

Supporting Information

Circular Linkage of Intramolecular Multi-Hydrogen Bonding Frameworks through Nucleophilic Substitutions of β -Dicarbonyls onto Cyanuric Chloride and Subsequent Tautomerisation

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Experimental Section

All reagents were commercial reagent grade and were used without further purification. ^1H and ^{13}C NMR spectra were recorded on a JEOL ECX-500 spectrometer (operating at 500.16 MHz for ^1H and 125.77 MHz for ^{13}C) using the residual solvent CDCl_3 as the internal reference for ^1H ($\delta = 7.26$ ppm) and ^{13}C ($\delta = 77.0$ ppm). UV-visible absorption spectra were recorded on a Shimadzu UV-2400 spectrometer using spectroscopic-grade CH_2Cl_2 . Mass spectra were recorded on a BRUKER micrOTOF using the positive-mode ESI-TOF method for acetonitrile solutions and sodium formate as the internal reference. Data for single crystal X-ray diffraction analyses were collected on a Rigaku R-AXIS RAPID diffractometer using a graphite monochromator with $\text{CuK}\alpha$ radiation ($\lambda = 1.54187$ Å). Data collection and reduction were performed using *RAPID AUTO*. The structures for crystallography were determined by direct methods using *SHELXL97*,^[S1] *Sir97*,^[S2] and *SHELEX-2014/5*^[S3] and were refined using *SHELXL97* and *SHELXL-2014/7S*^[S4] using the *Yadokari-XG* program.^[S5,S6] The crystal structures were rendered

using *ORTEP III*.^[S7] The crystallographic information file (CIF) data (CCDC-2014517, 2014518, 2014519, and 2014520) can be obtained free of charge from the Cambridge Crystallographic Data Centre^[S8]

Meldrum's acid tri-conjugate (3a). To a solution of cyanuric chloride (**1**, 1.0 mmol) and Meldrum's acid (**2a**, 5.0 mmol) in toluene (10 mL) was added diisopropylethylamine (DIEA, 5.3 mmol) at 0 °C and the resulting mixture was stirred overnight at room temperature. After removal of the solvent and DIEA under reduced pressure the residue was recrystallised from CHCl₃/MeOH, giving **3a** as a pale yellow solid (44.9 mg, 8.9%). ¹H NMR (CDCl₃): δ = 1.77 (s, 18H, CH₃) and 15.13 (s, 3H, NH) ppm; ¹³C NMR (CDCl₃): δ = 27.08, 79.03, 105.27, 149.76, and 163.46 ppm; UV-vis (CH₂Cl₂): λ_{max} (ϵ [M⁻¹cm⁻¹]): 319 (59,000) and 333 (60,000) nm; HR-ESI-TOF-Mass (positive-mode) (%intensity): 1037.2140 C₄₂H₄₂N₆O₂₄Na ([2M+Na]⁺), calcd: 1037.2143, found: 1037.2140 (100%); Crystal data: C₂₁H₂₁N₃O₁₂ = 507.41, monoclinic, space group *C* 2/*c* (No. 15), *a* = 28.349(11) Å, *b* = 9.848(3) Å, *c* = 19.498(7) Å, α = 90°, β = 124.168(5)°, γ = 90°, *V* = 4504(3) Å³, *Z* = 8, *D*_{calcd.} = 1.497 g/cm³, *T* = -180 °C, *R*₁ = 0.0502 (*I* > 2 σ (*I*)), *wR*₂ = 0.1301 (all data), GOF = 1.009, CCDC-2014517.

1,3-cyclohexanedione tri-conjugate (3b). To a solution of 1,3-cyclohexanedione (**2b**, 5.3 mmol) and a dispersion of 60 % sodium hydride in mineral oil (5.5 mmol) in toluene (10 mL), was slowly added cyanuric chloride (**1**, 1.0 mmol) in toluene (10 mL) and the resulting mixture was refluxed overnight. After cooling to room temperature, the resulting red suspension was filtered and washed with toluene. The solid was dispersed in water and an aqueous acetic acid solution was added until precipitation was completed. The solid was collected by filtration and subsequently recrystallised from CHCl₃/MeOH to afford **3b** as a pale yellow solid (134 mg, 33.0%). ¹H NMR (CDCl₃): δ = 2.01 (quin, *J* = 6.5 Hz, 6H, CH₂CH₂CH₂), 2.67 (t, *J* = 6.5 Hz, 12H, CH₂CH₂CH₂), and 16.41 (s, 3H, NH) ppm; ¹³C NMR (CDCl₃): δ = 18.34, 38.82, 99.69, 149.49, and 199.22 ppm; UV-vis (CH₂Cl₂): λ_{max} (ϵ [M⁻¹cm⁻¹]): 236 (43,000), 348 (60,000), and 362 (61,000) nm; HR-ESI-TOF-Mass (positive-mode) (%intensity): C₂₁H₂₁N₃O₆Na ([M+Na]⁺), calcd: 434.1323, found: 434.1325 (100%); Crystal data: C_{3.67}H_{4.17}N_{0.5}O_{1.17} = 73.91, hexagonal, space group *P* 6₃/*m* (No. 176), *a* = 13.202(7) Å, *b* = 13.202(7) Å, *c* = 6.454(4) Å, α = 90°, β = 90°, γ = 120°, *V* = 974.2(12) Å³, *Z* = 12, *D*_{calcd.} = 1.512 g/cm³, *T* = -180 °C, *R*₁ = 0.0502 (*I* > 2 σ (*I*)), *wR*₂ = 0.1171 (all data), GOF = 1.013, CCDC-2014518.

Dimedone tri-conjugate (3c). To a solution of dimedone (**2c**, 5.3 mmol) and a dispersion of 60 % sodium hydride in mineral oil (220 mg, 5.5 mmol) in toluene (10 mL), was slowly added cyanuric chloride (**1**, 1.0 mmol) in toluene (10 mL) and the resulting mixture was refluxed overnight. After cooling to room temperature, the resulting red suspension was filtered and washed with toluene. The solid was dispersed in water and an aqueous acetic acid solution was added until precipitation was completed. The solid was collected by filtration and subsequently recrystallised from CHCl₃/MeOH to afford **3c** as a pale yellow solid (199 mg, 40.2%). ¹H NMR (CDCl₃): δ = 1.08 (s, 18H, CH₃), 2.55 (s, 12H, CH₂), and 16.43 (s, 3H, NH) ppm; ¹³C NMR (CDCl₃): δ = 28.26, 30.18, 52.34, 98.54, 149.36, and 198.84 ppm; UV-vis (CH₂Cl₂): λ_{max} (ϵ [M⁻¹cm⁻¹]): 238 (32,000), 346 (48,000), and 361 (51,000) nm; HR-ESI-TOF-Mass (positive-mode) (%intensity): C₂₇H₃₃N₃O₆Na ([M+Na]⁺), calcd: 518.2262, found: 518.2268 (100%); Crystal data: C₂₇H₃₃N₃O₆·CH₂Cl₂ = 580.49, triclinic, space group *P*-1 (No. 2), *a* = 11.2710(11) Å, *b* =

11.3037(2) Å, $c = 12.5205(8)$ Å, $\alpha = 73.166(14)^\circ$, $\beta = 87.132(18)^\circ$, $\gamma = 65.188(16)^\circ$, $V = 65.188(16)$ Å³, $Z = 2$, $D_{\text{calcd.}} = 1.396$ g/cm³, $T = -180$ °C, $R_1 = 0.0530$ ($I > 2\sigma(I)$), $wR_2 = 0.1694$ (all data), GOF = 1.097, CCDC-2014519.

Diethyl malonate tri-conjugate (3d). To a solution of diethyl malonate (**2d**, 5.3 mmol) and a dispersion of 60 % sodium hydride in mineral oil 5.5 mmol) in toluene (10 mL), was slowly added cyanuric chloride (**1**, 1.0 mmol) in toluene (10 mL) and the resulting mixture was refluxed overnight. After cooling to room temperature, the resulting red suspension was filtered and washed with toluene. The solid was dispersed in water and an aqueous acetic acid solution was added until precipitation was completed. The solid was collected by filtration and subsequently recrystallised from CHCl₃/MeOH to afford **3d** as a yellow powder (332 mg, 67.0%). ¹H NMR (CDCl₃): $\delta = 1.32$ (t, $J = 7.05$ Hz, 18H, CH₂CH₃), 4.33 (q, $J = 7.15$ Hz, 12H, CH₂CH₃), and 13.95 (s, 3H, NH) ppm; ¹³C NMR (CDCl₃): $\delta = 14.17$, 61.14, 83.31, 147.75, and 167.71 ppm; UV-vis (CH₂Cl₂): λ_{max} (ϵ [M⁻¹cm⁻¹]): 229 (18,000) and 317 (60,000) nm; HR-ESI-TOF-Mass (positive-mode) (%intensity): C₂₄H₃₃N₃O₁₂Na ([M+H]⁺), calcd: 578.1956, found: 578.1953 (100%).

1,3-cyclohexanedione tri-enol ether (4b). To a solution of cyanuric chloride (**1**, 1.0 mmol) and 1,3-cyclohexanedione (**2b**, 5.3 mmol) in toluene (10 mL) was added diisopropylethylamine (DIEA, 5.5 mmol) at 0 °C and the resulting mixture was stirred overnight at room temperature. After removal of the solvent and DIEA under reduced pressure the residue was recrystallised from CHCl₃/MeOH, giving **4b** as a white solid (86.9 mg, 21.1%). ¹H NMR (CDCl₃): $\delta = 2.13$ (quin, $J = 6.4$ Hz, 6H, CH₂CH₂CH₂), 2.47 (t, $J = 7.1$ Hz, 6H, CH₂CH₂CH₂), 2.65 (ddd, $J = 6.0$ 6.4 1.0 Hz, 6H, CH₂CH₂CH₂), and 5.97 (s, 3H, CH) ppm; ¹³C NMR (CDCl₃): $\delta = 21.18$, 27.98, 36.69, 118.26, 169.79, 171.85, and 198.91 ppm; UV-vis (CH₂Cl₂): λ_{max} (ϵ [M⁻¹cm⁻¹]): 233 (59,000) nm; HR-ESI-TOF-Mass (positive-mode) (%intensity): C₂₁H₂₁N₃O₆Na ([M+Na]⁺), calcd: 434.1323, found: 434.1344 (100%).

Dimedone tri-enol ether (4c). To a solution of cyanuric chloride (**1**, 1.0 mmol) and dimedone (**2c**, 5.3 mmol) in toluene (10 mL) was added diisopropylethylamine (DIEA, 5.5 mmol) at 0 °C and the resulting mixture was stirred overnight at room temperature. After removal of the solvent and DIEA under reduced pressure the residue was recrystallised from CHCl₃/MeOH, giving **4c** as a white solid (257 mg, 51.9%). ¹H NMR (CDCl₃): $\delta = 1.14$ (s, 18H, CH₃), 2.32 (s, 6H, CH₂), 2.52 (s, 6H, CH₂), and 5.97 (s, 3H, CH) ppm; ¹³C NMR (CDCl₃): $\delta = 28.20$, 33.45, 41.79, 50.78, 117.18, 168.12, 171.92, and 198.88 ppm; UV-vis (CH₂Cl₂): λ_{max} (ϵ [M⁻¹cm⁻¹]): 233 (58,000) nm; HR-ESI-TOF-Mass (positive-mode) (%intensity): C₂₇H₃₃N₃O₆Na ([M+Na]⁺), calcd: 518.2262, found: 518.2263 (100%); Crystal data: C₂₇H₃₃N₃O₆ = 495.56, monoclinic, space group $P 2_1/c$ (No. 14), $a = 17.963(2)$ Å, $b = 7.3777(8)$ Å, $c = 20.201(2)$ Å, $\alpha = 90^\circ$, $\beta = 105.543(3)^\circ$, $\gamma = 90^\circ$, $V = 2579.3(5)$ Å³, $Z = 4$, $D_{\text{calcd.}} = 1.276$ g/cm³, $T = -180$ °C, $R_1 = 0.0375$ ($I > 2\sigma(I)$), $wR_2 = 0.0782$ (all data), GOF = 1.002, CCDC-2014520.

