Supplementary Material

DNA alkylation promoted by an electron-rich quinone methide intermediate

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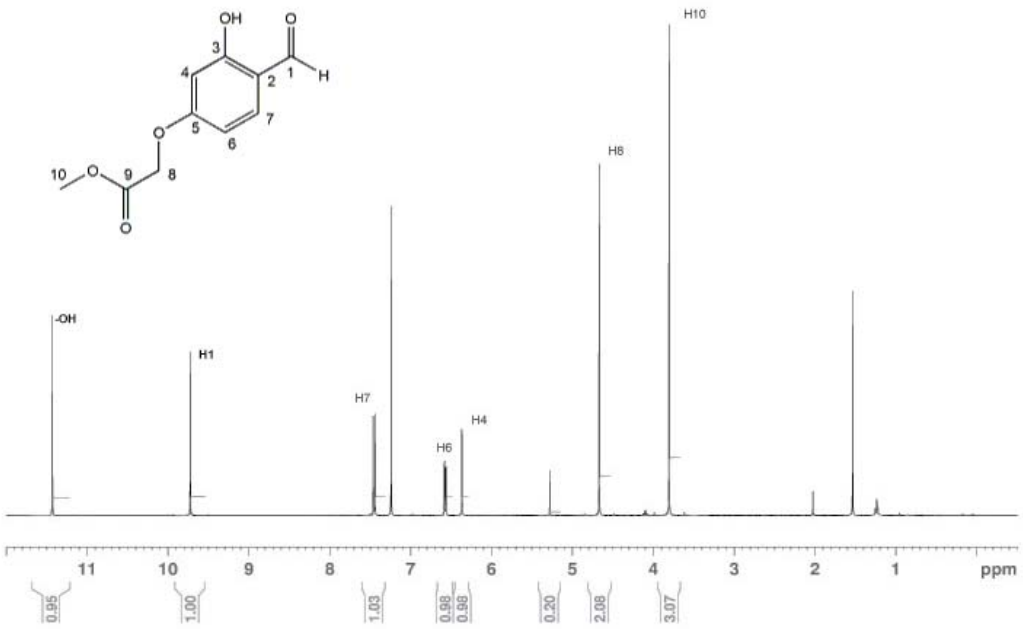
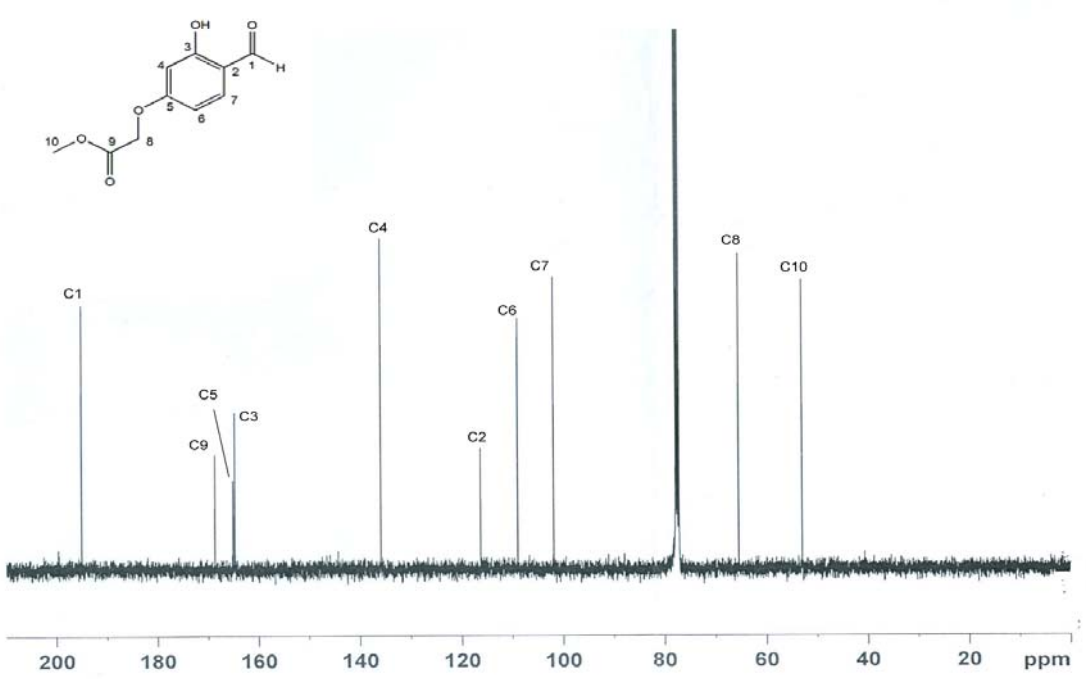
Appendix A

