

Supporting Information

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

Colorless prismatic crystals from chloroform-hexane, trigonal space group $P3_1$, $a = 13.4187(3) \text{ \AA}$, $b = 13.4187(3) \text{ \AA}$, $c = 28.8186(6) \text{ \AA}$, $\gamma = 120.0^\circ$, $V = 4493.9(2) \text{ \AA}^3$, $Z = 12$, $\rho = 1.301 \text{ g/cm}^3$, $\mu = 0.724 \text{ mm}^{-1}$. 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.

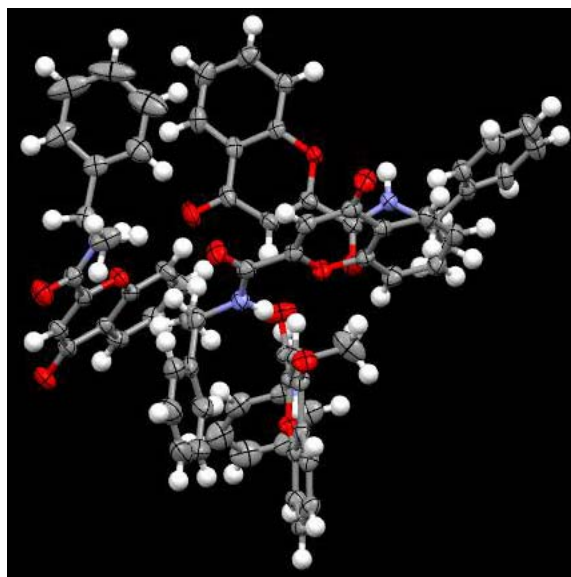


Figure S1. Perspective view of **1a**.

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

Colorless prismatic crystals from chloroform-hexane, triclinic space group $P1$, $a = 5.9167(9) \text{ \AA}$, $b = 10.9747(17) \text{ \AA}$, $c = 12.2265(18) \text{ \AA}$, $\alpha = 64.4240(19)^\circ$, $\beta = 82.5940(19)^\circ$, $\gamma = 89.9950(19)^\circ$, $V = 708.78(19) \text{ \AA}^3$, $Z = 2$, $\rho = 1.28 \text{ g/cm}^3$, $\mu = 0.088 \text{ mm}^{-1}$. 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.

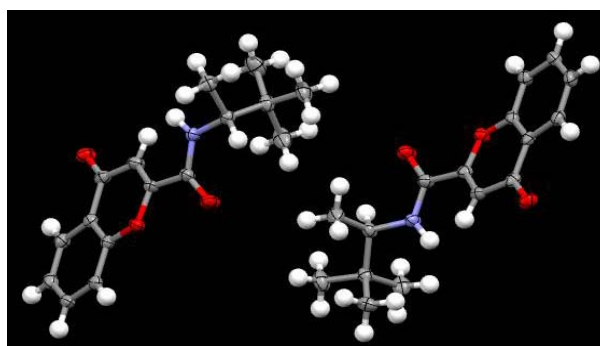


Figure S2. Perspective view of **1b**.

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

Colorless prismatic crystals from chloroform-hexane, monoclinic space group $P2_12_12_1$, $a = 12.2096(9) \text{ \AA}$, $b = 13.7443(10) \text{ \AA}$, $c = 18.0044(14) \text{ \AA}$, $V = 3021.4(4) \text{ \AA}^3$, $Z = 4$, $\rho = 1.290 \text{ g/cm}^3$, $\mu = 0.088 \text{ mm}^{-1}$. 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.

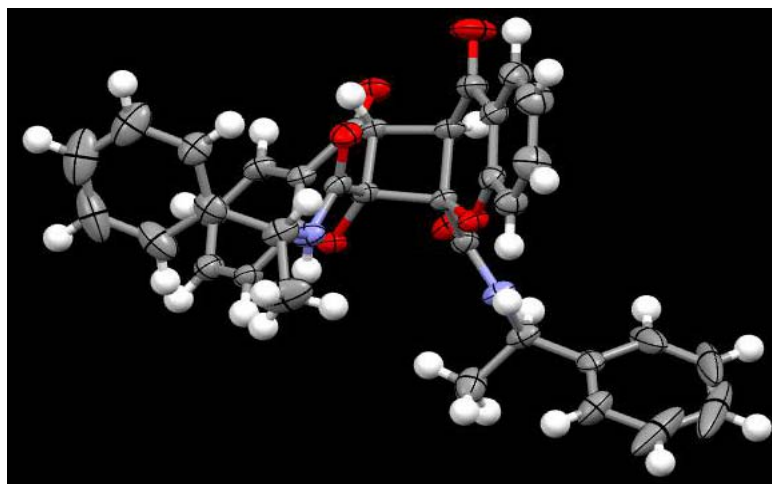


Figure S3. Perspective view of **2a**.

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

Colorless prismatic crystals from chloroform-hexane, monoclinic space group $P2_12_12_1$, $a = 9.7337(10) \text{ \AA}$, $b = 13.9495(14) \text{ \AA}$, $c = 22.104(2) \text{ \AA}$, $V = 3001.3(5) \text{ \AA}^3$, $Z = 4$, $\rho = 1.298 \text{ g/cm}^3$, $\mu = 0.088 \text{ mm}^{-1}$. 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.

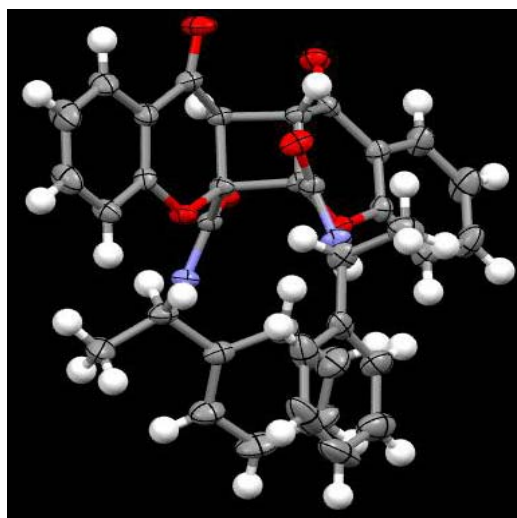


Figure S4. Perspective view of **2'a**.

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

Colorless prismatic crystals from chloroform-hexane, monoclinic space group $P2_12_12_1$, $a = 7.704(18) \text{ \AA}$, $b = 14.23(3) \text{ \AA}$, $c = 26.50(6) \text{ \AA}$, $V = 2906(11) \text{ \AA}^3$, $Z = 4$, $\rho = 1.249 \text{ g/cm}^3$, $\mu = 0.086 \text{ mm}^{-1}$. 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.

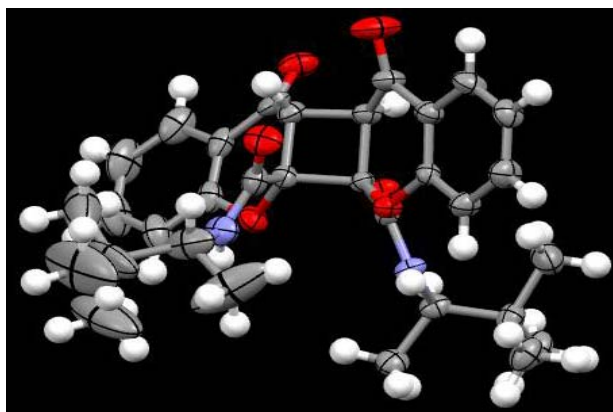


Figure S5. Perspective view of **2b**.

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

Colorless prismatic crystals, monoclinic space group $P2_12_12_1$, $a = 8.021(3) \text{ \AA}$, $b = 15.273(5) \text{ \AA}$, $c = 21.484(7) \text{ \AA}$, $V = 2631.9(15) \text{ \AA}^3$, $Z = 4$, $\rho = 1.389 \text{ g/cm}^3$, $\mu = 0.107 \text{ mm}^{-1}$. 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.

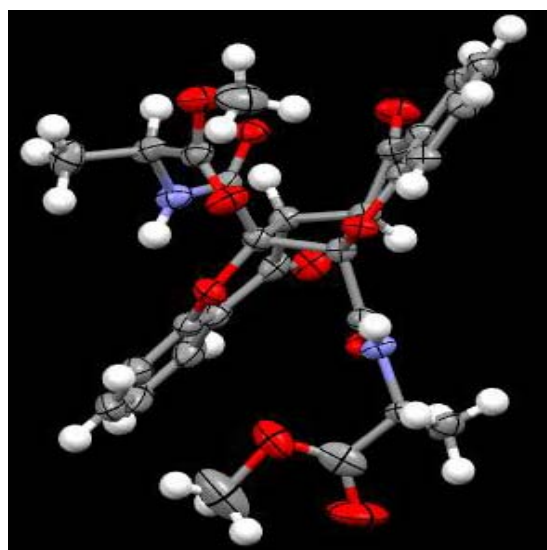


Figure S6. Perspective view of **2c**.

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 $P6_5$, $a = 12.380(5) \text{ \AA}$, $b = 12.380(5) \text{ \AA}$, $c = 42.393(17) \text{ \AA}$, $\gamma = 120.00^\circ$, $V = 5627(4) \text{ \AA}^3$, $Z = 6$, $\rho = 1.317 \text{ g/cm}^3$, $\mu = 0.098 \text{ mm}^{-1}$. 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.

