

Supplementary Material

Phenolic compounds from the stems of *Flickingeria fimbriata*

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ABSTRACT

Chemical investigation of *Flickingeria fimbriata* (Bl.) Hawkes (Orchidaceae) resulted in the isolation and identification of one new dihydrophenanthrene, 1,2,5,6,7-pentamethoxy-9,10-dihydrophenanthrene (**1**), together with seven known dihydrophenanthrenes, erianthridin (**2**), coelonin (**3**), 4-methoxy-9,10-dihydrophenanthrene-1,2,7-triol (**4**), lusianthridin (**5**), ephemeralhol A (**6**), flavanthridin (**7**), and hircinol (**8**), four known phenanthrenes, epheranthol B (**9**), nudol (**10**), denthysinin (**11**), and confusarin (**12**), and one known bibenzyl, batatasin III (**13**). The structure of the new compound was elucidated by spectroscopic analysis (HRMS, 1D and 2D NMR). All the compounds were isolated from *F. fimbriata* for the first time except for compounds **5** and **12**, and compounds **1**, **3**, **4**, **8**, **10**, **11**, and **13** were obtained from this genus for the first time. Compounds **1–4** showed moderate cytotoxic activity against HepG2 cells.

Keywords: *Flickingeria fimbriata*; Orchidaceae; 9,10-dihydrophenanthrene; cytotoxicity

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Figure S1. HRESIMS spectrum of **1**

