**Stereospecific decarboxylative allylation of sulfones**

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## Supporting Information

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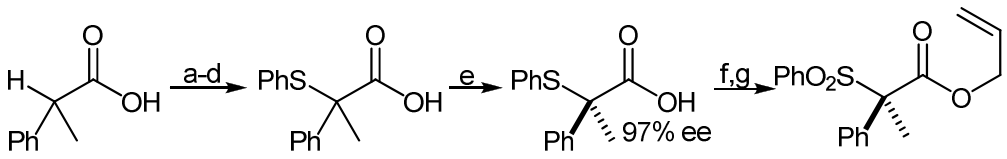
**Experimental:**

**General Information:**
All reactions were run in flame-dried glassware under an Ar atmosphere using standard Schlenk techniques. Toluene was dried over activated alumina and then distilled over sodium. Commercially available reagents were used without additional purification unless otherwise stated. Tris(dibenzylideneacetone) dipalladium (0), $Pd(PPh_3)_4$, and rac-BINAP were purchased from Strem and stored in a glovebox under an Ar atmosphere. All drying during reaction workups was performed using anhydrous powedered magnesium sulfate. Compound purification was effected by flash chromatography using 230x400 mesh, 60 Å porosity, silica obtained from Sorbent Technologies. $^1$H NMR and $^{13}$C NMR spectra were obtained on a Bruker Avance 400 or a Bruker Avance 500 DRX, or a Bruker AVIII 500 spectrometer and referenced to residual protio solvent signals (some spectra were taken using a broadband observe probe and a dual 13C/1H Cryoprobe). Structural assignments are based on $^1$H, $^{13}$C, DEPT-135, COSY, HSQC and IR spectroscopies.

**Procedure for the synthesis of 1a and 1g:** 2-phenyl-2-(phenylthio)propanoic acid (27.3 mmol) and (*S*)-α-methyl benzyl amine were added to a fritted filter—equipped with a screw valve. EtOH (18.2 mL) and $H_2O$ (18.2 mL) were added and the mixture was heated to reflux. Upon dissolution the filter was loosly capped and cooled to 0 °C. After precipitation had ceased the valve was open and the solvent removed by vacumn filtration. The diastereomeric salt was recrystallized (5X) using 4.2 mL/g of salt of a 3:1 EtOH:$H_2O$ mixture. After the fifth recrystallization, the free acid was recovered by the addition of 3 M HCl and extraction with ethyl acetate to afford 2-phenyl-2-(phenylthio)propanoic acid (1.67 mmol) in 97% ee. The acid was esterified by a standard DCC/DMAP prep followed by *m*CPBA oxidation of the sulfide ester to the sulfonyl ester.[1]

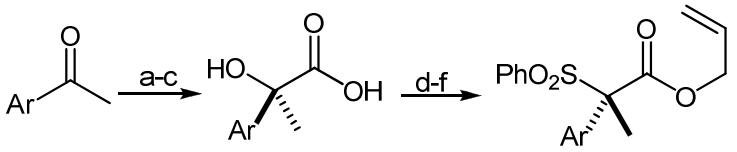



a) $H_2SO_4$, EtOH b) NBS, $Br_2$ (cat.), $CCl_4$, c) NaSPh, EtOH d) LiOH, $H_2O$, MeOH, THF e) phenethyl amine, EtOH:$H_2O$ 3:1 Recrystalize 5X f) allyl alcohol, DCC, DMAP, $CH_2Cl_2$ g) *m*CPBA, $CH_2Cl_2$

**Syntheses of 1b-f,h, i-k:** These compounds were made by the methods outlined by Weaver, Morris, and Tunge.[2]

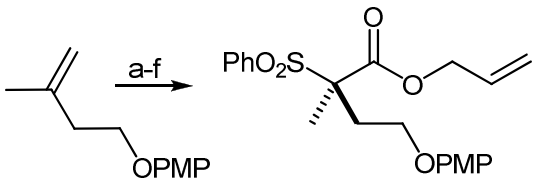
[1] Weaver, J. D.; Tunge, J. A. *Org. Lett*. **2008**, *10*, 4657.

[2] Weaver, J. D.; Morris, D. K.; Tunge, J. A. *Synlett* **2010**, 470.



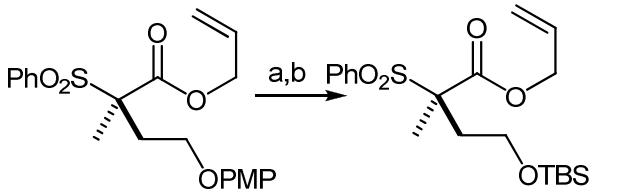

a) MePPh$_3$Br, KO*t*Bu, THF b) AD-mix-α–or-β c) Pt/C, NaHCO$_3$, Air, H$_2$O, 70 °C d) K$_2$CO$_3$, Bromide Acetone, rt e) 1) MsCl, DMAP, Pyr, -5 - 0 °C, 2) NaSPh, EtOH, 0 °C-rt f) *m*CPBA, CH$_2$Cl$_2$

**Syntheses of 1i-k:** These compounds were made by the methods outlined by Weaver, Morris, and Tunge.[3]




a) AD-mix-α–or-β b) Pt/C, NaHCO$_3$, Air, H$_2$O, 70 °C c) K$_2$CO$_3$, Bromide Acetone, rt d) MsCl, DMAP, Pyr, rt, e) NaSPh, EtOH, rt f) *m*CPBA, CH$_2$Cl$_2$

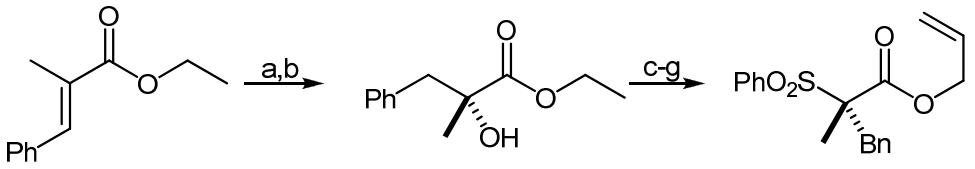
**Synthesis of 1i: 1j** was subjected to oxidative removal of the PMP group and silylation. **1j** (0.175 mmol) was dissolved in MeCN (1.75 mL) and H$_2$O (0.44 mL) and cooled to 0 °C. CAN (cerric ammonium nitrate) (0.525 mmol) was added and the reaction was stirred for 10 min. The reaction was purified by flash chromatography (9:1-1:1 hexanes:Ethyl acetate) to afford the corresponding free alcohol (0.161 mmol). The free alcohol (0.137 mmol) was subjected to TBSCl (0.686 mmol) and imidazole (0.822 mmol) were dissolved in DMF (2.0 mL) for 3h at room temperature. The reaction was extracted with ethyl acetate (15 mL) and washed (4 x 5 mL) with H$_2$O and dried and concentrated and the crude product was purified by column chromatography (9:1 hexanes:ethyl acetate) which coeluted with a silyl contaminant which was removed by sequential azeotroping with toluene to afford pure **1i** (0.112 mmol).




a) CAN, MeCN, H$_2$O, 0 °C b) TBSCl, Imidazole, DMF

**Syntheses of 1l,m:** The corresponding ethyl ester was synthesized as outlined in the afformentioed prep.[2] The ethyl esters (0.639 mmol) were saponified by the addition of LiOH (1.278 mmol), H$_2$O (81 μL), MeOH (0.5 mL) and THF (1.3 mL) to afford the corresponding acid (0.619 mmol). The acids were esterified with the corresponding allyl alcohols via standard DCC/DMAP couplings.[1]

[3] Weaver, J. D.; Morris, D. K.; Tunge, J. A. *Synlett* **2010**, 470.




a) AD-mix-α–or-β b) TFAA, Pd/C, $H_2$ c) MsCl, DMAP, Pyr, rt, d) NaSPh, EtOH, rt e) *m*CPBA, $CH_2Cl_2$ f) LiOH, $H_2O$, MeOH, THF g) allyl alcohol, DCC, DMAP, $CH_2Cl_2$

**Representative procedure for the palladium catalyzed decarboxylation of α-phenyl substituted acetic esters (Procedure A):** To a flame dried Schlenk tube was added (R)-cinnamyl 2-(4-chlorophenyl)-2-(phenylsulfonyl)propanoate (56 mg, 0.127 mmol) and then taken into the glovebox where toluene (0.64 mL), and $Pd(PPh_3)_4$ (2.9 mg, 0.00254 mmol) were added under an atmosphere of argon. The solution was allowed to stir 10 min.-2h at room temperature, until a noticeable change in solution color occurred, more time resulted in the formation of Pd-black. The reaction was quenched and purified by loading the reaction mixture onto a silica column, where it was purified by flash column chromatography using 90:10 hexanes:EtOAc, yielding (S,E)-(4-(phenylsulfonyl)pent-1-ene-1,4-diyl)dibenzene in 99% yield as an 8.3:1 mixture of linear to branched homoallylic sulfones.

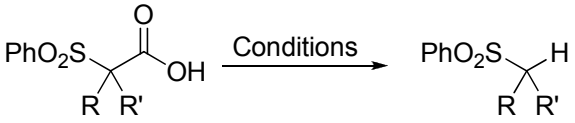
**General procedure for the palladium catalyzed decarboxylative coupling of α-alkyl substituted acetic esters (Procedure B):** To a flame dried Schlenk tube was added (R)-allyl 4-(4-methoxyphenoxy)-2-methyl-2-(phenylsulfonyl)butanoate (0.065g 0.160 mmol) and then taken into the glovebox where toluene (0.8 mL), $Pd_2dba_3$ (7.3 mg, 0.0080 mmol) and (±)-BINAP (10.0 mg, 0.0160 mmol) under an atmosphere of Argon. The solution was heated to 95°C and the progress of the reaction monitored by TLC. In general α,α-dialkyl substrates required 9-15h for the reaction to reach completion. After 12h, the reaction was quenched and purified by loading the reaction mixture onto a silica column, where it was purified by flash column chromatography using 90:10 hexanes:EtOAc. This afforded (S)-1-methoxy-4-(3-methyl-3-(phenylsulfonyl)hex-5-enyloxy)benzene in 95% yield.

**Procedure for the "Raney-Ni" hydrogenation of the homoallylic sulfones 2k:**
Into a 50 mL Schlenk flask with stirbar was placed sulfone **2k** (500mg,, 1.38mmol) and then Raney Nickel (~0.75g) (the "Raney-Ni" was prepared by decantation of the water, and 4 subsequent rinsings with absolute ethanol) was added along with ethanol (10 mL) and the mixture refluxed under an Ar atmosphere for 23h (excessive).

**Initial source of enantioenrichment for compounds 1a,g:** The source of enantio enrichment for these two substrates originated from there resolution with chiral non racemic α-Me, benzyl amine.

