Supporting Information

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Heracleumate, A New Enynic Ester from the Roots of *Heracleum rapula* Franch.

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Spectra data of compounds **2**–**5**

9-epoxyfalcarindiol (**2**): light yellow oil, $[\alpha]_D^{25.4}$ +97.2 (*c* 0.1, MeOH); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.95 (1H, ddd, *J* = 17.1, 10.2, 5.4 Hz, H-2), 5.48 (1H, dt, *J* = 17.1, 1.2 Hz, H-1a), 5.28 (1H, dt, *J* = 10.2, 1.1 Hz, H-1b), 4.95 (1H, t, *J* = 5.7 Hz, H-3), 4.29 (1H, dd, *J* = 7.7, 4.1 Hz, H-8), 3.19 (1H, dd, *J* = 7.6, 4.3 Hz, H-10), 3.07 (1H, ddd, *J* = 6.9, 5.4, 4.3 Hz, H-9), 2.35 (1H, d, *J* = 4.7 Hz, 8-OH), 2.02 (1H, d, *J* = 6.6 Hz, 3-OH), 1.62 – 1.46 (4H, m, H_2-11/H_2-12), 1.37 – 1.25 (8H, m, H_2-13~16), 0.89 (3H, t, *J* = 6.9 Hz, H_3-17); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.7 (C-2), 117.7 (C-1), 78.9 (C-7), 76.4 (C-4), 70.8 (C-5), 70.0 (C-6), 63.6 (C-3), 62.3 (C-8), 59.7 (C-9), 57.6 (C-10), 31.9 (C-15), 29.5 (C-11), 29.3 (C-14), 28.2 (C-13), 26.8 (C-12), 22.8 (C-16), 14.2 (C-17); HRESIMS *m/z* 299.1616 $[M+Na]^+$ (calculated for $C_{17}H_{24}O_3Na^+$, 299.1618; EIMS (70 eV) *m*/*z* (rel. int.) 207 (49), 191 (13), 177 (9), 135 (33), 105 (31), 91 (63), 81 (67), 71 (57), 57 (100), 43 (59).

3(*R*), 8(*S*)-falcarindiol (**3**): colorless oil, $[\alpha]_D^{25.3}$ +198.6 (*c* 0.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.93 (1H, ddd, *J* = 16.2, 10.2, 5.4 Hz, H-2), 5.60 (1H, dt, *J* = 11.1, 7.6 Hz, H-10), 5.51 (1H, m, H-9), 5.47 (1H, d, *J* = 17.1 Hz, H-1a), 5.25 (1H, d, *J* = 10.1 Hz, H-1b), 5.20 (1H, d, *J* = 8.4 Hz, H-8), 4.93 (1H, d, *J* = 5.4 Hz, H-3), 2.10 (2H, q, *J* = 7.5 Hz, H_2-11), 1.38 (2H, p, *J* = 7.1 Hz, H_2-12), 1.30 – 1.25 (8H, m, H_2-13~16), 0.87 (3H, t, *J* = 6.9 Hz, H_3-17); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.9 (C-2), 134.8 (C-10), 127.8 (C-9), 117.5 (C-1), 80.0 (C-4), 78.4 (C-7), 70.4 (C-5), 68.8 (C-6), 63.6 (C-3), 58.7 (C-8), 31.9 (C-11), 29.4 (C-12), 29.3 (C-13), 29.2 (C-14), 27.8 (C-15), 22.8 (C-16), 14.2 (C-17); HRESIMS *m/z* 283.1664 $[M+Na]^+$ (calculated for $C_{17}H_{24}O_2Na^+$, 283.1669; EIMS (70 eV) *m*/*z* (rel. int.) 207 (2),178 (29), 157 (32), 129 (100), 115 (53), 105 (31), 91 (67), 55 (60).

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oplopantriol B (**4**): yellow oil, $[\alpha]_D^{25.8}$ +187.4 (*c* 0.08, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60 (1H, ddt, *J* = 10.6, 7.3, 1.5 Hz, H-10), 5.51 (1H, ddt, *J* = 10.6, 7.5, 1.5 Hz, H-9), 5.20 (1H, d, *J* = 8.0 Hz, H-11), 4.37 (1H, t, *J* = 6.6 Hz, H-16), 3.65 (2H, t, *J* = 6.5 Hz, H-1), 2.11 (2H, m, H-8), 1.74 (2H, m, H-17), 1.57 (2H, m, H-2), 1.39 – 1.26 (10H, m, H_2-3~7), 1.01 (3H, t, *J* = 7.4 Hz, H_3-18); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.5 (C-10), 128.1 (C-9), 81.1 (C-15), 79.2 (C-12), 69.1 (C-14), 69.0 (C-13), 64.1 (C-16), 63.2 (C-1), 58.8 (C-11), 32.9 (C-2), 30.8 (C-17), 29.42(C-5), 29.3 (C-4), 29.2 (C-6), 29.0 (C-7), 27.7 (C-8), 25.7 (C-3), 9.5 (C-18); HRESIMS *m/z* 293.2118 $[M+H]^+$ (calculated for $C_{18}H_{29}O_3^+$, 293.2111).

18-*O*-acetyloplopantriol B (**5**): yellow oil, $[\alpha]_D^{25.4}$ +121.6 (*c* 0.07, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (1H, ddd, *J* = 17.2, 10.2, 1.0 Hz, H-17), 5.58 (1H, ddt, *J* = 10.7, 7.2, 1.0 Hz, H-9), 5.51 (1H, ddt, *J* = 10.7, 8.1, 1.0 Hz, H-10), 5.46 (1H, dt, *J* = 17.2, 1.0 Hz, H-18a), 5.24 (1H, dt, *J* = 10.2, 1.0 Hz, H-18b), 5.19 (1H, d, *J* = 8.2 Hz, H-11), 4.92 (1H, d, *J* = 5.3 Hz, H-16), 4.05 (2H, t, *J* = 6.8 Hz, H-1), 2.10 (2H, m, H-8), 2.04 (3H, s, $CO\underline{CH_3}$), 1.64 – 1.57 (2H, m, H-2), 1.38 – 1.26 (10H, m, H_2-3~7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7 ($\underline{CO}CH_3$), 136.0 (C-17), 134.5 (C-9), 128.0 (C-10), 117.3 (C-18), 80.0 (C-12), 78.5 (C-15), 70.3 (C-14), 68.8 (C-13), 64.9 (C-1), 63.5 (C-16), 58.6 (C-11), 29.3 (C-8), 29.2 (C-7), 29.22 (C-6), 29.1 (C-5), 28.7 (C-4), 27.7 (C-3), 25.9 (C-2), 21.2($CO\underline{CH_3}$); HRESIMS *m/z* 355.1839 $[M+Na]^+$ (calculated for $C_{20}H_{28}O_4Na^+$, 355.1880); EIMS (70 eV) *m/z* (rel. int.) 197 (7), 191 (13), 171 (13), 135 (27), 129 (82), 115 (54), 105 (34), 91 (76), 81 (48), 55 (100).

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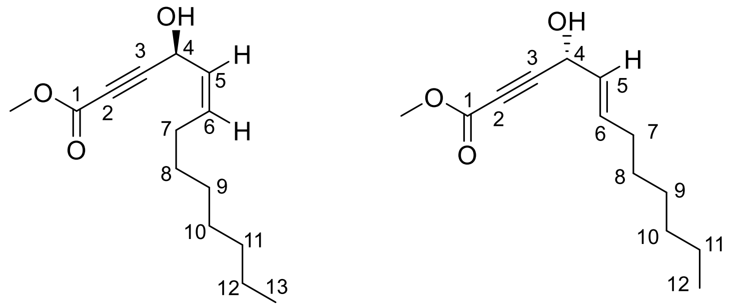
Table S1: The NMR data of **1** and (4R)-4-hydroxy-dodec-5-en-2-ynoic acid methyl ester.



1

(4*R*)-4-hydroxy-dodec-5-en-2-ynoic acid methyl ester

Position	**1**		**(4*R*)-4-hydroxy-dodec-5-en-2-ynoic acid methyl ester**	
	δ_C, mult.	δ_H (*J* in Hz)	δ_C, mult.	δ_H (*J* in Hz)
1	153.9, C		153.8, C	
2	76.2, C		76.9, C	
3	87.0, C		86.5, C	
4	58.1, CH	5.25, d (8.4)	62.6, CH	4.94, t (6)
5	126.8, CH	5.54, ddt (10.4, 8.4, 1.6)	126.6, CH	5.57, ddt (15.6, 6.4, 1.5)
6	135.8, CH	5.67, dtd (10.4, 7.5, 1.2)	135.8, CH	5.91, dtd (15.6, 6.8, 1)
7	27.9, CH_2	2.14-2.10, m	28.6, CH_2	2.06, q (7.2)
8	29.4, CH_2	1.40-1.37, m	28.8, CH_2	1.43-1.21, m[a]
9	29.3, CH_2	1.33-1.25[a]	28.8, CH_2	1.43-1.21, m[a]
10	29.2, CH_2	1.33-1.25 [a]	31.6, CH_2	1.43-1.21, m[a]
11	31.9, CH_2	1.33-1.25 [a]	22.5, CH_2	1.43-1.21, m[a]
12	22.8, CH_2	1.33-1.25 [a]	14.0, CH_3	0.87, t (7.2 Hz)
13	14.2, CH_3	0.88, t (6.9 Hz)		
OMe	53.0, CH_3	3.78, s	52.8, CH_3	3.78, s

[a] Overlapped signal.

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Table S2: Conformational analysis of twelve optimized conformers of 4*S*-**1** at the B3LYP/6-311G(d,p) level in methanol.

