Supplementary Materials

Experimental Procedure:

C_{60} was obtained via standard methods.[1] A solution of C60 (72 mg, 0.1 mmol) and digermirane **1** (69 mg, 0.1 mmol) in toluene (30 ml) was placed in a pyrex tube. After degassed by four freeze-pump-thaw cycles under reduced pressure, the reaction mixture was irradiated with a 400W high-pressure mercury lamp for 1.5 hr. Separation by preparative HPLC (Japan Analytical Industry LC-08) using toluene as eluent afforded **2** (86mg, 61%). **2**: FAB MS, m/z 1416-1412 (**2**), 723 - 720 (C_{60}); The ^1H and ^{13}C NMR spectra of **2** were acquired in the binary solvent system (CS_2/CD_2Cl_2=3:1) by Bruker DRX750, DRX500 and AC300. The variable-temperature ^1H NMR measurement was carried out in the binary solvent system (CS_2/*p*-$(CD_3)_2C_6D_4$=1:10). All proton peaks are referenced to the peak of tetramethylsilane as internal standard. Chemical shifts of ^{13}C NMR were expressed downfield of the signal for the carbon atom in CS2 as an internal standard (δ=195.0).

2: ^1H NMR (300 MHz, CS_2/CD_2Cl_2) δ 6.87-7.38(m, 12H), 4.13(dq, J=7.4, 15.2 Hz, 1H), 3.86(dq, J=7.4, 15.2 Hz, 1H), 3.45(dq, J=7.2, 14.5 Hz, 1H), 3.33(dq, J=7.6, 14.8 Hz, 1H), 3.26(dq, J=7.0, 15.1 Hz, 1H), 3.12(dq, J=7.2, 14.3 Hz, 1H), 2.49-3.00(m, 10H), 2.60(d, J=14.3 Hz, 1H), 2.40(d, J=14.3 Hz, 1H), 1.54(t, J=7.4 Hz, 3H), 1.31(t, J=7.4 Hz, 3H), 0.87(t, J=7.5 Hz, 3H), 0.78(t, J=7.3 Hz, 3H), 0.77(t, J=7.4 Hz, 3H), 0.71(t, J=7.4 Hz, 3H), 0.54(t, J=7.3 Hz, 3H), 0.50(t, J=7.3 Hz, 3H); ^{13}C NMR (75 MHz, CS_2/CD_2Cl_2) δ 162.7, 161.9, 150.6, 150.2, 149.8, 149.7, 149.2, 148.7, 148.6, 148.5, 148.4, 148.0, 147.7, 147.6, 147.3, 147.2, 147.1, 146.6, 146.0, 145.6, 145.5, 145.3, 145.2, 145.1, 145.0, 144.8, 144.6, 144.5, 144.4, 144.2, 143.4, 143.3, 143.2, 142.7, 142.5, 142.3, 142.2, 142.1, 141.5, 141.1, 140.2, 139.8, 139.3, 139.1, 137.4, 135.9, 129.6, 129.4, 128.9, 128.2, 127.5, 127.3, 127.2, 126.6, 125.3, 124.4, 124.1, 66.2, 65.9, 32.4, 32.1, 31.8, 31.4, 29.9, 29.8, 29.5, 21.5, 19.4, 15.2, 14.9, 14.8, 14.0, 13.8, Some peaks were overlapped.

References

1. (a) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354. (b) Krätschmer, W.; Fostiropoulos, K.; Huffman, D. R. *Chem. Phys. Lett.* **1990**,

170, 167. (c) Parker, D. H.; Wurtz, P.; Chatterjee, K.; Lykke, K. R.; Hunt, J. E.; Pellin, M. J.; Hemminger, J. C.; Gruen, D. M.; Stock, L. M. *J. Am. Chem. Soc.* **1991**, *113*, 7499.

Supplemental Figures

UV-VIS spectra of C60 (---), **1**(···), and **2** (__) from 190 to 820 nm in hexane and time dependent spectral changes of a toluene solution of C_{60} and **1** upon irradiation.

FTIR spectrum of **2**.

^{1}H, ^{13}C DEPT, HH COSY, HC COSY, and 187.5 MHz INADEQUATE NMR spectra of **2**.

