Electronic Supplementary Information (ESI)

Higher-Order Human Telomeric G-Quadruplex DNA

Metalloenzyme Catalyzed Diels-Alder Reaction: An Unexpected Inversion of Enantioselectivity Modulated by K⁺ and NH₄⁺ ions†

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Materials

All DNA oligodeoxynucleotides were purchased from Sangon (Shanghai, China). 3-(N-morpholino)propanesulfonic acid (MOPS) was purchased from Sangon (Shanghai, China). Cu(NO$_3$)$_2$·3H$_2$O (>99.5%), KCl (>99.5%) and NH$_4$Cl (>99.5%) were purchased from the Shanghai Chemical Reagent Company of the Chinese Medicine Group. Water was distilled and deionized (specific resistance of 18.2 MΩ at 25 ºC) using a Milli-Q A10 water purification system. All experiments were carried out in 20 mM MOPS buffer (pH 6.5) unless otherwise stated. Other reagents and solvents were obtained from commercial sources and used without further purification. Dienophiles 1a-f were prepared according to the literature.$^{1}$ All of the racemic products were prepared by the Diels-Alder reaction using Cu(NO$_3$)$_2$ as catalyst in methanol.

![Chemical structures of 1a-f](image-url)
Methods

Circular dichroism (CD) spectra were recorded on a dual beam DSM 1000 CD spectrophotometer (Olis, Bogart, GA) with a 10 mm path-length quartz cell. Each measurement was recorded from 220 to 320 nm at 4 °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. The molarities are related to G-quadruplex unit. CD samples of all G-quadruplexes were prepared at a concentration (G4 unit) of 5 μM by using a MOPS buffer solution (20 mM, pH = 6.5) consisting of different concentration of KCl or NH₄Cl as required.

The precise DNA strand concentrations were determined by measuring the UV absorbance of sample at 260 nm using the molar extinction coefficient values provided by the manufacturer. UV-Vis experiments were carried out on a Shimadzu 2450 spectrophotometer (Shimadzu, Japan) equipped with a Peltier temperature control accessory. All UV-Vis spectra were measured using a sealed quartz cell with a path length of 1.0 cm.

¹H NMR spectra were recorded on 400 MHz in CDCl₃ and ¹³C NMR spectra were recorded on 100 MHz in CDCl₃ using TMS or residual protic solvent signals as internal standard. Data for ¹H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, coupling constant(s) in Hz, integration).

The enantioselectivity was determined by chiral HPLC analysis using Daicel chiralcel ODH, OJ-H column or chiralpak ADH, AD column with a UV-detector by using isopropanol and n-hexane as eluents at 25 °C.
**General procedure**

To a MOPS buffer (0.5 mL, 20 mM, pH 6.5) containing KCl (150 mM) or NH₄Cl (25 mM), an aqueous solution of HT45 (final G4 unit conc. of 50 μM) was added. After stirred for a half hour at 4 °C, a solution of Cu(NO₃)₂ (final conc. of 10 μM for K⁺ case and 16.7 μM for NH₄⁺ case) was added. Then, aza-chalcone 1 in CH₃CN (final conc. of 1 mM for K⁺ case and 0.5 mM for NH₄⁺ case, 1 equiv.) was added. The reaction was initiated by the addition of freshly distilled cyclopentadiene 2 (100 equiv.). The mixture was stirred for 12 hours (1a), 48 hours (1b-e) and 72 hours (1f) at 4 °C, respectively. Followed by the extraction with diethyl ether (3 × 5 mL), the solvent was removed under reduced pressure. The residue was directly analyzed by ¹H-NMR and HPLC. The conversions were determined by ¹H-NMR and HPLC (only for 3a) of the crude product.² The diastereoselectivity (endo/exo) and enantiomeric excess (ee) were determined by chiral HPLC.

**HPLC analysis condition**

Product 3a: Daicel Chiralcel-ODH, n-hexane/i-PrOH 98:2, flow rate 0.5 mL/min, λ = 212 nm).
Product 3b: Daicel Chiralcel-ODH, n-hexane/i-PrOH 98:2, flow rate 0.5 mL/min, λ = 212 nm).
Product 3c: Daicel Chiralpak-ADH, n-hexane/i-PrOH 95:5, flow rate 1.0 mL/min, λ = 212 nm).
Product 3d: Daicel Chiralcel-OJH, n-hexane/i-PrOH 90:10, flow rate 0.5 mL/min, λ = 212 nm).
Product 3e: Daicel Chiralpak-AD, n-hexane/i-PrOH 90:10, flow rate 1.0 mL/min, λ = 254 nm).
Product 3f: Daicel Chiralpak-ADH, n-hexane/i-PrOH 90:10, flow rate 1.0 mL/min, λ =254 nm).
**Calculation the conversion of 1a**

The procedure to determine the conversion of 1a by HPLC was according to the literature.\textsuperscript{2}

Conversions of 1a were calculated using the formula:

\[
\text{Conversion (\%)} = \frac{A_{3a}}{A_{3a} + A_{1a}/f}
\]

Where \(A_{1a}\) and \(A_{3a}\) are the HPLC peak areas of 1a and 3a, respectively. And \(f\) is the correction factor determined to be 0.73 from a calibration curve.

