Supporting Information

Controllable Stereoinversion in DNA-catalyzed Olefin Cyclopropanation via Cofactor Modification

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Materials and Methods

Unless otherwise noted, all chemicals and reagents for chemical reactions were obtained from commercial suppliers (Sigma-Aldrich, Acros, TCI, Frontier scientific) and used without further purification. The DNA sequences were all purchased from Sangon (Shanghai, China). The DNA strand concentrations were determined by measuring the UV absorbance of sample at 260 nm by using the molar extinction coefficient values provided by the manufacturer. Water purified on a Milli-Q A10 water purification system (specific resistance of 18.2 MΩ at 25 °C) was used for all experiments.

High Performance Liquid Chromatography (HPLC). The enantioselectivity was determined by Agilent HPLC 1260 analysis using Daicel chiralcel OJH column and Daicel CHIRALPAK-IJ column with a UV-detector by using ethanol, isopropanol and n-hexane as eluents at 25 °C.

Circular Dichroism (CD) Spectroscopy. All CD spectra were recorded on a dual beam DSM 1000 CD spectrophotometer (Olis, Bogart, GA) with a 10 mm or 1.5 mm path-length quartz cell. Each measurement was recorded from 220 to 400 nm at 20 °C under N₂ purge. The scan rate was 0.5 nm per second. The average scan for each sample was subtracted by a background CD spectrum of corresponding buffer solution.

UV Melting Experiment. UV melting experiments were carried out on Shimadzu 2450
spectrophotometer (Shimadzu, Japan) equipped with a Peltier temperature control accessory. A sealed quartz cell with a path length of 1.0 cm was used. The UV melting curves of the G-quadruplexes and G4-based biocatalysts were monitored by UV absorption at 295 nm with a heating rate of 0.5 °C/min. Data were analyzed by using Origin 8 software. The melting temperatures ($T_m$) can be obtained from the best sigmoidal curve fit of the melting profile.

**UV-Vis Absorption Titration Experiments.** Absorption spectra were measured on Shimadzu 2600 spectrophotometer (Shimadzu, Japan) with a 1 cm path-length quarter cell. UV-vis absorption titrations were carried out by the stepwise addition of G-quadruplex solution to a cell containing FeTMPyPn ($n = 4, 3, 2$). Absorption spectra were recorded in the range of 300-550 nm at room temperature. The titration was terminated when the wavelength and intensity of the Soret band for FeTMPyPn did not change any more upon three successive additions of G-quadruplexes.

**Nuclear Magnetic Resonance (NMR) Titration.** NMR titration experiments were performed on Bruker-700MHz NMR instrument in potassium phosphate buffer (10mM, pH 7.0), containing 5% D$_2$O. The strand concentration of NMR samples was 0.25 mM. Before experiment the samples were heated at 95 °C for 3 min and annealed to room temperature.

**Isothermal Titration Calorimetry (ITC).** ITC measurements were carried out at 25
°C using a MicroCal TM ITC 200 titration calorimeter (MicroCal, GE). Experiments were performed in potassium phosphate buffer (10mM, pH 7.0). The reference cell in the ITC was filled with ultrapure water (18.2 MΩ). A pre-folded G-quadruplex DNA was loaded into the calorimeter cell. Then the syringe was loaded with FeTMPyPn (n = 4, 3, 2) (1.5 mM) in corresponding buffers. Following the auto-equilibration and an initial 60 s delay, the FeTMPyPn titrant divided into 25 injections was added into the cell with 250s injection intervals. The stir rate was 1000 rpm. All data were recorded with the GE Instruments software provided. Calorimetric data were further analyzed according to relevant model using MicroCal ORIGIN software and MATLAB. Data analysis gives ΔH (binding enthalpy change, k_{cal/mol}), K_a (binding constant, M^{-1}), and n (number of bound FeTMPyPn cofactor) whereas the change in Gibbs energy and the entropic contribution were determined by the relationships ΔG = -RTlnK_a and ΔG = ΔH-TΔS, respectively.

**Fluorescence quench titration assay.** Fluorescently labelled oligonucleotide was dissolved in assay buffer (potassium phosphate buffer 10 mM, pH 7.0), which is in agreement with the catalytic buffer. The resultant strand concentration of oligonucleotide was 100 nM. FeTMPyPn (n = 4, 3, 2) was prepared at a concentration of 5 mM in water and diluted to an appropriate concentration before titration. The fluorescence experiments were recorded on a FLS920 fluorescence spectrometer (Edinburgh) with a 1 cm path length quartz cuvette at 20 °C. Fluorescence intensity of FAM-labeled DNA was recorded after the addition of FeTMPyPn. Interval time
between two titration points was 10-15 minutes in order to reach the binding equilibrium. Each quench titration assay was conducted in triplicate. If not stated otherwise, the titration curve was fitting as one site specific binding by using software Origin 8.1.
**General Procedures**

**Typical procedure for cyclopropanation bioconversions under anaerobic conditions.** Reactions (1 mL) were conducted in 10 mL Schlenk tubes (Synthware Glass, Beijing). G4-based biocatalysts were added to the tube with a small stir bar in phosphate buffer (10 mM, pH = 7.0) and a solution of the reductant (Na$_2$S$_2$O$_4$, or NADPH) were combined in tube and degassed by bubbling argon through the solution for 5 min. The headspace of tube was made anaerobic by flushing argon over the solution (with no bubbling). A styrene solution in DMSO (20 µL, typically 1.5 M) was added to the reaction vial via a glass syringe, and left to stir for about 30s. An EDA solution in DMSO was then added (20 µL, 0.5 M) and the reaction was left to stir for appropriate time. The final concentrations of the reagents were typically: 30 mM styrene, 10 mM EDA, 5 mM Na$_2$S$_2$O$_4$ or 0.5 mM NADPH, 12.5 µM mA9A-FeTMPyPn (n = 4, 3, 2). After 2 hours of reaction, the product was extracted with ethyl acetate (3 × 2 mL). The organic layer was washed with brine (1 × 5 mL). After a short flash chromatography containing anhydrous Na$_2$SO$_4$ and the evaporation of solvent, the crude product was analyzed by HPLC, using 2-methylanisole as internal standard.

