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(4 + 3) Cycloadditions of Allenyl Ether-Derived Oxygen-Stabilized Oxyallyl Cations with Furans

authored by

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GENERAL EXPERIMENTAL INFORMATION.

All reactions were performed in flame-dried glassware under nitrogen atmosphere. Solvents were distilled prior to use. Reagents were used as purchased from Aladdin, Macklin, Innochen, or TCI unless otherwise noted. Chromatographic separations were performed using Silica Gel, AR, 200-300 mesh. $^1$H and $^{13}$C NMR spectra were obtained on Varian VI-400, VI-500 and VI-600 spectrometers using CDCl$_3$ as the solvent. Infrared spectra were obtained on Thermo Scientific Nicolet iS 50. TLC analysis was visualized using UV, p-anisoldehyde and phosphomolybdic acid stains. High-resolution mass spectra were obtained using AB SCIEX X500R QTOF. All spectral data obtained for new compounds are reported here.

PREPARATION OF ALLENYL ETHERS 5b-s.$^1$

\[
\begin{align*}
S1b-n &\xrightarrow{K_2CO_3, DMF} S2b-n \\
S1o-r &\xrightarrow{NaH, THF} S2b-r \\
S1s &\xrightarrow{NaH, THF} S2s
\end{align*}
\]

General procedure for Synthesis of S2b-n Using S2b as an Example.

To a stirred suspension of phenol $S1b$ (1.00 g, 10.63 mmol) and potassium carbonate (1.76 g, 12.7 mmol, 1.2 equiv) in DMF (53 mL) was added propargyl bromide (1.90 g, 15.9 mmol, 1.5 equiv). The reaction was stirred at rt for 3 h before being quenched with H$_2$O. The mixture was extracted three times with EtOAc. The combined organic layers were washed with equal volume of sat aq NaCl and dried over anhyd MgSO$_4$. After filtration and concentration, the crude product was purified using silica gel flash column chromatography [eluent: 5% EtOAc/Hexane] to give phenyl propargyl ether $S2b$ (1.24 g, 88% yield).
General procedure for Synthesis of S2o-r Using S2o as an Example.

To a solution of benzyl alcohols S1o (1.00 g, 9.25 mmol) in THF (46 mL) was added NaH (333 mg, 13.9 mmol, 1.5 equiv) and propargyl bromide (1.32 g, 11.1 mmol, 1.2 equiv) at 0°C. The reaction was stirred at rt and the reaction progress was monitored using TLC analysis. After the reaction was complete (the reaction time is usually within 2 h), the reaction was quenched with sat aq NH₄Cl. The quenched mixture was poured into H₂O and extracted three times with EtOAc. The combined organic layers were washed with equal volume of sat aq NaCl and dried over anhyd MgSO₄. After filtration and concentration, the crude product was purified using silica gel flash column chromatography [eluent: 5% EtOAc/Hexane] to give benzyl propargyl ether S2o (0.90 g, 67% yield).

Procedure for Synthesis of S2s.

To a solution of propargyl alcohol S11 (1.00 g, 17.86 mmol) in THF (3 mL) was added NaH (0.78 g, 19.6 mmol, 1.1 equiv) at 0°C. After stirred at rt for 1h, the mixture was cooled to 0°C. At this temperature, prenyl bromide (2.66 g, 17.8 mmol, 1.0 equiv) was added dropwise to the mixture. The reaction was stirred at rt for 12 h and then quenched with sat aq NH₄Cl. The quenched mixture was extracted three times with Et₂O. The combined organic layers were washed with equal volume of sat aq NaCl and dried over anhyd MgSO₄. After filtration and concentration, the crude product was purified using silica gel flash column chromatography [eluent: 5% EtOAc/Hexane] to give prenyl propargyl ether S2s (1.50 g, 68% yield).

CHARACTERIZATIONS OF ARYL PROPARGYL ETHERS S2b-s.

S2b: 1.24 g (88% yield); yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.40 – 7.33 (m, 2H), 7.10 – 7.02 (m, 3H), 4.75 (d, J = 2.4 Hz, 2H), 2.57 (t, J = 2.4 Hz, 1H); ¹³C NMR
(125 MHz, CDCl$_3$) $\delta$ 157.6, 129.5, 129.4, 121.7, 121.5, 115.0, 114.9, 74.5, 55.8; IR (KBr) cm$^{-1}$ 3297s, 3056m, 3036m, 2914m, 2960m, 1599s, 1494s, 1244s, 1212s, 1173s, 1039s, 754s, 691s; HRMS: C$_9$H$_8$O for [M+H]$^+$, calculated 133.0648, found 133.0647.

![S2c]

**S2c**: 1.17 g (90% yield); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28 – 7.21 (m, 2H), 6.94 – 6.87 (m, 2H), 4.66 (d, $J$ = 2.4 Hz, 2H), 2.52 (t, $J$ = 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.1, 129.4, 126.6, 116.3, 78.2, 75.9, 56.1; IR (KBr) cm$^{-1}$ 3288s, 2917w, 2869w, 1571m, 1491s, 1289m, 1233s, 1212s, 1173s, 1090s, 1027s, 926m, 822s; HRMS: C$_9$H$_7$ClO for [M+H]$^+$, calculated 167.0258, found 167.0259.

![S2d]

**S2d**: 0.80 g (66% yield); colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 – 7.36 (m, 2H), 6.89 – 6.82 (m, 2H), 4.65 (d, $J$ = 2.4 Hz, 2H), 2.52 (t, $J$ = 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.6, 132.3, 116.8, 113.9, 78.1, 75.9, 56.0; IR (KBr) cm$^{-1}$ 3274m, 2917m, 2125m, 1628m, 1485m, 1024m, 1229s, 825s; HRMS: C$_9$H$_7$BrO for [M-H]$^-$, calculated 210.9759, found 211.0937.

![S2e]

**S2e**: 0.80 g (66% yield); colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.18 – 7.10 (m, 3H), 6.93 – 6.89 (m, 1H), 4.67 (d, $J$ = 2.4 Hz, 2H), 2.54 (t, $J$ = 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.3, 130.6, 124.8, 122.8, 118.4, 113.9, 78.0, 76.0, 56.0; IR (KBr) cm$^{-1}$ 3295s, 3074w, 2914m, 2854m, 1590s, 1575s, 1474s, 1281m, 1212s, 1028s, 831m, 771s, 679s; HRMS: C$_9$H$_7$BrO for [M+H]$^+$, calculated 210.9753, found 210.9756.
**S2f:** 0.84 g (69% yield); colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (dd, $J = 7.9$, 1.6 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.06 (dd, $J = 8.3$, 1.3 Hz, 1H), 6.89 (td, $J = 7.7$, 1.4 Hz, 1H), 4.77 (d, $J = 2.4$ Hz, 2H), 2.53 (t, $J = 2.4$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.0, 133.6, 128.4, 122.9, 114.2, 112.5, 78.0, 76.2, 56.9; IR (KBr) cm$^{-1}$ 3288 s, 3065 m, 2916 m, 1589 s, 1574 s, 1476 s, 1446 s, 1279 s, 1050 s, 922 s, 756 s; HRMS: C$_9$H$_7$BrO for [M+H]$^+$, calculated 210.9680, found 210.9584.

**S2g:** 1.02 g (87% yield); white solid; mp 40-41°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 – 7.53 (m, 2H), 6.78 – 6.72 (m, 2H), 4.65 (d, $J = 2.4$ Hz, 2H), 2.52 (t, $J = 2.4$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.4, 138.3, 117.4, 84.0, 78.1, 76.0, 55.9; IR (KBr) cm$^{-1}$ 3274 m, 3089 m, 3069 m, 2129 m, 1509 m, 1563 m, 1480 s, 1277 s, 1019 s, 817 s, 793 m; HRMS: C$_9$H$_7$IO for [M+H]$^+$, calculated 257.9536, found 257.9538.

**S2h:** 1.06 g (86% yield); yellow oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.60 (d, $J = 8.4$ Hz, 2H), 7.08 (d, $J = 8.4$ Hz, 2H), 4.77 (d, $J = 2.4$ Hz, 2H), 2.58 (t, $J = 2.4$ Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 159.9, 126.9, 126.9, 114.9, 77.8, 76.2, 55.8; IR (KBr) cm$^{-1}$ 3303 s, 1613 m, 1589 m, 1512 s, 1419 w, 1300 s, 1229 m, 1175 m, 1157 m, 1107 s, 1068 m, 836 s; HRMS: C$_{10}$H$_7$F$_3$O for [M+Na]$^+$, calculated 223.0347, found 223.0935.
S2i: 1.00 g (80% yield); yellow solid; mp 103-104°C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.24 (d, \(J = 9.0\) Hz, 2H), 7.07 (d, \(J = 9.0\) Hz, 2H), 4.82 (d, \(J = 1.8\) Hz, 2H), 2.61 (t, \(J = 2.4\) Hz, 1H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 162.3, 142.2, 125.9, 115.0, 77.1, 76.8, 56.3; IR (KBr) cm\(^{-1}\) 3258s, 3110m, 3084m, 1587s, 1489s, 1326s, 1245s, 1104s, 1020s, 972s, 843s, 716s, 664s; HRMS: C\(_9\)H\(_7\)NO\(_3\) for [M+Na]^+, calculated 200.0318, found 200.0316.

S2j: 1.09 g (85% yield); white solid; mp 68-69°C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.98 (d, \(J = 9.0\) Hz, 2H), 7.04 (d, \(J = 9.0\) Hz, 2H), 4.79 (d, \(J = 2.4\) Hz, 2H), 2.61 – 2.56 (m, 4H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 196.8, 161.3, 131.1, 130.5, 114.6, 77.8, 77.3, 77.0, 76.8, 76.2, 55.9, 26.4; IR (KBr) cm\(^{-1}\) 3219s, 3083m, 2997m, 2920m, 2866m, 2122s, 1665s, 1603s, 1576s, 1505s, 1377s, 1279s, 1241s, 1185s, 1021s, 959s, 826s; HRMS: C\(_{11}\)H\(_{10}\)O\(_2\) for [M+H]^+, calculated 175.0754, found 175.0742.

S2k: 1.26 g (93% yield); yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.09 (d, \(J = 8.4\) Hz, 2H), 6.90 – 6.84 (m, 2H), 4.64 (d, \(J = 2.4\) Hz, 2H), 2.49 (t, \(J = 2.4\) Hz, 1H), 2.28 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 155.5, 130.9, 129.9, 114.8, 78.8, 75.3, 55.9, 20.5; IR (KBr) cm\(^{-1}\) 3283s, 2866w, 1610w, 1587w, 2159s, 1289m, 1265w, 1218m, 1176m, 1031s, 923m, 804s; HRMS: C\(_{10}\)H\(_{10}\)O for [M+H]^+, calculated 147.0804, found 147.0806.
**S2l:** 1.05 g (80% yield); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.09 (d, $J = 8.4$ Hz, 2H), 6.90 – 6.84 (m, 2H), 4.64 (d, $J = 2.4$ Hz, 2H), 2.49 (t, $J = 2.4$ Hz, 1H), 2.28 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.5, 151.7, 116.2, 114.6, 79.0, 75.3, 56.6, 55.7; IR (KBr) cm$^{-1}$ 3288s, 3001m, 2954m, 2835m, 1507s, 1455s, 1208s, 1109s, 1039s, 923s, 825s, 752m; HRMS: C$_{10}$H$_{10}$O for [M+H]$^+$, calculated 163.0754, found 163.0754.

