Supporting Information

X-Ray diffraction analysis data of **1a**

Colorless prismatic crystals from chloroform-hexane, trigonal space group $P3_1$, a = 13.4187(3) Å, b = 13.4187(3) Å, c = 28.8186(6) Å, γ = 120.0 °, V = 4493.9(2) Å^3, Z = 12, ρ = 1.301 g/cm^3, μ = 0.724 mm^{-1}. The structure was solved by the direct method of full matrix least-squares, where the final R and wR were 0.1240 and 0.3327 for 9005 reflections. CCDC 1010749.

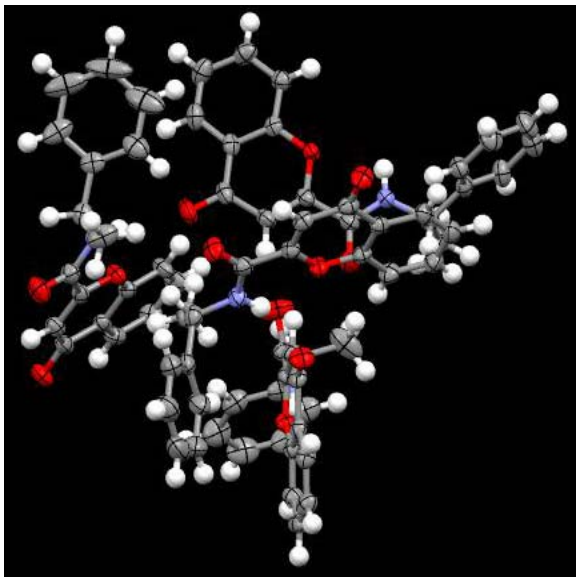


Figure S1. Perspective view of **1a**.

X-Ray diffraction analysis data of **1b**

Colorless prismatic crystals from chloroform-hexane, triclinic space group $P1$, a = 5.9167(9) Å, b = 10.9747(17) Å, c = 12.2265(18) Å, α = 64.4240(19) °, β = 82.5940(19) °, γ = 89.9950(19) °, V = 708.78(19) Å^3, Z = 2, ρ = 1.28 g/cm^3, μ = 0.088 mm^{-1}. The structure was solved by the direct method of full matrix least-squares, where the final R and wR were 0.0398 and 0.1003 for 9005 reflections. CCDC 1010750.

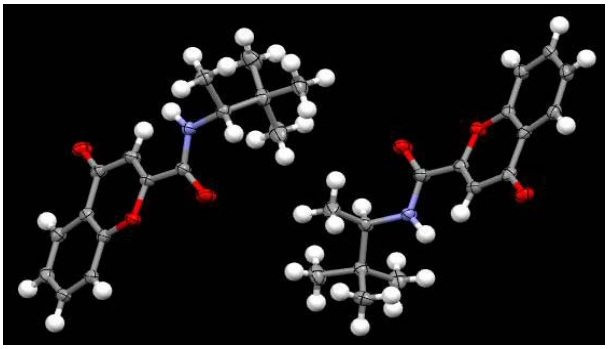


Figure S2. Perspective view of **1b**.

X-Ray diffraction analysis data of photodimer **2a**

Colorless prismatic crystals from chloroform-hexane, monoclinic space group $P2_12_12_1$, a = 12.2096(9) Å, b = 13.7443(10) Å, c = 18.0044(14) Å, V = 3021.4(4) Å^3, Z = 4, ρ = 1.290 g/cm^3, μ = 0.088 mm^{-1}. The structure was solved by the direct method of full matrix least-squares, where the final R and wR were 0.0469 and 0.1150 for 5358 reflections. CCDC 1010751.

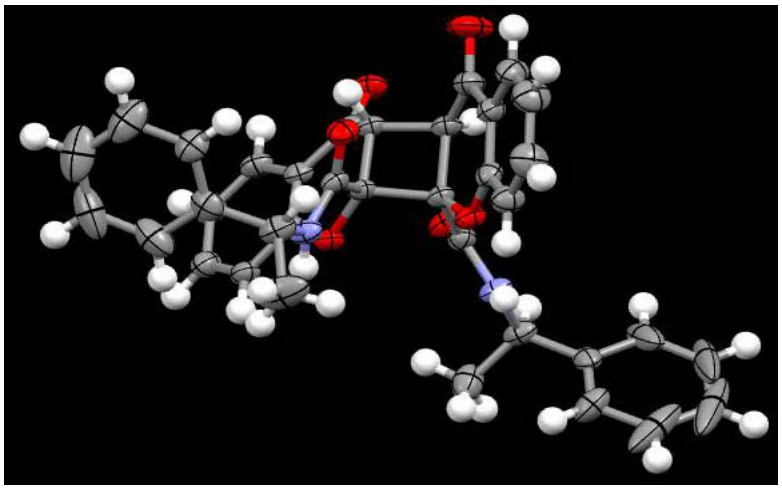


Figure S3. Perspective view of **2a**.

X-Ray diffraction analysis data of photodimer **2'a**

Colorless prismatic crystals from chloroform-hexane, monoclinic space group $P2_12_12_1$, a = 9.7337(10) Å, b = 13.9495(14) Å, c = 22.104(2) Å, V = 3001.3(5) Å^3, Z = 4, ρ = 1.298 g/cm^3, μ = 0.088 mm^{-1}. The structure was solved by the direct method of full matrix least-squares, where the final R and wR were 0.0424 and 0.0944 for 5287 reflections. CCDC 1010752.

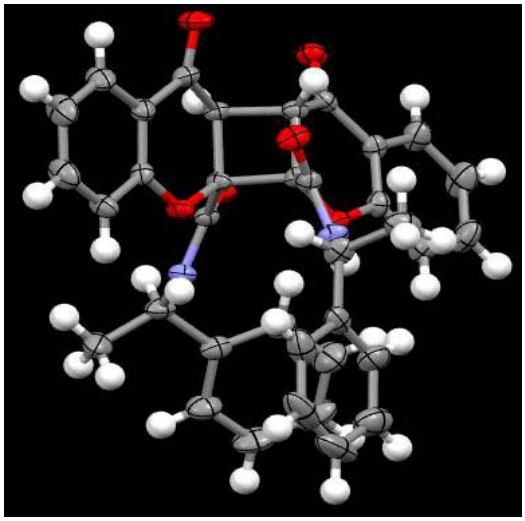


Figure S4. Perspective view of **2'a**.

X-Ray diffraction analysis data of photodimer **2b**

Colorless prismatic crystals from chloroform-hexane, monoclinic space group $P2_12_12_1$, a = 7.704(18) Å, b = 14.23(3) Å, c = 26.50(6) Å, V = 2906(11) Å^3, Z = 4, ρ = 1.249 g/cm^3, μ = 0.086 mm^{-1}. The structure was solved by the direct method of full matrix least-squares, where the final R and wR were 0.0629 and 0.1531 for 5433 reflections. CCDC 1010753. The absolute configuration could be determined on the basis of the configuration of (*R*)-1-(*t*-butyl)ethylamine.

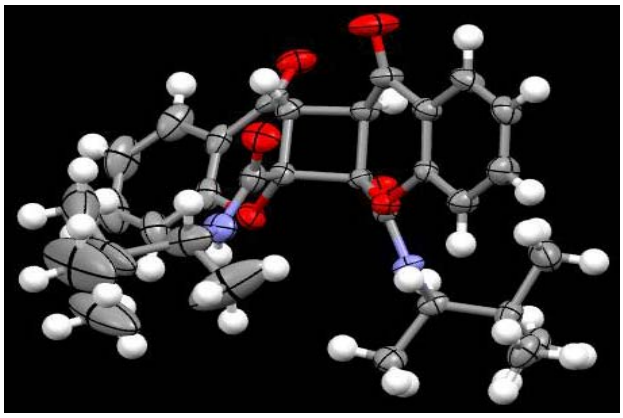


Figure S5. Perspective view of **2b**.

X-Ray diffraction analysis data of photodimer **2c**

Colorless prismatic crystals, monoclinic space group $P2_12_12_1$, a = 8.021(3) Å, b = 15.273(5) Å, c = 21.484(7) Å, V = 2631.9(15) Å^3, Z = 4, ρ = 1.389 g/cm^3, μ = 0.107 mm^{-1}. The structure was solved by the direct method of full matrix least-squares, where the final R and wR were 0.0535 and 0.0896 for 5909 reflections. CCDC 1010754. The absolute configuration could be determined on the basis of the configuration of (*S*)-alanine function.

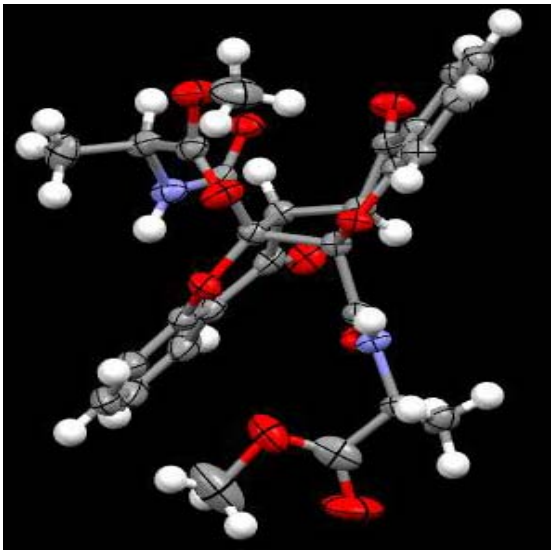


Figure S6. Perspective view of **2c**.

X-Ray diffraction analysis data of photodimer **2'c**

This crystal included each one molecule of acetone and *N*-methylbenzamide. Colorless prismatic crystals, monoclinic space group $P6_5$, a = 12.380(5) Å, b = 12.380(5) Å, c = 42.393(17) Å, γ = 120.00 °, V = 5627(4) Å^3, Z = 6, ρ = 1.317 g/cm^3, μ = 0.098 mm^{-1}. The structure was solved by the direct method of full matrix least-squares, where the final R and wR were 0.0631 and 0.1416 for 6805 reflections. CCDC 1010755.

