Supporting Information

Kinetic Analysis of a Cysteine-Derived Thiyl-Catalyzed Asymmetric Vinyl Cyclopropane Cycloaddition Reflects Numerous Attractive Non-Covalent Interactions

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I. General information

A. Materials and Instrumentation

UV reactions were conducted with an unfiltered BLAK-RAY MODEL B 100AP UV lamp (365 nm filter removed). Kinetic data were acquired using an Agilent 1100 series analytical chiral HPLC equipped with a photodiode array detector (254 nm) with a Chiralpak IB column (5 μm particle size, 4.5 x 250 mm). Enantiomeric excesses were also determined on the same instrument, using Chiralpak IA and IB columns. Optical rotations were recorded on a Perkin Elmer Polarimeter 341 at the sodium D line (1.0 dm path length) at 20 °C. Kinetics data were processed and analyzed using Origin 2018.[1] Normal-phase column chromatography was performed with either silica gel 60 Å (32-63 microns) or with a Biotage Isolera One flash purification system equipped with Ultra HP-Sphere 25 μm columns. All reaction solvents were purified using a Seca Solvent Purification System by Glass Contour (in which the solvents were dried over alumina and dispensed under an argon atmosphere). All reagents were purchased from commercial sources and used as received unless otherwise noted.

B. Abbreviations

cat = catalyst

[1] Origin, Version 2018. OriginLab Corporation, Northampton, MA, USA.

CV = column volumes

DCM = dichloromethane

DFT = density functional theory

DIPEA = diisopropylethylamine

ee = enantiomeric excess

h = hour

HATU = *O*-(7-azabenzotriazol-1-yl)-*N,N,N',N'*-tetramethyluronium hexafluorophosphate

HPLC = high-performance liquid chromatography

RT = room temperature

TBVE = *tert*-butyl vinyl ether

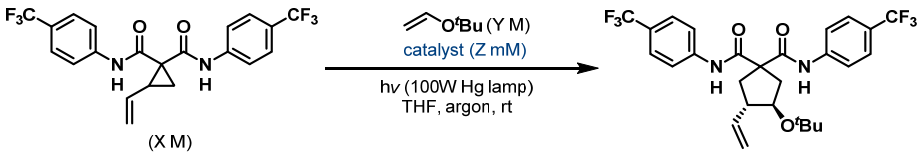
THF = tetrahydrofuran

VCP = vinylcyclopropane

W = Watt

II. Kinetics Procedures

Syntheses of the catalysts used in the following kinetics procedures have been previously reported by our group.[2] Although the reactions in our initial report were carried out in 2:1 hexanes/THF, these kinetic studies were carried out in pure THF for the sake of consistency.



A. General Procedure for Kinetics Experiments

[2] Ryss, J. M.; Turek, A. K.; Miller, S. J. Disulfide-Bridged Peptides That Mediate Enantioselective Cycloadditions Through Thiyl Radical Catalysis. *Org. Lett.* **2018**, *20*, 1621–1625.

An oven-dried quartz Schlenk tube[3] equipped with a magnetic stir bar was charged with the vinylcyclopropane (X M) and the peptide catalyst (Z mM), and the solids were dissolved in tetrahydrofuran (3 or 4 mL) freshly pulled from a solvent purification system and added using a gastight syringe. *Tert*-butyl vinyl ether (Y M) was added via gastight syringe, with the needle submerged in the reaction mixture to prevent evaporation of the reagent. The Schlenk tube was sealed with a Precision Seal® rubber septum, which was secured with copper wire. The reaction mixture was subjected to five freeze-pump-thaw cycles, backfilling with argon. After warming to room temperature, the Schlenk tube was wrapped in aluminum foil and was placed in front of a UV lamp that had been warmed up for at least 30 minutes. A fan was positioned above the flask for additional temperature control. The foil was removed and a timer was started simultaneously. Reaction aliquots (30 µL) were collected at evenly spaced time points as follows: a 50 µL gastight syringe fitted with a 6-inch needle was purged with argon five times in a separate Schlenk tube, and 30 µL of the reaction mixture (plus gas bubble) was collected.[4] The aliquot was added to a 1 mL volumetric flask, and a timepoint was recorded at this point. The needle was flushed into the volumetric flask[5] and the sample was diluted to 1 mL with 10% IPA/hexanes, filtered through a plug of Kimtech® laboratory wipe, and analyzed by HPLC (Chiralpak IB, 10% IPA/hexanes, 1 mL/min, 8.5 min, 5 µL injection volume, 254 nm) to determine conversion of starting material (retention time of vinylcyclopropane starting material = 6.8 minutes).

The enantiomeric excesses of the product and remaining VCP were determined by HPLC using the following conditions:

Product: Chiralpak IA, 5% IPA/hexanes, 1 mL/min, 30 min, 5 µL injection volume, 254 nm

VCP: Chiralpak IB, 2% IPA/hexanes, 1.2 mL/min, 25 min, 40 °C, 5 µL injection volume, 254 nm

B. Determination of Calibration Curve

The absorbance data obtained by HPLC were converted to concentration data using a response factor determined from a modified Beer's Law plot shown below (Figure S1). These data were obtained as follows: A 5 mM stock solution of the VCP substrate in THF was prepared in a 5 mL volumetric flask. Samples of varying concentration were obtained by taking aliquots of the stock solution and diluting to 1 mL with 10% IPA/hexanes in a volumetric flask. Repeated twice for each concentration. The solutions were analyzed by HPLC (Chiralpak IB, 10% IPA/hexanes, 1 mL/min, 8.5 min, 5 µL injection volume, 254 nm) to determine the absorbance at each concentration. This procedure was repeated with a second stock solution. The peaks corresponding

[3] Prepared by Daryl Smith, glassblower at Yale University. No reaction or very sluggish reaction rates were observed when standard glass Schlenk tubes were used.

[4] Attempts to purge the gas bubble resulted in irreproducible data.

[5] The volume in the syringe needle was determined to be 3.4 µL. The needle volume for a standard 2-inch removable needle is reported to be 1.13 µL (https://www.hamiltoncompany.com/laboratory-products/syringes/80230). This is multiplied by three to estimate the needle volume for a 6-inch removable needle.

to VCP substrate were integrated, and the resulting areas from all experiments were simultaneously plotted against the absolute concentration of each sample (Figure S1). The data were fit to a linear equation (1). The slope obtained from this fit determines the response factor used to convert absorbance data to concentration. All data have been obtained on a single HPLC instrument; therefore, the path length is assumed to be constant for the calibration plot and kinetics data collection.

$$Area = response\ factor \times [VCP] \quad (1)$$

Run 1

VCP mass: 12.2 mg

Stock solution concentration: 5.52 mM

Run 2

VCP mass: 14.7 mg

Stock solution concentration: 6.65 mM

Table S1. Data for calibration curve

	Run 1			**Run 2**		
Volume of stock solution used (μL)	[VCP] (mM)	area (mAU)	area (mAU)	[VCP] (mM)	area (mAU)	area (mAU)
300	1.65	10300	10900	1.99	11400	14200
250	1.38	9070	9220	1.66	9530	12000
200	1.10	7280	7350	1.33	9100	9510
150	0.83	5480	5560	1.00	6950	7330
100	0.55	3670	3670	0.66	4660	4820
50	0.28	1840	1850	0.33	2390	2410
20	0.11	745	726	0.13	951	982
10	0.06	381	379	0.07	485	500

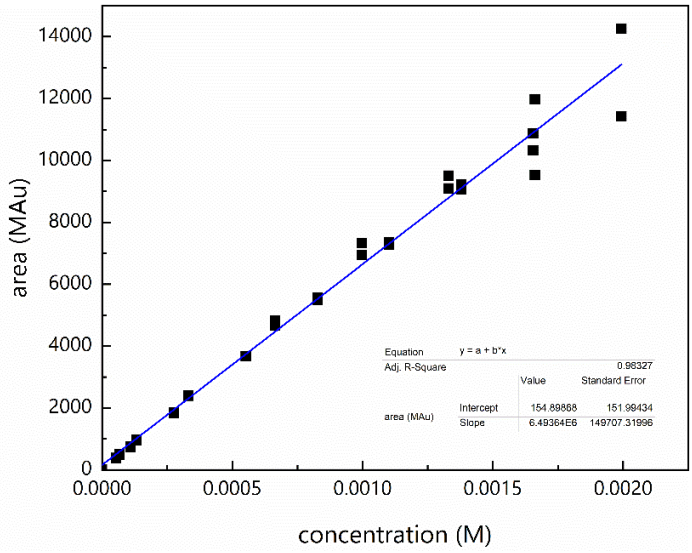


Figure S1. Calibration curve to determine HPLC response factor.

$$Response\ factor = 6.4936 \times 10^6$$

Using this correction factor, the absorbance data collected from each kinetics experiment were converted to concentration data. Duplicate experiments were co-plotted on a single graph. Unless specifically stated otherwise, all data analysis was carried out using duplicate data sets simultaneously. The data were analyzed using the method described by Burés.[6] This method was chosen due to the fact that an *in situ* method for monitoring conversion was not used, leading to errors and artifacts when the data were converted to rate. A direct comparison of the concentration profiles was thus more suitable for analysis of these data. In some cases, a parallel analysis is also presented.

[6] Burés, J. Variable Time Normalization Analysis: General Graphical Elucidation of Reaction Orders from Concentration Profiles. *Angew. Chem. Int. Ed.* **2016**, *55*, 16084–16087.

C. Different Excess Experiments

The initial concentrations used for the different excess experiments (Experiments 1−3) for the **1**-catalyzed reaction follow in Table S2.

Table S2. Concentrations for different excess experiments with catalyst **1**

Expt	$[VCP]_0$ (M)	$[TBVE]_0$ (M)	$[1]_T$ (mM)
1	0.05	0.1	2.5
2	0.05	0.2	2.5
3	0.075	0.1	2.5

The [VCP] vs. time plots for experiments 1 and 2 overlay, indicating that increased $[TBVE]_0$ does not affect the reaction rate (Figure S2a). The variable time normalization analysis was also carried out, which shows that the plots overlay when the normalization assumes a zeroth-order rate dependence on [TBVE] (Figure S2b). The plots in which the normalization assumes a first-order rate dependence are also shown, and do not overlay (Figure S2c).

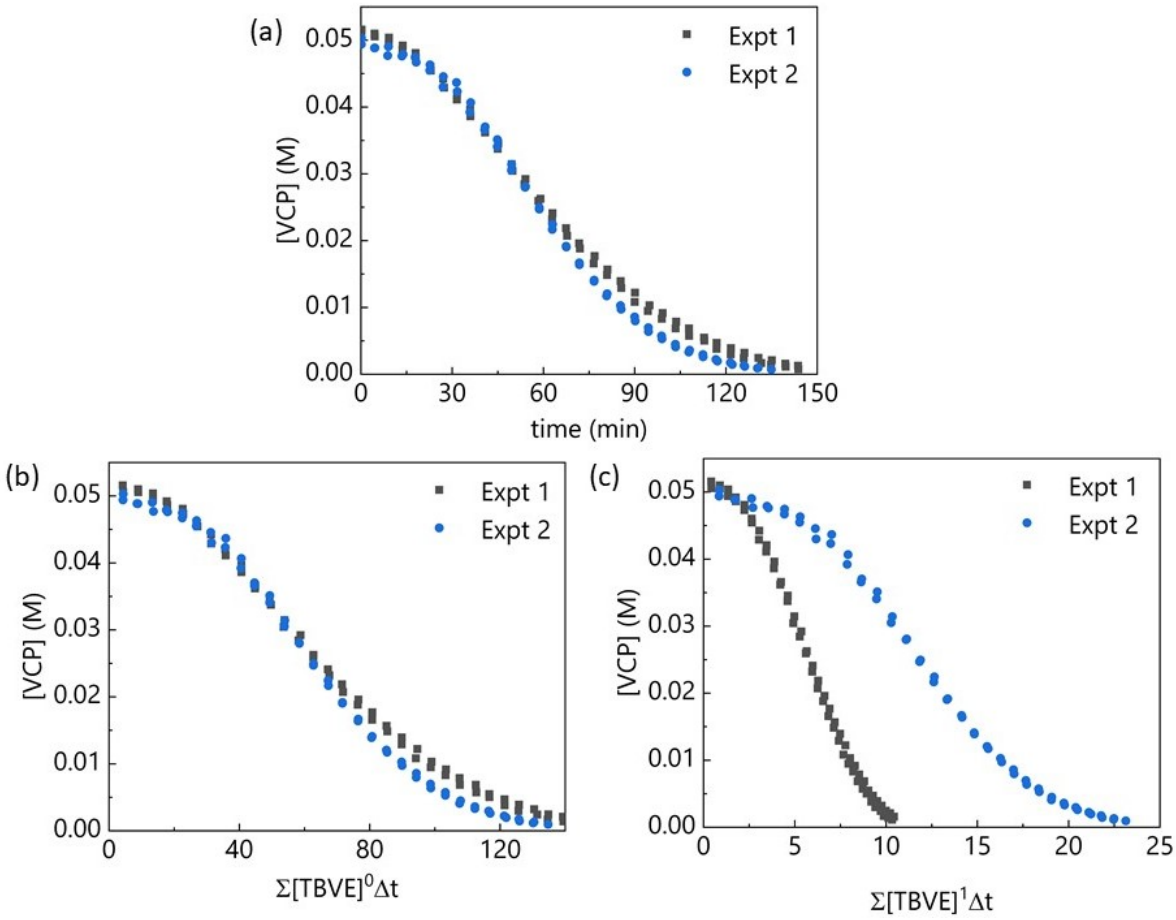


Figure S2. Different excess experiment maintaining $[VCP]_0$ and changing $[TBVE]_0$. Duplicate experiments are simultaneously plotted and analyzed. (a) Raw concentration profiles (b) Variable time normalization analysis assuming zeroth-order dependence on [TBVE] (c) Variable time normalization analysis assuming first-order dependence on [TBVE].

Analysis of experiments 1 and 3 reveals a half-order rate dependence on [VCP], consistent with VCP ground state dimerization. These experiments have been time-adjusted to align the initial data points on the y-axis (Figure S3a and b).[7] Using the variable time normalization approach, overlay is achieved when a 0.5-order dependence of reaction rate on [VCP] is assumed (Figure S3c). The deterioration of overlap toward the end of the reaction could be consistent with a change in rate dependence on [VCP], due to decreased VCP aggregation as the overall [VCP] also decreases. For comparison, we also present the plots that have been normalized assuming first-order dependence on [VCP], which do not display overlap (Figure S3d).

[7] Baxter, R. D.; Sale, D.; Engle, K. M.; Yu, J.-Q.; Blackmond, D. G. Mechanistic Rationalization of Unusual Kinetics in Pd-Catalyzed C–H Olefination. *J. Am. Chem. Soc.* **2012**, *134*, 4600–4606.

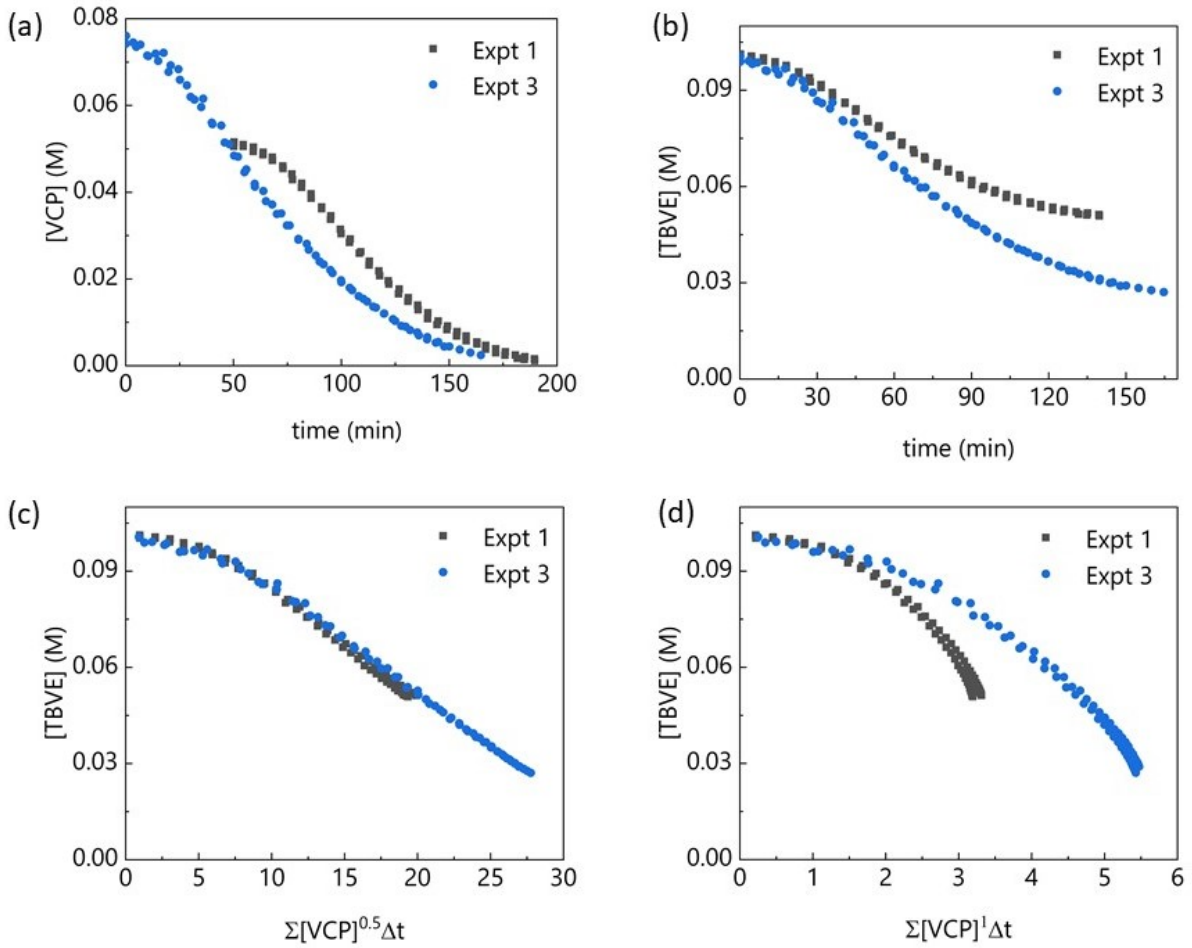


Figure S3. Different excess experiment maintaining $[TBVE]_0$ and changing $[VCP]_0$. Duplicate experiments are simultaneously plotted in each graph. (a) Time-adjusted concentration profiles showing change in [VCP] over time. (b) Raw concentration profiles showing change in [TBVE] over time. (c) Variable time scale normalization assuming half-order rate dependence on [VCP]. (d) Variable time scale normalization assuming first-order rate dependence on [VCP].

The kinetic order of VCP was also verified using the analysis outlined by Blackmond.[8] The reaction rate has already been established to be independent of [TBVE], so the rate equation for the reaction can be written as:

$$rate = \frac{d[VCP]}{dt} = k[VCP]^x$$

A plot of rate vs. $[VCP]^x$ should therefore display as a straight line. The raw temporal data can be represented as an empirically determined seventh-order polynomial:

$$[VCP] = a + bt + ct^2 + dt^3 + ft^4 + gt^5 + ht^6 + jt^7$$

Differentiation of this polynomial provides an equation describing rate as a function of time.

$$\frac{d[VCP]}{dt} = b + 2ct + 3dt^2 + 4ft^3 + 5gt^4 + 6ht^5 + 7jt^6$$

If the data are truncated to exclude the induction period, the remainder of the rate vs. $[VCP]^{1/2}$ plot looks to be linear, indicating that the reaction exhibits half-order kinetics with respect to [VCP], consistent with the conclusion obtained from the Burés analysis (Figure S4d). For comparison, both the full and truncated data sets are shown in Figure S4, along with the plots comparing first- and half-order dependence of rate on [VCP].

[8] (a) Blackmond, D. G. Reaction Progress Kinetic Analysis: A Powerful Methodology for Mechanistic Studies of Complex Catalytic Reactions. *Angew. Chem. Int. Ed.* **2005**, *44*, 4302–4320. (b) Mathew, J. S.; Klussmann, M.; Iwamura, H.; Valera, F.; Futran, A.; Emanuelsson, E. A. C.; Blackmond, D. G. Investigations of Pd-Catalyzed ArX Coupling Reactions Informed by Reaction Progress Kinetic Analysis. *J. Org. Chem.* **2006**, *71*, 4711–4716. (c) Blackmond, D. G. Kinetic Profiling of Catalytic Organic Reactions as a Mechanistic Tool. *J. Am. Chem. Soc.* **2015**, *137*, 10852–10866.

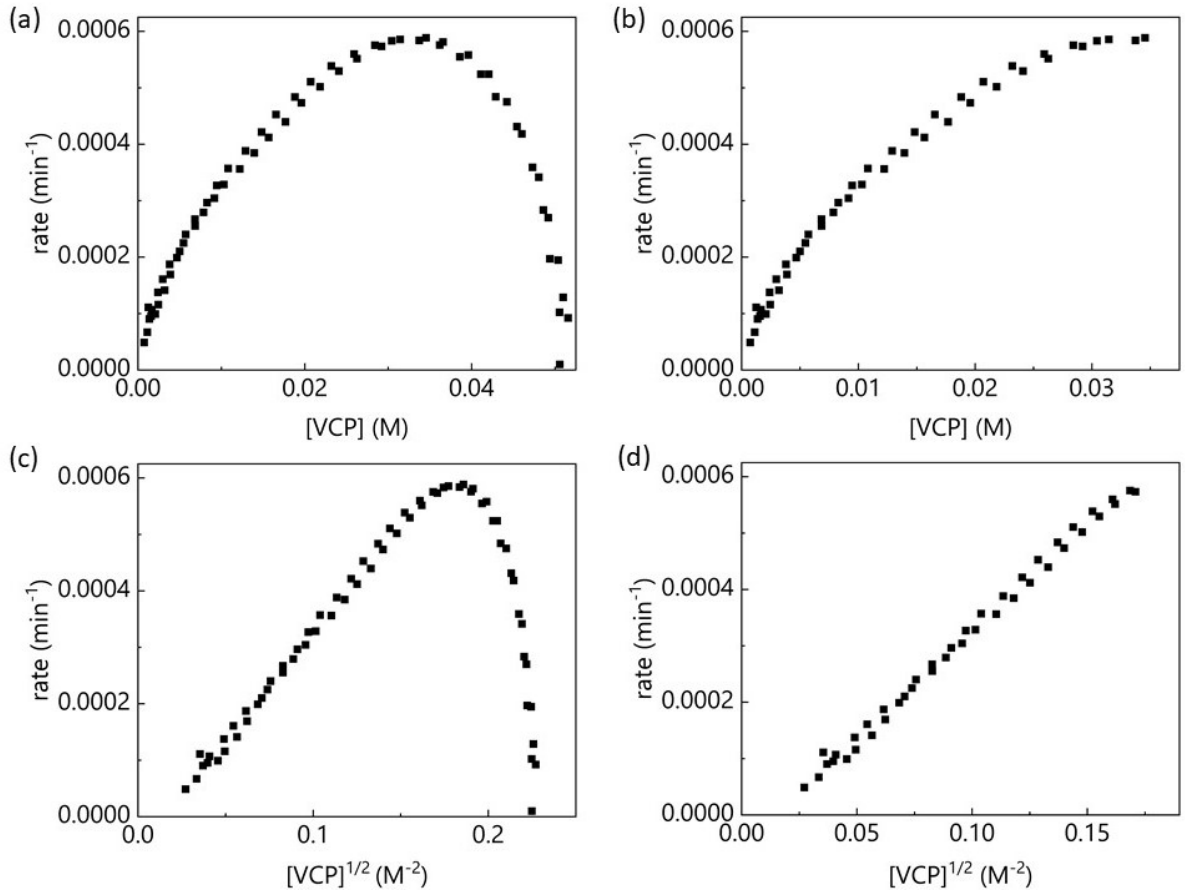


Figure S4. Data for experiment 1. Duplicate experiments are simultaneously plotted in each graph. (a) Rate vs. [VCP]. (b) Rate vs. [VCP], truncated to exclude induction period. (c) Rate vs. $[VCP]^{1/2}$. (d) Rate vs. $[VCP]^{1/2}$, truncated to exclude induction period.