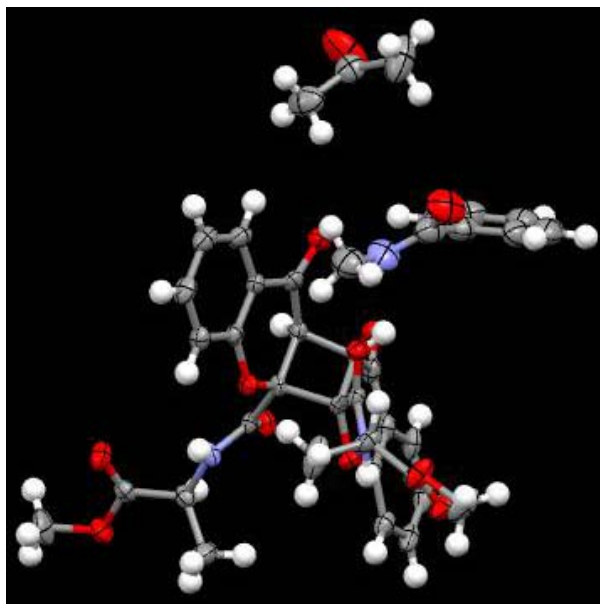
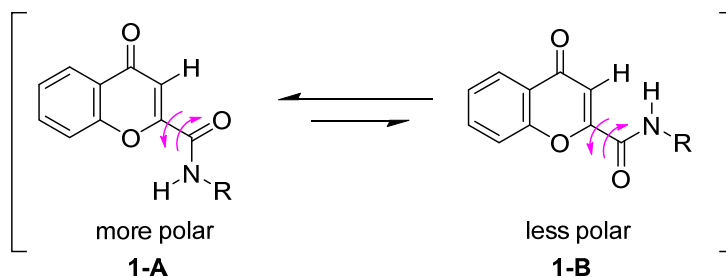


Figure S7. Perspective view of **2'c**.

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**

comps	Ground state conformation	$\Delta H_B - \Delta H_A$ (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

^aDifferences 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. ^bDipole 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**

comps	Triplet excited state conformation	$\Delta H_B - \Delta H_A$ (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

^aDifferences 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. ^bDipole moment obtained from DFT (RB3LYP 6-31G) calculation in Gaussian 09W.