**Initial source of enantioenrichment for compounds 1b-f,h-m:** The source of enantio enrichment for these compounds originates from the ADH of the corresponding 1,1-disubstituted olefin. The details of the procedure have been published.[2]

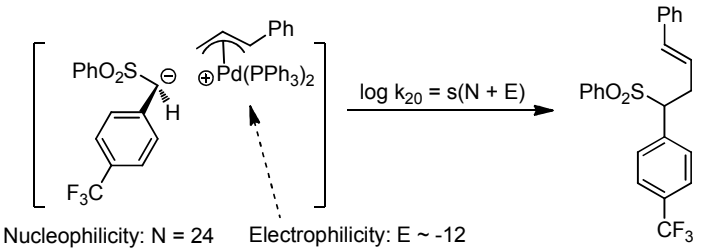
**Table S-1:** Effect of Pd(II) on the rate of decarboxylation of α-sulfonyl acetates




| R | R' | Conditions | Time | Conversion |
|---|---|---|---|---|
| Me | H | $CsCO_3$ (2.5 eq)<br>d-Tol (.2M), 23 °C<br>MTBE (4 uL) | 36 h | 59% |
| Me | H | $CsCO_3$ (2.5 eq)<br>$Pd(OAc)_2$ (0.1 eq)<br>d-Tol (.2M), 23 °C<br>MTBE (4 uL) | 36 h | 59% |
| Me | Bn | $Et_3N$(1.2 eq)<br>d-Tol, 95 °C<br>1,4-dioxane (26.0 uL) | 0.75 h | 25% |
| Me | Bn | $Et_3N$(1.2 eq)<br>$Pd(OAc)_2$ (0.1 eq)<br>d-Tol, 95 °C<br>1,4-dioxane (26.0 uL) | 0.75 h | 27% |
| Me | Bn | $CsCO_3$ (1.5 eq))<br>d-Tol, 95 °C<br>1,4-dioxane (18.5 uL) | 13 h | 59% |
| Me | Bn | $CsCO_3$ (2.5 eq)<br>$Pd(OAc)_2$ (0.1 eq)<br>d-Tol, 95 °C<br>1,4-dioxane (18.5 uL) | 13 h | 77% |
| H | H | KOAc (0.2 eq)<br>d-Tol, 95 °C<br>1,4-dioxane (26.0 uL) | 1 h | 24% |
| H | H | $Pd(OAc)_2$ (0.1 eq)<br>d-Tol, 95 °C<br>1,4-dioxane (26.0 uL) | 1 h | 34% |
| H | H | $Et_3N$ (1.0 eq)<br>d-Tol, 95 °C<br>1,4-dioxane (1.0) | 2 min<br>5 min | 8%<br>17% |
| H | H | $[Pd(allyl)Cl]_2$ (0.5 eq)<br>$PPh_3$ (2.0 eq)<br>$Et_3N$ (1.0 eq)<br>d-Tol, 95 °C<br>1,4-dioxane (1.0) | 2 min<br>5 min | 8%<br>23% |

**Conclusion:** The addition of Pd(OAc)2 (a mimic for (allyl)PdOAc) or (π-allyl)$Pd(PPh_3)_2$ does not substantially affect the rate of decarboxylation of α-sulfonyl acetates.

**Estimation of the barrier for the reaction of a palladium allyl complex ion-paired with an α-sulfonyl anion.**




$\log k_{20} = 0.51(24 - 12) = 6.12$

$k_{20} = 1.32 \times 10^6$

the Eyring equation give, $\Delta G^{\ddagger} = 8.9$ kcal/mol

$$\ln(1.32 \times 10^6) = \frac{k_b T}{h} e^{\frac{-\Delta G^{\ddagger}}{(293)*1.985}}$$

Using Mayr's electrophilicity and nucleophilicity parameters, the rate of the above reaction can be predicted.[4] Using a *very* conservative estimate for the effective concentration of ions within contact or solvent-separated ion pairs of 1 M, gives a barrier for the above reaction of 8.9 kcal/mol. Thus, the suggestion of a barrier of less than 9.9 kcal/mol for our related reaction is reasonable.

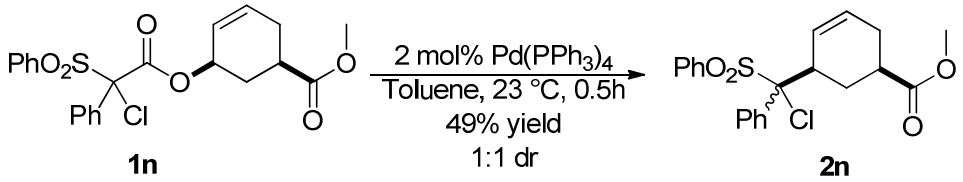
This calculation is meant to shed light on whether the barrier to allylation is potentially lower than 9.9 kcal/mol or whether that assumption is outlandish. This calculation clearly supports a low barrier for allylation, however the absolute number is likely to be inaccurate because of the following assumptions.

The electrophilicity of the pi-allyl complex is an estimate.

The nucleophilicity of our alpha-sulfonyl anions may be somewhat different than that of the above anion. Our sulfonyl anions are more substituted and Mayr has shown that increased substitution of nucleophiles can increase or decrease the nucleophilicity of anions.

[4] (a) Seeliger, F.; Mayr, H. *Org. Biomol. Chem.* **2008**, *6*, 3052. (b) Kuhn, O.; Mayr, H. *Angew. Chem. Int. Ed.* **1999**, *38*, 343.

**Double inversion in decarboxylative coupling of sulfonyl esters.**



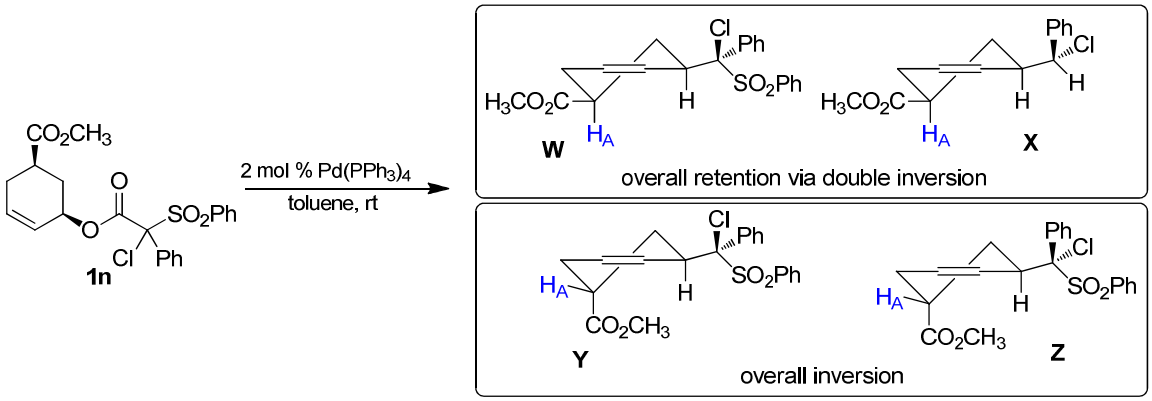

**1n** **2n**

**Synthesis and decarboxylation of compound 1n:** In a procedure adapted from Marshall,[53] 3-cyclohexene carboxylic acid (8.19 mmol) and $NaHCO_3$ (24.6 mmol) and $H_2O$ (13.7 mL) were mixed and cooled to 0 °C. Then a solution of KI (49.1 mmol) and $I_2$ (8.60 mmol) dissolved in $H_2O$ (20.3 mL) was added. The reaction mixture was allowed to warm to room temperature and stir for 24 h. The resulting solution was extracted with $CHCl_3$ (4 x 20 mL). The $CHCl_3$ was washed with $Na_2SO_3$ (0.5 g) and dried and concentrated *in vacuo*. The crude oil was sufficiently clean for further reactions. The bicyclic iodolactone (8.19 mmol) was subjected to elimination with DBU (12.29 mmol) in refluxing THF (55 mL). After 11 h the reaction mixture was quenched by pouring over 0.5 N HCl (30 mL)and extracting the aqueous layer (3 x 30 mL ) with $Et_2O$. The combined organic layer was washed with brine, dried and concentrated *in vacuo* to afford 6-oxabicyclo[3.2.1]oct-3-en-7-one in 86% crude yield as a brown oil. Without further purification, 6-oxabicyclo[3.2.1]oct-3-en-7-one (7.089 mmol) was subjected to methanolysis by the addition $NaHCO_3$ (7.089 mmol) in MeOH (35 mL). The reaction was stirred for 12 h at room temperature and concentrated *in vacuo* and then extracted with $Et_2O$ (35 mL) and washed with $H_2O$ (15 mL), brine (15 mL), dried and concentrated *in vacuo*. The crude product was purified by flash column chromatoghraphy (1:9 Hexanes:$Et_2O$) to afford the isolated alcohol in 41% isolated yield (2.91 mmol). The alcohol (0.5 mmol) was coupled to α-phenyl sulfonyl acetic acid (0.5 mmol) via standard DCC/DMAP coupling (0.5 and 0.05 mmol) in DCM (2 mL) overnight at room temperature. The reaction mixture was filtered over a plug of silica and concentrated *in vacuo* and used without further purification. The sulfonyl ester was chlorinated by the addition of NCS (0.55 mmol), $K_2CO_3$ (1.5 mmol) in DCM (2.5 mL). After 15 h the reaction was extracted with $Et_2O$ (5 mL) and washed with $H_2O$ (5 mL). The organic layer was passed through a silica plug and concentrated to afford the crude compound **1n**. Crude **1n** was purified via flash column chromatography (8:2-7:3 Hexanes:ethyl acetate) to afford a white amorphous solid in 78% yield over 2 steps (0.39 mmol). The decarboxylation was carried out via the method described for α-phenyl substituted sulfonyl esters.

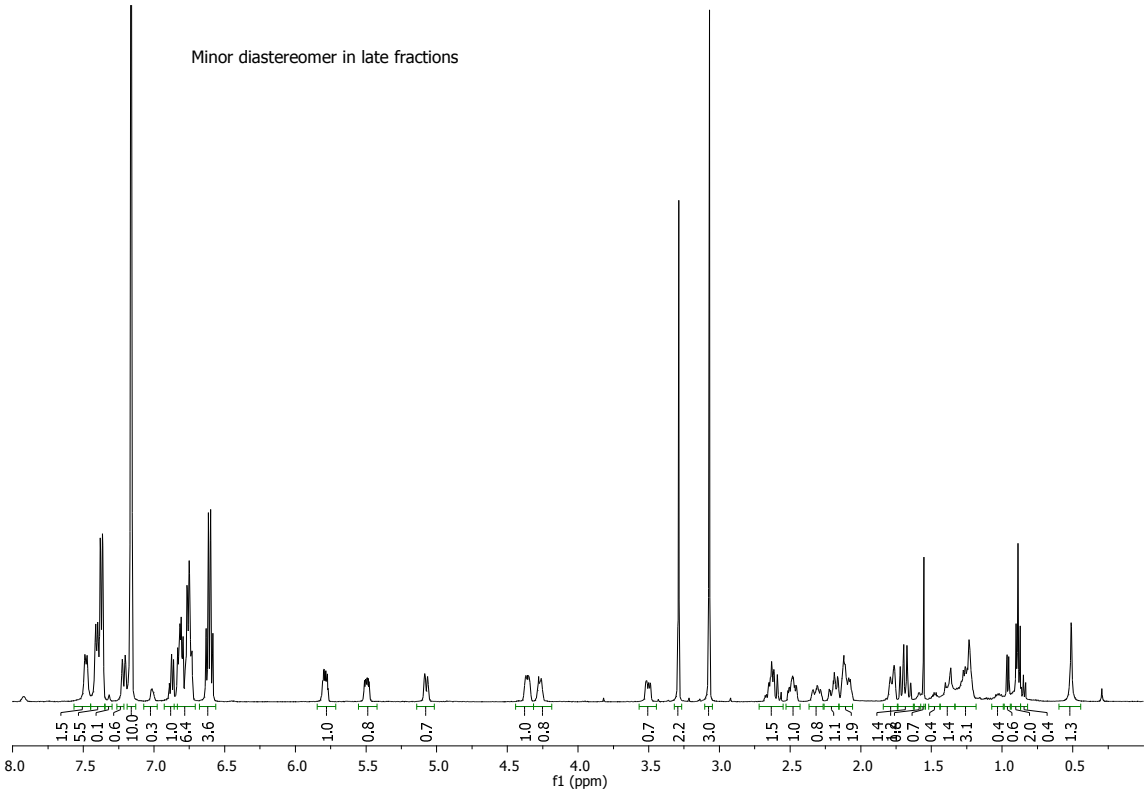
**Procedure for the decarboxylation of 1n (stereochemical anaylsis):** To a flame dried Schlenk tube equipped with stir bar was added **1n** (75 mg, 0.168 mmol) and then it was taken into the glovebox where toluene (0.84 mL), and $Pd(PPh_3)_4$ (3.9 mg, 0.00336 mmol) were added under an atmosphere of argon. The solution was capped and removed from the glovebox and allowed to stir 30 min. at room temperature. The reaction was quenched and purified by loading the reaction mixture onto a silica column, where it was purified by flash column chromatography using 90:10-85:15 hexanes:EtOAc, yielding a 1:1 mix of diastereomers **2n** in 49% yield. While the diastereomers were not resolved the early fractions were enriched in one diastereomer and the later fractions the other diastereomer.

