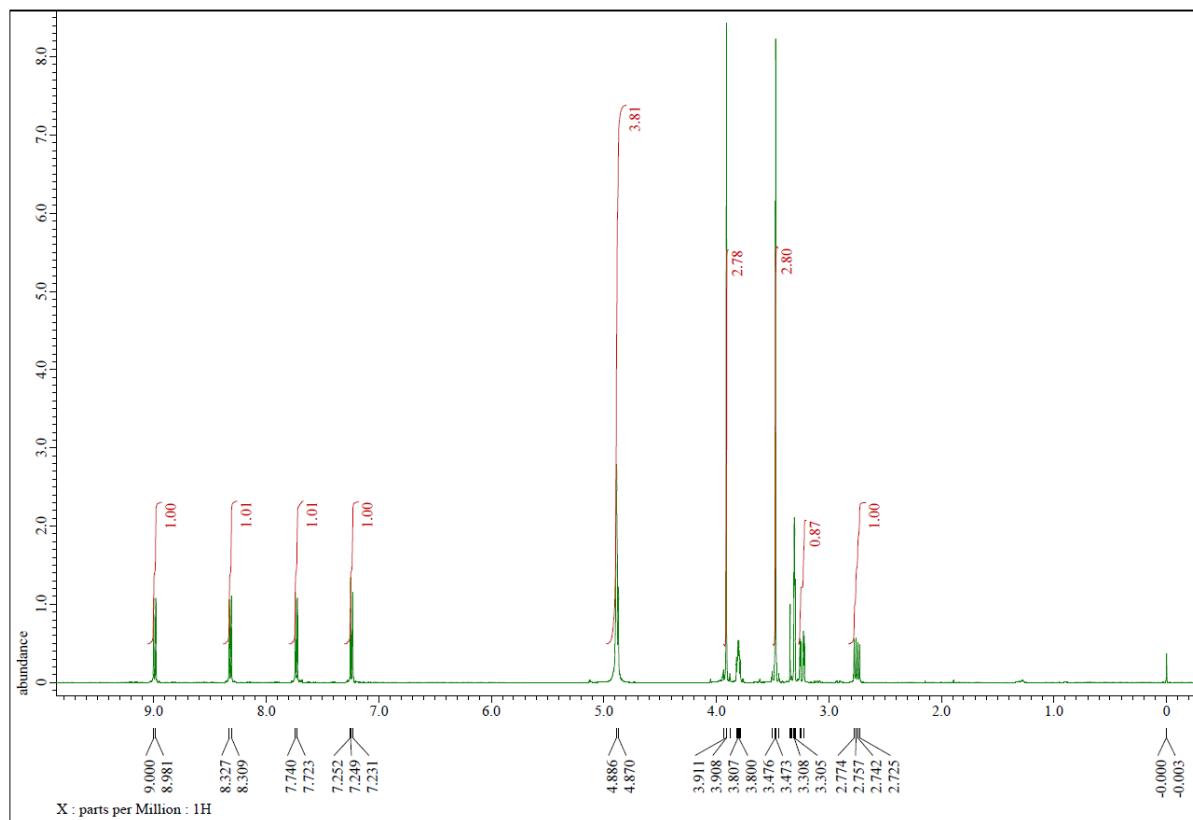


# Supplementary Materials: Identification of two new phenanthrenes from Dendrobii Herba and their cytotoxicity towards human hypopharynx squamous carcinoma cell (FaDu)

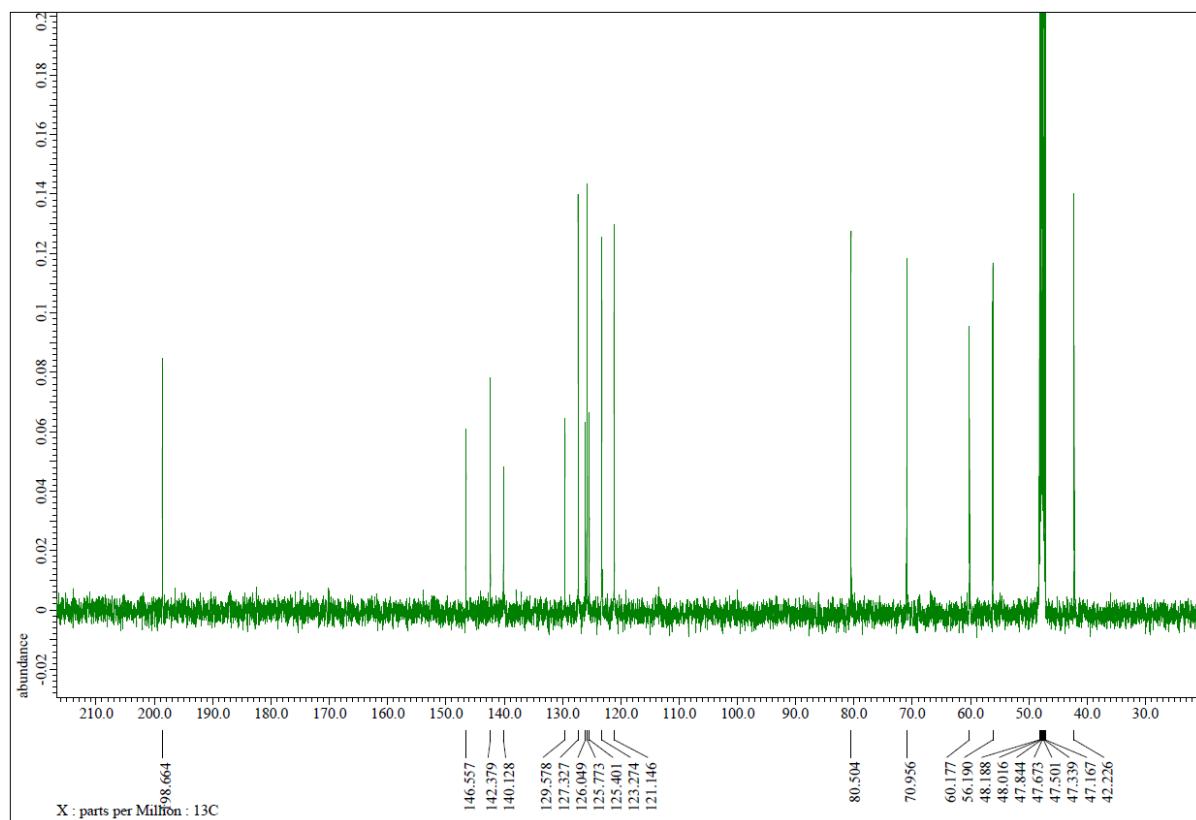
Bomi Nam, Seung Mok Ryu, Dongho Lee, Chan-Hun Jung, Chang Hyun Jin, Jin-Baek Kim, Ik-Soo Lee\* and Ah-Reum Han\*

Table S1.  $^1\text{H}$ -NMR (500 MHz) and  $^{13}\text{C}$ -NMR (125 MHz) spectral data of **2** and **3** in  $\text{DMSO}-d_6$  ( $\delta$  in ppm)

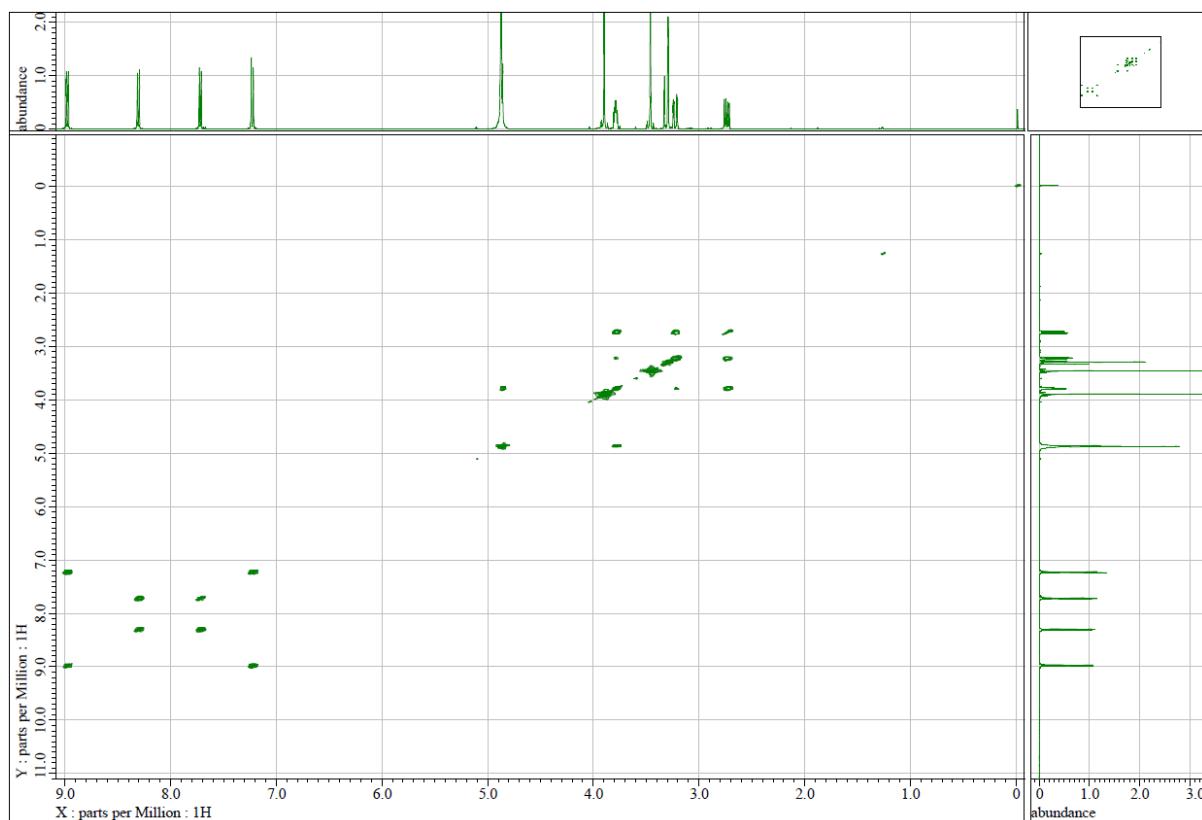
Position	<b>2</b>		<b>3</b>	
	$\delta_{\text{H}}$	$\delta_{\text{C}}$	$\delta_{\text{H}}$	$\delta_{\text{C}}$
1		179.9		180.8
2		158.5		158.9
3	6.22 (1H, s)	110.8	6.29 (1H, s)	117.8
4		188.8		189.0
5	9.24 (1H, d, $J = 9.8$ Hz)	129.4	9.36 (1H, d, $J = 9.5$ Hz)	128.8
6	7.19 (1H, dd, $J_{1,2} = 9.8, 1.8$ Hz)	123.8	7.26 (1H, dd, $J_{1,2} = 9.5, 2.8$ Hz)	123.1
7		157.0		158.3
8	7.02 (1H, brs)	109.9	7.25 (1H, d, $J = 2.8$ Hz)	110.3
9	7.87 (2H, d, $J = 8.3$ Hz)	131.2	8.08 (1H, d, $J = 8.3$ Hz)	132.9
10		128.5	7.97 (1H, d, $J = 8.3$ Hz)	130.2
4a		127.0		127.4
4b		122.4		123.9
8a		141.2		139.5
10a		121.6		122.4
2-OCH <sub>3</sub>			3.86 (3H, s)	57.0



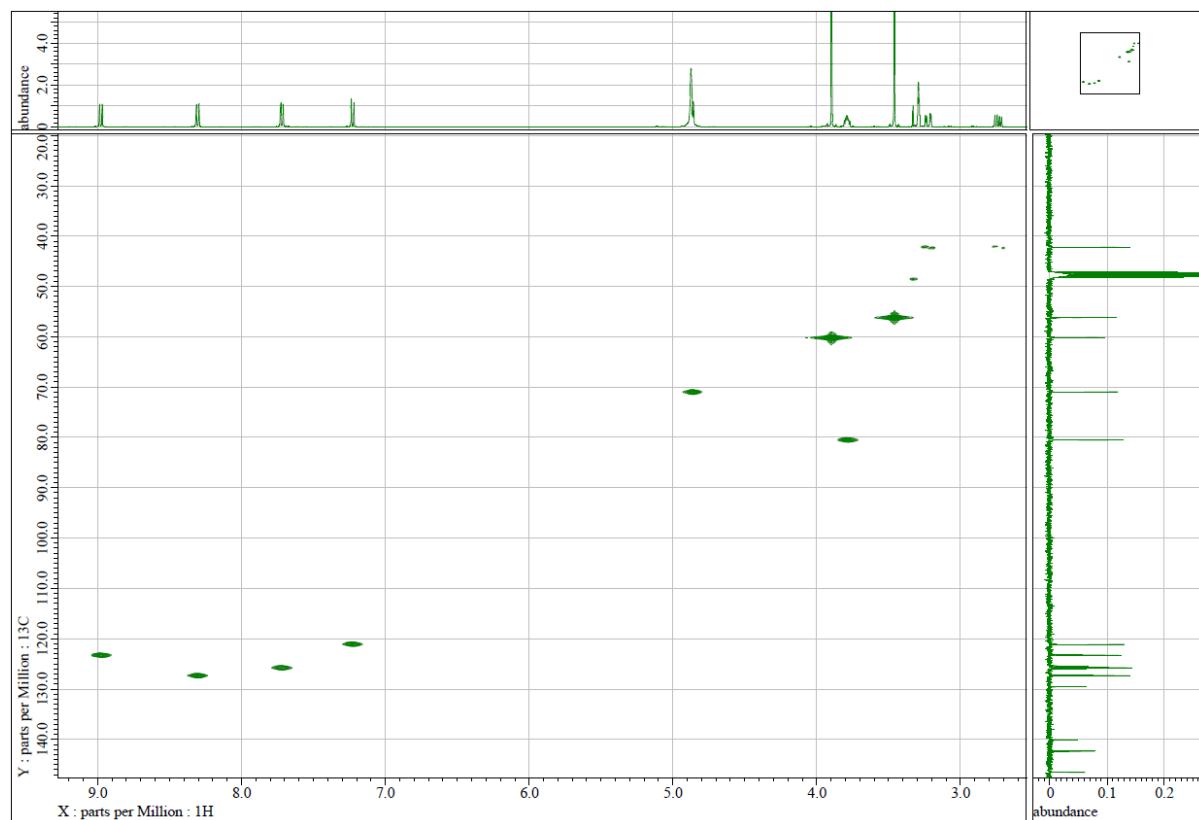
**Figure S1.**  $^1\text{H}$ -NMR (500 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **1**.



