Non-covalent Interactions in the Diastereoselective Synthesis of *cis*-2,3-dihydrobezofurans: Experimental and Computational Studies

Omar Jamis-Oliva,[‡] Roger López,[‡] Antonio Galdámez, Sebastián Gallardo-Fuentes,[*†] Marcelo Vilches-Herrera.[*]

Experimental Details

General Procedure for the synthesis of DHBs **2a-f**. In a 15 mL pressure tube were placed 0.5 mmol of compound 1, 1 equiv of Cs_2CO_3 and 4 mL of THF at 60°C. The reaction was monitored by TLC and stirred until the reaction was completed. The reac-tion mixture was cooled to room temperature and the solvent was removed in vacuum. The residue was purified by silica gel chromatography (eluent: heptane/ethyl acetate = 20:1 to heptane/ethyl acetate 8:1) to afford the corresponding products **2a-f**.

methyl (E)-3-((2S,3S)-3-(2-oxopropyl)-2,3-dihydrobenzofuran-2-yl)acrylate **2a**. 80% yield. Colorless oil. ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.22 (d, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 6.98 – 6.92 (m, 2H), 6.90 (d, *J* = 5.3 Hz, 1H), 6.24 (d, *J* = 15.7 Hz, 1H), 5.56 – 5.50 (m, 1H), 4.18 (q, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 2.80 (dd, *J* = 7.0, 3.6 Hz, 2H), 2.22 (s, 3H). ^{13}C-NMR (101 MHz, Chloroform-*d*) δ 206.47, 166.20, 158.48, 142.61, 128.80, 124.34, 122.92, 121.18, 109.91, 83.49, 51.74, 44.90, 40.53, 30.25. (QTOF-MS/UHPLC) m/z: $[M+H]^+$ Calcd for $C_{15}H_{17}O_4$ 261.1121, found 261.1120.

methyl (E)-3-((2S,3S)-5-methyl-3-(2-oxopropyl)-2,3-dihydrobenzofuran-2-yl)acrylate **2b**. 81% yield. Colorless oil. ^{1}H-NMR (400 MHz, Chloroform-d) δ 6.91 (d, *J* = 7.9 Hz, 1H), 6.86 (s, 1H), 6.79 (dd, *J* = 15.7, 5.4 Hz, 1H), 6.68 (d, *J* = 8.1 Hz, 1H), 6.12 (d, *J* = 15.7 Hz, 1H), 5.41 – 5.36 (m, 1H), 4.02 (q, *J* = 7.9 Hz, 1H), 3.70 (s, 3H), 2.67 (dd, *J* = 7.1, 3.4 Hz, 2H), 2.23 (s, 3H), 2.10 (s, 3H). ^{13}C-NMR (101 MHz, Chloroform-*d*) δ 206.54, 166.25, 156.39, 142.78, 130.54, 129.28, 129.14, 124.86, 122.83, 109.43, 83.57, 51.72, 44.90, 40.58, 30.25, 20.80. HRMS (QTOF-MS/UHPLC) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}O_4$ 274.1205, found 275.1278.

methyl (E)-3-((2S,3S)-5-bromo-3-(2-oxopropyl)-2,3-dihydrobenzofuran-2-yl)acrylate **2c**. 73% yield. White solid. Mp 178 °C. ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.0 Hz, 1H), 7.23 (s, 1H), 6.83 (dd, *J* = 15.7, 5.4 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.17 (d, *J* = 15.7 Hz, 1H), 5.50 (dd, *J* = 8.3, 5.9 Hz, 1H), 4.12 (q, *J* = 7.6 Hz, 1H), 3.77 (s, 3H), 2.74 (d, *J* = 7.2 Hz, 2H), 2.18 (s, 3H). ^{13}C-NMR (101 MHz, Chloroform-*d*) δ 205.99, 166.07, 157.69, 141.86, 131.80, 131.63, 127.49, 123.26, 112.99, 111.50, 84.08, 51.82, 44.68, 40.45, 30.18.

methyl (E)-3-((2S,3S)-5-chloro-3-(2-oxopropyl)-2,3-dihydrobenzofuran-2-yl)acrylate **2d**. 70% yield White solid. Mp 153 °C ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 9.1 Hz, 1H), 7.23 (s, 1H), 6.97 (dd, *J* = 15.7, 5.4 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.31 (d, *J* = 15.7 Hz, 1H), 5.68 – 5.60 (m, 1H), 4.25 (q, *J* = 7.6 Hz, 1H), 3.91 (s, 3H), 2.88 (d, *J* = 7.2 Hz, 2H), 2.32 (s, 3H). ^{13}C-NMR (101 MHz, Chloroform-*d*) δ 206.00, 166.08, 157.17, 141.91, 131.27, 128.71, 125.93, 124.64, 123.23, 110.87, 84.12, 51.82, 44.66, 40.51, 30.19. HRMS (QTOF-MS/UHPLC) m/z: $[M+H]^+$ Calcd for $C_{15}H_{16}ClO_4$ 295.0732, found 295.0742.

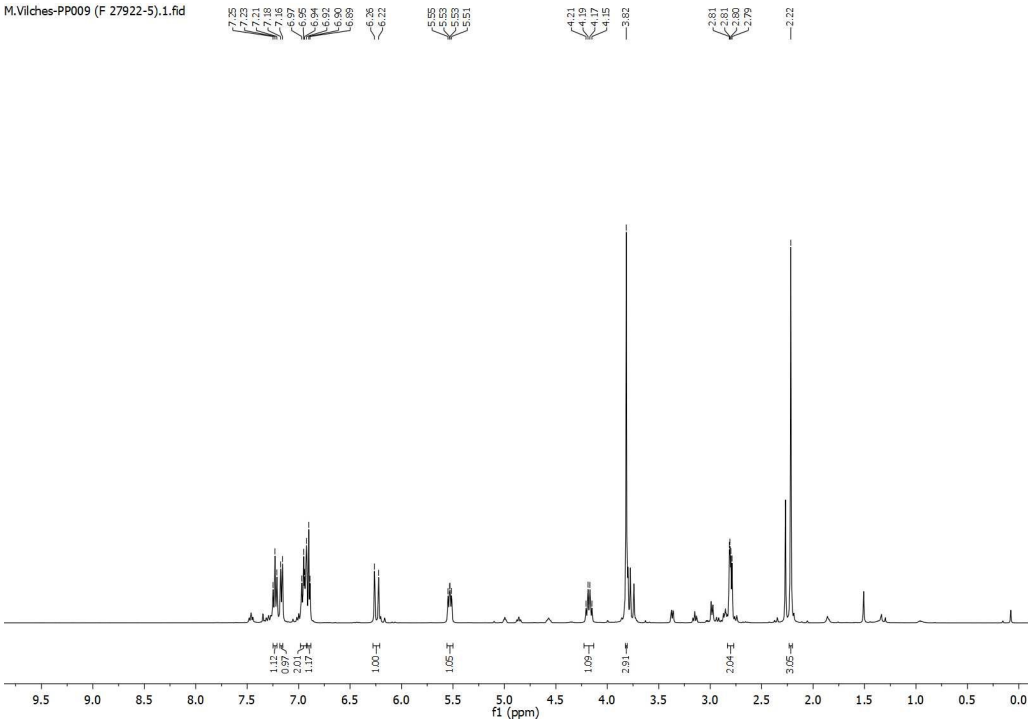
methyl (E)-3-((2S,3S)-5-methoxy-3-(2-oxopropyl)-2,3-dihydrobenzofuran-2-yl)acrylate **2e**. 85% yield. Brown solid. Mp 164 °C ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 6.80 (dd, *J* = 15.7, 5.4 Hz, 1H), 6.72 – 6.64 (m, 3H), 6.13 (d, *J* = 15.7 Hz, 1H), 5.42 – 5.36 (m, 1H), 4.03 (q, *J* = 7.6 Hz, 1H), 3.71 (s, 6H), 2.67 (d, *J* = 7.2 Hz, 2H), 2.11 (s, 3H). ^{13}C-NMR (101 MHz, Chloroform-*d*) δ 206.41, 166.25, 154.61, 152.50, 142.68, 130.39, 122.89, 113.64, 110.68, 109.89, 83.76, 56.02, 51.75, 44.76, 40.95, 30.28. HRMS (QTOF-MS/UHPLC) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}O_5$ 291.1227, found 291.1234.

methyl (E)-3-((2S,3S)-5-fluoro-3-(2-oxopropyl)-2,3-dihydrobenzofuran-2-yl)acrylate **2f**. 77% yield colorless oil. ^{1}H-NMR (400 MHz, Chloroform-d) δ 6.80 (dd, *J* = 10.8, 5.9 Hz, 3H), 6.74 – 6.67 (m, 1H), 6.12 (d, *J* = 15.7 Hz, 1H), 5.47 – 5.39 (m, 1H), 4.05 (q, *J* = 7.6 Hz, 1H), 3.71 (s, 3H), 2.67 (d, *J* = 7.1 Hz, 2H), 2.11 (s, 3H). ^{13}C-NMR (101 MHz, Chloroform-d) δ 206.06, 166.14, 142.14, 123.12, 115.09, 114.85, 111.83, 111.59, 110.17, 110.08, 84.10, 51.80, 44.63, 40.75, 30.21. HRMS (QTOF-MS/UHPLC) m/z: $[M+H]^+$ Calcd for $C_{15}H_{16}FO_4$ 279.1027, found 279.1023.

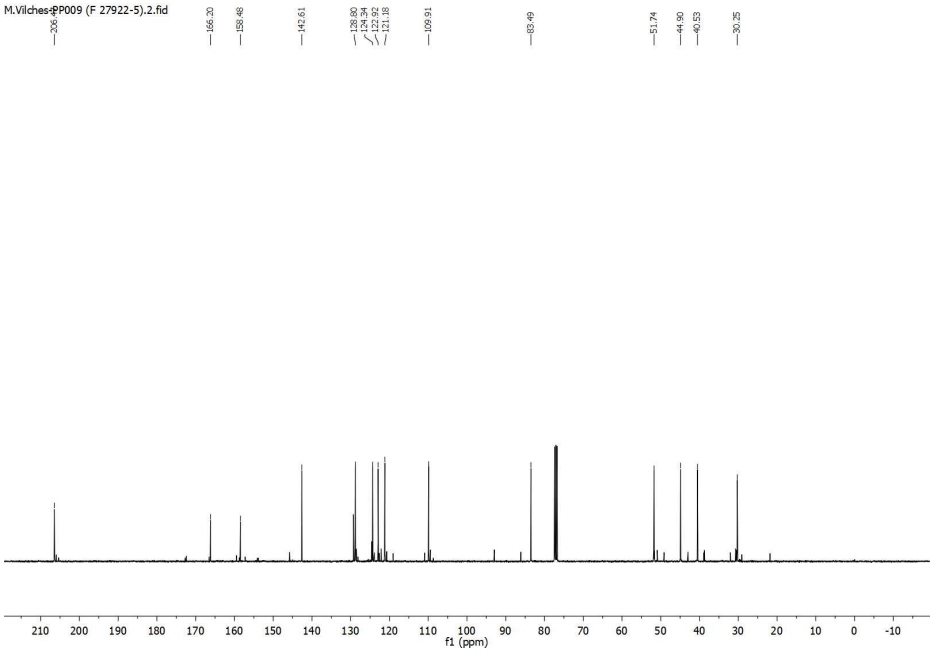
methyl (E)-3-((2S,3S)-6-methoxy-3-(2-oxopropyl)-2,3-dihydrobenzofuran-2-yl)acrylate **2g**. 67% yield pale yellow oil ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 8.4 Hz, 1H), 7.05 (dd, *J* = 15.7, 5.2 Hz, 1H), 6.63 (d, *J* = 6.9 Hz, 2H), 6.37 (d, *J* = 15.7 Hz, 1H), 5.67 (dd, *J* = 8.6, 5.5 Hz, 1H), 4.24 (q, *J* = 7.8 Hz, 1H), 3.98 (s, 3H), 3.96 (s, 3H), 2.90 (dd, *J* = 6.7, 3.1 Hz, 2H), 2.35 (s, 3H). ^{13}C-NMR (101 MHz, Chloroform-*d*) δ 206.68, 166.22, 160.83, 159.72, 142.66, 124.47, 122.80, 121.26, 106.73, 96.52, 84.27, 55.49, 51.73, 45.09, 39.99, 30.28. HRMS (QTOF-MS/UHPLC) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}O_5$ 291.1227, found 261.1237.

