Electronic Supplementary Information

Brönsted acid-promoted dimerization of *o*-alkynylbenzaldehydes: a one-step synthesis of functionalized Kagan's ether analogues

Hao Zhang, Wei-Chen Cui, Zhi-Long Hu, Shu-Yan Yu, Shaozhong Wang,* Zhu-Jun Yao*

State Key Laboratory of Coordination Chemistry and Nanjing National Laboratory of Microstructures, Institute of Chemical Biology and Drug Innovation, School of Chemistry and Chemical Engineering, Nanjing University, 22 Hankou Road, Nanjing, Jiangsu 210093, China

yaoz@nju.edu.cn or wangsz@nju.edu.cn

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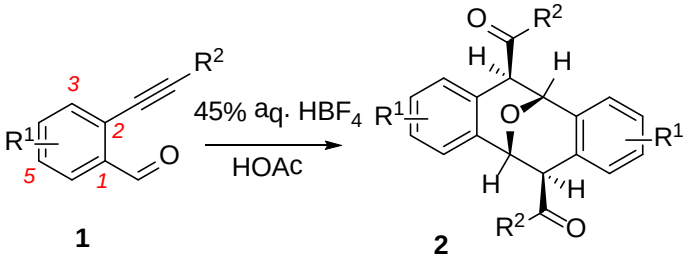
1. General methods

Unless otherwise stated, all commercial reagents and solvents were used without further purification. All solvents and triethylamine were dried and distilled according to standard procedures. All reactions were performed under nitrogen atmosphere unless otherwise noted. Petroleum ether and ethyl acetate were obtained from commercial suppliers and used without further distillations. All melting points were uncorrected. IR spectra were recorded on an FT-IR instrument. ^{1}H NMR spectra were recorded at 300 MHz or 400 MHz and ^{13}C NMR spectra were recorded at 75 or 100 MHz, respectively, and assigned in parts per million (δ). Flash column chromatographies were performed on 300-400 mesh silica gel. X-ray crystallographic structure was determined on a Bruker SMART 1000 diffractometer, MoKa radiation (λ = 0.71073 Å), at 120 K.

2. Representative procedure for the dimerization and characterizations of products 2b-2p.



1 **2**

To a solution of **1b** (3.10 g, 15.0 mmol) in acetic acid (40 mL) was added tetrafluoroboric acid (14 mL, 45% in water) at room temperature under nitrogen atmosphere. The reaction was heated to 90 ^{o}C and continued stirring for 3 hrs until the starting material was consumed by TLC monitoring. The mixture was cooled down to room temperature, and diluted with dichloromethane (200 mL) and water (100 mL). The whole mixture was stirred for 30 mins and the organic layer was separated. The aqueous phase was extracted with dichloromethane (100 mL x 3). The combined organic layers were washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (ethyl acetate/petroleum ether = 1:30) to afford **2b** as a white solid (2.45 g, 76% yield).

(5*R,6*R**,11*R**,12*R**)-5,6,11,12-Tetrahydro-5,11-epoxydibenzo[*a*,*e*][8]annulene-6,12-diyl)bis(phenylmethanone) (2b).** Yield: 76%; white solid; m.p. 177-180 °C; ^{1}H NMR ($CDCl_3$, 300 MHz):

δ 8.07-8.09 (m, 4H), 7.54-7.64 (m, 6H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 2H), 6.94 (d, *J*= 7.8 Hz, 2H), 5.59 (s, 2H), 4.77 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 198.2, 136.7, 136.2,133.1, 130.4, 130.0, 128.9,128.5, 127.7, 127.7, 124.5, 71.4, 54.2; IR (KBr) ν_{max}: 1686, 1447, 1202, 1085, 1005, 753, 687 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{22}O_3Na$ [M+Na$^+$] 453.1467; Found: 453.1462.

(5*R,6*R**,11*R**,12*R**)-3,9-Dichloro-5,6,11,12-tetrahydro-5,11-epoxydibenzo[*a,e*][8]annulene-6,12-diyl)bis(phenylmethanone) (2c).** Yield: 73%; white solid; m.p. 218-220 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.02-8.06 (m, 4H), 7.55-7.66 (m, 6H), 7.35-7.36 (d, 2H, *J* = 2.1Hz), 7.17-7.21 (dd, 2H, J_1 = 8.1 Hz, J_2 = 2.1 Hz), 6.89-8.92 (d, 2H, *J* = 8.1 Hz), 5.55 (s, 2H), 4.71 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.2, 137.9, 135.7, 133.4, 133.3, 131.8, 129.0, 128.4, 128.2, 124.5, 70.9, 53.4 ppm; IR (KBr) ν_{max}: 3057, 2951, 1684, 1260, 1021, 1094, 969, 774, 691 cm^{-1}; HRMS (ESI) calculated for $C_{30}H_{20}Cl_2O_3Na$ [M+Na$^+$] 521.0687, found: 521.0677.

(5*R,6*R**,11*R**,12*R**)-4,10-Difluoro-5,6,11,12-tetrahydro-5,11-epoxydibenzo[*a,e*][8]annulene-6,12-diyl)bis(phenylmethanone) (2d).** Yield: 65%; yellow solid; m.p. 180-182 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.17 (d, *J* = 7.5 Hz, 4H), 7.64 (t, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 4H), 7.23 (t, *J* = 6.0 Hz, 2H), 7.05 (t, *J* = 9.3 Hz, 2H),6.80 (d, *J* = 7.5 Hz, 2H), 5.79 (s, 2H), 4.91 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.5,159.5, 157.1, 135.5, 133.5, 133.4, 129.0, 128.9, 128.7, 128.6, 126.1, 123.4, 114.4, 114.2, 67.8, 51.1; IR (KBr) ν_{max}: 1687, 1463, 1263, 1205, 1024, 794, 773, 693, 532cm^{-1}; ESI-MS (m/z): 467 [M+H$^+$]; HRMS (ESI) Calcd for $C_{30}H_{20}O_3F_2Na$ [M+Na$^+$] 489.1278; Found: 489.1279.

(5*R,6*R**,11*R**,12*R**)-Dimethyl-6,12-dibenzoyl-5,6,11,12-tetrahydro-5,11-epoxydibenzo-[*a,e*][8]annulene-3,9-dicarboxylate (2e).** Yield: 63%; white solid; m.p. 189-193 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08-8.10 (m, 6H), 7.85 (d, *J* =6.3 Hz, 2H), 7.67 (t, *J* = 5.1 Hz, 2H), 7.60 (t, *J* = 6.0 Hz, 2H), 7.04 (d, *J* = 6.3 Hz, 2H), 5.69 (s, 2H), 4.85 (s, 2H), 3.95 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.2, 166.6, 136.7, 135.7,135.4, 133.5, 130.8, 130.0, 129.2, 128.8, 128.6, 125.8, 71.2, 54.3, 52.3; IR (KBr) ν_{max}: 1710,1438, 1295, 1203, 1083, 760, 695 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{26}O_7Na$ [M+Na$^+$] 569.1576; Found: 569.1596.

(5*R,6*R**,11*R**,12*R**)-3,9-Dinitro-5,6,11,12-tetrahydro-5,11-epoxydibenzo[*a,e*][8]annulene-6, 12-diyl)bis(phenylmethanone) (2f).** Yield: 67%; white solid; m.p. 190-192 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.27 (d, *J* = 2.1 Hz, 2H), 8.09(d, *J* = 7.2 Hz, 6H), 7.72 (t, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 4H), 7.19 (d, *J* = 8.4 Hz, 2H), 5.75 (s, 2H), 4.92 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 196.0, 147.4, 137.5, 137.4, 135.2,134.1, 132.0, 129.5, 128.5, 123.0, 119.8, 71.0, 54.0; IR (KBr) ν_{max}: 1683, 1523, 1350, 1261,1205, 1083, 1004, 690 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{20}O_7N_2Na$ [M+Na$^+$] 543.1168; Found: 543.1155.

(5*R,6*R**,11*R**,12*R**)-2,4,8,10-Tetrachloro-5,6,11,12-tetrahydro-5,11-epoxydibenzo[*a,e*][8]an nulene-6,12-diyl)bis(phenylmethanone) (2g).** Yield: 70%; white solid; m.p. 293-297°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07-8.10 (m, 4H), 7.57-7.68 (m, 6H), 7.33 (d, 2H, *J* = 1.8 Hz), 7.29 (d, 2H, *J* = 2.1 Hz), 5.48 (s, 2H), 4.92 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.6, 139.5, 135.8, 135.4, 134.0, 133.7, 129.2, 128.8, 128.3, 127.5, 123.3, 70.5, 51.8; IR (KBr) ν_{max}: 3085, 2937, 1689, 1264, 1092, 839, 777, 687 cm^{-1}. HRMS calculated for $C_{30}H_{18}Cl_4O_3Na$ [M+Na$^+$]: 590.9878, found: 590.9889.

(5*R,6*R**,11*R**,12*R**)-6,12-Dibenzoyl-5,6,11,12-tetrahydro-5,11-epoxydibenzo[*a,e*][8]annulen e-3,9-dicarbonitrile (2h).** Yield: 63%; white solid; m.p. 293-297°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03-8.06 (m, 4H), 7.68-7.71 (m, 4H), 7.60-7.65 (m, 4H), 7.52 (dd, 2H, J_1 = 8.1 Hz, J_2 = 1.5 Hz), 7.11 (d, 2H, *J* = 4.8 Hz), 5.63 (s, 2H), 4.79 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.1, 137.5, 135.4, 135.2, 133.9, 131.6, 131.3, 129.4, 128.4, 128.3, 118.1, 112.0, 70.6, 54.0; IR (KBr) ν_{max}: 3052, 2923, 2853, 2361, 2229, 1685, 1266, 1082, 1004, 974, 829, 783, 691 cm^{-1}; HRMS calculated for $C_{32}H_{20}N_2O_3Na$ [M+Na$^+$] 503.1366, found: 503.1360.

(5*R,6*R**,11*R**,12*R**)-3,9-Bis(trifluoromethyl)-5,6,11,12-tetrahydro-5,11-epoxydibenzo[a,e][8]annulene-6,12-diyl)bis(phenylmethanone) (2i).** Yield: 72%; white solid; m.p. 246-249 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04-8.07 (m, 4H), 7.57-7.68 (m, 8H), 7.48 (d, 2H, *J* = 7.8 Hz), 7.11 (d, 2H, *J* = 8.4 Hz), 5.66 (s, 2H), 4.82 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.8, 137.0, 135.5, 134.0, 133.6, 131.2, 130.7, 130.3, 129.9, 129.4, 129.4, 129.1, 128.4, 125.4, 124.8, 124.7, 124.7, 124.6, 121.8, 121.4, 121.3, 121.2, 70.9, 53.8; IR (KBr) ν_{max} 3084, 3059, 2942, 2932, 1688, 1344, 1240, 1121, 1104, 830, 696 cm^{-1}; HRMS calculated for $C_{32}H_{20}F_6O_3Na$ [M+Na$^+$] 589.1214, found:

589.1218.

(5*R,6*R**,11*R**,12*R**)-3,9-Dimethoxy-2,8-dinitro-5,6,11,12-tetrahydro-5,11-epoxydibenzo[*a,e*][8]annulene-6,12-diyl)bis(phenylmethanone) (2j).** Yield: 20%; white solid; m.p. 342 °C (dec.); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17-8.14 (m, 4H), 7.76-7.63 (m, 6H),7.60 (s, 2H), 7.38 (s, 2H), 5.49 (s, 2H), 5.27 (s, 2H), 4.07 (s, 6H); ^{13}C NMR (75MHz, $CDCl_3$): δ 197.9, 151.0, 142.4, 138.3, 135.5, 133.5, 129.2, 128.8, 126.4, 122.7, 111.0, 70.7, 56.8; IR (KBr) ν_{max}: 3055, 2937, 2361, 1676, 1521, 1278, 1064, 1010, 860, 787, 685 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{24}N_2O_9$ [M-H]$^-$: 579.1409; Found: 579.1426.

(5*R,6*R**,11*R**,12*R**)-3,9-Di-*tert*-butyl-5,6,11,12-tetrahydro-5,11-epoxydibenzo[*a,e*][8]annulene-6,12-diyl)bis(phenylmethanone) (2k).** Yield: 84%; white solid; m.p. 250-253 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06-8.10 (m, 4H), 7.52-7.66 (m, 6H), 7.35 (d, 2H, J = 1.8 Hz), 7.20-7.24 (dd, 2H, J_1 = 8.1 Hz, J_2 = 1.8 Hz), 6.88-6.90 (d, 2H, J = 8.4 Hz), 5.52 (s, 2H), 4.72 (s, 2H), 1.34 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.7, 156.8, 136.9, 133.5, 130.3, 130.2, 128.5, 127.6, 127.4, 125.8, 124.5, 54.1, 35.1, 31.0; IR (KBr) ν_{max}: 3054, 2962, 2869, 1680, 1237, 1071, 938, 824, 688 cm^{-1}. HRMS calculated for $C_{38}H_{38}O_3Na$ [M+Na$^+$] 565.2719, found: 565.2724.

(5*R,6*R**,11*R**,12*R**)-5,6,11,12-Tetrahydro-5,11-epoxydibenzo[*a,e*][8]annulene-6,12-diyl)bis((4-chlorophenyl)methanone) (2*l*).** Yield: 80%; white solid; m.p. 223-225 °C;^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97-8.01 (m, 4H),7.50-7.54 (m, 4H), 7.29-7.38 (m, 4H), 7.15-7.21 (dt, 2H, J = 7.0 Hz), 6.91-6.93 (d, 2H, J = 7.8 Hz), 5.54 (s, 2H), 4.69 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.0, 139.6, 136.4, 134.5, 130.3, 129.9, 129.6, 129.2, 127.8, 127.7, 124.5, 71.2, 54.2; IR (KBr) ν_{max} 3062, 2926, 1685, 1231, 1084, 1005, 960, 831, 761, 617 cm^{-1}; HRMS calculated for $C_{30}H_{20}Cl_2O_3Na$ [M+Na$^+$]: 521.0682, found: 521.0682.

(5*R,6*R**,11*R**,12*R**)-5,6,11,12-Tetrahydro-5,11-epoxydibenzo[a,e][8]annulene-6,12-diyl)bis((4-fluorophenyl)methanone) (2m).** Yield: 82%; ehite solid; m.p. 236-239 °C; ^{1}H NMR (300 MHz, CD_3CN): δ 8.08-8.12 (m, 4H), 7.39-7.29 (m, 4H), 7.16-7.25 (m, 6H), 76.91-6.94 (m, 2H), 5.56 (s, 2H), 4.71 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.6, 167.3, 163.9, 136.4, 132.5, 132.5, 131.2, 131.1, 130.3, 129.7, 127.8, 127.7, 124.5, 116.1, 115.9, 71.3, 54.1; IR (KBr) ν_{max}:

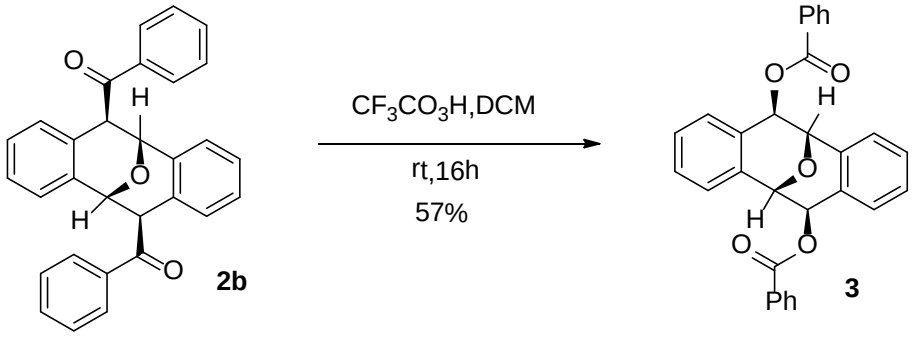
3068, 2927, 1680, 1230, 1079, 1007, 970, 840, 744, 605 cm^{-1}; HRMS calcd for $C_{30}H_{20}F_2O_3Na$ [M+Na^+]: 489.1273, found: 489.1268.

(5*R,6*R**,11*R**,12*R**)-5,6,11,12-Tetrahydro-5,11-epoxydibenzo[*a,e*][8]annulene-6,12-diyl)bis((4-(*tert*-butyl)phenyl)methanone) (2n).** Yield: 67%; white solid; m.p. 292-298 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05-8.02 (d, *J* = 8.4 Hz, 4H), 7.57-7.54 (d, *J* = 8.1Hz, 4H), 7.43-7.40 (d, *J* = 8.1 Hz, 2H), 7.32-7.27 (t, 2H, *J* = 7.2 Hz), 7.18-7.13 (t, 2H, *J* = 7.2 Hz), 6.93-6.90 (d, 2H, *J* = 7.8 Hz), 5.59 (s, 2H), 4.77 (s, 2H), 1.37 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.7, 156.8, 136.9, 133.5, 130.4, 130.2, 128.5, 127.6, 127.4, 125.8, 124.5, 54.1, 35.1, 31.0; IR (KBr) ν_{max}: 3026, 2959, 2867, 1687, 1262, 1080, 968, 828, 748, 619 cm^{-1}; HRMS calcd for $C_{38}H_{38}O_3Na$ [M+Na^+] 565.2713, found: 565.2714.