[5] Marshall, J. A.; Xie, S. J. Org. Chem. 1995, 60, 7230..

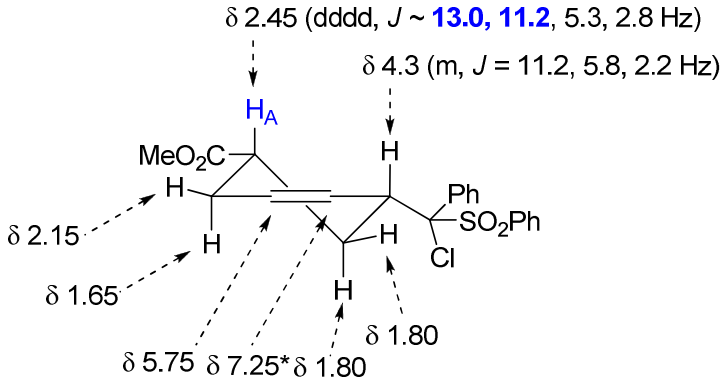
**Determination of the stereospecificity of decarboxylative allylation of a sulfone.**




If the substrate, **1n**, undergoes decarboxylative allylation through a double-inversion mechanism, then diastereomeric products **W** and **X** will form. Alternatively if the intermediate sulfonyl anion binds to Pd prior to reductive elimination, then diastereomeric products **Y** and **Z** are expected. As can be seen, the two sets of products differ by the orientation of $H_A$; in **W** and **X** it is axial, while it is equatorial in **Y** and **Z**. Thus, we can determine the stereospecificity of the reaction by analysis of the coupling constants for $H_A$.



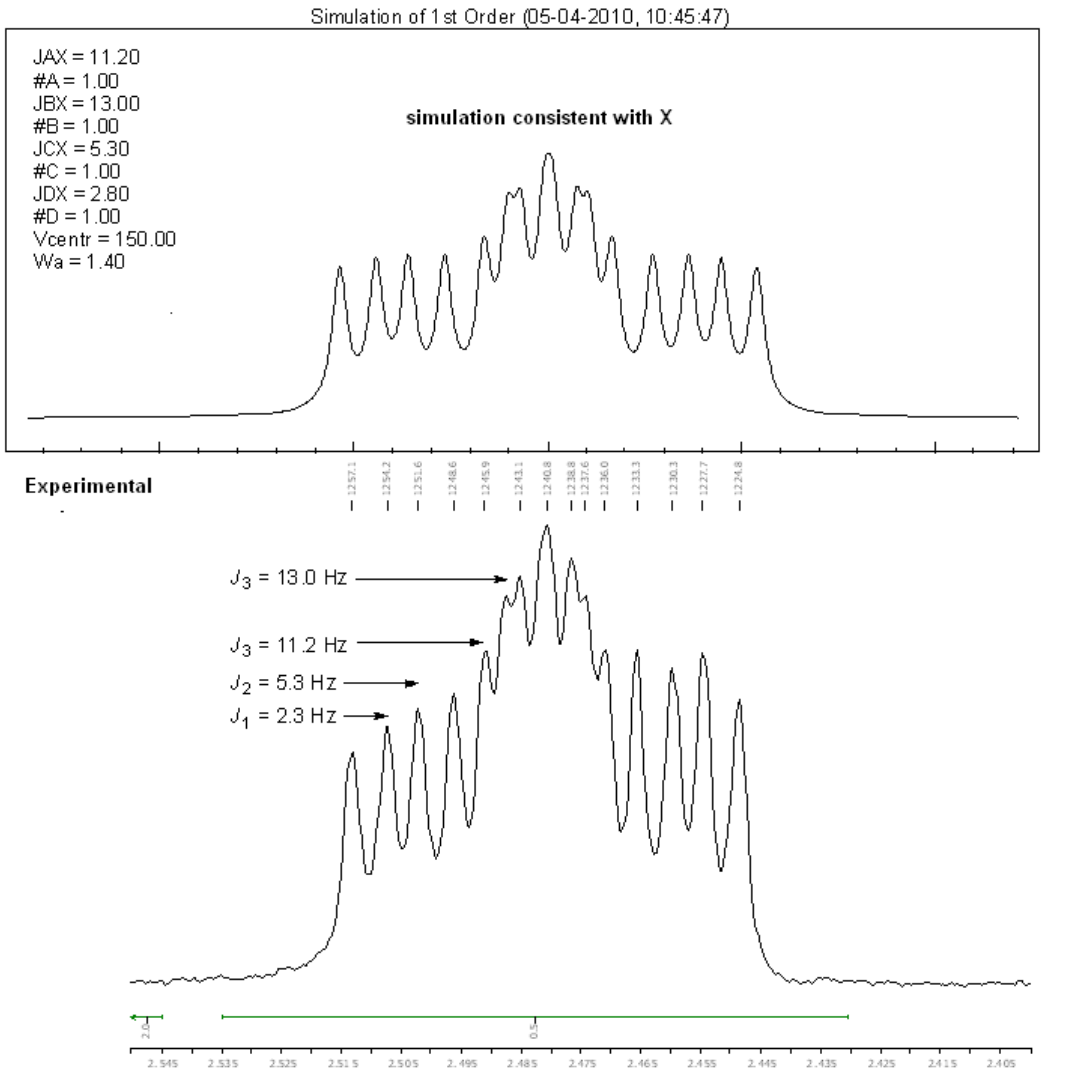
**Assignment and stereochemistry of diastereomer 1**: (minor component of late column fractions).

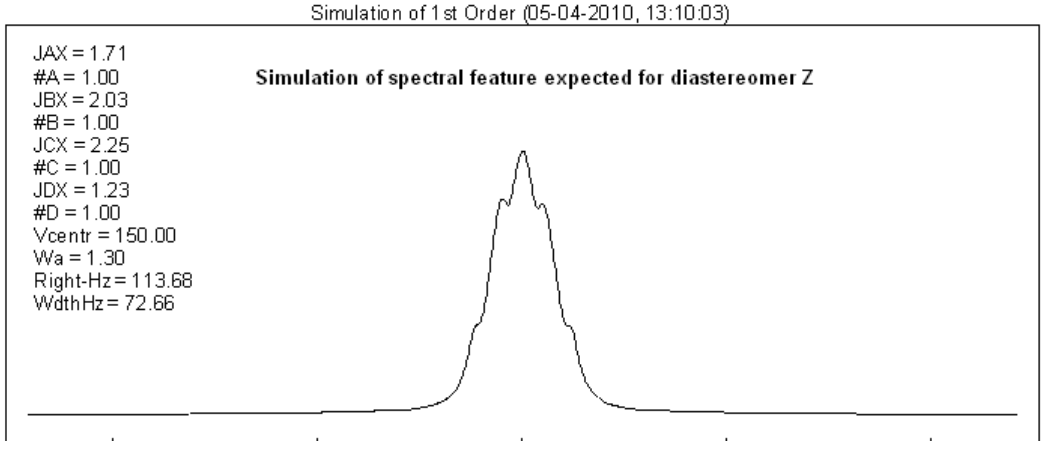



The peak for $H_A$ (2.45 ppm) is a well resolved dddd. Analysis of the coupling constants reveals two large coupling constants that are only fitting with an axially oriented $H_A$ as in **X**. A simulation of $H_A$ using the measured coupling constants and WINDNMR[6] is shown above the experimental spectrum on page S9.

A simulated spectrum for the alternative epimer **Z** is also shown below the experimental spectrum on page S9. This spectral feature was simulated using the Karplus relation and the H—C—C—H angles (-58.9, 54.7, 52.0 and -66.1) of the minimum energy structure of **Z** (determined using MM2 calculations within Chem3D).

[6] Reich, H. J. WinDNMR: Dynamic NMR Spectra for Windows *J. Chem. Educ. Software* **3D2**


Simulation of 1st Order (05-04-2010, 10:45:47)
JAX = 11.20
#A = 1.00
JBX = 13.00
#B = 1.00
JCX = 5.30
#C = 1.00
JDX = 2.80
#D = 1.00
Vcentr = 150.00
Wa = 1.40
simulation consistent with X
Experimental
J3 = 13.0 Hz
J3 = 11.2 Hz
J2 = 5.3 Hz
J1 = 2.3 Hz


Simulation of 1st Order (05-04-2010, 13:10:03)
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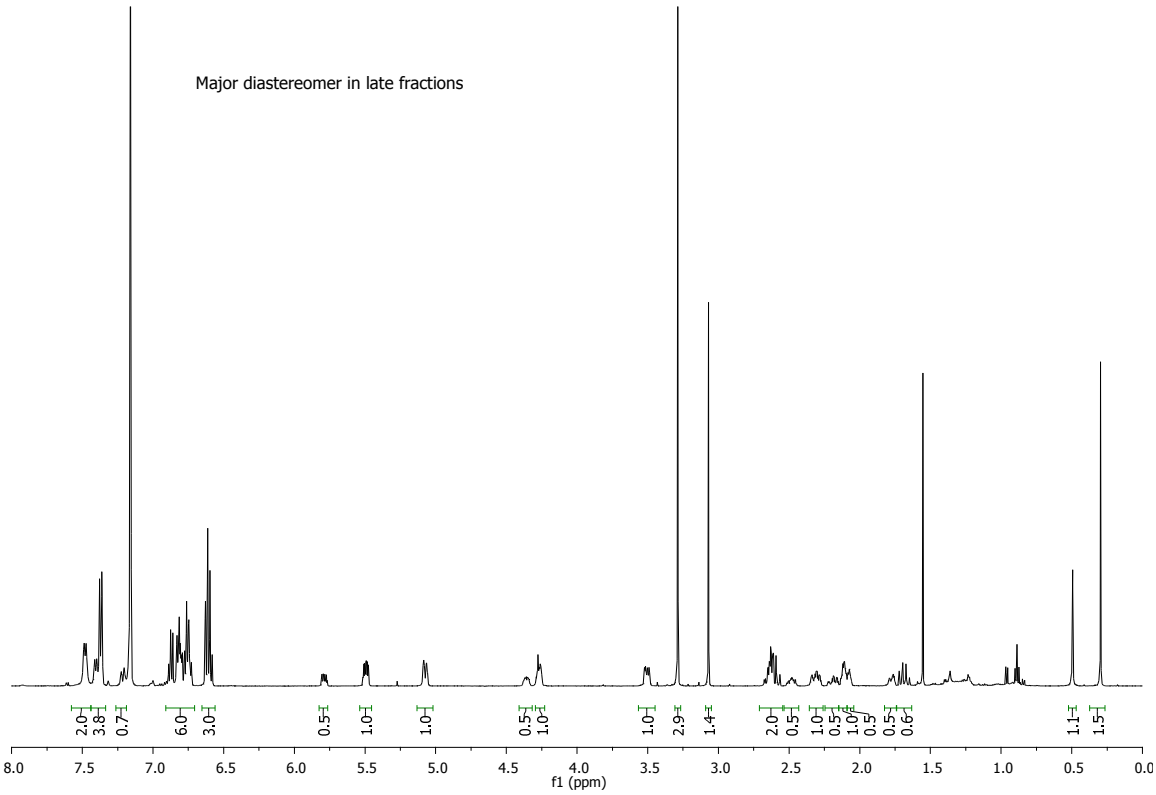
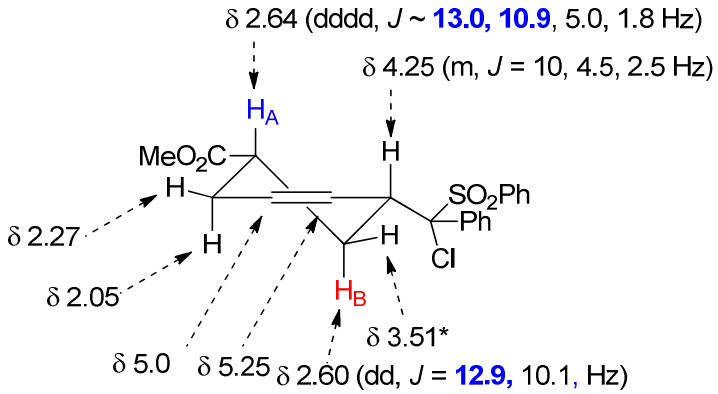
#A = 1.00
JBX = 2.03
#B = 1.00
JCX = 2.25
#C = 1.00
JDX = 1.23
#D = 1.00
Vcentr = 150.00
Wa = 1.30
Right-Hz = 113.68
WdthHz = 72.66
Simulation of spectral feature expected for diastereomer Z




