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Supplementary Materials:

Dehydrogenative Transformation of Alcoholic Substrates in Aqueous Media Catalyzed by an Iridium Complex Having a Functional Ligand with α-Hydroxypyridine and 4,5-Dihydro-1*H*-imidazol-2-yl Moieties

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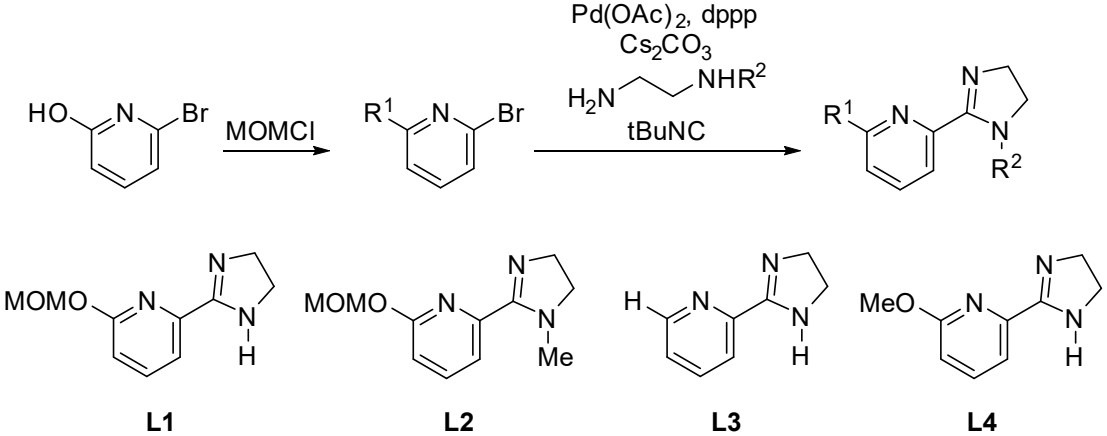
1. General information

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on JEOL ECX-500 and ECS-400 spectrometers at room temperature. Gas chromatography (GC) analyses were performed on a GL-Sciences GC353B gas chromatograph with a capillary column (GL-Sciences and InertCap Pure WAX). Elemental analyses were carried out at the Microanalysis Center of Kyoto University. Silica-gel column chromatography was carried out by using Wako-gel C-200. The compounds, $[Cp^*IrCl_2]_2$ (Cp^* = η^5-pentamethylcyclopentadienyl) [1] and $[Cp^*Ir(OH_2)_3](OTf)_2$ [2]were prepared according to the literature method. The diol **7c** was prepared by the reduction of 2-benzoylbenzoic acid using $LiAlH_4$ [3]. The diols **7e**, **7f** and **7g** were prepared by the reduction of the corresponding dicarboxylic acids using BH_3-THF [3]. All other reagents are commercially available and were used as received.

2. Typical procedures for synthesis of ligands L1-L4

*Synthesis of ligands **L1**-**L4***

These ligands were synthesized according to the literature method [4].



Preparation of 2-bromo-6-(methoxymethoxy)pyridine

K_2CO_3 (1.43 g, 10.3 mmol) and dry THF (40 mL) were added in the two-necked round bottomed flask under argon atmosphere. Then, 2-bromo-6-hydroxypyridine (1.18 g, 6.8 mmol) and chloromethyl methyl ether (640 μL, 8.43 mmol) were added in the solution and stirred for 24 hours at room temperature. The reaction mixture was filtered through Celite and the filtrate was evaporated. The crude product was purified by column chromatography (535 mg, 2.4 mmol, 35% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (t, *J* = 8 Hz, 1H, aromatic), 7.11 (t, *J* = 7 Hz, 1H, aromatic), 6.76 (d, *J* = 8 Hz, 1H, aromatic), 5.49 (s, 2H, CH_3OCH_2O-), 3.52 (s, 3H, CH_3OCH_2O-). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.3, 141.0, 138.7, 121.4, 109.7, 92.7, 57.5. Anal. Calcd for $C_7H_8NO_2Br$: C, 38.56; H, 3.70; N, 6.42. Found: C, 38.63; H, 3.74; N, 6.45.

*Preparation of compound **L1***

In two-necked round-bottomed flask connected with the Dimroth condenser, 2-bromo-6-(methoxymethoxy)pyridine (394 mg, 1.81 mmol), $PdCl_2$ (17.2 mg, 0.096 mmol, 5 mol%), dppp [1,3-bis(diphenylphosphino)propane] (76.7 mg, 0.19 mmol, 10 mol%), Cs_2CO_3 (770.0 mg, 2.4 mmol, 1.3 equiv.), toluene (9.0 mL), *tert*-butyl isocyanide (315 μL, 2.8 mmol, 1.5 equiv.), ethylenediamine (620 μL, 9.3 mmol, 5.1 equiv.) were placed in this order. The reaction mixture was refluxed in oil bath (125 °C) for 16 hours. After cooling to room temperature, the reaction mixture was filtered through Celite and washed with ethyl acetate. The crude product was obtained after evaporation of the filtrate. After purifying by column chromatography, the product was obtained (slightly yellow solid, 350 mg, 1.69 mmol, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7 Hz, 1H, aromatic), 7.12 (m, 1H, aromatic), 7.70 (t, *J* = 8 Hz, 1H, aromatic), 6.89 (d, *J* = 8 Hz, 1H, -NH-), 5.54 (s, 2H, CH_3OCH_2O-), 4.05 (t, *J* = 10 Hz, 2H, $-NH_2$-), 3.59 (m, 2H, $-NH_2$-), 3.53 (s, 3H, CH_3OCH_2O-). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.1, 161.7, 144.7, 146.1, 139.8, 116.2, 113.0, 92.0, 57.3.

Ligands **L2–L4** were prepared by the similar procedures for the compound **L1.**

*Compound **L2*** (slightly yellow solid, 68%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (t, *J* = 8 Hz, 1H, aromatic), 7.54 (d, *J* = 7 Hz, 1H, aromatic), 6.86 (d, *J* = 8 Hz, 1H, aromatic), 5.54 (s, 2H, CH_3OCH_2O-), 3.86 (t, *J* = 10 Hz, 2H, $-N(CH_2)$-), 3.52 (s, 3H, CH_3OCH_2O-), 3.48 (t, *J* = 8 Hz, 2H, $-NH_2$-), 3.08 (s, 3H, $-N(CH_3)$-).

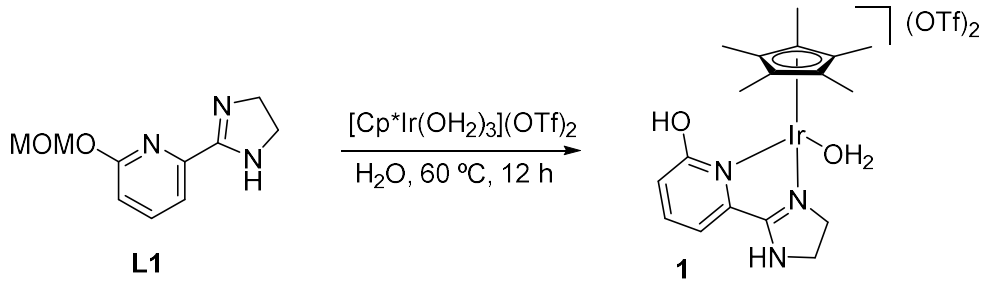
*Compound **L3*** [5] (slightly yellow oil, 75%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, *J* = 5 Hz, 1H, aromatic), 8.14 (d, *J* = 8 Hz, 1H, aromatic), 7.77 (m, 1H, aromatic), 7.36 (m, 1H, aromatic), 4.10 (t, *J* = 10 Hz, 2H, $-N(CH_2)$-), 3.59 (m, 2H, $-N(CH_2)$-).

*Compound **L4*** [6] (white solid, 89%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7 Hz, 1H, aromatic), 7.63 (t, *J* = 8 Hz, 1H, aromatic), 6.81 (d, *J* = 8 Hz, 1H, aromatic), 4.05 (t, *J* = 9 Hz, 2H, $-N(CH_2)$-), 3.94 (s, 3H, OCH_3), 3.57 (t, *J* = 9 Hz, 2H, $-N(CH_2)$-).

*3. Preparation of complexes **1** - **4**:*



In a two-necked round-bottomed flask under argon atmosphere, $[Cp^*Ir(OH_2)_3](OTf)_2$ (1.14 g, 1.68 mmol), 2-(4,5-dihydro-1*H*-imidazol-2yl)-6-(methoxymethoxy)pyridine (348 mg, 1.68 mmol),

and degassed distilled water (10 mL) were placed. The mixture was stirred at 60 °C for 12 hours. After cooling to room temperature, the mixture was washed with CH_2Cl_2 (15 mL x 3) and Et_2O (10 mL x 1). Evaporation of the water layer under vacuum gave a crude product of complex **1** as a yellow powder. The product was purified by recrystallization from water (orange crystals, 965 mg, 1.20 mmol, 71%).

Analysis: ^{1}H NMR (400 MHz, methanol-d_4): δ 8.13 (t, J = 7.2 Hz, 1H, aromatic), 7.63 (d, J = 7.2 Hz, 1H, aromatic), 7.33 (d, J = 8.0 Hz, 1H, aromatic), 4.34 (t, J = 10 Hz, 2H, -N(CH_2)-), 4.10 (t, J = 11 Hz, 2H, -N(CH_2)-), 1.77 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (100 MHz, methanol-d_4): δ 173.2, 165.6, 144.9, 144.8, 123.3(q, CF_3), 118.2, 117.4, 89.6, 53.8, 47.0, 9.7. ^{1}H NMR (500 MHz, D_2O) [6]: δ 7.97 (dd, J = 8.0 Hz, 7.0 Hz, 1H, aromatic), 7.42 (d, J = 7.0 Hz, 1H, aromatic), 7.23 (d, J = 8.0 Hz, 1H, aromatic), 4.27 (t, J = 10.5 Hz, 2H, -N(CH_2)-), 4.02 (t, J = 10.5 Hz, 2H, -N(CH_2)-), 1.70 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (125 MHz, D_2O): δ 172.5, 165.0, 144.1, 143.5, 120.3 (q, J_{CF} = 316 Hz), 117.2, 117.1, 88.6, 53.1, 46.4, 9.27. Anal. Calcd for $C_{20}H_{26}N_3O_8IrF_6S_2$: C, 29.78; H, 3.25; N, 5.21. Found: C, 29.42; H, 3.25; N, 5.14.

Complexes **2**-**4** were prepared by the similar procedures for complex **1**.

Complex **2** (61%): Analysis: ^{1}H NMR (400 MHz, methanol-d_4): δ 8.15 (t, J = 8.0 Hz, 1H, aromatic), 7.92 (d J = 8.0 Hz, 1H, aromatic), 7.35 (d, J = 8.0 Hz, 1H, aromatic), 4.20 (m, 4H, -N(CH_2CH_2)N-), 3.50 (s, 3H, NCH_3), 1.75 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (100 MHz, methanol-d_4): δ 171.3, 165.7, 144.9, 144.8, 123.3, 120.0, 117.4, 89.8, 56.7, 51.9, 35.7, 9.8. Anal. Calcd for $C_{21}H_{29}N_3O_8IrF_6S_2$•$2H_2O$: C, 29.40; H, 3.88; N, 4.90. Found: C, 29.50; H, 3.62; N, 4.92.

Complex **3** (75%): Analysis: ^{1}H NMR (400 MHz, methanol-d_4): δ 9.24 (d, J = 5.2Hz, 1H, aromatic), 8.45 (t, J = 7.6 Hz, 1H, aromatic), 8.23 (d, J = 7.6 Hz, 1H, aromatic), 8.02 (t, J = 6.4 Hz, 1H, aromatic), 4.38 (t, J = 10 Hz, 2H, -N(CH_2)-), 4.18 (t, J = 11 Hz, 2H, -N(CH_2)-), 1.80 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (100 MHz, methanol-d_4): δ 172.5, 154.3, 148.0, 143.2, 132.1, 126.8, 123.3, 89.8, 53.6, 47.4, 9.12. Anal. Calcd for $C_{20}H_{26}N_3O_7IrF_6S_2$: C, 30.38; H, 3.31; N, 5.31. Found: C, 30.29; H, 3.32; N, 5.27.

Complex **4** (88%): Analysis: ^{1}H NMR (400 MHz, methanol-d_4): δ 8.36 (t, J = 7.6 Hz, 1H, aromatic), 7.80 (d, J = 1.2 Hz, 1H, aromatic), 7.69 (d, J = 9.2 Hz, 1H, aromatic), 4.36 (m, 2H, -N(CH_2-)), 4.13 (m, 2H, -N(CH_2)-), 4.34 (s, 3H, OCH_3), 1.76 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (100 MHz, methanol-d_4): δ 173.1, 165.9, 146.2, 145.7, 123.4, 119.4, 114.4, 89.9, 59.1, 54.0, 47.1, 9.8. Anal. Calcd for $C_{21}H_{28}N_3O_8IrF_6S_2$•$2H_2O$: C, 29.44; H, 3.76; N, 4.90. Found: C, 29.72; H, 3.73; N, 4.84.

4. General procedures for the dehydrogenative oxidation of 1-phenylethanol. (Table 1 and Table 2):

In a flask under argon atmosphere, catalyst **1** (0.0025 mmol, 0.25 mol%), 1-phenylethanol (1.0 mmol), degassed distilled water (3.0 mL) and 0.1M Na_2CO_3 aq. (25 μL) were placed. The mixture was stirred under reflux for 20 hours in an oil bath (135 °C). After cooling to room temperature, the mixture was diluted with THF (10 mL). The conversion of 1-phenylethanol and the yield of acetophenone were determined by GC analysis using biphenyl as an internal standard.

5. General procedure for the dehydrogenative oxidation of secondary alcohols (Table 3):

In a flask under argon atmosphere, catalyst **1** (0.0025 mmol, 0.25 mol%), secondary alcohol (1.0 mmol), degassed distilled water (3.0 mL) and 0.1 M Na_2CO_3 aq. (25 μL) were placed. The mixture was stirred under reflux for 20 hours in an oil bath (135 °C). After cooling to room temperature, the produced ketones were isolated by column chromatography on silica gel (eluent: hexane / ethyl acetate).

4'-Methylacetophenone (**6b**) [7]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (m, 2H, aromatic), 7.26 (m, 2H, aromatic), 2.58 (s, 3H, -$COCH_3$), 2.41 (s, 3H, -CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 197.8, 143.8, 134.7, 129.2, 128.4, 26.5, 21.6.

4'-Methoxyacetophenone (**6c**) [8]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (m, 2H, aromatic), 6.93 (m, 2H, aromatic), 3.87 (s, 3H, OCH_3), 2.56 (s, 3H, -$COCH_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 196.8, 163.5, 130.6, 130.3, 114.0, 55.5, 26.3.

4'-(N, N-dimethylamino)acetophenone (**6d**) [7]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 6.8 Hz, 2H, aromatic), 6.64 (m, 2H, aromatic), 3.03 (s, 6H), 2.49 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 196.4, 153.4, 130.5, 125.1, 110.6, 40.0, 26.0.

4′-Trifluoromethylacetophenone (**6e**) [9]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.4 Hz, 2H, aromatic), 7.71 (d, *J* = 7.6 Hz, 2H, aromatic), 2.63 (s, 3H, -$COCH_3$). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 197.1, 139.8, 134.4 (q, J_{CF} = 32.4 Hz), 128.7, 125.8 (d, J_{CF} = 2.8 Hz), 123.7 (q, J_{CF} = 271.8 Hz), 26.9.

4′-Fluoroacetophenone (**6f**) [9]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (m, 2H, aromatic), 7.08 (t, *J* = 8.8 Hz, 2H, aromatic), 2.54 (s, 3H, -$COCH_3$). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 196.5, 165.8 (d, J_{CF} = 253.6 Hz), 133.6, 131.0 (d, J_{CF} = 8.5 Hz), 115.6 (d, J_{CF} = 21.9 Hz), 26.5.

4′-Chloroacetophenone (**6g**) [10]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (ddd, *J* = 8.4, 2.4, 1.6 Hz, 2H, aromatic), 7.42 (dt, *J* = 8.8, 2.0 Hz, 2H, aromatic), 2.59 (s, 3H, -$COCH_3$). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 196.7, 139.6, 135.5, 129.6, 128.9, 26.6.

3′-Methylacetophenone (**6h**) [11]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (m, 2H, aromatic), 7.33 (m, 2H, aromatic), 2.57 (s, 3H, -$COCH_3$), 2.40 (s, 3H, -CH_3). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 198.4, 138.3, 137.1, 133.9, 128.8, 128.4, 125.6, 26.7, 21.3.

3′-Methoxyacetophenone (**6i**) [8]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (m, 1H, aromatic), 7.45 (m, 1H, aromatic), 7.33 (m, 1H, aromatic), 7.07 (m, 1H, aromatic), 3.81 (s, 3H, -OCH_3) 2.56 (s, 3H, -$COCH_3$). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 197.9, 159.8, 138.5, 129.6, 121.1, 119.6, 112.4, 55.4, 26.7.

3′-Chloroacetophenone (**6j**) [11]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (m, 1H, aromatic), 7.79 (m, 1H, aromatic), 7.49 (m, 1H, aromatic), 7.37 (t, *J* = 8.0 Hz, 1H, aromatic), 2.56 (s, 3H, -$COCH_3$). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 196.8, 138.6, 134.9, 133.1, 130.0, 128.4, 126.5, 26.7.

1-Indanone (**6k**) [12]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.6 Hz, 1H, aromatic), 7.54 (m, 1H, aromatic), 7.44 (m, 1H, aromatic), 7.32 (m, 1H, aromatic), 3.09 (t, *J* = 6.0 Hz, 2H), 2.70-2.63 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 207.0, 155.2, 137.2, 134.6, 127.2, 126.7, 123.6, 36.2, 25.8.

