

Supporting Information

Phytotoxic *ent*-Isopimarane-Type Diterpenoids from *Euphorbia hylonoma*

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1. Experimental Section

Computational details for ECD spectra of compounds **2** and **7**.

Based on the known relative configuration, **2-A** (3*S*, 5*S*, 9*R*, 10*R*, 11*R*, 12*S*, 13*R*), **2-B** (3*R*, 5*R*, 9*S*, 10*S*, 11*S*, 12*R*, 13*S*), **7**-(2*R*, 3*S*, 5*S*, 9*R*, 10*R*, 11*R*, 13*R*) were employed for the conformational random search using the Charmm force field in the Best module of Discovery studio 2.5.5 (Accelrys, San Diego, CA, 2009) software package. The conformational search results with an energy cut off of 17 kJ/mol (approximately 4 kcal/mol) was selected to further geometry optimization and ECD calculation. As a result, the conformer structures **2a-2b** of compound **2** and the conformer structures **7a-7e** of compound **7** were built, as shown in Figures S1 and S3.

The geometry of the molecules was optimized with Gaussian 09 package at B3LYP/6-31G(d) computational level. The minimum nature of the structure was confirmed by frequency calculations at the same computational level.

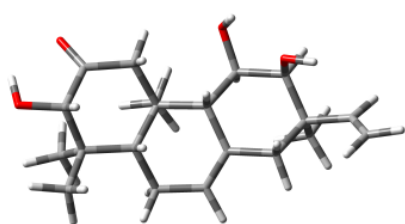
Then quantum chemical theoretical calculations (Diedrich and Grimme, 2003) for ECD were carried out in methanol using time-dependent density functional theory (TDDFT) with B3LYP functional and dgdzvp forcefield basis set with 60 electronic transitions. The energies, oscillator strengths, and rotational strengths of the electronic excitations of all the conformers were calculated using the TDDFT method at the B3LYP/dgdzvp level.

Based on the relativity energy, boltzmann weighted average of the different low energy conformations was calculated for compounds **2** and **7**. The ECD for each molecule is calculated based on boltzmann weighted average of the conformations search results.

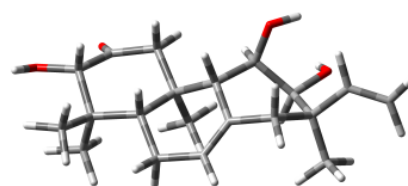
The conformational geometries optimization of conformers of compound **2** at the B3LYP/6-31G(d) level afforded one conformer accounting for more than 99% (conformer **2a**), as shown in Figure S1. Thus, the calculated ECD curve of **2** is the same as that of conformer **2a**, as shown in Figure S2.

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- (2) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.



2a (99.98%)



2b (0.02%)

Figure S1. Two lowest energy conformers of compound **2** with (3*S*, 5*S*, 9*R*, 10*R*, 11*R*, 12*S*, 13*R*) configuration.

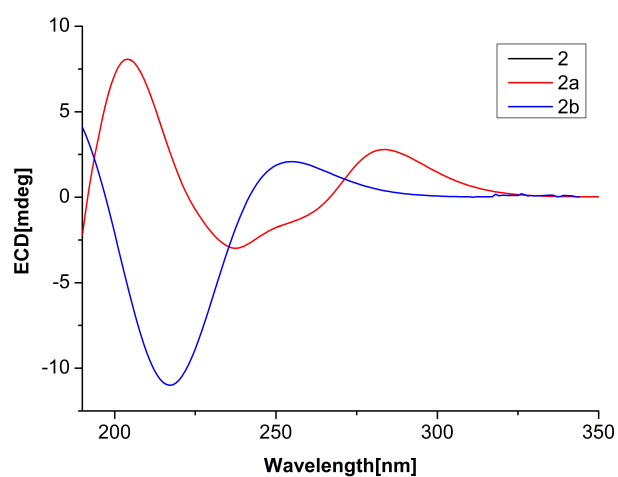
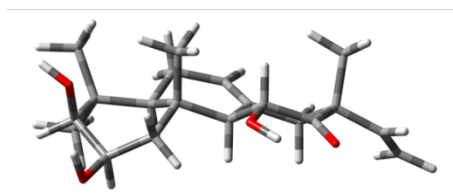
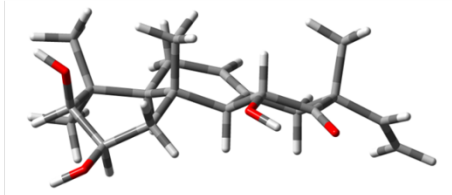


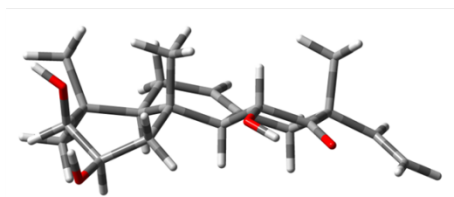
Figure S2. Comparison of the computed ECD spectra for **2** and the two energy lowest conformers (**2a–2b**) with (3*S*, 5*S*, 9*R*, 10*R*, 11*R*, 12*S*, 13*R*) configuration. The calculations were performed with TDDFT method at the B3LYP/dgdzvp level (solvent: MeOH).



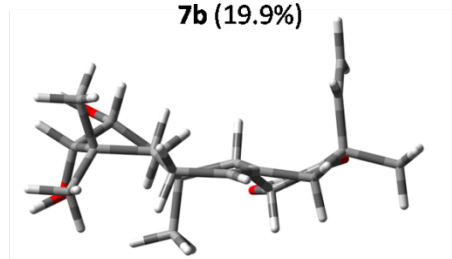
7a (76.9%)



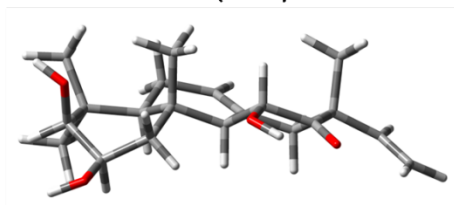
7b (19.9%)



7c (2.0%)



7d (0.6%)



7e (0.06%)

Figure S3. Five lowest energy conformers of compound **7** with (2*R*, 3*S*, 5*S*, 9*R*, 10*R*, 11*R*, 13*R*) configuration.

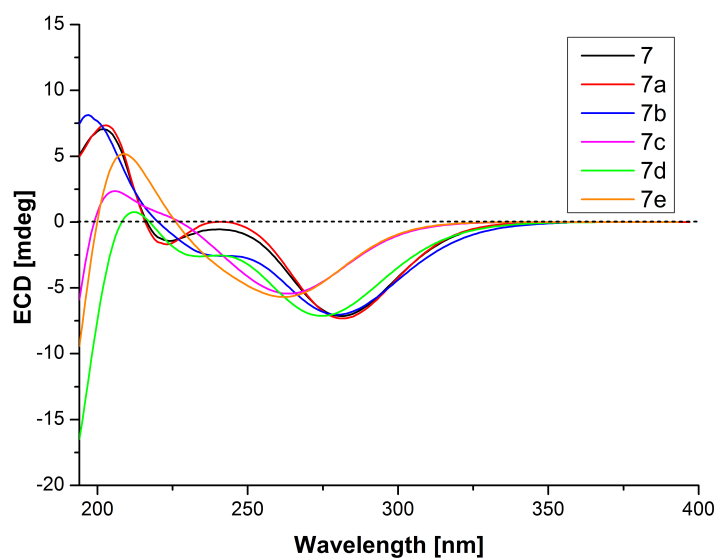


Figure S4: Comparison of the computed ECD spectra for **7** and the five energy lowest conformers (**7a–7e**) with (2*R*, 3*S*, 5*S*, 9*R*, 10*R*, 11*R*, 13*R*) configuration. The calculations were performed with TDDFT method at the B3LYP/dgdzvp level (solvent: MeOH).

2. Crystal Data and Structure Refinement for Compounds 1, 2, and 7

Table SI1 Crystal data and structure refinement for compound 1

Identification code	Compound 1
Empirical formula	C ₂₀ H ₃₀ O ₄ , H ₂ O
Formula weight	352.46
Temperature/K	290.2(2)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	6.3769(3)
b/Å	13.3424(6)
c/Å	11.4964(5)
α /°	90.00
β /°	100.294(5)
γ /°	90.00
Volume/Å ³	962.40(7)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.216
μ/mm^{-1}	0.694
F(000)	384.0
Crystal size/mm ³	0.1 × 0.05 × 0.04
Radiation	CuK α (λ = 1.54184)
2 Θ range for data collection/°	7.82 to 139.8
Index ranges	-5 ≤ h ≤ 7, -15 ≤ k ≤ 16, -13 ≤ l ≤ 13
Reflections collected	5682
Independent reflections	3390 [R_{int} = 0.0269, R_{sigma} = 0.0385]
Data/restraints/parameters	3390/4/258
Goodness-of-fit on F^2	1.022
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0380, wR_2 = 0.0938
Final R indexes [all data]	R_1 = 0.0468, wR_2 = 0.0991
Largest diff. peak/hole / e Å ⁻³	0.19/-0.14
Flack parameter	0.0(2)

Table SI2 Crystal data and structure refinement for compound **2**.

Identification code	Compound 2
Empirical formula	C ₂₀ H ₃₀ O ₄ , H ₂ O
Formula weight	352.45
Temperature/K	296.56(10)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	11.0078(9)
b/Å	6.8749(8)
c/Å	12.6547(12)
α /°	90
β /°	98.677(8)
γ /°	90
Volume/Å ³	946.72(16)
Z	2
ρ_{calc} /cm ³	1.236
μ /mm ⁻¹	0.087
F(000)	384.0
Crystal size/mm ³	0.22 × 0.15 × 0.14
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	6.514 to 52.014
Index ranges	-13 ≤ h ≤ 13, -7 ≤ k ≤ 8, -15 ≤ l ≤ 14
Reflections collected	3645
Independent reflections	2594 [R_{int} = 0.0441, R_{sigma} = 0.1019]
Data/restraints/parameters	2594/1/239
Goodness-of-fit on F ²	1.002
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0631, wR_2 = 0.1134
Final R indexes [all data]	R_1 = 0.1126, wR_2 = 0.1435
Largest diff. peak/hole / e Å ⁻³	0.26/-0.27
Flack parameter	-3.1(10)

Table SI3 Crystal data and structure refinement for compound 7.	
Identification code	Compound 7
Empirical formula	C ₂₀ H ₃₀ O ₄ · 0.75(H ₂ O)
Formula weight	347.95
Temperature/K	291.9(9)
Crystal system	orthorhombic
Space group	P2 ₂ 12 ₁
a/Å	6.16925(15)
b/Å	23.4813(6)
c/Å	26.4016(7)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å ³	3824.58(17)
Z	8
ρ _{calc} /g/cm ³	1.209
μ/mm ⁻¹	0.682
F(000)	1516.0
Crystal size/mm ³	0.16 × 0.03 × 0.02
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	7.52 to 139.5
Index ranges	-5 ≤ h ≤ 7, -27 ≤ k ≤ 28, -31 ≤ l ≤ 32
Reflections collected	13072
Independent reflections	6954 [R _{int} = 0.0248, R _{sigma} = 0.0380]
Data/restraints/parameters	6954/12/500
Goodness-of-fit on F ²	1.037
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0381, wR ₂ = 0.0943
Final R indexes [all data]	R ₁ = 0.0441, wR ₂ = 0.1001
Largest diff. peak/hole / e Å ⁻³	0.12/-0.13
Flack parameter	0.23(16)

3. 1D and 2D NMR, HRESIMS, IR, UV, and ECD Data of Compounds 1–10 and 14–16

Figure SI1. ^1H NMR spectrum of compound 1 (CDCl_3)

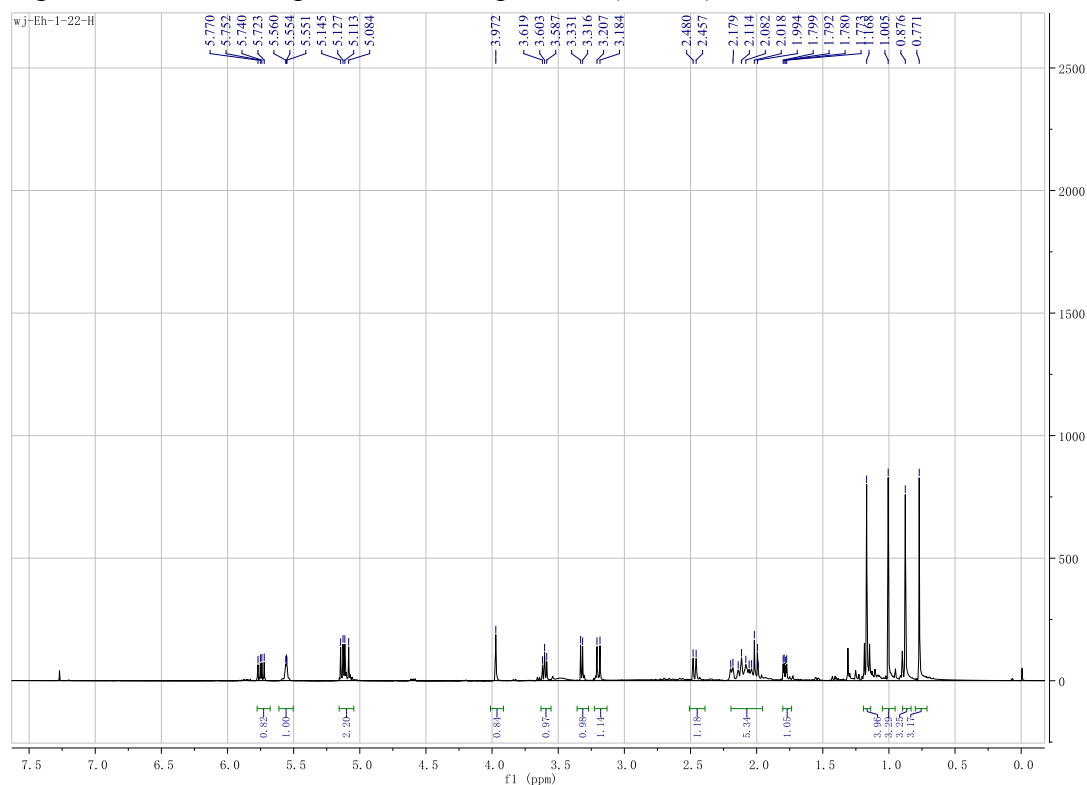


Figure SI2. ^{13}C NMR spectrum of compound 1 (CDCl_3)

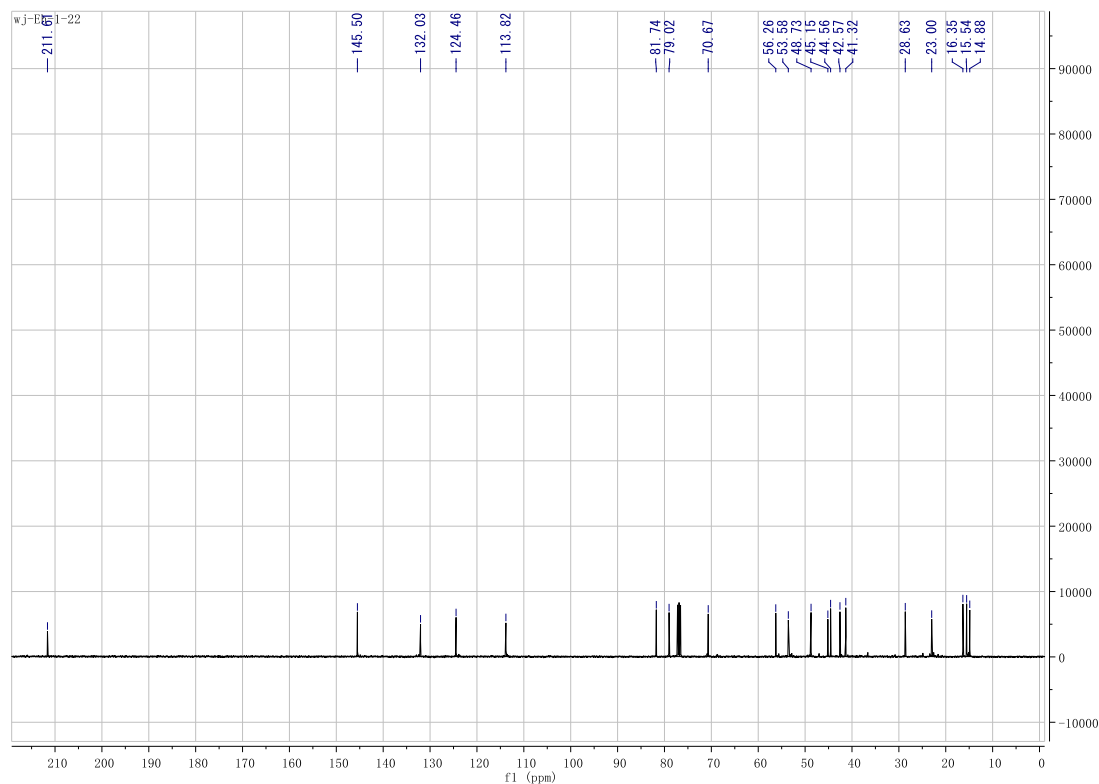


Figure SI3. DEPT spectrum of compound **1** (CDCl₃)

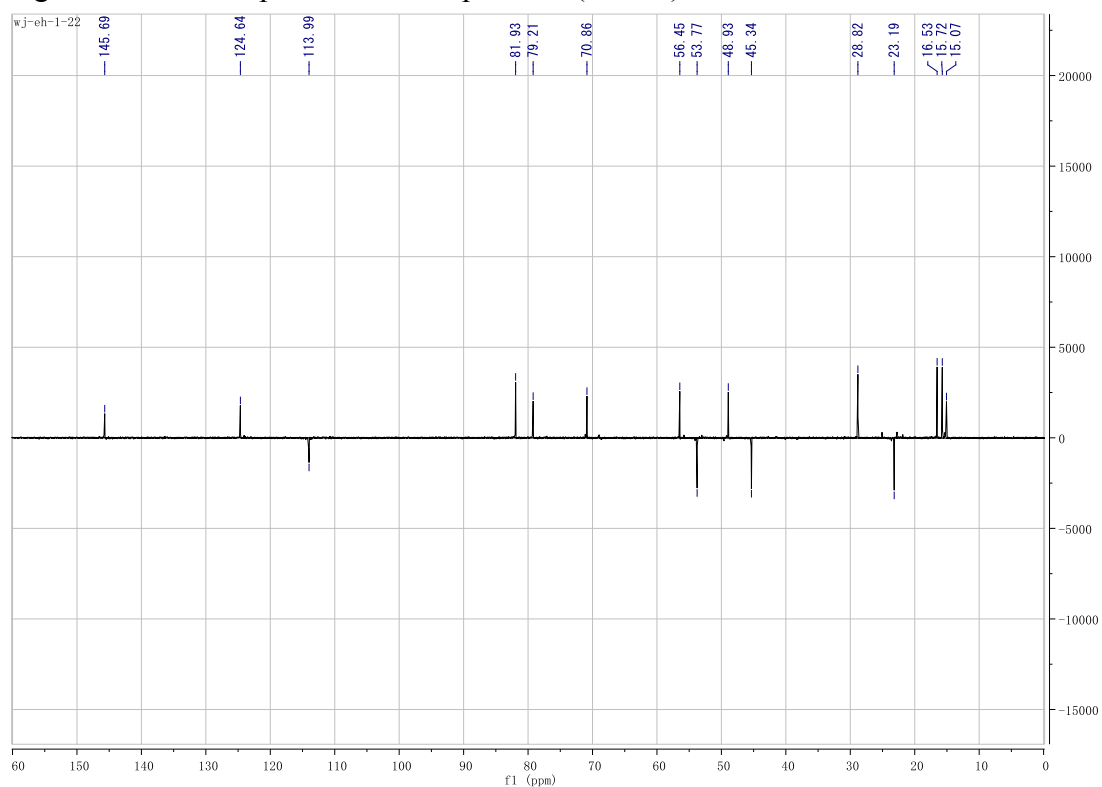


Figure SI4. ¹H-¹H COSY spectrum of compound **1** (CDCl₃)

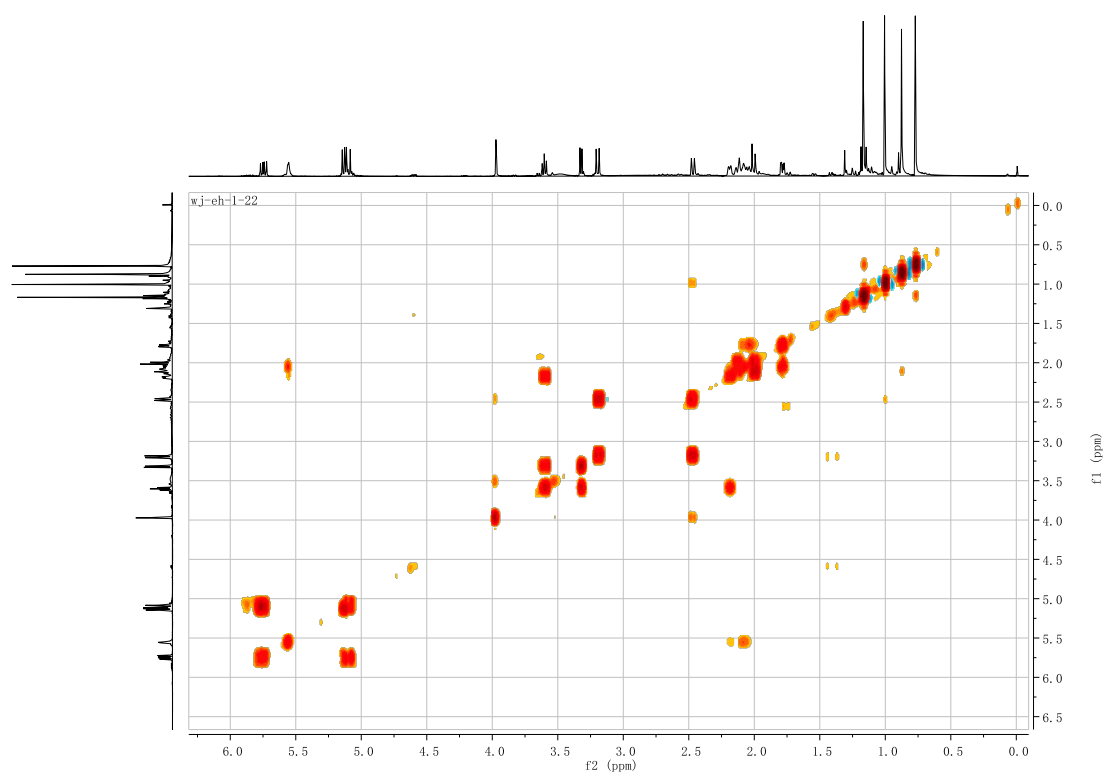


Figure SI5. HSQC spectrum of compound **1** (CDCl₃)

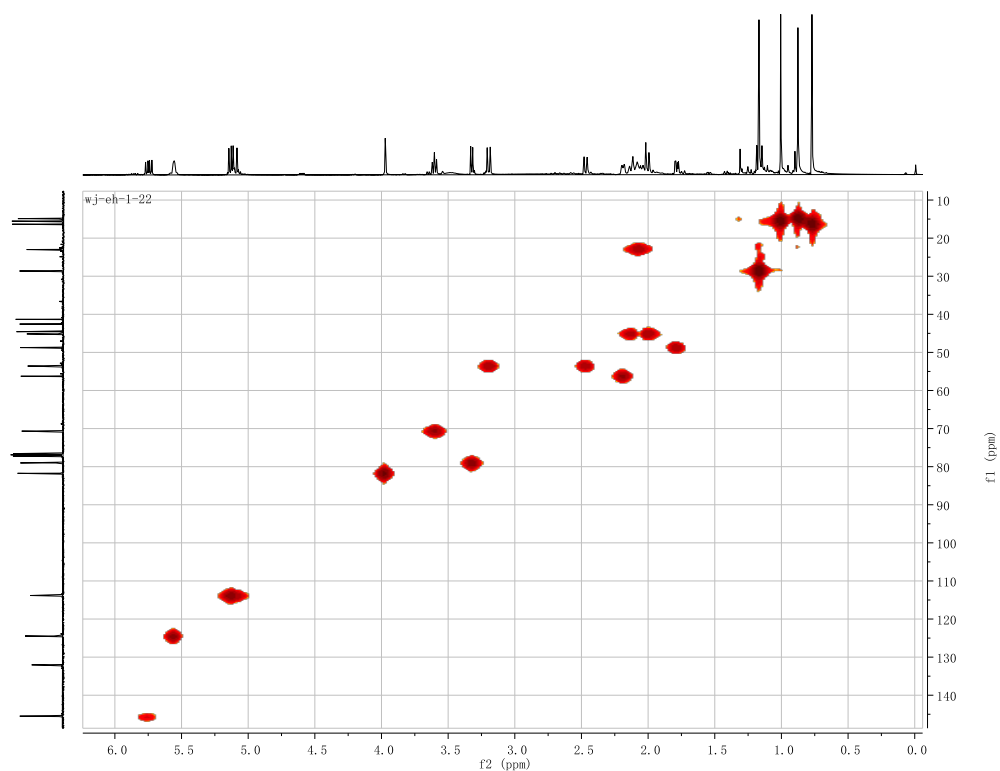


Figure SI6. HMBC spectrum of compound **1** (CDCl₃)

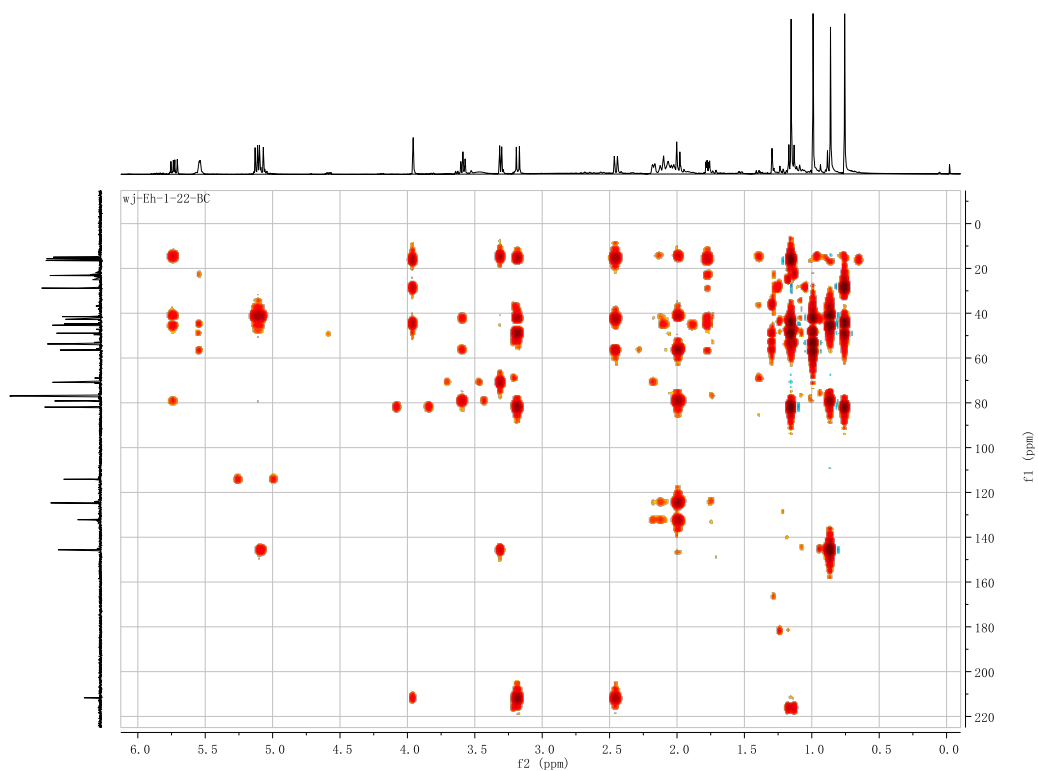


Figure SI7. NOESY spectrum of compound **1** (CDCl₃)

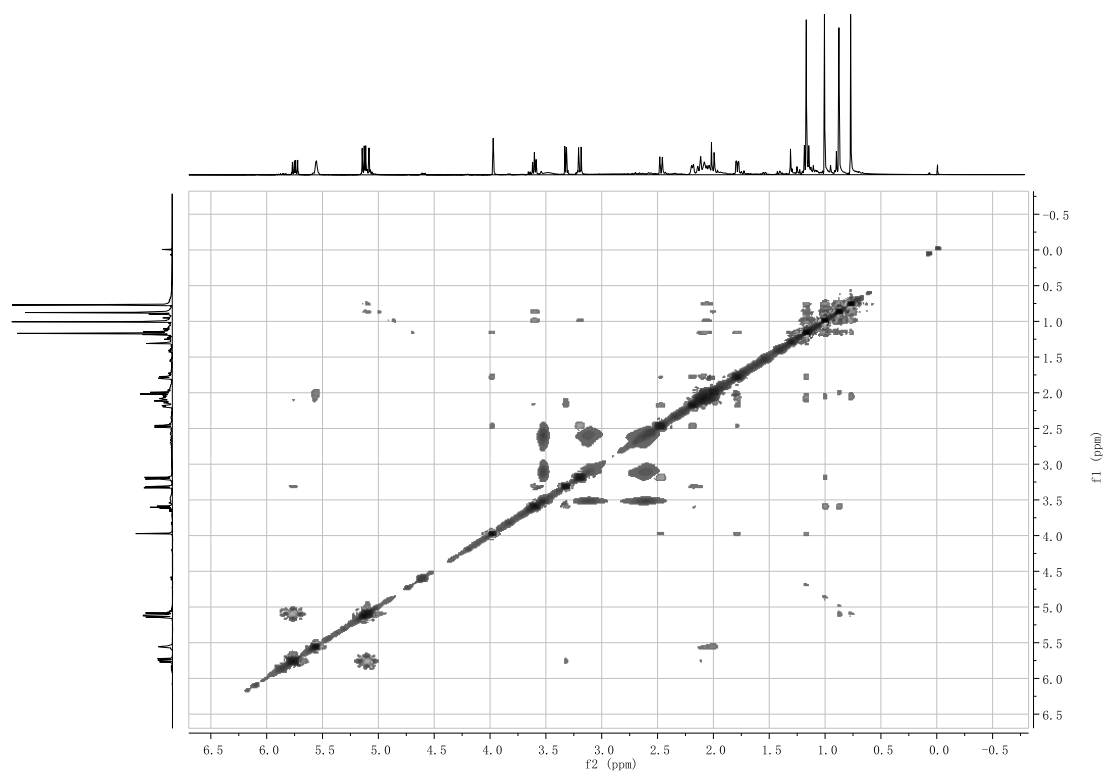


Figure SI8. HRESIMS spectrum of compound **1** (CDCl₃)

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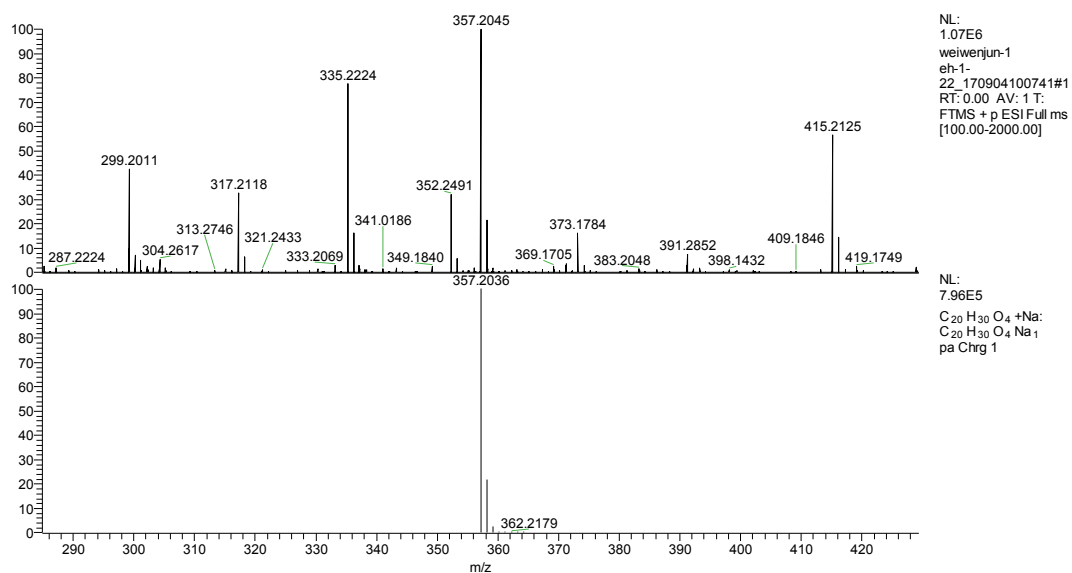


Figure SI9. IR spectrum of compound **1** (CDCl₃)

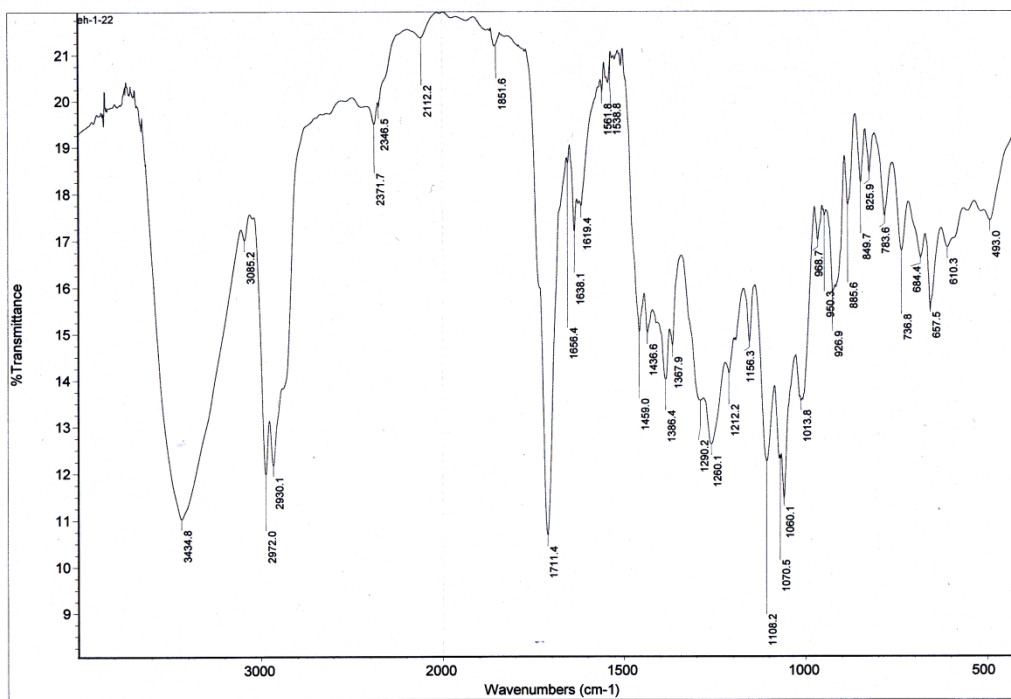


Figure SI10. ¹H NMR spectrum of compound **2** (CDCl₃)

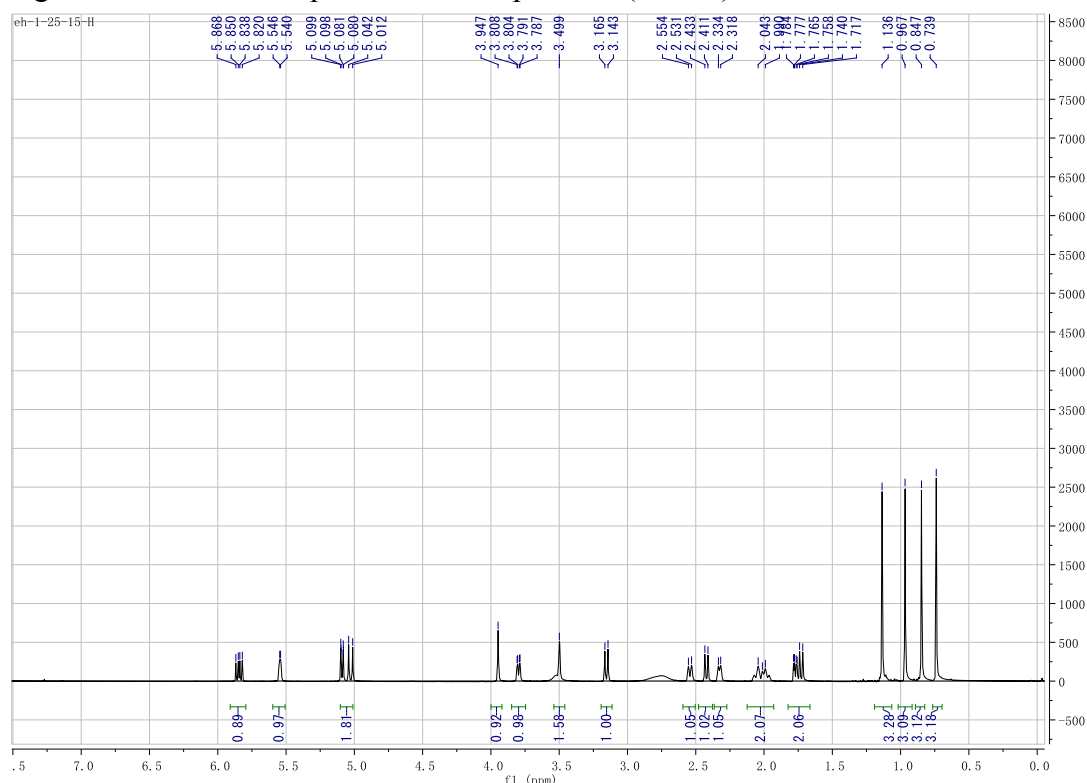


Figure SI11. ^{13}C NMR spectrum of compound **2** (CDCl_3)

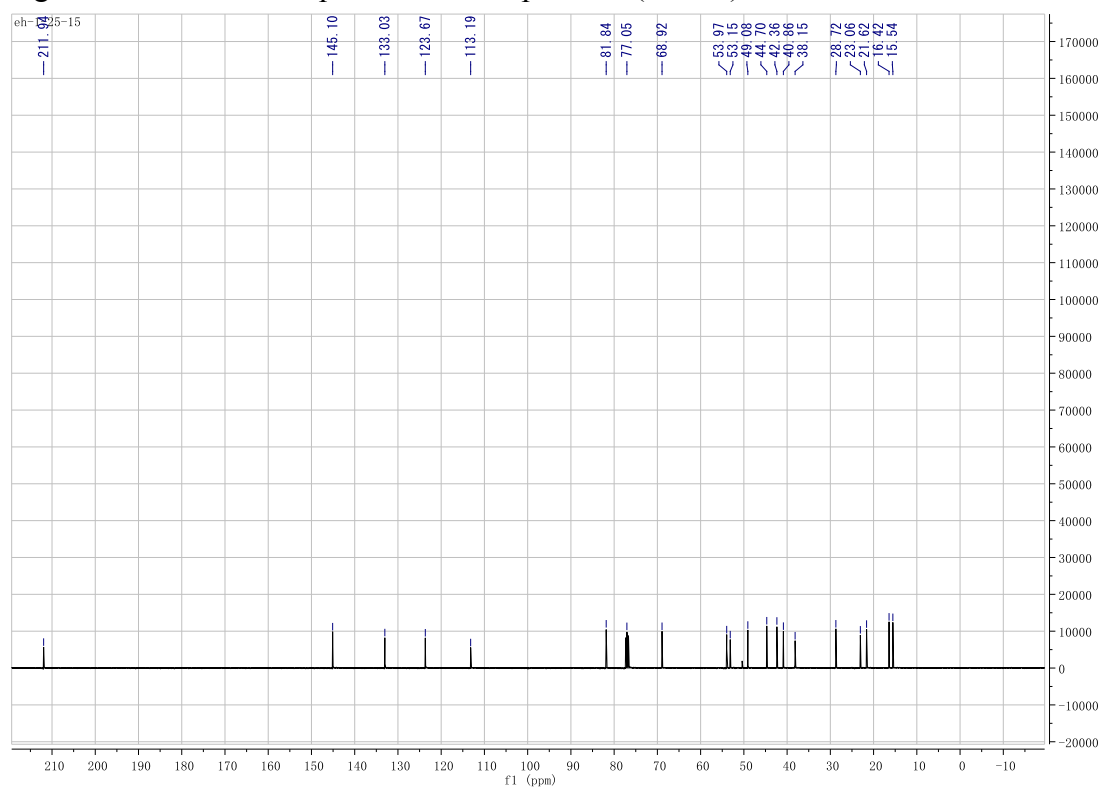


Figure SI12. DEPT spectrum of compound **2** (CDCl_3)