**Kinetic measurements**

All kinetic measurements were performed using UV-Vis spectroscopy (Shimadzu 2450) at 298 K by monitoring the disappearance of the absorption of 1a at 326 nm.\textsuperscript{2b}

Typical procedure is described as follows: HT45 (final G4 unit conc. 50 μM) was added to MOPS (20 mM, pH 6.5) containing KCl (150 mM) or NH\textsubscript{4}Cl (25 mM) in a quartz cuvette. After stirring for 15 min, Cu\textsuperscript{2+} ion (final conc. 10 μM in K\textsuperscript{+} media or 16.7 μM in NH\textsubscript{4}\textsuperscript{+} media) was added. After stirring for another 15 min, 4 μL of a fresh solution of 1a in CH\textsubscript{3}CN was added, resulting in a final concentration of 20 μM. The determination was made after 2 (final conc. 4 mM) was added with the cuvette sealed tightly.

The following equations were used to calculate \(k_{\text{app}}\) and \(k_{\text{rel}}\):

\[
k_{\text{app}} = d[A_{1a}] / dt \cdot (d \cdot (\varepsilon_{1a} - \varepsilon_{3a}) \cdot [1a]^0 \cdot [2]^0)^{-1}
\]

\[
k_{\text{rel}} = k_{\text{app-catalyst}} / k_{\text{app-no catalyst}}
\]

Where \(d[A_{1a}] / dt\) is the slope of the absorption of 1a vs. time during the first 15% of the reaction, and \(d\) is the path length of the cuvette. \(\varepsilon_{1a}\) (22173 M\textsuperscript{-1}cm\textsuperscript{-1}) and \(\varepsilon_{3a}\) (177 M\textsuperscript{-1}cm\textsuperscript{-1}) are the molar extinction coefficient of 1a and 3a at 326 nm, respectively.
References


1H NMR spectra

(3-phenylbicyclo[2.2.1]hept-5-en-2-yl)(pyridin-2-yl)methanone (3a)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.67 (m, 1H), 8.00 (m, 1H), 7.81 (m, 1H), 7.49 – 7.39 (m, 1H), 7.36 – 7.23 (m, 4H), 7.17 (m, 1H), 6.49 (m, 1H), 5.82 (m, 1H), 4.53 (m, 1H), 3.54 (s, 1H), 3.45 (d, $J = 3.9$ Hz, 1H), 3.09 (s, 1H), 2.07 (d, $J = 8.4$ Hz, 1H), 1.62 (m, 1H).
pyridin-2-yl(3-p-tolylbicyclo[2.2.1]hept-5-en-2-yl)methanone (3b)

\[
\text{δ 8.67 (d, } J = 4.6 \text{ Hz, 1H), 8.00 (d, } J = 7.8 \text{ Hz, 1H), 7.81 (td, } J = 7.7, 1.3 \text{ Hz, 1H), 7.44 (dd, } J = 7.0, 5.3 \text{ Hz, 1H), 7.21 (d, } J = 8.0 \text{ Hz, 2H), 7.08 (d, } J = 7.9 \text{ Hz, 2H), 6.49 (dd, } J = 5.4, 3.3 \text{ Hz, 1H), 5.81 (dd, } J = 5.6, 2.7 \text{ Hz, 1H), 4.52 (dd, } J = 4.9, 3.7 \text{ Hz, 1H), 3.53 (s, 1H), 3.41 (d, } J = 5.0 \text{ Hz, 1H), 3.05 (s, 1H), 2.30 (s, 3H), 2.06 (d, } J = 8.4 \text{ Hz, 1H), 1.59 (dd, } J = 8.5, 1.1 \text{ Hz, 1H).}
\]

\[
\begin{align*}
\text{1H NMR (400 MHz, CDCl}_3, \text{ endo isomer):} \\
\delta & 8.67 \text{ (d, } J = 4.6 \text{ Hz, 1H), 8.00 \text{ (d, } J = 7.8 \text{ Hz, 1H), 7.81 \text{ (td, } J = 7.7, 1.3 \text{ Hz, 1H), 7.44 \text{ (dd, } J = 7.0, 5.3 \text{ Hz, 1H), 7.21 \text{ (d, } J = 8.0 \text{ Hz, 2H), 7.08 \text{ (d, } J = 7.9 \text{ Hz, 2H), 6.49 \text{ (dd, } J = 5.4, 3.3 \text{ Hz, 1H), 5.81 \text{ (dd, } J = 5.6, 2.7 \text{ Hz, 1H), 4.52 \text{ (dd, } J = 4.9, 3.7 \text{ Hz, 1H), 3.53 \text{ (s, 1H), 3.41 \text{ (d, } J = 5.0 \text{ Hz, 1H), 3.05 \text{ (s, 1H), 2.30 \text{ (s, 3H), 2.06 \text{ (d, } J = 8.4 \text{ Hz, 1H), 1.59 \text{ (dd, } J = 8.5, 1.1 \text{ Hz, 1H).}}}
\end{align*}
\]
(3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-en-2-yl)(pyridin-2-yl)methanone (3c)