**S2m:** 0.77 g (60% yield); yellow oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.40 (dd, $J = 4.0$, 3.4 Hz, 1H), 7.93 – 7.87 (m, 1H), 7.58 (dd, $J = 11.5$, 6.7 Hz, 3H), 7.47 (t, $J = 7.9$ Hz, 1H), 7.01 (d, $J = 7.6$ Hz, 1H), 4.95 (d, $J = 2.4$ Hz, 2H), 2.64 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.4, 134.6, 127.5, 126.6, 125.7, 125.6, 125.5, 122.1, 121.3, 105.6, 78.7, 75.6, 56.2; IR (KBr) cm$^{-1}$ 3291s, 3053s, 3056m, 1628m, 1622m, 1509s, 1507s, 1461m, 1398s, 1360s, 1268s, 1235s, 1095s, 1065s, 1015s, 988s, 786s, 765m; HRMS: C$_{13}$H$_{10}$O for [M+H]$^+$, calculated 183.0804, found 183.0803.

**S2n:** 0.71 g (56% yield); white solid; mp 54-55°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 – 7.72 (m, 3H), 7.47 – 7.41 (m, 1H), 7.35 (ddd, $J = 8.1$, 7.0, 1.2 Hz, 1H), 7.23 (d, $J = 1.3$ Hz, 1H), 7.18 (dd, $J = 8.9$, 2.6 Hz, 1H), 4.79 (d, $J = 2.4$ Hz, 2H), 2.54 (t, $J = 2.4$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.5, 134.3, 129.6, 129.3, 127.7, 126.9, 126.5, 124.1, 118.8, 107.5, 78.5, 75.7, 55.9; IR (KBr) cm$^{-1}$ 3053m, 3056m, 1628m, 1622m, 1509m, 1435m, 1253s, 1250s, 1009s, 881s, 738s; HRMS: C$_{13}$H$_{10}$O for [M+H]$^+$, calculated 183.0804, found 183.0805.
**S2o**

**S2o**: 0.90 g (67% yield); yellow oil; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.40 (d, \(J = 4.4\) Hz, 4H), 7.38 – 7.31 (m, 1H), 6.88 (t, \(J = 5.9\) Hz, 2H), 5.52 (d, \(J = 5.9\) Hz, 2H), 4.66 (s, 1H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 137.29, 128.4, 128.1, 127.9, 79.6, 73.6, 71.6, 57.0; IR (KBr) cm\(^{-1}\) 3288s, 3086m, 3026m, 2859m, 1497s, 1455s, 1345m, 1089s, 1024s, 931m, 909m, 738s, 697s; HRMS: C\(_{10}\)H\(_{10}\)O for [M+H]\(^+\), calculated 147.0810, found 147.0806.

**S2p**

**S2p**: 0.99 g (78% yield); yellow oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.33 (d, \(J = 8.5\) Hz, 2H), 6.93 (d, \(J = 8.6\) Hz, 2H), 4.59 (s, 2H), 4.18 (d, \(J = 2.4\) Hz, 2H), 3.85 (s, 3H), 2.50 (dd, \(J = 2.4, 1.5\) Hz, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 159.4, 129.8, 129.7, 129.3, 113.9, 113.8, 71.2, 56.7; IR (KBr) cm\(^{-1}\) 3283s, 2994w, 2940w, 2905w, 2834w, 1607s, 1513s, 1248s, 1173m, 1078s, 1034m, 1025s, 816s; HRMS: C\(_{11}\)H\(_{12}\)O\(_2\) for [M+Na]\(^+\), calculated 199.0730, found 199.0735.

**S2q**

**S2q**: 0.90 g (75% yield); yellow oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.66 (d, \(J = 8.0\) Hz, 2H), 7.52 (d, \(J = 8.0\) Hz, 2H), 4.71 (s, 2H), 4.26 (d, \(J = 2.4\) Hz, 2H), 2.53 (t, \(J = 2.2\) Hz, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 141.5, 127.9, 125.4, 74.0, 70.8, 70.7, 70.5, 57.5; IR (KBr) cm\(^{-1}\) 3304s, 2857m, 1619m, 1450m, 1414m, 1325s, 1161s, 1131s, 1090s, 1066s, 1018m, 819s; HRMS: C\(_{11}\)H\(_9\)F\(_3\)O for [M-H]\(^+\), calculated 213.0533, found 213.0532.
S2r: 0.85 g (65% yield); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 – 7.11 (m, 5H), 4.65 (q, $J = 6.5$ Hz, 1H), 3.97 (ddd, $J = 83.4$, 15.7, 2.4 Hz, 1H), 2.40 (t, $J = 2.4$ Hz, 1H), 1.47 (d, $J = 6.5$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.4, 128.6, 127.8, 126.5, 80.0, 76.7, 74.1, 55.5, 23.8; IR (neat) cm$^{-1}$ 3295s, 3031m, 2977m, 2931m, 1493m, 1452s, 1372m, 1208s, 1093s, 1056m, 761s, 702s; HRMS: C$_{11}$H$_{12}$O for [M+Na]$^+$, calculated 183.0786, found 183.0782. [$\alpha$]$_D^{25}$ = +0.2, (0.1 $\times$ 10$^{-3}$ g/mL, MeOH).

S2s: 1.5g (68% yield); brown oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.34 (tdd, $J = 5.8$, 2.7, 1.3 Hz, 1H), 4.12 (d, $J = 2.4$ Hz, 2H), 4.06 (d, $J = 7.1$ Hz, 2H), 2.42 (t, $J = 2.4$ Hz, 1H), 1.76 (s, 3H), 1.71 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.3, 120.2, 80.1, 74.1, 65.9, 56.7, 25.8, 17.9; IR (neat) cm$^{-1}$ 3463w, 2956w, 2924m, 2854m, 1636w, 1461m, 1378w, 738w; HRMS: C$_8$H$_{12}$O for [M+H]$^+$, calculated 125.0961, found 125.0966.

**General Procedure for Synthesis of Allenyl ethers 5b-s Using 5b as an Example.**

To a solution of S2b (1.00 g, 7.57 mmol) in THF (38 mL) was added t-BuOK (1.0 M solution in THF, 2.27 mL, 2.27 mmol, 0.30 equiv) at 0°C. The reaction was stirred at rt for 1 h before being concentrated under reduced pressure. Subsequently, the residue was first suspended in Et$_2$O and then filtered through Celite™. The filtrate was concentrated under reduced pressure and the crude residue was purified using silica gel flash column chromatography [eluent: 5% EtOAc/Hexane] to give the desired allenyl ether 5b (0.90 g, 90% yield).

**Characterizations of Allenyl Ethers 5a-q.**
5b: 1.30 g (91% yield); yellow oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.35 (td, $J = 8.5, 7.5$ Hz, 2H), 7.13 – 7.04 (m, 3H), 6.88 (t, $J = 6.0$ Hz, 1H), 5.48 (d, $J = 6.0$ Hz, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 202.8, 157.2, 129.5, 122.8, 117.9, 116.8, 89.6; IR (KBr) cm$^{-1}$ 3032m, 2913m, 2854m, 1592s, 1485s, 1437m, 1336m, 1223s, 1163m, 1099m, 988m, 884s, 750s; HRMS: C$_{9}$H$_{8}$O for [M+H]$^+$, calculated 133.0648, found 133.0649.

5c: 1.23 g (95% yield); yellow oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.31 – 7.27 (m, 2H), 7.05 – 7.00 (m, 2H), 6.83 (t, $J = 6.0$ Hz, 1H), 5.48 (d, $J = 6.0$ Hz, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 202.6, 155.7, 129.5, 127.8, 118.2, 117.9, 90.0; IR (KBr) cm$^{-1}$ 3030w, 2964m, 1676m, 1593s, 1488s, 1440s, 1340m, 1238s, 1168s, 1091s, 1008s, 889m, 823s, 682m; HRMS: C$_{9}$H$_{7}$ClO for [M+H]$^+$, calculated 167.0264, found 167.0279.

5d: 1.09 g (89% yield); yellow oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.47 – 7.41 (m, 2H), 7.00 – 6.95 (m, 2H), 6.82 (t, $J = 6.0$ Hz, 1H), 5.48 (d, $J = 6.0$ Hz, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 202.6, 156.2, 132.4, 118.7, 117.7, 115.2, 90.0; IR (KBr) cm$^{-1}$ 3032m, 2913m, 2854m, 1578m, 1482s, 1438m, 1331m, 1233s, 1167m, 1066m, 884m, 816s; HRMS: C$_{9}$H$_{7}$BrO for [M+H]$^+$, calculated 210.9753, found 210.9745.
**5e:** 0.84 g (69% yield); yellow oil; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.27 (t, $J = 8.4$ Hz, 1H), 7.23 – 7.18 (m, 2H), 7.02 (dt, $J = 7.0$, 2.0 Hz, 1H), 6.82 (t, $J = 6.0$ Hz, 1H), 5.50 (d, $J = 6.0$ Hz, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 202.7, 157.9, 130.6, 125.9, 122.7, 120.0, 117.4, 115.6, 89.9; IR (KBr) cm$^{-1}$ 3065w, 3015w, 2979m, 2917m, 1591s, 1472s, 1434s, 1223s, 1021s, 992s, 882s, 766s; HRMS: C$_9$H$_7$BrO for [M+H]$^+$, calculated 210.9753, found 210.9580.

![Br](image)

**5f:** 0.88 g (72% yield); yellow oil; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.58 (dd, $J = 7.9$, 1.5 Hz, 1H), 7.30 (td, $J = 8.2$, 1.5 Hz, 1H), 7.16 (dd, $J = 8.2$, 1.3 Hz, 1H), 6.97 (td, $J = 7.8$, 1.3 Hz, 1H), 6.87 (t, $J = 6.0$ Hz, 1H), 5.48 (d, $J = 6.0$ Hz, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 202.4, 171.1, 153.7, 133.6, 128.4, 124.3, 118.4, 117.3, 113.3, 90.5, 60.4, 21.1, 14.3; IR (KBr) cm$^{-1}$ 3443s, 3035w, 2925m, 1730m, 1623m, 1474s, 1326s, 1240s, 1165m, 1126s, 1067s, 824m, 750s; HRMS: C$_9$H$_7$BrO for [M+H]$^+$, calculated 210.9759, found 211.0247.

![I](image)

**5g:** 0.93 g (79% yield); white solid; mp 29-30°C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.64 – 7.59 (m, 2H), 6.89 – 6.84 (m, 2H), 6.81 (t, $J = 6.0$ Hz, 1H), 5.48 (d, $J = 6.0$ Hz, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 202.6, 157.1, 138.4, 119.1, 117.5, 90.0, 85.4; IR (KBr) cm$^{-1}$ 3077w, 3029w, 1961m, 1637w, 1583m, 1571m, 1479s, 1437s, 1330s, 1244s, 1172s, 1015m, 844s, 809s; HRMS: C$_9$H$_7$IO for [M-H]$^+$, calculated 256.9469, found 256.9467.