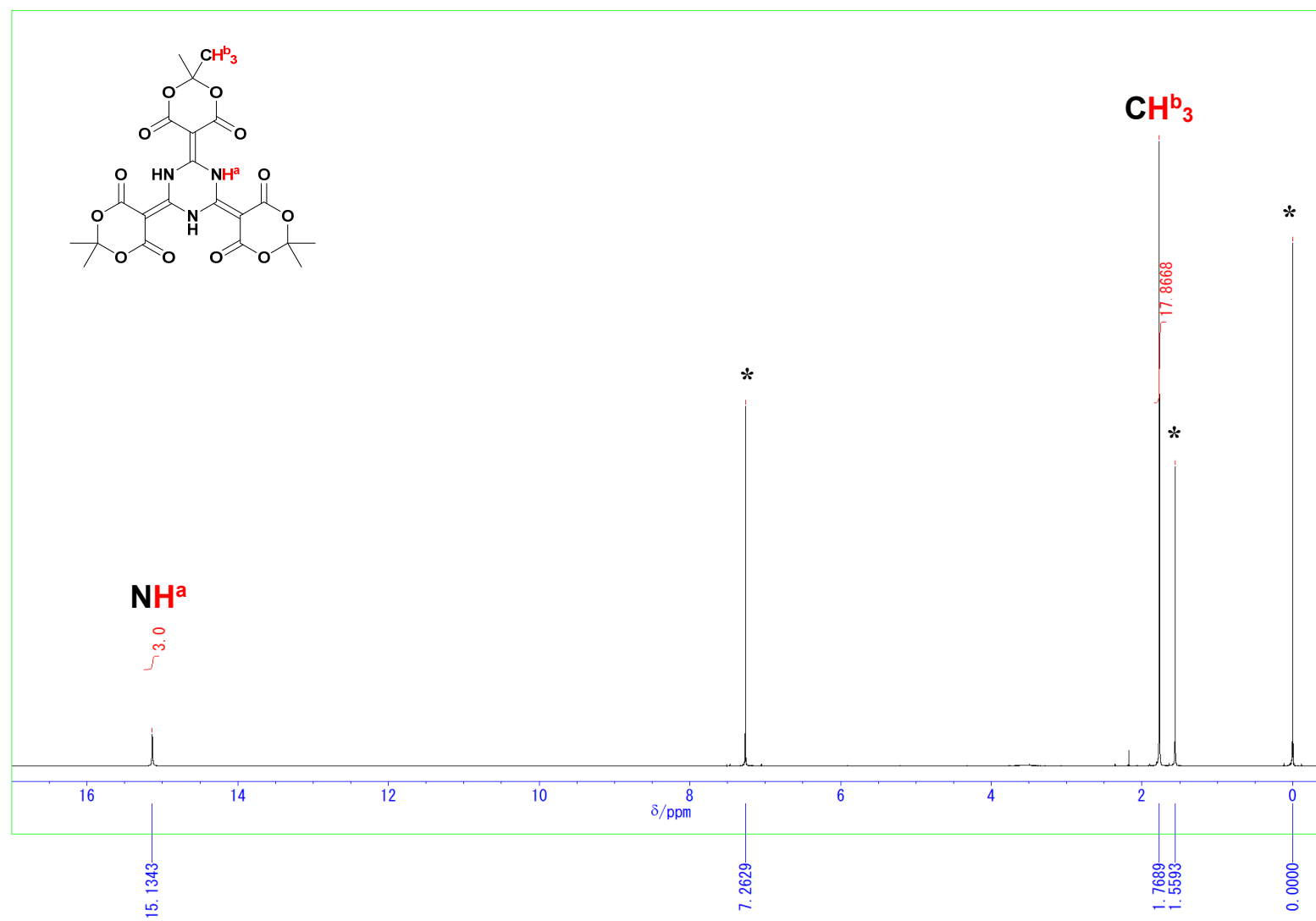


Figure S1. ^1H NMR spectrum of **3a** in CDCl_3 . *: solvent or impurity.

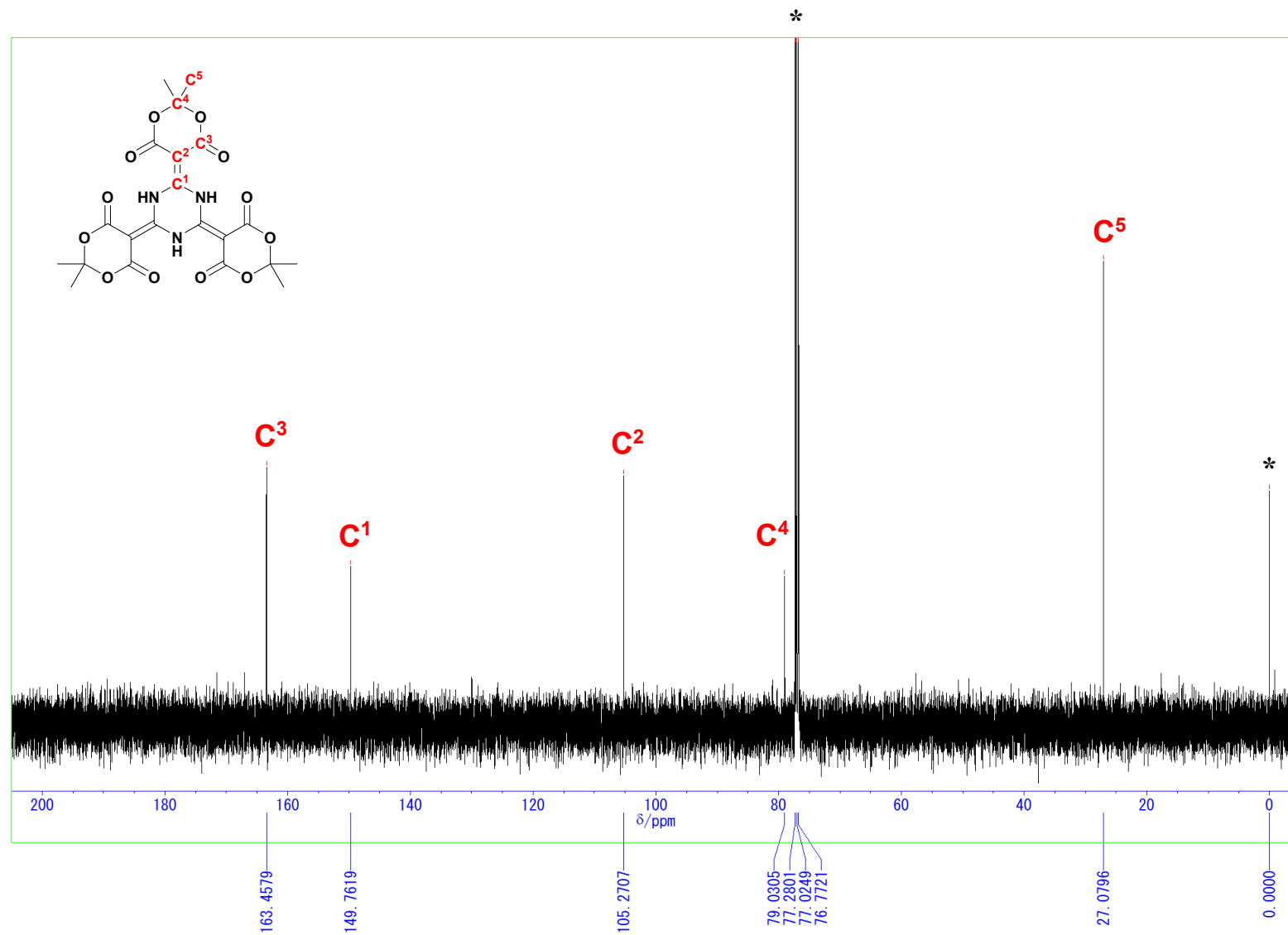


Figure S2. ^{13}C NMR spectrum of **3a** in CDCl_3 . *: solvent or impurity.

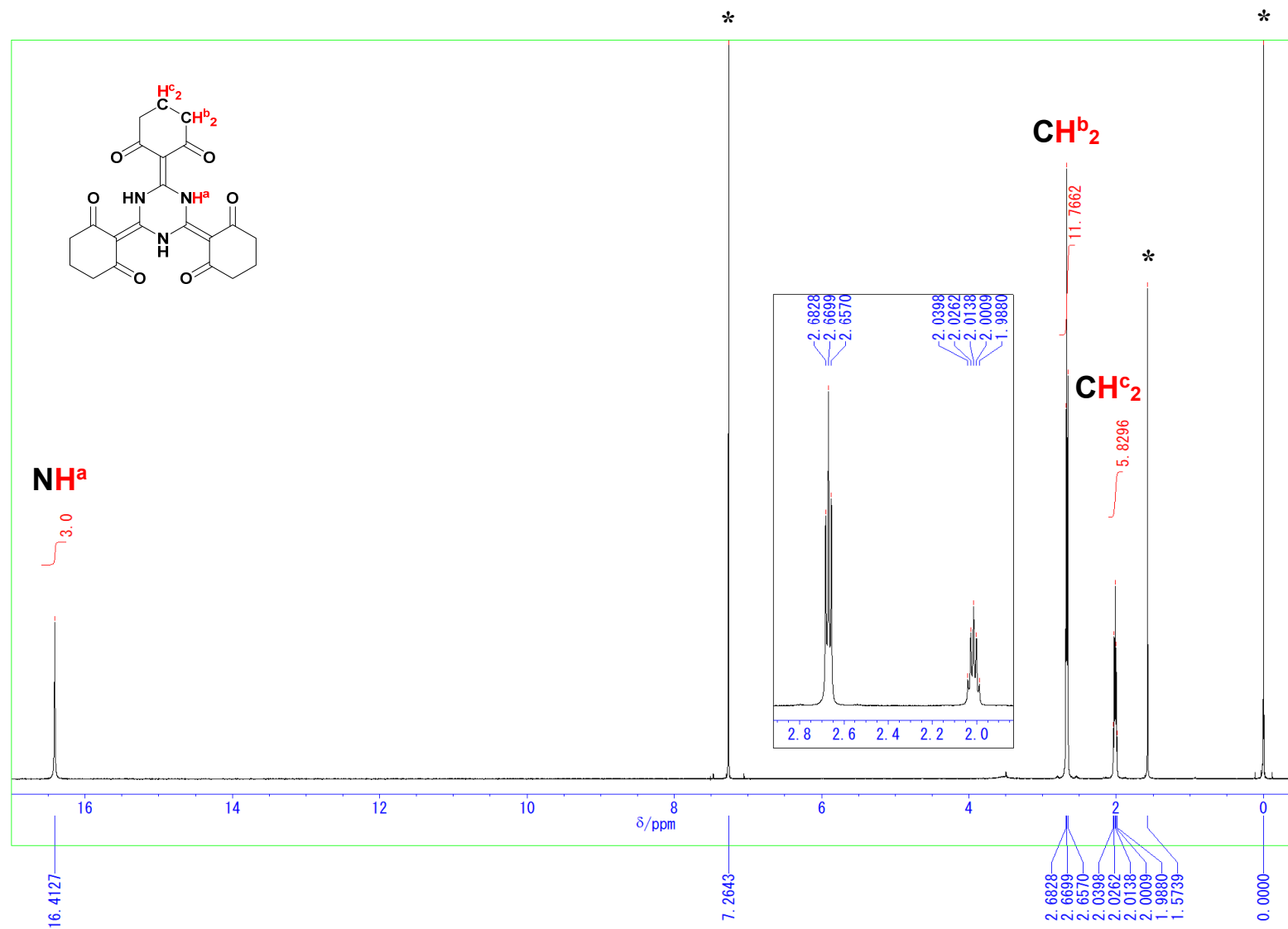


Figure S3. ^1H NMR spectrum of **3b** in CDCl_3 . *: solvent or impurity.