**Assignment and stereochemistry of diastereomer 2**: (major component of late column fractions).




Analysis of the $^1$H NMR spectrum shows that the peaks the peak for $H_A$ (dddd) and $H_B$ (dd) partially overlap. Below is an expansion of these overlapping peaks as well as a simulation of the spectrum using the coupling constants that were determined. While the simulation is not perfect, it provides excellent agreement, even in the absence of line-broadening. It is important to note that the observed coupling pattern for $H_A$ *requires* that it has two large couplings. Thus, $H_A$ is axial. As further evidence $H_A$ and $H_B$ couple to one another with a $J$ of ~ 13 Hz. Thus, the spectrum unambiguously establishes that $H_A$ is axial.

A simulated spectrum for the alternative epimer **Y** is shown below the experimental spectrum. This spectral feature was simulated using the Karplus relation and the H—C—

C—H angles of the minimum energy structure of **Y** (determined using MM2 calculations within Chem3D).

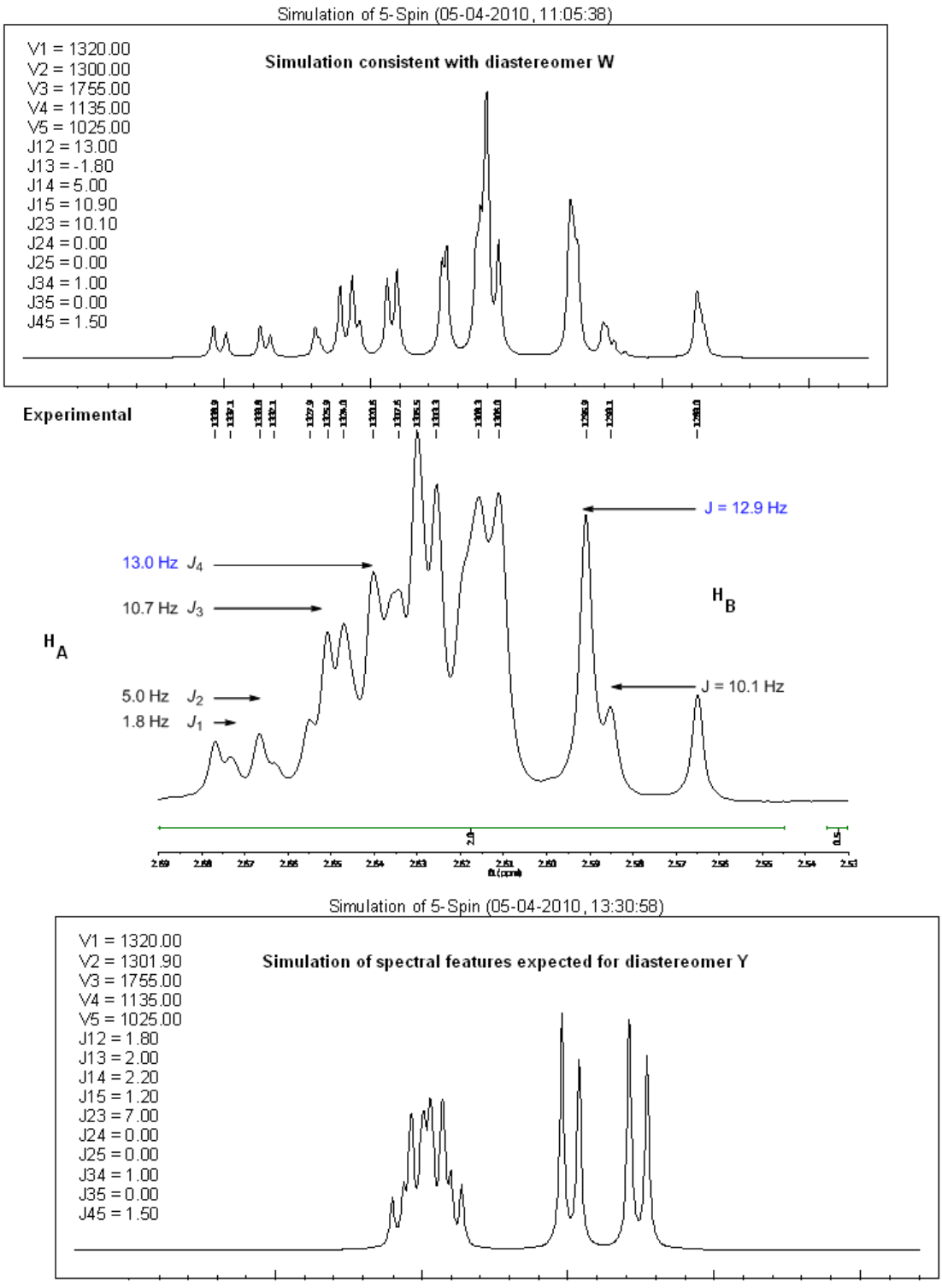
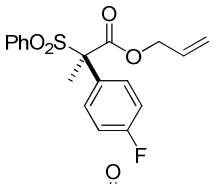
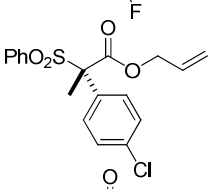
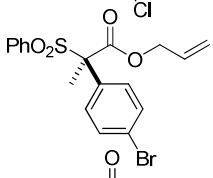
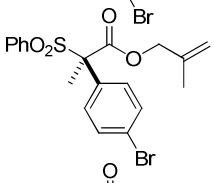
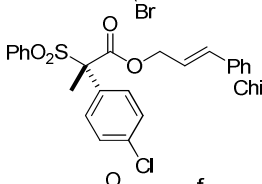
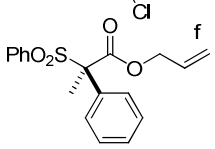
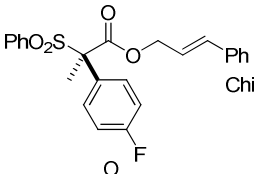
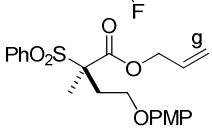
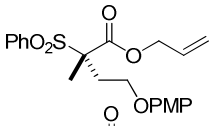
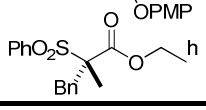
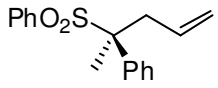


**Table S-2:** Table of reactant ee's and conditions for enantiomeric separation

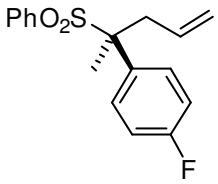
| Reactant | Support[a] | Flow Rate[b] | Hex:IPA[c] | $R_{t's}$ (min.)[d] | % ee |
|---|---|---|---|---|---|
|  | Chiracel OD-H | 1 | 99:1 | 20.0 & 23.5[e] | 46.2% |
|  | Chiracel OD-H | 1 | 99:1 | 20.6[e] & 24.3 | 88.8% |
|  | Chiracel AD | 1 | 99:1 | 38.5 & 45.0[e] | 96.8% |
|  | Chiracel AS | .25 | 98:2 | 30.5 & 41.7[e] | 80.0% |
|  | Chiracel AD | 1 | 90:10 | 16.4[e] & 21.6 | 60.7% |
|  | Chiracel OD-H | 1 | 99:1 | 24.4 & 27.5[e] | 97% |
|  | Chiracel AD | 1 | 91:9 | 17.6 & 20.0[e] | 72.8% |
|  | Chiracel AD | 1 | 85:15 | 20.8 & 25.2[e] | 93.6% |
|  | Chiracel AD | 1 | 85:15 | 20.8[e] & 25.2 | 100% |
|  | Chiracel OD-H | 1 | 90:10 | 8.2 & 15.2[e] | 97.7% |

[a] Columns purchased from Diacel. [b] Flow rate = ml/min, [c] Volume/volume ratio of hexanes to isopropanol. [d] $R_{t's}$ are given in minutes for both enantiomers. [e] Retention time of major enantiomer. [f] The decarboxylated product 2g came from the same sulfide acid and makes the assumption that niether esterification nor oxidation of the sulfide to the sulfone will cause racemization. [g] The ester leading to the decarboxylated product 2i was made from this ester and assumes that oxidative cleavage of PMP group and silylation do not effect the stereocenter. [h] The esters leading to the decarboxylated products 2l and 2m were made from this ester via saponification and esterification with the appropriate alcohols.



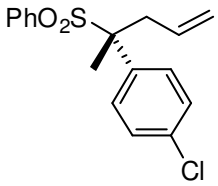

**2a: (S)-(2-phenylpent-4-en-2-ylsulfonyl)benzene**:

Colorless amorphous solid isolated by flash column chromatography using: 95:5 hexanes:EtOAc as eluent: 93% ee (Chiracel AD, 99:1 Hexanes/isopropanol, 1 mL/min, 210 nm, major $R_t$ = 18.0 , minor $R_t$ = 21.7 min.) $[\alpha]_D^{25}$ = -46.7 (*c* .00075, DCM): Matches previously characterized compound Weaver, J. D.; Tunge, J. A. *Org. Lett.* **2008**, *10*, 4657.




**2b: (S)-1-fluoro-4-(2-(phenylsulfonyl)pent-4-en-2-yl)benzene**:

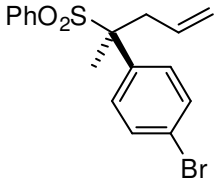
Colorless amorphous solid isolated by flash column chromatography using: 9:1 hexanes:EtOAc as eluent: 41.7% ee (Chiracel AD, 99:1 hexanes/isopropanol, 1 mL/min, 210 nm, major $R_t$ = 19.2, minor $R_t$ = 24.1 min.) $[\alpha]_D^{25}$ = -12.5 (*c* .00325, DCM): $\upsilon_{max}$: 1300, 1147: **HRMS** calcd for [M+NH4] 322.1277 found 322.1276: **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.52 (dt, *J* = 5.0, 4.3 Hz, 1H, *p*ArC*H*-SO2R), 7.34 (d, *J* = 0.7 Hz, 2H, ArCH-(q)C), 7.33 (s, 2H, *m*ArC*H*-SO2R), 7.28 – 7.23 (m, 2H, *o*ArC*H*-SO2R), 6.97 – 6.91 (m, 2H, ArCH-(q)C), 5.37 (dddd, *J* = 17.0, 10.0, 8.4, 5.8 Hz, 1H, -CH2C*H*CH2), 5.14 (ddd, *J* = 17.0, 2.8, 1.7 Hz, 1H, -CH2CHCH*H*), 5.04 (d, *J* = 10.0 Hz, 1H, -CH2CHC*H*H), 3.34 (dd, *J* = 14.1, 5.6 Hz, 1H, (q)CC*H*H-R), 2.84 (dd, *J* = 14.1, 8.4 Hz, 1H, (q)CCH*H*-R), 1.67 (s, 3H, Me(q)C): **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 163.7 (s, CF), 161.7 (s, CF), 134.8 (s, qAr*C*(q)C), 133.6 (s, *p*Ar*C*H-SO2R), 131.2 – 130.9 (m, F-Ar*C*H(q)*C*), 130.7 (S, RCH2*C*HCH2), 128.3 (s, *o*Ar*C*H-SO2R), 120.2 (s, RCH2CH*C*H2), 115.1 (s, F-Ar*mC*H), 114.9 (s, F-Ar*mC*H), 68.1 (s, RRRR*C*), 37.9 (s, (q)C*C*H2R), 19.4 (s, R*C*H3).