![F$_3$C](image)
**5h:** 1.10 g (89% yield); yellow oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.61 (d, $J = 8.6$ Hz, 2H), 7.17 (d, $J = 8.6$ Hz, 2H), 6.87 (t, $J = 6.0$ Hz, 1H), 5.52 (d, $J = 6.0$ Hz, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 202.7, 159.3, 127.0, 126.9, 126.9, 116.9, 116.6, 90.0; IR (KBr) cm$^{-1}$ 2924m, 2853m, 1740m, 1615s, 1515s, 1328s, 1244s, 1166s, 1123s, 1066s, 1012s, 837s; HRMS: C$_{10}$H$_7$F$_3$O for [M+H]$^+$, calculated 201.0522, found 201.0529.

![5i](image)

**5i:** 1.08 g (85% yield); yellow solid; mp 92-93°C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.27 – 8.23 (m, 2H), 7.19 – 7.14 (m, 2H), 6.88 (t, $J = 6.0$ Hz, 1H), 5.55 (d, $J = 6.0$ Hz, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 202.6, 162.1, 125.9, 116.3, 116.3, 90.3; IR (KBr) cm$^{-1}$ 3077w, 2929w, 1612s, 1622s, 1585s, 1490s, 1342s, 1262s, 1107s, 1015s, 947s, 843s, 751s; HRMS: C$_9$H$_7$NO$_3$ for [M+H]$^+$, calculated 178.0497, found 178.0500.

![5j](image)

**5j:** 1.11 g (87% yield); white solid; mp 63-64°C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.91 – 7.86 (m, 2H), 7.06 – 7.01 (m, 2H), 6.79 (t, $J = 6.0$ Hz, 1H), 5.43 (d, $J = 6.0$ Hz, 2H), 2.50 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 202.8, 196.7, 161.0, 131.9, 130.5, 116.6, 116.1, 89.9, 26.5; IR (KBr) cm$^{-1}$ 3068w, 3044w, 1666s, 1597s, 1578s, 1503s, 1420s, 1354s, 1234s, 1182s, 1019s, 959s, 902s, 837s, 961s; HRMS: C$_{11}$H$_{10}$O$_2$ for [M+H]$^+$, calculated 175.0754, found 175.0749.

![5k](image)

**5k:** 1.10 g (82% yield); yellow oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.17 (d, $J = 8.4$ Hz, 2H), 7.03 (d, $J = 8.4$ Hz, 2H), 6.89 (d, $J = 6.0$ Hz, 1H), 5.49 (d, $J = 6.0$ Hz, 2H), 2.37 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 202.8, 155.1, 132.3, 130.0, 118.4, 116.9, 89.6,
20.7; IR (KBr) cm\(^{-1}\) 3029w, 2916m, 2857m, 1610m, 1583m, 1503s, 1434s, 1342s, 1226s, 1175m, 1015m, 994m, 878m, 872s; HRMS: C\(_{10}\)H\(_{10}\)O for [M+H]\(^+\), calculated 147.0804, found 147.0804.

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\begin{center}
\text{H}_3\text{CO} \quad 5l
\end{center}
\]

5l: 1.12 g (86% yield); yellow oil; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.03 (dd, \(J = 9.8, 3.0\) Hz, 2H), 6.89 – 6.83 (m, 2H), 5.45 (d, \(J = 6.0\) Hz, 2H), 3.81 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 202.5, 155.4, 151.0, 119.4, 118.4, 114.5, 89.9, 55.7; IR (KBr) cm\(^{-1}\) 2942w, 2901w, 2836m, 1506s, 1437m, 1339m, 1223s, 1035m, 1012m, 991m, 878m, 872s; HRMS: C\(_{10}\)H\(_{10}\)O\(_2\) for [M+H]\(^+\), calculated 163.0754, found 163.0753.

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\begin{center}
\text{5m}
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\]

5m: 0.57 g (45% yield); colorless oil; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.38 – 8.33 (m, 1H), 7.92 – 7.87 (m, 1H), 7.61 (d, \(J = 8.2\) Hz, 1H), 7.60 – 7.55 (m, 1H), 7.46 (t, \(J = 7.9\) Hz, 1H), 7.17 (d, \(J = 7.6\) Hz, 1H), 7.08 (t, \(J = 6.0\) Hz, 1H), 5.56 (d, \(J = 6.0\) Hz, 1H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 203.1, 153.3, 134.7, 127.6, 126.6, 126.0, 125.8, 125.6, 122.6, 122.0, 118.2, 109.6, 89.7; IR (KBr) cm\(^{-1}\) 3053s, 2976m, 1672m, 1592s, 1577s, 1509s, 1428s, 1390s, 1262s, 1238s, 1175s, 1157s, 890s, 788s, 768s; HRMS: C\(_{13}\)H\(_{10}\)O for [M+H]\(^+\), calculated 183.0804, found 183.0804.

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\begin{center}
\text{5n}
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\]

5n: 0.62 g (49% yield); white solid; mp 57-58°C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.83 (dd, \(J = 8.4, 5.8\) Hz, 2H), 7.80 (d, \(J = 8.2\) Hz, 1H), 7.50 (t, \(J = 7.5\) Hz, 1H), 7.45 – 7.41 (m, 2H), 7.31 (dd, \(J = 9.0, 2.4\) Hz, 1H), 7.01 (t, \(J = 6.0\) Hz, 1H), 5.53 (d, \(J = 6.0\) Hz, 2H), 5.49 (d, \(J = 7.2\) Hz, 1H), 4.83 (t, \(J = 7.8\) Hz, 1H), 4.31 (dd, \(J = 8.0, 5.8\) Hz, 2H), 3.91 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 204.1, 153.4, 134.7, 127.5, 126.2, 125.8, 125.6, 122.5, 122.0, 118.1, 109.7, 89.6; IR (KBr) cm\(^{-1}\) 3053s, 2976m, 1672m, 1592s, 1577s, 1509s, 1428s, 1390s, 1262s, 1238s, 1175s, 1157s, 890s, 788s, 768s; HRMS: C\(_{13}\)H\(_{10}\)O for [M+H]\(^+\), calculated 183.0804, found 183.0804.
$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 203.0, 171.2, 155.1, 134.2, 130.0, 129.7, 127.8, 127.1, 126.6, 124.5, 118.9, 117.7, 110.9, 89.7, 60.4, 21.1, 14.2; IR (KBr) cm$^{-1}$ 3053w, 3021w, 2946w, 1626s, 1594s, 1505s, 1434s, 1250s, 1202s, 1010s, 1025s, 835s, 746s; HRMS: C$_{13}$H$_{10}$O for [M+H]$^+$, calculated 183.0804, found 183.0805.

5o: 1.09 g (81% yield); yellow oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.40 (d, $J$ = 4.4 Hz, 3H), 7.37 – 7.32 (m, 1H), 6.88 (t, $J$ = 6.0 Hz, 1H), 5.52 (d, $J$ = 6.0 Hz, 2H), 4.66 (s, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 201.4, 137.3, 128.5, 127.9, 127.8, 121.7, 91.2, 70.7; IR (KBr) cm$^{-1}$ 3086m, 3036m, 2866m, 1953s, 1491m, 1456s, 1435s, 1375m, 1349s, 1188s, 1042s, 884s, 739s, 694s; HRMS: C$_{10}$H$_{10}$O for [M+H]$^+$, calculated 147.0804, found 147.0805.

5p: 1.10 g (86% yield); colorless oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.33 (d, $J$ = 8.5 Hz, 2H), 6.93 (d, $J$ = 8.6 Hz, 2H), 6.86 (t, $J$ = 6.0 Hz, 1H), 5.52 (d, $J$ = 6.0 Hz, 2H), 4.59 (s, 2H), 3.84 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 201.4, 159.4, 129.6, 129.4, 121.5, 113.9, 90.9, 70.5, 55.3; IR (KBr) cm$^{-1}$ 3445s, 2935w, 2836m, 1953s, 1456s, 1435s, 1375m, 1349s, 1188s, 1042s, 884s, 739s, 694s; HRMS: C$_{11}$H$_{12}$O$_2$ for [M+K]$^+$, calculated 215.0474, found 215.0559.

5q: 0.97 g (80% yield); yellow oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J$ = 8.0 Hz, 2H), 7.49 (d, $J$ = 8.0 Hz, 2H), 6.88 (t, $J$ = 6.0 Hz, 1H), 5.51 (d, $J$ = 6.0 Hz, 2H), 4.71 (s, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 201.1, 141.5, 127.6, 125.4, 125.3, 121.5, 91.6, 69.6; IR (KBr) cm$^{-1}$ 3448s, 2932w, 1955m, 1732s, 1662m, 1444m, 1420m, 1327s,
1166s, 1126s, 1067m, 1018s, 824s; HRMS: C_{11}H_{9}F_{3}O for [M-H]^+, calculated 213.0533, found 213.0523.

5r: 0.64 g (64% yield); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (ddd, $J$ = 6.6, 4.6, 1.9 Hz, 5H), 6.97 – 6.55 (m, 1H), 5.52 – 5.44 (m, 1H), 5.39 – 5.32 (m, 1H), 5.01 – 4.93 (m, 1H), 1.78 – 1.55 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.3, 143.4, 128.5, 127.6, 126.2, 120.4, 90.2, 76.8, 23.5; IR (neat) cm$^{-1}$ 3031m, 2978m, 2929m, 1953m, 1727m, 1450s, 1374m, 1350s, 1196s, 1069m, 1028m, 760s, 699s; HRMS: C$_{11}$H$_{12}$O for [M+Na]$^+$, calculated 183.0786, found 183.0782. $\alpha$$_D^{25}$ = -0.1, (0.08 $\times$ 10$^{-3}$ g/mL, MeOH).

5s: 0.66g (66% yield); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.73 (t, $J$ = 5.9 Hz, 1H), 5.43 (d, $J$ = 5.9 Hz, 1H), 5.40 (ddddd, $J$ = 8.4, 5.6, 2.8, 1.4 Hz, 1H), 5.30 (s, 1H), 4.07 (d, $J$ = 7.0 Hz, 1H), 1.75 (d, $J$ = 10.6 Hz, 3H), 1.67 (d, $J$ = 12.7 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.3, 138.1, 121.3, 119.9, 90.4, 65.3, 60.4, 53.4, 25.8, 18.1; IR (neat) cm$^{-1}$ 3685w, 2956w, 2925m, 2855m, 1636w, 1465m, 1378w, 738w; HRMS: C$_8$H$_{12}$O for [M+H]$^+$, calculated 125.0961, found 125.0966.

**GENERAL PROCEDURE FOR (4 + 3) CYCLOADDITION USING 5B AND FURAN AS AN EXAMPLE.**

![Diagram](image-url)
To a solution of allenyl ether 5b (26 mg, 0.2 mmol) in CH$_2$Cl$_2$ (4 mL) containing anhyd 4Å MS were added KH$_2$PO$_4$ (54 mg, 0.40 mmol, 2.0 equiv) and furan (27 mg, 0.40 mmol, 2.0 equiv) at –30 °C. After which, a dry-ice chilled solution of DMDO (7.5 mL, 0.08 M solution in CH$_2$Cl$_2$, 3.0 equiv) was added via syringe pump over 1 h. The reaction mixture was stirred at this temperature for another 1 h before being filtered through Celite™. The filtrate was concentrated under reduced pressure and purified by silica gel flash column chromatography [eluent: 20% EtOAc/Hexane] to afford the desired cycloadduct 8b (35 mg, 81% yield).

