Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Supplementary Information

Long-Range Intramolecular Photoredox Reaction via Coupled Charge and Proton Transfer of Triplet Excited Anthraquinones Mediated by Water

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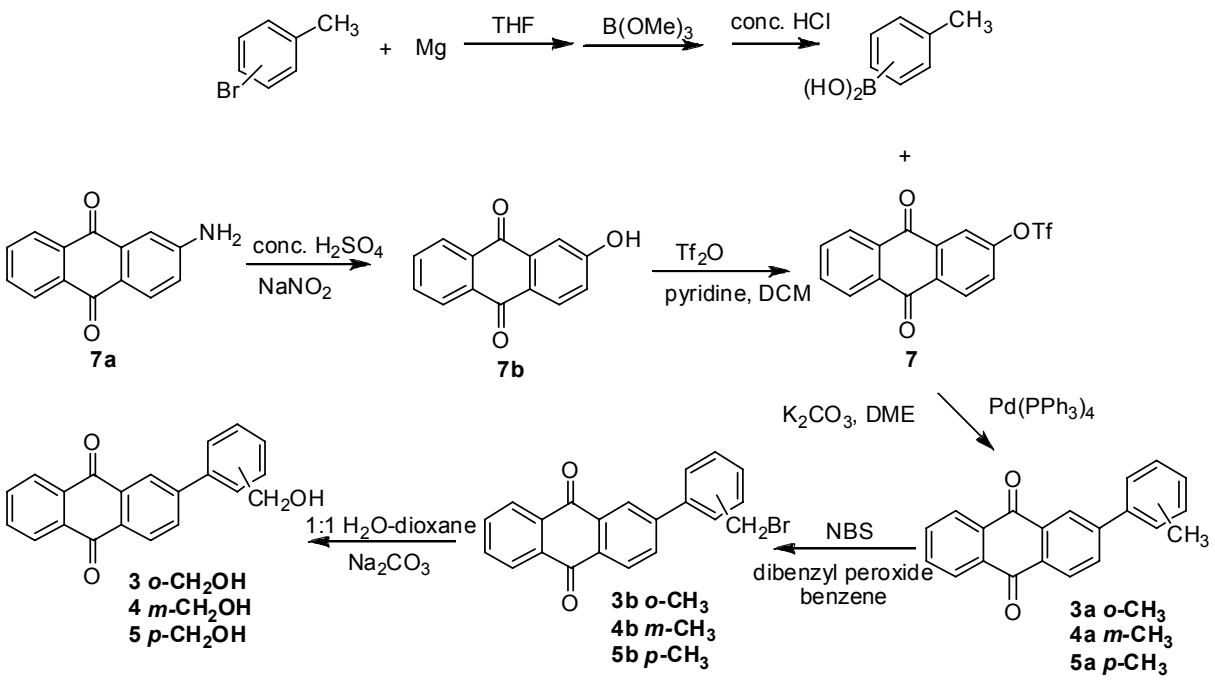
Preparation



Preparation of precursors methylphenyl boronic acid and 7

Preparation of methylphenyl boronic acid

Bromomethyl benzene (ortho, meta and para) (0.3, 1.8mmol) in 20 mL of THF was added dropwise into THF solution with Mg under N_2 at room temperature and the mixture was stirred for 2 hours. After the reaction, the Grignard solution under N_2 was transferred into a solution of $B(OMe)_3$ at -30^oC in 0.5 hour. After the addition, the solution was warmed up and stirred for overnight at room temperature to give a white paste. The solution was washed with conc. HCl to give white precipitates. The precipitates were recrystallized by water to give methyl phenyl boronic acid (white needle crystals, 70-80% yield). ^1H NMR ($CDCl_3$, 300 MHz) (*o*-methylphenyl)boronic acid: δ 8.20 (d, H, J = 8.1 Hz), 7.42-7.30 (m, H),7.35-7.25 (m, 2H), 2.81

(s, 3H); (*m*-methylphenyl)boronic acid: δ 8.06-8.01 (m, 2H), 7.42-7.38 (m, 2H), 2.47 (s, 3H); (*p*-methylphenyl)boronic acid: δ 8.11 (d, 2H, J = 8.1 Hz), 7.30 (d, 2H, J = 8.1 Hz), 2.43 (s, 3H).

Preparation of 7

$NaNO_2$ (0.56 g, 8.1 mmol) was added in three portions into a solution of **7a** (1.5g, 6.8 mmol) in conc. H_2SO_4 (15 mL) cooled in an ice bath. After the addition, the mixture was stirred in the ice bath for 10 min and warmed up to room temperature and stirred for 4 hours. The mixture was poured onto 100 mL of ice and transferred to 500 mL flask and refluxed for 45 min. After cooling, the brown solid was filtered, washed with water and dissolved in 10 mL of 1 M NaOH. The dark red solution was washed 3 × 25mL dichloromethane. The combined aqueous layers was acidified with conc. HCl and extracted with 5 × 25 mL EtOAc, dried over anhydrous $MgSO_4$. A yellow brown powder **7b** (1.1 g, 70% yield) was obtained after removal of solvent. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.30-8.24 (m, 2H), 8.21 (d, 1H, J = 8.5 Hz), 7.94-7.88 (m, 2 H), 7.67 (d, 1H, J = 2.6 Hz), 7.34 (dd, 1H, J = 2.6 Hz, 8.5 Hz).

A solution of **7b** (0.90, 4.0 mmol) in 50 mL of dichloromethane in a cold water bath was flushed with N_2. Pyridine (1.95 mL, 24.1 mmol) was added dropwise into the above solution, then Tf_2O (2.0 mL, 12 mmol) was added. After the addition, the mixture was warmed up to room temperature and stirred for overnight. After the reaction, the solvent was removed and the residue was washed with 2 × 25 mL water. The combined aqueous solutions were extracted with 2 × 25 mL EtOAc. The collected organic layers were dried over anhydrous $MgSO_4$. After removal of solvent, a brown powder was purified by column chromatography with silica gel using CH_2Cl_2 as an eluent, to give **c** (white powder, 1.4 g) in 98% yield. ^{1}H NMR ($CDCl_3$, 300

MHz) δ 8.44 (d, 1H, J = 8.8 Hz), 8.36-8.29 (m, 2H), 8.18 (d, 1H, J = 2.2 Hz), 7.87-7.80 (m, 2H), 7.67 (dd, 1H, J = 8.8, 2.2 Hz).

Preparation of 2-(*o*-hydroxymethylphenyl)-9,10-anthraquinone (3)

A mixture of (*o*-methylphenyl)boronic acid (0.50 g, 2.4 mmol), **7** (0.27 g, 2 mmol), anhydrous K_2CO_3 (1.93g, 14 mmol) and $Pd(PPh_3)_4$ (100 mg) was added into a 100 mL flask contained 60 mL of DME saturated with N_2. The mixture was refluxed for 3 days under N_2. After the reaction, solvent was removed and the residue was dissolved in 100 DCM and washed with 2 × 25 mL of 1 M NaOH. The solution was dried over anhydrous $MgSO_4$. After removal of solvent, a brown powder was purified by column chromatography with silica gel using CH_2Cl_2 as an eluent, to give 2-(*o*-methylphenyl)-9,10-anthraquinone (**3a**) (yellow powder, 0.41 g, mp. 160-161^oC) in 70% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ 8.39-8.24 (m, 4H), 7.84-7.71 (m, 3H), 7.34-7.25 (m, 4H), 2.31 (s, 3H); ^{13}C ($CDCl_3$, 75 MHz) 183.44, 183.20, 148.41, 140.11, 135.38, 135.12, 134.38, 134.31, 133.84 (2C), 133.55, 132.19, 130.96, 129.73, 128.64, 128.08, 127.52, 127.46, 127.44, 126.38, 20.64; IR (neat from CH_2Cl_2 solution, NaCl plates) v 3054, 1673, 1588, 1327, 1289, 930, 707 cm^{-1}.

A mixture of **3a** (0.30 g, 1.0 mmol) and NBS (0.21 g, 1.2 mmol) in benzene (30 mL) was refluxed for overnight under N_2. After the reaction, the solution was washed with 2 × 25 mL water and the collected organic layer was dried over anhydrous $MgSO_4$. After the removal of solvent, a brown residue (**3b**) was obtained. The brown residue and Na_2CO_3 (0.42 g, 5.0 mmol) in 1:1 H_2O-dioxane were refluxed for overnight under N_2. After the reaction, the mixture was acidized by 10 mL of 1 M HCl and extracted with 2 × 25 mL DCM. The collected extracts were

dried over anhydrous $MgSO_4$ and evaporated to give brown powders. The crude product was purified by column chromatography with silica gel using 20% EtOAc-CH_2Cl_2 as an eluent to give yellow powder. The yellow powder was further purified with recrystallization from ethanol to give 2-(*o*-hydroxymethylphenyl)-9,10-anthraquinone (**3**) (yellow needle crystals, 0.22 g, mp.184-185^oC) in 70% yield. ^1H NMR ($CDCl_3$, 500 MHz) δ 8.36 (d, 1H, *J* = 7.7 Hz), 8.34-8.30 (m, 3H), 7.85 (dd, 1H, *J* = 7.7, 1.8 Hz), 7.83-7.78 (m, 2H), 7.60 (d, 1H, *J* = 7.0 Hz), 7.46 (td, 1H, *J* = 7.5, 1.5 Hz), 7.41 (td, 1H, *J* = 7.5, 1.5 Hz), 7.34 (dd, 1H, *J* = 7.5, 1.5 Hz), 4.63 (s, 2H), 1.63 (s, broad OH peak); ^{13}C NMR ($CDCl_3$, 125 MHz) 183.39, 183.16, 147.16, 139.74, 138.08, 135.12, 134.45, 134.38, 133.84 (2C), 133.63, 132.53, 130.11, 129.22, 129.10, 128.35, 128.05, 127.63, 127.52, 127.50, 63.24; IR (neat from CH_2Cl_2 solution, NaCl plates) *v* 3384, 3060, 2884, 1673, 1588, 1330, 1294, 707 cm^{-1}; MS (EI) *m/z* 314 (M^+, 100), 297 (28), 283 (19); HRMS, calculated for $C_{21}H_{14}O_3$ 314.09429; observed 314.09436.

Preparation of 2-(*m*-hydroxymethylphenyl)-9,10-anthraquinone (4)

By following the same synthetic procedure of **3**, 2-(*m*-methylphenyl)-9,10-anthraquinone (**4a**) (yellow powder, 0.30g, m.p. 137-138^oC) in 70% yield was obtained. ^1H NMR ($CDCl_3$, 300 MHz) δ 8.47 (d, 1H, *J* = 1.5 Hz), 8.34-8.25 (m, 3H), 7.97 (dd, 1H, *J* = 8.1, 1.5 Hz), 7.81-7.73 (m, 2H), 7.49 (d, 2H, *J* = 8.1 Hz), 7.36 (t, 1H, *J* = 8.1 Hz), 7.22 (d, 1H, *J* = 8.1 Hz), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) 183.43, 183.06, 147.15, 139.05 (2C), 134.35, 134.22, 134.02, 133.84, 133.80, 132.54, 132.25, 129.84, 129.24, 128.25, 128.18, 127.47, 127.40, 125.72, 124.62, 21.74; IR (neat from CH_2Cl_2 solution, NaCl plates) *v* 3060, 3027, 2912, 1670, 1588, 1330, 1278, 932, 770, 707 cm^{-1}.

