Supporting Information for "The Rhodium Carbenoid-Initiated Claisen Rearrangement: Scope and Mechanistic Observations"

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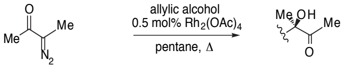
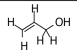
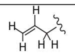
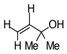
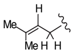
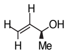
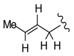
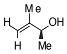
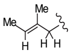
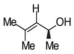
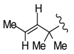
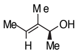
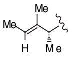
Materials and Methods

Unless otherwise stated, reactions were performed in flame-dried glassware under a nitrogen atmosphere using freshly distilled solvents. All commercially-obtained reagents were used as received. Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm). Silica gel (particle size 0.032-0.063 mm) was used for flash chromatography. High-performance liquid chromatography (HPLC) was performed with either a Rainin Microsorb 80-199-C5 or 80-120-C5 column. ^{1}H and ^{13}C NMR chemical shifts are reported as δ values relative to internal chloroform (^{1}H δ 7.27 ppm, ^{13}C δ 77.0 ppm) or benzene (^{1}H, δ 7.15 ppm). Melting points are uncorrected. High resolution mass spectra were acquired at The University of Illinois Mass Spectrometry Center. Single crystal X-Ray analyses were performed by Ms. Susan DeGala (Yale University).

Table 1.



12a

Entry	Allylic Alcohol [ee]	[3,3] Product (yield) [ee]^a
1		 (51)
2		 (59)
3	 [98]	 (64) [93]
4	 [82]	 (59) [79]
5	 [75]	 (60) [41]
6	 [92]	 (60) [91]

[a] %ee's were determined by Mosher ester analysis of the derived diols

General Procedure for Preparation of α-Hydroxyketones in Table 1 (Entry 3).

To a stirred solution of 3-diazo-2-butanone (**12a**, 78 mg, 0.795 mmol, 1.0 equiv) and (*S*)-(+)-3-buten-2-ol (83 μL, 0.958 mmol, 1.2 equiv) in pentane (8 mL) was added $Rh_2(OAc)_4$ (1.7 mg, 0.004 mmol, 0.005 equiv). The mixture was immersed in a preheated oil bath and heated under reflux for 15 min, after which it was cooled and concentrated under reduced pressure (0°C). Flash chromatography of the resulting residue (8:1 pentane:Et_2O eluent) afforded α-hydroxyketone (72 mg, 64% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.52 (m, 1H), 5.32 (m, 1H), 3.71 (s, 1H), 2.37 (m, 2H), 2.19 (s, 3H), 1.64 (d, *J*=6.5 Hz, 3H), 1.34 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 211.9, 129.6, 124.4, 78.8, 42.6, 24.9, 24.0, 18.0; **IR** (thin film/NaCl) 3477 (br m), 3027 (w), 2976 (m), 2935 (m), 2921 (m), 2858 (w), 1711 (s), 1451 (w), 1357 (m), 1161 (m), 972 (s) cm^{-1}; **HRMS** (EI) *m/z* found: 143.1075, [calc'd for $C_8H_{15}O_2$ (M+H): 143.1072]; **$[\alpha]_D^{20}$** -35.8° (*c* 3.6, $CHCl_3$).

Entry 2

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.01 (t, *J*=7.2 Hz, 1H), 3.70 (br s, 1H), 2.39 (m, 2H), 2.17 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H), 1.34 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 212.2, 135.5, 117.4, 78.9, 38.0, 25.8, 24.8, 23.8, 18.0; **IR** (thin film/NaCl) 3480 (br s), 2975 (s), 2928 (s), 2861 (m), 1710 (s), 1451 (m), 1375 (s), 1355 (s), 1164 (s), 1118 (s), 1098 (s), 940 (m) cm^{-1}; **HRMS** (EI) *m/z* found: 157.1234, [calc'd for $C_9H_{17}O_2$ (M+H): 157.1229].

Entry 4

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.25 (q, *J*=6.7 Hz, 1H), 3.41 (br s, 1H), 2.43 (d, *J*=13.9 Hz, 1H), 2.36 (d, *J*=13.9 Hz, 1H), 2.21 (s, 3H), 1.60 (s, 3H), 1.56 (d, *J*=6.7 Hz, 3H), 1.33 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 212.4, 131.4, 123.8, 79.3, 48.9, 25.5, 24.3, 17.1, 13.5; **IR** (thin film/NaCl) 3479 (br m), 2978 (m), 2924 (m), 2863 (w), 1709 (s), 1451 (m), 1357 (m), 1157 (m), 1116 (m), 967 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 157.1231, [calc'd for $C_9H_{17}O_2$ (M+H): 157.1229]; **$[\alpha]_D^{20}$** -23.7° (*c* 1.9, $CHCl_3$).

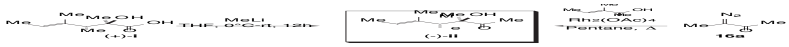
Entry 5

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.57 (dq, *J*=1.4, 15.7 Hz, 1H), 5.45 (dq, *J*=6.3, 15.6 Hz, 1H), 2.16 (s, 3H), 1.69 (dd, *J*=1.4, 6.3 Hz, 3H), 1.31 (s, 3H), 1.05 (s, 3H), 0.95 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 213.1, 137.1, 124.2, 82.7, 42.5, 27.1, 23.3, 21.9, 20.4, 18.2; **IR** (thin film/NaCl) 3471 (br s), 3027 (w), 2971 (s), 2939 (s), 2880 (m), 1701 (s), 1449 (m), 1358 (s), 1127 (s), 1065 (w), 982 (s) cm^{-1}; **HRMS** (EI) *m/z* found: 171.1384, [calc'd for $C_{10}H_{19}O_2$ (M+H): 171.1385]; **$[\alpha]_D^{20}$** -40.7° (*c* 2.8, $CHCl_3$).

Entry 6

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.26 (m, 1H), 3.47 (br s, 1H), 2.50 (q, *J*=7.0 Hz, 1H), 2.17 (s, 3H), 1.51 (m, 6H), 1.32 (s, 3H), 1.17 (d, *J*=7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 212.2, 137.5, 121.5, 81.6, 49.1, 24.2, 24.0, 13.1, 13.0; **IR** (thin film/NaCl) 3472 (br m), 2975 (m), 2936 (m), 1708 (s), 1451 (m), 1356 (m), 1160 (m), 969 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 171.1390, [calc'd for $C_{10}H_{19}O_2$ (M+H): 171.1385]; **$[\alpha]_D^{20}$** -32.6° (*c* 10.7, $CHCl_3$).

General Procedure for Determination of Relative and Absolute Stereochemistry of α-Hydroxyketones in Table 1.

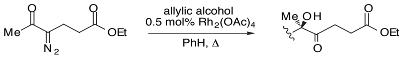


Addition of methyllithium to α-hydroxyacid (+)-**i** of established relative and absolute stereochemistry[1] provided α-hydroxyketone (-)-**ii**. This compound was spectroscopically identical to that derived from Claisen rearrangement with diazoketone **16a** and 3-methyl-3-penten-2-ol. Comparison of optical rotation data established that (-)-**ii** prepared by both routes shared the same absolute stereochemistry as well.

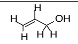
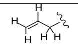
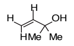
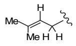
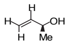
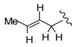
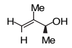
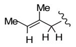
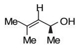
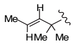
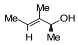
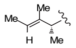
Preparation of α-hydroxyketone (-)-ii from α-hydroxyacid (+)-i.

To a stirred solution of α-hydroxyacid (+)-**i** (342 mg, 2.37 mmol, 1.0 equiv) in THF (25 mL) at 0°C was added dropwise a solution of methyllithium (1.4M, 6.0 mL, 8.40 mmol, 3.5 equiv). The resulting mixture was allowed to warm to room temperature and stirred for 12 h after which it was recooled to 0°C, quenched with H_2O (10 mL), and acidified with 1N HCl (5 mL). The heterogeneous mixture was extracted with Et_2O (4 x 50 mL) and the combined organic layers dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash chromatography (10:1 pentane:Et_2O eluent) afforded α-hydroxyketone (-)-**ii** (77 mg, 23% yield) that was identical spectroscopically to that obtained by Claisen rearrangement with α-diazoketone **16a**. Absolute stereochemistry was assigned by optical rotation: **$[\alpha]_D^{20}$** -31.0° (*c* 2.1, $CHCl_3$).

Table 2.



16b

Entry	Allylic Alcohol	[3,3] Product (yield)
1		 (58)
2		 (49)
3		 (51)
4		 (51)
5		 (49)
6		 (53)

Preparation of α-diazoketone 12b.[2]

To a stirred solution of diketone **iii** (2.10 g, 8.46 mmol, 1.0 equiv)[3] and *p*-NBSA (3.61 g, 15.8 mmol, 1.9 equiv) in CH_2Cl_2 (50 mL) at 0°C was added dropwise DBU (2.5 mL, 16.7 mmol, 2.0 equiv). The resulting mixture was stirred for 20 min at 0°C and then concentrated. Flash chromatography (3:2 hexanes:EtOAc eluent) afforded **16b** (688 mg, 44% yield) as an orange oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.15 (q, *J*=7.1 Hz, 2H), 2.59 (m, 4H), 2.23 (s, 3H), 1.27 (t, *J*=7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.0, 172.6, 60.7, 31.9, 25.2, 19.0, 14.1; **IR** (thin film/NaCl) 2983 (m), 2935 (m), 2080 (s), 1733 (s), 1636 (s), 1374 (s), 1327 (s), 1196 (s), 1018 (m), 977 (w), 847 (w) cm^{-1}. Due the unstable nature of this compound, satisfactory HRMS results could not be obtained.

General Procedure for Preparation of α-Hydroxyketones in Table 2 (Entry 3).

