Electronic supplementary information for

Screening and application of boron difluoride complex of curcumin as a colorimetric and ratiometric fluorescent probe for bisulfite

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I. Synthesis and characterization of curcumin (Cur) derivatives

1.1 Synthesis of **Cur-BF_2**

Boron trifluoride diethyl ether (0.85 g, 5.98 mmol) was added dropwise to the solution of **Cur** (0.73 g, 1.98 mmol) in 20 mL dichloromethane at room temperature and then stirred for 30 min. The mixture was concentrated under reduced pressure and dissolved in 10 mL acetone with heating. After cooling, brick red solid precipitated was filtered, washed and dried to obtain brick red solid (0.74 g, 89.0%).[1]H NMR (400 MHz, DMSO-d_6) δ 10.09 (s, 2H), 7.95 (s, 1H), 7.91 (s, 1H), 7.48 (d, J = 1.4 Hz, 2H), 7.35 (dd, J = 8.3, 1.4 Hz, 2H), 7.04 (s, 1H), 7.00 (s, 1H), 6.88 (d, J = 8.2 Hz, 2H), 6.46 (s, 1H), 3.86 (s, 6H). The data were in agreement with those reported in the literature.[1]

1.2 Synthesis of **Cur-Me**

Cur (3.68 g, 10.00 mmol), potassium carbonate (2.76 g, 19.97 mmol) and dimethyl sulfate (3.81 g，30.21 mmol) were added to 60 mL acetone at room temperature and then the mixture was refluxed for 4 h. After cooling, the mixture was concentrated under reduced pressure and 100 mL water was added. The resulted solution was extracted with ethyl acetate (100 mL×2) and the combined organic phase was washed with saturated saline, dried over anhydrous sodium sulfate and concentrated. The crude product was recrystallized from 50 mL methanol to give golden yellow solid (3.37 g, 85.1%). [1]H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.59 (s, 1H), 7.14 (d, J = 8.2 Hz, 2H), 7.08 (s, 2H), 6.88 (d, J = 8.3 Hz, 2H), 6.50 (d, J = 15.7 Hz, 2H), 5.82 (s, 1H), 3.93 (s, 6H)， 3.92 (s, 6H). The data were in agreement with those reported in the literature.[2]

1.3 Synthesis of **Cur-Me-BF_2**

Boron trifluoride diethyl ether (0.85 g, 5.98 mmol) was added dropwise to the solution of **Cur-Me** (0.79 g, 1.99 mmol) in 20 mL dichloromethane at room temperature and then stirred for 30 min. After removing the solvent by concentration under reduced pressure, the crude product was recrystallized from 10 mL acetone to obtain purple solid (0.79 g, 90.4%). [1]H NMR (400 MHz, DMSO-d_6) δ 8.00 (s, 1H), 7.96 (s, 1H), 7.50 (s, 2H),7.47 (d, J = 8.4 Hz, 2H), 7.13 (s, 1H), 7.11 – 7.07 (m, 3H), 6.52 (s, 1H), 3.85 (s, 12H). The data were in agreement with those reported in the literature.[1]

1.4 Synthesis of **Cur- DMBA**

Two drops of piperidine was added to the solution of **Cur** (0.57 g, 1.55 mmol) and terephthalaldehyde (0.47 g, 3.15 mmol) in 20 mL toluene at room temperature and then the mixture was refluxed for 4 h. The residue obtained by concentration under reduced pressure was purified by column chromatography on silica gel (cyclohexane: acetone = 4:1, v/v) to afford crude product. Finally, it was recrystallized from 8 mL ethanol to give red solid (0.24 g, 36.0%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.72 (d, *J* = 15.4 Hz, 1H), 7.51 (d, *J* = 16.1 Hz, 1H), 7.41 (d, *J* = 8.9 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.96 (d, *J* = 15.9 Hz, 2H), 6.92-6.81 (m, 3H), 6.59 (d, *J* = 8.8 Hz, 2H), 5.90 (d, *J* = 7.5 Hz, 2H), 3.92 (s, 3H), 3.89 (s, 3H), 2.99 (s, 6H). The data were in agreement with those reported in the literature.[3]

