Supporting Information

Readily Functionalized AAA-DDD Triply Hydrogen-Bonded Motifs

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^{1}H NMR and ^{13}C NMR Spectra of Intermediates, AAA and DDD compounds

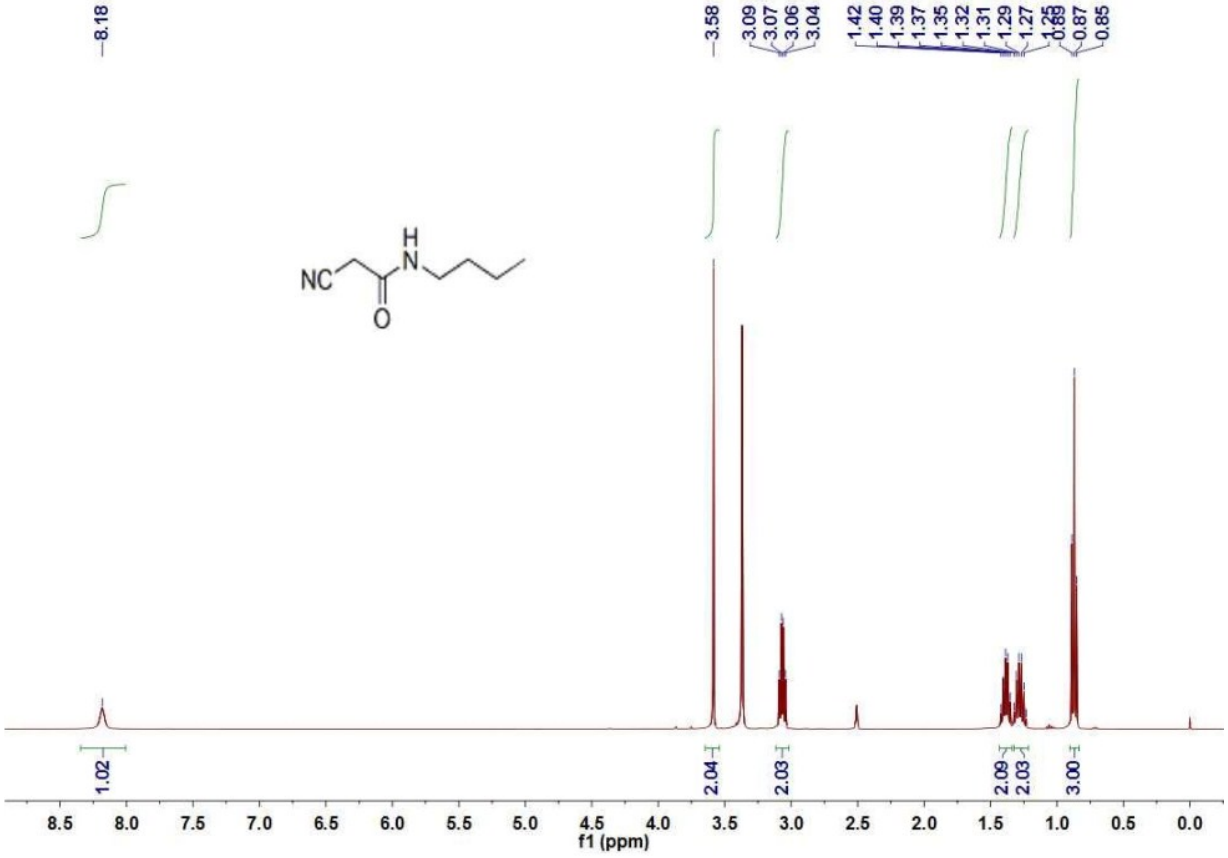


Figure S1. ^{1}H NMR of **1a** in DMSO-d_6.

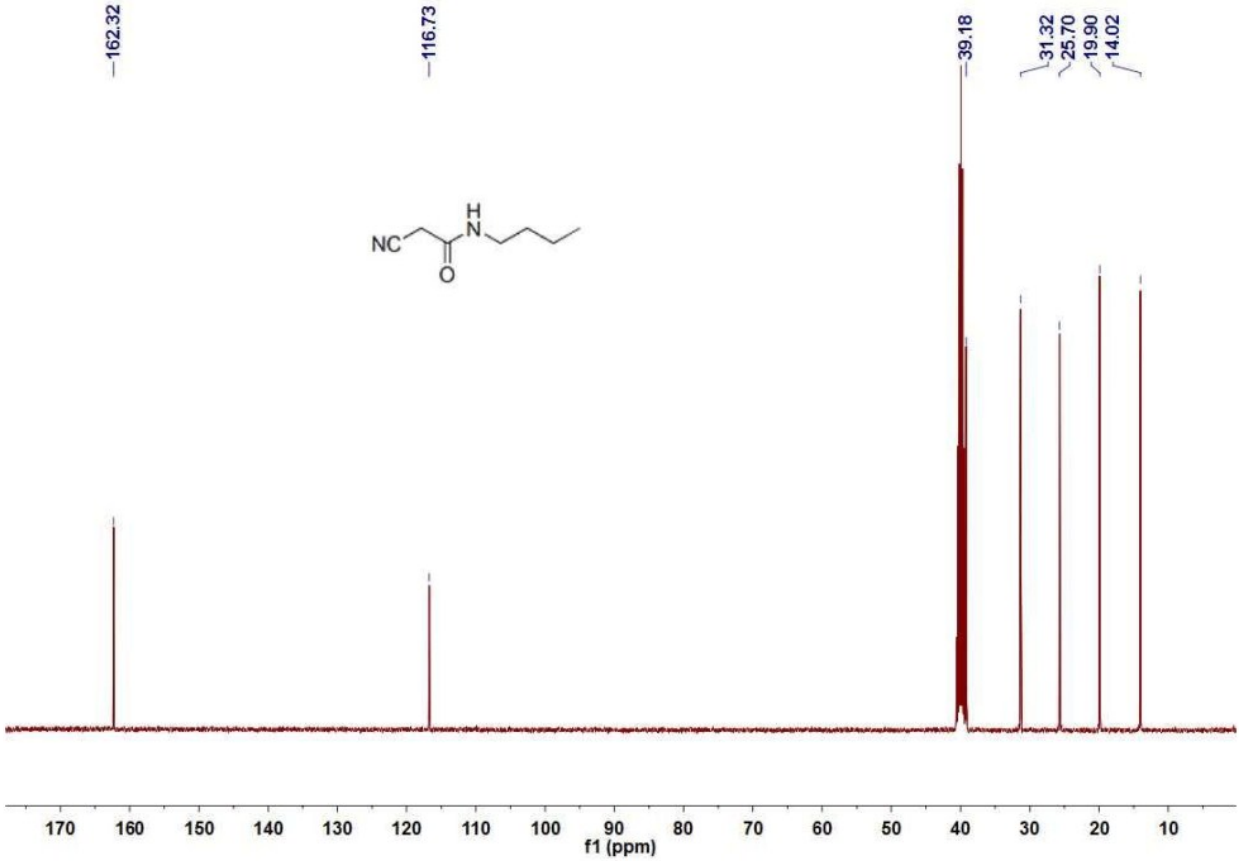


Figure S2. ^{13}C NMR of **1a** in DMSO-d_6.

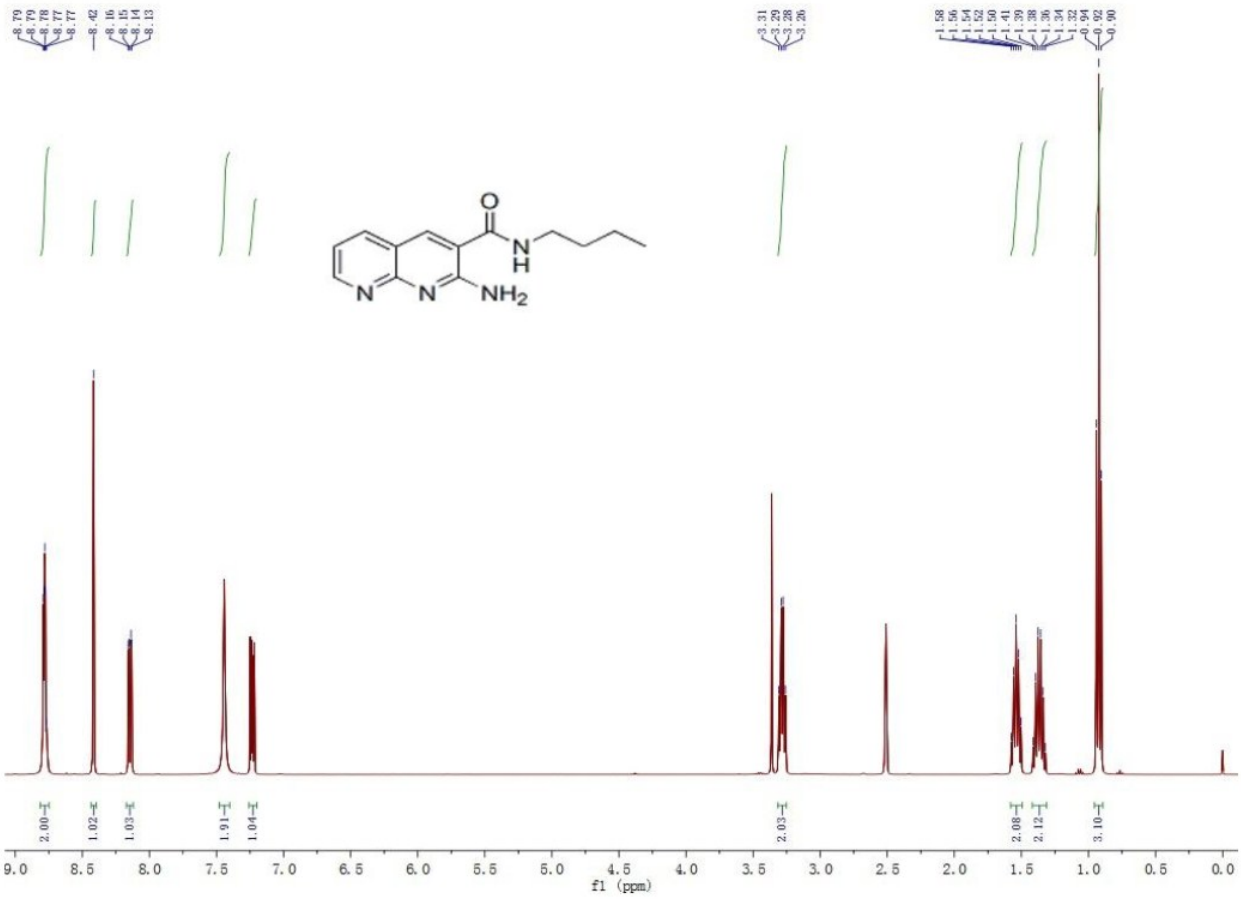


Figure S3. ^{1}H NMR of **2a** in DMSO-d_6.