α-Tetralone (**6l**) [12]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (m, 1H, aromatic), 7.45 (m, 1H, aromatic), 7.32-7.18 (m, 2H, aromatic), 2.92 (m, 2H), 2.61 (m, 2H), 2.07 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 198.1, 144.4, 133.2, 132.9, 128.7, 126.9, 126.4, 39.0, 29.5, 23.1

Propiophenone (**6m**) [11]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (m, 2H, aromatic), 7.52 (m, 1H, aromatic), 7.43 (m, 2H, aromatic), 2.99 (q, *J* = 7.2 Hz, 2H, CH_2CH_3), 1.21 (t, *J* = 7.2 Hz, 3H, CH_2CH_3). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 200.8, 136.9, 132.9, 128.6, 128.0, 31.8, 8.3.

*6. Procedure for the quantitative analysis of the evolved hydrogen gas in the dehydrogenative oxidation of 1-indanol (**5k**) or 1,2-benzenedimethanol(**7a**) catalyzed by complex **1** (eq. 1).*

The reaction setup is shown in Figure S1. In a flask connected with a gas burette through a condenser under argon atmosphere, catalyst **1** (20.3 mg, 0.025 mmol), distilled water (30 mL), 0.1M Na_2CO_3 aq. (250 μL) and 1-indanol (1.35 g, 10 mmol) were placed. The mixture was stirred under reflux for 20 h in an oil bath (135 °C). The yield of 1-indanone was determined by ^{1}H NMR($CDCl_3$) using triphenylmethane as an internal standard. The volume of evolved gas was measured by a gas burette. The molar amount of hydrogen was calculated using the ideal gas law. The purity of evolved hydrogen gas was confirmed by GC analysis as shown in Figure S2.

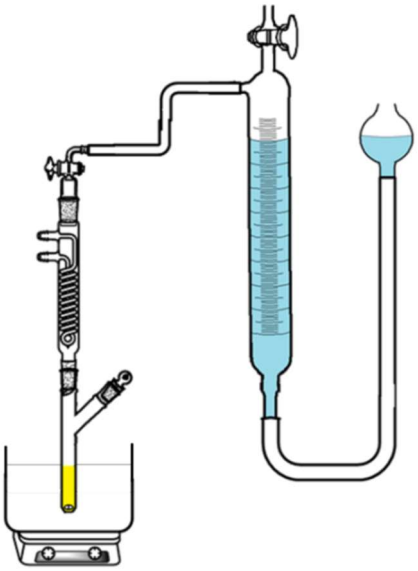


Figure S1. Reaction setup for the quantitative analysis of the evolved hydrogen gas.

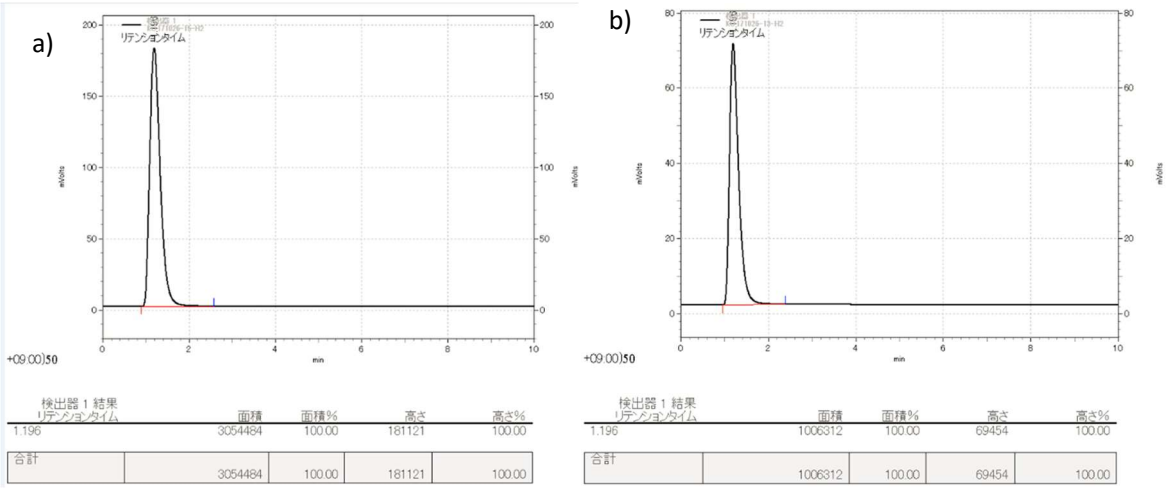


Figure S2. GC analyses of the hydrogen gas. a) The chromatogram of the evolved gas by the reaction of 1-indanol. b) The chromatogram of the standard gas of pure hydrogen.

7. Experiments for the isolation of catalytic active species

*Preparation of monocationic complex **9***

In a flask under argon atmosphere, complex **1** (101.6 mg, 0.126 mmol) was placed. 0.1 M Na_2CO_3 aq. (1.25 mL) was added and stirred for 10 minutes at room temperature. Then, the solvent water was evaporated by the vacuum pump and the deposed dark green powder remained. The powder was dissolved in dry CH_2Cl_2 and filtered by Celite under argon atmosphere. The filtrate organic layer was washed by distilled water (10 mL x 4) under argon atmosphere, then the solvent was removed by evaporation and the dark green powder was obtained (27.2 mg, 0.041 mmol, 33%).

*Complex **9***

^{1}H NMR (500 MHz, D_2O): δ 7.52 (t, J = 7.5 Hz, 1H, aromatic), 6.88 (br, 1H, aromatic), 6.67 (d, J = 8.0 Hz, aromatic), 4.10 (br, 2H, -CH_2-), 3.86 (br, 2H, -CH_2-), 1.68 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (125 MHz, D_2O): δ 170.7, 143.7, 139.4, 122.2, 120.3 (q, J_{CF} = 316 Hz), 110.8, 87.6 (br), 53.2, 9.53.

In the $^{13}C\{^1H\}$ NMR spectra, the quartet signal which was assigned to the carbon in trifluoromethanesulfonate was observed. Thus, the complex **9** must contain trifluoromethanesulfonate as a counter anion, suggesting that **9** would be a mono-cationic species.

*NMR Analysis of the reaction of complex **1** with Na_2CO_3 in D_2O.*

In an NMR tube, complex **1** (4.0 mg, 0.0050 mmol), 0.1 M Na_2CO_3 aq. (25.0-100.0 μL, 0.5-2.0 equiv.), D_2O (0.4 mL) were placed. *tert*-BuOH (2.0 μL) was added as an internal standard. The color of the solution immediately changed to green. Then, the sample analyzed by ^1H NMR spectroscopy. All spectral data are shown in Figure S3. When 0.5 equivalent of Na_2CO_3 was added, all aromatic peaks were shifted to upfield. This observation suggests that the one proton, probably on the hydroxy group on the pyridine ring, would be abstracted by the base and the α-hydroxypyridine structure must be changed to the α-pyridonate structure. Further addition of Na_2CO_3 did not cause the change of chemical shift of signals, therefore, other protons in the mono-cationic complex **9** would be difficult to be abstracted. On the basis of these observations, we conclude that the complex **1** easily release one proton in the presence of base to afford the mono-cationic complex **9**, which must be a catalytically active species for the dehydrogenative oxidation of alcoholic substrates in aqueous media.

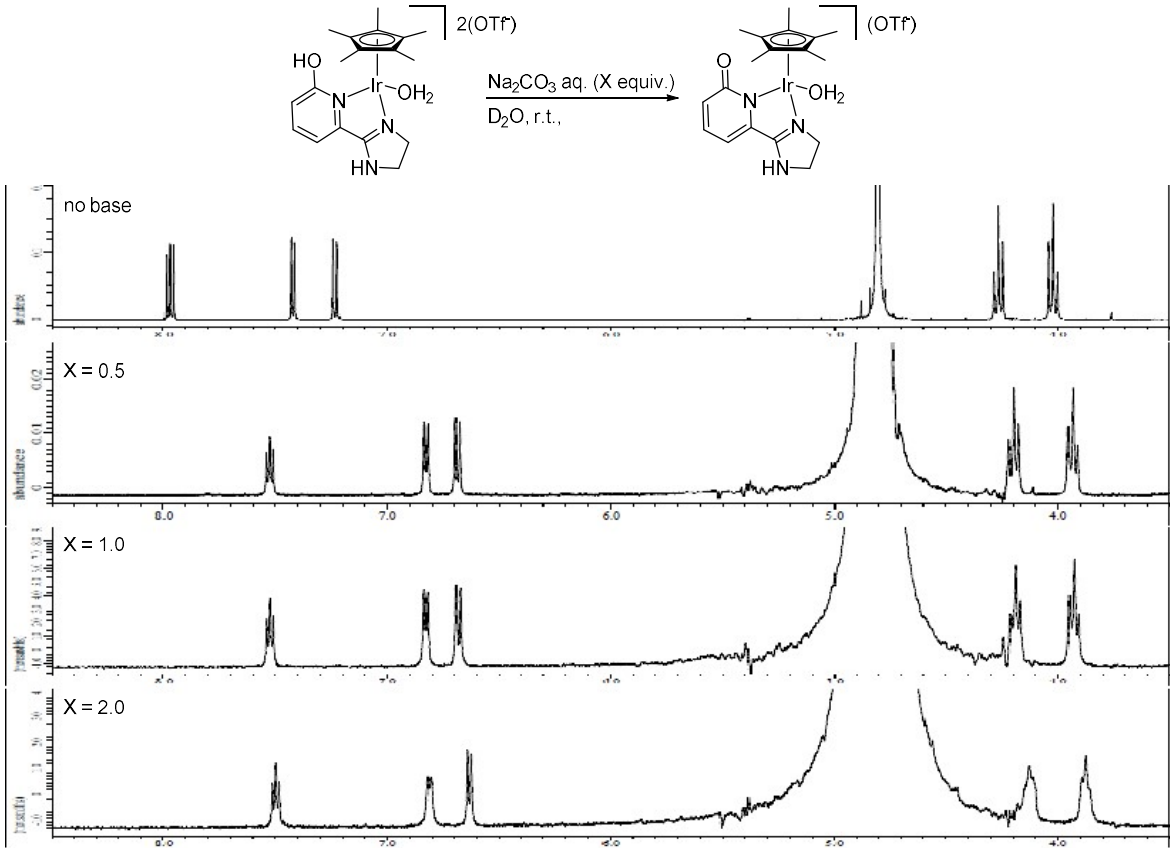


Figure S3: ^1H NMR(D_2O) experiment for detection of the active species.

Figure S3. ^1H NMR(D_2O) experiment for detection of the active species.

8. General procedure for the dehydrogenative lactonization of benzylic diols (Table 4):

In two-necked test tube under argon atmosphere, catalyst **1** (0.0025 mmol, 0.25 mol%), diol (1.0 mmol), distilled water (1.5 mL) and 0.1 M Na_2CO_3 aq. (25 μL, 0.0025 mmol, 0.25 mol%) were placed. The mixture was stirred under reflux for 20 hours in an oil bath (135 °C). After cooling to room temperature, the solvent was evaporated. The yield of the product was determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. The product was isolated by silica gel column chromatography (eluent: hexane / ethyl acetate).

Phthalide (**8a**) [13]: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.5 Hz, 1H, aromatic), 7.71 (td, *J* = 7.5, 1.0 Hz, 1H, aromatic), 7.56-7.52 (m, 2H, aromatic), 5.34 (s, 2H, -CH_2-). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 171.2, 146.6, 134.1, 129.0, 125.6, 125.6, 122.2, 69.7.

3-Phenyl-1(3H)-isobenzofuranone (**8b**) [14]: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.5 Hz, 1H, aromatic), 7.66 (t, *J* = 7.5 Hz, 1H, aromatic), 7.56 (t, *J* = 7.5 Hz, 1H, aromatic), 7.41-7.36 (m, 3H, aromatic), 7.34 (d, *J* = 7.5 Hz, 1H, aromatic), 7.30-7.27 (m, 2H, aromatic). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 170.7, 149.8, 136.5, 134.5, 129.5, 129.4, 129.1, 127.1, 125.8, 125.7, 123.0, 82.9.

Naphtho[2,3-c]furan-1(3H)-one (**8c**) [13]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H, aromatic), 8.06 (d, *J* = 8.4 Hz, 1H, aromatic), 7.96 (d, *J* = 8.4 Hz, 1H, aromatic), 7.92 (s, 1H, aromatic), 7.67 (td, *J* = 6.8, 1.2 Hz, 1H, aromatic), 7.61 (t, *J* = 8.0 Hz, 1H, aromatic), 5.5 (s, 2H, -CH_2-). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 171.1, 140.1, 136.3, 133.2, 130.0, 129.1, 128.2, 127.1, 127.1, 123.5, 120.1, 69.8.

1H,3H-Naphtho[1,8-cd]pyran-1-one (**8d**) [13]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (dd, *J* = 7.6, 0.8 Hz, 1H, aromatic), 8.08 (d, *J* = 8.0 Hz, 1H, aromatic), 7.81 (d, *J* = 8.4 Hz, 1H, aromatic), 7.62 (dd, *J* = 8.0, 7.2 Hz, 1H, aromatic), 7.53 (t, *J* = 7.2 Hz, 1H, aromatic), 7.34 (dd, *J* = 7.2, 0.8 Hz, 1H, aromatic), 5.79 (s, 2H, -CH_2-). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 170.3, 139.0, 137.3, 132.7, 131.9, 130.7, 130.2, 128.8, 128.7, 128.6, 128.5, 69.2.

3,4-Dihydro-1H-2-Benzopyran-1-one (**8ea**) [15], *1,4-Dihydro- 3H-2-Benzopyran-3-one* (**8eb**) [16]: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (dd, *J* = 6.4, 0.8 Hz 1H), 7.55 (td, *J* = 6.0, 1.2 Hz, 1H), 7.41(t, *J* = 6.0 Hz, 1H), 7.27 (m, 1H), 4.55 (t, *J* = 4.8 Hz, 2H), 3.08 (t, *J* = 4.8 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 165.0, 139.5, 133.6, 130.1, 127.5, 127.2, 125.1, 67.2, 27.6. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.23 (m, 4H), 5.32 (s, 2H), 3.72 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 170.7, 131.5, 130.9, 128.6, 126.9, 124.5, 69.9, 36.1.

6-Methyl-1(3H)-Isobenzofuranone (**8fa**) [13], *5-Methyl- 1(3H)-Isobenzofuranone* (**8fb**) [13]: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 5.27 (s, 2H), 2.50 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 171.2, 143.8, 139.1, 135.1, 125.6, 125.3, 121.8, 69.6, 21.1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.29 (s, 1H), 5.29 (s, 2H), 2.47 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 171.1, 147.1, 145.2, 130.0, 125.3, 122.9, 122.4, 69.4, 21.9.

6-Fluoro-1(3H)-Isobenzofuranone (**8ga**) [17]: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 2.5, 7.0 Hz, 1H, aromatic), 7.49 (m, 1H, aromatic), 7.42 (td, *J* = 2.5, 8.5 Hz, 1H, aromatic), 5.32 (s, 2H, -CH_2-). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 170.1 (d, J_{CF} = 3.5 Hz), 163.2 (d, J_{CF} = 248.0 Hz), 142.0, 127.9 (d, J_{CF} = 9.6 Hz), 123.9 (d, J_{CF} = 8.4 Hz), 122.2 (d, J_{CF} = 23.9 Hz), 112.3 (d, J_{CF} = 23.9 Hz), 69.6 (s).

5-Fluoro-1(3H)-Isobenzofuranone (**8gb**) [17]: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (dd, *J* = 8.5, 5.0 Hz, 1H, aromatic), 7.25 (td, *J* = 8.8, 2.0 Hz, 1H, aromatic), 7.20 (dd, *J* = 7.5, 1.5 Hz, 1H, aromatic), 5.32 (s, 2H, -CH_2-). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 170.0, 166.7 (d, J_{CF} = 255.1 Hz), 149.4 (d, J_{CF} = 10.8 Hz), 128.2 (d, J_{CF} = 9.5 Hz), 122.0, 117.5 (d, J_{CF} = 23.8 Hz), 109.6 (d, J_{CF} = 23.9 Hz), 69.1 (d, J_{CF} = 3.6 Hz).