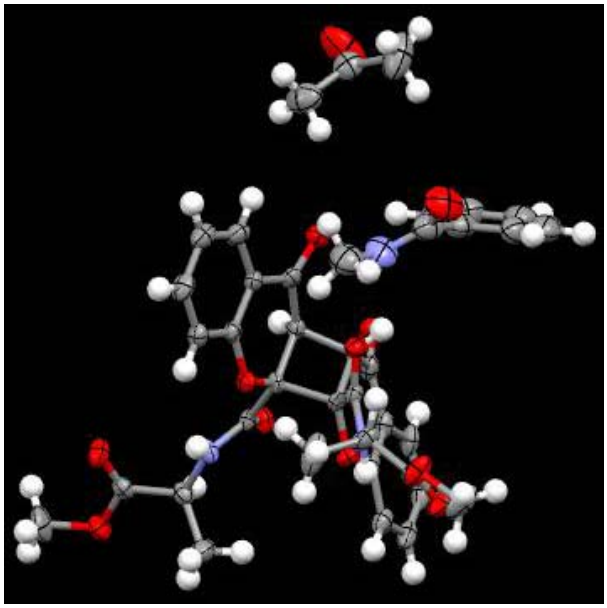
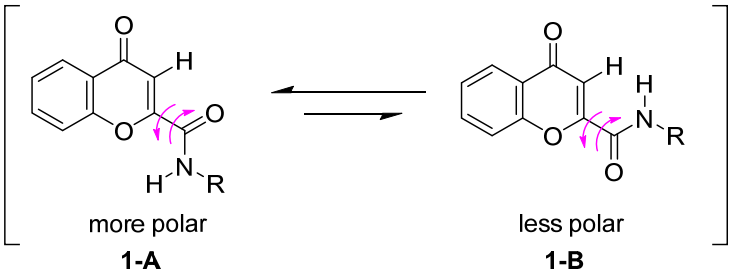


Figure S7. Perspective view of **2'c**.

Conformational calculation using Gaussian 09 program.

Total energy and dipole moment for two conformations, **1-A** and **1-B,** were estimated by DFT calculation using RB3LYP 6-31G in Gaussian 09W. (Scheme S1, Table S1 and S2).



Scheme S1. Conformational change of **1**.

Table S1. Conformational analysis and the dipole moment of ground state of **1a–c**

compds	Ground state conformation	ΔH_B- ΔH_A (kcal mol^{-1})[a]	Dipole moment (Deby)
1a	A (more stable)	5.78	6.75
1a	B (less stable)		2.21
1b	A (more stable)	5.98	6.88
1b	B (less stable)		2.16
1c	A (more stable)	5.80	7.01
1c	B (less stable)		3.15

[a]Differences in total energy between stable conformation A and less stable conformation B in the ground state obtained from DFT (RB3LYP 6-31G) calculation in Gaussian 09W. [b]Dipole moment obtained from DFT (RB3LYP 6-31G) calculation in Gaussian 09W.

Table S2. Conformational analysis and the dipole moment of triplet excited state of **1a–c**

compds	Triplet excited state conformation	ΔH_B- ΔH_A (kcal mol^{-1})[a]	Dipole moment (Deby)
1a	A (more stable)	7.37	5.93
1a	B (less stable)		1.80
1b	A (more stable)	7.76	5.94
1b	B (less stable)		1.33
1c	A (more stable)	7.14	5.61
1c	B (less stable)		0.61

[a]Differences in total energy between stable conformation A and less stable conformation B in the ground state obtained from DFT (RB3LYP 6-31G) calculation in Gaussian 09W. [b]Dipole moment obtained from DFT (RB3LYP 6-31G) calculation in Gaussian 09W.