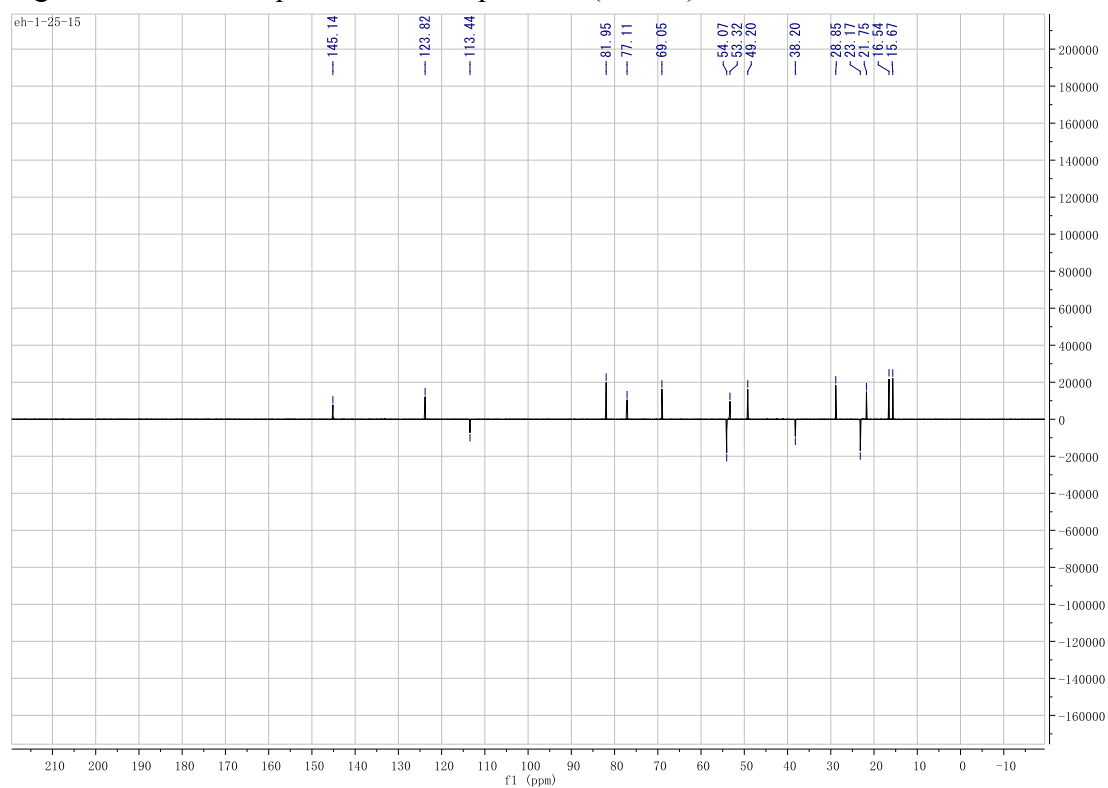


Figure SI13. ^1H - ^1H COSY spectrum of compound **2** (CDCl_3)

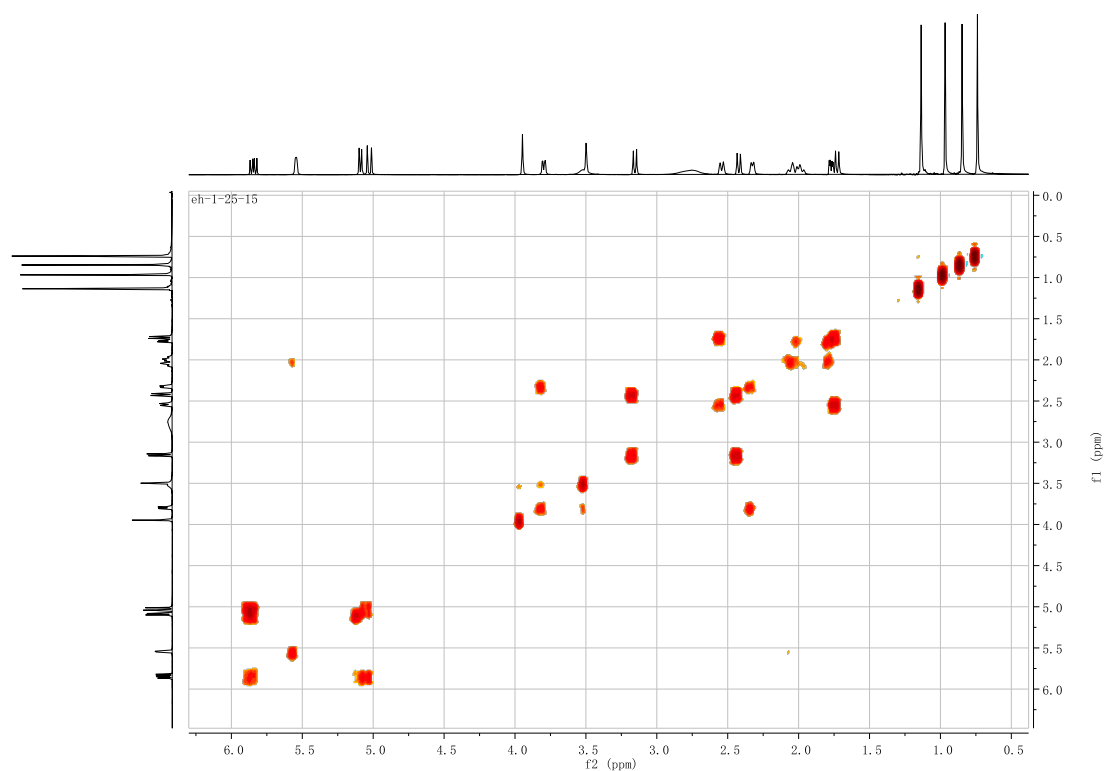


Figure SI14. HSQC spectrum of compound **2** (CDCl_3)

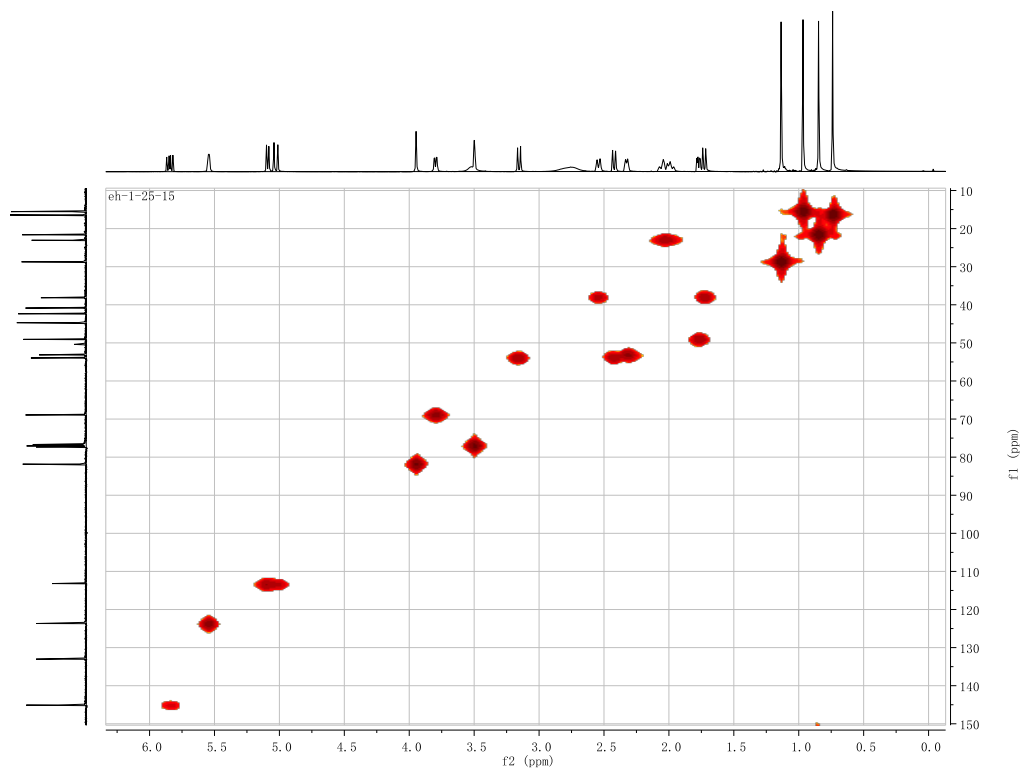


Figure SI15. HMBC spectrum of compound **2** (CDCl₃)

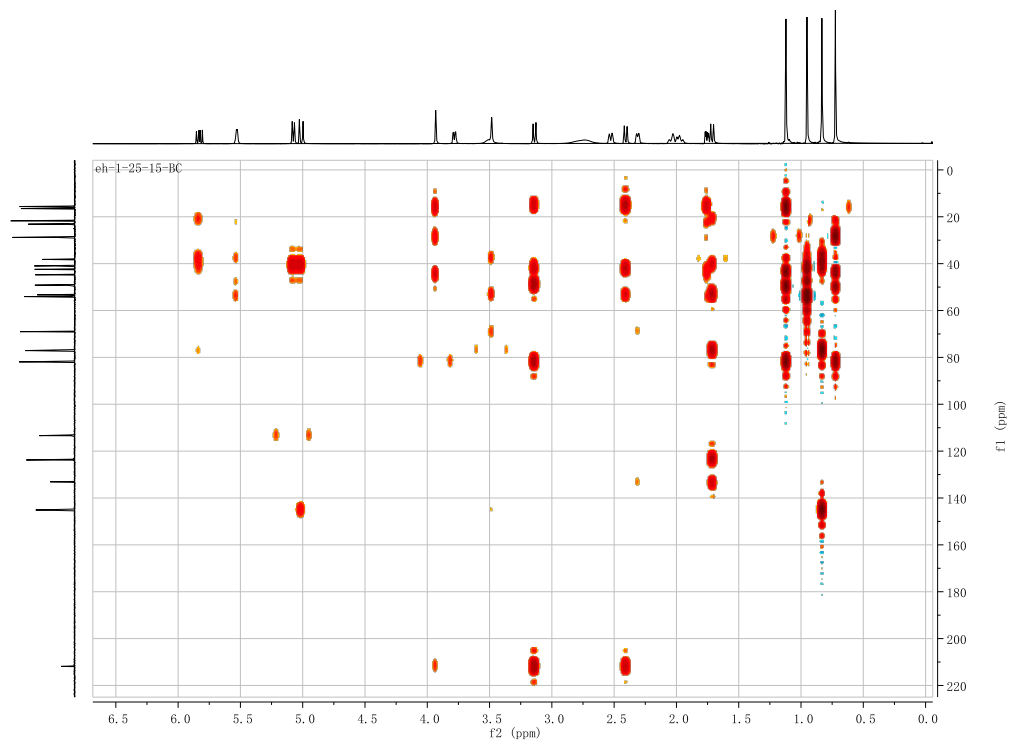


Figure SI16. NOESY spectrum of compound **2** (CDCl₃)

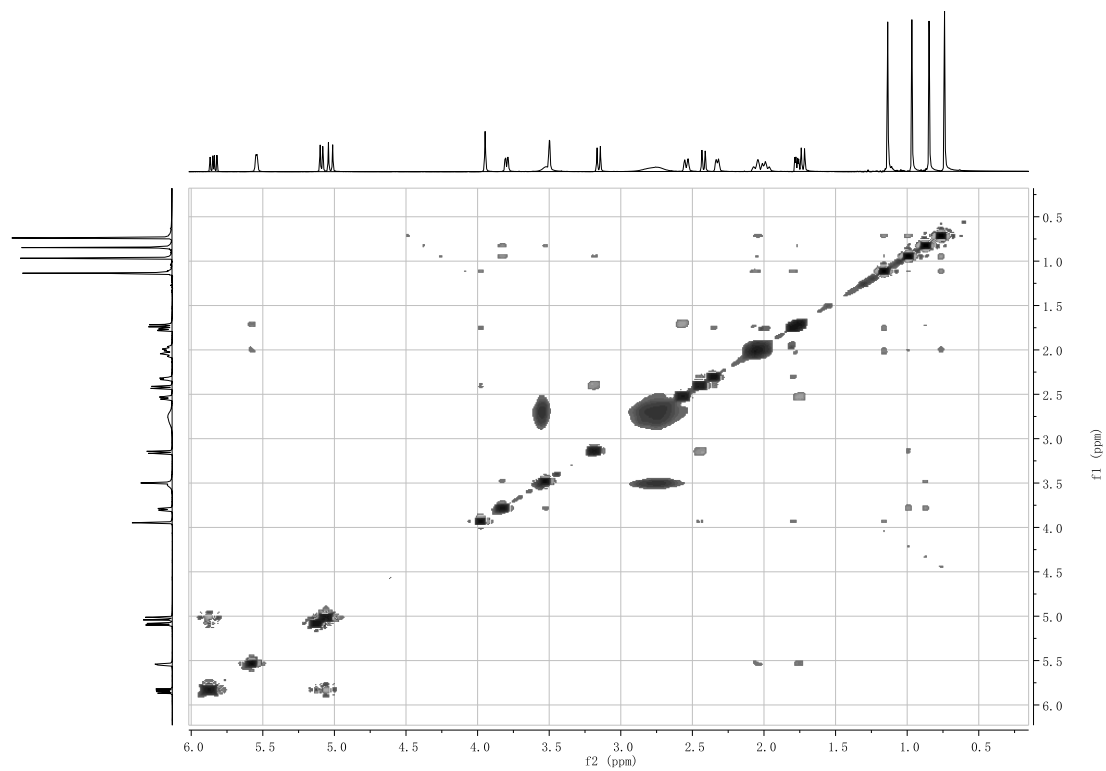


Figure SI17. HRESIMS spectrum of compound **2** (CDCl₃)

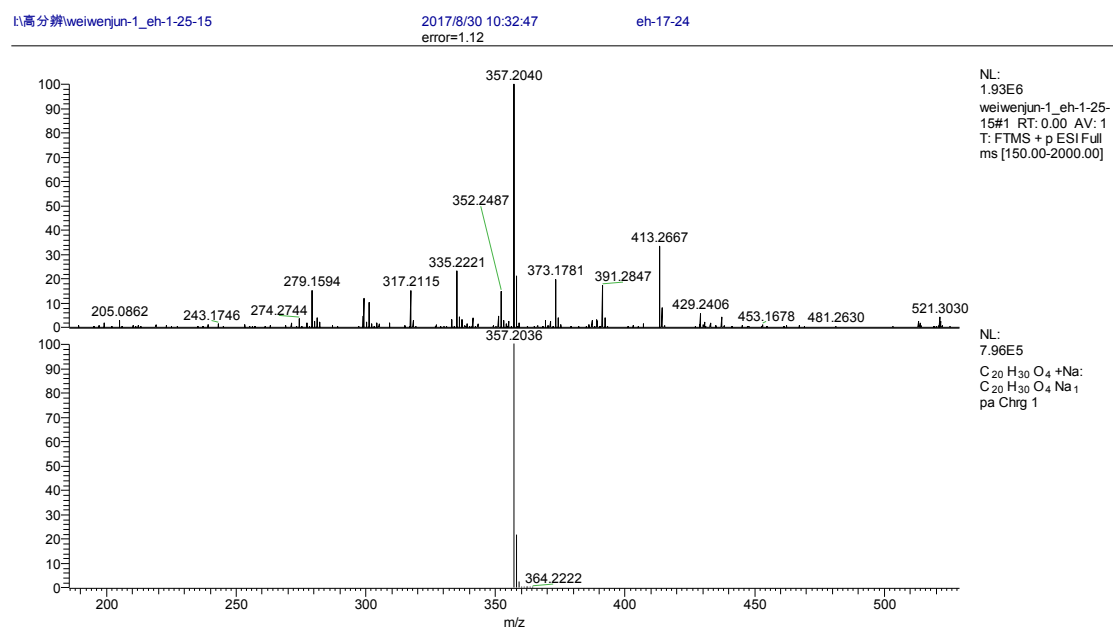


Figure SI18. IR spectrum of compound **2** (CDCl₃)

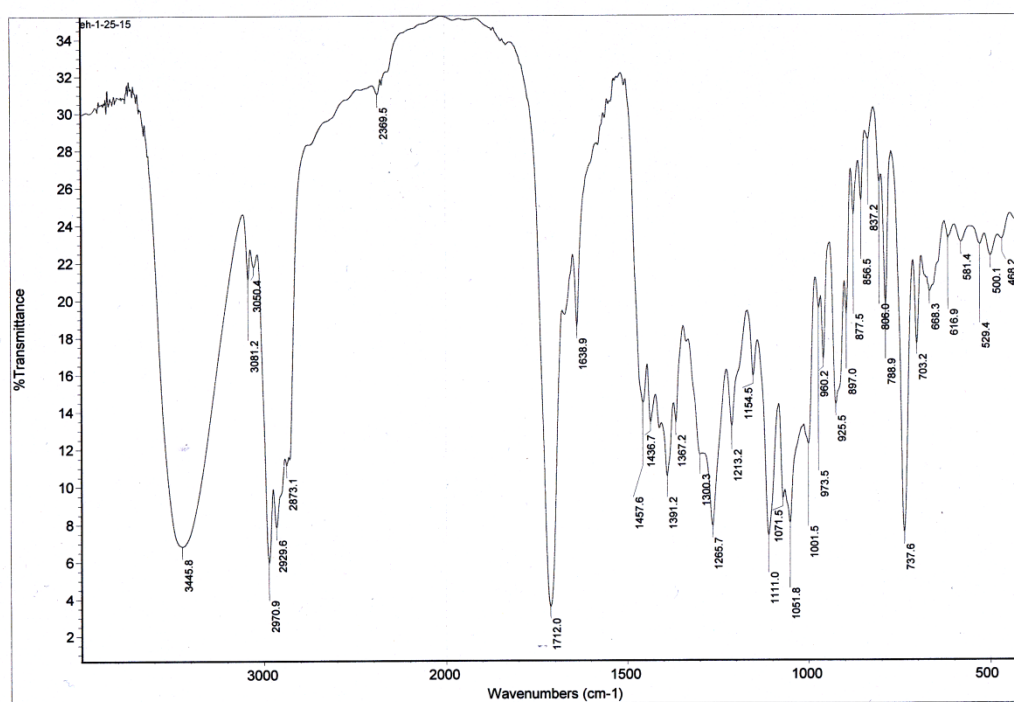


Figure SI19. ^1H NMR spectrum of compound **3** (CDCl_3)

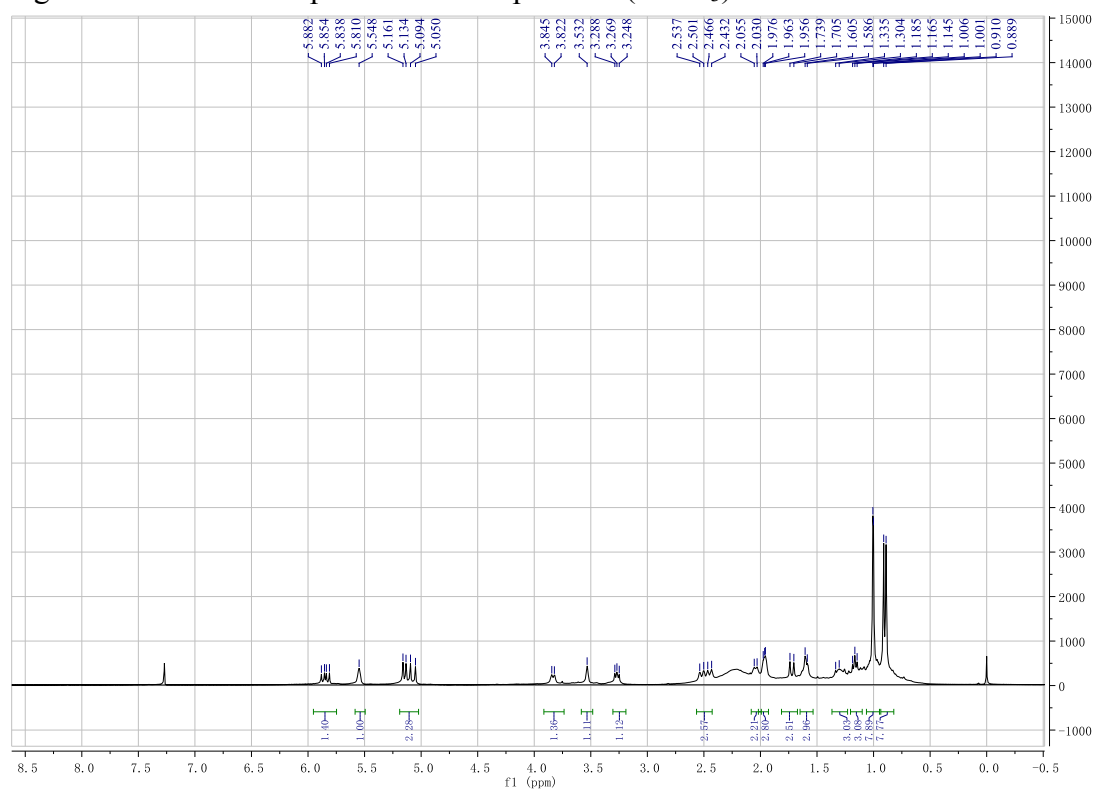


Figure SI20. ^{13}C NMR spectrum of compound **3** (CDCl_3)

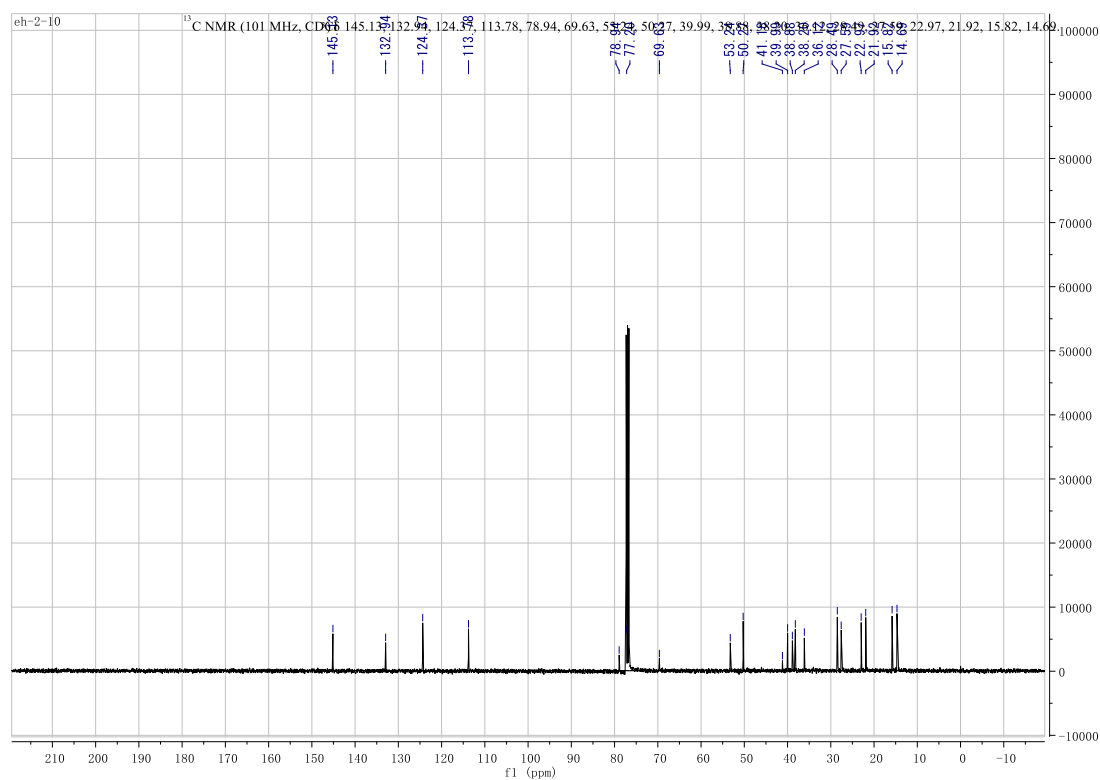


Figure SI21. DEPT spectrum of compound **3** (CDCl₃)

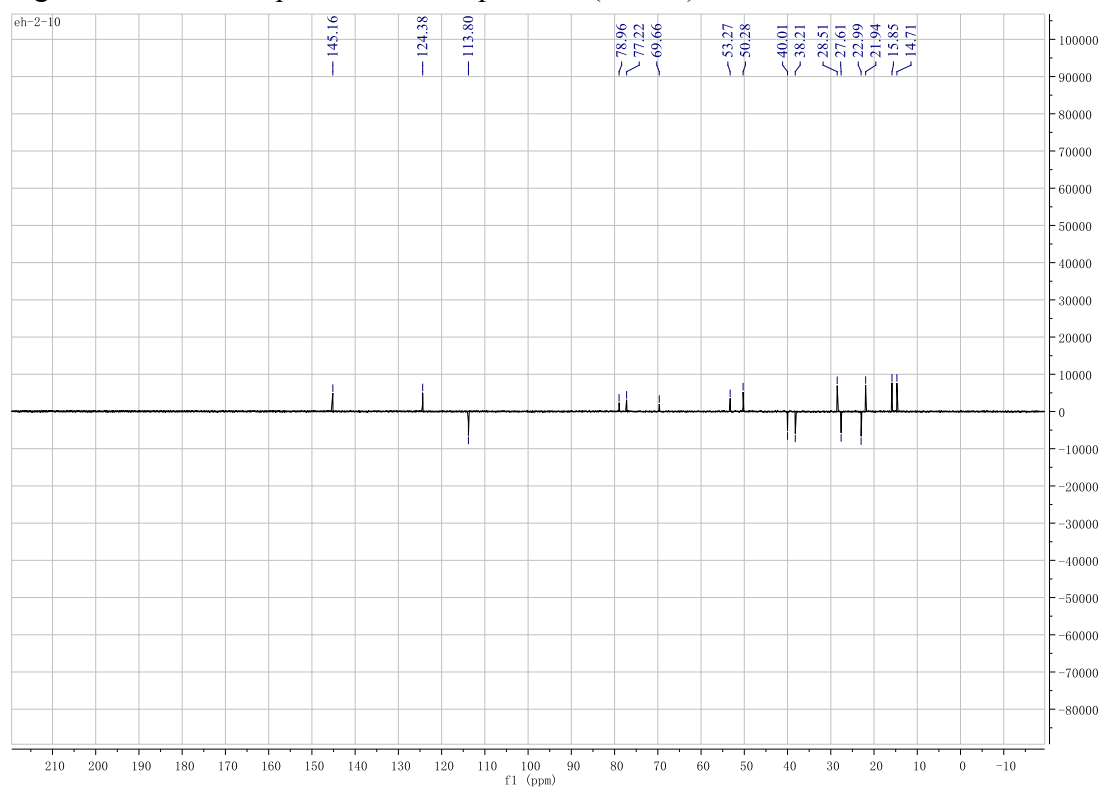


Figure SI22. ¹H-¹H COSY spectrum of compound **3** (CDCl₃)

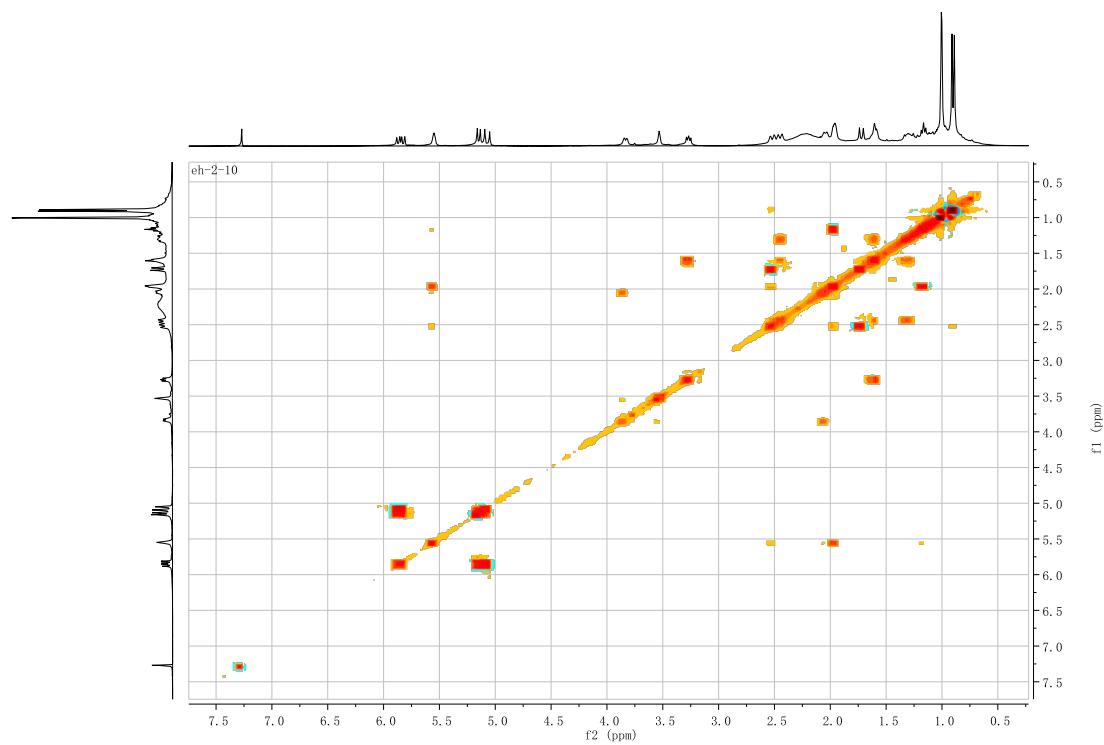


Figure SI23. HSQC spectrum of compound **3** (CDCl₃)

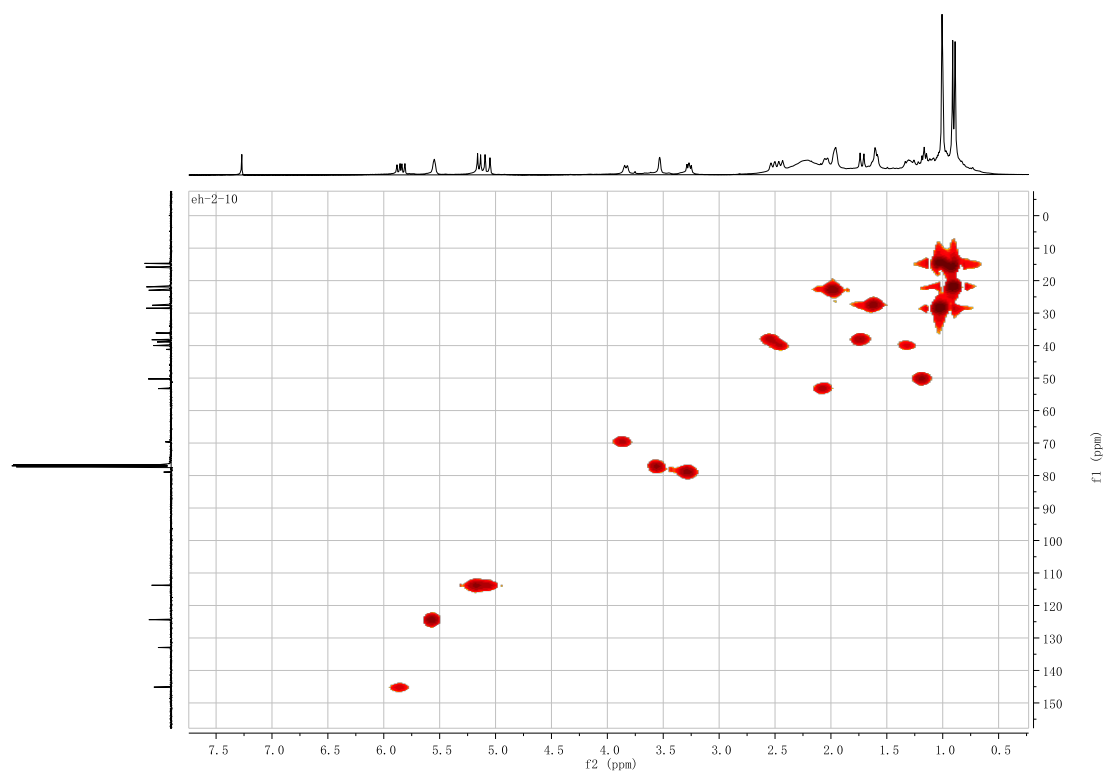


Figure SI24. HMBC spectrum of compound **3** (CDCl₃)

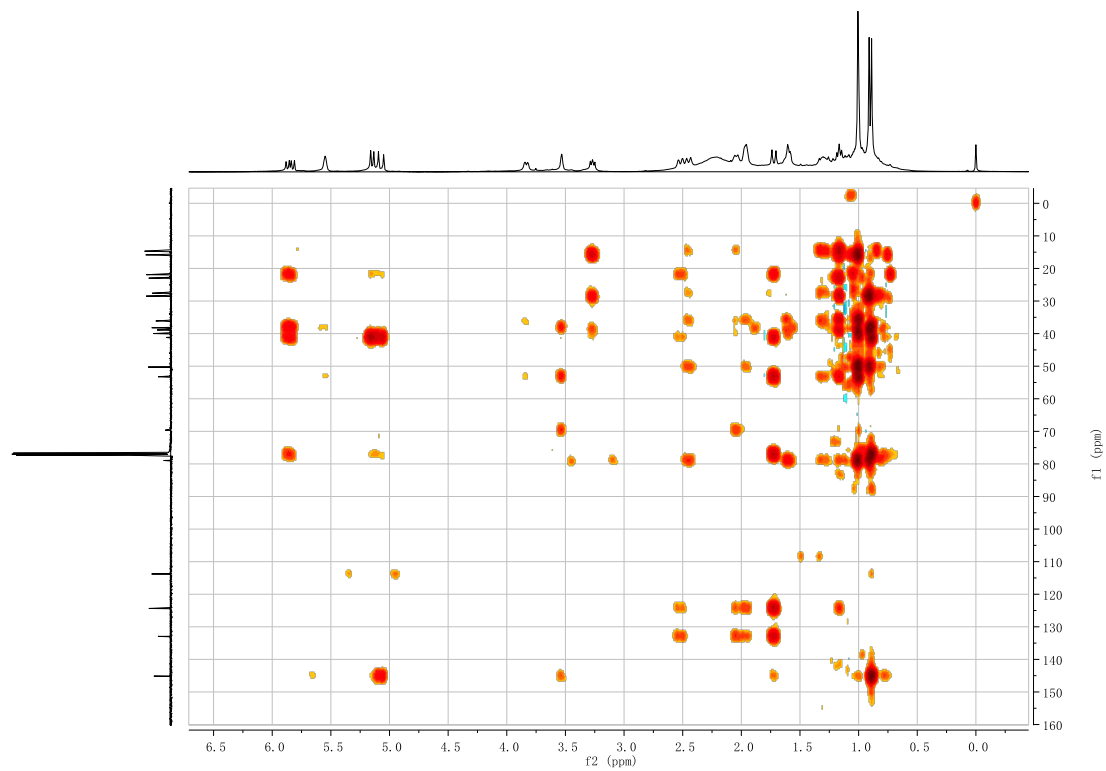


Figure SI25. NOESY spectrum of compound **3** (CDCl₃)

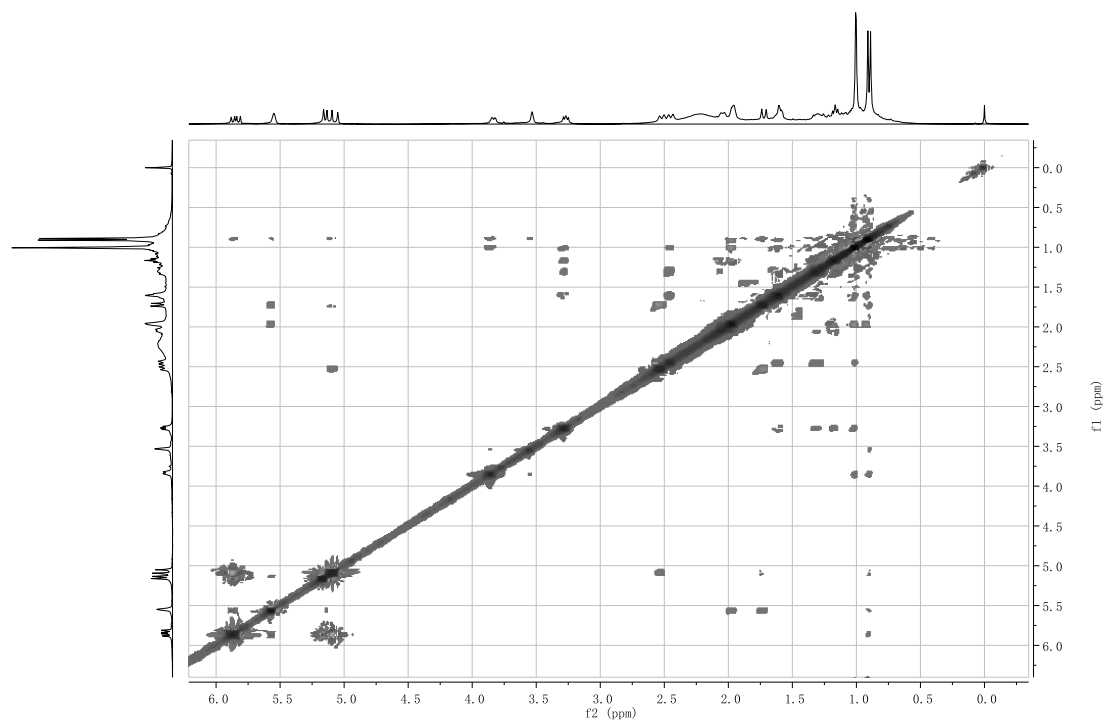
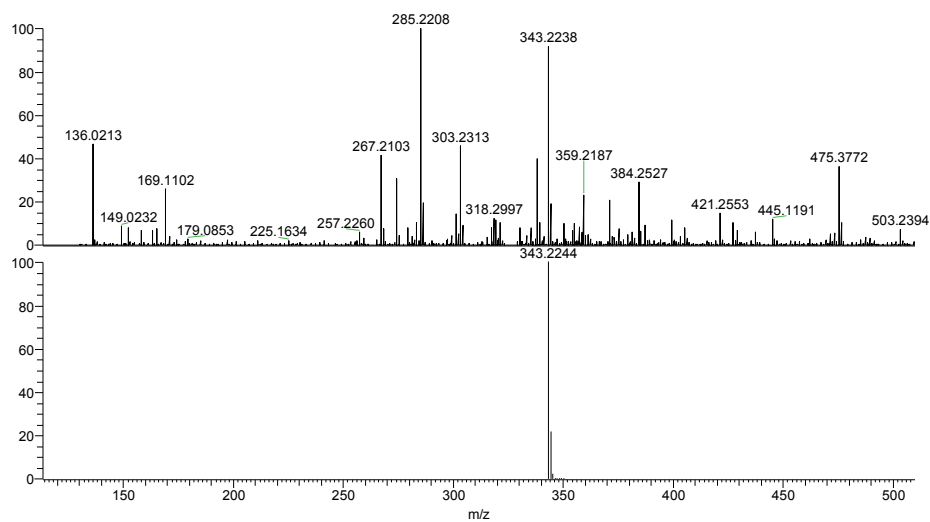


Figure SI26. HRESIMS spectrum of compound **3** (CDCl₃)

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170911170104#1 RT:
0.00 AV: 1 T: FTMS + p
ESI Full ms
[100.00-2000.00]

NL:
7.98E5
C₂₀H₃₂O₃+Na:
C₂₀H₃₂O₃Na₁
pa Chrg 1

Figure SI27. IR spectrum of compound **3** (CDCl₃)

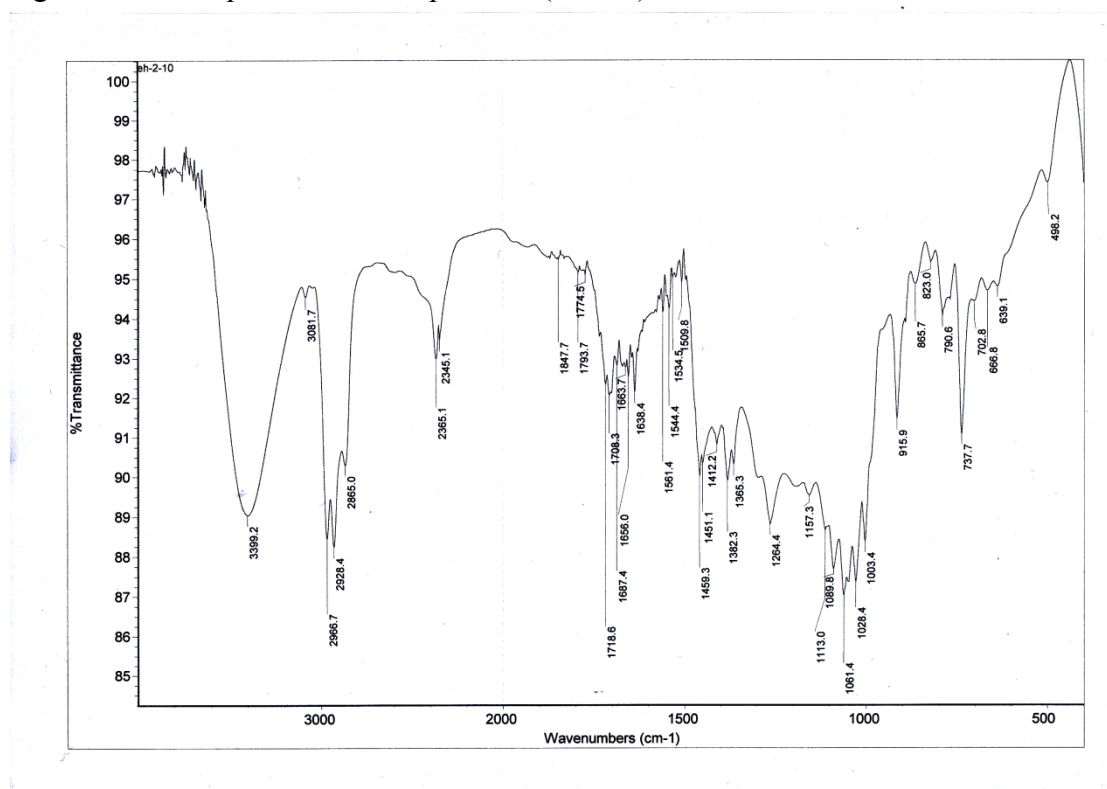


Figure SI28. ¹H NMR spectrum of compound **4** (CDCl₃)