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10. ^{1}H and ^{13}C NMR Spectora of products

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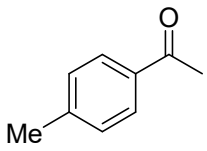

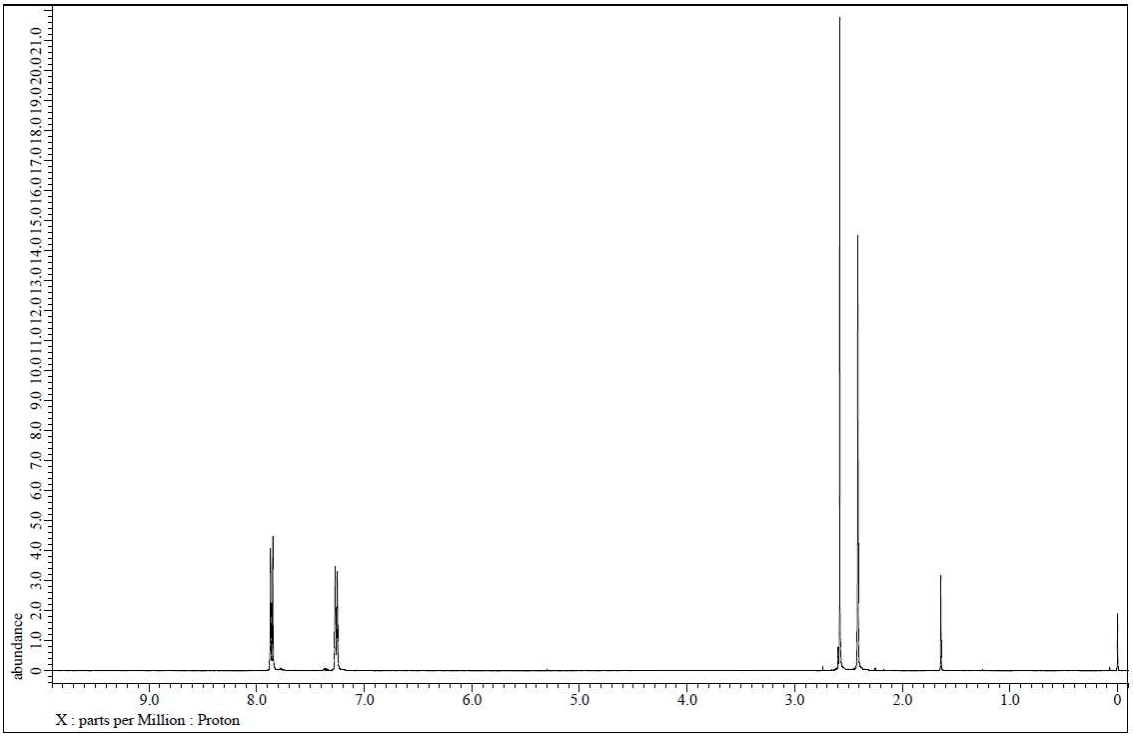

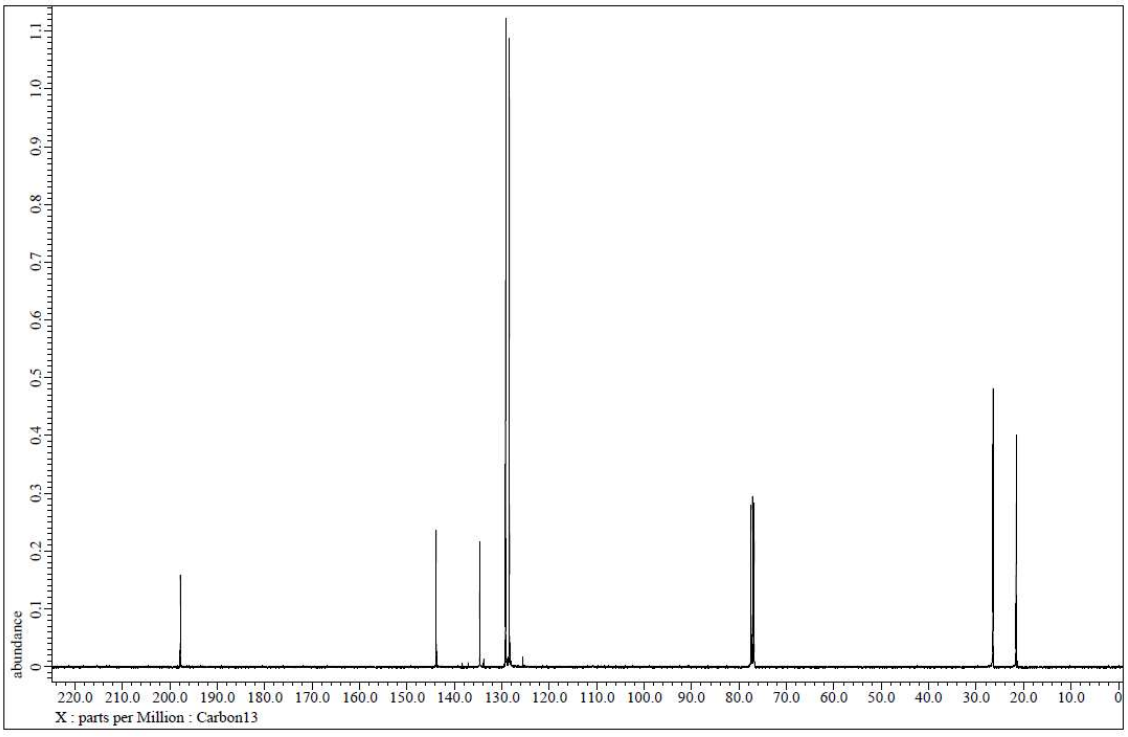

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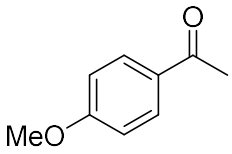
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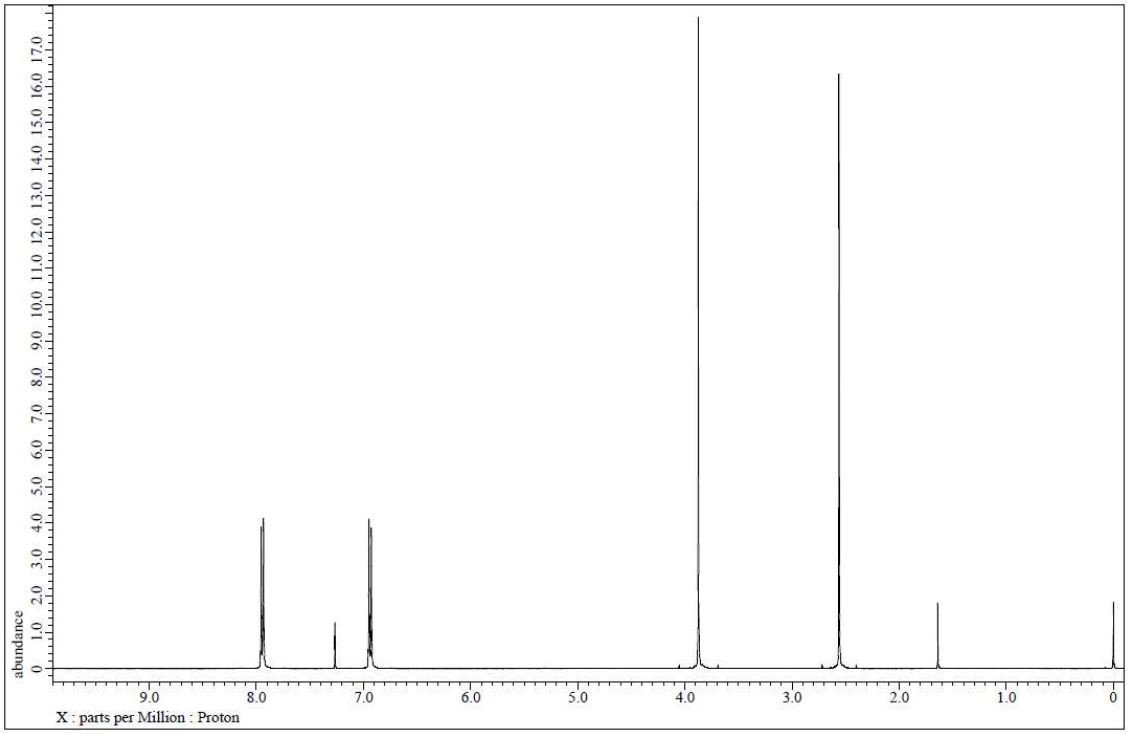
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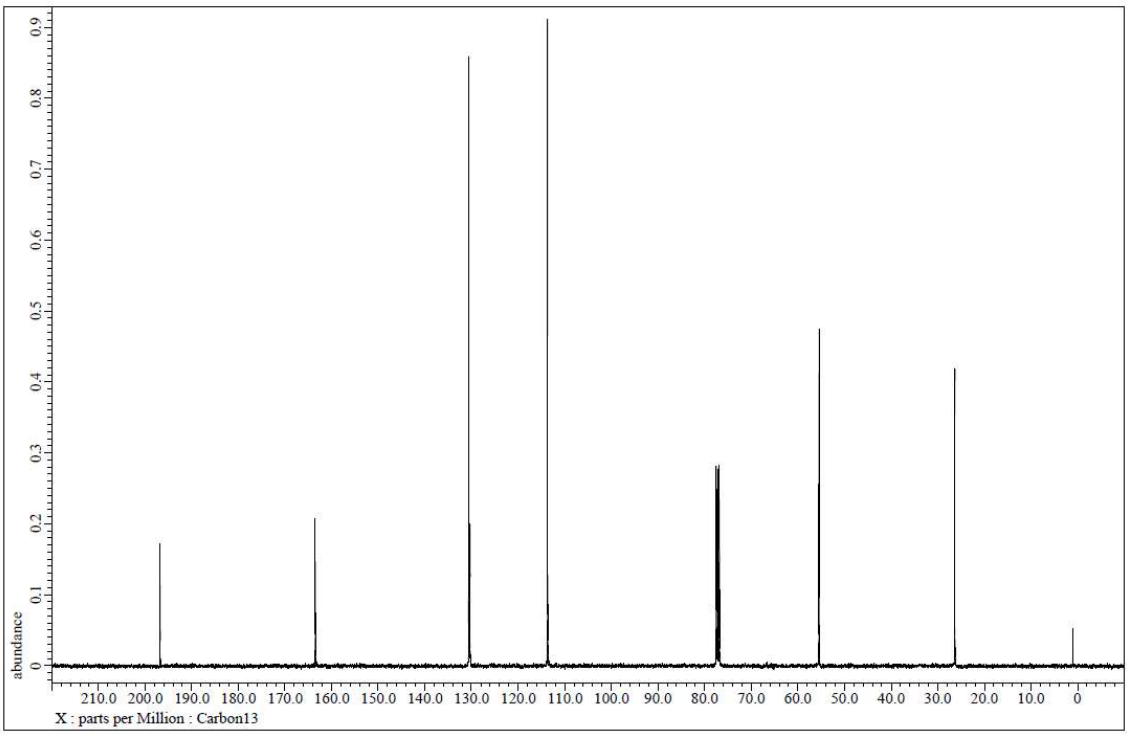
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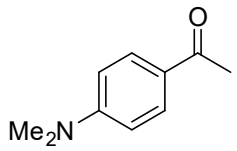
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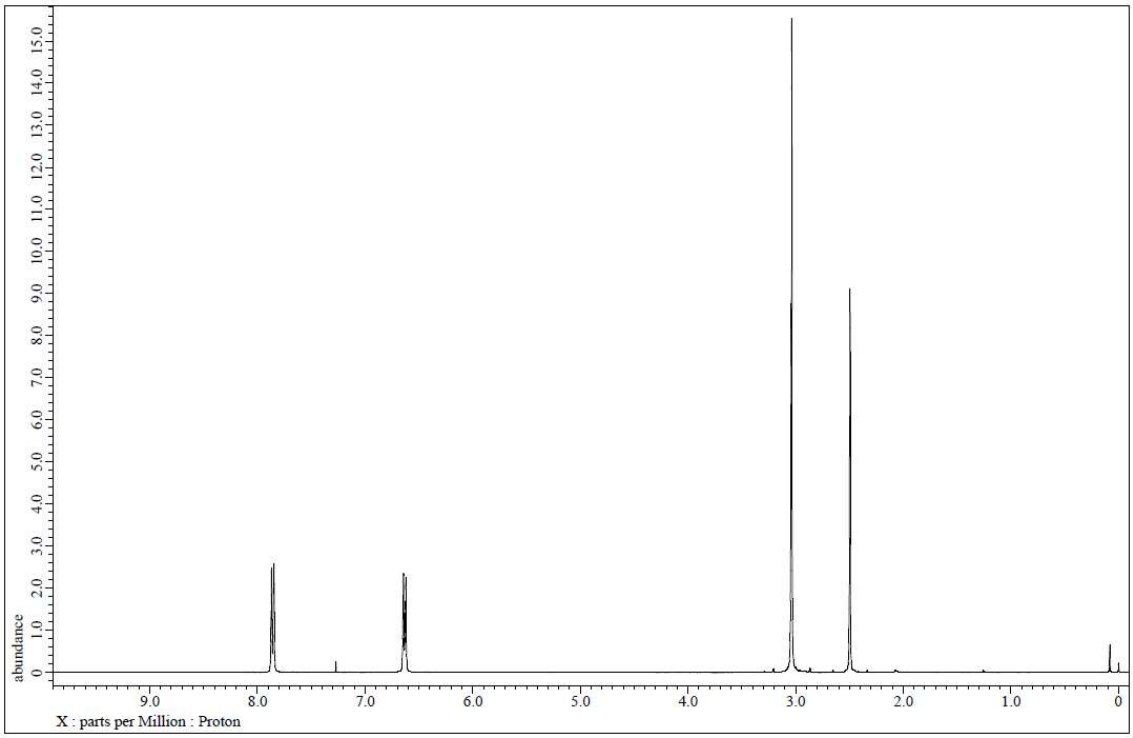
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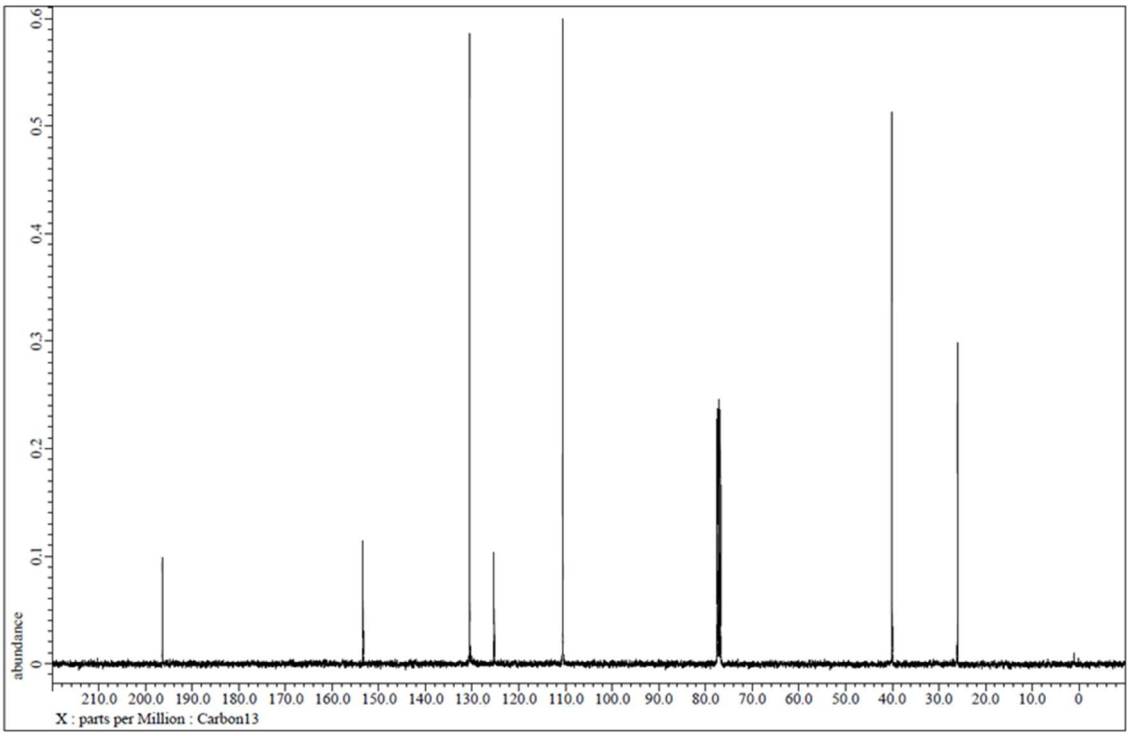
abundance
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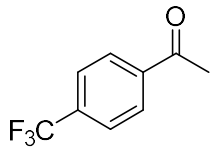
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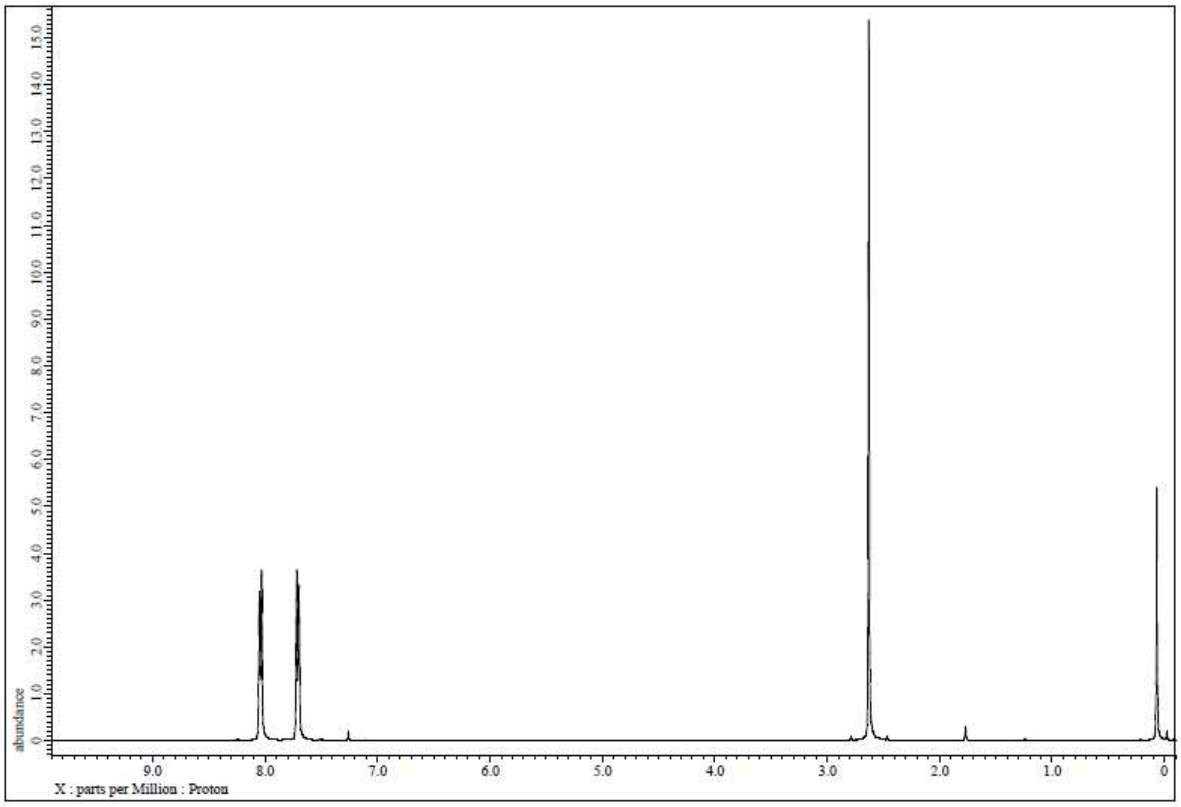
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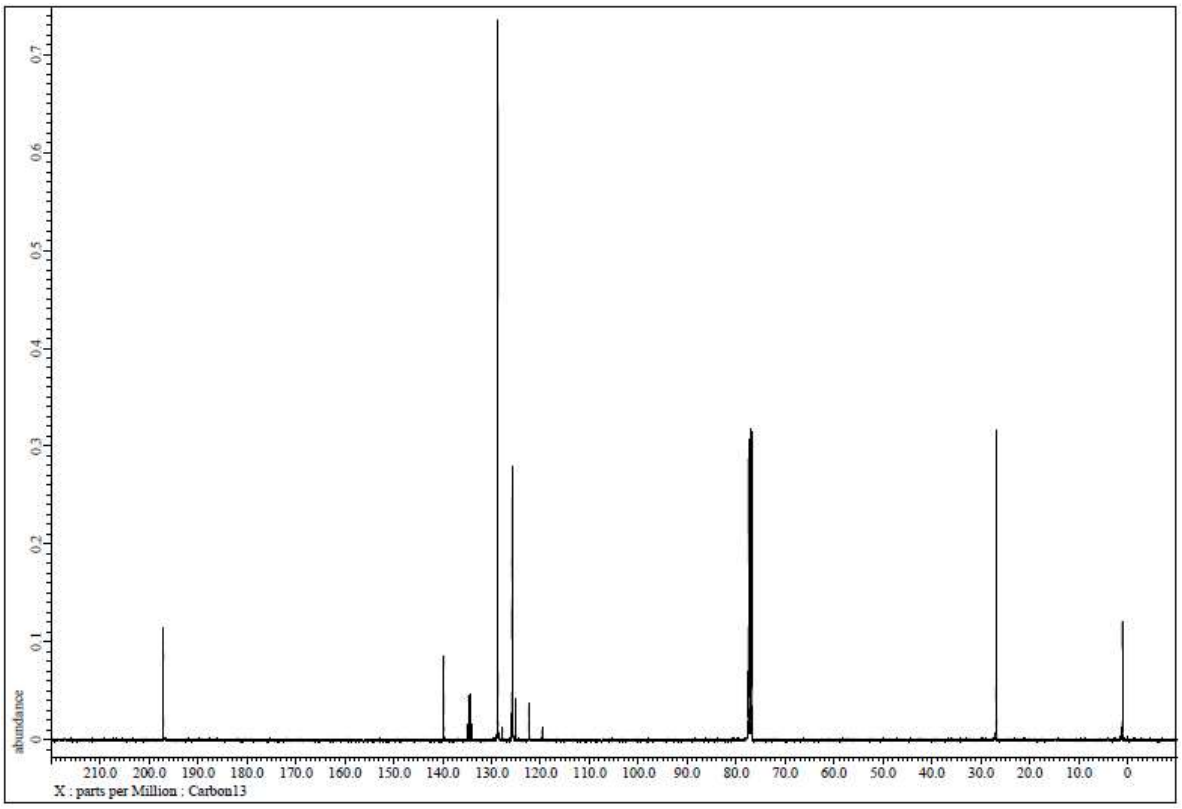
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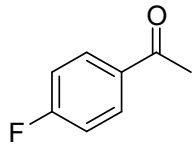
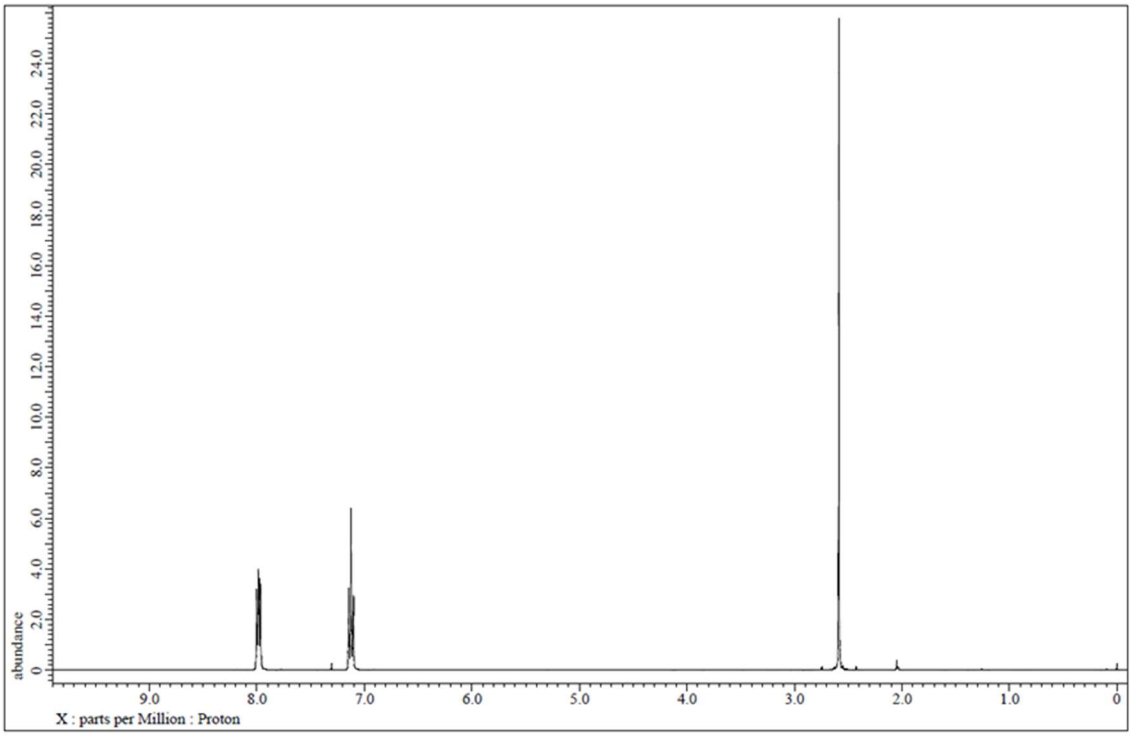
Compound 6f


