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Supplementary Information

High-capacity organic cathode active materials of 2,2′-bis-*p*-benzoquinone derivatives for rechargeable batteries

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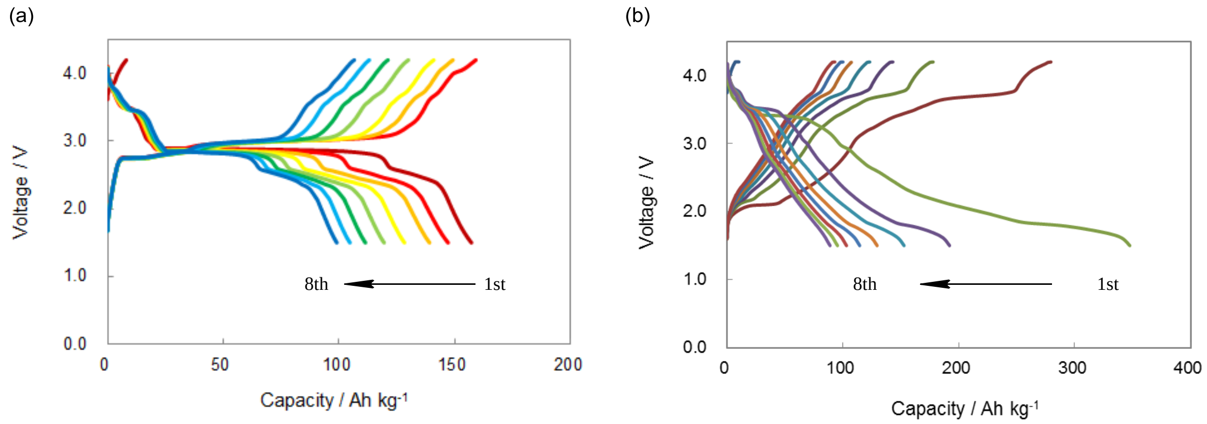


Fig. S1 Charge-discharge curves and cycle-life performance over eight cycles for (a) BQ and (b) NDQ cells in 1.0 M $LiPF_6$-EC/DEC.

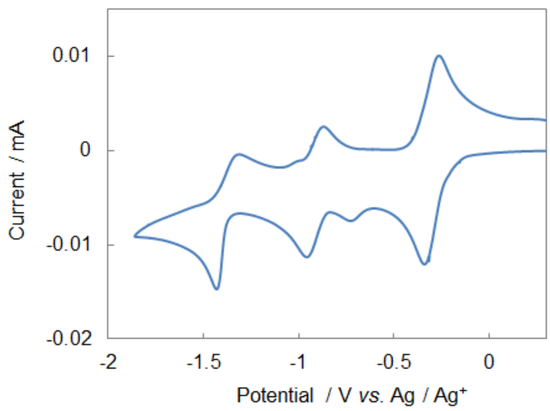


Fig. S2 CV of NDQ in acetonitrile.

Table S1 Electrochemical parameters and the enrgy levels of LUMO and HOMO for BQ and BBQ.

Sample	$E_{1p,\,c}$ in solution CV (V)	Discharge voltage (V)	LUMO level (eV)	HOMO level (eV)
BQ	-0.91	2.8	-3.947	-7.797
BBQ	-0.76	2.9	-4.251	-7.736
NDQ	-0.34	1.8-3.4	-4.645	-7.404

DFT calculations were carried out on the B3LYP/6-31+G* level.

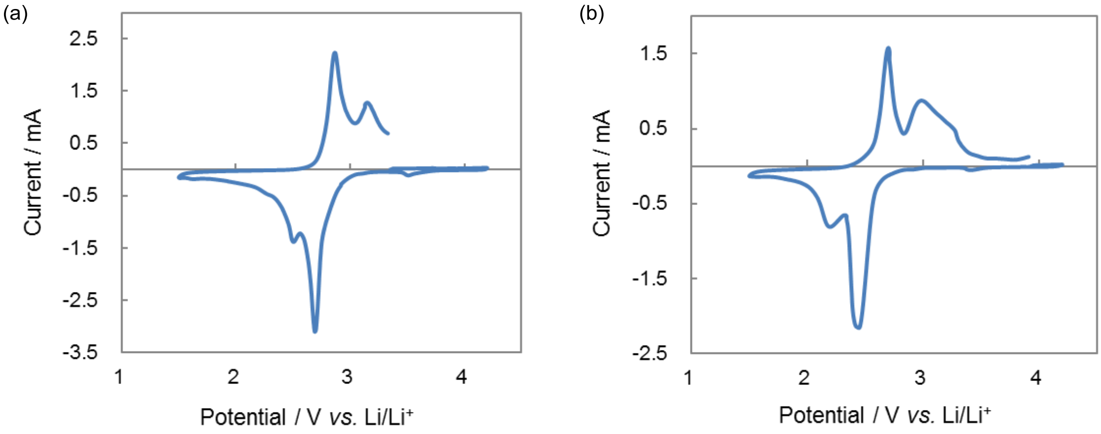


Fig. S3 Electrode CVs of (a) Br_2- and (b) Me_2-BBQ cells (1.0 M $LiPF_6$-EC/DEC) at initial cycle.

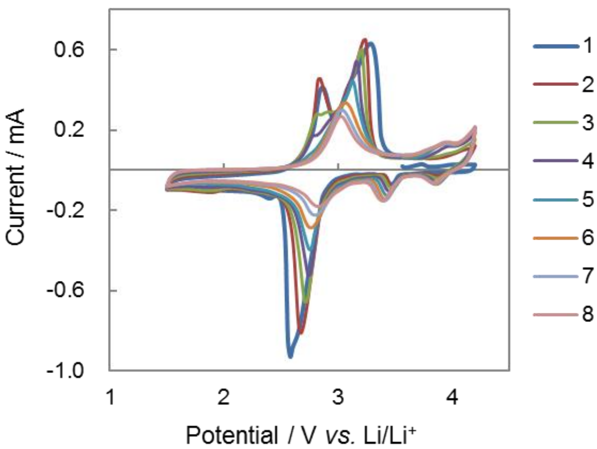


Fig. S4 Electrode CVs of BBQ cells (1.0 M $LiPF_6$-EC/DEC) from first to eighth cycles.

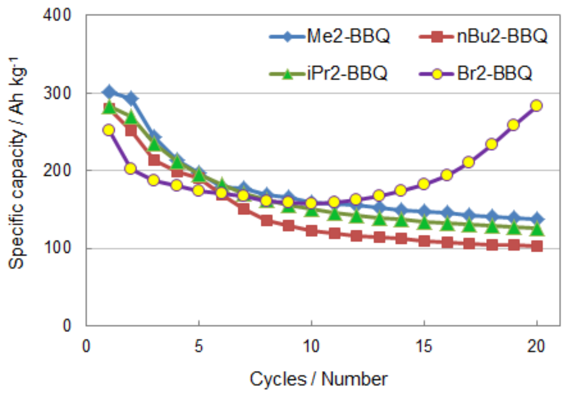


Fig. S5 Cycle-life performance over twenty cycles for cells based on R_2-BBQ (R = Br, Me, *n*Bu, and *i*Pr) in 2.75 M LiTFSI-tetraglyme systems.

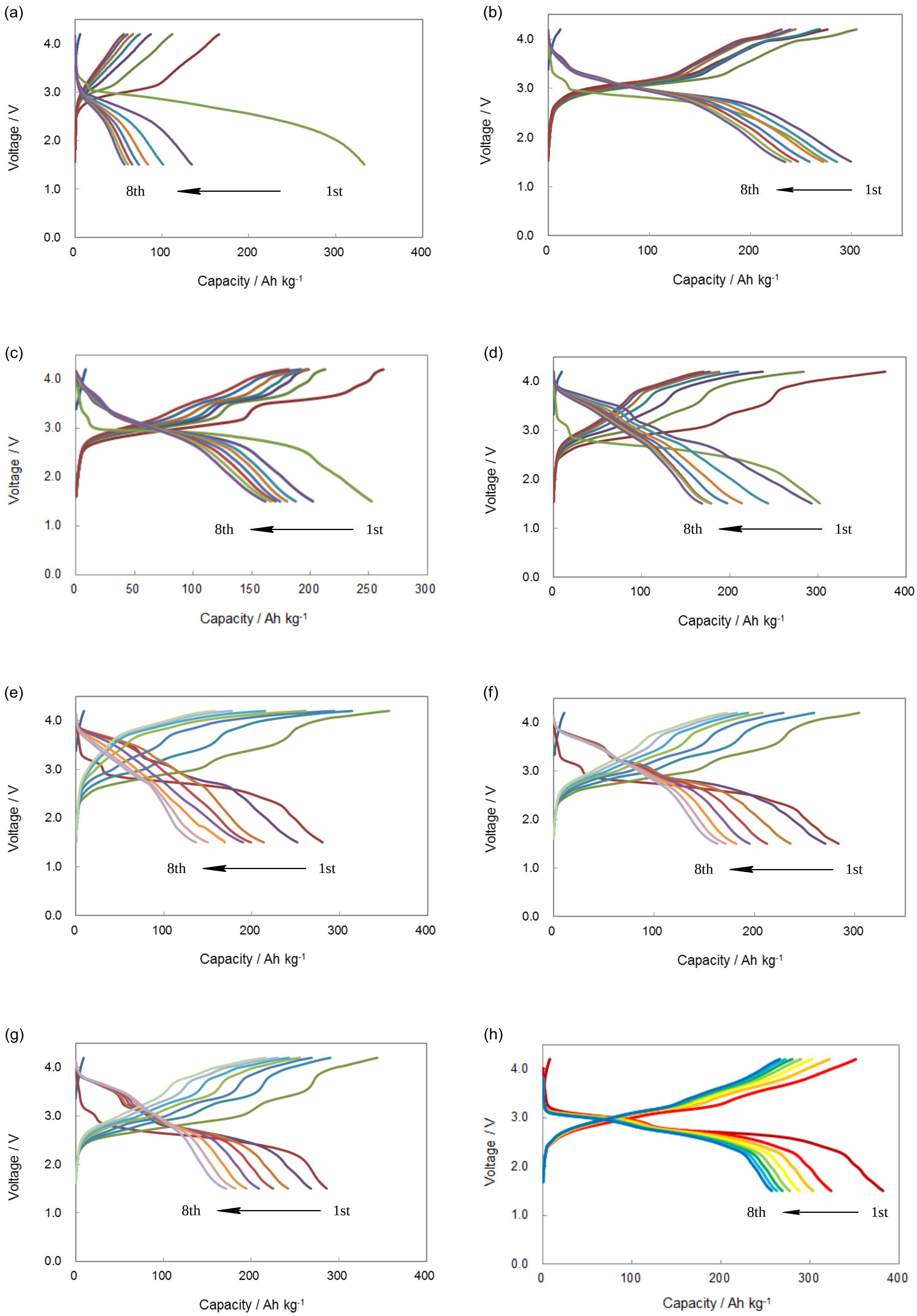


Fig. S6 Charge-discharge curves and cycle-life performance over eight cycles for (a) F_2-, (b) Cl_2-, (c) Br_2-, (d) Me_2-, (e) *n*Bu_2-, (f) *i*Pr_2-, (g) *t*Bu_2-, and (h) $(OMe)_2$-BBQ cells in 2.75 M LiTFSI-tetraglyme systems.

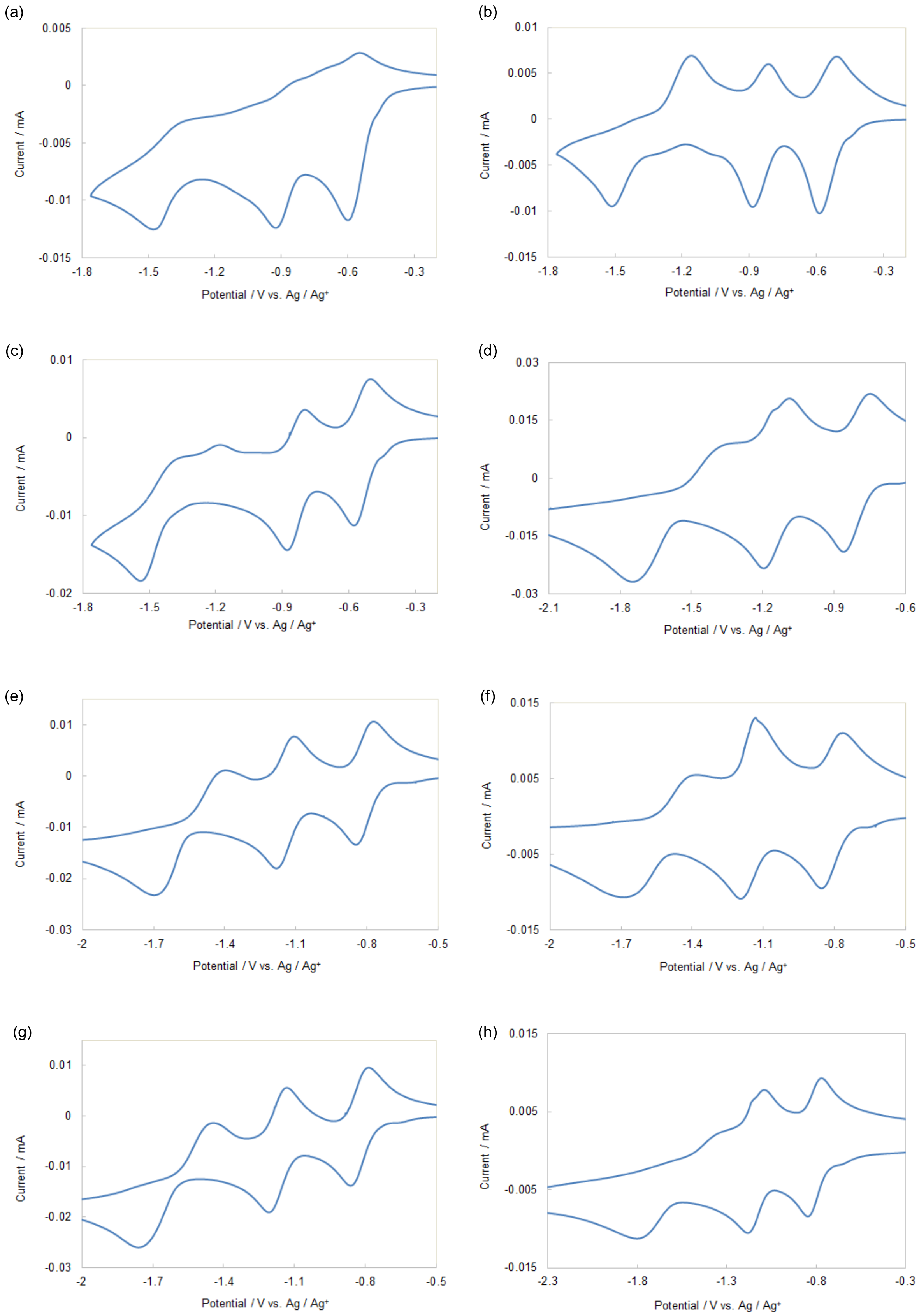


Fig. S7 CV of (a) F_2-, (b) Cl_2-, (c) Br_2-, (d) Me_2-, (e) *n*Bu_2-, (f) *i*Pr_2-, (g) *t*Bu_2-, and (h) $(OMe)_2$-BBQ in acetonitrile.

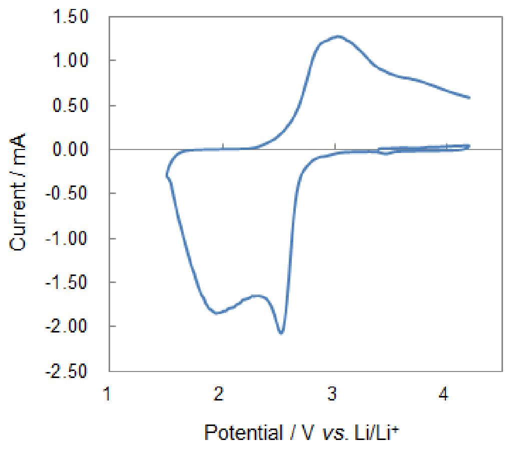


Fig. S8 Electrode CV of $(OMe)_2$-BBQ cells at initial cycle.

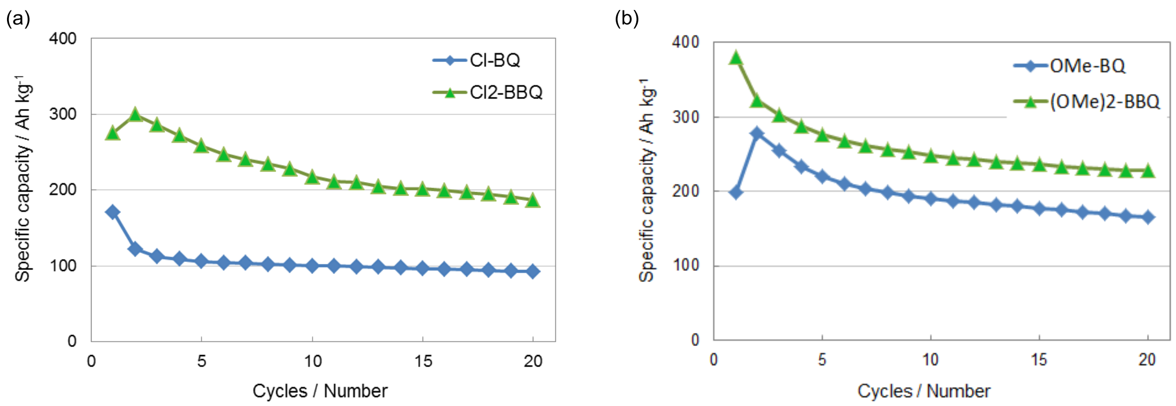
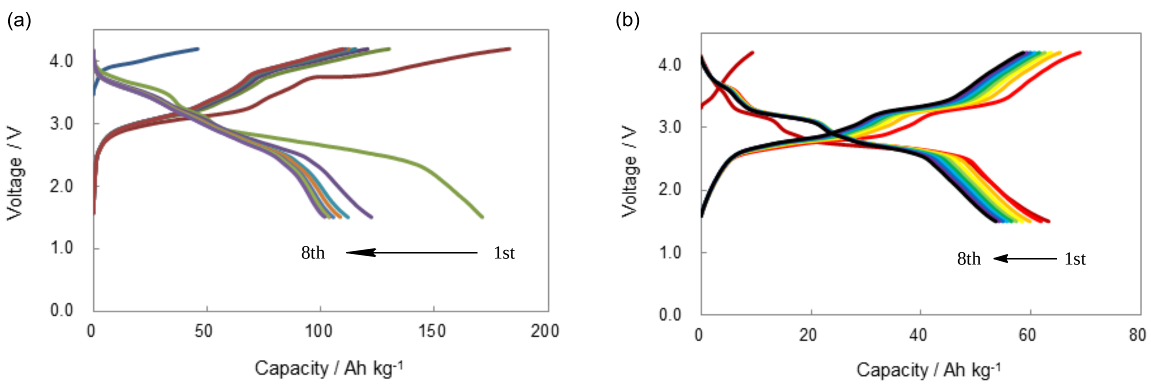


Fig. S9 Cycle-life performance over twenty cycles for cells based on (a) Cl-BQ and Cl_2-BBQ, and (b) OMe-BQ and $(OMe)_2$-BBQ in 2.75 M LiTFSI-tetraglyme systems.



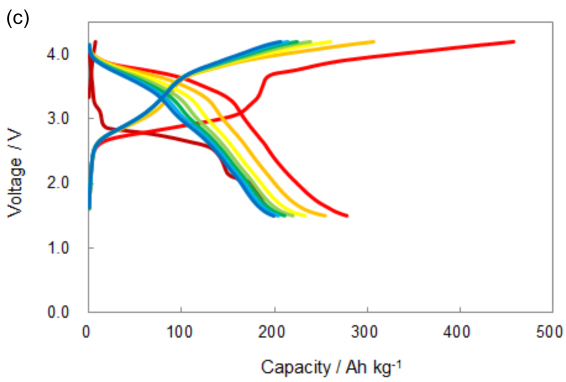


Fig. S10 Charge-discharge curves and cycle-life performance over eight cycles for (a) Cl-BQ, (b) Me-BQ, and (c) OMe-BQ in 2.75 M LiTFSI-tetraglyme systems.

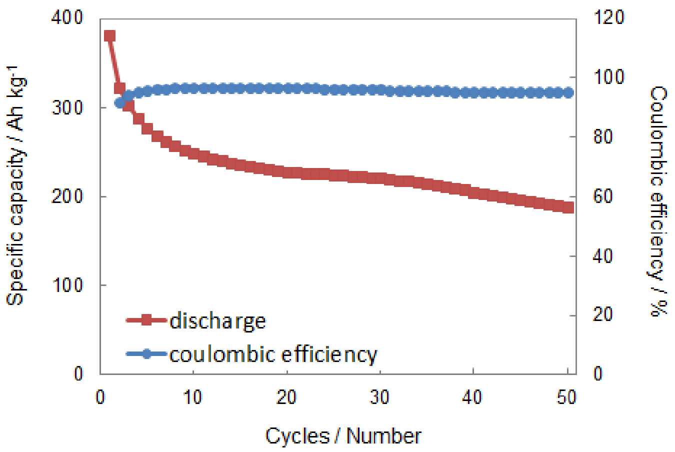


Fig. S11 Cycle-life performance over 50th cycles for cells based on $(OMe)_2$-BBQ in 2.75 M LiTFSI-tetraglyme systems.

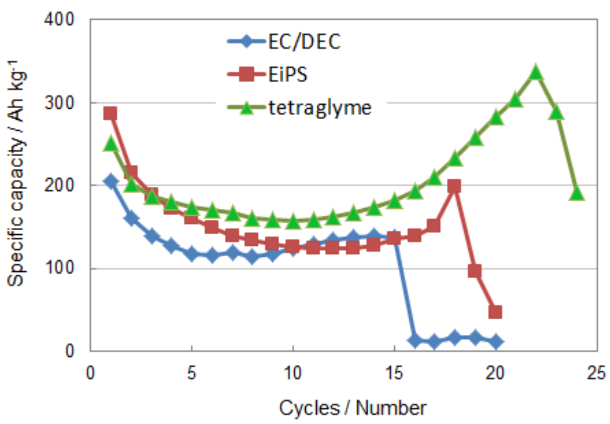


Fig. S12 Cyclability for Br_2-BBQ cells in 1.0 M $LiPF_6$-EC/DEC, 1.0 M LiTFSI-EiPS, and 2.75 M LiTFSI-tetraglyme systems.

Electrolyte effects in charge-discharge curves and cycle performance

Effects of the electrolyte in the BBQ cell was examined by preparing cells with three different electrolytes: EiPS with 1.0 M $LiN(SO_2CF_3)_2$ (LiTFSI), tetraglyme with 2.75 M LiTFSI, and a mixture of EC (30 vol%) and DEC (70 vol%) with 1.0 M $LiPF_6$. The cyclability for the BBQ cells in different electrolytes is shown in Fig. S12, and the charge-discharge curves over eight cycles are depicted in Fig. S13. The LiTFSI-EiPS system provided the highest initial capacity of 429 Ah kg^{-1}, which exceeded the theoretical value involving three electrons (376 Ah kg^{-1}). However, its discharge capacity significantly faded to 370 Ah kg^{-1} in the second cycle. In the LiTFSI-tetraglyme system, the cell afforded an initial capacity of 358 Ah kg^{-1}, and surprisingly increased to 368 Ah kg^{-1} in the second cycle. Although the initial capacity in the tetraglyme system was smaller than in the EiPS system, tetraglyme afforded the highest cycle retention rate (the ratios of the 20th capacity to the 1st in the tetraglyme, EiPS, and EC/DEC systems were 67, 47, and 52%, respectively), and its capacity remained at 239 Ah kg^{-1} at the 20th cycle.

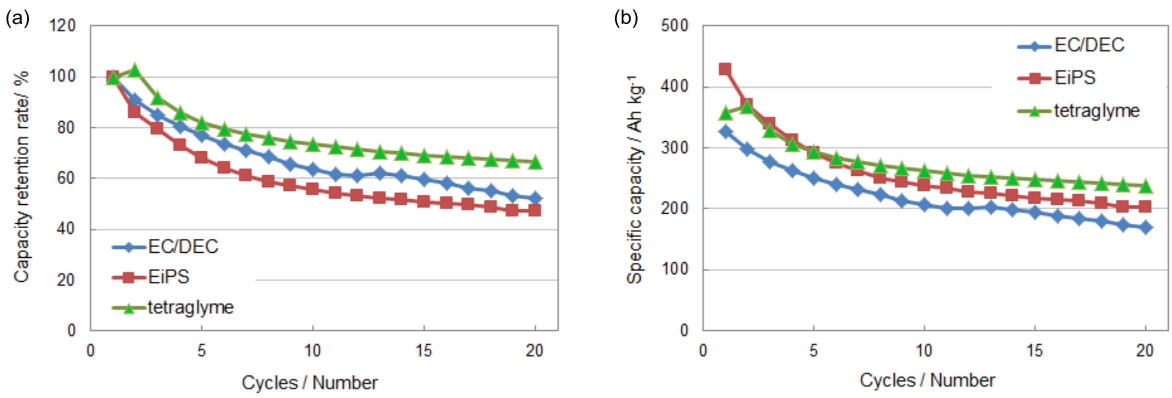


Fig. S13 Cyclability over twenty cycles for BBQ cells in 1.0 M $LiPF_6$-EC/DEC, 1.0 M LiTFSI-EiPS, and 2.75 M LiTFSI-tetraglyme systems: plots of (a) capacity retention rate versus cycle number and (b) capacity retention rate versus cycle number.

