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Efficient and Strategical Installations of Quaternary Ammonium Groups in Metal-Organic Frameworks for Hydroxide Conductivity

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General Methods

Solvents and reagents: Chemical reagents and catalysts were used without further purification from merchandise's supply (Sigma-Aldrich, Alfa-Aesar, TCI, Daejung, and etc.).

Thin layer chromatography (TLC) analysis and flash column chromatography: TLC was analyzed on pre-coated silica gel 60 F254 plates with proper eluents. TLC plates were visualized with 254 nm wavelength UV light. Flash column chromatography was performed for separation on silica gel (400-630 mesh) with proper eluents.

Nuclear Magnetic Resonance (NMR): ^1H and ^{13}C NMR spectra were measured on 400 MHz or 500 MHz (FT AM 400 or 500, Bruker AVANCE; 100 MHz and 125 MHz for ^{13}C) in the center for research facilities at Chungbuk National University. Chemical shifts were displayed in "ppm" and referenced to TMS (tetramethylsilane) or the appropriate solvent residual peak ($CHCl_3$, DMSO, etc.). Coupling constants, *J,* are announced in Hz (Hertz). Abbreviation codes were employed to show peak multiplicities; singlet = s, doublet = d, triplet = t, quartet = q, broad = br, and multiplet = M.

Gas Chromatography Mass Spectrometry (GC-MS): GC-MS measurements were performed using GC-MS-QP2020 Nx (Shimadzu) and He for carrier gas.

Liquid Chromatography Mass Spectrometry (LC-MS): LC-MS measurements were performed using QTRAP 4500 (SCIEX).

High-Resolution Mass Spectrometry (HR-MS): HR-MS measurements were performed using maXis 4G hybrid LC-TOF system (Bruker BioScience).

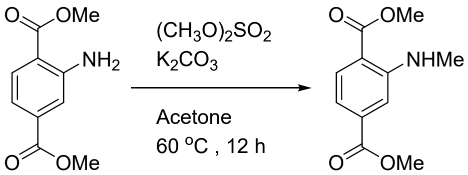
Powder X-ray diffraction (PXRD): PXRD patterns of MOFs were measured at room temperature on a Rigaku Miniflex 600 (40 kV & 15 mA for CuKa, $\lambda = 1.5406$ Å), with a scan speed of 2 sec/step, a step size of 0.02 ° in 2θ, and a 2θ range of 5-30 °, respectively.

N_2 adsorption: Approximately 100 mg of MOF samples were evacuated under vacuum for easy handling. Then samples were transferred to a pre-weighed sample tube, and degassed at 110 °C on an Micromeritics ASAP2020 for a minimum of 24 h or until the outgas rate was <5 μm Hg/min. The sample tube was re-weighted to obtain a consistent mass for the degassed MOF materials. N_2 adsorption data was collected with fully activated samples on ASAP2020 using high purity N_2 gas (99.999%).

Acid digestion of MOF for NMR: In case of Zr-based MOF, approximately 10 mg of MOFs were fully dried under vacuum (at least 24 h), and digested with sonication in 580 μL of DMSO-d_6 and 20 μL of HF (48% aqueous solution) until clearly dissolved.

Scanning Electron Microscope (SEM): SEM images of UiO-66 MOFs were taking using ZEISS Ultra Plus Field Emission Scanning Electron Microscope.

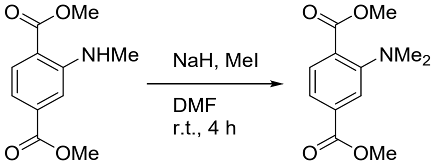
Detailed Procedures of BDC-Based Ligand Synthesis



Dimethyl-2-(methylamino)terephtahalate (**2**)[S1]

Dimethyl 2-aminoterephthalate (**1**, 2.0 g, 9.6 mmol), K_2CO_3(4.2 g, 30 mmol) and $(CH_3O)_2SO_2$ (3.0 mL, 32 mmol) were dissolved in acetone (30 mL). Then the mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the solvent was removed by evaporation and added water. Then the solution was extracted with ethyl acetate and distilled water. $MgSO_4$ was added to the organic layer to remove residual water, and the solvent was evaporated. The crude product was purified by silica gel column chromatography (EtOAc:*n*-hexane = 1:10). And a yellow solid was obtained (**2**, 1.3 g, 57%).

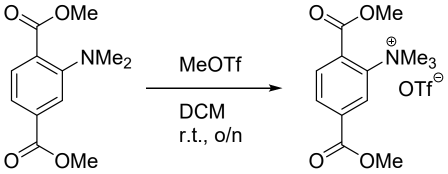
Dimethyl-2-(methylamino)terephtahalate (**2**): ^{1}H NMR (DMSO-*d*$_6$, 500 MHz, ppm) δ 7.87 (d, *J* = 8.2 Hz, 1H), 7.61 (q, *J* = 5.0 Hz, 1H), 7.21 (d, *J* = 1.6 Hz, 1H), 7.10 (dd, *J* = 8.2, 1.6 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 2.88 (d, *J* = 5.0 Hz, 3H); ^{13}C NMR (DMSO-*d*$_6$, 125 MHz, ppm) δ 167.46, 166.00, 150.92, 134.67, 131.48, 114.08, 112.47, 111.39, 52.29, 51.76, 29.23.



Dimethyl-2-(dimethylamino)terephtahalate (**3**)[S1]

A two neck round bottom flask was charged NaH(900 mg of 60% dispersion in oil, 23 mmol). And change the inside of the flask to N_2 conditions. Then NaH was washed with *n*-hexane (10 mL) for 3 times. After cooling the solutions to 0 °C and adding dry DMF (5 mL). A solution of dimethyl-2-(methylamino)terephtahalate (**2**, 600 mg, 2.69 mmol) is dissolved in DMF (8 mL) was added by dropwise for 1 h at 0 °C. And MeI (1.7 mL, 0.027 mmol) was added to the mixture and was stirred at room temperature for 4 h. After completion, H_2O was added to the mixture, and extraction with ethyl acetate and brine. $MgSO_4$ was added to the organic layer to remove residual water, and the solvent was evaporated. The crude product was purified by silica gel column chromatography (EtOAc:*n*-hexane = 1:10). And a yellow solid was obtained (**3**, 440 mg, 69%).

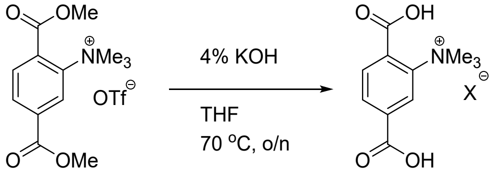
Dimethyl-2-(dimethylamino)terephtahalate (**3**): ^{1}H NMR (DMSO-*d*$_6$, 500 MHz, ppm) δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 1.5 Hz, 1H), 7.35 (dd, *J* = 8.0, 1.5 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 2.81 (s, 6H); ^{13}C NMR (DMSO-*d*$_6$, 125 MHz, ppm) δ 168.05, 165.92, 150.89, 132.45, 131.06, 123.82, 117.97, 116.41, 52.29, 52.17, 42.59.



2,5-Bis(methoxycarbonyl)-N,N,N-trimethylbenzenaminium trifluoromethanesulfonate (**4**)[S2]

Dimethyl-2-(dimethylamino)terephtahalate (**3**, 390 mg, 1.64 mmol) was dissolved in DCM (10 mL). Then methyl triflate (350 μL, 3.28 mmol) was added by dropwise and stirred at room temperature overnight. After completion, the solvent was removed by evaporation. The crude product was purified by silica gel column chromatography (MeOH:DCM = 1:10). And a white solid was obtained (**8**, 449 mg, 68%).

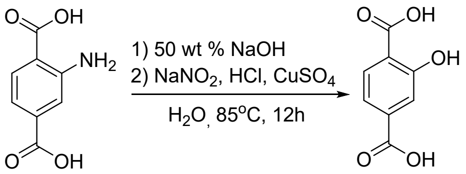
2,5-Bis(methoxycarbonyl)-*N,N,N*-trimethylbenzenaminium trifluoromethanesulfonate (**4**): ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 8.47 (d, *J* = 1.4 Hz, 1H), 8.25 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 4.03 (s, 3H), 3.95 (s, 3H), 3.76 (s, 9H); ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 167.73, 164.38, 143.21, 133.06, 132.52, 130.95, 130.78, 123.07, 57.20, 54.60, 53.09.



2,5-Dicarboxy-N,N,N-trimethylbenzenaminium cation (**A**)[S2]

2,5-Bis(methoxycarbonyl)-*N*,*N*,*N*-trimethylbenzenaminium trifluoromethanesulfonate (**4**, 400 mg, 0.997 mmol) was dissolved in THF (5 mL). Then, 4% KOH solution (5 mL) was added to a solution. The solution was stirred at 70 °C overnight. After completion (monitored by TLC), THF and water was removed under reduced pressure. Then mixture was acidified to pH 2 with 1.0 M aqueous HCl. The solution was collected by filtration with MeOH, and evaporated of MeOH. BDC-NMe_3X (**A**, 341 mg, 90%-calculated with OTf based molecular weight) was obtained as a white solid.

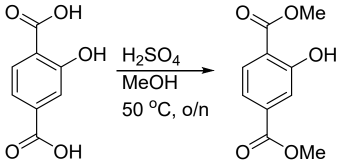
2,5-Dicarboxy-*N,N,N*-trimethylbenzenaminium cation (**A**): ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 8.15 (d, *J* = 1.3 Hz, 1H), 7.92 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 3.79 (s, 9H); ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 169.94, 165.89, 143.05, 134.05, 133.26, 132.36, 131.40, 123.26, 57.36.



2-Hydroxyterephthalic acid (**6**)[S3]

A 500 mL round bottom flask was charged with 2-aminoterephthalic acid (**5**, 2.0 g, 11 mmol) dissolved in diluted water (30 mL). Then, 2.0 g of a 50 wt% NaOH was added to suspension. When the solution becomes clear, lower it to 0°C, then $NaNO_2$ (1.2 g, dissolved in 2.0 mL distill water) was added to the mixture. Diluted with 16.0 mL of distilled water and 6.0 mL of conc. HCl. The solution turns beige color. After stirring for 4 h at room temperature, $CuSO_4$ (3.5 g) was added, and refluxed at 85 °C for 24 h. It is then washed with water and filtered to obtain a white solid (**6**, 1.8 g, 90%).

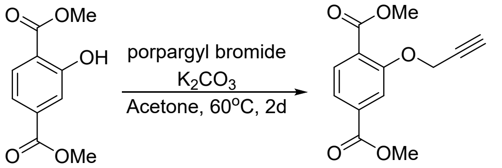
2-Hydroxyterephthalic acid (**6**): ^{1}H NMR (DMSO-*d*$_6$, 500 MHz, ppm) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.45 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.42 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR(DMSO-*d*$_6$, 125 MHz, ppm) δ 171.08, 166.41, 160.55, 136.88, 130.72, 119.54, 117.72, 116.87.



Dimethyl 2-hydroxyterephthalate (**7**)[S3]

BDC-OH (**6**, 1.0 g, 5.5 mmol) were dissolved in MeOH (50 mL). Add 2.5 mL of H_2SO_4 to the suspension. The mixture was stirred at 60 °C for overnight. Then the solution was extracted with dichloromethane and distilled water, and work-up with $NaHCO_3$. The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. The mixture solid was purified by silica gel column chromatography (EtOAc:*n*-hexane = 1: 15), and a white solid was obtained (**7**, 0.61 g, 52 %).

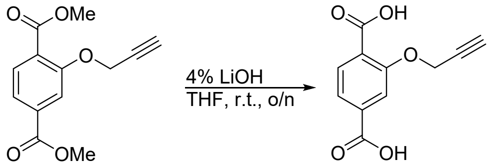
Dimethyl 2-hydroxyterephthalate (**7**): ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 10.74 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 1.5 Hz, 1H), 7.51 (dd, *J* = 8.3, 1.6 Hz, 1H), 3.97 (s, 3H), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 169.95, 165.98, 161.29, 136.42, 130.01, 119.68, 118.89, 115.66, 52.62, 52.47.



Dimethyl 2-(prop-2-yn-1-yloxy)terephthalate (**8**)

To a sealed flask was added BDCE-OH (**7**, 1.05 g, 4.99 mmol), K_2CO_3(1.73 g, 12.5 mmol), propargyl bromide (490 µL, 6.5 mmol) dissolved in acetone (30 mL). The mixture was stirred at 60 °C for 2 days. Then the solution was extracted with ethyl acetate and distilled water. $MgSO_4$ was added to the organic layer to remove residual water, and the solvent was evaporated. The crude product was purified by silica gel column chromatography (EtOAc:*n*-hexane = 1:7). And an ivory solid was obtained (**8**, 0.93 g, 75 %).