^{1}H and ^{13}C-NMR spectra of compounds **2a-2f**

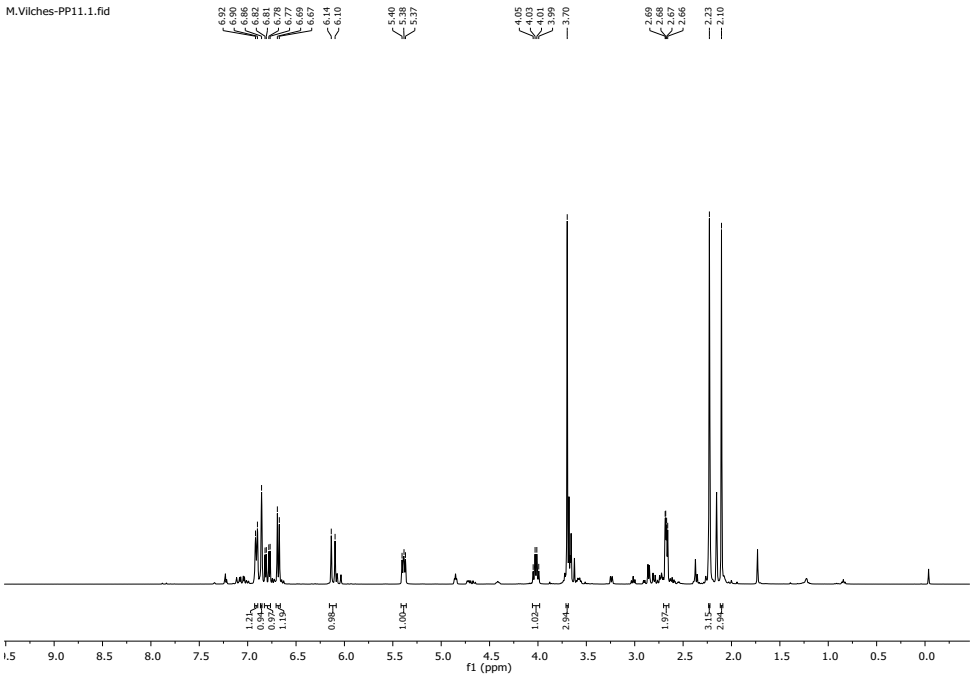
^{1}H-NMR **2a**



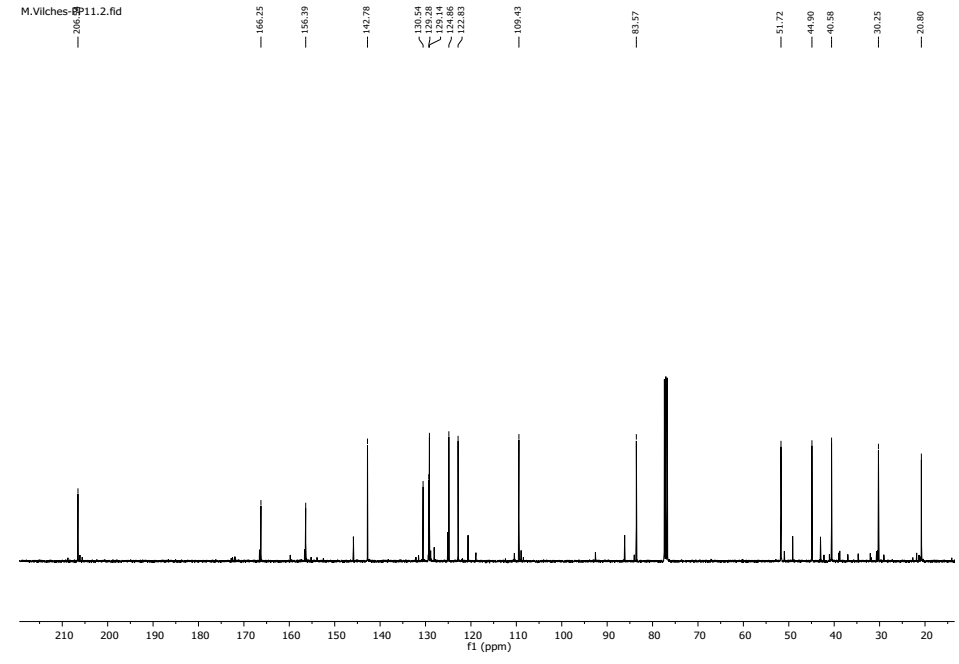
^{13}C-NMR **2a**



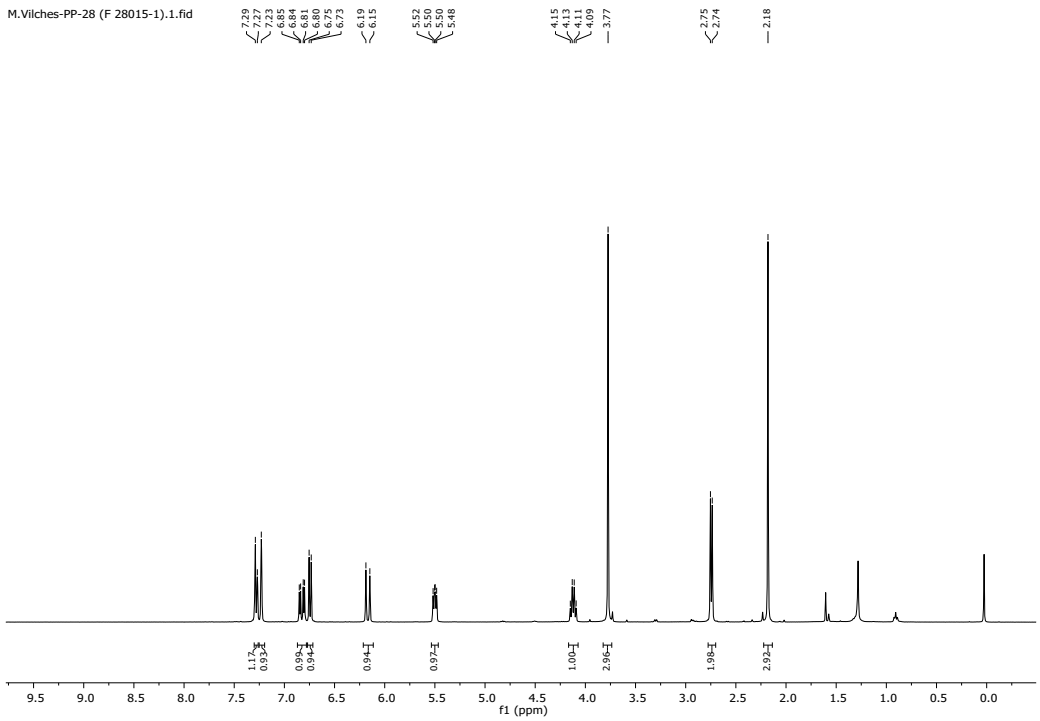
^{1}H-NMR **2b**



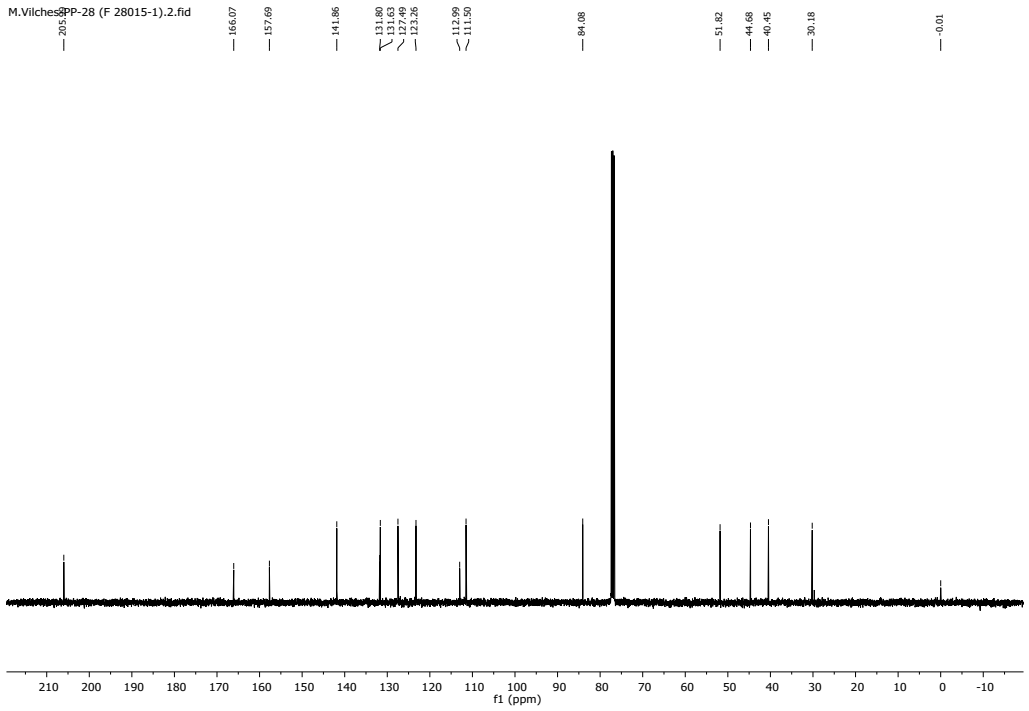
^{13}C-NMR **2b**



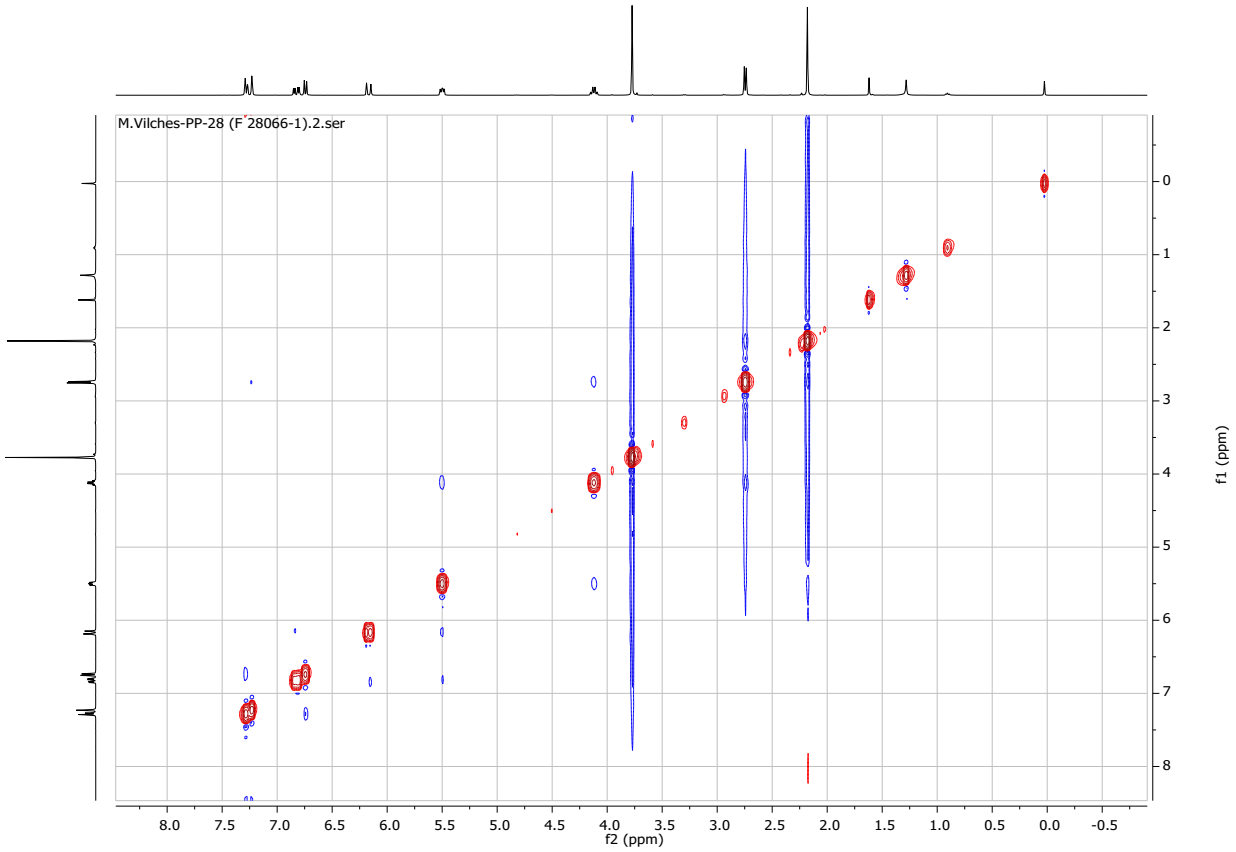
^{1}H-NMR **2c**



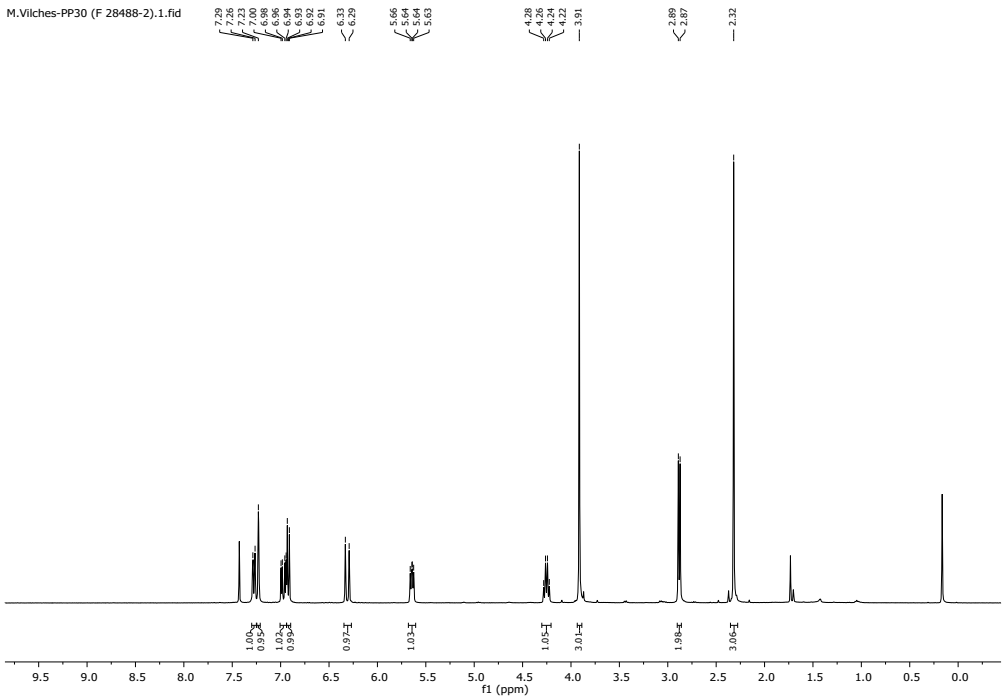
^{13}C-NMR **2c**


M.Vilches-PP-28 (F 28015-1).2.fid
205.5
166.07
157.69
141.86
131.80
131.63
127.49
123.26
112.99
111.50
84.08
51.82
44.68
40.45
30.18
-0.01
f1 (ppm)

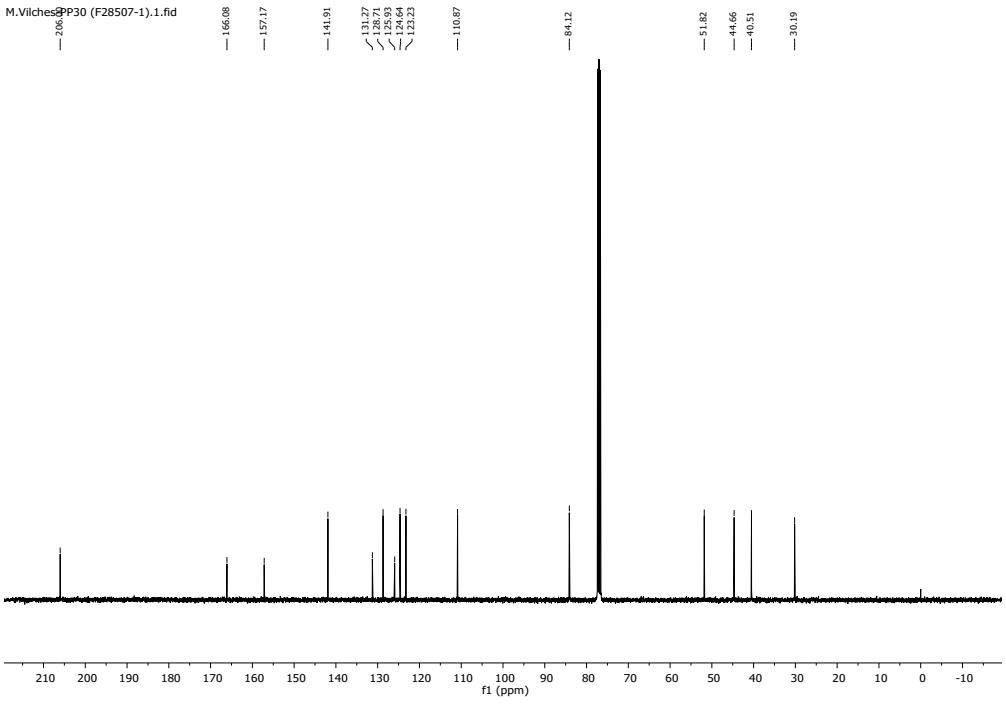
NOESY **2c**


M.Vilches-PP-28 (F 28066-1).2.ser
f2 (ppm)
f1 (ppm)

