Understanding the mechanism of transition metal-free anti addition to alkynes: the selenoboration case

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1. General Information

Solvents and reagents: Solvents and reagents were obtained from commercial suppliers and dried and/or purified (if needed) by standard procedures, as specified in “Purification of Laboratory Chemicals”.\textsuperscript{1} Tetrahydrofuran was dried by distillation from sodium benzophenone ketyl. Phenylselenium pinacolborane (PhSe-Bpin) was synthesized in the laboratory of Prof. Stephen A. Westcott at Mount Allison University, Sackville, NB (Canada).\textsuperscript{2} Tricyclohexylphosphine was purchased from Sigma-Aldrich Inc. All reactions were conducted in oven and flame-dried glassware under an inert atmosphere of argon, using Schlenk-type techniques. Flash chromatography was performed on standard silica gel (Merck Kieselgel 60 F254 400-630 mesh). Thin layer chromatography was performed on Merck Kieselgel 60 F254 which was developed using standard visualizing agents: UV fluorescence (254 and 366 nm) or potassium permanganate/Δ. NMR spectra were recorded at a Varian Goku 400 or a Varian Mercury 400 spectrometer. \textsuperscript{1}H NMR and \textsuperscript{13}C{\textsuperscript{1}H} NMR chemical shifts (δ) are reported in ppm with the solvent resonance as the internal standard (CHCl\textsubscript{3}: 7.26 ppm (\textsuperscript{1}H)) and (CDCl\textsubscript{3}: 77.16 ppm (\textsuperscript{13}C)). \textsuperscript{11}B{\textsuperscript{1}H} NMR chemical shifts (δ) are reported in ppm relative to (CH\textsubscript{3})\textsubscript{2}O···BF\textsubscript{3}. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, hept = heptuplet, br = broad, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra (HRMS) were recorded using a 6210 Time of Flight (TOF) mass spectrometer from Agilent Technologies (Waldborn, Germany) with an ESI interface and it was performed at the Servei de Recursos Científics i Tècnics (Universitat Rovira I Virgili, Tarragona). GC-MS analyses were performed on a HP6890 gas chromatograph and an Agilent Technologies 5973 Mass selective detector (Waldborn, Germany) equipped with an achiral capillary column HP-5 (30m, 0.25mm i. d., 0.25μm thickness) using He as the carrier gas. Substrates 1 and 2 were commercially available.

\textsuperscript{1} D. D. Perrin, W. L. F. Armarego, \textit{Purification of Laboratory Chemicals}, Pergamon Press, 1988, 3rd Ed.
\textsuperscript{2} a) S. A. Westcott, J. D. Webb, D. I. McIsaac and C. M. Vogels, WO Pat., 2006/089402 A1, 2006;
2. Experimental Procedures and Spectral data

I.- General Procedure A: Synthesis of alkynoates

An oven-dried Schlenck equipped with a magnetic stir bar was charged with 2 mmol of the appropriate alkyne and dissolved in 3 mL of THF. At -78 °C, 1.05 eq. of nBuLi (1.6M) were added dropwise. After stirring for 30 min, 1 eq. of the chloroformate or carbamoyl chloride was added drop wise. After 8 h stirring the reaction was allowed to rise to room temperature and let it react overnight. The reaction was quenched with 2mL of saturated Na₂S₂O₄ and extracted 3 times with 5mL of DCM. All the organic layers were collected and dry over MgSO₄ and evaporated to dryness. The crude residue was analysed by ¹H NMR. Then the products were purified by silica gel flash chromatography.

General Procedure A: Synthesis of alkynamides

An oven-dried Schlenck equipped with a magnetic stir bar was charged with 2 mmol of the appropriate alkyne and dissolved in 3 mL of THF. At -78 °C, 1.05 eq. of nBuLi (1.6M) were added dropwise. After stirring for 30 min, 1 eq. of carbamoyl chloride was added drop wise. After 8 h stirring the reaction was allowed to rise to room temperature and let it react overnight. The reaction was quenched with 2mL of saturated Na₂S₂O₄ and extracted 3 times with 5mL of DCM. All the organic layers were collected and dry over MgSO₄ and evaporated to dryness. The crude residue was analysed by ¹H NMR. Then the products were purified by silica gel flash chromatography.
Spectral data of Alkynoates

Ethyl 3-(4-methoxyphenyl)propionate

Flash column chromatography yielded 3 (367.6 mg, 90 %) as a colourless oil.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.53 – 7.49 (m, 2H), 6.87 – 6.84 (m, 2H), 4.26 (q, $J$ = 7.1 Hz, 2H), 3.80 (s, 3H), 1.32 (t, $J$ = 7.1 Hz, 3H). $^{13}$C $^1$H NMR (CDCl$_3$, 100 MHz) $\delta$ 161.5, 154.4, 135.0, 114.3, 111.4, 86.9, 80.2, 62.0, 55.4, 14.2.

HRMS (ESI) for C$_{12}$H$_{13}$O$_3$ [M+H]$^+$: calculated: 205.0865, found: 205.0862.

Characterization data matches literature$^3$

Propyl 3-(4-methoxyphenyl)propionate

Flash column chromatography yielded 4 (388.5 mg, 89 %) as a yellowish oil.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.55 – 7.51 (m, 2H), 6.89 – 6.85 (m, 2H), 4.17 (t, $J$ = 6.8 Hz, 2H), 3.82 (s, 3H), 1.77 – 1.68 (m, 2H), 0.98 (t, $J$ = 7.4 Hz, 3H). $^{13}$C $^1$H NMR (CDCl$_3$, 100 MHz) $\delta$ 161.5, 154.6, 135.0, 114.3, 111.4, 87.0, 80.2, 67.6, 55.5, 22.0, 10.5.

HRMS (ESI) for C$_{13}$H$_{15}$O$_3$ [M+H]$^+$: calculated: 219.1021, found: 219.1018.

Isopropyl 3-(4-methoxyphenyl)propionate

Flash column chromatography yielded 5 (379.8 mg, 87 %) as a white solid.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.56 – 7.52 (m, 2H), 6.89 – 6.86 (m, 2H), 5.15 (hept, $J$ = 6.3 Hz, 1H), 3.83 (s, 3H), 1.33 (d, $J$ = 6.3 Hz, 6H). $^{13}$C $^1$H NMR (CDCl$_3$, 100 MHz) $\delta$ 161.5, 154.1, 135.0, 114.4, 111.6, 86.6, 80.6, 69.9, 55.5, 21.9.

HRMS (ESI) for C$_{13}$H$_{15}$O$_3$ [M+H]$^+$: calculated: 219.1021, found: 219.1017.

$^3$ P. R. Andrews, R. I. Brinkworth, A. C. Partridge, J. A. Reiss, *Aus. J. Chem.* 1988, **41**, 1717.
**Spectral data of Alkynamides**

3-(4-methoxyphenyl)-N,N-dimethylpropiolamide

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\end{align*}
\]

Flash column chromatography yielded 6 (281.1 mg, 92 %) as a colourless oil.

\(^1\text{H NMR}\) (CDCl\(_3\), 400 MHz) \(\delta \) 7.54 – 7.43 (m, 2H), 6.93 – 6.80 (m, 2H), 3.83 (s, 3H), 3.28 (s, 3H), 3.02 (s, 3H).

\(^{13}\text{C} \{^1\text{H}\} \text{ NMR}\) (CDCl\(_3\), 100 MHz) \(\delta \) 161.0, 155.1, 134.2, 114.3, 112.6, 90.8, 81.0, 77.2, 55.5, 38.6, 34.3.

\(\text{HRMS (ESI)}\) for C\(_{12}\)H\(_{14}\)NO\(_2\) \([\text{M+H]}^+\): calculated: 204.1025, found: 204.1023.

3-(4-methoxyphenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-one

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\end{align*}
\]

Flash column chromatography yielded 7 (330.3 mg, 96 %) as a colourless oil.

\(^1\text{H NMR}\) (CDCl\(_3\), 400 MHz) \(\delta \) 7.52 – 7.45 (m, 2H), 6.90 – 6.84 (m, 2H), 3.83 (s, 3H), 3.76 – 3.68 (m, 2H), 3.56 – 3.49 (m, 2H), 2.02 – 1.90 (m, 4H).

\(^{13}\text{C} \{^1\text{H}\} \text{ NMR}\) (CDCl\(_3\), 100 MHz) \(\delta \) 161.0, 152.7, 134.3, 114.3, 112.7, 89.3, 82.1, 77.2, 55.5, 48.3, 45.5, 25.6, 24.9.

\(\text{HRMS (ESI)}\) for C\(_{14}\)H\(_{15}\)NNaO\(_2\) \([\text{M+Na]}^+\): calculated: 252,1000, found: 252.1001.

**II.- General Procedure B: \(\beta\)-selenation of alkynoates and alkynamides**

In the glove-box, an oven-dried resealable vial equipped with a magnetic stir bar was charged with 0.2 mmol of the alkynoate or ynamide compound. Then, the vial was charged with 1.1 eq. of pinB-SePh solved in 0.15mL of dry MeOH. After 16 h at 50\(^\circ\)C the reaction was evaporated to dryness. The crude residue was analysed by GC-MS and \(^1\text{H NMR}\) using naphthalene as an internal standard. Then the products were purified by silica gel flash chromatography.
Spectral data of β-selenated products

**Ethyl (Z)-3-phenyl-3-(phenylselanyl)acrylate**

Flash column chromatography yielded Z-8 (49.0 mg, 74 %) as a yellowish solid.

\[ ^1H\text{ NMR} (\text{CDCl}_3, 400 \text{ MHz}) \delta 7.25 – 7.20 (m, 2H), 7.11 – 6.96 (m, 8H), 6.32 (s, 1H), 4.30 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H). \]

\[ ^13C\{^1H\text{ NMR} (\text{CDCl}_3, 100 \text{ MHz}) \delta 166.9, 161.4, 139.2, 136.4, 129.3, 128.7, 128.5, 128.1, 128.0, 127.6, 117.1, 60.7, 14.5. \]

**HRMS (ESI) for C_{17}H_{17}O_{2}Se [M+H]^+: calculated: 333.0394, found: 333.0391.**

**Methyl (Z)-3-(phenylselanyl)non-2-enoate**

Flash column chromatography yielded Z-9 (51.4 mg, 79 %) as a yellowish oil.

\[ ^1H\text{ NMR} (\text{CDCl}_3, 400 \text{ MHz}) \delta 7.69 – 7.65 (m, 2H), 7.43 – 7.38 (m, 1H), 7.36 – 7.32 (m, 2H), 6.16 (s, 1H), 3.76 (s, 3H), 2.17 – 2.13 (m, 2H), 1.34 – 1.26 (m, 2H), 1.17 – 1.10 (m, 2H), 1.05 – 0.97 (m, 4H), 0.79 (t, J = 7.3 Hz, 3H). \]

\[ ^13C\{^1H\text{ NMR} (\text{CDCl}_3, 100 \text{ MHz}) \delta 167.7, 164.4, 137.7, 129.3, 129.2, 127.6, 113.2, 51.5, 37.9, 31.4, 29.8, 28.5, 22.5, 14.1. \]

**HRMS (ESI) for C_{16}H_{23}O_{2}Se [M+H]^+: calculated: 327.0863, found: 327.0855.**

**Ethyl (Z)-3-(4-methoxyphenyl)-3-(phenylselanyl)acrylate**

Flash column chromatography yielded Z-10 (52.0 mg, 72 %) as a yellowish oil.

\[ ^1H\text{ NMR} (\text{CDCl}_3, 400 \text{ MHz}) \delta 7.24 – 7.21 (m, 2H), 7.11 – 7.07 (m, 1H), 7.04 – 6.95 (m, 4H), 6.58 – 6.54 (m, 2H), 6.30 (s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.68 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H). \]

\[ ^13C\{^1H\text{ NMR} (\text{CDCl}_3, 100 \text{ MHz}) \delta 166.9, 161.0, 159.6, 136.1, 131.8, 130.2, 129.7, 128.5, 127.9, 116.7, 113.0, 60.6, 55.3, 14.5. \]

**HRMS (ESI) for C_{18}H_{19}O_{3}Se [M+H]^+: calculated: 363.0499, found: 363.0495.**
**Propyl (Z)-3-(4-methoxyphenyl)-3-(phenylselanyl)acrylate**

Flash column chromatography yielded **Z-11** (54.0 mg, 72 %) as a yellowish oil.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.24 – 7.22 (m, 2H), 7.11 – 7.07 (m, 1H), 7.03 – 6.95 (m, 4H), 6.57 – 6.54 (m, 2H), 6.31 (s, 1H), 4.19 (t, J = 6.7 Hz, 2H), 3.68 (s, 3H), 1.78 – 1.69 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H).