**Synthesis of cyclopropane products.** Under inert gas conditions, [Cu(MeCN)$_4$]PF$_6$ (52 mg) was dissolved in 20 mL anhydrous dichloromethane. Under stirring, olefin (140 mmol) was added to the solution and stirred for further 90 min at room temperature. Subsequently, a solution of ethyl diazoacetate or butyldiazoacetate (14 mmol) in 20 mL anhydrous dichloromethane was dropped to the solution over 4 hours.
The reaction mixture was allowed to stir at room temperature overnight. The pure product was obtained after flash chromatography.

**Synthesis of cofactor FeTMPyPn.**

The pH of an aqueous solution of H$_2$TMPyP (0.15 mmol) in 60 ml water was adjusted to 2 (with 1 M HCl), and a 40-fold molar excess FeCl$_2$.4H$_2$O was added and the solution was stirred and heated under reflux. The course of the metalation was followed by the decrease of the fluorescence of the metal-free porphyrin using UV light at 356 nm. The metalation was completed in 24 hours. The solution was filtered through a filter paper. The Fe porphyrin was precipitated as the PF$_6^-$ salt with a saturated aqueous solution of NH$_4$PF$_6$ (2 ml). The precipitate was thoroughly washed with diethyl ether (5 × 5 mL). The dried precipitate was then dissolved in acetone (the smallest possible amount) and precipitated as the chloride salt with saturated acetone solution of methyl-tri-noctylammonium chloride (2 mL). The precipitate was washed with acetone and dissolved in the smallest possible amount of water. The whole precipitation procedure was repeated once again to ensure high purity.
A solution of R-OH (50 mmol) and 2,2,6-trimethyl-4H-1,3-dioxin-4-one (50 mmol) in 10 mL of toluene was placed in a 50-ml flask. The flask was immersed in an oil bath that had been preheated to 150 °C, and the solution was vigorously stirred. The evolution of acetone became apparent within several minutes, heating was continued for a total of 6 hours. The reaction was cooled, and then the toluene was removed, and the product was distilled. To the solution of first step product (10 mmol) in acetonitrile (12 ml) was added Et$_3$N (13 mmol). The reaction mixture was cooled in an ice bath and a solution of p-ABSA (11 mmol) in acetonitrile (12 ml) was added slowly. The reaction mixture was allowed to warm to r.t. After stirring for 10h, solvent was removed under reduced pressure. The residue was dissolved in ether (60 ml) and washed with 5% aqueous KOH solution. To a solution of the crude product in ethyl ether was added 5% KOH (50 ml), and the reaction mixture was stirred for 1h. The organic phase was separated, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. Purification by vacuum distillation provided the desired diazo esters as yellow liquid.
Supplementary Results

Figure S1. UV-melting spectra of mA9A and mA9A-FeTMPyPn (n = 4, 3, 2).
Figure S2. (a) The diagrams of site-specific FAM labelled mA9A G-quadruplex. (b) CD spectra of FAM labelled mA9A (FAM labelled G4 strand concentration 15 μM, potassium phosphate buffer 10 mM, pH 7.0).
Figure S3. FeTMPyPn (n = 4, 3, 2)-dose-responsive FAM-mA9A emission spectra.
Synthesis and Characterization

(1RS, 2RS)-Ethyl 2-phenylcyclopropane-1-carboxylate. Prepared using general procedure, starting from styrene. Purified by column chromatography (SiO$_2$, EtOAc: pentane = 1: 10), to afford the product as a white solid.

HPLC analysis condition: Daicel Chiralcel-OJH, n-hexane, flow rate 1 mL/min, $\lambda$ = 225 nm. 2-methylanisole as internal standard.
(1RS, 2RS)-Ethyl 2-(4-methylphenyl) cyclopropane-1-carboxylate. Prepared using general procedure, starting from 4-methylstyrene. Purified by column chromatography (SiO$_2$, EtOAc: pentane = 1: 10), to afford the product as a white solid.

HPLC analysis condition: Daicel Chiralcel-OJH, n-hexane, flow rate 1 mL/min, $\lambda$ = 225 nm. 2-methylanisole as internal standard.
(1RS, 2RS)-Ethyl 2-(4-methoxyphenyl) cyclopropane-1-carboxylate. Prepared using general procedure, starting from 4-methoxystyrene. Purified by column chromatography (SiO$_2$, EtOAc: pentane = 1: 20), to afford the product as liquid.

HPLC analysis condition: Daicel Chiralcel-OJH, n-hexane: ethanol = 98: 2, flow rate 0.8 mL/min, $\lambda = 225$ nm. 2-methylanisole as internal standard.
(1RS, 2RS)-Ethyl 2-(4-chlorophenyl) cyclopropane-1-carboxylate. Prepared using general procedure, starting from 4-chlorostyrene. Purified by column chromatography (SiO₂, EtOAc: pentane = 1: 50), to afford the product as a white solid.