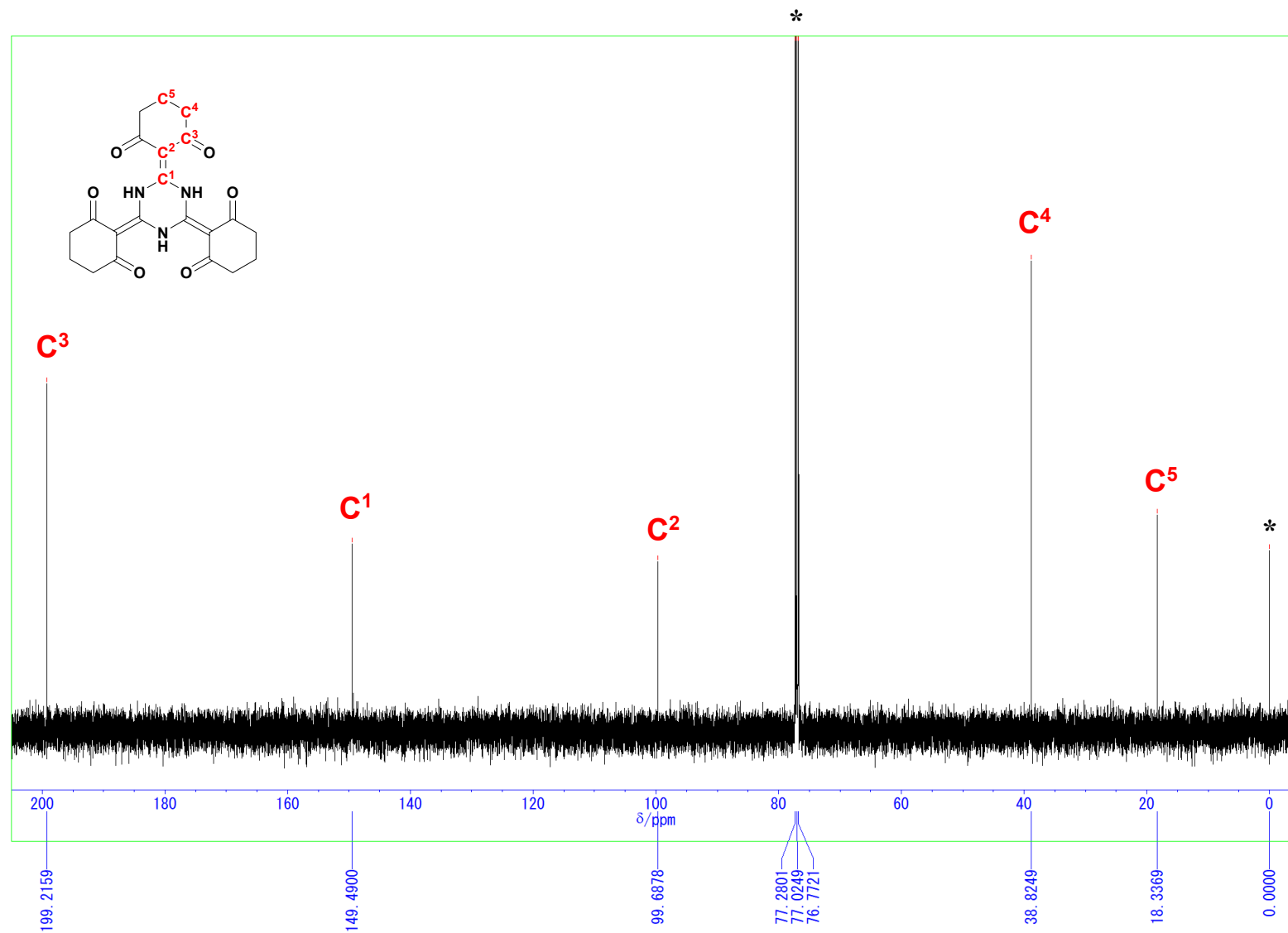


Figure S4. ^{13}C NMR spectrum of **3b** in CDCl_3 . *: solvent or impurity.

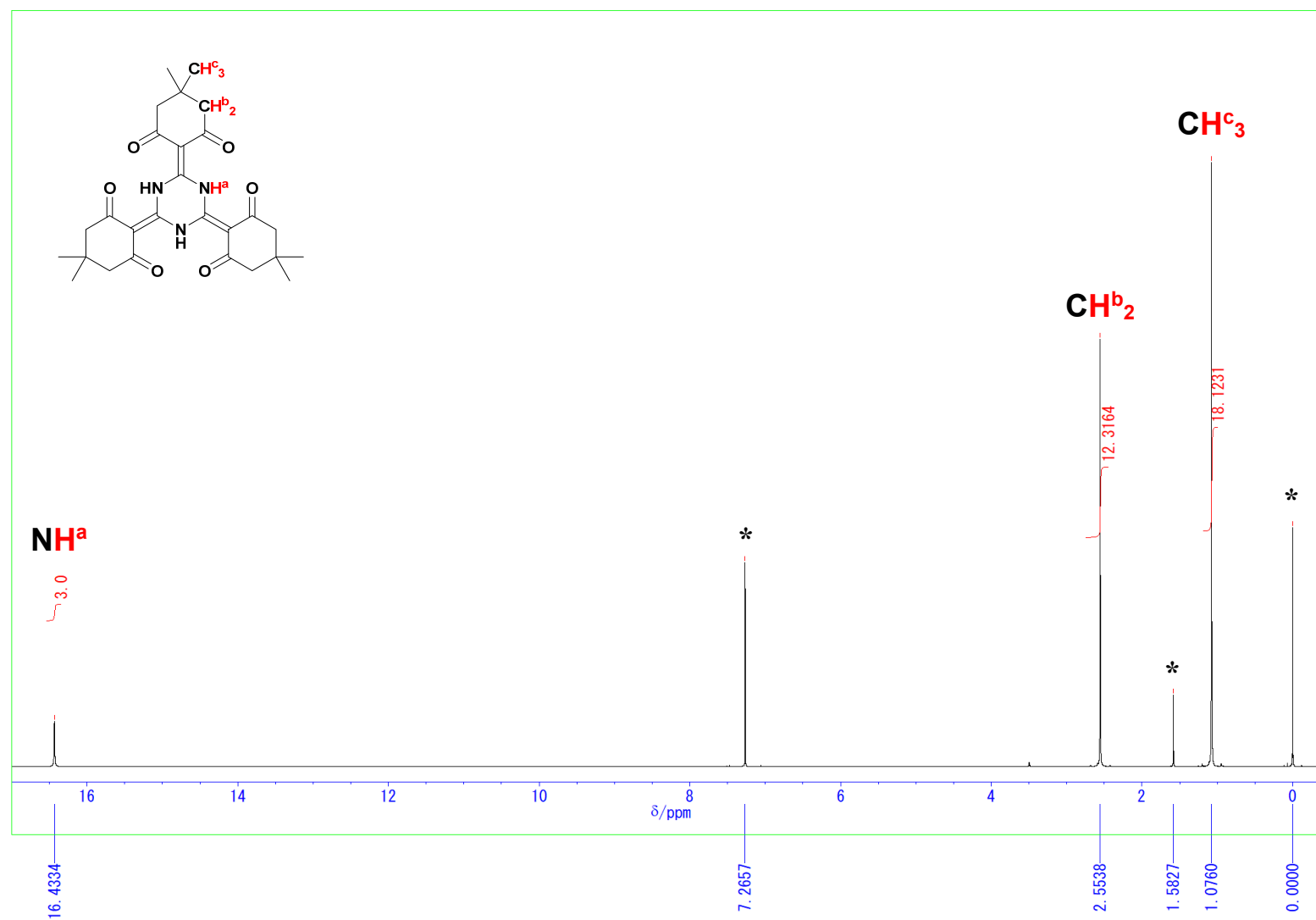


Figure S5. ^1H NMR spectrum of **3c** in CDCl_3 . *: solvent or impurity.

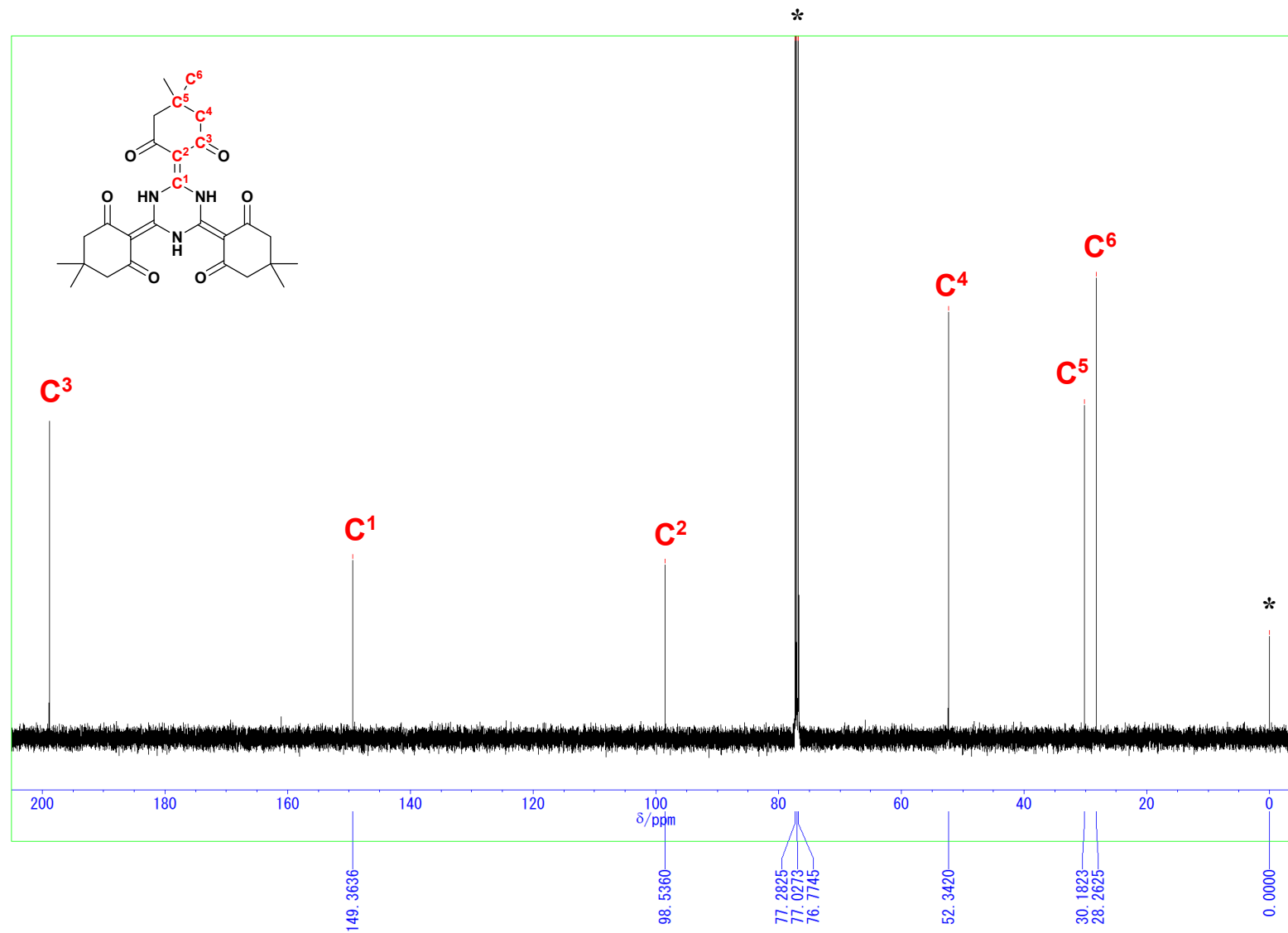


Figure S6. ^{13}C NMR spectrum of **3c** in CDCl_3 . *: solvent or impurity.