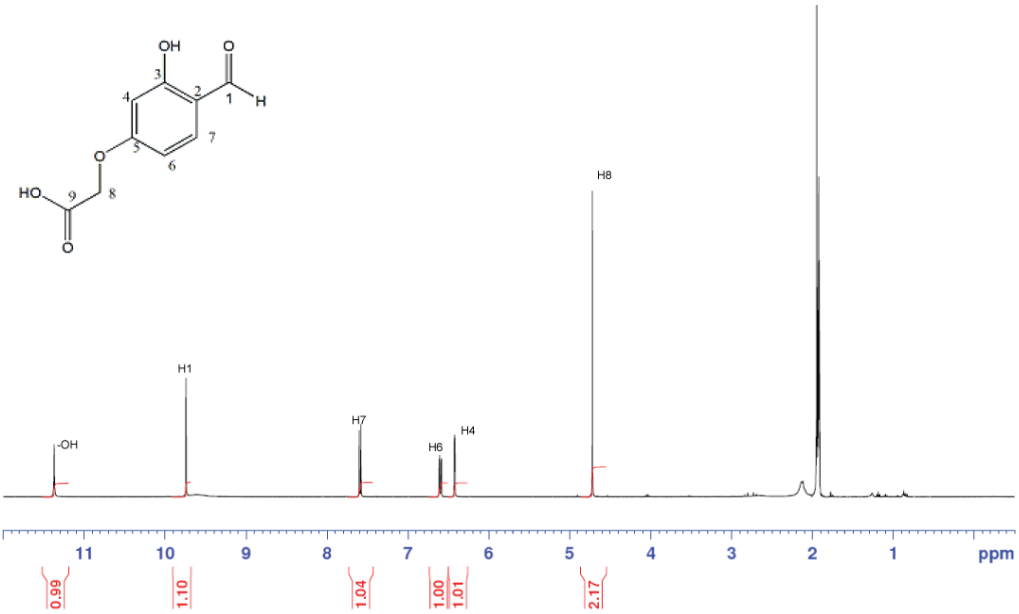
^{1}H NMR (400 MHz) spectrum of methyl 2-(4-formyl-3-hydroxyphenoxy)acetate (**2**) in CD_3CN



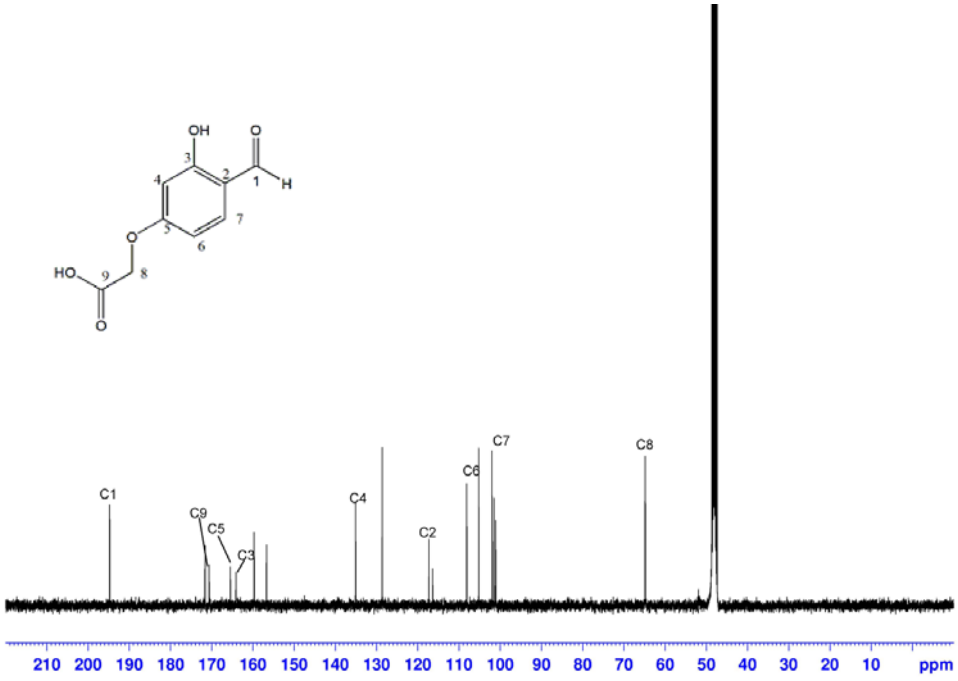
^{13}C NMR (100 MHz) spectrum of methyl 2-(4-formyl-3-hydroxyphenoxy)acetate (**2**) in CD_3CN



