Supporting Information

Synthesis of Bicyclic Enediynes That Possess a Photosensitive Triggering Device and Exhibit Strong DNA Cleaving Activity.

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General Methods

NMR spectra were recorded on a JEOL Model EX-270 (270 MHz for $^1$H, 67.8 MHz for $^{13}$C), or a JEOL Model EP-400 (400 MHz for $^1$H, 100 MHz for $^{13}$C) instrument in the indicated solvents. Chemical shifts are reported in unit of parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (CHCl$_3$: $\delta$=7.26 ppm for $^1$H, CH$_2$Cl$_2$: $\delta$=5.32 ppm for $^1$H, CDCl$_3$: $\delta$=77.0 ppm for $^{13}$C). Data are reported as follows: chemical shift, multiplicity (s; singlet, d; doublet, t; triplet, q; quartet, m; multiplet, br; broad), coupling constants (Hz) and integration.

IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrophotometer.

All reactions were monitored by thin-layer chromatography using E. Merck silica gel plates (60F-254) pre-coated plates (0.25 mm). TLC visualization was done with UV light and/or 5% ethanolic p-anisaldehyde or 10% ethanolic phosphomolybdic acid followed by heating.

Flash column chromatography was performed on Silica Gel 60 N, purchased from Kanto Chemical Co. or Silica gel BW-820MH, purchased from Fuji Silisia Co.

High performance liquid chromatography (HPLC) for qualitative and quantitative analyses were performed on a Waters® 2695 Separation Module using a Senshu Pak Silica-3301-N column.

ESI-TOF Mass spectra were obtained on Waters LCT Premier XE. HRMS (ESI-TOF) were calibrated with angioestensin I (SIGMA), bradykinin (SIGMA), and neurotensin (SIGMA) as external standards.
**Preparation of diyne**

![Diagram of diyne synthesis](image)

1. **4-(1-Ethoxyethoxy)-2-butyn-1-ol (21)**

   To a solution of 1,4-dihydroxy-2-butyne (44.9 g, 522 mmol, 1.0 eq.) and PPTS (502 mg, 2.00 mmol, 0.00380 eq.) in CH$_2$Cl$_2$ (600 mL) and THF (200 mL) was added ethyl vinyl ether (50.0 mL, 522 mmol, 1.0 eq.) dropwise at room temperature. After being stirred for 3 h, the reaction mixture was quenched by adding NET$_3$ (1.0 mL) and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (40% EtOAc in hexane) to give 4-(1-Ethoxyethoxy)-2-butyn-1-ol (21) (38.0 g, 240 mmol, 46%).

   ![NMR spectrum of 4-(1-Ethoxyethoxy)-2-butyn-1-ol (21)](image)

   - $^1$H NMR (270 MHz, CDCl$_3$) δ 4.84 (d, $J = 5.6$ Hz, 1H), 4.31 (d, $J = 1.6$ Hz, 2H), 4.25 (dt, $J = 2.0$, 1.6 Hz, 2H), 3.71-3.45 (m, 2H), 1.34 (d, $J = 5.6$ Hz, 3H), 1.21 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (67.8 MHz, CDCl$_3$) δ 98.3, 98.2, 84.1, 80.9, 80.8, 80.8, 76.6, 76.5, 60.4, 52.6, 50.2, 50.1, 19.3, 19.3, 14.9, 14.8; FT-IR (neat) 3519, 2982, 2933, 1643, 1446, 1386, 1340, 1128, 1020, 855, 611 cm$^{-1}$; HRMS (ESI-TOF): [M+H]$^+$ calcd for C$_8$H$_{15}$O$_3$, 159.1021; found 159.1024.

2. **1-(1-ethoxyethoxy)hepta-2,6-diyn-4-ol (22)**

   A solution of alcohol (21) (24.9 g, 157 mmol, 1.0 eq.), TEMPO (245 mg, 1.57 mmol, 0.010 eq.), NaHCO$_3$ (2.65 g, 31.5 mmol, 0.20 eq.), KBr (1.87 g, 15.7 mmol, 0.10 eq) in CH$_2$Cl$_2$ (150 mL) was cooled to 0°C. To the solution was added aqueous NaClO solution dropwise and stirred at the same temperature for 1 h. The reaction mixture was poured into 50% aqueous Na$_2$S$_2$O$_3$ solution and the aqueous layer was extracted with EtOAc twice. The combined organic layer was washed with 50% aqueous Na$_2$S$_2$O$_3$ solution and brine, dried over MgSO$_4$ and filtered. After removal of the solvent, the residue was used for the next reaction without further purification.
A mixture of magnesium turning (8.39 g, 345 mmol, 2.2 eq.) and HgCl₂ (426 mg, 1.57 mmol, 0.010 eq.) was stirred for 30 min and then dry Et₂O (100 mL) was added. After being cooled to 0 °C, a propargyl bromide (1.18 mL, 15.7 mmol, 0.10 eq.) was added to the suspension. After the reaction was occurred, the reaction mixture was added a solution of propargyl bromide (22.4 mL, 298 mmol, 1.9 eq.) in dry Et₂O (100 mL) dropwise at −20 ~ 15 °C. After being stirred at 0 °C for 30 min, the solution of above residue in dry Et₂O (50.0 mL) was added dropwise to the reaction mixture at 0 °C. After being stirred at 0 °C for 30 min, the reaction mixture was poured into saturated aqueous NH₄Cl solution and the aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over MgSO₄, and filtered. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (25% EtOAc in hexane) to give 1-(1-ethoxyethoxy)hepta-2,6-diyne-4-ol (22) (7.71 g, 39.3 mmol, 25% for 2 steps).

1H NMR (270 MHz, CDCl₃) δ 4.85 (q, J = 5.3 Hz, 1H), 4.55 (qt, J = 6.0, 1.6 Hz, 1H), 4.26 (d, J = 1.6 Hz, 2H), 3.72-3.46 (m, 2H), 2.64 (ddd, J = 6.0, 2.6, 2.6 Hz, 2H), 2.25 (d, J = 6.0 Hz, 1H), 2.12 (t, J = 2.6 Hz, 1H), 1.34 (d, J = 5.3, Hz, 3H), 1.21 (t, J = 7.0 Hz, 3H); 13C NMR (67.8 MHz, CDCl₃) δ 98.5, 85.1, 81.5, 79.3, 71.2, 60.7, 60.6, 52.6, 28.2, 19.6, 15.1; FT-IR (neat) 3415, 3292, 2980, 2919, 1637, 1387, 1127, 1052, 927, 857, 647 cm⁻¹; MS (ESI-TOF): [M+H]⁺ calcd for C₁₁H₁₇O₃ 197.25; found 197.25.

