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Electronic Supplementary Information for

# $SO_2$ Conversion to Sulfones: Development and Mechanistic Insights of a Sulfonylative Hiyama Cross-Coupling

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# 1. Experimental details

## *1.1. General considerations*

All reactions and manipulations were performed at 20 ºC in a recirculating MBraun LabMaster DP inert atmosphere (Ar) drybox and/or using standard vacuum Schlenk line procedures, if not otherwise stated. Glassware was dried overnight at 60 ºC before use. All NMR spectra were obtained using a Bruker AVANCE Neo 400 MHz spectrometer. Chemical shifts for $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra were referenced to solvent impurities. Reagents were purchased from commercial suppliers, stored in the glovebox and used as received. $SO_2$ was released by thermal degradation with a heat gun (T ~ 500-600°C) of $K_2S_2O_5$ (purchased from Aldrich). Solvents were thoroughly dried by standard methods and distilled immediately before use. **1c**,[1] **1e-1f**,[2] and **8c**,[3] were synthesized according to adapted literature procedures.

## *1.2. Experimental set-up*

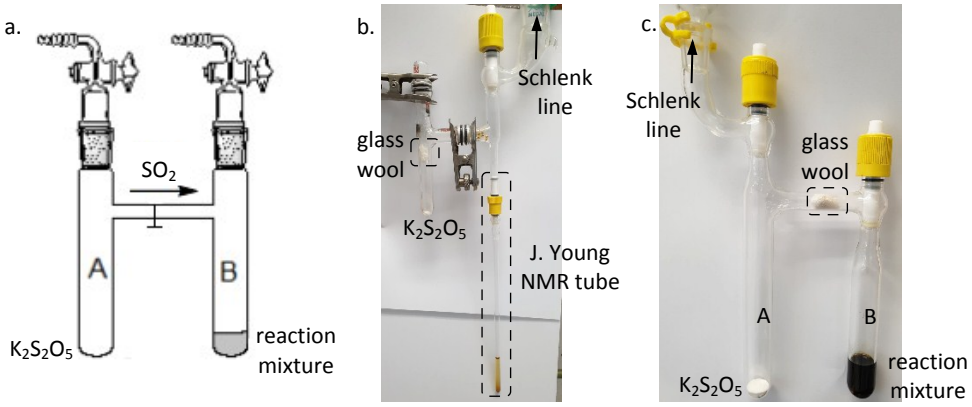



*Figure S1. a. Scheme of the experimental set-up for $SO_2$ generation and condensation; b. Picture of the set-up for NMR-scale reactions; c. Picture of the set-up for scale-up reactions (1 mmol). Use of glass wool avoid the bumping of $K_2S_2O_5$ in the reaction mixture.*

### *1.3. Screening of the reaction conditions*

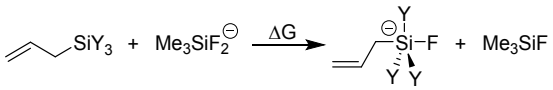
All the listed experiments were performed under argon in 2.5 mL J. Young NMR tubes at the 0.1 mmol scale, according to adapted general procedure (described below, ***1.5.***a).

| Fluoride source (eq.) | $SO_2$ source (eq.) | Catalyst (mol%) | Ligand (mol%) | Temperature (°C) | Yield in **3a** (%) |
|---|---|---|---|---|---|
| TBAF·$3H_2O$ (1) | $SO_2$ (1) | $Pd(acac)_2$ (5) | - | 80 °C | 12 |
| TBAF·$3H_2O$ (1) | DABSO (0.5) | $Pd(acac)_2$ (5) | - | 80 °C | 0 |
| TBAT (1) | $SO_2$ (1) | $Pd(acac)_2$ (5) | - | 80 °C | 17 |
| CsF (1) | $SO_2$ (1) | $Pd(acac)_2$ (5) | - | 80 °C | 0 |
| CsF (3) | $SO_2$ (1) | $Pd(acac)_2$ (5) | - | 80 °C | traces |
| TBAT (2) | $SO_2$ (1) | $Pd(acac)_2$ (5) | - | 80 °C | 8 |
| TBAT (0.9) | $SO_2$ (1) | $Pd(acac)_2$ (5) | - | 80 °C | 13 |
| TBAT (1) | $SO_2$ (2) | $Pd(acac)_2$ (5) | - | 80 °C | 26 |
| TBAT (1) | $SO_2$ (4) | $Pd(acac)_2$ (5) | - | 80 °C | 0 |
| TBAT (1) | $SO_2$ (2) | $Pd(dba)_2$ (5) | - | 80 °C | 5 |
| TBAT (1) | $SO_2$ (2) | $Pd(OAc)_2$ (5) | - | 80 °C | 12 |
| TBAT (1) | $SO_2$ (2) | $Pd(Cl)_2$ (5) | - | 80 °C | 15 |
| TBAT (1) | $SO_2$ (2) | $Pd(OCOCF_3)_2$ (5) | - | 80 °C | traces |
| TBAT (1) | $SO_2$ (2) | $Pd(acac)_2$ (5) | XPhos (10) | 80 °C | 41 |
| TBAT (1) | $SO_2$ (2) | $Pd(acac)_2$ (5) | Xantphos (10) | 80 °C | 78 |
| TBAT (1) | $SO_2$ (2) | $Pd(acac)_2$ (5) | $P(Ph)_3$ (10) | 80 °C | 33 |
| TBAT (1) | $SO_2$ (2) | $Pd(acac)_2$ (5) | $P(Cy)_3$ (10) | 80 °C | 30 |
| TBAT (1) | $SO_2$ (2) | $Pd(acac)_2$ (5) | CataCXium A (10) | 80 °C | 33 |
| TBAT (1) | $SO_2$ (2) | $Pd(acac)_2$ (5) | dppb (10) | 80 °C | 42 |
| TBAT (1) | $SO_2$ (2) | $Pd(acac)_2$ (5) | Xantphos (5) | 80 °C | 65 |
| TBAT (1) | $SO_2$ (2) | $Pd(acac)_2$ (5) | Xantphos (10) | 100°C | 60 |
| TBAT (1) | $SO_2$ (2) | $Pd(acac)_2$ (5) | Xantphos (10) | t.a. | 0 |
| TBAF (1M, THF) (1) | $SO_2$ (2) | $Pd(acac)_2$ (5) | Xantphos (10) | 80 °C | 71 |
| TBAT (1) | $SO_2$ (2) | - | - | | 0 |

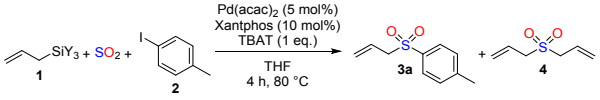
*Table S1: Influence of the reaction conditions on the sulfonylative Hiyama cross-coupling*

### *1.4. Fluoro-affinity of allylsilanes*

The fluoro-affinity of different organosilanes were quantified by the Gibbs free energy variation for the fluoride transfer from $Me_3SiF_2^-$ to the orgaosilane (see equation below, computational details are described in ***2.***).




Even though the poor fluorophile trimethyl(allyl)silane does not lead to the obtention of the diallyl sulfone **4**, the cross-coupling is also found to be diminished and thus despite a higher temperature or reaction time.




| $Y_3$ | Temperature (°C) | Time (h) | Yield **3a** (%) | Yield **4** (%) | **4**/**3a** ratio | $\Delta G$ (kcal.mol$^{-1}$) |
|---|---|---|---|---|---|---|
| $(OMe)_3$ (**1b**) | 80 | 4 | 51 | 23 | 0.45 | 2.98 |
| $(OEt)_3$ (**1a**) | 80 | 4 | 78 | 10 | 0.13 | 3.60 |
| $Me_2(OMe)$ (**1c**) | 80 | 4 | 74 | 7 | 0.09 | 11.94 |
| $Me_3$ (**1d**) | 80 | 4 | 54 | 0 | 0 | 15.60 |
| $Me_3$ (**1d**) | 80 | 24 | 68 | 0 | 0 | 15.60 |
| $Me_3$ (**1d**) | 100 | 4 | 71 | 0 | 0 | 15.60 |

*Table S2: Influence of the allylsilane on the formation of diallyl sulfone*

### *1.5. Synthesis and characterization of allylsulfones*

a) General procedure for NMR-scale experiments

In a glovebox, an oven dried 2.5 mL NMR tube equipped with a J. Young valve was charged with $Pd(acac)_2$ (1.52 mg, 0.005 mmol, 5 mol%), Xantphos (5.79 mg, 0.01 mmol, 10 mol%), TBAT (53.99 mg, 0.1 mmol, 1 eq.) and the electrophile (0.1 mmol, 1 eq.) followed by 400 µL of $d_8$-THF. To the resulting homogeneous yellow solution were sequentially added the silane (0.11 mmol, 1,1 eq.) and mesitylene (5 µL) as an internal standard. The tube was then sealed, brought out of the glovebox and connected to a fitted small vacuum line involving a flask containing $K_2S_2O_5$ (88.93 mg, 0.4 mmol, 4 eq.). The tube was degassed by freezing the solution in liquid nitrogen and evacuation under vacuum. After three evacuation/argon cycles, under static vacuum, $K_2S_2O_5$ was heated at 600 °C with a heat gun. Degradation released pale yellow $SO_2$ vapors which were condensed in the NMR tube cooled under liquid nitrogen (~ 2 minutes). The valve of the NMR tube was then closed, the mixture warmed to room temperature and immersed in a pre-heated oil bath at 80 °C (oil temperature). Yields of sulfones were determined by $^1$H NMR integration versus mesitylene as an internal standard ($\delta_H$ = 6.74 and 2.22 ppm in $d_8$-THF).

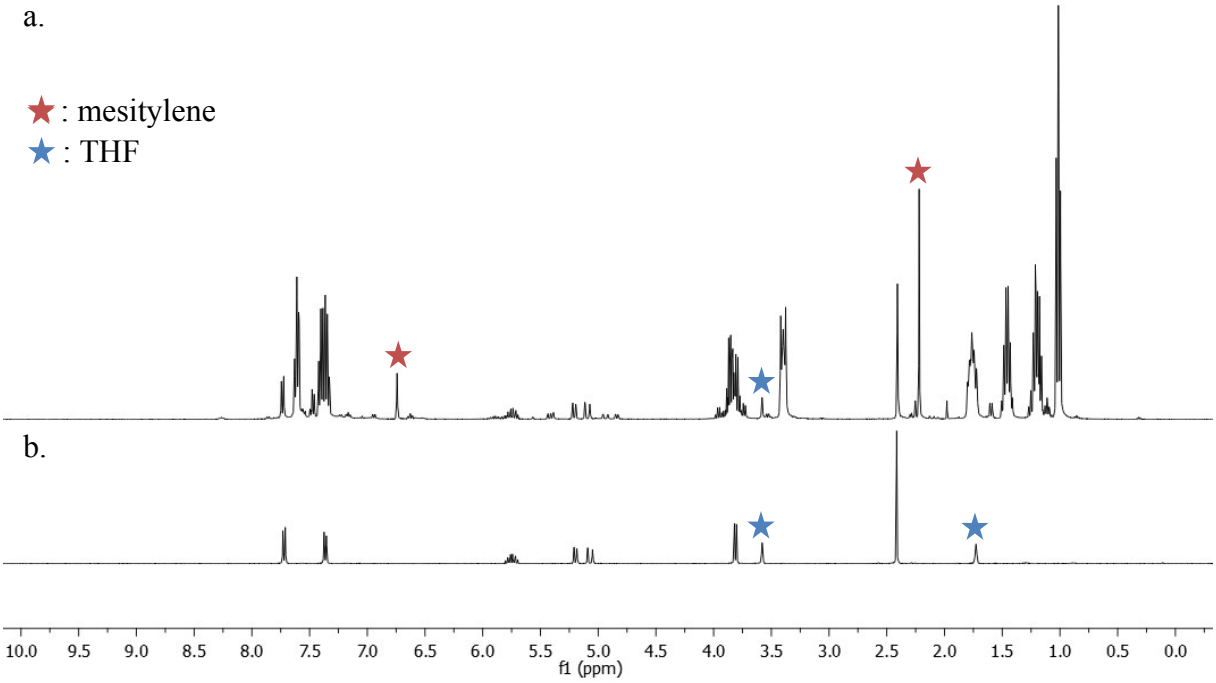
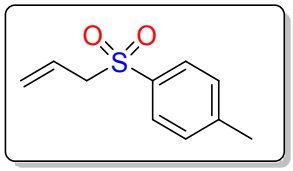



*Figure S3: Representative $^1H$ NMR spectra obtained in* $d_8$*-THF for the formation of* ***3a****. a. Crude reaction mixture after heating 4 h at 80 °C. Yield = 78%; b. Isolated spectrum of* ***3a****.*

b) General procedure for preparative scale experiments

In a glovebox, the catalytic chamber (chamber B, see Figure S1) of an oven dried 2*20 mL two-chambers set-up was charge with $Pd(acac)_2$ (15.23 mg, 0.05 mmol, 5 mol%), Xantphos (57.86 mg, 0.1 mmol, 10 mol%) and the electrophile (1 mmol, 1 eq.) followed by 3 mL of THF. To the resulting homogeneous yellow solution were added the silane (0.11 mmol, 1,1 eq.) and TBAF (1 mL, 1M solution in THF, 1 mmol, 1 eq.). The chamber B was then sealed and the two-chambers set-up brought out of the glovebox. The chamber A (see Figure S1) is then filled with $K_2S_2O_5$ (889.28 mg, 4 mmol, 4 eq.) and connected to a vacuum line. The whole system was degassed by freezing the solution in liquid nitrogen and evacuation under vacuum. After three evacuation/argon cycles, under static vacuum, $K_2S_2O_5$ was heated at 600 °C with a heat gun. Degradation released pale yellow $SO_2$ vapors which were condensed in the chamber B cooled under liquid nitrogen (~ 2 minutes). The chamber B was then sealed, the mixture warmed to room temperature and immersed in a pre-heated oil bath at 80 °C (oil temperature). After 4 h, the reaction mixture was then quenched with 5 mL $H_2O$. The aqueous phase was extracted with $EtOA_c$ (3 x 5 mL) and the combined organic phases were dried with $MgSO_4$. The volatiles were then removed under vacuum and the resulting crude mixture was purified by column chromatography on silica gel (eluent: *n*-pentane/ethyl acetate).

- Allyl 4-methylphenyl sulfone (**3a**)

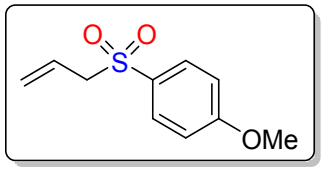


Obtained as a pale oil in 69% yield (135 mg) using 9:1 *n*-pentane/ethyl acetate for the column chromatography.

The spectroscopic data are in agreement with those reported in the literature.[4]

**$^1$H NMR** (400 MHz, $d_8$-THF) $\delta$ (ppm) = 7.72 (d, $J$ = 8.2 Hz, 2H, Ar), 7.36 (d, $J$ = 7.9 Hz, 2H, Ar), 5.75 (ddt, $J$ = 17.5, 10.3, 7.3 Hz, 1H, $CH_2$=C*H*-$CH_2$), 5.24 – 5.17 (m, 1H, C*H*$_2$=CH-$CH_2$), 5.07 (dd, $J$ = 17.1, 1.4 Hz, 1H, C*H*$_2$=CH-$CH_2$), 3.81 (d, $J$ = 7.3 Hz, 2H, $CH_2$=CH-C*H*$_2$), 2.41 (s, 3H, $C_6H_4$-C*H*$_3$). **$^{13}$C{$^1$H}-NMR** (400 MHz, $d_8$-THF) $\delta$ (ppm) = 144.8 (*C*(Ar)-$CH_3$), 137.5 (*C*(Ar)-$SO_2$), 130.0 (*C*(Ar) *meta*), 129.2 (*C*(Ar) *ortho*), 127.0 ($CH_2$=*C*H-$CH_2$), 123.3 (*C*H$_2$=CH-$CH_2$), 60.9 ($CH_2$=CH-*C*H$_2$), 21.3 (*C*H$_3$).

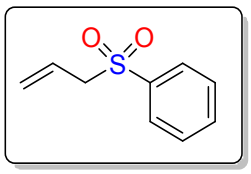
- Allyl 4-methoxyphenyl sulfone (**3b**)




Obtained as a pale oil in 75% yield (159 mg) using 9:1 *n*-pentane/ethyl acetate for the column chromatography.

The spectroscopic data are in agreement with those reported in the literature.[4] **$^1$H NMR** (400 MHz, $d_8$-THF) $\delta$ (ppm) = 7.76 (d, $J$ = 8.9 Hz, 2H, Ar), 7.05 (d, $J$ = 8.9 Hz, 2H, Ar), 5.76 (ddt, $J$= 17.5, 10.2, 7.4 Hz, 1H, $CH_2$=C*H*-$CH_2$), 5.26 – 5.15 (m, 1H, C*H*$_2$=CH-$CH_2$), 5.07 (dd, $J$= 17.1, 1.3 Hz, 1H, C*H*$_2$=CH-$CH_2$), 3.86 (s, 3H, $C_6H_4$-OC*H*$_3$), 3.79 (d, $J$ = 7.3 Hz, 2H, $CH_2$=CH-C*H*$_2$). **$^{13}$C{$^1$H}-NMR** (400 MHz, $d_8$-THF) $\delta$ (ppm) = 164.5 (*C*(Ar)-$OCH_3$), 131.9 (*C*(Ar)-$SO_2$), 131.3 (*C*(Ar) *ortho*), 127.2 ($CH_2$=*C*H-$CH_2$), 123.2 (*C*H$_2$=CH-$CH_2$), 114.6 (*C*(Ar) *meta*), 61.2 ($CH_2$=CH-*C*H$_2$), 55.8 ($OCH_3$).

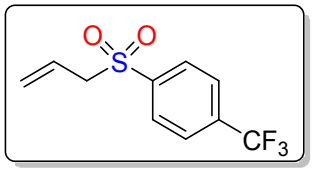
- Allyl phenyl sulfone (**3c**)



TBAT was used as the fluoride source instead of TBAF (1M). Obtained as a pale oil in 82% yield (176 mg) using 9:1 *n*-pentane/ethyl acetate for the column chromatography. The spectroscopic data are in agreement with those reported in the literature.[4]

**$^1$H NMR** (400 MHz, $d_8$-THF) $\delta$ (ppm) = 7.88 – 7.82 (m, 2H, Ar), 7.68 – 7.61 (m, 1H, Ar), 7.59 – 7.51 (m, 2H, Ar), 5.76 (ddt, $J$ = 17.4, 10.2, 7.3 Hz, 1H, $CH_2$=C*H*-$CH_2$), 5.25 – 5.17 (m, 1H, C*H*$_2$=CH-$CH_2$), 5.08 (ddd, $J$ = 17.1, 2.7, 1.3 Hz, 1H, C*H*$_2$=CH-$CH_2$), 3.88 – 3.82 (m, 2H, $CH_2$=CH-C*H*$_2$). **$^{13}$C{$^1$H}-NMR** (400 MHz, $d_8$-THF) $\delta$ (ppm) = 140.3 (*C*(Ar)-$SO_2$), 133.9 (*C*(Ar) *para*), 129.5 (*C*(Ar) *meta*), 129.2 (*C*(Ar) *ortho*), 126.8 ($CH_2$=*C*H-$CH_2$), 123.5 (*C*H$_2$=CH-$CH_2$), 60.8 ($CH_2$=CH-*C*H$_2$).

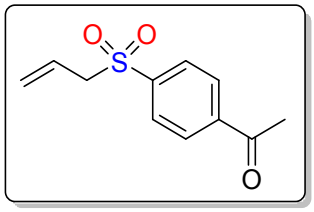
- Allyl 4-trifluoromethylphenyl sulfone (**3d**)



Obtained as a white solid in 33% yield (83 mg) using 9:1 *n*-pentane/ethyl acetate for the column chromatography.

**$^1$H NMR** (400 MHz, $d_8$-THF) $\delta$ (ppm) = 8.06 (d, $J$ = 8.2 Hz, 2H, Ar), 7.92 (d, $J$ = 8.3 Hz, 2H, Ar), 5.78 (ddt, $J$ = 17.5, 10.2, 7.4 Hz, 1H, $CH_2$=C*H*-$CH_2$), 5.34 – 5.18 (m, 1H, C*H*$_2$=CH-$CH_2$), 5.19 – 5.05 (m, 1H, C*H*$_2$=CH-$CH_2$), 3.96 (d, $J$ = 7.4 Hz, 2H, $CH_2$=CH-C*H*$_2$). **$^{13}$C{$^1$H}-NMR** (400 MHz, $d_8$-THF) $\delta$ (ppm) = 143.9 (*C*(Ar)-$SO_2$), 135.2 (q, $J_{C-F}$ = 32.7 Hz, *C*(Ar)-$CF_3$), 130.1 (*C*(Ar) *ortho*), 126.9 (q, $J_{C-F}$ = 3.8 Hz *C*(Ar) *meta*), 126.3 ($CH_2$=*C*H-$CH_2$), 124.43 (q, $J_{C-F}$ = 272.8 Hz, *C*$F_3$), 124.2 (*C*H$_2$=CH-$CH_2$), 60.5 ($CH_2$=CH-*C*H$_2$).

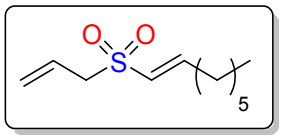
- Allyl 4-acethylphenyl sulfone (**3e**)



Obtained as a tan oil in 39% yield (87 mg) using 1:1 *n*-pentane/ethyl acetate for the column chromatography.

**$^1$H NMR** (400 MHz, $d_8$-THF) $\delta$ (ppm) = 8.18 – 8.10 (m, 2H, Ar), 8.00 – 7.92 (m, 2H, Ar), 5.77 (ddt, $J$ = 17.5, 10.2, 7.4 Hz, 1H, $CH_2$=C*H*-$CH_2$), 5.22 (ddt, $J$ = 10.2, 1.5, 0.8 Hz, 1H, C$H_2$=CH-$CH_2$), 5.09 (dq, $J$ = 17.1, 1.3 Hz, 1H, C$H_2$=CH-$CH_2$), 3.95 – 3.89 (m, 2H, $CH_2$=CH-C$H_2$), 2.61 (s, 3H, C(O)C$H_3$). **$^{13}$C{$^1$H}-NMR** (400 MHz, $d_8$-THF) $\delta$ (ppm) = 196.4 (*C*(O)$CH_3$), 143.5 (*C*(Ar)-$SO_2$), 141.7 (*C*(Ar)-C(O)$CH_3$), 129.5 (*C*(Ar) *meta*), 129.2 (*C*(Ar) *ortho*), 126.5 ($CH_2$=*C*H-$CH_2$), 123.9 (*C*$H_2$=CH-$CH_2$), 60.6 ($CH_2$=CH-*C*$H_2$), 26.5 (C(O)*C*$H_3$).

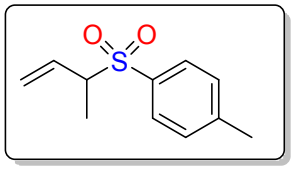
- Allyl *E*-oct-1-enyl sulfone (**3f**)



Obtained as a pale yellow oil in 52% yield (83 mg) using 9:1 *n*-pentane/ethyl acetate for the column chromatography.

**$^1$H NMR** (400 MHz, $d_8$-THF) $\delta$ (ppm) = 6.75 (dt, $J$ = 14.9, 6.9 Hz, 1H, CH=C*H*-$(CH_2)_5$-$CH_3$), 6.35 (dt, $J$ = 15.1, 1.4 Hz, 1H, C*H*=CH-$(CH_2)_5$-$CH_3$), 5.82 (ddt, $J$ = 17.6, 10.4, 7.3 Hz, 1H, $CH_2$=C*H*-$CH_2$), 5.34 – 5.25 (m, 2H, C$H_2$=CH-$CH_2$), 3.67 (d, $J$ = 7.3 Hz, 2H, $CH_2$=CH-C$H_2$), 2.25 (td, $J$ = 8.1, 1.3 Hz, 2H, CH=CH-C$H_2$-$(CH_2)_3$-$CH_2$-$CH_3$), 1.55 – 1.41 (m, 2H, CH=CH-$CH_2$-$(CH_2)_3$-C$H_2$-$CH_3$), 1.33 (m, 6H, CH=CH-$CH_2$-(C$H_2$)$_3$-$CH_2$-$CH_3$), 0.90 (t, $J$ = 6.8 Hz, 3H, CH=CH-$(CH_2)_5$-C$H_3$). **$^{13}$C{$^1$H}-NMR** (400 MHz, $d_8$-THF) $\delta$ (ppm) = 149.2 ($SO_2$-CH=*C*H), 129.4 ($SO_2$-*C*H=CH), 127.3 ($CH_2$=*C*H-$CH_2$), 123.0 (*C*$H_2$=CH-$CH_2$), 59.5 ($CH_2$=CH-*C*$H_2$), 32.3 (CH=CH-*C*$H_2$-$(CH_2)_4$-$CH_3$), 32.0 (CH=CH-$CH_2$-*C*$H_2$-$(CH_2)_3$-$CH_3$), 29.5 (CH=CH-$(CH_2)_2$-*C*$H_2$-$(CH_2)_2$-$CH_3$), 28.5 (CH=CH-$(CH_2)_3$-*C*$H_2$-$CH_2$-$CH_3$), 23.2 (CH=CH-$(CH_2)_4$-*C*$H_2$-$CH_3$), 14.2 (CH=CH-$(CH_2)_5$-*C*$H_3$).

