Electronic Supplementary Information

Electron doping of single-walled carbon nanotubes using pyridine-boryl radicals

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1. Materials. SWCNTs (Meijo-eDIPS) with a diameter of 1.5 ± 0.5 nm were purchased from Meijo Nano Carbon. *N*-methylpyrrolidone (NMP) and anhydrous pentane were purchased from FUJIFILM Wako Pure Chemicals Corp (Tokyo, Japan). Methanol was purchased from Kanto Chemical (Tokyo, Japan). Bis(pinacolato)diboron, 4-cyanopyridine, 4-methoxypyridine, and 4-phenylpyridine were purchased from Tokyo Chemical Industry.

2. General. ESR spectroscopy was conducted at room temperature using an EMX 8/2.7 (Bruker, America). Optical absorption measurements were performed using a V-670 spectrophotometer (JASCO, Tokyo Japan). The in-plane electrical conductivity and in-plane Seebeck coefficient were measured using a ZEM-3 measurement system (ADVANCE RIKO, Yokohama Japan) under a helium atmosphere at ~0.01 MPa from 30 to 100 °C. Scanning electron microscopy (SEM) was carried out using an SU-9000 microscope (Hitachi High Technologies, Tokyo Japan) with an accelerating voltage of 5.0 kV. X-ray photoelectron spectroscopy was conducted at room temperature using an AXIS-ULTRA spectrometer (Shimadzu, Kyoto Japan), in which indium was used as the substrate. Au film (Au 4f7/2 84.140 eV) was measured with each sample as the internal standard.

3. Fabrication of SWCNT sheets and doping of SWCNT film. The SWCNT films were fabricated according to the published procedure.[1] SWCNTs (5.0 mg) were dispersed in NMP (250 mL) using a bath-type sonicator (Branson 5010) for 1 hour. The dispersion was filtered through a polytetrafluoroethylene membrane (pore diameter: 1.0 μm). The obtained film was removed from the membrane and washed by dipping it in methanol to remove residual NMP, followed by vacuum-drying at 80 °C for 8 hours. The thickness of the films was 15 ± 5 μm. The free-standing SWCNT sheets were cut by scissors to the specified size.

4. Fabrication of SWCNT-coated quartz substrate. SWCNTs (1.0 mg) were suspended in ethanol (20 mL) by sonication in a bath-type sonicator for 1 h. The SWCNT suspension was dropped on a quartz substrate (70 × 8.0 mm).

5. Doping of SWCNTs with B_2pin_2 and 4-substituted pyridine.

Doping of SWCNTs with B_2pin_2 and 4-cyanopyridine. Pristine SWCNT film immersed in a pentane (1.5 mL) solution of B_2pin_2 (20.0 mg, 7.88×10^{-2} mmol, 1.0 equiv.) was added to a pentane (1.5 mL) solution of 4-cyanopyridine (4.1 mg, 3.96×10^{-2} mmol, 0.5 equiv.) at 30 °C under nitrogen, and then the mixture was shaken for 3 hours. After taking the films out of the solution, the doped SWCNT film was dried under vacuum at room temperature for 1 hour.

Doping of SWCNTs with B_2pin_2 and 4-phenylpyridine. Pristine SWCNT film immersed in a pentane (1.5 mL) solution of B_2pin_2 (20.0 mg, 7.88×10^{-2} mmol, 1.0 equiv.) was added to a pentane (1.5 mL) solution of 4-phenylpyridine (6.2 mg, 3.96×10^{-2} mmol, 0.5 equiv.) at 30 °C under nitrogen, and then the mixture was shaken for 24 hours. After taking the films out of the solution, the doped SWCNT film was dried under vacuum at room temperature for 1 hour.

Doping of SWCNTs with B_2pin_2 and 4-methoxylpyridine. Pristine SWCNT film immersed in a pentane (1.5 mL) solution of B_2pin_2 (20.0 mg, 7.88×10^{-2} mmol, 1.0 equiv.) was added to a pentane (1.5 mL) solution of 4-methoxypyridine (8.00 µL, 3.96×10^{-2} mmol, 0.5 equiv.) at 30 °C under nitrogen, and then the mixture was shaken for 24 hours. After taking the films out of the solution, the doped SWCNT film was dried under vacuum at room temperature for 1 hour.