To a stirred solution of ethyl 4-diazo-5-oxohexanoate (**16b**, 82 mg, 0.446 mmol, 1.0 equiv) and 3-buten-2-ol (46 μL, 0.531 mmol, 1.2 equiv) in benzene (5 mL) was added $Rh_2(OAc)_4$ (1.0 mg, 0.023 mmol, 0.005 equiv). The resulting mixture was immersed in a preheated oil bath and heated under reflux for 15 min. The mixture was cooled and concentrated and the residue purified by flash chromatography (4:1 pentane:Et_2O eluent) to provide the α-hydroxyketone (52 mg, 51% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.55 (m, 1H), 5.34 (m, 1H), 4.14 (q, *J*=7.2 Hz, 2H), 2.88 (ddd, *J*=6.2, 7.4, 18.4 Hz, 1H), 2.80 (ddd, *J*=5.9, 6.7, 18.5 Hz, 1H), 2.64 (ddd, *J*=5.8, 7.4, 17.2 Hz, 1H), 2.57 (ddd, *J*=6.5, 6.6, 17.3 Hz, 1H), 2.33-2.45 (m, 2H), 1.66 (m, 3H), 1.37 (s, 3H), 1.25 (t, *J*=7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 212.6, 172.5, 130.1, 124.5, 78.7, 60.7, 42.9, 31.4, 28.0, 25.0, 18.0, 14.2; **IR** (thin film/NaCl) 3492 (br m), 2981 (s), 2936 (m), 1735 (s), 1713 (s), 1375 (m), 1207 (s), 1178 (s), 1033 (m), 857 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 229.1445, [calc'd for $C_{12}H_{21}O_4$ (M+H): 229.1440].

Entry 1

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74 (m, 1H), 5.10-5.15 (comp m, 2H), 4.13 (q, *J*=7.1 Hz, 2H), 2.89 (ddd, *J*=6.0, 7.4, 18.5 Hz, 1H), 2.81 (ddd, *J*=5.8, 6.9, 18.5 Hz, 1H), 2.65 (ddd, *J*=5.8, 7.4, 17.3 Hz, 1H), 2.58 (ddd, *J*=6.2, 6.8, 17.3 Hz, 1H), 2.50 (ddt, *J*=0.9, 7.4, 14.1 Hz, 1H), 2.45 (ddt, *J*=1.2, 7.2, 14.1 Hz, 1H), 1.40 (s, 3H), 1.25 (t, *J*=7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 212.3, 172.5, 132.3, 119.1, 78.5, 60.7, 44.0, 31.4, 28.0, 25.1, 14.1; **IR** (thin film/NaCl) 3492 (br m), 2981 (m), 2934 (m), 1735 (s), 1713 (s), 1451 (w), 1375 (m), 1349 (m), 1208 (s), 1177 (s), 1033 (m), 1003 (m), 923 (w), 857 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 215.1282, [calc'd for $C_{11}H_{19}O_4$ (M+H): 215.1283].

Entry 2

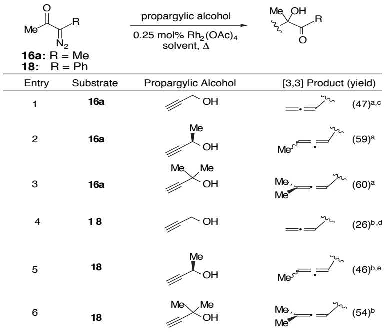
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.05 (m, 1H), 4.15 (q, *J*=7.1 Hz, 1H), 3.49 (s, 1H), 2.90 (dt, *J*=6.9, 18.3 Hz, 1H), 2.80 (dt, *J*=6.3, 18.5 Hz, 1H), 2.66 (ddd, *J*=6.1, 7.4, 17.3 Hz, 1H), 2.58 (dt, *J*=6.4, 17.2 Hz, 1H), 2.43 (m, 2H), 1.72 (s, 3H), 1.64 (s, 3H), 1.40 (s, 3H), 1.27 (t, *J*=7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 212.9, 172.5, 136.1, 117.5, 79.0, 60.7, 38.2, 31.3, 28.1, 25.9, 25.1, 18.1, 14.2; **IR** (thin film/NaCl) 3488 (br m), 2981 (m), 2917 (m), 1735 (s), 1714 (s), 1449 (w), 1376 (m), 1205 (s), 1179 (s), 1092 (m), 1035 (m), 1007 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 243.1589, [calc'd for $C_{13}H_{23}O_4$ (M+H): 243.1596].

Entry 4
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 5.28 (m, 1H), 4.14 (q, *J*=7.1 Hz, 2H), 3.40 (s, 1H), 2.92 (dt, *J*=6.7, 18.7 Hz, 1H), 2.87 (dt, *J*=6.7, 18.7 Hz, 1H), 2.63 (dt, *J*=6.8, 17.2 Hz, 1H), 2.55 (dt, *J*=6.6, 17.2 Hz, 1H), 2.48 (d, *J*=13.9 Hz, 1H), 2.35 (d, *J*=13.9 Hz, 1H), 1.59 (m, 6H), 1.36 (s, 3H), 1.26 (t, *J*=7.2 Hz, 3H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 213.2, 172.6, 131.5, 124.3, 79.0, 60.7, 49.0, 31.7, 28.1, 25.8, 17.3, 14.1, 13.5; **IR** (thin film/NaCl) 3493 (br m), 2981 (m), 2930 (m), 2863 (w), 1736 (s), 1712 (s), 1449 (m), 1376 (m), 1206 (s), 1166 (s), 1034 (m), 1007 (m) cm^{-1}; **HRMS** (EI) *m/z* found: 243.1590, [calc'd for $C_{13}H_{23}O_4$ (M+H): 243.1596].

Entry 5
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 5.62 (dq, *J*=1.4, 15.6 Hz, 1H), 5.51 (dq, *J*=6.3, 15.6 Hz, 1H), 4.14 (q, *J*=7.2 Hz, 2H), 2.93 (ddd, *J*=6.1, 7.1, 18.7 Hz, 1H), 2.77 (dt, *J*=6.4, 18.8 Hz, 1H), 2.56 (m, 2H), 1.73 (dd, *J*=1.4, 6.3 Hz, 3H), 1.35 (s, 3H), 1.26 (t, *J*=7.2 Hz, 3H), 1.08 (s, 3H), 1.00 (s, 3H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 213.7, 172.8, 136.9, 124.7, 82.7, 60.6, 42.8, 34.2, 28.4, 23.2, 22.1, 20.9, 18.3, 14.2; **IR** (thin film/NaCl) 3510 (br m), 1976 (s), 2937 (m), 2880 (w), 1736 (s), 1711 (s), 1449 (w), 1375 (s), 1349 (m), 1208 (s), 1178 (s), 981 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 257.1759, [calc'd for $C_{14}H_{25}O_4$ (M+H): 257.1753].

Entry 6
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 5.27 (m, 1H), 4.15 (q, *J*=7.1 Hz, 2H), 2.86 (m, 2H), 2.65 (td, *J*=7.3, 17.1 Hz, 1H), 2.52 (q, *J*=7.0 Hz, 1H), 2.43 (dt, *J*=6.5, 17.1 Hz, 1H), 1.52 (m, 6H), 1.36 (s, 3H), 1.27 (t, *J*=7.2 Hz, 3H), 1.17 (d, *J*=7.0 Hz, 3H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 212.9, 172.6, 137.6, 121.8, 81.4, 60.7, 49.4, 31.7, 28.2, 24.2, 14.2, 13.3, 13.2, 13.1; **IR** (thin film/NaCl) 3479 (br s), 2979 (s), 2933 (s), 1737 (s), 1709 (s), 1449 (m), 1375 (s), 1207 (s), 1164 (s), 1033 (m), 1002 (m) cm^{-1}; **HRMS** (EI) *m/z* found: 257.1745, [calc'd for $C_{14}H_{25}O_4$ (M+H): 257.1753].

Table 3.



[a] Reactions were performed in refluxing pentane. [b] Reactions were performed in refluxing benzene. [c] A 21% yield of OH-insertion product was also obtained. [d] A 28% yield of OH-insertion product and a 7% yield of [2,3]-rearranged product were also obtained. [e] A 4% yield of [2,3]-rearranged product was also isolated

General Procedure for the Preparation of Allenic α-Hydroxyketones in Table 3 (Entry 5). To a stirred solution of 1-diazo-1-phenyl-2-propanone (**18**, 148 mg, 0.924 mmol, 1.0 equiv) and 3-butyn-2-ol (87 μL, 1.11 mmol, 1.2 equiv) in benzene (10 mL) was added $Rh_2(OAc)_4$ (1.0 mg, 0.0023 mmol, 0.0025 equiv). The mixture was immersed in a preheated oil bath, heated under reflux for 15 min, then cooled and concentrated. The resulting residue was purified by flash chromatography (CH_2Cl_2 eluent) affording [3,3]-rearranged α-hydroxyketone (86 mg, 46% yield) and a small amount of [2,3]-rearranged α-hydroxyketone (8 mg, 4% yield).

[3,3]-Product (2.5:1 mixture of diastereomers): ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.11 (m, 2H), 8.09 (m, 2H), 7.58 (m, 1H), 7.48 (m, 2H), 5.34-5.48 (comp m, 2H), 4.54 (s, 1H), 4.52 (s, 1H), 1.74 (dd, *J*=3.2, 7.1 Hz, 3H), 1.67 (s, 3H), 1.66 (s, 3H), 1.65 (dd, *J*=3.4, 7.3 Hz, 3H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 204.2, 202.2, 133.2, 130.2, 130.1, 128.3, 128.2, 97.0, 90.6, 90.4, 76.8, 26.3, 26.1, 13.4, 13.3; **IR** (thin film/NaCl) 3446 (br m), 3061 (w), 2983 (w), 2927 (w), 2858 (w), 1964 (w), 1674 (s), 1597 (m), 1448 (m), 1370 (m), 1239 (s), 1133 (m), 1095 (m), 946 (m), 697 (s) cm^{-1}; **HRMS** (EI) *m/z* found: 202.0997, [calc'd for $C_{13}H_{14}O_2$ (M+): 202.0994].