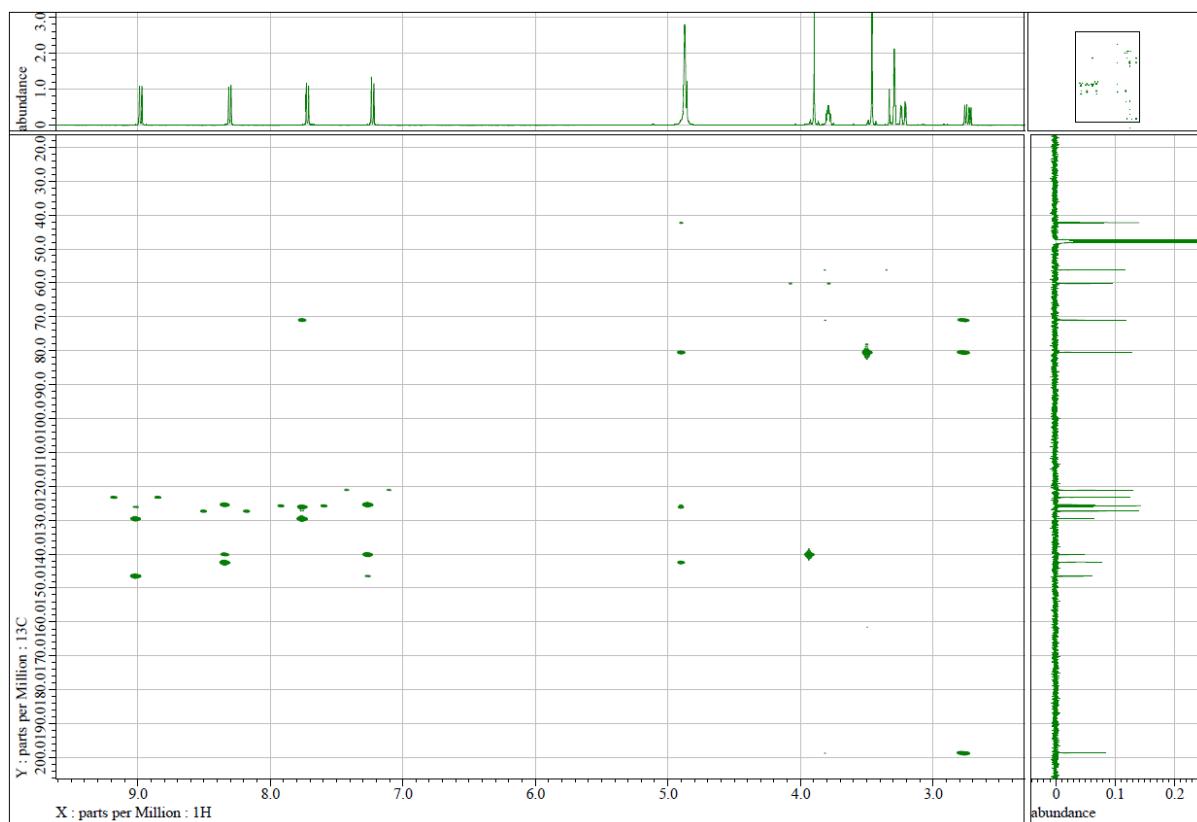
**Figure S2.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound 1.



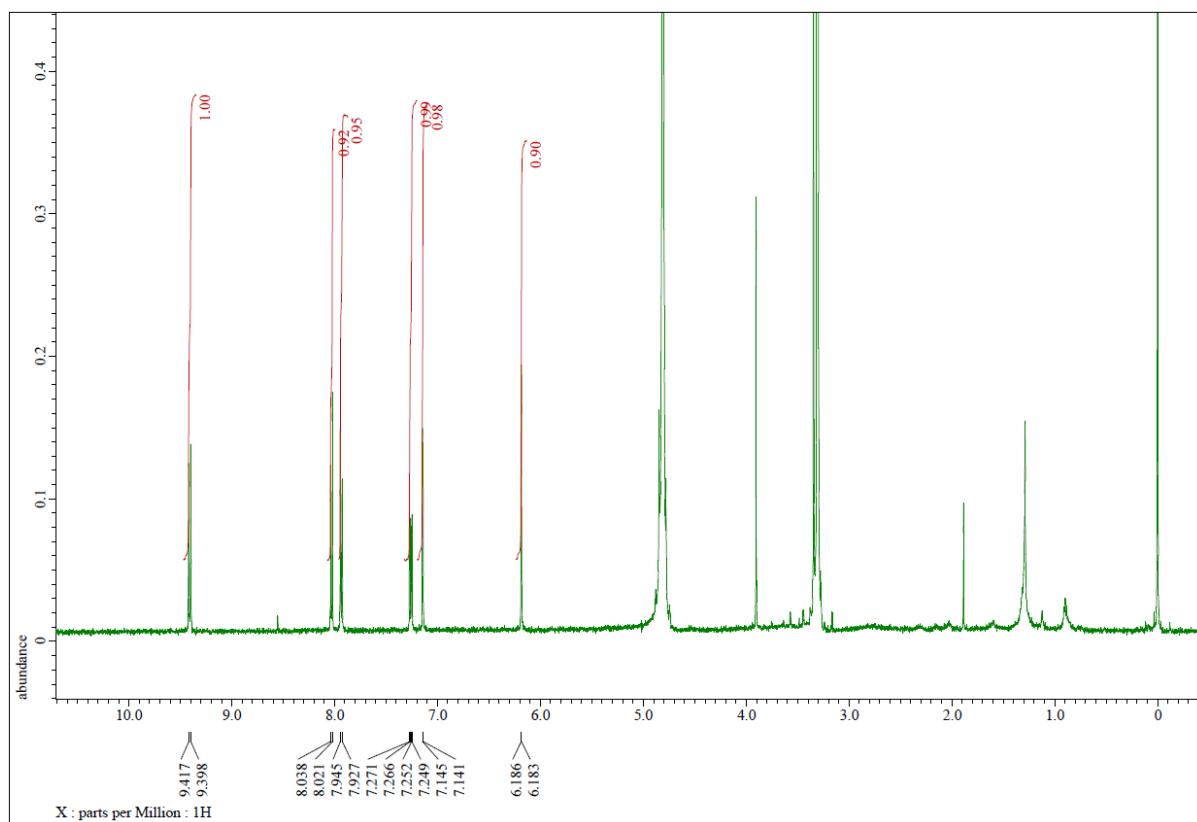
**Figure S3.**  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of compound **1**.



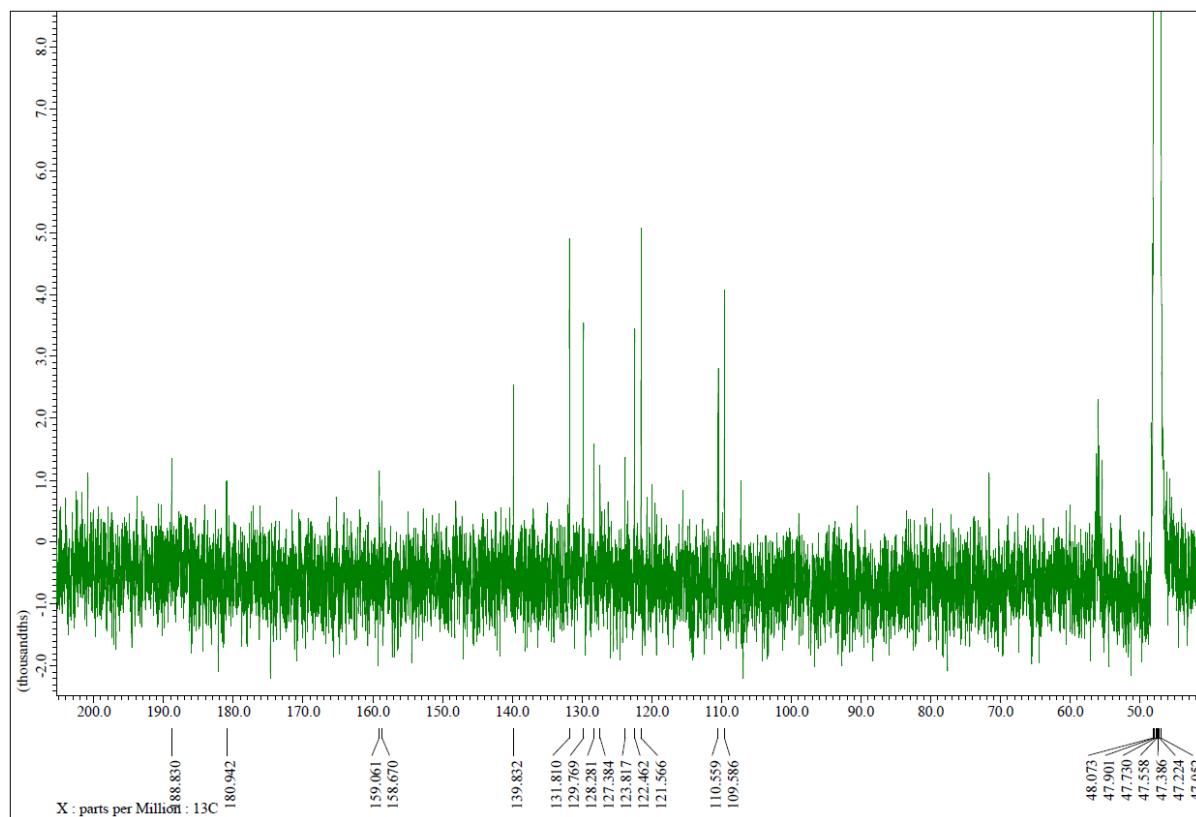
**Figure S4.**  $^1\text{H}$ - $^{13}\text{C}$  HMQC NMR spectrum of compound 1.



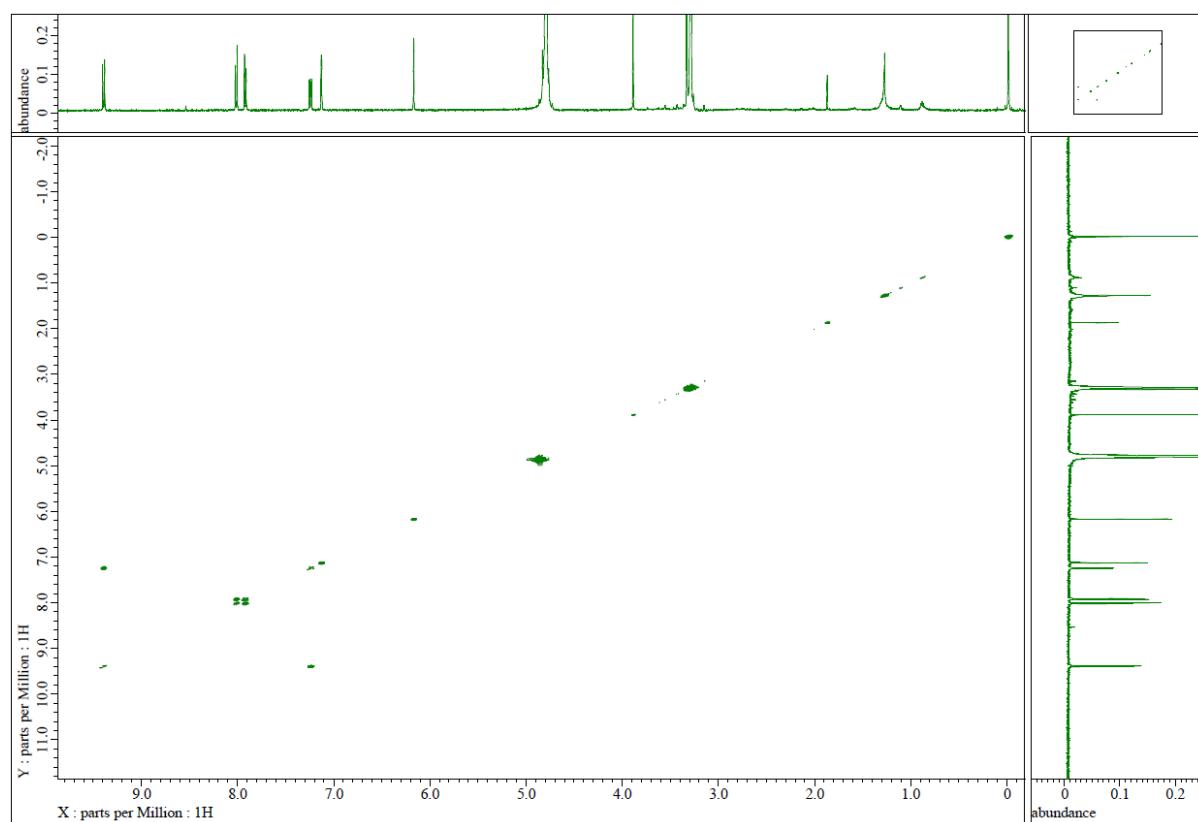
**Figure S5.**  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of compound **1**.



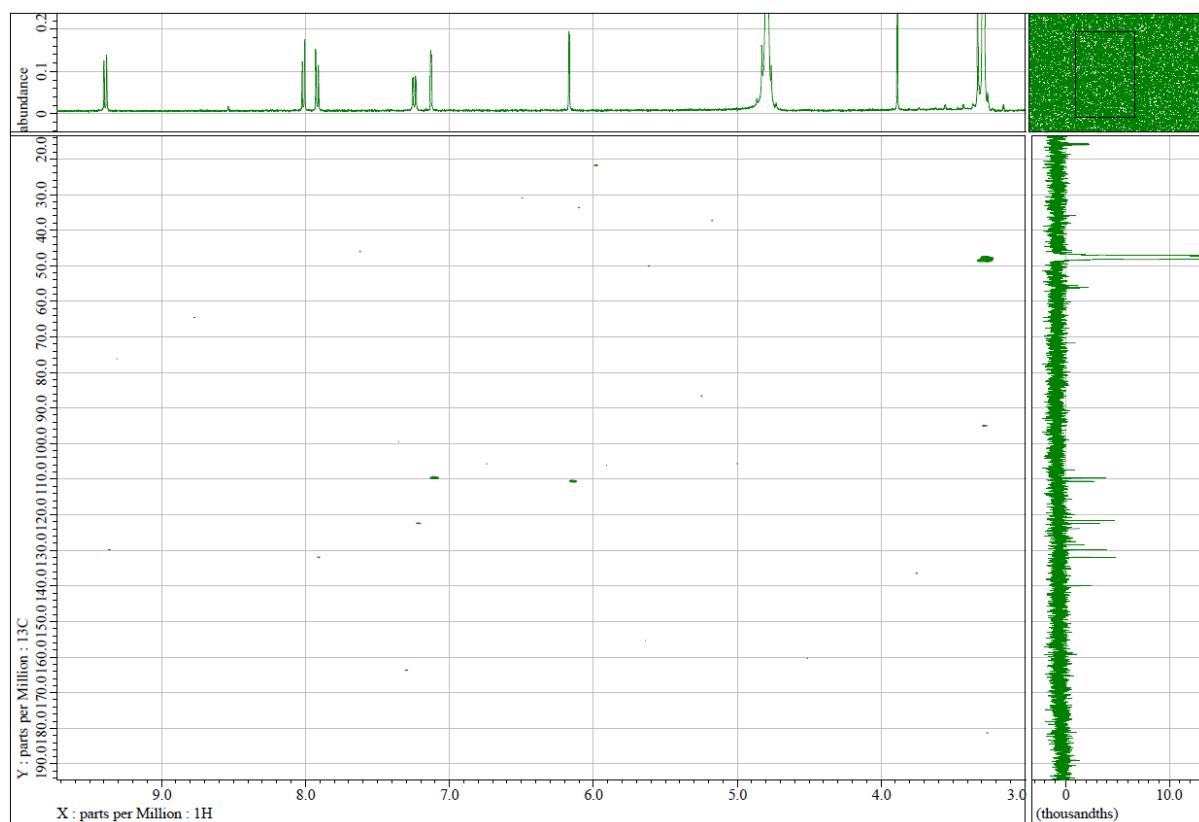
**Figure S6.**  $^1\text{H}$ -NMR (500 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **2**.



