Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

$K_2S_2O_8$-Mediated Metal-Free Direct C-H Functionalization of Quinones Using Arylboronic acids

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General Information:

All the reagents were purchased commercially and used without further purification. ^{1}H NMR and ^{13}C NMR were recorded with Bruker 400MHz. ^{1}H NMR (400MHz) and ^{13}C NMR (100MHz) spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard. 19F NMR recorded in Bruker 376.5 MHz. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broadresonance. All the NMR spectra were acquired at ambient temperature. Analytical thin layer chromatography (TLC) was performed using Silica Gel 60 Å F254 pre-coated plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp and staining with I_2 on silica gel. High-resolution mass spectra (HRMS) were recorded on Bruker Compass DataAnalysis 4.1, HRMS-ESI Mass Spectrometer with Quadrupole Time of Flight (Q-TOF) Analyzer, Source Type ESI, in positive mode. Instrument micrOTOF-Q III 8228888.20471.

General Procedure A: Arylation of Benzoquinones

To a solution of benzoquinone (1.0 equiv.) in 1:1 v/v of DCE (2 mL) and H_2O (2 mL) was added potassium persulfate (2.0 equiv.) and corresponding phenylboronic acid (1.5 equiv) at ambient temperature and heated at reflux. Progress of the reaction was monitored by TLC. Upon complete consumption of quinone, the reaction mixture was allowed to cool to ambient temperature and diluted with ethyl acetate and water. The organic phase was separated, extrcated two more times with ethyl acetate, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by silica gel column chromatography using hexane / ethyl acetate as eluent.

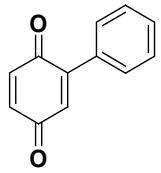
General Procedure B: Arylation of Naphthoquinones

To a solution of 1,4-naphthoquinone (1.0 equiv.) in 1:1 v/v of DCE (2 mL) and H_2O (2 mL) was added potassium persulfate (2.0 equiv.), phenylboronic acid (1.5 equiv.) and triethylamine (10.0 equiv.) at ambient temperature and heated at reflux. Progress of the reaction was monitored by TLC. Upon complete consumption of quinone, the reaction mixture was allowed to cool to ambient temperature and diluted with ethyl acetate and water. The organic phase was separated, extracted two more times with ethyl acetate, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by silica gel column chromatography using hexane / ethyl acetate as eluent.

General Procedure C: Arylation of Heterocycles

To a solution of heterocyic (1.0 equiv.) compound in 1:1 v/v of DCE (2 mL) and H_2O (2 mL) was added potassium persulfate (2.0 equiv.), and corresponding phenylboronic acid (1.5 equiv.) at ambient temperature and heated at reflux. Progress of the reaction was monitored by TLC. Upon complete consumption of the heterocycle, the reaction mixture was allowed to cool to ambient temperature and diluted with ethyl acetate and water. The organic phase was separated, extracted two more times with ethyl acetate, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by silica gel column chromatography using hexane / ethyl acetate as eluent.

Preparation of 2-Phenylcyclohexa-2,5-diene-1,4-dione (3aa):

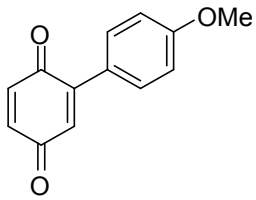


The reaction was carried out according to **general method A** using 1,4-benzoquinone **1a** (100 mg, 0.925 mmol), phenylboronic acid **2a** (169.3 mg, 1.388 mmol), potassium persulfate (500.6 mg, 1.852 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 1h.30 min.

The title compound **3aa** (170 mg, 72% yield) was obtained as yellow solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05).

m.p.: 112 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.49-7.43 (m, 5H), 6.93-6.78 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.6, 186.7, 146.0, 137.1, 136.2, 132.7, 130.1, 129.3, 128.6. The spectral data of the compound **3aa** was complies with the values reported in the literature.[1,3]

Preparation of 2-(4-Methoxyphenyl) cyclohexa-2,5-diene-1,4-dione (3ab):

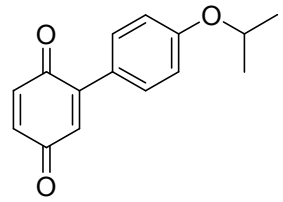


The reaction was carried out according to **general method A** using 1,4-benzoquinone **1a** (100 mg, 0.925 mmol), 4-Methoxyphenylboronic acid **2b** (214.2 mg, 1.388 mmol), potassium persulfate (500.6 mg, 1.852 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 24 h.

The title compound **3ab** (153 mg, 77% yield) was obtained as yellow solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05).

m.p.: 107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.85-6.79 (m, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.6, 187.1, 161.5, 145.2, 137.0, 136.3, 131.1, 130.9, 125.0, 114.2, 55.4. The spectral data of the compound **3ab** was complies with the values reported in the literature.[3]

Preparation of 2-(4-Isopropoxyphenyl) cyclohexa-2,5-diene-1,4-dione (3c):

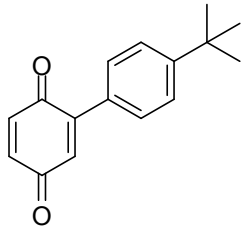


The reaction was carried out according to **general method A** using 1,4-benzoquinone **1a** (100 mg, 0.925 mmol), 4-isopropoxyphenylboronic acid **2c** (250 mg, 1.388 mmol), Potassium persulfate (500.6 mg, 1.852 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 5 h.

The title compound **3ac** (157 mg, 70% yield) was obtained as dark red solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05).

m.p.: 98-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.6 Hz, 2H), 6.94 (d, *J* =8.4 Hz, 2H), 6.85-6.78 (m, 3H), 4.64-4.58 (m, 1H), 1.36 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.7, 187.1, 159.9, 145.3, 137.0, 136.5, 136.2, 130.9, 124.6, 115.7, 70.1, 22.0. HRMS (ESI-micrOTOF-III): calcd. for $C_{15}H_{14}O_3Na$ 265.0835; found 265.0835.

Preparation of 2-(4-*tert*-butylphenyl) cyclohexa-2,5-diene-1,4-dione (3ad):

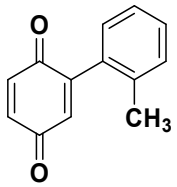


The reaction was carried out according to **general method A** using 1,4-benzoquinone **1a** (100 mg, 0.925 mmol), 4-tert-butylyphenylboronic acid **2d** (247.3 mg, 1.388 mmol), potassium persulfate (500.6 mg, 1.852 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 3 h.

The title compound **3ad** (145 mg, 65% yield) was obtained as yellow solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05).

m.p.: 71-74 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.43 (m, 4H), 6.87-6.80 (m, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.7, 186.9, 153.7, 145.8, 137.1, 136.2, 132.1, 129.8, 129.1, 125.6, 34.8, 31.2. The spectral data of the compound **3ad** was complies with the values reported in the literature.[1]

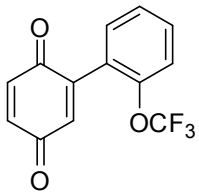
Preparation of 2-*O*-Tolylcyclohexa-2,5-diene-1,4-dione (3ae):



The reaction was carried out according to **general method A** using 1,4-benzoquinone **1a** (100 mg, 0.925 mmol), 2-methylphenylboronic acid **2e** (1.388 mmol, 189 mg), potassium persulfate (500.6 mg, 1.852 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 2 h 30 min.

The title compound **3ae** (110 mg, 60% yield) was obtained as yellow oil after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (t, *J* = 7.6 Hz, 1H), 7.27-7.22 (m, 2H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.89-6.83 (m, 2H), 6.72 (d, *J* = 2.0 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.7, 186.2, 148.5, 136.9, 136.4, 136.1, 134.5, 133.1, 130.4, 129.5, 129.2, 125.8, 20.3. The spectral data of the compound **3ae** was complies with the values reported in the literature.[3]

Preparation of 2-(2-(Trifluoromethoxy) phenyl)cyclohexa-2,5-diene-1,4-dione (3af):

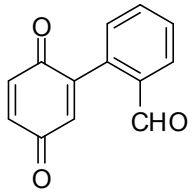


The reaction was carried out according to **general method A** using 1,4-benzoquinone **1a** (100 mg, 0.925 mmol), 2-trifluromethoxyphenylboronic acid **2f** (286 mg, 1.388 mmol), potassium persulfate (500.6 mg, 1.852 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 20 min.

The title compound **3af** (167 mg, 67% yield) was obtained as dark yellow oil after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05).^{1}H NMR

(400 MHz, $CDCl_3$): δ 7.49 (td, *J* =7.9, 1.6 Hz, 1H), 7.39-7.34 (m, 2H), 7.30-7.27 (m, 1H), 6.91-6.82 (m, 3H); ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -57.19 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.1, 185.0, 146.8, 144.0, 136.9, 136.5, 135.3, 131.2, 126.8, 126.6, 121.7, 120.7 (t, J_{C-F}= 258.5 Hz), 119.1. HRMS (ESI-microTOF-III): calcd. for $C_{13}H_7F_3O_3Na$ 291.0239; found 291.0239.

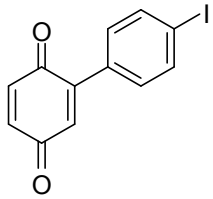
Preparation of 2-(3,6-Dioxocyclohexa-1,4-dienyl)benzaldehyde (3ag):



The reaction was carried out according to **general method A** using 1,4-Benzoquinone **1a** (100 mg, 0.925 mmol), 2-Formylphenylboronic acid **2g** (208.2 mg, 1.388 mmol), potassium persulfate (500.6 mg, 1.852 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 30 min.

The title compound **3ag** (88.5 mg, 45% yield) was obtained as yellow semi solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05). ^1H NMR (400 MHz, $CDCl_3$): δ 9.93 (s, 1H), 7.93 (d, *J* = 6.4 Hz, 1H), 7.73-7.67 (m, 2H), 7.33 (d, *J* = 6.8 Hz, 1H), 6.92-6.86 (m, 2H), 6.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6, 187.2, 185.3, 149.1, 137.1, 136.8, 134.9, 134.2, 133.7, 133.6, 132.0, 130.4, 130.2. HRMS (ESI-micrOTOF-III): calcd. for $C_{13}H_8O_3Na$ 235.0366; found 235.0864.

Preparation of 2-(4-Iodophenyl) cyclohexa-2,5-diene-1,4-dione (3ah):

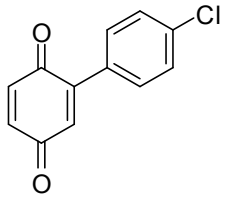


The reaction was carried out according to **general method A** using 1,4-benzoquinone **1a** (100 mg, 0.925 mmol), 4-iodophenylboronic acid **2h** (344.2 mg, 1.388 mmol), potassium persulfate (500.6 mg, 1.852 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 15 min.

The title compound **3ah** (224 mg, 78% yield) was obtained as yellow solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05). m.p.: 133-

135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 6.89-6.82 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.2, 186.2, 145.0, 137.8, 137.0, 136.4, 132.6, 132.1, 130.8, 96.9. The spectral data of the compound **3ah** was complies with the values reported in the literature.[2]

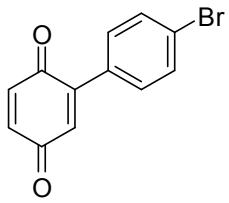
Preparation of 2-(4-Chlorophenyl) cyclohexa-2,5-diene-1,4-dione (3ai):



The reaction was carried out according to **general method A** using 1,4-benzoquinone **1a** (100 mg, 0.925 mmol), 4-chlorophenylboronic acid **2i** (217.2 mg, 1.388 mmol), potassium persulfate (500.6 mg, 1.852 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 40 min.

The title compound **3ai** (71 mg, 35% yield) was obtained as yellow solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05). m.p.: 134-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (s, 5H), 6.88-6.82 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.3, 186.3, 144.8, 137.0, 136.6,136.4, 132.7, 131.0, 130.6, 128.9. The spectral data of the compound **3ai** was complies with the values reported in the previous literature.[3]

Preparation of 2-(4-Bromophenyl) cyclohexa-2,5-diene-1,4-dione (3aj):

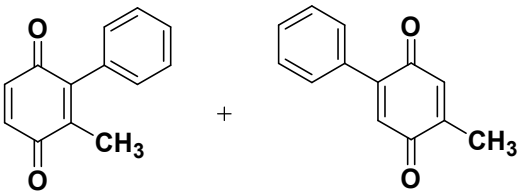


The reaction was carried out according to **general method A** using 1,4-benzoquinone **1a** (100 mg, 0.925 mmol), 4-bromophenylboronic acid **2j** (278.9 mg, 1.388 mmol), potassium persulfate (500.6 mg, 1.852 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 25 min.

The title compound **3aj** (133.5 mg, 55% yield) was obtained as yellow solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05). m.p.: 114-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 6.88-6.82 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.3, 186.2, 144.9, 137.0, 136.4, 132.7,

131.9, 131.5, 130.8, 124.9. The spectral data of the compound **3aj** complies with the values reported in the literature.[3]

Preparation of 2-Methyl-3-phenylcyclohexa-2,5-diene-1,4-dione (3bk):



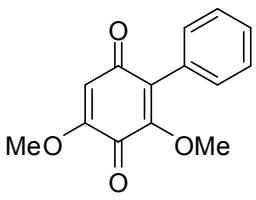
ka kb

The reaction was carried out according to **general method A** using 2-methyl-1,4-benzoquinone **1b** (100 mg, 0.820 mmol), phenylboronic acid **2a** (1.230 mmol, 149.9 mg), potassium persulfate (443 mg, 1.640 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 3h.

The title compound **3bka** (97.5 mg, 60% yield) was obtained as yellow semi solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.41 (m, 5H), 6.80 (d, J = 2.4 Hz, 1H), 6.68 (t, J = 2.0 Hz, 1H), 2,14 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.6, 187.0, 146.22, 146.18, 133.2, 133.1, 132.8, 129.9, 129.2, 128.4, 16.3. HRMS (ESI-micrOTOF-III): calcd. for $C_{13}H_{10}O_2$ (M+H) 199.0759; found 199.0754.

The title compound **3bkb** (97.5 mg, 12% yield) was obtained as yellow semi solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.41 (m, 5H), 6.85 (s, 1H), 6.71 (d, J = 1.5 Hz, 1H), 2.11 (d, J = 1.48 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.1, 186.8, 145.9, 145.6, 133.8, 132.7, , 129.9, 129.5, 129.3, 128.5, 15.4. HRMS (ESI-micrOTOF-III): calcd. for $C_{13}H_{10}O_2$ (M+H) 199.0759; found 199.0754.

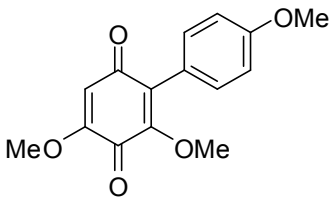
Preparation of 3,5-Dimethoxy-2-phenylcyclohexa-2,5-diene-1,4-dione (3cl):



The reaction was carried out according to **general method A** using 3,5-dimethoxy -1,4-benzoquinone **1c** (100 mg, 0.595 mmol), phenylboronic acid **2a** (0.893 mmol, 109 mg), potassium persulfate (322 mg, 1.190 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 3h 20 min.

The title compound **3cl** (99 mg, 68% yield) was obtained as orange solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05). m.p.: 112-114 ^{o}C.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.37 (m, 3H), 7.30-7.28 (m, 2H), 5.96 (s, 1H), 3.85 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.6, 178.6, 157.3, 153.9, 130.6, 130.1, 130.1, 129.3, 128.8, 127.8, 107.2, 61.2, 56.5. The spectral data of the compound **3cl** was complies with the values reported in the literature.[1]

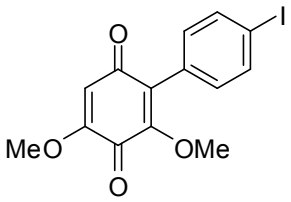
Preparation of 3,5-Dimethoxy-2-(4-methoxyphenyl) cyclohexa-2,5-diene-1,4-dione (3cm):



The reaction was carried out according to **general method A** using 3,5-dimethoxy-1,4-benzoquinone **1c** (100 mg, 0.595 mmol), 4-Methoxyphenylboronic acid **2b** (136 mg, 0.893 mmol), Potassium persulfate (322 mg, 1.190 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 2h 30 min.

The title compound **3cm** (121 mg, 74% yield) was obtained as dark red solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05). m.p.: 170-171 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 5.94 (s, 1H), 3.84 (s, 6H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.0, 178.6, 160.1, 157.4, 153.7, 132.2, 129.4, 122.1, 113.5, 107.2, 61.1, 56.5, 55.3. HRMS (ESI-micrOTOF-III): calcd. for $C_{15}H_{14}O_5Na$ 297.0733; found 297.0733.

Preparation of 2-(4-Iodophenyl)-3,5-dimethoxycyclohexa-2,5-diene-1,4-dione (3cn):

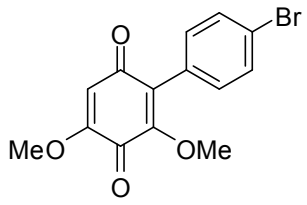


The reaction was carried out according to **general method A** using 3,5-dimethoxy -1,4-benzoquinone **1c** (100 mg, 0.595 mmol), 4-iodoPhenylboronic acid **2h** (221.3 mg, 0.893 mmol), potassium persulfate (322 mg, 1.190 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 50 min.

The title compound **3cn** (167.5 mg, 76% yield) was obtained as light orange solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05).

m.p.: 206 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 7.6 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 5.95 (s, 1H), 3.85 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2, 178.4, 157.4, 153.9, 137.1, 132.4, 129.5, 128.4, 107.1, 95.2, 61.4, 56.5. HRMS (ESI-micrOTOF-III): calcd. for $C_{13}H_{11}IO_4Na$ 292.9594; found 292.9594.

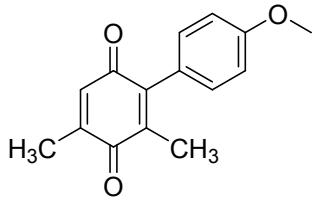
Preparation of 2-(4-Bromophenyl)-3,5-dimethoxycyclohexa-2,5-diene-1,4-dione (3co):



The reaction was carried out according to **general method A** using 3,5-dimethoxy -1,4-benzoquinone **1c** (100 mg, 0.595 mmol), 4-bromophenylboronic acid **2o** (179.3 mg, 0.893 mmol), potassium persulfate (322 mg, 1.190 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 1h 40 min.

The title compound **3co** (126.5 mg, 66% yield) was obtained as light orange solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05). m.p.: 202 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 7.6 Hz, 2H), 7.18 (d, J = 7.2 Hz, 2H), 3.85 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2, 178.3, 157.4, 153.9, 132.3, 131.1, 128.9, 129.3, 123.2, 107.1, 61.3, 61.5. HRMS (ESI-micrOTOF-III): calcd. for $C_{13}H_8O_3Na$ 344.9733; found 377.9733.

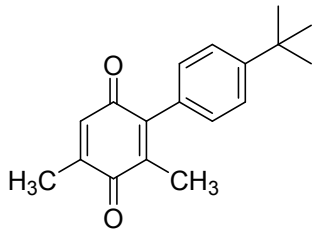
Preparation of 4'-methoxy-4,6-dimethyl-[1,1'-biphenyl]-2,5-dione (3dp):



The reaction was carried out according to **general method A** using 2,6-dimethyl -1,4-benzoquinone **1d** (100 mg, 0.734 mmol), 4-methoxyphenylboronic acid **2a** (167.4 mg, 1.10 mmol), potassium persulfate (397 mg, 1.47 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 24 h.

The title compound **3dp** (50 mg, 28% yield) was obtained as light yellow orange solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05). m.p.: 86-88 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.64 (s, 1H), 3.84 (s, 3H)), 2.10 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.6, 186.9, 159.8, 145.5, 143.3, 141.2, 133.2, 131.1, 125.1, 113.6, 15.8, 14.1. HRMS (ESI-micrOTOF-III): calcd. for $C_{15}H_{14}O_3(M+H)^+$ 243.1016; found 243.1014.

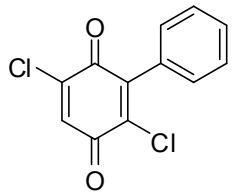
Preparation of 4'-(tert-butyl)-4,6-dimethyl-[1,1'-biphenyl]-2,5-dione (3dq):



The reaction was carried out according to **general method A** using 2,6-dimethyl -1,4-benzoquinone **1d** (100 mg, 0.734 mmol), 4-tert-butylphenylboronic acid **2d** (196.1 mg, 1.10 mmol), potassium persulfate (397 mg, 1.47 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 24 h.

The title compound **3dq** (50 mg, 28% yield) was obtained as inseparable mixture of light yellow oil after passing through a short silica gel column chromatography in hexane alone. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.66 (s, 1H), 2. 11(s, 3H)), 1.99(s, 3H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.6, 188.1, 187.5, 186.8, 151.4, 145.8, 145.4, 143.6, 141.4, 133.3, 133.2, 129.9, 129.3, 125.0, 34.7, 34.2, 15.9, 15.8, 14.1. HRMS (ESI-micrOTOF-III): calcd. for $C_{18}H_{20}O_2(M+H)^+$ 269.1536; found 269.1529.

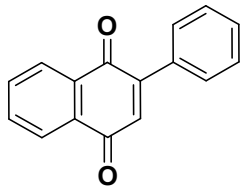
Preparation of 2,5-Dichloro-3-phenylcyclohexa-2,5-diene-1,4-dione (3er):



The reaction was carried out according to **general method A** using 2,5-dichloro -1,4-benzoquinone **1e** (100 mg, 0.397 mmol), phenylboronic acid **2a** (72.6 mg, 0.595 mmol), potassium persulfate (214.6 mg, 0.793 mmol), 4 mL of 1:1 v/v of DCE-water.Conditions: 80 °C, 1h 30 min.

The title compound **3er** (29 mg, 20% yield) was obtained as yellow solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05). m.p.: 102-105^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.47 (m, 3H), 7.31-7.28 (m, 2H), 7.23 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.6, 177.0, 144.5, 143.8, 141.0, 133.0, 130.7, 129.9, 129.6, 128.3. The spectral data of the compound **3er** was complies with the values reported in the literature.[1]

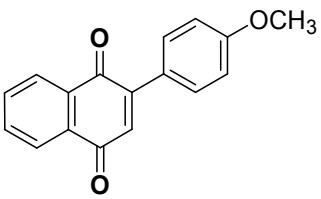
Preparation of 2-phenylnaphthalene-1,4-dione (5a):



The reaction was carried out according to **general method B** using 1,4-naphthoquinone **4a** (100 mg, 0.632 mmol), phenylboronic acid **2a** (116 mg, 0.949 mmol), potassium persulfate (342 mg, 1.265 mmol), tryethylamine (0.9 mL, 6.322 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 8h.

The title compound **5a** (21 mg, 14% yield) was obtained as yellow solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05). m.p.: 106-109 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20-8.12 (m, 1H), 8.14-8.12 (m, 1H), 7.79-7.77 (m, 2H), 7.59-7.57(m, 2H), 7.48 (t, J = 2.4, 3H), 7.10 (S, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.2, 184.4, 148.2, 135.2, 133.9, 133.8, 133.4, 132.5, 132.1, 130.0, 129.4, 128.5, 127.1, 126.0. The spectral data of the compound **5a** was complies with the values reported in the literature.[5]

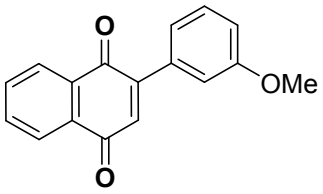
Preparation of 2-(4-methoxyphenyl)naphthalene-1,4-dione (5b):



The reaction was carried out according to **general method B** using 1,4-naphthoquinone **4a** (100 mg, 0.632 mmol), 4-methoxyphenylboronic acid **2b** (116 mg, 0.949 mmol), potassium persulfate (342 mg, 1.265 mmol), tryethylamine (0.9 mL, 6.322 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 7h 30 min.

The title compound **5b** (65 mg, 14% yield) was obtained as yellow solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05). m.p.: 131-133 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17-8.08 (m, 2H), 7.75 (t, 2H), 7.79 (m, 2H), 7.57 (t, J = 8, 2H), 7.03 (S, 1H), 6.98 (d, J = 8, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.3, 184.9, 161.45, 147.5, 133.8, 133.8, 132.7, 132.3, 131.2, 127.1, 126.0, 125.8, 114.2, 55.5. The spectral data of the compound **3w** was complies with the values reported in the literature.[5]

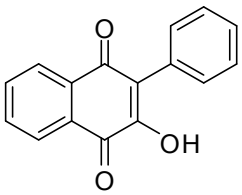
Preparation of 2-(3-methoxyphenyl)naphthalene-1,4-dione (5c):



The reaction was carried out according to **general method B** using 1,4-naphthoquinone **4a** (100 mg, 0.632 mmol), 3-methoxyphenylboronic acid **2l** (116 mg, 0.949 mmol), potassium persulfate (342 mg, 1.265 mmol), Tryethylamine (0.9 mL, 6.322 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 7h 30 min.

The title compound **5c** (65 mg, 14% yield) was obtained as yellow solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05). m.p.: 130-132 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18-8.11 (m, 2H), 7.77 (d, J = 2.8, 2H), 7.38 (t, J = 8.0, 1H), 7.15 (d, J = 7.2, 1H), 7.10 (d, J = 15.6, 2H), 7.02 (d, J = 7.6, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.1, 184.3, 159.5, 148.0, 135.3, 134.7, 133.8, 133.77, 132.5, 132.1, 129.5, 127.0, 125.96, 121.8, 115.9, 114.9, 55.4. HRMS (ESI-micrOTOF-III): calcd. for $C_{18}H_{14}O_4(M+H)^+$ 295.0965; found 265.0964.

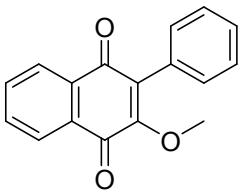
Preparation of 2-Hydroxy-3-phenylnaphthalene-1,4-dione (5d):



The reaction was carried out according to **general method B** using 2-hydroxy-1,4-naphthoquinone **4b** (100 mg, 0.575 mmol), phenylboronic acid **2a** (105.1 mg, 0.862 mmol), potassium persulfate (310 mg, 1.150 mmol), tryethylamine (0.6 mL, 5.742 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 6h.

The title compound **5d** (65 mg, 45% yield) was obtained as dark yellow solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05). m.p.: 141-143 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 7.6 Hz, 1H), 8.16 (d, *J* = 7.6 Hz, 1H), 7.82 (t, *J* = 7.2 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.58 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.45-7.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.7, 181.9, 152.2, 135.3, 133.1, 132.9, 130.7, 130.0, 129.4, 128.7, 127.9, 127.3, 126.1, 122.2. The spectral data of the compound **3y** was complies with the values reported in the literature.[4]

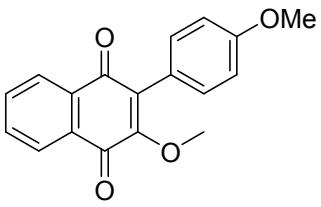
Preparation of 2-methoxy-3-phenylnaphthalene-1,4-dione (5e)



The reaction was carried out according to **general method B** using 2-methoxy-1,4-naphthoquinone **4c** (100 mg, 0.531 mmol), phenylboronic acid **2a** (97.2 mg, 0.797 mmol), potassium persulfate (287 mg, 1.063 mmol), tryethylamine (0.7 mL, 5.314 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 24h.

The title compound **5e** was obtained in trace as yellow semi solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05).^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14-8.12 (m, 2H), 7.76-7.73 (m, 2H), 7.45-7.41 (m, 3H), 7.37-7.35 (m, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.9, 182.1, 157.2, 134.3, 133.6, 132.1, 131.0, 130.6, 129.8, 128.8, 128.0, 126.8, 126.3, 115.4, 61.6. HRMS (ESI-micrOTOF-III): calcd. for $C_{17}H_{12}O_3(M+H)^+$ 265.0859; found 265.0860

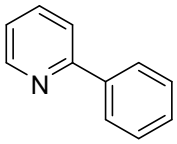
Preparation of 2-methoxy-3-(4-methoxyphenyl)naphthalene-1,4-dione (5f)



The reaction was carried out according to **general method B** using 2-methoxy-1,4-naphthoquinone **4c** (100 mg, 0.531 mmol), 4-methoxy phenylboronic acid **2b** (121 mg, 0.797 mmol), potassium persulfate (287 mg, 1.063 mmol), tryethylamine (0.7 mL, 5.314 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 24h.

The title compound **5f** (24mg, 15% yield) was obtained as dark red solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05). m.p.: 192-194 ^{o}C.^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13-8.11 (m, 2H), 7.74-7.72 (m, 2H), 7.35-7.33 (m, 2H), 6.99-6.97 (m, 2H), 3.88 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.2, 182.1, 160.0, 157.1, 134.2, 133.5, 132.2, 132.1, 131.6, 131.6, 126.8, 126.3, 122.9, 113.6, 61.5, 55.43. HRMS (ESI-micrOTOF-III): calcd. for C_{18} $H_{14}O_4(M+H)^+$ 295.0965; found 265.0964.

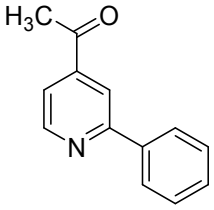
Preparation of 2-Phenylpyridine (7a):



The reaction was carried out according to **general method C** using pyridine **6a** (100 mg, 1.266 mmol), phenylboronic acid **2a** (231.5 mg, 1.90 mmol), potassium persulfate (684 mg, 2.532 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 5 min.

The title compound **7a** (in trace) was obtained as oil after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 4.4 Hz, 1H), 8.40 (d, *J* = 7.6 Hz, 2H), 7.80-7.73 (m, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.44-7.41 (m, 1H), 7.26-7.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 149.3, 139.0, 137.2, 129.2, 128.8, 127.0, 122.2, 120.8, 29.7. The spectral data of the compound **7a** was complies with the values reported in the literature.[3]

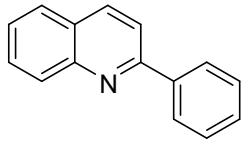
Preparation of 1-(2-phenylpyridin-4-yl) ethanone (7b):



The reaction was carried out according to **general method C** using 4-acetylpyridine **6b** (100 mg, 0.510 mmol), phenylboronic acid **2a** (93 mg, 0.761 mmol), potassium persulfate (505 mg, 1.870 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 10 min.

