Supporting Information

A Concise Asymmetric Total Synthesis of (+)-Epilupinine

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General Procedures and Methods
All the reactions were carried out under an argon atmosphere. Anhydrous solvents and reagents were commercial grade and used as supplied. NMR spectra were recorded on a Bruker AVANCE III 500 (500 MHz). Chemical shifts were reported in parts per million (ppm). For $^1$H NMR spectra (CDCl$_3$), the residual solvent peak was used as the internal reference (7.26 ppm), whereas the central solvent peak was used as the reference (77.0 ppm) for $^{13}$C NMR spectra. Mass spectra were recorded on a Waters/Micromass LCT PREMIER. Infrared (IR) spectra were recorded on a JASCO FT/IR-4200 spectrometer using KBr plate. Specific rotation was recorded on a JASCO P-2200 polarimeter. Analytical thin layer chromatography (TLC) was performed with E. Merck pre-coated TLC plates, silica gel 60F$_{254}$, layer thickness 0.25 mm. Reaction components were visualized by ninhydrin in 3% acetic acid in nBuOH or p-anisaldehyde in 10% sulfuric acid in ethanol. Flash column chromatography was performed on Kanto Chemical 60 N (0.04-0.05 mm) mesh silica gel. Melting point was measured with AS ONE ATM-01.

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• $^1$H NMR and $^{13}$C NMR spectra of synthetic intermediates (4, 5, 6, 7, 9, 11), (+)-epilupinine, and $^{19}$F NMR spectra of MTPA ester of (+)-epilupinine and (±)-tashiromine. S30–S44
Additional optimization for the cascade reaction

Table S1. Optimization of Cascade Reaction with Various Asymmetric Organocatalysts in MeOH

| Entry | Catalyst (mol %) | Yield (%) | Specific Rotation | ee (%) |
|-------|------------------|-----------|-------------------|--------|
| 1a    | A (10)           | 8         | +19.1             | -      |
| 2     | A (20)           | 15        | +20.4             | -      |
| 3     | A (10)           | 25        | -                 | 33     |
| 4a    | B (10)           | 6         | +17.6             | -      |
| 5a    | C (10)           | 6         | +11.2             | -      |
| 6     | C (10)           | 29        | -                 | 13     |
| 7     | G (30)           | 14        | +7.5              | <5     |
| 8a    | H (10)           | 6         | +11.4             | -      |
| 9     | H (10)           | 20        | +11.5             | -      |
| 10    | I (10)           | 17        | -                 | 37     |

Reaction Condition: 0.095 mmol of 5, 0.19 mmol of PhSH, 0.28 mmol of K₂CO₃, 2.4 mL of MeOH, 0.14 mmol of NaBH₄, *Purified by preparative thin layer chromatography
Table S2. Optimization of Cascade Reaction with Various Solvents Using Catalyst A

**Reaction Condition**: 0.095 mmol of 5, 0.019 mmol of catalyst A, 0.19 mmol of PhSH, 0.28 mmol of K$_2$CO$_3$, 2.4 mL of solvent and MeOH, 0 °C to rt; NaBH$_4$, MeOH, 0 °C to rt

| entry | solvent | yield (%) | specific rotation | ee (%) |
|-------|---------|-----------|-------------------|--------|
| 0$^a$ | MeOH    | 15        | +20.4             | -      |
| 1     | DMSO    | decomp.   | -                 | -      |
| 2     | MeCN    | n.r.      | -                 | -      |
| 3     | CHCl$_3$| 71        | +0.7              | -      |
| 4     | $^t$PrOH| $^b$      | -                 | -      |

$^a$MeOH was not added to reaction mixture in reduction. $^b$The Ns group was removed but the Mannich reaction did not proceed.
Table S3. Optimization of Cascade Reaction with Various Asymmetric Organocatalysts in CHCl₃

|| entry | catalyst (mol %) | yield (%) | specific rotation | ee (%) |
|-------|----------------|-----------|-------------------|--------|
| 0     | A (20)         | 71        | -0.7              | -      |
| 1     | B (20)         | .         | -                 | -      |
| 2     | C (20)         | 73        | +14.4             | 61     |
| 3     | C (50)         | 61        | +12.9             | 59     |
| 4     | D (20)         | 33        | -                 | <5     |
| 5     | E (20)         | 28        | -2.9              | -      |
| 6     | F (20)         | trace     | -                 | 11     |
| 7     | G (20)         | .         | -                 | -      |
| 8     | H (20)         | 57        | -9.0              | -      |
| 9     | H (100)        | 68        | -17.2             | 69     |
| 10    | D-prolinol (20) | 57        | -4.0              | -      |

Reaction Condition: 0.095 mmol of 5, 0.19 mmol of PhSH, 0.28 mmol of K₂CO₃, 2.4 mL of CHCl₃ and MeOH, 0.14 mmol of NaBH₄. * The Ns group was removed but the Mannich reaction did not proceed.
Table S4. Optimization of Cascade Reaction with Various Conditions Using Catalyst C

| entry | solvent | additive (eq) | yield (%) | specific rotation | ee (%) |
|-------|---------|---------------|-----------|--------------------|--------|
| 0     | CHCl₃   | -             | 73        | +14.4              | 61     |
| 1     | CH₂Cl₂  | -             | 29        | 10.9               | -      |
| 2     | toluene | -             | 42        | +12.4              | -      |
| 3     | Et₂O    | -             | -         | -                  | -      |
| 4     | THF     | -             | decomp.   | -                  | -      |
| 5     | CHCl₃   | AcOH (3.0)    | 49        | +5.6               | -      |
| 6     | CHCl₃   | AcOH (6.0)    | decomp.   | -                  | -      |
| 7ᵇ    | CHCl₃   | -             | 26        | +15.2              | -      |

**Reaction Condition**: 0.095 mmol of 5, 0.019 mmol of catalyst C, 0.19 mmol of PhSH, 0.28 mmol of K₂CO₃, 2.4 mL of CHCl₃ and MeOH, 0.14 mmol of NaBH₄. *= was insoluble in Et₂O, b0.095 mmol of PhSH and 0.095 mmol of K₂CO₃ were used.
Table S5. Optimization of Cascade Reaction with Various Solvents Using L-proline (I)

![Image of the reaction scheme](image)

| entry | solvent  | yield (%) | specific rotation | ee (%) |
|-------|----------|-----------|-------------------|--------|
| 0\(^a\) | MeOH | 17 | - | 37 |
| 0\(^b\) | CHCl\(_3\) | 68 | -17.2 | 69 |
| 1 | DMF | 30 | +13.5 | - |
| 2 | DMSO | decomp. | - | - |
| 3 | THF | 24 | +9.6 | - |
| 4 | 1,4-dioxane | 32 | +5.9 | - |
| 5 | AcOEt | 34 | +9.9 | - |
| 6 | MeNO\(_2\) | decomp. | - | - |

**Reaction Condition:** 0.095 mmol of 5, 0.095 mmol of L-proline (I), 0.19 mmol of PhSH, 0.28 mmol of K\(_2\)CO\(_3\), 2.4 mL of solvent and MeOH, 0.14 mmol of NaBH\(_4\). \(^a\)0.0095 mmol of L-proline (I) was used. \(^b\)D-proline (H) was used.
Table S6. Optimization of Cascade Reaction with Various Condition Using L-proline (I) in CHCl₃