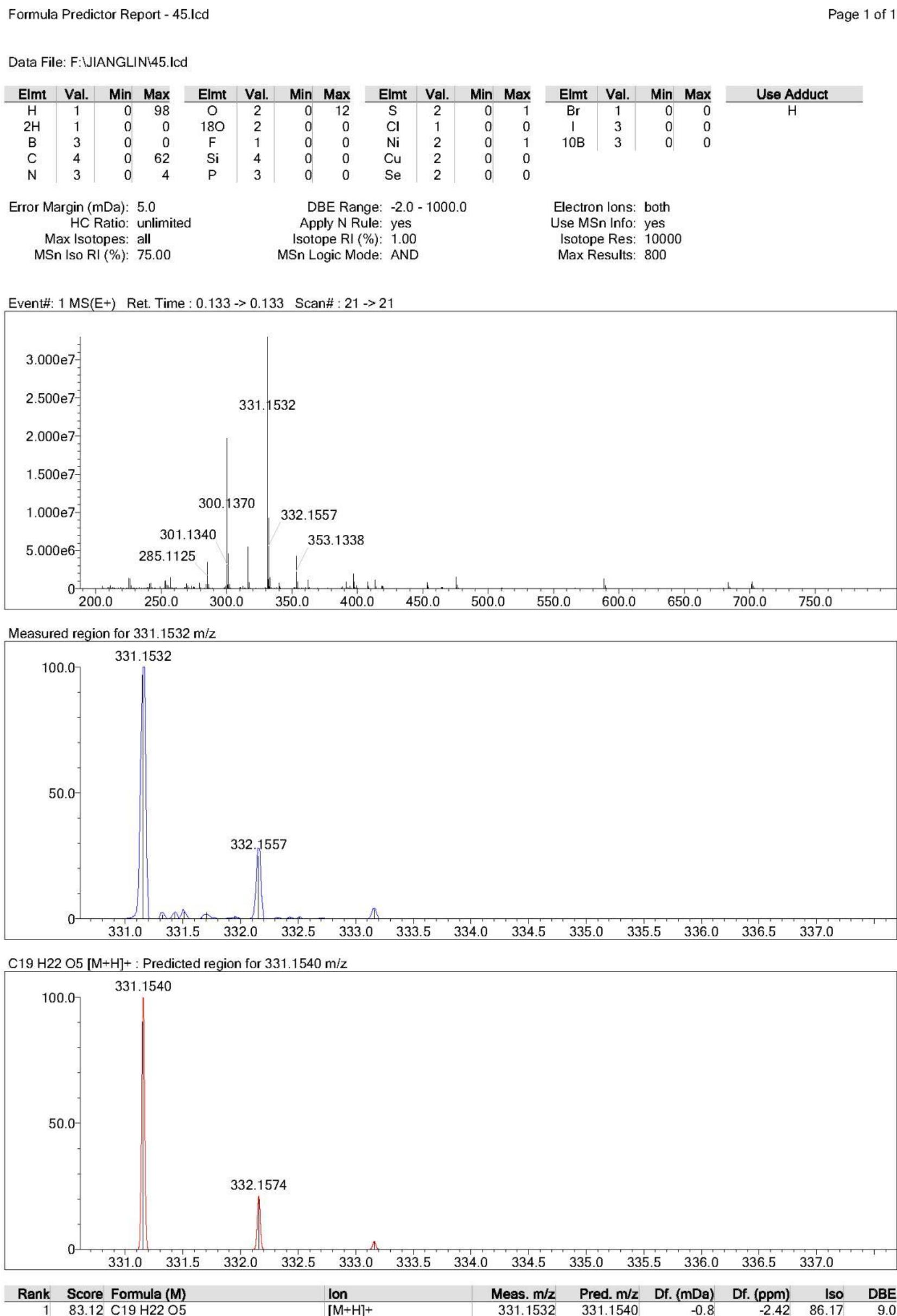


Figure S2. IR (KBr disc) spectrum of **1**

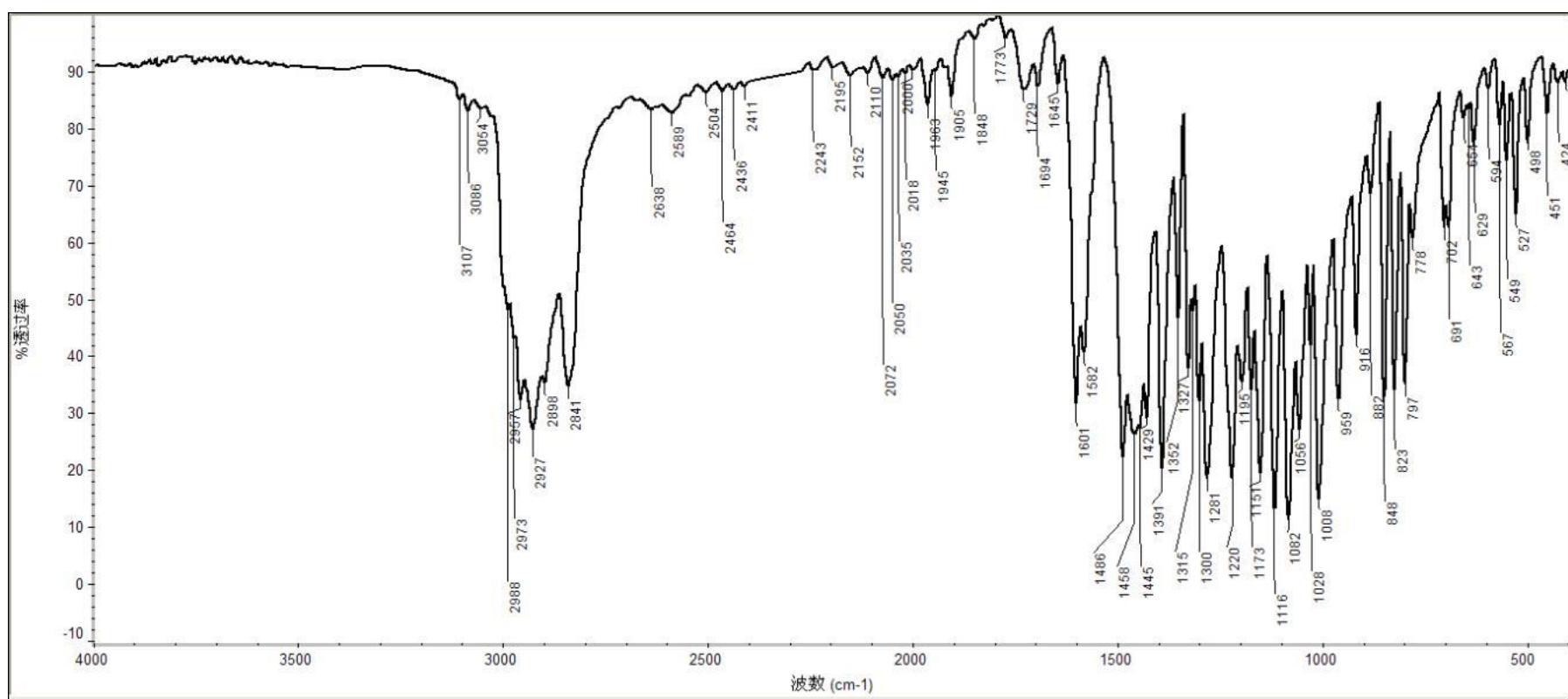


Figure S3. ^1H NMR (400 MHz, CDCl_3) spectrum of **1**

