Supplementary Materials

Semi-synthesis of Harringtonolide Derivatives and Their Antiproliferative Activity

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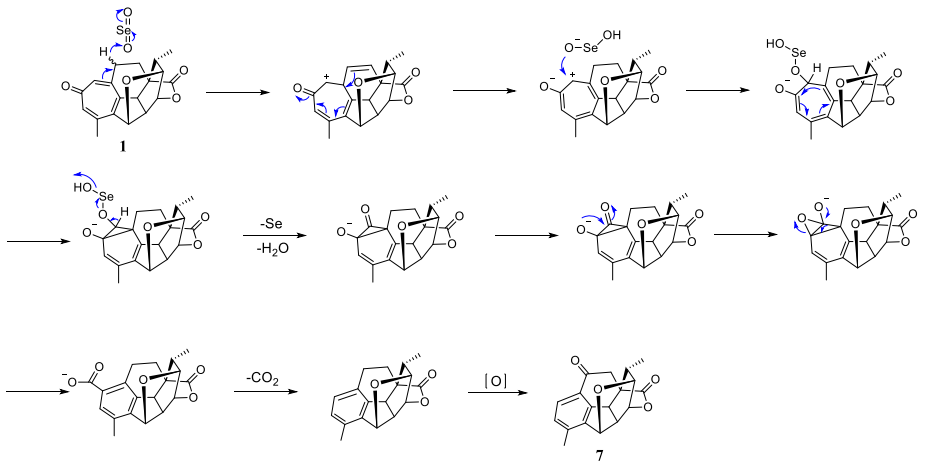
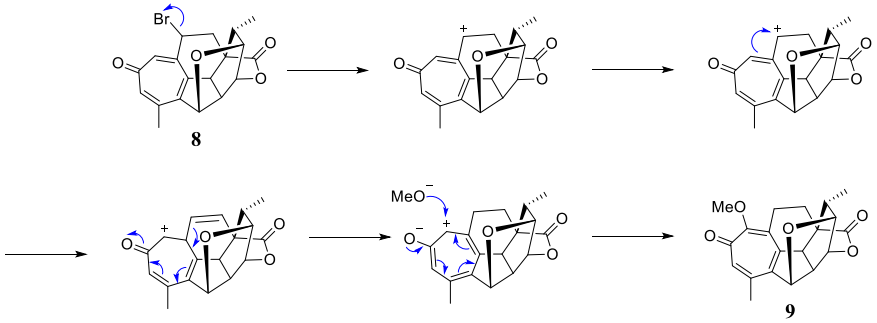
Scheme S1



A possible mechanism for the formation of **7** is presented in Scheme S1. The initial oxidation of allylic in HO (**1**) by SeO_2 was accompanied by the formation of $HSeO_2^-$ anion [1] and carbocation, which would rearrange to cycloheptatriene carbocation. Subsequently, $HSeO_2^-$ attacked the cycloheptatriene carbocation, while that followed by electrocyclic annulation to give cyclopropanes intermediate. The subsequent elimination of Se and H_2O led to the cyclopropenone intermediate [2-3], which then attacked by oxygen anion. Subsequent rearrangement occurs in the manner as indicated arrows, giving carboxylic acid intermediate. Further decarboxylation [4] of this intermediate and oxidation by SeO_2 would yield compound **7**.

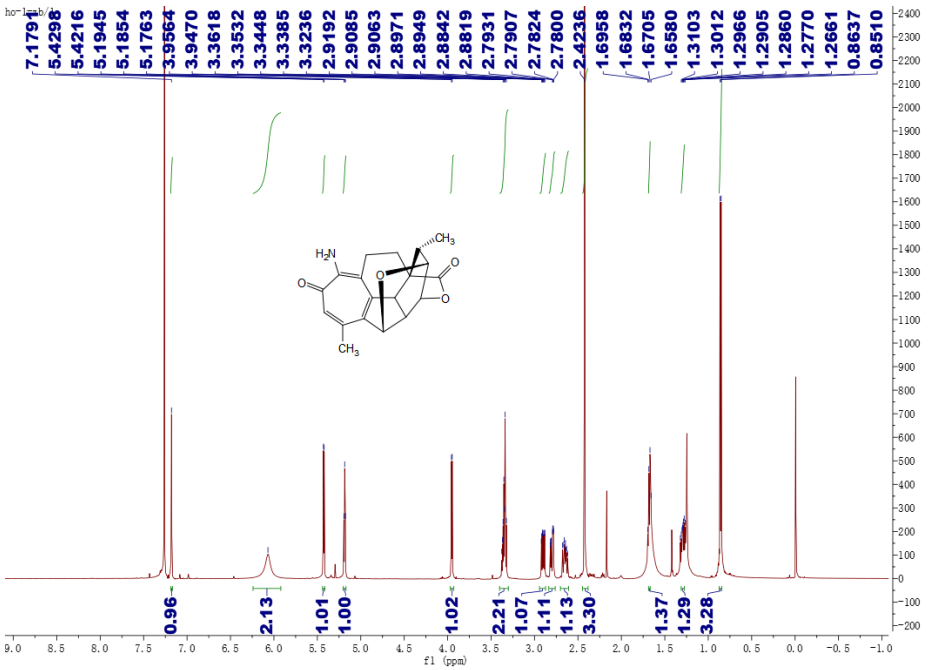
Scheme S2



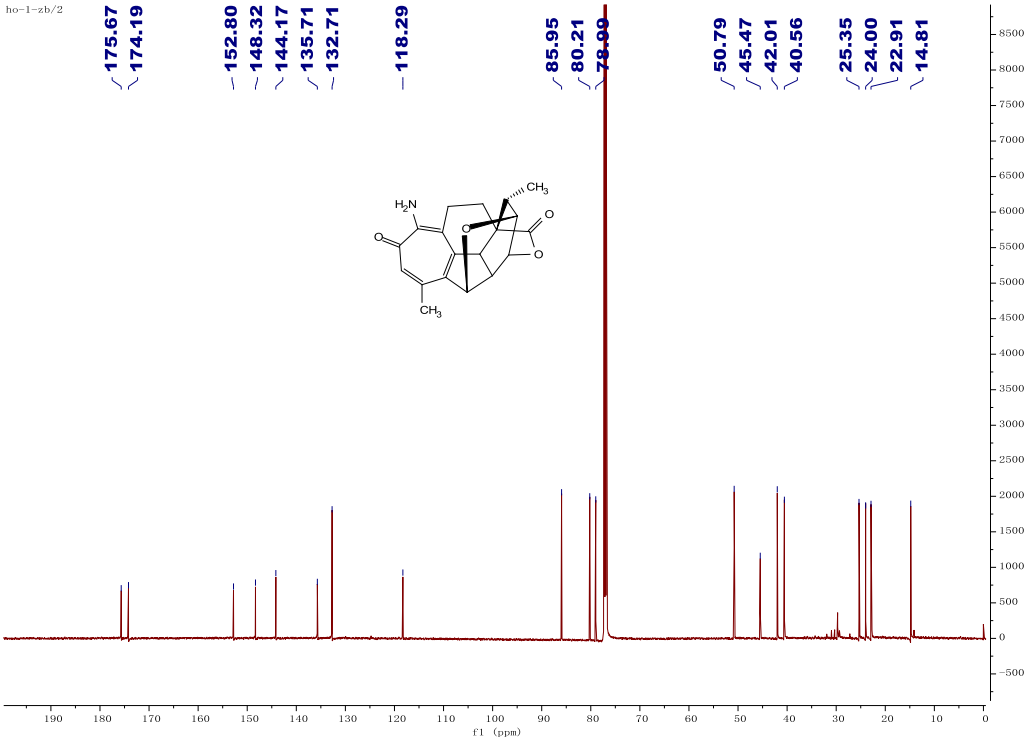
A possible mechanism for the formation of **9** is presented in Scheme S2. Under the attacked of nucleophile (methoxy anion), leaving of bromine atoms in compound **8** yield an allylic carbocation, which then rearranged to a more stable form–cycloheptatriene carbocation too. Subsequently, this carbocation intermediate was attacked by methoxy anion, and then further electron transfer occurs in the manner as indicated arrows to produce **9**.