HPLC analysis condition: Daicel Chiralcel-OJH, n-hexane: ethanol = 98: 2, flow rate 0.5 mL/min, λ = 225 nm. 2-methylanisole as internal standard.
(1RS, 2RS)-Ethyl 2-(4-fluorophenyl) cyclopropane-1-carboxylate. Prepared using general procedure, starting from 4-fluorostyrene. Purified by column chromatography (SiO₂, EtOAc: pentane = 1: 50), to afford the product as a white solid.

HPLC analysis condition: Daicel Chiralcel-OJH, n-hexane: ethanol = 98: 2, flow rate 0.5 mL/min, λ = 225 nm. 2-methylanisole as internal standard.
(1RS, 2RS)-Ethyl 2-(3,4-difluorophenyl) cyclopropane-1-carboxylate. Prepared using general procedure, starting from 3,4-difluorostyrene. Purified by column chromatography (SiO₂, EtOAc: pentane = 1: 50), to afford the product as pale yellow liquid.

HPLC analysis condition: Daicel CHIRALPAK-IJ, n-hexane: isopropanol = 98: 2, flow rate 0.3 mL/min, λ = 235 nm. 2-methylanisole as internal standard.
(1RS, 2RS)-Ethyl 2-methyl-2-phenylcyclopropane-1-carboxylate. Prepared using general procedure, starting from 2-phenyl-1-propene. Purified by column chromatography (SiO$_2$, EtOAc: pentane = 1: 10), to afford the product as a white solid.

HPLC analysis condition: Daicel Chiralcel-OJH, n-hexane, flow rate 1 mL/min, $\lambda = $ 225 nm. Thioanisole as internal standard.
(1RS, 2RS)-tert-Butyl 2-phenylcyclopropane-1-carboxylate. Prepared using general procedure, starting from styrene and $t$-BuDA. Purified by column chromatography (SiO$_2$, EtOAc: pentane = 1: 30), to afford the product as pale yellow liquid.

HPLC analysis condition: Daicel CHIRALPAK-IJ, n-hexane, flow rate 1 mL/min, $\lambda$ = 225 nm. Thioanisole as internal standard.
(1RS, 2RS)-2-methyl-1-(1-methylethyl)propyl 2-phenylcyclopropane-1-carboxylate. Prepared using general procedure, starting from 2-Methyl-1-(1-methylethyl)propyl 2-diazoacetate. Purified by column chromatography (SiO$_2$, EtOAc: pentane = 1:30), to afford the product as pale yellow liquid.

HPLC analysis condition: Daicel CHIRALPAK-IJ, n-hexane, flow rate 0.8 mL/min, $\lambda = 225$ nm. 4-Methoxystrene as internal standard.
(1RS, 2RS)-1,2-dimethyl-1-(1-methylethyl)propyl 2-phenylcyclopropane-1-carboxylate. Prepared using general procedure, starting from 2,3,4-Trimethyl-3-pentyl diazoacetate. Purified by column chromatography (SiO$_2$, EtOAc: pentane = 1: 50), to afford the product as pale yellow liquid.

HPLC analysis condition: Daicel CHIRALPAK-IJ, n-hexane, flow rate 0.5 mL/min, $\lambda = 225$ nm. 4-Methoxystrene as internal standard.
(1RS, 2RS)-dicyclohexylmethyl 2-phenylcyclopropane-1-carboxylate. Prepared using general procedure, starting from 2,3,4-Trimethyl-3-pentyl diazoacetate. Purified by column chromatography (SiO$_2$, EtOAc: pentane = 1: 30), to afford the product as pale yellow liquid.

HPLC analysis condition: Daicel Chiralcel-OJH, n-hexane, flow rate 0.6 mL/min, $\lambda$ = 235 nm. Thioanisole as internal standard.
HPLC Traces of Products

(1) Racemic trans product catalyzed by FeTMPyP4

(2) Racemic trans product catalyzed by FeTMPyP3

(3) Racemic trans product catalyzed by FeTMPyP2
(4) Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP2

Signal 1: VW01 A, Wavelength=225 nm
Peak RetTime Type Width Area Height Area %
# [min] [min] [nAU*sec] [nAU]
------------------------------------------------
1 17.670 MM 0.4352 352,819 16.3153 12.9558
2 24.068 VB 0.5528 3172.1334 87.7477 87.0358
Totals: 3644.70807 104.07927

(5) Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP3

Signal 1: VW01 A, Wavelength=225 nm
Peak RetTime Type Width Area Height Area %
# [min] [min] [nAU*sec] [nAU]
------------------------------------------------
1 17.698 MM 0.4853 734,51807 25.22478 18.8658
2 25.001 BB 0.5467 3159.02954 87.49763 81.1358
Totals: 3893.59761 112.67242

(6) Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP2

Signal 1: VW01 A, Wavelength=225 nm
Peak RetTime Type Width Area Height Area %
# [min] [min] [nAU*sec] [nAU]
------------------------------------------------
1 17.606 HH 0.4342 3670.93481 128.31760 73.2711
2 24.872 HH 0.5489 1342.79650 37.10339 26.7822
Totals: 5013.72131 165.41899
(1) Racemic trans product catalyzed by FeTMPyP4

![Graph showing UV/Vis spectra for FeTMPyP4 catalyzed reaction]

Signal 1: Wavelength = 225 nm

| Peak Ret Time | Width | Area       | Height | Area       |
|---------------|-------|------------|--------|------------|
|               | [min] | [min] [AU*sec] | [AU]  | %          |
| 1             | 22.490 | 0.4960 2707.4430 | 98.9305 | 59.7884   |
| 2             | 26.602 | 0.5702 2623.10059 | 76.67128 | 49.2116   |