Figure S8. ^{1}H NMR spectrum of **1a**

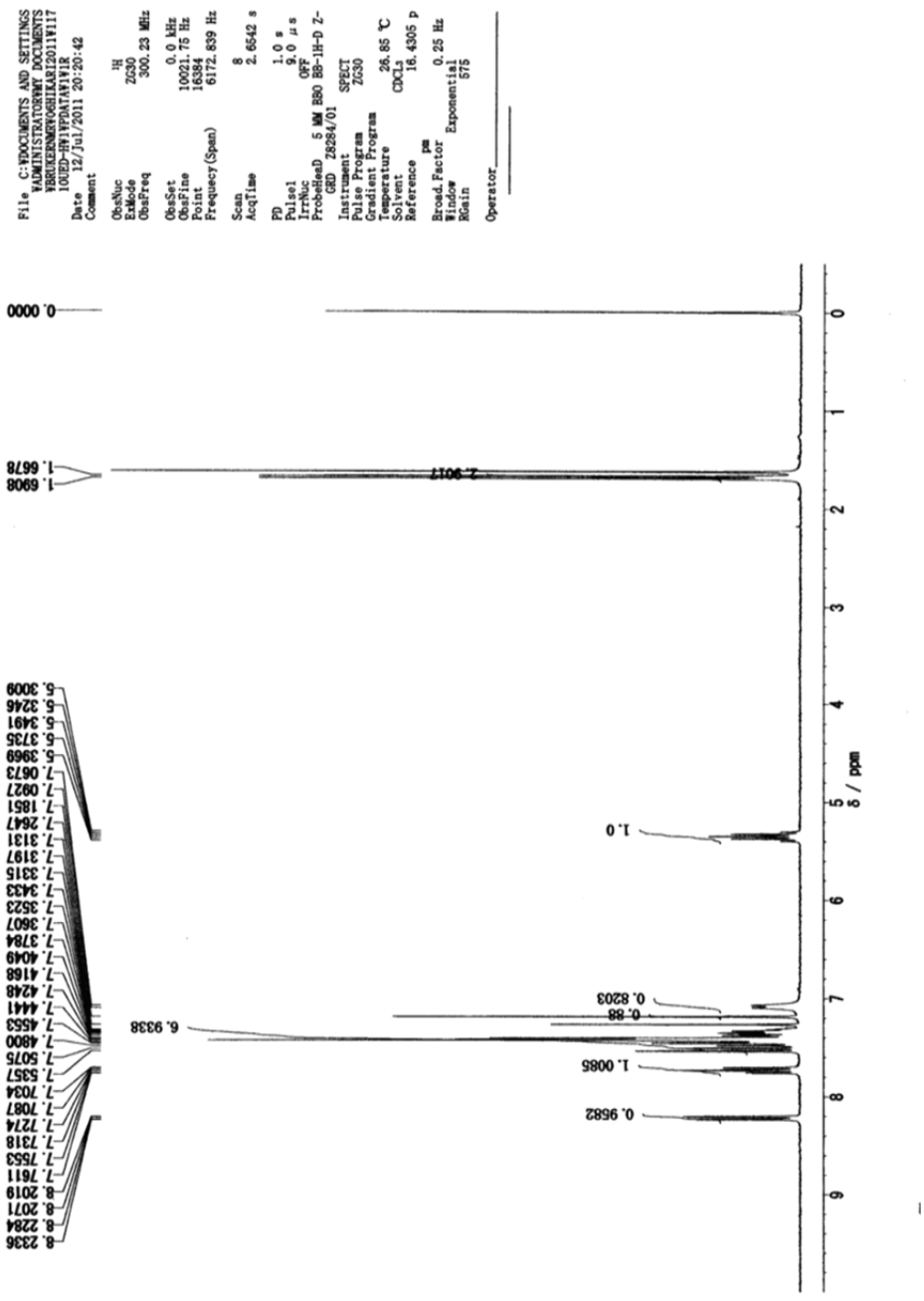


Figure S9. ^{13}C NMR spectrum of **1a**

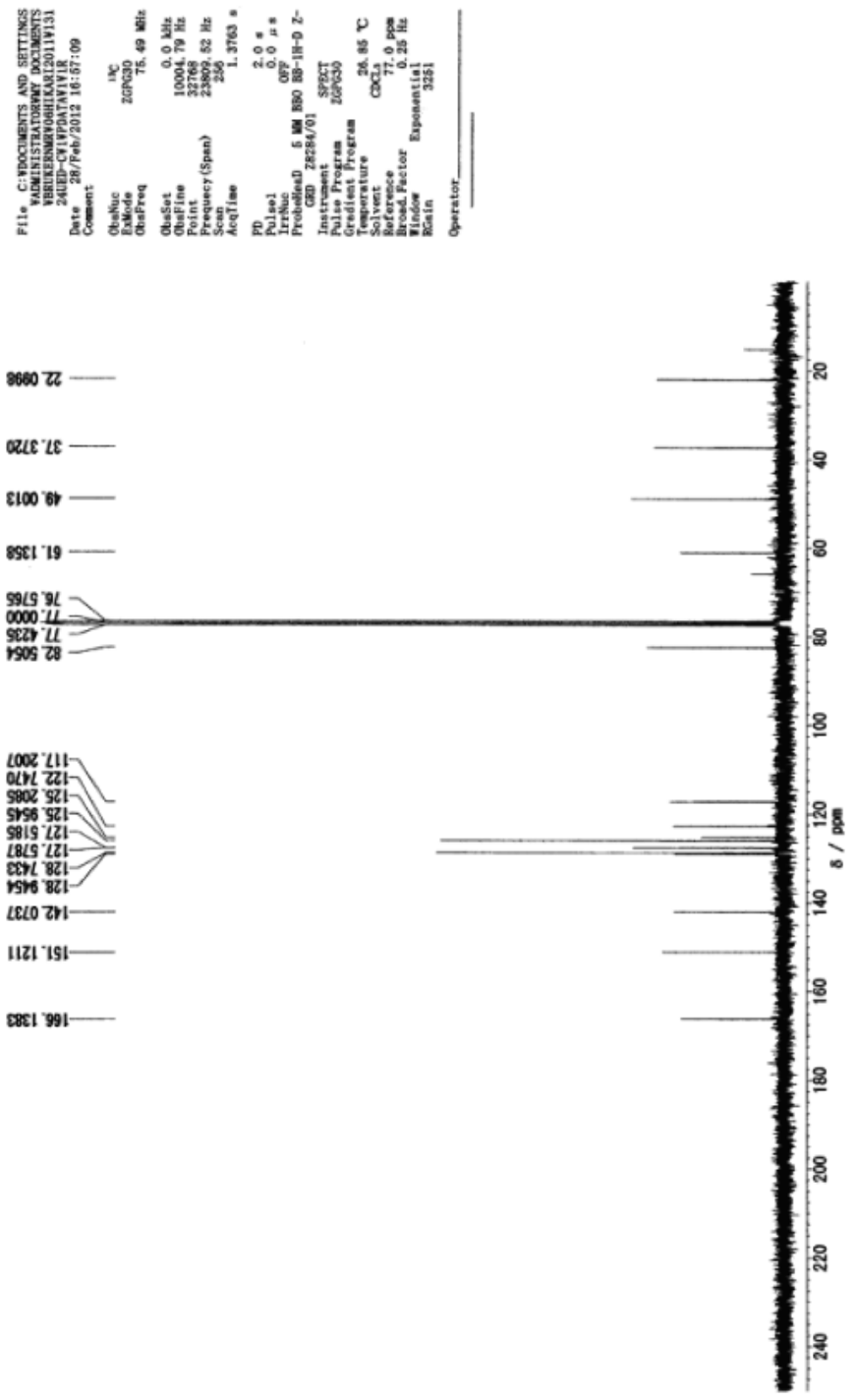


Figure S10. ^{1}H NMR spectrum of **1b**

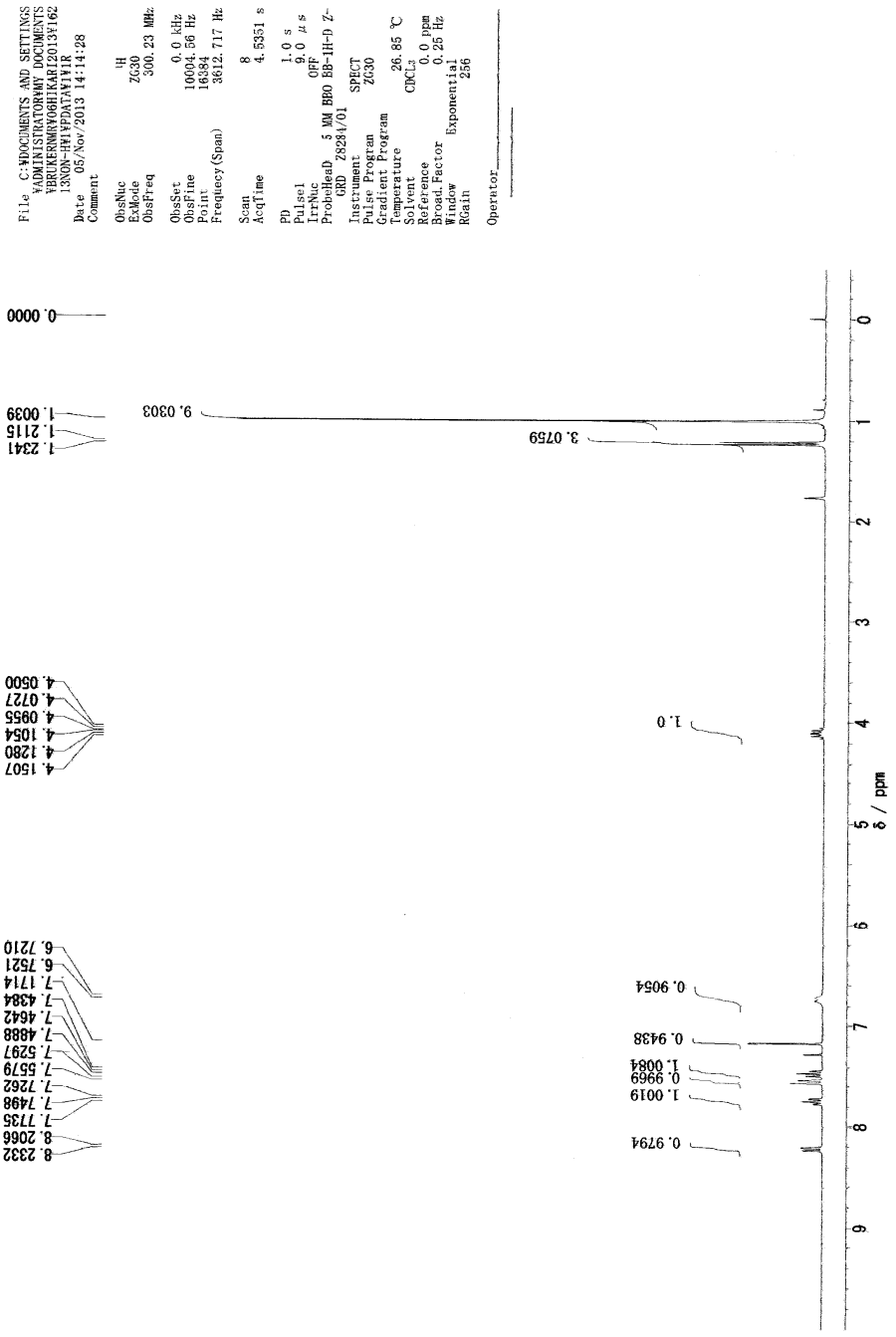


