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

authored by

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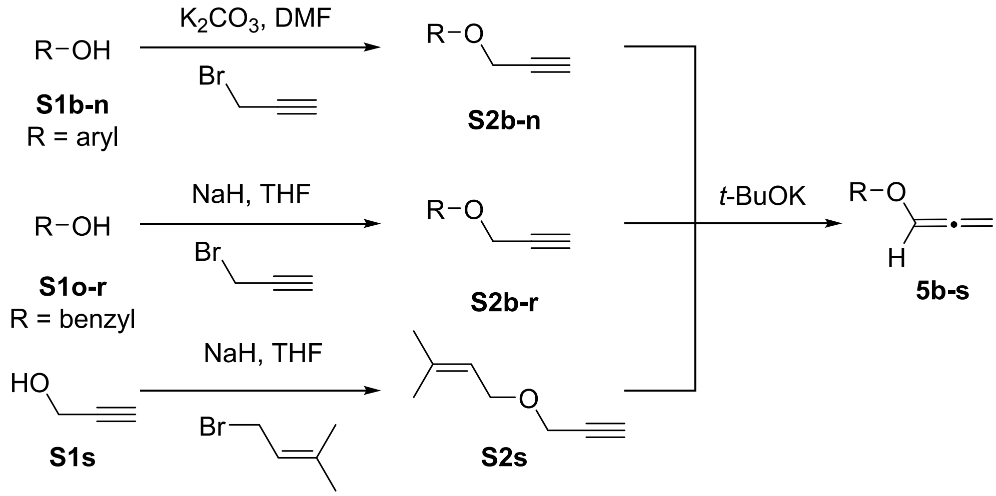
GENERAL EXPERIMENTAL INFROMATION.

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-anisoladehyde 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]



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_2O. 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).

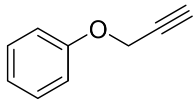
General procedure for Synthesis of S2o-r Using S2o as an Example.

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 NH_4Cl. The quenched mixture was poured into H_2O and 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 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 NH_4Cl. The quenched mixture was extracted three times with Et_2O. 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 prenyl propargyl ether **S2s** (1.50 g, 68% yield).

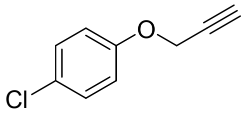
CHARACTERIZATIONS OF ARYL PROPARGYL ETHERS S2b-s.



S2b

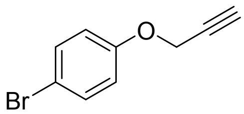
S2b: 1.24 g (88% yield); yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.10 – 7.02 (m, 3H), 4.75 (d, J = 2.4 Hz, 2H), 2.57 (t, J = 2.4 Hz, 1H); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 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_9H_8O for $[M+H]^+$, calculated 133.0648, found 133.0647.



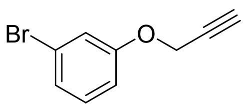
S2c

S2c: 1.17 g (90% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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_9H_7ClO for $[M+H]^+$, calculated 167.0258, found 167.0259.



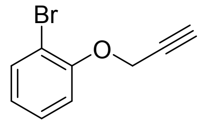
S2d

S2d: 0.80 g (66% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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_9H_7BrO for $[M-H]^+$, calculated 210.9759, found 211.0937.



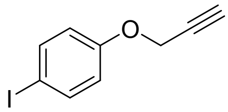
S2e

S2e: 0.80 g (66% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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_9H_7BrO for $[M+H]^+$, calculated 210.9753, found 210.9756.



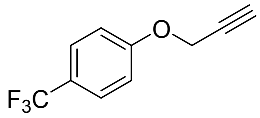
S2f

S2f: 0.84 g (69% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 154.0, 133.6, 128.4, 122.9, 114.2, 112.5, 78.0, 76.2, 56.9; IR (KBr) cm^{-1} 3288s, 3065m, 2916m, 2862m, 1589s, 1574s, 1476s, 1446s, 1279s, 1229s, 1050s, 1018s, 922s, 756s; HRMS: C_9H_7BrO for $[M+H]^+$, calculated 210.9680, found 210.9584.



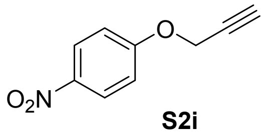
S2g

S2g: 1.02 g (87% yield); white solid; mp 40-41°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 157.4, 138.3, 117.4, 84.0, 78.1, 76.0, 55.9; IR (KBr) cm^{-1} 3274m, 3089m, 3069m, 2129m, 1509m, 1563m, 1480s, 1277s, 1019s, 817s, 793m; HRMS: C_9H_7IO for $[M+H]^+$, calculated 257.9536, found 257.9538.



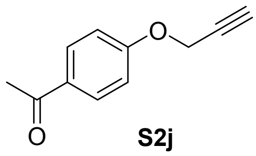
S2h

S2h: 1.06 g (86% yield); yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 159.9, 126.9, 126.9, 114.9, 77.8, 76.2, 55.8; IR (KBr) cm^{-1} 3303s, 1613m, 1589m, 1512s, 1419w, 1300s, 1229m, 1175m, 1157m, 1107s, 1068m, 836s; HRMS: $C_{10}H_7F_3O$ for $[M+Na]^+$, calculated 223.0347, found 223.0935.



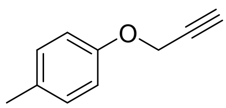
S2i

S2i: 1.00 g (80% yield); yellow solid; mp 103-104°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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: $C_9H_7NO_3$ for $[M+Na]^+$, calculated 200.0318, found 200.0316.



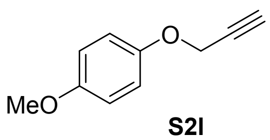
S2j

S2j: 1.09 g (85% yield); white solid; mp 68-69°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.



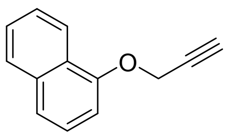
S2k

S2k: 1.26 g (93% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.



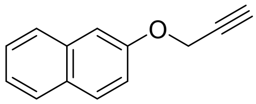
S2l

S2l: 1.05 g (80% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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: $C_{10}H_{10}O_2$ for $[M+H]^+$, calculated 163.0754, found 163.0754.