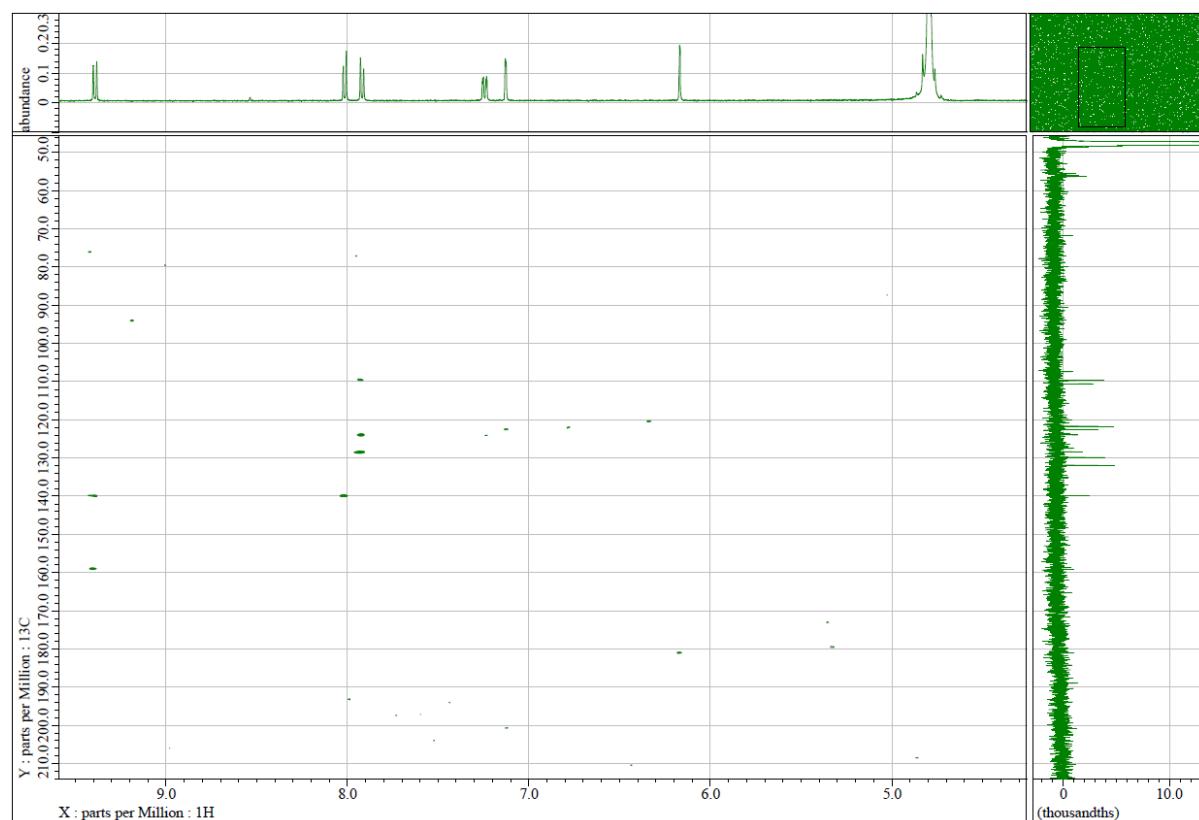
**Figure S7.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound 2.



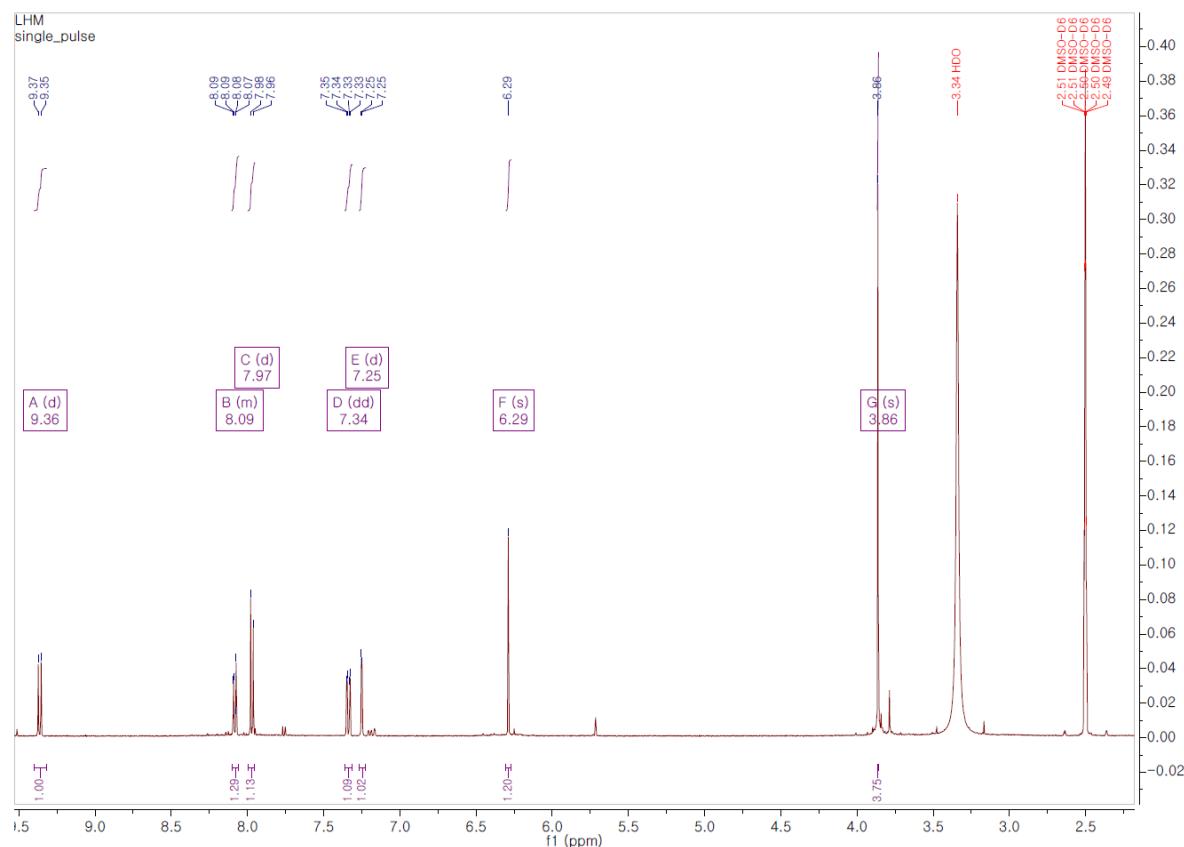
**Figure S8.**  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of compound 2.



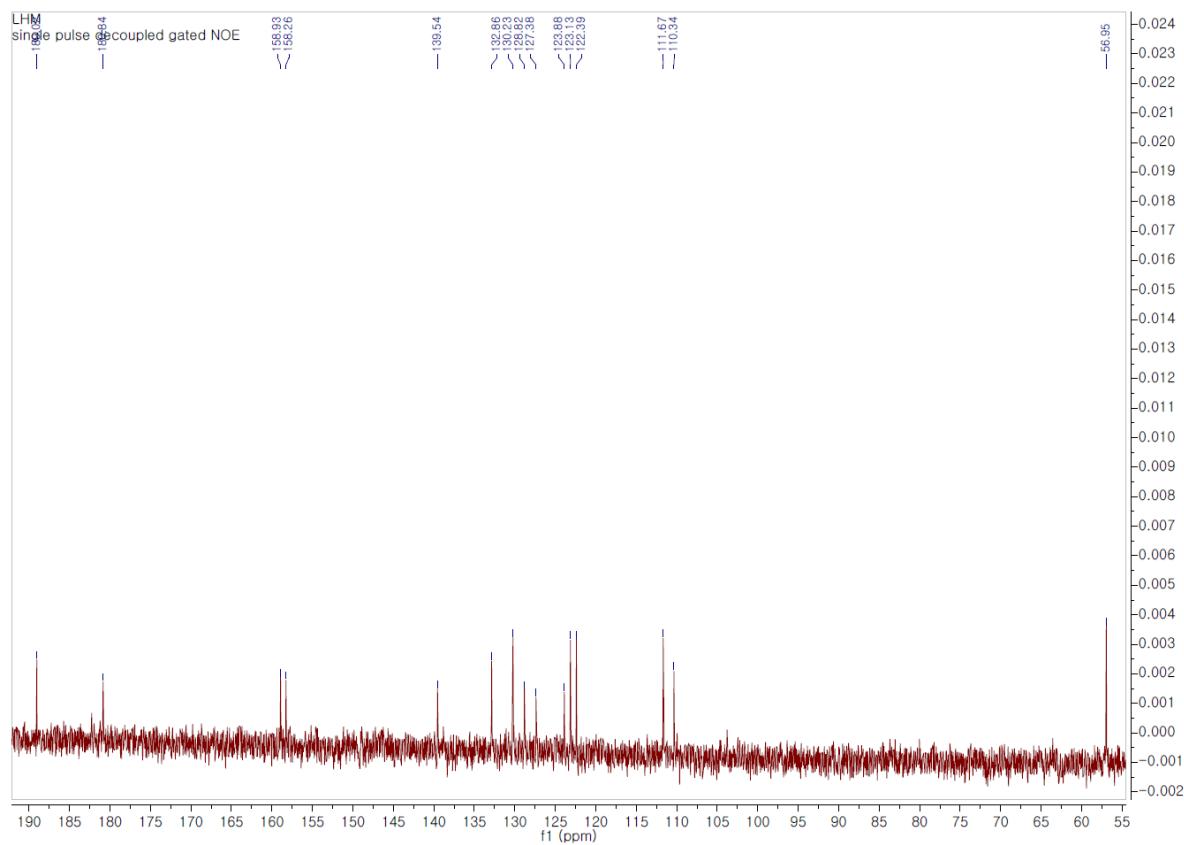
**Figure S9.**  $^1\text{H}$ - $^{13}\text{C}$  HMQC NMR spectrum of compound 2.



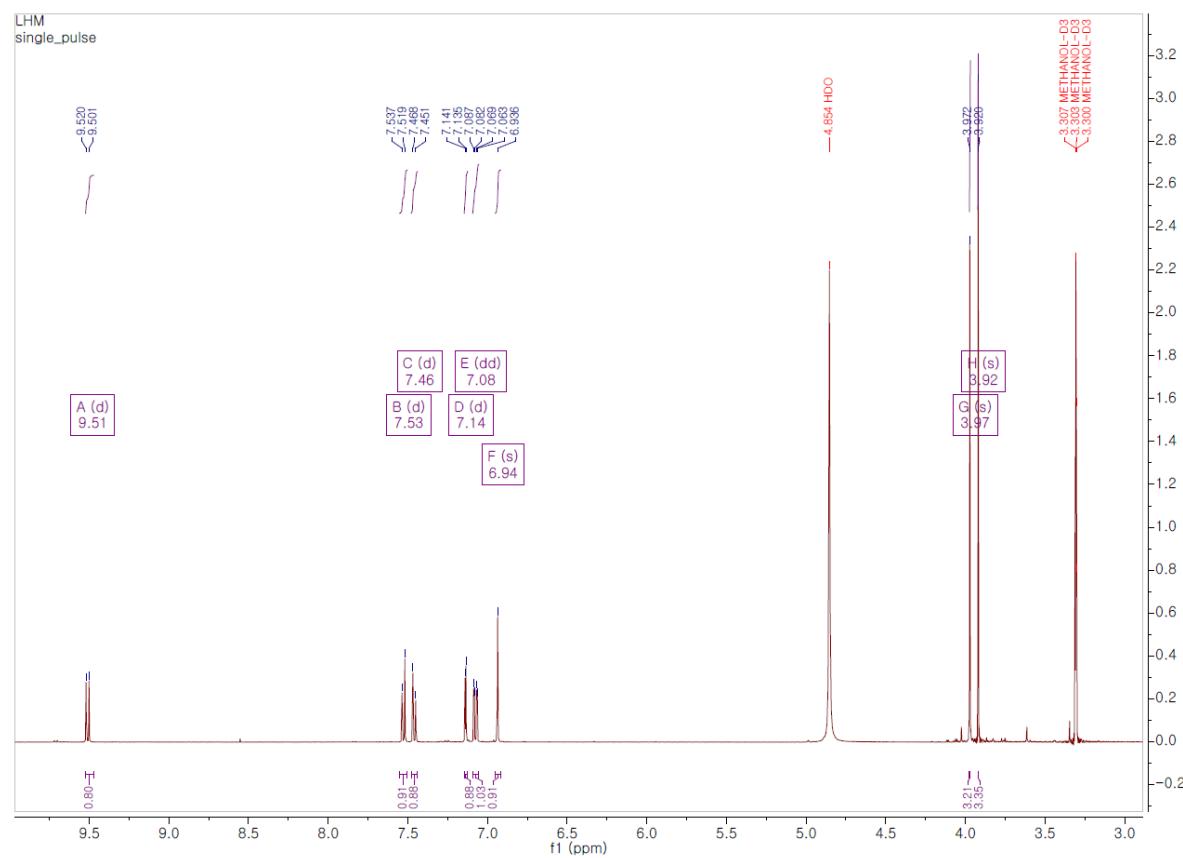
**Figure S10.**  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of compound 2.