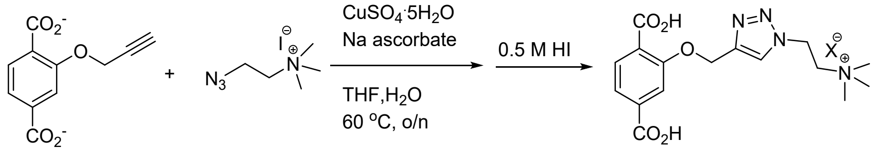
Dimethyl 2-(prop-2-yn-1-yloxy)terephthalate (**8**): ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.83 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 1.4 Hz, 1H), 7.69 (dd, J = 8.0, 1.4 Hz, 1H), 4.85 (d, J = 2.4 Hz, 2H), 3.94 (s, 3H), 3.91 (s, 3H), 2.55 (t, J = 2.4 Hz, 1H); ^{13}C ($CDCl_3$, 125 MHz, ppm) NMR δ 166.03, 165.94, 156.59, 134.29, 131.59, 125.20, 122.29, 115.02, 77.63, 76.53, 56.96, 52.57, 52.41.



2-(Prop-2-yn-1-yloxy)terephthalic acid (**B**)[S4]

Dimethyl 2-(prop-2-yn-1-yloxy)terephthalate (**8**, 0.99 g, 4 mmol) was dissolved in THF (20 mL). Then, 4% LiOH aqueous solution (20 mL) was added to a solution. The mixture was stirred at room temperature overnight. After completion (monitored by TLC), THF was removed under reduced pressure. The remaining aqueous phase was adjusted to pH 2 with 1.0 M aqueous HCl. The white precipitate was collected by filtration, washed with distilled water and dried under vacuum to afford BDC-OCH_2CCH (**B**, 0.8 g, 90 %).

2-(Prop-2-yn-1-yloxy)terephthalic acid (**B**): ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 13.19 (s, 2H), 7.77 – 7.69 (m, 2H), 7.60 (dd, *J* = 7.9, 1.4 Hz, 1H), 4.95 (d, *J* = 2.4 Hz, 2H), 3.63 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 166.91, 166.58, 155.44, 134.30, 130.49, 126.46, 121.81, 114.35, 79.01, 78.79, 56.24.

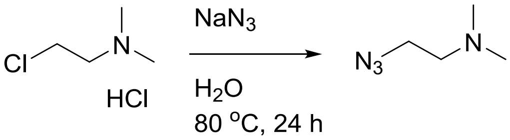


*2-(4-((2,5-Dicarboxyphenoxy)methyl)-1H-1,2,3-triazol-1-yl)-N,N,N-trimethylethanaminium iodide (**C**)*[S5]

Dimethyl 2-(prop-2-yn-1-yloxy)terephthalate (**8**, 100 mg, 0.402 mmol) was dissolved in THF (1 mL). Then, 4% LiOH aqueous solution (1 mL) was added to a solution. The mixture was stirred at room temperature overnight. After completion (monitored by TLC), mixture was removed under reduced pressure. TMAZ and $CuSO_4 \cdot 5H_2O$ (6 mg dissolved in 40 μL, H_2O), Na ascorbate (34 mg dissolved in 160 μL, H_2O) were added to the remaining mixture. The solution was stirred at 50 °C for 1 day. And then, the solution was cooled to 0 °C, add 0.5 M aqueous HI(2.0 equiv.) to the remaining aqueous phase. The orange solid was collected by filtration, washed with distilled water and dried under vacuum to afford BDC-triazole-NMe_3X (**C**, 82 mg, 42 %-calculated with iodide based molecular weight).

2-(4-((2,5-Dicarboxyphenoxy)methyl)-1H-1,2,3-triazol-1-yl)-*N,N,N*-trimethylethanaminium iodide (**C**): ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 13.13 (s, 2H), 8.30 (s, 1H), 7.78 (d, *J* = 1.5 Hz, 1H), 7.69 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.59 (dt, *J* = 7.9, 1.4 Hz, 1H), 5.34 (s, 2H), 4.98 (t, *J* = 6.8 Hz, 2H), 3.93 (t, *J* = 6.8 Hz, 2H), 3.11 (s, 9H); ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 167.41, 167.05, 156.66, 143.47, 134.89, 130.90, 126.94, 125.76, 122.10, 114.90, 63.61, 62.59, 53.20, 43.84. ESI-MS(+) *m/z* calcd. For $C_{16}H_{21}N_4O_5^+$ [*M*]$^+$: 349.1506, found [*M*]$^+$: 349.1506.

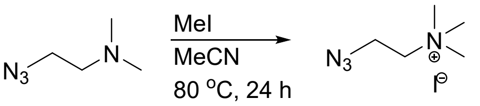
Detail Procedures for Azide Synthesis



*2-Azido-N,N-dimethylethanamine (**DMAZ**)*

2-Chloro-N,N-dimethylethanamine (144 mg, 1 mmol), NaN_3 (195 mg, 3 mmol) and H_2O (40 mL) were added to a round bottom flask. The mixture was refluxed at 80 °C for 24 h. After completion, 1 M NaOH was added to adjust pH 10. And the solution was extracted with DCM and H_2O. The organic layer was dried by $MgSO_4$ and evaporated. **DMAZ** (95%) was obtained as a yellow oil.

2-Azido-*N,N*-dimethylethanamine (**DMAZ**): ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ 3.35 (t, *J* = 6.2 Hz, 2H), 2.53 – 2.47 (m, 2H), 2.27 (s, 6H); ^{13}C NMR (D_2O, 125 MHz, ppm) δ 56.44, 48.23, 43.87.



2-Azido-N,N,N-trimethylethanaminium iodide (**TMAZ**)[S6]

2-Azido-*N,N*-dimethylethanamine (**DMAZ**, 114 mg, 1 mmol) was dissolved in MeCN (2 mL) at 0 °C. And then, MeI (3 equiv.) was added at 0 °C. The mixture was refluxed at 80 °C for 24 h. After the reaction was over, solvent was evaporated and recrystallized at 0 °C. The solids were filtered and washed by DCM. TMAZ (204 mg, 80%) was obtained as a colorless solid.

2-Azido-*N,N,N*-trimethylethanaminium iodide (**TMAZ**): ^1H NMR (DMSO-d_6, 500 MHz) δ 3.95 (td, *J* = 3.6, 1.8 Hz, 2H), 3.53 (dd, *J* = 6.5, 5.0 Hz, 2H), 3.10 (s, 9H); ^{13}C NMR (D_2O, 125 MHz, ppm) δ 64.37, 53.76, 53.73, 53.70, 44.77.

Detail Procedures for MOF Synthesis and Modifications

UiO-66

BDC (41.5 mg, 0.25 mmol), $ZrCl_4$ (55 mg, 0.25 mmol), formic acid (833 μL), H_2O (10 μL) and DMF (7 mL) were placed in a vial, and the mixture was heated in conventional oven at 120 ^{o}C for 24 h and then cooled to room temperature. UiO-66 powder was isolated by centrifugation. The solids were washed three times with 15 mL of DMF and then with 15 mL of MeOH three times. The solid material was then rinsed with 15 mL of MeOH and left to soak for 3 days with fresh MeOH exchanged every 12 h. After 3 days, the solid materials were centrifuged and dried under vacuum.

UiO-66-NH_2

$ZrCl_4$ (125 mg, 0.54 mmol), HCl (1 mL), DMF (5 mL) were placed in a vial, and being sonicated for 20 minutes until fully dissolved. Then, BDC-NH_2 (134 mg, 0.75 mmol) solution in DMF (10 mL) were added to vial, and the mixture was sonicated for the additional 20 minutes, and then heated in conventional oven at 80 ^{o}C for 12 h. After cooling to room temperature, UiO-66-NH_2 powder was isolated by centrifugation. The solids were washed three times with 15 mL of DMF and then with 15 mL of EtOH three times. The solid material was then rinsed with 15 mL of EtOH and left to soak for 3 days with fresh EtOH exchanged every 12 h. After 3 days, the solid materials were centrifuged and dried under vacuum.

UiO-66-OCH_2CCH

BDC-O-CH_2CCH (**B**, 58 mg, 0.25 mmol), $ZrCl_4$ (55 mg, 0.25 mmol), formic acid (833 μL), H_2O (10 μL) and DMF (7 mL) were placed in a vial, and the mixture was heated in conventional oven at 65 ^{o}C for 24 h and then cooled to room temperature. UiO-66-OCH_2CCH powder was isolated by centrifugation. The solids were washed three times with 15 mL of DMF and then with 15 mL of MeOH three times. The solid material was then rinsed with 15 mL of MeOH and left to soak for 3 days with fresh MeOH exchanged every 12 h. After 3 days, the solid materials were centrifuged and dried under vacuum.

UiO-66-NMe_3X (by PSE)

BDC-NMe_3OTf (**A**, 90 mg, 0.24 mmol) were dissolved in 4 % KOH solution. Then the solution was adjusted to pH 7 with 1 M aqueous HCl. And UiO-66 MOFs (77 mg, 0.046 mmol) were added to the solution. The reaction mixture was heated in conventional oven at 85 ^{o}C for 24 h. After completion, the UiO-66 MOFs were washed with fresh H_2O (10 x 3 mL) and washed again with fresh MeOH (10 mL) for 3 days with centrifugation. Then solid was dried under vacuum for 1 day to remove volatile substrates and solvents.

UiO-66-triazole-NMe_3X (by PSE)

BDC-triazole-NMe_3I (**C**, 33.8 mg, 0.071 mmol) were dissolved in 4 % KOH solution (1.5 mL). Then the solution was adjusted to pH 7 with 1 M aqueous HCl. And UiO-66 MOFs (40 mg, 0.024 mmol) were added to the solution. The reaction mixture was stirred at room temperature for 24 h. After completion, the UiO-66 MOFs were washed with fresh H_2O (10 x 3 mL) and washed again with fresh MeOH (10 mL) for 3 days with centrifugation. Then solid was dried under vacuum for 1 day to remove volatile substrates and solvents.

UiO-66-triazole-NMe$_3$X (by PSM)

UiO-66-OCH$_2$CCH (40 mg, 0.12 mmol) and TMAZ (36 mg, 0.14 mmol) were placed in a scintillated vial (20 mL). Then DMF (2 mL), $CuSO_4 \cdot H_2O$ (3 mg dissolved in 40 µL H_2O), sodium ascorbate (34.8 mg dissolved in 160 µL H_2O) were added to vial. The reaction mixture was heated at 50 °C for 24 h. After completion, UiO-66 MOFs were washed with fresh DMF (10 x 3 mL) and washed again with fresh MeOH (10 mL) for 3 days with centrifugation. Then solid was dried under vacuum for 1 day to remove volatile substrates and solvents.

Hydroxide ion conductivity measurement using impedance spectroscopy

The ionic conductivity of UiO-66-X and UiO-66-X in (*n*-Bu)$_4$NOH was determined using impedance analysis. The powder of samples (ca. ~80 mg) was ground and pressed to the pellet using a 7 mm standard die. The thickness of the pellet was measured by a digimatic micrometer (Absolute, Mitutoyo Co. Ltd., Japan, accuracy 0.001 mm). The pellet was then coated between the silver electrodes and silver wire for impedance analysis. Quasi-four probe AC impedance measurements were carried out using Bio-Logic SP-200. The temperature and humidity conditions were controlled by a humidity and temperature-controlled incubator (TH-ME-25, JEIOTECH., Korea). The applied frequency range for the measurement was from 3M to 1 Hz against the open circuit potential with a sinus amplitude of 20 mV.