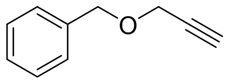
S2m

S2m: 0.77 g (60% yield); yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, 2913m, 2862m, 1622m, 1580m, 1503m, 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.



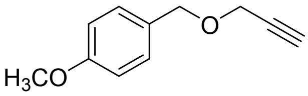
S2n

S2n: 0.71 g (56% yield); white solid; mp 54-55°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.



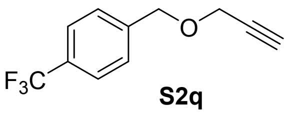
S2o

S2o: 0.90 g (67% yield); yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.



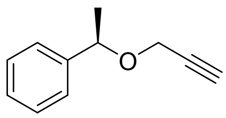
S2p

S2p: 0.99 g (78% yield); yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.



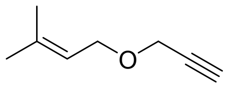
S2q

S2q: 0.90 g (75% yield); yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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: $C_{11}H_9F_3O$ for $[M-H]^+$, calculated 213.0533, found 213.0532.



S2r

S2r: 0.85 g (65% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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 × 10^{-3} g/mL, MeOH).



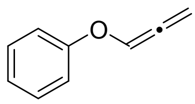
S2s

S2s: 1.5g (68% yield); brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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: $C_8H_{12}O$ for $[M+H]^+$, calculated 125.0961, found 125.0966.

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

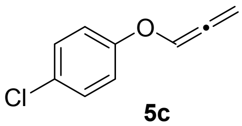
To a solution of **S2b** (1.00 g, 7.57 mmol) in THF (38 mL) was added *t*-BuOK (1.0 *M* solution in THF, 2.27 mL, 2.27 mmol, 0.30 equiv) at 0°C. The reaction was stirred at rt for 1 h before being concentrated under reduced pressure. Subsequently, the residue was first suspended in Et_2O and then filtered 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.



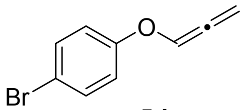
5b

5b: 1.30 g (91% yield); yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, 1009m, 988m, 884s, 750s; HRMS: C_9H_8O for $[M+H]^+$, calculated 133.0648, found 133.0649.



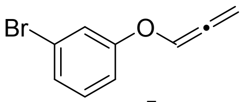
5c

5c: 1.23 g (95% yield); yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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_9H_7ClO for $[M+H]^+$, calculated 167.0264, found 167.0279.



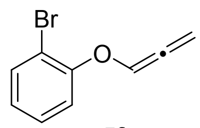
5d

5d: 1.09 g (89% yield); yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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_9H_7BrO for $[M+H]^+$, calculated 210.9753, found 210.9745.



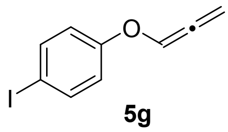
5e

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_9H_7BrO for $[M+H]^+$, calculated 210.9753, found 210.9580.



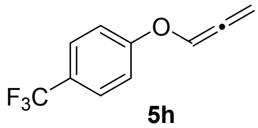
5f

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_9H_7BrO for $[M+H]^+$, calculated 210.9759, found 211.0247.



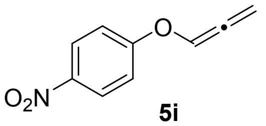
5g

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_9H_7IO for $[M-H]^+$, calculated 256.9469, found 256.9467.



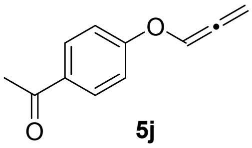
5h

5h: 1.10 g (89% yield); yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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: $C_{10}H_7F_3O$ for $[M+H]^+$, calculated 201.0522, found 201.0529.



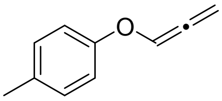
5i

5i: 1.08 g (85% yield); yellow solid; mp 92-93°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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: $C_9H_7NO_3$ for $[M+H]^+$, calculated 178.0497, found 178.0500.



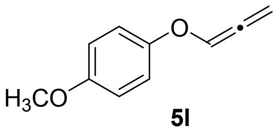
5j

5j: 1.11 g (87% yield); white solid; mp 63-64°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.



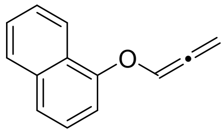
5k

5k: 1.10 g (82% yield); yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.



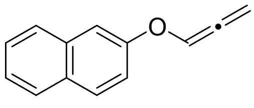
5l

5l: 1.12 g (86% yield); yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, 818s, 759s; HRMS: $C_{10}H_{10}O_2$ for $[M+H]^+$, calculated 163.0754, found 163.0753.



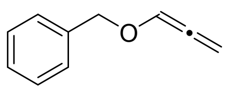
5m

5m: 0.57 g (45% yield); colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.



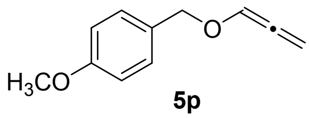
5n

5n: 0.62 g (49% yield); white solid; mp 57-58°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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); ^{13}C NMR (150 MHz, $CDCl_3$) δ 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, 2917w, 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.



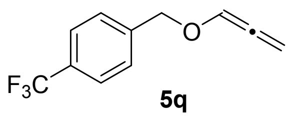
5o

5o: 1.09 g (81% yield); yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.



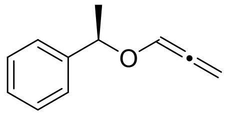
5p

5p: 1.10 g (86% yield); colorless oil; ^1H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, 1953m, 1723s, 1613s, 1514s, 1442m, 1302m, 1249s, 1173s, 1111w, 1035s, 821s; HRMS: $C_{11}H_{12}O_2$ for $[M+K]^+$, calculated 215.0474, found 215.0559.



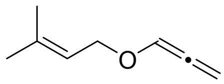
5q

5q: 0.97 g (80% yield); yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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: $C_{11}H_9F_3O$ for $[M-H]^+$, calculated 213.0533, found 213.0523.