Figure S1：NMR spectra for all compounds

Compound 2

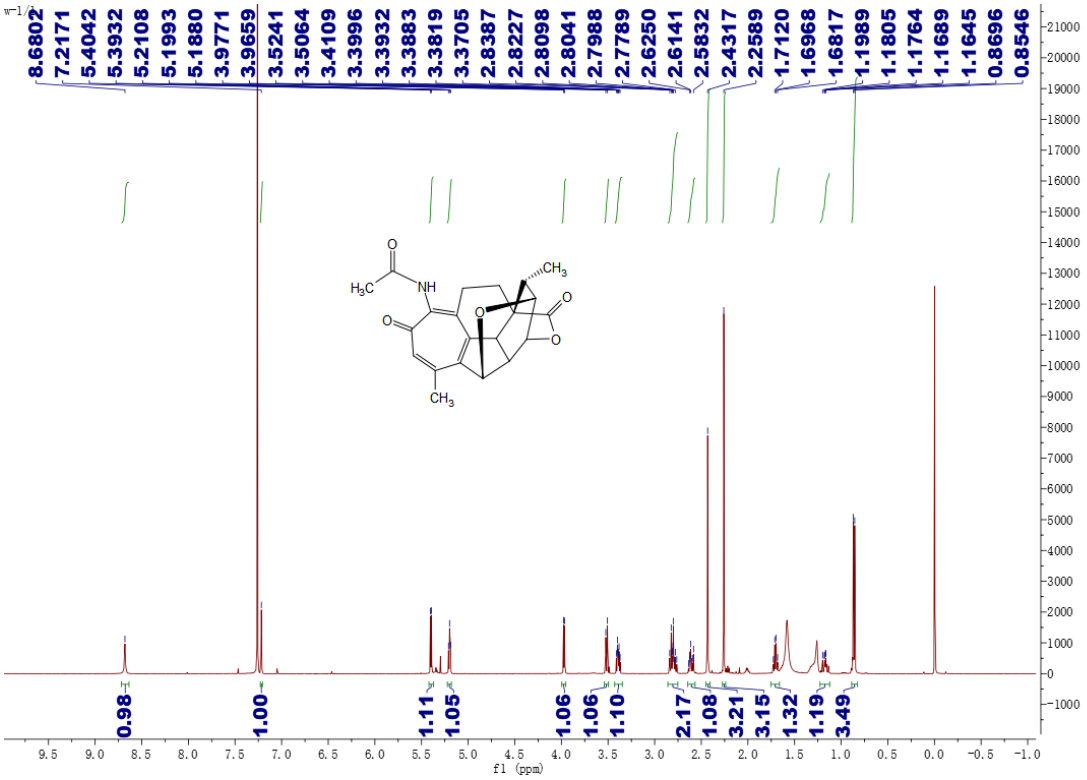


^{1}H-NMR spectrum (600 MHz, $CDCl_3$) for 2

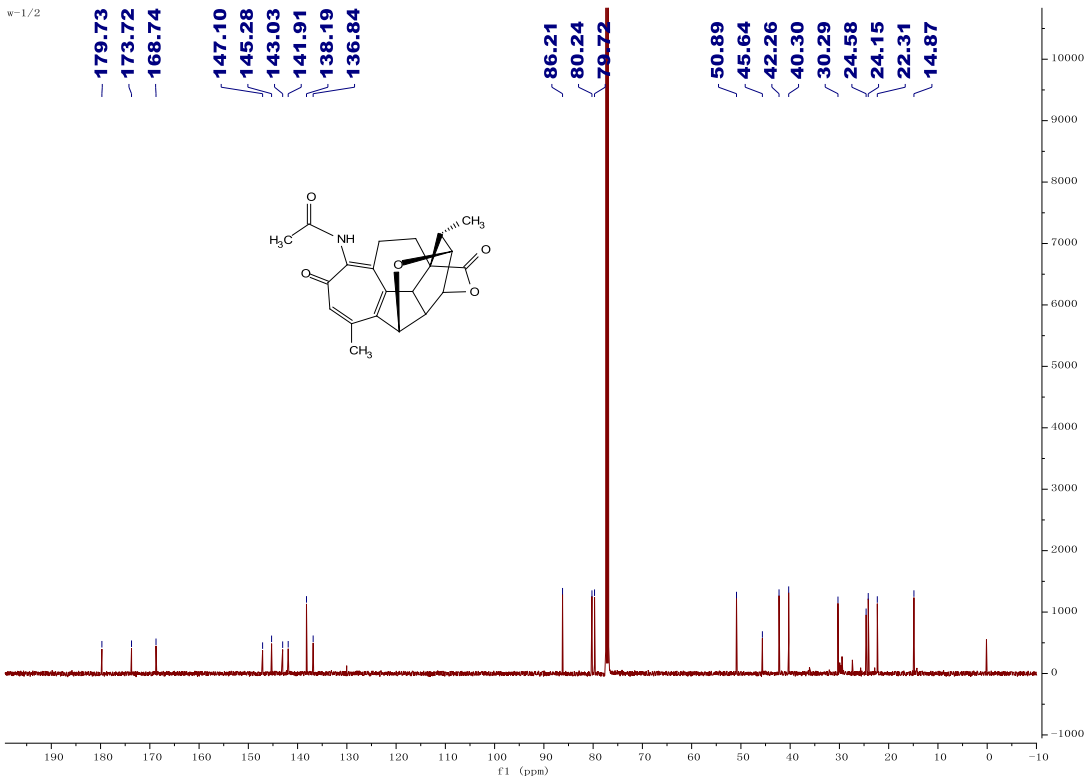


^{13}C-NMR spectrum (151 MHz, $CDCl_3$) for 2

Compound 3

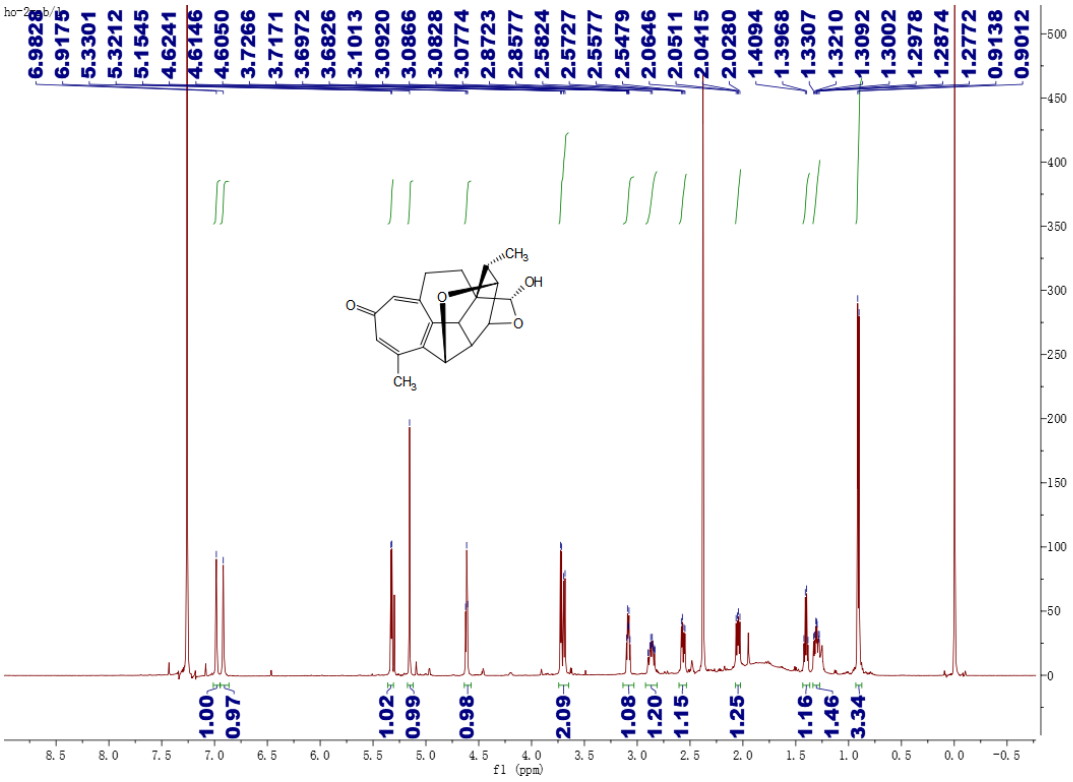


^{1}H-NMR spectrum (500 MHz, $CDCl_3$) for 3

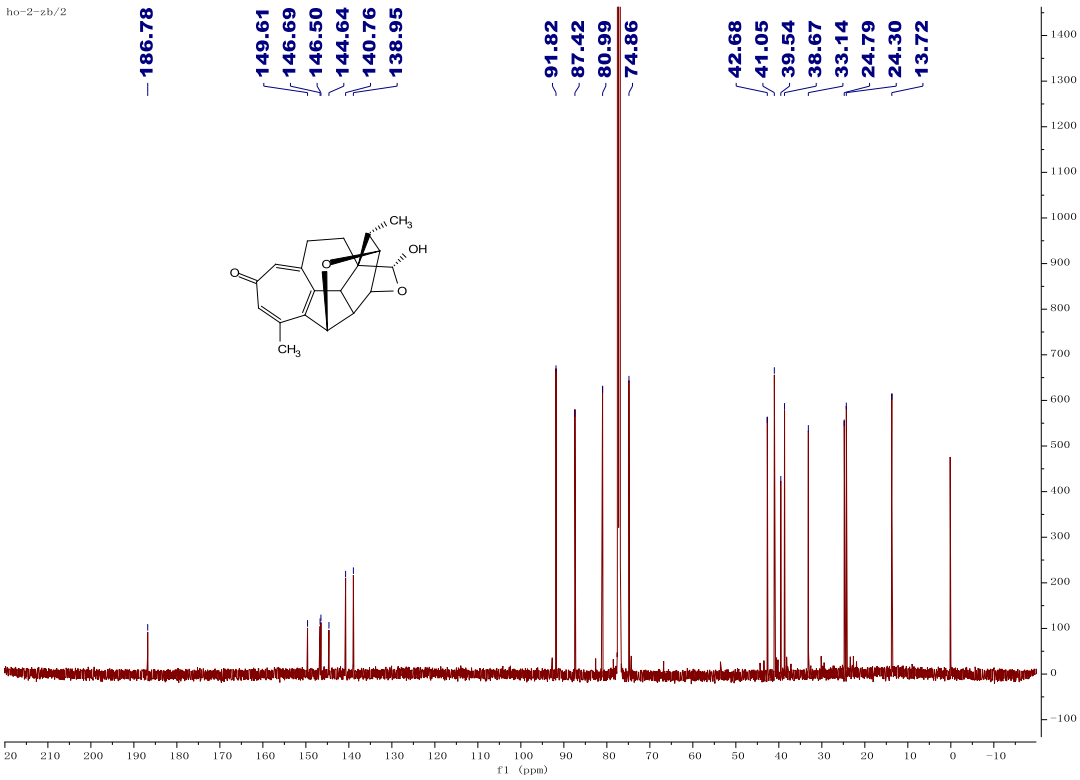


^{13}C-NMR spectrum (126 MHz, $CDCl_3$) for 3

Compound 4

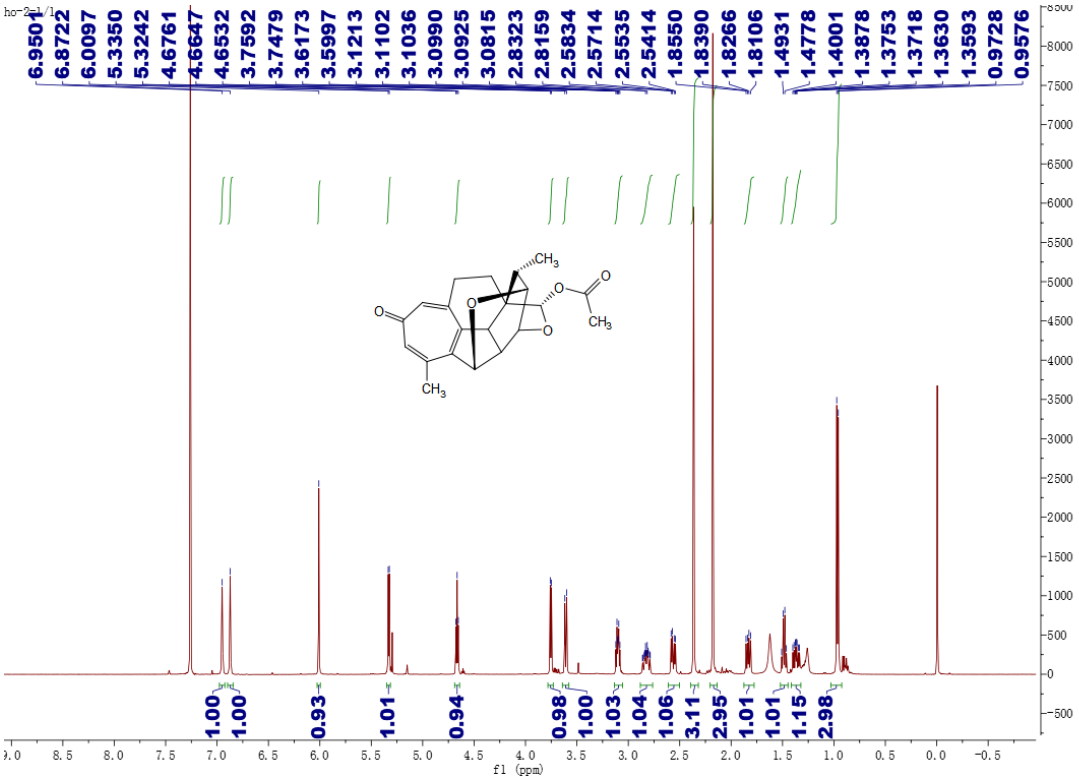


^{1}H-NMR spectrum (600 MHz, $CDCl_3$) for 4

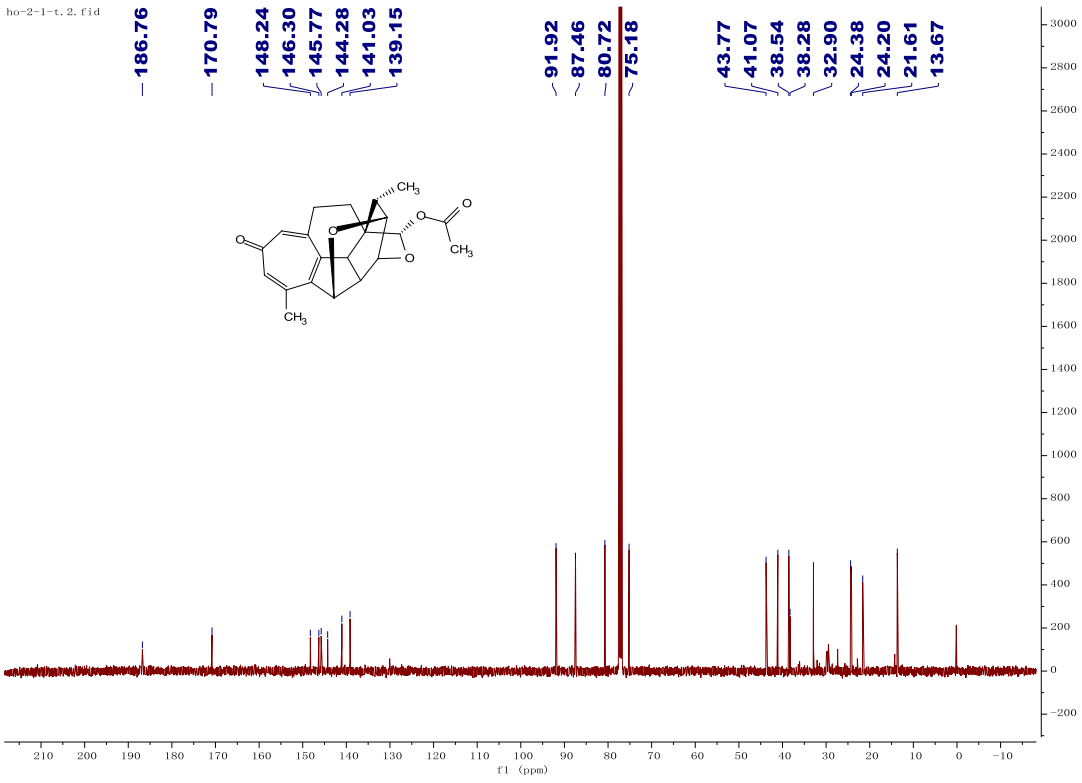


^{13}C-NMR spectrum (151 MHz, $CDCl_3$) for 4

