

Electronic Supporting Information for
**Small-molecule poly (ADP-ribose) polymerase (PARP) and PD-
L1 inhibitor conjugates as dual-action anticancer
agents**

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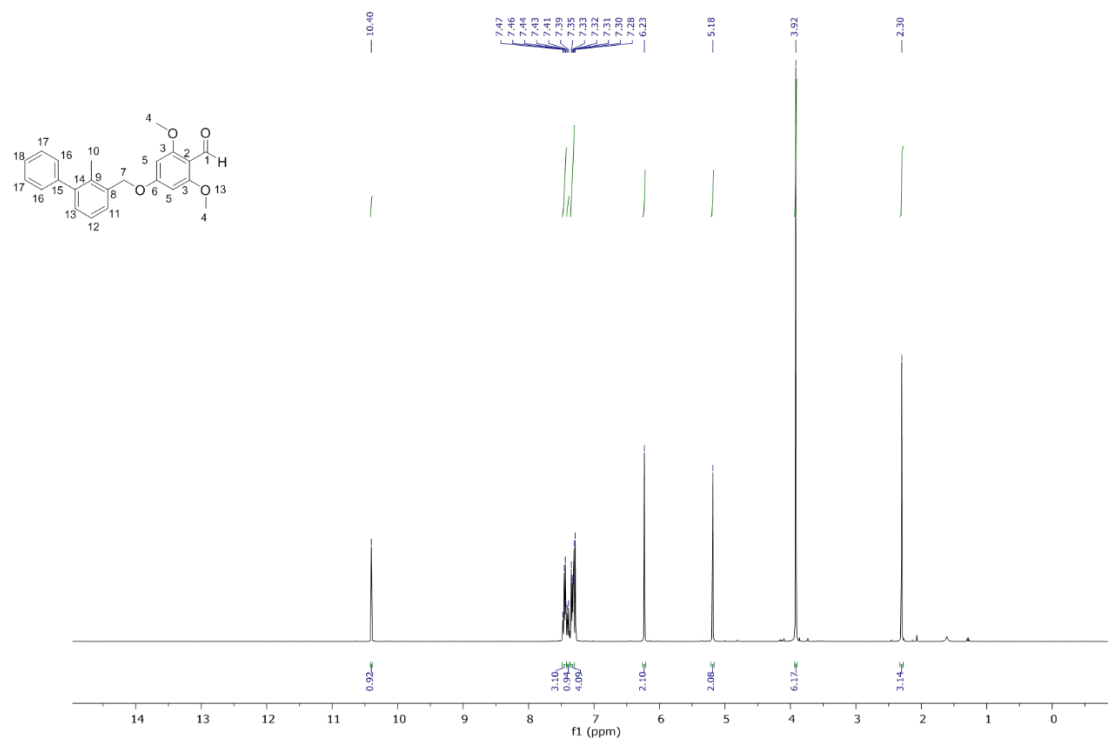


Figure S1. ^1H NMR spectrum of **6** (400 MHz, CDCl_3)

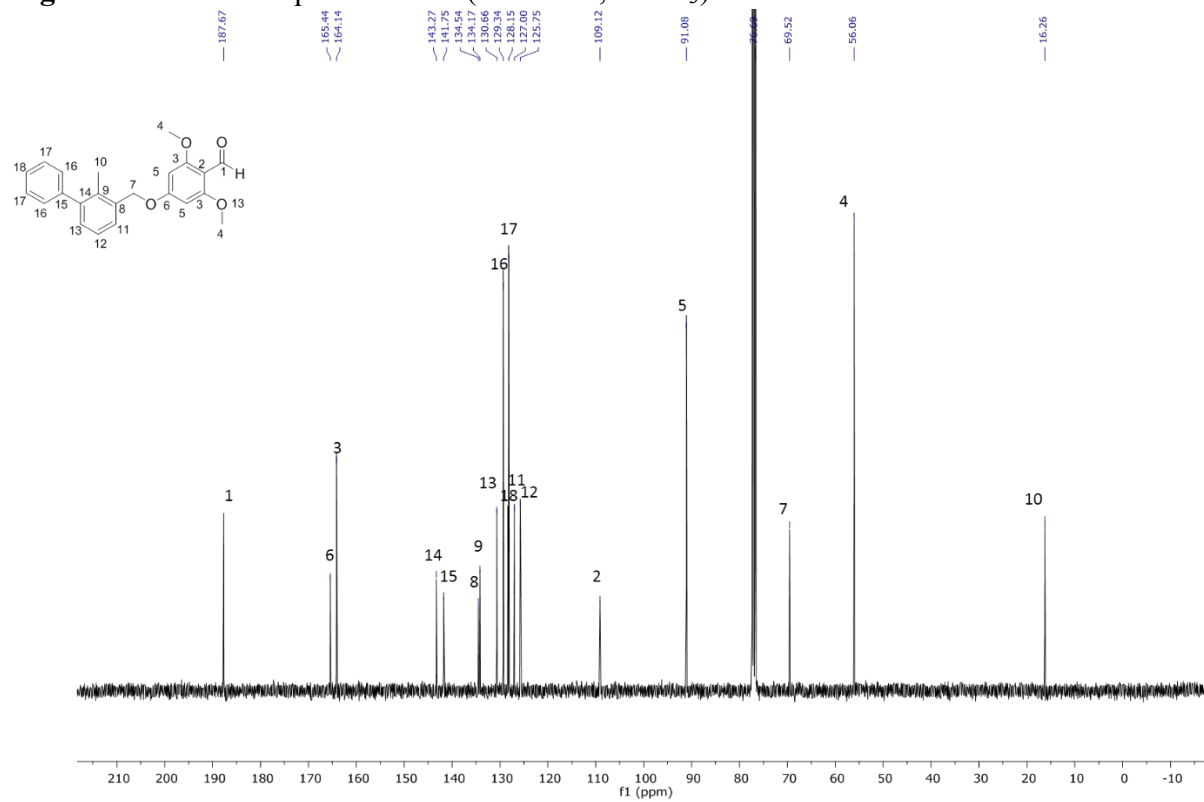


Figure S2. ^{13}C NMR spectrum of **6** (400 MHz, CDCl_3)

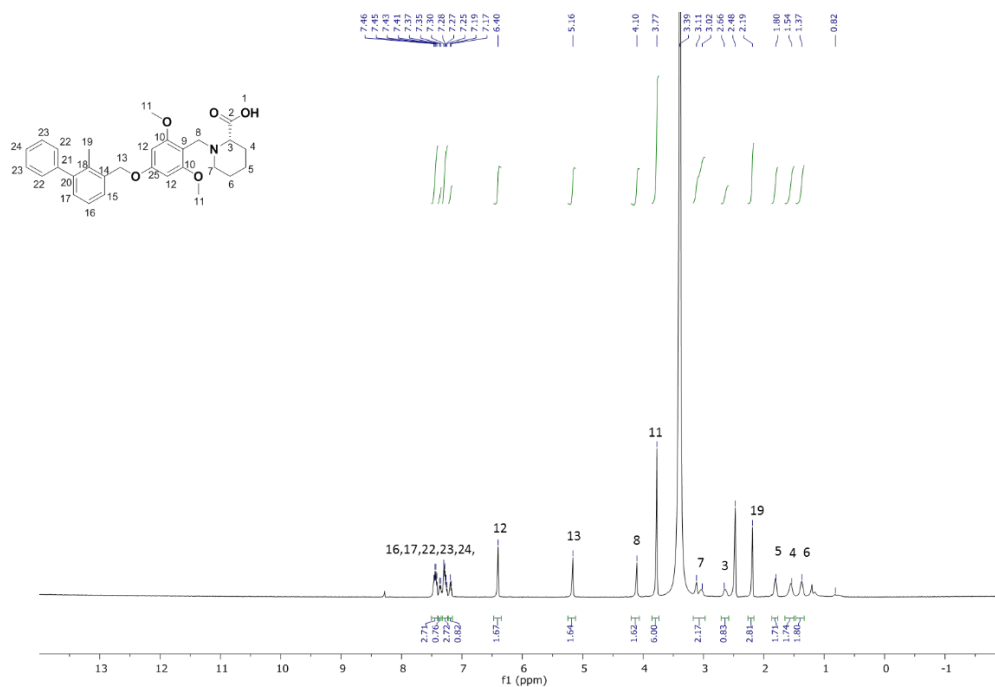


Figure S3. ^1H NMR spectrum of **8** (400 MHz, $\text{DMSO-}d_6$)

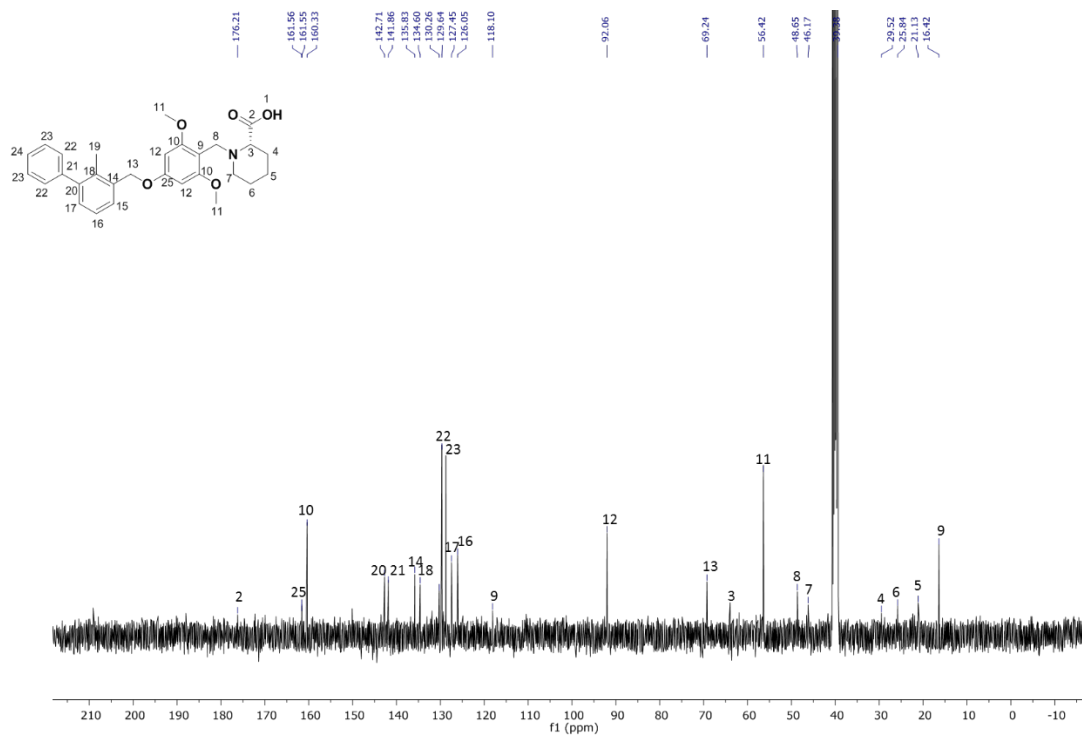


Figure S4. ^{13}C NMR spectrum of **8** (400 MHz, $\text{DMSO-}d_6$)

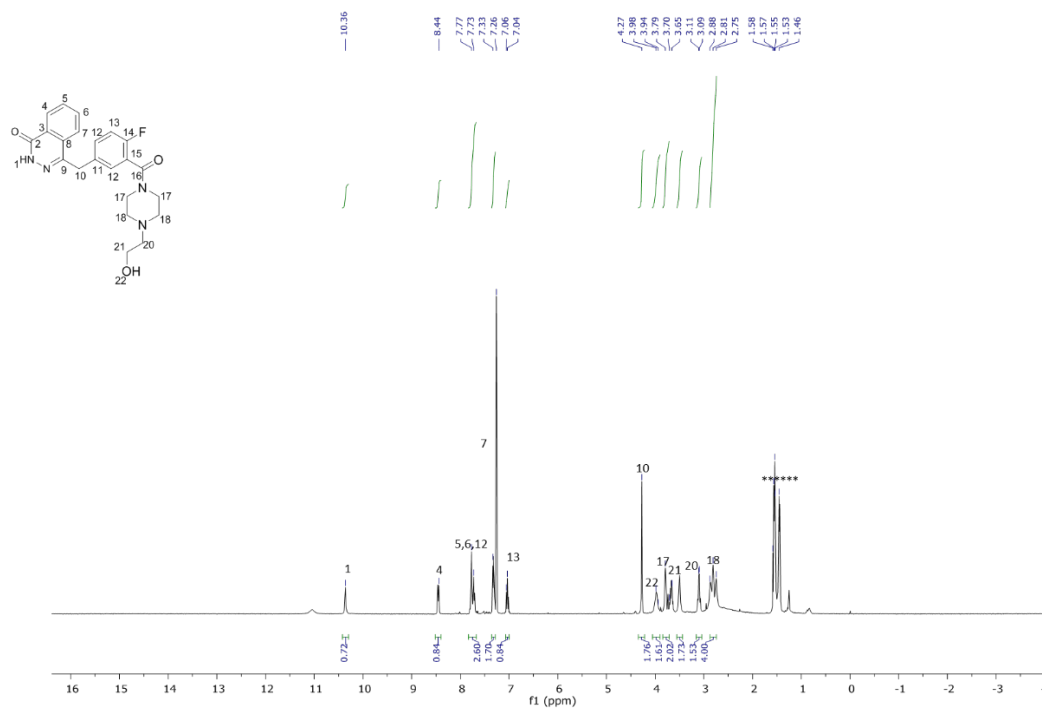


Figure S5. ¹H NMR spectrum of **11** (400 MHz, CDCl₃)