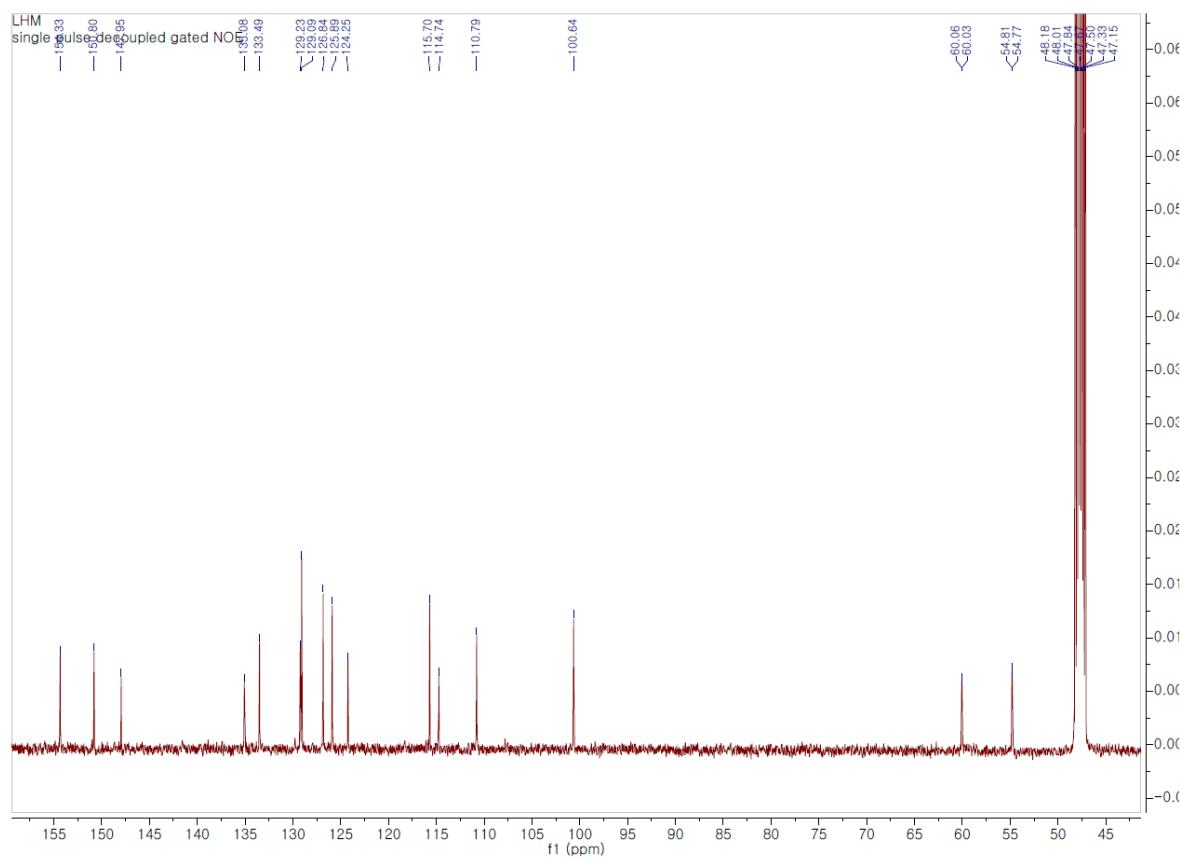
**Figure S11.**  $^1\text{H}$ -NMR (500 MHz,  $\text{DMSO}-d_6$ ) spectrum of compound 3.



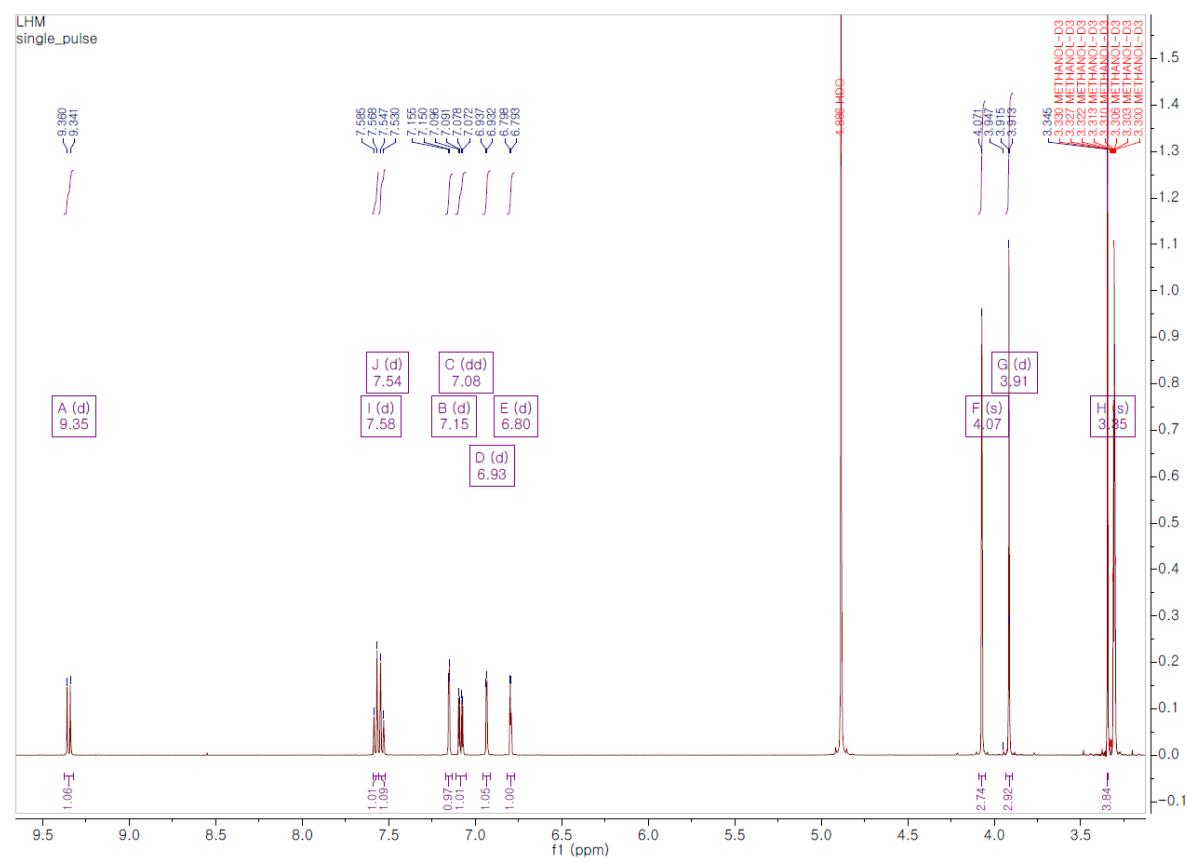
**Figure S12.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{DMSO}-d_6$ ) spectrum of compound 3.



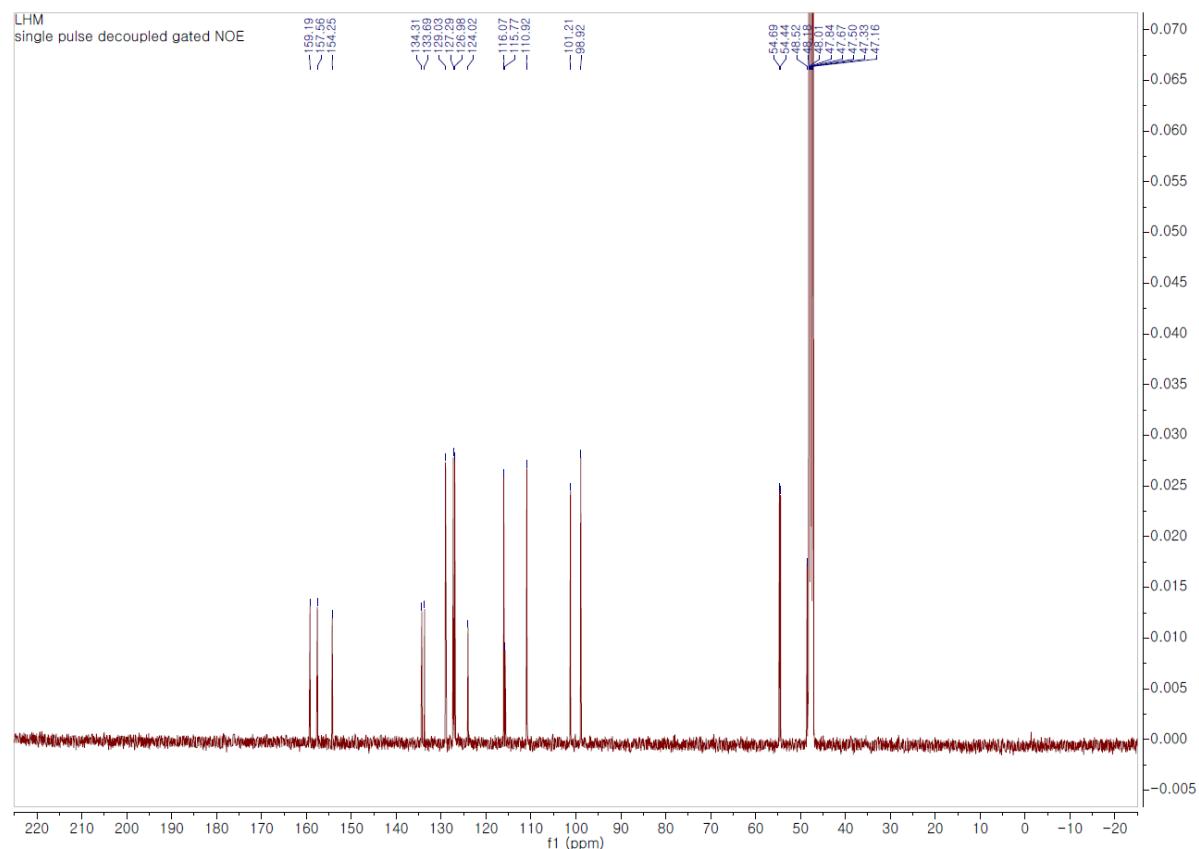
**Figure S13.**  $^1\text{H}$ -NMR (500 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound 4.



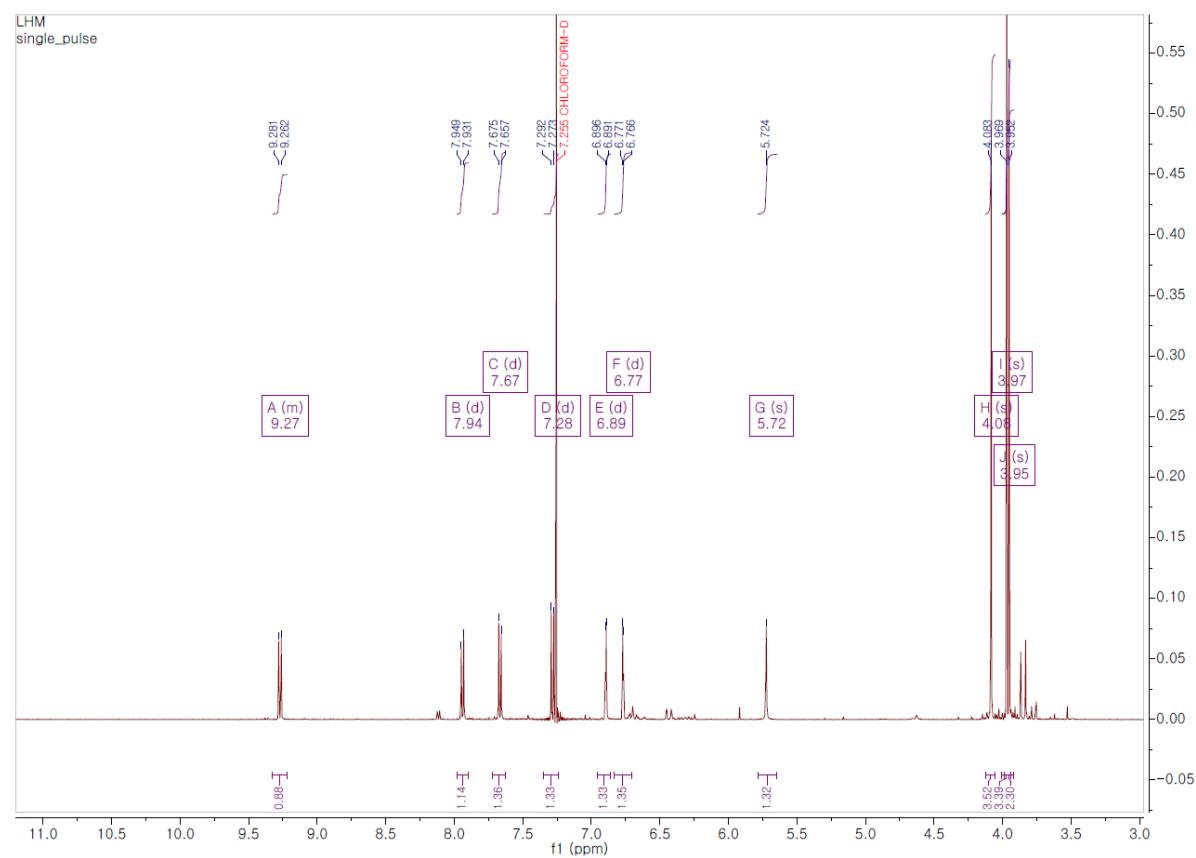
**Figure S14.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound 4.