Figure S8. ¹H NMR spectrum of 1a

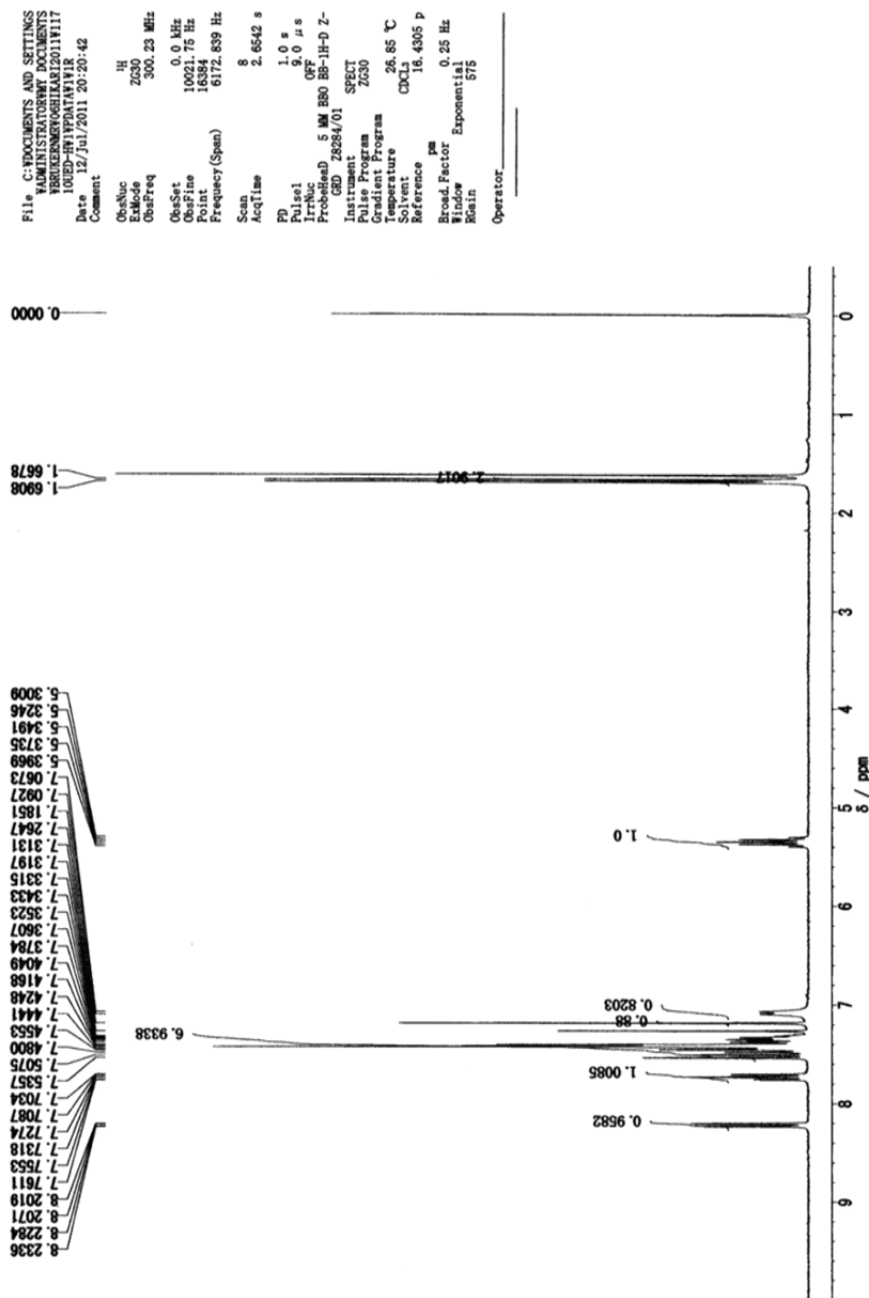


Figure S9. ^{13}C NMR spectrum of **1a**

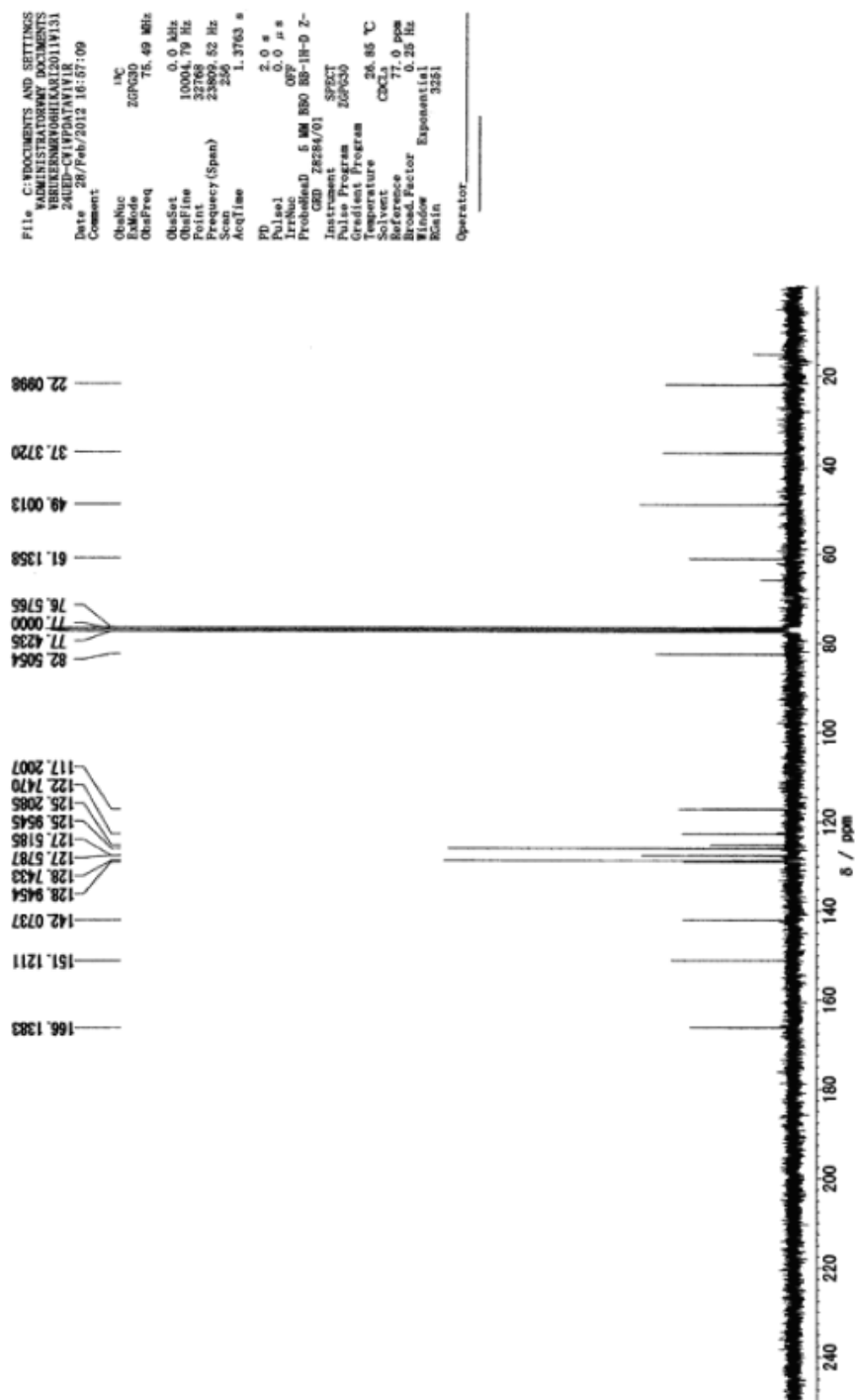


Figure S10. ¹H NMR spectrum of **1b**

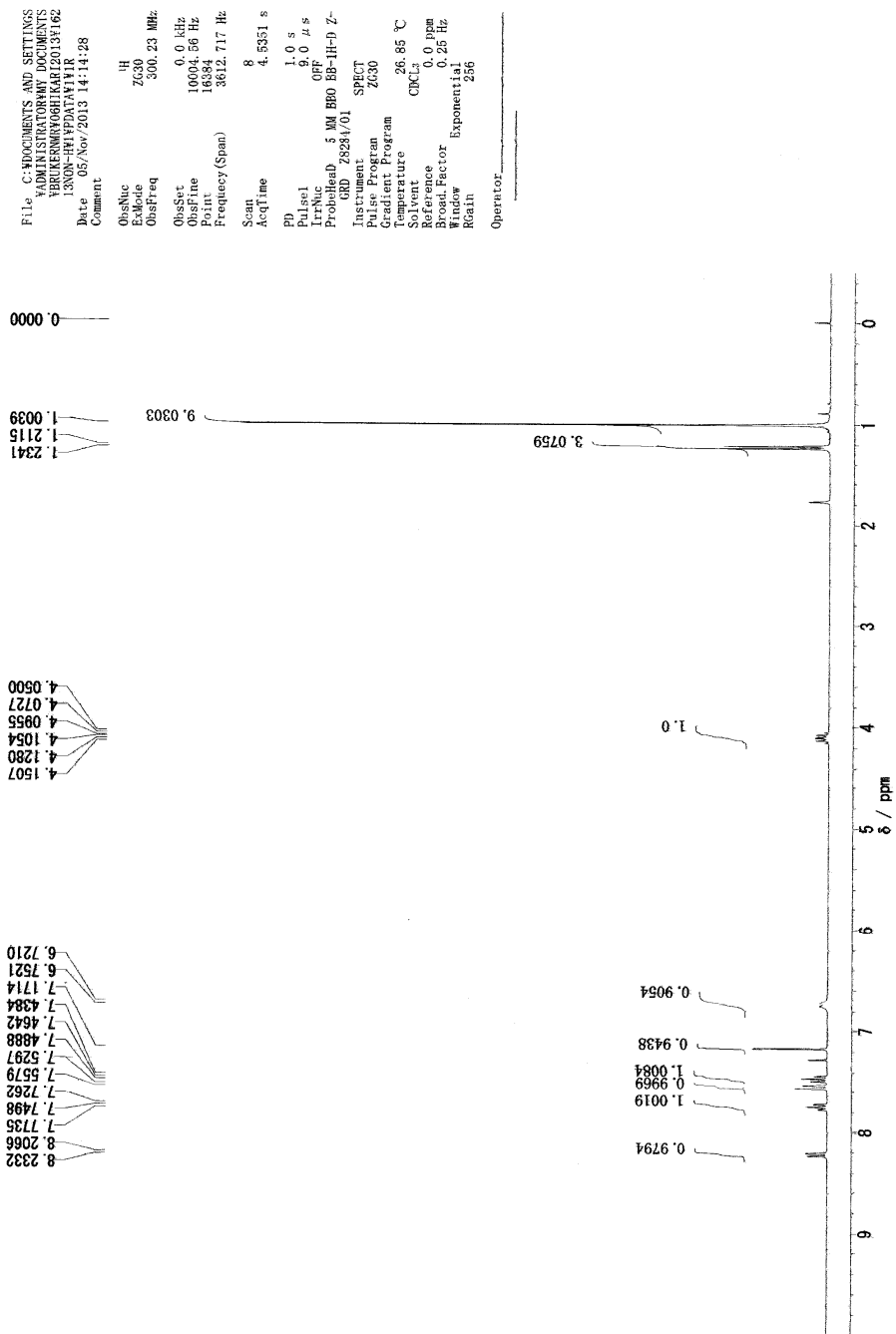


Figure S11. ¹³C NMR spectrum of 1b

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 ObsFreq: 75.49 MHz
 ObsSft: 0.0 kHz
 ObsFLine: 10003.05 Hz
 Point: 32769
 Frequency (Span): 18115.94 Hz
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 PD: 2.0 s
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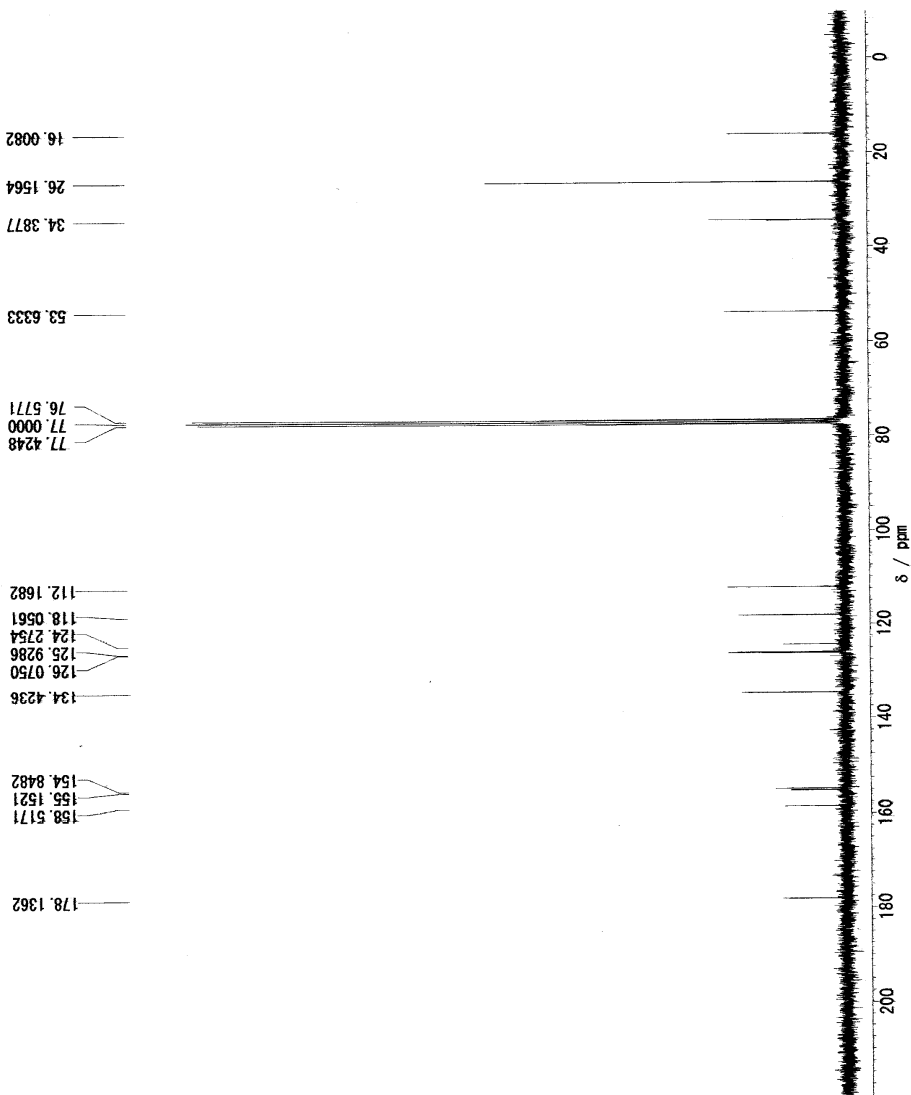