1-(1-ethoxyethoxy)-4-([t]-butyldimethylsilyloxy)-hepta-2,6-diyne (7)

To a stirred solution of mixture of alcohol (22) (20.0 g, 102 mmol, 1.0 eq.), imidazole (17.3 g, 255 mmol, 2.5 eq.) in DMF (100 mL) was added TBSCl (18.4 g, 122 mmol, 1.2 eq.) at 0 °C. After being stirred at room temperature for 8 h, the reaction mixture was poured into 1 M HCl and the aqueous layer was extracted with Et₂O twice. The combined organic layers were washed with 1 M HCl, water, saturated aqueous NaHCO₃ solution and brine, dried over MgSO₄, and filtered. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (10% EtOAc in hexane) to give 1-(1-ethoxyethoxy)-4-([t]-butyldimethylsilyloxy)-hepta-2,6-diyne (7) (26.3 g, 84.7 mmol, 83%).

1H NMR (270 MHz, CDCl₃) δ 4.85 (q, J = 5.3 Hz, 1H), 4.54 (t, J = 6.3, 1.6 Hz, 1H), 4.24 (s, 2H), 3.68-3.45 (m, 2H), 2.55 (dd, J = 6.4, 2.6 Hz, 2H), 2.01 (s, 1H), 1.32 (d, J = 5.3, Hz, 3H), 1.21 (t, J = 7.0 Hz, 3H), 0.90 (s, 9H), 0.14 (s, 3H), 0.12 (s, 3H); 13C NMR (67.8 MHz, CDCl₃) δ 98.4, 85.9, 80.8, 80.3, 70.3, 61.9, 60.9, 52.7, 29.1, 25.7, 19.8, 18.2, 15.3, −4.7, −5.0; FT-IR (neat) 3314, 2931, 2858, 1472, 1362, 1257, 1127, 1089, 930, 838, 779, 642 cm⁻¹; HRMS (ESI-TOF): [M+NH₄]⁺ calcd for C₁₇H₃₄N₂O₄Si₁ 328.2308, found 328.2303.
**Preparation of the o-nitro benzyl alcohol 11.**

4-(2-(2-Azidoethoxy)ethoxy)-3-methoxybenzaldehyde (25)

To a solution of 2-(2-chloroethoxy)ethanol (23) (12.2 mL, 110 mmol, 1.0 eq.), NEt₃ (46.0 mL, 330 mmol, 3.0 eq.) and NMe₃·HCl (100 mg, 1.1 mmol, 0.01 eq.) in CH₂Cl₂ (220 mL) was added TsCl (23.0 g, 121 mmol, 1.1 eq.) in several portions at 0 °C. After being stirred at room temperature for 1 h, the reaction mixture was poured into 1 M HCl and the aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with saturated aqueous NaHCO₃ solution and brine, dried over MgSO₄, and filtered. After removal of the solvent, the residue was used for the next reaction without further purification.

To a solution of above residue in DMF (100 mL) was added Vaniline (24) (13.39 g, 88.0 mmol, 0.80 eq.) and potassium carbonate (15.2 g, 110 mmol, 1.0 eq.) at room temperature. After being stirred at 70 °C for 12 h, the reaction mixture was added sodium azide (17.1g, 264 mmol, 2.4 eq.) and TBAI (16.2 g, 44.0 mmol, 0.40 eq.) at room temperature. After being stirred at 70 °C for another 12 h, the reaction mixture was poured into 1 M HCl and the aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with 1 M HCl, water, saturated aqueous NaHCO₃ solution and brine, dried over MgSO₄, and filtered. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (40% EtOAc in hexane) to give 4-(2-(2-azidoethoxy)ethoxy)-3-methoxybenzaldehyde (25) (21.4 g, 77.0 mmol, 70% for 3 steps).

1H NMR (400 MHz, CDCl₃) δ 10.4 (s, 1H), 7.43 (dd, J = 8.3, 2.0 Hz, 1H), 7.41 (d, J = 2.0 Hz, 1H), 7.02 (d, J = 8.3 Hz, 1H), 4.28 (t, J = 4.9 Hz, 2H), 3.94 (t, J = 4.9 Hz, 2H), 3.92 (s, 3H), 3.76 (t, J = 4.9 Hz, 2H), 3.41 (t, J = 4.9 Hz, 2H); 13C NMR (67.8 MHz, CDCl₃) δ 190.6, 153.5, 149.7, 130.1, 126.2, 111.9, 109.2, 76.5, 70.1, 69.2, 68.3, 55.7, 50.4; FT-IR (neat) 2937, 2102, 1681, 1586, 1509, 1465, 1424, 1267, 1134, 1030, 940, 810, 780, 731, 657, 592 cm⁻¹; HRMS (ESI-TOF): [M+NH₄]⁺ calcd for C₁₂H₁₉N₄O₄ 283.1406; found 283.1409.
4-(2-(2-Azidoethoxy)ethoxy)-5-methoxy-2-nitrobenzylalcohol (11)

To a solution of aldehyde (25) (18.5 g, 69.7 mmol, 1.0 eq.) and sodium nitrate (742 mg, 10.5 mmol, 0.15 eq.) in CH$_2$Cl$_2$ (210 mL) was added fuming HNO$_3$ (29.0 mL, 70.0 mmol, 10 eq.) dropwisely at $-78^\circ$C over 30 min. After being stirred at $-78^\circ$C for 30 min, the reaction mixture was warm up to room temperature. After being stirred at room temperature for 3 h, the reaction mixture was poured into ice, quenched by adding NaHCO$_3$ and the aqueous layer was extracted with EtOAc three times. The combined organic layers were washed with saturated aqueous NaHCO$_3$ solution and brine, dried over MgSO$_4$, and filtered. After removal of the solvent, the residue was used for the next reaction without further purification.