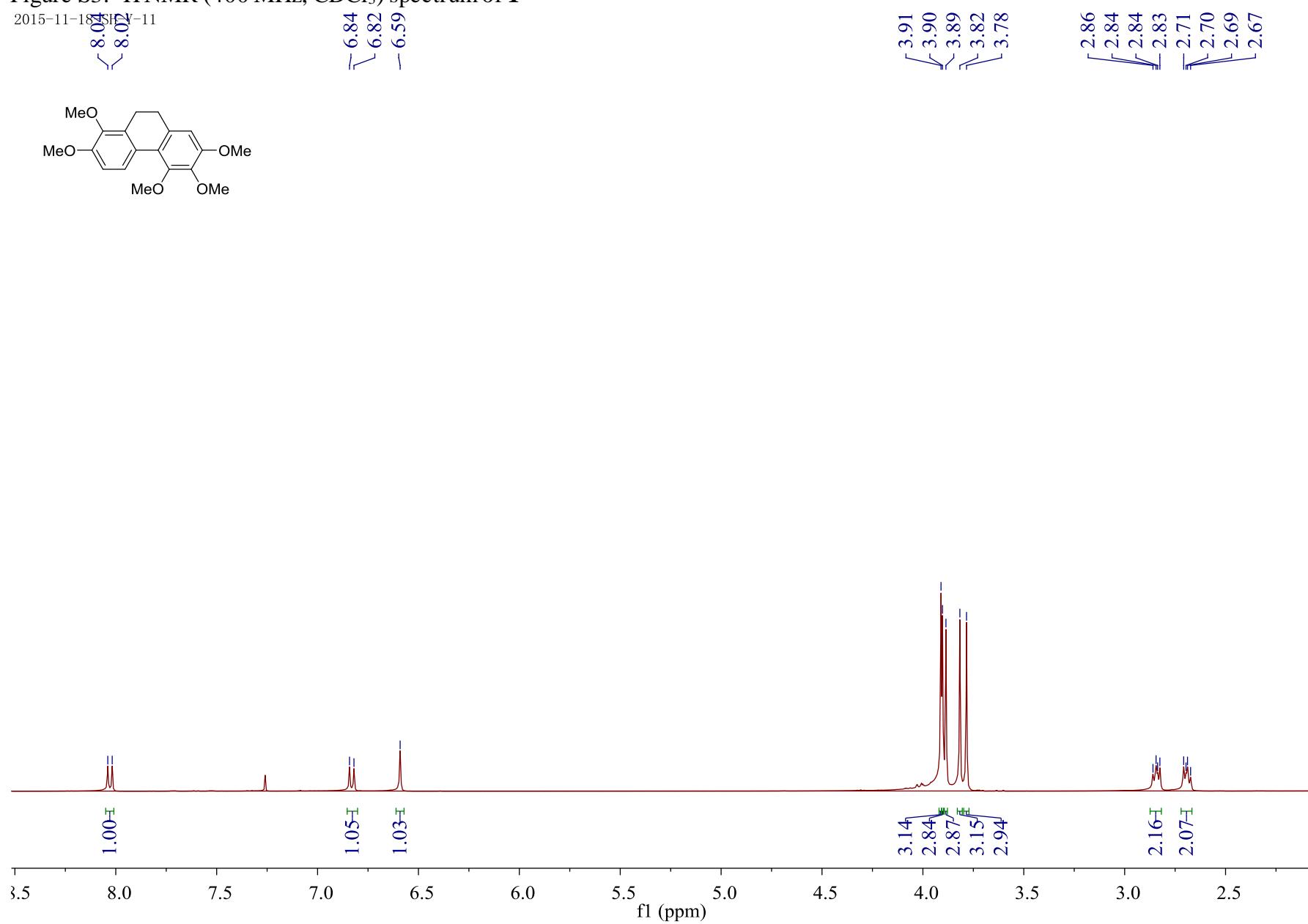


Figure S4. ^{13}C NMR (100 MHz, CDCl_3) spectrum of **1**

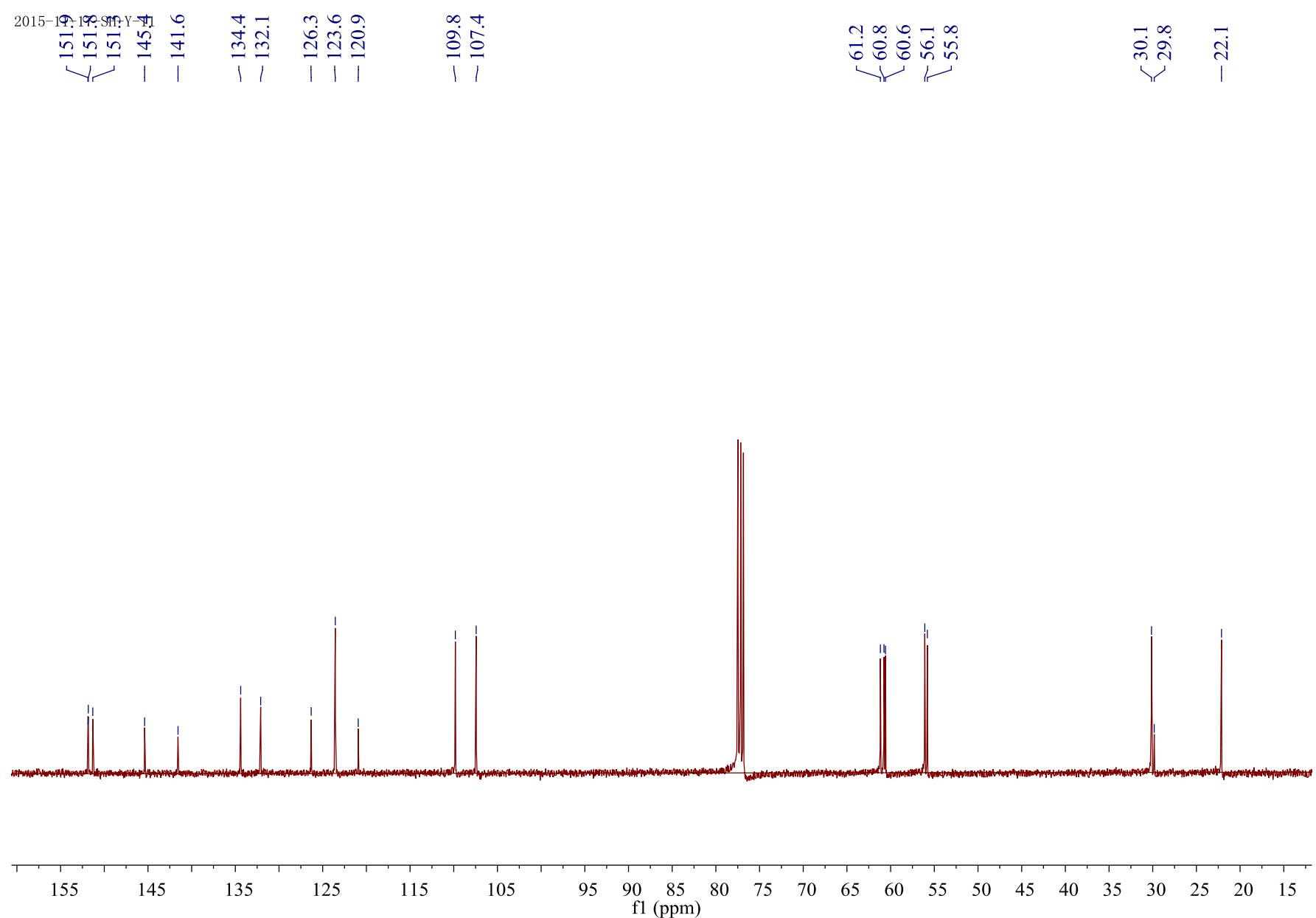