$^{13}$C $\{^1$H$\}$ NMR (CDCl$_3$, 100 MHz) $\delta$ 167.0, 160.9, 159.5, 136.1, 131.7, 130.2, 129.7, 128.5, 127.8, 116.7, 113.0, 66.2, 55.3, 22.2, 10.6.

HRMS (ESI) for C$_{19}$H$_{21}$O$_3$Se [M+H]$^+$: calculated: 377.0656, found: 377.0651.

**Isopropyl (Z)-3-(4-methoxyphenyl)-3-(phenylselanyl)acrylate**

Flash column chromatography yielded **Z-12** (51.8 mg, 69 %) as a yellowish oil.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.23 – 7.21 (m, 2H), 7.11 – 7.07 (m, 1H), 7.03 – 6.95 (m, 4H), 6.57 – 6.53 (m, 2H), 6.27 (s, 1H), 5.17 (hept, J = 6.2 Hz, 1H), 3.67 (s, 3H), 1.32 (d, J = 6.3 Hz, 6H).

$^{13}$C $\{^1$H$\}$ NMR (CDCl$_3$, 100 MHz) $\delta$ 166.5, 160.6, 159.5, 136.1, 131.8, 130.2, 129.7, 128.5, 127.8, 117.2, 113.0, 67.9, 55.3, 22.2.

HRMS (ESI) for C$_{19}$H$_{21}$O$_3$Se [M+H]$^+$: calculated: 377.0656, found: 377.0648.

**(Z)-3-(4-methoxyphenyl)-N,N-dimethyl-3-(phenylselanyl)acrylamide**

Flash column chromatography yielded **Z-13** (54.8 mg, 76 %) as a colourless oil.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.26 – 7.20 (m, 2H), 7.09 – 6.95 (m, 5H), 6.60 (s, 1H), 6.58 – 6.54 (m, 2H), 3.68 (s, 3H), 3.08 (brs, 6H).

$^{13}$C $\{^1$H$\}$ NMR (CDCl$_3$, 100 MHz) $\delta$ 167.1, 159.3, 156.1, 135.9, 132.6, 130.8, 130.2, 128.3, 127.4, 117.1, 113.0, 55.3, 24.9.

HRMS (ESI) for C$_{19}$H$_{20}$NO$_2$Se [M+H]$^+$: calculated: 362.0659, found: 362.0651.
(Z)-3-(4-methoxyphenyl)-3-(phenylselanyl)-1-(pyrrolidin-1-yl)prop-2-en-1-one

Flash column chromatography yielded **Z-14** (49.2 mg, 69 %) as a colourless oil.  
**^1H NMR** (CDCl₃, 400 MHz) δ 7.25 – 7.20 (m, 2H), 7.08 – 7.03 (m, 1H), 7.01 – 6.93 (m, 4H), 6.58 – 6.52 (m, 2H), 6.45 (s, 1H), 3.67 (s, 3H), 3.55 (brs, 4H), 1.93 (brs, 4H).  
**^13C {^1H} NMR** (CDCl₃, 100 MHz) δ 165.3, 159.2, 156.9, 136.2, 132.6, 130.9, 130.2, 128.3, 127.5, 117.6, 112.9, 77.2, 55.3, 46.4 (brs), 25.7 (brs).  
**HRMS** (ESI) for C₂₀H₂₂NO₂Se [M+H]^+: calculated: 388.0816, found: 388.0811.

**III.- General Procedure C: Insertion of pinB-SeR into alkynoates or alkynamides**

In the glove-box, an oven-dried resealable vial equipped with a magnetic stir bar was charged with 0.2 mmol of the alkynoate or ynamide compound. Then, 15mol% of tricyclohexylphosphine in 0.15ml of dry THF was added. After stirring in the glove-box for 5 min the vial was charged with 1.1 eq. of pinB-SePh. After 16 h at room temperature the reaction was evaporated to dryness. The crude residue was analysed by GC-MS and ^1H NMR using naphthalene as an internal standard. Then the products were purified by silica gel flash chromatography.
Spectral data of inserted products

(Z)-3-phenyl-2-(phenylselanyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate. No isolated product 15.

\[ \text{Structure Image} \]

\(^1\)H NMR of main signals (CDCl\(_3\), 400 MHz) \( \delta \) 3.97 (q, \( J = 7.1 \) Hz, 2H), 1.26 (s, 12H), 0.94 (t, \( J = 7.2 \) Hz, 3H).

Ethyl (Z)-3-(4-methoxyphenyl)-2-(phenylselanyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate

Flash column chromatography yielded 16 (4.9 mg, 5 %) as a yellowish oil.

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta \) 7.29 – 7.35 (m, 3H), 7.19 – 7.16 (m, 3H), 6.92 – 6.88 (m, 2H), 4.01 (q, \( J = 7.2 \) Hz, 2H), 3.82 (s, 3H), 1.29 (s, 12H), 0.94 (t, \( J = 7.1 \) Hz, 3H).

\(^{13}\)C \(^{1}\)H NMR (CDCl\(_3\), 100 MHz) \( \delta \) 169.4, 159.8, 134.5, 132.9, 131.0, 129.9, 129.0, 127.2, 113.5, 83.9, 62.8, 55.4, 25.0, 13.7. \(^{11}\)B NMR (128.3 MHz, CDCl\(_3\)) \( \delta \) 28.3.

HRMS (ESI) for C\(_{24}\)H\(_{30}\)BO\(_5\)Se [M+H]^+: calculated: 489.1352, found: 489.1358.

Propyl (Z)-3-(4-methoxyphenyl)-2-(phenylselanyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate

Flash column chromatography yielded 17 (23.1 mg, 23 %) as a yellowish oil.

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta \) 7.40 – 7.33 (m, 3H), 7.17 – 7.14 (m, 3H), 6.91 – 6.88 (m, 2H), 3.93 (t, \( J = 6.7 \) Hz, 2H), 3.82 (s, 3H), 1.41 – 1.32 (m, 2H), 1.29 (s, 12H), 0.70 (t, \( J = 7.4 \) Hz, 3H).

\(^{13}\)C \(^{1}\)H NMR (CDCl\(_3\), 100 MHz) \( \delta \) 169.9, 159.8, 134.3, 132.3,
131.5, 131.2, 129.9, 129.0, 128.3 (bs), 127.0, 113.4, 83.8, 68.6, 55.3, 25.0, 21.6, 10.3.

$^{11}$B NMR (128.3 MHz, CDCl$_3$) δ 27.9.

HRMS (ESI) for C$_{50}$H$_{62}$B$_2$NaO$_{10}$Se$_2$ [2M+Na]$^+$: calculated: 1027.2757, found: 1027.2789.

Isopropyl (Z)-3-(4-methoxyphenyl)-2-(phenylselanyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate

Flash column chromatography yielded 18 (31.1 mg, 31 %) as a yellowish oil.

$^1$H NMR (CDCl$_3$, 400 MHz) δ 7.41 – 7.36 (m, 3H), 7.18 – 7.15 (m, 3H), 6.92 – 6.89 (m, 2H), 4.85 (hept, $J = 6.3$ Hz, 1H), 3.82 (s, 3H), 1.29 (s, 12H), 0.95 (d, $J = 6.3$ Hz, 6H).

$^{13}$C { $^1$H} NMR (CDCl$_3$, 100 MHz) δ 169.6, 159.9, 132.6, 131.5, 131.4, 130.0, 129.0, 128.3, 127.1, 113.4, 83.6, 71.3, 55.3, 25.0, 21.3. $^{11}$B NMR (128.3 MHz, CDCl$_3$) δ 27.8.

HRMS (ESI) for C$_{25}$H$_{31}$BNaO$_5$Se [M+Na]$^+$: calculated: 525.1327, found: 525.1332.

(Z)-3-(4-methoxyphenyl)-N,N-dimethyl-2-(phenylselanyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylamide

No Isolated Product 23

$^1$H NMR (CDCl$_3$, 400 MHz) δ 7.25 – 7.21 (m, 2H), 7.19 – 7.13 (m, 2H), 7.09 – 6.98 (m, 3H), 6.63 – 6.57 (m, 2H), 3.69 (s, 3H), 3.09 (brs, 6H), 1.06 (s, 13H). $^{11}$B NMR (128.3 MHz, CDCl$_3$) δ 27.3.
(Z)-3-(4-methoxyphenyl)-N,N-dimethyl-2-(phenylselanyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylamide

No Isolated Product 24

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.24 – 7.19 (m, 2H), 7.14 – 7.09 (m, 2H), 7.08 – 6.95 (m, 3H), 6.60 – 6.54 (m, 2H), 3.68 (s, 3H), 3.56 (brs, 4H), 1.92 (brs, 4H), 1.04 (s, 12H).

IV.- General Procedure D: One pot α-selenation of alkynoates

In the glove-box, an oven-dried resealable vial equipped with a magnetic stir bar was charged with 0.2 mmol of the alkynoate or ynamide compound. Then, 15 mol% of tricyclohexylphosphine in 0.15 ml of dry THF was added. After stirring in the glove-box for 5 min the vial was charged with 1.1 eq. of pinB-SePh. After 16 h at room temperature the reaction was evaporated to dryness. The crude residue was solved in 2 mL of THF and 0.2 mL of K$_2$CO$_3$ (2M) water solution was added dropwise. The reaction was heated to reflux for 2h. Then the reaction was extracted with DCM and filtered through a pad of Celite and MgSO$_4$. The solvent was removed and the residue was analysed by GC-MS and $^1$H NMR using naphthalene as an internal standard. Then the products were purified by silica gel flash chromatography.

Spectral data of α-selenated products

Ethyl (Z)-3-phenyl-2-(phenylselanyl)acrylate
Flash column chromatography yielded 19 (14.6 mg, 22 %) as a yellowish oil.

$^{1}$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.15 (s, 1H), 7.66 – 7.64 (m, 2H), 7.42 – 7.37 (m, 5H), 7.22 – 7.19 (m, 3H), 4.07 (q, J = 7.1 Hz, 2H), 1.04 (t, J = 7.1 Hz, 3H). $^{13}$C $^{1}$H NMR (CDCl$_3$, 100 MHz) $\delta$ 166.8, 145.0, 138.4, 135.3, 134.4, 131.9, 130.4, 129.2, 128.3, 127.2, 124.5, 62.0, 13.9.

HRMS (ESI) for C$_{17}$H$_{17}$O$_2$Se [M+H]$^+$: calculated: 333.0394, found: 333.0392.

$\text{Ethyl (Z)-3-(4-methoxyphenyl)-2-(phenylselanyl)acrylate}$

Flash column chromatography yielded 20 (15.2 mg, 21 %) as a yellowish oil.