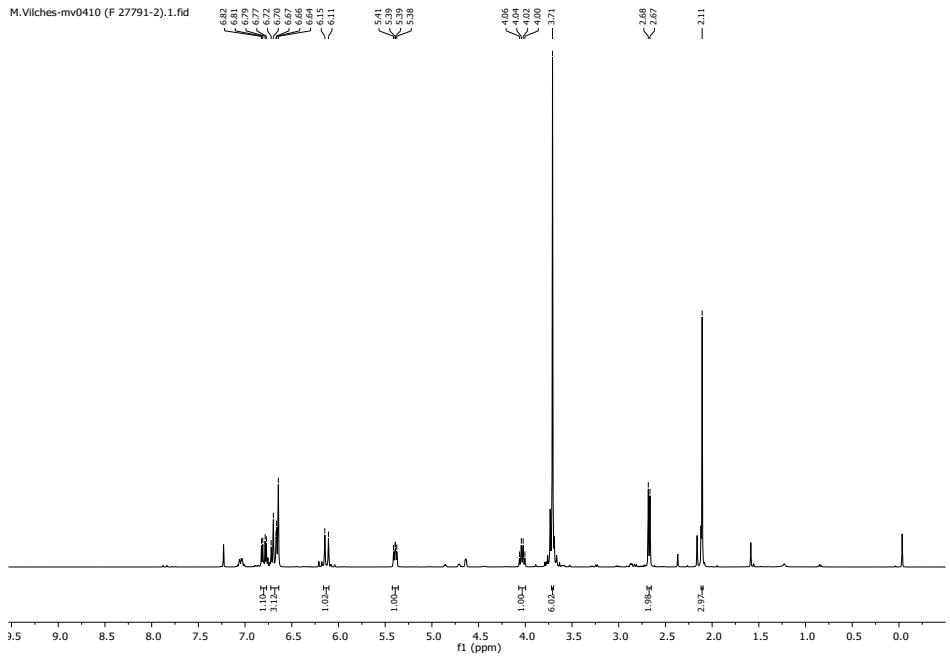
^{1}H-NMR **2d**



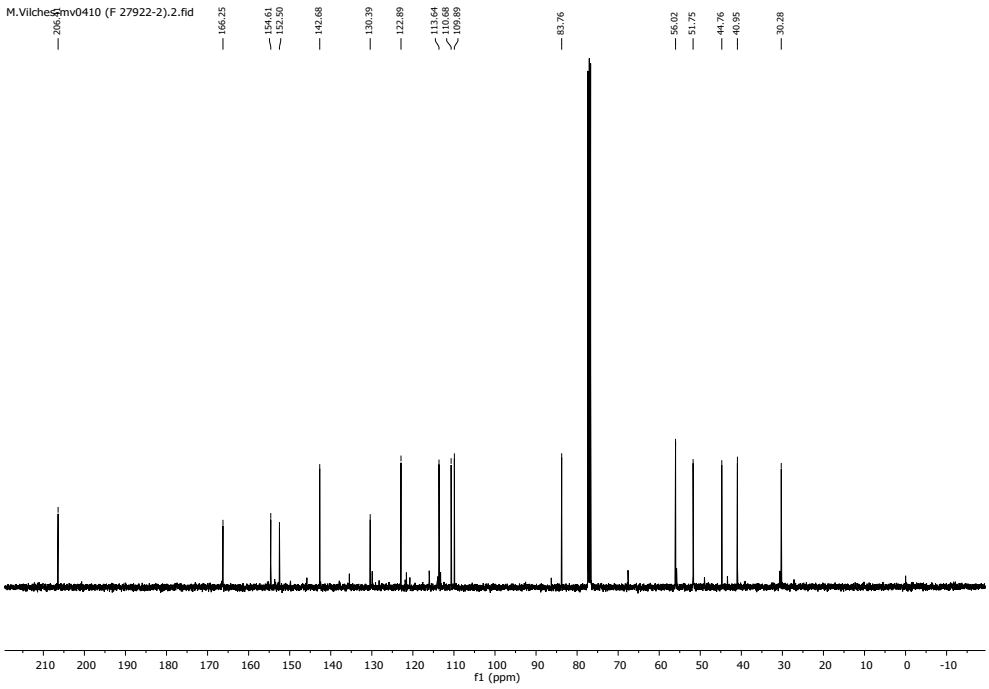
^{13}C-NMR **2d**



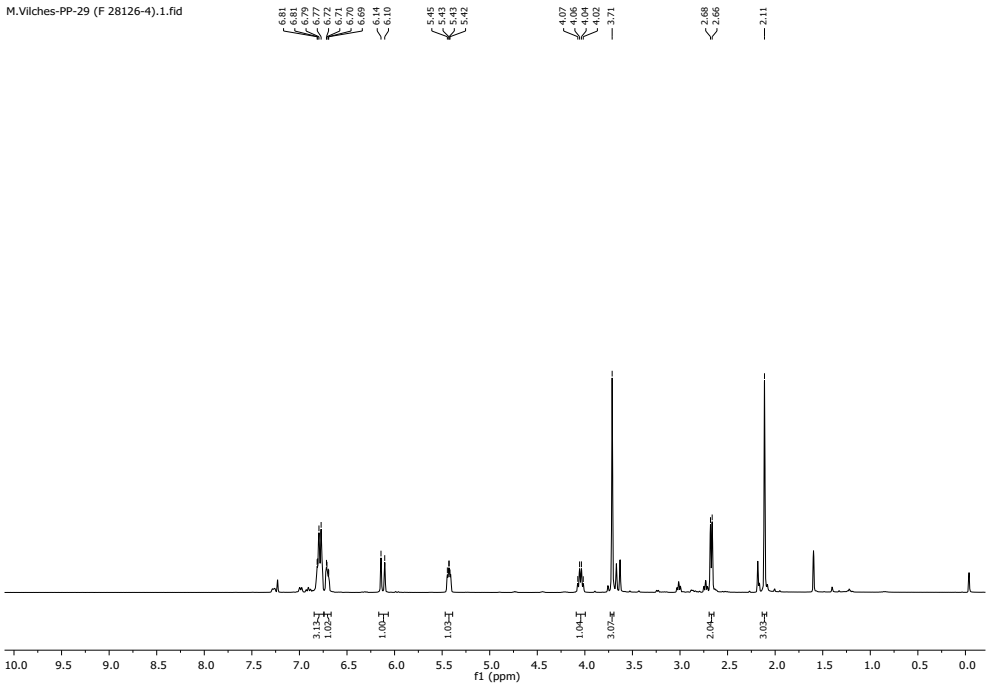
^{1}H-NMR **2e**



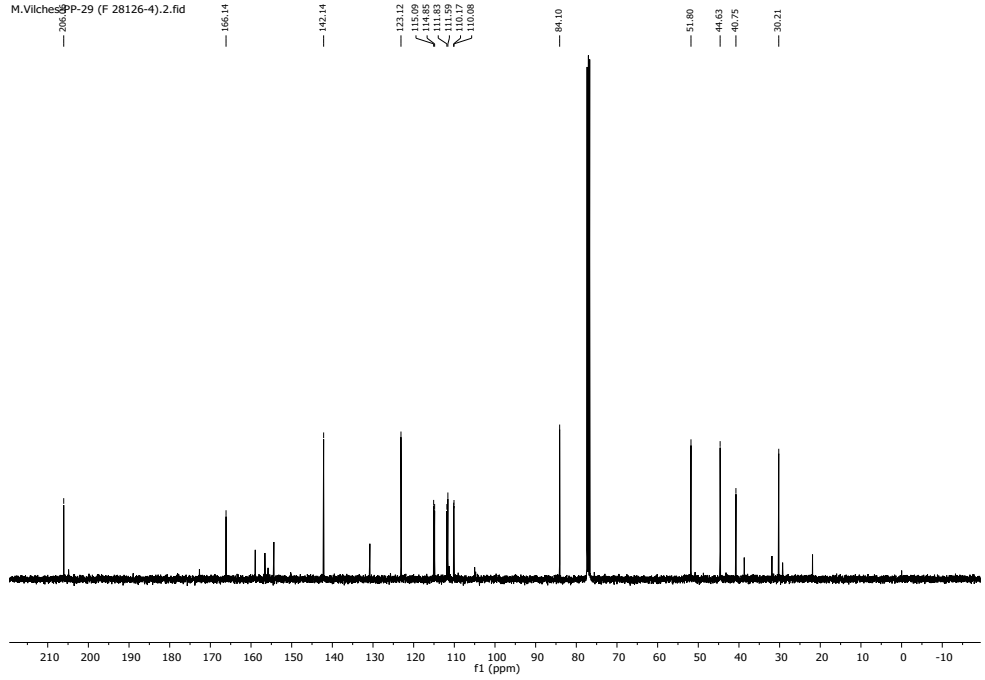
^{13}C-NMR **2e**



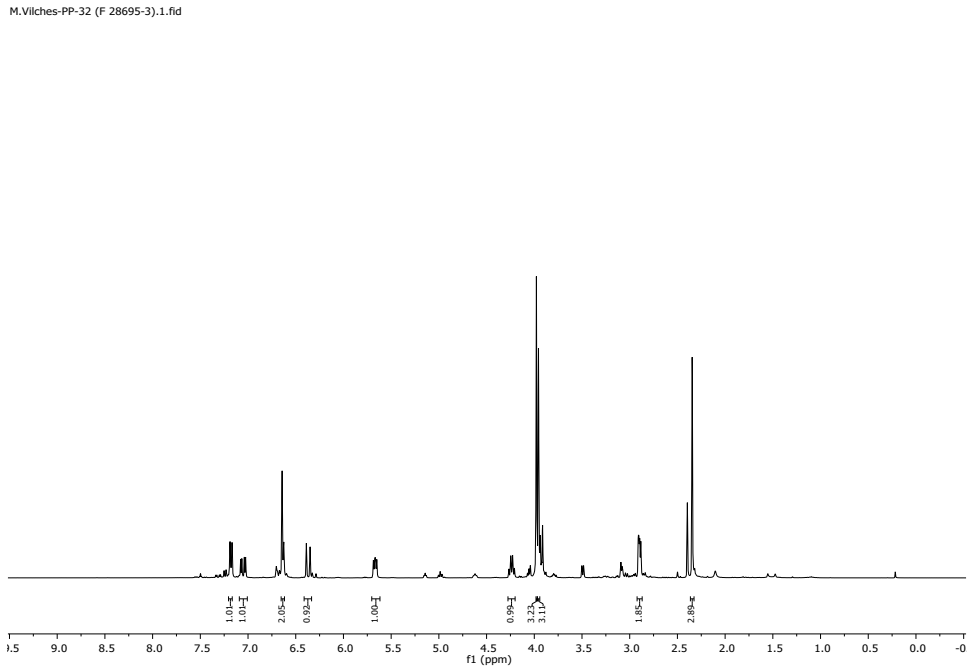
^{1}H-NMR **2f**



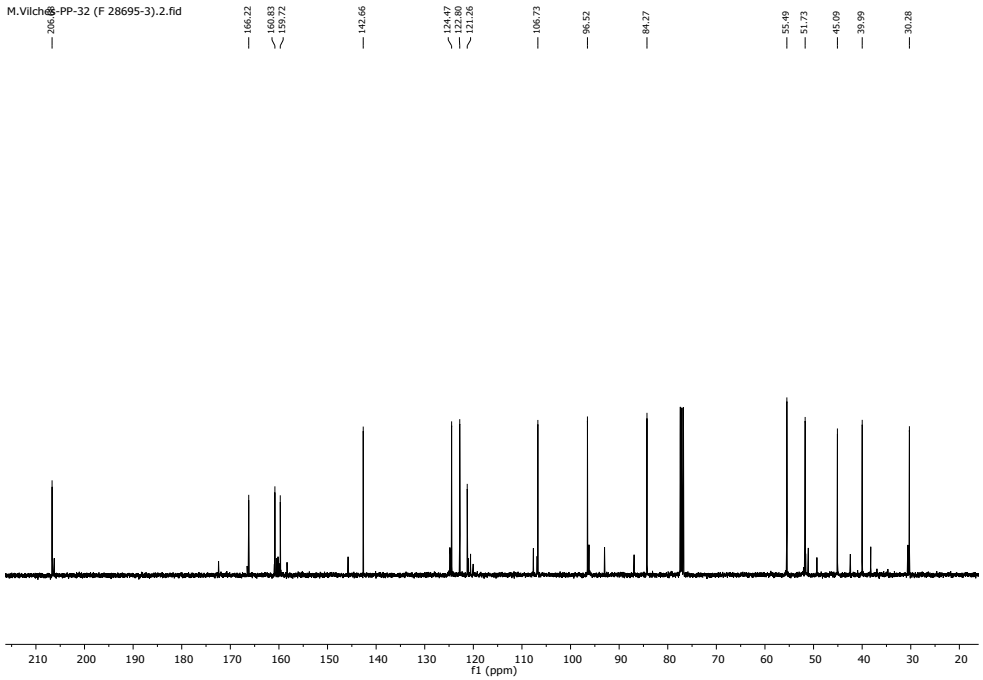
^{13}C-NMR **2f**



^{1}H-NMR **2g**



^{13}C-NMR **2g**



Computational Section

Summary of Energies

Table S1: Relative free energy and total energy profiles for the Cs_2CO_3–catalyzed intramolecular vinylogous Michael reaction of model substrate **1a**. Geometries were optimized at the SMD(THF)–ωB97X–D/def2-TZVP level. The vibrational entropy contribution was computed by means of QRRHO approximation.

Structure	Total Energy [a.u]	G(T) [a.u]	qh-G(T) [a.u]	[kcal/mol]
Cs_2CO_3	-304.356187	-304.385148	-304.382861	
1a	-882.162381	-881.947022	-881.941562	
Cs_2CO_3 + 1a	-1186.518568	-1186.332170	-1.186,324423	0.0
TS1a	-1186.532375	-1186.322567	-1186.313262	7.0
$CsHCO_3$	-284.723793	-284.735437	-284.733758	
Int1a	-901.802461	-901.602592	-901.597299	
CsHCO3 + int1a	-1186.526254	-1186.338029	-1186.331057	-4.2
TS2a-cis	-901.798328	-901.597080	-901.592192	
TS2a-cis + $CsHCO_3$	-1186.522121	-1186.332517	-1186.325950	-1.0
TS2a-trans	-901.793994	-901.595998	-901.589567	
TS2a-trans + $CsHCO_3$	-1186.517787	-1186.331435	-1186.323325	0.7
2a-trans	-882.191788	-881.972690	-881.967655	-16.4
2a-cis	-882.188819	-881.968073	-881.963648	-13.9

Transition State Conformations

We conducted a comprehensive conformational search to identify relevant transition state (TS) conformations for each cyclization pathway involving a chelating mode. In the case of the cis pathway, we identified two distinct cyclization modes resembling the Exo and Endo approaches observed in the Diels-Alder reaction. Four significant conformations were computationally characterized for the low-lying approach (Endo-like), denoted as **TS2a-cis**, **TS2a-cis-b**, **TS2a-cis-c**, and **TS2a-cis-d** in Figure S1. The energetics of these structures are summarized in Table S2