Totals: 533.24438 176.62433

(2) Racemic trans product catalyzed by FeTMPyP3

![Graph showing UV/Vis spectra for FeTMPyP3 catalyzed reaction]

Signal 1: Wavelength = 225 nm

| Peak Ret Time | Width | Area       | Height | Area       |
|---------------|-------|------------|--------|------------|
|               | [min] | [min] [AU*sec] | [AU]  | %          |
| 1             | 23.333 | 0.4669 3607.62500 | 119.14697 | 50.0601   |
| 2             | 28.016 | 0.6321 3598.96021 | 86.85062 | 49.9399   |

Totals: 7266.58521 206.01059

(3) Racemic trans product catalyzed by FeTMPyP2

![Graph showing UV/Vis spectra for FeTMPyP2 catalyzed reaction]

Signal 1: Wavelength = 225 nm

| Peak Ret Time | Width | Area       | Height | Area       |
|---------------|-------|------------|--------|------------|
|               | [min] | [min] [AU*sec] | [AU]  | %          |
| 1             | 23.620 | 0.4530 608.94950 | 20.75915 | 50.6158   |
| 2             | 28.471 | 0.5904 594.13354 | 15.48888 | 49.3842   |

Totals: 1203.08313 36.14603
(4) Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP4

![Graph showing trans product from cyclopropanation catalyzed by mA9A-FeTMPyP4]

| Peak RetTime Type | Width | Area | Height | Area % |
|------------------|-------|------|--------|--------|
| 1                | 22.724 BP | 0.4883 | 1773.1781 | 60.51929 | 15.2097 |
| 2                | 26.848 BB | 0.7975 | 5885.0578 | 197.88266 | 84.7903 |
| Totals:          | 1.16592e4 | 258.40193 |

(5) Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP3

![Graph showing trans product from cyclopropanation catalyzed by mA9A-FeTMPyP3]

| Peak RetTime Type | Width | Area | Height | Area % |
|------------------|-------|------|--------|--------|
| 1                | 22.692 BB | 0.4586 | 2293.7512 | 77.30296 | 19.6923 |
| 2                | 26.934 BB | 0.7756 | 9360.0735 | 381.16884 | 80.3277 |
| Totals:          | 1.16538e4 | 258.67180 |

(6) Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP2

![Graph showing trans product from cyclopropanation catalyzed by mA9A-FeTMPyP2]

| Peak RetTime Type | Width | Area | Height | Area % |
|------------------|-------|------|--------|--------|
| 1                | 22.772 BB | 0.6087 | 4332.1704 | 103.30273 | 73.5773 |
| 2                | 27.425 BB | 0.5466 | 1483.9227 | 41.7602 | 26.4227 |
| Totals:          | 5616.09314 | 147.47876 |
(1) Racemic trans product catalyzed by FeTMPyP4

![Graph of signal 1: VM01 A, Wavelength=225 nm]

| Peak RetTime | Width | Area | Height | Area % |
|--------------|-------|------|--------|--------|
| 1            | 17.329 | 0.3045 | 930.77545 | 46.88914 | 58.1834 |
| 2            | 24.342 | 0.4425 | 923.97205 | 32.21429 | 49.8166 |

Totals: 1854.74750 79.10344

(2) Racemic trans product catalyzed by FeTMPyP3

![Graph of signal 1: VM01 A, Wavelength=225 nm]

| Peak RetTime | Width | Area | Height | Area % |
|--------------|-------|------|--------|--------|
| 1            | 17.824 | 0.3126 | 927.31396 | 59.02786 | 51.1998 |
| 2            | 22.663 | 0.3989 | 4696.38379 | 179.25935 | 18.8002 |

Totals: 5623.69775 378.28722

(3) Racemic trans product catalyzed by FeTMPyP2

![Graph of signal 1: VM01 A, Wavelength=225 nm]

| Peak RetTime | Width | Area | Height | Area % |
|--------------|-------|------|--------|--------|
| 1            | 17.758 | 0.3457 | 7474.04639 | 316.19681 | 49.9475 |
| 2            | 22.448 | 0.4440 | 7489.76221 | 281.14175 | 50.0525 |

Totals: 1.49638e+6 597.33817
(4) Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP4

Additional Info: Peak(s) manually integrated

| Peak Set | Time | Width | Area | Height | Area % |
|----------|------|-------|------|--------|--------|
| 1        | 17.560 | 0.3003 | 2313.20581 | 118.69658 | 21.0114 |
| 2        | 22.148 | 0.4773 | 8666.06348 | 307.39966 | 78.9886 |

Totals: 1.10093e6 426.69624

(5) Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP3

Additional Info: Peak(s) manually integrated

| Peak Set | Time | Width | Area | Height | Area % |
|----------|------|-------|------|--------|--------|
| 1        | 17.256 | 0.2975 | 4117.81585 | 213.84589 | 24.0873 |
| 2        | 21.711 | 0.4339 | 1,2977644 | 468.30869 | 75.9127 |

Totals: 1.70551e6 674.15417

(6) Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP2

Additional Info: Peak(s) manually integrated

| Peak Set | Time | Width | Area | Height | Area % |
|----------|------|-------|------|--------|--------|
| 1        | 16.950 | 0.3482 | 6344.62169 | 283.86646 | 73.0086 |
| 2        | 21.284 | 0.3869 | 2345.86286 | 101.04584 | 26.9920 |