Figure S5. DEPT 135 (100 MHz, CDCl_3) spectrum of **1**

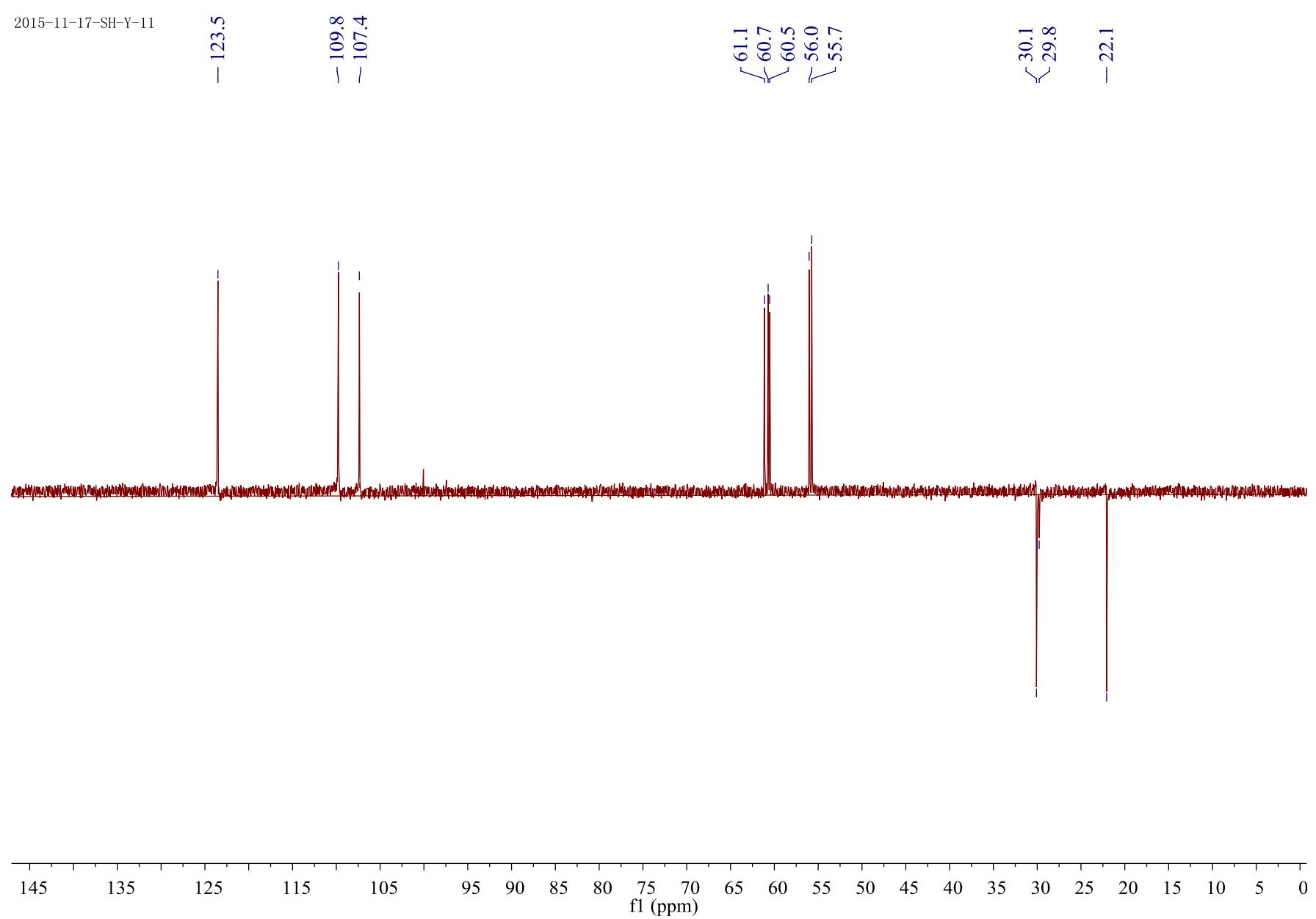


Figure S6. ^1H - ^1H COSY spectrum of **1** in CDCl_3