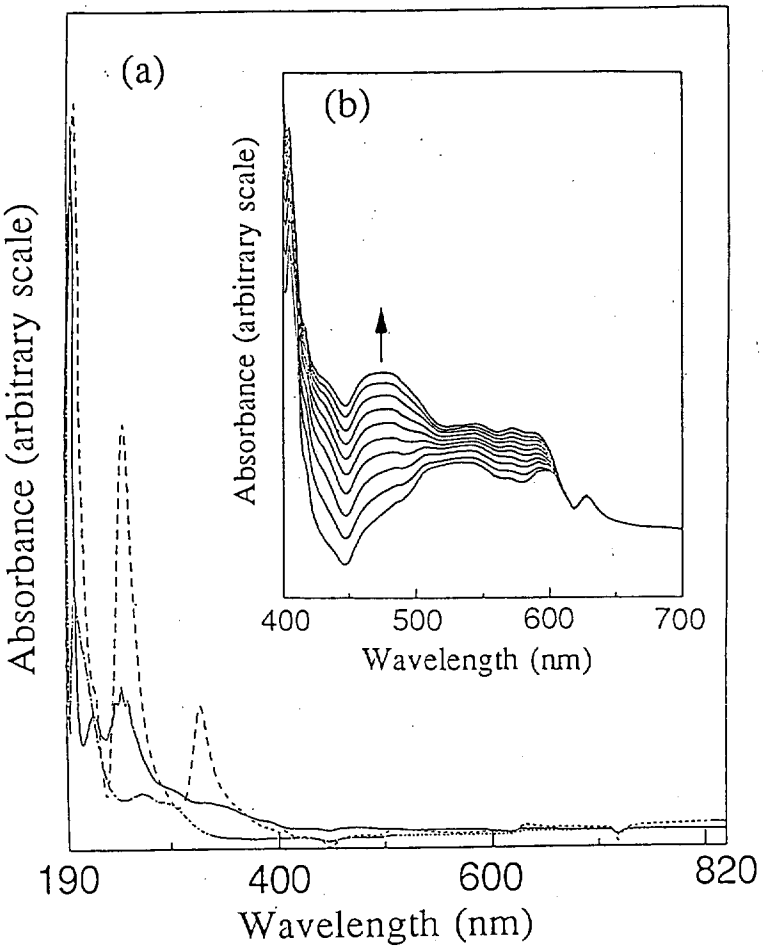
CV and DPV voltammograms of **2**.

The optimized structures of the Cs-form and twist-form of **2a** and the 5-membered and 6-membered bent-form of **2b** calculated with the AM1 method.

The transient absorption spectra obtained by laser flash photolysis of C_{60} with digermirane.