**Reaction Condition:** 0.095 mmol of 5, 0.095 mmol of L-proline, 0.19 mmol of PhSH, 0.28 mmol of K₂CO₃, 2.4 mL of CHCl₃ and MeOH, 0 °C to rt

| entry | additive (eq) | temp (°C) | conc. (M) | yield (%) | specific rotation | ee (%) |
|-------|---------------|-----------|-----------|-----------|-------------------|--------|
| 0°    | -             | rt        | 0.04      | 68        | -17.2             | 69     |
| 1°    | H₂O (10)      | rt        | 0.04      | 26        | -9.8              | -      |
| 2     | MeOH (20)     | rt        | 0.04      | 30        | +11.5             | -      |
| 3     | -             | 0         | 0.04      | 61        | +18.7             | 76     |
| 4     | -             | -15       | 0.04      | 38        | +8.4              | -      |
| 5     | -             | 0         | 0.1       | 54        | +19.9             | -      |
| 6     | -             | 0         | 0.01      | 31        | +21.4             | 77     |
| 7     | -             | -15       | 0.005     | 44        | +17.3             | -      |

**Remarks:** MeOH was used.
Table S7. Optimization of Cascade Reaction with Various Bases Using L-proline (I) in CHCl₃

**Reaction Condition**: 0.095 mmol of 5, 0.095 mmol of L-proline (I), 0.19 mmol of PhSH, 0.28 mmol of Base, 2.4 mL of CHCl₃ and MeOH, 0.14 mmol of NaBH₄. a13.5 mmol of 5, 13.5 mmol of L-proline (I), 27.0 mmol of PhSH, 40.5 mmol of Cs₂CO₃, 335 mL of CHCl₃ and MeOH was used, bPhSH was not added.

| entry | base (eq)            | yield (%) | specific rotation | ee (%) |
|-------|----------------------|-----------|-------------------|--------|
| 0     | K₂CO₃ (3.0)          | 61        | +18.7             | 76     |
| 1     | Li₂CO₃ (3.0)         | n.r.      | -                 | -      |
| 2ᵃ    | Cs₂CO₃ (3.0)         | 70        | +19.2             | 83     |
| 3     | Cs₂CO₃ (1.5)         | 37        | +15.7             | -      |
| 4     | Tl₂CO₃ (3.0)         | n.r.      | -                 | -      |
| 5     | Triton B (3.0)       | 53        | +7.4              | -      |
| 6ᵇ    | Trimethyl Benzyl Ammonium salt (3.0) | 30 | - | 61 |
| 7     | Me₂NOH (3.0)         | n.r.      | -                 | -      |
Table S8. Optimization of Cascade Reaction with Various Condition Using cesium salt (J) in CHCl₃

**Reaction Condition:** 0.095 mmol of 5, 0.095 mmol of L-proline (I), 0.19 mmol of additive, 0.28 mmol of Cs₂CO₃, 2.4 mL of CHCl₃ and MeOH, 0 °C to rt.

| entry | Catalyst (mol %) | additive (2.0 eq) | yield (%) | specific rotation | ee (%) |
|-------|------------------|-------------------|-----------|-------------------|--------|
| 0ᵇ    | I (100)          | PhSH              | 70        | +19.2             | 83     |
| 1     | J (100)          | PhSH              | 35        | -                 | 92     |
| 2     | J (20)           | PhSH              | 38        | -                 | 65     |
| 3     | J (100)          | PhSCs             | ᵇ         | -                 | -      |

*b*The Ns group was removed but the Mannich reaction did not proceed.
Experimental Detail

**N,N-bis(5-hexenyl)-2-nitrobenzenesulfonamide (8)**

\[ \text{N}_2\text{N}_2 + \text{Br} \quad \text{K}_2\text{CO}_3 \quad \text{DMF, 100 °C} \quad \rightarrow \quad \text{8} \]

To a solution of 6 (7.56 g, 37.4 mmol) in DMF (375 mL) were added K\(_2\)CO\(_3\) (31.0 g, 224 mmol) and 7 (10.0 mL, 74.8 mmol) at room temperature. The reaction mixture was heated to 100 °C for 16 h. The reaction was quenched with water and the mixture was extracted with Et\(_2\)O (x3). The combined organic layers were washed with brine, dried over anhydrous MgSO\(_4\), filtered, and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (Hexane/AcOEt = 9/1 to 4/1) to give 8 (13.4 g, 36.6 mmol, 98%) as a pale yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\), \(\delta\)): 8.01 (m, 1H), 7.69-7.65 (m, 2H), 7.61 (m, 1H), 5.73 (ddt, \(J = 17.0, 10.1, 6.7\) Hz, 2H), 4.97 (dq, \(J = 17.1, 1.7\) Hz, 2H), 4.94 (ddt, \(J = 10.8, 2.1, 1.0\) Hz, 2H), 3.28 (t, \(J = 7.6\) Hz, 4H), 2.03 (q, \(J = 7.2\) Hz, 4H), 1.54 (quint, \(J = 7.7\) Hz, 4H), 1.35 (quint, \(J = 7.6\) Hz, 4H); \(^13\)C NMR (125 MHz, CDCl\(_3\), \(\delta\)): 148.1, 138.2, 133.9, 133.2, 131.5, 130.8, 124.1, 114.9, 47.0, 33.2, 27.4, 25.7; IR (KBr): 3076, 2932, 1640, 1545, 1373, 1347, 1160, 1124, 996, 912, 740 cm\(^{-1}\); HRMS-ESI (m/z): [M + H]\(^+\) calcd for C\(_{18}\)H\(_{27}\)N\(_2\)O\(_4\)S, 367.1692; found, 367.1689.

**N,N-bis(5-oxopentyl)-2-nitrobenzenesulfonamide (5)**

\[ \text{O}_3, \text{CH}_2\text{Cl}_2, -78 °C; \quad \text{PPh}_3, -78 °C \text{ to rt} \quad \rightarrow \quad \text{5} \]

Ozone was bubbled through a solution of 8 (13.4 g, 36.6 mmol) in CH\(_2\)Cl\(_2\) (200 mL) at -78 °C until the color of the solution changed to blue. After bubbling of argon until the blue color disappeared, to the mixture was added PPh\(_3\) (28.8 g, 110 mmol) at -78 °C. The mixture was stirred at room temperature for 1 h and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (CH\(_2\)Cl\(_2\)/AcOEt = 1/0 to 19/1) to give 5 (11.7 g, 31.6 mmol, 86%) as a pale yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\), \(\delta\)): 9.74 (t, \(J = 1.4\) Hz, 2H), 8.01 (m, 1H), 7.71-7.68 (m, 2H), 7.62 (m, 1H), 3.30 (t, \(J = 7.0\) Hz, 4H), 2.46 (td, \(J = 6.7, 1.3\) Hz, 4H), 1.62-1.57 (m, 8H); \(^13\)C NMR (125 MHz, CDCl\(_3\), \(\delta\)): 201.7, 148.1, 133.5, 133.4, 131.6, 130.7, 124.2, 47.0, 43.1, 27.4, 18.9; IR (KBr): 2929, 2729, 1720, 1542, 1373, 1343, 1160, 1141, 745 cm\(^{-1}\); HRMS-ESI (m/z): [M + H]\(^+\) calcd for C\(_{16}\)H\(_{23}\)N\(_2\)O\(_6\)S, 371.1277; found, 371.1278.
To a solution of 5 (5.00 g, 13.5 mmol) in CHCl₃ (335 mL) were added Cs₂CO₃ (13.2 g, 40.5 mmol), L-proline (I) (1.55 g, 13.5 mmol) and PhSH (2.76 mL, 27.0 mmol) at 0 °C, and the mixture was stirred at 0 °C for 12 h. To the mixture were added MeOH (335 mL) and NaBH₄ (766 mg, 20.2 mmol), and the mixture was stirred at room temperature for 10 min. The reaction was quenched with saturated aqueous solution of NaHCO₃, and the mixture was extracted with CHCl₃ (x3). The combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (AcOEt/MeOH = 3/1) to give 1 (1.60 g, 9.45 mmol, 70%) as a yellow oil. ¹H NMR (500 MHz, CDCl₃, δ): 3.64 (dd, J = 10.9, 3.6 Hz, 1H), 3.55 (dd, J = 10.9, 5.8 Hz, 1H), 2.85-2.75 (m, 2H), 2.06-1.98 (m, 2H), 1.89 (m, 1H), 1.83 (m, 1H), 1.76 (m, 1H), 1.72-1.65 (m, 3H), 1.63-1.56 (m, 2H), 1.41 (m, 1H), 1.29-1.14 (m, 3H); ¹³C NMR (125Hz, CDCl₃, δ): 64.6, 64.3, 56.9, 56.6, 43.9, 29.7, 28.2, 25.5, 25.0, 24.5; IR (KBr): 3351, 2928, 1443, 1370, 1113, 1092, 1069, 769 cm⁻¹; HRMS-ESI (m/z): [M + H⁺] calcd for C₁₀H₂₀NO, 170.1545; found, 170.1546; [α]D²⁹ +19.2 (c 0.60, EtOH).