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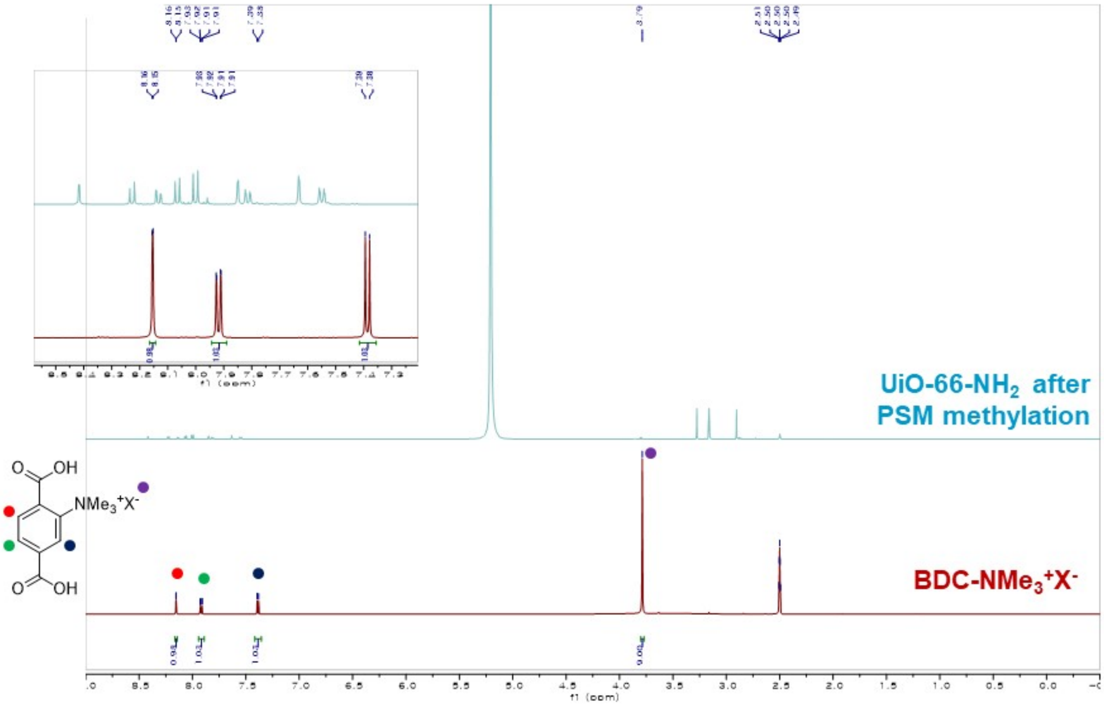
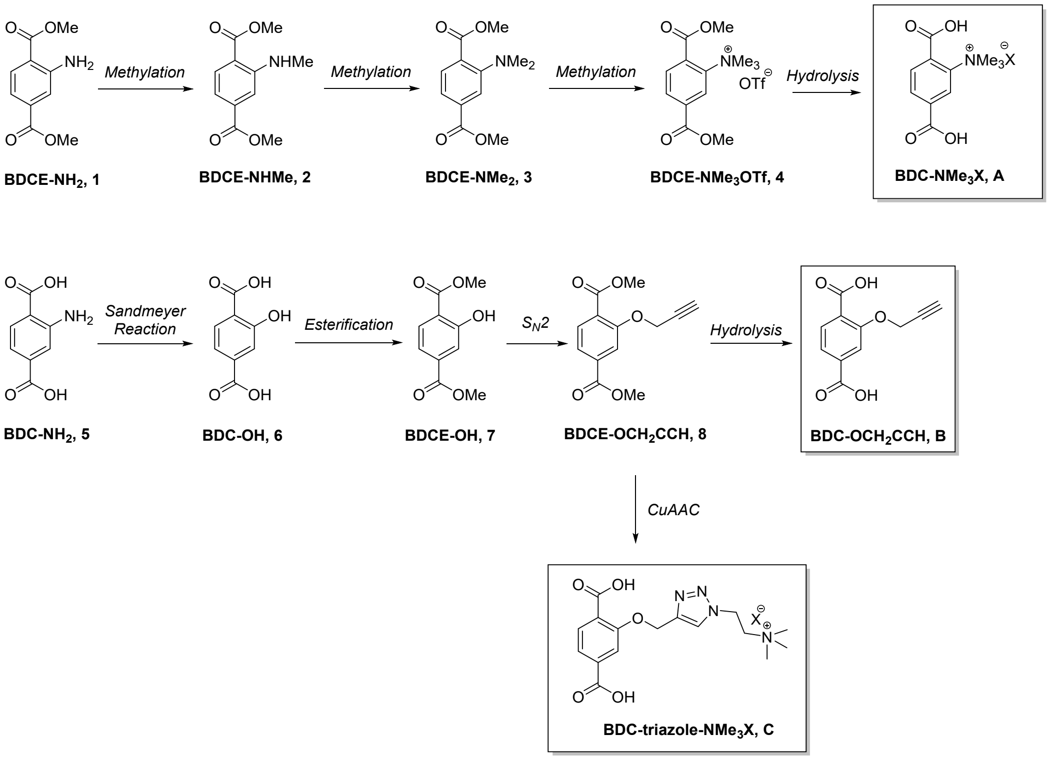


Fig. S1 Acid digested ^{1}H NMR of UiO-66-NH$_2$ after PSM methylation trials.



Scheme S1. Synthetic schemes for preparation of ligands **A**, **B** and **C.**

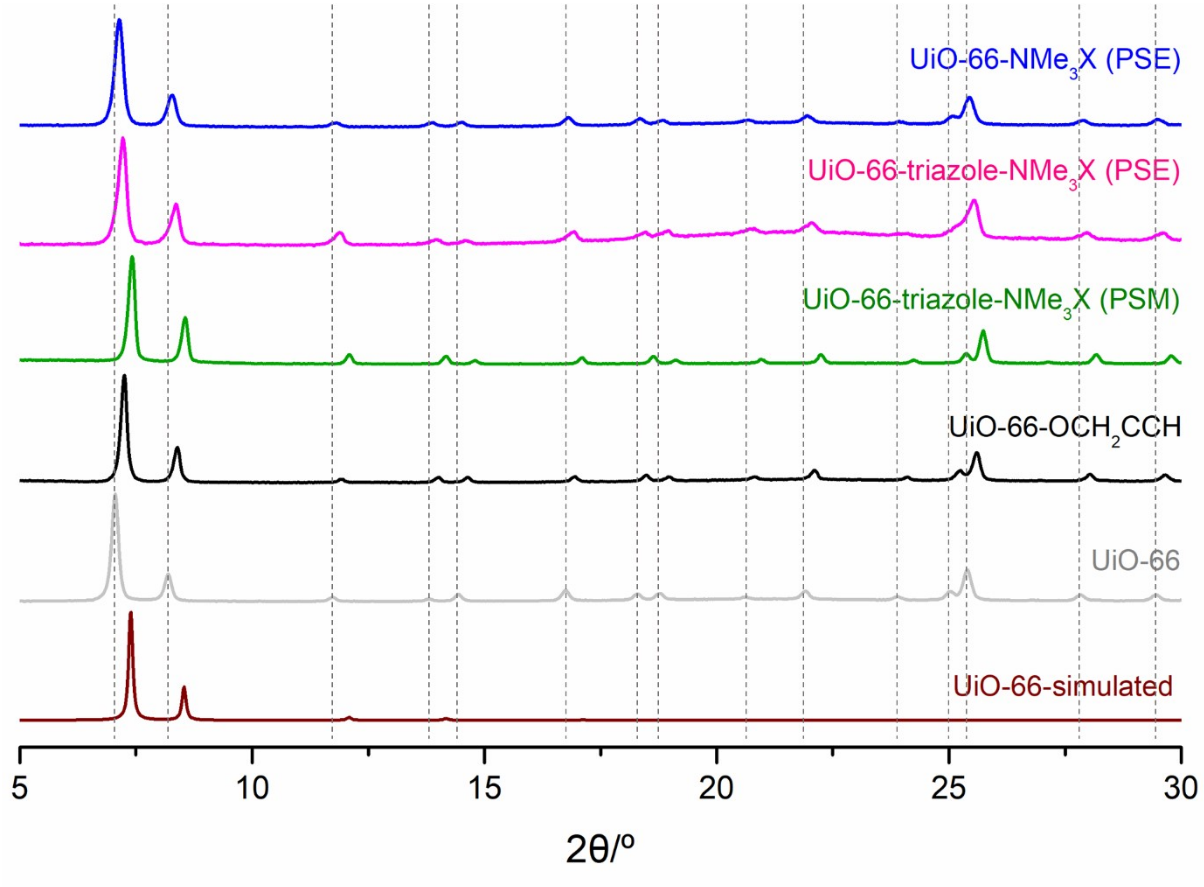


Fig. S2 PXRD patterns of simulated and synthesized UiO-66s in this study.

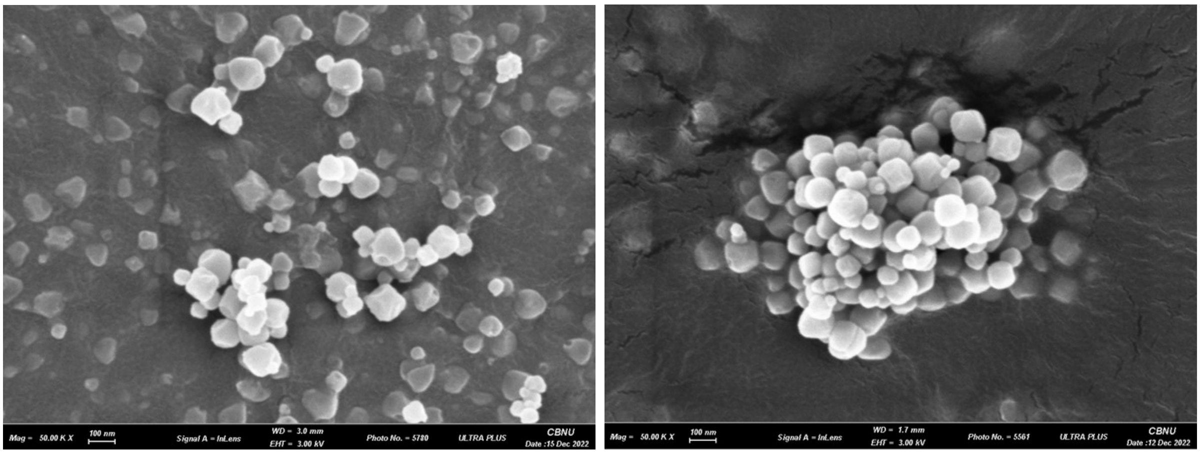


Fig. S3 SEM images of UiO-66-NMe$_3$$^+X^-$.

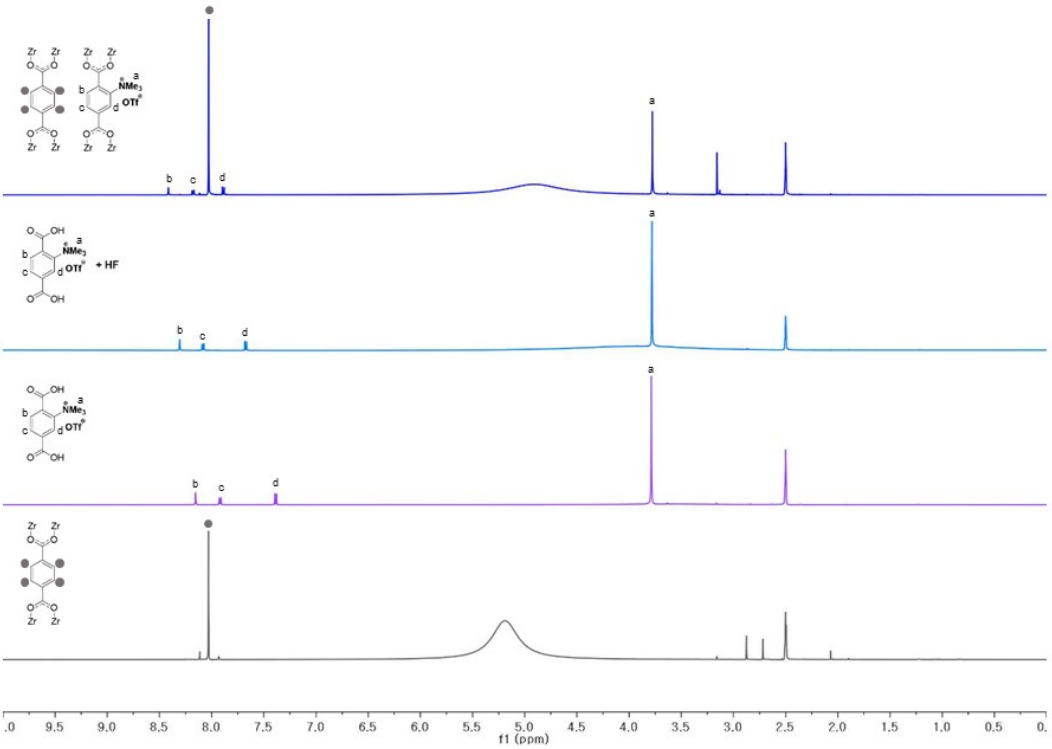


Fig. S4 ^{1}H NMR of UiO-66-NMe$_3$X (by PSE) after acid digestion (blue), BDC-NMe$_3$X + 48% aqueous HF (cyan), BDC-NMe$_3$X (purple), and parent UiO-66 after acid digestion (black).