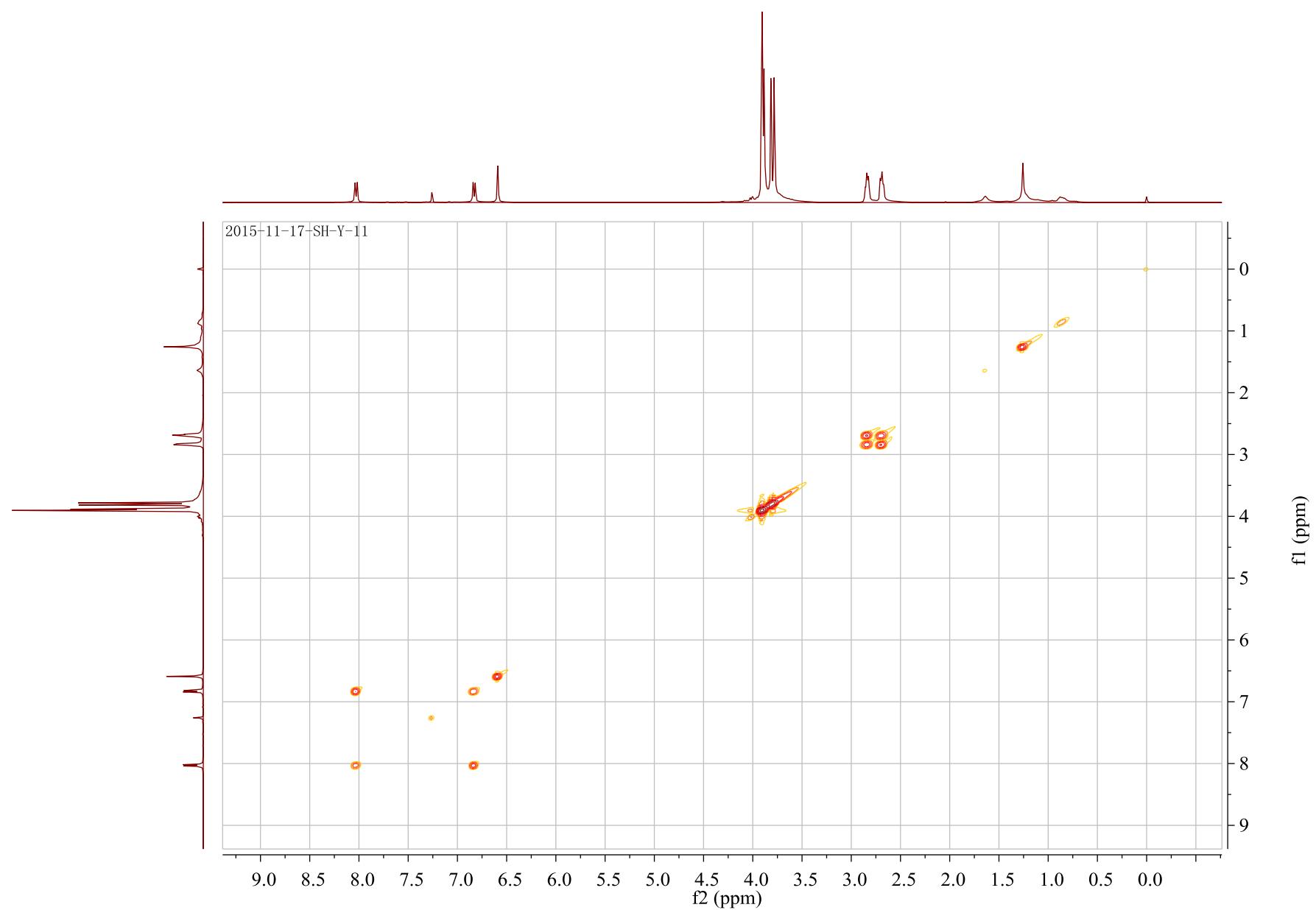


Figure S7. HSQC spectrum of **1** in CDCl_3

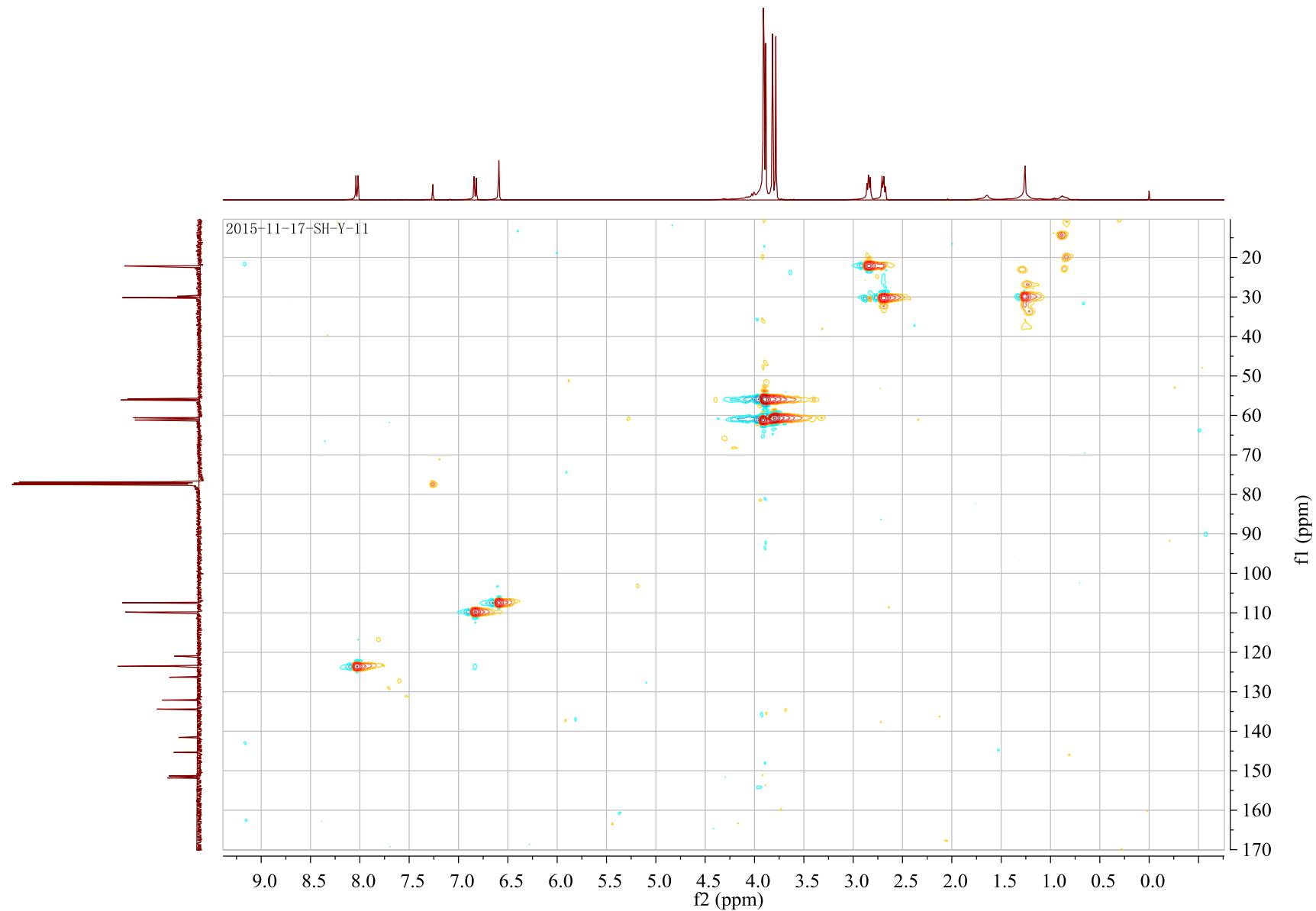


Figure S8. HMBC spectrum of **1** in CDCl_3