$^{1}$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.17 (s, 1H), 7.75 – 7.72 (m, 2H), 7.40 – 7.37 (m, 2H), 7.22 – 7.18 (m, 3H), 6.93 – 6.90 (m, 2H), 4.08 (q, J = 7.1 Hz, 2H), 3.83 (s, 3H), 1.06 (t, J = 7.1 Hz, 3H). $^{13}$C $^{1}$H NMR (CDCl$_3$, 100 MHz) $\delta$ 167.0, 161.0, 145.8, 132.7, 131.3, 129.8, 129.2, 127.7, 127.0, 113.8, 70.7, 61.9, 55.5, 14.0.

HRMS (ESI) for C$_{18}$H$_{19}$O$_3$Se [M+H]$^+$: calculated: 363.0499, found: 363.0507

$\text{Propyl (Z)-3-(4-methoxyphenyl)-2-(phenylselanyl)acrylate}$

Flash column chromatography yielded 21 (9.7 mg, 13 %) as a yellowish oil.

$^{1}$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.20 (s, 1H), 7.77 – 7.73 (m, 2H), 7.39 – 7.36 (m, 2H), 7.22 – 7.18 (m, 3H), 6.93 – 6.89 (m, 2H), 4.00 (t, J = 6.7 Hz, 2H), 3.83 (s, 3H), 1.53 – 1.44 (m, 2H), 0.81 (t, J = 7.4 Hz, 3H). $^{13}$C $^{1}$H NMR (CDCl$_3$, 100 MHz) $\delta$ 167.1, 161.0, 146.2, 136.0, 132.7, 131.0, 129.2, 127.7, 126.8, 120.4, 113.8, 67.6, 55.5, 21.9, 10.5.

HRMS (ESI) for C$_{19}$H$_{21}$O$_3$Se [M+H]$^+$: calculated: 377.0656, found: 377.0651

$\text{Isopropyl (Z)-3-(4-methoxyphenyl)-2-(phenylselanyl)acrylate}$

Flash column chromatography yielded 22 (23.3 mg, 31 %) as a yellowish oil.

$^{1}$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.15 (s, 1H), 7.73 – 7.70 (m, 2H), 7.40 – 7.37 (m, 2H), 7.23 – 7.17 (m, 3H), 6.94 – 6.90 (m, 2H), 4.91 (hept, J = 6.2 Hz, 1H), 3.84 (s, 3H), 1.04
(d, J = 6.3 Hz, 6H). $^{13}$C $^{1^H}$ NMR (CDCl$_3$, 100 MHz) $\delta$ 166.5, 160.9, 145.3, 132.6, 131.4, 130.2, 129.2, 127.8, 126.9, 121.4, 113.8, 69.5, 55.5, 21.5.

**HRMS** (ESI) for C$_{19}$H$_{21}$O$_3$Se $[\text{M+H}]^+$: calculated: 377.0656, found: 377.0651

3. $^1$H, $^{13}$C and $^{11}$B spectra
1H NMR

13C NMR
\[ ^{1}H \text{NMR} \]

\[ ^{13}C \text{NMR} \]
$^1$H NMR

$^{13}$C NMR
$^{1}H$ NMR of the crude

$^{1}H$ NMR

$^{1}H$ NMR
$^1$H NMR of the reaction crude

[Chemical structure image]

$^1$H NMR of the reaction crude

[Chemical structure image]
4. X-ray Diffraction data for (Z)-3-phenyl-3-(phenylselanyl)acrylate (Z-8)

Table 1. Crystal data and structure refinement for mo_MGC007f1_0m.

| Identification code      | mo_MGC007f1_0m          |
|--------------------------|-------------------------|
| Empirical formula        | C17 H16 O2 Se           |
| Formula weight           | 331.26                  |
| Temperature              | 100(2) K                |
| Wavelength               | 0.71073 Å               |
| Crystal system           | Triclinic               |
| Space group              | P1                      |
| Unit cell dimensions     | a = 6.7562(4) Å, a = 107.8301(18)°. |
|                         | b = 7.5182(5) Å, b = 98.9760(17)°. |
|                         | c = 8.7692(5) Å, g = 113.0598(18)°. |
| Volume                   | 370.28(4) Å³            |
| Z                        | 1                       |
| Density (calculated)     | 1.486 Mg/m³             |
| Absorption coefficient   | 2.533 mm⁻¹              |
| F(000)                   | 168                     |
| Crystal size             | 0.20 x 0.10 x 0.10 mm³  |
| Theta range for data collection | 2.571 to 28.312°.         |
| Index ranges             | -8≤h≤8, -8≤k≤9, -11≤l≤11 |
| Reflections collected    | 4368                    |
| Completeness to theta =28.312° | 96.6%             |
| Absorption correction    | Multi-scan              |
| Max. and min. transmission | 0.786 and 0.652          |
| Refinement method        | Full-matrix least-squares on F² |
| Data / restraints / parameters | 2430/ 3/ 182           |
| Goodness-of-fit on F²    | 1.303                   |
| Final R indices [I>2sigma(I)] | R1 = 0.0187, wR2 = 0.0573 |
| R indices (all data)     | R1 = 0.0198, wR2 = 0.0729 |
| Flack parameter          | x =-0.022(8)            |
| Largest diff. peak and hole | 0.446 and -0.409 e.Å⁻³  |
Table 2. Bond lengths [Å] and angles [°] for mo_MGC007f1_0m.

| Bond lengths---- |          |
|------------------|----------|
| C1-C2            | 1.342(6) |
| C1-C6            | 1.483(5) |
| C1-Se1           | 1.910(4) |
| C2-C3            | 1.469(5) |
| C3-O1            | 1.226(5) |
| C3-O2            | 1.341(5) |
| C4-O2            | 1.451(4) |
| C4-C5            | 1.505(6) |
| C6-C7            | 1.398(6) |
| C6-C11           | 1.400(5) |
| C7-C8            | 1.399(5) |
| C8-C9            | 1.378(6) |
| C9-C10           | 1.391(6) |
| C10-C11          | 1.390(5) |
| C12-C13          | 1.394(6) |
| C12-C17          | 1.395(6) |
| C12-Se1          | 1.927(4) |
| C13-C14          | 1.389(6) |
| C14-C15          | 1.388(6) |
| C15-C16          | 1.388(7) |
| C16-C17          | 1.390(6) |

| Angles---------- |        |
|------------------|--------|
| C2-C1-C6         | 120.0(3)|
| C2-C1-Se1        | 122.1(3)|
| C6-C1-Se1        | 118.0(3)|
| C1-C2-C3         | 122.8(4)|
| O1-C3-O2         | 123.3(3)|
| O1-C3-C2         | 124.7(4)|
| O2-C3-C2         | 112.0(3)|
| O2-C4-C5         | 107.5(3)|
| C7-C6-C11        | 119.5(3)|
| C7-C6-C1         | 119.8(4)|
| C11-C6-C1        | 120.7(4)|
| C6-C7-C8         | 119.6(4)|
| Bond             | Angle (°) |
|------------------|-----------|
| C9-C8-C7         | 120.3(4)  |
| C8-C9-C10        | 120.7(4)  |
| C11-C10-C9       | 119.5(4)  |
| C10-C11-C6       | 120.5(4)  |
| C13-C12-C17      | 120.0(4)  |
| C13-C12-Se1      | 121.6(3)  |
| C17-C12-Se1      | 118.3(3)  |
| C14-C13-C12      | 119.9(4)  |
| C15-C14-C13      | 119.7(4)  |
| C14-C15-C16      | 120.7(4)  |
| C15-C16-C17      | 119.7(4)  |
| C16-C17-C12      | 120.0(4)  |
| C3-O2-C4         | 116.1(3)  |
| C1-Se1-C12       | 99.41(16) |
| Bond                  | Torsion Angle [°] |
|----------------------|-------------------|
| C6-C1-C2-C3          | 179.5(4)          |
| Se1-C1-C2-C3         | -0.5(6)           |
| C1-C2-C3-O1          | 4.8(7)            |
| C1-C2-C3-O2          | -173.7(4)         |
| C2-C1-C6-C7          | -64.9(6)          |
| Se1-C1-C6-C7         | 115.1(4)          |
| C2-C1-C6-C11         | 114.9(5)          |
| Se1-C1-C6-C11        | -65.1(5)          |
| C11-C6-C7-C8         | 0.2(6)            |
| C1-C6-C7-C8          | -180.0(4)         |
| C6-C7-C8-C9          | -0.1(7)           |
| C7-C8-C9-C10         | -0.4(7)           |
| C8-C9-C10-C11        | 0.9(7)            |
| C9-C10-C11-C6        | -0.9(6)           |
| C7-C6-C11-C10        | 0.3(6)            |
| C1-C6-C11-C10        | -179.5(4)         |
| C17-C12-C13-C14      | -3.0(6)           |
| Se1-C12-C13-C14      | -179.8(3)         |
| C12-C13-C14-C15      | 2.8(6)            |
| C13-C14-C15-C16      | -0.6(6)           |
| C14-C15-C16-C17      | -1.3(7)           |
| C15-C16-C17-C12      | 1.1(7)            |
| C13-C12-C17-C16      | 1.1(6)            |
| Se1-C12-C17-C16      | 178.0(3)          |
| O1-C3-O2-C4          | 0.6(6)            |
| C2-C3-O2-C4          | 178.0(3)          |
| C5-C4-O2-C3          | -178.6(4)         |
5. **Kinetic Studies**

Experimental Kinetic study of the *anti*-3,4-selenoboration of ethyl phenylpropiolate (1) with PhSe-Bpin.

Inside the glovebox, Stock solutions of Naphthalene (0.0483 M) and Tricyclohexylphosphine (0.09 M) were prepared in THF-\(d_8\). Then 10 µL of Ethyl phenylpropiolate (1) (0.061 mmol) were transferred into an oven-dried NMR tube and dissolved in 0.4 mL of the Naphthalene Stock solution (0.0193 mmol), followed by the addition of 0.1 mL of the Tricyclohexylphosphine Stock solution (0.009 mmol, 15 mol%). After that, 18.9 mg of PhSe-Bpin (0.067 mmol, 1.1 eq.) were weighted in a mass vial and dissolved in 0.1 mL of THF-\(d_8\). Before starting to acquire de 1H-NMR spectrums the 0.1 mL of PhSe-Bpin solution were added to the NMR tube through a septum cap. The formation of products was followed by NMR spectroscopy.
Figure S1 Progress of the reaction between 1 and pinB-SePh in THF-\textit{d}_8 followed by $^1$H-NMR

![Figure S1](image)

Figure S2 Kinetic profile for the reaction between 1 and pinB-SePh in THF-\textit{d}_8

Figure S2 shows that under NMR experimental conditions the formation of $\beta$-selenated Z-8 product is competitive with the formation of $\alpha$-selenated product 15. In this conditions we used larger amount of THF-d8 solvent, which in addition contains a percentage of water. The water impurity provides the source of protons similar to methanol solvent that allows the reaction to proceed yielding Z-8 product. According to the Karl Fischer Titration of commercial source (205 ppm = 0.021%), which corresponds to an approximate concentration of 0.0113 M. Interestingly, the amount of formed Z-8 product is roughly the same as water impurity, which as a limiting reactant (see Figure S2). In fact, it is well known that the water present in the solvents is the responsible for the Cu-borylation/protonation of $\alpha$,$\beta$-unsaturated carbonyl compounds.\(^4\)

**Kinetic simulations of the anti-3,4-selenoboration of ethyl phenylpropionate (1) with PhSe-Bpin, using PMe$_3$ as model phosphine.**

The kinetic simulation was carried out with the Acuchem software.\(^5\) All rate constants were calculated using Eyring approximation and transition state theory using the Gibbs free-energy values on Scheme 4 and Figure 3 of the main text. The default $\Delta G$ values provided by Gaussian

\(^4\) (a) Miyaura \textit{et al.}, \textit{Chem. Lett.} 2000, 982; (b) Hosomi \textit{et al}, \textit{Tetrahedron Lett}, 2000, 41, 6821

\(^5\) W. Braun, J. T. Herron, D. K. Kahaner, \textit{Int. J. Chem. Kinet.} \textbf{1988}, 20, 51
overestimate the entropic cost for bimolecular processes and in this case it results in the overestimation of key free-energy barriers and in low conversions. In order to reduce this error and to obtain a better fit in kinetic simulations, we corrected $\Delta G$ values by changing the reference state from an ideal gas standard state of 1 atm to 1 mol$^{-1}$ at 298.15 K. As a result the simulations estimate larger yields, which are closer to experimental results. Another factor that may influence the $\Delta G$ values, and consequently kinetic simulations, is the use of model PMe$_3$ phosphine. As discussed in the main text, the replacement of PMe$_3$ by PCy$_3$ reduces the free-energy barrier of its addition to alkyne by $\sim$ 3 kcal$\cdot$mol$^{-1}$. To account for this phosphine effect we applied a constant correction to all the barriers involving the phosphine obtaining a good fit with experimental yields. The simulation was carried out concentration conditions for experimental NMR kinetic study (Figure S3).