[2,3]-Product (2.4:1 mixture of diastereomers): ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.54 (m, 2H), 7.53 (m, 2H), 7.32-7.41 (comp m, 3H), 5.72 (m, 1H), 5.36-5.45 (comp m, 1H), 4.57 (s, 1H), 4.52 (s, 1H), 2.11 (s, 3H), 2.10 (s, 3H), 1.76 (dd, *J*=3.3, 7.3 Hz, 3H), 1.71 (dd, *J*=3.3, 7.3 Hz, 3H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 207.2, 203.9, 140.4, 128.6, 128.3, 128.3, 126.8, 94.0, 93.9, 90.6, 90.3, 82.0, 24.8, 24.7, 13.9; **IR** (thin film/NaCl) 3454 (br s), 3061 (w), 3029 (w), 2988 (w), 2925 (w), 1965 (m), 1713 (s), 1491 (m), 1447 (m), 1355 (s), 1175 (m), 1065 (m), 765 (m), 701 (s) cm^{-1}; **HRMS** (EI) *m/z* found: 202.0997, [calc'd for $C_{13}H_{14}O_2$ (M+): 202.0994].

Entry 1 ([3,3]-Product)

^{1}**H NMR** (500 MHz, $CDCl_3$) δ 5.22 (t, *J*=6.7 Hz, 1H), 5.00 (dd, *J*=6.9, 11.4 Hz, 1H), 4.97 (dd, *J*=6.6, 11.4 Hz, 1H), 4.03 (s, 1H), 2.25 (s, 3H), 1.48 (s, 3H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 209.5, 207.5, 95.3, 78.9, 76.9, 24.0, 23.5; **IR** (thin film/NaCl) 3464 (br m), 2988 (w), 2934 (w), 1955 (m), 1715 (s), 1362 (m), 1229 (w), 1172 (m), 1127 (s), 936 (w), 859 (m) cm^{-1}; **HRMS** (EI) *m/z* found: 126.0687, [calc'd for $C_7H_{10}O_2$ (M+): 126.0681].

Entry 1 (OH-Insertion Product)
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 4.22 (m, 2H), 4.07 (q, 7.0H, q), 2.44 (m, 1H), 2.20 (s, 3H), 1.33 (d, *J*=6.8 Hz, 3H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 210.1, 80.0, 79.0, 75.0, 57.0, 25.3, 16.9; **IR** (thin film/NaCl) 3278 (br s), 2985 (w), 2928 (w), 2867 (w), 2118 (w), 1720 (s), 1442 (w), 1362 (s), 1112 (s) cm^{-1}; **HRMS** (EI) *m/z* found: 126.0685, [calc'd for $C_7H_{10}O_2$ (M+): 126.0681].

Entry 2 ([3,3]-Product, 3:2 mixture of diastereomers)
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 5.39 (m, 1H), 5.15 (septet, *J*=3.0 Hz, 1H), 3.77 (br s, 1H), 2.26 (s, 3H), 2.24 (s, 3H), 1.73 (dd, *J*=3.3, 7.1 Hz, 3H), 1.46 (s, 3H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 209.8, 204.0, 95.8, 95.7, 77.5, 77.4, 24.1, 24.0, 23.4, 23.3, 13.9, 13.7; **IR** (thin film/NaCl) 3467 (br s), 2986 (m), 2930 (m), 2866 (w), 1962 (m), 1714 (s), 1444 (m), 1356 (s), 1131 (s), 1086 (m), 945 (m), 873 (m) cm^{-1}; **HRMS** (EI) *m/z* found: 140.0839, [calc'd for $C_8H_{12}O_2$ (M+): 140.0837].

Entry 3 ([3,3]-Product)
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 5.02 (septet, *J*=3.0 Hz, 1H), 3.96 (br s, 1H), 2.23 (s, 3H), 1.75 (t, *J*=3.0 Hz, 6H), 1.43 (s, 3H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 210.2, 201.2, 100.2, 94.3, 77.8, 23.9, 23.3, 20.2, 20.0; **IR** (thin film/NaCl) 3469 (br s), 2982 (s), 2934 (s), 2864 (m), 1968 (w), 1712 (s), 1445 (m), 1357 (s), 1196 (m), 1123 (s), 1085 (m), 940 (m), 800 (m) cm^{-1}; **HRMS** (EI) *m/z* found: 154.0995, [calc'd for $C_9H_{14}O_2$ (M+): 154.0994].

Entry 4 ([3,3] Product)
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.08 (m, 2H), 7.45-7.60 (comp m, 3H), 5.53 (t, *J*=6.6 Hz, 1H), 5.06 (dd, *J*=6.7, 11.6 Hz, 1H), 4.99 (dd, *J*=6.6, 11.6 Hz, 1H), 4.58 (s, 1H), 1.68 (s, 3H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 207.9, 201.8, 133.3, 130.1, 128.4, 96.6, 79.3, 76.3, 26.1; **IR** (thin film/NaCl) 3445 (br m), 3064 (w), 2989 (w), 2933 (w), 2933 (w), 1955 (m), 1676 (s), 1448 (m), 1368 (m), 1247 (s), 1131 (m), 1100 (m), 941 (m), 856 (m), 717 (s), 696 (m) cm^{-1}; **HRMS** (EI) *m/z* found: 188.0841, [calc'd for $C_{12}H_{12}O_2$ (M+): 188.0837].

Entry 4 ([2,3] Product)
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.52 (m, 2H), 7.32-7.53 (comp m, 3H), 5.81 (t, *J*=6.7 Hz, 1H), 5.03 (dd, *J*=6.7, 11.5 Hz, 1H), 5.00 (dd, *J*=6.6, 11.5 Hz, 1H), 4.61 (s, 1H), 2.12 (s, 3H); ^{13}**C**

NMR (125 MHz, $CDCl_3$) δ 207.4, 206.6, 140.2, 128.6, 128.4, 126.6, 93.7, 81.7, 79.3, 24.8; **IR** (thin film/NaCl) 3453 (br m), 3061 (w), 3028 (w), 1956 (m), 1714 (s), 1492 (m), 1356 (s), 1173 (m), 1063 (m), 855 (m), 765 (m), 701 (s) cm^{-1}; **HRMS** (EI) *m/z* found: 188.0842, [calc'd for $C_{12}H_{12}O_2$ (M+): 188.0837].

Entry 4 (OH-Insertion Product)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.41 (comp m, 5H), 5.09 (s, 1H), 4.32 (dd, *J*=2.5, 15.9 Hz, 1H), 4.07 (dd, *J*=2.4, 16.0 Hz, 1H), 2.49 (t, *J*=2.4 Hz, 1H), 5.09 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.6, 135.0, 128.9, 127.5, 85.6, 78.7, 75.5, 56.2, 25.7; **IR** (thin film/NaCl) 3286 (br s), 3063 (w), 3032 (w), 2905 (w), 2860 (w), 2117 (w), 1722 (s), 1418 (m), 1453 (m), 1355 (s), 1098 (s), 1073 (s), 1028 (m), 748 (m), 701 (s) cm^{-1}; **HRMS** (EI) *m/z* found: 187.0757, [calc'd for $C_{12}H_{11}O_2$ (M - H): 187.0759].

Entry 6 ([3,3]-Product)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (m, 2H), 7.41-7.56 (comp m, 3H), 5.32 (septet, *J*=2.8 Hz, 1H), 4.49 (s, 1H), 1.74 (d, *J*=2.8 Hz, 3H), 1.67 (d, *J*=2.8 Hz, 3H), 1.64 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 202.4, 201.2, 133.4, 133.1, 130.2, 128.1, 100.4, 95.7, 77.3, 26.2, 19.9, 19.5; **IR** (thin film/NaCl) 3449 (br m), 2982 (m), 2934 (w), 2911 (w), 1967 (w), 1675 (s), 1596 (m), 1448 (m), 1363 (m), 1448 (m), 1255 (s), 1127 (m), 1096 (m), 942 (m), 705 (s) cm^{-1}; **HRMS** (EI) *m/z* found: 216.1157, [calc'd for $C_{14}H_{16}O_2$ (M+): 216.1150].

Preparation and ^{1}H NMR Observation of Allyloxy Enol 7.

To a stirred solution of azibenzil (**6**, 50 mg, 0.225 mmol, 1.0 equiv) and allyl alcohol (16 μL, 0.235 mmol, 1.0 equiv) in C_6D_6 (3 mL) was added $Rh_2(OAc)_4$ (1.0 mg, 0.0023 mmol, 0.01 equiv) resulting in rapid N_2(g) loss and decolorization of the reaction mixture. ^{1}H NMR of an aliquot (1 mL) revealed complete conversion of **5** to **7**. **^{1}H NMR** (500 MHz, C_6D_6) δ 7.51 (m, 2H), 7.25 (m, 2H), 6.90-7.00 (comp m, 6H), 6.10 (br s, 1H), 5.66 (ddt, *J*=5.8, 10.4, 17.1 Hz, 1H), 5.00 (dq, *J*=1.6, 17.2 Hz, 1H), 4.94 (dq, *J*=1.2, 10.2 Hz, 1H), 3.84 (dt, *J*=1.3, 5.8 Hz, 2H).

Preparation and ^{1}H NMR Observation of Enol 8.

To a stirred solution of azibenzil (**5**, 45 mg, 0.202 mmol, 1.0 equiv) and 3-buten-2-ol (18 μL, 0.208 mmol, 1.0 equiv) in C_6D_6 (2 mL) at room temperature was added $Rh_2(OAc)_4$ (1.2 mg, 0.0027 mmol, 0.01 equiv) resulting in rapid conversion of **5** to enol **8** with concomitant loss of N_2(g). **^{1}H NMR** (500 MHz, C_6D_6) δ 7.51 (m, 2H), 7.26 (m, 2H), 6.91-7.00 (comp m, 6H), 6.12 (br s, 1H), 5.64 (ddd, *J*=6.6, 8.1, 10.5 Hz, 1H), 4.90 (m, 2H), 4.07 (m, 1H), 1.07 (d, *J*=6.4 Hz, 3H).