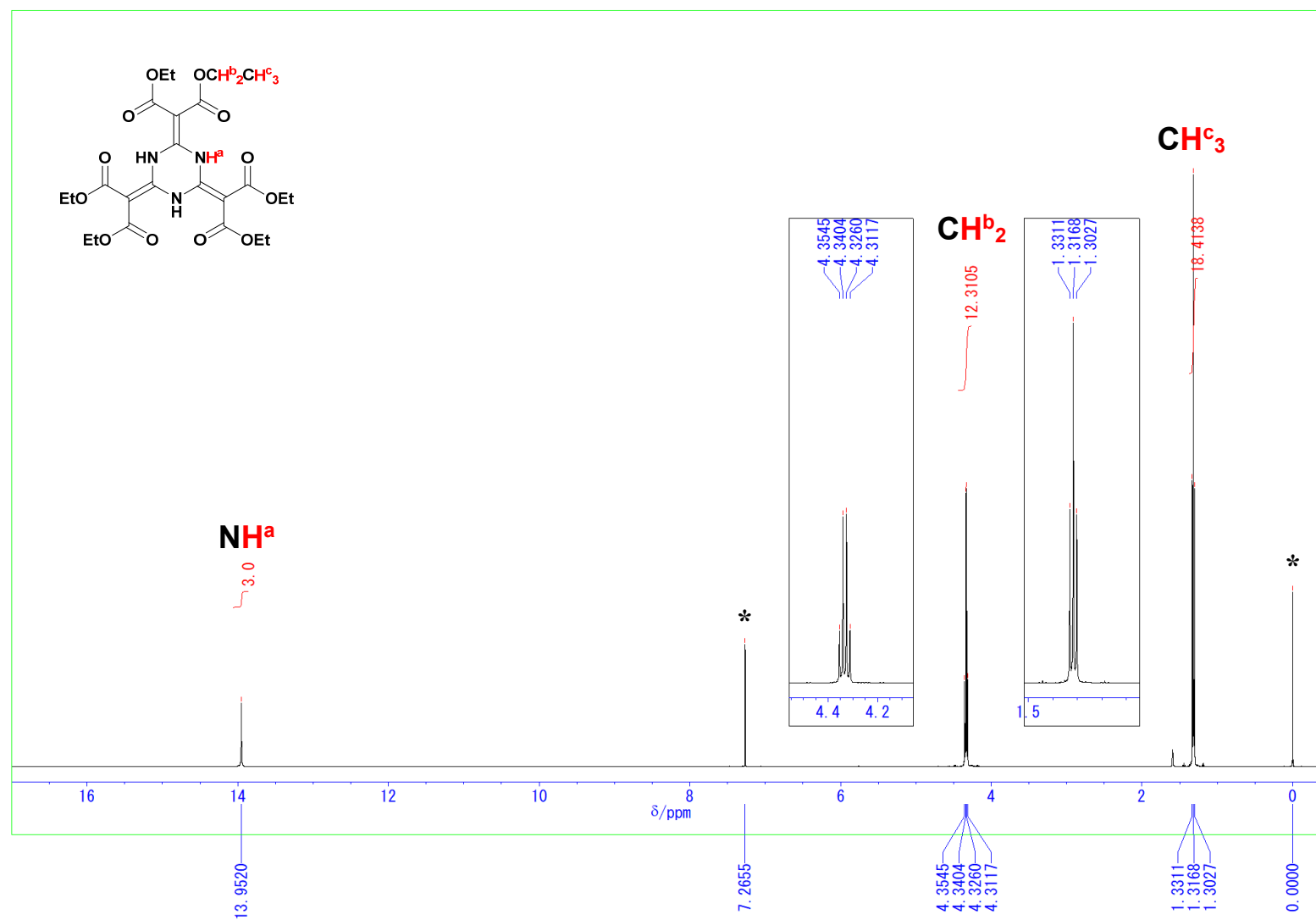


Figure S7. ^1H NMR spectrum of **3d** in CDCl_3 . *: solvent or impurity.

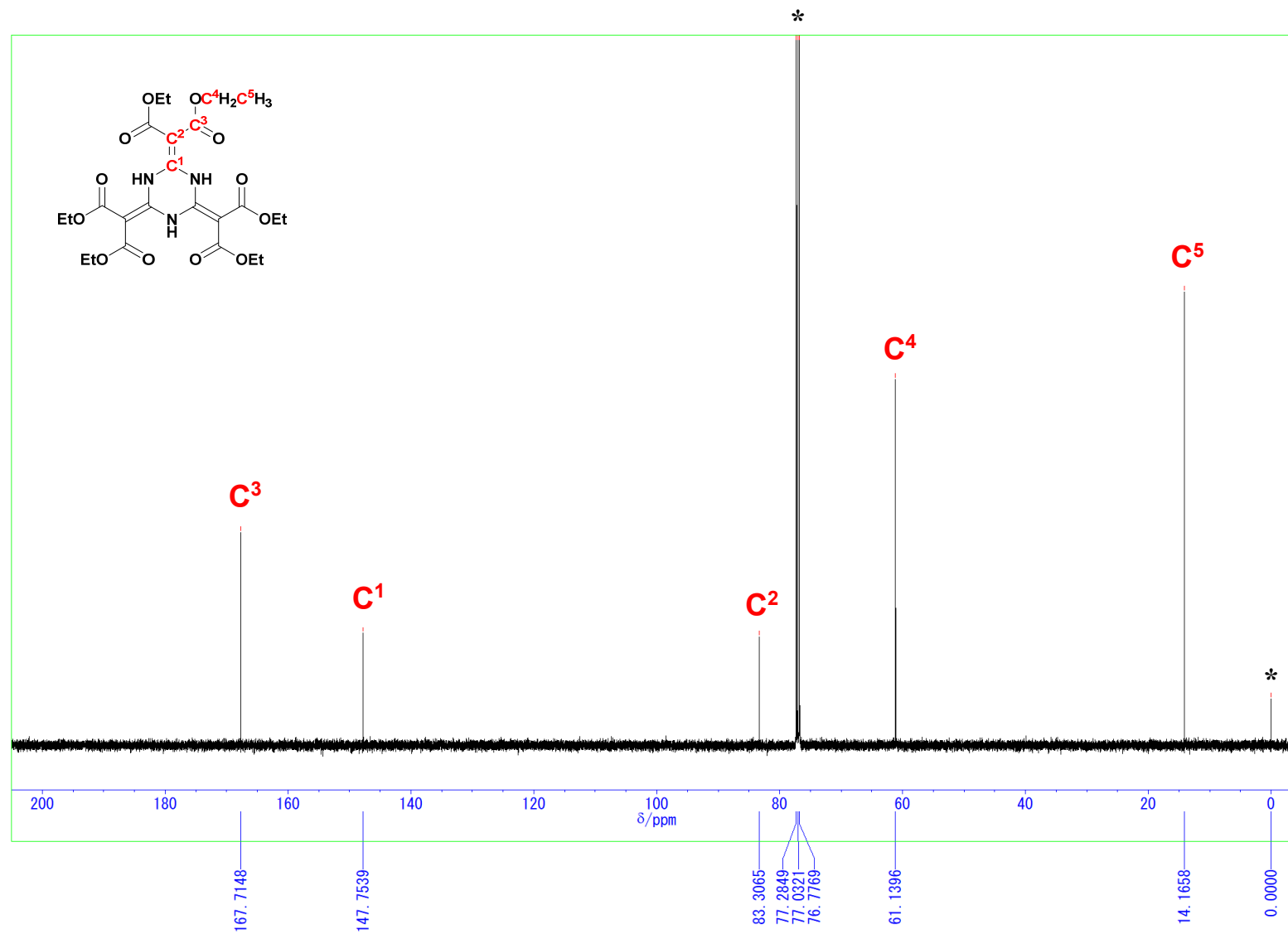


Figure S8. ^{13}C NMR spectrum of **3d** in CDCl_3 . *: solvent or impurity.

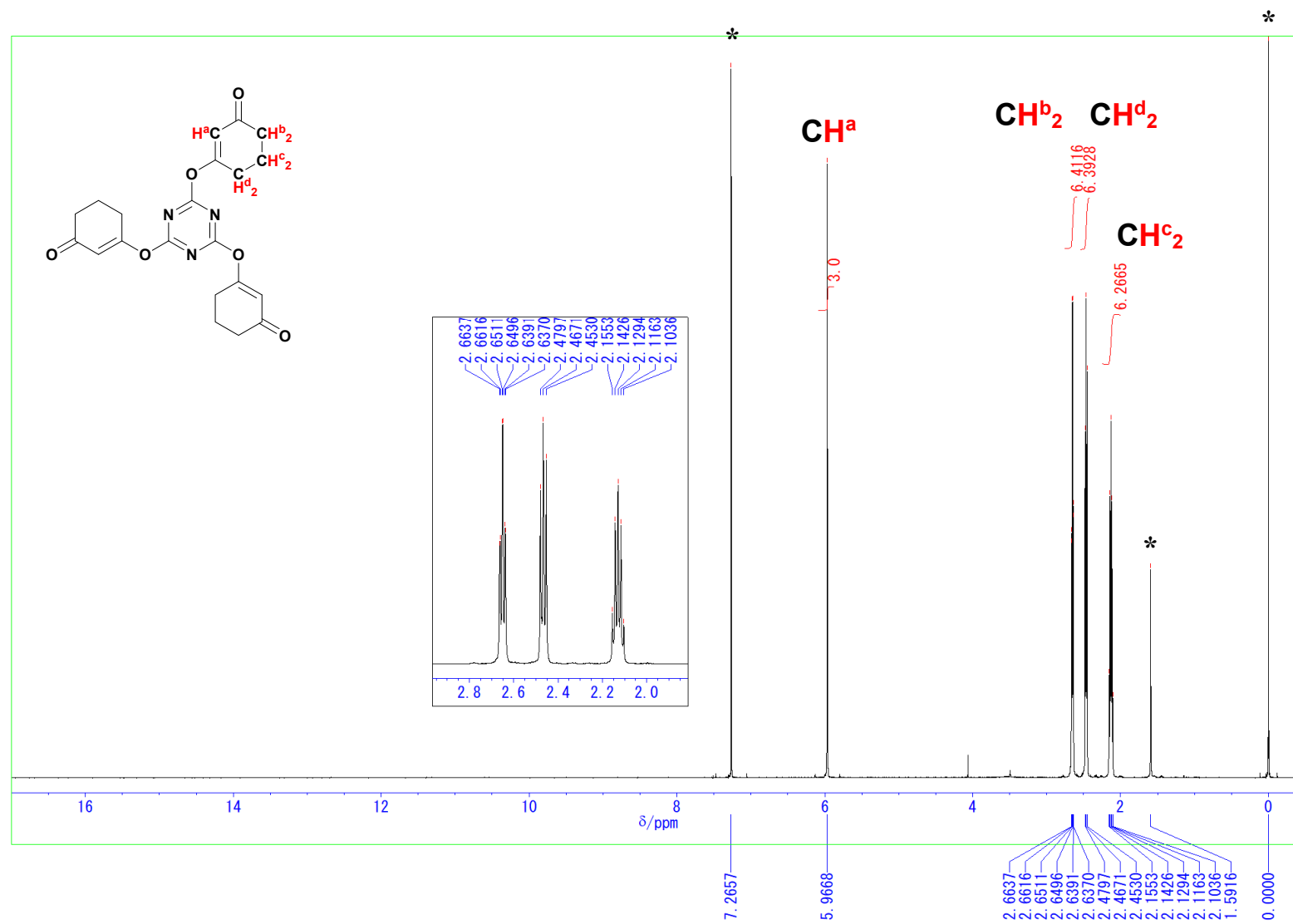


Figure S9. ^1H NMR spectrum of **4b** in CDCl_3 . *: solvent or impurity.