The title compound **7b** (in trace) was obtained as pale light yellow solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05). m.p.: 108 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (d, *J* =4.8, 1H), 8.17 (s, 1H), 8.04 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 4.0 Hz, 1H), 7.52-7.43 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 158.9, 150.8, 143.8, 138.6, 129.5, 128.9, 127.0, 119.7, 118.0, 26.8. The spectral data of the compound **7b** was complies with the values reported in the literature.[3]

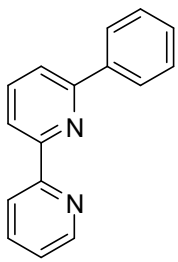
Preparation of 2-Phenylquinoline (7c):



The reaction was carried out according to **general method C** using quinoline **6c** (100 mg, 0.775 mmol), phenylboronic acid **2a** (142 mg, 1.163 mmol), potassium persulfate (419 mg, 1.550 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 5 min.

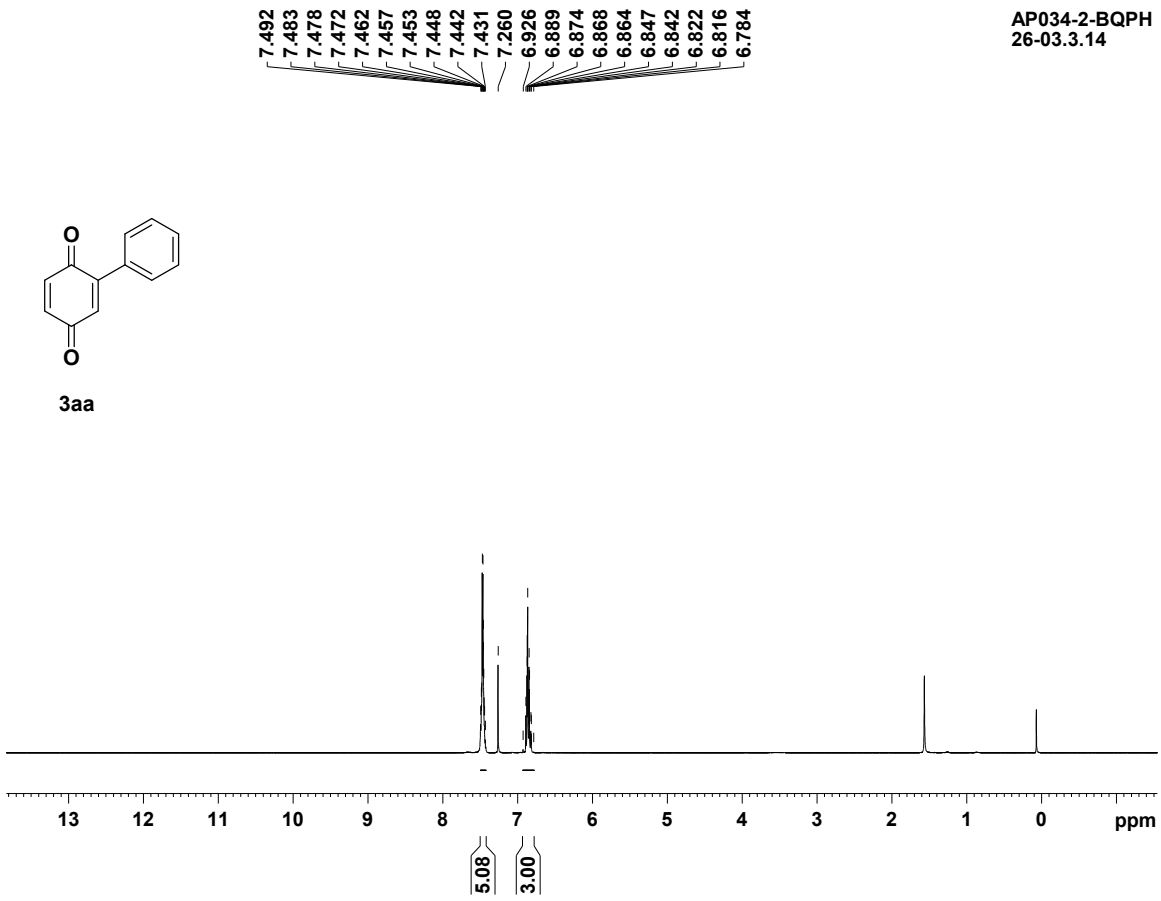
The title compound **7c** (67 mg, 42% yield) was obtained as pale yellow solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05).^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25-8.21 (m, 1H), 8.17 (d, *J* =8.0 Hz, 3H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 3H), 7.49-7.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 148.1, 139.4, 137.0, 129.8, 129.6, 129.4, 128.9, 127.7, 127.5, 127.2, 126.4, 119.1. The spectral data of the compound **7c** was complies with the values reported in the literature.[3]

Preparation of 6-phenyl-2,2'-bipyridine (7d):



The reaction was carried out according to **general method C** using 2,2'-bipyridine **6d** (100 mg, 0.640 mmol), phenylboronic acid **2a** (117 mg, 0.961 mmol), potassium persulfate (346 mg, 1.281 mmol), 4 mL of 1:1 v/v of DCE-water. Conditions: 80 °C, 10 min.

The title compound **7d** (67 mg, 42% yield) was obtained as pale yellow solid after passing through a short silica gel column chromatography (hexane/ethyl acetate, 95:05).m.p.: 74-77 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, J = 4.8 Hz, 1H), 8.65 (d, J = 8.0 Hz, 1H), 8.40 (d, J = 7.6 Hz, 1H), 8.16 (d, J = 7.2 Hz, 2H), 7.92-7.84 (m, 2H), 7.78 (d, J = 7.6 Hz, 1H), 7.53-7.50 (m, 2H), 7.46-7.42 (m, 1H), 7.35-7.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 156.2, 155.5, 148.8, 139.4, 137.7, 137.1, 129.0, 128.7, 127.0, 123.8, 121.5, 120.4, 119.4. HRMS (ESI-micrOTOF-III): calcd. for $C_{13}H_8O_3Na$ 232.1000; found 232.1000.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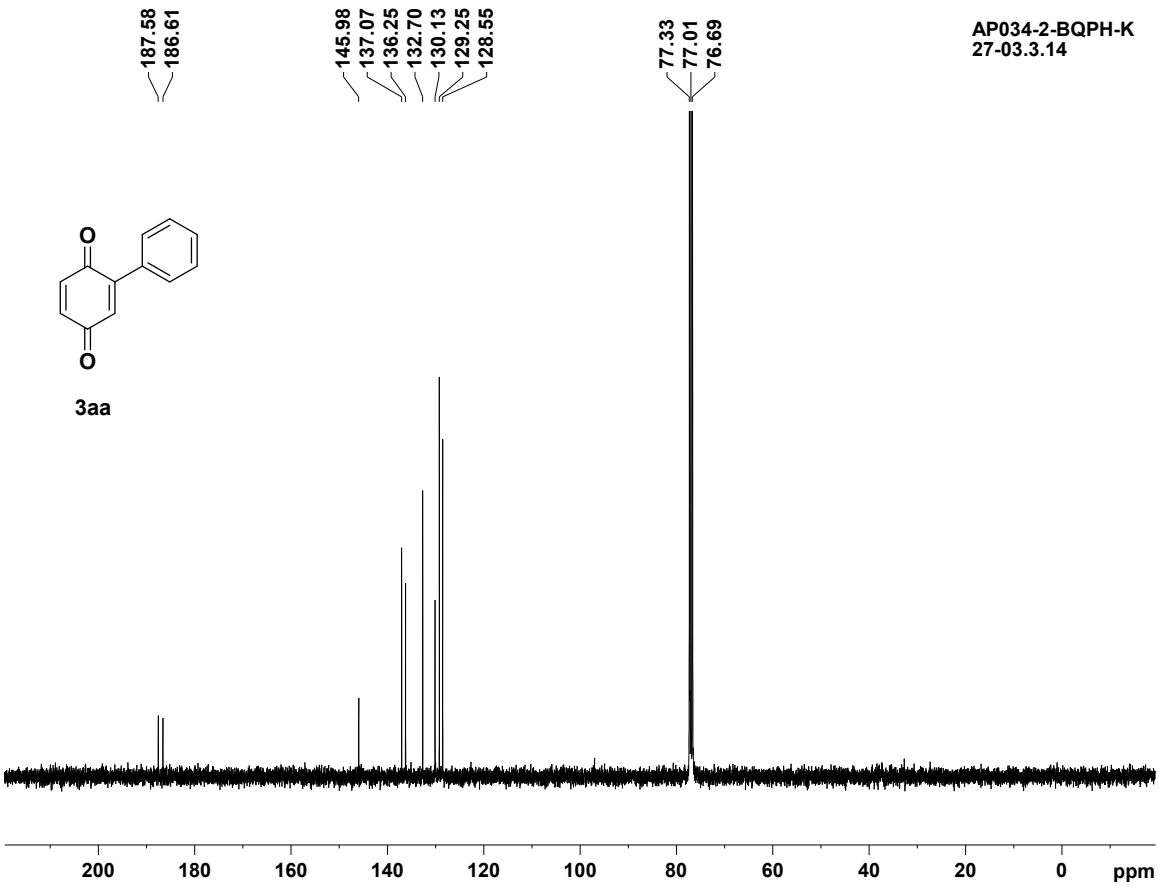
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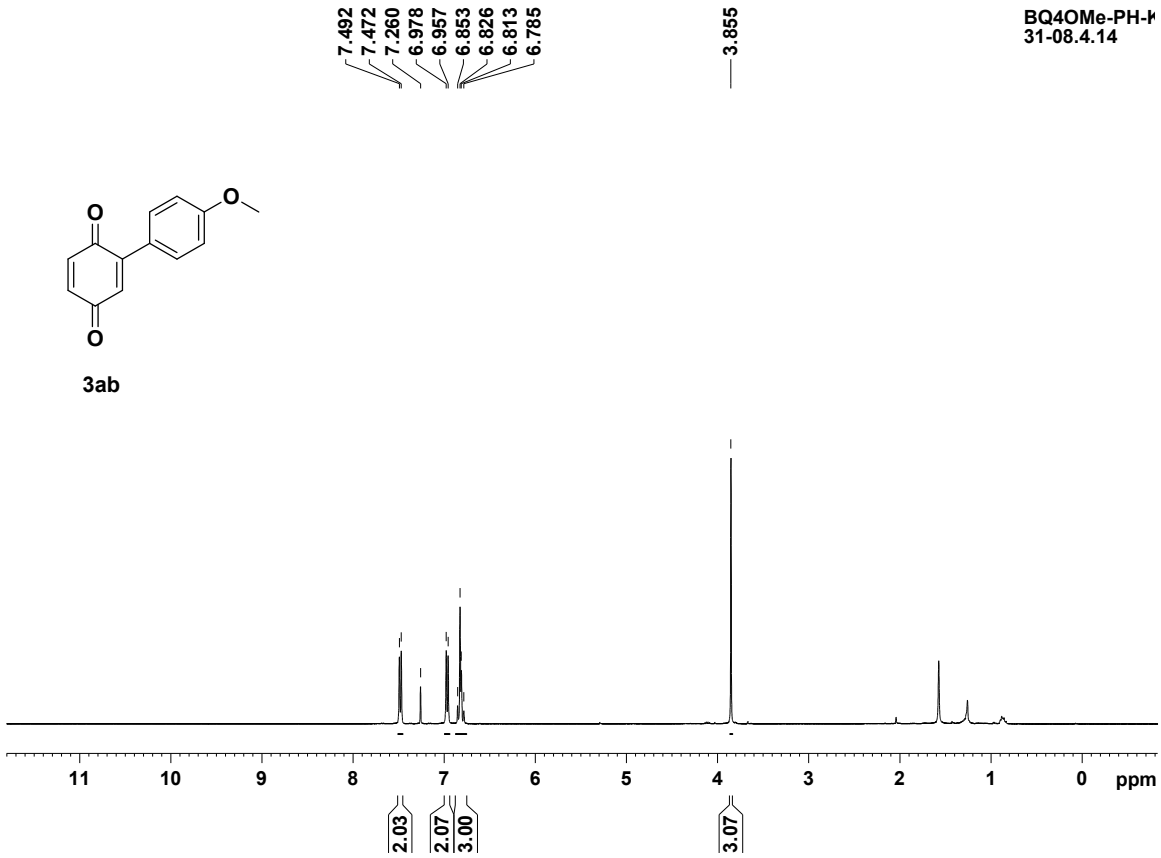
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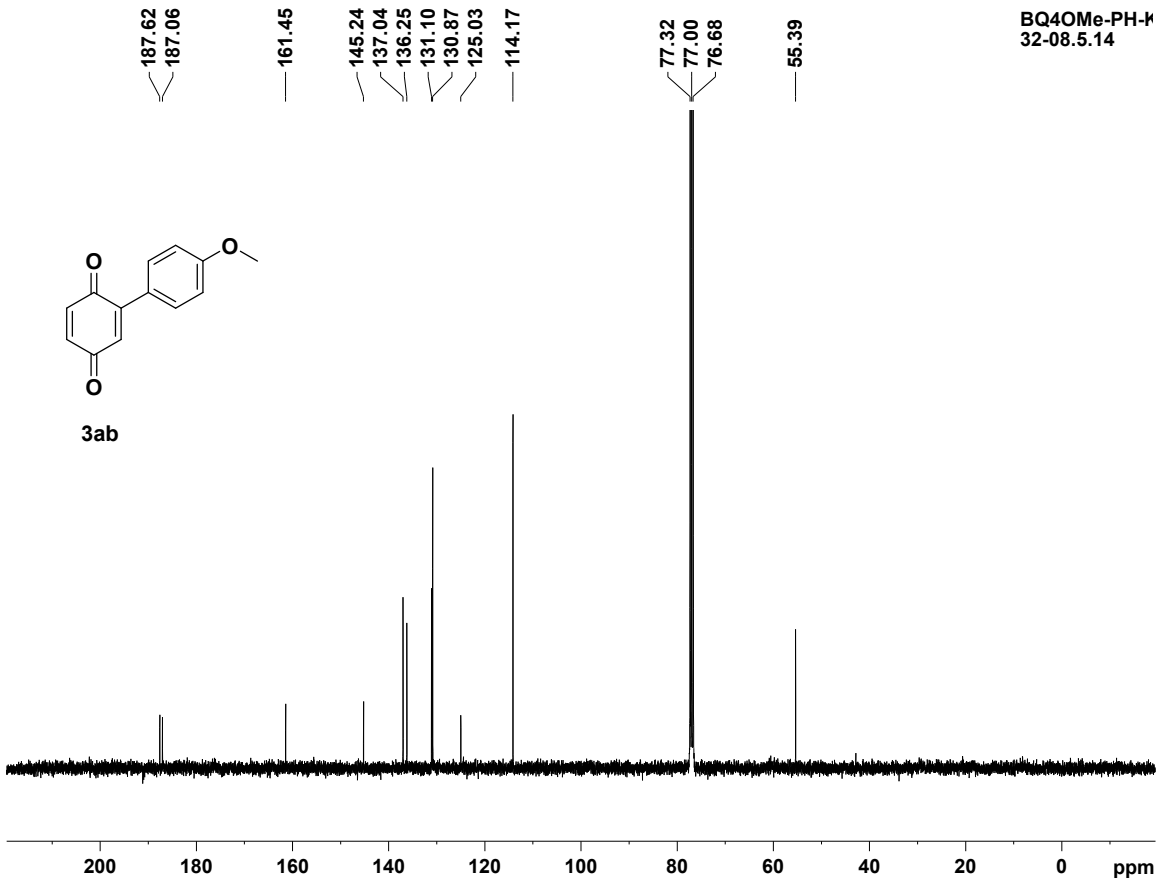
3.07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187.06
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145.24
137.04
136.25
131.10
130.87
125.03
114.17
77.32
77.00
76.68
55.39
BQ4OMe-PH-H
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O
O
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0
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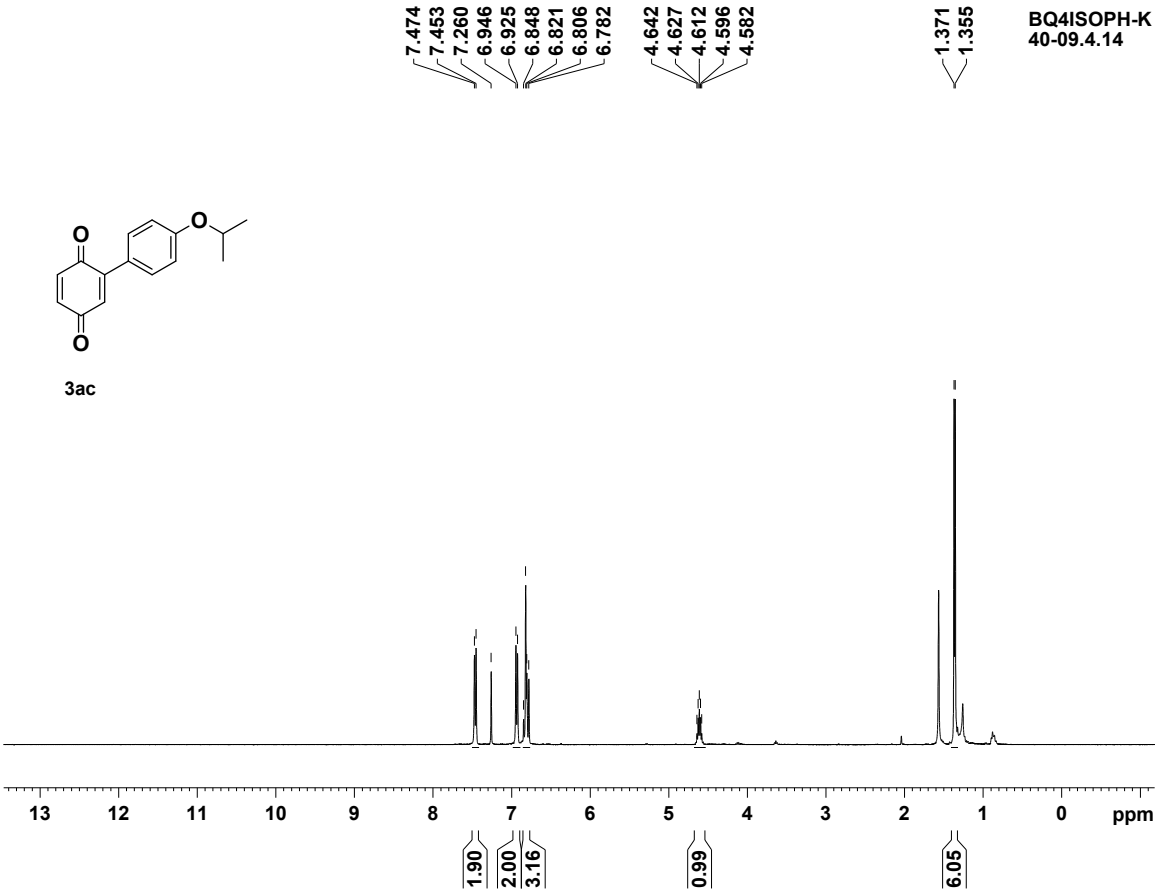
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6.925
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6.806
6.782
4.642
4.627
4.612
4.596
4.582
1.371
1.355
BQ4ISOPH-K
40-09.4.14
O
O
O
3ac
13
12
11
10
9
8
7
6
5
4
3
2
1
0
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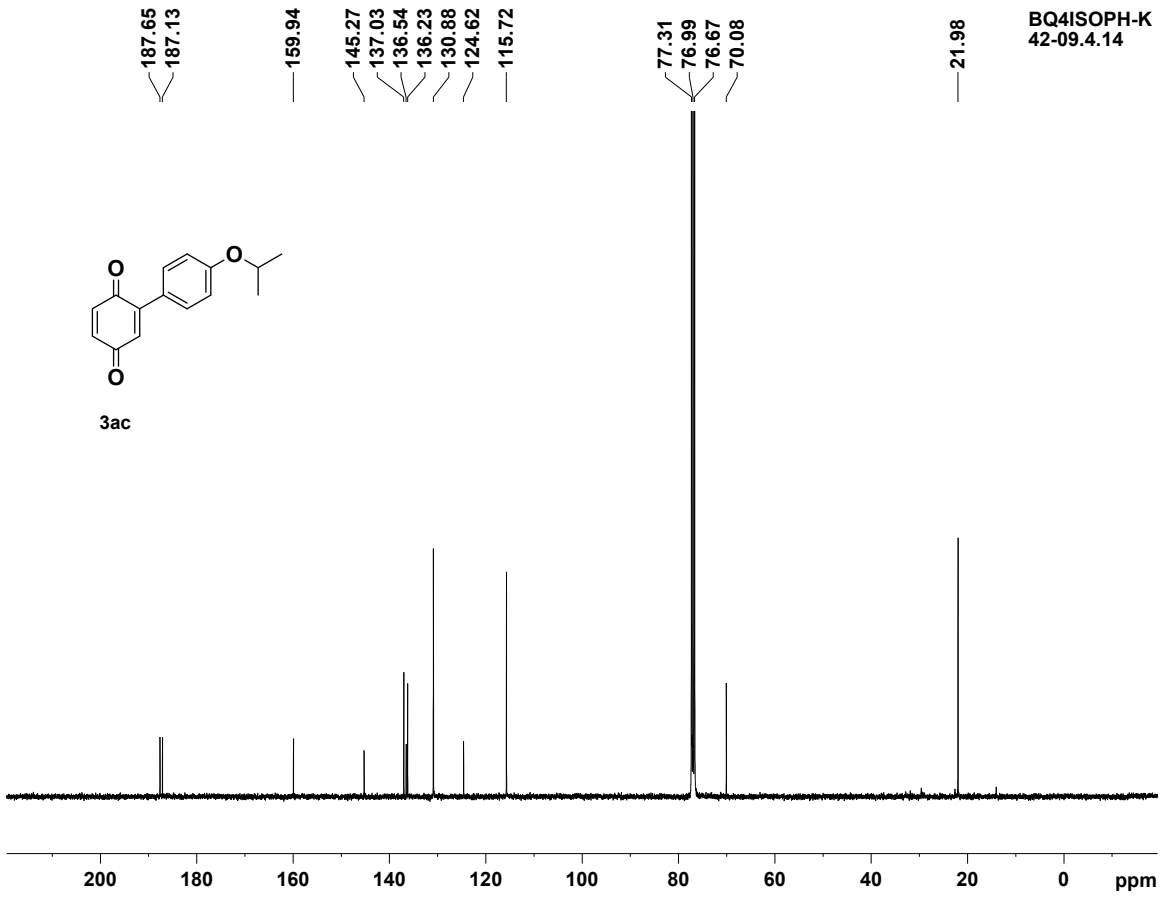
3.16
0.99
6.05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137.03
136.54
136.23
130.88
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115.72
77.31
76.99
76.67
70.08
21.98
BQ4ISOPH-K
42-09.4.14
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O
O
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120
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60
40
20
0
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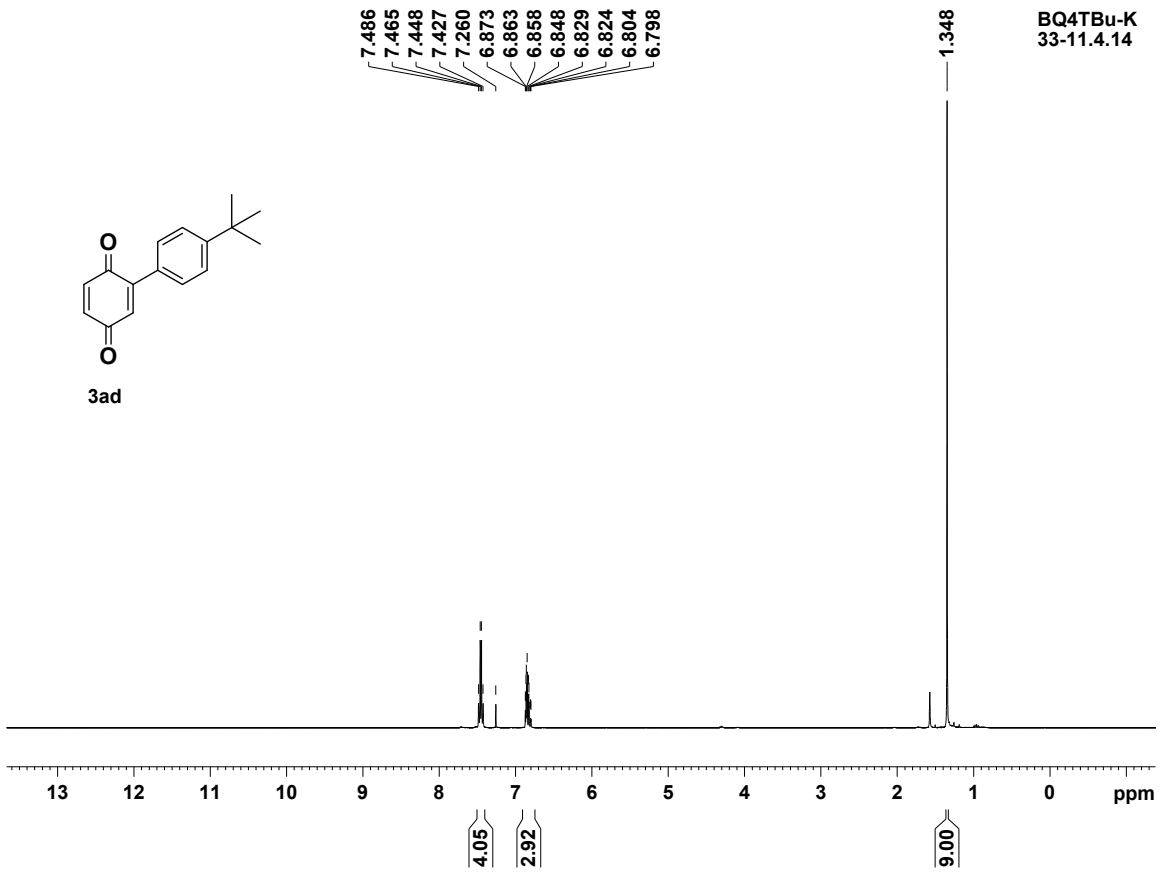
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7.448
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6.863
6.858
6.848
6.829
6.824
6.804
6.798
1.348
BQ4TBu-K
33-11.4.14
O
O
3ad
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12
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9
8
7
6
5
4
3
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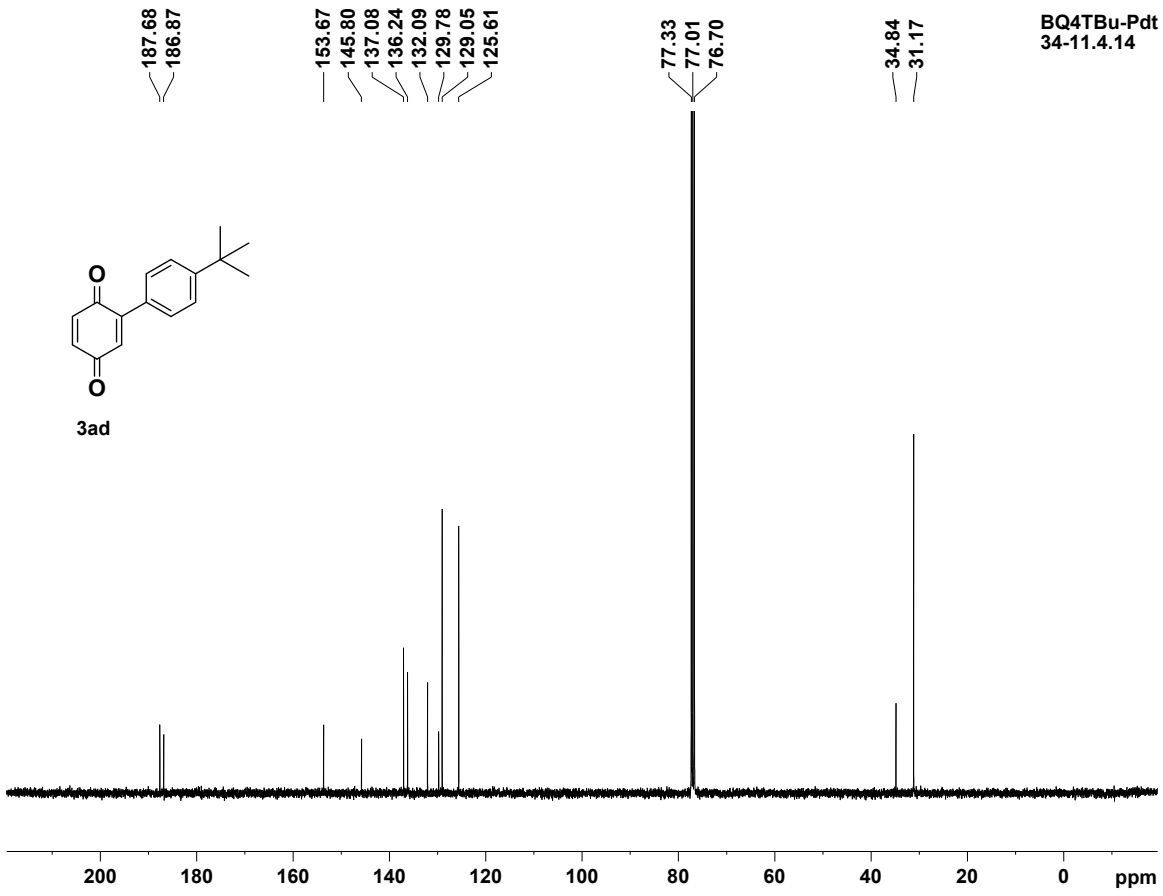
1
0
ppm
4.05
2.92
9.00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129.78
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125.61
77.33
77.01
76.70
34.84
31.17
BQ4TBu-Pdt
34-11.4.14
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O
3ad
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120
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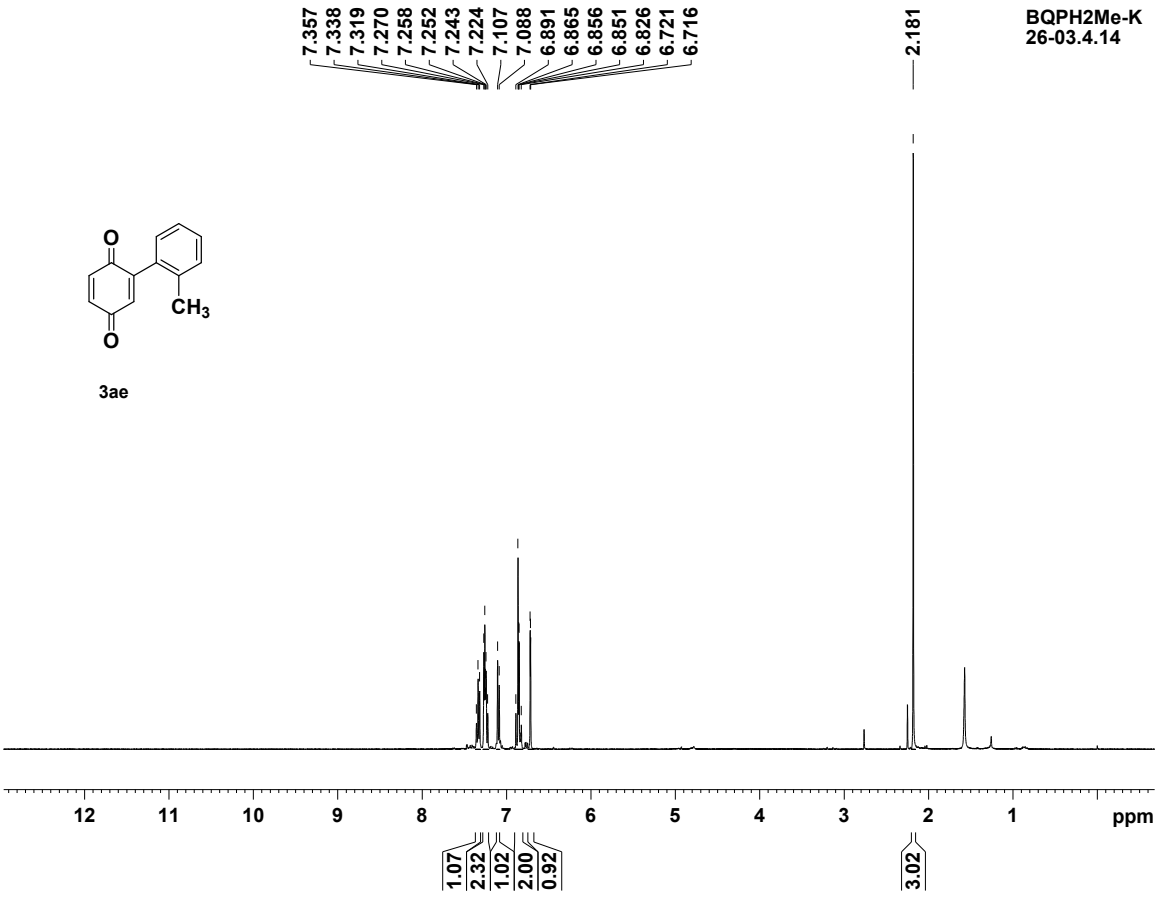
80
60
40
20
0
ppm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7.338
7.319
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7.252
7.243
7.224
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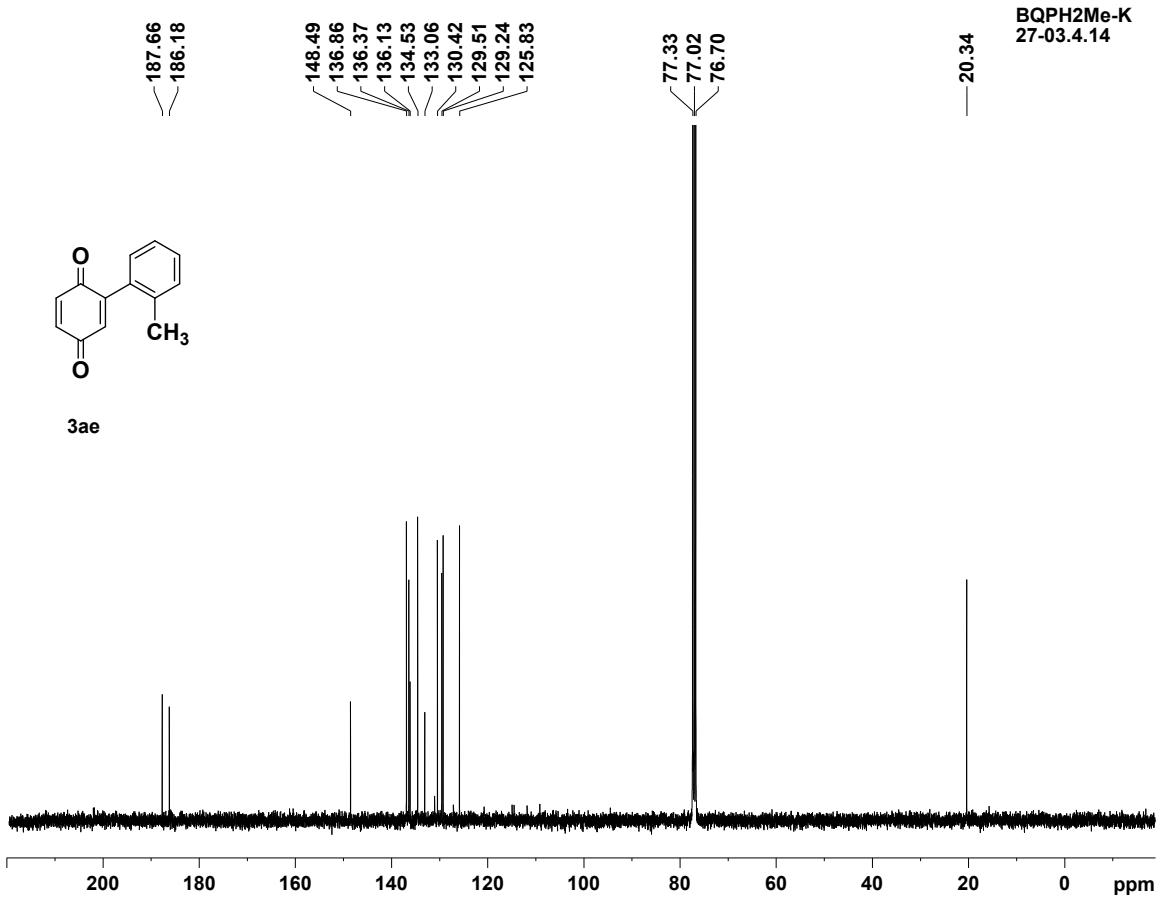
7.088
6.891
6.865
6.856
6.851
6.826
6.721
6.716
2.181
BQPH2Me-K
26-03.4.14
O
O
CH3
3ae
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.07
2.32
1.02
2.00
0.92
3.02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27-03.4.14
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136.86
136.37
136.13
134.53
133.06
130.42
129.51
129.24
125.83
77.33
77.02
76.70
20.34
O
O
CH3
3ae
200
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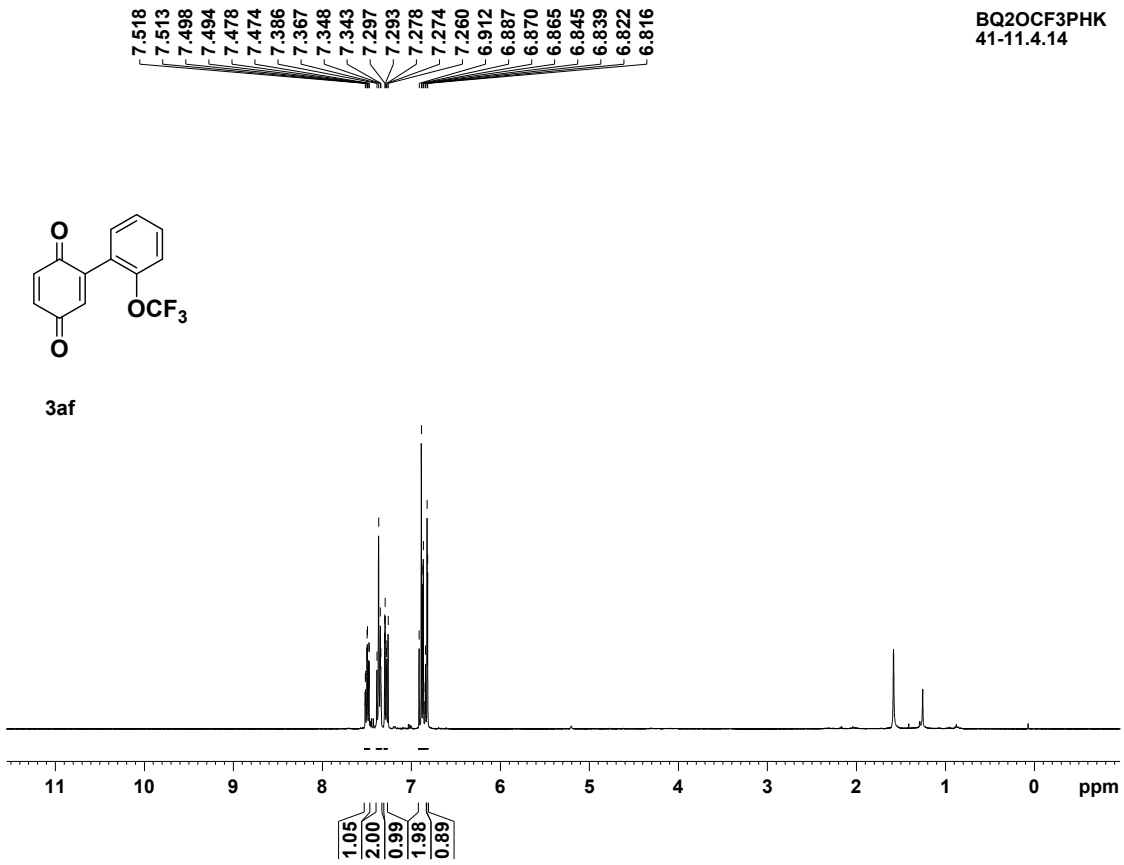
160
140
120
100
80
60
40
20
0
ppm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7.513
7.498
7.494
7.478
7.474
7.386
7.367
7.348
7.343
7.297
7.293
7.278
7.274
7.260
6.912
6.887
6.870
6.865
6.845
6.839
6.822
6.816
BQ2OCF3PHK
41-11.4.14
O
OCF3
O
3af
11
10
9
8
7
6
5
4
3
2
1
0
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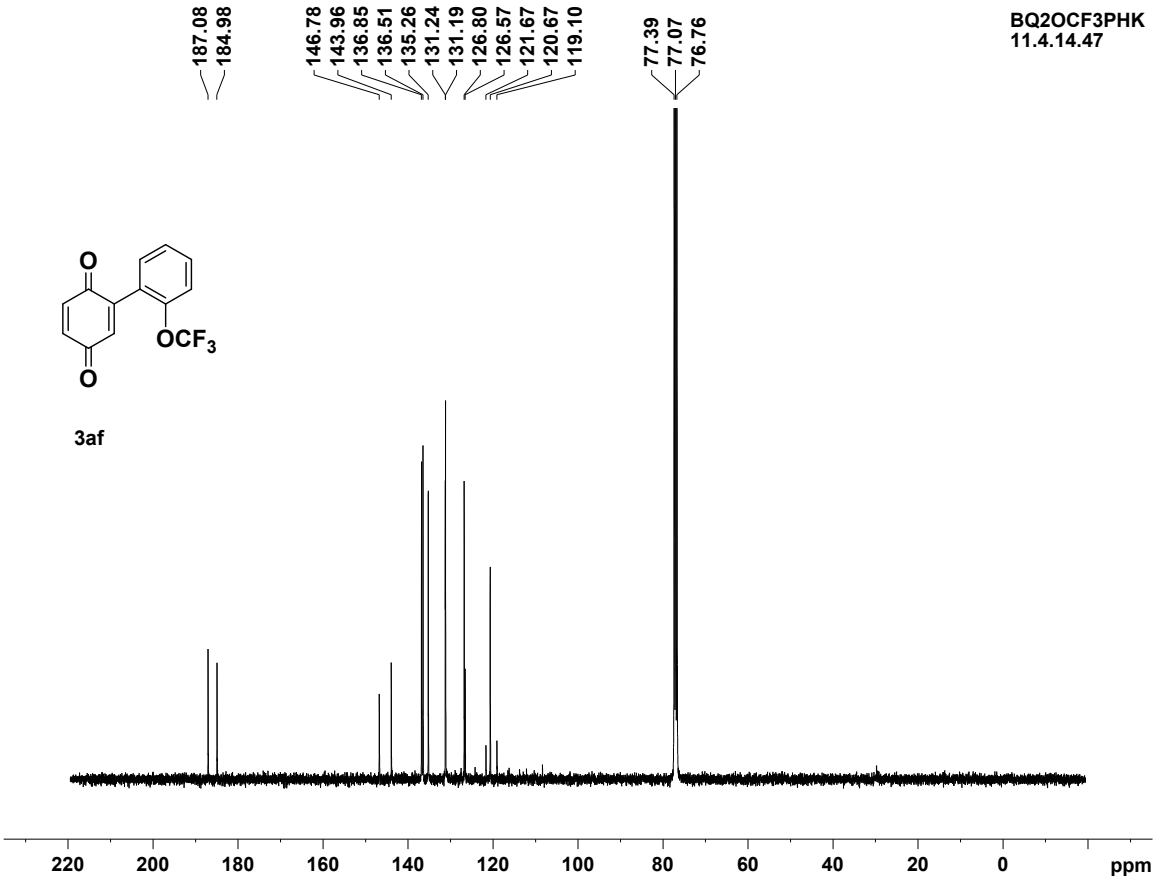
1.05
2.00
0.99
1.98
0.89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184.98
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143.96
136.85
136.51
135.26
131.24
131.19
126.80
126.57
121.67
120.67
119.10
77.39
77.07
76.76
BQ2OCF3PHK
11.4.14.47
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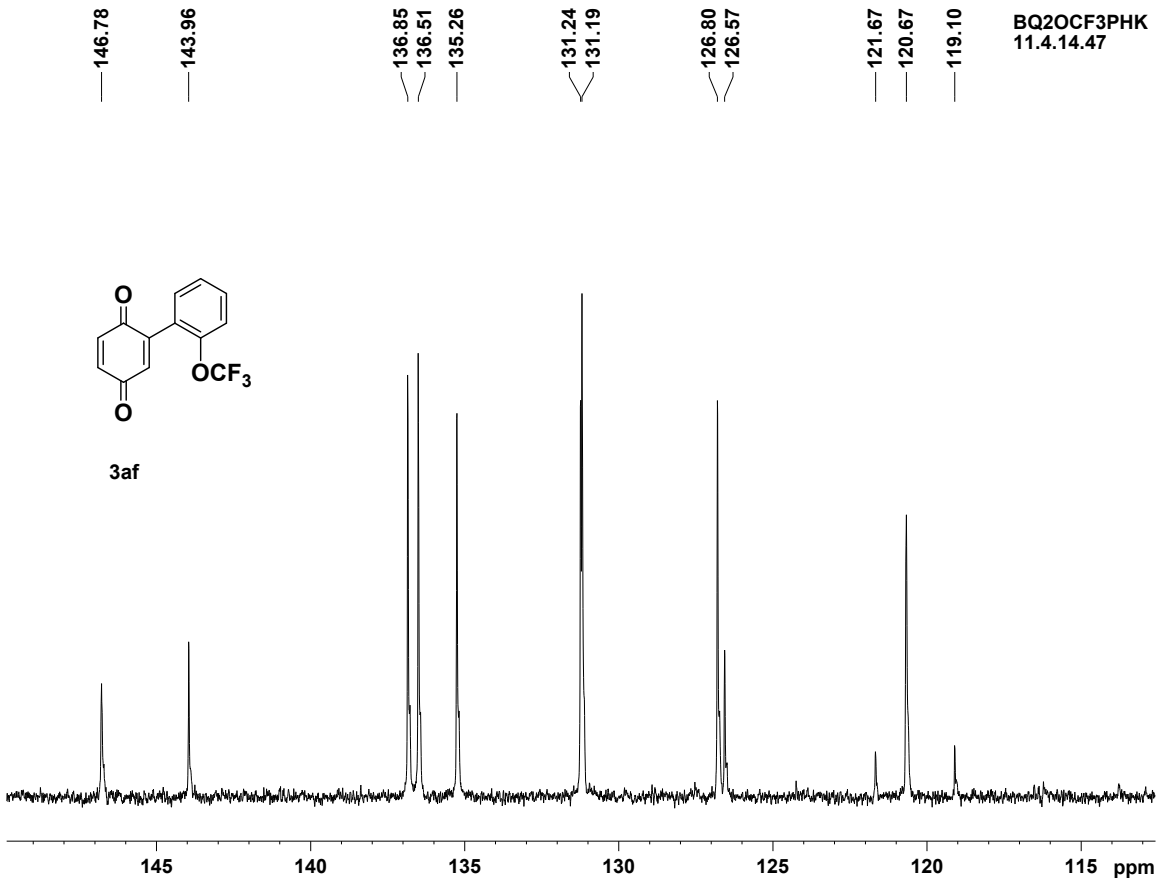
O
OCF3
3af
220
200
180
160
140
120
100
80
60
40
20
0
ppm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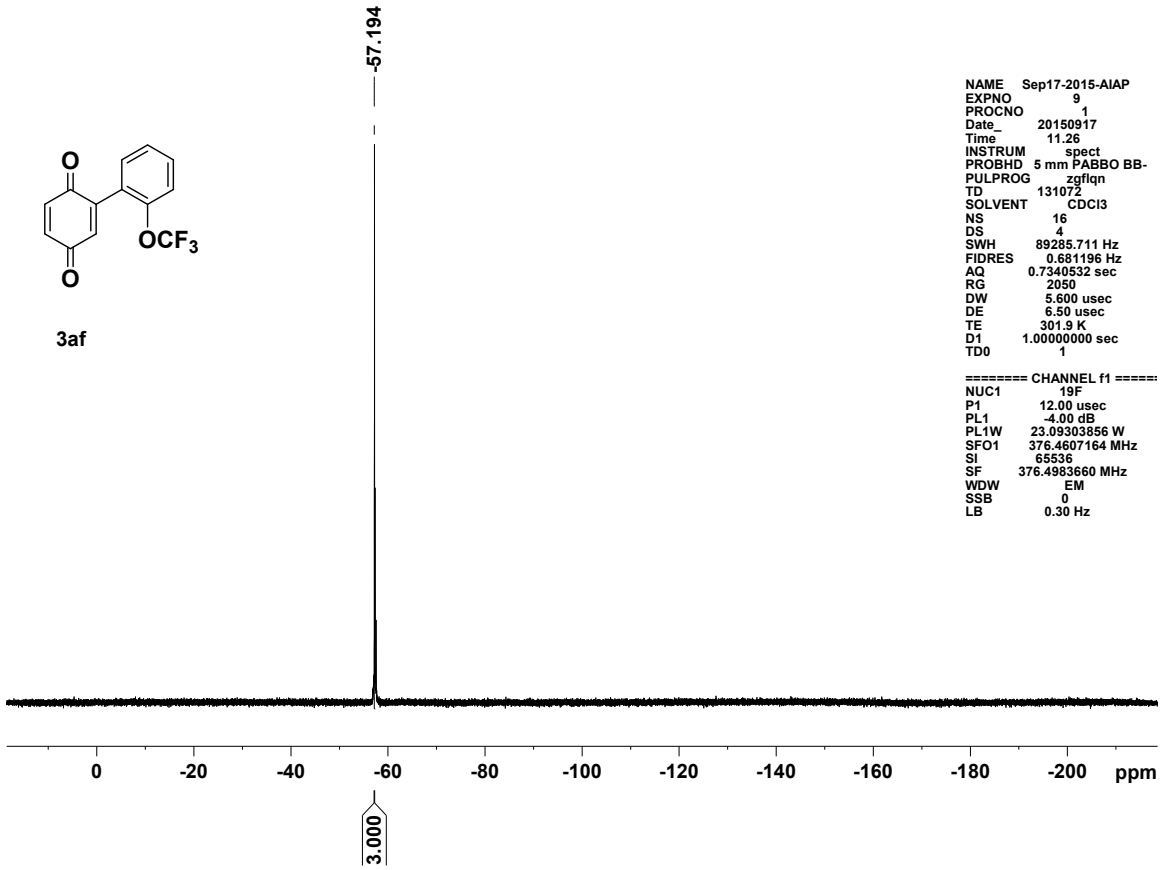
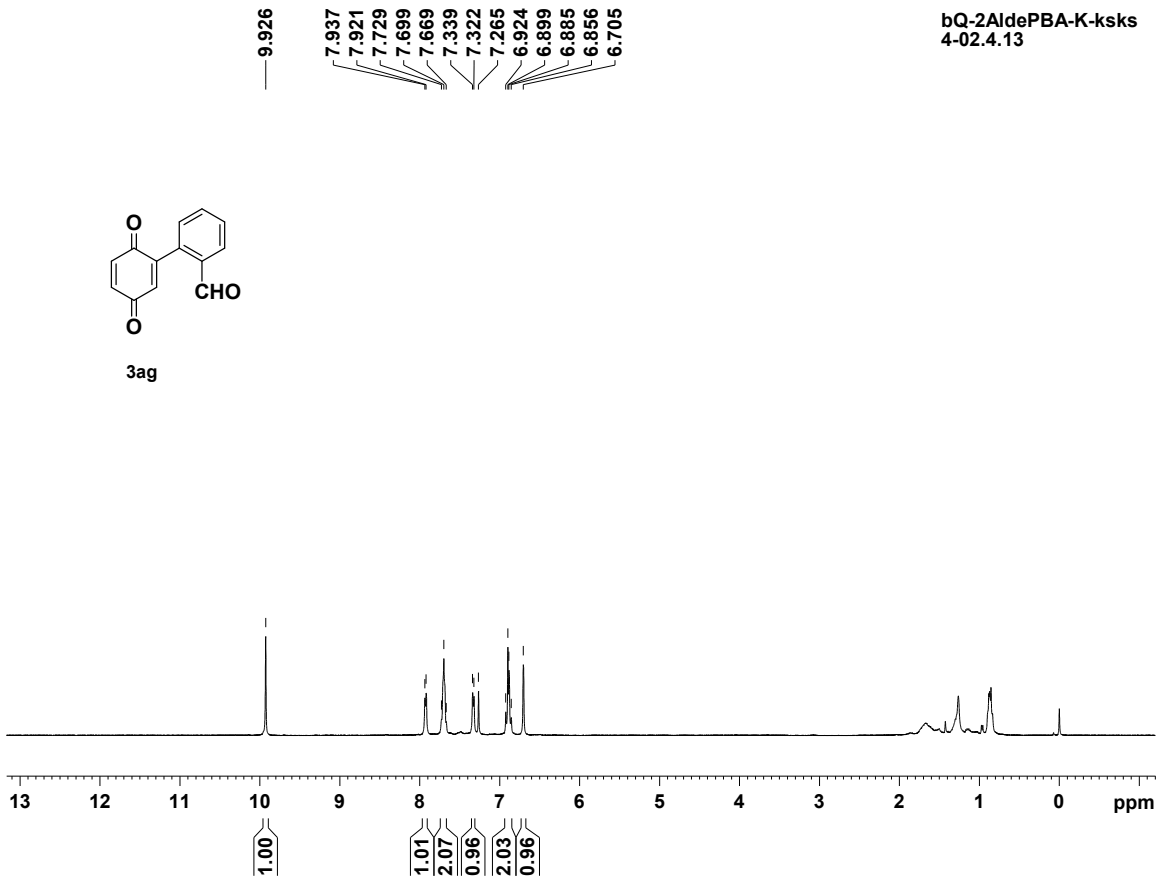
143.96
136.85
136.51
135.26
131.24
131.19
126.80
126.57
121.67
120.67
119.10
BQ2OCF3PHK
11.4.14.47
O
O
OCF3
3af
145
140
135
130
125
120
115
ppm