Totals: 8.69030396 384.91229
(1) Racemic trans product catalyzed by FeTMPyP4

(2) Racemic trans product catalyzed by FeTMPyP3

(3) Racemic trans product catalyzed by FeTMPyP2
(4) *Trans* product from the cyclopropanation catalyzed by mA9A-FeTMPyP4

![Graph showing cyclopropanation analysis](image)

| Signal | Peak | RetTime | Width | Height | Area  | Area % |
|--------|------|---------|-------|--------|-------|--------|
| 1      | 15.824 BB | 0.2507 | 1045.165316 | 63.17922 | 17.5529 |
| 2      | 18.662 BV  | 0.3497 | 4789.22412 | 216.04589 | 82.4471 |
| Totals |       |         |       |        | 5954.38928 | 279.22431 |

(5) *Trans* product from the cyclopropanation catalyzed by mA9A-FeTMPyP3

![Graph showing cyclopropanation analysis](image)

| Signal | Peak | RetTime | Width | Height | Area  | Area % |
|--------|------|---------|-------|--------|-------|--------|
| 1      | 15.862 BB | 0.2566 | 1054.52954 | 63.44704 | 23.5063 |
| 2      | 18.551 BV  | 0.3692 | 3431.63235 | 142.65867 | 76.4937 |
| Totals |       |         |       |        | 4486.16089 | 206.30572 |

(6) *Trans* product from the cyclopropanation catalyzed by mA9A-FeTMPyP2

![Graph showing cyclopropanation analysis](image)

| Signal | Peak | RetTime | Width | Height | Area  | Area % |
|--------|------|---------|-------|--------|-------|--------|
| 1      | 16.807 VB | 0.3287 | 2046.27869 | 101.11288 | 76.4640 |
| 2      | 18.683 BB  | 0.3570 | 697.94991 | 41.13651 | 25.1360 |
| Totals |       |         |       |        | 2733.32660 | 142.24939 |
(1) Racemic trans product catalyzed by FeTMPyP4

| Peak RetTime Type | Width | Area | Height | Area % |
|------------------|-------|------|--------|--------|
|                  | (min) | (μAU) | (μAU)  | (%)    |
| 1                | 16.296 | 0.271 | 3425.209235 | 210.83144 | 50.6160 |
| 2                | 17.134 | 0.2963 | 3335.0468 | 170.84022 | 49.3840 |
| Totals           |       |       |       | 6784.25293 | 381.86766 |

(2) Racemic trans product catalyzed by FeTMPyP3

| Peak RetTime Type | Width | Area | Height | Area % |
|------------------|-------|------|--------|--------|
|                  | (min) | (μAU) | (μAU)  | (%)    |
| 1                | 14.836 | 0.2539 | 7726.88379 | 467.84775 | 50.2703 |
| 2                | 17.077 | 0.3314 | 7643.77983 | 384.45569 | 49.7297 |
| Totals           |       |       |       | 1.5370764 | 892.30344 |

(3) Racemic trans product catalyzed by FeTMPyP2

| Peak RetTime Type | Width | Area | Height | Area % |
|------------------|-------|------|--------|--------|
|                  | (min) | (μAU) | (μAU)  | (%)    |
| 1                | 14.131 | 0.2636 | 1512.62354 | 87.19427 | 52.1810 |
| 2                | 16.959 | 0.3074 | 1386.17859 | 68.52614 | 47.8190 |
| Totals           |       |       |       | 2096.60212 | 155.71841 |
(4) **Trans** product from the cyclopropanation catalyzed by m9A-FeTMPyP4

![Graph 1]

Signal 1: WDI A, Wavelength=225 nm

| Peak | RetTime | Width | Area | Height | Area % |
|------|---------|-------|------|--------|-------|
| 1    | 14.202  | 0.2396| 874.29547 | 55.32927 | 17.1389 |
| 2    | 17.016  | 0.321 | 226.92725  | 50.41016 | 82.8611 |

Totals: 5896.66519 263.24512

(5) **Trans** product from the cyclopropanation catalyzed by m9A-FeTMPyP3

![Graph 2]

Signal 1: WDI A, Wavelength=225 nm

| Peak | RetTime | Width | Area | Height | Area % |
|------|---------|-------|------|--------|-------|
| 1    | 14.316  | 0.260 | 1031.82813 | 57.43111 | 29.3377 |
| 2    | 17.161  | 0.365 | 2485.24097  | 107.33364 | 70.6623 |

Totals: 3517.06903 164.74675

(6) **Trans** product from the cyclopropanation catalyzed by m9A-FeTMPyP2

![Graph 3]

Signal 1: WDI A, Wavelength=225 nm

| Peak | RetTime | Width | Area | Height | Area % |
|------|---------|-------|------|--------|-------|
| 1    | 14.460  | 0.3153| 2623.39624 | 117.16426 | 85.2797 |
| 2    | 17.225  | 0.2244| 644.42249  | 43.71943 | 19.7203 |

Totals: 3267.81873 160.88369

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(1) Racemic trans product catalyzed by FeTMPyP4

| Peak RetTime Type | Width  | Area     | Height | Area % |
|------------------|--------|----------|--------|--------|
| 1                | 18.633 | 0.3744   | 2981.03667 | 118.15169 | 49.2549 |
| 2                | 21.876 | 0.4324   | 3071.22632 | 105.16261 | 50.7451 |