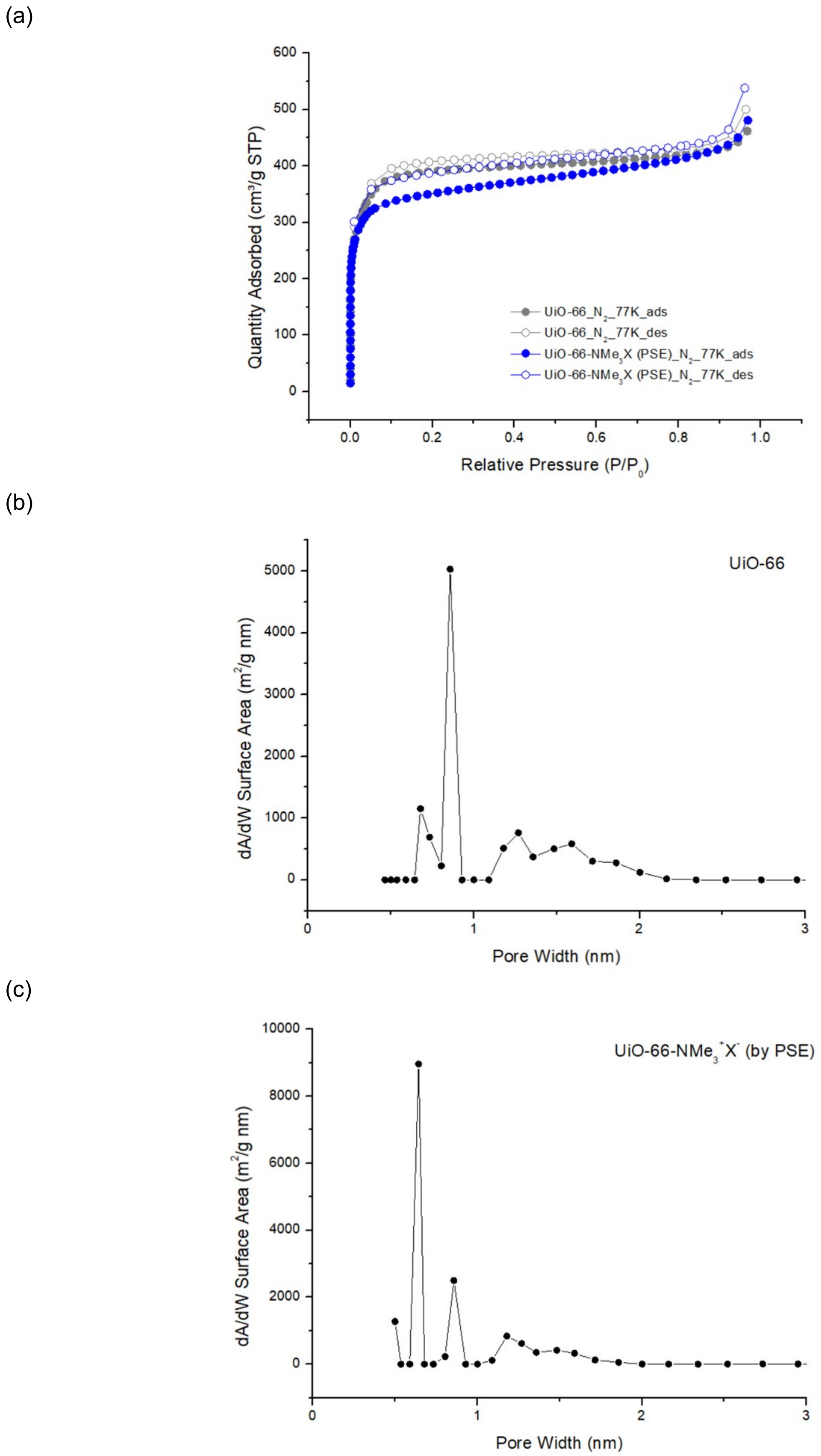


Fig. S5 (a) N_2 full isotherms (at 77 K) for UiO-66 (grey) and UiO-66-NMe_3X (by PSE, blue), (b) pore size distribution (PSD) for UiO-66, (c) PSD for UiO-66-NMe_3X (by PSE).

Table S1. BET surface area of a series of UiO-66s with quaternary ammonium groups.

MOF	BET surface (m^2/g)
UiO-66	1,589
UiO-66-OCH_2CCH	1,091
UiO-66-triazole-NMe_3X (by PSM)	426
UiO-66-triazole-NMe_3X (by PSE)	837
UiO-66-NMe_3X (by PSE)	1,385

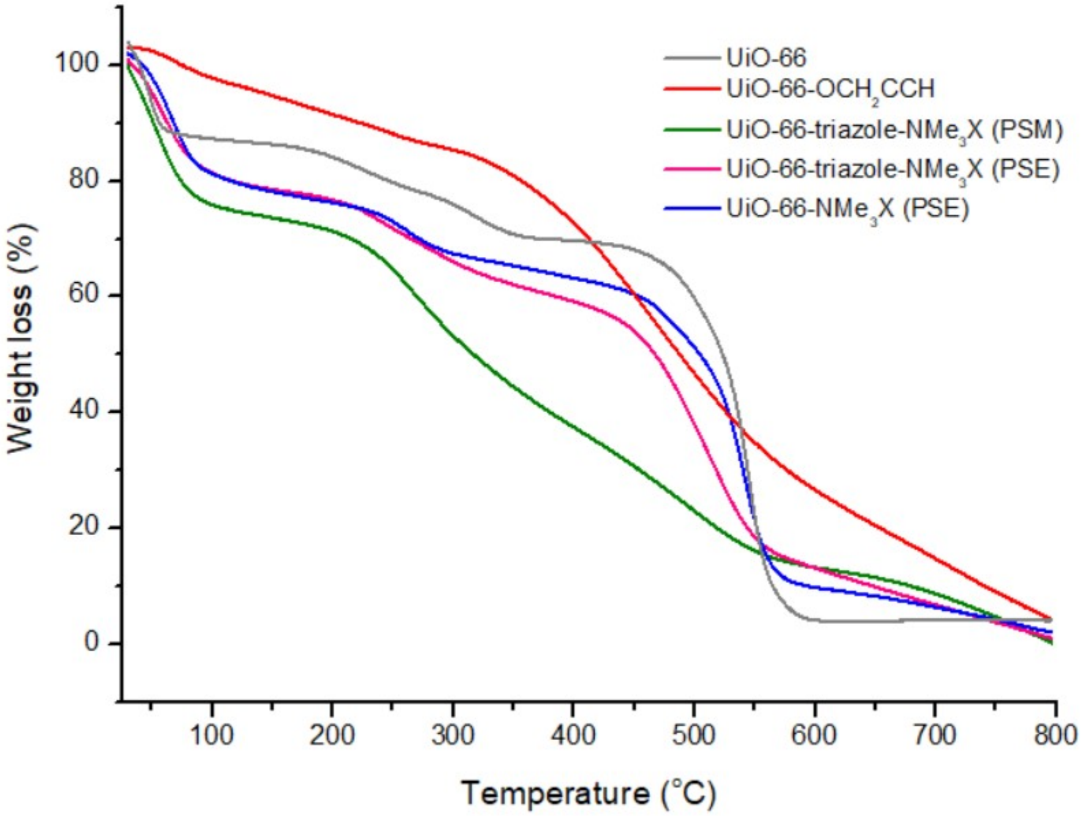


Fig. S6 TGA of a series of UiO-66s with quaternary ammonium groups.

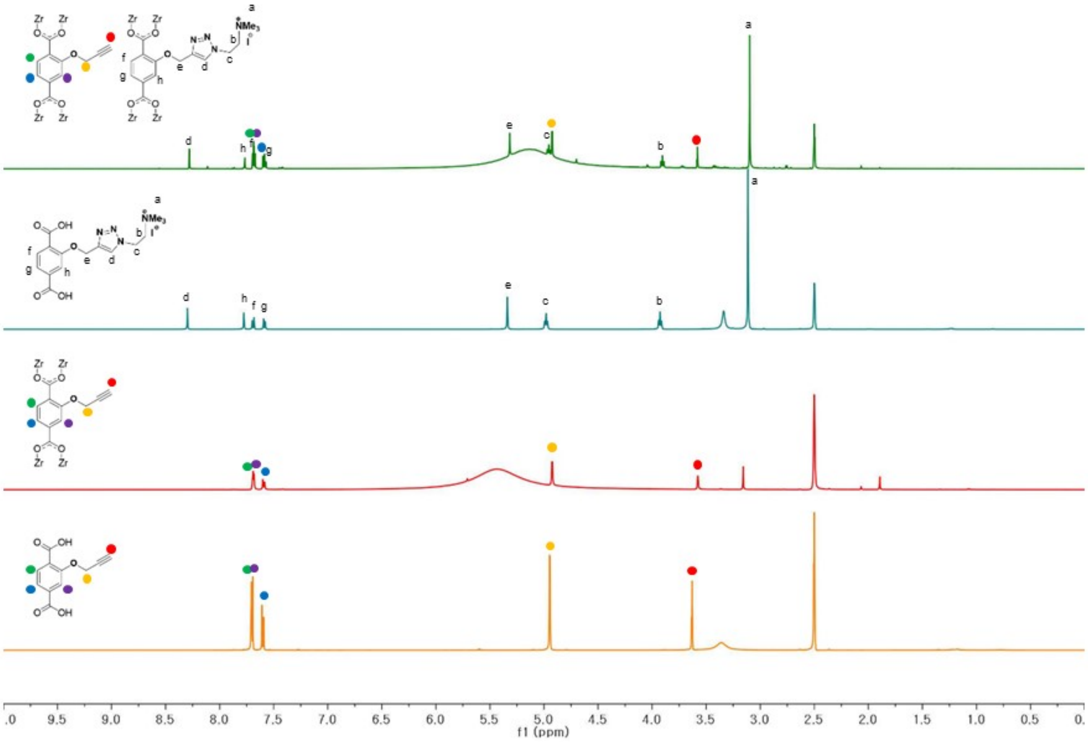


Fig. S7 ^{1}H NMR of UiO-66-triazole-NMe$_3$X (by PSM) after acid digestion (green), BDC-triazole-NMe$_3$X (cyan), UiO-66-OCH$_2$CCH after acid digestion (red), BDC-OCH$_2$CCH (orange).

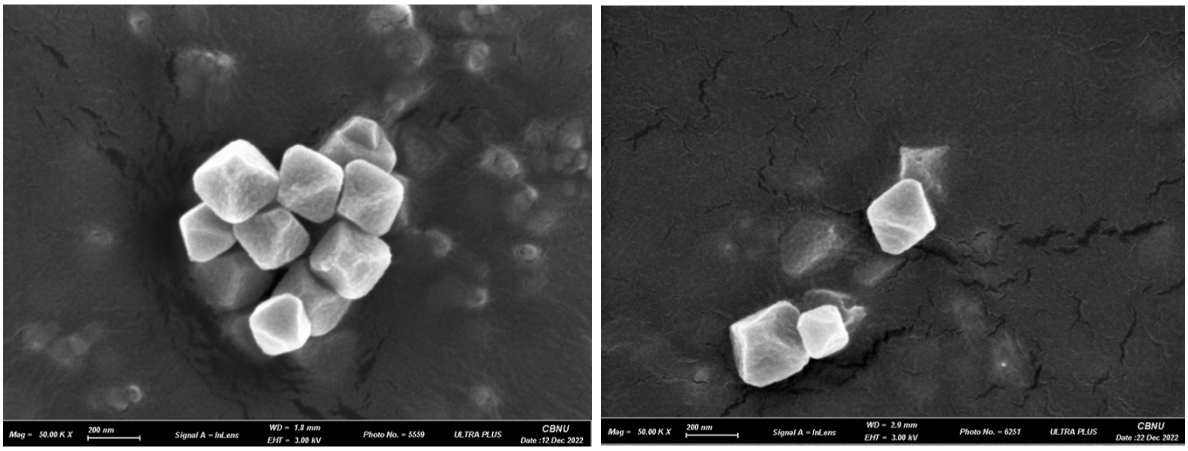


Fig. S8 SEM images of UiO-66-triazole-NMe$_3^+$X$^-$ (by PSM).