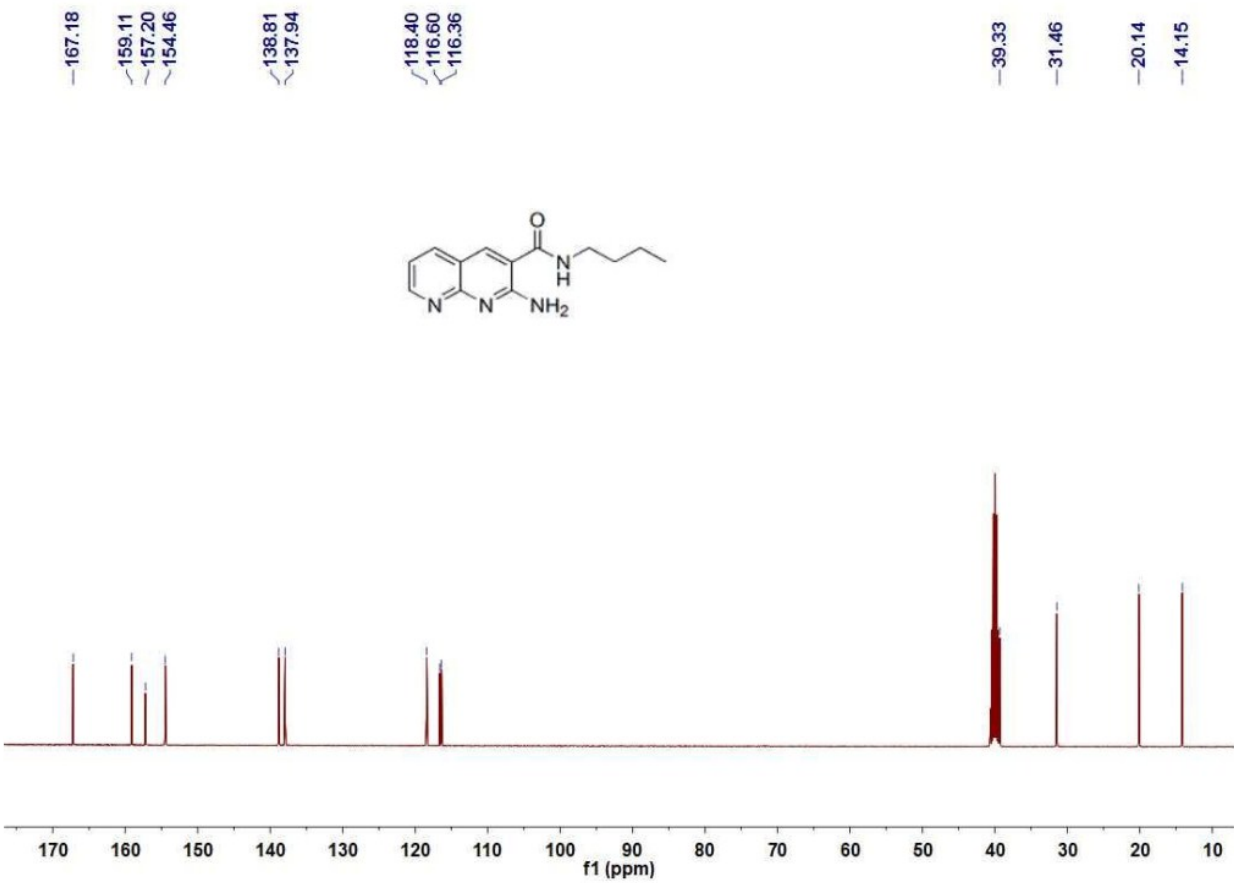


Figure S4. ^{13}C NMR of **2a** in DMSO-d_6.

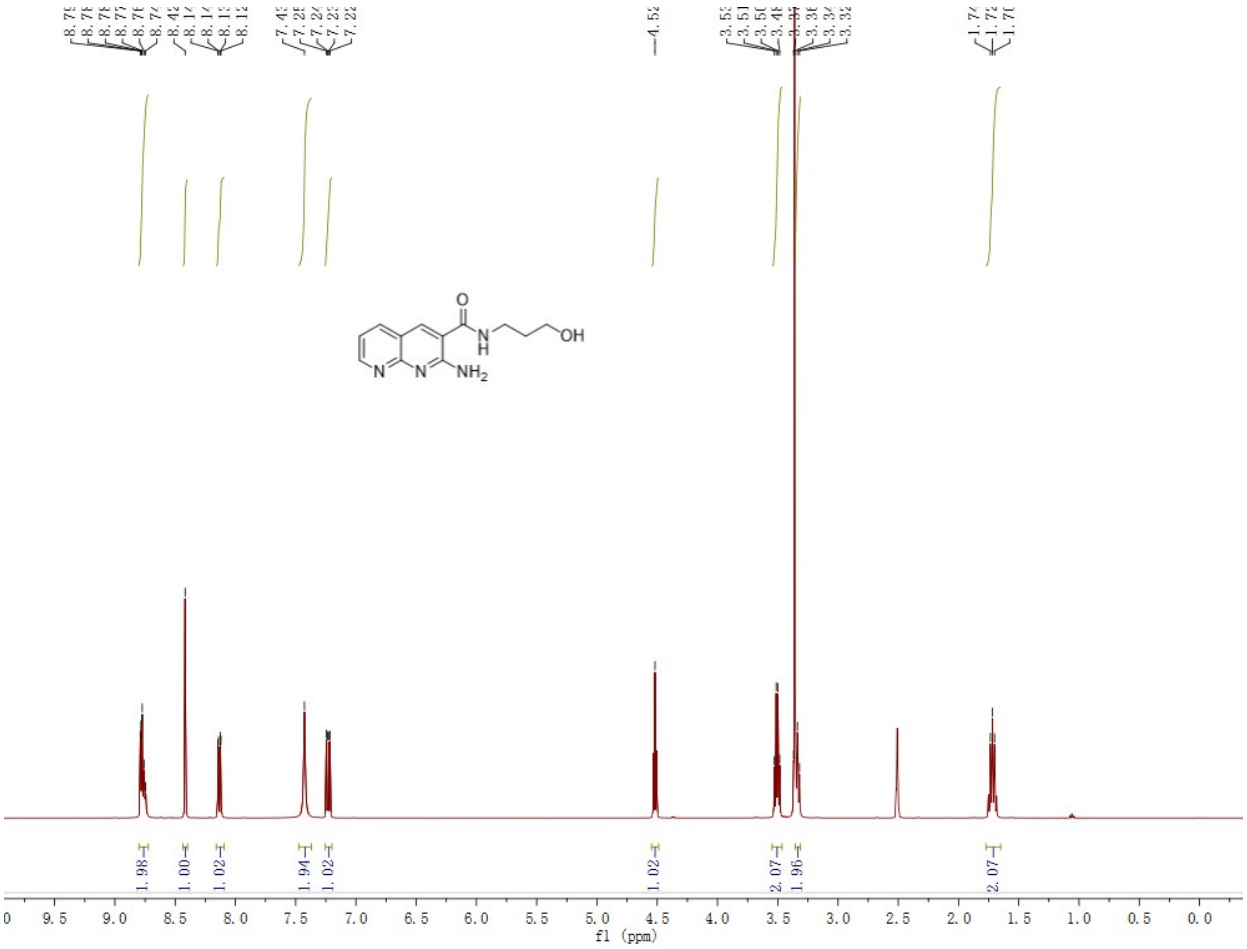


Figure S5. ^{1}H NMR of **2b** in DMSO-d_6.

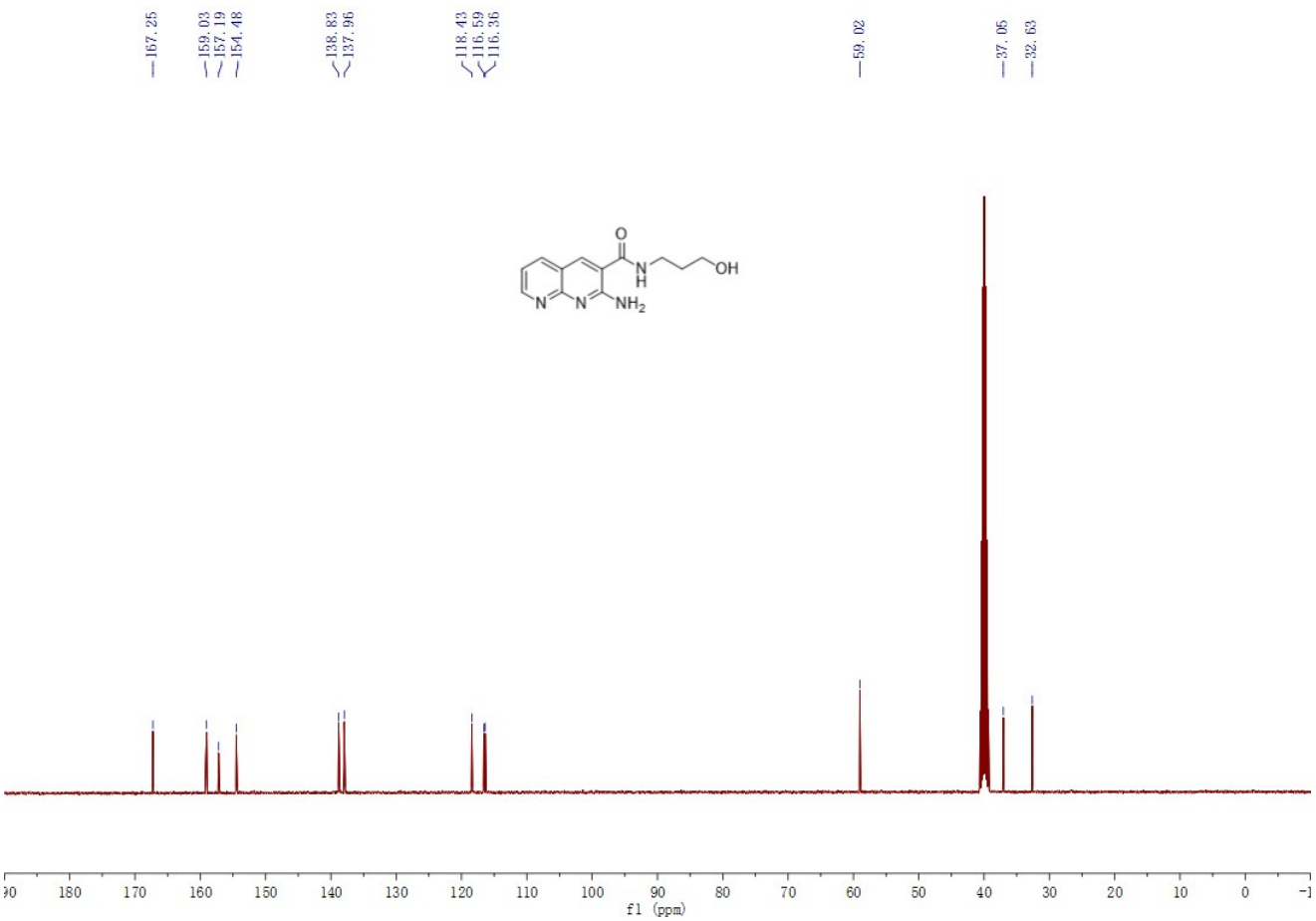


Figure S6. ^{13}C NMR of **2b** in DMSO-d_6.