-57.194
O
O
OCF3
3af
NAME Sep17-2015-AIAP
EXPNO 9
PROCNO 1
Date_ 20150917
Time 11.26
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgflqn
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 89285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340532 sec
RG 2050
DW 5.600 usec
DE 6.50 usec
TE 301.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 19F
P1 12.00 usec
PL1 -4.00 dB
PL1W 23.09303856 W
SFO1 376.4607164 MHz
SI 65536
SF 376.4983660 MHz
WDW EM
SSB 0
LB 0.30 Hz
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
3.000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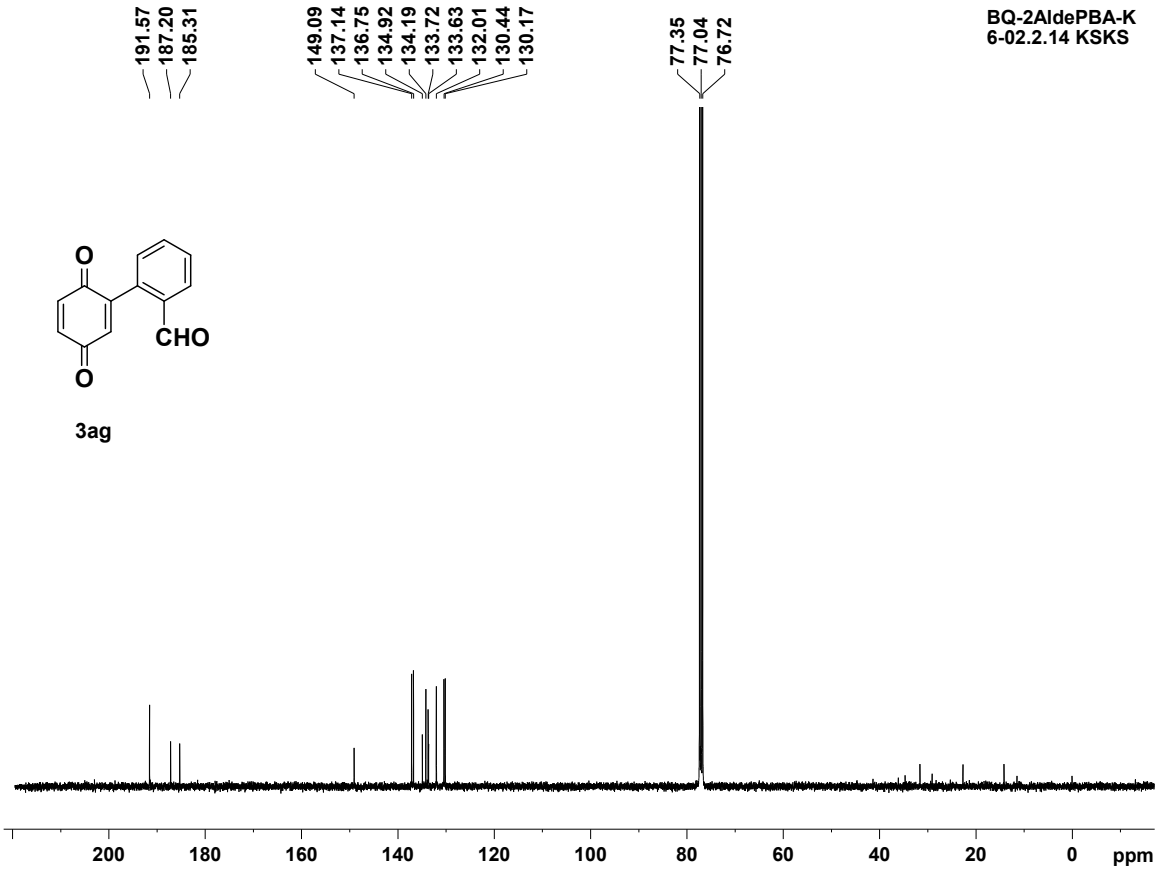
7.921
7.729
7.699
7.669
7.339
7.322
7.265
6.924
6.899
6.885
6.856
6.705
bQ-2AldePBA-K-ksks
4-02.4.13
O
CHO
O
3ag
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
2.07
0.96
2.03
0.96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185.31
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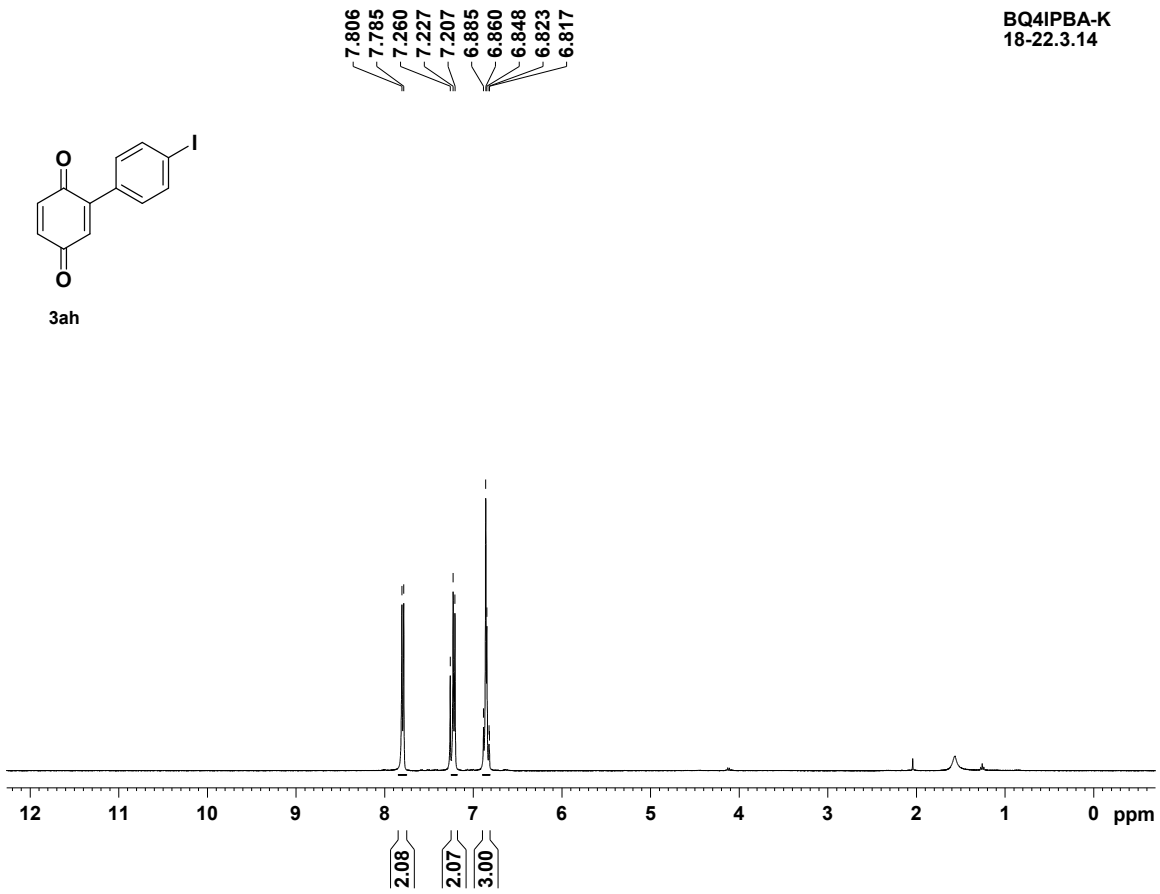
136.75
134.92
134.19
133.72
133.63
132.01
130.44
130.17
77.35
77.04
76.72
BQ-2AldePBA-K
6-02.2.14 KSKS
O
CHO
O
3ag
200
180
160
140
120
100
80
60
40
20
0
ppm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7.785
7.260
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7.207
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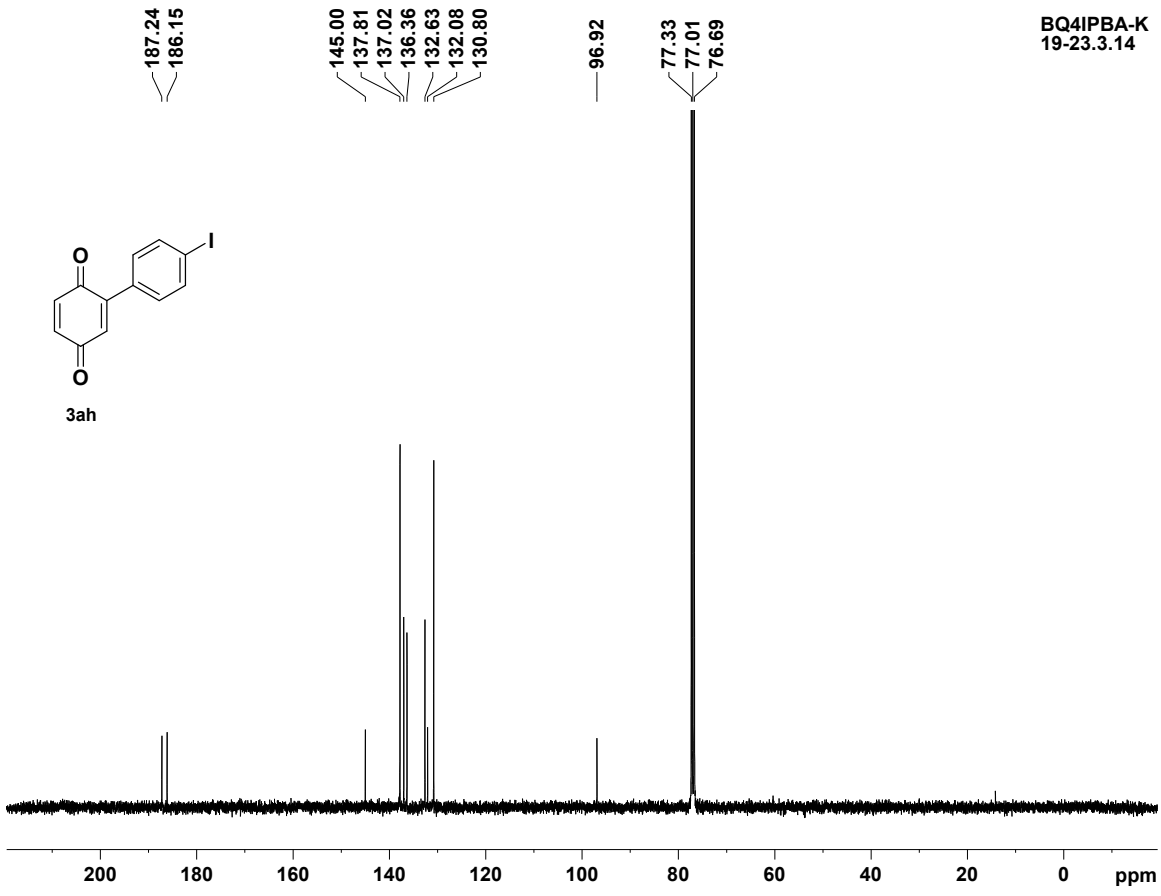
6.860
6.848
6.823
6.817
BQ4IPBA-K
18-22.3.14
O
I
O
3ah
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.08
2.07
3.00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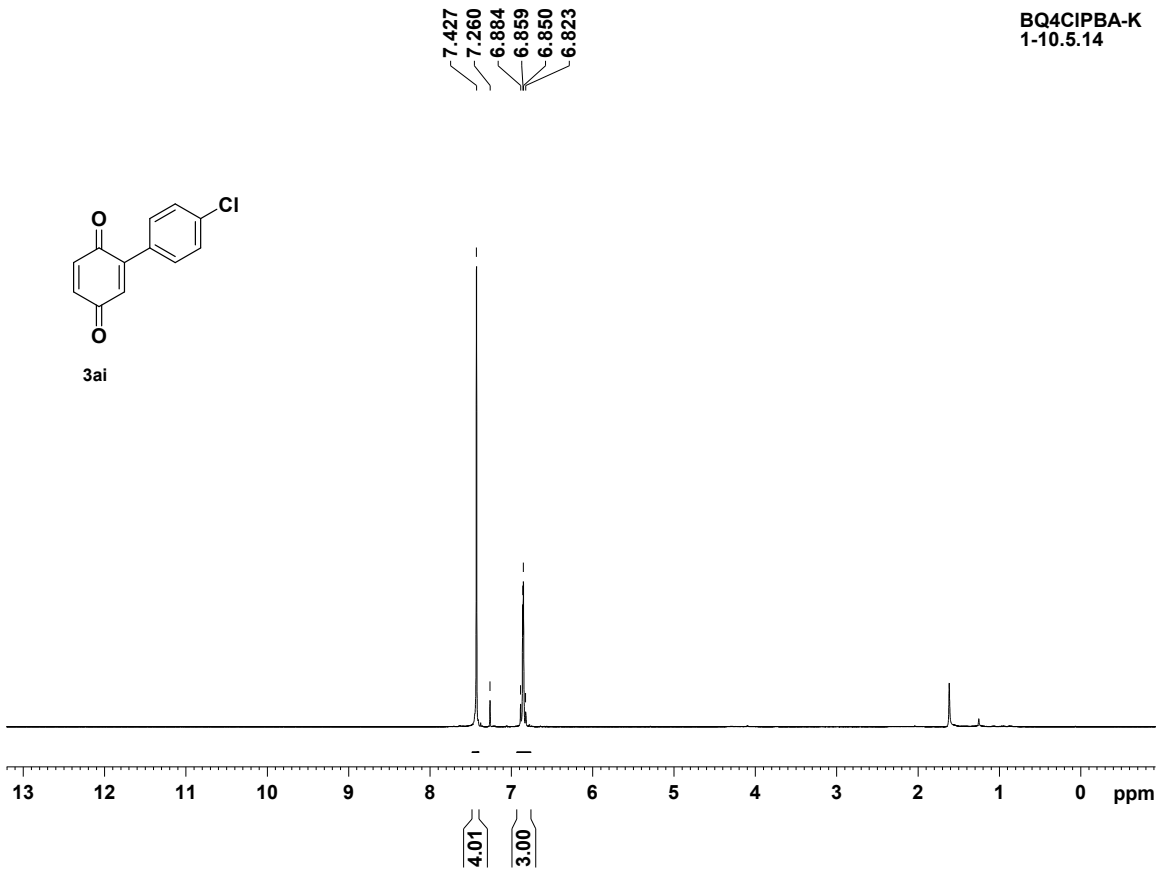
137.81
137.02
136.36
132.63
132.08
130.80
96.92
77.33
77.01
76.69
BQ4IPBA-K
19-23.3.14
O
O
I
3ah
200
180
160
140
120
100
80
60
40
20
0
ppm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6.884
6.859
6.850
6.823
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1-10.5.14
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Cl
O
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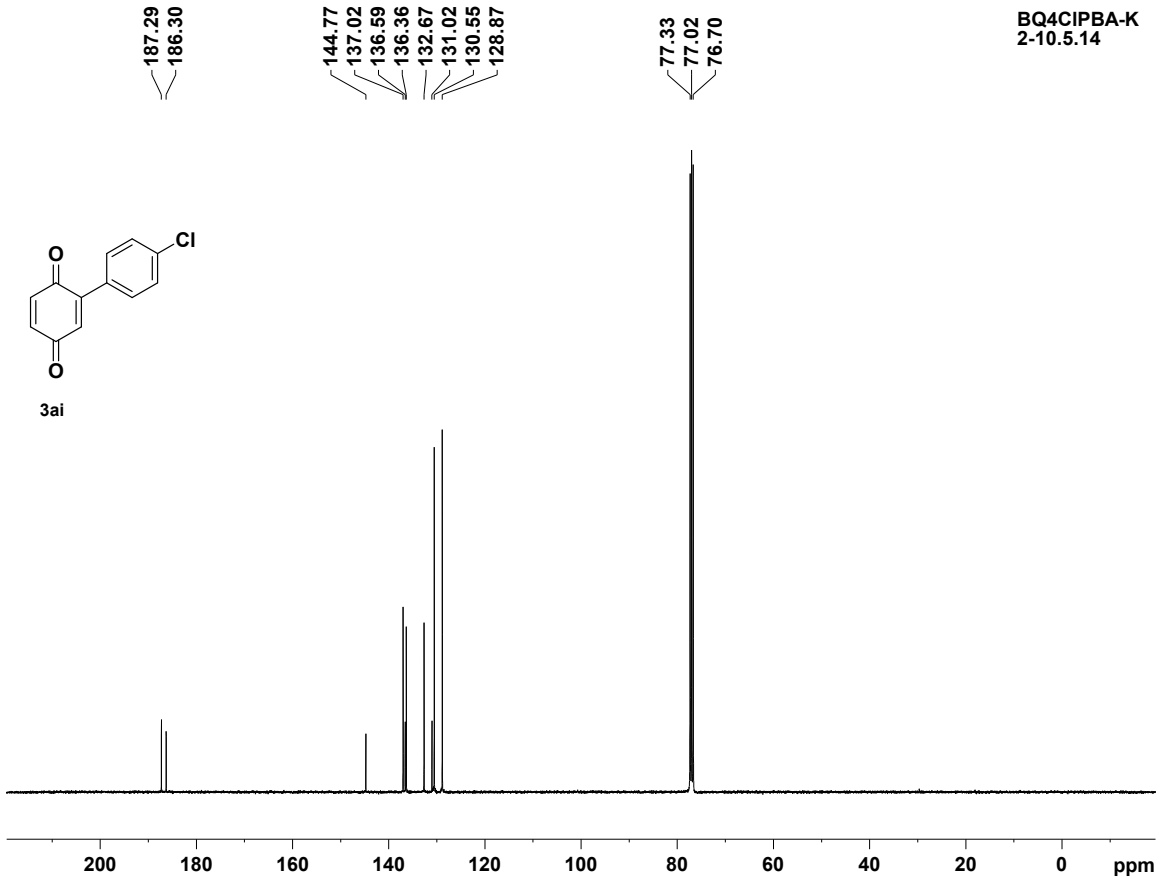
9
8
7
6
5
4
3
2
1
0
ppm
4.01
3.00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186.30
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137.02
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136.36
132.67
131.02
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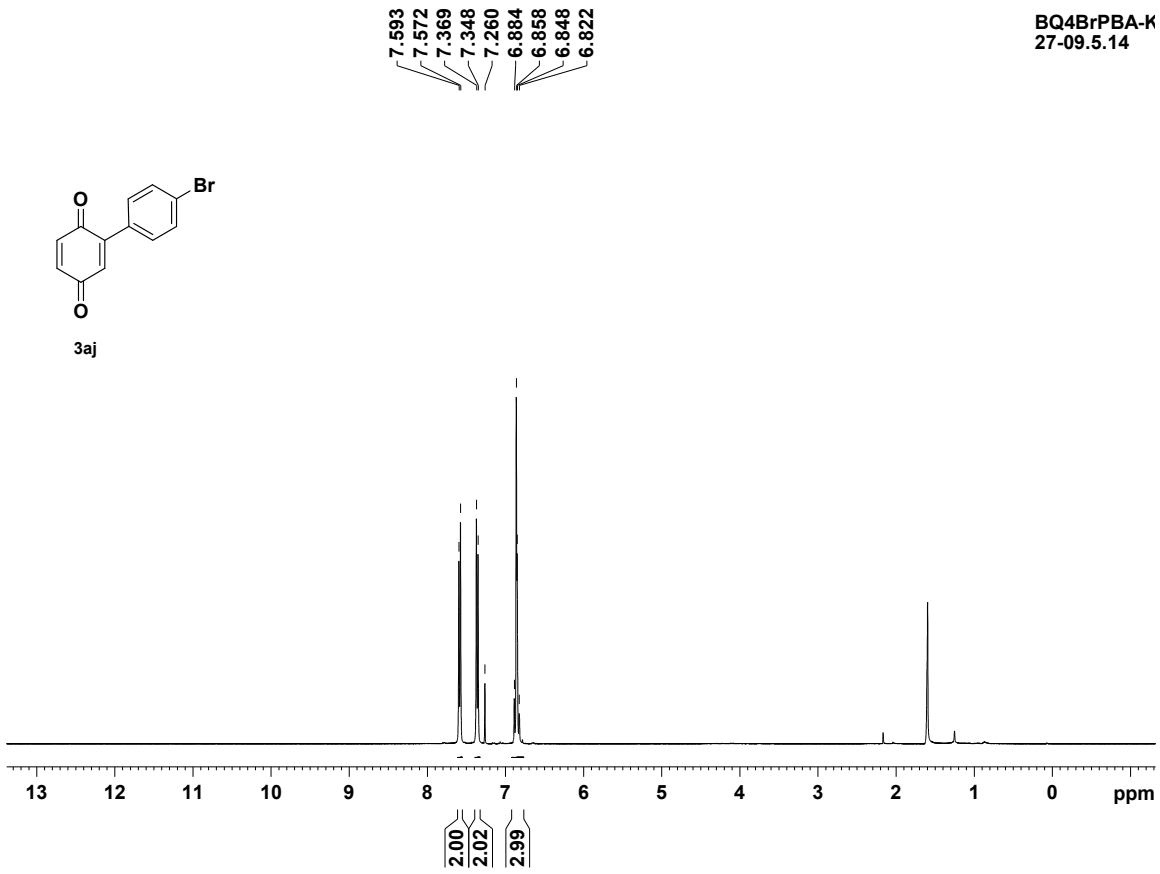
128.87
77.33
77.02
76.70
BQ4ClPBA-K
2-10.5.14
O
Cl
O
3ai
200
180
160
140
120
100
80
60
40
20
0
ppm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7.572
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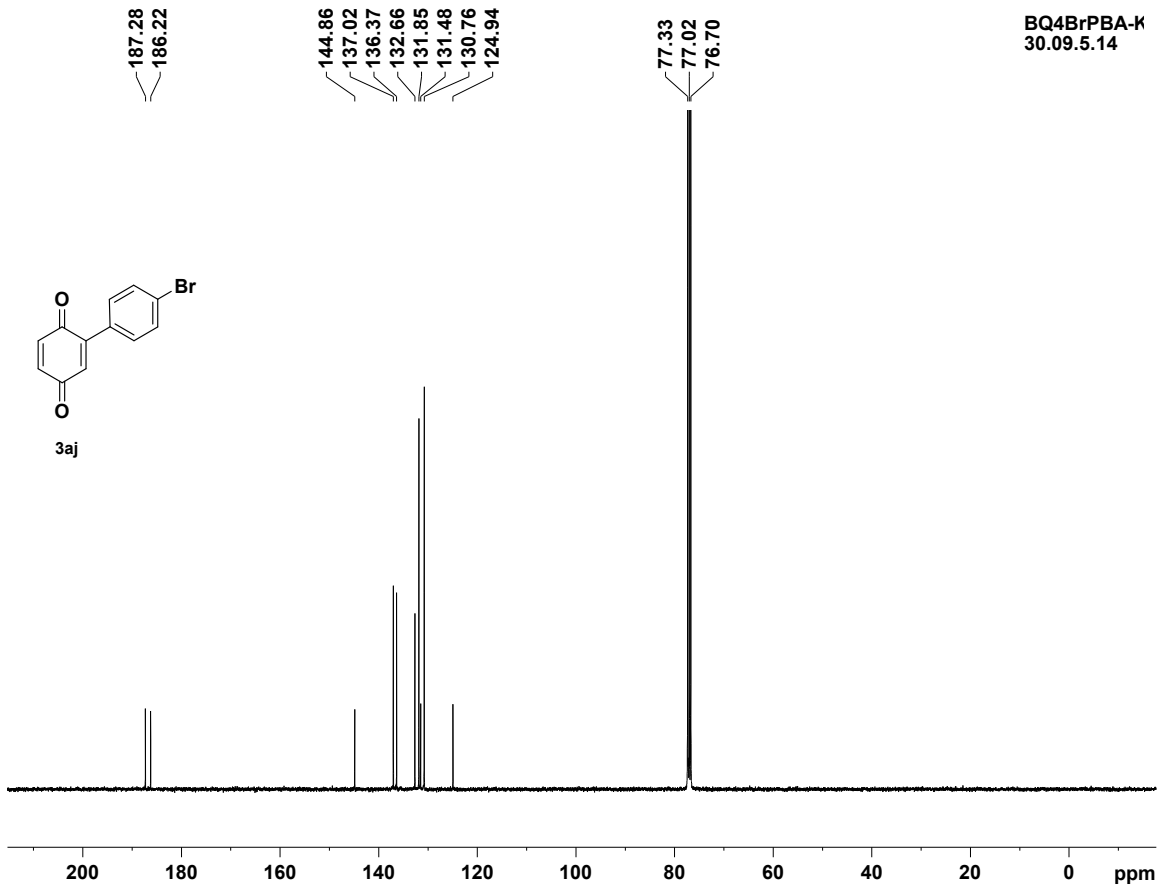
7.260
6.884
6.858
6.848
6.822
BQ4BrPBA-K
27-09.5.14
O
Br
O
3aj
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.02
2.99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186.22
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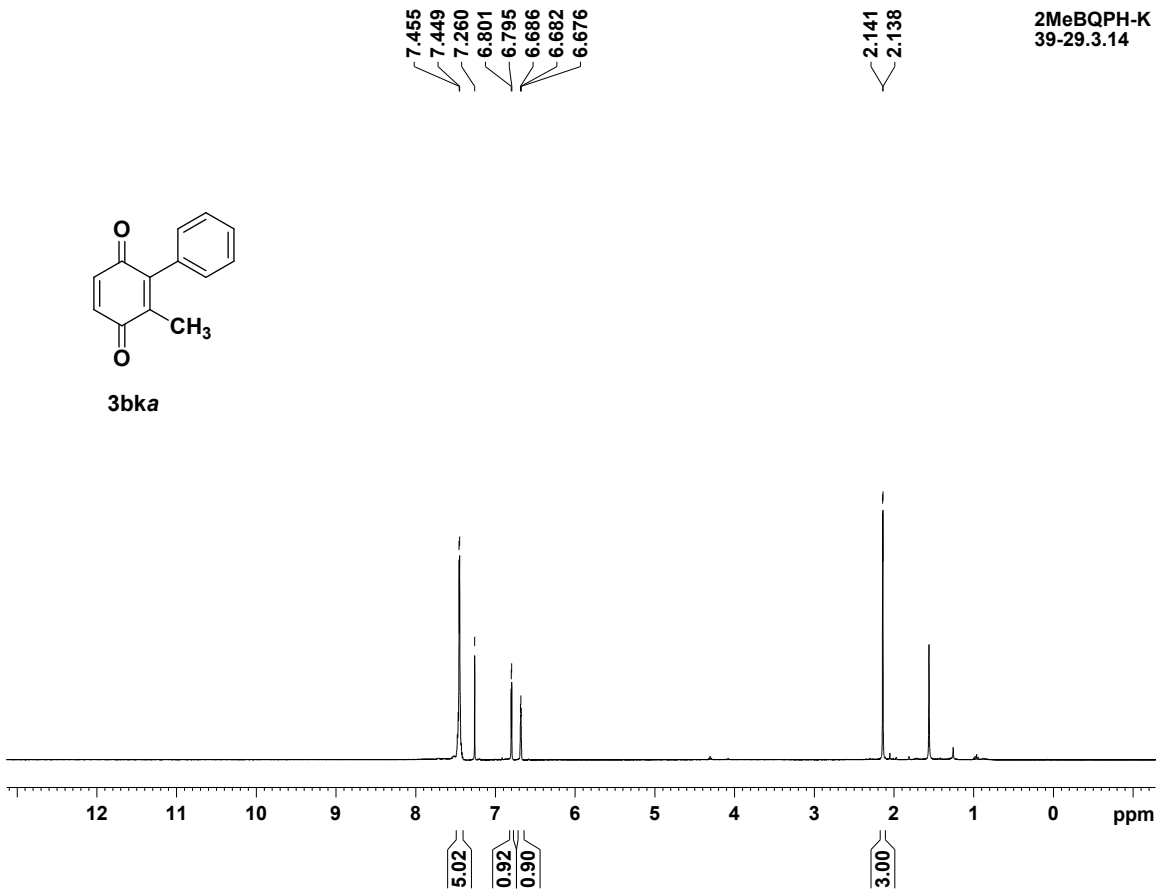
132.66
131.85
131.48
130.76
124.94
77.33
77.02
76.70
BQ4BrPBA-K
30.09.5.14
O
Br
O
3aj
200
180
160
140
120
100
80
60
40
20
0
ppm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7.449
7.260
6.801
6.795
6.686
6.682
6.676
2.141
2.138
2MeBQPH-K
39-29.3.14
O
CH3
O
12
11
10
9
8
7
6
5
4
3
2
1
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ppm
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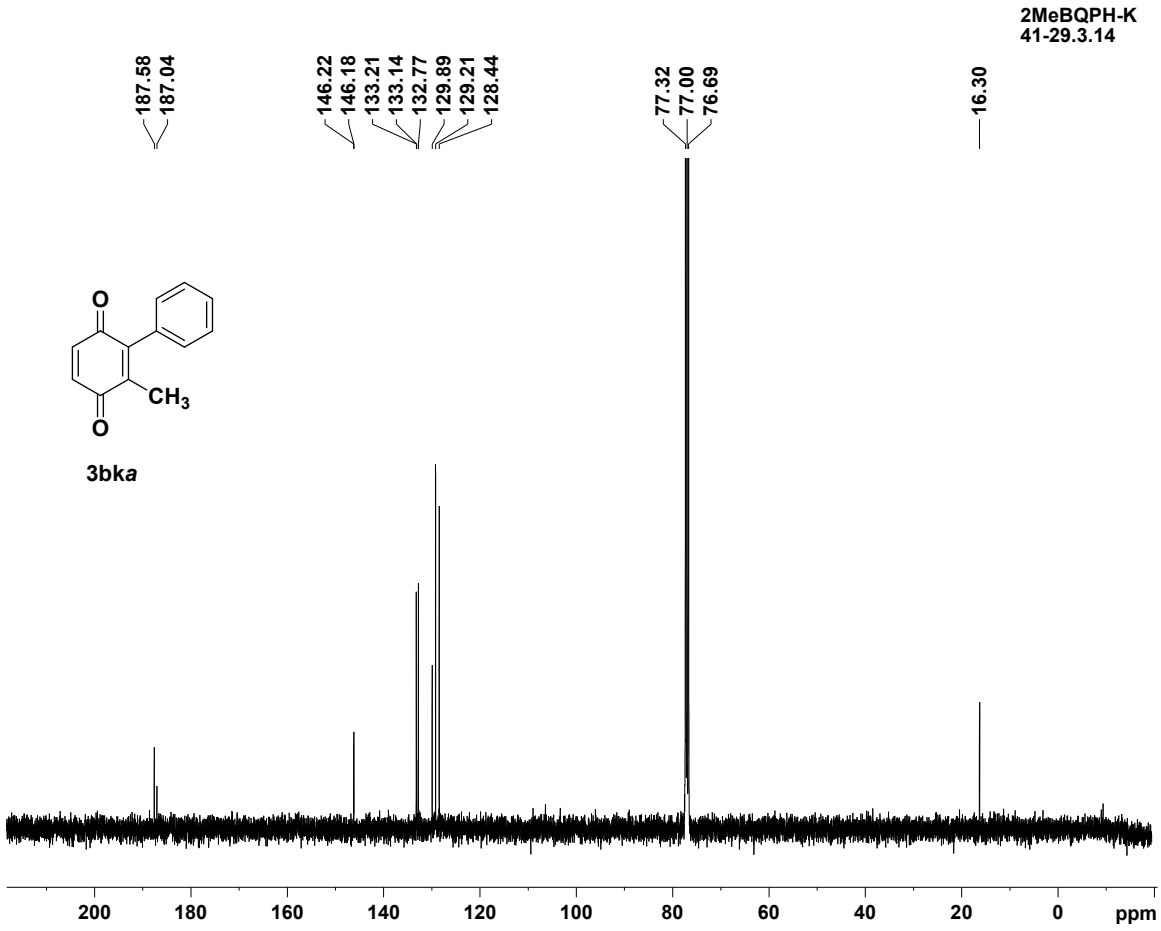
0.92
0.90
3.00