To a solution of above residue in MeOH (100 mL) was added NaBH$_4$ (1.32 g, 35.0 mmol, 0.50 eq.) in several portions at 0 °C. After being stirred at room temperature for 1 h, the reaction mixture was poured into 1 M HCl and the aqueous layer was extracted with EtOAc three times. The combined organic layers were washed with saturated aqueous NaHCO$_3$ solution and brine, dried over MgSO$_4$, and filtered. After removal of the solvent, the residue was recrystallized from EtOAc-hexane to give 4-(2-(2-azidoethoxy)ethoxy)-5-methoxy-2-nitrobenzyl alcohol (11) (16.7 g, 53.6 mmol, 79% for 2 steps).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (s, 1H), 7.17 (s, 1H), 4.96 (s, 2H), 4.27 (t, $J = 4.9$ Hz, 2H), 3.99 (s, 3H), 3.93 (t, $J = 4.9$ Hz, 2H), 3.76 (t, $J = 4.9$ Hz, 2H), 3.43 (t, $J = 4.9$ Hz, 2H); $^{13}$C NMR (67.8 MHz, CDCl$_3$) $\delta$ 154.3, 146.9, 139.2, 132.9, 110.8, 110.1, 70.1, 69.4, 68.9, 62.3, 56.2, 50.5; FT-IR (neat) 3537, 2934, 2104, 1577, 1518, 1458, 1325, 1274, 1215, 1128, 1070, 875, 803, 755 cm$^{-1}$; HRMS (ESI-TOF): [M+NH$_4$]$^+$ calcd for C$_{12}$H$_{20}$N$_5$O$_6$ 330.1414; found 330.1420.

2-(1-ethoxyethoxy)-4-butanolide (8)

A solution of 2-hydroxy-4-butanolide (10.5 mL, 135 mmol, 1.0 eq.) and PPTS (1.69 g, 6.75 mmol, 0.050 eq.) in CH$_2$Cl$_2$ (200 mL) was added ethyl vinyl ether (15.5 mL, 162 mmol, 1.2 eq.) dropwise at room temperature. After being stirred at room temperature for 3 h, the reaction mixture was quenched by adding NEt$_3$ (10.0 mL) and concentrated in vacuo. The residue was purified by flash column
chromatography on silica gel (20% EtOAc in hexane) to give 2-(1-ethoxyethoxy)-4-butanolide (8) (23.9 g, 128 mmol, 95%, Mixture of two diastereomers).

Mixture of diastereomers; \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta\) 5.11 (q, \(J = 5.3\) Hz, 1H), 4.96 (q, \(J = 5.3\) Hz, 1H), 4.51-4.37 (m, \(J = 4\) Hz), 4.28-4.18 (m, 2H), 3.81-3.48 (m, 4H), 2.58-2.46 (m, 2H), 2.36-2.21 (m, 2H), 1.40 (d, \(J = 5.3\) Hz, 3H), 1.30 (d, \(J = 5.3\) Hz, 3H), 1.22 (t, \(J = 7.0\) Hz, 3H), 1.21 (t, \(J = 7.0\) Hz, 3H); \(^13\)C NMR (67.8 MHz, CDCl\(_3\)) \(\delta\) 175.1, 174.9, 99.3, 98.9, 68.4, 67.5, 64.8, 64.7, 60.9, 60.7, 30.2, 29.9, 19.9, 19.5, 14.8, 14.7; FT-IR (neat) 3552, 29822, 2916, 1784, 1382, 1221, 1142, 1082, 949, 815, 712, 661, 510 cm\(^{-1}\).

**Syntjesis of the diol 10**

\[\text{OEE} \quad \text{OTBS} \quad \text{THF, -78 °C, 30 min} \quad \text{8 (1.5 eq.)} \quad \text{MeOH, rt, 4h, 65%} \quad \text{THF, -78 °C, 30 min} \quad \text{78%} \]

2-(4-(\(\text{r-Butyldimethylsilyloxy}\))-7-(1-ethoxyethoxy)hepta-1,5-diynyl))-3-(1-ethoxyethoxy)tetrahydro-furan-2-ol (9)

To a stirred solution of diyne (7) (4.20 g, 13.5 mmol, 1.0 eq.) in THF (40.0 mL) was added \(n\)-BuLi in hexane (2.77 M, 5.88 mL, 16.2 mmol, 1.2 eq.) dropwise at −78 °C. After being stirred at −78 °C for 1 h, the reaction mixture was added a solution of lactone 8 (3.51 g, 19.0 mmol, 1.4 eq.) in THF (20 mL) dropwise at −78 °C. After being stirred at 0 °C for 15 min, the reaction mixture was poured into saturated aqueous NH\(_4\)Cl solution and the aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over MgSO\(_4\), and filtered. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (25% EtOAc in hexane) to give coupling product (9) (4.45 g, 10.5 mmol, 78%, mixture of diastereomers).

Isomer 1 (less polar); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.83 (q, \(J = 5.3\) Hz, 1H), 4.71 (q, \(J = 5.3\) Hz, 1H), 4.60 (t, \(J = 6.3\) Hz, 1H), 4.43 (dd, \(J = 2.2\), 1.4 Hz, 1H), 4.24 (d, \(J = 1.4\) Hz, 1H), 3.78 (brs, 2H), 3.68-3.47 (m, 4H), 2.77 (d, \(J = 6.3\), 2H), 2.20-2.12 (m, 1H), 1.94-1.87 (m, 1H), 1.39 (d, \(J = 5.3\) Hz, 3H), 1.36 (d, \(J = 5.3\), Hz, 3H), 1.20 (t, \(J = 7.0\) Hz, 6H), 0.90 (s, 9H), 0.15 (s,
Isomer 2 (more polar); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.83 (q, $J = 5.3$ Hz, 1H), 4.77 (dq, $J = 5.3$, 1.9 Hz, 1H), 4.60 (t, $J = 6.3$, 1.5 Hz, 1H), 4.30 (dd, $J = 2.0$, 1.5 Hz, 1H), 4.24 (d, $J = 1.5$ Hz, 2H), 3.78 (brs, 2H), 3.66-3.50 (m, 4H), 2.77 (d, $J = 6.3$, 2H), 2.13-1.92 (m, 2H), 1.33 (d, $J = 5.3$, Hz, 3H), 1.32 (d, $J = 5.3$, Hz, 3H), 1.20 (t, $J = 6.8$ Hz, 3H), 1.16 (t, $J = 6.8$ Hz, 3H), 0.90 (s, 9H), 0.15 (s, 3H), 0.12 (s, 3H); $^{13}$C NMR (67.8 MHz, CDCl$_3$) $\delta$ 188.1, 188.0, 100.3, 100.2, 98.5, 98.4, 92.7, 85.2, 81.4, 80.5, 80.4, 78.7, 78.6, 78.5, 77.3, 77.1, 76.5, 61.7, 60.8, 60.7, 60.6, 58.6, 52.4, 34.5, 29.8, 29.7, 25.7, 25.6, 25.5, 25.3, 21.4, 19.8, 19.6, 19.5, 17.9, 15.2, 15.0, 14.8, −4.7, −4.8, −5.1, −5.2; FT-IR (neat) 3489, 2931, 2859, 2214, 1677, 1472, 1388, 1253, 1086, 928, 838, 780 cm$^{-1}$; HRMS (ESI-TOF): [M+NH$_4$]$^+$ calcd for C$_{25}$H$_{48}$N$_1$O$_2$Si$_1$ 502.3200, found 502.3199.