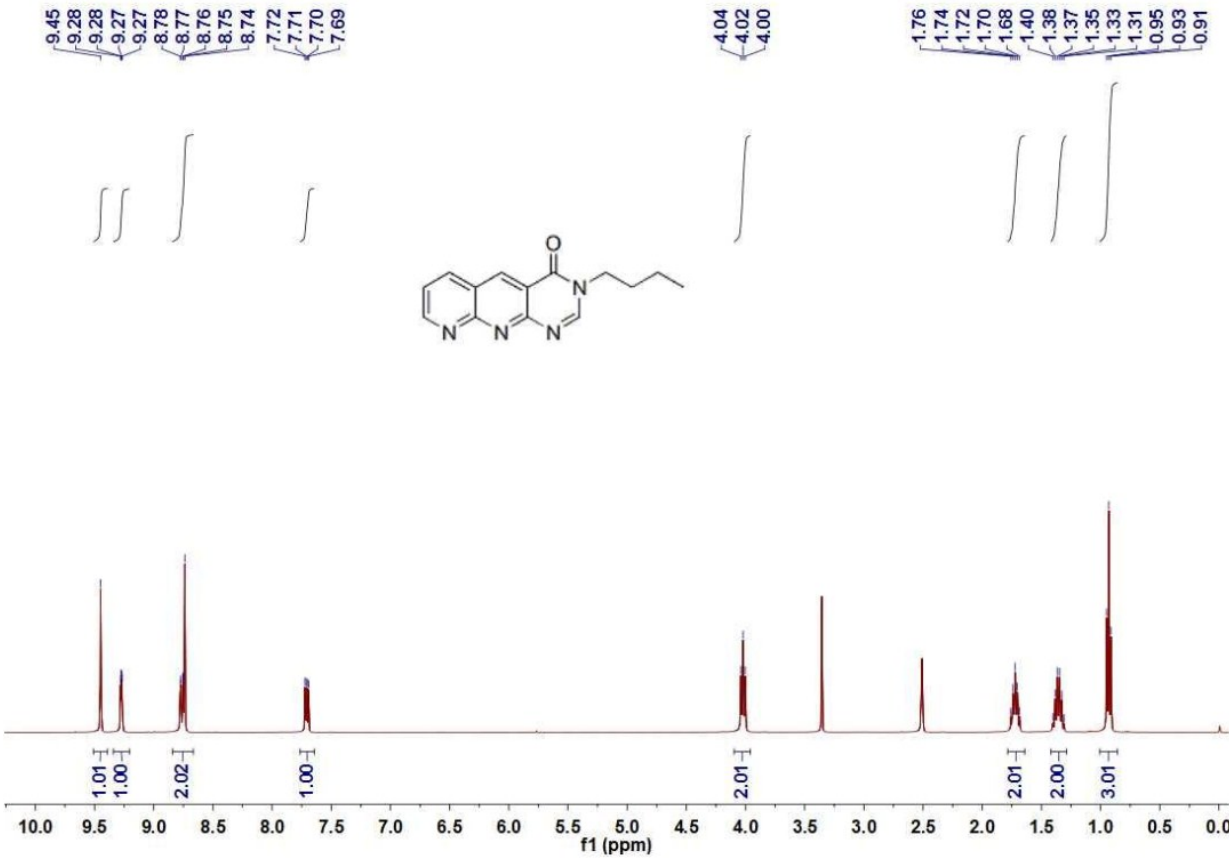


Figure S7. ^{1}H NMR of **3a** in DMSO-d_6.

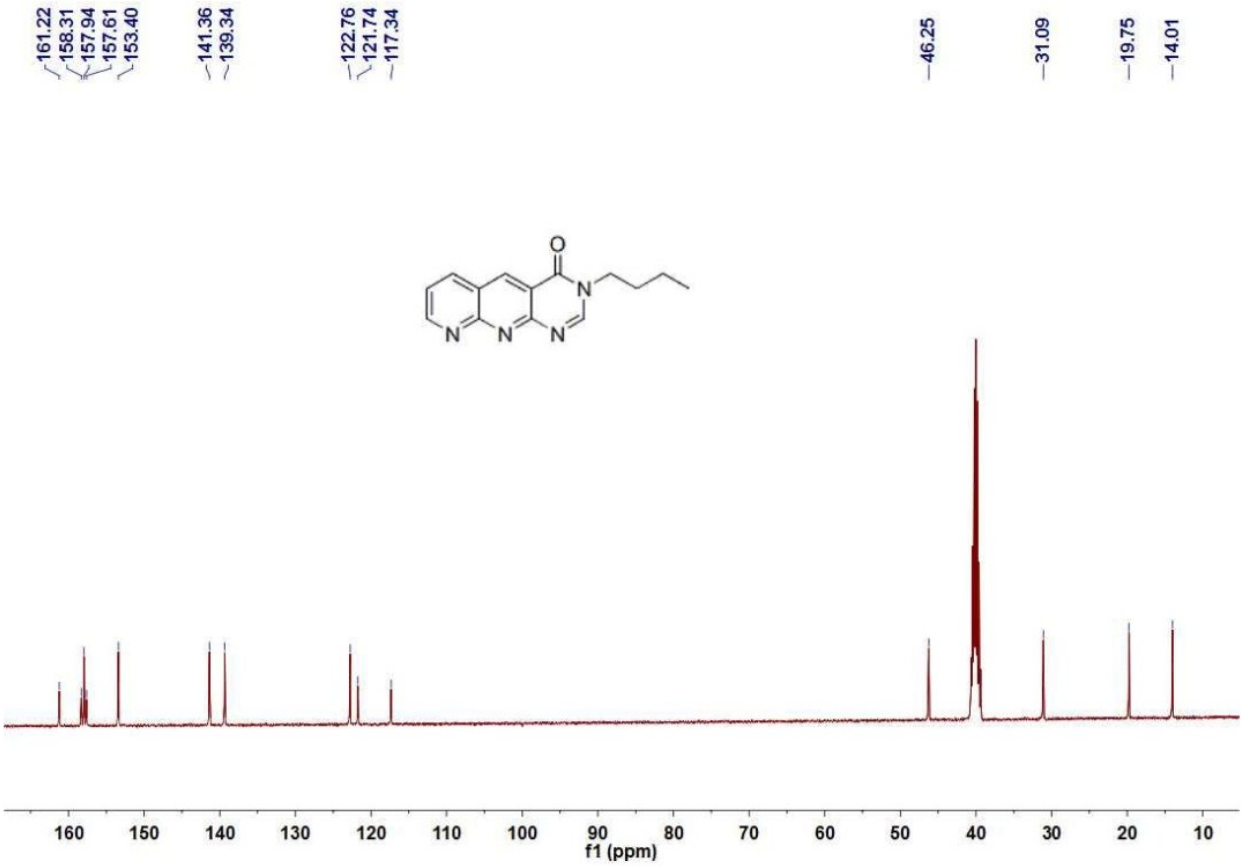


Figure S8. ^{13}C NMR of **3a** in DMSO-d_6.

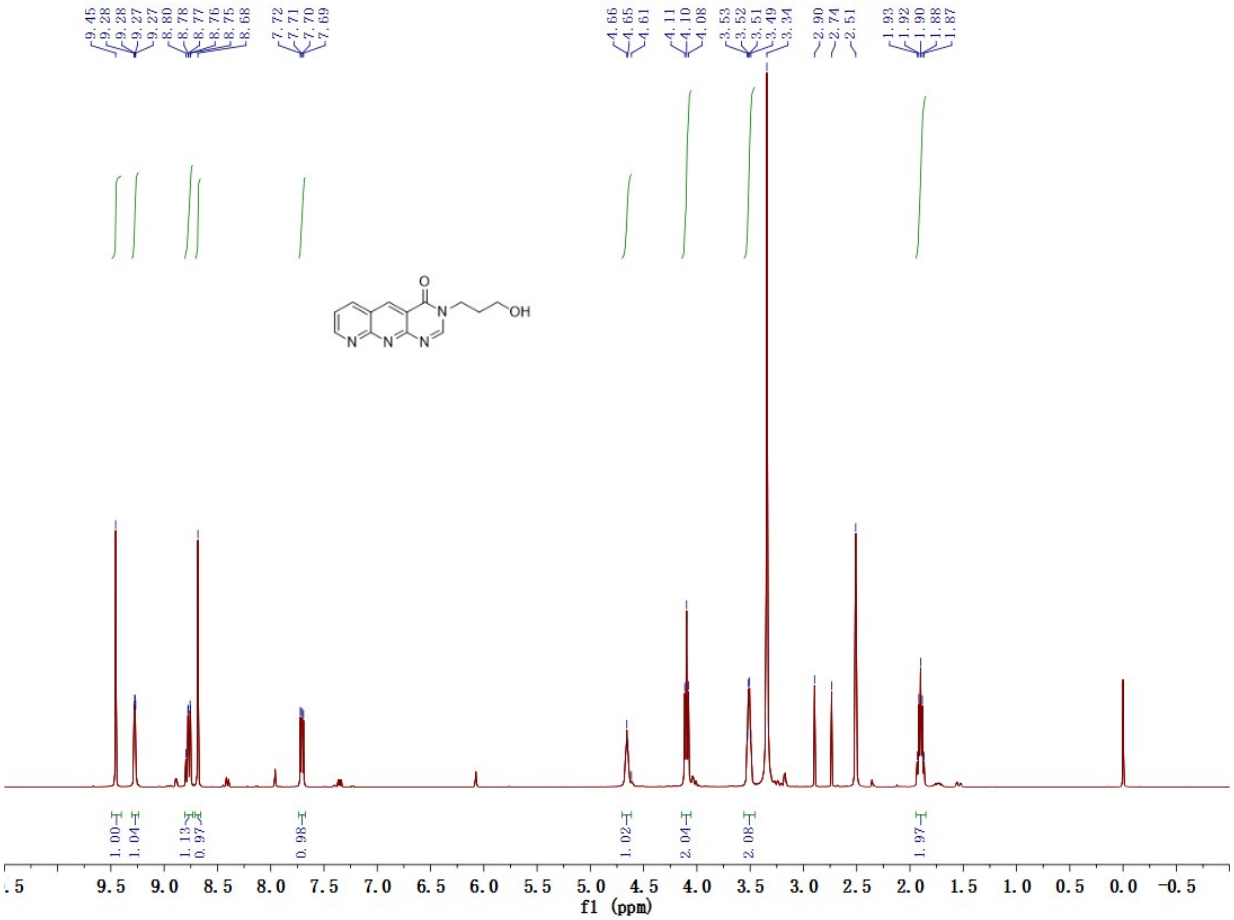


Figure S9. ^{1}H NMR of **3b** in DMSO-d_6.