3bk*a*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146.18
133.21
133.14
132.77
129.89
129.21
128.44
77.32
77.00
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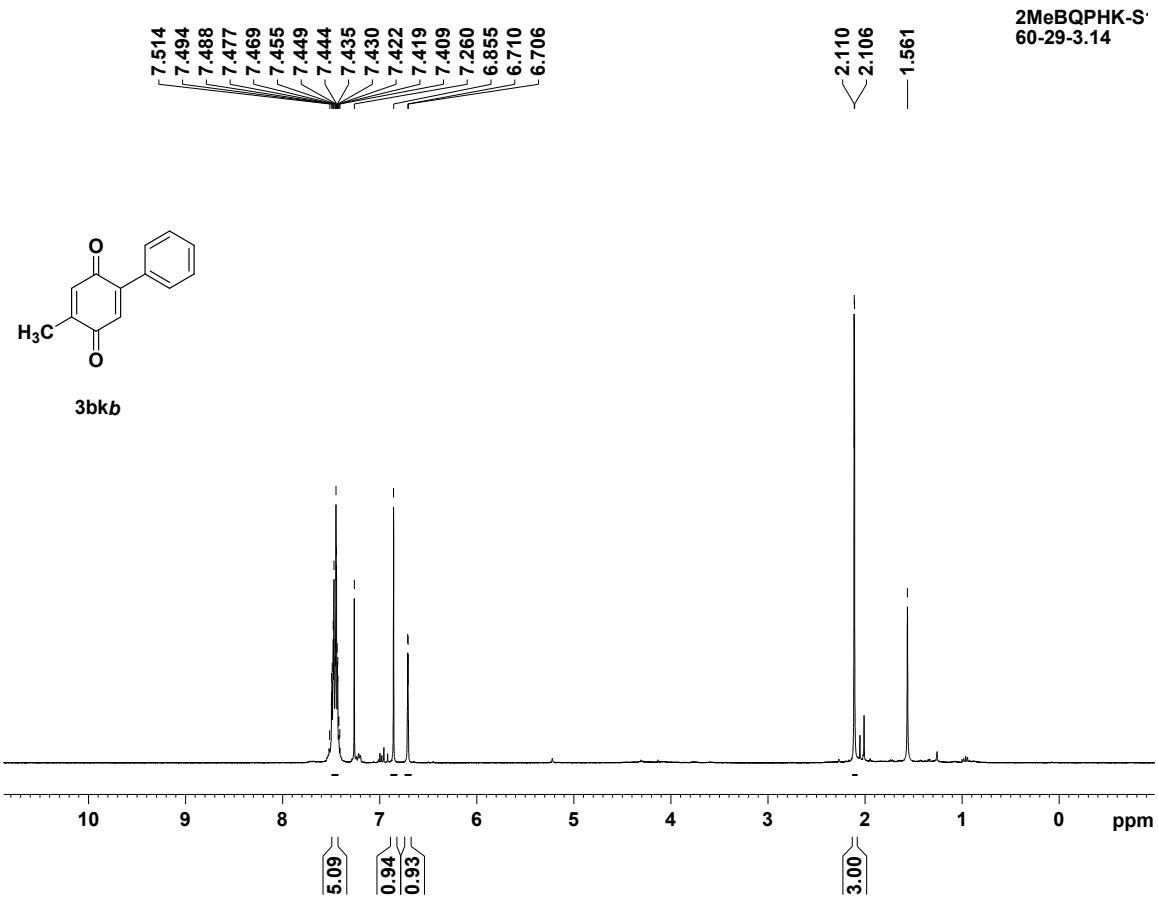
16.30
O
CH3
O
3bka
200
180
160
140
120
100
80
60
40
20
0
ppm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7.455
7.449
7.444
7.435
7.430
7.422
7.419
7.409
7.260
6.855
6.710
6.706
2.110
2.106
1.561
2MeBQPHK-S
60-29-3.14
O
H3C
O
3bkb
10
9
8
7
6
5
4
3
2
1
0
ppm
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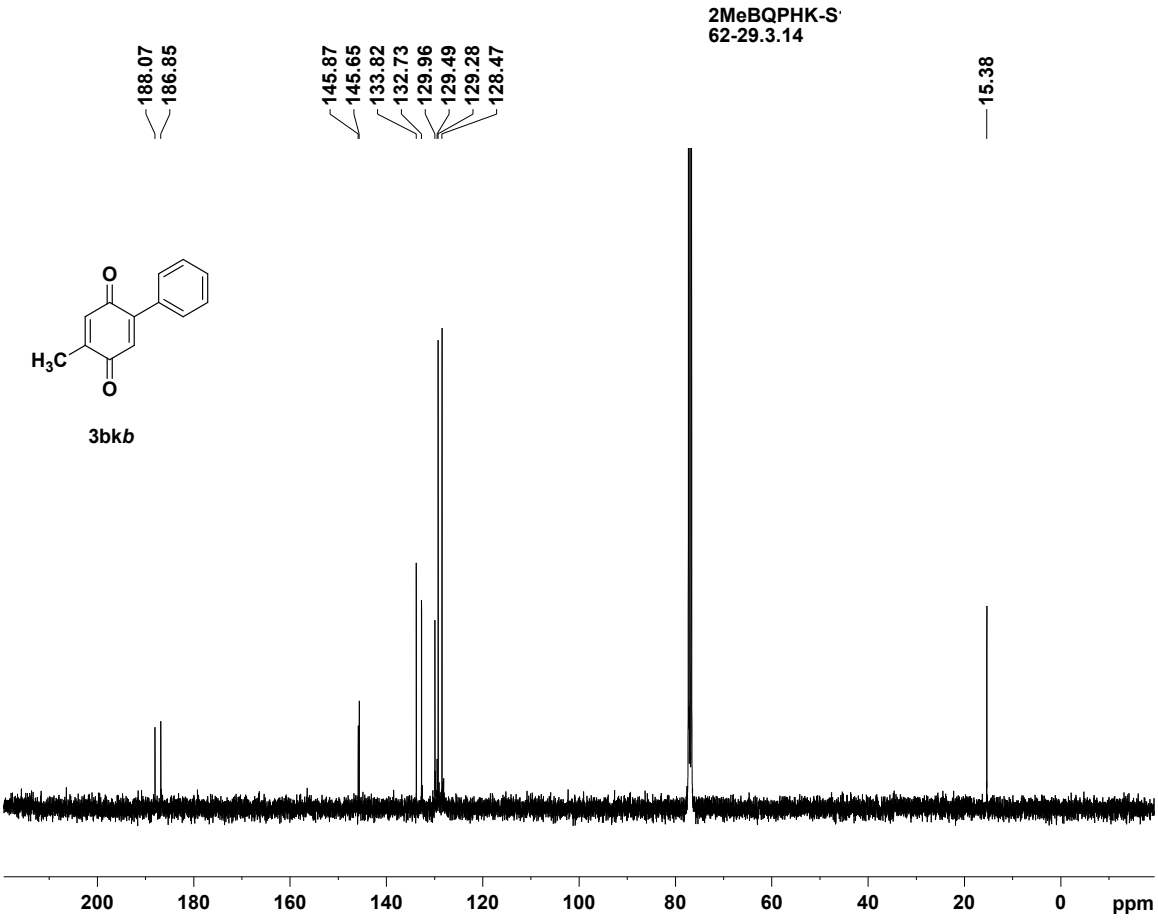
0.94
0.93
3.00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62-29.3.14
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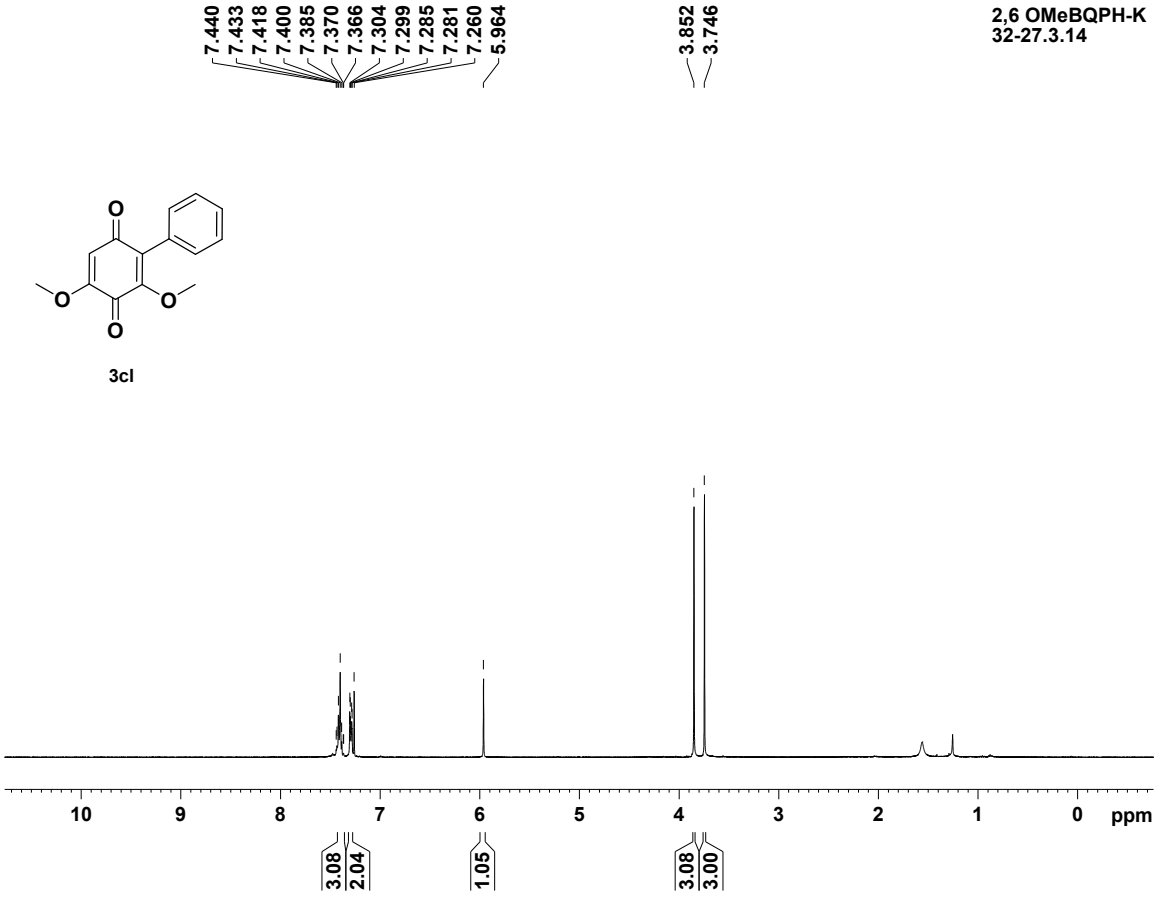
186.85
145.87
145.65
133.82
132.73
129.96
129.49
129.28
128.47
15.38
O
H3C
O
3bkb
200
180
160
140
120
100
80
60
40
20
0
ppm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7.304
7.299
7.285
7.281
7.260
5.964
3.852
3.746
2,6 OMeBQPH-K
32-27.3.14
O
O
O
O
3cl
10
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8
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6
5
4
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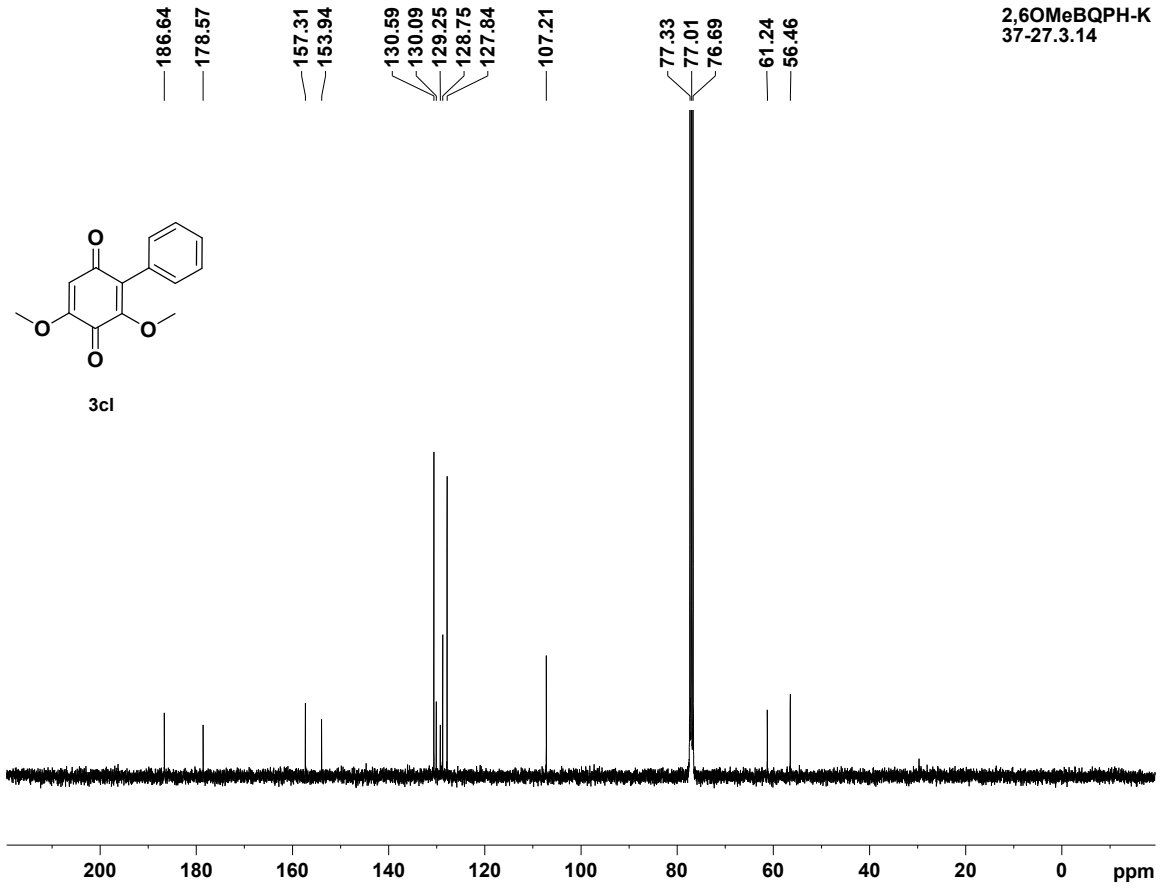
ppm
3.08
2.04
1.05
3.08
3.00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37-27.3.14
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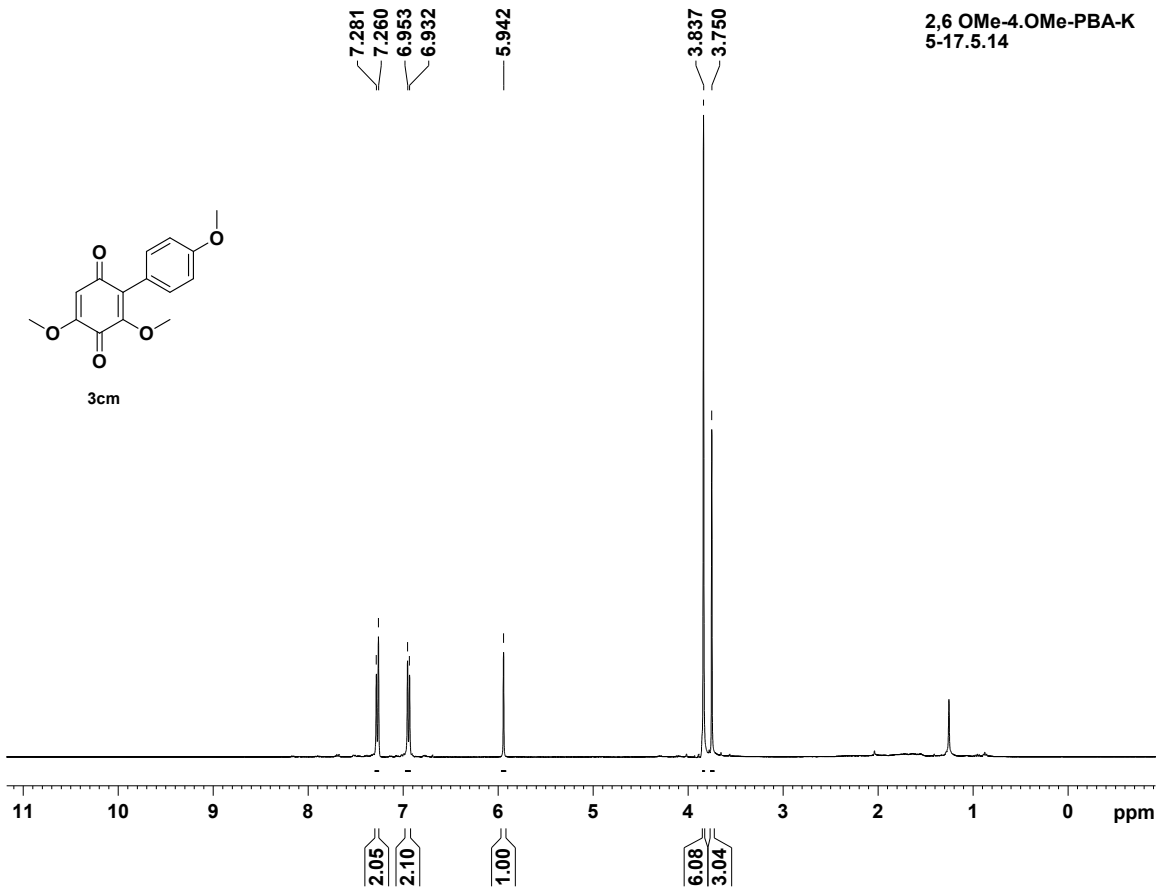
157.31
153.94
130.59
130.09
129.25
128.75
127.84
107.21
77.33
77.01
76.69
61.24
56.46
O
O
O
O
3cl
200
180
160
140
120
100
80
60
40
20
0
ppm