![8a](image)

**8a:** 16 mg (52% yield); yellow oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 6.33 – 6.30 (m, 2H), 5.05 (dd, $J = 5.0, 0.7$ Hz, 1H), 5.03 (d, $J = 5.0$ Hz, 1H), 3.99 (d, $J = 5.0$ Hz, 1H), 3.60 (s, 3H), 2.79 (dd, $J = 15.3, 4.9$ Hz, 1H), 2.39 (d, $J = 15.3$ Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 204.6, 134.7, 131.5, 86.9, 79.2, 78.4, 59.7, 45.9; IR (KBr) cm$^{-1}$ 3261w, 2967w, 2955m, 2923m, 1750s, 1610s, 1509s, 1401s, 1338m, 1260m, 1061m, 1020m, 962s, 848m, 729s; HRMS: C$_8$H$_{10}$O$_3$ for [M+H]$^+$, calculated 155.0703, found 155.0702.

![8b](image)

**8b:** 35 mg (81% yield); white solid; mp 52-53°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27 (dd, $J = 8.4$, 7.6 Hz, 2H), 6.99 (t, $J = 7.4$ Hz, 1H), 6.93 (d, $J = 8.0$ Hz, 2H), 6.40 (ddd, $J = 20.6$, 6.1, 1.5 Hz, 2H), 5.14 (dd, $J = 5.0$, 1.6 Hz, 1H), 5.08 (d, $J = 5.0$ Hz, 1H), 4.91 (d, $J = 5.0$ Hz, 1H), 2.88 (dd, $J = 15.4$, 4.9 Hz, 1H), 2.48 (d, $J = 15.4$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.1, 158.0, 135.2, 131.4, 129.6, 122.1, 115.7, 83.3, 79.4, 78.6, 46.0; IR (KBr) cm$^{-1}$ 3127w, 2965m, 2955m, 2923w, 1727s, 1610s, 1509s, 1401s,
1237s, 1175s, 1073s, 966s, 813s, 722s; HRMS: C_{13}H_{12}O_3 for [M+Na]^+, calculated 253.0835, found 253.0824.

8c: 36 mg (72% yield); yellow oil; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.25 – 7.20 (m, 2H), 6.90 – 6.81 (m, 2H), 6.40 (qd, \(J = 6.1, 1.5\) Hz, 2H), 5.16 – 5.05 (m, 2H), 4.85 (d, \(J = 5.0\) Hz, 1H), 2.89 (dd, \(J = 15.4, 4.9\) Hz, 1H), 2.49 (d, \(J = 15.4\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 201.9, 156.7, 135.3, 131.3, 129.4, 126.9, 117.0, 83.5, 79.3, 78.6, 46.0; IR (KBr) cm\(^{-1}\) 3089w, 2985m, 2955m, 2908m, 1716s, 1591s, 1481s, 1247s, 1208s, 1125s, 1069m, 820s, 734s; HRMS: C\(_{13}\)H\(_{11}\)ClO\(_3\) for [M+Na]^+, calculated 273.0289, found 273.0292.

8d: 40 mg (68% yield); white solid; mp 67-68°C; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40 – 7.32 (m, 2H), 6.83 – 6.75 (m, 2H), 6.39 (qd, \(J = 6.1, 1.5\) Hz, 2H), 5.15 – 5.05 (m, 2H), 4.85 (d, \(J = 5.0\) Hz, 1H), 2.87 (dd, \(J = 15.4, 5.0\) Hz, 1H), 2.47 (d, \(J = 15.4\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 201.8, 157.2, 135.4, 132.4, 131.2, 117.5, 114.2, 83.3, 79.3, 78.6, 45.9; IR (KBr) cm\(^{-1}\) 3096w, 2961m, 2926m, 1723s, 1585m, 1485s, 1279m, 1247s, 1176s, 1069s, 1125s, 968s, 822s, 729s; HRMS: C\(_{13}\)H\(_{11}\)BrO\(_3\) for [M+Na]^+, calculated 316.9784, found 316.9785.
**8e:** 32 mg (54% yield); white solid; mp 66-67°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.17 – 7.10 (m, 2H), 7.10 – 7.06 (m, 1H), 6.89 – 6.81 (m, 1H), 6.40 (qd, $J = 6.0$, 1.4 Hz, 2H), 5.13 (dd, $J = 5.0$, 1.4 Hz, 1H), 5.12 – 5.09 (m, 1H), 4.88 (d, $J = 5.0$ Hz, 1H), 2.90 (dd, $J = 15.4$, 5.0 Hz, 1H), 2.50 (d, $J = 15.4$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.6, 158.7, 135.4, 131.2, 125.2, 122.8, 119.1, 114.4, 83.2, 79.3, 78.6, 46.0; IR (KBr) cm$^{-1}$ 3063w, 2976m, 2927w, 2899w, 1714s, 1594s, 1472s, 1325s, 1243s, 1172s, 1072s, 967s, 861s, 763s, 735s, 672s; HRMS: C$_{13}$H$_{11}$BrO$_3$ for [M+Na]$^+$, calculated 316.9784, found 316.9771.

**8f:** 34 mg (57% yield); white solid; mp 54-55°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 – 7.24 (m, 1H), 7.03 – 6.96 (m, 1H), 6.93 (dd, $J = 8.6$, 0.8 Hz, 2H), 6.42 (dd, $J = 6.0$, 1.7 Hz, 1H), 6.37 (dd, $J = 6.0$, 1.6 Hz, 1H), 5.13 (dd, $J = 5.0$, 1.7 Hz, 1H), 5.07 (dd, $J = 3.8$, 1.1 Hz, 1H), 4.91 (d, $J = 5.0$ Hz, 1H), 2.88 (dd, $J = 15.4$, 5.0 Hz, 1H), 2.47 (d, $J = 15.4$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.0, 157.9, 135.2, 131.4, 129.5, 122.0, 115.7, 83.3, 79.3, 78.6, 45.9; IR (KBr) cm$^{-1}$ 3066w, 2989w, 2916w, 1711s, 1592s, 1491s, 1328m, 1326s, 1171s, 1056s, 964s, 874s, 749s, 728s, 689s; HRMS: C$_{13}$H$_{11}$BrO$_3$ for [M+Na]$^+$, calculated 316.9784, found 316.9781.
8g: 38 mg (55% yield); white solid; mp 42-43°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 – 7.22 (m, 2H), 6.99 (t, $J$ = 7.4 Hz, 1H), 6.96 – 6.89 (m, 2H), 6.39 (ddd, $J$ = 20.6, 6.1, 1.6 Hz, 2H), 5.17 – 5.03 (m, 2H), 4.91 (d, $J$ = 5.0 Hz, 1H), 2.88 (dd, $J$ = 15.4, 4.9 Hz, 1H), 2.48 (d, $J$ = 15.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.1, 158.0, 135.2, 131.4, 129.6, 122.1, 115.7, 83.3, 79.4, 78.6, 46.0; IR (KBr) cm$^{-1}$ 3089w, 3059w, 3032w, 2991m, 2914m, 2899m, 1714s, 1597s, 1493s, 1330m, 1244s, 1173s, 1090s, 965s, 861s, 754s, 731s, 689s; HRMS: C$_{13}$H$_{11}$IO$_3$ for [M+Na]$^+$, calculated 364.9645, found 364.9652.

8h: 46 mg (81% yield); yellow oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.56 (d, $J$ = 8.5 Hz, 2H), 6.99 (d, $J$ = 8.5 Hz, 2H), 6.44 (ddd, $J$ = 15.6, 6.1, 1.4 Hz, 2H), 5.20 – 5.09 (m, 2H), 4.99 (d, $J$ = 5.0 Hz, 1H), 2.93 (dd, $J$ = 15.4, 4.9 Hz, 1H), 2.52 (d, $J$ = 15.4 Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 201.5, 160.4, 135.5, 131.2, 126.9, 126.9, 115.4, 82.7, 79.3, 78.6, 45.9; IR (KBr) cm$^{-1}$ 3109w, 2975m, 2922m, 1719s, 1591s, 1612s, 1517s, 1321s, 1245s, 1161s, 1117s, 1059s, 998s, 886s, 725s; HRMS: C$_{14}$H$_{11}$F$_3$O$_3$ for [M+Na]$^+$, calculated 307.0552, found 307.0537.
8i: 42 mg (80% yield); yellow solid; mp 114-115°C; 1H NMR (400 MHz, CDCl₃) δ 8.22 – 8.16 (m, 2H), 6.98 – 6.91 (m, 2H), 6.47 – 6.40 (m, 2H), 5.18 (dd, J = 5.0, 1.0 Hz, 1H), 5.14 (d, J = 5.0 Hz, 1H), 5.03 (d, J = 5.0 Hz, 1H), 2.94 (dd, J = 15.4, 5.0 Hz, 1H), 2.52 (d, J = 15.4 Hz, 1H); 13C NMR (100 MHz, CDCl₃) δ 200.9, 162.9, 142.2, 135.8, 131.0, 125.8, 115.2, 82.6, 79.3, 78.7, 45.9; IR (KBr) cm⁻¹ 3115w, 3086m, 2924m, 1725s, 1590s, 1506s, 1345s, 1257s, 1171s, 1111s, 1079s, 1060s, 963s, 854s, 725s; HRMS: C₁₃H₁₁NO₅ for [M-H]⁺, calculated 260.0564, found 260.0564.

8j: 38 mg (74% yield); yellow oil; 1H NMR (400 MHz, CDCl₃) δ 7.95 – 7.88 (m, 2H), 6.97 – 6.89 (m, 2H), 6.42 (qd, J = 6.0, 1.5 Hz, 2H), 5.16 (dd, J = 5.0, 1.6 Hz, 1H), 5.14 – 5.10 (m, 1H), 5.02 (d, J = 5.0 Hz, 1H), 2.92 (dd, J = 15.4, 5.0 Hz, 1H), 2.55 (s, 3H), 2.51 (d, J = 15.4 Hz, 1H); 13C NMR (100 MHz, CDCl₃) δ 201.3, 196.7, 161.7, 135.5, 131.3, 131.2, 130.5, 114.9, 82.5, 79.2, 78.7, 45.9, 26.4; IR (KBr) cm⁻¹ 3082w, 2955m, 2924m, 2854m, 1725s, 1668s, 1598s, 1505s, 1419s, 1359s, 1253s, 1181s, 1055s, 964s, 829s, 732s; HRMS: C₁₅H₁₄O₄ for [M+Na]⁺, calculated 281.0784, found 281.0776.

8k: 28 mg (61% yield); yellow solid; mp 56-57°C; 1H NMR (400 MHz, CDCl₃) δ 7.07 (d, J = 8.2 Hz, 2H), 6.86 – 6.81 (m, 2H), 6.39 (ddd, J = 20.2, 6.1, 1.6 Hz, 2H), 5.13 (dd, J = 5.0, 1.7 Hz, 1H), 5.08 (d, J = 4.9 Hz, 1H), 4.86 (d, J = 5.0 Hz, 1H), 2.87 (dd, J = 15.4, 4.9 Hz, 1H), 2.48 (d, J = 15.4 Hz, 1H), 2.28 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ 202.1, 157.9, 135.2, 131.4, 129.5, 122.1, 115.7, 83.3, 79.4, 78.6, 45.9; IR (KBr) cm⁻¹
3077w, 3038w, 2961m, 2915w, 1723s, 1592s, 1485s, 1339m, 1241s, 1199m, 1083m, 1025s, 961s, 747m, 726s, 690m; HRMS: C_{14}H_{14}O_3 for [M+Na]^+, calculated 253.0835, found 253.0818.