We note that the data post-induction period also fit to the Michaelis–Menten equation (1) below, as shown in Figure S5.

$$rate = \frac{V_{max}[VCP]}{(K_m + [VCP])} \quad (1)$$

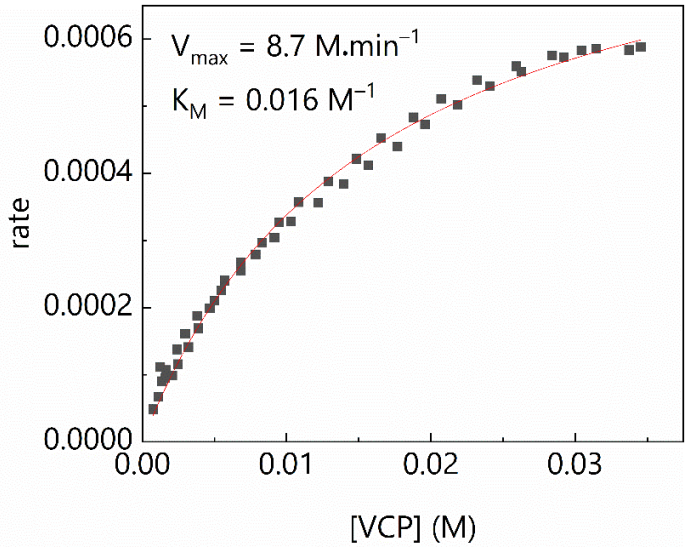


Figure S5. Data for experiment 1, truncated to exclude the induction period, fit to the Michaelis–Menten equation (1).

D. Catalyst Concentration Experiments

The concentrations used for experiments varying the concentration of catalyst **1** (Experiments 1, 4–10) follow in Table S3.

Table S3. Concentrations used to study effects of catalyst **1** concentration

Expt	$[VCP]_0$ (M)	$[TBVE]_0$ (M)	$[1]_T$ (mM)
4	0.05	0.1	1.25
5	0.05	0.1	1.62
6	0.05	0.1	2.0
1	0.05	0.1	2.5
7	0.05	0.1	3.0
8	0.05	0.1	3.5
9	0.05	0.1	4.19
10	0.05	0.1	4.85

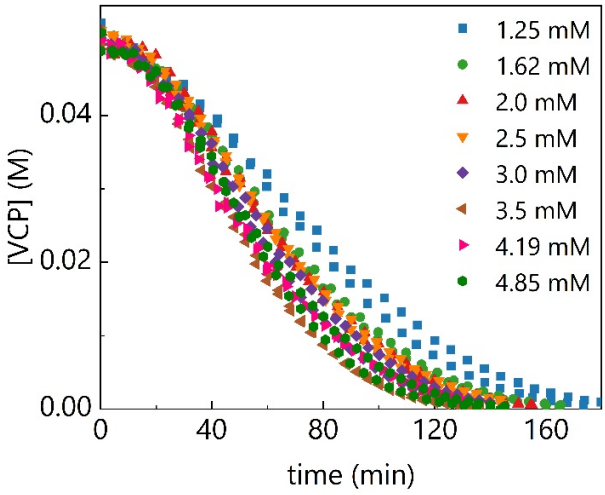


Figure S6. Raw concentration profiles with varying $[\mathbf{1}]_T$. Legend indicates [**1**] for each experiment, corresponding to experiments 1, 4–10. Duplicate experiments are simultaneously plotted and analyzed.

Given the induction period, we chose the maximum rate for each experiment as the point of comparison. These data are obtained from differentiation of the [VCP] vs. time data, which introduces some noisiness to the data. However, a general trend emerges in which the maximum rate increases with increasing $[\mathbf{1}]_T$ until $[\mathbf{1}]_T$ = 3.5 mM, after which the maximum rate decreases (Figure S7). This is consistent with changing catalyst order as $[\mathbf{1}]_T$ changes.

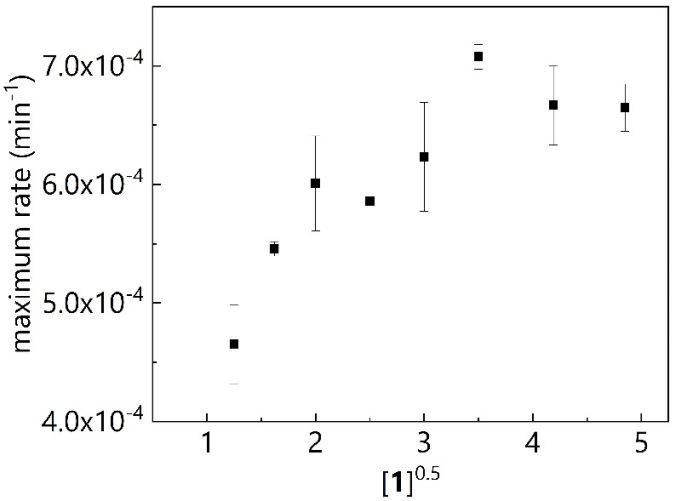


Figure S7. Effect of $[\mathbf{1}]_T$ on maximum rate of reaction. Error bars represent the standard deviation of two averaged runs.

We further attempted to quantify this trend by carrying out the normalized time scale method reported by Burés.[9] The changes resulting from these normalizations are small, so multiple plots are shown here to justify our subjective analysis as to what qualifies as "overlay."

At lower [**1**]$_T$, the data overlay when the catalyst order is assumed to be 0.5, consistent with a ground state dimer (Figure S8a). For comparison, the plots generated when catalyst order is assumed to be 1 are shown (Figure S8b). At higher [**1**]$_T$, the overlay improves as the hypothetical catalyst order is decreased, indicating that the catalyst is likely highly aggregated in solution (Figure S8c). In contrast, at higher [**1**]$_T$ a time scale normalization assuming 0.5 order in [**1**] does not provide overlay (Figure S8d).

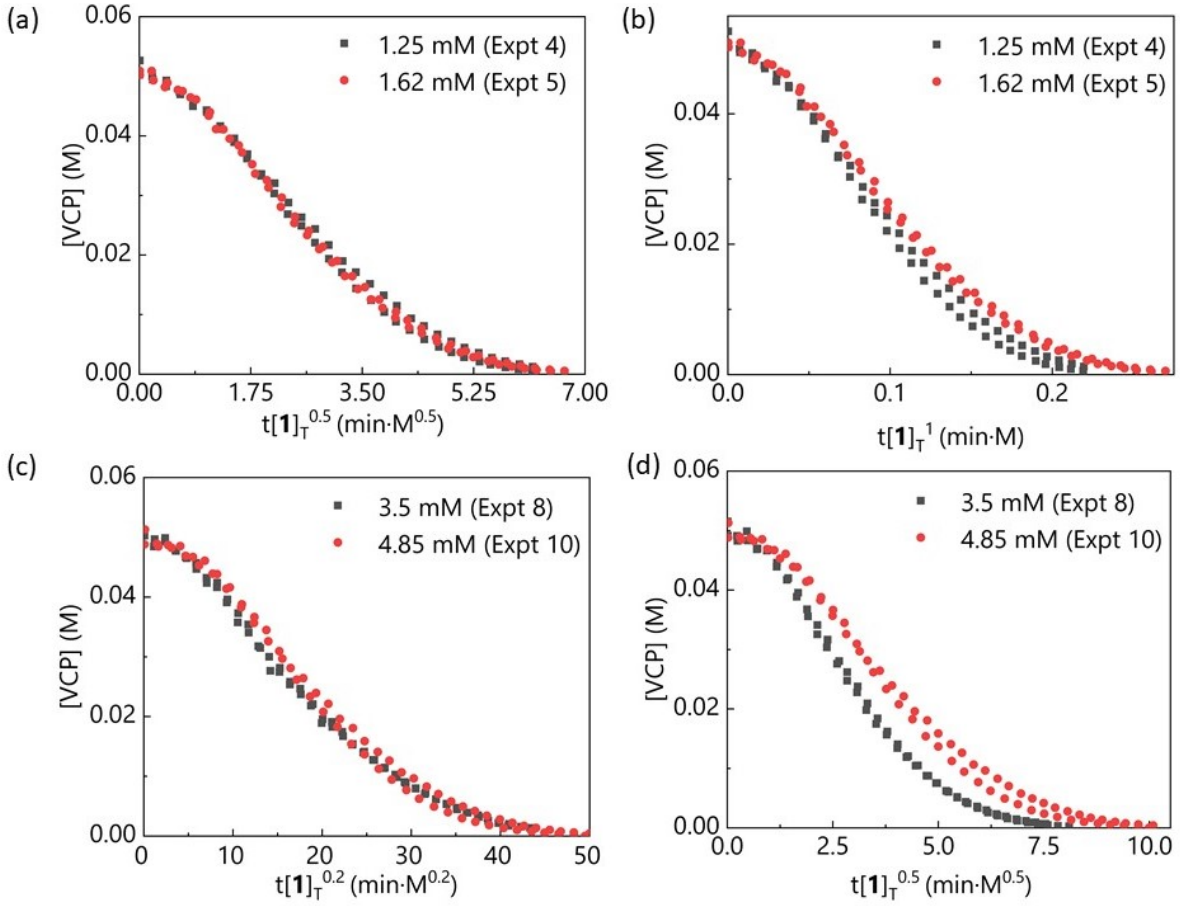


Figure S8. Variable time scale normalization for different regimes of [**1**]$_T$. Duplicate experiments are simultaneously plotted and analyzed. Legend indicates [**1**] for each experiment (a) Low [**1**]$_T$, assuming 0.5 order in **1**. (b) Low [**1**]$_T$, assuming first-order in **1**. (c) High [**1**]$_T$, assuming 0.2 order in **1**. (d) High [**1**]$_T$, assuming 0.5 order in **1**.

[9] Burés, J. A Simple Graphical Method to Determine the Order in Catalyst. *Angew. Chem. Int. Ed.* **2016**, *55*, 2028–2021. (b)

E. Same Excess Experiments

The concentrations used for the same excess experiments for the **1**-catalyzed reaction experiments (1, 11−12) follow in Table S4.

Table S4. Concentrations for same excess experiments with catalyst **1**

Expt	$[VCP]_0$ (M)	$[TBVE]_0$ (M)	$[1]_T$ (mM)	$[P]_{added}$ (M)
1	0.05	0.1	2.5	0
11	0.035	0.085	2.5	0
12	0.035	0.085	2.5	0.015

The $[VCP]_0$ and $[TBVE]_0$ used in experiment 11 are identical to the reaction concentrations of experiment 1 after the reaction proceeds to 30% conversion. Due to the induction period, the data are not expected to overlay at the beginning of the reaction, irrespective of possible product inhibition or catalyst degradation. For this analysis, only the data obtained in the post-induction period are compared. For experiment 1, the first data point post-induction period is defined as t = 0, and the data for experiment 4 are time-adjusted accordingly such that the experiments align at the appropriate [VCP] on the y-axis. Experiments 1 and 11 do not exhibit overlay, with experiment 11 exhibiting an overall slower reaction rate relative to experiment 1 (Figure S9). This is inconsistent with catalyst degradation or product inhibition. Possible explanations for this rate difference are (i) catalyst activation by TBVE, (ii) catalyst activation by product, or (iii) catalyst activation by VCP. The fact that the reaction exhibits a zeroth order dependence on [TBVE] eliminates possibility (i). To determine whether the product is activating the catalyst, a third experiment was performed (experiment 12), in which product—equal to the amount formed after 30% conversion—was added to the reaction (added product is 74:26 *trans*:*cis*, 76% ee *trans*, 55% ee *cis*). Experiments 11 and 12 overlay, indicating that the product does not affect the overall reaction rate and hypothesis (ii) is also not operative. Thus, we conclude that $[VCP]_0$ affects the overall reaction rate, either through H-bonding that disrupts catalyst aggregation, or simply through the ring-opening reaction that necessarily interferes with recombination of the thiyl radicals.

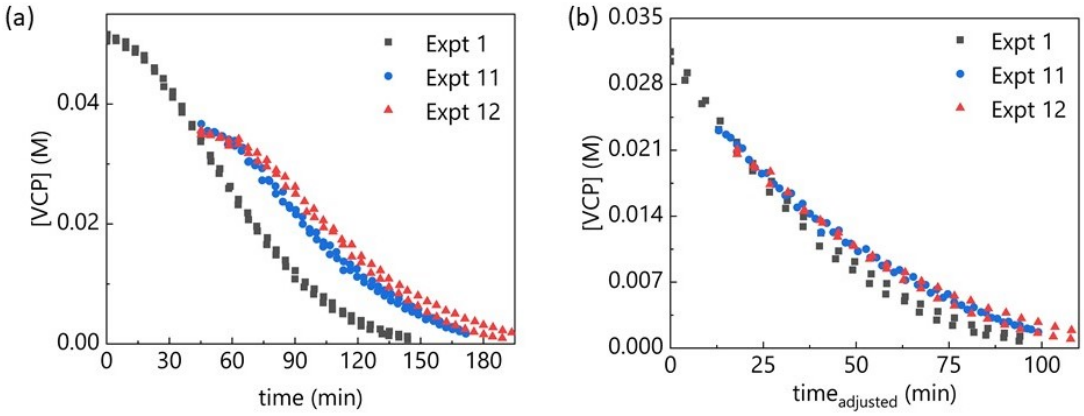


Figure S9. Same excess experiments. Duplicate experiments are simultaneously plotted and analyzed. (a) Raw concentration profiles. (b) Concentration profiles, truncated and time-adjusted to exclude the induction period.

We also observed that the maximum rate occurs consistently at 30% conversion, as opposed to a specific time or [VCP]. Data illustrating this phenomenon are shown below (Figure S10).

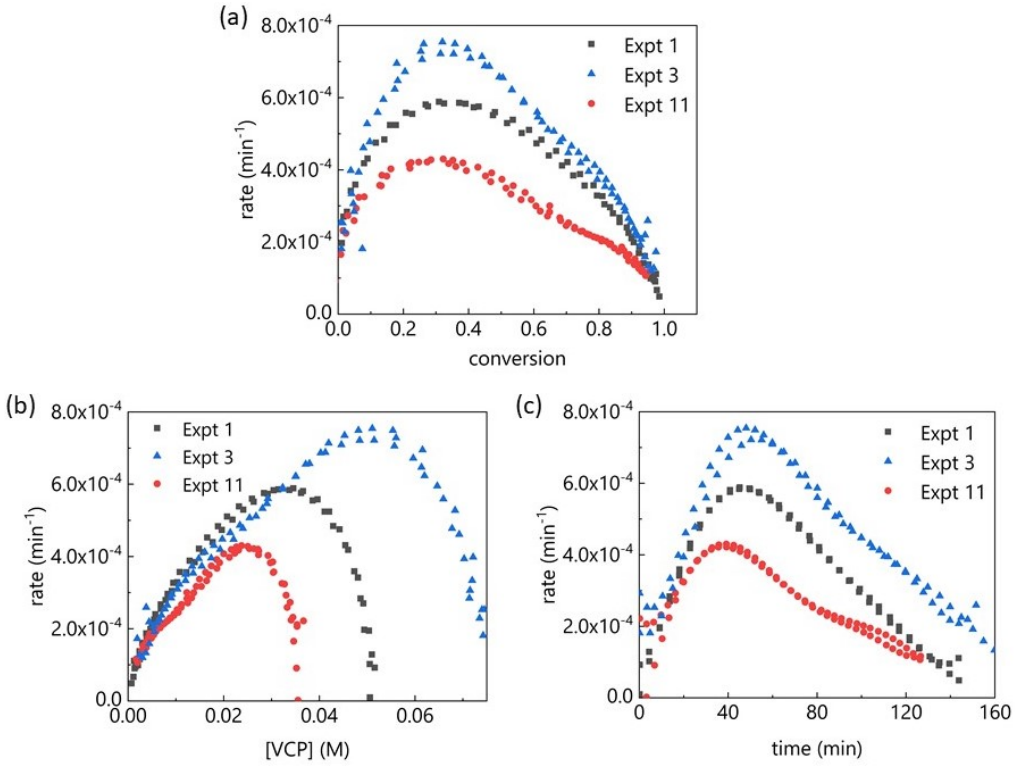


Figure S10. A comparison of rate data plotted (a) against conversion; (b) against [VCP]; (c) against time.

F. Experiments Using n-Butyl Disulfide as Catalyst

The concentrations used in the experiments for the (nBuS)$_2$-catalyzed reaction (Experiments 13−16) follow in Table S5.

Table S5. Concentrations for all experiments catalyzed by *n*-butyl disulfide

Expt	$[VCP]_0$ (M)	$[TBVE]_0$ (M)	$[(n\text{BuS})_2]_T$ (mM)
13	0.05	0.1	2.5
14	0.05	0.2	2.5
15	0.05	0.1	4.0
16	0.035	0.085	2.5

The data generated from these experiments are shown in the plots below (Figure S11). Experiments 13 and 14 demonstrate that the concentration of TBVE still has no effect on the rate of reaction, indicating that the rate-determining step is likely the same when *n*-butyl disulfide is used as the catalyst (Figure S11b and c). For comparison, the plots obtained when the reaction is assumed to be first-order in TBVE are shown, which do not display overlay (Figure S11d). Experiments 13 and 15 show overlay only when the reaction is assumed to be half-order in catalyst (Figure S11e). Under the same conditions with the full peptide catalyst, aggregation effects are observed. No such effects are observed with the simple disulfide catalyst, indicating that the peptide structure is responsible for catalyst aggregation, ostensibly due to H-bonding between the peptide backbones. Overlay between the plots generated from the "same-excess experiment" (experiments 13 and 16) is observed, indicating that the product "activation" observed with the full peptide catalyst is a function of the peptide backbone (again, ostensibly through H-bonding interactions) (Figure S11f).

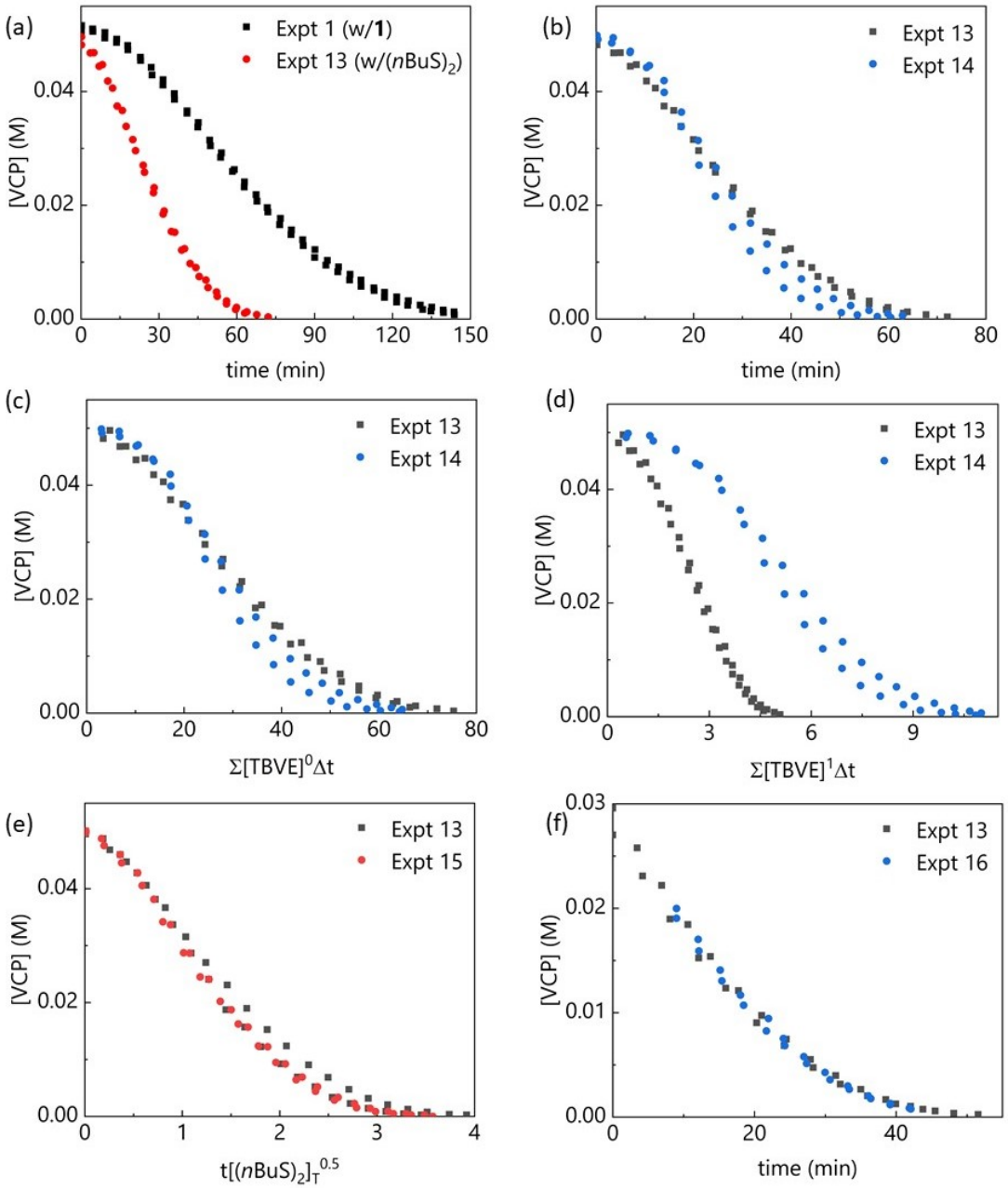


Figure S11. Kinetic analysis of $(n\text{BuS})_2$-catalyzed reaction. (a) Raw concentration profiles comparing the **1**-catalyzed reaction and the $(n\text{BuS})_2$-catalyzed reaction. (b) Raw concentration profiles for the different excess experiment maintaining $[\text{VCP}]_0$ and changing $[\text{TBVE}]_0$. (c) Variable time normalization analysis for different excess experiment, assuming zeroth-order dependence on [TBVE]. (d) Variable time normalization analysis for different excess experiment, assuming first-order dependence on [TBVE]. (e) Variable time normalization analysis for catalyst concentration experiment, assuming 0.5 order in $[(n\text{BuS})_2]_T$. (f) Raw concentration profiles for the same excess experiment.

G. Further Investigation of Induction Period

We attempted to account for the induction period by assuming irreversible homolysis of the catalyst analogous to the analysis reported by Blackmond and coworkers, fitting the entirety of the reaction data to equation 2.[10] However, this fails to provide a consistent fit across a range of $[VCP]_0$:$[TBVE]_0$ ratios, indicating that the data are not consistent with this model (Figure S12).

$$rate = \frac{V_{max}(1 - e^{-k_{diss}t})[VCP][TBVE]}{K_m + [VCP]} \quad (2)$$

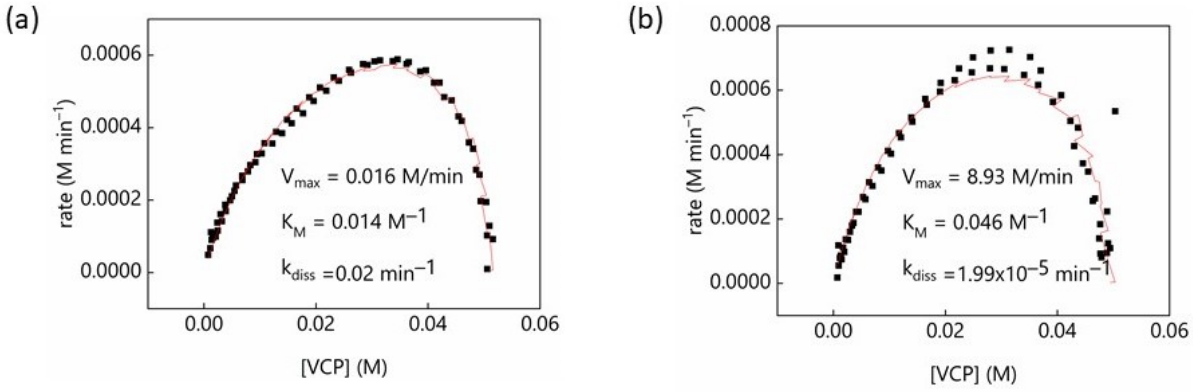


Figure S12. (a) Data from Experiment 1, fit to equation 2. (b) Data from Experiment 2, fit to equation 2. Duplicate experiments are simultaneously plotted and analyzed. The red line represents the smoothed (Lowess) best fit to Equation 2.

