Supporting Information

FOUR NEW CANTHARIDIN DERIVATIVES FROM THE CHINESE BLISTER BEETLES, *MYLABRIS PHALERATA*

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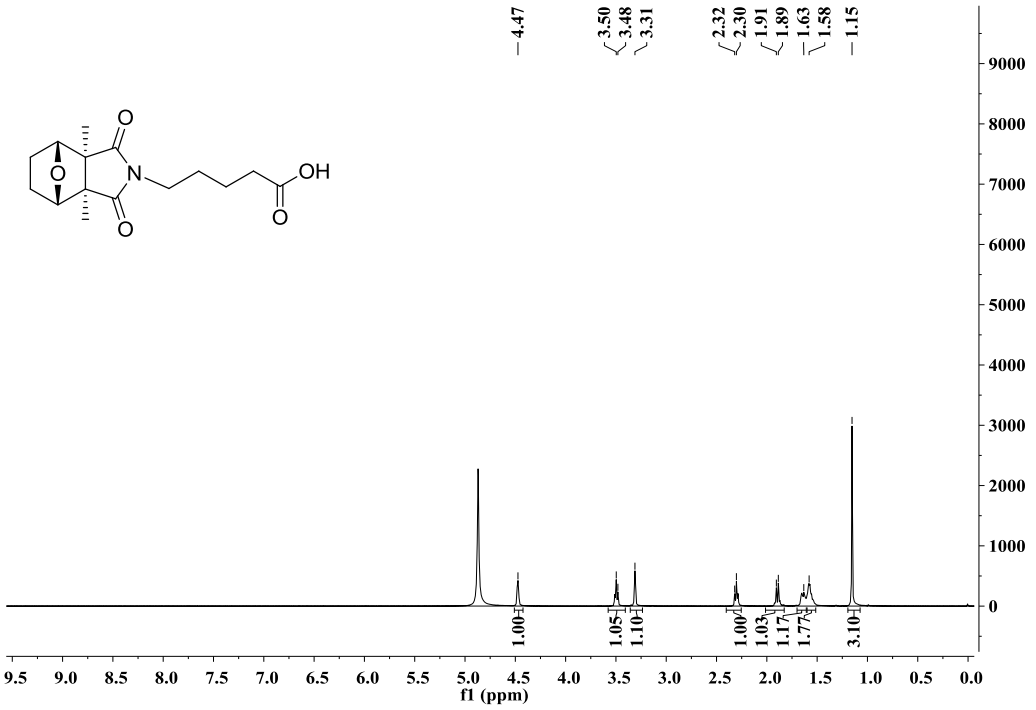

Figure S1. ^{1}H NMR spectrum of compound **1** in CD_3OD (400 MHz)

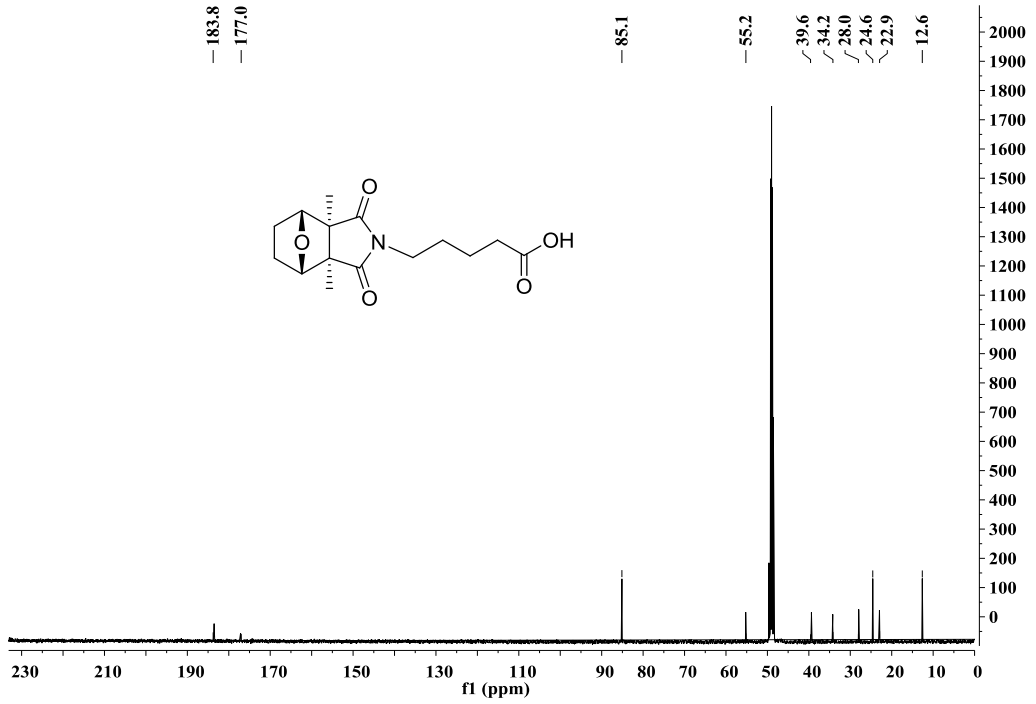

Figure S2. ^{13}C NMR spectrum of compound **1** in CD_3OD (100 MHz)

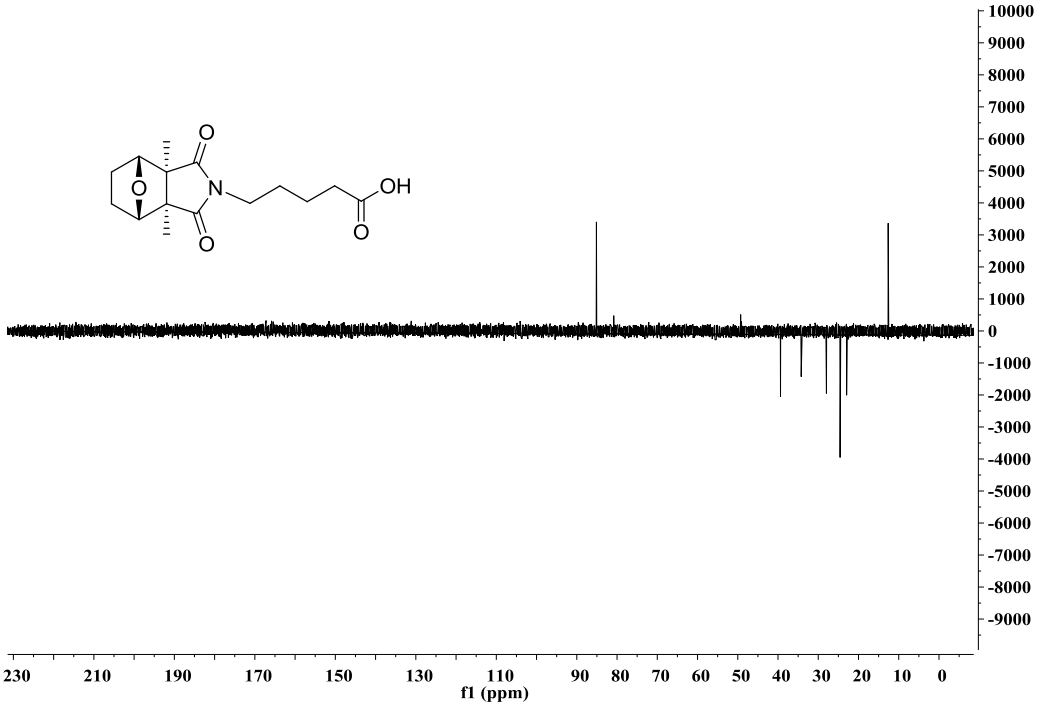

Figure S3. DEPT-135 spectrum of compound **1** in CD_3OD (100 MHz)

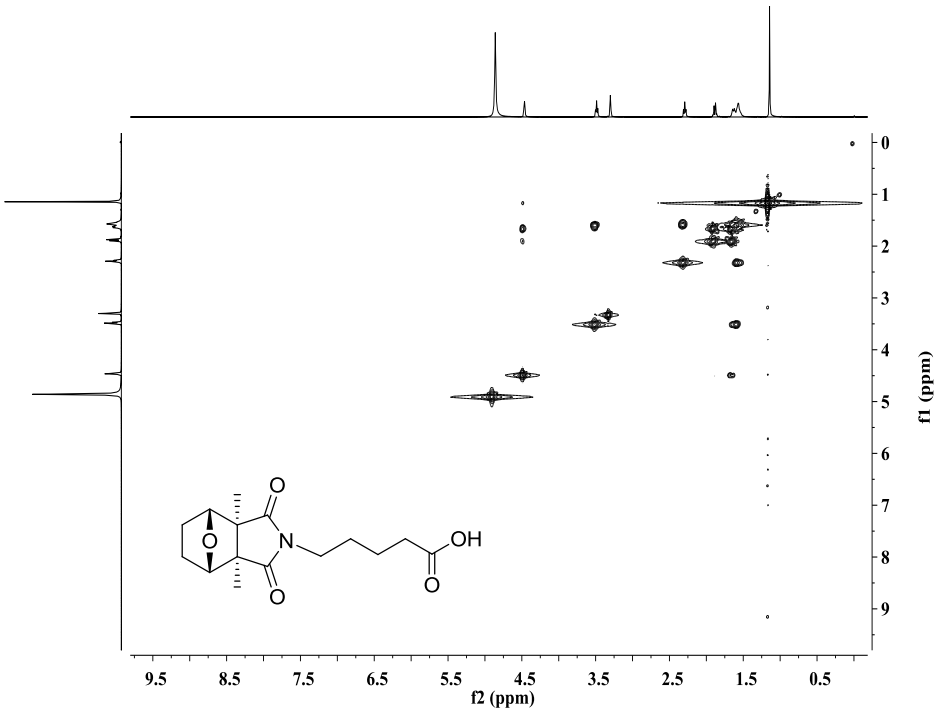

Figure S4. ^1H-^1H COSY spectrum of compound **1** in CD_3OD (400 MHz)

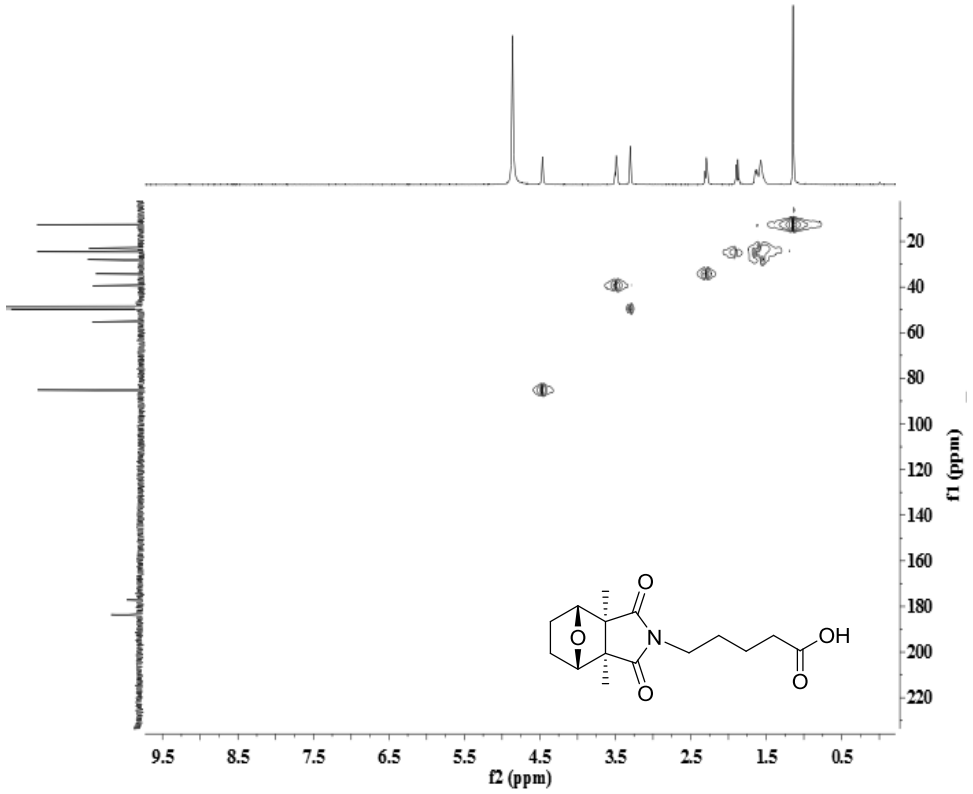

Figure S5. HSQC spectrum of compound **1** in CD_3OD (400 MHz)