2-(4-((t-Butyldimethylsilyloxy)-7-hydroxyhepta-1,5-diynyl))-2-methoxytetrahydro-furan-3-ol (10)

To a solution of hemiacetal (9) (5.41 g, 10.8 mmol, 1.0 eq.) and trimethyl orthoformate (2.36 mL, 21.6 mmol, 2.0 eq.) in dry MeOH (40.0 mL) was added a solution of PPTS (542 mg, 2.16 mmol, 0.20 eq.) in dry MeOH at room temperature. After being stirred at room temperature for 4 h, the reaction mixture was quenched by adding NEt$_3$ (1.00 mL). After removal of the solvent, the residue was purified by flash column chromatography on silica gel (40% EtOAc in hexane) to give 2-(4-((t-butyldimethylsilyloxy)-7-hydroxyhepta-1,5-diynyl))-2-methoxytetrahydro-furan-3-ol (10) (2.95 g, 8.32 mmol, 77%, mixture of diastereomers).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.61 (dd, $J = 10.2$, 7.1 Hz, 1H), 4.27 (s, 2H), 3.92 (dd, $J = 8.2$ Hz, 2H), 3.38 (s, 3H), 2.66 (dd, $J = 16.6$, 10.2 Hz, 2H), 2.33-2.27 (m, 1H), 2.00-1.94 (m, 1H), 0.90 (s, 9H), 0.14 (s, 3H), 0.13 (s, 3H); $^{13}$C NMR (67.8 MHz, CDCl$_3$) $\delta$ 106.0, 99.0, 85.5, 84.0, 82.6, 76.5, 67.0, 62.0, 50.9, 50.7, 31.5, 29.2, 25.8, 18.0, −4.9, −5.1; FT-IR (neat) 3421, 2931, 2857, 1472, 1253, 1110, 1031, 966, 838, 779, 668 cm$^{-1}$; HRMS (ESI-TOF): [M+NH$_4$]$^+$ calcd for C$_{18}$H$_{34}$N$_1$O$_5$Si$_1$ 372.2206; found 372.2206.
Synthesis of the 10-membered diynes 14b and 15b

2-(7-Bromo-4-(t-butyldimethylsilyloxy)hepta-1,5-diyln)-2-methoxytetrahydro-furan-3-ol (26)

To a stirred solution of propargyl alcohol (10) (2.66 g, 7.50 mmol, 1.0 eq.), CBr₄ (2.73 g, 8.25 mmol, 1.1 eq.) and 2,6-lutidine (2.18 mL, 18.8 mmol, 2.5 eq.) in dry MeCN (20.0 mL) was added PPh₃ (2.55 g, 9.75 mmol, 1.3 eq.) in several portions at 0 °C. After being stirred at room temperature for 15 min, the reaction mixture was poured into saturated aqueous NH₄Cl solution and the aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with water and brine, dried over Na₂SO₄, and filtered. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (25% EtOAc in hexane) to give 2-(7-bromo-4-(t-butyldimethylsilyloxy)hepta-1,5-diyln)-2-methoxytetrahydro-furan-3-ol (26) (2.69 g, 6.45 mmol, 86%, mixture of diastereomers).

¹H NMR (400 MHz, CDCl₃) δ 4.60 (dd, J = 10.2, 7.1 Hz, 1H), 4.27 (s, 2H), 3.92 (dd, J = 8.2 Hz, 2H), 3.38 (s, 3H), 2.66 (dd, J = 16.6, 10.2 Hz, 2H), 2.33-2.27 (m, 1H), 2.00-1.94 (m, 1H), 0.90 (s, 9H), 0.14 (s, 3H), 0.13 (s, 3H); ¹³C NMR (67.8 MHz, CDCl₃) δ 106.0, 99.0, 85.5, 84.0, 82.6, 76.5, 67.0, 62.0, 50.9, 50.7, 31.5, 29.2, 25.8, 18.0, −4.9, −5.1; FT-IR (neat) 3421, 2931, 2857, 1472, 1253, 1110, 1031, 966, 838, 779, 668 cm⁻¹; HRMS (ESI-TOF): [M+NH₄]⁺ calcld for C₁₈H₃₅N₂O₃Si 372.2206; found 372.2206.