H. Experiments Using Enantiopure VCP

The comparisons between (±)-VCP, (*R*)-VCP, and (*S*)-VCP were carried out using the standard reaction conditions ($[VCP]_0$ = 0.05 M, $[TBVE]_0$ = 0.1 M, $[cat]_T$ = 2.5 mM). These data are illustrated in Figure S13. Specific concentrations for the different and same excess experiments follow in Table S6.

[10] Rosner, T.; Pfaltz, A.; Blackmond, D. G. Observation of Unusual Kinetics in Heck Reactions of Aryl Halides: The Role of Non-Steady-State Catalyst Concentration. *J. Am. Chem. Soc.* **2001,** *123,* 4621–4622.

Table S6. Concentrations for all **1**-catalyzed experiments using enantiopure VCP

Expt	**[S-VCP]$_0$ (M)**	**[TBVE]$_0$ (M)**	**[1]$_T$ (mM)**
17	0.05	0.1	2.5
18	0.05	0.2	2.5
19	0.035	0.085	2.5
Expt	**[R-VCP]$_0$ (M)**	**[TBVE]$_0$ (M)**	**[1]$_T$ (mM)**
20	0.05	0.1	2.5
21	0.05	0.2	2.5
22	0.035	0.085	2.5

The following [VCP] vs. time plots were generated. Qualitative examination of the plots indicates that (*R*)-VCP reacts at a faster rate than (*S*)-VCP, and both react at faster rates than the racemic VCP (Figure S13a). Quantitatively, relative rate constants were determined by comparing the maximum rates for each reaction (Figure S11b). The data used to calculate the relative rate constants, as well as the rate constants themselves, are shown in Table 7.

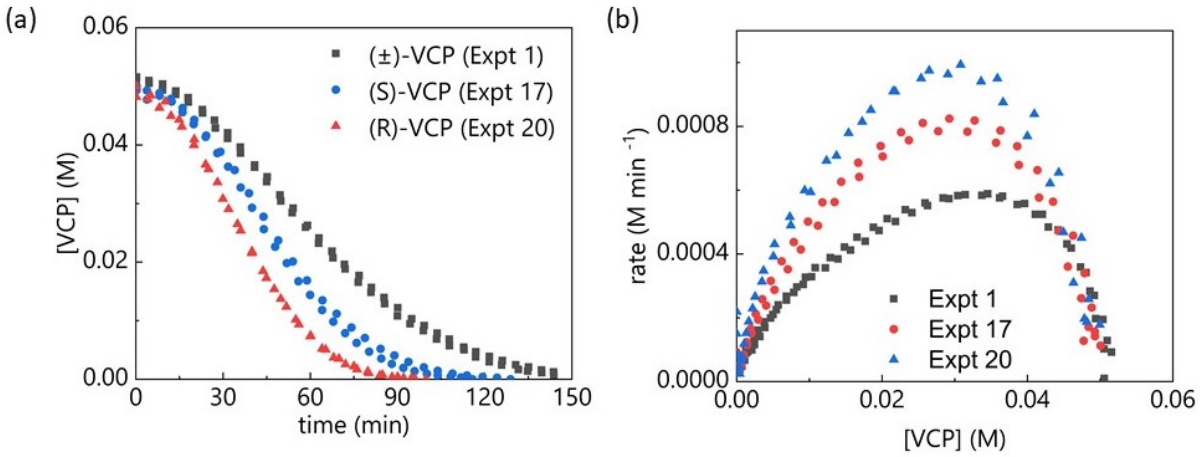


Figure S13. (a) Raw concentration profiles obtained from the **1**-catalyzed reaction, comparing racemic, (*S*)-, and (*R*)-VCP. Duplicate experiments are simultaneously plotted and analyzed. (b) Rate vs. concentration profiles obtained from the **1**-catalyzed reaction, comparing racemic, (*S*)-, and (*R*)-VCP.

These data can also be fit to equation 1 (post-induction period) (Figure S14).

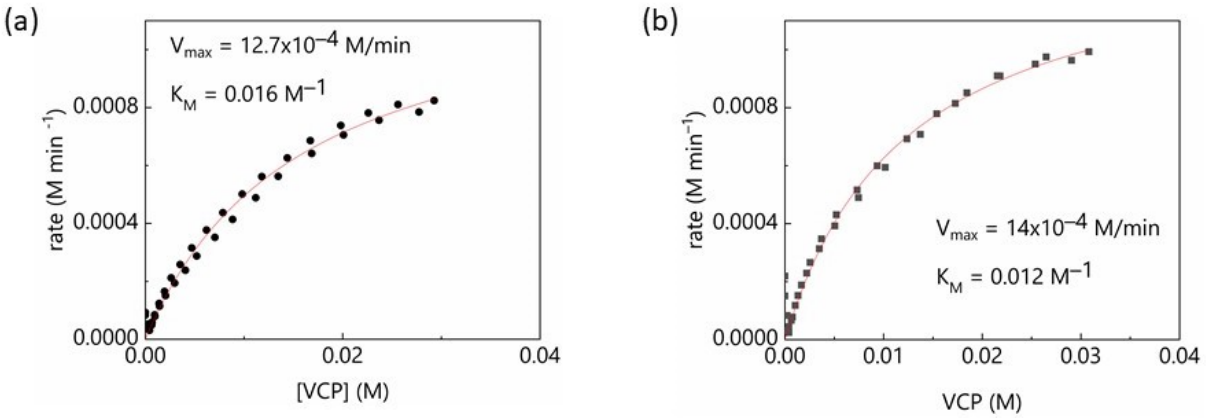


Figure S14. (a) Data for experiment 17, fit to equation 1. (b) Data for experiment 20, fit to equation 1.

Table S7. Determination of relative rates for reactions of racemic and enantiopure VCP

Expt	**Rate (Run 1) (M min^{-1})**	**Rate (Run 2) (M min^{-1})**	**Average Rate (M min^{-1})**	**k_{rel}**
1 **(±-VCP)**	5.88417x10^{-4}	5.83734x10^{-4}	5.84076x10^{-4}	1
17 **(S-VCP)**	7.84502x10^{-4}	8.24279x10^{-4}	8.04391x10^{-4}	1.4
20 **(R-VCP)**	9.92924x10^{-4}	9.63159x10^{-4}	9.78042x10^{-4}	1.7

The different excess experiments (S-VCP, experiments 17 and 18; R-VCP, experiments 20 and 21) indicate that these reactions are also zeroth-order in TBVE when enantiopure starting material is used, thus there is likely no change in rate-determining step for these reactions (Figure S15).

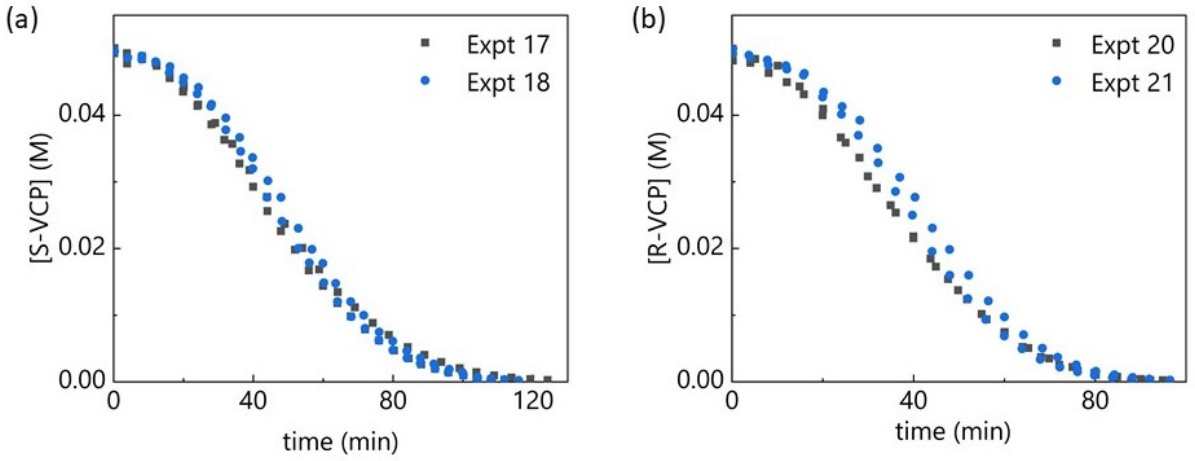


Figure S15. Different excess experiments using enantiopure VCP. Duplicate experiments are simultaneously plotted and analyzed. (a) Experiment with (*S*)-VCP. (b) Experiment with (*R*)-VCP.

The plots corresponding to the same excess experiments for both (*S*)- and (*R*)-VCP appear to show better, though imperfect, overlay than the same excess plot generated using racemic VCP (Figure S9b), which we interpreted as not displaying overlay. Any interpretation of these apparent differences is tenuous, though we suggest that this could result from differences in aggregation behavior related to the chirality of the dimers (or oligomers).

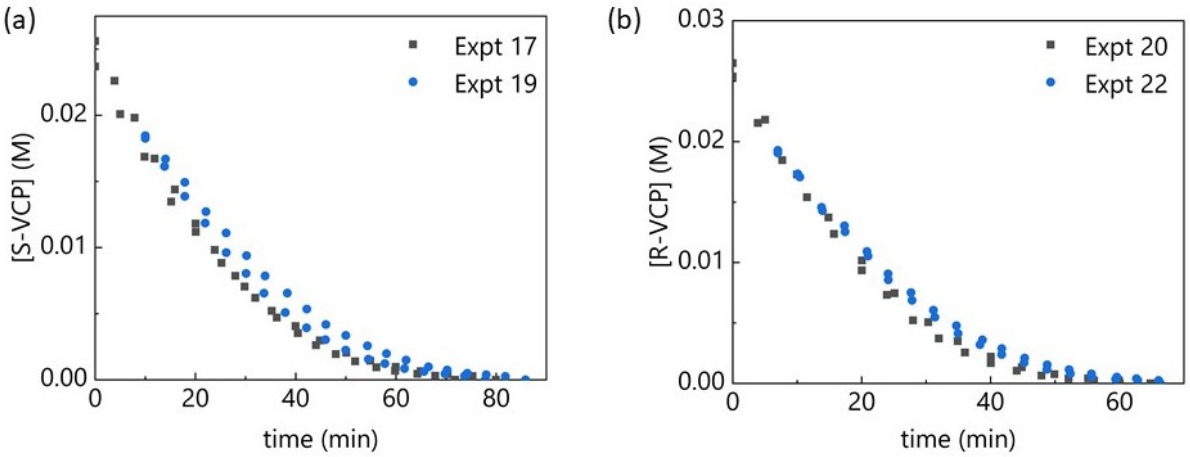


Figure S16. Same excess experiments using enantiopure VCP. Duplicate experiments are simultaneously plotted and analyzed. (a) Experiment with (*S*)-VCP. (b) Experiment with (*R*)-VCP.

I. Experiments Using Unsubstituted Catalyst

The comparisons between catalysts **1** and **2** were carried out using the standard reaction conditions ($[VCP]_0$ = 0.05 M, $[TBVE]_0$ = 0.1 M, $[cat]_T$ = 2.5 mM). Specific concentrations for the different and same excess experiments follow in Table S8.

Table S8. Concentrations for all **2**-catalyzed experiments using racemic VCP

Expt	$[VCP]_0$ (M)	$[TBVE]_0$ (M)	$[2]_T$ (mM)
23	0.05	0.1	2.5
24	0.05	0.2	2.5
25	0.035	0.085	2.5

A comparison between catalysts **1** and **2** illustrates that catalyst **1**, bearing the 4-proline substituent, catalyzes the reaction at a qualitatively faster rate than catalyst **2** (Figure S17a). The **2**-catalyzed reaction also appears to stall midway through the reaction, before proceeding to completion. This behavior precluded a quantitative comparison between the two catalysts, and we did not investigate this phenomenon further. The different excess experiment is also difficult to interpret due to the aforementioned stalling, but seems to be consistent with a scenario that is zeroth-order in TBVE, and we thus assume that there is no change in rate-determining step for the **2**-catalyzed reaction (Figure S17b). The same excess experiment does not result in overlay, consistent with the catalyst activation hypothesis proposed for the **1**-catalyzed reaction (Figure S17c and d).

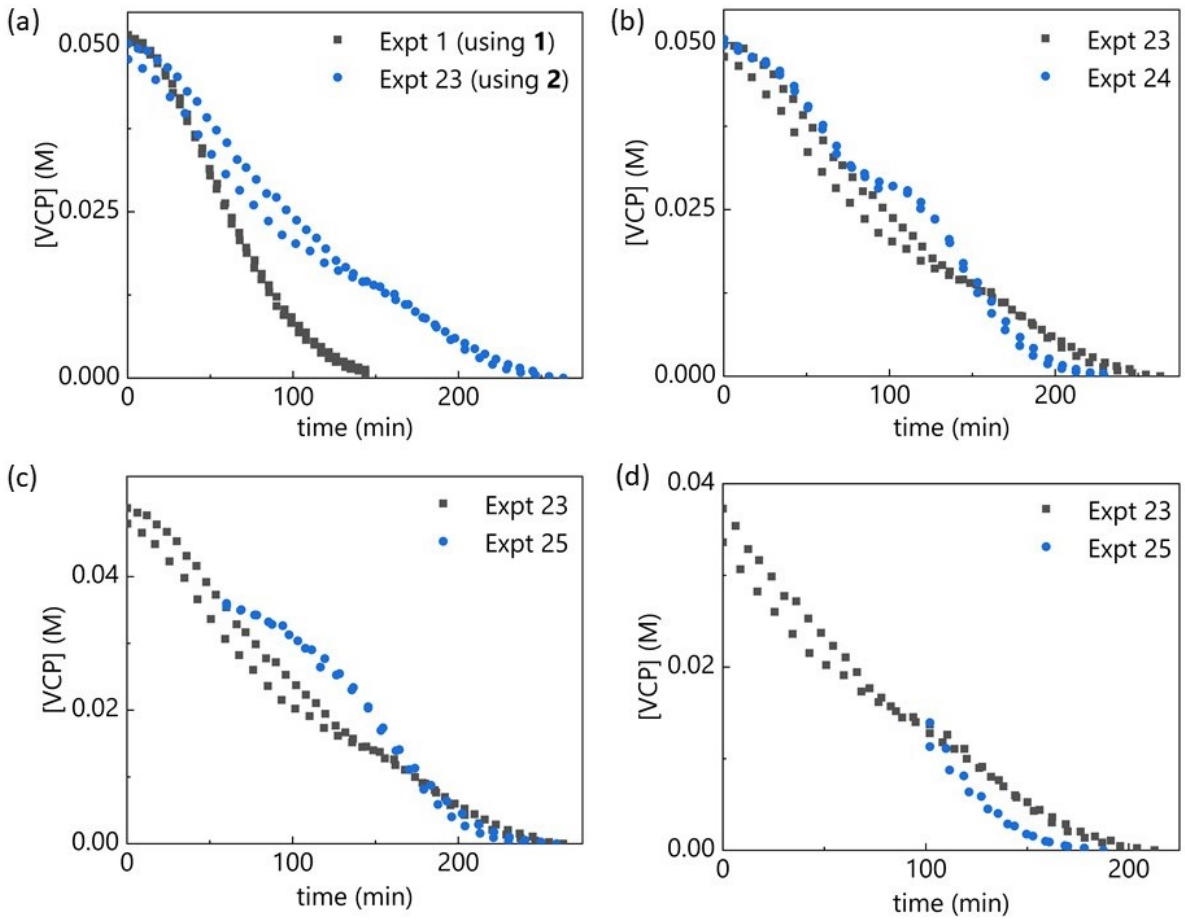


Figure S17. Data for the **2**-catalyzed reaction using racemic VCP. Duplicate experiments are simultaneously plotted and analyzed. (a) Raw concentration profile comparing catalysts **1** and **2**. (b) Different excess experiment. (c) Same excess experiment, raw data. (d) Same excess experiment, time-adjusted and truncated to remove the induction period.

J. Experiments Using Unsubstituted Catalyst and Enantiopure VCP

The comparisons between (±)-VCP, (*R*)-VCP, and (*S*)-VCP using the unsubstituted catalyst were carried out using the standard reaction conditions ($[VCP]_0$ = 0.05 M, $[TBVE]_0$ = 0.1 M, $[cat]_T$ = 2.5 mM). Specific concentrations for each experiment follow in Table S9.

Table S9. Concentrations for all **2**-catalyzed experiments using enantiopure VCP

Expt	**$[R\text{-}VCP]_0$ (M)**	**$[TBVE]_0$ (M)**	**$[2]_T$ (mM)**
26	0.05	0.1	2.5
Expt	**$[S\text{-}VCP]_0$ (M)**	**$[TBVE]_0$ (M)**	**$[2]_T$ (mM)**
27	0.05	0.1	2.5

As shown in Figure S18, as in the **1**-catalyzed reaction, (*R*)-VCP also reacts at the fastest rate in the **2**-catalyzed reaction, followed by (*S*)-VCP and then racemic VCP.

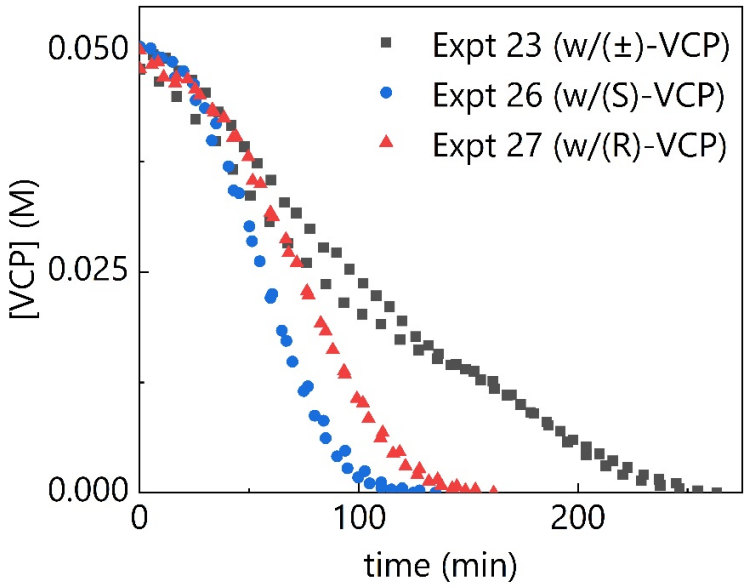
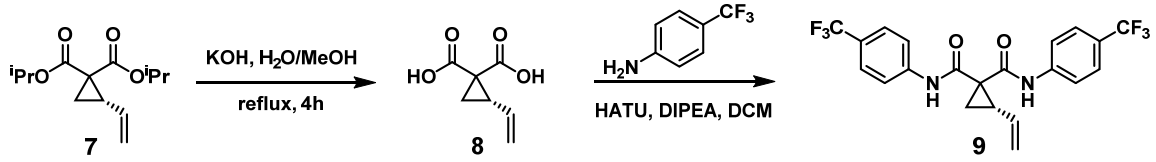


Figure S18. Raw concentration profiles obtained from the **2**-catalyzed reaction, comparing racemic, (*S*)-, and (*R*)-VCP. Duplicate experiments are simultaneously plotted and analyzed.

III. Synthesis of Enantiopure Vinylcyclopropanes

***S*-7** and ***R*-7** were accessed from (*S*)- and (*R*)-solketal through an adaptation of the methods reported in the literature.[11–13] A representative procedure for the synthesis of **S-7** is shown below.



(*S*)-2-vinylcyclopropane-1,1-dicarboxylic acid (S-8)

S-7 (6.1 g, 25.3 mmol, 1.0 equiv.) was dissolved in water (12.7 mL) and methanol (12.7 mL). Solid potassium hydroxide (5.7 g, 102 mmol, 4.0 equiv.) was added and the reaction mixture was stirred at 50 °C for 5 h. The reaction mixture was transferred to a separatory funnel, rinsing with water, and was acidified with HCl to pH < 2. The reaction mixture was extracted with ethyl acetate and the organic phase was washed with brine. The aqueous phase was back-extracted with ethyl acetate, and the combined organic phases were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford **S-8** as a colorless oil which was used in the subsequent reaction without further purification.

(*S*)-N,N'-bis(4-(trifluoromethyl)phenyl)-2-vinylcyclopropane-1,1-dicarboxamide (S-9)

S-8 was dissolved in DCM (63 mL), and HATU (21.1 g, 56 mmol, 2.2 equiv.) was added, followed by DIPEA (11.0 mL, 63 mmol, 2.5 equiv.). 4-Trifluoromethylaniline (7.0 mL, 56 mmol, 2.2 equiv.) was added and the reaction mixture was stirred at rt overnight. The reaction mixture was transferred to a separatory funnel and was diluted with DCM and washed with 1 N HCl, sat. aqueous sodium bicarbonate, and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude **S-9** was purified by silica gel column chromatography (5→25% ethyl acetate, hexanes). The semi-crude **S-9** was further purified by reversed-phase column chromatography on a Biotage Isolera One purification system (SNAP C18 120 g column; gradient = Ramp 20–100% MeCN/H_2O with 0.1% formic acid over 15 column volumes (CV), then 3 CV 100% MeCN with 0.1% formic acid; 75 mL/min flow rate; monitored λ = 210, 245 nm; 16 x 150 mm test tubes with 20 mL fractions). Fractions containing product were pooled and concentrated *in vacuo* to provide pure **S-9** as a white solid. Optical rotations were recorded on a Perkin Elmer Polarimeter 341 at the sodium D line (1.0 dm path length) at 20 °C, and determined to be $\mathbf{[\alpha]_D^{20} =}$

[11] Brard, M.; Lainé, C.; Réthoré, I. L.; Neveu, C.; Lemiègre, L.; Benvegnu, T. Synthesis of Archaeal Bipolar Lipid Analogues: A Way to Versatile Drug/Gene Delivery Systems. *J. Org. Chem.* **2007**, *72*, 8267–8279.
[12] Burgess, K.; Ho, K.-K.; Ke, C.-Y. Synthesis of a Valuable Cyclopropyl Chiron for Preparations of 2,3-Methanoamino Acids. *J. Org. Chem.* **1993**, *58*, 3767–3768.
[13] Carson, C. A.; Kerr, M. A. Total Synthesis of (+)-Phyllantidine. *Angew. Chem. Int. Ed.* **2006**, *45*, 6560–6563.

–38.2° (*c* = 0.01 g/mL, $CHCl_3$). All other spectral data matches that obtained for the racemic compound.[2]

(*R*)-2-vinylcyclopropane-1,1-dicarboxylic acid (R-8)

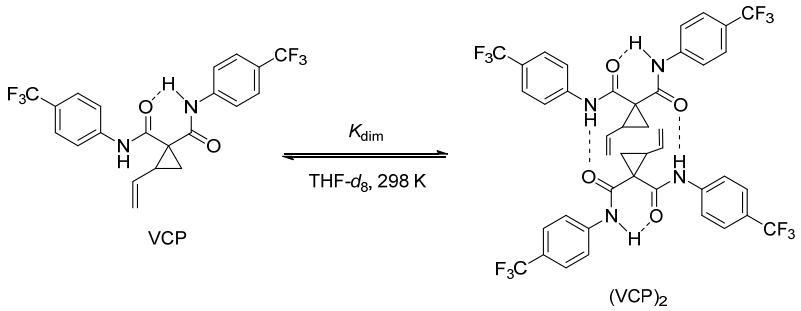
Synthesized by the same procedure as **S-8** using **R-7** (3.7 g, 15.4 mmol, 1.0 equiv.), water (7.7 mL), methanol (7.7 mL), and solid potassium hydroxide (3.5 g, 62 mmol, 4.0 equiv.) to afford **R-8** as a colorless oil which was used in the subsequent reaction without further purification.