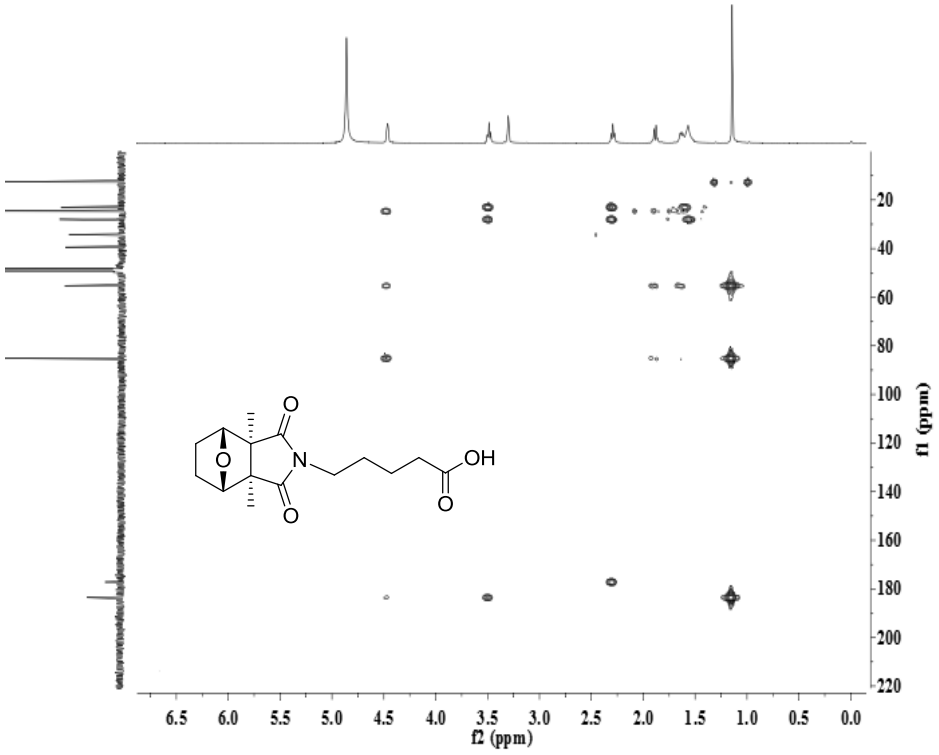

Figure S6. HMBC spectrum of compound **1** in CD_3OD (400 MHz)

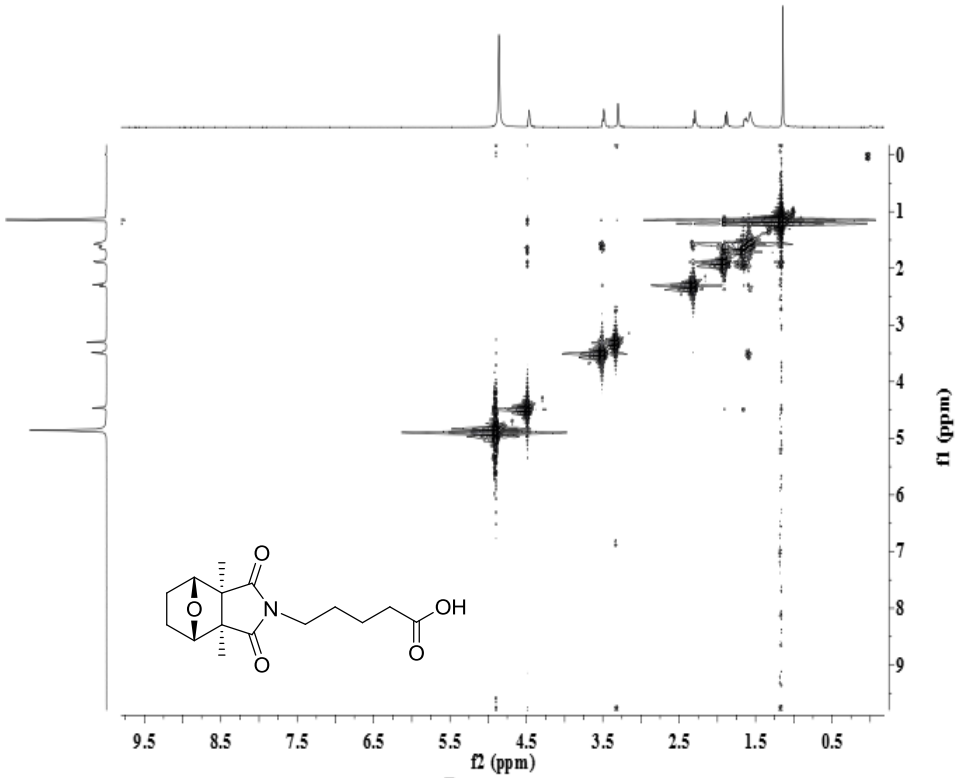

Figure S7. NOESY spectrum of compound **1** in CD_3OD (400 MHz)