Figure S11. ^{13}C NMR spectrum of **1b**

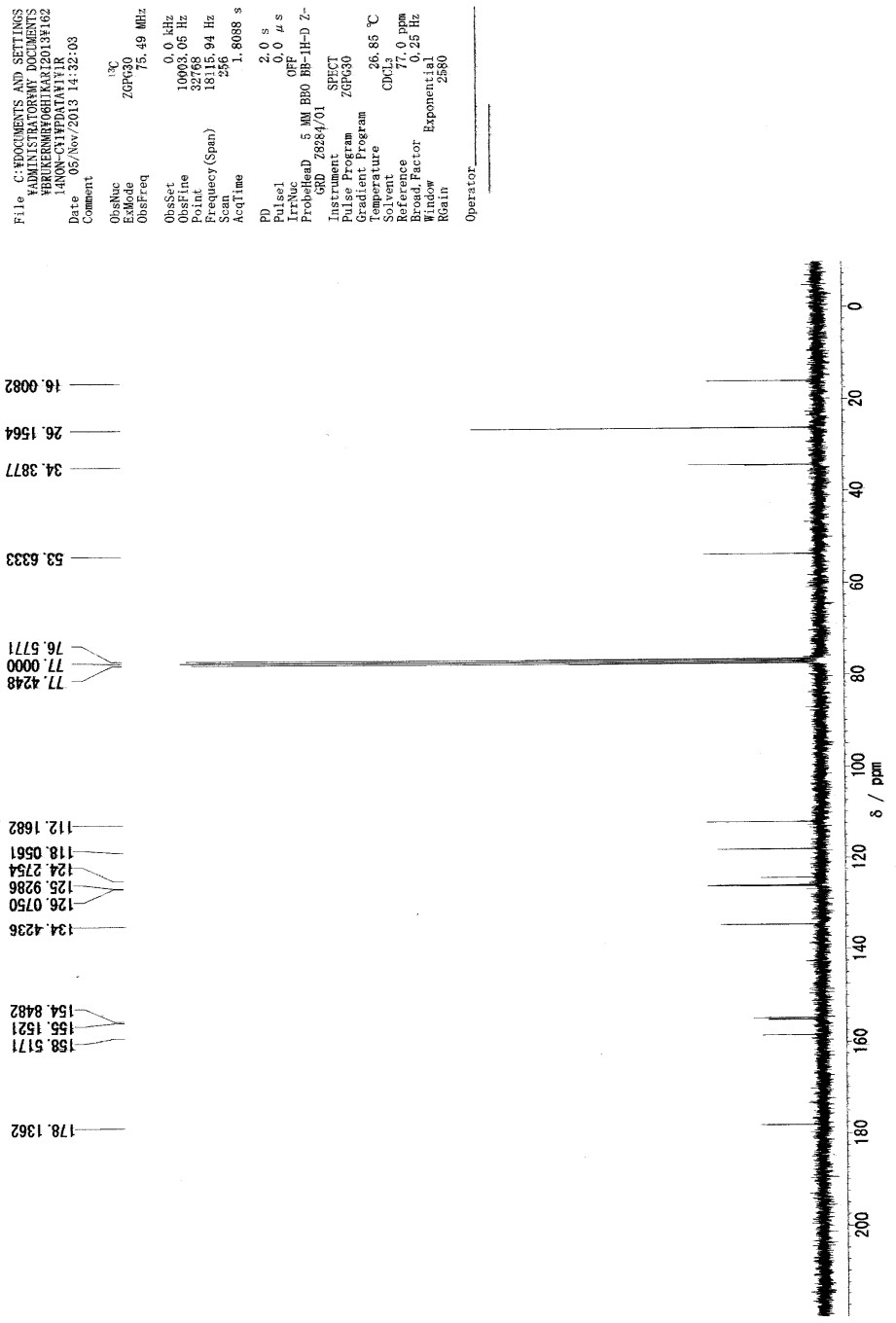


Figure S12. ^{1}H NMR spectrum of **1c**

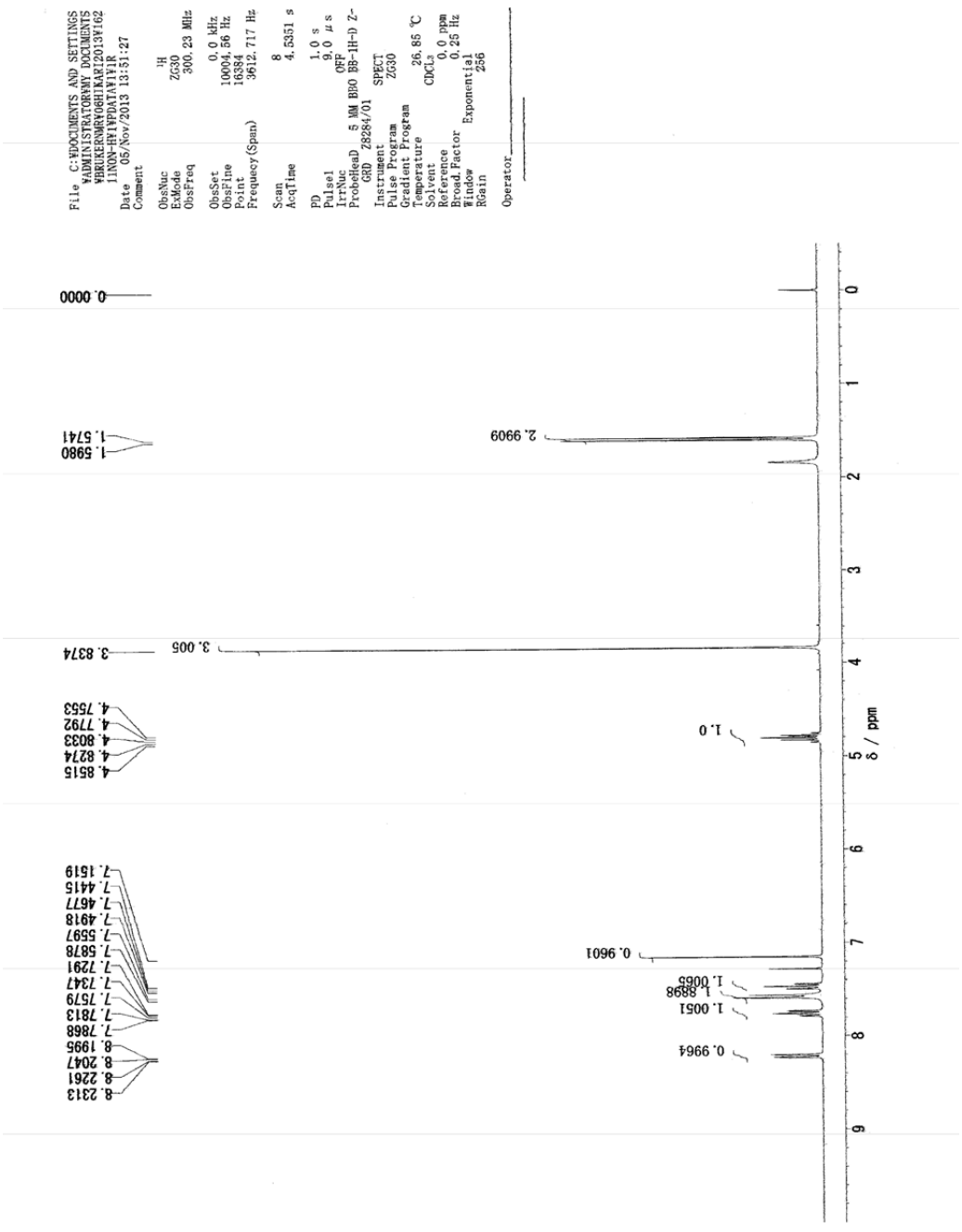


Figure S13. ^{13}C NMR spectrum of **1c**

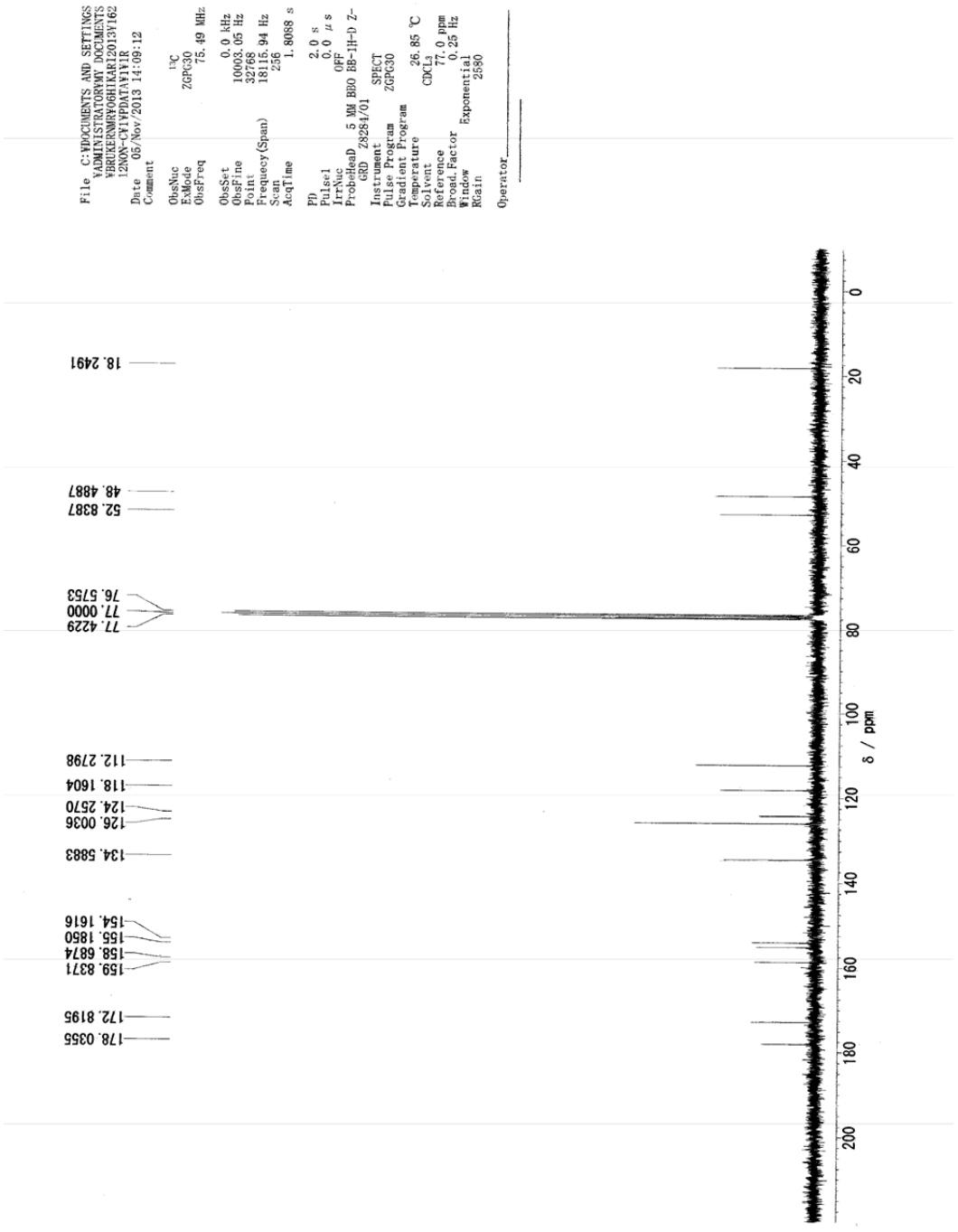