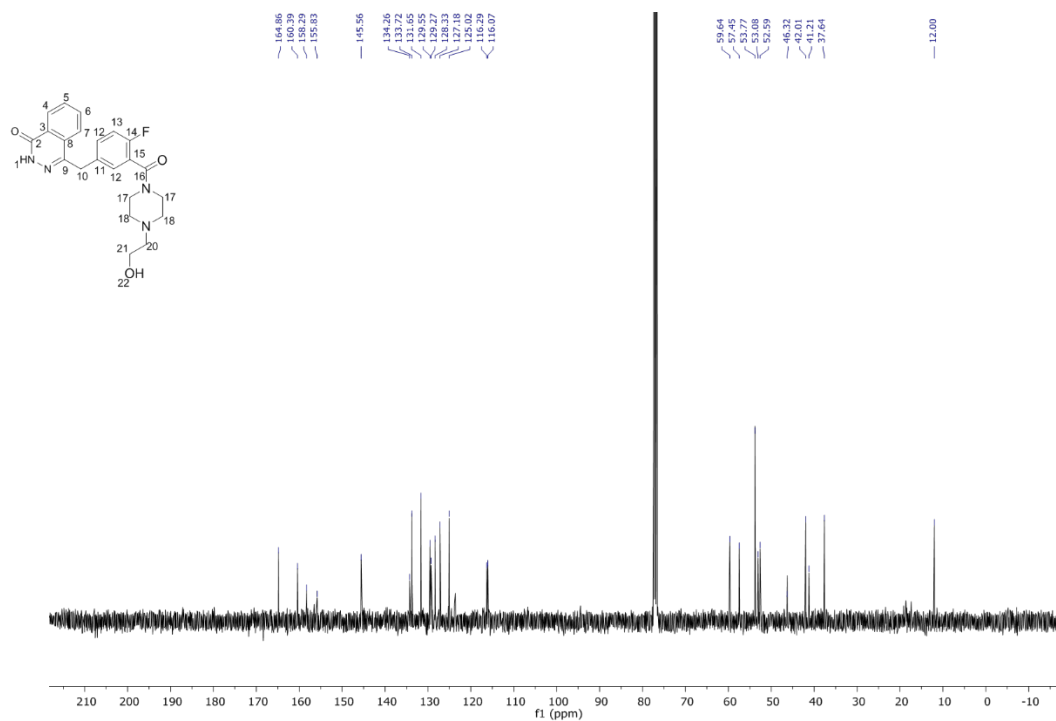


Figure S6. ¹³C NMR spectrum of **11** (400 MHz, CDCl₃)

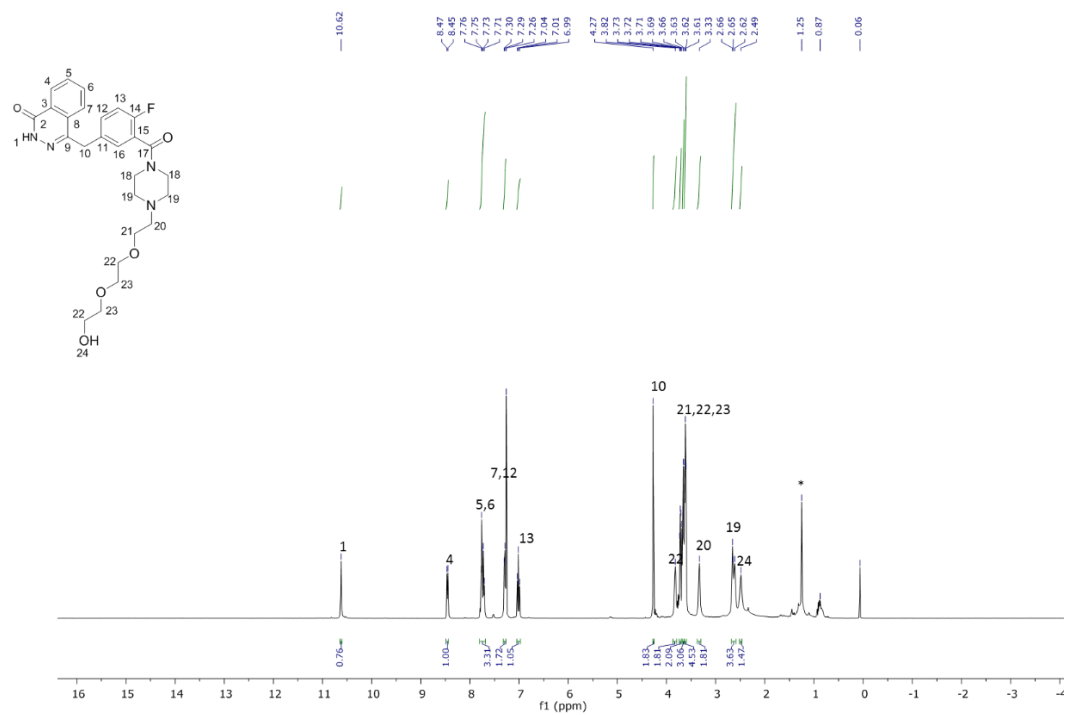


Figure S7. ¹H NMR spectrum of 13 (400 MHz, CDCl₃)

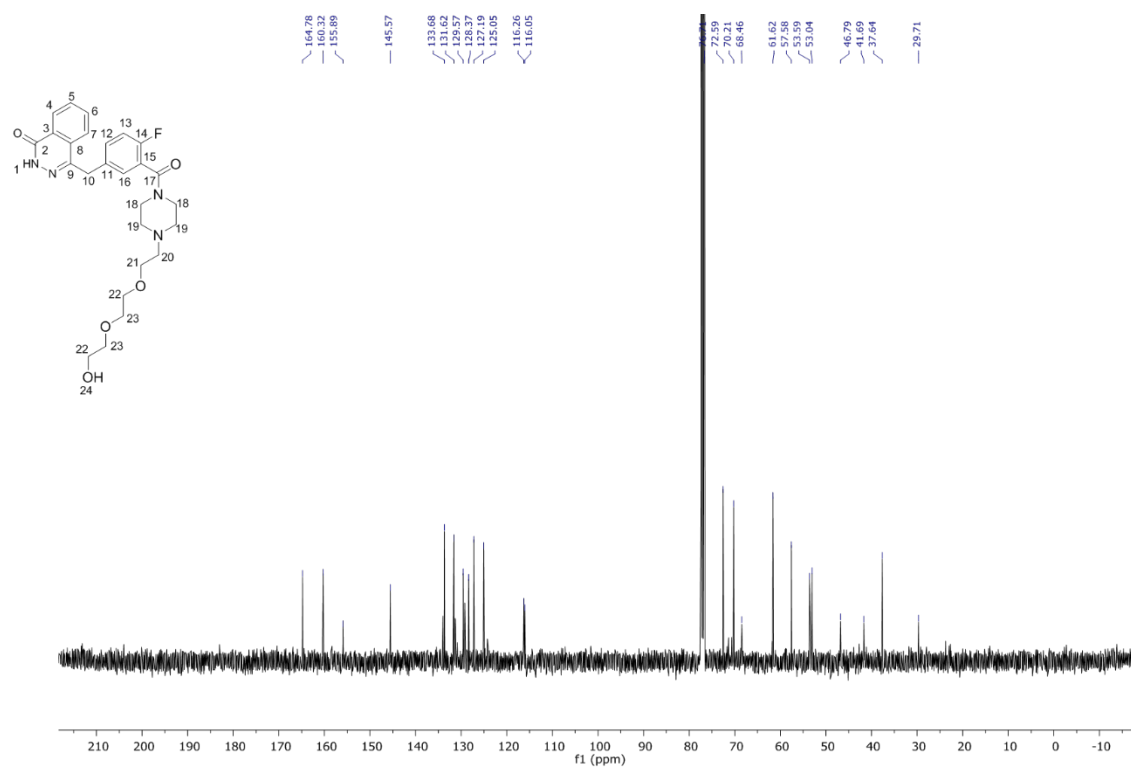


Figure S8. ¹³C NMR spectrum of 13 (400 MHz, CDCl₃)

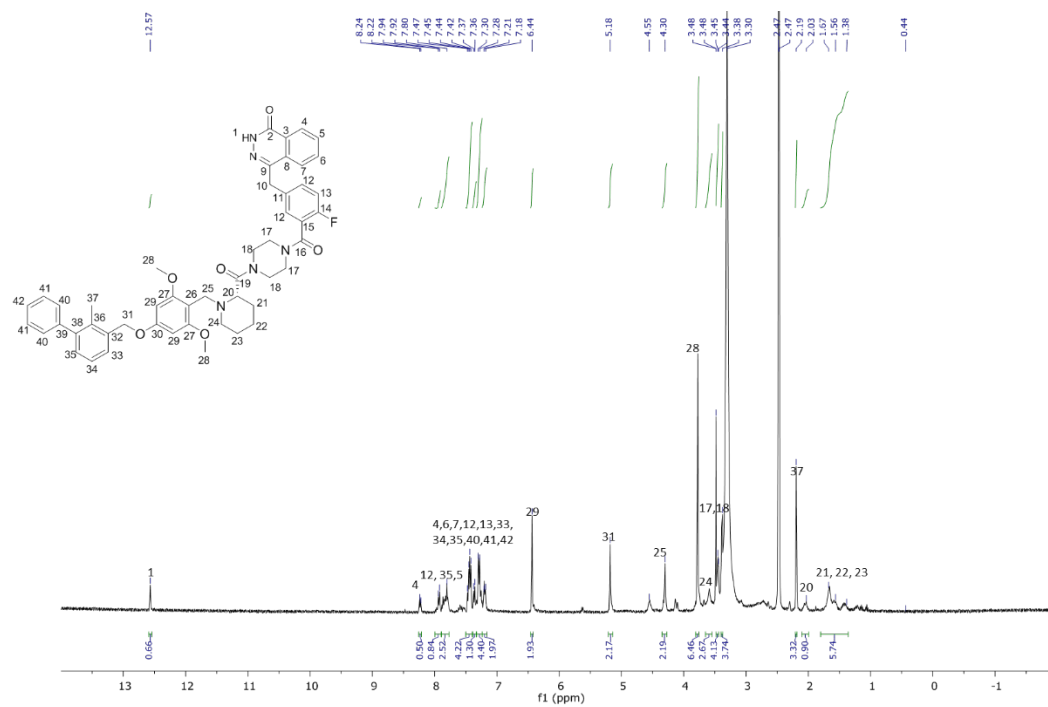


Figure S9. ^1H NMR spectrum of 1 (400 MHz, $\text{DMSO}-d_6$)

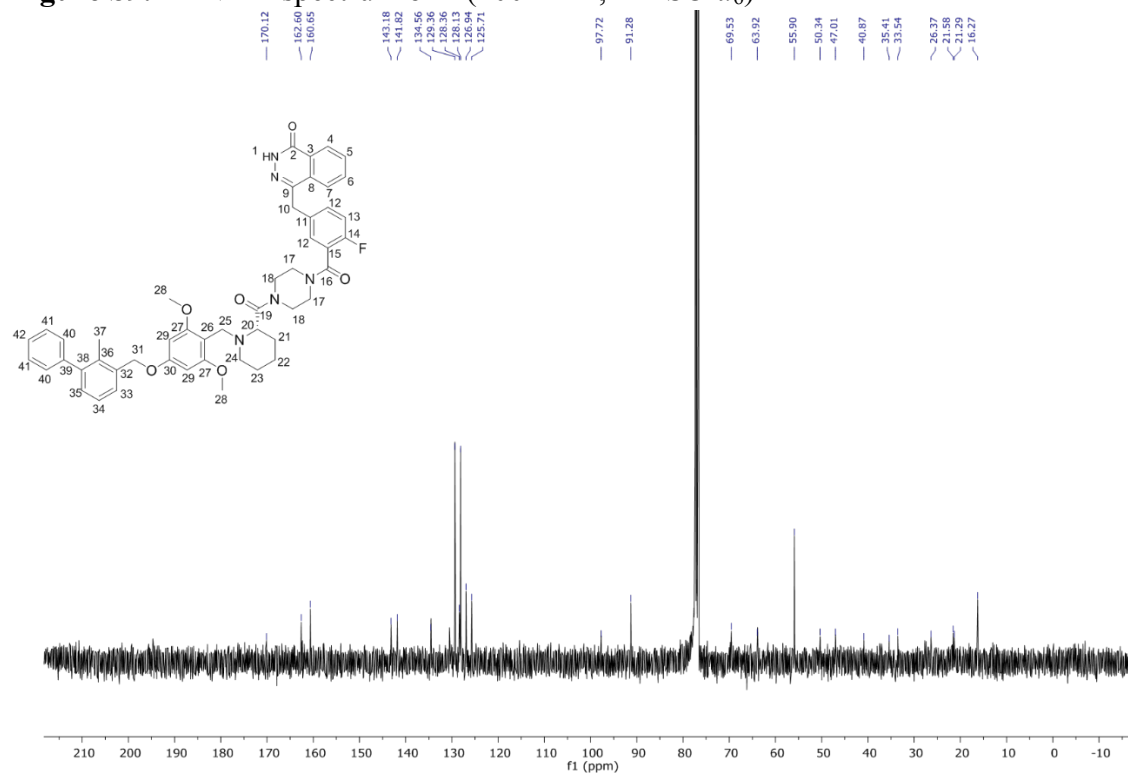


Figure S10. ^{13}C NMR spectrum of 1 (400 MHz, CDCl_3)