\[
\begin{align*}
\text{1H NMR (400 MHz, CDCl}_3, \text{ endo isomer): } & \delta 8.74 – 8.60 (m, 1H), 8.00 (d, J = 7.9 \text{ Hz}, 1H), 7.81 \\
& (td, J = 7.7, 1.7 \text{ Hz}, 1H), 7.44 (ddd, J = 7.5, 4.8, 1.1 \text{ Hz}, 1H), 7.28 – 7.18 (m, 2H), 6.86 – 6.78 (m, \\
& 2H), 6.48 (dd, J = 5.5, 3.2 \text{ Hz}, 1H), 5.81 (dd, J = 5.6, 2.7 \text{ Hz}, 1H), 4.49 (dd, J = 5.1, 3.5 \text{ Hz}, 1H), \\
& 3.77 (s, 3H), 3.53 (s, 1H), 3.39 (d, J = 4.5 \text{ Hz}, 1H), 3.02 (d, J = 1.2 \text{ Hz}, 1H), 2.06 (d, J = 8.4 \text{ Hz}, \\
& 1H), 1.60 (dd, J = 8.5, 1.6 \text{ Hz}, 1H).
\end{align*}
\]
(3-(4-chlorophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(pyridin-2-yl)methanone (3d)

$1^1$H NMR (400 MHz, CDCl$_3$, endo isomer): $\delta$ 8.67 (d, $J = 4.6$ Hz, 1H), 8.00 (d, $J = 7.8$ Hz, 1H), 7.83 (dd, $J = 8.5$, 6.9 Hz, 1H), 7.46 (dd, $J = 7.4$, 4.9 Hz, 1H), 7.25 – 7.10 (m, 4H), 6.48 (dd, $J = 5.4$, 3.2 Hz, 1H), 5.83 (dd, $J = 5.5$, 2.7 Hz, 1H), 4.46 (dd, $J = 5.1$, 3.5 Hz, 1H), 3.54 (s, 1H), 3.40 (d, $J = 5.1$ Hz, 1H), 3.05 (s, 1H), 2.01 (d, $J = 8.5$ Hz, 1H), 1.62 (d, $J = 8.6$ Hz, 1H).
(3-(4-nitrophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(pyridin-2-yl)methanone (3e)

$^1$H NMR (400 MHz, *endo* isomer):  δ 8.66 (d, $J = 4.5$ Hz, 1H), 8.07 (m, 3H), 7.84 (t, $J = 7.6$ Hz, 1H), 7.47 (m, 3H), 6.52 – 6.44 (m, 1H), 5.88 (dd, $J = 5.3$, 2.5 Hz, 1H), 4.51 – 4.44 (m, 1H), 3.66 – 3.50 (m, 2H), 3.13 (s, 1H), 2.00 (d, $J = 8.6$ Hz, 1H), 1.67 (d, $J = 8.4$ Hz, 1H).
(3-(naphthalen-1-yl)bicyclo[2.2.1]hept-5-en-2-yl)(pyridin-2-yl)methanone (3f)

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.70 – 8.57 (m, 1H), 8.18 – 7.98 (m, 2H), 7.87 – 7.76 (m, 2H), 7.70 (d, $J = 8.2$ Hz, 1H), 7.62 (d, $J = 7.2$ Hz, 1H), 7.49 – 7.37 (m, 4H), 6.68 – 6.57 (m, 1H), 5.97 – 5.89 (m, 1H), 4.74 – 4.65 (m, 1H), 4.07 (d, $J = 4.8$ Hz, 1H), 3.53 (s, 1H), 3.21 (s, 1H), 2.19 (dd, $J = 8.4$ Hz, 1H), 1.69 (dd, $J = 8.3$ Hz, 1H).
HPLC traces

1. Product 3a

Ee’s were determined by HPLC analysis (Daicel Chiralcel-ODH, n-hexane/i-PrOH 98:2, flow rate 0.5 mL/min, λ = 212 nm).