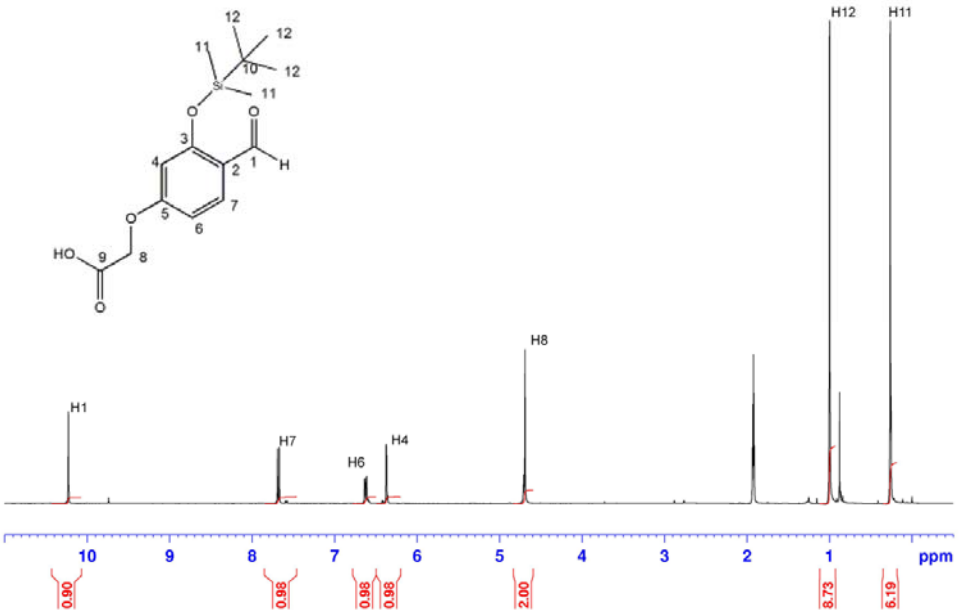
^{1}H NMR (400 MHz) spectrum of 2-(4-formyl-3-hydroxyphenoxy)acetic acid (**3**) in CD_3CN



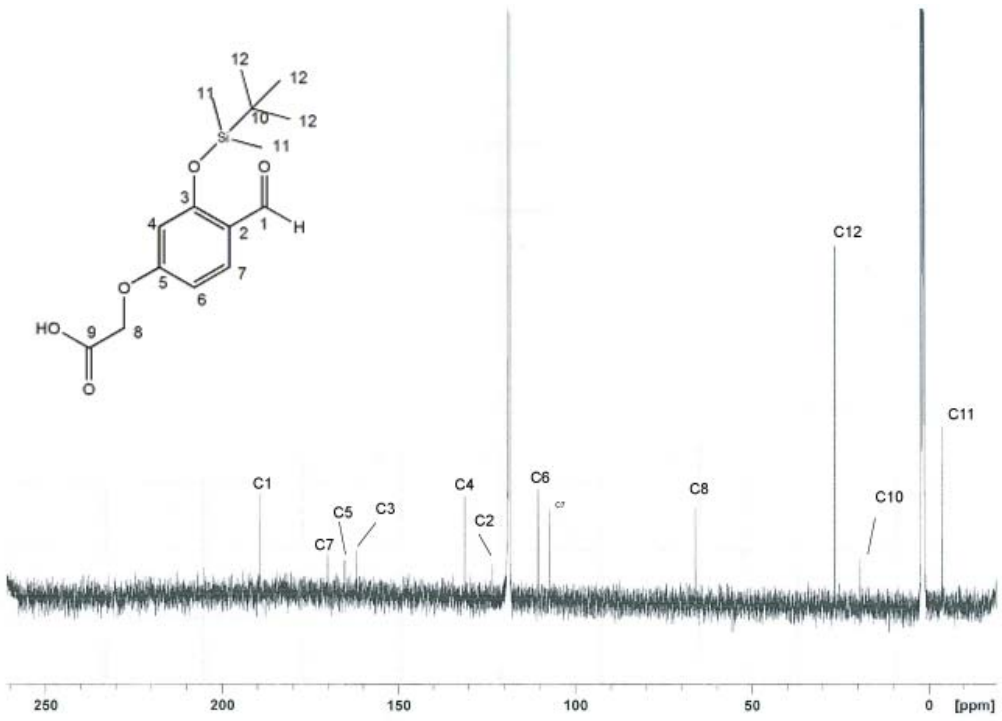
^{13}C NMR (125 MHz) spectrum of 2-(4-formyl-3-hydroxyphenoxy)acetic acid (**3**) in CD_3CN