Conformer	E (Hartree)	G (kcal/mol)	Percent (%)
4*S*-**1**-1	-772.5618542	-484789.88	19.68
4*S*-**1**-2	-772.5617699	-484789.83	18
4*S*-**1**-3	-772.5614247	-484789.61	12.49
4*S*-**1**-4	-772.561276	-484789.52	10.67
4*S*-**1**-5	-772.5611784	-484789.45	9.62
4*S*-**1**-6	-772.5610272	-484789.36	8.2
4*S*-**1**-7	-772.56046	-484789	4.49
4*S*-**1**-8	-772.560343	-484788.93	3.97
4*S*-**1**-9	-772.5602726	-484788.89	3.69
4*S*-**1**-10	-772.5602015	-484788.84	3.42
4*S*-**1**-11	-772.559983	-484788.7	2.71
4*S*-**1**-12	-772.5598395	-484788.61	2.33

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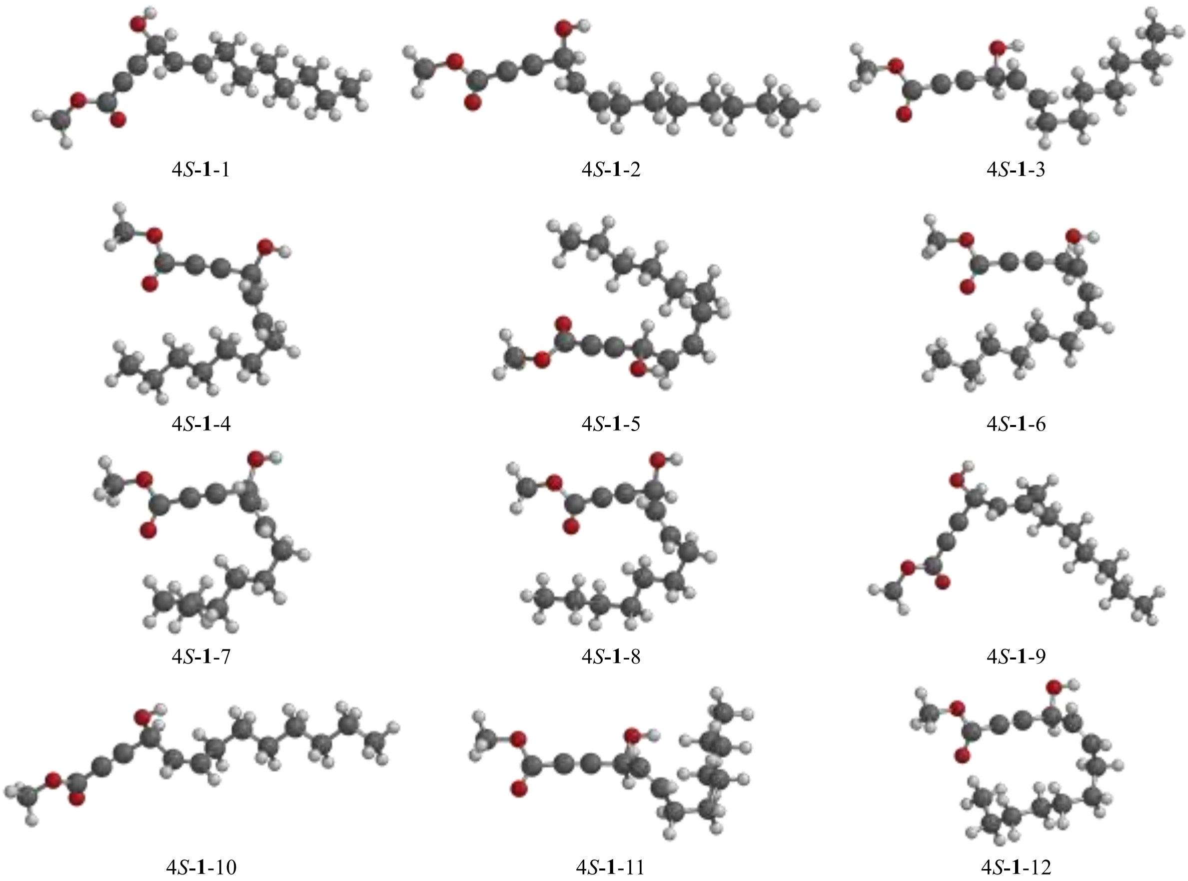

Figure S1: Twelve optimized conformers of 4*S*-**1** at the B3LYP/6-311G(d,p) level in methanol

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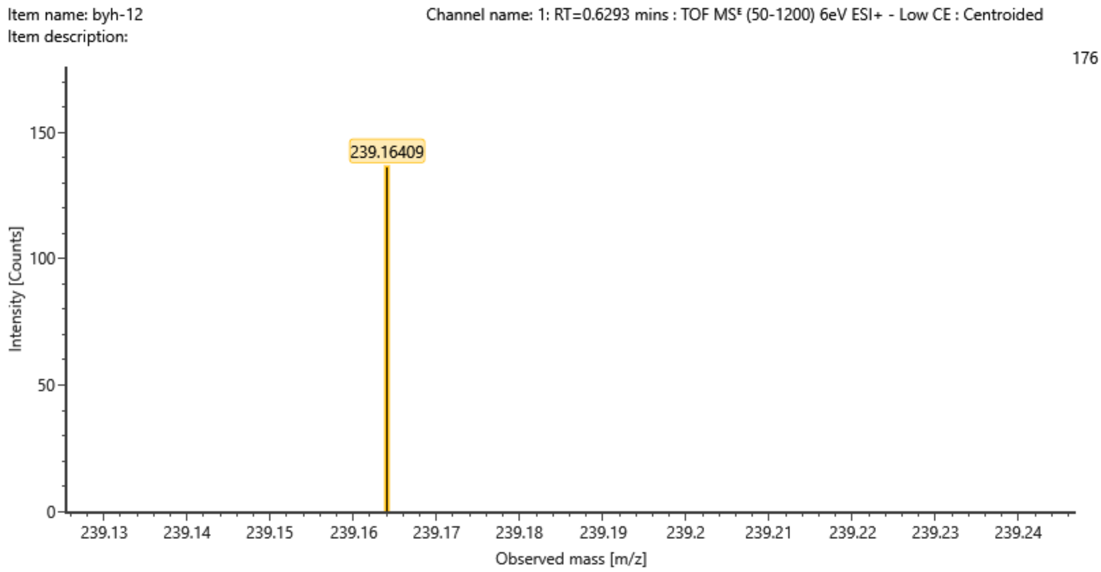

Figure S2: HR-ESI-MS spectrum of **1**

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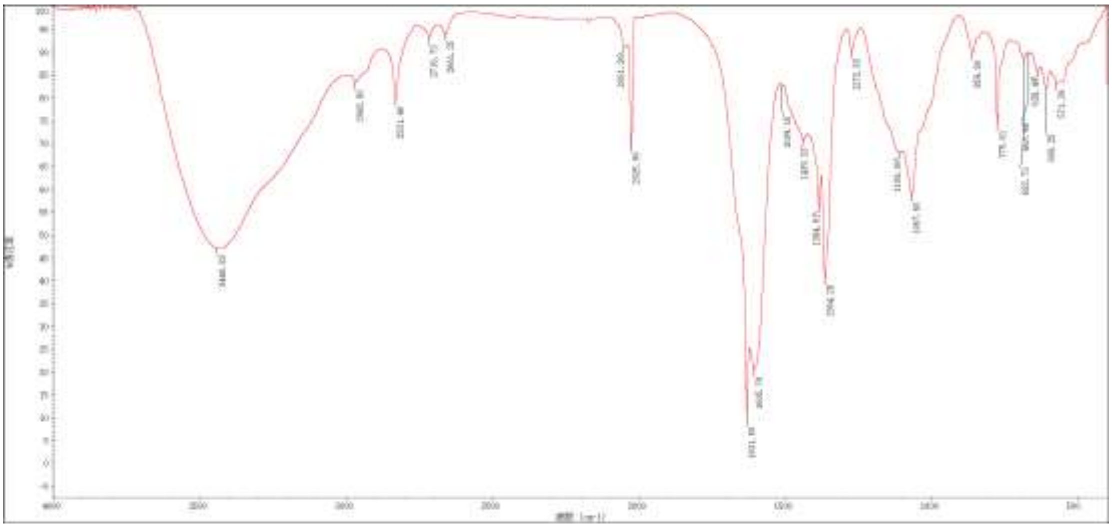

Figure S3: IR spectrum of **1**

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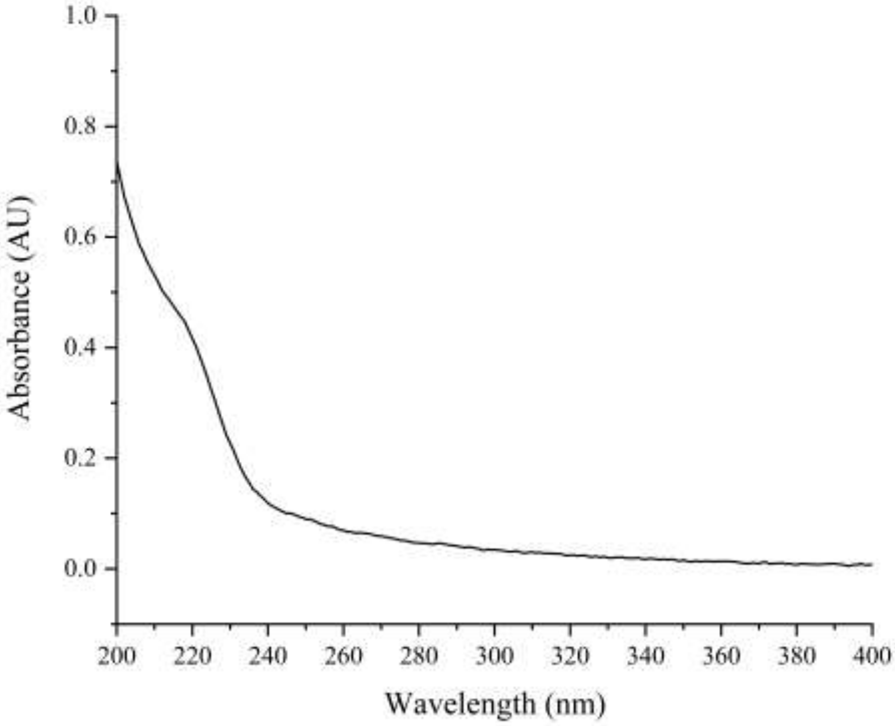