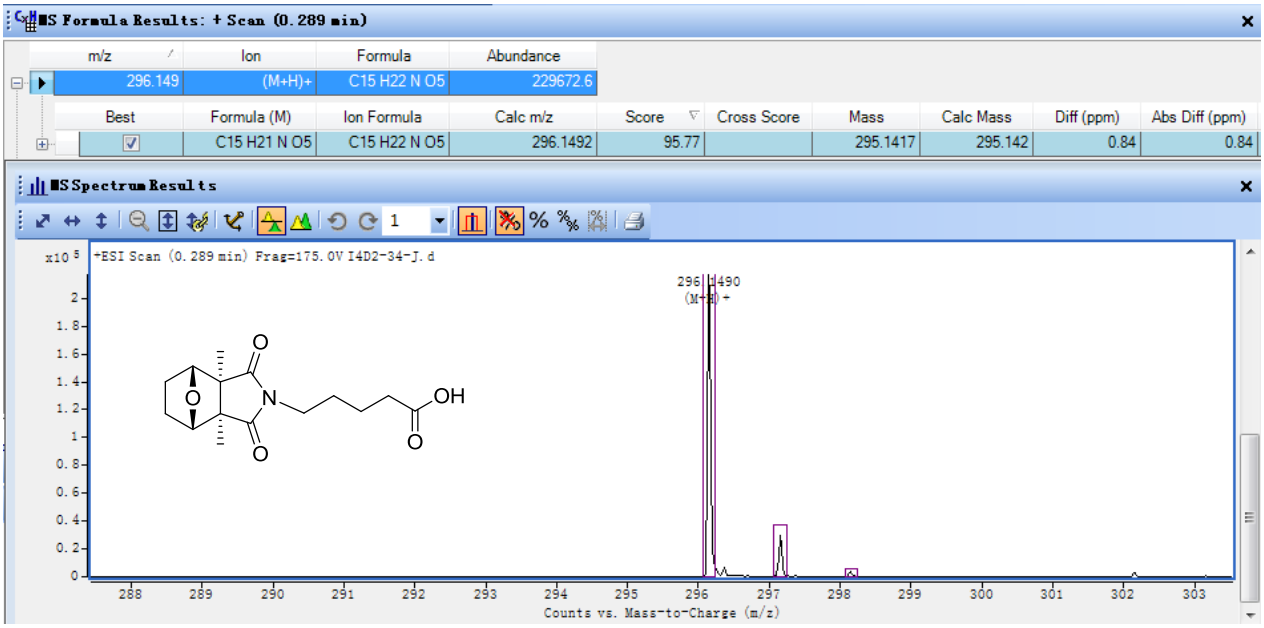

Figure S8. HR-ESI-MS spectrum of **1**

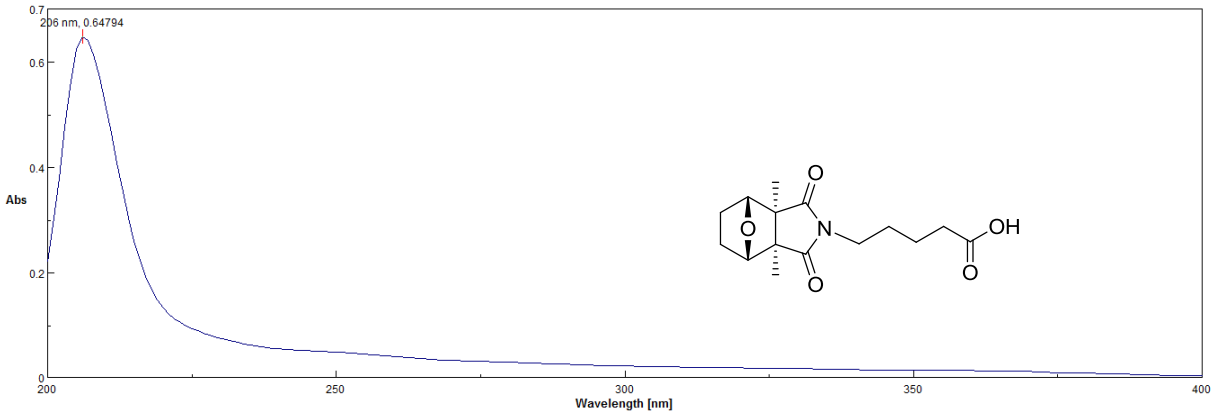

Figure S9. UV spectrum of **1** in MeOH

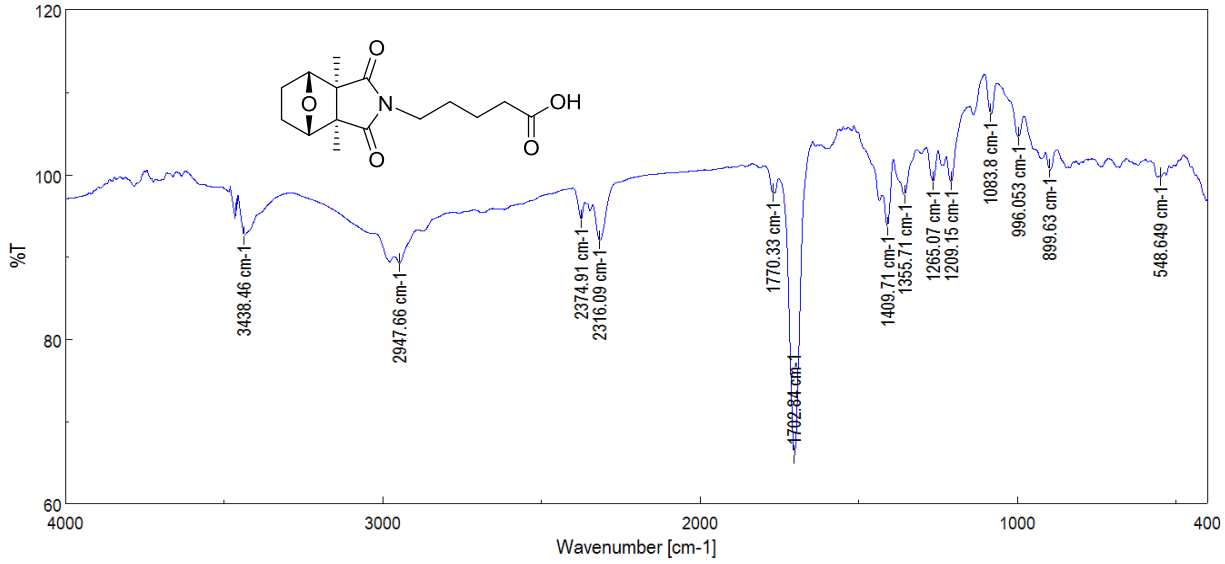

Figure S10. IR (KBr disc) spectrum of **1**

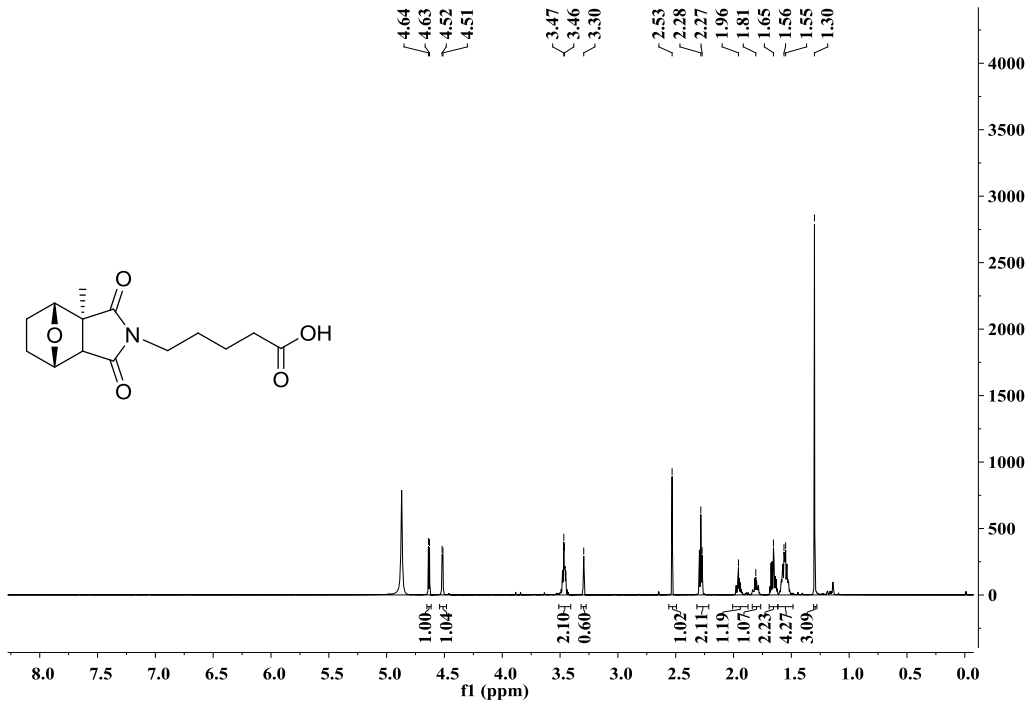

Figure S11. ^{1}H NMR spectrum of compound **2** in CD_3OD (600 MHz)

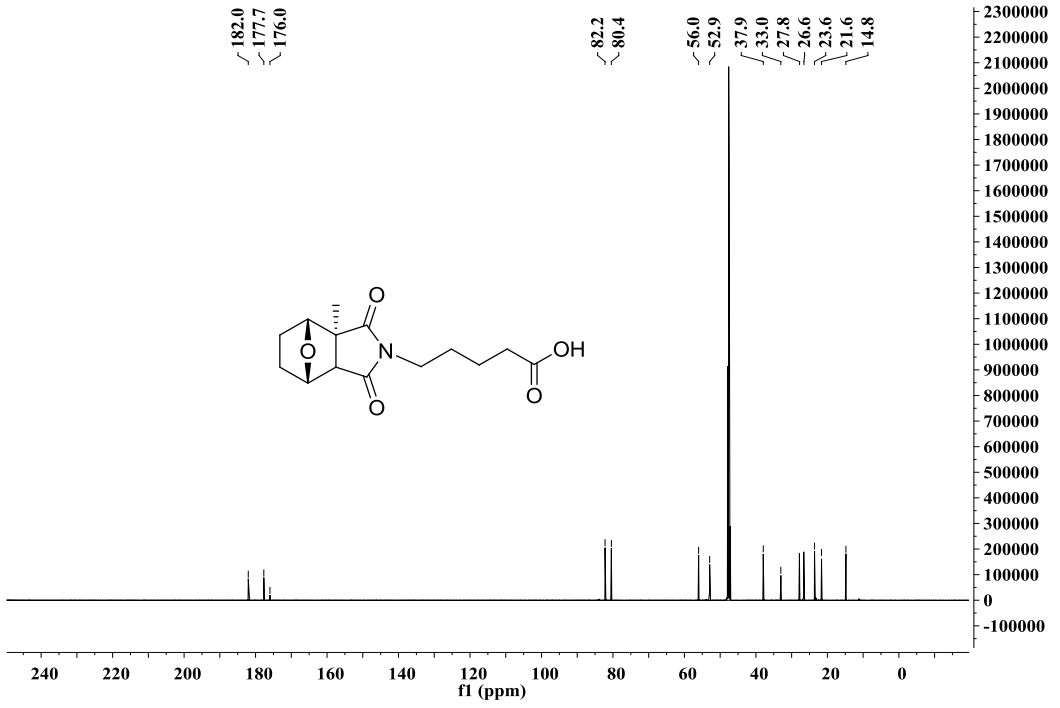

Figure S12. ^{13}C NMR spectrum of compound **2** in CD_3OD (150 MHz)

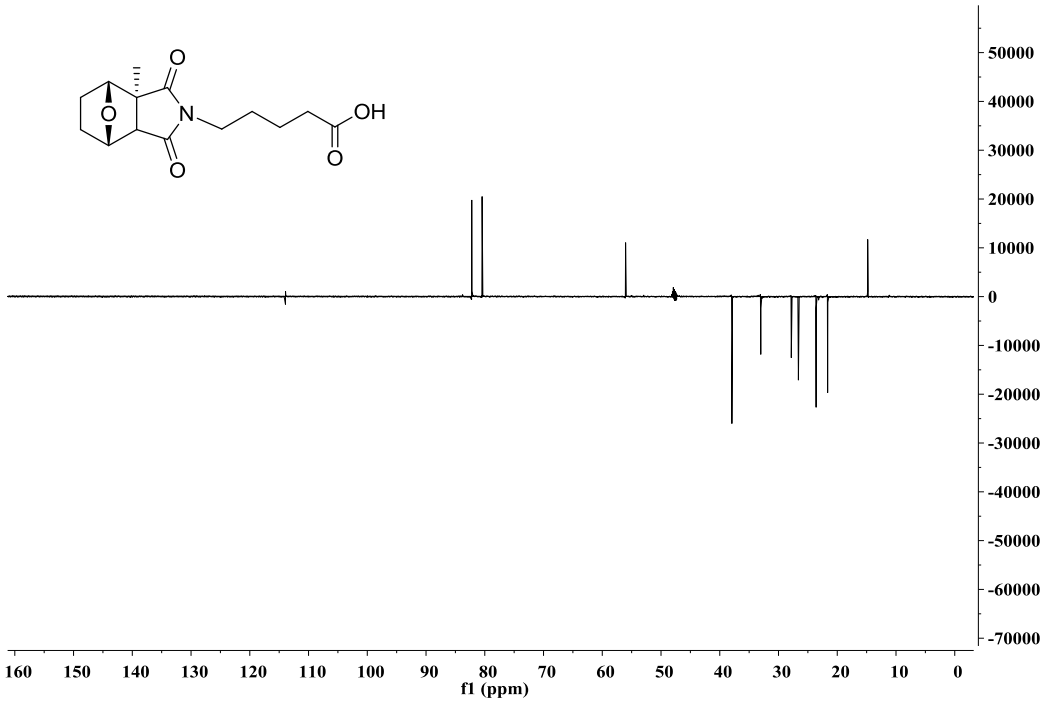

Figure S13. DEPT-135 spectrum of compound **2** in CD_3OD (150 MHz)

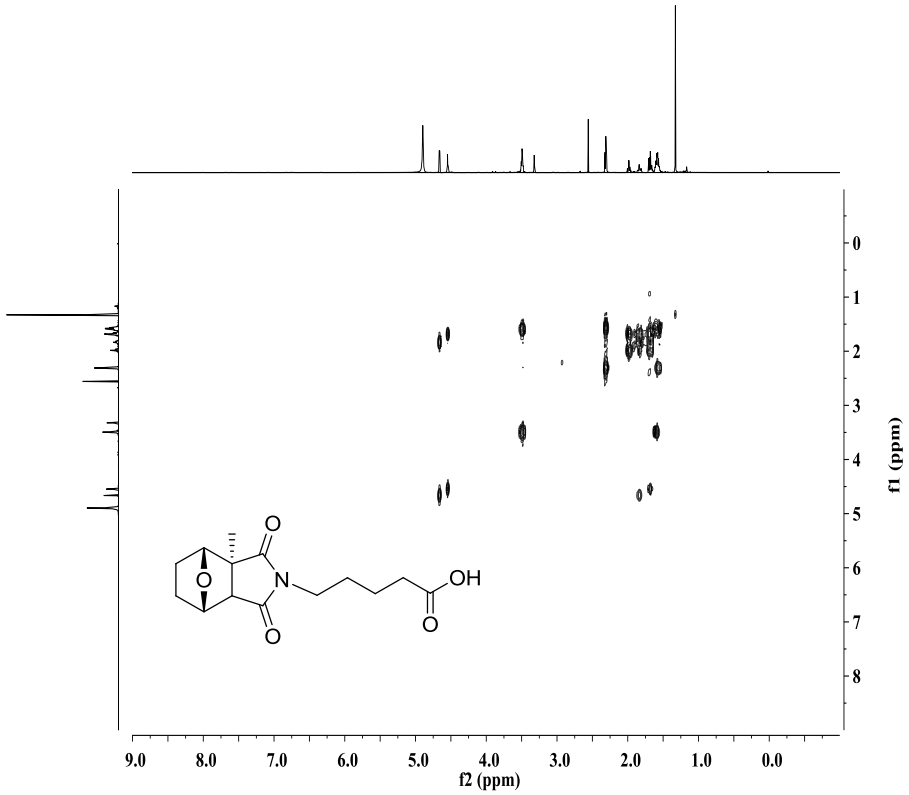

Figure S14. ^1H-^1H COSY spectrum of compound **2** in CD_3OD (600 MHz)

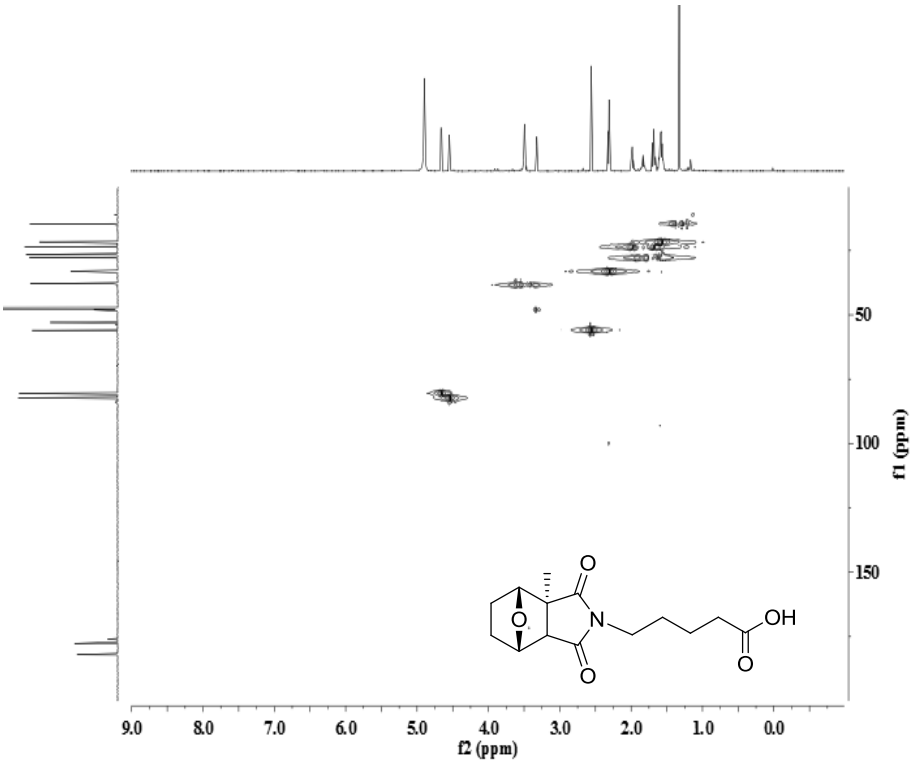

Figure S15. HSQC spectrum of compound **2** in CD_3OD (600 MHz)