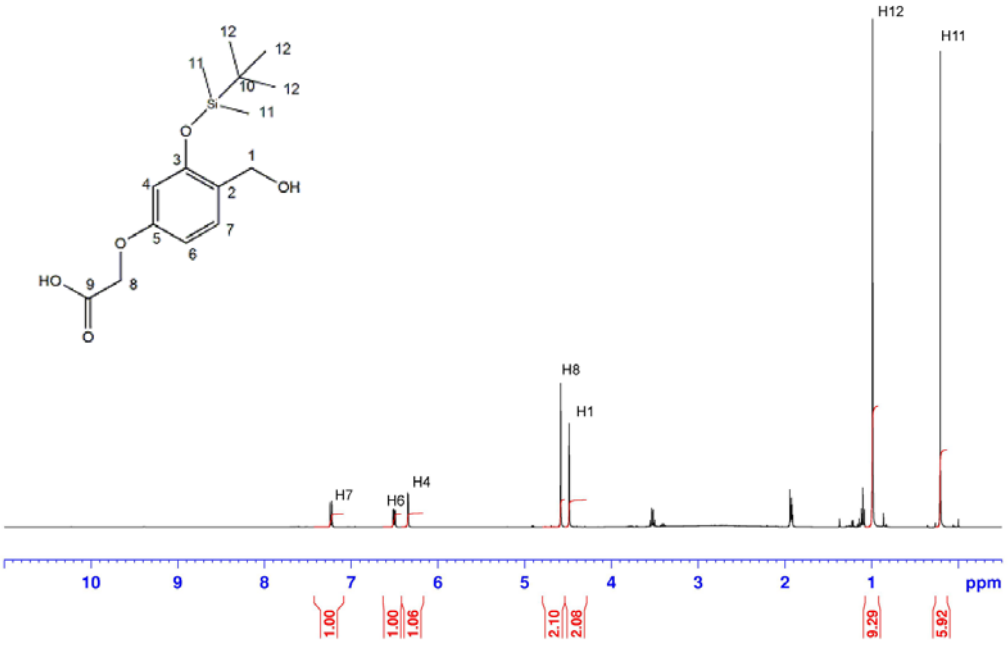
^{1}H NMR (400 MHz) spectrum of 2-(3-*tert*-butyldimethylsilyloxy-4-formylphenoxy)acetic acid (**4**) in CD_3CN



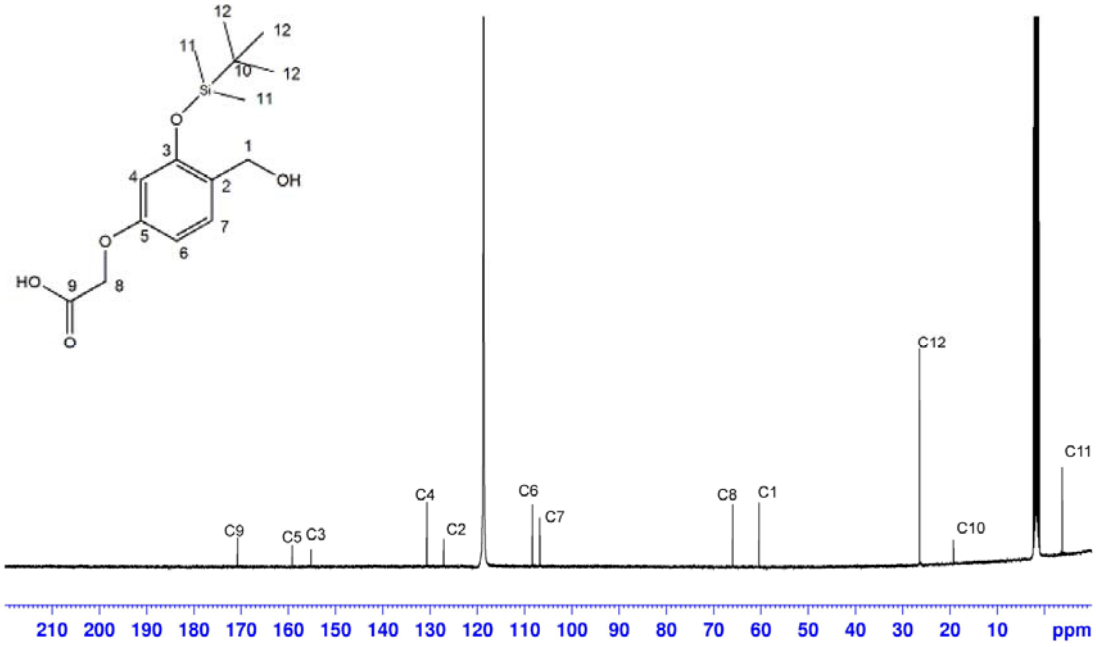
^{13}C NMR (125 MHz) spectrum of 2-(3-*tert*-butyldimethylsilyloxy-4-formylphenoxy)acetic acid (**4**) in CD_3CN