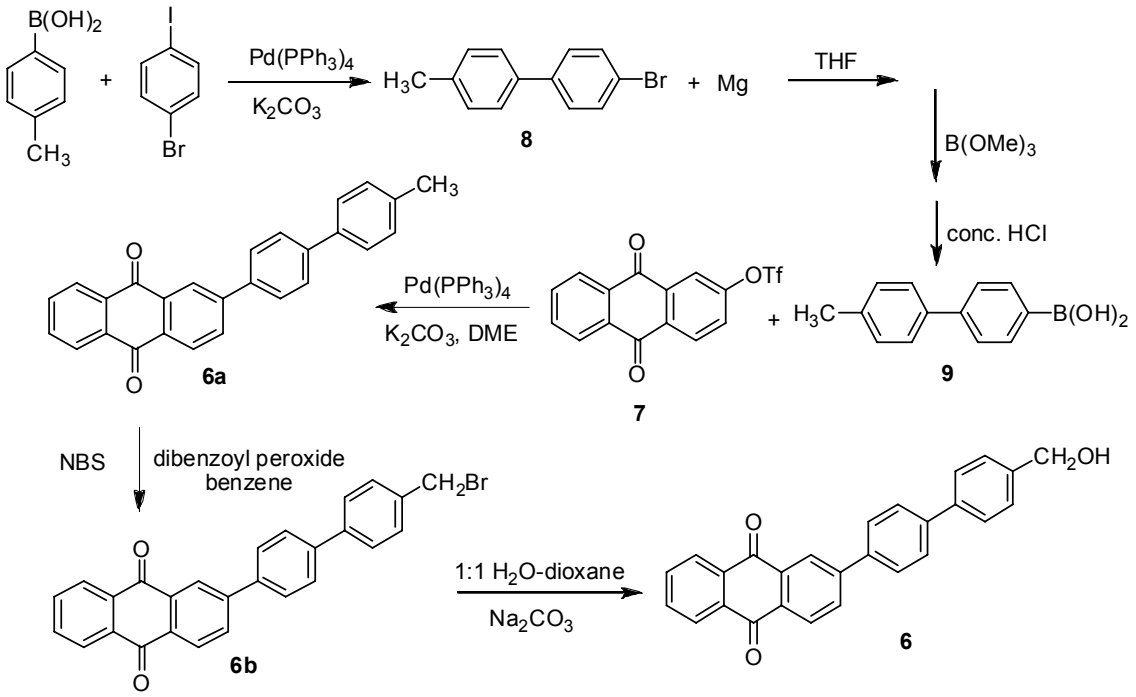
2-(*m*-Hydroxymethylphenyl)-9,10-anthraquinone (**4**) (yellow plate, 0.20 g, mp.158-161^{o}C) in 80% yield was obtained via bromination of **4a** followed with hydrolysis of **4b**. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.53 (d, 1H, *J* = 2.0 Hz), 8.37 (d, 1H, *J* = 8.1 Hz), 8.34-8.31 (m, 2H), 8.01 (dd, 1H, *J* = 8.1, 2.0 Hz), 7.83-7.79 (m, 2H), 7.73 (t, 1H, *J* = 1.8 Hz), 7.65 (dt, 1H, *J* = 7.7, 1.8 Hz), 7.50 (t, 1H, *J* = 7.7 Hz), 7.44 (d, 1H, *J* = 7.7 Hz), 4.81(s, 1H), 1.59 (s, broad OH peak); ^{13}C NMR ($CDCl_3$, 125 MHz) 183.46, 183.12, 146.90, 142.12, 139.53, 134.44, 134.31, 134.16, 133.90, 133.86, 132.64, 132.49, 129.62, 128.31, 127.59, 127.54, 127.47, 126.83, 126.07, 125.84, 65.37; IR (neat from CH_2Cl_2 solution, NaCl plates) *v* 3307, 2912, 2862, 1670, 1588, 1333, 1281, 707 cm^{-1}; MS (EI) *m/z* 314 (M^+, 100), 285 (67), 283 (18), 208 (11); HRMS, calculated for $C_{21}H_{14}O_3$ 314.09429; observed 314.09421.

Preparation of 2-(*p*-hydroxymethylphenyl)anthraquinone (5)

By following the same synthetic procedure of **3**, 2-(*p*-methylphenyl)-9,10-anthraquinone (**5a**) (yellow powder, 0.50g, m.p. 166-167^{o}C) in 75% yield was obtained. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.47 (d, 1H, *J* = 1.5 Hz), 8.34-8.25 (m, 3H), 7.97 (dd, 1H, *J* = 8.1, 1.5 Hz), 7.81-7.73 (m, 2H), 7.59 (d, 2H, *J* = 8.1 Hz), 7.28 (d, 1H, *J* = 8.1 Hz), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) 183.47, 183.06, 146.95, 139.21, 136.18, 134.34, 134.20, 133.85, 133.82, 132.26, 132.08, 130.07 (2C), 128.22, 127.46, 127.39, 127.35 (2C), 125.42, 21.45; IR (neat from CH_2Cl_2 solution, NaCl plates) *v* 3021, 2917, 1673, 1588, 1330, 1275, 812, 707 cm^{-1}.

2-(*p*-hydroxymethylphenyl)-9,10-anthraquinone (**5**) (yellow needle, 0.30 g, mp.199-201^{o}C) in 70% yield was obtained via bromination of **5a** followed with hydrolysis of **5b**. ^{1}H NMR (300MHz, $CDCl_3$) δ 8.54 (d, 1H, *J* = 2.0 Hz), 8.37 (d, 1H, *J* = 8.1 Hz), 8.35-8.31 (m, 2H), 8.01 (dd, 1H, *J* = 8.1, 2.0 Hz), 7.83-7.79 (m, 2H), 7.73 (d, 2H, *J* = 8.1 Hz), 7.51 (d, 2H, *J* = 8.1 Hz),

4.78 (s, 1H), 1.72 (s, broad OH peak); ^{13}C NMR ($CDCl_3$, 125 MHz) 183.48, 183.12, 146.74, 141.90, 138.52, 134.44, 134.31, 134.18, 133.91, 133.87, 132.53, 132.43, 128.33, 127.86 (2C), 127.76 (2C), 127.54, 127.48, 125.73, 65.13; IR (neat from CH_2Cl_2 solution, NaCl plates) *v* 3247, 2906, 2846, 1673, 1591, 1330, 1303, 820, 707 cm^{-1}; MS (EI) *m/z* 314 (M^+, 100), 318 (M^+, 60), 298 (16), 285 (79), 283 (16); HRMS, calculated for 314.09429; observed 314.09441.



Preparation of 8

A mixture of (*p*-methylphenyl)boronic acid (0.80 g, 5.9 mmol), *p*-bromoiodobenzene (8.4 g, 30 mmol), anhydrous K_2CO_3 (1.64g, 11.9 mmol) and $Pd(PPh_3)_4$ (0.69 g, 0.59 mmol) in 50 mL of DME (dimethoxyethane) was refluxed for 20 h under N_2. After the reaction, black solids were removed by filtration through Celite and rinsed by dichloromethane. After removal of solvent, white plate crystals were obtained and purified by column chromatography with silica gel using

neat hexane as an eluent to give **8** (white powder, 0.62 g) in 42 % yield. ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.53 (d, 2H, J = 8.5 Hz), 48-7.38 (m, 4H), 7.24 (d, 2H, J = 8.0 Hz).

Preparation of 9

A solution of **8** (0.50 g, 2.0 mmol) in 10 mL of THF (water and oxygen free) was added dropwise into the solution of THF with Mg under N_2. The mixture was refluxed for 1 h. After cooling, the Gringard reagent under N_2 was transferred into the solution of trimethyl borate in 10 mL of THF at -78^{o}C. After the addition, the mixture was warmed up to room temperature and stirred for overnight to give a white paste. The white paste was poured into 20 mL of cold water and acidified to pH 2 with 0.1 M H_2SO_4. The solution was extracted by 2 × 30 mL of ethyl ether and collected organic solution was dried over $MgSO_4$. After the removal of solvent, a white powder was obtained. Further purification was operated with column chromotagraphy on silica gel using 20% EtOAc-CH_2Cl_2 to give white powders (**9**, 0.20 g, 47% yield). ^{1}H-NMR (250 MHz, $CDCl_3$) δ 8.31 (d, 2H, J = 8.0 Hz), 7.73 (d, 2H, J = 8.0 Hz), 7.58 (d, 2H, J = 8.0 Hz), 7.29 (d, 2H, J = 8.0 Hz).

Preparation of 6a

By following the same synthetic procedure of **3**, 2-(*p*-methylbiphenyl)-9,10-anthraquinone (**6a**) (0.12 g, 83%, yellow powder, mp. 235~236^{o}C) was obtained. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.58 (d, 1H, J = 1.8 Hz), 8.38 (d, 1H, J = 8.0 Hz), 8.35-8.31 (m, 2H), 8.05 (dd, 1H, J = 1.8, 8.0 Hz), 7.82-7.78 (m, 4H), 7.72 (td, 2H, J = 1.8, 8.5 Hz), 7.50 (td, 2H, J = 1.8, 8.0 Hz), 7.27 (d, 2H, J = 8.0 Hz), 2.40 (s, 3H); ^{13}C-NMR ($CDCl_3$, 125 MHz) 183.49, 183.10, 146.65, 141.94, 137.86, 137.65, 137.54, 134.41, 134.27, 134.19, 133.92, 133.87, 132.36 (2C), 129.87 (2C), 128.33, 127.90 (2C), 127.83 (2C), 127.52, 127.46, 127.15 (2C), 125.58, 21.37; IR (neat from CH_2Cl_2 solution, NaCl plates) v 1668, 1588, 806, 705 cm^{-1}.

Preparation of 6

2- (*p*-hydroxymethylbiphenyl)-9,10-anthraquinone (**6**) was obtained by bromonation of **6a** followed by the hydrolysis of **6b** in 74% yield (**6**, 0.10 g, yellow powder, decomposed at 224^{o}C) ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.54 (d, 1H, *J* = 1.8 Hz), 8.34 (d, 1H, *J* = 8.1 Hz), 8.32-8.26 (m, 2H), 8.01 (dd, 1H, *J* = 1.8, 8.1 Hz), 7.80-7.73 (m, 4H), 7.68 (td, 2H, *J* = 1.8, 8.5 Hz), 7.61 (td, 2H, *J* = 1.8, 8.2 Hz), 7.42 (d, 2H, *J* = 8.2 Hz), 4.71 (s, 2H); ^{13}C-NMR ($CDCl_3$, 125 MHz) 183.50, 183.11, 146.56, 141.60, 140.66, 139.86, 138.06, 134.45, 134.31, 134.22, 133.93, 133.87, 132.44, 132.41, 128.37, 128.00 (2C), 128.99 (2C), 127.80 (2C), 127.54, 127.52, 127.48 (2C), 125.64, 65.31; IR (neat from CH_2Cl_2 solution, NaCl plates) *v* 3164, 2917, 2851, 1670, 1588, 1327, 1303, 803, 707 cm^{-1}; MS (EI) *m/z* 390 (M^+, 100), 374 (M^+, 25), 273 (12), 361 (25); HRMS, calculated for 390.12339; observed 390.12528.

Photolysis procedures for 3-6 and characterization of photolysis products

All photolysis were carried out in a 100 mL of quartz tube in H_2O-MeCN under argon purged. After the photolysis, solutions were extracted by 3 × 25 mL of DCM. The combined organic solutions were dried over anhydrous $MgSO_4$ and solvent was removed by reduced evaporation. Crude products were purified by prep. TLC.

Photolysis of 3

Compound **3** (3 mg in 25 mL MeCN and 25 mL H_2O, pH 1~7) was irradiated for 1 min at 300 nm (2 lamps) under argon, to give a yellow solution. After work-up in air, the brown residue was characterized by ^{1}H NMR to give **10** (8-45% yield). Further purification was obtained by prep. TLC (silica gel, CH_2Cl_2) to give **10** (yellow powder, 2 mg), ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.94 (s, 1H), 8.36 (d, 1H, *J* = 7.9 Hz), 8.32-8.26 (m, 3H), 8.02 (dd, 1H, *J* = 1.5, 7.6 Hz), 7.80-7.71 (m, 3H), 7.66 (dt, 1H, *J* = 1.5, 7.6 Hz), 7.54 (mt, 1H, *J* = 7.6 Hz), 7.44 (dd, 1H, *J* = 1.1, 7.6 Hz); ^{13}C-

NMR ($CDCl_3$, 125 MHz) 191.14, 182.76, 182.61, 144.08, 143.28, 135.32, 134.36, 133.37, 133.36, 133.27, 132.65, 130.68, 128.94, 128.68, 128.19, 127.34, 127.17, 127.15, 116.55; IR (neat from CH_2Cl_2 solution, NaCl plates) *v* 3053, 2917, 2846, 2747, 1690, 1676, 1591, 1330, 1292, 705 cm^{-1}.