5r

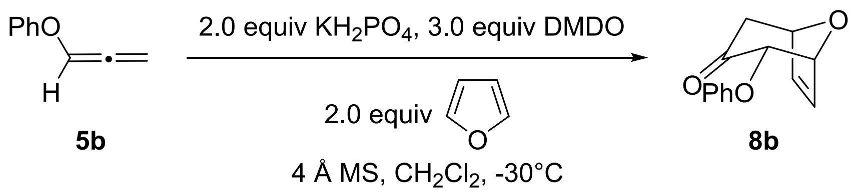
5r: 0.64 g (64% yield); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (ddd, *J* = 6.6, 4.6, 1.9 Hz, 5H), 6.97 – 6.55 (m, 1H), 5.52 – 5.44 (m, 1H), 5.39 – 5.32 (m, 1H), 5.01 – 4.93 (m, 1H), 1.78 – 1.55 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 143.4, 128.5, 127.6, 126.2, 120.4, 90.2, 76.8, 23.5; 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 × 10^{-3} g/mL, MeOH).



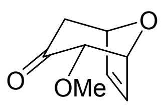
5s

5s: 0.66g (66% yield); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 6.73 (t, *J* = 5.9 Hz, 1H), 5.43 (d, *J* = 5.9 Hz, 1H), 5.40 (dddd, *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, $CDCl_3$) δ 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: $C_8H_{12}O$ for $[M+H]^+$, calculated 125.0961, found 125.0966.

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

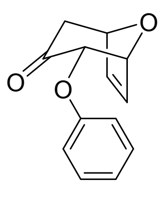


To a solution of allenyl ether **5b** (26 mg, 0.2 mmol) in CH_2Cl_2 (4 mL) containing anhyd 4Å MS were added KH_2PO_4 (54 mg, 0.40 mmol, 2.0 equiv) and furan (27 mg, 0.40 mmol, 2.0 equiv) at –30 °C. After which, a dry-ice chilled solution of DMDO (7.5 mL, 0.08 *M* solution in CH_2Cl_2,[2] 3.0 equiv) 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).



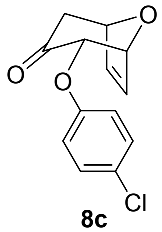
8a

8a: 16 mg (52% yield); yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 204.6, 134.7, 131.5, 86.9, 79.2, 78.4, 59.7, 45.9; IR (KBr) cm^{-1} 3261w, 2967w, 1750s, 1434s, 1338m, 1260m, 1116s, 1061m, 1020m, 962s, 848m, 729s; HRMS: $C_8H_{10}O_3$ for $[M+H]^+$, calculated 155.0703, found 155.0702.



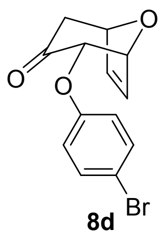
8b

8b: 35 mg (81% yield); white solid; mp 52-53°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.



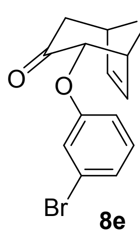
8c

8c: 36 mg (72% yield); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.



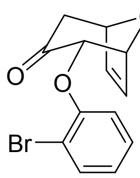
8d

8d: 40 mg (68% yield); white solid; mp 67-68°C; ^1H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.



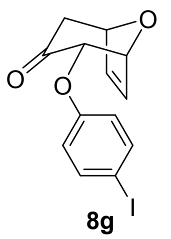
8e

8e: 32 mg (54% yield); white solid; mp 66-67°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 201.6, 158.7, 135.4, 131.2, 130.6, 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.



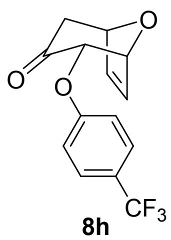
8f

8f: 34 mg (57% yield); white solid; mp 54-55°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.



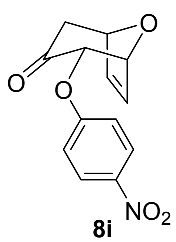
8g

8g: 38 mg (55% yield); white solid; mp 42-43°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.



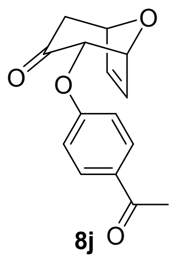
8h

8h: 46 mg (81% yield); yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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: $C_{14}H_{11}F_3O_3$ for $[M+Na]^+$, calculated 307,0552, found 307.0537.



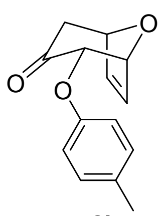
8i

8i: 42 mg (80% yield); yellow solid; mp 114-115°C; ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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: $C_{13}H_{11}NO_5$ for $[M\text{-}H]^+$, calculated 260.0564, found 260.0564.



8j

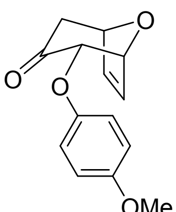
8j: 38 mg (74% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 2H), 6.97 – 6.89 (m, 2H), 6.42 (qd, *J* = 6.0, 1.5 Hz, 2H), 5.16 (dd, *J* = 5.0, 1.6 Hz, 1H), 5.14 – 5.10 (m, 1H), 5.02 (d, *J* = 5.0 Hz, 1H), 2.92 (dd, *J* = 15.4, 5.0 Hz, 1H), 2.55 (s, 3H), 2.51 (d, *J* = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 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: $C_{15}H_{14}O_4$ for $[M+Na]^+$, calculated 281.0784, found 281.0776.



8k

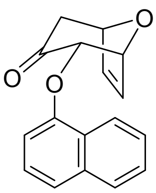
8k: 28 mg (61% yield); yellow solid; mp 56-57°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.2 Hz, 2H), 6.86 – 6.81 (m, 2H), 6.39 (ddd, *J* = 20.2, 6.1, 1.6 Hz, 2H), 5.13 (dd, *J* = 5.0, 1.7 Hz, 1H), 5.08 (d, *J* = 4.9 Hz, 1H), 4.86 (d, *J* = 5.0 Hz, 1H), 2.87 (dd, *J* = 15.4, 4.9 Hz, 1H), 2.48 (d, *J* = 15.4 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 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.



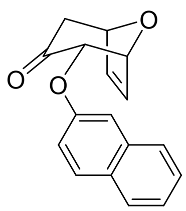
8l

8l: 23 mg (47% yield); yellow oil; ^{1}H 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); ^{13}C 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, 2918m, 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.



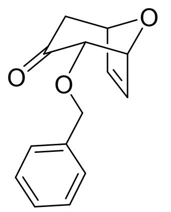
8m

8m: 24 mg (45% yield); white solid; mp 75-76°C; ^{1}H 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); ^{13}C 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.



