scheme S1B.
4. Mechanistic Investigation

4.1 The Intermediate 2a

![Scheme S2. Synthesis of glycal 3a via the intermediate 2a.](image)

**2a:** White solid; yield (93%); $^{31}$P NMR (162 MHz, Chloroform-$d$) $\delta$ 22.14; $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.87 – 7.76 (m, 9H), 7.66 (dt, $J = 10.8$, 5.4 Hz, 6H), 6.60 (dd, $J = 10.4$, 2.0 Hz, 1H), 5.47 (t, $J = 9.2$ Hz, 1H), 5.16 (dd, $J = 19.6$, 10.2 Hz, 1H), 4.85 (t, $J = 9.8$ Hz, 1H), 4.59 (dd, $J = 9.6$, 4.2 Hz, 1H), 4.14 (d, $J = 12.2$ Hz, 1H), 3.97 (dd, $J = 12.8$, 5.2 Hz, 1H), 1.96 (s, 3H), 1.86 (s, 3H), 1.85 (s, 3H), 1.37 (s, 3H); $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 170.13 (s, C), 169.71 (s, C), 169.23 (s, C), 169.11 (s, C), 135.50 (d, $J_{C-P} = 3.0$ Hz, 3CH), 134.55 (d, $J_{C-P} = 10.0$ Hz, 6CH), 130.38 (d, $J_{C-P} = 13.0$ Hz, 6CH), 120.83 (d, $J_{C-P} = 320.8$ Hz C), 116.01 (s, C), 115.16 (s, C), 74.13 (d, $J_{C-P} = 142.4$ Hz, CH), 70.30 (s, CH), 69.59 (s, CH), 67.78 (s, CH), 67.28 (s, CH$_2$), 61.38 (s, CH), 20.57 (s, CH$_3$), 20.54 (s, CH$_3$), 20.40 (s, CH$_3$), 19.88 (s, CH$_3$). HRMS Calcd. For C$_{32}$H$_{34}$O$_9$P$^+$ [M–OTf]$^+$, 593.1940. Found: 593.1935.
4.2 The Isotope-labeling Experiments

Scheme S3. The hydrolysis-elimination reaction of glycosylphosphonium 2a by D$_2$O/base. The major product 1D-3a (83%) was obtained, implying that the ylide species is the key intermediate.

Fig S2. $^1$H NMR (CDCl$_3$-d) of 3a and 1-D-3a
Scheme S4. $^{18}$O-labeling reaction.

Fig S3. The HRMS of O$^{18}$PPh$_3$
4.3 The Track Experiments (\(^{31}\text{P}-\text{NMR}\))

Fig. S4 The \(^{31}\text{P}\) NMR tracing of hydrolysis reaction of 2a with NaOH at room temperature in CH\(_2\)Cl\(_2\). We don’t observe any intermediate in this reaction condition, which imply that the formation and conversion of the intermediates are the fast processes.

Fig. S5 The \(^{31}\text{P}\) NMR tracing of treating 2a with \(^{4}\text{BuNa}\) and then water in hydropenic THF. We can observe the glycosyl ylide species, which indicate that glycosyl ylide could be one of key intermediates and both its formation and conversion are very fast.
4.4 Computation of Hydrolysis-E1cb Reaction.

Computational Methods

Density functional theory (DFT) investigations were performed to delineate the detailed mechanism of the hydrolysis-elimination reaction of glucosylphosphonium salt 2a. All density functional theory calculations were carried out with the Gaussian 16 programs. The geometry optimizations and frequency calculations of the reactants, transition states, and products were performed with the B3LYP method at the 6-31+G(d, p), and energy and frequency calculations at M06-2X/6-311+G(d, p)/IEF-PCM level. The Localized orbital locator (LOL) analysis and highest occupied molecular orbital (HOMO) distribution of transition state TS along its intrinsic reaction coordinate (IRC) are performed at B3LYP/6-31+G(d, p) level. The energies given in this work are M06-2X calculated Gibbs free energies in DCM solvent.

Scheme S5. The calculated reaction pathway by DFT at the m06-2x/6-311+G(d, p)/IEF-PCMDCM//b3lyp/6-31+G(d, p) level using 2a (glucose-triphenylphosphonium) as computational model substrate. A fast intermolecular addition reaction between the generated phosphorus-ylide and H$_2$O/D$_2$O/H$_2$O$_{18}$ molecule from two
different orientations (path a and path b) proceeded to give α/β-glucose-hydroxylphosphorane (Int-1 and Int-1'). Subsequently, the intermediates undergoes conformational conversion and deprotonation to respectively deliver INT-2 or INT-2', where the several equilibrium reactions and intermediates (Int-1-b, Int-2-b, Int-1'-b, and Int-2'-b) were involved. Finally, the elimination reaction undergoes to give the final glycal through a transition state TS (the barrier of 2.2 kcal/mol) or TS' (the barrier of 6.6 kcal/mol).

Fig. S6 The proposed reaction process and optimized structures for 2a', Int-1', Int-2', and TS'. The energy are shown in kcal mol\(^{-1}\).

Fig. S7. The IRC plots of TS calculated at the b3lyp/6-31+G(d, p) level.
Captions to Movies S1 and S2.

Animation of Reaction Coordinate (computational analysis) Move S1.

LOL analysis of TS. Localized orbital locator (LOL) analysis of transition state TS along its intrinsic reaction coordinate (IRC). This video show an axial P-C(glycosyl) bond cleavage and C=C bond formation with a nucleofugality leaving. The calculated methods see supporting computational details. The video was created using Multiwfn, VMD, and Windows Movie Maker.

Animation of Frontier Molecular Orbital for P-C Bond Cleavage and C=C Bond Forming Event (computational analysis) Move S2.

Orbital analysis of TS. Change in the HOMO involved in transition state TS along its intrinsic reaction coordinate (IRC). This video show the δ-electron heterolytic cleavage and π-electron formation with a nucleofugality leaving. The calculated methods see supporting computational details. The video was created using Multiwfn, VMD, and Windows Movie Maker.

Fig. S8. The IRC plots of TS' calculated at the b3lyp/6-31+G(d, p) level.

Compounds 1 (1 mmol) and triphenylphosphine (1.2 mmol) were dissolved in DCM (5 mL) in a Schlenk bottle under argon gas atmosphere, TMSOTf (1.1 mmol) was added under 0 °C and the mixture was stirred at room temperature for 5-6 h, and then corresponding phosphonium ylides 2 were obtained. Crude products not purified further and Lye added directly at room temperature. After the reaction was finished and then DCM was removed under reduced pressure, CH$_2$Cl$_2$ (10 mL) and water (10 mL) were subsequently added to the resulting mixture. The organic layer was separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (10 mL × 2). All combined organic solutions were dried with anhydrous Na$_2$SO$_4$, and the solvent was removed under reduced pressure. The residue was column chromatography to afford the corresponding products 3.


3a$^{[1]}$: Pale yellow liquid; yield (85%$^a$, 90%$^b$); $^1$H NMR (400 MHz, Chloroform-$d$) δ 6.45 (d, $J = 6.2$ Hz, 1H), 5.33 – 5.31 (m, 1H), 5.22 – 5.19 (m, 1H), 4.83 (dd, $J = 6.2$, 3.2 Hz, 1H), 4.38 (dd, $J = 12.0$, 5.8 Hz, 1H), 4.26 – 4.22 (m, 1H), 4.18 (dd, $J = 12.0$, 3.0 Hz, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 170.7 (s, C), 170.5 (s, C), 169.7 (s, C), 145.8 (s, CH), 99.1 (s, CH), 74.1 (s, CH), 67.6 (s, CH), 67.31 (s, CH), 61.5 (s, CH$_2$), 21.1 (s, CH$_3$), 20.9 (s, CH$_3$), 20.8 (s, CH$_3$). HRMS Calcd. For C$_{12}$H$_{17}$O$_7$ [M + H$^+$]$^+$, 273.0969. Found: 273.0966.
3b:\textsuperscript{[1b]}: Pale yellow liquid; yield (90%); \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.78 (d, \(J = 8.0\) Hz, 2H), 7.34 (d, \(J = 8.0\) Hz, 2H), 6.34 (d, \(J = 4.0\) Hz, 1H), 5.25 (t, \(J = 4.0\) Hz, 1H), 5.11 (t, \(J = 6.0\) Hz, 1H), 4.80 (dd, \(J = 6.0, 3.4\) Hz, 1H), 4.25 – 4.19 (m, 3H), 2.44 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H); \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 170.3 (s, C), 169.5 (s, C), 145.40 (s, CH), 145.2 (s, C), 132.6 (s, C) 123.0 (s, 2CH), 128.1 (s, 2CH), 99.0 (s, CH), 73.3 (s, CH), 67.1 (s, CH), 66.7 (s, CH), 66.5 (s, CH), 21.8 (s, CH), 21.0 (s, CH), 20.8 (s, CH). HRMS Calcd. For C\(_{17}\)H\(_{21}\)O\(_8\)S [M + H\(^+\)]\(^+\), 385.0952. Found: 385.0956.

![Chemical Structure](image1)

3c:\textsuperscript{[a]}: Pale yellow liquid; yield (87%); \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 6.48 (d, \(J = 6.2\) Hz, 1H), 5.35 (s, 1H), 5.23 – 5.20 (m, 1H), 4.89 (dd, \(J = 6.2, 3.4\) Hz, 1H), 4.48 (dd, \(J = 11.4, 6.0\) Hz, 1H), 4.37 – 4.33 (m, 2H), 3.07 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H); \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 169.8 (s, C), 169.1 (s, C), 144.8 (s, CH), 98.9 (s, CH), 73.1 (s, CH), 66.5 (s, CH), 66.4 (s, CH), 65.1 (s, CH), 37.4 (s, CH), 20.4 (s, CH), 20.3 (s, CH). HRMS Calcd. For C\(_{11}\)H\(_{17}\)O\(_8\)S [M + H\(^+\)]\(^+\), 309.0639. Found: 309.0640.

![Chemical Structure](image2)

3d:\textsuperscript{[b]}: Pale yellow liquid; yield (86%); \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.01 (d, \(J = 7.2\) Hz, 2H), 7.59 (t, \(J = 7.4\) Hz, 1H), 7.45 (t, \(J = 7.8\) Hz, 2H), 6.52 (d, \(J = 6.0\) Hz, 1H), 5.53 – 5.44 (m, 2H), 4.93 (dd, \(J = 5.0, 1.2\) Hz, 1H), 4.44 – 4.36 (m, 2H), 4.29 (d, \(J = 8.8\) Hz, 1H), 2.07 (s, 3H), 2.03 (s, 3H); \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 170.7 (s, C), 170.5 (s, C), 165.3 (s, C), 145.8 (s, CH), 133.7 (s, CH), 130.0 (s, 2CH), 129.3 (s, C), 128.7 (s, 2CH), 99.1 (s, CH), 74.1 (s, CH), 68.0 (s, CH), 67.3 (s, CH), 61.9 (s, CH), 21.1 (s, CH), 20.8 (s, CH). HRMS Calcd. For C\(_{17}\)H\(_{19}\)O\(_7\) [M + H\(^+\)]\(^+\), 335.1125. Found: 335.1123.
3e[^4c]: Pale yellow liquid; yield (80%); $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 6.38 (d, $J$ = 5.4 Hz, 1H), 4.82 (dd, $J$ = 6.2, 2.8 Hz, 1H), 3.98 – 3.84 (m, 1H), 3.87 (d, $J$ = 3.2 Hz, 1H), 3.69 – 3.61 (m, 2H), 3.53 (s, 3H), 3.45 (dd, $J$ = 8.4, 6.2 Hz, 1H), 3.41 (s, 3H), 3.40 (s, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 144.7 (s, CH), 99.7 (s, CH), 76.8 (s, CH), 76.4 (s, CH), 76.0 (s, CH), 71.0 (s, CH$_2$), 59.4 (s, CH$_3$), 59.4 (s, CH$_3$), 55.9 (s, CH$_3$). HRMS Calcd. For C$_9$H$_{17}$O$_4$ [M + H$^+$]$^+$, 189.1121. Found: 189.1125.