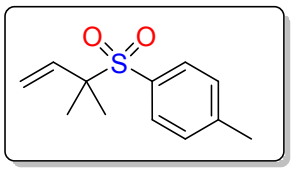
- 1-Methylallyl phenyl sulfone (**3g**)



Obtained as a pale yellow oil in 72% yield (151 mg) using 9:1 *n*-pentane/ethyl acetate for the column chromatography.
The spectroscopic data are in agreement with those reported in the literature.[5]

**$^1$H NMR** (400 MHz, $d_8$-THF) $\delta$ (ppm) = 7.69 (d, $J$ = 8.3 Hz, 2H, Ar), 7.36 (d, $J$ = 7.9 Hz, 2H, Ar), 5.80 (ddd, $J$ = 17.3, 10.4, 7.8 Hz, 1H, $CH_2$=C*H*-CH($CH_3$)), 5.16 (dt, $J$ = 10.4, 1.0 Hz, 1H, C*H*$_2$=CH-CH($CH_3$)), 5.02 (dt, $J$ = 17.2, 1.2 Hz, 1H, C*H*$_2$=CH-CH($CH_3$)), 3.82 – 3.65 (m, 1H, $CH_2$=CH-C*H*($CH_3$)), 2.41 (s, 3H, $C_6H_4$-C*H*$_3$), 1.34 (d, $J$ = 6.9 Hz, 3H, $CH_2$=CH-CH(C*H*$_3$)). **$^{13}$C{$^1$H}-NMR** (400 MHz, $d_8$-THF) $\delta$ (ppm) = 144.9 ($CH_2$=*C*H-CH($CH_3$)), 135.9 (*C*(Ar)-$SO_2$), 133.2 (*C*(Ar) *para*), 130.0 (*C*(Ar) *meta*), 129.9 (*C*(Ar) *ortho*), 120.7 (*C*H$_2$=CH-CH($CH_3$)), 64.3 ($CH_2$=CH-*C*H($CH_3$)), 21.3 (*C*H$_3$) 13.1 ($CH_2$=CH-CH(*C*H$_3$)).

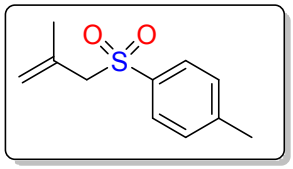
- 1,1-Dimethylallyl phenyl sulfone (**3h**)



Obtained as a pale oil in 51% yield (114 mg) using 9:1 *n*-pentane/ethyl acetate for the column chromatography.
The spectroscopic data are in agreement with those reported in the literature.[6]

**$^1$H NMR** (400 MHz, $d_8$-THF) $\delta$ (ppm) = 7.66 (d, $J$ = 8.2 Hz, 2H, Ar), 7.34 (d, $J$ = 8.0 Hz, 2H, Ar), 6.02 (dd, $J$ = 17.5, 10.7 Hz, 1H, $CH_2$=C*H*-C($CH_3$)$_2$), 5.17 (d, $J$ = 10.7 Hz, 1H, C*H*$_2$=CH-C($CH_3$)$_2$), 5.01 (d, $J$ = 17.5 Hz, 1H, C*H*$_2$=CH-C($CH_3$)$_2$), 2.41 (s, 3H, $C_6H_4$-C*H*$_3$), 1.36 (s, 6H, $CH_2$=CH-C($CH_3$)$_2$). **$^{13}$C{$^1$H}-NMR** (400 MHz, $d_8$-THF) $\delta$ (ppm) = 144.9 ($CH_2$=*C*H-C($CH_3$)$_2$), 138.5 (*C*(Ar)-$CH_3$), 134.1 (*C*(Ar)-$SO_2$), 131.4 (*C*(Ar) *meta*), 129.5 (*C*(Ar) *ortho*), 118.0 (*C*H$_2$=CH-C($CH_3$)$_2$), 64.7 ($CH_2$=CH-*C*($CH_3$)$_2$), 21.3 (*C*H$_3$), 20.8 ($CH_2$=CH-C(*C*H$_3$)$_2$).

- 2-Methylallyl phenyl sulfone (**3i**)



Obtained as a white solid in 28% yield (59 mg) using 9:1 *n*-pentane/ethyl acetate for the column chromatography.

The spectroscopic data are in agreement with those reported in the literature.[7]

**$^{1}$H NMR** (400 MHz, $d_8$-THF) $\delta$ (ppm) = 7.73 (d, $J$ = 8.3 Hz, 2H, Ar), 7.36 (d, $J$ = 8.0 Hz, 2H, Ar), 4.96 – 4.87 (m, 1H, C$H_2$=C(CH$_3$)-CH$_2$), 4.60 (d, $J$ = 0.7 Hz, 1H, C$H_2$=C(CH$_3$)-CH$_2$), 3.79 (s, 2H, CH$_2$=C(CH$_3$)-C$H_2$), 2.41 (s, 3H, C$_6$H$_4$-C$H_3$), 1.83 (s, 3H, CH$_2$=C(C$H_3$)-CH$_2$). **$^{13}$C{$^{1}$H}-NMR** (400 MHz, $d_8$-THF) $\delta$ (ppm) = 144.8 (CH$_2$=*C*(CH$_3$)-CH$_2$), 137.5 (*C*(Ar)-CH$_3$), 135.6 (*C*(Ar)-SO$_2$), 130.0 (*C*(Ar) *meta*), 129.2 (*C*(Ar) *ortho*), 119.7 (*C*H$_2$=C(CH$_3$)-CH$_2$), 64.3 (CH$_2$=C(CH$_3$)-*C*H$_2$), 22.6 (CH$_2$=C(*C*H$_3$)-CH$_2$), 21.3 (*C*H$_3$).

### *1.6. Hammett plot and mechanistic control experiments*

#### *1.6.1. Hammett plot*

The Hammet plot was obtained by considering the NMR yield of the reaction at t = 30 min.

#### *1.6.2. Mechanistic control experiments*

As soon as sulfur dioxide is added to the reaction mixture, a transient species can be observed and attributed to allylsulfinate (see spectrum below).

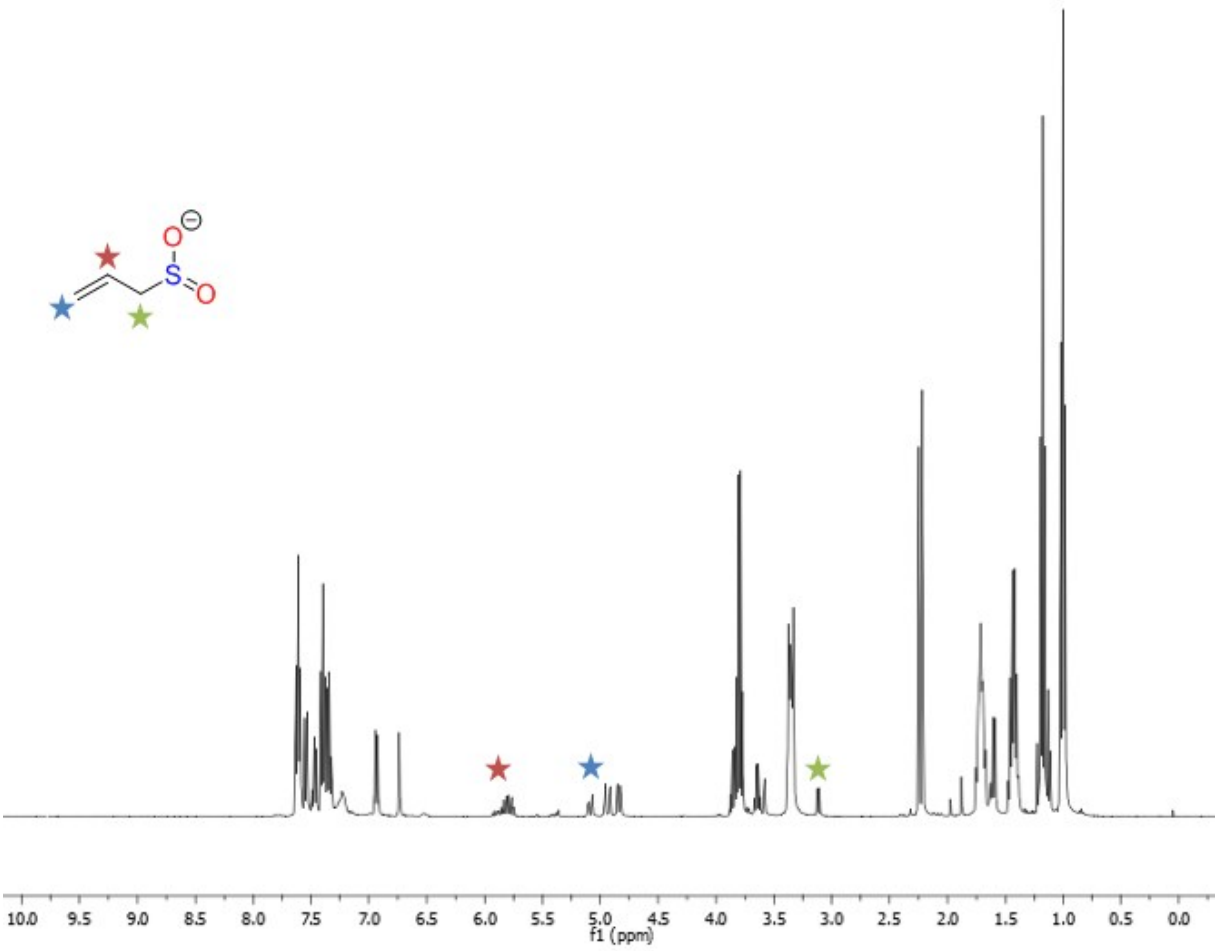



*Figure S4: Representative $^{1}H$ NMR monitoring of a sulfonylative Hiyama cross-coupling in* $d_8$-*THF.*

Reactions described on Scheme 4 were performed at the NMR scale according to below procedures. Yields were determined by $^{1}H$ NMR integration versus mesitylene as an internal standard.

a) Classical Hiyama cross-coupling (without $SO_2$)

In a glovebox, an oven dried 2.5 mL NMR tube equipped with a J. Young valve was charged with $Pd(acac)_2$ (1.52 mg, 0.005 mmol, 5 mol%), Xantphos (5.79 mg, 0.01 mmol, 10 mol%), TBAT (53.99 mg, 0.1 mmol, 1 eq.) and the electrophile (0.1 mmol, 1 eq.) followed by 400 µL of $d_8$-THF. To the resulting homogeneous yellow solution were sequentially added the silane (0.11 mmol, 1,1 eq.) and mesitylene (5 µL) as an internal standard. The tube was then sealed, brought out of the glovebox and immersed in a pre-heated oil bath at 80 °C (oil temperature).

b) Sulfonylative Hiyama cross-coupling

See general procedure for NMR-scale experiments (***1.4.***a) above.

c) Ethyl iodide trapping of sulfinate

In a glovebox, an oven dried 2.5 mL NMR tube equipped with a J. Young valve was charged with TBAT (53.99 mg, 0.1 mmol, 1 eq.) followed by 400 µL of $d_8$-THF. To the resulting homogeneous colourless solution were sequentially added the silane (0.1 mmol, 1 eq.), ethyl iodide (8 µL, 0.1 mmol, 1eq.) and mesitylene (5 µL) as an internal standard. The tube was then sealed, brought out of the glovebox and connected to a fitted small vacuum line involving a flask containing $K_2S_2O_5$ (88.93 mg, 0.4 mmol, 4 eq.). The tube was degassed by freezing the solution in liquid nitrogen and evacuation under vacuum. After three evacuation/argon cycles, under static vacuum, $K_2S_2O_5$ was heated at 600 °C with a heat gun. Degradation released pale yellow $SO_2$ vapors which were condensed in the NMR tube cooled under liquid nitrogen (~ 2 minutes). The valve of the NMR tube was then closed, the mixture warmed to room temperature and immersed in a pre-heated oil bath at 80 °C (oil temperature).

d) Direct cross-coupling of aryl sulfinate

In a glovebox, an oven dried 2.5 mL NMR tube equipped with a J. Young valve was charged with $Pd(acac)_2$ (1.52 mg, 0.005 mmol, 5 mol%), Xantphos (5.79 mg, 0.01 mmol, 10 mol%), sodium *para*-toluenesulfinate (17.82 mg, 0.1 mmol, 1 eq.) followed by 400 µL of $d_7$-DMF. To the resulting solution were sequentially added iodobenzene (11.2 µL, 0.1 mmol, 1 eq.) and mesitylene (5 µL) as an internal standard. The tube was then sealed, brought out of the glovebox and immersed in a pre-heated oil bath at 80 °C (oil temperature).

The reaction was carried in DMF due to solubility issues of sodium *para*-toluenesulfinate in THF. The coupling of *para*-tolyl(triethoxy)silane with phenyl iodide in DMF did not give any of the desired sulfone.