Figure S12. ¹H NMR spectrum of **1c**

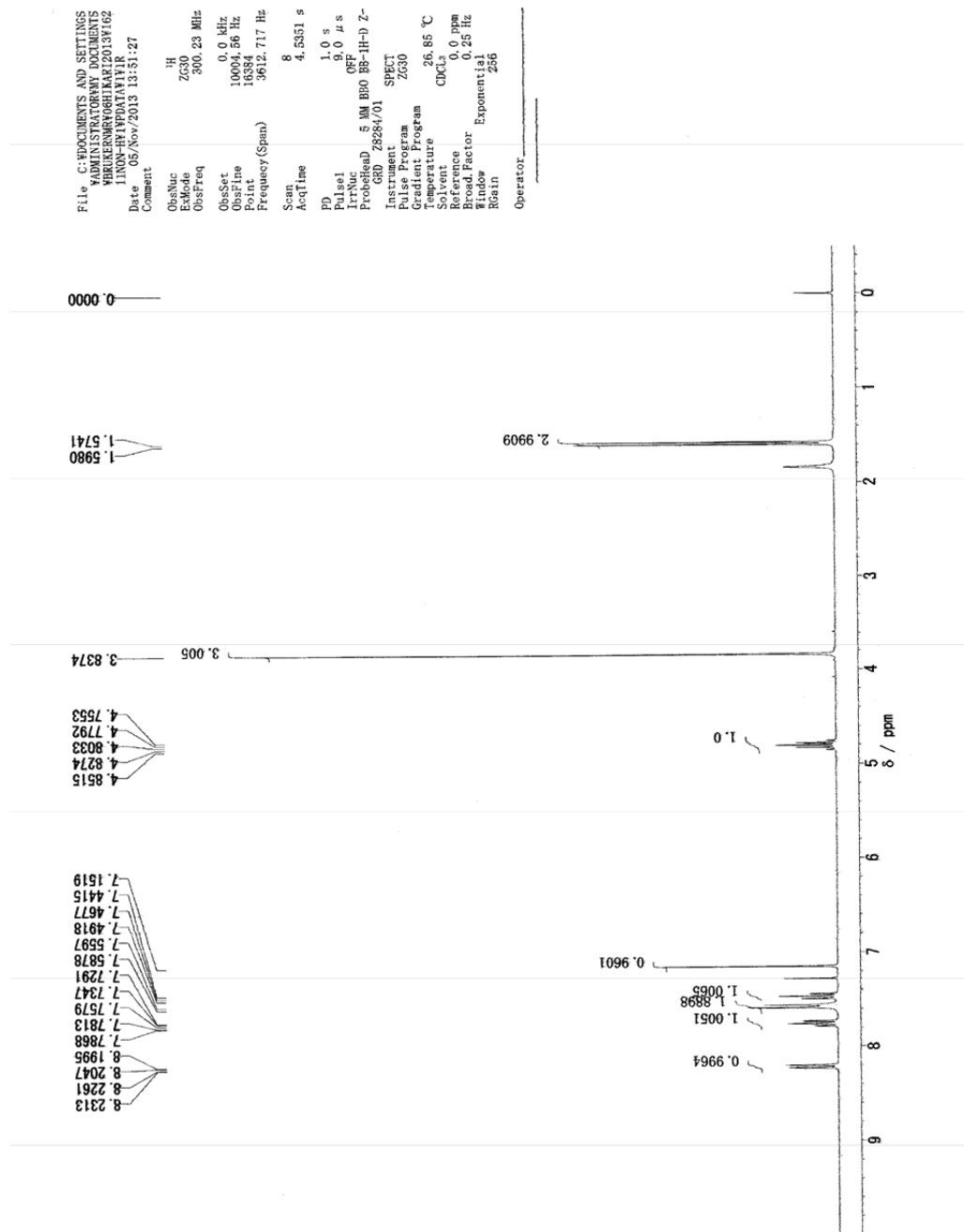


Figure S13. ¹³C NMR spectrum of 1c

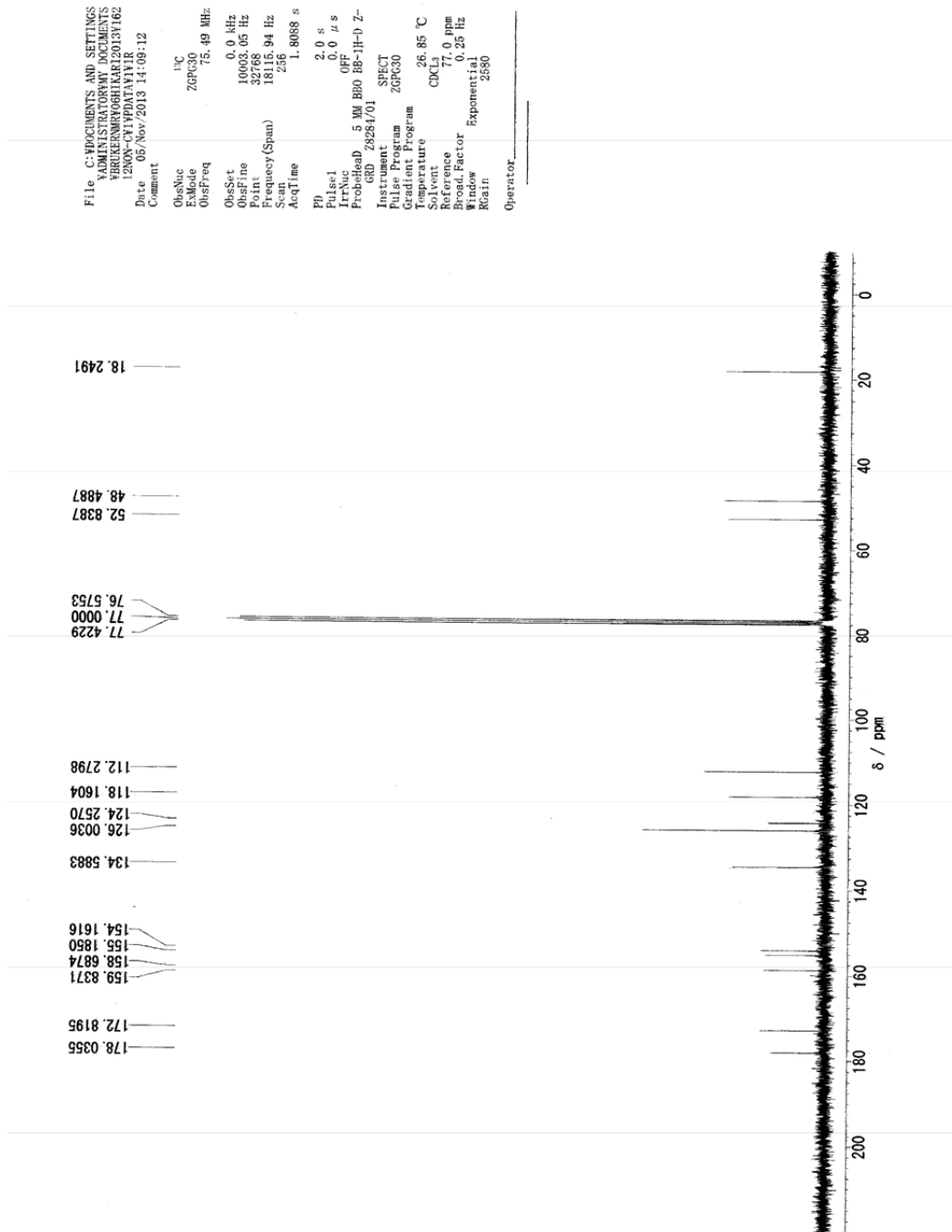


Figure S14. ¹H NMR spectrum of 2a

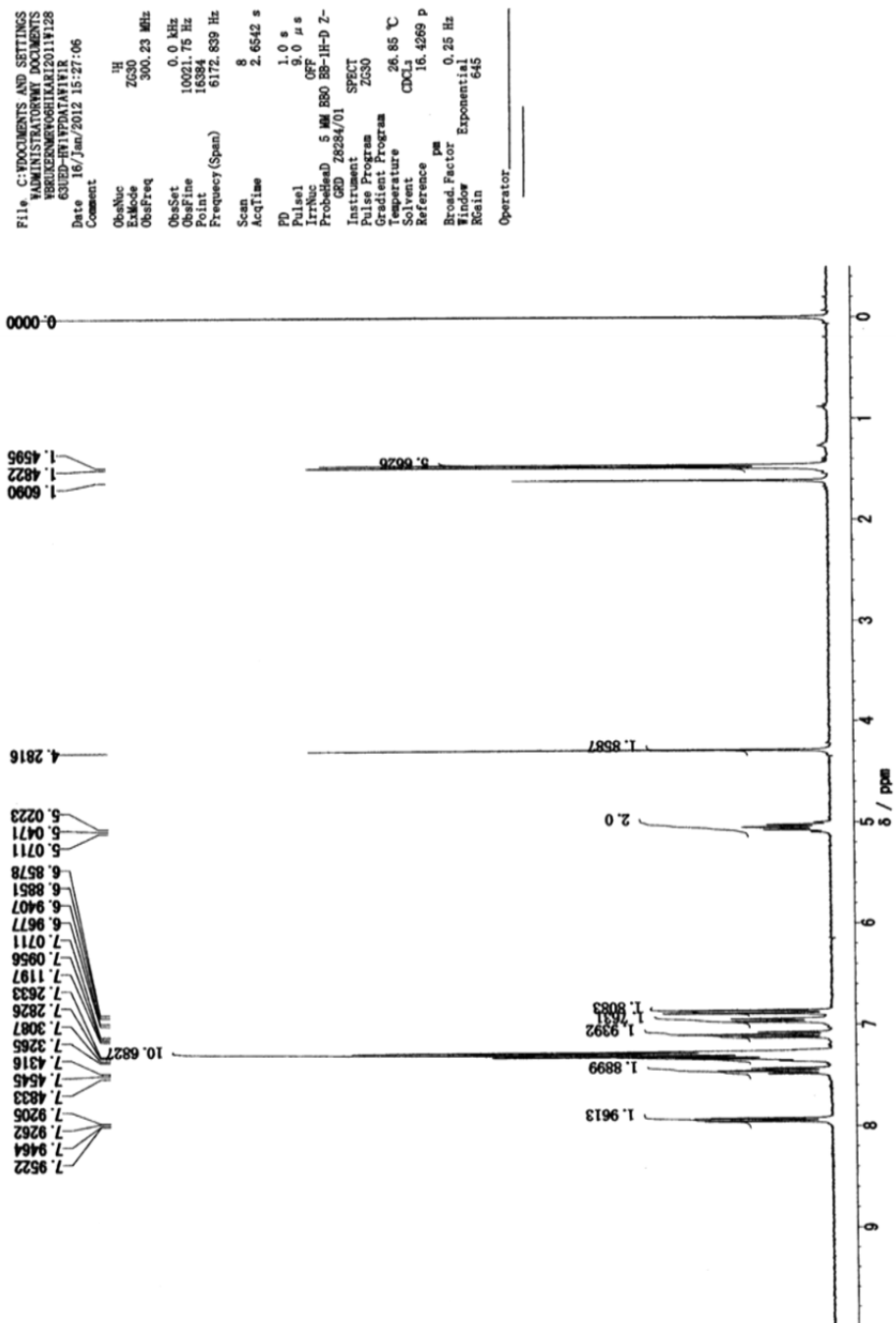


Figure S15. ¹³C NMR spectrum of 2a