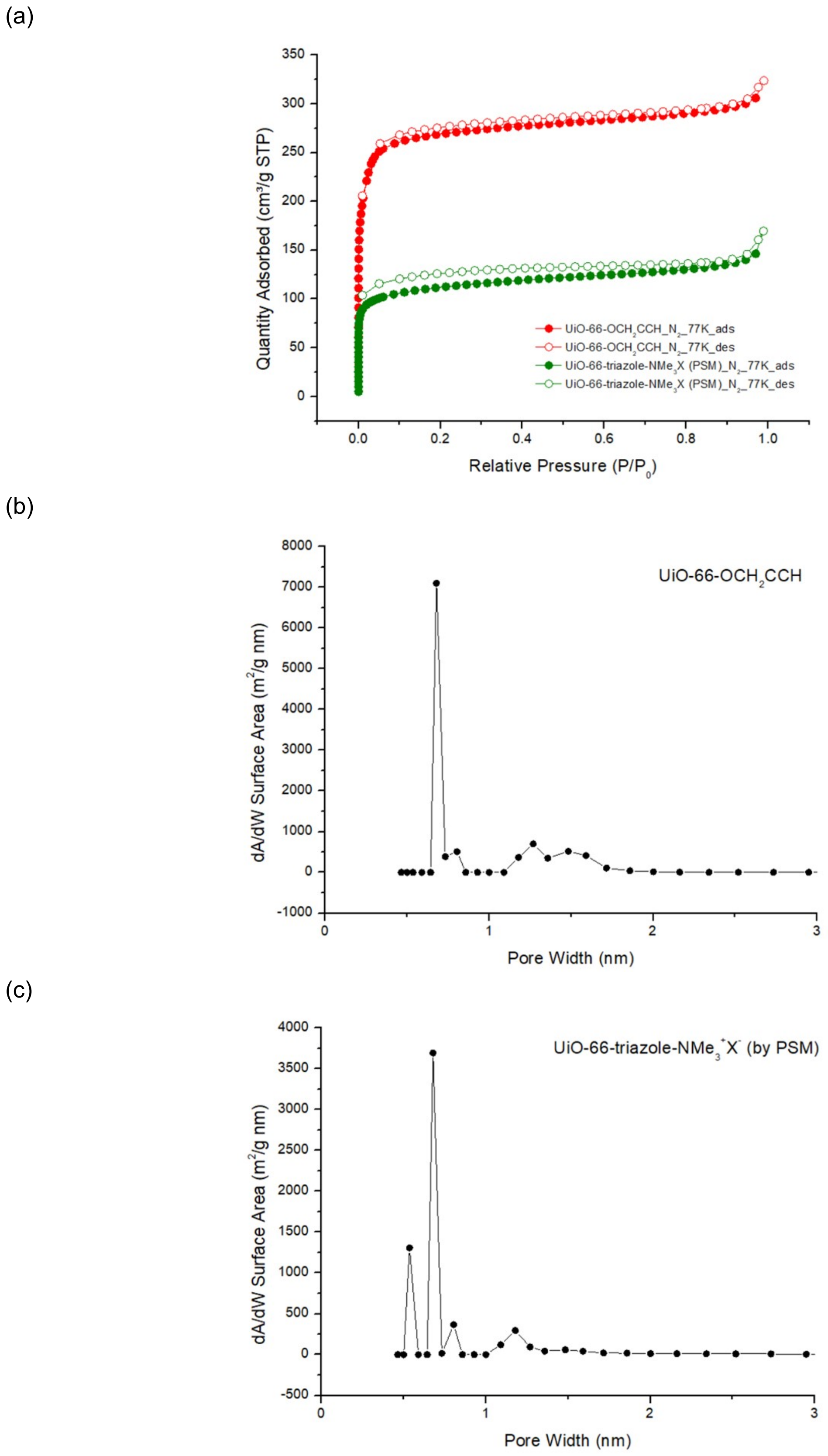


Fig. S9 (a) N_2 full isotherms (at 77 K) for UiO-66-OCH_2CCH (red) and UiO-66-triazole-NMe_3X (by PSM, green), (b) PSD of UiO-66-OCH_2CCH_3, (c) PSD of UiO-66-triazole-NMe_3X (by PSM).

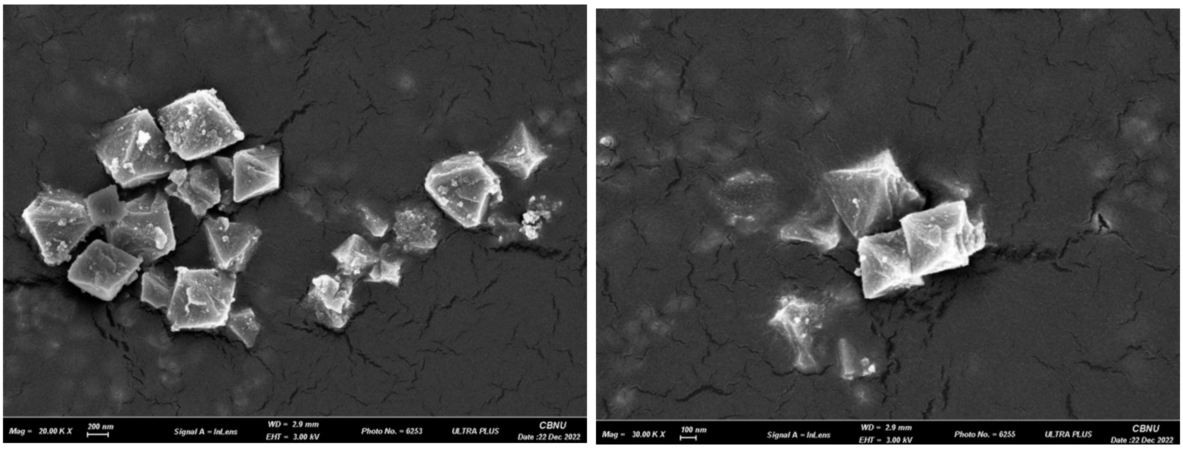


Fig. S10 SEM images of UiO-66-triazole-$NMe_3^+X^-$ (by PSE).

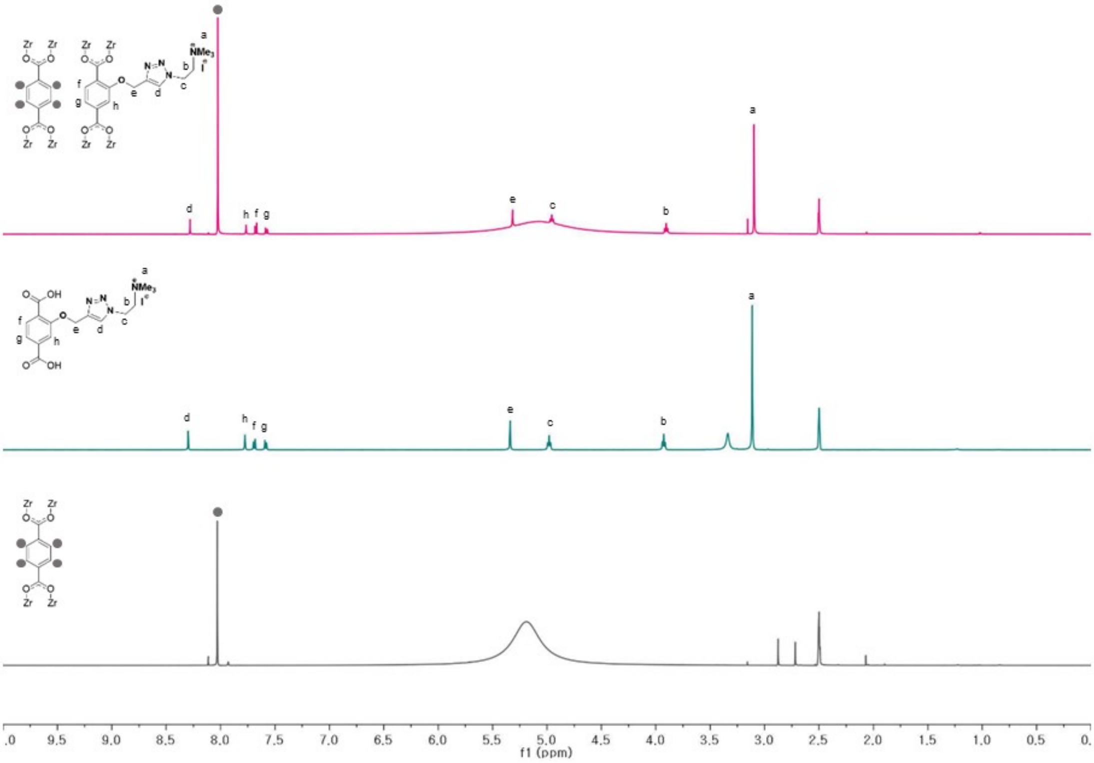
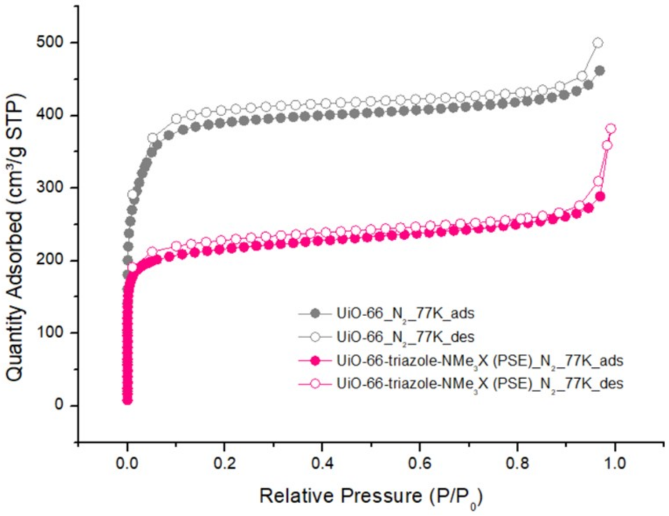


Fig. S11 ^{1}H NMR of UiO-66-triazole-NMe_3X (by PSE) after acid digestion (pink), BDC-triazole-NMe_3X, UiO-66 (cyan).

(a)



(b)

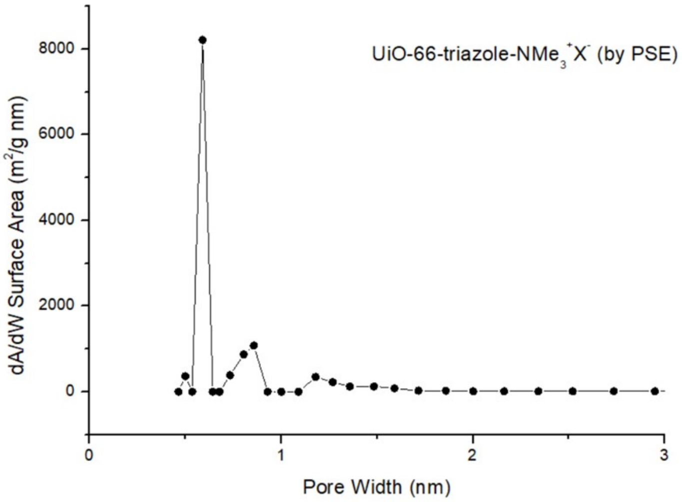


Fig. S12 (a) N_2 full isotherms (at 77 K) for UiO-66 and UiO-66-triazole-NMe_3X (by PSE), (b) PSD of UiO-66-triazole-NMe_3X (by PSE).