![Graph](image)

**Figure S3.** Simulated, kinetic profile of **15** and **Z-8** for the reaction between **1** and pinB-SePh catalysed by PMe$_3$ , using the concentration and temperature conditions of experiment in NMR kinetic study described in previous section.

Additionally, we repeated the simulation in “dry THF” (no water in the simulation) introducing both the equations of $\beta$- and $\alpha$-selenoboration reactions (blue line in Figure S4) and introducing exclusively the equations of $\alpha$-selenoboration reactions (green line in Figure S4).
Under these condition the β-selenated reaction (Scheme 4) is still competitive accumulating intermediate B which cannot evolve to products in the absence of proton source. As a consequence of this off-cycle reaction, the profile of α-selenated product 15 shows a sigmoidal profile analogous to that observed in the experiments (blue line in Figure S4). Interestingly, when β-selenated reaction is removed from the kinetic model the rate of formation of 15 increases significantly and the shape of curve is not sigmoidal anymore (green line in Figure S4).

**Figure S4.** Simulated, kinetic profile of 15 and Z-8 for the reaction between 1 and pinB-SePh catalysed by PMe₃, using the concentration and temperature conditions of experiment in NMR kinetic study described in previous section but excluding the presence of water (blue line) and supposing that β-selenation reaction is not operative (green line).
6. Additional Figures of the computational study

Figure S5. Computed free-energy profile (kcal mol\(^{-1}\)) for \textit{anti}-3,4-addition of PhSe-Bpin to of \(\alpha,\beta\)-acetylenic ester adapted from the proposal for analogous \textit{anti}-selective carboboration, silaboration and diboration.

Figure S6. Schematic representation of the possible paths of the stereoselectivity determining step yielding \textit{anti} isomer. Relative free-energies and barriers in kcal mol\(^{-1}\).
7. Cartesian coordinates in Å and the electronic energies for the computed structures

**TS1p:** $E = -997.212131$ a.u.

|    | X      | Y      | Z      |
|----|--------|--------|--------|
| C  | -2.196761 | -1.261651 | 0.276522 |
| O  | -2.798472 | -1.196316 | 1.329756 |
| O  | -2.830128 | -1.518849 | -0.898631 |
| C  | -4.232965 | -1.739126 | -0.777895 |
| H  | -4.729643 | -0.858859 | -0.366530 |
| H  | -4.586163 | -1.941190 | -1.786036 |
| H  | -4.433335 | -2.588971 | -0.124662 |
| C  | -0.795236 | -1.113278 | 0.107752 |
| C  | 0.238551  | -0.401306 | 0.003056 |
| C  | 1.694894  | -0.580442 | -0.049031 |
| C  | 2.212211  | -1.810831 | 0.377664 |
| C  | 2.577988  | 0.390679  | -0.518503 |
| C  | 3.576523  | -2.051810 | 0.338498 |
| H  | 1.520967  | -2.562902 | 0.737663 |
| C  | 3.946251  | 0.144452  | -0.562412 |
| H  | 2.196279  | 1.342145  | -0.869113 |
| C  | 4.451535  | -1.074893 | -0.131151 |
| H  | 3.960803  | -3.006354 | 0.678043 |
| H  | 4.616362  | 0.908734  | -0.937693 |
| H  | 5.517524  | -1.265203 | -0.160920 |
| P  | 0.343439  | 1.690017  | 0.052109 |
| C  | -1.168066 | 1.756622  | 1.679795 |
| H  | -1.786003 | 0.867222  | 1.815107 |
| H  | -0.407097 | 1.770407  | 2.461993 |
| H  | -1.785284 | 2.654073  | 1.761455 |
| C  | -1.705432 | 1.798736  | -1.160205 |
| H  | -1.294460 | 2.076651  | -2.132072 |
| H  | -2.190565 | 0.827043  | -1.256954 |
| H  | -2.439117 | 2.546766  | -0.852854 |
| C  | 0.436845  | 3.361567  | -0.069893 |
| H  | 1.240880  | 3.438923  | 0.663575 |
| H  | 0.859215  | 3.501772  | -1.066205 |
| H  | -0.298014 | 4.148498  | 0.119373 |

**1P:** $E = -997.221779$ a.u.

|    | X      | Y      | Z      |
|----|--------|--------|--------|
| C  | 2.005466 | -1.116883 | -0.990502 |
| O  | 2.557188  | -0.504495 | -1.896172 |
| O  | 2.734942  | -1.827532 | -0.081275 |
| C  | 4.136460  | 1.838490  | -0.316671 |
| H  | 4.563434  | -0.836739  | -0.217919 |
| H  | 4.558586  | -2.499204  | 0.437328 |
| H  | 4.359166  | -2.208642  | -1.317737 |
| C  | 0.598500  | -1.253152  | -0.792948 |
| C  | -0.222743 | -0.301961  | -0.342395 |
| C  | -1.703667 | -0.448405  | -0.253185 |
| C  | -2.236189 | -1.653416  | -0.212764 |
| C  | -2.586678  | 0.555897  | -0.658177 |
| C  | -3.609603  | -1.838944  | 0.287030 |
| H  | -1.546254  | -2.438535  | 0.498506 |
| C  | -3.963715  | 0.372918  | -0.582689 |
| H  | -2.201414  | 1.478776  | -1.082721 |
| C  | -4.480068  | -0.824222 | -0.102398 |

45
\[
\begin{array}{l}
\text{H} & -4.004838 & -2.779944 & 0.651587 \\
\text{H} & -4.631420 & 1.159274 & -0.914890 \\
\text{H} & -5.551770 & -0.970276 & -0.042113 \\
\text{P} & 0.484595 & 1.299433 & 0.117895 \\
\text{C} & 0.790096 & 2.330500 & -1.342238 \\
\text{H} & 1.407352 & 1.728347 & -2.014338 \\
\text{H} & -0.151347 & 2.570656 & -1.836660 \\
\text{H} & 1.310043 & 3.249750 & -1.065467 \\
\text{C} & 2.105483 & 1.096798 & 0.910461 \\
\text{H} & 2.091737 & 0.218541 & 1.555399 \\
\text{H} & 2.861246 & 0.956737 & 0.885443 \\
\text{H} & -0.645563 & 1.670474 & 2.202329 \\
\text{H} & 0.015648 & 3.192109 & 1.547715 \\
\end{array}
\]

\[
\text{TS}^\circ: \ E = -4041.629217 \text{ a.u.}
\]

\[
\begin{array}{l}
\text{C} & 0.334436 & 1.297885 & 1.659562 \\
\text{O} & 1.366010 & 0.766805 & 1.190420 \\
\text{O} & 0.455181 & 2.174329 & 2.697977 \\
\text{C} & 1.760528 & 2.288965 & 3.256298 \\
\text{H} & 2.457386 & 2.726205 & 2.538775 \\
\text{H} & 1.652272 & 2.940831 & 4.120287 \\
\text{H} & 2.136988 & 1.312351 & 3.563589 \\
\text{C} & -0.961289 & 0.985642 & 1.294753 \\
\text{C} & -1.832473 & 1.263871 & 0.344291 \\
\text{C} & -3.074695 & 0.495754 & 0.078102 \\
\text{C} & -3.757205 & -0.081179 & 1.152074 \\
\text{C} & -3.525197 & 0.245063 & -1.219340 \\
\text{C} & -4.876786 & -0.868986 & 0.931602 \\
\text{H} & -3.375006 & 0.082530 & 2.152962 \\
\text{C} & -4.649964 & -0.543457 & -1.439917 \\
\text{H} & -2.960610 & 0.614559 & -2.068442 \\
\text{C} & -5.333544 & -1.096535 & -0.364427 \\
\text{H} & -5.391329 & -1.316606 & 1.773858 \\
\text{H} & -4.978961 & -0.739889 & -2.453745 \\
\text{H} & -6.208452 & -1.712840 & -0.534110 \\
\text{P} & -1.391036 & 2.732908 & -0.624870 \\
\text{C} & 0.234585 & 2.622125 & -1.409054 \\
\text{H} & 0.970223 & 2.224700 & -0.706413 \\
\text{H} & 0.184699 & 1.940409 & -2.257188 \\
\text{H} & 0.528871 & 3.619475 & -1.743646 \\
\text{C} & -1.312584 & 4.109892 & 0.552504 \\
\text{H} & -2.309423 & 4.277695 & 0.962893 \\
\text{H} & -0.641164 & 3.835807 & 1.367970 \\
\text{H} & -0.959156 & 5.015241 & 0.055968 \\
\text{C} & -2.564774 & 3.285775 & -1.904863 \\
\text{H} & -2.462429 & 2.678356 & -2.803181 \\
\text{H} & -3.584340 & 3.194005 & -1.528212 \\
\text{H} & -2.356102 & 4.328559 & -2.151966 \\
\text{Se} & 0.220082 & -0.956537 & -1.397439 \\
\text{B} & 1.896355 & -0.471074 & -0.400734 \\
\text{O} & 2.613584 & -1.373466 & 0.355261 \\
\text{O} & 2.706214 & 0.403192 & -1.105340 \\
\text{C} & 3.987914 & -1.255585 & -0.062034 \\
\text{C} & 4.053141 & 0.205290 & -0.620668 \\
\end{array}
\]
| atom | x   | y   | z   |
|------|-----|-----|-----|
| C    | 4.889032 | -1.519118 | 1.132292 |
| H    | 4.773700  | -2.557502 | 1.447556  |
| H    | 5.937222  | -1.353233 | 0.867582  |
| C    | 4.626892  | -0.875559 | 1.971159  |
| C    | 4.213851  | -2.309204 | -1.145264 |
| H    | 5.254326  | -2.330757 | -1.477621 |
| H    | 3.953300  | -3.285703 | -0.734544 |
| H    | 3.566610  | -2.121713 | -2.004723 |
| C    | 4.328898  | 1.240727  | 0.467012  |
| H    | 5.370166  | 1.195970  | 0.795469  |
| H    | 6.033478  | 1.441819  | -2.098861 |
| C    | 4.728863  | -0.222211 | -2.634859 |
| H    | -0.759111 | -2.015658 | -0.134020 |
| H    | -0.404280 | -2.104915 | 1.210496  |
| C    | -1.894953 | -2.680750 | -0.598356 |
| C    | -1.188130 | -2.860374 | 2.077228  |
| H    | 0.477883  | -1.595291 | 1.576961  |
| C    | -2.672150 | -3.429258 | 0.275629  |
| H    | -2.173647 | -2.607299 | -1.643633 |
| C    | -2.321946 | -3.521122 | 1.619153  |
| H    | -0.907109 | -2.924907 | 3.122107  |
| H    | -3.556686 | -3.934098 | -0.095503 |
| H    | -2.927910 | -4.104368 | 2.302515  |