Figure S14. ^{1}H NMR spectrum of **2a**

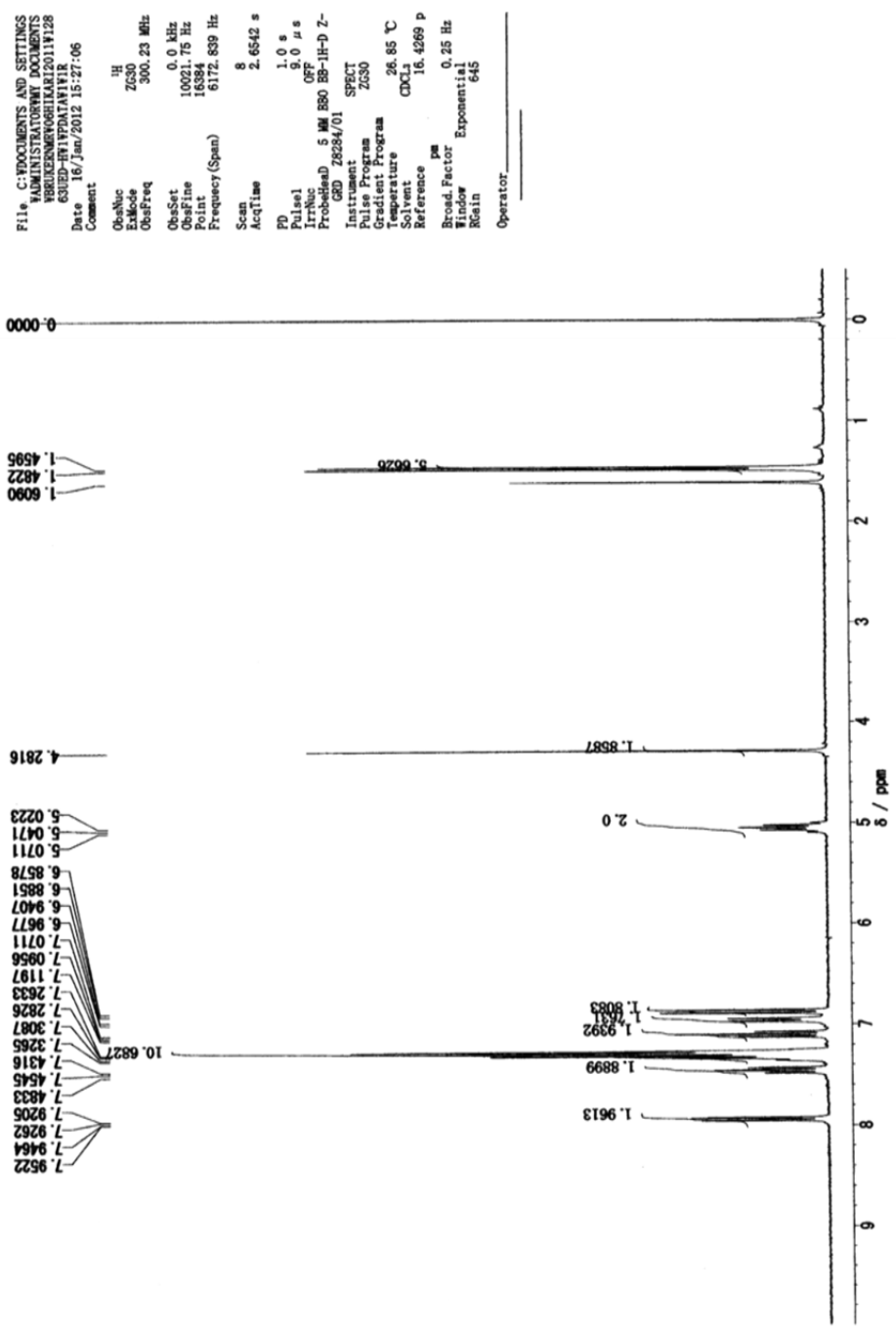


Figure S15. ^{13}C NMR spectrum of **2a**

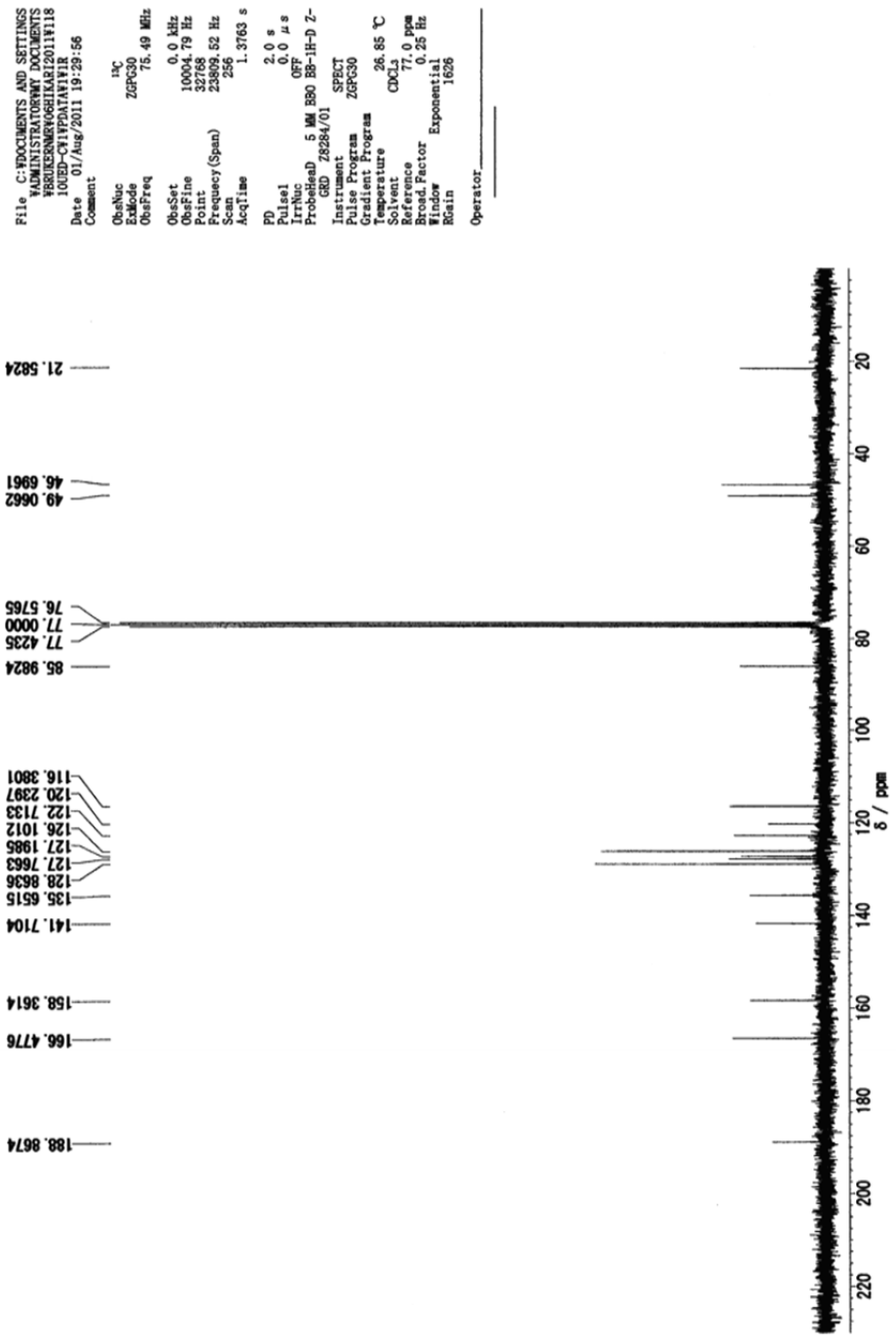


Figure S16. ***anti*-HH dimer 2'a**