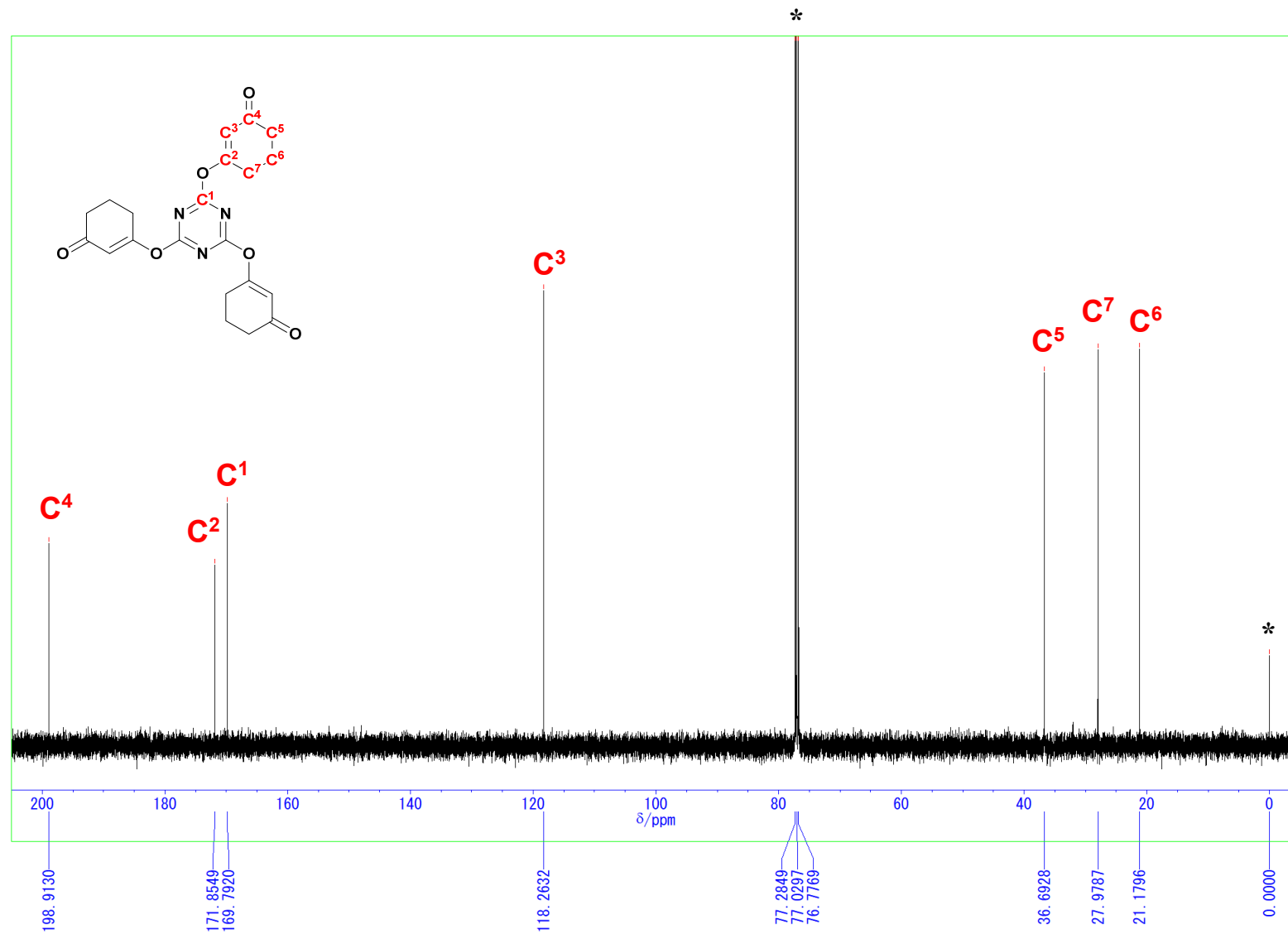


Figure S10. ^{13}C NMR spectrum of **4b** in CDCl_3 . *: solvent or impurity.

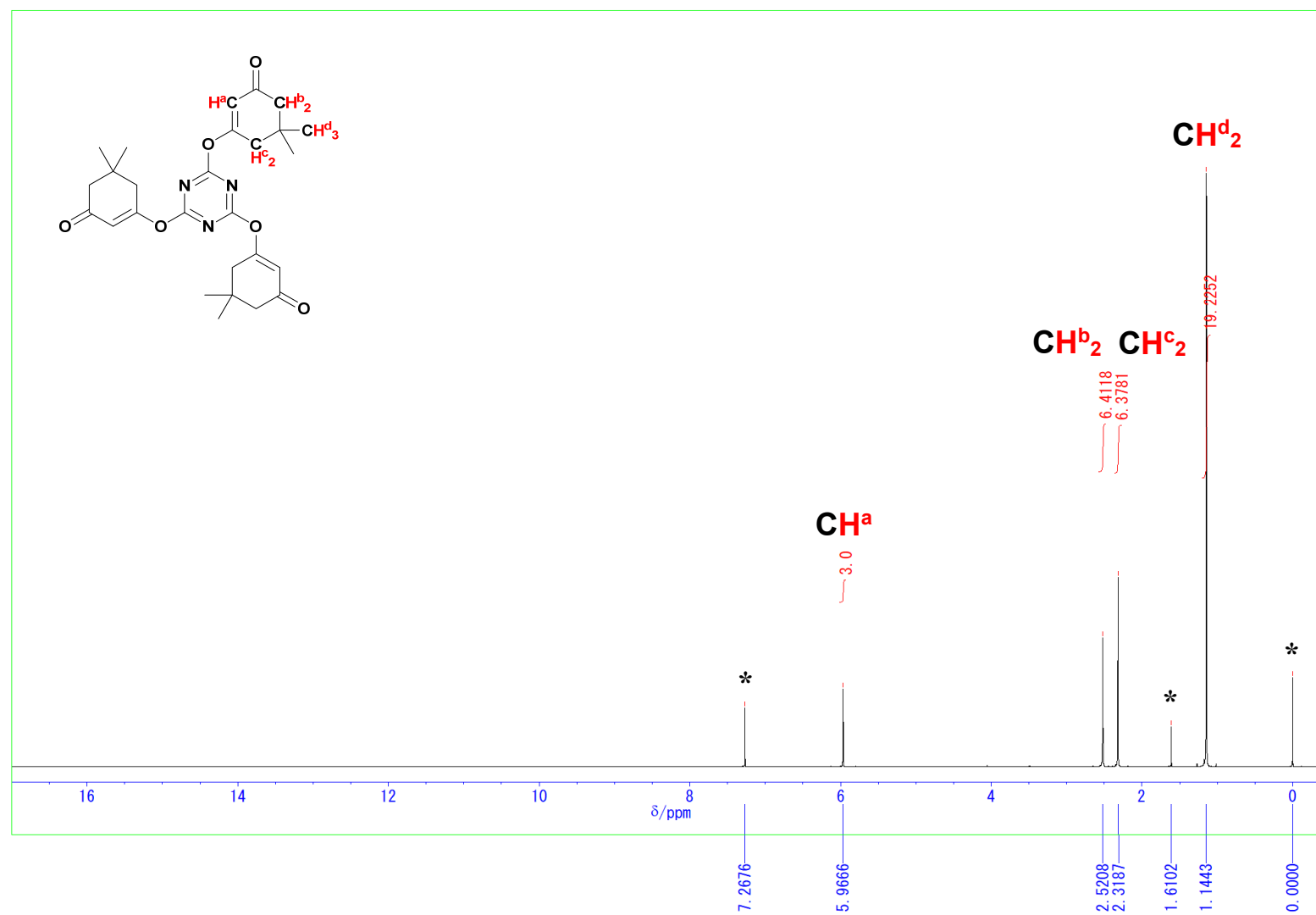


Figure S11. ^1H NMR spectrum of **4c** in CDCl_3 . *: solvent or impurity.

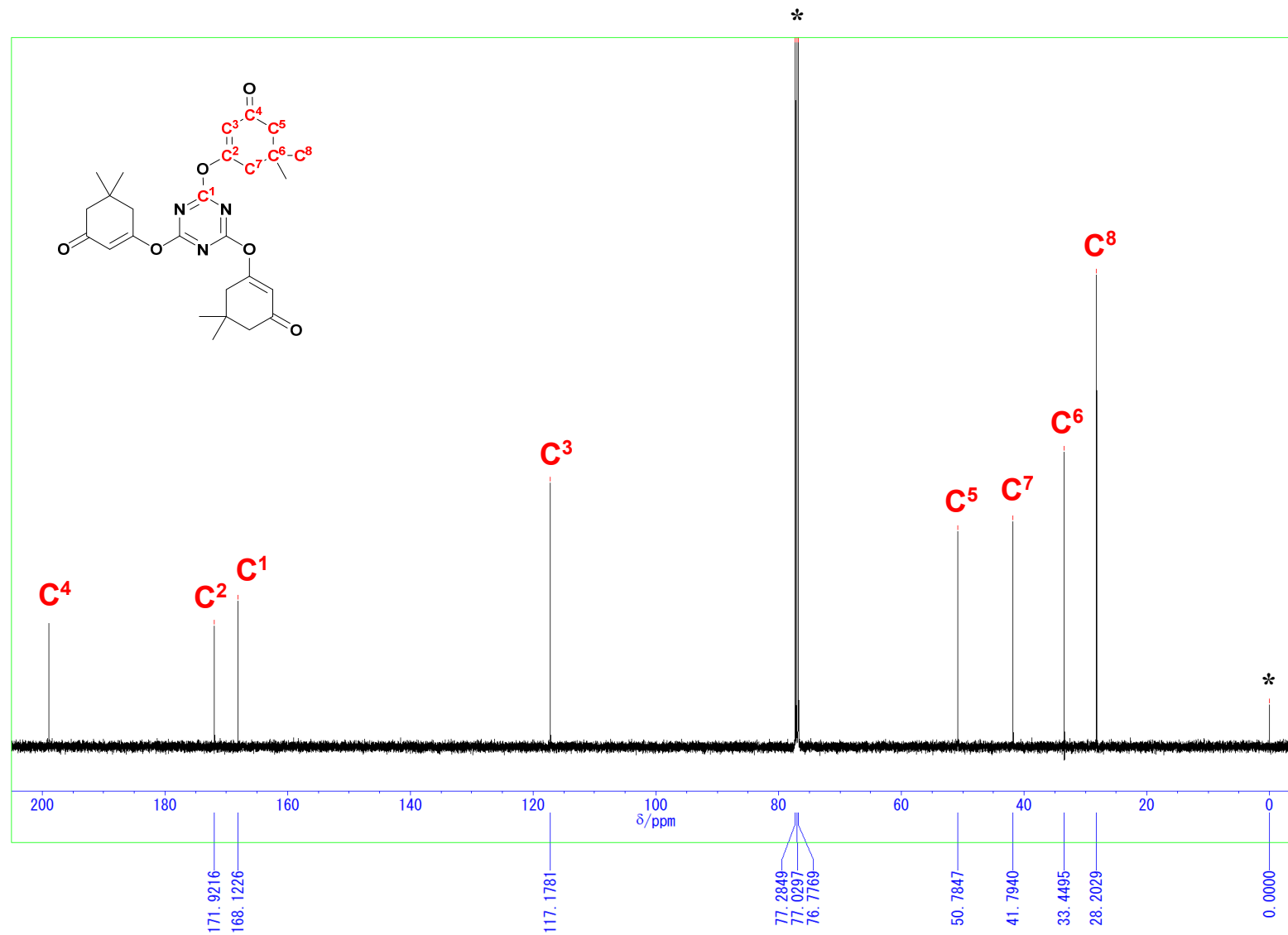


Figure S12. ^{13}C NMR spectrum of **4c** in CDCl_3 . *: solvent or impurity.