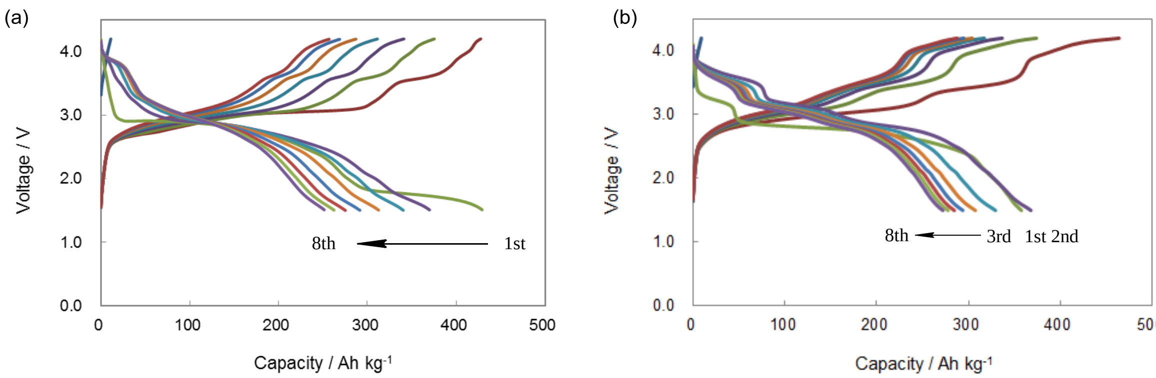


Fig. S14 Charge-discharge curves and cycle-life performance over eight cycles for BBQ cells in (a) 1.0 M LiTFSI-EiPS, and (b) 2.75 M LiTFSI-tetraglyme systems.

Experimental details of preparations for cathode active materials

Melting points were obtained with a Yanako micro melting point apparatus and are not corrected. Products were purified by flash chromatography on silica gel (Kanto Chemical Co., Inc., Silica Gel 60N (spherical, neutral), 63-210 μm). ^{1}H NMR spectra were recorded with JEOL-ECP-500 (500 MHz) and JEOL-ECP-400 (400 MHz) spectrometers in $CDCl_3$ or DMSO-d_6. Chemical shifts were reported in parts per million (δ) referenced to the solvent peak at 7.26 or 2.49 ppm. ^{13}C NMR spectra were recorded with JEOL-ECP-500 (126 MHz) and JEOL-ECP-400 (100 MHz) spectrometers in $CDCl_3$ or DMSO-d_6, and referenced to the solvent peak at 77.0 or 39.7 ppm. Coupling constants, *J*, were reported in Hertz (Hz), and splitting patterns were designated as s (singlet), d (doublet), t (triplet), sext (sextet), sept (septet), dd (double doublet), dt (double triplet) and m (multiplet). IR spectra were obtained on a JASCO FT/IR-4100 or a JASCO FT/IR-5300 spectrometer; absorptions were reported in reciprocal centimeters. Conventional mass spectra were recorded with SHIMADZU GCMS-QP2010Plus and JEOL MS-700 spectrometers, and high-resolution mass spectra were recorded with a JEOL MS-700 spectrometer. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

1,4,5,8-Naphthodiquinone (NDQ)

A mixture of **1** (570 mg, 3.00 mmol) and [bis(trifluoroacetoxy)iodo]benzene (3.02 g, 7.02 mmol) in acetone (20 mL) was stirred for 1.5 h at room temperature. Then, [bis(trifluoroacetoxy)iodo]benzene (3.44 g, 8.00 mmol) was added to the reaction mixture, and the mixture was stirred at room temperature. After stirring for 2.5 h, the mixture was filtered through a glass filter, and the residue was washed with acetone and benzene, and then dried over under reduced pressure to yield **NDQ** (86 mg, 15%) as a brown solid. M.p. 204.5–208.0 °C; IR (KBr): ν = 3065, 1685, 1642, 1606, 1299, 1132, 865 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.89 (s, 4H; vinyl-H); ^{13}C NMR (126 MHz, DMSO-d_6): δ = 186.0, 136.1, 126.3 ppm.

2,2'-Bis-*p*-benzoquinone (BBQ)

A mixture of **2** (2.75 g, 19.9 mmol), iodine (2.03 g, 8.01 mmol), iodic acid (1.04 g, 5.92 mmol), acetic acid (33 mL), water (7 mL), and sulfuric acid (1 mL) was heated to 60 °C for 5 h. After cooling to room temperature, the reaction mixture was poured into 10% aqueous $NaHSO_3$. The insoluble precipitate was filtered off using a glass filter, and then washed with diethyl ether. The aqueous layer was then separated and extracted with diethyl ether. The combined organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane–chloroform = 2/1) to yield **3** (3.90 g, 74%) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 2.8 Hz, 1H; ClC*H*), 6.85 (dd, *J* = 9.2, 3.2 Hz, 1H; ClC(OCH_3)CHC*H*), 6.74 (d, *J* = 8.7 Hz, 1H; ClC(OCH_3)C*H*), 3.81 (s, 3H; OCH_3), 3.74 (s, 3H; OCH_3) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 154.1, 152.5, 124.7, 114.6, 111.5, 85.9, 56.9, 55.8 ppm; LRMS (EI): *m*/*z* (%): 264 (100) [M^+], 249 (78), 122 (18), 107 (23), 79 (22).

A mixture of **3** (5.84 g, 22.1 mmol), copper (7.76 g, 122 mmol), 2,2'-bipyridine (347 mg, 2.22 mmol), and DMSO (40 mL) was heated at 150 °C under N_2 for 15 h. After cooling to room temperature, water (80 mL) was added with cooling by an ice bath. The mixture was then filtered through a pad of Celite and the pad was washed with diethyl ether. The aqueous layer was separated and extracted with diethyl ether. The combined organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane–chloroform = 1/1 and 100% chloroform) to yield **4** (1.99 g, 66%) as a white crystalline solid. M.p. 96.0–98.0 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 6.91 (d, *J* = 8.7 Hz, 2H; $CC(OCH_3)CH$), 6.86 (dd, *J* = 8.7, 3.2 Hz, 2H; $CC(OCH_3)CHCH$), 6.84 (d, *J* = 3.3 Hz, 2H; $CCHC(OCH_3)$), 3.78 (s, 6H; OCH_3), 3.73 (s, 6H; OCH_3) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 153.2, 151.2, 128.5, 117.1, 113.3, 112.4, 56.4, 55.6 ppm; LRMS (EI): *m*/*z* (%): 274 (100) [M^+], 259 (42), 244 (26), 228 (37), 213 (17).

To a mixture of **4** (551 mg, 2.01 mmol) in acetonitrile (15 mL), a solution of CAN (11.0 g, 6.00 mmol) in water (15 mL) was added at 0°C, the mixture was then warmed slowly to room temperature. After stirring for 1 h, water (60 mL) and dichloromethane (30 mL) was added to the mixture. The aqueous layer was then separated and extracted with dichloromethane. The combined organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: 100% chloroform and chloroform–ethyl acetate = 20/1) to yield **BBQ** (294 mg, 68%) as a yellow crystalline solid. M.p. 184.5–191.0 °C; IR (KBr): ν = 1657, 1594, 1351, 1293, 1280, 1101, 928, 918, 847 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 6.89 (d, *J* = 10.1 Hz, 2H; $CCOCH$), 6.86 (dd, *J* = 10.1, 2.3 Hz, 2H; $CCOCHCH$), 6.83 (d, *J* = 2.3 Hz, 2H; $CCHCO$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 186.2, 184.4, 139.9, 136.8, 136.6, 135.8 ppm; LRMS (EI): *m*/*z* (%): 214 (63) [M^+], 186 (23), 130 (28), 102 (36), 82 (58), 54 (69), 50 (27), 44 (100).

5,5'-Difluoro-2,2'-bis-*p*-benzoquinone (F$_2$-BBQ)

To a mixture of CAN (7.24 g, 13.2 mmol) in water (12 mL), a solution of **5** (625 mg, 4.00 mmol) in acetonitrile (12 mL) was added dropwise at room temperature. After stirring for 1.5 h, water (60 mL) was added to the mixture, and the mixture was filtered through a glass filter. The residue was washed with water and chloroform / hexane = 1 : 1, then dried over under reduced pressure to yield **F$_2$-BBQ** (195 mg, 39%) as a yellow solid. M.p. 183.0–185.0 °C; IR (KBr): ν = 1685, 1656, 1604, 1357, 1163, 921 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.87 (d, *J* = 7.6 Hz, 2H; $CCHCO$), 6.57 (d, *J* = 10.0 Hz, 2H; $CFCH$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.1 (d, *J* = 14.3 Hz), 178.3 (d, *J* = 24.8 Hz), 159.6 (d, *J* = 292.2 Hz), 139.4, 134.4 (d, *J* = 2.8 Hz), 115.7 (d, *J* = 9.5 Hz) ppm; LRMS (EI): *m*/*z* (%): 250 (100) [M^+], 129 (58), 73 (77), 69 (64), 60 (53), 57 (61), 55 (62); HRMS (EI): found [M^+] 250.0073, $C_{12}H_4F_2O_4^+$ requires 250.0078.

5,5'-Dichloro-2,2'-bis-*p*-benzoquinone (Cl_2-BBQ)

To a mixture of CAN (7.24 g, 13.2 mmol) in water (12 mL), a solution of **6** (690 mg, 4.00 mmol) in acetonitrile (12 mL) was added dropwise at room temperature. After stirring for 1.5 h, water (60 mL) was added to the mixture, and the mixture was filtered through a glass filter. The residue was washed with water, and dried over under reduced pressure. Then, the residue was purified by column chromatography on silica gel (eluent: 100% chloroform), and by washing with water and chloroform / hexane = 1 : 1, then dried over under reduced pressure to yield **Cl_2-BBQ** (176 mg, 31%) as a yellow solid. M.p. 196.0–199.0 °C; IR (KBr): ν = 1670, 1653, 1608, 1570, 1320, 1194, 1010, 910 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.12 (s, 2H; CClC*H*), 7.00 (s, 2H; CC*H*CO) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 182.8, 179.0, 143.1, 139.6, 136.0, 134.2 ppm; LRMS (EI): *m*/*z* (%): 286 (25), 284 (44), 282 (56) [M^+], 149 (75), 84 (44), 81 (50), 73 (37), 69 (100), 57 (48), 55 (40).

5,5'-Dibromo-2,2'-bis-*p*-benzoquinone (Br_2-BBQ)

To a mixture of CAN (7.24 g, 13.2 mmol) in water (12 mL), a solution of **7** (868 mg, 4.00 mmol) in acetonitrile (12 mL) was added dropwise at room temperature. After stirring for 1.5 h, water (60 mL) was added to the mixture, and the mixture was filtered through a glass filter. The residue was washed with water and chloroform / hexane = 1 : 1, then dried over under reduced pressure to yield **Br_2-BBQ** (187 mg, 25%) as a yellow solid. M.p. 188.5–191.0 °C; IR (KBr): ν = 1664, 1604, 1571, 1318, 1189, 984, 910, 438 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40 (s, 2H; CBrC*H*), 7.04 (s, 2H; CC*H*CO) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.7, 178.4, 139.0, 138.2, 137.7, 135.6 ppm; LRMS (EI): *m*/*z* (%): 374 (57), 372 (85), 370 (41) [M^+], 149 (40), 86 (44), 84 (63), 81 (49), 73 (41), 69 (100), 57 (45), 55 (43).

5,5'-Dimethyl-2,2'-bis-*p*-benzoquinone (Me_2-BBQ)

To a mixture of CAN (3.61 g, 6.60 mmol) in water (6 mL), a solution of **8** (304 mg, 2.00 mmol) in acetonitrile (6 mL) was added dropwise at room temperature. After stirring for 1 h, water (40 mL) was added to the mixture, and the mixture was filtered through a glass filter. The crude product obtained was washed with water, and then dried over under reduced pressure. The residue was recrystallized from chloroform / ethanol to yield **Me_2-BBQ** (164 mg, 68%) as a yellow solid. Decomposition 167.0 °C; IR (KBr): ν = 1649, 1629, 1577, 1234, 1205 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.81 (s, 2H; CC*H*CO), 6.70 (d, *J* = 1.6 Hz, 2H; C(CH_3)C*H*), 2.10 (d, *J* = 1.2 Hz, 6H; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.9, 184.7, 146.2, 139.5, 135.9, 133.6, 15.6 ppm; LRMS (EI): *m*/*z* (%): 242 (100) [M^+], 146 (82), 118 (24), 68 (41), 40 (37).

5,5'-Dimethoxy-2,2'-bis-*p*-benzoquinone ($(OMe)_2$-BBQ)

To a mixture of CAN (18.1 g, 33.0 mmol) in water (30 mL), a solution of **9** (1.68 g, 10.0 mmol) in acetonitrile (30 mL) was added dropwise at room temperature. After stirring for 1.5 h, water (150 mL) was added to the mixture, and the mixture was filtered through a glass filter. The residue was washed with water and methanol, then dried over under reduced pressure to yield **(OMe)$_2$-BBQ** (93 mg, 7%) as a yellow solid. Decomposition 214.0 °C; IR (KBr): ν = 1671, 1643, 1620, 1574, 1225, 1197, 1173, 998, 910 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.77 (s, 2H; C(OCH$_3$)C*H*), 6.04 (s, 2H; CC*H*CO), 3.87 (s, 6H; OCH$_3$) ppm; Measurement of ^{13}C NMR was unsuccesful because of low solubility of the product in general organic solvents; LRMS (EI): *m*/*z* (%): 274 (100) [M$^+$], 245 (47), 231 (37), 201 (21), 69 (24).

5,5'-Dibutyl-2,2'-bis-*p*-benzoquinone (*n*Bu$_2$-BBQ)

To a mixture of **2** (277 mg, 2.00 mmol) and TMEDA (621 mg, 5.40 mmol) in dry hexane (4 mL), *n*-butyllithium (1.6 M hexane solution, 2.91 g, 6.00 mmol) was added dropwise at room temperature under N$_2$. After stirring for 20 h, the reaction mixture was cooled by an ice bath, 1-bromobutane (1.154 g, 8.40 mmol) was then added dropwise to the mixture, and the mixture was warmed slowly to room temperature. After stirring for 12 h, the mixture was quenched by adding excess amount of water dropwise. The aqueous layer was separated and extracted with diethyl ether. The combined organic layer was then washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane–chloroform = 4/1) to yield **10** (84 mg, 22%) as a colorless liquid. IR (neat): ν = 2954, 2931, 1501, 1465, 1224, 1050 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.76 (d, *J* = 8.4 Hz, 1H; *C*C(OCH$_3$)C*H*), 6.73 (d, *J* = 3.2 Hz, 1H; CC*H*C(OCH$_3$)), 6.68 (dd, *J* = 8.8, 3.2 Hz, 1H; *C*C(OCH$_3$)CHC*H*), 3.78 (s, 3H; OCH$_3$), 3.76 (s, 3H; OCH$_3$), 2.58 (t, *J* = 7.2 Hz, 2H; Ar-CH$_2$), 1.59-1.52 (m, 2H; ArCH$_2$C*H*$_2$), 1.37 (sext, *J* = 7.2 Hz, 2H; C*H*$_2$CH$_3$), 0.93 (t, *J* = 7.6 Hz, 3H; CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 153.3, 151.7, 132.4, 116.1, 110.9, 110.3, 55.6, 55.3, 32.0, 29.9, 22,5, 13.9 ppm; LRMS (EI): *m*/*z* (%): 194 (90) [M$^+$], 152 (30), 151 (100), 137 (68), 121 (51), 91 (27), 77 (19).

To a mixture of CAN (3.77 g, 6.87 mmol) in water (15 mL), a solution of **10** (403 mg, 2.10 mmol) in acetonitrile (6 mL) was added dropwise at room temperature. After stirring for 1 h, water (60 mL) was added to the mixture. The mixture was filtered through a glass filter, and the residue was washed with water and then dried over under reduced pressure. The crude product obtained was recrystallized from chloroform / ethanol to yield ***n*Bu$_2$-BBQ** (220 mg, 65%) as a yellow crystalline solid. M.p. 167.5–169.0 °C; IR (KBr): ν = 2953, 2926, 1661, 1646, 923 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.80 (s, 2H; CC*H*CO), 6.65 (t, *J* = 1.6 Hz, 2H; C(*n*Bu)C*H*), 2.46 (dt, *J* = 7.8, 1.2 Hz, 4H; CC*H*$_2$), 1.55-1.48 (m, 4H; CCH$_2$C*H*$_2$), 1.41 (sext, *J* = 7.2 Hz, 4H; C*H*$_2$CH$_3$), 0.95 (t, *J* = 7.2 Hz, 6H; CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 186.8, 185.0, 150.0, 139.2, 136.2, 132.6, 29.8, 28.5, 22.4, 13.8 ppm; LRMS (EI): *m*/*z* (%): 328 (11), 327 (11) [M+H]$^+$, 155 (22), 138 (28), 137 (69), 136 (100), 107 (33), 91 (24), 90 (26), 89 (34), 77 (32).

5,5'-Diisopropyl-2,2'-bis-*p*-benzoquinone (*i*Pr$_2$-BBQ)

To a mixture of *n*-butyllithium (1.6 M hexane solution, 2.1 mL, 3.3 mmol) in dry THF (1 mL), a solution of **2** (279 mg, 2.00 mmol) in dry THF (1.6 mL) was added at room temperature under argon. After stirring for 1 h, acetone (480 mg, 8.20 mmol) dissolved in dry THF (2.2 mL) was slowly added. After stirring for 1 h, the mixture was quenched by adding excess amount of water dropwise. The aqueous layer was then separated and extracted with diethyl ether. The combined organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane–ether = 1/2) to yield **11** (186 mg, 47%) as a yellow liquid. IR (neat): ν = 3444, 2965, 2939, 2834, 1491, 1464, 1420, 1281, 1218, 1178, 1070, 1050, 1026 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.91 (d, *J* = 3.2 Hz, 1H; CC*H*C(OCH_3)), 6.85 (d, *J* = 8.6 Hz, 1H; CC(OCH_3)C*H*), 6.74 (dd, *J* = 8.8, 3.2 Hz, 1H; CC(OCH_3)CHC*H*), 4.25 (s, 1H; OH), 3.88 (s, 3H; OCH_3), 3.78 (s, 3H; OCH_3), 1.59 (s, 6H; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.5, 151.0, 137.1, 113.0, 111.9, 111.1, 72.4, 55.7, 55.6, 29.5 ppm; LRMS (EI): *m*/*z* (%): 196 (47) [M^+], 181 (98), 43 (100).

To a mixture of 10% palladium on carbon (43 mg) and **11** (372 mg, 1.90 mmol) in ethyl acetate (5 mL), a drop of sulfuric acid was added, then the mixture was stirred at room temperature under the atmosphere of hydrogen using a balloon. After stirring for 24 h, water (50 mL) was added dropwise to the mixture. The palladium on carbon was filtered off, and the aqueous layer was separated and extracted with diethyl ether. The combined organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane–chloroform = 4/1) to yield **12** (284 mg, 79%) as a yellow liquid. IR (neat): ν = 2959, 1501, 1464, 1281, 1220, 1048 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.84 (d, *J* = 2.4 Hz, 1H; CC*H*C(OCH_3)), 6.80 (d, *J* = 8.4 Hz, 1H; CC(OCH_3)C*H*), 6.70 (dd, *J* = 8.4, 2.4 Hz, 1H; CC(OCH_3)CHC*H*), 3.81 (s, 3H; OCH_3), 3.80 (s, 3H; OCH_3), 3.33 (sept, *J* = 6.8 Hz, 1H; CH), 1.23 (d, *J* = 7.6 Hz, 6H; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.7, 151.0, 138.4, 113.0, 111.2, 109.9, 56.0, 55.5, 26.8, 22.7 ppm; LRMS (EI): *m*/*z* (%): 180 (74) [M^+], 165 (100), 150 (50), 105 (17).

To a mixture of CAN (1.15 g, 2.10 mmol) in water (4 mL), a solution of **12** (115 mg, 0.63 mmol) in acetonitrile (4 mL) was added dropwise at room temperature. After stirring for 1 h, water (40 mL) was added to the mixture. The mixture was filtered through a glass filter, and the residue was washed with water and then dried over under reduced pressure. The crude product obtained was recrystallized from chloroform / ethanol to yield ***i*Pr$_2$-BBQ** (76 mg, 81%) as a yellow crystalline solid. M.p. 173.5–175.0 °C; IR (KBr): ν = 2966, 1653, 1600, 1233, 1048, 925 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.81 (s, 2H; CC*H*CO), 6.63 (s, 2H; C(*i*Pr)C*H*), 3.07 (sept, *J* = 6.4 Hz, 2H; CH), 1.16 (d, *J* = 6.8 Hz, 12H; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.4, 185.4, 155.3, 139.0, 136.4, 130.7, 26.8, 21.3 ppm; LRMS (EI): *m*/*z* (%): 300 (19), 299 (15), 298 (8) [M^+], 154 (27), 149 (100), 136 (26), 83 (27), 81 (28), 71 (44), 69 (43), 57 (35), 55 (27); HRMS (EI): found [M^+] 298.1193, $C_{18}H_{18}O_4^+$ requires 298.1205.

5,5'-Di-*tert*-butyl-2,2'-bis-*p*-benzoquinone (*t*Bu$_2$-BBQ)

To a mixture of sodium hydride (178 mg, 4.40 mmol) in DMF (3 mL), a solution of **13** (334 mg, 2.00

mmol) in DMF (3 mL) was added at room temperature under N_2. Then, methyl iodide (1.36 g, 9.60 mmol) was slowly added to the mixture, and stirred for 4 h at 40 °C. After cooling to room temperature, the mixture was quenched by adding excess amount of water dropwise. The aqueous layer was then separated and extracted with diethyl ether. The combined organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane–ether = 95/5) to yield **14** (323 mg, 83%) as a yellow liquid. IR (neat): ν = 2952, 2927, 1499, 1488, 1464, 1283, 1221, 1059, 1032 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.89 (d, *J* = 3.2 Hz, 1H; C(*t*Bu)C*H*), 6.88 (d, *J* = 8.8 Hz, 1H; C(*t*Bu)C(OCH_3)C*H*), 6.79 (dd, *J* = 8.4, 3.2 Hz, 1H; CC(OCH_3)CHC*H*), 3.80 (s, 3H; OCH_3), 3.77 (s, 3H; OCH_3), 1.36 (s, 9H; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.2, 152.8, 139.8, 114.2, 112.2, 109.7, 55.6, 55.5, 34.9, 29.6 ppm; LRMS (EI): *m*/*z* (%): 194 (56) [M^+], 179 (100), 164 (36), 151 (36).

To a mixture of CAN (2.71 g, 4.90 mmol) in water (10 mL), a solution of **14** (320 mg, 1.70 mmol) in acetonitrile (10 mL) was added dropwise at room temperature. After stirring for 1 h, water (60 mL) was added to the mixture. The mixture was filtered through a glass filter, and the residue was washed with water and then dried over under reduced pressure. The crude product obtained was recrystallized from chloroform / ethanol to yield ***t*Bu$_2$-BBQ** (150 mg, 56%) as a yellow crystalline solid. M.p. 194.0–196.0 °C; IR (KBr): ν = 2956, 2924, 1658, 1630, 1594, 1362, 1237, 914 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.75 (s, 2H; CC*H*CO), 6.68 (s, 2H; C(*t*Bu)C*H*), 1.31 (s, 18H; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.6, 185.6, 156.4, 138.0, 137.6, 131.9, 35.3, 29.0 ppm; LRMS (EI): *m*/*z* (%): 326 (48) [M^+], 311 (56), 285 (36), 284 (87), 283 (34), 269 (100), 201 (48), 41 (40).

Details of DFT calculations and Gaussian archives of optimized structures at the B3LYP/6-31+G* level

DFT calculations were carried out using GAUSSIAN 09 program.[1] Geometry optimization were performed using standard gradient techniques at the B3LYP level of theory using restricted (RB3LYP) and unrestricted (UB3LYP) methods for closed- and open-shell systems, respectively.[2] In every case, 6-31+G* was used as the basis set, and all ground states were verified by vibration frequency analysis. The calculated molecular structures were visualized by Gauss View 5.0.[3]

The singlet and triplet states of the BBQ dianion, the doublet and quartet states of the trianion, and singlet, triplet, and quintet states of the tetraanion were calculated and summarised in the following Table. BQ dianion and trianion are more stable in singlet and doublet states than in triplet and quartet states, respectively, while BBQ dianion and trianion are more stable in triplet and doublet states than in singlet and quartet states, respectively. Although the BBQ tetraanion had similar energies in singlet and triplet states, the singlet was determined as the most stable state considering that the triplet state was highly spin contaminated.

Species	Spin state	Energy (kJ mol^{-1})	<S^2> value[a]
BQ dianion	singlet	-1001446.2	——
	triplet	-1001326.5	2.082
BQ trianion	doublet	-1000698.6	0.751
	quartet	-1000623.0	3.822
BBQ dianion	singlet	-2000099.7	——
	triplet	-2000134.6	2.278
BBQ trianion	doublet	-1999622.3	1.360
	quartet	-1999553.6	4.089
BBQ tetraanion	singlet	-1998790.5	——
	triplet	-1998789.7	2.598
	quintet	-1998752.0	6.406

[a] Determined by the HF/6-31+G* level.