Photolysis of 4

Compound **4** (3 mg in 25 mL of MeCN and 25 mL of H_2O, pH 1~7) was irradiated for 1 min at 300 nm (2 lamps) under argon, to give a yellow solution. After work-up in air, the brown residue was characterized by ^1H NMR to give **11** (6-22% yield). Further purification was obtained by prep. TLC (silica gel, CH_2Cl_2) to give **11** (yellow powder, 1 mg), ^1H NMR ($CDCl_3$, 300 MHz) δ 10.07 (s, 1H), 8.52 (d, 1H, *J* = 1.8 Hz), 8.37 (d, 1H, *J* = 8.2 Hz), 8.33-8.25 (m, 2H), 8.18 (t, 1H, *J* = 1.8 Hz), 8.00 (dd, 1H, *J* = 2.0, 8.2 Hz), 7.97-7.88 (m, 2H), 7.81-7.73 (m, 2H), 7.64 (t, 1H, *J* = 7.6 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) 191.79, 182.88, 182.71, 145.25, 139.98, 137.17, 134.30, 134.18, 134.04, 133.57, 133.52, 133.06, 132.69, 132.36, 130.02, 129.92, 128.26 (2C), 127.35, 127.29, 125.65; IR (neat from CH_2Cl_2 solution, NaCl plates) *v* 3060, 2813, 2745, 1700, 1673, 1591, 1327, 705 cm^{-1}.

Photolysis of 5

Compound **5** (3 mg in 25 mL MeCN and 25 mL H_2O, pH 1~7) was irradiated for 1 min at 300 nm (2 lamps) under argon, to give a yellow solution. After work-up in air, the brown residue was characterized by ^1H NMR to give **12** (7-45% yield). Further purification was obtained by prep. TLC (silica gel, CH_2Cl_2) to give **12** (yellow powder, 1 mg), ^1H NMR ($CDCl_3$, 300 MHz) δ 10.04 (s, 1H), 8.52 (d, 1H, *J* = 1.8 Hz), 8.37 (d, 1H, *J* = 8.2 Hz), 8.32-8.25 (m, 2H), 8.03-7.94 (m, 3H), 7.83 (td, 2H, *J* = 1.8, 8.2 Hz), 7.80-7.73 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) 191.60, 182.92,

182.68, 145.24, 144.70, 136.26, 134.34, 134.23, 134.00, 133.55, 133.50, 132.92, 132.55, 130.43 (2C), 128.22, 128.00 (2C), 127.35, 127.30, 125.96; IR (neat from CH_2Cl_2 solution, NaCl plates) *v* 3049, 2917, 2725, 1700, 1673, 1591, 1333, 1278, 707 cm^{-1}.

Photolysis of 6

Compound **6** (2 mg in 25 mL MeCN and 25 mL H_2O, pH 1~7) was irradiated for 1 min at 300 nm (16 lamps) under argon, to give a yellow solution. After work-up in air, the brown residue was characterized by ^1H NMR to give **18** (15-23% yield). Further purification was obtained by prep. TLC (silica gel, CH_2Cl_2) to give **18** (yellow powder, 1 mg), ^1H NMR ($CDCl_3$, 500 MHz) δ 10.06 (s, 1H), 8.59 (d, 1H, *J* = 1.8 Hz), 8.40 (d, 1H, *J* = 8.1 Hz), 8.36-8.32 (m, 2H), 8.07 (dd, 1H, *J* = 1.8, 8.1 Hz), 7.98 (td, 2H, *J* = 1.8, 8.4 Hz), 7.85 (td, 2H, *J* = 1.8, 8.4 Hz), 7.83-7.80 (m, 4H), 7.79 (td, 2H, *J* = 1.8, 8.4 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) 192.05, 183.44, 183.06, 146.39, 146.18, 140.39, 139.22, 135.75, 134.51, 134.37, 134.24, 133.88, 133.83, 132.64, 132.47, 130.61, 128.42, 128.33, 128.19, 127.90, 127.56, 127.51, 125.75; IR (neat from CH_2Cl_2 solution, NaCl plates) *v* 2923, 2820, 1673, 1591, 1330, 809, 705 cm^{-1}.

Trapping of photolysis product of 3

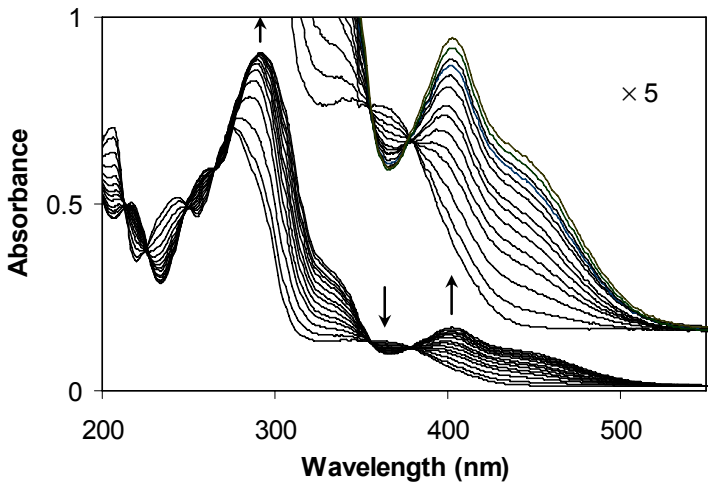
Photolysis of **3** (20 mg, 1:1 H_2O-MeCN, pH 1) was carried out in 100 mL of a quartz tube under argon to give yellow photoredox product **13**. Under Ar, NaOH (solid, 2 g) were added into the above solution to give a dark red solution which was converted to yellow solution with the addition of Ac_2O (2 mL). After the addition, the solution was extracted with 2 × 25 mL dichloromethane and the collected organic layer was dried over anhydrous $MgSO_4$. After the removal of solvent, a brown residue was obtained. The brown residue was purified by prep TLC by neat dichloromethane as an eluent to give **16** (10 mg, light red) ^1H NMR ($CDCl_3$, 300 MHz) δ 9.98 (s, 1H), 8.02 (dd, 1H, *J* = 1.5, 8.0Hz), 7.99 (d, 1H, *J* = 0.5, 9.0 Hz), 7.96-7.87 (m, 2H),

7.80 (s, 1H), 7.93 (td, 1H, J = 1.5, 8.0 Hz), 7.55-7.46 (m, 5H), 2.60 (s, 3H), 2.53 (s, 3H); ^{13}C-NMR ($CDCl_3$, 125 MHz) 192.31, 169.65 (2C), 145.35, 140.97, 140.69, 135.88, 134.35, 133.89, 131.19, 128.55, 128.50, 128.18, 127.09 (2C), 125.06, 124.89, 123.87, 123.53, 123.43, 122.60, 122.05 (2C), 21.00, 20.95;

UV-Vis studies

UV-Vis traces of phenylanthraquinones **3**-**6** in 1:1 H_2O-CH_3CN (~10^{-5} M, pH 1) were carried out in 3 cm quartz cuvette. The solutions were purged with Ar for 10 minutes and irradiated in Rayonet reactor, equipped with merry-go-round apparatus, at 300 nm. The cooling was achieved with a fan. The irradiation was stopped at regular time intervals and UV-VIS spectra were recorded.

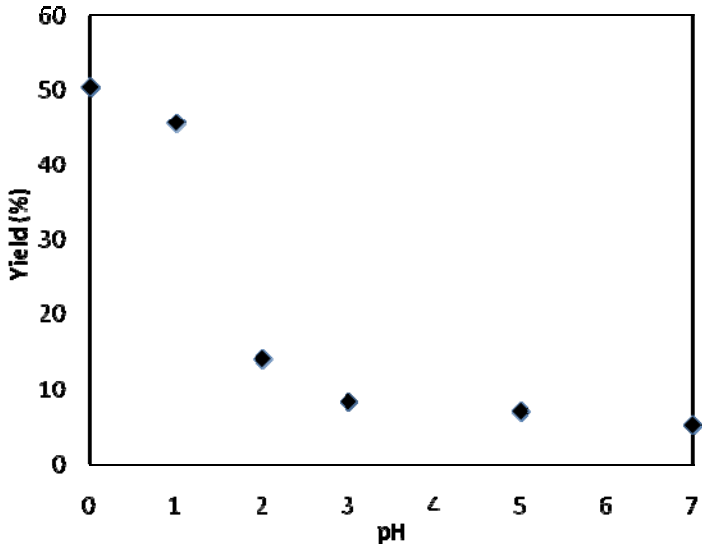
UV-Vis traces of 5



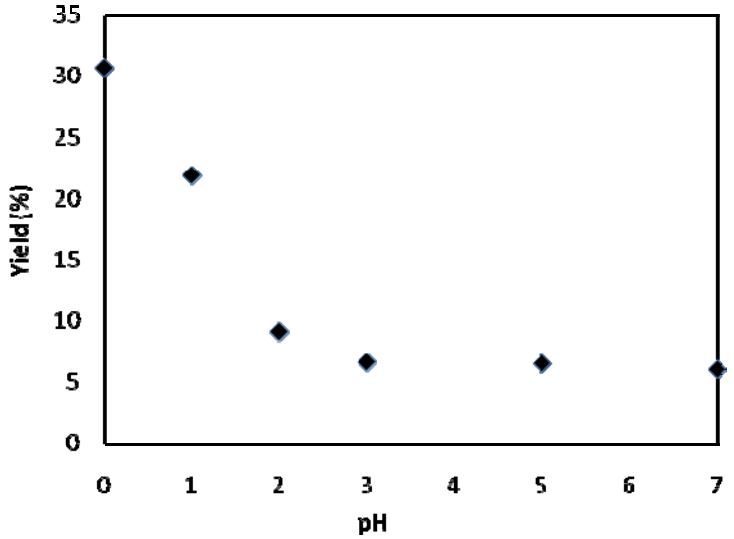
UV-Vis traces of photolysis of **5** (10^{-5} M, 1:1 H_2O-MeCN, pH 1, Ar purged, λ_{ex} = 300 nm, 2 lamps) showed the formation of two new bands at 297 and 408 nm, the latter being a completely new long wavelength band. These new bands are bleached within 40 min after aeration, to give rise to a spectrum identical to that of anthraquinone aldehyde **15**. Each trace represents 5 s of photolysis. Inset: five-fold expansion of the long wavelength region. Estimated conversion > 95%.

pH Effects on Photolysis efficiency of 3-6

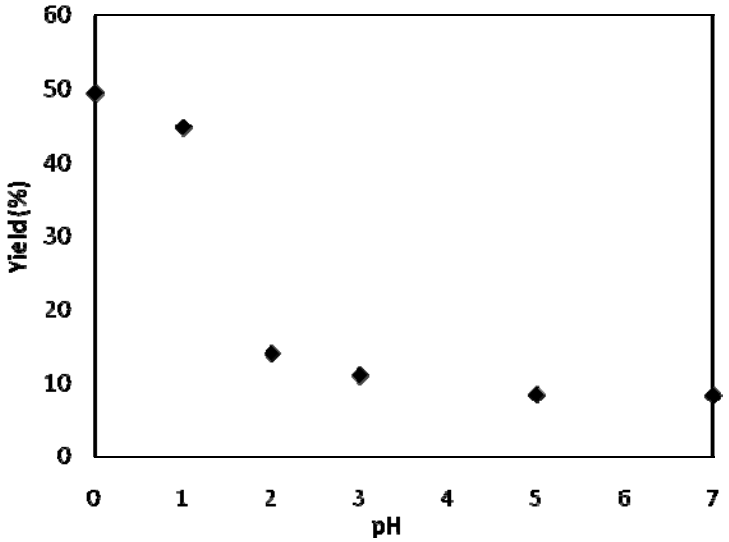
Solutions of **3**-**6** (1 mg 1:1 H_2O-CH_3CN, pH from 1 to 7) in a 100 mL of large quartz tube were purged with Ar for 15 minutes prior to photolysis and were irradiated (300 nm, 2 lamps for 1 min (**3**-**5**) and 8 lampls for 1 min (**6**). After work-up, the photolysis yield (%) were determined with proton NMR.