Compound 5

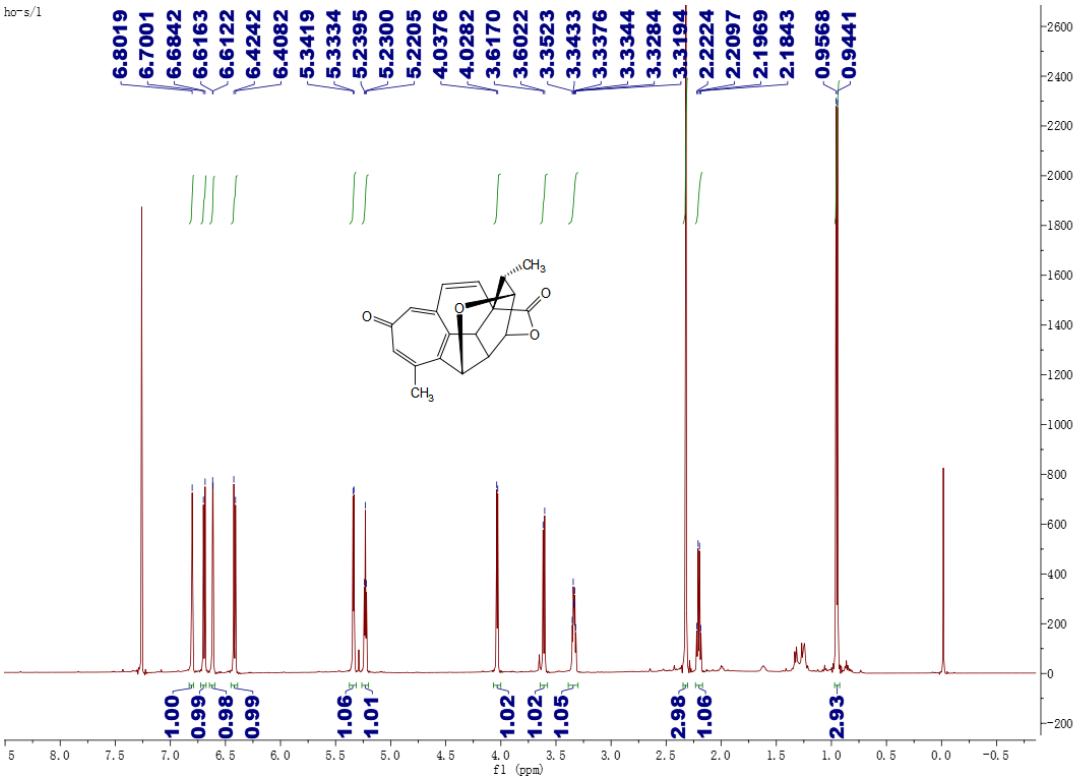


^{1}H-NMR spectrum (500 MHz, $CDCl_3$) for 5

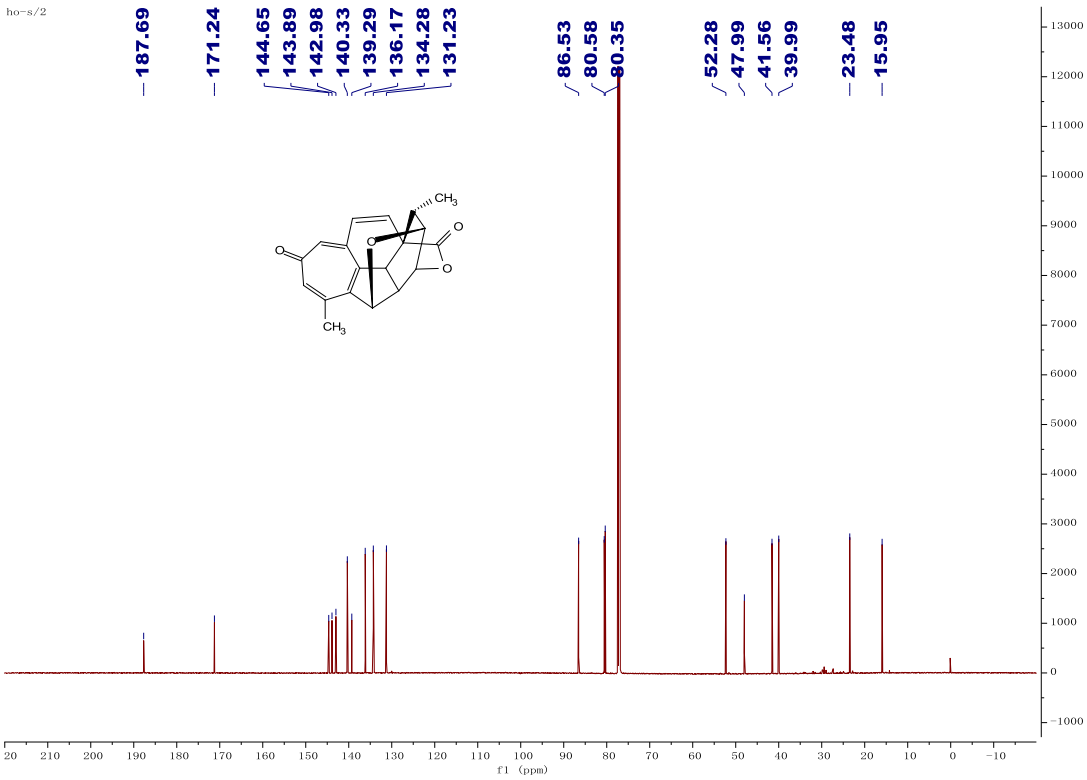


^{13}C-NMR spectrum (151 MHz, $CDCl_3$) for 5

Compound 6

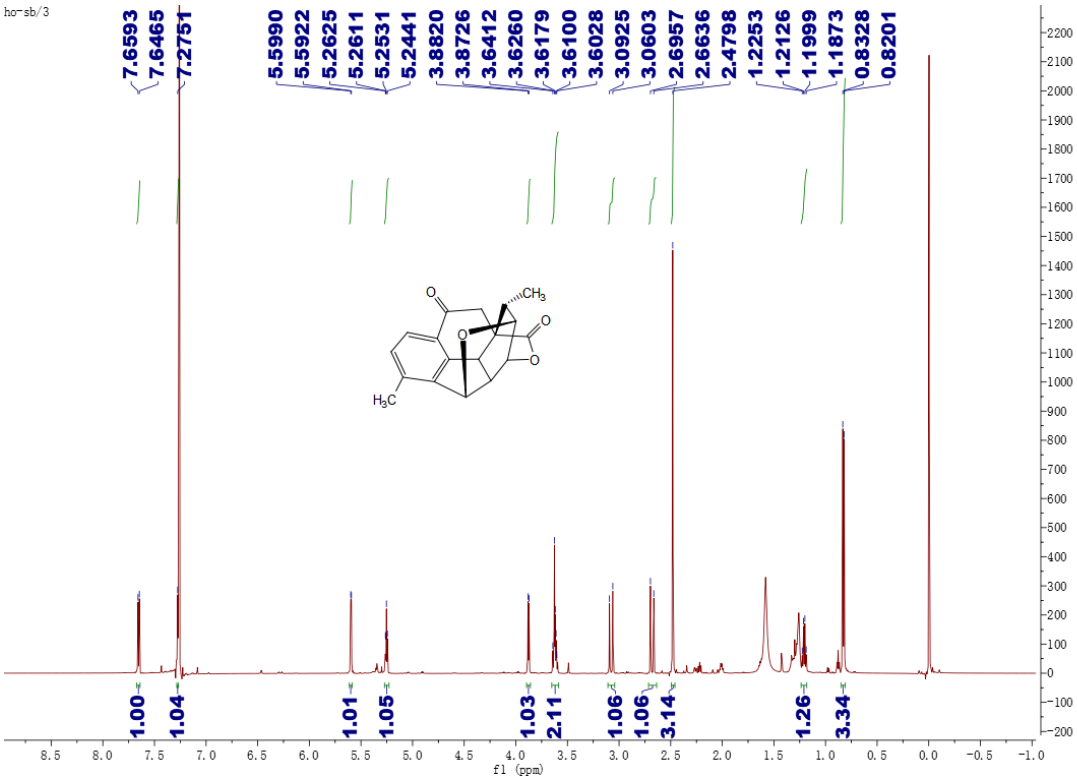


^{1}H-NMR spectrum (600 MHz, $CDCl_3$) for 6

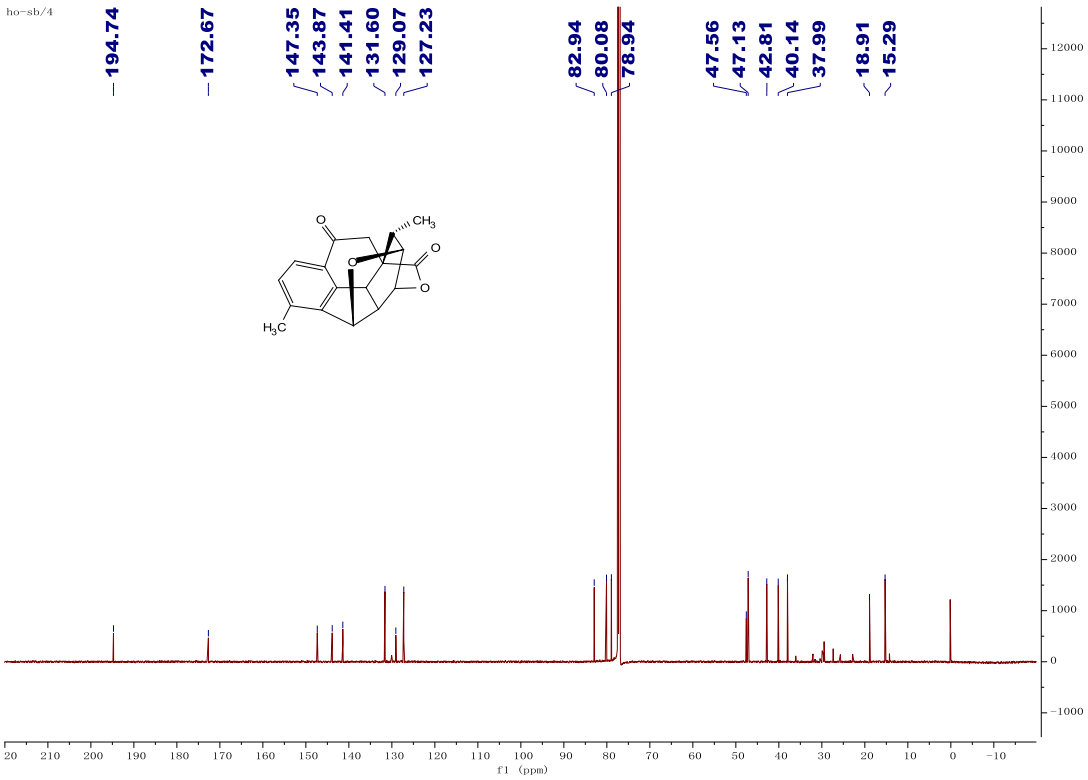


^{13}C-NMR spectrum (151 MHz, $CDCl_3$) for 6

Compound 7

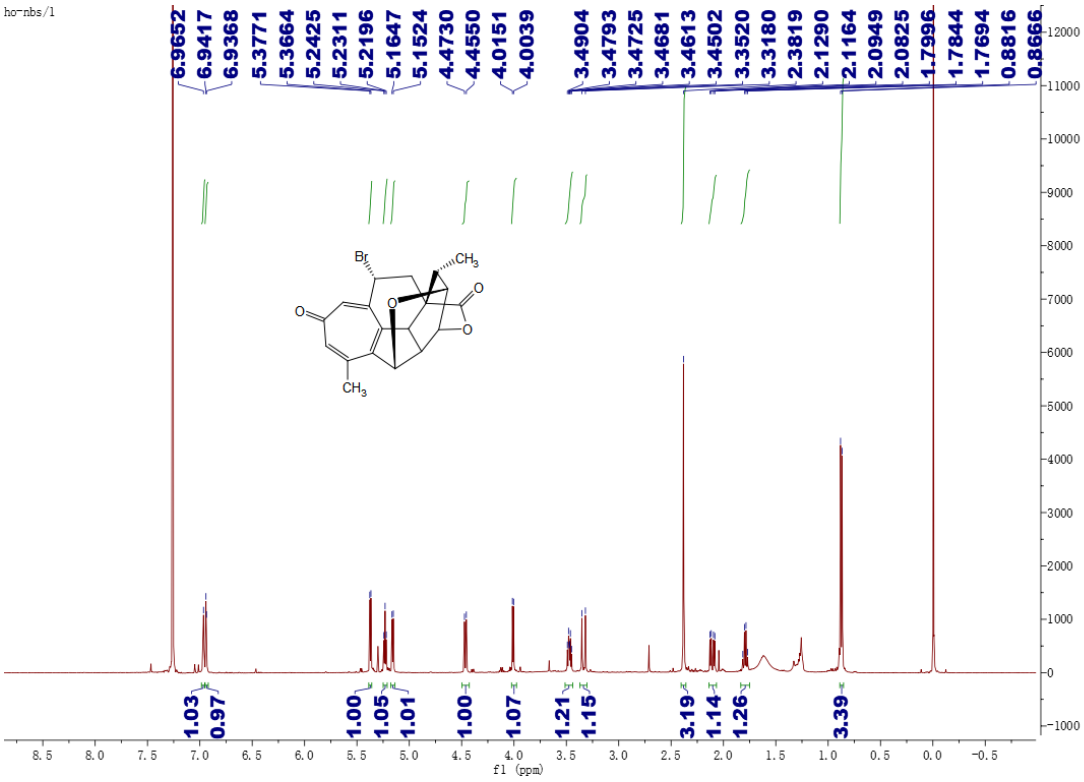


^{1}H-NMR spectrum (600 MHz, $CDCl_3$) for 7

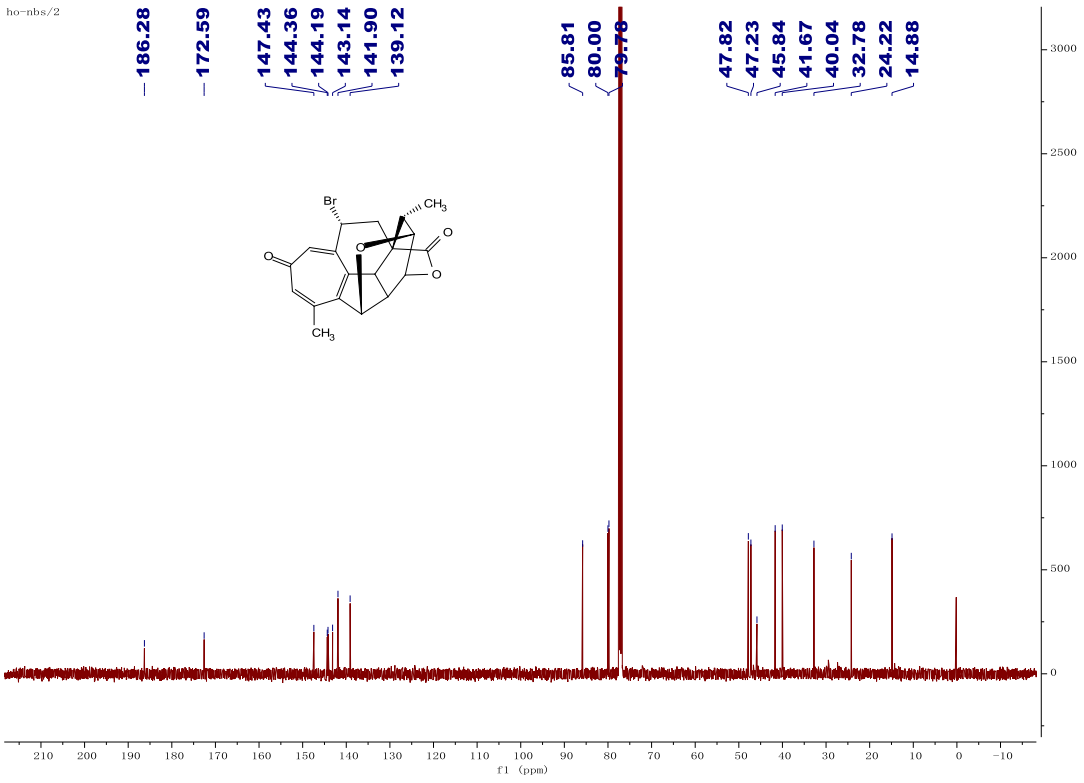


^{13}C-NMR spectrum (151 MHz, $CDCl_3$) for 7