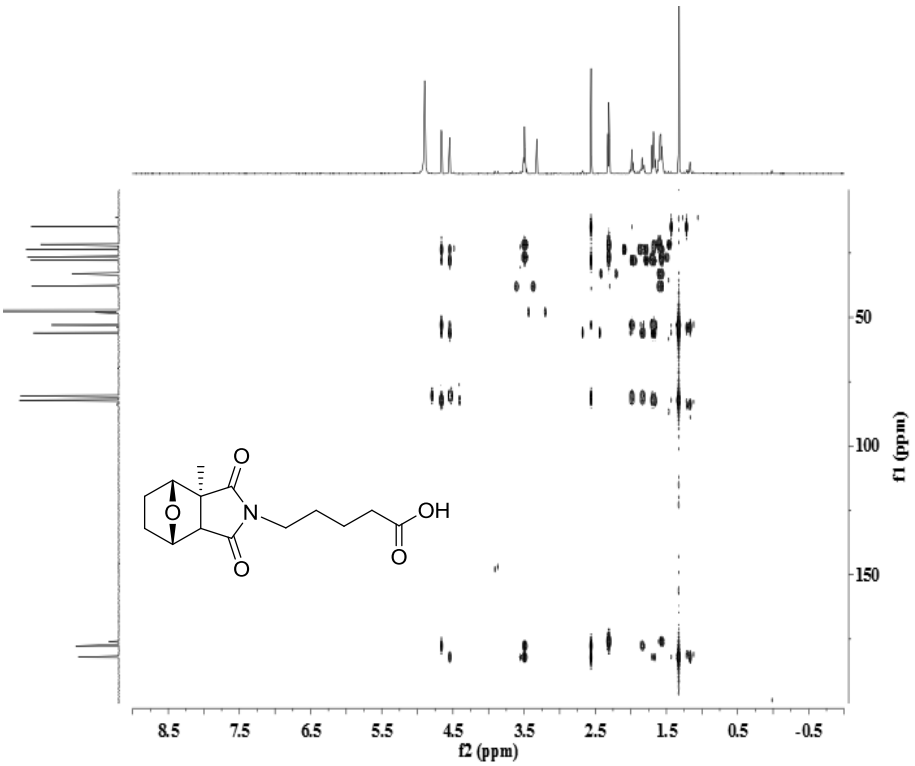

Figure S16. HMBC spectrum of compound **2** in CD_3OD (600 MHz)

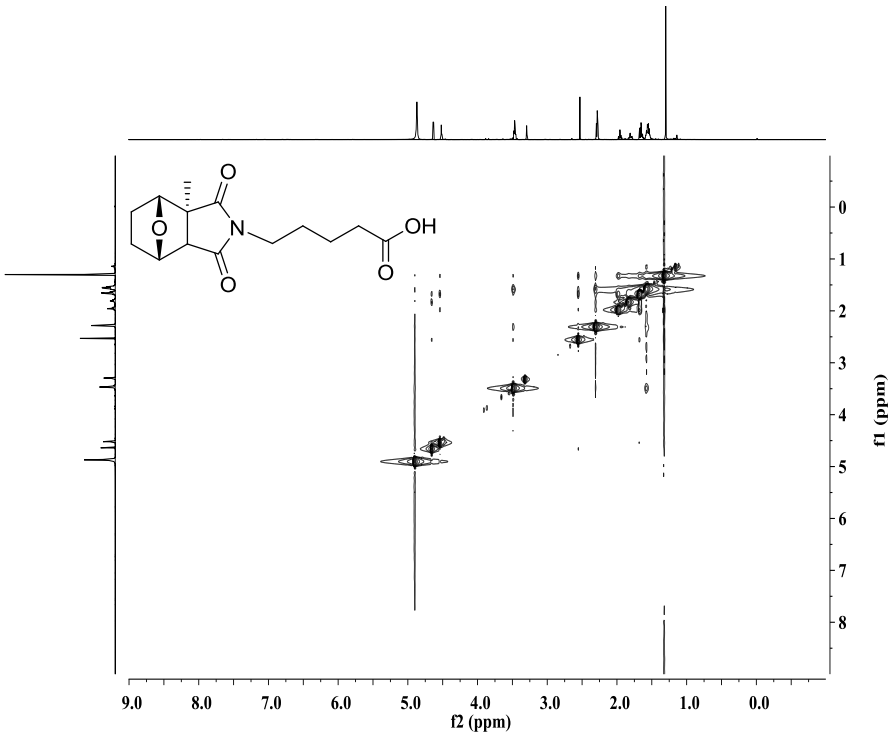

Figure S17. NOESY spectrum of compound **2** in CD_3OD (600 MHz)

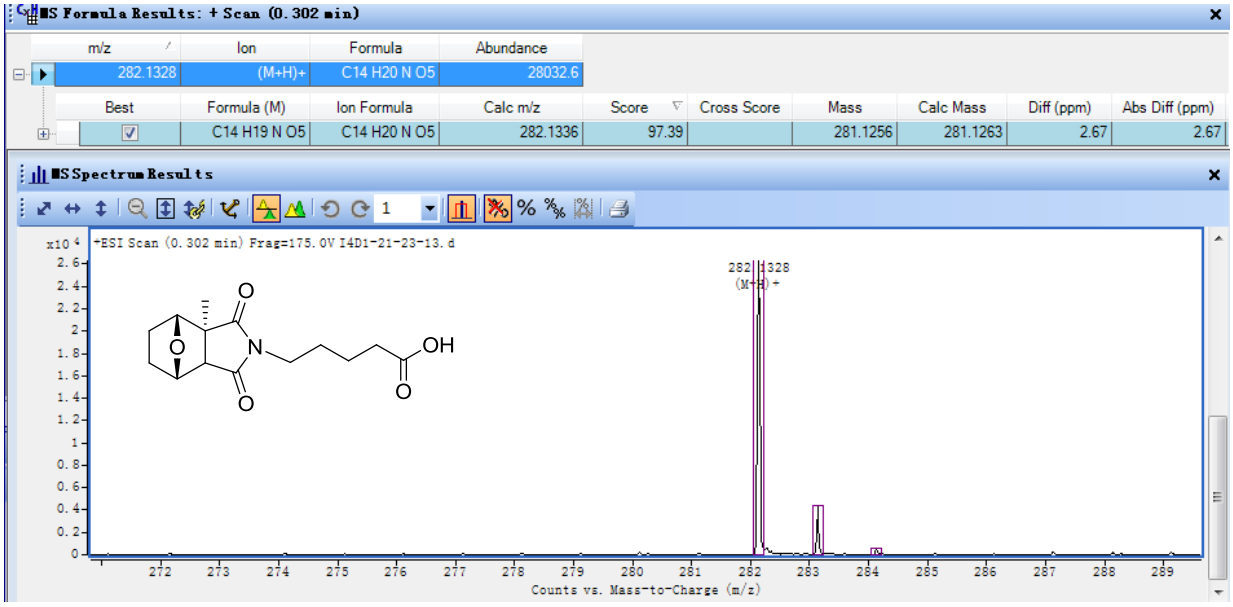

Figure S18. HR-ESI-MS spectrum of **2**

Figure S19. UV spectrum of **2** in MeOH

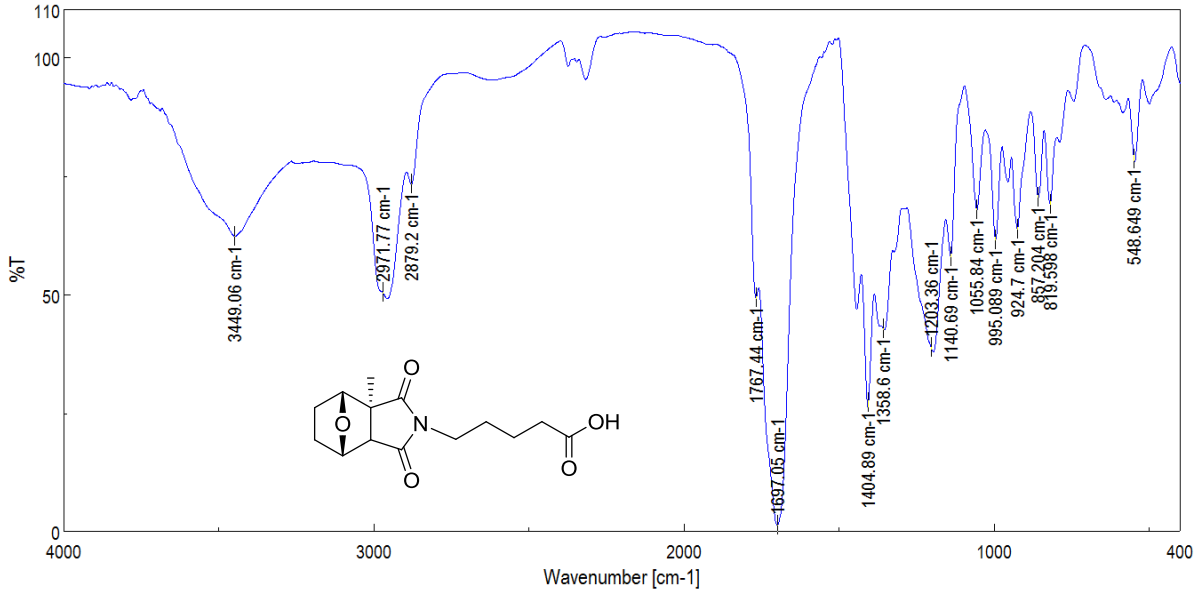

Figure S20. IR (KBr disc) spectrum of **2**

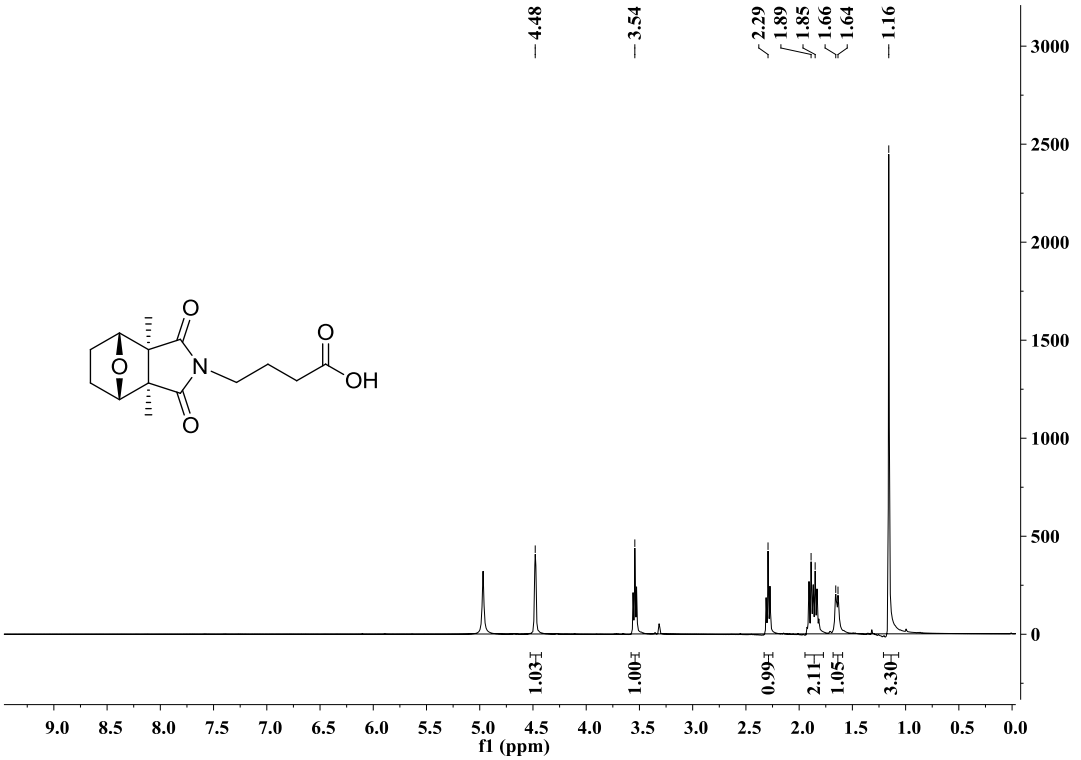

Figure S21. ^{1}H NMR spectrum of compound **3** in CD_3OD (400 MHz)