Recrystallization of (+)-epilupinine (1)

Triphenylacetic acid (1.59 g, 5.52 mmol) was added to a solution of 1 (935 mg, 5.52 mmol) in CHCl₃ at room temperature, and the mixture was concentrated under reduced pressure. The residue was recrystallized from CHCl₃/Et₂O at 0 °C in closed vessel. The mixture was filtrated, and the crystals were collected. The crystals were dissolved in 1M aqueous solution of HCl, and the mixture was extracted with Et₂O (x3). To the aqueous layer was added 3M aqueous solution of NaOH, and the mixture was extracted with nBuOH (x3). The combined organic layers were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to give 1 (496 mg, 2.93 mmol, 53%, 3 cycles) as a white solid. mp 77-78 °C [lit. 1 77-79 °C]; [α]D¹⁸ +31.5 (c 0.35, EtOH) [lit. [α]D²⁰ 31.8 (c 0.60, EtOH)].
Determination of ee (epilupinine)

To a solution of 1 (2.80 mg, 0.0165 mmol) in CH$_2$Cl$_2$ (100 µL) were added NEt$_3$ (3.46 µL, 0.0248 mmol) and (S)-MTPACl (3.71 µL, 0.0198 mmol) at 0 °C. The mixture was stirred at room temperature for 12 h. The reaction was quenched with saturated aqueous solution of NaHCO$_3$ and the mixture was extracted with AcOEt (x3). The combined organic layers were dried over anhydrous MgSO$_4$, filtered, and concentrated under reduced pressure. The residue was measured by $^{19}$F NMR without further purification, and the ee was determined by the integration ratio of the CF$_3$ peaks.

Benzyltrimethylammonium L-prolinate (S3)

To a 40% solution of benzyltrimethylammonium hydroxide (Triton B) in methanol (363 µL, 0.869 mmol) was added L-proline (I) (100 mg, 0.869 mmol) at room temperature. The mixture was stirred at room temperature for 1 h and concentrated under reduced pressure. The residue was used without further purification.

Benzyltrimethylammonium thiophenoate (S5)

To a 40% solution of benzyltrimethylammonium hydroxide (Triton B) in methanol (363 µL, 0.869 mmol) was added PhSH (88.8 µL, 0.869 mmol) at room temperature. The mixture was stirred at room temperature for 1 h and concentrated under reduced pressure. The residue was used without further purification.
Cesium L-prolineate (J)

\[
\begin{array}{c}
\text{OH} \\
\text{I} \\
\text{Cs}_2\text{CO}_3 \\
\text{H}_2\text{O}, \text{rt} \\
\text{OCs} \\
\text{J}
\end{array}
\]

To a solution of L-proline (I) (5.00 g, 43.4 mmol) in H₂O (45 mL) was added Cs₂CO₃ (7.08 g, 21.7 mmol) at room temperature, and the mixture was stirred at room temperature for 1 h. The mixture was concentrated under reduced pressure. The residue was used without further purification.

Cesium thiophenoate (S6)

\[
\begin{array}{c}
\text{PhSH} \\
\text{S4} \\
\text{Cs}_2\text{CO}_3 \\
\text{H}_2\text{O}, \text{rt} \\
\text{PhSCs} \\
\text{S6}
\end{array}
\]

To a solution of PhSH (500 µL, 4.86 mmol) in MeOH (25 mL) was added Cs₂CO₃ (796 mg, 2.44 mmol) at room temperature, and the mixture was stirred at room temperature for 1 h. The mixture was concentrated under reduced pressure. The residue was used without further purification.

\(N\)-(4-oxobutyl)-\(N\)-(5-oxopentyl)-2-nitrobenzenesulfonamide (9)

pale yellow oil; \(^1\)H NMR (500 MHz, CDCl₃, \(\delta\)): 9.77 (s, 1H), 9.64 (t, \(J = 1.4\) Hz, 1H), 8.03 (m, 1H), 7.74-7.71 (m, 2H), 7.65 (m, 1H), 3.35 (t, \(J = 7.4\) Hz, 2H), 3.34 (t, \(J = 7.1\) Hz, 2H), 2.56 (td, \(J = 7.0, 0.6\) Hz, 2H), 2.51-2.47 (m, 2H), 1.89 (quint, \(J = 7.1\) Hz, 2H), 1.64-1.59 (m, 4H); \(^{13}\)C NMR (125 MHz, CDCl₃, \(\delta\)): 201.7, 200.9, 148.0, 133.6, 133.2, 131.7, 130.7, 124.1, 47.0, 46.4, 43.0, 40.4, 27.4, 20.4, 18.9; IR (KBr): 2942, 2732, 1720, 1543, 1373, 1342, 1161, 1142, 745 cm\(^{-1}\); HRMS-ESI (m/z): [M + H]\(^+\) calcd for C₁₅H₂₁N₂O₆S, 357.1120; found, 357.1118.

\(N,N\)-bis(4-oxobutyl)-2-nitrobenzenesulfonamide (11)

pale yellow oil; \(^1\)H NMR (500 MHz, CDCl₃, \(\delta\)): 9.74 (s, 2H), 8.01 (m, 1H), 7.72-7.68 (m, 2H), 7.63 (m, 1H), 3.34 (t, \(J = 7.4\) Hz, 4H), 2.53 (td, \(J = 7.0, 0.6\) Hz, 4H), 1.88 (quint, \(J = 7.2\) Hz, 4H); \(^{13}\)C NMR (125 MHz, CDCl₃, \(\delta\)): 201.1, 148.2, 133.9, 133.3, 132.0, 131.1, 124.4, 46.8, 40.7, 20.7; IR (KBr): 2942, 2732, 1720, 1543, 1373, 1342, 1161, 1134, 755 cm\(^{-1}\); HRMS-ESI (m/z): [M + Na]\(^+\) calcd for C₁₄H₁₈N₂O₆SNa, 365.0783; found, 365.0786.

Reference
1. Su, D.; Wang, X.; Shao, C.; Xu, J.; Zhu, R.; Hu, Y. *J. Org. Chem.* 2011, 76, 188-194.
Computational Detail

Density functional theory calculations were performed with Gaussian 09 suite of programs.\textsuperscript{1} Geometries of all the molecules and transition states in the cationic form were optimized without any symmetry constrains using the B3LYP method combined with the 6-31G*(d,p) basis set. Vibrational analyses were performed at the same level of theory on all optimized geometries, to ensure that the optimized structures corresponded to local minima. The relative free energy ($\Delta G$) obtained from vibrational frequency calculation was reported in kcal/mol anywhere in the discussion.

Figure S1. Transition states (TS\textsubscript{Si}) for a) Cs-salt and b) K-salt using catalyst I.