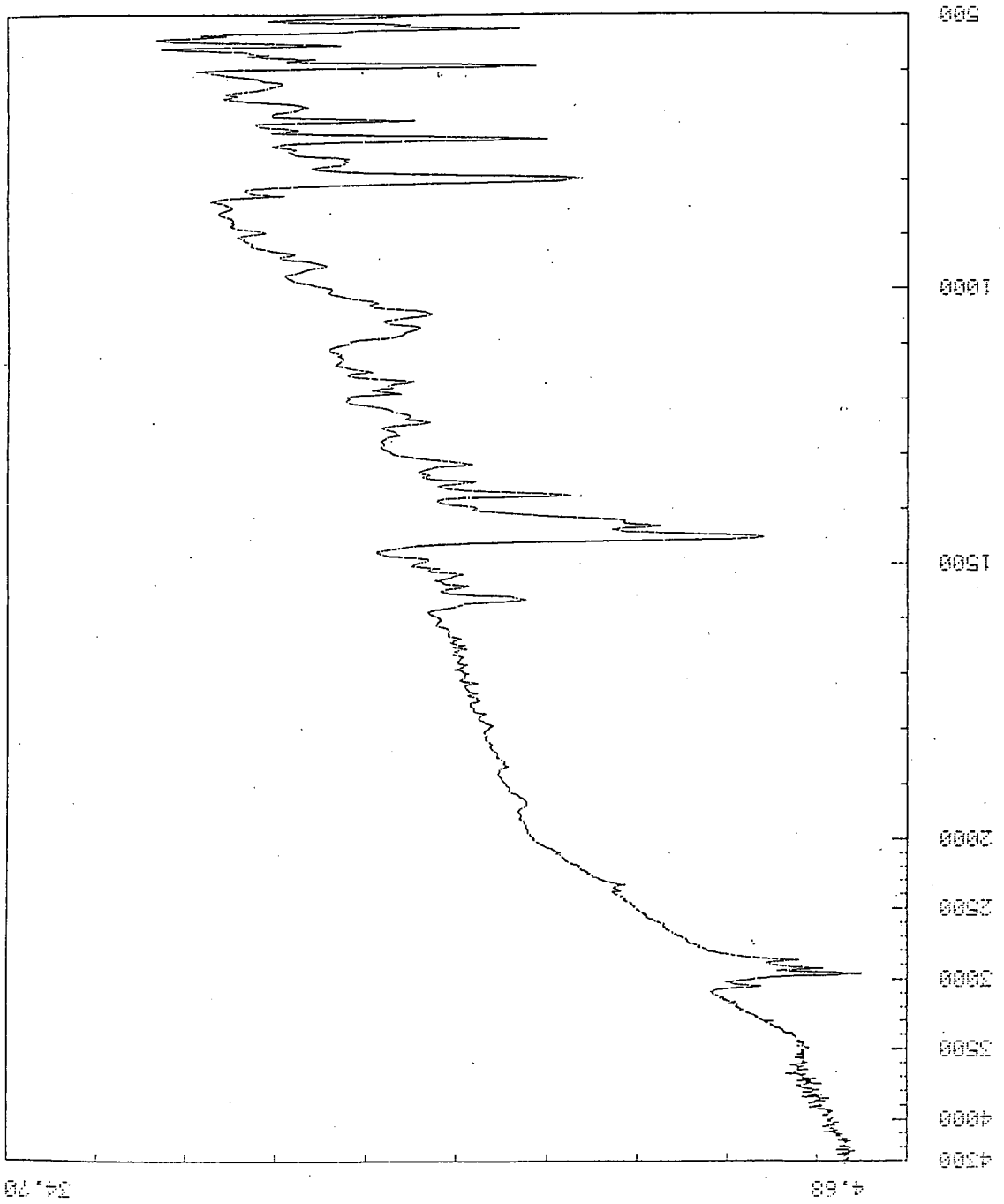
Supplemental Fig. 1 / T. Akasaka

UV-VIS spectra of C_{60}(---), **1**(...), and **2**(—) from 190 to 820 nm in hexane and time dependent spectral changes of a toluene solution of C_{60} and **1** upon irradiation