3f[^1b]: Pale yellow liquid; yield (91%); $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.33 (d, $J$ = 4.2 Hz, 9H), 7.26 (dd, $J$ = 17.0, 6.0 Hz, 6H), 6.42 (d, $J$ = 6.0 Hz, 1H), 4.88 (dd, $J$ = 6.0, 2.4 Hz, 1H), 4.83 (d, $J$ = 11.4 Hz, 1H), 4.65 (s, 1H), 4.62 (s, 1H), 4.56 (t, $J$ = 8.8 Hz, 3H), 4.21 (d, $J$ = 5.0 Hz, 1H), 4.09 – 4.03 (m, 1H), 3.89 – 3.75 (m, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 144.9 (s, CH), 138.5 (s, C), 138.3 (s, C), 138.1 (s, C), 128.6 (s, 2CH), 128.5 (s, 2CH), 128.5 (s, 2CH), 128.1 (s, 2CH), 127.9 (s, 2CH), 127.9 (s, 3CH), 127.8 (s, 2CH), 100.1 (s, CH), 76.9 (s, CH), 75.9 (s, CH), 74.5 (s, CH), 73.9 (s, CH$_2$), 73.6 (s, CH$_2$), 70.6 (s, CH$_2$), 68.7 (s, CH$_2$). HRMS Calcd. For C$_{27}$H$_{29}$O$_4$ [M + H$^+$]$^+$, 417.2060. Found: 417.2063.

3g: Pale yellow liquid; yield (87%); $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 6.68 (d, $J$ = 6.0 Hz, 1H), 5.41 (d, $J$ = 1.4 Hz, 1H), 5.02 – 4.98 (m, 2H), 4.83 (s, 1H), 3.79 (s, 3H), 2.12 (s, 3H), 1.99 (s, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 169.6 (s, C), 169.4 (s, C), 167.3 (s, C), 146.4 (s, CH), 97.3 (s, CH), 72.3 (s, CH), 67.4 (s, CH), 62.6 (s, CH), 52.4 (s, CH$_3$), 21.0 (s, CH$_3$), 20.9 (s, CH$_3$). HRMS Calcd. For C$_{11}$H$_{14}$NaO$_7$ [M + Na$^+$]$^+$, 281.0632. Found: 281.0635.
3h\[^{[1b-1d]}\]: Pale yellow liquid; yield (84\%); \(^{1}H\) NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 6.46 (d, \(J = 6.4\) Hz, 1H), 5.55 (s, 1H), 5.43 (d, \(J = 4.4\) Hz, 1H), 4.73 (d, \(J = 5.4\) Hz, 1H), 4.34 – 4.29 (m, 1H), 4.26 – 4.19 (m, 2H), 2.13 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H); \(^{13}C\) NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 170.7 (s, C), 170.5 (s, C), 170.3 (s, C), 145.6 (s, CH), 99.0 (s, CH), 73.0 (s, CH), 64.0 (s, CH), 62.1 (s, CH\(_2\)), 21.0 (s, CH\(_3\)), 20.9 (s, CH\(_3\)), 20.8 (s, CH\(_3\)). HRMS Calcd. For C\(_{12}\)H\(_{17}\)O\(_7\)[M + H\(^+\)]\(^+\), 273.0969. Found: 273.0970.

3i\[^{[1b]}\]: Pale yellow liquid; yield (90\%); \(^{1}H\) NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 6.59 (d, \(J = 5.4\) Hz, 1H), 4.98 – 4.93 (m, 3H), 4.19 (d, \(J = 12.2\) Hz, 1H), 3.97 (d, \(J = 12.0\) Hz, 1H), 2.09 (s, 3H), 2.06 (s, 3H); \(^{13}C\) NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 170.1 (s, C), 169.9 (s, C), 148.2 (s, CH), 97.5 (s, CH), 67.3 (s, CH), 63.7 (s, CH\(_2\)), 63.5 (s, CH), 21.3 (s, CH\(_3\)), 21.1 (s, CH\(_3\)). HRMS Calcd. For C\(_9\)H\(_{13}\)O\(_5\)[M + H\(^+\)]\(^+\), 201.0757. Found: 201.0755.

3j: Pale yellow liquid; yield (90\%); \(^{1}H\) NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 5.63 – 5.59 (m, 1H), 5.07 (t, \(J = 3.0\) Hz, 1H), 4.49 (s, 1H), 4.38 – 4.33 (m, 1H), 4.27 (dd, \(J = 11.8, 4.8\) Hz, 1H), 4.21 (d, \(J = 1.0\) Hz, 1H), 4.15 (dd, \(J = 11.8, 6.6\) Hz, 1H), 2.06 (s, 3H), 2.05 (s, 3H); \(^{13}C\) NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 170.5 (s, C), 169.9 (s, C), 169.6 (s, C), 158.2 (s, C), 87.3 (s, CH\(_2\)), 81.9 (s, CH), 76.2 (s, CH), 74.8 (s, CH), 62.9 (s, CH\(_2\)), 20.9 (s, CH\(_3\)), 20.7 (s, 2CH\(_3\)). HRMS Calcd. For C\(_{12}\)H\(_{17}\)O\(_5\)[M + H\(^+\)]\(^+\), 273.0969. Found: 273.0965.

3k\[^{[4e]}\]: Pale yellow liquid; yield (94\%); \(^{1}H\) NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 6.46 (d, \(J = 6.4\) Hz, 1H), 5.59 – 5.54 (m, 1H), 5.28 (d, \(J = 4.4\) Hz, 1H), 4.63 (d, \(J = 6.4\) Hz, 1H), 4.20 (q, \(J = 6.6\) Hz, 1H), 2.15 (s, 3H), 2.01 (s, 3H), 1.27 (s, 1H), 1.26 (s, 1H), 1.24 (s, 1H); \(^{13}C\) NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 170.8 (s, C), 170.5 (s, C), 146.3 (s, CH), 98.4 (s,
Pale yellow liquid; yield (92%); $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 6.41 (d, $J$ = 5.4 Hz, 1H), 5.34 – 5.29 (m, 1H), 5.01 (dd, $J$ = 8.0, 6.2 Hz, 1H), 4.76 (dd, $J$ = 6.2, 3.0 Hz, 1H), 4.13 – 4.04 (m, 1H), 2.07 (s, 3H), 2.03 (s, 3H), 1.29 (d, $J$ = 6.6 Hz, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 170.8 (s, C), 170.0 (s, C), 146.1 (s, CH), 98.9 (s, CH), 72.6 (s, CH), 72.0 (s, CH), 68.4 (s, CH), 21.2 (s, CH$_3$), 21.0 (s, CH$_3$), 16.7 (s, CH$_3$). HRMS Calcd. For C$_{10}$H$_{15}$O$_5$ [M + H$^+$]$^+$, 215.0914. Found: 215.0915.

Pale yellow liquid; yield (85%); $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.08 – 8.03 (m, 4H), 7.57 (dd, $J$ = 8.2, 6.8 Hz, 2H), 7.44 (t, $J$ = 7.8 Hz, 4H), 6.74 (d, $J$ = 2.2 Hz, 1H), 5.99 (s, 1H), 5.34 (t, $J$ = 2.6 Hz, 1H), 4.94 – 4.89 (m, 1H), 4.62 (dd, $J$ = 11.8, 4.2 Hz, 1H), 4.56 (dd, $J$ = 11.8, 6.2 Hz, 1H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 166.5 (s, C), 166.3 (s, C), 152.2 (s, CH), 133.3 (d, $J$ = 5.0 Hz, 2C), 129.8 (d, $J$ = 9.7 Hz, 5CH), 128.4(s, 5CH), 99.6 (s, CH), 83.8 (s, CH), 79.3 (s, CH), 64.1 (s, CH$_2$). HRMS Calcd. For C$_{19}$H$_{17}$O$_5$ [M + H$^+$]$^+$, 325.1071. Found: 325.1069.

Pale yellow liquid; yield (90%); $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.35 (dd, $J$ = 9.2, 5.8 Hz, 10H), 6.61 (d, $J$ = 2.4 Hz, 1H), 5.19 (s, 1H), 4.66 (t, $J$ = 4.6 Hz, 2H), 4.59 (d, $J$ = 7.4 Hz, 2H), 4.53 (s, 2H), 3.56 (dd, $J$ = 9.8, 6.4 Hz, 1H), 3.43 (dd, $J$ = 10.2, 5.2 Hz, 1H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 150.5 (s, CH), 138.3 (s, C), 137.9 (s, C), 128.5 (s, 4CH), 128.0 (s, 2CH), 127.8 (t, $J$ = 5.8 Hz, 4CH), 100.7 (s, CH), 84.9 (s, CH), 82.7 (s, CH), 73.5 (s, CH$_2$), 69.9 (s, CH$_2$), 69.7 (s, CH$_2$). HRMS Calcd. For C$_{19}$H$_{21}$O$_3$ [M + H$^+$]$^+$, 297.1485. Found: 297.1480.
3o: Pale yellow liquid; yield (90%); \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 6.55 (d, \(J = 1.8\) Hz, 1H), 5.15 (s, 1H), 4.49 (s, 1H), 4.41 (s, 1H), 3.46 (dd, \(J = 10.2, 6.8\) Hz, 1H), 3.39 (s, 3H), 3.36 (d, \(J = 5.4\) Hz, 1H), 3.27 (s, 3H). \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 149.9 (s, CH), 99.6 (s, CH), 83.7 (s, CH), 83.7 (s, CH), 72.3 (s, CH\(_2\)), 58.8 (s, CH\(_3\)), 54.1 (s, CH\(_3\)). HRMS Calcd. For \(C_7H_{13}O_3\) [M + H\(^+\)]\(^+\), 145.0859. Found: 145.0860.

4p: Pale yellow liquid; yield (85%); \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.94 – 7.91 (m, 2H), 7.40 (t, \(J = 7.4\) Hz, 1H), 7.29 (d, \(J = 7.8\) Hz, 2H), 7.07 (s, 1H), 6.22 (s, 1H), 5.13 (s, 2H), 1.89 (d, \(J = 0.7\) Hz, 3H); \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 166.3 (s, C), 149.6 (s, C), 140.0 (s, CH), 133.1 (s, CH), 130.1 (s, C), 129.8 (s, 2CH), 128.4 (s, 2CH), 121.0 (s, C), 113.5 (s, CH), 58.8 (s, CH\(_2\)), 9.7 (s, CH\(_3\)). HRMS Calcd. For \(C_{13}H_{13}O_3\) [M + H\(^+\)]\(^+\), 217.0859. Found: 217.0858.