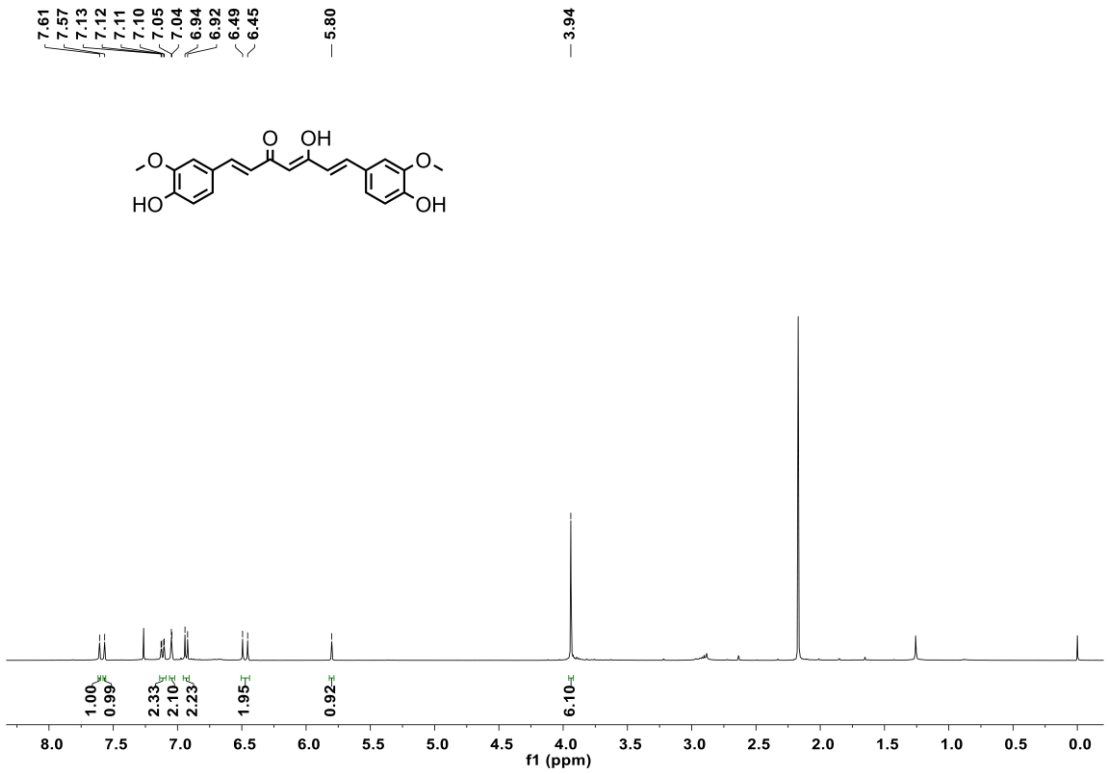

Fig. S1 ^{1}H NMR spectra of **Cur**.