(*R*)-N,N'-bis(4-(trifluoromethyl)phenyl)-2-vinylcyclopropane-1,1-dicarboxamide (R-9)

Synthesized by the same procedure as **S-9** using **R-8**, DCM (38.5 mL), HATU (12.9 g, 34 mmol, 2.2 equiv.), DIPEA (6.7 mL, 39 mmol, 2.5 equiv.), and 4-trifluoromethylaniline (4.3 mL, 34 mmol, 2.2 equiv.) to afford **S-9** as a white solid. $\mathbf{[\alpha]_D^{20}}$ **=** +37.1° (*c* = 0.01 g/mL, $CHCl_3$). All other spectral data matches that obtained for the racemic compound.[2]

IV. Vinylcyclopropane Binding Studies by NMR Titration

We performed NMR dilution experiments to investigate our hypothesis on the dimerization behavior of VCP in solution. In particular, we measured the shift of an amide N–H proton in THF-d_8 solutions of various VCP concentrations at constant temperature.[14]



Scheme S1. Proposed dimerization equilibrium for VCP.

A. General Procedure

For each production run across a concentration range, a stock solution of racemic or (*R*)-VCP at an appropriate concentration in THF-d_8 was prepared in a 1.00 mL volumetric flask. Each sample was prepared by diluting the appropriate amount of stock solution to 500 µL with THF-d_8 in a 5 mm Wilmad NMR tube using a gastight Hamilton® syringe. ^{1}H NMR spectra were recorded on a 500 MHz Agilent spectrometer. Samples were equilibrated in the spectrometer at 25 °C for

[14] (a) Wilcox, C. S., *Frontiers in Supramolecular Organic Chemistry and Photochemistry,*. VCH Weinheim: New York, 1991; (b) Horman, I.; Dreux, B., Estimation of association constants of biomolecular organic complexes. *Anal. Chem.* **1983,** *55* (8), 1219-1221.

100 s before acquisition. Proton chemical shifts are reported in ppm (δ) and referenced to residual solvent (THF-*d*$_8$, δ 3.58 ppm).[15] The lower-field amide N–H proton with δ ≈ 9.7 ppm was chosen for all runs.

B. Binding Studies with Racemic VCP

Run 1: 0.05 mM to 5 mM

Samples were prepared from a 10 mM stock solution of VCP in THF-*d*$_8$. The data are shown in Table S10 and plotted in Figure S19.

Table S10. Measured amide proton shifts for racemic VCP at concentrations from 0.05 mM to 5 mM.

[VCP] (mM)	0.05	0.075	0.10	0.25	0.50	1.0	1.5	2.5	5.0
$\delta_{N\text{-}\mathbf{H}}$ (ppm)	9.712	9.710	9.709	9.710	9.710	9.711	9.710	9.711	9.711

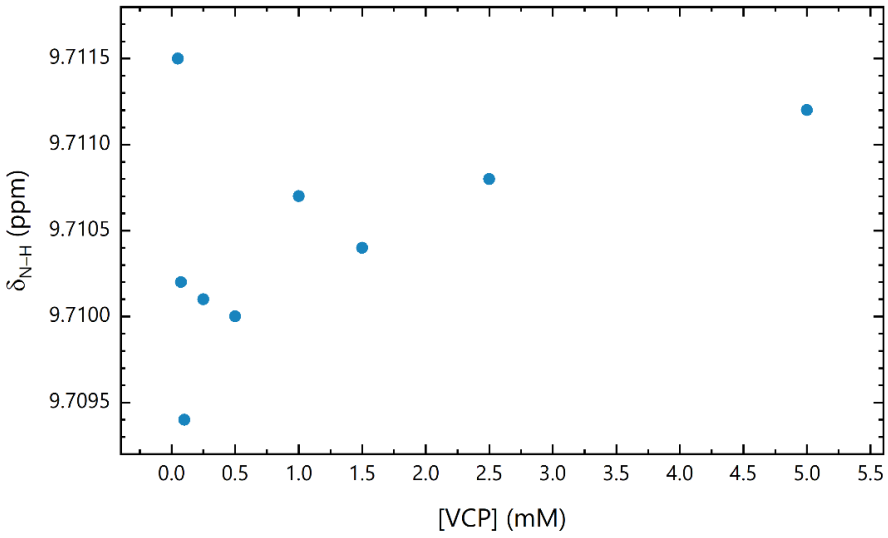


Figure S19. Measured amide proton shifts for racemic VCP at concentrations from 0.05 mM to 5 mM.

Run 2: 50 mM to 1000 mM

[15] Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I., NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010,** *29* (9), 2176-2179.

Samples were prepared from a 1000 mM stock solution of VCP in THF-d_8. The data are shown in Table S11 and plotted in Figure S20.

Table S11. Measured amide proton shifts for racemic VCP at concentrations from 50 mM to 1000 mM.

[VCP] (mM)	50	100	140	200	250	300	500	600	700	800	900	1000
$\delta_{N\text{-}H}$ (ppm)	9.716	9.722	9.724	9.730	9.732	9.738	9.758	9.781	9.761	9.785	9.798	9.806

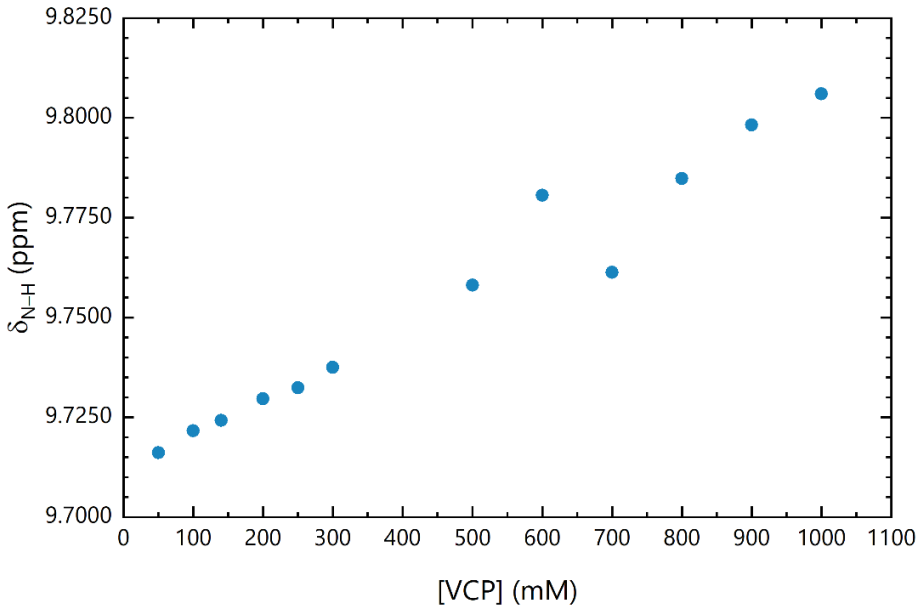


Figure S20. Measured amide proton shifts for racemic VCP from 50 mM to 1000 mM.

The observed changes in the chemical shift of the amide N–H proton (ca. 0.1 ppm over 20000-fold concentration change) suggest that the VCP dimerization/dissociation equilibrium does not shift measurably under the concentration regime being studied. Attempts to fit binding curves to the data were unsuccessful.[16]

C. Binding Studies with (*R*)-VCP

Run 1: 0.05 mM to 50 mM

[16] Bakowski, A.; Dressel, M.; Bauer, A.; Bach, T., Enantioselective radical cyclisation reactions of 4-substituted quinolones mediated by a chiral template. *Organic & Biomolecular Chemistry* **2011,** *9* (9), 3516-3529.

Samples were prepared from a 50 mM stock solution of VCP in THF-d_8. The data are shown in Table S12 and plotted in Figure S21.

Table S12. Measured amide proton shifts for (*R*)-VCP at concentrations from 0.05 mM to 50 mM.

[VCP] (mM)	0.05	0.1	0.25	0.5	1	5	10	20	50
$\delta_{N\text{-}\mathbf{H}}$ (ppm)	9.7132	9.7149	9.7146	9.7149	9.7148	9.7152	9.7166	9.7158	9.7202

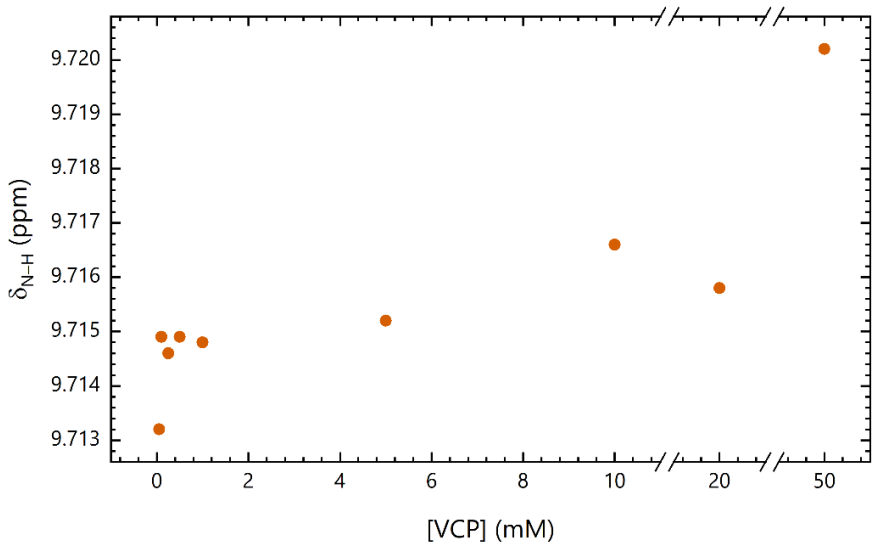


Figure S21. Measured amide proton shifts for (*R*)-VCP at concentrations from 0.05 mM to 50 mM.

A second run at concentrations above 50 mM was not performed as we observed similar behavior (i.e. small-magnitude shifts) between (*R*)- and racemic VCP in the lower concentration regime.

V. Computational Methods and Results

A. General Information

Calculations were performed on the Grace high-performance computing cluster supported by Yale University's Center for Research Computing.

Conformational searches were performed with CREST (version 2.11)[17] based on the xtb package (version 6.3.3).[18] Structures were preoptimized at the GFN2-xTB level using the analytical linearized Poisson-Boltzmann solvation model (ALPB)[19] for THF with the `--vtight` optimization convergence criteria. Optimized structures were then subjected to conformational searches at the i) GFN2-xTB/ALPB(THF) level (for the VCP monomers and dimers) or ii) multilevel GFN2-xTB/ALPB(THF)//GFN-FF/ALPB(THF) (for the intermediates $\mathbf{I}_{\boldsymbol{R}}$ and $\mathbf{I}_{\boldsymbol{S}}$) with an energy window of 10 kcal/mol. Two to four distinct conformers with the lowest energies were identified and then subjected to geometry optimization, as described below.

All DFT calculations were performed with the Gaussian 16 package (Revision C.01).[20] Geometry optimizations were performed with the dispersion-corrected density functional B3LYP-

[17] Pracht, P.; Bohle, F.; Grimme, S., Automated exploration of the low-energy chemical space with fast quantum chemical methods. *Phys. Chem. Chem. Phys.* **2020,** *22* (14), 7169-7192.

[18] Bannwarth, C.; Ehlert, S.; Grimme, S., GFN2-xTB—An Accurate and Broadly Parametrized Self-Consistent Tight-Binding Quantum Chemical Method with Multipole Electrostatics and Density-Dependent Dispersion Contributions. *J. Chem. Theory Comput.* **2019,** *15* (3), 1652-1671.

[19] (a) Sigalov, G.; Scheffel, P.; Onufriev, A., Incorporating variable dielectric environments into the generalized Born model. *J. Chem. Phys.* **2005,** *122* (9), 094511; (b) Sigalov, G.; Fenley, A.; Onufriev, A., Analytical electrostatics for biomolecules: Beyond the generalized Born approximation. *J. Chem. Phys.* **2006,** *124* (12), 124902.

[20] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16 Rev. C.01*, Wallingford, CT, 2016.

D3[21] with a Becke–Johnson (BJ) damping function[22] and the i) 6-31+G (d,p) (for the VCP monomers and dimers) or ii) 6-31G(d) (for the intermediates $\mathbf{I}_R$ and $\mathbf{I}_S$) basis set using the polarizable continuum model of solvation (PCM) for THF.[23] Optimized structures were verified by frequency calculations as minima with zero imaginary frequencies. For each species, the structures with the lowest free energies are reported.

For the VCP monomers and dimers, high-level free energies including improved solvation and high-level single-point energies were further computed based on the DFT-optimized geometries. Improved solvation free energies were computed using Truhlar's SMD solvation model[24] for THF at the M05-2X/6-31G(d) level of theory (*vide infra*).[25] High-level single-point energies were computed with the ORCA package (Version 4.2.1)[26] using the domain-based local pair natural orbital coupled cluster method with single, double, and perturbative triple excitations (DLPNO-CCSD(T))[27] with Ahlrichs' def2/TZVPP basis set,[28] with Hellweg's def2/TZVPP/C auxiliary basis set[29] using the `TightPNO` and `TightSCF` settings. The following equation was used to determine the final free energies:

$$G_{hl} = E_{0,CC} + \Delta G_{corr} + \Delta G_{solv,SMD},$$

[21] (a) Becke, A. D., Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993,** *98* (7), 5648-5652; (b) Lee, C.; Yang, W.; Parr, R. G., Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical Review B* **1988,** *37* (2), 785-789; (c) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010,** *132* (15), 154104; (d) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J., Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994,** *98* (45), 11623-11627; (e) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H., Results obtained with the correlation energy density functionals of becke and Lee, Yang and Parr. *Chem. Phys. Lett.* **1989,** *157* (3), 200-206.

[22] Grimme, S.; Ehrlich, S.; Goerigk, L., Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011,** *32* (7), 1456-1465.

[23] Amovilli, C.; Barone, V.; Cammi, R.; Cancès, E.; Cossi, M.; Mennucci, B.; Pomelli, C. S.; Tomasi, J., Recent Advances in the Description of Solvent Effects with the Polarizable Continuum Model. In *Adv. Quantum Chem.*, Löwdin, P.-O., Ed. Academic Press: 1998; Vol. 32, pp 227-261.

[24] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G., Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009,** *113* (18), 6378-6396.

[25] Zhao, Y.; Schultz, N. E.; Truhlar, D. G., Design of Density Functionals by Combining the Method of Constraint Satisfaction with Parametrization for Thermochemistry, Thermochemical Kinetics, and Noncovalent Interactions. *J. Chem. Theory Comput.* **2006,** *2* (2), 364-382.

[26] Neese, F., The ORCA program system. *WIRES Comput. Mol. Sci.* **2012,** *2* (1), 73-78.

[27] (a) Riplinger, C.; Neese, F., An efficient and near linear scaling pair natural orbital based local coupled cluster method. *J. Chem. Phys.* **2013,** *138* (3), 034106; (b) Lehtola, S.; Steigemann, C.; Oliveira, M. J. T.; Marques, M. A. L., Recent developments in libxc — A comprehensive library of functionals for density functional theory. *SoftwareX* **2018,** *7*, 1-5.

[28] Weigend, F.; Ahlrichs, R., Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005,** *7* (18), 3297-3305.

[29] Hellweg, A.; Hättig, C.; Höfener, S.; Klopper, W., Optimized accurate auxiliary basis sets for RI-MP2 and RI-CC2 calculations for the atoms Rb to Rn. *Theor. Chem. Acc.* **2007,** *117* (4), 587-597.

where $E_{0,CC}$ is the gas-phase electronic energy from DLPNO-CCSD(T); $\Delta G_{solv,SMD}$ is the difference in electronic energies computed at the M05-2X/6-31G(d) (gas phase) and M05-2X/6-31G(d)/SMD(THF) levels of theory, then adding a correction from 1 atm to 1 mol L^{-1} of RT ln(24.5) = +1.897 kcal/mol;[30] ΔG_{corr} is the thermal correction and zero-point vibrational energy (ZPVE) evaluated from the unscaled vibrational frequencies at the initial level of optimization.

For intermediates $\mathbf{I_R}$ and $\mathbf{I_S}$, high-level single-point energies were further computed. The following equation was used to determine the final free energy:

$$G_{hl} = E_{0,hl} + \Delta G_{corr},$$

where $E_{0,hl}$ is the electronic energy at the B3LYP-D3BJ/6-311+G(d,p)/PCM(THF) level, and ΔG_{corr} is the thermal correction and zero-point vibrational energy (ZPVE) evaluated from the unscaled vibrational frequencies at the initial level of optimization at 298.15 Kelvin.

All molecular structures were rendered in CYLView.[31] In all cases, the following color-coding scheme applies: H = white, C = grey, N = blue, O = red, F = lime, S = sulfur. Carbon-bound hydrogen atoms are omitted for clarity. Hydrogen bonding interactions are indicated with dotted lines.

B. Calculated high-level VCP conformer energies

Table S13. Energy components for high-level conformer energies in solution for VCP.

Species	Energies (au)					
	$E_{0,CC}$	ΔG_{corr}	$E_{M05-2X,gas}$	$E_{M05-2X,SMD}$	$\Delta G_{solv,SMD}{}^{a}$	G_{hl}
trans-VCP	–1666.43473	0.273197	–1668.74061	–1668.76967	–0.0260329	–1666.18757
cis-VCP	–1666.43416	0.273755	–1668.74021	–1666.43416	–0.0255793	–1666.18598
ΔG (au)						0.00159
$\Delta G_{dim,hl}$ (kcal/mol)						**+1.00**

[a] Including +1.897 kcal/mol correction

C. Calculated high-level VCP dimerization energies

Table S14. Energy components for high-level dimerization energies in solution for the heterochiral VCP dimer.

Species	Energies (au)					
	$E_{0,CC}$	ΔG_{corr}	$E_{M05-2X,gas}$	$E_{M05-2X,SMD}$	$\Delta G_{solv,SMD}{}^{a}$	G_{hl}
monomer	–1666.43473	0.273197	–1668.74061	–1668.76967	–0.0260329	–1666.18757

[30] Foresman, J. B.; Frisch, Æ., *Exploring Chemistry with Electronic Structure Methods*. 3 ed.; Gaussian, Inc.: Wallingford, CT, 2015.
[31] Legault, C. Y. *CYLView*, 1.0b; Université de Sherbrook, 2009.

heterochiral dimer	–3332.90642	0.571685	–3337.51749	–3337.55978	–0.0392668	–3332.37400
$\Delta G_{dim,hl}$ (au)						0.001139[b]
$\Delta G_{dim,hl}$ (kcal/mol)						**+0.715**

[a] Including +1.897 kcal/mol correction [b] $G_{hl}(\text{dimer}) - 2 \cdot G_{hl}(\text{monomer})$

Table S15. Energy components for high-level dimerization energies in solution for the homochiral VCP dimer.

Species	Energies (au)					
	$E_{0,CC}$	ΔG_{corr}	$E_{M05-2X,gas}$	$E_{M05-2X,SMD}$	$\Delta G_{solv,SMD}$ [a]	G_{hl}
monomer	–1666.43473	0.273197	–1668.74061	–1668.76967	–0.0260329	–1666.18757
homochiral dimer	–3332.90876	0.576434	–3337.51558	–3337.55824	–0.0396423	–3332.37196
$\Delta G_{dim,hl}$ (au)						0.003172[b]
$\Delta G_{dim,hl}$ (kcal/mol)						**+1.99**

[a] Including +1.897 kcal/mol correction [b] $G_{hl}(\text{dimer}) - 2 \cdot G_{hl}(\text{monomer})$

D. Calculated high-level $\mathbf{I_R}$ and $\mathbf{I_S}$ energies

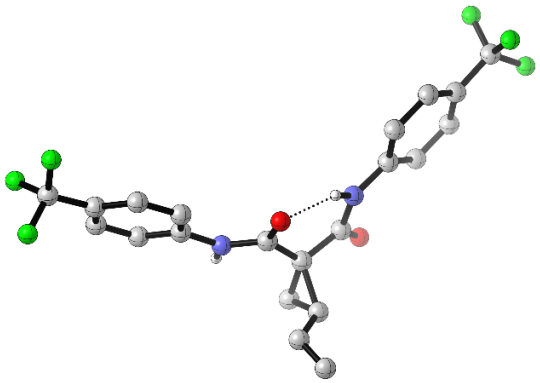
Table S16. Energy components for relative energies in solution for intermediates $\mathbf{I_R}$ and $\mathbf{I_S}$.