(5*R,6*R**,11*R**,12*R**)-5,6,11,12-Tetrahydro-5,11-epoxydibenzo[*a,e*][8]annulene-6,12-diyl)bis(*p*-tolylmethanone) (2o).** Yield: 87%; white solid; m.p. 180-182 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00-7.97 (d, 2H, *J* = 8.4 Hz), 7.30-7.38 (m, 8H), 7.17-7.22 (dt, 2H, J_1 = 7.8 Hz, J_2 = 1.5 Hz), 6.91-6.94 (d, 2H, *J* = 7.8 Hz), 5.57 (s, 2H), 4.75 (s, 2H), 2.45 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.7, 143.9, 136.8, 133.6, 130.3, 130.1, 129.5, 128.6, 127.6, 127.4, 124.5, 71.4, 53.9, 21.6; IR (KBr) ν_{max}: 3027, 2961, 2919, 1676, 1257, 1084, 970, 822, 727, 608 cm^{-1}; HRMS calcd for $C_{32}H_{26}O_3Na$ [M+Na^+]: 481.1774, found: 481.1767.

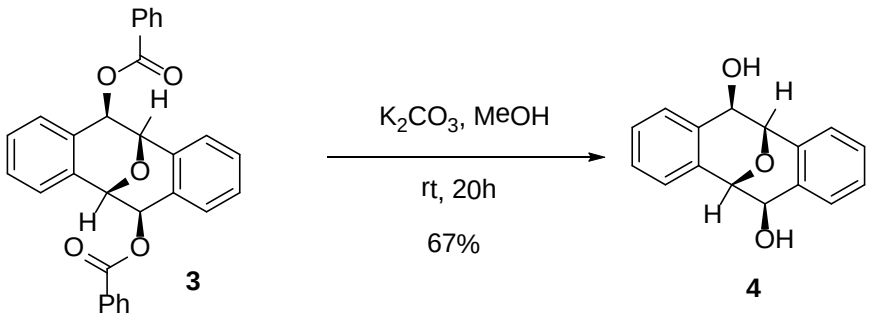
(5*R,6*R**,11*R**,12*R**)-Dimethyl 6,12-bis(4-(*tert*-butyl)benzoyl)-5,6,11,12-tetrahydro-5,11-epoxydibenzo[*a,e*][8]annulene-3,9-dicarboxylate (2p).** Yield: 65%; white solid; m.p.: 292-298 °C; ^{1}H NMR (300 MHz, CD_3CN): δ 8.09-8.03 (m, 6H), 7.84-7.84 (d, *J* = 4.8Hz, 2H),7.60 (d, *J* = 4.8 Hz, 4H), 7.03-7.01 (d, *J* = 4.8Hz, 2H), 5.68 (s, 2H), 4.84 (s, 2H), 3.95 (s, 6H), 1.38 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 134.7, 133.2, 131.0, 129.9, 129.8, 129.1, 128.8, 128.4, 128.3, 125.7, 73.4, 71.1; IR (KBr) ν_{max}: 3036, 2959, 2870, 1717, 1228, 1104, 995, 845, 617 cm^{-1}; HRMS calcd for $C_{42}H_{42}O_7Na$ [M+Na^+] 681.2823, found: 681.2818.

3. Experimental procedure for transformations of Kagan's Ethers



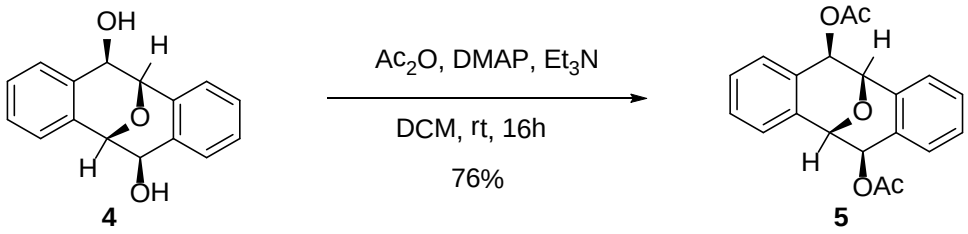
To a solution of trifluoroacetic anhydride (TFAA) (0.96 mL, 6.8 mmol) in dichloromethane (4 mL) was added 30% hydrogen peroxide (0.15 mL, 1.4 mmol) at 0 ºC and stirred for 1 h at room temperature. The resultant solution was directly used as 0.33 mol/L TFPA solution of dichloromethane.

To the above solution of trifluoroperoxyacetic acid (TFPA) in dichloromethane (0.33 M, 8 mL) was added the solution of **2b** (0.21 g, 0.5 mmol) at 0 °C. After stirring for 4 h at the room temperature, the second batch of TFPA solution in dichloromethane (0.33 M, 8 mL) was added at 0 °C. The mixture was stirred at room temperature for another 4 h. The reaction was quenched by adding saturated aq. sodium hydrogen sulfite, diluted with water and extracted with dichloromethane (15 mL x 3). The combined organic phases were washed with water and brine, dried over sodium sulfate, and concentrated. Purification by silica gel chromatography (petroleum ether/ethyl acetate = 80:1) afforded **3** (0.12 g, 57%) as a pale yellow solid. m.p. 199-201 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10-8.13 (m, 4H), 7.46-7.56 (m, 4H), 7.38-7.46 (m, 6H), 7.27-7.31 (m, 4H), 5.98 (s, 2H), 5.53 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 134.7, 133.2, 131.0, 129.9, 129.8, 129.1, 128.8, 128.4, 128.3, 125.7, 73.4, 71.1; IR (KBr) ν_{max}: 3061, 3032, 2965, 2930, 1707, 1270, 1094, 940, 709 cm^{-1}; HRMS calcd for $C_{30}H_{22}O_5Na$ [M+Na^{+}] 485.1360, found: 485.1367.

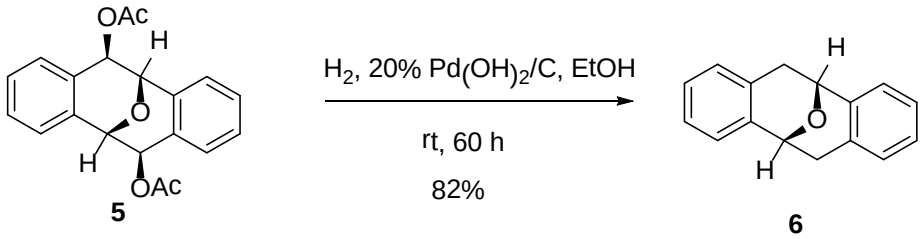


To the solution of **3** (4.6g, 10 mmol) in methanol (50mL) was added potassium carbonate (1.2 g)

at the room temperature. After stirring for 24 h, the mixture was filtered, and the filtrate was concentrated. Purification by silica gel chromatography (petroleum ether/ethyl acetate = 30:1) afforded **4** (1.7 g, 67%) as a white solid. m.p. 253-256 °C; ^{1}H NMR (300 MHz, CD_3OD): δ 7.18-7.30 (m, 8H,), 5.17 (s, 2H), 4.43 (s, 2H); ^{13}C NMR (75 MHz, CD_3OD): δ 134.5, 132.6, 130.2, 127.7, 127.4, 124.8, 76.0, 69.7; IR (KBr) ν_{max}: 3385, 3032, 3006, 2916, 2893, 1491, 1242, 1040, 902, 761, 609 cm^{-1}; HRMS calcd for $C_{16}H_{14}O_3Na$ [M+Na$^+$] 277.0835, found: 277.0842.



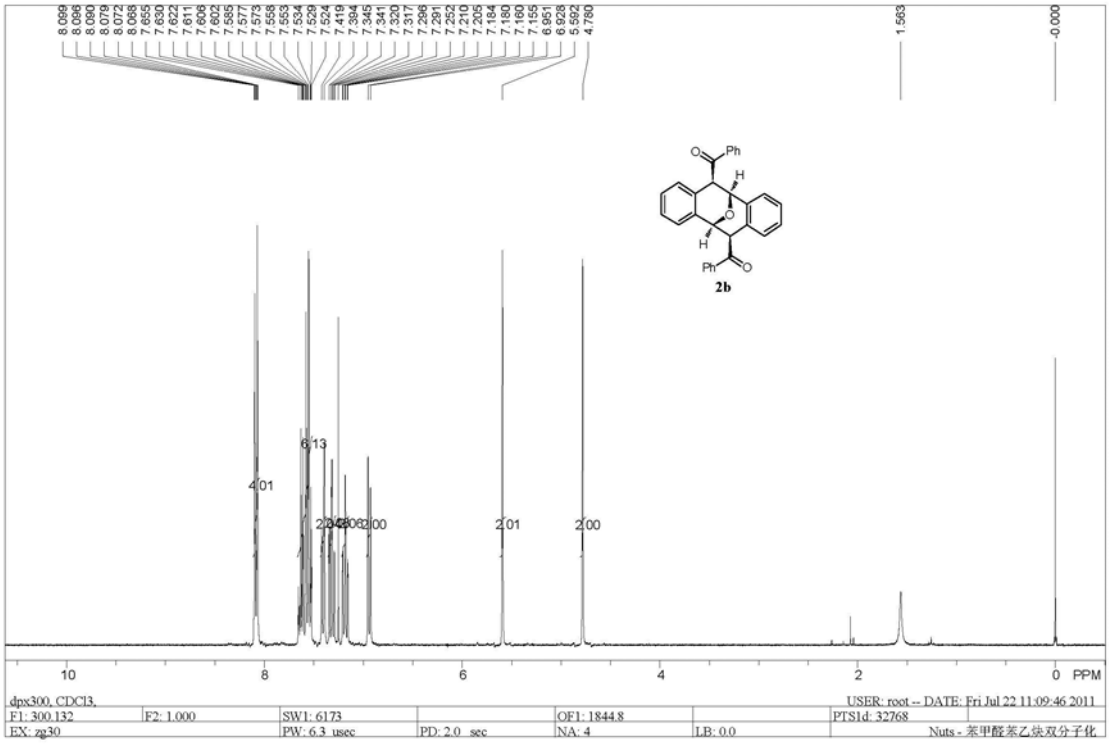
A solution of **4** (0.89 g, 5.0 mmol), DMAP (6 mg, 1 mol%) and triethylamine (2.2 mL, 8.97 mmol) in 50 mL dichloromethane was cooled down to –5 °C and treated with acetic anhydride (0.91 g, 9 mmol). After stirring for 12 h, the reaction was quenched by adding 20 mL water and diluted with dichloromethane. The mixture was washed successively with sat. aq. sodium bicarbonate and brine, dried over sodium sulfate, filtered and concentrated. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to afford **5** (1.28 g, 76%) as a white solid. m.p. 253-256 °C; ^{1}H NMR (300 MHz, CD_3Cl): δ 7.30-7.39 (m, 4H), 7.19-7.27 (m, 4H), 5.70 (s, 2H), 5.34 (s, 2H), 2.18 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.0, 134.3, 130.7, 129.1, 128.5, 128.4, 125.5, 73.1, 70.5, 21.2; IR (KBr) ν_{max}: 3067, 3031, 3010, 2975, 2947, 2848, 2361, 1726, 1242, 1024, 971, 765 cm^{-1}; HRMS calcd for $C_{20}H_{18}O_5Na$ [M+Na$^+$] 361.1046, found: 361.1043.

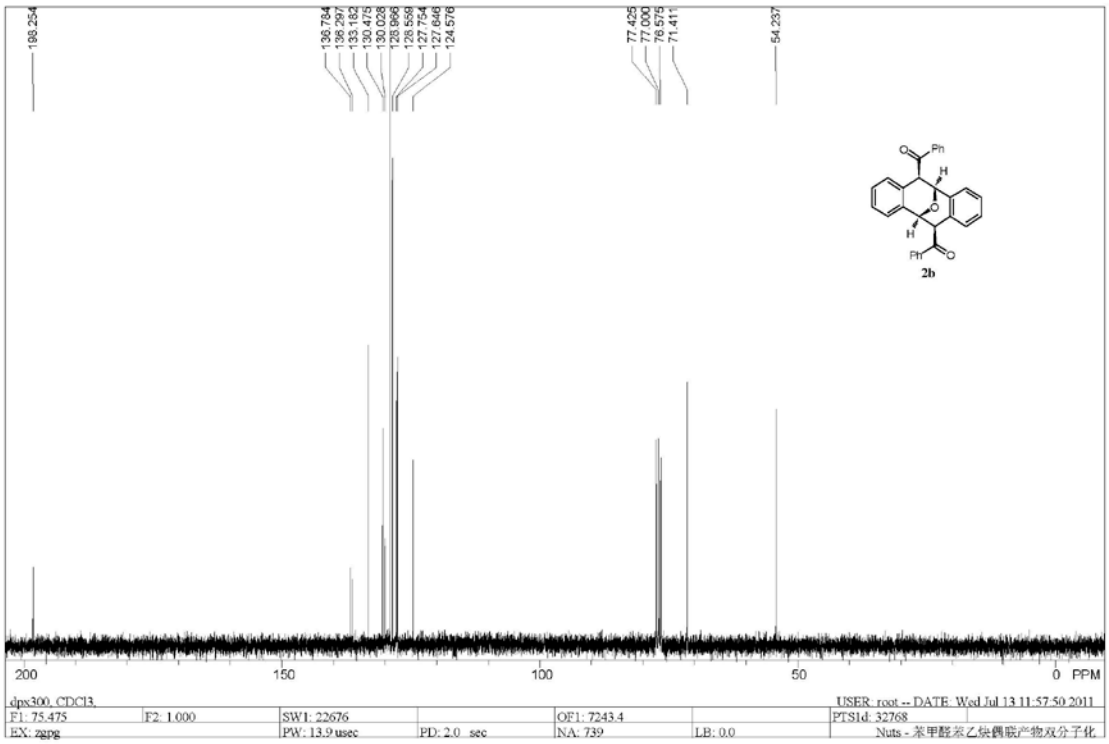


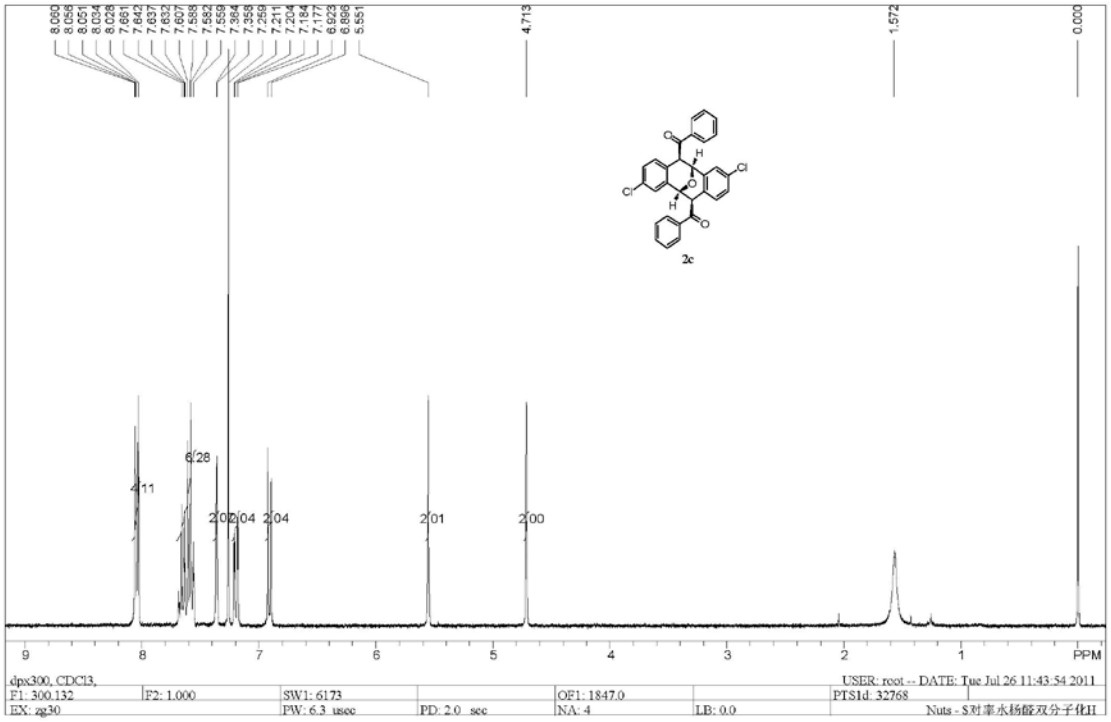
A mixture of diacetate **5** (1 g, 3 mmol) and 20% palladiumhydroxide on charcoal (200 mg) in ethanol (50 mL) was stirred under hydrogen at 40 psi (1 psi = 6.9 Kpa) at room temperature for 40 h. After removal of the catalyst by filtration, the solution was concentrated. The residue was

purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1) to afford **6** (0.54 g, 82%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.08-7.18 (m, 6H), 6.99-7.02 (m, 2H), 5.31-5.33 (d, J = 6.0 Hz, 2H), 5.54-5.62 (dd, J_1 = 16.2 Hz, J_2 = 6 Hz, 2H), 2.77-2.83 (d, J = 16.2 Hz, 6H) ppm. EI-MS (m/z): 222 (M^+).