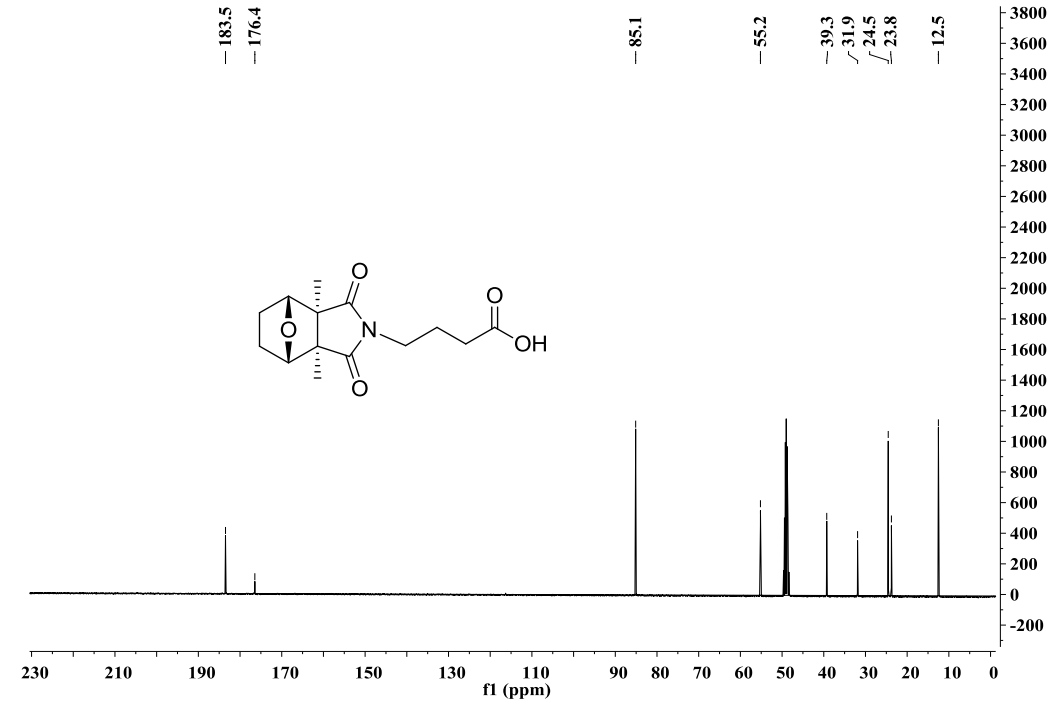

Figure S22. ^{13}C NMR spectrum of compound **3** in CD_3OD (100 MHz)

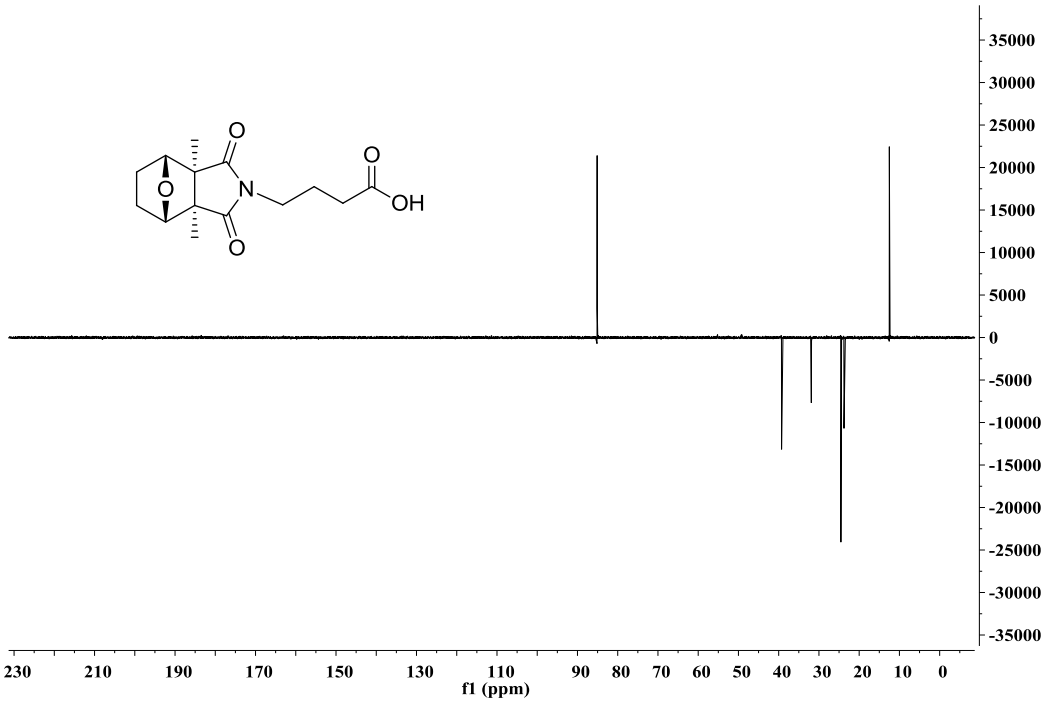

Figure S23. DEPT-135 spectrum of compound **3** in CD_3OD (100 MHz)

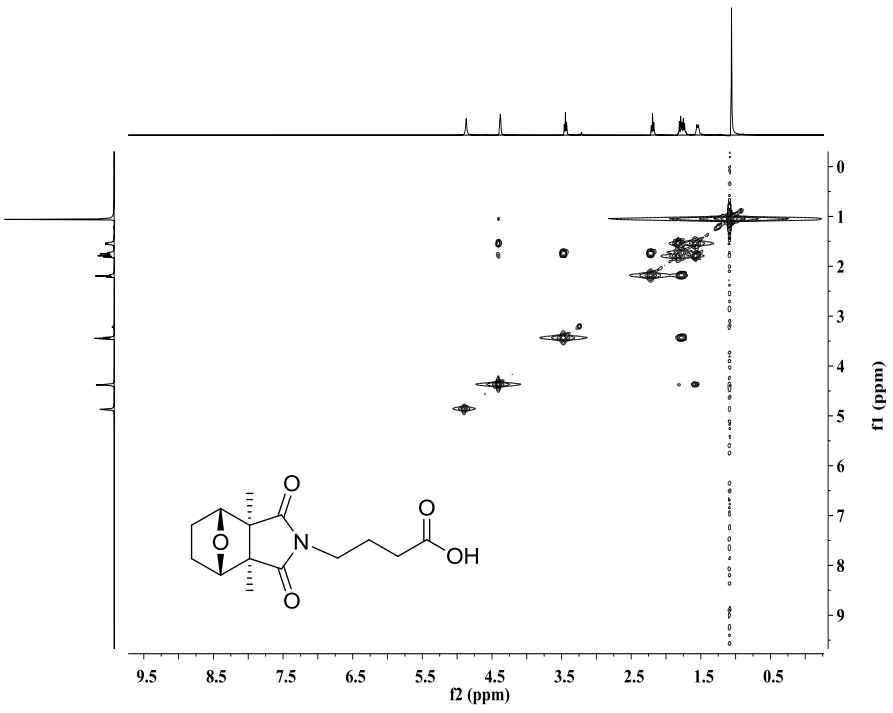

Figure S24. ^1H-^1H COSY spectrum of compound **3** in CD_3OD (400 MHz)

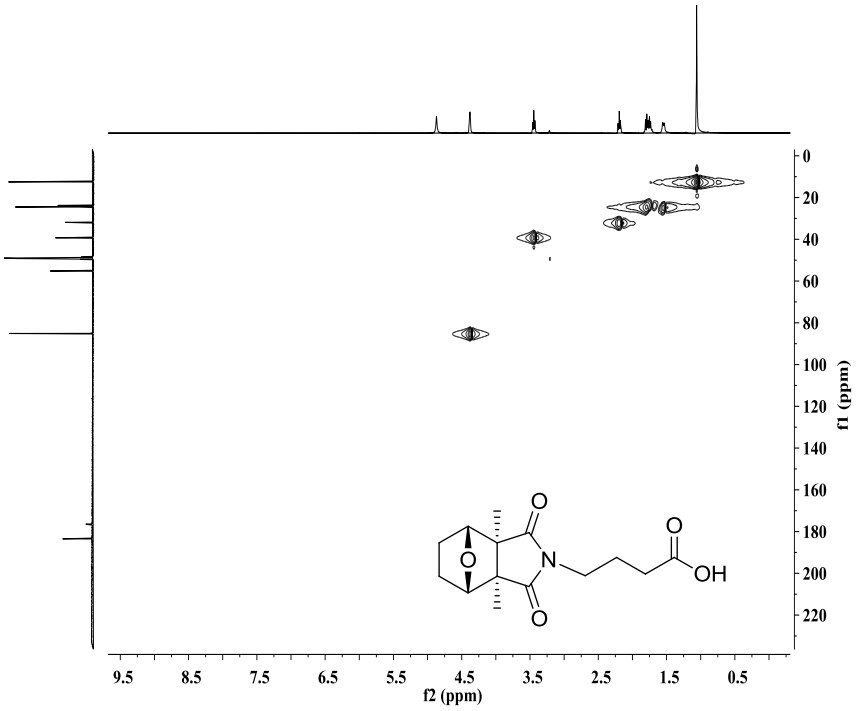

Figure S25. HSQC spectrum of compound **3** in CD_3OD (400 MHz)