3q: Pale yellow liquid; yield (89%); \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.38 – 7.32 (m, 10H), 6.28 (s, 1H), 4.64 – 4.56 (m, 4H), 4.49 (d, \(J = 12.4\) Hz, 2H), 3.56 (dd, \(J = 10.0, 6.4\) Hz, 1H), 3.40 (dd, \(J = 10.0, 6.4\) Hz, 1H), 1.72 (s, 3H); \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 144.3 (s, CH), 138.4 (d, \(J = 53.8\) Hz, C), 133.8 (d, \(J = 19.4\) Hz, C), 128.5 (d, \(J = 5.2\) Hz, 4CH), 127.9 (s, 2CH), 127.8 (s, 2CH), 127.7 (s, 2CH), 109.9 (s, CH), 85.9 (s, CH), 84.5 (s, CH), 73.6 (s, CH\(_2\)), 70.3 (s, CH\(_2\)), 69.7 (s, CH\(_2\)), 9.0 (s, CH\(_3\)). HRMS Calcd. For \(C_{20}H_{23}O_3\) [M + H\(^+\)]\(^+\), 311.1642. Found: 311.1645.
3r: Pale yellow liquid; yield (81%); $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 6.28 (d, $J = 5.4$ Hz, 1H), 5.43 (s, 1H), 5.03 (t, $J = 5.8$ Hz, 1H), 4.53 (s, 1H), 4.32 (t, $J = 8.6$ Hz, 2H), 4.17 (dd, $J = 10.6$, 3.8 Hz, 1H), 2.11 (s, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) 170.3 (s, C), 145.3 (s, CH), 102.2 (s, CH), 77.4 (s, CH), 74.3 (s, CH$_2$), 74.2 (s, CH), 72.1 (s, CH), 21.1 (s, CH$_3$). HRMS Calcd. For C$_8$H$_{11}$O$_4$ [M+H]$^+$, 171.0652. Found: 171.0650.

3s$^{[6a]}$: Pale yellow liquid; yield (87%); $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 6.40 (d, $J = 6.0$ Hz, 1H), 5.41 (s, 1H), 5.18 (t, $J = 9.4$ Hz, 1H), 5.08 (t, $J = 9.6$ Hz, 1H), 4.97 (t, $J = 8.8$ Hz, 1H), 4.82 (dd, $J = 6.0$, 3.2 Hz, 1H), 4.68 (d, $J = 8.0$ Hz, 1H), 4.44 (d, $J = 11.4$ Hz, 1H), 4.31 (dd, $J = 12.4$, 4.4 Hz, 1H), 4.21 – 4.11 (m, 2H), 4.05 (d, $J = 12.4$ Hz, 1H), 3.98 (t, 1H), 3.67 (d, 1H), 2.12 (s, 3H), 2.09 (s, 3H), 2.04 (s, 6H), 2.01 (s, 3H), 1.99 (s, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 170.8 (s, C), 170.6 (s, C), 170.4 (s, C), 170.1 (s, C), 169.4 (s, C), 169.3 (s, C), 145.6 (s, CH), 100.7 (s, CH), 99.2 (s, CH), 74.8 (s, CH), 74.5 (s, CH), 72.9 (s, CH), 72.1 (s, CH), 71.5 (s, CH), 68.7 (s, CH), 68.2 (s, CH), 61.9 (s, CH$_2$), 61.9 (s, CH$_2$), 21.1 (s, CH$_3$), 21.0 (s, CH$_3$), 20.8 (s, CH$_3$), 20.7 (s, 2CH$_3$), 20.7 (s, CH$_3$). HRMS Calcd. For C$_{24}$H$_{32}$NaO$_{15}$ [M+Na]$^+$, 583.1633. Found: 583.1636.

3t$^{[6a]}$: Pale yellow liquid; yield (89%); $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 6.40 (d, $J = 6.0$ Hz, 1H), 5.42 – 5.38 (m, 1H), 5.33 (d, $J = 2.8$ Hz, 1H), 5.18 (dd, $J = 10.4$, 8.0 Hz, 1H), 4.99 (dd, $J = 10.6$, 3.4 Hz, 1H), 4.83 (dd, $J = 6.0$, 3.4 Hz, 1H), 4.65 (d, $J = 8.0$ Hz, 1H), 4.43 (dd, $J = 11.4$, 2.0 Hz, 1H), 4.22 – 4.11 (m, 3H), 4.07 (dd, $J = 11.2$, 7.4 Hz, 1H), 3.99 (dd, $J = 7.0$, 5.8 Hz, 1H), 3.90 (t, $J = 6.8$ Hz, 1H), 2.15 (s, 3H), 2.11 (s, 3H), 2.08 (s, 3H), 2.05 (d, $J = 4.0$ Hz, 6H), 1.97 (s, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 170.6 (s, C), 170.5 (s, C), 170.3 (s, C), 170.2 (s, C), 170.1 (s, C), 169.4 (s, C), 145.6 (s, CH), 101.2 (s, CH), 99.1 (s, CH), 74.8 (s, CH), 74.3 (s, CH), 71.0 (s, CH), 70.9 (s, CH), 69.0 (s, CH), 68.9 (s, CH), 66.9 (s, CH), 62.0 (s, CH), 61.1 (s, CH), 21.2 (s, CH$_3$), 21.0
(s, CH₃), 20.8 (s, CH₃), 20.7 (s, CH₃), 20.7 (s, CH₃), 20.6 (s, CH₃). HRMS Calcd. For C₂₄H₃₃O₁₅ [M+H]+, 561.1814. Found: 561.1815.

3u[4c]: Pale yellow liquid; yield (90%); ¹H NMR (400 MHz, Chloroform-d) δ 6.43 (d, J = 6.2 Hz, 1H), 5.49 (d, J = 3.8 Hz, 1H), 5.40 (t, J = 10.0 Hz, 1H), 5.16 (t, J = 3.8 Hz, 1H), 5.04 (t, J = 10.0 Hz, 1H), 4.82 (dd, J = 10.2, 4.2 Hz, 2H), 4.35 (t, J = 4.6 Hz, 2H), 4.31 – 4.27 (m, 1H), 4.23 (dd, J = 12.4, 4.2 Hz, 1H), 4.11 – 3.99 (m, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.04 (d, J = 2.2 Hz, 6H), 2.02 (s, 3H), 2.00 (s, 3H); ¹³C NMR (100 MHz, Chloroform-d) δ 170.7 (s, C), 170.6 (s, C), 170.5 (s, C), 170.4 (s, C), 170.3 (s, C), 169.7 (s, C), 145.7 (s, CH), 98.7 (s, CH), 96.0 (s, CH), 74.3 (s, CH), 72.7 (s, CH), 70.6 (s, CH), 69.8 (s, CH), 69.6 (s, CH), 68.4 (s, CH), 68.4 (s, CH), 62.0 (s, CH), 61.8 (s, CH), 21.2 (s, CH₃), 20.9 (s, CH₃), 20.8 (d, J = 1.6 Hz, 2CH₃), 20.7 (s, CH₃), 20.7 (s, CH₃). HRMS Calcd. For C₂₄H₃₃O₁₅ [M+H]+, 561.1814. Found: 561.1812.

3v: Pale yellow liquid; yield (80%); ¹H NMR (400 MHz, Chloroform-d) δ 6.40 (d, J = 6.0 Hz, 1H), 5.38 (s, 1H), 5.29 – 5.24 (m, 1H), 5.18 (s, 1H), 5.11 (dd, J = 14.6, 4.4 Hz, 2H), 5.02 (dd, J = 10.8, 3.4 Hz, 1H), 4.82 – 4.75 (m, 1H), 4.19 (s, 2H), 4.01 (d, J = 6.4 Hz, 2H), 3.78 (dd, J = 11.0, 6.2 Hz, 1H), 3.61 (dd, J = 11.2, 4.0 Hz, 1H), 2.06 (s, 3H), 2.02 (d, J = 2.8 Hz, 6H), 1.96 (s, 6H), 1.90 (s, 3H); ¹³C NMR (100 MHz, Chloroform-d) δ 170.5 (s, C), 170.3 (s, C), 170.2 (s, C), 170.1 (s, C), 169.9 (s, C), 169.5 (s, C), 145.6 (s, CH), 98.4 (s, CH), 96.3 (s, CH), 74.5 (s, CH), 68.0 (s, 2CH), 67.4 (s, 2CH), 66.6 (s, CH), 66.4 (s, CH), 65.5 (s, CH₂), 61.7 (s, CH₂), 20.9 (s, CH₃), 20.8 (s, CH₃), 20.7 (d, J = 3.8 Hz, 2CH₃), 20.6 (d, J = 2.3 Hz, 2CH₃). HRMS Calcd. For C₂₄H₃₂O₁₅ [M+H]+, 561.1814. Found: 561.1817.
**3w:** White solid, yield (85%); $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 6.42 (d, $J = 6.2$ Hz, 1H), 5.40 (d, $J = 2.6$ Hz, 1H), 5.29 (dd, $J = 10.8$, 3.2 Hz, 1H), 5.19 (d, $J = 3.8$ Hz, 1H), 5.16 – 5.12 (m, 1H), 5.11 (d, $J = 3.6$ Hz, 1H), 5.05 (dd, $J = 10.8$, 3.6 Hz, 1H), 4.79 (dd, $J = 6.0$, 3.8 Hz, 1H), 4.20 (d, $J = 6.4$ Hz, 2H), 4.03 (d, $J = 6.6$ Hz, 2H), 3.81 (dd, $J = 11.2$, 6.1 Hz, 1H), 3.63 (dd, $J = 11.2$, 4.2 Hz, 1H), 2.08 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.98 (s, 6H), 1.92 (s, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 170.6 (s, C), 170.3 (s, C), 170.2 (s, C), 170.2 (s, C), 169.9 (s, C), 169.5 (s, C), 145.7 (s, CH), 98.5 (s, CH), 96.3 (s, CH), 74.5 (s, CH), 68.0 (s, 2CH), 67.5 (d, $J = 2.2$ Hz, 2CH), 66.6 (s, CH), 66.4 (s, CH), 65.6 (s, CH$_2$), 61.7 (s, CH$_2$), 21.0 (s, CH$_3$), 20.8 (s, CH$_3$), 20.7 (s, CH$_3$), 20.6 (s, CH$_3$), 20.6 (s, CH$_3$). HRMS Calcd. For C$_{24}$H$_{33}$O$_{15}$ [M + H$^+$]$^+$, 561.1814. Found: 561.1817.

**3x$^{[5]}$:** Pale yellow liquid; yield (85%); $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 6.43 (d, $J = 6.2$ Hz, 1H), 5.45 – 5.40 (m, 1H), 5.39 – 5.31 (m, 3H), 5.20 – 5.16 (m, 1H), 5.05 (t, $J = 10.0$ Hz, 1H), 4.84 (dd, $J = 10.6$, 4.0 Hz, 1H), 4.79 (dd, $J = 6.2$, 3.4 Hz, 1H), 4.68 (dd, $J = 10.4$, 4.0 Hz, 1H), 4.48 (dd, $J = 12.4$, 2.2 Hz, 1H), 4.37 (d, $J = 4.6$ Hz, 2H), 4.30 – 4.25 (m, 1H), 4.23 (dd, $J = 12.6$, 3.4 Hz, 1H), 4.17 (dd, $J = 12.4$, 3.4 Hz, 1H), 4.06 – 4.02 (m, 1H), 4.01 (d, $J = 2.0$ Hz, 1H), 3.99 (d, $J = 9.8$ Hz, 1H), 3.96 – 3.90 (m, 2H), 2.13 (s, 3H), 2.13 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 170.7 (s, C), 170.6 (s, 2C), 170.6 (s, C), 170.5 (s, 2C), 170.0 (s, C), 169.9 (s, C), 169.6 (s, C), 145.8 (s, CH), 98.7 (s, CH), 95.8 (s, CH), 95.8 (s, CH), 74.2 (s, CH), 72.8 (s, CH), 72.6 (s, CH), 72.0 (s, CH), 71.0 (s, CH), 70.1 (s, CH), 69.9 (s, CH), 69.4 (s, CH), 68.8 (s, CH), 68.6 (s, CH), 68.0 (s,
CH), 62.5 (s, CH₂), 62.1 (s, CH₂), 61.5 (s, CH₂), 21.2 (s, CH₃), 21.0 (s, CH₃), 20.9 (s, CH₃), 20.8 (s, CH₃), 20.7 (s, CH₃), 20.6 (s, CH₃). HRMS Calcd. For C₃₆H₄₉O₂₃ [M + H⁺]⁺, 848.2659. Found: 842.2660.