Preparation and ^{1}H NMR Observation of Enol 9.

To a stirred solution of azibenzil (**5**, 51 mg, 0.229 mmol, 1.0 equiv) and 2-methyl-2-propen-1-ol (20 µL, 0.238, 1.0 equiv) in C_6D_6 (2.5 mL) at room temperature was added $Rh_2(TFA)_4$ (1.6 mg, 0.0024 mmol, 0.01 equiv) resulting in rapid N_2(g) loss and decolorization of the reaction mixture. ^{1}H NMR analysis of an aliquot showed complete conversion of **5** to enol **9**. **^{1}H NMR** (500 MHz, C_6D_6) δ 7.52 (m, 2H), 7.26 (m, 2H), 6.92-7.00 (comp m, 6H), 6.16 (br s, 1H), 4.94 (s, 1H), 4.78 (s, 1H), 3.81 (s, 2H), 1.51 (s, 3H).

Preparation and ^{1}H NMR Observation of Enol 15.

To a stirred solution of 1-diazo-1-phenyl-2-propanone **18** (57 mg, 0.356 mmol, 1.0 equiv) and 3-buten-2-ol (31 mL, 0.358 mmol, 1.0 equiv) in C_6D_6 (4 mL) was added in one portion $Rh_2(OAc)_4$ (1.6 mg, 0.0036 mmol, 0.01 equiv) resulting in rapid conversion of **18** to **15** with concomitant loss of N_2(g) and decolorization. **^{1}H NMR** (500 MHz, C_6D_6) δ 7.29 (m, 2H), 7.00-7.15 (comp m, 3H), 5.90 (br s, 1H), 5.62 (m, 1H), 4.91 (d, *J*=1.0 Hz, 1H), 4.88 (m, 1H), 3.99 (m, 1H), 1.88 (s, 3H), 1.05 (d, *J*=6.4 Hz, 3H).

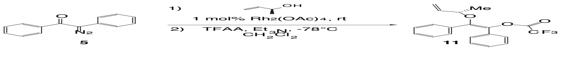
Preparation and ^{1}H NMR Observation of Enol 19.

To a stirred solution of 1-diazo-1-phenyl-2-propanone **18** (36 mg, 0.225 mmol, 1.0 equiv) and 3-butyn-2-ol (21 µL, 0.268 mmol, 1.2 equiv) in C_6D_6 (2.5 mL) was added $Rh_2(OAc)_4$ (1.0 mg, 0.0023 mmol, 0.01 equiv) resulting in rapid loss of N_2(g) and decolorization of the reaction mixture. Analysis by ^{1}H NMR revealed complete conversion of **5** to enol **19**. **^{1}H NMR** (500 MHz, C_6D_6) δ 7.29 (m, 2H), 7.00-7.13 (comp m, 3H), 6.13 (br s, 1H), 4.15 (qd, *J*=2.2, 6.6 Hz, 1H), 1.96 (d, *J*=2.2 Hz, 1H), 1.88 (s, 3H), 1.20 (d, *J*=6.6 Hz, 3H).

General Procedure for ^{1}H NMR Kinetic Measurements.

A solution of α-diazoketone (**5** or **18**) and alcohol in deuterated solvent (C_6D_6 or CD_2Cl_2) was treated with the appropriate rhodium(II) catalyst to effect complete decompositon of the diazo compound. Once nitrogen gas evolution was observed to have stopped (ca. 1 min), an aliquot of the mixture was transferred to an NMR tube. Rearrangement was monitored by ^{1}H NMR and the integration of enol resonances measured versus internal standard (residual alcohol for enols **7**, **8**, **9**, **15**, and **19**; added toluene for trifluoroacetate **11**) at regular time intervals at the desired temperature.

Preparation of Enol Trifluoroacetate 11.



To a stirred solution of azibenzil (**5**, 85 mg, 0.382 mmol, 1.0 equiv) and 3-buten-2-ol (40 µL, 0.462 mmol, 1.2 equiv) in CH_2Cl_2 (4 mL) was added $Rh_2(OAc)_4$ (1.7 mg, 0.0038 mmol, 0.01 equiv) resulting in decolorization of the reaction mixture and rapid N_2(g) loss. Once complete, the mixture was cooled to -78°C and treated with trifluoroacetic anhydride (80 µL, 0.566 mmol, 1.5 equiv) followed by Et_3N (0.12 mL, 0.863 mmol, 2.3 equiv). After 10 min the mixture was warmed to room temperature and concentrated and the residue purified by flash chromatography (4:1 pentane:CH_2Cl_2 eluent) to provide **11** (78 mg, 56% yield) as white needles. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29-7.37 (comp m, 5H), 7.13-7.20 (comp m, 5H), 5.81 (ddd, *J*=7.0, 10.3, 17.3 Hz, 1H), 5.11 (dt, *J*=1.1, 10.3 Hz, 1H), 4.99 (dt, *J*=1.1, 17.2 Hz, 1H), 4.22 (m, 1H), 1.30 (d, *J*=6.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.3 (q, *J*=42.6 Hz), 145.4, 138.5, 133.7, 132.4, 131.9, 130.1, 129.3, 128.5, 128.3, 128.2, 128.1, 116.3, 114.8 (q, *J*=283.7 Hz), 76.0, 20.7; **IR** (thin film/NaCl) 3085 (w), 3061 (w), 2982 (w), 2932 (w), 1801 (s), 1446 (m), 1358 (m), 1258 (s), 1222 (s), 1171 (s), 1135 (s), 1050 (m), 921 (m), 776 (m), 697 (s) cm^{-1}; **HRMS** (EI) *m/z* found: 362.1127, [calc'd for $C_{20}H_{17}F_3O_3$ (M+): 362.1130]; **m.p.** 57-59° C(pentane).

Preparation and X-Ray Crystallographic Analysis of Enol Acetate iv.

To a stirred solution of azibenzil (**5**, 733 mg, 3.30 mmol, 1.0 equiv) and methanol (0.15 mL, 3.70 mmol, 1.1 equiv) in CH_2Cl_2 (30 mL) was added $Rh_2(TFA)_4$ (22.0 mg, 0.033 mmol, 0.01 equiv) resulting in vigorous loss of N_2(g). The resulting pale green solution was added dropwise with careful air exclusion to a mixture of acetic anhydride (19 mL, 0.20 mol, 61 equiv) and BF_3•OEt_2 (63 mL, 0.50 mmol, 0.15 equiv) at -78°C. After stirring for 30 min at -78°C, the mixture was warmed to room temperature and concentrated under reduced pressure. The residue was redissolved in Et_2O (50 mL) and washed with sat. $NaHCO_3$ solution (careful-much CO_2(g) pressure) until washings were basic as indicated by pH paper. The organic phase was dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (1:1 hexanes:CH_2Cl_2 eluent) afforded enol acetate **iv** (780 mg, 88% yield) as a colorless viscous oil which solidified upon cooling (0°C) overnight. Recrystallization from heptane afforded crystals suitable for X-Ray analysis.

X-Ray Crystallography Report for Enol Acetate iv.

Data Collection

A colorless cut block crystal of $C_{17}H_{16}O_3$ having approximate dimensions of 0.24 x 0.28 x 0.30 mm was mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using ten (1^{o} in ω, 10s exposure, de-zingered) data frames, corresponded to a primitive monoclinic cell with dimensions: a = 7.8065(2) Å, b = 11.3336(5) Å, β = 94.158(2)o, c = 16.5721(6) Å and V = 1462.37(8) Å^3. For Z = 4 and F.W. = 268.31, the calculated density is 1.22 g/cm^3. The systematic absences of: h0l: h+l = 2n+1, 0k0: k = 2n+1; uniquely determine the space group to be: $P2_1/n$ (#14).

The data were collected at a temperature of 23 $\pm$ 1^{o}C to a maximum 2θ value of 61.0^{o}. One phi scan consisting of 179 data frames was collected with a scan width of 1^{o} and a detector-to-crystal distance, Dx, of 35mm. Each frame was exposed twice (for the purpose of de-zingering) for 60s. The data frames were processed and scaled using the DENZO software package. (Z. Otwinowski and W. Minor, “Processing of X-Ray Diffraction Data Collected in Oscillation Mode,” Methods in Enzymology, vol. 276: Macromolecular Crystallography, part A, 307-326, 1997, C.W. Carter, Jr. & R.M. Sweet, Eds., Academic Press).

Data Reduction

A total of 4330 reflections was collected. No decay correction was applied. The linear absorption coefficient, μ, for Mo-Kα radiation is 0.8 cm^{-1} and no absorption correction was applied. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques.[2] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement[3] was based on 2631 observed reflections ($I > 3.00\sigma(I)$) and 245 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \,||Fo| - |Fc|| \,/\, \Sigma\, |Fo| = 0.050$$

$$R_w = [(\Sigma\, w\, (|Fo| - |Fc|)^2 \,/\, \Sigma\, w\, Fo^2)]^{1/2} = 0.054$$

The standard deviation of an observation of unit weight[4] was 2.77. The weighting scheme was based on counting statistics and included a factor ($p = 0.010$) to downweight the intense reflections. Plots of $\Sigma\, w\, (|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.18 and -0.17 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[5] Anomalous dispersion effects were included in Fcalc[6]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[7] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[8] All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

References

(1) SIR92: Altomare, A., Burla, M.C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A., Polidori, G.; *J. Appl. Cryst.,* 27, 435-436 (1994).