BQ

1\1\GINC-HEX\FOpt\RB3LYP\6-31+G(d)\C6H4O2\YOKOJI\10-Aug-2015\0\\#B3LYP/6-31+G* opt=(ReadFC,Maxcycle=100) NoSymm freq=NoRaman geom=check guess=read\\bqb3+\\0,1\C,1.1473960993,0.6385839984,0.0000000008\C,-1.2455936404,1.2457168671,0.0000000035\C,-0.512664242,-1.1884288198,-0.0000000034\C,-1.6176902387,-0.1937182215,-0.0000000006\C,0.7752942945,-0.8008521598,0.\C,0.0423659446,1.6332890664,-0.0000000026\H,-2.0720010581,1.9520647157,0.0000000074\H,-0.8119264774,-2.2335912849,-0.0000000048\H,0.341651651,2.6784450456,-0.0000000088\O,2.3221669073,0.9923242349,0.0000000025\O,-2.7924601291,-0.5474613541,0.\H,1.6017108891,-1.5071845781,0.0000000059\\Version=EM64L-G09RevC.01\HF=-381.4704834\RMSD=3.710e-09\RMSF=1.597e-04\Dipole=0.0000008,0.0000037,0.\Quadrupole=-9.3959157,6.969247,2.4266688,-5.4190299,0.,0.\PG=C01 [X(C6H4O2)]\\@

BQ anion radical

1\1\GINC-HEX\FOpt\UB3LYP\6-31+G(d)\C6H4O2(1-,2)\YOKOJI\07-Sep-2015\0\\#B3LYP/6-31+G* opt=(ReadFC,Maxcy
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2004556137,0.000000001\C,0.7762825226,-0.7523958326,0.0000000001\C,0.0701615082,1.5934015139,0.0000000002\H,-
2.0533614742,1.9300581383,-0.0000000004\H,-0.8087995645,-2.2049257995,-0.0000000005\H,0.3385081895,2.64979014
72,-0.0000000005\O,2.3885404091,1.0121158865,0.0000000007\O,-2.8588325568,-0.567251678,0.0000000007\H,1.58306
96694,-1.4851929873,-0.0000000004\\Version=EM64L-G09RevC.01\HF=-381.5500259\S2=0.761125\S2-1=0.\S2A=0.7500
4\RMSD=5.840e-09\RMSF=4.801e-05\Dipole=0.0000022,0.0000005,0.\Quadrupole=-17.0104226,8.1357382,8.8746844,-8.
129647,0.,0.\PG=CS [SG(C6H4O2)]\\@

BQ dianion (singlet)

1\1\GINC-HEX\FOpt\RB3LYP\6-31+G(d)\C6H4O2(2-)\YOKOJI\07-Sep-2015\0\\#B3LYP/6-31+G* opt=(ReadFC,Maxcycl
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611783,0.0000000037\C,0.7825791502,-0.71404129,0.0000000021\C,0.0968597503,1.5649167725,0.0000000004\H,-2.041
7433894,1.919837133,0.0000000022\H,-0.8051207041,-2.190000515,-0.0000000042\H,0.3348278472,2.6348643575,-0.000
0000013\O,2.466028291,1.0351184497,-0.0000000061\O,-2.9363209113,-0.5902504951,-0.0000000047\H,1.5714528711,-1.
4749725858,0.0000000058\\Version=EM64L-G09RevC.01\HF=-381.4306621\RMSD=2.621e-09\RMSF=3.335e-05\Dipole=
0.0000002,0.000007,0.\Quadrupole=-26.5357374,10.0961101,16.4396273,-11.7316984,0.,0.\PG=C01 [X(C6H4O2)]\\@

BQ dianion (triplet)

1\1\GINC-HEX\FOpt\UB3LYP\6-31+G(d)\C6H4O2(2-,3)\YOKOJI\07-Sep-2015\0\\#B3LYP/6-31+G* opt=(ReadFC,Maxcy
cle=100) NoSymm freq=NoRaman geom=check guess=read\\bqdiani_tb3+\\-2,3\C,1.1517051528,0.6398139779,-0.00000
00037\C,-1.2504952668,1.2090974392,-0.0000000021\C,-0.5371206073,-1.1605380364,-0.0000000008\C,-1.6219724052,-
0.1949419362,-0.0000000034\C,0.7801736459,-0.7642009423,-0.0000000077\C,0.0668213364,1.6053601848,-0.00000000
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204715,-0.0000000041\O,2.3794228588,1.0094182017,0.0000000131\O,-2.8496660064,-0.5645403031,0.0000000041\H,1.
5828068154,-1.5043744054,-0.0000000029\\Version=EM64L-G09RevC.01\HF=-381.3850578\S2=2.010858\S2-1=0.\S2A=
2.000029\RMSD=4.382e-09\RMSF=6.300e-05\Dipole=0.0006022,0.000176,0.\Quadrupole=-9.4420042,-14.5613075,24.003
3117,2.0941194,0.,0.\PG=C01 [X(C6H4O2)]\\@

BQ radical trianion (doublet)

1\1\GINC-I7\FOpt\UB3LYP\6-31+G(d)\C6H4O2(3-,2)\YOKOJI\24-Sep-2015\0\\#B3LYP/6-31+G* opt=(ReadFC,Maxcycle
=100) NoSymm freq=NoRaman geom=check guess=read\\bqradtrianib3+\\-3,2\C,1.1759334645,0.6469238006,-0.000000
0037\C,-1.2589570636,1.1787564209,-0.0000000025\C,-0.5613350778,-1.139927229,-0.0000000013\C,-1.6462010964,-0.2
020868079,-0.0000000027\C,0.7886323578,-0.7338498394,-0.0000000007\C,0.0910377929,1.5847931815,-0.0000000011
\H,-2.0486933569,1.9375794324,-0.0000000015\H,-0.801197311,-2.2085933933,0.0000000037\H,0.3308731859,2.6534668
673,0.0000000096\O,2.4515378956,1.0306295218,-0.0000000046\O,-2.921783745,-0.5858559938,0.0000000007\H,1.5784
029539,-1.4926484511,0.0000000042\\Version=EM64L-G09RevC.01\HF=-381.1459255\S2=0.750385\S2-1=0.\S2A=0.75\R
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103823,0.,0.\PG=C01 [X(C6H4O2)]\\@

BQ trianion (quartet)

1\1\GINC-I7\FOpt\UB3LYP\6-31+G(d)\C6H4O2(3-,4)\YOKOJI\24-Sep-2015\0\\#B3LYP/6-31+G* opt=(ReadFC,Maxcycle
=100) NoSymm freq=NoRaman geom=check guess=read\\bqtriani_qb3+\\-3,4\C,1.1465935269,0.6375382051,0.0005394

374\C,-1.2518446907,1.2151280769,0.0000604907\C,-0.5361929961,-1.1660233197,-0.0004491558\C,-1.6168881742,-0.19
27050116,-0.0005580095\C,0.7815707376,-0.7702772742,0.0001821872\C,0.0659073767,1.6109034044,0.0007657824\H,-
2.0462786929,1.9631124019,-0.0000934307\H,-0.7868316804,-2.228014512,-0.0007447715\H,0.3165371537,2.672899725
1,0.0004527883\O,2.3805113446,1.0084339042,0.0007273884\O,-2.8508343641,-0.5635454061,-0.0012267105\H,1.57600
04589,-1.518258194,0.0003440037\\Version=EM64L-G09RevC.01\HF=-381.1171206\S2=3.760769\S2-1=0.\S2A=3.750024
\RMSD=9.435e-09\RMSF=2.076e-05\Dipole=-0.0003198,-0.0000959,-0.00115\Quadrupole=-5.8660167,-34.7434279,40.60
94447,10.1303205,-0.0116159,-0.0205312\PG=C01 [X(C6H4O2)]\\@

BBQ

1\1\GINC-HEX\FOpt\RB3LYP\6-31+G(d)\C12H6O4\YOKOJI\12-Jun-2014\0\\#B3LYP/6-31+G* opt=(ReadFC,Maxcycle=
100) NoSymm freq=NoRaman geom=check guess=read\\bbqb3+\\0,1\C,-1.2778582671,-1.4267324274,0.4361316144\C,-
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93,-0.4414232863\C,-0.7317500355,-0.1032558785,-0.0381814097\C,-2.7508698711,-1.6163630807,0.4284331341\H,-1.27
00518354,1.8306300507,-0.7749048935\H,-3.0920156125,-2.5870845395,0.7778938327\O,-0.5487332502,-2.3290135418,
0.831570026\O,-3.8252386423,1.5407150279,-0.8337297144\H,-4.6728577919,-0.7740987873,0.0189141313\C,3.0712338
981,-0.6550740049,-0.4414242718\C,0.7317500293,0.1032558913,-0.0381815187\C,2.7508699601,1.6163628783,0.428433
3068\C,1.2778583585,1.4267322155,0.436132027\C,3.5932714312,0.6508159938,0.0263997755\C,1.6022138223,-0.85758
87245,-0.4311026702\H,3.0920157774,2.5870841691,0.7778943972\H,1.2700516728,-1.8306296847,-0.7749060479\O,3.8
252384678,-1.5407146211,-0.8337312928\O,0.5487334258,2.329013131,0.8315710445\H,4.6728577939,0.7740987877,0.0
18913476\\Version=EM64L-G09RevC.01\HF=-761.742748\RMSD=6.903e-09\RMSF=2.699e-06\Dipole=0.,0.,0.0415335\Q
uadrupole=3.0018799,-4.9835492,1.9816693,16.7248217,0.0000039,-0.0000035\PG=C01 [X(C12H6O4)]\\@

BBQ anion radical

1\1\GINC-HEX\FOpt\UB3LYP\6-31+G(d)\C12H6O4(1-,2)\YOKOJI\12-Jun-2014\0\\#B3LYP/6-31+G* opt=(ReadFC,Maxc
ycle=100) NoSymm freq=NoRaman geom=check guess=read\\bbqradanib3+\\-1,2\C,-1.2585144815,-1.4673858664,0.329
5123518\C,-3.5747921519,-0.6318463078,0.0269395058\C,-1.6330455883,0.882427057,-0.331957872\C,-3.0705603905,0.
6980890418,-0.3485093217\C,-0.7244018479,-0.1165374765,-0.0304275964\C,-2.7242339941,-1.6331054684,0.341691391
\H,-1.2876360973,1.8755217011,-0.5887735852\H,-3.0709169042,-2.6275520533,0.6146420435\O,-0.5468158108,-2.4382
2992,0.6386828011\O,-3.8653397769,1.610626389,-0.6787163803\H,-4.6551040822,-0.7647790775,0.0269144395\C,3.070
5605998,-0.6980890962,-0.3485086705\C,0.7244020481,0.1165373891,-0.0304275161\C,2.7242337216,1.6331054991,0.34
16917827\C,1.2585142377,1.4673858553,0.3295123638\C,3.5747919957,0.6318463987,0.0269401689\C,1.6330459295,-0.
8824271656,-0.3319575022\H,3.0709165321,2.6275521259,0.6146424294\H,1.287636588,-1.8755218653,-0.5887731975
\O,3.8653402742,-1.6106263761,-0.6787154101\O,0.5468152842,2.4382298955,0.6386824182\H,4.6551039147,0.7647793
208,0.0269153563\\Version=EM64L-G09RevC.01\HF=-761.8470123\S2=0.770726\S2-1=0.\S2A=0.750203\RMSD=5.461e-
09\RMSF=1.914e-06\Dipole=-0.0000018,-0.0000004,0.1935648\Quadrupole=-14.0494731,-2.0548402,16.1043133,19.1016
06,-0.000003,0.0000029\PG=C01 [X(C12H6O4)]\\@

BBQ dianion (singlet)

1\1\GINC-HEX\FOpt\RB3LYP\6-31+G(d)\C12H6O4(2-)\YOKOJI\12-Jun-2014\0\\#B3LYP/6-31+G* opt=(CalcFC,Maxcyc
le=100) NoSymm freq=NoRaman geom=check guess=read\\bbqdiani_sb3+\\-2,1\C,-1.2495756318,-1.4986003841,0.2213
382639\C,-3.5676619366,-0.6127674767,0.0473699671\C,-1.665904756,0.8981794996,-0.2603430762\C,-3.0872454416,0.
7315898072,-0.2643001902\C,-0.7233088325,-0.1271184099,-0.0422303632\C,-2.7056199132,-1.6414525824,0.280357706
7\H,-1.3071095909,1.9020696644,-0.4418755316\H,-3.0584530652,-2.6502695869,0.4971730927\O,-0.548198019,-2.5285
388873,0.4154036359\O,-3.9225344585,1.6660807464,-0.525783855\H,-4.6496882494,-0.7576217608,0.0694310953\C,3.0
87325577,-0.731656962,-0.2631720628\C,0.7233219275,0.1271083688,-0.0420413817\C,2.7055348726,1.6415237519,0.28
07681309\C,1.2495084574,1.498656885,0.2213407273\C,3.5676473773,0.6127792531,0.0483036658\C,1.6659837043,-0.8
982451374,-0.2596069785\H,3.0583023939,2.6503953434,0.4974361296\H,1.3072428039,-1.902180638,-0.4409956269\O,
3.9226939096,-1.6662145503,-0.5241635154\O,0.5480718568,2.5286443166,0.4149325839\H,4.6496670144,0.757638739

4,0.0706575824\\Version=EM64L-G09RevC.01\HF=-761.7976553\RMSD=2.897e-09\RMSF=3.408e-06\Dipole=-0.000050 4,0.0000422,0.3337398\Quadrupole=-33.0328518,0.7610427,32.2718091,22.5885661,-0.0128397,0.0074347\PG=C01 [X(C 12H6O4)]\\@

BBQ dianion (triplet)

1\1\GINC-HEX\FOpt\UB3LYP\6-31+G(d)\C12H6O4(2-,3)\YOKOJI\12-Jun-2014\0\\#B3LYP/6-31+G* opt=(ReadFC,Maxc ycle=100) NoSymm freq=NoRaman geom=check guess=read\\bbqdiani_tb3+\\-2,3\C,-1.3258715512,-1.0347011127,1.030 4103049\C,-3.5446631596,-0.6070129483,-0.0136795176\C,-1.5394365194,0.4558584498,-0.9240795707\C,-2.975065382, 0.2627335761,-1.0193718036\C,-0.7372796096,-0.12742625,0.0352309775\C,-2.7648495522,-1.210422278,0.9459969114 \H,-1.0942372801,1.1204710879,-1.663504999\H,-3.2045837273,-1.8743365846,1.6916141165\O,-0.639969088,-1.662844 9436,1.8934913871\O,-3.6862381957,0.8204962627,-1.924442379\H,-4.6232213382,-0.7691712374,-0.0516736792\C,2.97 50660583,-0.262733432,-1.0193699972\C,0.7372796172,0.1274260559,0.0352314807\C,2.7648489209,1.2104221918,0.94 59987501\C,1.3258708885,1.0347008597,1.0304112614\C,3.5446631432,0.6070131063,-0.013677319\C,1.53943715,-0.45 58584297,-0.9240786687\H,3.204582575,1.874336504,1.6916162582\H,1.0942384003,-1.1204709252,-1.663504522\O,3.6 862394819,-0.8204959817,-1.9244401648\O,0.6399678509,1.6628444686,1.8934920499\H,4.6232213171,0.7691715604,-0. 051670877\\Version=EM64L-G09RevC.01\HF=-761.8109459\S2=2.021559\S2-1=0.\S2A=2.000233\RMSD=9.051e-09\RM SF=3.493e-06\Dipole=-0.0000002,0.,0.5073304\Quadrupole=-25.9708775,20.3556857,5.6151918,7.7762014,-0.0000092,0.0 000041\PG=C01 [X(C12H6O4)]\\@

BBQ radical trianion (doublet)

1\1\GINC-HEX\FOpt\UB3LYP\6-31+G(d)\C12H6O4(3-,2)\YOKOJI\12-Jun-2014\0\\#B3LYP/6-31+G* opt=(ReadFC,Maxc ycle=100) NoSymm freq=NoRaman geom=check guess=read\\bbqradtrianib3+\\-3,2\C,-1.256072923,-1.4807978561,0.42 48186724\C,-3.5537288613,-0.6072436752,-0.0552327445\C,-1.6537937136,0.8577107886,-0.3135345976\C,-3.074889599 6,0.7000816849,-0.4218240357\C,-0.7305694082,-0.1456219035,0.0590220951\C,-2.6920538729,-1.6193755417,0.346855 7947\H,-1.2612500439,1.8445720016,-0.5394508919\H,-3.0806170153,-2.6056100772,0.62014438\O,-0.5452388681,-2.48 10256276,0.8178273305\O,-3.8880000752,1.6407010305,-0.8268030191\H,-4.6344904314,-0.781851115,-0.1118256021\C, 3.074889702,-0.7000817351,-0.4218234483\C,0.7305694783,0.1456219712,0.0590222453\C,2.6920537407,1.6193755048, 0.3468564383\C,1.2560728089,1.4807979142,0.4248189048\C,3.5537288352,0.6072436098,-0.055231944\C,1.653793857 4,-0.8577107738,-0.3135343365\H,3.0806168876,2.6056100186,0.6201451212\H,1.2612502161,-1.8445719604,-0.5394508 111\O,3.8880003193,-1.640701099,-0.8268022957\O,0.5452385453,2.4810257649,0.8178272531\H,4.6344904217,0.78185 10755,-0.111824509\\Version=EM64L-G09RevC.01\HF=-761.6157972\S2=0.768778\S2-1=0.\S2A=0.750205\RMSD=8.474 e-09\RMSF=2.784e-06\Dipole=-0.0000019,-0.0000004,0.3268645\Quadrupole=-49.2702799,5.9054319,43.364848,21.0406 65,-0.0000072,0.0000001\PG=C01 [X(C12H6O4)]\\@

BBQ trianion (quartet)

1\1\GINC-HEX\FOpt\UB3LYP\6-31+G(d)\C12H6O4(3-,4)\YOKOJI\17-Jun-2014\0\\#B3LYP/6-31+G* opt=(ReadFC,Maxc ycle=100) NoSymm freq=NoRaman scf=xqc geom=check guess=read\\bbqtriani_qb3+\\-3,4\C,-1.2842671189,-1.4051815 606,-0.6060173101\C,-3.5458451484,-0.6334066644,0.0858514723\C,-1.5995559077,0.8087176347,0.435200155\C,-3.029 1632316,0.6269466423,0.5764245278\C,-0.7356827313,-0.1324022159,-0.1002233141\C,-2.7205192325,-1.5818598722,-0. 4698280489\H,-1.1985191344,1.7562671575,0.7869898712\H,-3.1347058875,-2.5215159617,-0.8395474335\O,-0.5727530 962,-2.3124873439,-1.1477562906\O,-3.7836940096,1.5174783662,1.1121725234\H,-4.6191213913,-0.817558773,0.16655 9936\C,3.0291615906,-0.6269462465,0.5764587169\C,0.735685319,0.132395031,-0.1002095913\C,2.7205187002,1.58186 57442,-0.4697860907\C,1.284269886,1.4051791028,-0.6059933114\C,3.5458418615,0.6334130493,0.0858988385\C,1.599 5569216,-0.808724409,0.4352177817\H,3.1347050507,2.5215252624,-0.8394964783\H,1.1985211688,-1.7562788881,0.78 69949815\O,3.7836927431,-1.5174772269,1.1122082172\O,0.5727572501,2.3124813694,-1.1477396286\H,4.6191163978,0. 8175698022,0.1666204761\\Version=EM64L-G09RevC.01\HF=-761.5896338\S2=3.770541\S2-1=0.\S2A=3.750158\RMSD =5.488e-07\RMSF=3.439e-05\Dipole=-0.0000024,-0.0000033,0.6381637\Quadrupole=-81.1018574,19.618495,61.4833625,- 23.7080612,-0.0009921,-0.000295\PG=C01 [X(C12H6O4)]\\@

BBQ tetraanion (signlet)

1\1\GINC-HEX\FOpt\RB3LYP\6-31+G(d)\C12H6O4(4-)\YOKOJI\16-Jun-2014\0\\#B3LYP/6-31+G* opt=(ReadFC,Maxcy
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61,0.8745945234\C,-3.532418039,-0.6331056249,-0.1363302079\C,-1.5893838612,0.6660062056,-0.6155060674\C,-3.0031
653406,0.4924983054,-0.8295389648\C,-0.7451874462,-0.1574182512,0.1576396787\C,-2.7287418197,-1.4681381578,0.6
728848325\H,-1.1287456698,1.5178645905,-1.1220294858\H,-3.1837422558,-2.336773485,1.1687691311\O,-0.642246323
6,-2.1220309819,1.6416649036\O,-3.7357929631,1.2944304007,-1.6014723876\H,-4.6140459882,-0.8206688787,-0.21062
27685\C,3.0031623435,-0.4925004681,-0.8295483905\C,0.7451879769,0.1574187701,0.1576364636\C,2.7287441939,1.46
81400442,0.6728710926\C,1.3158848589,1.3035079014,0.8745868904\C,3.5324175028,0.6331052917,-0.1363444837\C,1.
5893815907,-0.6660077082,-0.6155101862\H,3.183746406,2.3367769366,1.1687510771\H,1.1287415366,-1.5178672212,-
1.1220299982\O,3.7357872108,-1.2944344648,-1.6014824544\O,0.6422525711,2.1220340307,1.641658677\H,4.614045102
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ole=-0.0000001,0.0000002,0.180132\Quadrupole=-66.6988359,28.2781056,38.4207304,3.2724201,0.0001762,0.0000013\P
G=C01 [X(C12H6O4)]\\@

BBQ tetraanion (triplet)

1\1\GINC-HEX\FOpt\UB3LYP\6-31+G(d)\C12H6O4(4-,3)\YOKOJI\19-Jun-2014\0\\#B3LYP/6-31+G* opt=(CalcFC,Maxc
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33706761,0.7518266013,0.0026712716\C,-0.7351071286,-0.1502141051,0.0010623659\C,-2.7137372459,-1.6830613331,0.
0054381154\H,-1.3185397769,1.9152733109,-0.0003225933\H,-3.093640016,-2.7070756421,0.0072607166\O,-0.56993745
42,-2.6251415142,0.003606555\O,-3.9653492816,1.7622527222,0.0022507977\H,-4.6710914604,-0.793271028,0.00628530
92\C,3.1234396256,-0.7518288444,-0.0045526817\C,0.7351282461,0.1501901297,-0.001218827\C,2.7136503186,1.683055
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BBQ tetraanion (quintet)

1\1\GINC-HEX\FOpt\UB3LYP\6-31+G(d)\C12H6O4(4-,5)\YOKOJI\26-Dec-2014\0\\#B3LYP/6-31+G* opt=(ReadFC,Max
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6007860499,-0.7932409899,0.4588999543\H,3.1539266631,2.5176326202,-0.8398188142\H,1.1972797877,-1.733530596,0.
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7,-52.9685106,-0.2627032,-0.0405227\PG=C01 [X(C12H6O4)]\\@

Solubility study of BBQ derivatives

The solubilities of BBQ derivatives were measured for the non-substituted BBQ and R_2-BBQ (R = F, Cl, Br, Me, *n*Bu, and OMe) using tetraglyme as the electrolyte solution. The obtained solubilities and the related battery performance are summarized in the following table.

Solubility of the BBQs in tetraglyme and the related battery perormance.

Sample	Solubility in tetraglyme (g L^{-1})	Capacity retention[a] (%)
BBQ	4.0-5.0	67
F_2-BBQ	18-19	12
Cl_2-BBQ	9.0-10	68
Br_2-BBQ	3.0-4.0	>99[b]
Me_2-BBQ	7.0-8.0	46
nBu_2-BBQ	>23	37
$(OMe)_2$-BBQ	<1.0	60

[a] Ratio of the 20th capacity to the 1st value. [b] The capacity was rapidly decreased at around 25th cycle.

<u>Experimental method for solubility measurement</u>

R_2-BBQ (0.5 mg) was added to tetraglyme (0.5 mL), and the mixture was stirred at 20 °C for 5 min. The addition of 0.5 mg R_2-BBQ and stirring of the mixture were repeated, until undissolved R_2-BBQ remained after the stirring.