2,6 OMe-4.OMe-PBA-K
5-17.5.14
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7.260
6.953
6.932
5.942
3.837
3.750
3cm
11
10
9
8
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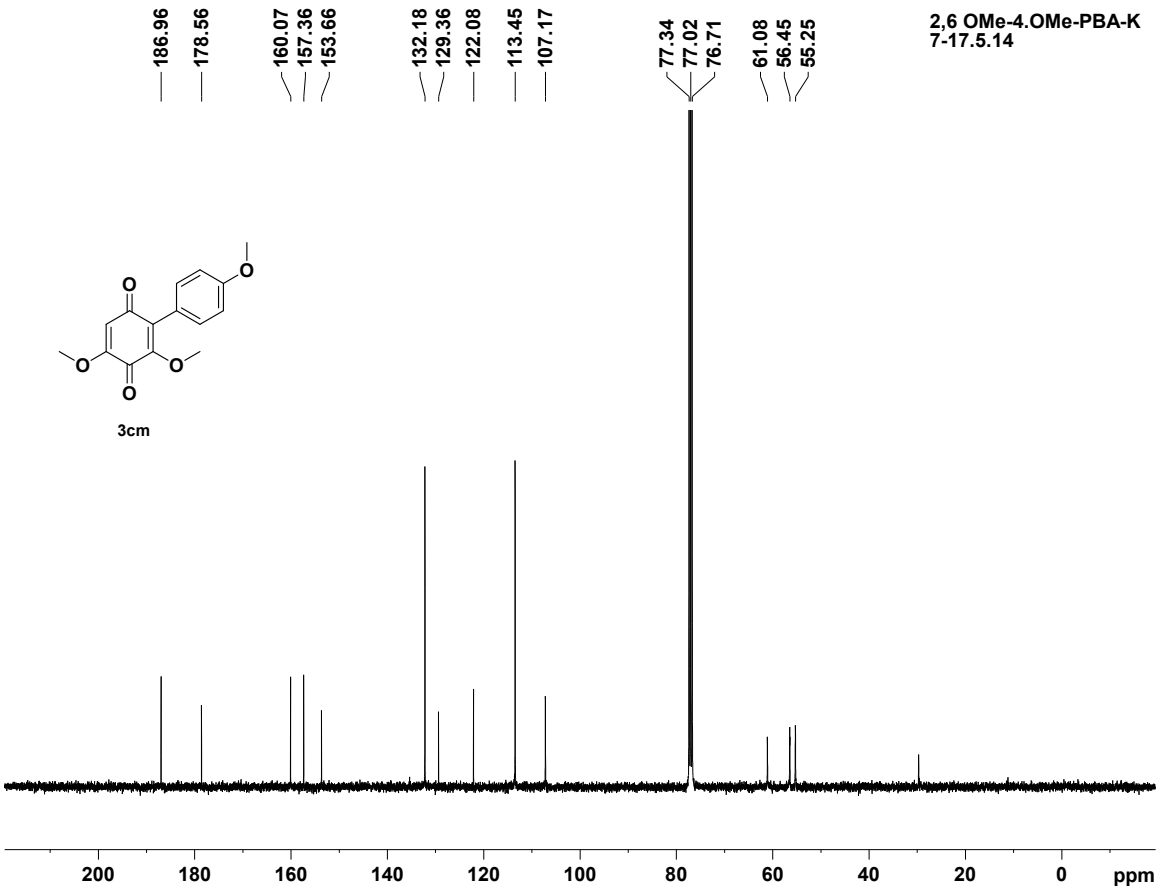
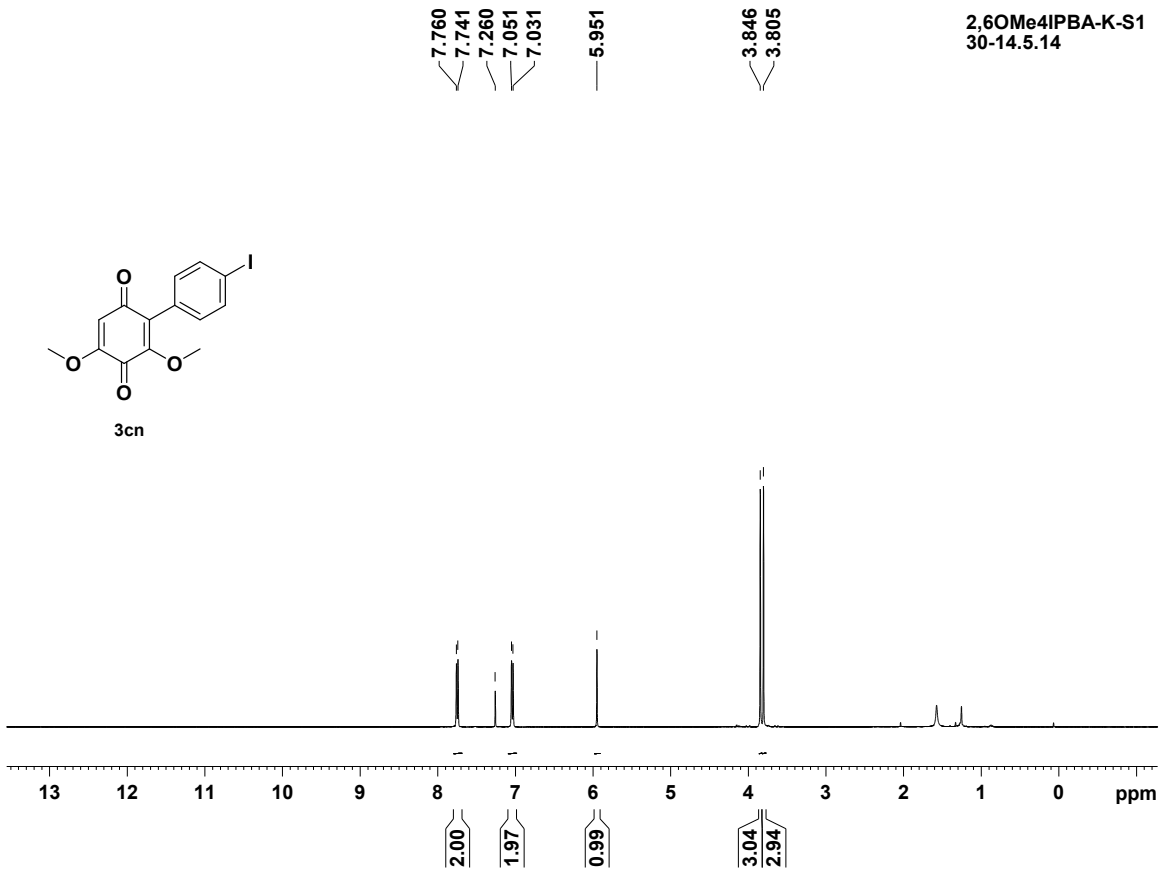
6
5
4
3
2
1
0
ppm
2.05
2.10
1.00
6.08
3.04


186.96
178.56
160.07
157.36
153.66
132.18
129.36
122.08
113.45
107.17
77.34
77.02
76.71
61.08
56.45
55.25
2,6 OMe-4.OMe-PBA-K
7-17.5.14
3cm
200
180
160
140
120
100
80
60
40
20
0
ppm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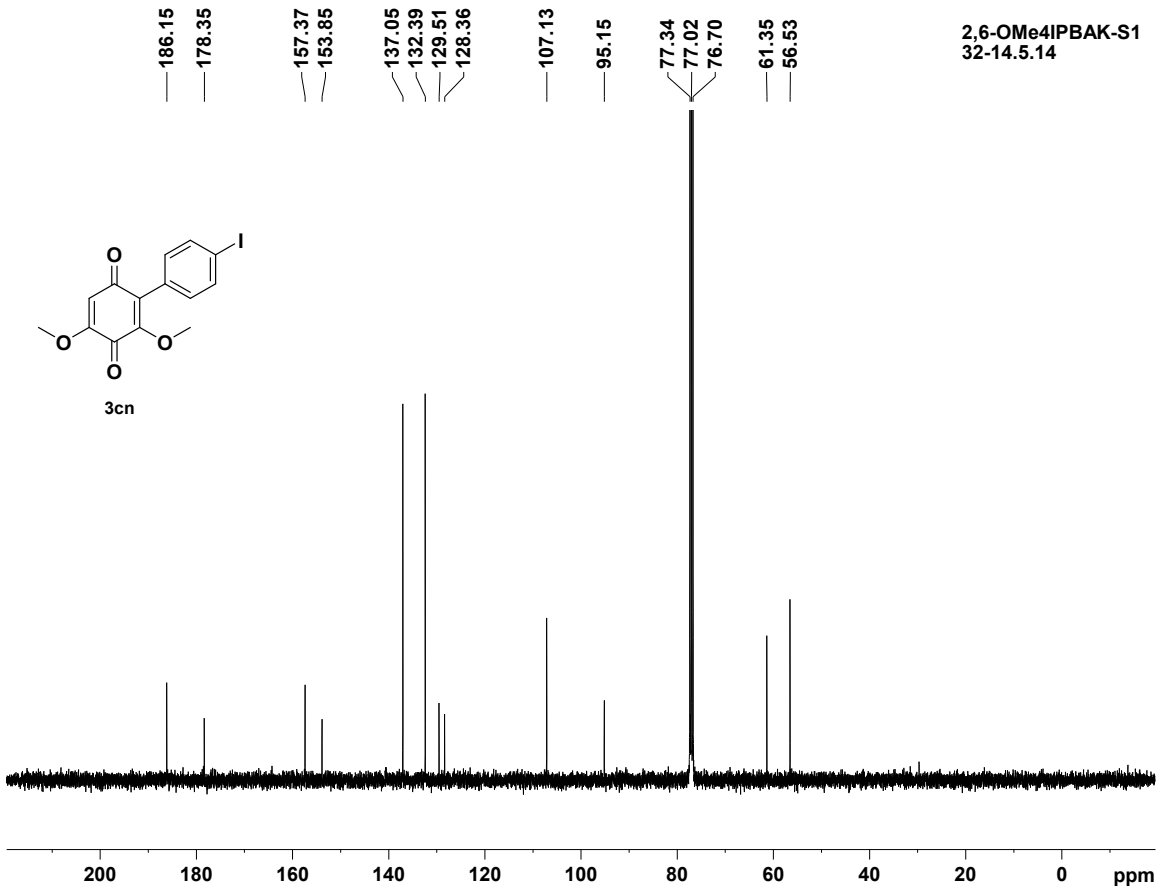
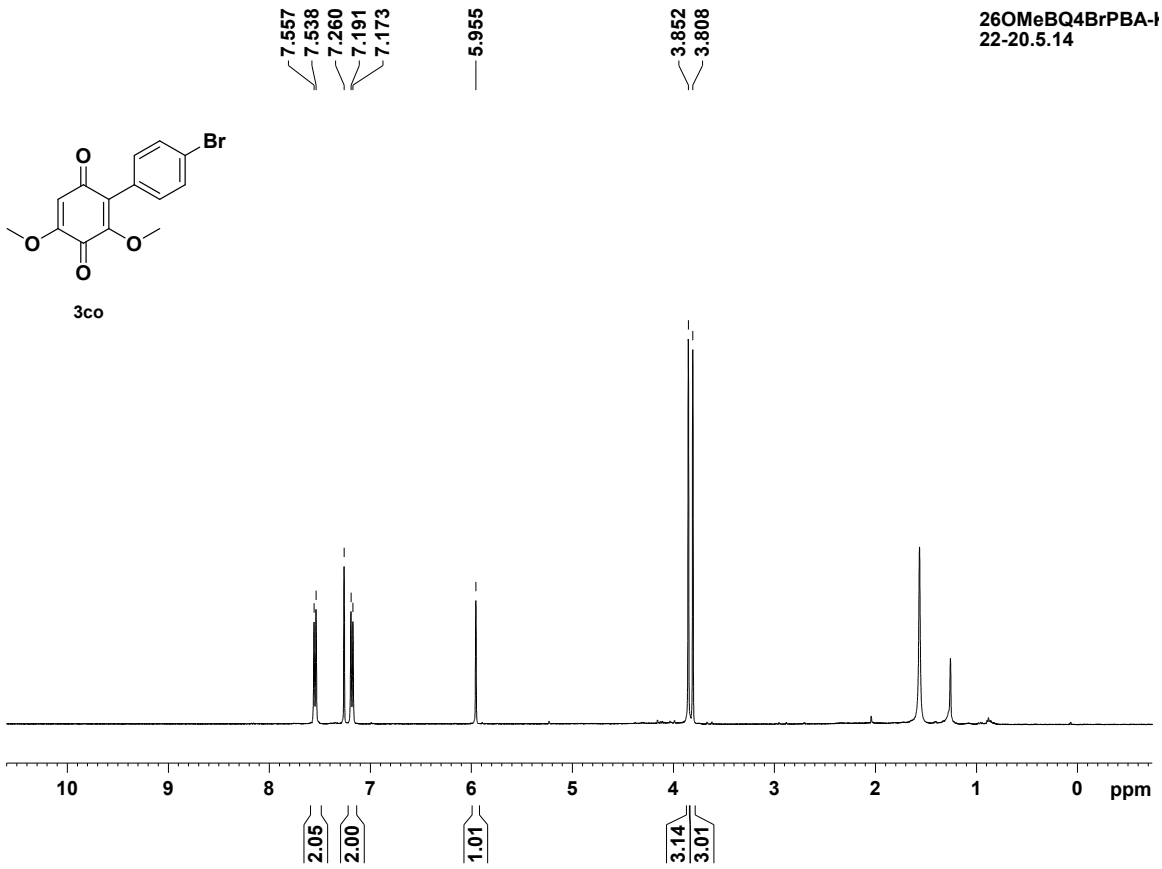
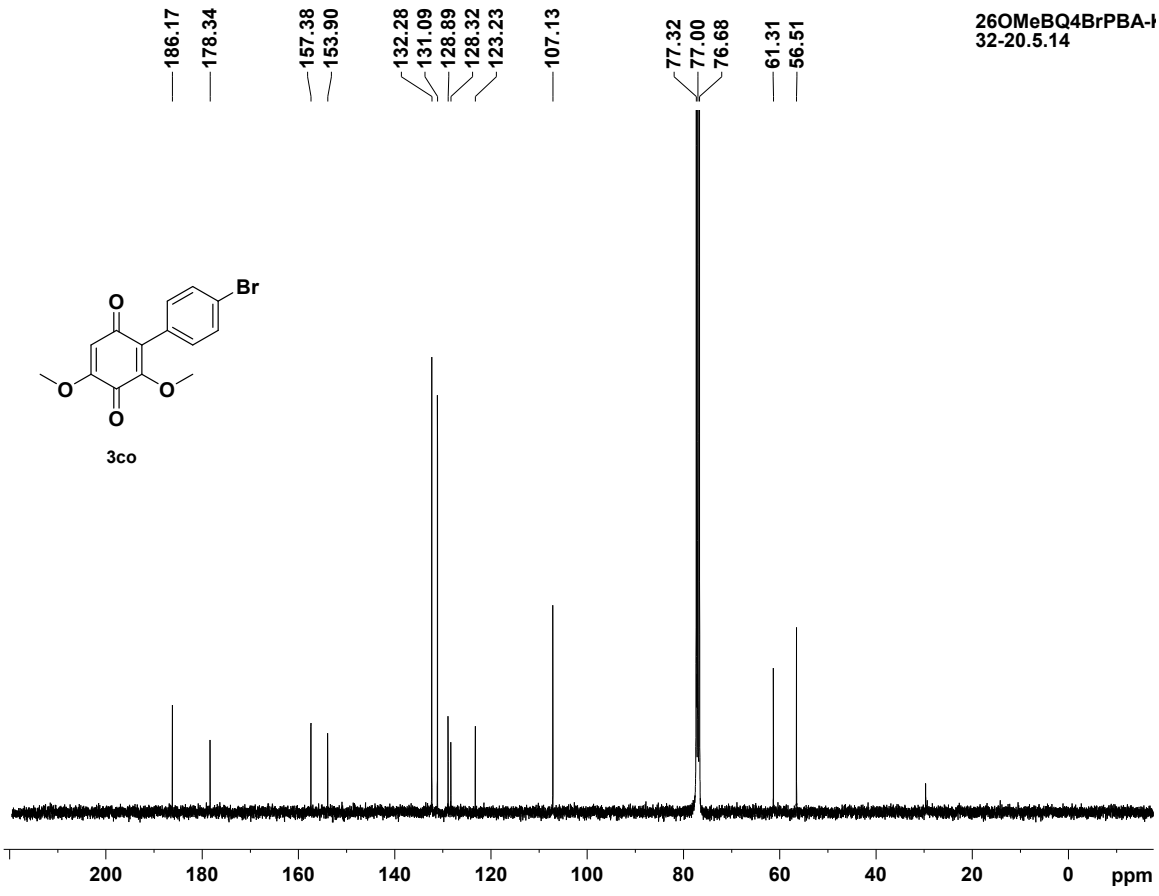
7.051
7.031
5.951
3.846
3.805
2,6OMe4IPBA-K-S1
30-14.5.14
O
I
O
O
O
3cn
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.97
0.99
3.04
2.94