Totals: 6052.26099 223.31429

(2) Racemic trans product catalyzed by FeTMPyP3

| Peak RetTime Type | Width  | Area     | Height | Area % |
|------------------|--------|----------|--------|--------|
| 1                | 18.804 | 0.3684   | 3712.28394 | 140.29503 | 49.3660 |
| 2                | 21.177 | 0.4430   | 3807.63623 | 125.42380 | 50.6340 |

Totals: 7519.92017 265.71883

(3) Racemic trans product catalyzed by FeTMPyP2

| Peak RetTime Type | Width  | Area     | Height | Area % |
|------------------|--------|----------|--------|--------|
| 1                | 18.142 | 0.3658   | 2957.25635 | 118.91586 | 49.2929 |
| 2                | 21.323 | 0.4309   | 3042.10400 | 104.17683 | 50.7071 |

Totals: 5999.36035 223.09469
(4) Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP4

| RetTime | Width | Area | Height | Area % |
|---------|-------|------|--------|--------|
| 18.202 | 0.4314| 896,164,675 | 35,623,072 | 22.772 |
| 21.558 | 0.4290| 3039,14722 | 105,672,458 | 77.227 |
| Totals: | | | | 3935,31396 | 139,29552 |

(5) Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP3

| RetTime | Width | Area  | Height | Area % |
|---------|-------|-------|--------|--------|
| 17.883 | 0.4640| 1297,94507 | 49,080,956 | 29.808 |
| 20.946 | 0.4361| 3056,37643 | 104,160,988 | 70.192 |
| Totals: | | | | 4354,31250 | 153,20980 |

(6) Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP2

| RetTime | Width | Area  | Height | Area % |
|---------|-------|-------|--------|--------|
| 17.843 | 0.3843| 4405,87988 | 166,697,458 | 85.6408 |
| 20.980 | 0.4468| 739,39587 | 24,194,50 | 14.3592 |
| Totals: | | | | 5149,27576 | 190,89195 |
(1) Racemic trans product catalyzed by FeTMPyP4

![UV spectrum of racemic trans product]

| Peak RetTime | Width | Area  | Height | Area % |
|--------------|-------|-------|--------|--------|
| 1            | 14.888 | 0.2872 | 676.2322 | 46.46402 49.3497 |
| 2            | 16.793 | 0.3916 | 699.34905 | 38.27814 53.6503 |
| Totals       |       | 1.775.59973 |       | 84.74415 |

(2) Racemic trans product catalyzed by FeTMPyP3

![UV spectrum of racemic trans product]

| Peak RetTime | Width | Area  | Height | Area % |
|--------------|-------|-------|--------|--------|
| 1            | 15.001 | 0.3079 | 691.40973 | 37.42679 51.5734 |
| 2            | 16.959 | 0.3505 | 649.22241 | 30.86210 48.4266 |
| Totals       |       | 1.340.63214 |       | 68.29600 |

(3) Racemic trans product catalyzed by FeTMPyP2

![UV spectrum of racemic trans product]

| Peak RetTime | Width | Area  | Height | Area % |
|--------------|-------|-------|--------|--------|
| 1            | 14.676 | 0.2744 | 630.75702 | 34.99970 50.4532 |
| 2            | 16.550 | 0.3541 | 619.42499 | 29.15617 49.5468 |
| Totals       |       | 1.250.10201 |       | 64.15587 |
(4) *Trans* product from the cyclopropanation catalyzed by mA9A-FeTMPyP4

![Graph](image1.png)

Signal 1: VWD1 A, Wavelength=225 nm

| Peak Ret Time Type | Width [min] | Area [µM×t] | Height [µM] | Area % |
|-------------------|------------|-------------|-------------|-------|
| 1 15.334 NM       | 0.3236     | 1698.9331   | 78.4533     | 45.1246 |
| 2 17.334 AV       | 0.3620     | 1909.7349   | 79.8723     | 54.8754 |

Totals: 3491.6659 136.2576

(5) *Trans* product from the cyclopropanation catalyzed by mA9A-FeTMPyP3

![Graph](image2.png)

Signal 1: VWD1 A, Wavelength=225 nm

| Peak Ret Time Type | Width [min] | Area [µM×t] | Height [µM] | Area % |
|-------------------|------------|-------------|-------------|-------|
| 1 15.348 MM       | 0.3336     | 1569.9331   | 78.4533     | 45.1246 |
| 2 17.334 AV       | 0.3620     | 1909.7349   | 79.8723     | 54.8754 |

Totals: 3479.10059 136.2576

(6) *Trans* product from the cyclopropanation catalyzed by mA9A-FeTMPyP2

![Graph](image3.png)

Signal 1: VWD1 A, Wavelength=225 nm

| Peak Ret Time Type | Width [min] | Area [µM×t] | Height [µM] | Area % |
|-------------------|------------|-------------|-------------|-------|
| 1 15.001 HF       | 0.3198     | 724.20697   | 37.74258    | 51.6815 |
| 2 16.959 FN       | 0.3618     | 677.08167   | 31.18903    | 48.3185 |

Totals: 1401.28864 68.93161
(1) Racemic trans product catalyzed by FeTMPyP4

| Peak RetTime Type | Width | Area [nAU^2] | Height [nAU] | Area % |
|------------------|-------|--------------|--------------|--------|
| 1                | 8.305 | 876.82204    | 69.01480     | 55.3834|
| 2                | 9.500 | 831.47778    | 61.91261     | 49.6166|
| Totals           |       | 1740.30072   | 130.93741    |        |