O
F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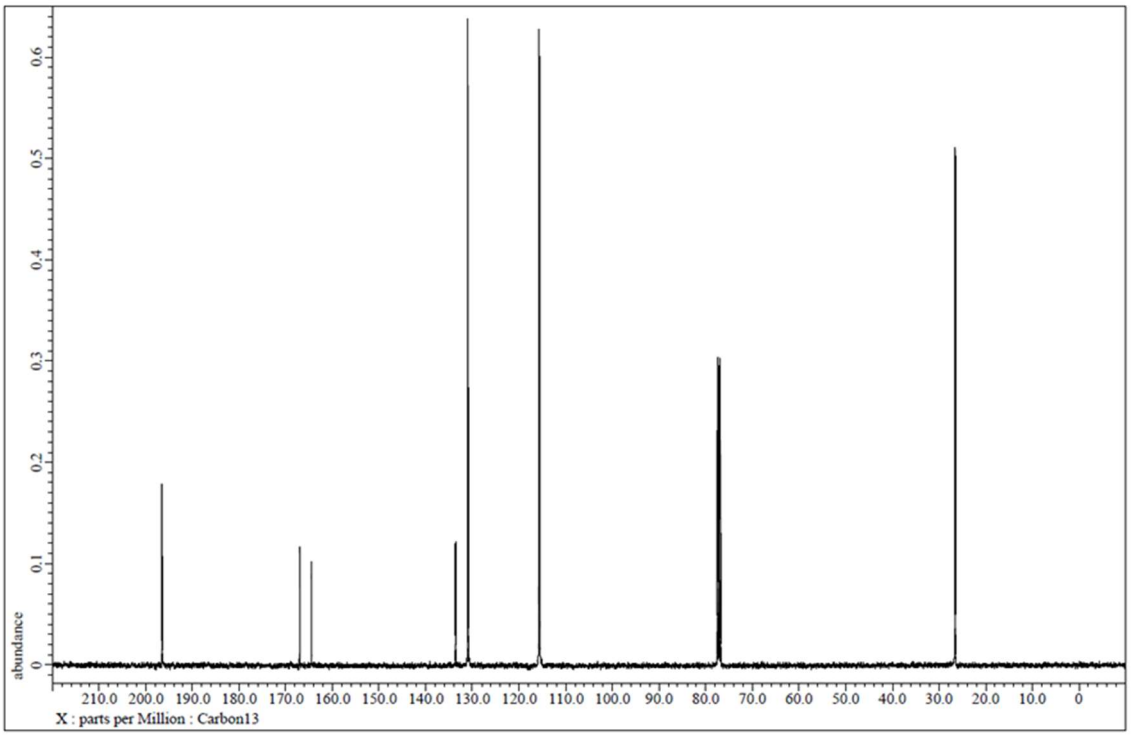
X : parts per Million : Proton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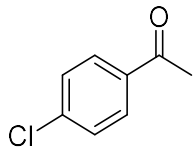
X : parts per Million : Carbon13

Compound **6g**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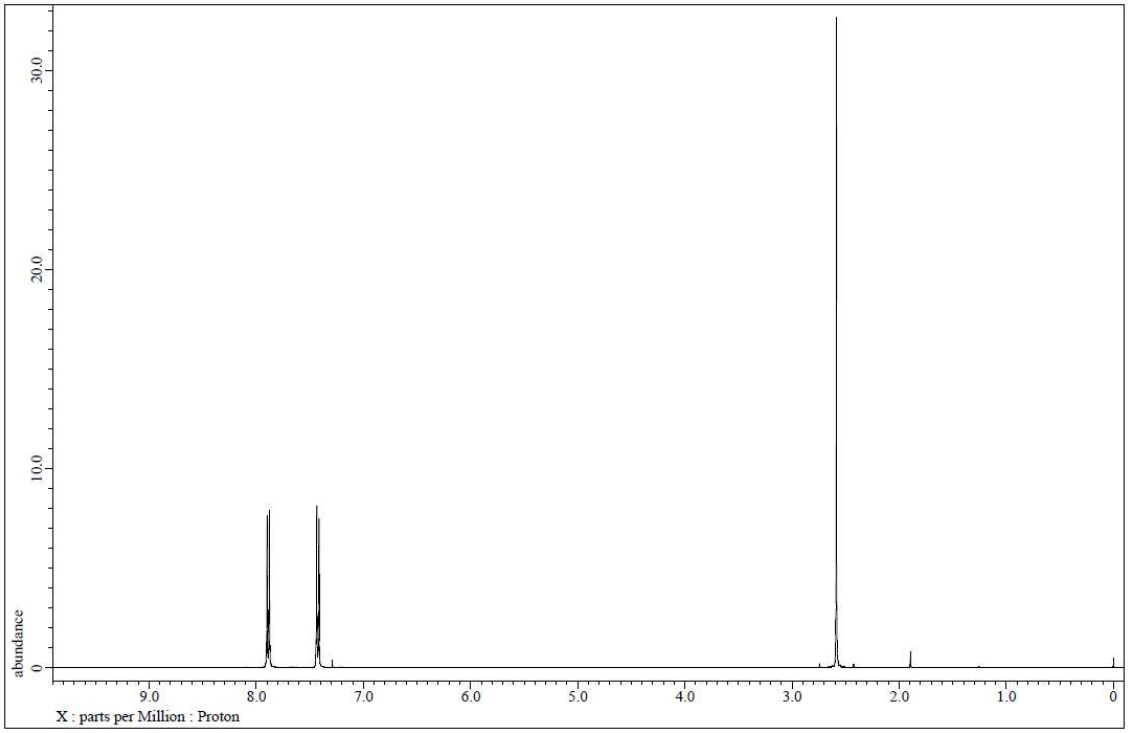
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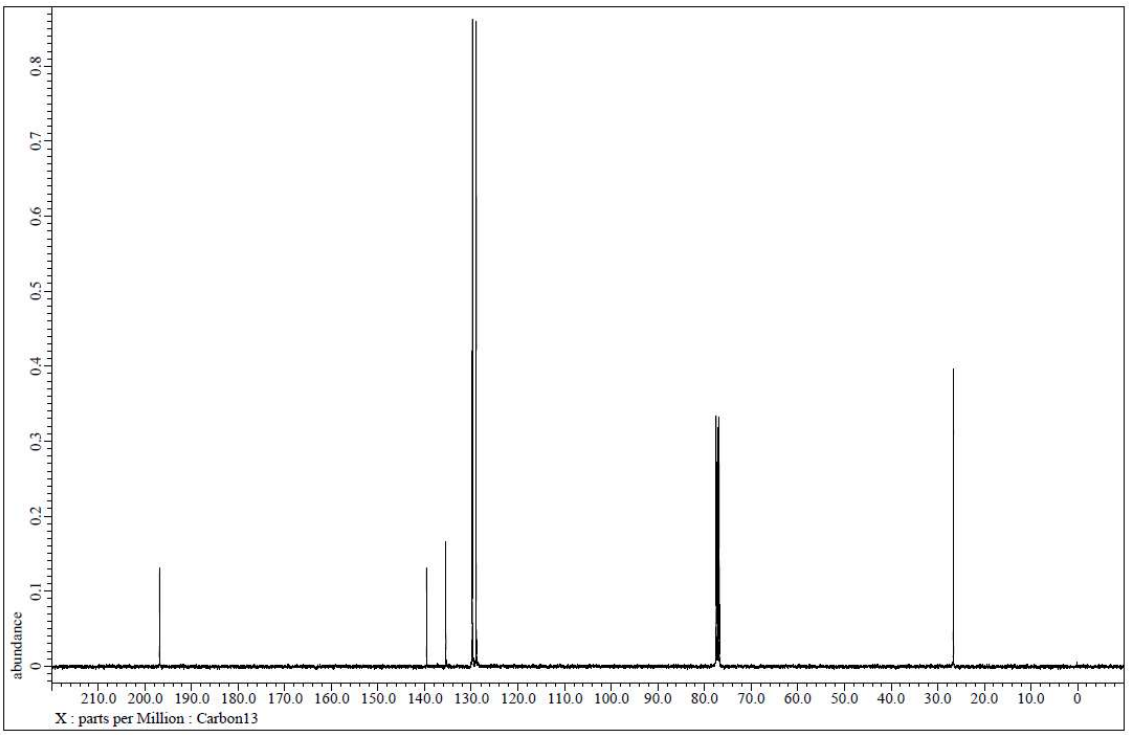
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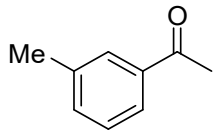
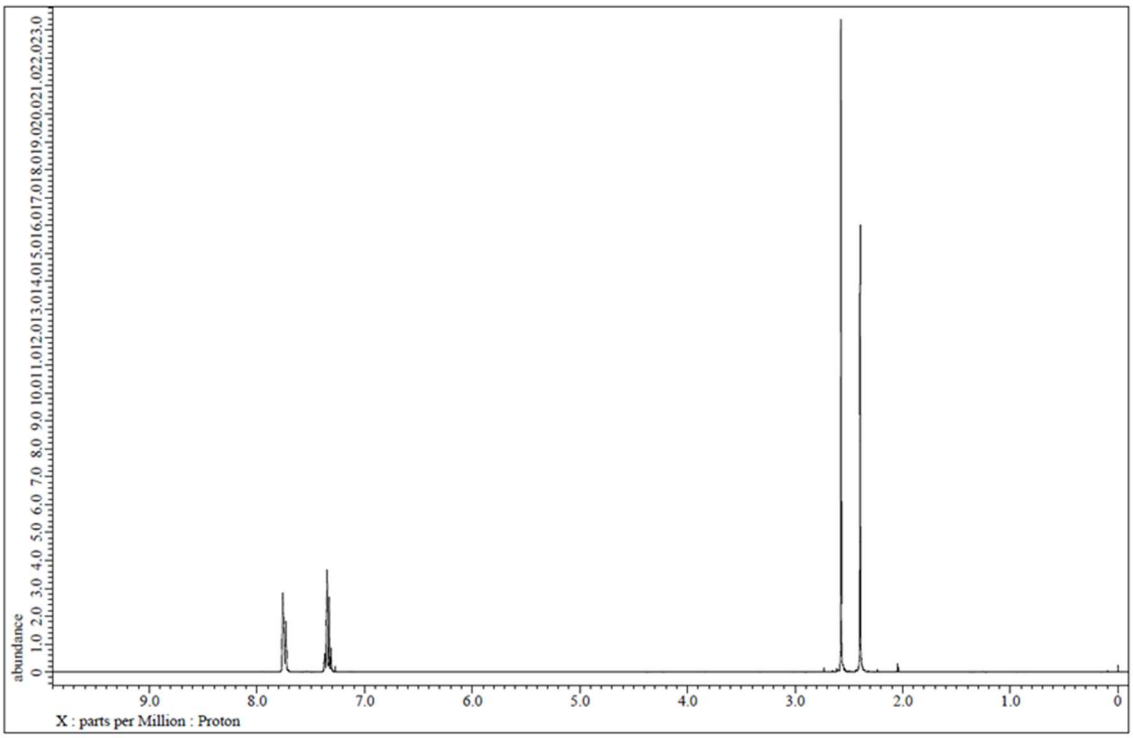
Compound **6h**