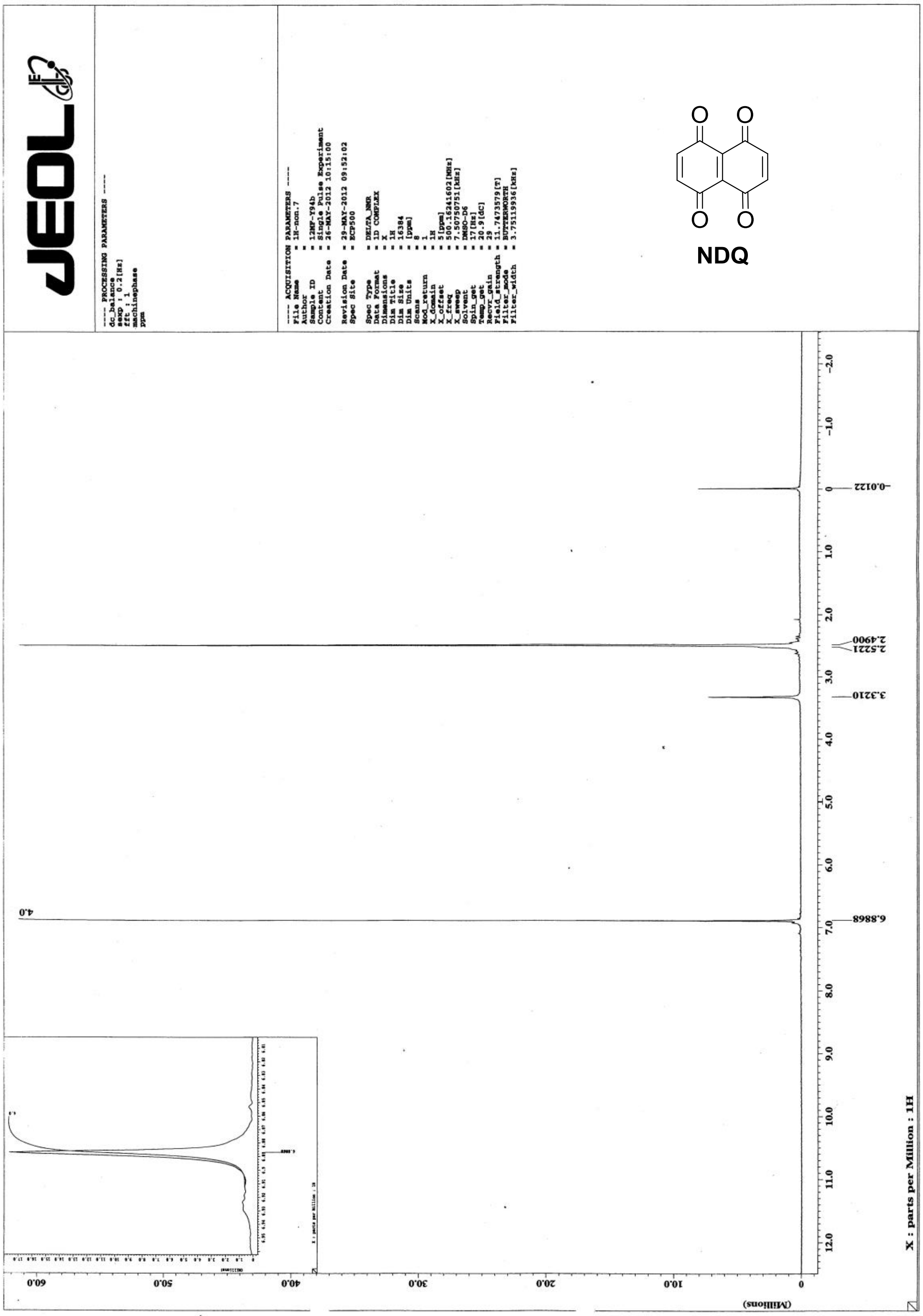
References

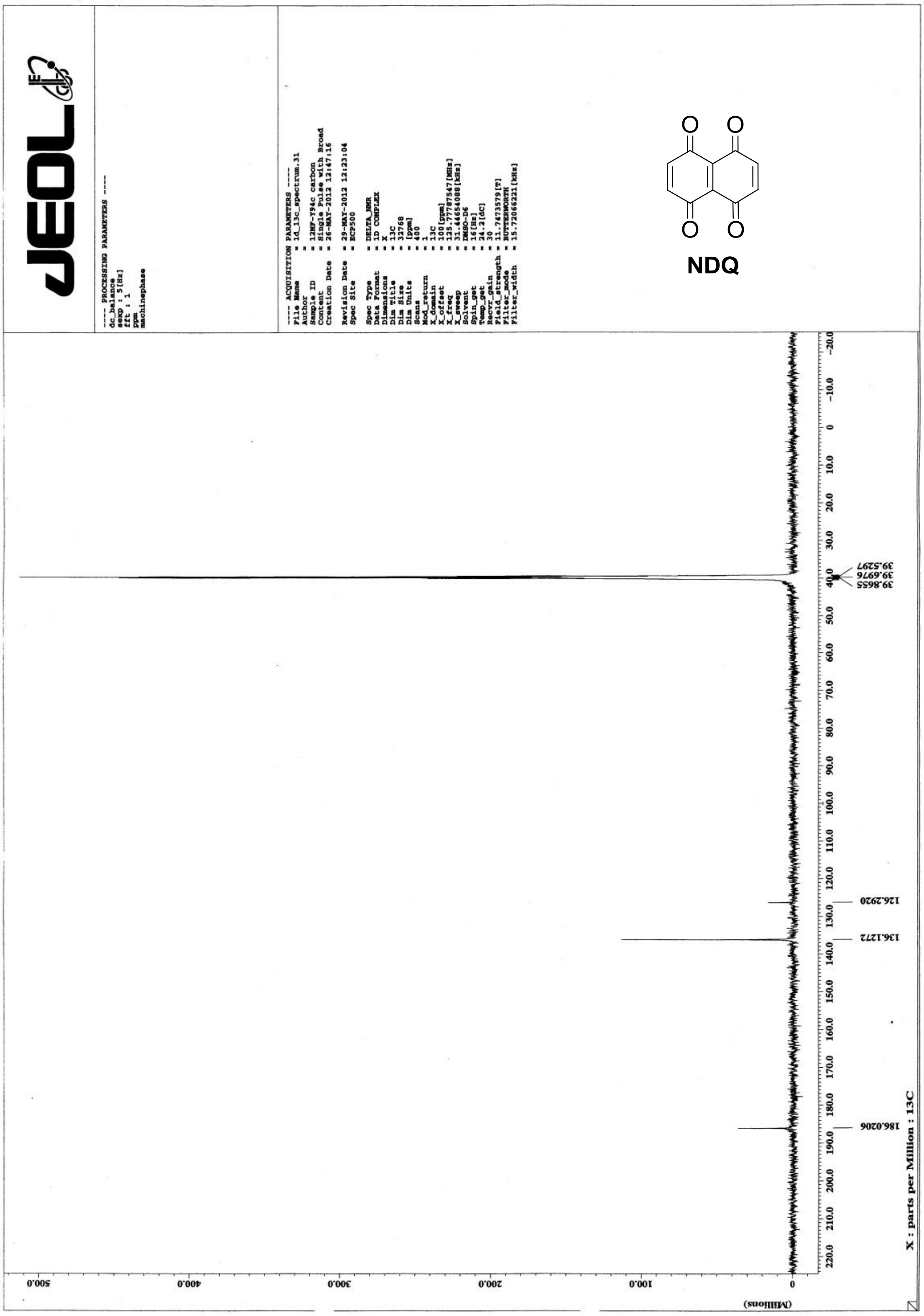
1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford CT, 2010.

2 W. J. Hehre, L. Radom, P. V. R. Schleyer and P. A. Pople, *Ab initio Molecular Orbital Theory*, Wiley, New York, 1986.

3 R. Dennington, T. Keith and J. Millam, Semichem Inc., Shawnee Mission, KS, 2009.

^{1}H and ^{13}C NMR of compounds involved in this study

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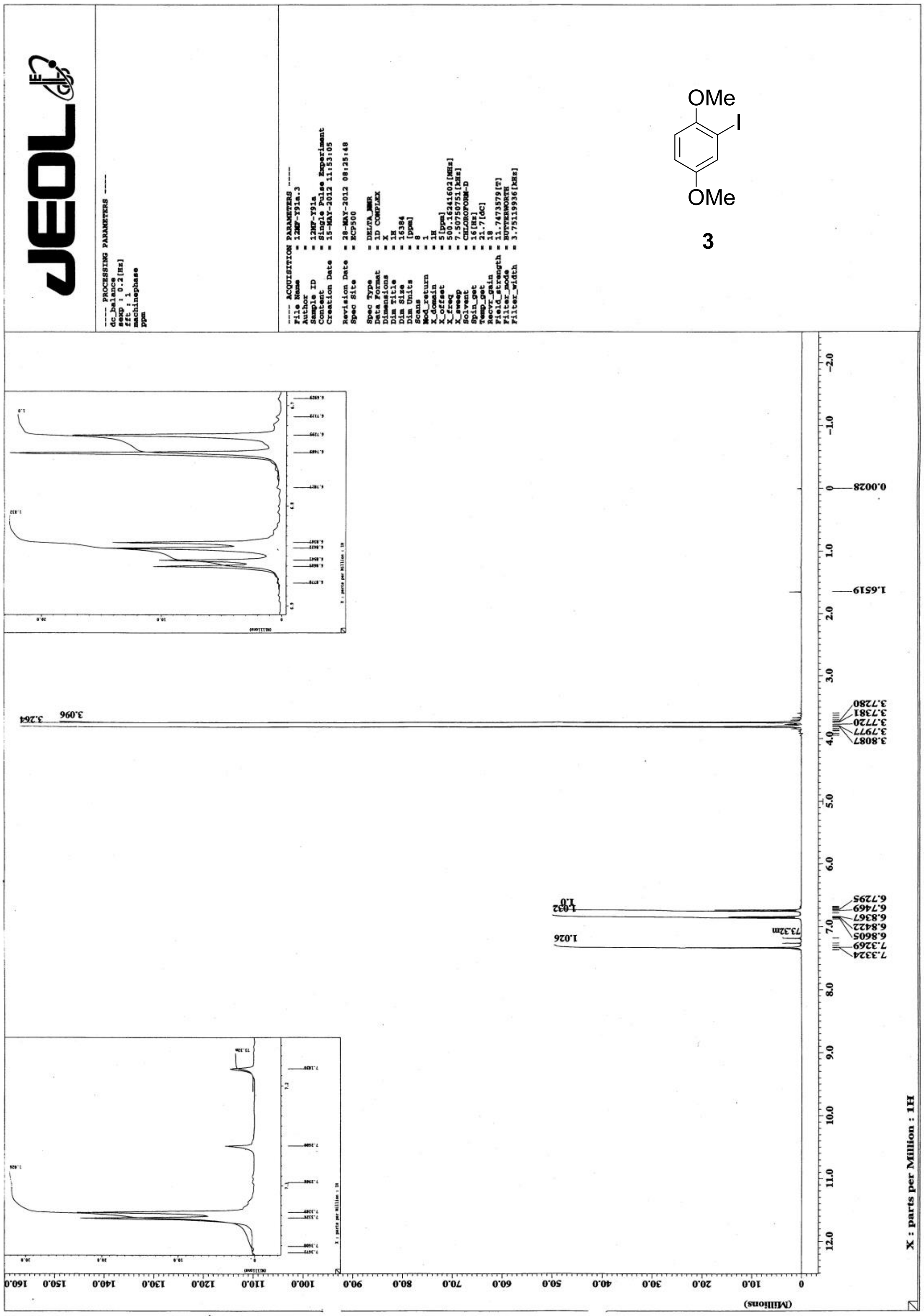
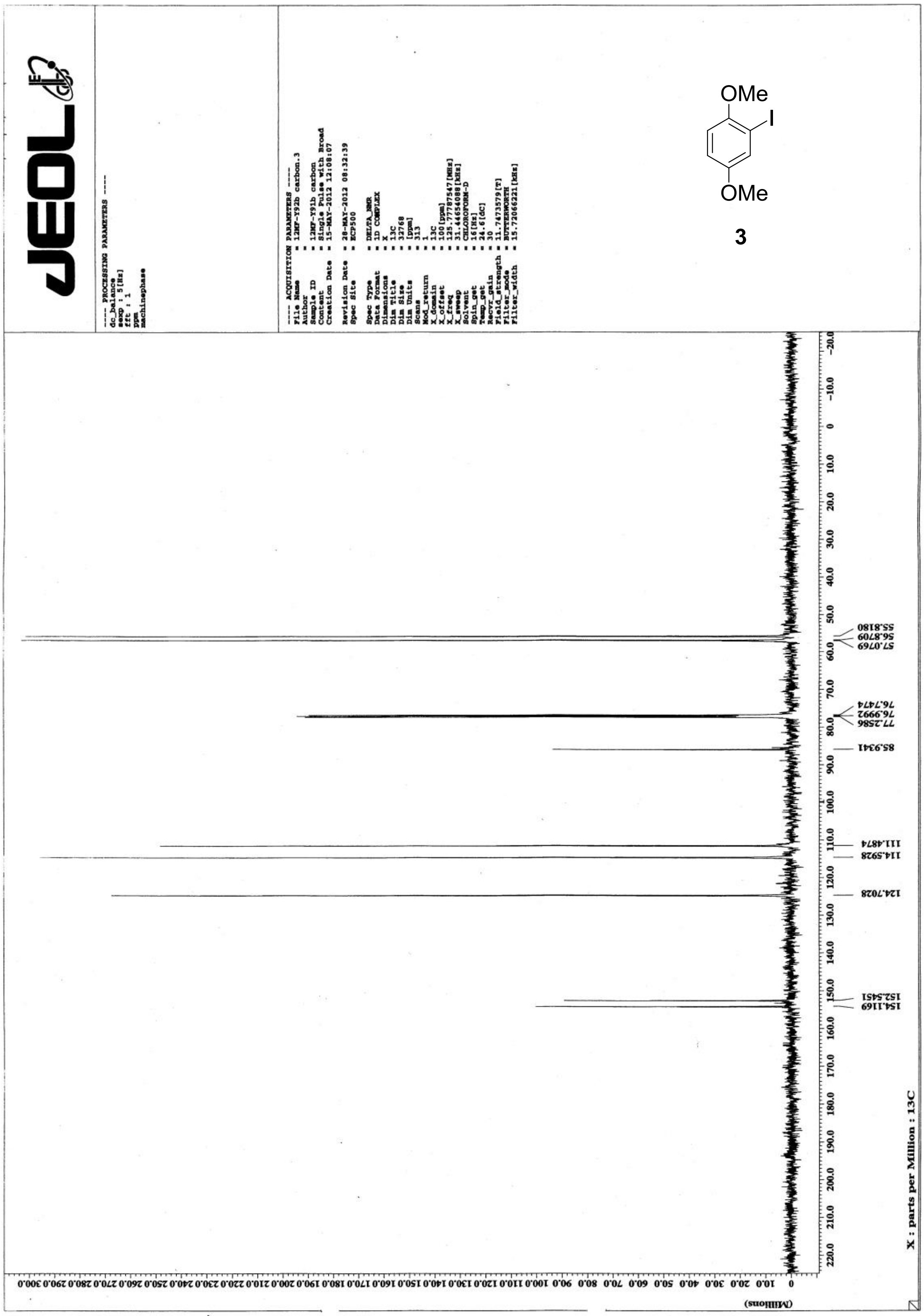
(Millions)


OMe
I
OMe
3
X : parts per Million : 1H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Revision Date = 28-MAY-2012 08:32:39
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OMe
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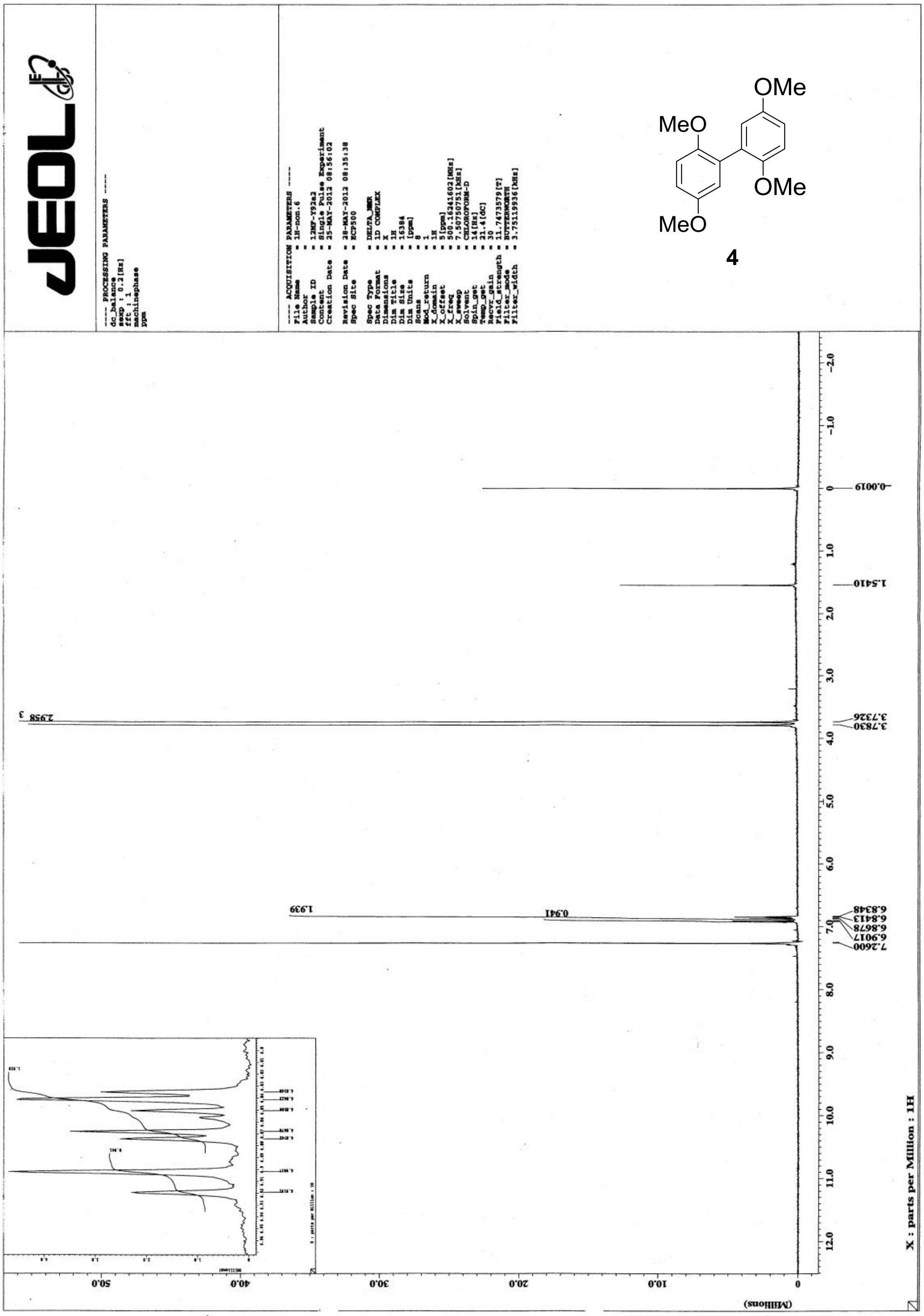
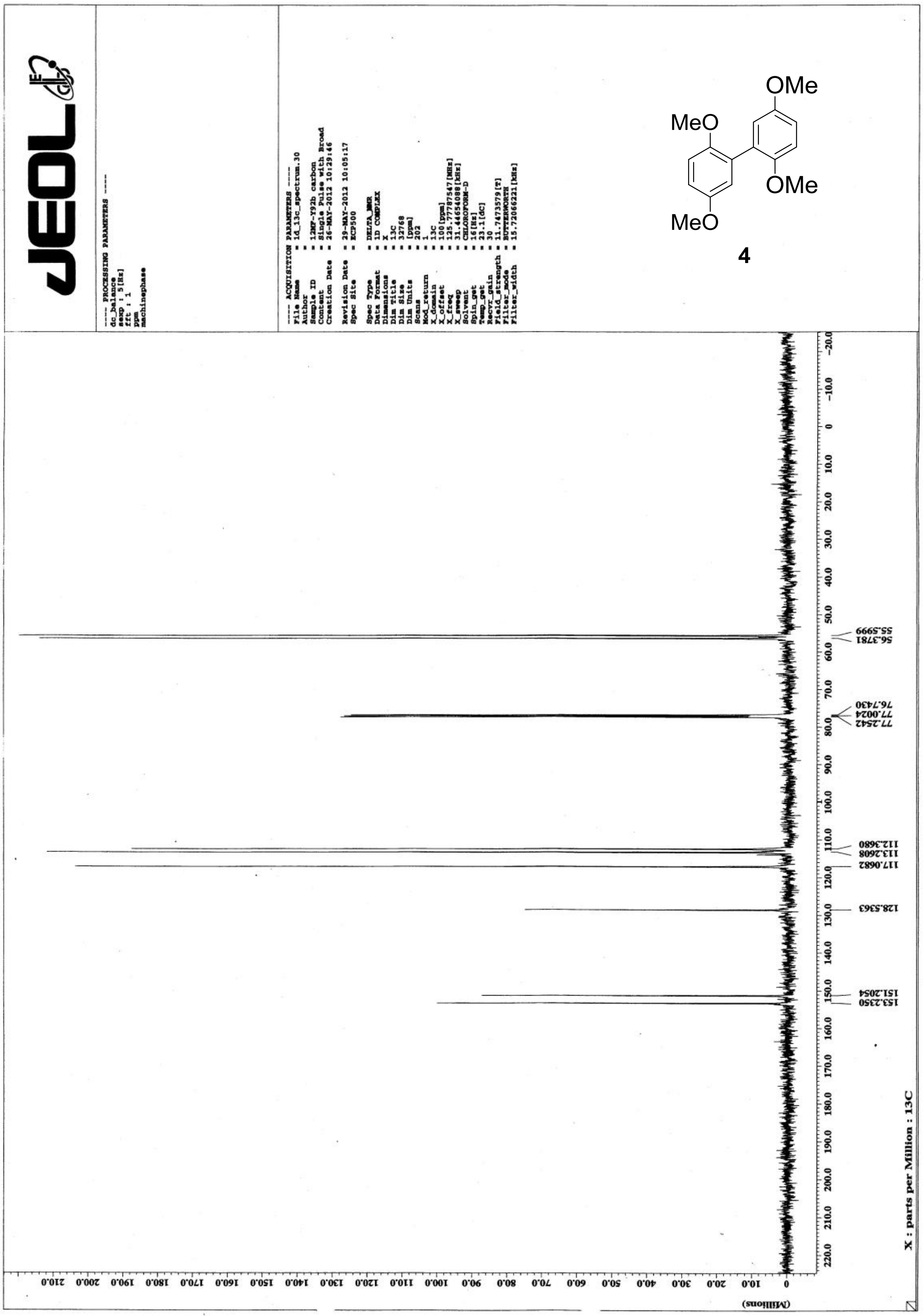
(Millions)


JEOL
MeO
OMe
OMe
MeO
4
X : parts per Million : 1H
(Millions)