6. Theoretical calculations. Density functional theory (DFT) calculations of 4-CNpy-boryl radical on the surface of SWCNT with chiral index of (8,8) and (10,0) were performed using

QuantumATK software package.[2] The supercells with five repeating unit cells for SWCNT (8,8) and three repeating unit cells for SWCNT (10,0) were used. The calculations were performed with 1 x 1 x 4 k-points sampling in the direction of tube repetition. The geometry optimization was carried out the SWCNT/boryl-radical complexes until the forces were minimized below 0.05 eV/Å^2. The optimization and energy levels of **4-CNpy-boryl radical**, **4-Phpy-boryl radical, 4-OMepy-boryl radical, 1** and **1'** were calculated at the UB3LYP/6-31G(d,p) and B3LYP/6-31G(d,p), respectively using Gaussian 16 program package.[3]

7. Supporting Figures.

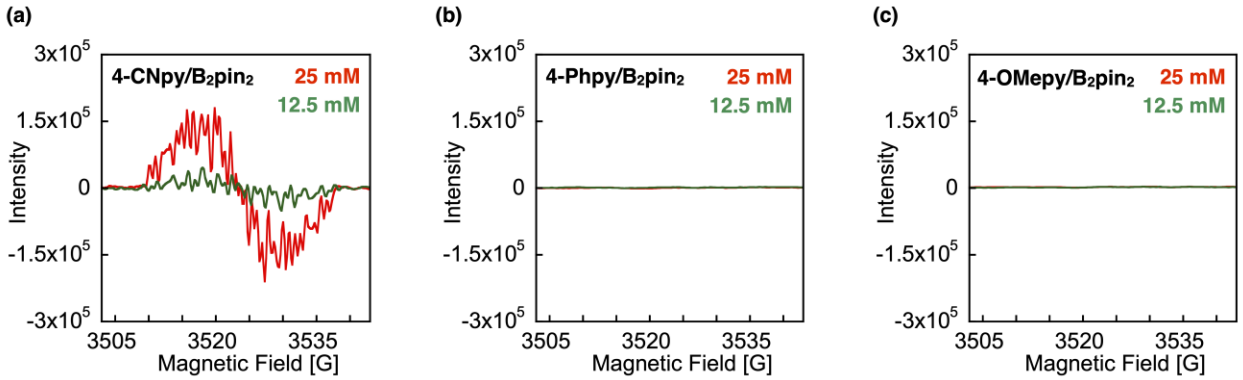

Fig. S1 ESR spectra of a pentane solution of (a) 4-CNpy/B_2pin_2, (b) 4-Phpy/B_2pin_2 and (c) 4-OMepy/B_2pin_2 at 25 °C under nitrogen. The spectra of 25 mM and 12.5 mM solutions were colored red and green, respectively.

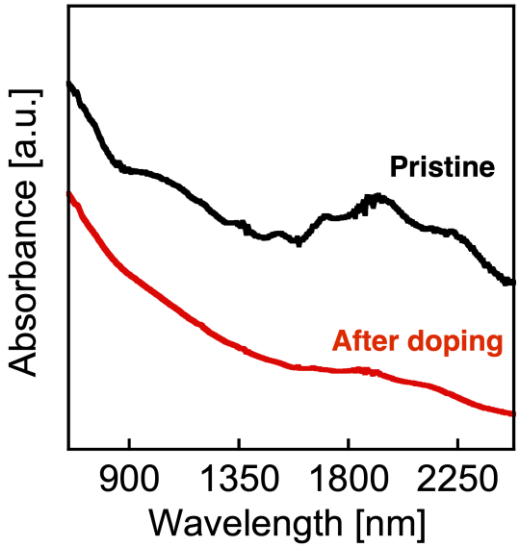

Fig. S2 UV-vis-NIR spectra of pristine SWCNT film (black) and the n-doped SWCNT film using B_2pin_2 and 4-CNpy (red) on quartz substrate.