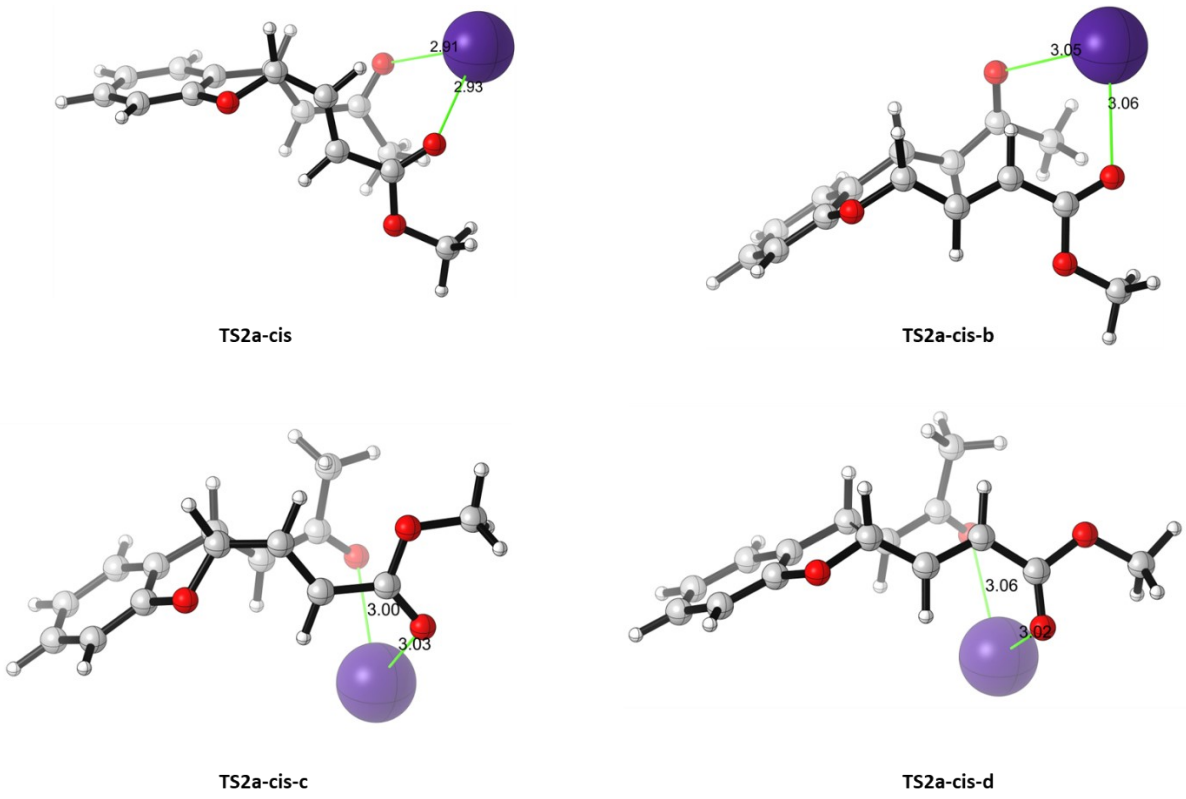
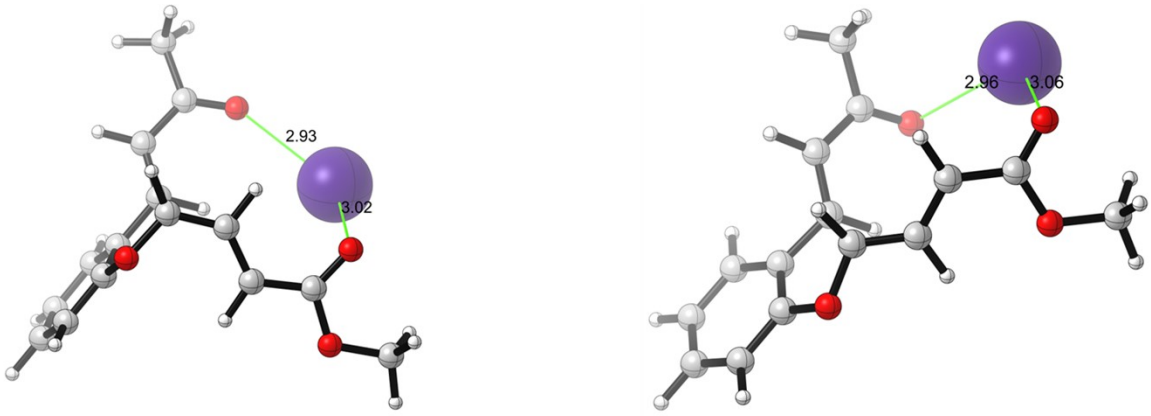


Figure S1: Transition state conformers for the low-lying pathway associated with the 5-exo-trig cyclization of intermediate int1a. Key bond lengths are given in angstroms (Å).

Table S2: Total energy and free energy differences ($\Delta\Delta G^{\ddagger}$ at 298 K) for the *cis*-cyclization pathway of intermediate **int1a** via **TS2a** (w.r.t. **TS2a-cis**). In all cases, the geometries were optimized at the SMD(THF)–ωB97x-D/def2-TZVP level. The vibrational entropy contribution was computed through QRRHO approximation.

Structure	Total Energy [a.u]	G(T) [a.u]	qh-G(T) [a.u]	$\Delta\Delta G^{\neq}$ [kcal/mol]
TS2a-cis	-901.798328	-901.588258	-901.584266	0.0
TS2a-cis-b	-901.791205	-901.581262	-901.577526	4.2
TS2a-cis-c	-901.796714	-901.586788	-901.582665	1.0
TS2a-cis-d	-901.794192	-901.584234	-901.580261	2.5

On the other hand, for the trans approach, two different conformations were computationally characterized, denoted as **TS2a-trans** and **TS2a-trans-b**. The energetics of these structures are summarized in Table S3



TS2a-trans **TS2a-trans-b**

Figure S2: Transition state conformers for the *trans*-approach associated with the 5-exo-trig cyclization of intermediate int1a. Key bond lengths are given in angstroms (Å).

Table S3: Total energy and free energy differences ($\Delta\Delta G^{‡}$ at 298 K) for the *trans*-cyclization pathway of intermediate **int1a** via **TS2a** (w.r.t. **TS2a-cis**). In all cases, the geometries were optimized at the SMD(THF)–ωB97x-D/def2-TZVP level. The vibrational entropy contribution was computed through QRRHO approximation.

Structure	Total Energy [a.u]	G(T) [a.u]	qh-G(T) [a.u]	$\Delta\Delta G^{\neq}$ [kcal/mol]
TS2a-trans	-901.793994	-901.586765	-901.581522	0.0
TS2a-trans-b	-901.786964	-901.578412	-901.574139	4.6

Computational analysis on the role of the Brønsted-base

K_2CO_3-catalyzed deprotonation

Table S4: Total energy and activation free energy ($\Delta G^{\ddagger}$ at 298 K) for the for the deprotonation of substrate **1a** by K2CO3. In all cases, the geometries were optimized at the SMD(THF)–ωB97x-D/def2-TZVP level. The vibrational entropy contribution was computed through QRRHO approximation.

Structure	Total Energy [a.u]	G(T) [a.u]	qh-G(T) [a.u]	$\Delta G^{\neq}$ [kcal/mol]
K2CO3	-1463.834748	-1463.858501	-1463.856881	
1a	-882.162381	-881.947022	-881.941562	
K2CO3 + 1a	-2345.997129	-2345.805523	-2345.798443	0.0
TS1a-K2CO3	-2345.957337	-2345.749471	-2345.738383	37.7

t-ButO$^-$K$^+$-catalyzed deprotonation

Table S5: Total energy and activation free energy ($\Delta G^{\ddagger}$ at 298 K) for the for the deprotonation of substrate **1a** by t-butOK. In all cases, the geometries were optimized at the SMD(THF)–ωB97x-D/def2-TZVP level. The vibrational entropy contribution was computed through QRRHO approximation.

Structure	Total Energy [a.u]	G(T) [a.u]	qh-G(T) [a.u]	$\Delta G^{\neq}$ [kcal/mol]
t-butOK	-833.059753	-832.978763	-832.977287	
1a	-882.162381	-881.947022	-881.941562	
t-butOK + 1a	-1715.222134	-1714.925785	-1714.918849	0.0
TS1a-tbutOK	-1715.196112	-1714.882772	-1714.872260	29.2

Cyclization of the naked anion

TS2a-cis-unc **TS2a-trans-unc**

Figure S3: Transition state structures for the 5-exo-trig cyclization of intermediate **int1a** without the presence of the Cs^+ counterion. Key bond lengths are given in angstroms (Å).

Table S6: Total energy and relative free energy ($\Delta\Delta G^{\ddagger}$ at 298 K) for the for the *5-exo-trig* cyclization of intermediate **int1a** without the presence of the Cs^+ counterion computed at the SMD(THF)–ωB97x-D/def2-TZVP level. The vibrational entropy contribution was computed through QRRHO approximation.

Structure	Total Energy [a.u]	G(T) [a.u]	qh-G(T) [a.u]	$\Delta\Delta G^{\neq}$ [kcal/mol]
TS2a-cis-unc	-881.634341	-881.420717	-881.417759	0.0
TS2a-trans-unc	-881.629294	-881.418581	-881.414465	2.1

Substituent effects

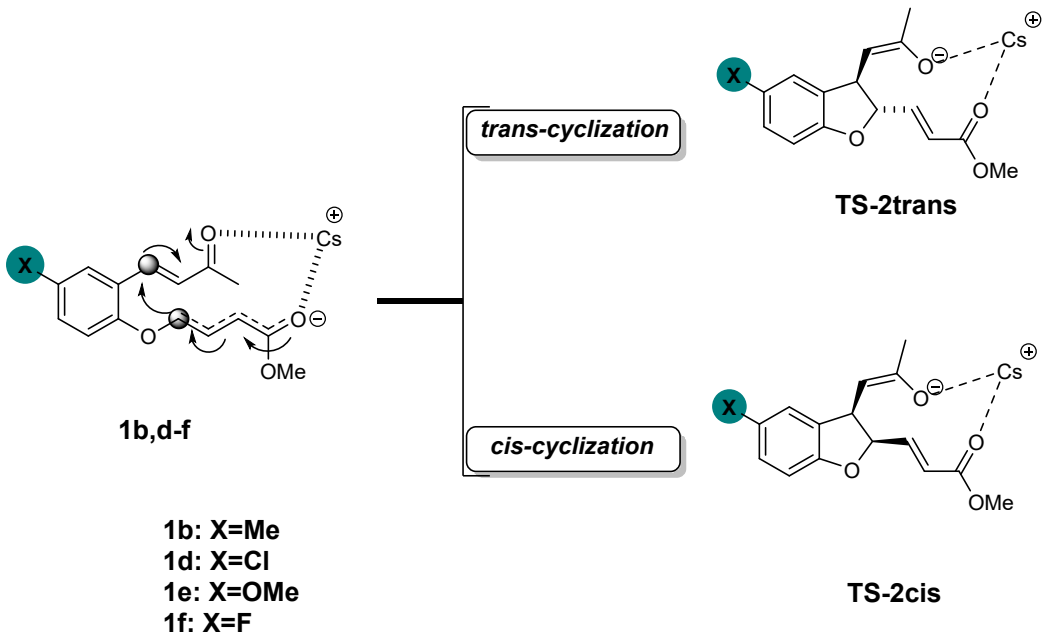


Table S7: Experimental and calculated selectivities for the studied substrates in this work. The computed diastereomeric ratio (d.r) was determined at the SMD(THF)–ωB97x-D/def2-TZVP level. Vibrational entropy contribution was calculated using the QRRHO approximation.

Structure	qh-G(T) [a.u]	$\Delta\Delta G^{\neq}$ [kcal/mol]	d.r (exp)	d.r (calc)
TS2b-cis	-940.878447	0.0		
TS2b-trans	-940.876098	1.47	**90:10**	**92:8**
TS2d-cis	-1361.208275	0.0		
TS2d-trans	-1361.205286	1.88	**100:0**	**96:4**
TS2e-cis	-1016.087758	0.0		
TS2e-trans	-1016.085249	1.57	**93:7**	**93:7**
TS2f-cis	-1000.847782	0.0		
TS2f-trans	-1000.844525	2.04	**100:0**	**97:3**

Cartesian coordinates SMD-(THF)-ωB97X-D/def2-tzvp

Cs_2CO_3

C	-0.00000500	1.33274400	-0.00004100
O	0.00000900	0.02108000	-0.00019800
O	1.11754800	1.95324500	-0.05599200
O	-1.11762300	1.95317200	0.05604900
Cs	-2.81256800	-0.35833400	-0.00322500
Cs	2.81257800	-0.35832900	0.00325000

1a

C	-3.19450300	0.30873300	-0.81781700
C	-3.02210100	0.20022300	0.56947000
C	-3.97684700	-0.50491800	1.29907400
C	-5.07330100	-1.08978200	0.68572600
C	-5.22319300	-0.98175900	-0.68950700
C	-4.28967700	-0.28503500	-1.43655500
H	-3.84350000	-0.59865200	2.37049800
H	-5.80144900	-1.62954700	1.27764600
H	-6.07256700	-1.43682300	-1.18414100
H	-4.39241100	-0.18769400	-2.51008000
C	-1.82203600	0.74133400	1.24879400
H	-1.83740100	1.77739000	1.56223300
C	-0.76409300	-0.03245900	1.51436400
H	-0.77900600	-1.07886400	1.22553600
C	0.48138700	0.42740500	2.13865600
O	1.39657200	-0.36484800	2.32548400
C	0.62873100	1.87443300	2.50903500
H	0.60937800	2.48118300	1.60043800
H	-0.19265700	2.20315400	3.14839900
H	1.57674200	2.02584600	3.02103400
O	-2.29101300	0.92758500	-1.62019000
C	-1.69853500	2.08058400	-1.11444300
H	-2.39849500	2.87202600	-0.87157400
C	-0.36342500	2.22644200	-1.05929700
H	-0.03388400	3.19483300	-0.69677700
C	0.63559500	1.26645800	-1.35270900
H	0.35914100	0.33625600	-1.83215200
C	1.99291900	1.42806500	-1.04198600
O	2.89844200	0.59880100	-1.23887000
C	3.61834900	2.73853100	0.06719800
H	4.36599900	2.69124900	-0.72719500
H	3.66630400	3.71359100	0.55145900
H	3.83661700	1.95841500	0.80034500
O	2.30446400	2.61874100	-0.43901500

Cs	1.97988800	-2.01734800	-0.27409000

TS1a

C	0.07247500	0.01612300	0.01201400
C	0.04907900	-0.01789200	1.41110000
C	1.28101200	-0.05327900	2.09231700
C	2.45833500	-0.20013600	1.36380000
C	2.44854100	-0.21155100	-0.02141300
C	1.25061200	-0.06732700	-0.70670900
H	-0.87279800	0.07892600	-0.51512100
H	3.39097200	-0.28866900	1.90451700
H	3.38137300	-0.31272800	-0.56215700
H	1.23251100	-0.04707300	-1.78867200
C	-1.58248500	-0.44291600	3.29188300
O	-3.91454300	-0.14260100	3.00872000
C	1.01145800	1.24598100	4.08093400
H	0.31457300	1.03082000	4.89268900
C	2.12676900	2.03464000	4.49337100
H	1.85858200	2.87567800	5.12631800
C	3.41716100	1.95019600	4.09007400
H	3.75739600	1.15224400	3.44708700
C	4.39721400	2.94835700	4.47094900
O	4.24621300	3.88241800	5.23056800
O	5.58055400	2.72582000	3.84755800
C	6.62713500	3.63833300	4.14873900
H	6.86831700	3.62467700	5.21278800
H	7.48920900	3.30709000	3.57261700
H	6.35897900	4.65584000	3.85922900
O	1.37769000	0.00128900	3.44086500
H	-0.83060000	-0.69217800	4.02650300
C	-1.26167300	-0.09643300	2.04267000
H	-2.09027100	0.07883700	1.36112600
C	-0.47415000	4.19152600	3.09802400
O	0.66827500	4.62652200	3.39062100
O	-1.53276000	4.86916500	3.05243700
O	-0.57906500	2.88335800	2.75994000
H	0.21224600	2.14263900	3.33236600
Cs	2.04511400	3.36830400	1.12026600
Cs	-3.40167400	2.87201100	2.00523800
C	-3.23479500	-1.06521800	5.09293100
H	-4.29982400	-1.12031400	5.30804300
H	-2.78002600	-2.05444600	5.18688900
H	-2.74221900	-0.41924000	5.82532600
C	-2.99472800	-0.51829600	3.71717400