186.15
178.35
157.37
153.85
137.05
132.39
129.51
128.36
107.13
95.15
77.34
77.02
76.70
61.35
56.53
2,6-OMe4IPBAK-S1
32-14.5.14
O
I
O
O
O
3cn
200
180
160
140
120
100
80
60
40
20
0
ppm


7.557
7.538
7.260
7.191
7.173
5.955
3.852
3.808
26OMeBQ4BrPBA-H
22-20.5.14
Br
O
O
O
O
3co
10
9
8
7
6
5
4
3
2
1
0
ppm
2.05
2.00
1.01
3.14
3.01


186.17
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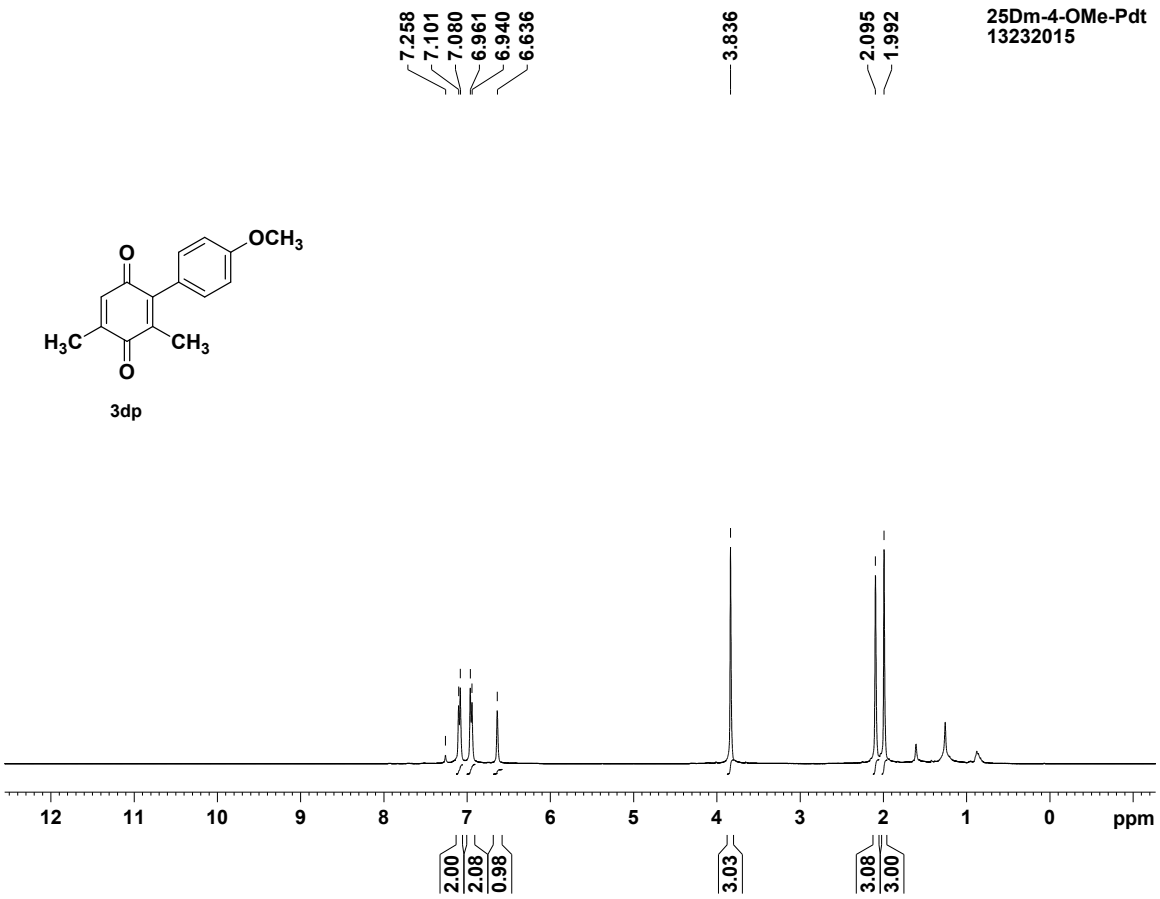
157.38
153.90
132.28
131.09
128.89
128.32
123.23
107.13
77.32
77.00
76.68
61.31
56.51
26OMeBQ4BrPBA-I
32-20.5.14
Br
O
O
O
O
3co
200
180
160
140
120
100
80
60
40
20
0
ppm


7.258
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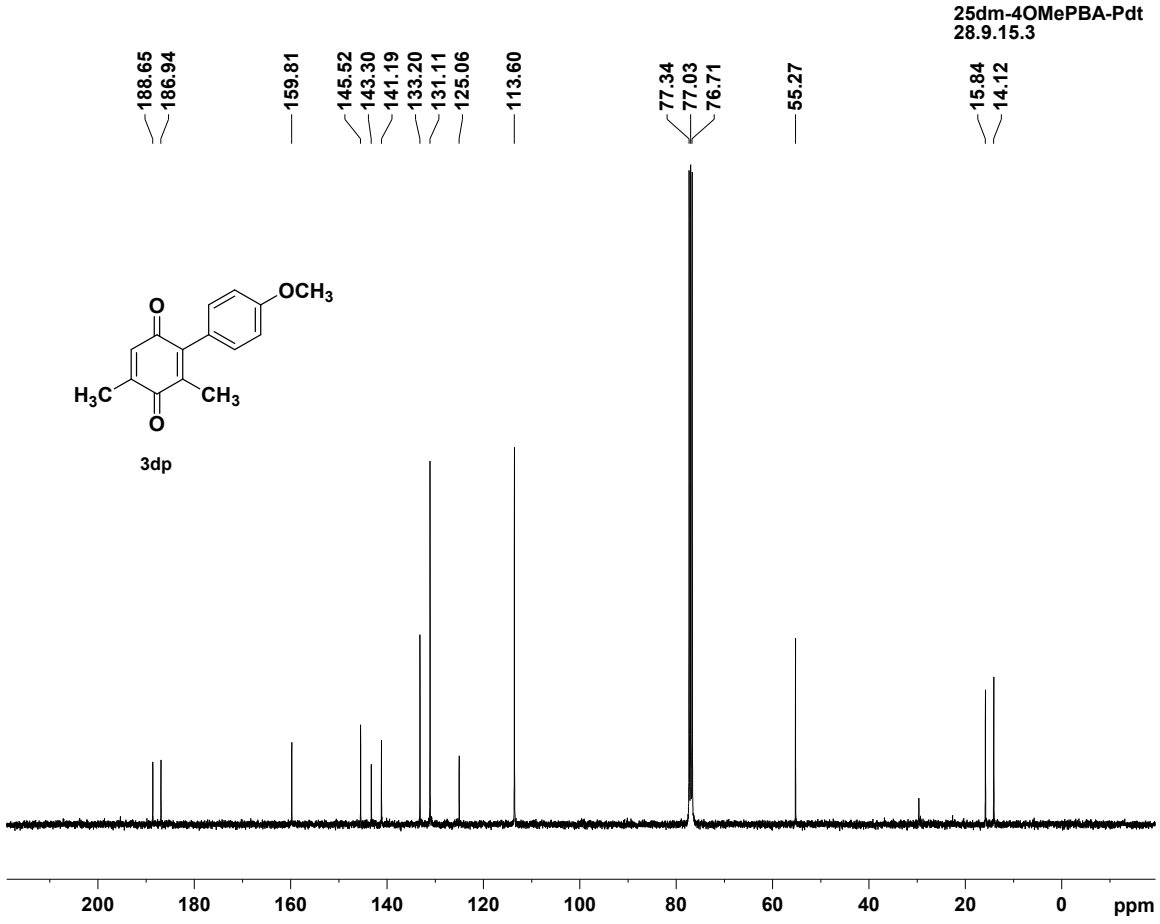
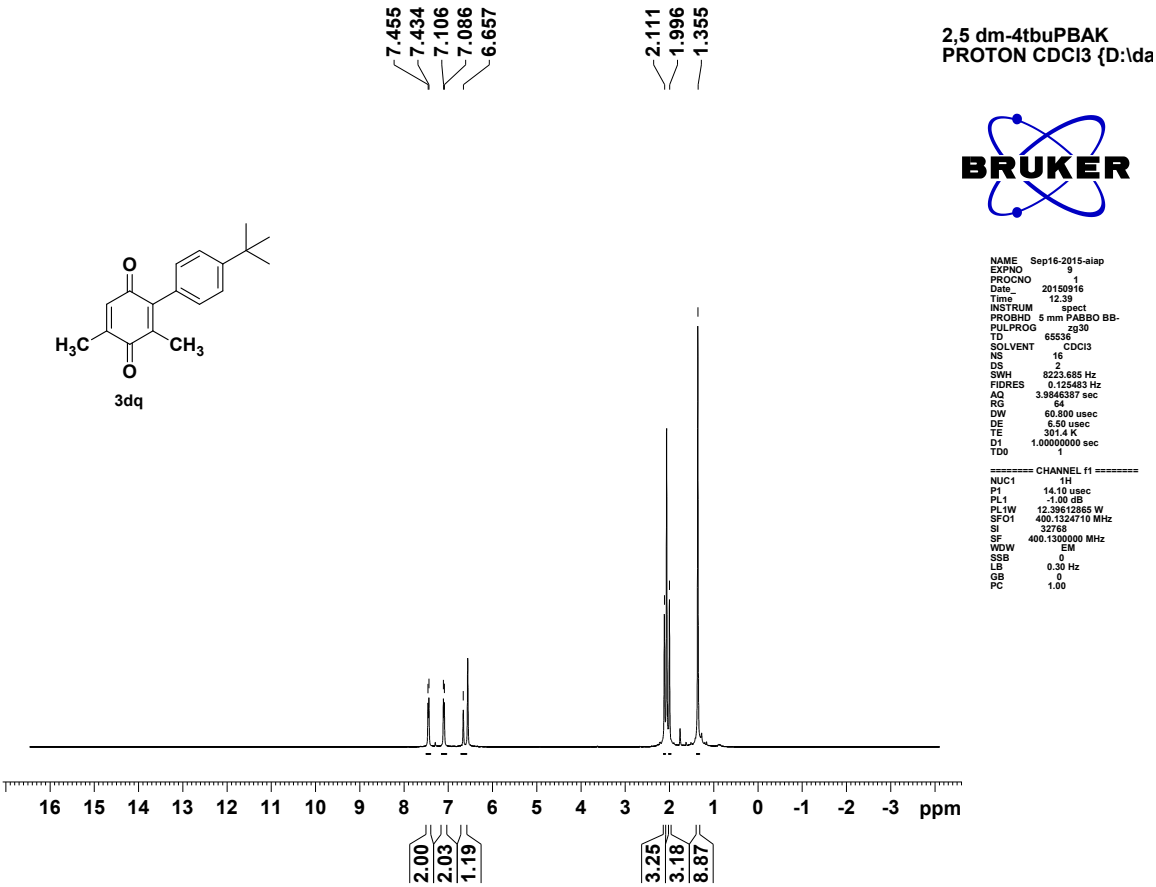
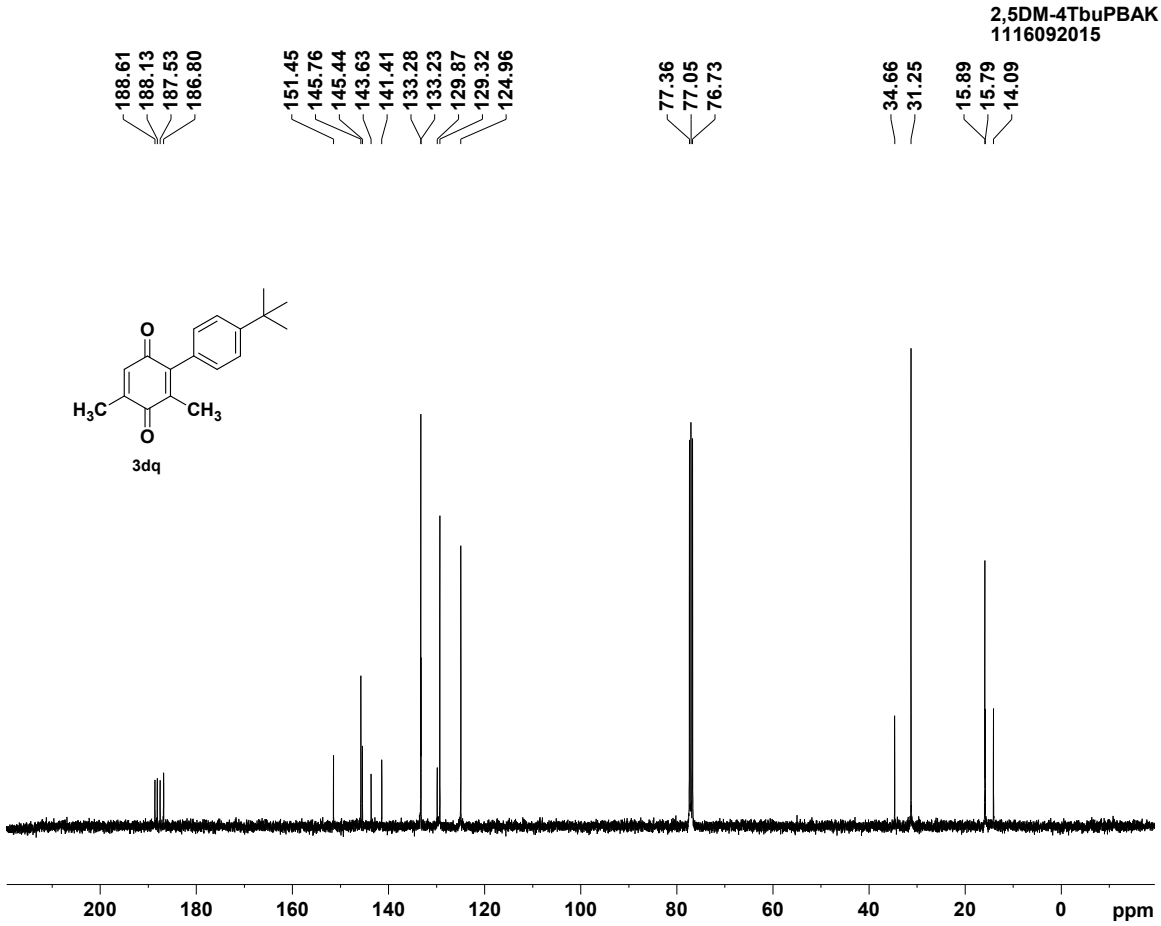
7.080
6.961
6.940
6.636
3.836
2.095
1.992
25Dm-4-OMe-Pdt
13232015
OCH3
O
H3C
CH3
O
3dp
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.08
0.98
3.03
3.08
3.00


25dm-4OMePBA-Pdt
28.9.15.3
188.65
186.94
159.81
145.52
143.30
141.19
133.20
131.11
125.06
113.60
77.34
77.03
76.71
55.27
15.84
14.12
OCH3
O
H3C
CH3
O
3dp
200
180
160
140
120
100
80
60
40
20
0
ppm


7.455
7.434
7.106
7.086
6.657
2.111
1.996
1.355
2,5 dm-4tbuPBAK
PROTON CDCl3 {D:\da
BRUKER
NAME Sep16-2015-aiap
EXPNO 9
PROCNO 1
Date_ 20150916
Time 12.39
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 64
DW 60.800 usec
DE 6.50 usec
TE 301.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.10 usec
PL1 -1.00 dB
PL1W 12.39612865 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
H3C
CH3
O
3dq
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 ppm
2.00
2.03
1.19
3.25
3.18
8.87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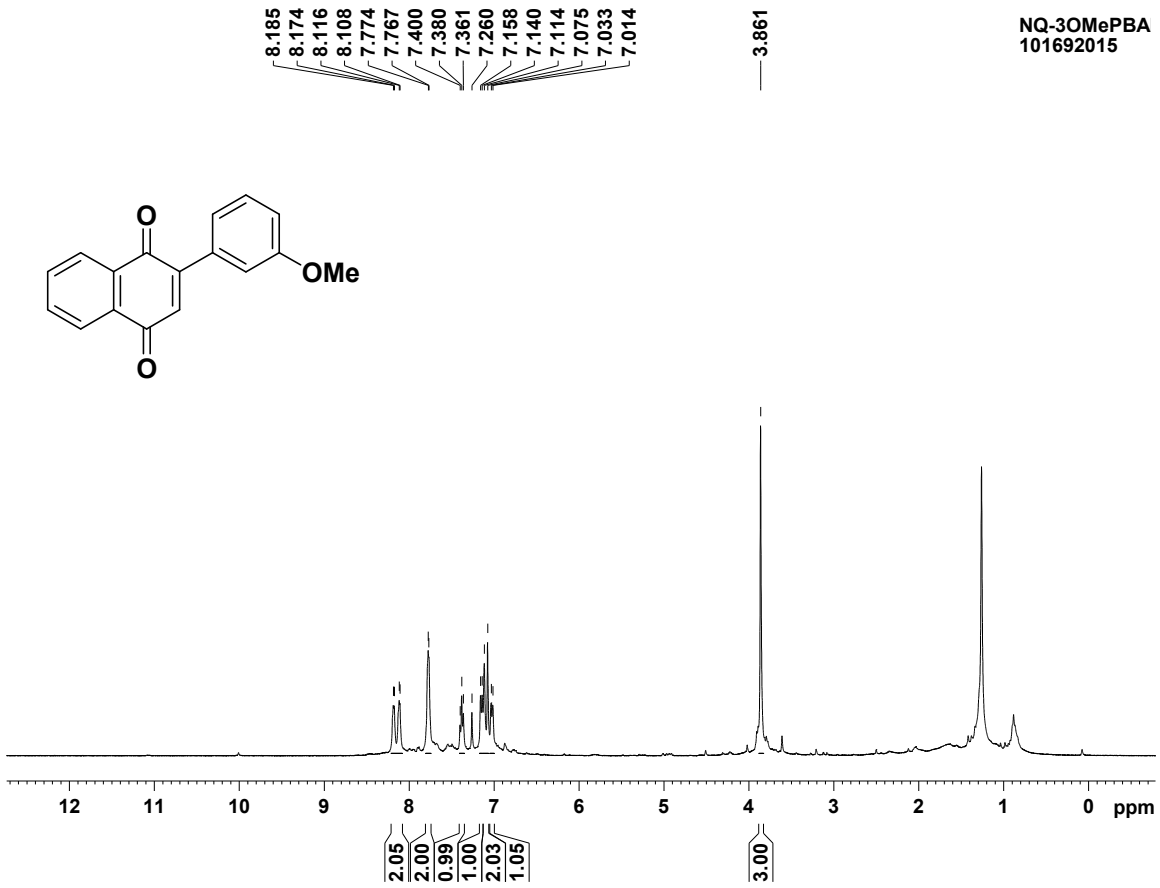
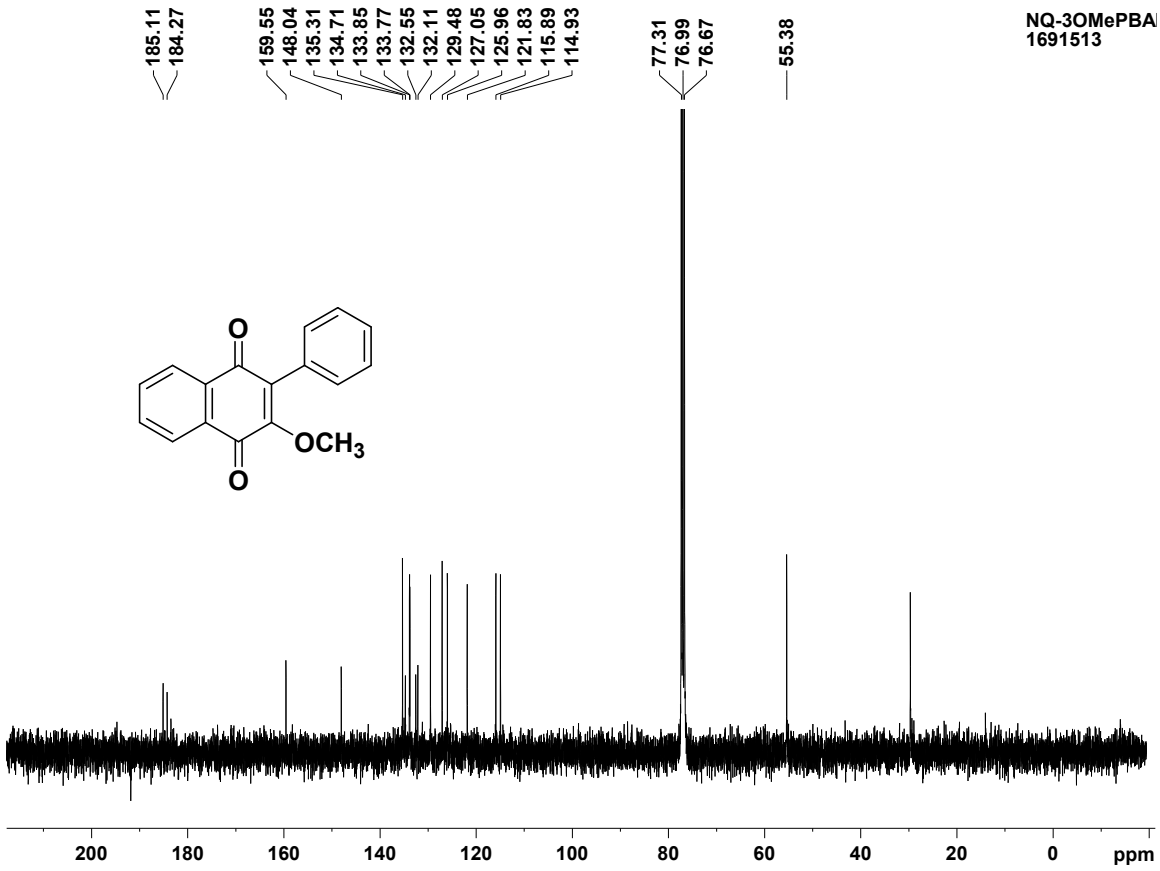
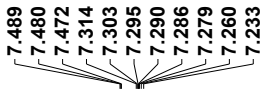
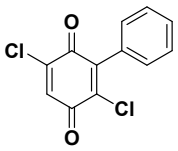
1116092015
188.61
188.13
187.53
186.80
151.45
145.76
145.44
143.63
141.41
133.28
133.23
129.87
129.32
124.96
77.36
77.05
76.73
34.66
31.25
15.89
15.79
14.09
O
H3C
CH3
O
3dq
200
180
160
140
120
100
80
60
40
20
0
ppm


8.185
8.174
8.116
8.108
7.774
7.767
7.400
7.380
7.361
7.260
7.158
7.140
7.114
7.075
7.033
7.014
3.861
NQ-3OMePBA
101692015
O
OMe
O
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.05
2.00
0.99
1.00
2.03
1.05
3.00

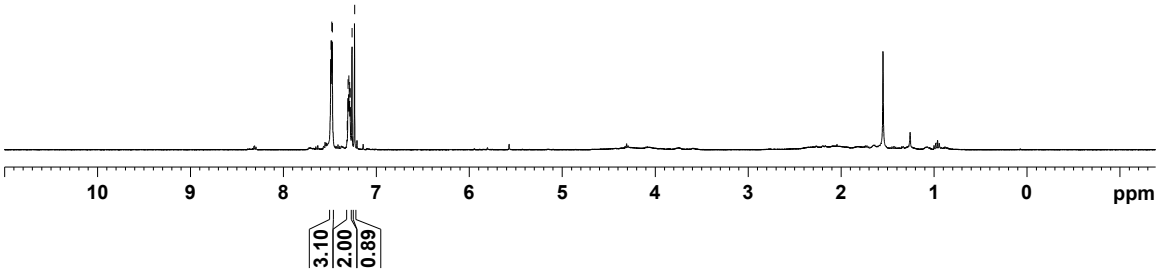

185.11
184.27
159.55
148.04
135.31
134.71
133.85
133.77
132.55
132.11
129.48
127.05
125.96
121.83
115.89
114.93
77.31
76.99
76.67
55.38
NQ-3OMePBA
1691513
O
OCH3
O
200
180
160
140
120
100
80
60
40
20
0
ppm