Figure S4: UV spectrum of **1**

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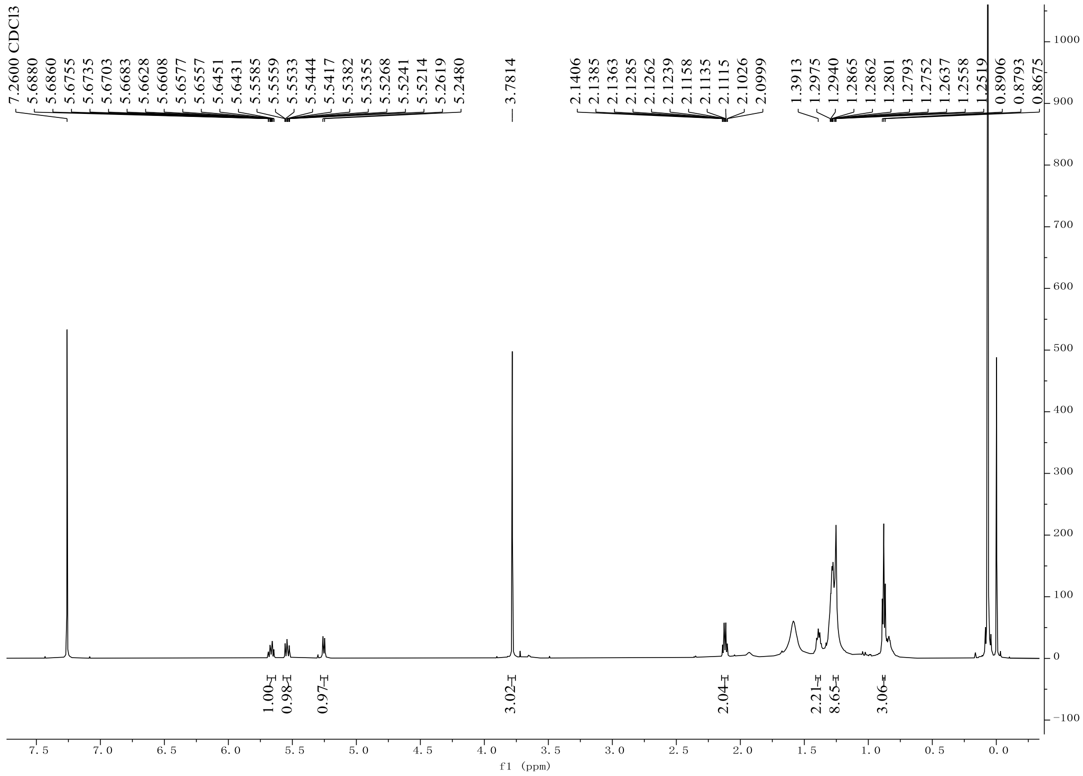

Figure S5: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1**

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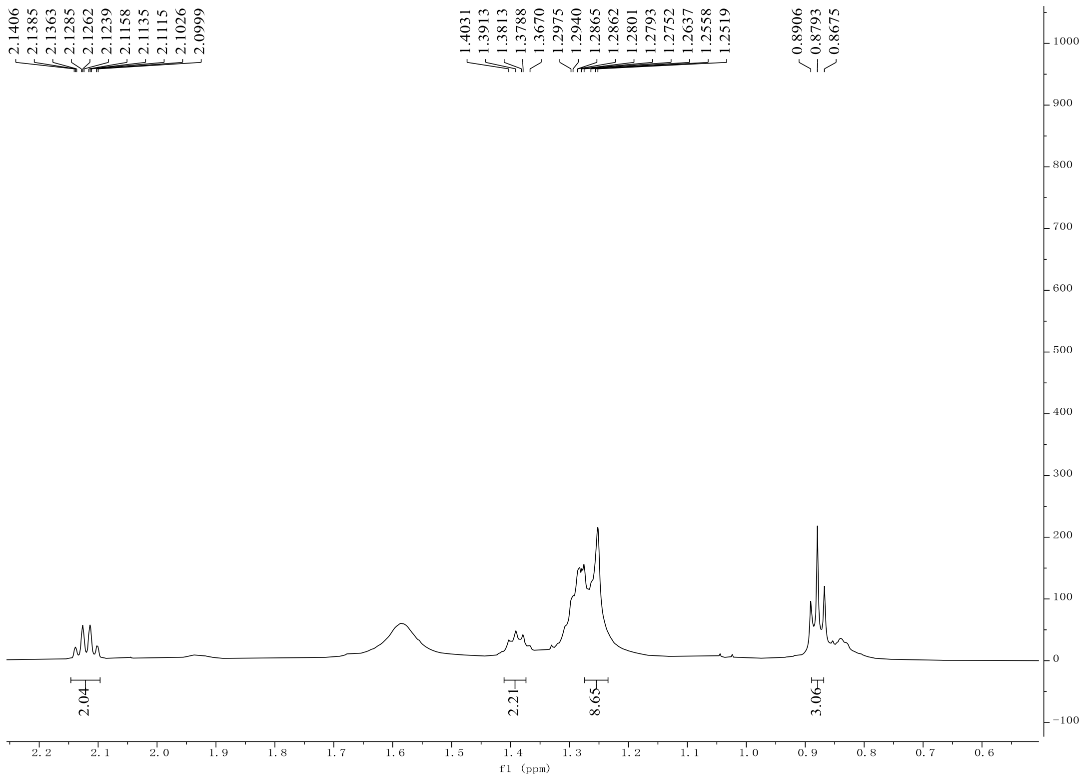

Figure S5-1: [1]H NMR (600 MHz, $CDCl_3$) spectrum of **1** (From δ_H 2.25 to δ_H 0.50)

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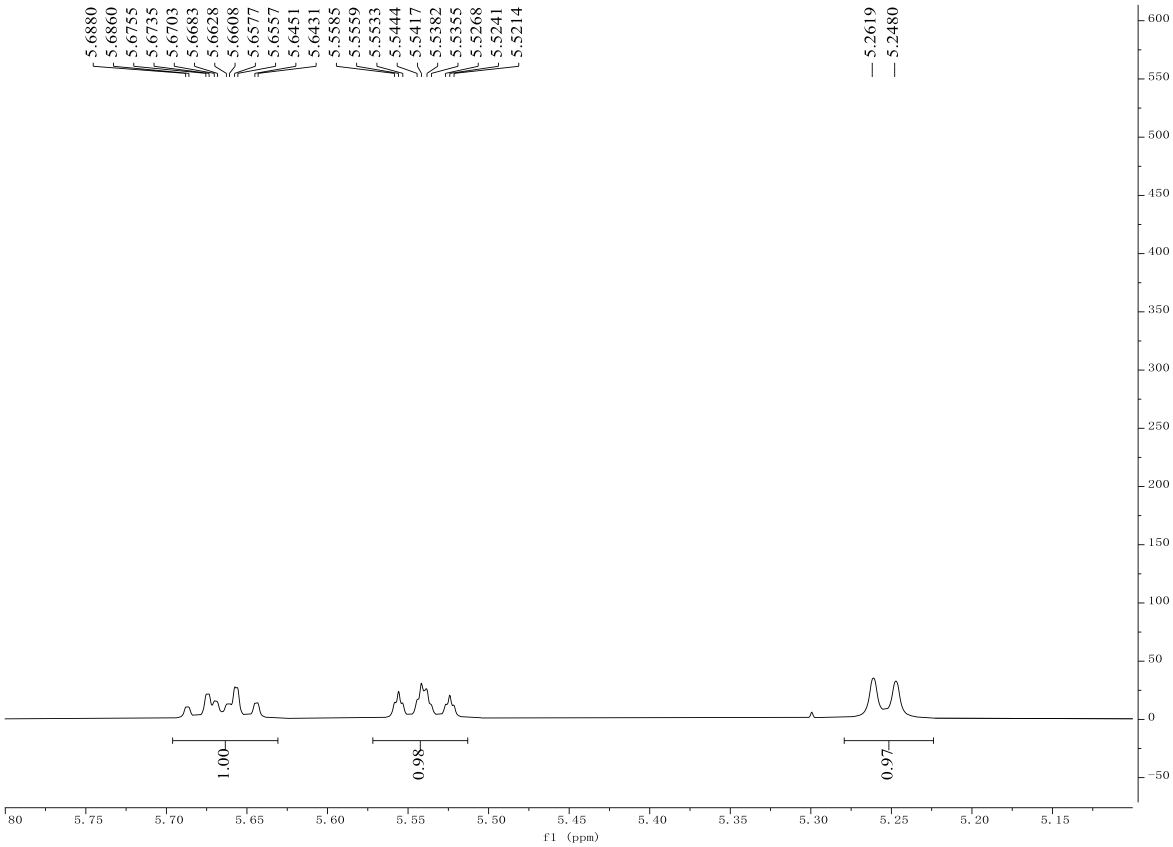

Figure S5-2: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1** (From δ_H 5.80 to δ_H 5.10)