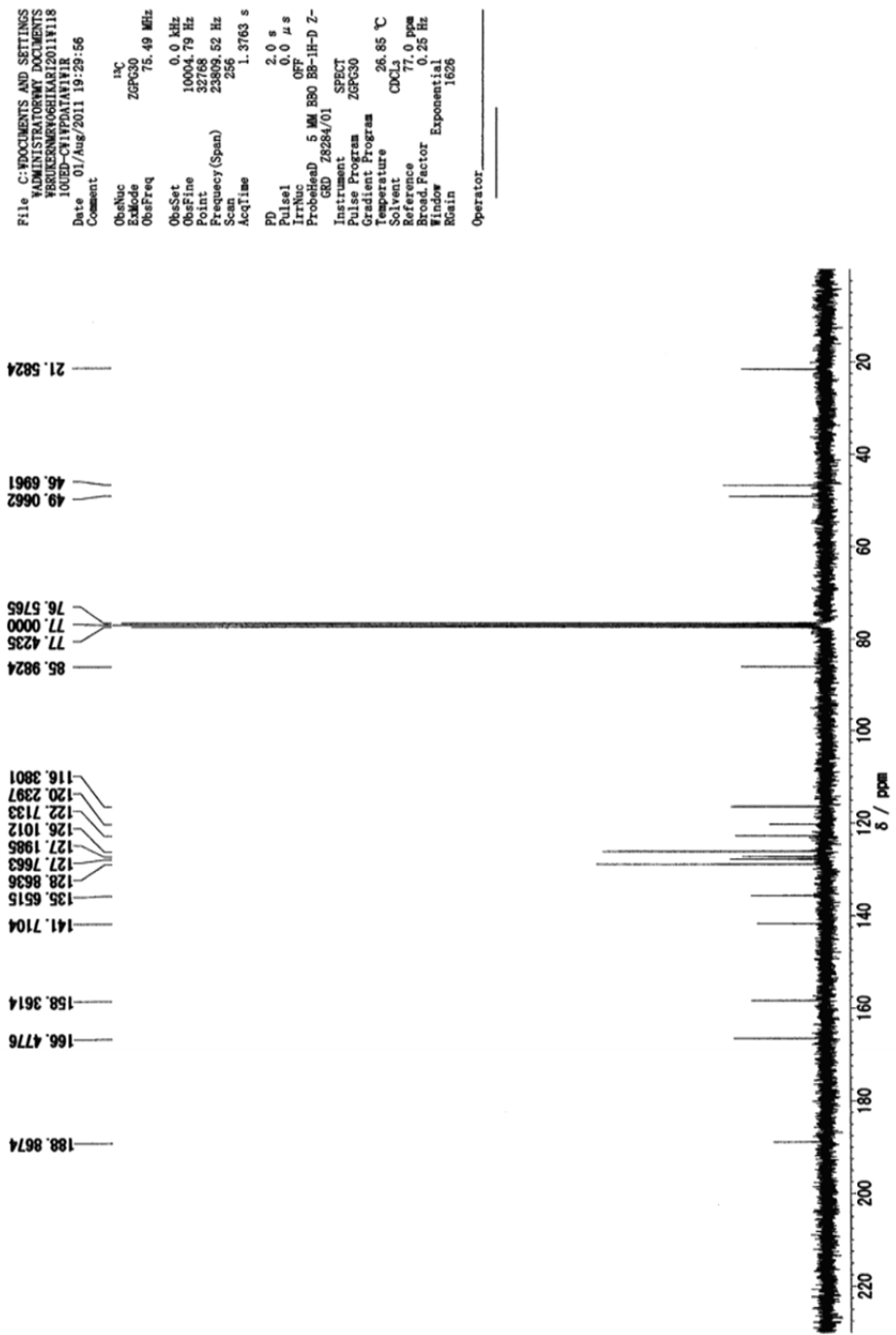


Figure S16. anti-HH dimer 2'a

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 ObsFine 10004.56 Hz
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PP
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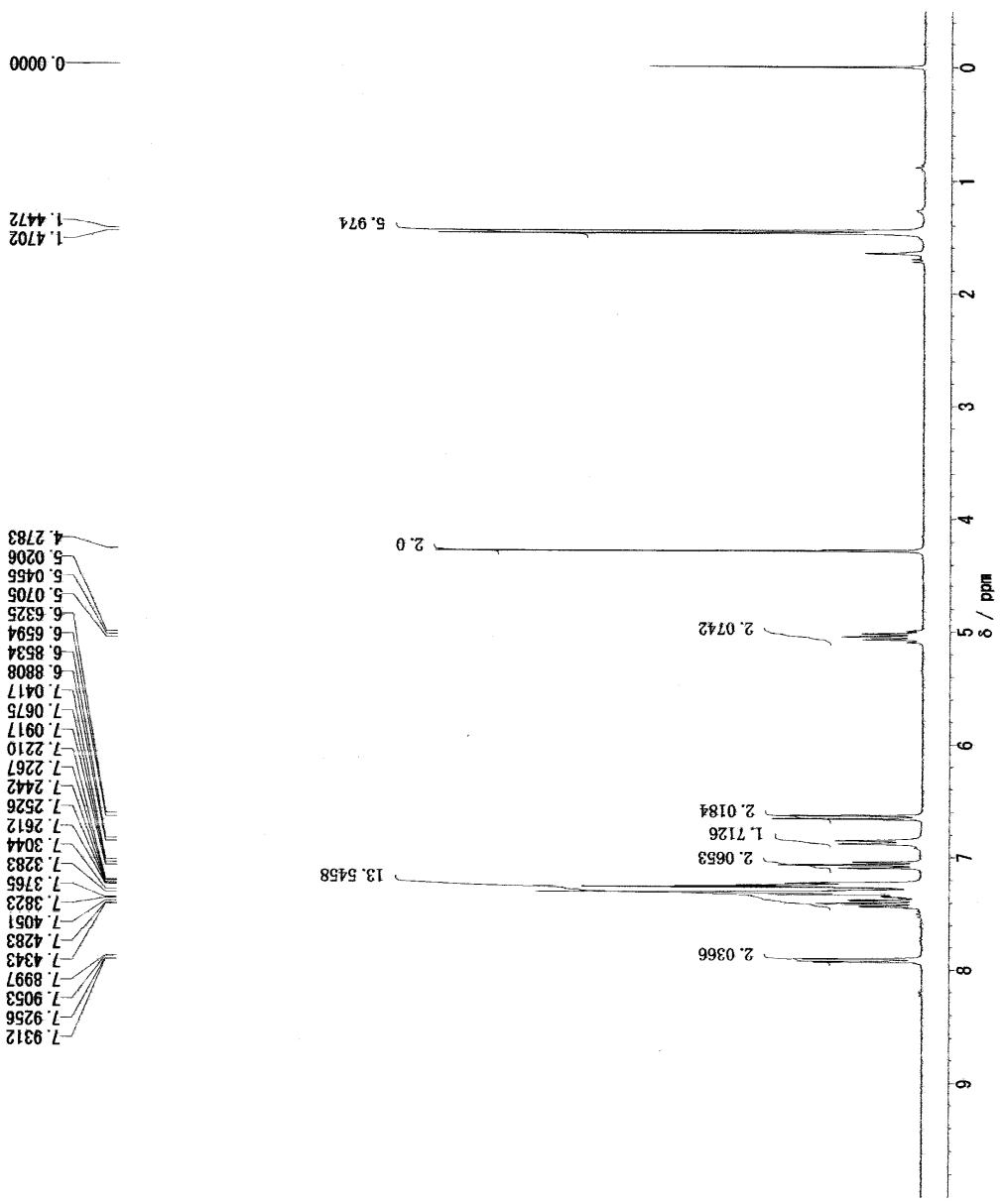