Me
O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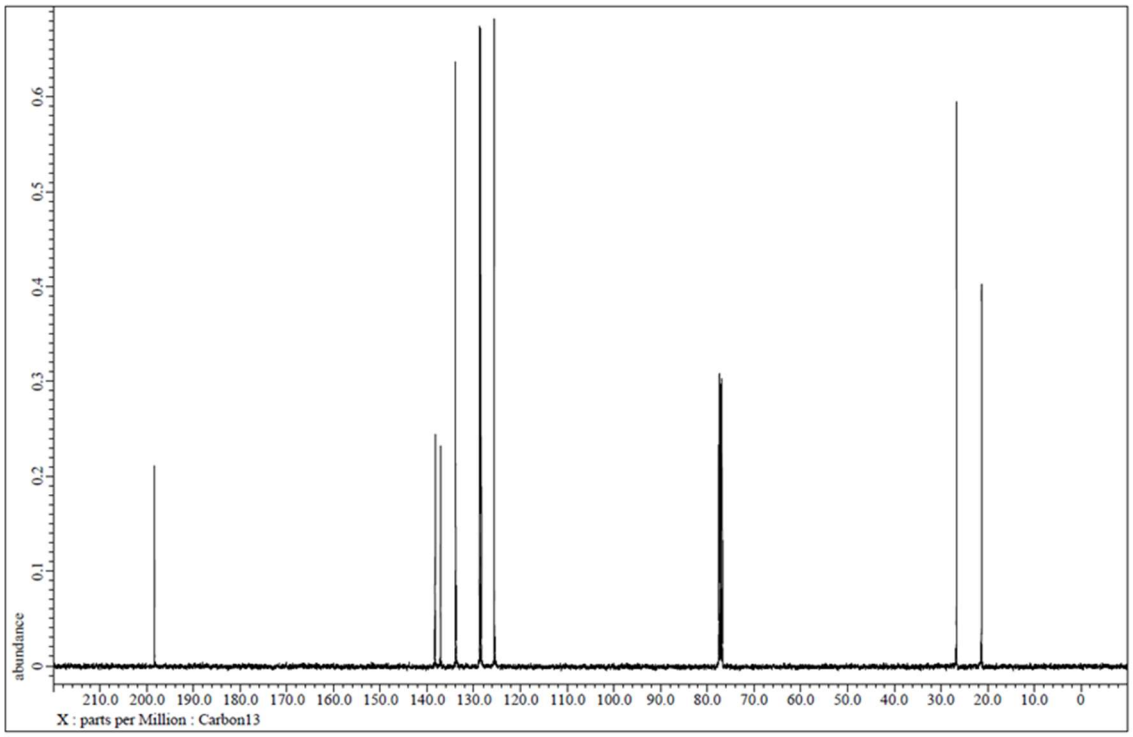
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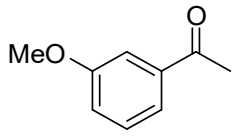
Compound **6i**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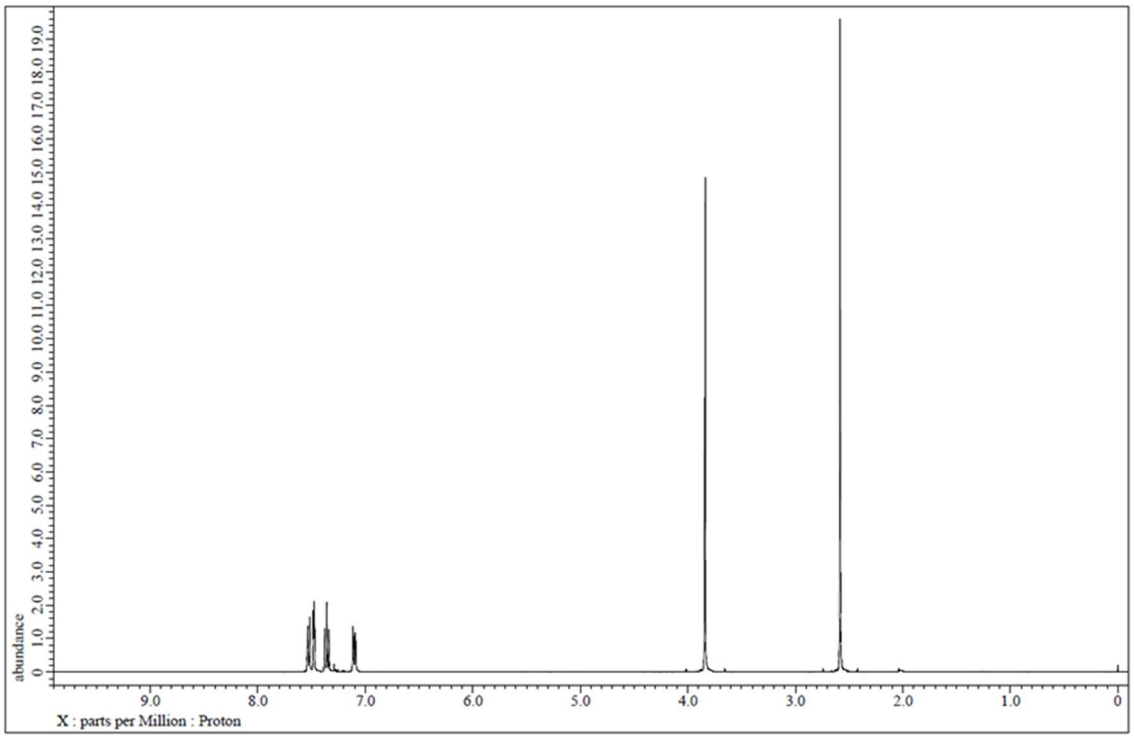
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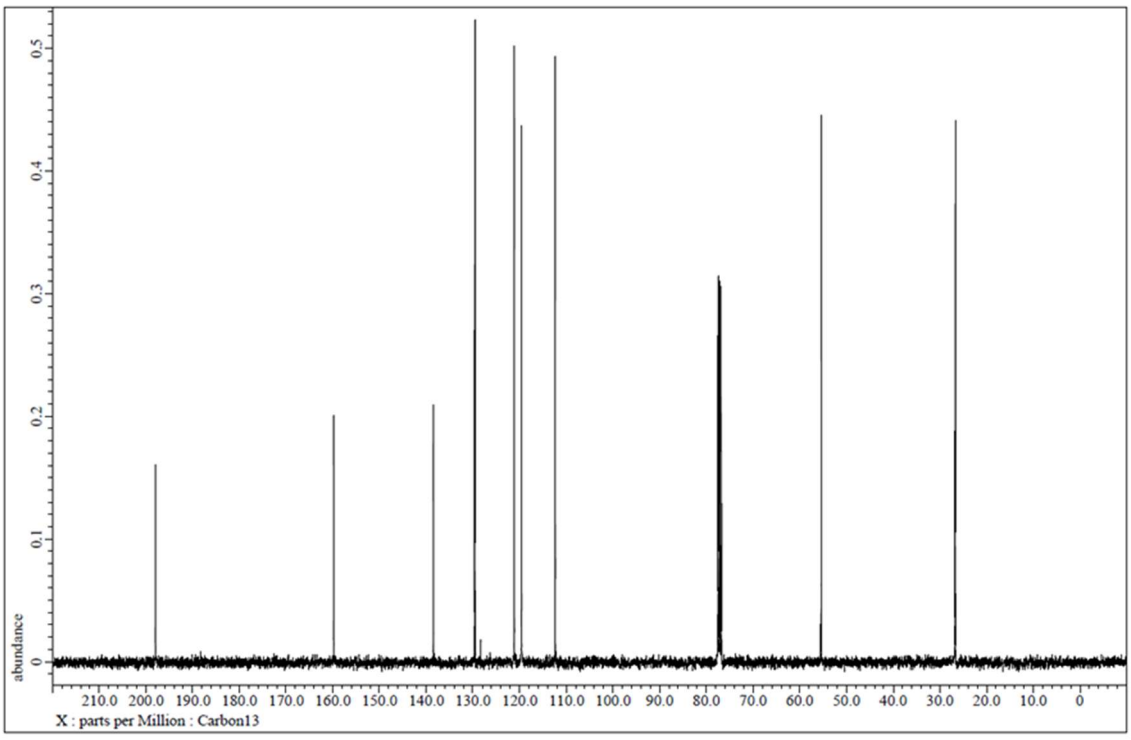
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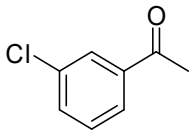
Compound **6j**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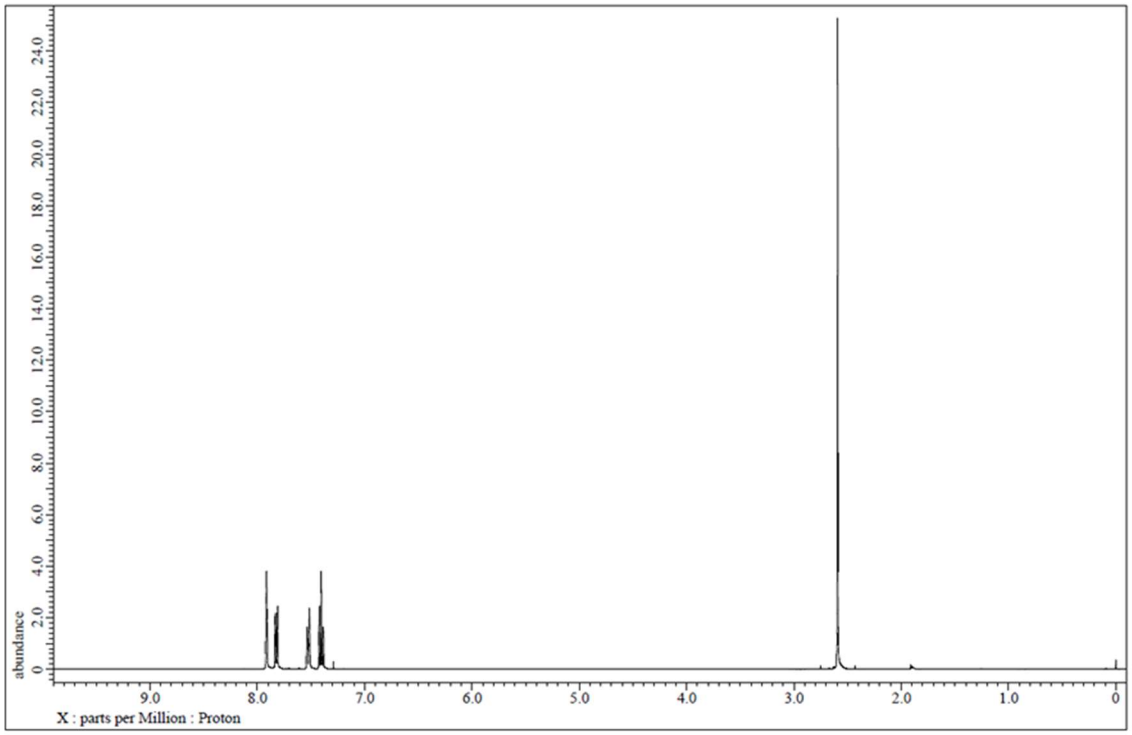
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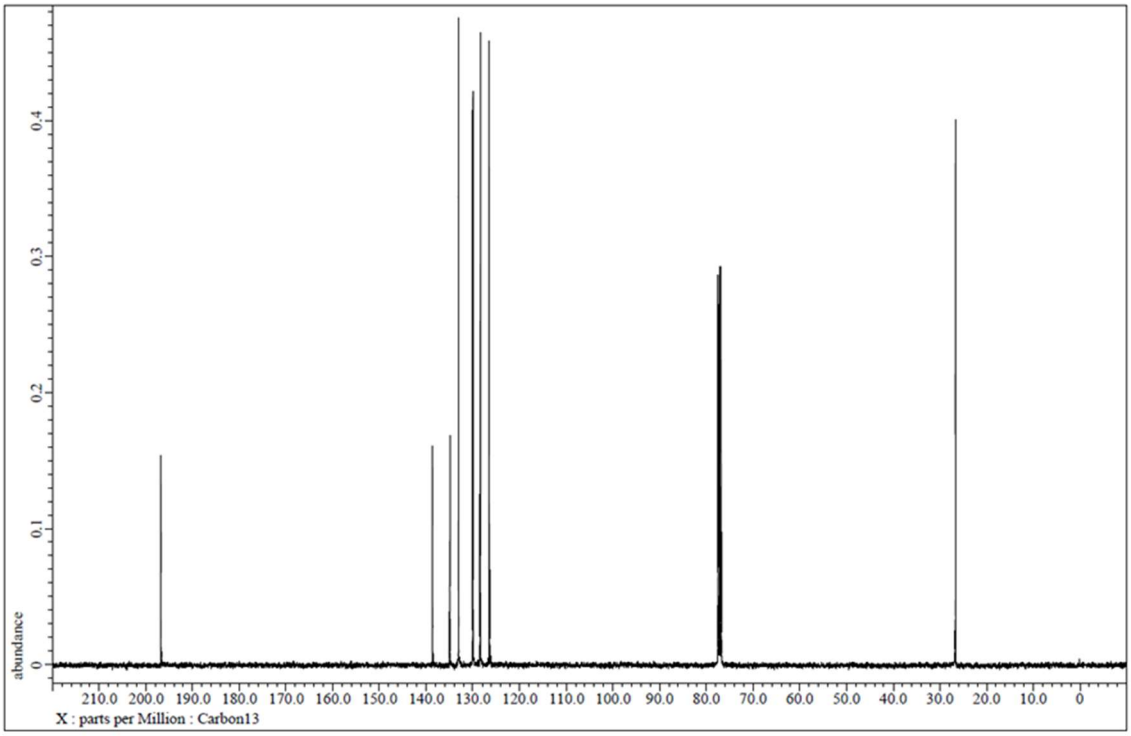
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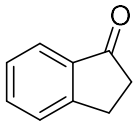

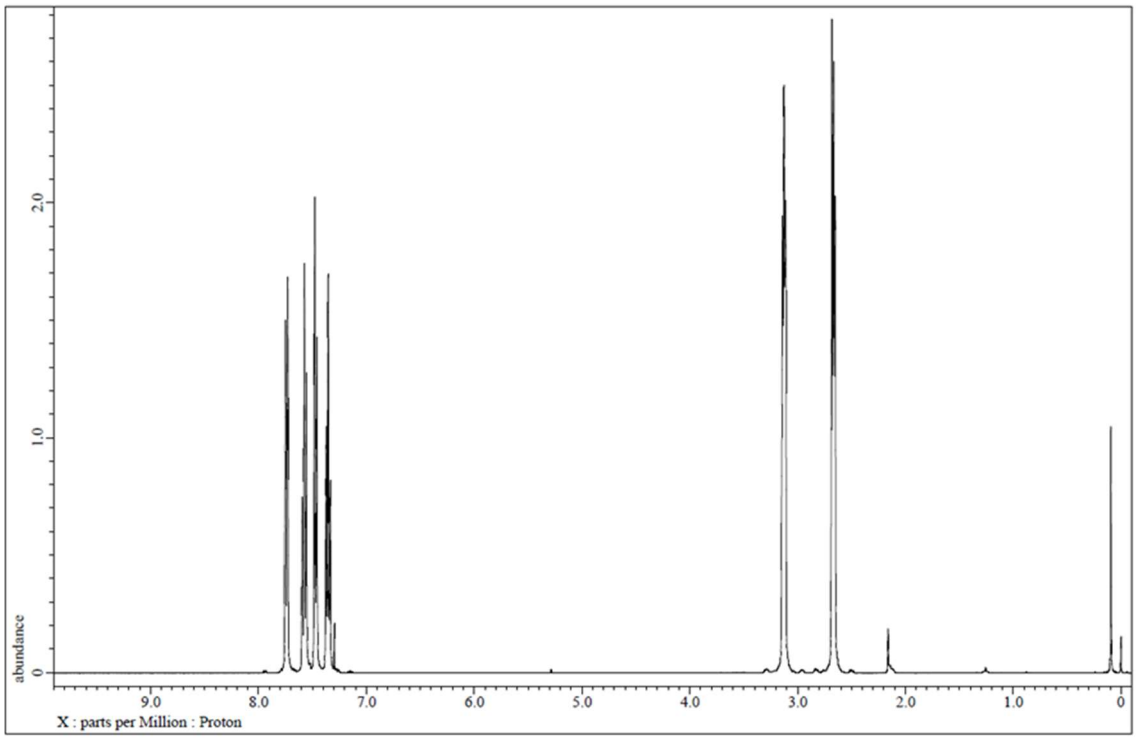
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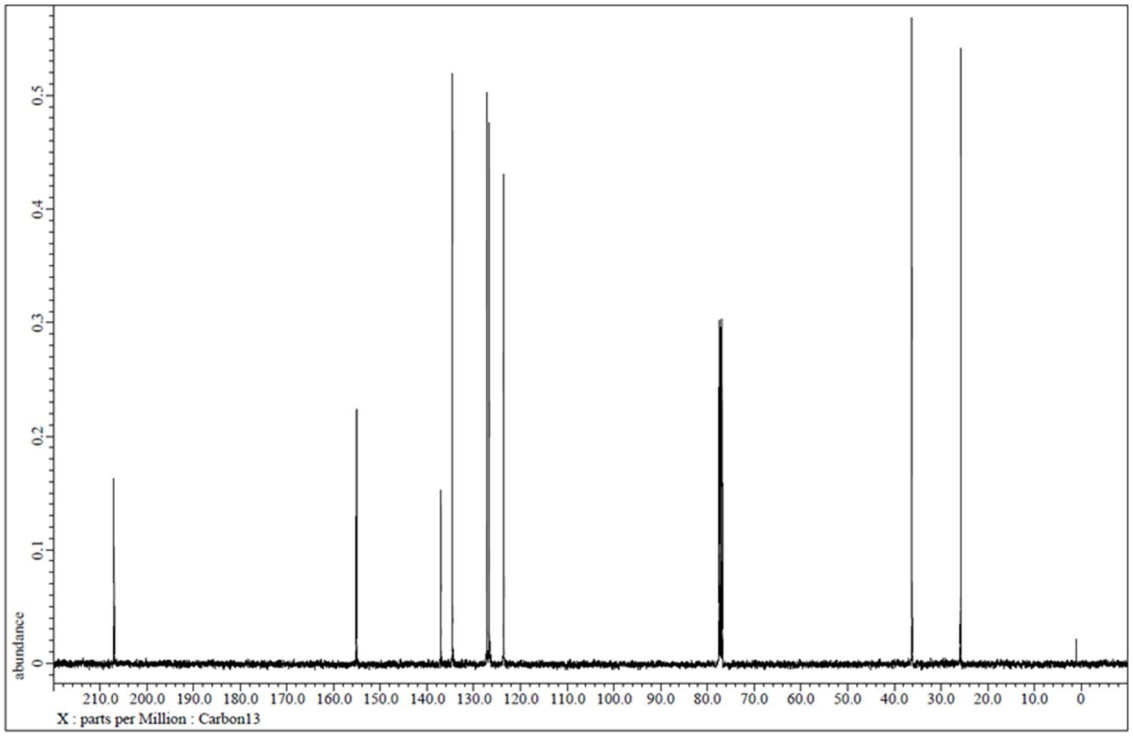
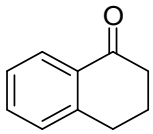
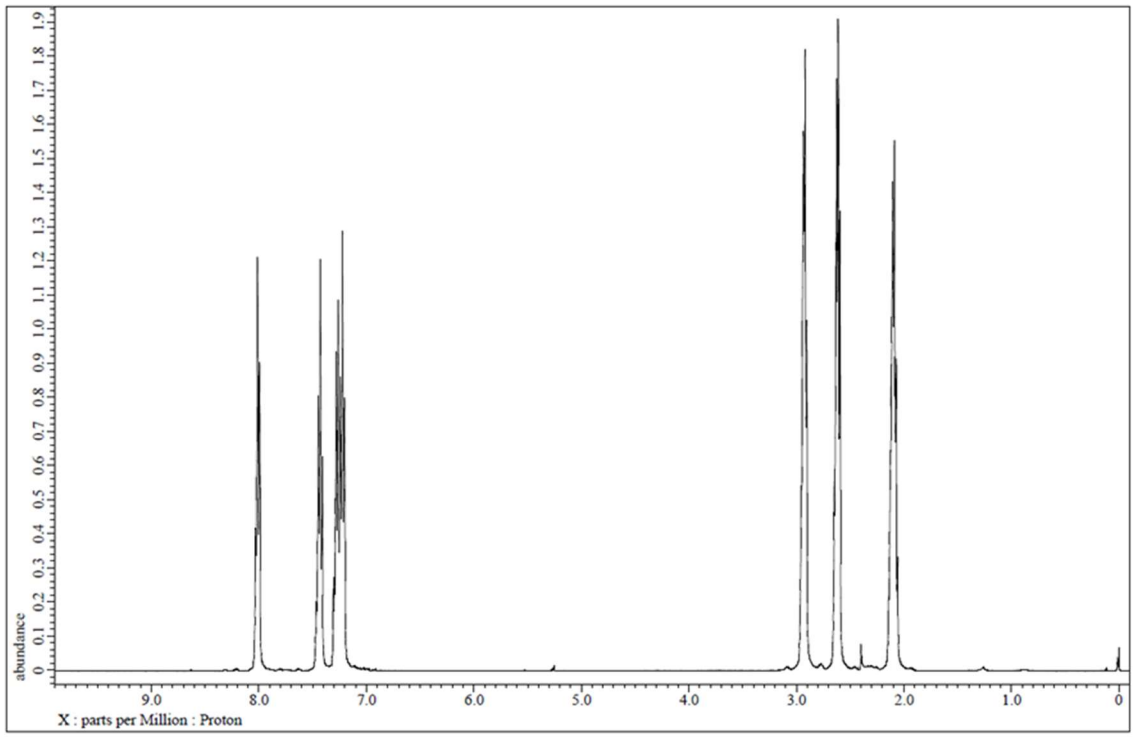
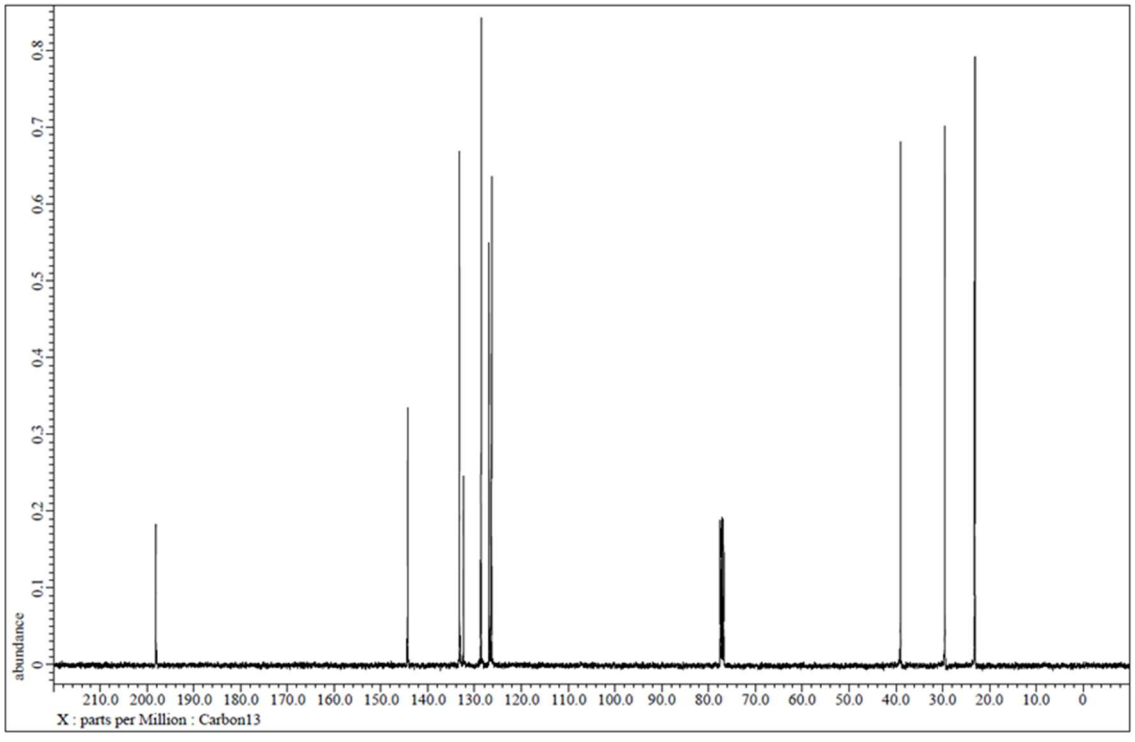
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