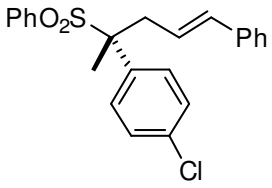

**2c: (R)-1-chloro-4-(2-(phenylsulfonyl)pent-4-en-2-yl)benzene**:

Colorless amorphous solid isolated by flash column chromatography using: 9:1 hexanes:EtOAc as eluent: 86.6% ee (Chiracel AD, 99:1 Hexanes/isopropanol, 1 mL/min, 210 nm, minor $R_t$ = 21.9, major $R_t$ = 27.1 min.) $[\alpha]_D^{25}$ = +42.8 (*c* .00375, DCM): $\upsilon_{max}$: 1303, 1143: **HRMS** calcd for [M+Na] 343.0536 found 343.0547: **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 1H, ArC*H*), 7.25 (s, 2H, ArC*H*), 7.24 (d, *J* = 0.5 Hz, 1H, ArC*H*), 7.13 (s, 2H, ArC*H*), 7.12 (s, 3H,

ArC*H*), 5.25 (dddd, *J* = 17.0, 10.0, 8.4, 5.8 Hz, 1H, RC*H*CHH), 5.03 (dd, *J* = 17.0, 1.1 Hz, 1H, RCHCH*H*), 4.93 (d, *J* = 10.0 Hz, 1H, RCHC*H*H), 3.22 (dd, *J* = 14.1, 5.6 Hz, 1H, RCH*H*CHCH2), 2.82 – 2.60 (m, 1H, RC*H*HCHCH2), 1.44 (s, 3H, RC*H*3). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 134.7 (s, (qaut)Ar*C*), 134.7 (s, (qaut)Ar*C*), 133.6 (s, Ar*C*H), 133.5 (s, (qaut)Ar*C*), 131.0 (s, Ar*C*H), 130.6 (s, R*C*HCH2), 130.4 (s, Ar*C*H), 128.4 (s, Ar*C*H), 128.2 (s, Ar*C*H), 120.3 (s, RCH*C*H2), 68.2 (s, RRRR*C*), 37.9 (s, R*C*H2CHCH2), 19.3 (s, R*C*H3).

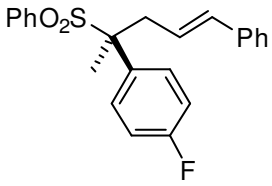



**2d: (S)-1-bromo-4-(2-(phenylsulfonyl)pent-4-en-2-yl)benzene**: Colorless amorphous solid isolated by flash column chromatography using: 9:1 hexanes:EtOAc as eluent: 95.8% ee (Chiracel AD, 99:1 Hexanes/isopropanol, 1 mL/min, 210 nm, major $R_t$ = 20.1, minor $R_t$ = 25.9 min.) $[\alpha]_D^{25}$ = -42.2 (*c* .00325, DCM): **υ$_{max}$**: 1302, 1146: **HRMS** calcd for [M+NH4] 382.0476 found 382.0500: **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 1H, ArC*H*), 7.37 (dd, *J* = 12.7, 6.7 Hz, 6H, ArC*H*), 7.15 (d, *J* = 8.8 Hz, 2H, ArC*H*), 5.35 (dddd, *J* = 16.9, 10.0, 8.4, 5.8 Hz, 1H, RC*H*CH2), 5.13 (ddd, *J* = 17.0, 2.7, 1.5 Hz, 1H, RCHC*H*H), 5.04 (d, *J* = 10.0 Hz, 1H, RCHCH*H*), 3.33 (dd, *J* = 14.1, 5.7 Hz, 1H, RC*H*HCHCH2), 2.83 (dd, *J* = 14.1, 8.4 Hz, 1H, RCH*H*CHCH2), 1.66 (s, 3H, RC*H*3).**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 134.9 (s, (q)Ar*C*), 134.2 (s, (q)Ar*C*), 133.9 (Ar*C*H), 131.4 (Ar*C*H), 131.2 (Ar*C*H), 131.1 (Ar*C*H), 130.6 (Ar*C*H), 128.6 (vinyl *C*H), 123.2 ((q)Ar*C*-Br), 120.6 ( RCH*C*H2), 68.5 (RRRRC), 38.1 (R*C*H2CHCH2), 19.4 (R*C*H3).



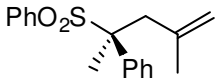

**2e: (R,E)-1-chloro-4-(5-phenyl-2-(phenylsulfonyl)pent-4-en-2-yl)benzene**: White amorphous solid isolated by flash column chromatography using: 9:1 hexanes:EtOAc as eluent (Isolated as a 8.3:1 mixture of linear and branched (dr ~1:1) regioisomers, 1-chloro-4-((2R)-3-phenyl-2-(phenylsulfonyl)pent-4-en-2-yl)benzene): 63.7% ee (Chiracel AD, 99.4:0.6 Hexanes/isopropanol, 1 mL/min, 210 nm, minor $R_t$ = 49.4, major $R_t$ = 55.5 min.): **υ$_{max}$**: 1302, 1147: **HRMS** calcd for [M+Na] 419.0849 found 419.0834: **$^1$H NMR** (500 MHz,

$CDCl_3$) δ 7.59 (t, *J* = 6.8 Hz, 1H, ArC*H*'s), 7.48 – 7.38 (m, 4H, ArC*H*'s), 7.35 – 7.17 (m, 9H, ArC*H*'s), 6.53 (d, *J* = 15.7 Hz, 1H, RCHC*H*Ph), 5.87 – 5.70 (m, 1H, RC*H*CHPh), 3.54 (dd, *J* = 14.1, 5.6 Hz, 1H, RC*H*HCHCHPh), 3.07 (dd, *J* = 14.2, 8.8 Hz, 1H, RCH*H*CHCHPh), 1.76 (s, 3H, RC*H*3). **$^{13}$C NMR** (126 MHz, $CDCl_3$) $^{13}$C NMR (126 MHz, $CDCl_3$) δ 136.8 ((q)Ar*C*), 135.3 ((q)Ar*C*), 135.0 ((q)Ar*C*), 133.9 (Ar*C*H), 133.8 ((q)Ar*C*), 130.7 (Ar*C*H), 130.6 (Ar*C*H), 128.7 (RCH*C*HPh), 128.6 (Ar*C*H), 128.5 (Ar*C*H), 128.3 (Ar*C*H), 127.8 (Ar*C*H), 126.4 (Ar*C*H), 122.6 (R*C*HCHPh), 68.7 (RRRR*C*), 37.4 (R*C*H2CHCHPh), 19.6 (R*C*H3).

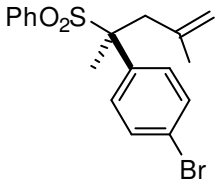



**2f: (S,E)-1-fluoro-4-(5-phenyl-2-(phenylsulfonyl)pent-4-en-2-yl)benzene**:

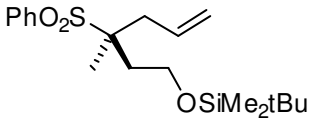
Slighty yellow amorphous solid isolated by flash column chromatography using: 9:1 hexanes:EtOAc as eluent (Isolated as a 8:1 mixture of regioisomer, 1-fluoro-4-((2S)-3-phenyl-2-(phenylsulfonyl)pent-4-en-2-yl)benzene): 96% ee (Chiracel AS, 99:1 Hexanes/isopropanol, 0.95 mL/min, 210 nm, minor $R_t$ = 42.7, major $R_t$ = 47.2 min.): **$\upsilon_{max}$**: 1301, 1146: **HRMS** calcd for [M+Na] 403.1144 found 403.1148: **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.53 (td, *J* = 6.1, 3.3 Hz, 1H, ArC*H*SO2R), 7.38 – 7.33 (m, 4H, ArC*H's*), 7.31 (dd, *J* = 8.9, 5.3 Hz, 2H, ArC*H*'s), 7.23 – 7.13 (m, 5H, ArC*H*'s), 6.96 (t, *J* = 8.7 Hz, 2H, ArC*H*'s), 6.49 (d, *J* = 15.7 Hz, 1H, RCHC*H*Ph), 5.75 (ddd, *J* = 14.7, 8.8, 5.9 Hz, 1H, RC*H*CHPh), 3.50 (dd, *J* = 14.1, 5.8 Hz, 1H, RC*H*HR), 3.03 (dd, *J* = 14.1, 8.8 Hz, 1H, Diastereotopic RC*H*HR), 1.72 (s, 3H, RC*H*3).**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 163.0 (d, *J* = 249.2 Hz, Ar*C*F), 136.9 ((q)ArC), 135.2 (RCH*C*HPh), 135.0 ((q)ArC), 133.8 (s, 1H), 131.3 (d, *J* = 8.2 Hz, 1H, RArCAr*C*H'sACH'sArCF), 130.6 (Ar*C*H), 128.7 (Ar*C*H), 128.6 (Ar*C*H), 128.3 (Ar*C*H), 127.8 (Ar*C*H), 126.4 (Ar*C*H), 122.7 (R*C*HCHPh), 115.3 (d, *J* = 21.3 Hz, RAr*C*H'sArCF), 68.6 (RRRR*C*), 37.5 (R*C*H2CHCHPh), 19.8 (R*C*H3).




**2g: (S)-(4-methyl-2-(phenylsulfonyl)pent-4-en-2-yl)benzene**: White amorphous solid isolated by flash column chromatography using: 95:5 hexanes:EtOAc as eluent: 93% ee (Chiracel AD, 99:1 Hexanes/isopropanol, 1 mL/min, 210 nm, major $R_t$ = 17.2, minor $R_t$ = 25.3 min.) $[\alpha]_D^{25}$ = -55.9 (*c* .0055, DCM): $\upsilon_{max}$: 1302, 1145: **HRMS** calcd for [M+NH4] 318.1528 found 318.1519: **$^1$H NMR** (500 MHz, $CDCl_3$) $^1$H NMR (500 MHz, $CDCl_3$) δ 7.47 (ddd, *J* = 8.6, 5.9, 2.6 Hz, 1H, ArC*H*SO2R), 7.37 (d, *J* = 7.5 Hz, 2H, ArC*H's*SO2R), 7.30 – 7.25 (m, 5H, ArC*H*), 7.21 (d, *J* = 6.8 Hz, 2H, ArC*H*), 4.77 (s, 1H, vinyl C*H*), 4.63 (s, 1H, vinyl C*H*), 3.38 (d, *J* = 14.0 Hz, 1H, diastereotopic C*H*2), 2.99 (d, *J* = 14.0 Hz, 1H, diastereotopic C*H*2), 1.67 (s, 3H, vinylC*H*3), 1.28 (s, 3H, quatCC*H*3). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 140.0 (Ar*C*H), 135.7 (RC(Me)CH2), 135.2 (Ar*C*), 133.5 (Ar*C*H), 130.6 (Ar*C*H), 129.3 (Ar*C*H), 128.7 (Ar*C*H), 128.3 (Ar*C*H), 128.1 (Ar*C*H), 116.8 (RCH(Me)*C*H2), 69.1 (RRRR-*C*), 40.6 (R*C*H2R), 24.5 (*C*H3vinyl), 19.4 ((q)C*C*H3).