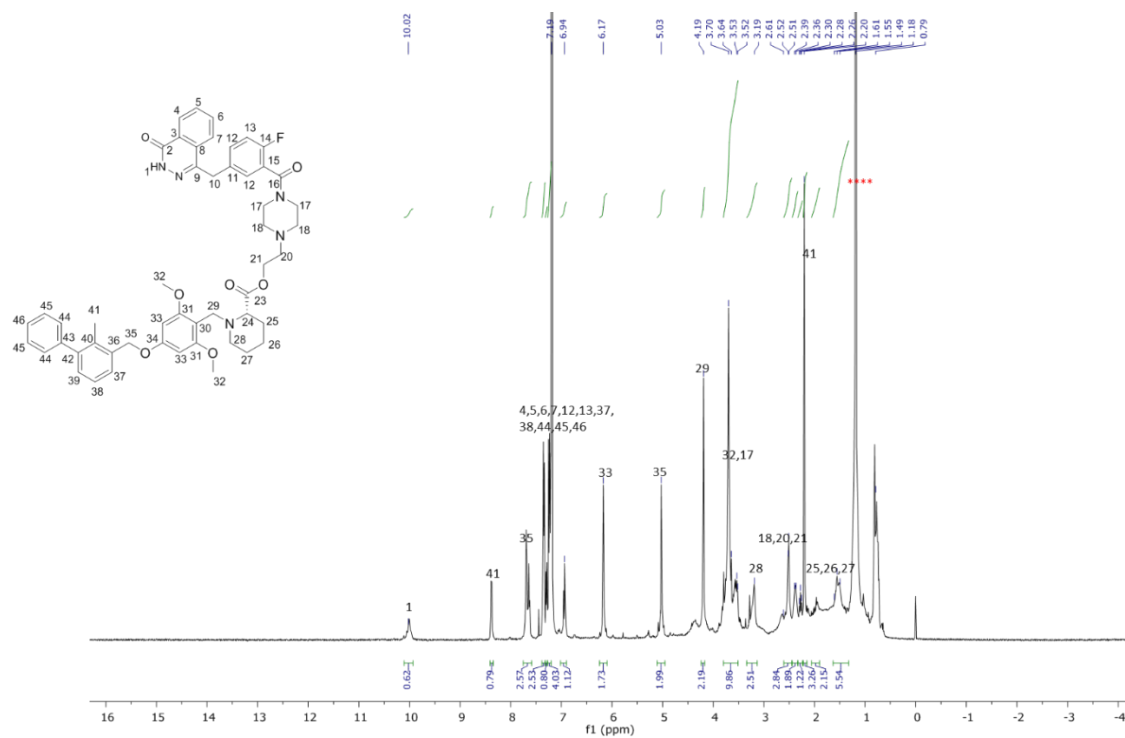


Figure S11. ^1H NMR spectrum of **2** (400 MHz, CDCl_3)

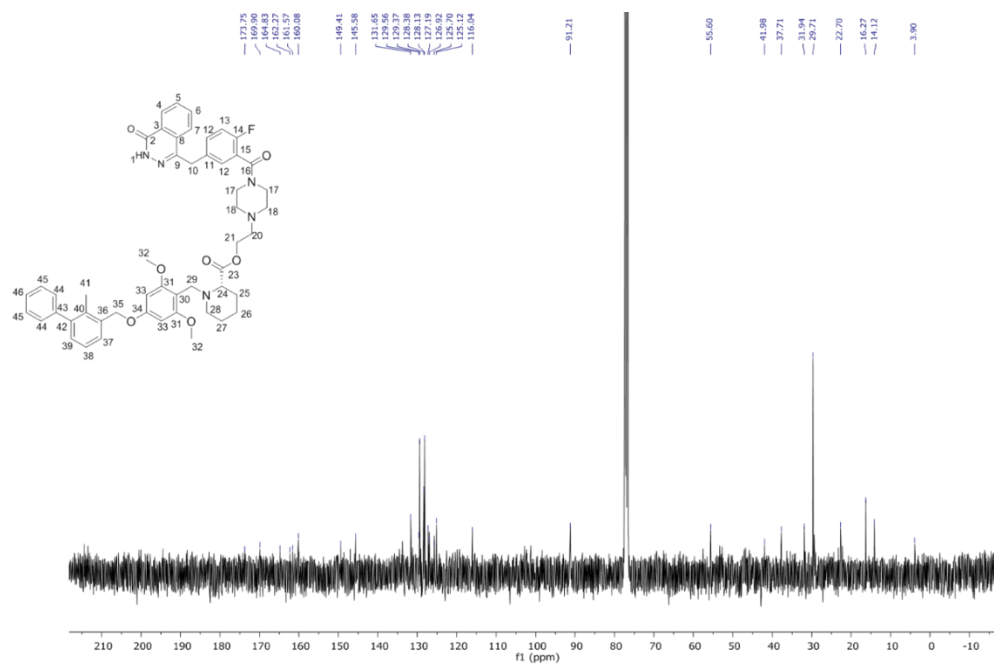


Figure S12. ^{13}C NMR spectrum of **2** (400 MHz, CDCl_3)

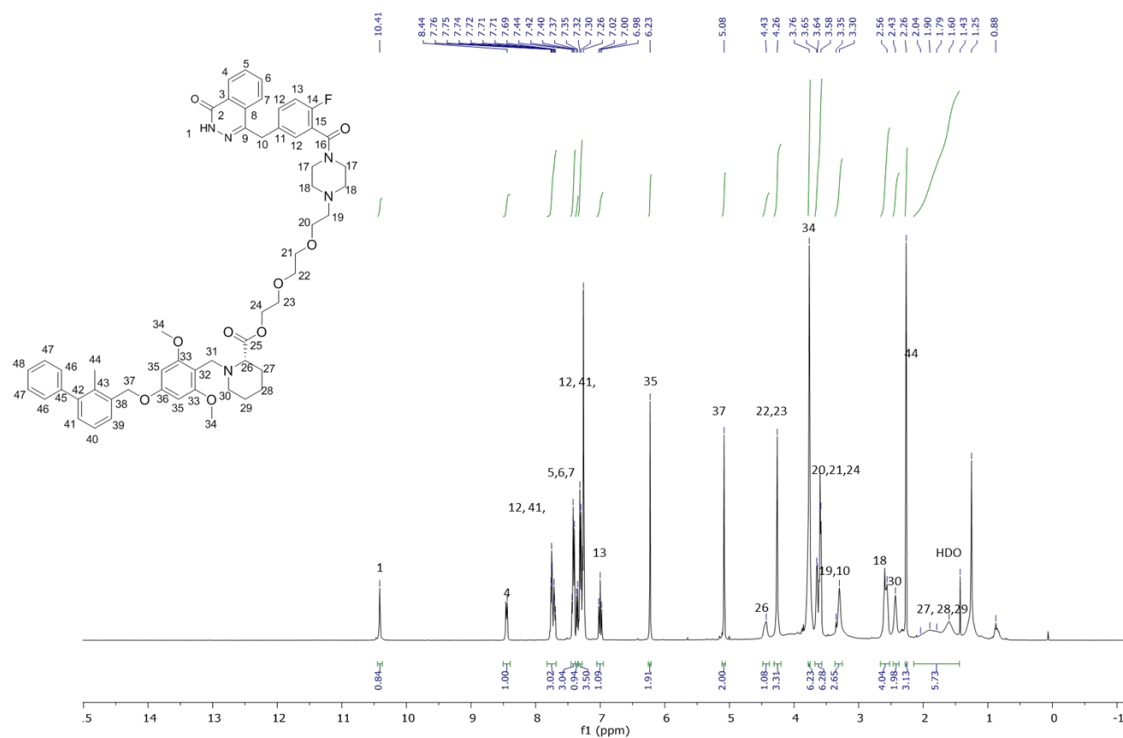


Figure S13. ¹H NMR spectrum of 3 (400 MHz, CDCl₃)

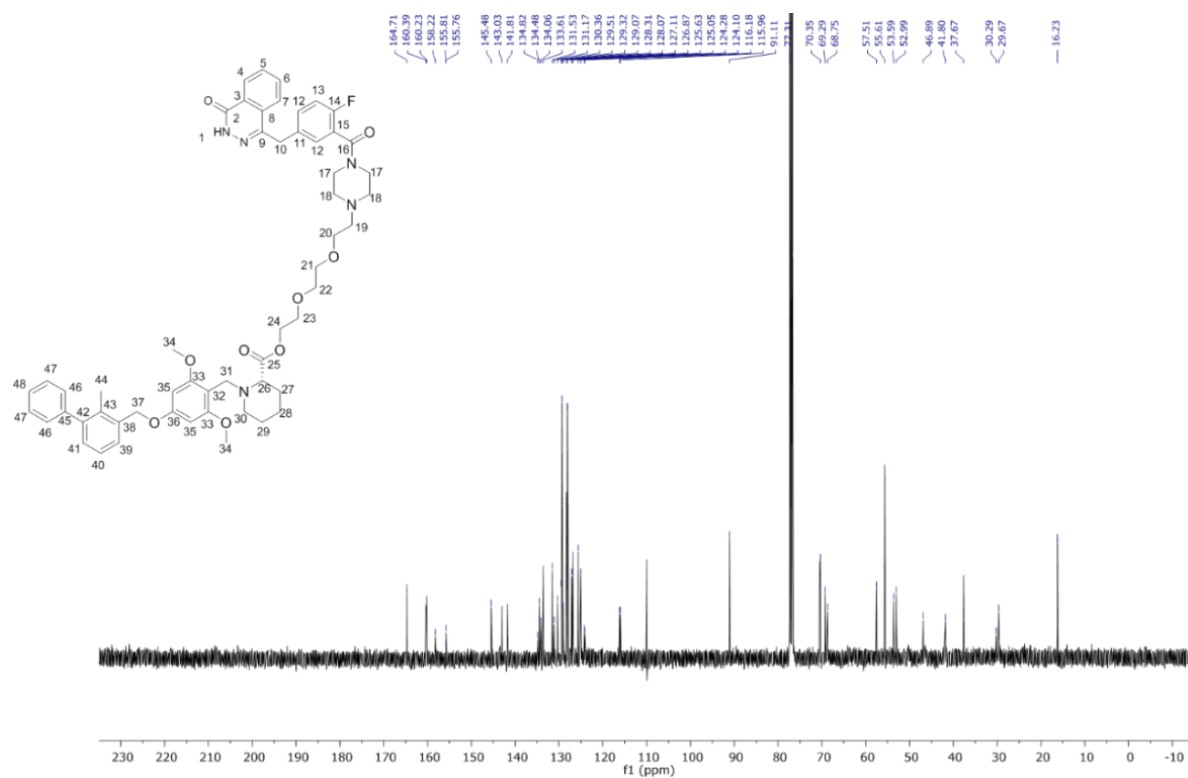


Figure S14. ¹³C NMR spectrum of 3 (400 MHz, CDCl₃)

