Catalytic asymmetric formal γ-allylation of deconjugated butenolides

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SUPPORTING INFORMATION: PART A

1. General information:

Infrared (FT-IR) spectra were recorded on Perkin Elmer Spectrum BX spectrophotometer and Bruker alfa FT-IR, ν_{max} in cm^{-1}. NMR spectra were recorded on Bruker Ultrashield spectrometer at 400 MHz (for ^{1}H-NMR) and 100 MHz (for ^{13}C-NMR). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ 7.26 for ^{1}H-NMR and $CDCl_3$: δ 77.16, for ^{13}C-NMR). For ^{1}H-NMR, data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, dt = doublet of triplets, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectrometry was performed on Micromass Q-TOF Micro instrument. Optical rotations were measured on JASCO P-2000 polarimeter. Melting points were measured using ANALAB μ-Thermocal 10 melting point apparatus. All melting points were measured in open glass capillary and values are uncorrected. Enantiomeric ratios were determined by Shimadzu LC-20AD HPLC instrument and SPD-20A UV/Vis detector using stationary phase chiral columns (25 cm × 0.46 cm) in comparison with authentic racemic compounds.

Unless stated otherwise, all reactions were carried out with distilled and dried solvents under an atmosphere of argon in oven (120 °C) dried glassware with standard vacuum line techniques. Organic solvents used for carrying out reactions were dried using standard methods. All work up and purification were carried out with reagent grade solvents in air. Thin layer chromatography was performed using Merck silica gel 60 F_{254} pre-coated plates (0.25 mm). Column chromatography was performed using silica gel (230-400 or 100-200 mesh). Catalyst **I** was synthesized according to previously reported procedure.[1]

2. Substrate preparation and characterization:

Preparation of β,γ-unsaturated butenolides:

α-Angelica lactone was purchased from Alfa Aesar and used as received.

Butenolides **1a-n** and **1p** were prepared according to the literature procedure.[2,3]

Butenolide **1o** was prepared according to the literature procedure.[4] The spectral data obtained are in accordance with those described in the literature.

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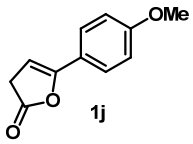
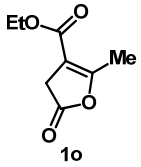
[1] M. S. Manna and S. Mukherjee, *Chem. Sci.*, 2014, **5**, 1627-1633.
[2] V. Kumar and S. Mukherjee, *Chem. Commun.*, 2013, **49**, 11203-11205.
[3] V. Kumar, B. Ray, P. Rathi and S. Mukherjee, *Synthesis*, 2013, **45**, 1641-1646.
[4] F. Gaudemar-Bardone, M. Mladenova and R. Couffignal, *Tetrahedron Lett.*, 1984, **25**, 1047-1048.

5-(4-Methoxyphenyl)furan-2(3*H*)-one (1j): yellow oil. **FT-IR (Thin film):** 1791, 1644, 1251, 1036 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.53 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 5.62 (s, 1H), 3.83 (s, 3H), 3.39 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 176.1, 160.6, 153.7, 126.2, 121.1, 114.0, 95.4, 55.3, 34.6.



Ethyl 2-methyl-5-oxo-4,5-dihydrofuran-3-carboxylate (1o): colorless oil. **FT-IR (Thin film):** 1818, 1710, 1338, 960 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 4.16 (q, *J* = 7.0 Hz, 2H), 3.38 (s, 2H), 2.33 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 172.7, 163.2, 162.9, 106.1, 60.4, 33.4, 14.1, 13.5.

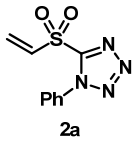


Preparation of vinyl sulfones:

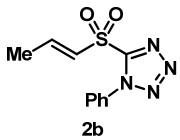
Vinyl sulfone **2a** was prepared according to the literature procedure.[5]

Vinyl sulfones **2b-h** were prepared according to the literature procedure.[6] The spectral data obtained are in accordance with those described in the literature.

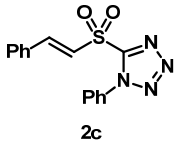
1-Phenyl-5-(vinylsulfonyl)-1*H*-tetrazole (2a): white solid. **m.p.** 69-75 °C; **FT-IR (Thin film):** 2624, 1641, 1493, 1271, 978 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 7.0 Hz, 2H), 7.64-7.62 (m, 3H), 7.14 (dd, *J* = 16.5, 9.8 Hz, 1H), 6.67 (d, *J* = 16.5 Hz, 1H), 6.50 (d, *J* = 9.8 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 154.1, 135.2, 134.6, 132.9, 131.5, 129.7, 125.2; **HRMS (ESI+):** Calcd. for $C_9H_8N_4O_2SNa$ ($[M+Na]^+$): 259.0266, Found: 259.0261.



(*E*)-1-Phenyl-5-(prop-1-en-1-ylsulfonyl)-1*H*-tetrazole (2b): colorless oil. **FT-IR (Thin film):** 3288, 1599, 1495, 1335, 1148, 1020 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.68-7.65 (m, 2H), 7.63-7.57 (m, 3H), 7.20-7.11 (m, 1H), 6.77 (dd, *J* = 15.0, 1.4 Hz, 1H), 2.08 (dd, *J* = 7.0, 1.3 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 154.7, 150.9, 133.1, 131.4, 129.6, 128.4, 125.3, 17.9; **HRMS (ESI+):** Calcd. for $C_{10}H_{10}N_4O_2SNa$ ($[M+Na]^+$): 273.0422, Found: 273.0421.

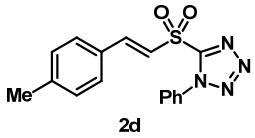


(*E*)-1-Phenyl-5-(styrylsulfonyl)-1*H*-tetrazole (2c): white solid. **m.p.** 119 °C; **FT-IR (Thin film):** 3063, 1604, 1496, 1344, 1148, 976 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.72-7.58 (m, 6H), 7.55-7.50 (m, 3H), 7.47-7.43 (m, 2H), 7.21 (d, *J* = 15.4 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 154.9, 149.4, 133.1, 132.7, 131.4, 131.1, 129.6, 129.4, 129.3, 125.4, 122.9; **HRMS (ESI+):** Calcd. for $C_{15}H_{12}N_4O_2SNa$ ($[M+Na]^+$): 335.0579, Found: 335.0579.



[5] E. Rodrigo, S. Morales, S. Duce, J. L. G. Ruano and M. B. Cid, *Chem. Commun.*, 2011, **47**, 11267-11269.

[6] P. Mauleón, I. Alonso, M. R. Rivero and J. C. Carretero, *J. Org.Chem.*, 2007, **72**, 9924-9935.

(*E*)-5-((4-Methylstyryl)sulfonyl)-1-phenyl-1*H*-tetrazole (2d): white solid. **m.p.** 155 °C; 

FT-IR (Thin film): 1639, 1603, 1491, 1259, 1148 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.69-7.59 (m, 6H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 5.5 Hz, 2H), 7.13 (d, *J* = 15.3 Hz, 1H), 2.41 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 155.1, 149.6, 143.8, 133.2, 131.4, 130.0, 129.6, 129.4, 128.5, 125.5, 121.6, 21.7; **HRMS (ESI+):** Calcd. for $C_{16}H_{14}N_4O_2SNa$ ($[M+Na]^+$): 349.0735, Found: 349.0731.

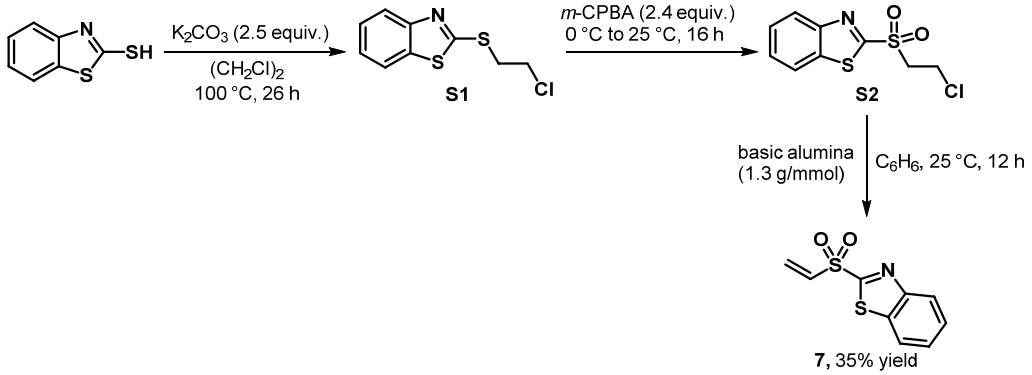
(*E*)-5-((3-Chlorostyryl)sulfonyl)-1-phenyl-1*H*-tetrazole (2e): white solid. **m.p.** 96 °C; **FT-IR (Thin film):** 1611, 1348, 1149, 838 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.69-7.66 (m, 2H), 7.64 (d, *J* = 5.0 Hz, 1H), 7.62-7.58 (m, 3H), 7.52 (s, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.40-7.37 (m, 1H), 7.25 (d, *J* = 15.1 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 154.6, 147.5, 135.3, 133.0, 132.9, 132.4, 131.5, 130.5, 129.6, 128.9, 127.4, 125.3, 124.5; **HRMS (ESI+):** Calcd. for $C_{15}H_{11}ClN_4O_2SNa$ ($[M+Na]^+$): 369.0189, Found: 369.0192.

(*E*)-5-((4-Bromostyryl)sulfonyl)-1-phenyl-1*H*-tetrazole (2f): white solid. **m.p.** 150 °C; **FT-IR (Thin film):** 3581, 1601, 1491, 1344, 1269, 1148 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.71-7.69 (m, 3H), 7.64-7.60 (m, 5H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 17.5 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 154.8, 147.9, 133.0, 132.7, 131.5, 130.6, 130.1, 129.7, 127.5, 125.3, 123.6; **HRMS (ESI+):** Calcd. for $C_{15}H_{11}BrN_4O_2SNa$ ($[M+Na]^+$): 412.9684, Found: 412.9687.

(*E*)-5-((2-(Naphthalen-2-yl)vinyl)sulfonyl)-1-phenyl-1*H*-tetrazole (2g): white solid. **m.p.** 147 °C; **FT-IR (Thin film):** 3060, 1599, 1493, 1332, 1149, 973, 754, 605 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.97 (s, 1H), 7.88 (d, *J* = 8.8 Hz, 3H), 7.86 (d, *J* = 7.0 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.67-7.54 (m, 5H), 7.30 (d, *J* = 15.3 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 155.0, 149.5, 135.1, 133.1, 132.9, 132.6, 131.4, 129.6, 129.3, 129.0, 128.7, 128.6, 127.9, 127.3, 125.5, 123.4, 122.8; **HRMS (ESI+):** Calcd. for $C_{19}H_{14}N_4O_2SNa$ ($[M+Na]^+$): 385.0735, Found: 385.0738.

(*E*)-5-((2-(Furan-2-yl)vinyl)sulfonyl)-1-phenyl-1*H*-tetrazole (2h): white solid. **m.p.** 92-94 °C; **FT-IR (Thin film):** 1616, 1341, 1146, 842 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.69-7.66 (m, 2H), 7.64-7.58 (m, 4H), 7.46 (d, *J* = 14.9 Hz, 1H), 7.03 (d, *J* = 14.9 Hz, 1H), 7.86 (d, *J* = 3.4 Hz, 1H), 6.58-6.56 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 155.0, 147.8, 147.4, 134.8, 133.1, 131.1, 129.6, 125.4, 120.3, 119.7, 113.3; **HRMS (ESI+):** Calcd. for $C_{13}H_{10}N_4O_3SNa$ ($[M+Na]^+$): 325.0371, Found: 325.0374.

Preparation of 2-(vinylsulfonyl)benzo[*d*]thiazole (7):

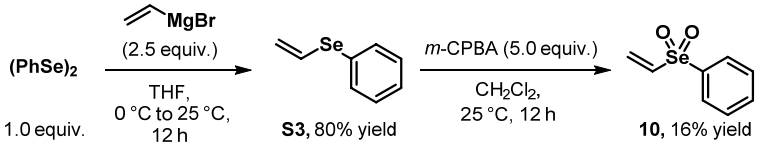


In a 100 mL round bottom flask, benzo[*d*]thiazole-2-thiol (1.0 g, 5.97 mmol, 1.0 equiv.) and K_2CO_3 (2.0 g, 14.9 mmol, 2.5 equiv.) were taken in 28 mL of dichloroethane under argon atmosphere. The resulting mixture was heated to reflux for 26 h. The reaction mixture was then allowed to attain room temperature and 15 mL of distilled water was added. Organic phase was separated and the aqueous phase was extracted with EtOAc (3 × 15 mL). Combined organic phase was dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain **S1** as a yellow liquid which was used in the next step without any further purification or characterization.

This yellow liquid was taken in 15 mL of dry CH_2Cl_2 under argon. The resulting mixture was cooled to 0 °C. *m*-CPBA (1.6 g, 9.10 mmol, 5 equiv.) was then added and the mixture was stirred at 0 °C temp for 16 h. 20% Aqueous $NaHSO_3$ solution was added to the reaction mixture. Organic phase was separated and aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL). Combined organic layer was washed with sat. $NaHCO_3$ solution and brine. Organic phase was dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain **S2** as a white solid which was used in the next step without any further purification or characterization.

The white solid was taken in 15 mL dry benzene and 1.2 g basic alumina was added. Stirring was continued for 12 h. The reaction mixture was filtered through silica gel (100-200 mesh) and eluted with CH_2Cl_2. Organic phase was concentrated under reduced pressure to obtain a white solid (470 mg, 2.09mmol, 35% over 3 steps). **m.p.** 86 °C; **FT-IR (Thin film):** 2637, 1641, 1470, 1328, 1270, 1147 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.18 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.62-7.54 (m, 2H), 6.97 (dd, *J* = 16.5, 9.8 Hz , 1H), 6.71 (d, *J* = 16.5 Hz, 1H), 6.32 (d, *J* = 9.8 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 165.8, 152.7, 136.8, 135.8, 132.2, 128.0, 127.6, 125.3, 122.2; **HRMS (ESI+):** Calcd. for $C_9H_7NO_2S_2Na$ ($[M+Na]^+$): 247.9816, Found: 247.9841.

Preparation of (vinylselenonyl)benzene (10):



Vinyl phenyl selenone **10** was prepared according to the literature procedure.[7] The spectral data obtained are in agreement with those described in the literature.

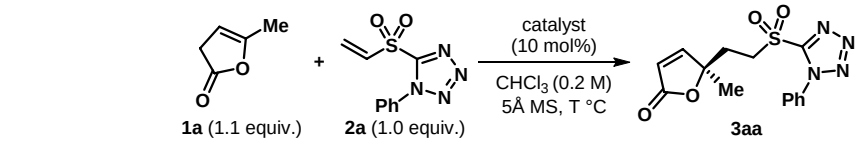
S3: Colorless oil (80% yield based on recovered starting). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.53-7.51 (m, 2H), 7.32-7.62 (m, 3H), 6.85 (dd, *J* = 16.9, 9.5 Hz, 1H), 5.78 (d, *J* = 9.5 Hz, 1H), 5.54 (d, *J* = 16.9 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 133.0, 129.3, 129.2, 127.6, 127.4, 119.4.