3y: White solid; yield (86%); ¹H NMR (400 MHz, Chloroform-d) δ 6.44 (dd, J = 6.2, 1.2 Hz, 1H), 5.51 – 5.47 (m, 1H), 5.05 (dd, J = 8.4, 6.4 Hz, 1H), 4.83 (dd, J = 6.2, 3.0 Hz, 1H), 4.49 (dd, J = 12.4, 5.0 Hz, 1H), 4.28 (ddd, J = 13.6, 7.0, 3.0 Hz, 2H), 3.69 (s, CH₂), 3.04 (d, J = 14.8 Hz, 1H), 2.47 – 2.33 (m, 2H), 2.12 (s, 3H), 2.10 (s, 3H), 2.08 (s, 1H), 2.08 – 2.00 (m, 1H), 1.93 (d, J = 18.6 Hz, 1H), 1.64 (ddd, J = 14.0, 9.4, 4.6 Hz, 1H), 1.43 (ddd, J = 13.0, 9.4, 3.8 Hz, 1H), 1.09 (s, 3H), 0.86 (s, 3H); ¹³C NMR (100 MHz, Chloroform-d) δ 214.2 (s, C), 170.7 (s, C), 170.6 (s, C), 145.8 (s, CH), 98.9 (s, CH), 74.1 (s, CH), 73.2 (s, CH), 68.1 (s, CH), 61.3 (s, CH₂), 58.0 (s, C), 48.6 (s, CH₂), 48.1 (s, CH), 42.8 (s, CH), 42.5 (s, CH₂), 27.0 (s, CH₂), 24.9 (s, CH₂), 21.1 (s, CH₃), 20.9 (s, CH₃), 19.8 (s, CH₃), 19.7 (s, CH₃). HRMS Calcd. For C₂₀H₂₉O₉S [M + H⁺]⁺, 445.1527. Found: 445.1530.

3z: Pale yellow liquid; yield (80%); ¹H NMR (400 MHz, Chloroform-d) δ 7.55 – 7.51 (m, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.39 – 7.30 (m, 2H), 7.10 (dd, J = 12.0, 6.2 Hz, 2H), 6.45 – 6.40 (m, 1H), 5.40 (t, J = 18.8 Hz, 1H), 5.30 – 5.25 (m, 1H), 4.83 – 4.75 (m, 1H), 4.41 – 4.19 (m, 1H), 4.19 – 4.12 (m, 1H), 4.09 – 3.97 (m, 1H), 3.76 (q, J = 7.2 Hz, 1H), 2.10 – 2.03 (m, 2H), 2.00 (d, J = 6.0 Hz, 3H), 1.85 (s, 1H), 1.53 (dd, J = 7.2, 2.6 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-d) δ 172.5 (s, C), 170.4 (s, C), 170.3 (s, C), 160.7 (d, J = 248.8 Hz, C), 145.7 (s, CH), 141.0 (s, C), 135.3 (s, C), 131.0 (s, CH), 129.0 (s, 2CH), 128.5 (s, 2CH), 128.2 (s, CH), 127.8 (s, CH), 123.4 (s, CH), 115.0 (s, CH), 99.2 (s, CH), 84.8 (s, CH).
73.9 (s, CH), 68.1 (s, CH), 67.7 (s, CH), 61.4 (s, CH₂), 44.9 (s, CH), 20.9 (s, CH₃), 20.6 (s, CH₃), 17.9 (s, CH₃). HRMS Calcd. For C₂₅H₂₆FO₇ [M + H⁺]^+, 457.1657. Found: 457.1655.

3aa: White solid; yield (86%); ¹H NMR (400 MHz, Chloroform-d) δ 6.44 (d, J = 6.2 Hz, 1H), 5.44 – 5.35 (m, 1H), 5.22 (dd, J = 8.2, 6.4 Hz, 1H), 4.80 (dd, J = 6.2, 3.0 Hz, 1H), 4.31 (dd, J = 12.0, 5.6 Hz, 1H), 4.24 – 4.12 (m, 2H), 2.07 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.83 (s, 6H), 1.69 (s, 6H); ¹³C NMR (100 MHz, Chloroform-d) δ 176.1 (s, C), 170.7 (s, C), 170.5 (s, C), 145.7 (s, CH), 99.4 (s, CH), 74.3 (s, CH), 67.9 (s, CH), 66.6 (s, CH), 61.6 (s, CH₂), 40.8 (s, C), 38.6 (s, CH₂), 36.4 (s, CH₂), 27.8 (s, CH), 21.1 (s, CH₃), 20.8 (s, CH₃). HRMS Calcd. For C₂₁H₂₉O₇ [M + H⁺]^+, 393.1908. Found: 393.1906.

3ab: White solid; yield (82 %); ¹H NMR (400 MHz, Chloroform-d) δ 8.13 (t, J = 3.6 Hz, 1H), 8.03 (dd, J = 8.8, 2.2 Hz, 1H), 6.98 (d, J = 9.0 Hz, 1H), 6.49 (d, J = 6.2 Hz, 1H), 5.39 (dt, J = 11.8, 5.2 Hz, 2H), 4.88 (dd, J = 6.2, 3.4 Hz, 1H), 4.52 – 4.34 (m, 2H), 4.29 – 4.17 (m, 1H), 3.86 (d, J = 6.6 Hz, 2H), 2.69 (s, 3H), 2.16 (dt, J = 20.0, 6.6 Hz, 1H), 2.06 (d, J = 6.0 Hz, 3H), 2.05 – 2.00 (m, 3H), 1.04 (d, J = 6.8 Hz, 6H); ¹³C NMR (100 MHz, Chloroform-d) δ 170.5 (s, C), 170.3 (s, C), 168.1 (s, C), 162.6 (s, C), 162.5 (s, C), 160.5 (s, C), 145.7 (s, CH), 132.7 (s, CH), 125.7 (s, C), 120.4 (s, C), 115.3 (s, C), 112.7 (s, CH), 103.0 (s, C), 98.8 (s, CH), 75.7 (s, CH₂), 73.8 (s, CH), 68.1 (s, CH), 66.8 (s, CH), 61.4 (s, CH₂), 28.1 (s, CH₃), 21.0 (s, CH₃), 20.7 (s, CH₃), 19.0 (s, CH₃), 17.6 (s, CH₃). HRMS Calcd. For C₂₇H₃₁N₂O₈ [M + H⁺]^+, 543.1796. Found: 543.1795.
**3ac:** White solid; yield (81 %); $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.14 (d, $J = 8.2$ Hz, 2H), 7.06 (d, $J = 8.0$ Hz, 2H), 6.42 – 6.37 (m, 1H), 5.42 – 5.35 (m, 1H), 5.23 (dd, $J = 8.8$, 6.6 Hz, 1H), 4.77 (dd, $J = 6.2$, 3.0 Hz, 1H), 4.12 – 4.05 (m, 1H), 4.03 (dd, $J = 12.4$, 2.6 Hz, 1H), 3.88 (dd, $J = 12.4$, 5.4 Hz, 1H), 3.68 (q, $J = 7.2$ Hz, 1H), 2.42 (d, $J = 7.2$ Hz, 2H), 2.00 (s, 3H), 1.97 (s, 3H), 1.86 – 1.77 (m, 1H), 1.46 (d, $J = 7.2$ Hz, 3H), 0.86 (d, $J = 6.6$ Hz, 6H); $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 173.2 (s, C), 170.6 (s, C), 170.3 (s, C), 145.7 (s, CH), 140.9 (s, CH), 137.0 (s, CH), 129.5 (s, 2CH), 127.1 (s, 2CH), 99.3 (s, CH), 74.0 (s, CH), 68.3 (s, CH), 67.3 (s, CH), 61.4 (s, CH$_2$), 45.1 (s, CH), 45.0 (s, CH$_2$), 30.2 (s, CH), 22.4 (s, 2CH), 21.0 (s, CH$_3$), 20.7 (s, CH$_3$), 18.0 (s, CH$_3$). HRMS Calcd. For C$_{23}$H$_{31}$O$_7$ [M + H$^+$]$^+$, 419.2064. Found: 419.2060.

**3ad:** White solid; yield (93%); $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.58 (d, $J = 8.2$ Hz, 1H), 8.47 (s, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 1H), 6.51 (d, $J = 6.2$ Hz, 1H), 5.38 (d, $J = 4.0$ Hz, 2H), 4.89 (d, $J = 3.8$ Hz, 1H), 4.63 (dd, $J = 12.2$, 3.2 Hz, 1H), 4.55 (dd, $J = 12.2$, 5.8 Hz, 1H), 4.45 (s, 1H), 2.11 (s, 3H), 2.05 (s, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 170.5 (s, C), 169.8 (s, C), 162.1 (s, C), 145.9 (s, CH), 140.1 (s, C), 137.6 (s, CH), 136.8 (s, C), 126.4 (s, C), 125.7 (s, CH), 125.2 (s, CH), 124.7 (s, CH), 122.6 (s, CH), 99.1 (s, CH), 74.1 (s, CH), 67.5 (s, CH), 67.4 (s, CH), 61.5 (s, CH$_2$), 21.1 (s, CH$_3$), 21.0 (s, CH$_3$). HRMS Calcd. For C$_{19}$H$_{19}$O$_7$ [M + H$^+$]$^+$, 391.0846. Found: 391.0850.
3ae: White solid; yield (90%); \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.77 (d, \(J = 7.6\) Hz, 2H), 7.57 (d, \(J = 7.4\) Hz, 2H), 7.40 (t, \(J = 7.4\) Hz, 2H), 7.32 (t, \(J = 7.4\) Hz, 2H), 6.48 (d, \(J = 6.0\) Hz, 1H), 5.39 (s, 1H), 5.28 – 5.22 (m, 1H), 4.84 (dt, \(J = 7.8, 4.0\) Hz, 1H), 4.41 (t, \(J = 6.6\) Hz, 3H), 4.27 – 4.16 (m, 3H), 4.05 (d, \(J = 28.4\) Hz, 2H), 2.91 (s, 2H), 2.55 – 2.42 (m, 1H), 2.10 (s, 3H), 2.02 (s, 3H), 1.87 (d, \(J = 8.2\) Hz, 2H), 1.59 (s, 2H); \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 173.1 (s, C), 170.7 (s, C), 170.5 (s, C), 155.2 (s, C), 145.8 (s, CH), 144.1 (s, 2C), 141.5 (s, 2C), 127.8 (s, 2CH), 127.2 (s, 2CH), 125.1 (s, 2CH), 120.1 (s, 2CH), 99.2 (s, CH), 74.1 (s, CH), 67.6 (s, CH), 67.4 (s, CH\(_2\)), 67.4 (s, CH), 61.4 (s, CH\(_2\)), 47.5 (s, CH), 43.2 (s, CH\(_2\)), 43.2 (s, CH\(_2\)), 40.9 (s, CH), 27.8 (s, CH\(_2\)), 27.7 (s, CH\(_2\)), 21.1 (s, CH\(_3\)), 20.9 (s, CH\(_3\)). HRMS Calcd. For C\(_{31}\)H\(_{34}\)NO\(_9\) [M + H\(^+\)]\(^+\), 564.2228. Found: 564.2230.