Species	Energies (au)		
	$E_{0,hl}$	ΔG_{corr}	G_{hl}
$\mathbf{I_R}$	–3713.23944	1.10959	–3712.129849
$\mathbf{I_S}$	–3713.246291	1.11214	–3712.134156
ΔG_{hl} (kcal/mol)			2.70[a]

[b] $G_{hl}(\mathbf{I_R}) - G_{hl}(\mathbf{I_S})$

E. Coordinates and energies at initial level of optimization

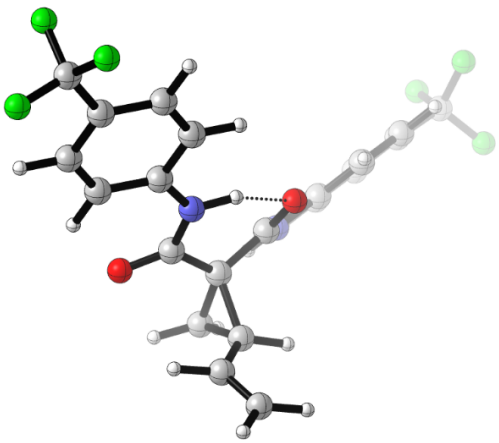
VCP: *trans* conformer



B3LYP–D3(BJ)/6–31+G(d,p)/PCM(THF)
Charge: 0
Multiplicity: 1
Electronic Energy: –1669.10419679
Imaginary Frequencies: 0
Temperature: 298.000 Kelvin
Pressure: 1.00000 Atm
Zero–point correction: 0.339660
Thermal correction to Energy: 0.367419
Thermal correction to Enthalpy: 0.368363
Thermal correction to Gibbs Free Energy: 0.273197
Sum of electronic and zero–point Energies: –1668.764537
Sum of electronic and thermal Energies: –1668.736777
Sum of electronic and thermal Enthalpies: –1668.735834
Sum of electronic and thermal Free Energies: –1668.831000

C	0.447910000	3.514846000	–1.193553000
C	0.064736000	3.682188000	0.248969000
C	1.081582000	3.920099000	1.293379000
C	0.836479000	4.587470000	2.426454000
H	1.615864000	4.751594000	3.163376000
H	–0.148627000	4.990789000	2.647128000
H	2.081577000	3.530796000	1.106093000
H	–0.909161000	4.124262000	0.440771000
C	–0.019485000	2.290092000	–0.450768000
C	0.937922000	1.225252000	0.025908000
O	0.658934000	0.498455000	0.988302000
N	2.103568000	1.129243000	–0.672138000
C	3.208163000	0.285988000	–0.444835000
C	4.229973000	0.308039000	–1.408788000
C	5.360514000	–0.483510000	–1.253863000
C	5.482681000	–1.310518000	–0.131834000
C	4.469986000	–1.330768000	0.830247000
C	3.331745000	–0.540829000	0.682256000
H	2.547454000	–0.566096000	1.423126000
H	4.559997000	–1.968856000	1.702068000
C	6.722864000	–2.128296000	0.064277000
F	6.492487000	–3.265043000	0.769984000
F	7.688017000	–1.446308000	0.751449000
F	7.292553000	–2.500844000	–1.111171000
H	6.139574000	–0.460142000	–2.007084000
H	4.135842000	0.943943000	–2.283766000
H	2.167100000	1.705118000	–1.500089000
C	–1.455707000	1.870143000	–0.720233000
O	–2.161437000	2.516758000	–1.495783000
N	–1.882117000	0.787298000	–0.008987000
C	–3.138121000	0.164900000	–0.025744000
C	–4.210971000	0.587699000	–0.828153000
C	–5.422012000	–0.099536000	–0.775814000
C	–5.582948000	–1.200683000	0.068958000
C	–4.514277000	–1.624222000	0.868293000
C	–3.303848000	–0.946368000	0.821252000
H	–2.478388000	–1.275126000	1.444856000
H	–4.626535000	–2.476960000	1.528243000
C	–6.871135000	–1.962781000	0.078481000
F	–6.870493000	–2.997180000	–0.817253000
F	–7.940384000	–1.190090000	–0.245025000
F	–7.139344000	–2.520460000	1.288945000
H	–6.245793000	0.234236000	–1.396733000
H	–4.092571000	1.442821000	–1.476114000
H	–1.187849000	0.401740000	0.631192000
H	1.502251000	3.612481000	–1.431781000
H	–0.232691000	3.895986000	–1.945249000

VCP: *cis* conformer

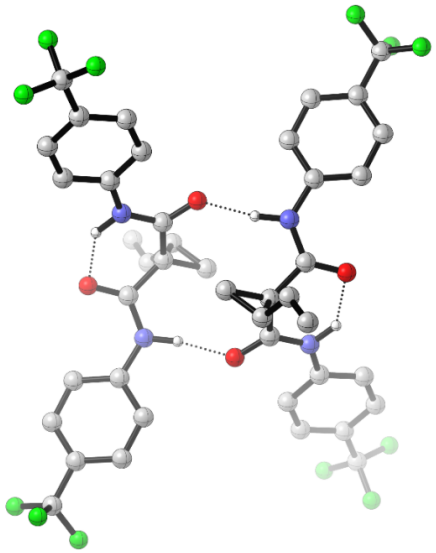


Charge: 0
Multiplicity: 1
Electronic Energy: –-1669.10365420
Imaginary Frequencies: 0

Temperature: 298.000 Kelvin
Pressure: 1.00000 Atm
Zero–point correction: 0.339924
Thermal correction to Energy: 0.367581
Thermal correction to Enthalpy: 0.368525
Thermal correction to Gibbs Free Energy: 0.273755
Sum of electronic and zero–point Energies: –1668.763730
Sum of electronic and thermal Energies: –1668.736073
Sum of electronic and thermal Enthalpies: –1668.735130
Sum of electronic and thermal Free Energies: –1668.829899

C	-0.346950000	-3.539806000	1.211360000
C	0.017386000	-3.646093000	-0.242300000
C	1.268649000	-4.284195000	-0.700452000
C	1.396769000	-4.874984000	-1.894081000
H	2.328614000	-5.344507000	-2.192296000
H	0.574679000	-4.909937000	-2.604880000
H	2.108572000	-4.264937000	-0.009661000
H	-0.815460000	-3.733384000	-0.936092000
C	0.048998000	-2.272644000	0.501411000
C	1.443128000	-1.749021000	0.818617000
O	2.134602000	-2.279147000	1.689457000
N	1.852741000	-0.715316000	0.031107000
C	3.073685000	-0.026766000	0.050489000
C	4.146772000	-0.360373000	0.893400000
C	5.326328000	0.379038000	0.831481000
C	5.455181000	1.444862000	-0.062411000
C	4.385610000	1.780347000	-0.901624000
C	3.206615000	1.049993000	-0.845541000
H	2.380603000	1.309897000	-1.500097000
H	4.473199000	2.605391000	-1.599520000
C	6.707393000	2.264466000	-0.087062000
F	7.798549000	1.568794000	0.324907000
F	6.629001000	3.359658000	0.729335000
F	6.991563000	2.746077000	-1.326573000
H	6.150931000	0.113721000	1.483441000
H	4.052689000	-1.187256000	1.580749000
H	1.151012000	-0.393318000	-0.637160000
C	-0.966491000	-1.273409000	0.003642000
O	-0.694931000	-0.485658000	-0.912960000
N	-2.182107000	-1.315853000	0.616875000
C	-3.346686000	-0.576470000	0.334229000
C	-4.445533000	-0.779329000	1.186506000
C	-5.635499000	-0.096021000	0.975640000
C	-5.742648000	0.802747000	-0.091980000
C	-4.653667000	1.002937000	-0.943057000
C	-3.454541000	0.322850000	-0.737391000
H	-2.612130000	0.488310000	-1.391199000
H	-4.730662000	1.698130000	-1.771196000
C	-7.042593000	1.502447000	-0.347959000
F	-6.884864000	2.670617000	-1.020255000
F	-7.711117000	1.793033000	0.799141000
F	-7.897973000	0.745089000	-1.098778000
H	-6.473892000	-0.259482000	1.643126000
H	-4.364694000	-1.472854000	2.017920000
H	-2.250175000	-1.930678000	1.416047000
H	0.374865000	-3.897850000	1.936606000
H	-1.384144000	-3.709741000	1.478930000

Heterochiral VCP dimer

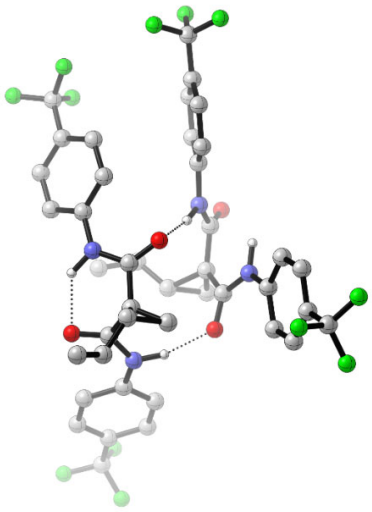


B3LYP–D3(BJ)/6–31+G(d,p)/PCM(THF)
Charge: 0
Multiplicity: 1
Electronic Energy: –3338.23871750
Imaginary Frequencies: 0
Temperature: 298.000 Kelvin
Pressure: 1.00000 Atm
Zero–point correction: 0.681812
Thermal correction to Energy: 0.738839
Thermal correction to Enthalpy: 0.739782
Thermal correction to Gibbs Free Energy: 0.571685
Sum of electronic and zero–point Energies: –3337.556905
Sum of electronic and thermal Energies: –3337.499879
Sum of electronic and thermal Enthalpies: –3337.498935
Sum of electronic and thermal Free Energies: –3337.667033

C	1.404575000	–0.966752000	–3.230794000
C	1.184441000	–1.480226000	–1.847143000
C	0.327864000	–2.654826000	–1.580529000
C	0.538994000	–3.499862000	–0.566593000
H	–0.100185000	–4.362455000	–0.413481000
H	1.355225000	–3.357739000	0.136947000
H	–0.495944000	–2.831574000	–2.269155000
H	2.007128000	–1.343299000	–1.156146000
C	0.544705000	–0.133895000	–2.295685000
C	–0.948864000	–0.181240000	–2.551300000

O	–1.415014000	–0.623017000	–3.600658000
N	–1.715206000	0.270773000	–1.512240000
C	–3.125121000	0.296377000	–1.446334000
C	–3.937263000	–0.607592000	–2.141296000
C	–5.319488000	–0.572610000	–1.960943000
C	–5.895274000	0.358517000	–1.094867000
C	–5.084275000	1.270662000	–0.407278000
C	–3.707831000	1.242341000	–0.586918000
H	–3.073687000	1.940627000	–0.051380000
H	–5.524944000	1.999521000	0.264413000
C	–7.375560000	0.389559000	–0.863331000
F	–7.699399000	0.062316000	0.421988000
F	–8.055641000	–0.465361000	–1.663188000
F	–7.903935000	1.628839000	–1.072374000
H	–5.943428000	–1.284004000	–2.488598000
H	–3.492068000	–1.335326000	–2.803846000
H	–1.247504000	0.522712000	–0.636926000
C	1.220133000	1.101388000	–1.763705000
O	2.399552000	1.067299000	–1.386917000
N	0.486211000	2.250017000	–1.777349000
C	0.851488000	3.516516000	–1.280513000
C	2.183533000	3.921711000	–1.114518000
C	2.456607000	5.190901000	–0.609928000
C	1.416770000	6.063738000	–0.280161000
C	0.087657000	5.664962000	–0.460020000
C	–0.192118000	4.398563000	–0.957915000
H	–1.223669000	4.087668000	–1.090768000
H	–0.726103000	6.336390000	–0.210980000
C	1.716965000	7.405174000	0.316741000
F	1.705933000	7.374780000	1.683362000
F	2.939043000	7.875064000	–0.039796000
F	0.808732000	8.349309000	–0.043282000
H	3.487728000	5.499478000	–0.481494000
H	2.988854000	3.249169000	–1.367514000
H	–0.485762000	2.164403000	–2.044892000
H	0.866205000	–1.440723000	–4.043772000
H	2.382127000	–0.562826000	–3.467036000
C	1.883117000	1.898288000	1.775776000
C	1.488636000	0.467448000	1.997366000
C	2.475946000	–0.669143000	1.858374000
O	2.412060000	–1.660861000	2.595599000
N	3.366455000	–0.517034000	0.842629000
C	4.353198000	–1.419480000	0.404512000
C	4.766356000	–2.534562000	1.146796000
C	5.754522000	–3.373733000	0.632184000
C	6.330353000	–3.112398000	–0.611755000
C	5.917471000	–1.996997000	–1.352362000
C	4.936605000	–1.155303000	–0.848243000
H	4.605556000	–0.296445000	–1.422273000
H	6.358143000	–1.787603000	–2.321192000
C	7.386142000	–4.009021000	–1.182541000
F	7.000325000	–4.571482000	–2.364471000
F	7.717460000	–5.030814000	–0.357167000
F	8.541044000	–3.335971000	–1.455209000
H	6.071827000	–4.234283000	1.209033000
H	4.317654000	–2.742559000	2.106400000
H	3.168664000	0.249875000	0.199773000
C	0.057233000	0.096976000	1.688406000
O	–0.688733000	0.886784000	1.089971000
N	–0.324905000	–1.128493000	2.129223000
C	–1.564215000	–1.766609000	1.932491000
C	–2.743114000	–1.061182000	1.661237000
C	–3.928210000	–1.755168000	1.433981000
C	–3.953236000	–3.149300000	1.501740000
C	–2.784561000	–3.854524000	1.814664000
C	–1.597005000	–3.166521000	2.029616000
H	–0.687993000	–3.712941000	2.257289000
H	–2.797697000	–4.936577000	1.880902000
C	–5.211966000	–3.895477000	1.181422000
F	–6.328735000	–3.153908000	1.388988000
F	–5.346966000	–5.030539000	1.917371000
F	–5.256717000	–4.290090000	–0.127238000
H	–4.830207000	–1.201283000	1.203393000
H	–2.730952000	0.015953000	1.618926000
H	0.417424000	–1.679665000	2.558628000
C	1.651401000	1.442157000	3.191814000
C	2.777741000	1.267728000	4.130467000
C	2.676505000	1.432574000	5.453900000
H	3.536257000	1.310353000	6.104527000
H	1.732047000	1.696792000	5.923145000
H	3.739901000	1.003505000	3.692951000
H	0.711229000	1.741016000	3.648281000
H	2.907796000	2.099422000	1.483483000
H	1.140127000	2.539684000	1.319799000

Homochiral VCP dimer



B3LYP–D3(BJ)/6–31+G(d,p)/PCM(THF)
Charge: 0
Multiplicity: 1
Electronic Energy: –3338.24234425
Imaginary Frequencies: 0
Temperature: 298.000 Kelvin
Pressure: 1.00000 Atm
Zero–point correction: 0.682109
Thermal correction to Energy: 0.738869
Thermal correction to Enthalpy: 0.739812
Thermal correction to Gibbs Free Energy: 0.576434
Sum of electronic and zero–point Energies: – 3337.560236
Sum of electronic and thermal Energies: – 3337.503476
Sum of electronic and thermal Enthalpies: – 3337.502532
Sum of electronic and thermal Free Energies: – 3337.665910

C	1.404575000	–0.966752000	–3.230794000
C	1.184441000	–1.480226000	–1.847143000
C	0.327864000	–2.654826000	–1.580529000
C	0.538994000	–3.499862000	–0.566593000
H	–0.100185000	–4.362455000	–0.413481000
H	1.355225000	–3.357739000	0.136947000
H	–0.495944000	–2.831574000	–2.269155000
H	2.007128000	–1.343299000	–1.156146000
C	0.544705000	–0.133895000	–2.295685000
C	–0.948864000	–0.181240000	–2.551300000
O	–1.415014000	–0.623017000	–3.600658000
N	–1.715206000	0.270773000	–1.512240000
C	–3.125121000	0.296377000	–1.446334000
C	–3.937263000	–0.607592000	–2.141296000
C	–5.319488000	–0.572610000	–1.960943000
C	–5.895274000	0.358517000	–1.094867000
C	–5.084275000	1.270662000	–0.407278000
C	–3.707831000	1.242341000	–0.586918000
H	–3.073687000	1.940627000	–0.051380000
H	–5.524944000	1.999521000	0.264413000
C	–7.375560000	0.389559000	–0.863331000
F	–7.699399000	0.062316000	0.421988000
F	–8.055641000	–0.465361000	–1.663188000
F	–7.903935000	1.628839000	–1.072374000
H	–5.943428000	–1.284004000	–2.488598000
H	–3.492068000	–1.335326000	–2.803846000
H	–1.247504000	0.522712000	–0.636926000
C	1.220133000	1.101388000	–1.763705000
O	2.399552000	1.067299000	–1.386917000
N	0.486211000	2.250017000	–1.777349000
C	0.851488000	3.516516000	–1.280513000
C	2.183533000	3.921711000	–1.114518000
C	2.456607000	5.190901000	–0.609928000
C	1.416770000	6.063738000	–0.280161000
C	0.087657000	5.664962000	–0.460020000
C	–0.192118000	4.398563000	–0.957915000
H	–1.223669000	4.087668000	–1.090768000
H	–0.726103000	6.336390000	–0.210980000
C	1.716965000	7.405174000	0.316741000
F	1.705933000	7.374780000	1.683362000
F	2.939043000	7.875064000	–0.039796000
F	0.808732000	8.349309000	–0.043282000
H	3.487728000	5.499478000	–0.481494000
H	2.988854000	3.249169000	–1.367514000
H	–0.485762000	2.164403000	–2.044892000
H	0.866205000	–1.440723000	–4.043772000
H	2.382127000	–0.562826000	–3.467036000
C	1.883117000	1.898288000	1.775776000
C	1.488636000	0.467448000	1.997366000
C	2.475946000	–0.669143000	1.858374000
O	2.412060000	–1.660861000	2.595599000
N	3.366455000	–0.517034000	0.842629000
C	4.353198000	–1.419480000	0.404512000
C	4.766356000	–2.534562000	1.146796000
C	5.754522000	–3.373733000	0.632184000
C	6.330353000	–3.112398000	–0.611755000
C	5.917471000	–1.996997000	–1.352362000
C	4.936605000	–1.155303000	–0.848243000
H	4.605556000	–0.296445000	–1.422273000
H	6.358143000	–1.787603000	–2.321192000
C	7.386142000	–4.009021000	–1.182541000
F	7.000325000	–4.571482000	–2.364471000
F	7.717460000	–5.030814000	–0.357167000
F	8.541044000	–3.335971000	–1.455209000
H	6.071827000	–4.234283000	1.209033000
H	4.317654000	–2.742559000	2.106400000
H	3.168664000	0.249875000	0.199773000
C	0.057233000	0.096976000	1.688406000
O	–0.688733000	0.886784000	1.089971000
N	–0.324905000	–1.128493000	2.129223000
C	–1.564215000	–1.766609000	1.932491000
C	–2.743114000	–1.061182000	1.661237000
C	–3.928210000	–1.755168000	1.433981000
C	–3.953236000	–3.149300000	1.501740000
C	–2.784561000	–3.854524000	1.814664000
C	–1.597005000	–3.166521000	2.029616000
H	–0.687993000	–3.712941000	2.257289000
H	–2.797697000	–4.936577000	1.880902000
C	–5.211966000	–3.895477000	1.181422000
F	–6.328735000	–3.153908000	1.388988000
F	–5.346966000	–5.030539000	1.917371000
F	–5.256717000	–4.290090000	–0.127238000
H	–4.830207000	–1.201283000	1.203393000
H	–2.730952000	0.015953000	1.618926000
H	0.417424000	–1.679665000	2.558628000
C	1.651401000	1.442157000	3.191814000
C	2.777741000	1.267728000	4.130467000
C	2.676505000	1.432574000	5.453900000

H	3.536257000	1.310353000	6.104527000
H	1.732047000	1.696792000	5.923145000
H	3.739901000	1.003505000	3.692951000
H	0.711229000	1.741016000	3.648281000
H	2.907796000	2.099422000	1.483483000
H	1.140127000	2.539684000	1.31979900

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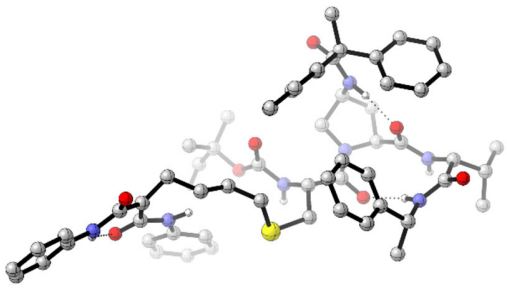

B3LYP–D3(BJ)/6–31G(d)/PCM(THF)
Charge: 0
Multiplicity: 2
Electronic Energy: –3712.31176358
Imaginary Frequencies: 0
Temperature: 298.150 Kelvin
Pressure: 1.00000 Atm
Zero–point correction: 1.225356
Thermal correction to Energy: 1.298530
Thermal correction to Enthalpy: 1.299474
Thermal correction to Gibbs Free Energy: 1.109590
Sum of electronic and zero-point Energies: –3711.086408
Sum of electronic and thermal Energies: –3711.013233
Sum of electronic and thermal Enthalpies: –3711.012289
Sum of electronic and thermal Free Energies: –3711.202174

N	2.888620000	2.046353000	0.481780000
C	2.334987000	1.970877000	1.841125000
H	1.937784000	2.947972000	2.142340000
H	1.537494000	1.235103000	1.908872000
C	3.556235000	1.586573000	2.687469000
H	3.423901000	1.873192000	3.730301000
C	4.685951000	2.372696000	1.995087000
H	4.672920000	3.408163000	2.345349000
H	5.672592000	1.953164000	2.201071000
C	4.332003000	2.337909000	0.486286000
H	4.526228000	3.296354000	-0.004383000
C	5.088292000	1.213692000	-0.225053000
N	5.979038000	1.562815000	-1.172568000
H	6.019616000	2.523338000	-1.484383000
C	6.757410000	0.542372000	-1.864847000
C	7.964876000	1.155789000	-2.605099000
H	8.457063000	0.299755000	-3.079448000
C	5.928698000	-0.332796000	-2.824991000
N	4.704276000	0.124007000	-3.161102000
H	4.308980000	0.916426000	-2.662611000
C	3.801948000	-0.603347000	-4.042656000
H	4.437731000	-1.247133000	-4.658256000
O	6.432253000	-1.365212000	-3.273406000
O	4.913167000	0.032562000	0.090649000
C	2.260635000	1.821696000	-0.691731000
C	0.775212000	1.403166000	-0.649275000
H	0.704459000	0.502353000	-0.032686000
C	0.300344000	1.080727000	-2.074251000
H	0.908013000	0.271524000	-2.479990000
H	0.441665000	1.950025000	-2.721710000
N	-0.026985000	2.405543000	0.021564000
C	-0.781228000	2.115906000	1.121376000
O	-1.514565000	3.180988000	1.474253000
C	-2.208946000	3.228699000	2.781040000
C	-3.260489000	2.123714000	2.882536000
H	-3.940753000	2.166657000	2.028930000
H	-3.849408000	2.277670000	3.792969000
H	-2.798412000	1.137291000	2.927018000
C	-2.875318000	4.602352000	2.748976000
H	-2.126594000	5.390473000	2.620472000
H	-3.403645000	4.775945000	3.691498000
H	-3.592896000	4.664315000	1.926676000
O	-0.749391000	1.030955000	1.697991000
H	-0.162819000	3.307887000	-0.414736000
O	2.863242000	1.930729000	-1.769520000
H	7.126388000	-0.151788000	-1.104197000
C	7.547207000	2.134065000	-3.711855000
H	8.427295000	2.463584000	-4.273323000
H	6.847178000	1.673877000	-4.416236000
H	7.071727000	3.037476000	-3.307881000
C	8.948021000	1.798769000	-1.620618000
H	9.841383000	2.150033000	-2.147726000
H	8.502442000	2.661590000	-1.111562000
H	9.263347000	1.083103000	-0.853293000
C	3.083584000	0.414100000	-4.942103000
H	3.815961000	0.977773000	-5.528711000
H	2.395702000	-0.082614000	-5.631031000
H	2.510394000	1.116459000	-4.328841000
C	2.816810000	-1.491438000	-3.282806000
C	1.895861000	-2.265672000	-4.003379000
C	2.796685000	-1.557071000	-1.885017000
C	0.972336000	-3.078841000	-3.346671000
C	1.862930000	-2.360866000	-1.225943000
C	0.951230000	-3.127327000	-1.951455000
H	1.904120000	-2.241199000	-5.089910000
H	3.511935000	-0.987675000	-1.304046000
H	0.271193000	-3.673674000	-3.925509000
H	1.840698000	-2.380008000	-0.142627000
H	0.231547000	-3.750723000	-1.430272000
C	-4.890052000	-1.255000000	0.812341000

C	-3.840559000	-1.424364000	-0.264989000
C	-2.652008000	-0.810052000	-0.240833000
C	-1.612209000	-0.936604000	-1.305474000
H	-0.631953000	-1.160124000	-0.880185000
H	-1.852642000	-1.726755000	-2.020319000
H	-2.392839000	-0.154276000	0.588423000
H	-4.111050000	-2.076565000	-1.094095000
C	-6.187534000	-0.722502000	0.265451000
C	-6.385325000	0.719425000	0.016926000
O	-7.514143000	1.245040000	-0.026704000
N	-5.231984000	1.441514000	-0.140070000
C	-5.091210000	2.830378000	-0.338125000
C	-6.103943000	3.758802000	-0.051076000
C	-5.855329000	5.118647000	-0.237294000
C	-4.618229000	5.569148000	-0.701919000
C	-3.613758000	4.638950000	-0.978619000
C	-3.843669000	3.279661000	-0.798152000
H	-3.057259000	2.561478000	-1.008665000
H	-2.641276000	4.970277000	-1.331290000
H	-6.643242000	5.831895000	-0.012808000
H	-7.063250000	3.415057000	0.305949000
H	-4.382394000	0.901635000	-0.271463000
C	-7.218267000	-1.738936000	-0.049501000
O	-6.919560000	-2.942142000	-0.038908000
N	-8.461350000	-1.252371000	-0.349457000
C	-9.618286000	-1.959334000	-0.698423000
C	-9.673812000	-3.358059000	-0.826189000
C	-10.878245000	-3.966127000	-1.179038000
C	-12.029634000	-3.211490000	-1.408844000
C	-11.970651000	-1.820672000	-1.281963000
C	-10.778483000	-1.197835000	-0.930299000
H	-10.734961000	-0.116234000	-0.832390000
H	-12.856286000	-1.216825000	-1.457392000
H	-10.911376000	-5.047835000	-1.275295000
H	-8.782885000	-3.941697000	-0.648316000
H	-8.534020000	-0.234202000	-0.282129000
H	-4.508878000	-0.589046000	1.594663000
H	-5.101436000	-2.230241000	1.260366000
S	-1.469615000	0.663900000	-2.230650000
N	3.785454000	0.153079000	2.650283000
H	4.148959000	-0.225215000	1.774936000
C	3.379482000	-0.671522000	3.642840000
O	2.903529000	-0.261963000	4.703744000
C	3.482753000	-2.192254000	3.327943000
C	3.580426000	-2.947400000	4.674802000
H	4.455249000	-2.631743000	5.248628000
H	2.692368000	-2.744069000	5.275666000
C	2.170641000	-2.628194000	2.649730000
C	1.085965000	-1.758088000	2.482908000
C	2.010202000	-3.961272000	2.237836000
C	-0.110465000	-2.194621000	1.908840000
C	0.820058000	-4.400286000	1.659122000
C	-0.248630000	-3.515997000	1.489262000
H	1.142862000	-0.732261000	2.823798000
H	2.831929000	-4.660683000	2.356589000
H	-0.924727000	-1.488573000	1.796809000
H	0.729914000	-5.434688000	1.339899000
H	-1.177548000	-3.852321000	1.037352000
C	4.733884000	-2.455547000	2.468496000
C	5.999863000	-2.208420000	3.027153000
C	4.679367000	-2.847758000	1.127037000
C	7.162449000	-2.358831000	2.275871000
C	5.842106000	-2.993035000	0.366633000
C	7.089183000	-2.753758000	0.936628000
H	6.078860000	-1.872818000	4.056888000
H	3.725210000	-3.023145000	0.650670000
H	8.127112000	-2.159212000	2.734574000
H	5.762296000	-3.264469000	-0.682124000
H	7.994302000	-2.862989000	0.345812000
H	3.653512000	-4.023176000	4.495893000
H	-4.438267000	6.630666000	-0.842094000
H	-12.960473000	-3.698273000	-1.683564000
C	-1.166763000	3.142358000	3.896091000
H	-0.673641000	2.168290000	3.900263000
H	-0.411248000	3.925686000	3.772830000
H	-1.655578000	3.288198000	4.864693000