abundance
0.5
0.4
0.3
0.2
0.1
0
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13

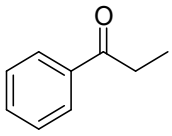
Compound **61**

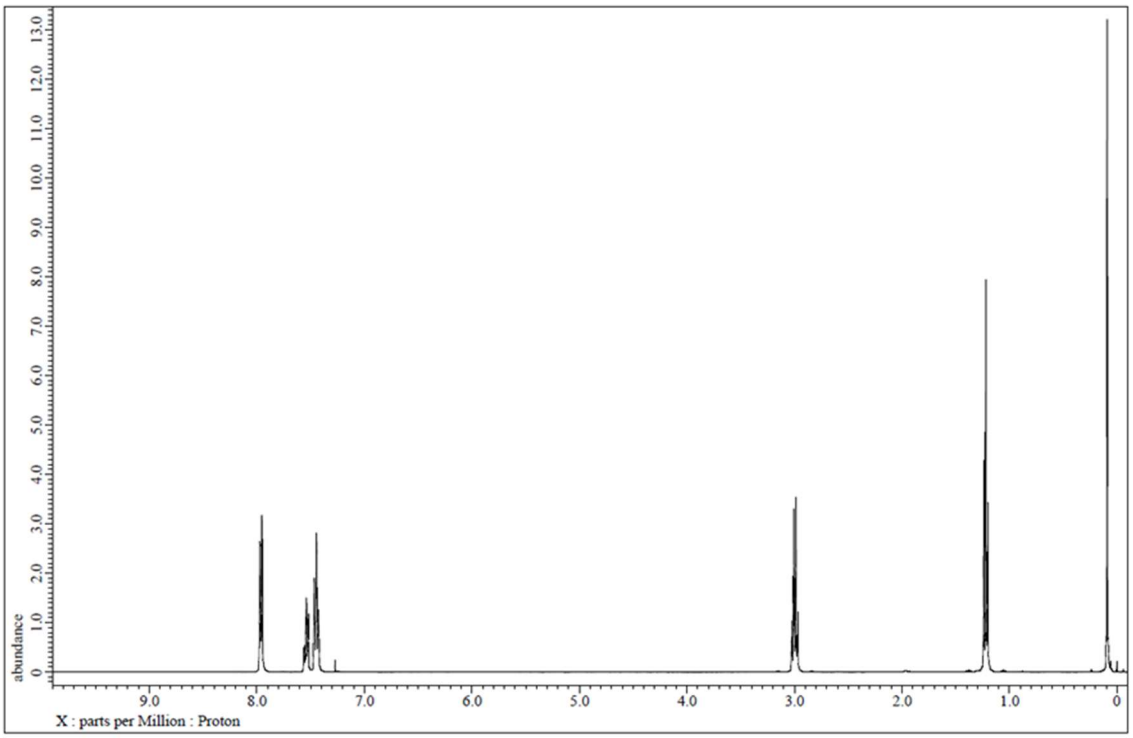


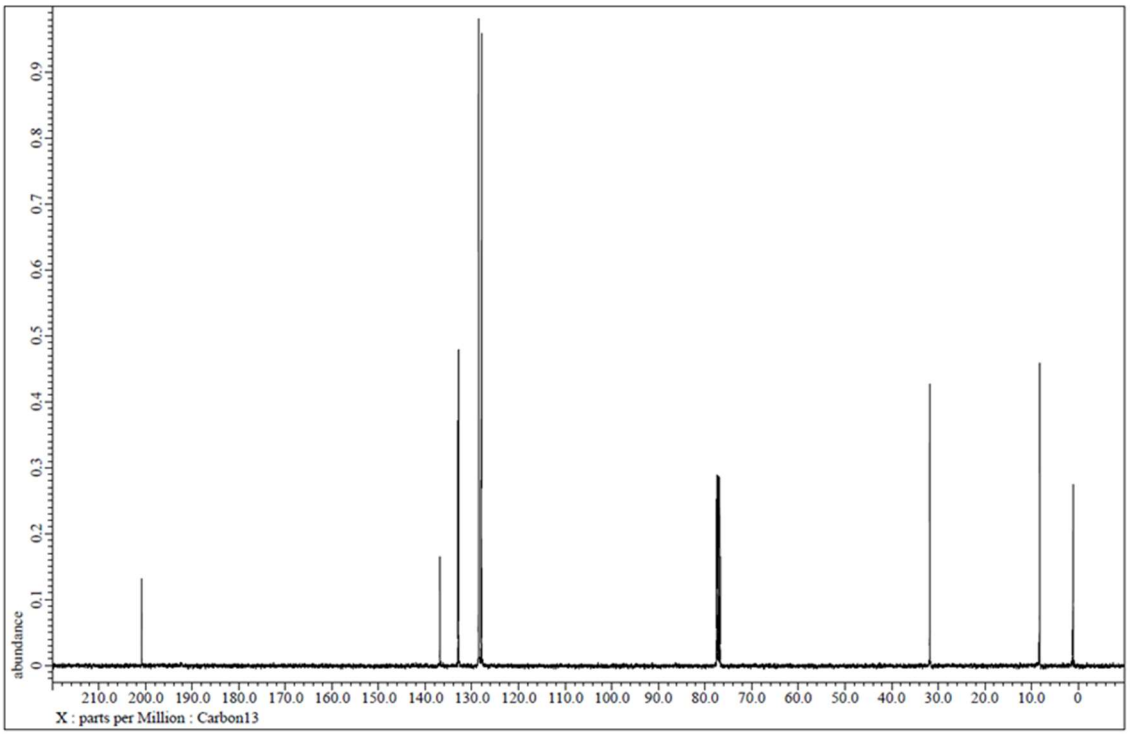

abundance
X : parts per Million : Proton


abundance
X : parts per Million : Carbon13

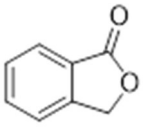
Compound **6m**

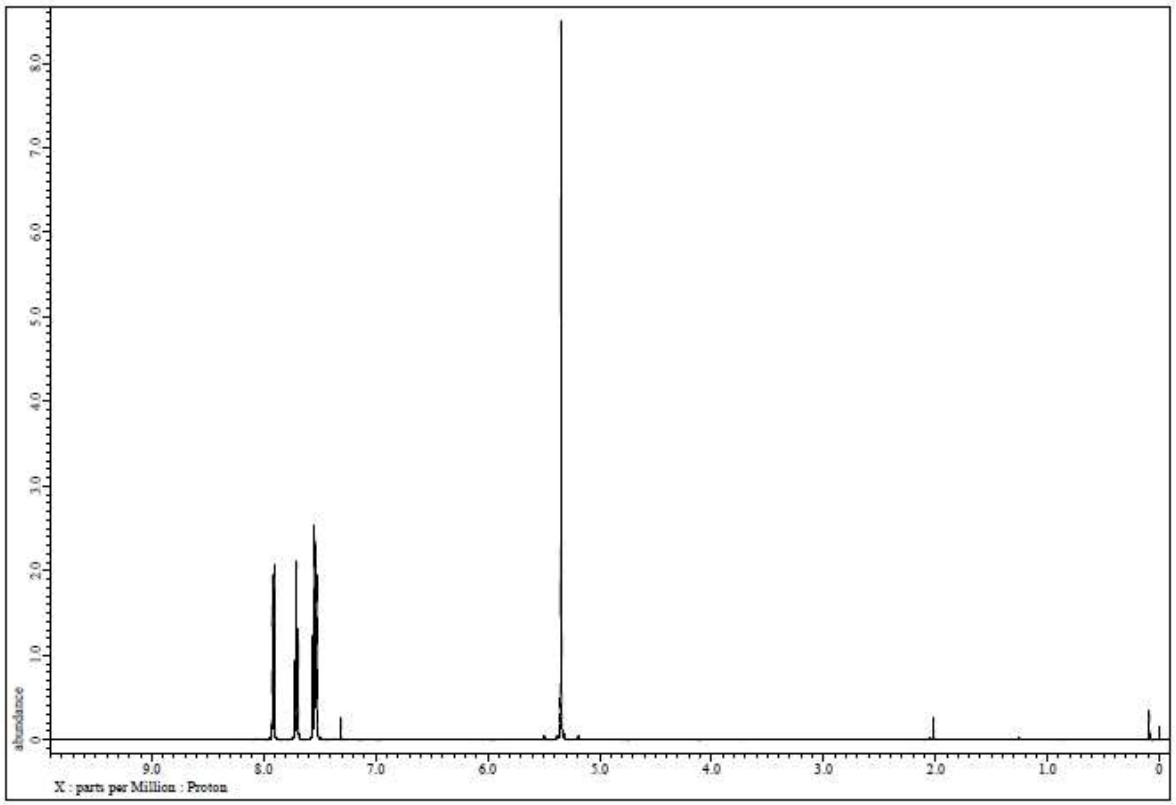


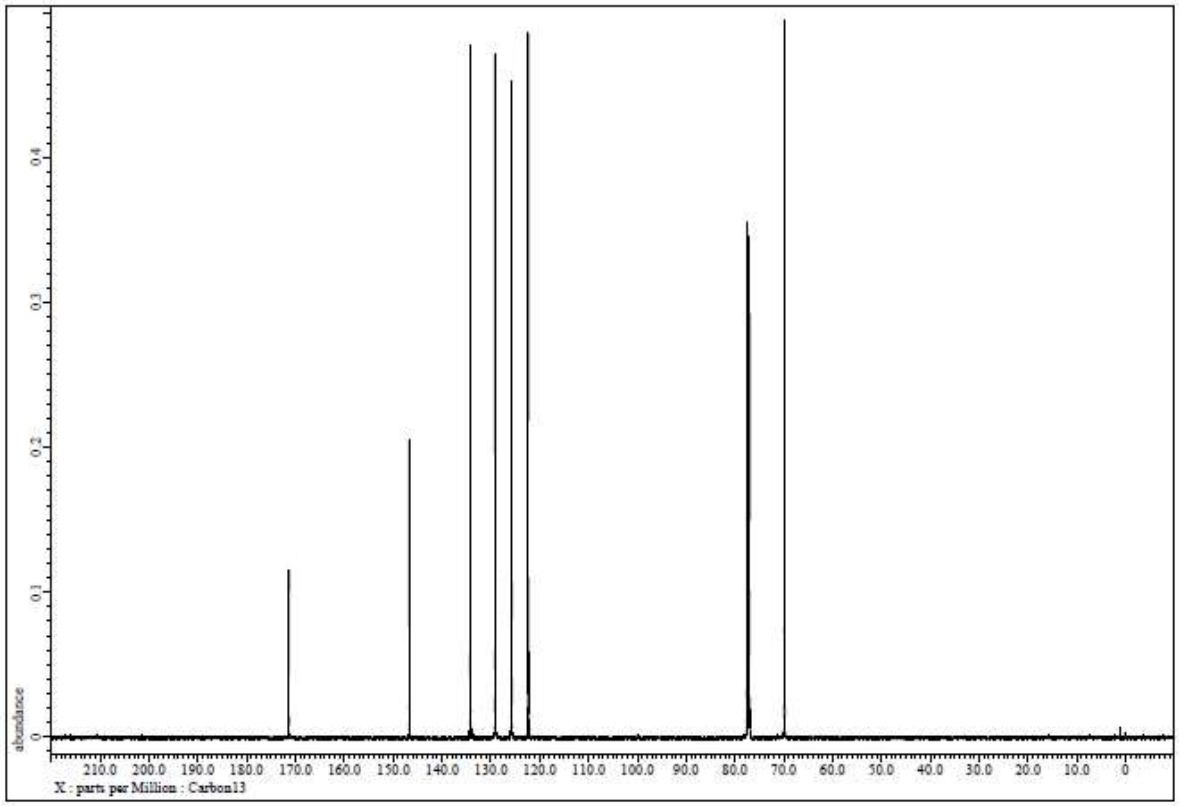

abundance
X : parts per Million : Proton


abundance
X : parts per Million : Carbon13

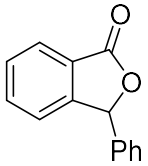
Compound **8a**