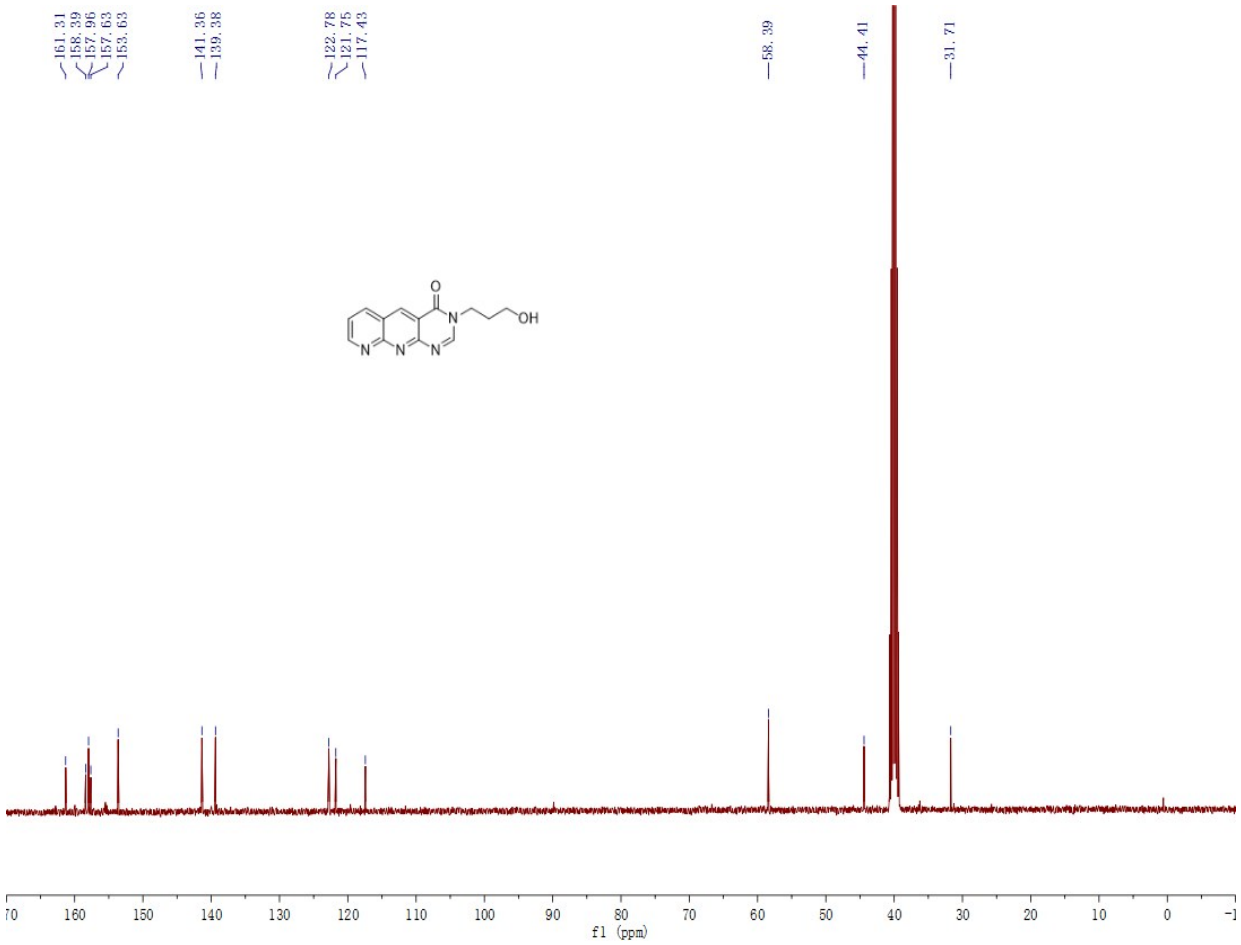


Figure S10. ^{13}C NMR of **3b** in DMSO-d_6.

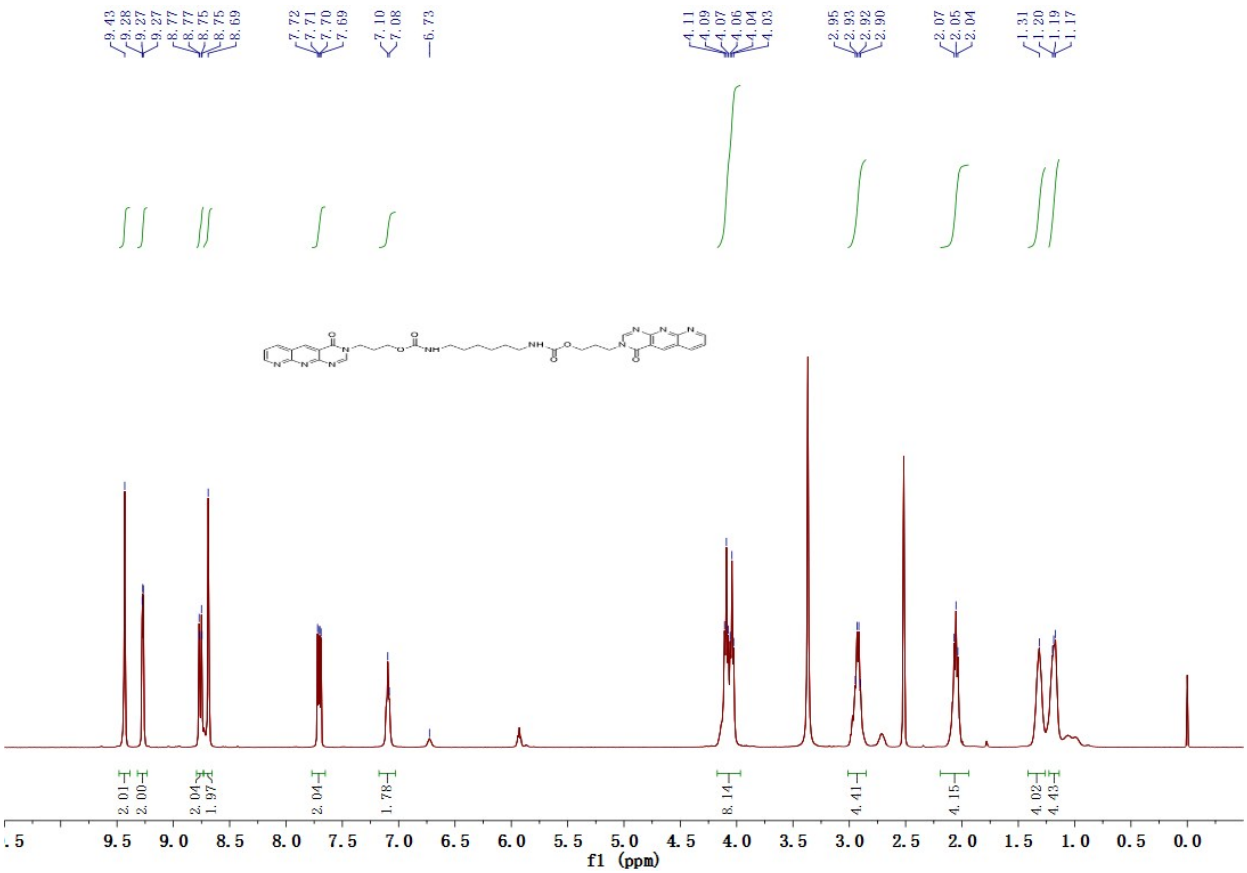


Figure S11. ^{1}H NMR of **5** in DMSO-d_6.

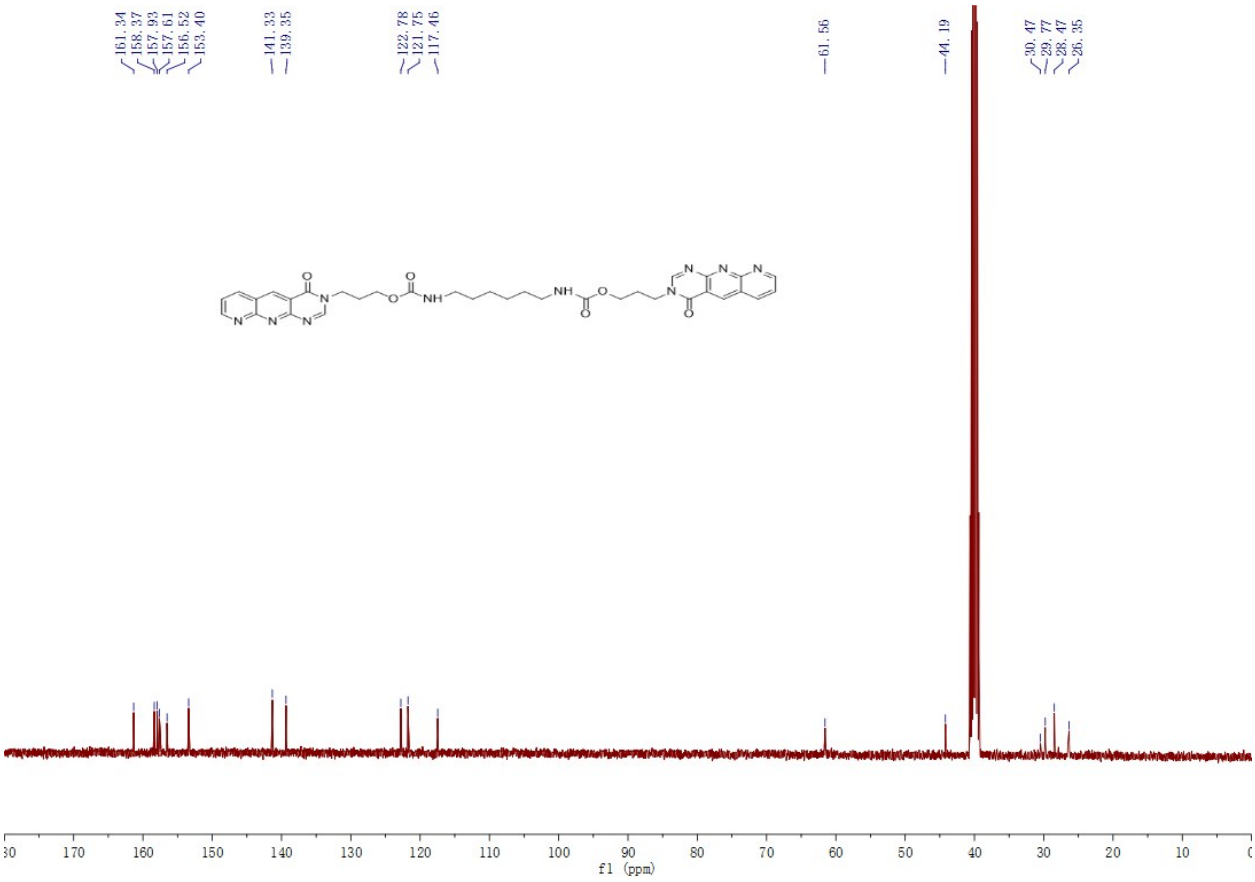


Figure S12. ^{13}C NMR of **5** in DMSO-d_6.