3af: White solid; yield (64%); \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 6.45 (d, \(J = 6.0\) Hz, 1H), 5.37 – 5.13 (m, 3H), 4.85 (dd, \(J = 6.0, 3.6\) Hz, 1H), 4.33 – 4.18 (m, 3H), 2.20 (dd, \(J = 13.4, 7.2\) Hz, 1H), 2.05 (d, \(J = 11.4\) Hz, 9H), 1.87 (ddd, \(J = 22.4, 15.4, 6.8\) Hz, 6H), 1.59 (d, \(J = 10.8\) Hz, 3H), 1.26 (d, \(J = 8.4\) Hz, 3H), 1.21 (s, 2H), 1.11 – 0.91 (m, 6H), 0.91 – 0.84 (m, 2H), 0.81 (s, 2H); \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 178.1 (s, C), 170.3 (s, C), 169.5 (s, C), 145.7 (s, CH), 145.3 (s, C), 135.6 (s, C), 122.4 (s, CH), 120.5 (s, CH), 98.5 (s, CH), 73.8 (s, CH), 67.4 (s, CH), 66.7 (s, CH), 61.4 (s, CH\(_2\)), 50.8 (s, CH), 46.7 (s, C), 45.2 (s, CH), 38.2 (s, CH\(_2\)), 37.0 (s, CH\(_2\)), 34.9 (s, CH), 34.6 (s, C), 27.4 (s, CH\(_2\)), 25.6 (s, CH\(_2\)), 22.5 (s, CH\(_2\)), 21.4 (s, CH\(_3\)), 21.1 (s, CH\(_3\)), 20.9 (s, 2CH\(_3\)), 18.1 (s, CH\(_2\)), 17.0 (s, CH\(_3\)), 14.1 (s, CH\(_3\)). HRMS Calcd. For C\(_{30}\)H\(_{43}\)O\(_7\) [M + H\(^+\)]\(^+\), 515.3003. Found: 515.3000.
3ag\textsuperscript{[10c]}: Pale yellow liquid; yield (90%\textsuperscript{a}, 88%\textsuperscript{b}); \textsuperscript{1}H NMR (400 MHz, Chloroform-\textit{d}) \(\delta\) 8.04 (t, \(J = 8.6\) Hz, 4H), 7.90 (d, \(J = 8.0\) Hz, 2H), 7.59 – 7.48 (m, 3H), 7.42 (t, \(J = 7.8\) Hz, 4H), 7.34 (t, \(J = 7.8\) Hz, 2H), 6.64 (d, \(J = 6.2\) Hz, 1H), 5.94 (d, \(J = 9.2\) Hz, 2H), 5.04 – 4.98 (m, 1H), 4.81 (dd, \(J = 11.4, 7.6\) Hz, 1H), 4.75 – 4.69 (m, 1H), 4.58 (dd, \(J = 11.4, 4.6\) Hz, 1H); \textsuperscript{13}C NMR (100 MHz, Chloroform-\textit{d}) \(\delta\) 165.9 (s, C), 165.5 (s, C), 165.2 (s, C), 145.4 (s, CH), 133.1 (s, CH), 132.9 (s, CH), 132.8 (s, CH), 129.6 (s, 3C), 129.4 (s, 2CH), 129.3 (s, 2CH), 128.2 (s, 2CH), 128.1 (s, 3CH), 128.0 (s, 3CH), 98.8 (s, CH), 72.8 (s, CH), 64.7 (s, CH), 64.4 (s, CH), 62.2 (s, CH\textsubscript{2}). HRMS Calcd. For C\textsubscript{27}H\textsubscript{23}O\textsubscript{7} [M + H\textsuperscript{+}]\textsuperscript{+}, 459.1438. Found: 459.1436.

3ah\textsuperscript{[6a]}: Pale yellow liquid; yield (88%); \textsuperscript{1}H NMR (400 MHz, Chloroform-\textit{d}) \(\delta\) 8.04 (t, \(J = 8.6\) Hz, 4H), 7.90 (d, \(J = 8.0\) Hz, 2H), 7.59 – 7.48 (m, 3H), 7.42 (t, \(J = 7.8\) Hz, 4H), 7.34 (t, \(J = 7.8\) Hz, 2H), 6.64 (d, \(J = 6.2\) Hz, 1H), 5.94 (d, \(J = 9.2\) Hz, 2H), 5.04 – 4.98 (m, 1H), 4.81 (dd, \(J = 11.4, 7.6\) Hz, 1H), 4.75 – 4.69 (m, 1H), 4.58 (dd, \(J = 11.4, 4.6\) Hz, 1H); \textsuperscript{13}C NMR (100 MHz, Chloroform-\textit{d}) \(\delta\) 165.9 (s, C), 165.5 (s, C), 165.2 (s, C), 145.4 (s, CH), 133.1 (s, CH), 132.9 (s, CH), 132.8 (s, CH), 129.6 (s, 3C), 129.4 (s, 2CH), 129.3 (s, 2CH), 128.2 (s, 2CH), 128.1 (s, 3CH), 128.0 (s, 3CH), 98.8 (s, CH), 72.8 (s, CH), 64.7 (s, CH), 64.4 (s, CH), 62.2 (s, CH\textsubscript{2}). HRMS Calcd. For C\textsubscript{27}H\textsubscript{23}O\textsubscript{7} [M + H\textsuperscript{+}]\textsuperscript{+}, 459.1438. Found: 459.1436.

3ai\textsuperscript{[6a]}: Pale yellow liquid; yield (92%); \textsuperscript{1}H NMR (400 MHz, Chloroform-\textit{d}) \(\delta\) 8.02 (dd, \(J = 13.4, 7.8\) Hz, 4H), 7.55 (dd, \(J = 16.2, 7.8\) Hz, 2H), 7.42 (q, \(J = 7.4\) Hz, 4H), 6.54 (d, \(J = 6.2\) Hz, 1H), 5.71 (s, 1H), 5.54 – 5.49 (m, 1H), 5.01 (dd, \(J = 6.0, 3.0\) Hz, 1H), 4.36 (d, \(J =
6.8 Hz, 1H), 1.45 (d, J = 6.6 Hz, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 166.2 (s, C), 165.6 (s, C), 146.3 (s, CH), 133.5 (s, CH), 133.3 (s, CH), 130.0 (s, C), 129.8 (s, C), 128.6 (s, 4CH), 128.5 (s, 4CH), 98.9 (s, CH), 72.8 (s, CH), 72.1 (s, CH), 68.9 (s, CH), 16.8 (s, CH$_3$). HRMS Calcd. For C$_{20}$H$_{19}$O$_5$ [M + H$^+$]$^+$, 339.1227. Found: 339.1230.

3aj: Pale yellow liquid; yield (83%); $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.13 – 8.04 (m, 6H), 7.62 – 7.53 (m, 3H), 7.49 – 7.39 (m, 6H), 6.21 – 6.17 (m, 1H), 5.68 (t, J = 2.8 Hz, 1H), 4.83 – 4.78 (m, 1H), 4.75 – 4.70 (m, 2H), 4.69 (s, 1H), 4.46 (d, J = 1.2 Hz, 1H); $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 166.3 (s, C), 165.7 (s, C), 165.4 (s, C), 158.5 (s, C), 133.8 (s, CH), 133.7 (s, CH), 133.3 (s, CH), 130.1 (s, 2CH), 130.0 (s, 2CH), 129.9 (s, 2CH), 129.7 (s, C), 129.2 (s, C), 128.9 (s, C), 128.7 (s, 2CH), 128.6 (s, 2CH), 128.5 (s, 2CH), 87.9 (s, CH), 82.5 (s, CH), 77.5 (s, CH$_2$), 75.7 (s, CH$_2$), 64.0 (s, CH). HRMS Calcd. For C$_{27}$H$_{23}$O$_7$ [M + H$^+$]$^+$, 459.1438. Found: 459.1435.

3f$^{[1b]}$: Pale yellow liquid; yield (91%); $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.33 (d, J = 4.2 Hz, 9H), 7.26 (dd, J = 17.0, 6.0 Hz, 6H), 6.42 (d, J = 6.0 Hz, 1H), 4.88 (dd, J = 6.0, 2.4 Hz, 1H), 4.83 (d, J = 11.4 Hz, 1H), 4.65 (s, 1H), 4.62 (s, 1H), 4.56 (t, J = 8.8 Hz, 3H), 4.21 (d, J = 5.0 Hz, 1H), 4.09 – 4.03 (m, 1H), 3.89 – 3.75 (m, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 144.9 (s, CH), 138.5 (s, C), 138.3 (s, C), 138.1 (s, C), 138.0 (s, C), 132.6 (s, 2CH), 128.5 (s, 2CH), 128.5 (s, 2CH), 128.1 (s, 2CH), 127.9 (s, 2CH), 127.8 (s, 3CH), 127.7 (s, 2CH), 100.1 (s, CH), 76.9 (s, CH), 75.9 (s, CH), 74.5 (s, CH), 73.9 (s, CH$_2$), 73.6 (s, CH$_2$), 70.6 (s, CH$_2$), 68.7 (s, CH$_2$). HRMS Calcd. For C$_{27}$H$_{29}$O$_4$ [M + H$^+$]$^+$, 417.2060. Found: 417.2063.

3m: Pale yellow liquid; yield (85%); $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.08 – 8.03 (m, 4H), 7.57 (dd, J = 8.2, 6.8 Hz, 2H), 7.44 (t, J = 7.8 Hz, 4H), 6.74 (d, J = 2.2 Hz, 1H), 5.99 (s, 1H), 5.34 (t, J = 2.6 Hz, 1H), 4.94 – 4.89 (m, 1H), 4.62 (dd, J = 11.8, 4.2 Hz,
\( ^{13}\text{C} \text{ NMR (100 MHz, Chloroform-}d\text{)} \delta 166.5 (s, C), 166.3 (s, C), 152.2 (s, CH), 133.3 (d, \ J = 5.0 \text{ Hz}, 2C), 129.8 (d, \ J = 9.7 \text{ Hz}, 5CH), 128.4 (s, 5CH), 99.6 (s, CH), 83.8 (s, CH), 79.3 (s, CH), 64.1 (s, CH). \text{HRMS Calcd. For } C_{19}H_{17}O_5 [M+H]^+, 325.1071. \text{Found: 325.1069.}

\begin{align*}
\text{3n}^{[11]}: & \text{ Pale yellow liquid; yield (86%); } \text{\textsuperscript{1}H NMR (400 MHz, Chloroform-}d\text{)} \delta 7.35 (dd, \ J = 9.2, 5.8 \text{ Hz}, 10H), 6.61 (d, \ J = 2.4 \text{ Hz}, 1H), 5.19 (s, 1H), 4.66 (t, \ J = 4.6 \text{ Hz}, 2H), 4.59 (d, \ J = 7.4 \text{ Hz}, 2H), 4.53 (s, 2H), 3.56 (dd, \ J = 9.8, 6.4 \text{ Hz}, 1H), 3.43 (dd, \ J = 10.2, 5.2 \text{ Hz}, 1H); \text{\textsuperscript{13}C NMR (100 MHz, Chloroform-}d\text{)} \delta 150.5 (s, CH), 138.3 (s, C), 137.9 (s, C), 128.5 (s, 4CH), 128.0 (s, 2CH), 127.8 (t, \ J = 5.7 \text{ Hz}, 4CH), 100.7 (s, CH), 84.9 (s, CH), 82.7 (s, CH), 73.5 (s, CH\textsubscript{2}), 69.9 (s, CH\textsubscript{2}), 69.7 (s, CH\textsubscript{2}). \text{HRMS Calcd. For } C_{19}H_{21}O_3 [M+H]^+, 297.1485. \text{Found: 297.1480.}