10: white solid (16% yield). **m.p.** 99-114 °C; **FT-IR (Thin film):** 3045, 1640, 1446, 985, 936 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.64-7.62 (m, 3H), 7.14 (dd, *J* = 16.5, 9.0 Hz , 1H), 6.68 (d, *J* = 16.5 Hz, 1H), 6.49 (d, *J* = 9.0 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 140.8, 138.6, 134.2, 131.2, 131.1, 130.2, 130.1, 126.6; **HRMS (ESI+):** Calcd. for $C_8H_8O_2SeNa$ (M^+): 238.9580, Found: 238.9583.

[7] M. Tiecco, D. Chianelli, L. Testaferri, M. Tingoli and D. Bartoli, *Tetrahedron*, 1986, **42**, 4889-4896.

3. Optimization of reaction conditions:

Table 1. Optimization of catalyst for the enantioselective vinylogous Michael addition of α-angelica lactone 1a to vinyl PT-sulfone 2a



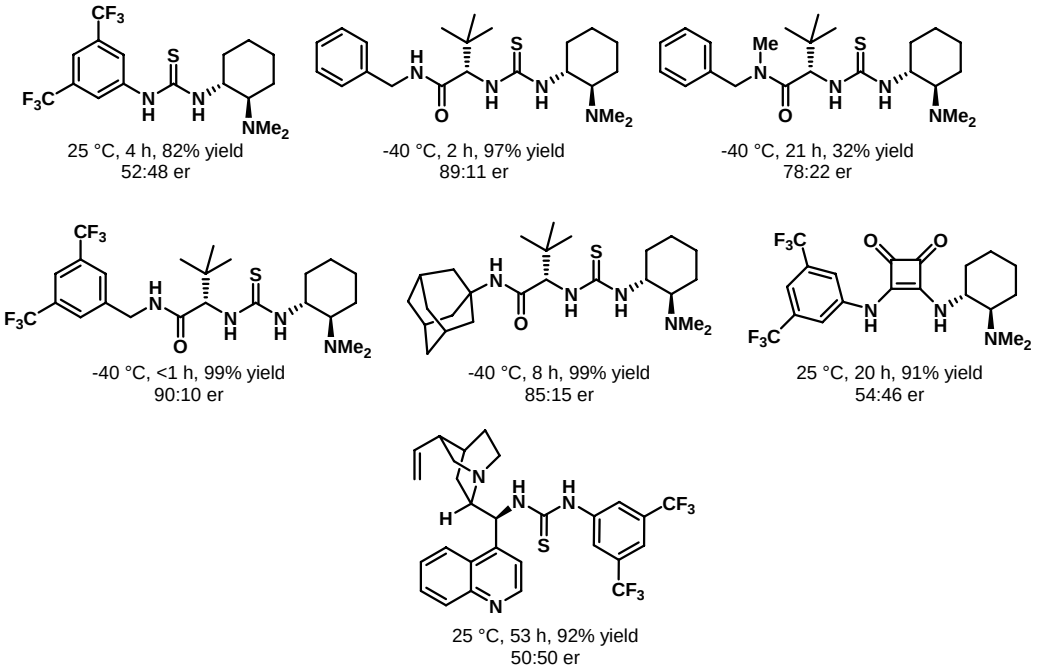
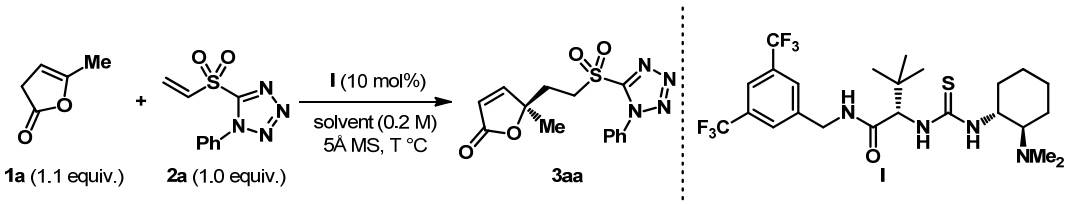
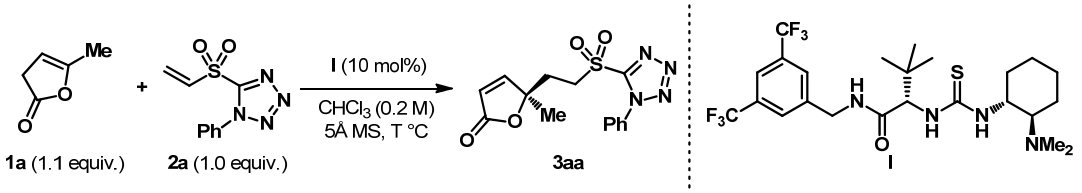


Table 2. Optimization of solvent



solvent	T/°C	t/h	yield (%)	er
CH_2Cl_2	–40	1	99	88:12
CH_2Cl_2	–80	6.5	99	91:9
$CHCl_3$	–40	<1	99	90:10
$PhCH_3$	–40	24	94	85:15
MTBE	–40	8	99	79.5:20.5
$(CH_2Cl)_2$	–40	26	50(conv.)	83:17
$PhCF_3$	–10	3.5	89	81:19

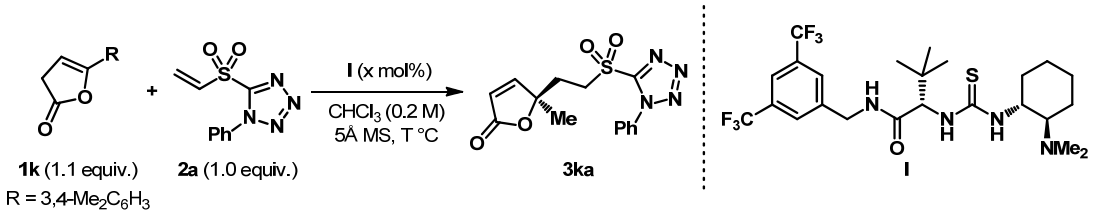
Table 3. Optimization of temperature



1a (1.1 equiv.) **2a** (1.0 equiv.) **3aa** **I**

T/°C	t/h	yield (%)	er
25	0.5	95	83:17
0	2	99	86:14
–20	1.5	99	86.5:13.5
–40	7.5	99	90:10
–60	1	99	91.5:9.5

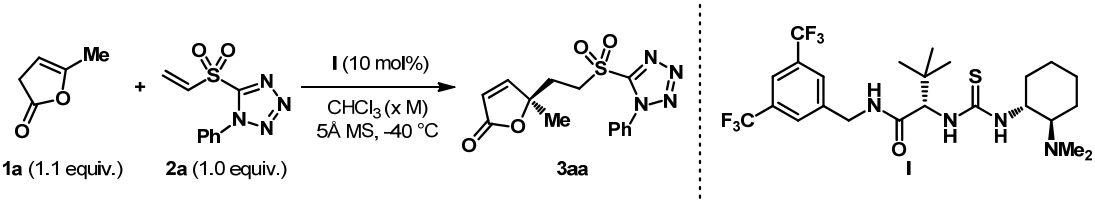
Table 4. Optimization of catalyst loading



1k (1.1 equiv.) **2a** (1.0 equiv.) **3ka** **I**
R = 3,4-$Me_2C_6H_3$

x	t/h	yield (%)	er
10	0.2	98	94:6
5	20	75 (conv.)	82:18
2	74	90	84:16

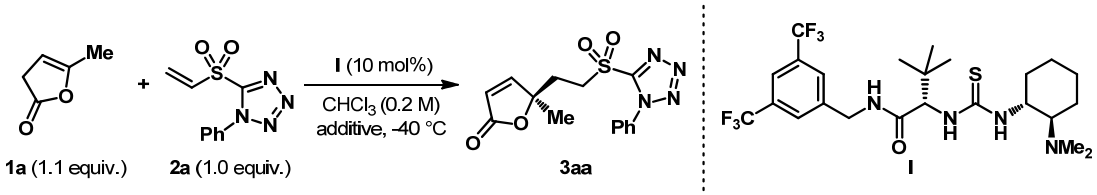
Table 5. Optimization of concentration



1a (1.1 equiv.) **2a** (1.0 equiv.) **3aa** **I**

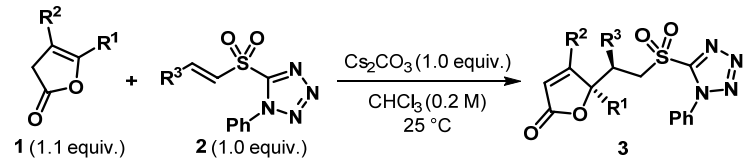
x/M	T/°C	t/h	yield (%)	er
0.5	0	1.5	99	85:15
0.2	0	2	99	86:14
0.05	–40	16	88	91:9

Table 6. Optimization of additive



additive	t/h	yield (%)	er
none	7.5	99	90:10
5Å MS	1	99	90:10
4Å MS	1.5	99	90:10
3Å MS	1	99	90:10

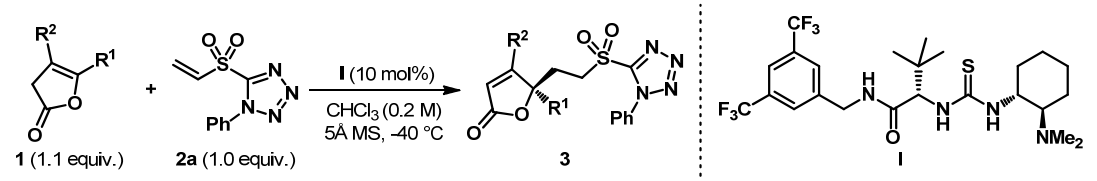
4. General procedure for the preparation of racemic products (*rac*-3):



In a glass-vial, **1** (0.146 mmol, 1.1 equiv.), **2** (0.133 mmol, 1.0 equiv.) and Cs_2CO_3 (0.133 mmol, 1.0 equiv) were taken along with 0.65 mL of $CHCl_3$ under positive argon pressure. The resulting solution was stirred at room temperature until TLC reveals the complete consumption of **2**. The racemic product (*rac*-**3**) samples for HPLC analysis were obtained by scratching the TLC plate (Merck silica-gel 60 F_{254} pre-coated plates of 0.25 mm thickness).

5. Scope with respect to butenolides and vinyl PT-sulfones:

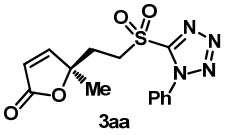
General procedure for the catalytic enantioselective vinylogous Michael addition of deconjugated butenolides 1 to vinyl sulfones 2a:



In an oven and vacuum dried Schlenk tube, 80 mg 5Å MS (activated by heating at 200 °C under high vacuum for 1 h prior to use), vinyl sulfone **2a** (20.0 mg, 0.084 mmol, 1.0 equiv.) and catalyst **I** (4.3 mg, 0.008 mmol, 0.1 equiv.) were taken under argon atmosphere. Dry $CHCl_3$ (0.2 mL) was added to it and the solution was cooled to –40 °C under a positive argon pressure. A solution of **1** (0.092 mmol, 1.1 equiv.) in 0.2 mL of $CHCl_3$ was added to it and the

resulting mixture was stirred at –40 °C until TLC (30% EtOAc/Petroleum ether) revealed complete conversion of **2a**. The reaction mixture was brought to 25 °C, solvent was removed under reduced pressure and the residue was purified by column chromatography to obtain the desired product.

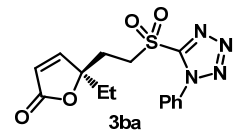
(*R*)-5-Methyl-5-(2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)furan-2(5*H*)-one (3aa):



3aa

Purified by silica gel (230-400 mesh) column chromatography (40% EtOAc/Petroleum ether) to afford a colorless oil (28.0 mg, 0.083 mmol, 99% yield). **FT-IR (Thin film):** 2918, 1758, 1152 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.67-7.65 (m, 2H), 7.65-7.57 (m, 3H), 7.45 (d, *J* = 5.6 Hz, 1H), 6.14 (d, *J* = 5.6 Hz, 1H), 3.75-3.57 (m, 2H), 2.61-2.54 (m, 1H), 2.41-2.34 (m, 1H), 1.56 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.2, 158.7, 152.9, 132.6, 131.5, 129.6, 124.9, 121.7, 86.2, 51.09, 30.3, 23.9; **HRMS (ESI+):** Calcd. for $C_{14}H_{14}N_4O_4SNa$ ($[M+Na]^+$): 357.0633, Found: 357.0634; **Optical rotation:** $[\alpha]_D^{24}$ –31.2 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 90:10 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (70:30 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 21.9 min, τ_{major} = 24.7 min). See Supporting Information: Part B for HPLC chromatograms.

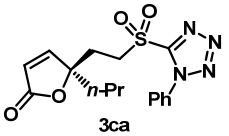
(*R*)-5-Ethyl-5-(2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)furan-2(5*H*)-one (3ba):



3ba

Purified by silica gel (230-400 mesh) column chromatography (50% EtOAc/Petroleum ether) to obtain a white solid (24.0 mg, 0.069 mmol, 82% yield). **m.p.** 92-94 °C; **FT-IR (Thin film):** 2926, 1755, 1653, 1154, 1017 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.68-7.66 (m, 2H), 7.63-7.57 (m, 3H), 7.39 (d, *J* = 5.6 Hz, 1H), 6.20 (d, *J* = 5.6 Hz, 1H), 3.72-3.56 (m, 2H), 2.65-2.57 (m, 1H), 2.42-2.35 (m, 1H), 2.00-1.82 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.4, 157.3, 153.1, 132.8, 131.6, 129.8, 124.9, 123.0, 89.0, 50.9, 30.2, 29.2, 7.6; **HRMS (ESI+):** Calcd. for $C_{15}H_{16}N_4O_4SNa$ ($[M+Na]^+$): 371.0790, Found: 371.0792; **Optical rotation:** $[\alpha]_D^{24}$ –14.8 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 89:11 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (70:30 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 21.2 min, τ_{major} = 23.6 min). See Supporting Information: Part B for HPLC chromatograms.

(*R*)-5-(2-((1-Phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)-5-propylfuran-2(5*H*)-one (3ca):

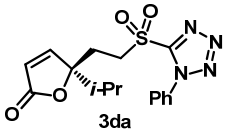


3ca

Purified by silica gel (230-400 mesh) column chromatography (40% EtOAc/Petroleum ether) to obtain a thick colorless oil (26.0 mg, 0.072 mmol, 85% yield). **FT-IR (Thin film):** 2925, 1761, 1635, 1153 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.67-7.57 (m, 5H), 7.40 (d, *J* = 5.6 Hz, 1H), 6.17 (d, *J* = 5.6 Hz, 1H), 3.71-3.55 (m, 2H), 2.63-2.56 (m, 1H), 2.41-2.33 (m, 1H), 1.90-1.75 (m, 2H), 1.32-1.25 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.4, 157.6, 153.0, 132.7, 131.6, 129.8, 124.9, 122.7, 88.8, 50.9, 39.1, 29.4, 16.7,

13.9; **HRMS (ESI+):** Calcd. for $C_{16}H_{18}N_4O_4SNa$ ($[M+Na]^+$): 385.0946, Found: 385.0948; **Optical rotation:** $[\alpha]_D^{24}$ –11.8 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 86:14 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (70:30 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 20.3 min, τ_{major} = 22.0 min). See Supporting Information: Part B for HPLC chromatograms.