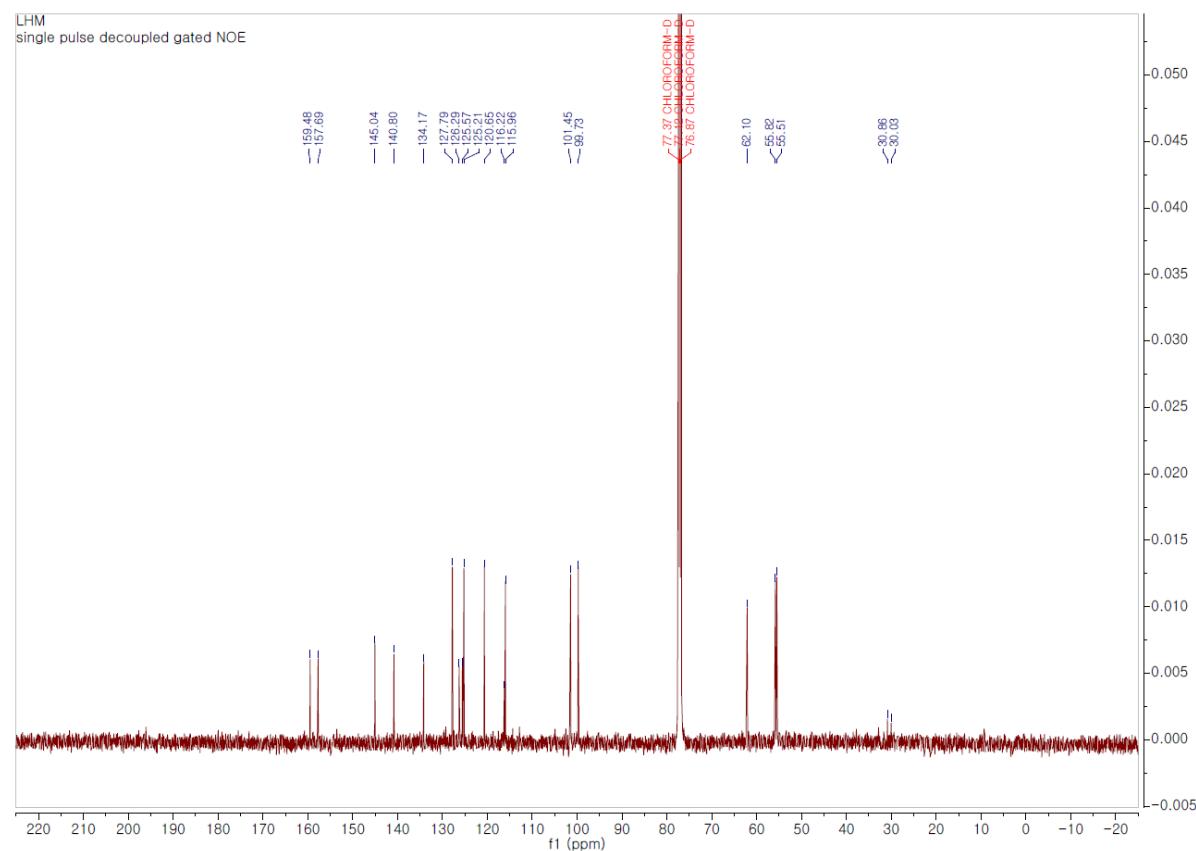
**Figure S15.**  $^1\text{H}$ -NMR (500 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **5**.



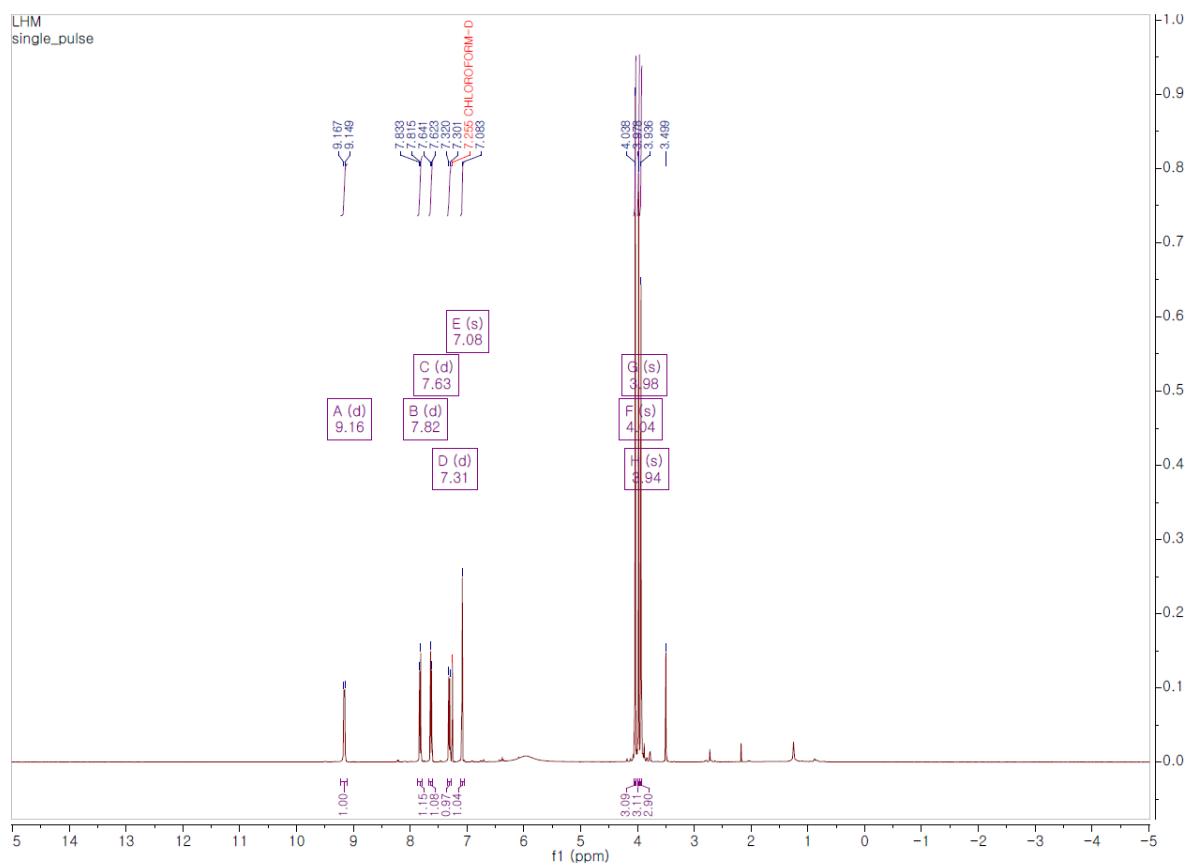
**Figure S16.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound 5.



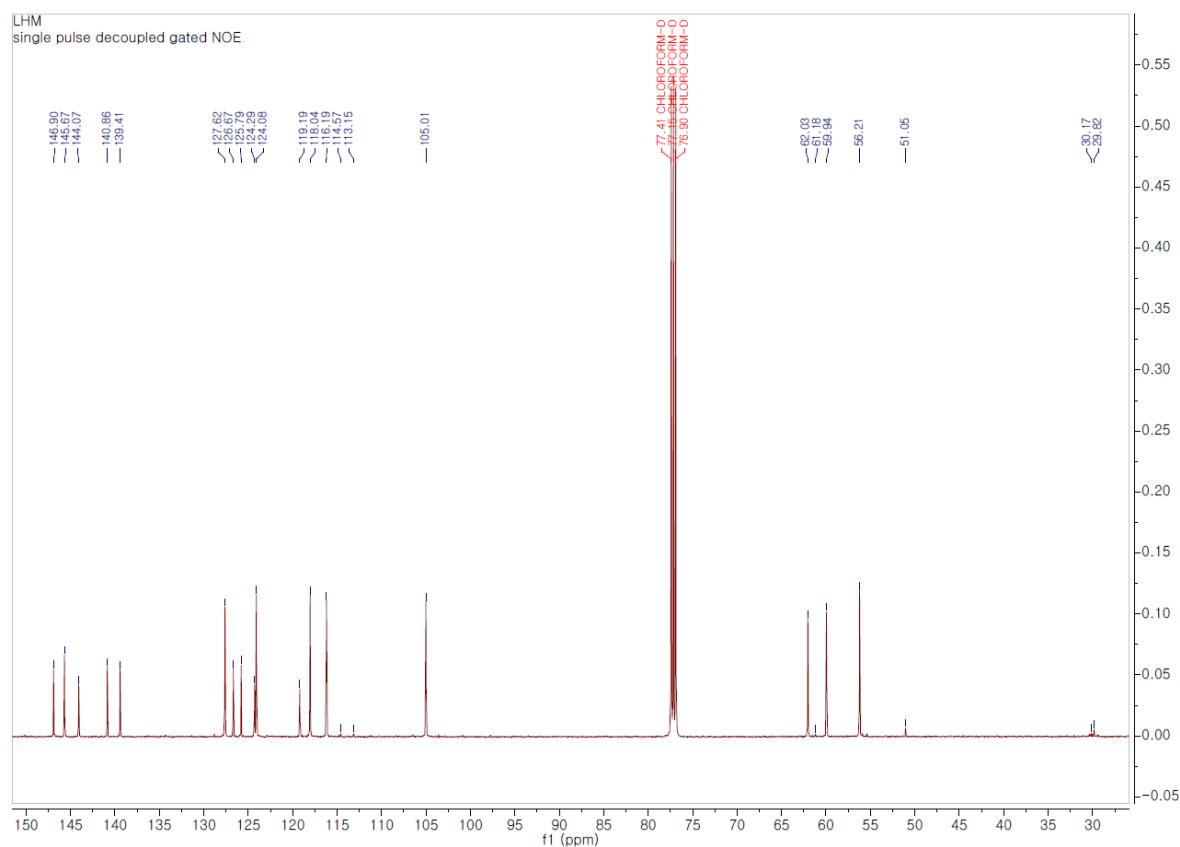
**Figure S17.**  $^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound 6.



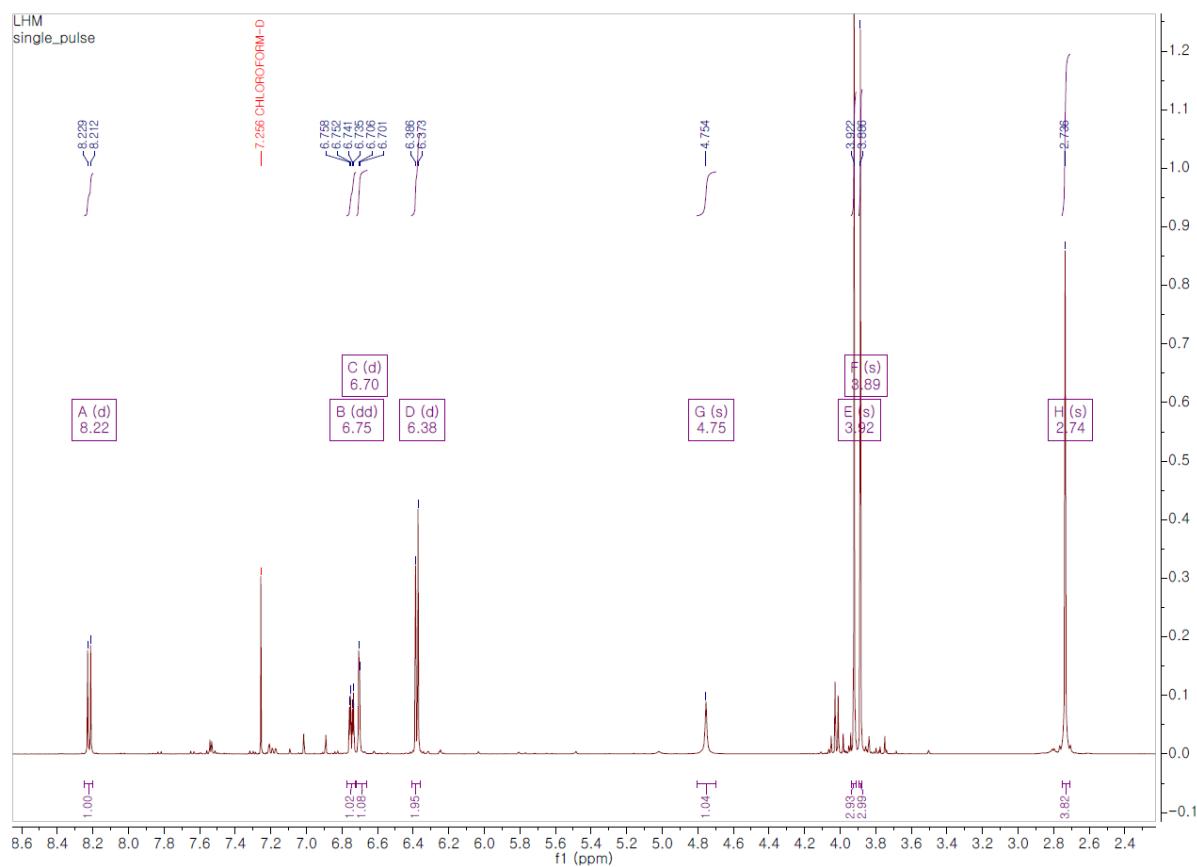
**Figure S18.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of compound 6.



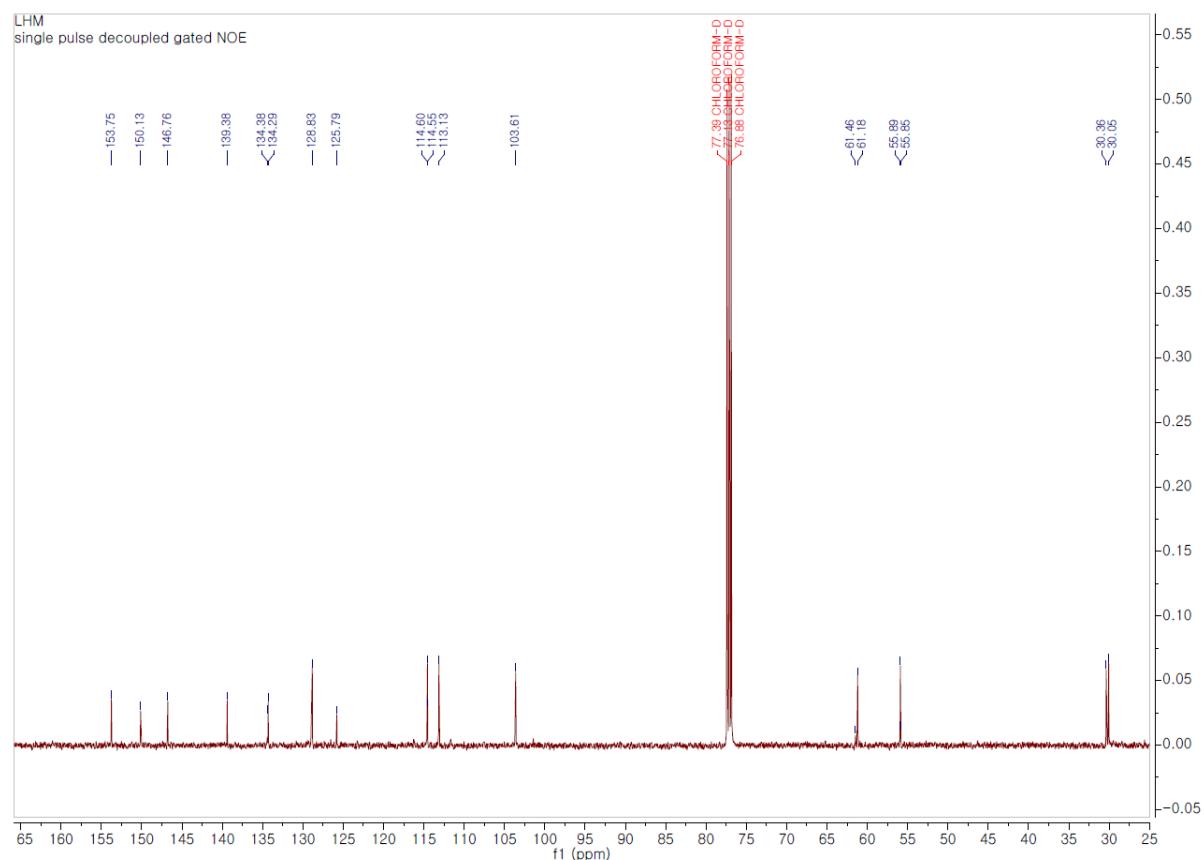
**Figure S19.**  $^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound 7.