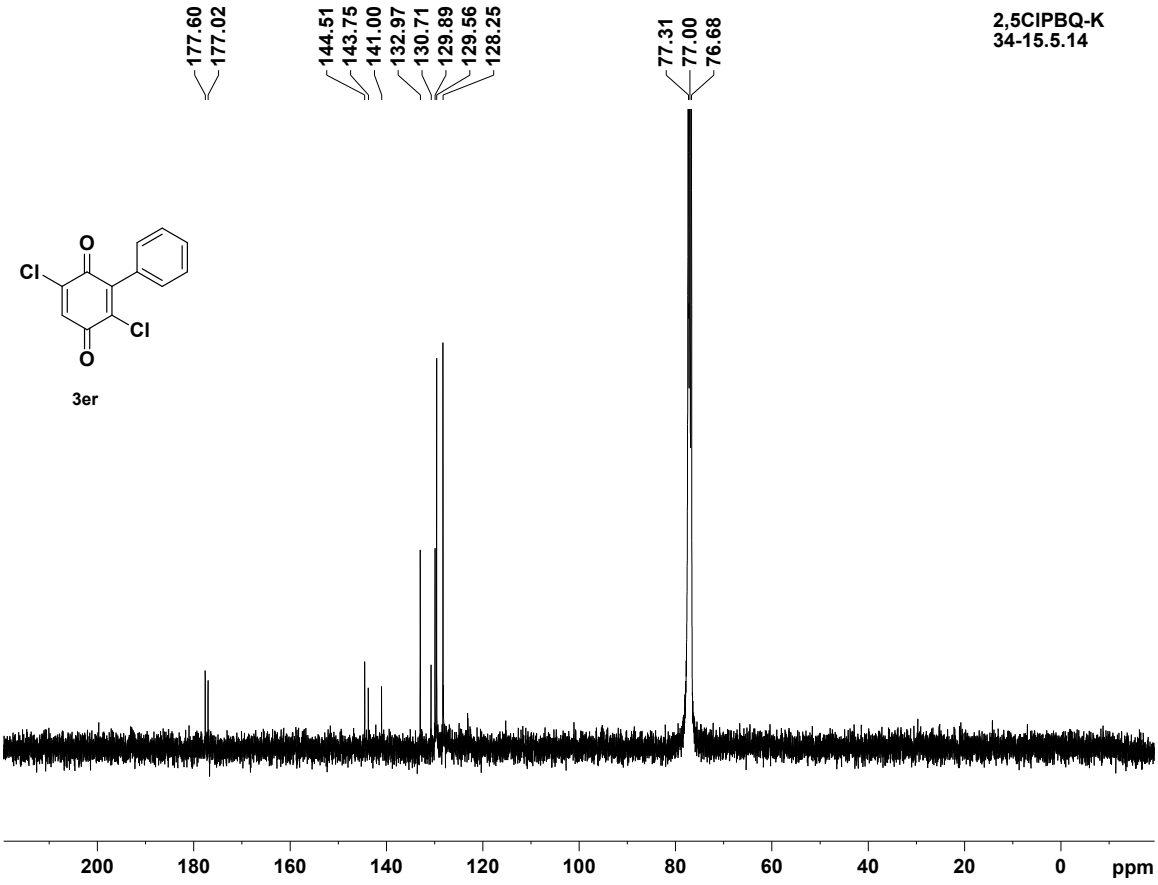


BQ2,5ClPBA-K
33-29.3.14



3er

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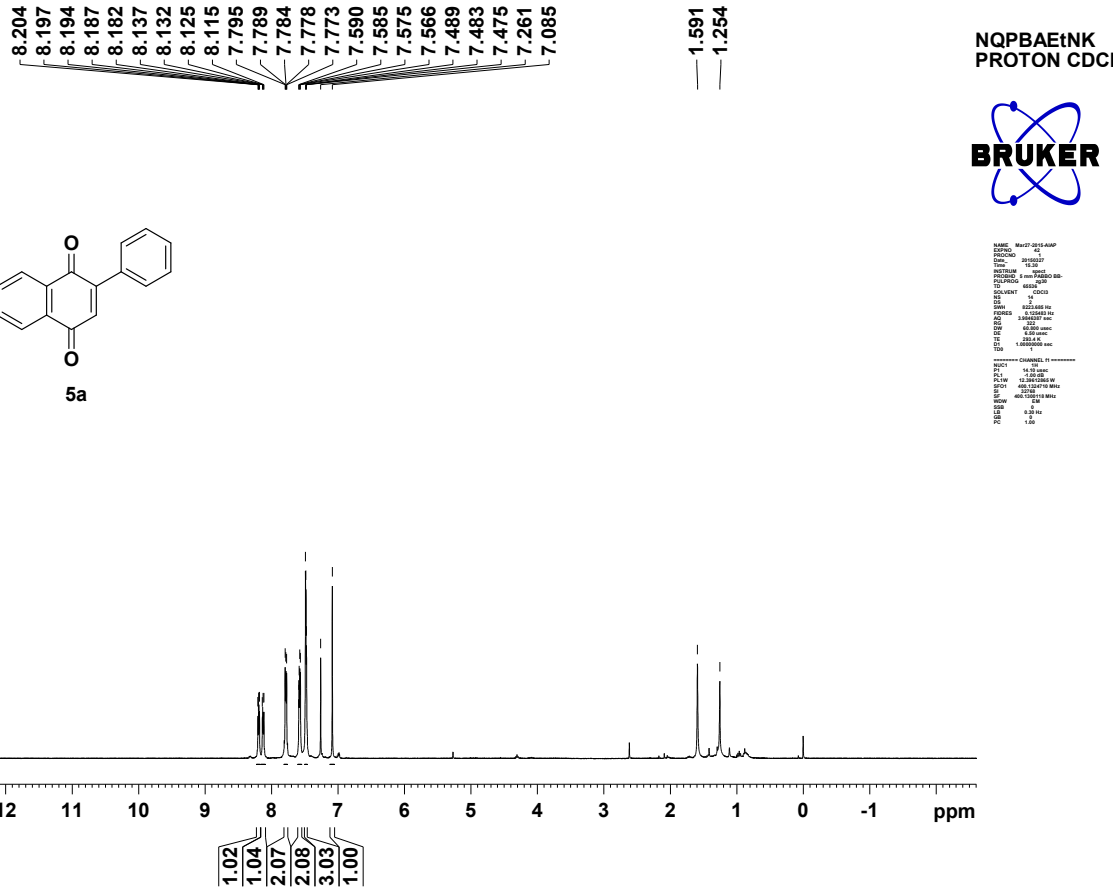
177.02
144.51
143.75
141.00
132.97
130.71
129.89
129.56
128.25
77.31
77.00
76.68
2,5ClPBQ-K
34-15.5.14
O
Cl
Cl
O
3er
200
180
160
140
120
100
80
60
40
20
0
ppm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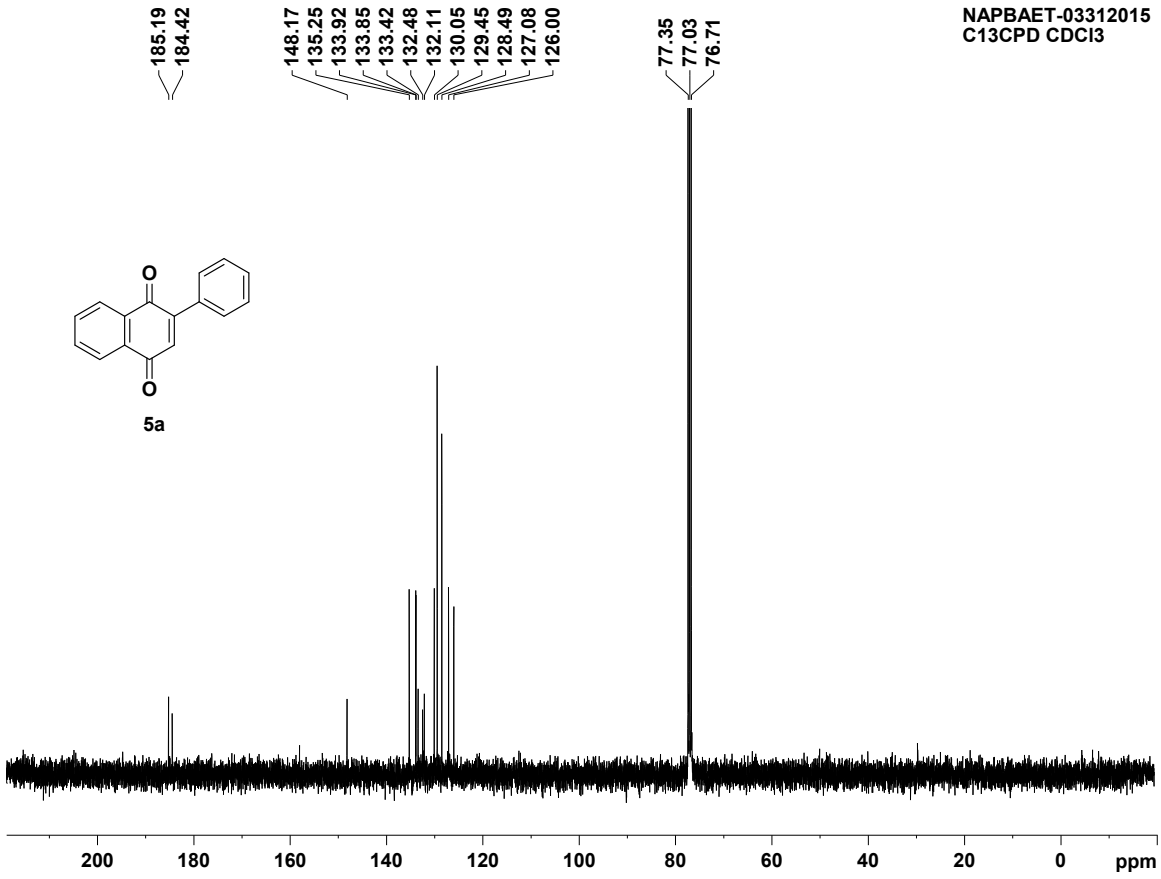
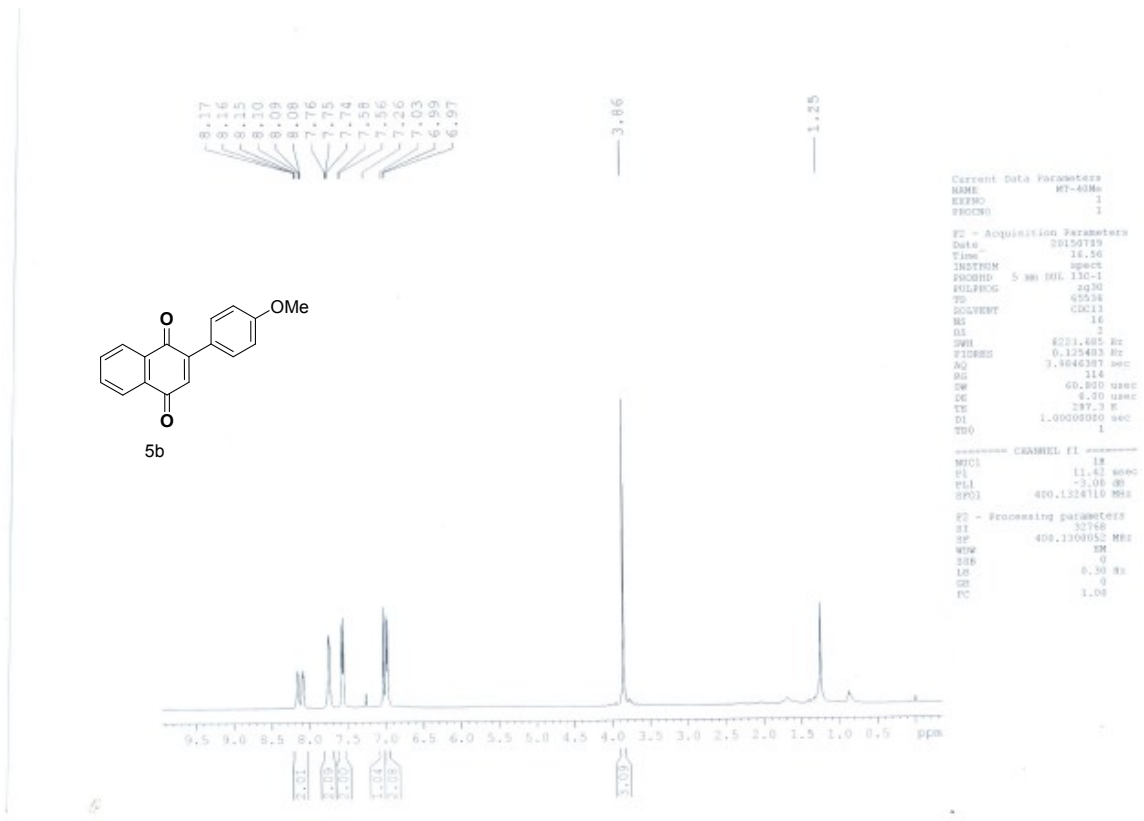
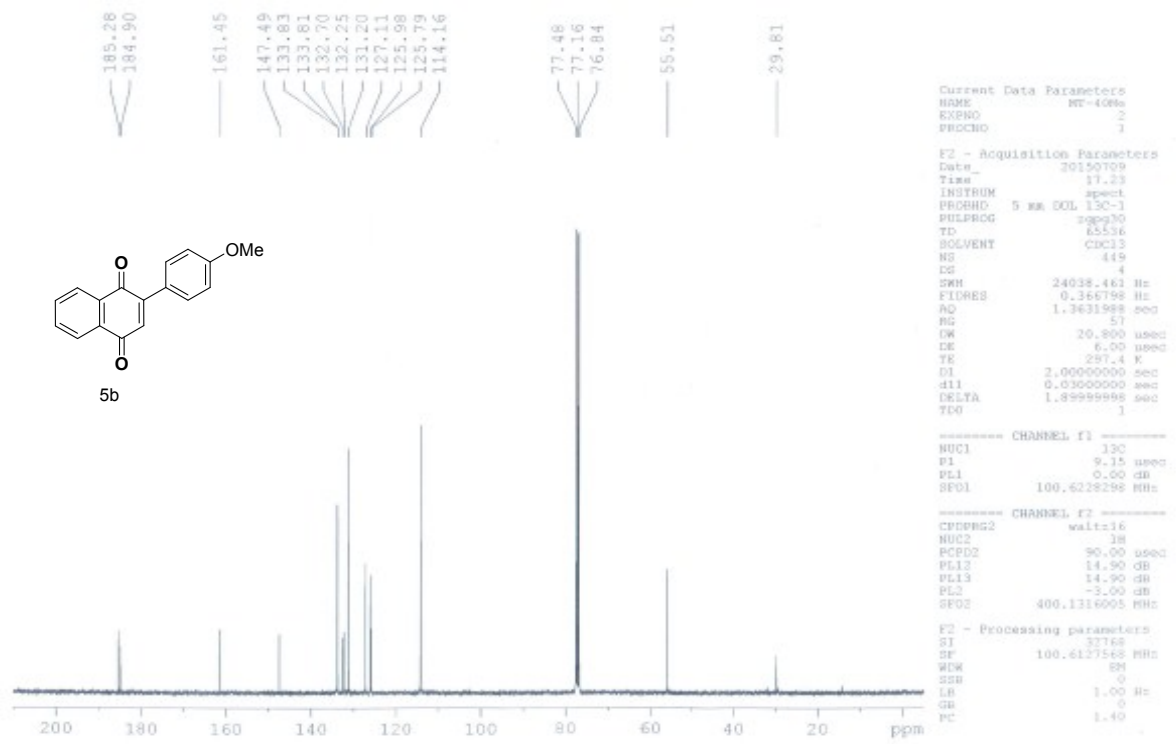
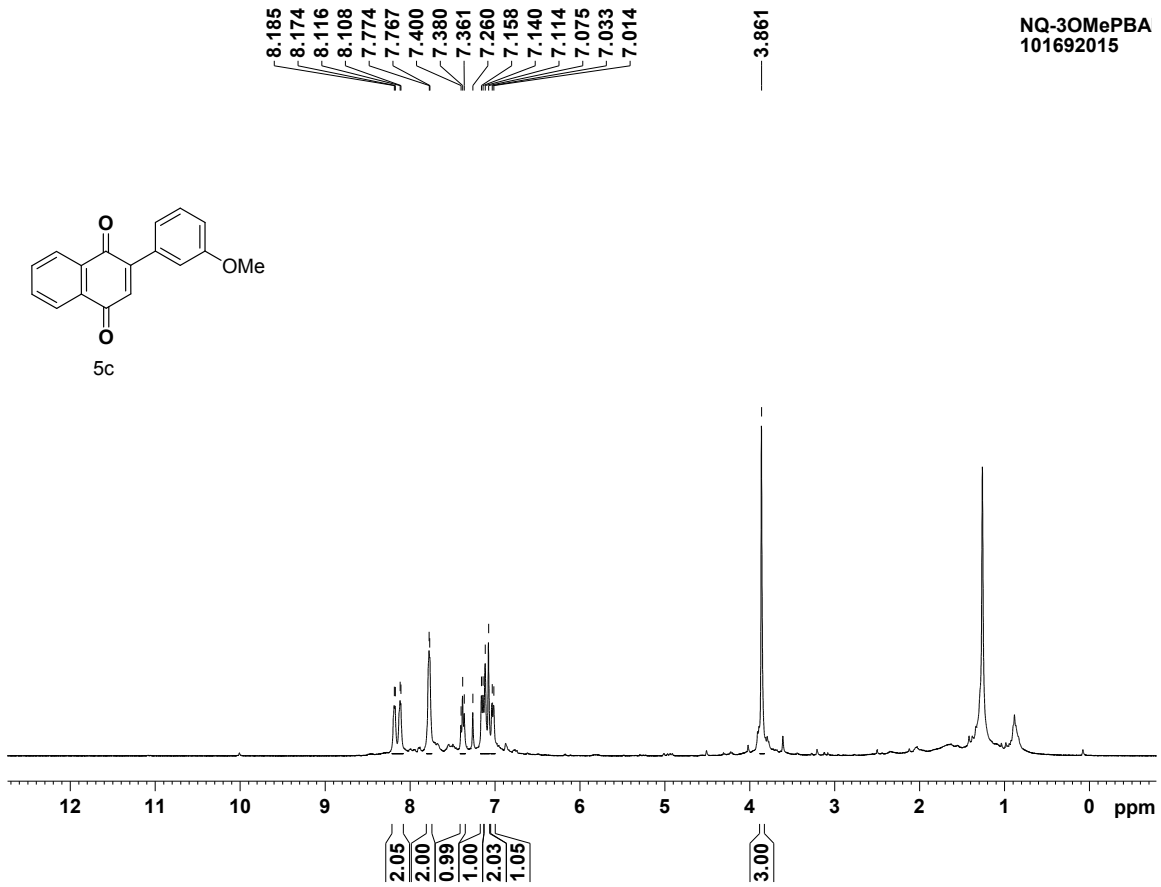
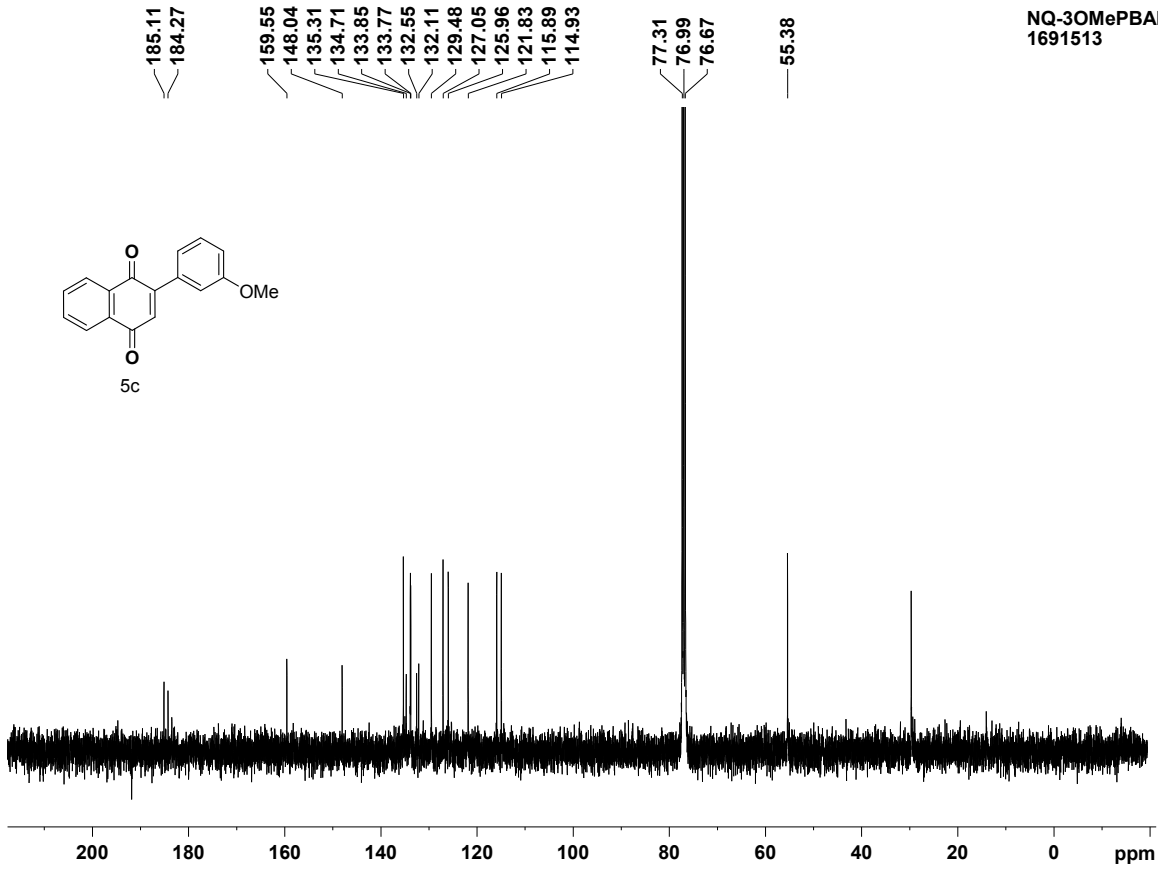
8.197
8.194
8.187
8.182
8.137
8.132
8.125
8.115
7.795
7.789
7.784
7.778
7.773
7.590
7.585
7.575
7.566
7.489
7.483
7.475
7.261
7.085
1.591
1.254
NQPBAEtNK
PROTON CDCl
BRUKER
O
O
5a
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.02
1.04
2.07
2.08
3.03
1.00

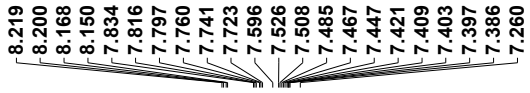

185.19
184.42
148.17
135.25
133.92
133.85
133.42
132.48
132.11
130.05
129.45
128.49
127.08
126.00
77.35
77.03
76.71
NAPBAET-03312015
C13CPD CDCl3
O
O
5a
200
180
160
140
120
100
80
60
40
20
0
ppm


8.17
8.16
8.15
8.10
8.09
8.08
7.76
7.75
7.74
7.58
7.56
7.26
7.03
6.99
6.97
3.86
1.25
OMe
O
O
5b
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.01
1.00
1.00
1.04
1.00
3.00
Current Data Parameters
NAME MT-40Me
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date 20150729
Time 16.56
INSTRM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125403 Hz
AQ 3.9846387 sec
RG 114
DW 60.800 usec
DE 6.50 usec
TE 297.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.42 usec
PL1 -3.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300052 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

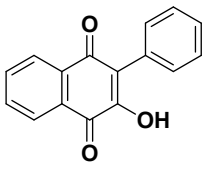

185.28
184.90
161.45
147.49
133.83
133.81
132.70
132.25
131.20
127.11
125.98
125.79
114.16
77.48
77.16
76.84
55.51
29.81
OMe
O
O
5b
200
180
160
140
120
100
80
60
40
20
ppm
Current Data Parameters
NAME MT-406a
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150709
Time 17.23
INSTRUM spect
PROBHD 5 mm DCH 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 449
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 57
DW 20.800 usec
DE 6.00 usec
TE 297.4 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.15 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL12 14.90 dB
PL13 14.90 dB
PL2 -3.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127568 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


8.185
8.174
8.116
8.108
7.774
7.767
7.400
7.380
7.361
7.260
7.158
7.140
7.114
7.075
7.033
7.014
3.861
NQ-3OMePBA
101692015
O
OMe
O
5c
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.05
2.00
0.99
1.00
2.03
1.05
3.00

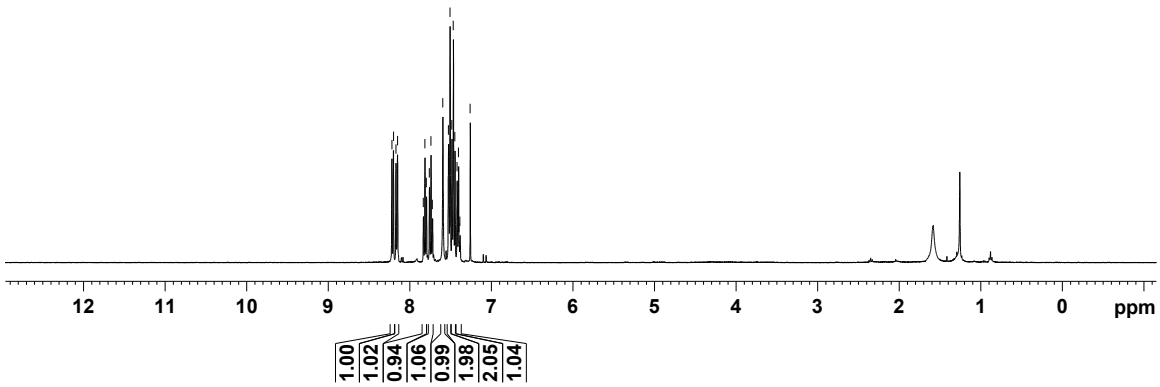

185.11
184.27
159.55
148.04
135.31
134.71
133.85
133.77
132.55
132.11
129.48
127.05
125.96
121.83
115.89
114.93
77.31
76.99
76.67
55.38
NQ-3OMePBA
1691513
O
O
OMe
5c
200
180
160
140
120
100
80
60
40
20
0
ppm

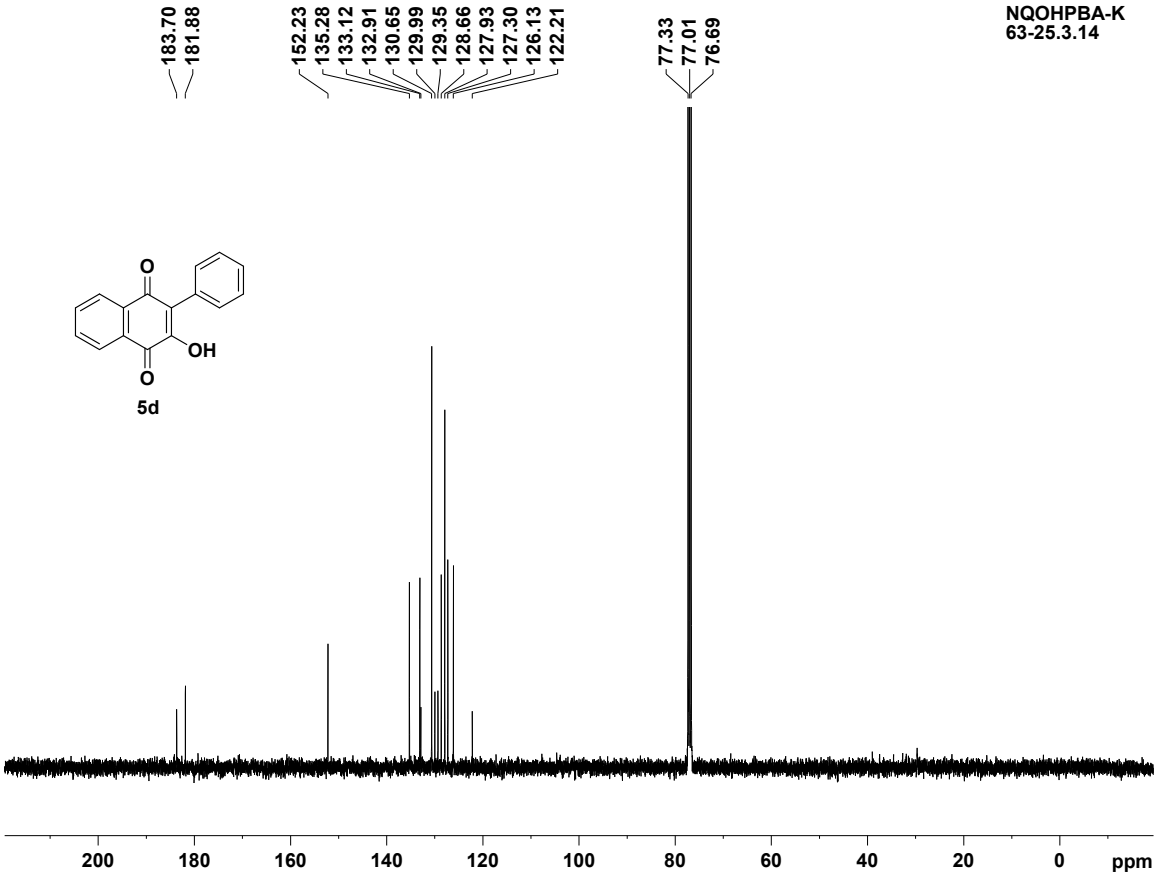


NQOHPBQ-K
16-25.3.14



5d

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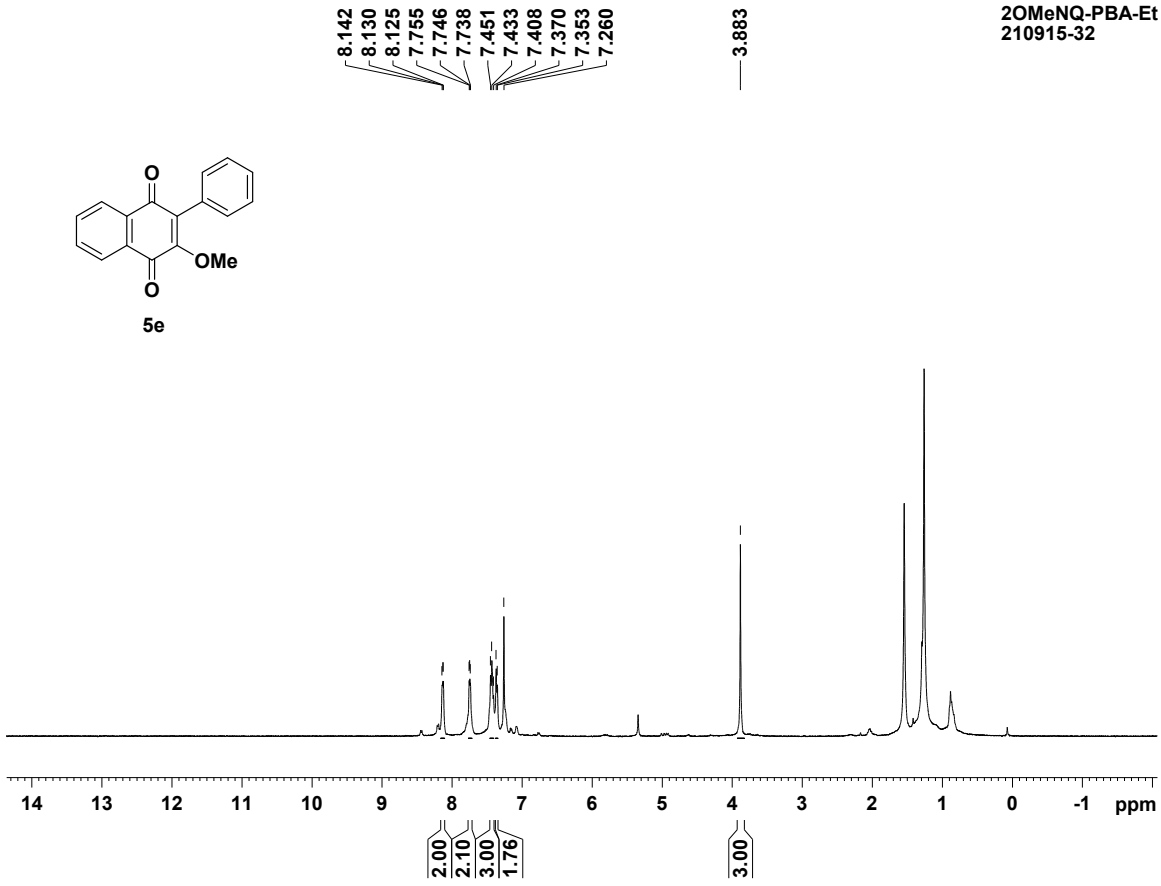
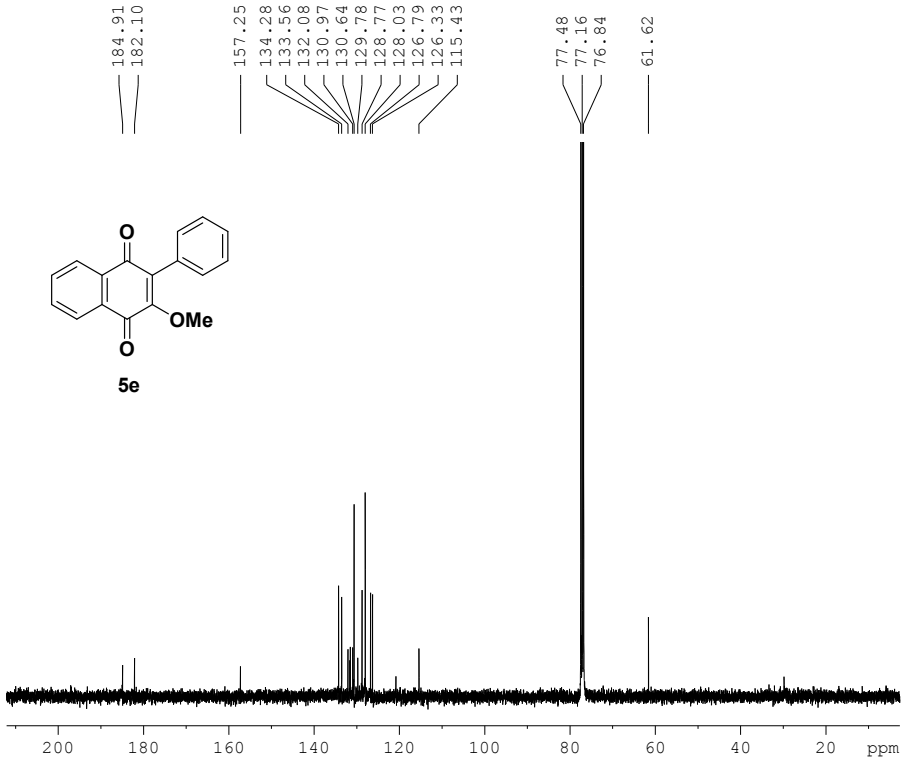
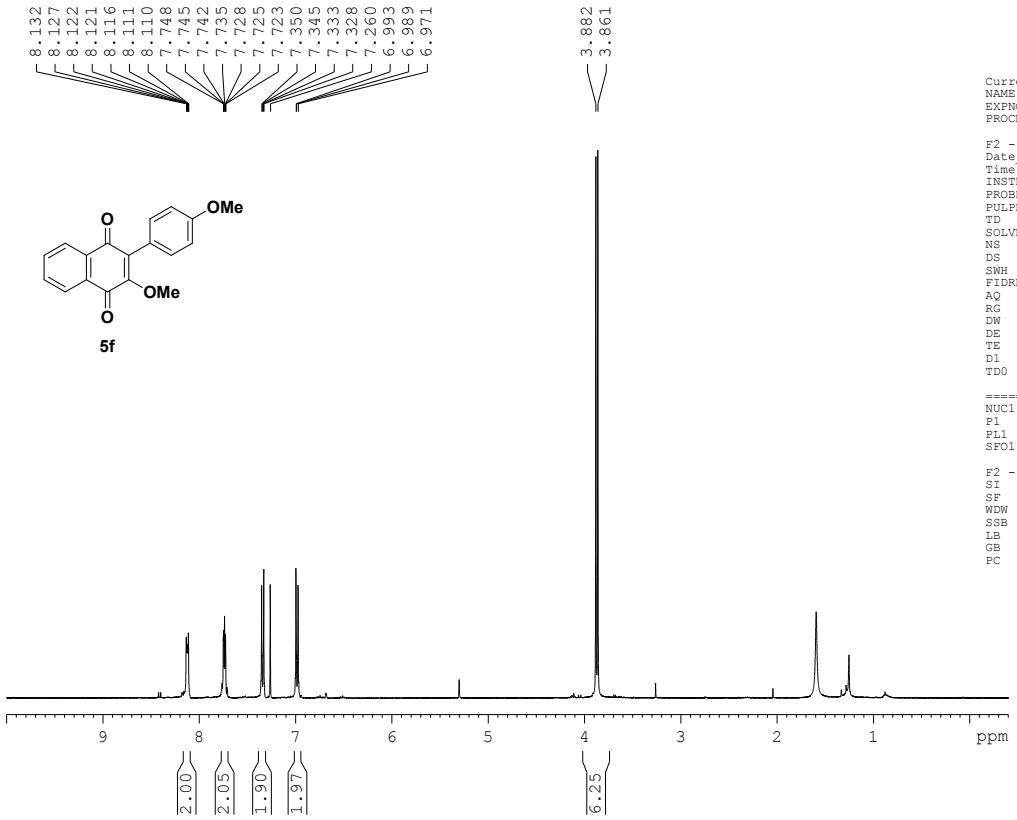
181.88
152.23
135.28
133.12
132.91
130.65
129.99
129.35
128.66
127.93
127.30
126.13
122.21
77.33
77.01
76.69
NQOHPBA-K
63-25.3.14
O
OH
O
5d
200
180
160
140
120
100
80
60
40
20
0
ppm