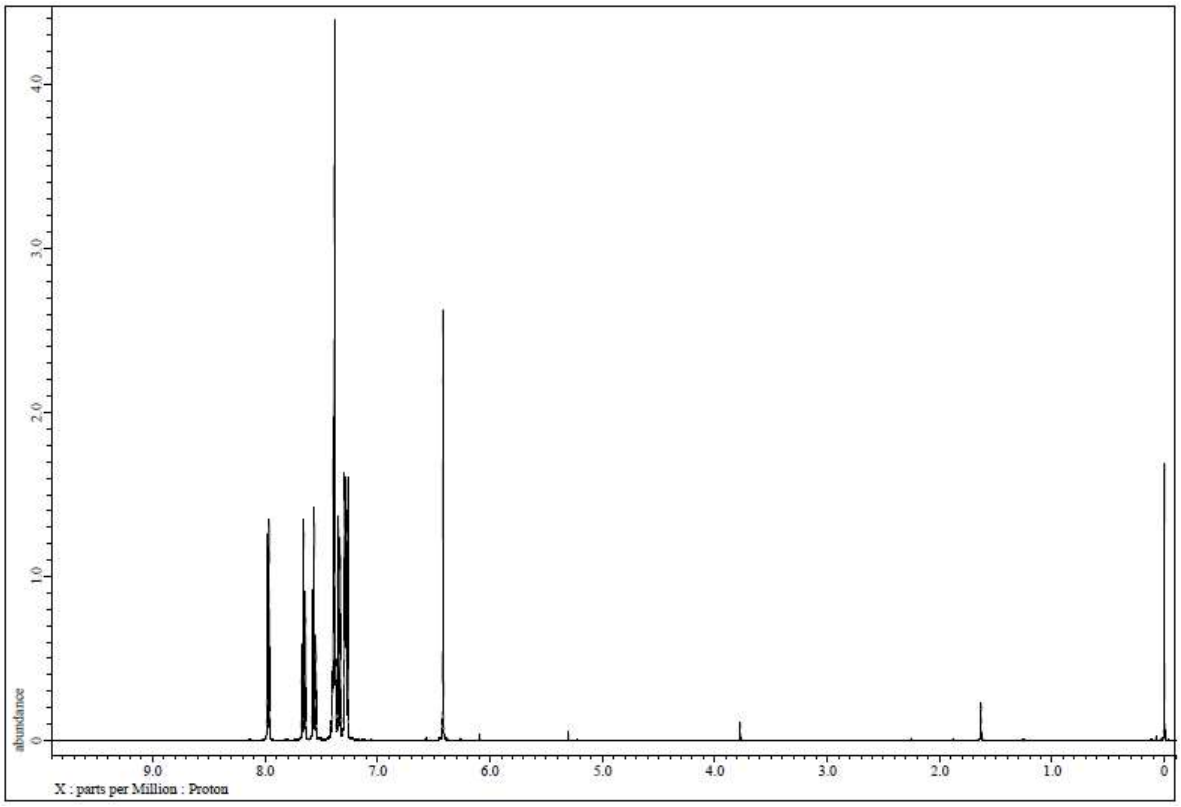


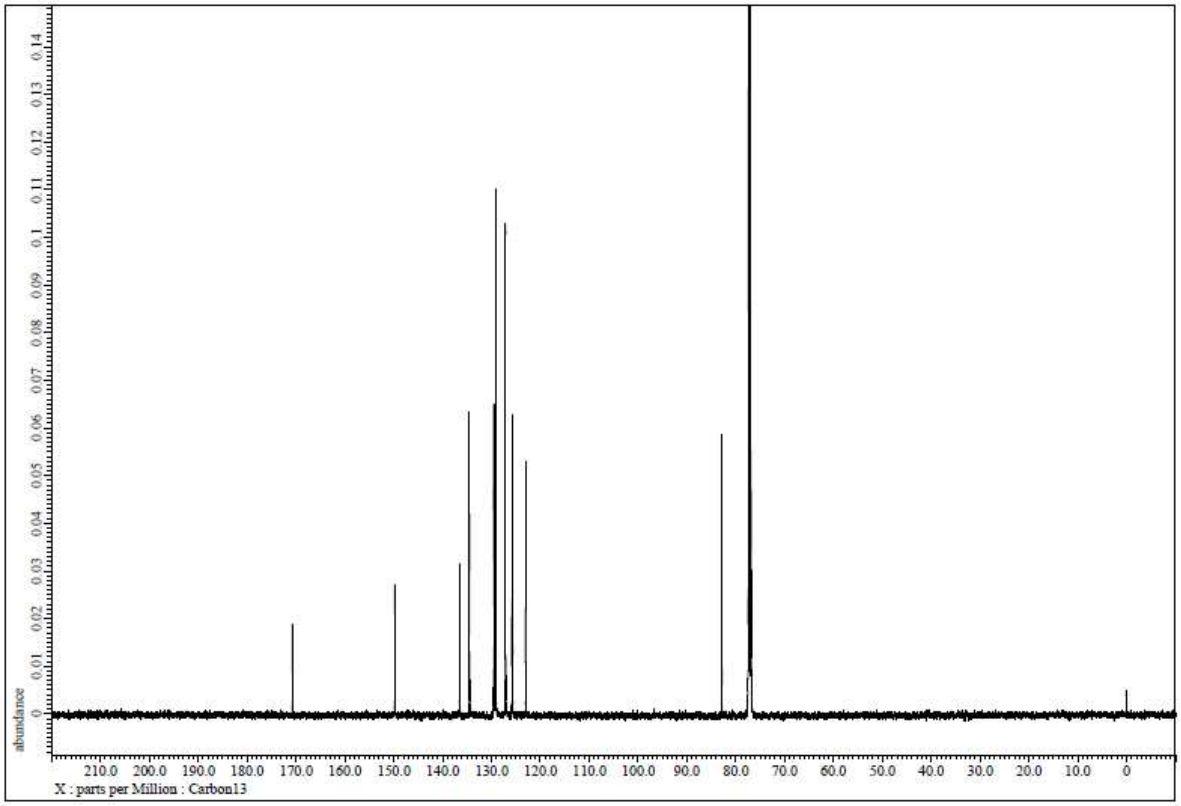

abundance
X : parts per Million : Proton


abundance
X : parts per Million : Carbon13

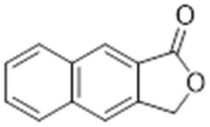
Compound **8b**

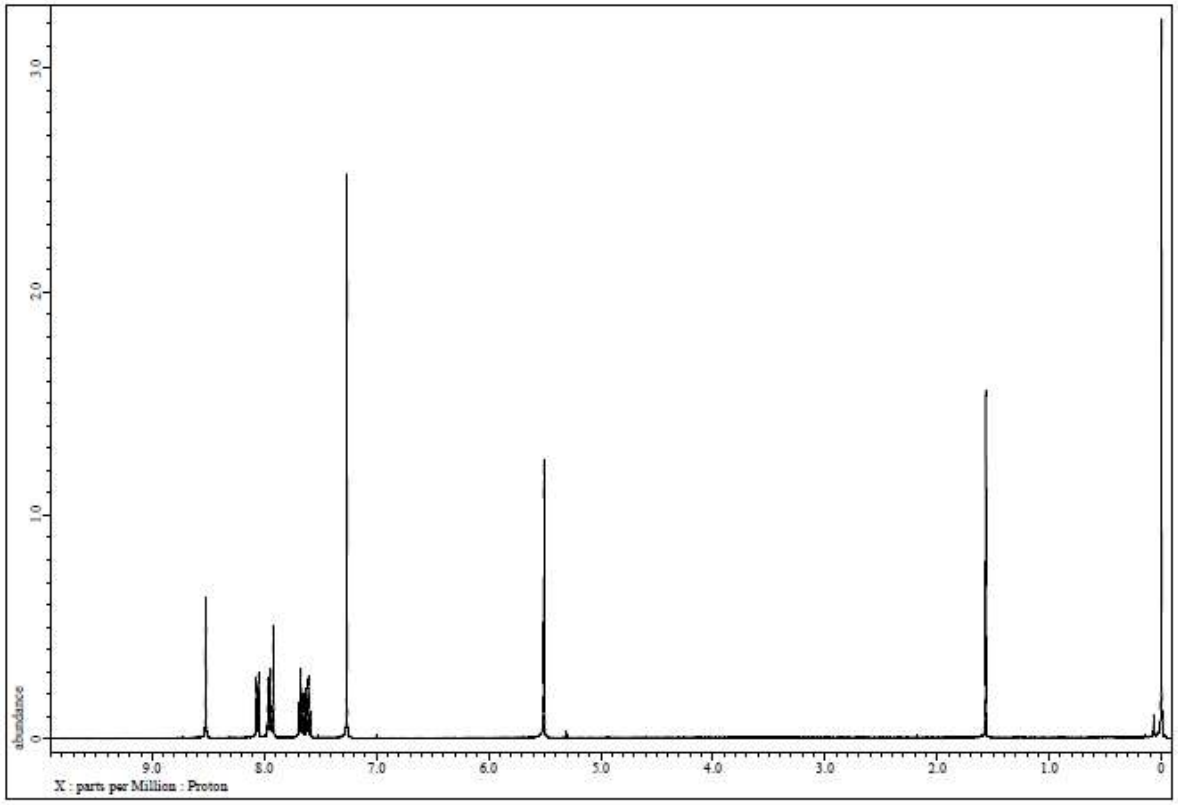

O
O
Ph

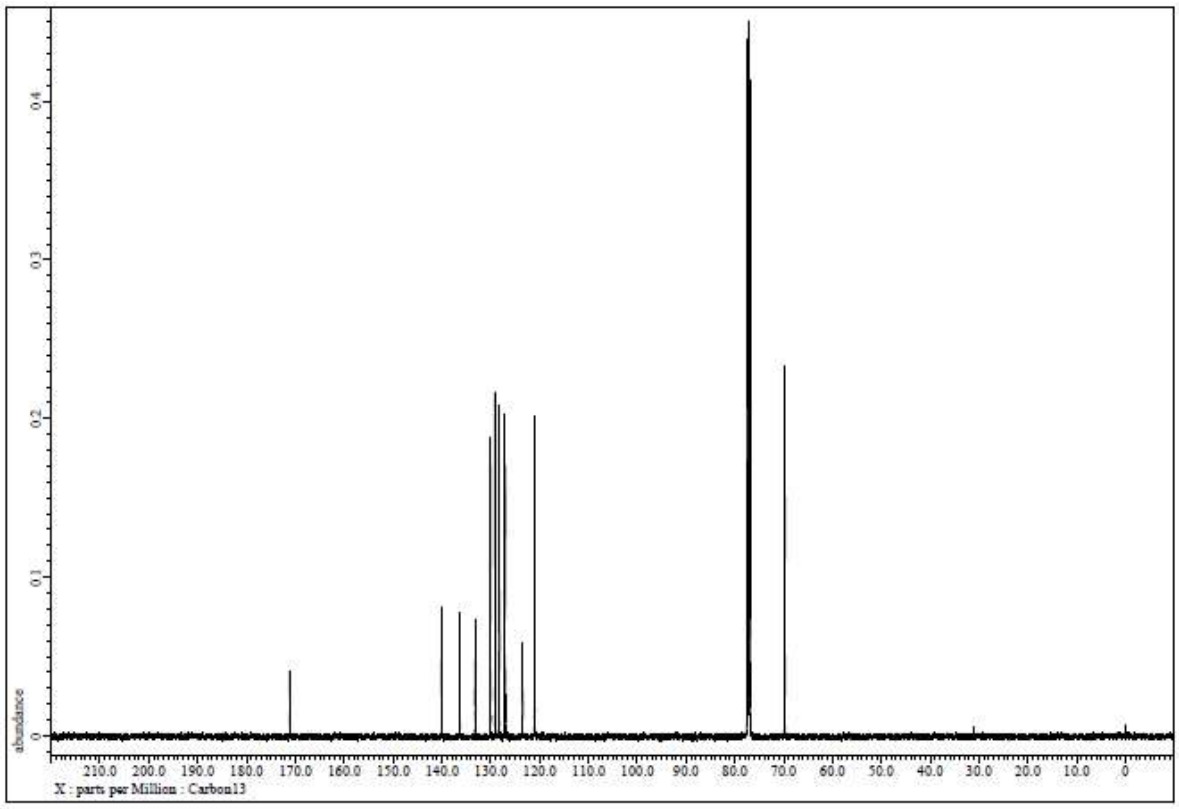

abundance
X : parts per Million : Proton


abundance
X : parts per Million : Carbon13

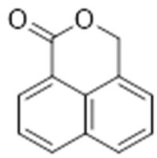
Compound **8c**

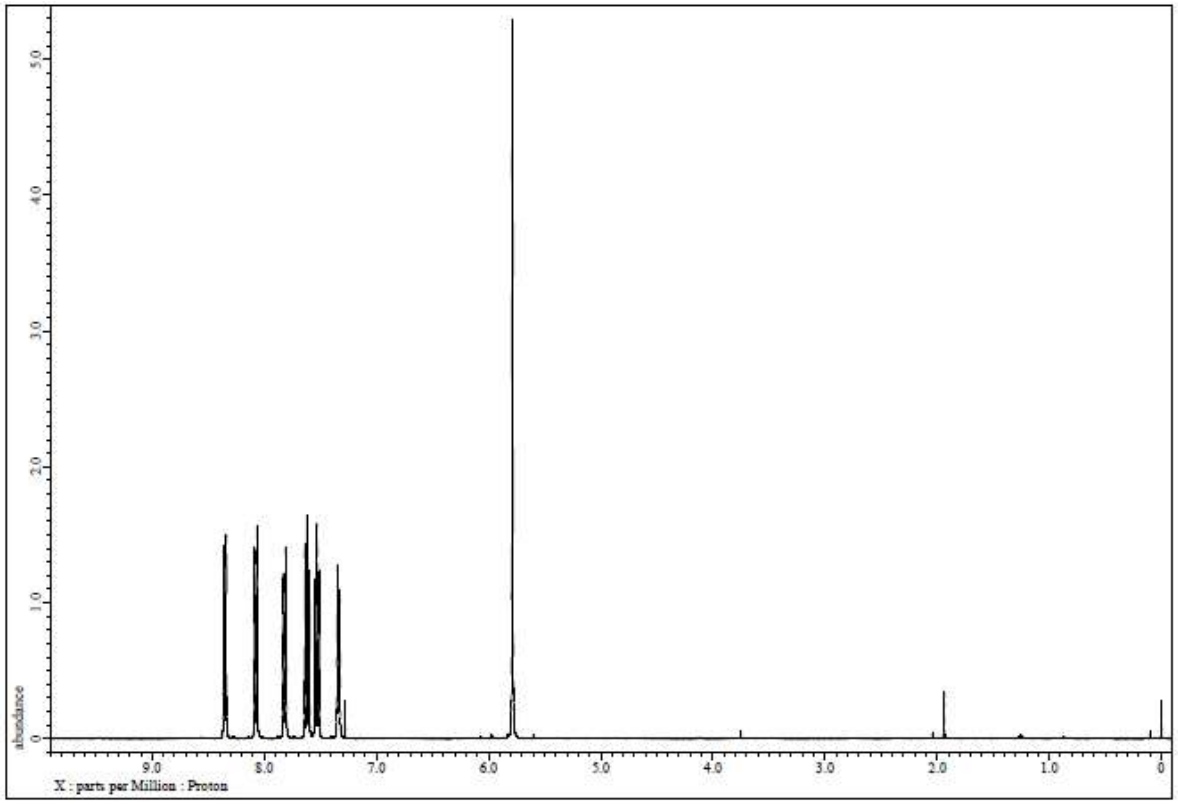

O
O

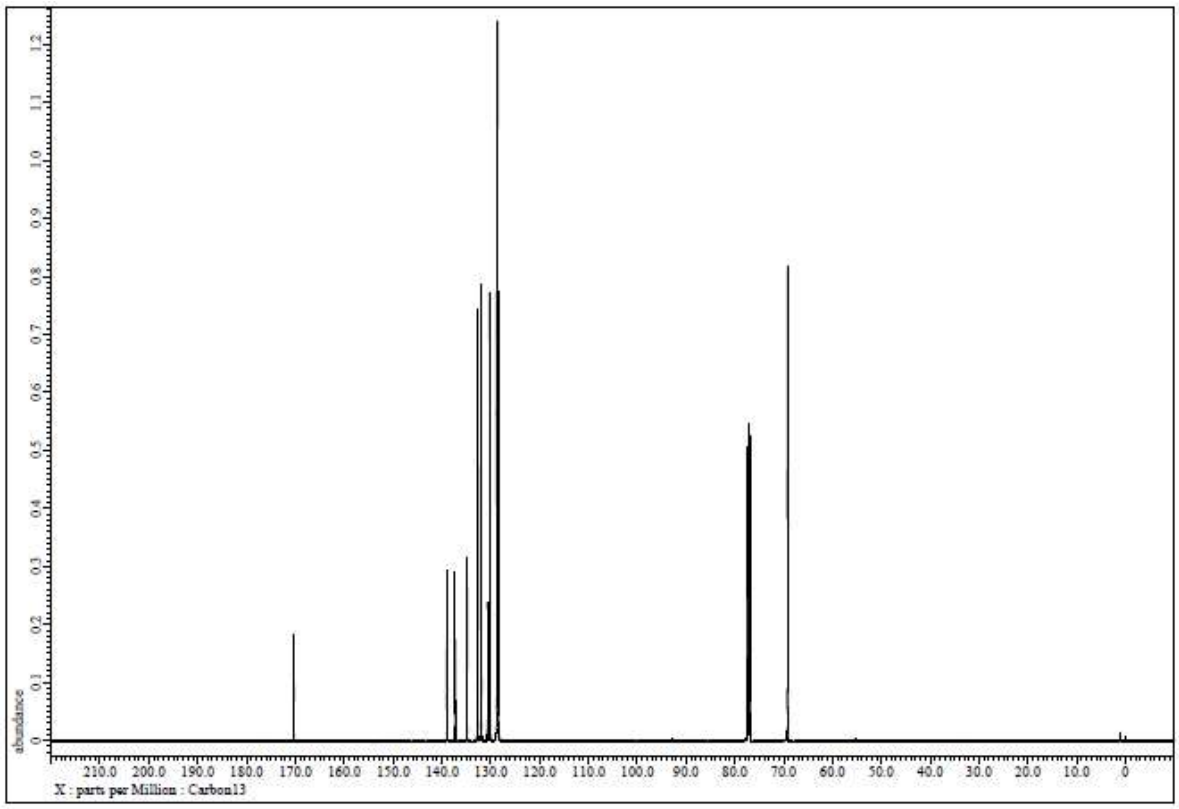

abundance
X : parts per Million : Proton


abundance