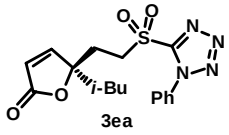
(*S*)-5-Isopropyl-5-(2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)furan-2(5*H*)-one (3da):



3da

Purified by silica gel (230-400 mesh) column chromatography (30% EtOAc/Petroleum ether) to obtain thick colorless oil (29.0 mg, 0.080 mmol, 95% yield). **FT-IR (Thin film)**: 2973, 1652, 1187, 1167 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.68-7.66 (m, 2H), 7.63-7.57 (m, 3H), 7.43 (d, *J* = 5.6 Hz, 1H), 6.22 (d, *J* = 5.6 Hz, 1H), 3.67-3.51 (m, 2H), 2.70-2.62 (m, 1H), 2.44-2.37 (m, 1H), 2.15-2.08 (m, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.4, 156.4, 153.1, 132.7, 131.6, 129.8, 124.9, 123.5, 91.5, 50.9, 35.0, 27.1, 17.6, 16.7; **HRMS (ESI+):** Calcd. for $C_{16}H_{18}N_4O_4SNa$ ($[M+Na]^+$): 385.0946, Found: 385.0944; **Optical rotation:** $[\alpha]_D^{24}$ –5.23 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 88:12 er. The enantiomeric ratio was determined by HPLC analysis using column Phenomenex Cellulose-2 (80:20 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 19.5 min, τ_{major} = 21.1 min). See Supporting Information: Part B for HPLC chromatograms.

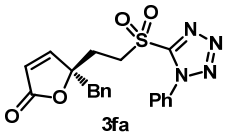
(*R*)-5-Isobutyl-5-(2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)furan-2(5*H*)-one (3ea):



3ea

Purified by silica gel (230-400 mesh) column chromatography (30% EtOAc/Petroleum ether) to obtain a colorless oil (31.0 mg, 0.082 mmol, 98% yield). **FT-IR (Thin film)**: 2959, 1758, 1344, 1152 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.63-7.58 (m, 3H), 7.44 (d, *J* = 5.6 Hz, 1H), 6.18 (d, *J* = 5.6 Hz, 1H), 3.65-3.55 (m, 2H), 2.64-2.56 (m, 1H), 2.40-2.32 (m, 1H), 1.89-1.84 (m, 1H), 1.72-1.68 (m, 1H), 1.65-1.58 (m, 1H), 0.92 (d, *J* = 6.7 Hz, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.4, 157.9, 153.1, 132.8, 131.6, 129.8, 124.9, 122.6, 88.9, 50.9, 45.8, 30.1, 24.1, 23.9, 23.8; **HRMS (ESI+):** Calcd. for $C_{17}H_{20}N_4O_4SNa$ ($[M+Na]^+$): 399.1103, Found: 399.1105; **Optical rotation:** $[\alpha]_D^{24}$ –29.1 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 85:15 er. The enantiomeric ratio was determined by HPLC analysis using column Phenomenex Cellulose-1 (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 210 nm, τ_{major} = 33.9 min, τ_{minor} = 40.2 min). See Supporting Information: Part B for HPLC chromatograms.

(*R*)-5-Benzyl-5-(2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)furan-2(5*H*)-one (3fa):

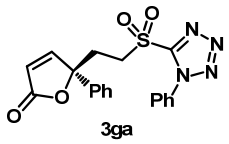


3fa

Purified by silica gel (230-400 mesh) column chromatography (20% EtOAc/Petroleum ether) to obtain a colorless oil (32.0 mg, 0.078 mmol, 93% yield). **FT-IR (Thin film):** 2924, 1756, 1629, 1153 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.67-7.65 (m, 2H), 7.64-7.58 (m, 3H), 7.37 (d, *J* =

5.6 Hz, 1H), 7.30-7.26 (m, 3H), 7.13 (d, *J* = 6.8 Hz, 2H), 6.01(d, *J* = 5.6 Hz, 1H), 3.73-3.56 (m, 2H), 3.19 (d, *J* = 13.9 Hz, 1H), 3.11 (d, *J* = 13.9 Hz, 1H), 2.70-2.63 (m, 1H), 2.49-2.42 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.0, 157.0, 153.0, 133.0, 132.7, 131.6, 130.2, 129.8, 128.6, 127.6, 124.9, 123.1, 88.3, 50.9, 44.0, 29.1; **HRMS (ESI+):** Calcd. for $C_{20}H_{18}N_4O_4SNa$ ($[M+Na]^+$): 433.0946, Found: 433.0948; **Optical rotation:** $[\alpha]_D^{24}$ +9.32 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 80:20 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (70:30 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 23.4 min, τ_{major} = 25.9 min). See Supporting Information: Part B for HPLC chromatograms.

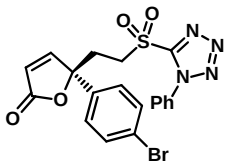
(*R*)-5-Phenyl-5-(2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)furan-2(5*H*)-one (3ga):



3ga

Purified by silica gel (230-400 mesh) column chromatography (20% EtOAc/Petroleum ether) to obtain a crystalline solid (33.0 mg, 0.083 mmol, 99% yield). **m.p.** 157 °C; **FT-IR (Thin film):** 2923, 1764, 1154 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 5.5 Hz, 1H), 7.64-7.57 (m, 5H), 7.46-7.38 (m, 5H), 6.15 (d, *J* = 5.5 Hz, 1H), 3.81-3.74 (m, 1H), 3.61-3.54 (m, 1H), 2.99-2.91 (m, 1H), 2.64-2.57 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.0, 158.2, 153.0, 136.4, 132.8, 131.6, 129.8, 129.4, 129.0, 125.0, 124.7, 120.6, 88.9, 51.5, 32.4; **HRMS (ESI+):** Calcd. for $C_{19}H_{16}N_4O_4SNa$ ($[M+Na]^+$): 419.0790, Found: 419.0793; **Optical rotation:** $[\alpha]_D^{24}$ +240.5 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 93:7 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IC column (80:20 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 23.1 min, τ_{major} = 24.8 min). See Supporting Information: Part B for HPLC chromatograms.

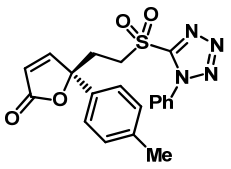
(*R*)-5-(4-Bromophenyl)-5-(2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)furan-2(5*H*)-one (3ha):



3ha

Purified by silica gel (230-400 mesh) column chromatography (40% EtOAc/Petroleum ether) to obtain a thick colorless oil (32.0 mg, 0.067 mmol, 80% yield). **FT-IR (Thin film):** 2924, 1768, 1634, 1154,1017 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.66 (d, *J* = 5.6 Hz, 2H), 7.63 (s, 2H), 7.60-7.56 (m, 4H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.16 (d, *J* = 5.6 Hz, 1H), 3.79-3.72 (m, 1H), 3.61-3.53 (m, 1H), 2.96-2.89 (m, 1H), 2.63-2.56 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 170.7, 157.7, 153.0, 135.5, 132.7, 132.6, 131.6, 129.8, 126.4, 124.9, 123.3, 120.8, 88.5, 51.3, 32.3; **HRMS (ESI+):** Calcd. For $C_{19}H_{15}BrN_4O_4SNa$ ($[M+Na]^+$): 496.9895, Found: 496.9898; **Optical rotation:** $[\alpha]_D^{24}$ +65.7 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 85:15 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (70:30 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 22.2 min, τ_{major} = 24.3 min). See Supporting Information: Part B for HPLC chromatograms.

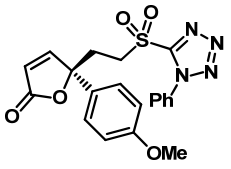
(*R*)-5-(2-((1-Phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)-5-(p-tolyl)furan-2(5*H*)-one (3ia):



3ia

Purified by silica gel (230-400 mesh) column chromatography (20% EtOAc/Petroleum ether) to obtain a thick colorless oil (30.0 mg, 0.073 mmol, 87% yield). **FT-IR (Thin film):** 2925, 1764, 1625, 1156 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.67 (d, *J* = 5.5 Hz, 1H), 7.64-7.56 (m, 5H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.12 (d, *J* = 5.5 Hz, 1H), 3.80-3.73 (m, 1H), 3.62-3.54 (m, 1H), 2.96-2.88 (m, 1H), 2.61-2.54 (m, 1H), 2.35 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.2, 158.4, 153.1, 139.0, 133.3, 132.7, 131.6, 130.0, 129.8, 125.0, 124.6, 120.3, 89.0, 51.6, 32.3, 21.0; **HRMS (ESI+):** Calcd. for $C_{20}H_{18}N_4O_4SNa$ ($[M+Na]^+$): 433.0946, Found: 433.0946; **Optical rotation:** $[\alpha]_D^{24}$ +107.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 94:6 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (70:30 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 21.6 min, τ_{major} = 23.8 min). See Supporting Information: Part B for HPLC chromatograms.

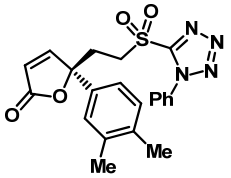
(*R*)-5-(4-Methoxyphenyl)-5-(2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)furan-2(5*H*)-one (3ja):



3ja

Purified by silica gel (230-400 mesh) column chromatography (40% EtOAc/Petroleum ether) to obtain a colorless oil (35.0 mg, 0.082 mmol, 98% yield). **FT-IR (Thin film):** 2924, 1749, 1649, 1187, 1168 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.66 (d, *J* = 5.5 Hz, 1H), 7.64-7.56 (m, 5H), 7.31 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.11 (d, *J* = 5.5 Hz, 1H), 3.80 (s, 3H), 3.78-3.72 (m, 1H), 3.62-3.54 (m, 1H), 2.94-2.87 (m, 1H), 2.60-2.53 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.1, 159.9, 158.4, 153.0, 132.7, 131.5, 129.7, 128.0, 126.1, 124.9, 120.2, 114.7, 88.8, 55.3, 51.5, 32.2; **HRMS (ESI+):** Calcd. for $C_{20}H_{18}N_4O_5SNa$ ($[M+Na]^+$): 449.0896, Found: 449.0895; **Optical rotation:** $[\alpha]_D^{24}$ +58.20 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 95:5 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (80:20 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{major} = 28.9 min, τ_{minor} = 32.4 min). See Supporting Information: Part B for HPLC chromatograms.

(*R*)-5-(3,4-Dimethylphenyl)-5-(2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)furan-2(5*H*)-one (3ka):

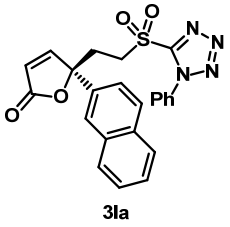


3ka

Purified by silica gel (230-400 mesh) column chromatography (20% EtOAc/Petroleum ether) to obtain a white solid (35.0 mg, 0.082 mmol, 98% yield). **m.p.** 136 °C; **FT-IR (Thin film):** 2937, 1767, 1533 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.66 (d, *J* = 5.5 Hz, 1H), 7.64-7.57 (m, 5H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.15 (s, 1H), 7.10 (d, *J* = 7.9 Hz, 1H), 6.11 (d, *J* = 5.5 Hz, 1H), 3.80-3.72 (m, 1H), 3.62-3.55 (m, 1H), 2.95-2.88 (m, 1H), 2.60-2.54 (m, 1H), 2.27 (d, *J* = 10.2 Hz, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.3, 158.5, 153.1, 137.9, 137.7, 133.6, 132.8, 131.6, 130.5, 129.8, 125.8, 125.0, 122.1, 120.2, 89.0, 51.6, 32.3 19.9, 19.4; **HRMS (ESI+):** Calcd. for $C_{21}H_{20}N_4O_4SNa$ ($[M+Na]^+$): 447.1103, Found: 447.1101; **Optical rotation:** $[\alpha]_D^{24}$ +151.0 (*c*

1.0, $CHCl_3$) for an enantiomerically enriched sample with 94:6 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 31.6 min, τ_{major} = 38.3 min). See Supporting Information: Part B for HPLC chromatograms.

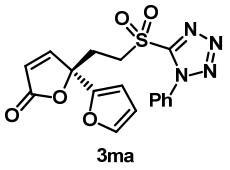
(*R*)-5-(Naphthalen-2-yl)-5-(2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)furan-2(5*H*)-one



3la

(3la): Purified by silica gel (230-400 mesh) column chromatography (40% EtOAc/Petroleum ether) to obtain a colorless oil (37.0 mg, 0.083 mmol, 99% yield). **FT-IR (Thin film):** 2922, 1769, 1634, 1155 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.90-7.88 (m, 2H), 7.87-7.84 (m, 2H), 7.78 (d, *J* = 5.6 Hz, 1H), 7.61-7.58 (m, 3H), 7.56-7.53 (m, 4H), 7.44 (dd, *J* = 8.6, 1.6 Hz, 1H), 6.17 (d, *J* = 5.6 Hz, 1H), 3.86-3.78 (m, 1H), 3.63-3.55 (m, 1H), 3.10-3.02 (m, 1H), 2.72-2.65 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.1, 158.2, 153.1, 133.4, 133.1, 133.0, 132.7, 131.5, 129.7, 129.5, 128.2, 127.7, 127.1, 127.0, 124.9, 124.2, 121.8, 120.6, 89.1, 51.6, 32.2; **HRMS (ESI+):** Calcd. for $C_{23}H_{18}N_4O_4SNa$ ($[M+Na]^+$): 469.0946, Found: 469.0943; **Optical rotation:** $[\alpha]_D^{24}$ +118.90 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 92:8 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2column (70:30 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 35.4 min, τ_{major} = 37.7 min). See Supporting Information: Part B for HPLC chromatograms.

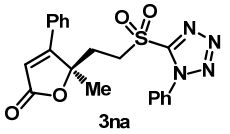
(*R*)-2-(2-((1-Phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)-[2,2'-bifuran]-5(2*H*)-one (3ma):



3ma

Purified by silica gel (230-400 mesh) column chromatography (40% EtOAc/Petroleum ether) to obtain a white solid (32.0 mg, 0.083 mmol, 99% yield). **m.p.** 99-102 °C; **FT-IR (Thin film):** 2922, 1771,1764, 1629, 1152 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.67-7.65 (m, 2H), 7.63-7.57 (m, 4H), 7.45 (s, 1H), 6.43 (d, *J* = 3.2 Hz, 1H), 6.38 (d, *J* = 3.2 Hz, 1H), 6.25 (d, *J* = 5.6 Hz, 1H), 3.83-3.71 (m, 2H), 3.04-2.97 (m, 1H), 2.70-2.62 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 170.6, 155.1, 153.0, 148.1, 143.9, 132.7, 131.6, 129.8, 124.9, 122.3, 110.8, 108.8, 84.7, 51.2, 29.3; **HRMS (ESI+):** Calcd. for $C_{17}H_{14}N_4O_5SNa$ ($[M+Na]^+$): 409.0583, Found: 409.0582; **Optical rotation:** $[\alpha]_D^{24}$ +27.82 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 85:15 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (80:20 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 22.8 min, τ_{major} = 29.7 min). See Supporting Information: Part B for HPLC chromatograms.