C: \( \mathcal{E} = -4041.651954 \) a.u.
\[ E = -4041.647466 \text{ a.u.} \]
H 4.834213  2.156183 -0.486342
H 5.763430 -1.758544 -1.963875
P 1.280730 -2.877780  0.419836
C 0.643122 -3.236531 -1.239639
H -0.219120 -2.578120 -1.384680
H 1.406969 -3.008760 -1.984409
H 0.337170 -4.281422 -1.320632
C 0.177159 -2.803274  2.553959
H -0.944778 -2.554294  1.188245
H -0.349685 -4.201520  1.558540
C 2.547587  4.128106  0.830889
H 3.051986  4.486066 -0.065524
H 3.282950  3.682942  1.501780
H 2.068816  4.973467  1.326312
Se -0.127779  0.933006 -1.152968
B -1.764592  0.204866  0.067219
O -3.009800  0.844814 -0.113199
O -1.891041 -1.178345 -0.347684
C -3.832517 -0.009623 -0.906309
C -3.293914 -1.425633 -0.523095
C -5.286496  0.235350 -0.531426
H -5.578215  1.234998 -0.858650
H -5.942877 -0.491221 -1.019150
H -5.426320  0.176951  0.547587
C -3.611736  0.313523 -2.384912
H -4.308139 -0.237848 -3.022018
H -3.772515  1.383122 -2.530066
H -2.589146  0.085623 -2.689077
C -3.863456 -1.910887  0.811449
H -4.925225 -2.155783  0.733444
H -3.328641 -2.812315  1.121165
H -3.729545 -1.146391  1.579766
C -3.473942 -2.489251 -1.594364
H -3.075664 -3.442431 -1.235822
H -4.532856 -2.630901 -1.827483
H -2.946048 -2.215923 -2.508111
C 0.171265  2.672406 -0.405127
C -0.774596  3.291401  0.415830
C 1.363214  3.339233 -0.701130
C -0.511553  4.550511  0.947325
H -1.716522  2.798660  0.623200
C 1.612977  4.600047 -0.172335
H 2.092558  2.864127 -1.348008
C 0.679568  5.208715  0.660884
H -1.252374  5.022949  1.582506
H 2.540380  5.107490 -0.413067
H 0.875641  6.189995  1.076150

D:  \( E = -4041.674424 \) a.u.
C -0.586262 -0.699909  1.472387
O -1.697716 -0.026506  1.880018
O -0.415437 -1.823583  2.211718
C 0.716605 -1.834626  3.084208
H 0.721581 -0.934687  3.703996
H 0.597782 -2.711449  3.718286
\[ H \ 4.261149 \ -1.1210145 \ 1.156402 \\
H \ 5.023460 \ 0.328675 \ 0.711566 \\
H \ 3.349977 \ 0.290670 \ 1.318494 \\
C \ 0.689554 \ -0.707962 \ 2.260202 \\
C \ 0.686339 \ 0.681421 \ 2.147416 \\
C \ 1.559513 \ -1.328758 \ 3.155134 \\
C \ 1.549338 \ 1.441407 \ 2.931012 \\
H \ 0.005269 \ 1.159503 \ 1.450507 \\
C \ 2.419165 \ -0.562734 \ 3.937507 \\
H \ 1.566281 \ -2.410250 \ 3.238408 \\
C \ 2.415562 \ 0.824729 \ 3.830936 \\
H \ 1.535436 \ 2.522264 \ 2.840903 \\
H \ 3.095634 \ -1.052852 \ 4.628702 \\
H \ 3.081176 \ 1.420673 \ 4.444056 \\
\]

\( D^* : E = -4041.682009 \ \text{a.u.} \)

\[
\begin{array}{ccc}
C & -0.866377 & -0.036734 & -1.438096 \\
O & 0.249443 & -0.570011 & -2.038916 \\
O & -2.012921 & -0.404929 & -2.031323 \\
C & -2.245193 & -1.814093 & -2.039681 \\
H & -2.278425 & -2.192581 & -1.013277 \\
H & -3.212111 & -1.958913 & -2.515638 \\
H & -1.466977 & -2.328033 & -2.607314 \\
C & -0.771865 & 0.865599 & -0.452024 \\
C & 0.497440 & 1.468434 & -0.031115 \\
C & 1.012837 & 1.286265 & 1.317069 \\
C & 0.502406 & 0.246610 & 2.123736 \\
C & 2.043735 & 2.066718 & 1.883396 \\
C & 0.986585 & 0.013951 & 3.401532 \\
H & -0.251448 & -0.406885 & 1.703264 \\
C & 2.539102 & 1.814186 & 3.155752 \\
H & 2.475743 & 2.893182 & 1.330290 \\
C & 2.015763 & 0.787597 & 3.934068 \\
H & 0.565521 & -0.798666 & 3.984828 \\
H & 3.336123 & 2.437630 & 3.545961 \\
H & 2.394935 & 0.598948 & 4.930497 \\
P & 1.222804 & 2.567174 & -1.139128 \\
C & 1.172595 & 4.353756 & -0.717404 \\
O & 0.126289 & 4.664522 & -0.728134 \\
H & 1.568607 & 4.528047 & 0.281906 \\
H & 1.737373 & 4.942871 & -1.443268 \\
C & 0.389559 & 2.503064 & -2.746217 \\
H & 0.522183 & 1.516869 & -3.189898 \\
H & -0.675429 & 2.695185 & -2.609444 \\
H & 0.822925 & 3.267405 & -3.393401 \\
C & 2.978567 & 2.214092 & -1.481604 \\
H & 3.543650 & 2.201376 & -0.549287 \\
H & 3.031223 & 1.219761 & -1.930882 \\
H & 3.400424 & 2.961732 & -2.155953 \\
Se & -2.385763 & 1.590501 & 0.361160 \\
B & 1.195774 & -1.203547 & -1.273849 \\
O & 2.504376 & -1.260538 & -1.670283 \\
O & 0.918092 & -1.939993 & -0.157442 \\
C & 3.221723 & -1.941470 & -0.610023 \\
C & 2.083579 & -2.761692 & 0.087060 \\
C & 4.322572 & -2.784177 & -1.229884 \\
H & 5.067803 & -2.129014 & -1.684223 \\
\end{array}
\]

52
|   | E 4.817335 | -3.386377 | -0.463333 |
|---|------------|----------|----------|
| H | 3.931453   | -3.445115 | -2.002440 |
| C | 3.810323   | -0.870069 | 0.301746  |
| H | 4.407752   | -1.316076 | 1.099622  |
| H | 4.458341   | -0.222219 | -0.292336 |
| H | 3.023855   | -0.260815 | 0.754303  |
| C | 1.821341   | -4.102541 | -0.594950 |
| H | 2.633081   | -4.809439 | -0.411697 |
| H | 0.895936   | -4.520233 | -0.195521 |
| H | 1.703631   | -3.975935 | -1.673874 |
| C | 2.261213   | -2.947490 | 1.582672  |
| H | 1.414133   | -3.511813 | 1.978016  |
| H | 3.175243   | -3.511872 | 1.787561  |
| H | 2.305684   | -1.989972 | 2.099338  |
| C | -3.486481  | 0.011831  | 0.499788  |
| C | -4.543684  | -0.193689 | -0.384714 |
| C | -3.224822  | -0.925438 | 1.497347  |
| C | -5.329109  | -1.336214 | -0.275428 |
| H | -4.728140  | 0.531387  | -1.167820 |
| C | -4.002984  | -2.075805 | 1.593316  |
| H | -2.418800  | -0.746634 | 2.199083  |
| C | -5.055001  | -2.282861 | 0.707567  |
| H | -6.151272  | -1.491171 | -0.964672 |
| H | -3.792333  | -2.803722 | 2.368053  |
| H | -5.664159  | -3.175524 | 0.786681  |

### TDOH-: \( E = -4041.677367 \, \text{a.u.} \)

|   | C  -0.330836 | 0.904208 | -1.840888 |
|---|-------------|---------|----------|
| O | 0.955723    | 0.677348 | -2.170205 |
| O | -1.134913   | 1.102411 | -2.892751 |
| C | -0.741315   | 0.500694 | -4.123998 |
| H | -0.600296   | -0.575836 | -3.999469 |
| H | -1.561170   | 0.692148 | -4.812029 |
| H | 0.179558    | 0.944368 | -4.501253 |
| C | -0.713094   | 1.008384 | -0.552163 |
| C | 0.334148    | 0.949405 | 0.497103  |
| C | 0.202012    | -0.043655 | 1.571130 |
| C | -0.549857   | -1.212745 | 1.340619 |
| C | 0.805836    | 0.069358 | 2.838321  |
| C | -0.695610   | -2.189050 | 2.312933 |
| H | -1.002659   | -1.357423 | 0.369088 |
| C | 0.676448    | -0.921944 | 3.805595  |
| H | 1.397459    | 0.942793 | 3.092300  |
| C | -0.081010   | -2.059728 | 3.556722 |
| H | -1.293038   | -3.066271 | 2.088958 |
| H | 1.164478    | -0.792320 | 4.765331 |
| H | -0.192878   | -2.825515 | 4.314316 |
| P | 0.968279    | 2.530719 | 0.856202 |
| C | 0.142164    | 3.472911 | 2.192772 |
| H | 0.611757    | 4.447617 | 2.339753 |
| H | -0.904700   | 3.601180 | 1.911384 |
| H | 0.174674    | 2.902816 | 3.121346 |
| C | 0.822910    | 3.594604 | -0.604980 |
| H | 1.318762    | 3.110606 | -1.447650 |
| H | -0.227069   | 3.751733 | -0.851125 |
| H | 1.300329    | 4.552791 | -0.393633 |
| C | 2.744915    | 2.593721 | 1.249756 |

|   | P 0.968279 | 2.530719 | 0.856202 |
|---|------------|----------|----------|
| C | 0.142164   | 3.472911 | 2.192772 |
| H | 0.611757   | 4.447617 | 2.339753 |
| H | -0.904700  | 3.601180 | 1.911384 |
| H | 0.174674   | 2.902816 | 3.121346 |
| C | 0.822910   | 3.594604 | -0.604980 |
| H | 1.318762   | 3.110606 | -1.447650 |
| H | -0.227069  | 3.751733 | -0.851125 |
| H | 1.300329   | 4.552791 | -0.393633 |
| C | 2.744915   | 2.593721 | 1.249756 |

53
|    |    |    |    |    |
|----|----|----|----|----|
| H  | 2.979927 | 2.018263 | 2.143360 |
| H  | 3.281649 | 2.163245 | 0.402647 |
| H  | 3.043161 | 3.633085 | 1.400849 |
| Se | -2.554828 | 1.460600 | -0.150990 |
| B  | 1.727917 | -0.097515 | -1.286787 |
| O  | 3.067466 | 0.177815 | -1.139923 |
| O  | 1.393949 | -1.388615 | -0.976021 |
| C  | 3.670882 | -0.960541 | -0.484831 |
| C  | 2.610504 | -2.108391 | -0.709181 |
| C  | 5.024950 | -1.216096 | -1.130231 |
| H  | 5.678893 | -0.363000 | -0.940671 |
| H  | 5.490778 | -2.107542 | -0.702149 |
| H  | 4.937127 | -1.345429 | -2.207949 |
| C  | 3.862517 | -0.609855 | 0.986676 |
| H  | 4.317720 | -1.439454 | 1.531202 |
| H  | 4.526739 | 0.253625 | 1.061752 |
| H  | 2.908066 | -0.369619 | 1.456612 |
| C  | 2.892564 | -2.947631 | -1.954082 |
| H  | 3.791605 | -3.556461 | -1.837547 |
| H  | 2.041198 | -3.608669 | -2.123064 |
| H  | 3.008077 | -2.310956 | -2.833816 |
| C  | 2.391205 | -3.008581 | 0.497015 |
| H  | 1.609496 | -3.732890 | 0.260332 |
| H  | 3.307058 | -3.554401 | 0.741054 |
| H  | 2.063300 | -2.441111 | 1.368735 |
| C  | -3.364414 | -0.289418 | -0.158872 |
| C  | -3.248790 | -1.109887 | -1.279579 |
| C  | -4.059117 | -0.734040 | 0.962706 |
| C  | -3.805422 | -2.383686 | -1.263258 |
| H  | -2.718183 | -0.747352 | -2.152048 |
| C  | -4.633582 | -2.001277 | 0.963690 |
| C  | -4.121534 | -0.102774 | 1.840786 |
| C  | -4.501072 | -2.831578 | -0.143889 |
| C  | -3.703737 | -3.024482 | -2.131502 |
| H  | -5.167775 | -2.346075 | 1.841338 |
| H  | -4.937807 | -3.823052 | -0.136003 |