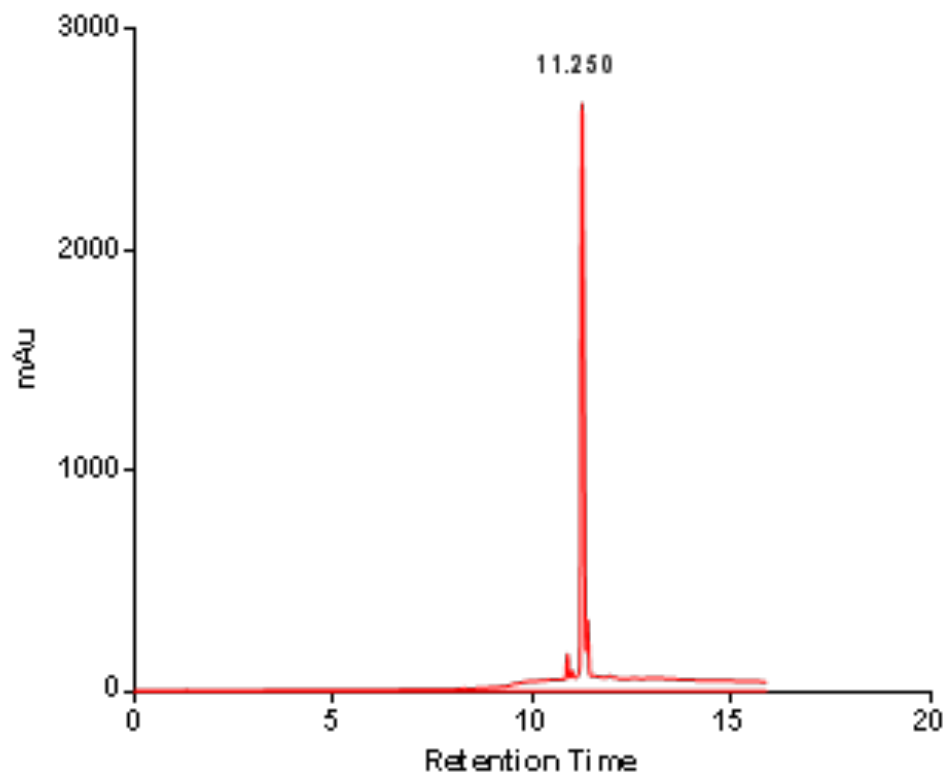


Figure S15: HPLC Chromatogram of Compound 1; RT: 11.250 min, 99.98% Purity

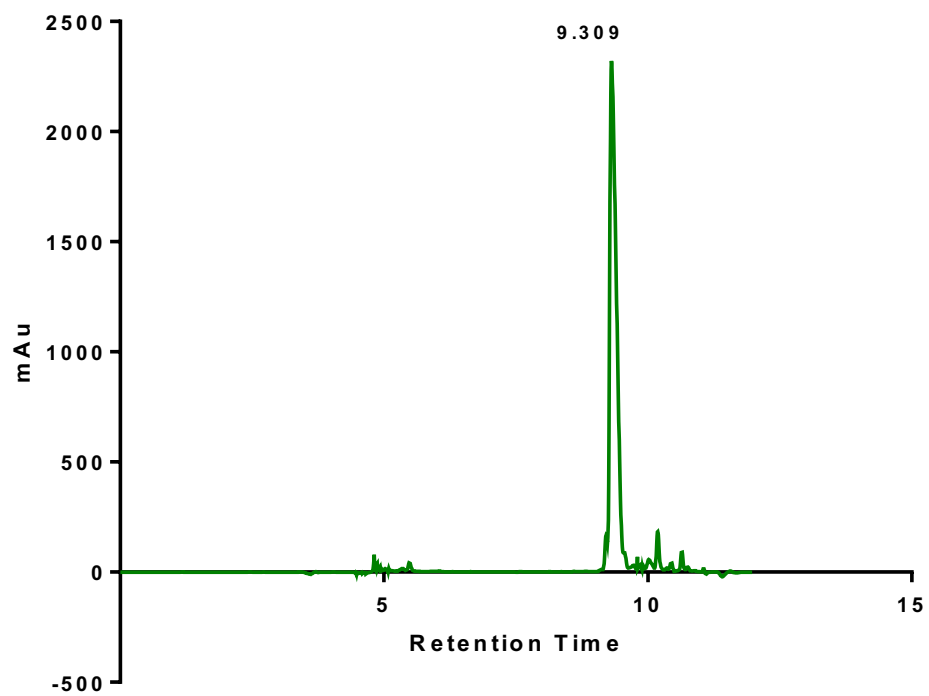


Figure S16: HPLC Chromatogram of Compound 2; RT: 9.308 min, 95.06% Purity

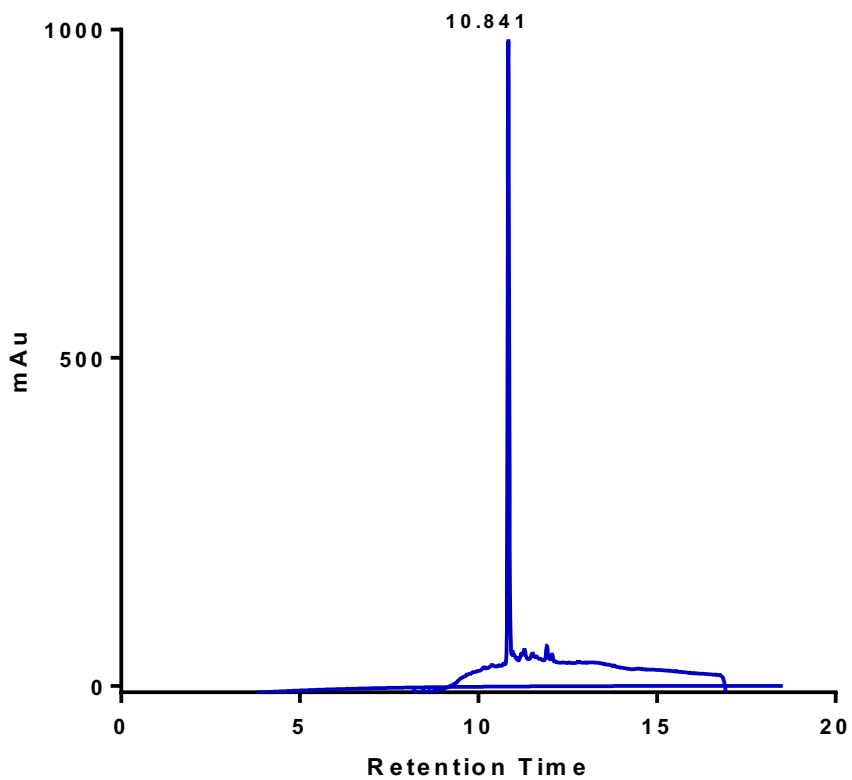


Figure S17: HPLC Chromatogram of Compound 3; RT: 10.841min, 99.10%

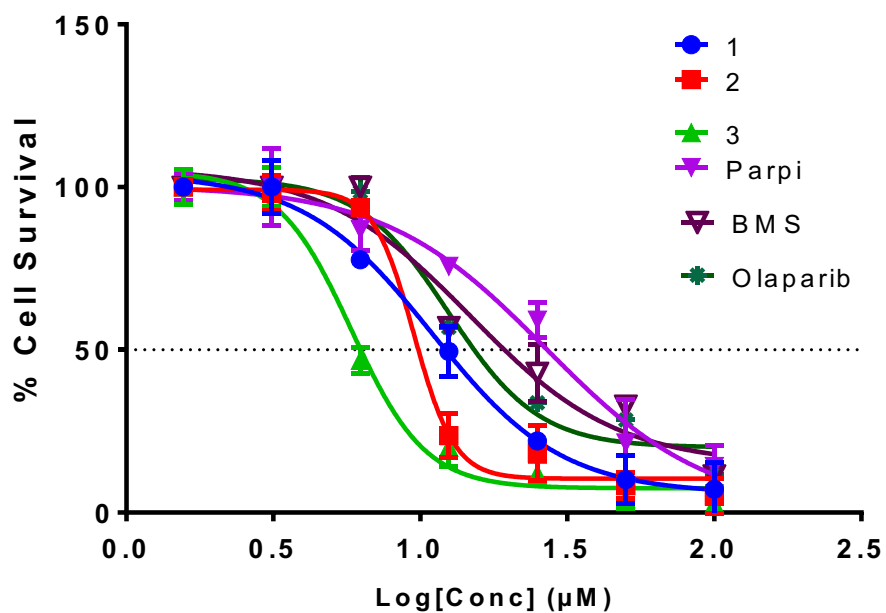


Figure S18: Dose-response curves of MDA-MB-231 cells in response to compounds

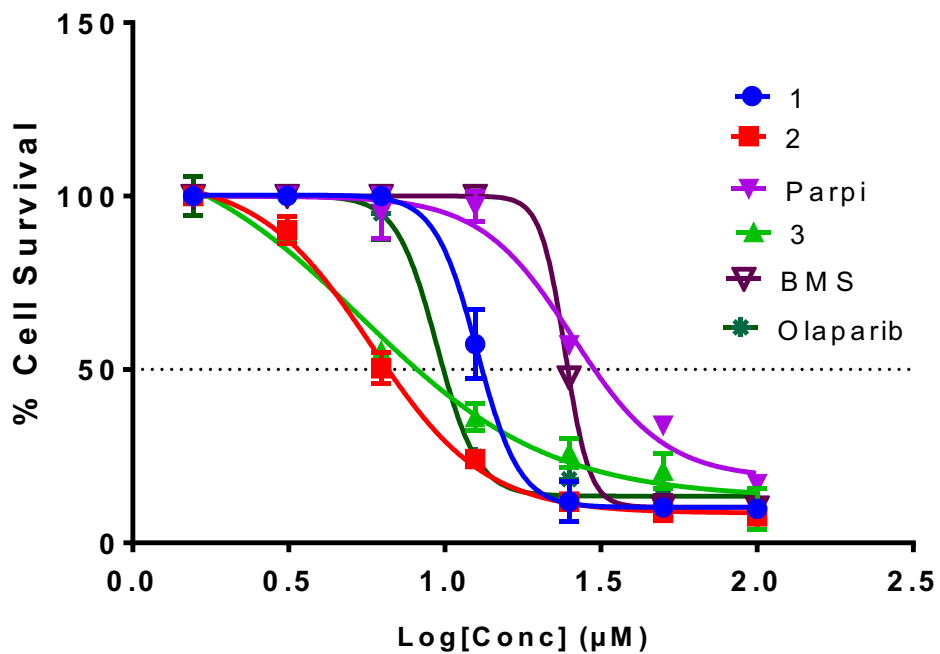


Figure S19: Dose-response curves of A2780 cells in response to compounds

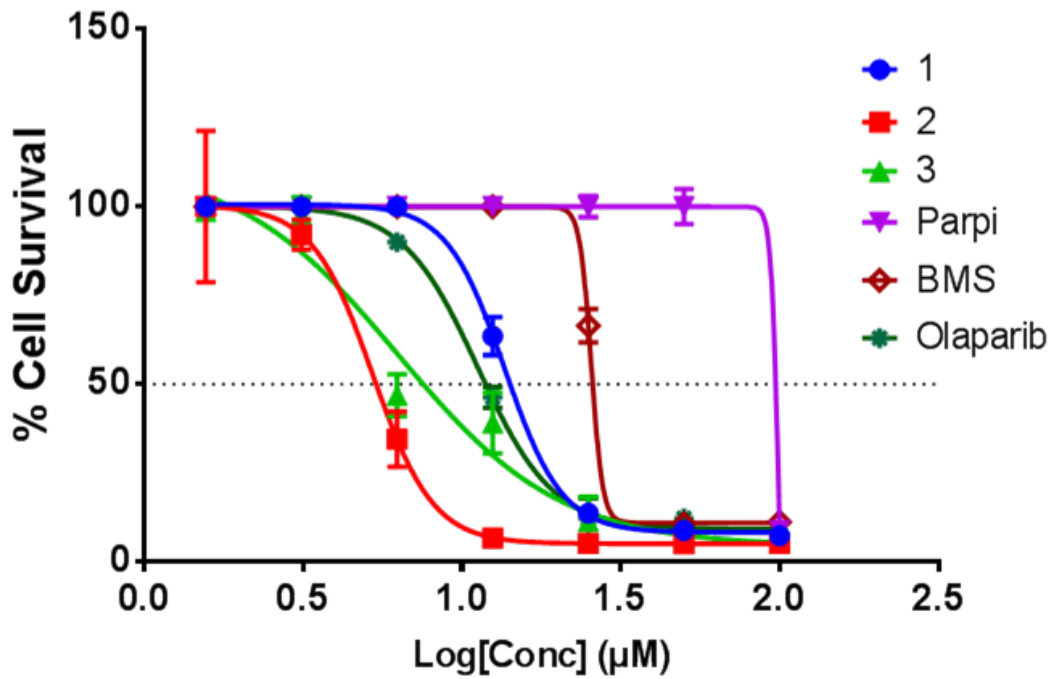


Figure S20: Dose-response curves of OVCAR8 cells in response to compounds

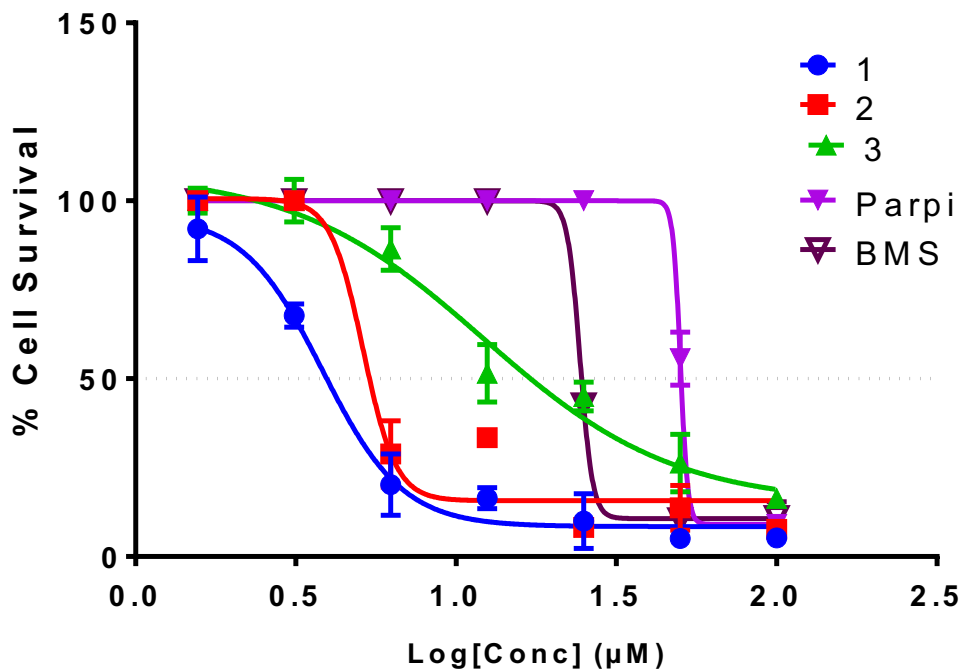


Figure S21: Dose-response curves of SKOV3 cells in response to compounds

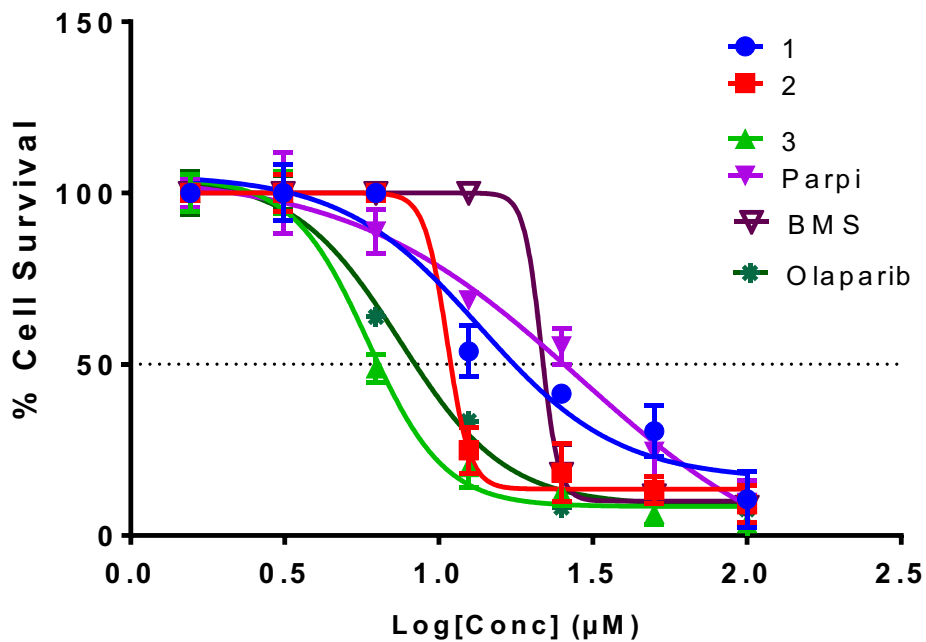


Figure S22: Dose-response curves of H460 cells in response to compounds

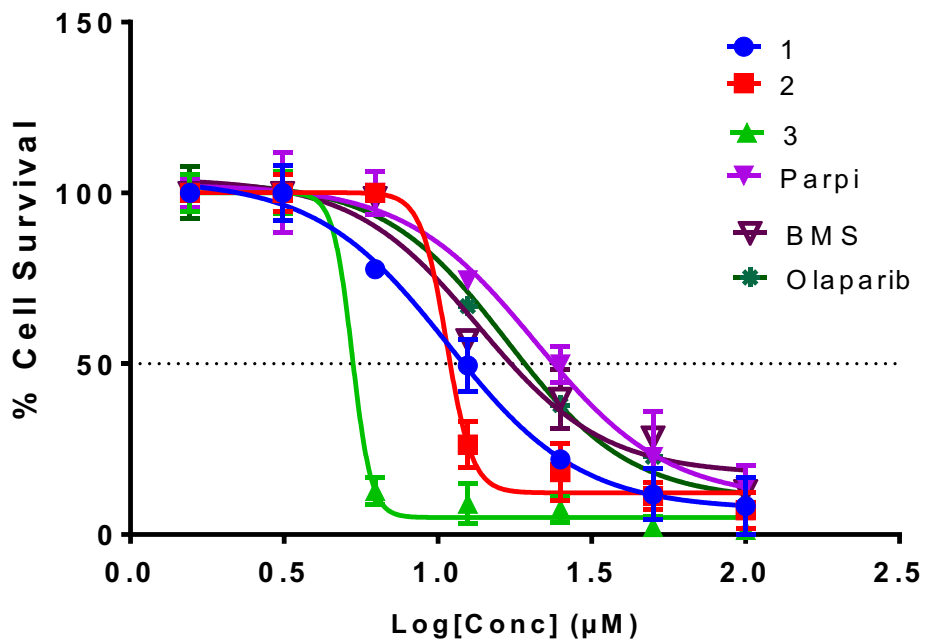


Figure S23: Dose-response curves of HCC1937 cells in response to compounds

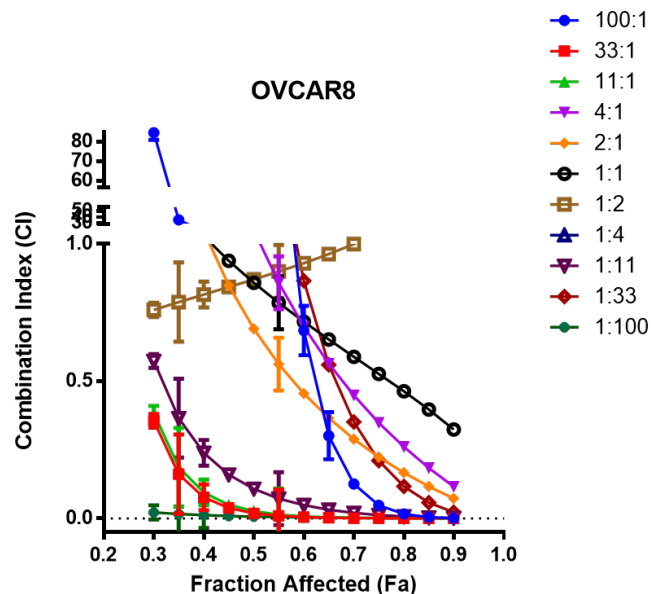


Figure S24: Combination Index values for olaparib-BMS001 combinations presented as a function of fraction affected (Fa) for OVCAR8 cells. Fa= 0.9 indicates 90% cell death. Each data point is presented as mean \pm SD obtained from three independent biological experiments. Ratios of combination of Olaparib to BMS001 are indicated (legend).

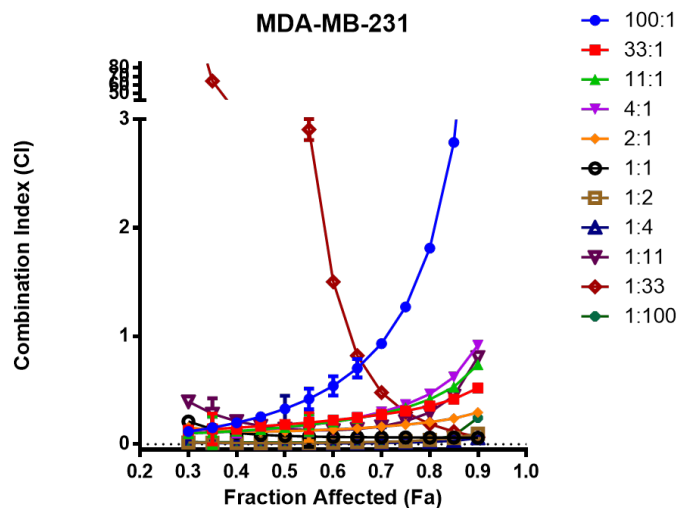