8l: 23 mg (47% yield); yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 6.93 – 6.86 (m, 2H), 6.83 – 6.78 (m, 2H), 6.39 (ddd, J = 20.2, 6.1, 1.5 Hz, 2H), 5.14 – 5.03 (m, 2H), 4.78 (d, J = 5.0 Hz, 1H), 3.75 (s, 3H), 2.86 (dd, J = 15.4, 4.9 Hz, 1H), 2.47 (d, J = 15.4 Hz, 1H);
^13C NMR (100 MHz, CDCl_3) δ 202.5, 154.8, 152.1, 135.1, 131.4, 117.3, 114.6, 84.6, 79.4, 78.6, 55.7, 45.9; IR (KBr) cm\(^{-1}\) 3093w, 3043w, 2999m, 2956m, 2849s, 1723s, 1512s, 1233s, 1173s, 1079m, 1025s, 964s, 825s, 734s; HRMS: C_{14}H_{14}O_4 for [M+Na]^+, calculated 269.0784, found 269.0777.

8m: 24 mg (45% yield); white solid; mp 75-76°C; ^1H NMR (400 MHz, CDCl_3) δ 8.28 – 8.20 (m, 1H), 7.85 – 7.77 (m, 1H), 7.54 – 7.44 (m, 3H), 7.35 (t, J = 8.0 Hz, 1H), 6.85 (d, J = 7.6 Hz, 1H), 6.54 (dd, J = 6.1, 1.7 Hz, 1H), 6.44 (dd, J = 6.1, 1.6 Hz, 1H), 5.26 (dd, J = 5.0, 1.7 Hz, 1H), 5.12 (t, J = 5.7 Hz, 2H), 2.95 (dd, J = 15.4, 4.9 Hz, 1H), 2.54 (d, J = 15.4 Hz, 1H); ^13C NMR (100 MHz, CDCl_3) δ 201.7, 153.7, 135.4, 134.6, 131.4, 127.5, 126.5, 125.8, 125.6, 125.5, 122.0, 121.7, 106.9, 83.6, 79.4, 78.6, 46.0; IR (KBr) cm\(^{-1}\) 3080m, 2961w, 1730s, 1576m, 1264s, 1238s, 1110s, 961s, 1015s, 770s, 735s; HRMS: C_{17}H_{14}O_3 for [M+Na]^+, calculated 289.0835, found 289.0828.
**8n**: 23 mg (43% yield); white solid; mp 112–113°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 (dd, $J = 8.1, 3.7$ Hz, 2H), 7.69 (d, $J = 8.2$ Hz, 1H), 7.46 – 7.39 (m, 1H), 7.37 – 7.31 (m, 1H), 7.22 – 7.15 (m, 2H), 6.41 (ddd, $J = 26.3, 6.1, 1.7$ Hz, 2H), 5.20 (dd, $J = 5.0, 1.7$ Hz, 1H), 5.08 (dd, $J = 8.2, 5.0$ Hz, 2H), 2.92 (dd, $J = 15.4, 4.9$ Hz, 1H), 2.50 (d, $J = 15.4$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.9, 155.8, 135.3, 134.3, 131.4, 129.7, 129.6, 127.7, 127.0, 126.6, 124.2, 118.7, 109.0, 83.3, 79.3, 78.7, 46.0; IR (KBr) cm$^{-1}$ 3052w, 2978w, 1724s, 1269s, 1510s, 1360s, 1252s, 1171s, 1072s, 962s, 832, 738s; HRMS: C$_{17}$H$_{14}$O$_3$ for [M+Na]$^+$, calculated 289.0835, found 289.0821.

**8o**: 21 mg (46% yield); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 – 7.27 (m, 5H), 6.32 (ddd, $J = 15.6, 6.1, 1.6$ Hz, 2H), 5.01 – 4.95 (m, 2H), 4.91 (dd, $J = 5.0, 1.6$ Hz, 1H), 4.64 (d, $J = 12.1$ Hz, 1H), 4.13 (d, $J = 5.0$ Hz, 1H), 2.76 (dd, $J = 15.4, 4.9$ Hz, 1H), 2.38 (d, $J = 15.4$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 205.0, 137.6, 134.6, 131.8, 128.5, 128.0, 127.9, 84.2, 79.8, 78.4, 73.6, 46.0; IR (KBr) cm$^{-1}$ 3083w, 3053w, 3027w, 2932w, 2855m, 1724s, 1493m, 1451m, 1324m, 1143s, 1042m, 1015s, 964s, 826s, 731s; HRMS: C$_{14}$H$_{14}$O$_3$ for [M+Na]$^+$, calculated 253.0835, found 253.0838.
**8p**: 28 mg (54% yield); yellow oil; 
$^1$H NMR (600 MHz, CDCl$_3$) δ 7.32 (d, $J=8.5$ Hz, 2H), 6.91 (d, $J=8.5$ Hz, 2H), 6.32 (ddd, $J=19.5$, 6.1, 1.4 Hz, 2H), 5.00 (d, $J=4.7$ Hz, 1H), 4.92 (d, $J=11.7$ Hz, 1H), 4.89 (dd, $J=4.9$, 1.4 Hz, 1H), 4.59 (d, $J=11.7$ Hz, 1H), 4.13 (d, $J=5.0$ Hz, 1H), 3.83 (s, 3H), 2.76 (dd, $J=15.4$, 4.9 Hz, 1H), 2.38 (d, $J=15.4$ Hz, 1H); 
$^{13}$C NMR (150 MHz, CDCl$_3$) δ 205.1, 159.5, 134.6, 131.8, 129.7, 113.9, 83.8, 79.9, 78.4, 73.2, 55.3, 46.0; 
IR (KBr) cm$^{-1}$ 3088w, 3003w, 2964m, 2841m, 1714s, 1611s, 1398s, 1327m, 1241m, 1179s, 1118s, 1068s, 963s, 825s, 727s, 617m; 
HRMS: C$_{15}$H$_{16}$O$_4$ for [M+Na]$^+$, calculated 283.0941, found 283.0936.

![8q](image)

**8q**: 48 mg (80% yield); yellow oil; 
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.61 (d, $J=8.1$ Hz, 2H), 7.49 (d, $J=8.0$ Hz, 2H), 6.37 – 6.30 (m, 2H), 5.09 – 5.00 (m, 2H), 4.98 (dd, $J=5.1$, 1.3 Hz, 1H), 4.69 (d, $J=12.5$ Hz, 1H), 4.14 (d, $J=5.1$ Hz, 1H), 2.78 (dd, $J=15.4$, 4.9 Hz, 1H), 2.39 (d, $J=15.4$ Hz, 1H); 
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 204.8, 141.8, 134.9, 131.6, 127.8, 125.5, 125.4, 84.6, 79.7, 78.4, 72.8, 46.0; IR (KBr) cm$^{-1}$ 2963m, 2912m, 2874w, 1721s, 1620m, 1398m, 1332s, 1107s, 1119s, 1017s, 961s, 833s, 737s; 
HRMS: C$_{15}$H$_{13}$F$_3$O$_3$ for [M+H]$^+$, calculated 299.0890, found 299.1618.

![8r](image)

**8r (isomer 1)**: 18 mg (37% yield); white solid; mp 98-99°C; 
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.31 – 7.22 (m, 5H), 6.25 (ddd, $J=33.4$, 6.1, 1.7 Hz, 2H), 4.87 (dd, $J=3.8$, 1.1 Hz, 1H), 4.75 (q, $J=6.5$ Hz, 1H), 4.62 (dd, $J=5.1$, 1.7 Hz, 1H), 3.86 (d, $J=5.1$ Hz, 2H), 2.92 (s, 3H); 
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 208.3, 159.7, 134.4, 131.5, 129.7, 128.7, 125.9, 125.4, 82.9, 79.9, 78.4, 72.9, 45.9; IR (KBr) cm$^{-1}$ 3015w, 2955w, 2928w, 2851w, 1711s, 1616s, 1509s, 1455s, 1388s, 1349s, 1250s, 1193s, 1066s, 962s, 820s, 727s, 617m; 
HRMS: C$_{15}$H$_{16}$O$_3$ for [M+Na]$^+$, calculated 283.0941, found 283.0936.

S24
Hz, 1H), 2.61 (dd, J = 15.4, 4.9 Hz, 1H), 2.26 (d, J = 15.4 Hz, 1H), 1.42 (d, J = 6.5 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 205.9, 143.3, 134.5, 131.9, 128.7, 127.9, 126.4, 82.9, 80.2, 79.2, 78.3, 45.9, 24.2; IR (KBr) cm$^{-1}$ 2972m, 2950m, 2895w, 1722s, 1417m, 1339w, 1283s, 1178s, 1047m, 1028, 969s, 888s, 763s; HRMS: C$_{15}$H$_{16}$O$_3$ for [M+Na]$^+$, calculated 267.0992, found 267.0997; [$\alpha$]$_D^{25}$ = +95, (1.0 × 10$^{-3}$ g/mL, CH$_2$Cl$_2$)

8r (isomer 2): 9 mg (18% yield); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 (dd, J = 5.1, 3.5 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.24 – 7.20 (m, 1H), 6.27 (ddd, J = 31.1, 6.1, 1.6 Hz, 1H), 4.99 (dd, J = 4.8, 1.7 Hz, 1H), 4.90 (dd, J = 3.8, 1.1 Hz, 1H), 4.69 (q, J = 6.4 Hz, 1H), 4.00 (d, J = 4.9 Hz, 1H), 2.58 (ddd, J = 15.4, 4.9 Hz, 1H), 2.27 (d, J = 15.4 Hz, 1H), 1.43 (d, J = 6.5 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 202.9, 142.5, 134.7, 131.8, 128.5, 127.8, 126.4, 82.7, 78.9, 78.3, 45.8, 23.7; IR (KBr) cm$^{-1}$ 3030w, 2973m, 2928w, 1728s, 1493m, 1452m, 1376m, 1338m, 1100s, 1031s, 969s, 850s, 826s; HRMS: C$_{15}$H$_{16}$O$_3$ for [M+Na]$^+$, calculated 267.0992, found 267.0997; [$\alpha$]$_D^{25}$ = -25, (1.0 × 10$^{-3}$ g/mL, CH$_2$Cl$_2$)

8s (isomer 1): 9.8 mg (22% yield); yellow solid; mp 68-69°C; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.32 (ddd, J = 15.4, 6.1, 1.5 Hz, 2H), 5.06 (dd, J = 5.1, 1.6 Hz, 1H), 5.02 (d, J = 4.9 Hz, 1H), 4.26 – 4.13 (m, 2H), 3.57 (dd, J = 11.4, 6.9 Hz, 1H), 3.02 (dd, J = 6.8, 3.6 Hz, 1H), 2.78 (dd, J = 15.4, 4.9 Hz, 1H), 2.37 (d, J = 15.4 Hz, 1H), 1.34 (d, J = 4.2 Hz, 3H), 1.27 (d, J = 11.5 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 205.0, 134.7, 131.8, 85.7, 79.87, 78.4, 71.4, 62.4, 57.7, 45.9, 24.7, 19.0; IR (KBr) cm$^{-1}$ 3473w, 2963s, 2926s, 2855w, 1726m, 1728s, 1499m, 1459m, 1380w, 1333w, 1245w, 1150s, 1115m, 964s, 730s; HRMS: C$_{12}$H$_{16}$O$_4$ for [M+H]$^+$, calculated 225.1121, found 225.1127.
8s (isomer 2): 9.8 mg (22% yield); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.36 – 6.27 (m, 2H), 5.02 (d, $J$ = 4.8 Hz, 2H), 4.18 (d, $J$ = 5.0 Hz, 1H), 3.95 (dd, $J$ = 11.5, 5.9 Hz, 1H), 3.78 (dd, $J$ = 11.5, 4.9 Hz, 1H), 3.07 – 3.00 (m, 1H), 2.78 (dd, $J$ = 15.4, 4.9 Hz, 1H), 2.38 (d, $J$ = 15.3 Hz, 1H), 1.29 (d, $J$ = 3.4 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 204.3, 134.8, 131.6, 85.5, 79.6, 78.4, 70.4, 61.6, 57.8, 45.9, 24.7, 18.9; IR (KBr) cm$^{-1}$ 3519w, 2961s, 2965s, 2854w, 1786m, 1728s, 1493m, 1462m, 1380w, 1363w, 1209s, 1188s, 1046s, 888s, 729s; HRMS: C$_{12}$H$_{16}$O$_4$ for [M+H]$^+$, calculated 225.1121, found 225.1127.