\text{3o: Yellow liquid, yield (80%); } \text{\textsuperscript{1}H NMR (400 MHz, Chloroform-}d\text{)} \delta 6.55 (d, \ J = 1.8 \text{ Hz}, 1H), 5.15 (s, 1H), 4.49 (s, 1H), 4.41 (s, 1H), 3.46 (dd, \ J = 10.2, 6.8 \text{ Hz}, 1H), 3.39 (s, 3H), 3.36 (d, \ J = 5.4 \text{ Hz}, 1H), 3.27 (s, 3H); \text{\textsuperscript{13}C NMR (100 MHz, Chloroform-}d\text{)} \delta 149.9 (s, CH), 99.6 (s, CH), 83.7 (s, CH), 83.7 (s, CH), 72.3 (s, CH\textsubscript{2}), 58.8 (s, CH), 54.1 (s, CH). \text{HRMS Calcd. For } C_7H_{13}O_3 [M+H]^+, 145.0859. \text{Found: 145.0860.}

\text{4p: Pale yellow liquid; yield (85%); } \text{\textsuperscript{1}H NMR (400 MHz, Chloroform-}d\text{)} \delta 7.94 – 7.91 (m, 2H), 7.40 (t, \ J = 7.4 \text{ Hz}, 1H), 7.29 (d, \ J = 7.8 \text{ Hz}, 2H), 7.07 (s, 1H), 6.22 (s, 1H), 5.13 (s, 2H), 1.89 (d, \ J = 0.8 \text{ Hz}, 3H); \text{\textsuperscript{13}C NMR (100 MHz, Chloroform-}d\text{)} \delta 166.3 (s, C), 149.6 (s, C), 140.0 (s, CH), 133.1 (s, CH), 130.1 (s, C), 129.8 (s, 2CH), 128.4 (s, 2CH), 121.0 (s, C), 113.5 (s, CH), 58.8 (s, CH\textsubscript{2}), 9.7 (s, CH\textsubscript{3}). \text{HRMS Calcd. For } C_{13}H_{13}O_5 [M+H]^+, 217.0859. \text{Found: 217.0858.}

Compounds 1 (1 mmol) and triphenylphosphine (1.2 mmol) were dissolved in DCM (5 mL) in a Schlenk bottle under argon gas atmosphere, TMSOTf (1.1 mmol) was added under 0 °C and the mixture was stirred at room temperature for 5-6 h, and then corresponding phosphonium ylides 2 were obtained. Crude products not purified further and potassium t-butoxide and deuterium oxide added directly at room temperature. After the reaction was finished and then DCM was removed under reduced pressure. The residue was column chromatography to afford the corresponding products 1D-3.

8. The Analytical and Spectral Characterization Data of Deuterated Compounds 1D-3.

D-3a\textsuperscript{12b}: Pale yellow liquid; yield (83%); \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 5.34 (dd, \(J = 5.4, 3.2\) Hz, 1H), 5.22 (dd, \(J = 7.4, 6.0\) Hz, 1H), 4.84 (d, \(J = 3.2\) Hz, 1H), 4.40 (dd, \(J = 12.0, 5.8\) Hz, 1H), 4.25 (dd, \(J = 10.8, 5.4\) Hz, 1H), 4.21 – 4.17 (m, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H); \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 170.6 (s, C), 170.4 (s, C), 169.6 (s, C), 145.7 (s, CH), 98.8 (s, CH), 74.0 (s, CH), 67.4 (s, CH), 67.2 (s, CH), 61.4 (s, CH\(_2\)), 21.0 (s, CH\(_3\)), 20.8 (s, CH\(_3\)), 20.7 (s, CH\(_3\)). HRMS Calcd. For C\(_{12}\)H\(_{16}\)DO\(_7\) [M+H\(^+\)]\(^+\), 274.1032. Found: 274.1030.
**D-3b**: Pale yellow liquid; yield (83%); $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.78 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 5.25 (dd, $J = 4.8$, 3.8 Hz, 1H), 5.12 (t, $J = 5.8$ Hz, 1H), 4.80 (d, $J = 3.4$ Hz, 1H), 4.22 (m, $J = 13.0$, 9.6, 5.4 Hz, 3H), 2.44 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 170.3 (s, C), 169.5 (s, C), 145.4 (s, 2C), 145.2 (s, CH), 130.0 (s, 2CH), 128.1 (s, 2CH), 99.0 (s, CH), 73.3 (s, CH), 67.1 (s, CH$_2$), 66.7 (s, CH), 66.5 (s, CH), 21.8 (s, CH$_3$), 21.0 (s, CH$_3$), 20.8 (s, CH$_3$). HRMS Calcd. For C$_{17}$H$_{20}$DO$_8$ [M + H$^+$]$^+$, 386.1014. Found: 386.1015.

**D-3f$^{12b}$**: Pale yellow liquid; yield (93%); $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.41 – 7.21 (m, 16H), 4.85 (dd, $J = 15.4$, 6.8 Hz, 2H), 4.66 – 4.52 (m, 5H), 4.21 (dd, $J = 6.0$, 2.2 Hz, 1H), 4.06 (dd, $J = 7.2$, 4.0 Hz, 1H), 3.90 – 3.74 (m, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 144.9 (s, CH), 138.5 (s, C), 138.3 (s, C), 138.1 (s, C), 128.5 (s, 2CH), 128.5 (s, 2CH), 128.4 (s, 2CH), 128.1 (s, 2CH), 127.9 (s, 2CH), 127.9 (s, 3CH), 127.8 (s, 2CH), 100.1 (s, CH), 76.9 (s, CH), 75.9 (s, CH), 74.5 (s, CH), 73.9 (s, CH$_2$), 73.6 (s, CH$_2$), 70.6 (s, CH$_2$), 68.7 (s, CH$_2$). HRMS Calcd. For C$_{27}$H$_{28}$DO$_4$ [M + H$^+$]$^+$, 418.2123. Found: 418.2125.

**D-3g**: White solid; yield (82%); $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 5.40 (dd, $J = 4.2$, 2.6 Hz, 1H), 5.03 – 4.95 (m, 2H), 4.82 (d, $J = 1.2$ Hz, 1H), 3.78 (s, 3H), 2.10 (s, 3H), 1.97 (s, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 169.7 (s, C), 169.4 (s, C), 167.4 (s, C), 146.5 (s, CH), 97.4 (s, CH), 72.4 (s, CH), 67.5 (s, CH), 62.6 (s, CH), 52.5 (s, CH), 21.1 (s, CH$_3$), 21.0 (s, CH$_3$). HRMS Calcd. For C$_{11}$H$_{14}$DO$_7$ [M + H$^+$]$^+$, 260.0875. Found: 260.0873.
**D-3h:** Pale yellow liquid; yield (85%); $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 5.55 (d, $J$ = 2.8 Hz, 1H), 5.45 – 5.40 (m, 1H), 4.73 (s, 1H), 4.32 (dd, $J$ = 11.4, 5.6 Hz, 1H), 4.28 – 4.16 (m, 2H), 2.13 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 170.7 (s, C), 170.5 (s, C), 169.7 (s, C), 145.8 (s, CH), 99.1 (s, CH), 74.1 (s, CH), 67.6 (s, CH), 67.3 (s, CH), 61.5 (s, CH$_2$), 21.1 (s, CH$_3$), 20.9 (s, CH$_3$), 20.8 (s, CH$_3$). HRMS Calcd. For C$_{12}$H$_{16}$DO$_7$ [M + H]$^+$, 274.1032. Found: 274.1030.

![Chemical structure](image)

**D-3i:** Pale yellow liquid; yield (90%); $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 4.97 (s, 3H), 4.20 (d, $J$ = 12.0 Hz, 1H), 3.97 (d, $J$ = 12.2 Hz, 1H), 2.08 (d, $J$ = 12.6 Hz, 6H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 170.1 (s, C), 169.9 (s, C), 148.2 (s, CH), 97.5 (s, CH), 67.3 (s, CH), 63.7 (s, CH$_2$), 63.5 (s, CH), 21.3 (s, CH$_3$), 21.1 (s, CH$_3$). HRMS Calcd. For C$_9$H$_{12}$DO$_5$ [M + H]$^+$, 202.0820. Found: 202.0825.

![Chemical structure](image)

**D-3q:** Pale yellow liquid; yield (90%); $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.39 – 7.29 (m, 10H), 4.63 – 4.55 (m, 4H), 4.49 (d, $J$ = 13.0 Hz, 2H), 3.59 – 3.53 (m, 1H), 3.43 – 3.37 (m, 1H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 144.2 (s, CH), 138.5 (s, C), 138.0 (s, C), 128.4 (d, $J$ = 5.0 Hz, C), 127.7 (t, $J$ = 12.2 Hz, C), 109.8 (s, C), 85.8 (s, C), 84.4 (s, C), 73.5 (s, C), 70.2 (s, C), 69.6 (s, C), 9.0 (s, C). HRMS Calcd. For C$_{20}$H$_{22}$DO$_3$ [M + H]$^+$, 312.1704. Found: 312.1700.

![Chemical structure](image)

**D-3s:** Pale yellow liquid; yield (87%); $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 5.38 (dd, $J$ = 5.6, 3.4 Hz, 1H), 5.15 (t, $J$ = 9.4 Hz, 1H), 5.04 (t, $J$ = 9.6 Hz, 1H), 4.97 – 4.90 (m, 1H), 4.78 (d, $J$ = 3.4 Hz, 1H), 4.66 (d, $J$ = 8.0 Hz, 1H), 4.41 (dd, $J$ = 11.4, 2.2 Hz, 1H), 4.27 (dd, $J$ = 12.4, 4.6 Hz, 1H), 4.12 (ddd, $J$ = 8.8, 8.0, 4.1 Hz, 2H), 4.03 (dd, $J$ = 12.4, 2.2 Hz, 1H), 3.95 (dd, $J$ = 7.4, 5.8 Hz, 1H), 3.66 (ddd, $J$ = 10.0, 4.4, 2.4 Hz, 1H), 2.
08 (s, 3H), 2.05 (s, 3H), 2.01 (d, \( J = 2.2 \) Hz, 6H), 1.98 (s, 3H), 1.96 (s, 3H); \(^{13}\)C NMR (100 MHz, Chloroform-\( d \)) \( \delta \) 170.8 (s, C), 170.6 (s, C), 170.4 (s, C), 170.1 (s, C), 169.4 (s, C), 169.3 (s, C), 145.6 (s, CH), 100.7 (s, CH), 99.2 (s, CH), 74.8 (s, CH), 74.5 (s, CH), 72.9 (s, CH), 72.1 (s, CH), 71.5 (s, CH), 68.7 (s, CH), 68.2 (s, CH), 61.9 (s, CH\(_2\)), 21.1 (s, CH\(_3\)), 21.0 (s, CH\(_3\)), 20.8 (s, CH\(_3\)), 20.7 (s, 2CH\(_3\)), 20.6 (s, CH\(_3\)). HRMS Calcd. For C\(_{24}\)H\(_{32}\)DO\(_{15}\) [M+H\(^+\)], 562.1877. Found: 562.1875.