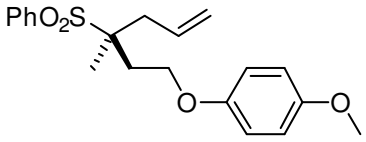



**2h: (S)-1-bromo-4-(4-methyl-2-(phenylsulfonyl)pent-4-en-2-yl)benzene:**
Off white amorphous solid: Isolated by flash column chromatography using 90:10 hexanes:EtOAc eluent; 80% ee (Chiracel AD, 99:1 hexanes/isopropanol, 1 mL/min, 210 nm, major $R_t$ = 17.4, minor $R_t$ = 25.5 min.) $[\alpha]_D^{25}$ = -55.7 (*c* .0215, DCM): $\upsilon_{max}$: 1301, 1145: **HRMS** calcd for [M+H] 379.0367 found 379.0347: **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.51 (dt, *J* = 8.7, 4.2 Hz, 1H, ArC*H*), 7.37 (d, *J* = 8.9 Hz, 2H, ArC*H*'s), 7.33 (d, *J* = 4.5 Hz, 4H, ArC*H*'s), 7.24 (d, *J* = 8.6 Hz, 2H, ArCC*H*'sCH'sCBr), 4.78 (s, 1H, RC(CH3)C*H*H), 4.61 (s, 1H, RC(CH3)CH*H*), 3.30 (d, *J* = 14.1 Hz, 1H, RC*H*HC(CH3)CH2), 2.95 (d, *J* = 14.1 Hz, 1H, RCH*H*C(CH3)CH2), 1.64 (s, 3H, RC(C*H*3)CH2), 1.29 (s, 3H, (q)CC*H*3). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 139.6 ((q)Ar*C*), 135.0 (R*C*(CH3)CH2), 134.9 ((q)Ar*C*), 133.8 (ArCH), 131.3 (ArCH's), 131.0 (ArCH's), 130.6 (ArCH's), 128.5 (ArCH's), 123.1 (Ar*C*Br), 117.1 (RC(Me)*C*H2), 68.7 (RRRR*C*), 40.6 (R*C*H2R), 24.5 (RC(*C*H3)CH2), 19.3 ((q)*C*H3).




**2i: (S)-tert-butyldimethyl(3-methyl-3-(phenylsulfonyl)hex-5-enyloxy)silane**:

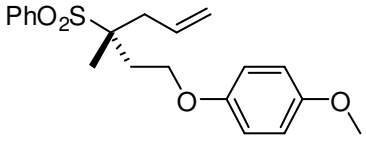
Colorless amorphous solid: Isolated by flash column chromatography using 9:1 hexane:EtOAc then 1:1 hexane:$CH_2Cl_2$ eluent: 92.4% ee ( The enantioenrichment was determined using the free alcohol. **2i** was converted to the corresponding alcohol by stirring overnight in a 4:1:1 solution of AcOH:$H_2O$:THF the alcohol was then separated using Chiracel AD, 90:10 Hexanes/isopropanol, 1 mL/min, 210nm, minor $R_t$ = 19.1, major $R_t$ = 21.7) $[\alpha]_D^{25}$ = +5.0 (*c* .002, DCM): $\upsilon_{max}$: 1302, 1146, 1077: **HRMS** calcd for [M+H] 369.1920found 369.1917: **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2H, *o*ArC*H*'s), 7.64 (t, *J* = 7.5 Hz, 1H, *p*ArC*H*), 7.54 (t, *J* = 7.7 Hz, 2H, *m*ArC*H*'s), 5.85 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H, RCH2C*H*CH2), 5.18 – 5.01 (m, 2H, RCH2CHC*H*2), 3.83 (t, *J* = 7.2 Hz, 2H, RCH2C*H*2OSiR), 2.58 (dd, *J* = 14.4, 7.2 Hz, 1H, RC*H*HCHCH2), 2.36 (dd, *J* = 14.4, 7.3 Hz, 1H, RCH*H*CHCH2), 1.93 (ddt, *J* = 22.2, 14.5, 7.3 Hz, 2H, RC*H*2CH2OSiR), 1.27 (s, 3H, quatC*Me*), 0.85 (s, 9H, RSiMe2*tBu*), 0.02 (s, 6H, RSi*Me*2tBu). **$^{13}$C NMR** $^{13}$C NMR (126 MHz, $CDCl_3$) δ 136.0 (quat Ar*C*), 133.9 (vinyl-*C*H), 132.4 (ArCH), 130.7 (ArCH), 129.4 – 128.8 (ArCH), 119.7 (vinyl *C*H2), 65.2 (CCC-*C*), 59.2 (R*C*H2OR), 38.8 (quatC*C*H2vinyl), 36.3 (R*C*H2CH2OR), 26.1 (RSiMe2C(*C*H3)3), 20.1 (quatC*C*H3), 18.4 (RSiMe2*C*Me3), -5.1 (RSi(*C*H3)2tBu).




**2j: (S)-1-methoxy-4-(3-methyl-3-(phenylsulfonyl)hex-5-enyloxy)benzene**:

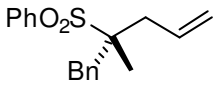
Colorless amorphous solid isolated by flash column chromatography using 9:1 hexanses:EtOAc as eluent; 91.5% ee (The enantioenrichment was determined using the free alcohol. **2j** was converted to the corresponding alcohol by a CAN oxidative removal of *p*-methoxy phenol in a 1:1 solution of MeCN/$H_2O$ at 0°C for 10min. The alcohol was then separated using Chiracel AD, 90:10 Hexanes/isopropanol, 1 mL/min, 210 nm, minor $R_t$ = 19.1, major $R_t$ = 21.7 min.) $[\alpha]_D^{25}$ = +3.8 (*c* .00725, DCM): $\upsilon_{max}$: 1510, 1300, 1231, 1145, 1075, 1037: **HRMS** calcd for [M+NH4] 378.1739found 378.1717: **$^1$H NMR** $^1$H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 2H, *o*ArCH'sSO2R), 7.65 (t, *J* = 7.5 Hz, 1H, *p*ArCHSO2R), 7.55 (t, *J* = 7.8 Hz, 2H,

*m*ArCH'sSO2R), 6.81 (s, 4H, RO*Ar*OMe), 5.90 – 5.75 (m, 1H, RC*H*CH2), 5.13 (dd, *J* = 24.2, 13.5 Hz, 2H, RCHC*H*2), 4.19 (t, *J* = 7.2 Hz, 2H, RC*H*2OAr), 3.75 (s, 3H, ArOC*H*3), 2.62 (dd, *J* = 14.1, 7.3 Hz, 1H, (q)CCH*H*vinyl), 2.39 (dd, *J* = 14.1, 7.3 Hz, 1H, (q)CC*H*Hvinyl), 2.27 – 2.08 (m, 2H, (q)CC*H*2CH2OAr), 1.32 (s, 3H, (q)CC*H*3). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 154.2 (RO-(q)ArC), 152.8 (RO-(q)ArC), 135.7 (R*C*HCH2), 134.0 (Ar*C*SO2R), 131.8 (Ar*C*HSO2R), 130.7 (Ar*C*HSO2R), 129.1 (Ar*C*HSO2R), 120.3 (RCH*C*H2), 115.7 (ROAr*C*H's), 114.9 (ROAr*C*H's), 64.9 ((q)*C*), 64.6 (R*C*H2OAr), 55.9 (ArO*C*H3), 38.8 ((q)C*C*H2vinyl), 33.1 ((q)C*C*H2CH2R), 20.2 (R*C*H3).



**2k: (R)-1-methoxy-4-(3-methyl-3-(phenylsulfonyl)hex-5-enyloxy)benzene**:

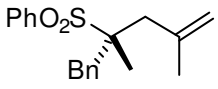
Colorless amorphous solid: 9:1 Hex:EtOAc 100% ee (The enantioenrichment was determined using the free alcohol. **2k** was converted to the corresponding alcohol by oxidative removal of *p*-methoxy phenol with CAN (cerric ammonium nitrate) in a 1:1 solution of $MeCN/H_2O$ at 0°C for 10 min. The alcohol was then separated using Chiracel AD, 90:10 Hexanes/isopropanol, 1 mL/min, 210 nm, major $R_t$ = 19.1 min., minor expected at $R_t$ = 21.7 min. was not detected). Matches previously characterized compound **2j**.



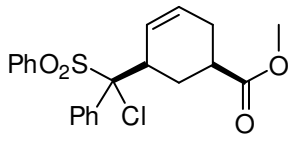
**2l: (R)-(2-methyl-1-phenylpent-4-en-2-ylsulfonyl)benzene**:

Yellow amorphous solid isolated by flash column chromatography using 95:5 hexanes:EtOAc as eluent; 93% ee (Chiracel OD-H, 98:2 Hexanes/isopropanol, 1 mL/min, 210nm, major $R_t$ = 16.8, minor $R_t$ = 18.1 min.) $[\alpha]_D^{25}$ = +14.2 (*c* .00425, DCM): $\upsilon_{max}$: 1301, 1144: **HRMS** calcd for [M+Na] 323.1082found 323.1093: **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 2H, *o*ArCH'sSO2R), 7.66 (t, *J* = 7.5 Hz, 1H, *p*ArCHSO2R), 7.56 (t, *J* = 7.7 Hz, 2H, *m*ArCH'sSO2R), 7.31 – 7.20 (m, 3H, ArC*H*'sCH2R), 7.11 (dd, *J* = 7.7, 1.7 Hz, 2H, ArC*H*'sCH2R), 5.92 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1H, RC*H*CH2), 5.08 (dd, *J* = 10.2, 1.9 Hz, 1H, RCHCH*H*), 4.99 (dd, *J* = 17.0, 1.8 Hz, 1H, RCHC*H*H), 3.07 (dd, *J* = 46.3, 13.3 Hz, 2H, RC*H*2Ph), 2.38 (ddd, *J* = 52.4, 15.3,

7.0 Hz, 2H, RC*H*2vinyl), 1.21 (s, 3H, RC*H*3). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 136.1 (Ar*C*), 135.3 (Ar*C*), 133.9 (Ar*C*H), 133.0 (R*C*HCH2), 131.3 (Ar*C*H), 130.8 (Ar*C*H), 129.1 (Ar*C*H), 128.4 (Ar*C*H), 127.3 (Ar*C*H), 119.0 (RCH*C*H2), 66.5 ((q)*C*), 39.5 (R*C*H2Ph), 38.4 (R*C*H2vinyl), 19.4 (R*C*H3)

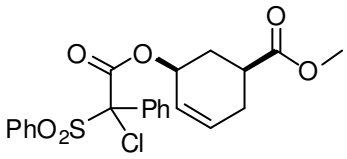



**2m: (R)-(2,4-dimethyl-1-phenylpent-4-en-2-ylsulfonyl)benzene**: Off white amorphous solid isolated by flash column chromatography using: 95:5 Hex:EtOAc as eluent; 93% ee (Chiracel AD, 98:2 Hexanes/isopropanol, 1 mL/min, 210nm, major $R_t$ = 18.6, minor $R_t$ = 20.0 min.) $[\alpha]_D^{25}$ = +9.2 (*c* .003, DCM): **$\upsilon_{max}$**: 1300, 1143: **HRMS** calcd for [M+Na] 337.1238 found 337.1236: **$^1$H NMR** $^1$H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.81 (m, 2H, oArCH'sSO2R), 7.64 (t, *J* = 7.5 Hz, 1H, *p*ArCHSO2R), 7.54 (t, *J* = 7.7 Hz, 2H, *m*ArCH'sSO2R), 7.33 – 7.19 (m, 3H, RCH2ArCH's), 7.15 (d, *J* = 8.0 Hz, 2H, RCH2ArCH's), 4.91 (s, 1H, RCMeC*H*H), 4.66 (s, 1H, RCMeCH*H*), 3.13 – 2.94 (m, 2H, RC*H*2Ph), 2.48 (dd, *J* = 37.7, 13.9 Hz, 2H, RC*H*2CMeCH2), 1.69 (s, 3H, RC(C*H*3)CH2), 1.33 (s, 3H, (q)CC*H*3).**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 140.7 (R*C*(Me)CH2), 136.4 (Ar*C*), 135.6 (Ar*C*), 133.8 (Ar*C*HSO2R), 131.5 (Ar*C*H'S), 130.9 (Ar*C*H'S), 129.0 (Ar*C*H'S), 128.3 (Ar*C*H'S), 127.2 (Ar*C*H), 117.6 (RC(Me)*C*H2), 67.1 (RRRR*C*), 41.8 (R*C*H2C(Me)CH2), 40.9 (R*C*H2Ph), 25.0 (RC(*C*H3)CH2), 19.6 ((q)*C*H3).