Table S1. Parameters for Transition states (TS\textsubscript{Si}) with Cs-salt and K-salt

| Distance (Å) | Cs-salt | K-salt |
|-------------|---------|--------|
| C1-C2       | 2.551   | 2.501  |
| O--H        | 2.880   | 3.224  |
| C2-H        | 1.085   | 1.083  |
| N-C2        | 1.333   | 1.32   |
| C2-C3       | 1.499   | 1.492  |
Figure S2. Energy profile diagram for formation of enantiomers and diasteromers of Epilupinione using catalyst A

Cartesian coordinates of all calculated intermediates and transition states

A-Cs

1 1
C     -2.41360100  -1.31250700  -0.34649500
H     -2.07607800  -1.06036300  -1.34249600
C     -1.37152700  -1.58196100   0.68505200
H     -0.60084300  -0.78989900   0.60777200
H     -0.83464000  -2.49008700   0.35450600
C     -1.93899200  -1.76626800   2.10530700
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| H    | -2.120618 | -0.783598 | 2.562852 |
| H    | -1.204539 | -2.276666 | 2.737311 |
| C    | -3.258789 | -2.565052 | 2.056821 |
| H    | -3.688998 | -2.676485 | 3.058782 |
| H    | -3.072040 | -3.576354 | 1.670031 |
| N    | -3.706495 | -1.455802 | -0.159598 |
| C    | -4.728091 | -1.082521 | -1.198432 |
| H    | -5.496033 | -0.497522 | -0.673092 |
| H    | -5.200498 | -2.015293 | -1.535203 |
| C    | -4.189998 | -0.274105 | -2.392186 |
| H    | -4.998314 | -0.254952 | -3.136497 |
| H    | -3.363872 | -0.811203 | -2.879240 |
| C    | -3.786530 | 1.200590  | -2.076637 |
| H    | -3.309542 | 1.474035  | 0.104687 |
| C    | -1.575277 | 1.830895  | -0.968346 |
| H    | -1.102980 | 1.851546  | -1.951079 |
| C    | -1.206457 | 2.361868  | 1.449906 |
| C    | 0.679659  | 2.507087  | -0.116355 |
| C    | 0.075427  | 2.754502  | 2.227016 |
| H    | -1.985522 | 3.137877  | 1.512557 |
| H    | -1.644033 | 1.424989  | 1.829296 |
| C    | 1.002669  | 3.357156  | 1.141139 |
| H    | 0.853736  | 3.083224  | -1.033301 |
| H    | 0.536845  | 1.862160  | 2.666073 |
| H    | -0.139230 | 3.459410  | 3.036210 |
| H    | 2.063508  | 3.311802  | 1.397171 |
| H    | 0.737338  | 4.405002  | 0.954138 |
| N    | -0.754897 | 2.215115  | 0.053971 |
| C    | 1.602460  | 1.256838  | -0.201330 |
| O    | 1.133273  | 0.069384  | 0.054880 |
| O    | 2.825670  | 1.512815  | -0.517756 |
| C    | -4.283689 | -1.848680 | 1.164387 |
| H    | -5.150938 | -2.487226 | 0.960241 |
| H    | -4.651320 | -0.931806 | 1.647335 |
| Cs   | 4.069219  | -1.135019 | -0.347982 |

**TS**

**Si-Cs**

| C    | -4.249703 | -1.140786 | -2.108234 |

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**Notes:**

- The table lists atomic coordinates in angstroms (Å).
- The table represents a molecular structure with selected atoms and their corresponding coordinates.
- The structure includes hydrogens (H), carbons (C), nitrogens (N), oxygens (O), and a cesium (Cs) atom.
- The TS (transition state) and Si-Cs structures are highlighted, indicating potential energy minima or saddle points in the molecular dynamics.

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**Image:**

- The image contains a series of coordinates for various atoms, arranged in a tabular format.
- The coordinates are organized by atom type, with X, Y, and Z components listed for each atom.
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | -3.184322  | -0.075922  | -2.481625  |
| C       | -2.635565  | 0.745646   | -1.318597  |
| C       | -2.088624  | -1.222073  | 0.209585   |
| N       | -3.277605  | -1.816332  | 0.106870   |
| C       | -3.727462  | -2.298023  | -1.230529  |
| C       | -1.580835  | -0.634442  | 1.492135   |
| C       | -2.698875  | -0.283110  | 2.490584   |
| C       | -3.734922  | -1.425094  | 2.546650   |
| C       | -4.332755  | -1.674739  | 1.152470   |
| H       | -4.638361  | -1.588040  | -3.033940  |
| H       | -5.103520  | -0.656270  | -1.616262  |
| H       | -3.645360  | 0.598096   | -3.219968  |
| H       | -2.351189  | -0.567206  | -3.010542  |
| H       | -3.369061  | 1.223741   | -0.667260  |
| H       | -1.352902  | -1.441669  | -0.557118  |
| H       | -2.878837  | -2.791342  | -1.721134  |
| H       | -4.509325  | -3.049343  | -1.074408  |
| H       | -0.922385  | 0.203560   | 1.237286   |
| H       | -0.897577  | -1.384461  | 1.927194   |
| H       | -2.270059  | -0.105358  | 3.483161   |
| H       | -3.196378  | 0.648719   | 2.185926   |
| H       | -3.258629  | -2.343720  | 2.915605   |
| H       | -4.550749  | -1.182399  | 3.237503   |
| H       | -4.997809  | -0.845714  | 0.868154   |
| H       | -4.926625  | -2.595702  | 1.140112   |
| C       | -1.323312  | 1.185428   | -1.308866  |
| H       | -0.617211  | 0.718539   | -1.992753  |
| C       | 0.685736   | 2.405449   | -0.469388  |
| C       | -1.548906  | 3.035036   | 0.374918   |
| C       | 0.831923   | 3.393499   | 0.717562   |
| H       | 0.984761   | 2.906380   | -1.402147  |
| C       | -0.526773  | 4.133221   | 0.749529   |
| H       | -2.417860  | 3.427633   | -0.169434  |
| H       | -1.921104  | 2.512788   | 1.269928   |
| H       | 1.687488   | 4.057170   | 0.577870   |
| H       | 0.985297   | 2.835896   | 1.650822   |
| H       | -0.543458  | 4.930535   | -0.003455  |
| H       | -0.742747  | 4.583328   | 1.723662   |
| N       | -0.771719  | 2.117427   | -0.491569  |
| C       | 1.611253   | 1.168910   | -0.319924  |
| O       | 1.107305   | -0.011489  | -0.111242  |
| Atom | x         | y         | z         |
|------|-----------|-----------|-----------|
| O    | 2.86781800| 1.43901500| -0.41066100|
| Cs   | 4.05492300| -1.22733600| 0.00257500|
| A'-Cs|           |           |           |
| C    | -2.74319900| -1.32686200| 0.76841800|
| H    | -1.77814400| -0.78855700| 0.85275300|
| C    | -2.88265800| -2.68861600| 1.38157200|
| H    | -2.45008700| -2.63869900| 2.39050000|
| H    | -2.20806900| -3.35651600| 0.82038100|
| C    | -4.32499400| -3.23728400| 1.40023300|
| H    | -4.87339300| -2.81407800| 2.25269400|
| H    | -4.30993000| -4.32319600| 1.54050800|
| C    | -5.04468400| -2.86928100| 0.08658500|
| H    | -6.07889800| -3.23148900| 0.09285400|
| H    | -4.54029000| -3.34692700| -0.76456800|
| N    | -3.70755400| -0.73265300| 0.11548300|
| C    | -3.50327200| 0.64210200 | -0.45398200|
| H    | -2.62460400| 1.06431900 | 0.04076800 |
| H    | -4.39055600| 1.23435800 | -0.19501600|
| C    | -3.26656600| 0.64783400 | -1.98126400|
| H    | -4.20150000| 0.48094500 | -2.53546400|
| H    | -2.57196300| -0.16457200| -2.23878800|
| C    | -2.61901700| 2.00516200 | -2.42314900|
| H    | -2.53978200| 1.99220900 | -3.51938800|
| H    | -3.29844400| 2.83253600 | -2.16693500|
| C    | -1.27178100| 2.20347800 | -1.76688000|
| H    | -0.47633200| 1.52947700 | -2.08364400|
| C    | -1.09747600| 3.00707300 | -0.67863400|
| H    | -1.90760600| 3.67751300 | -0.38569800|
| C    | 0.07059500 | 3.96355700 | 1.32525300 |
| C    | 1.11979700 | 2.11947300 | 0.08123600 |
| C    | 1.18966900 | 3.34508100 | 2.19132300 |
| H    | 0.32786300 | 4.99009100 | 1.01864200 |
| H    | -0.89097900| 4.00038200 | 1.85522200 |
| C    | 2.11254500 | 2.67285300 | 1.14492900 |
| H    | 1.58046700 | 2.13354600 | -0.91746900|
| H    | 0.76802700 | 2.58741400 | 2.86187800 |
| H    | 1.70818600 | 4.09568600 | 2.79659800 |
| H    | 2.73727400 | 1.88110200 | 1.56960600 |
| H    | 2.76859600 | 3.42344000 | 0.68449200 |
| N    | -0.00250400| 3.05885600 | 0.15741400 |
|   |         |         |         |
|---|---------|---------|---------|
| C | 0.76321800 | 0.61722600 | 0.36086700 |
| O | -0.38492300 | 0.30391800 | 0.84254700 |
| O | 1.71957100  | -0.21065900 | 0.07318700 |
| C | -5.05925600 | -1.34564700 | -0.10666100 |
| H | -5.75072400 | -0.86258500 | 0.59652800 |
| H | -5.36993900 | -1.07434300 | -1.12005900 |
| Cs| 4.09102800  | -1.61616200 | -0.37566600 |