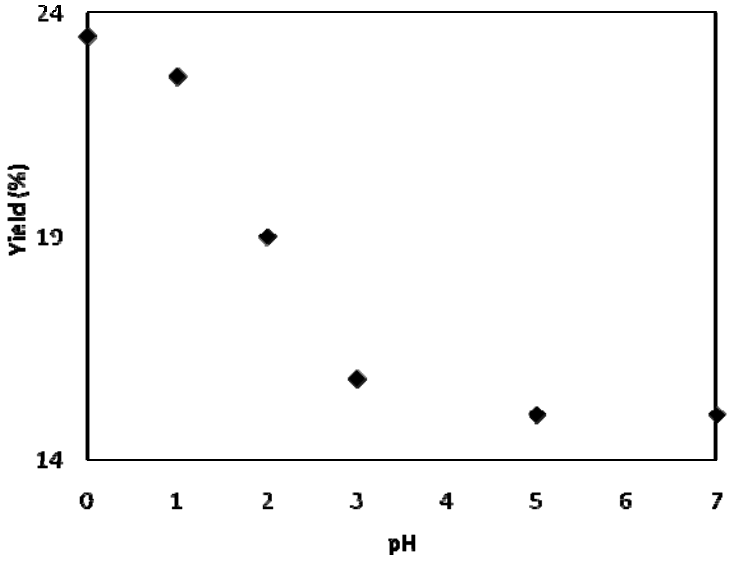
pH effect on the photolysis efficiency of **3** (1:1 H2O-MeCN, pH 0~7, argon purged) determined by ^{1}H NMR (photolysis yield of the formation of **10**)



pH effect on the photolysis efficiency of **4** (1:1 H2O-MeCN, pH 0~7, argon purged) determined by ^{1}H NMR (photolysis yield of the formation of **11**)



pH effect on the photolysis efficiency of **5** (1:1 H2O-MeCN, pH 0~7, argon purged) determined by ^{1}H NMR (photolysis yield of the formation of **12**)



pH effect on the photolysis efficiency of **6** (1:1 H2O-MeCN, pH 0~7, argon purged) determined by ^{1}H NMR (photolysis yield of the formation of **18**)

Quantum Yield of Photoredox Reactions of 3-6

Quantum yields were measured using NMR using the reaction of 2-(hydroxymethyl)anthraquinone (**1**) as a secondary actinometer ($\Phi = 0.8$).

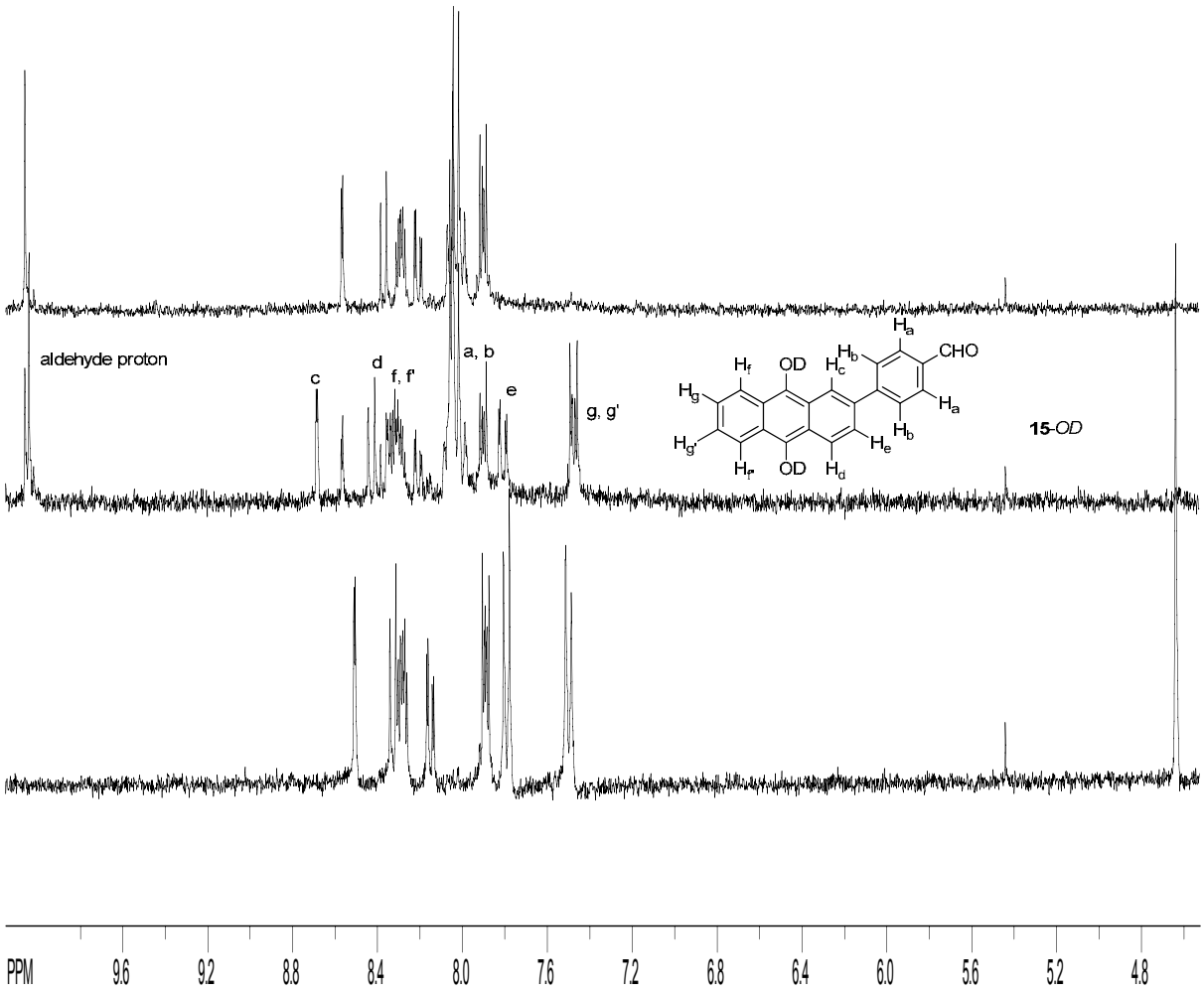
Compounds **3-6** (10^{-4} M) in 100 mL of 1:1 H_2O-MeCN (pH 1) solution was irradiated for 1 min at 300 nm, 2 lamps in Rayonet reactor with Ar-purging and cooling by water. After extraction with CH_2Cl_2, drying over anhydrous $MgSO_4$, solvent was evaporated and ^1H NMR was recorded. All conversions were kept below 30% and repeated twice. The conversion determined by ^1H was compared to an identical run using **1**. Quantum yield of photoredox reactions of **3-6** were estimated to be 0.6, 0.3, 0.5 and 0.1 respectively.

Concentration effects on photolysis conversions of 3

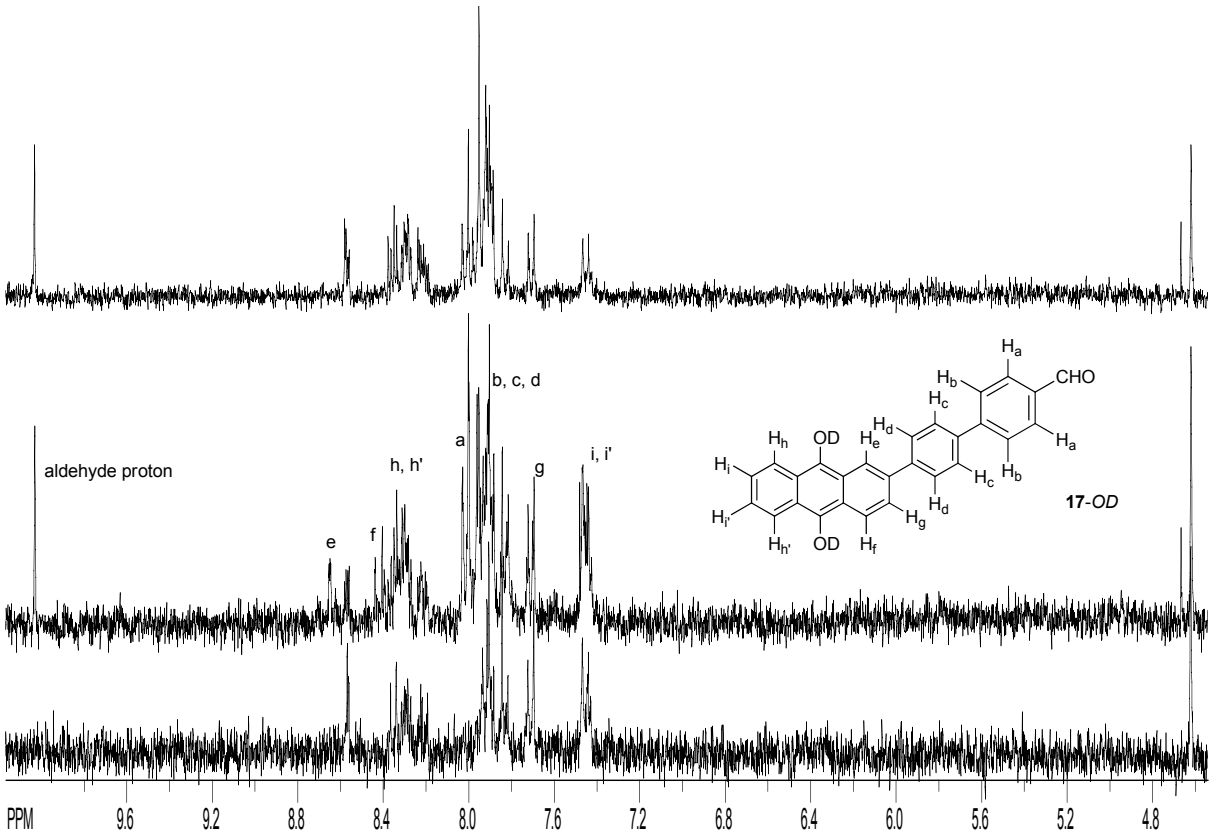
Photolysis of **3** (10^{-7}~10^{-5} M, 1:1 H_2O-MeCN, pH 1, argon saturated**)** was carried out in a 3 mL of quartz cuvette and the absorption intensity of product **7** at 387 nm was determined with UV-Vis spectroscopy. The rates at different concentrations were determined by taking the slope of the plot of absorbance *vs* time (0~20s). The rate constant was obtained by taking the slope of the plot of rates *vs* concentration. The experimental results showed the rates were reasonably linear with respective to concentrations of **3** and the rate constant 1.6×10^{-3} $L \cdot mol^{-1} \cdot s^{-1}$.

Proton NMR studies of 5 and 6 in the NMR tubes

NMR studies of **5 and 6** (10^{-4} M, 10% D_2O-CD_3CN, pD1, argon purged, λ_{ex} 300 nm, 16 lamps, 10 min) were carried out in NMR tubes to give yellow species that is consistent with photoredox products **15-** *OD* (100% conversion) and **17-***OD* (50% conversion) respectively. After aeration, the yellow color disappeared and gave rise to the NMR spectrum identical of that of **12** and **18**. (Vide infra)



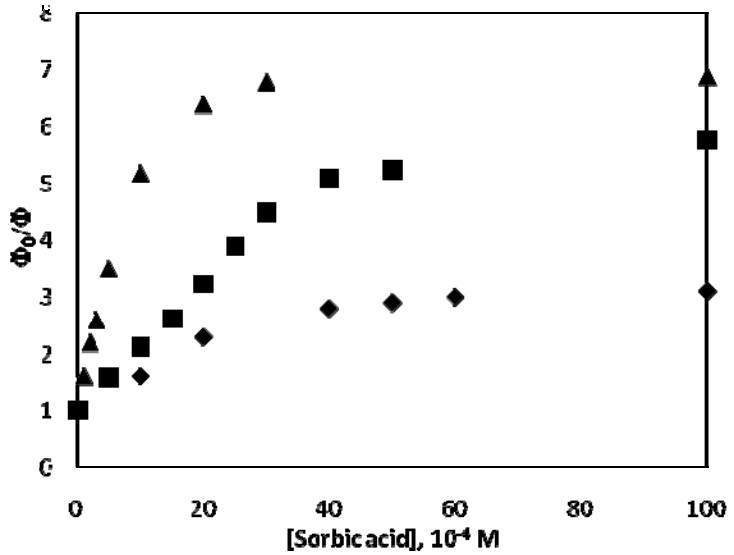
Proton NMR Studies of photolysis of **5** in 10% D_2O-CD_3CN (pD 1, argon saturated). Every spectrum represents **5** prior to photolysis, middle spectrum is **15**-*OD*, and top spectrum is that of **12** (formed upon aeration of **15**-*OD*). ^{1}H NMR (300 Hz) of **15**-*OD* δ 10.04 (s, 1H, aldehyde proton), 8.69 (d, H_c, J = 1.8 Hz), 8.43 (d, H_d, J = 9.2 Hz), 8.37-8.25 (m, H_f and $H_{f'}$), 8.07-8.00 (m, $2H_a$ and $2H_b$), 7.81 (dd, H_e, J = 9.1, 1.8 Hz), 7.52-7.43 (m, H_g and $H_{g'}$).