(1S⁺,10S⁺)-5-(t-Butyldimethylsilyloxy)-1-methoxy-9,13-dioxabicyclo[8.3.0]tridec-2,6-diyne (14b) and (1R⁺,10S⁺)-5-(t-Butyldimethylsilyloxy)-1-methoxy-9,13-dioxabicyclo[8.3.0]tridec-2,6-diyne (15b)

To a stirred suspension of NaH (120 mg, 5.00 mmol 20 eq.) in THF (100 mL) and H₂O (2.00 mL) was added to a solution of bromoalcohol (26) (104 mg, 0.250 mmol, 1.0 eq.) in THF (25.0 mL) dropwisely at room temperature over 30 min. After being stirred at the same temperature for 6 h, the reaction mixture was poured into saturated aqueous NH₄Cl solution and the aqueous layer was extracted with Et₂O twice. The combined organic layers were washed with brine, dried over Na₂SO₄ and filtered. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (5 – 10% EtOAc in hexane) to give
5-(t-butyldimethylsilyloxy)-1-methoxy-9,13-dioxabicyclo[8.3.0] tridec-2,6-diyne (14) (33.7 mg, 0.110 mmol, 44%, mixture of two diastereomers)

Trans isomer 14b; $^1$H NMR (400 MHz, CDCl$_3$) δ 4.78 (brs, 1H), 4.40 (dd, $J = 16.6, 2.4$ Hz, 1H), 4.27 (dt, $J = 10.6, 9.3$ Hz, 1H), 4.17 (dd, $J = 16.6, 2.4$ Hz, 0.5 H), 4.15 (dd, $J = 16.6, 2.4$ Hz, 0.5 H), 3.99-3.88 (m, 2H, d), 3.42 (s, 1.5H), 3.40 (s, 1.5H), 2.69 (dd, $J = 16.9, 6.7$ Hz, 0.5H), 2.61 (dd, $J = 17.0, 6.7$ Hz, 1H), 2.51 (dd, $J = 16.9, 6.7$ Hz, 0.5H), 2.26-2.17 (m, 1H), 0.89 (s, 9H), 0.88 (s, 4.5 H), 0.13 (s, 1.5 H), 0.12 (s, 1.5H), 0.10 (s, 1.5H), 0.09 (s, 1.5H); $^{13}$C NMR (99.5 MHz, CDCl$_3$) δ 99.5, 99.2, 88.4, 88.3, 87.5, 86.1, 86.0, 85.9, 85.7, 85.4, 83.4, 83.1, 64.3, 64.2, 63.8, 63.5, 60.1, 59.8, 51.1, 51.0, 30.1, 29.9, 28.3, 27.6, 25.8, 25.7, 18.2, 18.1, −4.5, −4.6, −4.8, −4.9; FT-IR (neat) 2930, 2856, 1729, 1471, 1349, 1255, 1084, 1031, 1007, 839, 779, 669 cm$^{-1}$; HRMS (ESI-TOF): [M+NH$_4$]$^+$ calcd for C$_{18}$H$_{32}$N$_1$O$_4$Si$_1$ 354.2101; found 354.2101.

Cis isomer 15b; $^1$H NMR (400 MHz, CDCl$_3$) δ 4.78 (dt, $J = 4.5, 2.0$ Hz, 1H), 4.48 (dd, $J = 16.9, 2.0$ Hz, 1H), 4.13 (dt, $J = 8.1, 2.1$ Hz, 1H), 4.04 (dd, $J = 16.9, 2.9$ Hz, 1H), 3.90 (d, $J = 5.3$ Hz, 1H), 3.82 (dt, $J = 8.2, 2.0$ Hz, 1H), 3.33 (s, 3H), 2.64 (dd, $J = 8.0, 4.5$ Hz, 2H), 2.43-2.33 (m, 1H), 1.97-1.88 (m, 1H), 0.88 (s, 9H), 0.12 (s, 3H), 0.09 (s, 3H); $^{13}$C NMR (99.5 MHz, CDCl$_3$) δ 104.4, 89.7, 86.5, 85.1, 80.9, 66.3, 64.0, 61.3, 32.4, 30.8, 25.8, 18.1, −4.7, −4.9; FT-IR (neat) 2932, 2858, 1728, 1471, 1357, 1252, 1101, 839, 782, 670 cm$^{-1}$; HRMS (ESI-TOF): [M+NH$_4$]$^+$ calcd for C$_{18}$H$_{32}$N$_1$O$_4$Si$_1$ 354.2101; found 354.2103.
Synthesis of the 10-membered diyne 14a and 14a

A mixture of methylfuranoside (10) (2.70 g, 7.62 mmol, 1.0 eq.) and alcohol (11) (11.8 g, 38.0 mmol, 5.0 eq.) and pulverized activated MS-5A (3.81 g, 0.50 g/mmol) in dry CH₂Cl₂ (35 mL) was stirred for 30 min at room temperature under argon. Then the mixture was added a solution of PPTS (955 mg, 0.380 mmol, 0.50 eq.) in dry CH₂Cl₂ (5.0 mL) at room temperature. After being stirred at room temperature for 15 h, the reaction mixture was poured into saturated aqueous NaHCO₃ solution and the aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with 1 M HCl, brine, saturated aqueous NaHCO₃ solution and brine, dried over MgSO₄, and filtered. After removal of the solvent, the resulting mixture was crystallized from EtOAc-hexane, filtered and the resulting filtrate was concentrated in vacuo. The residue was recrystallized from EtOAc-hexane twice, and the resulting residue was purified by flash column chromatography on silica gel (20 – 30% EtOAc in toluene) to give 2-(4-(2-(2-azidoethoxy)ethoxy)-5-methoxy-2-nitrobenzylxylo)-2-(4-(t-butyldimethylsilyloxy)-7-hydroxyhepta-1,5-diynyl)tetrahydro-furan-3-ol (12) as a colorless liquid (2.27g, 3.58 mmol, 47%, mixture of diastereomers).
1H NMR (400 MHz, CDCl₃) δ 7.74 (s, 1H), 7.14 (s, 1H), 5.12 (s, 2H), 4.58 (dd, J = 10.0, 6.8 Hz, 1H), 4.25-4.21 (6H), 3.98-3.94 (4H), 3.76 (t, J = 4.9 Hz, 2H), 3.42 (t, J = 4.9 Hz, 2H), 2.68-2.61 (m, 2H), 2.38-2.29 (m, 1H), 2.09-2.02 (m, 1H), 0.87 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H); 13C NMR (67.8 MHz, CDCl₃) δ 153.9, 146.7, 139.2, 130.4, 110.2, 109.9, 105.7, 85.9, 85.4, 83.9, 77.7, 76.2, 70.1, 69.4, 67.3, 63.0, 61.7, 56.2, 50.6, 31.6, 29.1, 25.5, 18.0, −4.7, −5.2; FT-IR (neat) 3405, 2929, 2857, 2103, 1579, 1521, 1462, 1327, 1277, 1217, 1072, 1028, 937, 838, 780, 667 cm⁻¹; HRMS (ESI-TOF): [M+H]⁺ calcd for C₂₉H₄₃N₄O₁₀Si₁Brₑ 635.2748; found 635.2748.