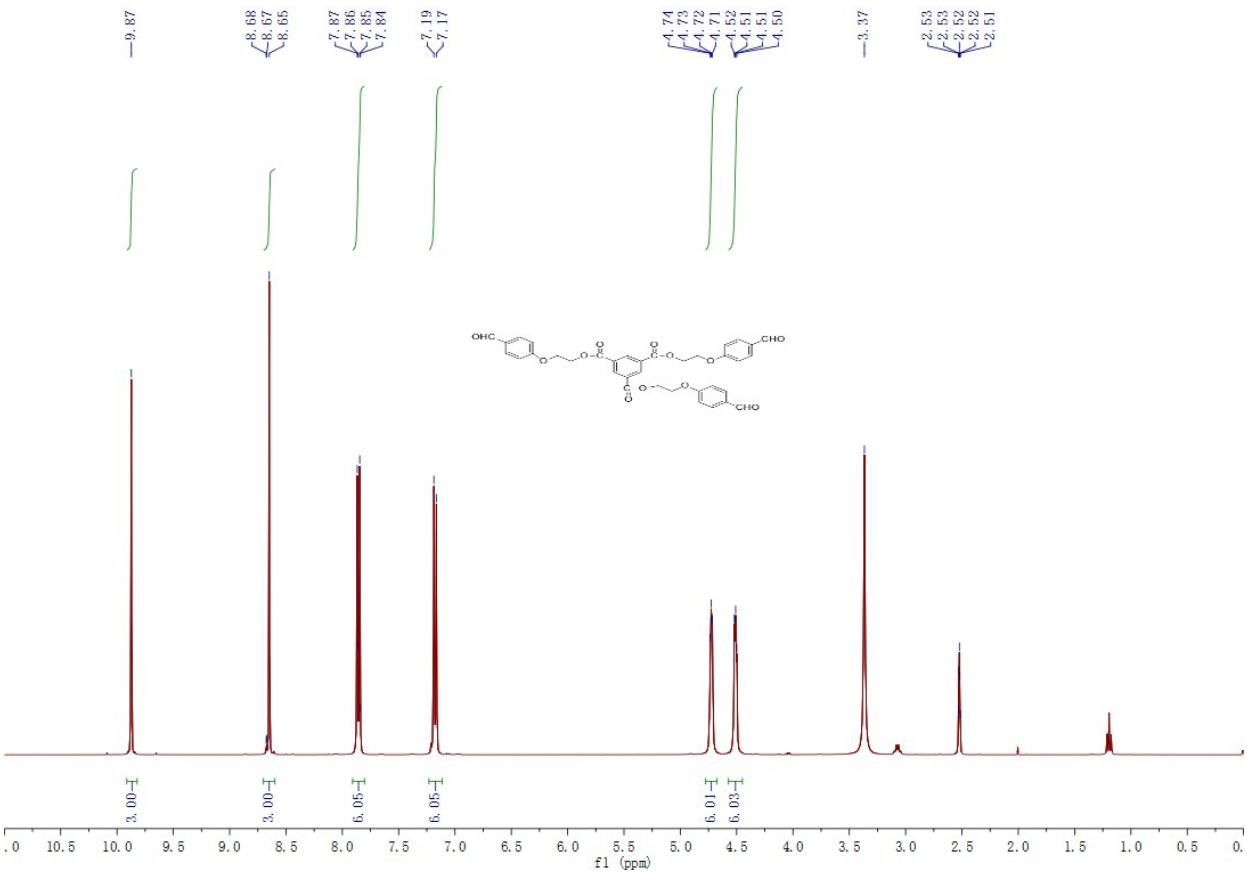


Figure S13. ^{1}H NMR of **6** in DMSO-d_6.

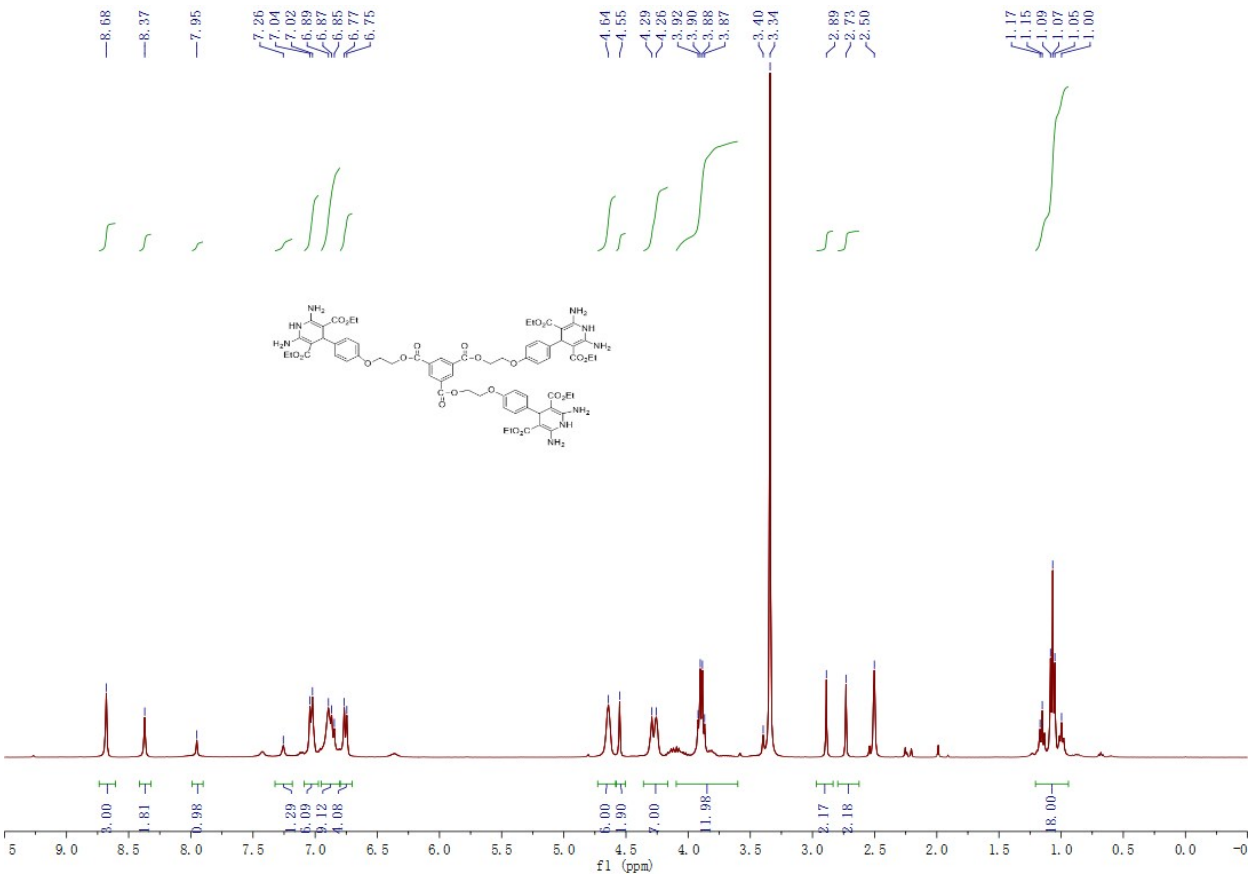


Figure S14. ^{1}H NMR of **7** in DMSO-d_6.