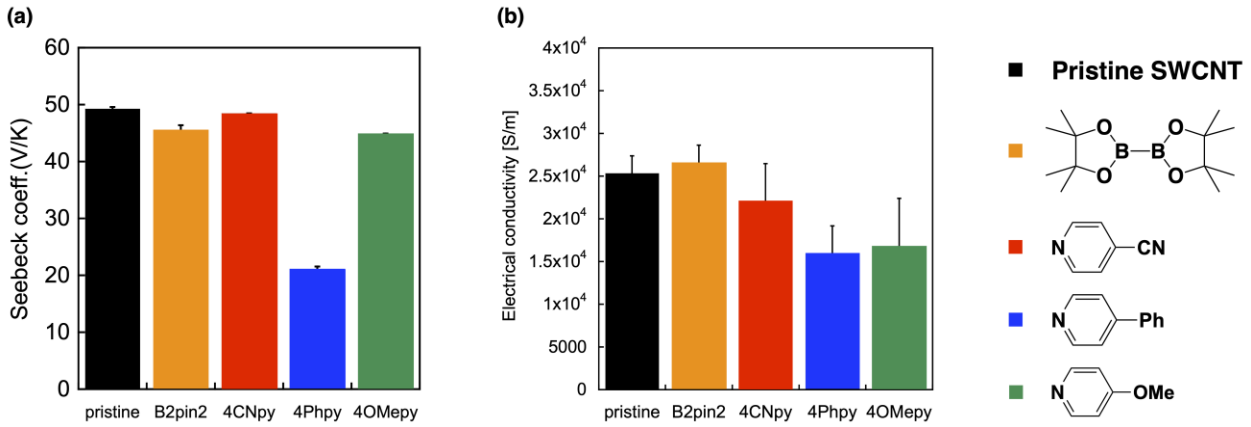

Fig. S3 (a) Seebeck coefficient and (b) electrical conductivities of the pristine SWCNT film (black) at 30 °C, the SWCNT film after immersing in a pentane solution of B_2pin_2 (orange), 4-CNpy (red), 4-Phpy (blue) and 4-OMepy (green) in air.