Int1a

C	-3.19450300	0.30873300	-0.81781700
C	-3.02210100	0.20022300	0.56947000
C	-3.97684700	-0.50491800	1.29907400
C	-5.07330100	-1.08978200	0.68572600
C	-5.22319300	-0.98175900	-0.68950700

C	-4.28967700	-0.28503500	-1.43655500
H	-3.84350000	-0.59865200	2.37049800
H	-5.80144900	-1.62954700	1.27764600
H	-6.07256700	-1.43682300	-1.18414100
H	-4.39241100	-0.18769400	-2.51008000
C	-1.82203600	0.74133400	1.24879400
H	-1.83740100	1.77739000	1.56223300
C	-0.76409300	-0.03245900	1.51436400
H	-0.77900600	-1.07886400	1.22553600
C	0.48138700	0.42740500	2.13865600
O	1.39657200	-0.36484800	2.32548400
C	0.62873100	1.87443300	2.50903500
H	0.60937800	2.48118300	1.60043800
H	-0.19265700	2.20315400	3.14839900
H	1.57674200	2.02584600	3.02103400
O	-2.29101300	0.92758500	-1.62019000
C	-1.69853500	2.08058400	-1.11444300
H	-2.39849500	2.87202600	-0.87157400
C	-0.36342500	2.22644200	-1.05929700
H	-0.03388400	3.19483300	-0.69677700
C	0.63559500	1.26645800	-1.35270900
H	0.35914100	0.33625600	-1.83215200
C	1.99291900	1.42806500	-1.04198600
O	2.89844200	0.59880100	-1.23887000
C	3.61834900	2.73853100	0.06719800
H	4.36599900	2.69124900	-0.72719500
H	3.66630400	3.71359100	0.55145900
H	3.83661700	1.95841500	0.80034500
O	2.30446400	2.61874100	-0.43901500
Cs	1.97988800	-2.01734800	-0.27409000

$CsHCO_3$

C	2.09606000	0.03813400	-0.00013300
O	1.54120600	1.14798700	-0.00028700
O	1.57160700	-1.09751000	-0.00032700
O	3.47543500	0.06966900	0.00037400
Cs	-1.25519500	-0.00615100	0.00004100
H	3.75340200	-0.85168300	0.00046800

TS2a-cis

C	-3.74921700	0.21109700	-0.77309700
C	-3.38097600	-0.72787900	0.18935200
C	-4.37816800	-1.31050100	0.96104900
C	-5.71199400	-0.97221500	0.77093600
C	-6.05418200	-0.02886700	-0.18874600
C	-5.07506200	0.56925600	-0.96786000
H	-4.10254200	-2.03078400	1.72268600
H	-6.48005400	-1.43971500	1.37419100
H	-7.09248700	0.24219700	-0.33705100

H	-5.32624800	1.30340500	-1.72301900
C	-1.93097600	-0.97457200	0.38290100
H	-1.51149600	-1.90488900	0.02146400
C	-1.25006400	-0.30324600	1.37284100
H	-1.71087200	0.54082700	1.87074200
C	0.12440500	-0.57880500	1.63223100
O	0.75004100	-1.49246500	1.06669000
C	0.86208800	0.27147400	2.64047400
H	0.26568100	1.10357500	3.01275300
H	1.16734300	-0.35444800	3.48321600
H	1.77171900	0.66437900	2.17888600
O	-2.77129300	0.79694900	-1.50538400
C	-1.61963000	0.01385300	-1.60924000
H	-1.74001200	-0.82883900	-2.28386100
C	-0.38224200	0.58444600	-1.40931200
H	0.45828700	-0.00911800	-1.75360400
C	-0.11812100	1.70192700	-0.64858400
H	-0.92276100	2.31887000	-0.27486500
C	1.21502000	2.08209800	-0.31255800
O	2.25731700	1.52447800	-0.65245900
C	2.54357800	3.60623700	0.89665000
H	3.16405600	3.88910400	0.04437300
H	2.37837500	4.47368900	1.53308600
H	3.05632000	2.82803000	1.46512600
O	1.25705000	3.17885400	0.47913700
Cs	3.23841900	-1.23135700	-0.41927600

TS2a-trans

C	3.03378200	-1.15094000	0.42725300
C	2.72147500	-0.03237200	-0.34172900
C	3.45832600	0.19962600	-1.49981700
C	4.46752300	-0.66610600	-1.89289500
C	4.75529300	-1.78044900	-1.11486400
C	4.04342100	-2.02654500	0.04662600
H	3.22579100	1.07220800	-2.09925000
H	5.02632600	-0.47118500	-2.79938700
H	5.54410600	-2.46133300	-1.41082800
H	4.26251600	-2.88425700	0.66998600
C	1.62514600	0.87546000	0.07185100
H	0.63792700	0.61193700	-0.28607000
C	1.85033000	2.19716400	0.37380100
H	2.85612800	2.53410500	0.59459400
C	0.77647500	3.13128300	0.49917200
O	-0.41654000	2.83085600	0.33956700
C	1.11534300	4.55602400	0.86752100
H	0.79486000	4.73729900	1.89736300
H	2.18133300	4.76976700	0.79417600
H	0.55907100	5.24183500	0.22635500

O	2.37268500	-1.38189000	1.58178000
C	1.31447700	-0.50976700	1.85073600
H	1.52699600	0.19007200	2.64837600
C	0.02564700	-0.92959200	1.59849700
H	-0.74982900	-0.28847100	2.01088900
C	-0.37814200	-1.99910000	0.81989500
H	0.34420300	-2.69048500	0.40733100
C	-1.75917500	-2.26178400	0.58842600
O	-2.71824500	-1.58536700	0.96173000
C	-3.30654300	-3.69865900	-0.45708000
H	-3.77636600	-2.90172900	-1.03747600
H	-3.27138000	-4.61025300	-1.05096200
H	-3.89460400	-3.87124600	0.44579000
O	-1.95887100	-3.38405600	-0.14528400
Cs	-2.47199200	0.97745300	-0.61704700

TS2a'-cis

C	3.34432600	0.48520200	0.44301100
C	2.81626800	-0.60631700	-0.24188200
C	3.29611300	-0.88224200	-1.51670300
C	4.29940700	-0.10768300	-2.08346700
C	4.82802500	0.95974500	-1.37056800
C	4.35081900	1.26592400	-0.10494900
H	2.88905900	-1.72880600	-2.05726100
H	4.66817800	-0.33960500	-3.07455200
H	5.61034900	1.56951300	-1.80613100
H	4.73485500	2.11055900	0.45313600
C	1.79152100	-1.43578000	0.43258400
H	2.16441800	-2.06676000	1.23052700
C	0.67172700	-1.86920300	-0.25617000
H	0.39976500	-1.37096100	-1.18219100
C	-0.21484300	-2.87860000	0.21207100
O	-1.25555900	-3.17940500	-0.40039000
C	0.08850500	-3.58205400	1.51775100
H	1.07396400	-4.05197400	1.50249300
H	0.08033900	-2.86831000	2.34638600
H	-0.66751200	-4.34386100	1.69962400
O	2.84043600	0.79928800	1.65729400
C	1.64305200	0.13797300	1.97569100
H	1.72905900	-0.49342700	2.85022000
C	0.45090900	0.78726400	1.69724000
H	-0.43789500	0.31358400	2.10781600
C	0.26755500	1.86576100	0.86628700
H	1.11123400	2.38591700	0.43298100
C	-1.03866200	2.38602200	0.60102800
O	-2.10822000	1.95112800	1.02181100
C	-2.26422700	4.02856300	-0.55899800
H	-2.79729800	4.37792200	0.32639800

H	-2.04353800	4.87079500	-1.21177000
H	-2.89092100	3.30873500	-1.08964500
O	-1.00798200	3.46224800	-0.21578000
Cs	-2.71557100	-0.53212500	-0.52198300

2a-cis

C	0.78813800	1.82782300	0.64037600
C	1.57449000	0.80507600	0.13168000
C	2.39274400	1.04821000	-0.95279000
C	2.41428800	2.32629600	-1.50919500
C	1.62875700	3.33838600	-0.97502000
C	0.79485200	3.10379800	0.11508800
H	3.01814800	0.26563500	-1.36439200
H	3.05078700	2.53105400	-2.36062300
H	1.65655600	4.32773300	-1.41510700
H	0.17058100	3.88420200	0.53067000
C	1.35157100	-0.41909400	0.98431000
H	2.15919600	-0.48416600	1.71724500
C	1.28133200	-1.74208200	0.24015000
H	0.61726200	-1.68228900	-0.62532600
C	2.62812100	-2.27813400	-0.20070800
O	3.66408400	-1.91549800	0.30687000
C	2.58804200	-3.30508100	-1.29513500
H	1.79806700	-4.03608300	-1.11118900
H	2.34309400	-2.79830300	-2.23336600
H	3.55070300	-3.80272400	-1.39516000
O	0.02879700	1.43469700	1.69634200
C	0.05220700	-0.00078400	1.73546900
H	0.10281700	-0.29607600	2.78450400
C	-1.19633800	-0.56945000	1.14096800
H	-1.31833500	-1.64298800	1.24345200
C	-2.13796700	0.12581200	0.51826400
H	-2.07262800	1.19894700	0.39766300
C	-3.32783200	-0.55030900	-0.04054100
O	-3.55441200	-1.73530900	0.00815600
C	-5.33319800	-0.19716800	-1.21028000
H	-5.94919600	-0.68723000	-0.45588800
H	-5.86214800	0.65630000	-1.62734800
H	-5.09135500	-0.90940300	-1.99960400
O	-4.14282800	0.33108500	-0.62490900
H	0.86607500	-2.52420600	0.88697700

2a-trans

C	0.78066900	1.66350500	0.71409400
C	1.38277100	1.16226400	-0.42905000
C	1.93685700	2.02806700	-1.35050700
C	1.87795200	3.39846800	-1.10797600

C	1.27486100	3.88034300	0.04723200
C	0.71233000	3.01699800	0.98241400
H	2.41077900	1.64886100	-2.24844300
H	2.30301300	4.09149800	-1.82281600
H	1.23538700	4.94815600	0.22486600
H	0.23664300	3.38651800	1.88159000
C	1.33047000	-0.34088800	-0.37848000
H	0.90908000	-0.76124700	-1.29153800
C	2.70231200	-0.95770200	-0.13708000
H	3.13291100	-0.60219100	0.80483600
C	2.70782400	-2.46981600	-0.12848900
O	1.72247600	-3.11502100	-0.40724000
C	4.00647200	-3.11989900	0.25552900
H	4.84377800	-2.65104300	-0.26478700
H	4.16871100	-2.96895800	1.32668100
H	3.97930200	-4.18714400	0.04402300
O	0.28945100	0.69347900	1.52462900
C	0.34359400	-0.55163300	0.80704600
H	0.71625100	-1.30522200	1.50323300
C	-1.00814500	-0.96302400	0.32778700
H	-1.04449800	-1.93792100	-0.14859600
C	-2.11154100	-0.23376100	0.42225000
H	-2.11227200	0.74073100	0.89249200
C	-3.39572900	-0.73087700	-0.11379700
O	-3.56971300	-1.79115300	-0.66392000
C	-5.66770000	-0.20129400	-0.38363600
H	-6.01914500	-1.10802300	0.10962300
H	-6.31713900	0.63450200	-0.13480400
H	-5.65576100	-0.35751000	-1.46264800
O	-4.37025300	0.16045600	0.08912800
H	3.39928800	-0.63761700	-0.91850600

TS2a-cis-b

C	-0.05007500	0.52124200	-0.06386300
C	-0.14895600	-0.12272100	1.17171300
C	0.95257200	-0.84237100	1.62522500
C	2.12656600	-0.90495300	0.88845300
C	2.20700800	-0.24025000	-0.32768600
C	1.12063600	0.47215800	-0.80920800
H	0.88277300	-1.34997900	2.58033200
H	2.97279800	-1.46674700	1.26323700
H	3.11828000	-0.28179200	-0.91198900
H	1.16119000	0.97992600	-1.76473800
C	-1.39667000	-0.01368700	1.96437600
H	-1.51692900	0.88694100	2.55647200
C	-2.13253800	-1.10169100	2.36010700
H	-1.98885000	-2.05414800	1.86220400
C	-3.19589300	-1.01024100	3.31084200

O	-3.49892800	0.02048100	3.93503900
C	-4.00219300	-2.27083700	3.55186500
H	-4.35895200	-2.29551500	4.58271300
H	-4.87199100	-2.26987400	2.88516900
H	-3.43147800	-3.17569900	3.34269400
O	-1.11686800	1.18012400	-0.57767700
C	-2.26593400	1.13431900	0.21656600
H	-2.42478800	2.02414900	0.81345500
C	-3.29097900	0.29155600	-0.14041700
H	-3.08518200	-0.42621400	-0.92950600
C	-4.45416500	0.15435000	0.59081700
H	-4.63548700	0.84113400	1.40747300
C	-5.41453400	-0.88312200	0.44819100
O	-6.39152100	-1.04085700	1.18600700
C	-6.08997800	-2.82140100	-0.70916100
H	-7.10912900	-2.47127400	-0.88118700
H	-5.74761800	-3.38957800	-1.57240200
H	-6.07837600	-3.45937800	0.17653600
O	-5.18557700	-1.73676000	-0.57482300
Cs	-6.52529200	0.39852200	3.88664100

TS2a-cis-c

C	-0.03067800	-0.10522100	-0.01514000
C	-0.01047800	-0.03603400	1.37622100
C	1.21794700	-0.03046600	2.02271200
C	2.39997500	-0.07926100	1.29418700
C	2.35487900	-0.15792900	-0.09170700
C	1.13824200	-0.17129100	-0.75811100
H	1.24604400	0.00544500	3.10568600
H	3.35286500	-0.06218700	1.80800000
H	3.27476900	-0.20246800	-0.66204700
H	1.08721000	-0.22461800	-1.83835000
C	-1.32434200	-0.09647400	2.07356000
H	-1.68037500	0.80598700	2.55401300
C	-1.72486300	-1.32862500	2.55897300
H	-1.16320200	-2.20618800	2.25378200
C	-2.84838800	-1.55859800	3.40995900
O	-3.14159600	-2.69279600	3.82704800
C	-3.70456600	-0.38278700	3.81780900
H	-4.52862700	-0.73072400	4.43810500
H	-3.11921100	0.35064100	4.37793600
H	-4.10648200	0.12402800	2.93778200
O	-1.24142300	-0.12824600	-0.62438500
C	-2.22022700	0.48477600	0.16164900
H	-2.10044900	1.56321500	0.21618400
C	-3.47728600	-0.07673300	0.25884800
H	-4.23142300	0.57754100	0.68257900
C	-3.79776400	-1.39927600	0.06617400