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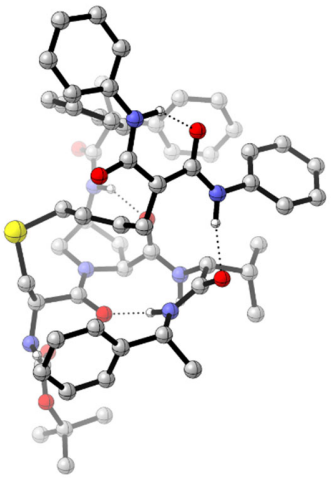

B3LYP–D3(BJ)/6–31G(d)/PCM(THF)
Charge: 0
Multiplicity: 2
Electronic Energy: –3712.32371933
Imaginary Frequencies: 0
Temperature: 298.000 Kelvin
Pressure: 1.00000 Atm
Zero-point correction: 1.225793

Thermal correction to Energy: 1.298795
Thermal correction to Enthalpy: 1.299739
Thermal correction to Gibbs Free Energy: 1.112135
Sum of electronic and zero-point Energies: –3711.097926
Sum of electronic and thermal Energies: –3711.024925
Sum of electronic and thermal Enthalpies: –3711.023981
Sum of electronic and thermal Free Energies: –3711.211584

N	-2.320525000	-1.050903000	-1.875068000
C	-1.975363000	-1.267768000	-3.291099000
H	-2.883605000	-1.478739000	-3.868078000
H	-1.471923000	-0.395996000	-3.709655000
C	-1.062507000	-2.502213000	-3.247408000
H	-1.108821000	-3.060593000	-4.181206000
C	-1.645980000	-3.305482000	-2.064499000
H	-2.525387000	-3.861216000	-2.401469000
H	-0.933936000	-4.015284000	-1.642909000
C	-2.094646000	-2.242282000	-1.046221000
H	-3.036889000	-2.518924000	-0.564576000
C	-1.049145000	-1.920750000	0.025552000
N	-1.473602000	-2.052415000	1.297096000
H	-2.442909000	-2.295000000	1.449643000
C	-0.665584000	-1.684168000	2.443499000
C	-0.655689000	-2.799241000	3.515950000
H	-0.071952000	-2.395333000	4.346150000
C	-1.070960000	-0.339160000	3.063878000
N	-2.118663000	0.323037000	2.548863000
H	-2.537882000	0.035197000	1.664530000
C	-2.604642000	1.556747000	3.194990000
H	-1.716464000	2.086109000	3.548240000
O	-0.421155000	0.089787000	4.036681000
O	0.093861000	-1.547243000	-0.266932000
C	-2.985200000	-0.015068000	-1.329225000
C	-3.460390000	1.137327000	-2.230716000
H	-3.477273000	0.825255000	-3.275680000
C	-2.570239000	2.378779000	-2.068835000
H	-2.346486000	2.557086000	-1.013057000
H	-3.121830000	3.245125000	-2.443720000
N	-4.817431000	1.495049000	-1.835552000
C	-5.729833000	0.472707000	-1.756672000
O	-6.793049000	0.860146000	-1.026659000
C	-7.804127000	-0.116748000	-0.586616000
C	-8.571681000	-0.655748000	-1.793663000
H	-9.393346000	-1.292859000	-1.449524000
H	-7.918388000	-1.240071000	-2.442499000
H	-8.998312000	0.171674000	-2.370183000
C	-8.713282000	0.725864000	0.306494000
H	-8.154563000	1.126359000	1.158711000
H	-9.534025000	0.110993000	0.688363000
H	-9.138381000	1.562195000	-0.257138000
O	-5.573586000	-0.613509000	-2.300554000
H	-4.883164000	2.167271000	-1.077468000
O	-3.245265000	0.013836000	-0.117610000
H	0.353202000	-1.558648000	2.068627000
C	-2.064217000	-3.121746000	4.029986000
H	-2.580200000	-2.226102000	4.394505000
H	-2.687344000	-3.583760000	3.253593000
H	-2.008095000	-3.834747000	4.858781000
C	0.060110000	-4.041340000	2.977994000
H	0.115512000	-4.814613000	3.751522000
H	-0.472379000	-4.462242000	2.116985000
H	1.081268000	-3.802534000	2.663941000
C	-3.451961000	1.200138000	4.423926000
H	-4.322991000	0.599109000	4.145532000
H	-2.846118000	0.625662000	5.129909000
H	-3.801700000	2.110467000	4.920867000
C	-3.324389000	2.456579000	2.207972000
C	-2.664556000	3.578920000	1.693045000
C	-4.652422000	2.227607000	1.830884000
C	-3.315588000	4.463336000	0.832417000
C	-5.315025000	3.117910000	0.984209000
C	-4.648479000	4.239706000	0.482534000
H	-1.633929000	3.766694000	1.977624000
H	-5.182935000	1.356674000	2.203130000
H	-2.785405000	5.327950000	0.444433000
H	-6.346696000	2.926504000	0.706459000
H	-5.165032000	4.931711000	-0.176297000
C	0.897812000	2.386954000	1.865966000
C	0.454277000	1.671411000	0.600183000
C	0.407498000	2.259323000	-0.601473000
C	0.157722000	1.506952000	-1.868581000
H	1.077292000	1.456612000	-2.460938000
H	-0.155527000	0.482555000	-1.666253000
H	0.625080000	3.321685000	-0.694216000
H	0.306695000	0.597169000	0.668505000
C	2.393619000	2.260997000	1.893986000
C	3.067075000	1.023988000	2.333006000
O	4.255325000	0.762739000	2.045600000
N	2.316048000	0.146963000	3.065631000
C	2.777035000	-1.102562000	3.545428000
C	2.355279000	-1.512427000	4.817611000
C	2.740478000	-2.755676000	5.314162000
C	3.554996000	-3.595393000	4.552393000
C	3.970098000	-3.184720000	3.283928000
C	3.581847000	-1.948642000	2.769907000
H	3.896554000	-1.641542000	1.781457000
H	4.593493000	-3.834841000	2.679929000
H	2.405088000	-3.064173000	6.299973000
H	1.717309000	-0.857262000	5.400632000
H	1.399694000	0.418347000	3.420807000
C	3.104660000	3.369392000	1.197116000
O	2.490526000	4.392220000	0.861808000
N	4.430842000	3.159278000	0.936915000
C	5.291265000	3.915320000	0.131416000

C	4.944888000	5.146206000	-0.452091000
C	5.870196000	5.804045000	-1.262869000
C	7.135130000	5.265160000	-1.501320000
C	7.477388000	4.042523000	-0.916293000
C	6.566635000	3.371531000	-0.108527000
H	6.831106000	2.416967000	0.338556000
H	8.456590000	3.606585000	-1.091915000
H	5.592513000	6.753868000	-1.711419000
H	3.966082000	5.562779000	-0.267401000
H	4.774740000	2.254107000	1.273526000
H	0.418447000	1.961919000	2.749622000
H	0.649211000	3.447318000	1.811177000
S	-1.012928000	2.335599000	-3.021891000
N	0.338038000	-2.163113000	-3.036942000
H	0.569244000	-1.780981000	-2.119608000
C	1.316865000	-2.770664000	-3.760425000
O	1.086755000	-3.429304000	-4.774297000
C	2.758491000	-2.606831000	-3.204583000
C	3.742100000	-3.112153000	-4.287117000
H	3.598401000	-2.593242000	-5.236617000
H	4.771437000	-2.957437000	-3.953650000
C	3.028804000	-1.121912000	-2.892673000
C	3.136895000	-0.630072000	-1.585935000
C	3.190538000	-0.212382000	-3.950330000
C	3.481687000	0.700335000	-1.345153000
C	3.510556000	1.124113000	-3.711524000
C	3.683322000	1.583913000	-2.403203000
H	2.963360000	-1.286014000	-0.741856000
H	3.073508000	-0.548327000	-4.975670000
H	3.602637000	1.032410000	-0.324436000
H	3.636800000	1.802474000	-4.550705000
H	3.955897000	2.617442000	-2.210368000
C	2.947515000	-3.509322000	-1.972081000
C	4.159077000	-3.462325000	-1.263458000
C	1.988560000	-4.441899000	-1.564713000
C	4.382750000	-4.286122000	-0.163234000
C	2.204671000	-5.266016000	-0.457052000
C	3.398539000	-5.185083000	0.255890000
H	4.929575000	-2.760577000	-1.565952000
H	1.065752000	-4.549087000	-2.121343000
H	5.329318000	-4.223958000	0.366311000
H	1.435682000	-5.972888000	-0.158524000
H	3.566048000	-5.819189000	1.121339000
H	3.582383000	-4.177876000	-4.462054000
H	3.860451000	-4.562130000	4.941176000
H	7.845635000	5.788703000	-2.133756000
C	-7.125176000	-1.223036000	0.223372000
H	-6.479231000	-1.835022000	-0.407593000
H	-6.522118000	-0.784337000	1.025690000
H	-7.887941000	-1.864678000	0.676244000

VI. Complete Raw Data for Kinetics Experiments

Experiment 1

$[VCP]_0$ = 0.05 M VCP, $[TBVE]_0$ = 0.1 M TBVE, $[\mathbf{1}]_T$ = 2.5 mM

Run 1: 88.5 mg VCP, 55 μL TBVE, 14.9 mg **1**, 4 mL THF

Product: 78:22 *trans*/*cis*, 75% ee *trans*, 51% ee *cis*

Run 2: 88.4 mg VCP, 55 μL TBVE, 15.0 mg **1**, 4 mL THF

Product: 77:23 *trans*/*cis*, 73% ee *trans*, 49% ee *cis*

Run 1			Run 2		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.3	11185	0.00172	0.2	10969	0.00169
4.5	11056	0.00170	4.6	10963	0.00169
9.2	10928	0.00168	9.2	10713	0.00165
13.8	10671	0.00164	13.7	10543	0.00162
18.0	10581	0.00163	18.1	10262	0.00158
22.9	10281	0.00158	23.0	9856	0.00152
27.1	9593	0.00148	27.4	9302	0.00143
31.6	9258	0.00143	31.6	8916	0.00137
36.0	8594	0.00132	36.0	8372	0.00129
40.9	7934	0.00122	40.9	7848	0.00121
45.2	7494	0.00115	45.0	7316	0.00113
49.6	6821	0.00105	49.9	6602	0.00102
54.1	6336	0.00098	53.8	6164	0.00095
59.1	5697	0.00088	58.4	5623	0.00087
63.0	5228	0.00081	62.9	5030	0.00077
67.5	4738	0.00073	67.8	4491	0.00069
71.8	4250	0.00065	72.0	4080	0.00063
76.8	3838	0.00059	76.6	3591	0.00055
81.1	3397	0.00052	80.9	3216	0.00050
85.4	3069	0.00047	85.6	2796	0.00043
90.1	2648	0.00041	90.0	2346	0.00036
94.9	2268	0.00035	94.4	2053	0.00032
99.2	1987	0.00031	99.0	1797	0.00028
103.7	1705	0.00026	103.5	1485	0.00023
107.9	1486	0.00023	107.9	1242	0.00019
112.8	1185	0.00018	112.9	1086	0.00017
117.0	1015	0.00016	116.9	825	0.00013

121.6	843	0.00013	121.6	645	0.00010
126.1	694	0.00011	125.9	522	0.00008
130.7	532	0.00008	131.6	362	0.00006
135.1	453	0.00007	134.8	299	0.00005
139.5	343	0.00005	139.6	244	0.00004
143.7	273	0.00004	143.8	161	0.00002

Experiment 2

$[VCP]_0$ = 0.05 M VCP, $[TBVE]_0$ = 0.2 M TBVE, $[\mathbf{1}]_T$ = 2.5 mM

Run 1: 88.5 mg VCP, 110 μL TBVE, 14.8 mg **1**, 4 mL THF

Product: 77:23 *trans*/*cis*, 75% ee *trans*, 50% ee *cis*

Run 2: 88.6 mg VCP, 110 μL TBVE, 14.9 mg **1**, 4 mL THF

Product: 77:23 *trans*/*cis*, 74% ee *trans*, 51% ee *cis*

Run 1			**Run 2**		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	10910	0.00168	0.2	10713	0.00165
4.6	10596	0.00163	4.5	10591	0.00163
8.8	10341	0.00159	9.1	10637	0.00164
13.9	10387	0.00160	13.5	10329	0.00159
17.8	10292	0.00158	18.2	10130	0.00156
22.7	10046	0.00155	22.7	9866	0.00152
27.1	9664	0.00149	27.0	9324	0.00144
31.4	9472	0.00146	31.7	9177	0.00141
36.1	8821	0.00136	35.9	8507	0.00131
40.8	8031	0.00124	40.7	7935	0.00122
44.9	7617	0.00117	44.9	7388	0.00114
49.6	6814	0.00105	49.5	6619	0.00102
54.2	6092	0.00094	54.0	6067	0.00093
58.6	5409	0.00083	58.6	5359	0.00083
63.0	4865	0.00075	62.9	4698	0.00072
67.5	4156	0.00064	67.5	4128	0.00064
71.9	3555	0.00055	71.8	3617	0.00056
76.7	3015	0.00046	76.7	3056	0.00047
80.8	2543	0.00039	81.0	2612	0.00040

85.5	2111	0.00033	85.3	2230	0.00034
90.2	1729	0.00027	90.0	1859	0.00029
94.5	1384	0.00021	94.5	1514	0.00023
99.0	1148	0.00018	98.9	1243	0.00019
103.5	885	0.00014	103.4	972	0.00015
107.8	720	0.00011	108.1	781	0.00012
112.5	563	0.00009	112.5	640	0.00010
117.2	424	0.00007	116.7	480	0.00007
122.1	315	0.00005	121.5	374	0.00006
126.2	253	0.00004	126.0	283	0.00004
130.4	195	0.00003	130.6	207	0.00003
			134.9	154	0.00002

Experiment 3

$[VCP]_0$ = 0.075 M, $[TBVE]_0$ = 0.1 M, $[\mathbf{1}]_T$ = 2.5 mM

Run 1: 132.8 mg VCP, 55 µL TBVE, 14.8 mg **1**, 4 mL THF

Product: 78:22 *trans*/*cis*, 75% ee *trans*, 51% ee *cis*

Run 2: 132.7 mg VCP, 55 µL TBVE, 14.9 mg **1**, 4 mL THF

Product: 78:22 *trans*/*cis*, 74% ee *trans*, 50% ee *cis*

Run 1			**Run 2**		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	16493.8	0.002539993	0.2	16103	0.00248
3.5	16164.2	0.002489236	4.9	15940	0.00245
6.8	16053.1	0.002472127	10.0	15508	0.00239
10.5	15478.5	0.00238364	15.1	15239	0.00235
13.9	15604.2	0.002402997	19.9	14690	0.00226
17.6	15646.8	0.002409558	25.2	14297	0.00220
20.9	15018.7	0.002312832	30.1	13442	0.00207
24.5	14828.3	0.002283511	35.1	12933	0.00199
28.4	14019.7	0.002158989	40.3	12078	0.00186
31.9	13304.5	0.002048851	45.9	11159	0.00172
36.0	13352.8	0.002056289	50.3	10504	0.00162
40.0	12152.7	0.001871477	55.1	9674	0.00149

44.3	12007.2	0.001849071	59.9	8946	0.00138
48.1	11073.8	0.00170533	65.0	8227	0.00127
52.1	10606	0.00163329	70.1	7590	0.00117
56.0	9816.76563	0.001511751	74.8	7011	0.00108
59.9	9096.85449	0.001400887	80.1	6298	0.00097
63.9	8735.18457	0.001345191	84.9	5802	0.00089
67.9	8058.78809	0.001241028	89.9	5206	0.00080
72.1	7609.93506	0.001171906	94.9	4783	0.00074
76.0	7011.39453	0.001079733	100.0	4173	0.00064
80.1	6437.13184	0.000991298	105.0	3770	0.00058
84.0	6094.90869	0.000938597	110.2	3343	0.00051
88.2	5592.66455	0.000861253	114.8	2953	0.00045
91.8	5069.98047	0.000780761	119.8	2605	0.00040
95.9	4631.78467	0.00071328	125.0	2238	0.00034
99.9	4273.52051	0.000658109	129.8	1949	0.00030
103.9	3892.38818	0.000599415	135.2	1666	0.00026
108.1	3475.7334	0.000535252	139.9	1429	0.00022
112.0	3207.16528	0.000493893	144.9	1188	0.00018
116.0	2904.14526	0.000447229	150.1	965	0.00015
119.9	2803.37646	0.000431711	154.9	804	0.00012
124.0	2326.36816	0.000358253	159.8	655	0.00010
127.8	1986.84778	0.000305968	164.7	525	0.00008
131.9	1778.34143	0.000273859	169.9	416	0.00006
135.9	1606.49841	0.000247396			
139.8	1317.06042	0.000202823			
143.8	1148.85522	0.00017692			
147.8	955.83124	0.000147195			
151.6	824.24896	0.000126932			

Experiment 4

$[VCP]_0$ = 0.05 M, $[TBVE]_0$ = 0.1 M, $[\mathbf{1}]_T$ = 1.25 mM

Run 1: 88.5 mg VCP, 55 µL TBVE, 7.4 mg **1**, 4 mL THF

Product: 76:24 *trans*/*cis*, 73% ee *trans*, 29% ee *cis*

Run 2: 88.6 mg VCP, 55 µL TBVE, 7.5 mg **1**, 4 mL THF

Product: 77:23 *trans*/*cis*, 75% ee *trans*, 51% ee *cis*

Run 1			Run 2		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	11416	0.05264	0.2	10895	0.05023
5.8	10828	0.04992	6.0	10717	0.04941
12.0	10690	0.04929	11.9	10477	0.04831
17.9	10279	0.04739	18.1	10179	0.04693
23.8	9750	0.04495	24.0	9981	0.04602
29.8	9606	0.04429	29.9	9541	0.04399
35.7	8915	0.04110	35.8	9029	0.04163
42.0	8441	0.03892	42.0	8578	0.03955
47.6	7848	0.03619	47.8	8006	0.03691
53.9	7221	0.03329	54.0	7284	0.03359
59.7	6573	0.03031	59.8	6950	0.03204
65.7	5822	0.02684	65.9	6242	0.02878
71.7	5398	0.02489	71.8	5709	0.02632
77.7	4785	0.02206	77.8	5286	0.02437
83.9	4200	0.01937	83.8	4700	0.02167
89.6	3706	0.01709	90.0	4120	0.01899
95.9	3119	0.01438	95.8	3713	0.01712
102.5	2687	0.01239	102.0	3284	0.01514
108.4	2256	0.01040	108.1	2871	0.01324
113.5	1909	0.00880	113.9	2485	0.01146
119.6	1605	0.00740	120.2	2030	0.00936
126.0	1266	0.00584	125.8	1754	0.00809
132.4	993	0.00458	131.9	1447	0.00667
138.0	797	0.00368	138.0	1190	0.00549
143.7	616	0.00284	143.8	966	0.00446
150.4	456	0.00210	150.1	778	0.00359
155.3	345	0.00159	155.9	596	0.00275
161.9	244	0.00113	161.8	471	0.00217
167.7	181	0.00083	168.1	360	0.00166

173.6	127	0.00058	173.9	267	0.00123
			179.8	202	0.00093

Experiment 5

$[VCP]_0$ = 0.05 M, $[TBVE]_0$ = 0.1 M, $[\mathbf{1}]_T$ = 1.62 mM

Run 1: 88.5 mg VCP, 55 µL TBVE, 9.7 mg **1**, 4 mL THF

Product: 75:25 *trans*/*cis*, 73% ee *trans*, 48% ee *cis*

Run 2: 88.5 mg VCP, 55 µL TBVE, 9.7 mg **1**, 4 mL THF

Product: 76:24 *trans*/*cis*, 72% ee *trans*, 49% ee *cis*

Run 1			**Run 2**		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	11040	0.05090	0.2	10893	0.05023
4.8	11037	0.05089	5.5	10695	0.04931
10.0	10449	0.04818	10.9	10608	0.04891
15.0	10347	0.04771	16.8	10301	0.04749
19.9	10074	0.04645	22.1	9998	0.04610
27.0	9408	0.04338	27.5	9542	0.04399
29.9	8921	0.04113	32.7	8911	0.04109
35.2	8573	0.03953	38.6	8328	0.03840
40.0	8069	0.03720	43.9	7752	0.03522
45.1	7297	0.03364	49.6	7059	0.03254
50.2	6793	0.03132	55.4	6427	0.02963
55.0	6093	0.02809	60.5	5734	0.02644
60.3	5501	0.02536	65.9	5220	0.02407
65.3	5060	0.02333	71.4	4637	0.02138
70.0	4554	0.02100	76.9	4122	0.01901
75.0	4069	0.01876	82.8	3567	0.01644
80.0	3572	0.01647	87.7	3168	0.01461
85.0	3099	0.01429	93.3	2717	0.01253
90.1	2722	0.01255	99.8	2273	0.01048
94.6	2412	0.01112	104.3	1962	0.00905
99.5	2057	0.00948	109.8	1668	0.00769
104.9	1699	0.00783	115.4	1321	0.00609

109.9	1493	0.00688	121.0	1079	0.00497
115.8	1186	0.00547	126.9	856	0.00389
120.1	930	0.00429	131.9	674	0.00311
124.9	795	0.00367	137.6	524	0.00241
129.8	618	0.00285	143.0	406	0.00187
135.7	472	0.00217	148.4	300	0.00138
139.8	353	0.00163	153.9	221	0.00102
144.9	280	0.00129	159.6	163	0.00075
149.9	208	0.00096	165.3	117	0.00054
154.5	149	0.00069	139.6	597	0.00275
160.0	106	0.00049	144.1	488	0.00225
164.9	79	0.00036	148.6	411	0.00190

Experiment 6

$[VCP]_0$ = 0.05 M, $[TBVE]_0$ = 0.1 M, $[\mathbf{1}]_T$ = 2.0 mM

Run 1: 88.5 mg VCP, 55 μL TBVE, 12.0 mg **1**, 4 mL THF

Product: 78:22 *trans*/*cis*, 75% ee *trans*, 51% ee *cis*

Run 2: 88.6 mg VCP, 55 μL TBVE, 11.9 mg **1**, 4 mL THF

Product: 78:22 *trans*/*cis*, 75% ee *trans*, 50% ee *cis*

Run 1			**Run 2**		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	10844	0.05000	0.2	11180	0.05155
5.0	10472	0.04828	5.1	10967	0.05057
9.8	10684	0.04853	10.4	10202	0.05003
14.9	10418	0.04804	15.1	10697	0.04932
20.0	9924	0.04576	19.9	10477	0.04830
25.2	9495	0.04313	25.0	9933	0.04580
29.8	8926	0.04115	30.1	9341	0.04307
35.0	8450	0.03896	35.2	8803	0.04059
39.9	7730	0.03564	40.0	8199	0.03780
45.1	7022	0.03238	45.2	7446	0.03433
50.0	6769	0.03075	50.1	6827	0.03148
55.0	5903	0.02722	54.8	6143	0.02832