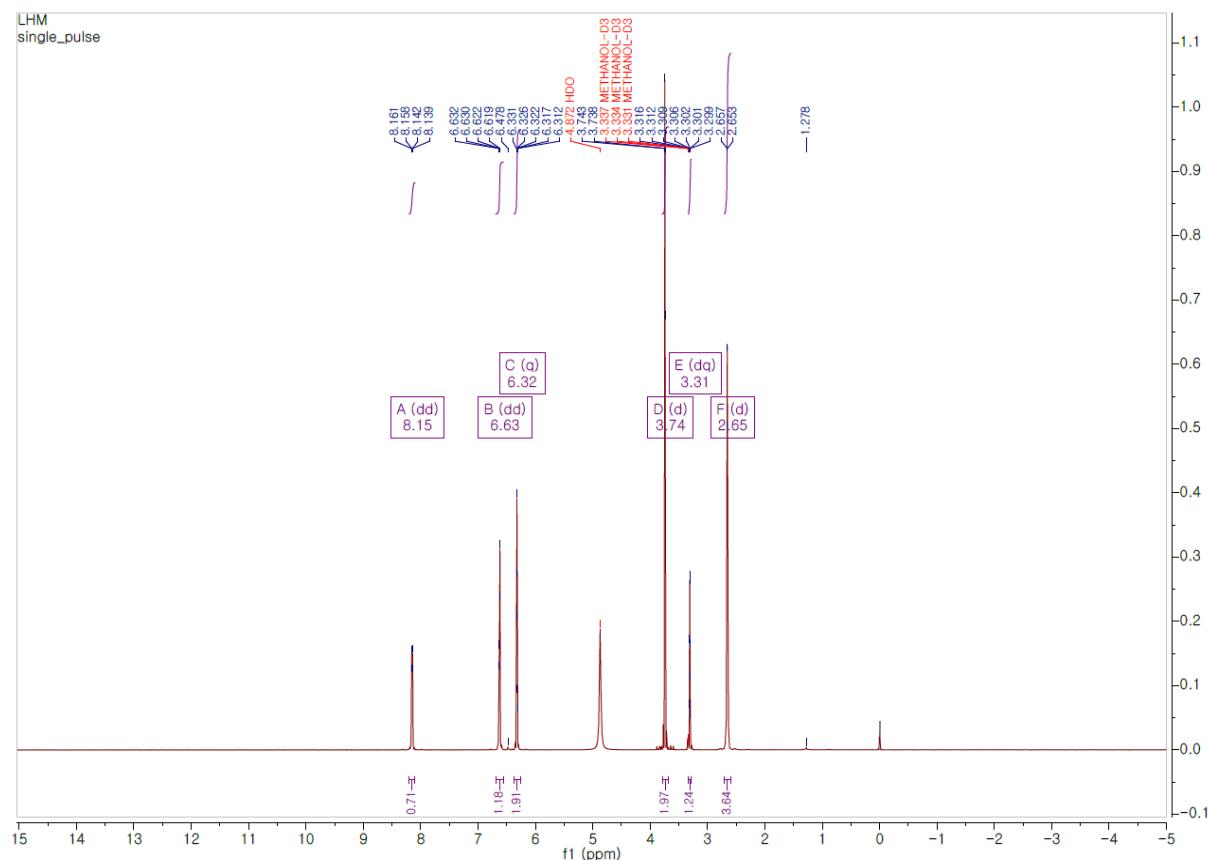
**Figure S20.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of compound 7.



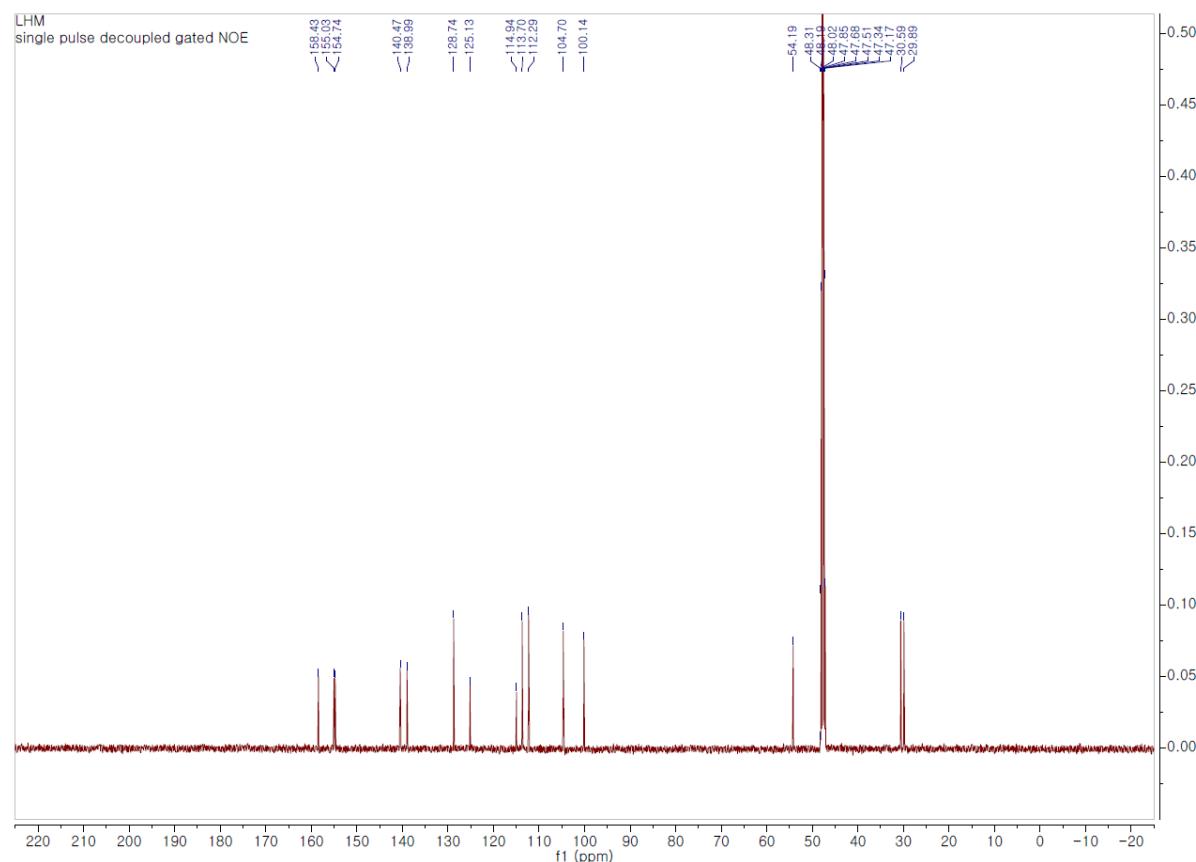
**Figure S21.**  $^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound 8.



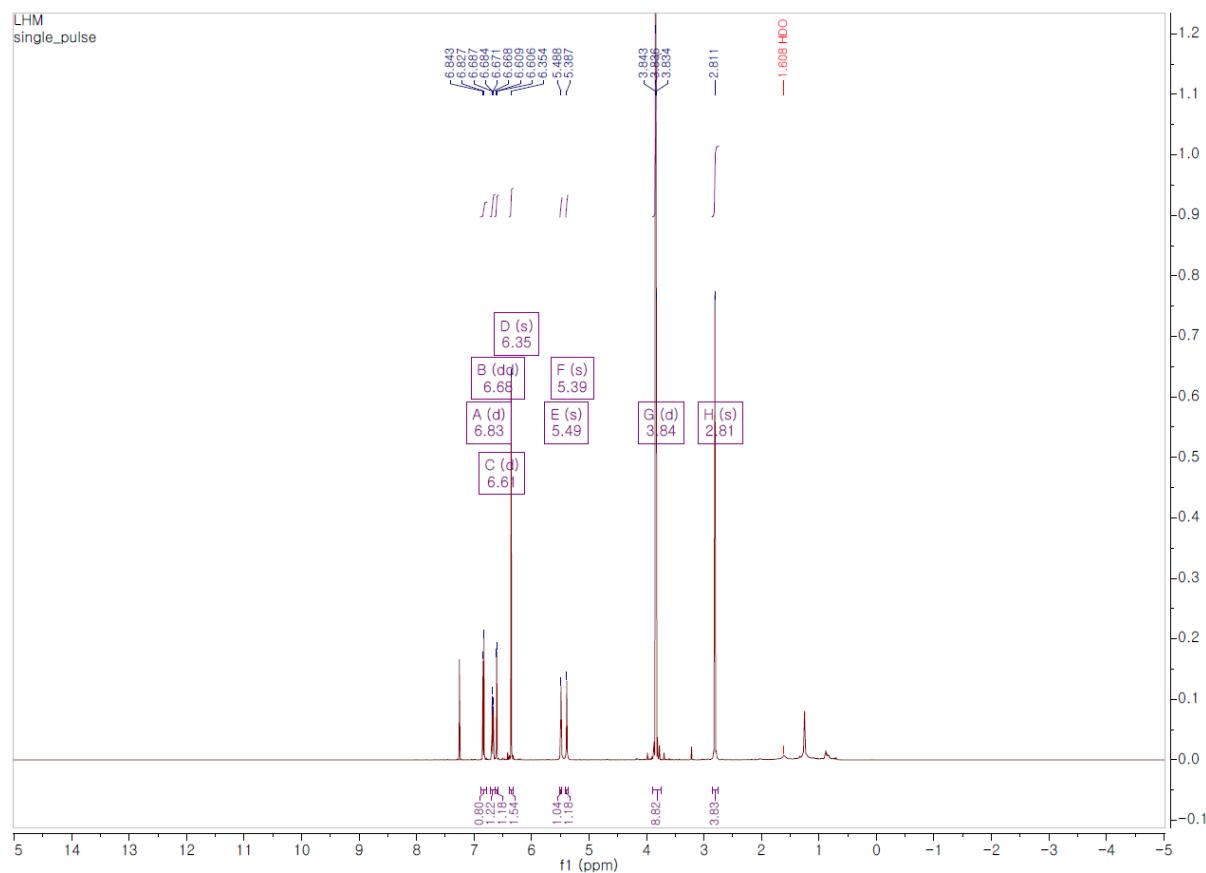
**Figure S22.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of compound 8.



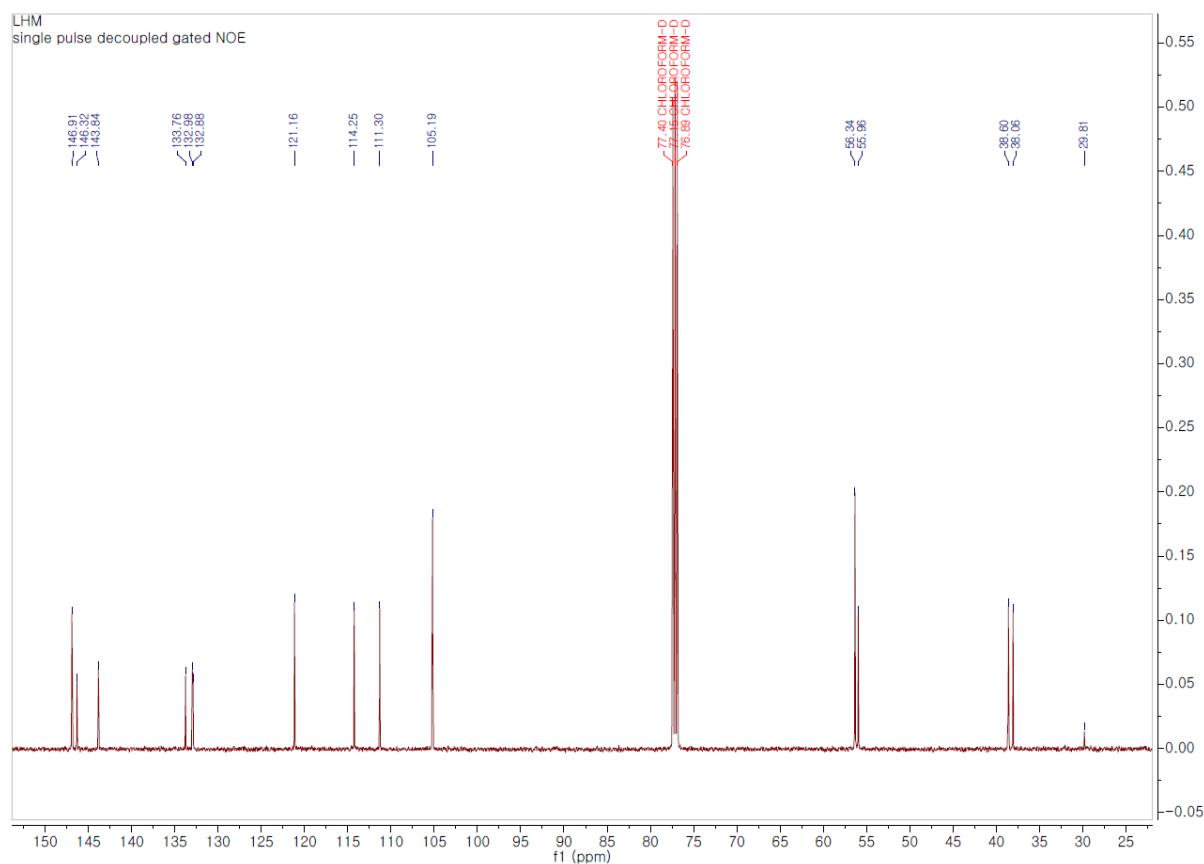
**Figure S23.**  $^1\text{H}$ -NMR (500 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound 9.