Figure S17. anti-HH dimer 2'a

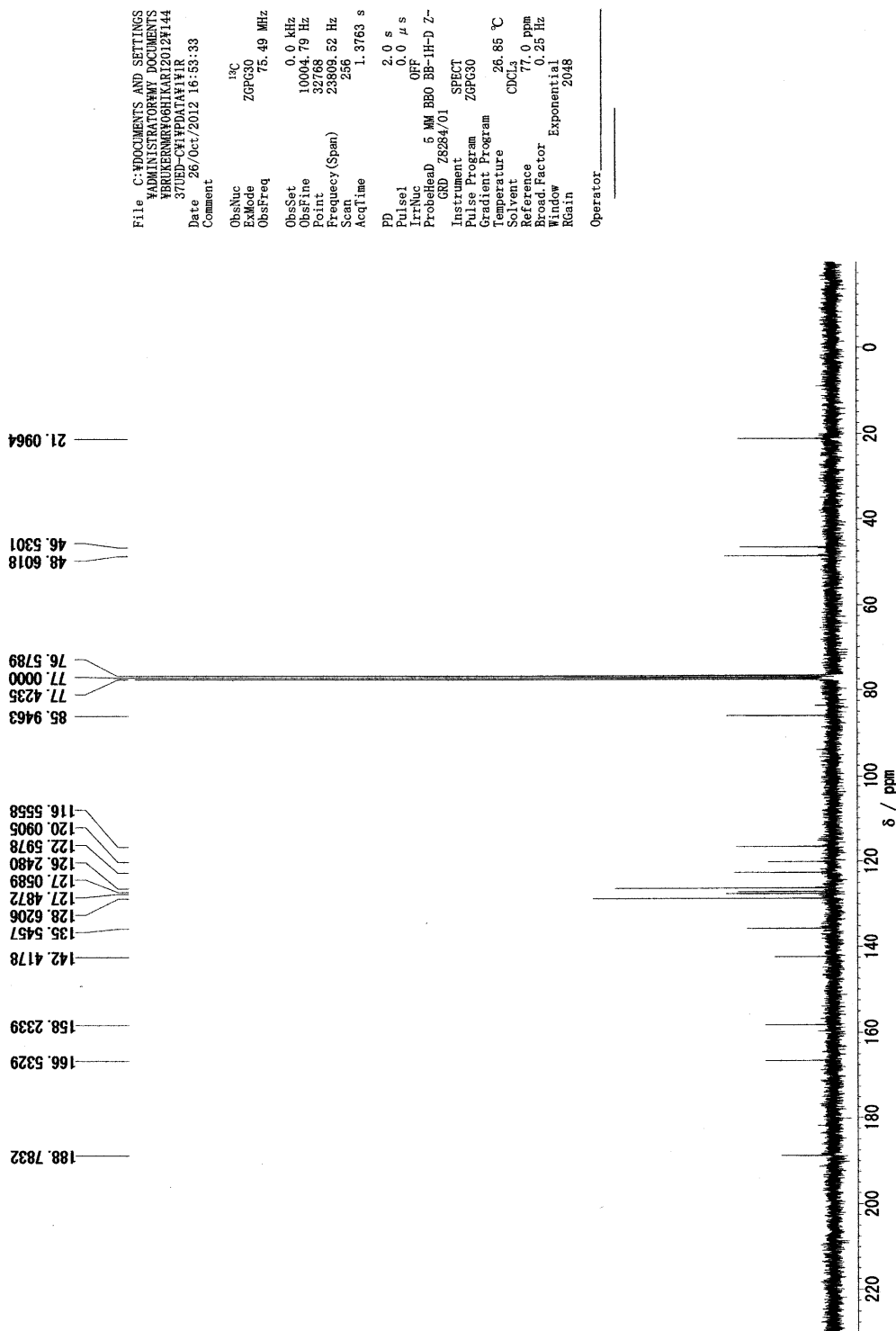


Figure S18. ¹H NMR spectrum of 2b

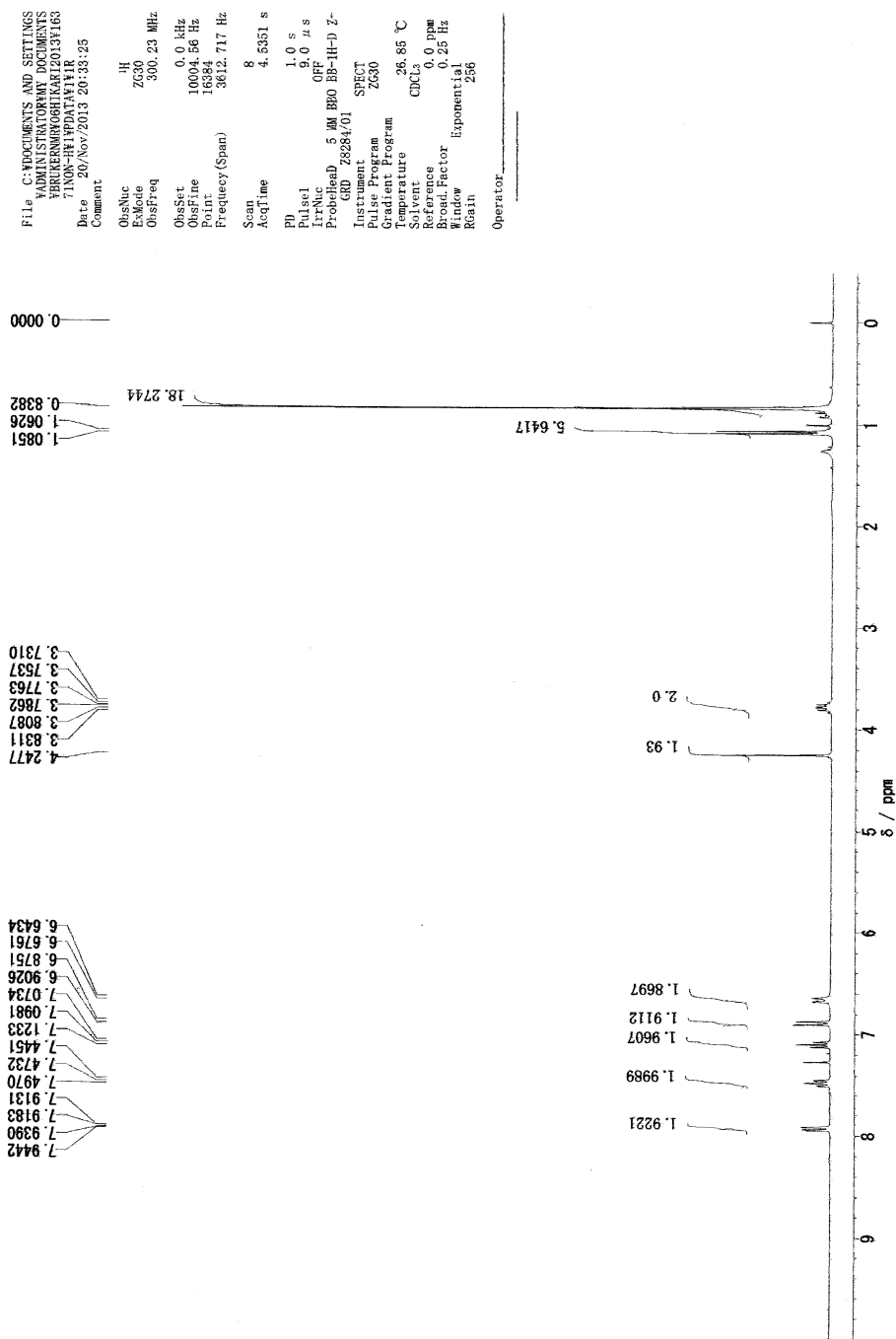


Figure S19. ¹³C NMR spectrum of 2b

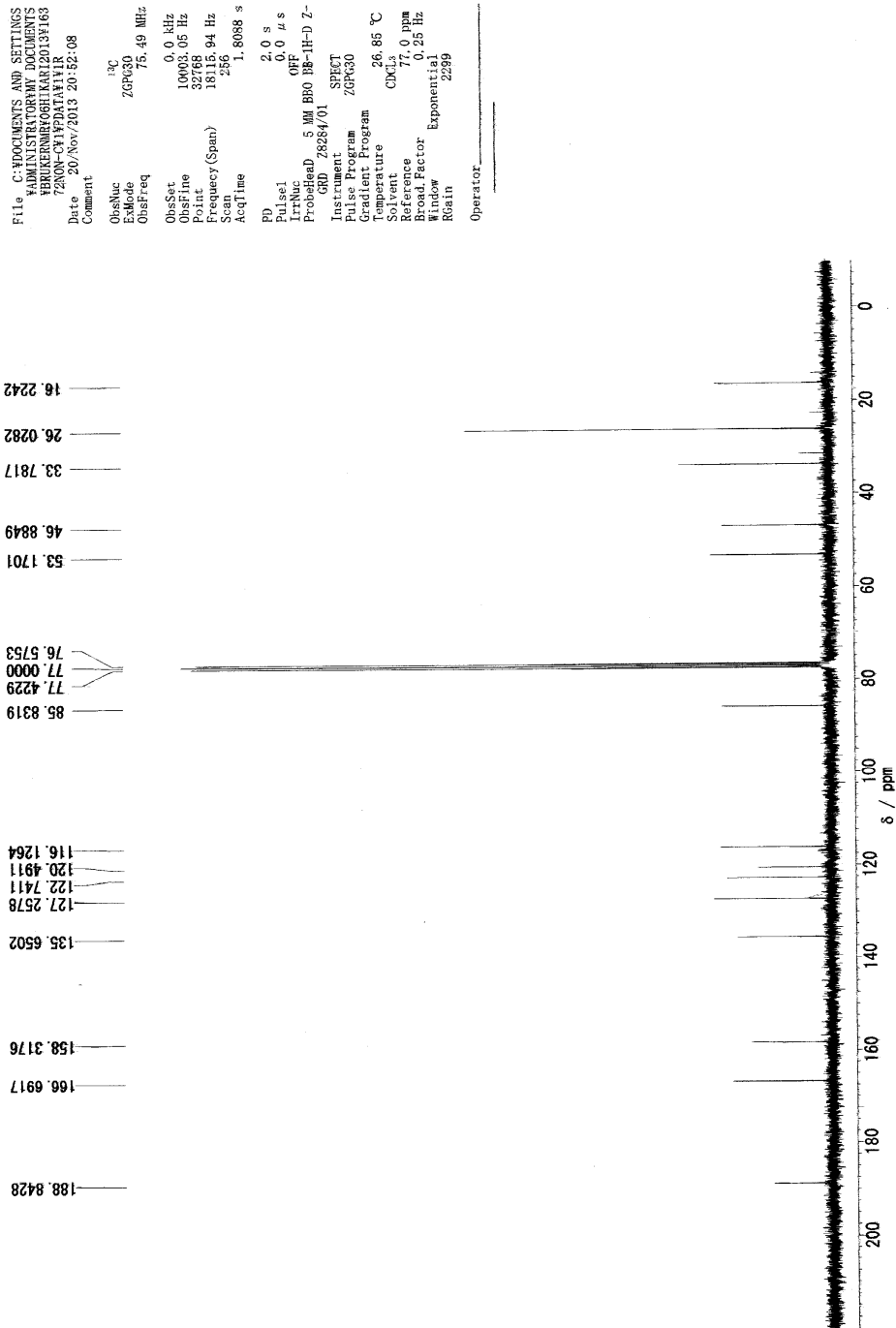