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least-Squares:

Function minimized $\Sigma w(|F_o|-|F_c|)^2$

where $w = 1/\sigma^2(F_o)$

and $\sigma^2(F_o) = [S^2(C+R^2B) + (pF_o^2)^2]/Lp^2$

S = Scan rate

C = Total integrated peak count

R = Ratio of scan time to background counting time

B = Total background count
Lp = Lorentz-polarization factor
p = p-factor

(4) Standard deviation of an observation of unit weight:

$$[\Sigma w(|F_o|-|F_c|)/\sigma]/(N_o-N_v)$$

where N_o = number of observations and N_v = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; *Acta Crystallogr.*, 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{17}H_{16}O_3$
Formula Weight	268.31
Crystal Color, Habit	colorless, cut block
Crystal Dimensions	0.24 X 0.28 X 0.30 mm
Crystal System	monoclinic
Lattice Type	Primitive

Lattice Parameters	a = 7.8065(2)Å b = 11.3336(5) Å c = 16.5721(6) Å β = 94.158(2)^{o} V = 1462.37(8) Å^{3}
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.219 g/cm^{3}
F_{000}	568.00
μ(MoKα)	0.83 cm^{-1}

B. Intensity Measurements

Nonius KappaCCD

Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Take-off Angle	2.8^{o}
Crystal to Detector Distance	35 mm
Temperature	23.0^{o}C
Scan Rate	60s/frame
Scan Width	1^{o}/frame

$2\theta_{max}$	61.0°
No. of Reflections Measured	Total: 4330
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	Σ w $(\lvert Fo\rvert - \lvert Fc\rvert)^2$
Least Squares Weights	$1/\sigma^2(Fo)$
p-factor	0.0100
Anomalous Dispersion	All non-hydrogen atoms
No. Observations $(I>3.00\sigma(I))$	2631
No. Variables	245
Reflection/Parameter Ratio	10.74
Residuals: R; Rw	0.050 ; 0.054
Goodness of Fit Indicator	2.77
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.18 e-/Å^3
Minimum peak in Final Diff. Map	-0.17 e-/Å^3

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}

O(1)	0.0390(1)	0.07059(8)	0.16594(5)	4.83(2)
O(2)	0.2446(1)	-0.03678(9)	0.11463(6)	5.87(3)
O(3)	-0.1777(1)	-0.10860(9)	0.17913(6)	5.39(2)
C(1)	0.0506(1)	0.0010(1)	0.23709(7)	4.03(3)
C(2)	-0.0706(2)	-0.0804(1)	0.24566(7)	4.12(3)
C(3)	0.1484(2)	0.0450(1)	0.10895(8)	4.20(3)
C(4)	0.1320(3)	0.1320(2)	0.0413(1)	6.12(5)
C(5)	-0.3525(2)	-0.1335(3)	0.1916(2)	8.02(6)
C(6)	0.1970(1)	0.0297(1)	0.29413(7)	3.65(3)
C(7)	0.2449(2)	0.1466(1)	0.30961(9)	4.67(3)
C(8)	0.3864(2)	0.1739(2)	0.36100(10)	5.34(4)
C(9)	0.4838(2)	0.0857(2)	0.39738(9)	5.28(4)
C(10)	0.4392(2)	-0.0304(1)	0.38315(9)	4.90(3)
C(11)	0.2973(2)	-0.0583(1)	0.33185(8)	4.12(3)
C(12)	-0.0918(1)	-0.1436(1)	0.32292(7)	4.03(3)
C(13)	-0.1067(2)	-0.0801(1)	0.39371(8)	4.54(3)
C(14)	-0.1264(2)	-0.1368(2)	0.46621(9)	5.27(4)
C(15)	-0.1327(2)	-0.2579(2)	0.4687(1)	5.82(4)
C(16)	-0.1205(2)	-0.3213(2)	0.3992(1)	6.48(5)
C(17)	-0.0999(2)	-0.2654(1)	0.3261(1)	5.54(4)
H(1)	0.165(3)	0.095(2)	-0.005(2)	8.7(5)
H(2)	0.198(3)	0.192(2)	0.054(2)	11.1(7)
H(3)	0.015(4)	0.152(2)	0.028(2)	11.0(7)
H(4)	-0.412(3)	-0.132(2)	0.144(2)	9.7(6)
H(5)	-0.401(4)	-0.061(2)	0.226(2)	13.8(9)
H(6)	-0.360(3)	-0.200(3)	0.220(2)	12.4(9)
H(7)	0.178(2)	0.202(1)	0.2841(9)	5.1(3)
H(8)	0.419(2)	0.253(1)	0.3732(9)	6.2(4)
H(9)	0.588(2)	0.107(1)	0.433(1)	7.1(4)
H(10)	0.508(2)	-0.096(1)	0.4082(9)	5.6(3)
H(11)	0.267(2)	-0.144(1)	0.3207(8)	5.0(3)
H(12)	-0.101(2)	0.004(2)	0.3927(9)	5.5(3)
H(13)	-0.132(2)	-0.093(1)	0.516(1)	5.7(3)
H(14)	-0.148(2)	-0.299(1)	0.518(1)	7.1(4)
H(15)	-0.120(2)	-0.401(2)	0.398(1)	8.4(5)

H(16)	-0.084(2)	-0.311(1)	0.2788(10)	5.6(3)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Anisotropic Displacement Parameters

atom	U11	U22	U33	U12	U13	U23
O(1)	0.0559(5)	0.0764(6)	0.0520(6)	0.0134(4)	0.0086(4)	0.0213(4)
O(2)	0.0907(8)	0.0728(7)	0.0619(7)	0.0132(6)	0.0221(6)	0.0020(5)
O(3)	0.0515(6)	0.1047(8)	0.0481(6)	-0.0055(5)	-0.0010(4)	0.0019(5)
C(1)	0.0461(7)	0.0631(8)	0.0450(7)	0.0082(6)	0.0100(5)	0.0128(6)
C(2)	0.0442(7)	0.0708(8)	0.0417(7)	0.0038(6)	0.0045(5)	0.0033(6)
C(3)	0.0552(8)	0.0608(8)	0.0436(7)	-0.0074(7)	0.0026(6)	0.0021(6)
C(4)	0.094(1)	0.087(1)	0.0515(10)	-0.014(1)	0.0037(9)	0.0177(9)
C(5)	0.0527(9)	0.175(3)	0.076(1)	-0.026(1)	-0.0081(9)	0.015(2)
C(6)	0.0445(6)	0.0532(7)	0.0424(7)	0.0017(6)	0.0123(5)	0.0070(5)
C(7)	0.0656(9)	0.0542(8)	0.0601(9)	0.0045(7)	0.0213(7)	0.0134(7)
C(8)	0.076(1)	0.0648(9)	0.0649(10)	-0.0222(8)	0.0205(8)	-0.0074(8)
C(9)	0.0596(9)	0.086(1)	0.0550(9)	-0.0141(8)	0.0069(7)	-0.0047(8)
C(10)	0.0540(8)	0.0745(10)	0.0569(8)	0.0041(7)	0.0000(6)	0.0035(7)
C(11)	0.0491(7)	0.0543(8)	0.0531(8)	0.0020(6)	0.0042(6)	0.0023(6)
C(12)	0.0400(6)	0.0670(9)	0.0468(7)	-0.0049(6)	0.0074(5)	0.0043(6)
C(13)	0.0515(8)	0.0706(10)	0.0513(8)	-0.0080(7)	0.0105(6)	-0.0011(7)
C(14)	0.0598(9)	0.095(1)	0.0469(8)	-0.0141(8)	0.0097(7)	-0.0007(8)
C(15)	0.0666(9)	0.100(1)	0.0554(10)	-0.0078(9)	0.0108(7)	0.0210(9)
C(16)	0.093(1)	0.071(1)	0.084(1)	-0.0055(9)	0.0235(9)	0.0185(10)
C(17)	0.081(1)	0.0692(10)	0.0619(10)	-0.0074(8)	0.0195(8)	-0.0003(8)

The general temperature factor expression:

$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 3. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
O(1)	C(1)	1.416(1)	O(1)	C(3)	1.350(2)

O(2)	C(3)	1.192(2)	O(3)	C(2)	1.372(2)
O(3)	C(5)	1.423(2)	C(1)	C(2)	1.337(2)
C(1)	C(6)	1.466(2)	C(2)	C(12)	1.487(2)
C(3)	C(4)	1.491(2)	C(6)	C(7)	1.395(2)
C(6)	C(11)	1.388(2)	C(7)	C(8)	1.380(2)
C(8)	C(9)	1.369(2)	C(9)	C(10)	1.378(2)
C(10)	C(11)	1.383(2)	C(12)	C(13)	1.388(2)
C(12)	C(17)	1.383(2)	C(13)	C(14)	1.381(2)
C(14)	C(15)	1.375(2)	C(15)	C(16)	1.367(2)
C(16)	C(17)	1.386(2)			

Table 4. Bond Lengths(Å) for the Hydrogen Atoms

atom	atom	distance	atom	atom	distance
C(4)	H(1)	0.93(2)	C(4)	H(2)	0.87(2)
C(4)	H(3)	0.95(3)	C(5)	H(4)	0.89(3)
C(5)	H(5)	1.09(3)	C(5)	H(6)	0.90(3)
C(7)	H(7)	0.90(2)	C(8)	H(8)	0.95(2)
C(9)	H(9)	0.99(2)	C(10)	H(10)	0.99(2)
C(11)	H(11)	1.01(1)	C(13)	H(12)	0.96(2)
C(14)	H(13)	0.96(2)	C(15)	H(14)	0.95(2)
C(16)	H(15)	0.90(2)	C(17)	H(16)	0.96(2)