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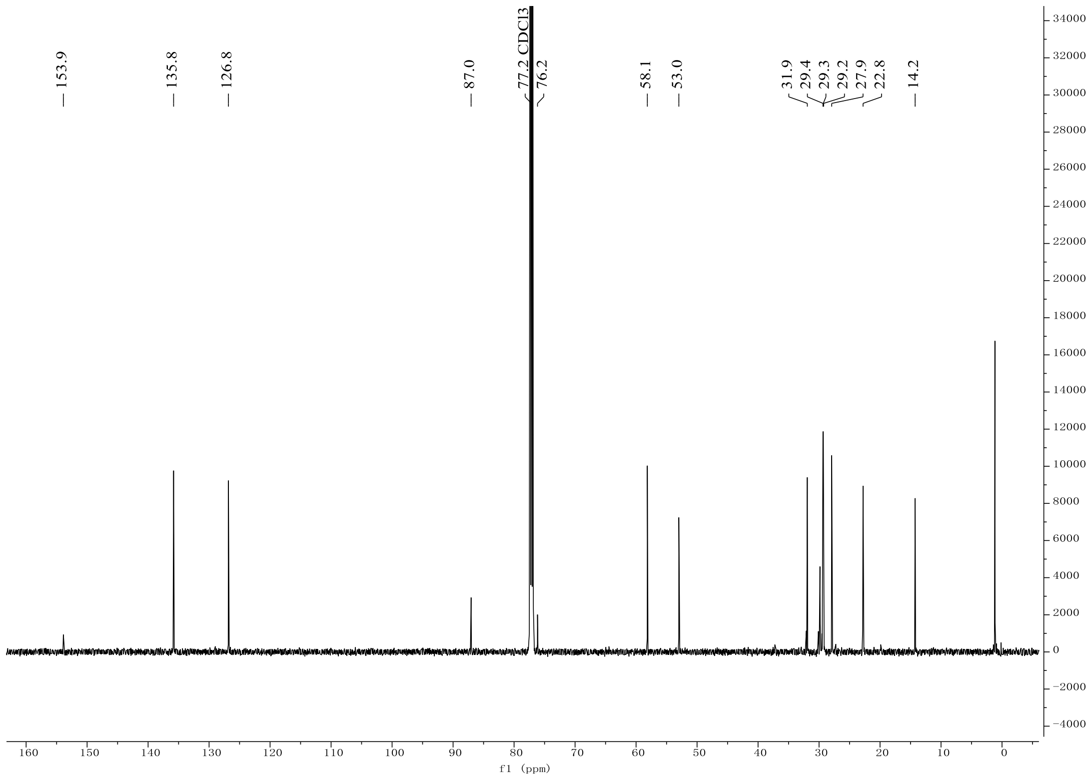

Figure S6: ^{13}C-NMR (150 MHz, $CDCl_3$) spectrum of **1**

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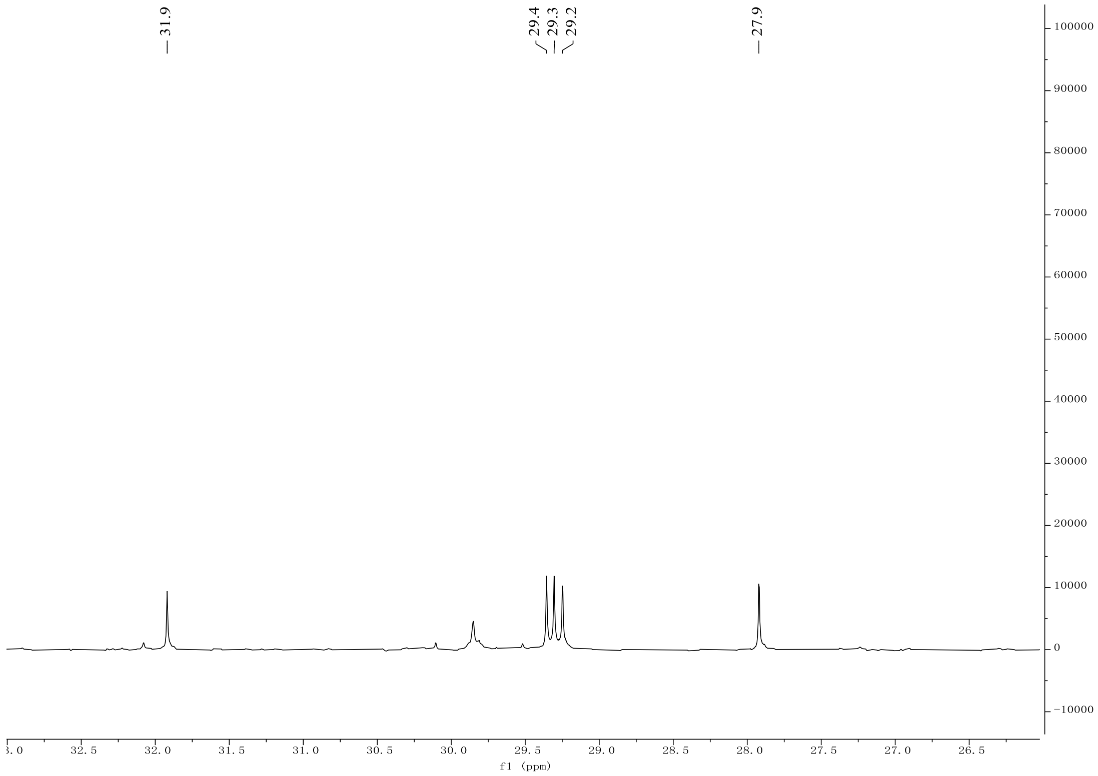

Figure S6-1: ^{13}C-NMR (150 MHz, $CDCl_3$) spectrum of **1** (From δ_C 33.0 to δ_C 26.0)

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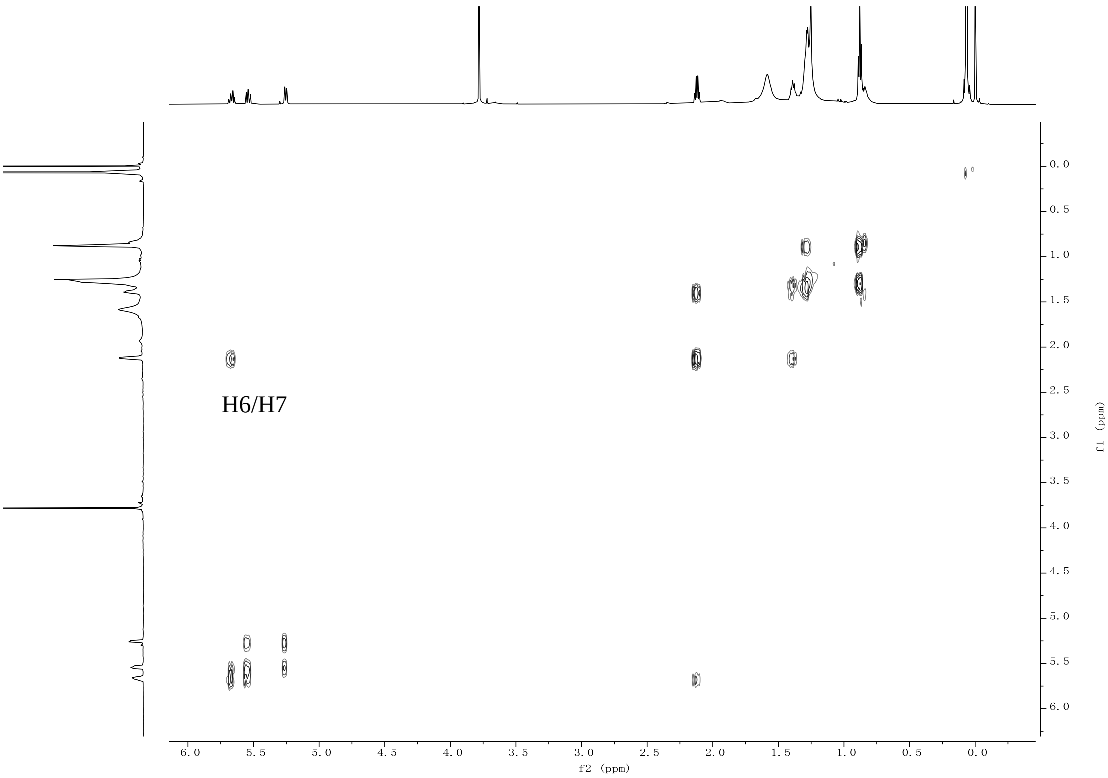

Figure S7: ^{1}H-^{1}H COSY spectrum of **1**

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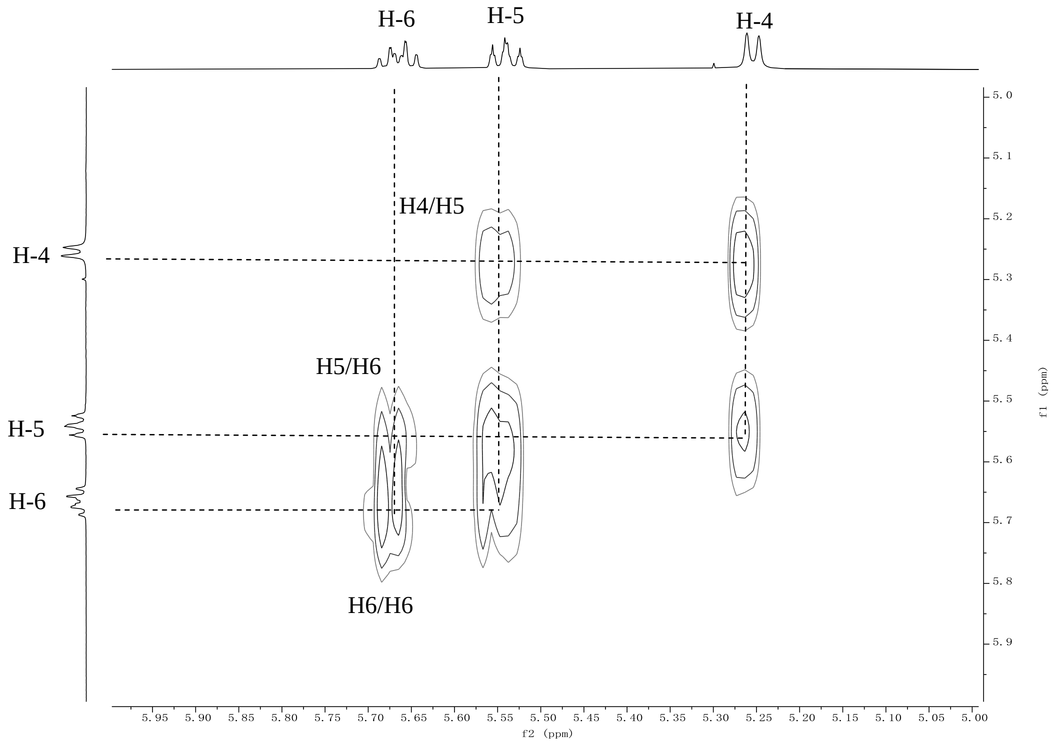