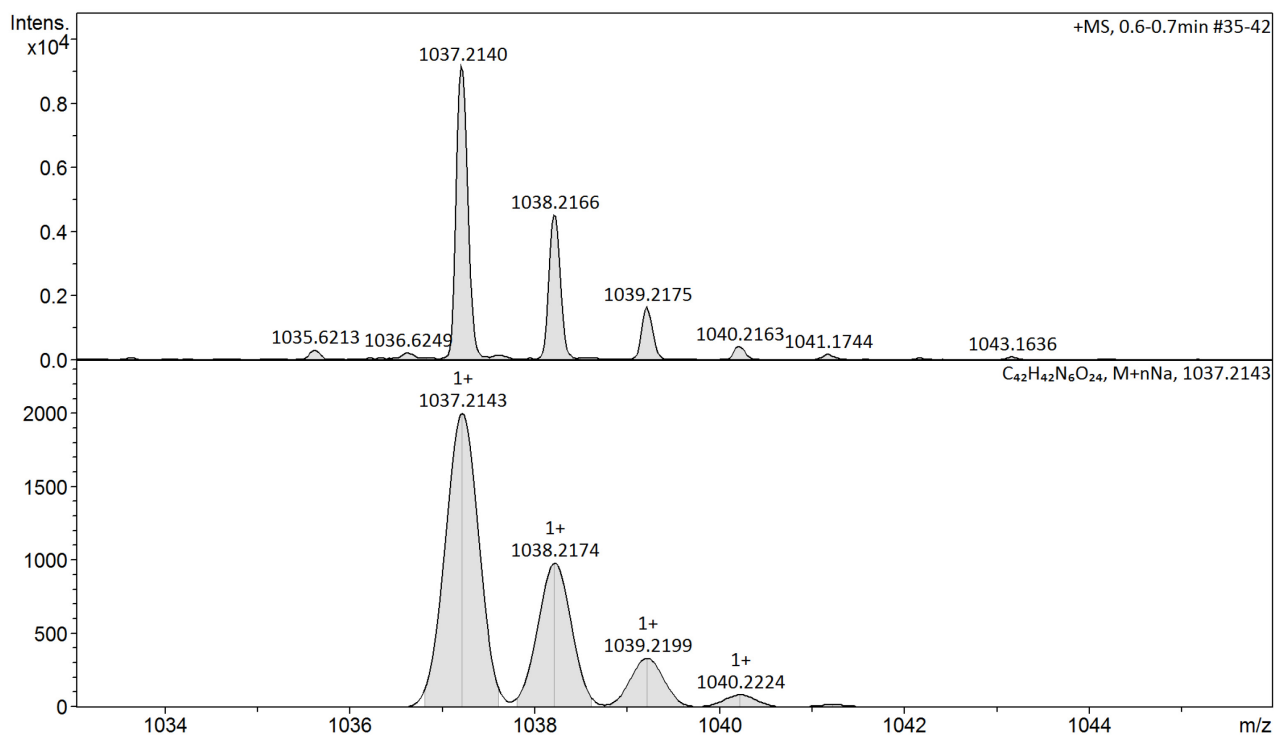


Figure S13. ESI-TOF mass spectrum of 3a. Upper: found; lower: calcd.

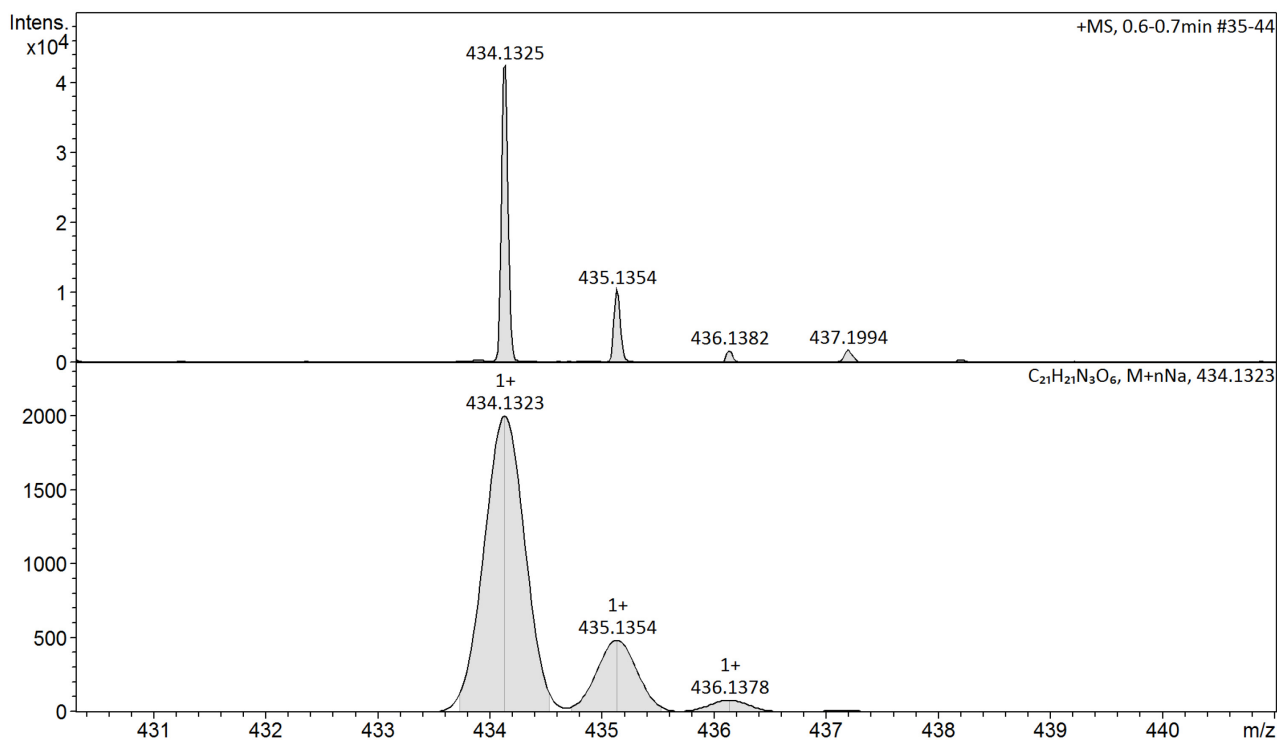


Figure S14. ESI-TOF mass spectrum of 3b. Upper: found; lower: calcd.

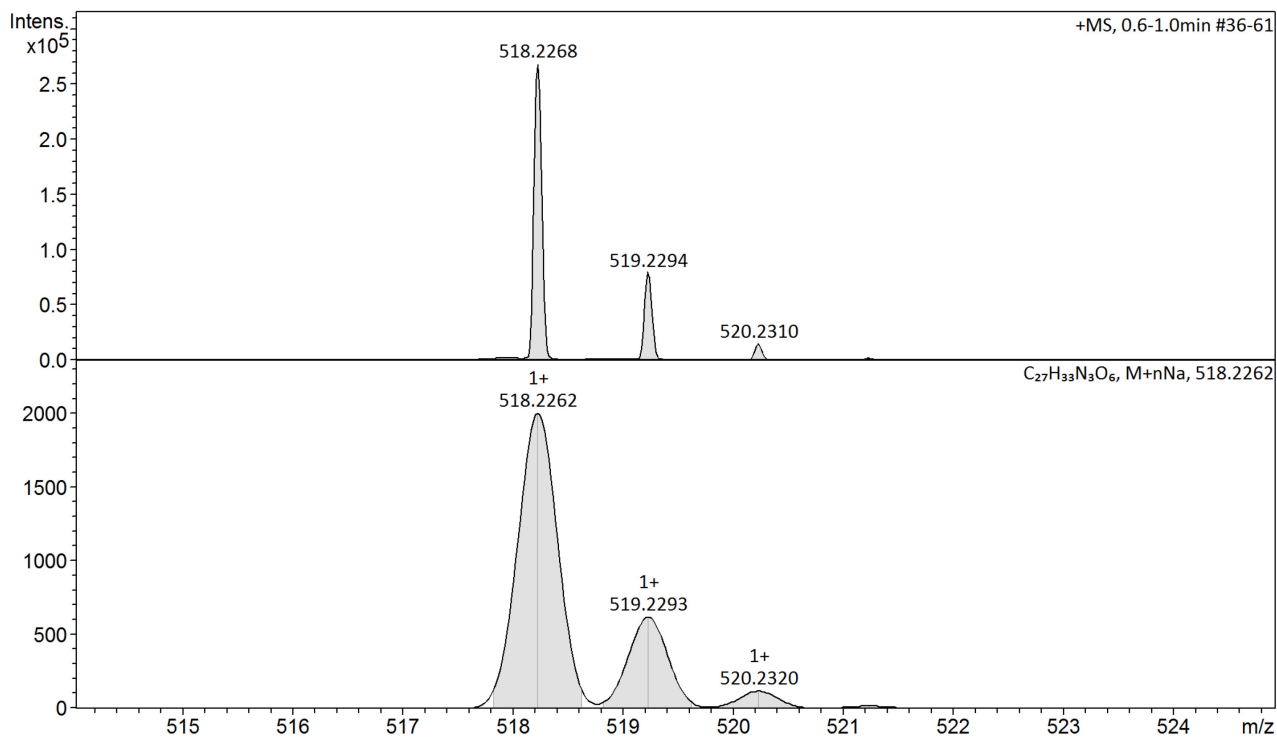


Figure S15. ESI-TOF mass spectrum of **3c**. Upper: found; lower: calcd.

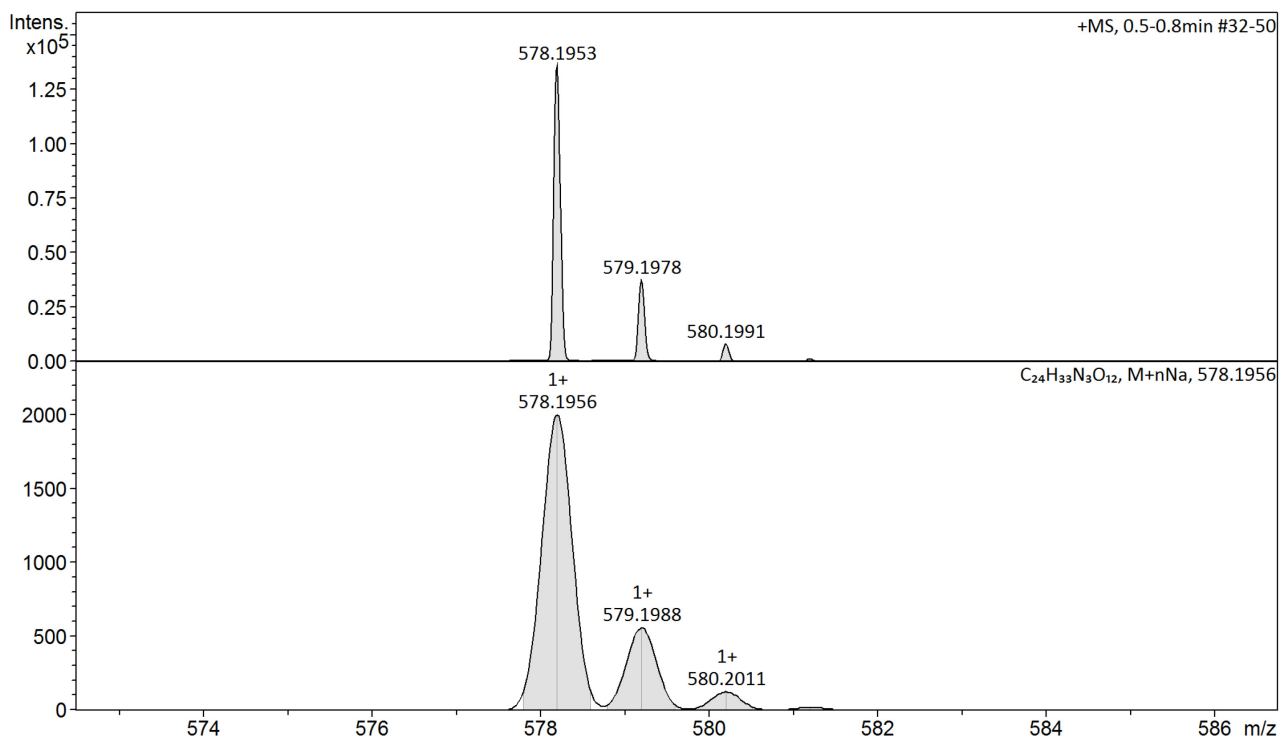


Figure S16. ESI-TOF mass spectrum of **3d**. Upper: found; lower: calcd.