(*R*)-5-Methyl-4-phenyl-5-(2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)furan-2(5*H*)-one

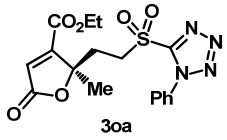


3na

(3na): Purified by silica gel (230-400 mesh) column chromatography (30% EtOAc/Petroleum ether) to obtain a colorless oil (34.0 mg, 0.080 mmol, 96% yield). **FT-IR (Thin film):** 1752, 1609, 1151 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.64-7.62 (m, 2H), 7.60-7.56 (m, 5H), 7.52-7.51

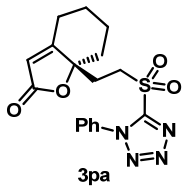
(m, 3H), 6.34 (s, 1H), 3.77-3.70 (m, 1H), 3.64-3.56 (m, 1H), 2.82-2.74 (m, 1H), 2.70-2.62 (m, 1H), 1.79 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 170.2, 169.2, 153.1, 132.7, 131.6, 131.5, 129.7, 129.5, 129.1, 127.4, 125.0, 116.1, 86.9, 51.4, 31.2, 25.1; **HRMS (ESI+):** Calcd. For $C_{20}H_{18}N_4O_4SNa$ ($[M+Na]^+$): 433.0946, Found: 433.0942; **Optical rotation:** $[\alpha]_D^{24}$ –8.24 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 83:17 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (70:30 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 42.2 min, τ_{major} = 55.8 min). See Supporting Information: Part B for HPLC chromatograms.

(*R*)-Ethyl-2-methyl-5-oxo-2-(2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)-2,5-dihydrofuran-3-carboxylate (3oa): Purified by silica gel (230-400 mesh) column chromatography (40% EtOAc/Petroleum ether) to obtain a colorless oil (34.0 mg, 0.084 mmol, 99% yield). **FT-IR (Thin film):** 2922, 1766, 1153 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.68-7.66 (m, 2H), 7.63-7.59 (m, 3H), 6.72 (s, 1H), 4.44-4.36 (m, 2H), 3.75-3.52 (m, 2H), 2.74-2.59 (m, 2H), 1.70 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 168.8, 160.3, 159.0, 153.0, 132.8, 131.5, 129.8, 127.4, 124.9, 86.7, 62.7, 51.0, 30.1, 24.1, 14.0; **HRMS (ESI+):** Calcd. for $C_{17}H_{18}N_4O_6SNa$ ($[M+Na]^+$): 429.0845, Found: 429.0847; **Optical rotation:** $[\alpha]_D^{24}$ –10.5 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 81:19 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (80:20 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 15.1 min, τ_{major} = 25.5 min). See Supporting Information: Part B for HPLC chromatograms.



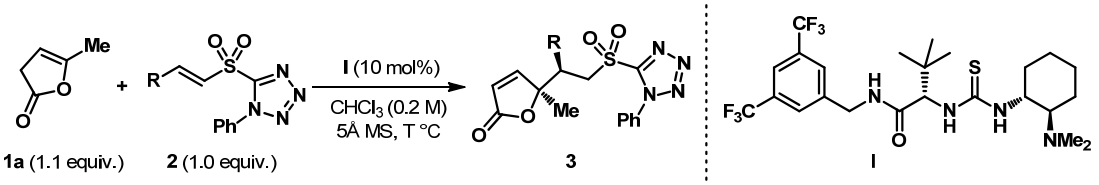
3oa

(*R*)-7a-(2-((1-Phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)-5,6,7,7a-tetrahydrobenzofuran-2(4*H*)-one (3pa): Purified by silica gel (230-400 mesh) column chromatography (40% EtOAc/Petroleum ether) to obtain a colorless oil (31.0 mg, 0.083 mmol, 99% yield). **FT-IR (Thin film):** 2929, 1750, 1653, 1152 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.68-7.65 (m, 2H), 7.63-7.58 (m, 3H), 5.80 (s, 1H), 3.71-3.63 (m, 1H), 3.57-3.51 (m, 1H), 2.86 (d, *J* = 12.5 Hz, 1H), 2.55-2.44 (m, 2H), 2.38-2.32 (m, 2H), 2.11 (d, *J* = 12.5 Hz, 1H), 1.89-1.84 (m, 1H), 1.72 (s, 1H), 1.56-1.53 (m, 1H), 1.42-1.32 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 173.3, 171.2, 153.1, 132.7, 131.5, 129.7, 124.9, 114.0, 86.0, 50.8, 38.7, 27.4, 27.3, 27.2, 22.1; **HRMS (ESI+):** Calcd. for $C_{17}H_{18}N_4O_4SNa$ ($[M+Na]^+$): 397.0946, Found: 397.0943; **Optical rotation:** $[\alpha]_D^{24}$ +0.73 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 83:17 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (70:30 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 14.2 min, τ_{major} = 15.6 min). See Supporting Information: Part B for HPLC chromatograms.



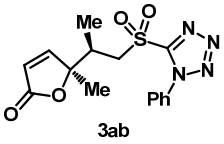
3pa

Scope of the enantioselective vinylogous Michael addition with respect to vinyl sulfones 2:



The same procedure as described above has been followed except for the reaction temperature. The specific temperature in which each reaction has been conducted is provided below.

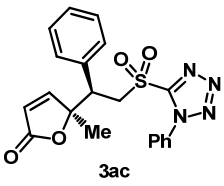
(*S*)-5-Methyl-5-((*R*)-1-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)propan-2-yl)furan-2(5*H*)-one



3ab

(3ab): This reaction was carried out in 0.077 mmol scale at −40 °C for 96 h. Purified by silica gel (230-400 mesh) column chromatography (40% EtOAc/Petroleum ether) to obtain a colorless oil (25.0 mg, 0.072 mmol, 93% yield). **FT-IR (Thin film):** 2921, 1750, 1523, 1154 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.67-7.65 (m, 2H), 7.65-7.58 (m, 3H), 7.42 (d, *J* = 5.6 Hz, 1H), 6.13 (d, *J* = 5.6 Hz, 1H), 4.04 (dd, *J* = 14.8, 1.8 Hz, 1H), 3.49 (dd, *J* = 14.8, 9.7 Hz), 2.76-2.68 (m, 1H), 1.57 (s, 3H), 1.20 (d, *J* = 6.9 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.3, 157.9, 153.6, 132.8, 131.6, 129.7, 125.1, 121.9, 89.3, 57.5, 34.9, 22.6, 15.6; **HRMS (ESI+):** Calcd. for $C_{15}H_{16}N_4O_4SNa$ ($[M+Na]^+$): 371.0790, Found: 371.0794; **Optical rotation:** $[\alpha]_D^{24}$ −1.9 (*c* 0.5, $CHCl_3$) for an enantiomerically enriched sample with 90:10 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1column (70:30 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 11.0 min, τ_{major} = 12.6 min). See Supporting Information: Part B for HPLC chromatograms.

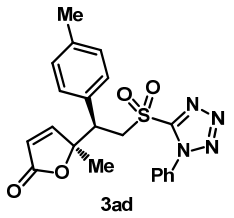
(*S*)-5-Methyl-5-((*R*)-1-phenyl-2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)furan-2(5*H*)-one



3ac

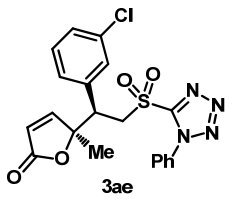
(3ac): This reaction was carried out in 0.064 mmol scale at −40 °C for 57 h. Purified by silica gel (230-400 mesh) column chromatography (40% EtOAc/Petroleum ether) to obtain a colorless oil (25.0 mg, 0.061 mmol, 95% yield). **FT-IR (Thin film):** 2924, 2360, 1762, 1523, 1155 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.60-7.56 (m, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.26-7.24 (m, 4H), 7.07-7.05 (m, 2H), 5.86 (d, *J* = 5.7 Hz, 1H), 4.27-4.12 (m, 2H), 3.81-3.78 (m, 1H), 1.55 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.2, 157.8, 153.3, 134.8, 132.6, 131.4, 129.5, 129.0, 128.6, 128.4, 125.2, 121.7, 88.8, 56.6, 46.9, 23.5; **HRMS (ESI+):** Calcd. for $C_{20}H_{18}N_4O_4SNa$ ($[M+Na]^+$): 433.0946, Found: 433.0945; **Optical rotation:** $[\alpha]_D^{24}$ −33.9 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 93:7 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (70:30 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{major} = 12.1 min, τ_{minor} = 13.7 min). See Supporting Information: Part B for HPLC chromatograms.

(*S*)-5-Methyl-5-((*R*)-2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)-1-(p-tolyl)ethyl)furan-2(5*H*)-one (3ad): This reaction was carried out at 0 °C for 96 h. Purified by silica gel (230-400 mesh) column chromatography (40% EtOAc/Petroleum ether) to obtain a colorless oil (11.0 mg, 0.026 mmol, 31% yield). **FT-IR (Thin film):** 2921, 1766, 1351, 1157 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.60-7.56 (m, 1H), 7.54-7.50 (m, 2H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 5.6 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 2H), 6.94 (d, *J* = 7.7 Hz, 2H), 5.88 (d, *J* = 5.6 Hz, 1H), 4.19 (d, *J* = 6.6 Hz, 2H), 3.76 (t, *J* = 6.6 Hz, 1H), 2.29 (s, 3H), 1.54 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.3, 157.9, 153.4, 138.5, 132.7, 131.7, 131.4, 129.7, 129.5, 128.2, 125.2, 121.7, 88.9, 56.7, 46.5, 23.5, 21.0; **HRMS (ESI+):** Calcd. for $C_{21}H_{20}N_4O_4SNa$ ($[M+Na]^+$): 447.1103, Found: 447.1106; **Optical rotation:** $[\alpha]_D^{24}$ –33.23 (*c* 0.9, $CHCl_3$) for an enantiomerically enriched sample with 89:11 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (80:20 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{major} = 17.7 min, τ_{minor} = 24.5 min). See Supporting Information: Part B for HPLC chromatograms.



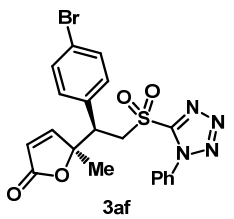
3ad

(*S*)-5-((*R*)-1-(3-Chlorophenyl)-2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)-5-methylfuran-2(5*H*)-one (3ae): This reaction was carried out at 0 °C for 4 h. Purified by silica gel (230-400 mesh) column chromatography (40% EtOAc/Petroleum ether) to obtain a colorless thick oil (36.0 mg, 0.081 mmol, 96% yield). **FT-IR (Thin film):** 2926, 1761, 1361, 1156 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.61-7.52 (m, 3H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.26-7.18 (m, 3H), 7.05 (s, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 5.88 (d, *J* = 5.6 Hz, 1H), 4.27-4.17 (m, 2H), 3.79-3.75 (m, 1H), 1.57 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 170.9, 157.6, 153.2, 136.9, 134.8, 132.5, 131.5, 130.3, 129.6, 128.9, 128.8, 126.3, 125.1, 121.9, 88.4, 56.5, 46.5, 23.4; **HRMS (ESI+):** Calcd. for $C_{20}H_{17}ClN_4O_4SNa$ ($[M+Na]^+$): 467.0557, Found: 467.0559; **Optical rotation:** $[\alpha]_D^{24}$ –35.3 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 88:12 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IC column (80:20 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{major} = 15.5 min, τ_{minor} = 20.2 min). See Supporting Information: Part B for HPLC chromatograms.



3ae

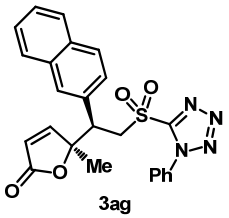
(*S*)-5-((*R*)-1-(4-Bromophenyl)-2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)-5-methylfuran-2(5*H*)-one (3af): This reaction was carried out at 0 °C and continued for 72 h. Purified by silica gel (230-400 mesh) column chromatography (40% EtOAc/Petroleum ether) to get a crystalline solid (34.0 mg, 0.069 mmol, 83% yield). **m.p.** 176 °C; **FT-IR (Thin film):** 2922, 1733, 1652, 1187 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.61-7.52 (m, 3H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.22 (d, *J* =



3af

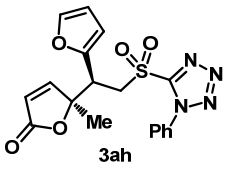
5.6 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 2H), 5.87 (d, *J* = 5.6 Hz, 1H), 4.33 (dd, *J* = 15.0, 2.2 Hz, 1H), 4.24-4.18 (m, 1H), 3.78 (dd, *J* = 10.4, 1.8 Hz, 1H), 1.59 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.0, 157.7, 153.3, 134.0, 132.6, 132.2, 131.5, 129.9, 129.6, 125.0, 122.8, 121.9, 88.4, 56.6, 46.2, 23.4; **HRMS (ESI+):** Calcd. for $C_{20}H_{17}BrN_4O_4SNa$ ($[M+Na]^+$): 511.0052, Found: 511.0053; **Optical rotation:** $[\alpha]_D^{24}$ –59.3 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 84:16 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (80:20 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{major} = 37.3 min, τ_{minor} = 43.3 min). See Supporting Information: Part B for HPLC chromatogram.

(*S*)-5-Methyl-5-((*R*)-1-(naphthalen-2-yl)-2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)furan-2(5*H*)-one (3ag): This reaction was carried out at 0 °C for 80 h. Purified by silica gel (230-400 mesh) column chromatography (40% EtOAc/Petroleum ether) to obtain a colorless oil (34.0 mg, 0.074 mmol, 88% yield). **m.p** 167 °C; **FT-IR (Thin film):** 2924, 1762, 1599, 1156 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.81-7.78 (m, 1H), 7.72 (d, *J* = 7.7 Hz, 2H), 7.52-7.50 (m, 4H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 5.6 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 3H), 5.83 (d, *J* = 5.6 Hz, 1H), 4.44-4.37 (m, 1H), 4.30-4.25 (m, 1H), 3.98-3.95 (m, 1H), 1.58 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.1, 157.8, 153.2, 132.9, 132.8, 132.4, 132.0, 131.3, 129.3, 128.9, 128.2, 127.9, 127.7 126.9, 126.8, 125.0, 121.7, 88.9, 56.7, 47.2, 23.6; **HRMS (ESI+):** Calcd. for $C_{24}H_{20}N_4O_4SNa$ ($[M+Na]^+$): 483.1103, Found: 483.1115; **Optical rotation:** $[\alpha]_D^{24}$ –42.9 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 87:13 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (70:30 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 33.2 min, τ_{major} = 37.5 min). See Supporting Information: Part B for HPLC chromatograms.