Figure S25: The combination Index values for olaparib-BMS001 combinations presented as a function of fraction affected (Fa) for MDA-MB-231 cells. Fa= 0.9 indicates 90% cell death. Each data point is presented as mean \pm SD obtained from three independent biological experiments. Ratios of combination of Olaparib to BMS001 are indicated (legend).

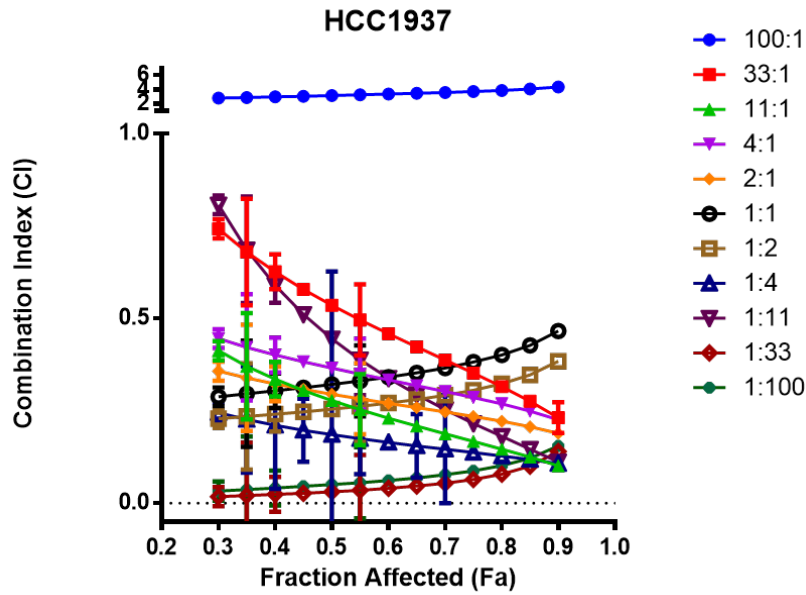


Figure S26: The combination Index values for olaparib-BMS001 combinations presented as a function of fraction affected (Fa) for HCC1937 cells. Fa= 0.9 indicates 90% cell death. Each data point is presented as mean \pm SD obtained from three independent biological experiments. Ratios of combination of Olaparib to BMS001 are indicated (legend).

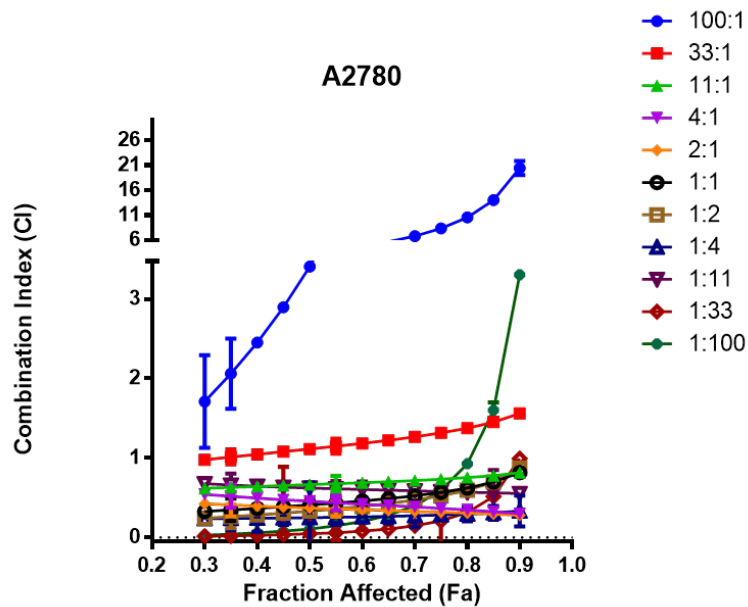


Figure S27: The combination Index values for olaparib-BMS001 combinations presented as a function of fraction affected (Fa) for A2780 cells. Fa= 0.9 indicates 90% cell death. Each data point is presented as mean \pm SD obtained from three independent biological experiments. Ratios of combination of Olaparib to BMS001 are indicated (legend).

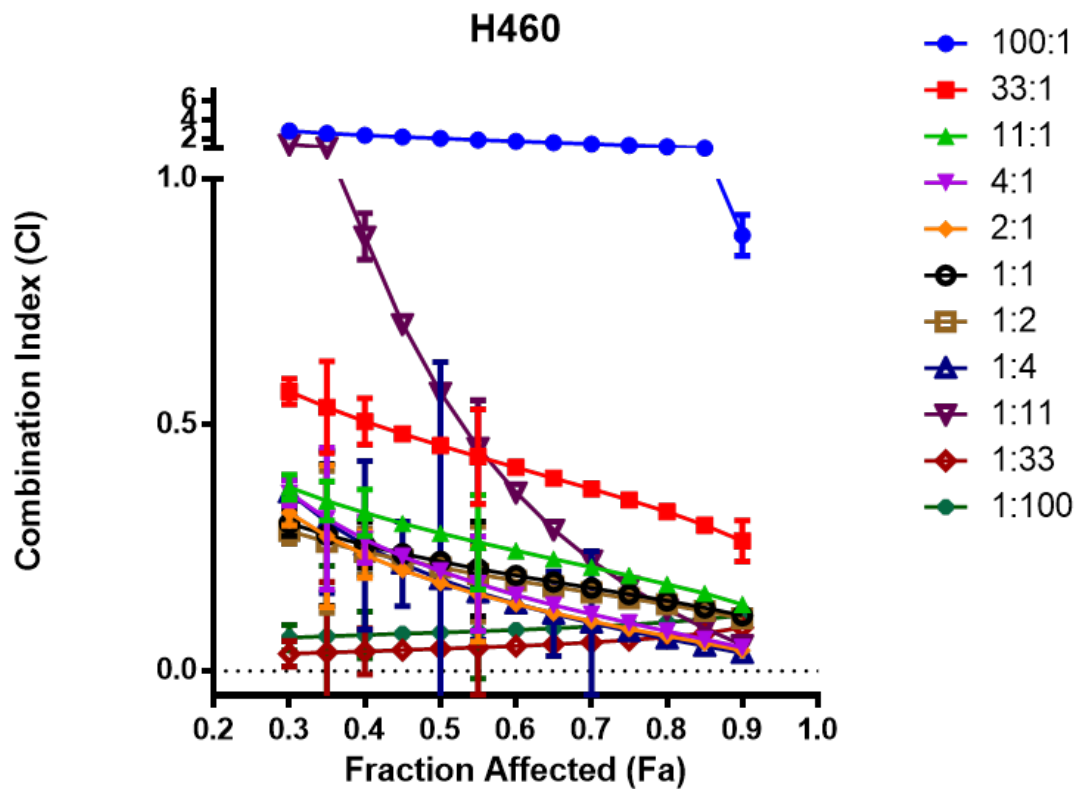


Figure S28: The combination Index values for olaparib-BMS001 combinations presented as a function of fraction affected (Fa) for H460 cells. Fa= 0.9 indicates 90% cell death. Each data point is presented as mean \pm SD obtained from three independent biological experiments. Ratios of combination of Olaparib to BMS001 are indicated (legend).