Proton NMR Studies of photolysis of **6** in 10% D_2O-CD_3CN (pD 1, argon saturated). Every spectrum represents **6** prior to photolysis, middle spectrum is **17**-*OD*, and top spectrum is that of **18** (formed upon aeration of **17**-*OD*). ^{1}H NMR (300 Hz) of **17**-*OD* δ 10.03 (s, 1H, aldehyde proton), 8.65 (dd, H_e, J = 1.7, 0.6 Hz), 8.42 (dd, H_f, J = 9.3, 0.6 Hz), 8.35-8.27 (m, H_h and $H_{h'}$), 8.01 (dd, $2H_a$, J = 8.6, 1.2 Hz), 7.97-7.87 (m, $2H_b$, $2H_c$, $2H_d$ and H_g), 7.49-7.40 (m, Hi and $H_{i'}$).

Triplet quenching studies

Photolyses of **3-5** (10^{-4} M, 1:1 H_2O-MeCN, pH1, argon purged, λ_{ex} 350 nm) were carried out in 100 mL of quartz tube in the presence of sorbic acid (0 ~ 0.01 M). After workup in air, the photolysis yield (the formation of **10-12**, 25 ~ 40%) were determined with proton NMR. The maximum quencher concentration of sorbic acid was 10^{-2} M due to its relatively low solubility in 1:1 H_2O–CH_3CN.

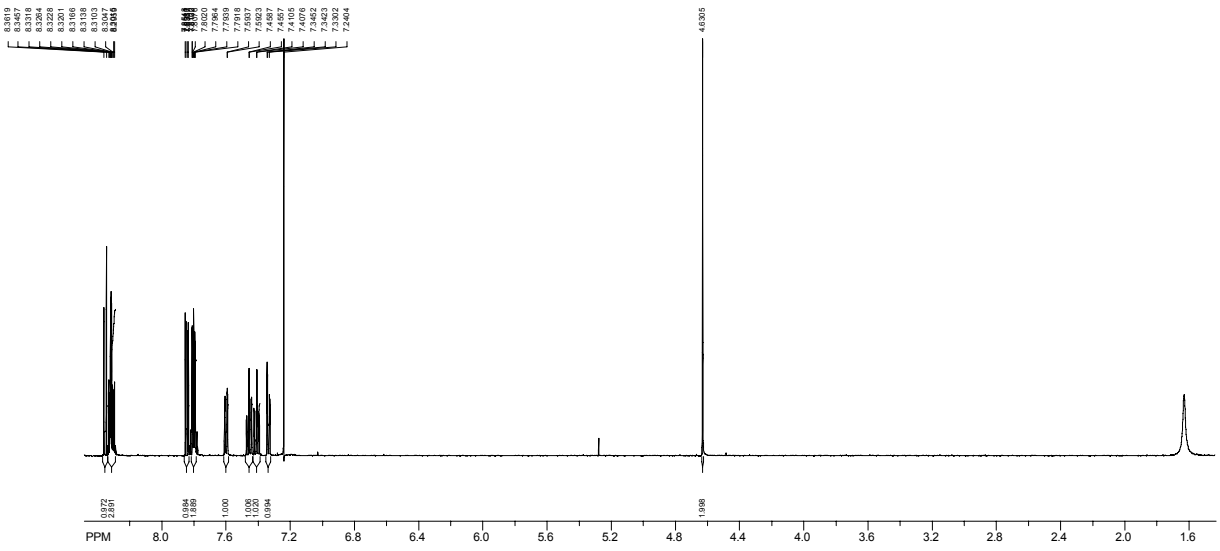


Stern-Volmer plot of quenching of photoredox reaction for **3** (♦), **4** (▲) and **5** (■) in the presence of sorbic acid. Φ_0/Φ refer to the yields in the absence and presence quencher.
From the slopes of the quenching plots, it was estimated that the reactive triplet lifetimes of **3**, **4** and **5** are 90 ns, 1 μs and 0.23 μs, respectively, assuming the bimolecular triplet quenching rate constant is diffusion-controlled in water (5×10^{-9} $M^{-1}s^{-1}$)[1]

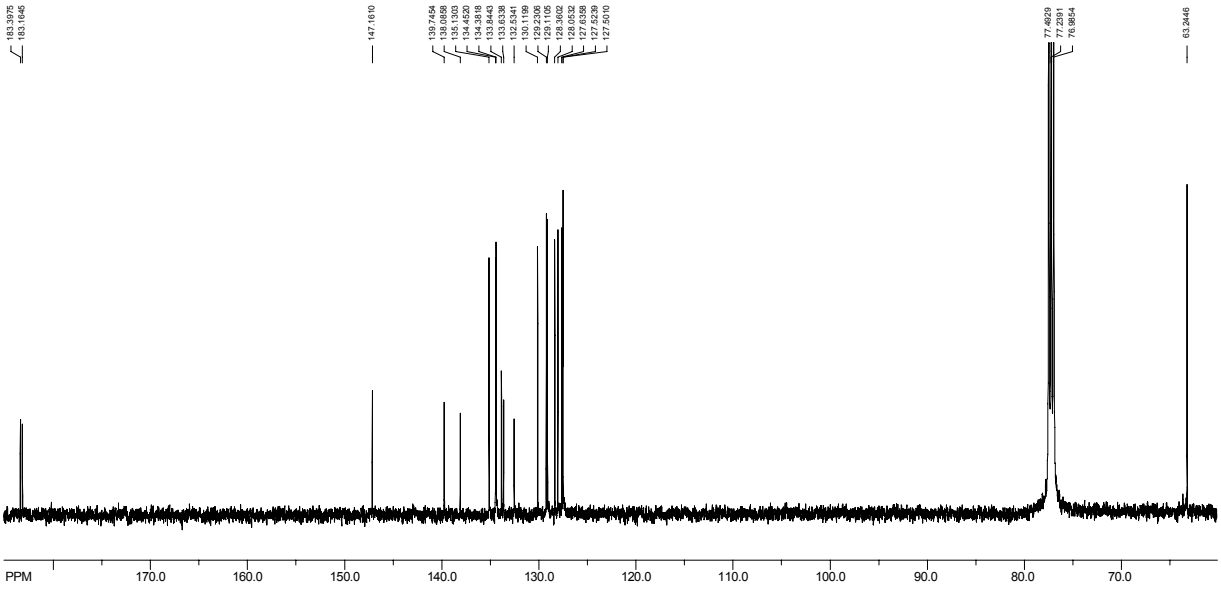
[1] S. L. Murov, Handbook of Photochemistry, Marcel Dekker, New York, 1973.