2-(4-(2-(2-Azidoethoxy)ethoxy)-5-methoxy-2-nitrobenzyloxy)-2-(7-bromo-4-(t-butyl-dimethylsilyloxy)hepta-1,5-diynyl)tetrahydrofuran-3-ol (13)

To a stirred solution of propargyl alcohol (12) (147 mg, 0.230 mmol, 1.0 eq.), CBr₄ (84.0 mg, 0.253 mmol, 1.1 eq.) and 2,6-lutidine (59.0 mL, 0.506 mmol, 2.2 eq.) in dry MeCN (1.5 mL) was added PPh₃ (72.4 mg, 0.276 mmol, 1.2 eq.) in several portions at 0 °C. After being stirred at room temperature for 15 min, the reaction mixture was poured into saturated aqueous NH₄Cl solution and the aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with water and brine, dried over Na₂SO₄, and filtered. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (30% EtOAc in hexane) to give 2-(4-(2-(2-azidoethoxy)ethoxy)-5-methoxy-2-nitrobenzyloxy)-2-(7-bromo-4(t-butyldimethylsilyloxy) -hepta-1,5-diynyl)tetrahydro-furan-3-ol (13) (132 mg, 0.189 mmol, 82%, mixture of diastereomers.)

1H NMR (400 MHz, CDCl₃) δ 7.74 (s, 1H), 7.15 (s, 1H), 5.12 (s, 2H), 4.58 (t, J = 8.0, Hz, 1H), 4.26-4.24 (4H), 3.98-3.89 (9H), 3.76 (t, J = 4.9 Hz, 2H), 3.42 (t, J = 4.9 Hz, 2H), 2.67 (d, J = 8.0 Hz, 2H), 2.40-2.31 (m, 1H), 2.10-2.02 (m, 1H), 0.88 (s, 9H), 0.14 (s, 3H), 0.11 (s, 3H); FT-IR (neat) 3405, 2929, 2857, 2103, 1759, 1520, 1327, 1277, 1217, 1171, 1071, 1028, 938, 838, 780, 755, 542 cm⁻¹; HRMS (ESI-TOF): [M+H]⁺ calcd for C₂₉H₄₃N₄O₁₀Si₁Br₁ 697.1826; found 697.1830.
To a stirred suspension of NaH (800 mg, 33.0 mmol 20 eq.) in THF (700 mL) and H₂O (5.0 mL) was added to a solution of bromoalcohol (13) (1.15 g, 1.65 mmol, 1.0 eq.) in THF (100 mL) dropwisely at room temperature over 2 h. After being stirred at room temperature for 3 h, the reaction mixture was poured into saturated aqueous NH₄Cl solution and the aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over Na₂SO₄ and filtered. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (20% EtOAc in toluene) to give (1RS,10S*)-1-(4-(2-(2-Azidoethoxy)ethoxy)-5-methoxy-2-nitrobenzoyloxy)-9,13-dioxabicyclo[8.3.0]tridec-2,6-diyne (14a) (292mg, 0.484 mmol, 30%) and (1'S,10'S*)-1-(4-(2-(2-Azidoethoxy)ethoxy)-5-methoxy-2-nitrobenzoyloxy)-5-(t-butyldimethylsilyl-oxy)-9,13-dioxabicyclo[8.3.0]tridec-2,6-diyne (15a) (117mg, 0.193 mmol, 12%).

Trans isomer 14a; ¹H NMR (400 MHz, CDCl₃) δ 7.76 (s, 1H), 7.50 (s, 1H), 5.19 (s, 1H), 5.17 (s, 1H), 4.78 (t, J = 7.3 Hz, 0.75H), 4.66 (t, J = 5.9 Hz, 0.25H), 4.44-4.31 (m, 2H), 4.24 (t, J = 4.9 Hz, 2H), 4.01 (s, 3H), 4.00-3.95 (m, 2H), 3.92 (t, J = 4.9 Hz, 2H), 3.75 (t, J = 5.3 Hz, 2H), 3.42 (t, J = 5.3 Hz, 2H), 2.67-2.54 (m, 1H), 2.47-2.38 (m, 1H), 2.36-2.16 (m, 2H); ¹³C NMR (67.8 MHz, CDCl₃) δ 154.1, 154.0, 146.5, 138.8, 132.2, 132.3, 110.6, 110.5, 109.8, 99.5, 99.2, 88.6, 87.8, 87.0, 86.8, 85.9, 85.1, 83.2, 83.0, 70.3, 69.5, 69.0, 64.6, 64.5, 63.5, 63.3, 63.2, 60.1, 59.8, 56.3, 56.2, 50.7, 30.1, 29.7, 28.5, 27.8, 25.7, 18.1, 4.8, 4.7, 5.0; FT-IR (neat) 2930, 2857, 2104, 1579, 1521, 1463, 1327, 839, 780 cm⁻¹; HRMS (ESI-TOF): [M+H]^+ caleld for C₂₉H₄₀N₄O₅Si₁ 617.2643; found 617.2650.

Cis isomer 15a; ¹H NMR (400 MHz, CDCl₃) δ 7.73 (s, 1H), 7.10 (s, 1H), 5.05 (s, 2H), 4.74 (t, J = 7.2 Hz, 1H), 4.52 (d, J = 17.0 Hz, 1H), 4.24 (t, J = 4.9 Hz, 2H), 4.17 (dd, J = 16.5, 8.0 Hz, 1H), 4.05 (d, J = 4.9 Hz, 1H), 4.02 (d, J = 17.0 Hz, 1H), 3.95 (m, 1H), 3.95 (s, 3H), 3.92 (t, J = 4.9 Hz, 2H), 3.75 (t, J = 5.3 Hz, 2H), 3.42 (t, J = 5.3 Hz, 2H), 2.67 (s, 1H), 2.63 (d, J = 2.4 Hz, 1H), 2.49-2.36 (m, 1H), 2.06-1.94 (m, 1H), 0.88 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ¹³C NMR (67.8 MHz, CDCl₃) δ 153.8, 146.9, 140.0, 139.7, 130.4, 110.6, 110.1, 108.8, 104.3, 89.5, 86.3, 86.0, 76.5, 71.6, 70.3, 69.5, 69.0, 67.0, 63.9, 62.7, 61.3, 56.7, 56.2, 50.7, 30.8, 29.7, 25.7, 25.7, 18.1, 4.8, 4.7, 4.9; FT-IR (neat) 2918, 2860, 2110, 1584, 1518, 1463, 1327, 1278, 1220, 1132, 1070, 1034, 929, 839, 780 cm⁻¹; HRMS (ESI-TOF): [M+H]^+ caleld for C₂₉H₄₁N₄O₅Si₁ 617.2643; found 617.2639.
$^1$H NMR of 14 and 15