3ag

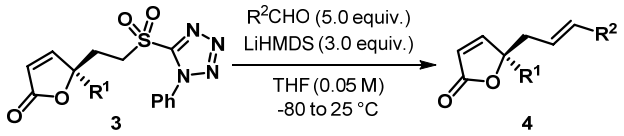
(*S*)-5-((*R*)-1-(Furan-2-yl)-2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)-5-methylfuran-2(5*H*)-one (3ah): This reaction was carried out at 0 °C for 36 h. Purified by silica gel (230-400 mesh) column chromatography (40% EtOAc/Petroleum ether) to obtain a colorless oil (32.0 mg, 0.079 mmol, 95% yield). **FT-IR (Thin film):** 2920, 1760, 1600, 1151 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.63-7.50 (m, 6H), 7.33 (s, 1H), 6.22-6.21 (m,1H), 6.16 (d, *J* = 3.1 Hz, 1H), 6.08 (d, *J* = 5.7 Hz, 1H), 4.12 (dd, *J* = 14.5, 11.5 Hz, 1H), 3.98 (dd, *J* = 11.5, 2.1 Hz, 1H), 3.80 (dd, *J* = 14.5, 2.1 Hz, 1H), 1.43 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.0, 157.7, 153.0, 147.4, 143.3, 132.7, 131.5, 129.6, 125.2, 122.1, 110.6, 110.5, 88.0, 54.4, 40.9, 23.4; **HRMS (ESI+):** Calcd. for $C_{18}H_{16}N_4O_5SNa$ ($[M+Na]^+$): 423.0739, Found: 423.0739; **Optical rotation:** $[\alpha]_D^{24}$ –41.15 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 87:13 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IC column (80:20 *n*-Hexane/EtOH, 1.0 mL/min, 20



3ah

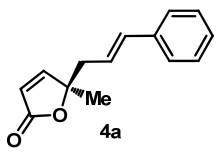
°C, 210 nm, τ_{major} = 26.9 min, τ_{minor} = 30.9 min). See Supporting Information: Part B for HPLC chromatograms.

6. General procedure for the formal γ-allylation of butenolides through Julia-Kocienski olefination of 3:

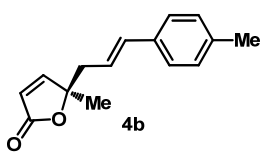


To a solution of **3** (1.0 equiv.) in 0.5 mL dry THF, was added freshly prepared LiHMDS (3.0 equiv.) [prepared by adding 2.0 M solution of *n*-BuLi in hexane drop wise over a period of 5 min to a pre-cooled solution of HMDS in THF at –20 °C and then stirring at –10 °C for 30 min prior to use] drop wise over a period of 5 min at –78 °C and stirred at that temperature for 45 min. Then a solution of aldehyde (5.0 equiv.) in 0.5 mL dry THF was added drop wise over a period of 5 min. The resulting solution was stirred at –78 °C for 40 min and then it was slowly brought it to 25 °C and stirred until TLC (20% EtOAc/Petroleum ether) shows complete consumption of **3**. The reaction mixture was then diluted with 10 mL of saturated aqueous NH_4Cl solution. The aqueous phase was extracted with CH_2Cl_2 (3 × 6 mL). Organic phase was dried over anh. Na_2SO_4 and concentrated under reduced pressure.

(*R*)-5-Cinnamyl-5-methylfuran-2(5*H*)-one (4a): This reaction was carried out with 30.0 mg (0.089 mmol) of **3aa**. Purified by silica gel (230-400 mesh) column chromatography (4% EtOAc/Petroleum ether) to obtain a colorless oil (19.0 mg, 0.088 mmol, 99% yield). **FT-IR (Thin film):** 3584, 1749, 1018 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.40 (d, *J* = 5.5 Hz, 1H), 7.34-7.28 (m, 4H), 7.26-7.22 (m, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.11-6.03 (m, 2H), 2.65 (d, *J* = 7.3 Hz, 2H), 1.51 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 172.2, 160.1, 136.6, 134.8, 128.5, 127.6, 126.2, 122.3, 120.9, 88.5, 42.1, 23.5; **HRMS (ESI+):** Calcd. for $C_{14}H_{14}O_2Na$ ($[M+Na]^+$): 237.0891, Found: 237.0895; **Optical rotation:** $[\alpha]_D^{24}$ –95.5 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 90:10 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 9.2 min, τ_{major} = 10.0 min). See Supporting Information: Part B for HPLC chromatograms.

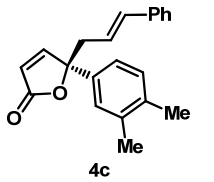


(*R*,*E*)-5-Methyl-5-(3-(*p*-tolyl)allyl)furan-2(5*H*)-one (4b): This reaction was carried out with 26.0 mg (0.077 mmol) of **3aa**. Purified by silica gel (230-400 mesh) column chromatography (4% EtOAc/Petroleum ether) to obtain a colorless oil (6.0 mg, 0.026 mmol, 34% yield). **FT-IR (Thin film):** 1752, 1019 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.40 (d, *J* = 5.5 Hz,



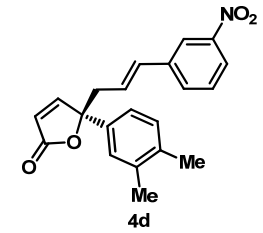
1H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 6.42 (d, *J* = 15.7 Hz, 1H), 6.04-5.98 (m, 2H), 2.64 (d, *J* = 7.3 Hz, 2H), 2.33 (s, 3H); 1.50 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 172.3, 160.2, 137.6, 134.7, 133.8, 129.7, 129.3, 126.1, 121.2, 120.9, 115.2, 88.6, 42.2, 23.5, 21.1; **HRMS (ESI+):** Calcd. for $C_{15}H_{16}O_2Na$ ($[M+Na]^+$): 251.1048, Found: 251.1050; **Optical rotation:** $[\alpha]_D^{24}$ –66.2 (*c* 0.5, $CHCl_3$) for an enantiomerically enriched sample with 90:10 er, assuming no erosion in er during the reaction.

(*R*)-5-Cinnamyl-5-(3,4-dimethylphenyl)furan-2(5*H*)-one (4c): This reaction was carried out with 30.0 mg (0.072 mmol) of **3ka**. Purified by silica gel (230-400 mesh) column chromatography (2% EtOAc/Petroleum ether) to obtain a colorless oil (22.0 mg, 0.072 mmol, 99% yield). **FT-IR (Thin film):** 1756, 1018 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.67 (d, *J* = 5.6 Hz, 1H), 7.28-7.26 (m, 4H), 7.25-7.18 (m, 2H), 7.16-7.11 (m, 2H), 6.44 (d, *J* = 16.1 Hz, 1H), 6.07 (d, *J* = 5.6 Hz, 1H), 6.02-5.94 (m, 1H), 3.05-2.91 (m, 2H), 2.27 (d, *J* = 7.7 Hz, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 172.2, 159.0, 137.2, 136.9, 136.7, 135.9, 134.9, 129.9, 128.5, 127.6, 126.9, 126.2, 122.5, 121.9, 120.4, 91.0, 43.2, 19.9, 19.4; **HRMS (ESI+):** Calcd. for $C_{21}H_{20}O_2Na$ ($[M+Na]^+$): 327.1361, Found: 327.1361; **Optical rotation:** $[\alpha]_D^{24}$ +52.54 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 93:7 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (95:5 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 13.5 min, τ_{major} = 15.1 min). See Supporting Information: Part B for HPLC chromatograms.



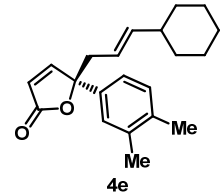
4c

(*R*,*E*)-5-(3,4-Dimethylphenyl)-5-(3-(3-nitrophenyl)allyl)furan-2(5*H*)-one (4d): This reaction was carried out with 33.0 mg (0.077 mmol) of **3ka**. Purified by silica gel (230-400 mesh) column chromatography (2% EtOAc/Petroleum ether) to obtain a colorless oil (19.0 mg, 0.054 mmol, 70% yield). **FT-IR (Thin film):** 1754, 1526, 1018 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.09 (s, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 5.5 Hz, 1H), 7.61-7.57 (m, 1H), 7.50-7.43 (m, 1H), 7.18-7.09 (m, 3H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.16-6.09 (m, 2H), 3.11-3.05 (m, 1H), 2.97-2.92 (m, 1H), 2.27 (d, *J* = 7.7 Hz, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 172.0, 158.8, 148.5, 138.4, 137.4, 137.1, 135.5, 132.8, 132.0, 130.1, 129.4, 126.1, 125.5, 122.4, 122.2, 120.9, 120.4, 90.6, 43.0, 19.9, 19.4; **HRMS (ESI+):** Calcd. for $C_{21}H_{19}NO_4Na$ ($[M+Na]^+$): 372.1212, Found: 372.1213; **Optical rotation:** $[\alpha]_D^{24}$ +60.6 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 93:7 er, assuming no erosion in er during the reaction.



4d

(*R*,*E*)-5-(3-Cyclohexylallyl)-5-(3,4-dimethylphenyl)furan-2(5*H*)-one (4e): This reaction was carried out with 25.0 mg (0.058 mmol) of **3ka**. Purified by silica gel (230-400 mesh) column chromatography (4% EtOAc/Petroleum ether) to obtain a yellow thick oil (6.0 mg, 0.019 mmol, 33% yield). **FT-IR (Thin film):** 3584, 2376,2313, 1751, 1511, 1019 cm^{-1}; **^{1}H-NMR (400 MHz,**

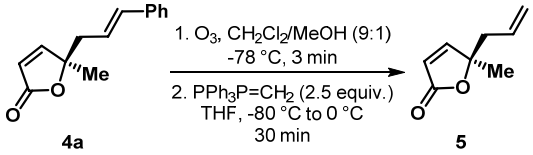


4e

$CDCl_3$): δ 7.58 (d, *J* = 5.5 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 1H), 6.05 (d, *J* = 5.6 Hz, 1H), 5.46-5.41 (m, 1H), 5.19-5.05 (m, 1H), 2.79-2.67 (m, 2H), 2.25 (d, *J* = 6.4 Hz, 1H), 1.88-1.86 (m, 1H), 1.68-1.59 (m, 4H), 1.26-1.09 (m, 4H), 1.03-0.94 (m, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 172.4, 159.0, 142.7, 137.0, 136.7, 129.8, 126.3, 122.5, 120.3, 91.1, 42.8, 40.6, 32.9, 32.8, 26.0, 25.9, 19.9, 19.4; **HRMS (ESI+):** Calcd. for $C_{12}H_{26}O_2Na$ ($[M+Na]^+$): 333.1830, Found: 333.1828; **Optical rotation:** $[\alpha]_D^{24}$ +43.3 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 93:7 er, assuming no erosion in er during the reaction.

7. Synthetic elaboration of γ-allylated butenolides:

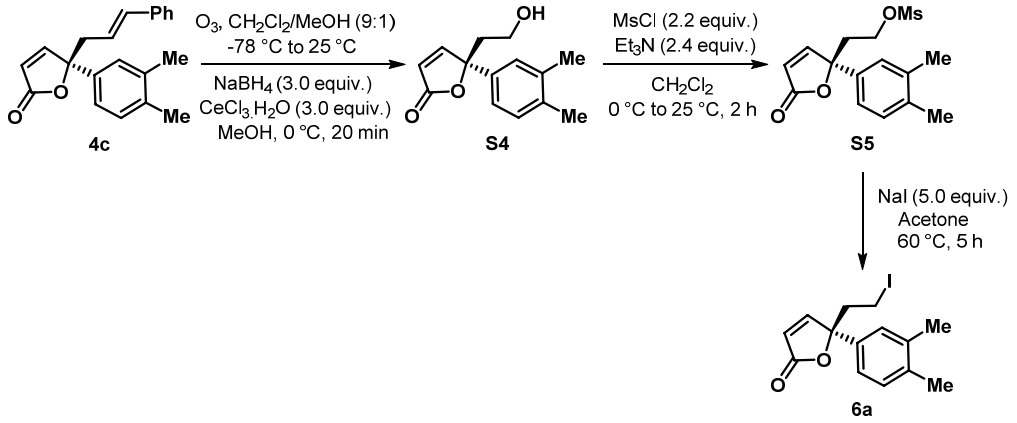
Preparation of 5 from 4a:



To a solution of **4a** (60.0 mg, 0.28 mmol) in 10 mL CH_2Cl_2/MeOH (9:1) at –78 °C ozone gas was bubbled until the reaction was complete (solution becomes blue within 3 min). Dimethylsulfide (0.1 mL) was then added to the reaction mixture at –78 °C, stirred for another 1 hour at 0 °C. The reaction mixture was passed through a short pad of celite, and eluted with CH_2Cl_2. The filtrate was concentrated and used directly for the next step.

To a solution of methyltriphenylphosphonium bromide (720.0 mg, 2.01 mmol, 3.0 equiv.) in dry THF (6.0 mL) at –78 °C, *n*-BuLi (1.67 mL, 2.0 M in hexane, 1.67 mmol, 2.5 equiv.) was slowly added and the reaction mixture was stirred at –78 °C for 40 min. The mixture was warmed to 0 °C and stirred for another 40 min. A solution of crude aldehyde in dry THF (1.5 mL) was introduced drop wise, and the resulting mixture was stirred at 0°C until TLC (30% EtOAc/Petroleum ether) revealed complete conversion of aldehyde (<1 h). The reaction mixture was filtered through a short pad of silica gel, and eluted with 100 mL 40% EtOAc/Petroleum ether. Purified by silica gel (230-400 mesh) column chromatography (10% EtOAc/Petroleum ether) to obtain a colorless oil (30.0 mg, 0.224 mmol, 80% yield). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.35 (d, *J* = 5.6 Hz, 1H), 6.03 (d, *J* = 5.6 Hz, 1H), 5.73-5.62 (m, 1H), 5.17-5.10 (m, 2H), 2.50 (d, *J* = 7.4 Hz, 2H), 1.46 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 173.1, 160.0, 131.1, 120.9, 120.1, 88.1, 42.9, 23.5; **HRMS (ESI+):** Calcd. for $C_8H_{10}O_2Na$ ($[M+Na]^+$): 161.0578, Found: 161.0576; **Optical rotation:** $[\alpha]_D^{24}$ –42.43 (*c* 0.62, $CHCl_3$) for an enantiomerically enriched sample with 90:10 er, assuming no erosion in er during the reaction.

Conversion of 4c to γ-iodoethyl butenolide 6a:



Ozonolysis was carried out following the general procedure as described above. The reaction was performed with 18.0 mg of **4c** (0.060 mmol).

After ozonolysis, aldehydes were taken in an oven dried 10 mL round bottom flask under argon atmosphere along with 0.5 mL dry MeOH. It was cooled to 0 °C followed by the addition of hydrated cerium(III)chloride (67.0 mg, 0.180 mmol, 3.0 equiv.). After 5 min sodium borohydride (7.0 mg, 0.18 mmol, 3.0 equiv.) was added portion wise. Add 6 mL 1(N) HCl solution (aq.) to it. Extract the aqueous phase with Et_2O (3 × 7 mL). The combined organic phase was dried over anh.Na_2SO_4 and concentrated under reduced pressure to get **S4** as yellow oil which was used in the next step without any further purification or characterization.