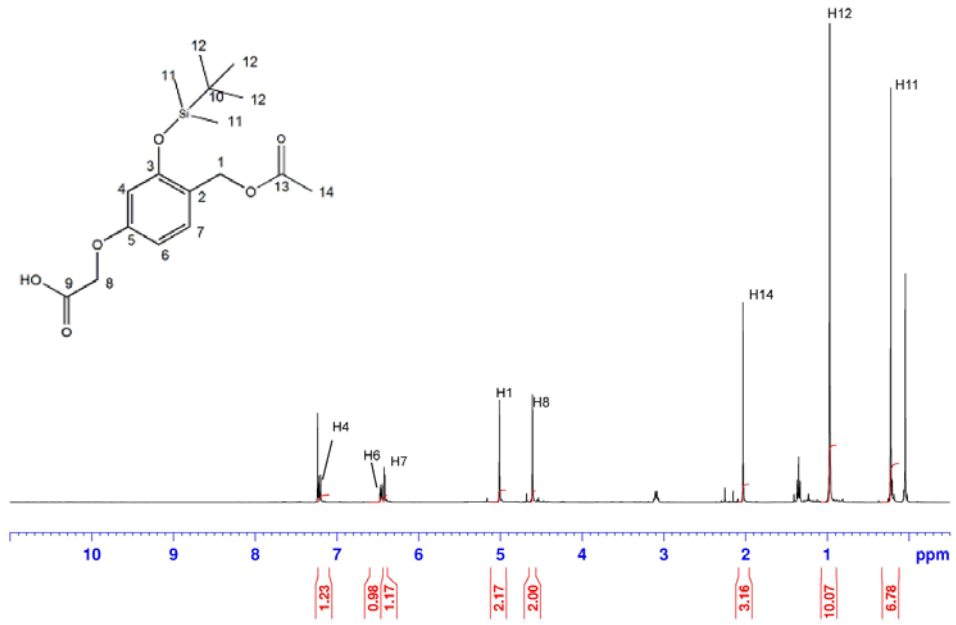
^{1}H NMR (400 MHz) spectrum of 2-(3-*tert*-butyldimethylsilyloxy-4-(hydroxymethyl)-phenoxy)acetic acid (**5**) in CD_3CN