**TS_{Re-Cs}**

|   |         |         |         |
|---|---------|---------|---------|
| C | -2.92138000 | -0.75297900 | 0.96713900 |
| H | -3.71279000 | -0.15672000 | 1.41716700 |
| C | -1.64001000 | -0.91044400 | 1.76309500 |
| H | -1.85330900 | -0.63535600 | 2.80535000 |
| H | -0.86242100 | -0.22413300 | 1.39957800 |
| C | -1.07879700 | -2.34717400 | 1.67191700 |
| H | -1.67843400 | -3.04667900 | 2.27157600 |
| H | -0.60058800 | -2.35512200 | 2.07527000 |
| C | -1.07634700 | -2.78306800 | 0.19354900 |
| H | -0.61724600 | -3.77138800 | 0.06510700 |
| H | -0.48260800 | -2.06058200 | -0.38145900 |
| N | -3.38029700 | -1.76098500 | 0.18868500 |
| C | -4.70409500 | -1.58313400 | -0.45932100 |
| H | -5.43891500 | -1.32166900 | 0.31382900 |
| H | -5.00673900 | -2.54108400 | -0.89516600 |
| C | -4.65719600 | -0.47885400 | -1.53657200 |
| H | -5.66888300 | -0.36368400 | -1.94679900 |
| H | -4.01282300 | -0.79646300 | -2.36898300 |
| C | -4.16824700 | 0.88950200  | -0.99943100 |
| H | -4.29782700 | 1.63141500  | -1.80083800 |
| H | -4.82399500 | 1.22219100  | -0.17678200 |
| C | -2.70511900 | 0.88835900  | -0.53946300 |
| H | -2.00070800 | 0.41276500  | -1.22517300 |
| C | -2.22041400 | 1.91794300  | 0.27596700 |
| H | -2.91757800 | 2.38407100  | 0.97754400 |
| C | -0.52940000 | 3.35179400  | 1.40448200 |
| C | 0.07564800  | 2.23681900  | -0.70711700 |
| C | 0.84847000  | 3.86680400  | 0.91914100 |
| H | -1.26571600 | 4.16343900  | 1.48117200 |
| H | -0.46432700 | 2.84610500  | 2.37421300 |
| C | 0.84062200  | 3.58281800  | -0.60348800 |
| H | -0.40665600 | 2.12214500  | -1.68450800 |
|   |   |   |   |
|---|---|---|---|
| H | 1.65259900 | 3.30500200 | 1.40726200 |
| H | 0.98663000 | 4.92707500 | 1.15019400 |
| H | 1.83736600 | 3.50336500 | -1.04126700 |
| H | 0.28813700 | 4.36706400 | -1.13612000 |
| N | -0.96147000 | 2.39055300 | 0.34445800 |
| C | 1.05205600 | 1.03593600 | -0.53229800 |
| O | 0.94738900 | 0.25668400 | 0.49949600 |
| O | 1.93914700 | 0.92934200 | -1.46085300 |
| C | -2.51687000 | -2.84663900 | -0.34476600 |
| H | -2.98973100 | -3.79896500 | -0.07052200 |
| H | -2.51897900 | -2.79038500 | -1.44712200 |
| Cs | 3.74585600 | 1.04224900 | -0.15307000 |

**A''-Cs**

|   |   |   |   |
|---|---|---|---|
| C | 2.25644000 | -1.37980400 | -0.04089000 |
| H | 1.67123100 | -1.54048100 | 0.85699500 |
| C | 1.52243500 | -1.17719800 | -1.32267400 |
| H | 0.70421100 | -0.45730500 | -1.12632500 |
| H | 0.98685000 | -2.12138100 | -1.53142500 |
| C | 2.43403400 | -0.78996000 | -2.50098200 |
| H | 2.66678000 | 0.28307800 | -2.45222700 |
| H | 1.90980900 | -0.95711200 | -3.44789600 |
| C | 3.74201100 | -1.60651500 | -2.45551400 |
| H | 4.41316600 | -1.32749800 | -3.27605700 |
| H | 3.51766200 | -2.67595100 | -2.57016600 |
| N | 3.56465100 | -1.48651200 | 0.05808400 |
| C | 4.25991000 | -1.64896800 | 1.38164100 |
| H | 5.26207900 | -1.22449500 | 1.24950700 |
| H | 4.38076900 | -2.72493900 | 1.57147500 |
| C | 3.57390300 | -0.94455100 | 2.56823300 |
| H | 4.25126200 | -1.08478900 | 3.42183300 |
| H | 2.63788600 | -1.44912900 | 2.84577200 |
| C | 3.31591000 | 0.57538200 | 2.35294300 |
| H | 3.31440800 | 1.05194300 | 3.34466500 |
| H | 4.16890000 | 1.01722100 | 1.81393100 |
| C | 2.01567600 | 0.91585100 | 1.64242000 |
| H | 1.09639400 | 0.63431900 | 2.15695200 |
| C | 1.94952500 | 1.71579200 | 0.52830500 |
| H | 2.88150300 | 2.00272500 | 0.03587800 |
| C | 0.87335300 | 3.04518100 | -1.29825100 |
| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| C    | -0.49665100 | 2.27102000 | 0.59906600 |
| C    | -0.60304900 | 3.42988200 | -1.54088600 |
| H    | 1.49976500  | 3.93940200 | -1.15162300 |
| H    | 1.29262000  | 2.46893000 | -2.13391000 |
| C    | -1.20315900 | 3.45936400 | -0.11432300 |
| H    | -0.37989700 | 2.47428500 | 1.67144700  |
| H    | -1.09598900 | 2.65810500 | -2.14342900 |
| H    | -0.69508500 | 4.38758500 | -2.06247900 |
| H    | -2.29066100 | 3.35616500 | -0.09191100 |
| H    | -0.94004800 | 4.39840100 | 0.38861300  |
| N    | 0.82393200  | 2.23463900 | -0.05570600 |
| C    | -1.35495200 | 0.97893200 | 0.49390800  |
| O    | -1.04929200 | 0.04851000 | -0.36374900 |
| O    | -2.38153200 | 0.94827600 | 1.27390600  |
| C    | 4.47449600  | -1.36965300 | -1.12643700 |
| H    | 4.92491900  | -0.36728200 | -1.09788400 |
| H    | 5.28007900  | -2.09947100 | -0.98418900 |
| Cs   | -3.91438900 | -1.24912300 | 0.04391300  |