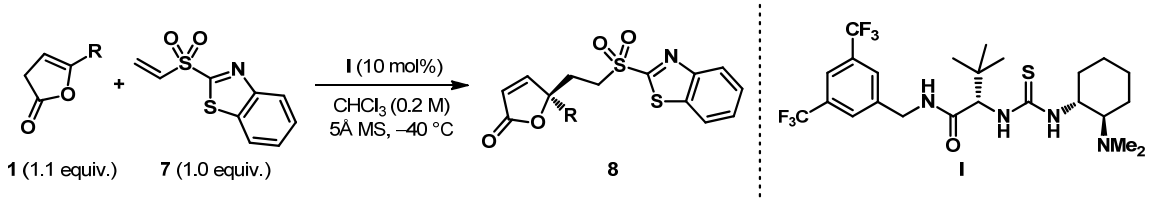
The yellow oil was taken in 0.6 mL dry CH_2Cl_2 and cooled it to 0 °C. To this was added methanesulfonyl chloride (0.010 mL, 0.132 mmol, 2.2 equiv.) and triethylamine (0.02 mL, 0.144 mmol, 2.4 equiv.) sequentially at 0 °C. The resulting reaction mixture was allowed to warm to room temperature and stir for 2 h. Solvent was removed under reduced pressure and the residue was diluted with 10 mL CH_2Cl_2 and 6 mL of distilled water. Organic phase was separated from aqueous phase. The aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phase was dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain **S5** as a thick yellow oil which was used in the next step without any further purification or characterization.

The thick yellow oil was taken in 0.6 mL dry acetone. To this was added sodium iodide (44.0 mg, 0.300 mmol, 5.0 equiv.) and the resulting mixture was heated at 60 °C for 5 h. The reaction mixture was cooled to r.t. and diluted with water (5 mL). Organic phase was separated from aqueous phase. The aqueous phase was extracted with CH_2Cl_2 (3 × 6 mL). The combined organic phase was dried over anh. Na_2SO_4 and concentrated under reduced pressure. The reaction mixture was purified by silica gel (230-400 mesh) column chromatography (10% EtOAc/Petroleum ether) to obtain a yellow oil (16.0 mg, 0.047 mmol, 78% yield). **FT-IR (Thin film):** 2921,1761, 1019 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.63

(d, *J* = 5.5 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.11 (s, 1H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.07 (d, *J* = 5.5 Hz, 1H), 3.08 (dt, *J* = 11.8, 5.0 Hz, 1H), 2.93 (dt, *J* = 11.8, 4.6 Hz, 1H), 2.76 (dt, *J* = 14.1, 4.6 Hz, 1H), 2.51 (dt, *J* = 14.1, 5.0 Hz, 1H), 2.25 (d, *J* = 8.4 Hz, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.8, 158.5, 137.6, 137.2, 134.4, 130.2, 125.8, 122.2, 119.8, 91.8, 44.3, 19.9, 19.4, –4.1; **HRMS (ESI+):** Calcd. for $C_{14}H_{15}IO_2Na$ ($[M+Na]^+$): 365.0015, Found: 365.0015; **Optical rotation:** $[\alpha]_D^{24}$ +89.7 (*c* 2.8, $CHCl_3$) for an enantiomerically enriched sample with 93:7 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 7.8 min, τ_{major} = 8.3 min). See Supporting Information: Part B for HPLC chromatograms.

8. Scope with respect to vinyl BT-sulfone and vinyl phenyl selenone:

General procedure for the catalytic enantioselective vinylogous Michael addition of deconjugated butenolides to vinyl BT-sulfones:

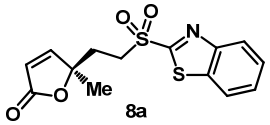


1 (1.1 equiv.) **7** (1.0 equiv.) **8** **I**

In an oven and vacuum dried Schlenk tube, 80 mg 5Å MS (activated by heating at 200 °C under high vacuum for 1 h prior to use), vinyl BT-sulfone **7** (18.0 mg, 0.084 mmol, 1.0 equiv.) and the catalyst **I** (4.3 mg, 0.008 mmol, 0.1 equiv.) were taken under argon atmosphere. Dry $CHCl_3$ (0.2 mL) was added to it and the solution was cooled to –40 °C under a positive argon pressure. A solution of **1** (0.092 mmol, 1.1 equiv.) in 0.2 mL of dry $CHCl_3$ was added to it and the resulting mixture was stirred at –40 °C until TLC (40% EtOAc/Petroleum ether) revealed complete conversion of **7**. The reaction mixture was warmed to r.t., solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography.

The corresponding racemic Michael adducts (*rac*-**8**) were prepared following general procedure as described above for *rac*-**3**.

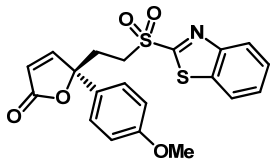
(*R*)-5-(2-(Benzo[*d*]thiazol-2-ylsulfonyl)ethyl)-5-methylfuran-2(5*H*)-one (8a): Purified by silica gel (230-400 mesh) column chromatography (50% EtOAc/Petroleum ether) to afford a white solid (26.0 mg, 0.080 mmol, 96% yield). **m.p.** 127 °C; **FT-IR (Thin film):** 3584, 2375, 2313, 1755, 1018 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.22 (d, *J* = 8.2 Hz, 1H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.66-7.59 (m, 2H), 7.38 (d, *J* = 5.6 Hz, 1H), 6.10 (d, *J* = 5.6 Hz, 1H), 3.54 (dt, *J* = 14.3, 4.8 Hz, 1H), 3.36 (dt, *J* = 12.1, 4.2 Hz, 1H), 2.50 (dt, *J* =



8a

14.3, 4.8 Hz, 1H), 2.33 (dt, *J* = 12.1, 4.2 Hz, 1H), 1.53 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.3, 164.9, 158.7, 152.5, 136.6, 128.3, 127.8, 125.5, 122.3, 121.8, 86.5, 49.6, 30.2, 24.0; **HRMS (ESI+):** Calcd. for $C_{14}H_{13}NO_4S_2Na$ ($[M+Na]^+$): 346.0184, Found: 346.0186; **Optical rotation:** $[\alpha]_D^{24}$ –24.2 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 95:5 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (70:30 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 30.8 min, τ_{major} = 33.2 min). See Supporting Information: Part B for HPLC chromatograms.

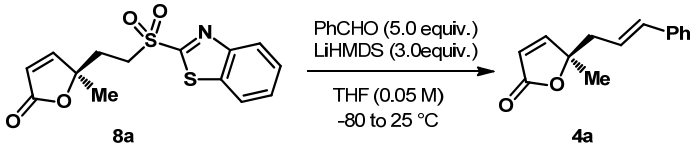
(*R*)-5-(2-(Benzo[*d*]thiazol-2-ylsulfonyl)ethyl)-5-(4-methoxyphenyl)furan-2(5*H*)-one (8b):



8b

Purified by silica gel (230-400 mesh) column chromatography (50% EtOAc/Petroleum ether) to afford a white solid (34.0 mg, 0.082 mmol, 98% yield). **m.p.** 124 °C; **FT-IR (Thin film):** 1764, 1325, 1148, 1026 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.20 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.66-7.58 (m, 3H), 7.23 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 1H), 6.07 (d, *J* = 5.5 Hz, 1H), 3.78 (s, 3H), 3.57 (dt, *J* = 14.2, 4.4 Hz, 1H), 3.38 (dt, *J* = 12.4, 4.0 Hz, 1H), 2.79 (dt, *J* = 14.2, 4.0 Hz, 1H), 2.50 (dt, *J* = 12.4, 4.4 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.3, 164.8, 159.8, 158.6, 152.5, 136.6, 128.2, 127.8, 126.0, 125.5, 122.3, 120.0, 114.6, 89.0, 55.3, 50.0, 32.0; **HRMS (ESI+):** Calcd. for $C_{20}H_{17}NO_5S_2Na$ ($[M+Na]^+$): 438.0446, Found: 438.0449; **Optical rotation:** $[\alpha]_D^{24}$ +285.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 95:5 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (70:30 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{major} = 10.7 min, τ_{minor} = 12.8 min). See Supporting Information: Part B for HPLC chromatograms.

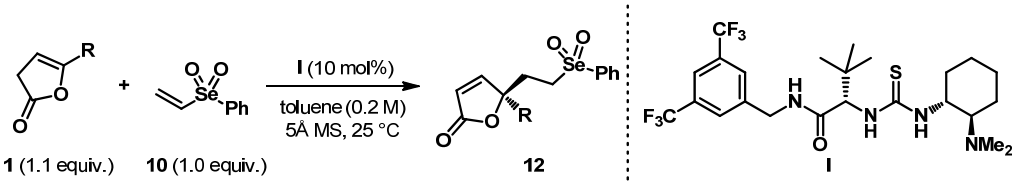
Determination of the absolute configuration of 8a:



8a **4a**

Absolute configuration of compound **8a** was determined by converting it to compound **4a** following general Julia-Kocienski olefination procedure described above and comparing the optical rotation and HPLC chromatograms with those of (*R*)-**4a** obtained from (*R*)-**3aa**. **Optical rotation:** $[\alpha]_D^{24}$ –100.6 (*c* 0.2, $CHCl_3$) for an enantiomerically enriched sample with 95:5 er. From the direction of optical rotation, the absolute configuration of **4a** was found to be (*R*). Therefore, the absolute configuration of **8a** can also be taken as (*R*).

General procedure for the catalytic enantioselective vinylogous Michael addition of deconjugated butenolides 1 to vinyl phenyl selenone 10:

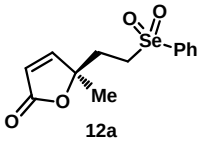


1 (1.1 equiv.) **10** (1.0 equiv.) **12** **I**

In an oven and vacuum dried Schlenk tube, 80 mg 5Å MS (activated by heating at 200 °C under high vacuum for 1 h prior to use), vinyl phenyl selenone **10** (18.0 mg, 0.084 mmol, 1.0 equiv.) and catalyst **I** (4.3 mg, 0.008 mmol, 0.1 equiv.) were taken in dry $CHCl_3$ (0.2 mL) under argon atmosphere. To this was added a solution of compound **1** (0.092 mmol, 1.1 equiv.) in 0.2 mL of dry $CHCl_3$ and the resulting mixture was stirred at 25 °C until TLC (1% $MeOH/CH_2Cl_2$) revealed complete conversion of **10** (3 days). Solvent was removed under reduced pressure and the residue was purified by column chromatography.

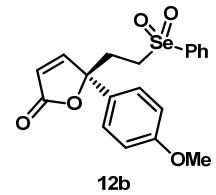
The corresponding racemic Michael adducts (*rac*-12) were prepared following general procedure as described above for *rac*-**3**.

(*R*)-5-Methyl-5-(2-(phenylselenonyl)ethyl)furan-2(5*H*)-one (12a): Purified by silica gel (230-400 mesh) column chromatography (3% $MeOH/CH_2Cl_2$) to afford a colorless oil (20.0 mg, 0.064 mmol, 76% yield). **FT-IR (Thin film):** 3584, 2312, 1750, 1018 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.75-7.72 (m, 1H), 7.66 (t, *J* = 7.5 Hz, 2H), 7.43-7.42 (m, 1H), 6.07 (d, *J* = 5.6 Hz, 1H), 3.47-3.40 (m, 1H), 3.32-3.25 (m, 1H), 2.55-2.48 (m, 1H), 2.44-2.36 (m, 1H), 1.52 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.2, 158.7, 140.9, 130.4, 126.9, 121.8, 86.6, 53.8, 29.9, 24.0; **HRMS (ESI+):** Calcd. for $C_{13}H_{14}O_4SeNa$ ($[M+Na]^+$): 336.9950, Found: 336.9951; **Optical rotation:** $[\alpha]_D^{24}$ −29.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 92:8 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IC column (40:60 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{major} = 20.1 min, τ_{minor} = 28.5 min). See Supporting Information: Part B for HPLC chromatograms.



12a

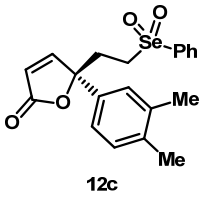
(*R*)-5-(4-Methoxyphenyl)-5-(2-(phenylselenonyl)ethyl)furan-2(5*H*)-one (12b): Purified by silica gel (230-400 mesh) column chromatography (3% $MeOH/CH_2Cl_2$) to afford a colorless oil (27.0 mg, 0.067 mmol, 79% yield). **FT-IR (Thin film):** 2312, 1760, 1512, 938 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.26 (d, *J* = 7.4 Hz, 2H), 8.09-7.97 (m, 4H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 6.42 (d, *J* = 5.3 Hz, 1H), 4.14 (s, 3H), 3.82 (dt, *J* = 12.0, 3.9 Hz, 1H), 3.62 (dt, *J* = 12.0, 3.5 Hz, 1H), 3.18 (dt, *J* = 13.6, 3.9 Hz, 1H), 2.88 (dt, *J* = 13.6, 4.2 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.2, 159.9, 158.5, 141.0, 134.6, 130.4, 128.0, 126.9, 126.0, 120.1, 114.7, 89.2, 55.3, 54.1, 31.7; **HRMS (ESI+):**



12b

Calcd. for $C_{19}H_{18}O_5SeNa$ ([M+Na]$^+$): 429.0212, Found: 429.0216; **Optical rotation:** $[\alpha]_D^{24}$ +89.4 (*c* 0.5, $CHCl_3$) for an enantiomerically enriched sample with 92:8 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IE column (40:60 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 23.9 min, τ_{major} = 29.4 min). See Supporting Information: Part B for HPLC chromatograms.

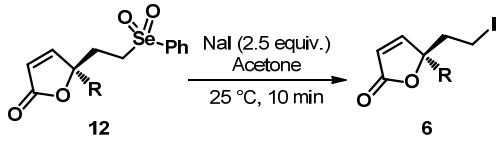
(*R*)-5-(3,4-Dimethylphenyl)-5-(2-(phenylselenonyl)ethyl)furan-2(5*H*)-one (12c): Purified by silica gel (100-200 mesh) column chromatography (1% MeOH/CH_2Cl_2) to afford a yellow oil (31.0 mg, 0.077 mmol, 92% yield). **FT-IR (Thin film):** 2362,1759 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.74-7.71 (m, 2H), 7.66- 7.62 (m, 3 H), 7.13 (d, *J* = 7.7 Hz, 1H), 7.07 (s, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.06 (d, *J* = 5.5 Hz, 1H), 3.48 (dt, *J* = 4.2, 12.2 Hz, 1H), 3.27 (dt, *J* = 12.2, 4.0 Hz, 1H), 2.82 (dt, *J* = 13.5, 4.2 Hz, 1H), 2.51 (dt, *J* = 13.5, 4.2 Hz, 1H), 2.23 (s, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.2, 158.6, 140.9, 137.9, 137.6, 134.6, 133.4, 130.5, 130.4, 126.9, 125.6, 121.9, 120.0, 89.3, 54.1, 31.7, 19.9, 19.4; **HRMS (ESI+):** Calcd. for $C_{20}H_{20}O_4SeNa$ ([M+Na]$^+$): 427.0419, Found: 427.0417; **Optical rotation:** $[\alpha]_D^{24}$ +67.9 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 91:9 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IE column (40:60 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 18.1 min, τ_{major} = 26.8 min). See Supporting Information: Part B for HPLC chromatograms.