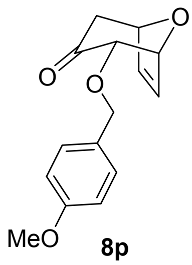
8n

8n: 23 mg (43% yield); white solid; mp 112-113°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, 1726s, 1269s, 1596s, 1510s, 1360s, 1252s, 1171s, 1072s, 962s, 832, 738s; HRMS: $C_{17}H_{14}O_3$ for $[M+Na]^+$, calculated 289.0835, found 289.0821.



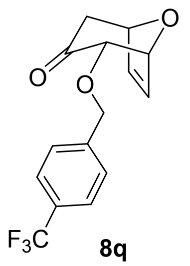
8o

8o: 21 mg (46% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, 2964m, 2932m, 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.



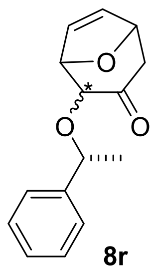
8p

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, 1513s, 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

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: $C_{15}H_{13}F_3O_3$ for $[M+H]^+$, calculated 299.0890, found 299.1618.

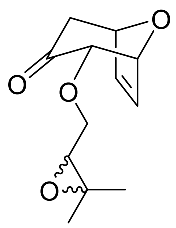


8r

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, 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, 2927w, 2856w, 1722s, 1417m, 1339w, 1215s, 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_2Cl_2)

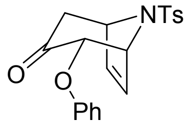
8r (isomer 2): 9 mg (18% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 5.1, 3.5 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.24 – 7.20 (m, 1H), 6.27 (ddd, J = 31.1, 6.1, 1.6 Hz, 1H), 4.99 (dd, J = 4.8, 1.7 Hz, 1H), 4.90 (dd, J = 3.8, 1.1 Hz, 1H), 4.69 (q, J = 6.4 Hz, 1H), 4.00 (d, J = 4.9 Hz, 1H), 2.58 (dd, 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_2Cl_2)



8s

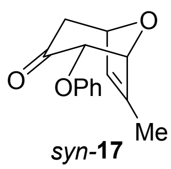
8s (isomer 1): 9.8 mg (22% yield); yellow solid; mp 68-69°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 (ddd, J = 15.4, 6.1, 1.5 Hz, 2H), 5.06 (dd, J = 5.1, 1.6 Hz, 1H), 5.02 (d, J = 4.9 Hz, 1H), 4.26 – 4.13 (m, 2H), 3.57 (dd, J = 11.4, 6.9 Hz, 1H), 3.02 (dd, J = 6.8, 3.6 Hz, 1H), 2.78 (dd, J = 15.4, 4.9 Hz, 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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.

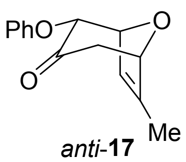


8t

8t: 56 mg (76% yield); white solid; mp 138-139°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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: $C_{20}H_{19}NO_4S$ for $[M+Na]^+$, calculated 392.0927, found 392.0932.



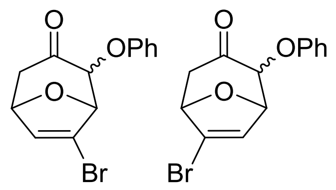
syn-**17**



anti-**17**

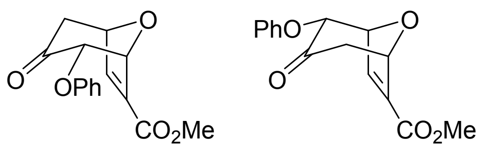
17: 18 mg (39% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m), 7.00 (t, *J* = 7.4 Hz), 6.95 – 6.89 (m), 6.01 – 5.97 (m), 5.93 – 5.89 (m), 5.05 (d, *J* = 4.7 Hz), 4.99 (d, *J* = 4.9 Hz), 4.88 (t, *J* = 4.8 Hz), 4.79 (d, *J* = 4.8 Hz), 2.92 – 2.83 (m), 2.52 (dd, *J* = 19.3, 15.4 Hz), 1.97 (s), 1.84 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 202.3, 158.0, 157.9, 145.6, 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, 1493s, 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

S3: 21 mg (35% yield, mixture of isomers); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 (ddd, *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, CDC_{l3}) δ 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, 1321s, 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.

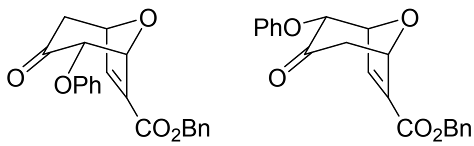


syn-**18** *anti*-**18**

syn-**18:** 27 mg (49% yield); white solid; mp 109-110°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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; ^1H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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^{-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 297.0719.

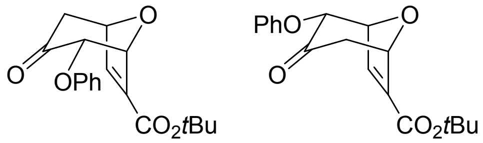
syn-**15** : *anti*-**15** = 1.6 ： 1.


syn-**19** *anti*-**19**

19: 26 mg (37% yield); *syn*-**19:** white solid; mp 90-91°C; ^1H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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^{-1} 3034m, 2962m, 2924w, 1730s, 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; ^1H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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^{-1} 2962m, 2924w, 1728s, 1627m, 1593s, 1494s, 1456m, 1347w, 1291m, 1250s, 1188s, 975s, 753s, 693; HRMS: $C_{21}H_{18}O_5$ for $[M+Na]^+$, calculated 373.1046, found 373.1052.

syn-**19** : *anti*-**19** = 1 : 1.

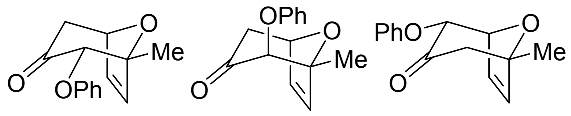


syn-**20** *anti*-**20**

syn-**20:** 19 mg (30% yield); white solid; mp 108-109°C; ^1H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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; ^1H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.