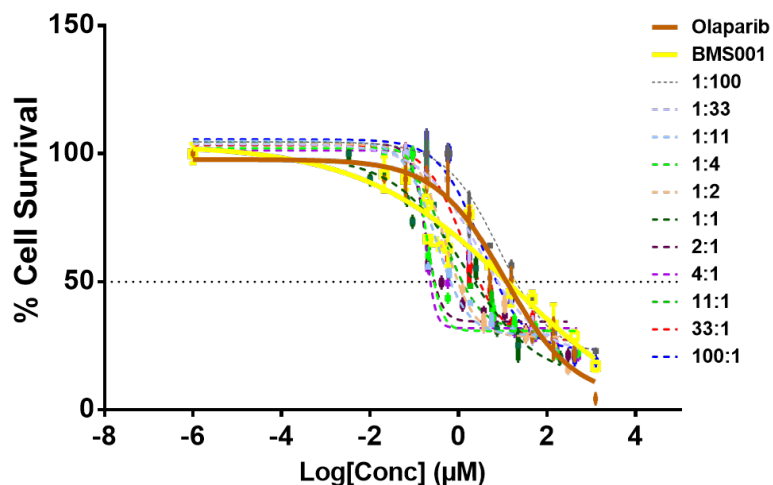


Figure S29: Dose-Response curve of OVCAR8 cell lines for Olaparib or BMS given as a monotherapy, or in combination. For both monotherapy and combination, cells were treated with three-fold serial dilution of Olaparib/BMS (maximum concentration was 1.25mM, minimum concentration = 12.5µM, same multiples were used for 100:1, 33:1, 11:1 and the reverse, eg. , 100:1 = 1.25mM Ola + 12.5µM BMS001). For 1:1 - the Olaparib: BMS001 concentration were set at 100µM: 100µM, the same multiples were used for 1:2, 2:1, 1:4, 4:1). Each data point is presented as mean \pm SD obtained from three independent biological experiments.

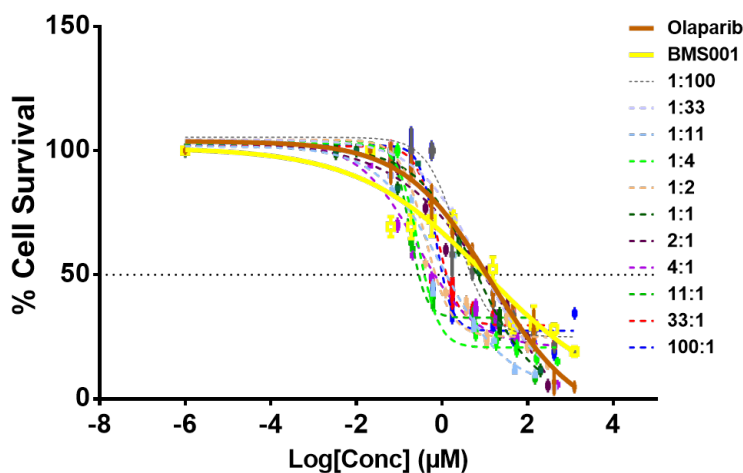


Figure S30: Dose-Response curve of MDA-MB-231 cell lines for Olaparib or BMS given as a monotherapy, or in combination. For both monotherapy and combination, cells were treated with three-fold serial dilution of Olaparib/BMS (maximum concentration was 1.25mM, minimum concentration = 12.5µM, same multiples were used for 100:1, 33:1, 11:1 and the reverse, e.g. 100:1 = 1.25mM Ola + 12.5µM BMS001). For 1:1 - the Olaparib: BMS001 concentration were set at 100µM: 100µM, the same multiples were used for 1:2, 2:1, 1:4, 4:1). Each data point is presented as mean \pm SD obtained from three independent biological experiments.

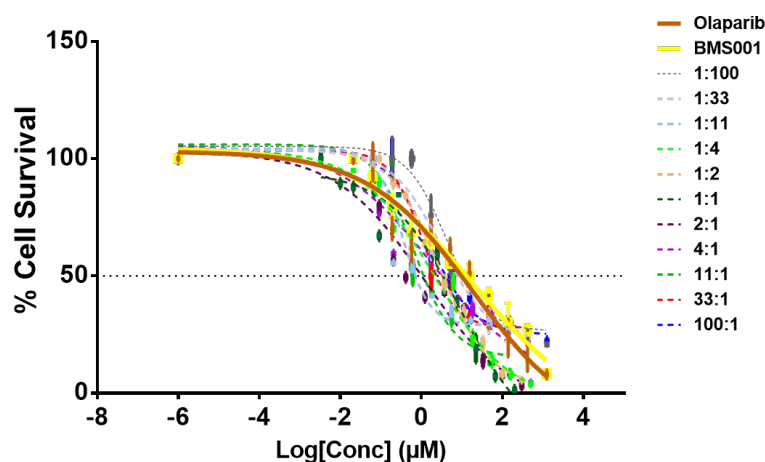


Figure S31: Dose-Response curve of HCC1937 cell lines for Olaparib or BMS given as a monotherapy, or in combination. For both monotherapy and combination, cells were treated with three-fold serial dilution of Olaparib/BMS (maximum concentration was 1.25mM, minimum concentration = 12.5 μ M, same multiples were used for 100:1, 33:1, 11:1 and the reverse, eg. , 100:1 = 1.25mM Ola + 12.5 μ M BMS001 stock).. For 1:1 - the Olaparib: BMS001 concentration were set at 100 μ M: 100 μ M, the same multiples were used for 1:2, 2:1, 1:4, 4:1). Each data point is presented as mean \pm SD obtained from three independent biological experiments.

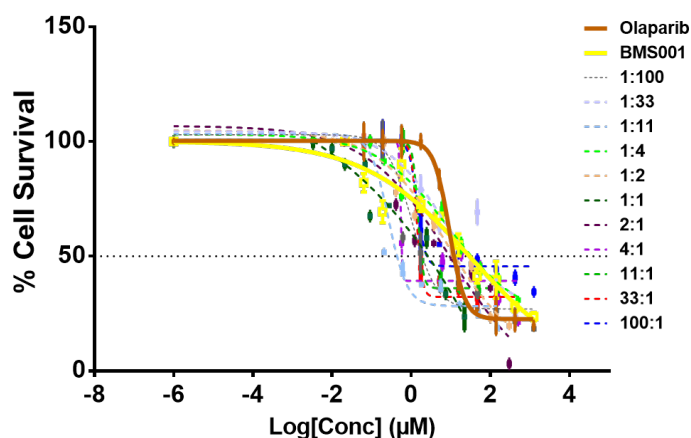


Figure S32: Dose-Response curve of HCC1937 cell lines for Olaparib or BMS given as a monotherapy, or in combination. For both monotherapy and combination, cells were treated with three-fold serial dilution of Olaparib/BMS (maximum concentration was 1.25mM, minimum concentration = 12.5 μ M, same multiples were used for 100:1, 33:1, 11:1 and the reverse, eg. , 100:1 = 1.25mM Ola + 12.5 μ M BMS001).For 1:1 - the Olaparib: BMS001 concentration were set at 100 μ M: 100 μ M, the same multiples were used for 1:2, 2:1, 1:4, 4:1). Each data point is presented as mean \pm SD obtained from three independent biological experiments.

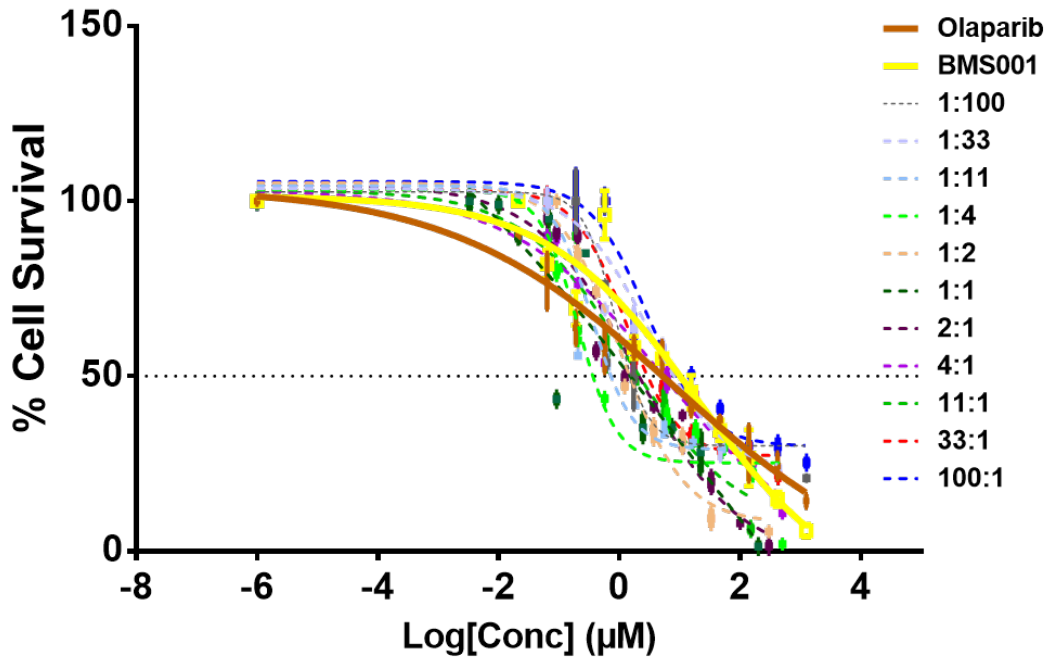


Figure S33: Dose-Response curve of H460 cell lines for Olaparib or BMS given as a monotherapy, or in combination. For both monotherapy and combination, cells were treated with three-fold serial dilution of Olaparib/BMS (maximum concentration was 1.25mM, minimum concentration = 12.5µM, same multiples were used for 100:1, 33:1, 11:1 and the reverse, eg. , 100:1 = 1.25mM Ola + 12.5µM BMS001).For 1:1 - the Olaparib: BMS001 concentration were set at 100µM: 100µM, the same multiples were used for 1:2, 2:1, 1:4, 4:1). Each data point is presented as mean \pm SD obtained from three independent biological experiments.

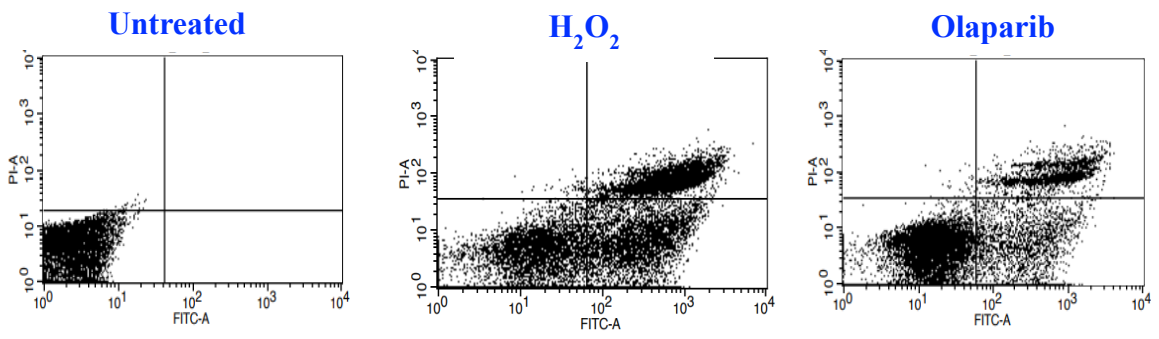


Figure S34: Apoptosis induced by olaparib in MDA-MB-231 cells with respective controls.