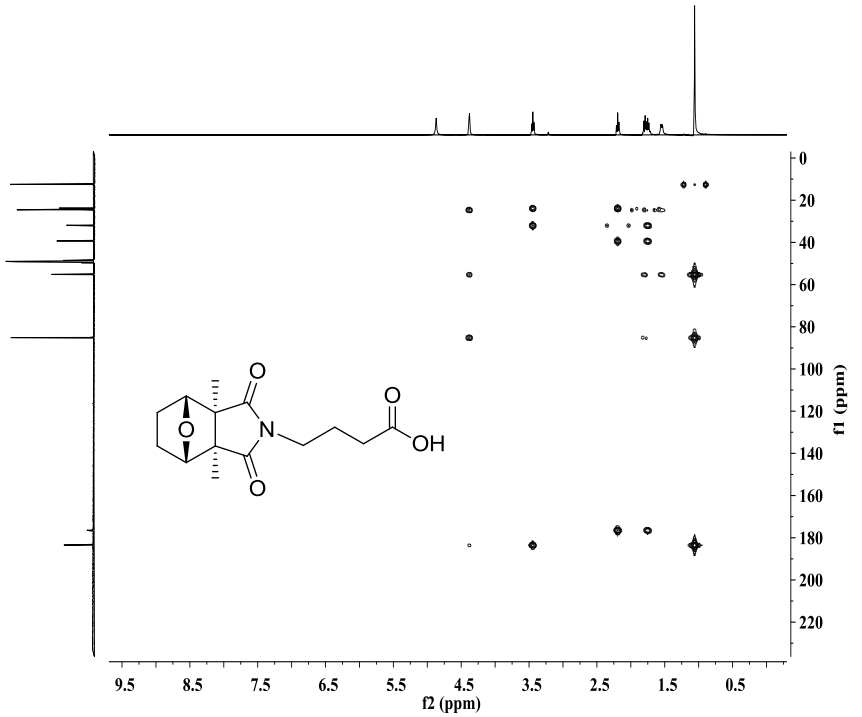

Figure S26. HMBC spectrum of compound **3** in CD_3OD (400 MHz)

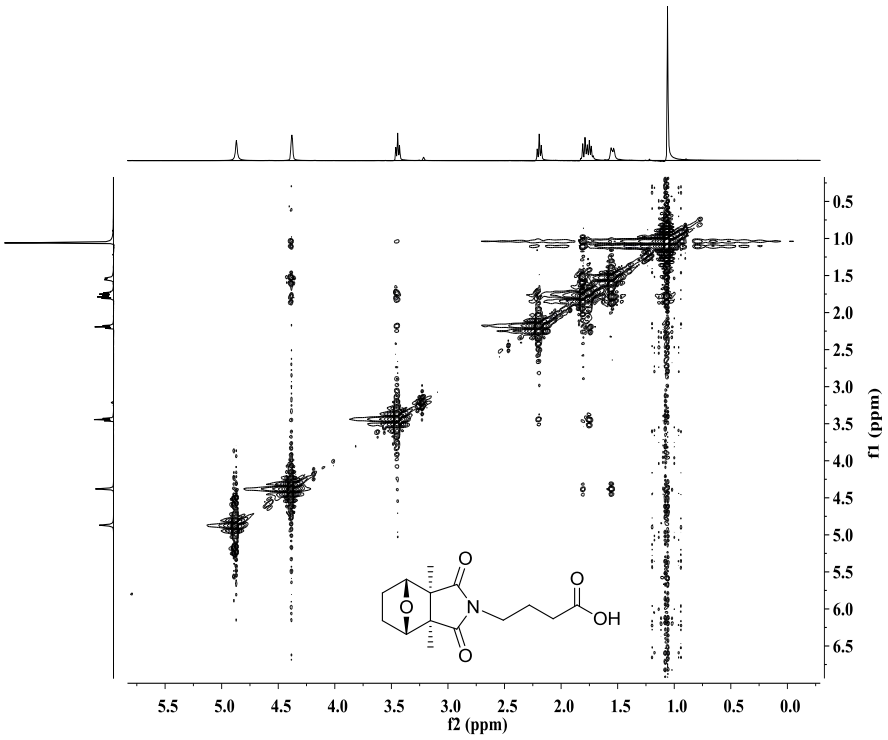

Figure S27. NOESY spectrum of compound **3** in CD_3OD (400 MHz)

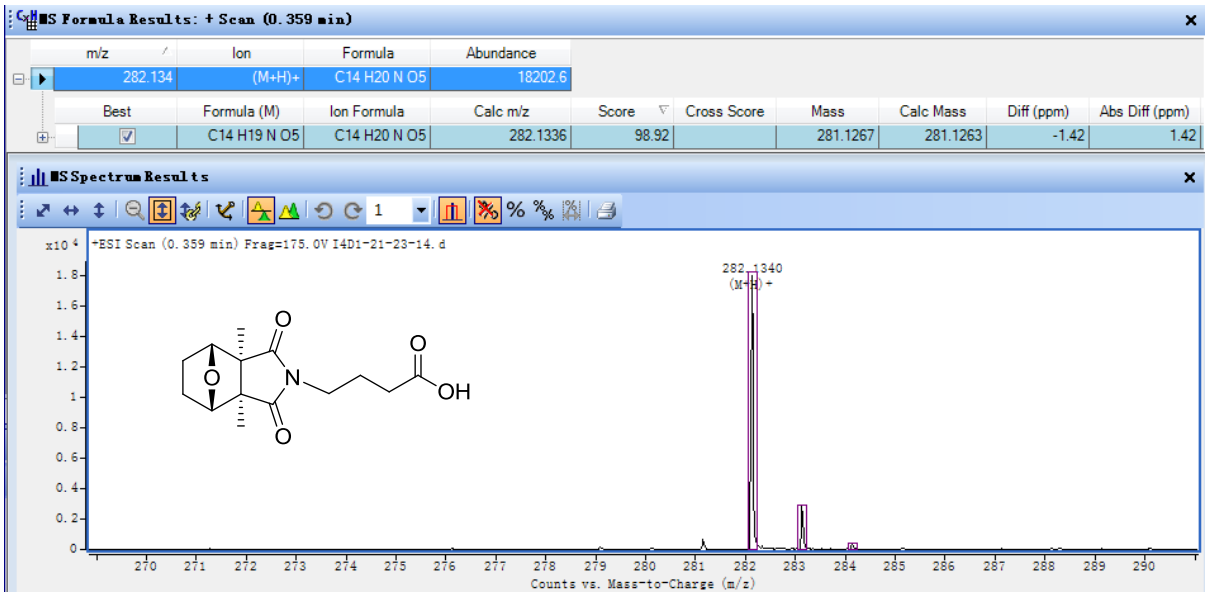

Figure S28. HR-ESI-MS spectrum of **3**

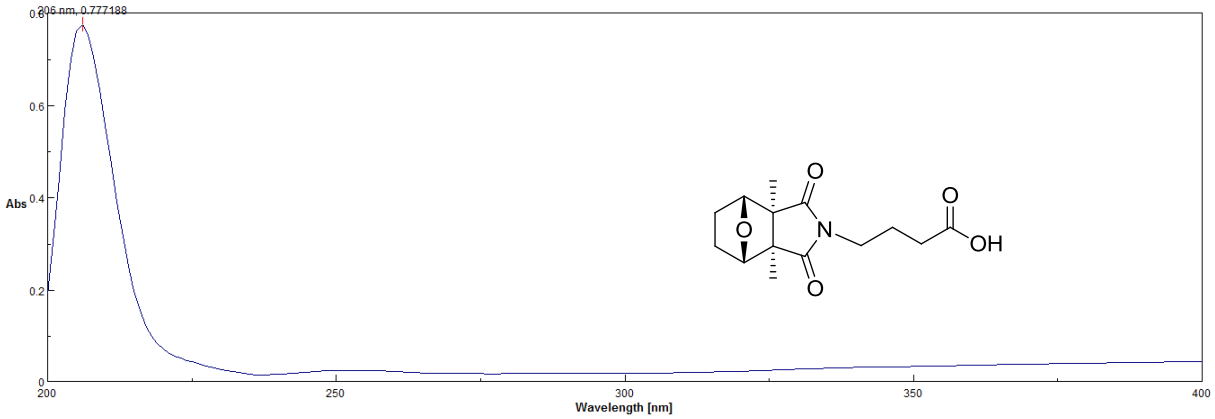

Figure S29. UV spectrum of **3** in MeOH

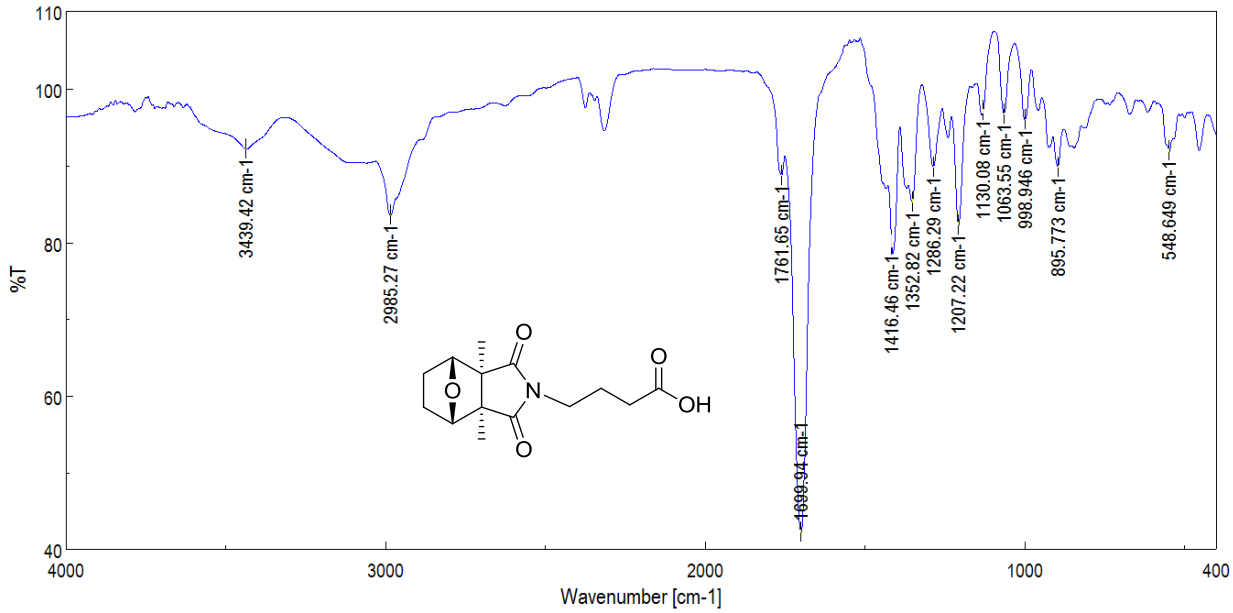

Figure S30. IR (KBr disc) spectrum of **3**

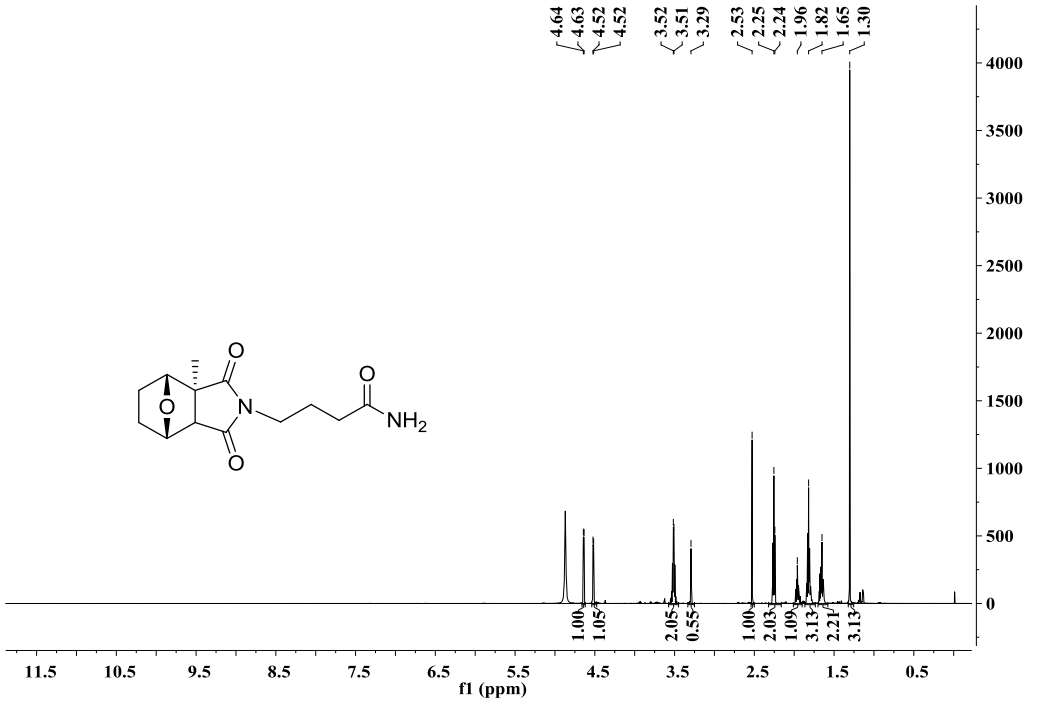

Figure S31. ^{1}H NMR spectrum of compound **4** in CD_3OD (600 MHz)