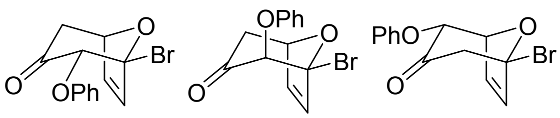
syn-**21** *syn*-**21'** *anti*-**21**

21: 19 mg (41% yield); yellow oil; *syn*-**21**’, *anti*-**21:** ^1H NMR (400 MHz, $CDCl_3$) δ 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 = 15.5, 4.6 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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, 1493s, 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.

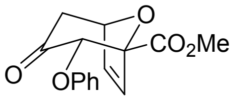
syn-**21** : *syn*-**21'** : *anti*-**21** = 2 : 1 : 3.



syn-**22** *syn*-**22'** *anti*-**22**

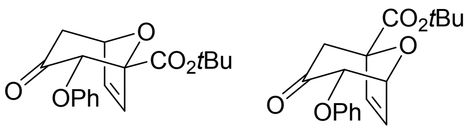
22: 22 mg (37% yield); yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.29 (m), 7.10 – 7.01 (m), 6.98 – 6.93 (m), 6.58 (d, J = 5.9 Hz), 6.47 – 6.39 (m), 6.36 (dd, J = 5.9, 1.8 Hz), 5.23 (dd, J = 4.9, 1.1 Hz), 5.17 (dd, J = 5.0, 1.7 Hz), 5.11 (d, J = 4.9 Hz), 4.97 – 4.94 (m), 2.98 (dd, J = 16.1, 5.2 Hz), 2.91 (dd, J = 15.4, 4.9 Hz), 2.52 (dd, J = 15.8, 6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 199.9, 158.9, 157.9, 135.4, 135.2, 134.7, 131.4, 129.5, 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, 1792s, 1732s, 1592s, 1491s, 1239s, 1174s, 1086s, 1039m, 1000s, 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’** = 4 : 1 : 1.



syn-**23**

syn-**23:** 39 mg (71% yield); yellow solid; mp 105-106°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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), 2.54 (d, *J* = 15.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 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, 2842m, 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.



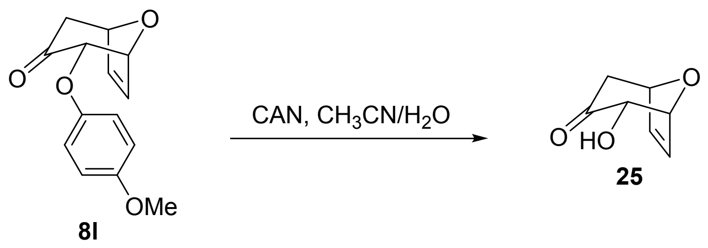
syn-**24** *anti*-**24**

syn-**24**: 20 mg (32% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, 1595s, 1494s, 1399m, 1296s, 1155s, 1130s, 1078s, 815s, 692s; HRMS: $C_{18}H_{20}O_5$ for $[M+Na]^+$, calculated 339.1203, found 339.1208.

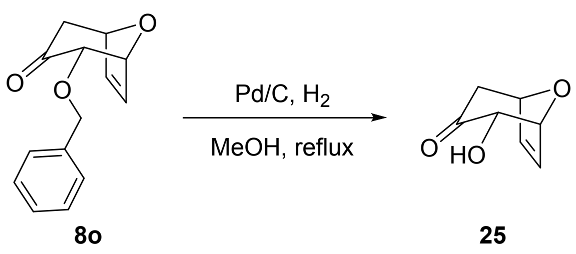
anti-**24:** 20 mg (32% yield); white solid; mp 106-107°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 2H), 7.00 – 6.95 (m, 1H), 6.92 – 6.88 (m, 2H), 6.55 (d, *J* = 6.0 Hz, 1H), 6.41 (dd, *J* = 6.0, 1.7 Hz, 1H), 5.18 (d, *J* = 5.1 Hz, 1H), 5.08 (s, 1H), 2.96 (dd, *J* = 15.6, 5.0 Hz, 1H), 2.51 (d, *J* = 15.6 Hz, 1H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 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.

syn-**24** : *anti*-**24** = 1 : 1.

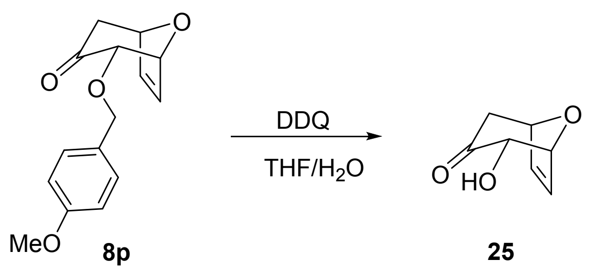
REMOVAL OF ARYL GROUPS ON CYCLOADDUCTS



To a solution of **8l** (60 mg, 0.23 mmol) in CH_3CN/H_2O (1.8:1, 1.2 mL) was added $Ce(NH_4)_2(NO_3)_6$ (315 mg, 0.58 mmol, 2.5 equiv) at 0°C. The reaction was stirred for 30 min before being quenched by sat aq NH_4Cl. 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** (19 mg, 56% yield).



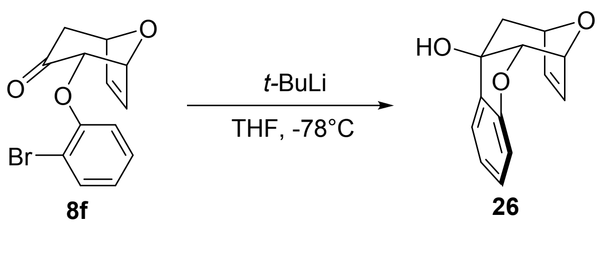
The benzyl ether **8o** (50 mg, 0.22 mmol) and 10% Pd/C (80 mg) were refluxed in methanol (2.5 ml) for 2 h under hydrogen atmosphere. The reaction mixture was allowed to cool to rt and the catalyst was filtered through Celite™. The catalyst was washed with methanol (2 × 5 mL). The crude product obtained 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_2O (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_4Cl. 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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: $C_7H_8O_3$ for $[M+Na]^+$, calculated 163.0366, found 163.0367.