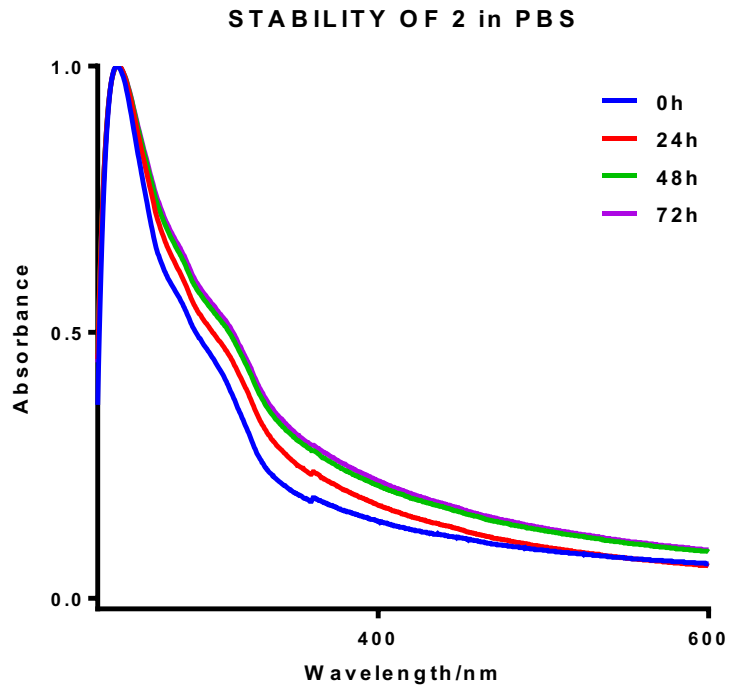


Figure S35: UV absorption profile of conjugate 2 in PBS

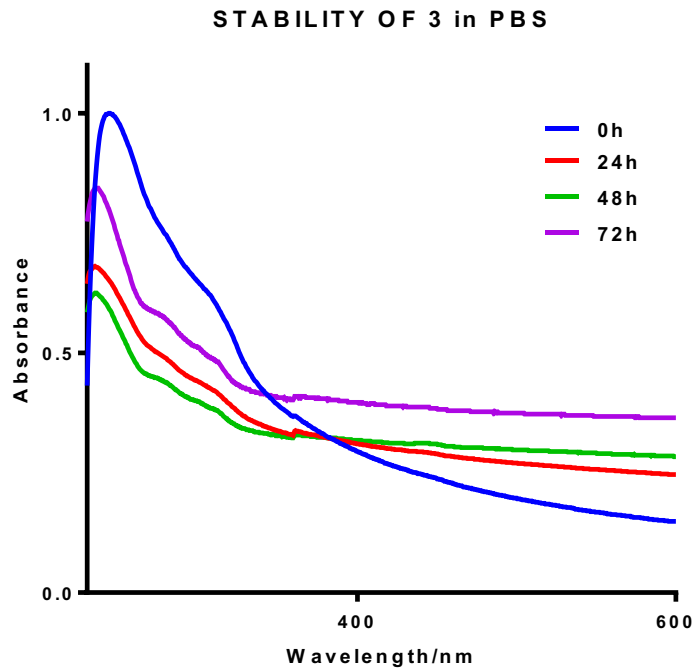


Figure S36: UV absorption profile of conjugate 3 in PBS

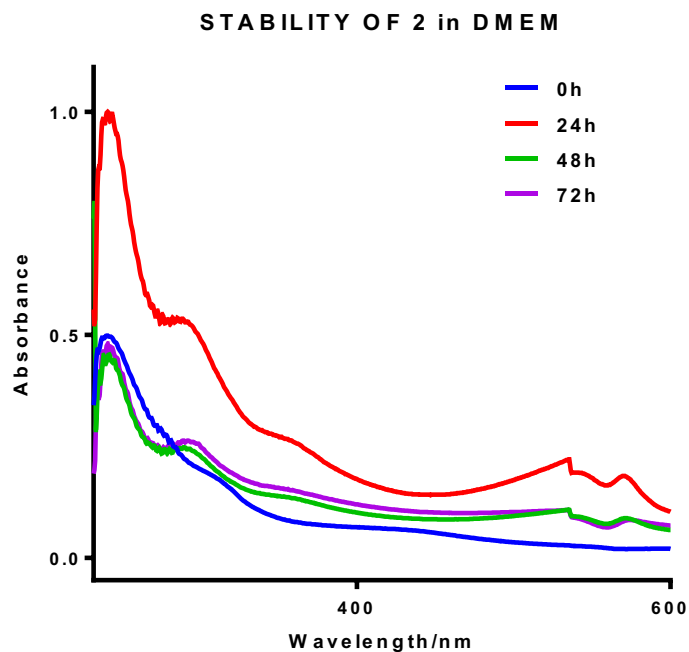


Figure S37: UV absorption profile of conjugate 2 in DMEM

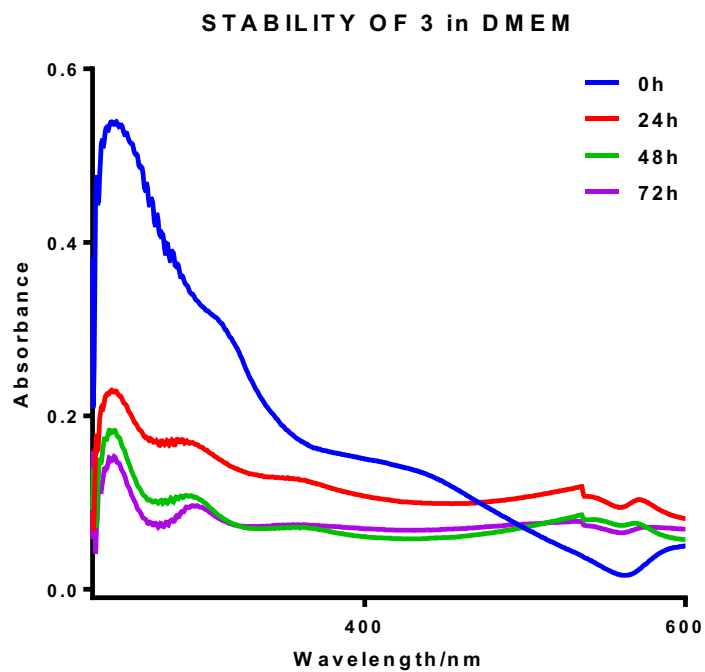


Figure S38: UV absorption profile of conjugate 3 in DMEM

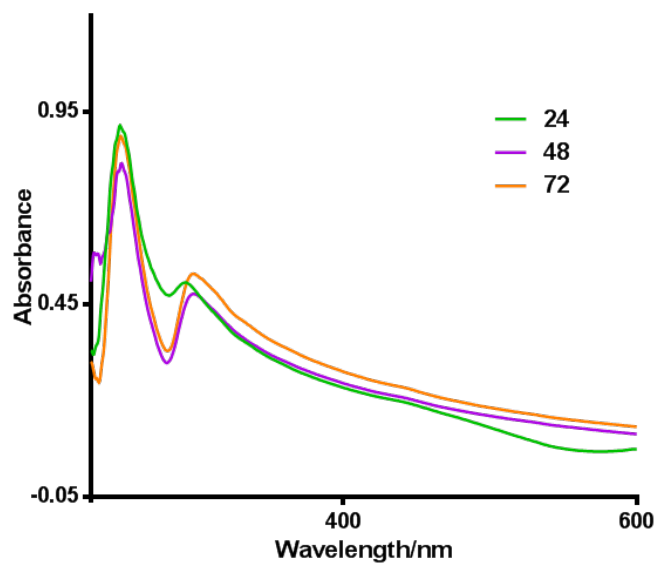


Figure S39: UV absorption profile of conjugate 1 in BSA after time points (in hours)

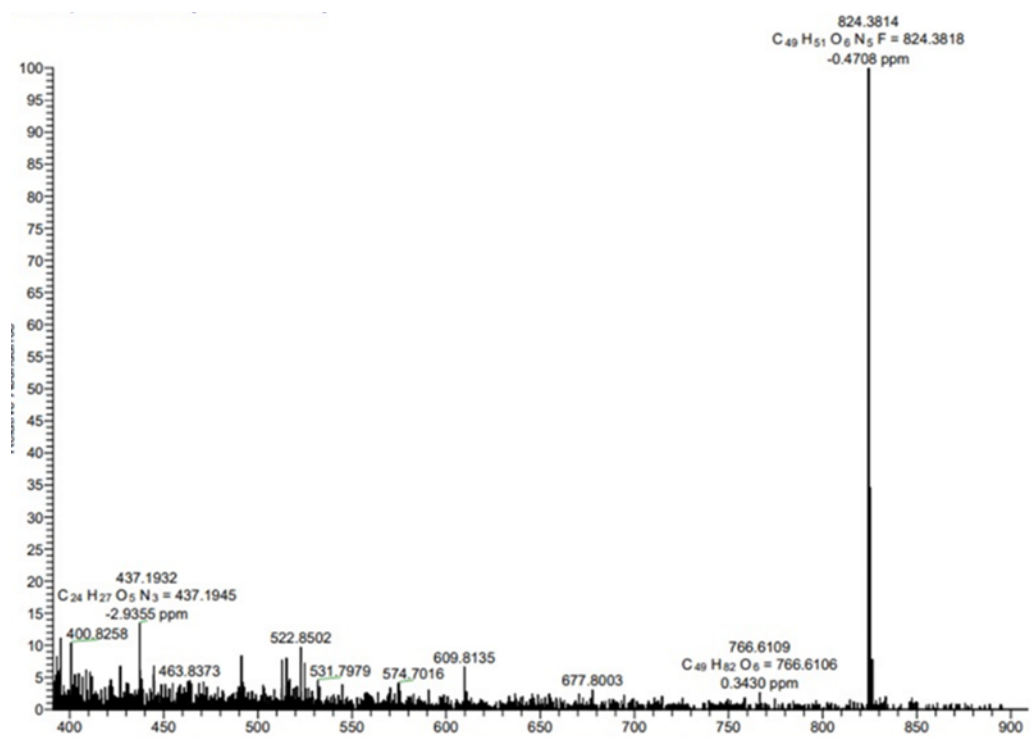


Figure S40: Mass spectra of an extract of Conjugate 1-BSA mix after 72 h

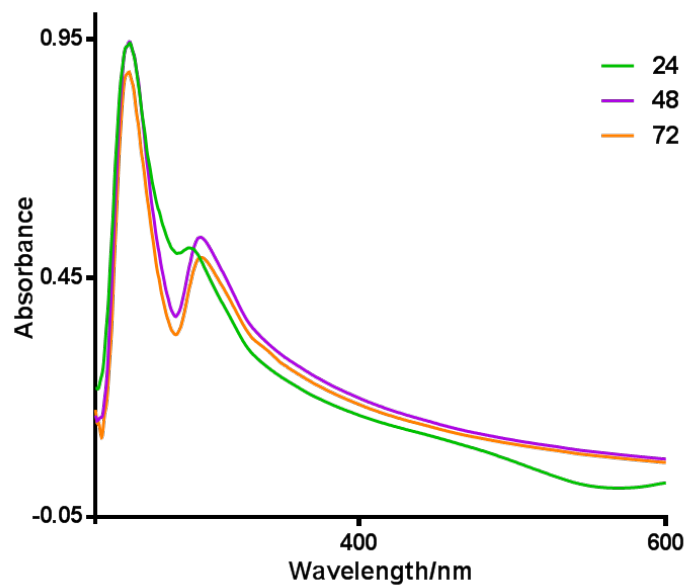


Figure S41: UV absorption profile of conjugate **2** in BSA after time points (in hours)

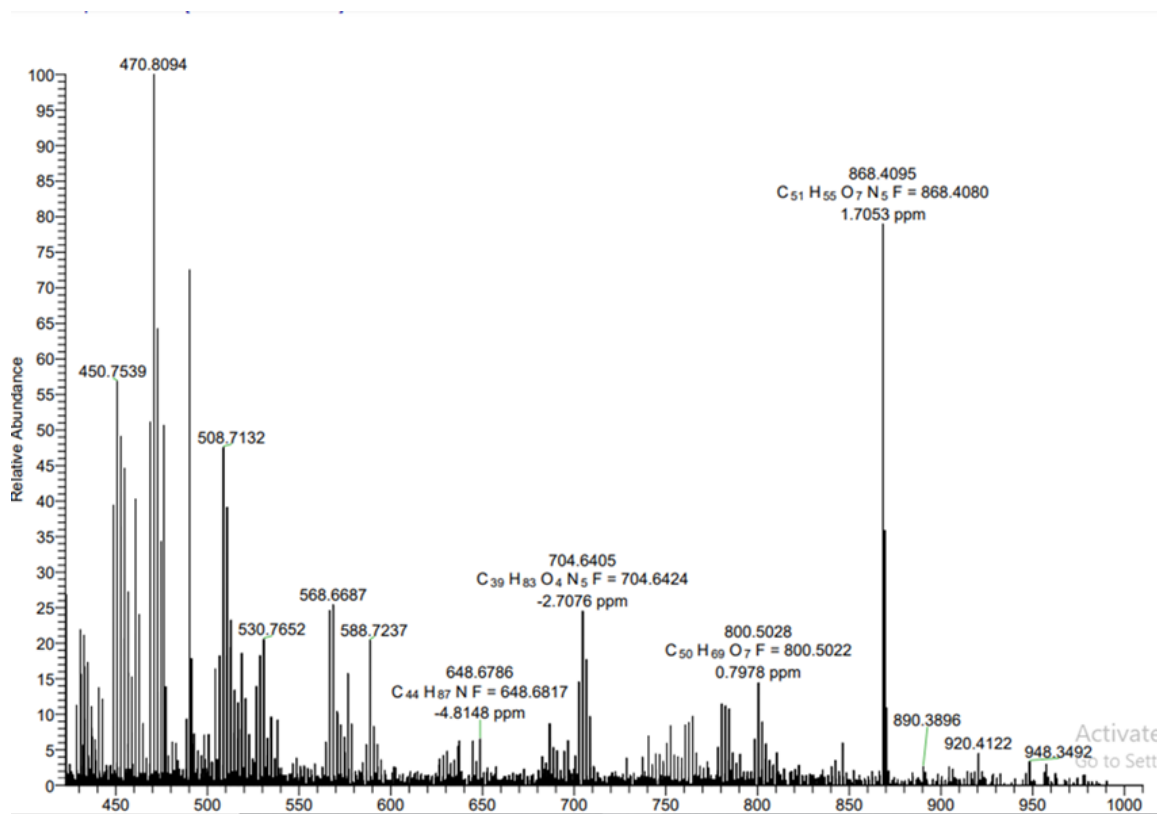


Figure S42: Mass spectra of an extract of Conjugate **2**-BSA mix after 72 h

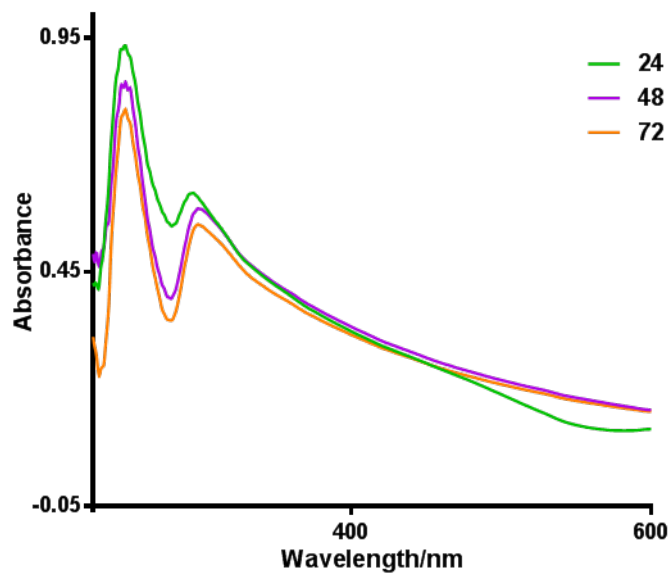


Figure S43: UV absorption profile of conjugate **3** in BSA after time points (in hours)