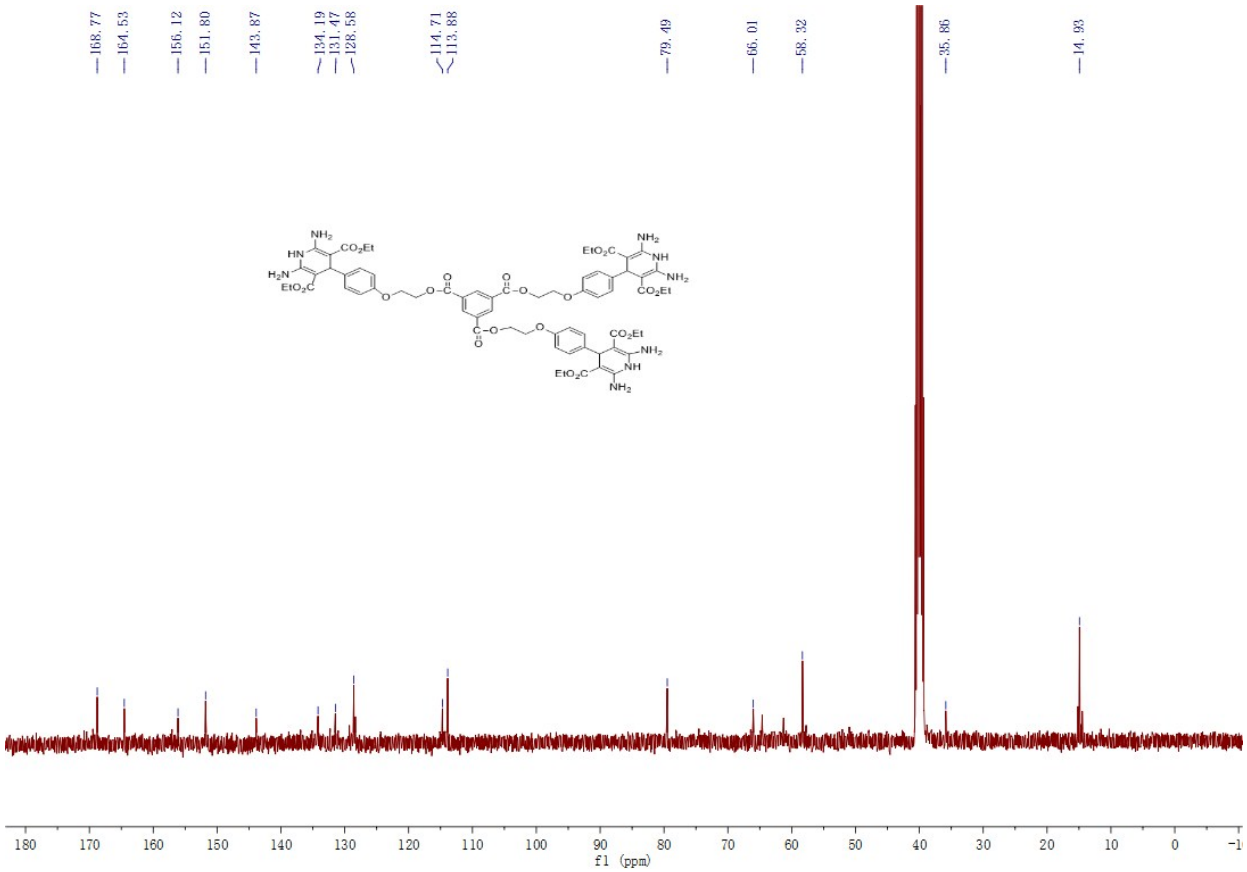
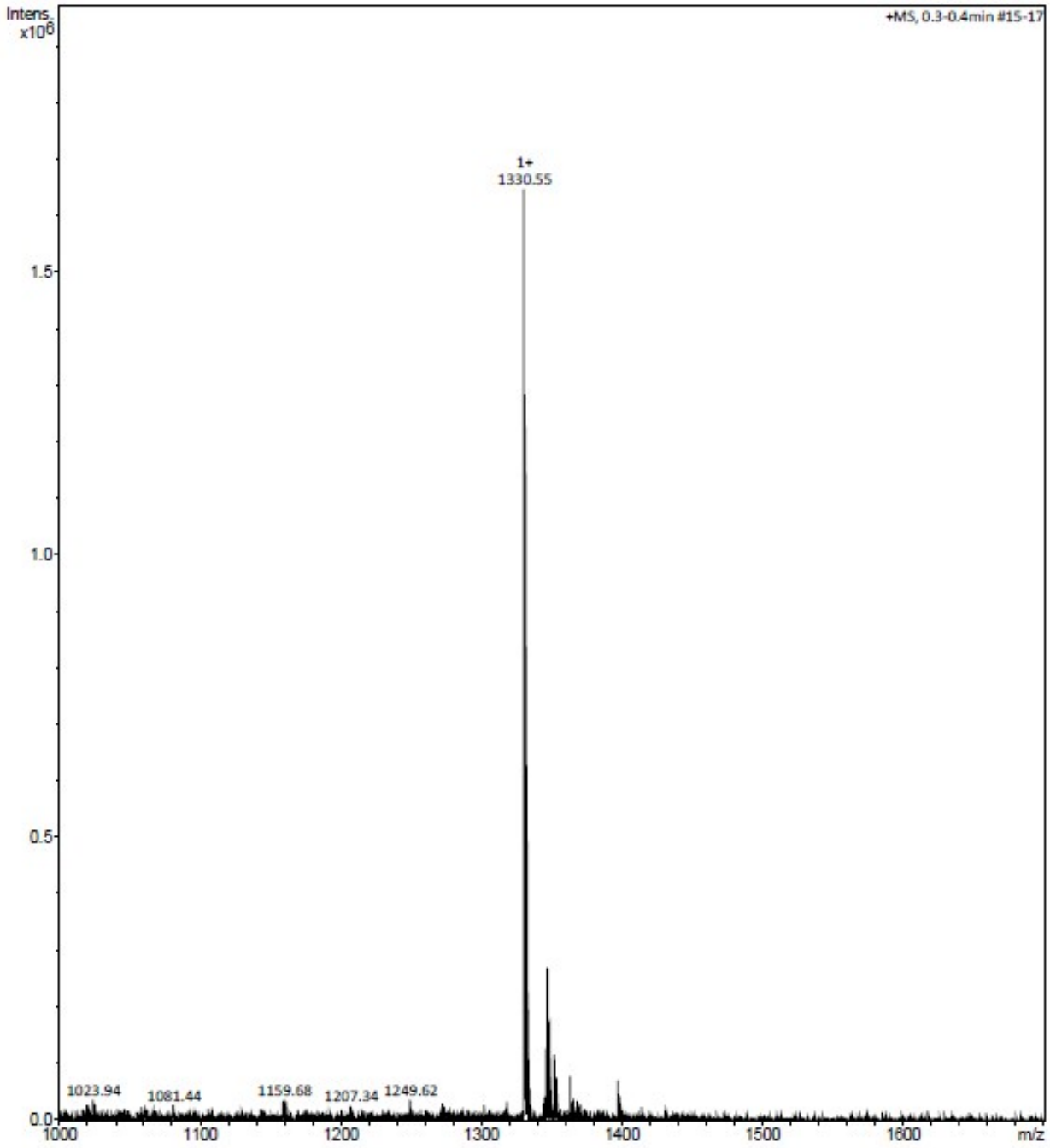


Figure S15. ^{13}C NMR of **7** in DMSO-d_6.

Mass Spectrum of Compound 7



Compound 3a X-Ray Crystal Structure

Table S1. Crystallography parameters for **3a** single crystal.

	3a
Chemical Formula	$C_{14}H_{14}N_4O$
Molecular Weight ($g \cdot mol^{-1}$)	254.28
Crystal System	Monoclinic
Space Group	P $2_1/c$
a (Å)	7.753 (2)
b (Å)	14.532 (4)
c (Å)	11.144 (3)
α (°)	90
β (°)	98.574 (6)
γ (°)	90
V (Å^3)	1241.7 (6)
Z	4
F(000)	532
T (K)	296 (2)
λ (Å)	0.71073
ρ_{calc} ($g \cdot cm^{-3}$)	1.350
μ (mm^{-1})	0.088
Reflections Collected	7080
Unique Reflections	1972
Absorption Correction	None
Refinement on	F^2
Parameters Refined	2437
$R(F_0)(I>2\sigma(I))$	0.0348
$R_w(F_0^2)(I>2\sigma(I))$	0.0915
$R(F_0)$(all data)	0.0444
$R_w(F_0^2)$(all data)	0.1021
GOF on F^2	1.069

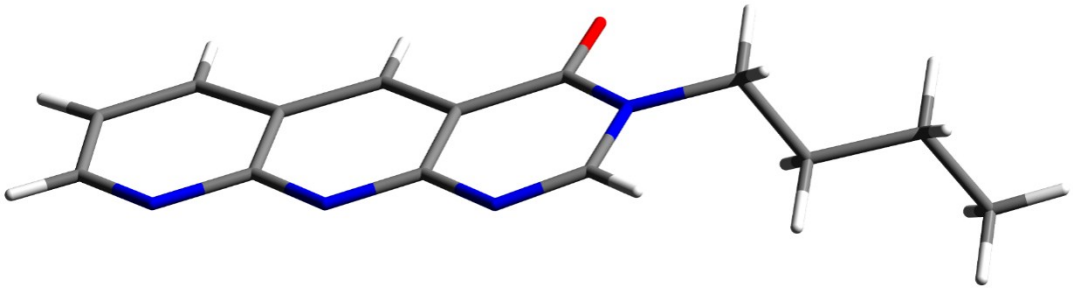


Figure S16. Stick representation of the X-ray crystal structure of compound **3a**. Blue, grey, white and red correspond to nitrogen, carbon, hydrogen and oxygen atoms, respectively.

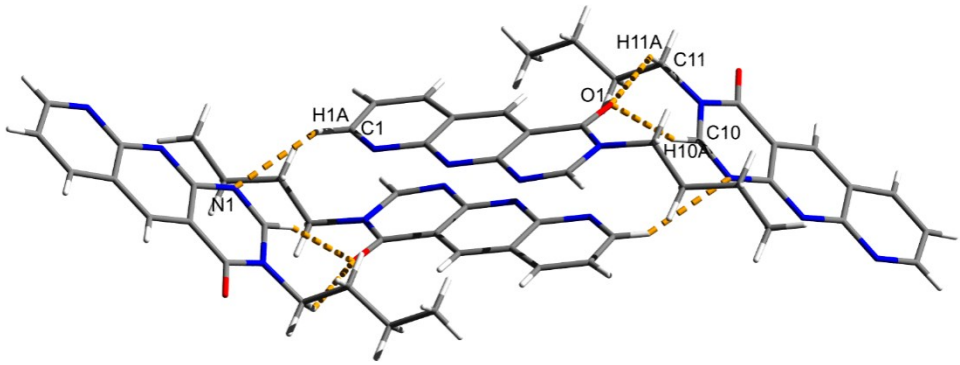


Figure S17. Stick representation of compound **3a** unit cell crystal structure. Blue, grey, white and red correspond to nitrogen, carbon, hydrogen and oxygen atoms, respectively.

^{1}H NMR Titrations

^{1}H NMR titration experiments were carried out at room temperature using deuterated chloroform as solvent. All ^{1}H NMR spectra were recorded on an Ascend™ 400 MHz spectrometer. In the titration experiment, **4** was assigned as the host, and **3a** was designated as the guest. The chemical shift monitored corresponded to the N-H proton of the 1,4-dihydro tautomer.

Preparation of host-guest solutions. In a clean and dry vial, 10 mL of a 0.01 mM solution of compound **4** in chloroform was prepared. Apart, in another clean and dry vial, 10 mL of a 0.01 mM solution of compound **3a** in chloroform was prepared. Via micro-injector nine aliquots of 1 mL each of compound **4** were taken and placed in nine empty vials previously labeled as: 0 Equivalents, 0.25 Equivalents, 0.50 Equivalents, 0.75 Equivalents, 1 Equivalent, 1.25 Equivalents, 1.50 Equivalents, 1.75 Equivalents and 2 Equivalents. To each one of these vials 0, 250 μL, 500 μL, 750 μL, 1.00 mL, 1.25 mL, 1.50 mL, 1.75 mL and 2.00 mL of compound **3a** solution were added, respectively. The solvent was removed from all vials by reduced pressure and 500 μL of $CDCl_3$ were added to each vial. Each prepared host-guest solution was transferred to an NMR tube and submitted to ^{1}H NMR spectrometry.