^{1}H NMR and ^{13}C NMR spectra of 3-6 and photolysis products 10-12, 16 and 18

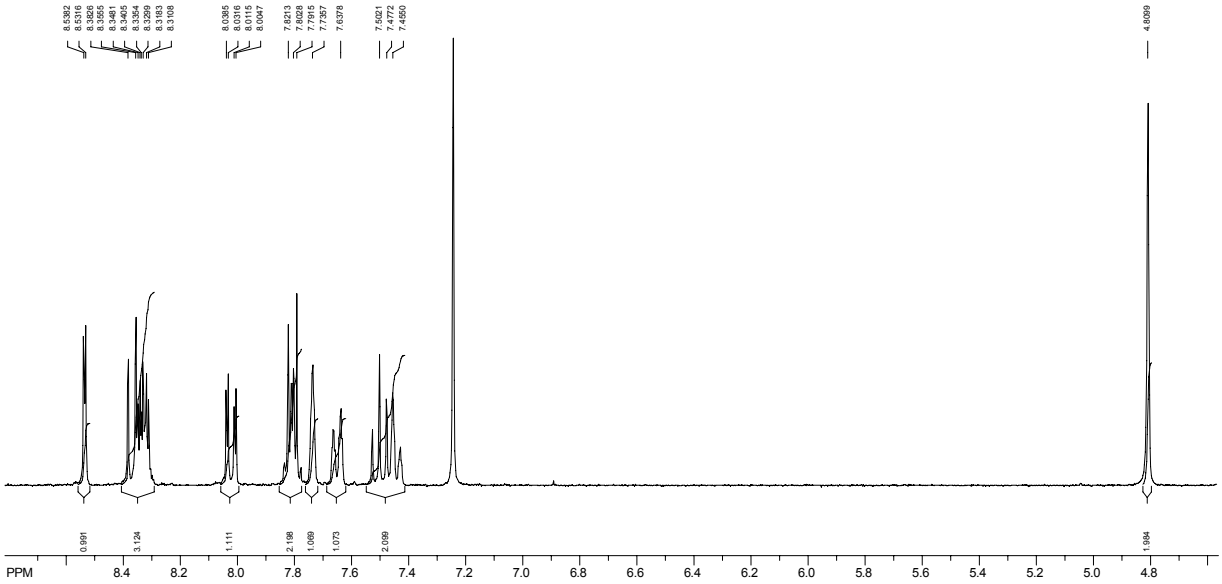
^{1}H NMR (500Hz, $CDCl_3$) of **3**



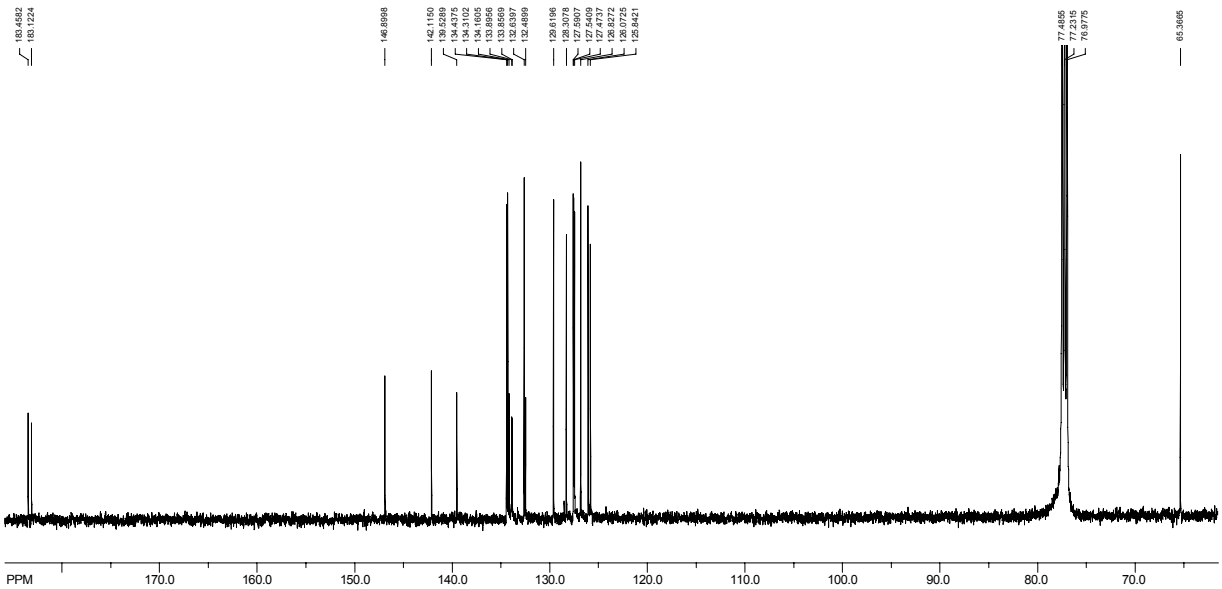
^{13}C NMR (125Hz, $CDCl_3$) of **3**



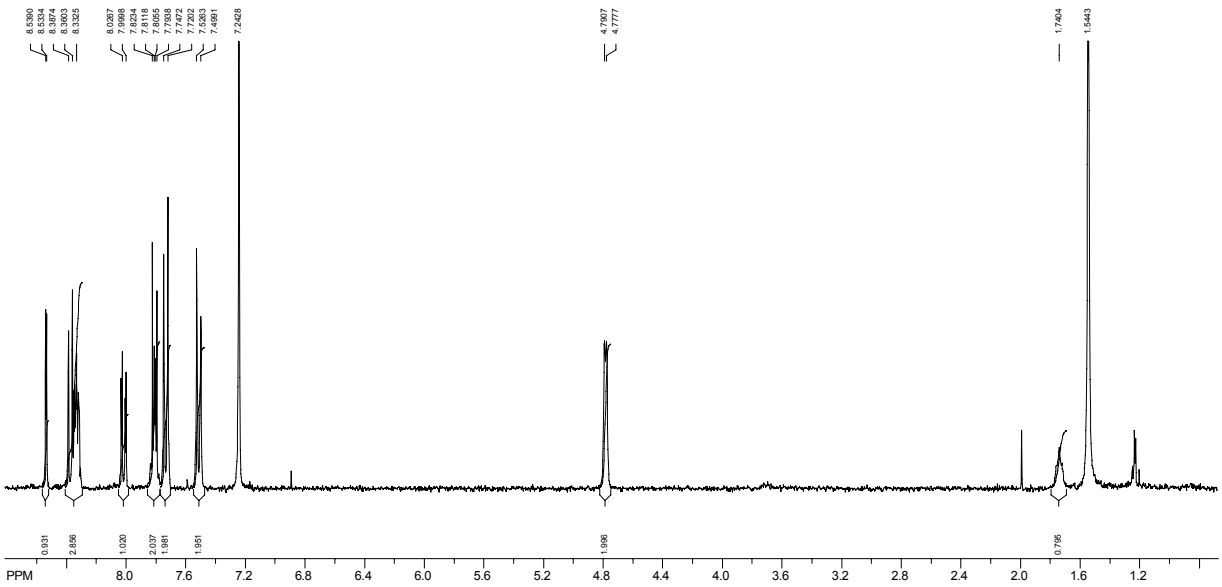
^{1}H NMR (300Hz, $CDCl_3$) of **4**



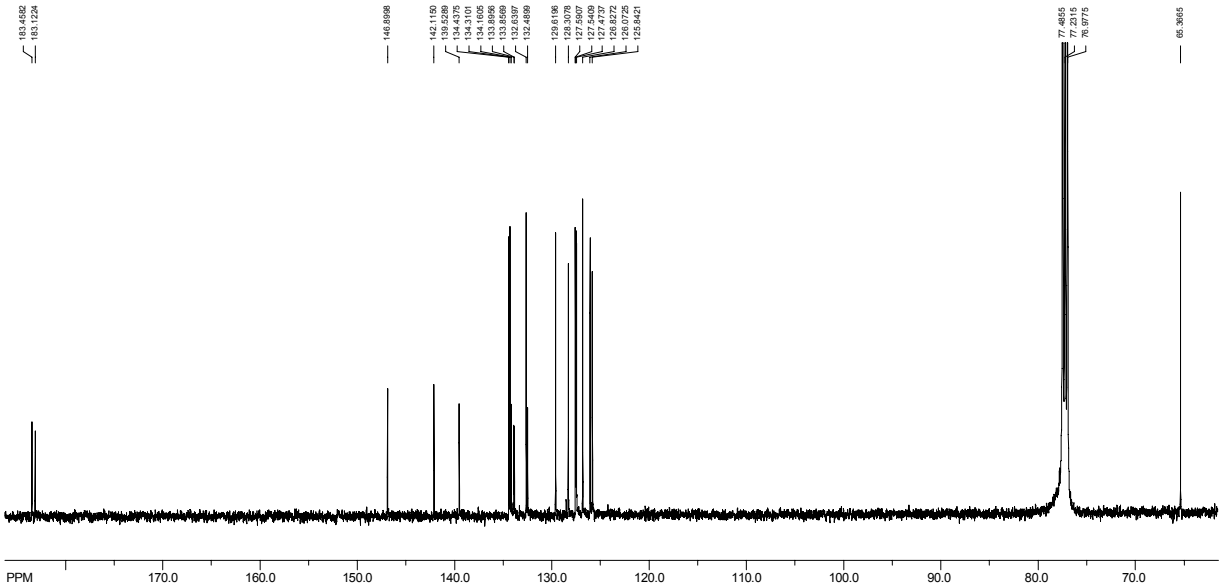
^{13}C NMR (125Hz, $CDCl_3$) of **4**



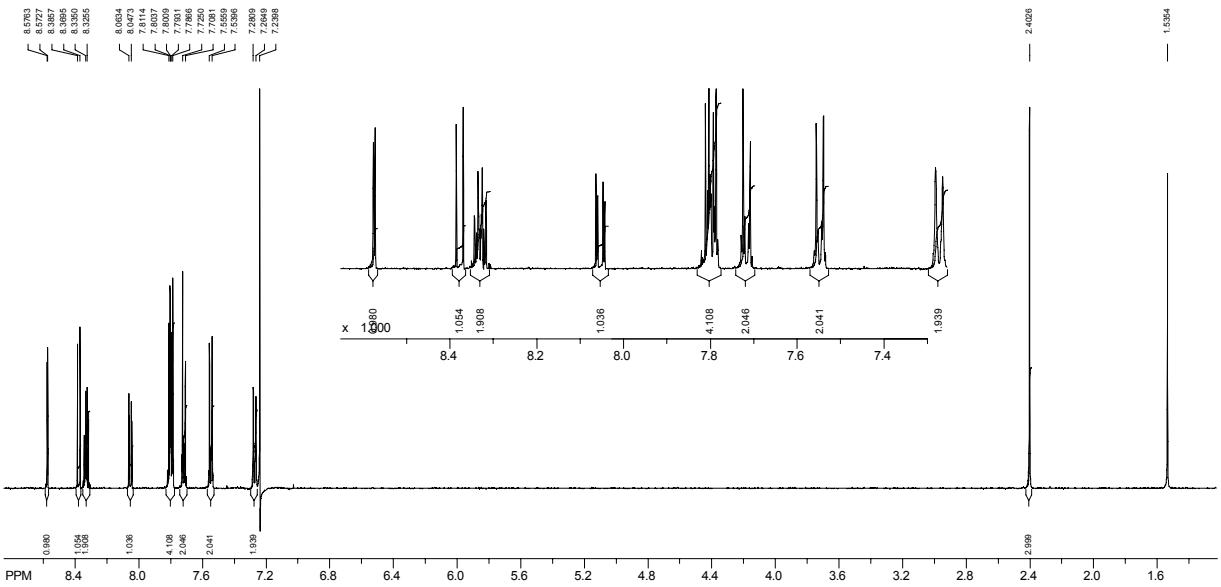
^{1}H NMR (300Hz, $CDCl_3$) of **5**



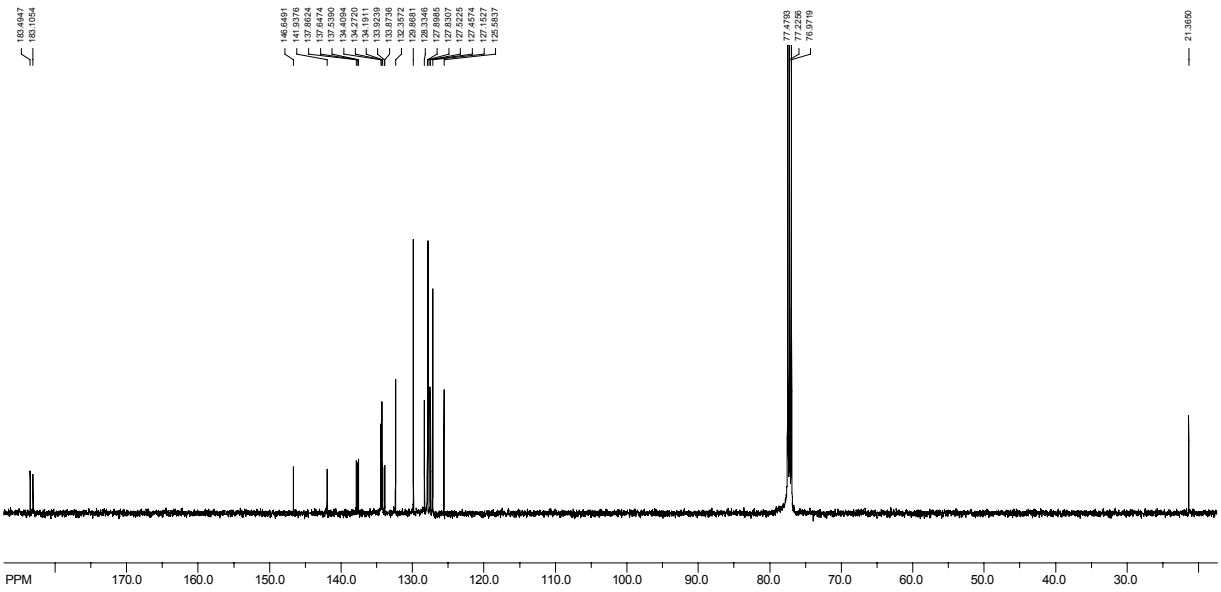