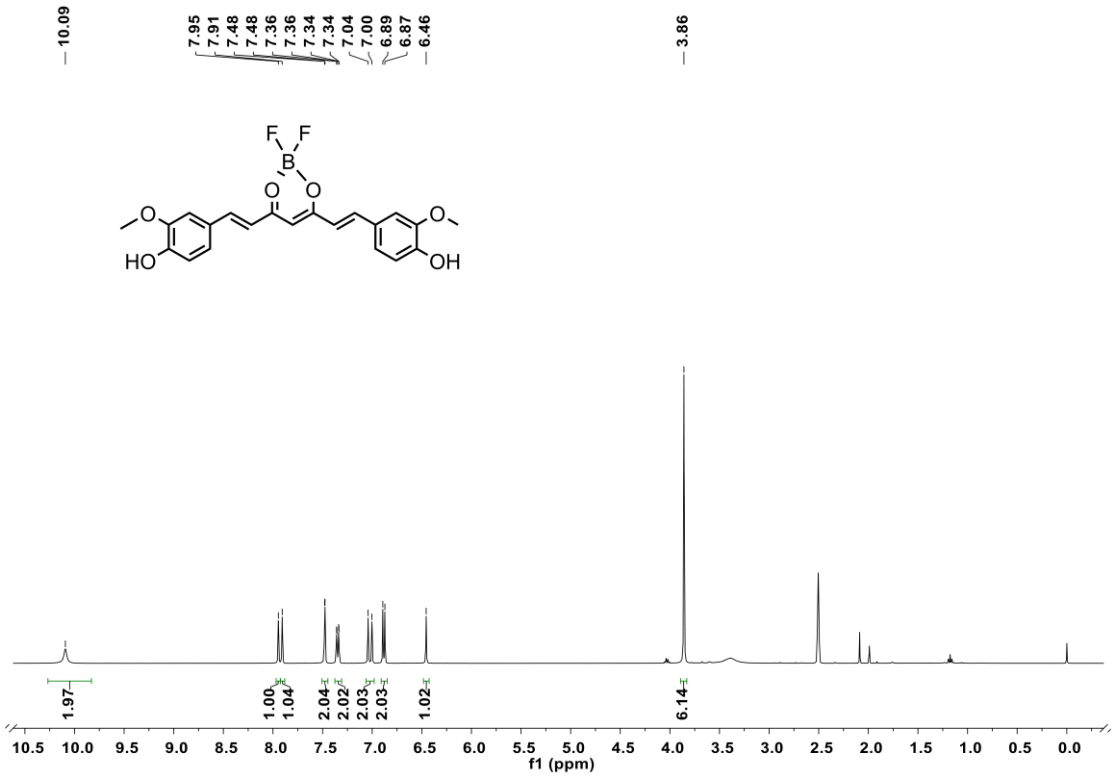

Fig. S2 ^{1}H NMR spectra of **Cur-BF$_2$**.

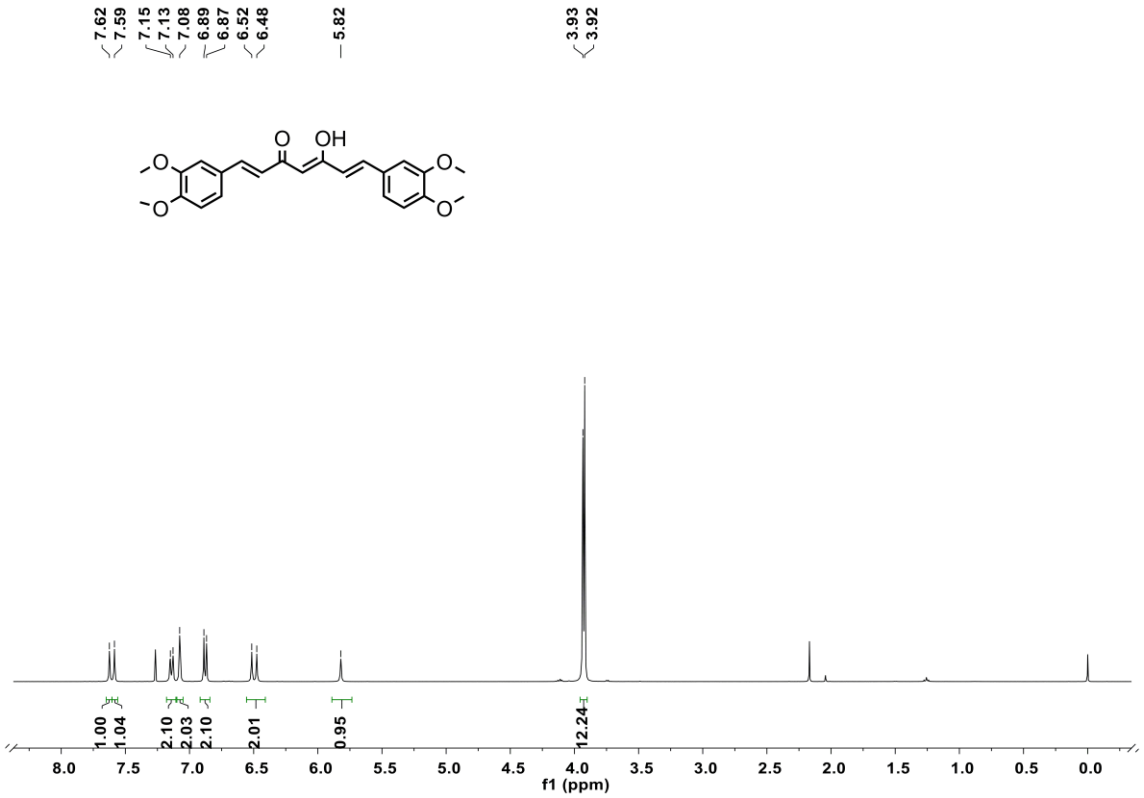

Fig. S3 ^{1}H NMR spectra of **Cur-Me**.