H	-3.07913400	-2.07634600	-0.37629200
C	-5.05108200	-1.98412700	0.43472200
O	-5.31555000	-3.18183300	0.34899900
C	-7.17444700	-1.67056300	1.40100600
H	-6.99246200	-2.37451900	2.21493100
H	-7.76249400	-0.83095800	1.76695800
H	-7.71644200	-2.17956200	0.60267400
O	-5.95762900	-1.11393600	0.92581200
Cs	-3.01830900	-4.71399800	1.60710900

TS2a-cis-d

C	0.30662900	-0.13800900	-0.08335900
C	0.05517100	0.05161300	1.27607300
C	1.11779000	0.42180700	2.09585700
C	2.38800800	0.62479500	1.57786800
C	2.60987200	0.44673000	0.21801800
C	1.57382000	0.06319200	-0.61667800
H	0.93341600	0.56160400	3.15476300
H	3.19877000	0.92270600	2.23052500
H	3.59858200	0.60166000	-0.19664300
H	1.73410300	-0.09482800	-1.67586100
C	-1.31407100	-0.15952100	1.80912900
H	-1.98343800	0.68670900	1.73385200
C	-1.55134600	-1.08677900	2.80030900
H	-0.77958700	-1.82703700	2.99499300
C	-2.74635700	-1.23368900	3.56849900
O	-2.87028600	-2.15730200	4.39314400
C	-3.88677200	-0.24968300	3.43790300
H	-4.82629500	-0.80254900	3.41729400
H	-3.89629800	0.38705900	4.32688600
H	-3.83182600	0.38761900	2.55781400
O	-0.68163100	-0.57413300	-0.89712300
C	-1.93853700	-0.63219400	-0.28629900
H	-2.50693000	0.28693700	-0.37039800
C	-2.55703600	-1.85925500	-0.19103800
H	-1.94665600	-2.73377900	-0.40697900
C	-3.82090700	-2.07893400	0.31283500
H	-4.47144000	-1.25068300	0.56193700
C	-4.33135700	-3.39680300	0.50413700
O	-3.75158300	-4.45893100	0.28302600
C	-6.15501500	-4.66360500	1.29315100
H	-5.56858200	-5.20750400	2.03706700
H	-7.14905200	-4.46550600	1.68947600
H	-6.23181600	-5.27161500	0.39061400
O	-5.58594000	-3.39357600	1.01501300
Cs	-2.06662800	-4.64173800	2.78822900

TS2a-trans-b

C	3.89770600	-0.93618500	-0.04469600
C	3.45807700	0.36180900	0.20930700
C	4.40283600	1.32710500	0.53462600
C	5.75139200	1.00395100	0.62083100
C	6.16218700	-0.29962500	0.38465800
C	5.23737000	-1.27700300	0.04457500
H	4.07013000	2.33837800	0.73735500
H	6.47527500	1.76811700	0.87400200
H	7.21176500	-0.55932800	0.45016800
H	5.54418800	-2.29378500	-0.16618000
C	2.00257800	0.65293300	0.20373200
H	1.45396200	0.30370500	1.07295100
C	1.44956500	1.70769400	-0.47812600
H	1.97382300	2.13492200	-1.32554200
C	0.18343400	2.27040000	-0.12022300
O	-0.47085900	1.93861500	0.87967900
C	-0.38311200	3.33380800	-1.03601300
H	-0.99878000	2.84479300	-1.79847600
H	-1.01735700	4.01708500	-0.47105200
H	0.39459700	3.89379400	-1.55570700
O	2.98644300	-1.87379700	-0.40073700
C	1.80174800	-1.31735800	-0.89223700
H	1.91412400	-0.86521000	-1.87340900
C	0.60352400	-1.83671900	-0.47445500
H	0.62629800	-2.44178100	0.42732200
C	-0.63023500	-1.59686800	-1.06941400
H	-0.69232900	-1.03968400	-1.99637800
C	-1.86314700	-2.09375800	-0.57511400
O	-2.97235500	-1.87241300	-1.06967100
C	-2.98246200	-3.30268300	1.11348700
H	-3.52864400	-3.94325300	0.41932300
H	-2.70932300	-3.87228900	2.00015800
H	-3.62632300	-2.46840800	1.40259700
O	-1.76340700	-2.84684100	0.55304100
Cs	-3.16143200	0.89878900	0.21052300

TS1a-K_2CO_3

C	0.00914800	0.04921400	-0.01522500
C	-0.00215800	0.02979800	1.39974400
C	1.22026900	0.03423800	2.08009800
C	2.42023100	0.05480700	1.40206800

C	2.40954200	0.06639900	0.00899300
C	1.22595000	0.06518800	-0.70405200
H	1.22181600	0.02860800	3.16317000
H	3.35634100	0.06026300	1.94538500
H	3.34665000	0.07152000	-0.53590000
H	1.24517200	0.04447900	-1.79002600
C	-1.28007000	0.00765900	2.08445200
H	-2.13934700	0.11381700	1.43326100
C	-1.50062900	-0.13813600	3.40231100
H	-0.69139300	-0.26788000	4.11245200
C	-2.83265800	-0.15813600	3.98336200
O	-2.96370600	-0.32001100	5.19738100
C	-4.05021800	0.00485100	3.11904800
H	-4.94046400	0.00948100	3.74411900
H	-4.00149500	0.93242100	2.54650400
H	-4.11679200	-0.81728300	2.40330200
O	-1.17673800	0.05375500	-0.61896000
C	-1.26003800	0.09208000	-2.04720100
H	-0.72793900	0.95617700	-2.45247500
C	-2.61486600	-0.00289600	-2.47939800
H	-2.76048000	0.20501700	-3.53664700
C	-3.69439300	-0.39966600	-1.76616300
H	-3.61954100	-0.62592400	-0.71133600
C	-4.99536200	-0.54129500	-2.39041600
O	-5.27718500	-0.34703600	-3.55614700
C	-7.24886500	-1.09857200	-1.99230900
H	-7.28080200	-1.86524600	-2.76819400
H	-7.85435300	-1.41025200	-1.14303500
H	-7.63952500	-0.16464900	-2.40009300
O	-5.93049500	-0.92909700	-1.49127700
H	-0.61857100	-0.96253000	-2.60533000
C	1.01175400	-1.70944100	-3.79265700
O	1.40366000	-0.49036800	-3.88008400
O	-0.04362400	-1.99362000	-3.07682200
O	1.62430400	-2.65250000	-4.38600700
K	3.27925000	-1.07836800	-5.50985400
K	-2.96550800	-0.94729600	7.62284700

TS1a-tbutOK

C	0.00025500	-0.00463700	0.00125900
C	-0.00132900	0.00259800	1.41380600
C	1.22471800	0.00958100	2.08615700
C	2.42059300	0.01197700	1.39844600
C	2.40202700	-0.00778700	0.00639900
C	1.21060500	-0.01474800	-0.69416000
H	1.23148700	0.03749400	3.16910300
H	3.36023300	0.02800500	1.93530700
H	3.33459700	-0.02486000	-0.54539200

H	1.20172300	-0.10025700	-1.77333800
C	-1.27514800	0.02357100	2.11012900
H	-2.12516400	0.28253800	1.48981200
C	-1.49097100	-0.25561200	3.40563300
H	-0.68711700	-0.56207300	4.06617000
C	-2.80836800	-0.20387900	4.02178300
O	-2.93537700	-0.50589700	5.20830200
C	-4.01136500	0.20840300	3.22356100
H	-4.89330100	0.19127800	3.85992300
H	-3.87587900	1.21161100	2.81554900
H	-4.15980800	-0.46899500	2.38014600
O	-1.19384200	-0.02509100	-0.59375500
C	-1.31128700	0.28037800	-1.98959100
H	-0.93329600	1.29298200	-2.17776000
C	-2.68053600	0.13079100	-2.40838500
H	-2.89230200	0.51950300	-3.40072800
C	-3.67892800	-0.49290300	-1.75615100
H	-3.53606400	-0.90979800	-0.76860400
C	-4.99616800	-0.63475100	-2.36178400
O	-5.34093800	-0.24486200	-3.45734200
C	-7.16750000	-1.47511500	-2.01942800
H	-7.16256100	-2.08400300	-2.92472600
H	-7.70242100	-1.99634400	-1.22789100
H	-7.65739000	-0.52374200	-2.23243800
O	-5.84687600	-1.27380300	-1.53149800
H	-0.59644100	-0.48066400	-2.74727700
O	0.20936300	-1.27090100	-3.49312300
K	-2.75837600	-1.45902800	7.52539200
C	0.58019300	-0.72515000	-4.70410700
C	1.68565200	0.33263600	-4.51588700
H	2.55146700	-0.11957800	-4.02390300
H	2.01838400	0.76808600	-5.46407500
H	1.32346100	1.14616800	-3.88024300
C	-0.61395200	-0.05472000	-5.41211700
H	-0.35111800	0.30852700	-6.41080800
H	-1.43575500	-0.76894600	-5.50965600
H	-0.97589600	0.79921900	-4.83288400
C	1.11934200	-1.83957100	-5.61309400
H	0.34351600	-2.59312100	-5.77315500
H	1.44388000	-1.46424800	-6.58961000
H	1.97007300	-2.33007000	-5.13207900

TS2b-cis

C	-0.01076700	0.01878000	-0.00121900
C	-0.00319500	-0.00350400	1.39178200
C	1.21891000	-0.01561500	2.04895700
C	2.42565200	0.00546200	1.35134500
C	2.37867100	0.01938400	-0.03909500

C	1.17075000	0.02717400	-0.72274400
H	1.22943300	-0.05108300	3.13354500
H	3.30432300	0.02677000	-0.60388500
H	1.14024400	0.03898900	-1.80515400
C	-1.31455800	-0.10382000	2.07883700
H	-1.70163700	0.77248200	2.58345500
C	-1.78438500	-1.33508700	2.47937500
H	-1.31124000	-2.23902500	2.11627600
C	-2.99827900	-1.45241500	3.21590400
O	-3.63951400	-0.46906100	3.62738500
C	-3.53991400	-2.83110900	3.51592600
H	-2.96226300	-3.62653300	3.04646400
H	-3.54922500	-2.98660900	4.59795500
H	-4.57456800	-2.89070900	3.16812400
O	-1.20894700	-0.00412100	-0.63808200
C	-2.24633300	0.51516400	0.13721800
H	-2.21197800	1.59766800	0.22315100
C	-3.44633500	-0.15782300	0.21386900
H	-4.27427800	0.42097800	0.60985500
C	-3.62833600	-1.51124500	0.03795800
H	-2.83066200	-2.13106800	-0.34562700
C	-4.85957300	-2.15047600	0.37068700
O	-5.88130200	-1.62003300	0.80375600
C	-5.98864600	-4.21256000	0.51825900
H	-6.84209300	-3.89821600	-0.08523000
H	-5.76325000	-5.25823000	0.31668500
H	-6.23673300	-4.08861500	1.57406400
O	-4.81844000	-3.48840900	0.17379700
Cs	-6.40984600	0.18940200	3.05151100
C	3.73581500	0.03018400	2.08966200
H	3.95416400	1.03175700	2.47079700
H	3.72114400	-0.64685600	2.94607500
H	4.56157400	-0.26263000	1.43979800

TS2b-trans

C	0.01954200	0.01894400	-0.01338100
C	0.01316600	0.00127500	1.37595800
C	1.23525600	-0.01938700	2.04552700
C	2.44749000	-0.00577300	1.36805100
C	2.41456800	0.02093600	-0.02578900
C	1.21700500	0.03115000	-0.71741600
H	1.22893200	-0.04168400	3.13015000
H	3.34582300	0.02661600	-0.58177400
H	1.19575800	0.03861900	-1.80007100
C	-1.27088600	0.01192500	2.11656200
H	-1.68498500	0.99089400	2.32280400
C	-1.63223200	-1.01262200	2.95967100
H	-1.13184100	-1.97068700	2.88439900

C	-2.71739400	-0.88311100	3.87875400
O	-3.40400200	0.14445400	3.99172800
C	-3.05707400	-2.07089800	4.74767600
H	-4.01722900	-2.48113400	4.42274400
H	-2.30714000	-2.85990600	4.69832900
H	-3.17520700	-1.74359400	5.78218800
O	-1.14651500	-0.01109900	-0.69844900
C	-2.29905600	0.04171800	0.08833300
H	-2.82015200	-0.90482000	0.15352900
C	-2.98186200	1.23520800	0.19024300
H	-3.96487000	1.15933500	0.64857900
C	-2.52627100	2.50009800	-0.13495500
H	-1.56872400	2.63889100	-0.61840900
C	-3.32722500	3.65389500	0.10223200
O	-4.43110300	3.69492200	0.64692300
C	-3.44264200	6.00008600	-0.08365200
H	-3.60226200	6.15699200	0.98542400
H	-2.81881700	6.79921100	-0.48020100
H	-4.40982200	6.00432600	-0.58890200
O	-2.73484400	4.79533100	-0.32780900
Cs	-3.83264600	2.99855900	3.52724800
C	3.75697100	-0.00709400	2.10781100
H	4.27376300	0.94992200	1.99681000
H	3.60843900	-0.18350200	3.17386200
H	4.42582300	-0.78223600	1.72724000

TS2d-cis

C	-0.02637700	0.02915100	-0.00883300
C	-0.01404600	-0.01384900	1.38467100
C	1.20683100	-0.06500000	2.04182400
C	2.38136400	-0.06261700	1.30643400
C	2.36576600	-0.02799800	-0.07763500
C	1.15048600	0.01835900	-0.74183500
H	1.23668600	-0.11488600	3.12277400
H	3.29232600	-0.03118200	-0.63614200
H	1.11264900	0.05046000	-1.82301900
C	-1.32234600	-0.09172900	2.07863800
H	-1.68249400	0.78574400	2.60025500
C	-1.82284700	-1.31767700	2.45105700
H	-1.37378500	-2.22627800	2.06998300
C	-3.03718700	-1.41681800	3.19346800
O	-3.64957200	-0.42404100	3.62231100
C	-3.60750000	-2.78650500	3.47846800
H	-3.06033800	-3.58672500	2.98166400
H	-3.59545600	-2.96207100	4.55741600
H	-4.65095400	-2.81394200	3.15454800
O	-1.22195100	0.05284500	-0.63995700
C	-2.24744800	0.59009000	0.14410000

H	-2.18471200	1.67015700	0.23837500
C	-3.46173300	-0.05601700	0.21650200
H	-4.27572600	0.53845800	0.61806600
C	-3.67320100	-1.40344200	0.03145500
H	-2.89137300	-2.03756600	-0.36128000
C	-4.91912800	-2.01822000	0.35883900
O	-5.92675000	-1.46867400	0.80000800
C	-6.09323900	-4.05633000	0.48741200
H	-6.94152400	-3.71720800	-0.10979000
H	-5.89085700	-5.10432400	0.27407200
H	-6.33493500	-3.93831300	1.54533300
O	-4.90865900	-3.35371500	0.14644100
Cs	-6.40842700	0.32831300	3.06984500
Cl	3.91317300	-0.10979300	2.14670500