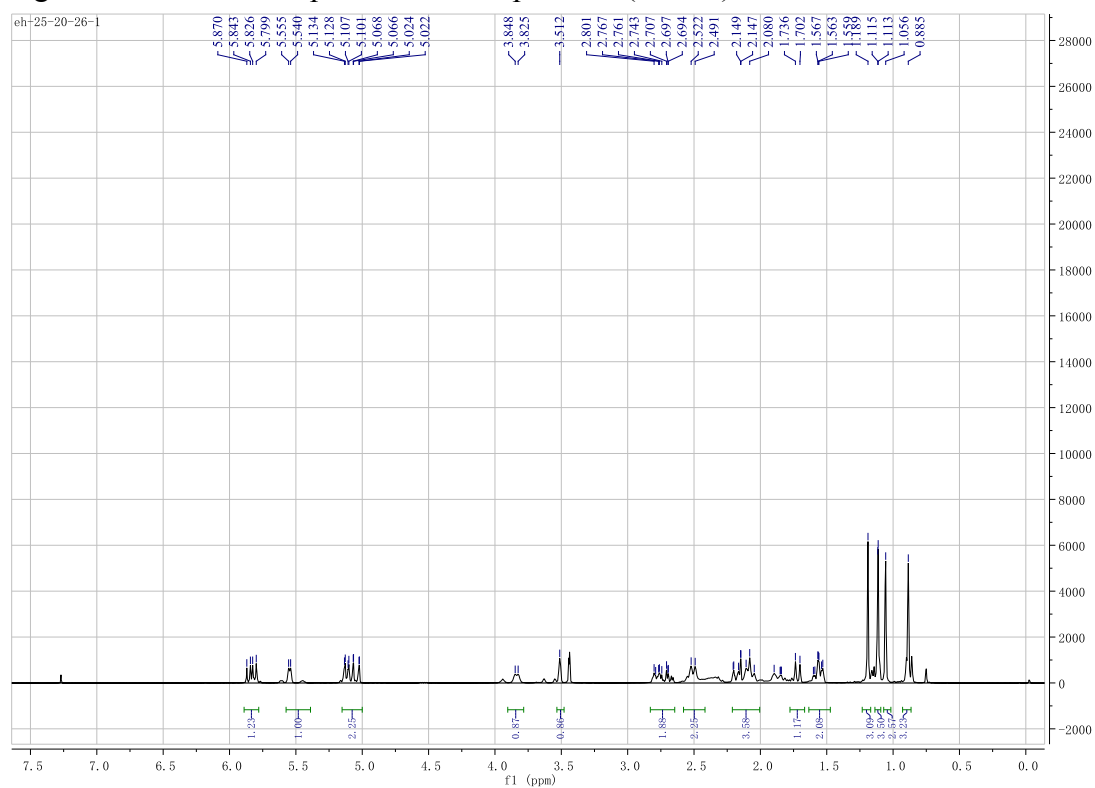


Figure SI29. ^{13}C NMR spectrum of compound **4** (CDCl_3)

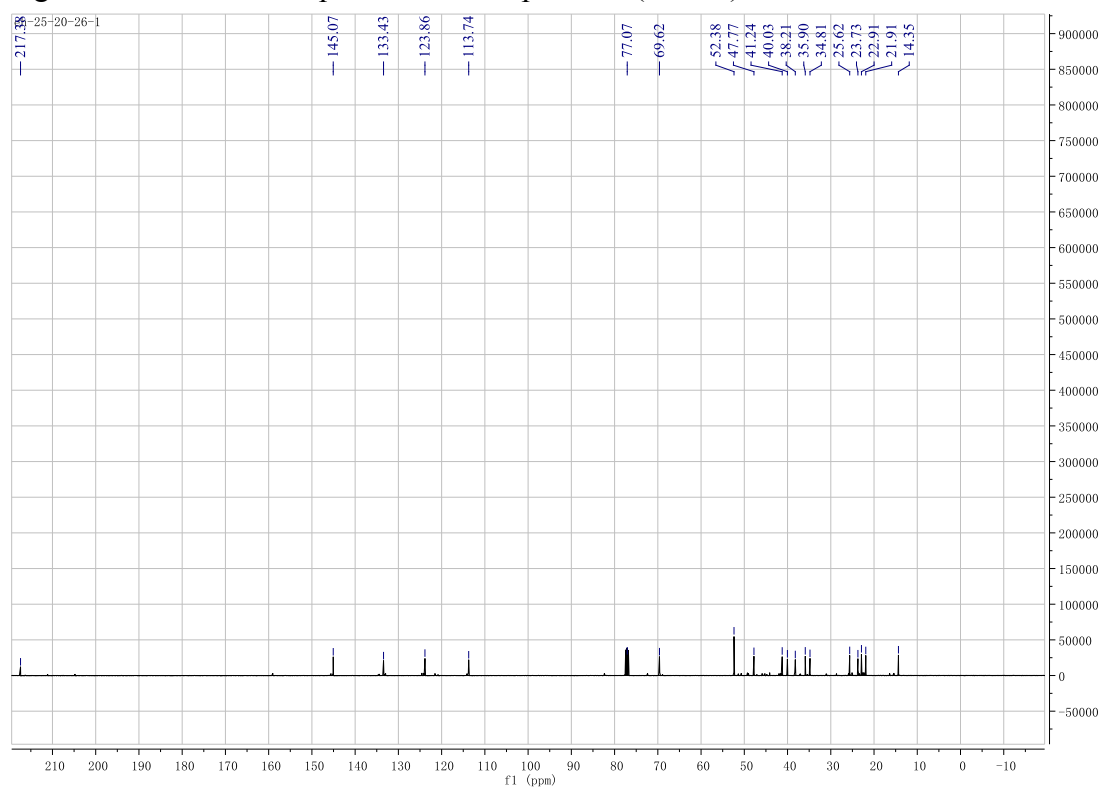


Figure SI30. DEPT spectrum of compound **4** (CDCl_3)

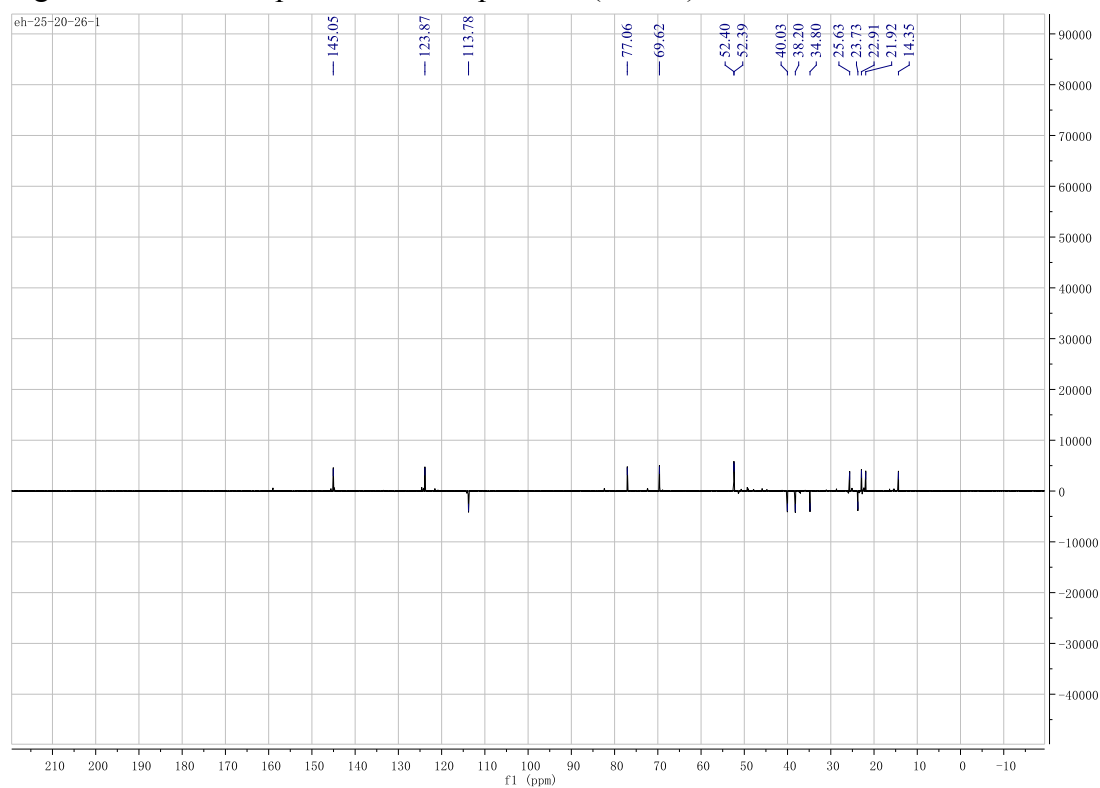


Figure SI31. ^1H - ^1H COSY spectrum of compound **4** (CDCl_3)

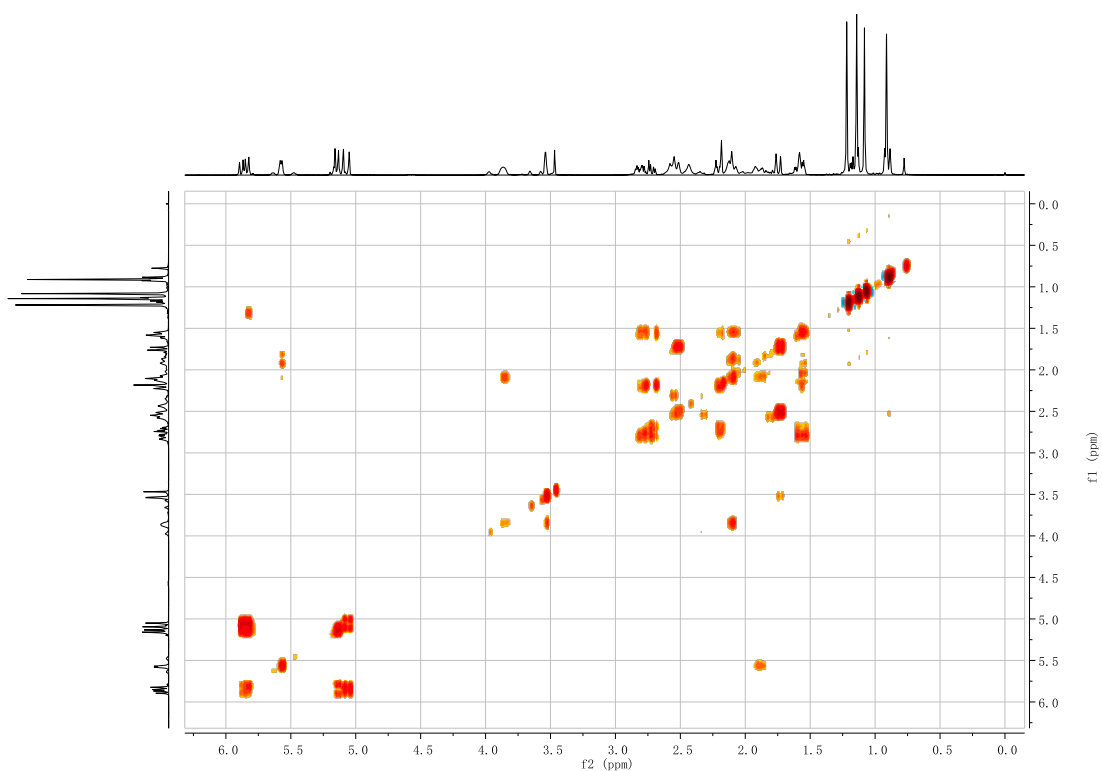


Figure SI32. HSQC spectrum of compound **4** (CDCl_3)

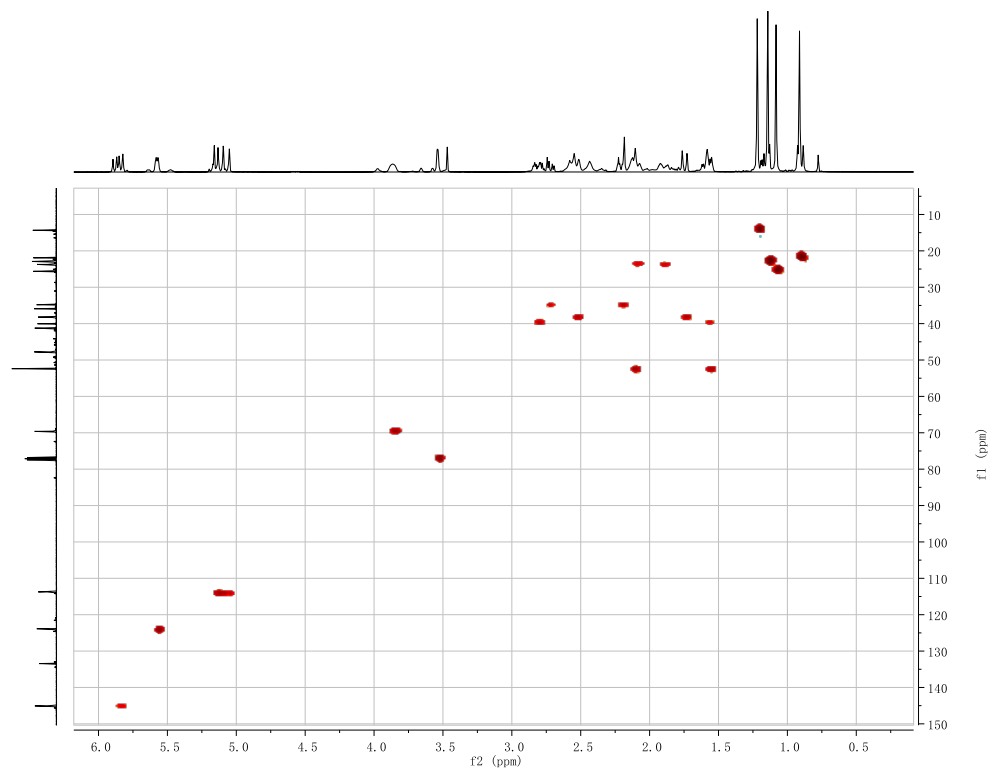


Figure SI33. HMBC spectrum of compound **4** (CDCl₃)

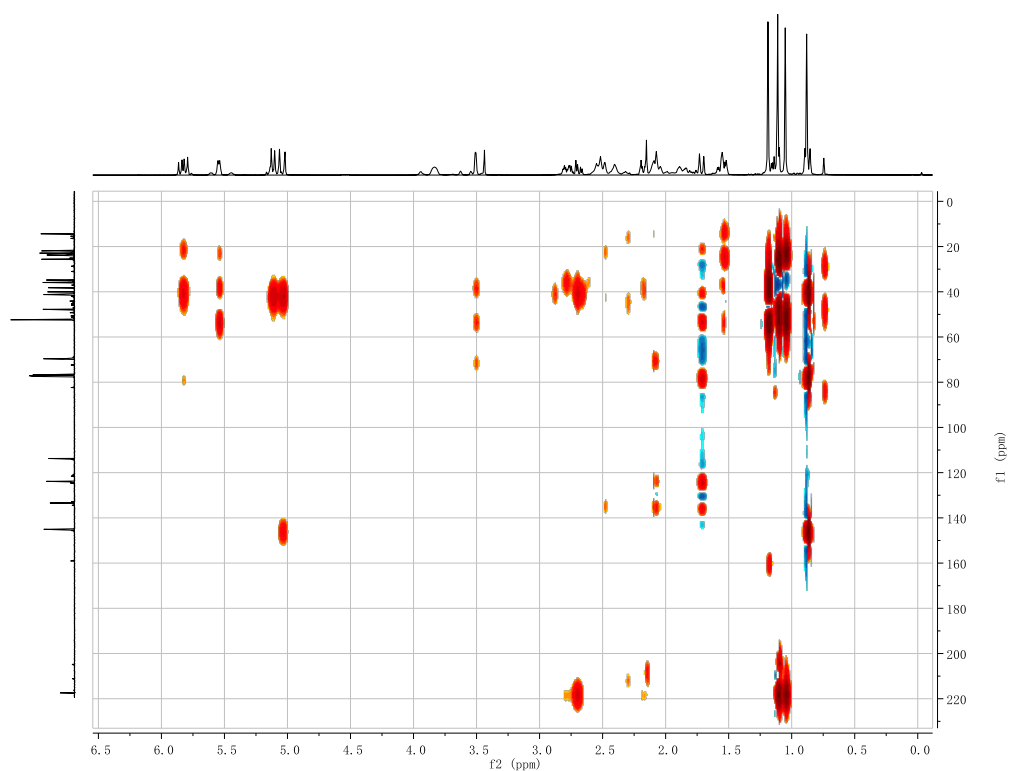


Figure SI34. NOESY spectrum of compound **4** (CDCl₃)

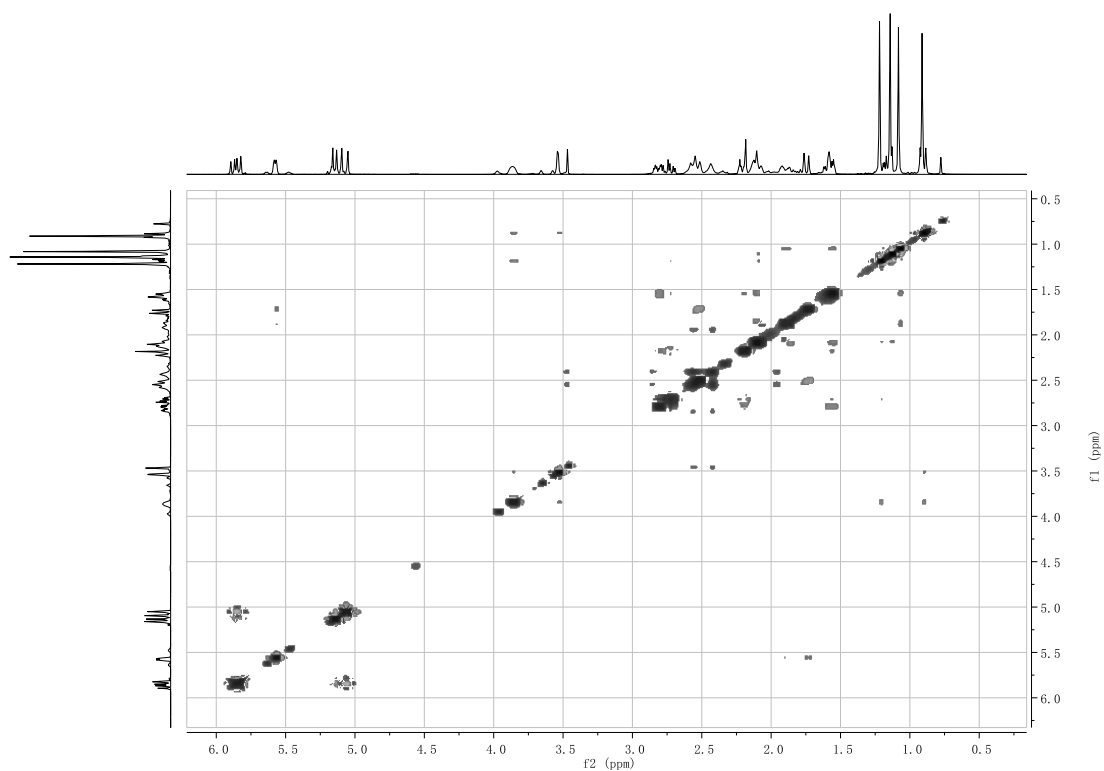


Figure SI35. HRESIMS spectrum of compound **4** (CDCl₃)

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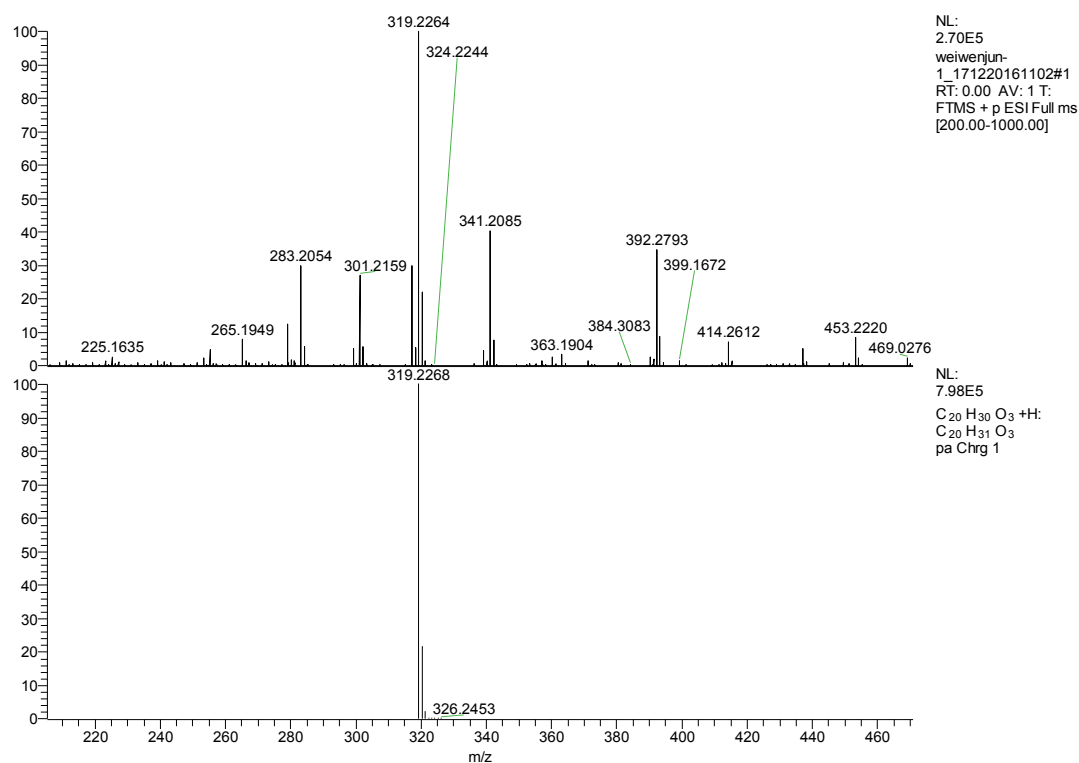


Figure SI36. IR spectrum of compound **4** (CDCl₃)

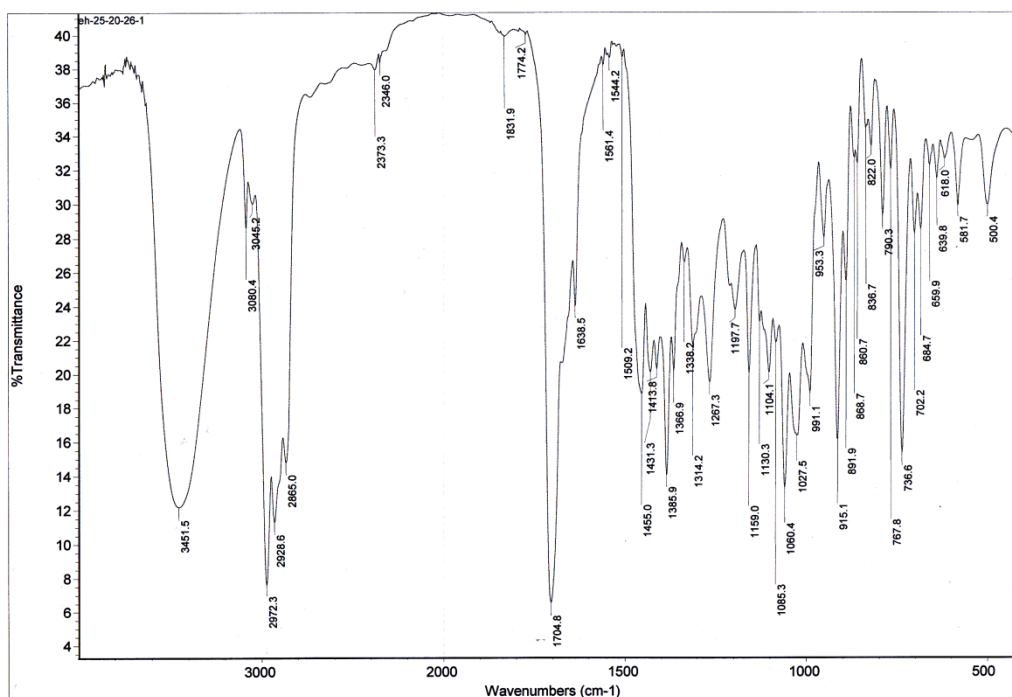


Figure SI37. ^1H NMR spectrum of compound **5** (CDCl_3)

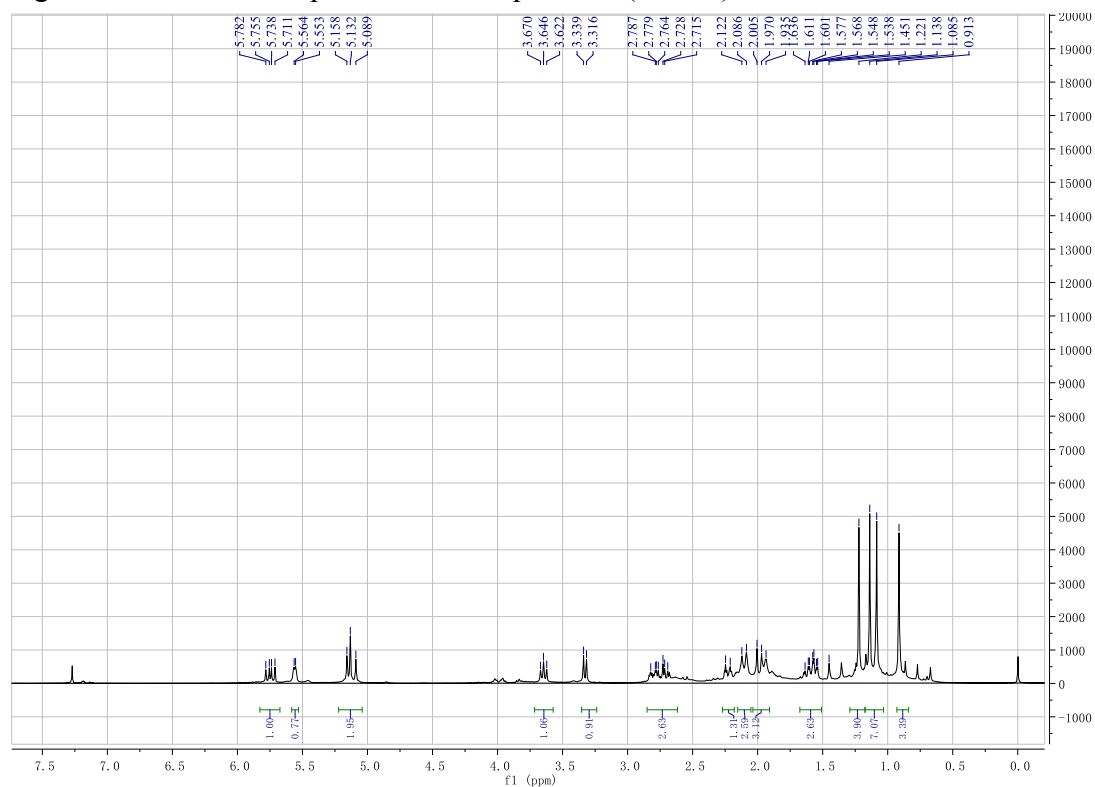


Figure SI38. ^{13}C NMR spectrum of compound **5** (CDCl_3)

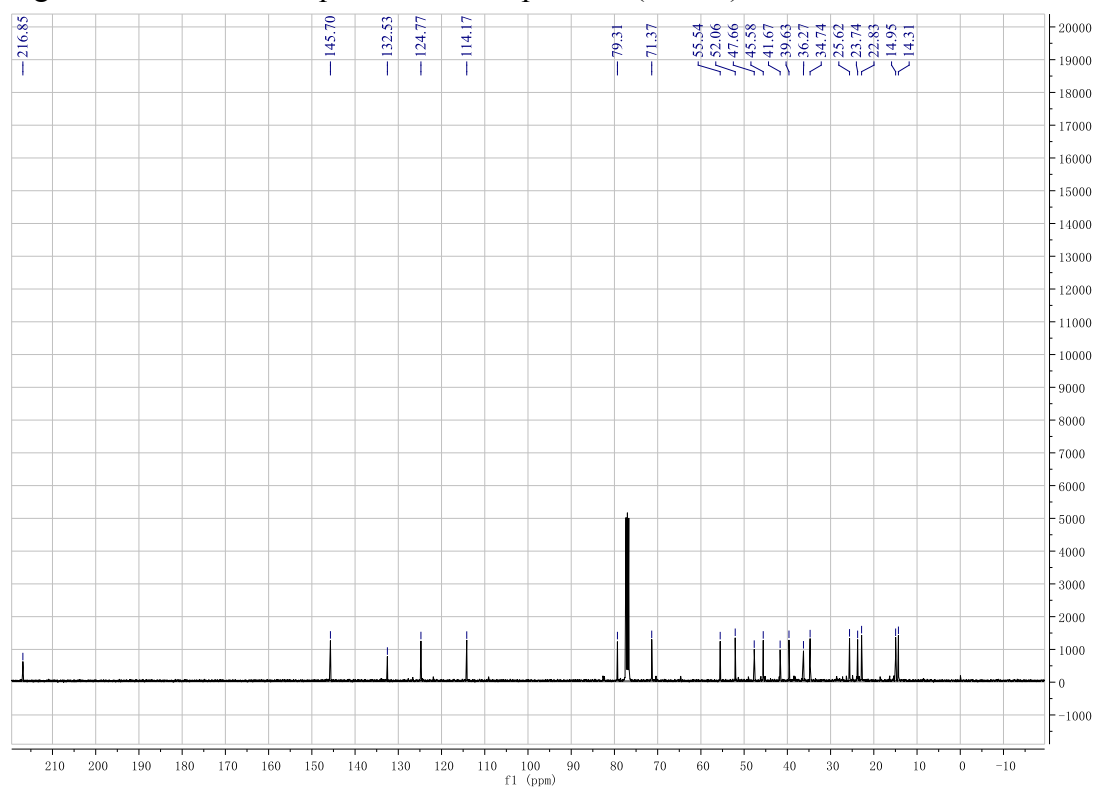


Figure SI39. DEPT spectrum of compound **5** (CDCl₃)

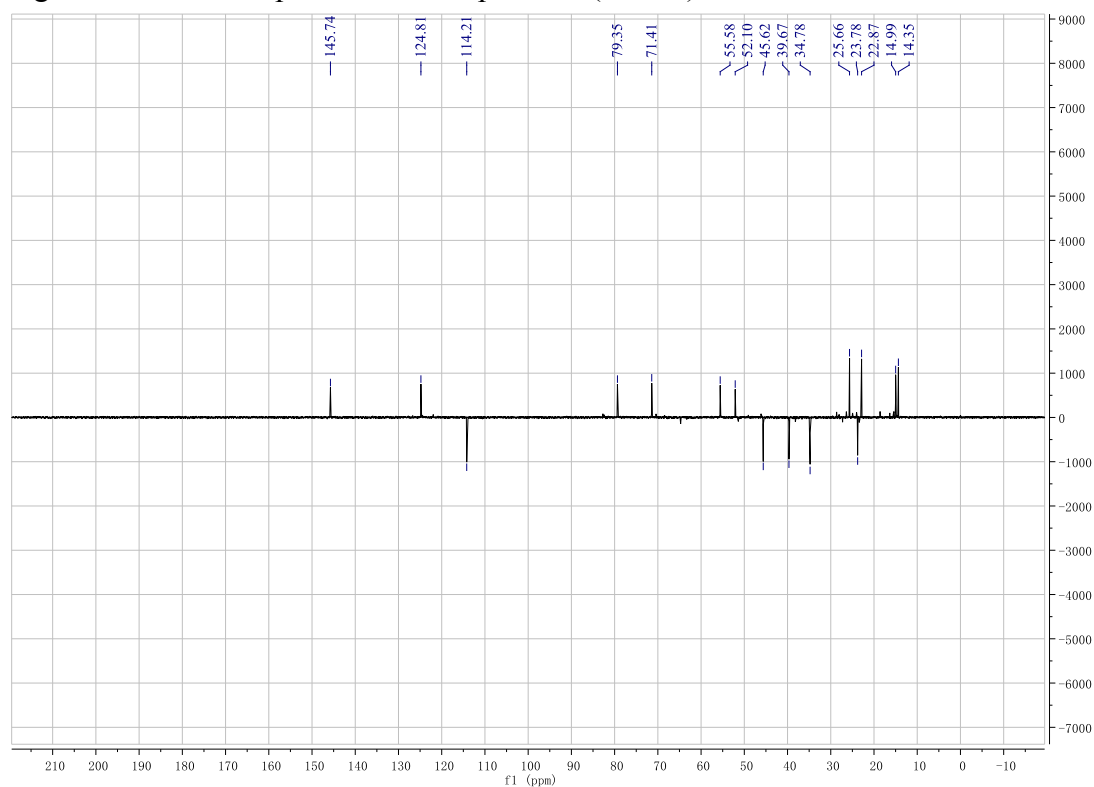


Figure SI40. ¹H-¹H COSY spectrum of compound **5** (CDCl₃)

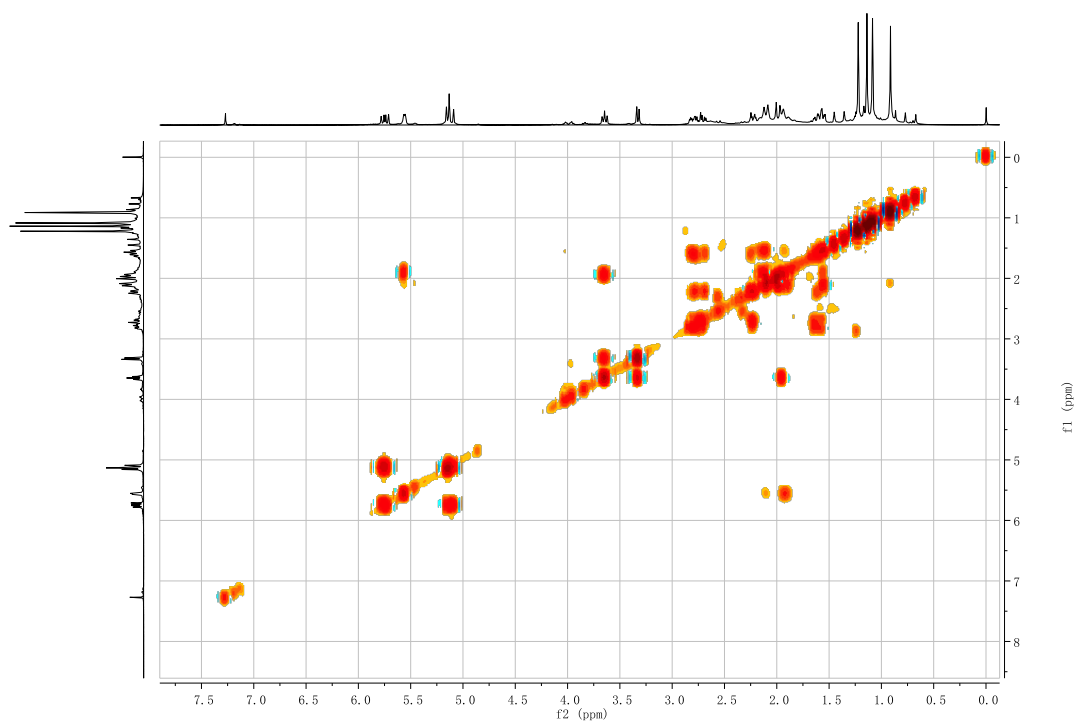


Figure SI41. HSQC spectrum of compound **5** (CDCl₃)

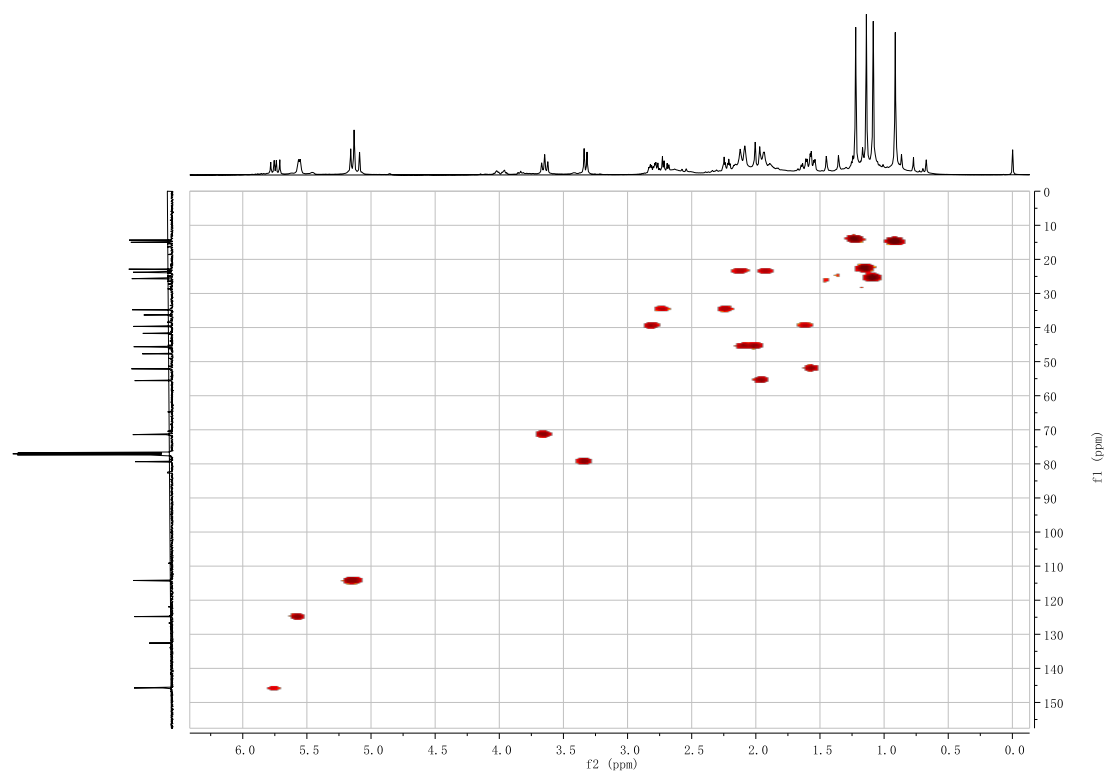


Figure SI42. HMBC spectrum of compound **5** (CDCl₃)

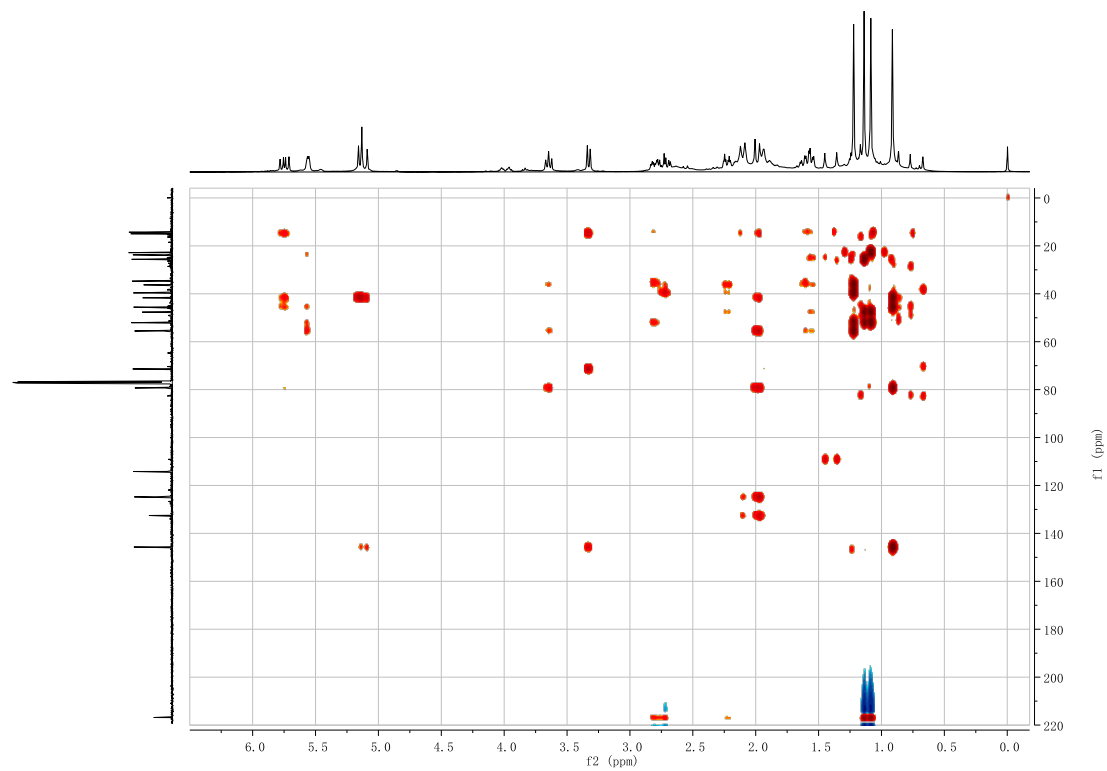


Figure SI43. NOESY spectrum of compound **5** (CDCl₃)