Figure S7-1: ^{1}H-^{1}H COSY spectrum of **1 (**From δ_H 6.00 to δ_H 5.00)

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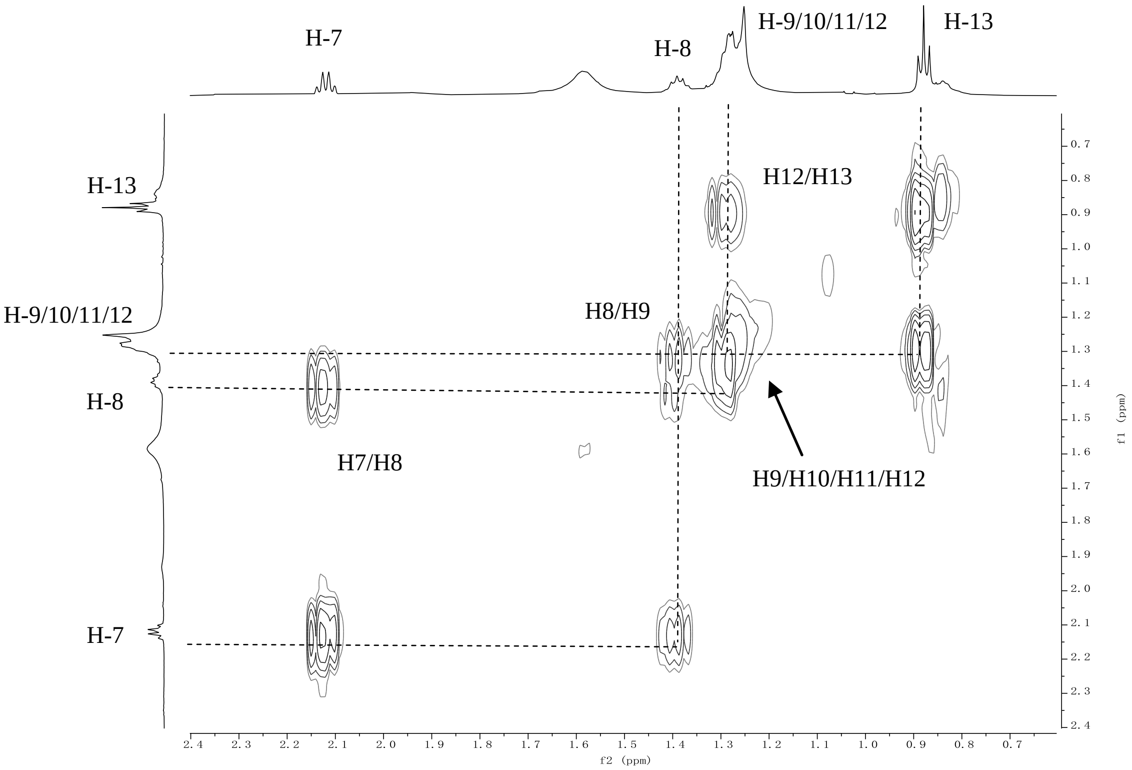

Figure S7-2: ^{1}H-^{1}H COSY spectrum of **1** (From δ_H 2.30 to δ_H 0.50)

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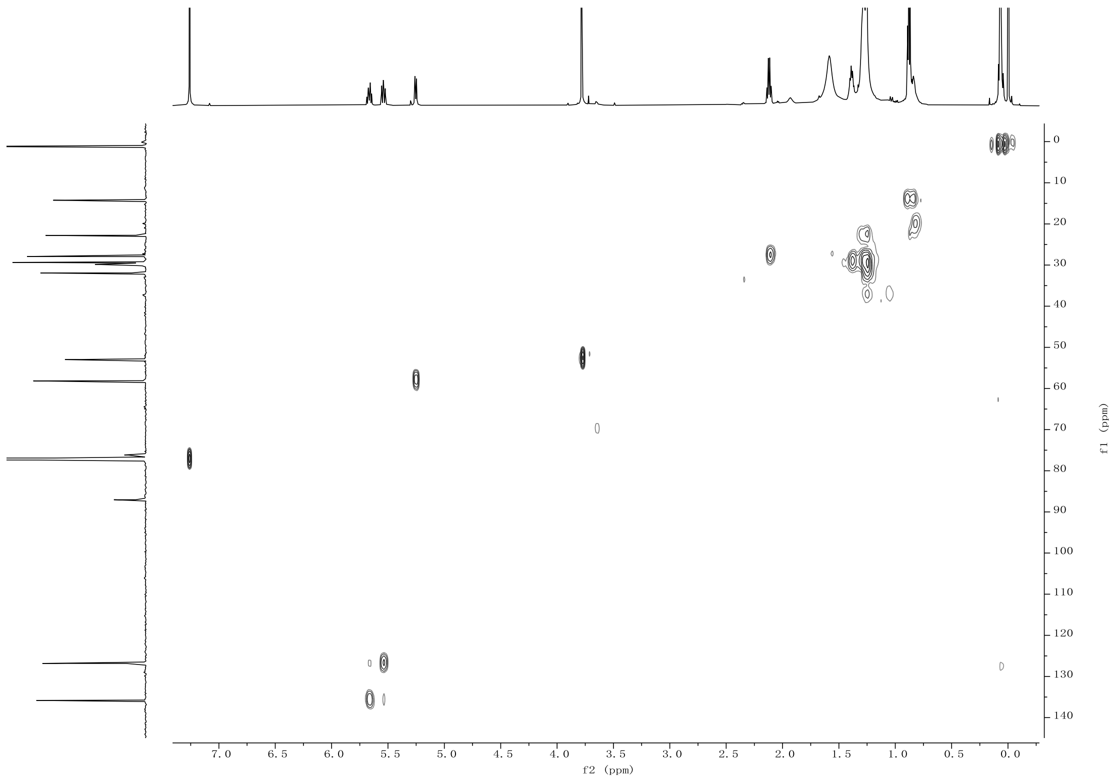

Figure S8: HSQC spectrum of **1**

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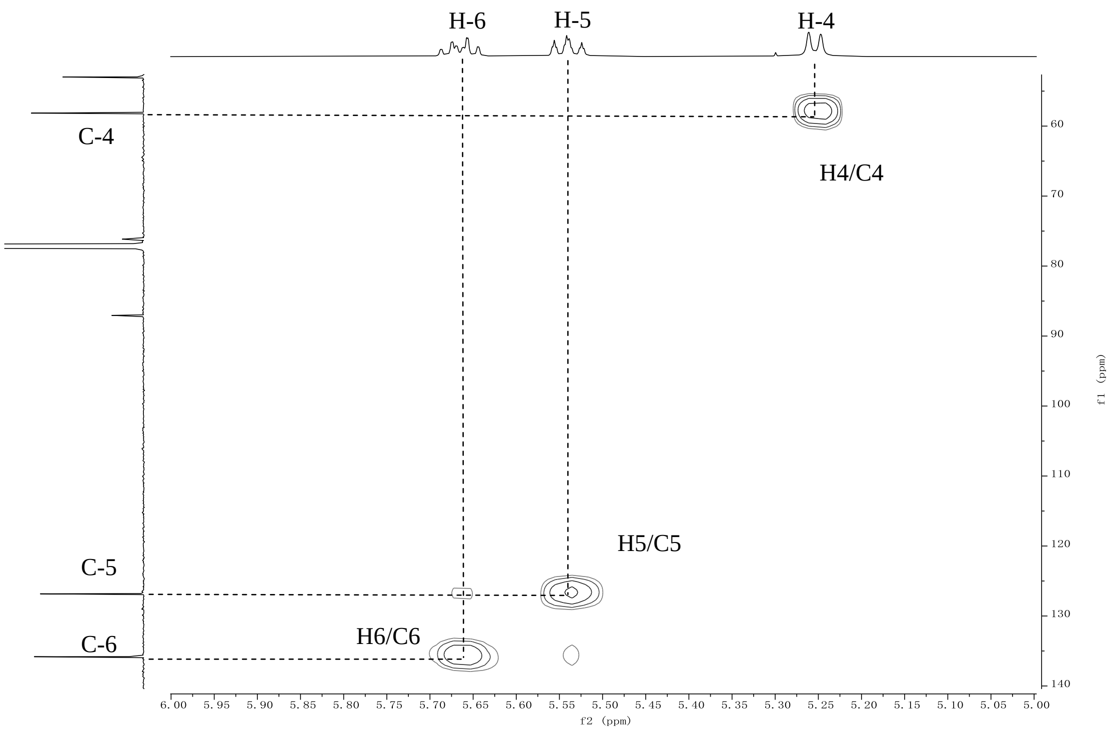

Figure S8-1: HSQC spectrum of **1** (From δ_H 6.00 to δ_H 5.00)