4. NMR spectra of new compounds



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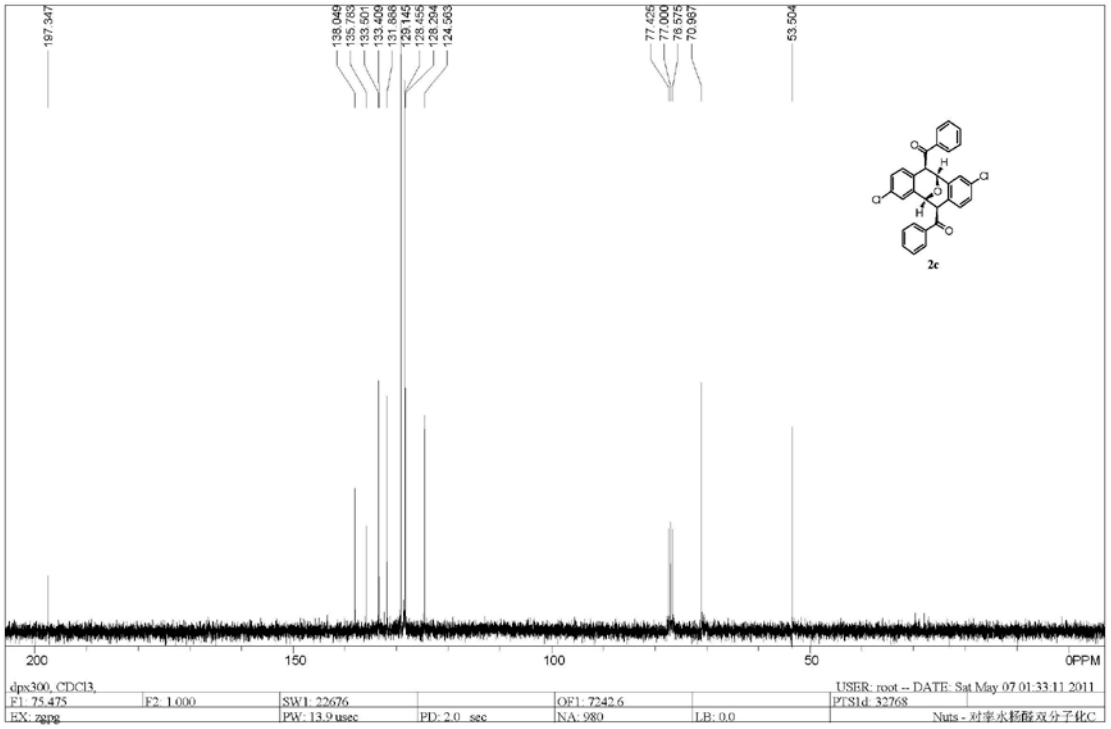
8.051
8.034
8.028
7.661
7.642
7.637
7.632
7.607
7.588
7.582
7.559
7.384
7.358
7.259
7.211
7.204
7.184
7.177
6.923
6.896
5.551
4.713
1.572
0.000
4.11
6.28
2.02
2.04
2.04
2.01
2.00
2c
9
8
7
6
5
4
3
2
1
PPM
dpx300, CDCl3,
USER: root -- DATE: Tue Jul 26 11:43:54 2011
F1: 300.132
F2: 1.000
SW1: 6173
OF1: 1847.0
PTS1d: 32768
EX: zg30
PW: 6.3 usec
PD: 2.0 sec
NA: 4
LB: 0.0
Nuts - $对苯水杨醛双分子化H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135.783
133.501
133.409
131.668
129.145
128.455
128.294
124.563
77.425
77.000
76.575
70.967
53.504
2c
200
150
100
50
0PPM
dpx300, CDCl3,
USER: root -- DATE: Sat May 07 01:33:11 2011
F1: 75.475
F2: 1.000
SW1: 22676
OF1: 7242.6
PTS1d: 32768
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PW: 13.9 usec
PD: 2.0 sec
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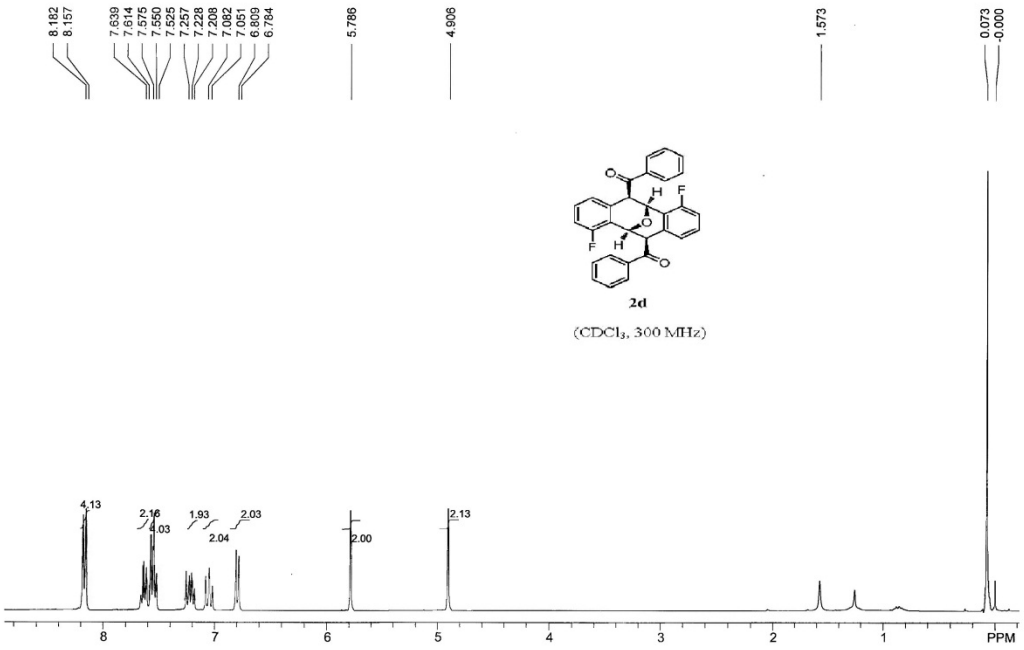
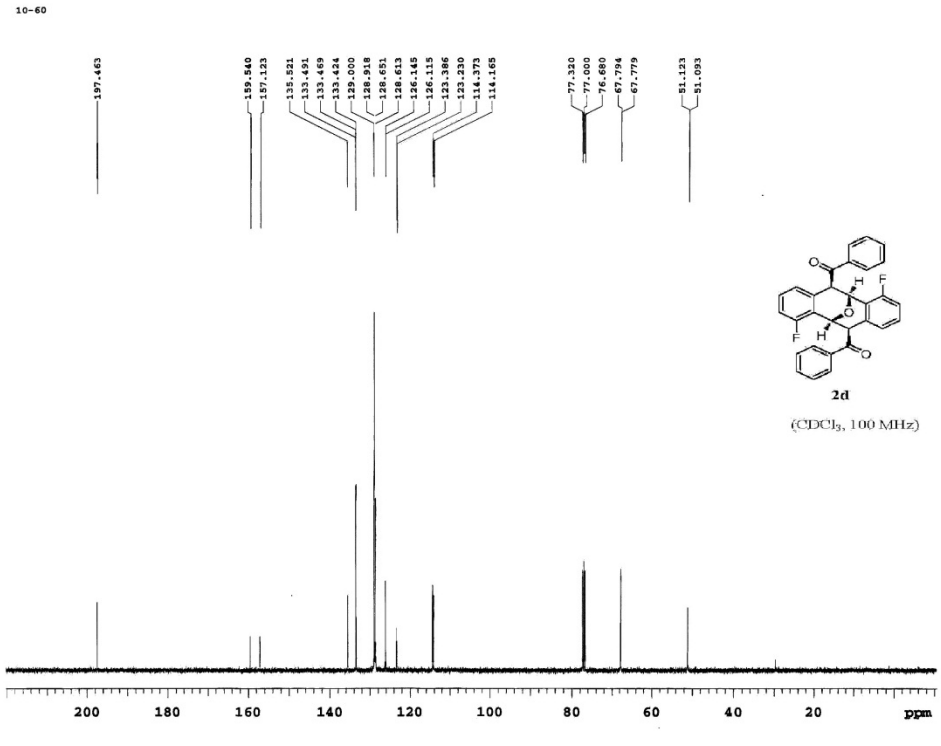
LB: 0.0
Nuts - 对苯水杨醛双分子化C



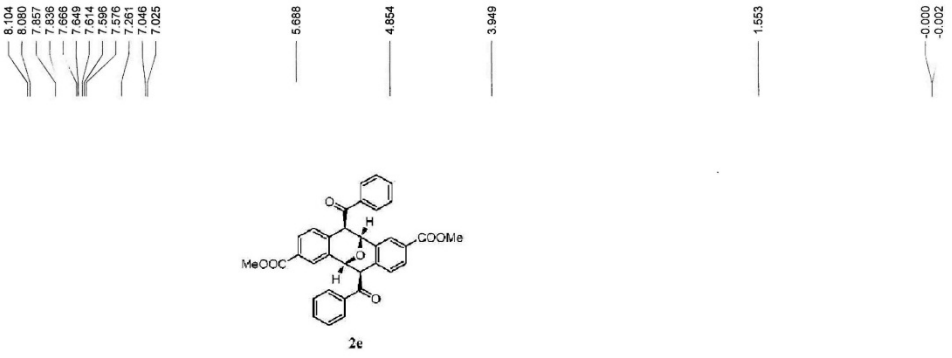
2d

($CDCl_3$, 300 MHz)



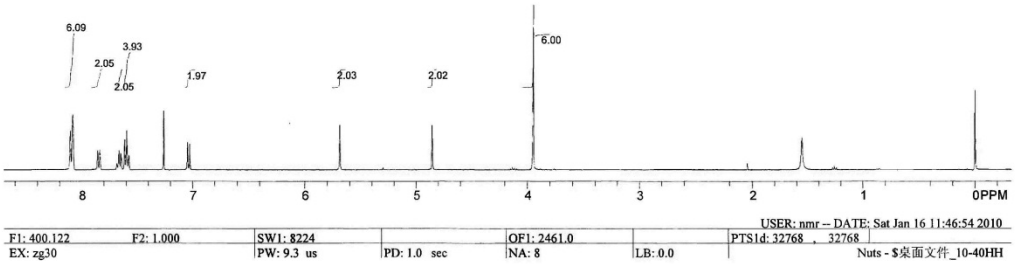
2d

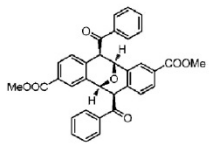
($CDCl_3$, 100 MHz)



2e

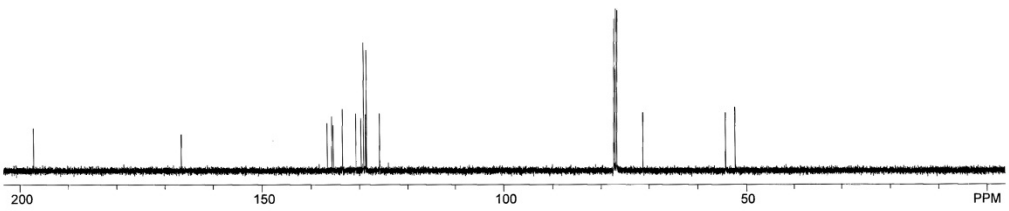
($CDCl_3$, 300 MHz)

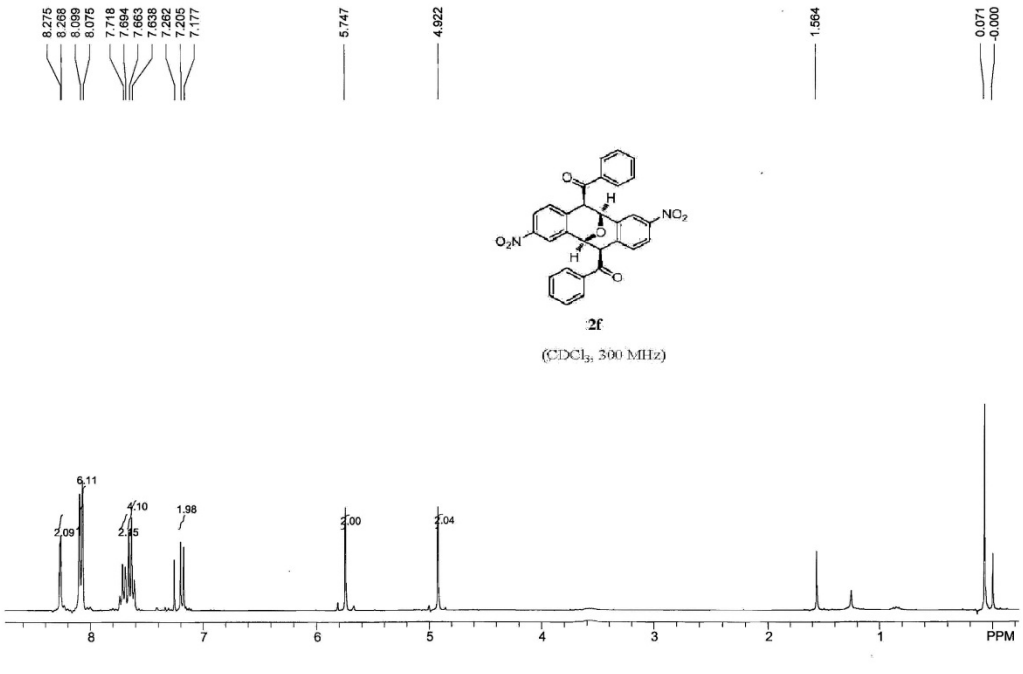




2e

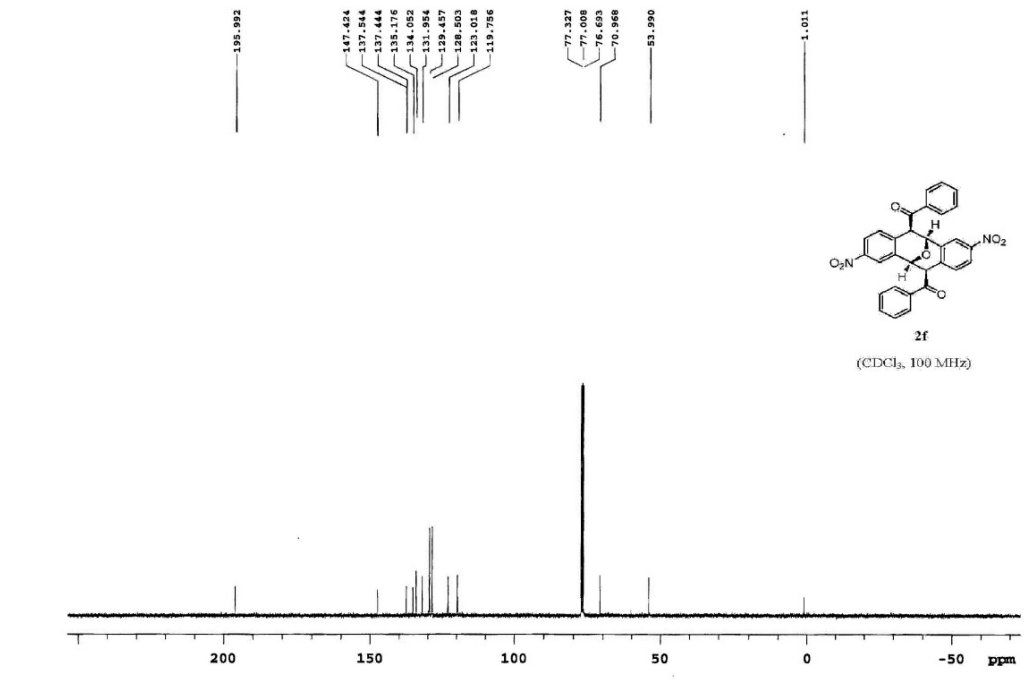
($CDCl_3$, 100 MHz)





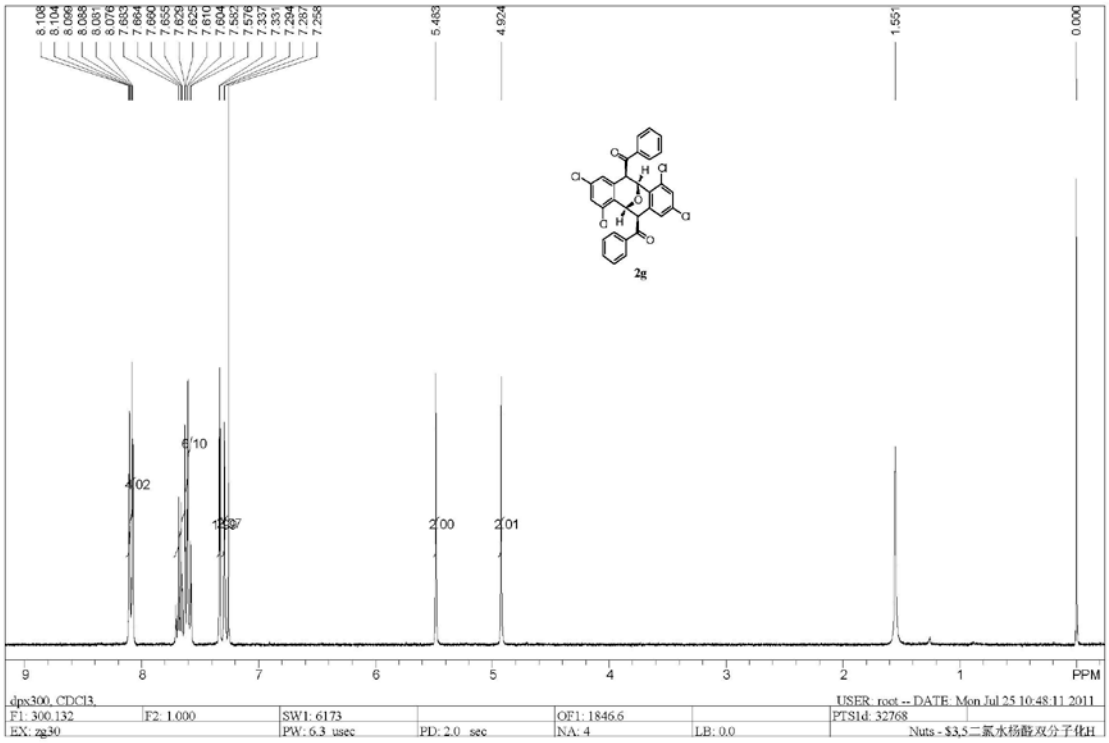
2f

($CDCl_3$, 300 MHz)