Compound 8

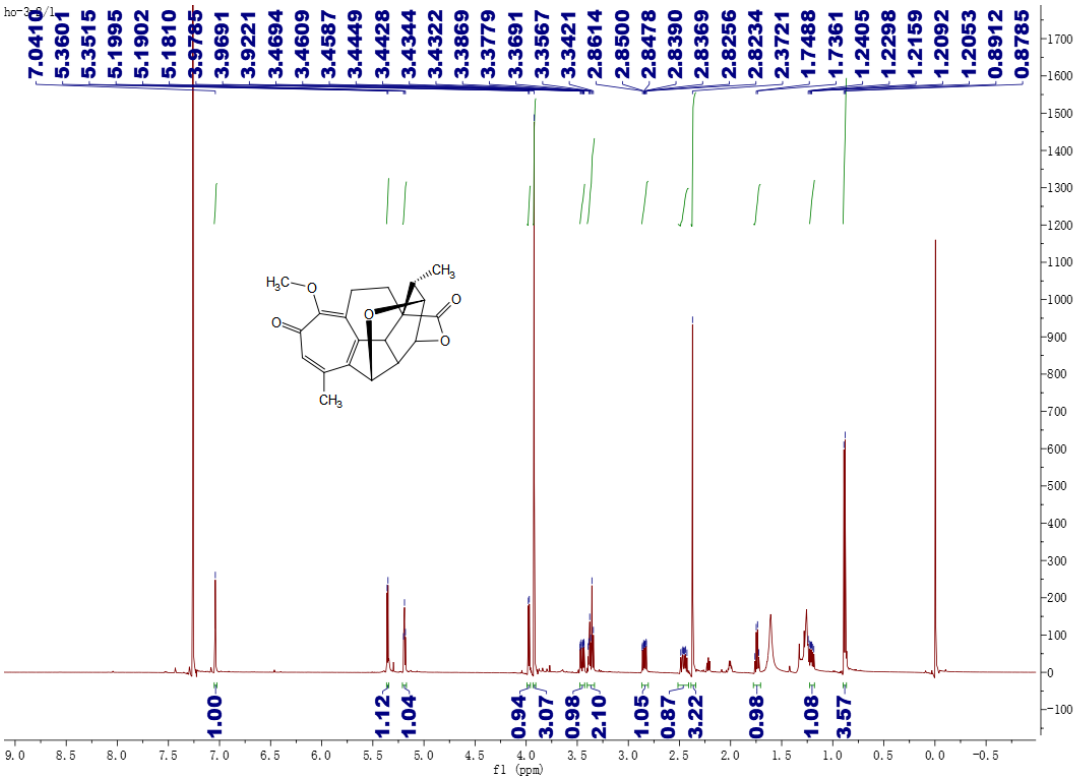


^{1}H-NMR spectrum (500 MHz, $CDCl_3$) for 8

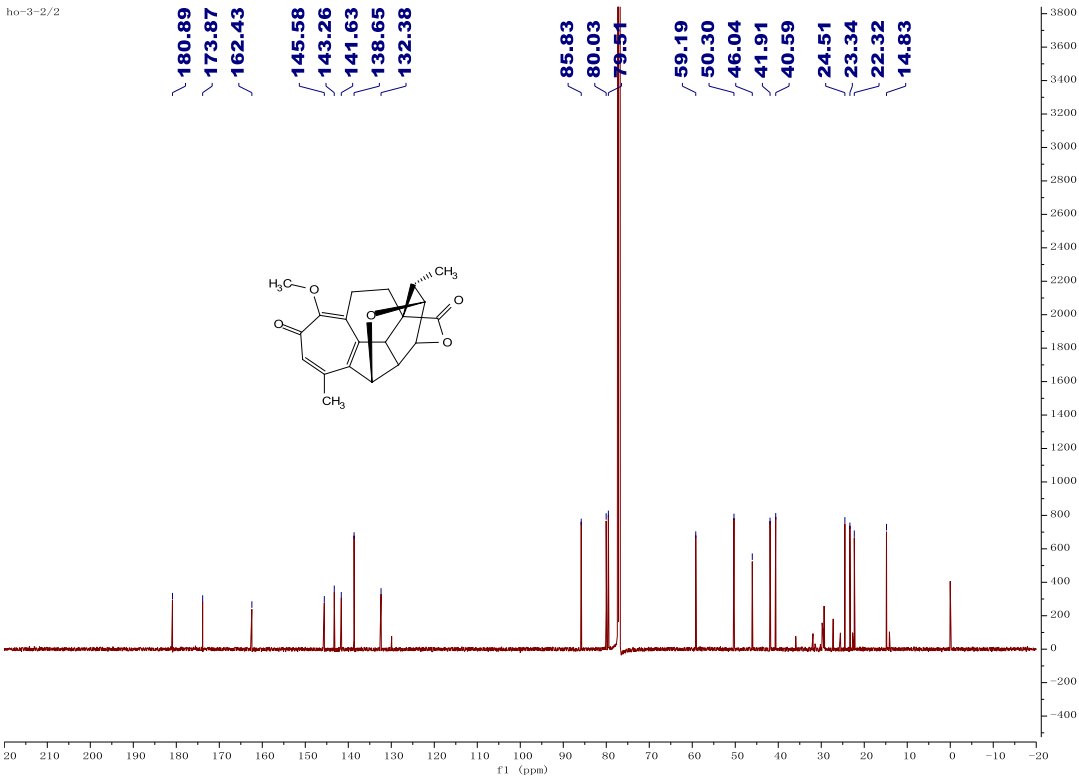


^{13}C-NMR spectrum (126 MHz, $CDCl_3$) for 8

Compound 9

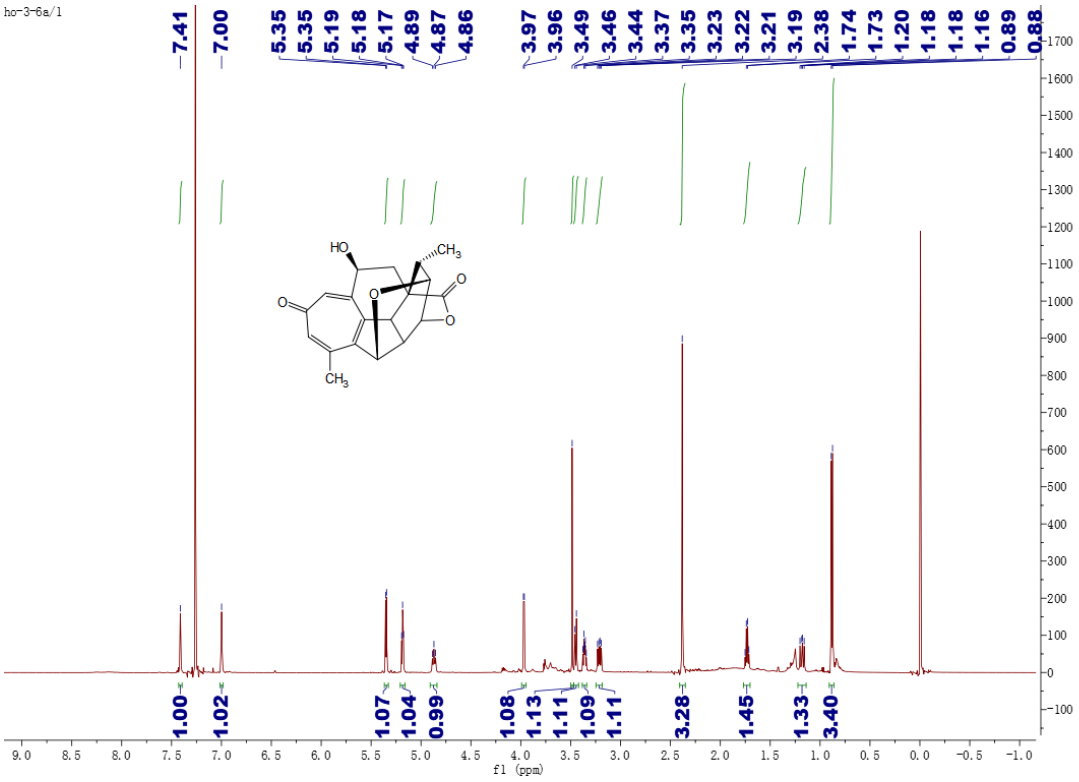


^{1}H-NMR spectrum (600 MHz, $CDCl_3$) for 9

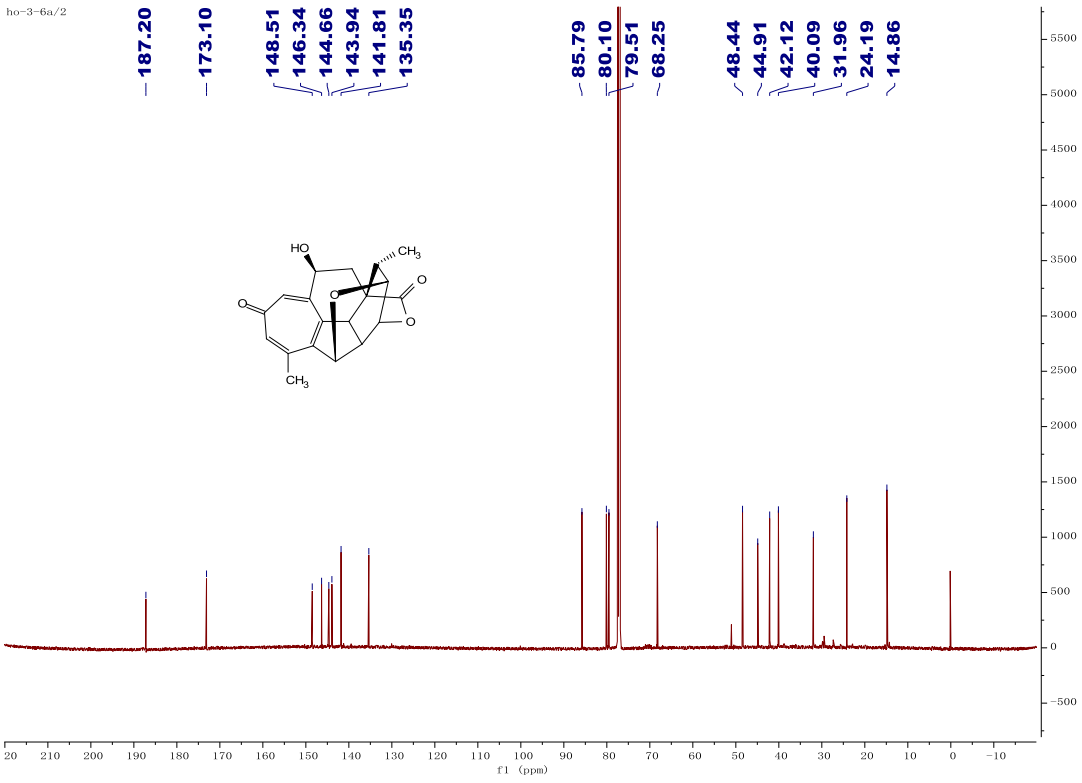


^{13}C-NMR spectrum (151 MHz, $CDCl_3$) for 9

Compound 10

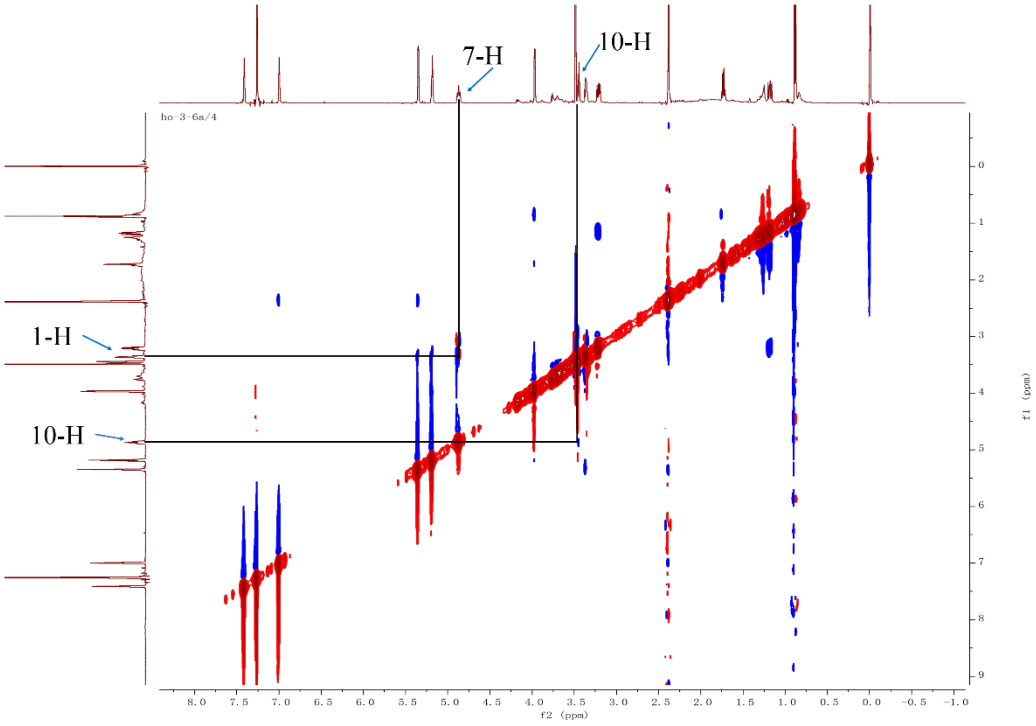


^{1}H-NMR spectrum (600 MHz, $CDCl_3$) for 10

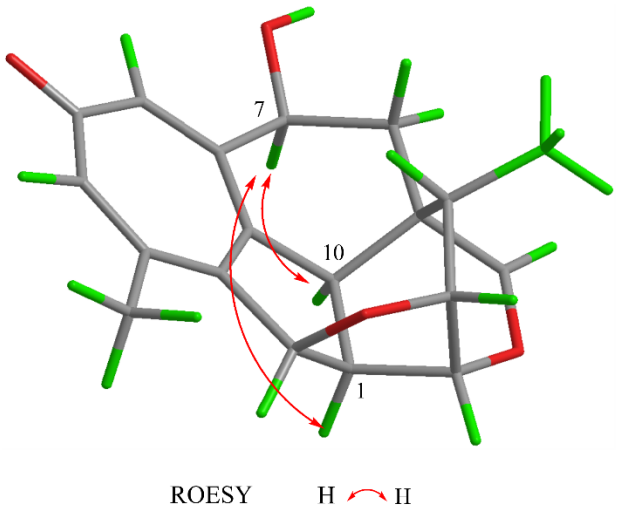


^{13}C-NMR spectrum (151 MHz, $CDCl_3$) for 10

ROESY Spectra of compound 10