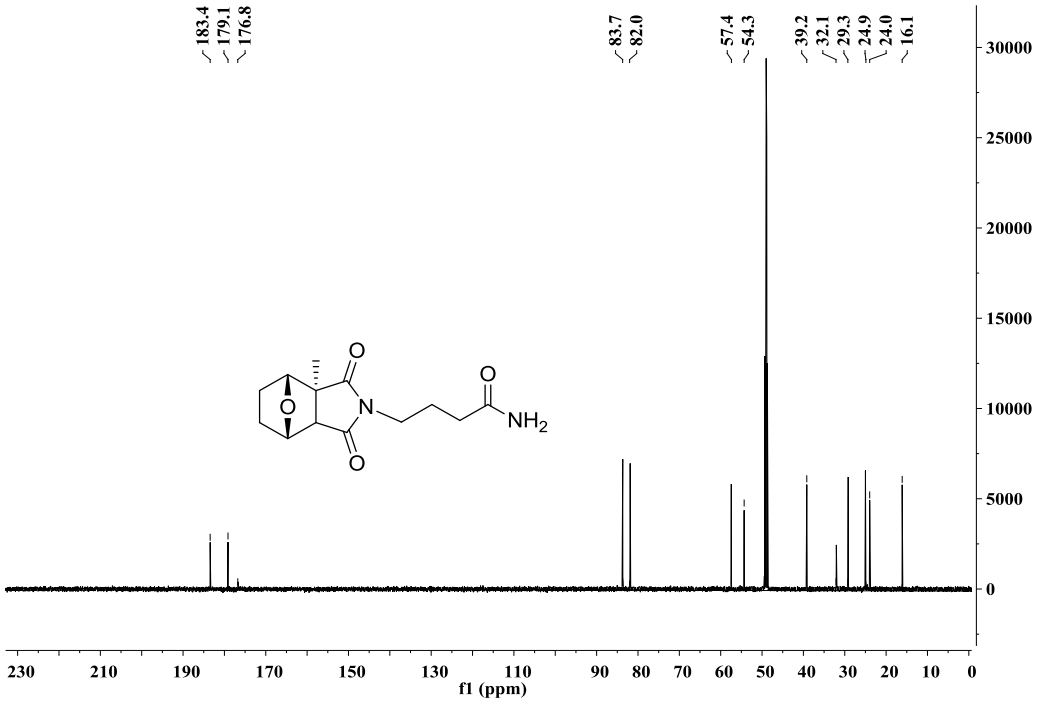

Figure S32. ^{13}C NMR spectrum of compound **4** in CD_3OD (150 MHz)

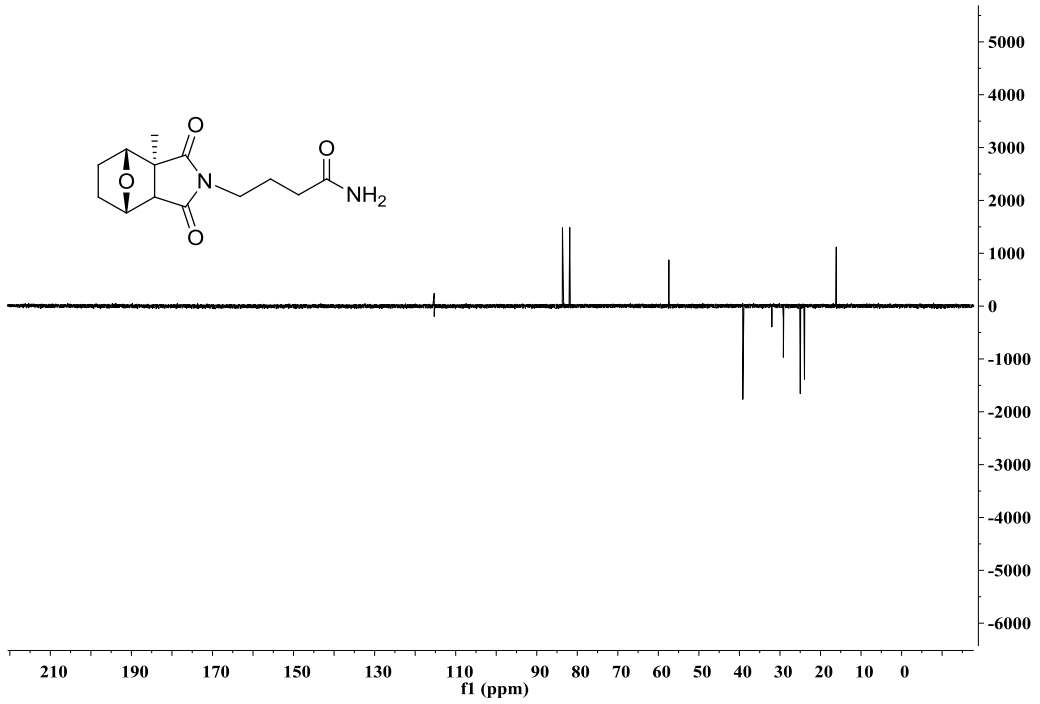

Figure S33. DEPT-135 spectrum of compound **4** in CD_3OD (150 MHz)

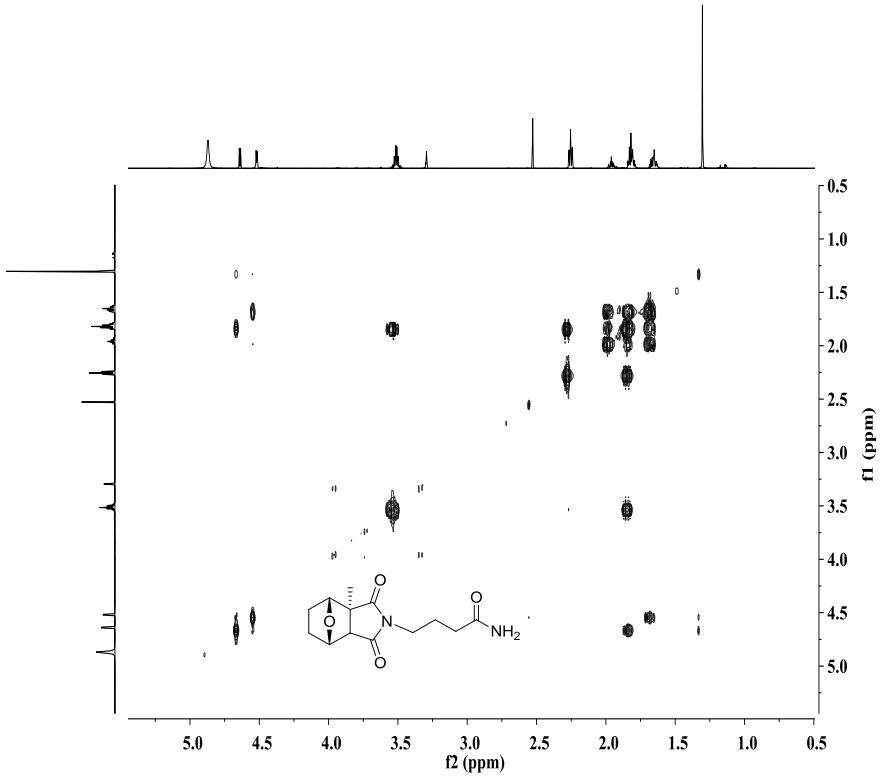

Figure S34. ^1H-^1H COSY spectrum of compound **4** in CD_3OD (600 MHz)

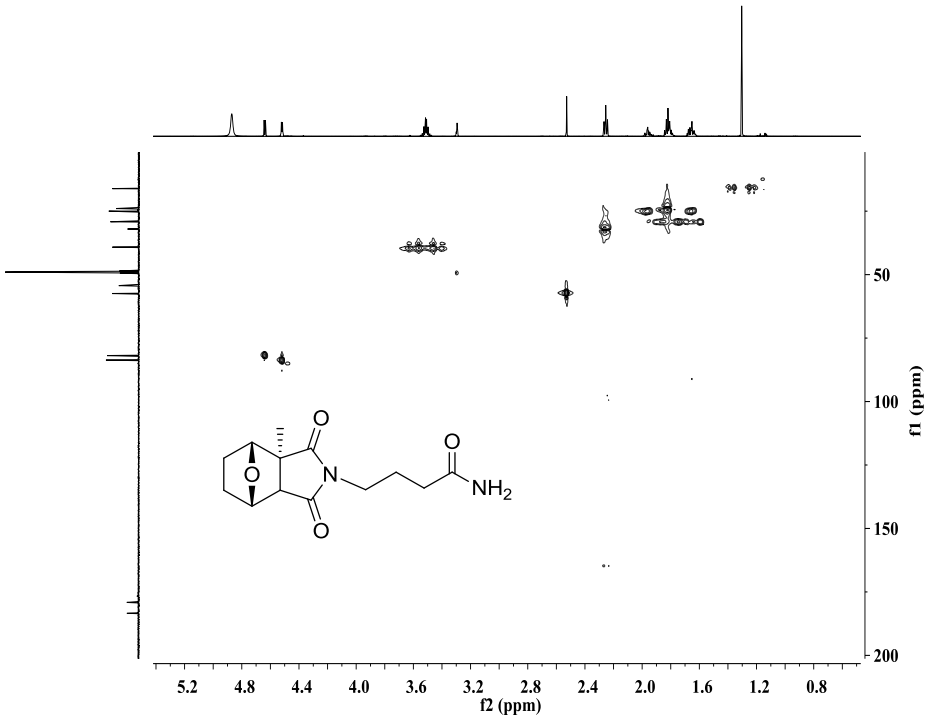

Figure S35. HSQC spectrum of compound **4** in CD_3OD (600 MHz)

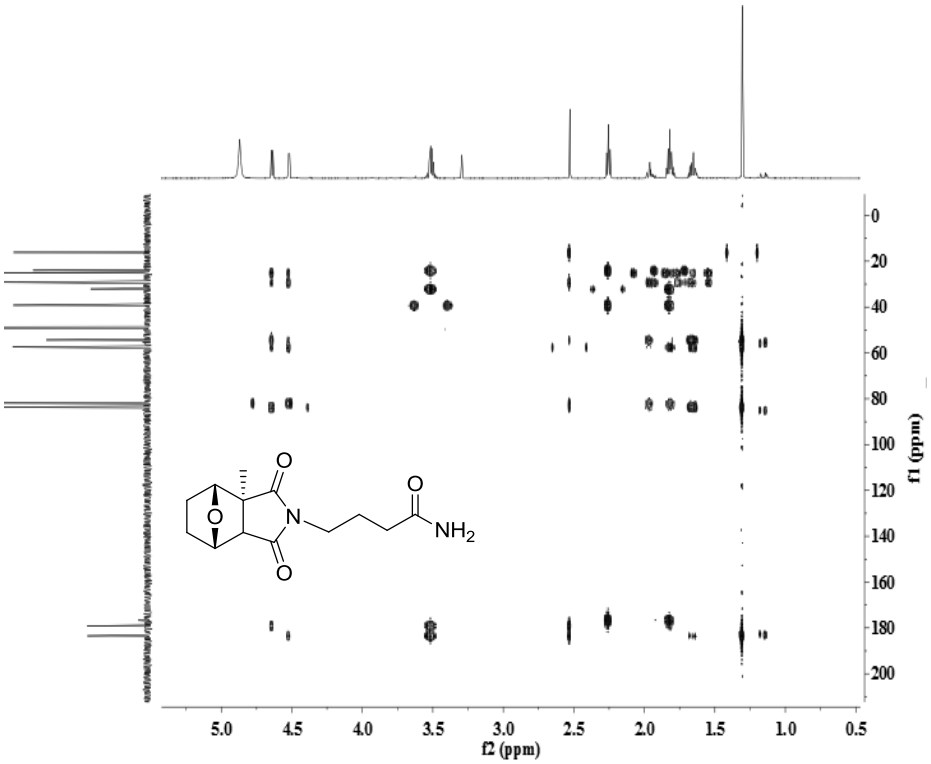

Figure S36. HMBC spectrum of compound **4** in CD_3OD (600 MHz)