2f

($CDCl_3$, 100 MHz)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8.104
8.098
8.088
8.081
8.076
7.683
7.664
7.660
7.655
7.629
7.625
7.610
7.604
7.582
7.576
7.337
7.331
7.294
7.287
7.258
5.483
4.924
1.555
0.000
2g
4.02
6.10
12.87
2.00
2.01
9
8
7
6
5
4
3
2
1
PPM
dpx300, CDCl3
USER: root -- DATE: Mon Jul 25 10:48:11 2011
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OF1: 1846.6
PTS1d: 32768
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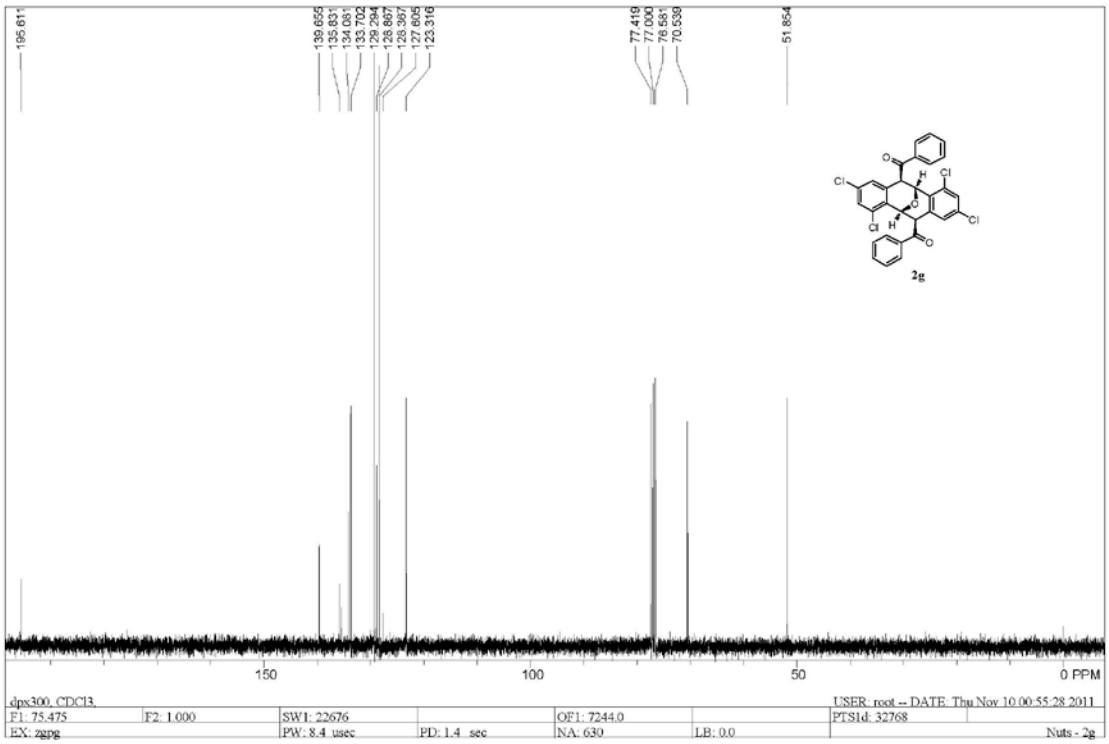
PD: 2.0 sec
NA: 4
LB: 0.0
Nuts - $3,5二氯水杨酚双分子化H


195.611
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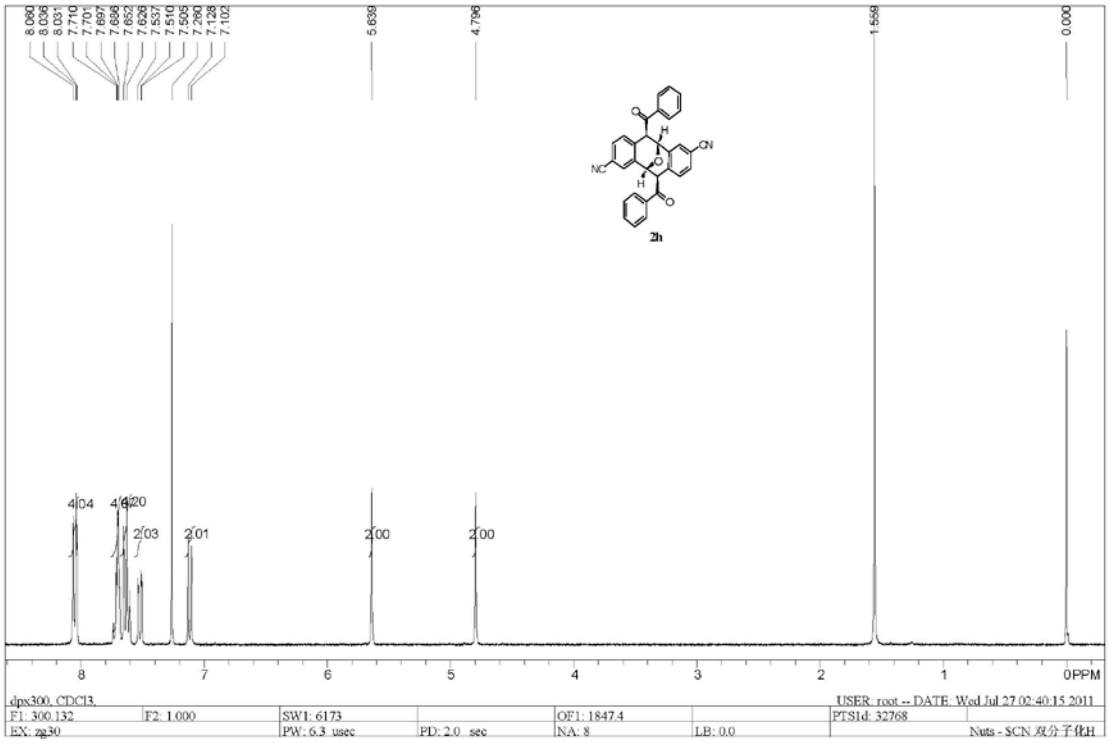
135.831
134.081
133.702
129.294
128.867
128.397
127.605
123.316
77.419
77.000
76.581
70.539
51.854
2g
150
100
50
0 PPM
dpx300, CDCl3
USER: root -- DATE: Thu Nov 10 00:55:28 2011
F1: 75.475
F2: 1.000
SW1: 22676
OF1: 7244.0
PTS1d: 32768
EX: zgpg
PW: 8.4 usec
PD: 1.4 sec
NA: 630
LB: 0.0
Nuts - 2g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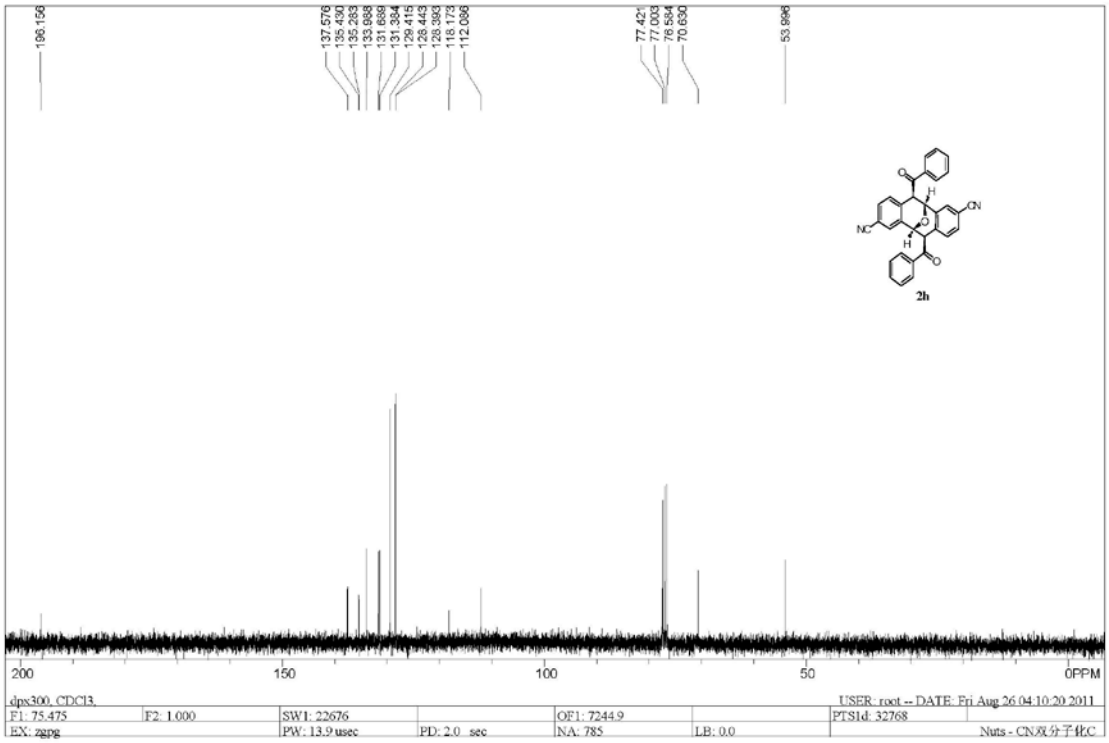
8.036
8.031
7.710
7.701
7.697
7.688
7.652
7.626
7.537
7.510
7.505
7.290
7.128
7.102
5.639
4.796
1.559
0.000
4.04
4.16
4.20
2.03
2.01
2.00
2.00
2h
8
7
6
5
4
3
2
1
0PPM
dpx300, CDCl3,
USER: root -- DATE: Wed Jul 27 02:40:15 2011
F1: 300.132
F2: 1.000
SW1: 6173
OF1: 1847.4
PTS1d: 32768
EX: zg30
PW: 6.3 usec
PD: 2.0 sec
NA: 8
LB: 0.0
Nuts - SCN 双分子化H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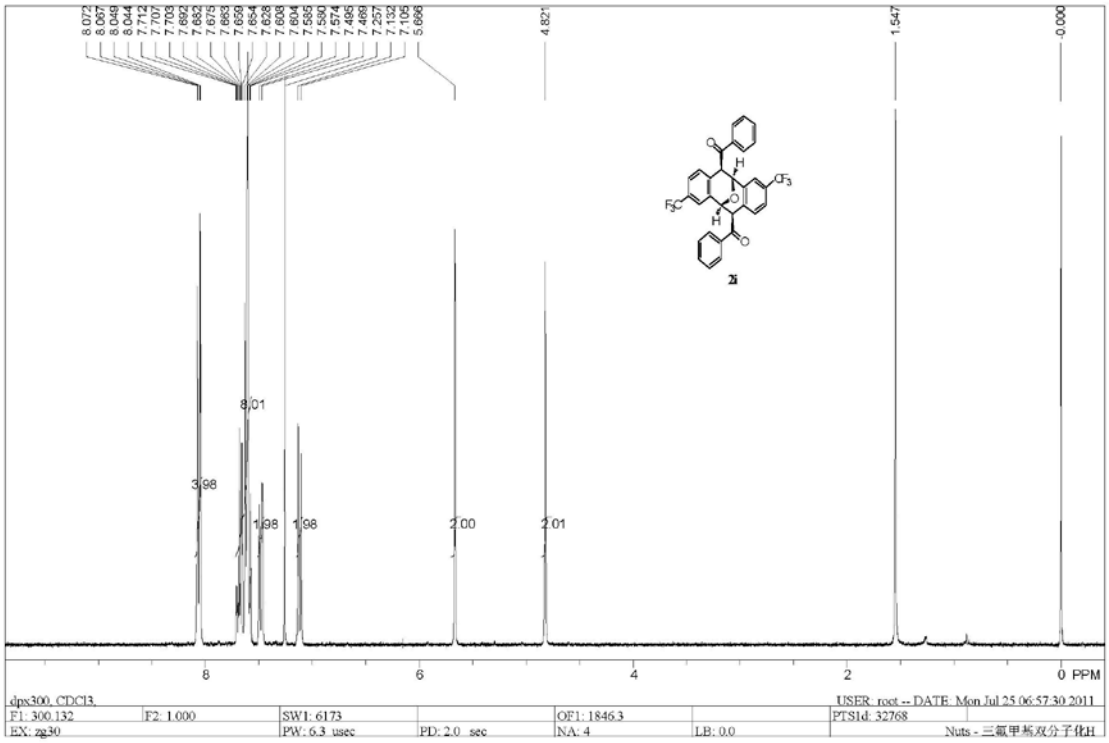
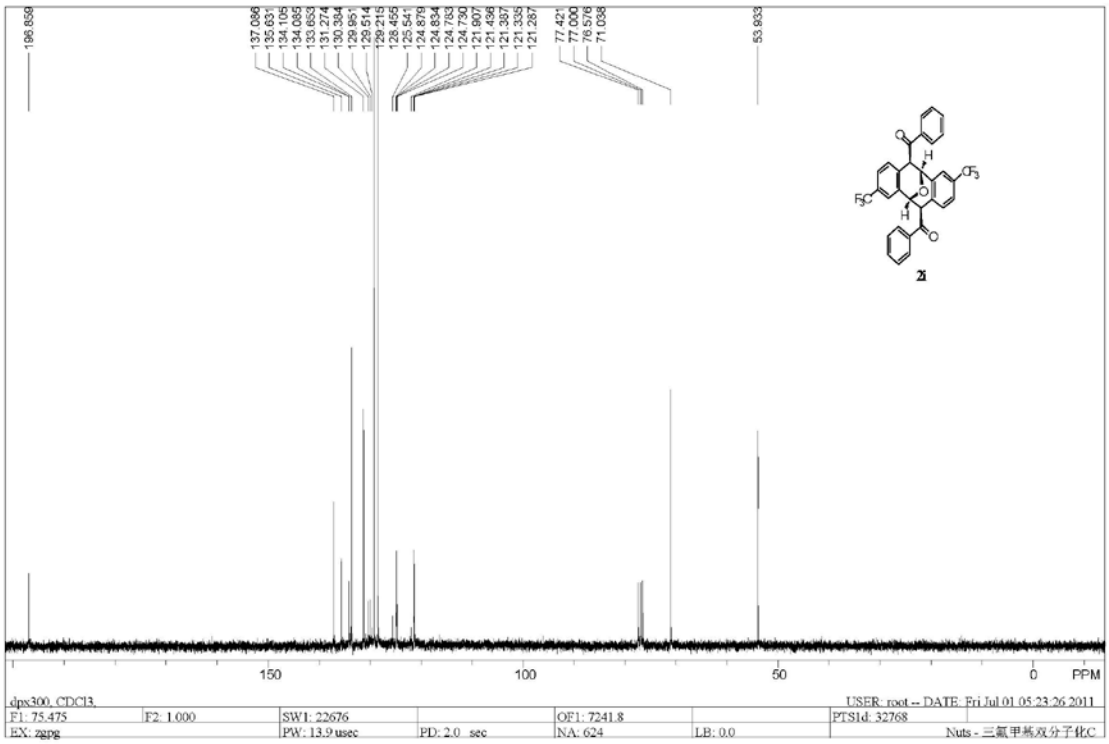
135.430
135.283
133.998
131.689
131.384
129.415
128.443
128.393
118.173
112.096
77.421
77.003
76.584
70.630
53.996
2h
200
150
100
50
0PPM
dpx300, CDCl3,
USER: root -- DATE: Fri Aug 26 04:10:20 2011
F1: 75.475
F2: 1.000
SW1: 22676
OF1: 7244.9
PTS1d: 32768
EX: zgpg
PW: 13.9 usec
PD: 2.0 sec
NA: 785
LB: 0.0
Nuts - CN双分子化C


8.072
8.067
8.049
8.044
7.712
7.707
7.703
7.692
7.682
7.675
7.663
7.659
7.654
7.628
7.608
7.604
7.585
7.580
7.574
7.485
7.469
7.257
7.132
7.105
6.898
4.821
1.547
0.000
8.01
3.98
1.98
1.98
2.00
2.01
8
6
4
2
0 PPM
dpx300, CDCl3
USER: root -- DATE: Mon Jul 25 06:57:30 2011
F1: 300.132
F2: 1.000
SW1: 6173
OF1: 1846.3
PTS1d: 32768
EX: zg30
PW: 6.3 usec
PD: 2.0 sec
NA: 4
LB: 0.0
Nuts - 三氟甲烯双分子化H