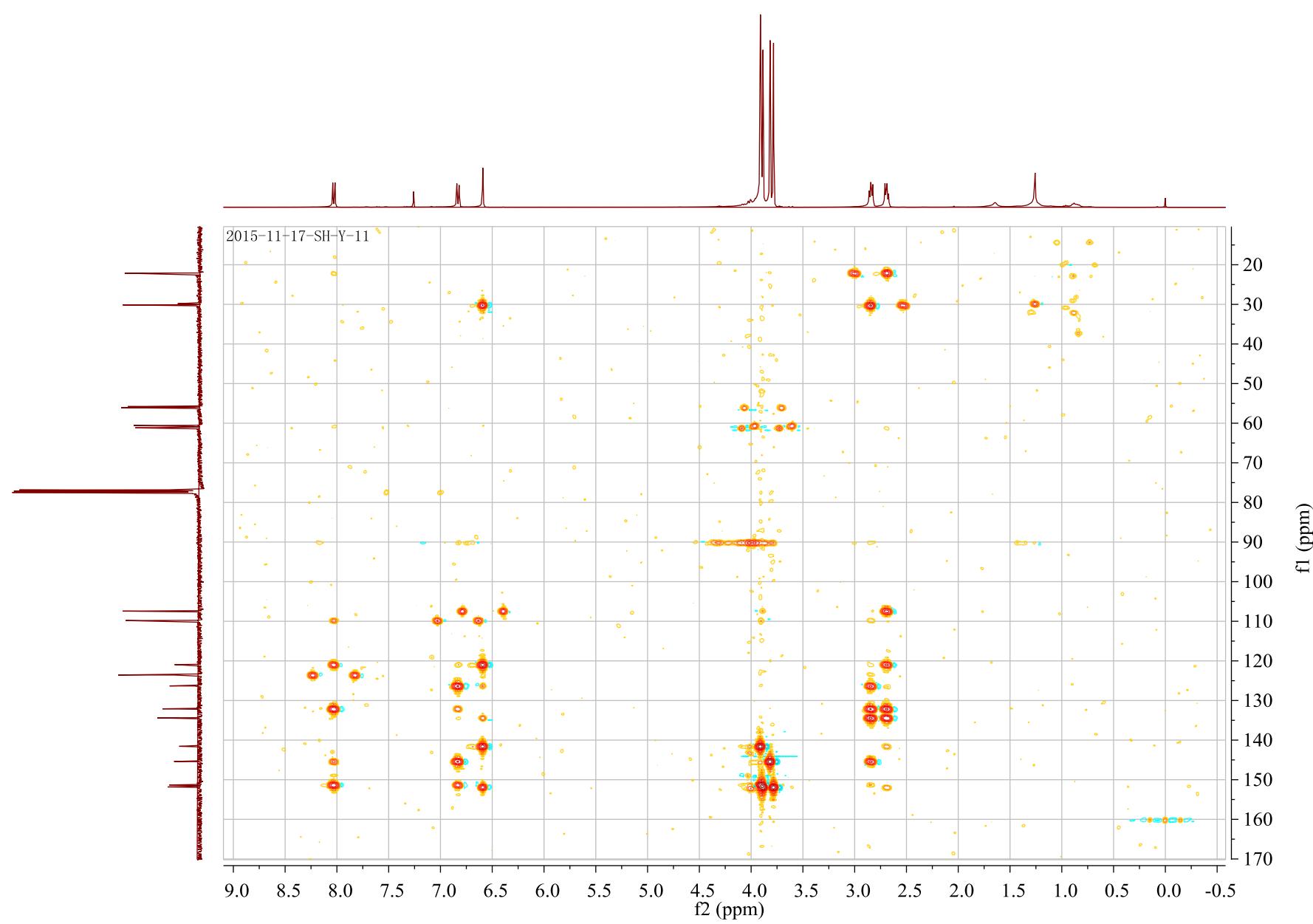


Figure S9. NOESY spectrum of **1** in CDCl_3

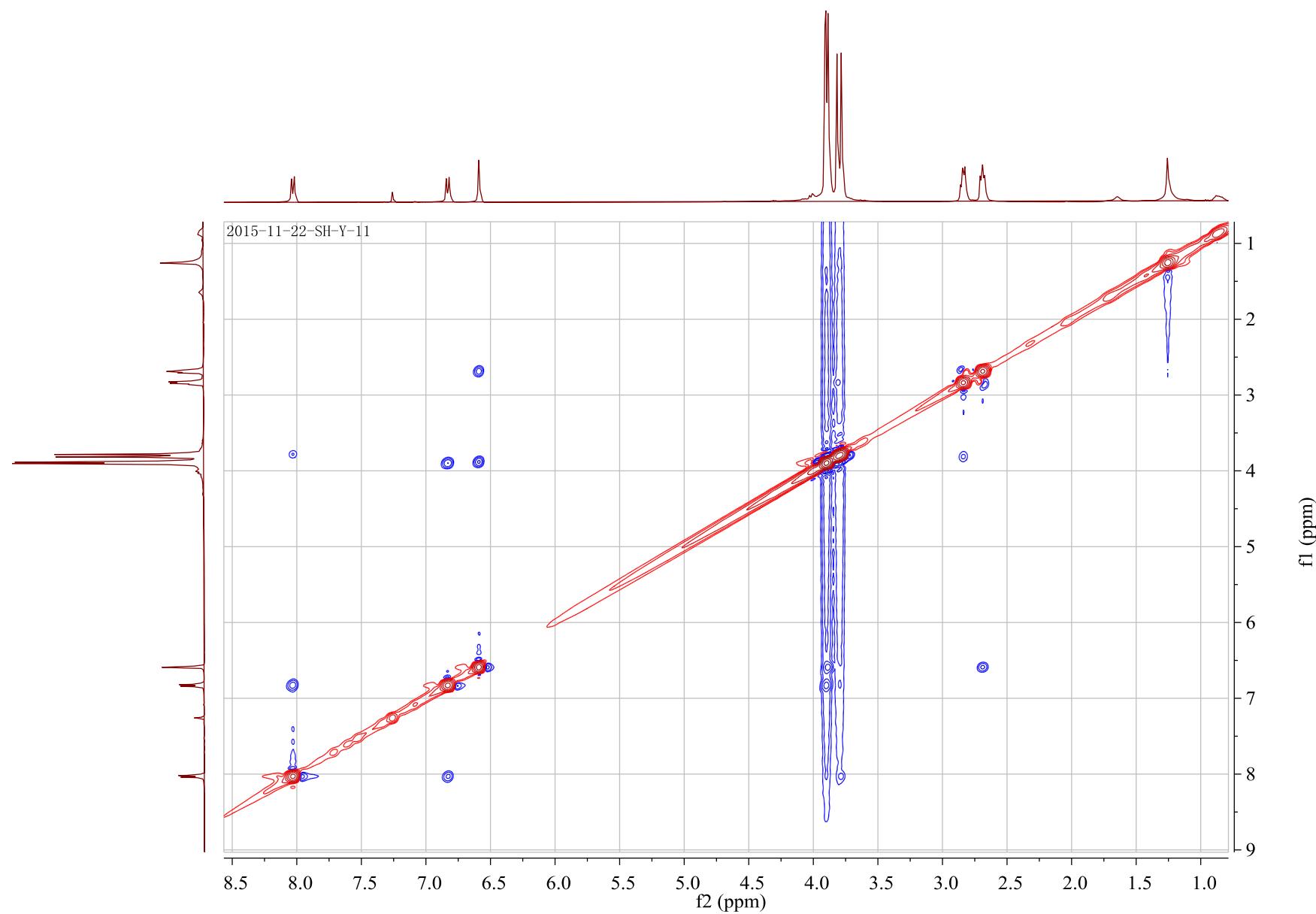
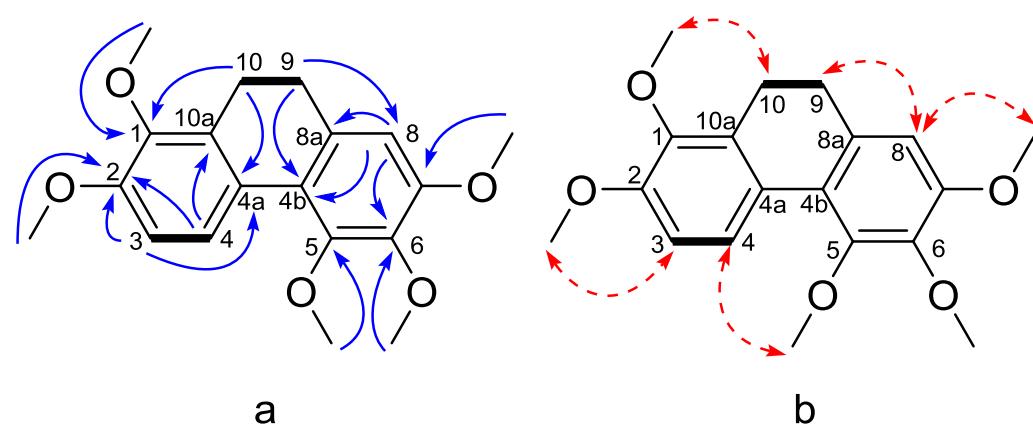