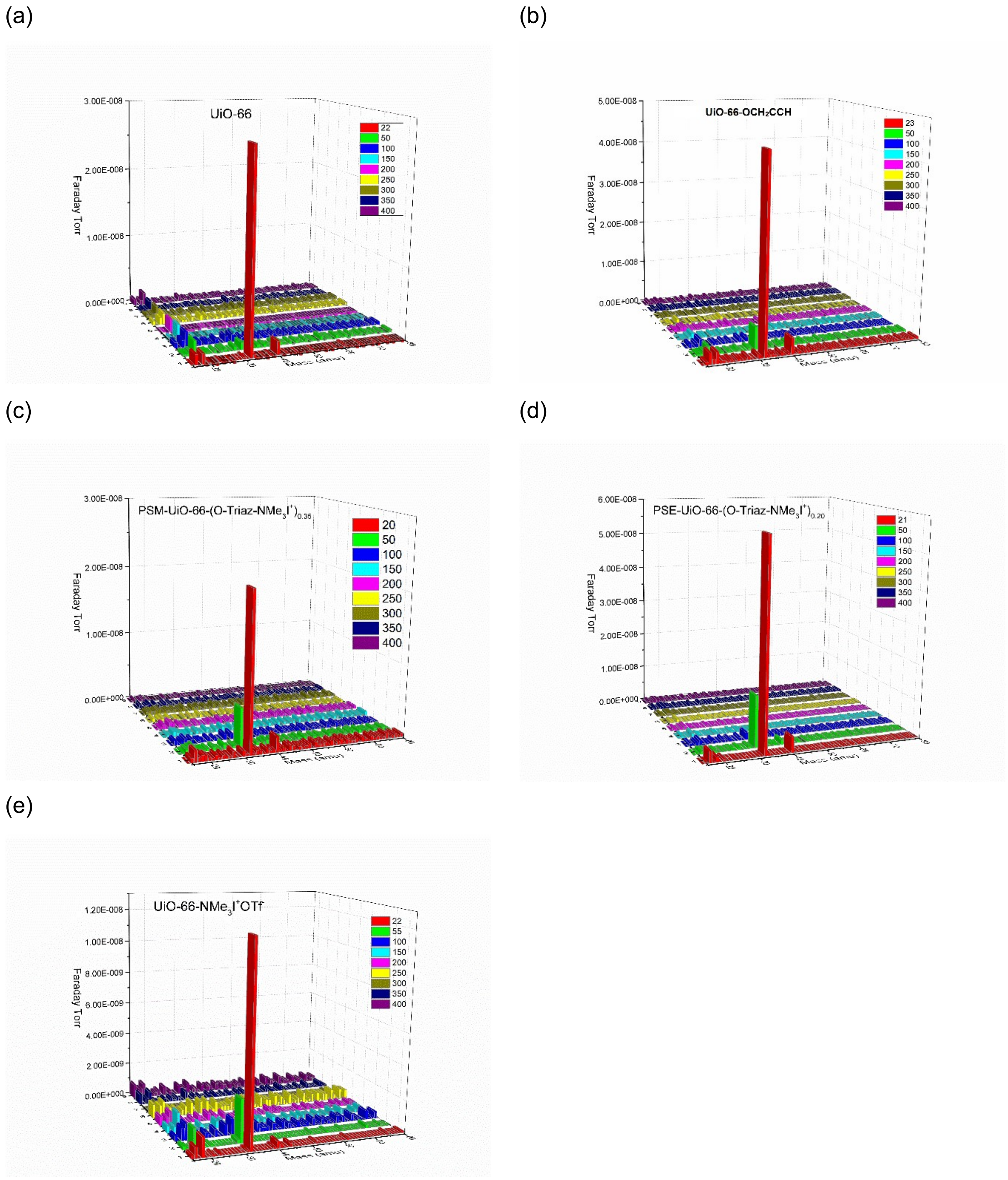


Fig. S13 Thermogravimetric-Mass Spectrometry (TG-MS) bar mode for a series of UiO-66s with quaternary ammonium groups; (a) UiO-66 (b) UiO-66-OCHCCH (c) UiO-66-triazole-NMe_3X (by PSM) (d) UiO-66-triazole-NMe_3X (by PSE) (e) UiO-66-NMe_3X (by PSE).

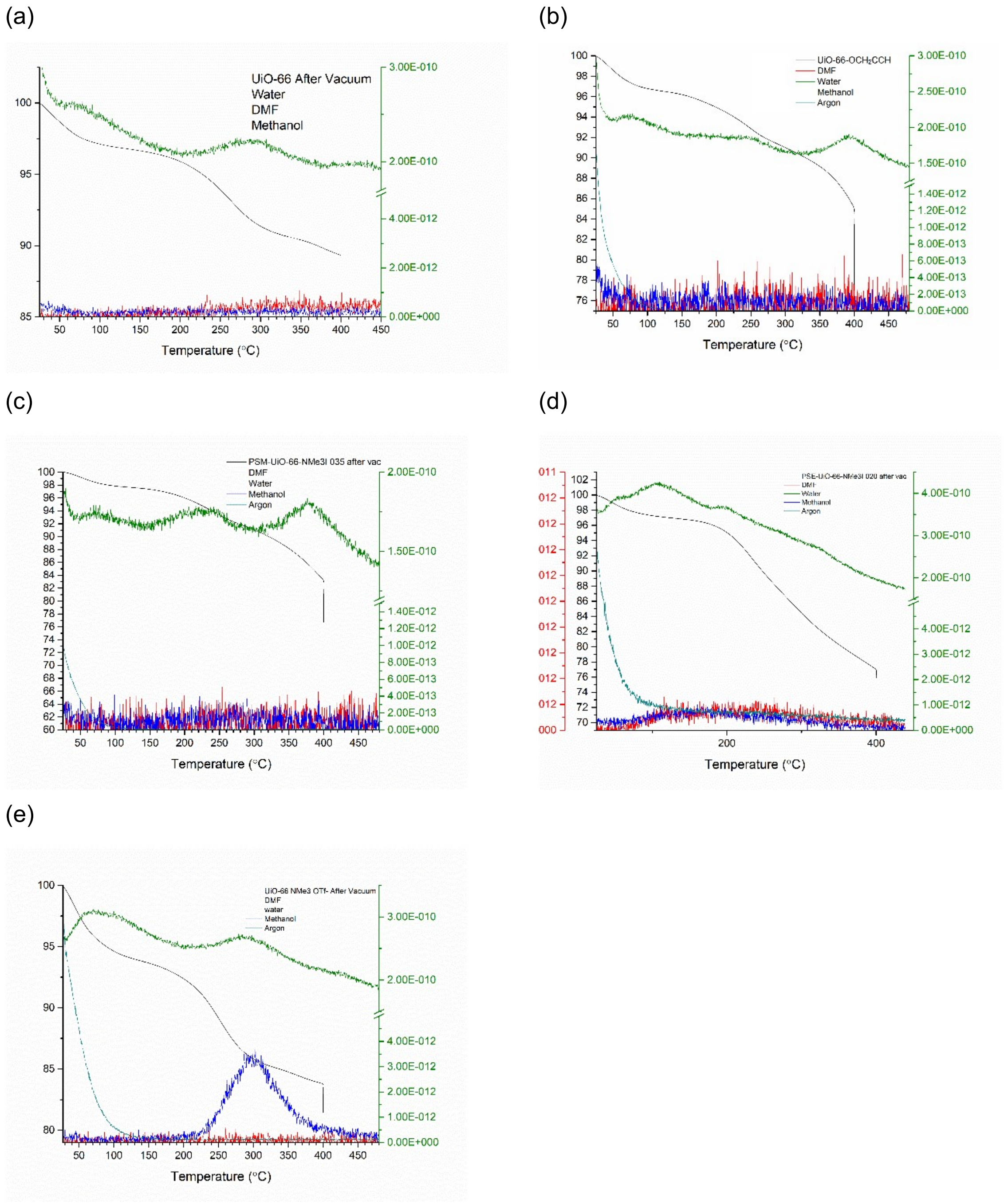


Fig. S14 TG-MS Mass profile mode for a series of UiO-66s with quaternary ammonium groups; (a) UiO-66 (b) UiO-66-OCH_2CCH (c) UiO-66-triazole-NMe_3X (by PSM) (d) UiO-66-triazole-NMe_3X (by PSE) (e) UiO-66-NMe_3X (by PSE).

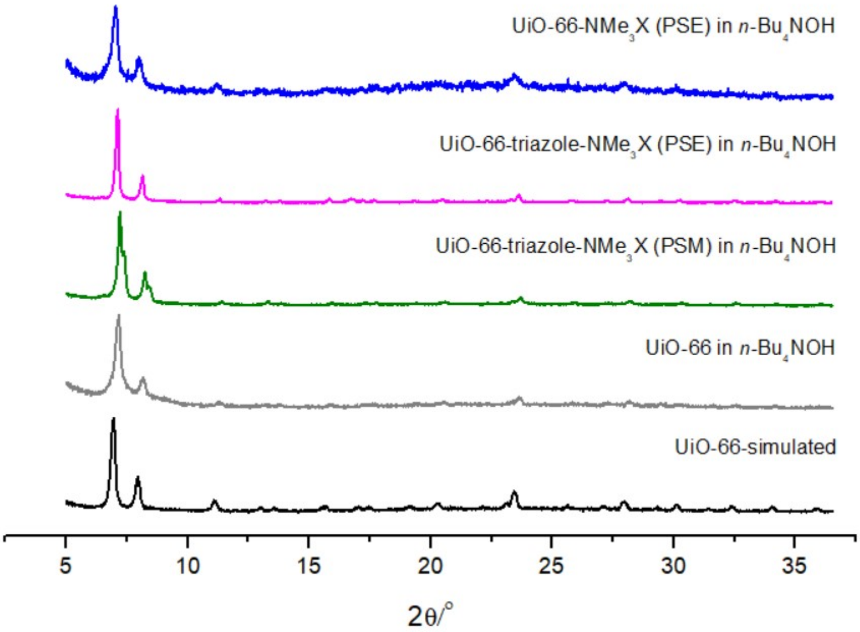


Fig. S15 PXRD patterns of UiO-66s in TBAH (n-Bu_4NOH).

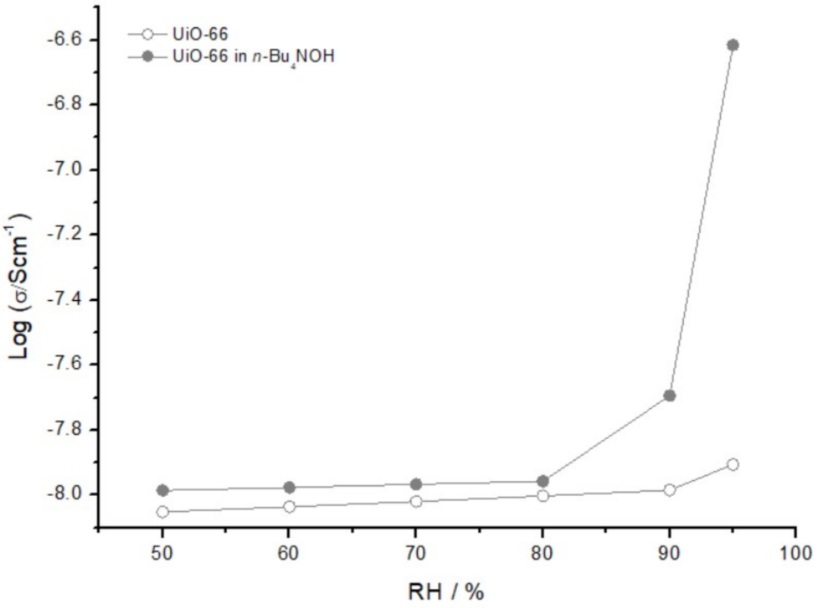


Fig. S16 Hydroxide conductivity of UiO-66 with/without TBAH.

Table S2. Hydroxide conductivities of UiO-66 with relative humidity controls.

Relative humidity – Temperature	Conductivity of UiO-66 (S/cm)	Conductivity of UiO-66 in *n*-Bu_4NOH (S/cm)
50% - 25 °C	8.8718×10^{-9}	1.0327×10^{-8}
60% - 25 °C	9.2004×10^{-9}	1.0552×10^{-8}
70% - 25 °C	9.5543×10^{-9}	1.0786×10^{-8}
80% - 25 °C	9.9365×10^{-9}	1.1032×10^{-8}
90% - 25 °C	1.0351×10^{-8}	2.0225×10^{-8}
95% - 25 °C	1.2421×10^{-8}	2.4270×10^{-7}

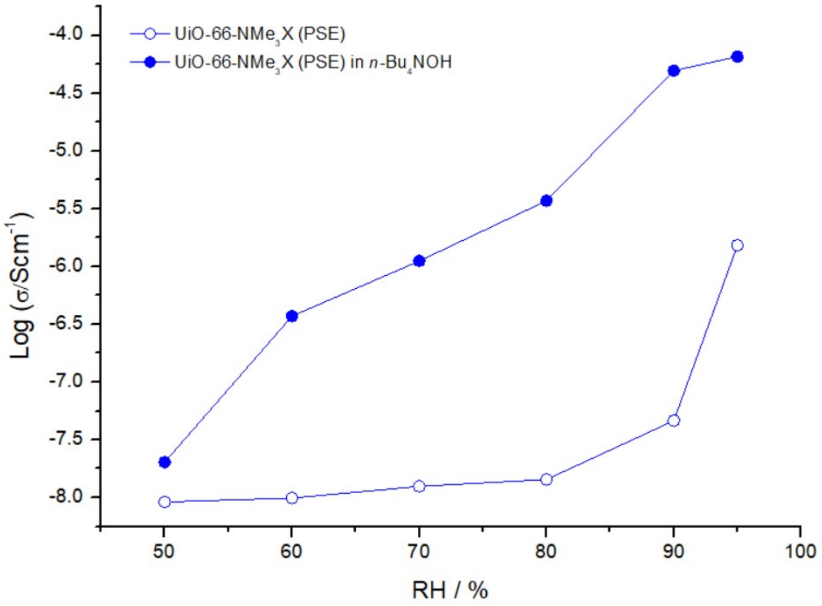


Fig. S17 Hydroxide conductivity of UiO-66-NMe_3X (by PSE) with/without TBAH.