E: $E = -4041.699920$ a.u.

|    |    |    |    |
|----|----|----|----|
| C  | -0.221848 | -1.843487 | -1.160123 |
| O  | -1.469099 | -1.457722 | -1.263428 |
| O  | 0.216488 | -2.759961 | -2.020410 |
| C  | -0.677173 | -3.128087 | -3.070154 |
| H  | -0.947937 | -2.258432 | -3.669757 |
| H  | -0.130238 | -3.849245 | -3.672068 |
| H  | -1.584011 | -3.579794 | -2.667048 |
| C  | 0.530563 | -1.303931 | -0.156221 |
| C  | -0.323847 | -0.326230 | 0.631958 |
| C  | 0.380923 | 0.969062 | 0.989521 |
| C  | 0.812432 | 1.785635 | -0.066821 |
| C  | 0.684550 | 1.384259 | 2.287708 |
| C  | 1.505412 | 2.960979 | 0.170985 |
| H  | 0.598091 | 1.482380 | -1.081400 |
| C  | 1.379768 | 2.569336 | 2.530622 |
| H  | 0.397708 | 0.792622 | 3.148918 |
| C  | 1.793478 | 3.363317 | 1.473658 |
| H  | 1.834948 | 3.560724 | -0.669418 |
| H  | 1.598914 | 2.859105 | 3.551783 |
H  2.339088  4.281216  1.657572
P  -0.967838  -1.264359  2.055391
C   0.333650  -1.981392   3.110806
H   0.828760   -2.779678  2.558367
H   1.086051  -1.242697   3.792077
H  -0.128854  -2.395113   4.009151
C  -1.900107  -2.710184   1.487499
H  -2.753032  -2.375679   0.899362
H  -1.250253  -3.342035   0.881901
C   2.231219  -3.264660   2.368311
C   -2.116673 -0.354429   3.135139
C   -1.810561   0.685378   2.654923
H   0.309321  -0.384318   1.048274
H  -2.154485  -0.830596   4.116369
Se  2.330375  -1.765970   0.202997
B  -1.659891  -0.171743  -0.428473
O   -1.607512   0.978769  -1.272445
C   -3.629424  1.040222  -0.148274
H   -3.831204  3.036914   0.709611
H   -3.704903  1.731951   1.891207
C   -5.520865   0.549485   0.752295
H   -5.648821  1.666808  -0.614695
H   -5.335438  -0.059656  -0.897769
C   -3.334956  2.088583   0.927529
H   -3.812041  3.036914   0.709611
H   -3.704903  1.731951   1.891207
C   -2.257489  2.264840   1.003859
C   -3.527395   0.605885  -2.671203
H   -4.524327   0.959779  -2.946200
H   -2.864048   0.725527  -3.530006
H   -3.577550  -0.456318  -2.424280
C   -2.933885   2.889829  -1.831436
H   -2.472269  3.038636  -2.809653
H   -3.950259  3.292973  -1.866881
H   -2.352261   3.443664  -1.094463
C   3.230534  -0.226263  -0.545707
C   4.066951   0.541417   0.257180
C   3.032161   0.114900  -1.881482
C   4.704651  1.657425  -0.277582
H   4.193482   0.285917   1.302703
C   3.657690   1.239006  -2.405629
H   2.374461  -0.491889  -2.494250
C   4.497310  2.010973  -1.605415
H   5.346417   2.261898   0.352840
H   3.495874   1.509576  -3.442688
H   4.986087   2.885828  -2.017770

**TS**: $E = -4041.674127$ a.u.
C  -0.377087  -1.561155  -1.591987
O  -1.517621  -1.003409  -1.629635
O  -0.060342  -2.465468  -2.488204
C  -1.037708  -2.734205  -3.501818
H  -1.264652  -1.824276  -4.056182
H  -0.582265   3.478374  -4.148131
H  -1.950441  -3.120396  -3.048524
C   0.514233  -1.183629  -0.555072
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| C       | -0.125803 | -0.239138 | 0.247986 |
| C       | 0.663982  | 0.675315  | 1.120908  |
| C       | 0.856511  | 1.988768  | 0.675279  |
| C       | 1.314529  | 0.263960  | 2.285835  |
| C       | 1.670164  | 2.862450  | 1.388560  |
| H       | 0.373933  | 2.306986  | -0.240194 |
| C       | 2.111396  | 1.145470  | 3.006406  |
| H       | 1.216562  | -0.760152 | 2.619396  |
| C       | 2.292642  | 2.449849  | 2.560690  |
| H       | 1.816531  | 3.871584  | 1.913576  |
| C       | -0.327287 | -2.804686 | 2.356400  |
| H       | 0.023278  | -2.290135 | 3.831553  |
| C       | -0.892757 | -3.693189 | 3.240995  |
| C       | -2.165403 | -2.893608 | 0.799910  |
| H       | -2.922233 | -2.383571 | 0.204748  |
| H       | -1.412828 | -3.324547 | 0.133946  |
| C       | -2.734839 | -1.265827 | 3.069233  |
| H       | -2.380858 | -0.562924 | 3.825128  |
| C       | -3.522785 | -0.789942 | 2.485453  |
| H       | -3.122101 | -2.162463 | 3.560127  |
| Se      | 2.296933  | -1.845313 | -0.407862 |
| B       | -1.525915 | 0.186911  | -0.521427 |
| O       | -2.774907 | 0.114133  | 0.175203  |
| O       | -1.462167 | 1.441045  | -1.193034 |
| C       | -3.392204 | 1.403086  | 0.099216  |
| C       | -2.786691 | 1.978078  | -1.219012 |
| C       | -4.903078 | 1.229871  | 0.080542  |
| H       | -5.240369 | 0.841872  | 1.044608  |
| H       | -5.400521 | 2.188502  | -0.091850 |
| H       | -5.206424 | 0.527990  | -0.695749 |
| C       | -2.963323 | 2.205747  | 1.328829  |
| C       | -3.449508 | 3.183655  | 1.365042  |
| H       | -3.241482 | 1.649378  | 2.226630  |
| H       | -1.879570 | 2.346585  | 1.337718  |
| C       | -3.501928 | 1.447147  | -2.462789 |
| H       | -4.491707 | 1.894903  | -2.581319 |
| H       | -2.898378 | 1.694763  | -3.338100 |
| H       | -3.604334 | 0.361415  | -2.412823 |
| C       | -2.696640 | 3.495303  | -1.267045 |
| H       | -2.278331 | 3.804467  | -2.227031 |
| H       | -3.686791 | 3.947851  | -1.161882 |
| H       | -2.049146 | 3.871276  | -0.474604 |
| C       | 3.179128  | -0.153680 | -0.722097 |
| C       | 4.113388  | 0.312662  | 0.195650  |
| C       | 2.861044  | 0.603349  | -1.847517 |
| C       | 4.733486  | 1.541169  | -0.015749 |
| H       | 4.330657  | -0.264746 | 1.086373  |
| C       | 3.472492  | 1.834388  | -2.044540 |
| H       | 2.124365  | 0.236369  | -2.552987 |
| C       | 4.411853  | 2.304915  | -1.130564 |
| H       | 5.451880  | 1.908496  | 0.707807  |
| H       | 3.216089  | 2.426503  | -2.915174 |
H 4.886527 3.266343 -1.286217

$T_{\text{SDF}}$: $E = -7086.061572$ a.u.

C  \ -1.031434  -0.699185  0.519940
O  \ -2.176506  -0.902818  1.234732
O  \ -0.161268  -1.716570  0.605801
C  \ -0.729393  -3.013980  0.802530
H  \ -1.535145  -3.191273  0.083209
H  \  0.078003  -3.721501  0.633752
H  \ -1.108445  -3.120817  1.819120
C  \ -0.766322  0.424001  -0.175084
C  \  0.415836  0.639162  -1.057830
C  \  0.906440  2.031093  -1.078914
C  \  0.911176  2.748441  0.132008
C  \  1.309703  4.103062  -2.226556
C  \  1.206621  4.103062  0.180016
C  \  0.653244  2.223468  1.044275
C  \  1.625206  4.091599  -2.175270
H  \  1.559580  2.249550  -3.192832
C  \  1.557011  4.794240  -0.977297
H  \  1.158319  4.618927  1.133476
H  \  1.916107  4.601534  -3.087018
H  \  1.782719  5.852964  -0.944410
P  \  0.128959  -0.115295  -2.614569
C  \ -1.118499  0.728813  -3.662469
H  \ -0.874763  1.786848  -3.760179
H  \ -1.175137  0.262741  -4.648588
H  \ -2.086606  0.639346  -3.164269
C  \ -0.564718  -1.779944  -2.454303
H  \  0.105907  -2.392300  -1.853001
H  \ -1.550784  -1.716409  -1.991080
H  \ -0.657344  -2.200113  -3.458345
C  \  1.640183  -0.267267  -3.630463
H  \  1.494469  0.216423  -4.597488
H  \  2.481194  0.191679  -3.108737
H  \  1.857385  -1.324806  -3.786465
Se  \ -2.221483  1.742608  -0.228926
B  \ -3.371475  -1.076187  0.589923
O  \ -4.535680  -1.122193  1.260531
O  \ -3.478854  -1.350186  -0.753480
C  \ -5.593430  -1.184304  0.256751
C  \ -4.836954  -1.802178  -0.969896
C  \ -6.735561  -2.032623  0.787502
H  \ -7.197499  -1.523663  1.634691
H  \ -7.496038  -2.174730  0.015060
H  \ -6.385200  -3.007443  1.124488
C  \ -6.057601  0.247244  0.006927
H  \ -6.888629  0.277776  -0.701002
H  \ -6.387375  0.673754  0.955278
H  \ -5.237355  0.860211  -0.371917
C  \ -4.801556  -3.327523  -0.937212
H  \ -5.784032  -3.755261  -1.146300
H  \ -4.099565  -3.678790  -1.696024
H  \ -4.463872  -3.687218  0.037632
C  \ -5.307359  -1.302711  -2.324136
H  \ -4.727404  -1.786866  -3.112522
H  \ -6.362081  -1.545764  -2.476697
|     | X     | Y     | Z     |
|-----|-------|-------|-------|
| H   | -5.176693 | -0.224494 | -2.410863 |
| C   | -1.983354  | 2.722792  | 1.411402  |
| C   | -1.740300  | 2.073574  | 2.620056  |
| C   | -2.072421  | 4.112756  | 1.368171  |
| C   | -1.565982  | 2.823655  | 3.778426  |
| H   | -1.687177  | 0.992543  | 2.653544  |
| C   | -1.921863  | 4.852578  | 2.536090  |
| H   | -2.227386  | 4.612649  | 0.419118  |
| C   | -1.660284  | 4.211353  | 3.742362  |
| H   | -1.366570  | 2.317473  | 4.715751  |
| C   | -1.565982  | 2.823655  | 3.778426  |
| H   | -1.989481  | 5.933607  | 2.497211  |
| C   | -2.072421  | 4.112756  | 1.368171  |
| H   | -2.227386  | 4.612649  | 0.419118  |
| C   | -1.660284  | 4.211353  | 3.742362  |
| H   | -1.366570  | 2.317473  | 4.715751  |
| C   | -1.565982  | 2.823655  | 3.778426  |
| H   | -1.989481  | 5.933607  | 2.497211  |
| C   | -2.072421  | 4.112756  | 1.368171  |
| H   | -2.227386  | 4.612649  | 0.419118  |
| C   | -1.660284  | 4.211353  | 3.742362  |
| H   | -1.366570  | 2.317473  | 4.715751  |
| C   | -1.565982  | 2.823655  | 3.778426  |
| H   | -1.989481  | 5.933607  | 2.497211  |
| C   | -2.072421  | 4.112756  | 1.368171  |
| H   | -2.227386  | 4.612649  | 0.419118  |
| C   | -1.660284  | 4.211353  | 3.742362  |
| H   | -1.366570  | 2.317473  | 4.715751  |
| C   | -1.565982  | 2.823655  | 3.778426  |
| H   | -1.989481  | 5.933607  | 2.497211  |
| C   | -2.072421  | 4.112756  | 1.368171  |
| H   | -2.227386  | 4.612649  | 0.419118  |
| C   | -1.660284  | 4.211353  | 3.742362  |
| H   | -1.366570  | 2.317473  | 4.715751  |
| C   | -1.565982  | 2.823655  | 3.778426  |
| H   | -1.989481  | 5.933607  | 2.497211  |
| C   | -2.072421  | 4.112756  | 1.368171  |
| H   | -2.227386  | 4.612649  | 0.419118  |
| C   | -1.660284  | 4.211353  | 3.742362  |
| H   | -1.366570  | 2.317473  | 4.715751  |
| C   | -1.565982  | 2.823655  | 3.778426  |
| H   | -1.989481  | 5.933607  | 2.497211  |
| C   | -2.072421  | 4.112756  | 1.368171  |
| H   | -2.227386  | 4.612649  | 0.419118  |
| C   | -1.660284  | 4.211353  | 3.742362  |
| H   | -1.366570  | 2.317473  | 4.715751  |
| C   | -1.565982  | 2.823655  | 3.778426  |
| H   | -1.989481  | 5.933607  | 2.497211  |
| C   | -2.072421  | 4.112756  | 1.368171  |
| H   | -2.227386  | 4.612649  | 0.419118  |