## *1.7. NMR spectra of isolated compounds*

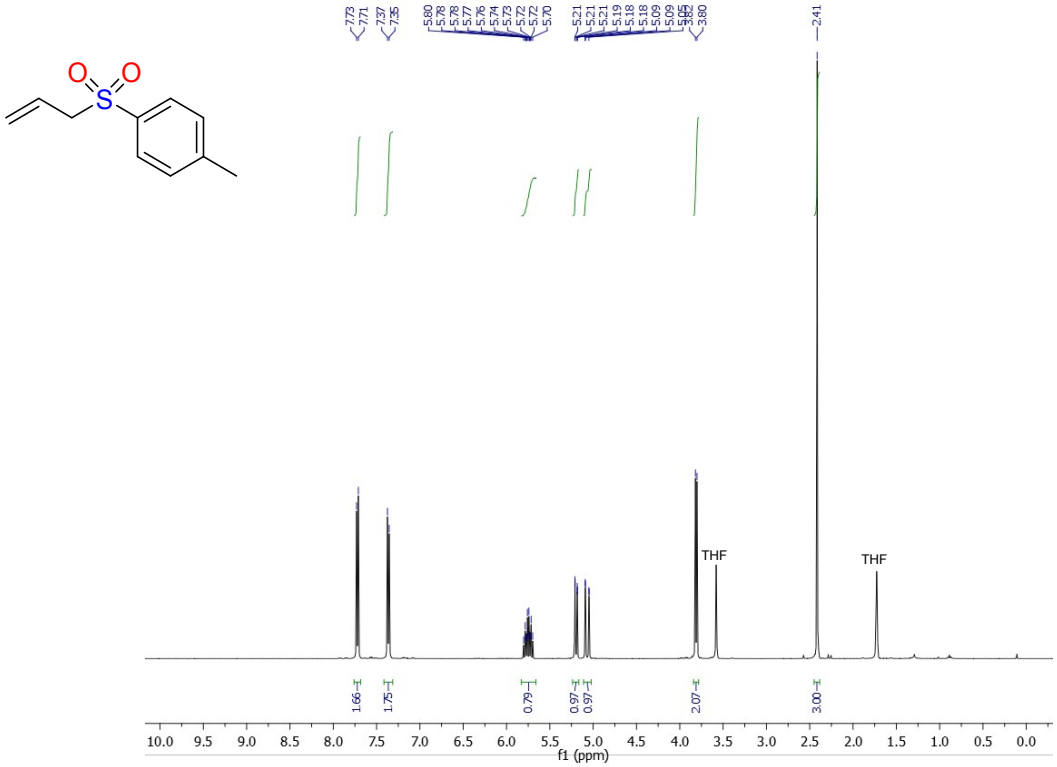



*Figure S5: $^{1}H$ NMR spectrum of (3a) in $d_8$–THF*

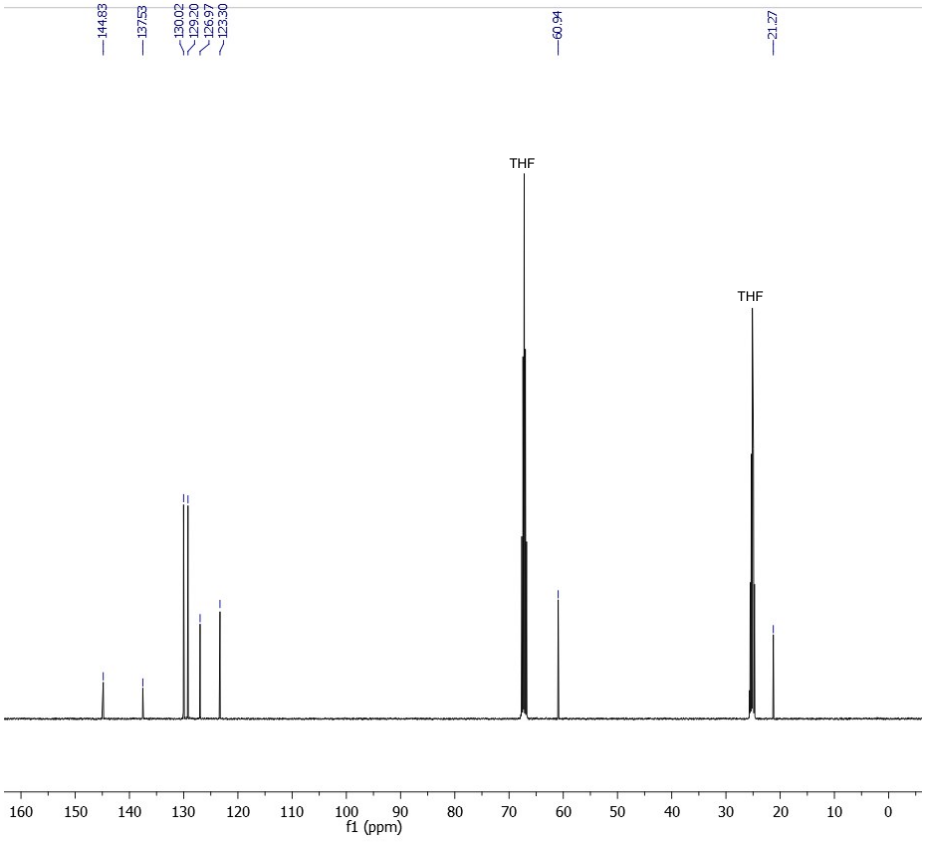



*Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum of (3a) in $d_8$–THF*

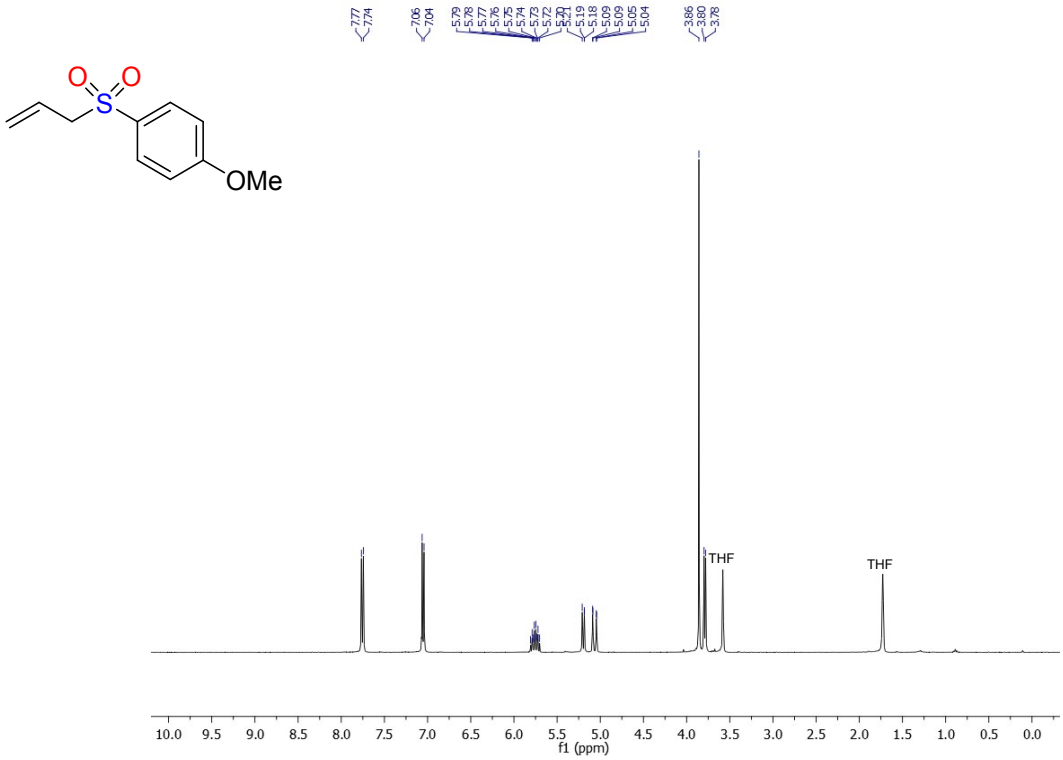



*Figure S7: $^{1}H$ NMR spectrum of (3b) in $d_8$–THF*

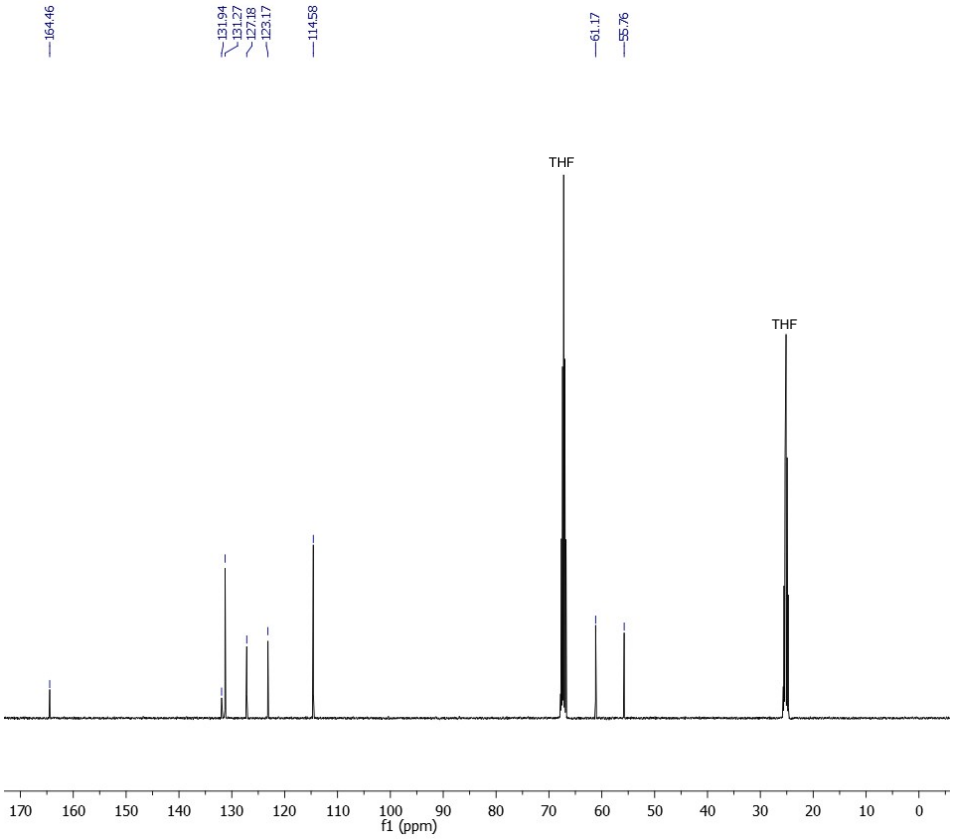



*Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum of (3b) in $d_8$–THF*

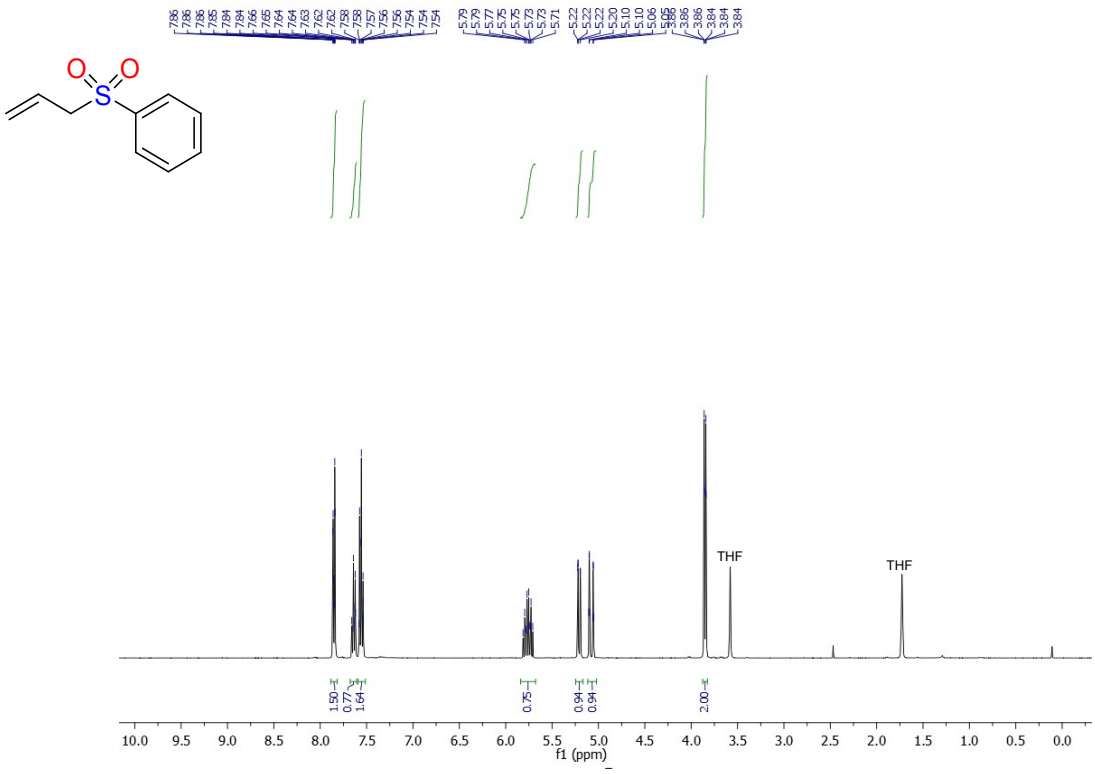



*Figure S9: $^{1}H$ NMR spectrum of (3c) in $d_8$–THF*

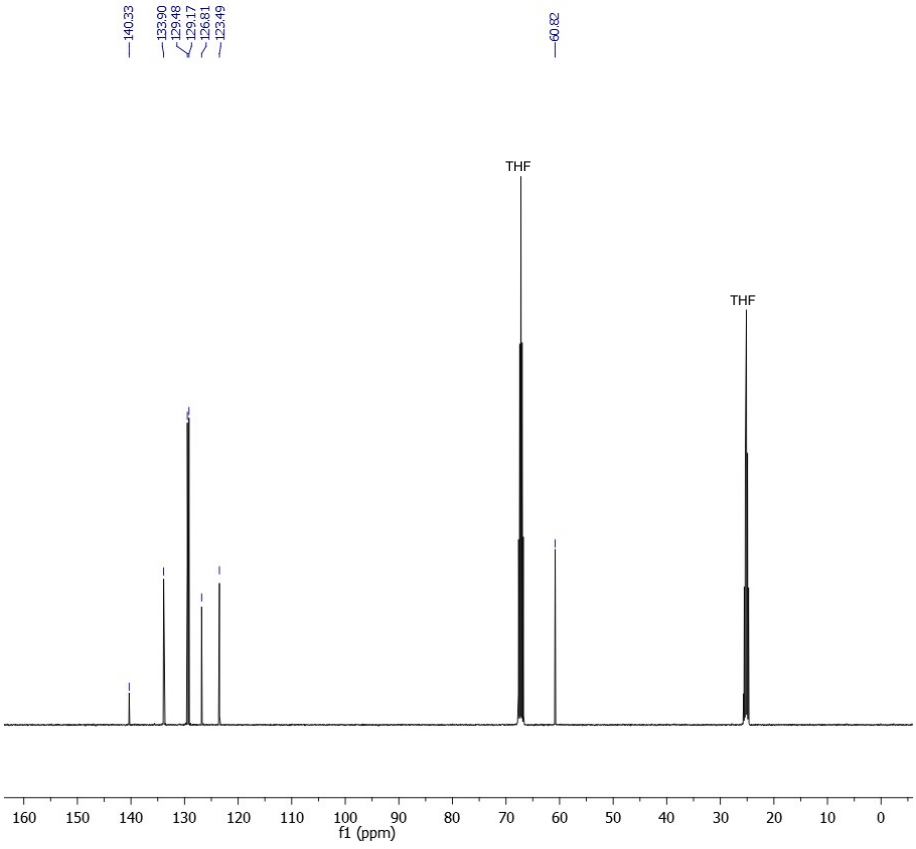



*Figure S10: $^{13}C\{^{1}H\}$ NMR spectrum of (3c) in $d_8$–THF*

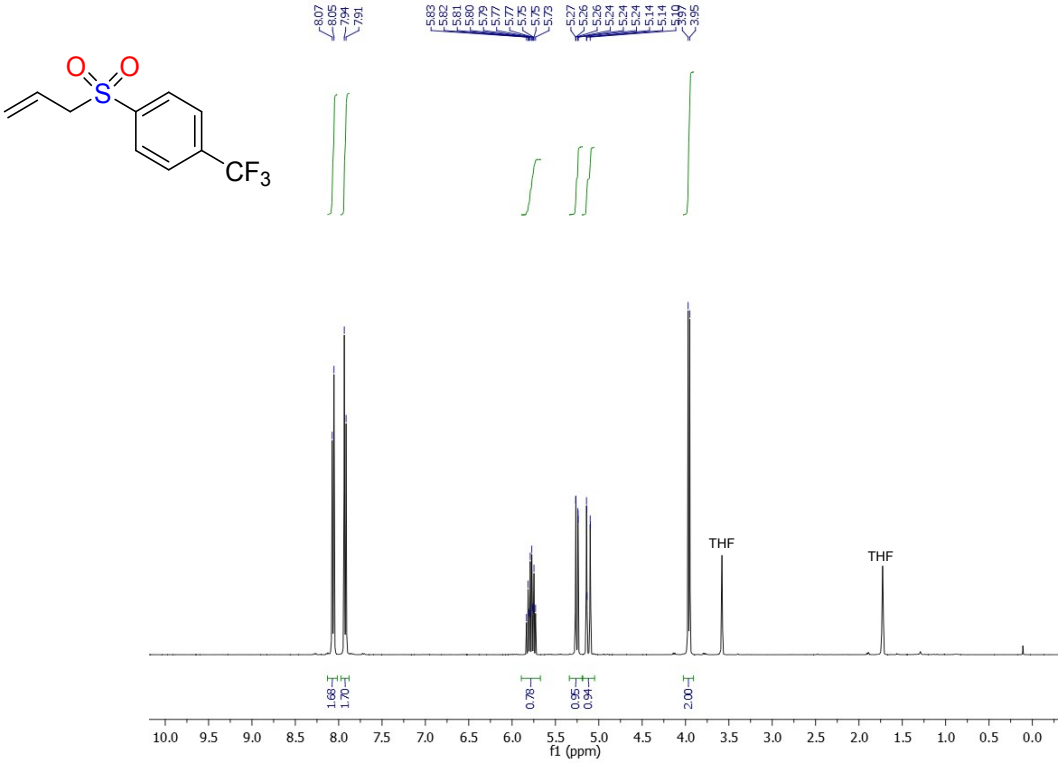



*Figure S11: $^{1}H$ NMR spectrum of (3d) in $d_8$–THF*

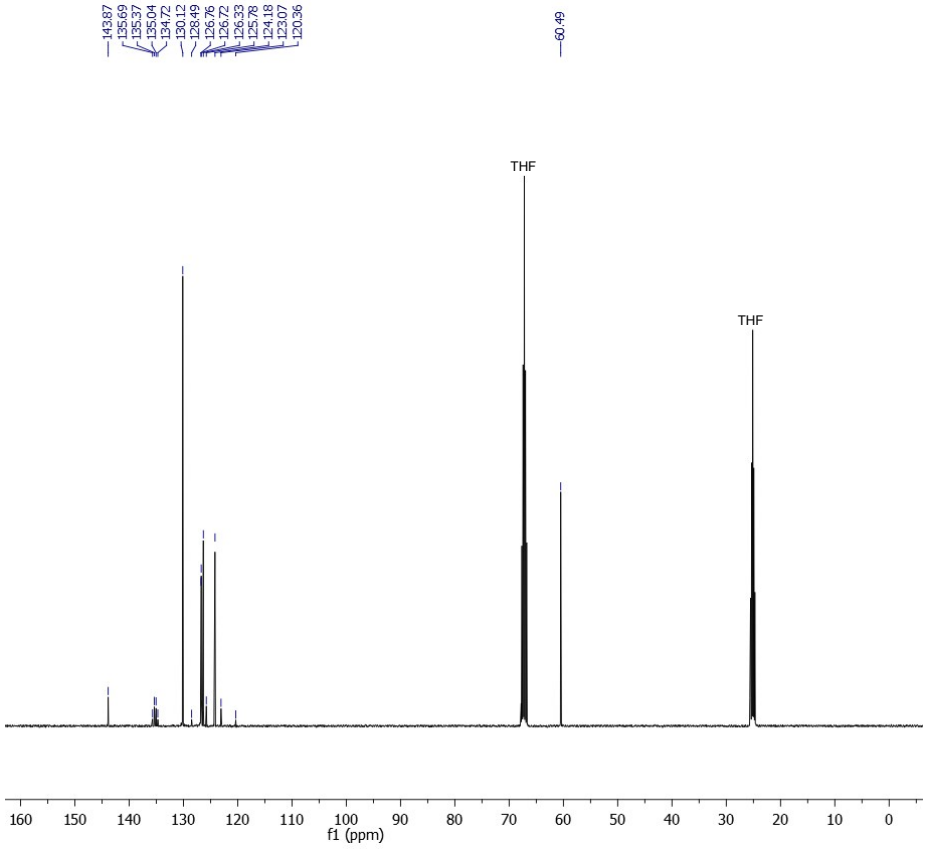



*Figure S12: $^{13}C\{^{1}H\}$ NMR spectrum of (3d) in $d_8$–THF*

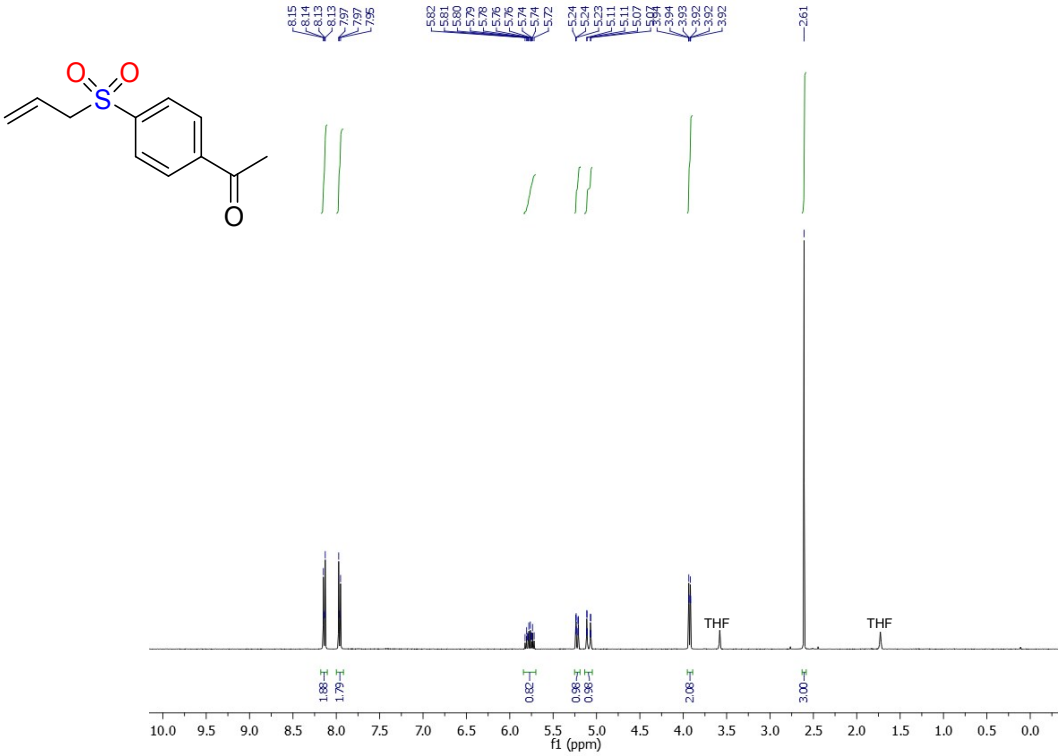



*Figure S13: $^{1}H$ NMR spectrum of (3e) in $d_8$–THF*

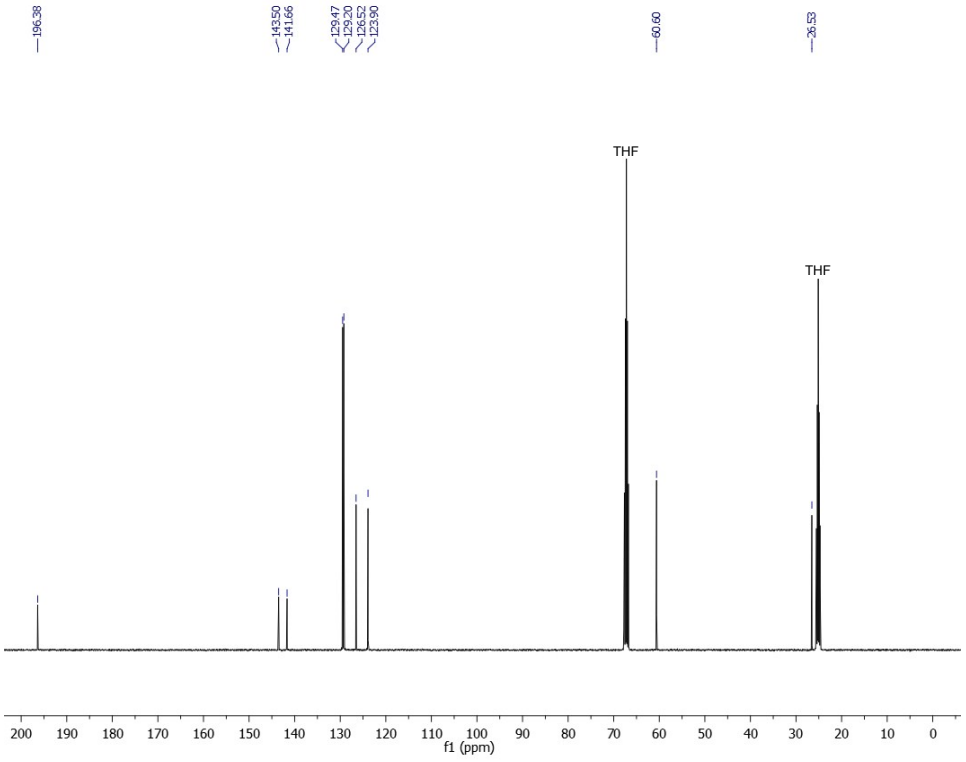



*Figure S14: $^{13}C\{^{1}H\}$ NMR spectrum of (3e) in $d_8$–THF*

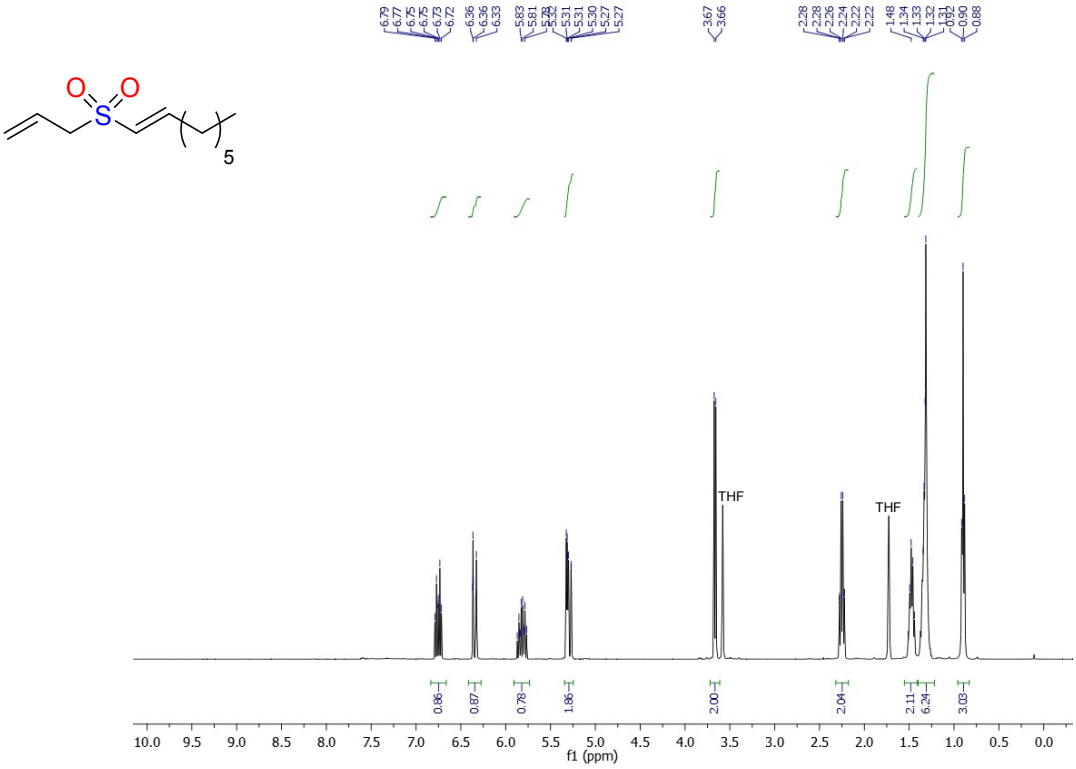



*Figure S15: $^{1}H$ NMR spectrum of (3f) in $d_8$–THF*

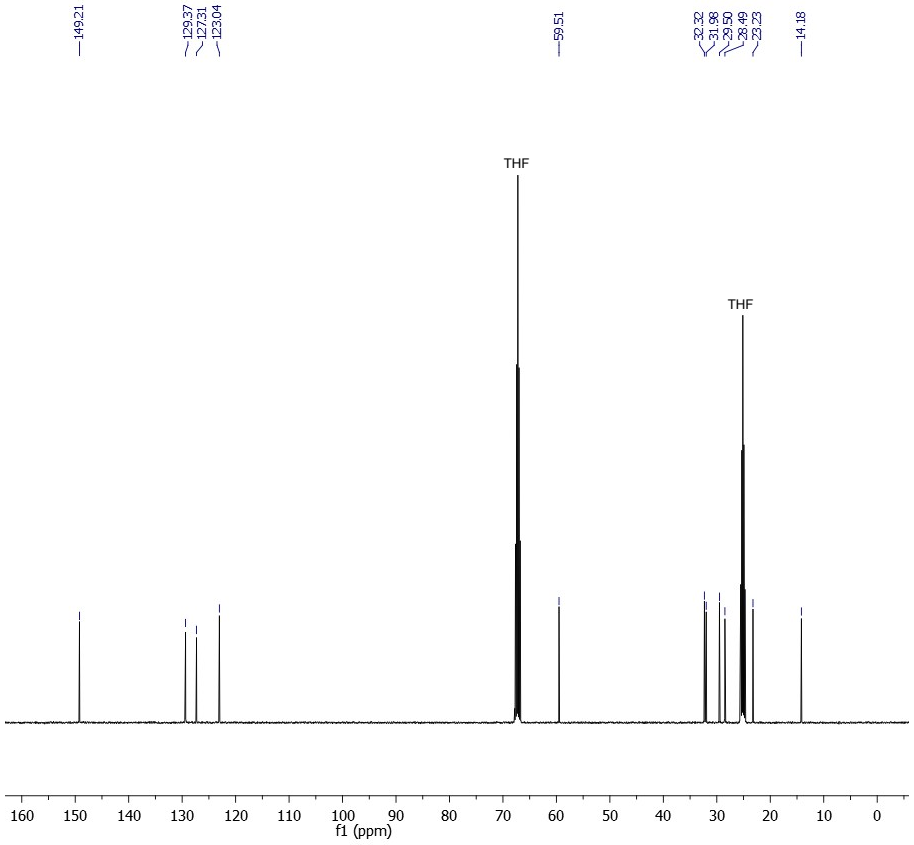



*Figure S16: $^{13}C\{^{1}H\}$ NMR spectrum of (3f) in $d_8$–THF*

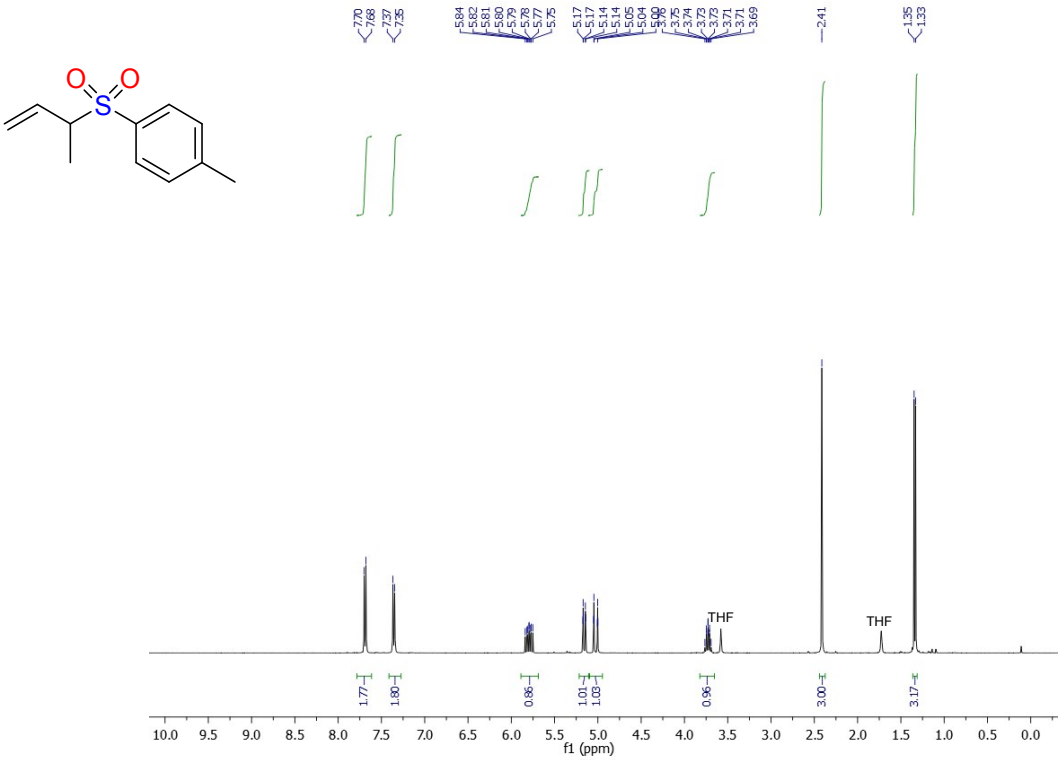



*Figure S17: $^{1}H$ NMR spectrum of (3g) in $d_8$–THF*

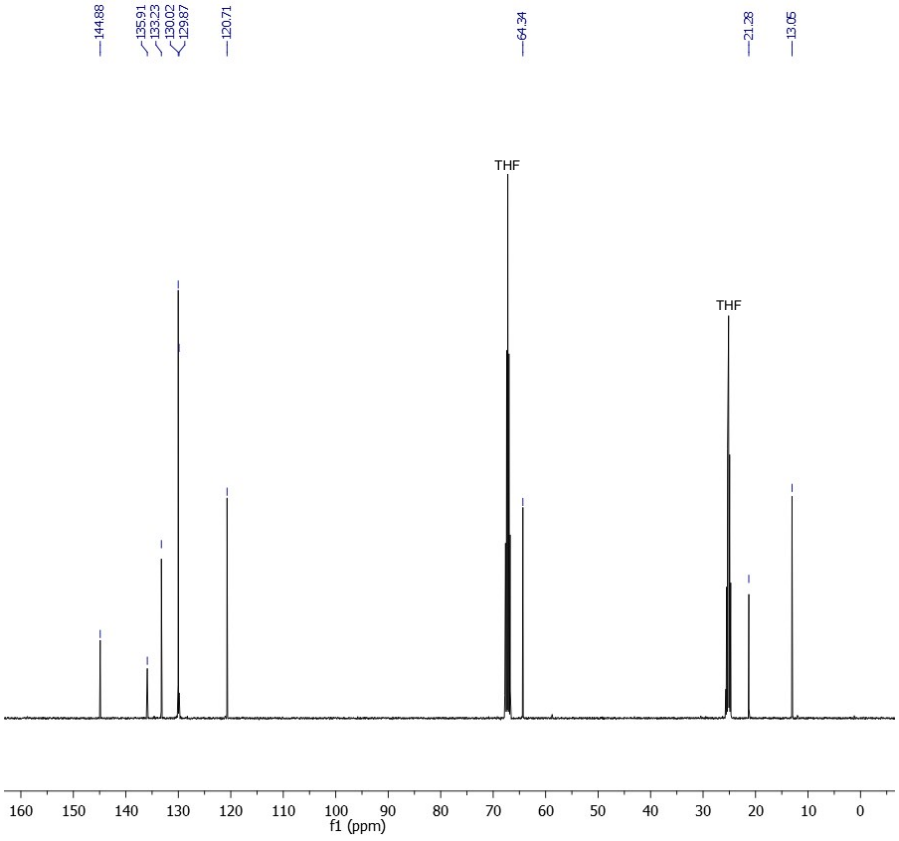



*Figure S18: $^{13}C\{^{1}H\}$ NMR spectrum of (3g) in $d_8$–THF*

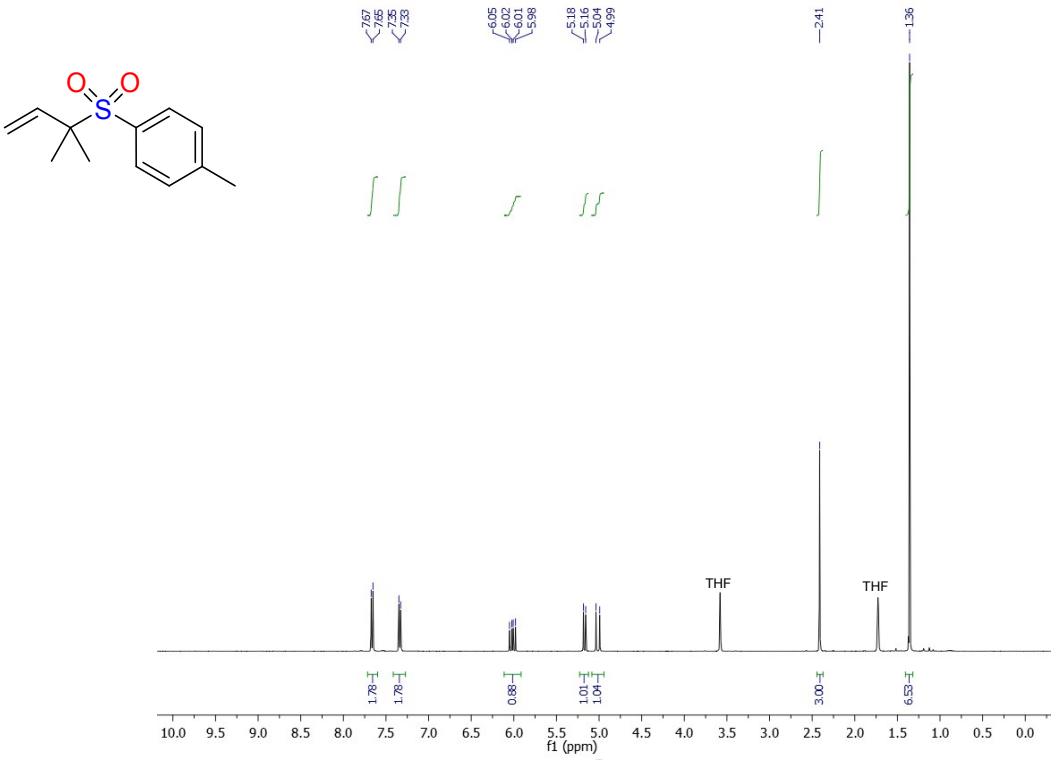



*Figure S19: $^{1}H$ NMR spectrum of (3h) in $d_8$–THF*

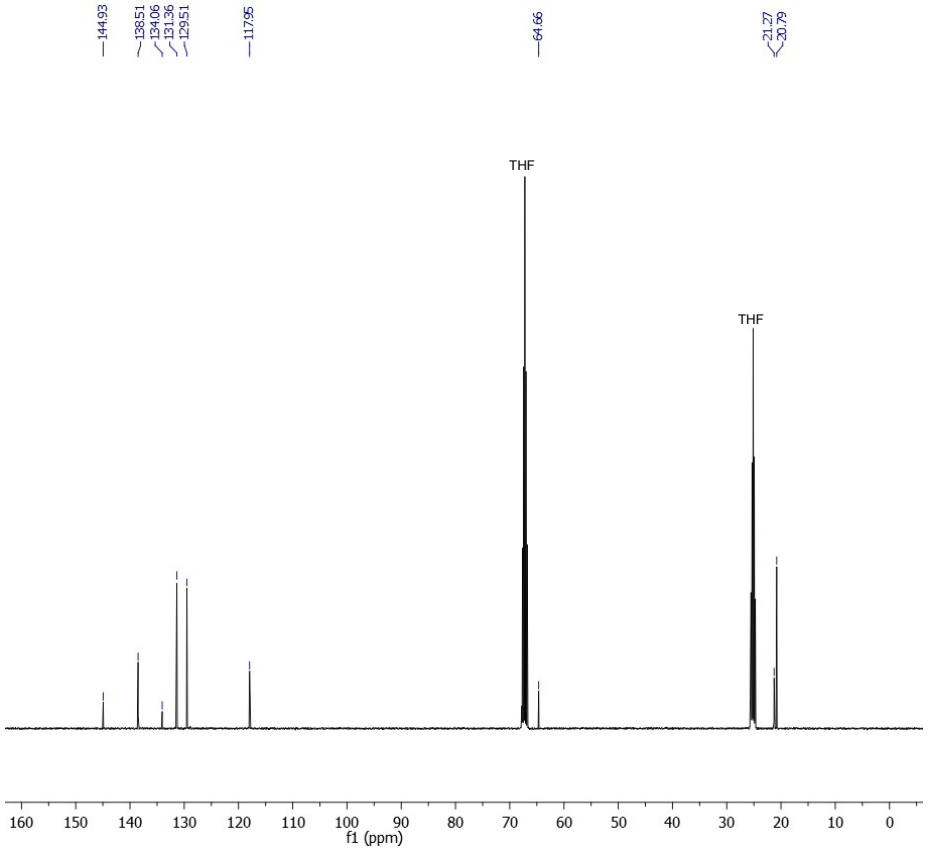



*Figure S20: $^{13}C\{^{1}H\}$ NMR spectrum of (3h) in $d_8$–THF*

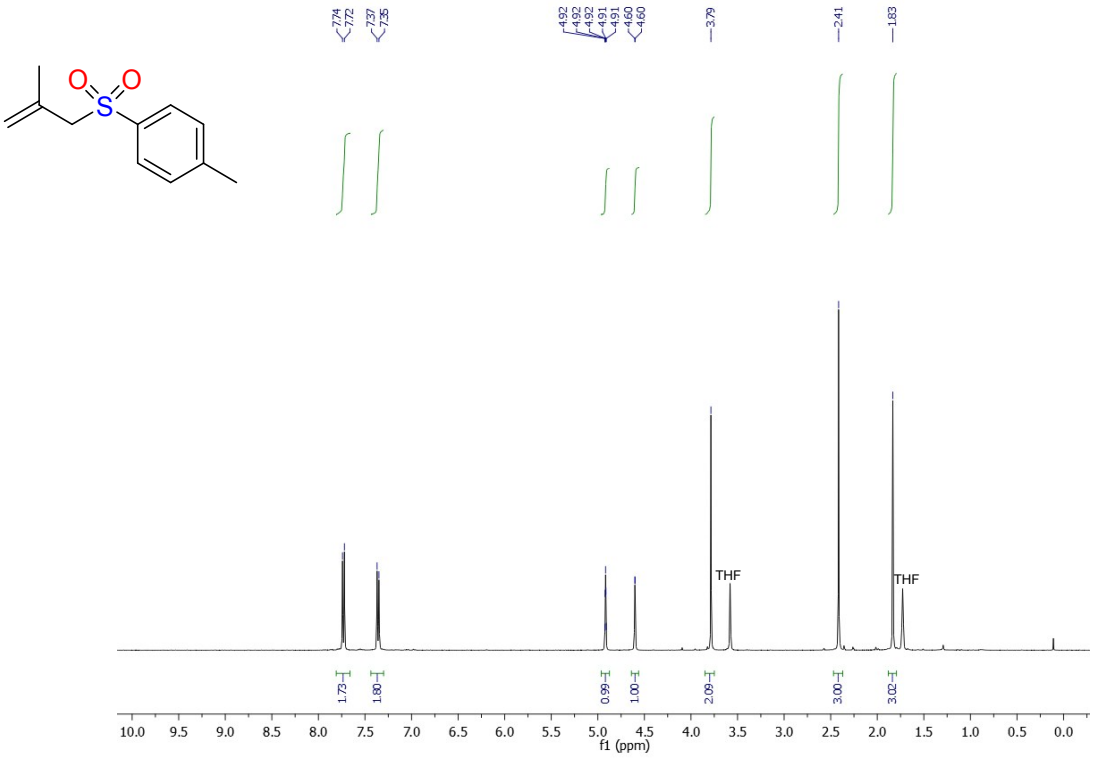



*Figure S21: $^{1}H$ NMR spectrum of (3i) in $d_8$–THF*

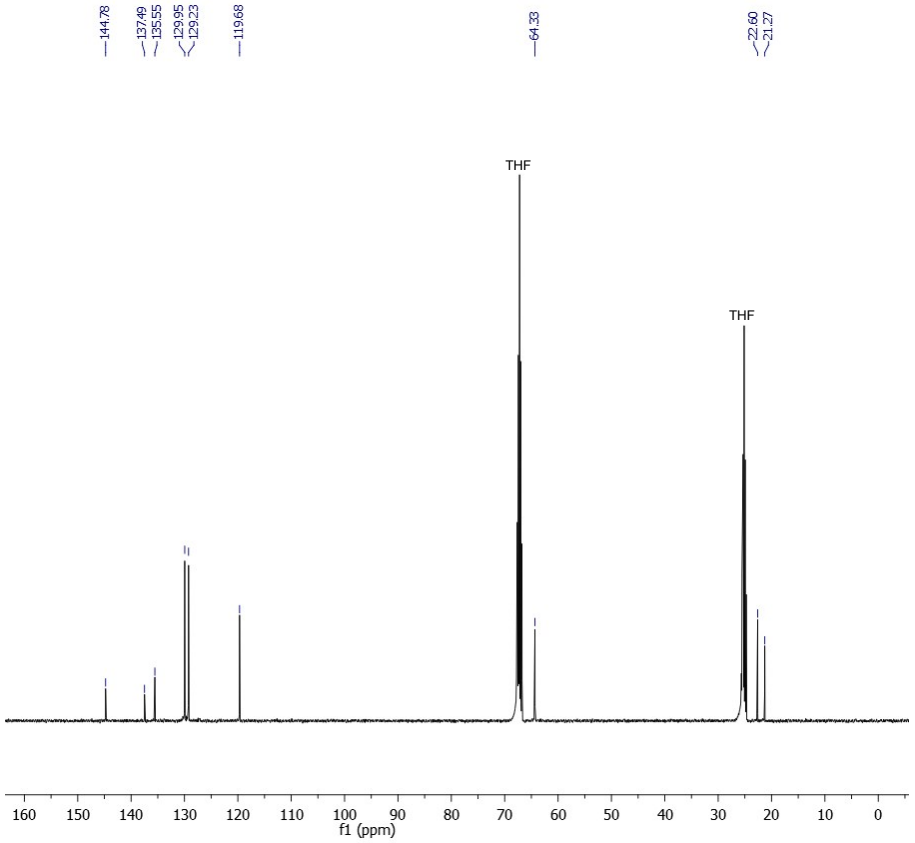



*Figure S22: $^{13}C\{^{1}H\}$ NMR spectrum of (3i) in $d_8$–THF*

## 2. Computational Details

Density functional theory[8] was applied to determine the structural and energetic features of the intermediates and transition states described herein. Calculations were performed using Gaussian09 version D.01 code.[9] The 6-311+G(d) basis set was used for atoms C, H, N, and O whereas 6-311++G(d,p) was used for P, Si, S and F (unless for the $CF_3$ moiety for which 6-311+G(d) was used). The Becke three-parameter hybrid functional B3LYP[10] was used with Grimme's D3 empirical dispersion.[11] All structures were optimized without geometrical constraint; stationary points were characterized by frequency calculations (one negative frequency for a transition state, no negative frequency for minima). Solvent effects (THF) were included in structure-optimization and frequency calculations using the PCM model implemented in the Gaussian code.[12] All relative energies (corrected for ZPE contributions) and Gibbs free energies (T= 298 K, P= 1 atm) are reported in kcal.mol$^{-1}$.

### *2.1. Computed potential energy surface for the formation of the sulfinate*

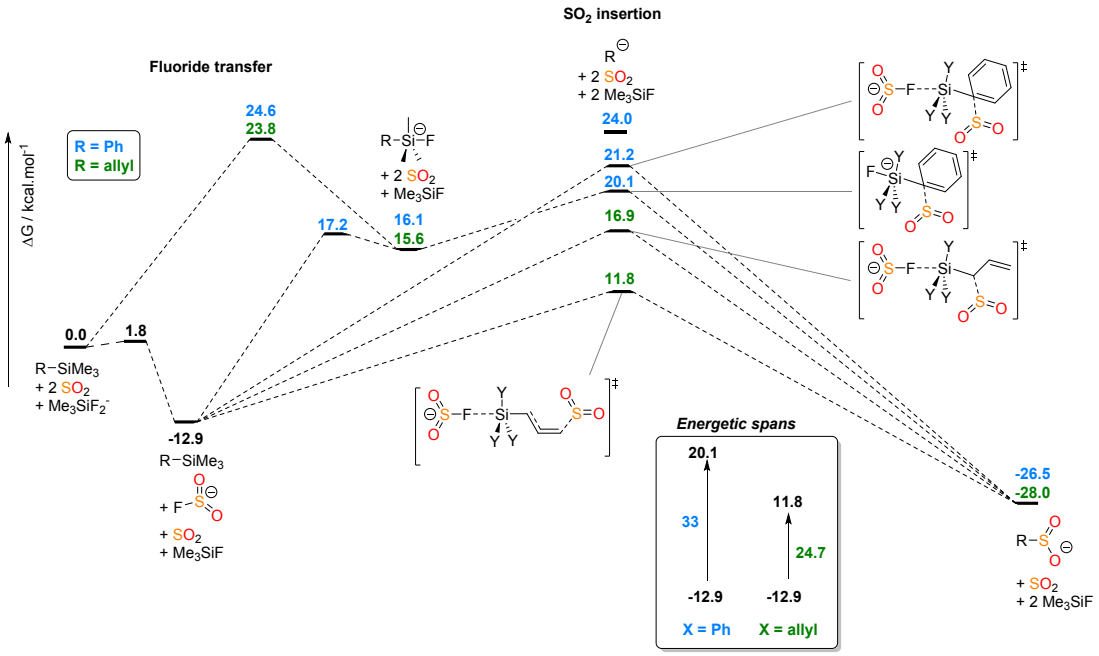



*Figure S23. Potential energy surface with different reaction pathways for the formation of* ***8a*** *and* ***8b****. Values given correspond to Gibbs free energies with respect to the starting material (G=0.0 kcal.mol$^{-1}$).*

### *2.2. Energies and frequencies of computed compounds and transition states*

All energies are in Hartree, imaginary frequencies are in $cm^{-1}$, the 3 displayed frequencies being the lowest ones.[13]

#### *2.2.1. Fluoro-affinity of allylsilanes*

$FSiMe_3$

| Element | X | Y | Z |
|---|---|---|---|
| Si | -0.00039800 | -0.00028300 | 0.00678600 |
| C | -1.78839099 | 0.13964500 | -0.52003801 |
| H | -1.87244499 | 0.13820601 | -1.61166704 |
| H | -2.38248110 | -0.69743198 | -0.14163300 |
| H | -2.24080396 | 1.06627500 | -0.15475300 |
| C | 0.77372801 | -1.61909997 | -0.51701301 |
| H | 1.79871595 | -1.70989096 | -0.14558101 |
| H | 0.20276000 | -2.47399211 | -0.14293700 |
| H | 0.80928200 | -1.69711006 | -1.60850894 |
| C | 1.01639700 | 1.47877204 | -0.51552802 |
| H | 0.58548301 | 2.41194892 | -0.14098001 |
| H | 2.04286790 | 1.40847194 | -0.14366600 |
| H | 1.06414795 | 1.55097198 | -1.60698497 |
| F | -0.00281200 | -0.00075200 | 1.66680801 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 133.2221 | 150.0940 | 150.7969 |
| Red. masses -- | 1.0099 | 1.0398 | 1.0441 |
| Frc consts -- | 0.0106 | 0.0138 | 0.0140 |
| IR Inten -- | 0.0012 | 0.0037 | 0.0020 |

Sum of electronic and zero-point Energies= -509.161188
Sum of electronic and thermal Energies= -509.152799
Sum of electronic and thermal Enthalpies= -509.151855
Sum of electronic and thermal Free Energies= -509.193018

HF = -509.274188643

$F_2SiMe_3^-$

| Element | X | Y | Z |
|---|---|---|---|
| Si | 0.00002300 | -0.00374000 | 0.00017400 |
| F | 1.82993305 | -0.00779900 | -0.00021700 |
| F | -1.82990003 | -0.00667100 | 0.00038200 |
| C | 0.00016900 | -0.40796900 | 1.86227906 |
| H | 0.00024400 | 0.52507699 | 2.44042206 |
| H | -0.89006698 | -0.96823102 | 2.15952492 |
| H | 0.89037102 | -0.96834201 | 2.15942097 |
| C | 0.00049700 | 1.81463504 | -0.57021999 |
| H | 0.00042600 | 1.85983098 | -1.66680098 |
| H | -0.88933599 | 2.34917307 | -0.22719900 |
| H | 0.89068800 | 2.34867191 | -0.22734299 |

| | | | |
|---|---|---|---|
| C | -0.00064800 | -1.40778697 | -1.28868306 |
| H | -0.00117300 | -2.37882304 | -0.77684897 |
| H | -0.89167899 | -1.37954795 | -1.92166102 |
| H | 0.89042199 | -1.38047802 | -1.92164397 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -59.1633 | 58.8019 | 77.2376 |
| Red. masses -- | 1.0447 | 1.0555 | 1.0637 |
| Frc consts -- | 0.0022 | 0.0022 | 0.0037 |
| IR Inten -- | 0.0174 | 0.1991 | 0.0683 |

Sum of electronic and zero-point Energies= -609.187295
Sum of electronic and thermal Energies= -609.178045
Sum of electronic and thermal Enthalpies= -609.177101
Sum of electronic and thermal Free Energies= -609.221013

HF = -609.301004925

## allylSiMe$_3$

| Element | X | Y | Z |
|---|---|---|---|