196.859
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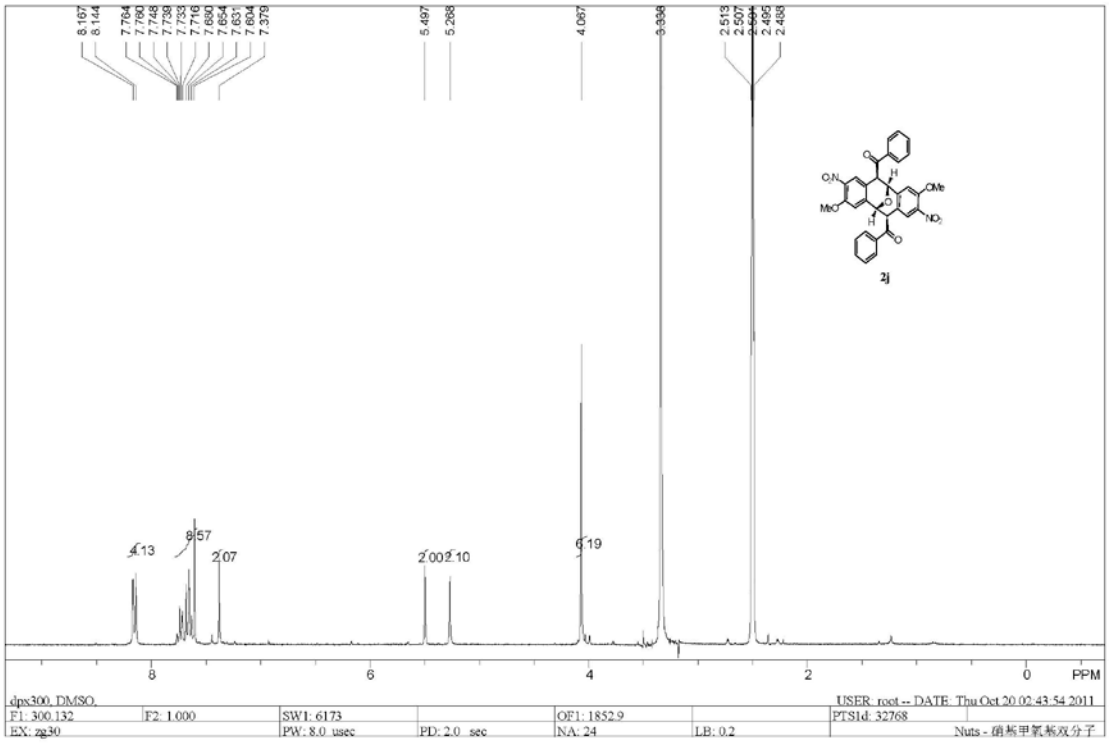
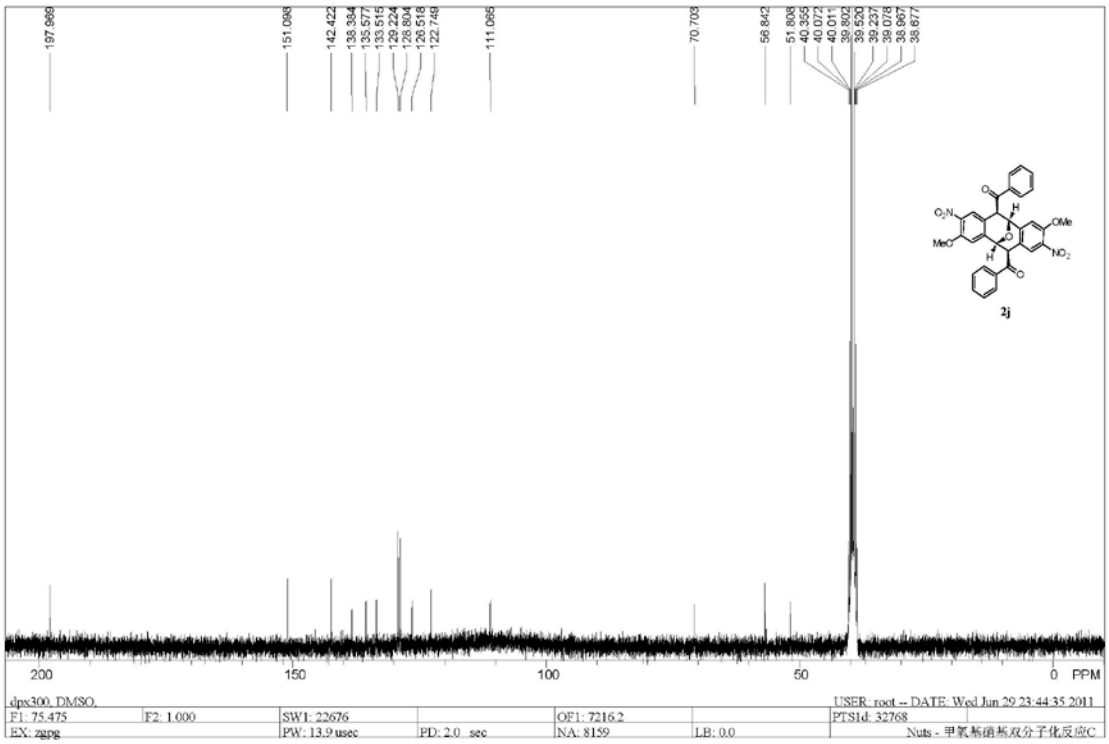
135.631
134.105
134.085
133.653
131.274
130.384
129.951
129.514
129.215
128.455
125.541
124.879
124.834
124.783
124.730
121.907
121.498
121.387
121.335
121.287
77.421
77.000
76.576
71.038
53.933
150
100
50
0 PPM
dpx300, CDCl3
USER: root -- DATE: Fri Jul 01 05:23:26 2011
F1: 75.475
F2: 1.000
SW1: 22676
OF1: 7241.8
PTS1d: 32768
EX: zgpg
PW: 13.9 usec
PD: 2.0 sec
NA: 624
LB: 0.0
Nuts - 三氟甲烯双分子化C


8.167
8.144
7.764
7.760
7.746
7.738
7.733
7.716
7.690
7.654
7.631
7.604
7.379
5.497
5.288
4.057
3.338
2.513
2.507
2.495
2.488
4.13
8.57
2.07
2.00
2.10
6.19
2j
8
6
4
2
0
PPM
dpx300_DMSO
USER: root -- DATE: Thu Oct 20 02:43:54 2011
F1: 300.132
F2: 1.000
SW1: 6173
OF1: 1852.9
PTS1d: 32768
EX: zg30
PW: 8.0 usec
PD: 2.0 sec
NA: 24
LB: 0.2
Nuts - 硝基甲氧基双分子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138.384
135.577
133.515
129.224
128.804
126.518
122.748
111.065
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56.842
51.808
40.355
40.072
40.011
39.802
39.520
39.237
39.078
38.967
38.677
2j
200
150
100
50
0
PPM
dpx300_DMSO
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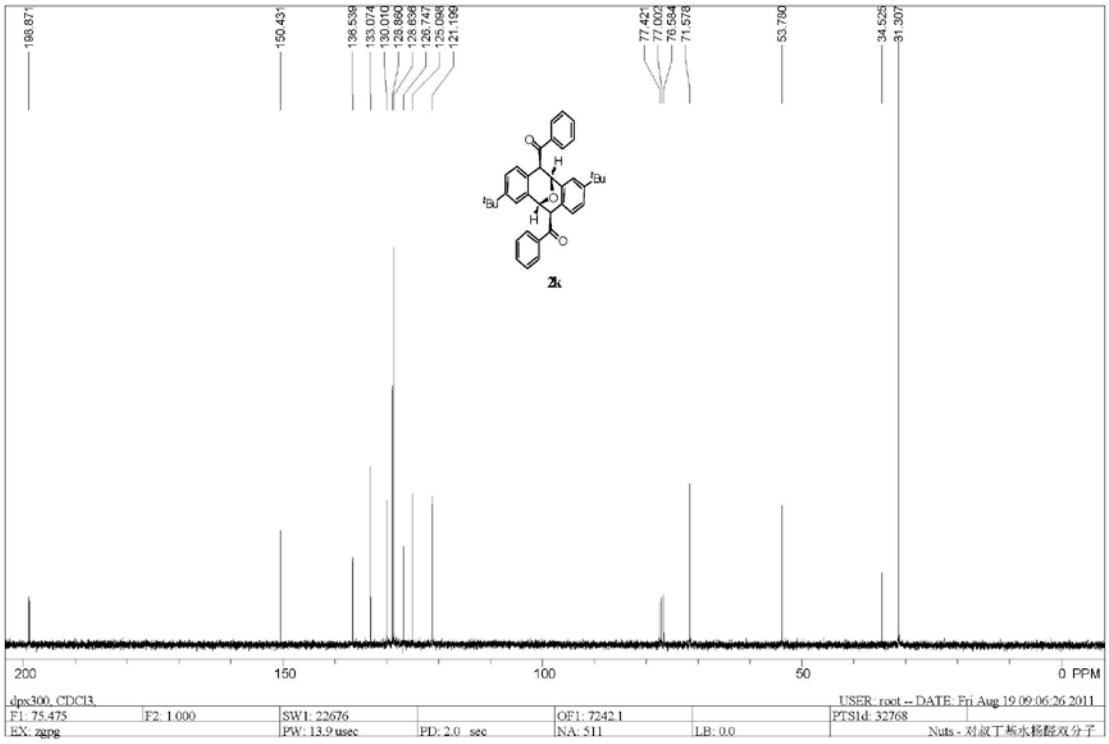
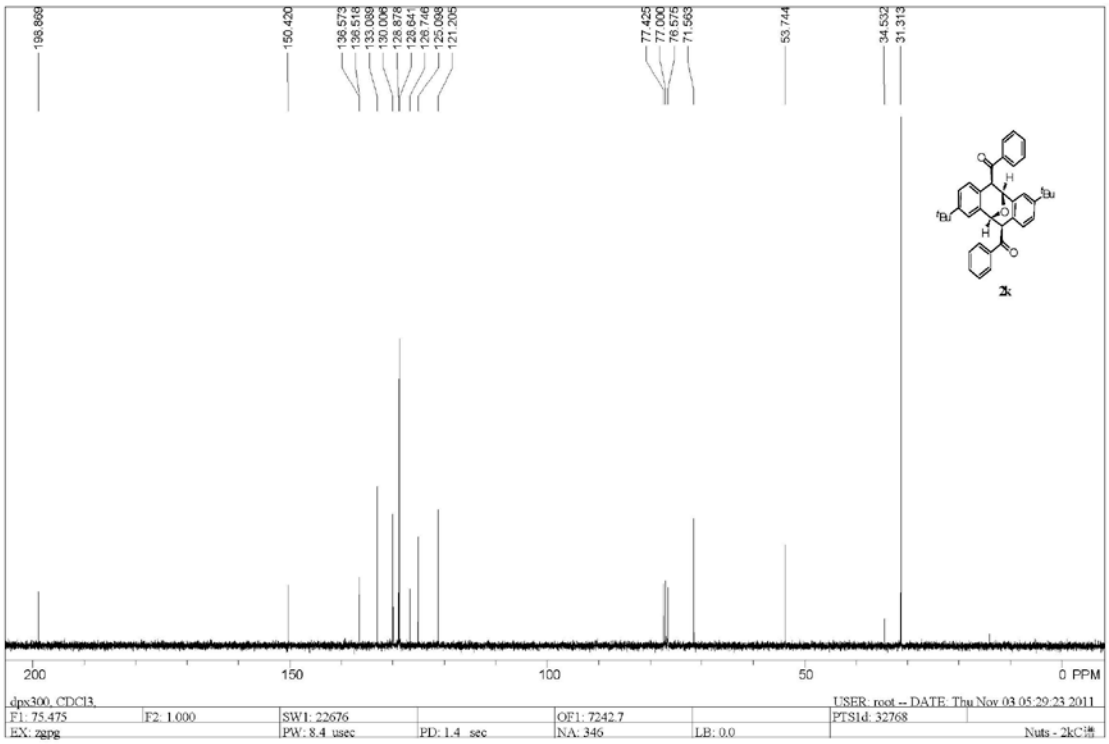
F1: 75.475
F2: 1.000
SW1: 22676
OF1: 7216.2
PTS1d: 32768
EX: zgpg
PW: 13.9 usec
PD: 2.0 sec
NA: 8159
LB: 0.0
Nuts - 甲氧基硝基双分子化反应C


198.87
150.43
136.53
133.07
130.01
128.86
128.63
126.74
125.09
121.19
77.42
77.00
76.58
71.57
53.78
34.52
31.30
tBu
tBu
H
H
O
O
O
2k
200
150
100
50
0 PPM
dpx300, CDCl3,
USER: root -- DATE: Fri Aug 19 09:06:26 2011
F1: 75.475
F2: 1.000
SW1: 22676
OF1: 7242.1
PTS1d: 32768
EX: zgpg
PW: 13.9 usec
PD: 2.0 sec
NA: 511
LB: 0.0
Nuts - 对叔丁炼水杨醛双分子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150.42
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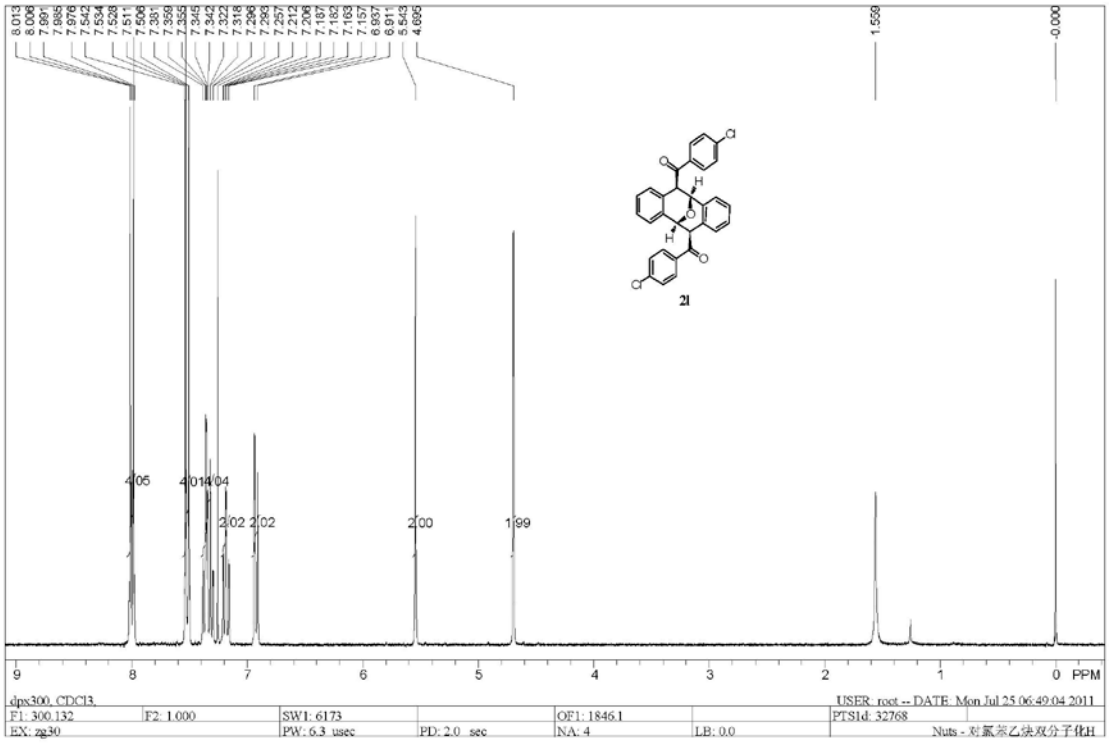
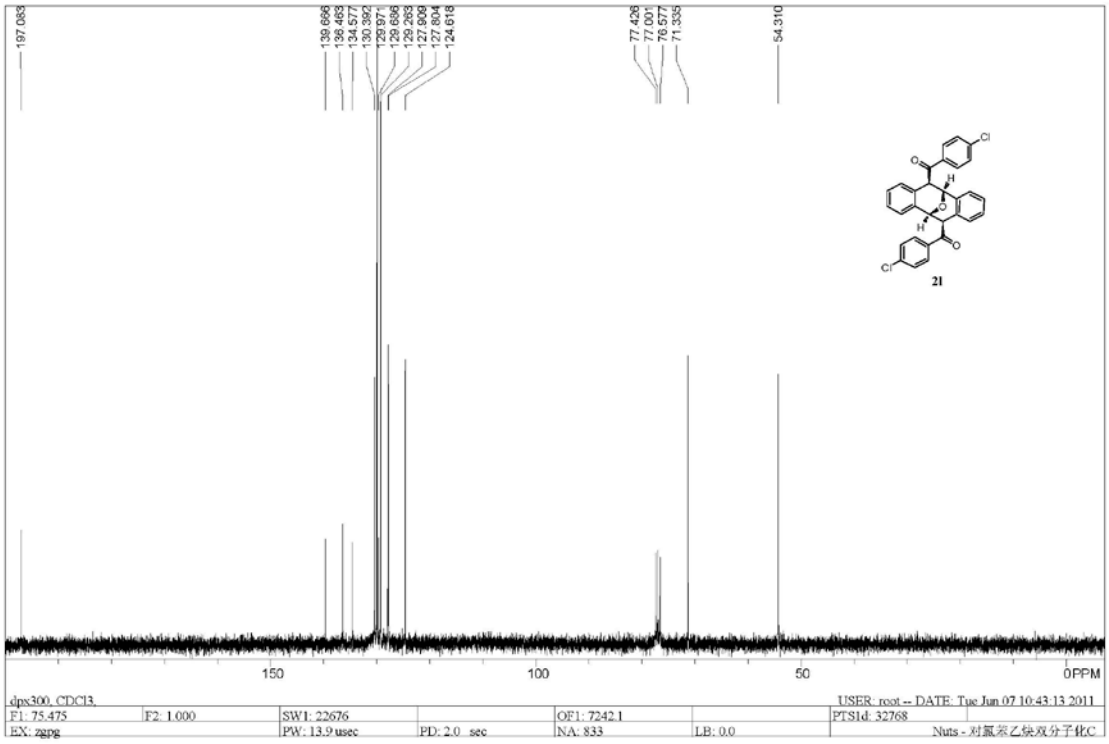
136.51
133.08
130.00
128.87
128.64
126.74
125.09
121.20
77.42
77.00
76.57
71.56
53.74
34.53
31.31
tBu
tBu
H
H
O
O
O
2k
200
150
100
50
0 PPM
dpx300, CDCl3,
USER: root -- DATE: Thu Nov 03 05:29:23 2011
F1: 75.475
F2: 1.000
SW1: 22676
OF1: 7242.7
PTS1d: 32768
EX: zgpg
PW: 8.4 usec
PD: 1.4 sec
NA: 346
LB: 0.0
Nuts - 2kC谱