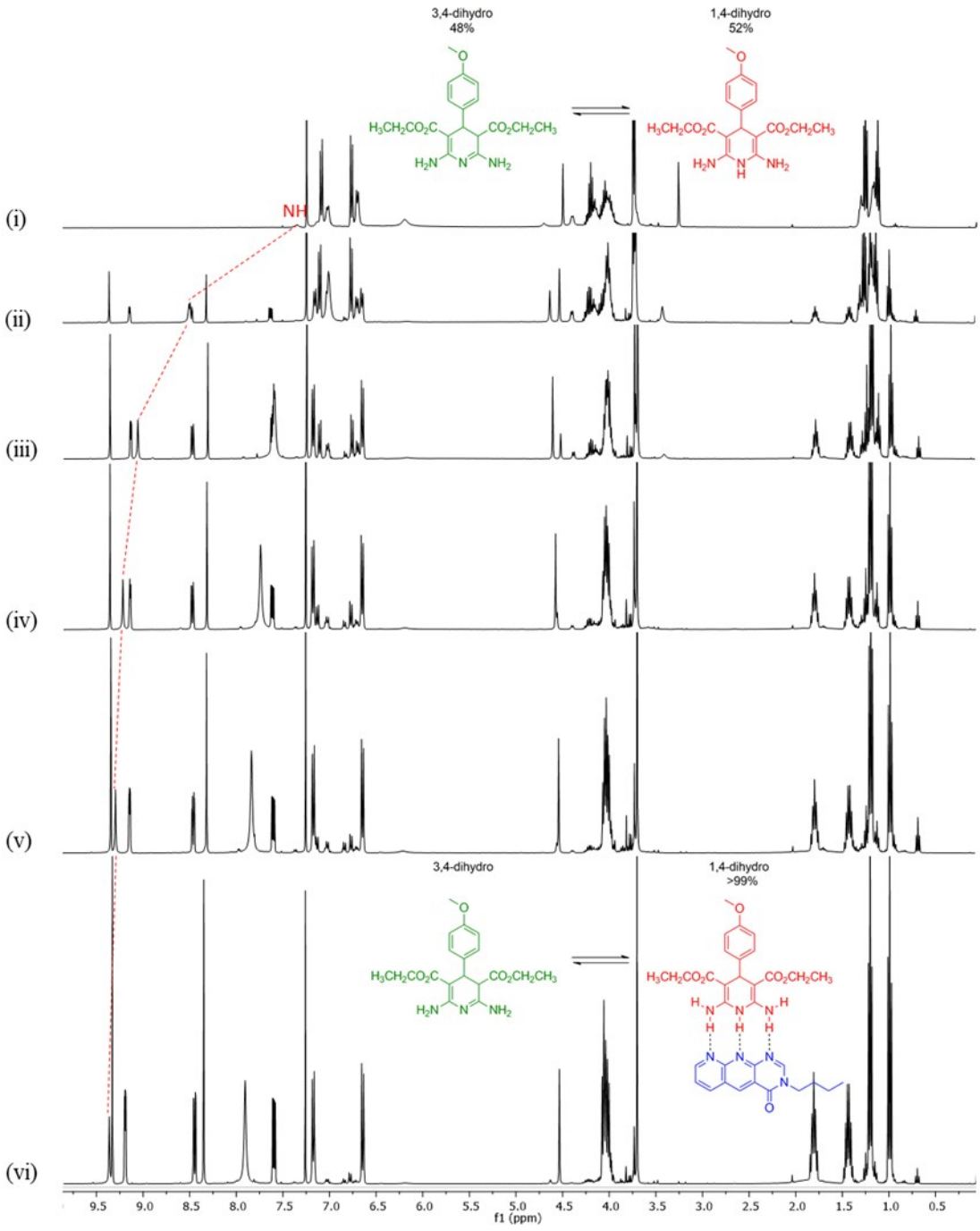


Figure S18. ^{1}H NMR spectra plot of DDD (compound **4**; 1,4-dihydro and 3,4-dihydro tautomers in red and green, respectively) with (i) 0 equivalents, (ii) 0.25 equivalents, (iii) 0.50 equivalents, (iv) 0.75 equivalents, (v) 1.0 equivalents, and (vi) 1.5 equivalents of AAA (compound **3a**).

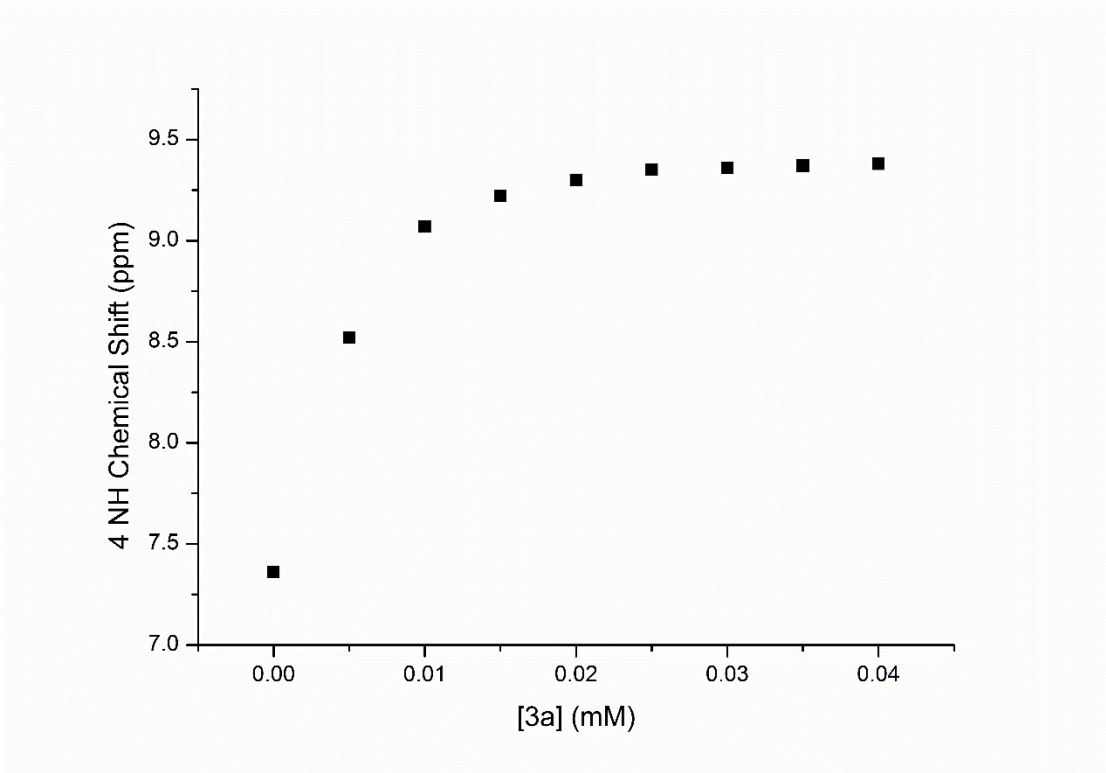


Figure S19. ^{1}H NMR titration isotherm of DDD compound **4** (host, 0.02 mM) and AAA compound **3a** (guest). Black squares correspond to the observed chemical shift at 0, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75 and 2.00 equivalents of AAA in solution.

Fluorescence Titrations

A fluorescence spectrometer F-700 (Hitachi High Technologies) was used to measure the fluorescence of the complex solution during titration. Contrary to the ^{1}H NMR titration, AAA (**3a**) was assigned as the host; meanwhile, DDD (**4**) was designated as the guest. The excitation and emission slit widths were both set to 20 nm. Separately, solutions of **3a** and **4** in chloroform ($5x10^{-7}$ and $5x10^{-6}$ M, respectively) were prepared. An aliquot of 2.5 μL of the guest solution was added to 1 mL of the host solution through a micro-injector and the mixture was stirred to homogenize the mixture. The emission spectrum was recorded until fluorescence intensity was constant. This procedure was repeated nine times with guest's aliquots of 2.5 μL, ten times with aliquots of 7.5 μL and 15 times with aliquots of 20 μL.

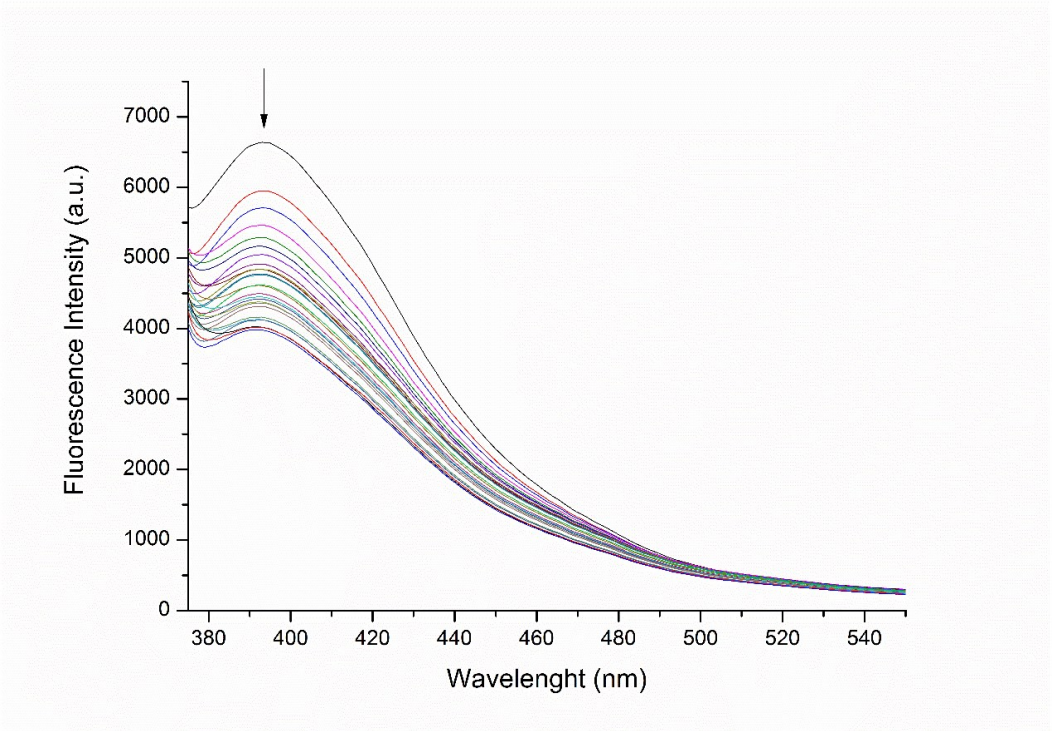


Figure S20. Fluorescence Spectra of **3a** (5×10^{-7} M in chloroform) in the presence of **4** (0, 2.5 x 10, 7.5 x 10, 20 x 15 μL of 5×10^{-6} M in chloroform). Arrow indicates the decrease in the emission intensity as compound **4** was added.

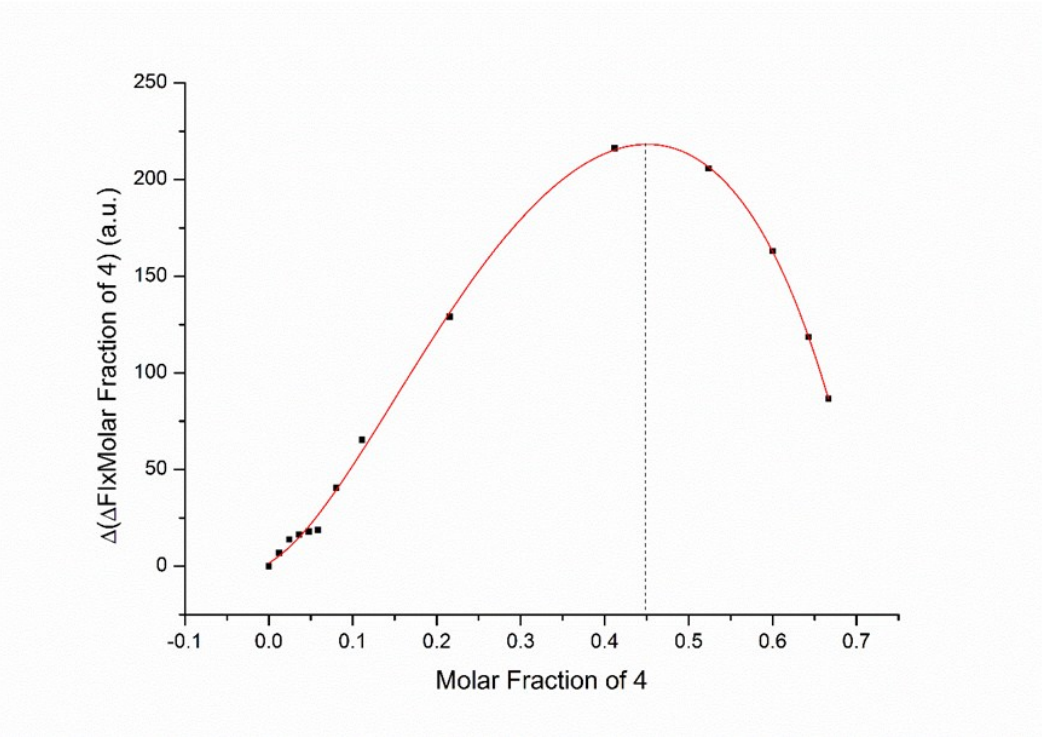


Figure S21. Job's Plot for determining the stoichiometry of **3a**:**4** complex.