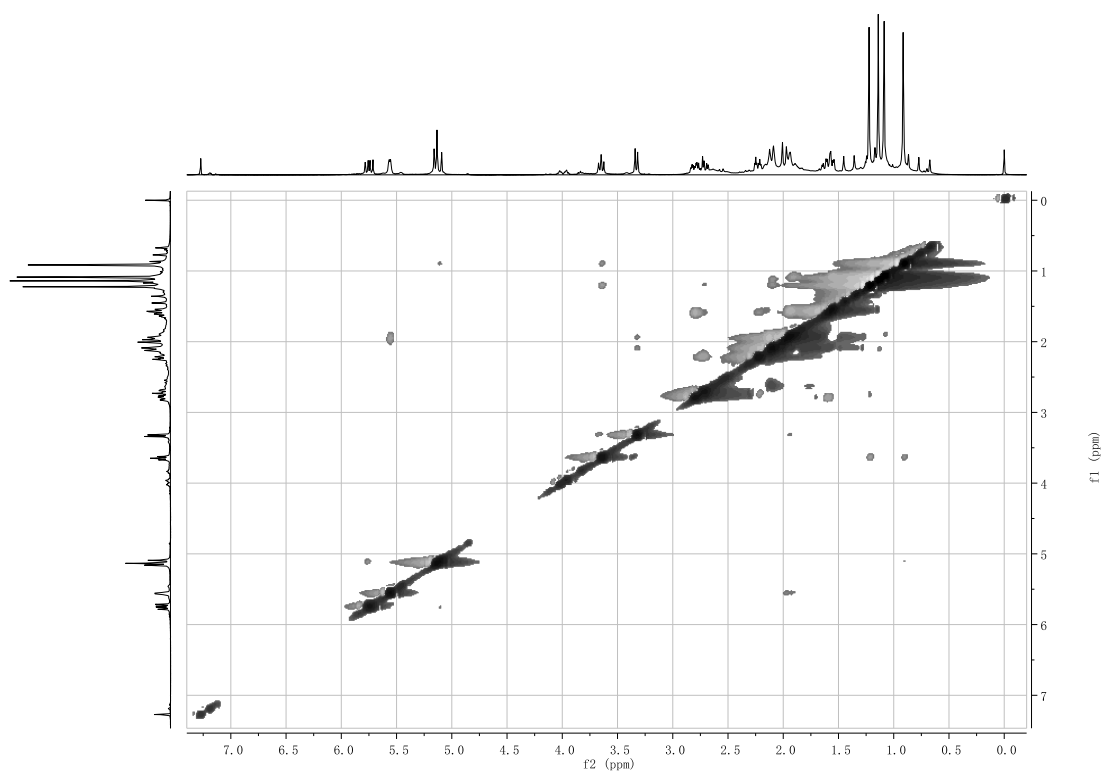


Figure SI44. HRESIMS spectrum of compound **5** (CDCl₃)

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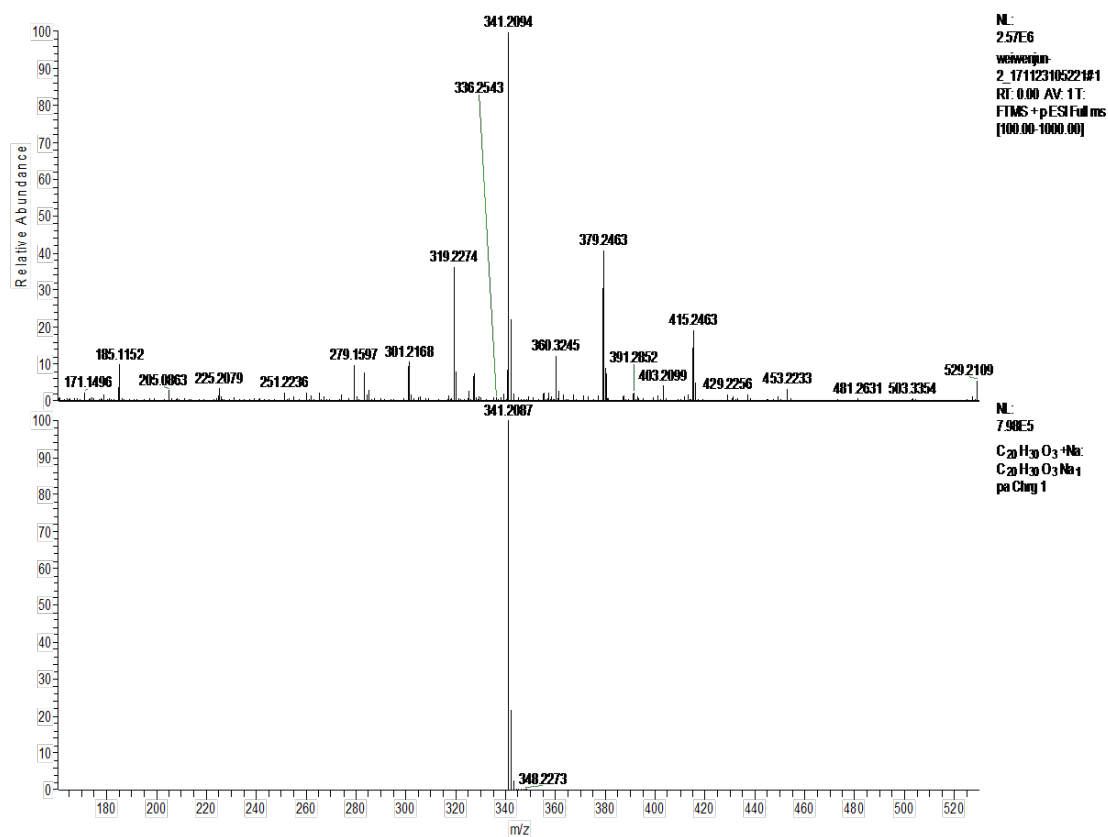


Figure SI45. IR spectrum of compound **5** (CDCl_3)

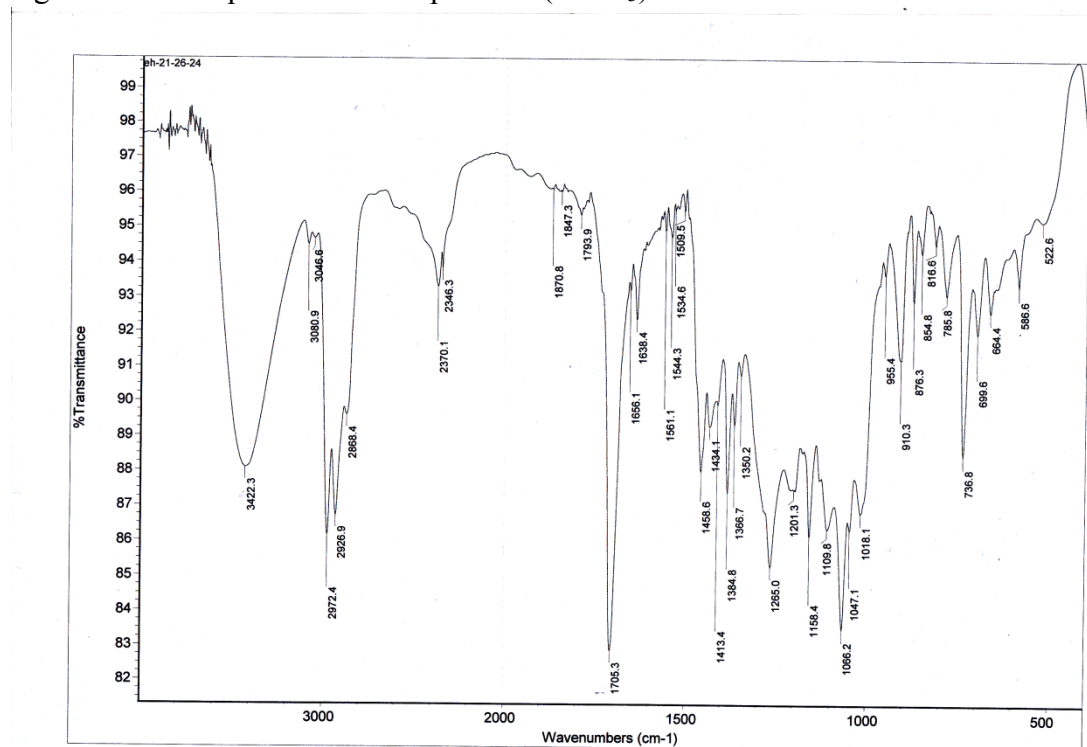


Figure SI46. ^1H NMR spectrum of compound **6** (CDCl_3)

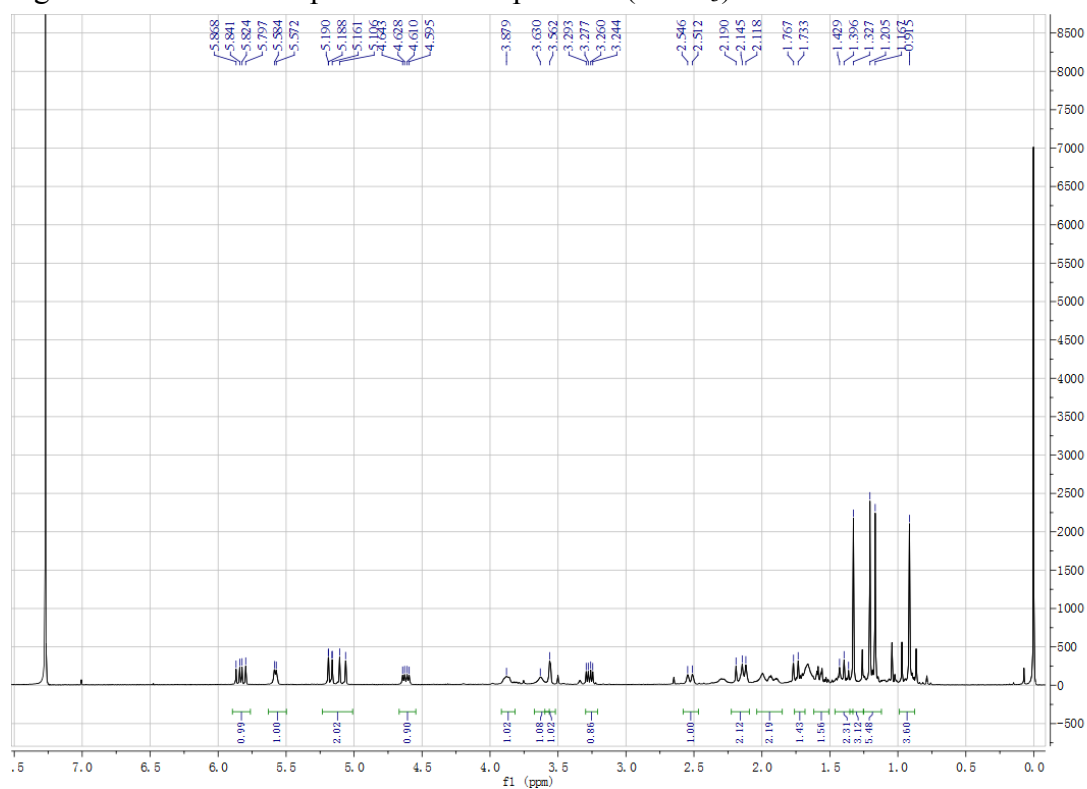


Figure SI47. ^{13}C NMR spectrum of compound **6** (CDCl_3)

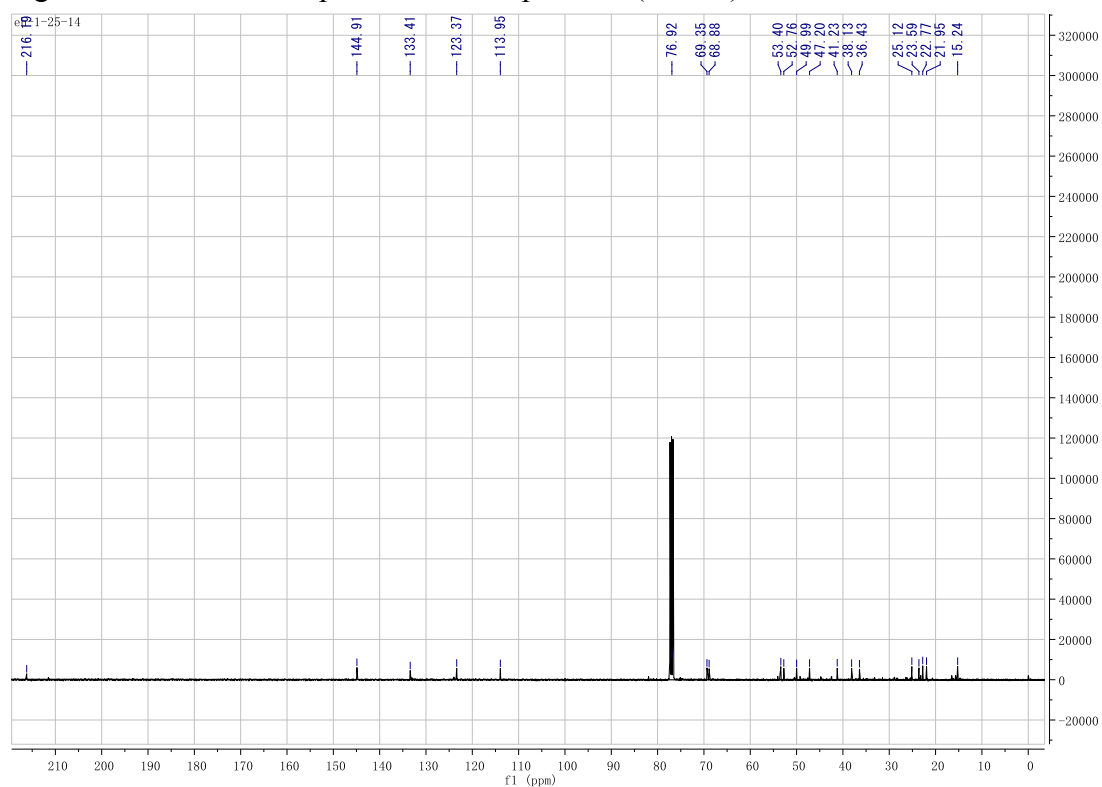


Figure SI48. DEPT spectrum of compound **6** (CDCl_3)

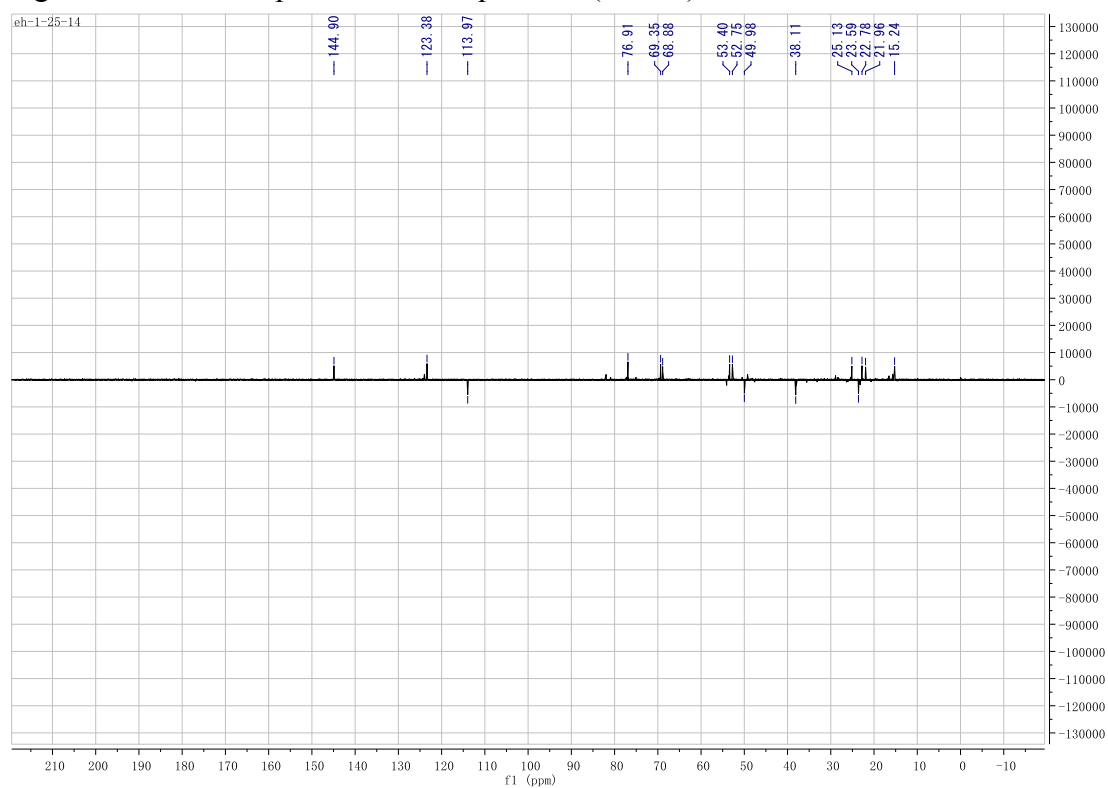


Figure SI49. ^1H - ^1H COSY spectrum of compound **6** (CDCl_3)

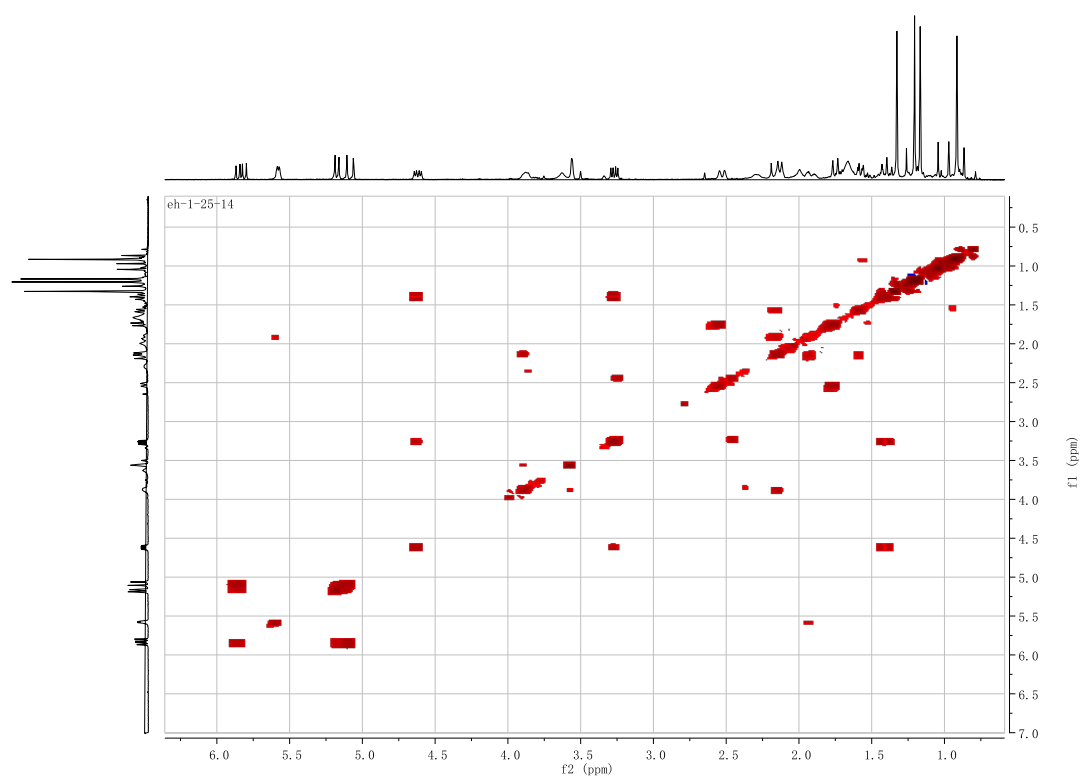


Figure SI50. HSQC spectrum of compound **6** (CDCl_3)

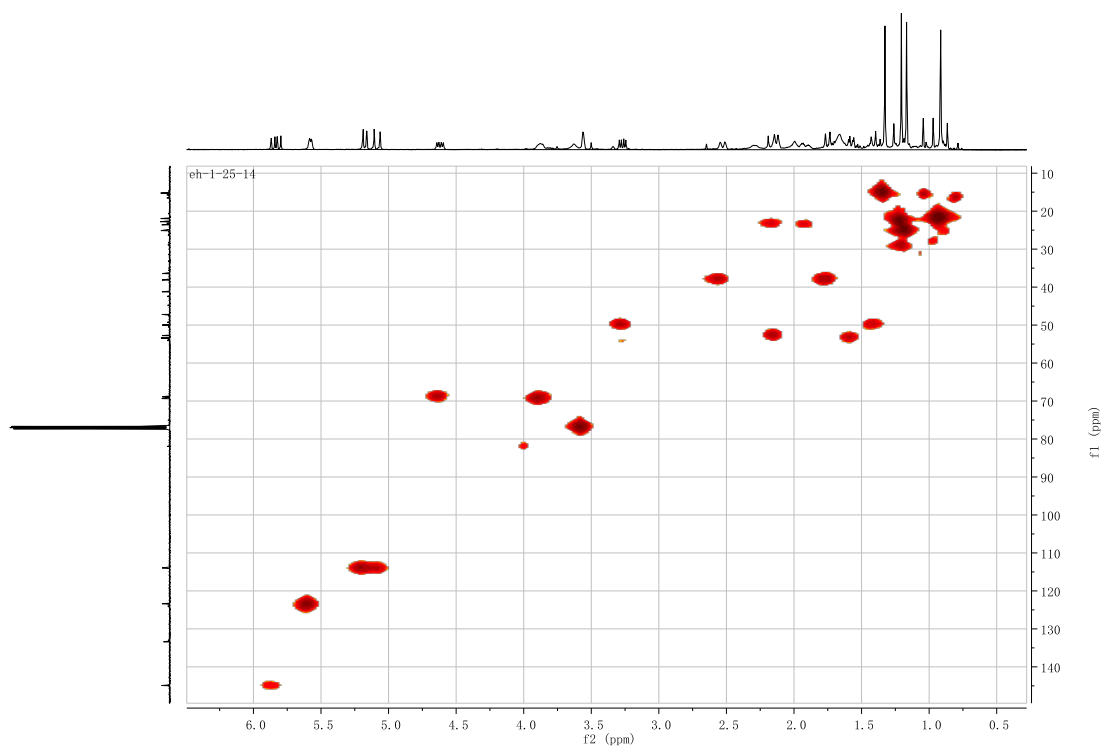


Figure SI51. HMBC spectrum of compound **6** (CDCl₃)

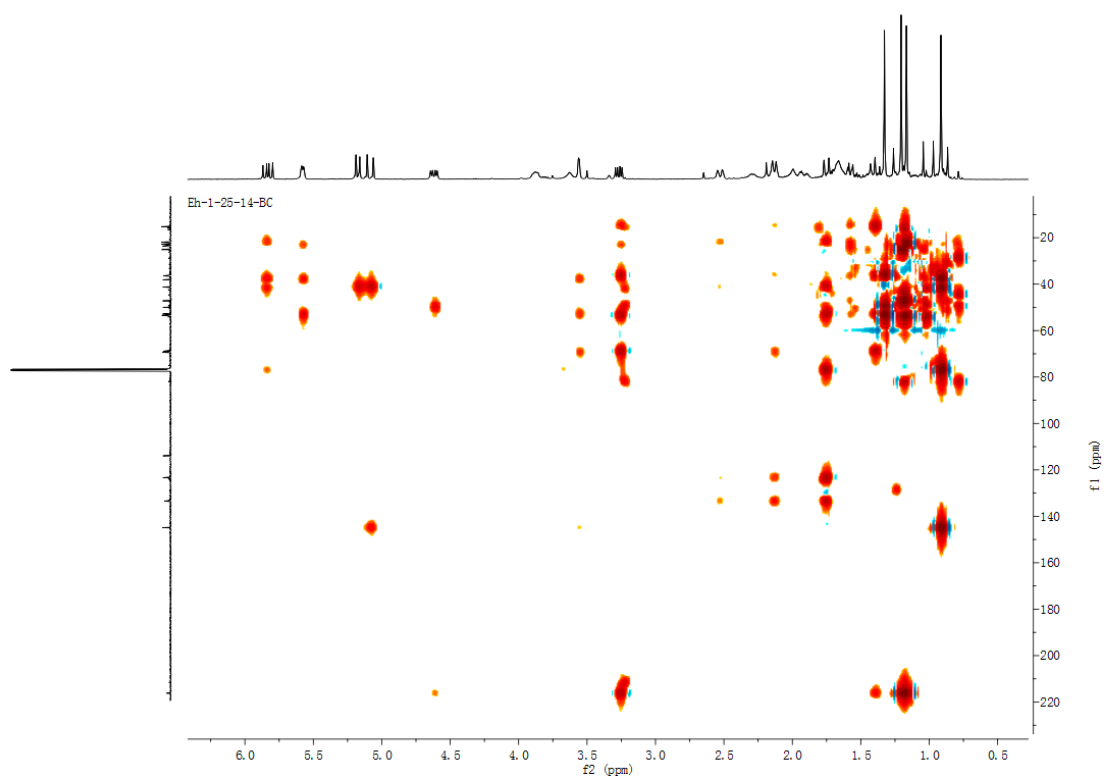


Figure SI52. NOESY spectrum of compound **6** (CDCl₃)

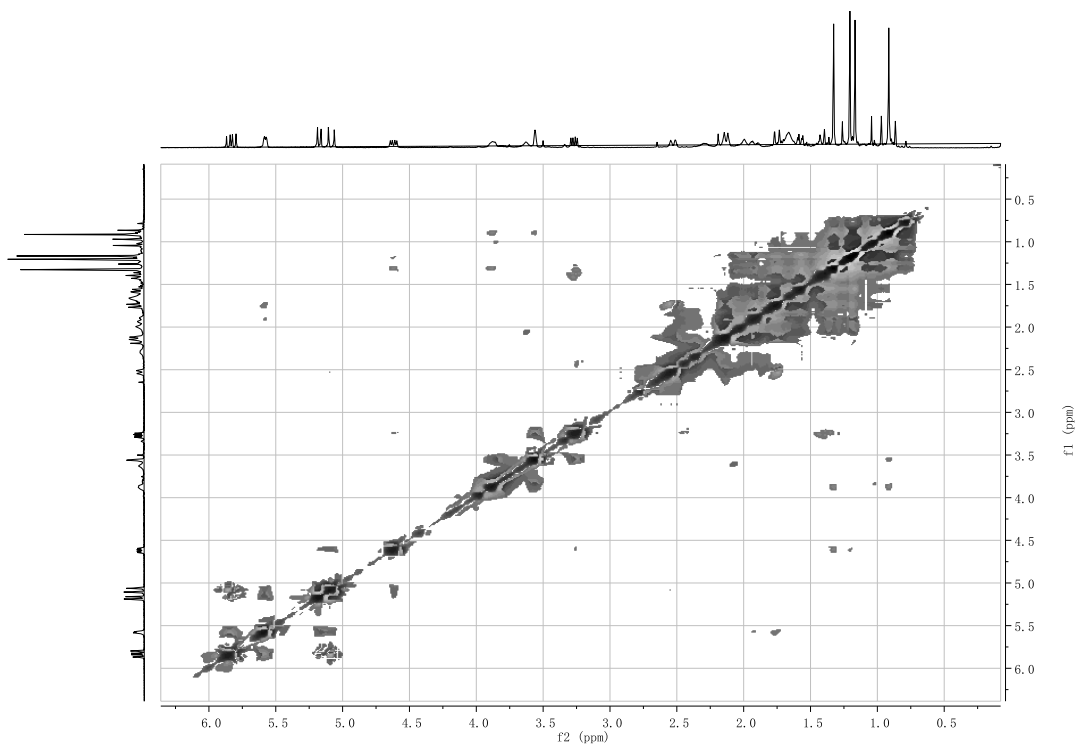


Figure SI53. HRESIMS spectrum of compound **6** (CDCl₃)

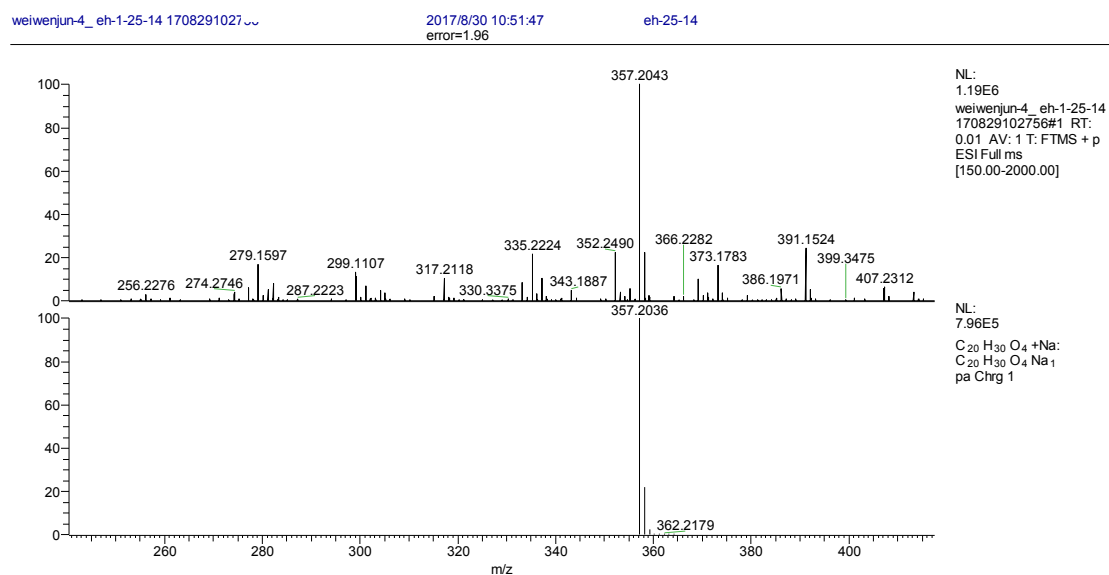


Figure SI54. IR spectrum of compound **6** (CDCl₃)

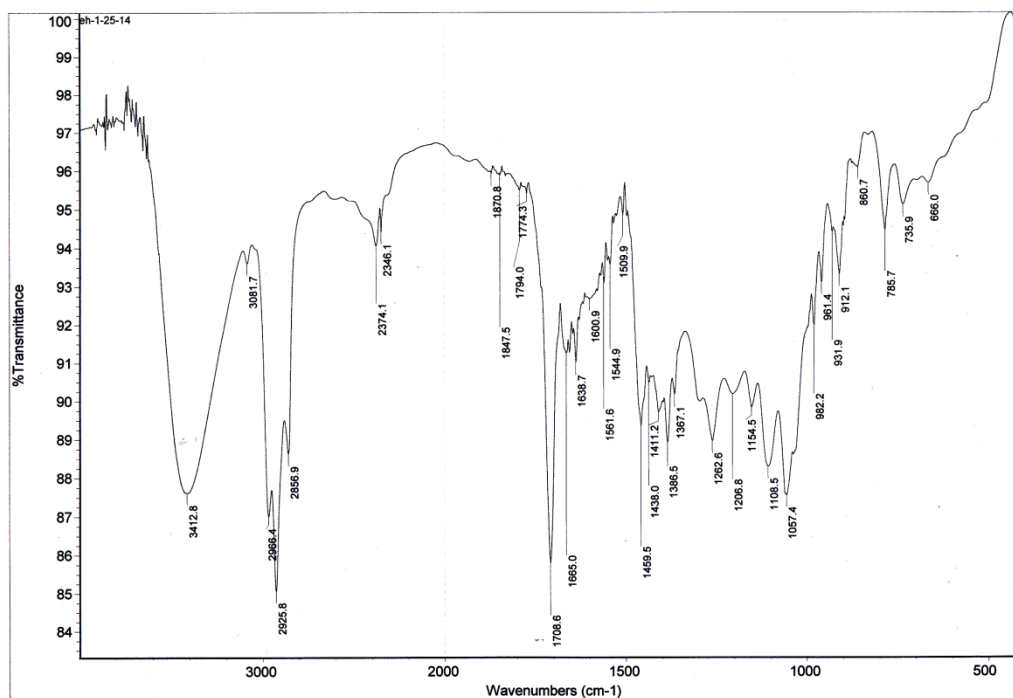


Figure SI55. ^1H NMR spectrum of compound **7** (CDCl_3)

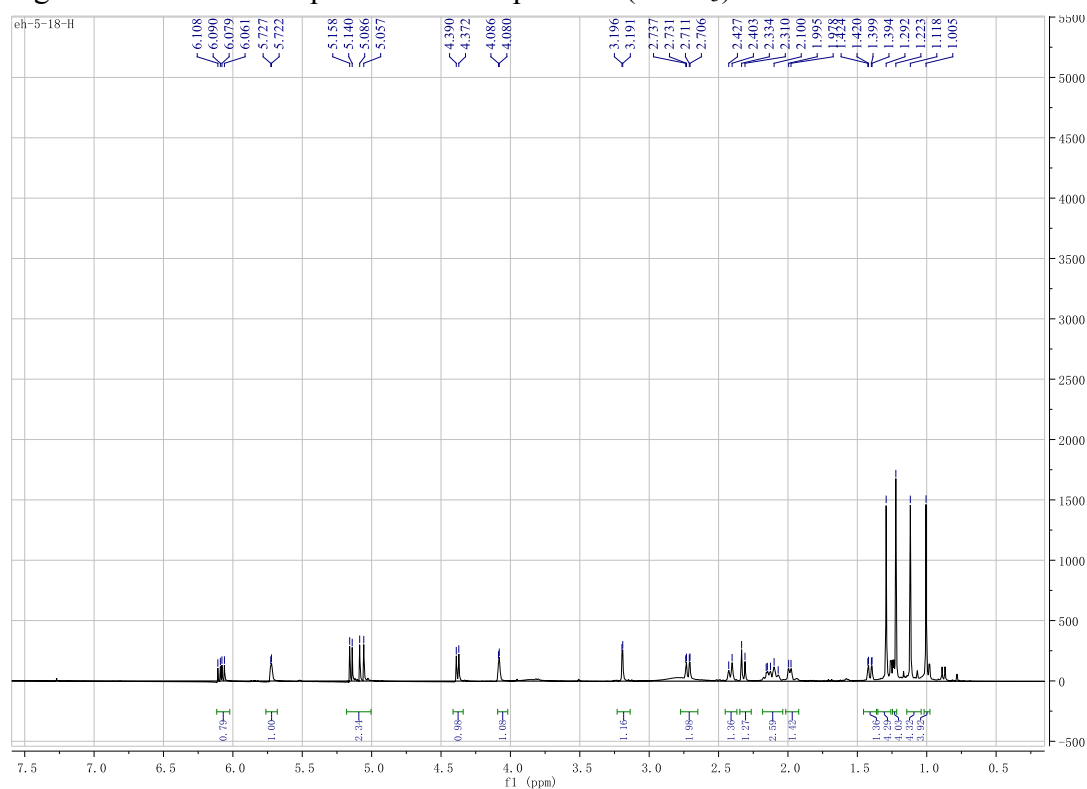


Figure SI56. ^{13}C NMR spectrum of compound **7** (CDCl_3)

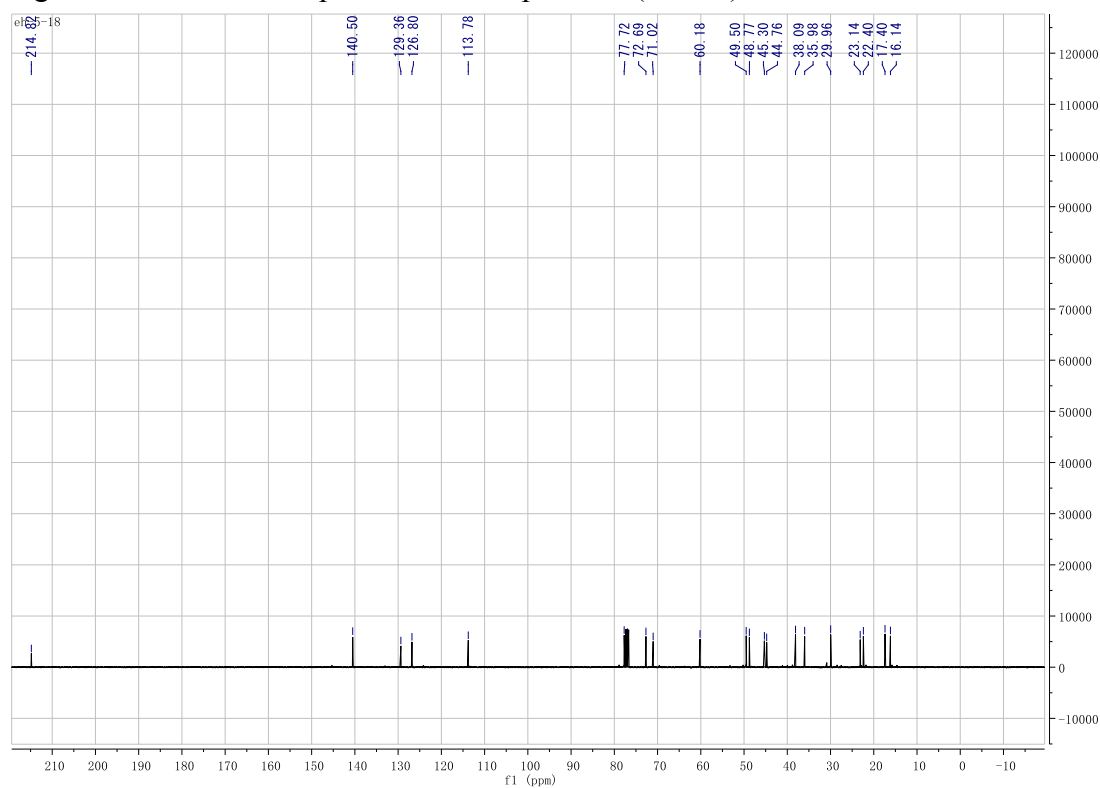


Figure SI57. DEPT spectrum of compound **7** (CDCl₃)

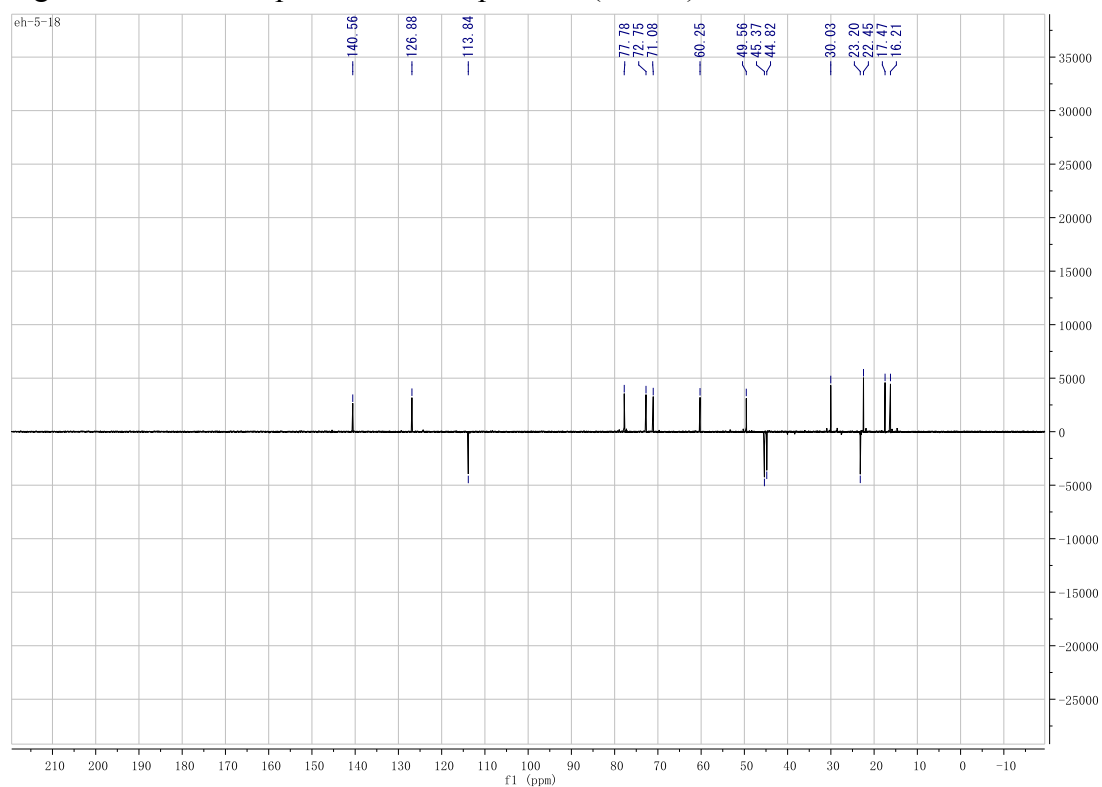


Figure SI58. ¹H–¹H COSY spectrum of compound **7** (CDCl₃)