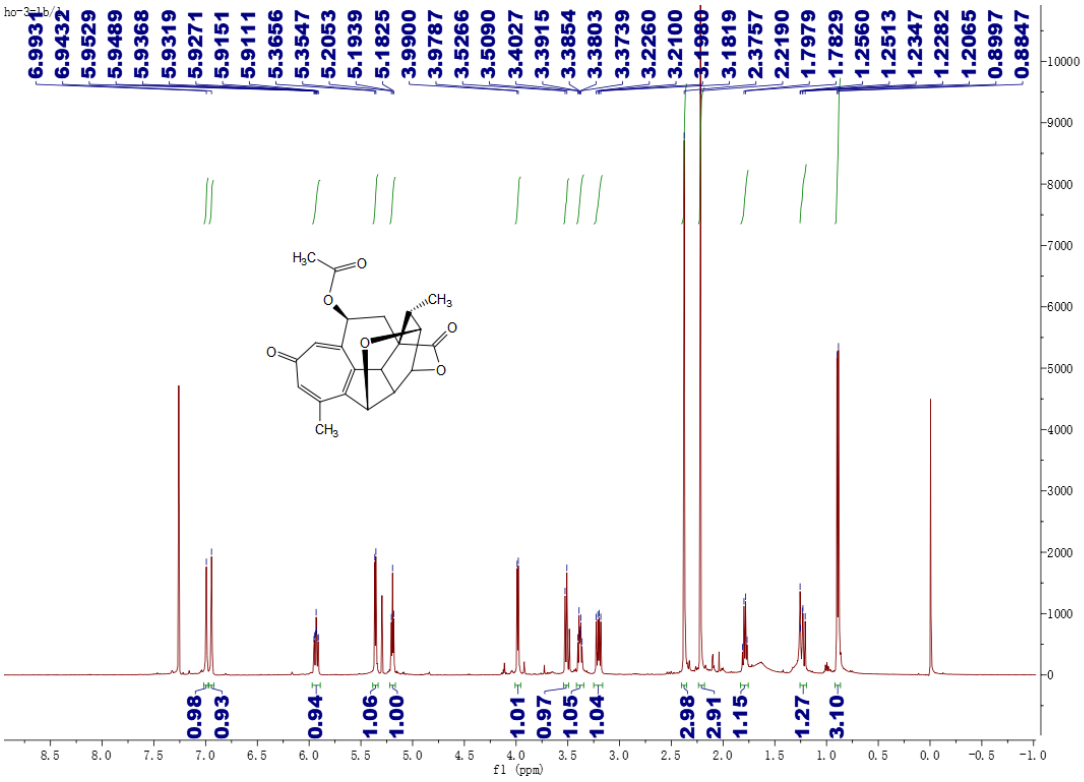


ROESY Spectra of compound 10

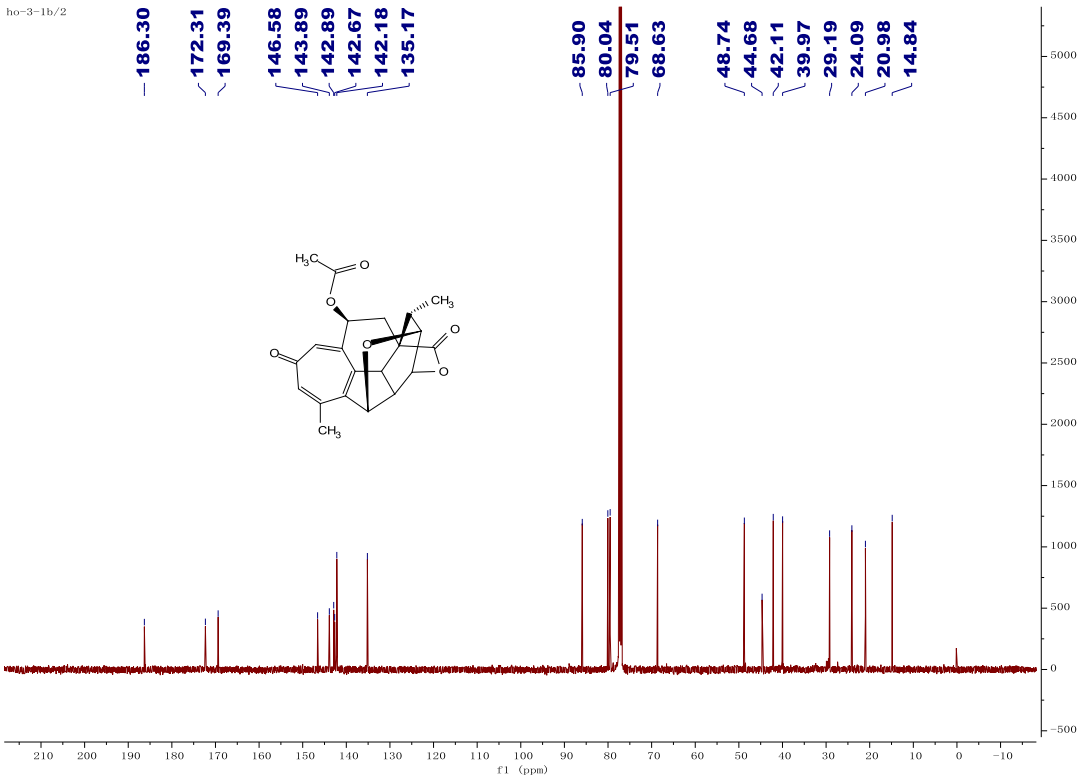


ROESY correlations of compound 10

Compound 10a

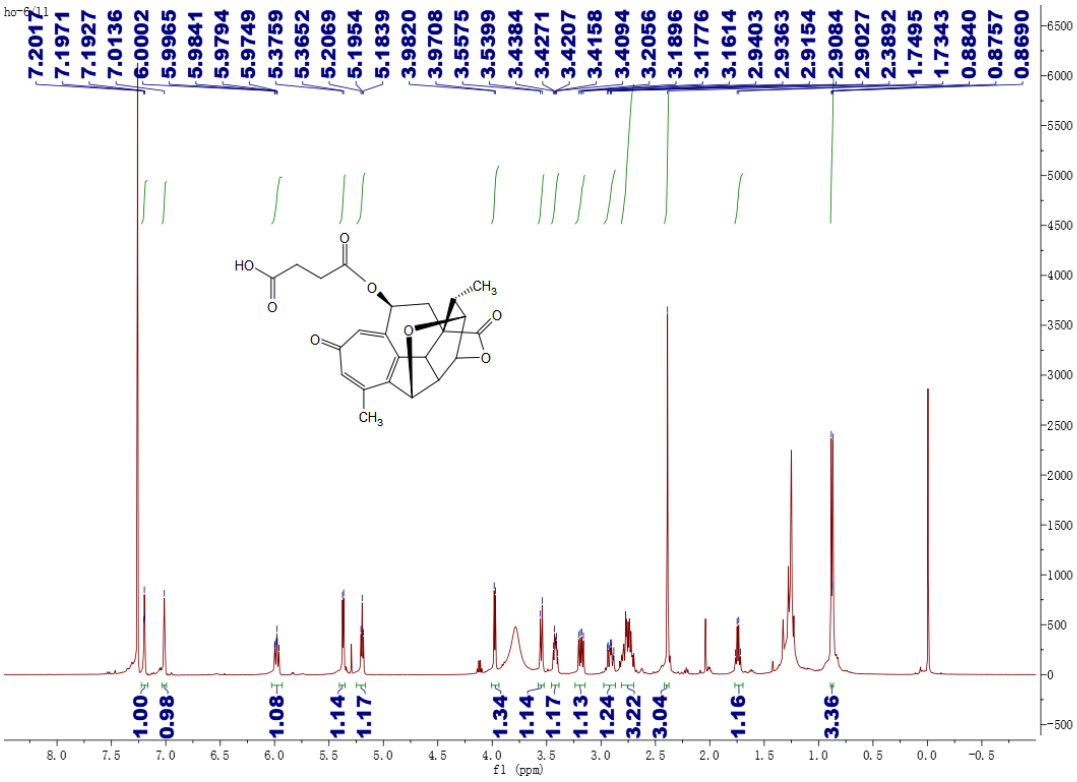


^{1}H-NMR spectrum (500 MHz, $CDCl_3$) for 10a

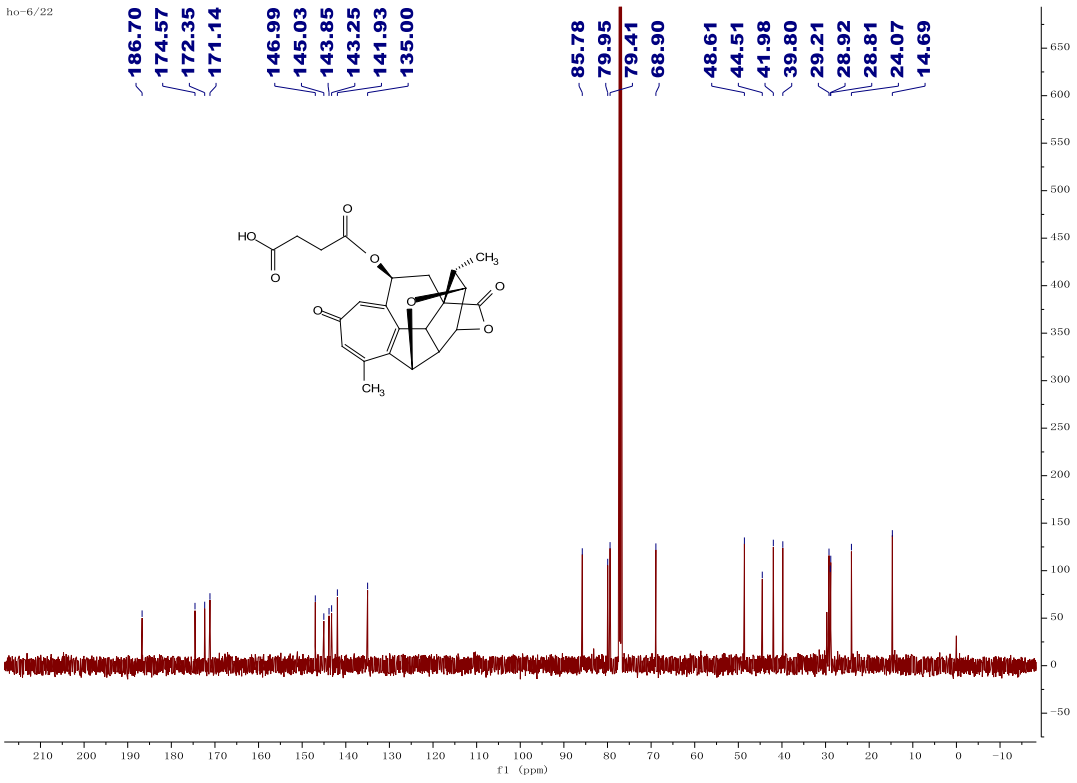


^{13}C-NMR spectrum (126 MHz, $CDCl_3$) for 10a

Compound 10b

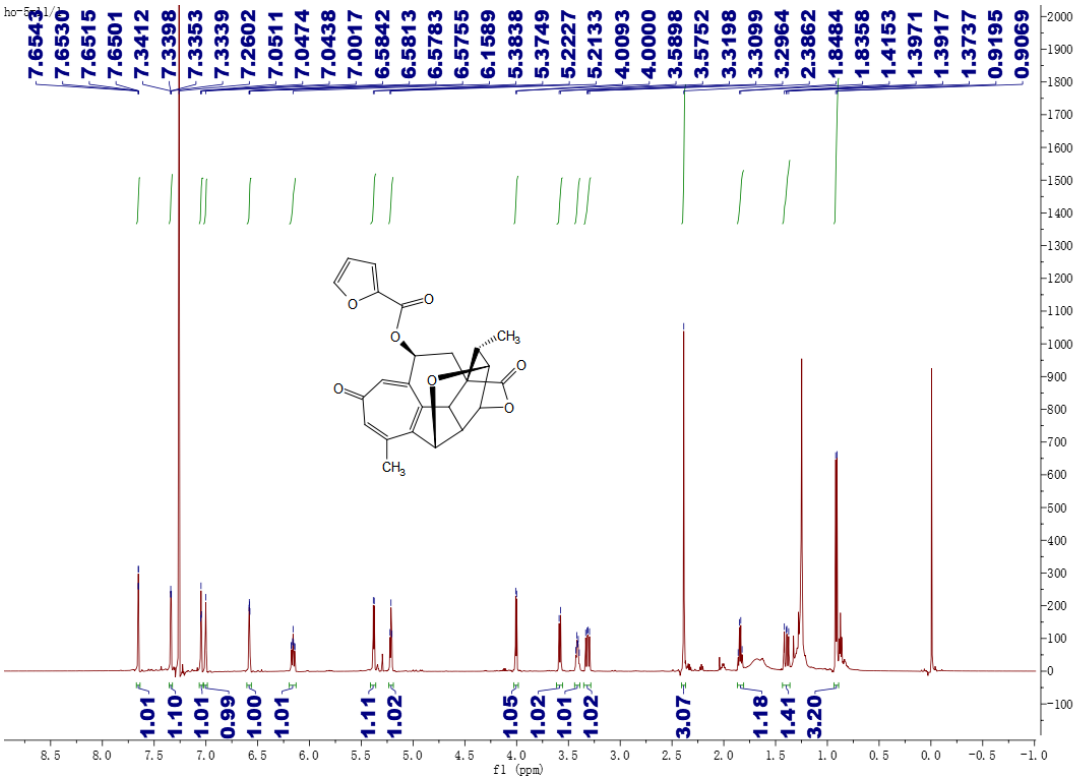


^{1}H-NMR spectrum (500 MHz, $CDCl_3$) for 10b

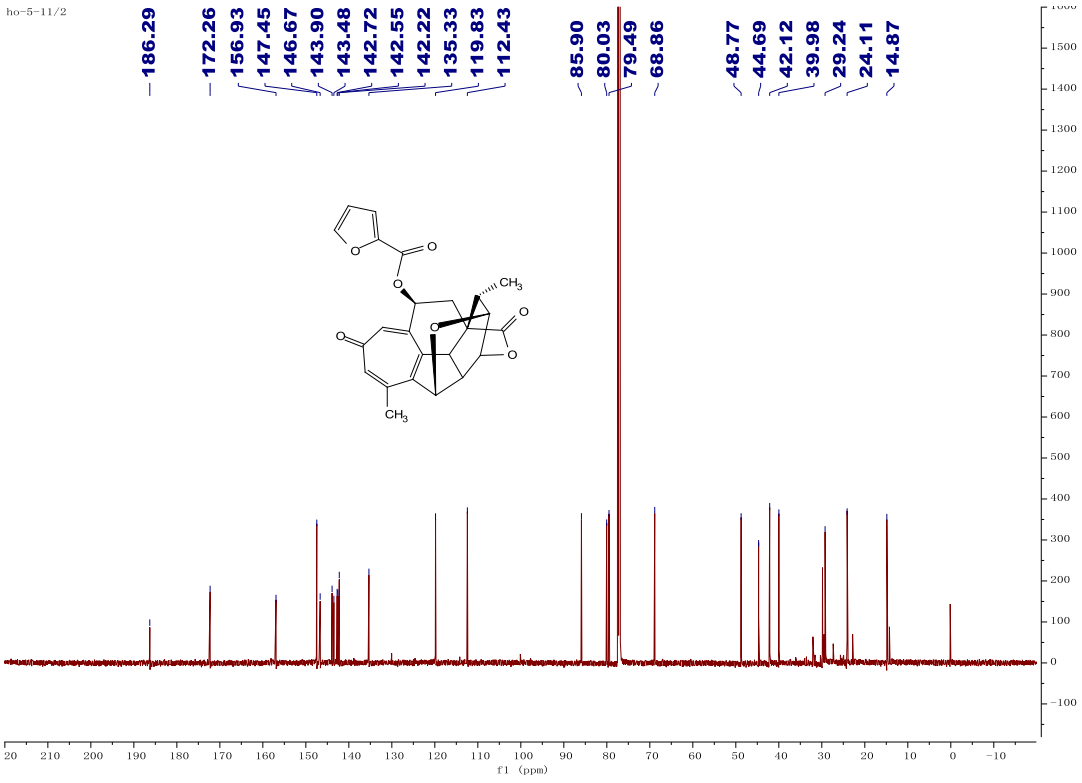


^{13}C-NMR spectrum (126 MHz, $CDCl_3$) for 10b

Compound 10c

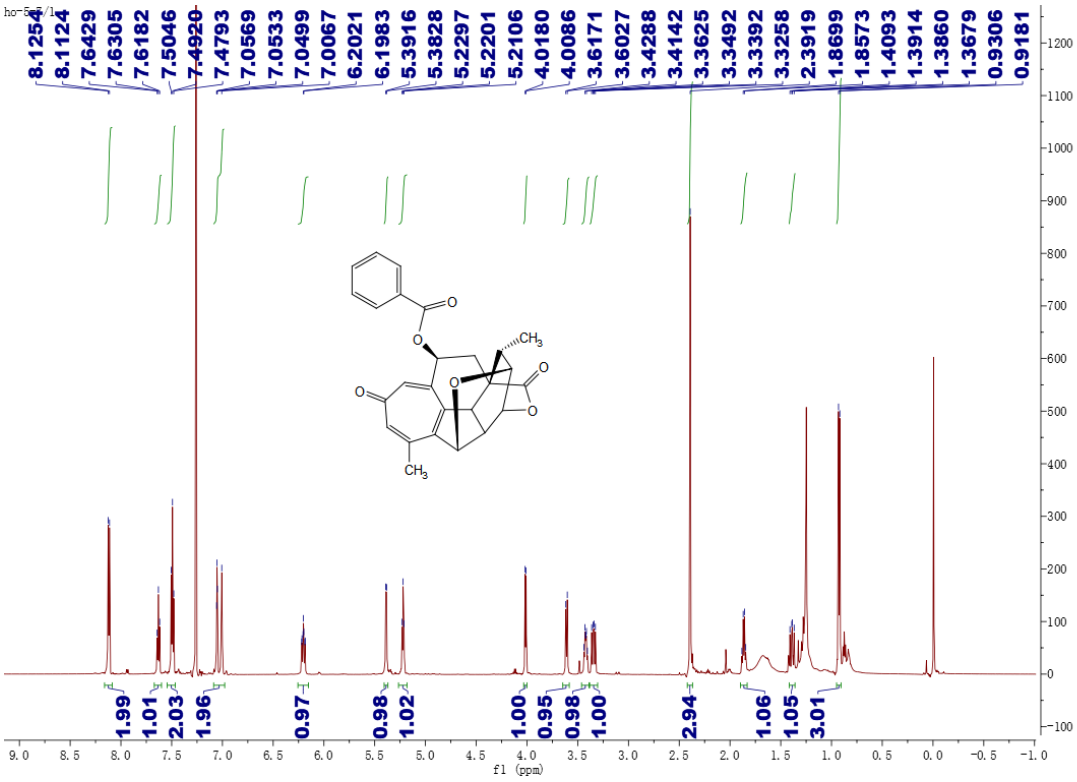