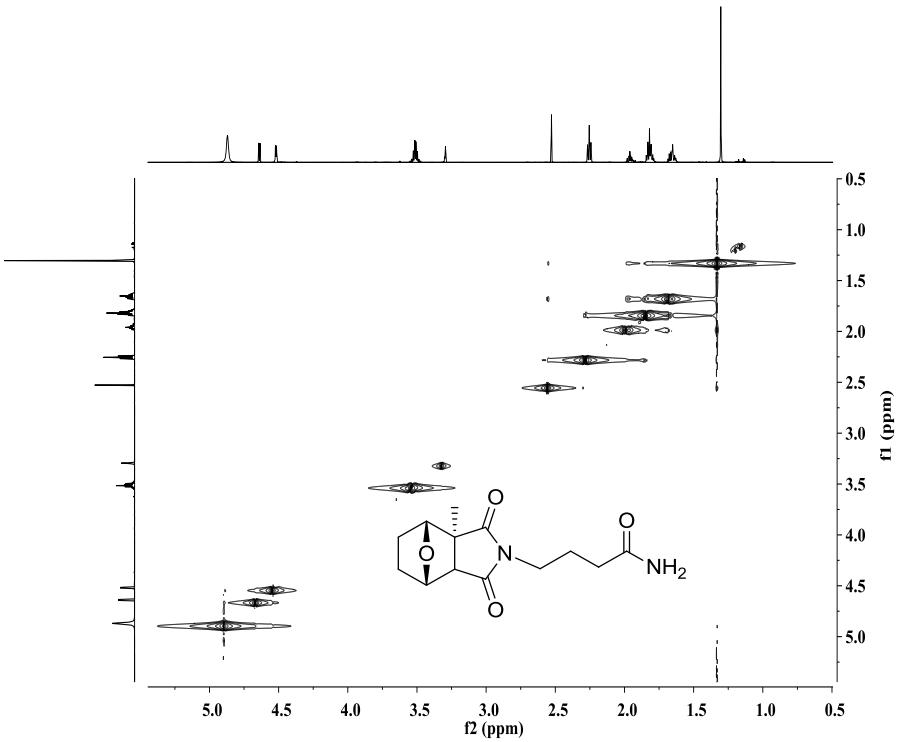

Figure S37. NOESY spectrum of compound **4** in CD_3OD (600 MHz)

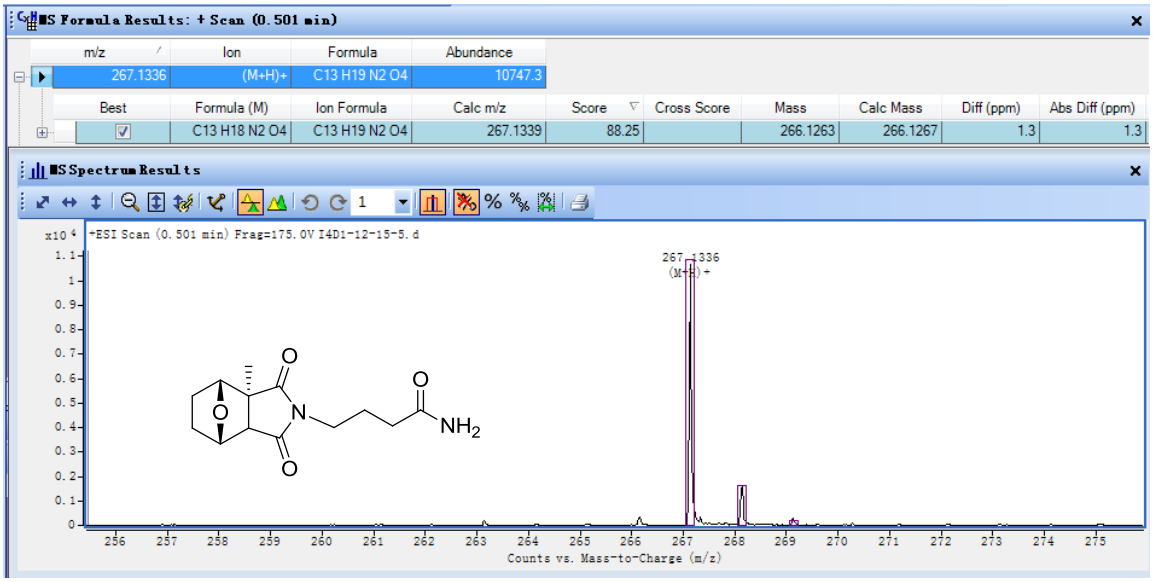

Figure S38. HR-ESI-MS spectrum of **4**

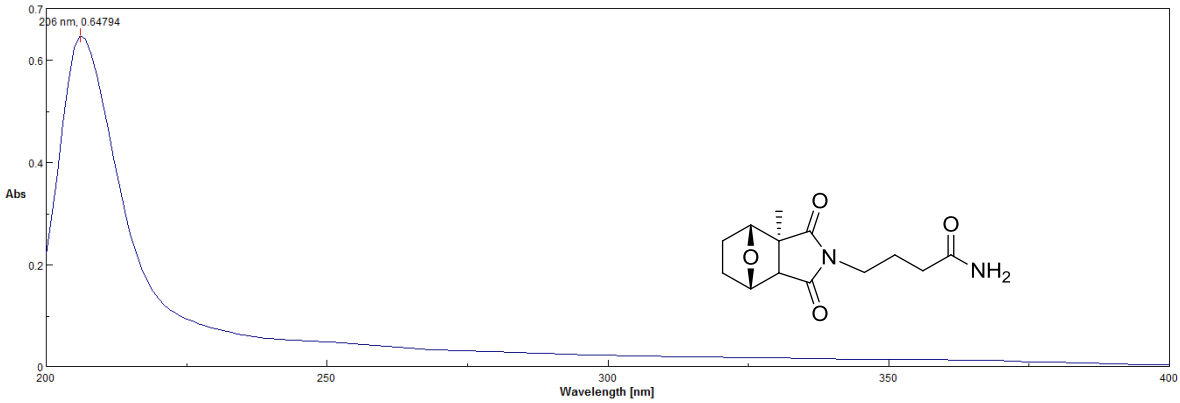

Figure S39. UV spectrum of **4** in MeOH

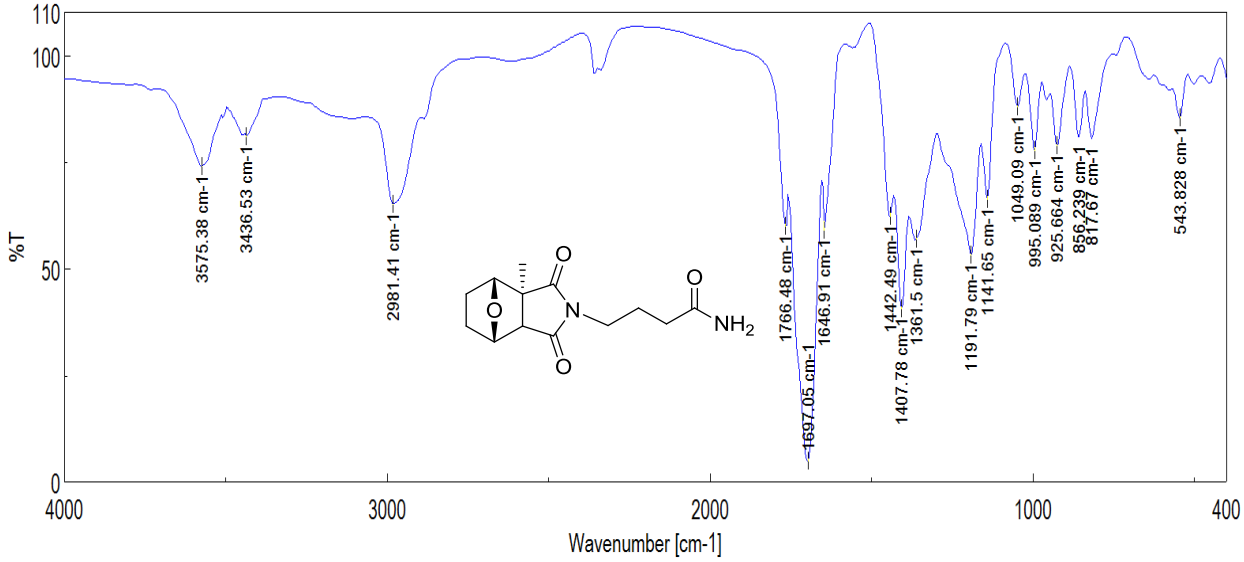

Figure S40. IR (KBr disc) spectrum of **4**

Table S1. Crystal data and structure refinement for **1**

Identification code	14
Empirical formula	$C_{15}H_{21}NO_5$
Formula weight	295.33
Temperature	293(2) K
Wavelength	1.54178Å
Crystal system, space group	monoclinic, P 21/n
Unit cell dimensions	a = 8.41720 (10) Å alpha = 90 °
	b = 10.23860 (10) Å beta =101.5320(10) °
	c = 17.71080 (10) Å gamma = 90 °
Volume	1495.51 (3) $Å^3$
Z, Calculated density	4, 1.312Mg/m^3
Absorption coefficient	0.817mm^{-1}
F(000)	632
Crystal size	0.45 x 0.35 x 0.28mm
Theta range for data collection	5.015 to 74.150 °
Limiting indices	-10<=h<=10, -12<=k<=12, -21<=l<=20
Reflections collected / unique	3033/ 2865 [R(int) = 0.0259]
Completeness to theta = 67.679 °	100 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.78202
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3033 / 0 / 194
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R_1 = 0.0376, wR_2 = 0.0984
R indices (all data)	R_1 = 0.0393, wR_2 = 0.0969

Calculation details for 2

The systematic random conformational analysis of the enantiomers of compound **2** was performed in the SYBYL 8.1 program by using MMFF94s molecular force field, which afforded 10 conformers of **2**, with an energy cutoff of 10 kcal mol^{-1} to the global minima. All the obtained conformers were further optimized using DFT at the B3LYP/6-31+G(d) level in gas phase by using Gaussian09 software,[1] and 6 conformers of **1** were selected. All of the optimized stable conformers were used for TDDFT computation of the excited stats at the same levels, with the consideration of the first 30 excitations. The overall ECD curves of **2** were weighted by Boltzmann

distribution of each conformer (with a half-bandwidth of 0.33 eV), with a UV correction of 10 nm. The calculated ECD spectra of **2** were subsequently compared with the experimental one. The ECD spectra were produced by SpecDis 1.6 software.[2]

[1] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[2] T. Bruhn, A. Schaumlöffel, Y. Hemberger, G. Bringmann, SpecDis version 1.60, University of Wuerzburg, Germany, 2012.