Supporting Information
Design, Synthesis and DNA-Cleaving Efficiency of Photoswitchable Dimeric Azobenzene Based Enediynes
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Figures S1

\[
\begin{align*}
\text{Br} & \quad \text{O} \\
& \quad \text{R} \\
& \quad \text{COOCH}_2\text{Ph} \\
& \quad \text{H} \\
& \quad \text{O} \\
& \quad \text{Br}
\end{align*}
\]

\[R = \text{CH}_2\text{Ph}\]

Figures S2

\[
\begin{align*}
\text{Br} & \quad \text{O} \\
& \quad \text{R} \\
& \quad \text{COOCH}_2\text{Ph} \\
& \quad \text{H} \\
& \quad \text{Br}
\end{align*}
\]

\[R = \text{CH}_2\text{Ph}\]
Figures S3

\[
\begin{align*}
\text{R} & = \text{CH(CH}_3\text{)}_2 \\
\text{Br} & \text{-} \text{COOCH}_2\text{Ph} \\
\text{N} & \text{COOCH}_2\text{Ph}
\end{align*}
\]

Figures S4

\[
\begin{align*}
\text{R} & = \text{CH(CH}_3\text{)}_2 \\
\text{Br} & \text{-} \text{COOCH}_2\text{Ph} \\
\text{N} & \text{COOCH}_2\text{Ph}
\end{align*}
\]
Figures S7

Figures S8
Figures S11

Figures S12
Figures S15

Figures S16
Figures S23

Figures S24
Figures S27

![Image of chemical structure 7]

Figures S28

![Image of chemical structure 7]
Figures S33

Figures S34
Figures S35

Figures S36
Figures S37

4e

Figures S38

4e
Figures S39

Figures S40
Figures S41

Figures S42
Thermal Isomerization Kinetics of 10 at 20 °C

T = 0

\[ y = 0.00538 \times r = 0.999 \]

Compound 1a

T = 60 min

\[ \ln \left( \frac{a}{a-x} \right) \]

Time in min

Figures S44

Figures S45

T = 180 min

Figures S46

T = 1800 min

Figures S47

\[ \text{y = 0.00538 x} \quad r = 0.999 \]

Compound 1a

Figure S47a
Thermal Isomerization Kinetics of 2a at 20 °C

T = 0

Figures S48

T = 90 min

Figures S49

T = 240 min

Figures S50

T = 300 min

Figures S51

T = 660 min

Figures S52

T = 960 min

Figures S53
Thermal Isomerization Kinetics of 2b at 20 °C

T = 0

T = 50 min

T = 180 min

T = 300 min

T = 450 min

T = 550 min

T = 900 min

Figures S54

Figures S55

Figures S56

Figures S57

Figures S58

Figures S59

Figures S60

Figures S61
Thermal Isomerization Kinetics of 2c at 20 °C

Figures S62

T = 0

Figures S63

T = 45 min

Figures S64

T = 150 min

Figures S65

T = 290 min

Figures S66

T = 350 min

Figures S67

T = 500 min

Figures S68

\[ y = 1.6 \times 10^{-3} \times 0.9972 \]
Bergman Cyclization Kinetics of 1a at 45 °C

\[
y = 0.00382x \quad R = 0.9957
\]
Bergman Cyclization Kinetics of aliphatic 1c at 30 °C

T = 0 h

Figures S76

T = 24 h

Figures S77

T = 30.5 h

Figures S78

T = 34 h

Figures S79

T = 41 h

Figures S80

Figures S81

\[ y = 0.0327x \quad R = 0.9947 \]

Compounds 2e
DNA binding study of compound 2a by UV

Figures S82
DNA binding study of compound 1a by UV

Figures 83
DNA-Binding Plots

Figure S84: For 1a

Figure S85: For 2a

Figure S86: For 1e

Figure S87: For 2e
DSC of enediynes 1a, 1b, 1c and 1e respectively

Figure S88

Figure S89

Figure S90

Figure S91
Figure S92: NOESY spectrum of enediynes 1a/2a
Figure S93: Energy minimized conformations of 1a (A), 2a (B), 1d (C)/ 2d (D), and 1e (E)/2e (F)
Gel Documentation
The gel documentation was carried with UVP-GELDOC, Cambridge UK. The cleavage efficiency was measured by densitometry using image processing software (Kodak 1D version V.3.6.3).

Energy Minimization
The energy minimizations were carried out in Silicon Graphics using PDB coordinates from the Dundee PRODRG 2.5 Server (beta).