^{1}H-NMR spectrum (600 MHz, $CDCl_3$) for 10c

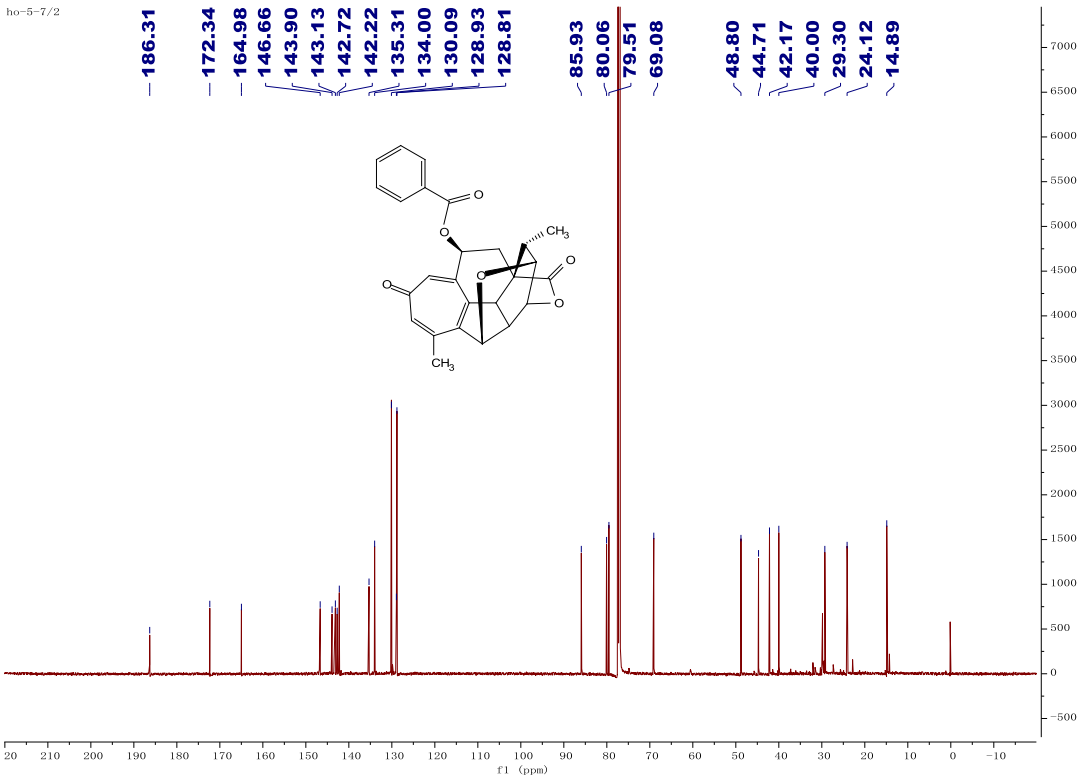


^{13}C-NMR spectrum (151 MHz, $CDCl_3$) for 10c

Compound 10d

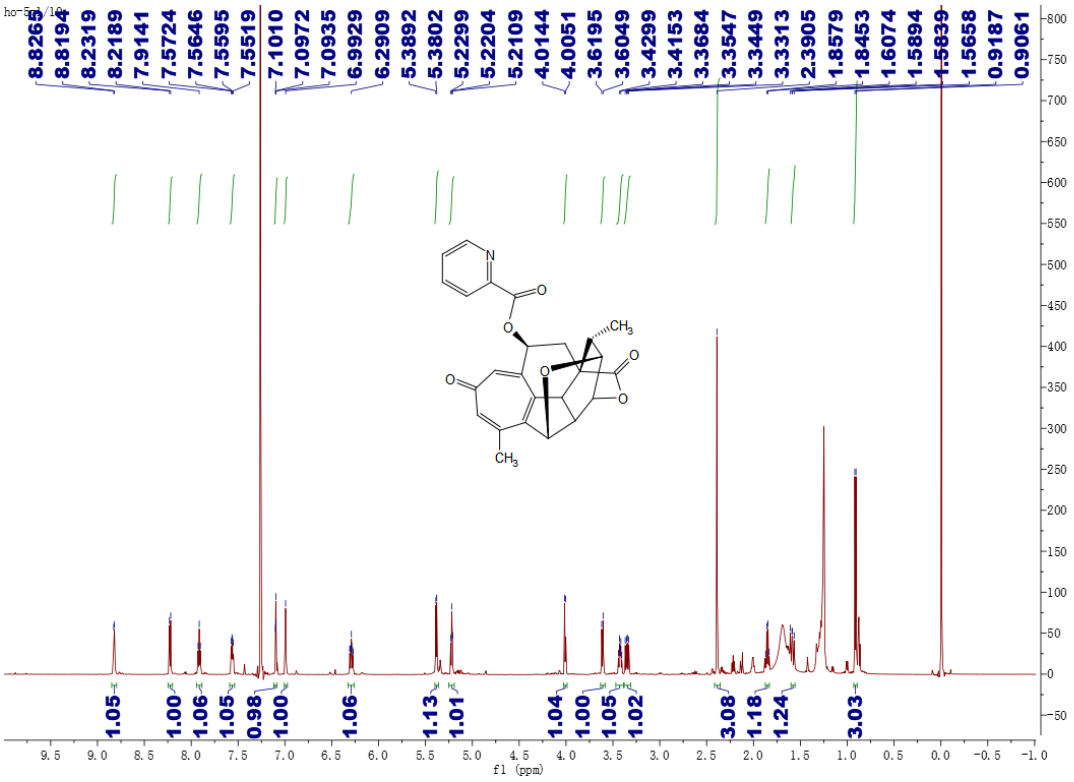


^{1}H-NMR spectrum (600 MHz, $CDCl_3$) for 10d

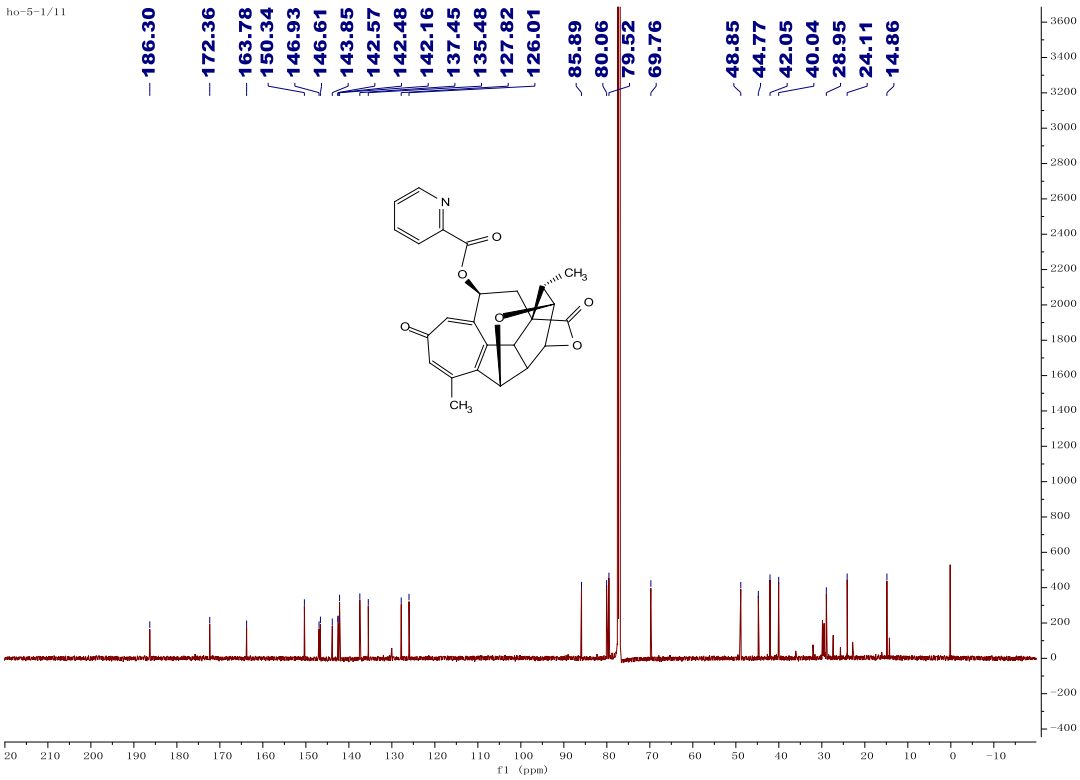


^{13}C-NMR spectrum (151 MHz, $CDCl_3$) for 10d

Compound 10e

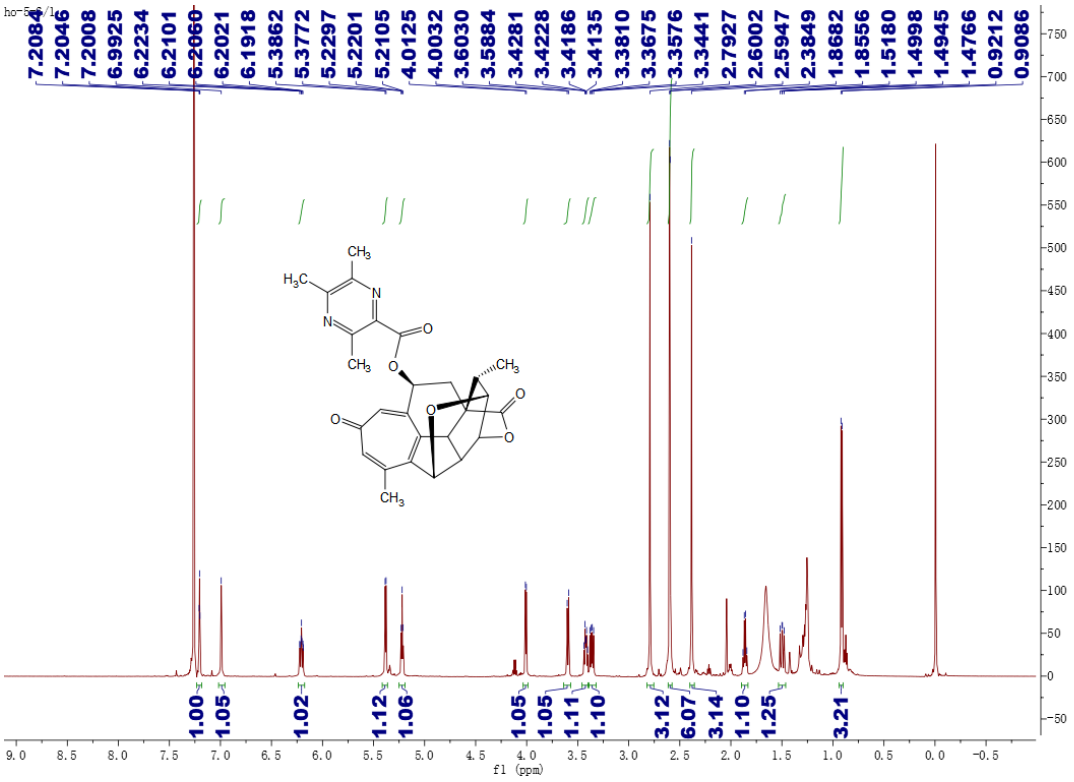


^{1}H-NMR spectrum (600 MHz, $CDCl_3$) for 10e

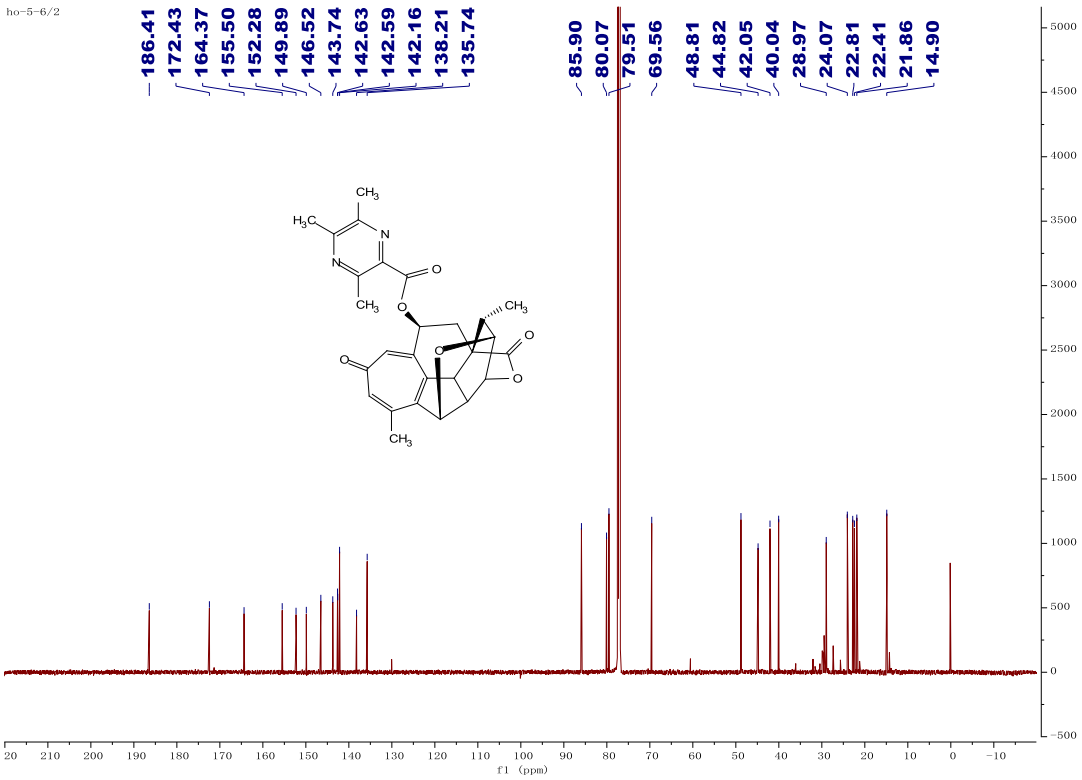


^{13}C-NMR spectrum (151 MHz, $CDCl_3$) for 10e

Compound 10f

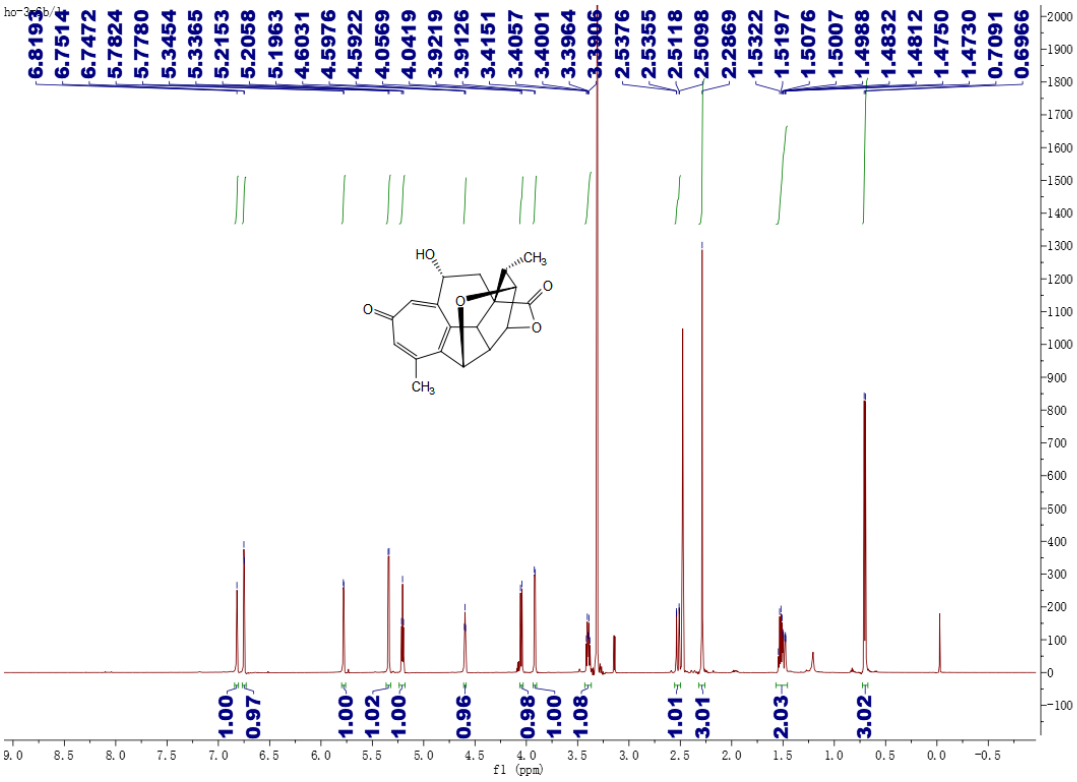