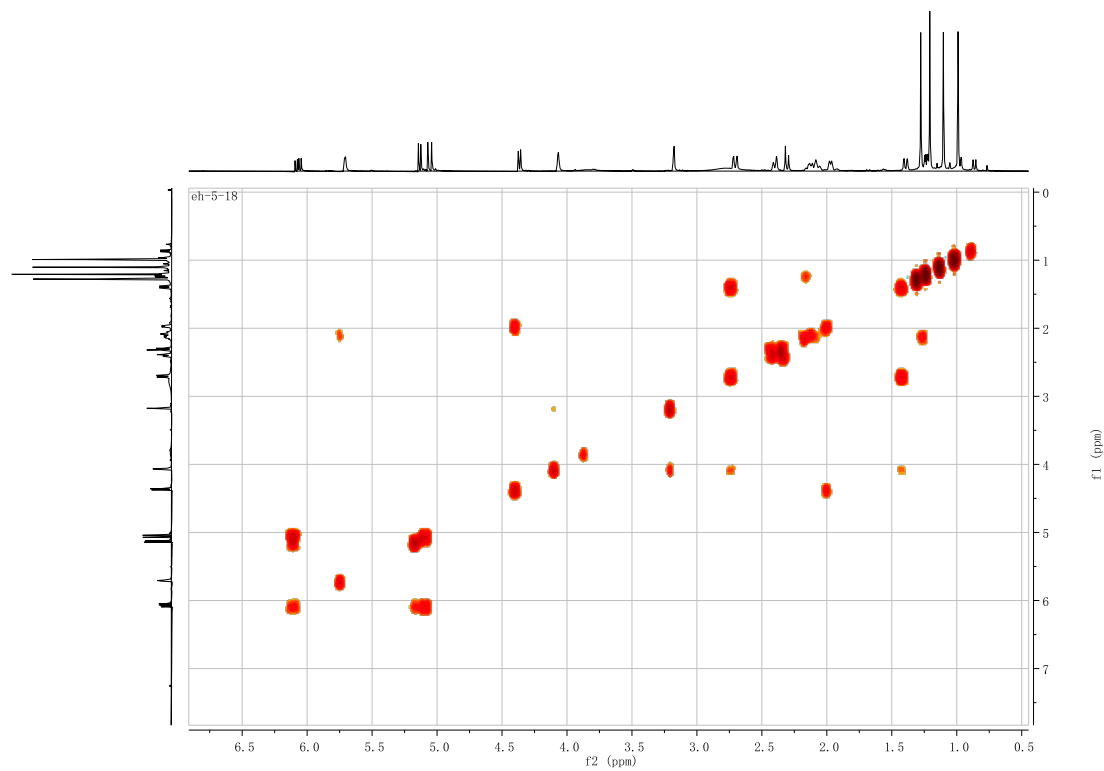


Figure SI59. HSQC spectrum of compound **7** (CDCl₃)

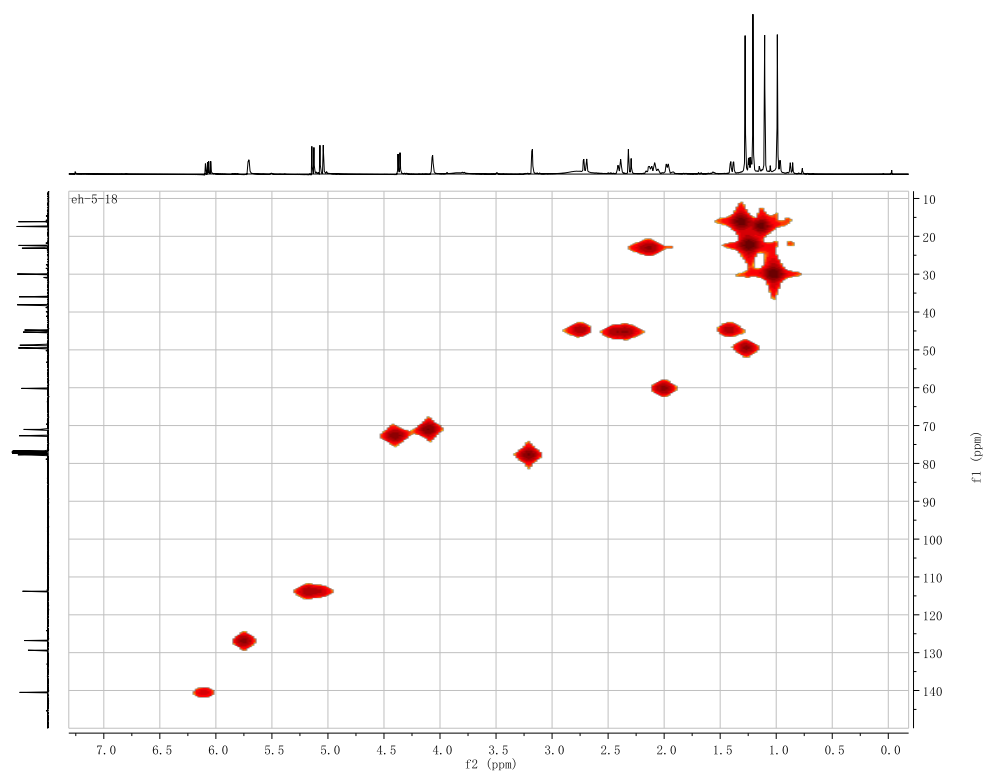


Figure SI60. HMBC spectrum of compound **7** (CDCl₃)

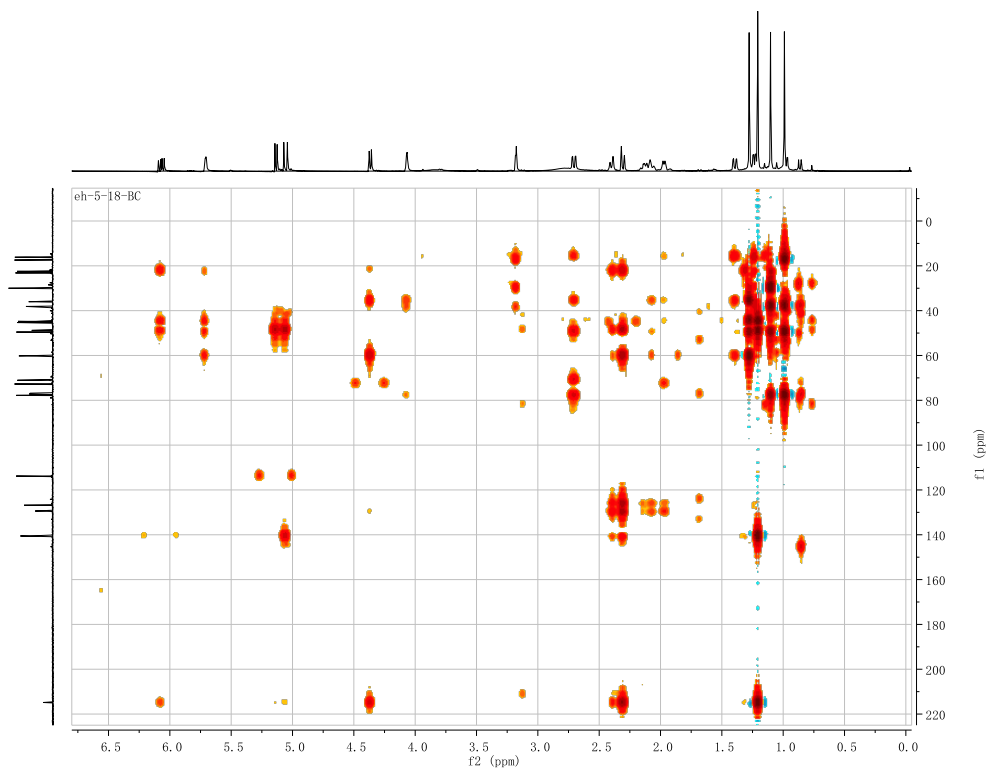


Figure SI61. NOESY spectrum of compound **7** (CDCl₃)

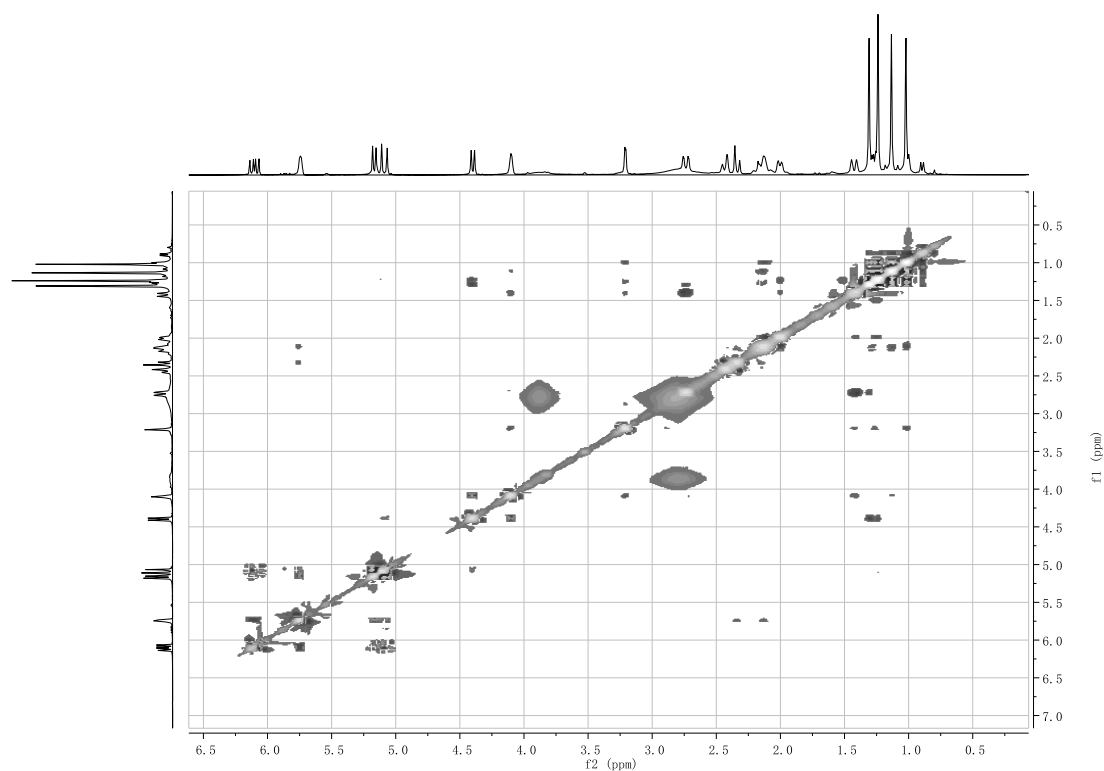


Figure SI62. HRESIMS spectrum of compound **7** (CDCl₃)

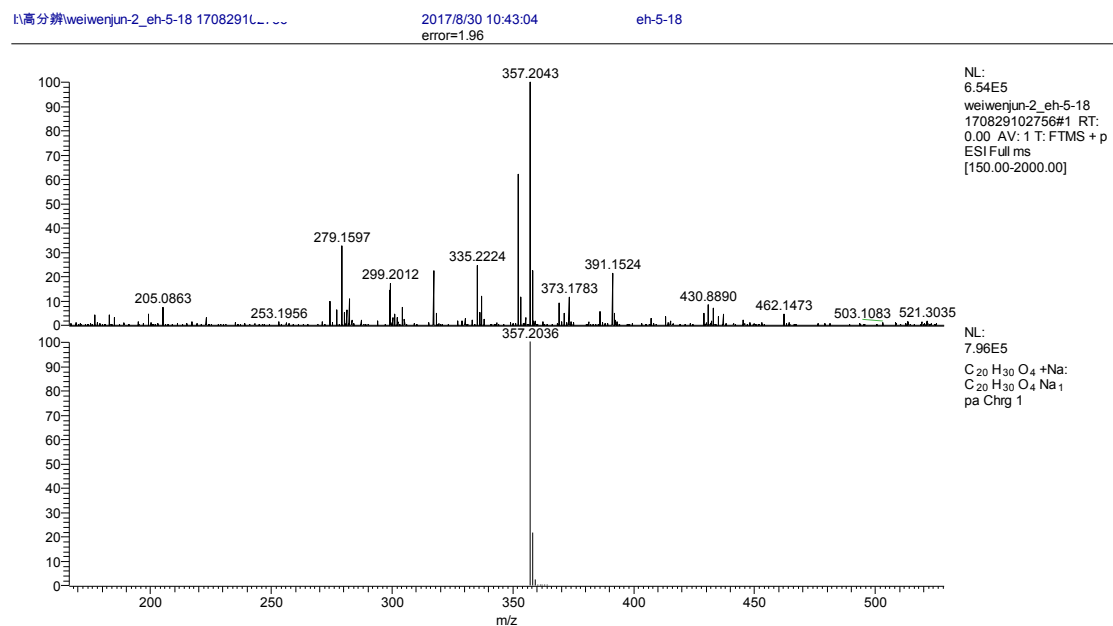


Figure SI63. IR spectrum of compound **7** (CDCl₃)

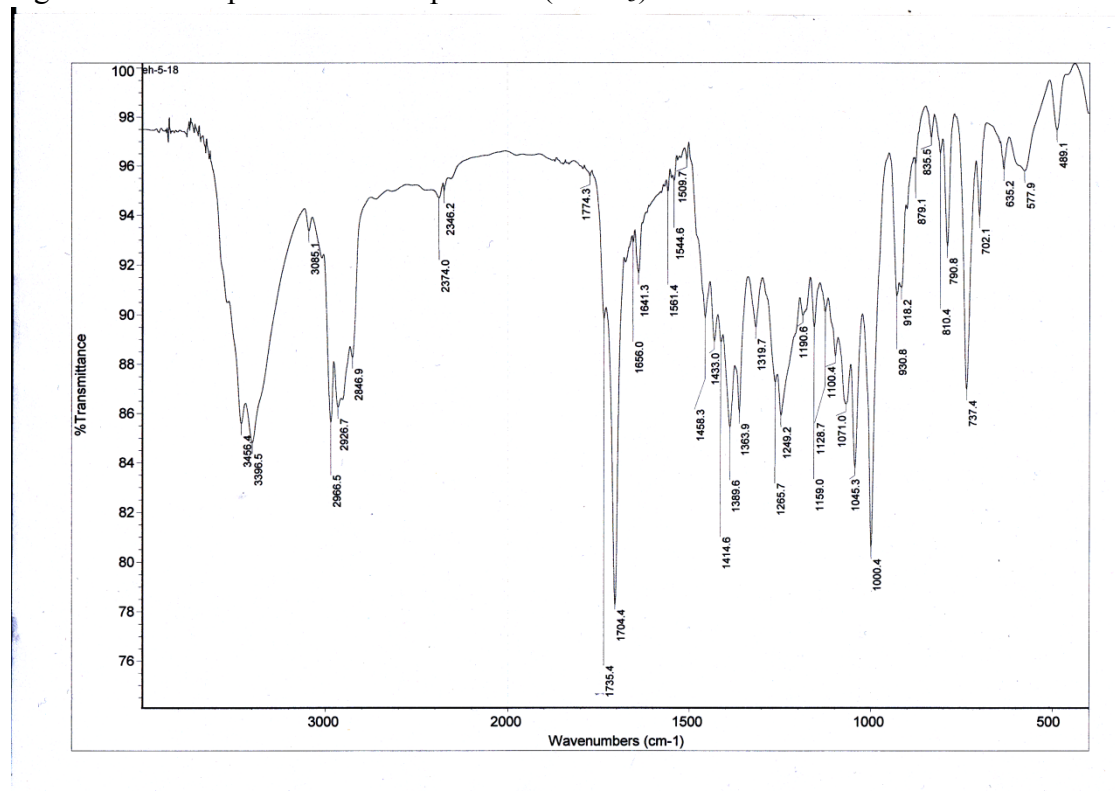


Figure SI64. ¹H NMR spectrum of compound **8** (CDCl₃)

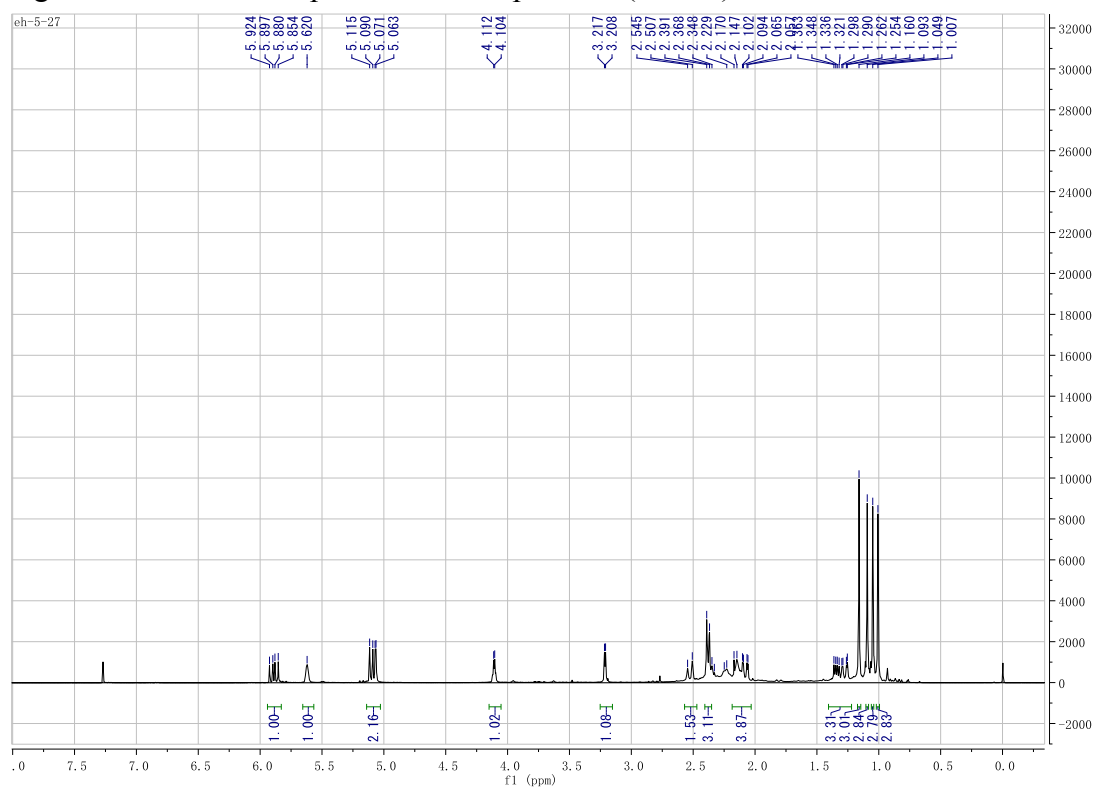


Figure SI65. ^{13}C NMR spectrum of compound **8** (CDCl_3)

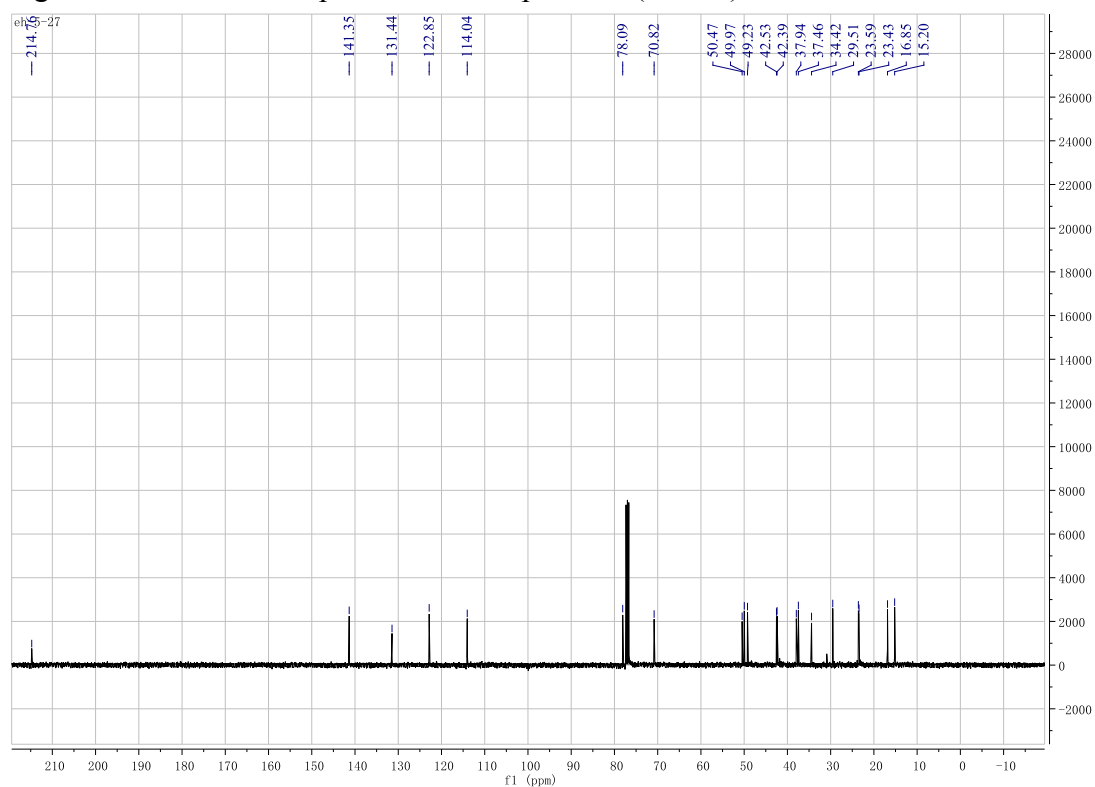


Figure SI66. DEPT spectrum of compound **8** (CDCl_3)

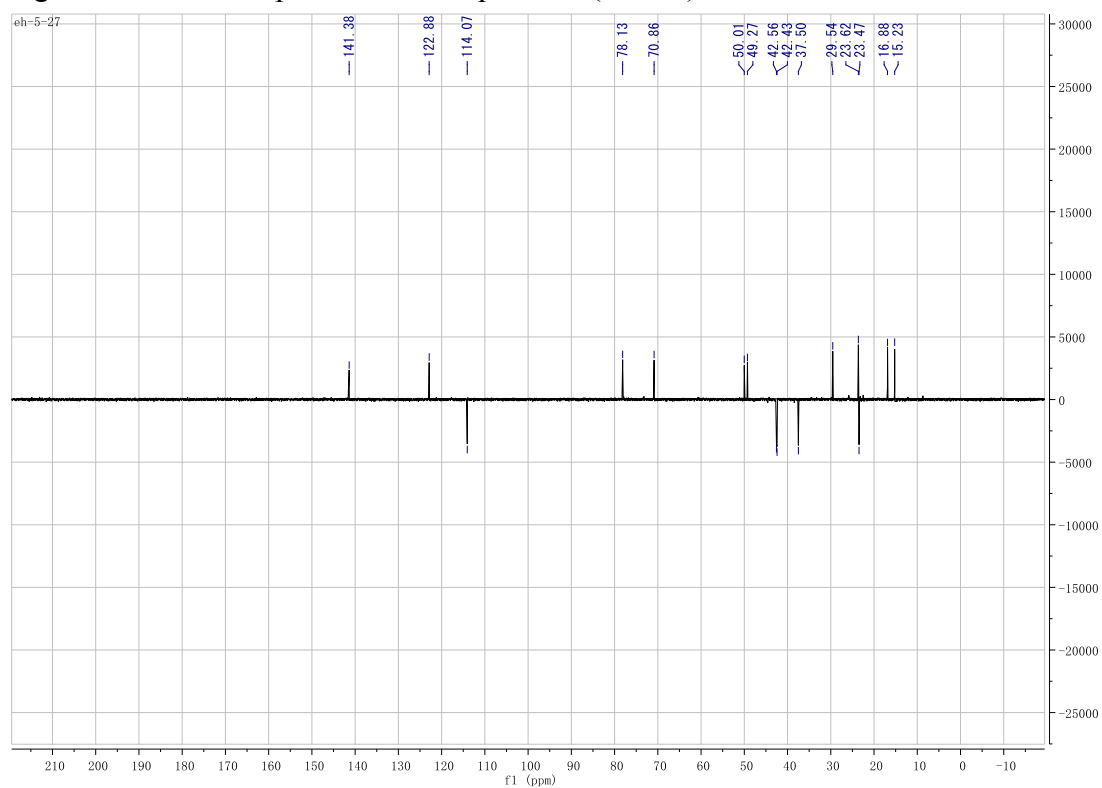


Figure SI67. ^1H - ^1H COSY spectrum of compound **8** (CDCl_3)

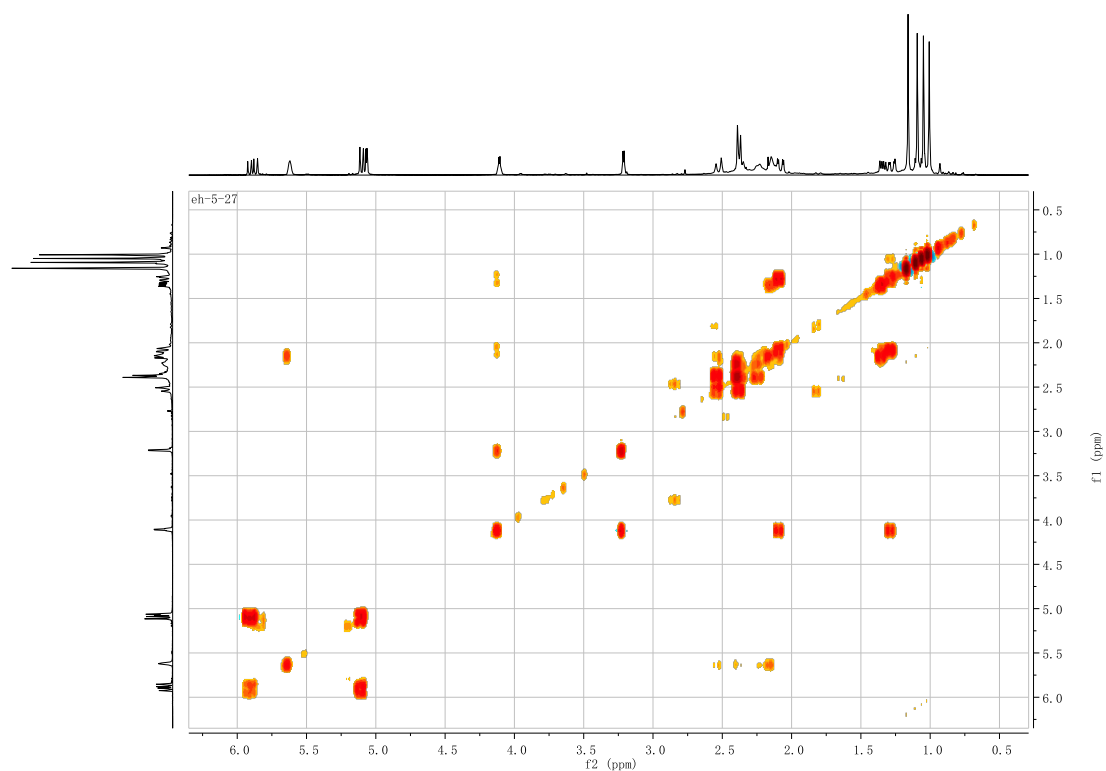


Figure SI68. HSQC spectrum of compound **8** (CDCl_3)

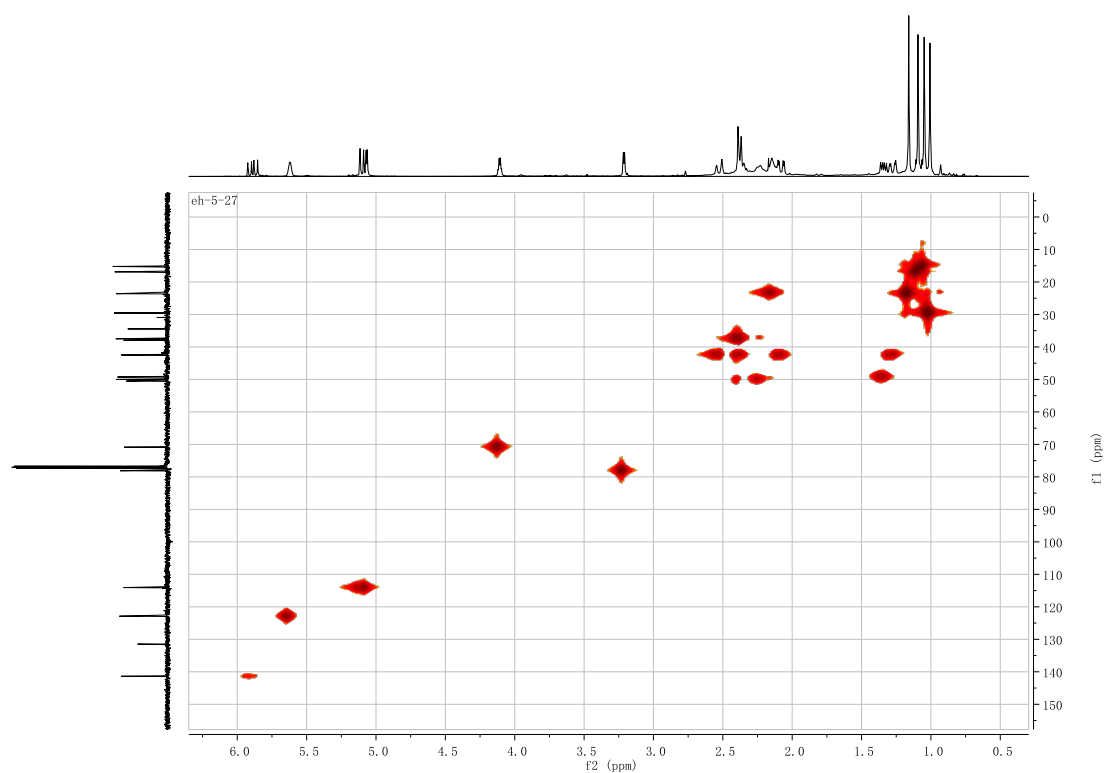


Figure SI69. HMBC spectrum of compound **8** (CDCl₃)

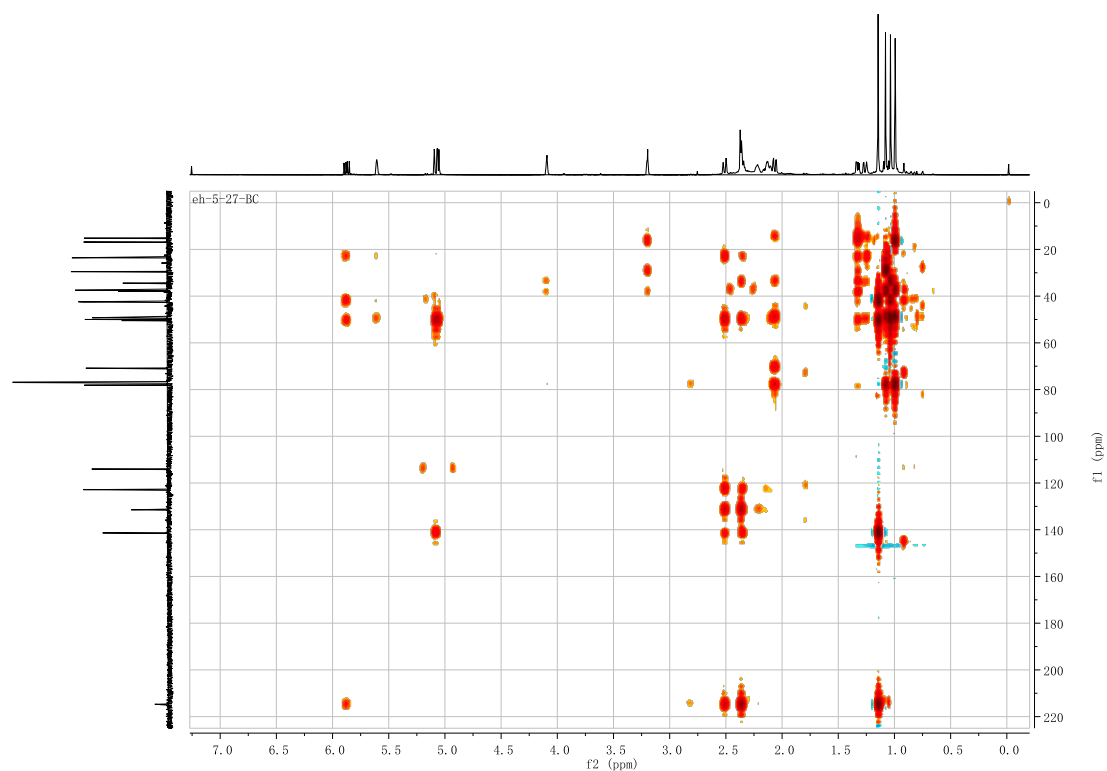


Figure SI70. NOESY spectrum of compound **8** (CDCl₃)

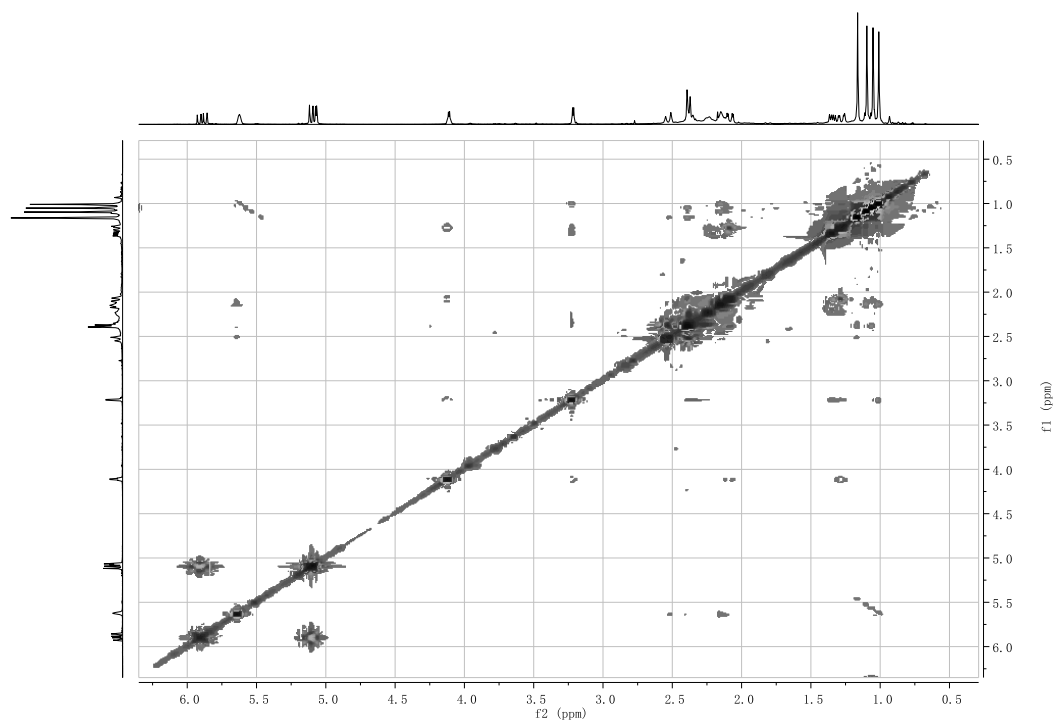


Figure SI71. HRESIMS spectrum of compound **8** (CDCl₃)

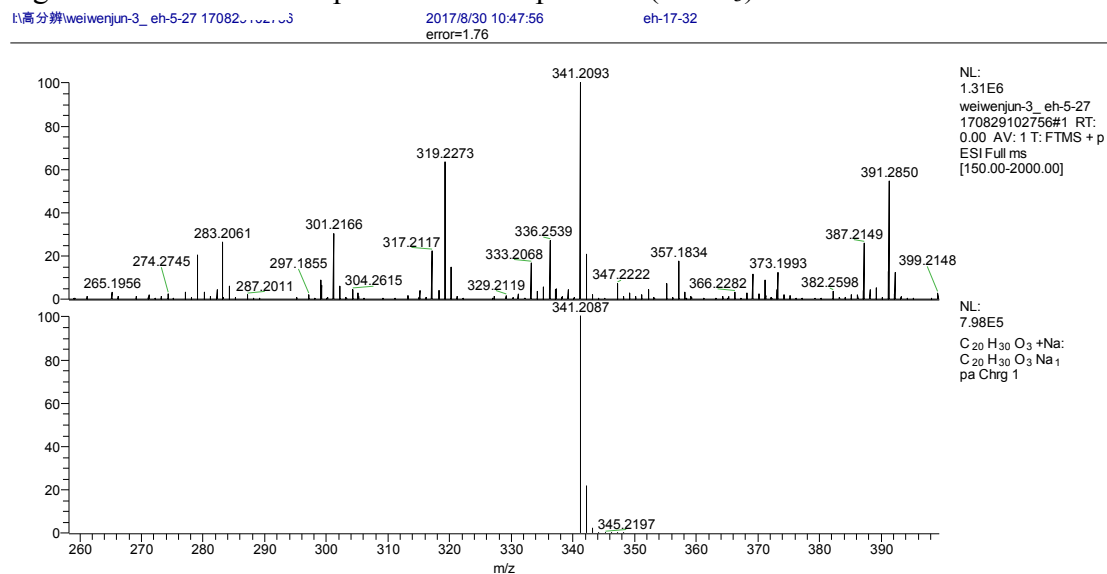


Figure SI72. IR spectrum of compound **8** (CDCl₃)

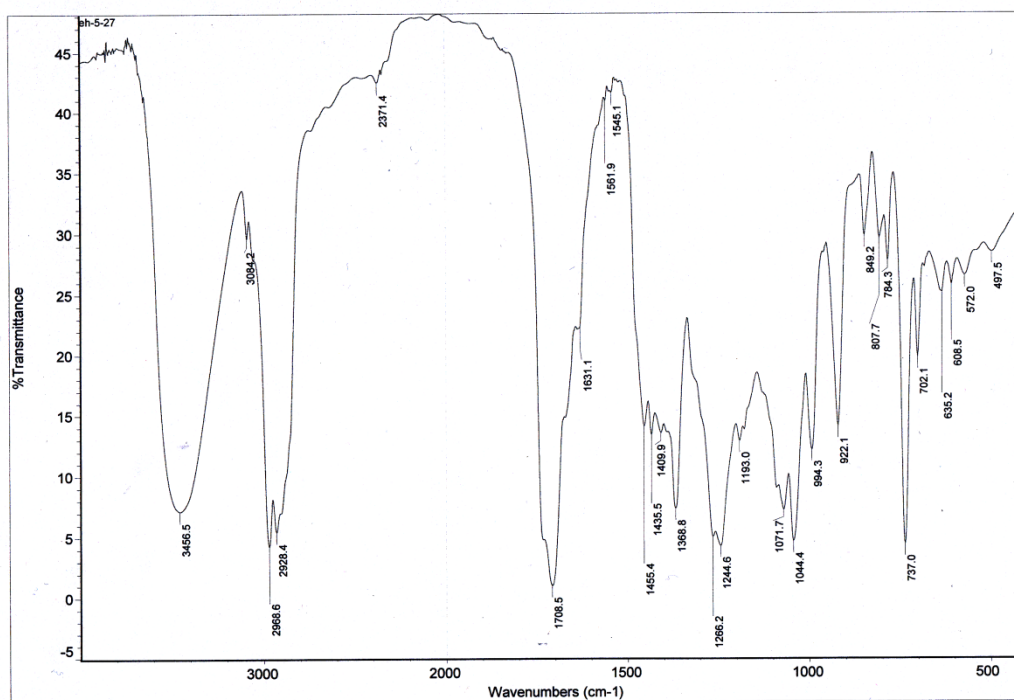


Figure SI73. ^1H NMR spectrum of compound **9** (CDCl_3)

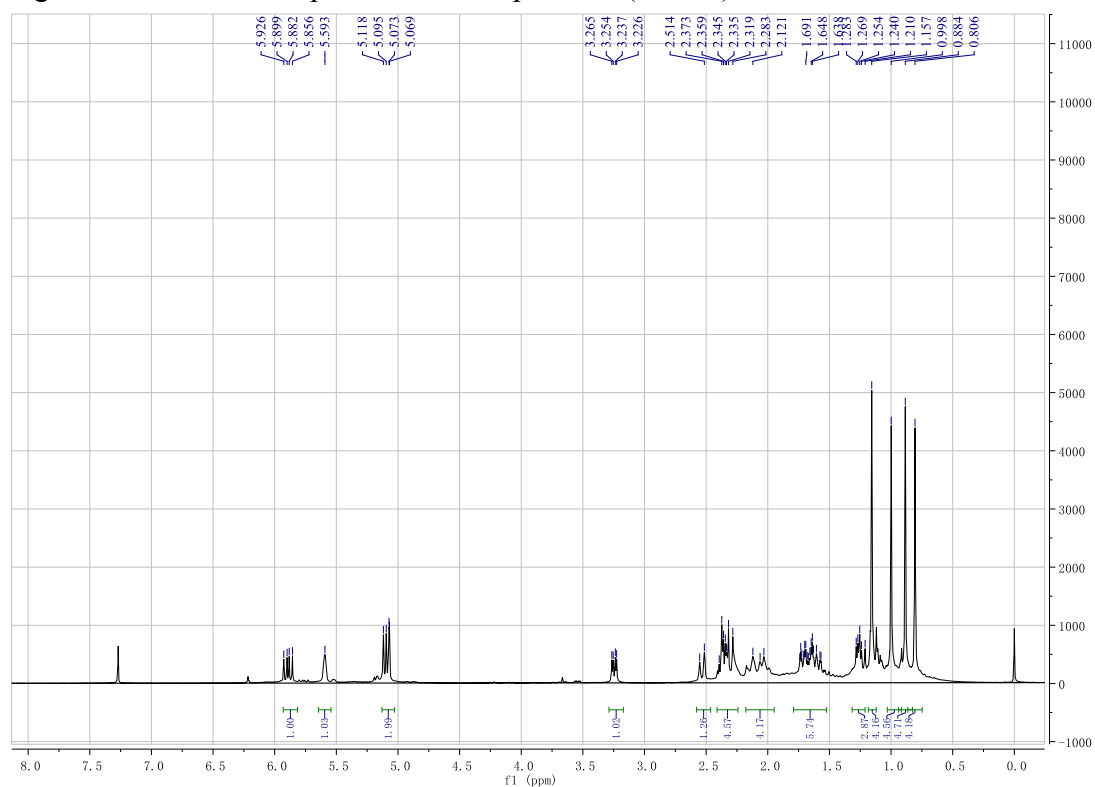


Figure SI74. ^{13}C NMR spectrum of compound **9** (CDCl_3)