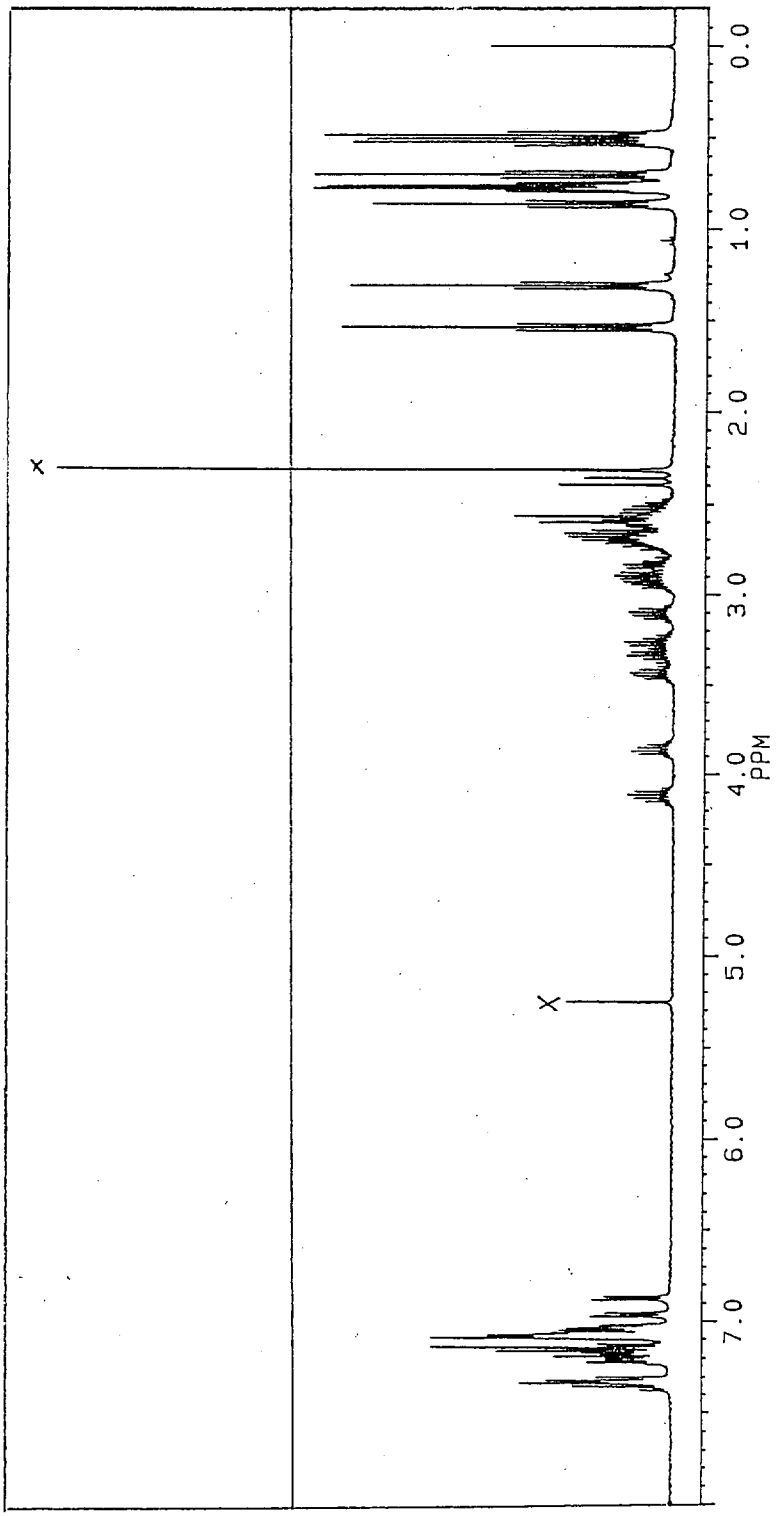
Supplemental Fig. 2 / T. Akasaka

FTIR spectrum of **2**

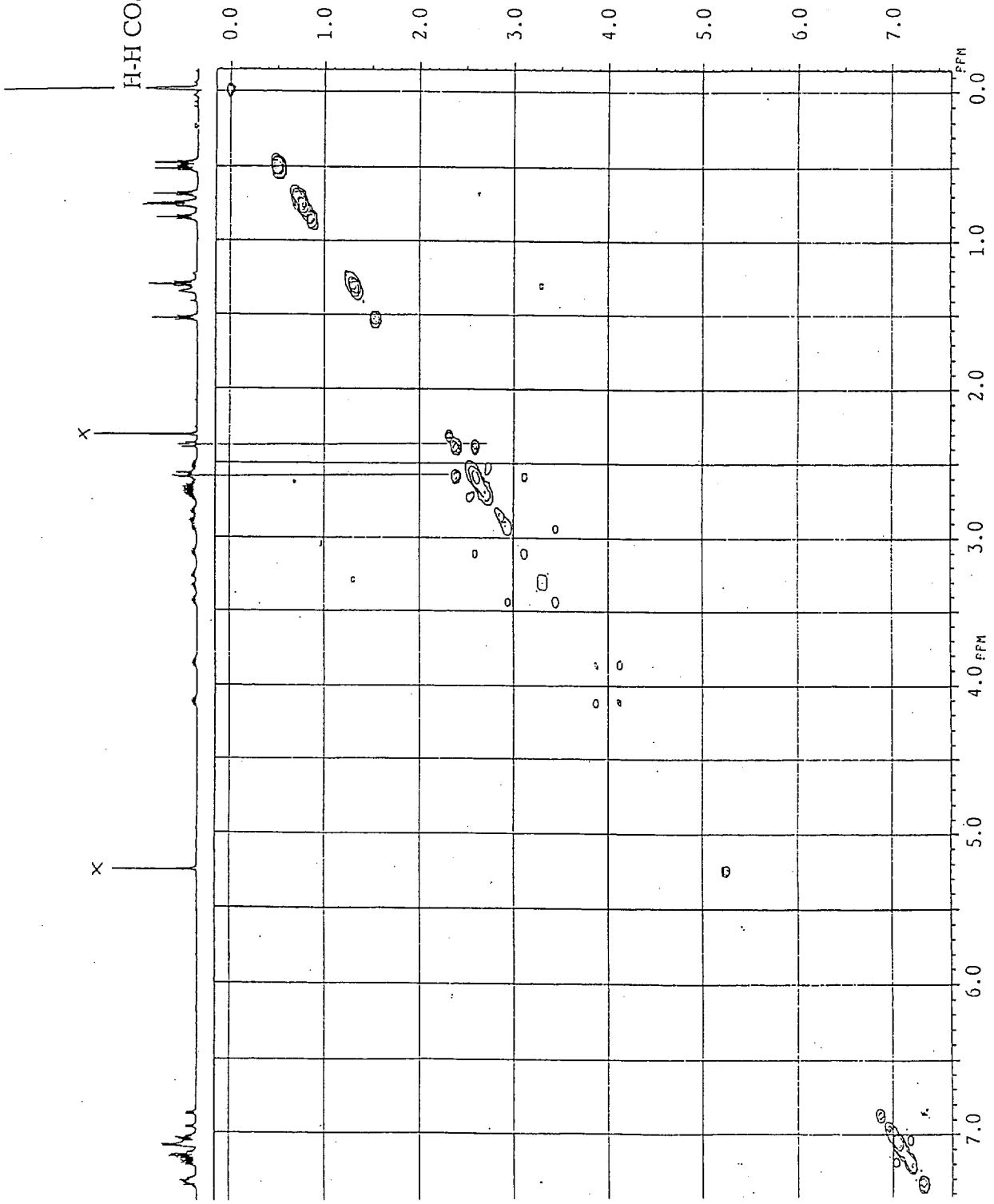


Supplemental Fig. 3 / T. Akasaka

^{1}H NMR spectrum of 2.