8.013
8.008
7.991
7.985
7.978
7.542
7.534
7.528
7.511
7.506
7.381
7.359
7.355
7.345
7.342
7.322
7.318
7.298
7.289
7.257
7.212
7.206
7.187
7.183
7.163
7.157
6.937
6.911
5.543
4.695
1.559
0.000
4.05
4.01
4.04
2.02
2.02
2.00
1.99
21
9
8
7
6
5
4
3
2
1
0 PPM
dpx300, CDCl3,
USER: root -- DATE: Mon Jul 25 06:49:04 2011
F1: 300.132
F2: 1.000
SW1: 6173
OF1: 1846.1
PTS1d: 32768
EX: zg30
PW: 6.3 usec
PD: 2.0 sec
NA: 4
LB: 0.0
Nuts - 对氯苯乙炔双分子化H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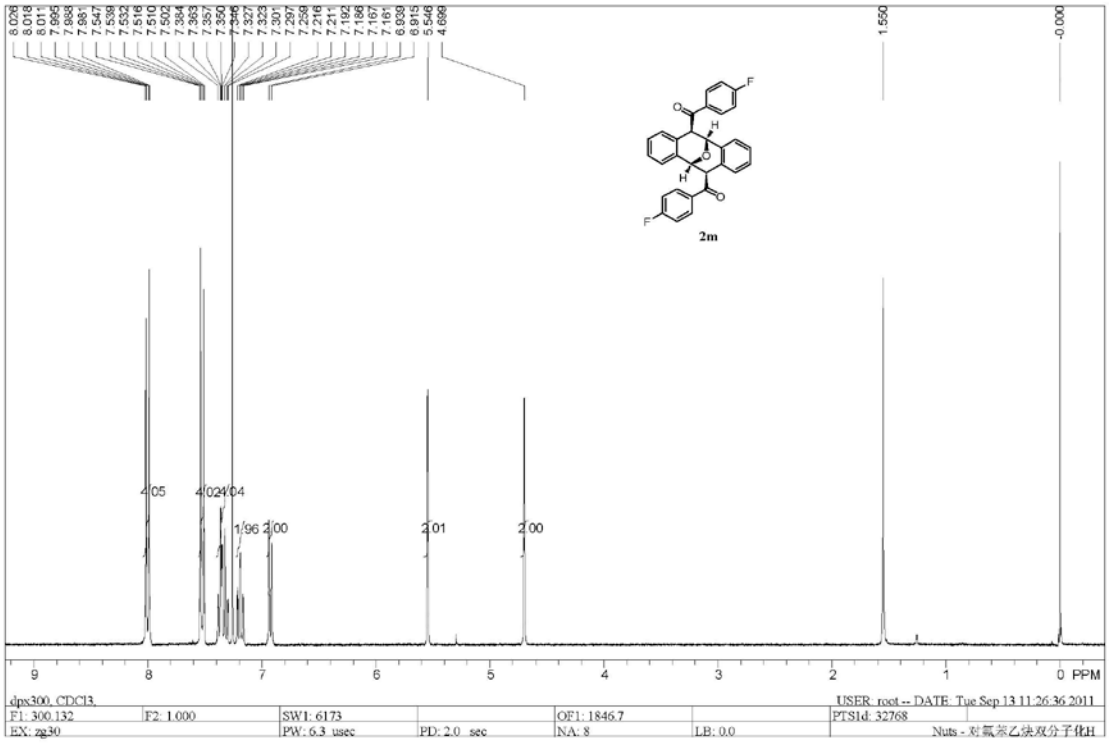
138.483
134.577
130.392
129.971
129.696
129.283
127.909
127.804
124.618
77.426
77.001
76.577
71.335
54.310
21
150
100
50
0PPM
dpx300, CDCl3,
USER: root -- DATE: Tue Jun 07 10:43:13 2011
F1: 75.475
F2: 1.000
SW1: 22676
OF1: 7242.1
PTS1d: 32768
EX: zgpg
PW: 13.9 usec
PD: 2.0 sec
NA: 833
LB: 0.0
Nuts - 对氯苯乙炔双分子化C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8.018
8.011
7.995
7.989
7.981
7.547
7.538
7.532
7.516
7.510
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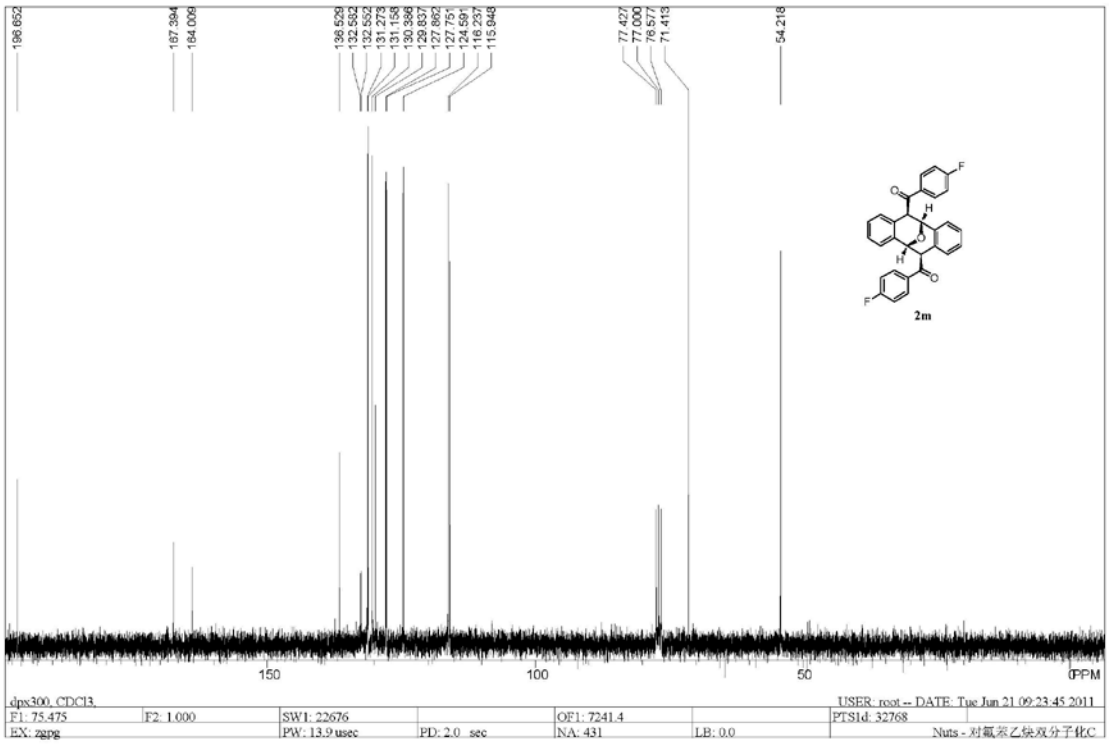
7.384
7.363
7.357
7.350
7.346
7.327
7.323
7.301
7.297
7.258
7.216
7.211
7.192
7.186
7.167
7.161
6.939
6.915
5.546
4.699
1.550
0.000
4.05
4.02
4.04
1.96
2.00
2.01
2.00
2m
9
8
7
6
5
4
3
2
1
0 PPM
dpx300, CDCl3
USER: root -- DATE: Tue Sep 13 11:26:36 2011
F1: 300.132
F2: 1.000
SW1: 6173
OF1: 1846.7
PTS1d: 32768
EX: zg30
PW: 6.3 usec
PD: 2.0 sec
NA: 8
LB: 0.0
Nuts - 对氟苯乙炔双分子化H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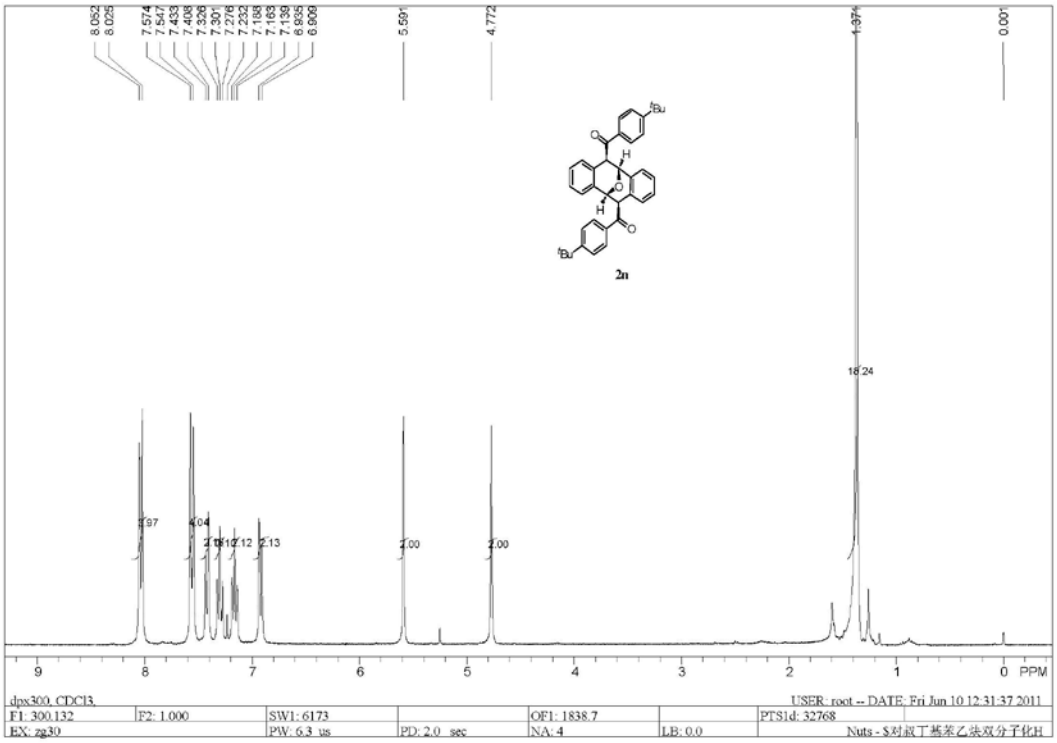
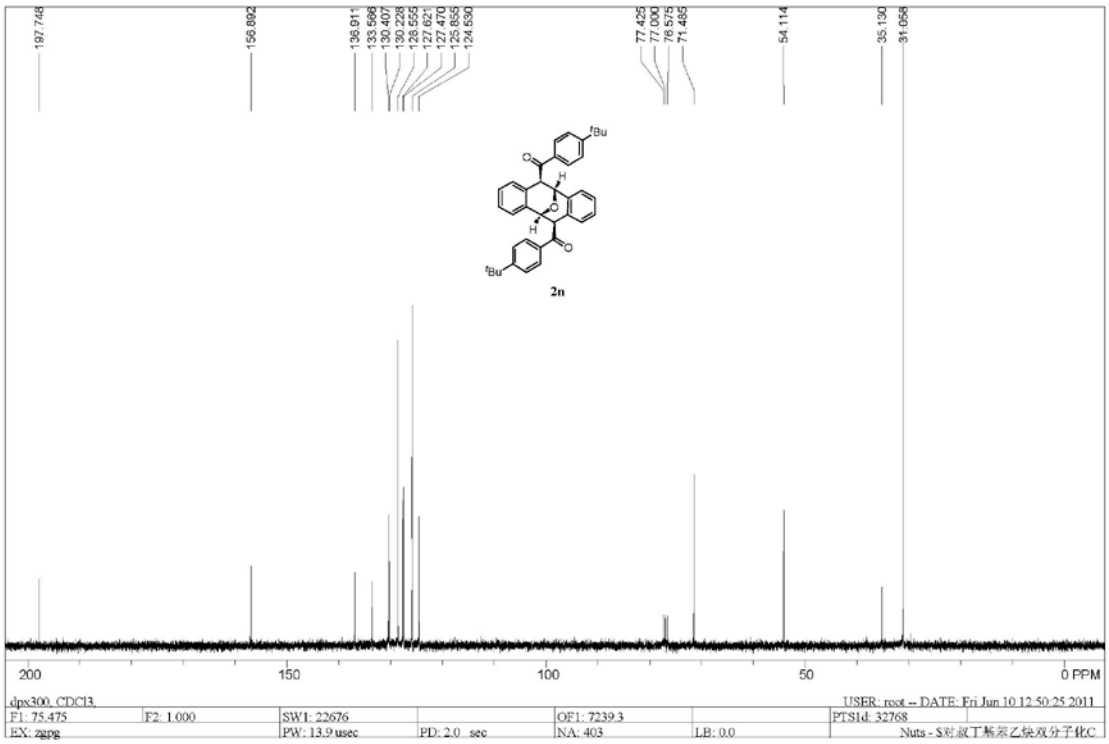
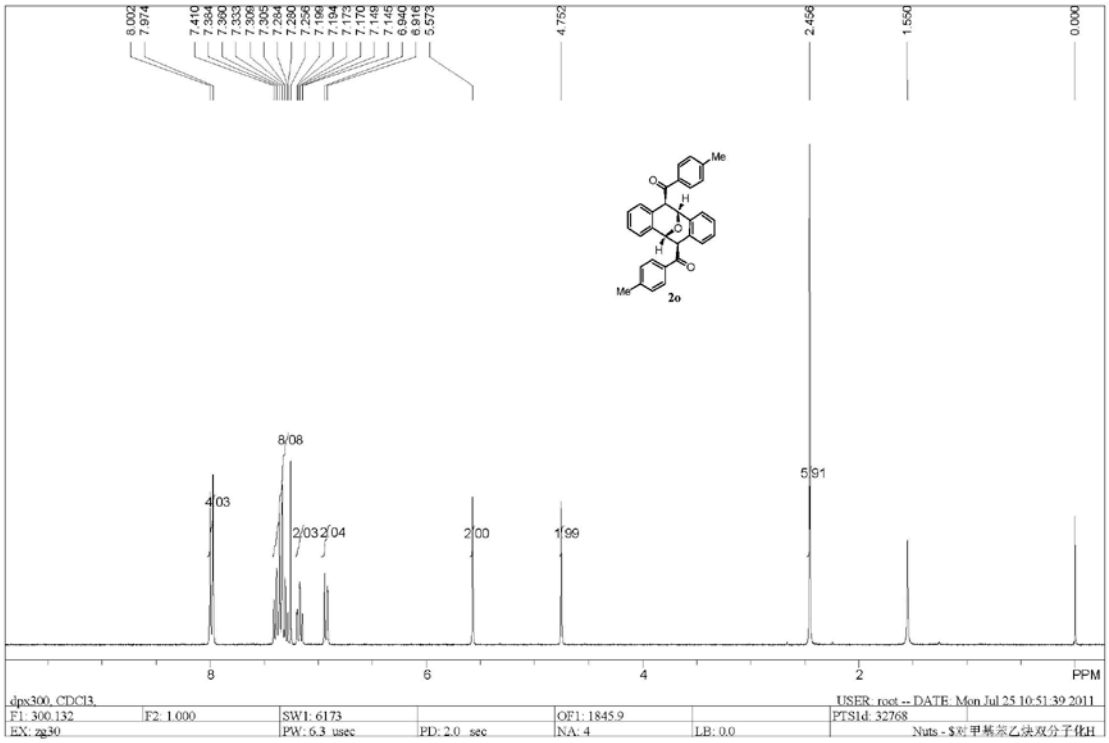
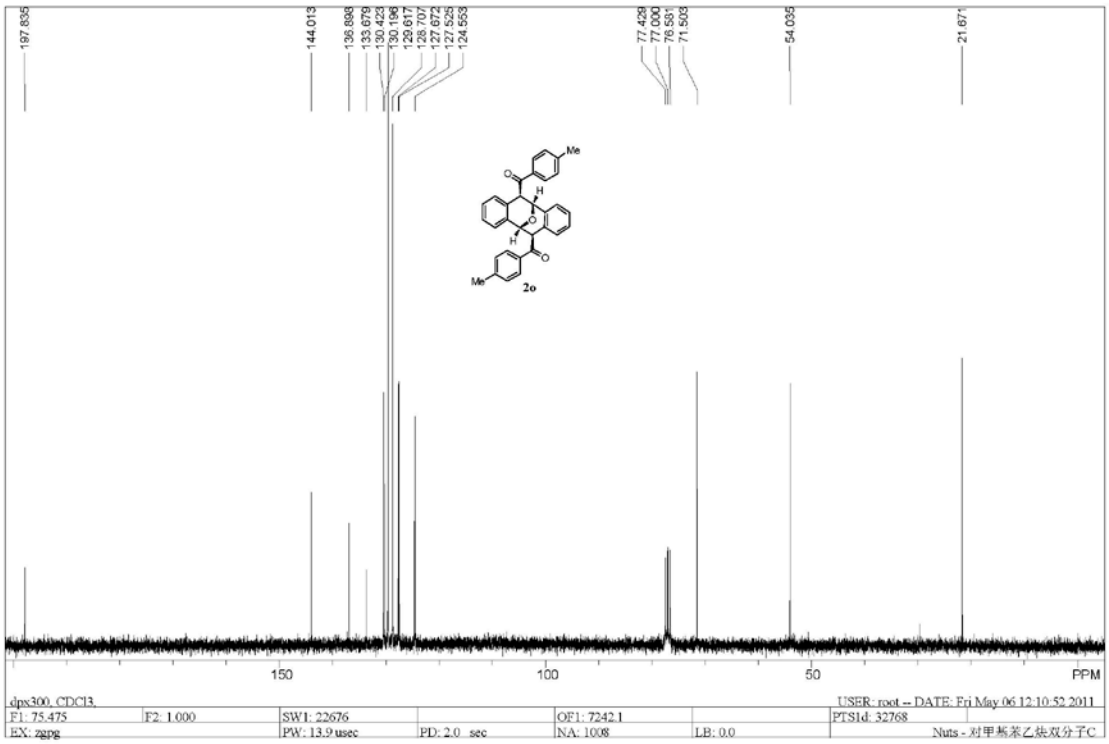
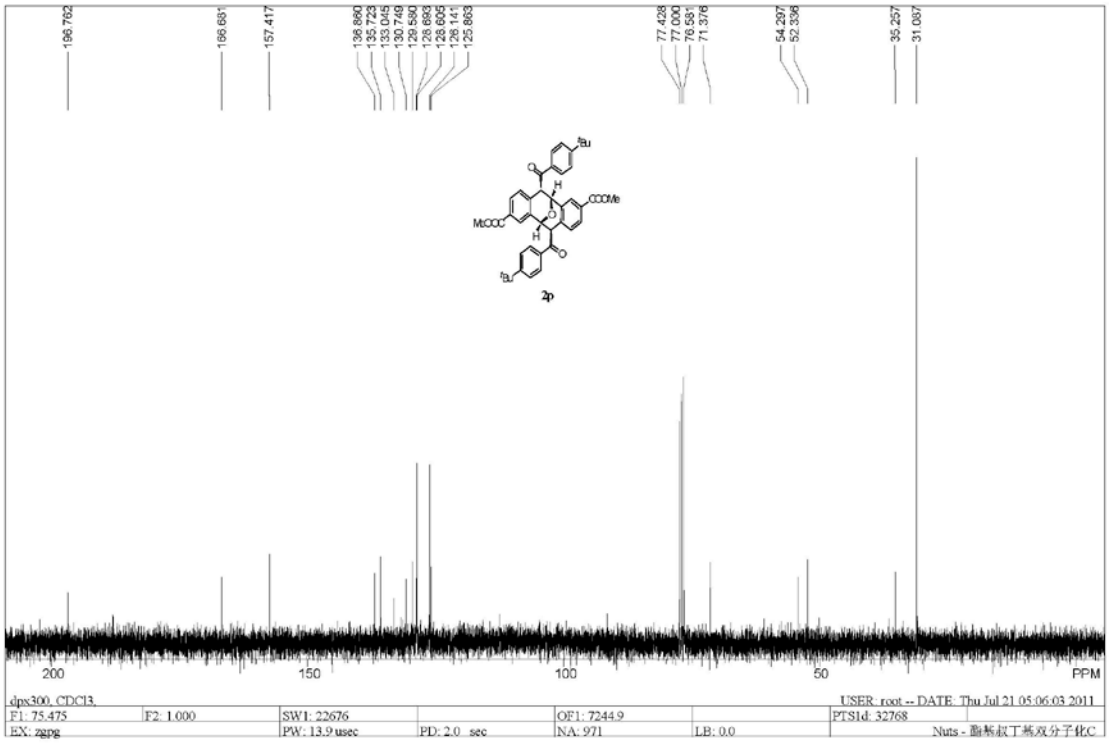
132.552
131.273
131.158
130.396
129.837
127.862
127.751
124.591
116.237
115.948
77.427
77.000
76.577
71.413
54.218
2m
150
100
50
0PPM
dpx300, CDCl3
USER: root -- DATE: Tue Jun 21 09:23:45 2011
F1: 75.475
F2: 1.000
SW1: 22676
OF1: 7241.4
PTS1d: 32768
EX: zgpg
PW: 13.9 usec
PD: 2.0 sec
NA: 431
LB: 0.0
Nuts - 对氟苯乙炔双分子化C