14a

14b

15a

15b

8% NOE
Synthesis of enediyne 1

To a solution of TBS-ether (14) (120 mg, 0.194 mmol, 1.0 eq) in THF (2.0 mL) was added TBAF in THF (1.0 M, 2.00 mL, 2.00 mmol, 10 eq) at 0 °C. After being stirred at room temperature for 30 min, the reaction mixture was poured into saturated aqueous NH₄Cl solution and the aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over Na₂SO₄ and filtered. After removal of the solvent, the residue was used for the next reaction without further purification.

To a solution of above residue and NEt₃ (220 mL, 1.55 mmol, 6.0 eq.) in dry CH₂Cl₂ (1.5 mL) was added MsCl (45.0 mL, 0.582 mmol, 3.0 eq.) at 0 °C. After being stirred at 0 °C for 30 min, the reaction mixture was poured into saturated aqueous NH₄Cl solution and the aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over Na₂SO₄ and filtered. After removal of the solvent, the residue was used for the next reaction without further purification.

To a solution of above residue in THF (1.0 mL) was added DBU (150 mL, 1.00 mmol, 5.0 eq.) at room temperature. After being stirred at room temperature, for 5 min the reaction mixture was poured into saturated aqueous NH₄Cl solution and the aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over Na₂SO₄ and filtered. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (15% EtOAc in toluene) to give (1R⁺,10S⁻)-(Z)-1-(4-(2-Azidoethoxy)ethoxy)-5-methoxy-2-nitrobenzyloxy)-9,13-dioxabicyclo[8.3.0]tridec-4-en-2,6-diyne (1) (30.0 mg, 0.0623 mmol, 32% for 3 steps) as a white amorphous.

¹H NMR (400 MHz, CDCl₃) δ 7.76 (s, 1H), 7.48 (s, 1H), 5.98 (d, J = 9.9 Hz, 1H), 5.82 (d, J = 9.8 Hz, 1H), 5.23 (d, J = 16.6 Hz, 2H), 5.18 (d, J = 16.6 Hz, 1H), 4.60 (t, J = 10.2 Hz, 1H), 4.54 (d, J =
17.5 Hz, 1H), 4.43 (d, J = 17.5 Hz, 1H), 4.24 (t, J = 4.9 Hz, 2H), 4.00 (m, 2H), 3.97 (s, 3H), 3.92 (t, J = 4.9 Hz, 2H), 3.75 (t, J = 5.3 Hz, 2H), 3.42 (t, J = 5.3 Hz, 2H), 2.39-2.20 (m, 2H); 13C NMR (99.5 MHz, CDCl₃) δ 154.2, 146.6, 138.9, 131.9, 125.5, 122.2, 110.8, 109.9, 99.7, 88.1, 87.9, 87.5, 70.4, 69.6, 69.1, 64.3, 63.4, 60.6, 56.3, 50.8, 29.8; FT-IR (neat) 2923, 2106, 1579, 1519, 1325, 1277, 1218, 1104, 1071, 1027, 876, 803, 739 cm⁻¹; HRMS (ESI-TOF): [M+NH₄]⁺ calcd for C₂₃H₂₈N₅O₈ 502.1938; found 502.1935.

3-(2-Hydroxyethyl)-3,4-tetrahydro-1H-isochroman-4-one (16)

To a solution of 10-membered enediyne (1) (4.20 mg, 13.0 mmol) in THF (1.50 mL) and H₂O (0.150 mL) was irradiated with 400 W high-pressure mercury lamp (Riko kagaku sangyo) through a Vycor filter at 5 °C. After being irradiated at 5 °C for 90 min, the reaction mixture was stirred at room temperature for 30 min. After removal of solvent, the residue was purified by flash column chromatography on silica gel (30% EtOAc in hexane) to give 3-(2-hydroxyethyl)-3,4-tetrahydro-1H-isochroman-4-one (16) (0.60 mg, 3.10 mmol, 25%).

¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, J = 7.5 Hz, 1H), 7.57 (dd, J = 7.5 Hz, 1H), 7.42 (dd, J = 7.5 Hz, 1H), 7.42 (dd, J = 7.5 Hz, 1H), 4.95 (s, 2H), 4.37 (dd, J = 6.2, 4.4 Hz, 1H), 3.88 (t, J = 5.8 Hz, 2H), 2.39-2.34 (m, 1H), 2.17-2.08 (m, 1H); FT-IR (neat) 3358, 2924, 2853, 1697, 1604, 1458, 1284, 1260, 1110, 1055, 801, 754 cm⁻¹; HRMS (ESI-TOF): [M+H]⁺ calcd for C₁₁H₁₅O₅ 193.0867; found 193.0866.
Huisgen [3+2] cycloaddition of the 10-membered enediyne 1 N-benzyl 4-pentyanoamide.

To a solution of the 10-membered enediyne 1 (2.0 mg, 4.1 mmol, 1.2 eq.) and N-benzyl 4-pentyanoamide (0.65 mg, 3.4 mmol, 1.0 eq.) in 2-methyl-2-propanol (0.20 mL) and H₂O (0.20 mL) was added 0.5 M aqueous solution of sodium ascorbate (14 mL, 7.0 mmol, 2.0 eq.) and 0.5 M aqueous solution of CuSO₄ (7.0 mL, 3.5 mmol, 1.0 eq.) at room temperature. After being stirred at room temperature for 4 h, the reaction mixture was poured into pH 8 aqueous NH₄Cl-NH₄OH buffer and the aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over Na₂SO₄ and filtered. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (40% acetone in toluene) to give click product (5-24) (1.6 mg, 2.4 mmol, 60%) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.73 (s, 1H), 7.59 (s, 1H), 7.50 (s, 1H), 7.30-7.18 (m, 5H), 6.00 (d, J = 9.7 Hz, 1H), 5.83 (d, J = 9.7 Hz, 1H), 5.20 (d, J = 5.8 Hz, 2H), 4.60 (t, J = 8.2 Hz, 1H), 4.58-4.51 (m, 3H), 4.43 (d, J = 18.0 Hz, 1H), 4.38 (d, J = 5.8 Hz, 2H), 4.18 (t, J = 4.3 Hz, 2H), 4.02-3.93 (m, 7H), 3.84 (t, J = 4.3 Hz, 2H), 3.10 (t, J = 4.3 Hz, 2H), 2.39-2.20 (m, 2H); FT-IR (neat) 3710, 2923, 2852, 2331, 1665, 1518, 1453, 1276, 1070, 1026, 850, 813, 736, 623 cm⁻¹; HRMS (ESI-TOF): [M+H]⁺ calcd for C₃₅H₃₈N₅O₉ 672.2670; found 672.2672.