| C | -1.44365597 | 0.69515097 | -1.07747304 |
| H | -1.09742904 | 0.34229699 | -2.04608107 |
| H | -2.51353192 | 0.65618497 | -0.89814502 |
| C | -0.59480202 | 1.15516400 | -0.15485600 |
| H | -1.00266504 | 1.49807501 | 0.79618502 |
| C | 0.88665301 | 1.29493999 | -0.31443399 |
| H | 1.24518001 | 0.70304102 | -1.16501403 |
| H | 1.40360796 | 0.91935402 | 0.57796001 |
| Si | 1.44796395 | 3.10161090 | -0.57927698 |
| C | 0.79319000 | 4.17225790 | 0.82978803 |
| H | 1.12179196 | 5.21095085 | 0.72204798 |
| H | -0.30085900 | 4.17432308 | 0.85578698 |
| H | 1.14714599 | 3.81346607 | 1.80176103 |
| C | 0.76701897 | 3.71486592 | -2.22658205 |
| H | 1.03652704 | 4.76087189 | -2.40428901 |
| H | 1.15870702 | 3.12561107 | -3.06205297 |
| H | -0.32429901 | 3.64228606 | -2.25439095 |
| C | 3.33434010 | 3.14177108 | -0.59949601 |
| H | 3.73826909 | 2.50727606 | -1.39493001 |
| H | 3.70720792 | 4.15747976 | -0.76669800 |
| H | 3.75103688 | 2.78912306 | 0.34939301 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 45.8756 | 70.3601 | 134.8255 |
| Red. masses -- | 2.4757 | 2.8714 | 1.0447 |
| Frc consts -- | 0.0031 | 0.0084 | 0.0112 |
| IR Inten -- | 0.1231 | 0.0650 | 0.0044 |

Sum of electronic and zero-point Energies= -526.496092
Sum of electronic and thermal Energies= -526.484597
Sum of electronic and thermal Enthalpies= -526.483653
Sum of electronic and thermal Free Energies= -526.532821

HF = -526.676627637

## allylSiMe$_3$F$^-$

| Element | X | Y | Z |
|---|---|---|---|
| C | -0.20242301 | -0.04070200 | -1.06762397 |
| H | 0.00664000 | -0.08573500 | -2.13468504 |
| H | -1.03511500 | -0.64058697 | -0.71052700 |
| C | 0.52529198 | 0.72984701 | -0.23934400 |
| H | 0.24591000 | 0.71441603 | 0.81671298 |
| C | 1.60681498 | 1.66693294 | -0.59084803 |
| H | 2.01527500 | 1.45289302 | -1.58831203 |
| H | 2.42996693 | 1.59631598 | 0.13393401 |
| C | 0.45963201 | 3.60594392 | 1.23009706 |
| H | 0.45873600 | 4.59039688 | 1.70236099 |
| H | -0.57205898 | 3.23275709 | 1.24625301 |
| H | 1.04914498 | 2.91989589 | 1.84832895 |
| C | -0.13093100 | 3.52047706 | -2.04227710 |
| H | -1.10293698 | 3.95155907 | -1.78207302 |
| H | 0.25059599 | 4.10877609 | -2.88455009 |
| H | -0.29305300 | 2.49477291 | -2.38329911 |
| C | 2.89028406 | 4.22866583 | -0.92740399 |
| H | 3.59242702 | 3.40743303 | -1.10166705 |
| H | 2.91037512 | 4.89032507 | -1.79947305 |
| H | 3.26461697 | 4.82013798 | -0.08400100 |
| Si | 1.09222102 | 3.66228390 | -0.57802498 |
| F | 0.65478402 | 5.53539181 | -0.58197898 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 88.8054 | 98.9997 | 111.5108 |
| Red. masses -- | 1.6080 | 1.8254 | 1.7937 |
| Frc consts -- | 0.0075 | 0.0105 | 0.0131 |
| IR Inten -- | 0.5295 | 2.1026 | 1.2362 |

Sum of electronic and zero-point Energies= -626.498718
Sum of electronic and thermal Energies= -626.486094
Sum of electronic and thermal Enthalpies= -626.485150
Sum of electronic and thermal Free Energies= -626.535962

HF = -626.680284135

## allylSiMe$_2$OMe

| Element | X | Y | Z |
|---|---|---|---|
| C | -1.44664097 | 0.78712302 | -1.05934405 |
| H | -1.09314299 | 0.31428301 | -1.97262895 |
| H | -2.52216697 | 0.83801299 | -0.92171502 |
| C | -0.60150498 | 1.28250802 | -0.15272100 |
| H | -1.01147497 | 1.74987996 | 0.74166399 |
| C | 0.89229298 | 1.29914701 | -0.26620799 |
| H | 1.23054802 | 0.63668603 | -1.07216799 |
| H | 1.35121500 | 0.93361199 | 0.66119897 |
| Si | 1.60210204 | 3.02170205 | -0.59438097 |

| | | | |
|---|---|---|---|
| C | 0.92610502 | 3.74100494 | -2.19128799 |
| H | 1.30025804 | 4.75349617 | -2.37142897 |
| H | 1.22166705 | 3.12774611 | -3.04890609 |
| H | -0.16652900 | 3.78276205 | -2.17480898 |
| C | 3.47969890 | 2.96492505 | -0.63925201 |
| H | 3.83319092 | 2.33036089 | -1.45845795 |
| H | 3.90907788 | 3.96022201 | -0.79136199 |
| H | 3.88860011 | 2.56413007 | 0.29316300 |
| O | 1.08436894 | 3.93935204 | 0.71567899 |
| C | 1.33574998 | 5.33184290 | 0.86168897 |
| H | 0.88354701 | 5.66252708 | 1.79852998 |
| H | 2.41030312 | 5.54666519 | 0.90163600 |
| H | 0.89373302 | 5.90911198 | 0.04120600 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 45.0064 | 58.3862 | 73.5298 |
| Red. masses -- | 2.8099 | 2.3850 | 2.8128 |
| Frc consts -- | 0.0034 | 0.0048 | 0.0090 |
| IR Inten -- | 0.0291 | 5.8949 | 0.5001 |

Sum of electronic and zero-point Energies= -601.762247
Sum of electronic and thermal Energies= -601.749612
Sum of electronic and thermal Enthalpies= -601.748668
Sum of electronic and thermal Free Energies= -601.801268

HF = -601.948683982

## allylSiMe$_2$OMeF$^-$

| Element | X | Y | Z |
|---|---|---|---|
| C | -0.07571800 | -0.03125500 | -1.05911505 |
| H | 0.09804000 | -0.02718200 | -2.13344908 |
| H | -0.83331001 | -0.71887600 | -0.69297302 |
| C | 0.60663801 | 0.77972102 | -0.23292200 |
| H | 0.36904499 | 0.70920902 | 0.83092499 |
| C | 1.59699500 | 1.81441295 | -0.59505200 |
| H | 1.99003398 | 1.65124297 | -1.60652006 |
| H | 2.44501591 | 1.79412401 | 0.10103900 |
| C | 0.30366901 | 3.59916592 | 1.27241695 |
| H | 0.07968900 | 4.56740808 | 1.72454906 |
| H | -0.61524802 | 3.00006890 | 1.29437602 |
| H | 1.02914202 | 3.07506990 | 1.90506995 |
| C | -0.28830001 | 3.53803611 | -1.99413204 |
| H | -1.25168705 | 4.01334286 | -1.78465605 |
| H | 0.12991600 | 4.05570412 | -2.86638308 |
| H | -0.46890801 | 2.49711609 | -2.27327800 |
| Si | 0.92939502 | 3.73358393 | -0.53212798 |
| F | 0.46803600 | 5.52477407 | -0.52055699 |
| O | 2.56393790 | 4.19144392 | -0.84440601 |
| C | 3.07585096 | 5.49755192 | -1.01072395 |
| H | 2.94592190 | 6.11317682 | -0.11316000 |
| H | 4.14895010 | 5.41323280 | -1.21968305 |
| H | 2.60179591 | 6.02812576 | -1.84423697 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 64.1790 | 83.8809 | 112.4479 |
| Red. masses -- | 2.1892 | 2.2714 | 1.5106 |
| Frc consts -- | 0.0053 | 0.0094 | 0.0113 |
| IR Inten -- | 1.5016 | 6.2682 | 0.1706 |

Sum of electronic and zero-point Energies= -701.771460
Sum of electronic and thermal Energies= -701.758003
Sum of electronic and thermal Enthalpies= -701.757059
Sum of electronic and thermal Free Energies= -701.810236