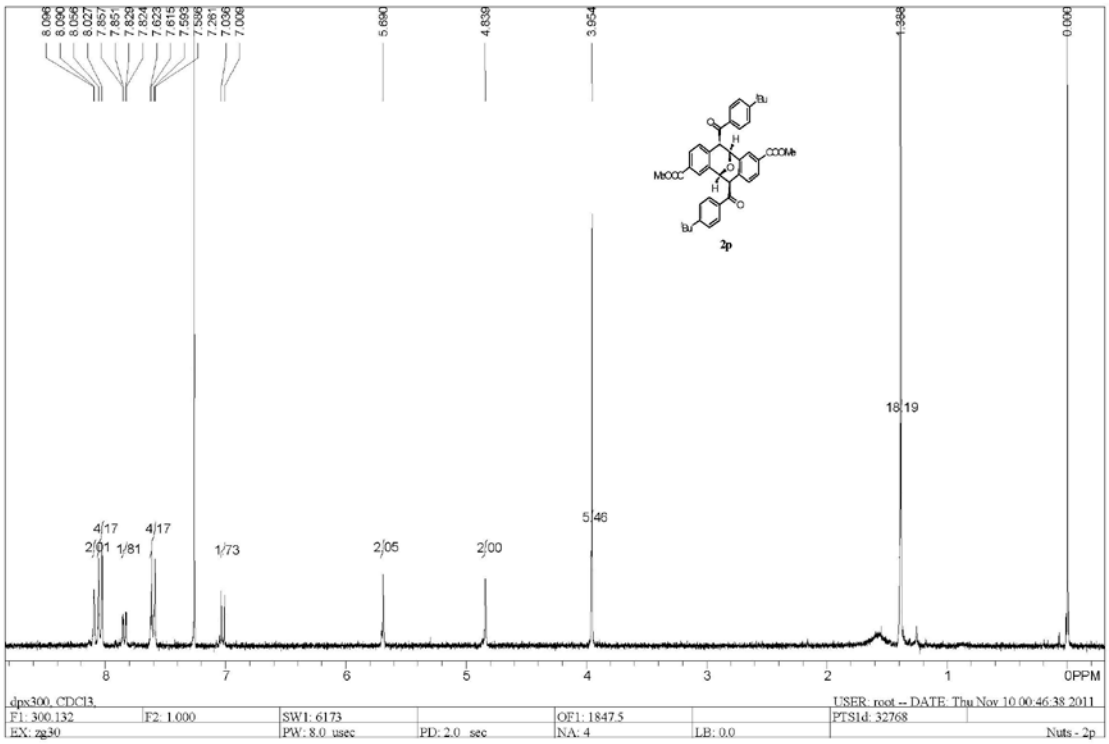

8.052
8.025
7.574
7.547
7.433
7.408
7.326
7.301
7.276
7.232
7.188
7.163
7.139
6.935
6.909
5.591
4.772
1.374
0.000
tBu
O
H
O
H
O
tBu
2n
18.24
1.97
4.04
2.10
2.12
2.13
2.00
2.00
9
8
7
6
5
4
3
2
1
0 PPM
dpx300_CDCl3_
USER: root -- DATE: Fri Jun 10 12:31:37 2011
F1: 300.132
F2: 1.000
SW1: 6173
OF1: 1838.7
PTS1d: 32768
EX: zg30
PW: 6.3 us
PD: 2.0 sec
NA: 4
LB: 0.0
Nuts - $对叔丁基苯乙炔双分子化H

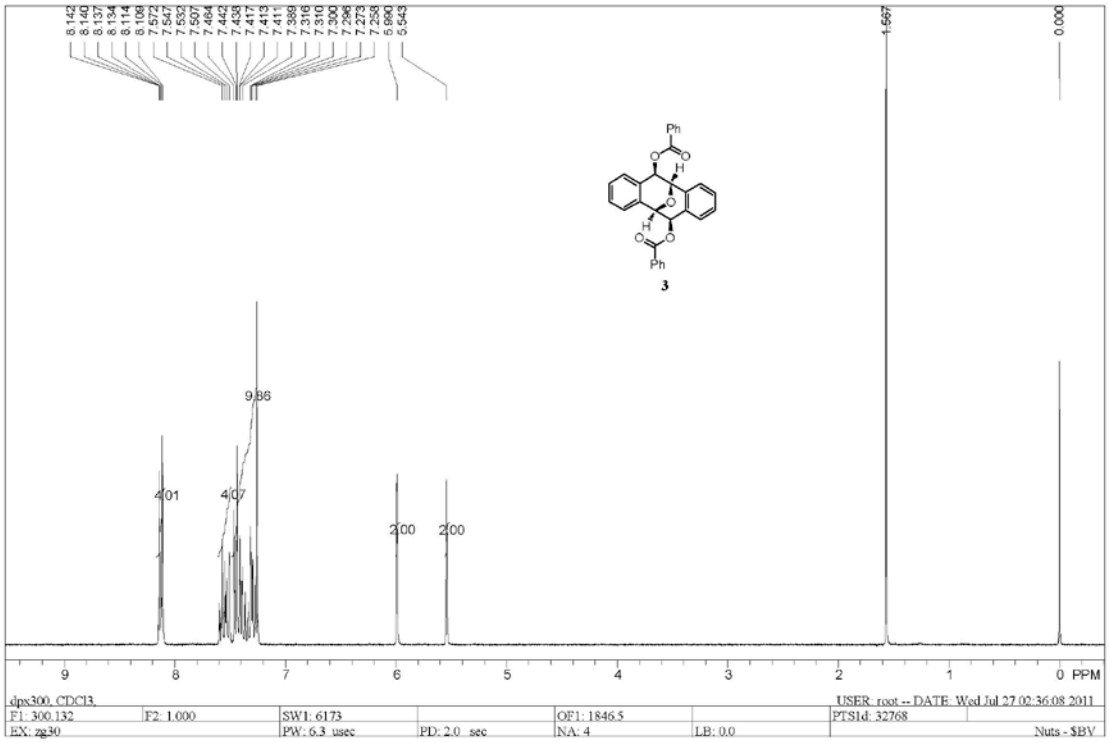

197.748
156.892
136.911
133.566
130.407
130.228
128.555
127.621
127.470
125.855
124.530
77.425
77.000
76.575
71.485
54.114
35.130
31.058
tBu
O
H
O
H
O
tBu
2n
200
150
100
50
0 PPM
dpx300_CDCl3_
USER: root -- DATE: Fri Jun 10 12:50:25 2011
F1: 75.475
F2: 1.000
SW1: 22676
OF1: 7239.3
PTS1d: 32768
EX: zgpg
PW: 13.9 usec
PD: 2.0 sec
NA: 403
LB: 0.0
Nuts - $对叔丁基苯乙炔双分子化C

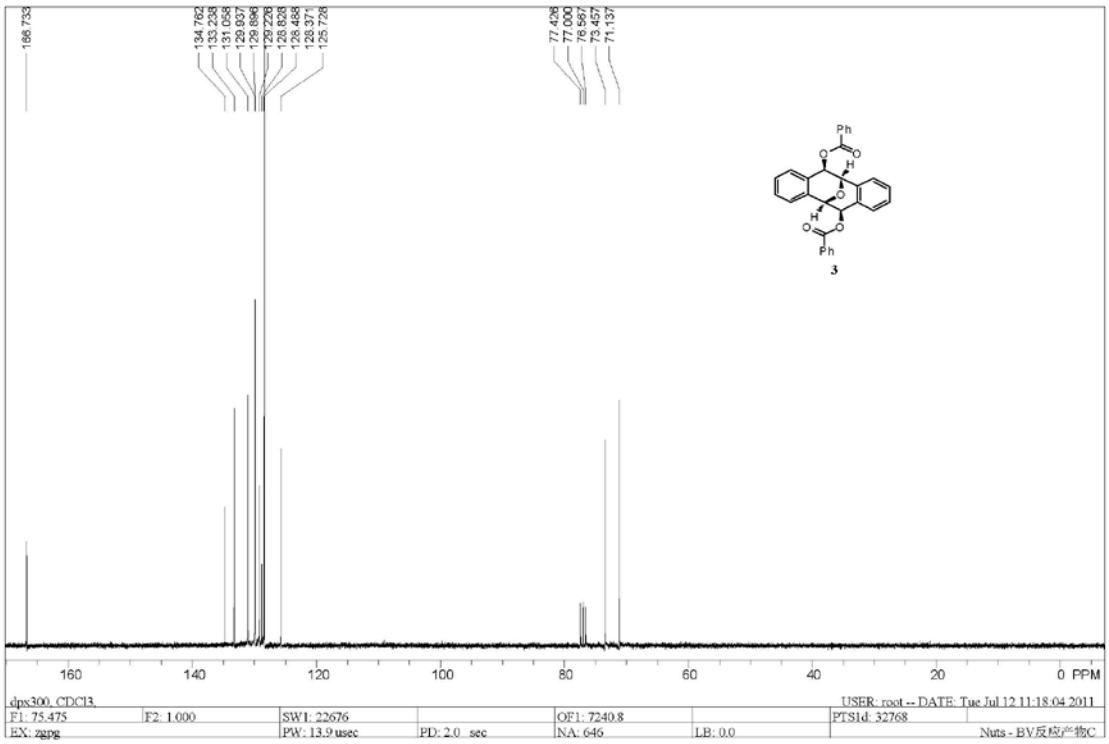

8.002
7.974
7.410
7.384
7.360
7.333
7.306
7.284
7.280
7.256
7.196
7.194
7.173
7.170
7.148
7.145
6.940
6.916
5.573
4.752
2.456
1.550
0.000
Me
O
H
O
H
O
Me
2o
8.08
4.03
2.03
2.04
2.00
1.99
5.91
8
6
4
2
PPM
dpx300, CDCl3,
USER: root -- DATE: Mon Jul 25 10:51:39 2011
F1: 300.132
F2: 1.000
SW1: 6173
OF1: 1845.9
PTS1d: 32768
EX: zg30
PW: 6.3 usec
PD: 2.0 sec
NA: 4
LB: 0.0
Nuts - $对甲基苯乙炔双分子化H

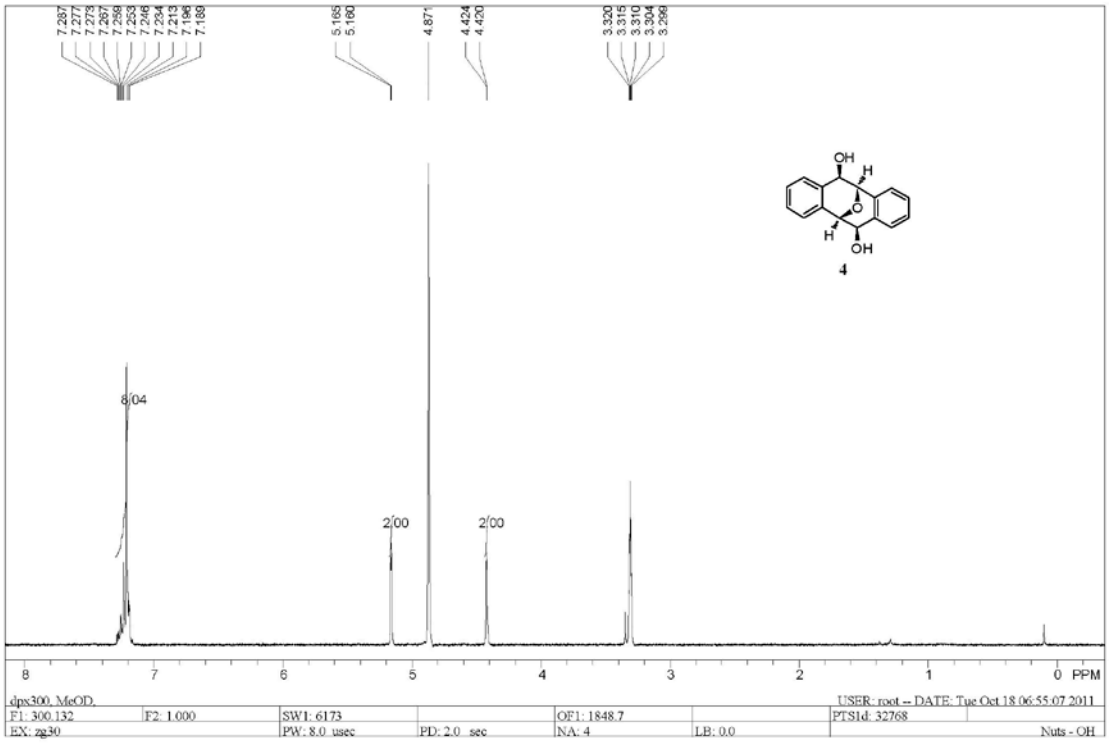

197.835
144.013
136.898
133.679
130.423
130.196
129.617
128.707
127.672
127.525
124.553
77.429
77.000
76.581
71.503
54.055
21.671
Me
O
H
O
H
O
Me
2o
150
100
50
PPM
dpx300, CDCl3,
USER: root -- DATE: Fri May 06 12:10:52 2011
F1: 75.475
F2: 1.000
SW1: 22676
OF1: 7242.1
PTS1d: 32768
EX: zgpg
PW: 13.9 usec
PD: 2.0 sec
NA: 1008
LB: 0.0
Nuts - 对甲基苯乙炔双分子C