(2) Racemic trans product catalyzed by FeTMPyP3

| Peak RetTime Type | Width | Area [nAU^2] | Height [nAU] | Area % |
|------------------|-------|--------------|--------------|--------|
| 1                | 8.874 | 722.56366    | 53.89403     | 50.3919|
| 2                | 10.223| 711.32303    | 43.93259     | 49.6081|
| Totals           |       | 1433.88708   | 97.02702     |        |

(3) Racemic trans product catalyzed by FeTMPyP2

| Peak RetTime Type | Width | Area [nAU^2] | Height [nAU] | Area % |
|------------------|-------|--------------|--------------|--------|
| 1                | 8.436 | 777.01953    | 61.62082     | 50.6113|
| 2                | 9.626 | 758.24988    | 55.37621     | 49.3887|
| Totals           |       | 1535.26941   | 116.99703    |        |
(4) **Trans** product from the cyclopropanation catalyzed by mA9A-FeTMPyP4

| Peak RetTime Type | Width | Area  | Height | Area % |
|------------------|-------|-------|--------|--------|
| #         | [min] | [min] | [nAU’s] | [nAU] |
| 1          | 8.573 | 0.293 | 77.96956 | 4.40032 | 9.0489 |
| 2          | 9.813 | 0.262 | 786.43921 | 49.70558 | 90.9591 |
| Totals:       |       |       | 862.40907 | 54.14290 |

(5) **Trans** product from the cyclopropanation catalyzed by mA9A-FeTMPyP3

| Peak RetTime Type | Width | Area  | Height | Area % |
|------------------|-------|-------|--------|--------|
| #         | [min] | [min] | [nAU’s] | [nAU] |
| 1          | 8.638 | 0.2073 | 151.08315 | 11.07085 | 19.7433 |
| 2          | 9.874 | 0.228 | 614.15540 | 40.98235 | 80.2567 |
| Totals:       |       |       | 765.33854 | 52.05319 |

(6) **Trans** product from the cyclopropanation catalyzed by mA9A-FeTMPyP2

| Peak RetTime Type | Width | Area  | Height | Area % |
|------------------|-------|-------|--------|--------|
| #         | [min] | [min] | [nAU’s] | [nAU] |
| 1          | 8.785 | 0.2137 | 929.03815 | 65.43421 | 67.8835 |
| 2          | 10.103 | 0.2351 | 439.13946 | 28.53935 | 32.1165 |
| Totals:       |       |       | 1368.57761 | 93.97356 |
(1) Racemic trans product catalyzed by FeTMPyP4

| Signal 1: VWD1 A, Wavelength=225 nm |
|-----------------------------------|
| Peak RetTime Type Width Area Height Area |
| # [min] [min] [mAU]* [mAU]% |
|-----------------------------------|
| 1 7.072 BB 0.1286 1343.86194 59.94378 49.9669 |
| 2 8.139 BB 0.1473 1345.69233 139.78761 50.0331 |
| Totals: 2689.50427 299.73131 |

(2) Racemic trans product catalyzed by FeTMPyP3

| Signal 1: VWD1 A, Wavelength=225 nm |
|-----------------------------------|
| Peak RetTime Type Width Area Height Area |
| # [min] [min] [mAU]* [mAU]% |
|-----------------------------------|
| 1 7.088 BB 0.1284 1805.69903 221.08999 49.9503 |
| 2 8.158 BB 0.1494 1860.39575 192.1677 50.0497 |
| Totals: 3717.09558 413.65176 |

(3) Racemic trans product catalyzed by FeTMPyP2

| Signal 1: VWD1 A, Wavelength=225 nm |
|-----------------------------------|
| Peak RetTime Type Width Area Height Area |
| # [min] [min] [mAU]* [mAU]% |
|-----------------------------------|
| 1 7.096 BB 0.1282 822.85834 97.11717 50.0823 |
| 2 8.169 VB 0.1685 820.18530 84.33962 49.9877 |
| Totals: 1623.04364 181.45679 |
(4) Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP4

![Graph of Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP4]

| Peak | RetTime | Width | Area    | Height | Area % |
|------|---------|-------|---------|--------|--------|
| 1    | 7.066   | 0.128 | 146.3738 | 17.2507 | 8.1401 |
| 2    | 8.131   | 0.147 | 160.4517 | 16.9557 | 91.8599 |

Totals: 1785.80510 186.91184

(5) Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP3

![Graph of Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP3]

| Peak | RetTime | Width | Area    | Height | Area % |
|------|---------|-------|---------|--------|--------|
| 1    | 7.105   | 0.128 | 262.0803 | 31.2437 | 16.1732 |
| 2    | 8.177   | 0.149 | 1357.9679 | 139.8162 | 83.8268 |

Totals: 1619.96820 171.05431

(6) Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP2

![Graph of Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP2]

| Peak | RetTime | Width | Area    | Height | Area % |
|------|---------|-------|---------|--------|--------|
| 1    | 7.056   | 0.127 | 1200.3136 | 151.2206 | 69.0204 |
| 2    | 8.104   | 0.161 | 565.5743 | 58.3376 | 30.9736 |

Totals: 1025.88782 209.56629
(1) Racemic trans product catalyzed by FeTMPyP4

```
Signal 1: VW01 A, Wavelength=225 nm
Peak RetTime Type Width Area Height Area %
1 10.713 MM 0.2456 1845.59424 125.22459 48.8721
2 12.730 MM 0.4078 1930.78052 78.90295 51.1279
Totals: 3776.37476 204.12755
```