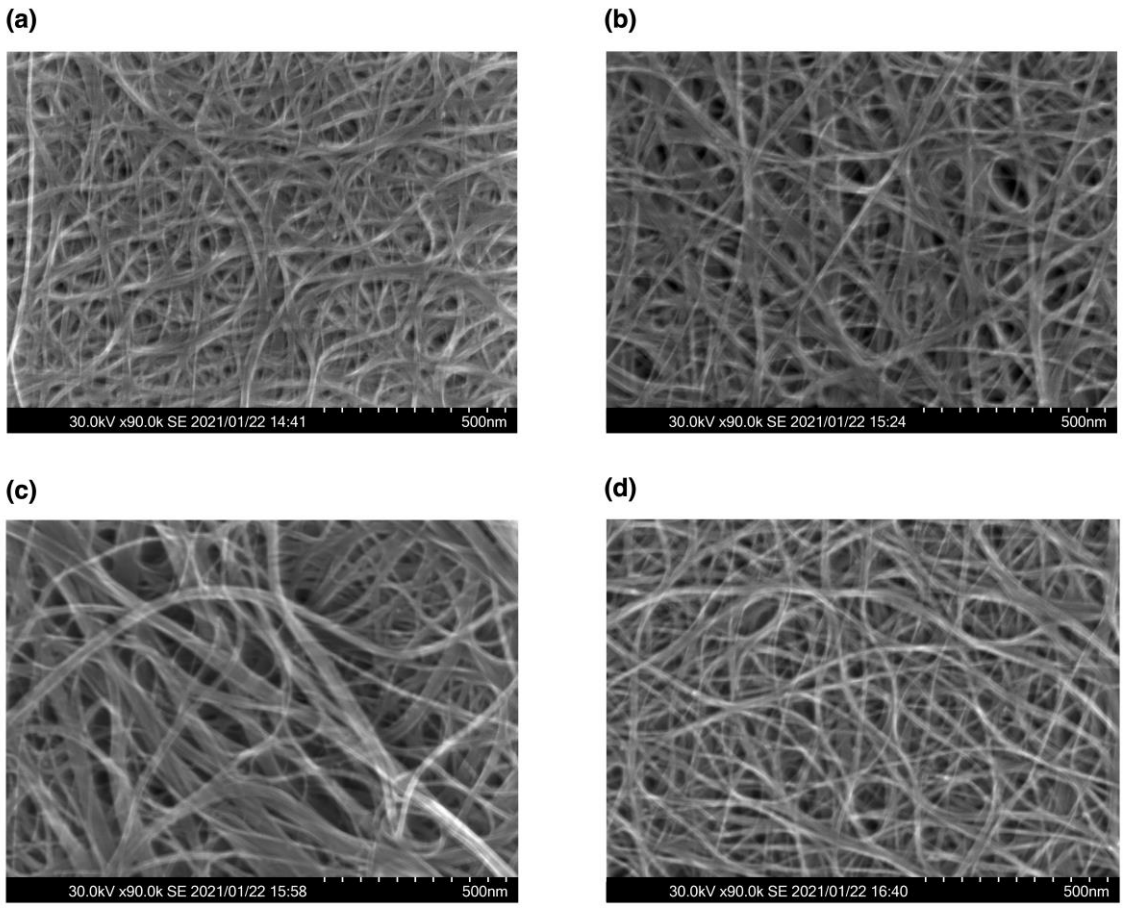

Fig. S4 Scanning electron microscopy of (a) pristine SWCNT film, n-doped SWCNT films using (b) 4-CNpy/B_2pin_2, (c) 4-Phpy/B_2pin_2 and (d) 4-OMepy/B_2pin_2.

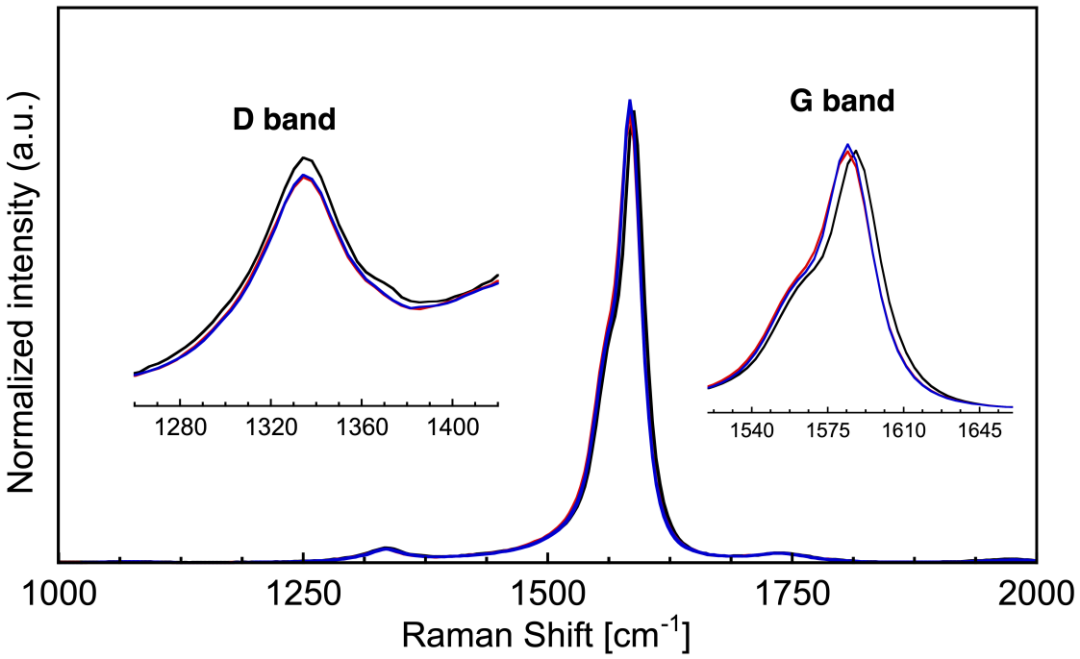

Fig. S5 Raman spectra of pristine SWCNT film (black), n-doped SWCNT films using 4-CNpy/B_2pin_2 (red), 4-Phpy/B_2pin_2 (blue) and 4-Phpy/B_2pin_2 (green).