^{13}C NMR (125Hz, $CDCl_3$) of **5**



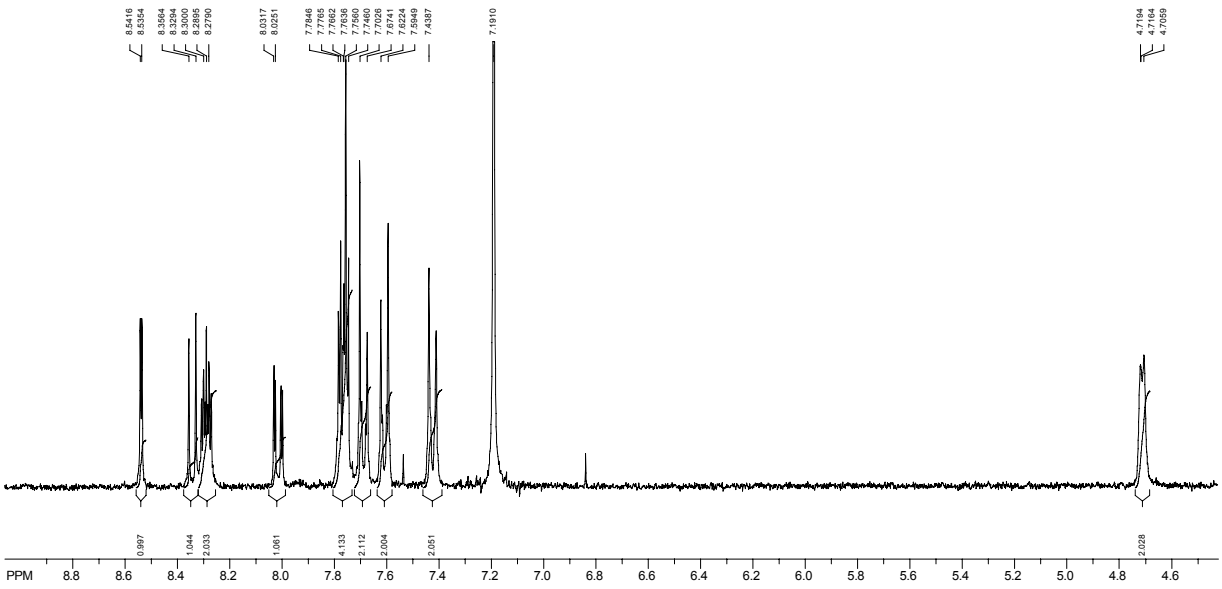
^{1}H NMR (500Hz, $CDCl_3$) of **6a**



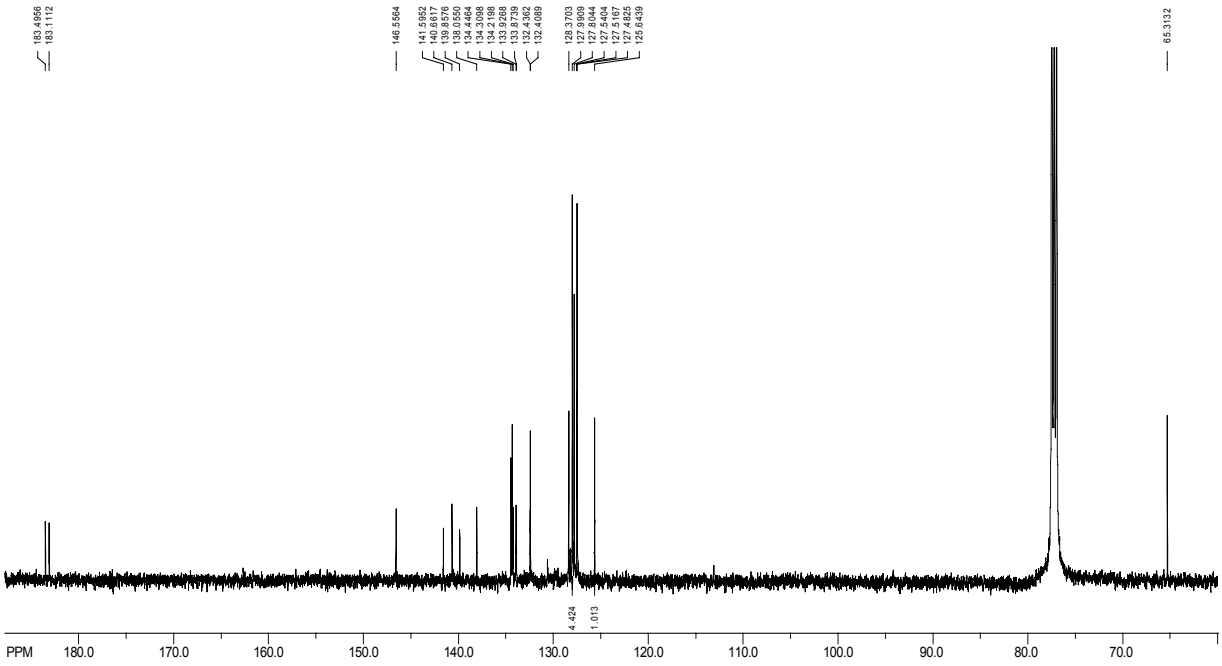
^{13}C NMR (125Hz, $CDCl_3$) of **6a**



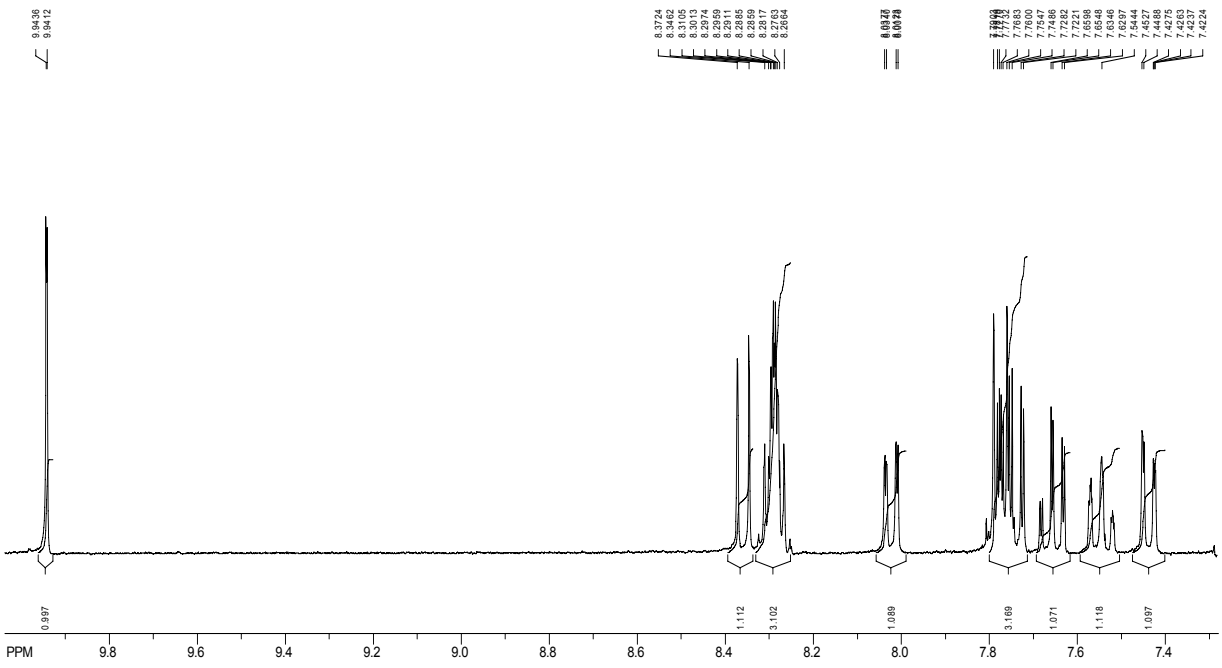
^{1}H NMR (300Hz, $CDCl_3$) of **6**



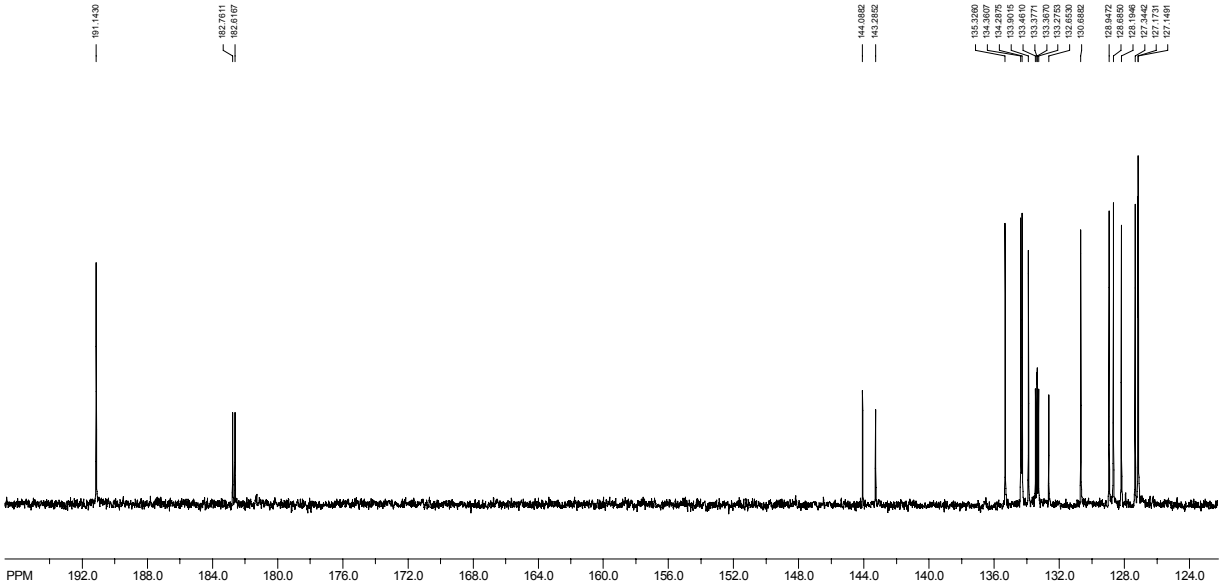
^{13}C NMR (125Hz, $CDCl_3$) of **6**



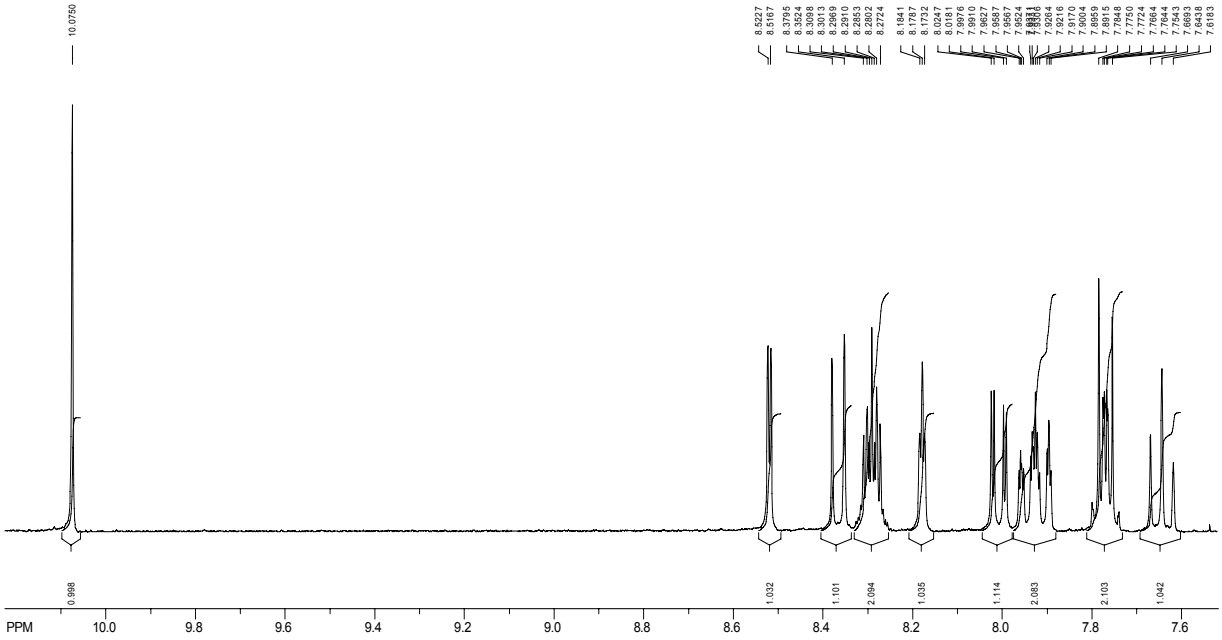
^{1}H NMR (300Hz, $CDCl_3$) of **10**



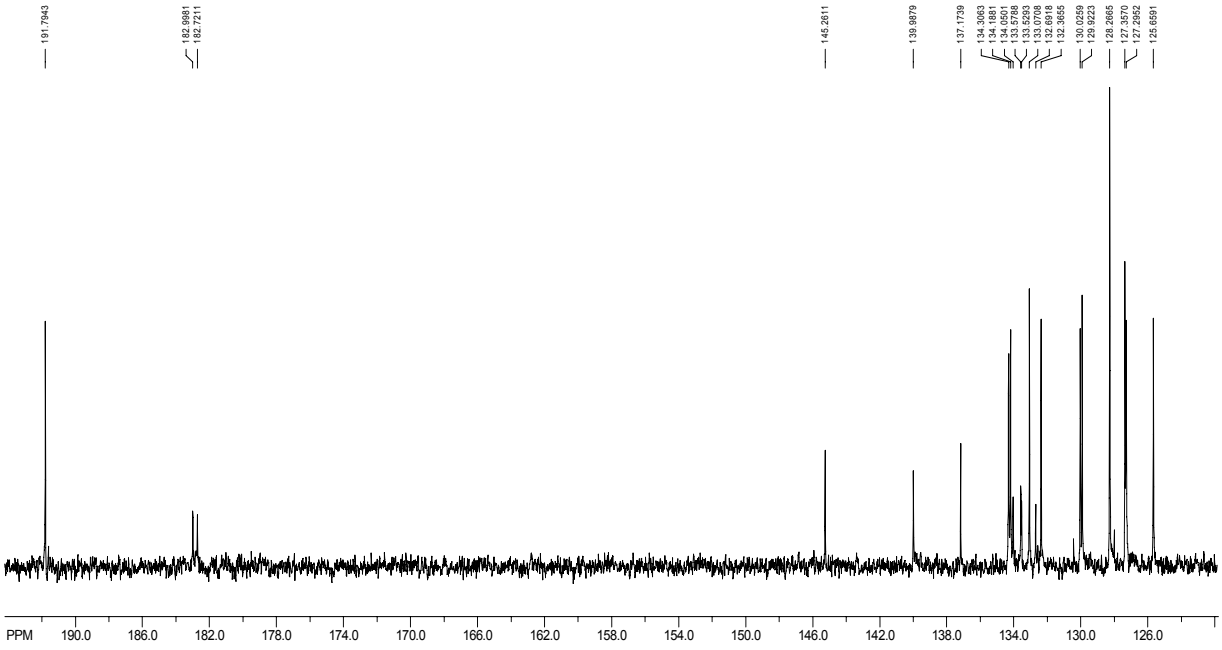
^{13}C NMR (125Hz, $CDCl_3$) of **10**