60.1	5282	0.02435	60.1	5445	0.02511
65.0	4781	0.02204	65.3	4912	0.02265
70.4	4189	0.01932	70.1	4359	0.02010
74.8	3758	0.01733	75.0	3882	0.01790
79.8	3243	0.01495	80.2	3462	0.01596
84.9	2827	0.01303	85.2	3027	0.01395
89.7	2364	0.01090	90.1	2607	0.01202
94.8	2023	0.00933	94.9	2265	0.01044
99.8	1720	0.00793	99.9	1937	0.00893
104.8	1417	0.00653	105.0	1603	0.00739
110.0	1153	0.00531	110.0	1336	0.00616
114.6	922	0.00419	114.8	1081	0.00498
120.0	745	0.00343	120.0	855	0.00394
125.0	589	0.00271	125.2	666	0.00307
130.0	442	0.00204	130.2	515	0.00238
134.9	354	0.00163	135.0	433	0.00188
140.1	249	0.00115	139.9	303	0.00140
145.1	189	0.00087	144.9	235	0.00109
150.0	138	0.00064	150.1	168	0.00078
154.4	107	0.00049	155.1	121	0.00056

Experiment 7

$[VCP]_0$ = 0.05 M, $[TBVE]_0$ = 0.1 M, $[\mathbf{1}]_T$ = 3.0 mM

Run 1: 88.6 mg VCP, 55 µL TBVE, 17.7 mg **1**, 4 mL THF

Product: 78:22 *trans*/*cis*, 75% ee *trans*, 51% ee *cis*

Run 2: 88.5 mg VCP, 55 µL TBVE, 17.9 mg **1**, 4 mL THF

Product: 77:23 *trans*/*cis*, 74% ee *trans*, 50% ee *cis*

Run 1			**Run 2**		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	10916	0.05033	0.2	10967	0.05057
3.8	10790	0.04975	4.6	10585	0.04880
8.3	10649	0.04910	8.9	10567	0.04872
12.6	10620	0.04897	13.3	10373	0.04783
15.8	10240	0.04721	18.0	10009	0.04615

20.1	9924	0.04576	22.6	9575	0.04415
24.2	9547	0.04402	27.1	9002	0.04150
28.2	9181	0.04233	31.9	8602	0.03966
32.0	8716	0.04019	35.9	7827	0.03609
36.2	8164	0.03764	40.4	7244	0.03340
39.9	7855	0.03622	45.0	6697	0.03088
43.9	7163	0.03303	49.5	5977	0.02756
47.6	6578	0.03033	54.0	5391	0.02486
52.1	6250	0.02882	58.5	4910	0.02264
55.9	5720	0.02638	62.9	4349	0.02005
59.9	5343	0.02464	67.7	3777	0.01741
64.2	4582	0.02113	72.0	3305	0.01524
68.0	4351	0.02006	76.3	2926	0.01349
71.8	3958	0.01825	80.8	2534	0.01168
75.8	3541	0.01633	85.6	2124	0.00979
79.9	3204	0.01477	89.8	1775	0.00818
84.5	2670	0.01231	94.4	1486	0.00685
88.0	2463	0.01136	98.7	1226	0.00565
91.9	2165	0.00998	103.4	976	0.00450
96.2	1812	0.00835	108.4	759	0.00350
100.2	1605	0.00740	112.4	604	0.00279
104.1	1353	0.00624	117.0	453	0.00209
108.3	1146	0.00528	121.4	356	0.00164
111.9	969	0.00447	125.9	273	0.00126
116.2	800	0.00369	130.4	202	0.00093
120.1	643	0.00297			
124.3	505	0.00233			
128.1	424	0.00195			
132.1	308	0.00142			
136.0	252	0.00116			
139.9	198	0.00091			

Experiment 8

$[VCP]_0$ = 0.05 M, $[TBVE]_0$ = 0.1 M, $[\mathbf{1}]_T$ = 3.5 mM

Run 1: 88.5 mg VCP, 55 µL TBVE, 20.7 mg **1**, 4 mL THF

Product ee/d.r. not measured for this run

Run 2: 88.6 mg VCP, 55 µL TBVE, 20.9 mg **1**, 4 mL THF

Product: 77:23 *trans*/*cis*, 74% ee *trans*, 51% ee *cis*

Run 1			Run 2		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	11175	0.05152	0.3	10659	0.04914
3.9	10649	0.04910	4.1	10469	0.04827
7.9	10820	0.04989	8.3	10479	0.04831
11.9	10158	0.04684	12.1	10189	0.04698
15.9	10109	0.04661	16.2	10150	0.04680
19.9	9522	0.04390	19.8	9668	0.04457
24.0	9045	0.04171	24.4	9107	0.04199
27.9	8427	0.03885	28.3	8576	0.03954
32.5	7714	0.03557	31.9	7971	0.03675
36.2	7056	0.03253	36.0	7397	0.03411
40.0	6583	0.03035	40.1	6863	0.03164
44.1	5985	0.02760	44.7	6083	0.02805
48.1	5368	0.02475	47.9	5680	0.02619
52.2	4940	0.02278	52.1	5158	0.02378
55.8	4293	0.01979	56.0	4537	0.02092
59.8	3789	0.01747	60.1	3994	0.01841
64.0	3396	0.01566	64.0	3515	0.01621
68.3	2909	0.01341	68.1	3046	0.01404
72.0	2578	0.01189	72.3	2614	0.01205
75.6	2264	0.01044	76.2	2276	0.01049
80.0	1901	0.00876	80.3	1895	0.00874
83.9	1630	0.00751	83.9	1632	0.00752
87.9	1348	0.00622	88.4	1311	0.00605
92.3	1126	0.00519	92.0	1102	0.00508
95.8	950	0.00438	96.1	890	0.00410
100.3	782	0.00360	100.1	720	0.00332
104.1	644	0.00297	104.2	555	0.00256
108.1	506	0.00233	108.0	444	0.00205
111.9	416	0.00192	112.0	341	0.00157

116.1	316	0.00146	116.0	259	0.00119
120.0	255	0.00117	120.1	192	0.00088
123.8	199	0.00092	124.1	148	0.00068
127.8	149	0.00069	128.1	103	0.00048
			132.1	73	0.00034
			136.6	59	0.00027

Experiment 9

$[VCP]_0$ = 0.05 M, $[TBVE]_0$ = 0.1 M, $[\mathbf{1}]_T$ = 4.19 mM

Run 1: 88.5 mg VCP, 55 μL TBVE, 24.9 mg **1**, 4 mL THF

Product: 77:23 *trans*/*cis*, 75% ee *trans*, 51% ee *cis*

Run 2: 88.5 mg VCP, 55 μL TBVE, 24.8 mg **1**, 4 mL THF

Product: 78:22 *trans*/*cis*, 74% ee *trans*, 50% ee *cis*

Run 1			**Run 2**		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	10902	0.05027	0.2	11067	0.05103
3.4	10507	0.04844	3.7	10772	0.04967
7.2	10814	0.04986	7.1	10689	0.04928
10.8	10348	0.04771	10.6	10383	0.04787
14.4	10085	0.04650	14.0	10132	0.04672
17.6	9911	0.04570	17.7	9695	0.04470
21.2	9182	0.04234	21.1	9371	0.04321
24.6	9028	0.04163	24.7	9193	0.04239
27.9	8481	0.03910	28.1	8585	0.03958
31.5	7754	0.03575	31.7	8086	0.03728
35.2	7380	0.03403	35.1	7675	0.03539
38.5	6888	0.03176	39.1	6825	0.03147
42.1	6504	0.02999	42.5	5995	0.02764
45.7	6102	0.02813	45.6	5957	0.02747
49.0	5500	0.02536	49.1	5597	0.02581
52.5	5343	0.02464	52.7	5141	0.02370
56.7	4784	0.02206	56.1	4728	0.02180
60.0	4238	0.01954	59.7	4101	0.01891
63.1	4139	0.01908	63.3	3959	0.01826

66.6	3782	0.01744	66.9	3623	0.01671
70.1	3336	0.01538	70.0	3312	0.01527
73.9	3059	0.01410	73.7	3027	0.01396
77.3	2755	0.01270	77.0	2764	0.01274
80.8	2487	0.01147	80.6	2462	0.01135
84.4	2227	0.01027	84.9	2135	0.00985
87.5	1954	0.00901	87.9	1915	0.00883
91.2	1731	0.00798	91.2	1722	0.00794
94.5	1572	0.00725	94.4	1520	0.00701
98.0	1329	0.00613	98.1	1339	0.00617
101.5	1152	0.00531	101.6	1172	0.00540
105.1	964	0.00445	105.1	1026	0.00473
108.3	844	0.00389	108.7	846	0.00390
112.3	689	0.00318	112.2	751	0.00346
115.5	548	0.00253	115.4	644	0.00297
118.9	470	0.00217	119.4	521	0.00240
122.3	372	0.00172	122.6	438	0.00202
			126.6	338	0.00156
			129.7	290	0.00134

Experiment 10

$[VCP]_0$ = 0.05 M, $[TBVE]_0$ = 0.1 M, $[\mathbf{1}]_T$ = 4.85 mM

Run 1: 88.4 mg VCP, 55 µL TBVE, 28.7 mg **1**, 4 mL THF

Product: 78:22 *trans*/*cis*, 73% ee *trans*, 49% ee *cis*

Run 2: 88.5 mg VCP, 55 µL TBVE, 28.7 mg **1**, 4 mL THF

Product: 77:23 *trans*/*cis*, 74% ee *trans*, 50% ee *cis*

Run 1			**Run 2**		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.4	11124	0.05129	0.2	10586	0.04881
4.3	10765	0.04890	4.8	10512	0.04847
7.9	10564	0.04871	9.1	10464	0.04825
11.9	10524	0.04852	13.6	10165	0.04687
16.0	10130	0.04671	18.0	9823	0.04529
19.9	9993	0.04608	22.5	9523	0.04391

23.9	9506	0.04383	27.0	8975	0.04138
28.0	9023	0.04160	31.7	8304	0.03829
32.0	8411	0.03878	35.9	7736	0.03567
36.1	7948	0.03665	40.6	7069	0.03259
40.0	7479	0.03448	45.1	6438	0.02968
44.2	6812	0.03094	49.8	5677	0.02618
47.8	6099	0.02812	54.2	5064	0.02335
52.0	5731	0.02642	58.5	4508	0.02078
56.2	5195	0.02395	63.1	3962	0.01827
60.1	4799	0.02213	67.7	3342	0.01541
63.9	4251	0.01960	72.0	2964	0.01367
68.2	3978	0.01807	76.6	2439	0.01125
72.0	3443	0.01587	80.8	2046	0.00944
76.3	3054	0.01408	85.6	1668	0.00769
80.1	2737	0.01262	89.8	1354	0.00624
84.0	2309	0.01065	94.6	1070	0.00493
88.0	2092	0.00965	99.1	861	0.00397
92.2	1820	0.00827	103.7	645	0.00297
96.0	1526	0.00703	108.1	515	0.00237
100.2	1252	0.00577	112.5	399	0.00184
104.0	1073	0.00495	117.3	290	0.00134
107.9	905	0.00417	121.6	217	0.00100
111.8	738	0.00340	126.4	161	0.00074
116.1	615	0.00279	130.6	117	0.00054
120.1	478	0.00220	135.2	82	0.00038
123.9	368	0.00170	140.2	59	0.00027
127.9	296	0.00136	143.8	0	0.00000
132.3	221	0.00102			
135.9	169	0.00077			
140.2	129	0.00059			
145.2	89	0.00041			

Experiment 11

$[VCP]_0$ = 0.035 M, $[TBVE]_0$ = 0.085 M, $[\mathbf{1}]_T$ = 2.5 mM

Run 1: 61.9 mg VCP, 47 µL TBVE, 15.0 mg **1**, 4 mL THF

Product: 78:22 *trans*/*cis*, 75% ee *trans*, 50% ee *cis*

Run 2: 61.8 mg VCP, 47 µL TBVE, 15.0 mg **1**, 4 mL THF

Product: 78:22 *trans*/*cis*, 74% ee *trans*, 50% ee *cis*

Run 1			Run 2		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	7954	0.00122	0.2	7648	0.00118
3.3	8008	0.00123	3.2	7705	0.00119
6.5	8009	0.00123	6.9	8209	0.00126
9.8	7476	0.00115	10.3	7513	0.00116
12.9	7215	0.00111	13.4	7614	0.00117
16.3	7166	0.00110	16.3	7349	0.00113
19.5	6981	0.00107	20.0	7094	0.00109
22.7	6585	0.00101	23.1	6609	0.00102
25.9	6457	0.00099	26.4	6558	0.00101
29.3	5915	0.00091	29.3	6350	0.00098
32.8	5888	0.00091	32.4	5928	0.00091
35.8	5429	0.00084	35.7	5703	0.00088
39.2	5143	0.00079	39.2	5505	0.00085
42.5	4917	0.00076	42.2	5009	0.00077
45.5	4683	0.00072	45.4	4842	0.00075
48.7	4336	0.00067	48.6	4597	0.00071
52.1	4016	0.00062	51.9	4151	0.00064
55.4	3777	0.00058	55.2	4030	0.00062
58.5	3514	0.00054	58.6	3675	0.00057
61.7	3239	0.00050	61.7	3562	0.00055
65.1	3095	0.00048	64.8	3323	0.00051
68.1	2665	0.00041	68.3	2978	0.00046
71.4	2667	0.00041	71.3	2880	0.00044
74.7	2427	0.00037	74.6	2710	0.00042
78.0	2261	0.00035	77.8	2406	0.00037
81.4	2085	0.00032	81.9	2313	0.00036
84.5	1899	0.00029	84.7	2084	0.00032
87.8	1743	0.00027	87.7	1969	0.00030
90.8	1564	0.00024	90.9	1799	0.00028

94.1	1458	0.00022	94.6	1640	0.00025
97.6	1273	0.00020	97.9	1454	0.00022
101.0	1163	0.00018	100.9	1350	0.00021
104.0	1056	0.00016	103.9	1244	0.00019
107.5	884	0.00014	107.6	987	0.00015
111.2	827	0.00013	110.9	936	0.00014
114.0	697	0.00011	114.2	817	0.00013
117.1	593	0.00009	117.3	680	0.00010
120.2	529	0.00008	120.3	611	0.00009
123.6	452	0.00007	123.3	525	0.00008
126.6	370	0.00006	126.4	430	0.00007

Experiment 12

$[VCP]_0$ = 0.035 M, $[TBVE]_0$ = 0.085 M, $[\mathbf{1}]_T$ = 2.5 mM, $[P]_0$ = 0.015 M

Product additive: 74:26 *trans*/*cis*, 76% ee *trans*, 55% ee *cis*

Run 1: 61.9 mg VCP, 47 μL TBVE, 14.9 mg **1**, 32.7 mg P, 4 mL THF

Product: 78:22 *trans*/*cis*, 73% ee *trans*, 47% ee *cis*

Run 2: 62.0 mg VCP, 47 μL TBVE, 14.8 mg **1**, 32.5 mg P, 4 mL THF

Product: 77:23 *trans*/*cis*, 74% ee *trans*, 50% ee *cis*

Run 1			Run 2		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	7723	0.03561	0.2	7573	0.03491
4.6	7539	0.03476	4.4	7598	0.03503
9.6	7482	0.03450	9.0	7441	0.03431
13.5	7160	0.03301	13.4	7359	0.03393
18.1	7227	0.03332	18.1	7404	0.03414
22.7	6893	0.03178	22.6	7090	0.03269
27.2	6603	0.03044	26.9	6909	0.03185
31.5	6412	0.02956	31.6	6642	0.03062
36.1	6142	0.02832	36.0	6279	0.02895
40.5	5679	0.02619	40.3	6039	0.02785
45.3	5422	0.02500	45.1	5674	0.02616

50.6	4767	0.02198	49.5	5152	0.02375
54.2	4575	0.02109	54.0	4878	0.02249
58.7	4206	0.01939	58.5	4463	0.02058
63.2	4058	0.01871	63.4	4152	0.01914
68.0	3581	0.01651	67.4	3767	0.01737
72.1	3151	0.01453	72.1	3585	0.01653
76.6	2944	0.01358	76.7	3172	0.01462
81.2	2559	0.01180	81.6	2884	0.01330
85.7	2347	0.01082	85.8	2653	0.01223
89.9	2051	0.00946	89.8	2357	0.01087
94.5	1823	0.00841	95.0	2123	0.00979
99.0	1563	0.00721	98.7	1920	0.00885
103.7	1369	0.00631	103.8	1742	0.00803
108.2	1139	0.00525	108.2	1561	0.00709
112.7	976	0.00450	112.6	1397	0.00644
117.3	790	0.00364	117.0	1200	0.00553
121.6	673	0.00310	121.4	1090	0.00503
126.3	535	0.00247	126.2	912	0.00420
130.4	431	0.00199	130.9	812	0.00374
135.1	345	0.00159	135.0	682	0.00315
139.3	263	0.00121	139.6	597	0.00275
144.0	210	0.00097	144.1	488	0.00225
			148.6	411	0.00190

Experiment 13

$[VCP]_0$ = 0.05 M, $[TBVE]_0$ = 0.1 M, $[(n\text{BuS})_2]_T$ = 2.5 mM

Run 1: 66.3 mg VCP, 41 µL TBVE, 1.5 µL $(n\text{BuS})_2$, 3 mL THF

Product: 76:24 *trans*/*cis*, racemic

Run 2: 66.5 mg VCP, 41 µL TBVE, 1.5 mg $(n\text{BuS})_2$, 3 mL THF

Product: 76:24 *trans*/*cis*, racemic

Run 1			Run 2		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	10449	0.04818	0.2	10757	0.04960
3.6	10145	0.04678	5.0	10154	0.04682
7.0	9636	0.04443	8.3	9697	0.04471
10.3	9071	0.04183	12.2	8802	0.04058
14.0	8117	0.03742	15.9	7950	0.03665
17.4	7343	0.03386	20.0	6842	0.03154
21.0	6419	0.02960	24.0	5862	0.02703
24.5	5594	0.02579	28.2	5009	0.02309
27.9	4813	0.02219	32.0	4114	0.01897
31.6	4000	0.01844	36.1	3306	0.01524
34.8	3336	0.01538	39.9	2680	0.01236
38.8	2628	0.01212	44.3	1960	0.00904
42.1	2113	0.00974	48.1	1487	0.00685
45.5	1619	0.00747	52.2	1030	0.00475
48.9	1197	0.00552	56.1	684	0.00315
52.5	865	0.00399	59.9	442	0.00204
56.1	578	0.00266	63.9	275	0.00127
59.6	365	0.00168	67.7	165	0.00076
63.1	224	0.00103	72.1	79	0.00036
66.5	127	0.00059	75.5	56	0.00026

Experiment 14

$[VCP]_0$ = 0.05 M, $[TBVE]_0$ = 0.2 M, $[(n\text{BuS})_2]_T$ = 2.5 mM

Run 1: 66.4 mg VCP, 83 µL TBVE, 1.5 µL $(n\text{BuS})_2$, 3 mL THF

Product: 76:24 *trans*/*cis*, racemic

Run 2: 66.3 mg VCP, 83 µL TBVE, 1.5 µL $(n\text{BuS})_2$, 3 mL THF

Product: 76:24 *trans*/*cis*, racemic

Run 1			Run 2		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	10811	0.04984	0.4	10659	0.04914
3.2	10524	0.04852	3.5	10722	0.04944
7.0	10162	0.04685	7.0	10206	0.04706
10.4	9588	0.04421	10.9	9663	0.04455
14.0	8640	0.03983	13.9	9088	0.04190
17.5	7338	0.03383	17.5	7888	0.03637
21.1	5864	0.02704	20.9	6806	0.03138
24.5	4679	0.02157	24.6	5775	0.02663
28.0	3513	0.01620	27.9	4691	0.02163
31.6	2591	0.01194	31.7	3658	0.01686
34.9	1845	0.00850	35.1	2856	0.01317
38.5	1186	0.00547	38.6	2070	0.00955
42.1	783	0.00361	42.2	1526	0.00704
45.8	459	0.00212	45.4	1137	0.00524
50.3	242	0.00112	48.7	776	0.00358
53.6	156	0.00072	52.2	514	0.00237
57.7	90	0.00042	56.0	332	0.00153
60.5	53	0.00024	59.9	204	0.00094
64.4	0	0.00000	62.9	137	0.00063
			65.1	106	0.00049

Experiment 15

$[VCP]_0$ = 0.05 M, $[TBVE]_0$ = 0.1 M, $[(n\text{BuS})_2]_T$ = 4.0 mM

Run 1: 66.4 mg VCP, 41 µL TBVE, 2.25 µL $(n\text{BuS})_2$, 3 mL THF

Product: 76:24 *trans*/*cis*, racemic

Run 2: 66.5 mg VCP, 41 µL TBVE, 2.25 µL $(n\text{BuS})_2$, 3 mL THF

Product: 76:24 *trans*/*cis*, racemic

Run 1			Run 2		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	10869	0.05011	0.2	10803	0.04981
2.6	10580	0.04878	3.0	10314	0.04756
5.5	9970	0.04597	5.8	9655	0.04452
8.3	9274	0.04276	9.0	8792	0.04054
10.8	8270	0.03813	12.2	7410	0.03416
13.4	7303	0.03367	15.4	6232	0.02873
16.4	6220	0.02868	18.0	5314	0.02450
19.4	5222	0.02408	21.1	4384	0.02021
22.8	4062	0.01873	24.0	3518	0.01622
25.5	3401	0.01568	27.1	2681	0.01236
28.5	2652	0.01223	29.8	2054	0.00947
31.3	1997	0.00921	33.0	1393	0.00642
33.9	1496	0.00690	36.0	955	0.00440
36.3	1127	0.00520	38.9	618	0.00285
39.5	724	0.00334	42.4	330	0.00152
42.1	491	0.00226	45.4	184	0.00085
44.5	309	0.00142	48.2	101	0.00047
47.3	188	0.00086	50.9	53	0.00024
50.1	101	0.00047	54.3	0	0.00000
53.0	56	0.00026			

Experiment 16

$[VCP]_0$ = 0.035 M, $[TBVE]_0$ = 0.085 M, $[(n\text{BuS})_2]_T$ = 2.5 mM

Run 1: 46.4 mg VCP, 35 μL TBVE, 1.5 μL $(n\text{BuS})_2$, 3 mL THF

Product: 76:24 *trans*/*cis*, racemic

Run 2: 46.5 mg VCP, 35 μL TBVE, 1.5 μL $(n\text{BuS})_2$, 3 mL THF

Product: 76:24 *trans*/*cis*, racemic

Run 1			Run 2		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	7710	0.03555	0.2	7684	0.03543
3.3	7437	0.03429	3.0	7662	0.03533
5.7	7010	0.03232	6.0	7193	0.03316
9.0	6720	0.03098	9.0	6788	0.03130
12.0	6081	0.02804	12.0	6230	0.02872
15.1	5282	0.02435	14.9	5552	0.02560
18.3	4606	0.02124	18.1	4957	0.02285
20.9	4132	0.01905	21.0	4334	0.01998
24.0	3452	0.01591	24.1	3693	0.01703
27.3	2831	0.01305	27.2	3053	0.01408
30.4	2324	0.01072	30.0	2535	0.01169
33.6	1791	0.00826	34.0	2048	0.00944
36.2	1484	0.00684	36.1	1634	0.00753
39.2	1113	0.00513	39.0	1256	0.00579
42.6	777	0.00358	42.0	929	0.00428
45.3	578	0.00266	45.2	646	0.00298
48.3	384	0.00177	48.1	440	0.00203
51.0	257	0.00119	51.2	283	0.00131
54.0	170	0.00078	53.9	187	0.00086