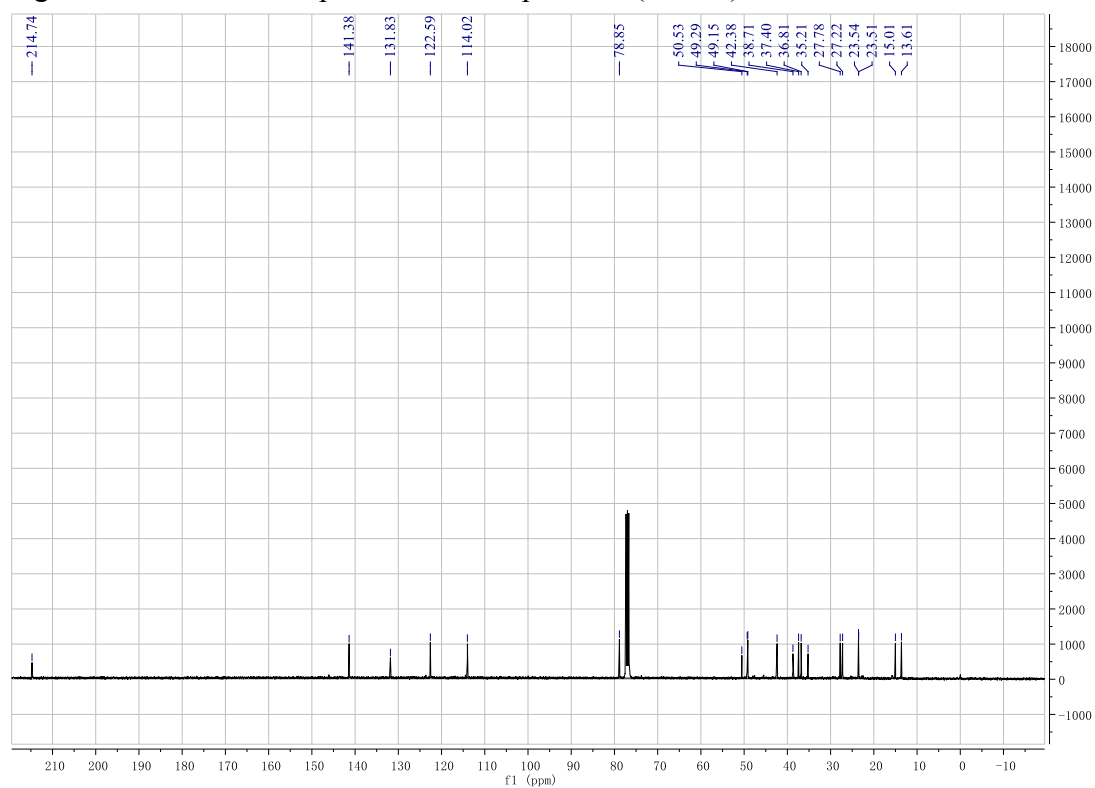


Figure SI75. DEPT spectrum of compound **9** (CDCl₃)

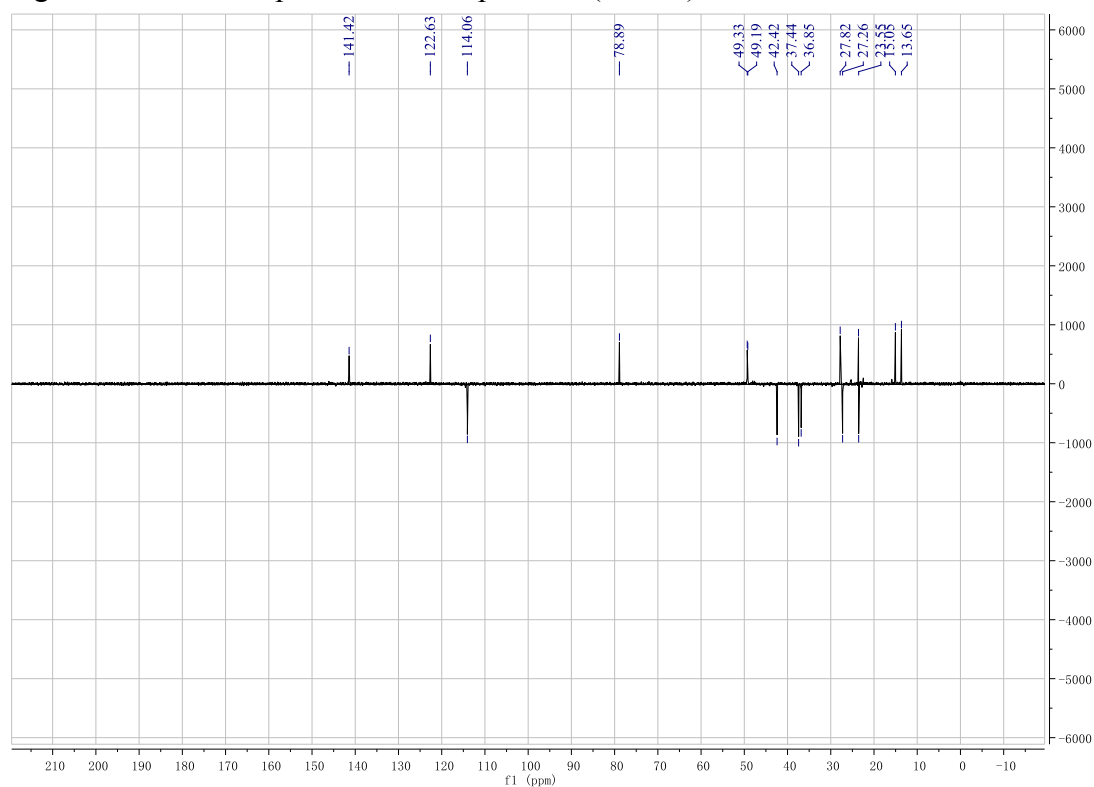


Figure SI76. ¹H-¹H COSY spectrum of compound **9** (CDCl₃)

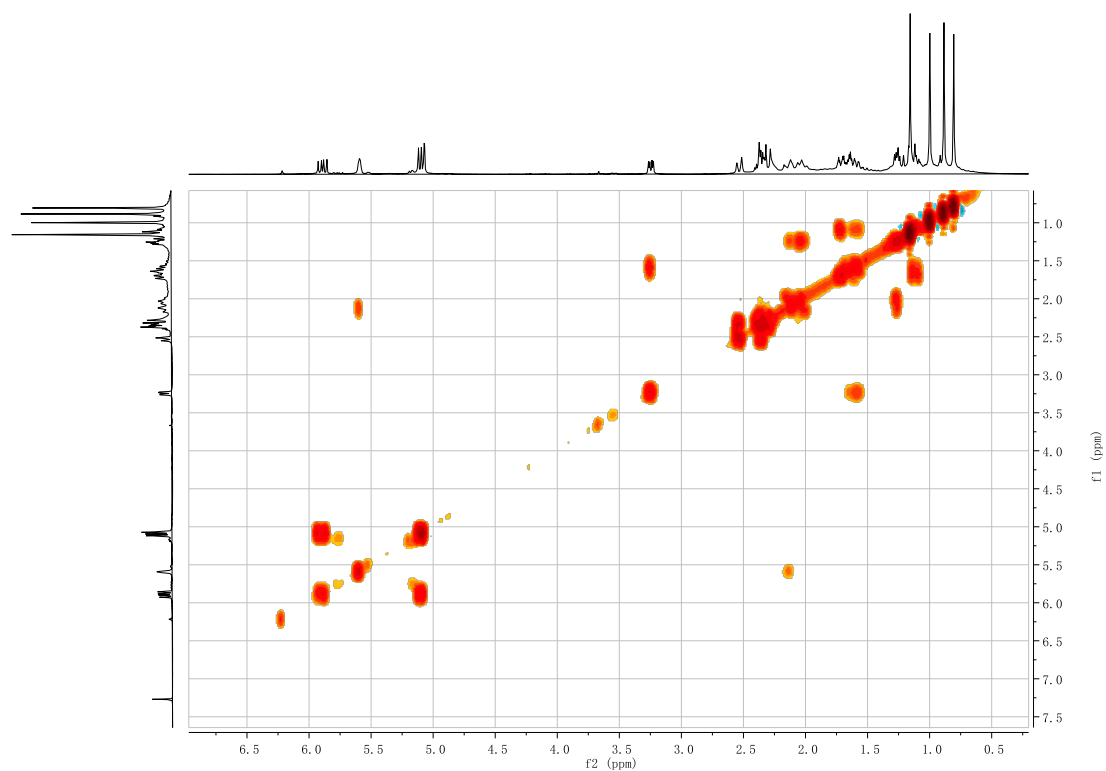


Figure SI77. HSQC spectrum of compound **9** (CDCl₃)

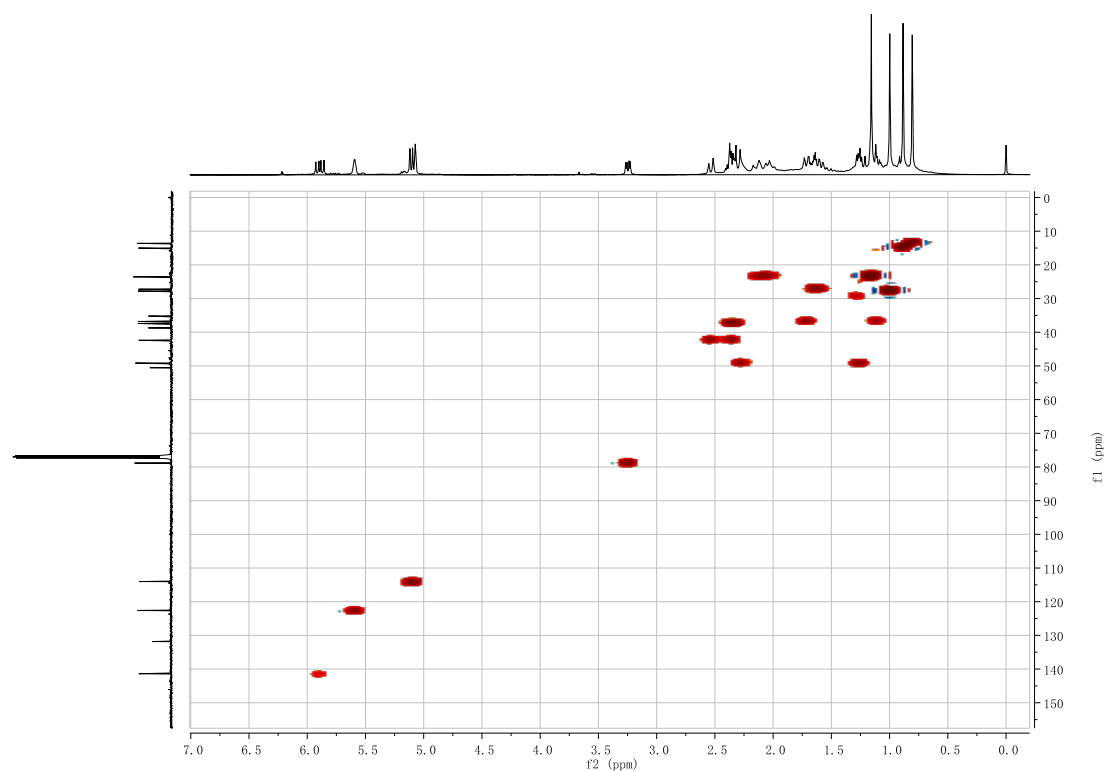


Figure SI78. HMBC spectrum of compound **9** (CDCl₃)

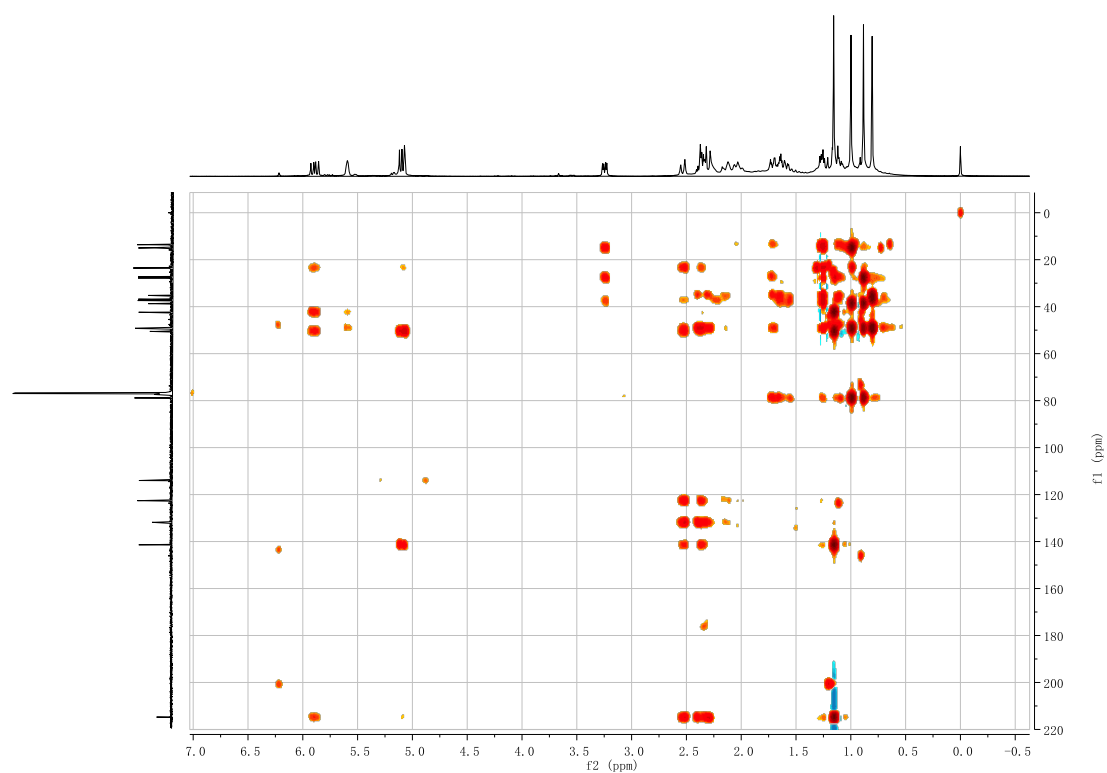


Figure SI79. NOESY spectrum of compound **9** (CDCl₃)

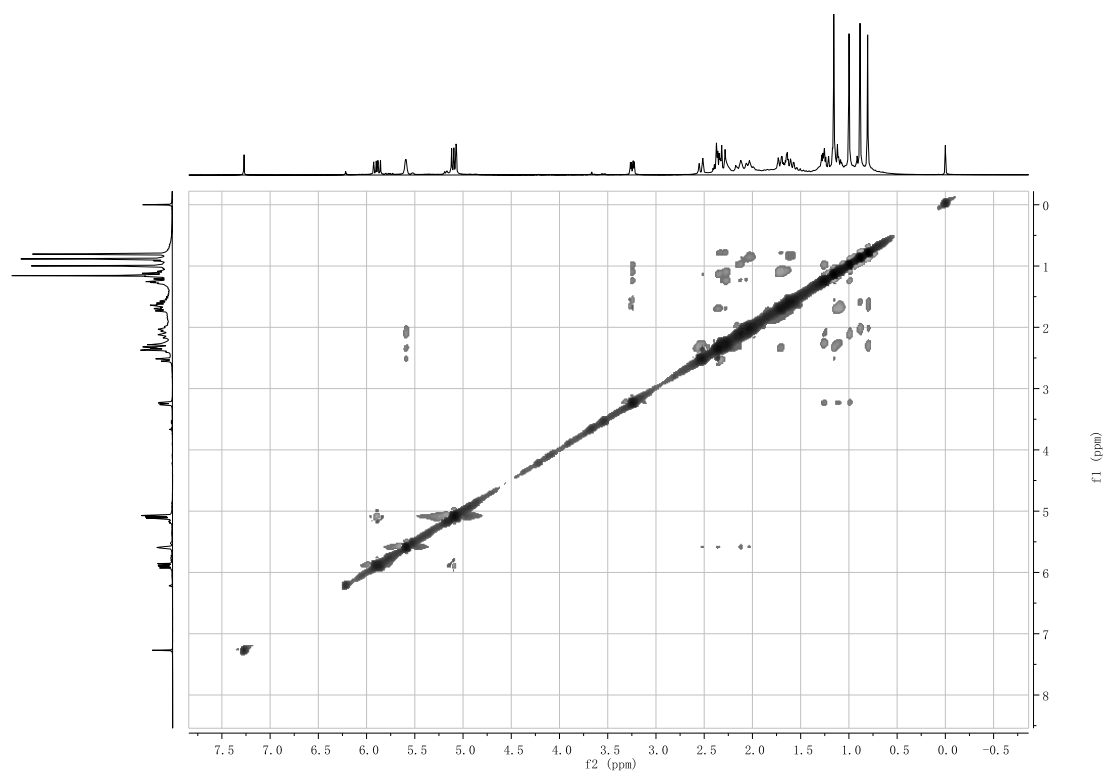


Figure SI80. HRESIMS spectrum of compound **9** (CDCl₃)

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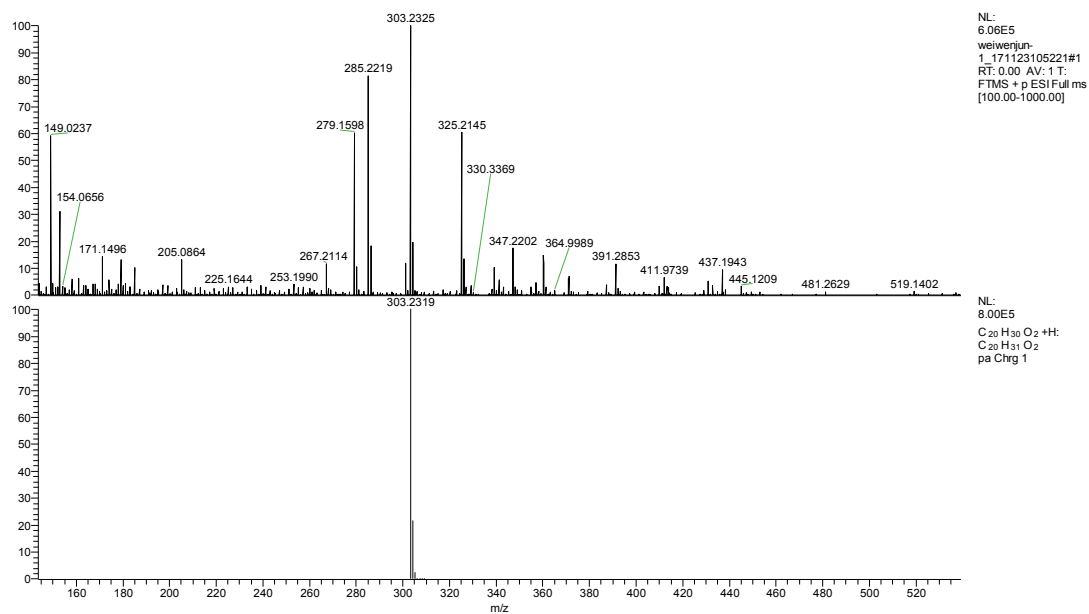


Figure SI81. IR spectrum of compound **9** (CDCl₃)

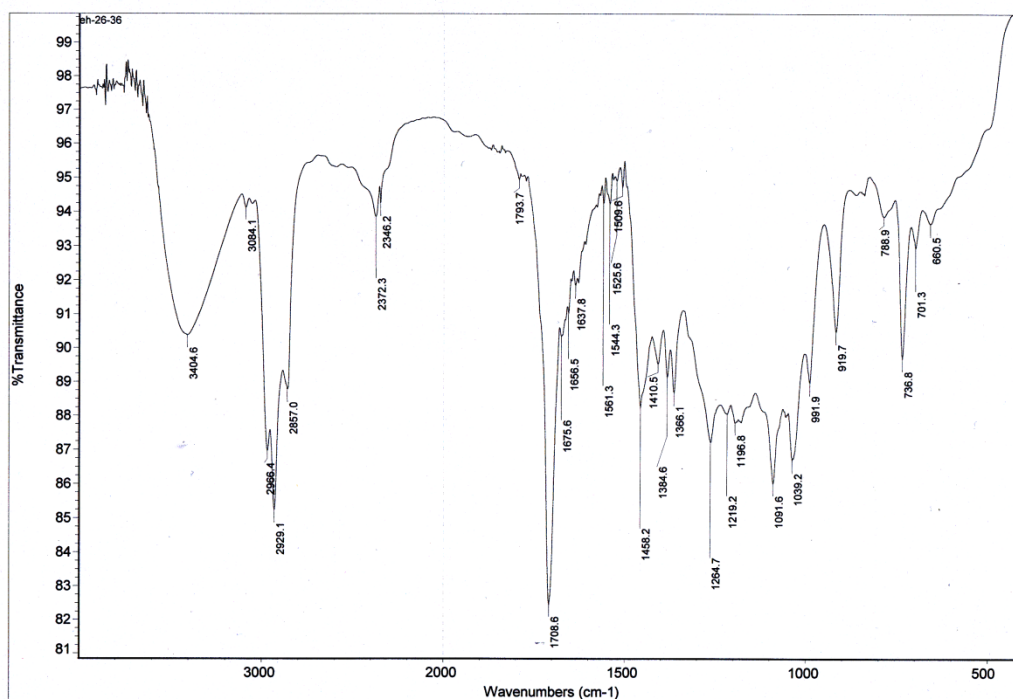


Figure SI82. ¹H NMR spectrum of compound **10** (CDCl₃)

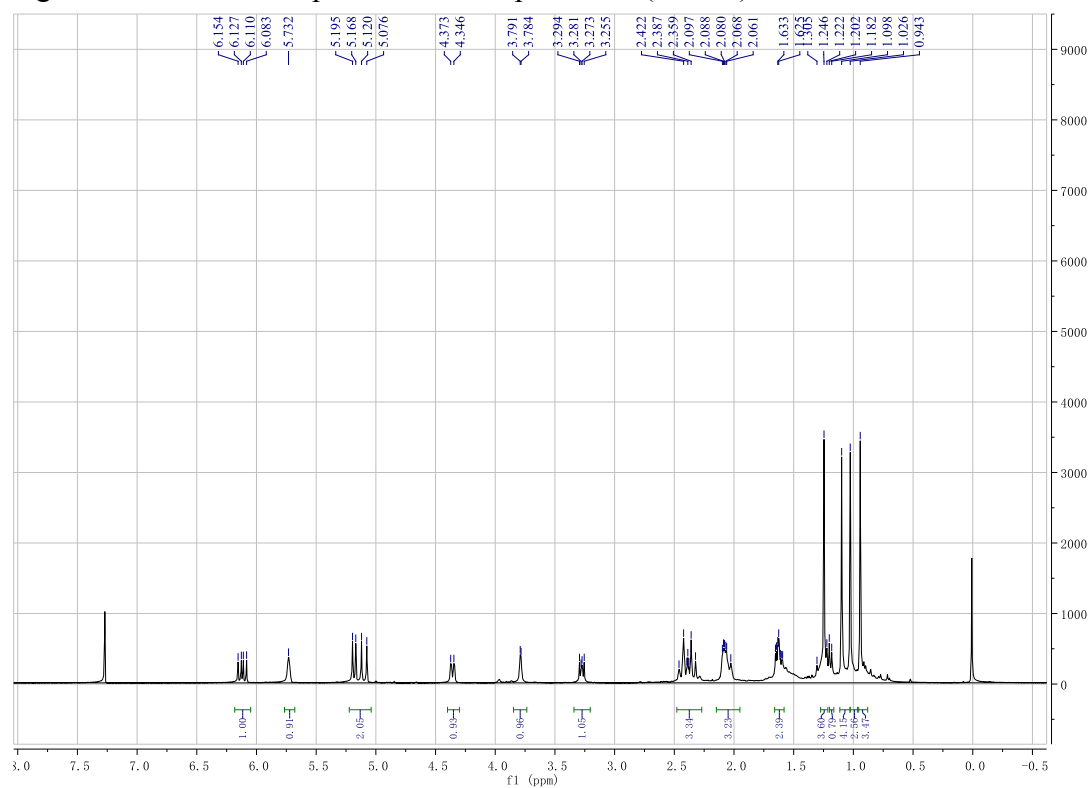


Figure SI83. ^{13}C NMR spectrum of compound **10** (CDCl_3)

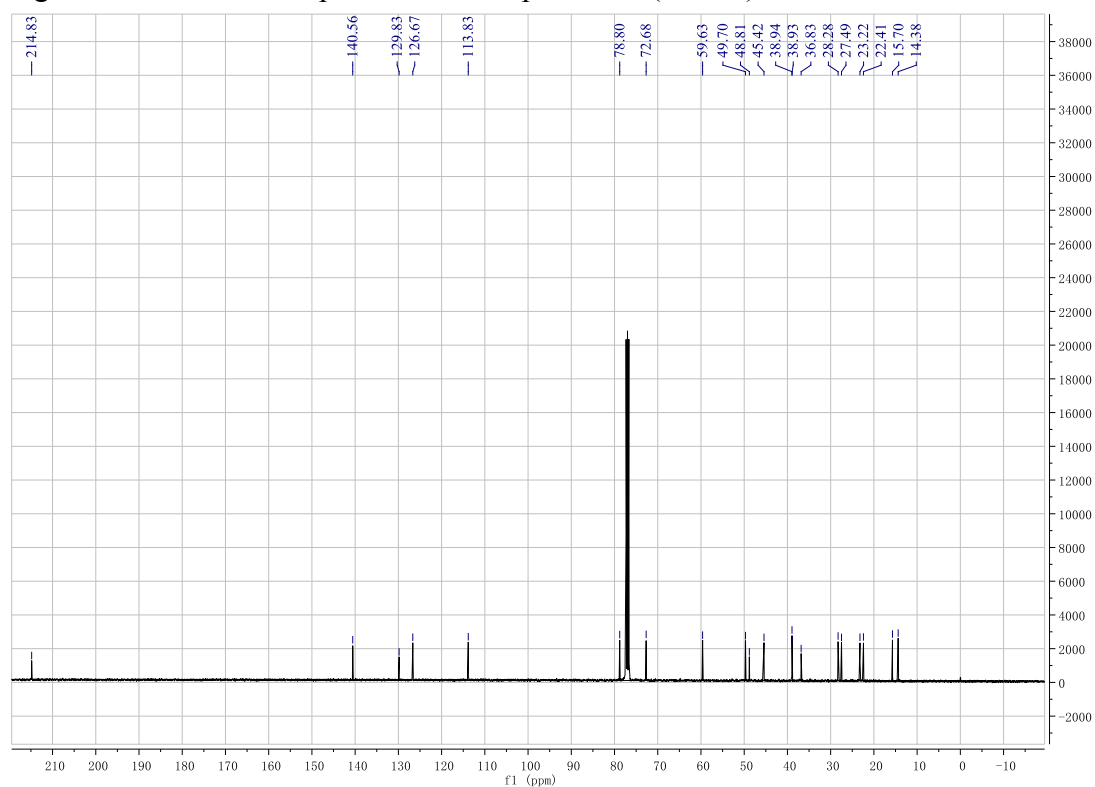


Figure SI84. DEPT spectrum of compound **10** (CDCl_3)

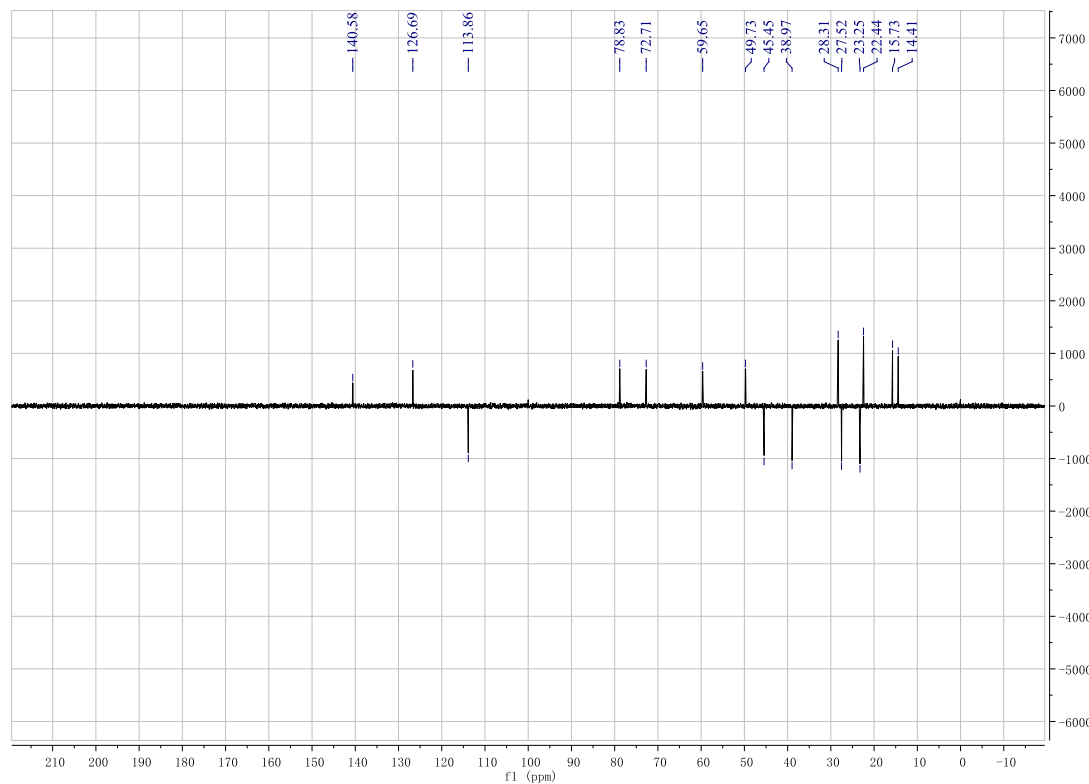


Figure SI85. ^1H - ^1H COSY spectrum of compound **10** (CDCl_3)

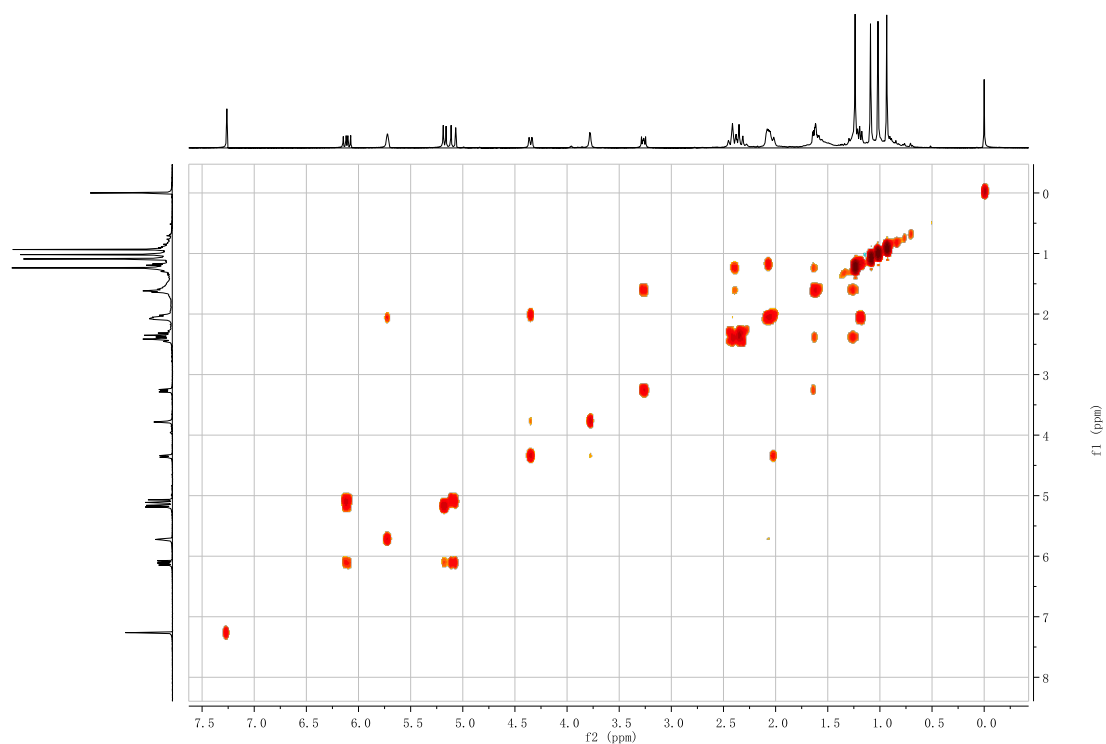


Figure SI86. HSQC spectrum of compound **10** (CDCl_3)

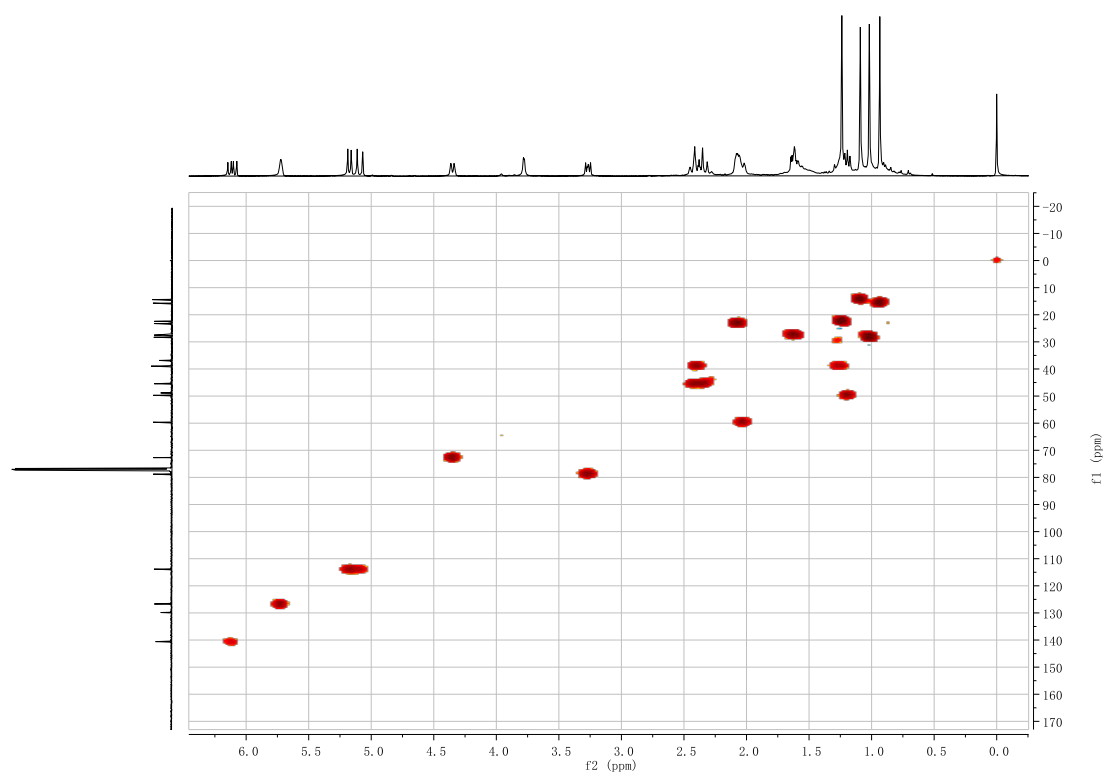


Figure SI87. HMBC spectrum of compound **10** (CDCl₃)

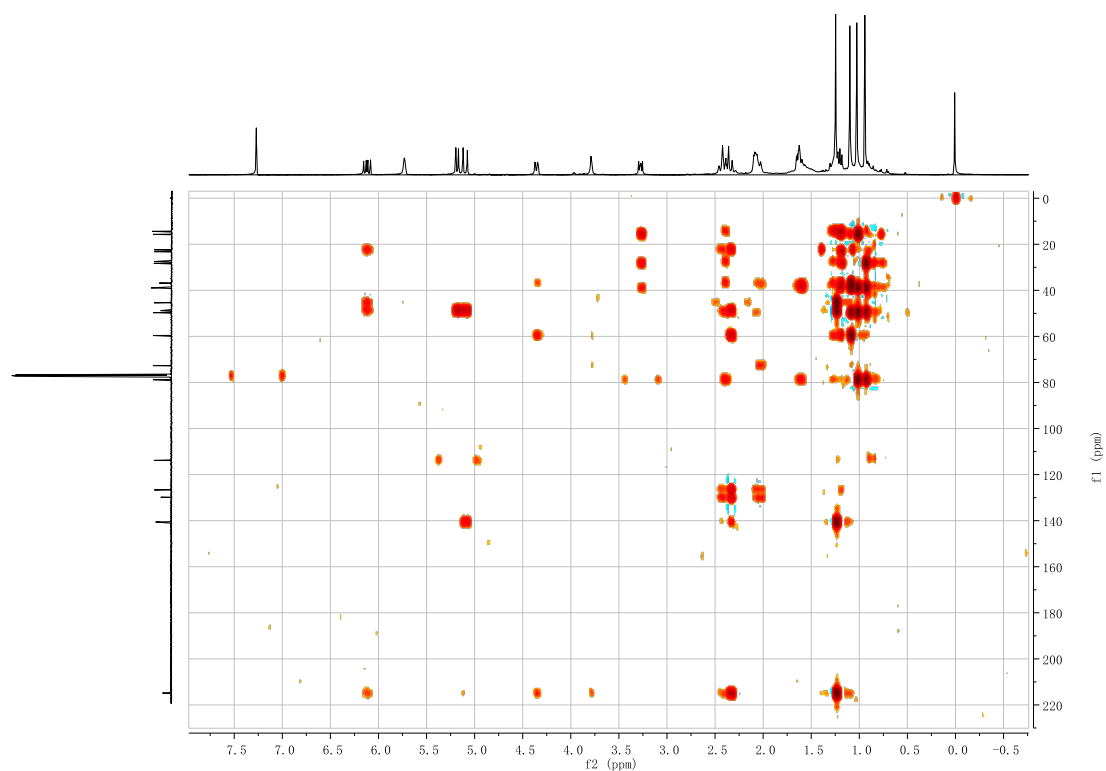


Figure SI88. NOESY spectrum of compound **10** (CDCl₃)

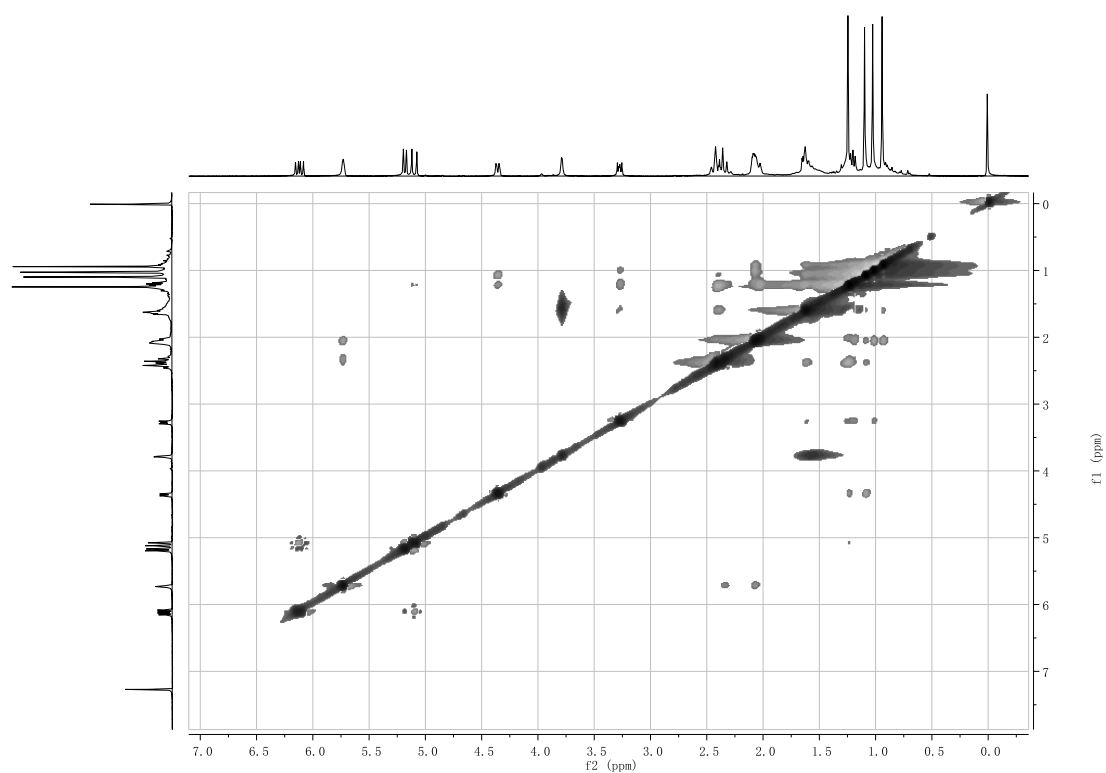


Figure SI89. HRESIMS spectrum of compound **10** (CDCl₃)