(2) Racemic trans product catalyzed by FeTMPyP3

```
Signal 1: VW01 A, Wavelength=225 nm
Peak RetTime Type Width Area Height Area %
1 10.785 MM 0.3124 2421.89723 172.01741 47.5126
2 12.908 VB 0.3132 2675.40975 176.80783 52.4874
Totals: 5097.30697 298.82510
```

(3) Racemic trans product catalyzed by FeTMPyP2

```
Signal 1: VW01 A, Wavelength=225 nm
Peak RetTime Type Width Area Height Area %
1 10.713 MM 0.2330 1747.02778 124.99615 48.2356
2 12.730 MM 0.3999 1875.54919 78.34403 51.7654
Totals: 3622.27699 203.34097
```
(4) **Trans** product from the cyclopropanation catalyzed by mA9A-FeTMPyP4

| Signal | Wavelength (nm) | Peak Ret Time (min) | Width (min) | Area (AU^2) | Height (AU) | Area % |
|--------|----------------|---------------------|-------------|-------------|-------------|--------|
| 1      | 10.556         | 2.2902              | 113,22777   | 6.50344     | 6.4336     |        |
| 2      | 12.732         | 3.3178              | 2440.62915  | 109.42220   | 95.5664    |        |
| Totals |                |                     |             |             |             | 255.38692 | 115.92564 |

(5) **Trans** product from the cyclopropanation catalyzed by mA9A-FeTMPyP3

| Signal | Wavelength (nm) | Peak Ret Time (min) | Width (min) | Area (AU^2) | Height (AU) | Area % |
|--------|----------------|---------------------|-------------|-------------|-------------|--------|
| 1      | 10.446         | 2.2120              | 836.29364   | 66.94638    | 18.1963    |        |
| 2      | 12.556         | 2.2563              | 3714.70581  | 225.94635   | 81.8507    |        |
| Totals |                |                     |             |             |             | 454.99945 | 290.69283 |

(6) **Trans** product from the cyclopropanation catalyzed by mA9A-FeTMPyP2

| Signal | Wavelength (nm) | Peak Ret Time (min) | Width (min) | Area (AU^2) | Height (AU) | Area % |
|--------|----------------|---------------------|-------------|-------------|-------------|--------|
| 1      | 10.403         | 2.2001              | 4474.54492  | 340.35177   | 65.5142    |        |
| 2      | 12.460         | 2.2690              | 2355.33862  | 130.09409   | 34.4858    |        |
| Totals |                |                     |             |             |             | 682.88354 | 470.34586 |
(1) Racemic trans product catalyzed by FeTMPyP4

![Graph](image)

**Signal 1: WM D1 A, Wavelength=235 nm**

| Peak RetTime Type | Width | Area | Height | Area % |
|------------------|-------|------|--------|-------|
|                  |       |      |        |       |
| 1                | 18.644 BB | 0.0510 | 2356.112255 | 112.14309 | 50.0232 |
| 2                | 22.166 BB | 0.0595 | 3355.90686 | 51.08897 | 49.9768 |

**Totals:** 4714.04159 2032.2396

(2) Racemic trans product catalyzed by FeTMPyP3

![Graph](image)

**Signal 1: WM D1 A, Wavelength=235 nm**

| Peak RetTime Type | Width | Area | Height | Area % |
|------------------|-------|------|--------|-------|
|                  |       |      |        |       |
| 1                | 38.623 BB | 0.3298 | 2511.602375 | 120.07256 | 49.8477 |
| 2                | 22.119 BB | 0.3981 | 2527.03816 | 97.14995 | 50.1595 |

**Totals:** 5038.71792 217.22240

(3) Racemic trans product catalyzed by FeTMPyP2

![Graph](image)

**Signal 1: WM D1 A, Wavelength=235 nm**

| Peak RetTime Type | Width | Area | Height | Area % |
|------------------|-------|------|--------|-------|
|                  |       |      |        |       |
| 1                | 38.361 BB | 0.3243 | 1803.07316 | 87.62695 | 50.2330 |
| 2                | 21.594 BB | 0.3893 | 1778.21704 | 87.62695 | 50.2330 |

**Totals:** 3982.8913 198.08391
(4) Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP4

Signal 1: VWD1 A, Wavelength=235 nm

| Peak RetTime | Width | Area     | Height | Area     |
|--------------|-------|----------|--------|----------|
| # [min]       | [min] | [nAU*]   | [nAU]  | %        |
| 1 18.435  | 0.322 | 1203.0667 | 57.58662 | 31.7402  |
| 2 21.767  | 0.389 | 2587.3576 | 101.72431 | 68.2598  |

Totals: 3790.44903 159.23092

(5) Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP3

Signal 1: VWD1 A, Wavelength=235 nm

| Peak RetTime | Width | Area     | Height | Area     |
|--------------|-------|----------|--------|----------|
| # [min]       | [min] | [nAU*]   | [nAU]  | %        |
| 1 18.426  | 0.369 | 1755.6017 | 75.77023 | 37.2007  |
| 2 21.796  | 0.429 | 5031.1950 | 117.54772 62.7993 |

Totals: 4826.79614 193.32193

(6) Trans product from the cyclopropanation catalyzed by mA9A-FeTMPyP2

Signal 1: VWD1 A, Wavelength=235 nm

| Peak RetTime | Width | Area     | Height | Area     |
|--------------|-------|----------|--------|----------|
| # [min]       | [min] | [nAU*]   | [nAU]  | %        |
| 1 18.481  | 0.314 | 2135.0352 | 104.36347 | 55.7904  |
| 2 21.830  | 0.393 | 1691.6054 | 66.73677 44.2086 |

Totals: 3926.93601 171.10024
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