8t: 56 mg (76% yield); white solid; mp 138-139°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 – 7.60 (m, 2H), 7.34 – 7.25 (m, 4H), 7.05 – 7.00 (m, 1H), 6.96 – 6.91 (m, 2H), 5.95 – 5.91 (m, 2H), 5.01 (dt, $J$ = 4.5, 2.8 Hz, 2H), 4.87 – 4.84 (m, 1H), 3.01 (dd, $J$ = 16.0, 4.3 Hz, 1H), 2.53 (dd, $J$ = 16.0, 1.4 Hz, 1H), 2.41 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.6, 157.5, 144.3, 134.9, 134.9, 130.7, 129.9, 129.1, 127.6, 122.3, 115.6, 83.5, 62.4, 60.5, 46.4, 21.6; (KBr) cm$^{-1}$ 3064w, 2923w, 1734s, 1597s, 1494s, 1349s, 1238s, 1166s, 1099m, 1089s, 1006s, 921s, 815s, 755s, 679s, 544s; HRMS: C$_{20}$H$_{19}$NO$_4$S for [M+Na]$^+$, calculated 392.0927, found 392.0932.

17: 18 mg (39% yield); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 – 7.24 (m), 7.00 (t, $J$ = 7.4 Hz), 6.95 – 6.89 (m), 6.01 – 5.97 (m), 5.93 – 5.89 (m), 5.05 (d, $J$ = 4.7 Hz), 4.99 (d, $J$ = 4.9 Hz), 4.88 (t, $J$ = 4.8 Hz), 4.79 (d, $J$ = 4.8 Hz), 2.92 – 2.83 (m), 2.52 (dd, $J$ = 19.3, 15.4 Hz), 1.97 (s), 1.84 (s); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.4, 202.3, 158.0, 157.9, 154.5, 143.0, 129.6, 129.5, 127.7, 124.3, 122.0, 121.9, 115.7, 115.5, 83.6,
82.3, 81.6, 81.4, 79.7, 79.0, 46.6, 45.0, 14.2, 12.8; IR (KBr) cm⁻¹ 3068w, 2964w, 2915w, 1716s, 1597s, 1448m, 1332m, 1240s, 1088m, 1052m, 964s, 877s, 746s, 687s; HRMS: C_{14}H_{14}O_3 for [M+Na]^+, calculated 253.0835, found 253.0833.

syn-17 : anti-17 = 1.7 : 1;

S3: 21 mg (35% yield, mixture of isomers); yellow oil; \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.33 – 7.24 (m, 2H), 7.08 (d, \(J = 8.2\) Hz, 1H), 7.04 – 6.96 (m, 2H), 6.96 – 6.87 (m, 1H), 6.46 (d, \(J = 2.0\) Hz, 1H), 6.45 (d, \(J = 2.0\) Hz, 1H), 6.40 (dd, \(J = 20.0, 6.1, 1.6\) Hz, 1H), 5.14 (dd, \(J = 5.0, 1.7\) Hz, 1H), 5.11 – 5.07 (m, 1H), 5.04 – 4.96 (m, 2H), 4.92 (d, \(J = 5.0\) Hz, 1H), 2.94 – 2.85 (m, 1H), 2.61 – 2.45 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 202.0, 200.7, 157.9, 157.3, 135.2, 133.8, 131.4, 129.9, 129.5, 129.5, 122.2, 122.0, 115.8, 115.7, 83.3, 83.1, 81.8, 79.8, 79.3, 78.6, 45.9, 45.7; IR (neat) cm⁻¹ 3092w, 2952m, 2919w, 1723s, 1592s, 1488s, 1401m, 1312s, 1235s, 1122s, 1071m, 1038m, 970s, 881s, 774s, 684s, 503s; HRMS: C_{13}H_{11}BrO_3 for [M+Na]^+, calculated 316.9784, found 3316.9782.

syn-18: 27 mg (49% yield); white solid; mp 109-110°C; \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.28 (dd, \(J = 13.1, 5.3\) Hz, 3H), 7.20 (d, \(J = 1.5\) Hz, 1H), 7.01 (t, \(J = 7.3\) Hz, 1H), 6.95 (d, \(J = 8.4\) Hz, 2H), 5.41 (d, \(J = 5.0\) Hz, 1H), 5.19 (d, \(J = 5.3\) Hz, 1H), 4.99 (d, \(J = 5.0\) Hz, 1H), 3.74 (s, 3H), 3.01 (dd, \(J = 15.9, 5.4\) Hz, 1H), 2.60 (d, \(J = 15.9\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 200.7, 162.0, 157.8, 144.0, 138.6, 129.5, 122.2, 115.8, 82.8, 79.3, 78.2, 52.0, 45.3; IR (KBr) cm⁻¹ 3012w, 2958m, 2823m, 2854w, 1719s, 1590s,
1496s, 1448s, 1357s, 1230s, 1086s, 975s, 749s; HRMS: C_{15}H_{14}O_{5} for [M+Na]^+, calculated 297.0733, found 297.0723.

**anti-18**: 17 mg (31% yield); white solid; mp 109-110°C; ^1^H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.28 (dd, \(J = 13.9, 5.9\) Hz, 3H), 7.19 (d, \(J = 1.8\) Hz, 1H), 7.02 (t, \(J = 7.4\) Hz, 1H), 6.93 (d, \(J = 8.1\) Hz, 2H), 5.27 (dd, \(J = 8.9, 3.5\) Hz, 2H), 4.96 (d, \(J = 5.3\) Hz, 1H), 3.79 (s, 3H), 2.95 (dd, \(J = 15.8, 5.0\) Hz, 1H), 2.73 (d, \(J = 15.8\) Hz, 1H); ^13^C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 201.3, 162.3, 157.8, 141.0, 140.9, 129.6, 122.4, 115.7, 82.0, 80.4, 78.3, 52.2, 45.7; IR (KBr) cm\textsuperscript{-1} 3080m, 3015w, 2953w, 1717s, 1586s, 1489s, 1290s, 1225s, 1089s, 975s, 751s, 687s; HRMS: C_{15}H_{14}O_{5} for [M+Na]^+, calculated 297.0733, found 297.0723.

**syn-15**: anti-15 = 1.6 : 1.

**19**: 26 mg (37% yield); syn-19: white solid; mp 90-91°C; ^1^H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.42 – 7.32 (m, 5H), 7.28 (ddd, \(J = 8.1, 6.2, 2.5\) Hz, 2H), 7.22 (d, \(J = 2.0\) Hz, 1H), 7.01 (dd, \(J = 10.6, 4.1\) Hz, 1H), 6.95 – 6.89 (m, 1H), 5.30 – 5.14 (m, 4H), 4.95 (d, \(J = 5.4\) Hz, 1H), 2.94 (dd, \(J = 15.8, 5.0\) Hz, 1H), 2.74 (d, \(J = 15.8\) Hz, 1H); ^13^C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 201.3, 161.7, 157.8, 141.2, 141.1, 135.1, 129.6, 128.7, 128.6, 128.4, 122.4, 115.7, 81.9, 80.4, 78.3, 67.0, 60.4, 45.7; IR (neat) cm\textsuperscript{-1} 3034m, 2962m, 1728s, 1623m, 1591s, 1494s, 1459m, 1347w, 1291m, 1242m, 1101s, 976s, 752s, 693; HRMS: C_{21}H_{18}O_{5} for [M+Na]^+, calculated 373.1046, found 373.1052.

**anti-19**: 25 mg (36% yield); white solid; mp 97-98°C; ^1^H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.36 – 7.26 (m, 5H), 7.27 – 7.20 (m, 3H), 7.01 – 6.95 (m, 1H), 6.86 (dd, \(J = 8.6, 0.8\) Hz, 2H), 6.86 (dd, \(J = 8.6, 0.8\) Hz, 1H), 5.43 (d, \(J = 5.0\) Hz, 3H), 5.23 – 5.14 (m, 1H), 4.97 (d, \(J = 5.0\) Hz, 1H), 3.00 (dd, \(J = 15.9, 5.4\) Hz, 1H), 2.59 (d, \(J = 15.9\) Hz, 1H); ^13^C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 200.8, 161.4, 157.9, 144.5, 138.7, 135.3, 129.5, 128.6, 128.3, 122.2, 115.8, 82.9, 79.3, 78.3, 66.9, 45.3; IR (neat) cm\textsuperscript{-1} 2962m, 2924w, 1728s,
1627m, 1593s, 1496s, 1347m, 1291m, 1250s, 1188s, 975s, 753s, 693; HRMS: C_{21}H_{18}O_5 for [M+Na]^+, calculated 373.1046, found 373.1052.


\[
\text{syn-19:} \quad \begin{array}{c}
\text{PhO} - O - \text{CO}_2 \text{Bu} \\
\text{PhO} - O - \text{CO}_2 \text{Bu}
\end{array}
\]

\[
\text{anti-19:} \quad \begin{array}{c}
\text{PhO} - O - \text{CO}_2 \text{Bu} \\
\text{PhO} - O - \text{CO}_2 \text{Bu}
\end{array}
\]

syn-20: 19 mg (30% yield); white solid; mp 108-109°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.31 - 7.25 (m, 2H), 7.09 (d, J = 2.0 Hz, 1H), 7.02 - 6.98 (m, 1H), 6.98 - 6.93 (m, 2H), 5.39 (d, J = 5.0 Hz, 1H), 5.18 - 5.14 (m, 1H), 4.96 (d, J = 5.1 Hz, 1H), 2.99 (dd, J = 15.9, 5.4 Hz, 1H), 2.58 (d, J = 15.9 Hz, 1H), 1.39 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 200.8, 160.7, 157.9, 142.7, 140.5, 129.5, 121.9, 115.4, 82.4, 81.7, 79.2, 78.2, 60.4, 45.4, 27.9, 21.1, 14.2; IR (neat) cm\(^{-1}\) 3451m, 2979w, 1731s, 1594s, 1494s, 1394m, 1363s, 1221s, 1241s, 1107s, 967s, 754s, 691s; HRMS: C\(_{18}\)H\(_{20}\)O\(_5\) for [M+Na]^+, calculated 339.1203, found 339.1208.