MeO
OMe
MeO
OMe
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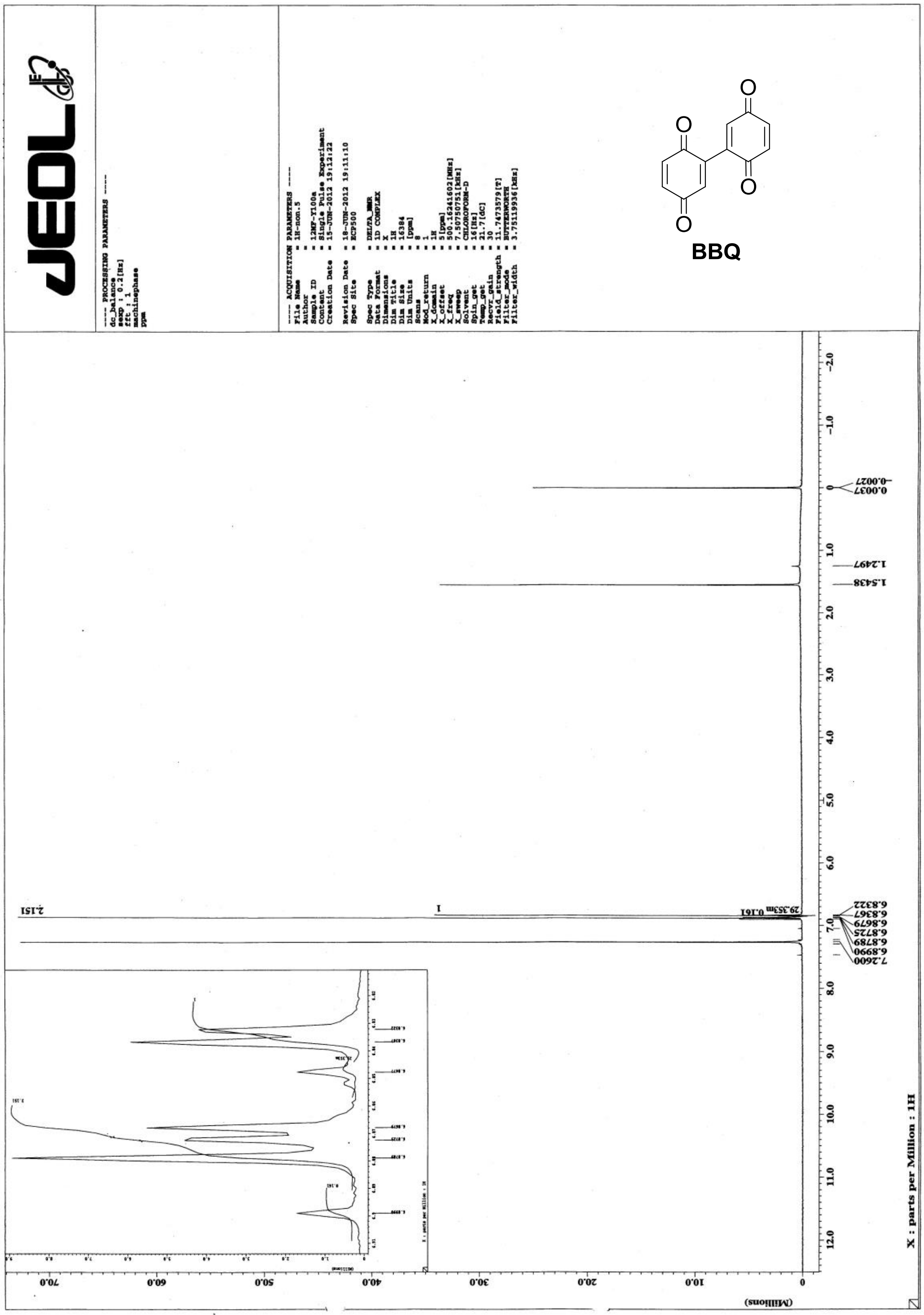
JEOL
BBQ
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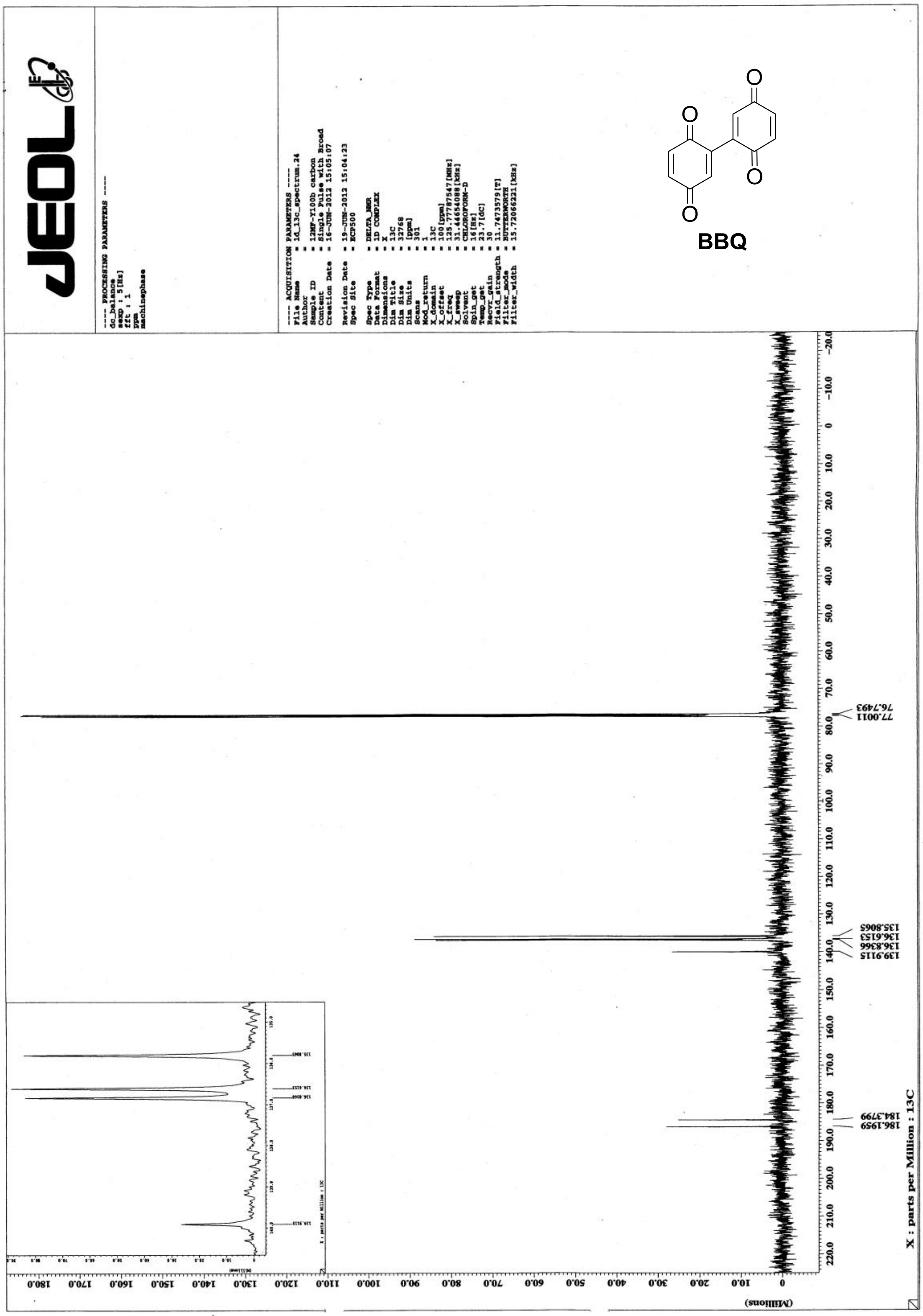
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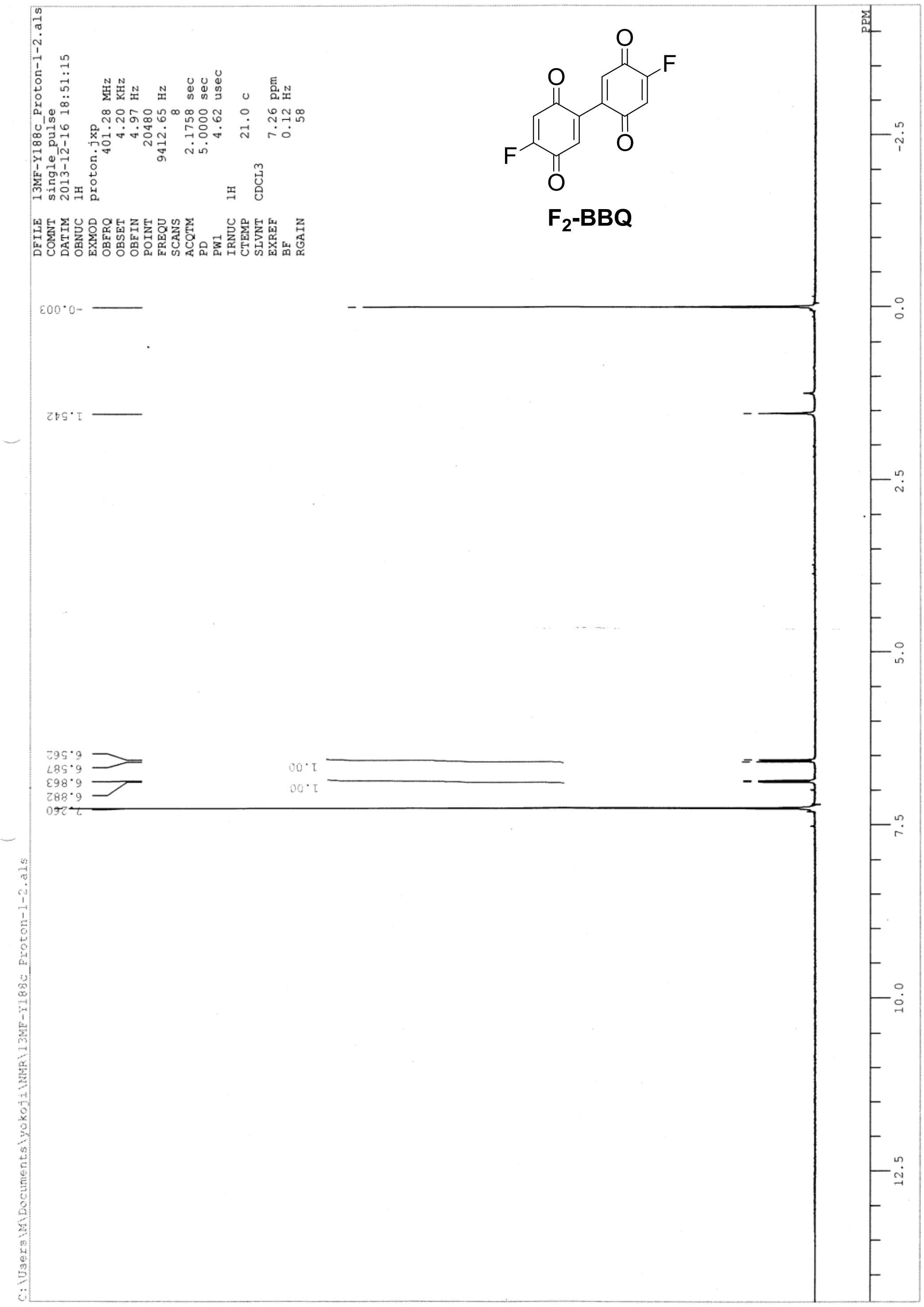
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OBSET 4.20 KHz
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PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 21.0 c
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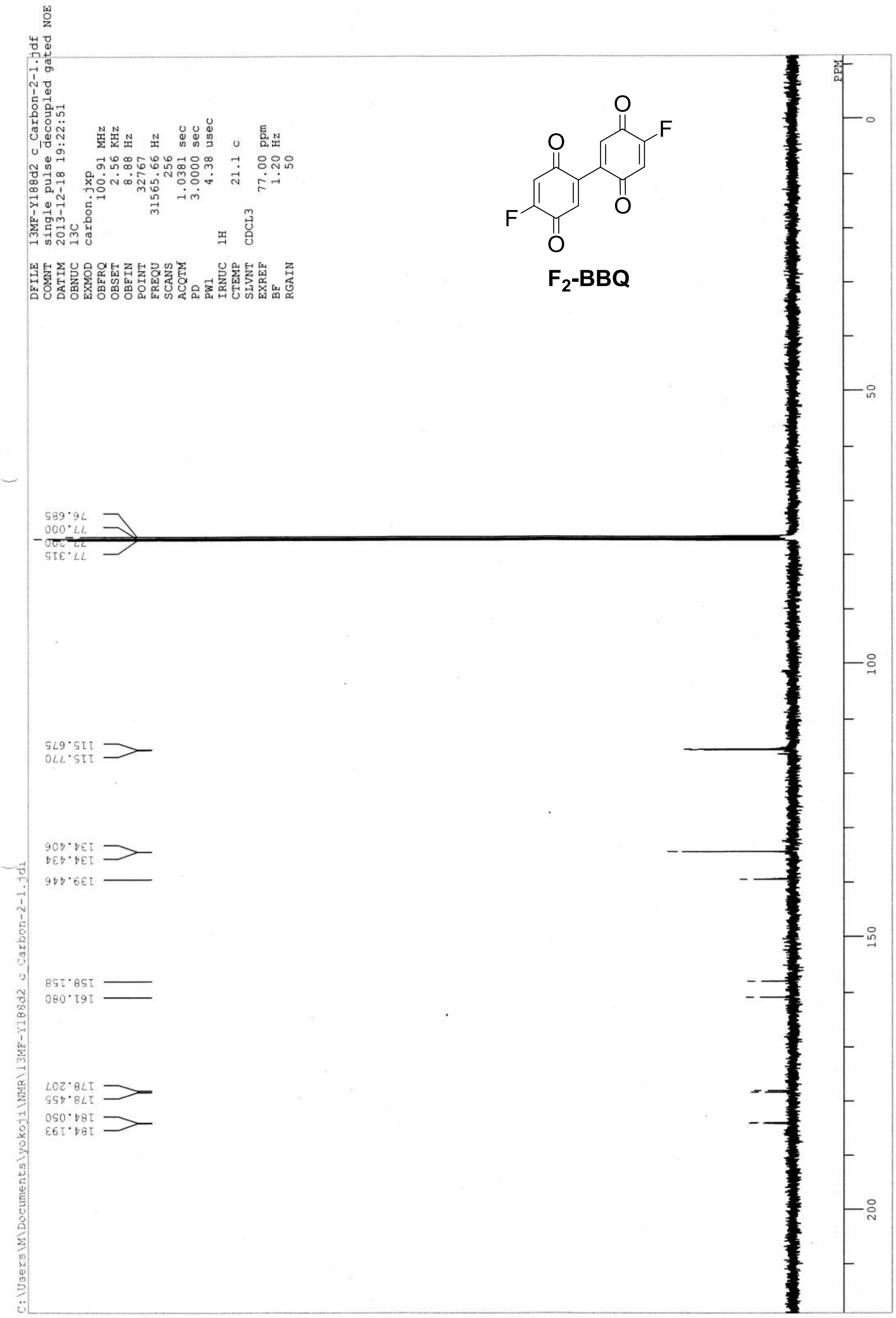
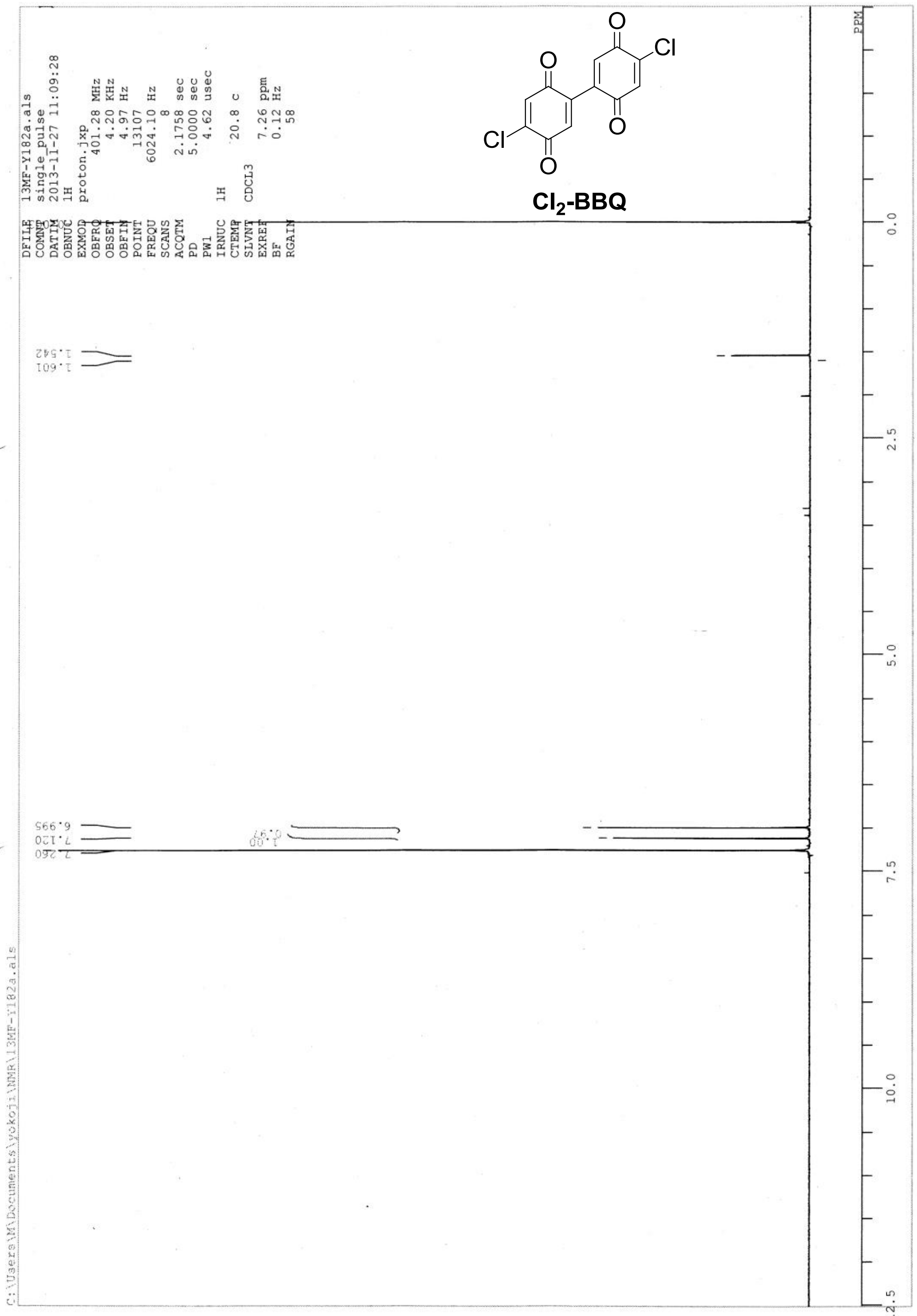
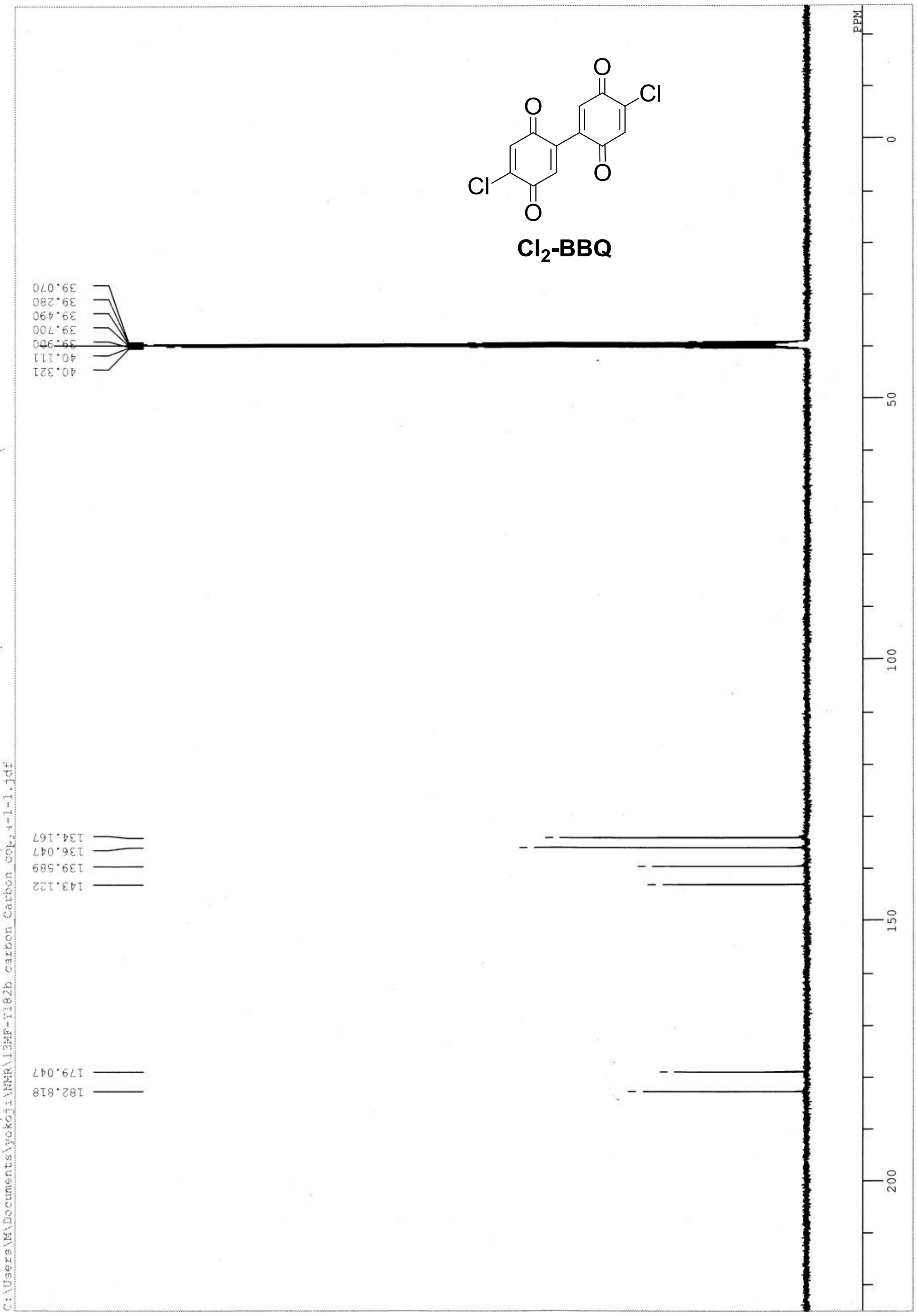
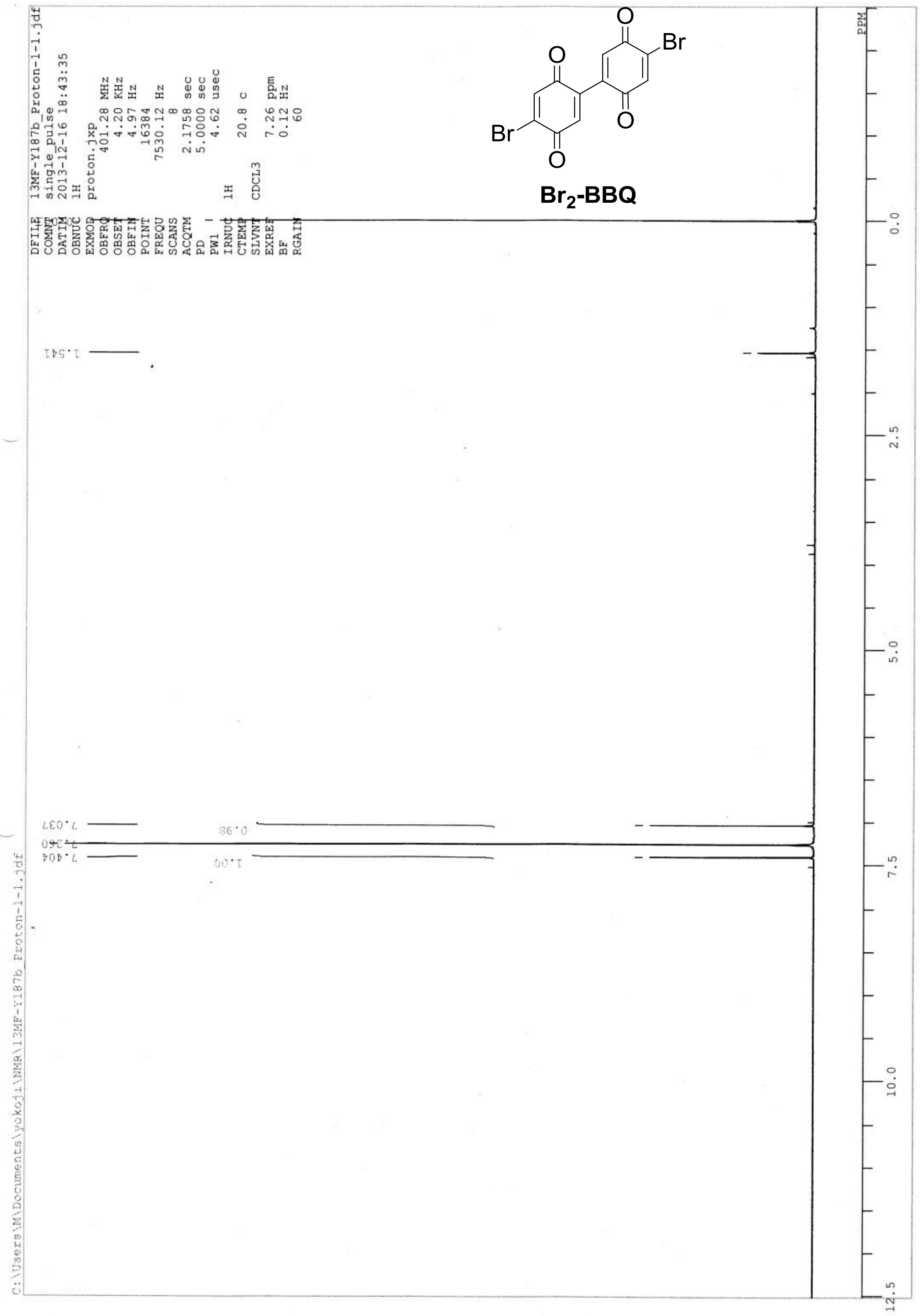
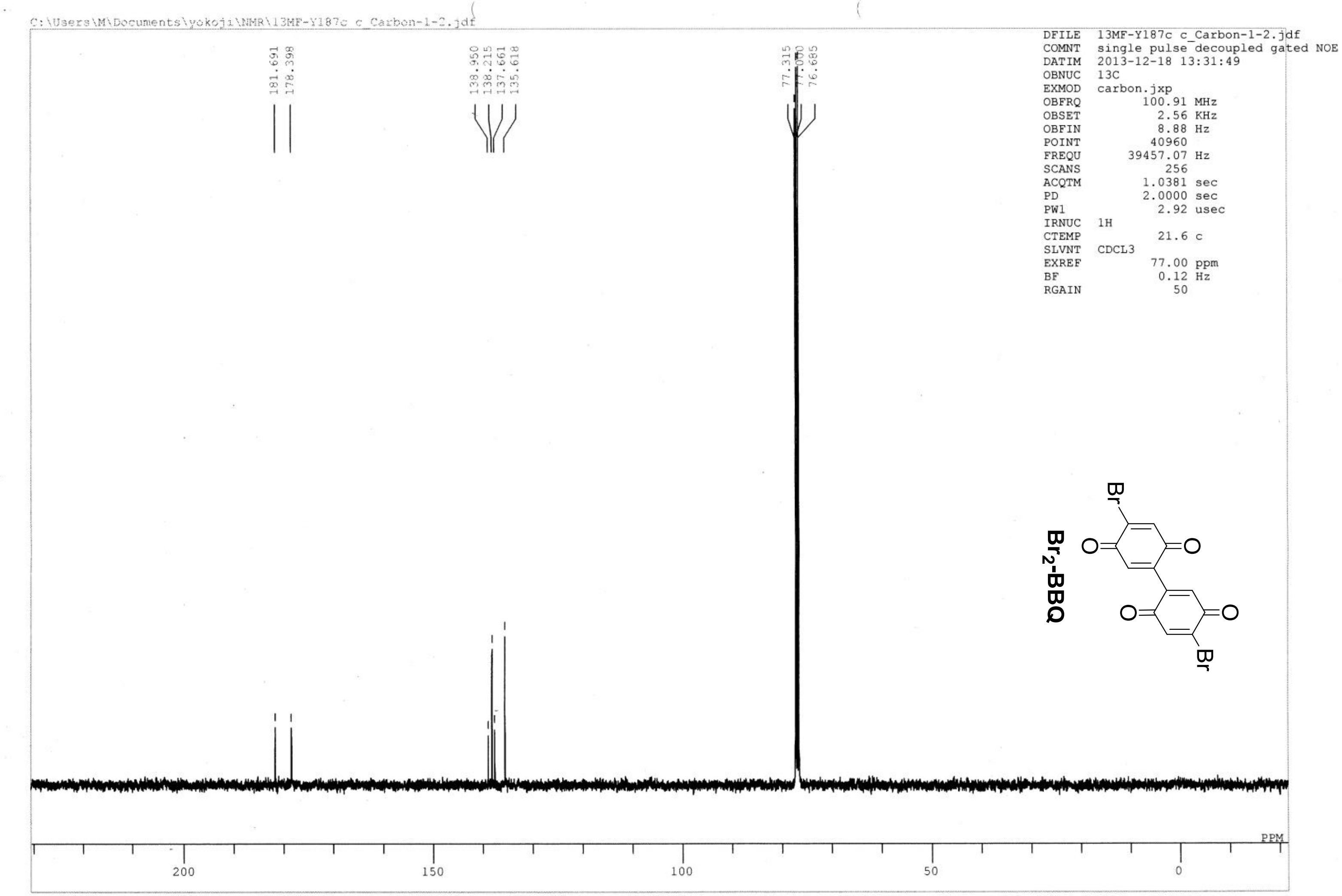
BF 0.12 Hz
RGAIN 58
F2-BBQ
-0.003
1.542
6.562
6.587
6.863
6.882
7.260
1.00
1.00
PPM
-2.5
0.0
2.5
5.0
7.5
10.0
12.5
C:\Users\M\Documents\yokoji\NMR\13MF-Y188c_Proton-1-2.als