Table 5. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
C(1)	O(1)	C(3)	117.24(10)	C(2)	O(3)	C(5)	117.7(1)
O(1)	C(1)	C(2)	118.0(1)	O(1)	C(1)	C(6)	114.4(1)
C(2)	C(1)	C(6)	127.5(1)	O(3)	C(2)	C(1)	118.1(1)
O(3)	C(2)	C(12)	118.7(1)	C(1)	C(2)	C(12)	123.2(1)
O(1)	C(3)	O(2)	122.6(1)	O(1)	C(3)	C(4)	111.1(1)
O(2)	C(3)	C(4)	126.3(1)	C(1)	C(6)	C(7)	121.0(1)
C(1)	C(6)	C(11)	121.3(1)	C(7)	C(6)	C(11)	117.7(1)
C(6)	C(7)	C(8)	121.2(1)	C(7)	C(8)	C(9)	120.2(1)
C(8)	C(9)	C(10)	119.8(2)	C(9)	C(10)	C(11)	120.3(1)

C(6)	C(11)	C(10)	120.9(1)	C(2)	C(12)	C(13)	119.9(1)
C(2)	C(12)	C(17)	121.5(1)	C(13)	C(12)	C(17)	118.5(1)
C(12)	C(13)	C(14)	121.1(1)	C(13)	C(14)	C(15)	119.8(2)
C(14)	C(15)	C(16)	119.7(2)	C(15)	C(16)	C(17)	121.0(2)
C(12)	C(17)	C(16)	119.9(2)				

Table 6. Bond Angles(°) for the Hydrogen Atoms

atom	atom	atom	angle	atom	atom	atom	angle
C(3)	C(4)	H(1)	108(1)	C(3)	C(4)	H(2)	108(1)
C(3)	C(4)	H(3)	111(1)	H(1)	C(4)	H(2)	111(2)
H(1)	C(4)	H(3)	103(1)	H(2)	C(4)	H(3)	114(2)
O(3)	C(5)	H(4)	108(1)	O(3)	C(5)	H(5)	107(1)
O(3)	C(5)	H(6)	110(1)	H(4)	C(5)	H(5)	105(1)
H(4)	C(5)	H(6)	115(2)	H(5)	C(5)	H(6)	108(2)
C(6)	C(7)	H(7)	115.9(9)	C(8)	C(7)	H(7)	123.0(9)
C(7)	C(8)	H(8)	122.1(9)	C(9)	C(8)	H(8)	117.8(9)
C(8)	C(9)	H(9)	119.0(10)	C(10)	C(9)	H(9)	121.2(10)
C(9)	C(10)	H(10)	121.4(8)	C(11)	C(10)	H(10)	118.2(8)
C(6)	C(11)	H(11)	119.4(8)	C(10)	C(11)	H(11)	119.7(8)
C(12)	C(13)	H(12)	119.7(9)	C(14)	C(13)	H(12)	119.2(9)
C(13)	C(14)	H(13)	120.9(9)	C(15)	C(14)	H(13)	119.3(9)
C(14)	C(15)	H(14)	121(1)	C(16)	C(15)	H(14)	119(1)
C(15)	C(16)	H(15)	122(1)	C(17)	C(16)	H(15)	116(1)
C(12)	C(17)	H(16)	120.1(9)	C(16)	C(17)	H(16)	119.9(9)

Table 7. Torsion Angles(°)

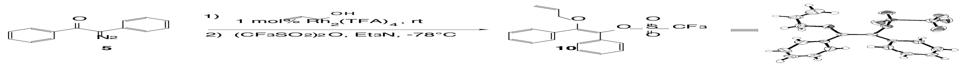
atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(1)	C(1)	C(2)	O(3)	13.1(2)	O(1)	C(1)	C(2)	C(12)	-168.5(1)
O(1)	C(1)	C(6)	C(7)	41.1(1)	O(1)	C(1)	C(6)	C(11)	-136.1(1)
O(2)	C(3)	O(1)	C(1)	4.5(2)	O(3)	C(2)	C(1)	C(6)	-167.9(1)
O(3)	C(2)	C(12)	C(13)	-128.8(1)	O(3)	C(2)	C(12)	C(17)	50.1(2)
C(1)	O(1)	C(3)	C(4)	-174.8(1)	C(1)	C(2)	O(3)	C(5)	-143.4(2)
C(1)	C(2)	C(12)	C(13)	52.8(2)	C(1)	C(2)	C(12)	C(17)	-128.3(2)
C(1)	C(6)	C(7)	C(8)	-177.6(1)	C(1)	C(6)	C(11)	C(10)	177.5(1)

C(2)	C(1)	O(1)	C(3)	-104.7(1)	C(2)	C(1)	C(6)	C(7)	-137.9(1)
C(2)	C(1)	C(6)	C(11)	44.9(2)	C(2)	C(12)	C(13)	C(14)	-180.0(1)
C(2)	C(12)	C(17)	C(16)	-179.7(1)	C(3)	O(1)	C(1)	C(6)	76.2(1)
C(5)	O(3)	C(2)	C(12)	38.1(2)	C(6)	C(1)	C(2)	C(12)	10.5(2)
C(6)	C(7)	C(8)	C(9)	0.6(2)	C(6)	C(11)	C(10)	C(9)	-0.3(2)
C(7)	C(6)	C(11)	C(10)	0.2(2)	C(7)	C(8)	C(9)	C(10)	-0.6(2)
C(8)	C(7)	C(6)	C(11)	-0.3(2)	C(8)	C(9)	C(10)	C(11)	0.5(2)
C(12)	C(13)	C(14)	C(15)	-0.5(2)	C(12)	C(17)	C(16)	C(15)	-0.1(3)
C(13)	C(12)	C(17)	C(16)	-0.8(2)	C(13)	C(14)	C(15)	C(16)	-0.5(2)
C(14)	C(13)	C(12)	C(17)	1.1(2)	C(14)	C(15)	C(16)	C(17)	0.8(3)

Table 8. Non-bonded Contacts out to 3.60 Å

atom	atom	distance	ADC	atom	atom	distance	ADC
O(1)	C(16)	3.582(2)	45502	O(2)	C(8)	3.467(2)	54502
O(2)	C(5)	3.485(3)	65501	O(2)	C(15)	3.537(2)	54404
O(3)	C(8)	3.451(2)	54502	C(10)	C(13)	3.581(2)	65501

Preparation and X-Ray Crystallographic Analysis of Enol Triflate 10



To a stirred solution of azibenzil (**5**, 101 mg, 0.454 mmol, 1.0 equiv) and allyl alcohol (37 μL, 0.544 mmol, 1.2 equiv) in CH_2Cl_2 (5 mL) was added $Rh_2(TFA)_4$ (3.8 mg, 0.006 mmol, 0.01 equiv) resulting in rapid N_2(g) loss and decolorization. The solution was cooled to -78°C and treated with triflic anhydride (0.11 mL, 0.654 mmol, 1.4 equiv) and Et_3N (0.25 mL, 1.80 mmol, 4.0 equiv) in rapid succession. The mixture was allowed to stir for 15 min at -78°C before being warmed to room temperature, diluted with CH_2Cl_2 (5 mL), and washed with sat. $NaHCO_3$ solution (3 x 10 mL). Combined aqueous phases were backwashed with CH_2Cl_2 (2 x 10 mL). Combined organic phases were dried over $MgSO_4$, filtered and rotavapped. The resulting residue was purified by flash chromatography (4:1 pentane:CH_2Cl_2 eluent) affording enol triflate **10** (121 mg, 69% yield) as a white solid. Recrystallization from pentane afforded crystals suitable for X-Ray analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16-7.36 (comp m, 10H), 5.98 (m, 1H), 5.26 (m, 2H), 4.22 (dt, *J*=1.3, 5.8 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.8, 134.5, 132.8, 131.7, 130.7, 130.0, 129.7, 129.2, 128.7, 128.6, 128.2, 118.4, 118.4 (q, *J*=318 Hz), 70.7; **IR** (thin film/NaCl) 3072 (m), 2938 (m), 2880 (w), 1967 (w), 1894 (w), 1654 (m), 1414 (s), 1214 (s), 1134 (s), 997 (s), 963 (s), 824 (s), 766 (m), 697 (s) cm^{-1}; **m.p.** 53-55° C(dec.) (pentane).

X-Ray Crystallography Report for Enol Triflate 10.

Data Collection

A colorless plate crystal of $C_{18}H_{15}O_4F_3S$ having approximate dimensions of 0.08 x 0.22 x 0.26 mm was mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using ten (1° in ω, 10s exposure, de-zingered) data frames, corresponded to a primitive orthorhombic cell with dimensions: a = 10.0680(2) Å, b = 17.4948(5) Å, c = 20.1991(5) Å and V = 3557.8(1) Å^3. For Z = 8 and F.W. = 384.37, the calculated density is 1.43 g/cm^3. The systematic absences of: 0kl: k = 2n+1; h0l: l = 2n+1; hk0: h = 2n+1; uniquely determine the space group to be: Pbca (#61).

The data were collected at a temperature of -90 $\pm$ 1°C to a maximum 2θ value of 61.0°. One phi scan consisting of 166 data frames was collected with a scan width of 1° and a detector-to-crystal distance, Dx, of 35mm. Each frame was exposed twice (for the purpose of de-zingering) for 50s. The data frames were processed and scaled using the DENZO software package. (Z. Otwinowski and W. Minor, "Processing of X-Ray Diffraction Data Collected in Oscillation Mode," Methods in Enzymology, vol. 276: Macromolecular Crystallography, part A, 307-326, 1997, C.W. Carter, Jr. & R.M. Sweet, Eds., Academic Press).

Data Reduction

A total of 5928 reflections was collected. No decay correction was applied. The linear absorption coefficient, μ, for Mo-Kα radiation is 2.3 cm^{-1} and no absorption correction was applied. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 6.74585e-07).