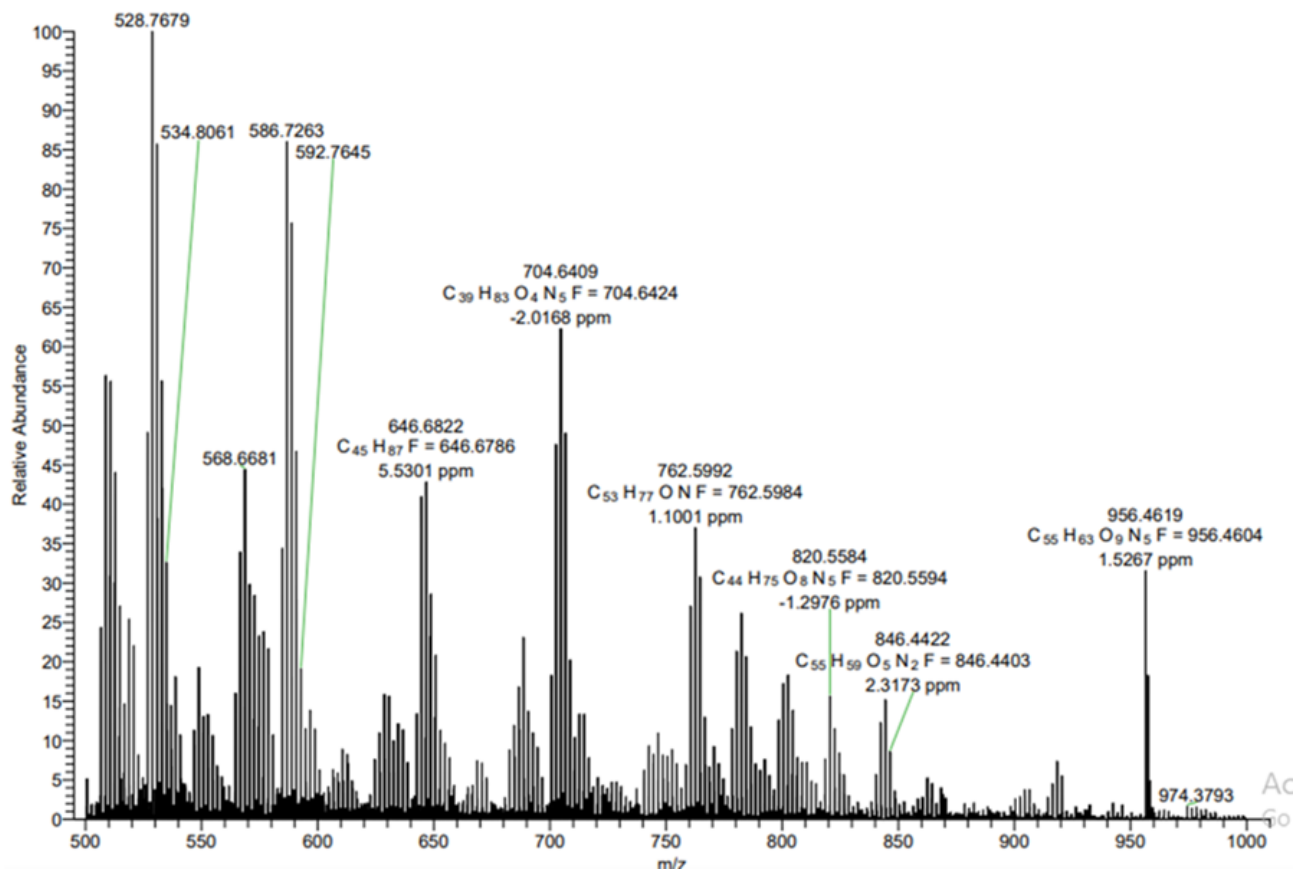


Figure S44: Mass spectra of an extract of Conjugate **3**-BSA mix after 72 h

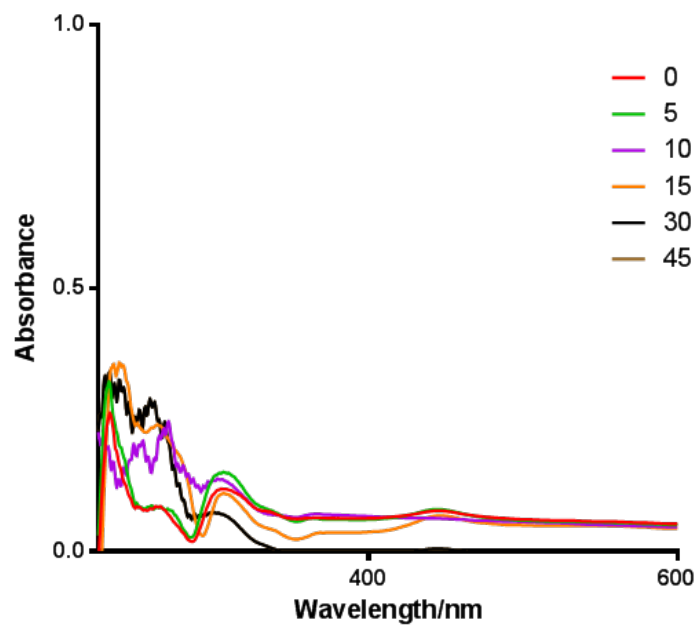


Figure S45: UV absorption profile of conjugate 1 incubated with liver microsomes at time points: 0, 5, 10, 15, 30, 45 minutes.

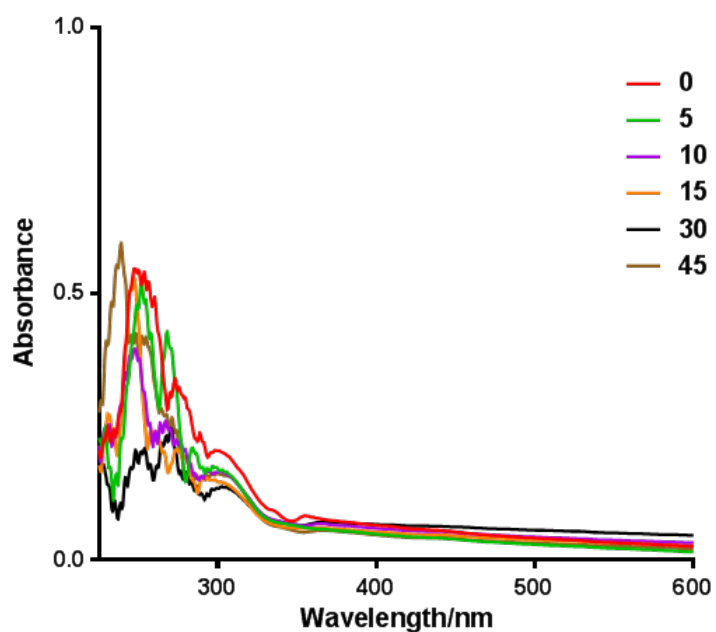


Figure S46: UV absorption profile of conjugate 2 incubated with liver microsomes at time points: 0, 5, 10, 15, 30, 45 minutes.

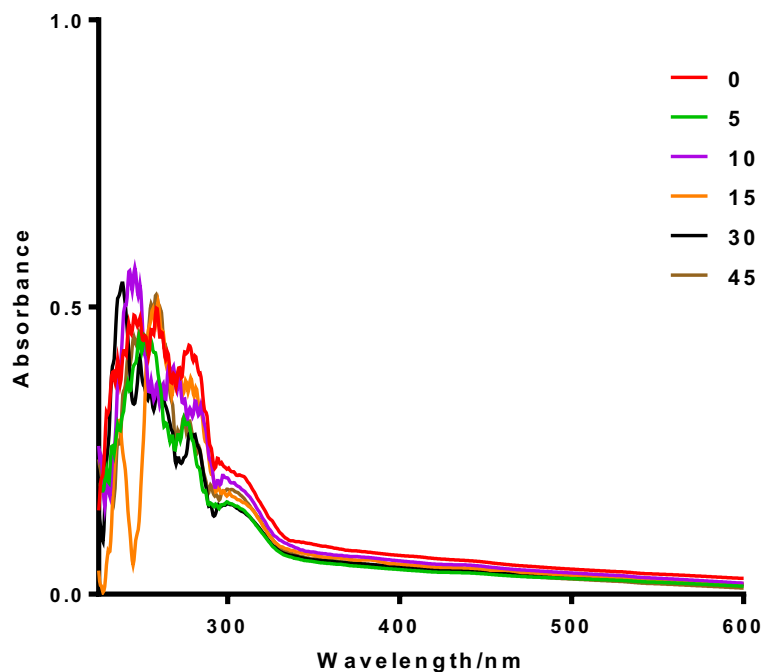


Figure S47: UV absorption profile of conjugate 3 incubated with liver microsomes at time points: 0, 5, 10, 15, 30 45minutes.

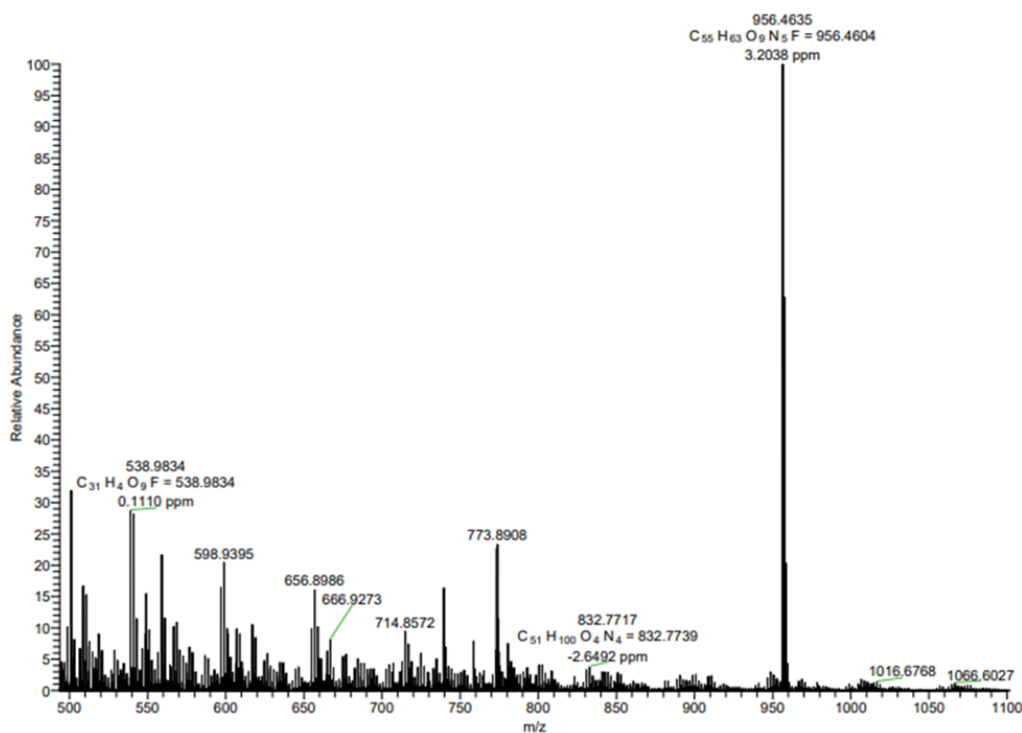


Figure S48: Mass spectra of an extract of Conjugate 3-microsome mix after 45minute incubation.