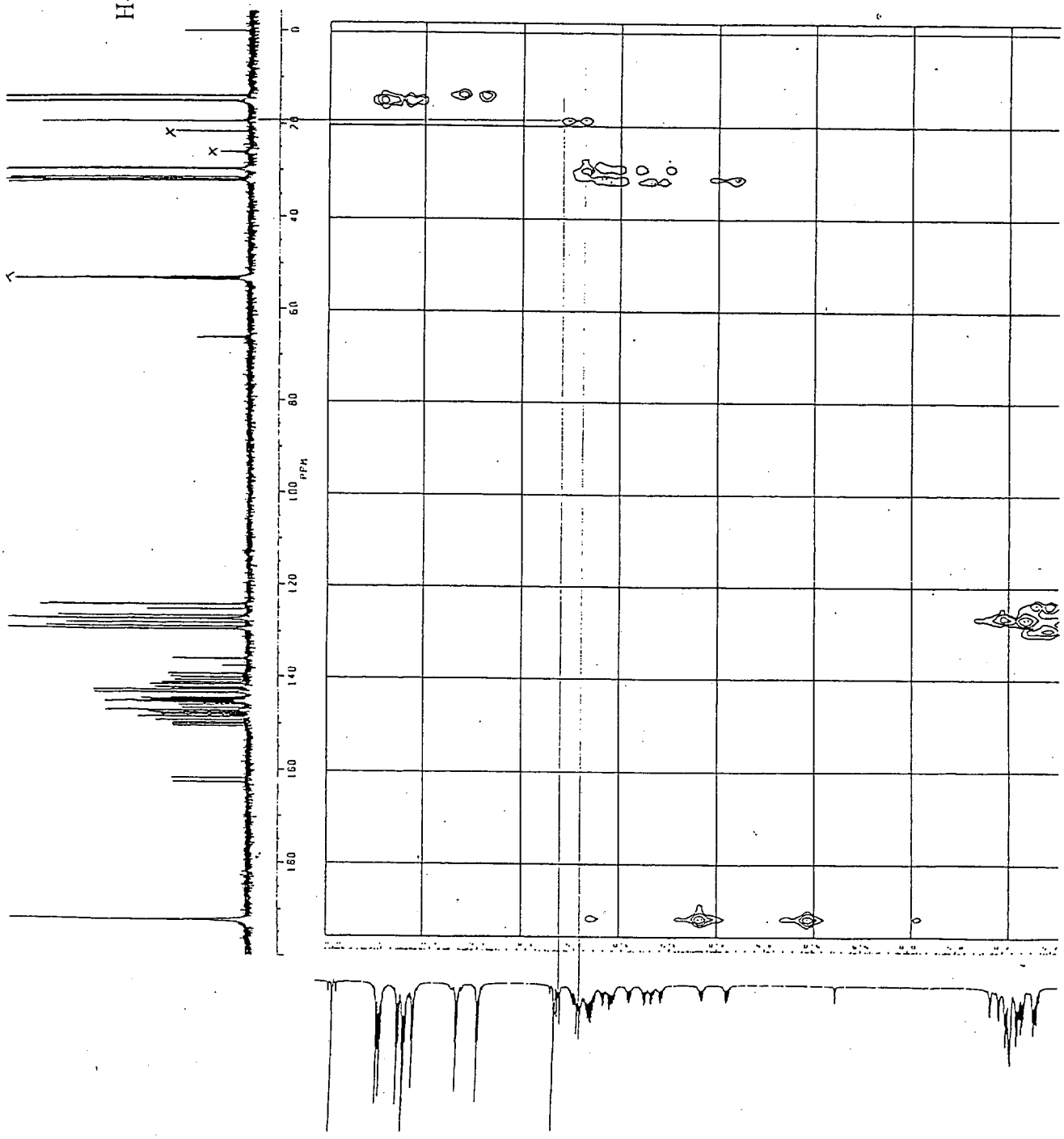
Supplemental Fig. 5 / T. Akasaka



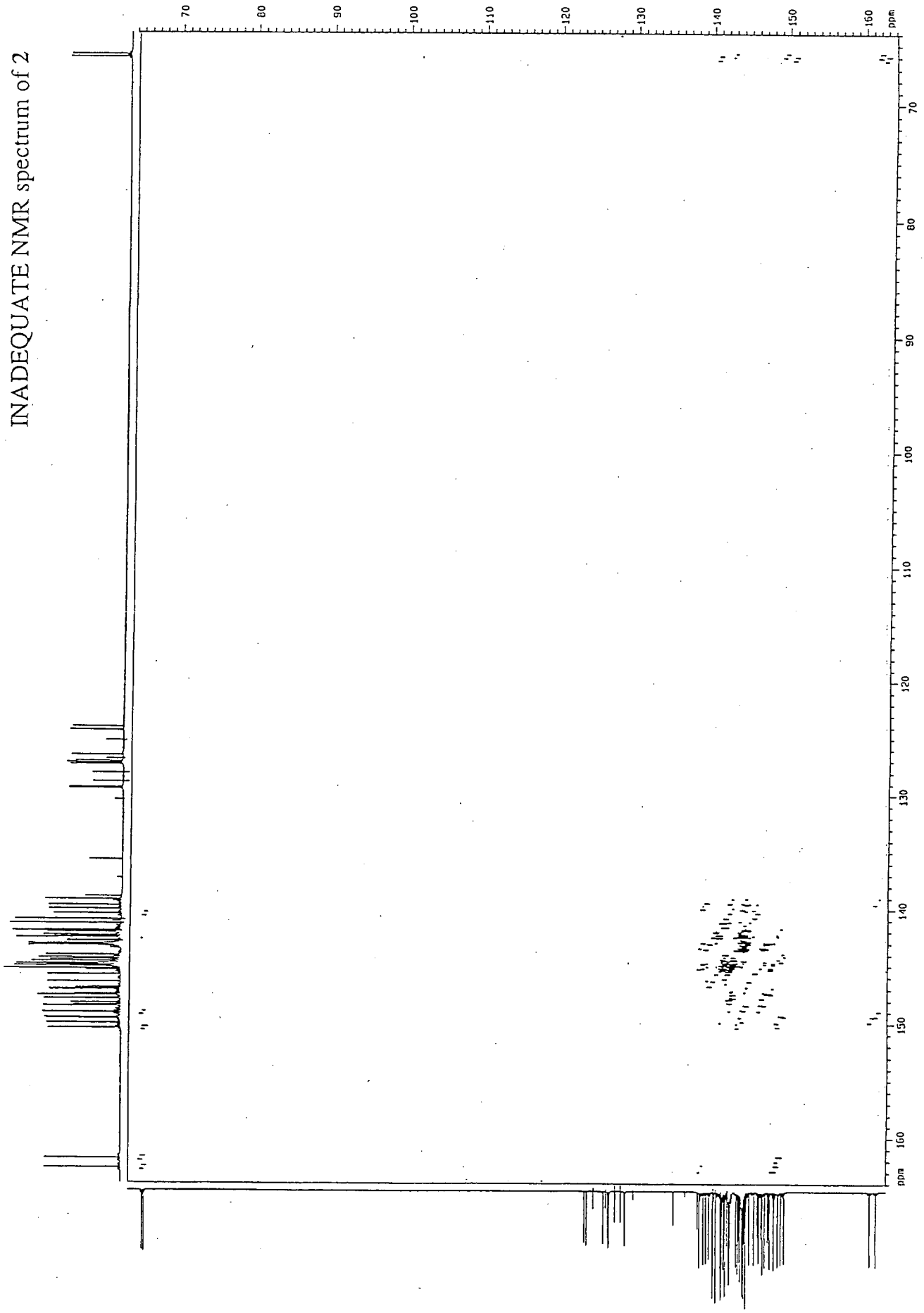
Supplemental Fig. 6 / T. Akasaka

T. Akasaka

H-C COSY NMR spectrum of 2.