Enediyne-polyamide hybrid (20)

To a solution of 10-membered enediyne (5-8) (5.3 mg, 11 mmol, 1.5 eq.) and alkyne (5-29) (10 mg, 7.3 mmol, 1.0 eq.) in 2-methyl-2-propanol (0.40 mL) and H₂O (0.40 mL) was added 0.5 M aqueous
solution of sodium ascorbate (30.0 mL, 15.0 mmol, 2.1 eq.) and 0.5 M aqueous solution of CuSO$_4$ (15.0 mL, 7.5 mmol, 1.1 eq.) at room temperature. After being stirred at room temperature for 2 h, the reaction mixture was concentrated in vacuo. The residue was dissolved in 50% aqueous MeCN and purified by reversed phase liquid HPLC (Inertsil ODS-3, 3 mm, 10 x 250 mm, 2 mL/min, with a linear gradient: 0.00 min [A]:[B]=95:5, 25.0 min [A]:[B]=60:40, 27.0 min [A]:[B]=10:90, 30.00 min [A]:[B]= 90:10, 32.00 min [A]:[B]=95:5, 0.1% formic acid in H$_2$O as solvent A, 0.1% formic acid in MeCN as solvent B, $t_R=21.4$ min) to give the enediyne-polyamide hybrid 20 (8.1 mg, 4.4 mmol, 60%) as a white solid.

HRMS (ESI-TOF): [M+NH$_4$]$^+$ calcd for C$_{89}$H$_{108}$N$_{27}$O$_{20}$ 1874.8264; found 1874.8220.

Plasmid DNA Cleavage Experiment

100 ng of supercoiled (form I) pGEX-4T-1 plasmid (GE Healthcare) and compounds 1 or 20 in DMSO were mixed in 25 mM Tris-HCl buffer (pH =7.4). The final volume was 10 mL containing 10% DMSO. 302/365 nm of UV irradiation was performed by using 3UV transilluminator NLMS-20E (6.4 mW/cm$^2$ at 302 nm and 6.7 mW/cm$^2$ at 365 nm) at room temperature. After UV irradiation, samples were electrophoresed on a 1% agarose gel in 0.5 x TBE buffer. The gel bands were stained by ethidium bromide and visualized by using LAS-3000 (Fujifilm).

(The gel band intensities were quantified by NIH ImageJ software. A correction factor of 1.47 was used for the supercoiled DNA (form I) assessment because intercalation of ethidium bromide to form I DNA is relatively weak as compared to that of nicked (form II) DNA.)
The transition state structures of TS-A and TS-B were optimized by density functional theory (B3LYP/6-31G(d)). The transition states were verified by only one imaginary frequency whose vibration indicating that it connects reactant and product. All the calculations were carried out using Gaussian03 program on TSUBAME super computer at Tokyo institute of Technology.

**TS-A**

Imaginary frequency: $475i \text{ cm}^{-1}$

Total energy = -650.623643 Hartree

Optimized geometry:

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**TS-B**

Imaginary frequency: $894i \text{ cm}^{-1}$

Total energy = -650.633109 Hartree

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\[ 14a \]
**Acquisition Parameters**

- **File Name**: tanaka090002_cyclize
- **Author**: JEOL LTD.
- **Sample ID**: 13C
- **Contact**: Single Pulse with Br
- **Creation Date**: 2-AUG-2009 10:17:38
- **Revision Date**: 2-AUG-2009 11:15:35
- **Spec Site**: RCP400SL

**Spec Type**: DELTA_MNR
**Data Format**: 1D COMPLEX
**Dimensions**: X
**Dim Title**: 13C
**Dim Size**: 32768
**Dim Units**: [ppm]
**Actual start time**: 2-AUG-2009 10:17:39
**Delay of start**: 0[s]
**Digital_filter**: FALSE
**End_time**: 5-AUG-2009 02:31:37
**Experiment**: single_pulse_mode
**Field_strength**: 9.281736[T]
**Filter_mode**: BUTTERWORTH
**Filter_width**: 12.4682793[kHz]
**Irr_code**: 146
**Irr_Domain**: 16
**Irr_freq**: 395.88252601[MHz]
**Irr_noise**: WAUGH
**Irr_offset**: 5[ppm]
**Irr_pwidth**: 40[us]
**Iterations**: 1
**Local_time**: 2-AUG-2009 10:17:39
**Obs_noise**: WAUGH
**Obs_pwidth**: 1[us]
**Proclda**: 2692
**Recvr_gain**: 30
**Relaxation_delay**: 0[s]
**Scans**: 187
**Solvent**: CHLOROFORM-D
**Spin_get**: 16[Hz]
**Spin_lock_90**: 1[us]
**Spin_lock_atta**: 29[dsn]
**Temp_get**: 28[OC]
**X0**: 10[us]
**X_acq_duration**: 1.333968[s]
**X_angle**: 30[deg]
**X_domain**: 13C
**X_freq**: 99.54737033[MHz]
**X_offset**: 100[ppm]
**X_points**: 32768
**X_prescans**: 4
**X_pulse**: 3.33333333[us]
**X_resolution**: 0.76103686[Hz]
**X_sweep**: 26.93759586[kHz]
**Tri**: 0
**Tri_noise**: WAUGH
**Tri_pwidth**: 1[us]
**Qua90**: 10[us]
**Qua_noise**: WAUGH
**Qua_pwidth**: 1[us]

**X**: parts per Million: 13C