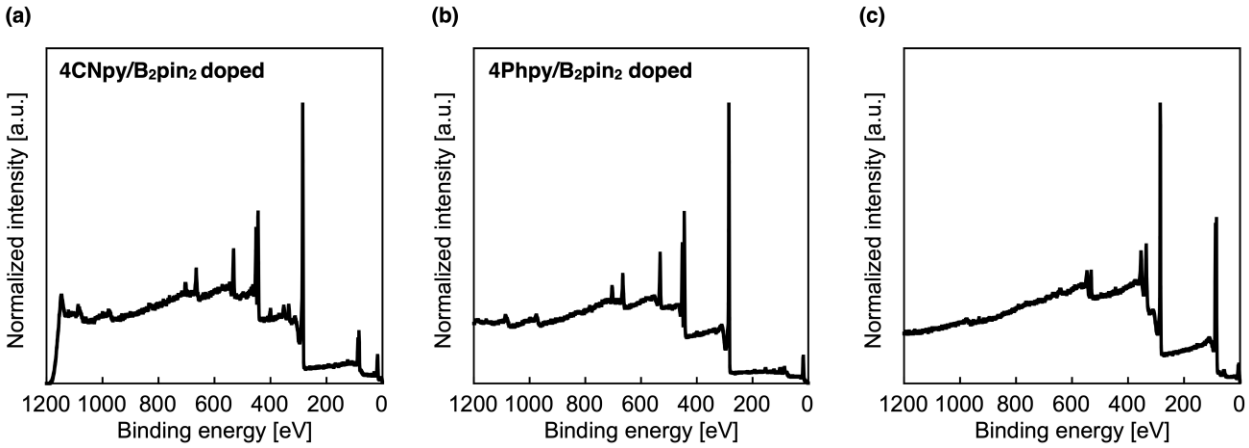

Fig. S6 XPS survey scans of the n-doped SWCNT films using (a) 4-CNpy/B_2pin_2, (b) 4-Phpy/B_2pin_2 and (c) 4-OMepy/B_2pin_2.

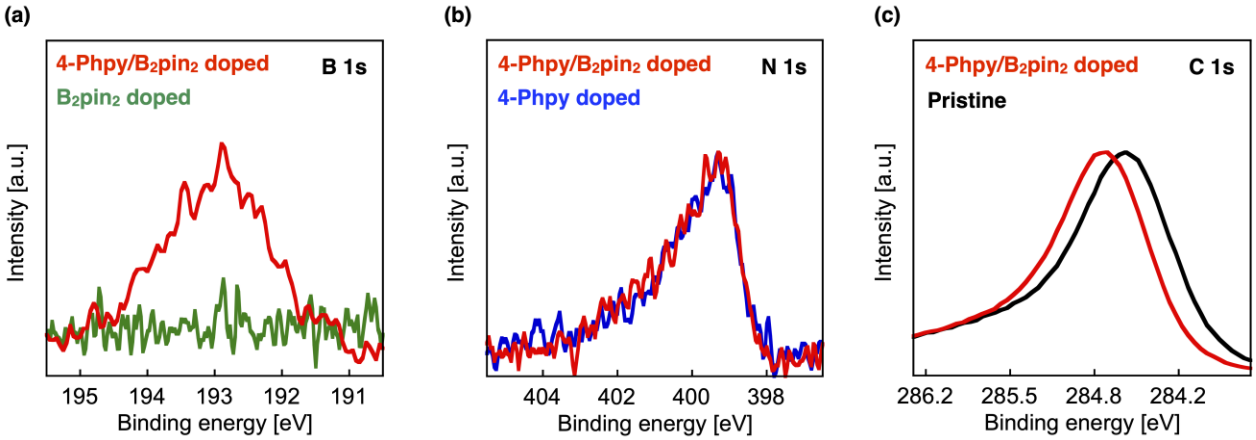

Fig. S7 XPS narrow scans of (a) B 1s, (b) N 1s, and (c) C 1s of the n-doped SWCNT films using 4-Phpy/B_2pin_2. The green line: the SWCNT film using B_2pin_2; the blue line: the SWCNT film using 4-Phpy; the black line: pristine SWCNT film.