TS2d-trans

C	-2.47861000	-1.08093400	1.15748900
C	-2.28911000	0.04398200	0.35763700
C	-3.21764000	0.31818900	-0.64038200
C	-4.29454700	-0.52732600	-0.83581200
C	-4.47539000	-1.65063900	-0.04549800
C	-3.56294100	-1.92585900	0.95698100
H	-3.08665000	1.19246100	-1.26506900
H	-5.32292000	-2.30383500	-0.20528000
H	-3.68816300	-2.79118600	1.59486300
C	-1.11169400	0.92002100	0.56307200
H	-0.21248100	0.62031200	0.04117200
C	-1.23880900	2.24744900	0.88830400
H	-2.17902000	2.61979800	1.27706900
C	-0.12619500	3.14385900	0.81836600
O	1.00933100	2.79799800	0.46081200
C	-0.34786400	4.58027900	1.22641700
H	-1.40355300	4.83840800	1.30532800
H	0.12203600	4.74359000	2.20050100
H	0.14036300	5.24416000	0.51137100
O	-1.62269500	-1.34749700	2.16369300
C	-0.52490600	-0.48527700	2.26178000
H	-0.59837200	0.20892700	3.08865000
C	0.69982700	-0.91285300	1.79585800
H	1.53771900	-0.27730500	2.07201500
C	0.96136500	-1.98115600	0.95751700
H	0.17832700	-2.67087500	0.67264200
C	2.28430000	-2.24778100	0.49922100
O	3.29274000	-1.57203400	0.70488100
C	3.63058900	-3.68670800	-0.79261700
H	4.36783500	-3.84439900	-0.00390300
H	3.49739200	-4.60652400	-1.35921200
H	3.98763300	-2.89664500	-1.45699600

O	2.35583400	-3.37161200	-0.25540800
Cs	2.75413100	0.91309500	-0.95164900
Cl	-5.44407400	-0.16961400	-2.10201700

TS2e-cis

C	-0.00310700	0.00424900	-0.05955300
C	0.02163700	-0.00166600	1.33566000
C	1.24392500	0.00622200	1.98367200
C	2.43529600	0.02838700	1.25817900
C	2.39479500	0.02820200	-0.13097100
C	1.16830600	0.01839600	-0.78921300
H	1.28799100	-0.01322200	3.06605900
H	3.30263700	0.04071300	-0.71733100
H	1.12850100	0.02203400	-1.87127700
C	-1.28206800	-0.09738400	2.03772900
H	-1.66321700	0.78401900	2.53776300
C	-1.74676000	-1.32493500	2.45464700
H	-1.27572300	-2.23255200	2.09824200
C	-2.95470700	-1.43319800	3.20211100
O	-3.59281000	-0.44406100	3.60469900
C	-3.49264600	-2.80759300	3.52737000
H	-2.91829300	-3.60953800	3.06498500
H	-3.49230500	-2.94675500	4.61167200
H	-4.53022500	-2.87337900	3.18950300
O	-1.21280100	-0.03917900	-0.68025100
C	-2.23685200	0.49690100	0.09878200
H	-2.19714900	1.58051100	0.17080400
C	-3.43804600	-0.17038300	0.20340100
H	-4.25800100	0.41543900	0.60563900
C	-3.62543900	-1.52586800	0.04745900
H	-2.83506600	-2.15153500	-0.34165600
C	-4.85275900	-2.15870000	0.40475400
O	-5.86673900	-1.62185900	0.84804200
C	-5.98441400	-4.21619500	0.59032900
H	-6.84639700	-3.90591000	-0.00309200
H	-5.76489600	-5.26455800	0.39634300
H	-6.21578600	-4.08044100	1.64852300
O	-4.81794900	-3.49886900	0.22023900
Cs	-6.38094900	0.18485900	3.09937000
C	4.80793400	0.05505700	1.30372300
H	4.91294700	0.94752100	0.67850900
H	5.58451300	0.06320400	2.06657400
H	4.92872200	-0.83745200	0.68140400
O	3.57726800	0.04514000	1.99322800

TS2e-trans

C	-0.02228900	-0.02882600	-0.06081600
C	0.00825600	-0.02776400	1.33257400
C	1.23770000	-0.03535100	1.97462900
C	2.42749600	-0.02845100	1.25189200
C	2.38155700	-0.02082800	-0.13751600
C	1.15385800	-0.02344200	-0.78806200
H	1.28043900	-0.03955400	3.05716100
H	3.28648500	-0.01839300	-0.72855600
H	1.10922900	-0.02920900	-1.86991200
C	-1.25644600	-0.00450000	2.10604400
H	-1.66355400	0.97892100	2.30337400
C	-1.59865100	-1.01461900	2.97280700
H	-1.10077100	-1.97425200	2.90180900
C	-2.66545100	-0.86941800	3.91165600
O	-3.34738000	0.16115100	4.02256700
C	-2.99087800	-2.04483100	4.80229400
H	-3.94886700	-2.46856100	4.48814000
H	-2.23478400	-2.82845100	4.76157000
H	-3.10706100	-1.70171300	5.83176700
O	-1.21001900	-0.06831300	-0.71455500
C	-2.33869900	-0.00727900	0.10273600
H	-2.85360700	-0.95438300	0.20211200
C	-3.02094200	1.18558300	0.21161100
H	-3.98761100	1.11489700	0.70445200
C	-2.57719900	2.44669400	-0.14570800
H	-1.63700500	2.57810300	-0.66400800
C	-3.36887700	3.60377600	0.10326000
O	-4.45247300	3.65372800	0.68683600
C	-3.48849800	5.94766300	-0.10677700
H	-3.60542100	6.11803200	0.96584700
H	-2.88029500	6.74109600	-0.53758500
H	-4.47504200	5.94700900	-0.57305500
O	-2.79196300	4.73915400	-0.36367900
Cs	-3.71547200	3.02520300	3.55249500
C	4.80012600	-0.03116500	1.29255300
H	4.91415300	0.86236300	0.67045600
H	5.57855000	-0.03507000	2.05352500
H	4.90891500	-0.92267500	0.66673400
O	3.57089900	-0.02906200	1.98514500

TS2f-cis

C	-0.02136300	0.02280600	-0.00861300
C	-0.01151000	-0.01720000	1.38492700
C	1.20923700	-0.05769500	2.04567600
C	2.37258600	-0.04928800	1.30216700
C	2.37231600	-0.01723500	-0.07677500
C	1.15513800	0.02049000	-0.74140500
H	1.25509100	-0.10396700	3.12650200

H	3.30799200	-0.01567800	-0.62040000
H	1.11598100	0.05097700	-1.82256700
C	-1.32168700	-0.09876300	2.07522800
H	-1.68341800	0.77741500	2.59811700
C	-1.82159300	-1.32565000	2.44690200
H	-1.37213900	-2.23373800	2.06502000
C	-3.03532300	-1.42584900	3.18946600
O	-3.64769700	-0.43376600	3.62076400
C	-3.60537700	-2.79590500	3.47361800
H	-3.05912800	-3.59562000	2.97496400
H	-3.59170000	-2.97289500	4.55234200
H	-4.64934400	-2.82276400	3.15132200
O	-1.22089600	0.03417800	-0.64072100
C	-2.24244300	0.57948400	0.13957900
H	-2.17455700	1.65963300	0.23313100
C	-3.46033300	-0.05963700	0.21485800
H	-4.27116900	0.53988300	0.61527900
C	-3.67809000	-1.40673600	0.03227200
H	-2.89909100	-2.04437600	-0.36031800
C	-4.92599500	-2.01606000	0.36068000
O	-5.93173200	-1.46229400	0.80126500
C	-6.10805000	-4.04951700	0.49243900
H	-6.95515000	-3.70882100	-0.10559500
H	-5.90956800	-5.09879800	0.28166200
H	-6.34953000	-3.92813000	1.55004600
O	-4.92098200	-3.35215500	0.14986600
Cs	-6.39984000	0.34064700	3.06765900
F	3.55769300	-0.07742300	1.95369500

TS2f-trans

C	-2.79272600	-1.16885300	0.75606700
C	-2.57113400	-0.00216300	0.02771100
C	-3.44044800	0.31256400	-1.01276700
C	-4.48242400	-0.54060900	-1.30504000
C	-4.70393300	-1.70345200	-0.59607000
C	-3.84866900	-2.01630600	0.44728600
H	-3.29697500	1.21467400	-1.59404900
H	-5.53474200	-2.34780500	-0.85225500
H	-3.99819900	-2.91364300	1.03360000
C	-1.41810800	0.87280000	0.34685500
H	-0.47990900	0.59411200	-0.11522600
C	-1.57699500	2.18823400	0.70483400
H	-2.54520100	2.54353300	1.03689700
C	-0.46817800	3.09060000	0.74904300
O	0.69209900	2.76344600	0.45987500
C	-0.72798400	4.50791700	1.19930900
H	-1.78651200	4.76647400	1.18750800
H	-0.35672300	4.62263500	2.22186800

H	-0.17185600	5.20247800	0.56817900
O	-1.99247500	-1.47932000	1.80001700
C	-0.95244100	-0.57816700	2.04492600
H	-1.14712000	0.09125300	2.87314900
C	0.33381400	-0.94256900	1.71203200
H	1.10818500	-0.28326700	2.09635300
C	0.73289400	-1.98071400	0.88833400
H	0.01498000	-2.69067700	0.50051300
C	2.10907500	-2.18997800	0.58623500
O	3.06089700	-1.48593100	0.92522200
C	3.65259900	-3.54524800	-0.56839200
H	4.29409200	-3.70935800	0.29890700
H	3.62199000	-4.44711500	-1.17720500
H	4.06015100	-2.72037000	-1.15710600
O	2.31206700	-3.29010700	-0.18110100
Cs	2.58914000	0.94930600	-0.83511800
F	-5.31529200	-0.22486700	-2.32266000

DFT-optimized stereodetermining transition state structures for the 5-exo-trig cyclization of int1a optimized at different levels of theory.

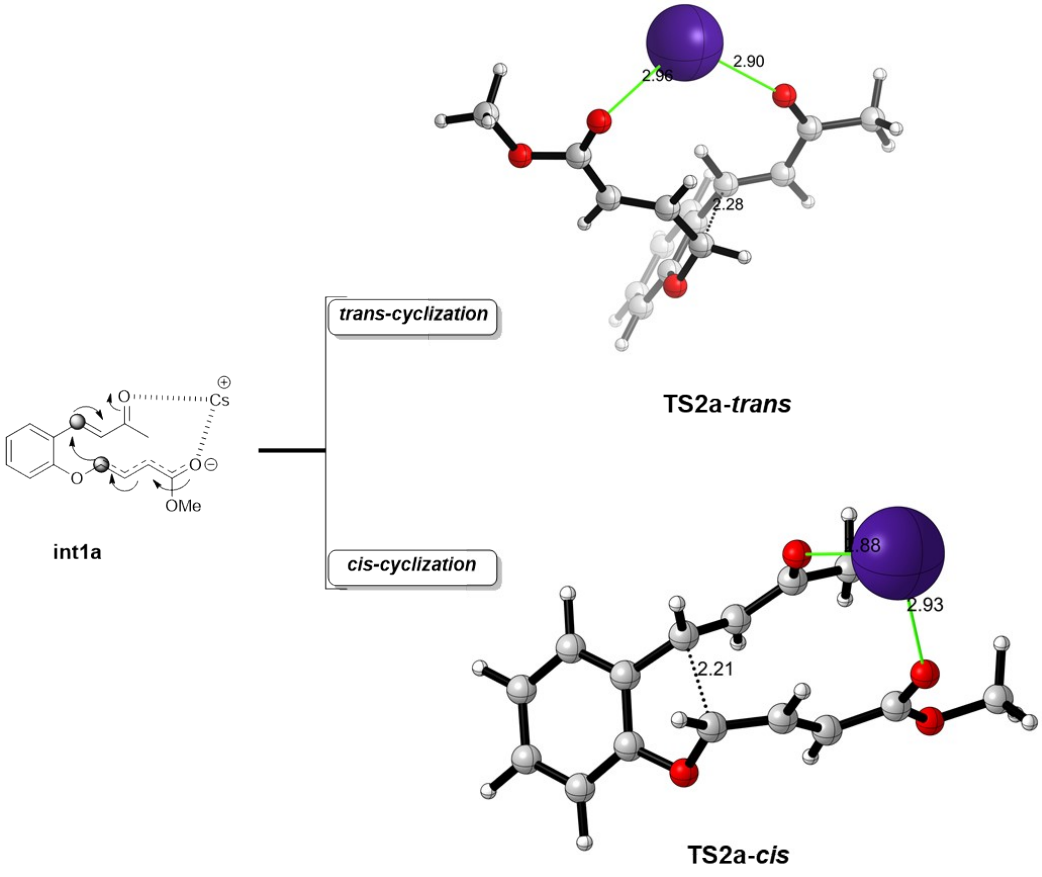


Figure S4: Computed SMD(THF)–M06–2X/def2-TZVP stereodetermining transition state structures for the *5-exo-trig* cyclization of **int1a.** Key bond lengths are given in angstroms (Å).

Table S8: Total energy and Free energy differences (ΔΔG‡ at 298 K) for the *5–exo–trig* cyclization of intermediate **int1a** via **TS2a**. TS structures were optimized at the SMD(THF)–M06–2X/def2-TZVP level. The vibrational entropy contribution was computed through QRRHO approximation

Structure	Total Energy [a.u]	G(T) [a.u]	qh-G(T) [a.u]	$\Delta\Delta G^{\neq}$ [kcal/mol]
TS2a-cis	-901.645604	-901.435314	-901.431886	0.0
TS2a-trans	-901.638433	-901.433393	-901.427548	3.0

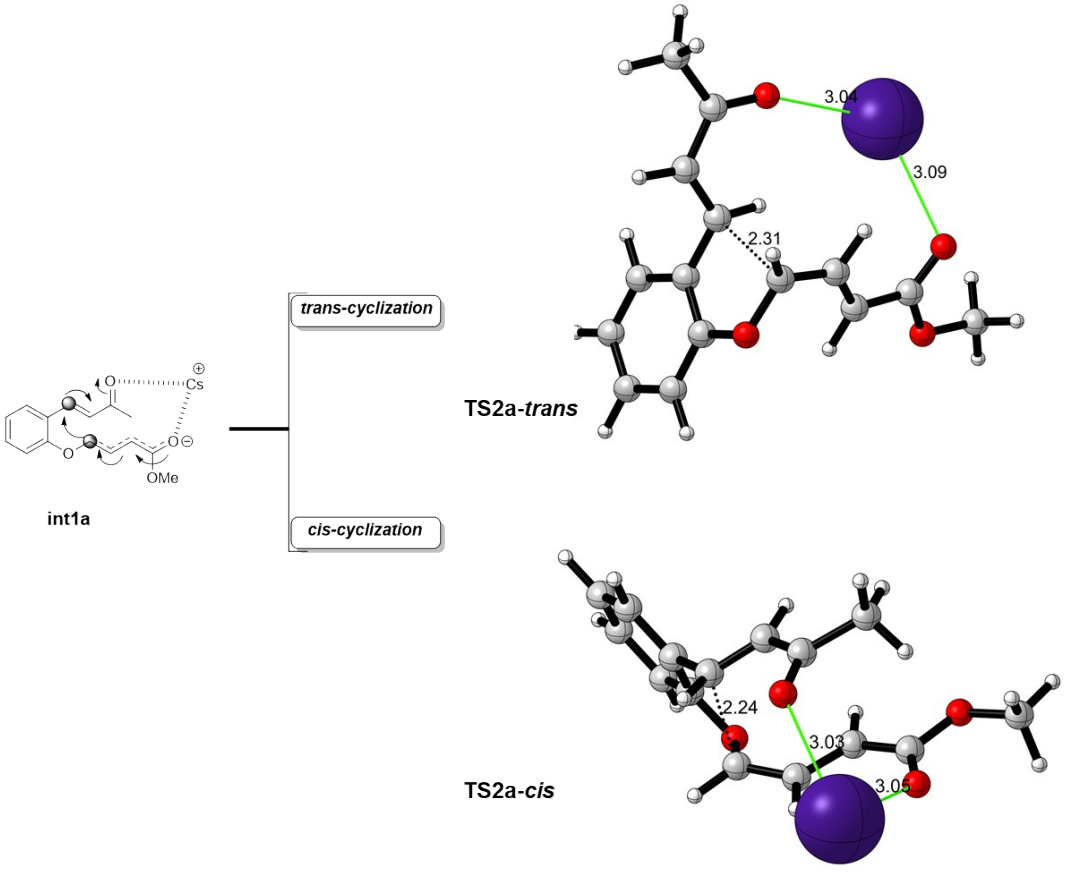


Figure S5: Computed SMD(THF)–M06–2X/LANL2DZ(Cs)/6-31+G(d,p) stereodetermining transition state structures for the *5-exo-trig* cyclization of **int1a**. Key bond lengths are given in angstroms (Å).

