Synthesis of Novel 10,11-Methylenedioxy-camptothecin Glycoside Derivatives and Investigation of Their Anti-tumor Effects in Vivo

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**Table S1** Ligand binding free energy for topotecan and FL118 in Top1/DNA complex (PDB code 1K4T) (kcal/mol)

| Compound | Top five scored conformation | Ligand binding free energy of 1K4T (kcal/mol) |
|----------|-----------------------------|---------------------------------------------|
| Topotecan | 1                           | -10.85                                      |
|          | 2                           | -10.01                                      |
|          | 3                           | -9.71                                       |
|          | 4                           | -9.64                                       |
|          | 5                           | -9.59                                       |
| FL118    | 1                           | -9.57                                       |
|          | 2                           | -9.34                                       |
|          | 3                           | -9.17                                       |
|          | 4                           | -9.14                                       |
|          | 5                           | -8.51                                       |

**Scheme S1 Synthesis of glycosyl donors.** Reagents and conditions: (a) pyridine/\(\text{Ac}_2\text{O}\), r.t., 12 h; (b) benzylamine, THF, r.t. 12 h.
Scheme S2 Synthesis of compounds 9-11. Reagents and conditions: (d) p-TsOH, toluene, reflux, 12h.
$^1$H NMR of compound 9a

$^{13}$C NMR of compound 9a
$^1$H NMR of compound 10a

$^{13}$C NMR of compound 10a
$^1$H NMR of compound 11a

$^{13}$C NMR of compound 11a
$^1$H NMR of compound 9b

$^{13}$C NMR of compound 9b
$^1$H NMR of compound 11b

$^{13}$C NMR of compound 11b
HRMS of compound 9a
HRMS of compound 10a
HRMS of compound 11a
HRMS of compound 9b
HRMS of compound 11b

Method: MeOH, flow rate = 1 mL/min, Agilent Eclipse Plus-C18 4.6*250 mm, 5 µm,
temp 25 deg, wavelength 254 nm.
Fig. S1 HPLC analysis of compound 11b

Compound 11b: Ret time: 5.637 min, Purity 99.56%.