Figure S10. ^1H - ^1H COSY, ^1H - ^{13}C HMBC and NOESY correlations of **1**



a. Selected ^1H - ^1H COSY (—) and HMBC (→) correlations of **1**

b. Key NOE correlations (↔) of **1**

Table S1. Cytotoxicity data for compounds **1–13**

Compound	Cell, IC ₅₀ (μ M \pm SD)
	HepG 2
1	16.60 \pm 0.58
2	22.67 \pm 0.41
3	25.18 \pm 0.54
4	28.10 \pm 0.72
5	no test
6	>50
7	>50
8	>50
9	>50
10	>50
11	>50
12	>50
13	>50

Experiment was performed in triplicate (n=3) from 3 independently performed experiments.

Spectroscopic data of the known compounds **2–13**

Erianthridin (**2**)

Colorless needles. ¹H NMR (CD₃OD, 400 MHz): 6.51 (1H, s, H-1), 8.04 (1H, d, J=8.51, H-5), 6.67 (1H, d, J=2.64, H-6), 6.64 (1H, s, H-8), 2.61 (2H, m, H-9), 2.61 (2H, m, H-10), 3.86 (3H, s, 3-OCH₃), 3.68 (3H, s, 4-OCH₃); ¹³C NMR (CD₃OD, 100 MHz): 112.4 (C-1), 150.1 (C-2), 141.5 (C-3), 152.7 (C-4), 121.3 (C-4a), 125.9 (C-4b), 129.5 (C-5), 114.3 (C-6), 156.9 (C-7), 115.5 (C-8), 140.8 (C-8a), 31.4 (C-9), 31.3 (C-10), 136.0 (C-10a), 61.5 (3-OCH₃), 60.7 (4-OCH₃).

Coelonin (**3**)

Colorless powder. ¹H NMR (CD₃OD, 400 MHz): 6.30 (1H, d, J=2.32, H-1), 6.39 (1H, d, J=2.32, H-3), 7.99 (1H, d, J=8.86, H-5), 6.60 (1H, dd, J=8.86, 2.69, H-6), 6.62 (1H, d, J=2.69, H-8), 2.63 (2H, s, H-9), 2.63 (2H, s, H-10), 3.82 (3H, s, 4-OCH₃); ¹³C NMR (CD₃OD, 100 MHz): 108.3 (C-1), 156.0 (C-2), 99.2 (C-3), 159.1 (C-4), 116.7 (C-4a), 126.2 (C-4b), 130.0 (C-5), 115.0 (C-6), 157.5 (C-7), 113.6 (C-8), 141.8 (C-8a), 31.2 (C-9), 31.8 (C-10), 140.5 (C-10a), 55.9 (4-OCH₃).

4-methoxy-9,10-dihydrophenanthrene-1,2,7-triol (**4**)

Light-yellow powder. ¹H NMR (CD₃OD, 400 MHz): 6.48 (1H, s, H-3), 8.20 (1H, d, J=8.60, H-5), 6.65 (1H, dd, J=8.60, 2.59, H-6), 6.62 (1H, d, J=2.59, H-8), 2.50 (2H, m, H-9), 2.28 (2H, m, H-10), 3.65 (3H, s, 4-OCH₃); ¹³C NMR (CD₃OD, 100 MHz): 141.1 (C-1), 155.3 (C-2), 99.7 (C-3), 157.7 (C-4), 117.5 (C-4a), 126.9 (C-4b), 130.3 (C-5), 113.5 (C-6), 156.0 (C-7), 114.7 (C-8), 140.7 (C-8a), 31.0 (C-9), 28.3 (C-10), 116.0 (C-10a), 55.9 (4-OCH₃).

Lusianthridin (**5**)

Brown amorphous solid. ¹H NMR (CD₃OD, 400 MHz): 6.31 (1H, d, J=2.54, H-1), 6.33 (1H, d, J=2.54, H-3), 8.16 (1H, d, J=7.24, H-5), 6.65 (1H, d, J=2.71, H-6), 6.63 (1H, s, H-8), 2.65 (2H, s, H-9), 2.65 (2H, s, H-10), 3.73 (3H, s, 2-OCH₃); ¹³C NMR (CD₃OD, 100 MHz): 106.2 (C-1), 160.6 (C-2), 101.7 (C-3), 156.2 (C-4), 115.2 (C-4a), 126.6 (C-4b), 130.3 (C-5), 113.8 (C-6), 156.6 (C-7), 115.2 (C-8), 140.5

(C-8a), 31.4 (C-9), 32.1 (C-10), 142.0 (C-10a), 55.7 (2-OCH₃).

Ephemeranthol A (6)

Colorless powder. ¹H NMR (CD₃OD, 400 MHz): 6.41 (1H, s, H-1), 8.19 (1H, m, H-5), 6.64 (1H, m, H-6), 6.63 (1H, t, J=2.03, H-8), 2.66 (2H, s, H-9), 2.66 (2H, s, H-10); ¹³C NMR (CD₃OD, 100 MHz): 104.4 (C-1), 152.0 (C-2), 135.5 (C-3), 148.9 (C-4), 116.8 (C-4a), 126.5 (C-4b), 130.2 (C-5), 113.9 (C-6), 156.5 (C-7), 115.3 (C-8), 140.5 (C-8a), 31.5 (C-9), 31.7 (C-10), 136.6 (C-10a).

Flavanthridin (7)

Brown amorphous solid. ¹H NMR (CDCl₃, 400 MHz): 6.57 (1H, s, H-1), 8.15 (1H, d, J=8.27, H-5), 6.75 (1H, d, J=8.27, H-6), 6.73 (1H, s, H-8), 2.70 (2H, s, H-9), 2.70 (2H, s, H-10), 3.90 (3H, s, 2-OCH₃), 3.70 (3H, s, 4-OCH₃); ¹³C NMR (CDCl₃, 100 MHz): 107.2 (C-1), 145.8 (C-2), 137.7 (C-3), 144.9 (C-4), 120.4 (C-4a), 125.4 (C-4b), 128.4 (C-5), 114.7 (C-6), 154.4 (C-7), 113.6 (C-8), 139.9 (C-8a), 30.0 (C-9), 30.3 (C-10), 129.8 (C-10a), 60.2 (2-OCH₃), 56.3 (4-OCH₃).