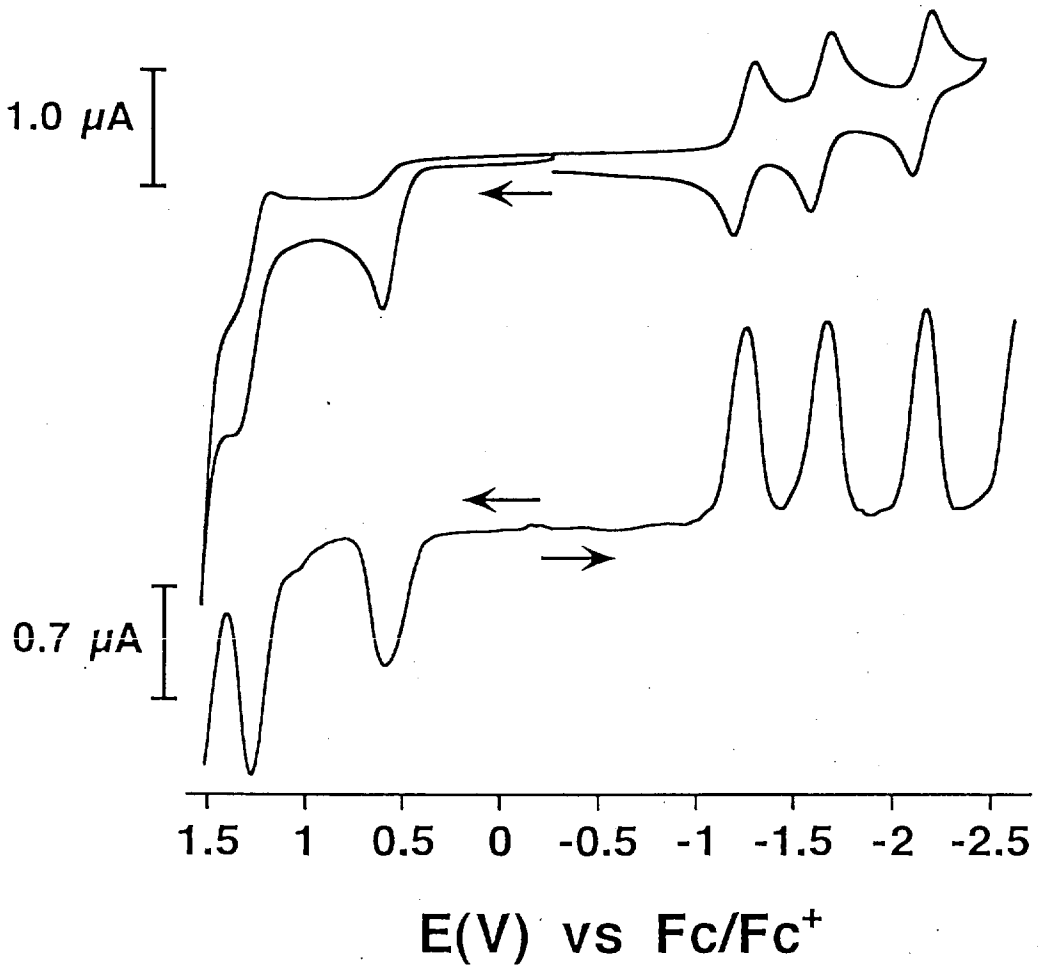
INADEQUATE NMR spectrum of 2



Supplemental Fig. 7 / T. Akasaka

Supplemental Fig. 8 / T. Akasaka

CV and DPV voltammograms of 2



Supplemental Fig. 9 / T. Akasaka

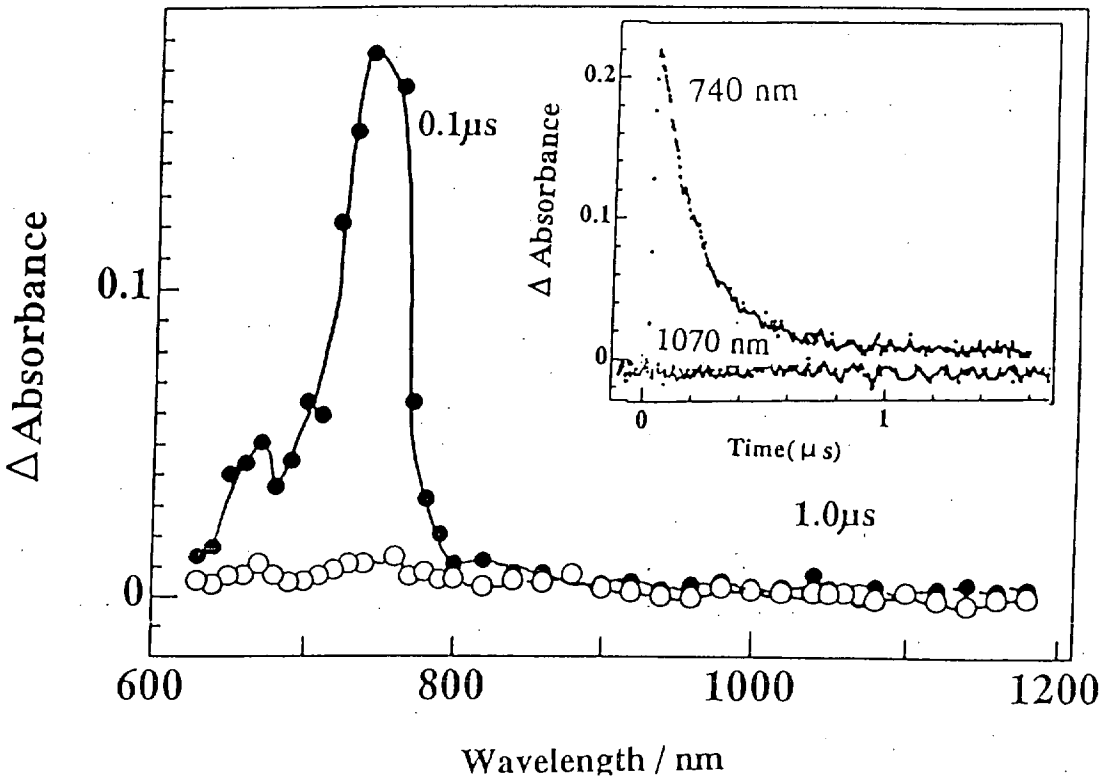