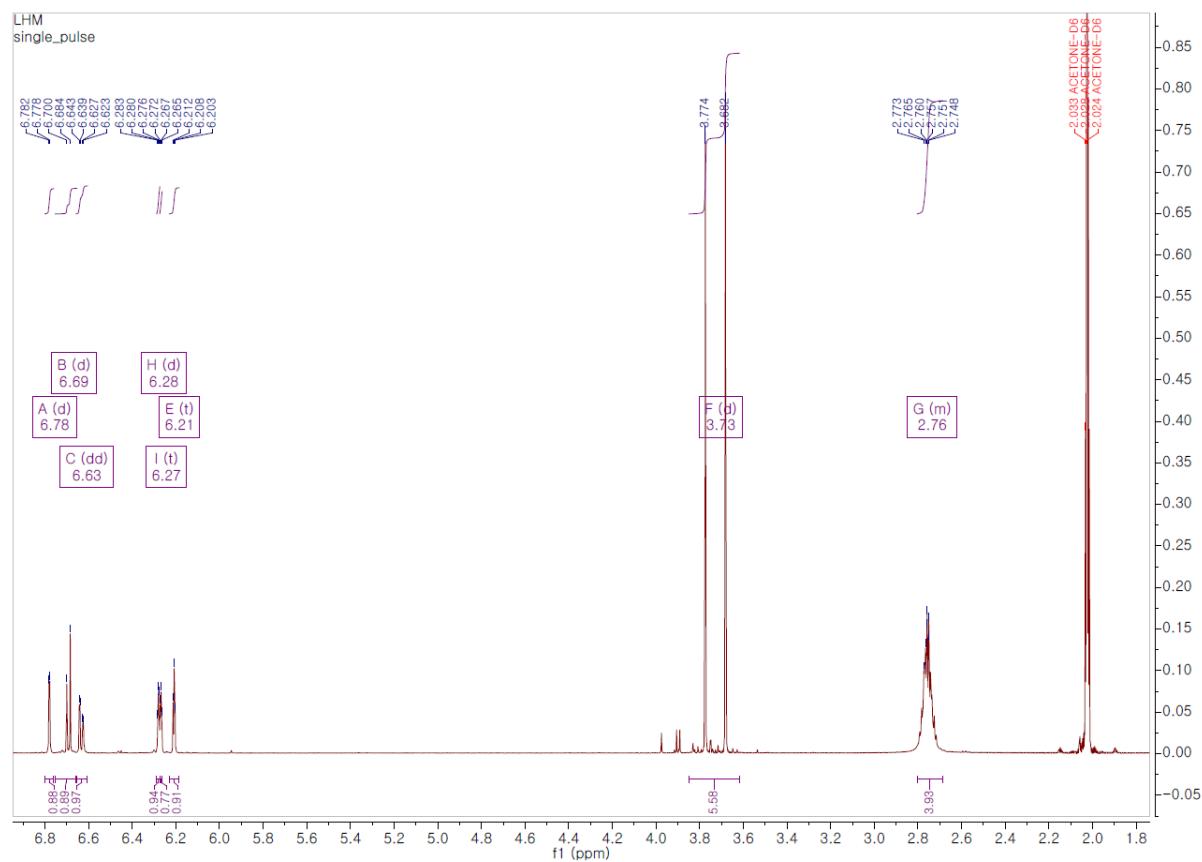
**Figure S24.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **9**.



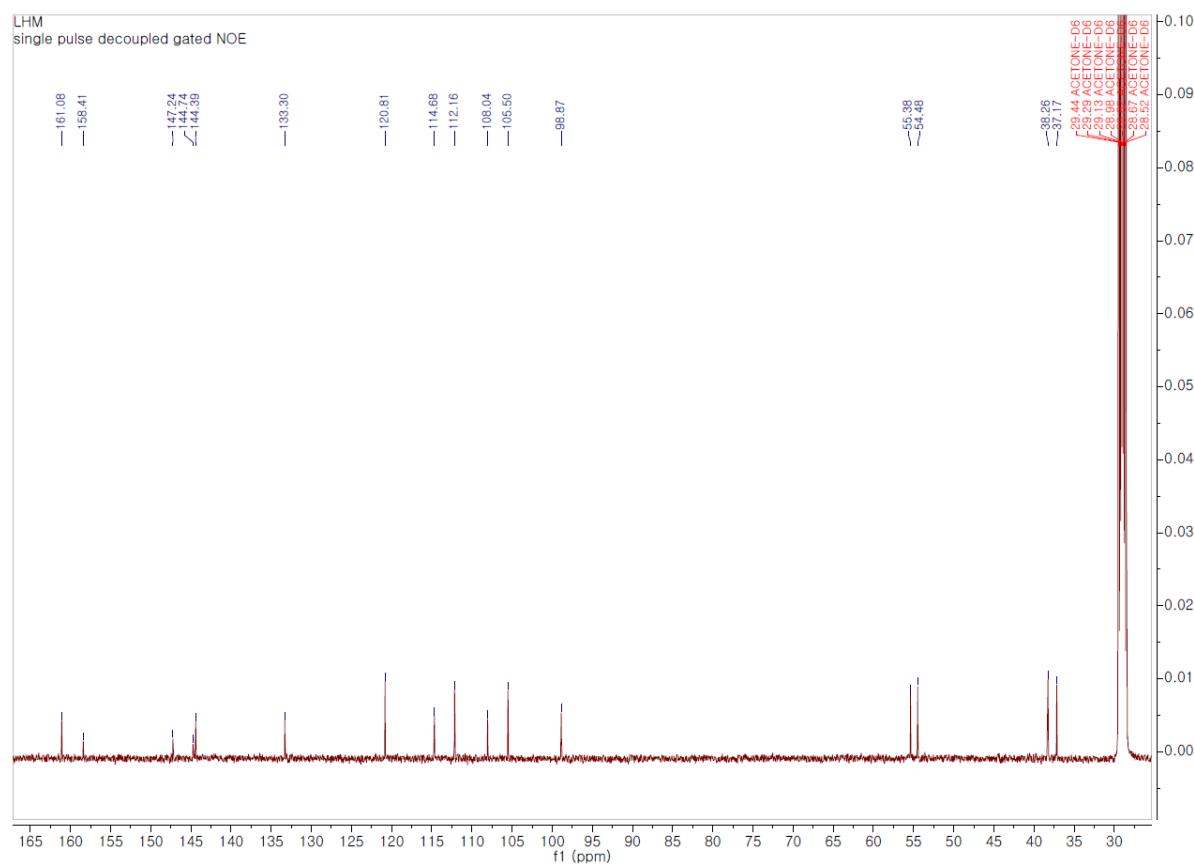
**Figure S25.**  $^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **10**.



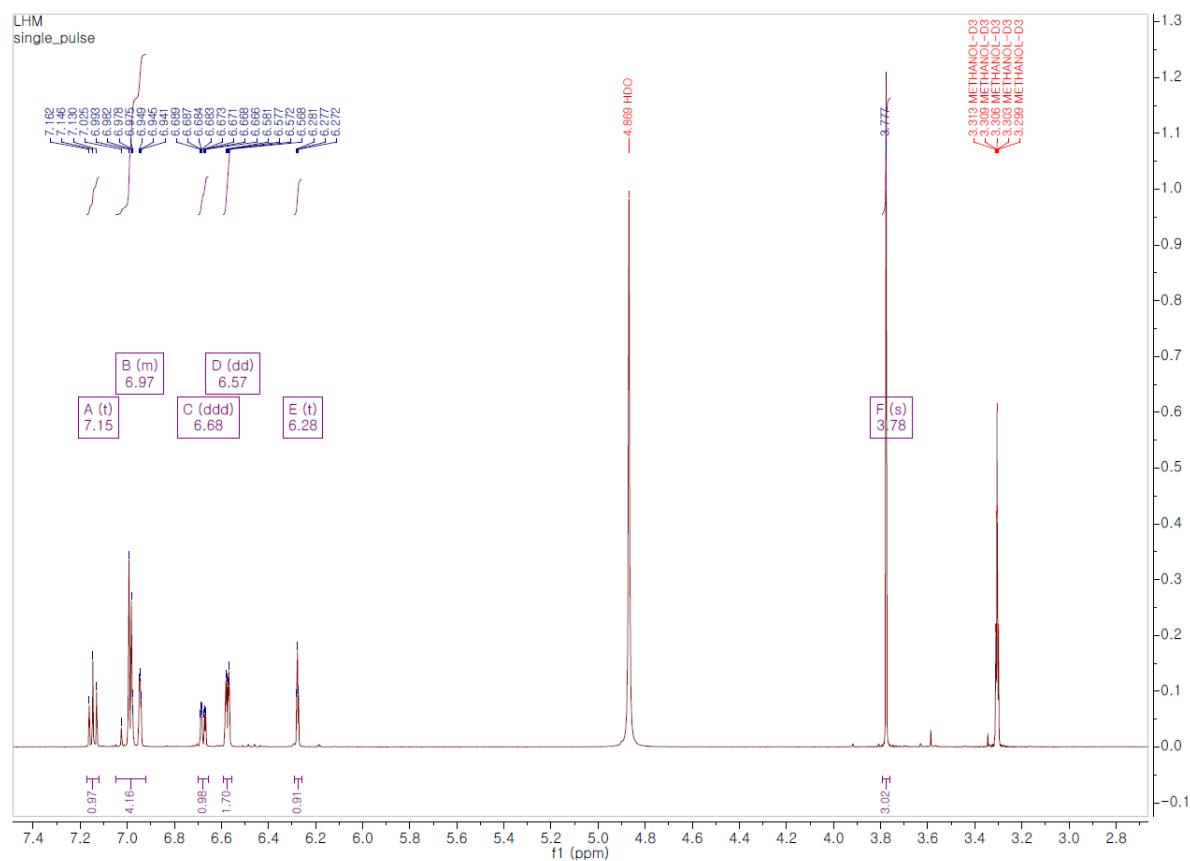
**Figure S26.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of compound **10**.



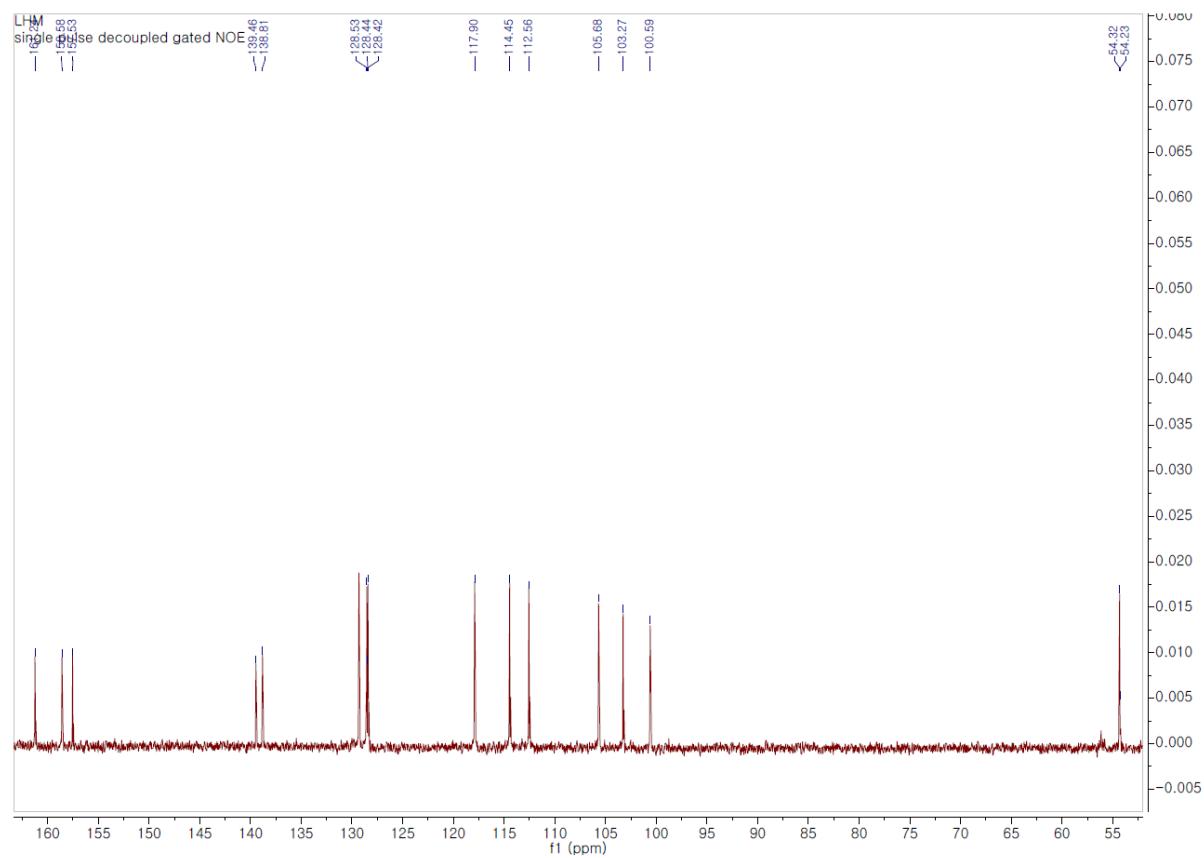
**Figure S27.** <sup>1</sup>H-NMR (500 MHz, acetone-*d*6) spectrum of compound 11.



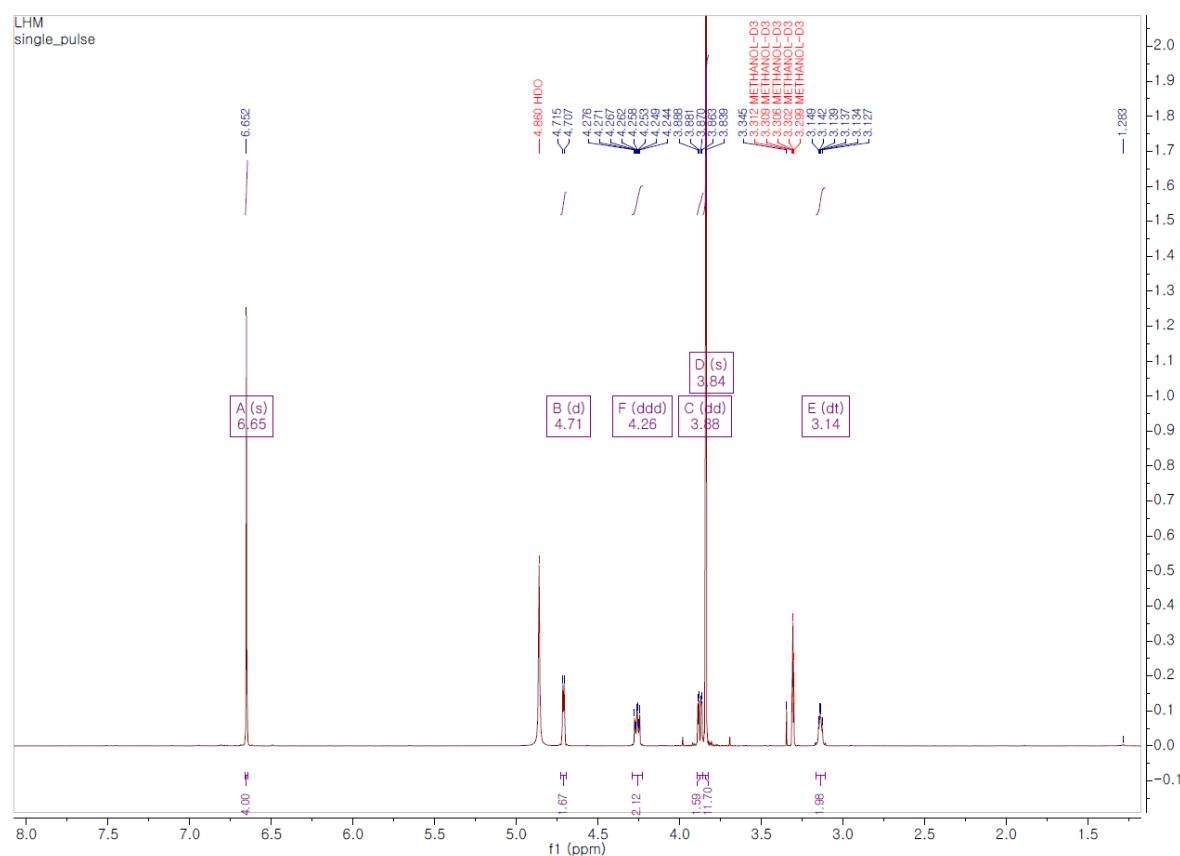
**Figure S28.**  $^{13}\text{C}$ -NMR (125 MHz, acetone-*d*6) spectrum of compound **11**.