12c

9. Synthetic transformations with vinyl selenone adducts:

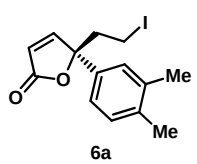
Replacement of the phenyl selenonyl group in 12 with iodide:



12 6

In an oven dried 10 mL round bottom flask, **12** (1.0 equiv.) was taken along with sodium iodide (2.5 equiv.) under argon atmosphere. To this was added 0.5 mL dry acetone and the reaction mixture was stirred at 25 °C for 10 min. The resulting mixture was diluted with water (5 mL). Organic phase was separated from aqueous phase. The aqueous phase was extracted with CH_2Cl_2 (3 × 6 mL). Combined organic phase was dried over anh. Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography.

(*R*)-5-(3,4-Dimethylphenyl)-5-(2-iodoethyl)furan-2(5*H*)-one (6a): This reaction was carried out with 14.0 mg (0.037 mmol) of **12c**. Purified by silica-gel (100-200 mesh) column chromatography (6% EtOAc/Petroleum ether) to obtain

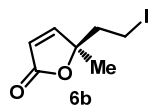


6a

a colorless oil (7.0 mg, 0.020 mmol, 55% yield); **Optical rotation:** $[\alpha]_D^{24}$ +83.9 (*c* 0.3, $CHCl_3$) for an enantiomerically enriched sample with 91:9 er. Other characterization data are reported above.

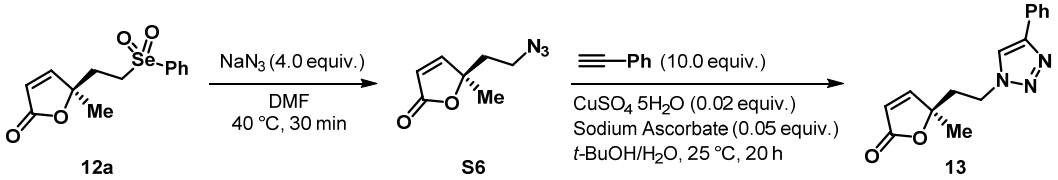
By comparing the optical rotation and HPLC chromatogram of this sample of **6a** with the one prepared from **4c**, the absolute configuration of vinyl selenone adduct (**12**) was determined to be (*R*).

(*R*)-5-(2-Iodoethyl)-5-methylfuran-2(5*H*)-one (6b): This reaction was carried out with 14.0 mg (0.045 mmol) of **12a**. Purified by silica-gel (230-400 mesh) column chromatography (10% EtOAc/Petroleum ether) to obtain a yellow oil (8.0 mg, 0.032 mmol, 71% yield). **FT-IR (Thin film):** 1752, 1018 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.39 (d, *J* = 5.5 Hz, 1H), 6.08 (d, *J* = 5.5 Hz, 1H), 3.13-3.06 (m, 1H), 2.99-2.92 (m, 1H), 2.57-2.49 (m, 1H), 2.36-2.28 (m, 1H), 1.48 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.9, 158.8, 121.2, 88.9, 42.7, 23.8, –4.6; **HRMS (ESI+):** Calcd. for $C_7H_9IO_2Na$ ($[M+Na]^+$): 274.9545, Found: 274.9542; **Optical rotation:** $[\alpha]_D^{24}$ –68.0 (*c* 0.5, $CHCl_3$) for an enantiomerically enriched sample with 92:8 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (80:20 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 7.5 min, τ_{major} = 7.8 min). See Supporting Information: Part B for HPLC chromatograms.



6b

Conversion of 12a to 13:



12a **S6** **13**

In an oven dried 10 mL round bottom flask, **12a** (17.0 mg, 0.05 mmol, 1.0 equiv.) was taken along with sodium azide (14.0 mg, 0.22 mmol, 4.0 equiv.) under argon atmosphere. To the reaction mixture 1.0 mL dry DMF was taken and the reaction mixture was stirred at 40 °C for 30 min. The reaction mixture was diluted with water (10 ml). Organic phase was separated and the aqueous phase was extracted with Et_2O (2 × 10 mL). Combined organic phase was dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain **S6** as a yellow oil which was used in the next step without any further purification or characterization.

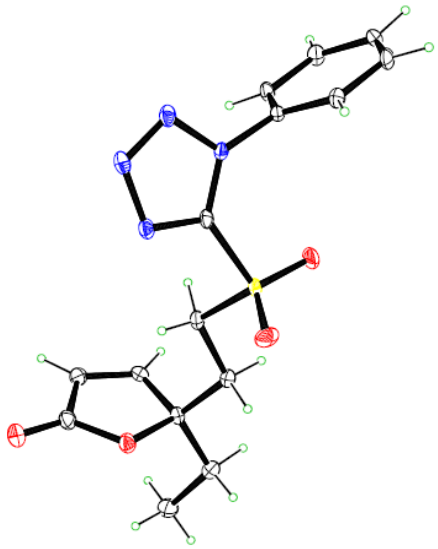
The yellow oil was taken in 0.6 mL *t*-BuOH/ H_2O (1:1). To this was added phenyl acetylene (0.05 mL, 0.5 mmol, 10.0 equiv.), copper(II)sulfate (0.2 mg, 0.001 mmol, 0.02 equiv.) and sodium ascorbate (0.5 mg, 0.0025 mmol, 0.05 equiv.). The resulting yellow mixture was stirred at 25 °C for 20 h. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and H_2O (5 mL). Organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (1 × 10 mL). The combined organic phase was dried over anh. Na_2SO_4 and concentrated under reduced pressure. Purified by silica-gel (230-400 mesh) column chromatography (10%

EtOAc/Petroleum ether) to obtain a yellow oil (12.0 mg, 0.045 mmol, 89% yield). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.79 (d, *J* = 7.4 Hz, 2H), 7.71 (s, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.35-7.31 (m, 1H), 7.25 (s, 1H), 5.96 (d, *J* = 5.6 Hz, 1H), 4.46-4.31 (m, 2H), 2.62-2.49 (m, 2H), 1.53 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.8, 159.1, 130.2, 128.9, 128.3, 125.7, 120.7, 120.2, 86.7, 45.3, 37.6, 24.5; **HRMS (ESI+):** Calcd. for $C_{15}H_{15}N_3O_2Na$ ($[M+Na]^+$): 292.1062, Found: 292.1064; **Optical rotation:** $[\alpha]_D^{24}$ –40.32 (*c* 0.5, $CHCl_3$) for an enantiomerically enriched sample with 88:12 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IC column (60:40 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{major} = 14.7 min, τ_{minor} = 17.2 min).See Supporting Information: Part B for HPLC chromatograms.

10. Single crystal X-ray diffraction analysis of 3ba and 3af:

Single crystal X-ray diffraction analysis of 3ba:

Single crystals of **3ba** (recrystallized from 1:1 pentane/CH_2Cl_2 at 0 °C) were mounted and the diffraction data were collected at 273 K on a Bruker SMART APEX CCD diffractometer using SMART/SAINT software. Intensity data were collected using graphite-monochromatized Mo-Ka radiation (71.073 pm). The structures were solved by direct methods using the SHELX-97 and refined by full-matrix least-squares on F^2. Empirical absorption corrections were applied with SADABS. All Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in geometric positions. Structure was drawn using Olex-2 and ORTEP-3. The crystallographic refinement parameters are given below:



ORTEP representation of the X-ray structure of enantiopure **3ba** (thermal ellipsoids at 30% probability)

Table 7. Crystal data and structure refinement for 3ba

Identification code	**3ba**	
Empirical formula	$C_{15}H_{16}N_4O_4S$	
Formula weight	348.38	
Temperature	100(2) K	
Wavelength	71.073 pm	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 583.34(5) pm	α = 90°.
	b = 1097.63(9) pm	β = 90°.
	c = 2492.2(2) pm	γ = 90°.
Volume	1.5957(2) nm^3	
Z	4	
Density (calculated)	1.450 Mg/m^3	
Absorption coefficient	0.229 mm^{-1}	
F(000)	728	
Crystal size	0.26 × 0.25 × 0.24 mm^3	
Theta range for data collection	3.08 to 24.9°	
Index ranges	$-6 \le h \le 6$, $-13 \le k \le 13$, $-29 \le l \le 29$	
Reflections collected	25586	
Independent reflections	2756	
Completeness to Θ = 25.242°	99.6%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2756/ 0 / 282	
Goodness-of-fit on F^2	1.081	
Final R indices [I > 2σ (I)]	$R1$ = 0.0448, ω$R2$ = 0.0726	
R indices (all data)	$R1$ = 0.0600, ω$R2$ = 0.0754	
Absolute structure parameter	0.00(12)	

Table 8. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (pm^2 × 10^{-1}) for 3ba. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
C(15)	-5955(10)	7085(4)	2873(2)	32(1)
S(1)	134(2)	9826(1)	1016(1)	23(1)
O(4)	-56(6)	5190(2)	2159(1)	35(1)
O(1)	1759(5)	10244(2)	1405(1)	33(1)
O(3)	-1542(5)	7066(2)	2251(1)	25(1)
N(1)	1621(6)	9494(2)	-45(1)	19(1)
N(2)	3136(6)	8780(3)	-309(1)	23(1)
C(1)	-1810(8)	9888(3)	-567(2)	24(1)
O(2)	-1480(6)	10654(2)	790(1)	35(1)
C(2)	163(8)	10330(3)	-347(1)	18(1)
C(5)	-2450(8)	11833(3)	-967(2)	25(1)
C(8)	-1275(9)	8517(3)	1261(2)	24(1)
C(12)	-3569(8)	5761(4)	1713(2)	25(1)
C(11)	-4705(9)	6798(3)	1707(2)	23(1)
N(3)	4147(6)	8111(3)	51(1)	24(1)
C(3)	911(8)	11511(3)	-427(2)	23(1)
C(9)	-2712(8)	8848(3)	1747(2)	23(1)
N(4)	3322(6)	8373(3)	549(1)	23(1)
C(13)	-1551(8)	5906(4)	2054(2)	26(1)
C(4)	-452(8)	12270(3)	-743(2)	24(1)
C(14)	-5012(11)	8119(4)	2533(2)	30(1)
C(6)	-3141(8)	10648(4)	-877(2)	25(1)
C(10)	-3557(8)	7720(3)	2055(2)	22(1)
C(7)	1760(7)	9217(3)	476(1)	18(1)

Table 9. Bond lengths [pm] and angles [°] for 3ba

C(15)-C(14)	151.9(6)
S(1)-O(2)	142.4(3)
S(1)-O(1)	143.1(3)
S(1)-C(8)	176.4(4)

S(1)-C(7)	177.6(4)
O(4)-C(13)	120.3(5)
O(3)-C(13)	136.4(5)
O(3)-C(10)	146.2(5)
N(1)-C(7)	133.7(4)
N(1)-N(2)	135.2(4)
N(1)-C(2)	146.0(5)
N(2)-N(3)	130.1(4)
C(1)-C(2)	136.5(6)
C(1)-C(6)	137.7(6)
C(2)-C(3)	138.2(5)
C(5)-C(4)	137.9(6)
C(5)-C(6)	138.0(5)
C(8)-C(9)	151.8(6)
C(12)-C(11)	131.8(6)
C(12)-C(13)	146.1(6)
C(11)-C(10)	149.1(5)
N(3)-N(4)	136.2(4)
C(3)-C(4)	139.5(6)
C(9)-C(10)	153.7(5)
N(4)-C(7)	131.2(5)
C(14)-C(10)	152.7(6)
O(2)-S(1)-O(1)	120.07(17)
O(2)-S(1)-C(8)	110.4(2)
O(1)-S(1)-C(8)	109.6(2)
O(2)-S(1)-C(7)	107.13(17)
O(1)-S(1)-C(7)	106.20(18)
C(8)-S(1)-C(7)	101.76(18)
C(13)-O(3)-C(10)	109.5(3)
C(7)-N(1)-N(2)	107.5(3)
C(7)-N(1)-C(2)	132.8(3)
N(2)-N(1)-C(2)	119.6(3)
N(3)-N(2)-N(1)	106.7(3)
C(2)-C(1)-C(6)	119.0(4)
C(1)-C(2)-C(3)	122.8(4)
C(1)-C(2)-N(1)	118.3(3)
C(3)-C(2)-N(1)	118.7(4)

C(4)-C(5)-C(6)	120.6(4)
C(9)-C(8)-S(1)	109.8(3)
C(11)-C(12)-C(13)	108.5(4)
C(12)-C(11)-C(10)	110.8(4)
N(2)-N(3)-N(4)	110.5(3)
C(2)-C(3)-C(4)	117.5(4)
C(8)-C(9)-C(10)	112.5(3)
C(7)-N(4)-N(3)	105.5(3)
O(4)-C(13)-O(3)	121.9(4)
O(4)-C(13)-C(12)	129.7(4)
O(3)-C(13)-C(12)	108.4(4)
C(5)-C(4)-C(3)	120.2(3)
C(15)-C(14)-C(10)	115.0(4)
C(1)-C(6)-C(5)	119.8(4)
O(3)-C(10)-C(11)	102.8(3)
O(3)-C(10)-C(14)	109.1(3)
C(11)-C(10)-C(14)	113.5(4)
O(3)-C(10)-C(9)	107.7(3)
C(11)-C(10)-C(9)	113.7(3)
C(14)-C(10)-C(9)	109.7(3)
N(4)-C(7)-N(1)	109.8(3)
N(4)-C(7)-S(1)	122.1(3)
N(1)-C(7)-S(1)	128.1(3)

Symmetry transformations used to generate equivalent atoms:

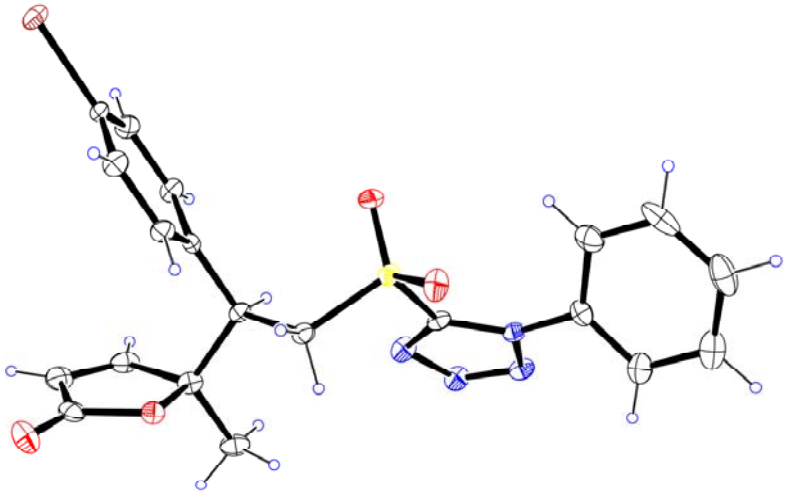
Table 10. Anisotropic displacement parameters ($pm^2 \times 10^{-1}$) for 3ba. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(15)	38(3)	32(2)	27(3)	2(2)	5(2)	-2(2)
S(1)	37(1)	11(1)	22(1)	1(1)	3(1)	2(1)
O(4)	41(2)	26(1)	38(2)	3(1)	-2(2)	10(2)
O(1)	48(2)	27(1)	25(2)	-7(1)	0(1)	-16(2)
O(3)	29(2)	19(1)	28(2)	-1(1)	-6(1)	1(1)
N(1)	23(2)	12(2)	22(2)	-1(1)	3(2)	1(2)
N(2)	24(2)	15(2)	31(2)	2(1)	5(2)	-1(2)