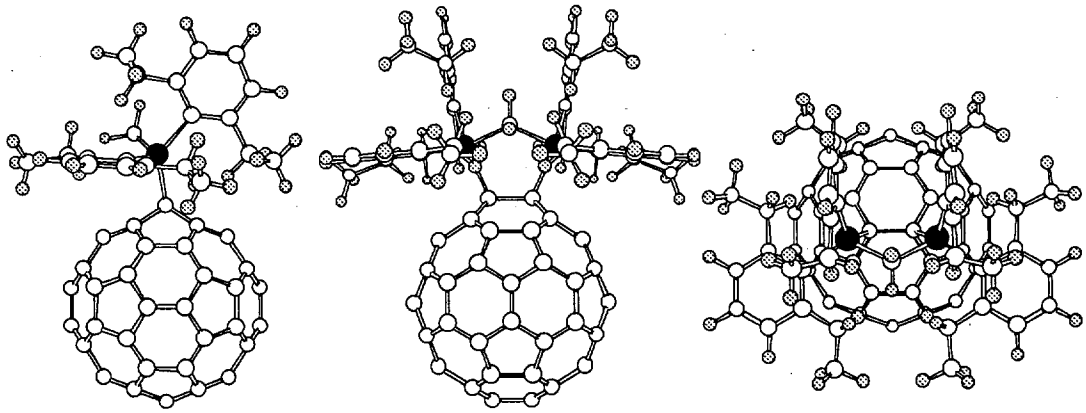


Figure. Transient absorption spectra obtained by 532 nm-laser flash photolysis of C_{60} (0.1×10^{-3} mol dm^{-3}) in the presence of **1** (3×10^{-3} mol dm^{-3}) in deaerated benzene. Time profiles at 720 and 1070 nm.