Figure S20. ¹H NMR spectrum of 2'b

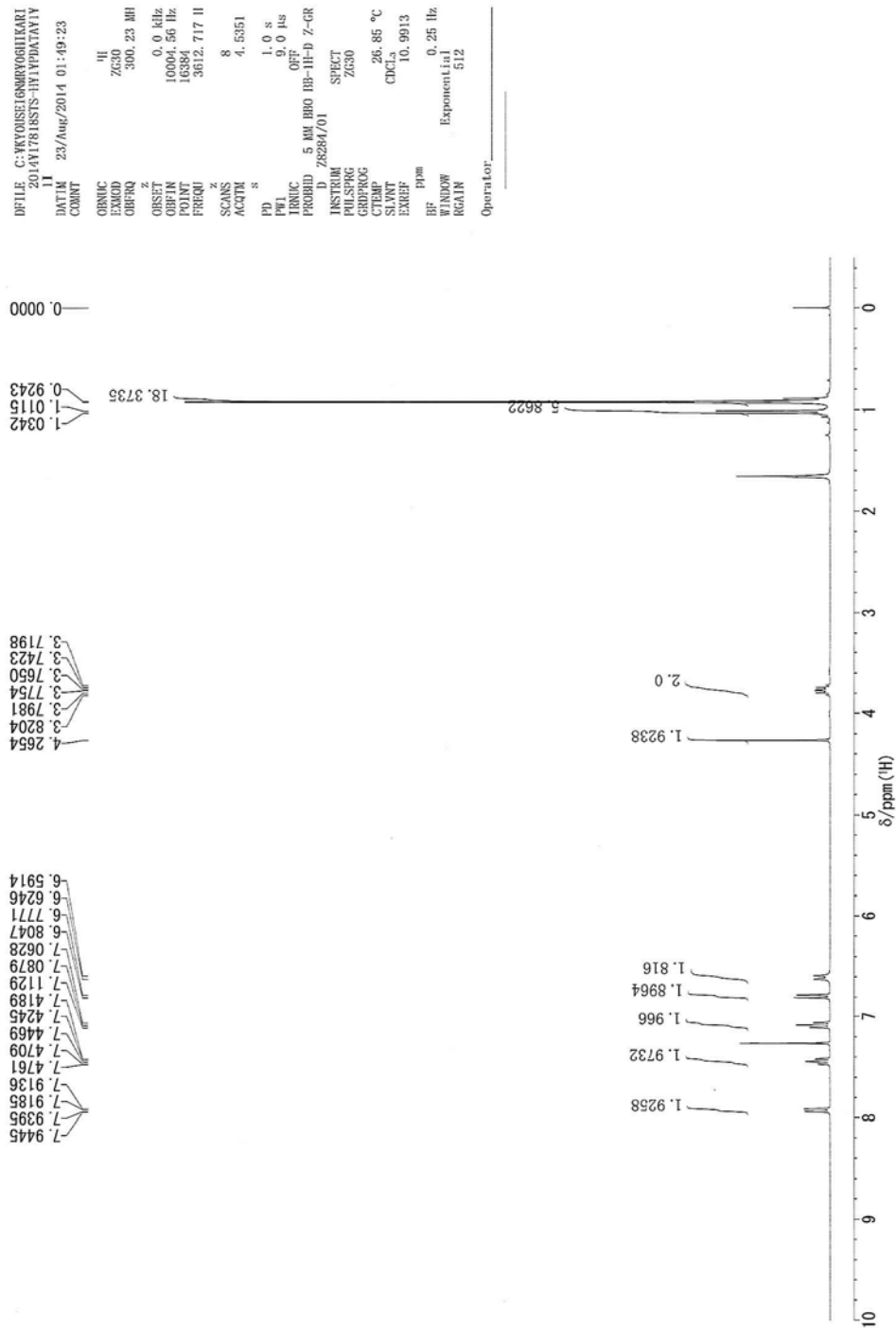


Figure S21. ¹³C NMR spectrum of 2'b

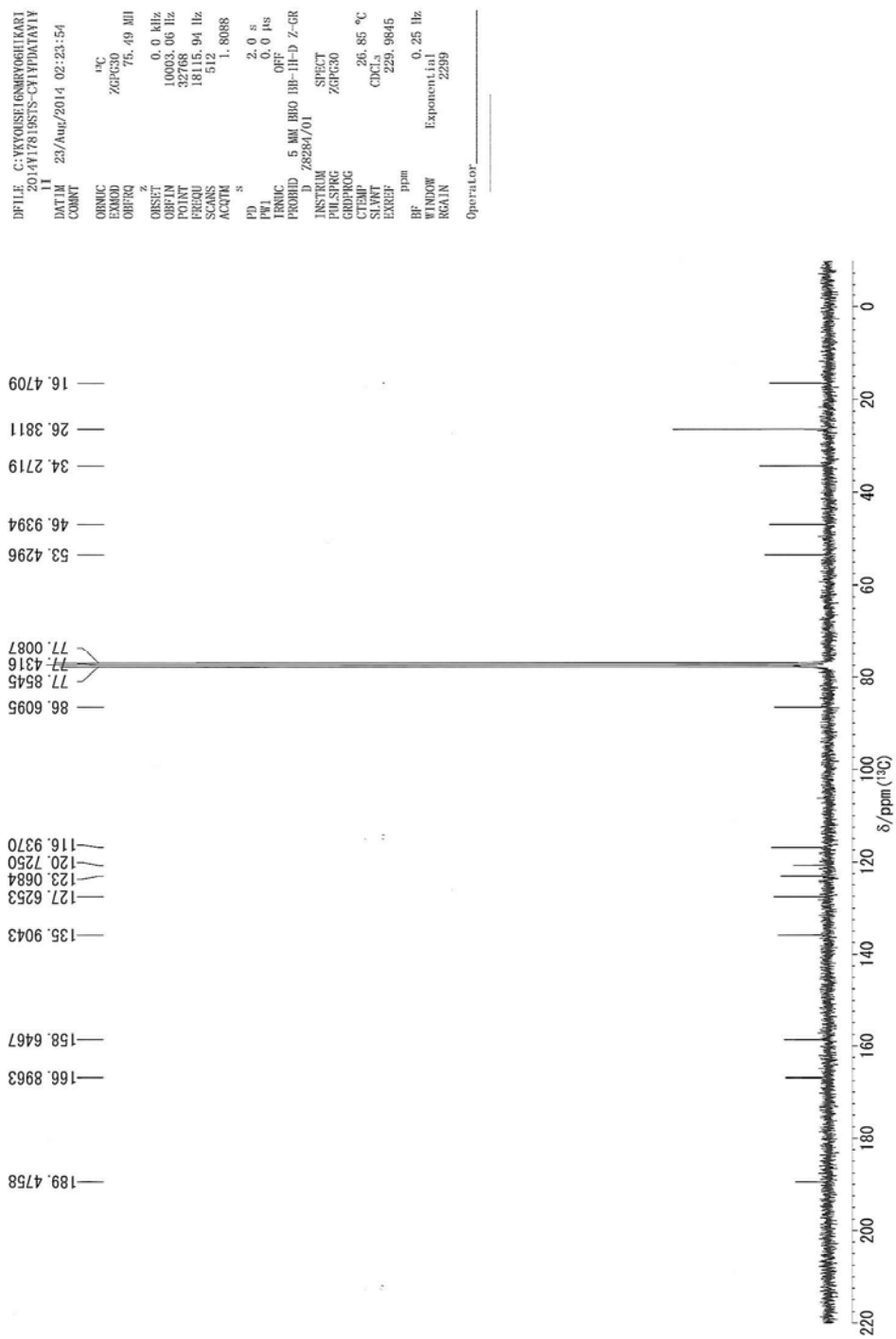


Figure S22. ¹H NMR spectrum of 2c

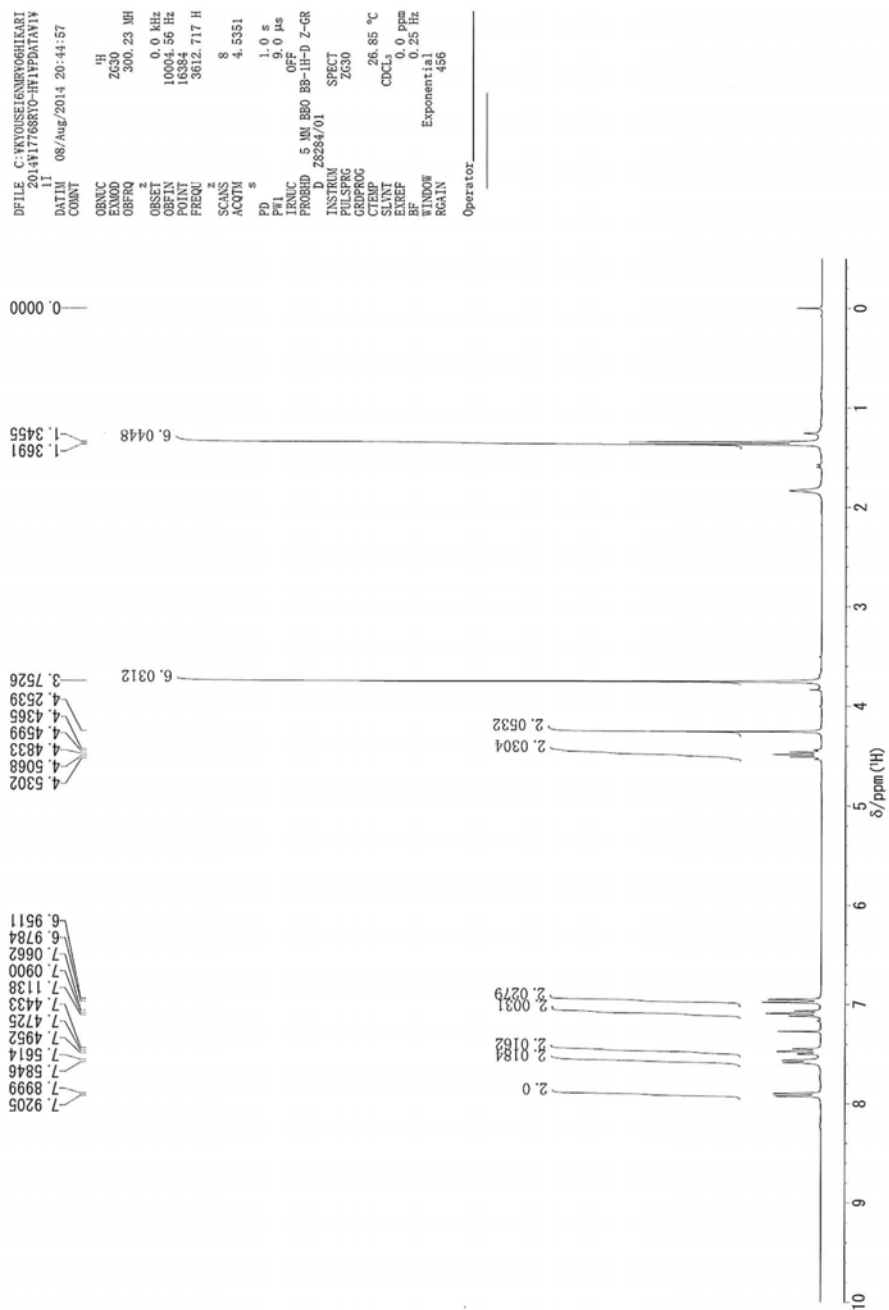