Hircinol (8)

Light-yellow powder. ¹H NMR (CD₃OD, 400 MHz): 6.50 (1H, d, J=2.37, H-1), 6.54 (1H, d, J=2.37, H-3), 8.03 (1H, d, J=8.7, H-4), 6.81 (1H, s, H-6), 7.05 (1H, dd, J=7.25, 8.15, H-7), 6.79 (1H, s, H-8), 2.61 (2H, m, H-9), 2.61 (2H, m, H-10), 3.91 (3H, s, 4-OCH₃); ¹³C NMR (CD₃OD, 100 MHz): 110.1 (C-1), 159.0 (C-2), 100.2 (C-3), 156.8 (C-4), 115.0 (C-4a), 122.1 (C-4b), 154.4 (C-5), 118.3 (C-6), 128.4 (C-7), 120.6 (C-8), 141.9 (C-8a), 32.3 (C-9), 32.0 (C-10), 144.6 (C-10a), 57.5 (4-OCH₃).

Epheranthol B (9)

Colorless powder. ¹H NMR (CD₃OD, 400 MHz): 7.13 (1H, s, H-1), 9.28 (1H, d, J=9.20, H-5), 7.10 (1H, dd, J=2.70, 9.20, H-6), 7.15 (1H, d, J=2.70, H-8), 7.52 (1H, d, J=8.81, H-9), 7.39 (1H, d, J=8.81, H-10), 3.87 (3H, s, 2-OCH₃), 3.97 (3H, s, 4-OCH₃); ¹³C NMR (CD₃OD, 100 MHz): 112.3 (C-1), 148.9 (C-2), 141.1 (C-3), 145.7 (C-4), 124.2 (C-4a), 120.3 (C-4b), 129.2 (C-5), 117.3 (C-6), 156.0 (C-7), 106.2 (C-8), 135.4 (C-8a), 128.2 (C-9), 125.6 (C-10), 127.0 (C-10a), 59.8 (2-OCH₃), 56.5 (4-OCH₃).

Nudol (10)

Light yellow powder. ¹H NMR (CD₃OD, 400 MHz): 7.15 (1H, s, H-1), 9.26 (1H, d, J=9.07, H-5), 7.08 (1H, d, J=9.07, H-6), 7.15 (1H, s, H-8), 7.45 (1H, s, H-9), 7.45 (1H, s, H-10), 3.94 (3H, s, 3-OCH₃), 4.00 (3H, s, 4-OCH₃); ¹³C NMR (CD₃OD, 100 MHz): 108.8 (C-1), 148.9 (C-2), 141.9 (C-3), 151.2 (C-4), 123.3 (C-4a), 129.4 (C-4b), 127.7 (C-5), 116.2 (C-6), 154.5 (C-7), 111.2 (C-8), 133.6 (C-8a), 126.4 (C-9), 125.9 (C-10), 118.1 (C-10a), 60.0 (3-OCH₃), 61.5 (4-OCH₃).

Denthyrsinin (11)

Colorless powder. ¹H NMR (CD₃OD, 400 MHz): 7.16 (1H, s, H-1), 9.10 (1H, d, J=9.31, H-5), 7.17 (1H, d, J=9.31, H-6), 7.82 (1H, d, J=9.11, H-9), 7.60 (1H, d, J=9.11, H-10), 3.99 (3H, s, 2-OCH₃), 3.86 (3H, s, 4-OCH₃), 3.92 (3H, s, 8-OCH₃); ¹³C NMR (CD₃OD, 100 MHz): 107.6 (C-1), 150.6 (C-2), 142.7 (C-3), 147.3 (C-4), 121.8 (C-4a), 126.5 (C-4b), 125.9 (C-5), 119.4 (C-6), 148.9 (C-7), 143.9 (C-8), 130.3 (C-8a), 120.3 (C-9), 129.7 (C-10), 128.4 (C-10a), 57.9 (2-OCH₃), 61.3 (4-OCH₃), 62.9 (8-OCH₃).

Confusarin (12)

Colorless crystal. ¹H NMR (CD₃OD, 400 MHz): 7.08 (1H, s, H-1), 9.08 (1H, d, J=9.3, H-5), 7.18 (1H, d, J=9.3, H-6), 7.85 (1H, d, J=9.1, H-9), 7.50 (1H, d, J=9.1, H-10), 3.92 (3H, s, 3-OCH₃), 3.92 (3H, s, 4-OCH₃), 4.00 (3H, s, 8-OCH₃); ¹³C NMR (CD₃OD, 100 MHz): 110.1 (C-1), 150.4 (C-2), 143.4 (C-3), 152.8 (C-4), 119.6 (C-4a), 130.7 (C-4b), 124.3 (C-5), 118.2 (C-6), 147.4 (C-7), 142.7 (C-8), 125.5 (C-8a), 120.5 (C-9), 127.8 (C-10), 128.4 (C-10a), 61.5 (3-OCH₃), 60.4 (4-OCH₃), 61.5 (8-OCH₃).

Batatasin III (13)

Colorless powder. ^1H NMR (CDCl_3 , 400 MHz): 6.32 (1H, d, $J=1.48$, H-1), 6.26 (1H, d, $J=1.64$, H-3), 6.26 (1H, d, $J=1.64$, H-5), 2.82 (2H, m, H-7), 2.82 (1H, m, H-7'), 6.76 (1H, d, $J=7.71$, H-5'), 7.14 (1H, t, $J=7.71$, H-4'), 6.68 (1H, d, $J=2.38$, H-3'), 6.65 (1H, s, H-1'), 3.75 (3H, s, 2-OCH₃); ^{13}C NMR (CDCl_3 , 100 MHz): 107.0 (C-1), 161.0 (C-2), 99.3 (C-3), 156.7 (C-4), 108.2 (C-5), 144.6 (C-6), 37.8 (C-7), 37.5 (C-7'), 143.7 (C-6'), 115.5 (C-5'), 129.7 (C-4'), 113.1 (C-3'), 155.6 (C-2'), 121.1 (C-1'), 55.4 (2-OCH₃).