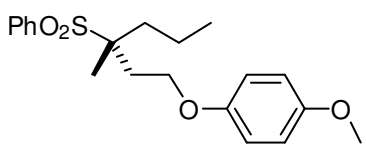



**2n: syn-methyl 5-(chloro(phenyl) (phenylsulfonyl) methyl)cyclohex-3-enecarboxylate:** White solid isolated by flash column chromatography using 90:10 hexanes:EtOAc as eluent; 1:1 dr: **$\upsilon_{max}$**: 1320, 1308, 1447, 1435, 1732, 1738, 1151: **HRMS** calcd for [M+NH4] 422.1193 found 422.1198. $^1$H NMR (500 MHz, $C_6D_6$) δ 7.48 (d, *J* = 7.1 Hz), 7.45 – 7.35 (m), 7.32 (s), 7.22 (s), 7.16 (s), 7.01 (s), 6.88 (t, *J* = 7.3 Hz), 6.86 – 6.71 (m), 6.61 (q, *J* = 8.2 Hz), 5.85 – 5.71 (m), 5.55 – 5.42 (m), 5.07 (d, *J* = 10.3 Hz), 4.44 – 4.32 (m), 4.27 (d, *J* = 9.4 Hz), 3.57 – 3.45 (m), 3.29 (s), 3.07 (s), 2.72 – 2.55 (m), 2.53 – 2.43 (m), 2.37 – 2.27 (m), 2.26 – 2.15 (m), 2.16 – 2.06 (m), 1.78 (d, *J* = 13.0 Hz), 1.68 (dd, *J* = 24.2, 12.7 Hz) **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ

175.1 (s, R*C*O$_2$CH$_3$), 174.8 (s, R*C*O$_2$CH$_3$), 136.4 (s), 136.3 (s), 135.3 (s), 134.7 (s), 133.6 (s), 133.6 (s), 131.3 (s), 131.2 (s), 130.6 (s), 129.8 (s), 129.5 (s), 129.4 (s), 129.4 (s), 129.2 (s), 128.7 (s), 128.5 (s), 128.5 (s), 128.3 (s), 127.3 (s), 125.6 (s), 95.4 (s, quat *C*), 95.2 (s, quat *C*), 51.7 (s), 51.5 (s), 44.7 (s), 43.6 (s), 40.0 (s), 39.8 (s), 32.3 (s), 29.3 (s), 28.7 (s), 28.3 (s), 28.0 (s), 23.4 (s), 14.7 (s).

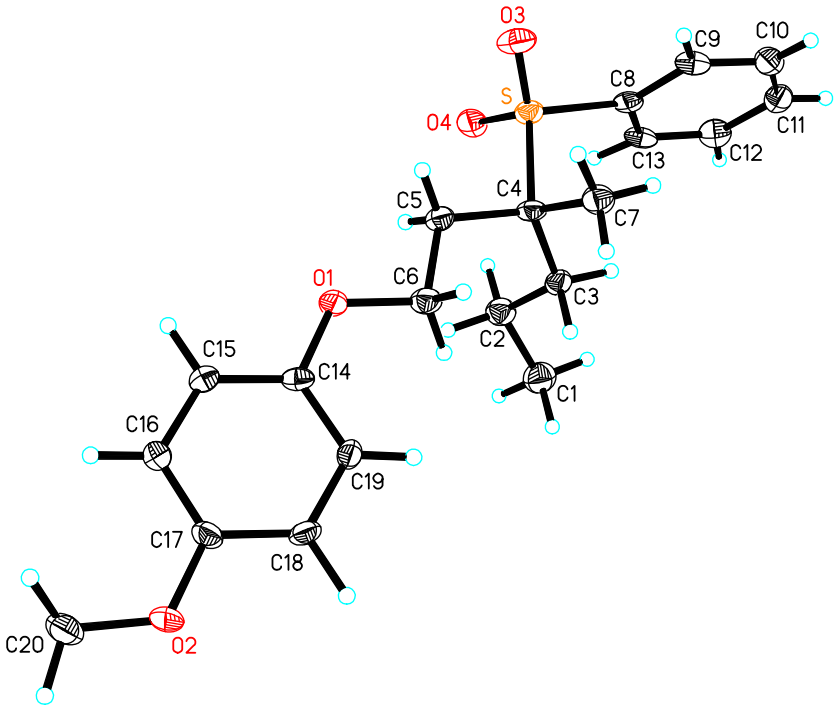



**1n: Syn-methyl 5-(2-chloro-2-phenyl-2-(phenylsulfonyl)acetoxy)cyclohex-3-enecarboxylate:** White amorphous solid isolated by flash column chromatography using 8:2-7:3 HexaneEtOAc; 1:1 dr: **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.72 – 7.50 (m, 10H, ArC*H*'s), 7.50 – 7.27 (m, 10H, ArC*H*'s), 5.88 (s, 2H), 5.68 – 5.48 (m, 4H), 3.63 (s, 3H), 3.61 (s, 3H), 2.69 (s, 2H), 2.41 (s, 2H), 2.27 (s, 4H), 1.78 (td, *J* = 12.5, 9.3 Hz, 1H), 1.67 (td, *J* = 12.5, 9.5 Hz, 1H), 1.57 (d, *J* = 3.8 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 174.3 (s), 174.2 (s), 164.3 (s), 134.7 (s), 134.7 (*apparent* m), 134.6 (s), 132.1 (s), 132.1 (s), 130.8 (s), 130.7 (s), 130.7 (s), 130.1 (s), 129.3 (s), 129.2 (s), 128.3 (s), 128.3 (s), 128.3 (s), 125.4 (s), 125.1 (s), 87.3 (s), 87.2 (s), 73.5 (s), 52.2 (s), 52.2 (s), 37.9 (s), 37.9 (s), 30.0 (s), 29.9 (s), 27.3 (s), 27.3 (s), 27.1 (s).




**4: (R)-1-methoxy-4-(3-methyl-3-(phenylsulfonyl)hexyloxy)benzene:** White solid: Filtered over a Celite plug and then a silica plug, to give the pure compound. X-ray quality crystals were grown from ethanol to afford clear colorless crystals. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.4 Hz, 2H, *o*ArCH'sSO2R), 7.64 (t, *J* = 7.4 Hz, 1H, *p*ArCHSO2R), 7.54 (t, *J* = 7.7 Hz, 2H, *m*ArCH'sSO2R), 6.81 (s, 4H, RO*Ar*OMe), 4.26 – 4.03 (m, 2H, RC*H*2OAr), 3.74 (s, 1H, ArOC*H*3), 2.25 (ddd, *J* = 14.5, 8.1, 6.1 Hz, 1H, RC*H*HCH2OAr), 2.11 (ddd, *J* = 14.6, 8.2, 6.0 Hz, 1H, RCH*H*CH2OAr), 1.81 (td, *J* = 13.2, 4.2 Hz, 1H, (q)CC*H*HEt), 1.71 – 1.55 (m, 1H, (q)CCH*H*Et), 1.55 – 1.45 (m, 1H,

(q)CCH2C*H*HMe), 1.45 – 1.34 (m, 1H, (q)CCH2C*H*HMe), 1.30 (s, 3H, (q)CC*H*3), 0.90 (t, *J* = 7.2 Hz, 3H, RCH2C*H*3). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 154.1 (MeO(q)Ar*C*RR), 152.9 (Ar(q)*C*OR), 136.0 (Ar(q)*C*SO2R), 133.9 (Ar-ρ*C*HSO2R), 130.6 (Ar-*mC*HSO2R), 129.1 (Ar-*oC*HSO2R), 115.7 (Ar-*oC*H's), 114.9 (Ar-*mC*H's), 65.4 ((q)*C*RRR), 64.7 (ArO*C*H2R), 56.0 (*C*H3OAr), 36.1 ((q)C*C*H2Et), 33.0 ((q)C*C*H2CH2OAr), 20.7 (*C*H3(q)C), 17.4 ((q)CH2*C*H2CH3), 14.8 ((q)CH2CH2*C*H3).



**Computational Methods**.
All calculations were performed with Gaussian 03[7] program. The 6-31+G* basis set was chosen for both density functional theory (DFT) and second-order Møller-Plesset[8] (MP2) calculations. The B3LYP[9] functional was used for all DFT computations. All geometry optimizations and transition state searches were conducted using B3LYP/6-31+G*; these were followed by single point MP2 energy calculations for these critical point structures. The transition state structures and corresponding energies were obtained using the QST2 algorithm.[10] The DFT and MP2 critical point energies are shown in Figure S1.

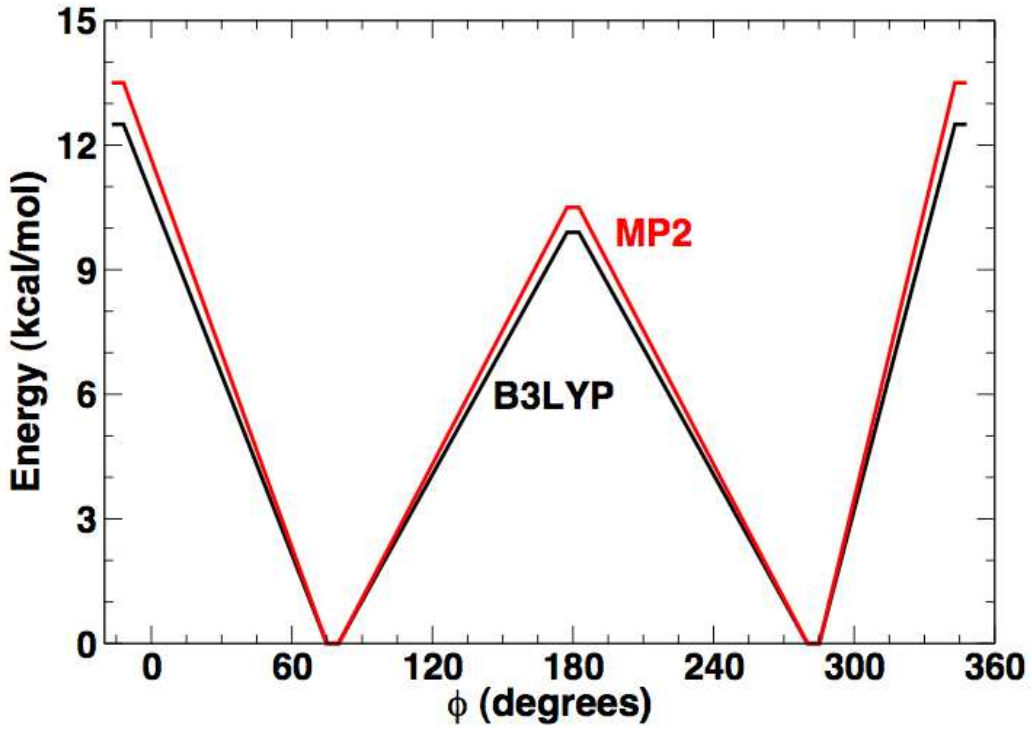


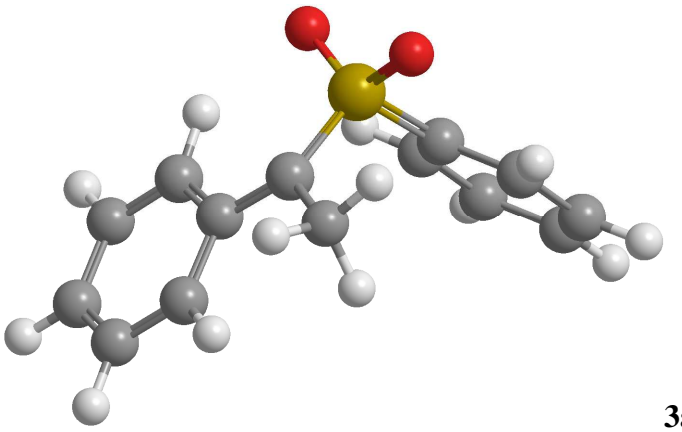

**Figure S1**. DFT (B3LYP/6-31+G*) and MP2 (MP2/6-31+G*//B3LYP/6-31+G*) energies at global minima and rotational barriers.