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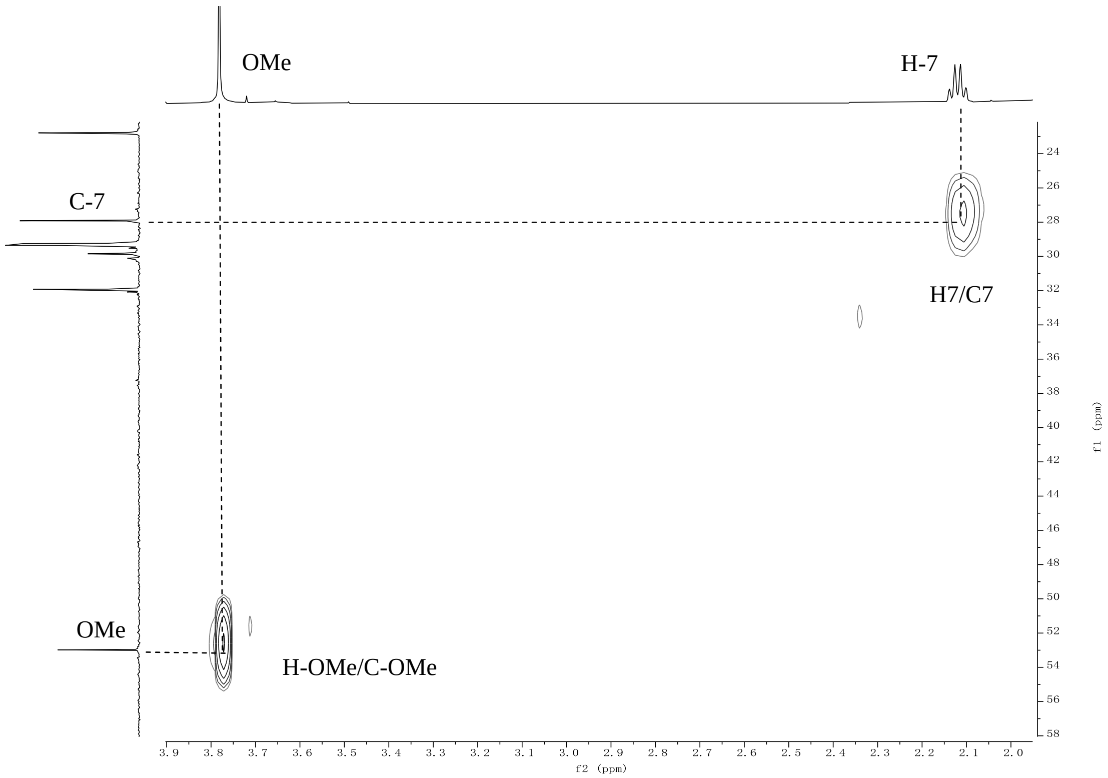

Figure S8-2: HSQC spectrum of **1** (From δ_H 3.90 to δ_H 1.95)

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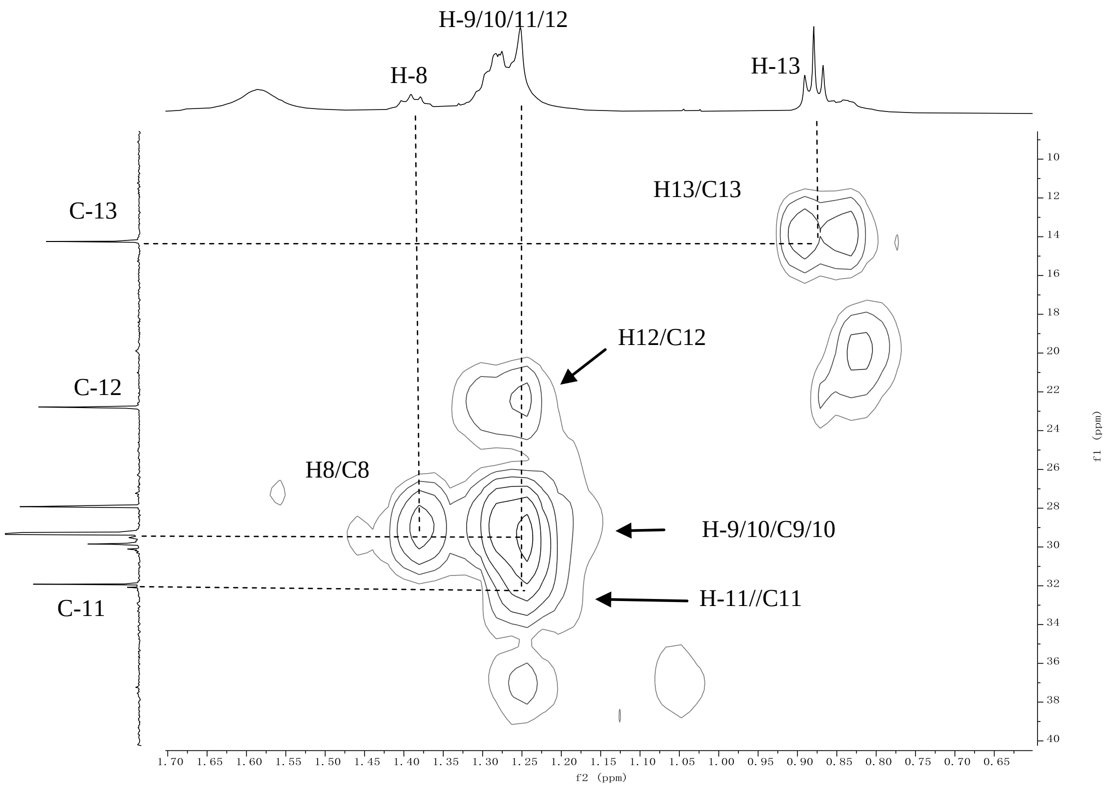

Figure S8-3: HSQC spectrum of **1 (**From δ_H 1.70 to δ_H 0.60)

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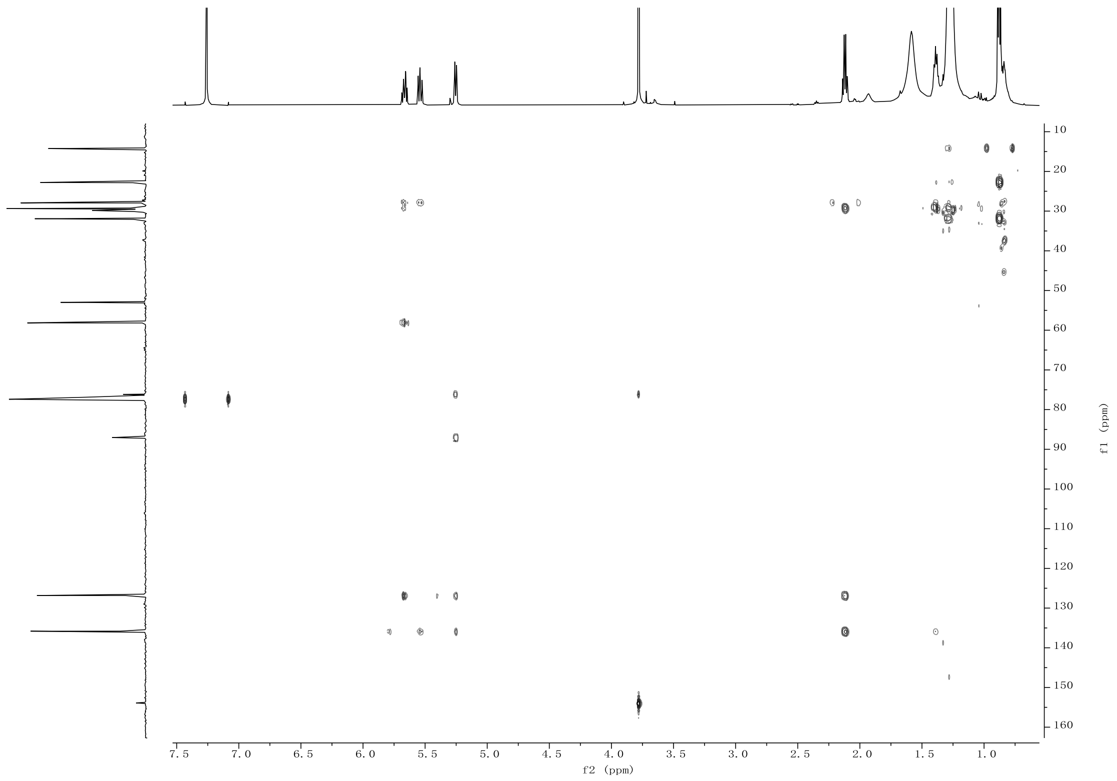

Figure S9: HMBC spectrum of **1**

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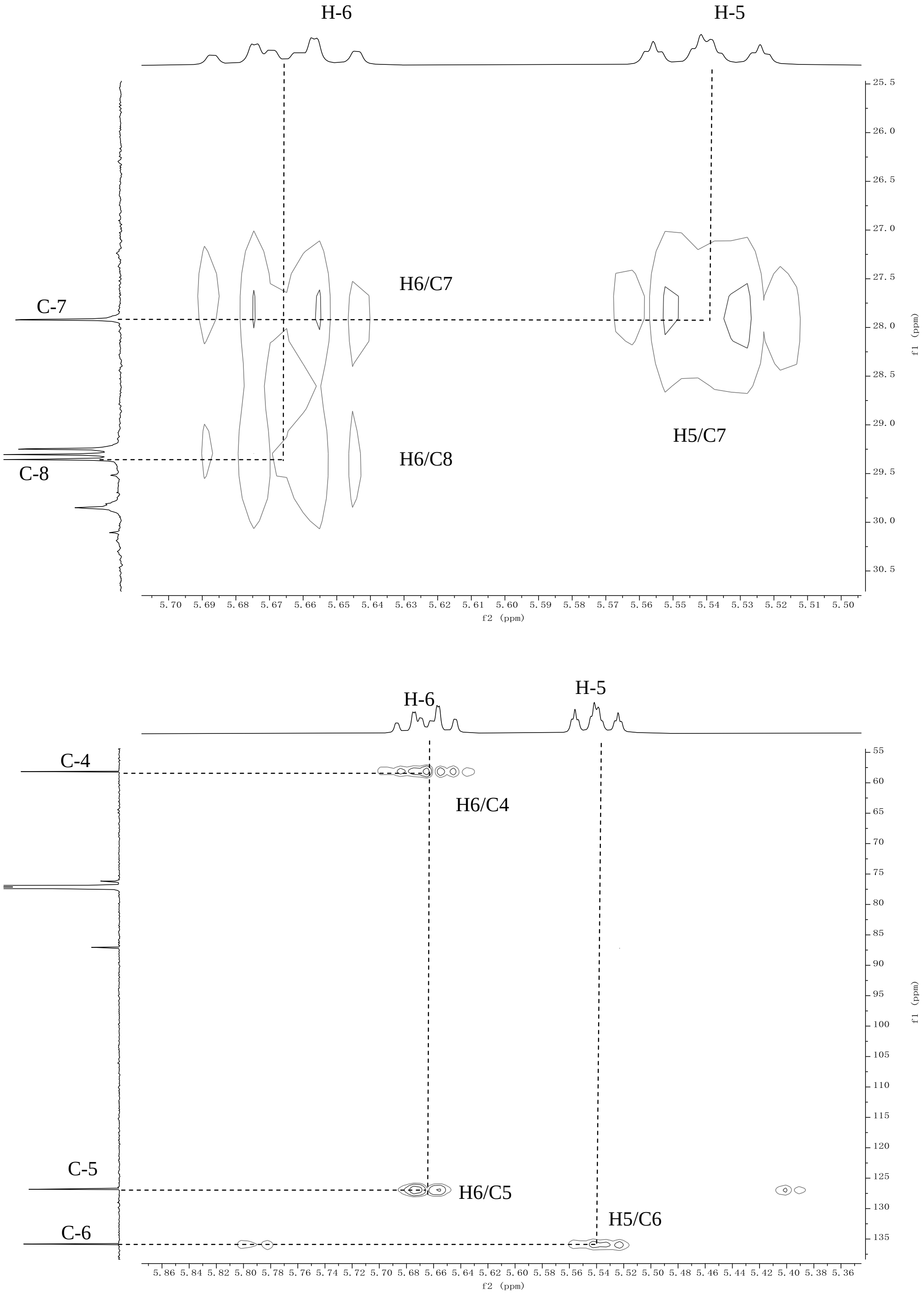