HF = -701.959120013

## allylSiOMe$_3$

| Element | X | Y | Z |
|---|---|---|---|
| C | -3.61613989 | -0.36729699 | 0.04063500 |
| H | -3.66644597 | -1.03211701 | 0.89936298 |
| H | -4.38688517 | -0.48521799 | -0.71440101 |
| C | -2.65382791 | 0.54764700 | -0.08305300 |
| H | -2.64436793 | 1.18477297 | -0.96588600 |
| C | -1.53248203 | 0.76823598 | 0.89135700 |
| H | -1.72383106 | 0.24726900 | 1.83563995 |
| H | -1.43306506 | 1.83442402 | 1.12833405 |
| Si | 0.11917300 | 0.19137999 | 0.24587700 |
| O | 0.19008200 | -1.46184397 | 0.28358701 |
| O | 1.31209099 | 0.80908000 | 1.21436799 |
| O | 0.29398701 | 0.73376399 | -1.30930400 |
| C | 0.73068100 | -2.32071900 | -0.71864599 |
| H | 1.82355905 | -2.35088801 | -0.65778202 |
| H | 0.34233099 | -3.32557797 | -0.54760402 |
| H | 0.43924901 | -1.99471700 | -1.72117496 |
| C | 2.56822300 | 0.19093899 | 1.49547899 |
| H | 2.98906589 | 0.66946602 | 2.38067389 |
| H | 2.44827199 | -0.87827098 | 1.69242299 |
| H | 3.26377797 | 0.32270801 | 0.66041899 |
| C | 1.52782094 | 1.00505197 | -1.97278798 |
| H | 2.17379189 | 1.64296305 | -1.36211598 |
| H | 2.06223392 | 0.07891600 | -2.20859098 |
| H | 1.30113995 | 1.52372599 | -2.90504909 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 27.2697 | 46.3004 | 60.1739 |
| Red. masses -- | 2.8692 | 3.0630 | 2.6643 |
| Frc consts -- | 0.0013 | 0.0039 | 0.0057 |
| IR Inten -- | 5.3245 | 1.0778 | 2.3730 |

Sum of electronic and zero-point Energies= -752.297607
Sum of electronic and thermal Energies= -752.282691
Sum of electronic and thermal Enthalpies= -752.281747
Sum of electronic and thermal Free Energies= -752.341339

HF = -752.496295063

## allylSiOMe$_3$F$^-$

| Element | X | Y | Z |
|---|---|---|---|
| C | -0.03704200 | -0.02022600 | -1.24291801 |
| H | 0.40411201 | -0.11158600 | -2.23371196 |
| H | -0.85414898 | -0.69832599 | -1.01038098 |
| C | 0.39205000 | 0.89819801 | -0.36649299 |
| H | -0.10307600 | 0.94289899 | 0.60407901 |
| C | 1.46000898 | 1.91070998 | -0.57492399 |
| H | 2.00504494 | 1.71461105 | -1.50543594 |
| H | 2.18500710 | 1.84792697 | 0.24736001 |
| Si | 0.87976098 | 3.78083396 | -0.58113497 |
| F | 0.38081601 | 5.47853804 | -0.55906898 |
| O | 2.52100492 | 4.26756001 | -0.72601497 |
| C | 3.01859188 | 5.58460188 | -0.85713297 |
| H | 2.78513908 | 6.20477009 | 0.01590500 |
| H | 4.10804605 | 5.52696323 | -0.95911998 |
| H | 2.61581397 | 6.09315920 | -1.74078798 |
| O | -0.03186200 | 3.53090191 | -2.00807309 |
| O | 0.17571300 | 3.56714106 | 0.97088999 |
| C | -0.87784702 | 4.44656515 | -2.67318511 |
| H | -0.33085901 | 5.31658888 | -3.05524111 |
| H | -1.33679795 | 3.92762399 | -3.52225804 |
| H | -1.67937303 | 4.81723213 | -2.02359009 |
| C | -0.51740700 | 4.51953411 | 1.75201595 |
| H | -0.85033703 | 4.02501822 | 2.67157197 |
| H | 0.11747800 | 5.36940193 | 2.02879596 |
| H | -1.39853597 | 4.91766024 | 1.23565102 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 39.5420 | 59.4832 | 71.6783 |
| Red. masses -- | 2.8786 | 2.9544 | 3.0763 |
| Frc consts -- | 0.0027 | 0.0062 | 0.0093 |
| IR Inten -- | 4.7772 | 2.8647 | 1.6293 |

Sum of electronic and zero-point Energies= -852.322224
Sum of electronic and thermal Energies= -852.306918
Sum of electronic and thermal Enthalpies= -852.305974
Sum of electronic and thermal Free Energies= -852.364591

HF = -852.522162510

## allylSiOEt$_3$

| Element | X | Y | Z |
|---|---|---|---|
| C | -1.39342296 | 0.38068399 | -0.66662699 |
| H | -1.28114104 | 0.04532200 | -1.69474900 |
| H | -2.38785100 | 0.31286100 | -0.23686400 |
| C | -0.36208799 | 0.85694802 | 0.03217600 |
| H | -0.53070903 | 1.18355894 | 1.05771303 |
| C | 1.03975201 | 1.01640296 | -0.47857699 |
| H | 1.17339802 | 0.49603099 | -1.43328094 |
| H | 1.75397694 | 0.57498598 | 0.22815600 |
| Si | 1.54977405 | 2.80125594 | -0.70978600 |

| | | | |
|---|---|---|---|
| O | 1.43763399 | 3.57123208 | 0.74883401 |
| C | 0.84645301 | 4.84035778 | 1.05541396 |
| H | 0.25998500 | 4.70424318 | 1.96831405 |
| H | 0.15583400 | 5.12875509 | 0.25709200 |
| O | 3.10867000 | 2.83816195 | -1.25881100 |
| O | 0.55217499 | 3.52374601 | -1.80958402 |
| C | 0.89016098 | 4.34033918 | -2.93720102 |
| H | 0.29013899 | 3.98400593 | -3.77924109 |
| H | 1.94400203 | 4.19775915 | -3.19580603 |
| C | 4.21818686 | 3.60468507 | -0.77283800 |
| H | 5.07198381 | 2.92423892 | -0.70943701 |
| H | 4.00459290 | 3.96543503 | 0.23805600 |
| C | 0.59667200 | 5.80587721 | -2.66081405 |
| H | -0.45282200 | 5.94584322 | -2.38991189 |
| H | 1.21358299 | 6.18716478 | -1.84289598 |
| H | 0.80493802 | 6.40764523 | -3.55068493 |
| C | 1.90866101 | 5.90774393 | 1.26177800 |
| H | 2.48348498 | 6.07827616 | 0.34765601 |
| H | 1.44203699 | 6.85471916 | 1.54955602 |
| H | 2.60441899 | 5.61423922 | 2.05190492 |
| C | 4.53264809 | 4.76457596 | -1.70328200 |
| H | 5.41362190 | 5.30710888 | -1.34701598 |
| H | 4.73696280 | 4.40525198 | -2.71500206 |
| H | 3.69888592 | 5.46974516 | -1.75394201 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 39.0007 | 43.9306 | 54.1521 |
| Red. masses -- | 3.5662 | 3.5481 | 3.3802 |
| Frc consts -- | 0.0032 | 0.0040 | 0.0058 |
| IR Inten -- | 0.8384 | 1.9554 | 2.3788 |

Sum of electronic and zero-point Energies= -870.202222
Sum of electronic and thermal Energies= -870.184259
Sum of electronic and thermal Enthalpies= -870.183315
Sum of electronic and thermal Free Energies= -870.249226

HF = -870.486948951

## allylSiOEt$_3$F$^-$

| Element | X | Y | Z |
|---|---|---|---|
| C | -0.06599000 | 0.15781701 | -1.22751606 |
| H | 0.27510700 | 0.14078900 | -2.26100898 |
| H | -0.82663798 | -0.56957501 | -0.95538300 |
| C | 0.41035900 | 1.04784405 | -0.34629899 |
| H | 0.01497000 | 1.01739502 | 0.66952699 |
| C | 1.40457594 | 2.12185597 | -0.59872299 |
| H | 1.85654104 | 2.00779796 | -1.59088504 |
| H | 2.21348906 | 2.05066299 | 0.14015000 |
| Si | 0.73911101 | 3.95808291 | -0.43603200 |
| F | 0.16284300 | 5.62454700 | -0.27808800 |
| O | 2.34471989 | 4.53189421 | -0.65128303 |
| C | 2.80557394 | 5.86541224 | -0.77699399 |
| H | 2.30207705 | 6.52215481 | -0.05965500 |
| H | 3.87371612 | 5.85750818 | -0.52231401 |

| | | | |
|---|---|---|---|
| O | -0.26686800 | 3.73883796 | -1.80604196 |
| O | 0.16602300 | 3.61258602 | 1.14584005 |
| C | -1.21140206 | 4.62777710 | -2.37400603 |
| H | -0.79866499 | 5.63988400 | -2.45471406 |
| H | -1.40613401 | 4.27132416 | -3.39418793 |
| C | -0.44637200 | 4.47602510 | 2.08670592 |
| H | -1.01697302 | 3.83997893 | 2.77668309 |
| H | -1.15852404 | 5.14833689 | 1.59654999 |
| C | 0.57665098 | 5.29110718 | 2.87157893 |
| H | 1.28718495 | 4.63080597 | 3.37827802 |
| H | 1.13587999 | 5.94521284 | 2.19854093 |
| H | 0.08550900 | 5.91202116 | 3.62966895 |
| C | -2.51906705 | 4.66584015 | -1.58924901 |
| H | -2.94214702 | 3.66066194 | -1.50116503 |
| H | -2.34429789 | 5.05455923 | -0.58371198 |
| H | -3.25599599 | 5.30712080 | -2.08648491 |
| C | 2.62397099 | 6.40868092 | -2.19100595 |
| H | 3.13070297 | 5.76618290 | -2.91766310 |
| H | 1.56335497 | 6.44802999 | -2.44982004 |
| H | 3.03921199 | 7.41933918 | -2.27849102 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 53.6373 | 56.4138 | 62.7441 |
| Red. masses -- | 3.0930 | 3.2301 | 3.0814 |
| Frc consts -- | 0.0052 | 0.0061 | 0.0071 |
| IR Inten -- | 1.5931 | 1.0935 | 1.4010 |

Sum of electronic and zero-point Energies= -970.225090
Sum of electronic and thermal Energies= -970.206519
Sum of electronic and thermal Enthalpies= -970.205575
Sum of electronic and thermal Free Energies= -970.271487

HF = -970.510805356

### *2.2.2. Formation of the sultinate*

$SO_2$

| Element | X | Y | Z |
|---|---|---|---|
| S | 0.36723700 | 2.31060505 | 7.78685093 |
| O | -0.32170501 | 3.59135199 | 7.92644501 |
| O | 1.01494706 | 1.75963497 | 8.97487831 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 499.1558 | 1127.5937 | 1278.5302 |
| Red. masses -- | 18.5513 | 18.0149 | 20.2749 |
| Frc consts -- | 2.7233 | 13.4955 | 19.5268 |
| IR Inten -- | 57.1188 | 52.6412 | 381.9765 |

Sum of electronic and zero-point Energies= -548.664618
Sum of electronic and thermal Energies= -548.661526
Sum of electronic and thermal Enthalpies= -548.660582

Sum of electronic and thermal Free Energies= -548.689503

HF = -548.671236713

## $FSO_2^-$

| Element | X | Y | Z |
|---|---|---|---|
| S | 0.11493900 | -1.63376606 | -0.00039500 |
| F | -1.77339005 | -1.56509101 | 0.00084900 |
| O | 0.39902601 | -0.86115998 | -1.24072504 |
| O | 0.40061200 | -0.86229998 | 1.24027205 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 287.6111 | 300.2414 | 428.4482 |
| Red. masses -- | 17.8874 | 18.2373 | 22.1383 |
| Frc consts -- | 0.8718 | 0.9686 | 2.3944 |
| IR Inten -- | 11.5757 | 87.1137 | 269.4793 |

Sum of electronic and zero-point Energies= -648.710736
Sum of electronic and thermal Energies= -648.706515
Sum of electronic and thermal Enthalpies= -648.705571
Sum of electronic and thermal Free Energies= -648.737981

HF = -648.719284708

## $allyl^-$

| Element | X | Y | Z |
|---|---|---|---|
| C | -1.51088405 | 0.40489000 | -0.71583498 |
| H | -1.30340505 | -0.64169800 | -0.93701297 |
| H | -2.55363202 | 0.70898902 | -0.71040398 |
| C | -0.49151900 | 1.31902099 | -0.45063800 |
| H | -0.84383798 | 2.33732390 | -0.24223500 |
| C | 0.89519298 | 1.17227697 | -0.40225300 |
| H | 1.54242802 | 2.01403499 | -0.17398600 |
| H | 1.37955499 | 0.21476300 | -0.59193498 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 259.7708 | 357.7850 | 432.7241 |
| Red. masses -- | 1.3085 | 1.1773 | 1.8598 |
| Frc consts -- | 0.0520 | 0.0888 | 0.2052 |
| IR Inten -- | 1.1952 | 741.2045 | 4.7677 |

Sum of electronic and zero-point Energies= -117.323988
Sum of electronic and thermal Energies= -117.319541
Sum of electronic and thermal Enthalpies= -117.318597
Sum of electronic and thermal Free Energies= -117.348929

HF = -117.386842748

## $allylSO_2^-$

| Element | X | Y | Z |
|---|---|---|---|
| C | -1.35658300 | 0.25180399 | -0.27944300 |
| H | -0.81307298 | -0.52442700 | 0.25387201 |
| H | -2.44027805 | 0.19034401 | -0.25715899 |
| C | -0.72156602 | 1.22856998 | -0.93504298 |
| H | -1.30738699 | 1.98729002 | -1.45002699 |
| C | 0.74953097 | 1.41574597 | -0.96423000 |
| H | 1.12961304 | 1.69563794 | -1.95080400 |
| H | 1.29581499 | 0.54724801 | -0.58868700 |
| S | 1.31382000 | 2.87515903 | 0.11825600 |
| O | 0.61651200 | 4.05869389 | -0.57215297 |
| O | 2.82459402 | 2.86813307 | -0.16837899 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 74.1650 | 92.6784 | 189.8145 |
| Red. masses -- | 3.1430 | 3.8312 | 3.1377 |
| Frc consts -- | 0.0102 | 0.0194 | 0.0666 |
| IR Inten -- | 4.3849 | 4.1295 | 1.3150 |

Sum of electronic and zero-point Energies= -666.070430
Sum of electronic and thermal Energies= -666.063545
Sum of electronic and thermal Enthalpies= -666.062601
Sum of electronic and thermal Free Energies= -666.101980

HF = -666.147650988

## $PhSiMe_3$

| Element | X | Y | Z |
|---|---|---|---|
| Si | 1.47111201 | -0.00969200 | 0.00000000 |
| C | 2.07206392 | 0.90138298 | -1.53980005 |
| H | 1.74324000 | 0.39654499 | -2.45330405 |
| H | 1.68729603 | 1.92557395 | -1.57192802 |
| H | 3.16519189 | 0.95853698 | -1.56414104 |
| C | 2.07208705 | 0.90152800 | 1.53970599 |
| H | 1.68734205 | 1.92572999 | 1.57173300 |
| C | 2.11965895 | -1.77929294 | 0.00008000 |
| H | 1.78961694 | -2.33339405 | 0.88414901 |
| H | 1.78963101 | -2.33346796 | -0.88394701 |
| H | 3.21427298 | -1.78358400 | 0.00008900 |
| C | -0.42352501 | -0.02298200 | 0.00001300 |
| C | -1.13973296 | 1.18760097 | -0.00004500 |
| C | -2.53401709 | 1.20937002 | -0.00003800 |
| H | -0.60574001 | 2.13495803 | -0.00009600 |
| C | -2.56307292 | -1.20213401 | 0.00008500 |
| C | -3.25040388 | 0.01105300 | 0.00002800 |
| H | -3.06196499 | 2.15821695 | -0.00008200 |
| H | -3.11307001 | -2.13839602 | 0.00013500 |
| H | -4.33583498 | 0.02416400 | 0.00003300 |
| H | 3.16521597 | 0.95866001 | 1.56403697 |
| H | 1.74325597 | 0.39679000 | 2.45326209 |
| C | -1.16647804 | -1.21473503 | 0.00007700 |
| H | -0.65440202 | -2.17266107 | 0.00012200 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 26.0169 | 84.3145 | 121.5663 |
| Red. masses -- | 3.3381 | 3.1953 | 2.7327 |
| Frc consts -- | 0.0013 | 0.0134 | 0.0238 |
| IR Inten -- | 0.0021 | 0.2383 | 0.2377 |

Sum of electronic and zero-point Energies= -640.844456
Sum of electronic and thermal Energies= -640.832186
Sum of electronic and thermal Enthalpies= -640.831242
Sum of electronic and thermal Free Energies= -640.882867

HF = -641.045509403

## $PhSiMe_3F^-$

| Element | X | Y | Z |
|---|---|---|---|
| Si | 1.36168206 | 0.02922300 | 0.00057300 |
| C | 1.56696498 | 1.81885803 | -0.65019602 |
| H | 0.77521300 | 2.10801196 | -1.34794700 |
| H | 1.54966497 | 2.54079700 | 0.17555401 |
| H | 2.53170800 | 1.93133199 | -1.14819598 |
| C | 1.27300501 | -0.33600399 | 1.88529098 |
| H | 0.68843901 | 0.44488299 | 2.38673401 |
| C | 1.61503005 | -1.37042499 | -1.28286099 |
| H | 1.66038895 | -2.34987903 | -0.79076701 |
| H | 0.81185001 | -1.41738605 | -2.02425599 |
| H | 2.56539202 | -1.23538804 | -1.80327797 |
| F | 3.29566002 | 0.01203100 | 0.21387900 |
| C | -0.66612399 | 0.01405400 | -0.08036600 |
| C | -1.43979001 | 1.16498303 | 0.16783500 |
| C | -2.83732891 | 1.14640999 | 0.21291700 |
| H | -0.94143701 | 2.11779904 | 0.33553699 |
| C | -2.79897499 | -1.21533501 | -0.22907400 |
| C | -3.52829099 | -0.04944300 | 0.01060600 |
| H | -3.38795209 | 2.06473804 | 0.40489900 |
| H | -3.31940889 | -2.15768790 | -0.38546699 |
| H | -4.61409283 | -0.07268900 | 0.04074800 |
| H | 2.24989796 | -0.40462601 | 2.36791992 |
| H | 0.73086798 | -1.27379704 | 2.05720592 |
| C | -1.40191197 | -1.17232096 | -0.27009100 |
| H | -0.87255198 | -2.10489202 | -0.45634699 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 30.6652 | 87.1161 | 108.5669 |
| Red. masses -- | 3.1465 | 3.8335 | 2.7561 |
| Frc consts -- | 0.0017 | 0.0171 | 0.0191 |
| IR Inten -- | 0.7985 | 0.7998 | 3.2065 |

Sum of electronic and zero-point Energies= -740.845215
Sum of electronic and thermal Energies= -740.831491
Sum of electronic and thermal Enthalpies= -740.830546
Sum of electronic and thermal Free Energies= -740.885196

HF = -741.047123814

## $Ph^-$

| Element | X | Y | Z |
|---|---|---|---|
| C | -3.24354196 | 0.66071898 | -0.22072200 |
| C | -1.84621596 | 0.67988002 | -0.22029801 |
| C | -1.16179597 | 1.90538001 | -0.22093400 |
| C | -1.79063594 | 3.17667294 | -0.22199200 |
| C | -3.20609808 | 3.08575392 | -0.22236800 |
| C | -3.92511511 | 1.88038695 | -0.22177000 |
| H | -3.78755307 | -0.28096700 | -0.22027799 |
| H | -1.29363406 | -0.26027799 | -0.21952400 |
| H | -0.06893300 | 1.84953403 | -0.22055800 |
| H | -3.80139589 | 4.00375509 | -0.22314499 |
| H | -5.01558113 | 1.88946199 | -0.22211100 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 359.6685 | 398.6895 | 603.7144 |
| Red. masses -- | 2.6289 | 3.9032 | 7.0779 |
| Frc consts -- | 0.2004 | 0.3655 | 1.5199 |
| IR Inten -- | 0.0011 | 23.3412 | 0.7004 |

Sum of electronic and zero-point Energies= -231.652171
Sum of electronic and thermal Energies= -231.647737
Sum of electronic and thermal Enthalpies= -231.646793
Sum of electronic and thermal Free Energies= -231.679633

HF = -231.737903992

## $PhSO_2^-$

| Element | X | Y | Z |
|---|---|---|---|
| C | -3.04858303 | 1.68083096 | 0.07317900 |
| C | -1.65701699 | 1.73153806 | -0.03074600 |
| C | -1.00349104 | 2.96581101 | -0.02299100 |
| C | -1.73905003 | 4.14655876 | 0.09169200 |
| C | -3.12945104 | 4.09185314 | 0.18862200 |
| H | 0.07812000 | 3.00828099 | -0.11113200 |
| H | -3.56003308 | 0.72283500 | 0.05961500 |
| H | -1.08447504 | 0.81364298 | -0.12135200 |
| H | -1.24192500 | 5.11106110 | 0.08278000 |
| S | -4.10193491 | 5.65522909 | 0.43406999 |
| O | -3.30264997 | 6.66352606 | -0.40956700 |
| O | -5.45307922 | 5.29028177 | -0.20509300 |
| C | -3.78480196 | 2.86126089 | 0.18917900 |
| H | -4.86726284 | 2.83769798 | 0.25440001 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 46.6995 | 135.1530 | 190.8861 |
| Red. masses -- | 6.6791 | 5.5625 | 7.1521 |

| | | | |
|---|---|---|---|
| Frc consts -- | 0.0086 | 0.0599 | 0.1535 |
| IR Inten -- | 1.3604 | 7.0461 | 0.4178 |

Sum of electronic and zero-point Energies= -780.416242
Sum of electronic and thermal Energies= -780.408539
Sum of electronic and thermal Enthalpies= -780.407594
Sum of electronic and thermal Free Energies= -780.449561

HF = -780.513319086

## TS: $F^-$ transfer from $F_2SiMe_3^-$ to $SO_2$

| Element | X | Y | Z |
|---|---|---|---|
| Si | 2.32052207 | -1.77358401 | 0.14601301 |
| C | 1.34828699 | -0.17533900 | -0.13734201 |
| H | 1.40064895 | 0.49458000 | 0.72527897 |
| H | 1.72683501 | 0.34885001 | -1.01861596 |
| H | 0.29424801 | -0.39854899 | -0.33346301 |
| C | 4.13026905 | -1.86145496 | -0.40524000 |
| H | 4.32626677 | -2.79620910 | -0.93846601 |
| H | 4.35517883 | -1.04716599 | -1.10121405 |
| H | 4.82028580 | -1.78877699 | 0.43967199 |
| C | 1.40317297 | -3.37688804 | 0.55555499 |
| H | 2.08672094 | -4.08671999 | 1.03546202 |
| H | 0.60254598 | -3.17686892 | 1.27609897 |
| H | 0.97109699 | -3.85266590 | -0.32474601 |
| F | 1.88766599 | -2.16165805 | -1.83792400 |
| F | 2.68458891 | -1.44054604 | 1.83995295 |
| S | 2.88990402 | -1.14573097 | -3.96170402 |
| O | 2.99821997 | 0.24890199 | -3.51920104 |
| O | 1.77451098 | -1.44354296 | -4.86683702 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -102.8094 | 32.5263 | 49.9668 |
| Red. masses -- | 9.3387 | 7.3313 | 4.6765 |
| Frc consts -- | 0.0582 | 0.0046 | 0.0069 |
| IR Inten -- | 295.6750 | 2.2848 | 0.1591 |

Sum of electronic and zero-point Energies= -1157.865200
Sum of electronic and thermal Energies= -1157.851041
Sum of electronic and thermal Enthalpies= -1157.850097
Sum of electronic and thermal Free Energies= -1157.907687

HF = -1157.98686694

## TS: $F^-$ transfer from $F_2SiMe_3^-$ to allylSiMe$_3$

| Element | X | Y | Z |
|---|---|---|---|
| Si | -3.55786705 | -0.05041500 | -0.01259000 |
| C | -2.87130690 | -1.71875298 | 0.50628197 |
| H | -2.84271097 | -2.40559793 | -0.34630299 |
| H | -1.86511397 | -1.63120306 | 0.90975302 |
| H | -3.52301192 | -2.16851807 | 1.26300597 |
| C | -3.20383596 | 0.55962402 | -1.75205696 |

| | | | |
|---|---|---|---|
| H | -2.18458891 | 0.92609102 | -1.84848297 |
| H | -3.35621905 | -0.24892101 | -2.47529697 |
| H | -3.89999604 | 1.36385703 | -2.01413608 |
| C | -3.75439310 | 1.23818302 | 1.33635497 |
| H | -2.78732610 | 1.63759899 | 1.63679194 |
| H | -4.38573694 | 2.06288910 | 0.98839098 |
| H | -4.24583387 | 0.79919797 | 2.21143293 |
| F | -5.19817209 | -0.48835000 | -0.22196600 |
| F | -1.15105796 | 0.61834502 | 0.28189400 |
| Si | 0.79664600 | 0.20039500 | 0.04211400 |
| C | 2.77780604 | -0.21844600 | -0.16625001 |
| C | 0.70364702 | -0.63945401 | 1.75672901 |
| H | -0.17305200 | -0.32668301 | 2.32522702 |
| H | 0.64587700 | -1.72786903 | 1.62935495 |
| H | 1.60181403 | -0.44119000 | 2.35182691 |
| C | 0.25114900 | -0.80280697 | -1.49038398 |
| H | 0.30214500 | -0.17031699 | -2.38493896 |
| H | 0.91040897 | -1.65903294 | -1.66957903 |
| H | -0.77455002 | -1.16010797 | -1.40541101 |
| C | 0.97995299 | 2.09740305 | -0.05338600 |
| H | 1.99610496 | 2.42067790 | -0.29476699 |
| H | 0.29952699 | 2.51591802 | -0.80087298 |
| H | 0.69464397 | 2.54119110 | 0.90665603 |
| H | 3.30701303 | 0.30118200 | 0.64399201 |
| H | 2.86150002 | -1.29895699 | 0.01864600 |
| C | 3.35461402 | 0.12530001 | -1.48207402 |
| C | 4.14080000 | 1.17214406 | -1.78380096 |
| H | 4.45557404 | 1.37850499 | -2.80303788 |
| H | 4.48757219 | 1.86351705 | -1.01828206 |
| H | 3.05212307 | -0.51954699 | -2.30995488 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -97.2073 | 31.5560 | 43.0801 |
| Red. masses -- | 8.4256 | 2.8026 | 3.7532 |
| Frc consts -- | 0.0469 | 0.0016 | 0.0041 |
| IR Inten -- | 258.6122 | 0.0956 | 0.7071 |