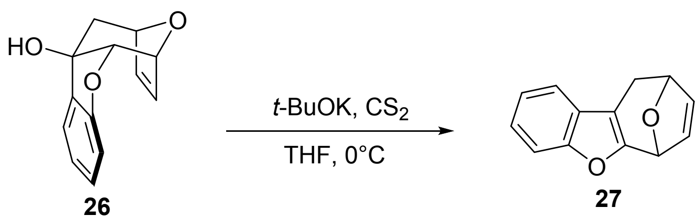
SYNTHESIS OF TETRACYCLIC COMPOUND 26.



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_4Cl. 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 compound **26** (91 mg, 62% yield).

26: 91 mg (62% yield); yellow solid; mp 138-139°C; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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, 2921w, 2845w, 1711s, 1613m, 1515s, 1467m, 1327m, 1242s, 1181s, 1112s, 1029s, 963s, 887m, 848s, 824s, 728m, 619m, 521m; HRMS: $C_{13}H_{12}O_4$ for $[M+Na]^+$, calculated 239.0679, found 239.0680.

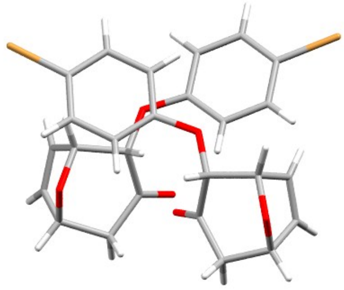
THE SYNTHESIS OF CYCLOHEPTA[*b*]BENZOFURAN 27.



To a solution of **26** (37 mg, 0.17 mmol) in THF (2.0 mL) was added *t*-BuOK (1.0*M* solution in THF, 0.34 mL, 0.34 mmol, 2.0 equiv) solution at 0°C. After stirred at rt for 30 min, CS_2 (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 NH_4Cl. The aqueous phase was extracted three times with Et_2O, and the combined organic layers were washed with H_2O and 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 cyclohepta[*b*]benzofuran **27** (26 mg, 76% yield)

27: 26 mg (76% yield); yellow solid; mp 91-92°C; ^1H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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).

Identification code	exp_5645
Empirical formula	$C_{13}H_{11}BrO_3$
Formula weight	295.13
Temperature / K	180.0(10)
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 9.4014(13) Å
	b = 10.3108(14) Å
	c = 13.260(2) Å
α/°, β/°, γ/°	91.303(12°), 109.661(13°), 101.101(11°)
Volume	1182.4(3) Å^3
Z	4
Density (calculated)	1.658 mg mm^{-3}
μ / mm^{-1}	3.469
F(000)	592
Crystal size	0.50 × 0.50 × 0.40 mm^3
2Θ range for data collection	6.56 to 52°

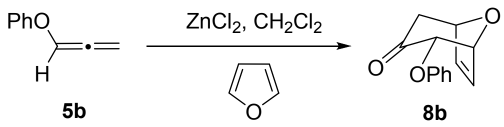
Index ranges	$-11 \le h \le 11$, $-12 \le k \le 12$, $-15 \le l \le 16$
Reflections collected	9135
Independent reflections	4642[R(int) = 0.0388 (inf-0.9Å)]
Data/restraints/parameters	4642/0/307
Goodness-of-fit on F^2	1.021
Final R indexes [$I>2\sigma(I)$ i.e. $F_o>4\sigma(F_o)$]	$R_1 = 0.0446$, $wR_2 = 0.0825$
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 REATION 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

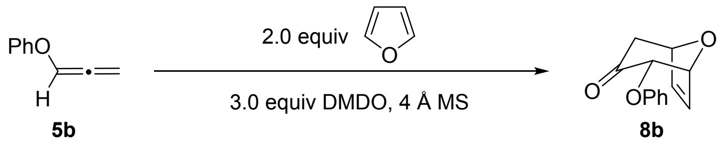


Entry[a]	Oxidant	Temp (°C)	Yield (%)[b]
1	DMDO	-78	52
2	*m*-CPBA	-78	41
3	Davis reagent	-78	0

[a]All reactions are carried out with 0.2 mmol **5b**, 0.4 mmol furan, 0.4 mmol $ZnCl_2$, 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

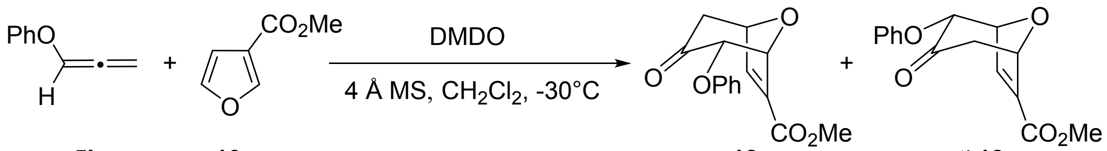


Entry[a]	Additive	solvent	Temp (°C)	Yield (%)[b]	Entry[a]	Additive	solvent	Temp (°C)	Yield (%)[b]
1	$ZnCl_2$	CH_2Cl_2	-78	53	17	$(PhO)_2P(O)OH$	CH_2Cl_2	-30	44
2	$ZnCl_2$	CH_2Cl_2	-30	70	18	K_2HPO_4	CH_2Cl_2	-30	61
3	$ZnCl_2$	CH_2Cl_2	0	18	19	Na_2HPO_4	CH_2Cl_2	-30	58
4	none	CH_2Cl_2	-78	29	20	KH_2PO_4	CH_2Cl_2	-30	81
5	none	CH_2Cl_2	-30	21	21	KH_2PO_4	CH_2Cl_2	-78	46
6	none	CH_2Cl_2	0	67	22	KH_2PO_4	CH_2Cl_2	-0	44
7	$BF_3{\cdot}OEt_2$	CH_2Cl_2	-30	32	23	KH_2PO_4	$CHCl_3$	-30	62
8	$InCl_3$	CH_2Cl_2	-30	29	24	KH_2PO_4	Et_2O	-30	59
9	$In(OTf)_3$	CH_2Cl_2	-30	41	25	KH_2PO_4	CH_3CN	-30	65
10	$MgBr_2$	CH_2Cl_2	-30	62	26	KH_2PO_4	toluene	-30	44
11	$ZnBr_2$	CH_2Cl_2	-30	23	27	KH_2PO_4	hexane	-30	74
12	$Zn(OTf)_3$	CH_2Cl_2	-30	50	28	KH_2PO_4	DMF	-30	3
13	$TiCl_4$	CH_2Cl_2	-78	0	29	KH_2PO_4	THF	-30	29
14	$SnCl_4$	CH_2Cl_2	-78	0	30	KH_2PO_4	MeOH	-30	0
15	$AlCl_3$	CH_2Cl_2	-78	0	31	KH_2PO_4	EtOAc	-30	59
16	H_3PO_4	CH_2Cl_2	-30	52					

[a]All reactions are carried out with 0.2 mmol **5b**, 0.4 mmol furan, 0.6 mmol DMDO (as a solution in CH_2Cl_2, added by syringe pump within 1 hour), and 0.4 mmol of the indicated additive. [b]Isolated yields.