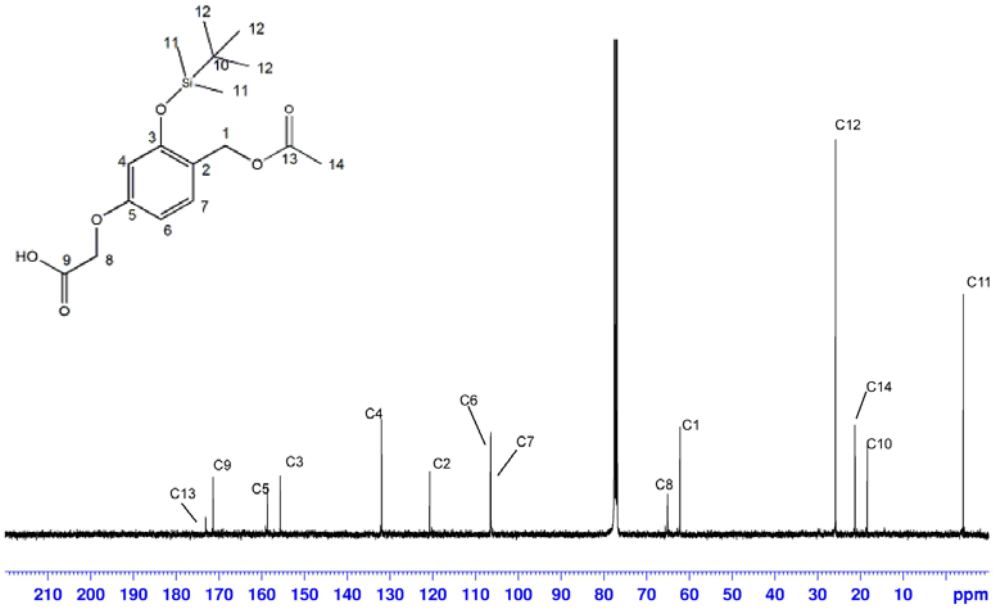
^{13}C NMR (100 MHz) spectrum of 2-(3-*tert*-butyldimethylsilyloxy-4-(hydroxymethyl)-phenoxy)acetic acid (**5**) in CD_3CN



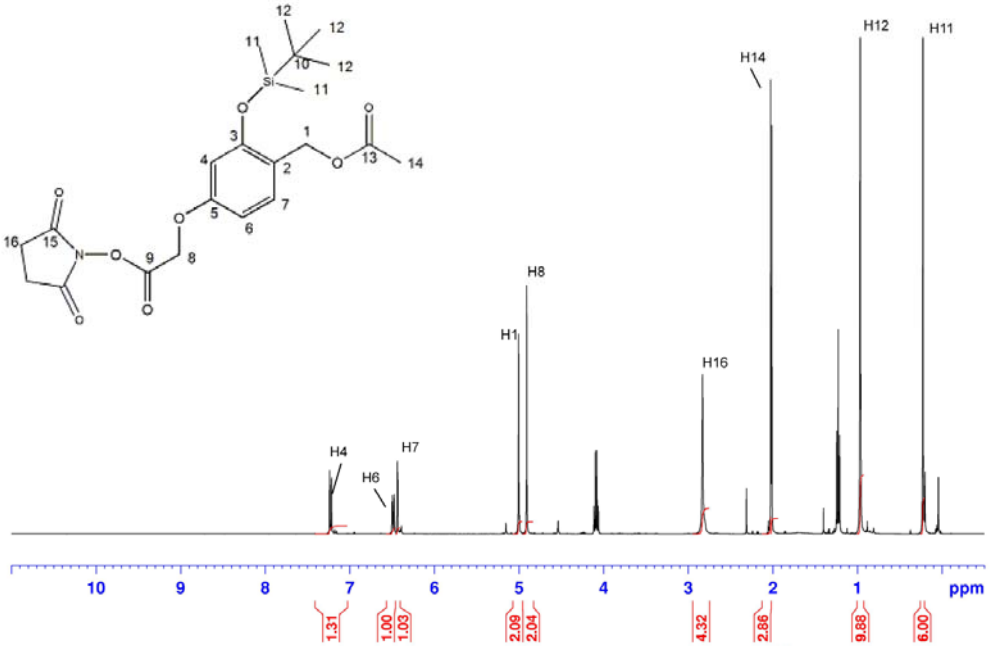
^{1}H NMR (400 MHz) spectrum of 2-(3-*tert*-butyldimethylsilyloxy-4-(acetoxymethyl)-phenoxy)acetic acid (**6**) in $CDCl_3$