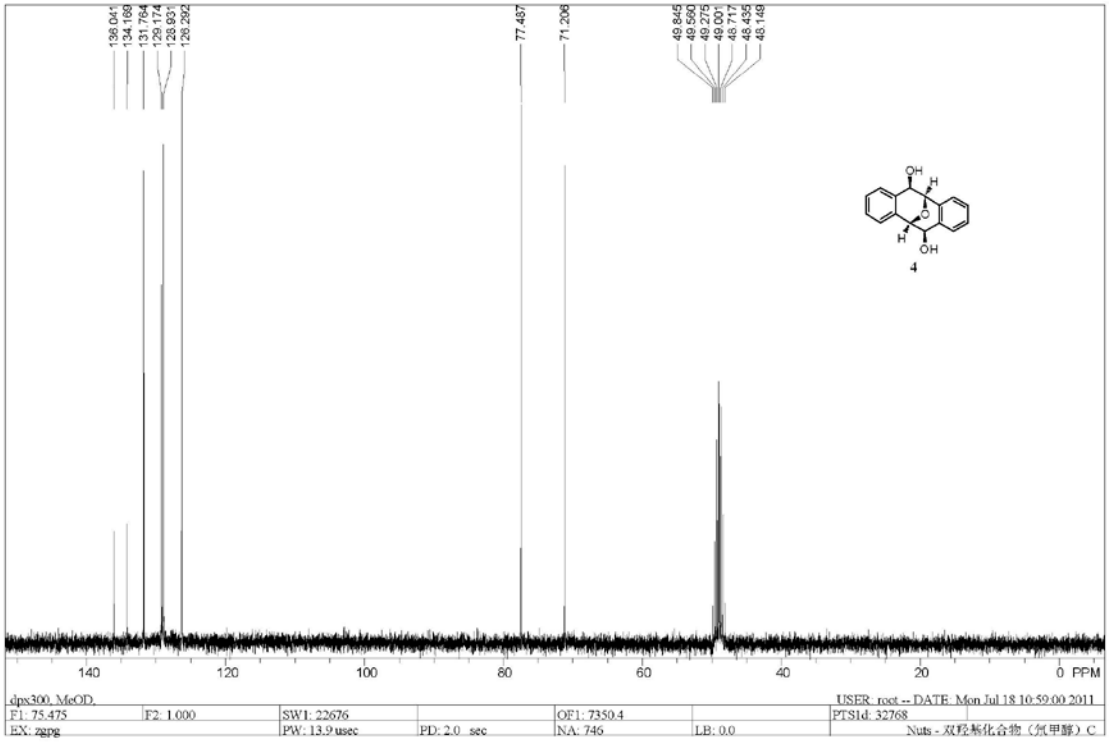

196.792
166.681
157.417
136.860
135.723
133.045
130.749
129.590
128.693
128.605
128.141
125.863
77.428
77.000
76.581
71.376
54.297
52.396
35.257
31.087
tBu
COOMe
MeOOC
O
H
O
tBu
2p
200
150
100
50
PPM
dpx300, CDCl3,
USER: root -- DATE: Thu Jul 21 05:06:03 2011
F1: 75.475
F2: 1.000
SW1: 22676
OF1: 7244.9
PTS1d: 32768
EX: zgpg
PW: 13.9 usec
PD: 2.0 sec
NA: 971
LB: 0.0
Nuts - 酚羟叔丁基双分子化C

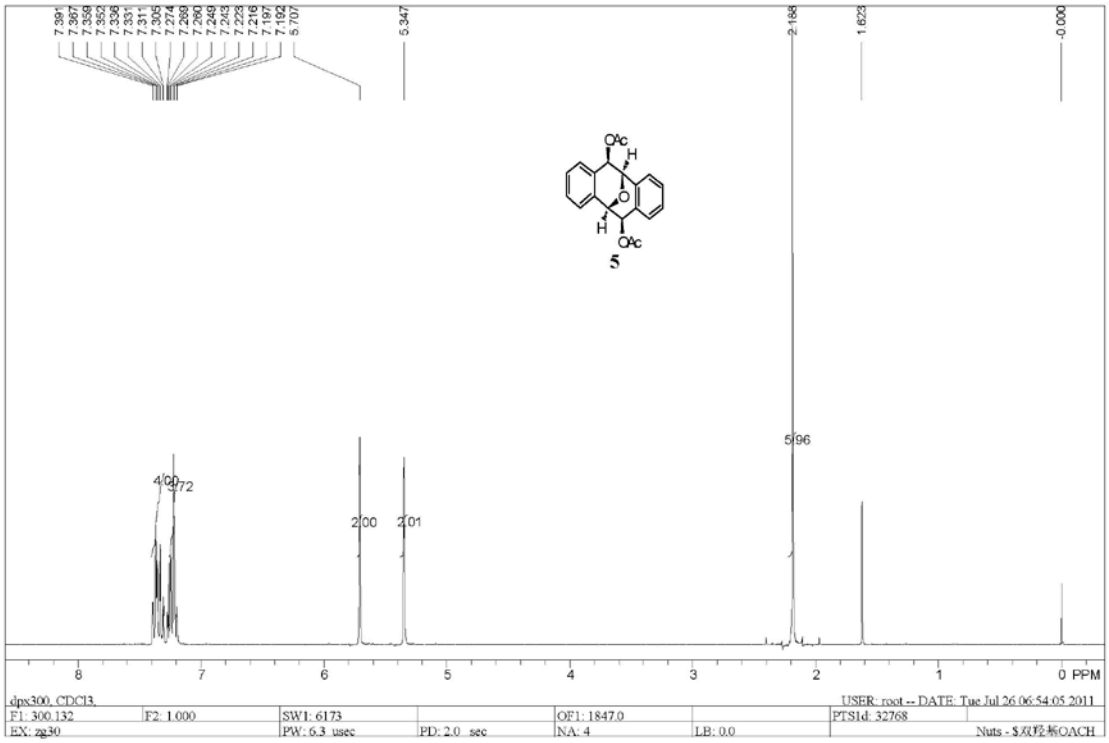

8.096
8.090
8.046
8.027
7.857
7.851
7.829
7.824
7.623
7.615
7.593
7.586
7.291
7.036
7.006
5.690
4.839
3.954
1.368
0.000
tBu
COOMe
MeOOC
O
H
O
tBu
2p
18.19
5.46
4.17
4.17
2.01
1.81
1.73
2.05
2.00
8
7
6
5
4
3
2
1
0PPM
dpx300, CDCl3,
USER: root -- DATE: Thu Nov 10 00:46:38 2011
F1: 300.132
F2: 1.000
SW1: 6173
OF1: 1847.5
PTS1d: 32768
EX: zg30
PW: 8.0 usec
PD: 2.0 sec
NA: 4
LB: 0.0
Nuts - 2p

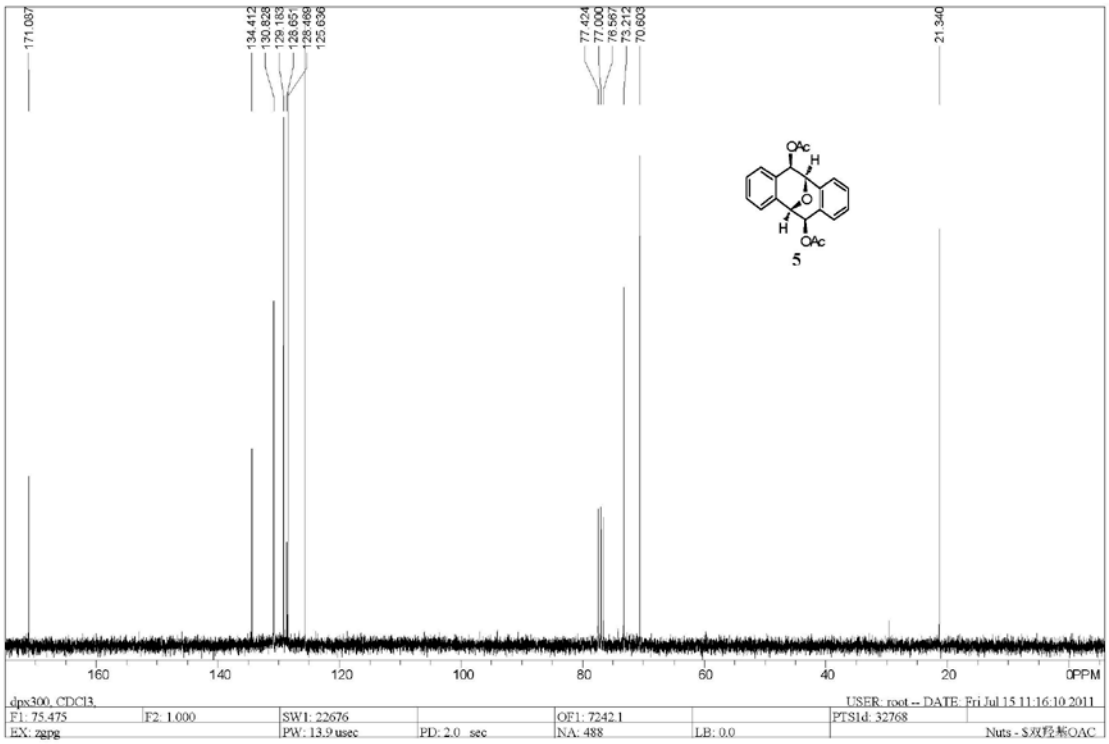

8.142
8.140
8.137
8.134
8.114
8.109
7.572
7.547
7.533
7.507
7.464
7.442
7.438
7.417
7.413
7.411
7.388
7.316
7.310
7.300
7.296
7.273
7.258
6.690
5.543
1.667
0.000
Ph
O
O
H
O
H
O
O
Ph
3
9.86
4.01
4.07
2.00
2.00
9
8
7
6
5
4
3
2
1
0 PPM
dpx300, CDCl3
USER: root -- DATE: Wed Jul 27 02:36:08 2011
F1: 300.132
F2: 1.000
SW1: 6173
OF1: 1846.5
PTS1d: 32768
EX: zg30
PW: 6.3 usec
PD: 2.0 sec
NA: 4
LB: 0.0
Nuts - $BV


166.733
134.762
133.238
131.058
129.937
129.896
129.226
128.828
128.488
128.371
125.728
77.426
77.000
76.567
73.457
71.137
Ph
O
O
H
O
H
O
O
Ph
3
160
140
120
100
80
60
40
20
0 PPM
dpx300, CDCl3
USER: root -- DATE: Tue Jul 12 11:18:04 2011
F1: 75.475
F2: 1.000
SW1: 22676
OF1: 7240.8
PTS1d: 32768
EX: zgpg
PW: 13.9 usec
PD: 2.0 sec
NA: 646
LB: 0.0
Nuts - BV反应产物C

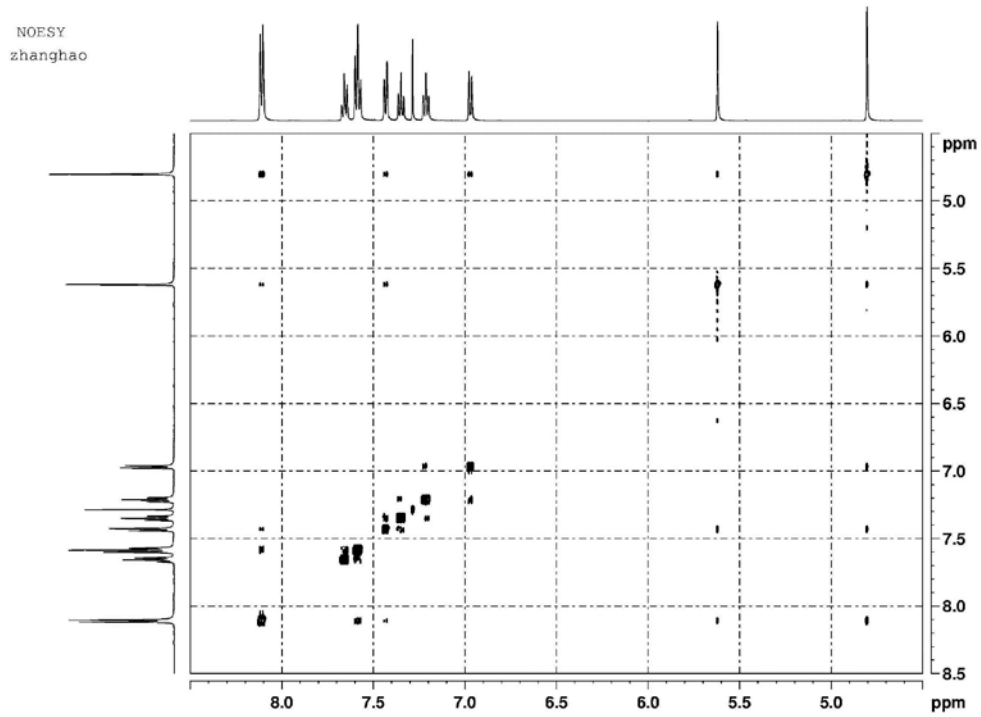

7.287
7.277
7.273
7.267
7.259
7.253
7.246
7.234
7.213
7.196
7.189
5.165
5.160
4.871
4.424
4.420
3.320
3.315
3.310
3.304
3.299
OH
H
O
H
OH
4
8.04
2.00
2.00
8
7
6
5
4
3
2
1
0 PPM
dpx300, MeOD
USER: root -- DATE: Tue Oct 18 06:55:07 2011
F1: 300.132
F2: 1.000
SW1: 6173
OF1: 1848.7
PTS1d: 32768
EX: zg30
PW: 8.0 usec
PD: 2.0 sec
NA: 4
LB: 0.0
Nuts - OH

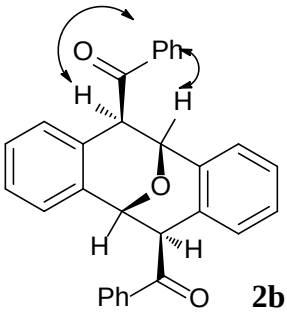

138.041
134.169
131.764
129.174
128.931
126.292
77.487
71.208
49.845
49.560
49.275
49.001
48.717
48.435
48.149
OH
H
O
H
OH
4
140
120
100
80
60
40
20
0 PPM
dpx300, MeOD
USER: root -- DATE: Mon Jul 18 10:59:00 2011
F1: 75.475
F2: 1.000
SW1: 22676
OF1: 7350.4
PTS1d: 32768
EX: zgpg
PW: 13.9 usec
PD: 2.0 sec
NA: 746
LB: 0.0
Nuts - 双羟基化合物（氘甲醇）C


7.391
7.387
7.359
7.352
7.336
7.331
7.311
7.305
7.274
7.269
7.260
7.249
7.243
7.223
7.216
7.197
7.192
5.707
5.347
2.188
1.625
0.000
OAc
H
O
H
OAc
5
5.96
4.00
3.72
2.00
2.01
8
7
6
5
4
3
2
1
0 PPM
dpx300, CDCl3,
USER: root -- DATE: Tue Jul 26 06:54:05 2011
F1: 300.132
F2: 1.000
SW1: 6173
OF1: 1847.0
PTS1d: 32768
EX: zg30
PW: 6.3 usec
PD: 2.0 sec
NA: 4
LB: 0.0
Nuts - $双乙酰OACH


171.087
134.412
130.828
129.153
128.657
128.498
125.636
77.424
77.000
76.567
73.212
70.603
21.340
OAc
H
O
H
OAc
5
160
140
120
100
80
60
40
20
0PPM
dpx300, CDCl3,
USER: root -- DATE: Fri Jul 15 11:16:10 2011
F1: 75.475
F2: 1.000
SW1: 22676
OF1: 7242.1
PTS1d: 32768
EX: zgpg
PW: 13.9 usec
PD: 2.0 sec
NA: 488
LB: 0.0
Nuts - S双乙酰OAC

5. NOESY spectrum of compound 2b





2b

6. Crystallographic structure of 2b

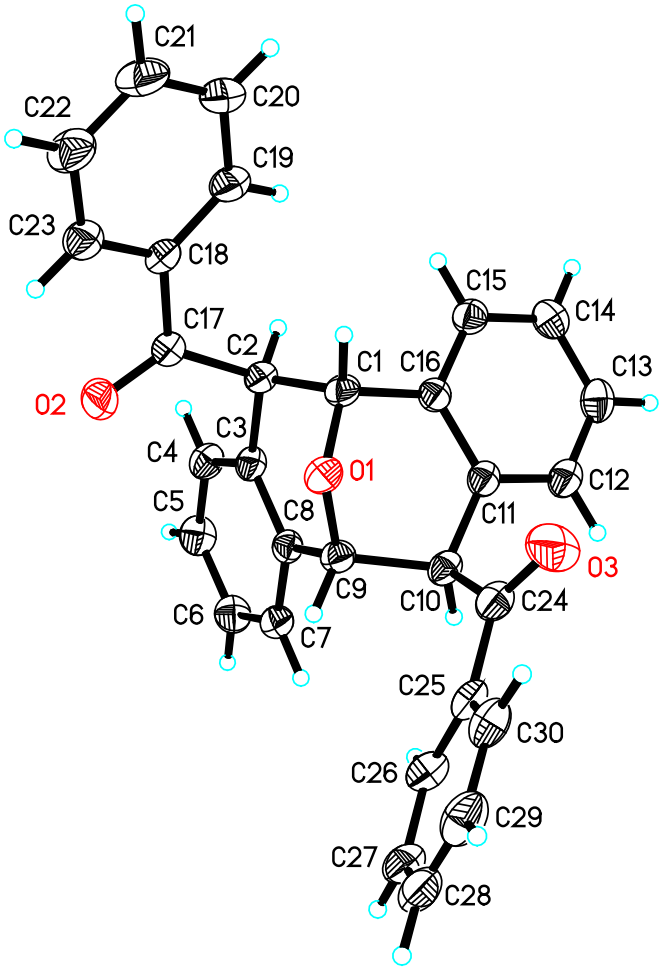


Fig. S1 X-ray structure of **2b**.

Empirical formula: $C_{30}H_{22}O_3$; Formula weight: 330.48; Temperature: 293(2) K; Wavelength: 0.71073 Å: Crystal system, space group: monoclinic, P2(1)/c, Unit cell dimensions: a = 13.7985(14) Å, alpha = 90 deg., b = 16.0801(16) Å, beta =101.502(2) deg., c = 9.8741(10) Å, gamma = 90 deg., Volume: 2145.5(4) Å3; Z = 4 , Calculated density: 1.333 Mg/m^3; F(000): 904; Crystal size: 0.45x 0.40 x 0.28 mm; final R indices [I > 2σ(I)], R1 = 0.0514, wR2 = 0.1072; R indices (all data): R1 = 0.0889, wR2 =0.1194;reflections collected/unique: 12516 / 4679 (Rint = 0.0920); number of observations [>2σ(I)] 4679, Parameters: 298.

References:

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2. Mancuso, R.; Salerno, G.; Mehta, S.; Jenks, William S.; Larock, R. C.; Gabriele, B. *J. Org. Chem*. **2010**, *75*, 897-901.

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4. Yao, B.; Li, Y.; Liang, Z.J.; Zhang, Y.H. *Org. Lett.* **2011**, *13*, 640-643.

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