Comparison study of (4 + 3) cycloaddition.

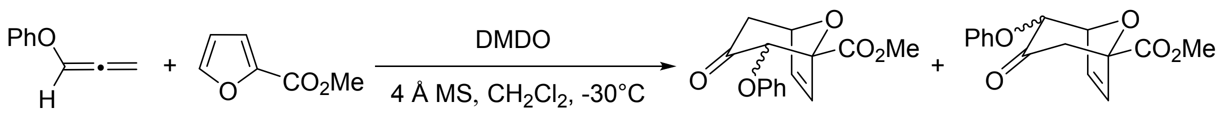
Supplementary Table 3. Comparison study using **5b** and **10**.



Entry[a]	Additive	Yield(%)[b]	Ratio (*syn* : *anti*)
1	$ZnCl_2$	29	1:1
2	$MgBr_2$	20	1.1:1
3	none	22	1:1

[a]Reactions are carried out with 0.2 mmol **5b**, 0.4 mmol **10**, 0.6 mmol DMDO (as a solution in CH_2Cl_2, added by syringe pump within 1 hour), and 0.4 mmol of the indicated additive. [b]Isolated yields.

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



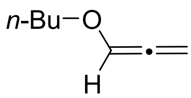
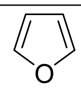
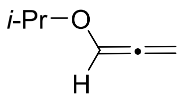
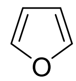
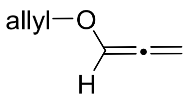
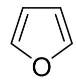
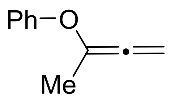
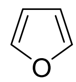
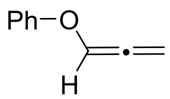
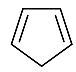
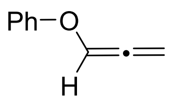
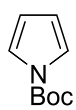
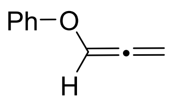
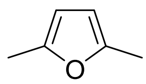
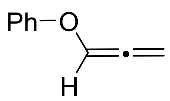
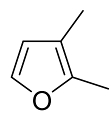
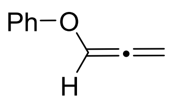
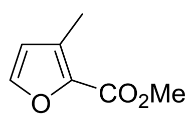
Entry[a]	Additive	Yield(%)[b]	Products
1	$ZnCl_2$	22	a mixture of regio- and diastereoisomers
2	$MgBr_2$	18	a mixture of regio- and diastereoisomers

[a]Reactions are carried out with 0.2 mmol **5b**, 0.4 mmol **15**, 0.6 mmol DMDO (as a solution in CH_2Cl_2, added by syringe pump within 1 hour), and 0.4 mmol of the indicated additive. [b]Isolated yields.

Study of Reaction Scope

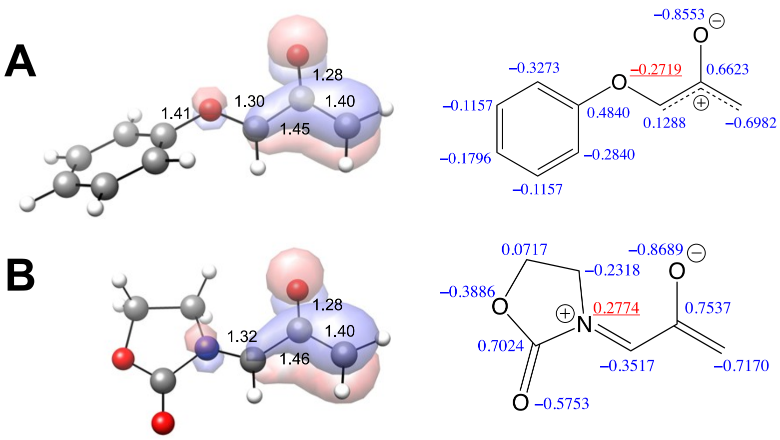
Some additional attempts are summarized in Supplementary Table 5. As mentioned in the main text, aliphatic allenyl ethers (except methoxyallene) couldn't give desired cycloadducts (Entry 1, 2). Although prenyloxyallene worked well in the cycloaddition, allyloxyallene didn't undergo the cycloaddition 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 $H_2PO_4^-$ and the allyl cation by steric effect (similar case with 3-Br furan).

Supplementary Table 5. Additional substrate scope

Entry[a]	Allenyl Ether	Diene	Product
1			–
2			–
3			–
4			–
5			–
6			–
7			–
8			–
9			–

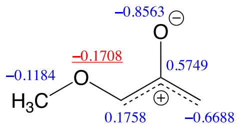
COMPUTATIONAL METHODOLOGY

DFT calculations were performed using the ORCA 4.0 suit of program.[3] All molecules were built using the Avogadro software.[4] Transition structures (TSs) were first guessed using the semi-empirical method PM6[5] of MOPAC 2016[6] 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 CH_2Cl_2 (ε = 8.93) was accounted for using the conductor-like polarizable continuum model (CPCM).[7] UCSF Chimera (version 1.12)[8] 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).

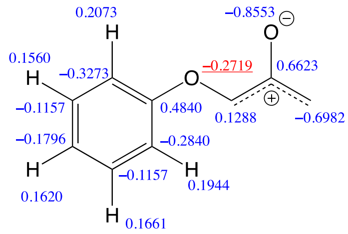


Supplementary Fig. 2 Optimized structures, HOMOs and partial ChelpG[9] partial atomic charges of **(A) 7b**, and **(B)** allenamide-oxyallyl. Distances are in Å. Orbitals were computed at HF/6-31+G(d,p)//B3LYP-D3/6-31+G(d,p) level of theory. The values of the aryloxyl oxygen and allenamide nitrogen are underlined and highlighted in red. The optimized geometries and the HOMOs for **7a**, **7c**, and **7l** are similar to that of **7b**.