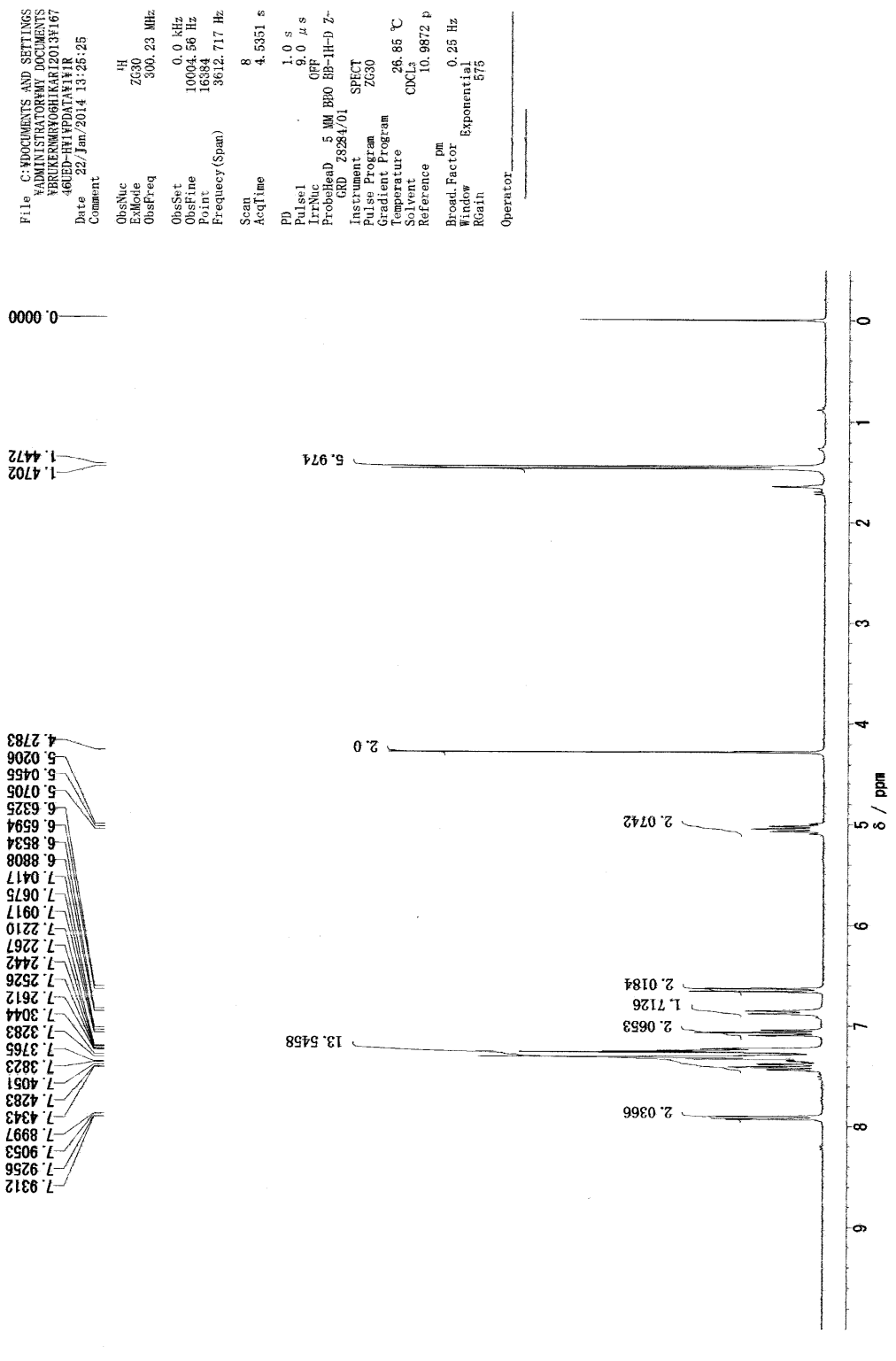


Figure S17. *anti*-HH dimer 2'a

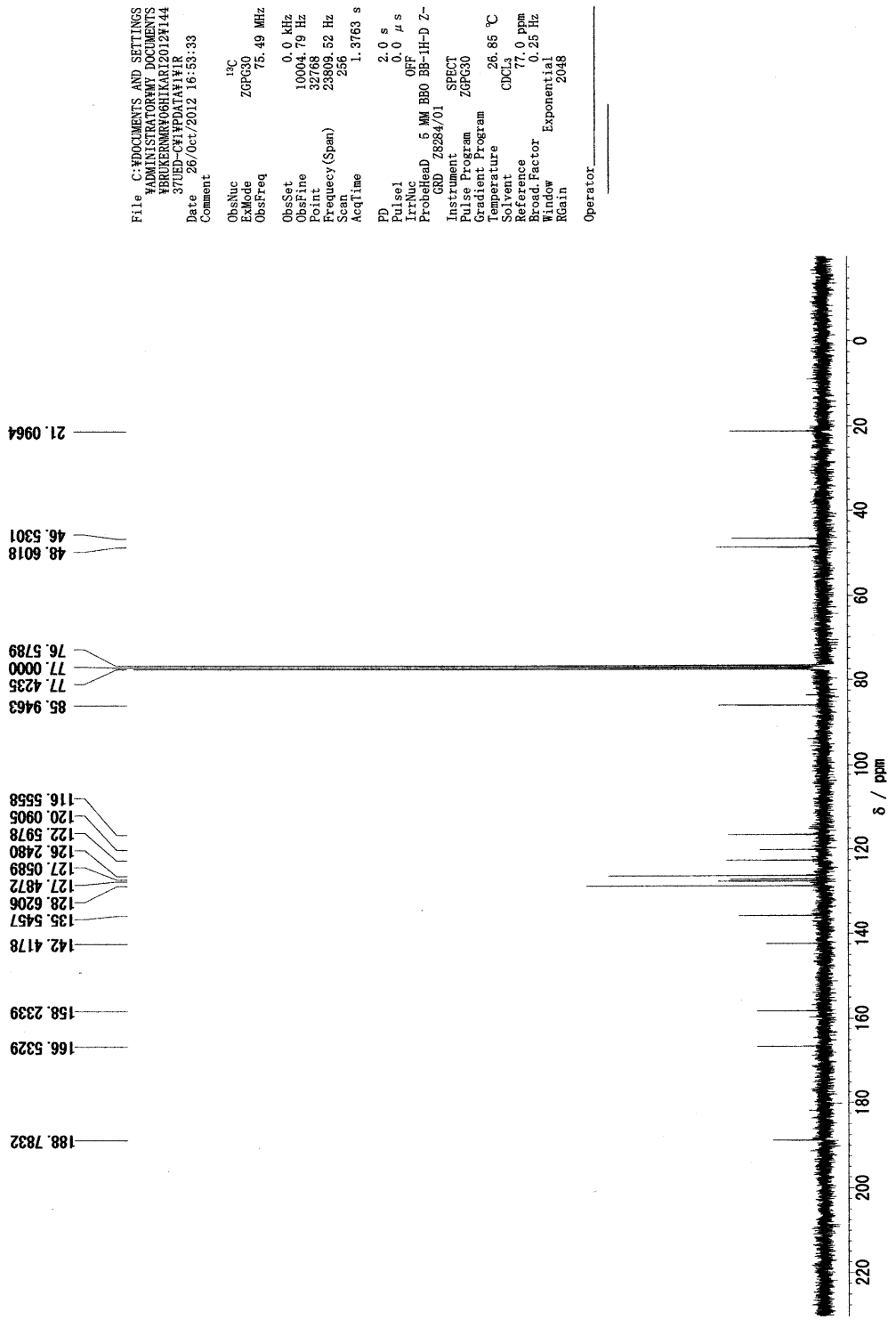


Figure S18. ^{1}H NMR spectrum of **2b**

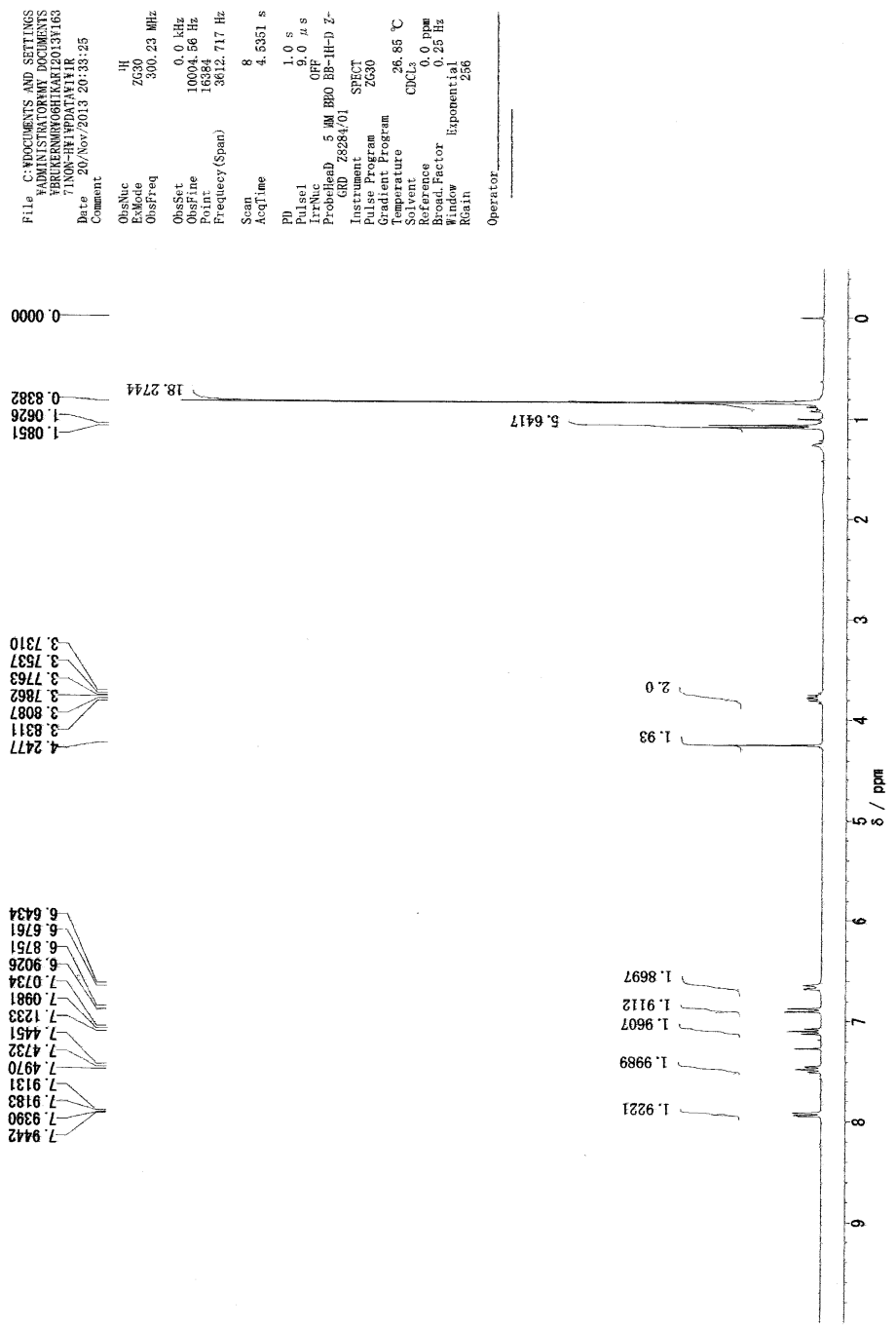


Figure S19. ^{13}C NMR spectrum of **2b**