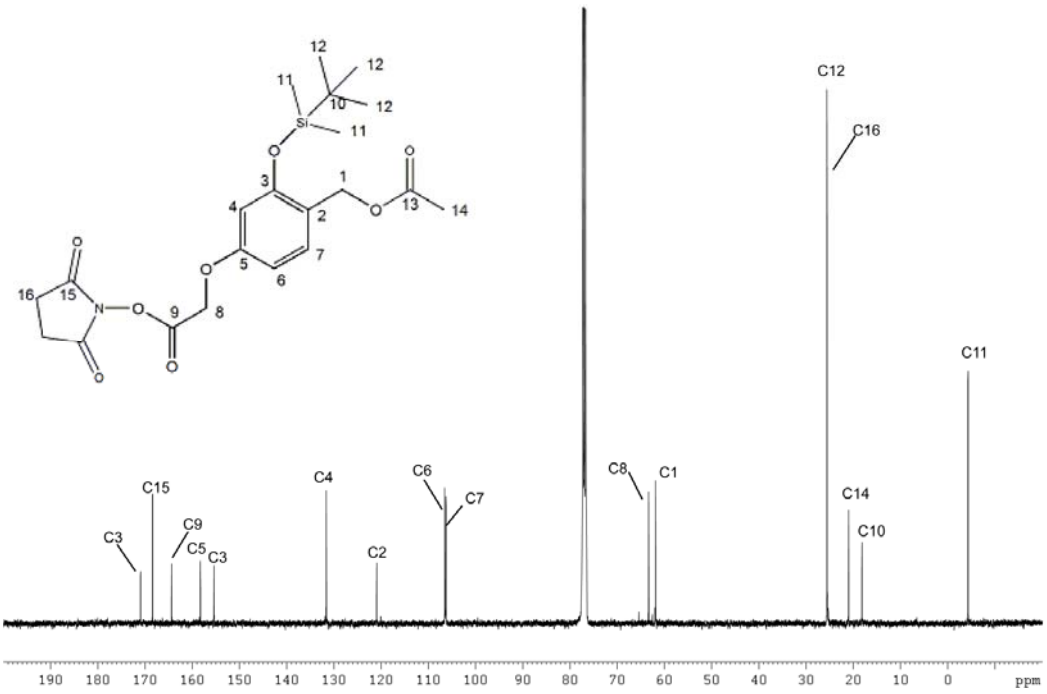
^{13}C NMR (100 MHz) spectrum of 2-(3-*tert*-butyldimethylsilyloxy-4-(acetoxymethyl)-phenoxy)acetic acid (**6**) in $CDCl_3$



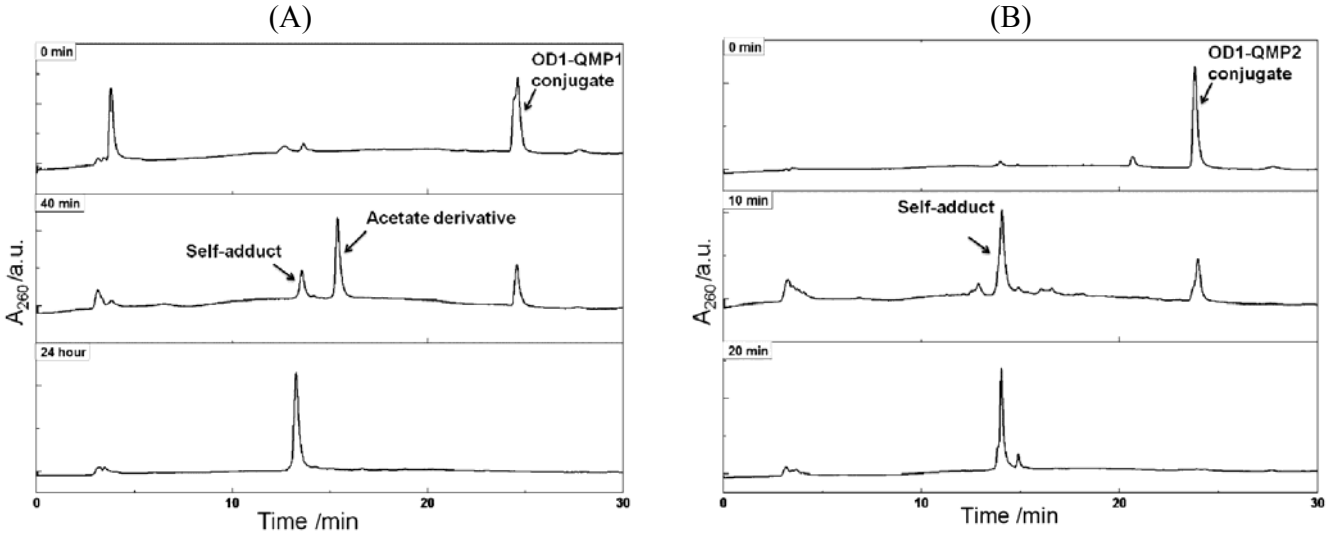
^{1}H NMR (400 MHz) spectrum of *N*-succinimidyl-2-(3-*tert*-butyldimethylsilyloxy-4-(acetoxymethyl)phenoxy) acetate (**7**) in $CDCl_3$