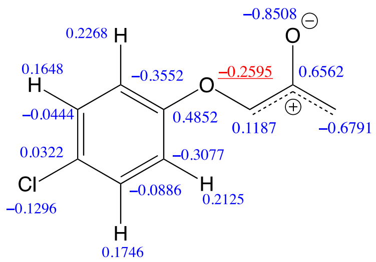
7a



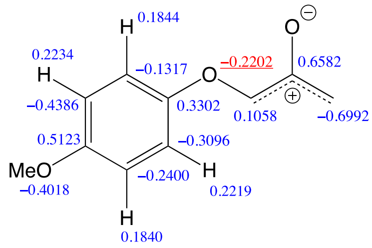
7b



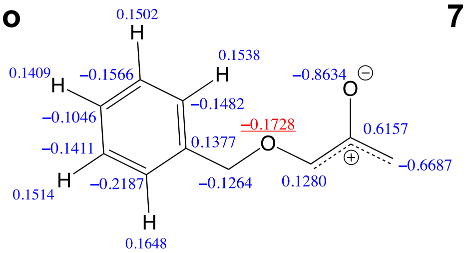
7c



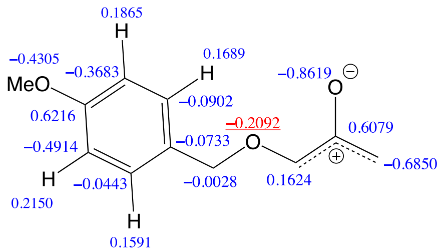
7l



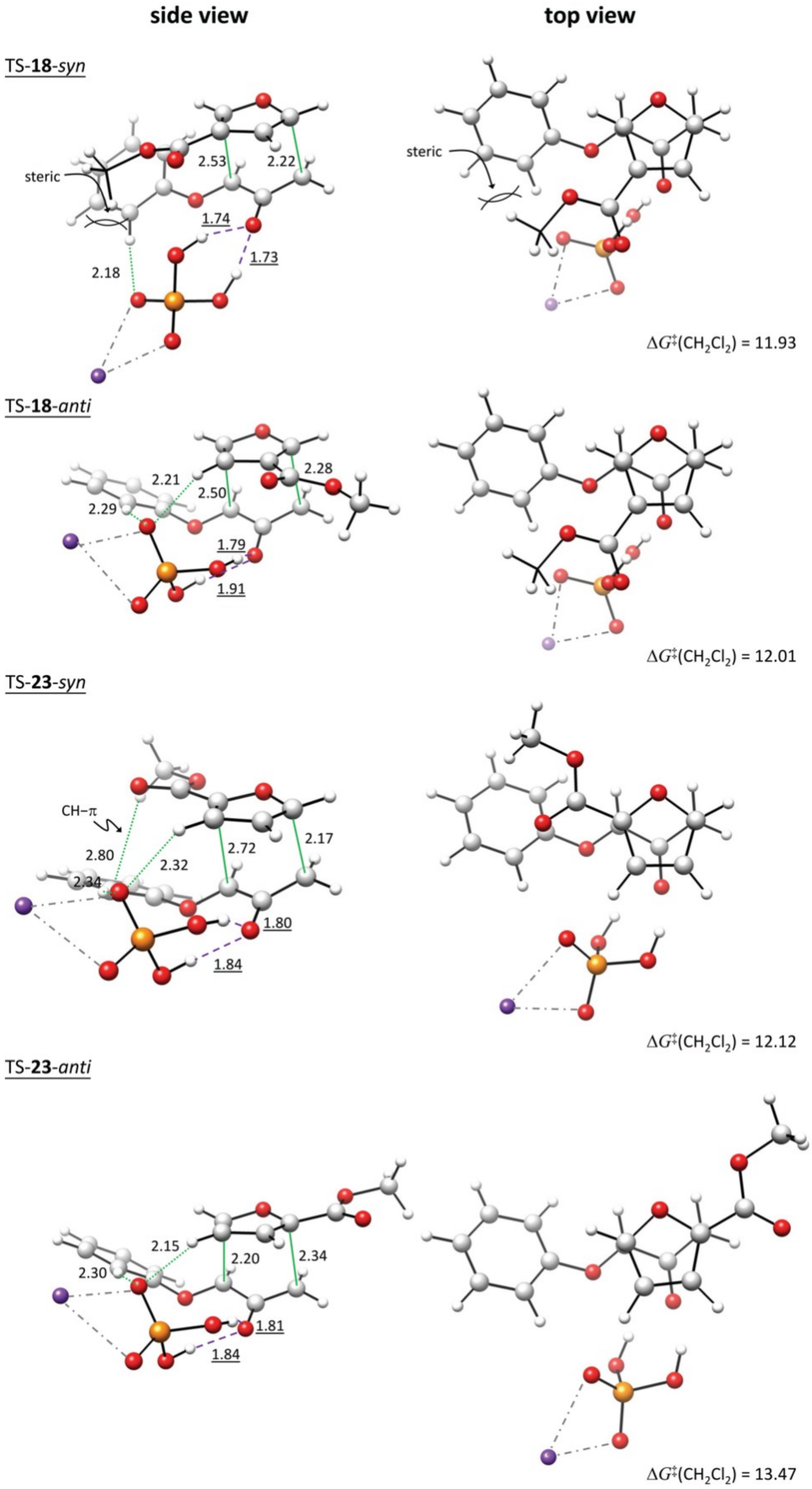
7o



7p



Supplementary Fig. 3 ChelpG[9] partial atomic charges of **7a**, **7b**, **7c**, **7l**, **7o** and **7p**. The values of the alkoxyl, 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**. $\Delta G^‡$ 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.

Structure	Energy (Eh)	Imaginary Frequency
5b	−497.77783812	0
10	−457.61619023	0
15	−457.61545818	0
KH_2PO_4	−1243.33978196	0
TS-18-*syn*	−2198.71488128	1
TS-18-*anti*	−2198.71474498	1
TS-23-*syn*	−2198.71384410	1
TS-23-*anti*	−2198.71169422	1

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