Sum of electronic and zero-point Energies= -1135.665281
Sum of electronic and thermal Energies= -1135.643193
Sum of electronic and thermal Enthalpies= -1135.642249
Sum of electronic and thermal Free Energies= -1135.715890

HF = -1135.96154511

## TS: $F^-$ transfer from $F_2SiMe_3^-$ to $PhSiMe_3$

| Element | X | Y | Z |
|---|---|---|---|
| Si | -3.61382389 | -0.16883400 | 0.06591000 |
| C | -2.67241001 | -1.73846197 | 0.47383499 |
| H | -2.65986991 | -2.41322708 | -0.38836500 |
| H | -1.64445400 | -1.52678299 | 0.75610900 |
| H | -3.16829991 | -2.26633906 | 1.29549205 |
| C | -3.47769094 | 0.52296901 | -1.67221296 |
| H | -2.57541299 | 1.12108600 | -1.78287995 |
| H | -3.45275688 | -0.28628999 | -2.40968204 |

| | | | |
|---|---|---|---|
| H | -4.35088015 | 1.14440000 | -1.89847803 |
| C | -3.80869198 | 1.08262098 | 1.44777906 |
| H | -2.89393806 | 1.66055703 | 1.57094896 |
| H | -4.63687897 | 1.76608300 | 1.23182094 |
| H | -4.03742886 | 0.57983702 | 2.39366293 |
| F | -5.19691706 | -0.79982901 | -0.00065700 |
| F | -1.21404600 | 0.80555099 | 0.14246801 |
| Si | 0.75219798 | 0.38859701 | -0.04817300 |
| C | 2.72118497 | -0.02007200 | -0.10663700 |
| C | 5.01421785 | 0.59855700 | 0.55372101 |
| C | 4.64105797 | -1.49180806 | -0.57233500 |
| C | 5.52274895 | -0.58777899 | 0.01971100 |
| H | 5.68608904 | 1.31464303 | 1.02127802 |
| H | 5.01870298 | -2.42140603 | -0.99203998 |
| H | 6.58669376 | -0.80251801 | 0.06540600 |
| C | 0.64352500 | -0.17618300 | 1.77949095 |
| H | -0.33987501 | -0.01790000 | 2.22345805 |
| H | 0.89253700 | -1.24218798 | 1.85067701 |
| H | 1.39257801 | 0.35113499 | 2.38102889 |
| C | 0.23405600 | -0.79005897 | -1.45779204 |
| H | 0.91964501 | -0.71637702 | -2.30882502 |
| H | 0.25142500 | -1.83450496 | -1.12601805 |
| H | -0.77731699 | -0.57603902 | -1.79985404 |
| C | 0.88949603 | 2.24504209 | -0.48306400 |
| H | 1.84484696 | 2.51734805 | -0.93999100 |
| C | 3.64471507 | 0.86391503 | 0.48713800 |
| H | 3.28632593 | 1.79797399 | 0.91725200 |
| H | 0.08108400 | 2.52040005 | -1.16429496 |
| H | 0.75985801 | 2.85967493 | 0.41543600 |
| C | 3.27229190 | -1.20551300 | -0.62804300 |
| H | 2.62205195 | -1.93970597 | -1.09678304 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -88.7008 | 30.2314 | 34.8347 |
| Red. masses -- | 8.0137 | 3.6640 | 4.6599 |
| Frc consts -- | 0.0371 | 0.0020 | 0.0033 |
| IR Inten -- | 213.6639 | 0.0130 | 2.2142 |

Sum of electronic and zero-point Energies= -1250.012179
Sum of electronic and thermal Energies= -1249.989102
Sum of electronic and thermal Enthalpies= -1249.988158
Sum of electronic and thermal Free Energies= -1250.064735

HF = -1250.32882891

## TS: $F^-$ transfer from $FSO_2^-$ to $PhSiMe_3$

| Element | X | Y | Z |
|---|---|---|---|
| C | -0.60013998 | -0.36954600 | 0.00720400 |
| C | -1.50818598 | -0.40142101 | 1.08185506 |
| C | -1.71569502 | -2.40308595 | -0.82504803 |
| C | -2.49302912 | -1.38715601 | 1.20998704 |
| H | -1.45443404 | 0.36232799 | 1.85385001 |
| C | -2.60380507 | -2.39562702 | 0.25286800 |
| H | -1.78471100 | -3.18359089 | -1.57919300 |

| | | | |
|---|---|---|---|
| H | -3.17331195 | -1.36763501 | 2.05828094 |
| H | -3.36684108 | -3.16334605 | 0.34502301 |
| Si | 0.91304898 | 0.94285601 | -0.15049300 |
| C | 0.15188700 | 2.31272507 | 0.94383001 |
| H | 0.30750501 | 2.09763598 | 2.00779700 |
| H | 0.61470002 | 3.27860308 | 0.73806399 |
| H | -0.92828602 | 2.40066910 | 0.78984201 |
| C | 0.81287998 | 1.20453203 | -2.04300809 |
| H | -0.11682200 | 0.84354198 | -2.48996401 |
| H | 0.91527402 | 2.26958299 | -2.26737499 |
| H | 1.64666998 | 0.69986498 | -2.54412889 |
| C | 2.14984202 | -0.32880500 | 0.57491899 |
| H | 3.18023491 | 0.02894800 | 0.60045898 |
| H | 1.84689403 | -0.60072702 | 1.59333301 |
| H | 2.11331105 | -1.25462306 | -0.01067100 |
| S | 4.49133301 | 2.87962508 | -1.71253598 |
| O | 5.24909592 | 3.58685589 | -0.67414403 |
| F | 2.48578906 | 2.15337110 | -0.27438799 |
| O | 4.98429108 | 1.54396403 | -2.06655407 |
| C | -0.74012399 | -1.40951896 | -0.93342900 |
| H | -0.06343700 | -1.45252800 | -1.78537703 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -66.5330 | 39.6955 | 43.0729 |
| Red. masses -- | 10.1570 | 8.5604 | 7.9235 |
| Frc consts -- | 0.0265 | 0.0079 | 0.0087 |
| IR Inten -- | 268.3546 | 3.6007 | 1.7901 |

Sum of electronic and zero-point Energies= -1289.526077
Sum of electronic and thermal Energies= -1289.508395
Sum of electronic and thermal Enthalpies= -1289.507451
Sum of electronic and thermal Free Energies= -1289.572901

HF = -1289.73602407

## TS: $SO_2$ insertion in allylSiMe$_3$ ($S_E2'$)

| Element | X | Y | Z |
|---|---|---|---|
| C | -0.44593200 | -0.64998502 | 0.55826002 |
| Si | 1.63514698 | -0.25486201 | 0.15521599 |
| C | 1.66282105 | 1.12338996 | 1.45388198 |
| H | 1.02430403 | 1.95529699 | 1.13886404 |
| H | 1.27581501 | 0.76472598 | 2.41247392 |
| H | 2.67232203 | 1.50613499 | 1.60839498 |
| C | 1.34782004 | 0.22279599 | -1.65604699 |
| H | 0.35348099 | 0.64772499 | -1.81660199 |
| H | 2.09020209 | 0.94493300 | -1.99973094 |
| H | 1.43174303 | -0.66468799 | -2.29196095 |
| C | 2.26080394 | -1.97400606 | 0.62623203 |
| H | 2.67387390 | -2.46465993 | -0.25932801 |
| S | -3.48505497 | -2.92207909 | 0.55173600 |
| H | 3.07950807 | -1.88095999 | 1.34414005 |
| H | 1.49074399 | -2.61936212 | 1.05190396 |
| S | 4.94786978 | -0.43309999 | -1.77717900 |
| O | 6.19888115 | -0.42359599 | -0.99949902 |

| | | | |
|---|---|---|---|
| F | 3.61122489 | 0.15526401 | -0.18717000 |
| O | 4.40857077 | -1.77490997 | -2.05752611 |
| H | -0.44441500 | -0.94282597 | 1.60986197 |
| H | -0.85075498 | 0.35113701 | 0.40171599 |
| C | -0.93169802 | -1.63236594 | -0.34246799 |
| H | -1.17924595 | -1.29676294 | -1.34850502 |
| C | -1.14420795 | -2.97071910 | -0.07181000 |
| H | -0.81843299 | -3.39448094 | 0.87361801 |
| H | -1.30193496 | -3.67460203 | -0.88234800 |
| O | -4.14740276 | -2.33828998 | -0.64719099 |
| O | -3.68627906 | -4.39161301 | 0.69458598 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -226.9814 | 23.3071 | 26.5453 |
| Red. masses -- | 11.3253 | 11.9835 | 8.8847 |
| Frc consts -- | 0.3438 | 0.0038 | 0.0037 |
| IR Inten -- | 2716.2545 | 2.9755 | 6.8961 |

Sum of electronic and zero-point Energies= -1723.866465
Sum of electronic and thermal Energies= -1723.845478
Sum of electronic and thermal Enthalpies= -1723.844534
Sum of electronic and thermal Free Energies= -1723.919877

HF = -1724.06542740

## TS: $SO_2$ insertion in allylSiMe$_3$ ($S_E2$)

| Element | X | Y | Z |
|---|---|---|---|
| C | -0.36277801 | -0.52551401 | 0.59381300 |
| Si | 1.82117701 | -0.24270099 | 0.15784299 |
| C | 1.84642196 | 1.18696904 | 1.40548694 |
| H | 2.86688399 | 1.49508595 | 1.63973999 |
| H | 1.31726205 | 2.05412507 | 0.99565500 |
| H | 1.34143198 | 0.91605198 | 2.33690596 |
| C | 1.46097803 | 0.13376100 | -1.66734505 |
| H | 0.52062398 | 0.67407298 | -1.80035305 |
| H | 2.26394105 | 0.72446299 | -2.11357403 |
| H | 1.38071597 | -0.80076301 | -2.23217607 |
| C | 2.25873303 | -1.99459100 | 0.72276098 |
| H | 2.85036111 | -1.93396103 | 1.64271700 |
| S | -2.82948089 | -0.08113700 | 1.71247494 |
| O | -3.57588696 | 0.55282700 | 0.60066801 |
| O | -2.59364796 | 0.80381101 | 2.87901402 |
| H | 1.39303195 | -2.63123202 | 0.90581399 |
| H | 2.89051104 | -2.47218108 | -0.03046100 |
| S | 5.08544588 | -0.70303798 | -1.79836702 |
| O | 6.33875513 | -0.54769999 | -1.04753101 |
| F | 3.68737292 | 0.03439400 | -0.17221200 |
| O | 4.58815289 | -2.08128095 | -1.91125202 |
| H | -0.26824099 | -0.81175703 | 1.63958204 |
| H | -0.61963600 | 0.51878202 | 0.43058199 |
| C | -0.94785702 | -1.49958003 | -0.31424001 |
| H | -1.16276598 | -1.13547301 | -1.31812000 |
| C | -1.21768999 | -2.79135203 | -0.04805200 |
| H | -1.04100895 | -3.22071910 | 0.93519503 |

| | | | |
|---|---|---|---|
| H | -1.61108398 | -3.45807910 | -0.80837798 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -247.0341 | 22.0915 | 26.9192 |
| Red. masses -- | 10.6069 | 7.7820 | 7.4194 |
| Frc consts -- | 0.3814 | 0.0022 | 0.0032 |
| IR Inten -- | 2949.4755 | 3.6137 | 2.9784 |

Sum of electronic and zero-point Energies= -1723.858783
Sum of electronic and thermal Energies= -1723.837326
Sum of electronic and thermal Enthalpies= -1723.836382
Sum of electronic and thermal Free Energies= -1723.912929

HF = -1724.05669580

## TS: $SO_2$ insertion in $PhSiMe_3$

| Element | X | Y | Z |
|---|---|---|---|
| C | -0.52568001 | -0.33981401 | 0.00310200 |
| C | -1.05511105 | -0.70589399 | 1.25342703 |
| C | -1.99081004 | -2.02473593 | -1.00549901 |
| C | -2.00485206 | -1.71550298 | 1.38921702 |
| H | -0.72756797 | -0.18159799 | 2.14707208 |
| C | -2.47482896 | -2.38230610 | 0.25512800 |
| H | -2.35780907 | -2.53272295 | -1.89294696 |
| H | -2.38572311 | -1.97875702 | 2.37204790 |
| H | -3.22075295 | -3.16535306 | 0.35190099 |
| Si | 1.71234500 | -0.02264300 | -0.09442400 |
| C | 1.81163204 | 1.05217898 | 1.46181095 |
| H | 2.45150089 | 0.54155999 | 2.18797803 |
| H | 2.30280495 | 1.99863899 | 1.21970606 |
| H | 0.86213702 | 1.27879500 | 1.94408906 |
| C | 1.67990804 | 0.72849101 | -1.83392298 |
| H | 0.69479102 | 0.91004801 | -2.26234508 |
| H | 2.22689295 | 1.67517805 | -1.82583106 |
| H | 2.22543693 | 0.05479400 | -2.50091100 |
| C | 1.89044201 | -1.90181506 | 0.09190900 |
| H | 2.93003893 | -2.18489289 | 0.26509100 |
| S | -0.87594700 | 2.07133198 | -0.20513400 |
| O | -1.44246900 | 2.37157798 | 1.13683605 |
| O | -1.88370502 | 2.07876301 | -1.29869294 |
| H | 1.27812898 | -2.28052998 | 0.91317600 |
| H | 1.54526603 | -2.39956093 | -0.81905800 |
| S | 5.24794197 | -0.86956197 | -1.39057302 |
| O | 5.63537121 | -1.87872398 | -0.39543200 |
| F | 3.62304497 | 0.14952300 | -0.18670200 |
| O | 4.43024302 | -1.37093902 | -2.50383711 |
| C | -1.04032302 | -1.01316297 | -1.12133002 |
| H | -0.68869102 | -0.74902701 | -2.11456990 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -223.9299 | 23.1763 | 29.8522 |
| Red. masses -- | 7.9496 | 9.9111 | 12.6123 |

| | | | |
|---|---|---|---|
| Frc consts -- | 0.2349 | 0.0031 | 0.0066 |
| IR Inten -- | 990.9600 | 7.7003 | 0.6263 |

Sum of electronic and zero-point Energies= -1838.202398
Sum of electronic and thermal Energies= -1838.180390
Sum of electronic and thermal Enthalpies= -1838.179445
Sum of electronic and thermal Free Energies= -1838.256114

HF = -1838.42109766

## TS: $SO_2$ insertion in $PhSiMe_3F^-$

| Element | X | Y | Z |
|---|---|---|---|
| C | 0.40062201 | -0.54039299 | -0.02594100 |
| C | 1.06648803 | -0.77102900 | -1.24608004 |
| C | 2.21353292 | -1.80059099 | 1.05951202 |
| C | 2.25515890 | -1.49468303 | -1.33137095 |
| H | 0.64989197 | -0.36620700 | -2.16530800 |
| C | 2.83762193 | -2.01256204 | -0.17263301 |
| H | 2.65857601 | -2.19722605 | 1.96845198 |
| H | 2.73283505 | -1.64928401 | -2.29543805 |
| H | 3.76905203 | -2.56833506 | -0.22774599 |
| Si | -1.77301097 | -0.29070899 | -0.00711000 |
| C | -1.81496203 | 0.85213500 | -1.53376198 |
| H | -2.41741896 | 0.37343600 | -2.31256795 |
| H | -2.33760500 | 1.77700198 | -1.26874197 |
| H | -0.85437602 | 1.12521505 | -1.96997905 |
| C | -1.81161797 | 0.44428700 | 1.75558496 |
| H | -0.85007203 | 0.71715301 | 2.19270897 |
| H | -2.44969702 | 1.33310199 | 1.75469804 |
| H | -2.28985000 | -0.27564600 | 2.42904902 |
| F | -3.60873699 | -0.21797501 | 0.00497800 |
| C | -1.84267604 | -2.18709111 | -0.24970400 |
| H | -2.87208390 | -2.55000591 | -0.29903799 |
| S | 0.77217400 | 2.07822299 | 0.23774099 |
| O | 1.33625400 | 2.46218300 | -1.07360804 |
| O | 1.73850095 | 2.11998296 | 1.35588706 |
| H | -1.32456398 | -2.47480297 | -1.17007303 |
| H | -1.32787395 | -2.70076108 | 0.56826800 |
| C | 1.02583301 | -1.07438600 | 1.12003899 |
| H | 0.57222801 | -0.92117202 | 2.09630489 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -105.2075 | 23.6674 | 57.0629 |
| Red. masses -- | 5.6578 | 9.3110 | 2.1559 |
| Frc consts -- | 0.0369 | 0.0031 | 0.0041 |
| IR Inten -- | 227.8497 | 3.5019 | 0.2480 |

Sum of electronic and zero-point Energies= -1289.522418
Sum of electronic and thermal Energies= -1289.504951
Sum of electronic and thermal Enthalpies= -1289.504007
Sum of electronic and thermal Free Energies= -1289.568327

HF = -1289.73234055

### *2.2.3. Reductive elimination*

allyl–Pd($PMe_3$)$_2$–Ph

| Element | X | Y | Z |
|---|---|---|---|
| Pd | -1.45955396 | -0.11114700 | 0.14976101 |
| C | 0.60236299 | -0.21547499 | 0.24187499 |
| C | 1.29027200 | -0.14600100 | 1.46661997 |
| C | 1.38933206 | -0.35128900 | -0.91477603 |
| C | 2.68389297 | -0.22495200 | 1.53848100 |
| H | 0.73089302 | -0.03589500 | 2.39292502 |
| C | 2.78440499 | -0.43302500 | -0.85505199 |
| H | 0.91134799 | -0.38755500 | -1.89010298 |
| C | 3.44127893 | -0.37328500 | 0.37481999 |
| H | 3.17906308 | -0.17180000 | 2.50514793 |
| H | 3.35854793 | -0.54004401 | -1.77232695 |
| H | 4.52431011 | -0.43631801 | 0.42559499 |
| C | -1.12036896 | 1.97732699 | -0.03581300 |
| H | -1.82923198 | 2.51419902 | 0.60979301 |
| H | -0.13303401 | 2.22065902 | 0.37334201 |
| C | -1.20149100 | 2.55110407 | -1.41883695 |
| H | -1.08877397 | 3.63945293 | -1.48319304 |
| C | -1.38253701 | 1.89829397 | -2.57028008 |
| H | -1.41330004 | 2.41996193 | -3.52344990 |
| H | -1.49485004 | 0.81763798 | -2.59527802 |
| P | -1.43765402 | -2.50011396 | 0.25686201 |
| P | -3.80464792 | 0.22584800 | -0.08088100 |
| C | -4.49445009 | -0.46073300 | -1.64714706 |
| H | -4.27740479 | -1.52742004 | -1.72195196 |
| H | -5.57583284 | -0.31114101 | -1.70368695 |
| H | -4.02009201 | 0.04186500 | -2.49185705 |
| C | -2.94752002 | -3.52241397 | 0.55078298 |
| H | -3.72476006 | -3.28294706 | -0.17644501 |
| H | -2.71035194 | -4.58637524 | 0.46800101 |
| H | -3.33559990 | -3.33055305 | 1.55253804 |
| C | -0.82413799 | -3.20684505 | -1.32888496 |
| H | 0.15615700 | -2.78402805 | -1.55120897 |
| H | -0.74469101 | -4.29562283 | -1.27155101 |
| H | -1.50663805 | -2.93919897 | -2.13800097 |
| C | -0.28462401 | -3.24075198 | 1.48518097 |
| H | -0.26663399 | -4.32961082 | 1.39121401 |
| H | 0.71693301 | -2.84155607 | 1.32895005 |
| H | -0.60351199 | -2.97452998 | 2.49497700 |
| C | -4.92357302 | -0.48774499 | 1.20037103 |
| H | -5.96782398 | -0.25020400 | 0.98051399 |
| H | -4.81139612 | -1.56976295 | 1.24934804 |
| H | -4.66429186 | -0.07311400 | 2.17648792 |
| C | -4.42535496 | 1.95732105 | -0.14340000 |
| H | -3.90055490 | 2.50480700 | -0.92626703 |
| H | -5.49926805 | 1.97070897 | -0.34549600 |
| H | -4.23939705 | 2.45306396 | 0.81088102 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 23.1467 | 29.8216 | 35.8658 |
| Red. masses -- | 4.1193 | 3.3640 | 3.3807 |

| | | | |
|---|---|---|---|
| Frc consts -- | 0.0013 | 0.0018 | 0.0026 |
| IR Inten -- | 0.0900 | 0.3881 | 0.6840 |

Sum of electronic and zero-point Energies= -1398.971002
Sum of electronic and thermal Energies= -1398.944858
Sum of electronic and thermal Enthalpies= -1398.943914
Sum of electronic and thermal Free Energies= -1399.027675

HF = -1399.35969134

## TS: reductive elimination from allyl–Pd($PMe_3$)$_2$–Ph to allylPh

| Element | X | Y | Z |
|---|---|---|---|
| C | -3.96363711 | 0.13088199 | -0.44205701 |
| C | -2.62624907 | -0.09306700 | -0.74511403 |
| C | -1.61816597 | 0.84085101 | -0.39019099 |
| C | -2.03696704 | 1.97363102 | 0.34824401 |
| C | -3.37875295 | 2.19208407 | 0.65042001 |
| C | -4.36028814 | 1.27945495 | 0.25471199 |
| H | -4.70914698 | -0.59580600 | -0.75572997 |
| H | -2.34902692 | -0.99685401 | -1.27999699 |
| H | -1.29594803 | 2.69567609 | 0.67962098 |
| H | -3.66132498 | 3.08630490 | 1.20056403 |
| H | -5.40512705 | 1.44920397 | 0.49362200 |
| Pd | -0.00850500 | 1.11903203 | -1.68959999 |
| P | 2.28312993 | 1.27150702 | -2.41652107 |
| P | -1.32984197 | 1.89987600 | -3.49814010 |
| C | 2.89504409 | 2.94544697 | -2.90211511 |
| H | 3.93895888 | 2.91449404 | -3.22775102 |
| H | 2.28033400 | 3.33512092 | -3.71568608 |
| H | 2.80701399 | 3.62812805 | -2.05449700 |
| C | 2.73417497 | 0.28049499 | -3.90956998 |
| H | 2.10827994 | 0.58269203 | -4.75169992 |
| H | 3.78538799 | 0.41490301 | -4.18093491 |
| H | 2.55002809 | -0.77815902 | -3.71527100 |
| C | 3.59917498 | 0.74092501 | -1.23120499 |
| H | 4.59917593 | 0.83190501 | -1.66521001 |
| H | 3.54664803 | 1.35415995 | -0.32885599 |
| H | 3.43340206 | -0.29912201 | -0.94057697 |
| C | -2.15764403 | 0.53793401 | -4.43028879 |
| H | -2.83671093 | 0.92791498 | -5.19426107 |
| H | -1.40507603 | -0.09191300 | -4.90897989 |
| H | -2.72529697 | -0.07655200 | -3.72880507 |
| C | -0.61241901 | 2.90028811 | -4.87689590 |
| H | 0.19359900 | 2.34156990 | -5.35741806 |
| H | -1.36614799 | 3.15032506 | -5.62955379 |
| H | -0.19325501 | 3.82584405 | -4.47647190 |
| C | -2.77740502 | 2.92957091 | -3.00589800 |
| H | -3.35673094 | 2.39165401 | -2.25436902 |
| H | -2.42855692 | 3.86175609 | -2.55708599 |
| H | -3.41346312 | 3.16146708 | -3.86505294 |
| C | 0.02691400 | 0.11056200 | 0.42865500 |
| H | 0.80830401 | -0.44248801 | -0.10515600 |
| H | 0.47690600 | 0.93577302 | 0.98133099 |
| C | -0.66166300 | -0.83915699 | 1.33540106 |
| C | -0.89996099 | -0.63836002 | 2.63541102 |
| H | -0.99696702 | -1.76860797 | 0.87805599 |
| H | -1.40994596 | -1.38082504 | 3.24102592 |

| | | | |
|---|---|---|---|
| H | -0.59876299 | 0.27920201 | 3.13457894 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -401.2722 | 22.3188 | 28.9055 |
| Red. masses -- | 5.2527 | 3.4058 | 3.3999 |
| Frc consts -- | 0.4983 | 0.0010 | 0.0017 |
| IR Inten -- | 158.9664 | 0.4133 | 0.0567 |

Sum of electronic and zero-point Energies= -1398.933307
Sum of electronic and thermal Energies= -1398.907108
Sum of electronic and thermal Enthalpies= -1398.906164
Sum of electronic and thermal Free Energies= -1398.990701