Selected spectral data
For compound 1a: δ_H (400 MHz, CDCl₃) 7.55 (dd, J = 8.4 Hz, 15.6 Hz, 2 x 2H), 7.29-7.16 (m, 12H), 6.99-6.94 (m, 10H), 6.86 (d, J = 8 Hz, 2H), 4.95 (m, 2H), 4.76 (d, J = 13.6 Hz, 2H), 4.66 (d, J = 13.6 Hz, 2H), 4.54 (s, 4H), 4.05 (s, 4H), 3.64 (bs, 4H), 3.18 (d, J = 4 Hz, 2H), 2.89 (dd, J = 8, 13.6 Hz, 2H), 2.80 (bs, 4H); δ_C (100 MHz, CDCl₃) 170.5, 168.0, 165.7, 154.9, 142.6, 135.8, 132.6, 129.7, 129.1, 129.03, 128.5, 128.3, 128.1, 127.9, 127.6, 127.5, 127.3, 126.8, 122.7, 117.8, 115.2, 98.1, 92.4, 88.0, 82.5, 68.9, 61.9, 52.8, 51.2, 40.8, 37.8, 18.2; HRMS: calcd for C₆₄H₅₄N₆O₁₀ + H⁺ 1067.3983 found 1067.3987.

For compound 2a: δ_H (400 MHz, CDCl₃) 7.38-7.08 (m, 22H), 6.79 (t, J = 7.6 Hz, 2H), 6.66 (d, J = 8.4 Hz, 2H), 6.51 (d, J = 8 Hz, 2H), 4.89, 4.83 (ABq, J = 16.0 Hz, 2 x 2H), 4.71 (m, 2H), 4.48, 4.38 (ABq, J = 16.0 Hz, 2 x 2H), 4.16 (m, 4H), 3.75 (bm, 4H), 3.35 (m, 2H), 3.01 (m, 2H), 2.94 (bm, 4H).

For compound 1c: δ_H (400 MHz, CDCl₃) 7.67 (t, J = 7.6 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.28-6.99 (m, 14H), 5.89, 5.81 (Abq, J = 9.6 Hz, 2 x 2H), 5.04 (2H, m), 4.84 (2H, m), 4.76, 4.73 (ABq, J = 12.6 Hz, 2 x 2H), 4.75 (m, obscured, 2H), 4.11 (s, 4H), 3.75 (bs, 4H), 3.29 (dd, J = 4.8, 14.0 Hz, 2H), 2.99 (dd, J = 4.0, 14.0 Hz, 2H), 2.86 (bs, 4H); δ_C (100 MHz, CDCl₃) 170.5, 168.0, 165.7, 155.0, 142.7, 135.7, 132.6, 129.1, 129.0, 128.5, 128.3, 126.8, 125.5, 122.7, 121.5, 117.9, 115.3, 102.7, 95.9, 88.4, 82.7, 69.0, 61.7, 52.8, 51.3, 40.8, 37.7, 18.4; HRMS: calcd for C₅₆H₅₀N₆O₁₀ + H⁺ 967.3669 found 967.3673.

For compound 2c: δ_H (400 MHz, CDCl₃) 7.22-6.99 (m, 14H), 6.82 (t, J = 7.4 Hz, 2H), 6.69 (d, J = 8.4 Hz, 2H), 6.53 (d, J = 7.6 Hz, 2H), 5.90, 5.82 (Abq, J = 9.2 Hz, 4H), 4.87 (m, 2H), 4.84,
4.77 (ABq, J = 14.2 Hz, 4H), 4.50, 4.37 (ABq, J = 14.8 Hz, 4H), 4.12 (m, 4H), 3.70 (m, 4H),
3.37 (dd, J = 4.4, 14.4 Hz, 2H), 3.03 (dd, J = 8.8, 14.0 Hz, 2H), 2.88 (m, 4H).

For compound 2i: δH (400 MHz, CDCl3) 7.66 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H),
7.38-7.21 (m, 12H), 7.15-7.0 (m, 10H), 6.94 (d, J = 8.0 Hz, 2H), 5.04 (m, 2H), 4.82, 4.75
(ABq, J = 14.4 Hz, 2H), 4.64 (s, 4H), 4.36 (s, 4H), 3.73 (t, J = 4.6 Hz, 4H), 3.26 (dd, J = 5.4,
14.4 Hz, 2H), 3.01-2.9 (m, 2H), 2.89 (t, J = 4.8 Hz, 4H); δC (100 MHz, CDCl3) 170.6, 168.1,
165.8, 155.0, 142.7, 135.8, 132.6, 129.8, 129.1, 129, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8,
127.5, 127.4, 126.8, 122.8, 117.8, 115.3, 98.1, 92.4, 88, 82.5, 68.9, 61.9, 52.8, 51.3, 40.9, 37.8,
18.2; MS (ES+) m/z 1067 (MH+), 1089 (MNa+); HRMS Calcd. For C62H54N6O10 + H+ 1067.3982 found 1067.3969.

For compound 2j: δH (400 MHz, CDCl3) 7.40-7.21 (m, 10H), 7.15-7.03 (m, 10H), 6.79 (t, J =
7.6 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 6.51 (d, J = 7.6 Hz, 2H), 4.95-4.80 (m, 6H), 4.47 (d, J =
15.6 Hz, 2H), 4.32 (d, J = 15.6 Hz, 4H), 4.18 (s, 4H), 3.75 (m, 4H), 3.38 (dd, J = 4.4, 14.0 Hz,
2H), 3.05 (dd, J = 5.2, 14.0 Hz, 2H), 2.92 (m, 4H).