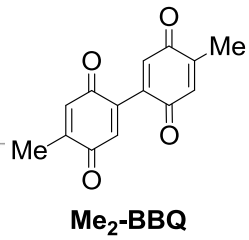

DFILE 13MF-Y188d2_c_Carbon-2-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2013-12-18 19:22:51
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 256
ACQTM 1.0381 sec
PD 3.0000 sec
PW1 4.38 usec
IRNUC 1H
CTEMP 21.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
F$_2$-BBQ
76.685
77.000
77.315
115.675
115.770
134.406
134.434
139.446
158.158
161.080
178.207
178.455
184.050
184.193
PPM
0
50
100
150
200
C:\Users\M\Documents\yokoji\NMR\13MF-Y188d2_c_Carbon-2-1.jdl


DFILE 13MF-Y182a.als
COMNT single_pulse
DATIM 2013-11-27 11:09:28
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 13107
FREQU 6024.10 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 58
O
Cl
Cl-BBQ
Cl2-BBQ
1.542
1.601
6.995
7.120
7.260
1.00
PPM
0.0
2.5
5.0
7.5
10.0
12.5
C:\Users\Mi\Documents\yokoji\NMR\13MF-Y182a.als

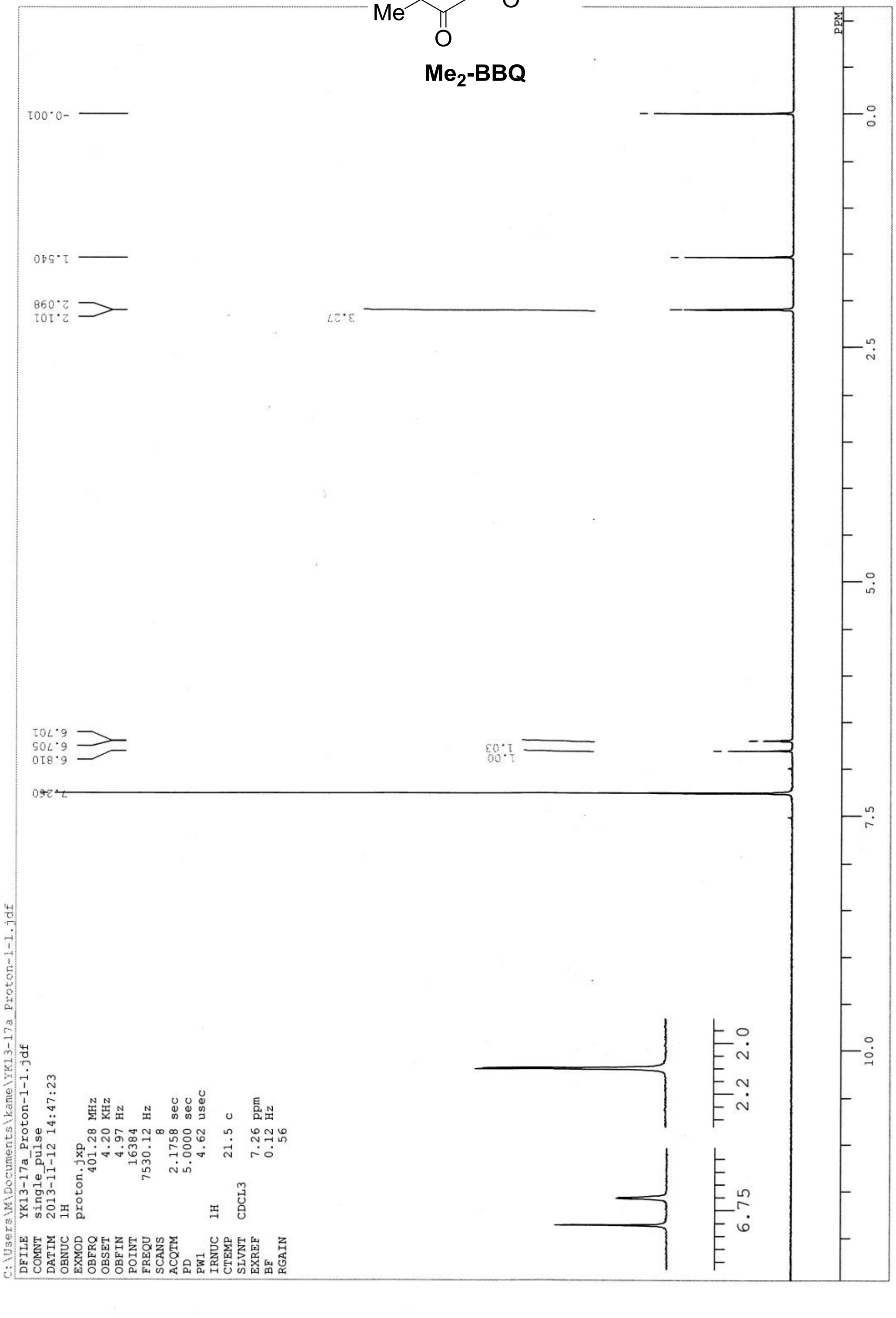

O
O
Cl
Cl
O
O
Cl$_2$-BBQ
39.070
39.280
39.490
39.700
39.900
40.111
40.321
134.167
136.047
139.589
143.122
179.047
182.818
PPM
0
50
100
150
200

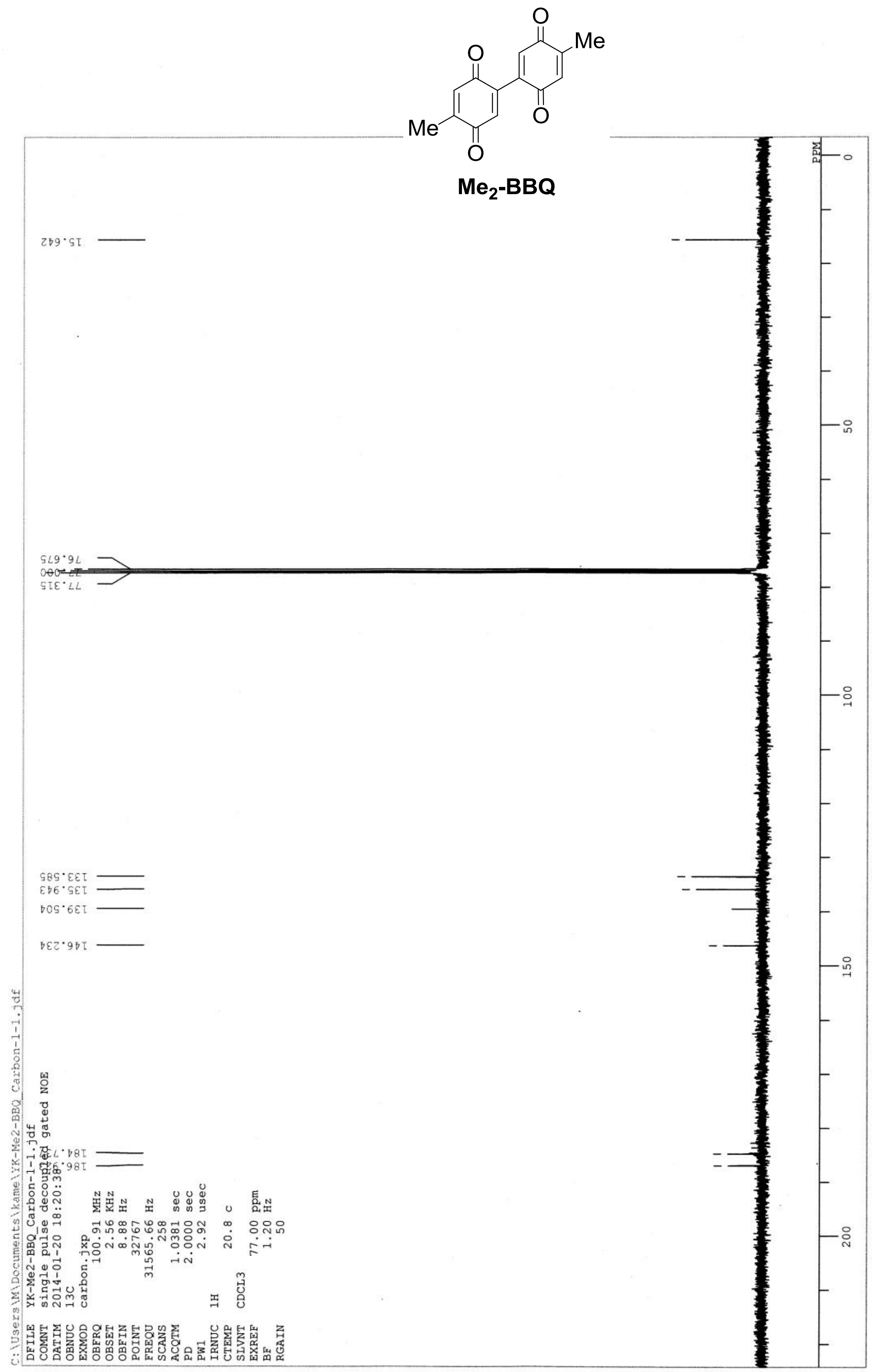

DFILE 13MF-Y187b_Proton-1-1.jdf
COMNT single_pulse
DATIM 2013-12-16 18:43:35
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 16384
FREQU 7530.12 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 60
O
Br
O
Br
O
O
Br2-BBQ
1.541
7.037
7.260
7.404
0.98
1.00
PPM
0.0
2.5
5.0
7.5
10.0
12.5
C:\Users\M\Documents\yokoji\NMR\13MF-Y187b_Proton-1-1.jdf


C:\Users\M\Documents\yokoji\NMR\13MF-Y187c c_Carbon-1-2.jdf
181.691
178.398
138.950
138.215
137.661
135.618
77.315
77.000
76.685
DFILE 13MF-Y187c c_Carbon-1-2.jdf
COMNT single pulse decoupled gated NOE
DATIM 2013-12-18 13:31:49
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 40960
FREQU 39457.07 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 21.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50
Br
O
Br₂-BBQ
PPM
200
150
100
50
0

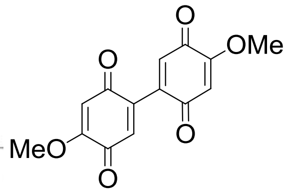


Me_2-BBQ

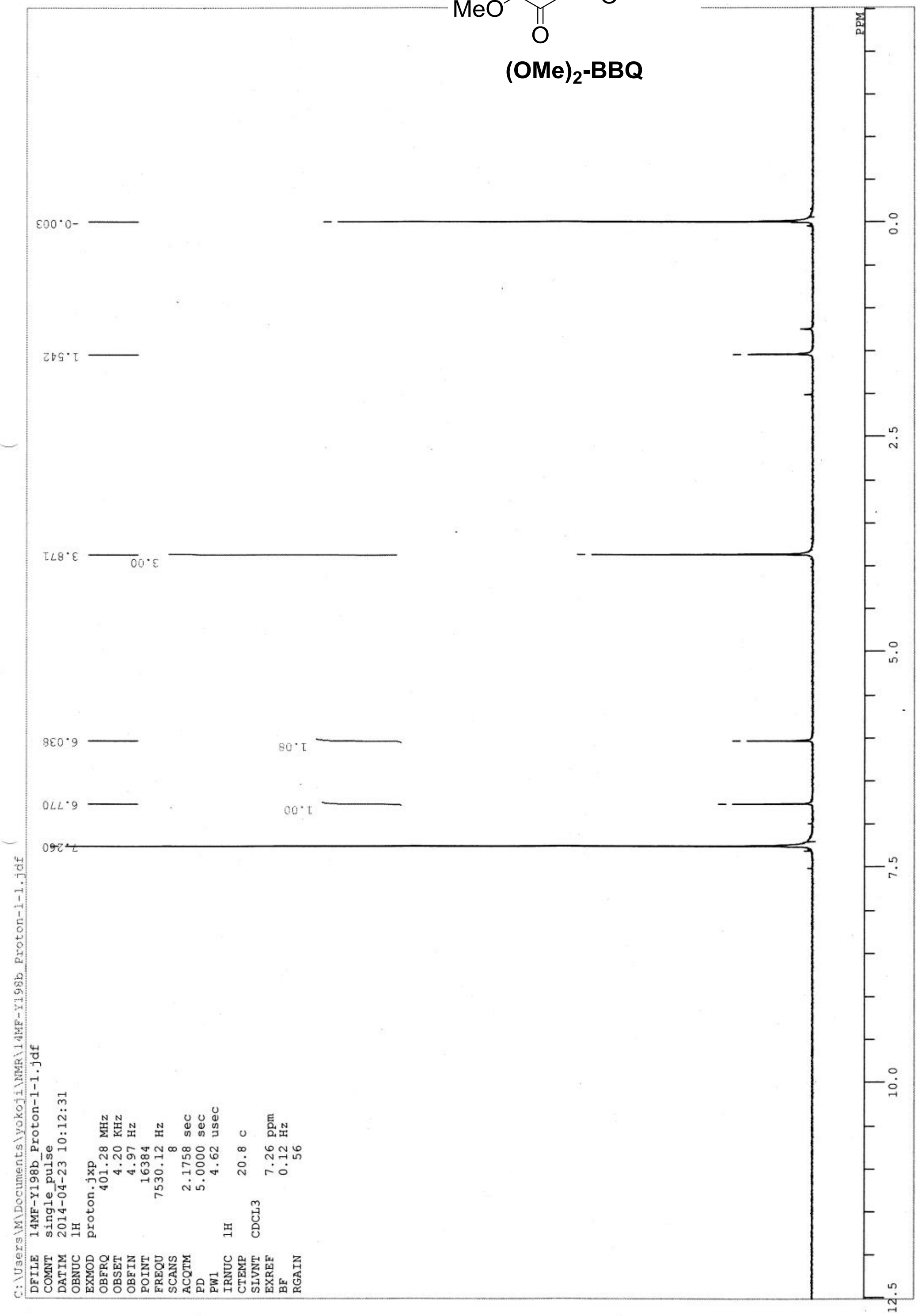

C:\Users\M\Documents\kame\YK13-17a_Proton-1-1.jdf
DFILE YK13-17a_Proton-1-1.jdf
COMNT single_pulse
DATIM 2013-11-12 14:47:23
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 16384
FREQU 7530.12 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 21.5 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 56
-0.001
1.540
2.098
2.101
6.701
6.705
6.810
7.260
3.27
1.03
1.00
6.75
2.2 2.0
PPM
0.0
2.5
5.0
7.5
10.0


C:\Users\M\Documents\kame\YK-Me2-BBQ_Carbon-1-1.jdf
DFILE YK-Me2-BBQ_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2014-01-20 18:20:38
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 258
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
146.234
139.504
135.943
133.585
77.315
76.675
15.642
PPM
200
150
100
50
0
Me
O
O
Me
O
O

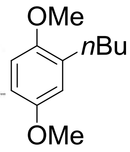
Me_2-BBQ



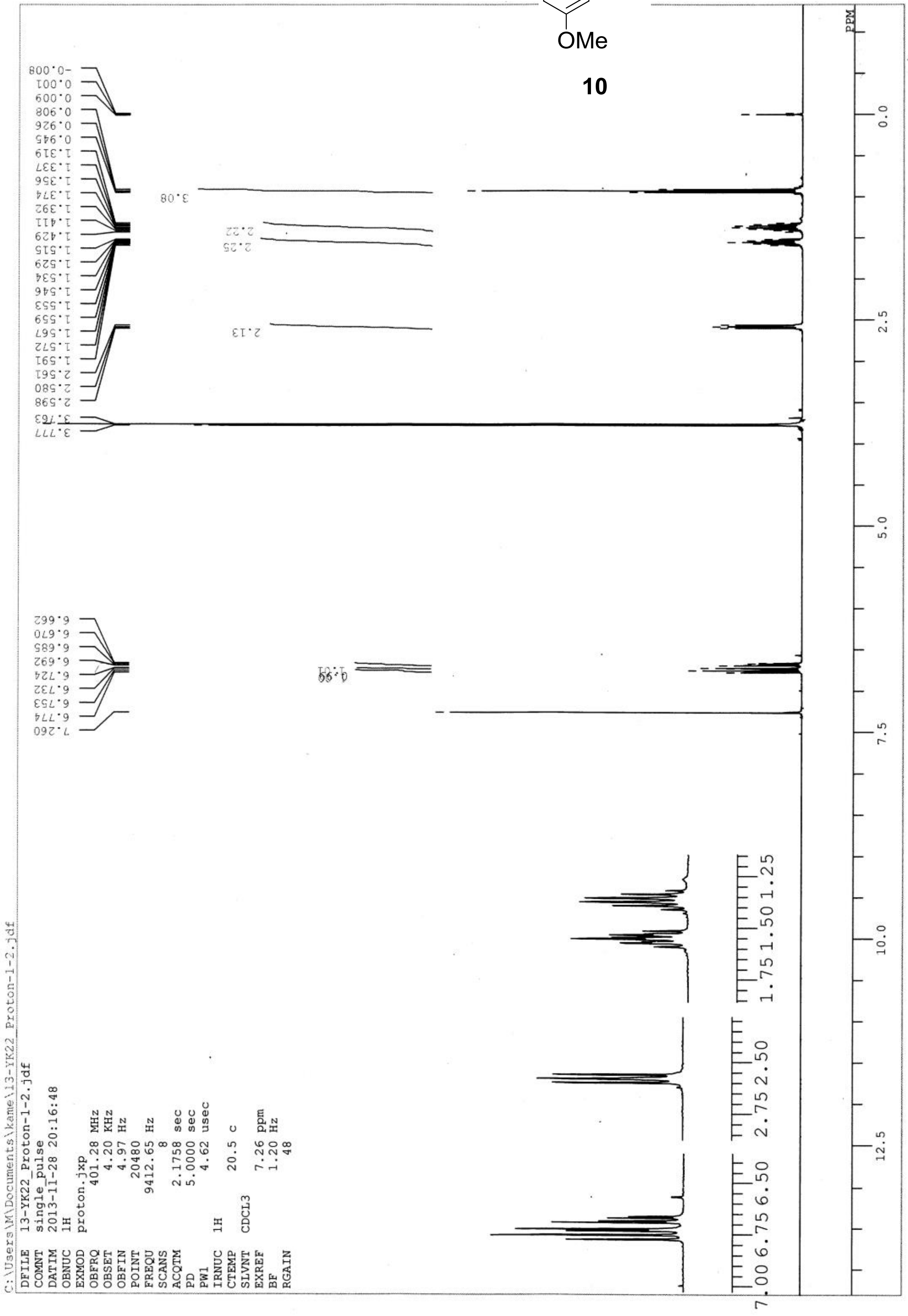
$(OMe)_2$-BBQ

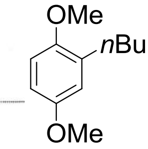


C:\Users\M\Documents\yokoji\NMR\14MF-Y198b_Proton-1-1.jdf
DFILE 14MF-Y198b_Proton-1-1.jdf
COMNT single_pulse
DATIM 2014-04-23 10:12:31
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 16384
FREQU 7530.12 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 56
-0.003
1.542
3.871
3.00
6.038
1.08
6.770
1.00
7.260
PPM
0.0
2.5
5.0
7.5
10.0
12.5

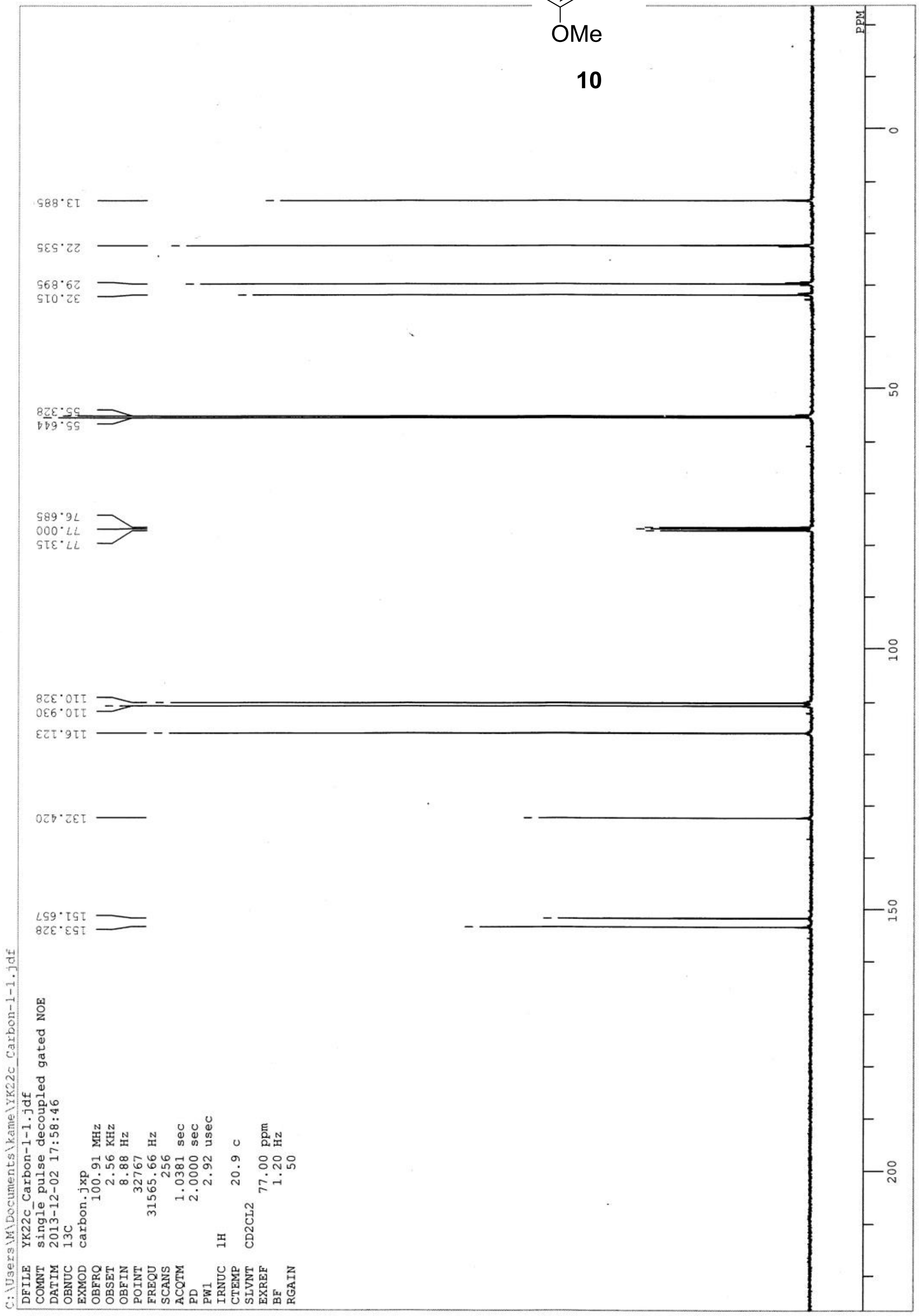

OMe
nBu
OMe

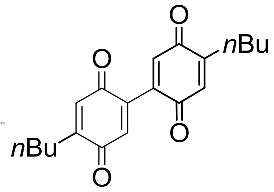
10


C:\Users\M\Documents\kame\13-YK22 Proton-1-2.jdf
DFILE 13-YK22_Proton-1-2.jdf
COMNT single_pulse
DATIM 2013-11-28 20:16:48
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 20480
FREQU 9412.65 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 20.5 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 1.20 Hz
RGAIN 48
PPM
0.0
2.5
5.0
7.5
10.0
12.5