Experiment 17

$[(R)\text{-VCP}]_0 = 0.05$ M, $[\text{TBVE}]_0 = 0.1$ M, $[\mathbf{1}]_T = 2.5$ mM

Run 1: 66.5 mg VCP, 41 µL TBVE, 11.2 mg, **1**, 3 mL THF

Product: 78:22 *trans*/*cis*, 75% ee *trans*, 57% ee *cis*

Run 2: 66.5 mg VCP, 41 µL TBVE, 11.0 mg **1**, 3 mL THF

Product: 78:22 *trans*/*cis*, 76% ee *trans*, 55% ee *cis*

Run 1			Run 2		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	10833	0.04995	0.2	10449	0.04818
5.1	10504	0.04843	4.1	10375	0.04783
10.1	10285	0.04742	8.1	10050	0.04634
14.9	9609	0.04430	12.1	9748	0.04494
20.1	8881	0.04095	15.8	9351	0.04311
25.0	7780	0.03587	20.0	8672	0.03998
29.9	6683	0.03081	24.0	7949	0.03665
35.0	5744	0.02649	28.1	7293	0.03363
40.0	4729	0.02180	31.9	6302	0.02906
44.9	3746	0.01727	36.1	5504	0.02538
49.8	2977	0.01372	40.0	4671	0.02154
55.0	2205	0.01017	43.8	4003	0.01846
60.1	1617	0.00746	47.6	3338	0.01539
65.3	1097	0.00506	51.8	2681	0.01236
69.9	757	0.00349	56.1	2028	0.00935
75.0	478	0.00221	60.0	1587	0.00732
79.8	288	0.00133	64.0	1131	0.00521
84.9	164	0.00075	68.1	804	0.00371
90.1	89	0.00041	72.1	553	0.00255
94.9	52	0.00024	76.1	363	0.00167
99.8	0	0.00000	80.1	227	0.00105
			84.0	141	0.00065
			88.2	86	0.00040
			92.1	50	0.00023
			96.1	0	0.00000

Experiment 18

$[(R)\text{-VCP}]_0 = 0.05$ M, $[\text{TBVE}]_0 = 0.2$ M, $[\mathbf{1}]_T = 2.5$ mM

Run 1: 66.5 mg VCP, 83 μL TBVE, 11.0 mg, **1**, 3 mL THF

Product: 76:24 *trans*/*cis*, 75% ee *trans*, 55% ee *cis*

Run 2: 66.5 mg VCP, 83 μL TBVE, 11.0 mg **1**, 3 mL THF

Product: 78:22 *trans*/*cis*, 76% ee *trans*, 56% ee *cis*

Run 1			Run 2		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	10678	0.04923	0.2	10834	0.04995
4.0	10565	0.04871	3.7	10630	0.04901
8.0	10304	0.04751	7.8	10471	0.04828
12.1	10175	0.04691	11.9	10284	0.04741
16.0	10034	0.04626	15.8	9977	0.04600
20.2	9426	0.04346	20.0	9265	0.04272
24.3	8959	0.04131	24.1	8706	0.04014
28.2	8513	0.03925	27.9	8020	0.03698
32.1	7601	0.03505	32.2	7126	0.03286
37.0	6656	0.03069	36.0	6191	0.02854
40.3	6007	0.02770	39.7	5421	0.02499
44.1	5003	0.02307	44.1	4240	0.01955
47.9	4304	0.01984	48.0	3466	0.01598
52.1	3467	0.01598	52.0	2703	0.01246
56.5	2629	0.01212	55.9	2029	0.00936
60.0	2111	0.00973	60.0	1489	0.00686
64.2	1534	0.00707	63.9	1075	0.00496
68.4	1094	0.00505	67.9	728	0.00336
71.7	799	0.00368	72.2	475	0.00219
75.8	551	0.00254	76.1	326	0.00150
80.1	342	0.00158	79.8	211	0.00097
84.2	228	0.00105	83.8	135	0.00062
88.2	143	0.00066	88.0	84	0.00039
91.9	92	0.00043	92.1	52	0.00024
96.5	53	0.00025	96.0	0	0.00000
100.2	0	0.00000			

Experiment 19

[(*R*)-VCP]$_0$ = 0.035 M, [TBVE]$_0$ = 0.085 M, [**1**]$_T$ = 2.5 mM

Run 1: 46.4 mg VCP, 35 µL TBVE, 11.1 mg, **1**, 3 mL THF

Product: 77:23 *trans*/*cis*, 75% ee *trans*, 54% ee *cis*

Run 2: 46.3 mg VCP, 35 µL TBVE, 11.1 mg **1**, 3 mL THF

Product: 77:23 *trans*/*cis*, 74% ee *trans*, 55% ee *cis*

Run 1			Run 2		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	7630	0.03518	0.2	7699	0.03550
3.4	7475	0.03446	3.6	7507	0.03461
6.8	7337	0.03383	6.9	7277	0.03355
10.5	7072	0.03261	10.5	7091	0.03270
14.0	6693	0.03086	14.1	6688	0.03083
17.6	6285	0.02898	18.1	6054	0.02791
21.0	5716	0.02635	21.1	5713	0.02634
24.5	5273	0.02431	24.7	5240	0.02416
28.0	4647	0.02143	28.1	4670	0.02153
31.7	4133	0.01906	31.7	4181	0.01928
35.1	3703	0.01707	34.8	3758	0.01733
38.6	3097	0.01428	38.5	3158	0.01456
42.1	2721	0.01255	42.1	2826	0.01303
45.6	2284	0.01053	45.6	2366	0.01091
48.8	1858	0.00857	48.8	1965	0.00906
52.5	1491	0.00687	52.4	1627	0.00750
56.0	1188	0.00548	55.9	1313	0.00605
59.6	893	0.00412	59.4	1036	0.00478
63.0	694	0.00320	63.5	782	0.00360
66.4	518	0.00239	66.5	624	0.00288
69.9	370	0.00171	70.0	454	0.00209
73.4	253	0.00117	73.5	334	0.00154
77.0	174	0.00080	76.9	246	0.00113
80.4	116	0.00053	80.4	171	0.00079
84.1	74	0.00034	84.3	114	0.00053
87.5	56	0.00026	87.4	85	0.00039
91.0	0	0.00000	90.8	54	0.00025

Experiment 20

$[(S)\text{-VCP}]_0 = 0.05$ M, $[\text{TBVE}]_0 = 0.1$ M, $[\mathbf{1}]_T = 2.5$ mM

Run 1: 66.3 mg VCP, 41 μL TBVE, 11.1 mg, **1**, 3 mL THF

Product: 77:23 *trans*/*cis*, 73% ee *trans*, 47% ee *cis*

Run 2: 66.4 mg VCP, 41 μL TBVE, 11.1 mg **1**, 3 mL THF

Product: 77:23 *trans*/*cis*, 71% ee *trans*, 47% ee *cis*

Run 1			Run 2		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	10689	0.04928	0.3	10857	0.05006
3.9	10355	0.04774	3.8	10690	0.04929
8.2	10498	0.04840	8.2	10593	0.04884
12.3	10281	0.04740	12.1	10381	0.04786
16.1	9881	0.04556	16.1	10041	0.04629
20.1	9603	0.04428	19.9	9441	0.04353
24.2	9021	0.04159	24.0	8974	0.04138
29.1	8422	0.03883	28.0	8372	0.03860
34.0	7741	0.03569	31.7	7872	0.03630
38.9	6889	0.03176	36.1	7100	0.03274
43.9	6017	0.02774	40.0	6348	0.02927
49.0	5137	0.02369	44.0	5554	0.02561
54.0	4356	0.02008	47.9	4903	0.02260
58.9	3657	0.01686	51.9	4297	0.01981
64.2	2920	0.01346	55.9	3625	0.01672
69.1	2425	0.01118	60.0	3119	0.01438
74.2	1916	0.00884	64.1	2560	0.01180
78.8	1527	0.00704	67.9	2129	0.00982
84.2	1129	0.00520	72.0	1704	0.00786
89.0	879	0.00405	76.0	1345	0.00620
93.8	644	0.00297	80.3	1020	0.00470
99.1	443	0.00204	84.5	765	0.00353
103.9	313	0.00144	88.1	568	0.00262
109.0	210	0.00097	92.0	421	0.00194
113.9	140	0.00065	95.9	303	0.00139
119.3	90	0.00042	100.1	204	0.00094
124.3	59	0.00027	103.9	146	0.00068
128.9	0	0.00000	108.3	96	0.00044
			111.9	66	0.00031

115.8	0	0.00000

Experiment 21

$[(S)\text{-VCP}]_0$ = 0.05 M, $[\text{TBVE}]_0$ = 0.2 M, $[\mathbf{1}]_T$ = 2.5 mM

Run 1: 66.3 mg VCP, 83 µL TBVE, 11.1 mg, **1**, 3 mL THF

Product: 77:23 *trans*/*cis*, 73% ee *trans*, 46% ee *cis*

Run 2: 66.4 mg VCP, 83 µL TBVE, 11.2 mg **1**, 3 mL THF

Product: 77:23 *trans*/*cis*, 73% ee *trans*, 45% ee *cis*

Run 1			Run 2		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.3	10772	0.04966	0.3	10735	0.04949
4.0	10540	0.04860	4.1	10552	0.04865
8.1	10498	0.04840	8.1	10602	0.04888
12.1	10417	0.04803	12.1	10411	0.04800
15.9	10059	0.04638	16.2	10258	0.04730
20.0	9755	0.04498	20.1	10041	0.04561
24.0	9369	0.04320	24.3	9578	0.04416
28.1	9032	0.04164	27.9	8965	0.04133
32.1	8197	0.03779	32.1	8585	0.03958
36.4	7498	0.03457	36.1	7952	0.03666
39.9	6938	0.03199	39.8	7298	0.03365
43.9	6002	0.02767	44.2	6544	0.03017
48.2	5223	0.02408	47.9	6003	0.02768
52.9	4346	0.02004	52.9	4996	0.02303
56.0	3874	0.01786	56.8	4312	0.01988
60.2	3223	0.01486	59.9	3857	0.01778
64.1	2611	0.01204	63.6	3204	0.01477
68.1	2121	0.00978	67.9	2610	0.01203
72.0	1738	0.00801	71.6	2168	0.01000
76.0	1351	0.00623	76.0	1620	0.00747
80.0	1034	0.00477	79.9	1324	0.00610
84.0	774	0.00357	84.0	1006	0.00464
87.8	599	0.00276	87.8	775	0.00357

92.0	428	0.00197	91.7	584	0.00269
95.8	309	0.00142	96.1	411	0.00189
100.1	217	0.00100	99.8	314	0.00145
104.2	149	0.00069	104.2	216	0.00010
108.0	108	0.00050	107.9	152	0.00007
111.9	77	0.00035	112.2	108	0.00005
115.9	52	0.00024	115.8	74	0.00003
120.3	0	0.00000	120.3	51	0.00002
			124.1	51	0.00023

Experiment 22

[(*S*)-VCP]$_0$ = 0.035 M, [TBVE]$_0$ = 0.085 M, [**1**]$_T$ = 2.5 mM

Run 1: 46.5 mg VCP, 35 µL TBVE, 11.0 mg, **1**, 3 mL THF

Product: 77:23 *trans*/*cis*, 73% ee *trans*, 45% ee *cis*

Run 2: 46.5 mg VCP, 35 µL TBVE, 11.1 mg **1**, 3 mL THF

Product: 77:23 *trans*/*cis*, 74% ee *trans*, 45% ee *cis*

Run 1			Run 2		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	7507	0.03461	0.2	7721	0.03560
4.1	7216	0.03327	4.0	7431	0.03426
8.1	7153	0.03298	8.1	7357	0.03392
12.3	6993	0.03224	12.1	7151	0.03297
16.2	6503	0.02998	16.2	6954	0.03206
20.1	6345	0.02925	20.2	6553	0.03021
24.3	5929	0.02734	23.7	6012	0.02772
27.9	5434	0.02505	28.1	5524	0.02547
32.1	5030	0.02319	32.0	5258	0.02424
36.0	4577	0.02110	36.1	4550	0.02098
39.9	3959	0.01825	40.0	4003	0.01846
43.9	3619	0.01669	43.9	3499	0.01613
47.8	3239	0.01493	47.9	3009	0.01387
52.0	2756	0.01271	52.0	2569	0.01185
56.0	2407	0.01110	56.2	2085	0.00961
60.1	2037	0.00939	60.1	1743	0.00804

63.8	1704	0.00786	63.7	1420	0.00655
68.3	1421	0.00655	67.9	1102	0.00508
72.1	1159	0.00534	72.2	853	0.00393
75.9	906	0.00418	76.0	656	0.00302
79.9	728	0.00336	80.0	486	0.00224
84.2	556	0.00256	84.5	337	0.00156
88.0	429	0.00198	87.8	264	0.00122
91.9	322	0.00149	91.7	184	0.00085
96.4	213	0.00098	95.6	135	0.00062
100.1	160	0.00074	99.8	96	0.00044
104.2	106	0.00049	103.7	63	0.00029
107.9	82	0.00038	107.8	0	0.00000
111.7	56	0.00026			
115.8	0	0.00000			

Experiment 23

$[VCP]_0$ = 0.05 M VCP, $[TBVE]_0$ = 0.1 M TBVE, $[\mathbf{2}]_T$ = 2.5 mM

Run 1: 66.4 mg VCP, 41 µL TBVE, 7.8 mg **2**, 3 mL THF

Product: 71:29 *trans*/*cis*, 12% ee *trans*, 1% ee *cis*

Run 2: 66.3 mg VCP, 41 µL TBVE, 7.7 mg **2**, 4 mL THF

Product: 71:29 *trans*/*cis*, 13% ee *trans*, 4% ee *cis*

Run 1			**Run 2**		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	10894	0.05023	0.2	10392	0.04791
6.4	10746	0.04955	9.0	10096	0.04655
12.0	10663	0.04916	17.0	9726	0.04484
18.0	10364	0.04779	25.7	9168	0.04227
24.1	10126	0.04669	34.7	8630	0.03979
30.1	9823	0.04529	42.6	7936	0.03659
36.0	9345	0.04309	50.7	7291	0.03362
42.0	9018	0.04158	59.3	6650	0.03066
47.9	8495	0.03917	67.7	6122	0.02823
53.7	8083	0.03727	76.2	5641	0.02601
0.0	7676	0.03539	85.1	5120	0.02361

66.3	7125	0.03285
71.6	6863	0.03164
77.8	6477	0.02986
84.0	6016	0.02774
89.9	5891	0.02716
95.9	5483	0.02528
102.1	5145	0.02372
108.0	4836	0.02230
114.2	4564	0.02104
119.8	4217	0.01944
126.0	3833	0.01767
131.8	3613	0.01666
136.5	3407	0.01571
142.1	3140	0.01448
148.7	3033	0.01398
155.7	2770	0.01277
162.0	2553	0.01177
167.8	2399	0.01106
173.9	2165	0.00998
180.1	1948	0.00898
185.9	1739	0.00802
192.0	1513	0.00697
197.8	1300	0.00599
203.8	1136	0.00524
209.8	954	0.00440
216.0	782	0.00361
222.7	617	0.00285
230.0	443	0.00204
237.1	328	0.00151
244.9	229	0.00105
252.8	142	0.00065
260.9	88	0.00041
269.0	0	0.00000
93.4	4666	0.02151
101.6	4383	0.02021
110.3	4144	0.01910
119.0	3756	0.01732
127.4	3506	0.01616
136.0	3290	0.01517
144.5	3152	0.01453
152.6	2977	0.01372
161.3	2735	0.01261
169.7	2400	0.01107
178.5	1973	0.00910
186.7	1656	0.00764
195.3	1250	0.00576
203.9	932	0.00429
212.8	657	0.00303
220.6	446	0.00206
229.0	295	0.00136
237.6	181	0.00084
246.4	98	0.00045
254.8	52	0.00024
263.4	0	0.00000

Experiment 24

$[VCP]_0$ = 0.05 M VCP, $[TBVE]_0$ = 0.2 M TBVE, $[\mathbf{2}]_T$ = 2.5 mM

Run 1: 66.4 mg VCP, 83 µL TBVE, 7.9 mg **2**, 3 mL THF

Product: 70:30 *trans*/*cis*, 11% ee *trans*, 3% ee *cis*

Run 2: 66.3 mg VCP, 83 µL TBVE, 7.9 mg **2**, 4 mL THF

Product: 70:30 *trans*/*cis*, 13% ee *trans*, 3% ee *cis*

Run 1			Run 2		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	10773	0.04967	0.2	10971	0.05059
8.7	10597	0.04886	8.7	10730	0.04947
17.0	10348	0.04771	17.2	10389	0.04790
25.5	10167	0.04688	25.3	10246	0.04724
33.8	9932	0.04579	33.9	9805	0.04521
42.5	9441	0.04353	42.8	9278	0.04278
50.9	8785	0.04050	50.7	8726	0.04024
59.9	8171	0.03768	59.6	8040	0.03707
68.1	7493	0.03455	68.1	7237	0.03337
77.3	6789	0.03130	76.6	6858	0.03162
85.0	6597	0.03042	85.2	6486	0.02991
93.9	6328	0.02918	93.3	6114	0.02819
102.2	6189	0.02854	102.0	6182	0.02850
111.0	6045	0.02787	110.9	5960	0.02748
119.0	5661	0.02610	118.8	5455	0.02515
127.5	5109	0.02355	127.4	5119	0.02360
136.4	4342	0.02002	136.1	4455	0.02054
144.6	3505	0.01616	144.6	3678	0.01696
153.1	2715	0.01252	153.2	3053	0.01408
161.6	2045	0.00943	161.5	2434	0.01122
169.8	1507	0.00695	170.3	1780	0.00821
178.6	997	0.00460	178.8	1268	0.00585
186.7	673	0.00310	186.9	912	0.00421
195.5	402	0.00185	196.3	566	0.00261
203.9	250	0.00115	204.4	356	0.00164
212.5	137	0.00063	212.6	230	0.00106
221.1	70	0.00032	221.1	122	0.00056
229.6	0	0.00000	229.0	87	0.00040

Experiment 25

$[VCP]_0$ = 0.035 M VCP, $[TBVE]_0$ = 0.085 M TBVE, $[\mathbf{2}]_T$ = 2.5 mM

Run 1: 46.4 mg VCP, 35 µL TBVE, 7.9 mg **2**, 3 mL THF

Product: 70:30 *trans*/*cis*, 13% ee *trans*, 3% ee *cis*

Run 2: 46.3 mg VCP, 35 µL TBVE, 7.8 mg **2**, 4 mL THF

Product: 70:30 *trans*/*cis*, 13% ee *trans*, 4% ee *cis*

Run 1			Run 2		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	7804	0.03598	0.2	7719	0.03559
9.0	7596	0.03502	8.6	7579	0.03494
18.4	7426	0.03424	17.1	7429	0.03425
27.6	7120	0.03283	25.4	7202	0.03320
37.9	6782	0.03127	34.0	7081	0.03265
47.7	6345	0.02925	43.2	6589	0.03038
56.8	5732	0.02643	51.5	6299	0.02904
66.4	5476	0.02525	59.4	6008	0.02770
75.8	4993	0.02302	68.3	5521	0.02546
85.6	4398	0.02028	76.7	5070	0.02338
94.6	3762	0.01734	85.6	4447	0.02050
104.4	3051	0.01407	93.3	3677	0.01696
113.8	2452	0.01131	102.4	3020	0.01392
123.5	1898	0.00875	110.4	2408	0.01110
133.1	1380	0.00636	119.1	1761	0.00812
142.4	976	0.00450	127.8	1274	0.00587
152.2	622	0.00287	136.0	872	0.00402
161.5	383	0.00177	144.1	573	0.00264
170.9	213	0.00098	153.1	336	0.00155
180.4	112	0.00051	161.3	196	0.00090
190.0	54	0.00025	170.3	93	0.00043
199.3	0	0.00000	178.5	0	0.00000

Experiment 26

[(*R*)-VCP]$_0$ = 0.05 M VCP, [TBVE]$_0$ = 0.1 M TBVE, [**2**]$_T$ = 2.5 mM

Run 1: 66.5 mg VCP, 41 µL TBVE, 7.9 mg **2**, 3 mL THF

Product: 70:30 *trans*/*cis*, 14% ee *trans*, 3% ee *cis*

Run 2: 66.5 mg VCP, 41 µL TBVE, 7.8 mg **2**, 4 mL THF

Product: 71:29 *trans*/*cis*, 13% ee *trans*, 1% ee *cis*

Run 1			Run 2		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	10948	0.05048	0.2	10939	0.05044
8.6	10689	0.04928	5.2	10910	0.05030
16.2	10190	0.04698	10.0	10685	0.04926
25.7	9638	0.04444	15.0	10582	0.04879
33.1	8646	0.03987	20.1	10352	0.04773
43.0	7422	0.03422	24.8	10030	0.04624
51.4	6175	0.02847	29.9	9439	0.04352
60.6	4878	0.02249	35.1	9064	0.04179
67.0	3732	0.01721	40.7	8012	0.03694
76.9	2613	0.01205	45.5	7353	0.03390
84.0	1770	0.00816	50.2	6542	0.03016
93.9	1034	0.00477	54.9	5682	0.02620
102.8	534	0.00246	59.8	4784	0.02206
110.4	257	0.00118	65.0	3979	0.01835
119.9	111	0.00051	69.8	3217	0.01483
127.8	56	0.00026	74.9	2499	0.01152
135.0	0	0.00000	79.9	1895	0.00874
			85.0	1341	0.00618
			90.2	896	0.00413
			94.9	601	0.00277
			99.8	378	0.00174
			105.0	229	0.00105
			110.4	122	0.00056
			114.9	82	0.00038
			120.1	54	0.00025
			124.8	0	0.00000

Experiment 27

[(*S*)-VCP]$_0$ = 0.05 M VCP, [TBVE]$_0$ = 0.1 M TBVE, [**2**]$_T$ = 2.5 mM

Run 1: 66.3 mg VCP, 41 µL TBVE, 7.9 mg **2**, 3 mL THF

Product: 70:30 *trans*/*cis*, 13% ee *trans*, 3% ee *cis*

Run 2: 66.3 mg VCP, 41 µL TBVE, 7.7 mg **2**, 4 mL THF

Product: 71:29 *trans*/*cis*, 13% ee *trans*, 1% ee *cis*

Run 1			Run 2		
time (min)	**area (mAU)**	**[VCP] (M)**	**time (min)**	**area (mAU)**	**[VCP] (M)**
0.2	10858	0.05006	0.2	10402	0.04796
8.5	10565	0.04871	5.7	10505	0.04844
16.9	10194	0.04700	11.1	10207	0.04706
25.5	9903	0.04566	16.4	10055	0.04636
34.0	9340	0.04306	22.0	10150	0.04680
42.7	8713	0.04017	27.6	9756	0.04498
51.6	7662	0.03533	33.3	9408	0.04338
59.8	6877	0.03171	38.6	9205	0.04244
68.1	5890	0.02716	44.1	8745	0.04032
76.5	4947	0.02281	49.7	8244	0.03801
85.0	3965	0.01828	55.2	7581	0.03495
93.4	2987	0.01377	61.0	6768	0.03121
102.0	2206	0.01017	66.8	6224	0.02870
111.0	1478	0.00681	71.8	5653	0.02606
118.7	999	0.00461	77.2	4853	0.02237
127.7	580	0.00267	82.7	4165	0.01920
136.1	329	0.00152	88.3	3511	0.01619
144.8	158	0.00073	93.7	2905	0.01340
153.2	79	0.00037	99.2	2313	0.01066
161.6	0	0.00000	104.5	1822	0.00840
			110.0	1345	0.00620
			115.8	966	0.00445
			121.4	660	0.00304
			126.8	438	0.00202
			132.0	280	0.00129
			137.7	176	0.00081
			142.7	108	0.00050
			148.7	60	0.00028
			153.7	0	0.00000