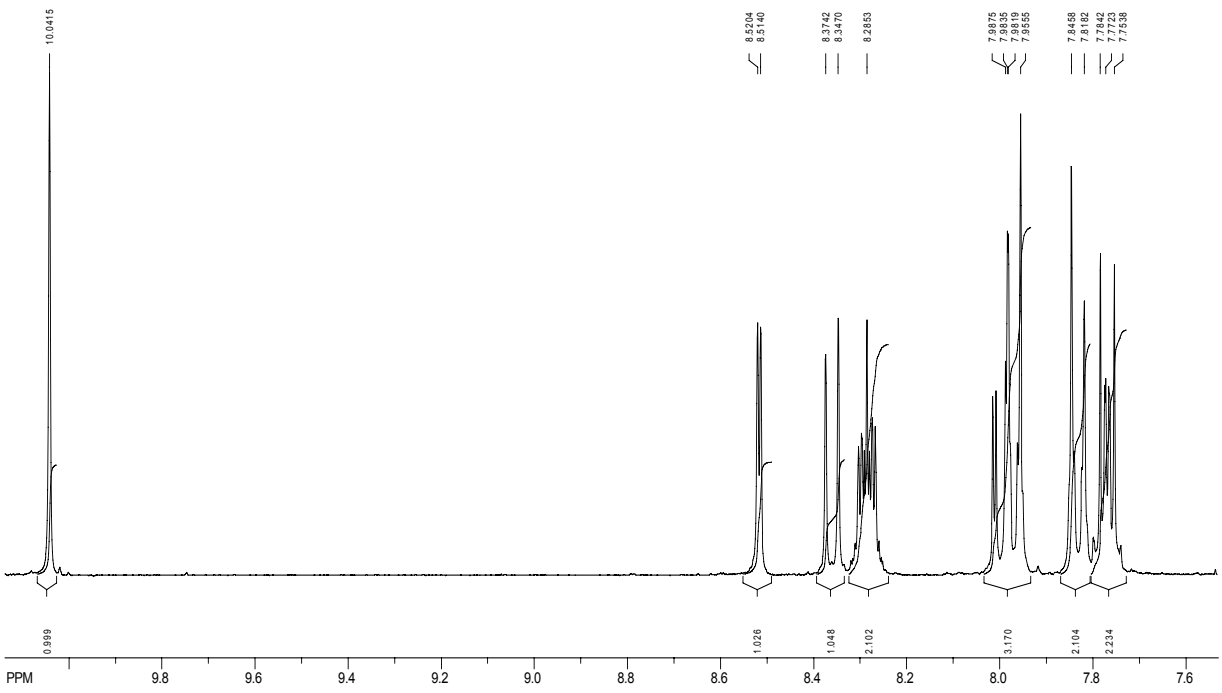
^{1}H NMR (300Hz, $CDCl_3$) of **11**



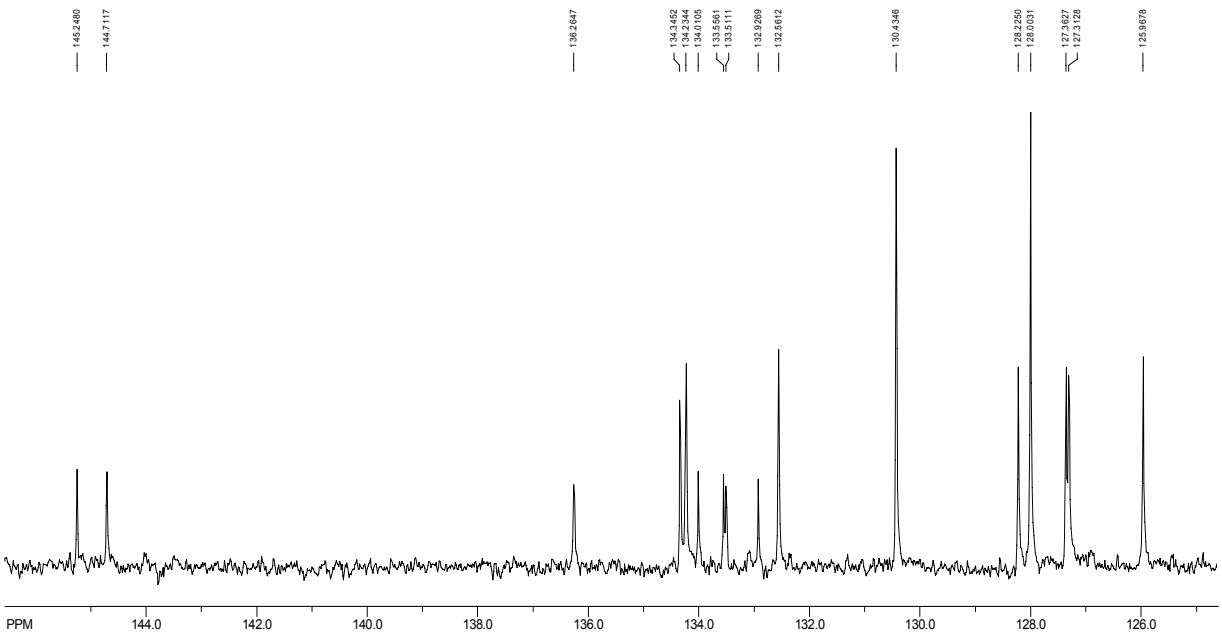
^{13}C NMR (75Hz, $CDCl_3$) of **11**



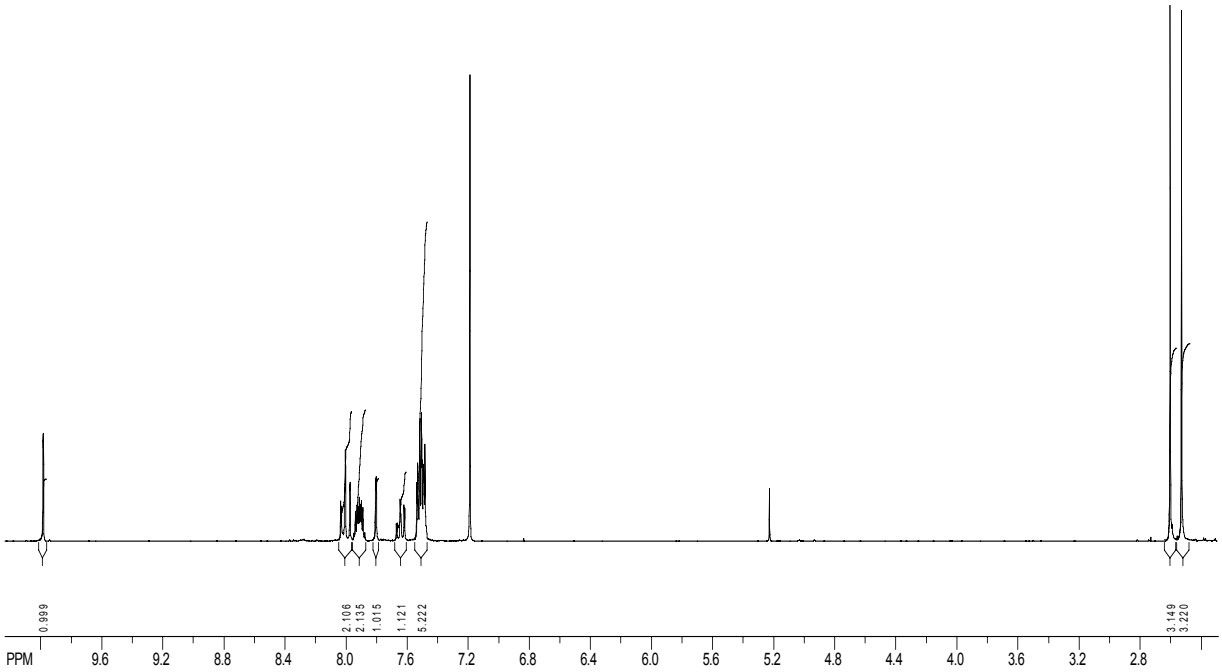
^{1}H NMR (300Hz, $CDCl_3$) of **12**



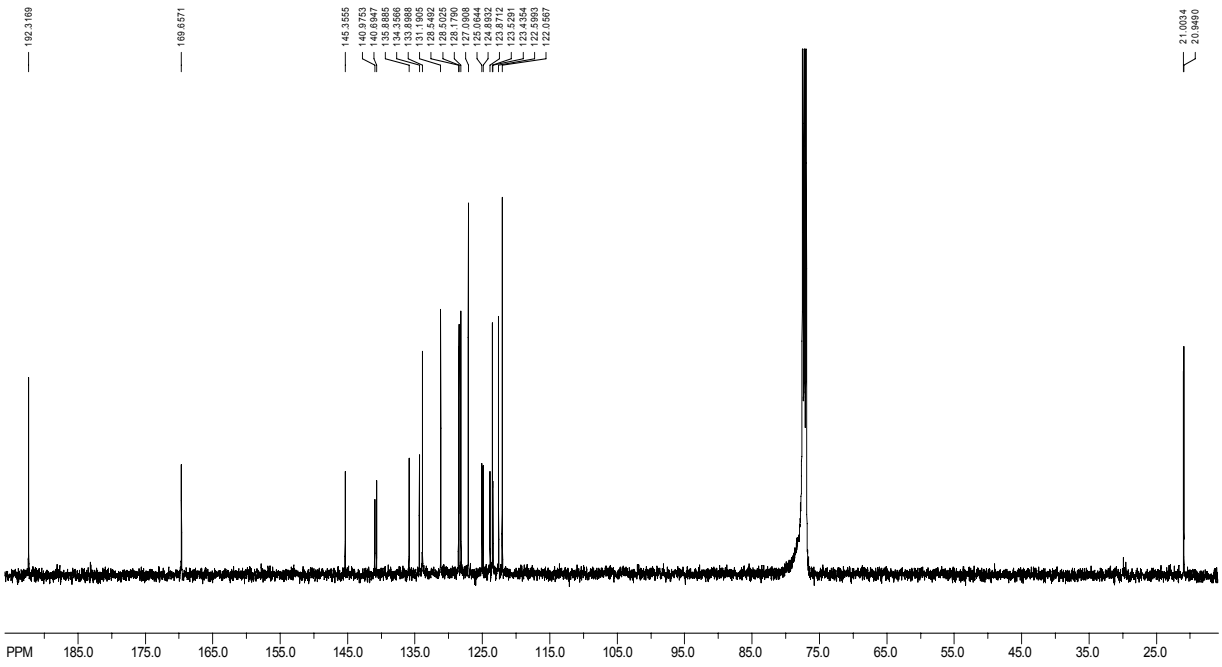
^{13}C NMR (75Hz, $CDCl_3$) of **12**



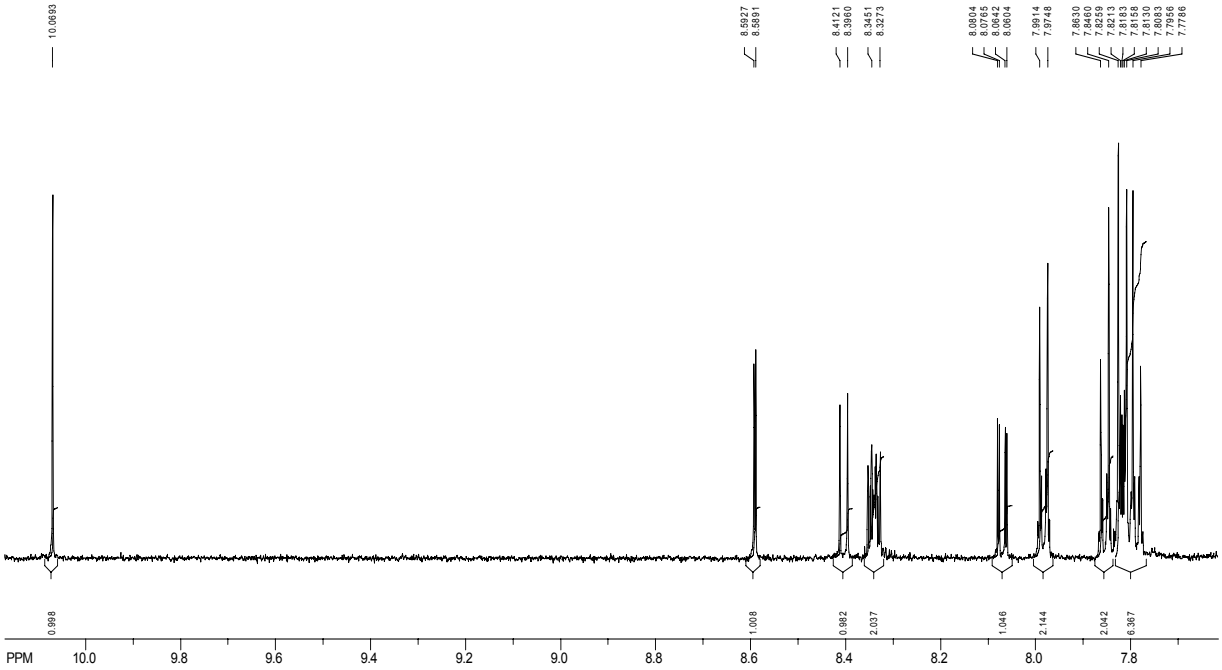
^{1}H NMR (300Hz, $CDCl_3$) of **16**



^{13}C NMR (125Hz, $CDCl_3$) of **16**



^{1}H NMR (500Hz, $CDCl_3$) of **18**



^{13}C NMR (125Hz, $CDCl_3$) of **18**