X : parts per Million : Carbon13

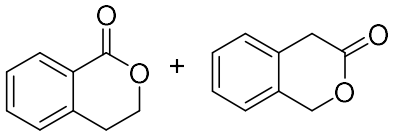
Compound **8d**

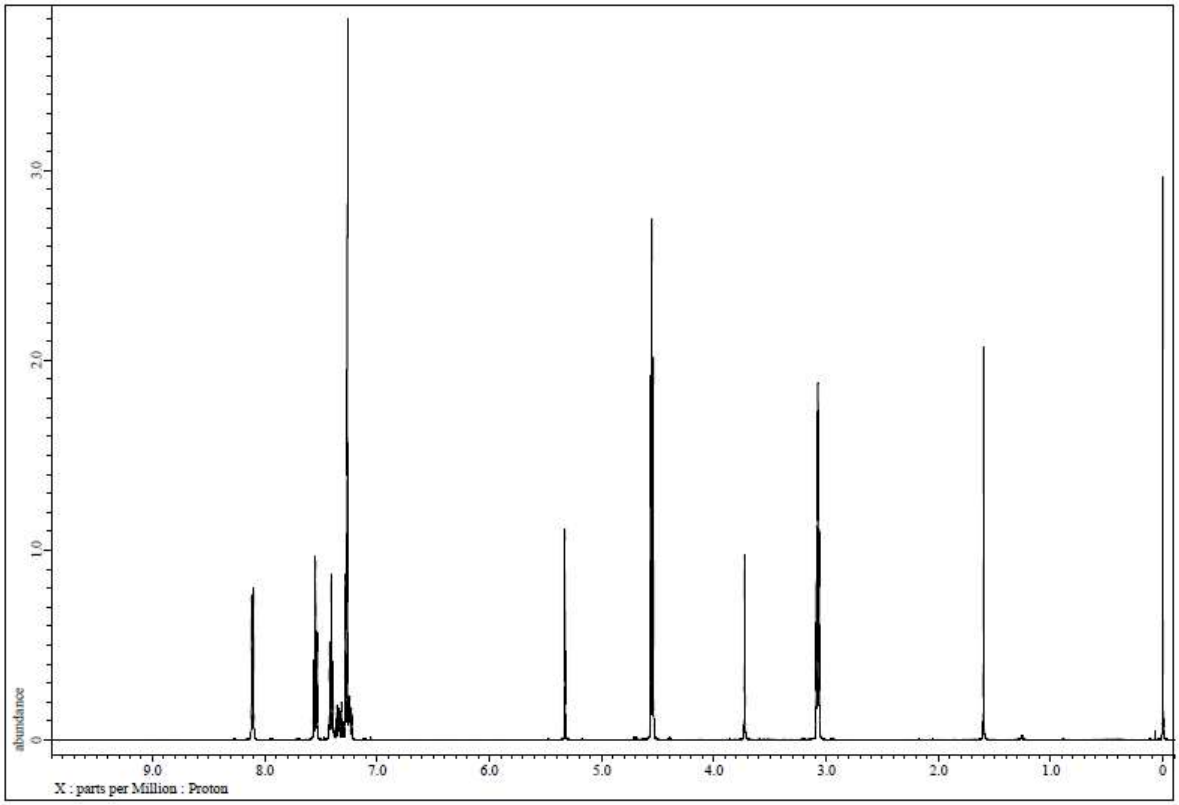


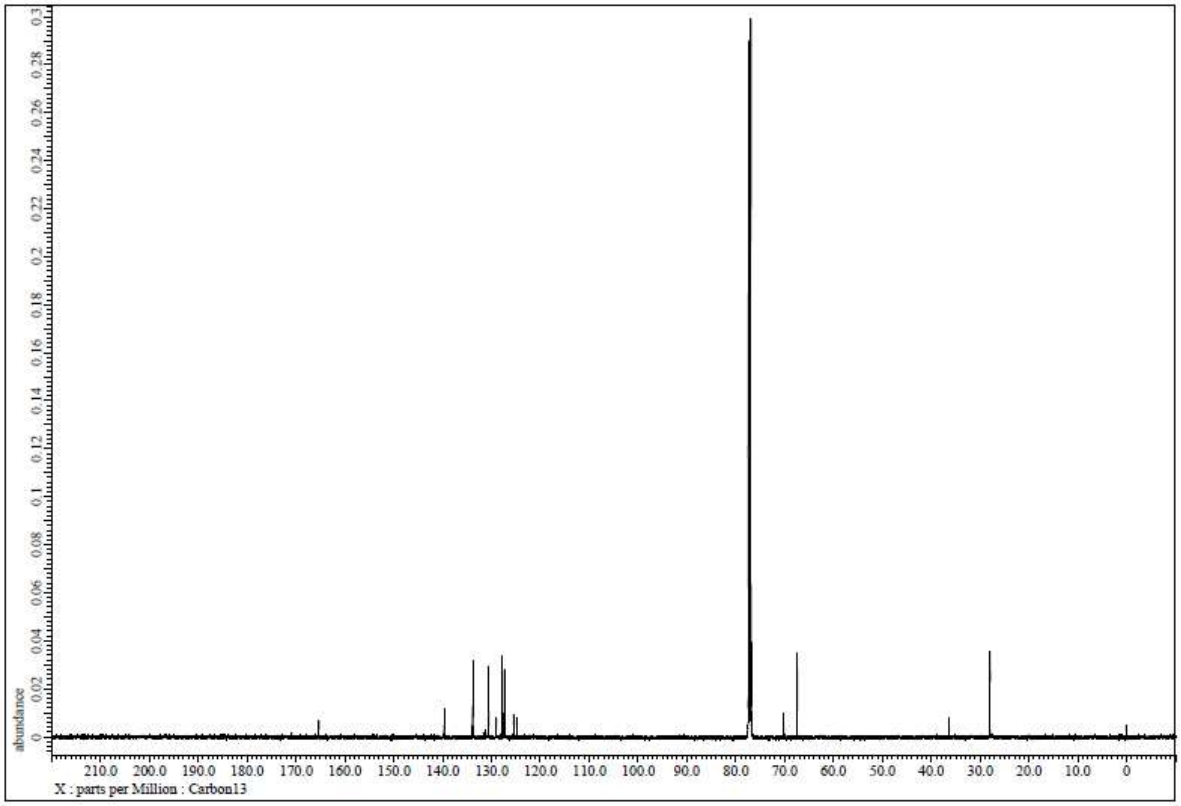

abundance
X : parts per Million : Proton


abundance
X : parts per Million : Carbon13

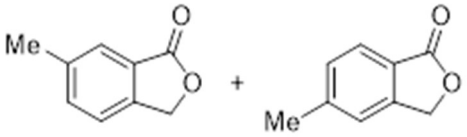
Compound **8ea**,**8eb**

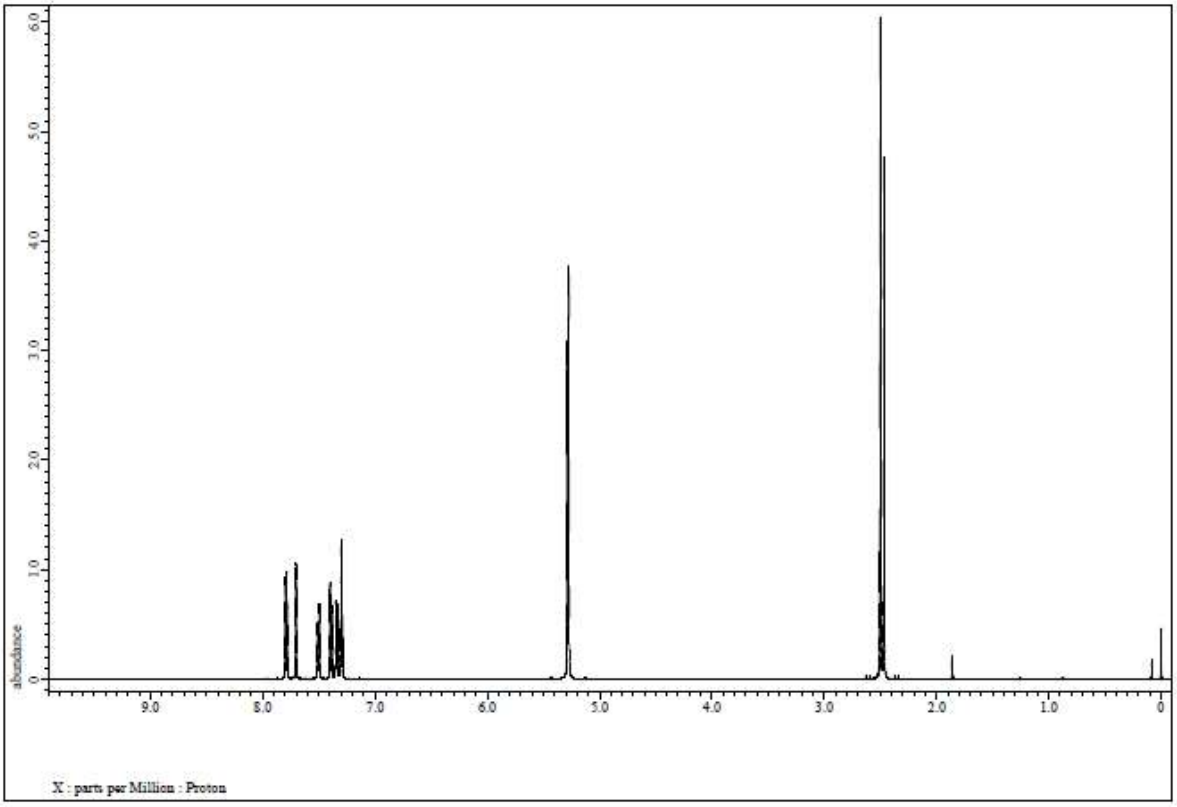


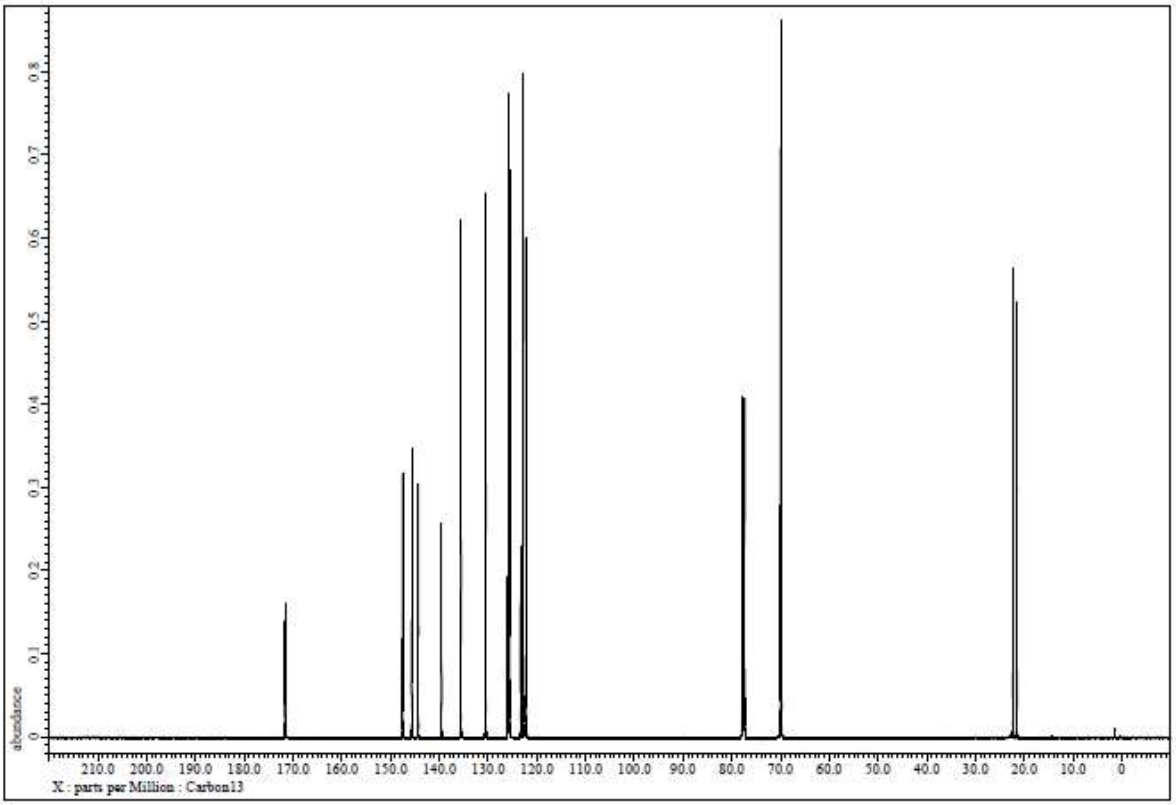




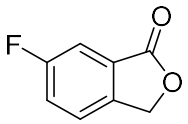
Compound **8fa**,**8fb**

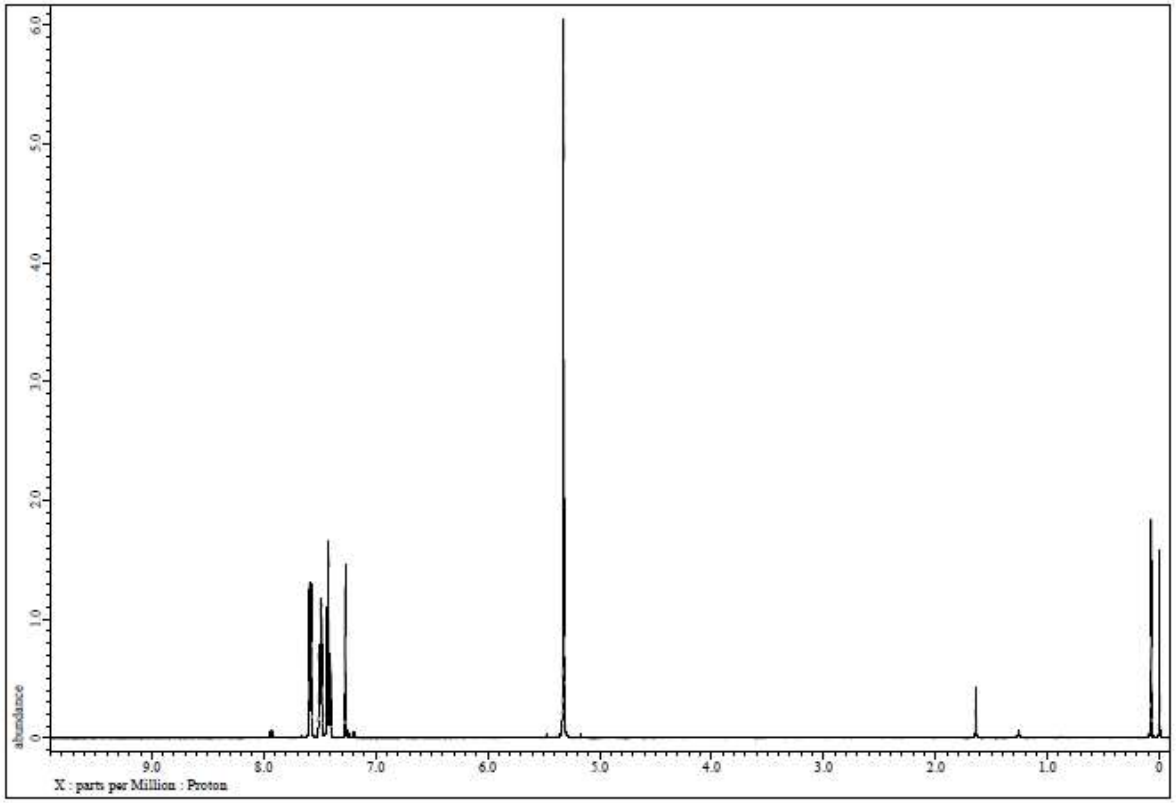


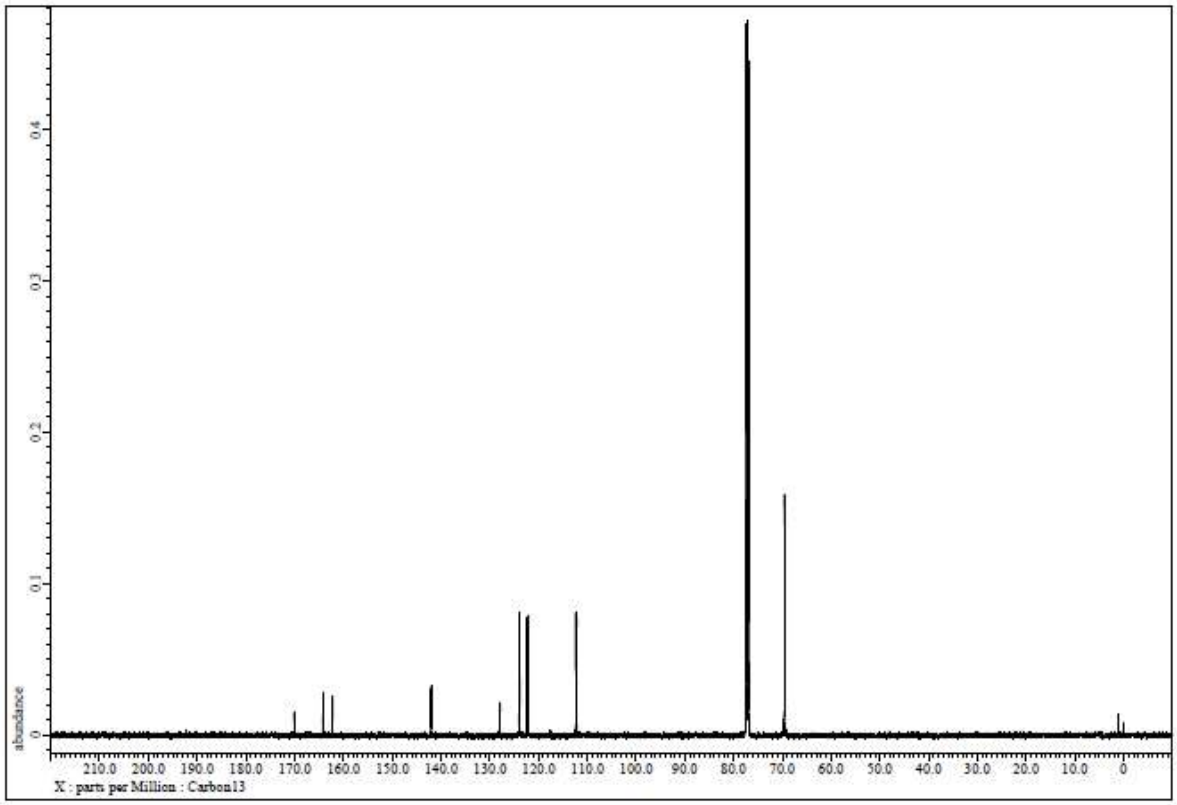




Compound **8ga**







Compound **8gb**