\[ \text{E} = -7086.08564 \text{ a.u.} \]
C 0.447612 2.986653 -1.014136
C -0.608156 3.557513 1.054488
C 0.495535 4.330013 -1.361973
H 0.810677 2.244162 -1.711534
C -0.559678 4.904711 0.711841
H -1.094271 3.277507 1.981820
C 0.003628 5.299959 -0.495721
H 0.920524 4.615480 -2.317343
H -0.973716 5.642887 1.389359
H 0.044489 6.348999 -0.763569
P 0.002893 0.789898 2.380811
C 1.065517 2.054622 3.185078
H 0.467724 2.620740 3.900989
H 1.887807 1.557856 3.697810
C 1.466339 2.735932 2.439067
C 0.713025 -0.853795 2.758077
H 1.007125 -1.385647 1.852334
H 1.578400 -0.726177 3.409459
H -0.057089 -1.440974 3.257818
C -1.509469 0.809547 3.391308
H -2.011667 1.771679 3.339403
H -2.186148 0.039031 3.026073
H -1.180326 0.596163 4.412584
Se 2.820050 0.490176 0.704403
B 2.410232 -2.229161 -1.008311
O 3.399915 -3.077056 -1.526185
O 1.951441 -2.586478 0.228075
C 3.691274 -3.991660 -0.458445
C 2.419373 -3.937682 0.453740
C 3.984722 -5.354599 -1.057606
H 4.884854 -5.295452 -1.671651
H 4.154887 -6.089885 -0.266675
H 3.162729 -5.695114 -1.685972
C 4.929455 -3.419182 0.223821
H 5.295156 -4.085857 1.007688
H 5.713138 -3.293655 -0.524775
H 4.714348 -2.440509 0.659686
C 1.307364 -4.869927 -0.015117
H 1.553199 -5.914895 0.186325
H 0.388109 -4.607619 0.511220
H 1.126961 -4.751536 -1.086275
C 2.683730 -4.115433 1.937775
H 1.737273 -4.060893 2.479692
H 3.135023 -5.091981 2.132115
H 3.346542 -3.337155 2.316726
C 3.415488 2.064892 -0.249100
C 3.582099 2.002786 -1.631576
C 3.662772 3.250498 0.434532
C 3.963828 3.141753 -2.329382
H 3.396428 1.070516 -2.154067
H 4.054776 4.386011 -0.269271
H 3.541534 3.292162 1.510622
C 4.197102 4.335099 -1.650316
H 4.085355 3.096226 -3.405386
H 4.235508 5.312198 0.263078
H 4.492520 5.221847 -2.198511
Se -1.617861 -1.628411 0.535766
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| B       | -1.761166 | 0.598835 | 0.101903 |
| O       | -2.617641 | 1.309155 | 1.001768 |
| O       | -2.291136 | 0.777378 | -1.203126 |
| C       | -3.820925 | 1.694333 | 0.689525 |
| C       | -3.403965 | 1.678923 | -1.173238 |
| C       | -4.910940 | 0.680313 | 0.340044 |
| H       | -5.005259 | 0.637649 | 1.777535 |
| H       | -5.877097 | 0.971511 | 0.269497 |
| O       | -4.661235 | -0.317911 | 0.334050 |
| C       | -4.235292 | 3.066491 | 0.860599 |
| H       | -5.124318 | 3.425861 | 0.334926 |
| H       | -4.479431 | 2.988242 | 1.923219 |
| H       | -3.436577 | 3.798085 | 0.739755 |
| C       | -4.490677 | 1.160281 | -2.108848 |
| C       | -5.354027 | 1.832070 | -2.098825 |
| C       | -4.097846 | 1.128486 | -3.128249 |
| H       | -4.822407 | 0.161370 | -1.833449 |
| C       | -2.933933 | 3.040391 | -1.691081 |
| H       | -2.464550 | 2.889625 | -2.665636 |
| H       | -3.773524 | 3.730647 | -1.808982 |
| H       | -2.197655 | 3.496893 | -1.032769 |
| C       | -3.286697 | -2.340929 | -0.076360 |
| C       | -3.701308 | -2.151913 | -1.396384 |
| C       | -4.092998 | -3.093579 | 0.782301 |
| C       | -4.902592 | -2.693449 | -1.842921 |
| H       | -3.093231 | -1.543064 | -2.053148 |
| C       | -5.288297 | -3.641036 | 0.329774 |
| H       | -3.779790 | -3.238070 | 1.809531 |
| H       | -5.700877 | -3.441564 | -0.984122 |
| H       | -5.215874 | -2.525666 | -2.867783 |
| H       | -5.903123 | -4.221181 | 1.008870 |
| C       | -6.635393 | -3.863478 | -1.334512 |

**TS_{E-G}: E = -7086.048128 a.u.**

| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | -0.670568 | 0.405142 | -1.302980 |
| O       | -1.650151 | 1.262028 | -1.499613 |
| O       | 0.228834  | 0.385639 | -2.238739 |
| C       | 0.378453  | 1.546453 | -3.072303 |
| H       | 0.639504  | 2.400862 | -2.445665 |
| H       | 1.195804  | 1.304039 | -3.743329 |
| H       | -0.541963 | 1.727316 | -3.624906 |
| C       | -0.681339 | -0.626688 | -0.352941 |
| C       | 0.499407  | -1.235732 | 0.089935 |
| C       | 0.477680  | -2.698606 | 0.347953 |
| C       | -0.156380 | -3.490350 | -0.619538 |
| C       | 1.196266  | -3.345096 | 1.361546 |
| C       | -0.080848 | -4.877999 | -0.574107 |
| H       | -0.679214 | -3.007570 | -1.435490 |
| C       | 1.252600  | -4.730108 | 1.418244 |
| H       | 1.736187  | -2.751804 | 2.085196 |
| C       | 0.617024  | -5.504470 | 0.450241 |
| H       | -0.567296 | -5.464378 | -1.345267 |
| H       | 1.808940  | -5.208897 | 2.215817 |
| H       | 0.674008  | -6.585660 | 0.492348 |
| P       | 0.392722  | -0.498246 | 2.800184 |
| C       | -0.403044 | -1.741501 | 3.912531 |
| H       | -0.462641 | -1.368902 | 4.938766 |
C  4.953725  -1.005323  -2.053222
H  5.886331  -1.553837  -1.892114
H  4.638328  -1.166887  -3.086894
H  5.143694   0.057780  -1.911232
C  3.556886  -2.975832  -1.452018
H  3.150859  -3.099921  -2.465024
H  4.453797  -3.599285  -1.413044
H  2.810574  -3.392754  -0.774202
C  2.935280  -0.661167  -0.986972
O  -0.900042  -1.003173  -0.502882
O  -0.604867  -1.991481  -0.962150
C  -1.261441  -3.212466  -0.625196
H  -1.047372  -3.499775  -0.406622
H  -0.856900  -3.958563  -0.206209
H  -2.338760  -3.106124  -0.766101
C  -0.418198   0.322265   0.779787
C   0.715298   1.020265   0.789031
C   0.884645   2.262719   1.605127
C   1.067872   2.186490   2.987238
C   0.962745   3.504208   0.971691
C   1.304821   3.337790   3.726759
H   1.019087   2.174342   3.470900
H   1.190561   4.657121   1.716333
C   0.855550   3.551732  -0.162093
C   1.363561   4.576179   3.093603
H   1.444036   3.269621   4.799220
H   1.239785   5.618357   1.218347
H   1.547091   5.473639   3.672246
Se  -1.976296   1.049233   1.690541
B  -2.244785   -0.017766  -1.480496
O  -3.497710   0.065040  -2.017158
O  -1.378312   0.942912  -1.923310
C  -3.550011   1.336619  -2.712153
C  -2.038253   1.611897  -3.021913
C  -4.430724   1.187916  -3.939563
H  -5.459122   1.000580  -3.626633
H  -4.413226   2.105416  -4.533743
H  -4.104874   0.355891  -4.562477
C  -4.144230   3.249274  -1.737848
H  -4.264763   3.328622  -2.205591
H  -5.125103   1.991746  -1.419305
H  -3.513478   3.215187  -0.851704
C  -1.560124   0.931253  -3.010350
H  -1.967732   1.418820  -5.189049

G:  \( E = -6625.035674 \) a.u.