Figure S23. ¹³C NMR spectrum of 2c

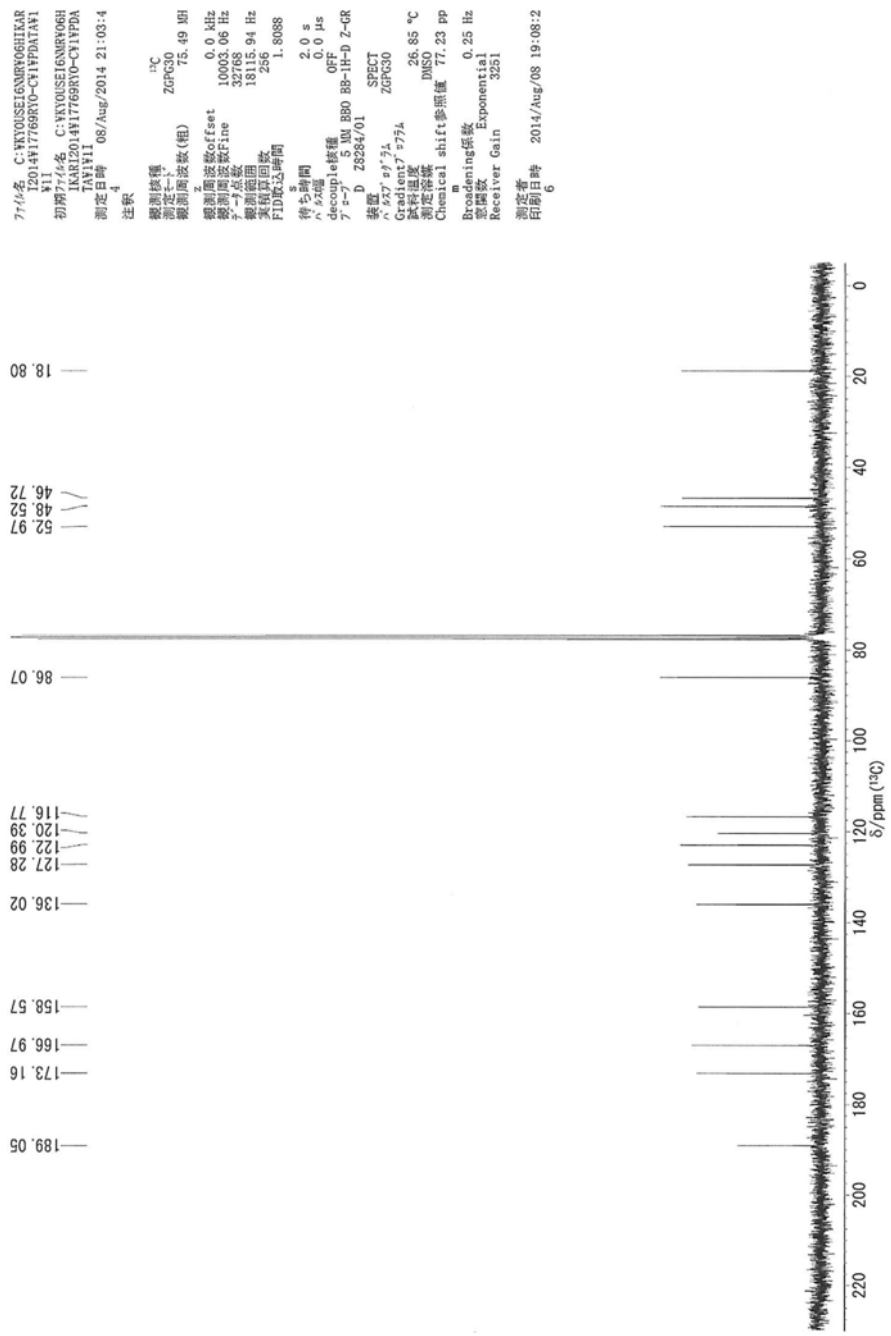


Figure S24. ¹H NMR spectrum of 2'c

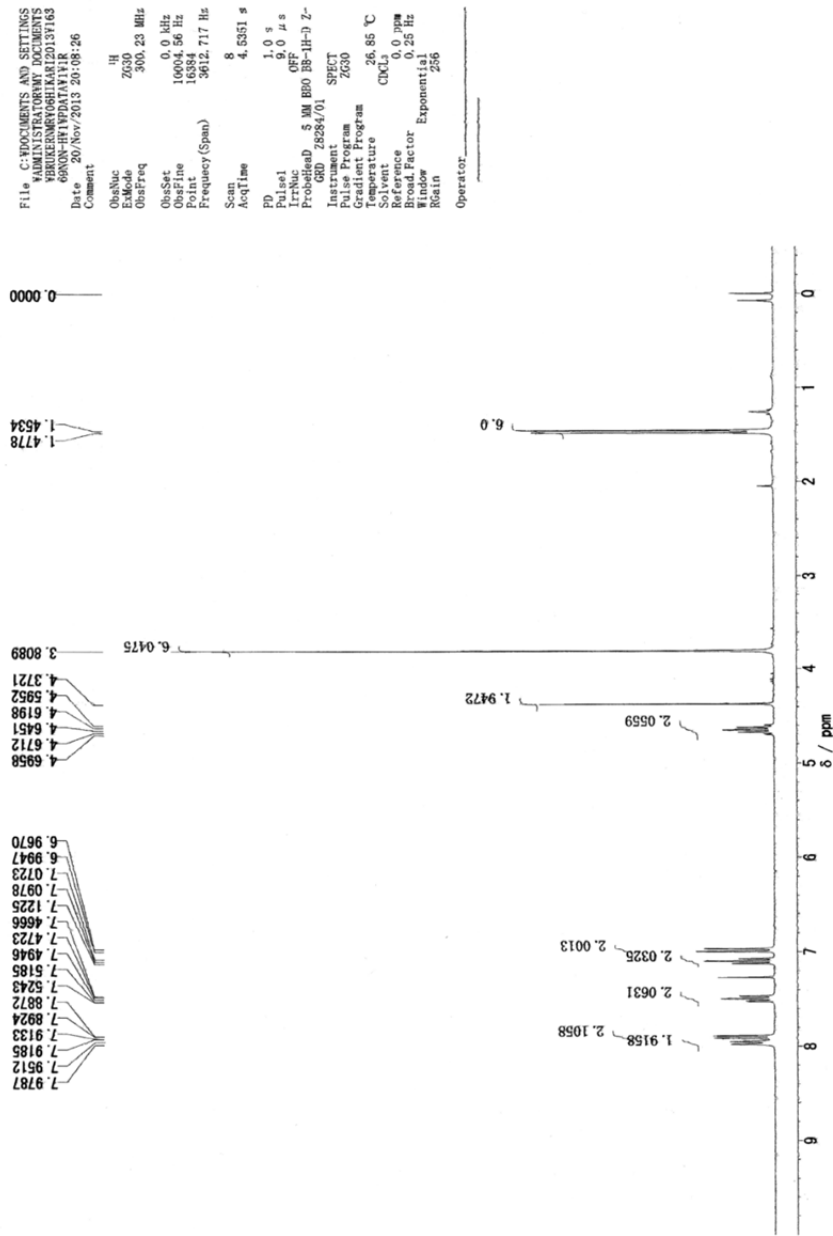


Figure S25. ^{13}C NMR spectrum of **2**'c