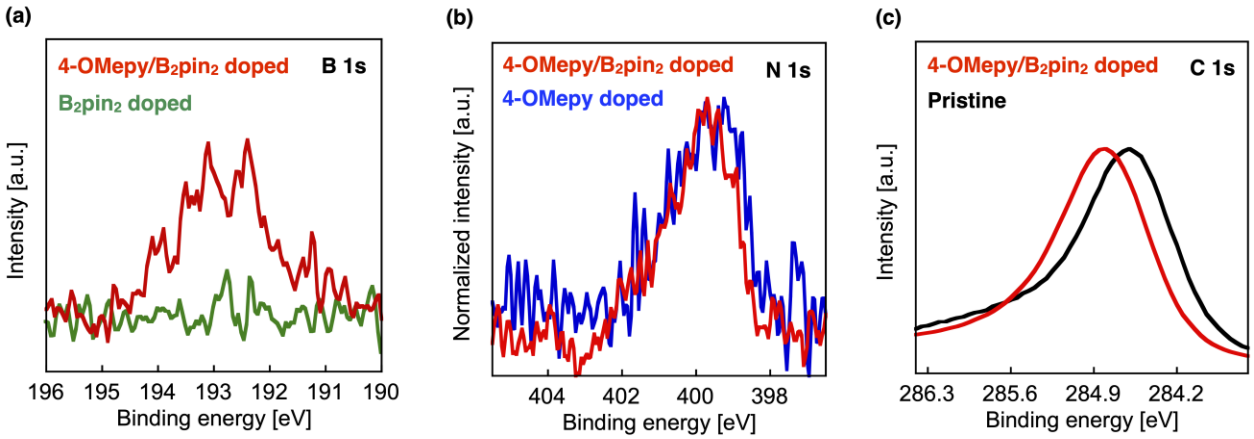

Fig. S8 XPS narrow scans of (a) B 1s, (b) N 1s, and (c) C 1s of the n-doped SWCNT films using 4-OMepy/B_2pin_2. The green line: the SWCNT film using B_2pin_2; the blue line: the SWCNT film using 4-OMepy; the black line: pristine SWCNT film.

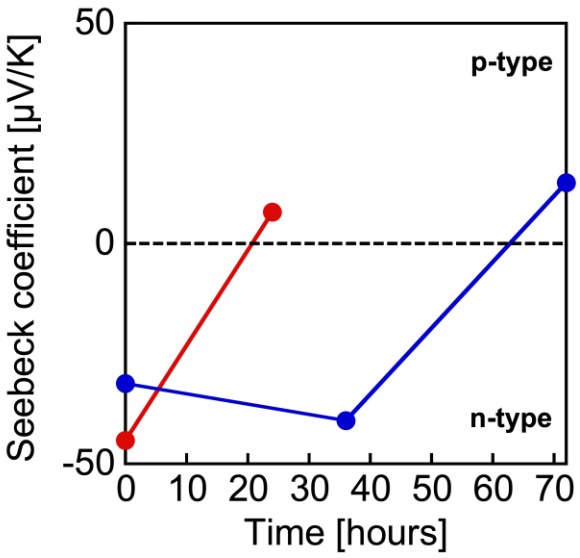

Fig. S9 Time course of the Seebeck coefficient of SWCNT film doped with 4-CNpy-boryl radical (red) and 4-Phpy/B_2pin_2 (blue) at 30 °C.

8. Supporting References.

S1. Y. Nakashima, N. Nakashima and T. Fujigaya, *Synth. Met.* 2017, **225**, 76.

S2. S. Smidstrup, T. Markussen, P. Vancraeyveld, J. Wellendorff, J. Schneider, T. Gunst, B. Verstichel, D. Stradi, P. A. Khomyakov, U. G. Vej-Hansen, M.-E. Lee, S. T. Chill, F. Rasmussen, G. Penazzi, F. Corsetti, A. Ojanperä, K. Jensen, M. L. N. Palsgaard, U. Martinez, A. Blom, M. Brandbyge and K. Stokbro, *Journal of Physics Condensed Matter*, 2019, **32**, 015901.

S3. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.