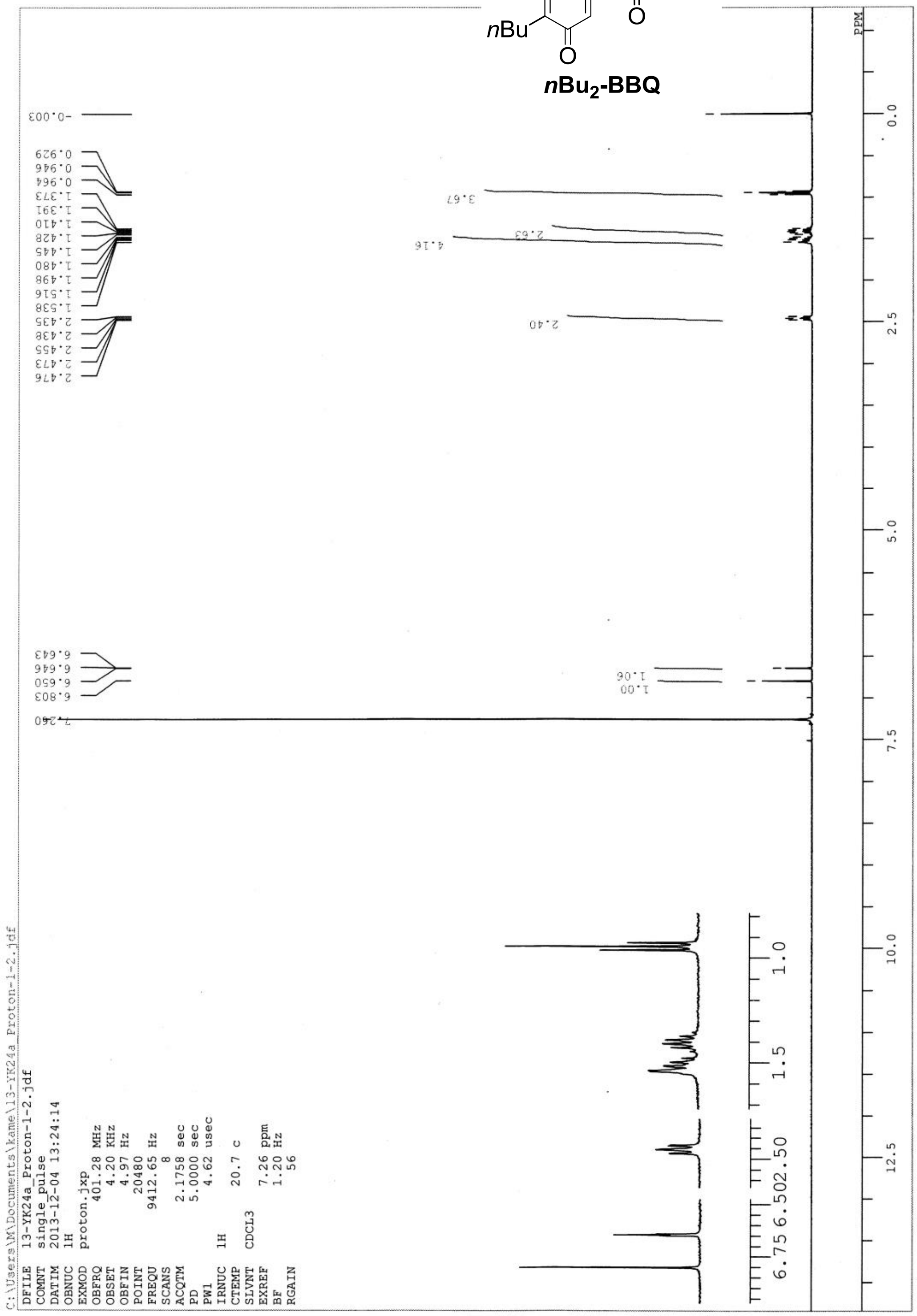

OMe
nBu
OMe

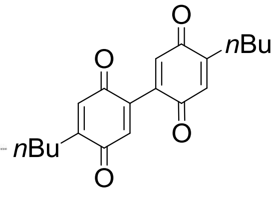
10


C:\Users\M\Documents\kame\YK22c_Carbon-1-1.jdf
DFILE YK22c_Carbon-1-1.jdf
COMNT single_pulse decoupled gated NOE
DATIM 2013-12-02 17:58:46
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 20.9 c
SLVNT CD2CL2
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
13.885
22.535
29.895
32.015
55.328
55.644
76.685
77.000
77.315
110.328
110.930
116.123
132.420
151.657
153.328
PPM
0
50
100
150
200



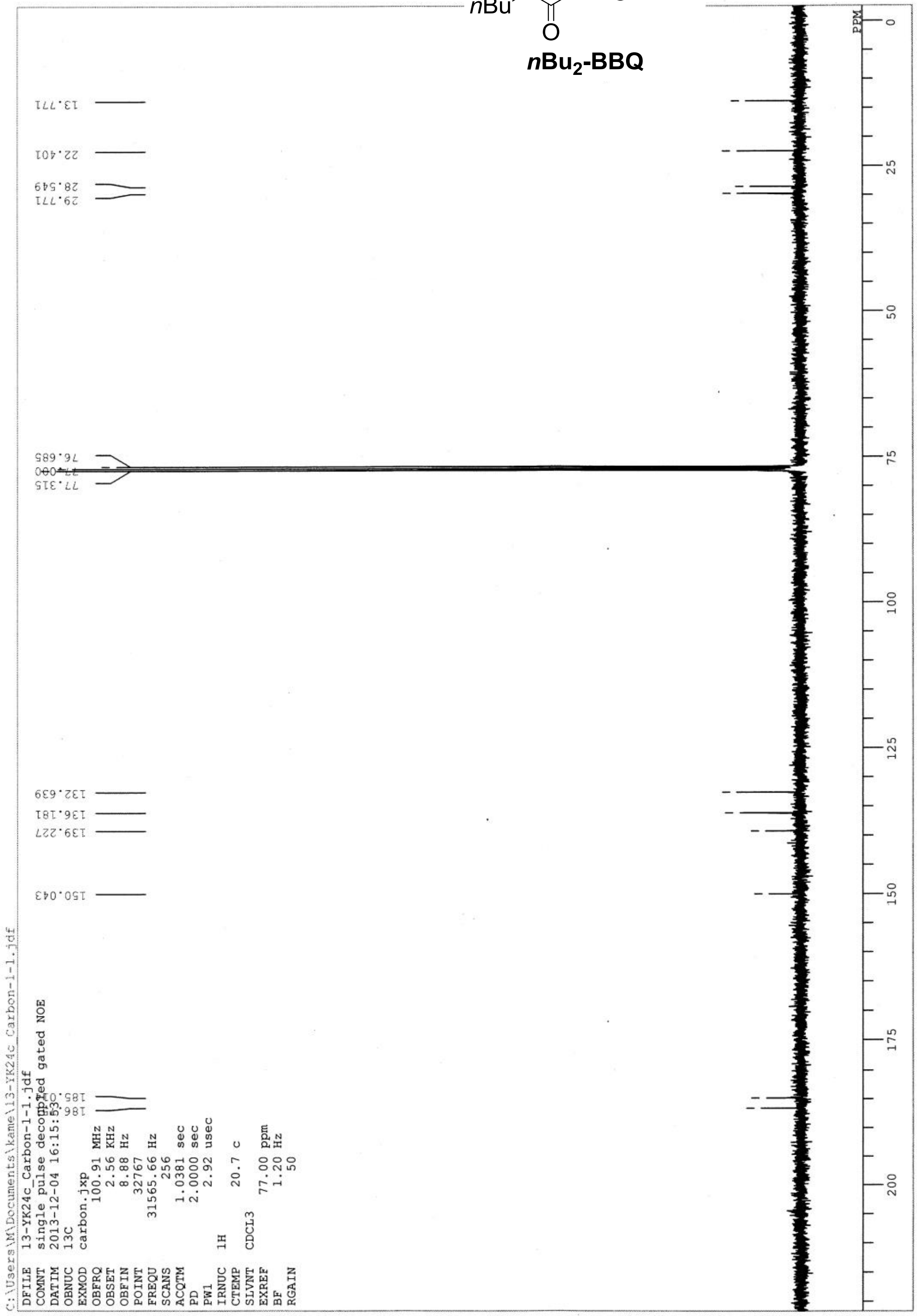
nBu$_2$-BBQ



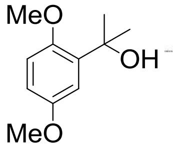


O
O
nBu
nBu
O
O

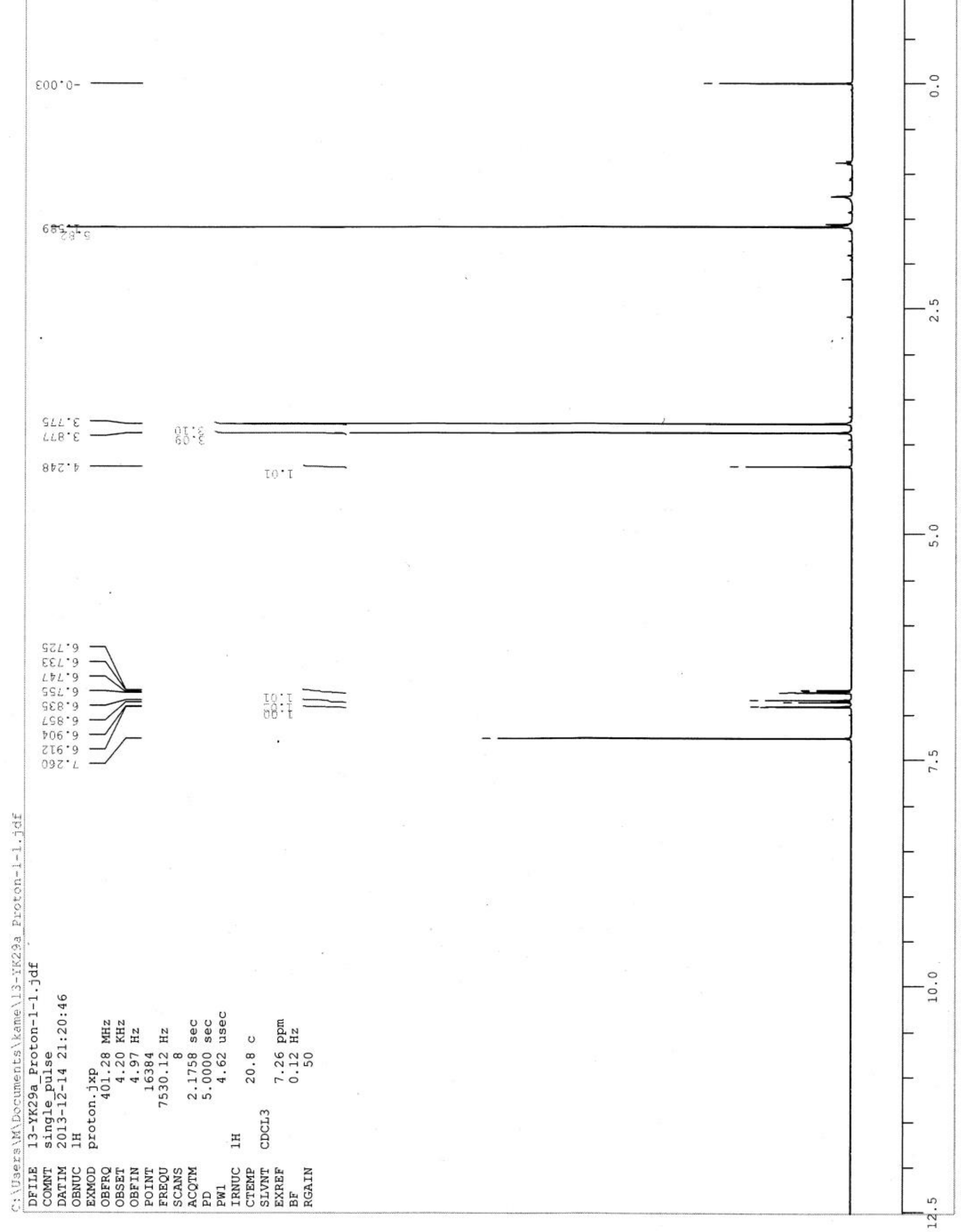
nBu$_2$-BBQ

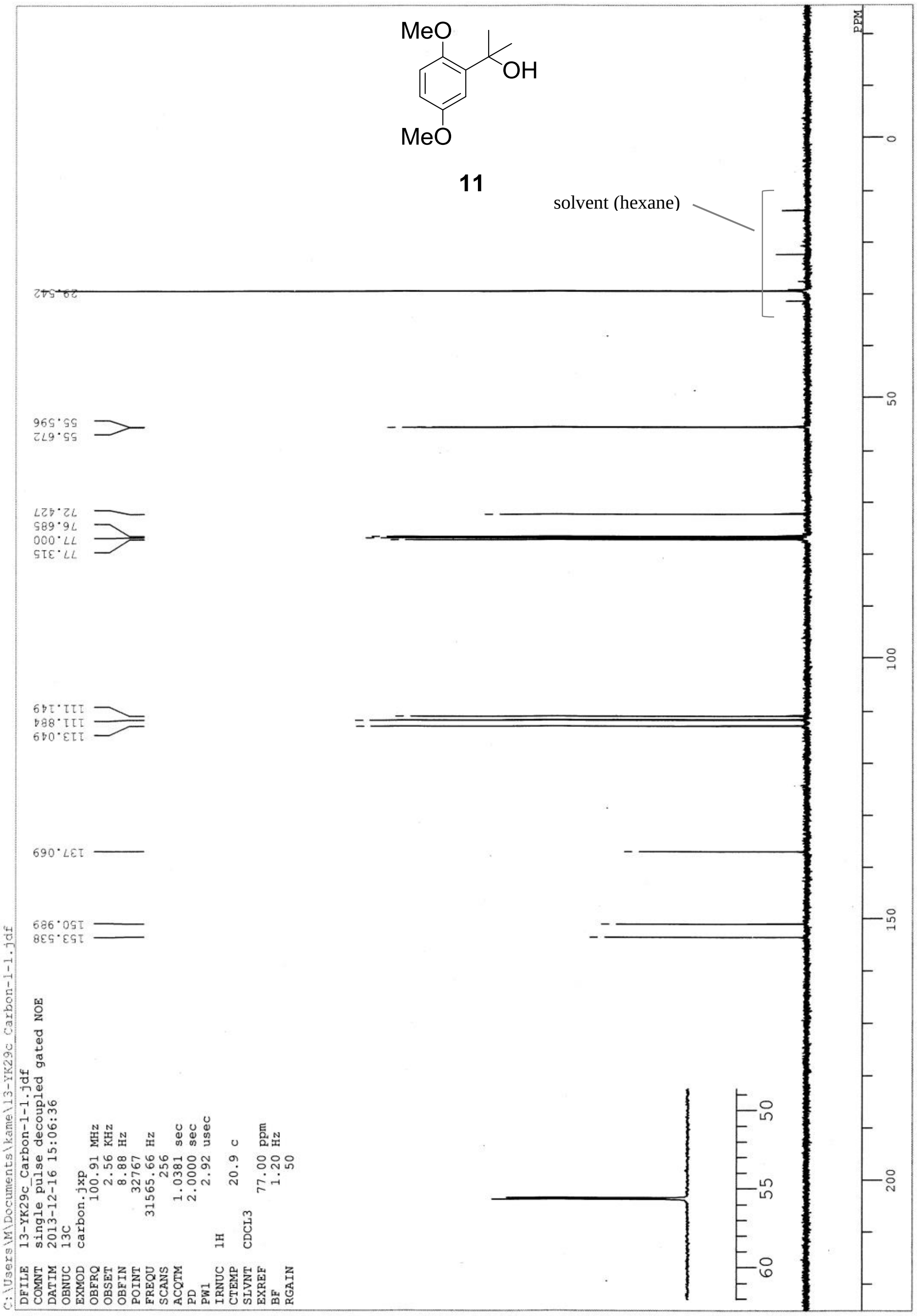


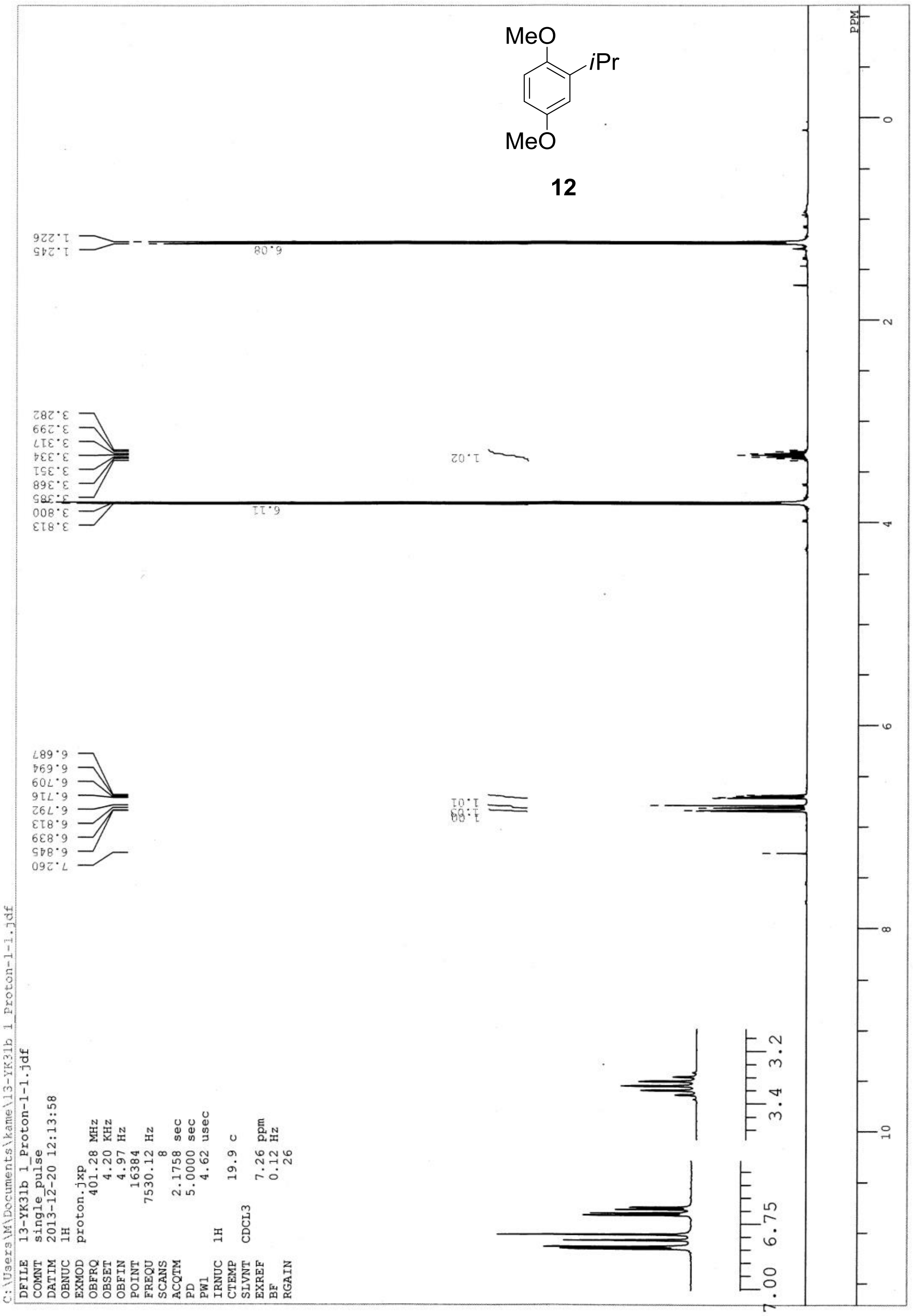
C:\Users\M\Documents\kame\13-YK24c_Carbon-1-1.jdf
DFILE 13-YK24c_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2013-12-04 16:15:53
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
13.771
22.401
28.549
29.771
76.685
77.315
132.639
136.181
139.227
150.043
PPM
0
25
50
75
100
125
150
175
200

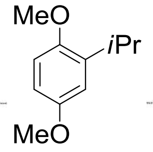

MeO
OH
MeO

11

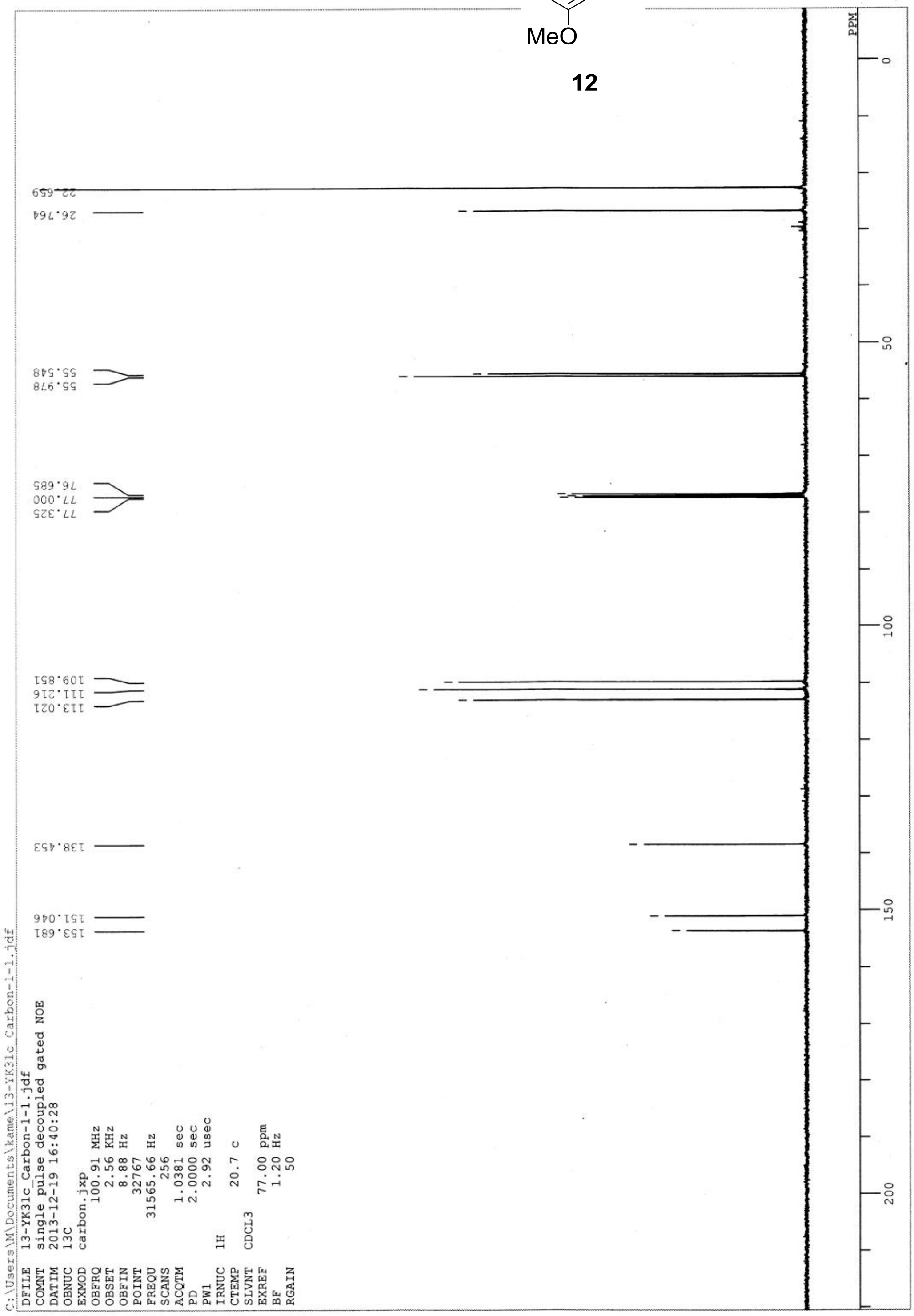

C:\Users\M\Documents\kame\13-YK29a_Proton-1-1.jdf
DFILE 13-YK29a_Proton-1-1.jdf
COMNT single_pulse
DATIM 2013-12-14 21:20:46
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 16384
FREQU 7530.12 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 50
-0.003
1.589
5.82
3.775
3.877
3.10
3.09
4.248
1.01
6.725
6.733
6.747
6.755
6.835
6.857
6.904
6.912
7.260
1.01
1.01
1.00
PPM
0.0
2.5
5.0
7.5
10.0
12.5

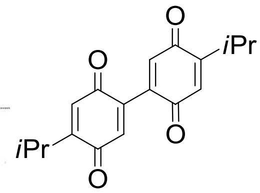

C:\Users\M\Documents\kame\13-YK29c_Carbon-1-1.jdf
DFILE 13-YK29c_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2013-12-16 15:06:36
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 20.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
MeO
OH
MeO
11
solvent (hexane)
29.542
55.596
55.672
72.427
76.685
77.000
77.315
111.149
111.884
113.049
137.069
150.989
153.538
PPM
0
50
100
150
200
50
55
60


MeO
iPr
MeO
12
C:\Users\M\Documents\kame\13-YK31b 1_Proton-1-1.jdf
DFILE 13-YK31b 1_Proton-1-1.jdf
COMNT single_pulse
DATIM 2013-12-20 12:13:58
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 16384
FREQU 7530.12 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 26
7.260
6.845
6.839
6.813
6.792
6.716
6.709
6.694
6.687
3.813
3.800
3.385
3.368
3.351
3.334
3.317
3.299
3.282
1.245
1.226
1.01
1.00
1.02
6.11
6.08
7.00 6.75
3.4 3.2
PPM
0
2
4
6
8
10