[7] Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

[8] Møller C.; Plesset M. S. Phys. Rev. 1934, 46, 618–622.

[9] Becke, A. D. J. Chem. Phys. 1993, 98, 5648-5652.

[10] Peng, C.; Schlegel, H. B. Israel J. of Chem., 1993, 33, 449; Peng, C.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J. J. Comp. Chem., 1996, 17, 49.



**3a**

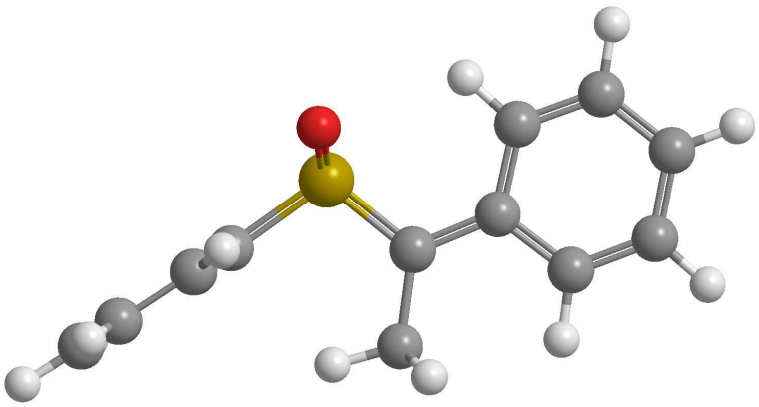
**Minimum Structures.**

$\phi = 77.4^{o}$:

| Atom | x | y | z |
|---|---|---|---|
| C | 0.0000 | 0.0000 | 0.0000 |
| C | 0.0000 | 0.0000 | 1.4014 |
| C | 1.2163 | 0.0000 | 2.0976 |
| C | 2.4228 | -0.0040 | 1.3928 |
| C | 2.4263 | -0.0043 | -0.0068 |
| C | 1.2094 | 0.0002 | -0.6993 |
| S | -1.5858 | -0.1350 | 2.3110 |
| C | -1.9486 | -1.7947 | 2.5239 |
| C | -1.3058 | -2.6142 | 3.5239 |
| C | -1.3621 | -4.0393 | 3.4064 |
| C | -0.7933 | -4.8929 | 4.3517 |
| C | -0.1219 | -4.3921 | 5.4715 |
| C | -0.0486 | -2.9971 | 5.6133 |
| C | -0.6205 | -2.1342 | 4.6852 |
| O | -1.3095 | 0.5600 | 3.5991 |
| O | -2.5704 | 0.4815 | 1.3759 |
| C | -2.6666 | -2.4467 | 1.3634 |
| H | -3.4521 | -3.1295 | 1.7243 |
| H | -2.0025 | -3.0476 | 0.7109 |
| H | -3.1569 | -1.6941 | 0.7421 |
| H | -1.8604 | -4.4837 | 2.5510 |
| H | -0.8733 | -5.9700 | 4.2016 |
| H | 0.3227 | -5.0581 | 6.2082 |
| H | 0.4568 | -2.5688 | 6.4793 |
| H | -0.5729 | -1.0655 | 4.8545 |
| H | 1.2082 | 0.0175 | 3.1824 |
| H | 3.3642 | -0.0012 | 1.9395 |
| H | 3.3678 | -0.0030 | -0.5526 |
| H | 1.2022 | 0.0112 | -1.7880 |
| H | -0.9496 | 0.0216 | -0.5262 |

$\phi = 282.6^{o}$:

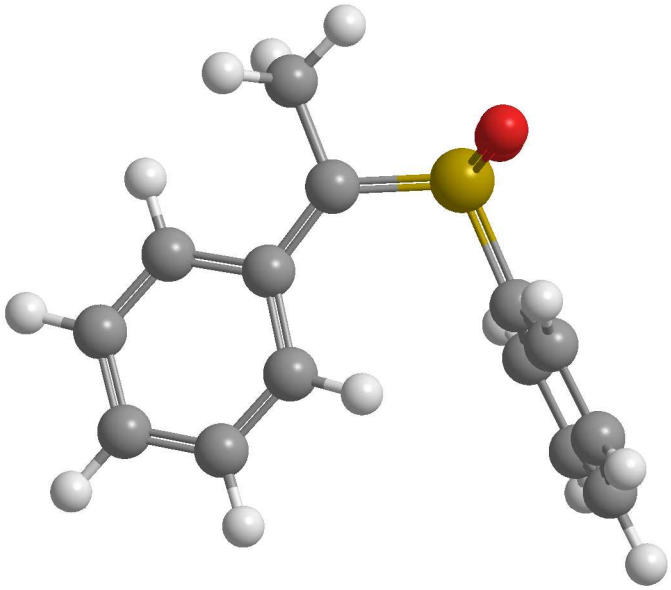
| Atom | x | y | z |
|---|---|---|---|
| C | 0.0000 | 0.0000 | 0.0000 |
| C | 0.0000 | 0.0000 | 1.4013 |
| C | 1.2164 | 0.0000 | 2.0975 |
| C | 2.4239 | -0.0002 | 1.3953 |
| C | 2.4275 | -0.0049 | -0.0050 |
| C | 1.2111 | -0.0043 | -0.6971 |
| S | -1.5766 | -0.1353 | 2.3266 |
| C | -1.9307 | -1.7950 | 2.5536 |
| C | -2.4702 | -2.6301 | 1.5066 |
| C | -2.3913 | -4.0534 | 1.6327 |
| C | -2.9196 | -4.9215 | 0.6772 |
| C | -3.5527 | -4.4379 | -0.4722 |
| C | -3.6441 | -3.0452 | -0.6247 |
| C | -3.1323 | -2.1679 | 0.3248 |
| O | -1.2589 | 0.4975 | 3.6390 |
| O | -2.5614 | 0.5437 | 1.4391 |
| C | -1.2822 | -2.4288 | 3.7639 |
| H | -0.3842 | -3.0312 | 3.5222 |
| H | -1.9855 | -3.1063 | 4.2740 |
| H | -0.9902 | -1.6655 | 4.4884 |
| H | -1.9008 | -4.4848 | 2.4992 |
| H | -2.8259 | -5.9963 | 0.8358 |
| H | -3.9637 | -5.1153 | -1.2181 |
| H | -4.1407 | -2.6301 | -1.5021 |
| H | -3.2592 | -1.1015 | 0.1849 |
| H | 1.2017 | 0.0218 | 3.1830 |
| H | 3.3653 | 0.0107 | 1.9424 |
| H | 3.3688 | -0.0040 | -0.5509 |
| H | 1.2043 | -0.0017 | -1.7856 |
| H | -0.9457 | 0.0181 | -0.5315 |



**Transition State Structures.**

$\phi = 180.0^{o}$:

| Atom | x | y | z |
|---|---|---|---|
| C | 2.7315 | -0.0024 | 1.2134 |
| C | 2.0719 | -0.2058 | 0.0001 |
| C | 2.7317 | -0.0023 | -1.2131 |
| C | 4.0607 | 0.4327 | -1.2112 |
| C | 4.7246 | 0.6551 | 0.0003 |
| C | 4.0605 | 0.4325 | 1.2117 |
| S | 0.3603 | -0.8508 | -0.0002 |
| C | -0.6592 | 0.5446 | -0.0001 |
| C | -2.0776 | 0.3531 | -0.0001 |
| C | -2.9581 | 1.4842 | -0.0001 |
| C | -4.3465 | 1.3493 | 0.0001 |
| C | -4.9578 | 0.0909 | 0.0004 |
| C | -4.1181 | -1.0375 | 0.0003 |
| C | -2.7351 | -0.9213 | 0.0000 |
| O | 0.2664 | -1.6676 | -1.2531 |
| O | 0.2662 | -1.6680 | 1.2524 |
| C | -0.0818 | 1.9381 | -0.0002 |
| H | -0.4006 | 2.5219 | 0.8838 |
| H | -0.4002 | 2.5217 | -0.8846 |
| H | 1.0098 | 1.9472 | 0.0000 |
| H | -2.5396 | 2.4861 | -0.0004 |
| H | -4.9598 | 2.2514 | 0.0001 |
| H | -6.0410 | -0.0117 | 0.0006 |
| H | -4.5561 | -2.0359 | 0.0004 |
| H | -2.1393 | -1.8278 | 0.0000 |
| H | 2.2018 | -0.2004 | -2.1400 |
| H | 4.5792 | 0.5932 | -2.1543 |
| H | 5.7593 | 0.9924 | 0.0004 |
| H | 4.5789 | 0.5928 | 2.1549 |
| H | 2.2015 | -0.2007 | 2.1402 |



$\phi$ = 345.6°:

| Atom | x | y | z |
|---|---|---|---|
| C | 0.0000 | 0.0000 | 0.0000 |
| C | 0.0000 | 0.0000 | 1.3959 |
| C | 1.1974 | 0.0000 | 2.1127 |
| C | 2.4124 | -0.0266 | 1.4210 |
| C | 2.4228 | -0.0478 | 0.0224 |
| C | 1.2161 | -0.0301 | -0.6863 |
| S | -1.5778 | 0.1371 | 2.2943 |
| C | -2.2980 | -1.4244 | 2.5060 |
| C | -1.9745 | -2.6585 | 1.8558 |
| C | -2.9982 | -3.6594 | 1.7163 |
| C | -2.7592 | -4.9110 | 1.1536 |
| C | -1.4922 | -5.2721 | 0.6785 |
| C | -0.4651 | -4.3230 | 0.8107 |
| C | -0.6853 | -3.0761 | 1.3834 |
| O | -1.2188 | 0.7574 | 3.6093 |
| O | -2.4149 | 1.0247 | 1.4208 |
| C | -3.6501 | -1.2446 | 3.1725 |
| H | -3.8486 | -2.0785 | 3.8630 |
| H | -4.4980 | -1.1953 | 2.4639 |
| H | -3.6801 | -0.3265 | 3.7694 |
| H | -4.0069 | -3.4312 | 2.0446 |
| H | -3.5891 | -5.6146 | 1.0751 |
| H | -1.3078 | -6.2489 | 0.2366 |
| H | 0.5441 | -4.5689 | 0.4787 |
| H | 0.1669 | -2.4201 | 1.5010 |
| H | 1.1613 | 0.0310 | 3.1972 |
| H | 3.3498 | -0.0285 | 1.9736 |
| H | 3.3689 | -0.0713 | -0.5147 |

| | | | |
|---|---|---|---|
| H | 1.2227 | -0.0392 | -1.7742 |
| H | -0.9464 | 0.0274 | -0.5304 |