Table S3. Hydroxide conductivities of UiO-66-NMe_3X (by PSE) with relative humidity and temperature controls.

Relative humidity – Temperature	Conductivity of UiO-66-NMe_3X (PSE) (S/cm)	Conductivity of UiO-66-NMe_3X (PSE) in *n*-Bu_4NOH (S/cm)
50% - 25 ^oC	9.1725×10^{-9}	2.0315×10^{-8}
60% - 25 ^oC	9.9162×10^{-9}	3.7244×10^{-7}
70% - 25 ^oC	1.2522×10^{-8}	1.1173×10^{-6}
80% - 25 ^oC	1.4332×10^{-8}	3.7244×10^{-6}
90% - 25 ^oC	4.6326×10^{-8}	4.9659×10^{-5}
95% - 25 ^oC	1.5287×10^{-6}	6.5724×10^{-5}
95% - 35 ^oC	2.1659×10^{-6}	8.5948×10^{-5}
95% - 45 ^oC	1.4004×10^{-5}	1.8622×10^{-4}
95% - 55 ^oC	1.8319×10^{-5}	3.7244×10^{-4}

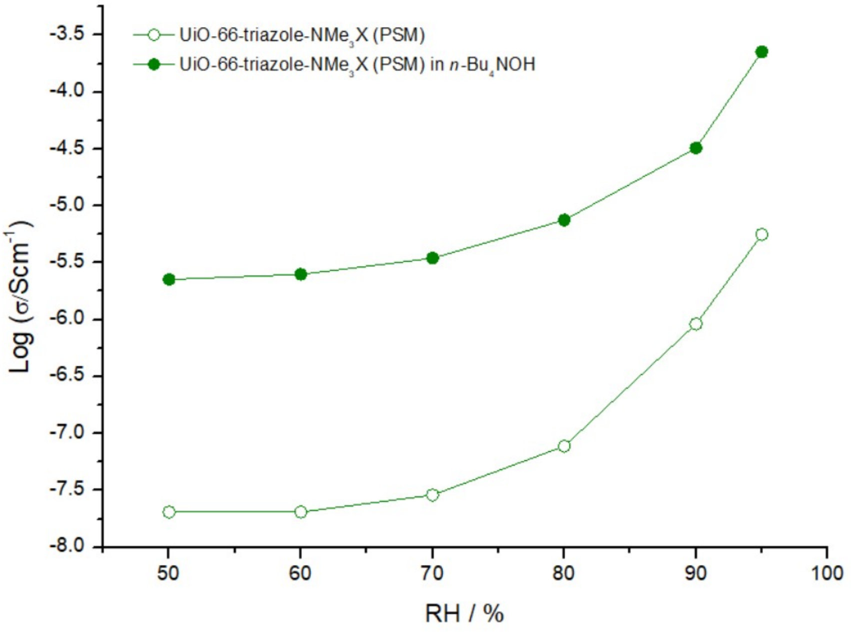


Fig. S18 Hydroxide conductivity of UiO-66-triazole-NMe$_3$X (by PSM) with/without TBAH.

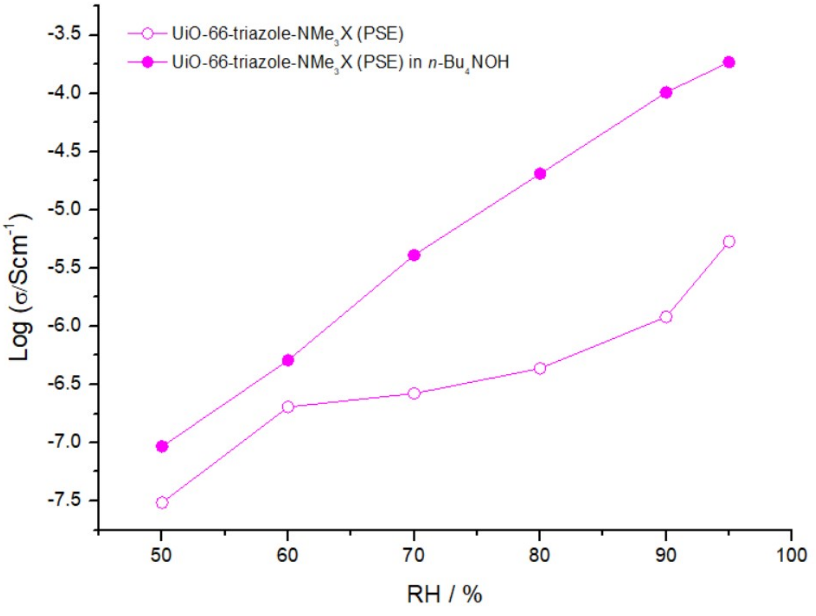


Fig. S19 Hydroxide conductivity of UiO-66-triazole-NMe$_3$X (by PSE) with/without TBAH.

Table S4. Hydroxide conductivities of UiO-66-triazole-NMe$_3$X (by PSM) with relative humidity and temperature controls.

Relative humidity – Temperature	Conductivity of UiO-66-triazole-NMe$_3$X (PSM) (S/cm)	Conductivity of UiO-66-triazole-NMe$_3$X (PSM) in *n*-Bu$_4$NOH (S/cm)
50% - 25 ^{o}C	2.0412×10^{-8}	2.2554×10^{-6}
60% - 25 ^{o}C	2.0412×10^{-8}	2.5061×10^{-6}
70% - 25 ^{o}C	2.8768×10^{-8}	3.4699×10^{-6}
80% - 25 ^{o}C	7.7454×10^{-8}	7.5182×10^{-6}
90% - 25 ^{o}C	9.1536×10^{-7}	3.2220×10^{-5}
95% - 25 ^{o}C	5.5938×10^{-6}	2.2555×10^{-4}
95% - 35 ^{o}C	1.6372×10^{-5}	2.5925×10^{-4}
95% - 45 ^{o}C	2.8769×10^{-5}	3.1326×10^{-4}

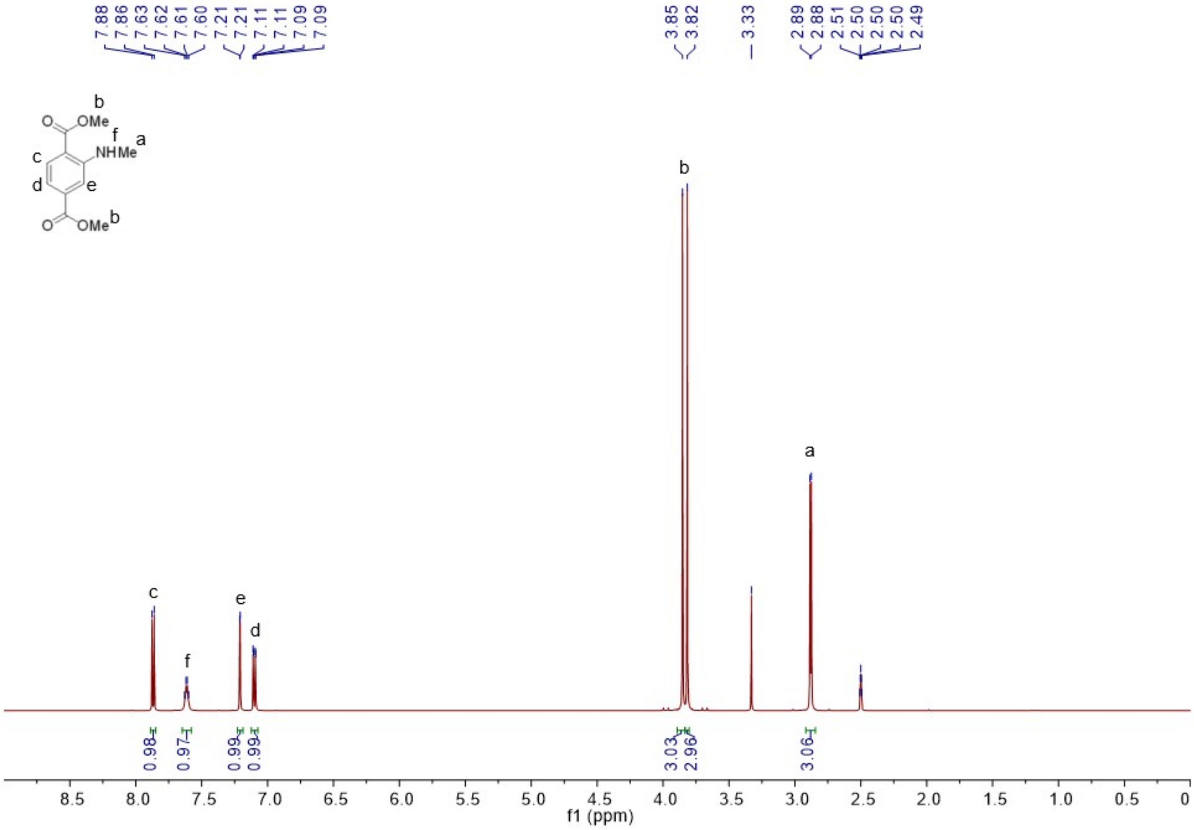
Table S5. Hydroxide conductivities of UiO-66-triazole-NMe$_3$X (by PSE) with relative humidity and temperature controls.

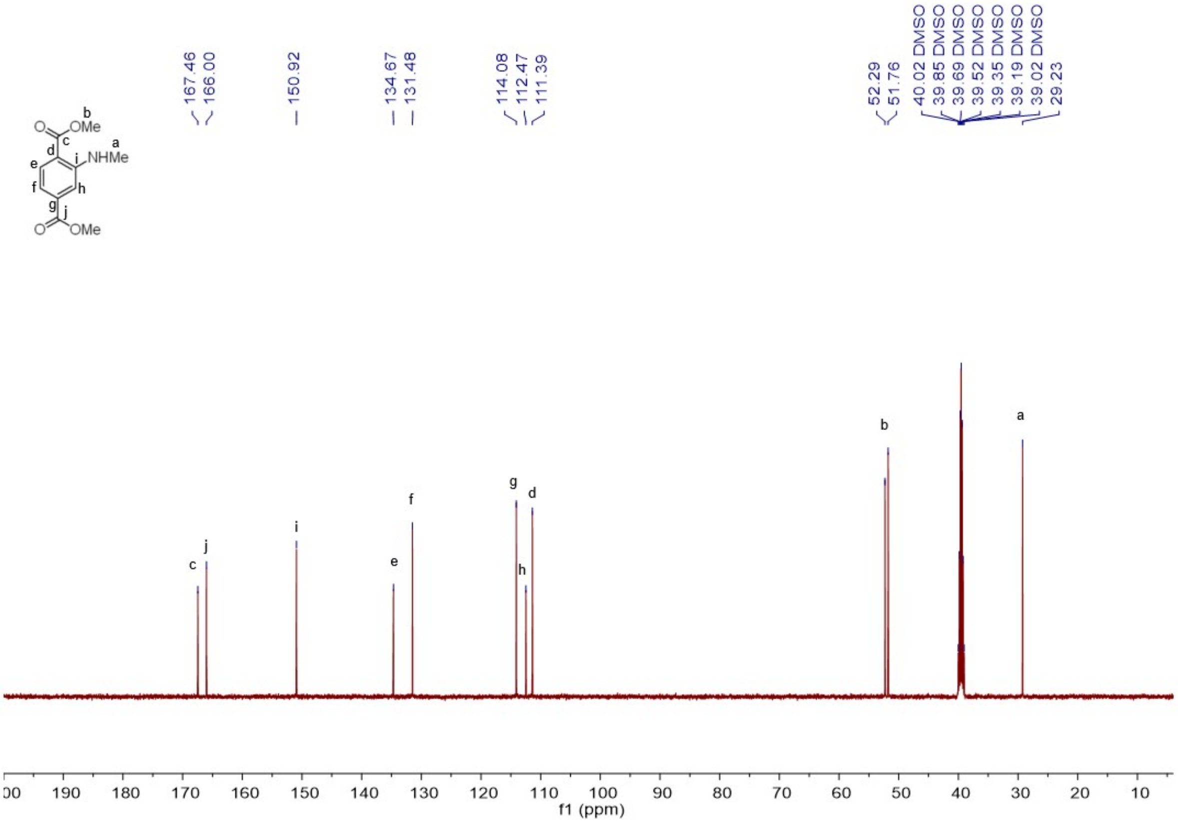
Relative humidity – Temperature	Conductivity of UiO-66-triazole-NMe$_3$X (PSE) (S/cm)	Conductivity of UiO-66-triazole-NMe$_3$X (PSE) in *n*-Bu$_4$NOH (S/cm)
50% - 25 ^{o}C	3.0528×10^{-8}	9.2954×10^{-8}
60% - 25 ^{o}C	2.0320×10^{-7}	5.1124×10^{-7}
70% - 25 ^{o}C	2.6493×10^{-7}	4.0900×10^{-6}
80% - 25 ^{o}C	4.3516×10^{-7}	2.0450×10^{-5}
90% - 25 ^{o}C	1.2041×10^{-6}	1.0225×10^{-4}
95% - 25 ^{o}C	5.3438×10^{-6}	1.8591×10^{-4}
95% - 35 ^{o}C	1.2974×10^{-5}	2.5562×10^{-4}
95% - 45 ^{o}C	3.0537×10^{-5}	4.0900×10^{-4}