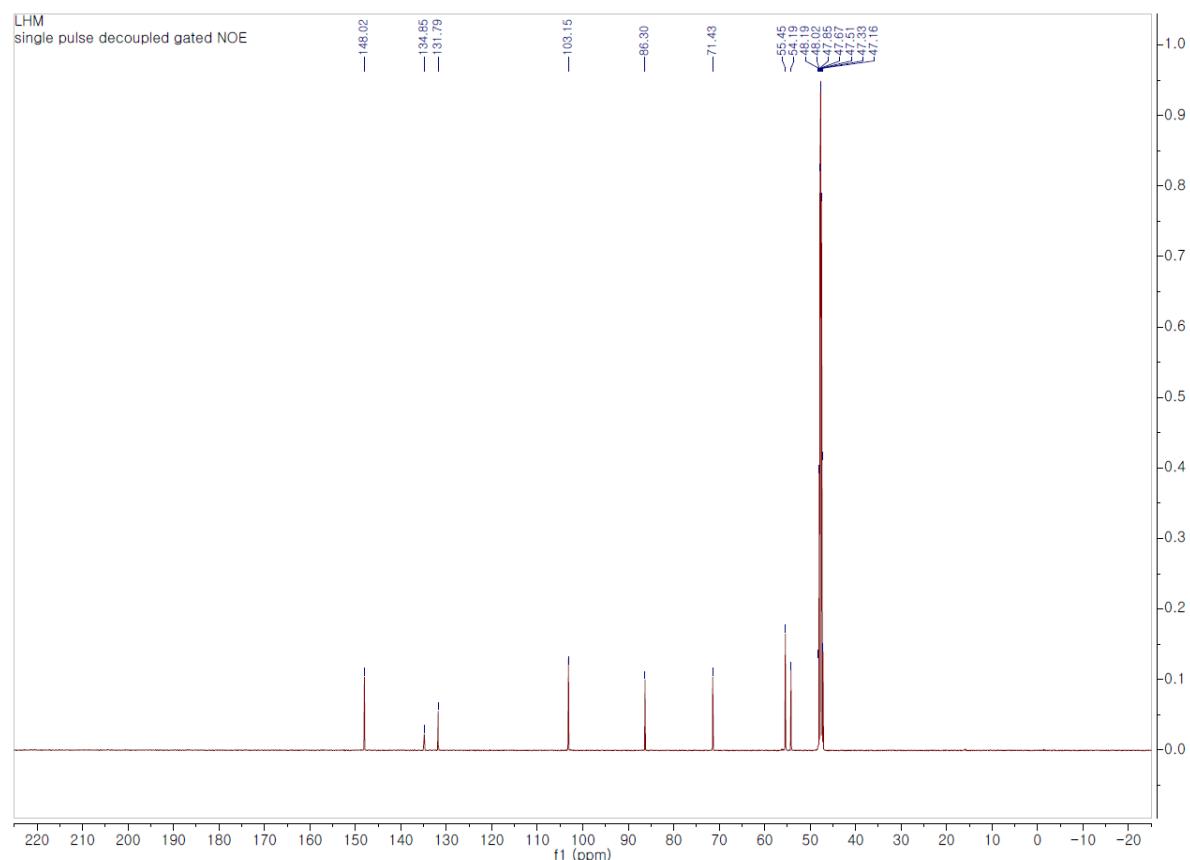
**Figure S29.**  $^1\text{H}$ -NMR (500 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **12**.



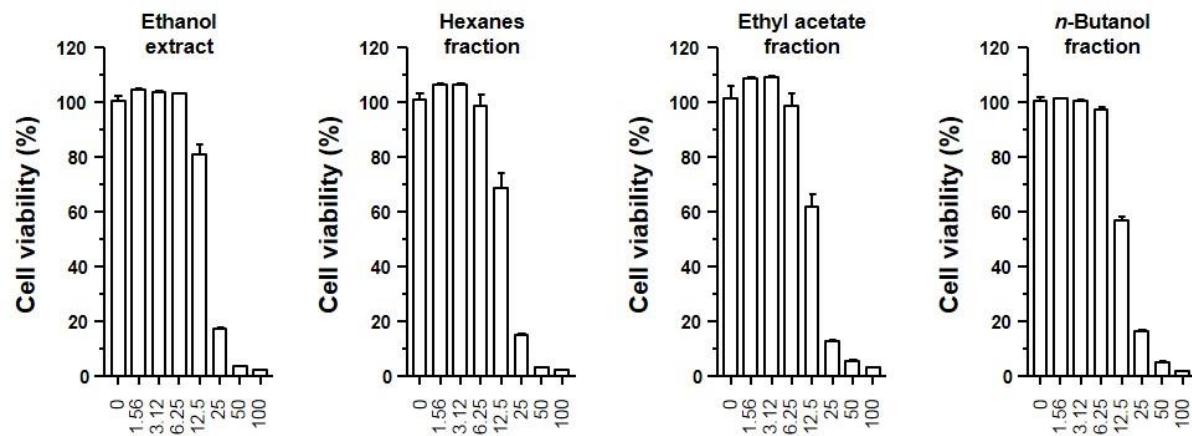
**Figure S30.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **12**.



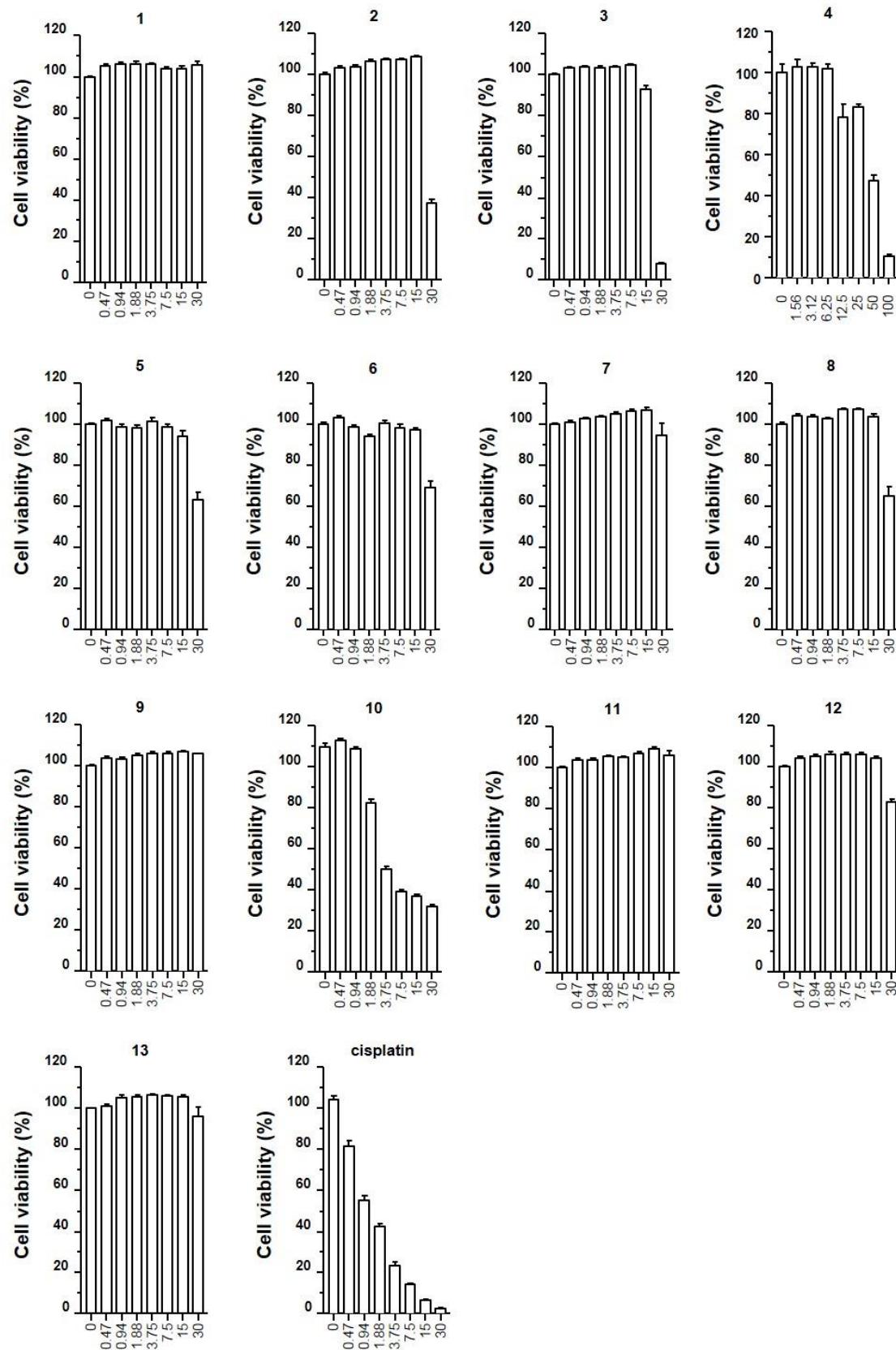
**Figure S31.** <sup>1</sup>H-NMR (500 MHz, CD<sub>3</sub>OD) spectrum of compound **13**.



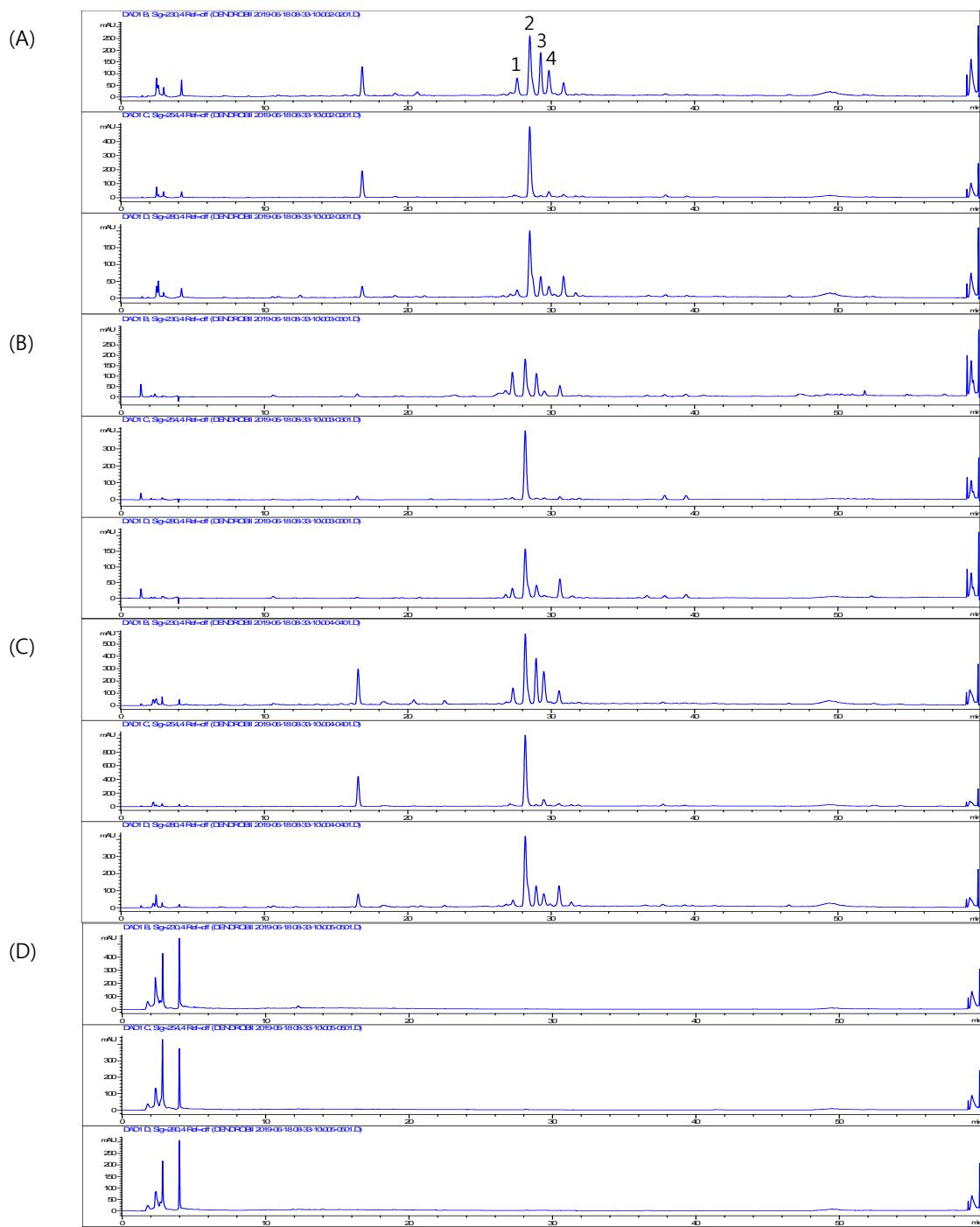
**Figure S32.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **13**.



**Figure S33.** Cytotoxic activities of extract and solvent fractions of *Dendrobii Herba* against FaDu cell line. Data are presented as means  $\pm \text{SD}$  ( $n = 6$ ).



**Figure S34.** Cytotoxic activities of compounds 1–13 from Dendrobii Herba against FaDu cell line. Data are presented as means  $\pm$  SD ( $n = 6$ ).



**Figure S35.** HPLC chromatograms of *Dendrobii Herba* (A) ethanol extract, (B) hexane soluble fraction, (C) Ethyl acetate soluble fraction and (D) *n*-butanol soluble fraction, detected at 230nm, 254nm and 280nm. Peak Identification by co-injection of each sample with standards: 1, moscatilin; 2, denthysrinin; 3, gigantol; 4, ephemeranthol A.