HF = -1399.31988685

## allyl$SO_2$–Pd($PMe_3$)$_2$–Ph

| Element | X | Y | Z |
|---|---|---|---|
| Pd | -1.89008498 | -1.23164201 | 0.06765000 |
| C | 0.14401700 | -1.07490504 | 0.31515500 |
| C | 0.71887702 | -1.18243802 | 1.58749294 |
| C | 0.98483801 | -0.79597002 | -0.76952398 |
| C | 2.09258008 | -1.00197995 | 1.77410495 |
| H | 0.09474900 | -1.39365995 | 2.45142293 |
| C | 2.35807610 | -0.61396098 | -0.58859003 |
| H | 0.57153797 | -0.70775902 | -1.77078295 |
| C | 2.91773200 | -0.71515203 | 0.68590403 |
| H | 2.51596498 | -1.08160806 | 2.77150011 |
| H | 2.98987508 | -0.38986099 | -1.44367194 |
| H | 3.98416495 | -0.57167101 | 0.82929701 |
| P | -1.49775100 | -3.49136305 | -0.38137099 |
| P | -4.30147791 | -1.24836004 | -0.28351101 |
| C | -5.28120422 | -2.80895209 | -0.23998800 |
| H | -5.27986479 | -3.21841311 | 0.77141398 |
| H | -6.31512308 | -2.59787107 | -0.52358598 |
| H | -4.88390589 | -3.55856991 | -0.92351198 |
| C | -2.31830096 | -4.65179920 | 0.78154600 |
| H | -3.39557600 | -4.50269222 | 0.78779000 |
| H | -2.10151696 | -5.68478823 | 0.49898201 |
| H | -1.93935394 | -4.47083712 | 1.78879595 |
| C | -2.05499506 | -4.02132988 | -2.05052495 |
| H | -1.49504006 | -3.46379089 | -2.80324197 |
| H | -1.87580502 | -5.08989620 | -2.19163704 |
| H | -3.11486912 | -3.81603909 | -2.19456601 |
| C | 0.23094000 | -4.10271692 | -0.35194400 |
| H | 0.24287000 | -5.17399216 | -0.56673700 |
| H | 0.82812297 | -3.57284093 | -1.09297097 |
| H | 0.67122602 | -3.91971493 | 0.62783903 |
| C | -5.28753710 | -0.20419399 | 0.86208302 |
| H | -6.34608221 | -0.25393501 | 0.59398001 |
| H | -5.15774012 | -0.55807102 | 1.88586998 |
| H | -4.94121408 | 0.82522702 | 0.80386698 |
| C | -4.69796515 | -0.55527300 | -1.93647599 |
| H | -4.25412893 | -1.17422795 | -2.71843505 |
| H | -5.77888584 | -0.50214100 | -2.08955193 |

| | | | |
|---|---|---|---|
| H | -4.26779890 | 0.44504899 | -1.98698401 |
| S | -2.04408908 | 1.10745800 | 0.58699399 |
| C | -0.41709200 | 2.01660490 | 0.45486799 |
| H | -0.08081100 | 1.87891304 | -0.57280600 |
| H | 0.25363499 | 1.48106098 | 1.12689900 |
| C | -0.58400100 | 3.44544005 | 0.83171499 |
| H | -0.84149200 | 3.63575912 | 1.87043798 |
| C | -0.45345101 | 4.46520376 | -0.01669900 |
| H | -0.20629101 | 4.30940199 | -1.06337595 |
| H | -0.58513701 | 5.49300909 | 0.30640700 |
| O | -2.94285607 | 1.81746197 | -0.40003899 |
| O | -2.44804692 | 1.29139698 | 2.03141689 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 26.3423 | 38.1403 | 44.3951 |
| Red. masses -- | 4.4319 | 3.8383 | 3.1741 |
| Frc consts -- | 0.0018 | 0.0033 | 0.0037 |
| IR Inten -- | 0.6694 | 4.8445 | 0.6704 |

Sum of electronic and zero-point Energies= -1947.687052
Sum of electronic and thermal Energies= -1947.657824
Sum of electronic and thermal Enthalpies= -1947.656880
Sum of electronic and thermal Free Energies= -1947.746606

HF = -1948.08849329

## TS: reductive elimination from allyl$SO_2$–Pd($PMe_3$)$_2$–Ph to allyl$SO_2$Ph

| Element | X | Y | Z |
|---|---|---|---|
| C | -3.77048492 | 0.37590900 | -0.18020400 |
| C | -2.42296696 | 0.07101200 | -0.33419499 |
| C | -1.47251701 | 1.10915399 | -0.40086901 |
| C | -1.88308597 | 2.43926001 | -0.18402401 |
| C | -3.23670697 | 2.72966194 | -0.03458600 |
| C | -4.18568277 | 1.70446599 | -0.03647800 |
| H | -4.50226212 | -0.42599499 | -0.17096400 |
| H | -2.09739709 | -0.95894301 | -0.43136999 |
| H | -1.14192998 | 3.23033500 | -0.14102399 |
| H | -3.55038500 | 3.76063490 | 0.09601700 |
| H | -5.23747396 | 1.93489397 | 0.09374800 |
| Pd | 0.00391200 | 1.03590298 | -1.98599303 |
| P | 2.34429193 | 1.39709198 | -2.37310195 |
| P | -1.53995299 | 0.83306003 | -3.75586390 |
| C | 3.51800799 | 0.22674100 | -1.56685197 |
| H | 4.55686903 | 0.51083797 | -1.75899506 |
| H | 3.32968211 | 0.22149099 | -0.49317199 |
| H | 3.34545588 | -0.78292900 | -1.94449401 |
| C | 2.97262001 | 3.02493596 | -1.77807701 |
| H | 2.76208210 | 3.10093999 | -0.71096998 |
| H | 4.04803085 | 3.12628698 | -1.95189095 |
| H | 2.44962406 | 3.83284307 | -2.29406595 |
| C | 2.94034195 | 1.37640202 | -4.12093782 |
| H | 4.01389122 | 1.57885301 | -4.18040895 |
| H | 2.73703790 | 0.39965001 | -4.56463718 |
| H | 2.40273499 | 2.13006806 | -4.69977283 |

| | | | |
|---|---|---|---|
| C | -2.39586401 | -0.79598302 | -3.89270806 |
| H | -3.11677289 | -0.79923201 | -4.71541977 |
| H | -1.65976202 | -1.58483303 | -4.05901194 |
| H | -2.92024708 | -1.00757396 | -2.95932102 |
| C | -0.90783298 | 1.06047595 | -5.47540522 |
| H | -0.11627100 | 0.33431199 | -5.67106724 |
| H | -1.70155203 | 0.93335599 | -6.21768904 |
| H | -0.48195601 | 2.06078601 | -5.57664585 |
| C | -2.97196603 | 1.99462795 | -3.72100592 |
| H | -3.51777411 | 1.86293304 | -2.78609395 |
| H | -2.61031294 | 3.02397895 | -3.75928092 |
| H | -3.64776111 | 1.82060003 | -4.56348801 |
| S | 0.26318201 | 0.67935598 | 0.64525402 |
| O | 1.20711303 | 1.81807005 | 0.86716598 |
| O | 0.80174500 | -0.69571102 | 0.42579499 |
| C | -0.63241100 | 0.55689502 | 2.28795695 |
| H | -1.18384004 | 1.49440205 | 2.37120891 |
| H | -1.32908404 | -0.27399799 | 2.18352890 |
| C | 0.34850001 | 0.36398000 | 3.38944101 |
| C | 0.50162601 | -0.78122401 | 4.05444908 |
| H | 0.97405899 | 1.21970201 | 3.62776995 |
| H | 1.23273695 | -0.88098902 | 4.85007286 |
| H | -0.10129000 | -1.65689695 | 3.83087397 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -242.4457 | 20.5945 | 23.0018 |
| Red. masses -- | 8.9700 | 4.5777 | 3.1356 |
| Frc consts -- | 0.3107 | 0.0011 | 0.0010 |
| IR Inten -- | 242.4618 | 0.0639 | 1.3092 |

Sum of electronic and zero-point Energies= -1947.625106
Sum of electronic and thermal Energies= -1947.595348
Sum of electronic and thermal Enthalpies= -1947.594404
Sum of electronic and thermal Free Energies= -1947.687441

HF = -1948.02304827

## allyl$SO_2$–Pd($PMe_3$)$_2$–($C_6H_4$)$CF_3$

| Element | X | Y | Z |
|---|---|---|---|
| Pd | -1.88749802 | -1.30296195 | -0.00416400 |
| C | 0.15903600 | -1.21579504 | 0.11414100 |
| C | 0.81580198 | -1.40520406 | 1.33765697 |
| C | 0.93787301 | -0.91234499 | -1.01104605 |
| C | 2.20062208 | -1.28550804 | 1.44147599 |
| H | 0.24609400 | -1.63381100 | 2.23307395 |
| C | 2.32228589 | -0.78862602 | -0.92157501 |
| H | 0.46503201 | -0.75745201 | -1.97617495 |
| C | 2.95537090 | -0.97199398 | 0.30950499 |
| H | 2.68823695 | -1.42515302 | 2.40003109 |
| H | 2.90486097 | -0.54231697 | -1.80258703 |
| P | -1.60563099 | -3.55368805 | -0.57664901 |
| P | -4.31255388 | -1.23794401 | -0.20353800 |
| C | -5.33396292 | -2.77122211 | -0.17111699 |
| H | -5.28306723 | -3.22845006 | 0.81826800 |

| | | | |
|---|---|---|---|
| H | -6.37596893 | -2.51542807 | -0.37759200 |
| H | -5.00620985 | -3.49841189 | -0.91291797 |
| C | -2.37040091 | -4.72750711 | 0.60938799 |
| H | -3.43866301 | -4.54713202 | 0.70493102 |
| H | -2.20891094 | -5.75642920 | 0.27972800 |
| H | -1.90838003 | -4.59045696 | 1.58845603 |
| C | -2.29852605 | -4.00081205 | -2.21851301 |
| H | -1.76081896 | -3.44687009 | -2.99001908 |
| H | -2.18208194 | -5.07167816 | -2.40222597 |
| H | -3.35359406 | -3.74033499 | -2.28655696 |
| C | 0.10145900 | -4.21239901 | -0.70174402 |
| H | 0.06446700 | -5.27210712 | -0.96514601 |
| H | 0.65897399 | -3.66744208 | -1.46246696 |
| H | 0.61843902 | -4.09065723 | 0.24975599 |
| C | -5.19120884 | -0.22536400 | 1.05189705 |
| H | -6.26688623 | -0.24742900 | 0.85969901 |
| H | -4.99468613 | -0.62207800 | 2.04886007 |
| H | -4.83029699 | 0.79968399 | 1.00778699 |
| C | -4.78260517 | -0.45141801 | -1.79339302 |
| H | -4.41139793 | -1.04606903 | -2.62999105 |
| H | -5.86798620 | -0.35311100 | -1.87539101 |
| H | -4.31900597 | 0.53464401 | -1.82253098 |
| S | -1.94403505 | 1.01093996 | 0.63508099 |
| C | -0.30386400 | 1.88390803 | 0.43754500 |
| H | -0.03225300 | 1.77623999 | -0.61268097 |
| H | 0.39097500 | 1.31028104 | 1.05126500 |
| C | -0.41187099 | 3.30212903 | 0.87242299 |
| H | -0.59555900 | 3.46201205 | 1.93166399 |
| C | -0.31530401 | 4.34653711 | 0.05009400 |
| H | -0.14185500 | 4.22086287 | -1.01523900 |
| H | -0.40164000 | 5.36532307 | 0.41418499 |
| O | -2.88381004 | 1.78857100 | -0.25600401 |
| O | -2.24580193 | 1.12976599 | 2.10966706 |
| C | 4.44660616 | -0.89537901 | 0.40128499 |
| F | 5.04387999 | -2.10327196 | 0.16831900 |
| F | 4.87837887 | -0.49954501 | 1.62426698 |
| F | 4.98474216 | -0.03770000 | -0.50149000 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 14.1901 | 21.2633 | 24.2111 |
| Red. masses -- | 17.1081 | 4.4185 | 8.0479 |
| Frc consts -- | 0.0020 | 0.0012 | 0.0028 |
| IR Inten -- | 0.5034 | 0.1747 | 1.6999 |

Sum of electronic and zero-point Energies= -2284.842877
Sum of electronic and thermal Energies= -2284.809878
Sum of electronic and thermal Enthalpies= -2284.808934
Sum of electronic and thermal Free Energies= -2284.909110

HF = -2285.24844083

## TS: reductive elimination from allyl$SO_2$–Pd($PMe_3$)$_2$–($C_6H_4$)$CF_3$ to allyl$SO_2$($C_6H_4$)$CF_3$

| Element | X | Y | Z |
|---|---|---|---|
| C | -3.75109696 | 0.04012200 | -0.41251299 |

| | | | |
|---|---|---|---|
| C | -2.38201594 | -0.12954400 | -0.51991397 |
| C | -1.52335501 | 0.99583101 | -0.58015102 |
| C | -2.07974505 | 2.28220296 | -0.37683299 |
| C | -3.45241189 | 2.44293308 | -0.27152199 |
| C | -4.29739904 | 1.32731795 | -0.30357200 |
| H | -4.40171003 | -0.82735300 | -0.41921899 |
| H | -1.96022499 | -1.12540197 | -0.59475303 |
| H | -1.42607296 | 3.14551806 | -0.32056999 |
| H | -3.86942101 | 3.43766809 | -0.16363899 |
| Pd | -0.00001100 | 1.02630603 | -2.08119893 |
| P | 2.36915398 | 1.40946400 | -2.39628911 |
| P | -1.47832596 | 0.77086502 | -3.88145208 |
| C | 3.50274396 | 0.23059900 | -1.54767096 |
| H | 4.54899979 | 0.52017999 | -1.68147802 |
| H | 3.25863504 | 0.20495901 | -0.48549700 |
| H | 3.35349011 | -0.77299500 | -1.95081902 |
| C | 2.96610498 | 3.03534508 | -1.76769197 |
| H | 2.70746803 | 3.11013007 | -0.71093702 |
| H | 4.04781103 | 3.13895202 | -1.89267600 |
| H | 2.46534991 | 3.84363198 | -2.30464602 |
| C | 3.02769709 | 1.39486694 | -4.12012386 |
| H | 4.10200214 | 1.60008204 | -4.13802481 |
| H | 2.84431195 | 0.41855201 | -4.57320118 |
| H | 2.51029110 | 2.14885712 | -4.71645021 |
| C | -2.21537495 | -0.90743297 | -4.07064819 |
| H | -2.91373897 | -0.93978399 | -4.91153479 |
| H | -1.42250001 | -1.63945699 | -4.23474789 |
| H | -2.74766207 | -1.17538202 | -3.15655589 |
| C | -0.77463400 | 1.06922400 | -5.55956507 |
| H | 0.07339800 | 0.40138900 | -5.72242594 |
| H | -1.51959205 | 0.90008700 | -6.34250689 |
| H | -0.41452599 | 2.09774494 | -5.62516594 |
| C | -2.97657609 | 1.84243298 | -3.88898897 |
| H | -3.57384396 | 1.63719106 | -3.00025892 |
| H | -2.67914295 | 2.89224505 | -3.86303401 |
| H | -3.58431101 | 1.66332304 | -4.78033209 |
| S | 0.13994800 | 0.73148298 | 0.61908901 |
| O | 0.98731399 | 1.94525504 | 0.80907899 |
| O | 0.79215002 | -0.59724599 | 0.45286500 |
| C | -0.82832098 | 0.60048097 | 2.21442890 |
| H | -1.44448400 | 1.50021505 | 2.23787808 |
| H | -1.46106398 | -0.27922699 | 2.10246110 |
| C | 0.10992100 | 0.50791502 | 3.36556005 |
| C | 0.32548901 | -0.61245102 | 4.05489588 |
| H | 0.64822000 | 1.41669405 | 3.61966491 |
| H | 1.02168202 | -0.63989800 | 4.88663006 |
| H | -0.19009900 | -1.53847301 | 3.81673694 |
| C | -5.77027321 | 1.49471200 | -0.13436501 |
| F | -6.48218679 | 0.55831802 | -0.81377703 |
| F | -6.16903591 | 1.38525605 | 1.17002797 |
| F | -6.21211910 | 2.70599890 | -0.55496401 |

==========

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -221.9987 | 13.3125 | 17.3272 |
| Red. masses -- | 10.2004 | 5.1141 | 17.1033 |
| Frc consts -- | 0.2962 | 0.0005 | 0.0030 |

IR Inten -- 218.0250 0.1058 0.0405

Sum of electronic and zero-point Energies= -2284.780441
Sum of electronic and thermal Energies= -2284.746897
Sum of electronic and thermal Enthalpies= -2284.745953
Sum of electronic and thermal Free Energies= -2284.849389

HF = -2285.18241921

## allyl$SO_2$–Pd($PMe_3$)$_2$–($C_6H_4$)$NMe_2$

| Element | X | Y | Z |
|---|---|---|---|
| Pd | -1.92783499 | -1.30543900 | 0.06100000 |
| C | 0.11074800 | -1.22501898 | 0.30954400 |
| C | 0.69212198 | -1.33913302 | 1.57468796 |
| C | 0.97275800 | -0.96758002 | -0.75946301 |
| C | 2.06553602 | -1.18915904 | 1.77429295 |
| H | 0.07042500 | -1.52577806 | 2.44651294 |
| C | 2.34773493 | -0.81397802 | -0.58219898 |
| H | 0.57719201 | -0.86248499 | -1.76675701 |
| C | 2.93728900 | -0.93088299 | 0.69491899 |
| H | 2.44707990 | -1.27158201 | 2.78407502 |
| H | 2.95495605 | -0.59867001 | -1.45232499 |
| P | -1.61020803 | -3.56889892 | -0.40734801 |
| P | -4.33761311 | -1.22485304 | -0.29101101 |
| C | -5.37700176 | -2.74713302 | -0.26533699 |
| H | -5.38737106 | -3.17076993 | 0.74023002 |
| H | -6.40326691 | -2.49415588 | -0.54247898 |
| H | -5.00968695 | -3.50147891 | -0.96058702 |
| C | -2.47558808 | -4.71065712 | 0.74246001 |
| H | -3.54752493 | -4.52612305 | 0.74305099 |
| H | -2.29113412 | -5.74854898 | 0.45486799 |
| H | -2.09745598 | -4.54854918 | 1.75327504 |
| C | -2.18216491 | -4.06519079 | -2.08245802 |
| H | -1.59120500 | -3.53183699 | -2.82904506 |
| H | -2.05450797 | -5.14052820 | -2.22858000 |
| H | -3.22983408 | -3.80726910 | -2.23156500 |
| C | 0.09531900 | -4.24190807 | -0.37801200 |
| H | 0.07155100 | -5.31070089 | -0.60454899 |
| H | 0.71405900 | -3.72377992 | -1.10953903 |
| H | 0.53661299 | -4.08322906 | 0.60554498 |
| C | -5.28662491 | -0.15183800 | 0.86012602 |
| H | -6.34578991 | -0.15813100 | 0.58961302 |
| H | -5.17327213 | -0.51650798 | 1.88213301 |
| H | -4.89950514 | 0.86347300 | 0.80816299 |
| C | -4.70433092 | -0.50028998 | -1.93761897 |
| H | -4.27917480 | -1.12554204 | -2.72495294 |
| H | -5.78203917 | -0.40664500 | -2.09432697 |
| H | -4.23844290 | 0.48457599 | -1.97463596 |
| S | -1.98411703 | 1.03205705 | 0.60731101 |
| C | -0.32397601 | 1.87774003 | 0.45705801 |
| H | -0.00662400 | 1.72810698 | -0.57493198 |
| H | 0.33384600 | 1.31380999 | 1.11859298 |
| C | -0.42967701 | 3.31163406 | 0.83643597 |
| H | -0.66823399 | 3.51139402 | 1.87800300 |
| C | -0.26770699 | 4.32686377 | -0.01226700 |
| H | -0.03828700 | 4.16277409 | -1.06175196 |

| | | | |
|---|---|---|---|
| H | -0.35520399 | 5.35869789 | 0.31310999 |
| O | -2.87012291 | 1.79033899 | -0.35634100 |
| O | -2.35805011 | 1.21662796 | 2.06079602 |
| N | 4.31998920 | -0.81587797 | 0.87817103 |
| C | 4.81406498 | -0.59966099 | 2.23150492 |
| C | 5.10058880 | -0.19971099 | -0.18648399 |
| H | 6.14868116 | -0.17116100 | 0.10841300 |
| H | 5.04018021 | -0.78465998 | -1.10672402 |
| H | 4.77559280 | 0.82749498 | -0.41149399 |
| H | 5.90058279 | -0.52681601 | 2.20853806 |
| H | 4.41434717 | 0.31832200 | 2.68852401 |
| H | 4.56072187 | -1.44055498 | 2.88053012 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 22.8449 | 25.8910 | 38.0057 |
| Red. masses -- | 4.0059 | 4.5356 | 3.0980 |
| Frc consts -- | 0.0012 | 0.0018 | 0.0026 |
| IR Inten -- | 0.6084 | 2.1642 | 2.3181 |

Sum of electronic and zero-point Energies= -2081.619571
Sum of electronic and thermal Energies= -2081.586064
Sum of electronic and thermal Enthalpies= -2081.585120
Sum of electronic and thermal Free Energies= -2081.684641

HF = -2082.09401290

## TS: reductive elimination from allyl$SO_2$–Pd($PMe_3$)$_2$–($C_6H_4$)$NMe_2$ to allyl$SO_2$($C_6H_4$)$NMe_2$

| Element | X | Y | Z |
|---|---|---|---|
| C | -3.68787098 | 0.33041799 | 0.01451300 |
| C | -2.33437109 | 0.08574700 | -0.14844500 |
| C | -1.41303504 | 1.14432800 | -0.21378700 |
| C | -1.87864494 | 2.44815111 | 0.02310100 |
| C | -3.23162293 | 2.70149803 | 0.18879300 |
| C | -4.18426085 | 1.65204096 | 0.16055299 |
| H | -4.36308002 | -0.51490402 | 0.02436700 |
| H | -1.98444104 | -0.93615901 | -0.25093001 |
| H | -1.17211103 | 3.27062988 | 0.06839800 |
| H | -3.54521704 | 3.72538400 | 0.34223300 |
| Pd | 0.03953700 | 1.07653296 | -1.84620500 |
| P | 2.34091210 | 1.27016497 | -2.40905309 |
| P | -1.53830099 | 1.00326204 | -3.62848401 |
| C | 3.47720003 | -0.00134900 | -1.70800197 |
| H | 4.52098083 | 0.22034000 | -1.94960105 |
| H | 3.34471798 | -0.03516600 | -0.62665701 |
| H | 3.21748710 | -0.98341602 | -2.10827589 |
| C | 3.13254690 | 2.83327198 | -1.83433104 |
| H | 2.98831391 | 2.90855789 | -0.75617701 |
| H | 4.20065594 | 2.85330009 | -2.07082891 |
| H | 2.64540505 | 3.68796897 | -2.30857301 |
| C | 2.81573510 | 1.24420500 | -4.19409084 |
| H | 3.89478707 | 1.36945605 | -4.32463408 |
| H | 2.51149607 | 0.29497299 | -4.63993216 |
| H | 2.29719210 | 2.04736495 | -4.72147799 |
| C | -2.45662999 | -0.59166598 | -3.78462911 |

| | | | |
|---|---|---|---|
| H | -3.19300389 | -0.55246198 | -4.59290218 |
| H | -1.75373495 | -1.40378594 | -3.98077989 |
| H | -2.96899891 | -0.80234897 | -2.84421706 |
| C | -0.95380300 | 1.25359702 | -5.36326790 |
| H | -0.19463000 | 0.50633502 | -5.60303783 |
| H | -1.77388000 | 1.17350805 | -6.08334017 |
| H | -0.49575099 | 2.24074888 | -5.45434284 |
| C | -2.93761396 | 2.20480394 | -3.53492808 |
| H | -3.46351409 | 2.06869507 | -2.58888888 |
| H | -2.54881310 | 3.22482800 | -3.56000590 |
| H | -3.63907194 | 2.06881404 | -4.36367607 |
| S | 0.39303100 | 0.76767099 | 0.70635402 |
| O | 1.32600403 | 1.92648995 | 0.90962303 |
| O | 0.93694299 | -0.61804003 | 0.53144801 |
| C | -0.42736101 | 0.66238397 | 2.39716697 |
| H | -0.95989001 | 1.60863304 | 2.50280094 |
| H | -1.14172804 | -0.15775301 | 2.33087993 |
| C | 0.59195399 | 0.45948201 | 3.46040797 |
| C | 0.73799902 | -0.67412901 | 4.14721680 |
| H | 1.25423098 | 1.29936004 | 3.65240598 |
| H | 1.49971795 | -0.77997899 | 4.91301298 |
| H | 0.09933700 | -1.53519595 | 3.97027206 |
| N | -5.53545523 | 1.90260196 | 0.27766699 |
| C | -5.99056005 | 3.24224210 | 0.62306499 |
| C | -6.45825911 | 0.79298401 | 0.47530699 |
| H | -5.62884903 | 3.56529093 | 1.60848701 |
| H | -7.07841206 | 3.25908589 | 0.63655901 |
| H | -5.66042614 | 3.97322798 | -0.11964000 |
| H | -6.42178202 | 0.09455600 | -0.36497599 |
| H | -7.47411299 | 1.17793000 | 0.53570098 |
| H | -6.24684477 | 0.23418801 | 1.39667797 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -225.5983 | 14.4861 | 24.0754 |
| Red. masses -- | 9.5127 | 3.8853 | 3.3030 |
| Frc consts -- | 0.2853 | 0.0005 | 0.0011 |
| IR Inten -- | 266.6476 | 0.0282 | 1.7597 |