anti-20: 28 mg (45% yield); white solid; mp 74-75°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.31 - 7.26 (m, 2H), 7.07 (d, J = 2.0 Hz, 1H), 7.04 - 6.99 (m, 1H), 6.96 - 6.91 (m, 2H), 5.24 (dd, J = 5.3, 2.0 Hz, 1H), 5.19 (dd, J = 5.0, 1.0 Hz, 1H), 4.95 (d, J = 5.3 Hz, 1H), 2.93 (dd, J = 15.7, 5.0 Hz, 1H), 2.72 (d, J = 15.7 Hz, 1H), 1.49 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 201.7, 161.3, 157.8, 155.9, 142.9, 139.6, 129.6, 129.6, 122.4, 120.5, 115.7, 115.3, 82.4, 82.0, 80.3, 78.4, 60.6, 45.7, 28.1, 21.1, 14.2; IR (neat) cm\(^{-1}\) 3451m, 2979w, 1731s, 1594s, 1494s, 1394m, 1363s, 1221s, 1241s, 1107s, 967s, 754s, 691s; HRMS: C\(_{18}\)H\(_{20}\)O\(_5\) for [M+Na]^+, calculated 339.1203, found 339.1208.

syn-20 : anti-20 = 1 : 1.5.

\[
\text{syn-20':} \quad \begin{array}{c}
\text{PhO} - O - \text{Me} \\
\text{PhO} - O - \text{Me}
\end{array}
\]

\[
\text{anti-20':} \quad \begin{array}{c}
\text{PhO} - O - \text{Me} \\
\text{PhO} - O - \text{Me}
\end{array}
\]

21: 19 mg (41% yield); yellow oil; syn-21', anti-21: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.32 - 7.23 (m), 7.15 - 7.09 (m), 7.03 - 6.96 (m), 6.96 - 6.90 (m), 6.42 (dd, J = 5.9, 1.7
Hz), 6.35 (dd, J = 5.9, 1.8 Hz), 6.18 (d, J = 5.9 Hz), 6.03 (d, J = 5.9 Hz), 5.13 (dd, J = 5.0, 1.8 Hz), 5.10 (dd, J = 3.1, 1.5 Hz), 4.89 (d, J = 5.0 Hz), 4.13 (s), 3.08 (dd, J = 5.9, 1.8 Hz), 2.72 (d, J = 15.2 Hz), 2.55 (d, J = 15.2 Hz), 2.33 (d, J = 15.5 Hz), 1.58 (s), 1.55 (s); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.9, 202.4, 158.6, 157.9, 138.2, 137.8, 133.1, 131.2, 129.5, 122.1, 121.9, 116.3, 115.6, 86.2, 85.4, 82.9, 82.1, 79.5, 78.3, 51.7, 44.2, 22.6, 18.3;

**syn-21**: $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 – 7.23 (m, 3H), 7.01 – 6.96 (m, 1H), 6.92 – 6.87 (m, 2H), 6.30 – 6.25 (m, 2H), 5.07 (dt, J = 5.0, 1.2 Hz, 1H), 4.59 (s, 1H), 2.90 (dd, J = 15.3, 5.0 Hz, 1H), 2.48 (d, J = 15.3 Hz, 1H), 1.59 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.9, 159.0, 134.7, 134.5, 129.4, 121.8, 115.7, 88.4, 86.8, 78.4, 45.7, 29.7, 20.2; IR (KBr) cm$^{-1}$ 2973w, 2931w, 1729s, 1596s, 1493w, 1338m, 1241s, 1174s, 1083s, 1019s, 961m, 853m, 827m, 753s, 691s; HRMS: C$_{14}$H$_{14}$O$_3$ for [M+Na]$^+$, calculated 253.0835, found 253.0834.

**syn-22**: $^{1}$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.36 – 7.29 (m), 7.10 – 7.01 (m), 6.98 – 6.93 (m), 6.58 (d, J = 5.9 Hz), 6.47 – 6.39 (m), 6.36 (dd, J = 5.9, 1.8 Hz), 5.23 (dd, J = 4.9, 1.1 Hz), 5.17 (dd, J = 5.0, 1.7 Hz), 5.11 (d, J = 4.9 Hz), 4.97 – 4.94 (m), 2.98 (dd, J = 16.1, 5.2 Hz), 2.91 (dd, J = 15.4, 4.9 Hz), 2.52 (dd, J = 15.8, 6.5 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.1, 199.9, 158.9, 157.9, 135.4, 135.2, 134.7, 131.4, 129.5, 122.7, 122.0, 116.6, 115.7, 94.2, 91.1, 83.3, 79.8, 79.3, 78.6, 45.9, 44.7; IR (KBr) cm$^{-1}$ 3102m, 2971m, 2919m, 1732s, 1592s, 1592s, 1491s, 1239s, 1174s, 1086s, 1039m, 934s, 817s, 742s; HRMS: C$_{13}$H$_{11}$BrO$_3$ for [M+Na]$^+$, calculated 316.9784, found 316.9786.

**syn-22** : **anti-22**: syn-22$^\prime$ = 4 : 1 : 1.
**syn-23:** 39 mg (71% yield); yellow solid; mp 105-106°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29 – 7.23 (m, 2H), 7.00 (t, $J = 7.4$ Hz, 1H), 6.91 (d, $J = 7.9$ Hz, 2H), 6.60 (d, $J = 6.0$ Hz, 1H), 6.45 (dd, $J = 6.0$, 1.7 Hz, 1H), 5.20 (d, $J = 5.0$ Hz, 1H), 5.07 (s, 1H), 3.75 (s, 3H), 2.97 (dd, $J = 15.7$, 5.0 Hz, 1H), 2.45 (d, $J = 15.7$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.3, 167.9, 158.5, 136.1, 130.4, 129.5, 122.5, 116.2, 88.2, 85.4, 79.5, 53.0, 45.3; IR (KBr) cm$^{-1}$ 3095w, 3062w, 2967m, 2949m, 2916m, 1759s, 1592s, 1485s, 1480s, 1279m, 1059s, 964s, 842s, 732s; HRMS: C$_{15}$H$_{14}$O$_5$ for [M+Na]$^+$, calculated 297.0733, found 297.0723.

**syn-24:** 20 mg (32% yield); colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28 – 7.22 (m, 2H), 7.00 – 6.95 (m, 1H), 6.92 – 6.88 (m, 2H), 6.55 (d, $J = 6.0$ Hz, 1H), 6.41 (dd, $J = 6.0$, 1.7 Hz, 1H), 5.18 (d, $J = 5.1$ Hz, 1H), 5.08 (s, 1H), 2.96 (dd, $J = 15.6$, 5.0 Hz, 1H), 2.51 (d, $J = 15.6$ Hz, 1H), 1.37 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 200.9, 167.6, 157.8, 155.8, 134.8, 132.5, 129.7, 129.6, 122.3, 120.6, 115.6, 115.4, 87.3, 83.7, 81.9, 79.9, 48.3, 27.9; IR (neat) cm$^{-1}$ 3703m, 2980w, 1733s, 1599s, 1493m, 1394s, 1399m, 1296s, 1155s, 1130s, 1078s, 815s, 692s; HRMS: C$_{18}$H$_{20}$O$_5$ for [M+Na]$^+$, calculated 339.1203, found 339.1208.

**anti-24:** 20 mg (32% yield); white solid; mp 106-107°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27 – 7.22 (m, 2H), 7.00 – 6.95 (m, 1H), 6.92 – 6.88 (m, 2H), 6.55 (d, $J = 6.0$ Hz, 1H), 6.41 (dd, $J = 6.0$, 1.7 Hz, 1H), 5.18 (d, $J = 5.1$ Hz, 1H), 5.08 (s, 1H), 2.96 (dd, $J = 15.6$, 5.0 Hz, 1H), 2.51 (d, $J = 15.6$ Hz, 1H), 1.37 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.9, 166.4, 158.6, 135.8, 130.9, 129.4, 122.2, 115.8, 89.0, 85.3, 83.4, 79.6, 45.3, 27.7; IR (neat) cm$^{-1}$ 3674m, 2979w, 1735s, 1599s, 1493s, 1370m, 1333s, 1291s, 1239s,
1165m, 1123m, 970m, 843m, 754m, 691m; HRMS: C_{18}H_{20}O_5 for [M+Na]^+, calculated 339.1203, found 339.1208.


**REMOVAL OF ARYL GROUPS ON CYCLOADDUCTS**

![Chemical structure](image)

To a solution of 8l (60 mg, 0.23 mmol) in CH₃CN/H₂O (1.8:1, 1.2 mL) was added Ce(NH₄)₂(NO₃)₆ (315 mg, 0.58 mmol, 2.5 equiv) at 0°C. The reaction was stirred for 30 min before being quenched by sat aq NH₄Cl. The mixture was extracted three times with EtOAc. The combined organic layers were washed with equal volume of sat aq NaCl and dried over anhyd MgSO₄. After filtration and concentration under reduced pressure, the crude product was purified using silica gel flash column chromatography [eluent: 20% EtOAc/Hexane] to give the desired 25 (19 mg, 56% yield).

![Chemical structure](image)

The benzyl ether 8o (50 mg, 0.22 mmol) and 10% Pd/C (80 mg) were refluxed in methanol (2.5 ml) for 2 h under hydrogen atmosphere. The reaction mixture was allowed to cool to rt and the catalyst was filtered through Celite™. The catalyst was washed with methanol (2 × 5 mL). The crude product obtained was purified by column chromatography [eluent: 20% EtOAc/Hexane] to get 25 (20 mg, 66% yield).
To a solution of 8p (50 mg, 0.19 mmol) in THF/H$_2$O (1.0 mL) was added DDQ (109 mg, 0.48 mmol, 2.5 equiv) at rt. The reaction was stirred for 4 h before being quenched with sat aq NH$_4$Cl. The mixture was extracted three times with EtOAc. The combined organic layers were washed with equal volume of sat aq NaCl and dried over anhyd MgSO$_4$. After filtration and concentration under reduced pressure, the crude product was purified using silica gel flash column chromatography [eluent: 20% EtOAc/Hexane] to give the desired 25 (20 mg, 74% yield).

25: yellow oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 6.32 (qd, $J = 6.1$, 1.4 Hz, 2H), 5.16 – 5.02 (m, 2H), 4.39 (dd, $J = 5.2$, 2.9 Hz, 1H), 3.55 (d, $J = 3.0$ Hz, 1H), 2.91 (dd, $J = 15.0$, 5.0 Hz, 1H), 2.50 (d, $J = 15.0$ Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 206.4, 134.6, 131.8, 80.7, 78.9, 78.5, 45.0; IR (KBr) cm$^{-1}$ 3363s, 2962w, 2862w, 1706s, 1490m, 1420m, 1277m, 1172s, 1142m, 1110s, 1086s, 1037s, 961s, 882s, 842s, 824s, 729s, 592s, 482s; HRMS: C$_7$H$_8$O$_3$ for [M+Na]$^+$, calculated 163.0366, found 163.0367.