^{1}H-NMR spectrum (600 MHz, $CDCl_3$) for 10f

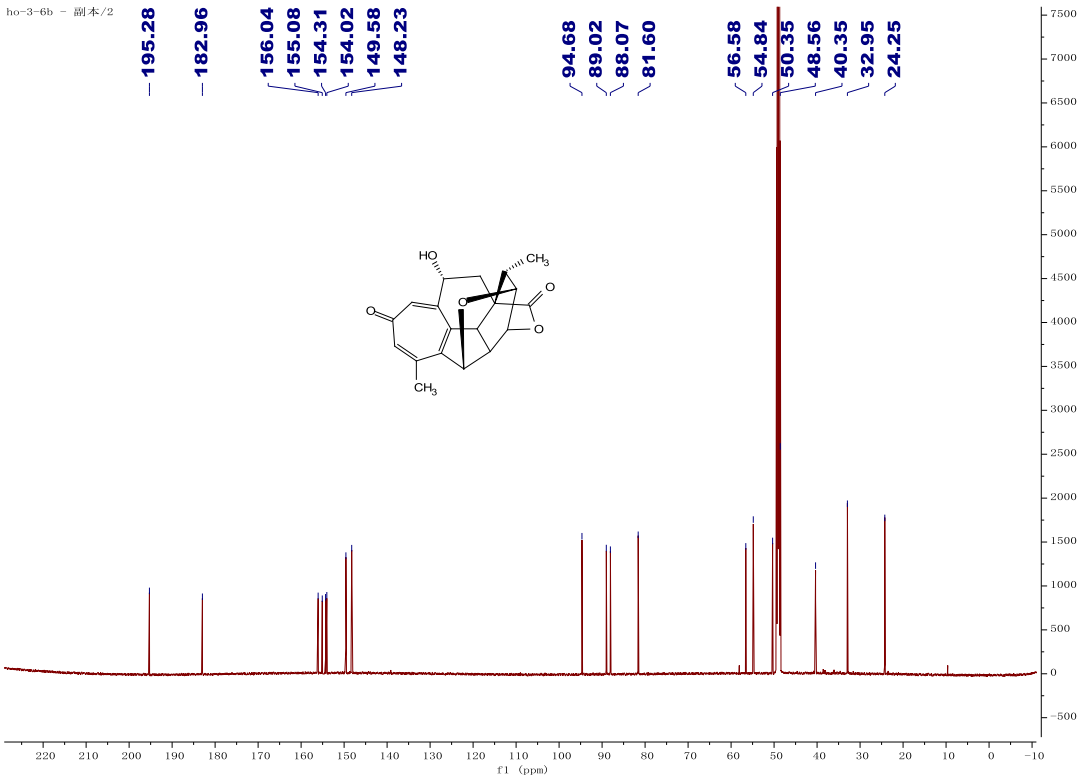


^{13}C-NMR spectrum (151 MHz, $CDCl_3$) for 10f

Compound 11

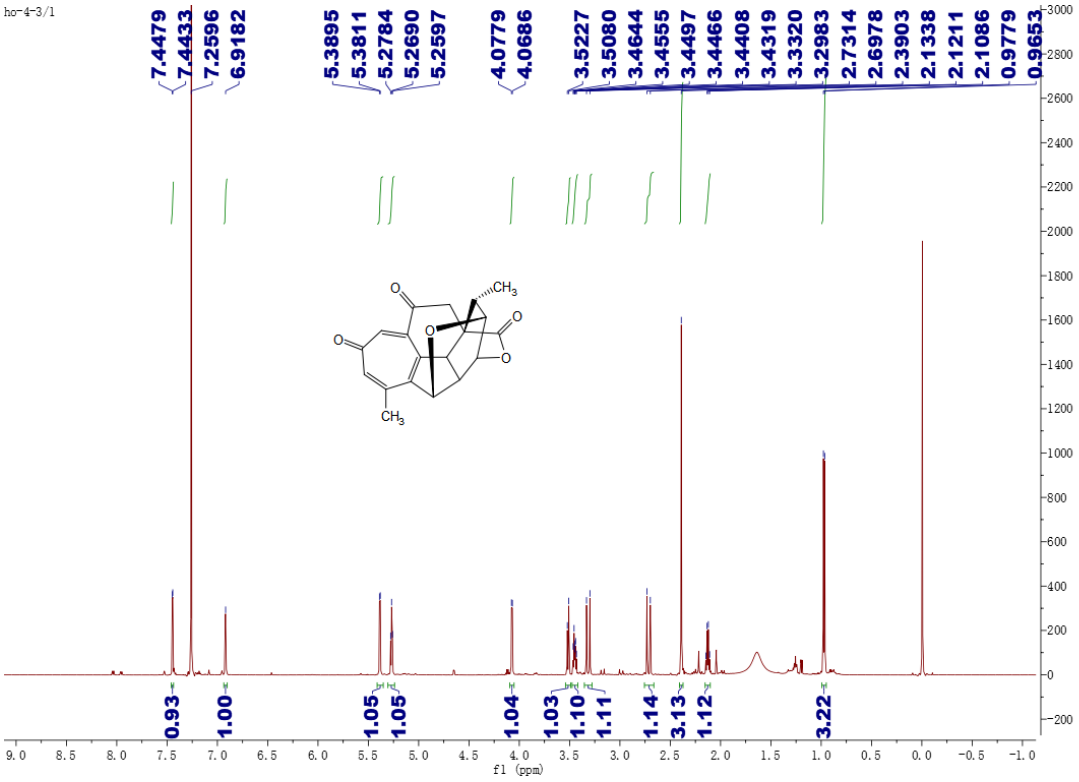


^{1}H-NMR spectrum (600 MHz, MeOD) for 11

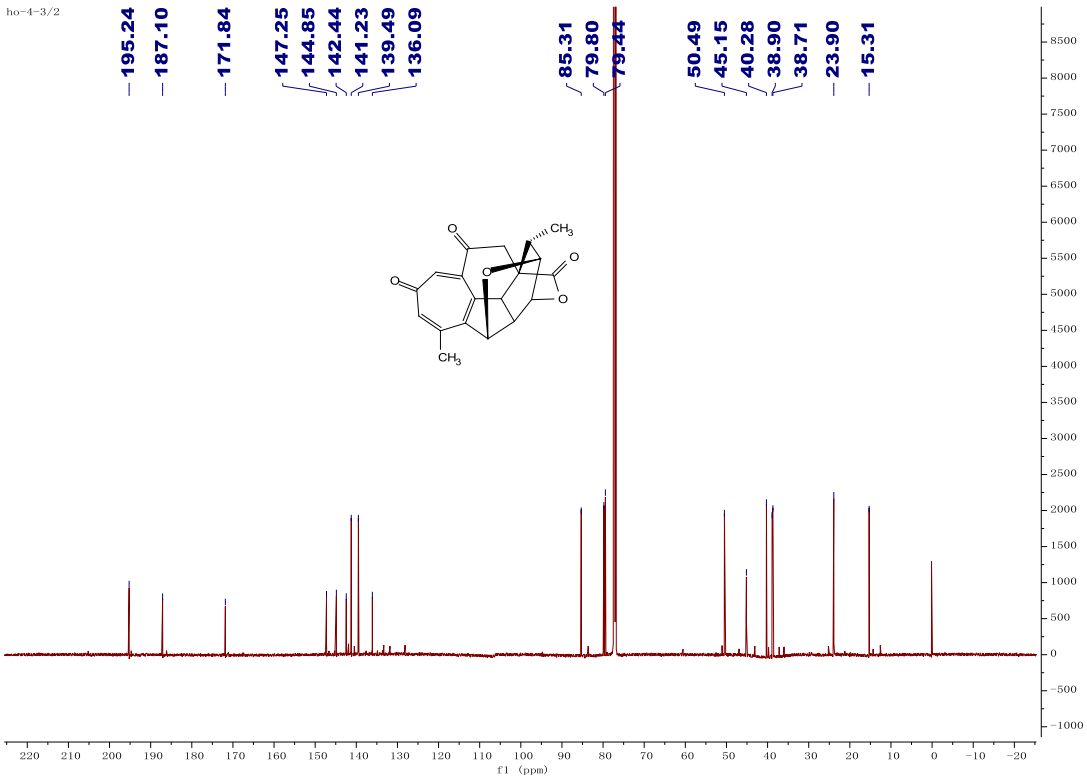


^{13}C-NMR spectrum (151 MHz, MeOD) for 11

Compound 12



^{1}H-NMR spectrum (600 MHz, $CDCl_3$) for 12



^{13}C-NMR spectrum (151 MHz, $CDCl_3$) for 12

References

1. Demidov, M.R.; Lapshina, M.Yu.; Osipov, D.V.; Osyanin, V.A.; Klimochkin, Y.N. Oxidative Rearrangement of 4*H*-Chromenes to 2-Aroylbenzofurans in the Presence of Selenium Dioxide. *Chem Heterocycl Comp* **2017**, 53, 1053–1056, doi:10.1007/s10593-017-2169-7.
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3. Karimi, S.; Ma, S.; Ramig, K.; Greer, E.M.; Szalda, D.J.; Subramaniam, G. Oxidative Ring-Contraction of 3*H*-1-Benzazepines to Quinoline Derivatives. *Tetrahedron Letters* **2015**, 56, 6886–6889, doi:10.1016/j.tetlet.2015.10.094.
4. Maier, W.F., Roth, W., Thies, I., Schleyer, P.V.R. Hydrogenolysis, iv. gas phase decarboxylation of carboxylic acids. *Chem. Ber.* **1982**, 115, 808-812, doi:10.1002/cber.19821150245