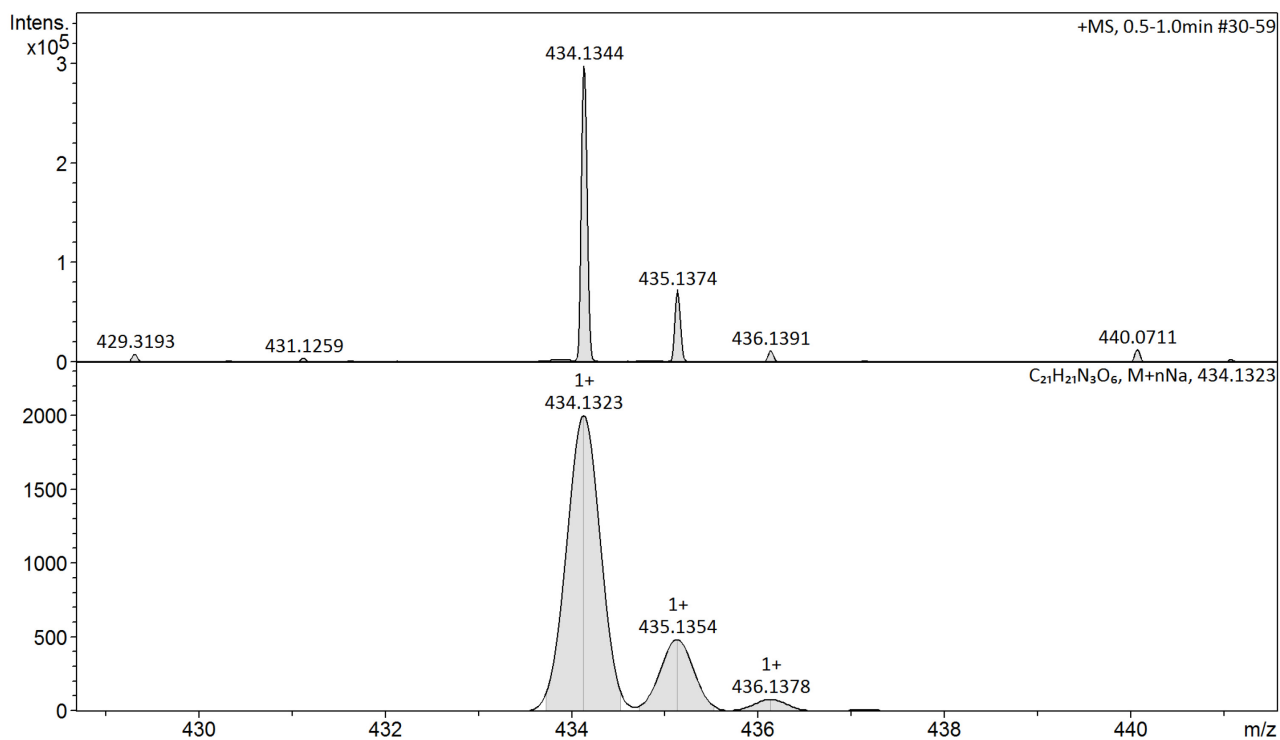


Figure S17. ESI-TOF mass spectrum of **4b**. Upper: found; lower: calcd.

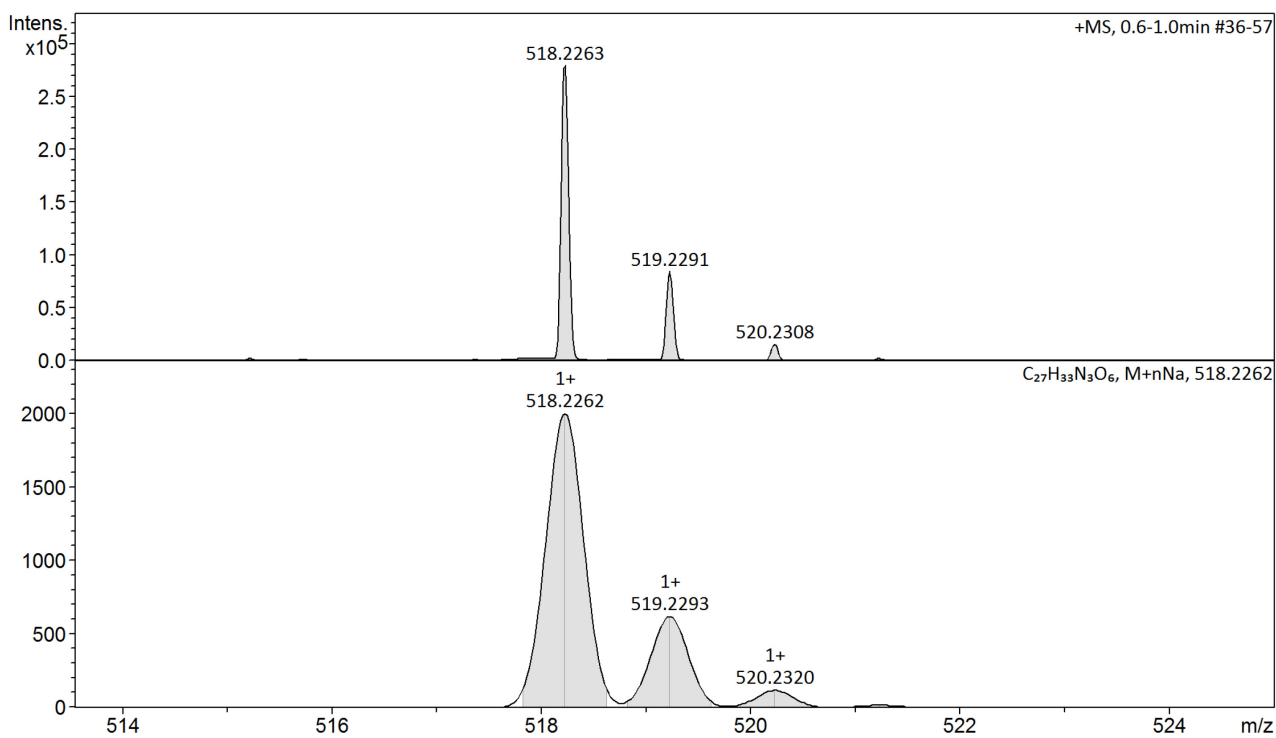


Figure S18. ESI-TOF mass spectrum of **4c**. Upper: found; lower: calcd.

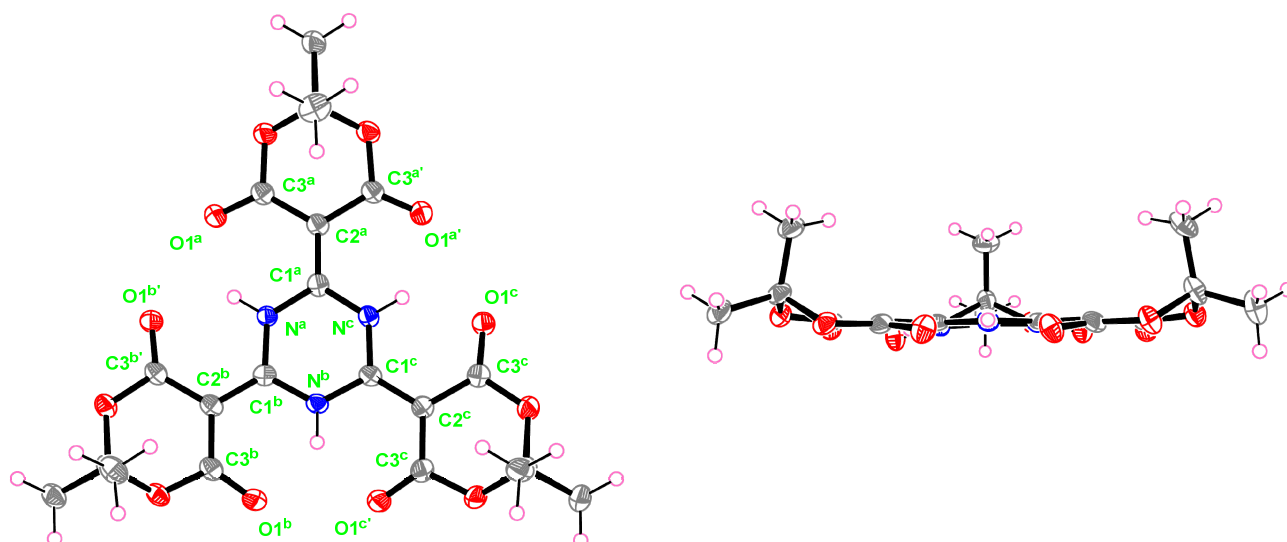


Figure S19. X-ray crystal structure of **3a**. Left: top view; right: side view. Thermal ellipsoids are set at 50% probability level. The bond distances (Å): $N^a-C1^a = 1.365(4)$, $C1^a-C2^a = 1.387(4)$, $C2^a-C3^a = 1.456(3)$, $C3^a-O1^a = 1.216(4)$, $C2^a-C3^a' = 1.456(5)$, $C3^a'-O1^a' = 1.216(3)$, $C1^b-N^a = 1.353(3)$, $N^b-C1^b = 1.365(3)$, $C1^b-C2^b = 1.393(4)$, $C2^b-C3^b = 1.447(4)$, $C3^b-O1^b = 1.218(3)$, $C2^b-C3^b' = 1.460(4)$, $C3^b'-O1^b' = 1.209(3)$, $C1^c-N^b = 1.369(4)$, $N^c-C1^c = 1.350(3)$, $C1^c-C2^c = 1.392(3)$, $C2^c-C3^c = 1.464(5)$, $C3^c-O1^c = 1.215(3)$, $C2^c-C3^c' = 1.445(4)$, $C3^c'-O1^c' = 1.218(4)$, $C1^c-N^a = 1.361(3)$. The bond angles (°): $C1^a-N^a-C1^b = 123.7(2)$, $N^a-C1^a-N^b = 116.2(2)$, $C1^b-N^b-C1^c = 123.5(2)$, $N^b-C1^b-N^c = 116.3(2)$, $C1^c-N^c-C1^a = 123.9(2)$, $N^c-C1^c-N^a = 116.2(2)$. The atom distances (Å): $N^a-O^a = 2.623(2)$, $N^a-O^b' = 2.649(3)$, $N^b-O^b = 2.635(3)$, $N^b-O^c' = 2.644(3)$, $N^c-O^c = 2.643(3)$, $N^c-O^a' = 2.680(3)$. Mean-plane deviation (calculated by C1~3, N, O1 = 21 atoms): 0.075 Å.