**D-3u:** Pale yellow liquid; yield (89%); \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 5.48 (d, \( J = 3.8 \) Hz, 1H), 5.38 (t, \( J = 10.0 \) Hz, 1H), 5.18 – 5.12 (m, 1H), 5.03 (t, \( J = 10.0 \) Hz, 1H), 4.83 – 4.78 (m, 2H), 4.34 (t, \( J = 4.8 \) Hz, 2H), 4.30 – 4.26 (m, 1H), 4.22 (dd, \( J = 12.4 \), 4.2 Hz, 1H), 4.07 (dd, \( J = 12.4 \), 4.2 Hz, 1H), 4.04 – 3.97 (m, 2H), 2.10 (s, 3H), 2.08 (s, 3H), 2.03 (d, \( J = 2.0 \) Hz, 6H), 2.01 (s, 3H), 1.99 (s, 3H); \(^{13}\)C NMR (100 MHz, Chloroform-\( d \)) \( \delta \) 170.6 (s, C), 170.5 (s, C), 170.4 (s, C), 170.0 (s, C), 169.5 (s, C), 145.6 (s, CH), 98.4 (s, CH), 95.8 (s, CH), 74.1 (s, CH), 72.5 (s, CH), 70.4 (s, CH), 69.6 (s, CH), 69.5 (s, CH), 68.3 (s, CH), 68.2 (s, CH), 61.9 (s, CH\(_2\)), 61.6 (s, CH\(_2\)), 21.1 (s, CH\(_3\)), 20.8 (s, CH\(_3\)), 20.7 (s, CH\(_3\)), 20.6 (s, CH\(_3\)), 20.5 (s, CH\(_3\)). HRMS Calcd. For C\(_{24}\)H\(_{32}\)DO\(_{15}\) [M+H\(^+\)], 562.1877. Found: 562.1875.

**D-3w:** White solid, yield (85%); \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 5.47 (d, \( J = 2.6 \) Hz, 1H), 5.35 (dd, \( J = 10.8 \), 3.2 Hz, 1H), 5.28 – 5.24 (m, 1H), 5.23 – 5.16 (m, 2H), 5.11 (dd, \( J = 10.8 \), 3.2 Hz, 1H), 4.86 (d, \( J = 3.4 \) Hz, 1H), 4.28 (t, \( J = 5.2 \) Hz, 2H), 4.10 (d, \( J = 6.6 \) Hz, 2H), 3.87 (dd, \( J = 11.2 \), 6.2 Hz, 1H), 3.70 (dd, \( J = 11.2 \), 4.2 Hz, 1H), 2.15 (s, 3H), 2.11 (d, \( J = 3.2 \) Hz, 6H), 2.05 (s, 6H), 1.99 (s, 3H); \(^{13}\)C NMR (100 MHz, Chloroform-\( d \)) \( \delta \) 170.6 (s, C), 170.3 (s, C), 170.2 (s, C), 170.2 (s, C), 169.9 (s, C), 169.5 (s, C), 145.7 (s, CH), 98.3 (s, CH), 96.3 (s, CH), 74.4 (s, CH), 68.0 (s, 2CH), 67.5 (s, CH), 66.6 (s, CH), 61.9 (s, CH), 21.1 (s, CH\(_3\)), 20.8 (s, CH\(_3\)), 20.6 (s, CH\(_3\)), 20.5 (s, CH\(_3\)).
66.4 (s, CH), 65.6 (s, CH\textsubscript{2}), 61.7 (s, CH\textsubscript{2}), 21.0 (s, CH\textsubscript{3}), 20.8 (s, CH\textsubscript{3}), 20.7 (s, CH\textsubscript{3}), 20.6 (s, CH\textsubscript{3}), 20.5 (s, CH\textsubscript{3}). HRMS Calcd. For C\textsubscript{24}H\textsubscript{32}DO\textsubscript{15} [M + H\textsuperscript{+}]\textsuperscript{+}, 562.1877. Found: 562.1873.

\[ \text{D-3x: Pale yellow liquid; yield (81%); } ^1\text{H NMR (400 MHz, Chloroform-}d\text{) } \delta 5.46 - 5.40 \text{ (m, 1H), 5.40 - 5.31 (m, 3H), 5.21 - 5.16 (m, 1H), 5.05 (t, } J = 10.0 \text{ Hz, 1H), 4.85 (dd, } J = 10.6, 4.0 \text{ Hz, 1H), 4.79 (d, } J = 3.2 \text{ Hz, 1H), 4.69 (dd, } J = 10.4, 4.0 \text{ Hz, 1H), 4.53 - 4.45 \text{ (m, 1H), 4.38 (d, } J = 4.6 \text{ Hz, 2H), 4.29 - 4.15 (m, 3H), 4.07 - 3.91 (m, 5H), 2.14 (d, } J = 0.8 \text{ Hz, 6H), 2.08 (s, 3H), 2.04 (s, 3H), 2.01 (d, } J = 1.6 \text{ Hz, 6H), 2.00 - 1.96 (m, 9H); } ^{13}\text{C NMR (100 MHz, Chloroform-}d\text{) } \delta 170.7 \text{ (s, C), 170.6 (s, 2C), 170.6 (s, C), 170.5 (s, 2C), 170.0 (s, C), 169.9 (s, C), 169.6 (s, C), 145.8 (s, CH), 98.7 (s, CH), 95.8 (s, CH), 95.7 (s, CH), 74.2 (s, CH), 72.8 (s, CH), 72.6 (s, CH), 72.0 (s, CH), 71.0 (s, CH), 70.1 (s, CH), 69.9 (s, CH), 69.4 (s, CH), 68.8 (s, CH), 68.6 (s, CH), 68.0 (s, CH), 62.5 (s, CH\textsubscript{2}), 62.1 (s, CH\textsubscript{2}), 61.5 (s, CH\textsubscript{2}), 21.2 (s, CH\textsubscript{3}), 21.0 (s, CH\textsubscript{3}), 20.9 (s, 2CH\textsubscript{3}), 20.8 (s, CH\textsubscript{3}), 20.7 (s, 3CH\textsubscript{3}), 20.6 (s, CH\textsubscript{3}). HRMS Calcd. For C\textsubscript{36}H\textsubscript{48}DO\textsubscript{23} [M + H\textsuperscript{+}]\textsuperscript{+}, 850.2722. Found: 850.2724.}\]

\[ \text{D-3aa: White solid; yield (88%); } ^1\text{H NMR (400 MHz, Chloroform-}d\text{) } \delta 5.42 - 5.35 \text{ (m, 1H), 5.23 (t, } J = 7.0 \text{ Hz, 1H), 4.81 (d, } J = 1.8 \text{ Hz, 1H), 4.32 (dd, } J = 12.0, 5.4 \text{ Hz, 1H), 4.25 - 4.14 \text{ (m, 2H), 2.08 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.83 (s, 6H), 1.73 - 1.64 \text{ (m, 6H); } ^{13}\text{C NMR (100 MHz, Chloroform-}d\text{) } \delta 176.1 \text{ (s, C), 170.7 (s, C), 170.5 (s, C), 145.7 \text{ (s, CH), 99.4 (s, CH), 74.3 (s, CH), 67.9 (s, CH), 66.6 (s, CH), 61.6 (s, CH\textsubscript{2}), 40.8 (s, C),}\]
38.6 (s, CH₂), 36.4 (s, CH₂), 27.8 (s, CH), 21.1 (s, CH₃), 20.8 (s, CH₃). HRMS Calcd. For C₂₁H₂₈DO₇ [M + H⁺]^+, 394.1971. Found: 394.1975.

**D-3ab:** Pale yellow liquid; yield (89%); ¹H NMR (400 MHz, Chloroform-d) δ 8.16 (dd, J = 5.6, 2.4 Hz, 1H), 8.06 (dd, J = 8.8, 2.2 Hz, 1H), 7.00 (d, J = 9.0 Hz, 1H), 5.53 – 5.28 (m, 2H), 4.90 (d, J = 3.4 Hz, 1H), 4.53 – 4.35 (m, 2H), 4.27 (d, J = 8.8 Hz, 1H), 3.88 (d, J = 6.6 Hz, 2H), 2.72 (s, 3H), 2.18 (dt, J = 13.4, 6.6 Hz, 1H), 2.09 (s, 3H), 2.04 (s, 3H), 1.07 (d, J = 6.8 Hz, 6H); ¹³C NMR (100 MHz, Chloroform-d) δ 170.5 (s, C), 170.3 (s, C), 168.1 (s, C), 162.6 (s, C), 162.5 (s, C), 160.5 (s, C), 145.7 (s, CH), 132.7 (s, CH), 132.1 (s, CH), 125.7 (s, C), 120.4 (s, C), 115.3 (s, C), 112.7 (s, CH), 103.0 (s, C), 98.8 (s, CH), 75.7 (s, CH₂), 73.8 (s, CH), 68.1 (s, CH), 66.8 (s, CH), 61.4 (s, CH₂), 28.1 (s, CH₃), 21.0 (s, CH₃), 20.7 (s, CH₃), 19.0 (s, CH₃), 17.6 (s, CH₃). HRMS Calcd. For C₂₆H₂₈D₉O₈S [M + H⁺]^+, 530.1702. Found: 530.1705.

**D-3ac:** Pale yellow liquid; yield (92%); ¹H NMR (400 MHz, Chloroform-d) δ 7.15 (d, J = 8.2 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 5.39 (dd, J = 6.4, 3.0 Hz, 1H), 5.24 (dd, J = 8.6, 6.4 Hz, 1H), 4.79 (d, J = 3.0 Hz, 1H), 4.15 – 4.00 (m, 2H), 3.90 (dd, J = 12.4, 5.6 Hz, 1H), 3.69 (m, 1H), 2.43 (d, J = 7.2 Hz, 2H), 2.02 (s, 3H), 1.99 (s, 3H), 1.90 – 1.75 (m, 1H), 1.47 (d, J = 7.2 Hz, 3H), 0.88 (d, J = 6.6 Hz, 6H); ¹³C NMR (100 MHz, Chloroform-d) δ 173.2 (s, C), 170.6 (s, C), 170.3 (s, C), 145.7 (s, CH), 140.9 (s, CH), 137.0 (s, CH), 129.5 (s, 2CH), 127.1 (s, 2CH), 99.3 (s, CH), 74.0 (s, CH), 68.3 (s, CH), 67.3 (s, CH), 61.4 (s, CH₂), 45.1 (s, CH), 45.0 (s, CH₂), 30.2 (s, CH), 22.4 (s, 2CH), 21.0
(s, CH₃), 20.7 (s, CH₃), 18.0 (s, CH₃). HRMS Calcd. For C_{23}H_{30}DO_{7}[M + H⁺], 420.2127. Found: 420.2126.

9. The Larger-scale (200 g) Reactions.

Fig. S9 The hundred gram-scale reaction process (schematic plot). The mixture of Glucose pentaacetate 1a (200 g), Ph₃P (1.1 eq), and TMSOTf (1.1 eq) in DCM (700‒800 mL) was stirred at room temperature for 10 h. The purified solid phosphonium 2a was separated from Et₂O (500 mL) and then the gycal 3a (370 g, 94%) was given by NaOH/H₂O (2 M) hydrolysis-elimination.

$^{31}$P NMR (CDCl₃-d) of intermediate 2a separated by simple filtration
1H NMR (CDCl$_3$-d) of intermediate 2a separated by simple filtration.

