Supporting Information for

“Independent Generation of 5-(2’-deoxycytidinyl)methyl Radical and the Formation of a Novel Crosslink Lesion between 5-methylcytosine and Guanine”

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1. Characterization of products isolated from 254-nm irradiation of d(mC\textsubscript{SPh}\textsuperscript{G}) and d(GmC\textsubscript{SPh}).

\textbf{d(mC\textsuperscript{G})}: \textsuperscript{1}H NMR (D\textsubscript{2}O): \(\delta 6.64 (s, 1H), 6.14 \text{ and } 6.06 (m, 2H), 5.03 (m, 1H), 4.31 (m, 1H), 4.22-3.83 (m, 6H), 3.55 (m, 2H), 2.47 (m, 4H). HRMS (ESI-FTICR) calcd 569.1510 [M + H]\textsuperscript{+}, found 569.1513; calcd 567.1353 [M - H]\textsuperscript{-}, found 567.1340. Negative-ion ESI-MS/MS (Figure S9 a).

\textbf{d(mCG)}: \textsuperscript{1}H NMR (D\textsubscript{2}O): \(\delta 8.06 (s, 1H), 7.44 (s, 1H), 6.25 (t, J = 6.7 Hz, 1H), 6.13 (m, 1H), 4.21 (m, 1H), 4.10 (m, 3H), 3.69 (m, 2H), 3.10 (m, 2H), 2.83-2.34 (m, 4H), 1.96 (s, 3H). HRMS (ESI-FTICR) calcd 571.1666 [M + H]\textsuperscript{+}, found 571.1651; calcd 569.1510 [M - H]\textsuperscript{-}, found 569.1501. Negative-ion ESI-MS/MS (Figure S10 a).

\textbf{d(FCG)}: \textsuperscript{1}H NMR (D\textsubscript{2}O) (Figure S5): \(\delta 9.49 (s, 1H), 8.63 (s, 1H), 8.07 (s, 1H), 6.27 (t, J = 6.2, 6.7 Hz, 1H), 6.06 (t, J = 6.2 Hz, 1H), 4.20 (m, 2H), 4.11 (m, 2H), 3.74 (m, 4H), 2.82 (m, 2H), 2.55 (m, 2H). HRMS (ESI-FTICR) calcd 585.1459 [M + H]\textsuperscript{+}, found 585.1479; calcd 583.1302 [M - H]\textsuperscript{-}, found 583.1328. Negative-ion ESI-MS/MS (Figure S10 b).

\textbf{d(HMC\textsuperscript{G})}: \textsuperscript{1}H NMR (D\textsubscript{2}O) (Figure S6): \(\delta 8.05 (s, 1H), 7.68 (s, 1H), 6.26 (t, J = 6.7, 7.2 Hz, 1H), 6.13 (m, 1H), 4.45 (m, 2H), 4.22 (m, 1H), 4.10 (m, 3H), 3.68 (m, 2H), 3.09 (m, 2H), 2.85-2.35 (m, 4H). HRMS (ESI-FTICR) calcd 585.1459 [M - H]\textsuperscript{-}, found 585.1462. Negative-ion ESI-MS/MS (Figure S10 c).

\textbf{d(G\textsuperscript{mC})}: \textsuperscript{1}H NMR (D\textsubscript{2}O): \(\delta 7.96 (s, 1H), 6.34 (m, 2H), 4.98 (t, J = 4.6, 5.1 Hz, 1H), 4.82 (m, 1H), 4.46 (m, 2H), 4.26(d, J = 16.4 Hz, 1H), 4.20 (d, J = 3.1 Hz, 2H), 4.03
(d, J = 15.9 Hz, 1H), 3.84 (d, J = 2.6 Hz, 2H), 2.45 and 2.32 (m, 4H). HRMS (ESI-FTICR) calcd 569.1510 [M + H]^+, found 569.1492; calcd 567.1353 [M - H]^{-}, found 567.1359. Negative-ion ESI-MS/MS and MS^n (Figure S9 b&c).

d(GmC): $^1$H NMR (D$_2$O) (Figure S7): δ 7.97 (s, 1H), 7.61 (s, 1H), 6.30 (t, J = 6.7 Hz, 1H), 6.20 (t, J = 6.2 Hz, 1H), 4.31-4.08 (m, 4H), 3.86 (m, 2H), 3.06 (m, 2H), 2.77 (m, 2H), 2.32 (m, 2H), 1.72 (s, 3H). HRMS (ESI-FTICR) calcd 569.1510 [M - H]^{-}, found 569.1492. Negative-ion ESI-MS/MS (Figure S11 a).

d(G$^{HM}$C): $^1$H NMR (D$_2$O) (Figure S8): 7.98 (s, 1H), 7.82 (s, 1H); 6.27 (m, 2H); 4.33-4.09 (m, 6H), 3.84 (m, 2H), 3.06 (m, 2H), 2.75 (m, 2H), 2.43 and 2.33 (m, 2H). HRMS (ESI-FTICR) calcd 585.1459 [M - H]^{-}, found 585.1447. Negative-ion ESI-MS/MS (Figure S11 b).
2. List of Figures in the Supporting Information:

Figure S1. $^1$H NMR of $^5$ in DMSO-$d_6$.

Figure S2. $^1$H NMR of d(mC$^{Sp}$G) (7) in D$_2$O.

Figure S3. $^1$H NMR of $^{10}$ in DMSO-$d_6$.

Figure S4. $^1$H NMR of d(GmC$^{Sp}$) (12) in D$_2$O.

Figure S5. $^1$H NMR of d($^F$CG) in D$_2$O.

Figure S6. $^1$H NMR of d($^{HM}$CG) in D$_2$O.

Figure S7. $^1$H NMR of d(GmC) in D$_2$O.

Figure S8. $^1$H NMR of d(G$^{HM}$C) in D$_2$O.

Figure S9. Product-ion spectra of the ESI-produced [M – H]$^-$ ions of d(mC$^G$) (a) and d(G$^m$C) (b). (c) MS$^3$ of ion of m/z 469 in (b).

Figure S10. Product-ion spectra of the ESI-produced [M – H]$^-$ ions of d(mCG) (a), d($^F$CG) (b), and d($^{HM}$CG) (c).

Figure S11. Product-ion spectra of the ESI-produced [M – H]$^-$ ions of d(GmC) (a) and d(G$^{HM}$C) (b).
Figure S1. $^1$H NMR of 5 in DMSO-$d_6$.

Figure S2. $^1$H NMR of d(mC$^{SPh}$G) (7) in D$_2$O.
Figure S3. $^1$H NMR of 10 in DMSO-$d_6$.

Figure S4. $^1$H NMR of d(GmC<sup>SPh</sup>) (12) in D<sub>2</sub>O.
Figure S5. $^1$H NMR of d(\text{\textsuperscript{\textit{F}}CG}) in D$_2$O.

Figure S6. $^1$H NMR of d(\text{\textsuperscript{\textit{HM}}CG}) in D$_2$O.
Figure S7. $^1$H NMR of d(GmC) in D$_2$O.

Figure S8. $^1$H NMR of d($^{15}$HC) in D$_2$O.
Figure S9. Product-ion spectra of the ESI-produced [M – H]- ions of d(mC^G) (a) and d(G^mC) (b). (c) MS^3 of ion of m/z 469 in (b).
Figure S10. Product-ion spectra of the ESI-produced [M – H]⁻ ions of d(mCG) (a), d((CG)) (b), and d(HMCG) (c).
Figure S11. Product-ion spectra of the ESI-produced \([M - H]^-\) ions of d(GmC) (a) and d(GHM'C) (b).