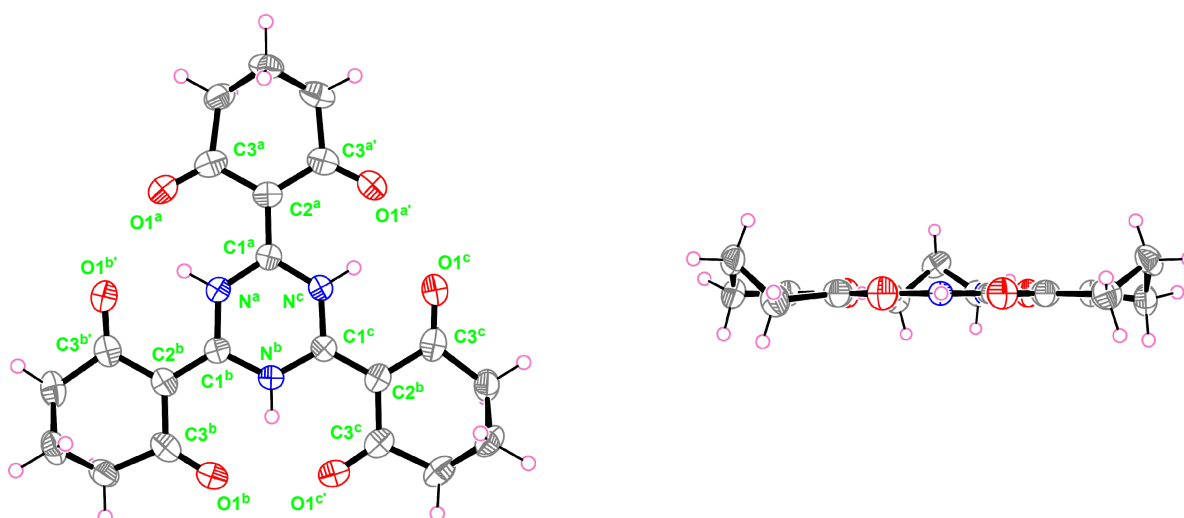


Figure S20. X-ray crystal structure of **3b**. Left: top view; right: side view. Thermal ellipsoids are set at 50% probability level. The bond lengths (Å): $N^a-C1^a = N^b-C1^b = N^c-C1^c = 1.365(0)$, $C1^a-C2^a = C1^b-C2^b = C1^c-C2^c = 1.400(0)$, $C2^a-C3^a = C2^b-C3^b = C2^c-C3^c = 1.464(0)$, $C3^a-O1^a = C3^b-O1^b = C3^c-O1^c = 1.231(0)$, $C2^a-C3^a' = C2^b-C3^b' = C2^c-C3^c' = 1.466(0)$, $C3^a'-O1^a' = C3^b'-O1^b' = C3^c'-O1^c' = 1.232(0)$, $C1^b-N^a = C1^c-N^b = C1^c-N^a = 1.367(0)$. The bond angles (°): $C1^a-N^a-C1^b = C1^b-N^b-C1^c = C1^c-N^c-C1^a = 124.1(0)$, $N^a-C1^a-N^b = N^b-C1^b-N^c = N^c-C1^c-N^a = 115.9(0)$. The atom distances (Å): $N^a-O^a = N^b-O^b = N^c-O^c = 2.591(0)$, $N^a-O^b' = N^b-O^c' = N^c-O^a' = 2.588(0)$. Mean-plane deviation (calculated by C1~3, N, O1 = 21 atoms): 0 Å.

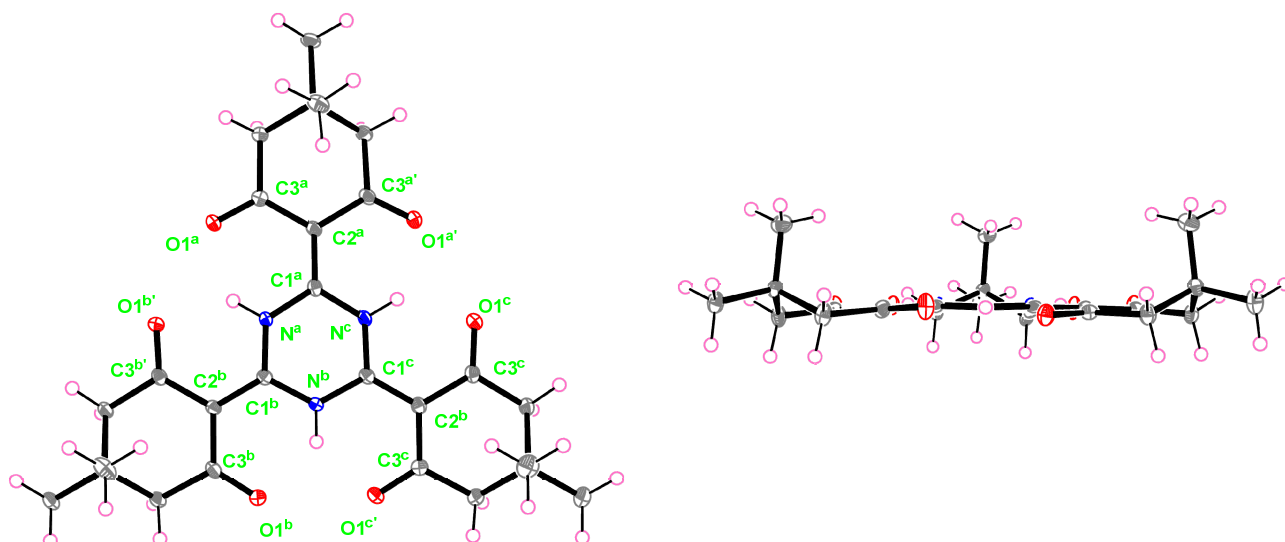


Figure S21. X-ray crystal structure of **3c**. Left: top view; right: side view. Thermal ellipsoids are set at 50% probability level. The solvent molecule was omitted for clarity. The bond distances (Å): $N^a-C1^a = 1.367(2)$, $C1^a-C2^a = 1.388(3)$, $C2^a-C3^a = 1.463(4)$, $C3^a-O1^a = 1.235(2)$, $C2^a-C3^{a'} = 1.475(2)$, $C3^{a'}-O1^{a'} = 1.226(3)$, $C1^b-N^a = 1.361(3)$, $N^b-C1^b = 1.364(3)$, $C1^b-C2^b = 1.402(2)$, $C2^b-C3^b = 1.465(3)$, $C3^b-O1^b = 1.228(3)$, $C2^b-C3^{b'} = 1.462(3)$, $C3^{b'}-O1^{b'} = 1.231(3)$, $C1^c-N^b = 1.367(2)$, $N^c-C1^c = 1.361(3)$, $C1^c-C2^c = 1.400(3)$, $C2^c-C3^c = 1.465(2)$, $C3^c-O1^c = 1.233(3)$, $C2^c-C3^{c'} = 1.460(3)$, $C3^{c'}-O1^{c'} = 1.239(2)$, $C1^c-N^a = 1.370(3)$. The bond angles (°): $C1^a-N^a-C1^b = 124.0(2)$, $N^a-C1^a-N^b = 116.4(2)$, $C1^b-N^b-C1^c = 123.6(2)$, $N^b-C1^b-N^c = 116.4(2)$, $C1^c-N^c-C1^c = 123.7(2)$, $N^c-C1^c-N^a = 115.9(2)$. The atom distances (Å): $N^a-O^a = 2.575(3)$, $N^a-O^{b'} = 2.582(2)$, $N^b-O^b = 2.601(2)$, $N^b-O^{c'} = 2.587(3)$, $N^c-O^c = 2.582(2)$, $N^c-O^{a'} = 2.593(2)$. Mean-plane deviation (calculated by C1~3, N, O1 = 21 atoms): 0.039 Å.

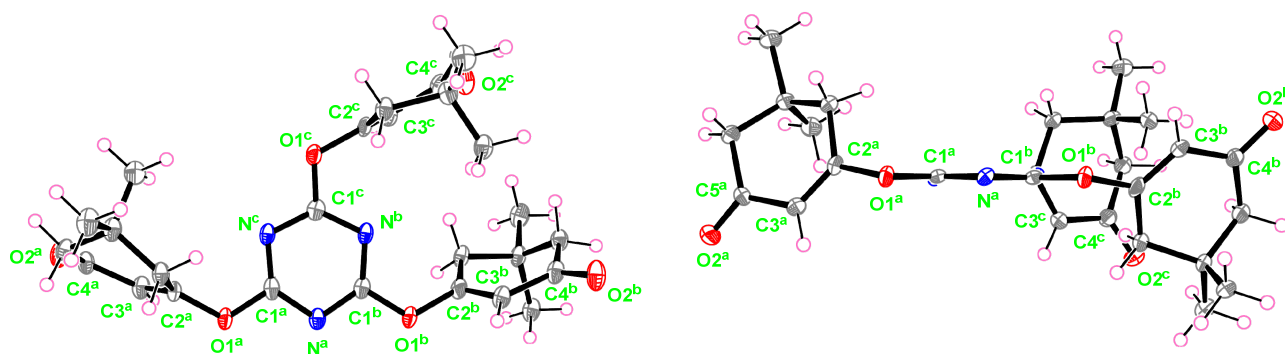


Figure S22. X-ray crystal structure of **4c**. Left: top view; right: side view. Thermal ellipsoids are set at 50% probability level. The bond distances (Å): $N^a-C1^a = 1.333(2)$, $C1^a-O1^a = 1.351(2)$, $O1^a-C2^a = 1.416(2)$, $C2^a-C3^a = 1.309(3)$, $C3^a-C4^a = 1.477(3)$, $C4^a-O2^a = 1.214(3)$, $C1^a-N^b = 1.324(3)$, $N^b-C1^b = 1.322(2)$, $C1^b-O1^b = 1.357(2)$, $O1^b-C2^b = 1.410(3)$, $C2^b-C3^b = 1.327(3)$, $C3^b-C4^b = 1.465(3)$, $C4^b-O2^b = 1.223(3)$, $C1^b-N^c = 1.333(2)$, $N^c-C1^c = 1.328(3)$, $C1^c-O1^c = 1.342(2)$, $O1^c-C2^c = 1.412(3)$, $C2^c-C3^c = 1.332(3)$, $C3^c-C4^c = 1.463(3)$, $C4^c-O2^c = 1.228(3)$, $C1^c-N^a = 1.322(2)$. The bond angles (°): $C1^a-N^a-C1^b = 111.4(2)$, $N^a-C1^a-N^b = 128.4(2)$, $C1^b-N^b-C1^c = 112.2(2)$, $N^b-C1^b-N^c = 127.5(2)$, $C1^c-N^c-C1^c = 111.9(2)$, $N^c-C1^c-N^a = 128.4(2)$.

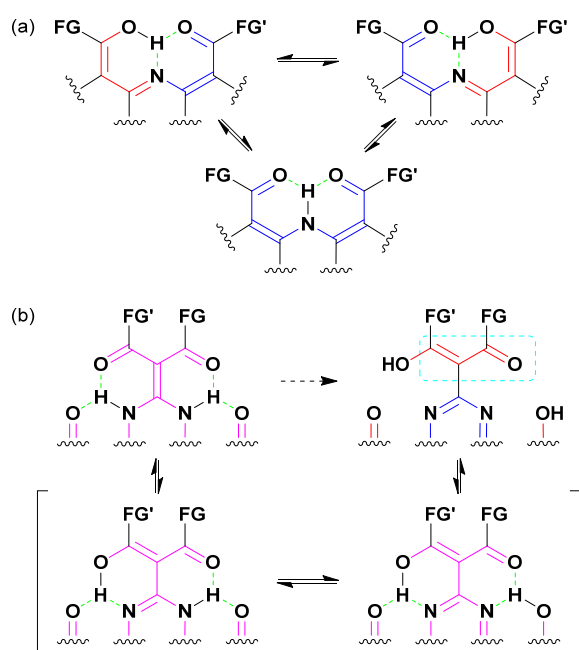


Chart S1. Tautomerism of multi-hydrogen bonding entities. (a) Delocalisation mechanism along single and double bonds. (b) Proposed mechanism of an independent enone moiety emerging.

References

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