(1) Racemic 3a

Retention times: 13.0, 14.7 (exo isomer) and 17.0, 22.0 (endo isomer) mins

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Totals: 1.48110e4 545.83416

*** End of Report ***
(2) Product 3a from the Diels-Alder reaction catalyzed by HT45-K-Cu

Retention times: 12.9, 14.4 (exo isomer) and 16.6, 21.3 (endo isomer) mins (92% ee)
(3) Product 3a from the Diels-Alder reaction catalyzed by HT45-NH$_4$-Cu

Retention times: 12.8, 14.3 (exo isomer) and 16.0, 20.8 (endo isomer) mins (-73% ee)
2. Product 3b

Ee’s were determined by HPLC analysis (Daicel Chiralcel-ODH, n-hexane/i-PrOH 98:2, flow rate 0.5 mL/min, λ = 212 nm).

(1) Racemic 3b

Retention times: 11.0, 12.6 (exo isomer) and 13.4, 18.1 (endo isomer) mins

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Area Percent Report
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Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

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Totals : | 1.21514e5 | 5328.91762 |
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*** End of Report ***
(2) Product 3b from the Diels-Alder reaction catalyzed by HT45-K-Cu

Retention times: 11.2, 12.9 (exo isomer) and 14.0, 18.8 (endo isomer) mins (50% ee)
(3) Product 3b from the Diels-Alder reaction catalyzed by HT45-NH₂-Cu

Retention times: 11.1, 12.8 (exo isomer) and 13.8, 18.6 (endo isomer) mins (-61% ee)
3. Product 3c

Ee’s were determined by HPLC analysis (Daicel Chiralpak-ADH, \(n\)-hexane/\(i\)-PrOH 95:5, flow rate 1.0 mL/min, \(\lambda = 212\) nm).

(1) Racemic 3c

Retention times: 13.8, 14.2 (exo isomer) and 16.6, 22.8 (endo isomer) mins

![HPLC chromatogram](image)

Area Percent Report

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Totals: 1.76214e4  780.05318

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*** End of Report ***
(2) Product 3c from the Diels-Alder reaction catalyzed by HT45-K-Cu

Retention times: 14.0, 14.4 (exo isomer) and 16.8, 23.4 (endo isomer) mins (52% ee)
(3) Product 3c from the Diels-Alder reaction catalyzed by HT45-NH₄-Cu

Retention times: 13.9, 14.2 (exo isomer) and 16.6, 22.9 (endo isomer) mins (-90% ee)
4. Product 3d

Ee’s were determined by HPLC analysis (Daicel Chiralcel-OJH, n-hexane/i-PrOH 90:10, flow rate 0.5 mL/min, λ = 212 nm).

(1) Racemic 3d

Retention times: 20.8, 26.9 (exo isomer) and 25.4, 44.4 (endo isomer) mins

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Area Percent Report

Sorted By : Signal
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Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

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Totals: 3.85330e4 693.09989

*** End of Report ***
(2) Product 3d from the Diels-Alder reaction catalyzed by HT45-K-Cu
Retention times: 20.4, 26.4 (exo isomer) and 24.5, 43.4 (endo isomer) mins (60% ee)
(3) Product 3d from the Diels-Alder reaction catalyzed by HT45-NH$_4$-Cu

Retention times: 20.3, 26.3 (exo isomer) and 24.6, 43.5 (endo isomer) mins (~90% ee)
5. Product 3e

Ee’s were determined by HPLC analysis (Daicel Chiralpak-AD, n-hexane/i-PrOH 90:10, flow rate 1.0 mL/min, λ = 254 nm).

(1) Racemic 3e

Retention times: 12.5, 16.0 (exo isomer) and 14.6, 18.1 (endo isomer) mins
(2) Product 3e from the Diels-Alder reaction catalyzed by HT45-K-Cu

Retention times: 12.5, 16.0 (exo isomer) and 14.6, 18.2 (endo isomer) mins (26% ee)
(3) Product **3e** from the Diels-Alder reaction catalyzed by HT45-NH$_4$-Cu

Retention times: 12.5, 15.9 (**exo** isomer) and 14.5, 18.1 (**endo** isomer) mins (-90% ee)
6. Product 3f

Ee’s were determined by HPLC analysis (Daicel Chiralpak-ADH, n-hexane/i-PrOH 90:10, flow rate 1.0 mL/min, \( \lambda = 254 \) nm).

(1) Racemic 3f

Retention times: 7.4 and 10.8 mins

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**Area Percent Report**

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Dilution: 1.0000
Use Multiplier & Dilution Factor with ISTDs

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*** End of Report ***
(2) Product 3f from the Diels-Alder reaction catalyzed by HT45-K-Cu

Retention times: 7.4 (major) and 10.7 (minor) mins (91% ee)

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Area Percent Report

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*** End of Report ***
(3) Product 3f from the Diels-Alder reaction catalyzed by HT45-NH$_4$-Cu

Retention times: 7.4 (minor) and 10.6 (major) mins (-82% ee)