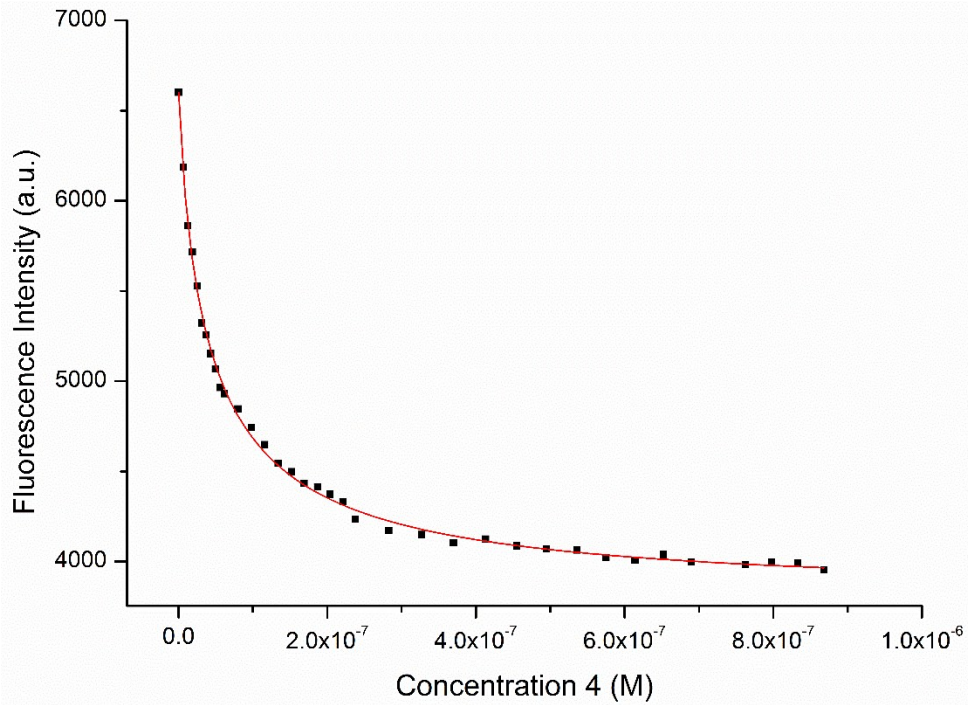


Figure S22. Change in fluorescence intensity of **3a** (5 x 10^{-7} M in chloroform) at 393 nm titrated with **4** (0, 2.5 x 10, 7.5 x 10, 20 x 15 μL of 5 x 10^{-6} M in chloroform). Black square marks correspond to the raw experimental data. The solid red line corresponds to the theoretical titration curve obtained fitting the data with a 1:1 binding model.

Viscosity Measurements

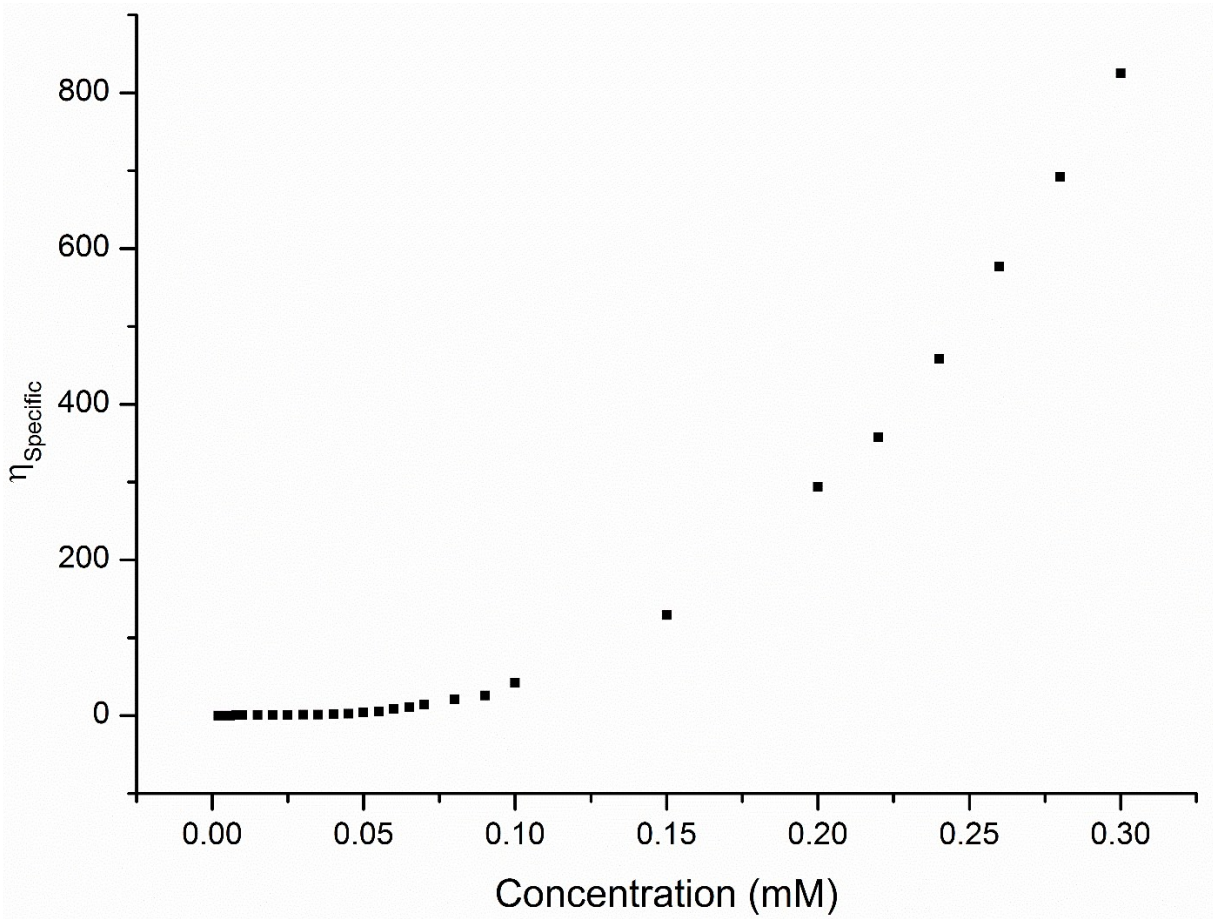


Figure S23. Specific viscosity of an equimolar mixture of **5** and **7** in 1,2-dichloroethane *versus* the concentration (298 K).

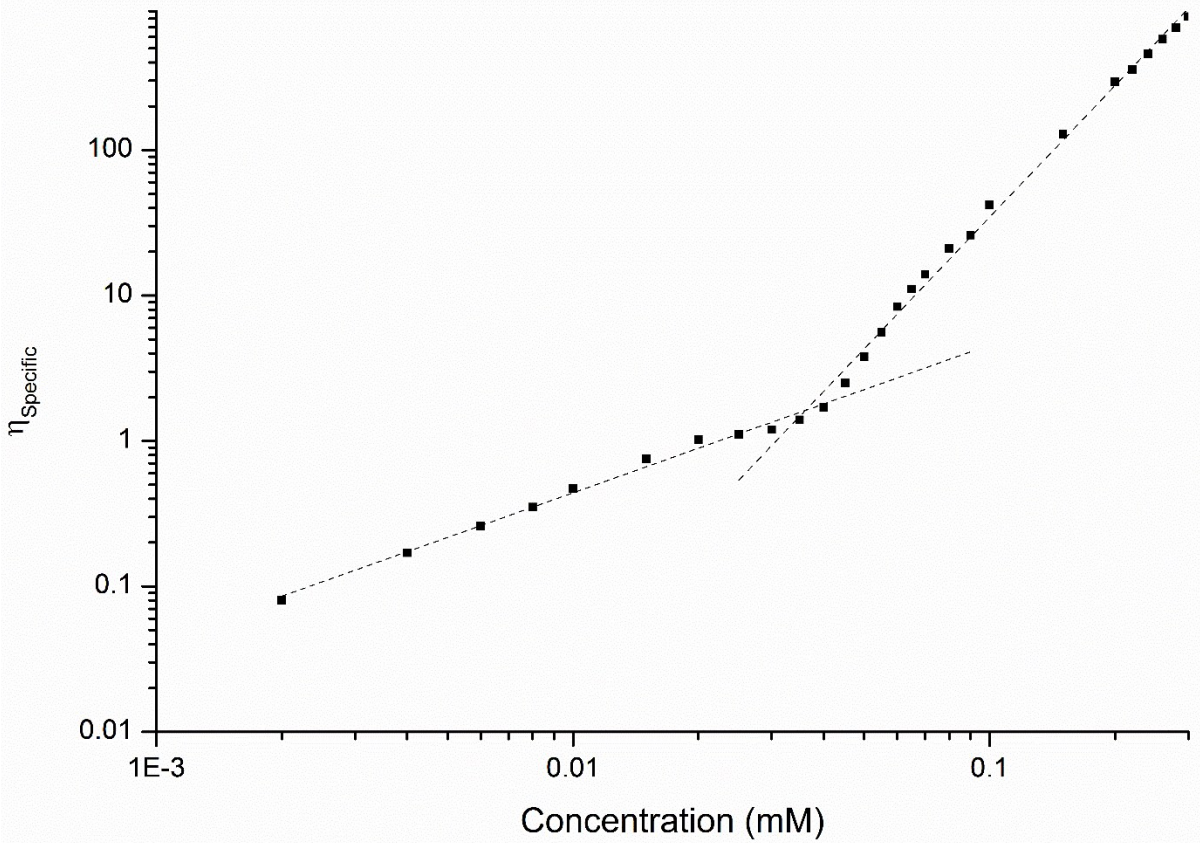


Figure S24. Double-logarithmic plot of the specific viscosity of an equimolar mixture of **5** and **7** in 1,2-dichloroethane versus its concentration (298 K). Black squares correspond to experimental data; dashed lines correspond to the linear fitting of the double logarithm when the total concentration was from 0.002 to 0.035 mM (calculated slope = 1.02), and from 0.040 to 0.30 mM (calculated slope = 3.00).