Table S9: Total energy and Free energy differences (ΔΔG‡ at 298 K) for the *5–exo–trig* cyclization of intermediate **int1a** via **TS2a**. TS structures were optimized at the SMD(THF)–M06–2X/ LANL2DZ(Cs)/6-31+G(d,p) level. The vibrational entropy contribution was computed by means of QRRHO approximation

Structure	Total Energy [a.u]	G(T) [a.u]	qh-G(T) [a.u]	$\Delta\Delta G^{\neq}$ [kcal/mol]
TS2a-cis	-901.062942	-900.844093	-900.840823	0.0
TS2a-trans	-901.055957	-900.840844	-900.835897	3.1

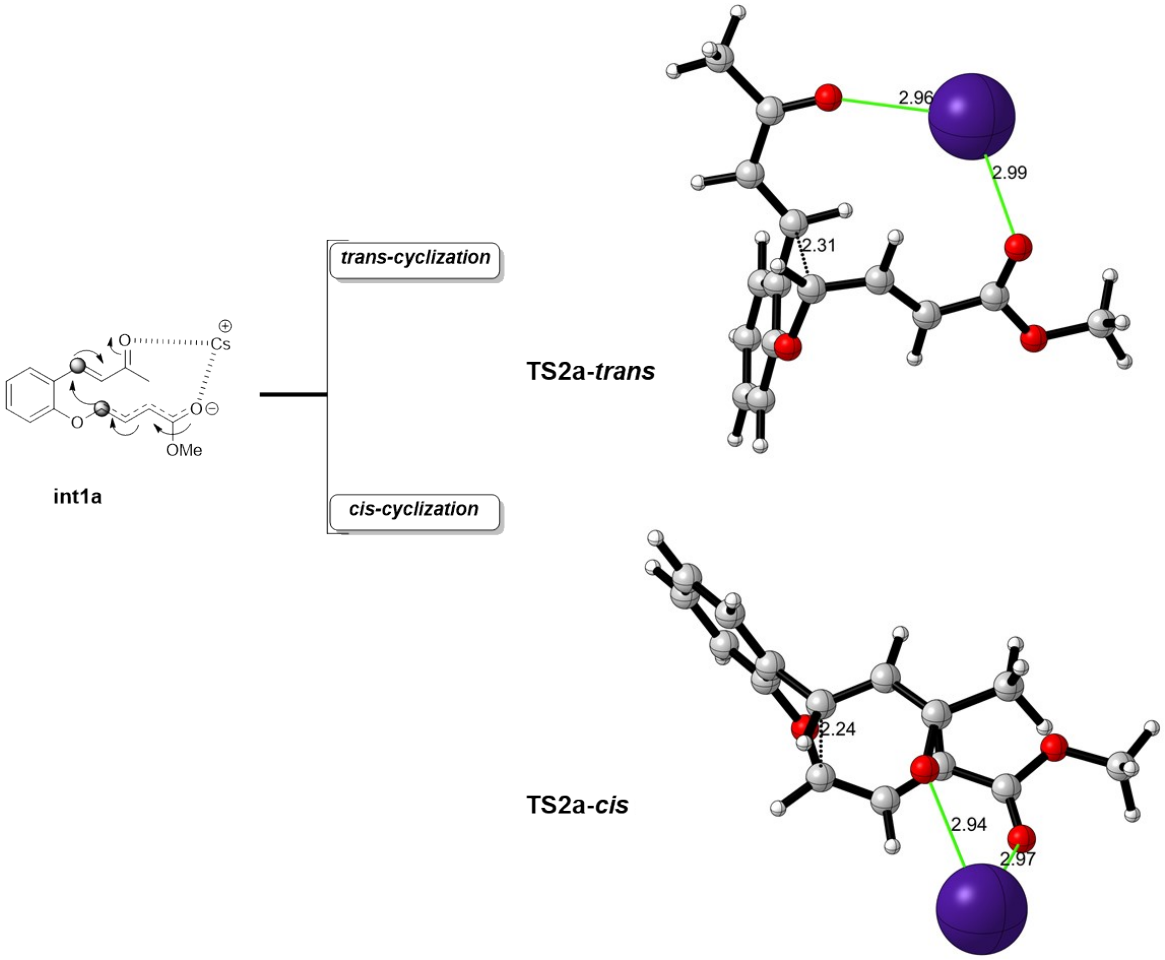


Figure S6: Computed SMD(THF)–M06–2X/SDD(Cs)/6-31+G(d,p) stereodetermining transition state structures for the *5-exo-trig* cyclization of **int1a.** Key bond lengths are given in angstroms (Å).

Table S10: : Total energy and Free energy differences (ΔΔG‡ at 298 K) for the *5–exo–trig* cyclization of intermediate **int1a** via **TS2a**. TS structures were optimized at the SMD(THF)–M06–2X/SDD(Cs)/6-31+G(d,p) level. The vibrational entropy contribution was computed by means of QRRHO approximation

Structure	**Total Energy [a.u]**	**G(T) [a.u]**	**qh-G(T) [a.u]**	$\Delta\Delta G^{\neq}$ **[kcal/mol]**
TS2a-cis	-901.332749	-901.114368	-901.110910	0.0
TS2a-trans	-901.325518	-901.110498	-901.105510	3.4

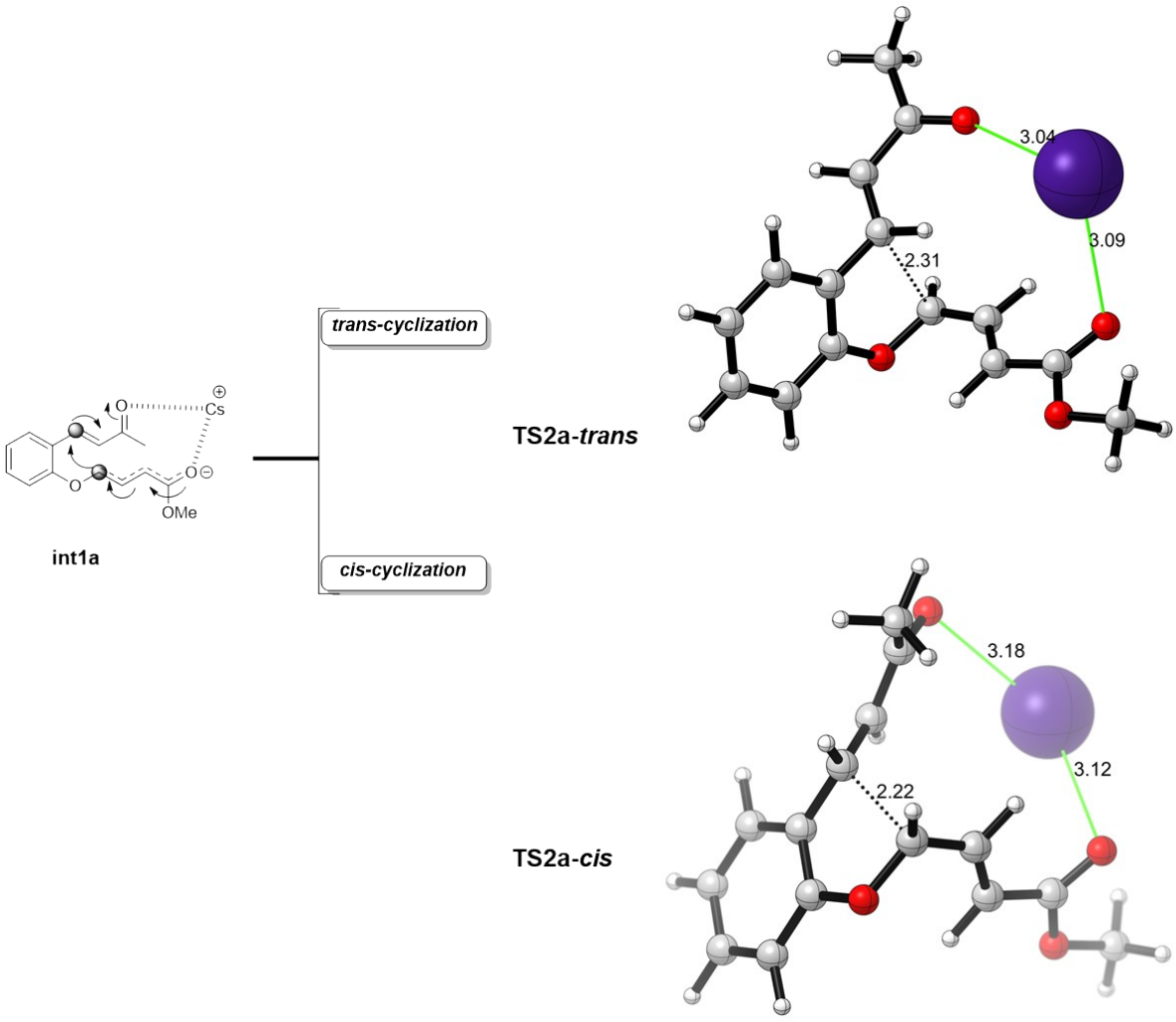


Figure S7: Computed SMD(THF)–ωB97X-D/LANL2DZ(Cs)/6-31+G(d,p) stereodetermining transition state structures for the *5-exo-trig* cyclization of **int1a.** Key bond lengths are given in angstroms (Å).

Table S11: Total energy and Free energy differences ($\Delta\Delta G^{\ddagger}$ at 298 K) for the *5–exo–trig* cyclization of intermediate **int1a** via **TS2a**. TS structures were optimized at the SMD(THF)–ωB97x-D/LANL2DZ(Cs)/6-31+G(d,p) level. The vibrational entropy contribution was computed by means of QRRHO approximation

Structure	Total Energy [a.u]	G(T) [a.u]	qh-G(T) [a.u]	$\Delta\Delta G^{\neq}$ [kcal/mol]
TS2a-cis	-901.227249	-901.009385	-901.005463	0.0
TS2a-trans	-901.223226	-901.008353	-901.003212	1.4

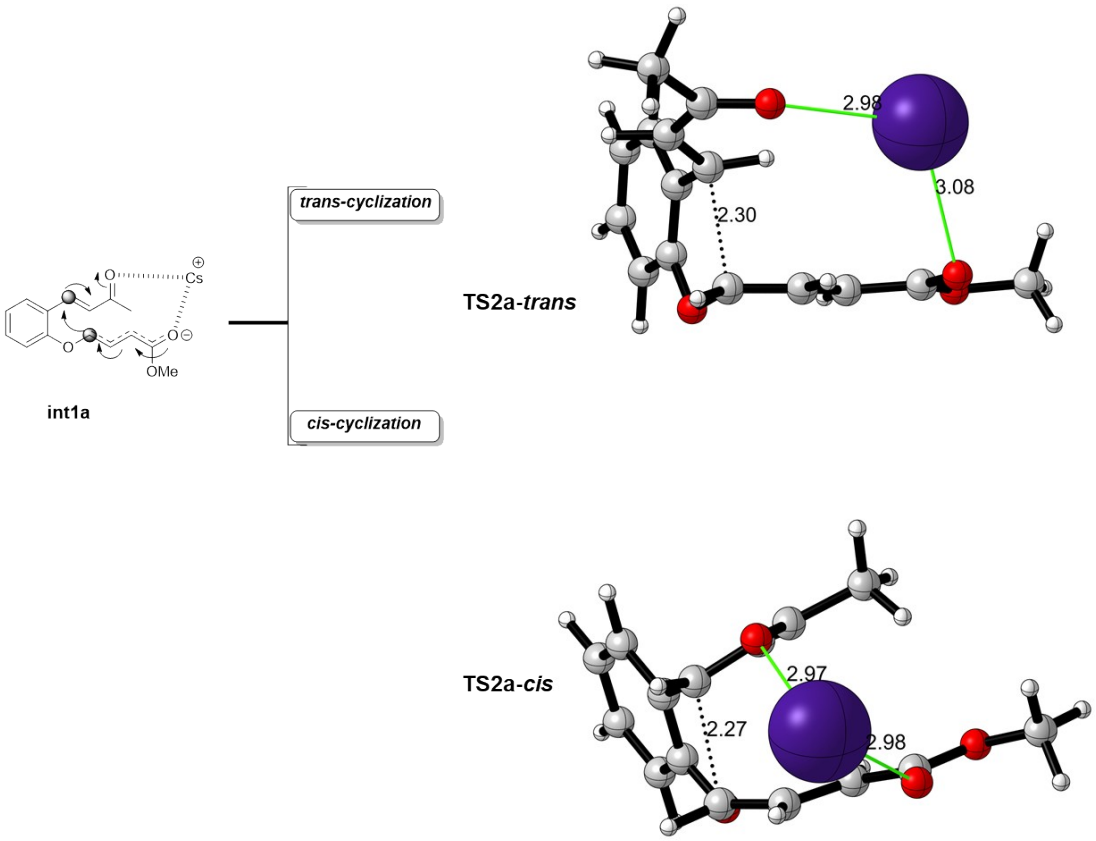


Figure S8: Computed SMD(THF)–ωB97X-D/ SDD(Cs)/6-31+G(d,p) stereodetermining transition state structures for the *5-exo-trig* cyclization of **int1a.** Key bond lengths are given in angstroms (Å).

Table S12: Total energy and Free energy differences ($\Delta\Delta G^{\ddagger}$ at 298 K) for the *5–exo–trig* cyclization of intermediate **int1a** via **TS2a**. TS structures were optimized at the SMD(THF)–ωB97x-D/SDD(Cs)/6-31+G(d,p) level. The vibrational entropy contribution was computed by means of QRRHO approximation

Structure	Total Energy [a.u]	G(T) [a.u]	qh-G(T) [a.u]	$\Delta\Delta G^{\neq}$ [kcal/mol]
TS2a-cis	-901.506780	-901.288190	-901.284642	0.0
TS2a-trans	-901.502452	-901.287455	-901.282380	1.4