Sum of electronic and zero-point Energies= -2081.561591
Sum of electronic and thermal Energies= -2081.527379
Sum of electronic and thermal Enthalpies= -2081.526435
Sum of electronic and thermal Free Energies= -2081.630196

HF = -2082.03252078

## allylS–Pd($PMe_3$)$_2$–Ph

| Element | X | Y | Z |
|---|---|---|---|
| Pd | -1.88349700 | -1.30377197 | -0.01281000 |
| C | 0.15956300 | -1.19686604 | 0.10774300 |
| C | 0.82122397 | -1.36984599 | 1.33168995 |
| C | 0.94325000 | -0.93337399 | -1.02426898 |
| C | 2.21282601 | -1.27726698 | 1.42469597 |
| H | 0.24935600 | -1.57398605 | 2.23301196 |
| C | 2.33496094 | -0.84052497 | -0.93914902 |

| | | | |
|---|---|---|---|
| H | 0.46788800 | -0.79102898 | -1.99129105 |
| C | 2.97786808 | -1.01240206 | 0.28773299 |
| H | 2.69886708 | -1.41133904 | 2.38759494 |
| H | 2.91714597 | -0.63097900 | -1.83277297 |
| P | -1.59569001 | -3.57078695 | -0.48183301 |
| P | -4.29908800 | -1.22767401 | -0.20797300 |
| C | -5.35962200 | -2.73623300 | -0.23672201 |
| H | -5.32318783 | -3.23273993 | 0.73413700 |
| H | -6.39611578 | -2.45695901 | -0.44154701 |
| H | -5.03358984 | -3.43935609 | -1.00323296 |
| C | -2.44620609 | -4.74451780 | 0.65134901 |
| H | -3.51999998 | -4.56946278 | 0.65747797 |
| H | -2.25555992 | -5.77620697 | 0.34516001 |
| H | -2.06790090 | -4.59821796 | 1.66460800 |
| C | -2.18845701 | -4.06222582 | -2.15370798 |
| H | -1.61361599 | -3.51862502 | -2.90556598 |
| H | -2.05808711 | -5.13580513 | -2.31174302 |
| H | -3.24017406 | -3.80834007 | -2.28301811 |
| C | 0.10908200 | -4.25272894 | -0.48353800 |
| H | 0.08251700 | -5.31792021 | -0.72603297 |
| H | 0.72046697 | -3.72381210 | -1.21388900 |
| H | 0.56326401 | -4.11093283 | 0.49699301 |
| C | -5.15808916 | -0.24707900 | 1.08970594 |
| H | -6.22459984 | -0.16467801 | 0.86524302 |
| H | -5.03234720 | -0.73797703 | 2.05641794 |
| H | -4.72140980 | 0.74926603 | 1.15231800 |
| C | -4.79218817 | -0.37891600 | -1.76299906 |
| H | -4.44814110 | -0.95716500 | -2.62265396 |
| H | -5.87695122 | -0.25783300 | -1.82148004 |
| H | -4.31231594 | 0.59990400 | -1.79311597 |
| S | -2.02235508 | 1.05865204 | 0.41040900 |
| C | -0.34469199 | 1.85819101 | 0.37774000 |
| H | 0.07861000 | 1.78357899 | -0.62471497 |
| H | 0.30892500 | 1.30780697 | 1.05595601 |
| C | -0.46877900 | 3.28383088 | 0.80850899 |
| H | -0.77678698 | 3.44135499 | 1.84162498 |
| C | -0.24590100 | 4.34010887 | 0.02470100 |
| H | 0.05139900 | 4.22438908 | -1.01480603 |
| H | -0.35091600 | 5.35674095 | 0.39121300 |
| H | 4.05894709 | -0.93924201 | 0.35713199 |

==========

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 23.1098 | 29.5151 | 41.9375 |
| Red. masses -- | 4.3265 | 3.5932 | 2.9755 |
| Frc consts -- | 0.0014 | 0.0018 | 0.0031 |
| IR Inten -- | 0.2592 | 1.6804 | 3.4153 |

Sum of electronic and zero-point Energies= -1797.234204
Sum of electronic and thermal Energies= -1797.206488
Sum of electronic and thermal Enthalpies= -1797.205544
Sum of electronic and thermal Free Energies= -1797.293233

HF = -1797.62688980

## TS: reductive elimination from allylS–Pd($PMe_3$)$_2$–Ph to allylSPh

==========

| Element | X | Y | Z |
|---|---|---|---|
| C | -4.11248589 | 1.08916795 | 0.15093499 |
| C | -2.84121203 | 0.54348898 | 0.01392900 |
| C | -1.68157899 | 1.35126102 | 0.15786199 |
| C | -1.88219905 | 2.71406293 | 0.51861101 |
| C | -3.16027308 | 3.24590993 | 0.62747997 |
| C | -4.29442596 | 2.44422698 | 0.44854701 |
| H | -4.97711277 | 0.44753399 | 0.00139000 |
| H | -2.74300909 | -0.49794000 | -0.26550400 |
| H | -1.02142596 | 3.34446001 | 0.72145301 |
| H | -3.27394009 | 4.29775381 | 0.87626803 |
| H | -5.29061508 | 2.86115408 | 0.54976702 |
| Pd | -0.08765500 | 1.34940195 | -1.33094203 |
| P | 2.19907188 | 1.69460905 | -2.02231097 |
| P | -1.48891103 | 1.40262699 | -3.23613000 |
| C | 2.66995597 | 3.06778002 | -3.16641498 |
| H | 3.74329710 | 3.06748009 | -3.37946105 |
| H | 2.12310290 | 2.96258211 | -4.10546494 |
| H | 2.39711308 | 4.02666187 | -2.72083998 |
| C | 2.92009902 | 0.23800500 | -2.90175796 |
| H | 2.36239195 | 0.05308900 | -3.82217503 |
| H | 3.97415900 | 0.39557901 | -3.14891601 |
| H | 2.83136201 | -0.64703900 | -2.26833105 |
| C | 3.42119002 | 1.92505801 | -0.65719903 |
| H | 4.45143795 | 1.92299700 | -1.02523696 |
| H | 3.22608089 | 2.87242007 | -0.14978300 |
| H | 3.29780006 | 1.12180805 | 0.07243200 |
| C | -2.46094608 | -0.12950200 | -3.58226991 |
| H | -3.13926196 | 0.01008800 | -4.42930603 |
| H | -1.78059304 | -0.95478100 | -3.80185509 |
| H | -3.04604101 | -0.38980800 | -2.69890189 |
| C | -0.77106100 | 1.75160205 | -4.90217304 |
| H | -0.01658100 | 0.99962699 | -5.14340401 |
| H | -1.53807497 | 1.74803603 | -5.68240213 |
| H | -0.28491199 | 2.72921205 | -4.88942099 |
| C | -2.82820201 | 2.66569996 | -3.13738489 |
| H | -3.40029407 | 2.50731492 | -2.22237706 |
| H | -2.38554406 | 3.66267610 | -3.09163404 |
| H | -3.49642897 | 2.60962892 | -4.00181723 |
| S | 0.01486500 | 0.56225002 | 0.97308302 |
| C | -0.52434802 | -1.20897603 | 1.05344796 |
| H | -1.49001801 | -1.23294306 | 1.56833196 |
| H | -0.65347201 | -1.59140003 | 0.04133800 |
| C | 0.50576502 | -1.99390399 | 1.80232298 |
| C | 1.25096297 | -2.95937896 | 1.26516402 |
| H | 0.63331598 | -1.73570502 | 2.85211706 |
| H | 1.98169100 | -3.50661302 | 1.85193300 |
| H | 1.15491998 | -3.23896909 | 0.21921501 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -234.9236 | 5.9195 | 18.0369 |
| Red. masses -- | 9.3538 | 3.0535 | 4.5239 |
| Frc consts -- | 0.3042 | 0.0001 | 0.0009 |
| IR Inten -- | 254.3414 | 0.0624 | 2.4693 |

Sum of electronic and zero-point Energies= -1797.189361
Sum of electronic and thermal Energies= -1797.161479
Sum of electronic and thermal Enthalpies= -1797.160535
Sum of electronic and thermal Free Energies= -1797.251168

HF = -1797.57882877

## allylS–Pd($PMe_3$)$_2$–($C_6H_4$)$CF_3$

| Element | X | Y | Z |
|---|---|---|---|
| Pd | -1.88598204 | -1.29953206 | -0.03005500 |
| C | 0.15171300 | -1.17875898 | 0.08615500 |
| C | 0.81773800 | -1.36504996 | 1.30731106 |
| C | 0.93463302 | -0.88863099 | -1.04154301 |
| C | 2.20361900 | -1.26199496 | 1.40552902 |
| H | 0.25078201 | -1.58613205 | 2.20654202 |
| C | 2.32107210 | -0.78339303 | -0.95989197 |
| H | 0.46015701 | -0.73164201 | -2.00560188 |
| C | 2.95957899 | -0.96716499 | 0.26870099 |
| H | 2.69320798 | -1.40274704 | 2.36326694 |
| H | 2.90234995 | -0.55076599 | -1.84579206 |
| P | -1.59449100 | -3.56011009 | -0.53855699 |
| P | -4.30073977 | -1.23582602 | -0.19844700 |
| C | -5.34816313 | -2.75245404 | -0.22561000 |
| H | -5.29298878 | -3.25750399 | 0.73988497 |
| H | -6.38952112 | -2.47824407 | -0.41114900 |
| H | -5.03005123 | -3.44547796 | -1.00430000 |
| C | -2.41776705 | -4.75579786 | 0.59024698 |
| H | -3.49242496 | -4.58883905 | 0.61694300 |
| H | -2.22493100 | -5.78083086 | 0.26405400 |
| H | -2.02326608 | -4.62295485 | 1.59911394 |
| C | -2.20594811 | -4.02685881 | -2.20982289 |
| H | -1.64377797 | -3.46787310 | -2.95990205 |
| H | -2.07077193 | -5.09692192 | -2.38615990 |
| H | -3.26064897 | -3.77780890 | -2.32195592 |
| C | 0.11666300 | -4.22524595 | -0.57547098 |
| H | 0.09555600 | -5.28704309 | -0.83236802 |
| H | 0.71233600 | -3.68335509 | -1.30937302 |
| H | 0.58540100 | -4.09540892 | 0.39993501 |
| C | -5.14515305 | -0.27586800 | 1.12318301 |
| H | -6.21613979 | -0.20391101 | 0.91772598 |
| H | -4.99688101 | -0.77415299 | 2.08282995 |
| H | -4.71903896 | 0.72482002 | 1.18730998 |
| C | -4.81933403 | -0.37437800 | -1.73736095 |
| H | -4.48726606 | -0.94335097 | -2.60780811 |
| H | -5.90526390 | -0.25688800 | -1.77715099 |
| H | -4.34378386 | 0.60660398 | -1.76547503 |
| S | -2.03727198 | 1.05550206 | 0.41832799 |
| C | -0.36381099 | 1.86497295 | 0.40722400 |
| H | 0.07453200 | 1.79163599 | -0.58880299 |
| H | 0.28409201 | 1.32334197 | 1.09810495 |
| C | -0.50465298 | 3.29110289 | 0.83193099 |
| H | -0.82806599 | 3.44976711 | 1.86002398 |
| C | -0.27786499 | 4.34551716 | 0.04709200 |
| H | 0.03515100 | 4.22794008 | -0.98752701 |
| H | -0.39470699 | 5.36267424 | 0.40831900 |
| C | 4.45007086 | -0.91304600 | 0.35371399 |

| | | | |
|---|---|---|---|
| F | 5.03195095 | -2.13266993 | 0.13303600 |
| F | 4.89507723 | -0.51046503 | 1.57114303 |
| F | 5.00077820 | -0.07444100 | -0.56060100 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 14.6651 | 20.3316 | 24.6052 |
| Red. masses -- | 16.3402 | 4.5762 | 7.2250 |
| Frc consts -- | 0.0021 | 0.0011 | 0.0026 |
| IR Inten -- | 0.2201 | 0.3964 | 0.8101 |

Sum of electronic and zero-point Energies= -2134.391125
Sum of electronic and thermal Energies= -2134.359765
Sum of electronic and thermal Enthalpies= -2134.358821
Sum of electronic and thermal Free Energies= -2134.456514

HF = -2134.78821559

## TS: reductive elimination from allylS–Pd($PMe_3$)$_2$–($C_6H_4$)$CF_3$ to allylS($C_6H_4$)$CF_3$

| Element | X | Y | Z |
|---|---|---|---|
| C | -3.96485400 | -0.31793100 | -0.60724998 |
| C | -2.59341192 | -0.17916100 | -0.48494399 |
| C | -1.99688303 | 1.09389400 | -0.21020301 |
| C | -2.90186310 | 2.18618798 | 0.01870300 |
| C | -4.26032495 | 2.03137302 | -0.10967800 |
| C | -4.82283497 | 0.77714199 | -0.44082800 |
| H | -4.37537003 | -1.29089200 | -0.85651797 |
| H | -1.96323001 | -1.04521894 | -0.64960200 |
| H | -2.49508190 | 3.16029501 | 0.26964101 |
| H | -4.90808201 | 2.89074492 | 0.03307200 |
| Pd | -0.25380901 | 1.39175403 | -1.46189499 |
| P | 2.06266308 | 1.00961900 | -2.05083990 |
| P | -1.42605400 | 2.21298099 | -3.33108997 |
| C | 2.85535908 | 1.88377404 | -3.47031212 |
| H | 3.91485906 | 1.62592995 | -3.55708098 |
| H | 2.34754300 | 1.61109102 | -4.39704323 |
| H | 2.76223803 | 2.96341896 | -3.33610010 |
| C | 2.48272896 | -0.74830300 | -2.43452311 |
| H | 1.92939103 | -1.07436299 | -3.31744409 |
| H | 3.55382395 | -0.87349600 | -2.61857796 |
| H | 2.19066000 | -1.38526595 | -1.59731805 |
| C | 3.24449611 | 1.37682199 | -0.68241900 |
| H | 4.27027178 | 1.10876405 | -0.95142603 |
| H | 3.20500708 | 2.44143391 | -0.44221899 |
| H | 2.94575310 | 0.82107598 | 0.20853300 |
| C | -2.94417691 | 1.26809800 | -3.76968002 |
| H | -3.46499395 | 1.72929800 | -4.61340284 |
| H | -2.67816997 | 0.24200299 | -4.03041506 |
| H | -3.60890794 | 1.23543894 | -2.90601397 |
| C | -0.57218802 | 2.35407495 | -4.95971298 |
| H | -0.20398401 | 1.37311006 | -5.26724005 |
| H | -1.24520504 | 2.73936105 | -5.73082495 |
| H | 0.28292301 | 3.02600002 | -4.86681986 |
| C | -2.09779406 | 3.91590500 | -3.11378789 |
| H | -2.72276402 | 3.94032502 | -2.21947503 |

| | | | |
|---|---|---|---|
| H | -1.27548504 | 4.62165880 | -2.98159599 |
| H | -2.69681001 | 4.22025394 | -3.97677898 |
| S | -0.38162601 | 1.12444699 | 0.93237501 |
| C | -0.02615500 | -0.66719103 | 1.28006196 |
| H | -0.97614902 | -1.11727202 | 1.58243704 |
| H | 0.31883299 | -1.15487504 | 0.36926800 |
| C | 0.99586803 | -0.74808300 | 2.36724710 |
| C | 2.21602011 | -1.26214194 | 2.21136808 |
| H | 0.69855100 | -0.34741801 | 3.33452511 |
| H | 2.92431998 | -1.30130100 | 3.03230405 |
| H | 2.54860401 | -1.66956997 | 1.26046205 |
| C | -6.28787804 | 0.62272602 | -0.52518100 |
| F | -6.90868998 | 0.48837200 | 0.70180601 |
| F | -6.90655088 | 1.69800401 | -1.09982502 |
| F | -6.67438221 | -0.47135401 | -1.23551297 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -152.8133 | 16.7599 | 20.1588 |
| Red. masses -- | 9.4638 | 15.6754 | 4.6474 |
| Frc consts -- | 0.1302 | 0.0026 | 0.0011 |
| IR Inten -- | 170.6936 | 0.0616 | 0.7069 |

Sum of electronic and zero-point Energies= -2134.353101
Sum of electronic and thermal Energies= -2134.321923
Sum of electronic and thermal Enthalpies= -2134.320979
Sum of electronic and thermal Free Energies= -2134.417698

HF = -2134.74730529

## allylS–Pd($PMe_3$)$_2$–($C_6H_4$)$NMe_2$

| Element | X | Y | Z |
|---|---|---|---|
| Pd | -1.93573403 | -1.26496601 | -0.00551200 |
| C | 0.10598700 | -1.11288798 | 0.11890200 |
| C | 0.78236300 | -1.25912201 | 1.33390701 |
| C | 0.89544898 | -0.82866400 | -0.99939400 |
| C | 2.16855693 | -1.12590694 | 1.43762302 |
| H | 0.22596900 | -1.47000301 | 2.24386191 |
| C | 2.28261399 | -0.69301897 | -0.91957998 |
| H | 0.43003300 | -0.69171500 | -1.97253394 |
| C | 2.96322608 | -0.85168898 | 0.30532300 |
| H | 2.62109804 | -1.23951900 | 2.41489697 |
| H | 2.82644892 | -0.45974001 | -1.82655299 |
| P | -1.58329105 | -3.52161288 | -0.46852100 |
| P | -4.35111189 | -1.24818695 | -0.21743900 |
| C | -5.37650394 | -2.78124404 | -0.25290501 |
| H | -5.33653879 | -3.27632809 | 0.71860301 |
| H | -6.41763496 | -2.52722192 | -0.46724299 |
| H | -5.02671814 | -3.47693205 | -1.01585400 |
| C | -2.41716003 | -4.71852589 | 0.65371799 |
| H | -3.49499011 | -4.56995916 | 0.64777100 |
| H | -2.19754100 | -5.74484491 | 0.34864599 |
| H | -2.05428004 | -4.56449890 | 1.67150497 |
| C | -2.14679909 | -4.02885914 | -2.14644098 |
| H | -1.57877600 | -3.47066092 | -2.89285707 |

| | | | |
|---|---|---|---|
| H | -1.98772204 | -5.09880114 | -2.30344796 |
| H | -3.20338702 | -3.80133390 | -2.28577900 |
| C | 0.13700999 | -4.16254997 | -0.45228401 |
| H | 0.13786200 | -5.22878408 | -0.69209403 |
| H | 0.74224102 | -3.61978102 | -1.17745399 |
| H | 0.57810801 | -4.00628614 | 0.53192002 |
| C | -5.24620199 | -0.28422001 | 1.06870496 |
| H | -6.31255579 | -0.22840600 | 0.83528203 |
| H | -5.11677980 | -0.76786900 | 2.03861308 |
| H | -4.83420897 | 0.72265899 | 1.13097501 |
| C | -4.85217285 | -0.41638201 | -1.77956605 |
| H | -4.48903513 | -0.99090999 | -2.63389301 |
| H | -5.93891001 | -0.31958401 | -1.84676802 |
| H | -4.39370012 | 0.57263398 | -1.81092095 |
| S | -2.12946796 | 1.09548199 | 0.41565999 |
| C | -0.46572000 | 1.92420995 | 0.39626500 |
| H | -0.03362800 | 1.85643101 | -0.60285503 |
| H | 0.19148400 | 1.38280797 | 1.07808399 |
| C | -0.61533803 | 3.34735990 | 0.82654500 |
| H | -0.93509197 | 3.49969912 | 1.85696304 |
| C | -0.40146500 | 4.40787506 | 0.04571900 |
| H | -0.09333500 | 4.29754591 | -0.99126202 |
| H | -0.52548403 | 5.42255020 | 0.41184101 |
| N | 4.36229515 | -0.76235998 | 0.38956001 |
| C | 4.94823694 | -0.56009799 | 1.70785105 |
| H | 4.72940397 | -1.40218198 | 2.36766601 |
| H | 6.03186703 | -0.49937001 | 1.61289001 |
| H | 4.59066582 | 0.35938099 | 2.19685888 |
| C | 5.06560421 | -0.11569200 | -0.71008301 |
| H | 4.74098921 | 0.92409903 | -0.87116498 |
| H | 6.13453007 | -0.11304900 | -0.49949101 |
| H | 4.92264700 | -0.66406101 | -1.64346099 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 17.7454 | 26.3104 | 29.1465 |
| Red. masses -- | 3.9822 | 4.3095 | 3.7039 |
| Frc consts -- | 0.0007 | 0.0018 | 0.0019 |
| IR Inten -- | 0.2243 | 1.6559 | 2.1578 |

Sum of electronic and zero-point Energies= -1931.165748
Sum of electronic and thermal Energies= -1931.133730
Sum of electronic and thermal Enthalpies= -1931.132785
Sum of electronic and thermal Free Energies= -1931.230584

HF = -1931.63136409

## TS: reductive elimination from allylS–Pd($PMe_3$)$_2$–($C_6H_4$)$NMe_2$ to allylS($C_6H_4$)$NMe_2$

| Element | X | Y | Z |
|---|---|---|---|
| C | -4.12468576 | 0.83014500 | -0.24117599 |
| C | -2.78791809 | 0.48860499 | -0.06813700 |
| C | -1.75829101 | 1.43858600 | -0.20732699 |
| C | -2.15818405 | 2.77100611 | -0.43509400 |
| C | -3.49264598 | 3.11250401 | -0.63078701 |
| C | -4.51993990 | 2.14759707 | -0.56100702 |

| | | | |
|---|---|---|---|
| H | -4.86048985 | 0.04107200 | -0.15086800 |
| H | -2.54624295 | -0.54911000 | 0.12652400 |
| H | -1.41307294 | 3.56027102 | -0.44527900 |
| H | -3.72453809 | 4.15330076 | -0.81722802 |
| Pd | -0.04180900 | 1.08582604 | -1.47204101 |
| P | 2.09845591 | 1.83938801 | -2.25494695 |
| P | -1.19675803 | 0.04569200 | -3.27138591 |
| C | 3.15623307 | 0.58089501 | -3.09971499 |
| H | 4.12427521 | 0.99879402 | -3.39219403 |
| H | 3.32157397 | -0.26552299 | -2.43001294 |
| H | 2.64345407 | 0.21309100 | -3.99057388 |
| C | 3.26286602 | 2.47424197 | -0.96987700 |
| H | 3.39427590 | 1.71606100 | -0.19497500 |
| H | 4.23891592 | 2.73047090 | -1.39254296 |
| H | 2.83338499 | 3.36094904 | -0.49863300 |
| C | 2.14266992 | 3.21490502 | -3.48963404 |
| H | 3.16805506 | 3.47090602 | -3.77365398 |
| H | 1.59014904 | 2.91982603 | -4.38411283 |
| H | 1.65867698 | 4.09881878 | -3.06939006 |
| C | -2.03231692 | -1.57754397 | -2.97763491 |
| H | -2.60846806 | -1.89481497 | -3.85227489 |
| H | -1.28528905 | -2.33995104 | -2.74735808 |
| H | -2.70624804 | -1.48669600 | -2.12463188 |
| C | -0.33086500 | -0.29959401 | -4.86807585 |
| H | 0.46639499 | -1.02745903 | -4.70251703 |
| H | -1.01656795 | -0.69270301 | -5.62483692 |
| H | 0.12156000 | 0.62060398 | -5.24391317 |
| C | -2.62074590 | 1.07316005 | -3.84062099 |
| H | -3.27255011 | 1.27646303 | -2.98928809 |
| H | -2.25126505 | 2.02838802 | -4.21897793 |
| H | -3.19246006 | 0.57245803 | -4.62773180 |
| S | 0.02867900 | 1.30075097 | 0.93338799 |
| C | -0.58772898 | -0.12046200 | 1.96610796 |
| H | -1.61734402 | 0.10286000 | 2.26079988 |
| H | -0.58124697 | -1.03132701 | 1.36713398 |
| C | 0.29567900 | -0.25509399 | 3.16474104 |
| C | 1.10606003 | -1.28838503 | 3.39419007 |
| H | 0.25918499 | 0.56720400 | 3.87745690 |
| H | 1.72599101 | -1.33952403 | 4.28367281 |
| H | 1.17635798 | -2.12251711 | 2.70075297 |
| N | -5.86167717 | 2.47343111 | -0.81059700 |
| C | -6.88411808 | 1.55582297 | -0.32511401 |
| H | -7.86773205 | 1.94756496 | -0.58161998 |
| H | -6.79309177 | 0.57795799 | -0.80228698 |
| H | -6.84173584 | 1.41024101 | 0.76537102 |
| C | -6.23118877 | 3.88199711 | -0.79612899 |
| H | -5.68871117 | 4.43575001 | -1.56508398 |
| H | -7.29315519 | 3.97583795 | -1.02020204 |
| H | -6.03750992 | 4.36445904 | 0.17465000 |

==========

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -262.0804 | 13.1910 | 22.1750 |
| Red. masses -- | 10.8889 | 4.1636 | 3.9207 |
| Frc consts -- | 0.4407 | 0.0004 | 0.0011 |
| IR Inten -- | 278.5000 | 0.3548 | 1.1991 |

Sum of electronic and zero-point Energies= -1931.119599
Sum of electronic and thermal Energies= -1931.087375
Sum of electronic and thermal Enthalpies= -1931.086430
Sum of electronic and thermal Free Energies= -1931.186193

HF = -1931.58228456

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13. Structures can be found in the cif document attached. Reports were directly generated from the .log file using the GEAC program (link: https://github.com/LaTruelle/Geac). E. Nicolas, http://doi.org/10.5281/zenodo.57101)