**TS’-Cs**

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| C    | -1.87382200 | -1.25711100 | 0.13888700 |
| H    | -1.15006400 | -1.59042000 | -0.59936500 |
| C    | -1.31265000 | -0.78208900 | 1.45990300  |
| H    | -0.57734300 | 0.00889400  | 1.29525400  |
| H    | -0.73917900 | -1.63005800 | 1.87469500  |
| C    | -2.39567000 | -0.35598600 | 2.46849300  |
| H    | -2.81362400 | 0.61850400  | 2.17815900  |
| H    | -1.94691900 | -0.22785300 | 3.45991900  |
| C    | -3.51831800 | -1.41071500 | 2.51259300  |
| H    | -4.31087100 | -1.11571800 | 3.21059000  |
| H    | -3.11309500 | -2.36873400 | 2.86634400  |
| N    | -3.10282400 | -1.80073800 | 0.06231200  |
| C    | -3.57982000 | -2.35570400 | -1.24139600 |
| H    | -4.67002800 | -2.42943400 | -1.17082000 |
| H    | -3.18913300 | -3.37512700 | -1.36757400 |
| C    | -3.20203300 | -1.45821000 | -2.44429500 |
| H    | -3.90446600 | -1.68554300 | -3.25573100 |
| H    | -2.20255400 | -1.71258500 | -2.82188500 |
| C    | -3.24323800 | 0.05585300  | -2.11140100 |
| H    | -3.32196600 | 0.61253700  | -3.05660000 |
| H    | -4.15623800 | 0.29487100  | -1.54346300 |
|  | x     | y     | z       |
|---|-------|-------|---------|
| C | -1.99903900 | 0.51966200 | -1.36033800 |
| H | -1.04214200 | 0.26055300 | -1.81616600 |
| C | -2.02384700 | 1.61912100 | -0.50509200 |
| H | -2.97918900 | 1.96179900 | -0.10563600 |
| C | -1.02680400 | 3.48513400 | 0.84156200  |
| C | 0.40921800  | 2.22608600 | -0.71555000 |
| C | 0.02158400  | 4.45884500 | 0.26801800  |
| H | -2.04404700 | 3.89199700 | 0.85465400  |
| H | -0.75524700 | 3.17650500 | 1.86037000  |
| C | 1.13866900  | 3.50714300 | -0.23115700 |
| H | 0.27161700  | 2.20122500 | -1.80410900 |
| H | 0.38431400  | 5.16711100 | 1.01891900  |
| H | -0.41039700 | 5.02876200 | -0.56356900 |
| H | 1.80033800  | 3.23329200 | 0.59657100  |
| H | 1.73925700  | 3.95160100 | -1.03095600 |
| N | -0.94516400 | 2.32564200 | -0.08522800 |
| C | 1.16386100  | 0.91822200 | -0.31562500 |
| O | 1.72434900  | 0.87671400 | 0.84839900  |
| O | 1.18489100  | -0.04669000 | -1.18404700 |
| C | -4.13531300 | -1.59559200 | 1.11725600  |
| H | -4.74436600 | -0.71708400 | 0.84920400  |
| H | -4.79608100 | -2.46969300 | 1.10244900  |
| Cs| 3.76719200  | -1.21551700 | 0.02769500  |

**A-K**

|  | x     | y     | z       |
|---|-------|-------|---------|
| C | 1.95091900 | 0.96497300 | -0.49578400 |
| H | 1.56474800 | 0.61156600 | -1.44101200 |
| C | 1.04647900 | 1.76450200 | 0.36762200 |
| H | 0.06824200 | 1.25683100 | 0.37467000 |
| H | 0.85495300 | 2.69805300 | -0.18778600 |
| C | 1.61811100 | 2.05606200 | 1.75818700 |
| H | 1.46642800 | 1.18673000 | 2.40679000 |
| H | 1.07984200 | 2.88998100 | 2.21673300 |
| C | 3.11496800 | 2.36718200 | 1.65082300 |
| H | 3.55679300 | 2.55320900 | 2.63429200 |
| H | 3.26923600 | 2.37486700 | 1.05413900 |
| N | 3.20069600 | 0.72776200 | -0.23895800 |
| C | 4.04890600 | -0.15674500 | -1.09087300 |
| H | 4.57418000 | -0.81999000 | -0.39279500 |
| H | 4.80417200 | 0.48726600 | -1.55592000 |
| C | 3.30514100 | -0.98924900 | -2.13576200 |
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | 4.08111600 | -1.39828300 | -2.79371300 |
| H    | 2.70274400 | -0.34079500 | -2.78380000 |
| C    | 2.46336100 | -2.17040700 | -1.58591900 |
| H    | 1.93451100 | -2.61003800 | -2.44003900 |
| H    | 3.16676600 | -2.94303700 | -1.24514300 |
| C    | 1.48191400 | -1.88408600 | -0.46858800 |
| H    | 1.87525200 | -1.87095100 | 0.54554500  |
| C    | 0.13207700 | -1.82545500 | -0.65381200 |
| H    | -0.26670300 | -1.88292800 | -1.66660900 |
| C    | -0.52952700 | -1.76204300 | 1.73448600  |
| C    | -2.25029100 | -1.59563600 | 0.01434400  |
| C    | -1.90539500 | -1.60028200 | 2.40533200  |
| H    | -0.05712000 | -2.72559300 | 1.97795400  |
| H    | 0.17419500  | -0.97128700 | 2.03164900  |
| C    | -2.89548300 | -2.08216700 | 1.32963900  |
| H    | -2.51850000 | -2.25351800 | -0.82002100 |
| H    | -2.08684700 | -0.54604300 | 2.64097200  |
| H    | -1.97788400 | -2.16729400 | 3.33685300  |
| H    | -3.90671600 | -1.69232300 | 1.45427200  |
| H    | -2.94943700 | -3.17620200 | 1.32516100  |
| N    | -0.82034000 | -1.70317000 | 0.30304500  |
| C    | -2.74309800 | -0.17729700 | -0.38007600 |
| O    | -1.94076500 | 0.81095100  | -0.36480700 |
| O    | -3.96256200 | -0.11754400 | -0.70160400 |
| C    | 3.85718900  | 1.19991700  | 1.00581700  |
| H    | 4.88123300  | 1.47402500  | 0.73547200  |
| H    | 3.91438500  | 0.33830200  | 1.68342900  |
| K    | -3.99018200 | 2.38170700  | -1.14443300 |

TS_{Sr-K}:

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | -3.62194700 | 0.06196100 | -2.11337600 |
| C    | -2.19955600 | 0.57143200 | -2.42190800 |
| C    | -1.39233600 | 1.02617500 | -1.21716000 |
| C    | -1.75361900 | -1.05409700 | 0.12378600 |
| N    | -3.07080100 | -1.08463600 | 0.03610500 |
| C    | -3.68024600 | -1.23759300 | -1.30185600 |
| C    | -1.03487200 | -0.85334700 | 1.41623400 |
| C    | -1.87023000 | -0.11886500 | 2.46860900 |
| C    | -3.29540400 | -0.68238200 | 2.48876100 |
| C    | -3.94078400 | -0.55808600 | 1.10991400 |
| H    | -4.14264200 | -0.12734400 | -3.05869600 |
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| H    | -4.19586500 | 0.84482800 | -1.60157100 |
| H    | -2.30115900 | 1.40487200 | -3.13101000 |
| H    | -1.64453000 | -0.20748200 | -2.96578300 |
| H    | -1.88397100 | 1.72039200 | -0.53738400 |
| H    | -1.21171500 | -1.52655200 | -0.68735000 |
| H    | -3.14271700 | -2.03814000 | -1.82156300 |
| H    | -4.71254300 | -1.56853400 | -1.16107000 |
| H    | -0.06692600 | -0.38978600 | 1.20315500 |
| H    | -0.78160700 | -1.86592600 | 1.77185600 |
| H    | -1.40060700 | -0.21718600 | 3.45170200 |
| C    | -0.01713000 | 0.95540300 | -1.21538600 |
| H    | 0.47009400 | 0.29531400 | -1.93031700 |
| C    | 2.29446800 | 1.35942900 | -0.42130100 |
| C    | 0.45210800 | 2.67470200 | 0.51836000 |
| C    | 2.80815300 | 2.22658400 | 0.74718800 |
| H    | 2.69941000 | 1.74082800 | -1.36871100 |
| C    | 1.78538200 | 3.36930700 | 0.83039600 |
| H    | -0.27309100 | 3.33243300 | 0.02649700 |
| H    | -0.01733700 | 2.27906400 | 1.43018400 |
| H    | 3.83136600 | 2.56235700 | 0.57459200 |
| H    | 2.80024300 | 1.64089900 | 1.67431300 |
| H    | 1.99748100 | 4.12690700 | 0.06794600 |
| H    | 1.77571600 | 3.86685100 | 1.80355900 |
| N    | 0.83532900 | 1.58024900 | -0.38549800 |
| C    | 2.75854800 | -0.10978700 | -0.30417700 |
| O    | 1.91408400 | -1.02934400 | -0.07152700 |
| O    | 4.00128700 | -0.27012800 | -0.44753400 |
| K    | 3.94326500 | -2.79843800 | -0.08305300 |