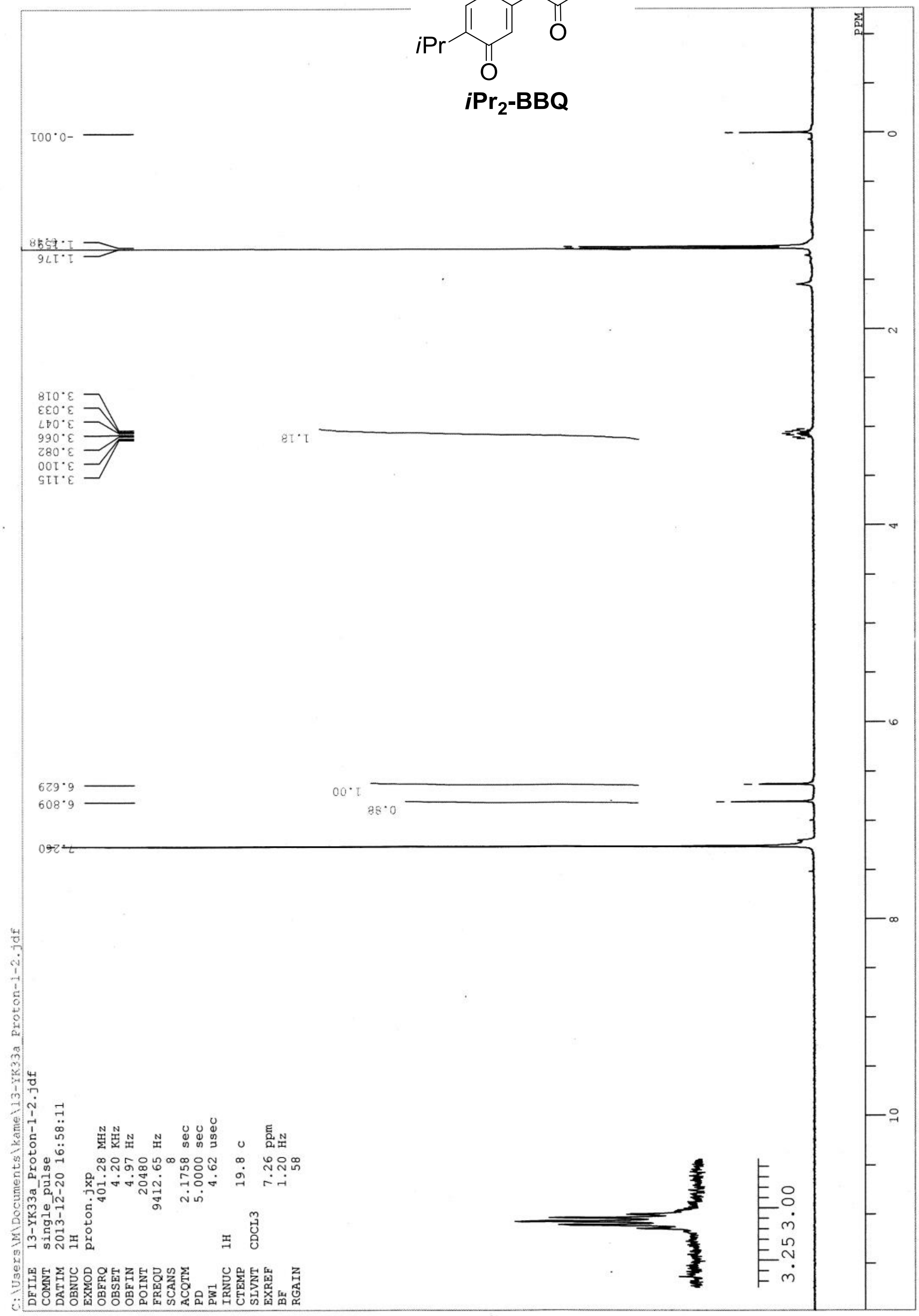

MeO
iPr
MeO

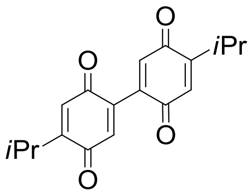
12


C:\Users\M\Documents\kame\13-YK31c_Carbon-1-1.jdf
DFILE 13-YK31c_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2013-12-19 16:40:28
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
22.659
26.764
55.548
55.978
76.685
77.000
77.325
109.851
111.216
113.021
138.453
151.046
153.681
PPM
0
50
100
150
200

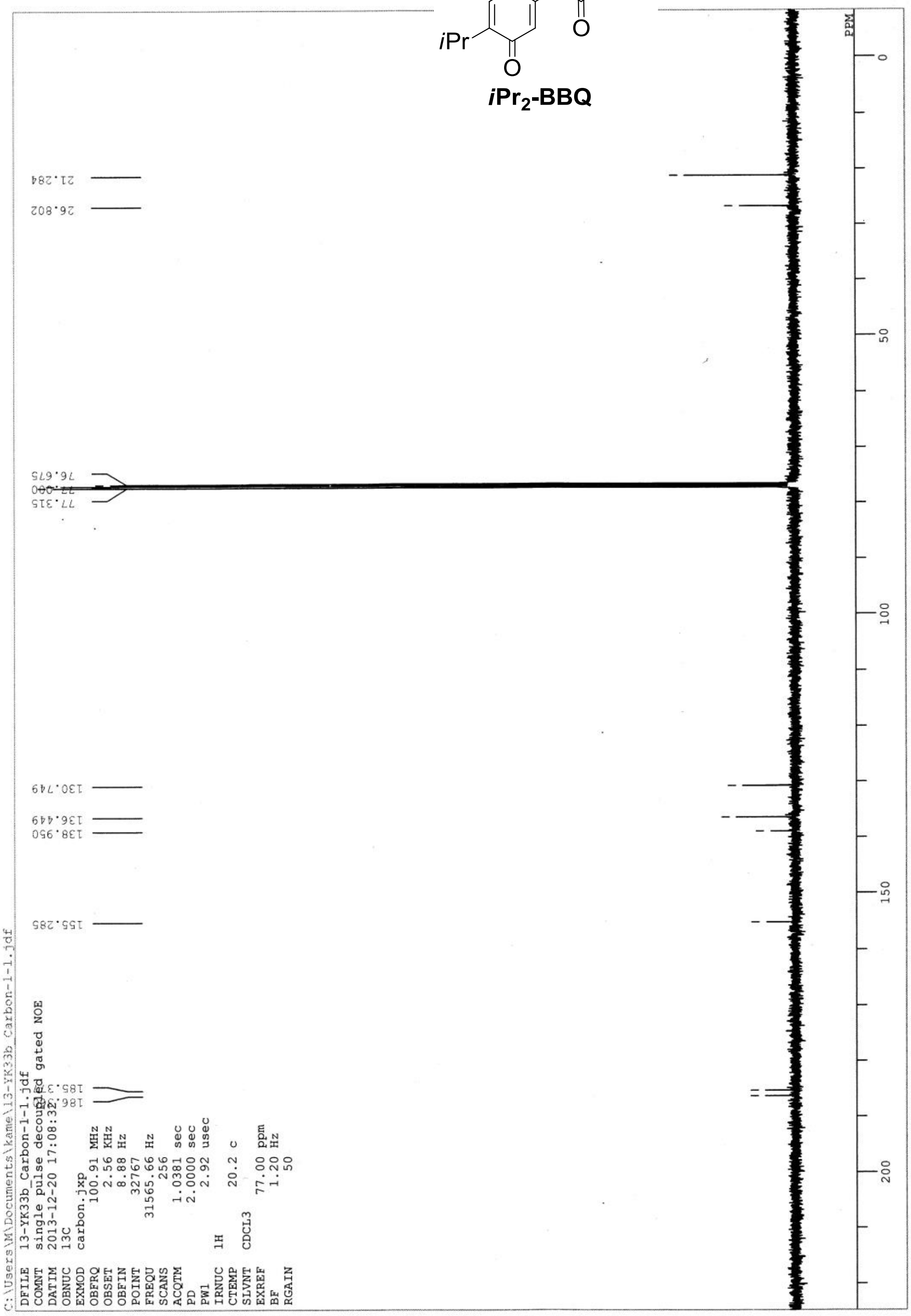


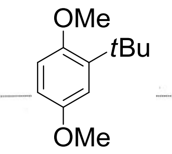
***i*Pr$_2$-BBQ**



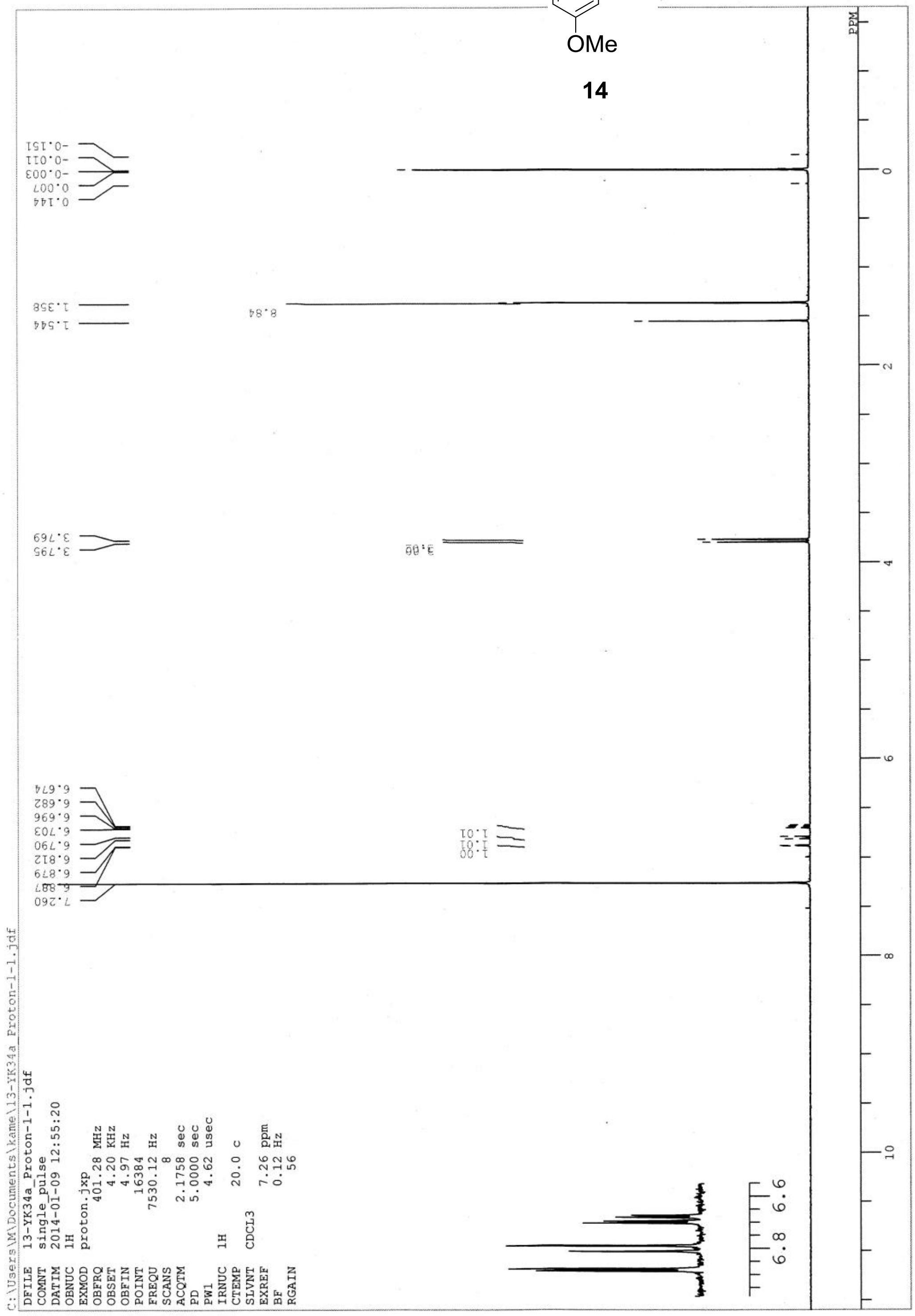

O
O
iPr
O
iPr
O

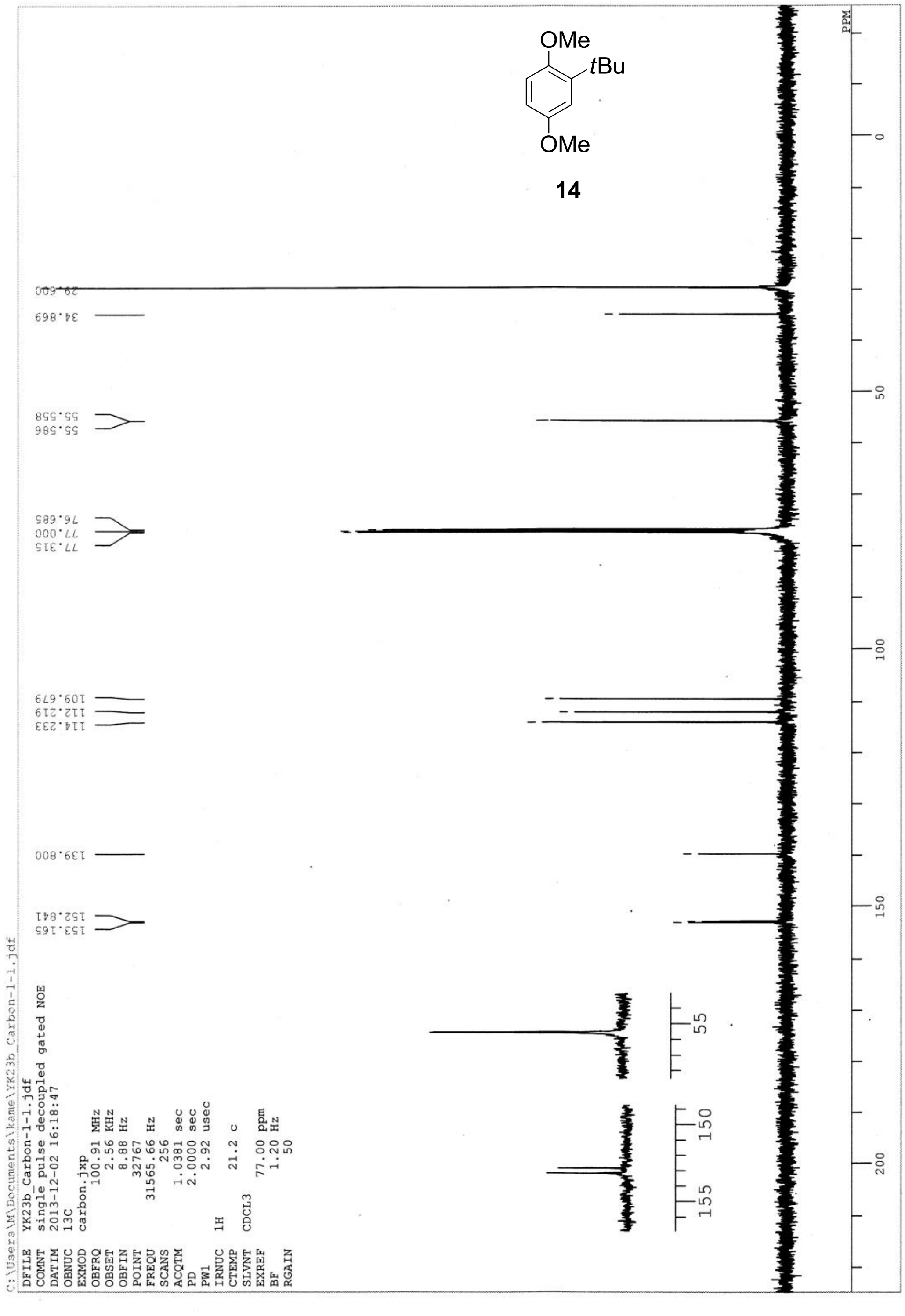
***i*Pr$_2$-BBQ**

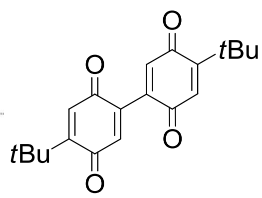

C:\Users\M\Documents\kame\13-YK33b_Carbon-1-1.jdf
DFILE 13-YK33b_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2013-12-20 17:08:32
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 20.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
21.284
26.802
76.675
77.000
77.315
130.749
136.449
138.950
155.285
PPM
0
50
100
150
200


OMe
tBu
OMe

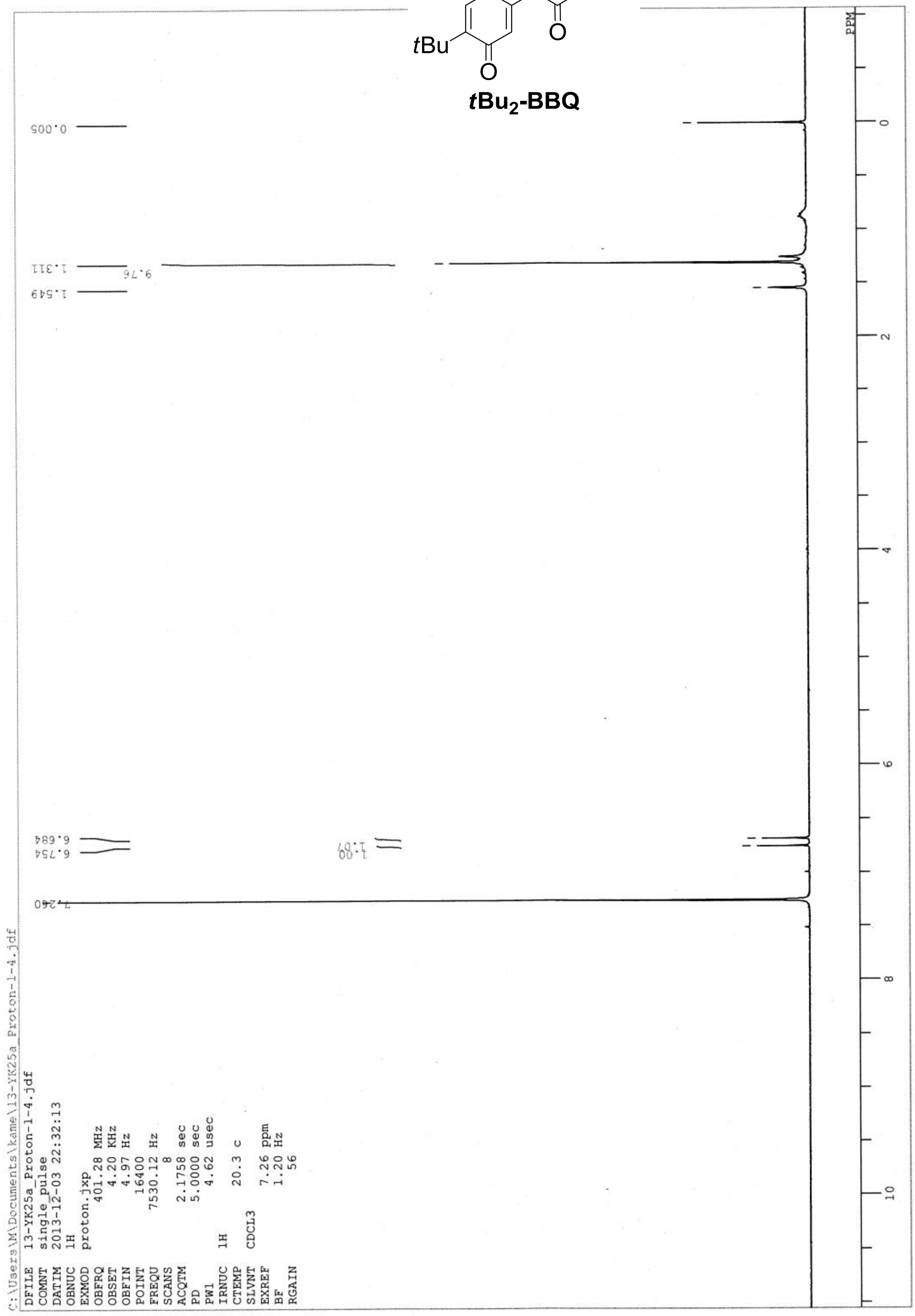
14

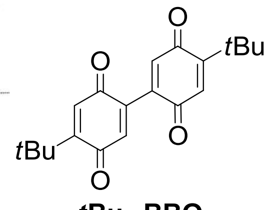

C:\Users\M\Documents\kame\13-YK34a_Proton-1-1.jdf
DFILE 13-YK34a_Proton-1-1.jdf
COMNT single_pulse
DATIM 2014-01-09 12:55:20
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 16384
FREQU 7530.12 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 20.0 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 56


OMe
tBu
OMe
14
C:\Users\M\Documents\kame\YK23b_Carbon-1-1.jdf
DFILE YK23b_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2013-12-02 16:18:47
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 21.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
153.165
152.841
139.800
114.233
112.219
109.679
77.315
77.000
76.685
55.586
55.558
34.869
29.600
PPM
0
50
100
150
200
55
150
155

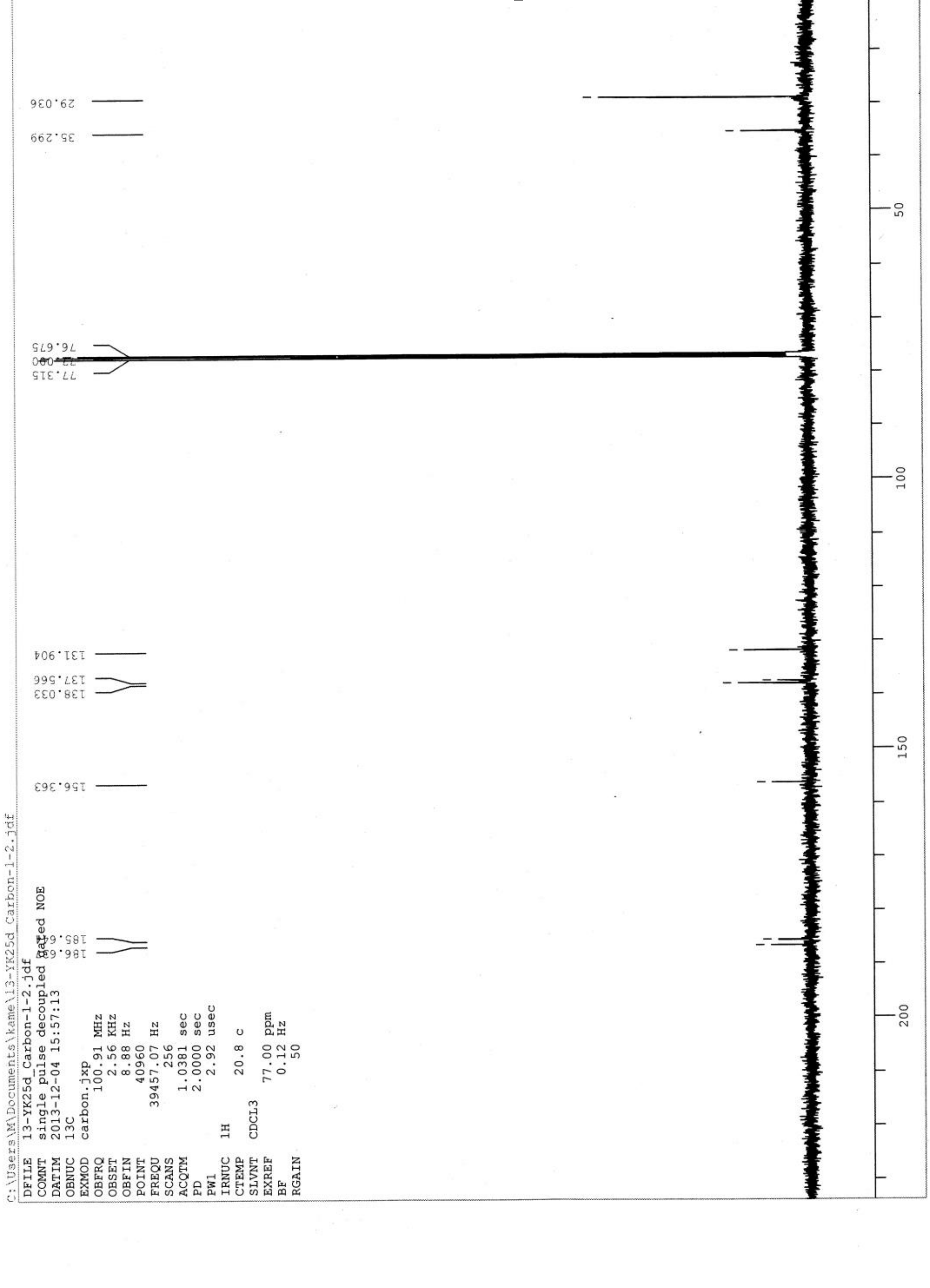

O
O
tBu
O
O
tBu

***t*Bu$_2$-BBQ**


C:\Users\M\Documents\kame\13-YK25a_Proton-1-4.jdf
DFILE 13-YK25a_Proton-1-4.jdf
COMNT single_pulse
DATIM 2013-12-03 22:32:13
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 16400
FREQU 7530.12 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 1.20 Hz
RGAIN 56
0.005
1.311
1.549
9.76
6.684
6.754
1.07
1.00
7.260
PPM
0
2
4
6
8
10



tBu$_2$-BBQ



C:\Users\M\Documents\kame\13-YK25d_Carbon-1-2.jdf
DFILE 13-YK25d_Carbon-1-2.jdf
COMNT single pulse decoupled gated NOE
DATIM 2013-12-04 15:57:13
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 40960
FREQU 39457.07 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50
29.036
35.299
76.675
77.000
77.315
131.904
137.566
138.033
156.363
PPM
0
50
100
150
200