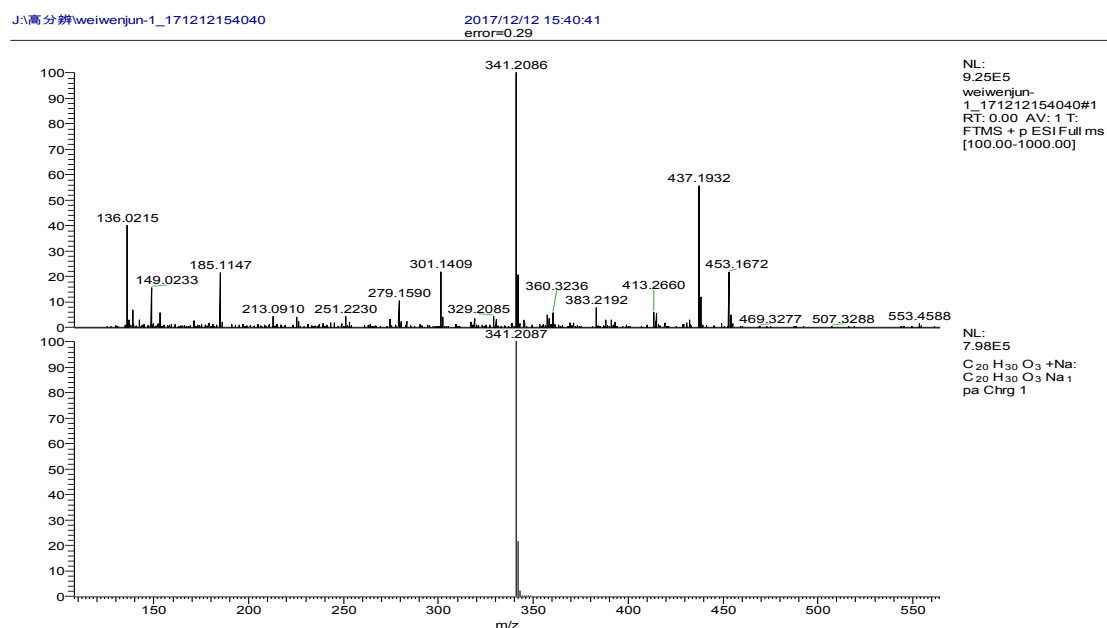


Figure SI90. IR spectrum of compound **10** (CDCl₃)

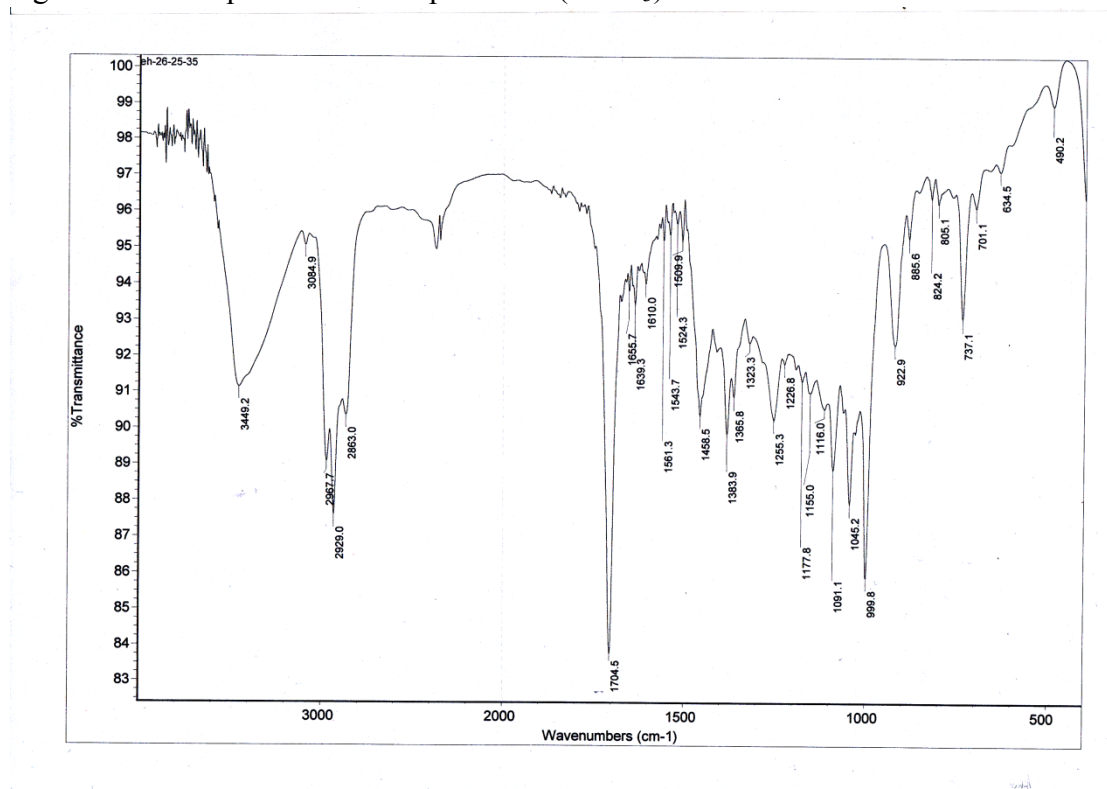


Figure SI91. ^1H NMR spectrum of compound **14** (CDCl_3)

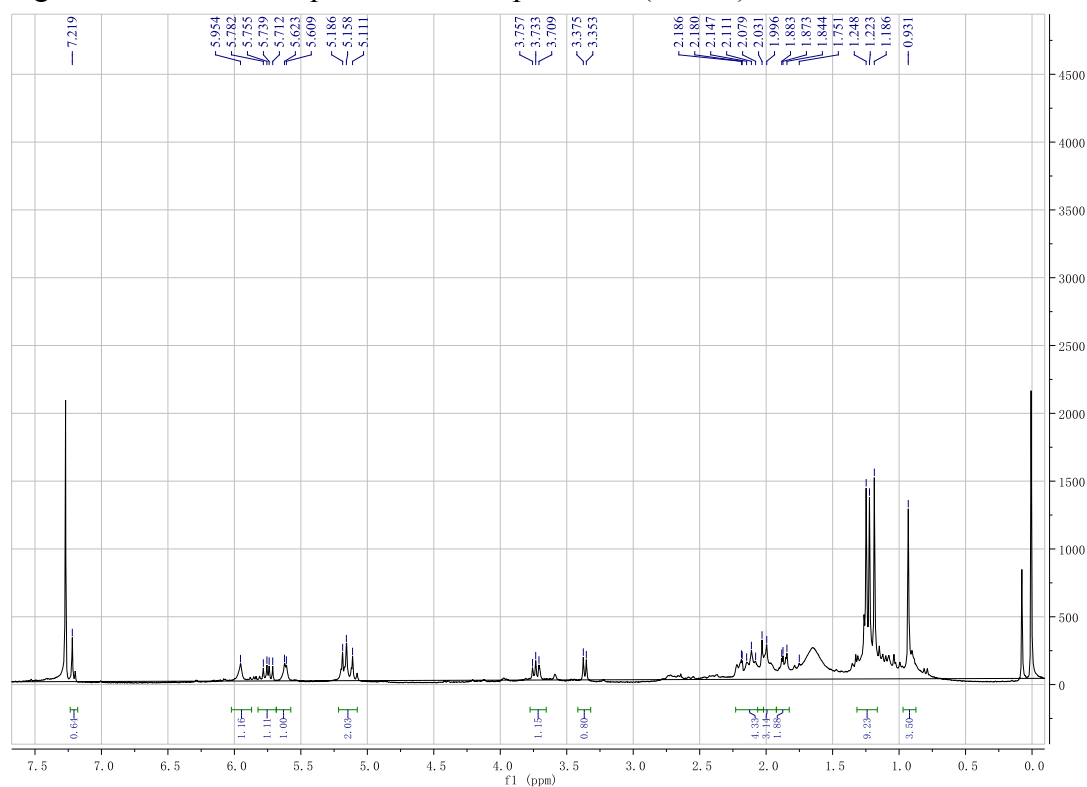


Figure SI92. ^{13}C NMR spectrum of compound **14** (CDCl_3)

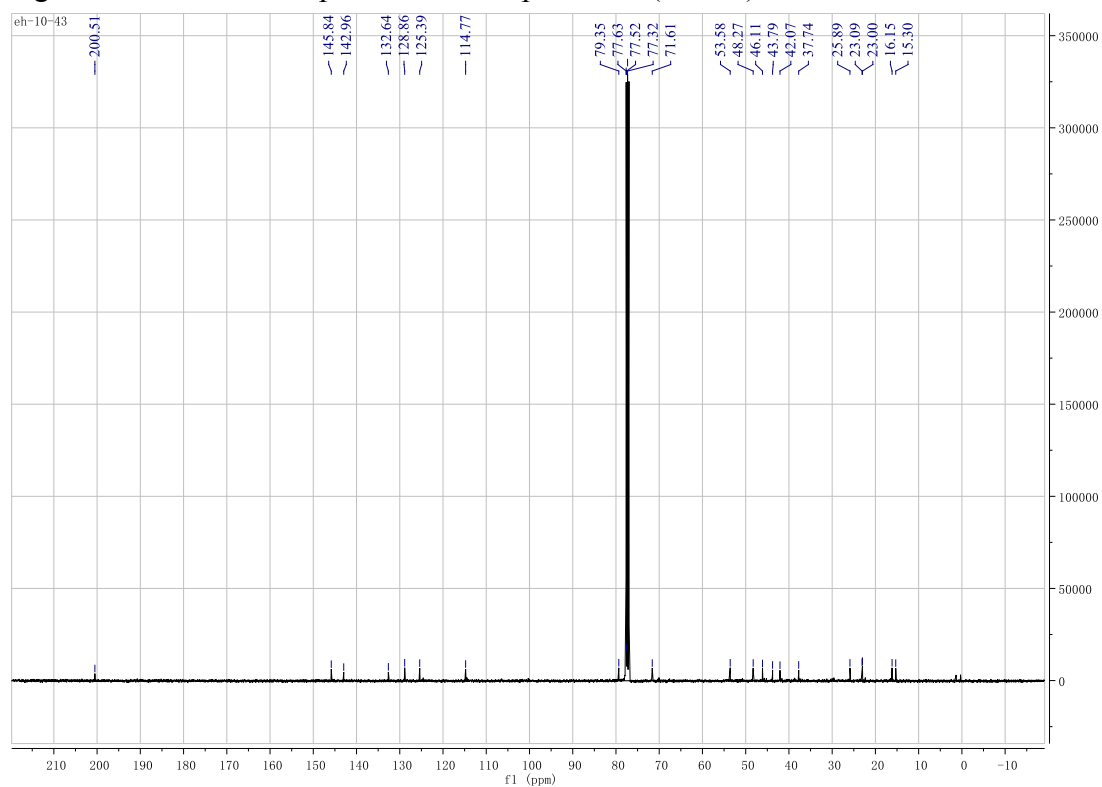


Figure SI93. DEPT spectrum of compound **14** (CDCl₃)

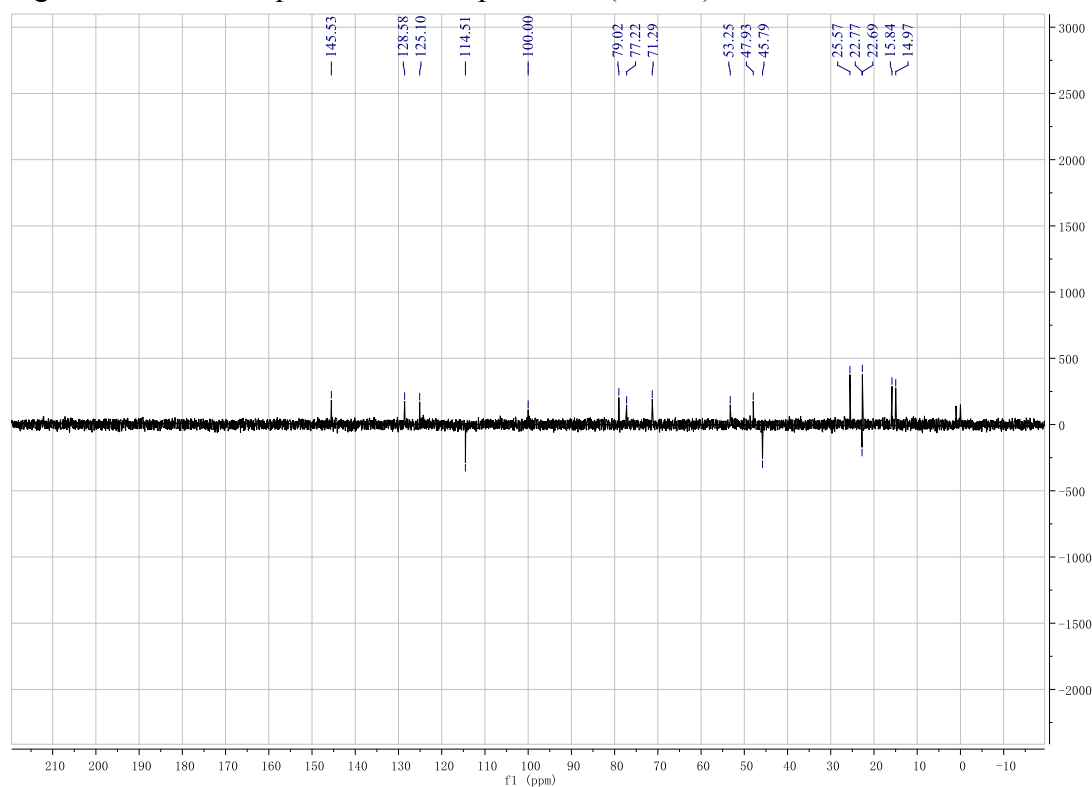


Figure SI94. ¹H-¹H COSY spectrum of compound **14** (CDCl₃)

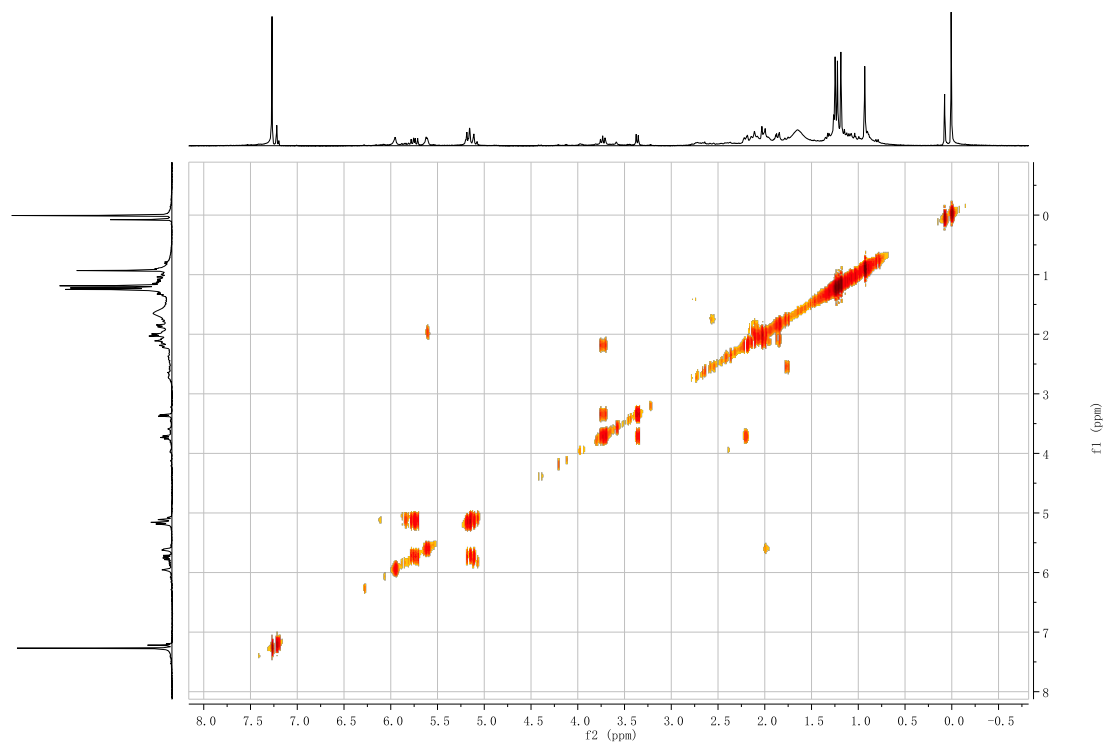


Figure SI95. HSQC spectrum of compound **14** (CDCl₃)

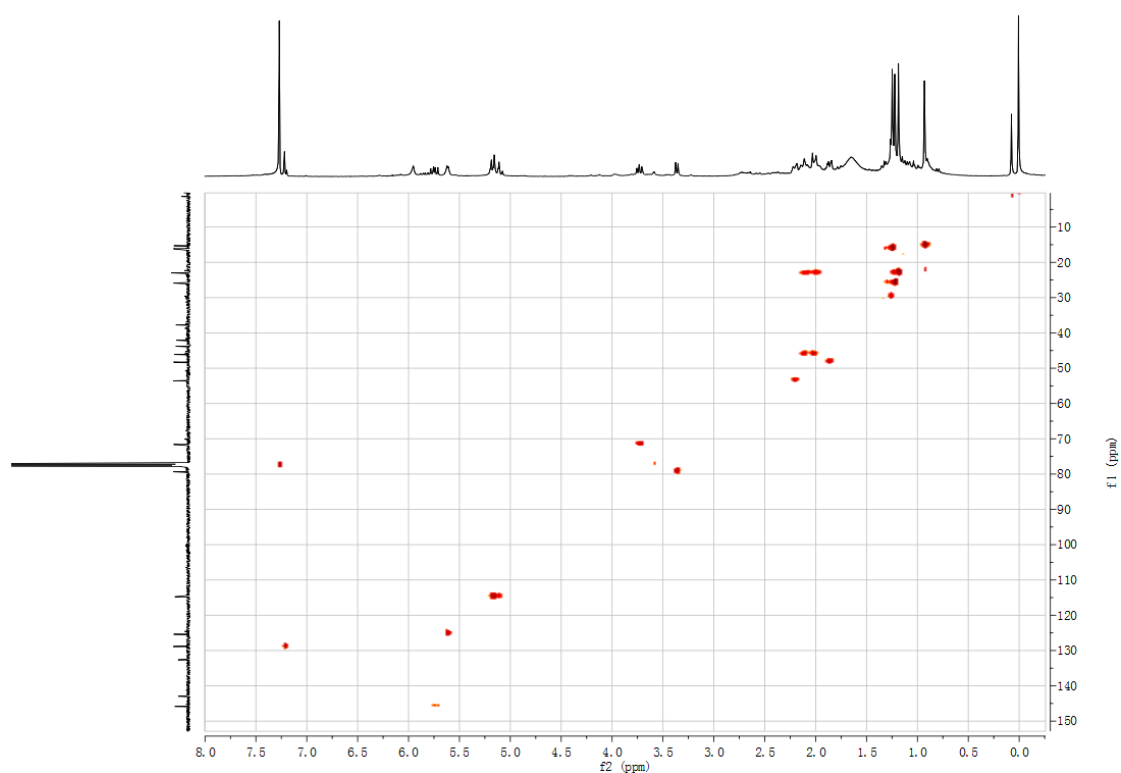


Figure SI96. HMBC spectrum of compound **14** (CDCl₃)

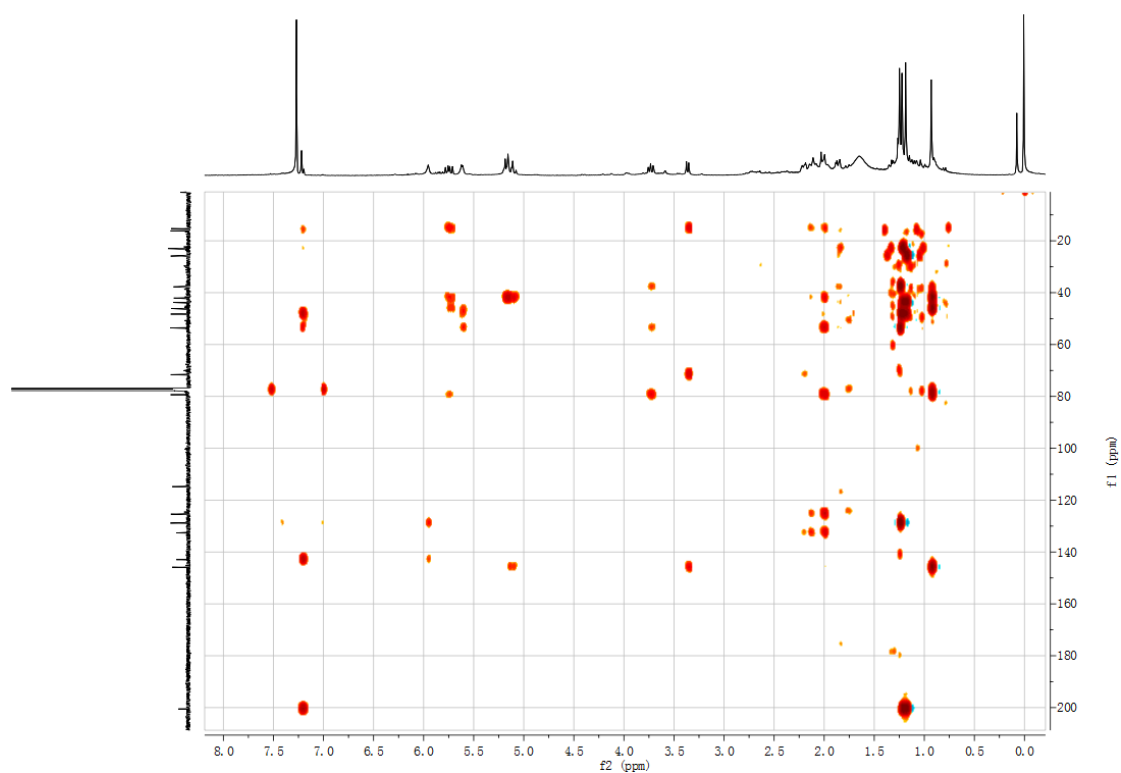


Figure SI97. NOESY spectrum of compound **14** (CDCl₃)

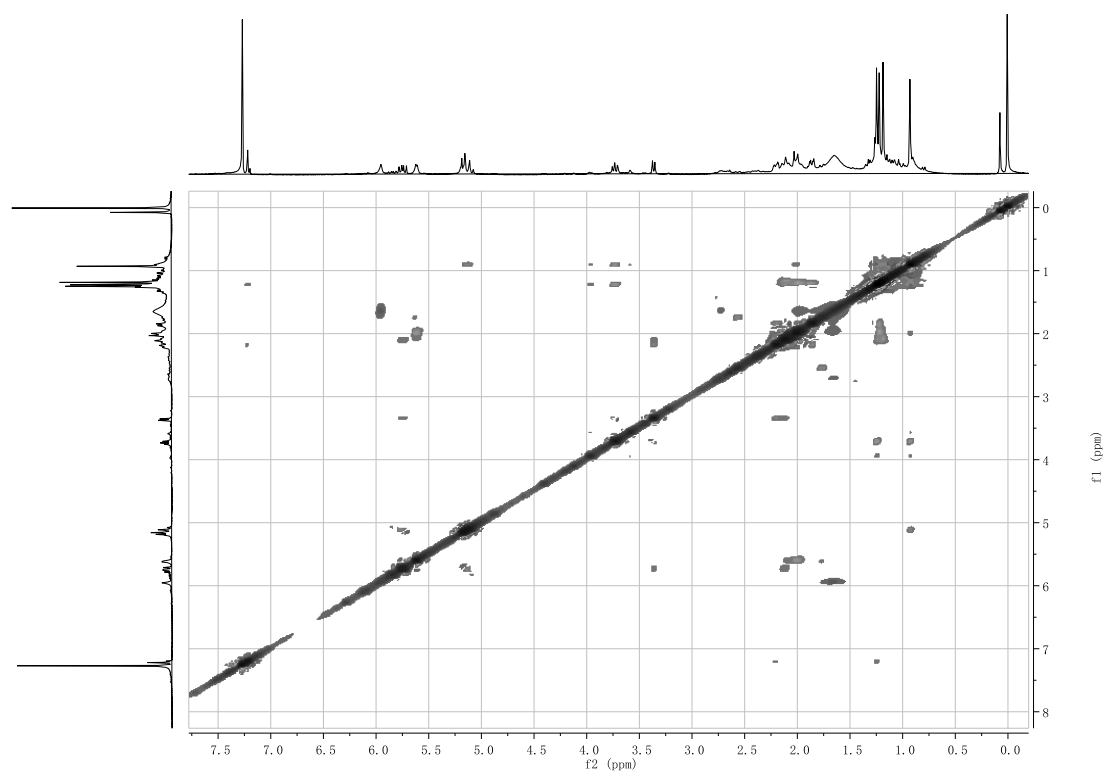


Figure SI98. HRESIMS spectrum of compound **14** (CDCl₃)

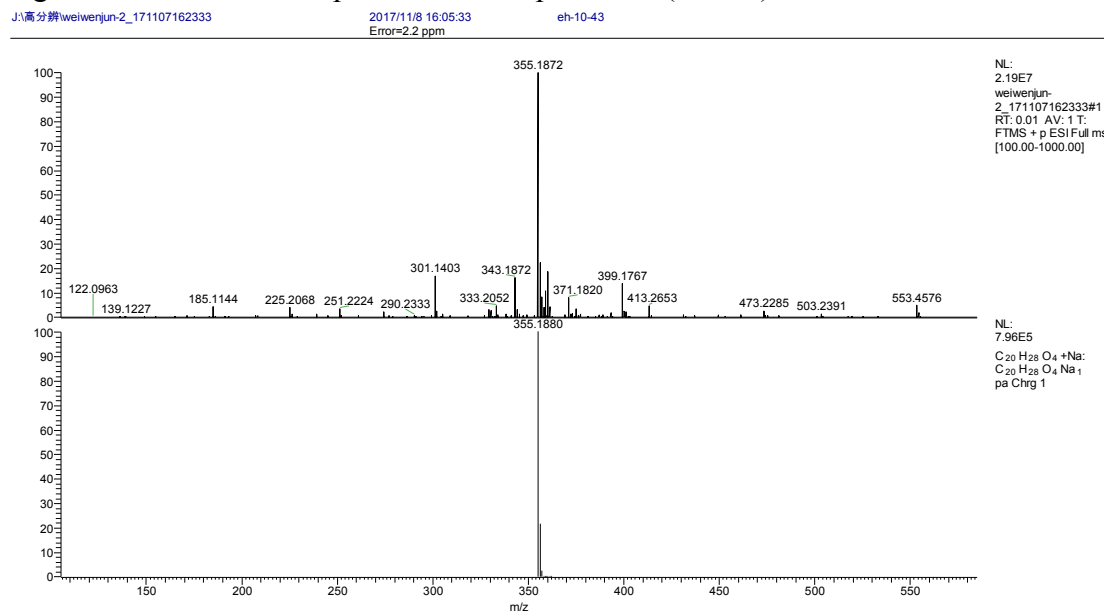


Figure SI99. IR spectrum of compound **14** (CDCl₃)

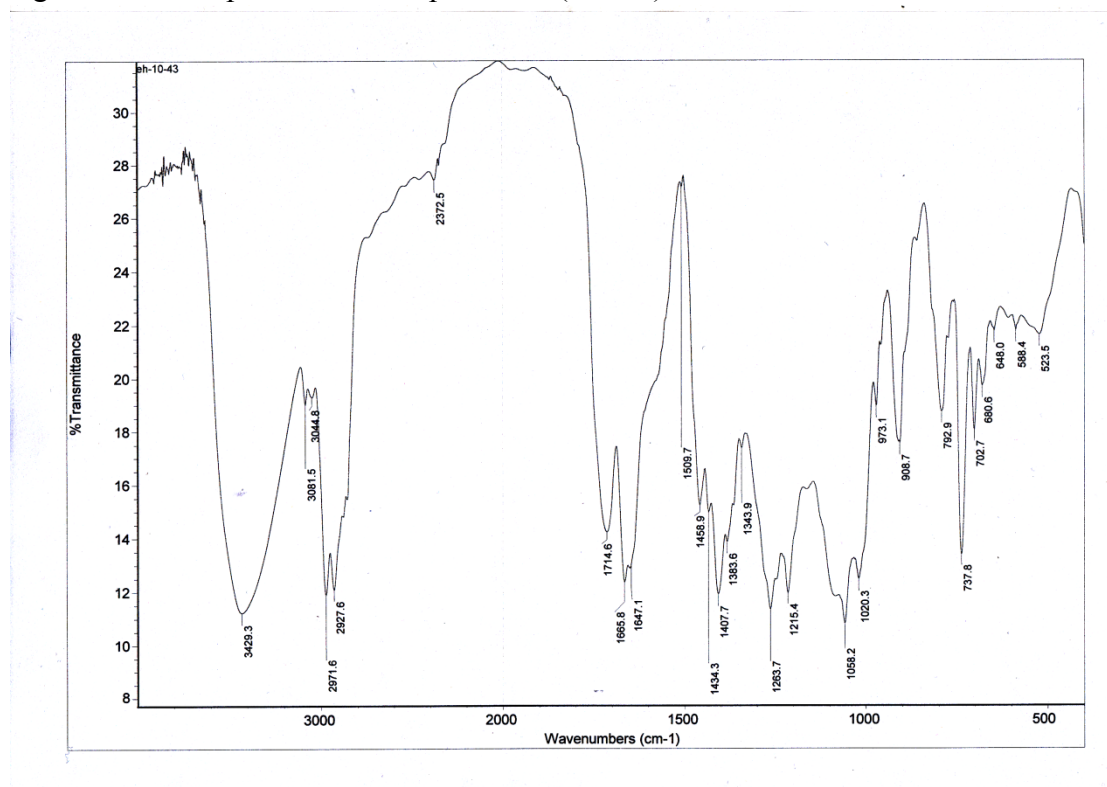


Figure SI100. ¹H NMR spectrum of compound **15** (CDCl₃)

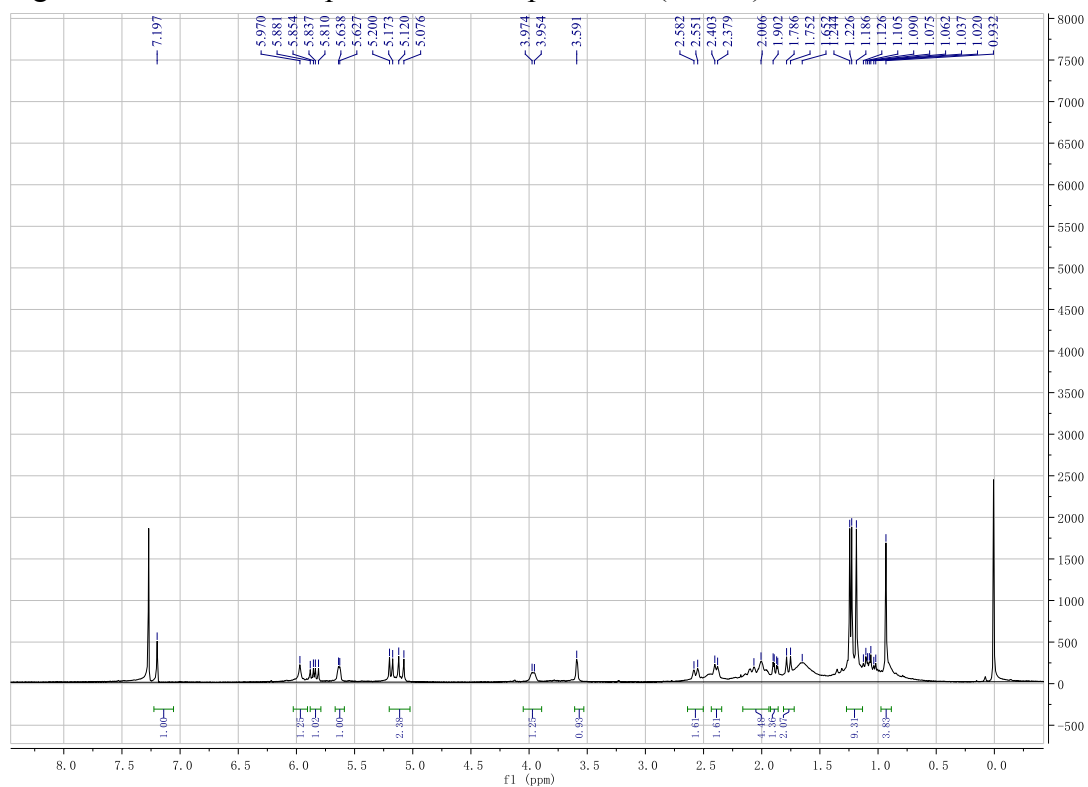


Figure SI101. ^{13}C NMR spectrum of compound **15** (CDCl_3)

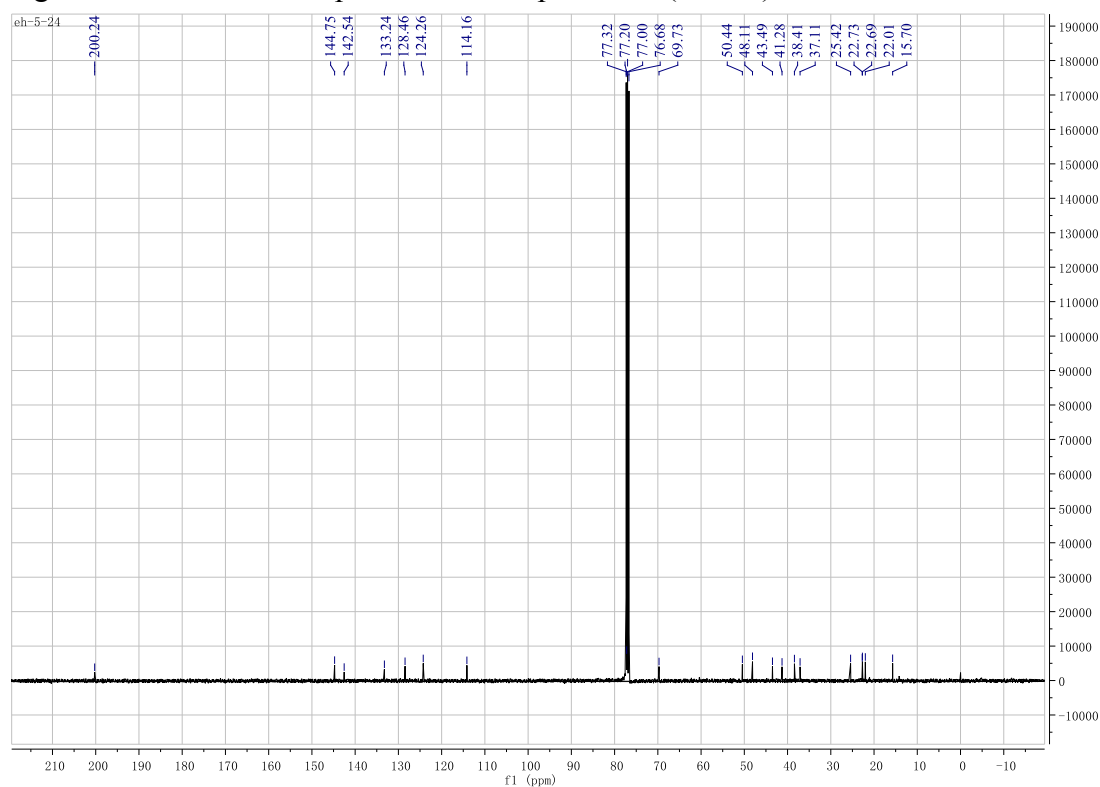


Figure SI102. DEPT spectrum of compound **15** (CDCl_3)

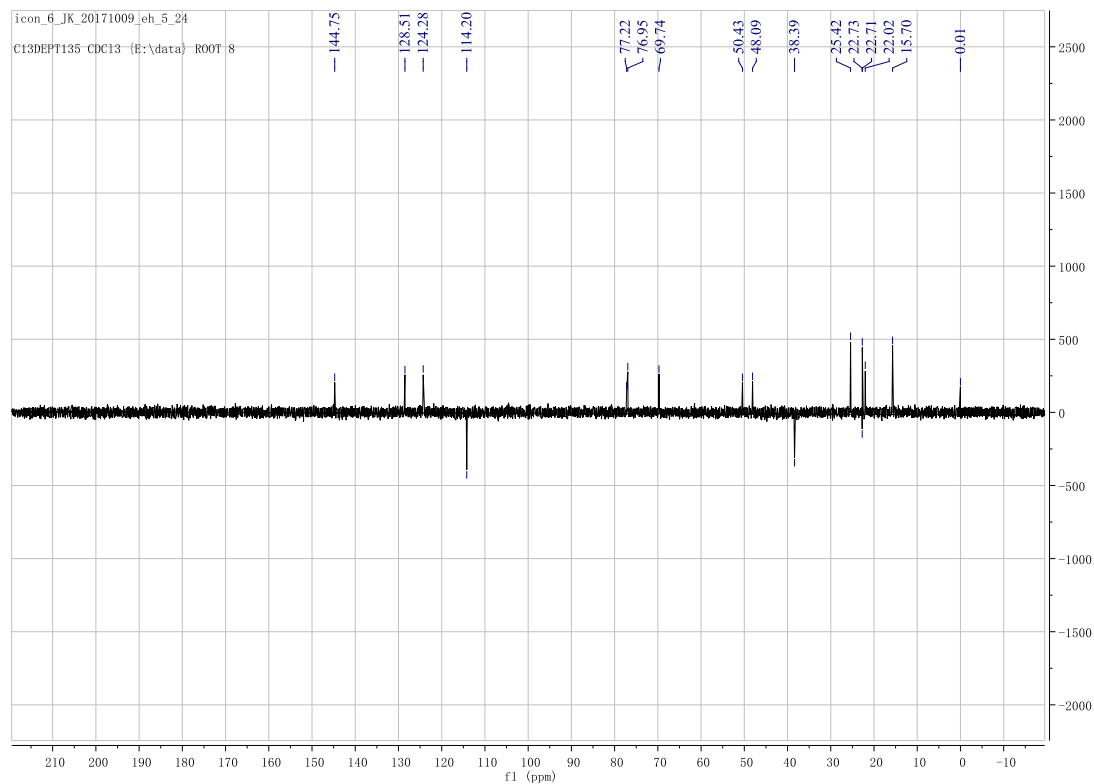


Figure SI103. ^1H - ^1H COSY spectrum of compound **15** (CDCl_3)

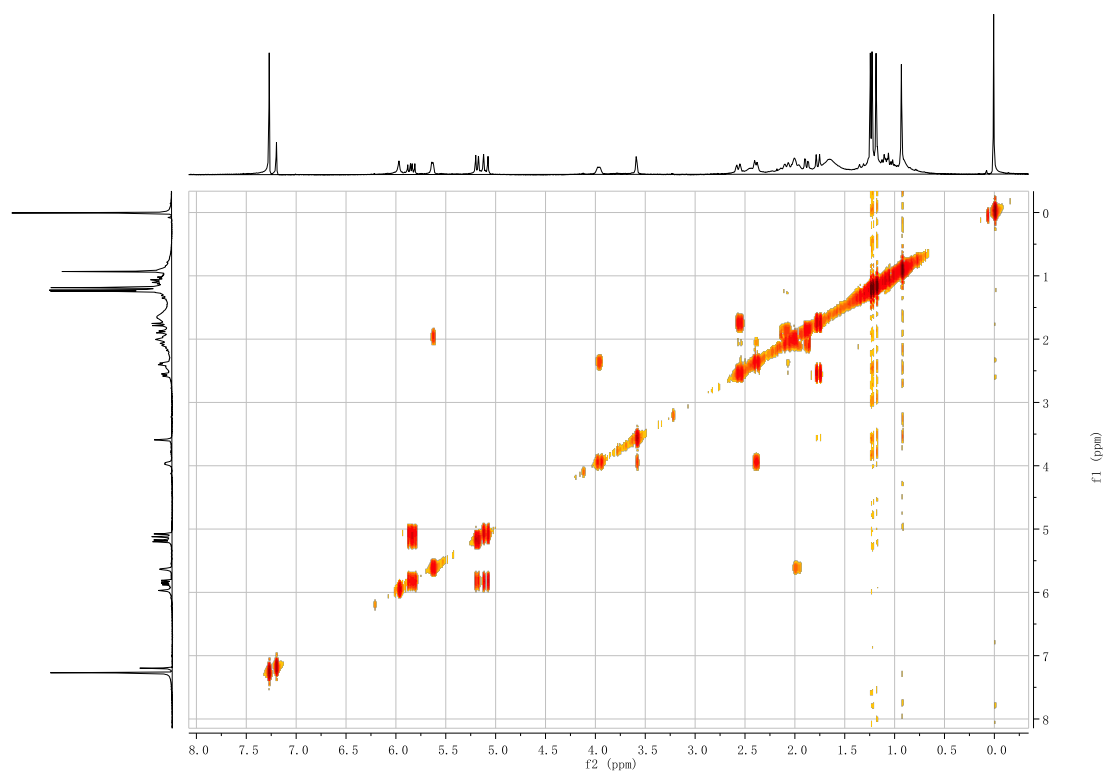


Figure SI104. HSQC spectrum of compound **15** (CDCl_3)