C(1)	31(3)	12(2)	29(2)	3(2)	3(2)	-2(2)
O(2)	48(2)	25(1)	31(2)	7(1)	11(2)	19(2)
C(2)	23(2)	14(2)	17(2)	1(1)	3(2)	3(2)
C(5)	35(3)	18(2)	23(2)	6(2)	1(2)	4(2)
C(8)	31(3)	14(2)	26(2)	1(2)	2(2)	3(2)
C(12)	32(3)	18(2)	24(2)	2(2)	3(2)	-6(2)
C(11)	29(3)	23(2)	18(2)	5(2)	0(2)	0(2)
N(3)	25(2)	15(2)	33(2)	4(1)	0(2)	-1(1)
C(3)	27(3)	16(2)	26(2)	-1(2)	0(2)	-2(2)
C(9)	29(3)	16(2)	24(2)	-2(2)	0(2)	1(2)
N(4)	27(2)	13(1)	28(2)	2(1)	-1(2)	0(2)
C(13)	30(3)	20(2)	27(2)	4(2)	3(2)	1(2)
C(4)	32(3)	11(2)	30(2)	2(2)	1(2)	-3(2)
C(14)	40(3)	25(2)	25(2)	-4(2)	3(2)	0(3)
C(6)	24(3)	21(2)	30(2)	-1(2)	-7(2)	1(2)
C(10)	24(3)	18(2)	23(2)	1(2)	-1(2)	5(2)
C(7)	21(3)	11(2)	23(2)	1(2)	2(2)	-1(2)

Single crystal X-ray diffraction analysis of 3af:

Single crystals of *rac*-**3af** (recrystalized from 1:1 pentane/CH_2Cl_2 at 0 °C) were mounted and the diffraction data were collected at 273 K on a Bruker SMART APEX CCD diffractometer using SMART/SAINT software. Intensity data were collected using graphite-monochromatized Mo-Ka radiation (71.073 pm). The structures were solved by direct methods using the SHELX-97 and refined by full-matrix least-squares on F^2. Empirical absorption corrections were applied with SADABS. All Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in geometric positions. Structure was drawn using Olex-2 and ORTEP-3. The crystallographic refinement parameters are given below:



ORTEP representation of the X-ray structure of *rac*-**3af** (thermal ellipsoids at 30% probability)

Table 11. Crystal data and structure refinement for 3af

Identification code	**3af**	
Empirical formula	$C_{20}H_{17}BrN_4O_4S$	
Formula weight	489.35	
Temperature	100(2) K	
Wavelength	71.073 pm	
Crystal system	Triclinic	
Space group	P_{-1}	
Unit cell dimensions	a = 817.72(5) pm	α = 70.184(2)°.
	b = 977.06(5) pm	β = 73.970(2)°.

	c = 1399.47(8) pm γ = 83.379(2)°.
Volume	1.01072(10) nm^3
Z	2
Density (calculated)	1.608 Mg/m^3
Absorption coefficient	2.173 mm^{-1}
F(000)	496
Crystal size	0.250 × 0.250 × 0.230 mm^3
Theta range for data collection	3.088 to 25.000°
Index ranges	$-9 \le h \le 9$, $-11 \le k \le 11$, $-16 \le l \le 16$
Reflections collected	35218
Independent reflections	3553 [R_{int} = 0.0677]
Completeness to Θ = 25.000°	99.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3553 / 0 / 272
Goodness-of-fit on F^2	1.025
Final R indices [I >2σ(I)]	$R1$ = 0.0303, ω$R2$ = 0.0598
R indices (all data)	$R1$ = 0.0437, ω$R2$ = 0.0627
Largest diff. peak and hole	0.421 and −0.343 e. $Å^{-3}$

Table 12. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (pm^2 × 10^{-1}) for 3af. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Br(1)	1583(1)	8520(1)	4517(1)	18(1)
S(2)	740(1)	7333(1)	10089(1)	14(1)
O(3)	5899(2)	5663(2)	8404(1)	15(1)
O(4)	-335(2)	6152(2)	10765(1)	21(1)
O(5)	137(2)	8484(2)	9308(1)	20(1)
N(6)	430(2)	8178(2)	11863(2)	14(1)
O(7)	7402(2)	4515(2)	7286(2)	27(1)

C(8)	2782(3)	6664(3)	7374(2)	15(1)
N(9)	2783(3)	9222(2)	11463(2)	19(1)
C(10)	2819(3)	9414(3)	5918(2)	17(1)
N(11)	2775(3)	8795(2)	10634(2)	18(1)
N(12)	1390(3)	8870(2)	12198(2)	17(1)
C(13)	2284(3)	6867(3)	6470(2)	16(1)
C(14)	3842(3)	7640(2)	8563(2)	12(1)
C(15)	3303(3)	9198(3)	6827(2)	15(1)
C(16)	6391(3)	7156(3)	9370(2)	20(1)
C(17)	6861(3)	7982(3)	7439(2)	19(1)
C(18)	3280(3)	7826(3)	7576(2)	13(1)
C(19)	5732(3)	7138(2)	8461(2)	15(1)
C(20)	-2583(3)	7840(3)	12098(2)	22(1)
C(21)	-2903(4)	6492(3)	14235(2)	28(1)
C(22)	7032(3)	5632(3)	7480(2)	20(1)
C(23)	-1327(3)	6954(3)	13576(2)	21(1)
C(24)	1314(3)	8150(2)	10904(2)	14(1)
C(25)	7606(3)	7119(3)	6892(2)	22(1)
C(26)	2707(3)	6591(3)	9541(2)	14(1)
C(27)	-4135(3)	7320(3)	12765(3)	29(1)
C(28)	-1197(3)	7632(3)	12521(2)	16(1)
C(29)	2295(3)	8244(3)	5754(2)	14(1)
C(30)	-4290(4)	6665(3)	13829(2)	32(1)

Table 13. Bond lengths [pm] and angles [°] for 3af

Br(1)-C(29)	190.1(2)
S(2)-O(4)	142.65(18)
S(2)-O(5)	142.77(17)
S(2)-C(26)	176.8(2)
S(2)-C(24)	177.8(2)
O(3)-C(22)	137.5(3)
O(3)-C(19)	145.8(3)
N(6)-C(24)	134.5(3)
N(6)-N(12)	135.4(3)
N(6)-C(28)	143.4(3)
O(7)-C(22)	119.8(3)

C(8)-C(13)	137.9(3)
C(8)-C(18)	138.7(3)
C(8)-H(8)	95.00
N(9)-N(12)	129.5(3)
N(9)-N(11)	136.1(3)
C(10)-C(29)	137.4(3)
C(10)-C(15)	137.6(3)
C(10)-H(10)	95.00
N(11)-C(24)	131.5(3)
C(13)-C(29)	137.7(3)
C(13)-H(13)	95.00
C(14)-C(18)	152.0(3)
C(14)-C(26)	153.4(3)
C(14)-C(19)	154.9(3)
C(14)-H(14)	100.00
C(15)-C(18)	139.3(3)
C(15)-H(15)	95.00
C(16)-C(19)	151.9(3)
C(16)-H(16A)	98.00
C(16)-H(16B)	98.00
C(16)-H(16C)	98.00
C(17)-C(25)	131.5(4)
C(17)-C(19)	149.1(3)
C(17)-H(17)	95.00
C(20)-C(28)	138.3(4)
C(20)-C(27)	138.3(4)
C(20)-H(20)	95.00
C(21)-C(30)	137.2(4)
C(21)-C(23)	138.2(4)
C(21)-H(21)	95.00
C(22)-C(25)	146.3(4)
C(23)-C(28)	137.7(3)
C(23)-H(23)	95.00
C(25)-H(25)	95.00
C(26)-H(26A)	99.00
C(26)-H(26B)	99.00
C(27)-C(30)	138.3(4)

C(27)-H(27)	95.00
C(30)-H(30)	95.00
O(4)-S(2)-O(5)	120.12(11)
O(4)-S(2)-C(26)	107.77(11)
O(5)-S(2)-C(26)	111.52(11)
O(4)-S(2)-C(24)	107.06(11)
O(5)-S(2)-C(24)	106.53(11)
C(26)-S(2)-C(24)	102.29(12)
C(22)-O(3)-C(19)	109.88(18)
C(24)-N(6)-N(12)	107.04(19)
C(24)-N(6)-C(28)	132.9(2)
N(12)-N(6)-C(28)	120.0(2)
C(13)-C(8)-C(18)	121.0(2)
C(13)-C(8)-H(8)	119.5
C(18)-C(8)-H(8)	119.5
N(12)-N(9)-N(11)	111.10(19)
C(29)-C(10)-C(15)	118.9(2)
C(29)-C(10)-H(10)	120.6
C(15)-C(10)-H(10)	120.6
C(24)-N(11)-N(9)	105.1(2)
N(9)-N(12)-N(6)	106.86(19)
C(29)-C(13)-C(8)	119.4(2)
C(29)-C(13)-H(13)	120.3
C(8)-C(13)-H(13)	120.3
C(18)-C(14)-C(26)	111.94(19)
C(18)-C(14)-C(19)	112.29(19)
C(26)-C(14)-C(19)	110.03(19)
C(18)-C(14)-H(14)	107.4
C(26)-C(14)-H(14)	107.4
C(19)-C(14)-H(14)	107.4
C(10)-C(15)-C(18)	121.5(2)
C(10)-C(15)-H(15)	119.2
C(18)-C(15)-H(15)	119.2
C(19)-C(16)-H(16A)	109.5
C(19)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(19)-C(16)-H(16C)	109.5

H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(25)-C(17)-C(19)	110.6(2)
C(25)-C(17)-H(17)	124.7
C(19)-C(17)-H(17)	124.7
C(8)-C(18)-C(15)	118.0(2)
C(8)-C(18)-C(14)	122.4(2)
C(15)-C(18)-C(14)	119.6(2)
O(3)-C(19)-C(17)	102.9(2)
O(3)-C(19)-C(16)	109.20(19)
C(17)-C(19)-C(16)	110.5(2)
O(3)-C(19)-C(14)	108.29(18)
C(17)-C(19)-C(14)	112.17(19)
C(16)-C(19)-C(14)	113.1(2)
C(28)-C(20)-C(27)	118.1(3)
C(28)-C(20)-H(20)	121.0
C(27)-C(20)-H(20)	121.0
C(30)-C(21)-C(23)	120.0(3)
C(30)-C(21)-H(21)	120.0
C(23)-C(21)-H(21)	120.0
O(7)-C(22)-O(3)	121.1(2)
O(7)-C(22)-C(25)	131.5(3)
O(3)-C(22)-C(25)	107.4(2)
C(28)-C(23)-C(21)	118.8(3)
C(28)-C(23)-H(23)	120.6
C(21)-C(23)-H(23)	120.6
N(11)-C(24)-N(6)	109.9(2)
N(11)-C(24)-S(2)	122.20(19)
N(6)-C(24)-S(2)	127.86(19)
C(17)-C(25)-C(22)	109.2(2)
C(17)-C(25)-H(25)	125.4
C(22)-C(25)-H(25)	125.4
C(14)-C(26)-S(2)	115.74(17)
C(14)-C(26)-H(26A)	108.3
S(2)-C(26)-H(26A)	108.3
C(14)-C(26)-H(26B)	108.3
S(2)-C(26)-H(26B)	108.3

H(26A)-C(26)-H(26B)	107.4
C(30)-C(27)-C(20)	120.2(3)
C(30)-C(27)-H(27)	119.9
C(20)-C(27)-H(27)	119.9
C(23)-C(28)-C(20)	122.2(2)
C(23)-C(28)-N(6)	117.7(2)
C(20)-C(28)-N(6)	120.0(2)
C(10)-C(29)-C(13)	121.1(2)
C(10)-C(29)-Br(1)	119.66(18)
C(13)-C(29)-Br(1)	119.21(18)
C(21)-C(30)-C(27)	120.6(3)
C(21)-C(30)-H(30)	119.7
C(27)-C(30)-H(30)	119.7

Symmetry transformations used to generate equivalent atoms:

Table 14. Anisotropic displacement parameters ($pm^2 \times 10^{-1}$) for 3ba. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	21(1)	22(1)	11(1)	-4(1)	-6(1)	-3(1)
S(2)	14(1)	17(1)	13(1)	-6(1)	-5(1)	-2(1)
O(3)	15(1)	13(1)	16(1)	-3(1)	-4(1)	-1(1)
O(4)	22(1)	23(1)	20(1)	-11(1)	-1(1)	-9(1)
O(5)	19(1)	26(1)	18(1)	-8(1)	-10(1)	5(1)
N(6)	15(1)	14(1)	14(1)	-5(1)	-6(1)	-1(1)
O(7)	23(1)	26(1)	33(1)	-15(1)	-3(1)	5(1)
C(8)	17(1)	11(1)	14(1)	0(1)	-4(1)	-1(1)
N(9)	20(1)	19(1)	19(1)	-6(1)	-6(1)	-5(1)
C(10)	22(2)	12(1)	16(1)	-1(1)	-5(1)	0(1)
N(11)	22(1)	17(1)	18(1)	-5(1)	-6(1)	-6(1)
N(12)	22(1)	14(1)	17(1)	-6(1)	-9(1)	-2(1)
C(13)	20(1)	14(1)	18(1)	-6(1)	-6(1)	-3(1)
C(14)	16(1)	9(1)	11(1)	-2(1)	-4(1)	-1(1)
C(15)	21(1)	11(1)	15(1)	-5(1)	-5(1)	-2(1)
C(16)	20(1)	17(1)	24(2)	-4(1)	-12(1)	-3(1)
C(17)	16(1)	16(1)	20(1)	4(1)	-7(1)	-6(1)

C(18)	10(1)	15(1)	13(1)	-6(1)	-2(1)	2(1)
C(19)	17(1)	11(1)	18(1)	-3(1)	-7(1)	-4(1)
C(20)	22(2)	20(1)	29(2)	-14(1)	-8(1)	6(1)
C(21)	34(2)	22(2)	25(2)	-11(1)	5(1)	-9(1)
C(22)	11(1)	26(2)	22(2)	-6(1)	-7(1)	2(1)
C(23)	25(2)	18(1)	21(2)	-11(1)	-2(1)	-3(1)
C(24)	19(1)	11(1)	14(1)	-3(1)	-8(1)	0(1)
C(25)	12(1)	29(2)	20(1)	0(1)	-2(1)	-4(1)
C(26)	18(1)	13(1)	14(1)	-4(1)	-6(1)	1(1)
C(27)	13(2)	21(2)	60(2)	-22(2)	-9(1)	3(1)
C(28)	17(1)	13(1)	21(1)	-11(1)	-2(1)	1(1)
C(29)	12(1)	22(1)	11(1)	-8(1)	-4(1)	1(1)
C(30)	26(2)	21(2)	42(2)	-15(1)	9(2)	-3(1)