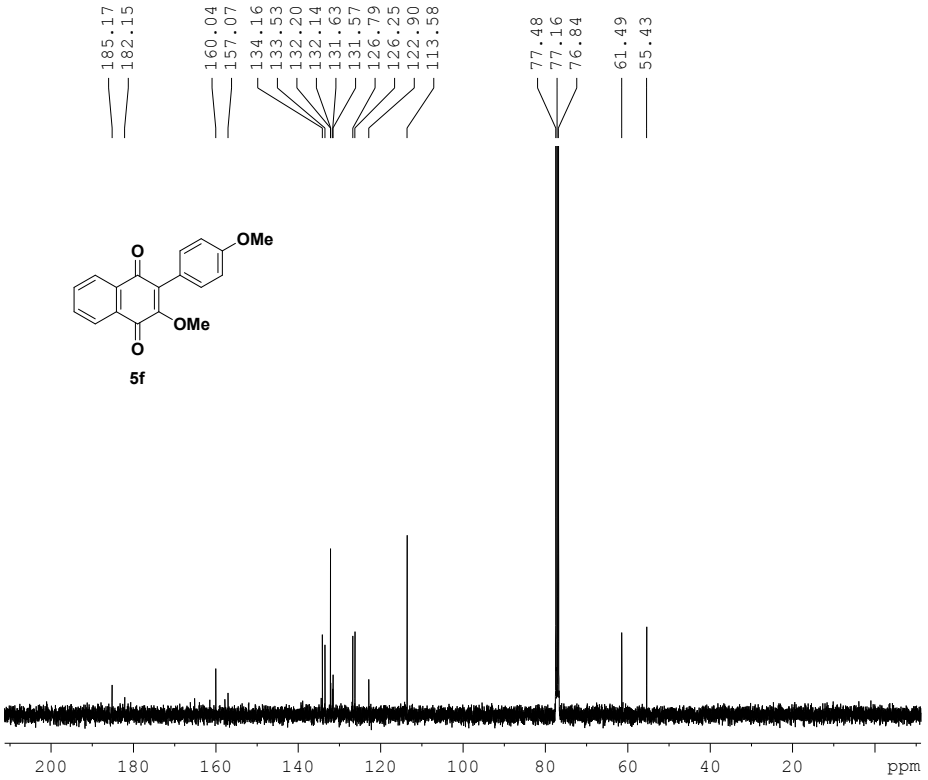

8.142
8.130
8.125
7.755
7.746
7.738
7.451
7.433
7.408
7.370
7.353
7.260
3.883
2OMeNQ-PBA-Et
210915-32
O
OMe
O
5e
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.00
2.10
3.00
1.76
3.00



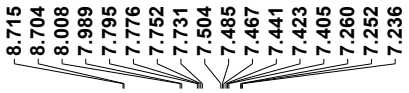

```
Current Data Parameters
NAME          M-NQ-2-OME
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151007
Time               10.34
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                   57
DW                20.800 usec
DE                 6.00 usec
TE                297.7 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.15 usec
PL1                0.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2              90.00 usec
PL12               14.90 dB
PL13               14.90 dB
PL2                -3.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127534 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



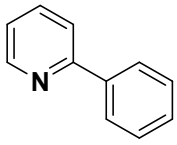

```
Current Data Parameters
NAME          M-NQ-20ME-4
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20151006
Time               16.09
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   228
DW                60.800 usec
DE                 6.00 usec
TE                296.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.42 usec
PL1                -3.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300051 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



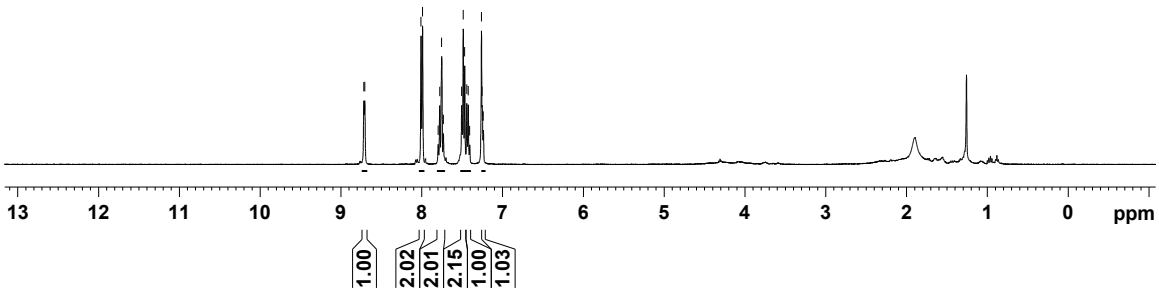

```
Current Data Parameters
NAME         M-NQ-20ME-4
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151006
Time               16.24
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                   64
DW                20.800 usec
DE                 6.00 usec
TE                296.5 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.15 usec
PL1                 0.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               14.90 dB
PL13               14.90 dB
PL2                -3.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127536 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

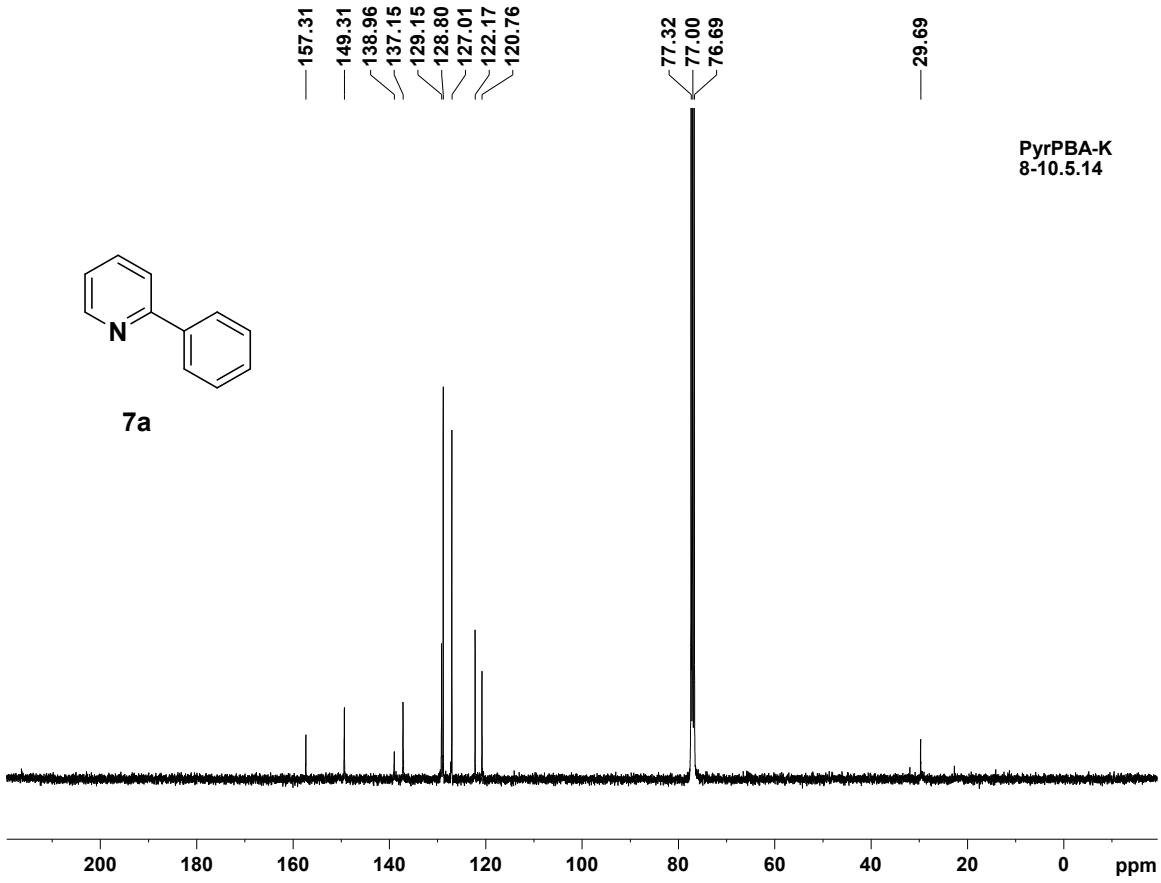


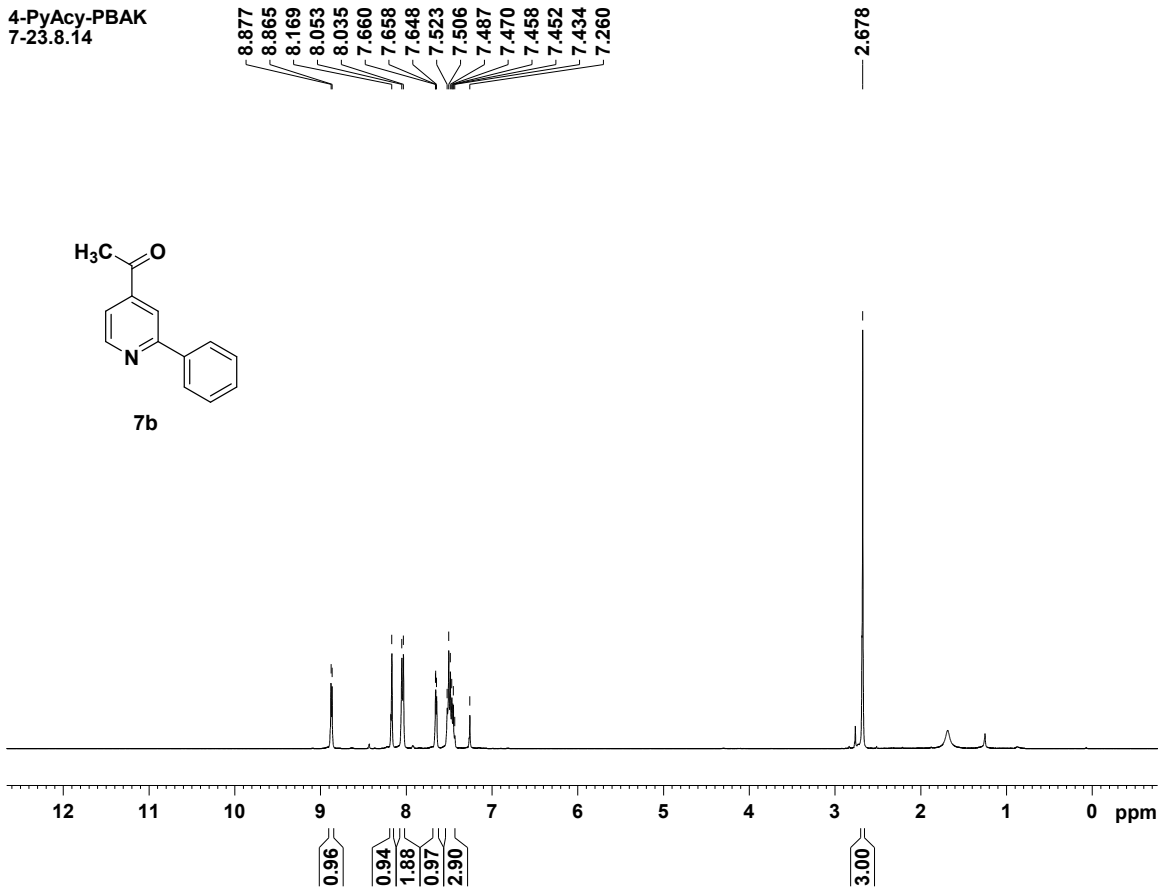
PyPBAK
5-10.5.14

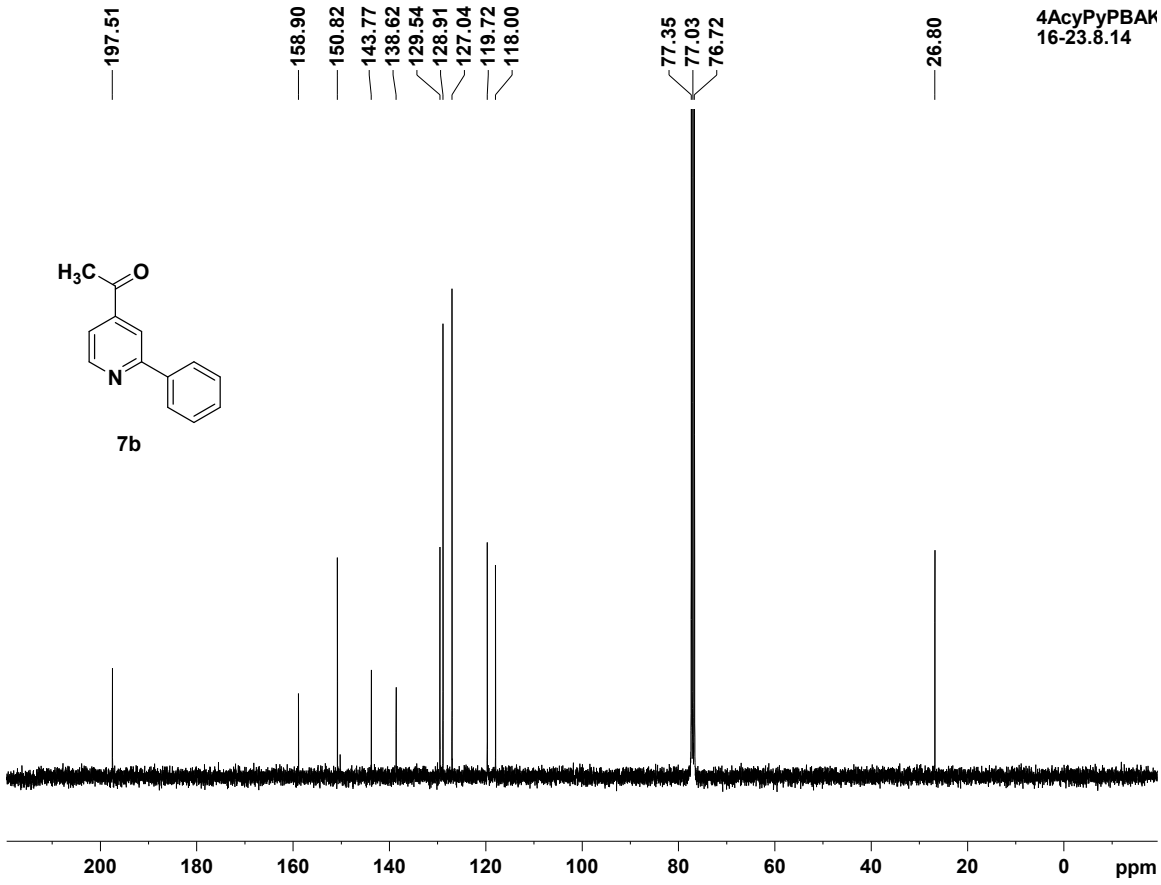


7a

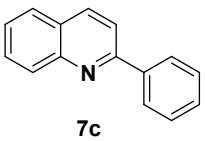



157.31
149.31
138.96
137.15
129.15
128.80
127.01
122.17
120.76
77.32
77.00
76.69
29.69
PyrPBA-K
8-10.5.14
N
7a
200
180
160
140
120
100
80
60
40
20
0
ppm

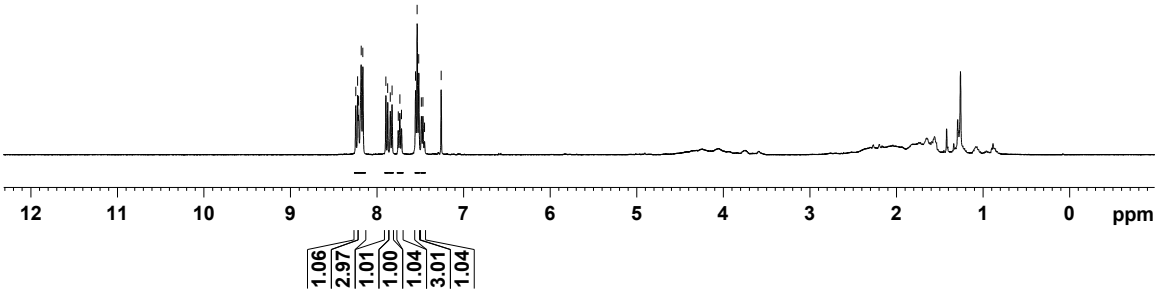

4-PyAcy-PBAK
7-23.8.14
8.877
8.865
8.169
8.053
8.035
7.660
7.658
7.648
7.523
7.506
7.487
7.470
7.458
7.452
7.434
7.260
2.678
H3C
O
N
7b
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.96
0.94
1.88
0.97
2.90
3.00

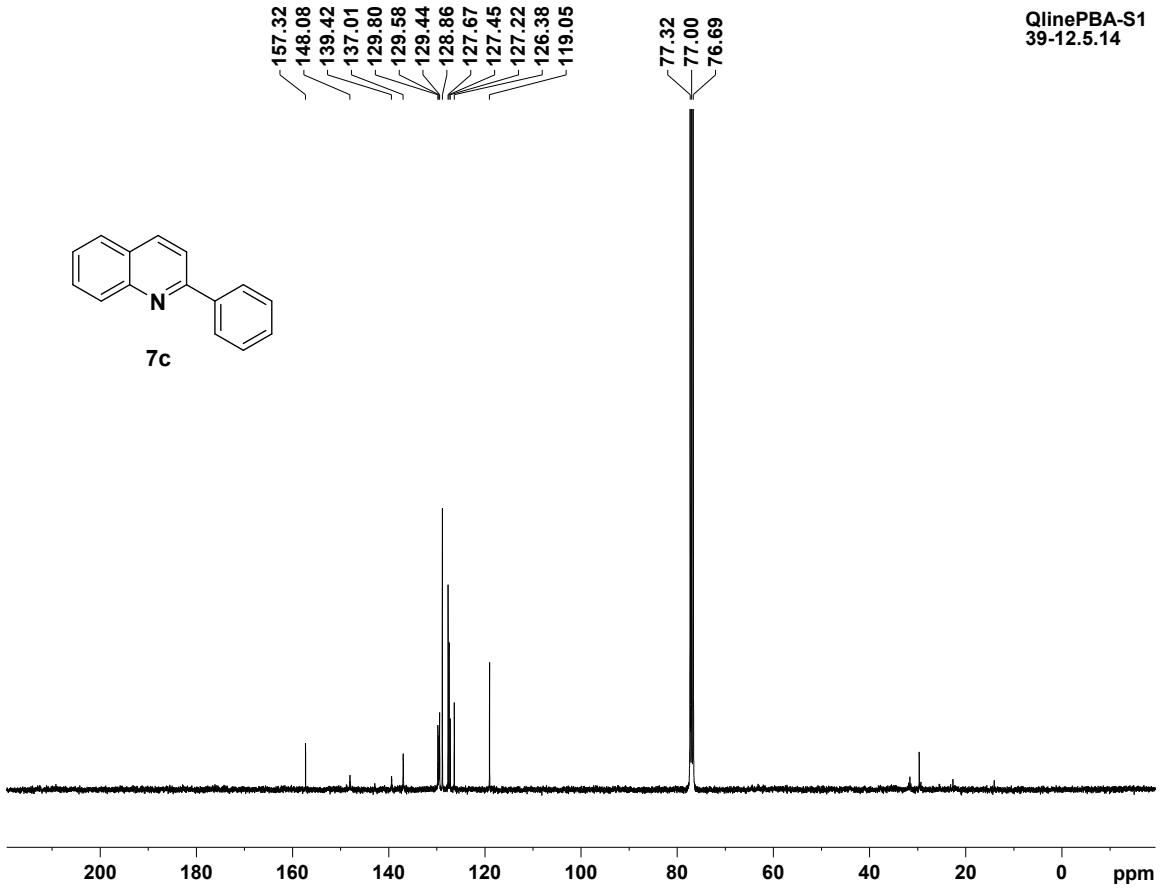

197.51
158.90
150.82
143.77
138.62
129.54
128.91
127.04
119.72
118.00
77.35
77.03
76.72
26.80
4AcyPyPBAK
16-23.8.14
H3C
O
N
7b
200
180
160
140
120
100
80
60
40
20
0
ppm

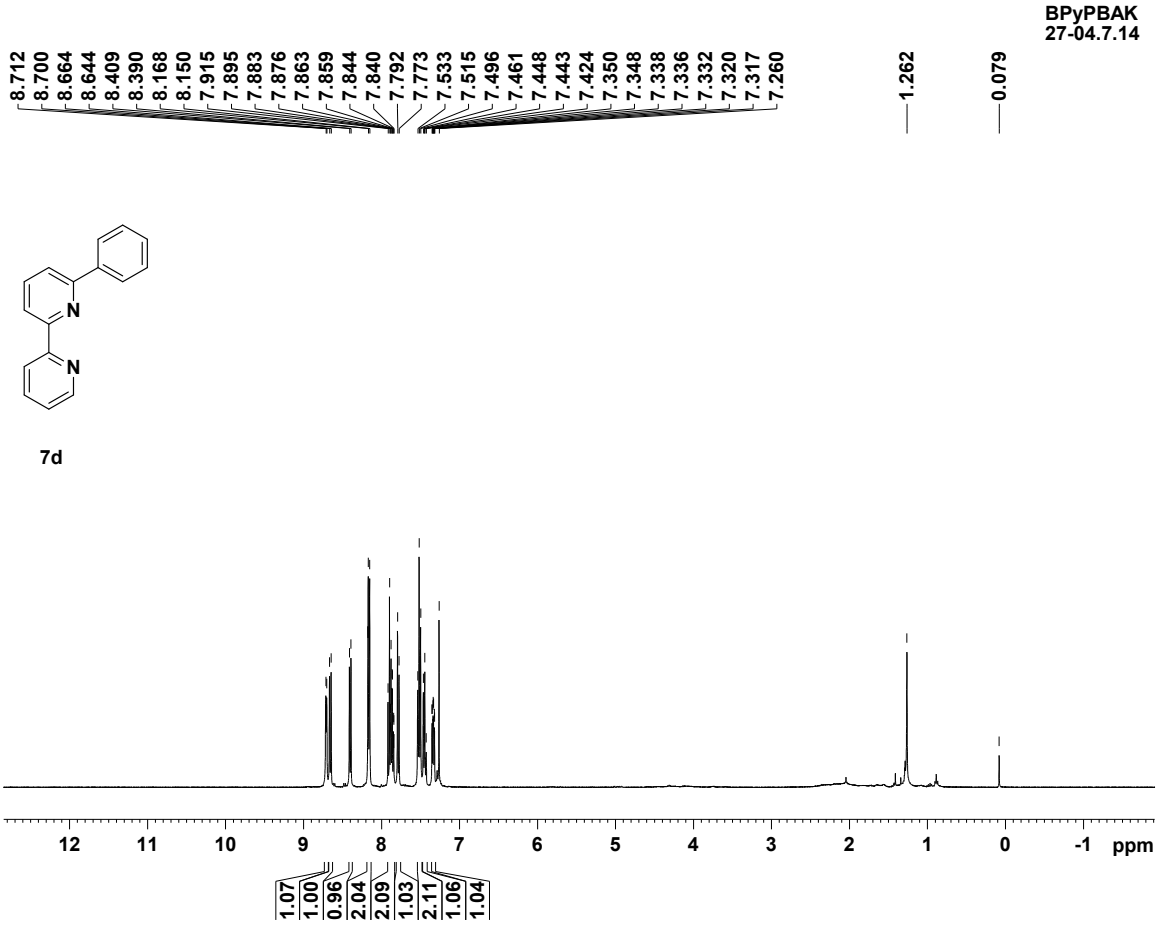
QlinePBAK-S1
33-12.5.14



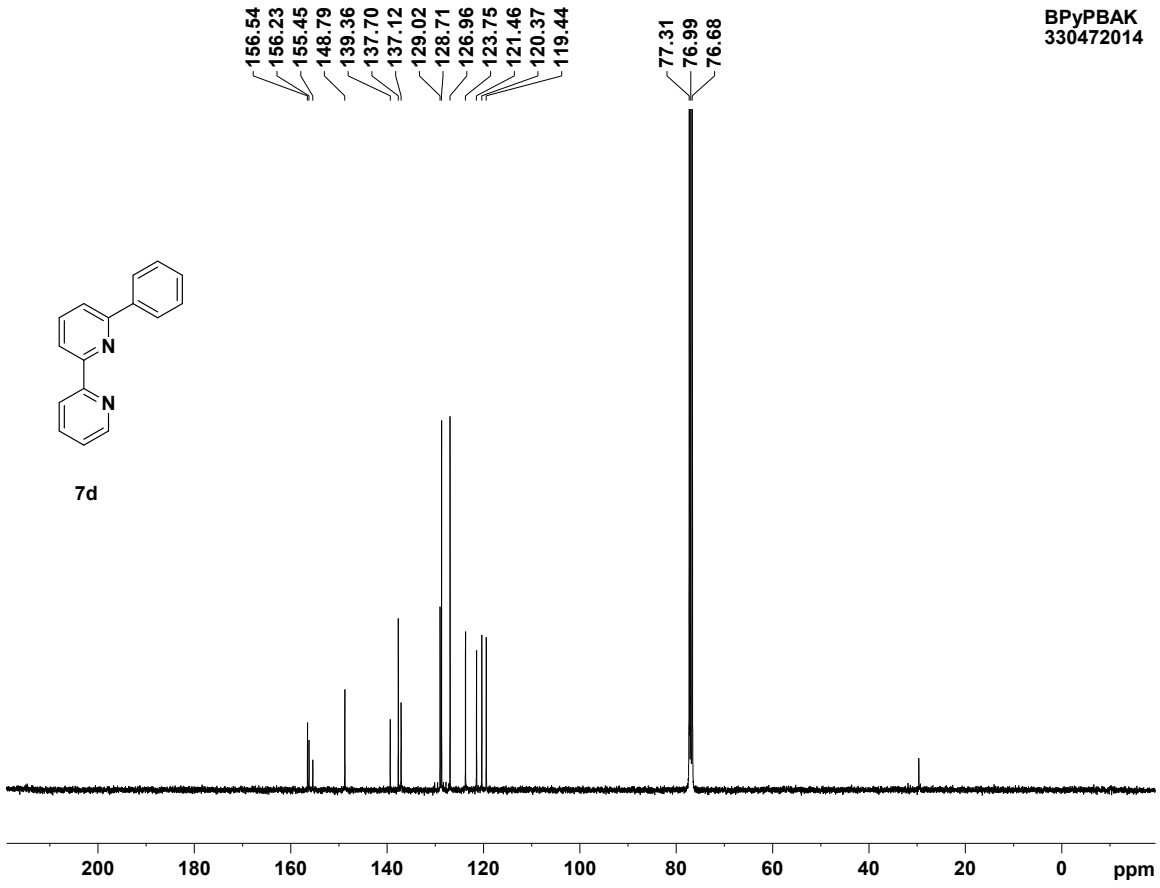
7c




157.32
148.08
139.42
137.01
129.80
129.58
129.44
128.86
127.67
127.45
127.22
126.38
119.05
77.32
77.00
76.69
QlinePBA-S1
39-12.5.14
N
7c
200
180
160
140
120
100
80
60
40
20
0
ppm


BPyPBAK
27-04.7.14
8.712
8.700
8.664
8.644
8.409
8.390
8.168
8.150
7.915
7.895
7.883
7.876
7.863
7.859
7.844
7.840
7.792
7.773
7.533
7.515
7.496
7.461
7.448
7.443
7.424
7.350
7.348
7.338
7.336
7.332
7.320
7.317
7.260
1.262
0.079
N
N
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.07
1.00
0.96
2.04
2.09
1.03
2.11
1.06
1.04

7d



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