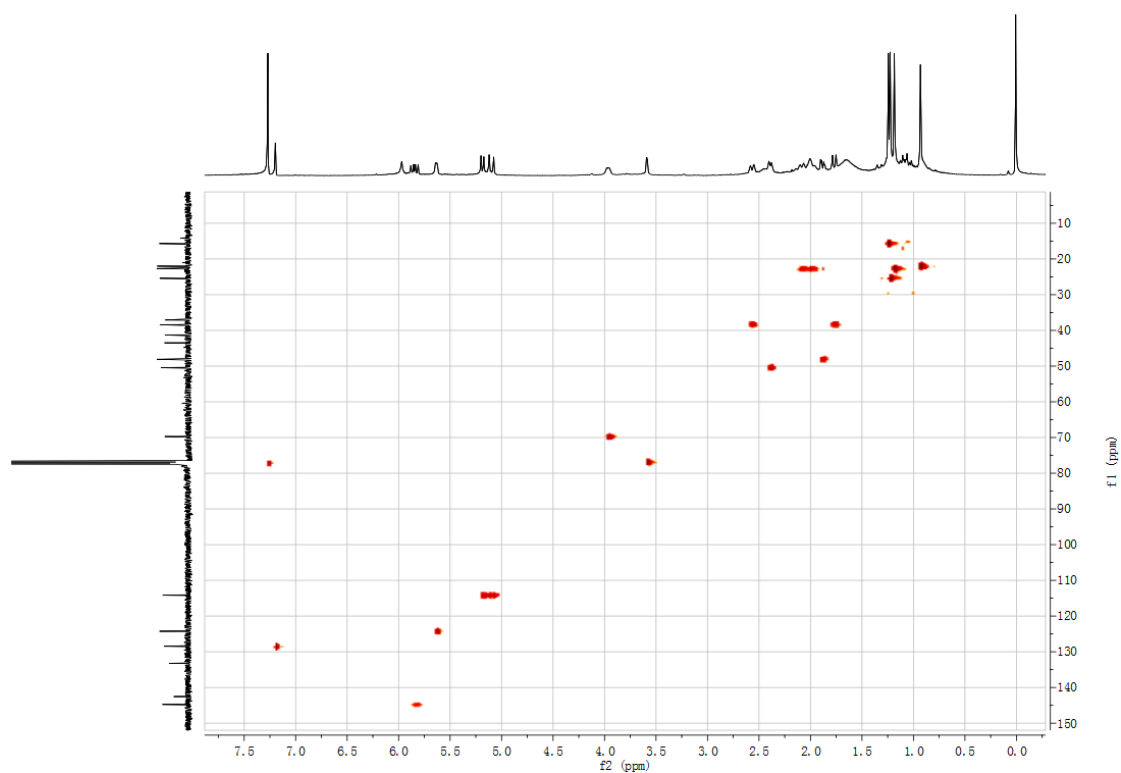


Figure SI105. HMBC spectrum of compound **15** (CDCl₃)

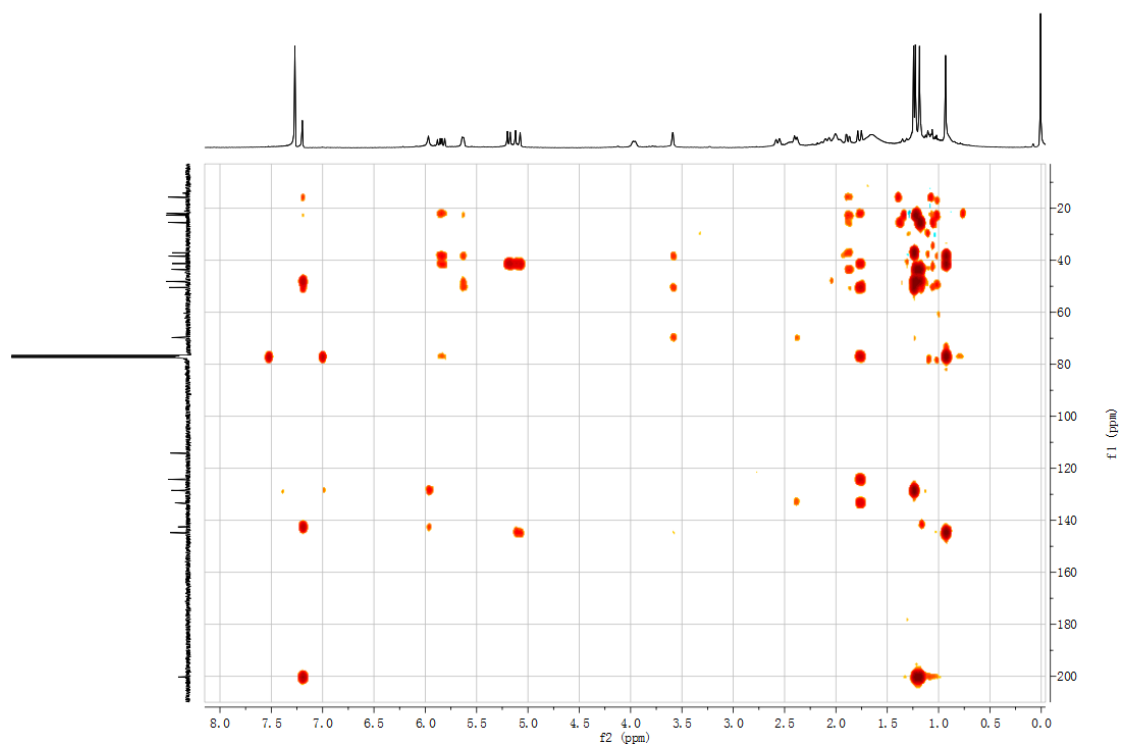


Figure SI106. NOESY spectrum of compound **15** (CDCl₃)

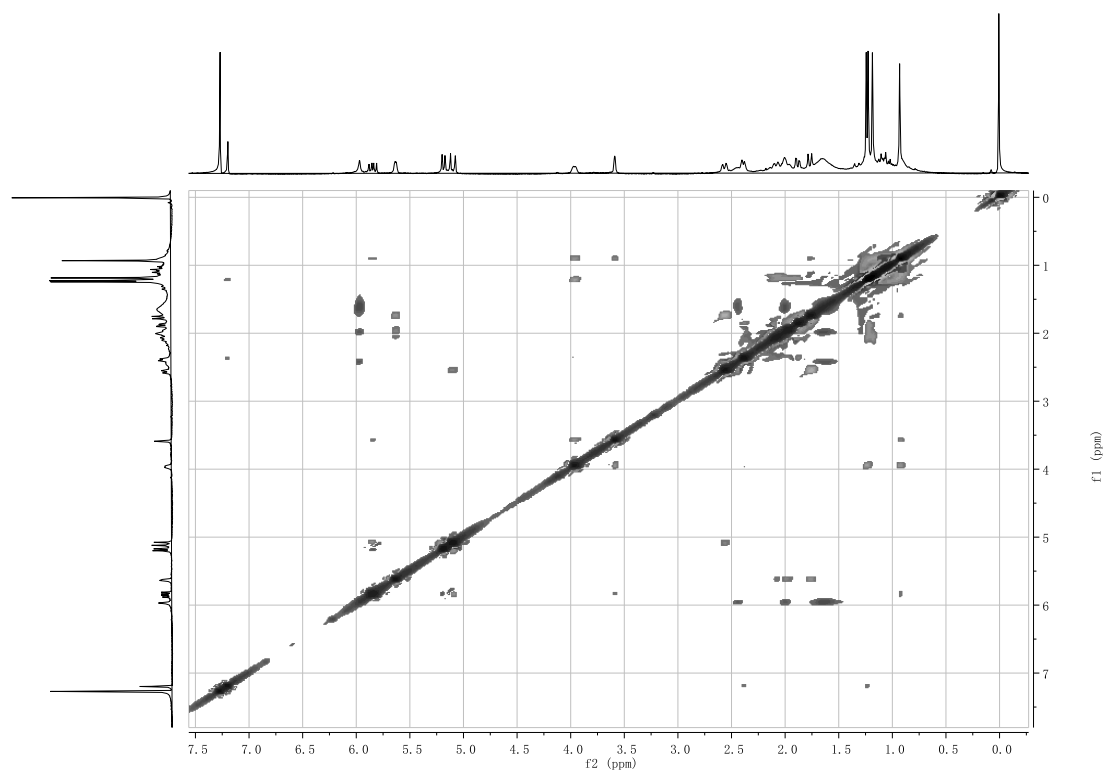


Figure SI107. HRESIMS spectrum of compound **15** (CDCl₃)

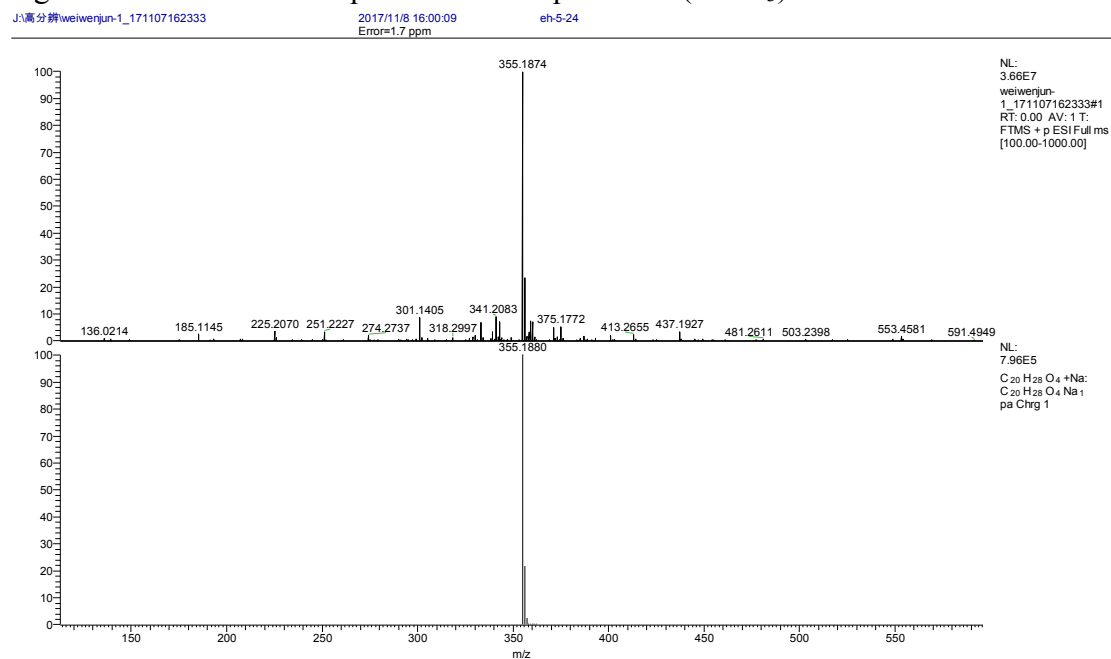


Figure SI108. IR spectrum of compound **15** (CDCl₃)

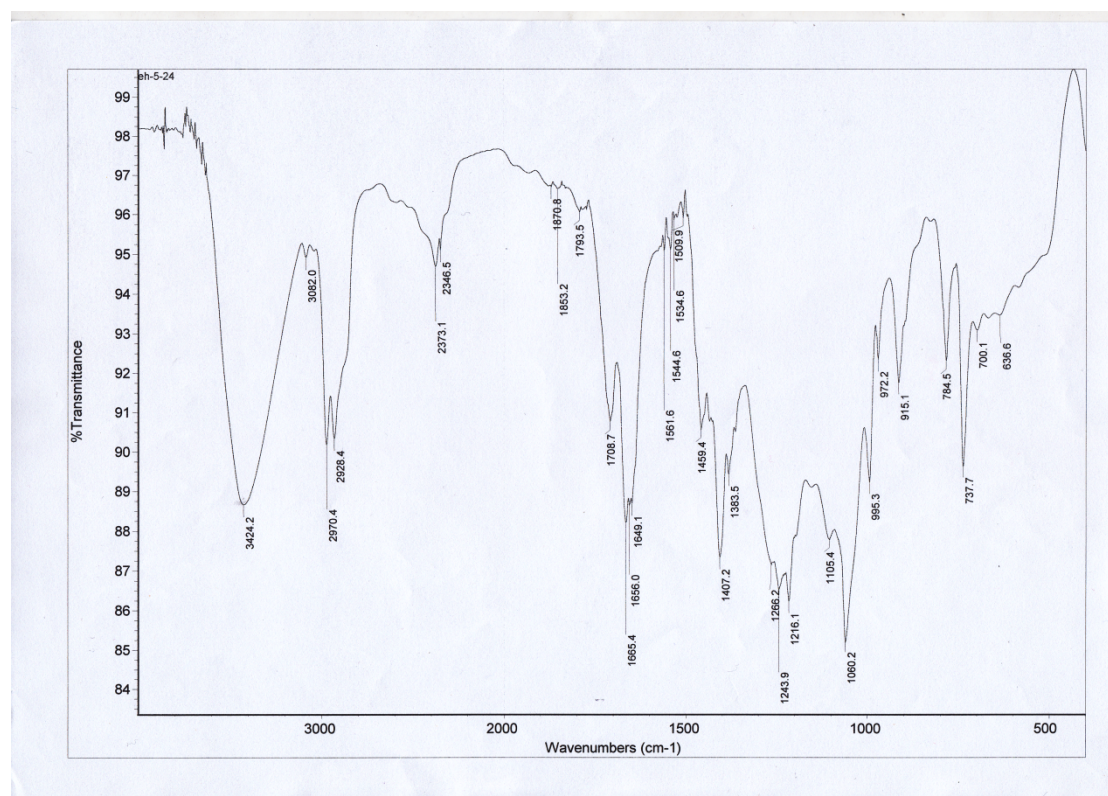


Figure SI109. ^1H NMR spectrum of compound **16** (CDCl_3)

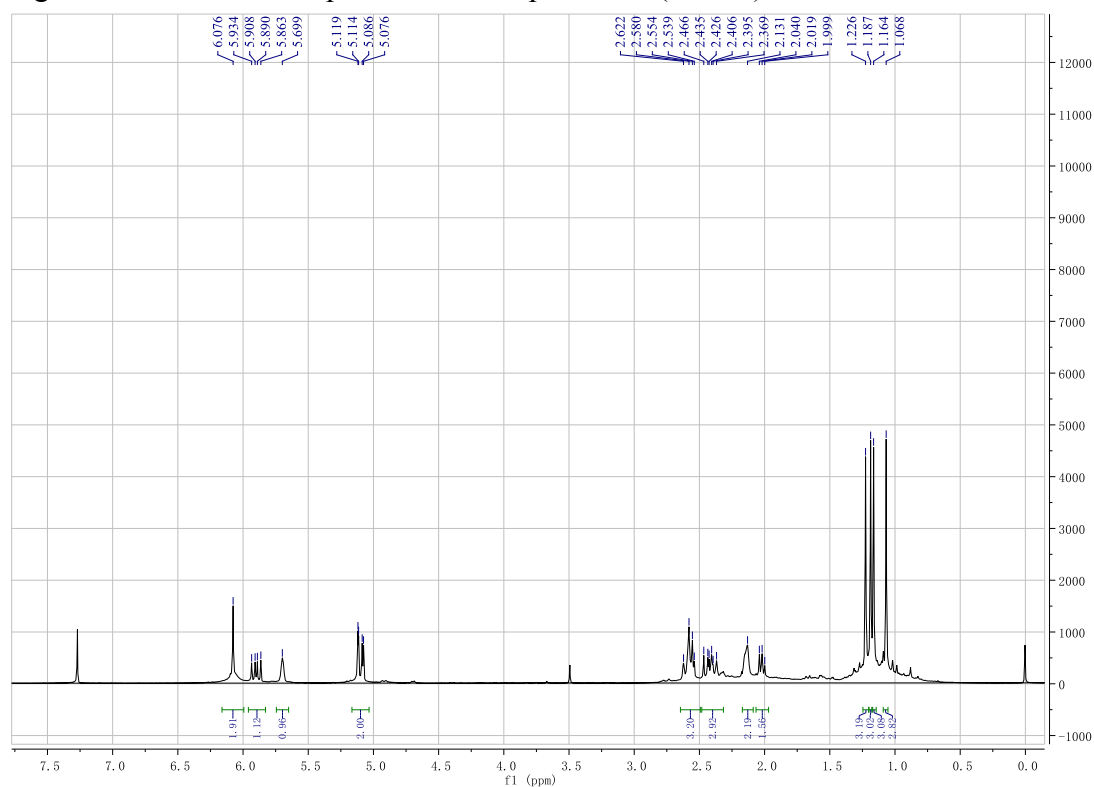


Figure SI110. ^{13}C NMR spectrum of compound **16** (CDCl_3)

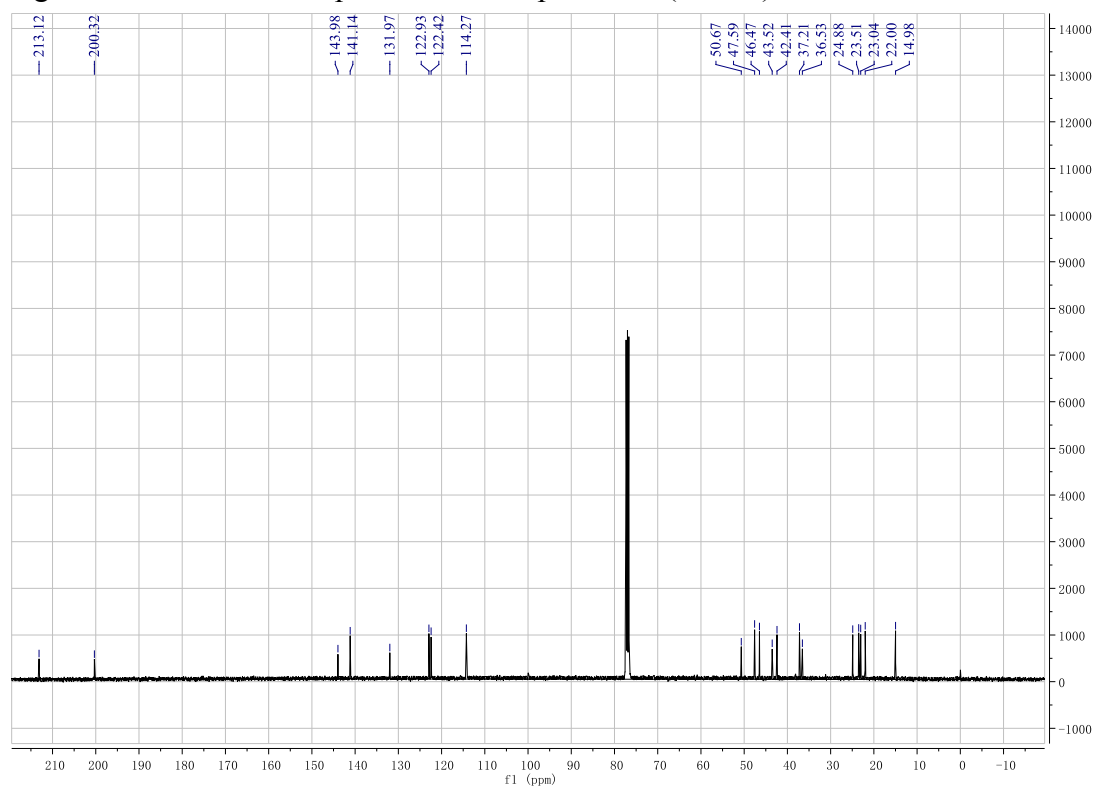


Figure SI111. DEPT spectrum of compound **16** (CDCl₃)

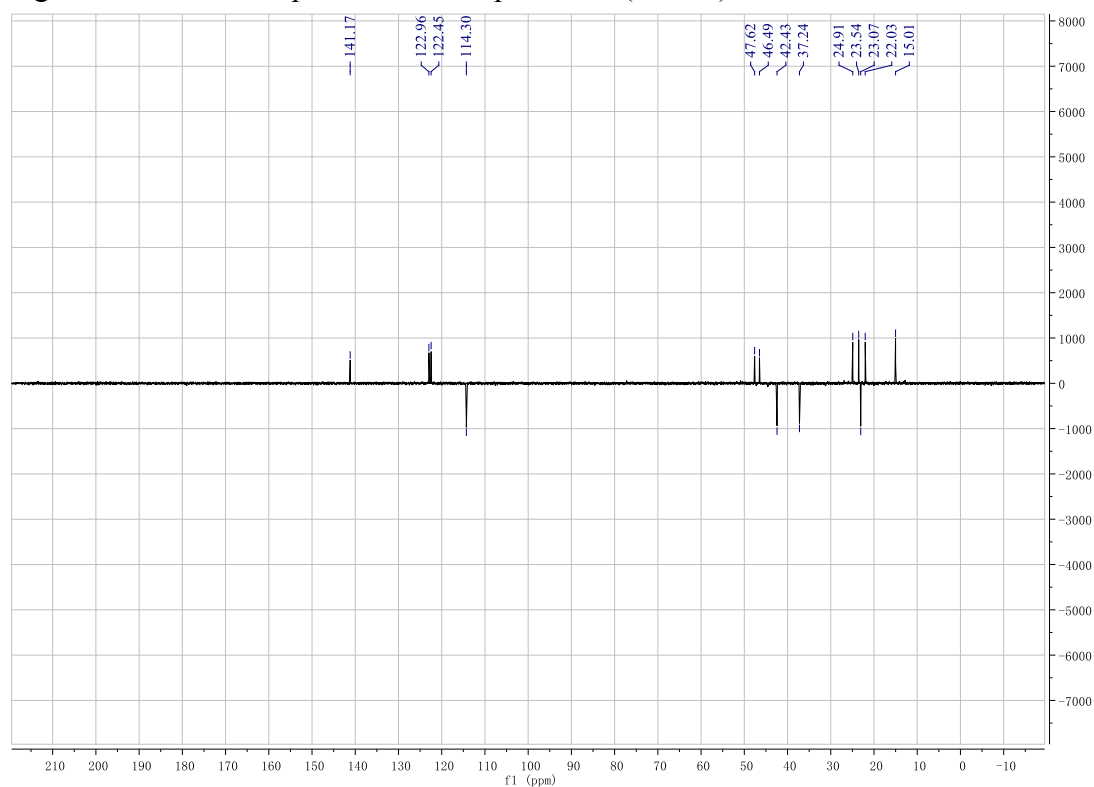


Figure SI112. ¹H-¹H COSY spectrum of compound **16** (CDCl₃)

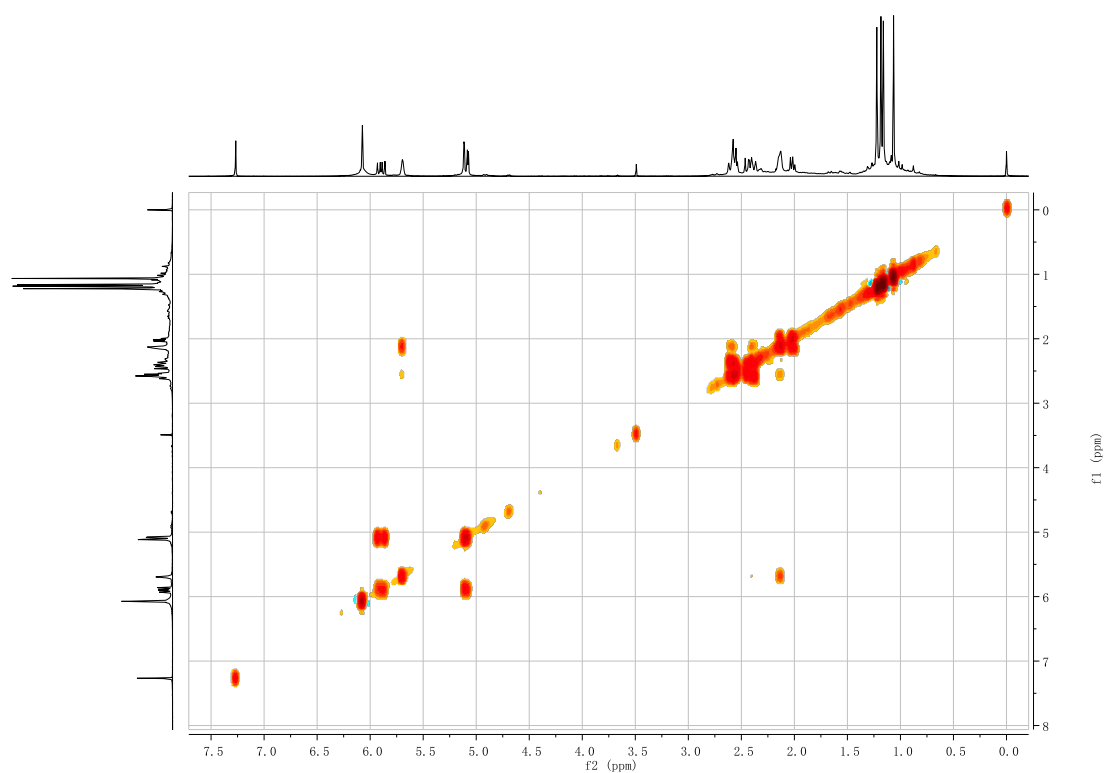


Figure SI113. HSQC spectrum of compound **16** (CDCl₃)

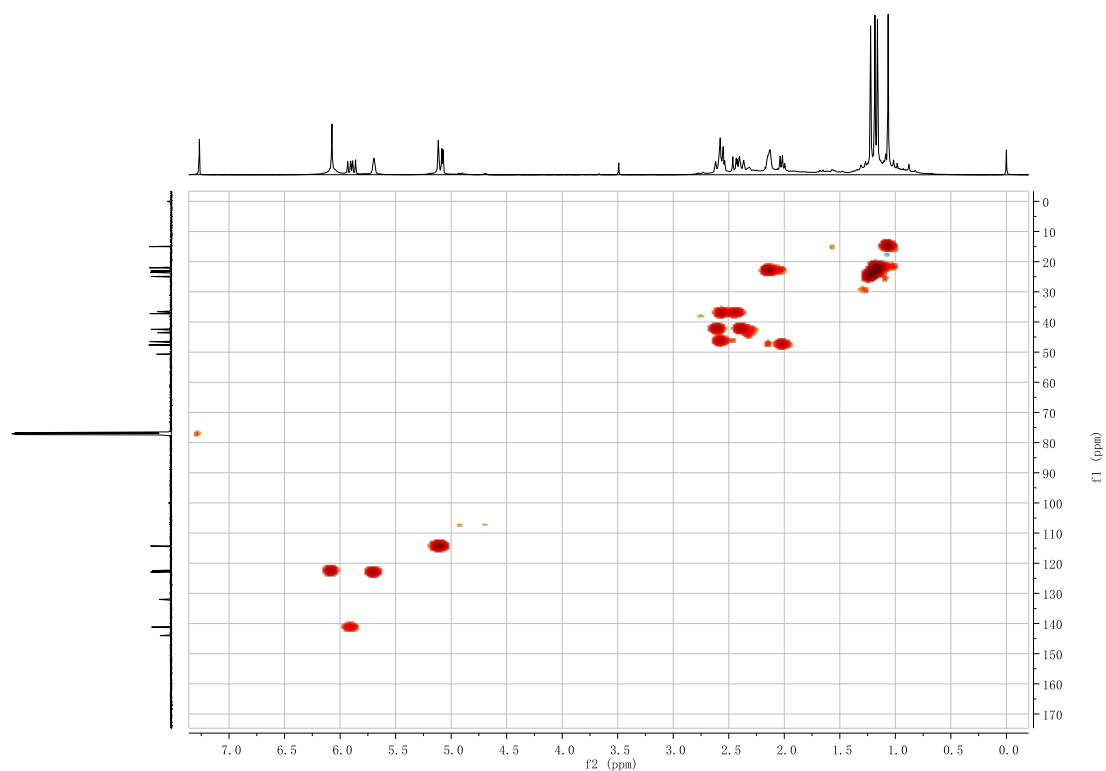


Figure SI114. HMBC spectrum of compound **16** (CDCl₃)

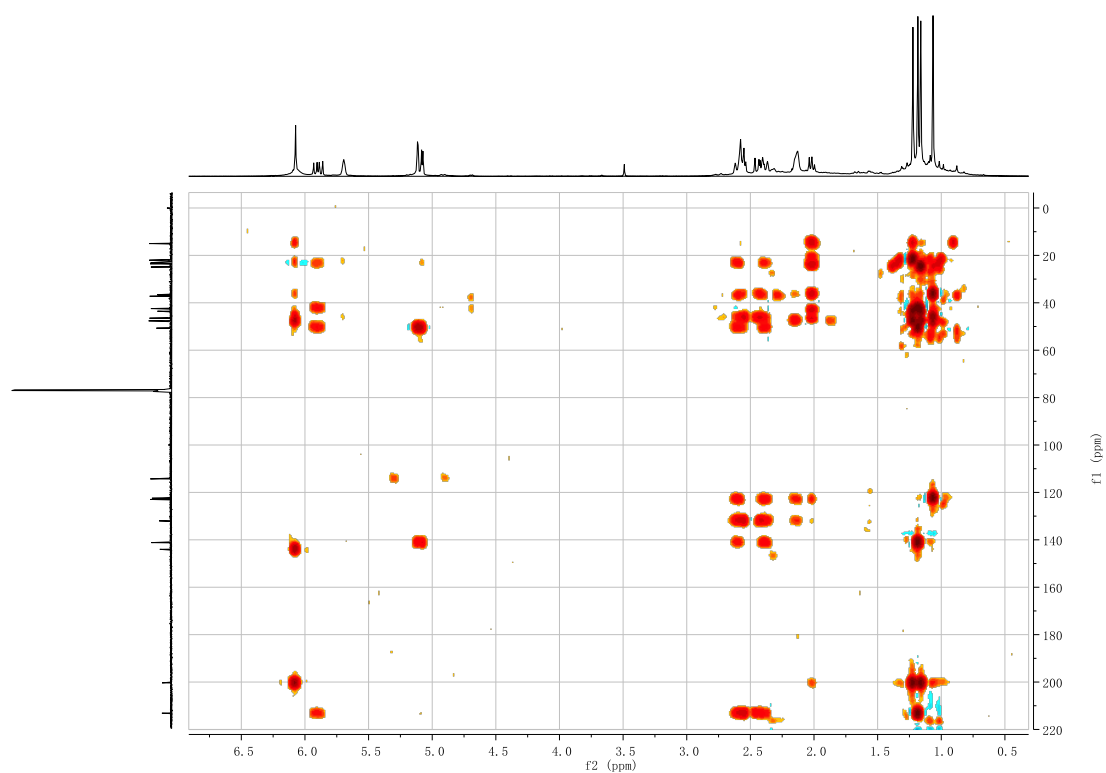


Figure SI115. NOESY spectrum of compound **16** (CDCl₃)

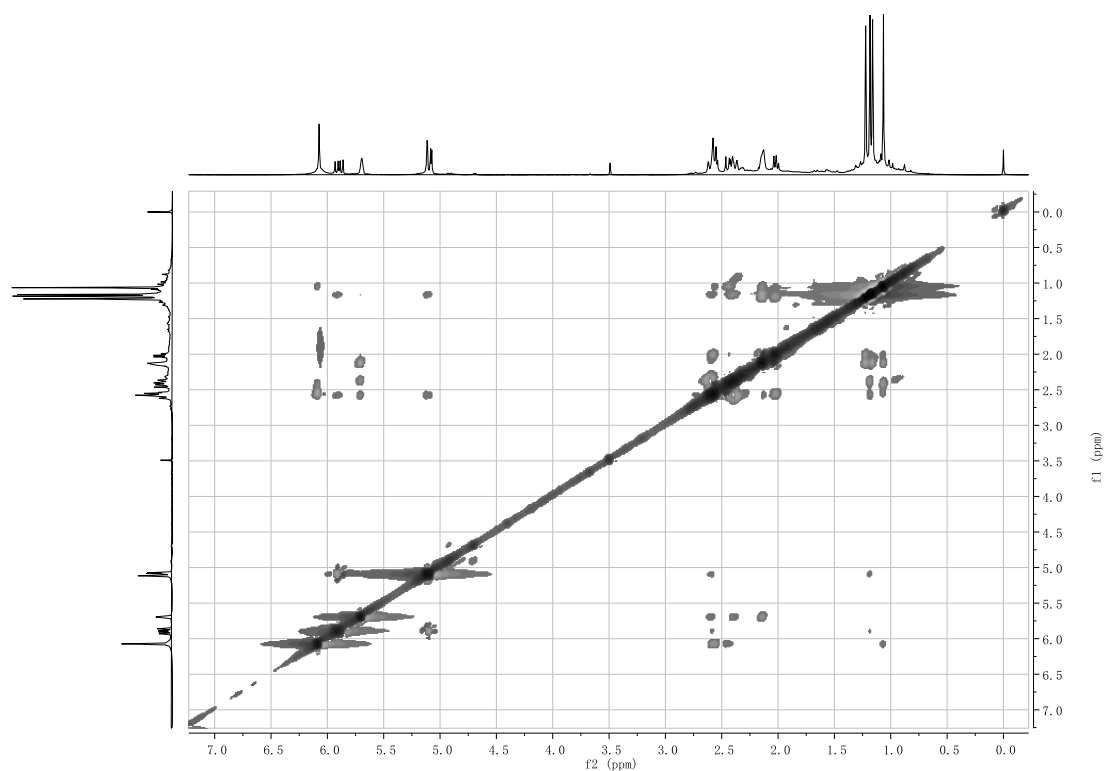


Figure SI116. HRESIMS spectrum of compound **16** (CDCl₃)

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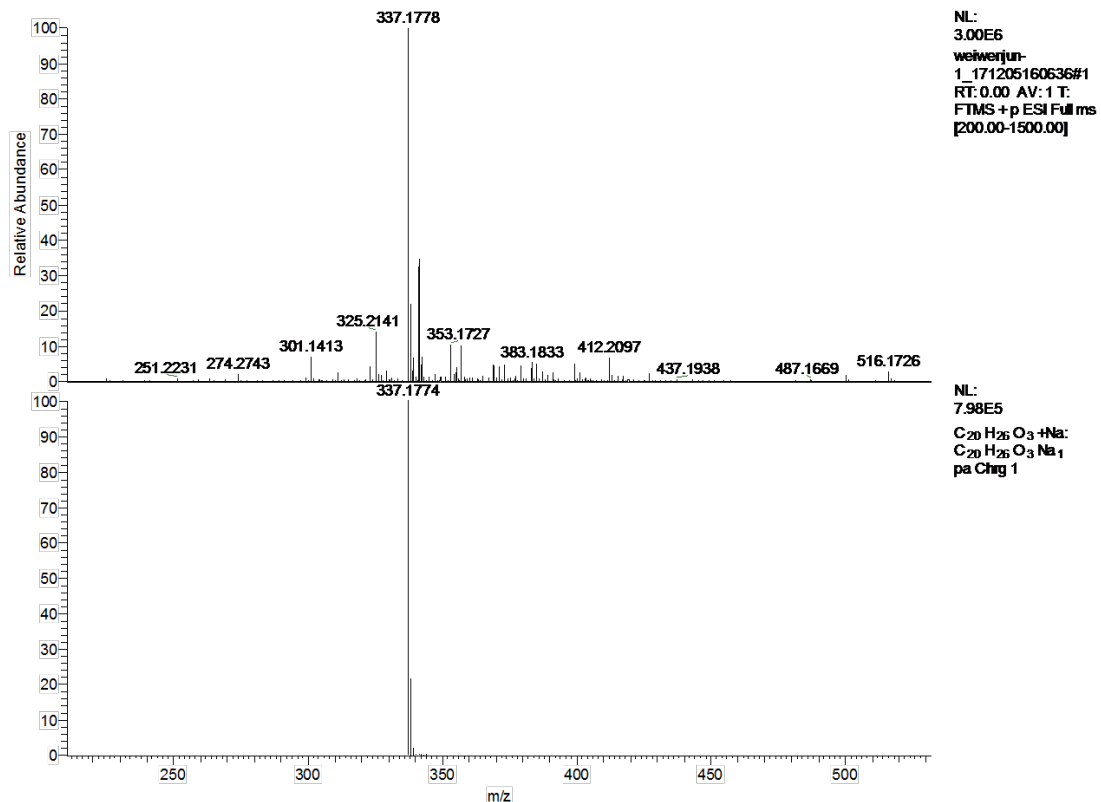


Figure SI117. IR spectrum of compound **16** (CDCl₃)

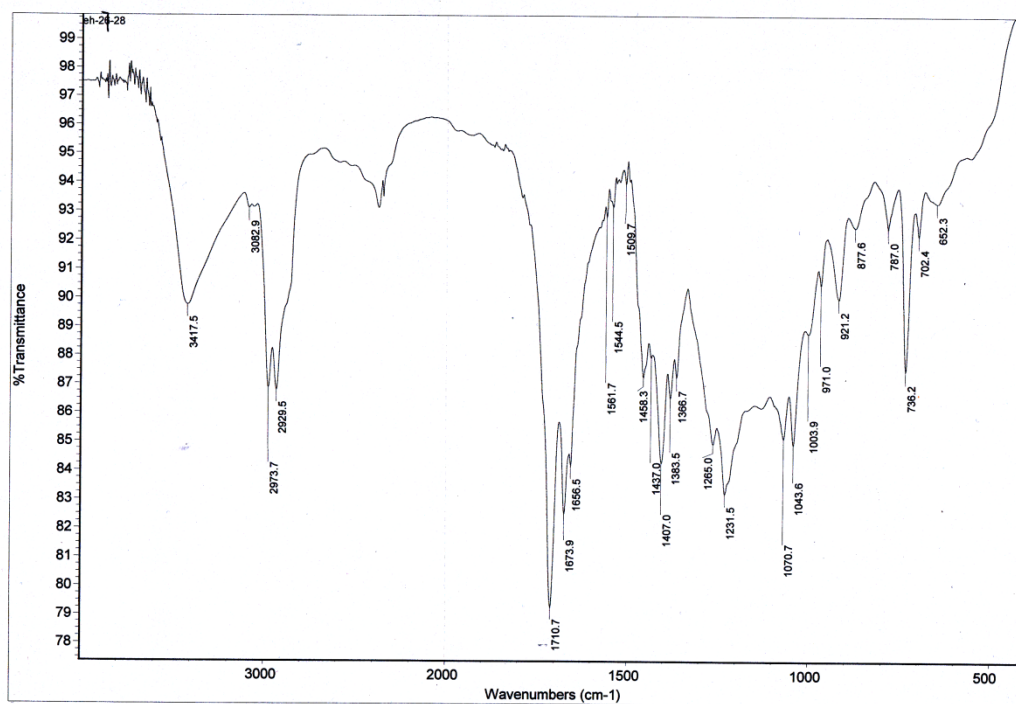


Figure SI118. UV and ECD spectra of compounds **1–6** and **8**

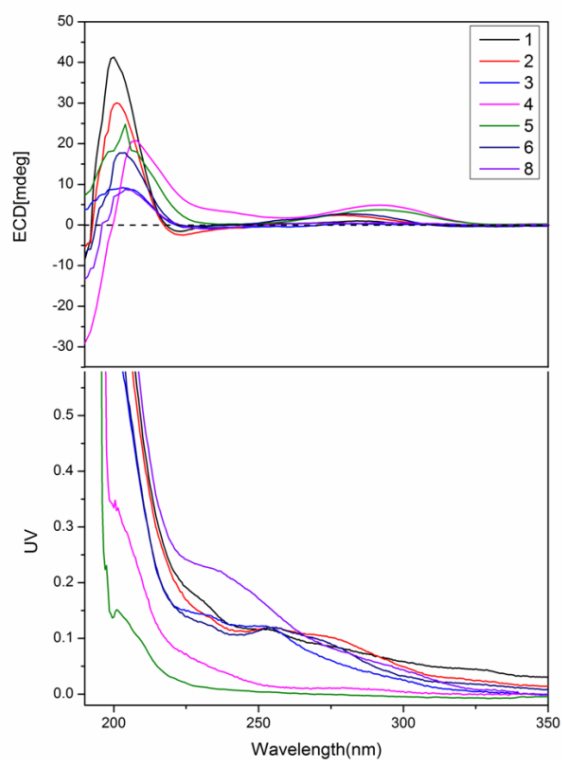


Figure SI119. UV and ECD spectra of compounds **7**, **9**, and **10**

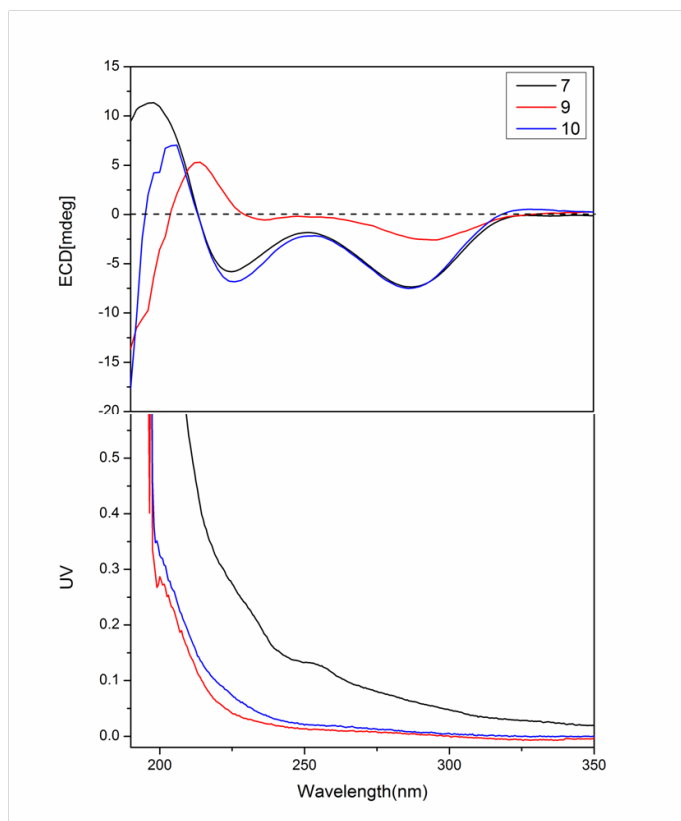


Figure SI120. UV and ECD spectra of compounds **14**–**16**