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement[3] was based on 2899 observed reflections ($I > 5.00\sigma(I)$) and 235 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \,||Fo| - |Fc|| \,/\, \Sigma \,|Fo| = 0.041$$

$$R_W = [(\Sigma\, w\, (|Fo| - |Fc|)^2 \,/\, \Sigma\, w\, Fo^2)]^{1/2} = 0.047$$

The standard deviation of an observation of unit weight[4] was 2.76. The weighting scheme was based on counting statistics and included a factor ($p = 0.010$) to downweight the intense reflections. Plots of $\Sigma\, w\, (|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.68 and -0.31 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[5] Anomalous dispersion effects were included in Fcalc[6]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[7] The values for the mass attenuation coefficients are those of Creagh and Hubbel[8]. All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

References

(1)SIR92: Altomare, A., Burla, M.C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A., & Polidori, G.; *J. Appl. Cryst.,* 27, 435-436 (1994).

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least-Squares:

Function minimized $\Sigma w(|F_o|-|F_c|)^2$

where $w = 1/\sigma^2(F_o^2)$

and $\sigma^2(F_o^2) = [S^2(C+R^2B) + (pF_o^2)^2]/Lp^2$

S = Scan rate

C = Total integrated peak count

R = Ratio of scan time to background counting time

B = Total background count

Lp = Lorentz-polarization factor

p = p-factor

(4) Standard deviation of an observation of unit weight:

$[\Sigma(|F_o|-|F_c|)/\sigma]/(N_o-N_v)$

where N_o = number of observations

N_v = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; *Acta Crystallogr.*, 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{18}H_{15}O_4F_3S$
Formula Weight	384.37
Crystal Color, Habit	colorless, plate

Crystal Dimensions	0.08 X 0.22 X 0.26 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 10.0680(2)Å b = 17.4948(5) Å c = 20.1991(5) Å V = 3557.8(1) $Å^3$
Space Group	Pbca (#61)
Z value	8
D_{calc}	1.435 g/cm^3
F_{000}	1584.00
μ(MoKα)	2.32 cm^{-1}

B. Intensity Measurements

Diffractometer	Nonius KappaCCD
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Take-off Angle	2.8°
Crystal to Detector Distance	35mm

Temperature	-90.0^{o}C
Scan Rate	50sec/frame
Scan Width	1o/frame
$2\theta_{max}$	61.0^{o}
No. of Reflections Measured	Total: 5928
Corrections	Lorentz-polarization Secondary Extinction (coefficient: 6.74585e-07)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma\ w\ (\lvert Fo\rvert - \lvert Fc\rvert)^2$
Least Squares Weights	$1/\sigma^2 Fo$
p-factor	0.0100
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>5.00\sigma(I)$)	2899
No. Variables	235
Reflection/Parameter Ratio	12.34
Residuals: R; Rw	0.041 ; 0.047
Goodness of Fit Indicator	2.76
Max Shift/Error in Final Cycle	0.00

Maximum peak in Final Diff. Map	0.68 e-/Å^3
Minimum peak in Final Diff. Map	-0.31 e-/Å^3

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
S(1)	-0.06773(5)	0.03668(3)	0.69126(2)	2.66(1)
F(1)	0.0015(1)	0.00404(9)	0.81077(7)	5.38(4)
F(2)	-0.1267(2)	0.1016(1)	0.80309(7)	6.62(4)
F(3)	0.0780(1)	0.11049(8)	0.77583(7)	5.32(4)
O(1)	-0.1175(1)	0.11472(7)	0.66303(6)	2.51(3)
O(2)	0.0510(1)	0.01252(9)	0.66127(7)	3.85(4)
O(3)	-0.1791(2)	-0.01178(9)	0.69691(8)	4.26(4)
O(4)	-0.1229(1)	0.07184(7)	0.53892(6)	2.94(3)
C(1)	-0.0374(2)	0.1568(1)	0.61568(9)	2.34(4)
C(2)	-0.0539(2)	0.1375(1)	0.55240(9)	2.36(4)
C(3)	-0.0266(2)	0.0654(1)	0.7756(1)	3.61(5)
C(4)	0.0446(2)	0.2170(1)	0.64538(9)	2.27(4)
C(5)	-0.0077(2)	0.2647(1)	0.6939(1)	2.90(5)
C(6)	0.0687(2)	0.3224(1)	0.7209(1)	3.32(5)
C(7)	0.1978(2)	0.3334(1)	0.7004(1)	3.28(5)
C(8)	0.2516(2)	0.2857(1)	0.6532(1)	3.06(5)
C(9)	0.1765(2)	0.2275(1)	0.62584(9)	2.66(4)
C(10)	-0.1997(2)	0.0695(1)	0.47868(10)	3.33(5)
C(11)	-0.3056(2)	0.0116(1)	0.4860(1)	3.67(5)
C(12)	-0.3456(2)	-0.0214(2)	0.5396(2)	5.00(7)
C(13)	0.0058(2)	0.1812(1)	0.49715(9)	2.40(4)
C(14)	-0.0127(2)	0.2599(1)	0.4920(1)	3.19(5)
C(15)	0.0480(2)	0.3003(1)	0.4416(1)	3.72(5)
C(16)	0.1266(2)	0.2629(1)	0.3957(1)	3.71(5)
C(17)	0.1434(2)	0.1847(1)	0.3998(1)	3.45(5)
C(18)	0.0823(2)	0.1437(1)	0.45000(10)	2.85(5)
H(1)	-0.0965	0.2576	0.7085	3.4818
H(2)	0.0319	0.3548	0.7539	3.9796
H(3)	0.2495	0.3736	0.7187	3.9308
H(4)	0.3409	0.2927	0.6394	3.6684

H(5)	0.2147	0.1946	0.5936	3.1944
H(6)	-0.2382	0.1182	0.4707	3.9974
H(7)	-0.1437	0.0562	0.4426	3.9974
H(8)	-0.3497	-0.0031	0.4464	4.3992
H(9)	-0.3054	-0.0091	0.5808	5.9970
H(10)	-0.4152	-0.0580	0.5379	5.9970
H(11)	-0.0670	0.2858	0.5232	3.8303
H(12)	0.0356	0.3540	0.4384	4.4657
H(13)	0.1690	0.2909	0.3615	4.4519
H(14)	0.1969	0.1589	0.3681	4.1432
H(15)	0.0928	0.0898	0.4522	3.4192

Table 2. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.0446(3)	0.0293(3)	0.0273(2)	0.0000(2)	-0.0021(2)	-0.0002(2)
F(1)	0.100(1)	0.0633(10)	0.0415(8)	-0.0006(8)	-0.0204(7)	0.0173(7)
F(2)	0.100(1)	0.112(1)	0.0401(8)	0.038(1)	0.0098(8)	-0.0189(8)
F(3)	0.0850(10)	0.0586(9)	0.0585(9)	-0.0149(8)	-0.0317(8)	-0.0028(7)
O(1)	0.0352(7)	0.0305(8)	0.0295(7)	-0.0002(6)	0.0043(6)	0.0041(6)
O(2)	0.0592(10)	0.0463(9)	0.0407(9)	0.0190(8)	0.0074(7)	0.0003(7)
O(3)	0.0636(10)	0.0410(9)	0.057(1)	-0.0194(8)	-0.0112(8)	0.0128(8)
O(4)	0.0491(8)	0.0326(8)	0.0302(7)	-0.0085(7)	-0.0070(6)	0.0004(6)
C(1)	0.0335(10)	0.028(1)	0.027(1)	0.0006(8)	0.0037(8)	0.0032(8)
C(2)	0.034(1)	0.026(1)	0.030(1)	0.0013(9)	-0.0022(9)	-0.0003(8)
C(3)	0.059(1)	0.046(1)	0.032(1)	0.004(1)	-0.006(1)	0.000(1)
C(4)	0.034(1)	0.028(1)	0.0246(9)	0.0017(8)	-0.0016(8)	0.0019(8)
C(5)	0.039(1)	0.036(1)	0.035(1)	-0.0005(9)	0.0046(9)	-0.0046(10)
C(6)	0.053(1)	0.035(1)	0.037(1)	0.002(1)	0.001(1)	-0.0096(10)
C(7)	0.047(1)	0.036(1)	0.041(1)	-0.007(1)	-0.008(1)	-0.0050(10)
C(8)	0.036(1)	0.042(1)	0.038(1)	-0.0037(10)	-0.0028(9)	0.003(1)
C(9)	0.037(1)	0.035(1)	0.028(1)	0.0028(9)	0.0002(9)	-0.0016(9)
C(10)	0.042(1)	0.054(1)	0.031(1)	-0.003(1)	-0.0079(9)	-0.005(1)
C(11)	0.043(1)	0.050(1)	0.047(1)	-0.004(1)	-0.008(1)	-0.002(1)
C(12)	0.048(1)	0.059(2)	0.083(2)	-0.007(1)	-0.012(1)	-0.001(1)

C(13)	0.034(1)	0.031(1)	0.0256(10)	0.0000(9)	-0.0044(8)	0.0020(9)
C(14)	0.056(1)	0.034(1)	0.032(1)	-0.001(1)	-0.0056(10)	-0.0017(9)
C(15)	0.064(1)	0.034(1)	0.044(1)	-0.006(1)	-0.013(1)	0.009(1)
C(16)	0.043(1)	0.059(2)	0.039(1)	-0.015(1)	-0.007(1)	0.018(1)
C(17)	0.037(1)	0.058(2)	0.036(1)	0.002(1)	0.0018(10)	0.007(1)
C(18)	0.036(1)	0.036(1)	0.036(1)	0.0026(9)	-0.0005(9)	0.0030(9)

The general temperature factor expression:
$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 3. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
S(1)	O(1)	1.562(1)	S(1)	O(2)	1.405(2)
S(1)	O(3)	1.410(2)	S(1)	C(3)	1.824(2)
F(1)	C(3)	1.318(3)	F(2)	C(3)	1.313(2)
F(3)	C(3)	1.316(3)	O(1)	C(1)	1.452(2)
O(4)	C(2)	1.370(2)	O(4)	C(10)	1.442(2)
C(1)	C(2)	1.332(3)	C(1)	C(4)	1.467(3)
C(2)	C(13)	1.480(3)	C(4)	C(5)	1.390(3)
C(4)	C(9)	1.398(3)	C(5)	C(6)	1.382(3)
C(6)	C(7)	1.378(3)	C(7)	C(8)	1.378(3)
C(8)	C(9)	1.382(3)	C(10)	C(11)	1.478(3)
C(11)	C(12)	1.292(3)	C(13)	C(14)	1.392(3)
C(13)	C(18)	1.390(3)	C(14)	C(15)	1.382(3)
C(15)	C(16)	1.383(3)	C(16)	C(17)	1.381(3)
C(17)	C(18)	1.385(3)			