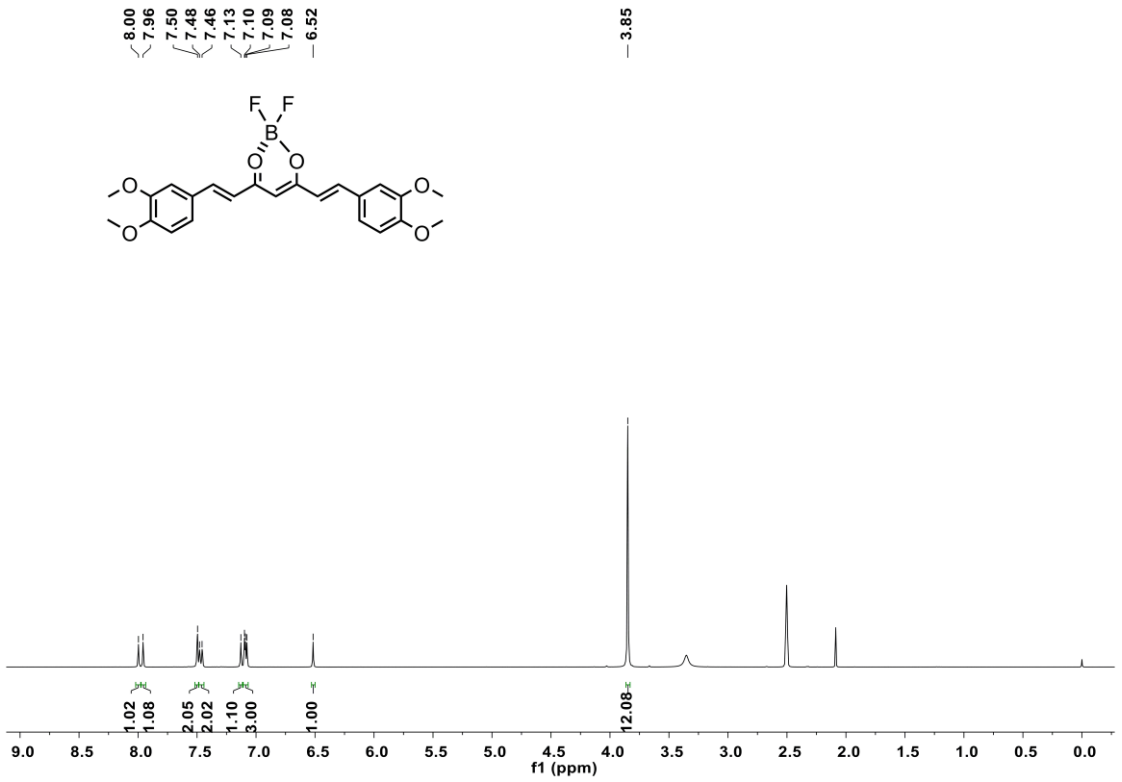

Fig. S4 ^{1}H NMR spectra of **Cur-Me-BF$_2$**.