A’-K:

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 1.87777300 | 0.51361400 | 0.59323300 |
| H    | 0.91718100 | 0.01215600 | 0.72585200 |
| C    | 1.87528000 | 1.99867600 | 0.51433900 |
| H    | 1.24420200 | 2.35317400 | 1.33831100 |
| H    | 1.29380600 | 2.23405500 | -0.38927400 |
| C    | 3.26757500 | 2.63761700 | 0.50557500 |
| Atoms | x      | y      | z       |
|-------|--------|--------|---------|
| H     | 3.65110000 | 2.70968100 | 1.53059300 |
| H     | 3.21016500 | 3.65857600 | 0.11823300 |
| C     | 4.21817700 | 1.78716500 | -0.34242300 |
| H     | 5.22890700 | 2.20546700 | -0.34887100 |
| H     | 3.87523300 | 1.76203700 | -1.38415100 |
| N     | 2.94141200 | -0.20987200 | 0.47595000 |
| C     | 2.90248100 | -1.69559600 | 0.57425600 |
| H     | 2.02390700 | -1.94944300 | 1.16873000 |
| H     | 3.79438100 | -1.97980300 | 1.13897900 |
| C     | 2.84712800 | -2.38488900 | -0.80911800 |
| H     | 3.69105000 | -3.07605600 | -0.90963000 |
| H     | 2.96401000 | -1.63392100 | -1.60011600 |
| C     | 1.51475400 | -3.14697300 | -1.02722000 |
| H     | 1.56516500 | -1.69559600 | 0.88427000 |
| H     | 1.46213000 | -2.38291800 | -0.31475700 |
| C     | 0.29049900 | -2.28135700 | -0.90072300 |
| H     | 0.11907700 | -1.53921200 | -1.67820100 |
| C     | -0.58432200 | -2.41366900 | 0.12892700 |
| H     | -0.38148600 | -3.17459200 | 0.88427000 |
| C     | -2.65179900 | -2.13472100 | 1.44536100 |
| C     | -2.38291800 | -0.86686000 | -0.62219500 |
| C     | -3.90636200 | -1.28444600 | 1.20571300 |
| H     | -2.88162600 | -3.20717400 | 1.35913200 |
| H     | -2.20859700 | -1.96272200 | 2.43348200 |
| C     | -3.88688900 | -1.05990500 | -0.31475700 |
| H     | -2.14988000 | -1.22556900 | -1.63292700 |
| H     | -3.82199100 | -0.32884500 | 1.73653400 |
| H     | -4.81452700 | -1.78174400 | 1.55607300 |
| H     | -4.48388300 | -0.21198400 | -0.65302400 |
| H     | -4.24853300 | -1.95623500 | -0.83057000 |
| N     | -1.73313400 | -1.71559800 | 0.37254200 |
| C     | -1.98963300 | 0.63540200 | -0.59366800 |
| O     | -1.13218600 | 1.07406100 | 0.24099400 |
| O     | -2.60832400 | 1.35660100 | -1.42778300 |
| C     | 4.28868300 | 0.36658000 | 0.20681900 |
| H     | 4.84230400 | 0.32371800 | 1.15219300 |
| H     | 4.78020800 | -0.31317500 | -0.49397700 |
| K     | -2.33098600 | 3.50948300 | -0.14368500 |

**TS\textsubscript{R2-K}**

| C       | x      | y      | z       |
|---------|--------|--------|---------|
| C       | 2.27066700 | 0.11083000 | 0.99271900 |
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| H       | 2.68265500 | -0.73684900| 1.53142900 |
| C       | 1.16933900 | 0.88961500 | 1.67212500 |
| H       | 1.23308400 | 0.67478800 | 2.74619500 |
| H       | 0.18378400 | 0.53878600 | 1.34482500 |
| C       | 1.27840300 | 2.39776400 | 1.40457800 |
| H       | 2.08135400 | 2.84223100 | 2.00612100 |
| H       | 0.34519300 | 2.88330000 | 1.70353200 |
| C       | 1.55757100 | 2.62202200 | -0.08396800|
| H       | 1.58002400 | 3.68702900 | -0.33667700|
| H       | 0.75369400 | 2.16526200 | -0.67372100|
| N       | 3.17053800 | 0.73190200 | 0.22108700 |
| C       | 4.28704800 | -0.07405900| -0.30287700|
| H       | 4.76462500 | -0.58056600| 0.54395000 |
| H       | 5.02374200 | 0.60829100 | -0.73521300|
| C       | 3.80218500 | -1.09905900| -1.33438100|
| H       | 4.66903400 | -1.68409000| -1.66020200|
| H       | 3.42633200 | -0.57988800| -2.22548900|
| C       | 2.71880900 | -2.05480000| -0.80110900 |
| H       | 2.53827100 | -2.81932700| -1.56776600|
| H       | 3.10515400 | -2.60143600| 0.07296500  |
| C       | 1.40229600 | -1.37207500| -0.44439500|
| H       | 1.01094500 | -0.68713100| -1.19596100|
| C       | 0.47920900 | -2.02918100| 0.36235400 |
| H       | 0.86005000 | -2.72284500| 1.11534600 |
| C       | -1.68926700| -2.56323600| 1.39880500 |
| C       | -1.65768300| -1.34605000| -0.72336300|
| C       | -3.11630000| -2.49349700| 0.82504200 |
| H       | -1.34261200| -3.59623700| 1.52077700 |
| H       | -1.60026500| -2.05076400| 2.36110900 |
| C       | -2.90299700| -2.25962400| -0.68134200|
| H       | -1.10884200| -1.45223000| -1.66269300|
| H       | -3.65607800| -1.65213700| 1.26929600 |
| H       | -3.68347600| -3.40330000| 1.03549300 |
| H       | -3.75650400| -1.79966200| -1.18180000|
| H       | -2.67800600| -3.20357000| -1.18968900|
| N       | -0.84768600| -1.89086800| 0.37965200 |
| C       | -2.06472200| 0.14371800 | -0.57958200|
| O       | -1.86427500| 0.74441100 | 0.51875700 |
| O       | -2.62536900| 0.63587500 | -1.59707700|
| C       | 2.90530200 | 2.00846900 | -0.47004300|
| H       | 3.72861300 | 2.68494600 | -0.20780400|
|   |          |          |          |
|---|----------|----------|----------|
| H | 2.95986200 | 1.83839700 | -1.55262700 |
| K | -3.47908500 | 2.70697100 | -0.31828400 |
| A''-K |          |          |          |
| C | -1.92193100 | 1.09451300 | 0.12161800 |
| H | -1.45104700 | 1.29433700 | 1.07565200 |
| C | -1.15894500 | 1.39521800 | -1.11366000 |
| H | -0.14329200 | 0.98808100 | -0.97247100 |
| H | -1.01049700 | 2.48795300 | -1.11840100 |
| C | -1.84974200 | 0.92265000 | -2.39531300 |
| H | -1.66452900 | -0.14906900 | -2.53835700 |
| H | -1.42047600 | 1.43447000 | -3.26084100 |
| H | -3.55144600 | -0.22019600 | -2.39531300 |
| H | -3.85784800 | 0.34396600 | 1.41640000 |
| H | -4.58124700 | -0.43156200 | 1.14645800 |
| H | -4.43039900 | 1.22672400 | 1.72815400 |
| C | -2.96419500 | -0.17899900 | 2.54394400 |
| H | -3.65596800 | -0.42631400 | 3.35757800 |
| H | -2.32171600 | 0.61544100 | 2.94365700 |
| H | -2.12282300 | -1.43012500 | 2.18971100 |
| H | -1.93398300 | -1.96861200 | 3.12808200 |
| H | -2.73073600 | -2.11272400 | 1.57947900 |
| C | -0.80118900 | -1.16233700 | 1.50628200 |
| H | -0.05853000 | -0.61625200 | 2.08577400 |
| C | -0.44537800 | -1.71666200 | 0.31469500 |
| H | -1.19803200 | -2.27436000 | -0.24558100 |
| C | 1.00295900 | -2.39020600 | -1.56650100 |
| C | 2.01675500 | -1.37454500 | 0.41311500 |
| C | 2.51667500 | -2.26913300 | -1.78064500 |
| H | 0.69857800 | -3.44354000 | -1.47400200 |
| H | 0.42497300 | -1.94186500 | -2.38319200 |
| C | 3.06702000 | -2.22056700 | -0.34636400 |
| H | 1.93169000 | -1.70804900 | 1.45459800 |
| H | 2.74874900 | -1.33903200 | -2.31097400 |
| H | 2.91715900 | -3.10041800 | -2.36647300 |
| H | 4.06713800 | -1.79192100 | -0.26692900 |
| H | 3.09852600 | -3.22947100 | 0.07952700 |
| N | 0.77046000 | -1.67465900 | -0.29901000 |
| Slow Step 1 | Slow Step 2 | Slow Step 3 |
|-------------|-------------|-------------|
| C           | 2.43081800  | 0.11823500  | 0.47734200  |
| O           | 1.77198400  | 1.00376100  | -0.15604700 |
| O           | 3.45645600  | 0.34617000  | 1.17804200  |
| C           | -3.94469400 | 0.46000600  | -1.09146900 |
| H           | -3.98657500 | -0.62509100 | -1.25076300 |
| H           | -4.96286500 | 0.80018700  | -0.87972100 |
| K           | 3.70043000  | 2.77384000  | 0.44642000  |