Table 4. Bond Lengths(Å) for the Hydrogen Atoms

atom	atom	distance	atom	atom	distance
C(5)	H(1)	0.95	C(6)	H(2)	0.95
C(7)	H(3)	0.95	C(8)	H(4)	0.95
C(9)	H(5)	0.95	C(10)	H(6)	0.95
C(10)	H(7)	0.95	C(11)	H(8)	0.95

C(12)	H(9)	0.95	C(12)	H(10)	0.95
C(14)	H(11)	0.95	C(15)	H(12)	0.95
C(16)	H(13)	0.95	C(17)	H(14)	0.95
C(18)	H(15)	0.95			

Table 5. Bond Angles(^{o})

atom	atom	atom	angle	atom	atom	atom	angle
O(1)	S(1)	O(2)	112.24(8)	O(1)	S(1)	O(3)	107.45(8)
O(1)	S(1)	C(3)	99.96(9)	O(2)	S(1)	O(3)	122.0(1)
O(2)	S(1)	C(3)	107.01(10)	O(3)	S(1)	C(3)	105.7(1)
S(1)	O(1)	C(1)	120.3(1)	C(2)	O(4)	C(10)	117.6(1)
O(1)	C(1)	C(2)	115.8(2)	O(1)	C(1)	C(4)	114.0(1)
C(2)	C(1)	C(4)	130.1(2)	O(4)	C(2)	C(1)	117.8(2)
O(4)	C(2)	C(13)	119.3(2)	C(1)	C(2)	C(13)	122.8(2)
S(1)	C(3)	F(1)	109.1(2)	S(1)	C(3)	F(2)	110.7(2)
S(1)	C(3)	F(3)	110.5(2)	F(1)	C(3)	F(2)	109.2(2)
F(1)	C(3)	F(3)	108.4(2)	F(2)	C(3)	F(3)	108.9(2)
C(1)	C(4)	C(5)	120.4(2)	C(1)	C(4)	C(9)	120.9(2)
C(5)	C(4)	C(9)	118.7(2)	C(4)	C(5)	C(6)	120.4(2)
C(5)	C(6)	C(7)	120.5(2)	C(6)	C(7)	C(8)	119.6(2)
C(7)	C(8)	C(9)	120.5(2)	C(4)	C(9)	C(8)	120.2(2)
O(4)	C(10)	C(11)	108.7(2)	C(10)	C(11)	C(12)	128.0(2)
C(2)	C(13)	C(14)	120.9(2)	C(2)	C(13)	C(18)	119.8(2)
C(14)	C(13)	C(18)	119.3(2)	C(13)	C(14)	C(15)	120.1(2)
C(14)	C(15)	C(16)	120.3(2)	C(15)	C(16)	C(17)	119.9(2)
C(16)	C(17)	C(18)	120.1(2)	C(13)	C(18)	C(17)	120.3(2)

Table 6. Bond Angles(^{o}) for the Hydrogen Atoms

atom	atom	atom	angle	atom	atom	atom	angle
C(4)	C(5)	H(1)	119.8	C(6)	C(5)	H(1)	119.8
C(5)	C(6)	H(2)	119.7	C(7)	C(6)	H(2)	119.7
C(6)	C(7)	H(3)	120.2	C(8)	C(7)	H(3)	120.2
C(7)	C(8)	H(4)	119.7	C(9)	C(8)	H(4)	119.7

C(4)	C(9)	H(5)	119.9	C(8)	C(9)	H(5)	119.9
O(4)	C(10)	H(6)	109.7	O(4)	C(10)	H(7)	109.7
C(11)	C(10)	H(6)	109.7	C(11)	C(10)	H(7)	109.7
H(6)	C(10)	H(7)	109.5	C(10)	C(11)	H(8)	116.0
C(12)	C(11)	H(8)	116.0	C(11)	C(12)	H(9)	120.0
C(11)	C(12)	H(10)	120.0	H(9)	C(12)	H(10)	120.0
C(13)	C(14)	H(11)	120.0	C(15)	C(14)	H(11)	120.0
C(14)	C(15)	H(12)	119.8	C(16)	C(15)	H(12)	119.8
C(15)	C(16)	H(13)	120.0	C(17)	C(16)	H(13)	120.0
C(16)	C(17)	H(14)	120.0	C(18)	C(17)	H(14)	120.0
C(13)	C(18)	H(15)	119.9	C(17)	C(18)	H(15)	119.9

Table 7. Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
S(1)	O(1)	C(1)	C(2)	86.3(2)	S(1)	O(1)	C(1)	C(4)	-96.7(2)
F(1)	C(3)	S(1)	O(1)	171.7(1)	F(1)	C(3)	S(1)	O(2)	-71.2(2)
F(1)	C(3)	S(1)	O(3)	60.2(2)	F(2)	C(3)	S(1)	O(1)	51.5(2)
F(2)	C(3)	S(1)	O(2)	168.6(2)	F(2)	C(3)	S(1)	O(3)	-60.0(2)
F(3)	C(3)	S(1)	O(1)	-69.3(2)	F(3)	C(3)	S(1)	O(2)	47.8(2)
F(3)	C(3)	S(1)	O(3)	179.3(1)	O(1)	C(1)	C(2)	O(4)	-12.3(2)
O(1)	C(1)	C(2)	C(13)	171.5(1)	O(1)	C(1)	C(4)	C(5)	-42.9(2)
O(1)	C(1)	C(4)	C(9)	136.9(2)	O(2)	S(1)	O(1)	C(1)	-5.2(2)
O(3)	S(1)	O(1)	C(1)	-142.0(1)	O(4)	C(2)	C(1)	C(4)	171.3(2)
O(4)	C(2)	C(13)	C(14)	131.4(2)	O(4)	C(2)	C(13)	C(18)	-49.2(2)
O(4)	C(10)	C(11)	C(12)	13.6(3)	C(1)	O(1)	S(1)	C(3)	108.0(1)
C(1)	C(2)	O(4)	C(10)	148.4(2)	C(1)	C(2)	C(13)	C(14)	-52.4(3)
C(1)	C(2)	C(13)	C(18)	126.9(2)	C(1)	C(4)	C(5)	C(6)	-178.7(2)
C(1)	C(4)	C(9)	C(8)	178.5(2)	C(2)	O(4)	C(10)	C(11)	-156.9(2)
C(2)	C(1)	C(4)	C(5)	133.5(2)	C(2)	C(1)	C(4)	C(9)	-46.7(3)
C(2)	C(13)	C(14)	C(15)	177.5(2)	C(2)	C(13)	C(18)	C(17)	-177.1(2)
C(4)	C(1)	C(2)	C(13)	-4.9(3)	C(4)	C(5)	C(6)	C(7)	-0.2(3)
C(4)	C(9)	C(8)	C(7)	0.6(3)	C(5)	C(4)	C(9)	C(8)	-1.7(3)
C(5)	C(6)	C(7)	C(8)	-0.9(3)	C(6)	C(5)	C(4)	C(9)	1.5(3)
C(6)	C(7)	C(8)	C(9)	0.7(3)	C(10)	O(4)	C(2)	C(13)	-35.3(2)
C(13)	C(14)	C(15)	C(16)	0.4(3)	C(13)	C(18)	C(17)	C(16)	-1.1(3)

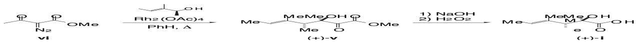
C(14)	C(13)	C(18)	C(17)	2.3(3)	C(14)	C(15)	C(16)	C(17)	0.8(3)
C(15)	C(14)	C(13)	C(18)	-1.9(3)	C(15)	C(16)	C(17)	C(18)	-0.5(3)

Table 8. Non-bonded Contacts out to 3.60 Å

atom	atom	distance	ADC	atom	atom	distance	ADC
F(1)	O(3)	3.232(2)	55608	F(1)	C(6)	3.318(3)	54603
F(1)	C(12)	3.420(3)	55608	F(2)	C(9)	3.293(2)	45608
F(2)	F(3)	3.377(2)	45608	F(2)	C(8)	3.557(3)	45608
F(3)	O(3)	3.296(2)	55608	F(3)	O(1)	3.306(2)	55608
F(3)	C(16)	3.319(3)	7	O(1)	C(16)	3.554(2)	45602
O(2)	C(10)	3.506(2)	55605	O(3)	C(7)	3.416(3)	54603
O(3)	C(6)	3.522(3)	54603	C(11)	C(12)	3.554(3)	45605
C(12)	C(18)	3.414(3)	55605	C(12)	C(12)	3.577(5)	45605

Notes and References

(1) α-hydroxyacid (+)-**i** is generated via oxidative decarboxylation of α-ketoester (+)-**v**, prepared from methyl diazoacetoacetate **vi** and *S*-3-methyl-3-penten-2-ol. For details regarding the assigment of relative stereochemistry of **i**, see: Wood, J. L.; Moniz, G. A.; Pflum, D. A.; Stoltz, B. M.; Holubec, A. A.; Dietrich, H.-J. *J. Am. Chem. Soc.* **1999**, *121*, 1748 and accompanying supporting information.



(2) The diazo transfer conditions were taken from: Taber, D. F.; Gleave, D. M.; Herr, R. J.; Moody, K.; Hennessy, M. J. *J. Org. Chem.* **1995**, *60*, 2283.

(3) Hickmott, P. W.; Ahmed, S. A. *J. Bangladesh Chem. Soc.* **1989**, *2*, 13.