C  -0.661167  -0.986972   0.039226
O  -1.900042  -1.003173  -0.602882
O  -0.604867  -1.991481   0.962150
C  -1.261441  -3.212466   0.625196
H  -1.047372  -3.499775  -0.406622
H  -0.856900  -3.958563  -1.306443
H  -2.338760  -3.106124   0.766101
C  -0.418198   0.322265   0.779787
C   0.715298   1.020265   0.789031
C   0.884645   2.262719   1.605127
C   1.067872   2.186490   2.987238
C   0.962745   3.504208   0.971691
C   1.304821   3.337790   3.726759
H   1.019087   2.174342   3.470900
H   1.190561   4.657121   1.716333
C   0.855550   3.551732  -0.162093
C   1.363561   4.576179   3.093603
H   1.444036   3.269621   4.799220
H   1.239785   5.618357   1.218347
H   1.547091   5.473639   3.672246
Se  -1.976296   1.049233   1.690541
B  -2.244785   -0.017766  -1.480496
O  -3.497710   0.065040  -2.017158
O  -1.378312   0.942912  -1.923310
C  -3.550011   1.336619  -2.712153
C  -2.038253   1.611897  -3.021913
C  -4.430724   1.187916  -3.939563
H  -5.459122   1.000580  -3.626633
H  -4.413226   2.105416  -4.533743
H  -4.104874   0.355891  -4.562477
C  -4.144230   3.249274  -1.737848
H  -4.264763   3.328622  -2.205591
H  -5.125103   1.991746  -1.419305
H  -3.513478   3.215187  -0.851704
C  -1.560124   0.931253  -3.010350
H  -1.967732   1.418820  -5.189049
|  |  |  |  |
|---|---|---|---|
| H  | -0.470899 | 0.985634 | -4.336205 |
| H  | -1.848418 | -0.122361 | -4.312114 |
| C  | -1.638395 | 3.076202 | -3.007064 |
| H  | -0.571720 | 3.158450 | -3.222846 |
| H  | -2.191046 | 3.632632 | -3.768759 |
| H  | -1.825965 | 3.524023 | -2.031723 |
| C  | -2.938530 | -0.550911 | 2.177766 |
| C  | -4.086457 | -0.909810 | 1.476035 |
| C  | -2.519217 | -1.306421 | 3.270626 |
| C  | -4.818777 | -2.024595 | 3.654072 |
| C  | -1.620754 | -1.021604 | 3.804170 |
| C  | -4.398266 | -2.784744 | 2.961241 |
| C  | -5.711542 | -2.302794 | 1.328348 |
| C  | -2.911759 | -3.020196 | 4.498651 |
| Se | 0.763771 | -1.271372 | -1.426638 |
| B  | 2.094307 | 0.733603 | 0.079714 |
| O  | 2.586318 | 1.518610 | -0.933037 |
| O  | 3.084601 | 0.044311 | 0.743162 |
| O  | 3.979876 | 1.174101 | -1.102358 |
| C  | 4.346663 | 0.591775 | 0.301259 |
| C  | 4.076207 | 0.133169 | -2.214639 |
| H  | 3.568834 | 0.520355 | -3.100996 |
| H  | 5.118675 | -0.073721 | -2.467240 |
| H  | 3.595126 | -0.802293 | -1.924499 |
| C  | 4.740561 | 2.432154 | -1.485985 |
| H  | 5.816589 | 2.239130 | -1.506944 |
| H  | 4.429581 | 2.752988 | -2.481848 |
| H  | 4.537627 | 3.241646 | -0.785424 |
| C  | 5.385033 | -0.516510 | 0.285162 |
| H  | 6.325346 | -0.155855 | -0.140745 |
| H  | 5.576196 | -0.846945 | 1.307808 |
| H  | 5.037255 | -1.374380 | -0.290107 |
| C  | 4.721998 | 1.676818 | 1.308792 |
| H  | 4.762254 | 1.228410 | 2.302850 |
| H  | 5.695555 | 2.116555 | 1.081120 |
| H  | 3.967707 | 2.468595 | 1.326020 |
| C  | 1.601113 | -2.873633 | -0.776052 |
| H  | 2.163102 | -2.944143 | 0.499341 |
| C  | 1.674353 | -3.972365 | -1.633591 |
| C  | 2.776733 | -4.122290 | 0.912264 |
| H  | 2.124951 | -2.085397 | 1.155049 |
| C  | 2.308488 | -5.138443 | -1.218742 |
| H  | 1.225305 | -3.915150 | -2.618385 |
| C  | 2.854386 | -5.217680 | 0.057628 |
| H  | 3.205452 | -4.177998 | 1.906074 |
| H  | 2.363948 | -5.987288 | -1.889953 |
| H  | 3.339930 | -6.129334 | 0.384930 |

\[ \text{TS}_{Ei}: E = -6625.000863 \text{ a.u.} \]

|  |  |  |  |
|---|---|---|---|
| C  | -0.625288 | 0.197492 | 0.751037 |
| O  | -1.880631 | 0.085268 | 0.428064 |
| O  | -0.308871 | -0.024713 | 1.992939 |
| C  | -1.345126 | -0.452053 | 2.908826 |
| H  | -1.912715 | -1.280386 | 2.493337 |
H  -0.812047  -0.755328  3.804453
H  -1.993857   0.402810  3.105233
C   0.292787   1.180543  0.087465
C   1.553364   0.959623 -0.283886
C   2.446672   2.052988 -0.773903
C   2.896906   3.045175  0.099346
C   2.904549   2.045073 -2.092494
C   3.773801   4.026705 -0.343984
H   2.551549   3.040957  1.126642
C   3.769344   3.038291 -2.538183
C   4.116093   4.792329  0.342001
H   4.107622   3.032629 -3.567497
H   4.886110   4.793444 -2.013768
Se  -0.573963   2.908607 -0.083666
B  -2.080625  -0.516355 -0.919591
O  -3.287871  -1.198674 -1.082116
O  -1.810953   0.313928 -2.011361
C  -3.928526  -0.626741 -2.238453
C  -2.713795  -0.080152 -3.056775
C  -4.737698  -1.702988 -2.940964
H  -5.564847  -2.013929 -2.298879
H  -5.153612  -1.320841 -3.877395
H  -4.123555  -2.576681 -3.156836
C  -4.839973   0.494869 -1.741871
H  -5.423280   0.932810 -2.555183
H  -5.524715   0.082379 -0.999043
H  -4.247013   1.280757 -1.267643
C  -2.040695  -1.164760 -3.896741
H  -2.649643  -1.429294 -4.764359
H  -1.078872  -0.784638 -4.462427
H  -1.856978  -2.063269 -3.304898
C  -3.021072   1.137068 -3.913429
H  -2.211360   1.433567 -4.455687
H  -3.803258   0.908012 -4.642716
H  -3.339815   1.977978 -3.298425
C  -1.359189   2.946976  1.678929
C  -2.745805   2.931804  1.813159
C  -0.548876   3.003230  2.813004
C  -3.320026   2.992630  3.080330
H  -3.367933   2.858543  0.929812
C  -1.126635   3.042661  4.076358
H  0.528858   3.004471  2.702263
C  -2.512887   3.045303  4.211318
H  -4.398750   2.985999  3.180849
H  -0.494107   3.080807  4.955264
H  -2.961446   3.085988  5.196695
Se  -0.262419  -1.899071  -0.717851
B  2.357028  -0.398917  -0.184556
O  3.028141  -0.909304  -1.258044
O  2.755592  -0.944994  1.009669
C  3.863168  -1.990968  -0.778880
C  3.997876  -1.644332  0.739491
C  3.129928  -3.304526  -1.027299
H  2.848093  -3.354694  -2.080163
H  3.772728  -4.156153  -0.792267
H  2.216709  -3.374848  -0.435011
C  5.170187   -1.959970  -1.554001
H  5.878439   -2.682311  -1.139231
H  4.977456   -2.227317  -2.594285
H  5.619024  -0.967421  -1.532788
C  4.113448  -2.843889  1.663208
H  5.026831  -3.402427  1.441883
H  4.164333  -2.499652  2.697850
H  3.262376  -3.516459  1.562486
C  4.113448  -2.843889  1.663208
H  5.026831  -0.297616  2.049940
H  6.101650  -1.094450  0.884086
H  5.032892  0.225539  0.359691
C  -0.767233  -2.934450  0.812596
C  0.151338  -3.099005  1.852601
C  -2.050387  -3.473998  0.924889
C  -0.213170  -3.803695  2.995543
H  1.127575  -2.631517  1.780335
C  -2.407337  -4.169133  2.075971
H  -2.766576  -3.317264  0.126915
C  -1.492937  -4.337267  3.112673
H  0.502683  -3.924719  3.800991
H  -3.406965  -4.579040  2.163229
H  -1.777015  -4.881135  4.005682

TS1P (PCy3): E = -1583.178416

C  -2.428029  -2.073723  -0.705198
O  -2.893678  -2.554598  0.307780
O  -3.189709  -1.360268  -1.579760
C  -4.557493  -1.227478  -1.204805
H  -4.651251  -0.637696  -0.289554
H  -5.043759  -0.717843  -2.033675
H  -5.009587  -2.205176  -1.037723
C  -1.078010  -2.170362  -1.135546
C  0.064653  -1.661185  -1.100886
C  1.451212  -1.856566  -1.520736
C  2.156550  -2.973223  -1.070637
C  2.094016  -0.922472  -2.337760
C  3.494578  -3.138595  -1.414185
H  1.646883  -3.695815  -0.444486
C  3.426135  -1.094710  -2.686258
H  1.539644  -0.058605  -2.689887
C  4.133641  -2.198986  -2.215497
H  4.038872  -4.002964  -1.052729
H  3.915528  -0.368303  -3.324313
H  5.176685  -2.327673  -2.478307
P  0.141996  0.315727  0.117012
C  -0.388363  -0.097792  1.863325
C  -1.229957  1.287833  -0.672821
C  1.675498  1.363827  0.308048
C  -1.882746  0.105412  2.161464
C  0.017254  -1.547241  2.200070
H  0.180128  0.576477  2.515986
|   | X     | Y     | Z     |
|---|-------|-------|-------|
| C | -1.467872 | 2.728556 | -0.196888 |
| C | -1.123798 | 1.270504 | -2.207905 |
| H | -2.115502 | 0.690707 | -0.416823 |
| C | 1.608037 | 2.616977 | 1.198049 |
| C | 2.818673 | 0.453321 | 0.804165 |
| H | 1.913854 | 1.675229 | -0.719251 |
| C | -2.192712 | -0.232830 | 3.623797 |
| H | -2.473347 | -0.559440 | 1.523408 |
| H | -2.190240 | 1.131741 | 1.949831 |
| C | -0.287424 | -1.87028 | 3.663645 |
| H | -0.553855 | -2.225536 | 1.558460 |
| H | 1.076880 | -1.710121 | 1.977868 |
| C | -2.773547 | 3.269766 | -0.787525 |
| H | -0.644116 | 3.356625 | -0.554105 |
| H | -1.476515 | 2.800754 | 0.893129 |
| C | -2.399673 | 1.846561 | -2.835362 |
| H | -0.256387 | 1.869263 | -2.519089 |
| H | -0.974757 | 0.250242 | -2.564388 |
| C | 2.948120 | 3.364599 | 1.187505 |
| H | 1.380717 | 2.317654 | 2.22752 |
| H | 0.814883 | 3.290861 | 0.881049 |
| C | 4.158396 | 1.192932 | 0.790781 |
| H | 2.593578 | 0.140485 | 1.832502 |
| H | 2.888285 | -0.453753 | 0.200160 |
| C | -1.773114 | -1.664071 | 3.960494 |
| H | -3.261267 | -0.096117 | 3.809903 |
| H | -1.661197 | 0.467992 | 4.279822 |
| H | 0.000910 | -2.906558 | 3.87696 |
| H | 0.312962 | -1.231200 | 4.319944 |
| C | -2.722097 | 3.243854 | -2.316454 |
| H | -2.953699 | 4.286749 | -0.428999 |
| H | -3.609432 | 2.652279 | -0.436149 |
| H | -2.304127 | 1.851556 | -3.924147 |
| H | -3.223543 | 1.160104 | -2.594746 |
| C | 4.098843 | 2.464603 | 1.637403 |
| H | 2.880768 | 4.247360 | 1.829002 |
| H | 3.146495 | 3.725238 | 0.171040 |
| H | 4.949304 | 0.529656 | 1.150105 |
| H | 4.407375 | 1.451870 | -0.245542 |
| H | -1.990596 | -1.887688 | 5.008154 |
| H | -2.357950 | -2.358191 | 3.346618 |
| H | -3.668463 | 3.595040 | -2.735736 |
| H | -1.946587 | 3.941702 | -2.655164 |
| H | 5.047380 | 3.005079 | 1.584632 |
| H | 3.947583 | 2.188137 | 2.687828 |