10. References


11. X-ray Crystal Structures of Compounds 2a’.

![Crystal structure diagram]

Table S2 Crystal data and structure refinement for 2a’. CCDC 2142375.

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Table S4 Bond Angles for 2a′.

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12. Copies of $^{31}$P NMR, $^1$H NMR, $^{13}$C NMR Spectra of Compounds 2.

$^{31}$P NMR (CDCl$_3$-d) of 2a

$^1$H NMR (CDCl$_3$-d) of 2a
$^{13}$C NMR (CDCl$_3$-d) of 2a

$^{31}$P NMR (CDCl$_3$-d) of 2a$'$
$^1$H NMR (CDCl$_3$-d) of 2a$'$

$^{13}$C NMR (CDCl$_3$-d) of 2a$'$
$^{31}$P NMR (CDCl$_3$-d) of 2f

$^1$H NMR (CDCl$_3$-d) of 2f
$^{13}$C NMR (CDCl$_3$-d) of 2f

$^{31}$P NMR (CDCl$_3$-d) of 2g
$^1$H NMR (CDCl$_3$-d) of 2g

$^{13}$C NMR (CDCl$_3$-d) of 2g
$^{31}$P NMR (CDCl$_3$-$d$) of 2h

$^1$H NMR (CDCl$_3$-$d$) of 2h
$^{13}\text{C NMR (CDCl}_3\text{-d)}$ of 2h

$^{31}\text{P NMR (CDCl}_3\text{-d)}$ of 2k
$^{1}H$ NMR (CDCl$_3$-d) of 2k

$^{13}C$ NMR (CDCl$_3$-d) of 2k
$^3$P NMR (CDCl$_3$-d) of 2m

$^1$H NMR (CDCl$_3$-d) of 2m
$^{13}$C NMR (CDCl$_3$-d) of 2m

$^{31}$P NMR (CDCl$_3$-d) of 2s
$^1$H NMR (CDCl$_3$-d) of 2s

$^{13}$C NMR (CDCl$_3$-d) of 2s
$^{31}$P NMR (CDCl$_3$-d) of 2t

$^1$H NMR (CDCl$_3$-d) of 2t
$^{13}$C NMR (CDCl$_3$-d) of 2t

$^{31}$P NMR (CDCl$_3$-d) of 2u
13. Copies of $^1$H NMR, $^{13}$C NMR Spectra of Compounds 3.
$^1$H NMR (CDCl$_3$-d) of 3a$^a$[1]

$^{13}$C NMR (CDCl$_3$-d) of 3a$^a$[1]
$^1$H NMR (CDCl$_3$-d) of 3a$^{[1b]}$

$^{13}$C NMR (CDCl$_3$-d) of 3a$^{[1b]}$
$^1$H NMR (CDCl$_3$-d) of 3b$^{[1b]}$

$^{13}$C NMR (CDCl$_3$-d) of 3b$^{[1b]}$
$^1$H NMR (CDCl$_3$-d) of 3c$^{[6a]}$

$^{13}$C NMR (CDCl$_3$-d) of 3c$^{[6a]}$
$\text{H NMR (CDCl}_3\text{-d)}$ of 3d

$\text{C NMR (CDCl}_3\text{-d)}$ of 3d

$\text{H NMR (CDCl}_3\text{-d)}$ of 3d

$\text{C NMR (CDCl}_3\text{-d)}$ of 3d
$^1$H NMR (CDCl$_3$-d) of 3e

$^{13}$C NMR (CDCl$_3$-d) of 3e
$^1$H NMR (CDCl$_3$-d) of 3f$^{[1b]}$
\[ ^1H \text{NMR (CDCl}_3-d) \text{ of 3g} \]

\[ ^{13}C \text{NMR (CDCl}_3-d) \text{ of 3g} \]
$^1$H NMR (CDCl$_3$-d) of 3h$^{[1b-1d]}$

$^{13}$C NMR (CDCl$_3$-d) of 3h$^{[1b-1d]}$
$^1$H NMR (CDCl$_3$-d) of 3i$^{[1b]}$

$^{13}$C NMR (CDCl$_3$-d) of 3i$^{[1b]}$
$^1$H NMR (CDCl$_3$-$d$) of $3j$

$^{13}$C NMR (CDCl$_3$-$d$) of $3j$
$^{1}H$ NMR (CDCl$_3$-d) of $3k^{[4c]}$

$^{13}C$ NMR (CDCl$_3$-d) of $3k^{[4c]}$
$^1$H NMR (CDCl$_3$-d) of 31$^{[1b]}$

$^1$C NMR (CDCl$_3$-d) of 31$^{[1b]}$
$^1$H NMR (CDCl$_3$-d) of 3m

$^{13}$C NMR (CDCl$_3$-d) of 3m
$^1$H NMR (CDCl$_3$-d) of 3n$^{[11]}$

$^{13}$C NMR (CDCl$_3$-d) of 3n$^{[11]}$
\[ \text{H NMR (CDCl}_3\text{-d)} \text{ of 3o} \]

\[ \text{^{13}C NMR (CDCl}_3\text{-d)} \text{ of 3o} \]
$^1$H NMR (CDCl$_3$-$d$) of 4p

$^1$H NMR (CDCl$_3$-$d$) of 4p

$^{13}$C NMR (CDCl$_3$-$d$) of 4p
$^1$H NMR (CDCl$_3$-d) of 3q

$^{13}$C NMR (CDCl$_3$-d) of 3q
S72

$^1$H NMR (CDCl$_3$-d) of 3r

$^{13}$C NMR (CDCl$_3$-d) of 3r
$^1\text{H NMR (CDCl}_3\text{-d)}$ of 3t$^{[6a]}$ 

$^{13}\text{C NMR (CDCl}_3\text{-d)}$ of 3t$^{[6a]}$
$^1$H NMR (CDCl$_3$-d) of 3u$^{[4c]}$

$^{13}$C NMR (CDCl$_3$-d) of 3u$^{[4c]}$
$^1$H NMR (CDCl$_3$-d) of 3w

$^{13}$C NMR (CDCl$_3$-d) of 3w
$^{1}H$ NMR (CDCl$_3$-d) of 3x$^5$

$^{13}C$ NMR (CDCl$_3$-d) of 3x$^5$
$^1$H NMR (CDCl$_3$-d) of 3y

eq

$^{13}$C NMR (CDCl$_3$-d) of 3y
$^1$H NMR (CDCl$_3$-d) of 3z

$^{13}$C NMR (CDCl$_3$-d) of 3z
$^1$H NMR (CDCl$_3$-$d$) of 3aa

$^{13}$C NMR (CDCl$_3$-$d$) of 3aa
$\textbf{1}^H$ NMR (CDCl$_3$-d) of 3ab

$\textbf{1}^3$C NMR (CDCl$_3$-d) of 3ab
H NMR (CDCl$_3$-$d$) of 3ac

$^{13}$C NMR (CDCl$_3$-$d$) of 3ac
$^1$H NMR (CDCl$_3$-d) of 3ad

$^{13}$C NMR (CDCl$_3$-d) of 3ad
$^1$H NMR (CDCl$_3$-d) of 3ae

$^{13}$C NMR (CDCl$_3$-d) of 3ae
$^1$H NMR (CDCl$_3$-d) of 3af

$^{13}$C NMR (CDCl$_3$-d) of 3af
$^1$H NMR (CDCl$_3$-$d$) of 3ag$^{[10c]}$

$^{13}$C NMR (CDCl$_3$-$d$) of 3ag$^{[10c]}$
$^1$H NMR (CDCl$_3$-$d$) of 3ah$^{[6a]}$

$^{13}$C NMR (CDCl$_3$-$d$) of 3ah$^{[6a]}$
$^1$H NMR (CDCl$_3$-d) of 3ai$^{[6a]}$

$^{13}$C NMR (CDCl$_3$-d) of 3ai$^{[6a]}$
$^{1}\text{H NMR (CDCl}_3\text{-d)}$ of 3aj

$^{13}\text{C NMR (CDCl}_3\text{-d)}$ of 3aj
$^1$H NMR (CDCl$_3$-d) of 3f$^{[1b]}$

$^{13}$C NMR (CDCl$_3$-d) of 3f$^{[1b]}$
$^1$H NMR (CDCl$_3$-d) of 3m

$^{13}$C NMR (CDCl$_3$-d) of 3m
$^{1}H$ NMR (CDCl$_3$-$d$) of 3n$^{[11]}$

$^{13}C$ NMR (CDCl$_3$-$d$) of 3n$^{[11]}$
$^1$H NMR (CDCl$_3$-d) of 30

$^{13}$C NMR (CDCl$_3$-d) of 30
14. Copies of $^1$H NMR, $^{13}$C NMR Spectra of Compounds 1D-3.
$^1$H NMR (CDCl$_3$-d) of $D$-3a

$^{13}$C NMR (CDCl$_3$-d) of $D$-3a
$^{13}$C NMR (CDCl$_3$-d) of D-3a

$^1$H NMR (CDCl$_3$-d) of D-3d
$^{13}$C NMR (CDCl$_3$-d) of D-3d

$^{13}$C NMR (CDCl$_3$-d) of D-3d
$^1$H NMR (CDCl$_3$-$d$) of $D$-3e

$^{13}$C NMR (CDCl$_3$-$d$) of $D$-3e
$^{13}$C NMR (CDCl$_3$-d) of $D$-3e

$^1$H NMR (CDCl$_3$-d) of $D$-3f
$^{13}$C NMR (CDCl$_3$-d) of $D$-3f

$^{13}$C NMR (CDCl$_3$-d) of $D$-3f
$^1$H NMR (CDCl$_3$-d) of $D$-3i

$^{13}$C NMR (CDCl$_3$-d) of $D$-3i
$^{13}$C NMR (CDCl$_3$-$d$) of $D$-3i

$^1$H NMR (CDCl$_3$-$d$) of $D$-3b
$^{13}$C NMR (CDCl$_3$-d) of $D$-3b
$^1$H NMR (CDCl$_3$-d) of $D$-3q

$^{13}$C NMR (CDCl$_3$-d) of $D$-3q
$^{13}$C NMR (CDCl$_3$-d) of $D$-3q

$^1$H NMR (CDCl$_3$-d) of $D$-3s
$^{13}$C NMR (CDCl$_3$-d) of D-3s

$^{13}$C NMR (CDCl$_3$-d) of D-3s
H NMR (CDCl$_3$-d) of D-3u

$^{13}$C NMR (CDCl$_3$-d) of D-3u
$^{13}$C NMR (CDCl$_3$-d) of $D$-3u

$^1$H NMR (CDCl$_3$-d) of $D$-3w
$^{13}$C NMR (CDCl$_3$-d) of $D$-3w
$^1$H NMR (CDCl$_3$-d) of D-3x

$^{13}$C NMR (CDCl$_3$-d) of D-3x
$^{13}$C NMR (CDCl$_3$-d) of $D$-3x

$^1$H NMR (CDCl$_3$-d) of $D$-3ab
$^{13}$C NMR (CDCl$_3$-$d$) of D-3ab

$^{13}$C NMR (CDCl$_3$-$d$) of D-3ab
$^1$H NMR (CDCl$_3$-$d$) of $D$-3ac

$^{13}$C NMR (CDCl$_3$-$d$) of $D$-3ac
$^{13}$C NMR (CDCl$_3$-d) of D-3ac

$^1$H NMR (CDCl$_3$-d) of D-3aa
$^{13}$C NMR (CDCl$_3$-d) of $D$-3aa

$^{13}$C NMR (CDCl$_3$-d) of $D$-3aa