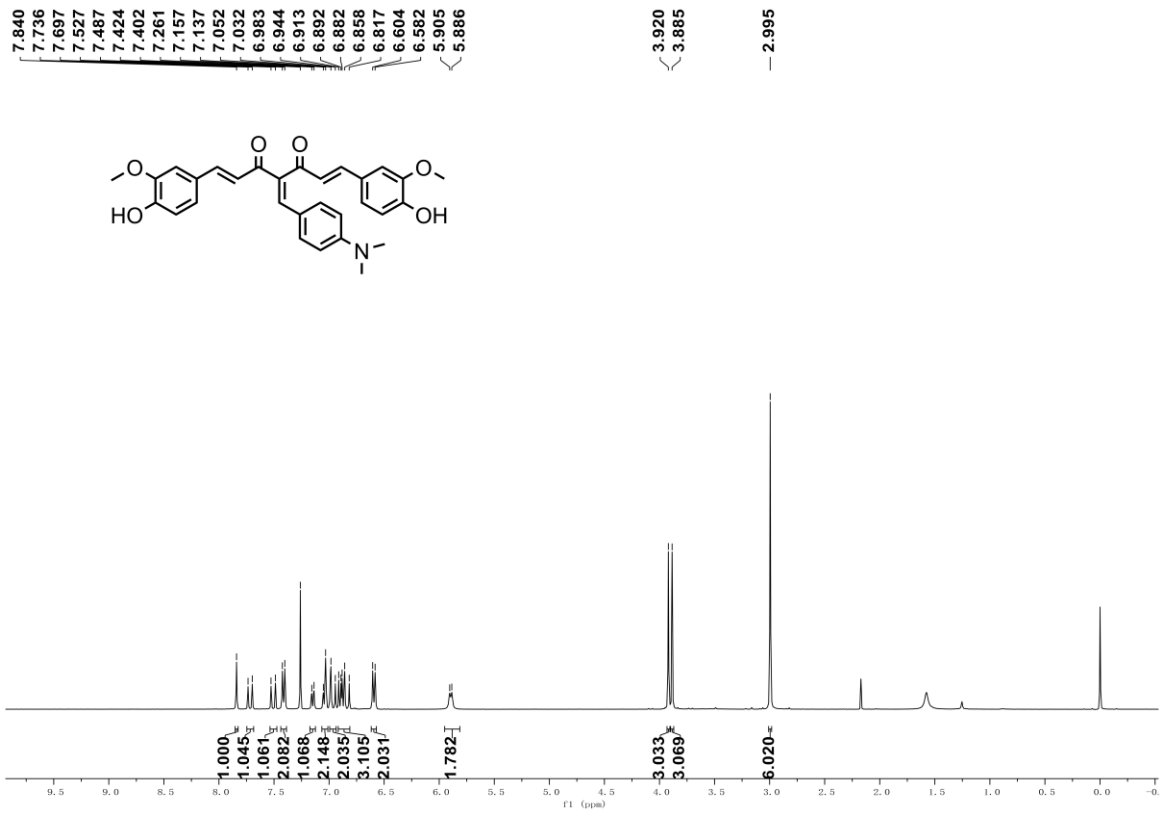

Fig. S5 ^{1}H NMR spectra of **Cur-DMBA**.