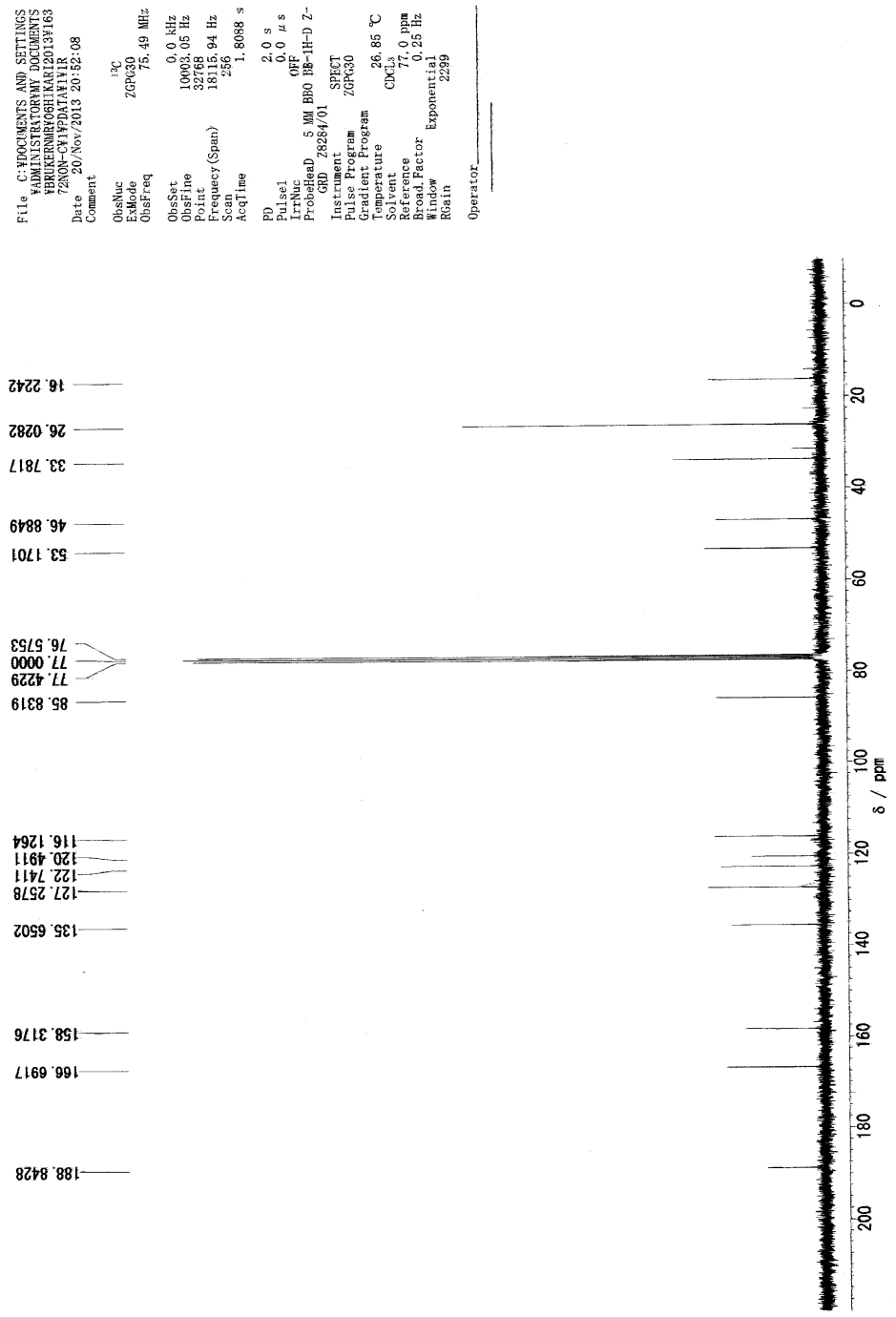


Figure S20. ^{1}H NMR spectrum of **2'b**

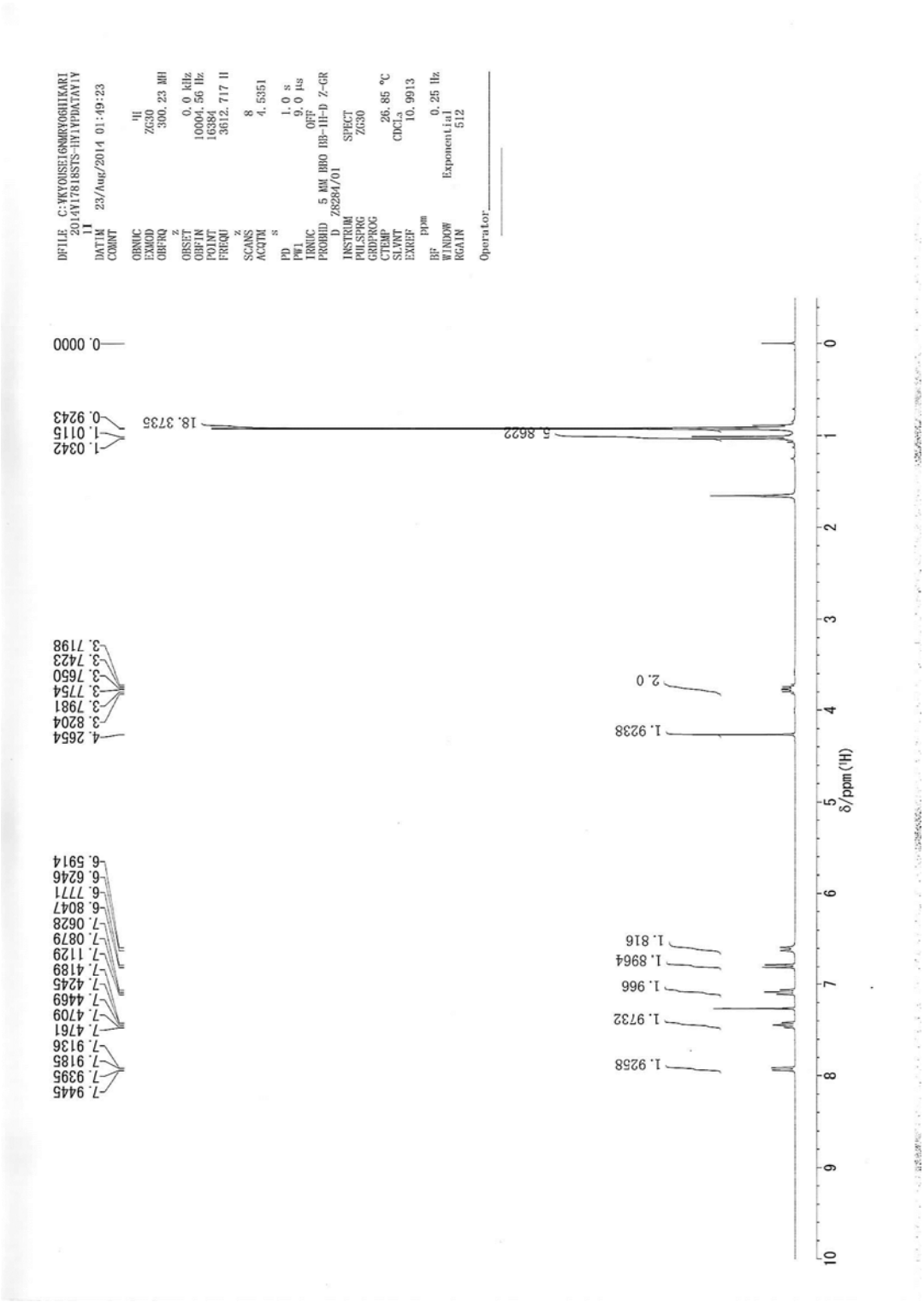


Figure S21. ^{13}C NMR spectrum of **2'b**

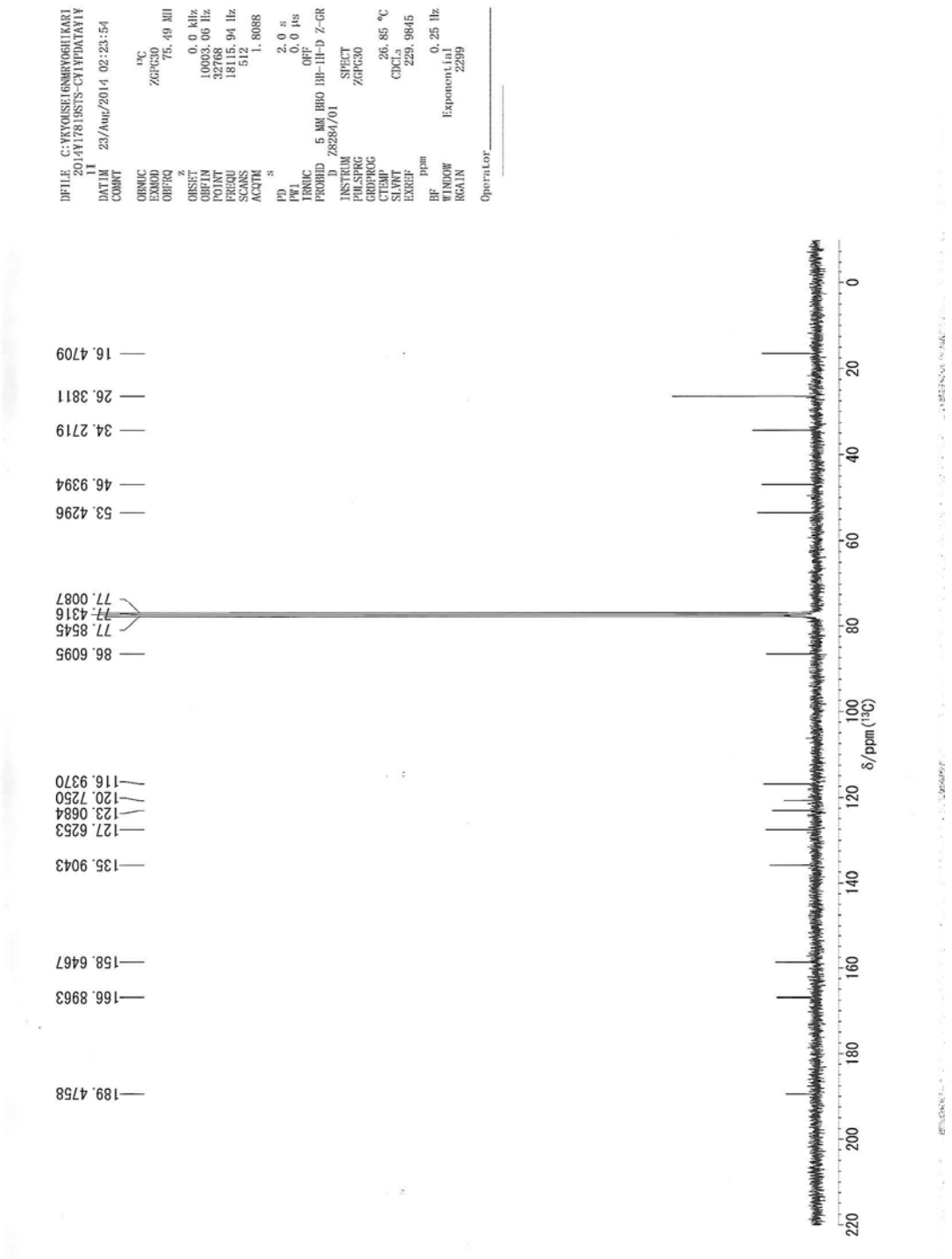


Figure S22. ^{1}H NMR spectrum of **2c**