^{13}C NMR (125 MHz) spectrum of *N*-succinimidyl-2-(3-*tert*-butyldimethylsilyloxy-4-(acetoxymethyl)phenoxy) acetate (**7**) in CD_3CN

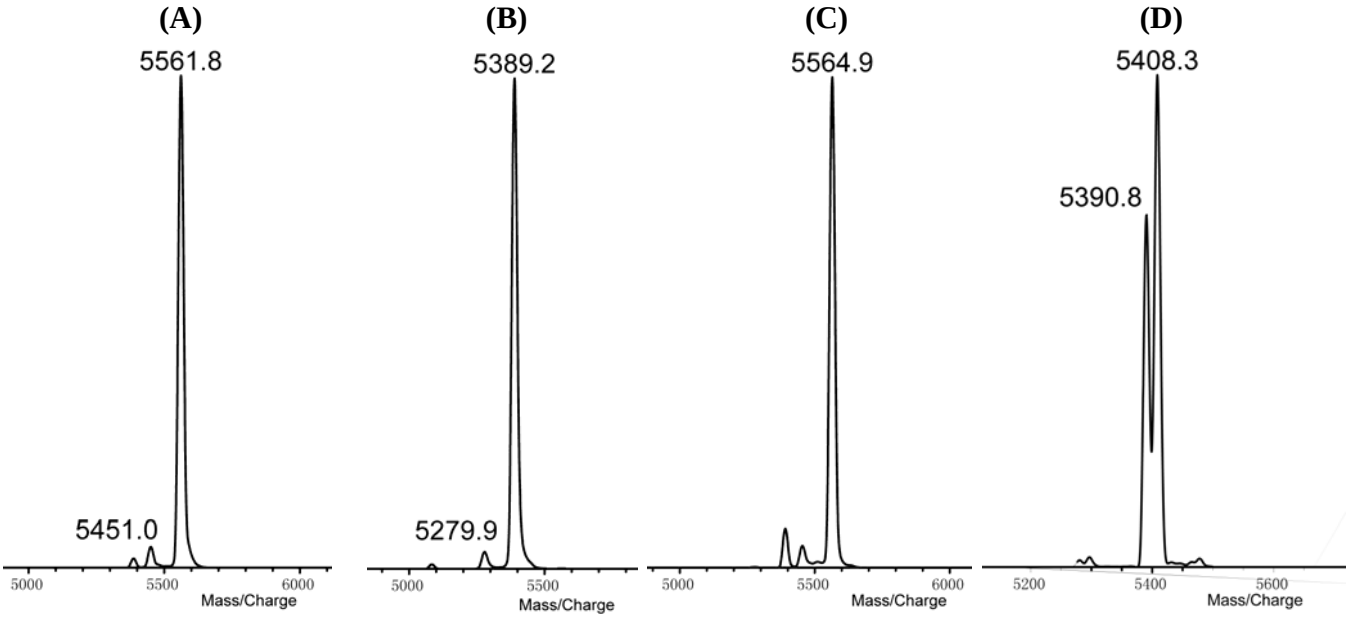


Appendix B



HPLC detection of self-adduct formation. (A) The DNA conjugate **OD1-QMP1** was treated with KF to generate the self-adduct (**OD1-QM1**) via a QM intermediate. Samples were analyzed by reverse phase chromatography at time of 0 min, 40 min and 24 h. The signal labeled acetate derivative lacks the TBDMS protecting group but has not yet eliminated the benzylic acetate to form the QM intermediate. (B) The electron rich conjugate **OD1-QMP2** was treated equivalently and analyzed after 0, 10 and 20 min. Samples were eluted with a linear gradient of 10–55% acetonitrile in aqueous triethylammonium acetate (50 mmol/L, pH 5.0) at 1 mL/min over 30 min.

Appendix C



MALDI-TOF analysis of (A) **OD1-QMP1 (**calc. *m/z* 5562.5), (B) **OD1-QM1** self-adduct (calc. *m/z* 5388.7) (C) **OD1-QMP2** (calc. *m/z* 5564.5) and (D) **OD1-QM2** self-adduct (calc. 5392.7). The *m/z* signal of 5408.3 corresponds to the water adduct of **OD1-QM2** (calc. mz 5409.7).