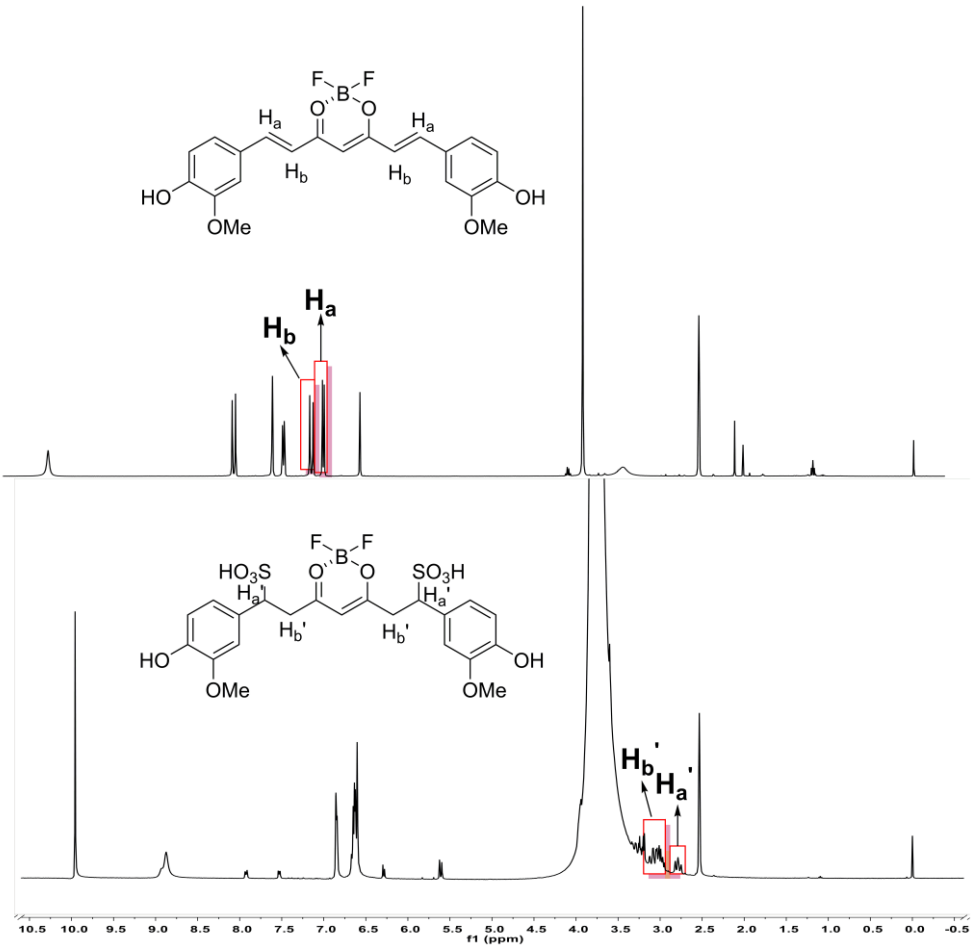

Fig. S6 Partial ^{1}H NMR spectra of probe **Cur-BF$_2$** (a) and **Cur-BF$_2$** with 20 equiv of $NaHSO_3$ (b) in DMSO-d_6 (400 MHz).

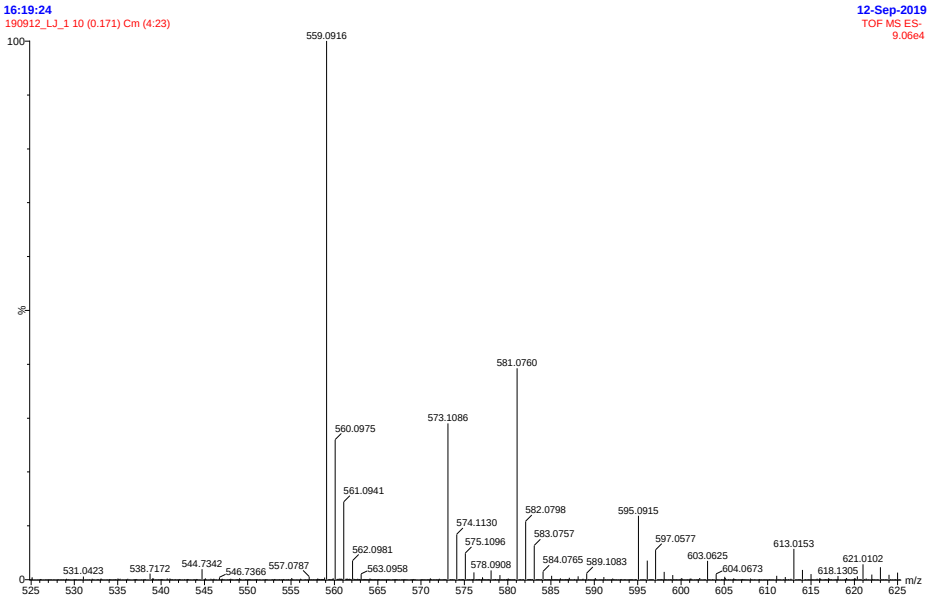

Fig. S7 HRMS spectra of **Cur-BF$_2$** with 20 equiv of $NaHSO_3$.

III. Cell viability assays of H1975 cells

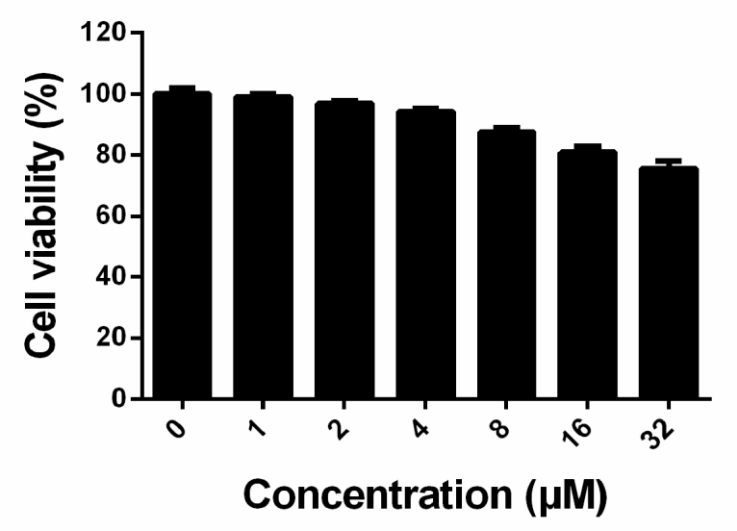

Fig. S8 Cell viability of H1975 cells after incubation with different concentrations of **Cur-BF_2** (0-32 μM) for 24h.

References

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