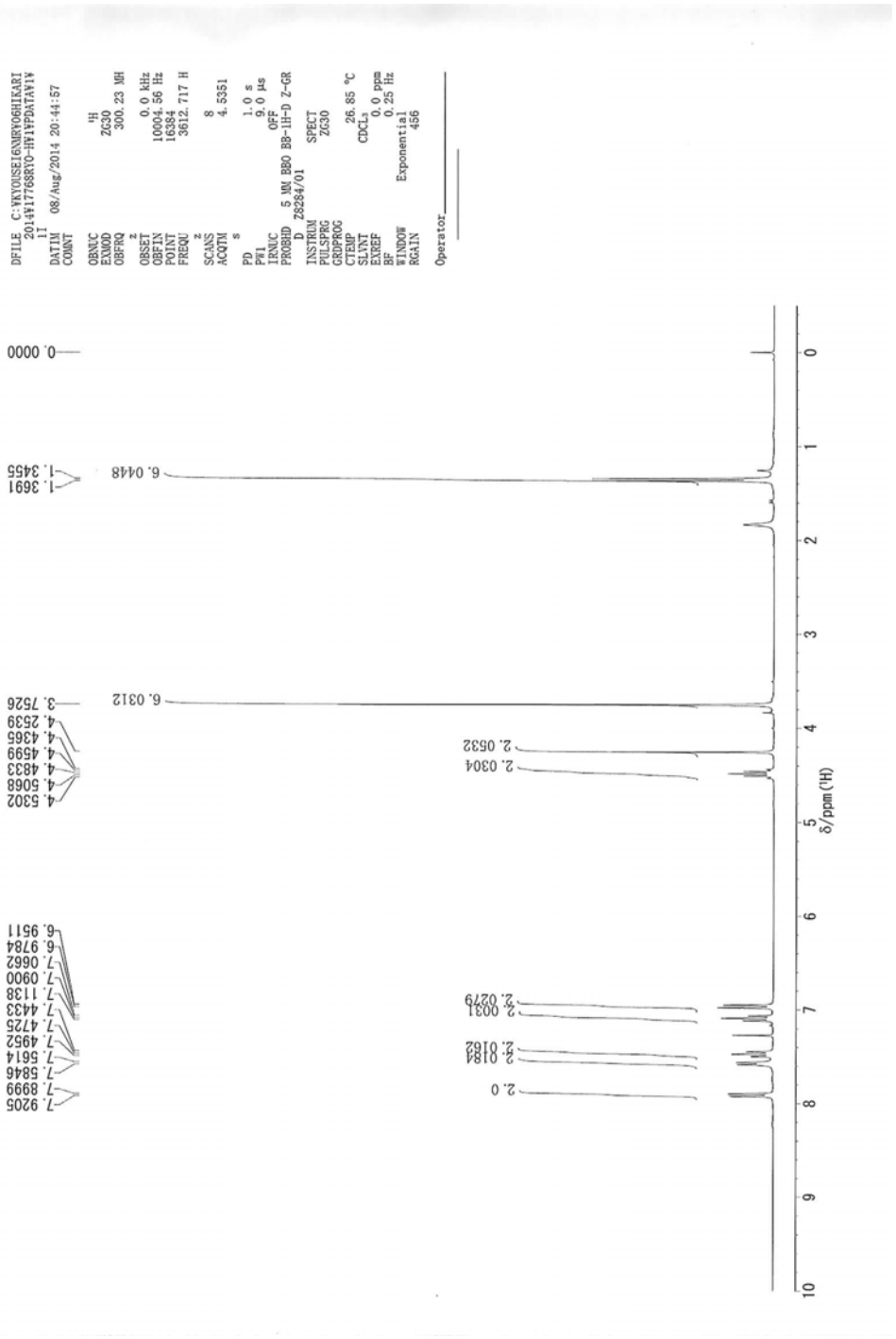


Figure S23. ^{13}C NMR spectrum of **2c**

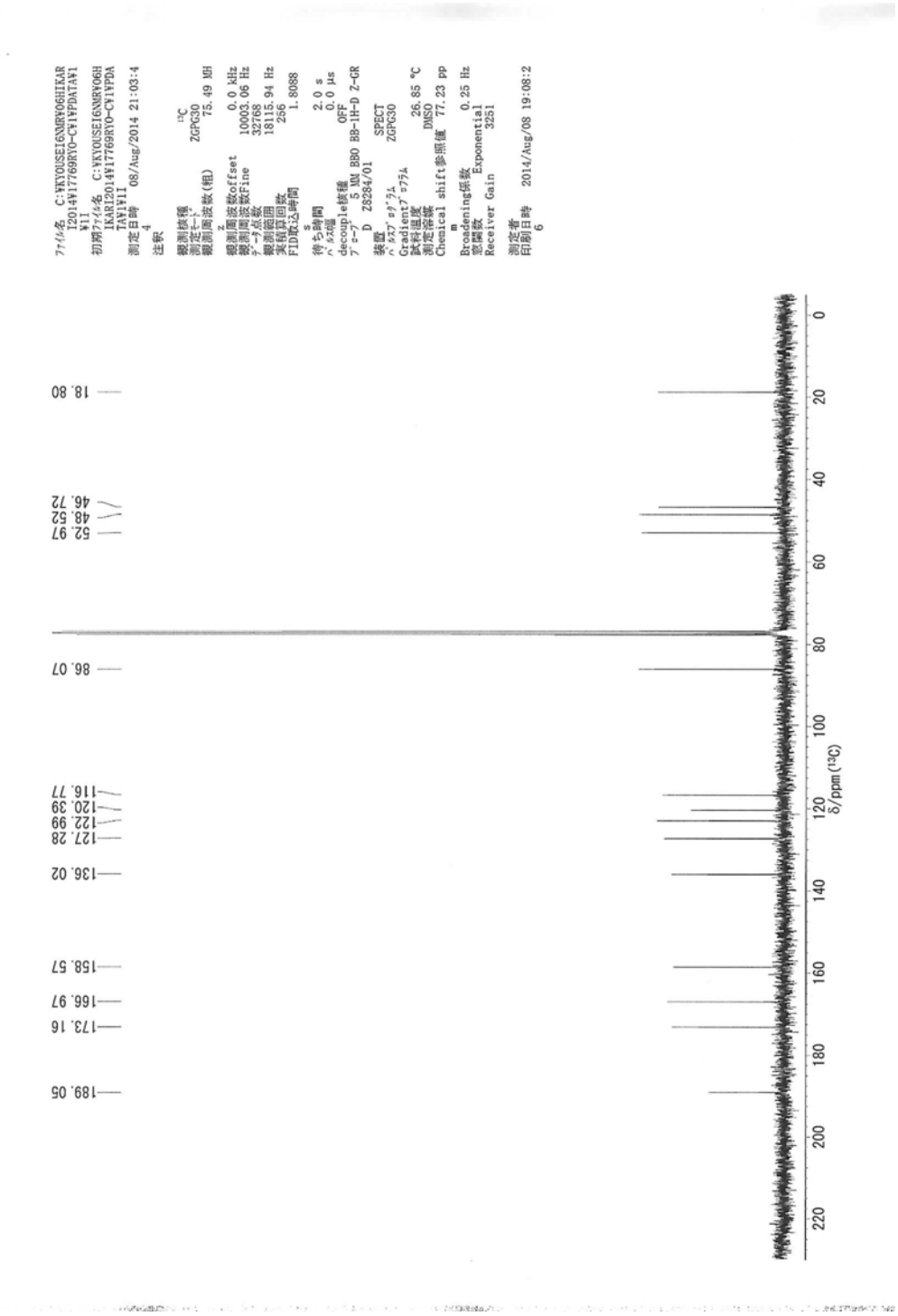


Figure S24. ^{1}H NMR spectrum of **2'c**

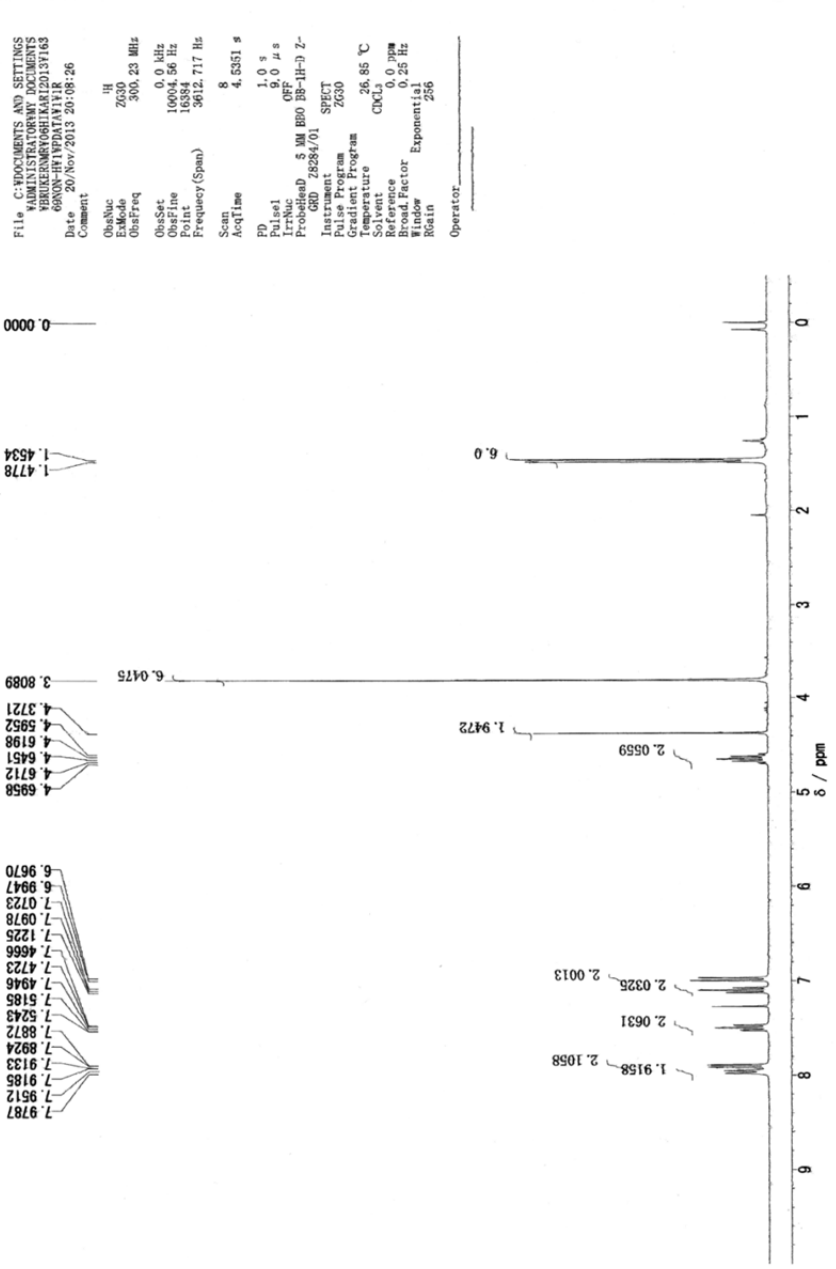


Figure S25. ^{13}C NMR spectrum of **2'c**