Figure S9-1: HMBC spectrum of **1** (δ_H 5.67, H-6; 5.54, H-5)

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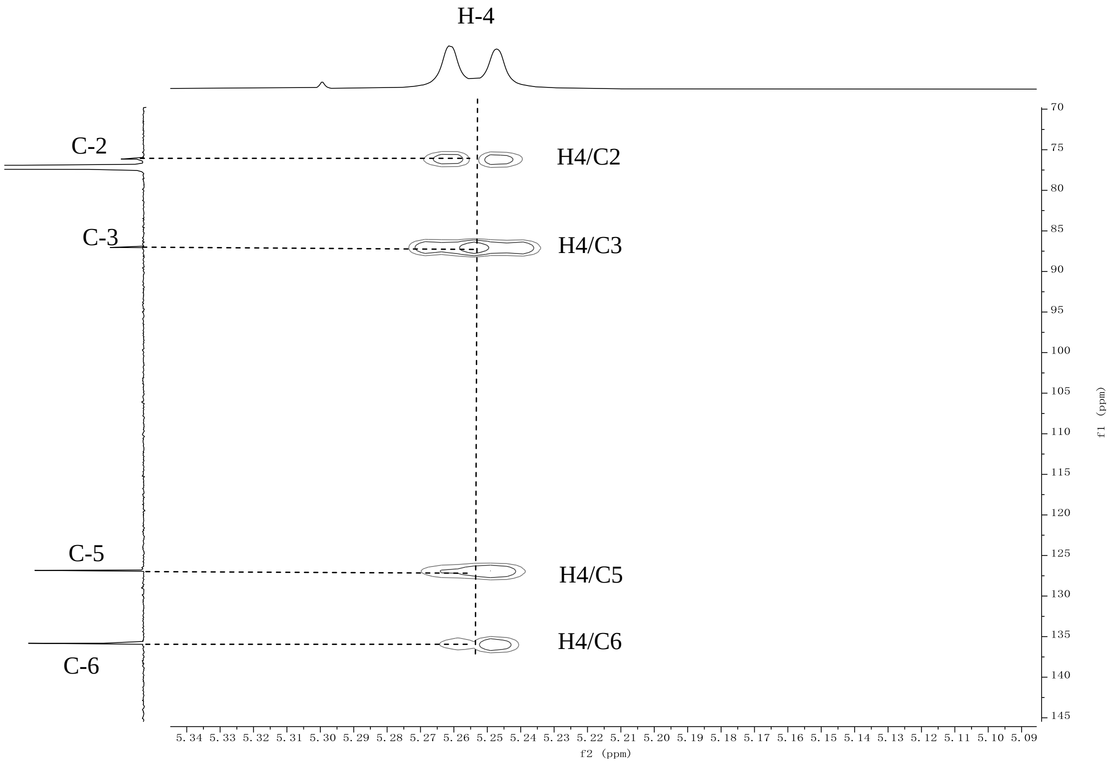

Figure S9-2: HMBC spectrum of **1** (δ_H 5.25, H-4)

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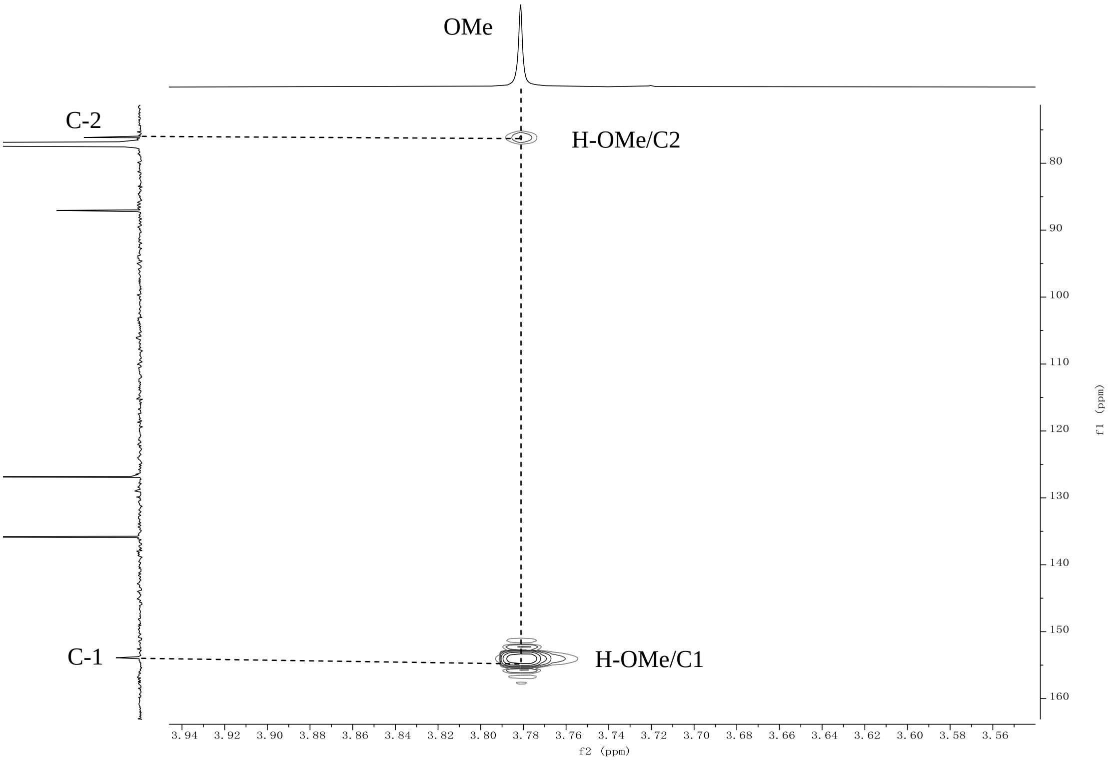

Figure S9-3: HMBC spectrum of **1** (δ_H 3.78, OMe)

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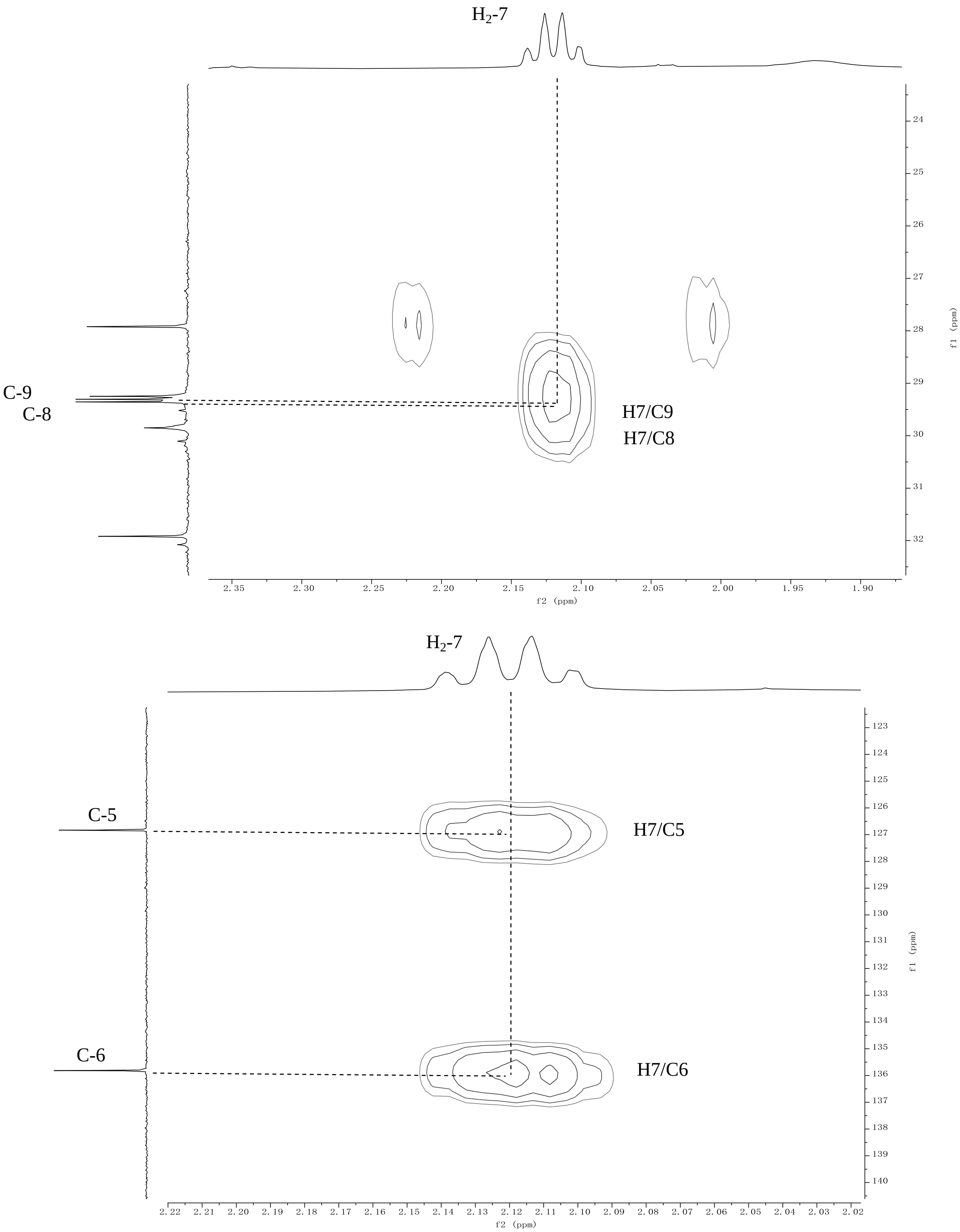