**SYNTHESIS OF TETRACYCLIC COMPOUND 26.**

To a solution of 8f (200 mg, 0.68 mmol) in THF (15.8 mL) was added $t$-BuLi (1.3 M solution in THF, 1.3 mL, 1.70 mmol, 2.5 equiv) at $-78$ °C. The reaction was stirred at $-78$ °C for 30 min before being quenched with sat aq NH$_4$Cl. The mixture was extracted three times with EtOAc. The combined organic layers were washed with equal volume
of sat aq NaCl and dried over anhyd MgSO₄. After filtration and concentration under reduced pressure, the crude product was purified using silica gel flash column chromatography [eluent: 20% EtOAc/Hexane] to give compound 26 (91 mg, 62% yield).

26: 91 mg (62% yield); yellow solid; mp 138-139°C; ¹H NMR (600 MHz, CDCl₃) δ 7.25 (t, J = 7.7 Hz, 1H), 7.15 (d, J = 7.4 Hz, 1H), 6.94 (t, J = 7.4 Hz, 1H), 6.84 (d, J = 8.1 Hz, 1H), 5.77 – 5.72 (m, 2H), 4.97 (d, J = 5.8 Hz, 1H), 4.95 – 4.92 (m, 1H), 4.68 (d, J = 5.8 Hz, 1H), 2.48 – 2.40 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 159.1, 133.8, 133.2, 130.6, 129.3, 121.6, 121.3, 110.5, 86.3, 78.0, 77.8, 34.5; IR (KBr) cm⁻¹ 3007w, 2987w, 2942w, 2857w, 2845w, 1711s, 1613m, 1515s, 1467m, 1327m, 1242s, 1181s, 1112s, 1029s, 963s, 887m, 848s, 824s, 728m, 619m, 521m; HRMS: C₁₃H₁₂O₄ for [M+Na]⁺, calculated 239.0679, found 239.0680.

THE SYNTHESIS OF CYCLOHEPTA[b]BENZOFURAN 27.

To a solution of 26 (37 mg, 0.17 mmol) in THF (2.0 mL) was added t-BuOK (1.0M solution in THF, 0.34 mL, 0.34 mmol, 2.0 equiv) solution at 0°C. After stirred at rt for 30 min, CS₂ (0.02 mL, 0.34 mmol, 2.0 equiv) was added. The reaction was stirred at rt for an additional 30 min. After the reaction was complete, the reaction was quenched using sat aq NH₄Cl. The aqueous phase was extracted three times with Et₂O, and the combined organic layers were washed with H₂O and sat aq NaCl, and dried over anhyd MgSO₄. After filtration and concentration under reduced pressure, the crude product was purified using silica gel flash column chromatography [eluent: 20% EtOAc/Hexane] to give the desired cyclohepta[b]benzofuran 27 (26 mg, 76% yield).
27: 26 mg (76% yield); yellow solid; mp 91-92°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 – 7.40 (m, 1H), 7.38 (dt, $J = 6.7$, 2.6 Hz, 1H), 7.23 – 7.16 (m, 2H), 6.63 (d, $J = 5.2$ Hz, 1H), 6.05 (dd, $J = 5.9$, 1.7 Hz, 1H), 5.43 (s, 1H), 5.22 (dd, $J = 5.9$, 1.3 Hz, 1H), 3.27 (dd, $J = 16.4$, 5.9 Hz, 1H), 2.40 (d, $J = 16.4$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.1, 153.9, 137.1, 128.7, 128.4, 123.2, 122.7, 118.3, 111.3, 106.1, 78.2, 75.6, 24.5; IR (KBr) cm$^{-1}$ 2963w, 2924w, 1443m, 1241m, 1121m, 1025s, 939s, 839s, 755s; HRMS: C$_{13}$H$_{10}$O$_2$ for [M+H]$^+$, calculated 199.0754, found 199.0747.
CRYSTALLOGRAPHIC DATA OF 8d (CCDC 1915744)

Supplementary Fig. 1  X-ray structure of 8d (dimer in a unit cell).

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Index ranges
-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -15 ≤ l ≤ 16

Reflections collected
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Independent reflections
4642 [R(int) = 0.0388 (inf-0.9 Å)]

Data/restraints/parameters
4642/0/307

Goodness-of-fit on F^2
1.021

Final R indexes [I>2σ (I) i.e. F_o>4σ (F_o)]
R_1 = 0.0446, wR_2 = 0.0825

Final R indexes [all data]
R_1 = 0.0715, wR_2 = 0.0932

Largest diff. peak/hole / e Å^-3
0.396/-0.851

Flack Parameters
N

Completeness
0.9979
DETAILED STUDIES OF REACTION CONDITIONS AND REACTION SCOPE

Study of other oxidants

In the beginning of our study of the allenyl ether (4 + 3) cycloaddition, the performance of other oxidants instead of DMDO was also investigated. While \( m \)-CPBA can carry out the reaction of \( 5b \) and furan to provide the cycloadduct with a slightly lower yield than that of DMSO, the Davis reagent gave a mixture of side products.

Supplementary Table 1. Survey of different oxidants

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<th>Entry</th>
<th>Oxidant</th>
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<th>Yield (%)</th>
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<td>2</td>
<td>( m )-CPBA</td>
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<td>3</td>
<td>Davis reagent</td>
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\(^a\)All reactions are carried out with 0.2 mmol \( 5b \), 0.4 mmol furan, 0.4 mmol \( \text{ZnCl}_2 \), and 0.6 mmol of the indicated oxidant. \(^b\)Isolated yields.
### Detailed optimization results of the cycloaddition of 5b with furan

**Supplementary Table 2. Optimization of (4 + 3) cycloaddition conditions**

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<th>Yield (%)</th>
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<th>Additive</th>
<th>solvent</th>
<th>Temp (°C)</th>
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*a* All reactions are carried out with 0.2 mmol 5b, 0.4 mmol furan, 0.6 mmol DMDO (as a solution in CH₂Cl₂, added by syringe pump within 1 hour), and 0.4 mmol of the indicated additive. *b* Isolated yields.
**Comparison study of (4 + 3) cycloaddition.**

**Supplementary Table 3.** Comparison study using 5b and 10.

![Chemical structure](image1)

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<th>Entry</th>
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<th>Yield(%)</th>
<th>Ratio (syn : anti)</th>
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<td>1:1</td>
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*Reactions are carried out with 0.2 mmol 5b, 0.4 mmol 10, 0.6 mmol DMDO (as a solution in CH₂Cl₂, added by syringe pump within 1 hour), and 0.4 mmol of the indicated additive. *Isolated yields.

**Supplementary Table 4.** Comparison study using 5b and 15.

![Chemical structure](image2)

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<tr>
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<td>MgBr₂</td>
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</tbody>
</table>

*Reactions are carried out with 0.2 mmol 5b, 0.4 mmol 15, 0.6 mmol DMDO (as a solution in CH₂Cl₂, added by syringe pump within 1 hour), and 0.4 mmol of the indicated additive. *Isolated yields.
Study of Reaction Scope

Some additional attempts are summarized in Supplementary Table 5. As mentioned in the main text, aliphatic allenyl ethers (except methoxyallene) couldn’t give desired cycloadducts (Entry 1, 2). Although prenyloxyallene worked well in the cycloaddition, allyloxyallene didn’t undergo the cycloaddition process (Entry 3), perhaps due to the competitive epoxidation reaction at the allyl group. Methyl-substituted allenyl ether couldn’t provide the cycloadduct either (Entry 4). Entry 5-9 in the table showed the reactions of 5b with a variety of dienes. It is surprised that methyl 3-methyl 2-furoate (Entry 9) didn’t work. However, according to the transition states shown in Supplementary Fig. 4, the 3-methyl group on the diene may interrupt the interaction between $\text{H}_3\text{PO}_4^-$ and the allyl cation by steric effect (similar case with 3-Br furan).

**Supplementary Table 5. Additional substrate scope**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Allenyl Ether</th>
<th>Diene</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$n$-Bu-O</td>
<td><img src="image1" alt="Diene 1" /></td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>i-Pr-O</td>
<td><img src="image1" alt="Diene 1" /></td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>allyl-O</td>
<td><img src="image1" alt="Diene 1" /></td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Ph-O</td>
<td><img src="image1" alt="Diene 1" /></td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Ph-O</td>
<td><img src="image1" alt="Diene 2" /></td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Ph-O</td>
<td><img src="image1" alt="Diene 3" /></td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>Ph-O</td>
<td><img src="image1" alt="Diene 4" /></td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>Ph-O</td>
<td><img src="image1" alt="Diene 4" /></td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>Ph-O</td>
<td><img src="image1" alt="Diene 5" /></td>
<td>-</td>
</tr>
</tbody>
</table>
COMPUTATIONAL METHODOLOGY

DFT calculations were performed using the ORCA 4.0 suit of program. All molecules were built using the Avogadro software. Transition structures (TSs) were first guessed using the semi-empirical method PM6 of MOPAC 2016 prior to DFT optimization by ORCA. Each TS without counterion was first determined, followed by the same calculations with the addition of a K⁺ ion. The nature of each stationary point was characterized using frequency calculation. TS were further validated by IRC calculations. Geometry optimizations and free-energy calculations were performed at the B3LYP-D3/6-31+G(d,p) level of theory. Solvation by CH₂Cl₂ (ε = 8.93) was accounted for using the conductor-like polarizable continuum model (CPCM). UCSF Chimera (version 1.12) was used for the visualization of geometries and orbitals. The coordinate files of TSs and stable structures 5b, 10 and 15 were provided separately (in “xyz” format).

Supplementary Fig. 2 Optimized structures, HOMOs and partial ChelpG partial atomic charges of (A) 7b, and (B) allenamide-oxyallyl. Distances are in Å. Orbitals were computed at HF/6-31+G(d,p)//B3LYP-D3/6-31+G(d,p) level of theory. The values of the aryloxyl oxygen and allenamide nitrogen are underlined and highlighted in red. The optimized geometries and the HOMOs for 7a, 7c, and 7l are similar to that of 7b.
Supplementary Fig. 3 ChelpG^9 partial atomic charges of 7a, 7b, 7c, 7l, 7o and 7p. The values of the alkoxy, aryloxyl or benzyloxyl oxygen (presumably forming two hydrogen bonds with H_2PO_4^-) are underlined and highlighted in red.
Supplementary Fig. 4 Proposed transition structures leading to cycloadducts 18 and 23. $\Delta G^\ddagger$ in kcal/mol at 298.15 K. Distances in Å (those of HBs underlined). C: grey, H: white, O: red, P: orange, K: purple.
**Supplementary Table 6.** Free energies (in Hatrees) and number of imaginary frequencies of the calculated structures.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Energy (Eh)</th>
<th>Imaginary Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>5b</td>
<td>−497.77783812</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>−457.61619023</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>−457.61545818</td>
<td>0</td>
</tr>
<tr>
<td>KH$_2$PO$_4$</td>
<td>−1243.33978196</td>
<td>0</td>
</tr>
<tr>
<td>TS-18-<em>syn</em></td>
<td>−2198.71488128</td>
<td>1</td>
</tr>
<tr>
<td>TS-18-<em>anti</em></td>
<td>−2198.71474498</td>
<td>1</td>
</tr>
<tr>
<td>TS-23-<em>syn</em></td>
<td>−2198.71384410</td>
<td>1</td>
</tr>
<tr>
<td>TS-23-<em>anti</em></td>
<td>−2198.71169422</td>
<td>1</td>
</tr>
</tbody>
</table>
REFERENCES


(3) Frank, N., Software update: the ORCA program system, version 4.0. Wiley Interdisciplinary Reviews: Computational Molecular Science 2018, 8 (1), e1327.