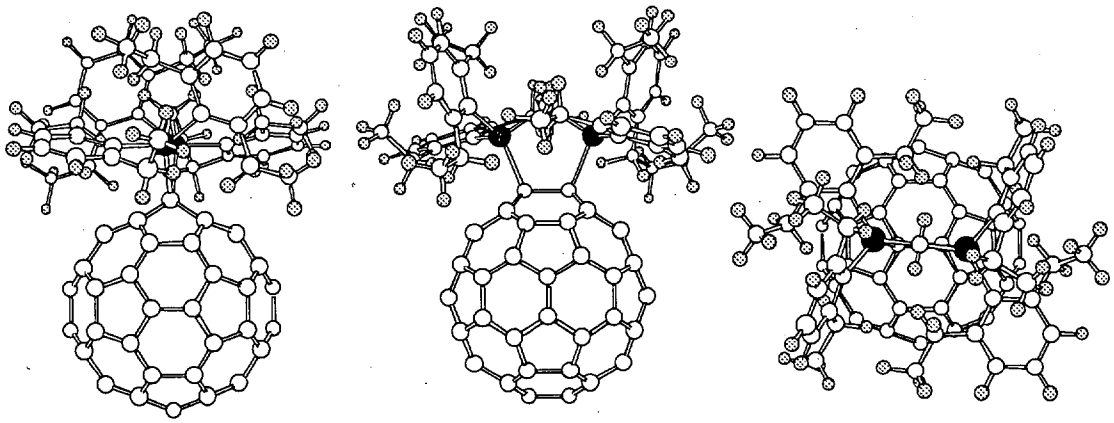
Supplemental Fig. 10 / T. Akasaka

Three views of the optimaized structure of the Cs-form of **2a**.



● = Ge ○ = C ⊘ = H

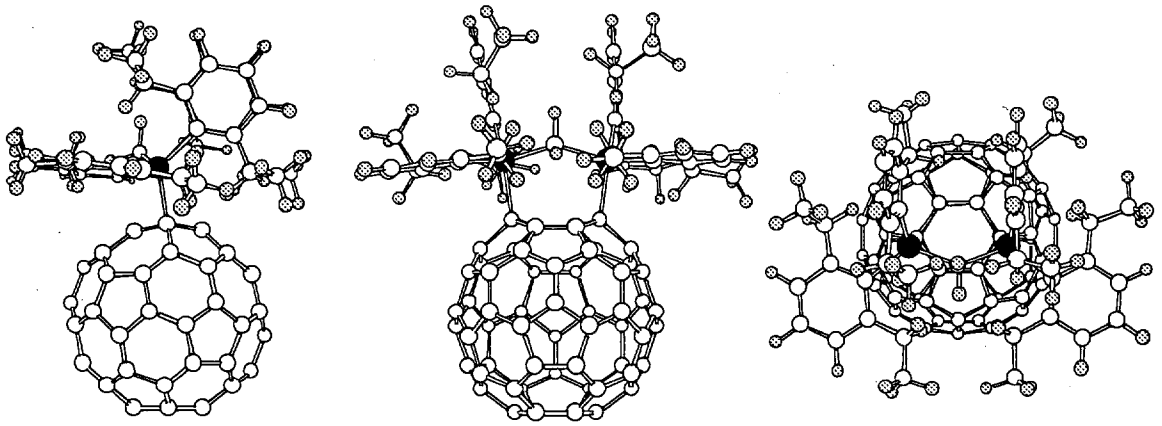
Three views of the optimaized structure of the twist-form of **2a**.



● = Ge ○ = C ⊘ = H

Supplemental Fig. 11 / T. Akasaka

Three views of the optimaized structure of the 5-membered bent-form of **2b**.



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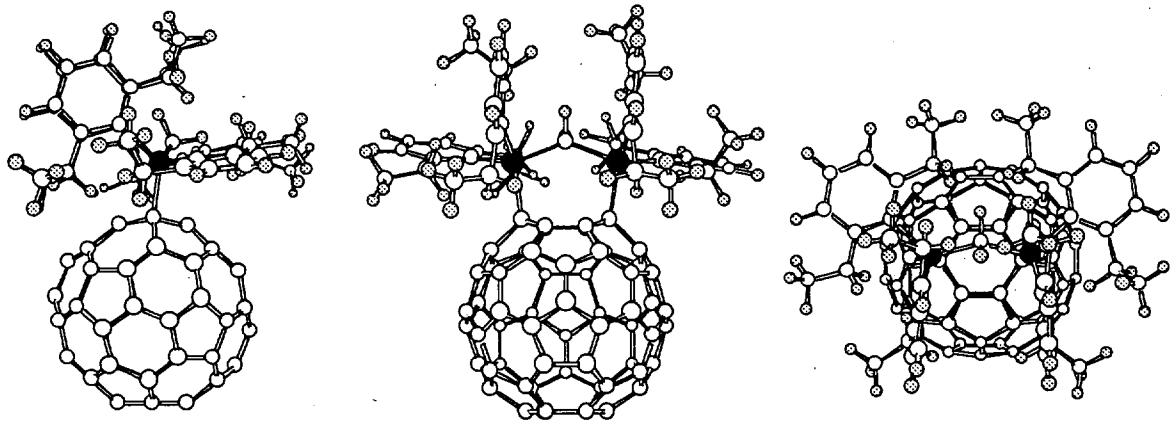
Three views of the optimaized structure of the 6-membered bent-form of **2b**.



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