Figure S9-4: HMBC spectrum of **1** (δ_H 2.14-2.10, H_2-7)

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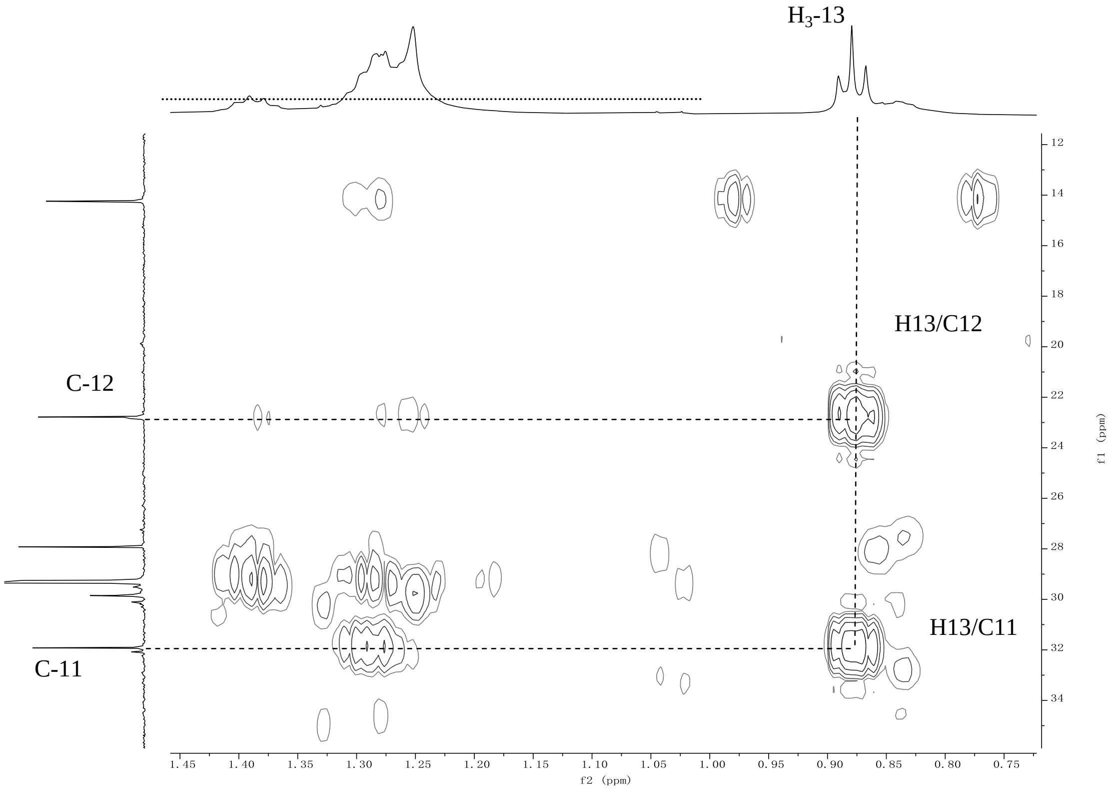

Figure S9-5: HMBC spectrum of **1** (δ_H 0.88, H-13)

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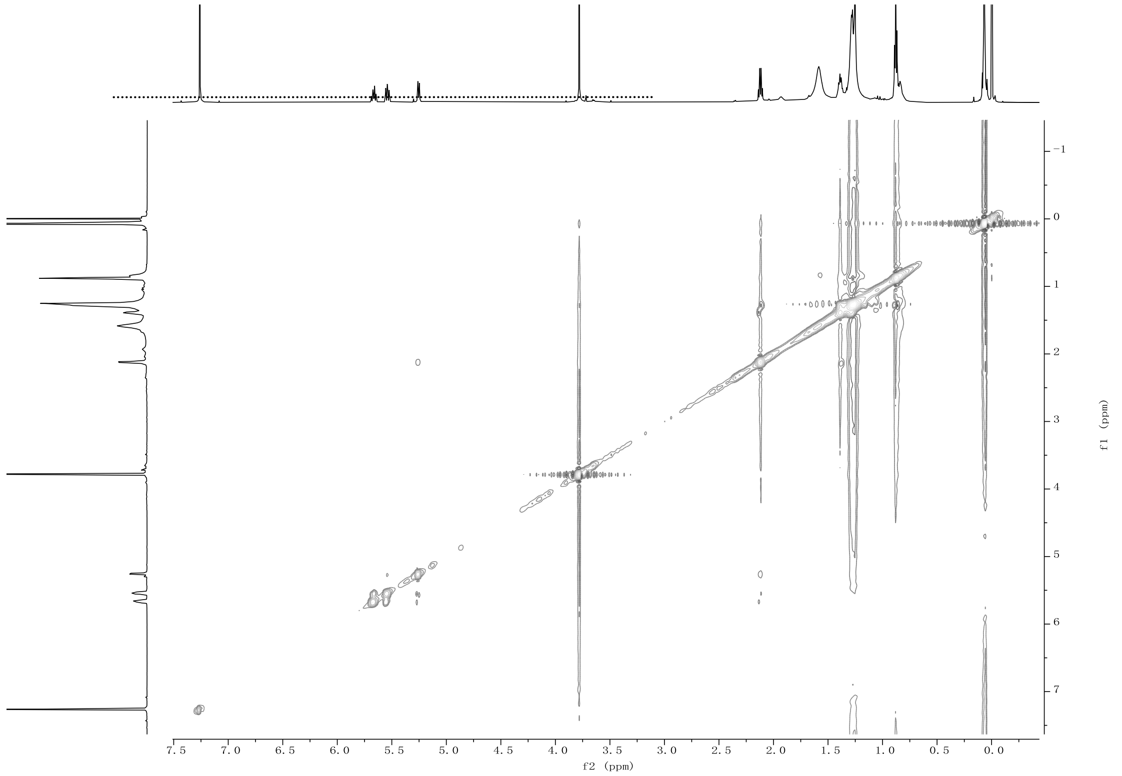

Figure S10: NOESY spectrum of **1**

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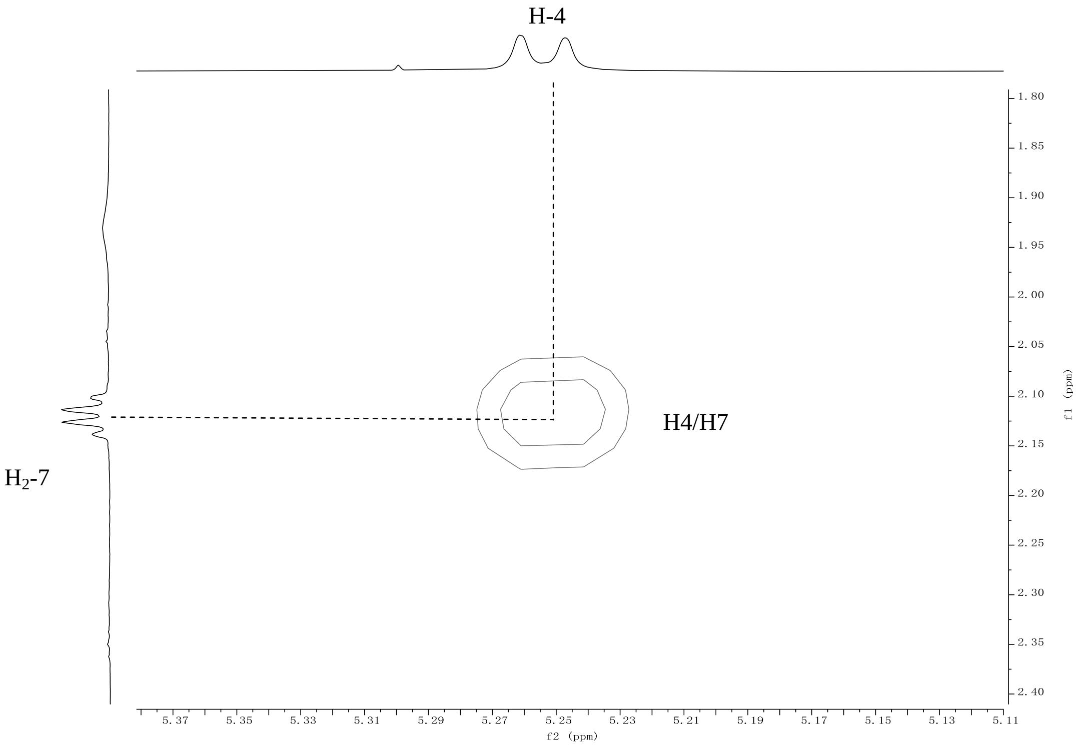

Figure S10-1: NOESY spectrum of **1** (δ_H 5.25, H-4)

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