**TS’-K**

| Slow Step 1 | Slow Step 2 | Slow Step 3 |
|-------------|-------------|-------------|
| C           | -1.81665000 | -0.99067400 | 0.02299100  |
| H           | -1.40818100 | -1.65825300 | -0.72951500 |
| C           | -1.14108900 | -1.02713900 | 1.36755300  |
| H           | -0.07852900 | -0.79095600 | 1.25704600  |
| H           | -1.18148300 | -2.08261000 | 1.68367800  |
| C           | -1.83463600 | -0.16100800 | 2.42225900  |
| H           | -1.62332700 | 0.89990400  | 2.23599900  |
| H           | -1.42831500 | -0.39066300 | 3.41200800  |
| C           | -3.34681100 | -0.39945200 | 2.38723900  |
| H           | -3.86899100 | 0.23861400  | 3.10743000  |
| H           | -3.56577600 | -1.43906400 | 2.66093500  |
| N           | -3.14034600 | -0.80425300 | -0.06620300 |
| C           | -3.78998600 | -0.92521200 | -1.39173600 |
| H           | -4.73250000 | -0.37560300 | -1.32722100 |
| H           | -4.04095700 | -1.97720600 | -1.57864700 |
| C           | -2.92988400 | -0.33768100 | -2.52217300 |
| H           | -3.59700800 | -0.09501200 | -3.35516400 |
| H           | -2.22753800 | -1.08625100 | -2.90882000 |
| C           | -2.14961900 | 0.91695000  | -2.08953000 |
| H           | -1.83644900 | 1.46136500  | -2.98921000 |
| H           | -2.81500400 | 1.60083200  | -1.54448100 |
| C           | -0.91885400 | 0.60254100  | -1.24809800 |
| H           | -0.17415600 | -0.01557000 | -1.74969200 |
| C           | -0.43400800 | 1.54577500  | -0.34339800 |
| H           | -1.14287700 | 2.23538300  | 0.11530100  |
| C           | 1.22244000  | 2.69866700  | 1.07725700  |
| C           | 2.00530600  | 1.15968400  | -0.64681000 |
| C           | 2.52071700  | 3.26930000  | 0.50154600  |
| H           | 0.42727600  | 3.43669900  | 1.21265400  |
| H           | 1.40124000  | 2.19431600  | 2.03527300  |
| C           | 3.18394200  | 2.02979700  | -0.12372600 |
| H           | 1.85081900  | 1.30655200  | -1.72048900 |
H                  3.14396500    3.74237800    1.26450300  
H                  2.29155900    4.01813300   -0.26448400  
H                  3.73462400    1.47859300    0.64562000  
N                  0.82571500    1.70349500    0.06450900  
C                  2.31158800   -0.33717400   -0.41276600  
O                  2.00063200   -0.85753700    0.70076400  
O                  2.93355200   -0.91106900   -1.34813800  
C                 -3.90230800   -0.11553800    0.99275000  
H                 -3.89749600    0.96680500    0.78956800  
H                 -4.93943000   -0.45347600    0.91465700  
K                  3.61448400   -2.90552600    0.15744900  

References
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$^1\text{H NMR (500 MHz), CDCl}_3$
$^{13}$C NMR (125 MHz), CDCl$_3$
$^{1}H$ NMR (500 MHz), CDCl$_3$
\[
\text{OHC-} - N - \text{CHO}
\]

\[^{13}\text{C NMR (125 MHz), CDCl}_3\]
$^1H$ NMR (500 MHz), CDCl$_3$
13C NMR (125 MHz), CDCl₆
$^{19}$F NMR (470 MHz), CDCl$_3$
(R)-MTPAO

\[ \text{H} \]

\[
\text{(S1)} \quad \begin{array}{c}
\text{N} \\
\text{S1} \quad (83\% \text{ ee})
\end{array}
\]

\[
\text{S2}
\]

\[
\text{H}
\]

\[ \text{19F NMR (470 MHz), CDCl}_3 \]

\[ \text{NMR spectrum} \]

\[
\text{\( \delta \) / ppm}
\]

\[
-71.5 \quad -71.2 \quad -71.25 \quad -71.3 \quad -71.36 \quad -71.4
\]
(R)-MTPAO

$^1^9F$ NMR (470 MHz), CDCl$_3$

S1
(92% ee)

S2

$^1^9F$ NMR (470 MHz), CDCl$_3$
(R)-MTPAO

S1

enantiomerically pure

$^{19}$F NMR (470 MHz), CDCl$_3$
$\text{OHC} \quad \text{Ns} \quad \text{CHO}$

$^1\text{H NMR (500 MHz), CDCl}_3$

Diagram of NMR spectrum with peaks at different ppm values.
$^{13}$C NMR (125 MHz), CDCl$_3$
$^{19}$F NMR (470 MHz), CDCl$_3$
OHC\[\begin{array}{c}
\text{N} \\
\text{Ns} \\
11
\end{array}\]
\text{CHO}

$^1$H NMR (500 MHz), CDCl$_3$
$^{13}$C NMR (125 MHz), CDCl$_3$