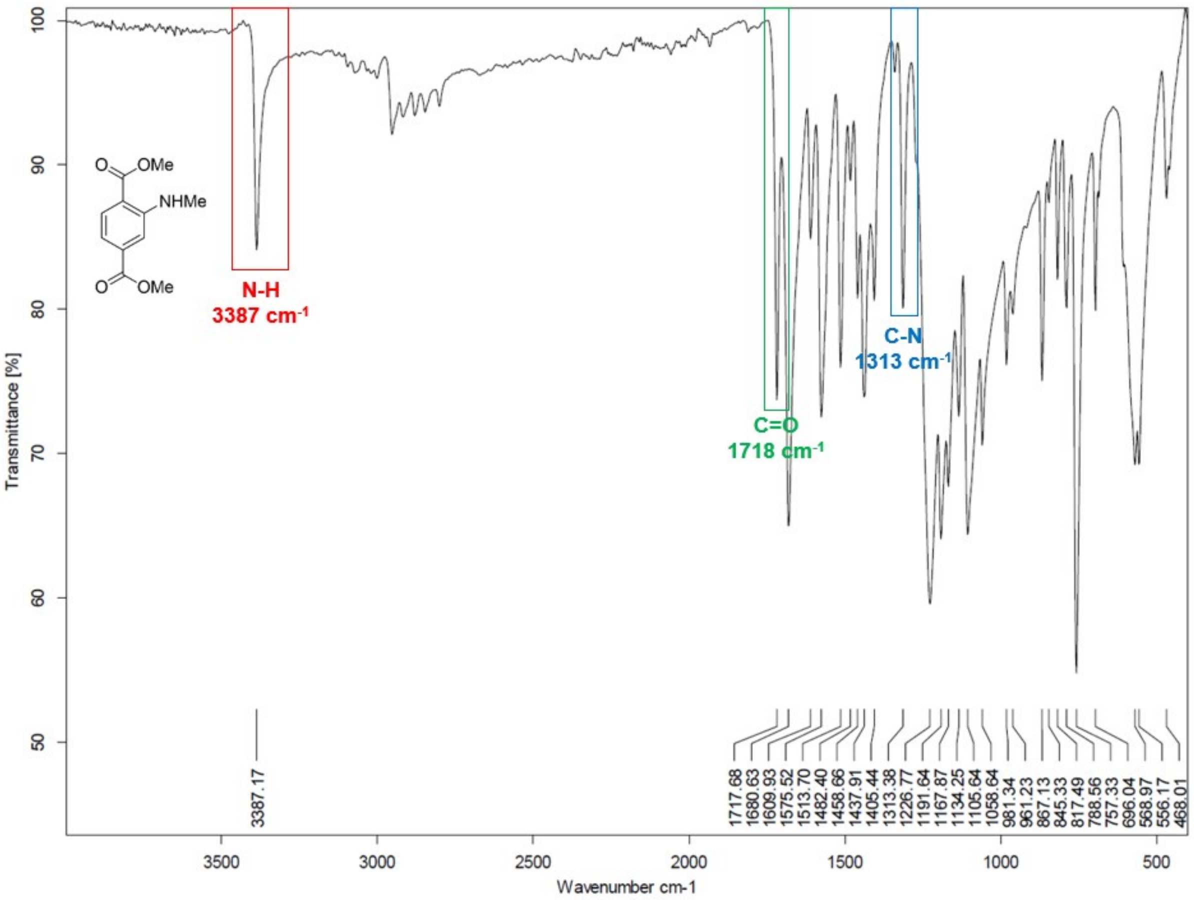
Appendix

NMR, IR and MS Spectra of the Obtained Compounds

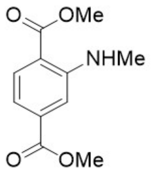
Dimethyl-2-(methylamino)terephtahalate (BDCE-NHMe)



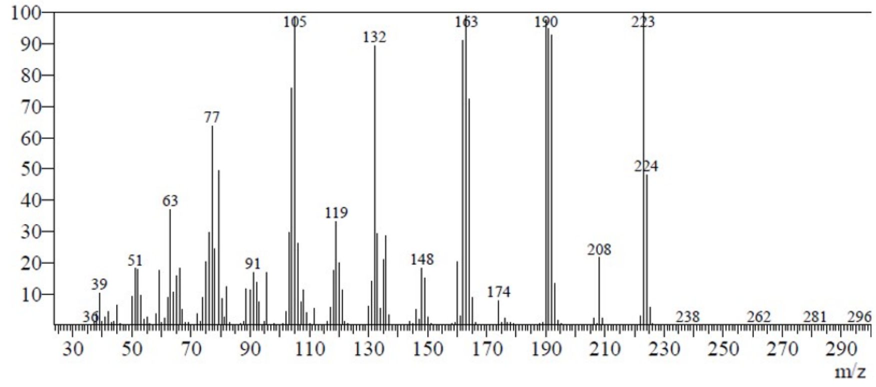




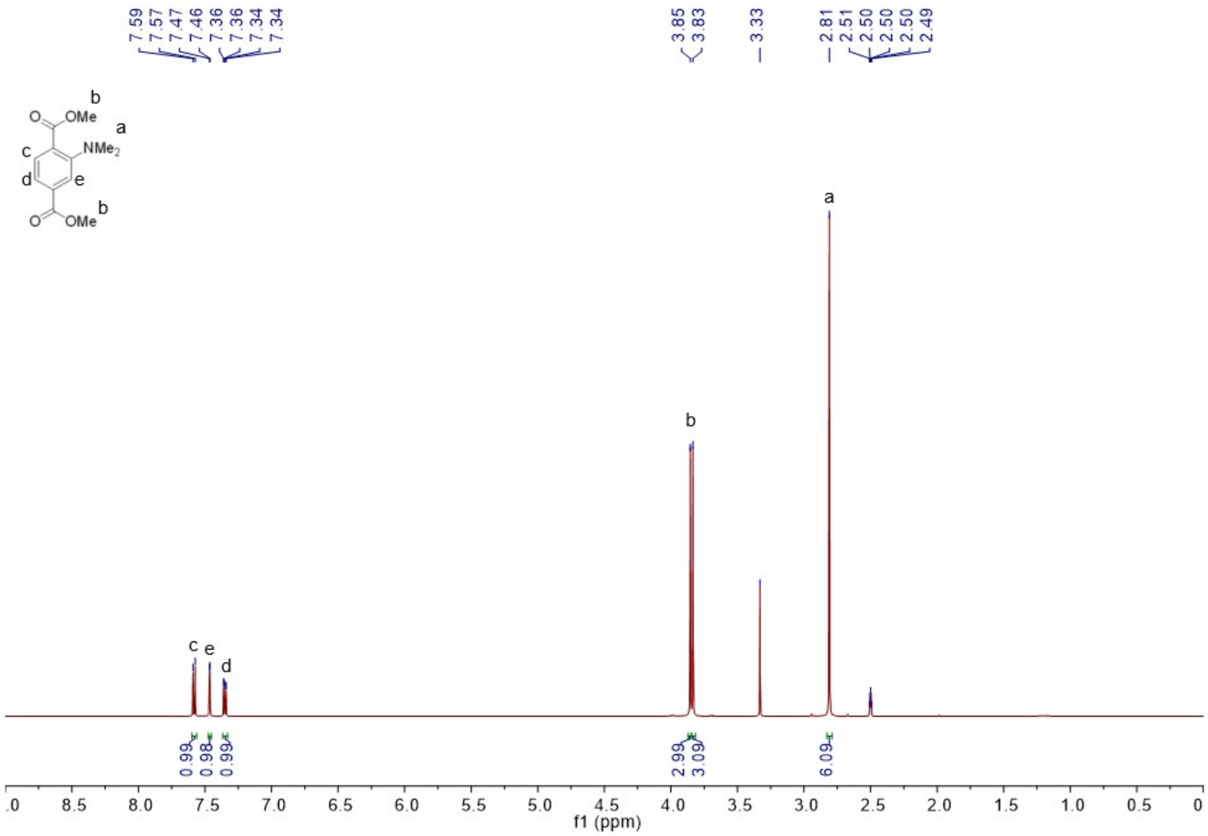
[GC-MS Data]

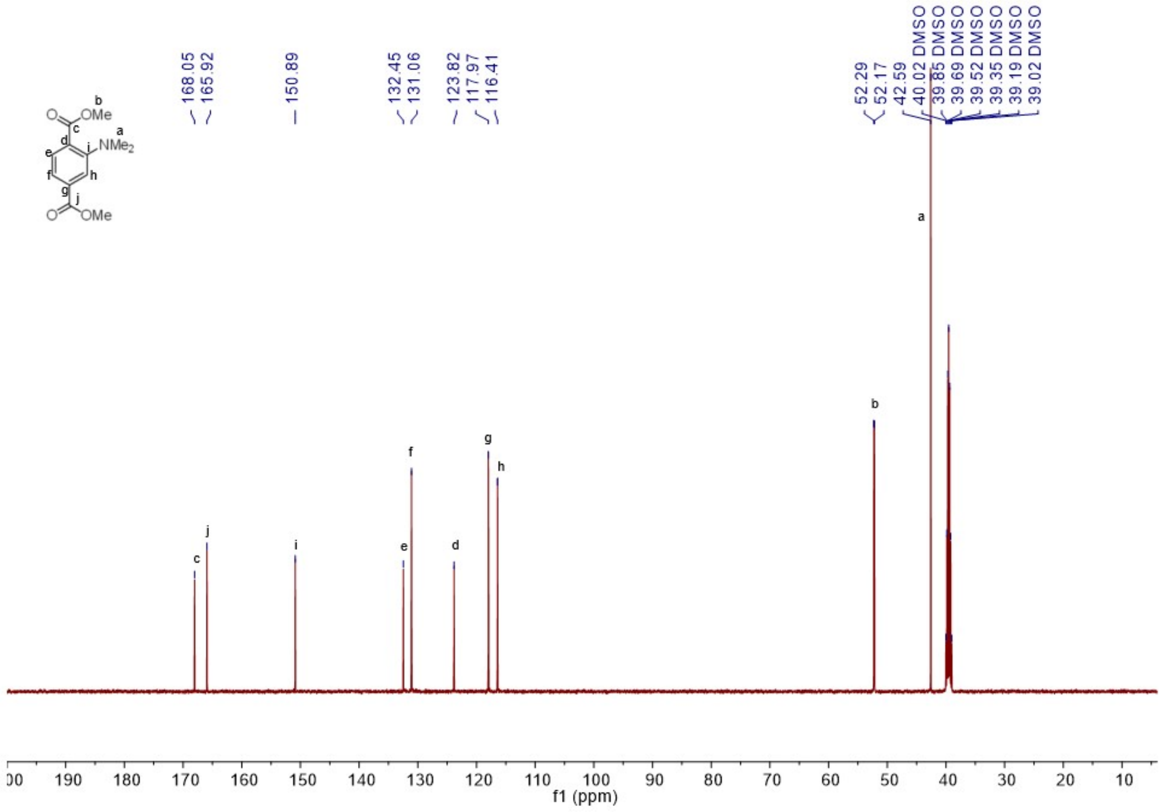


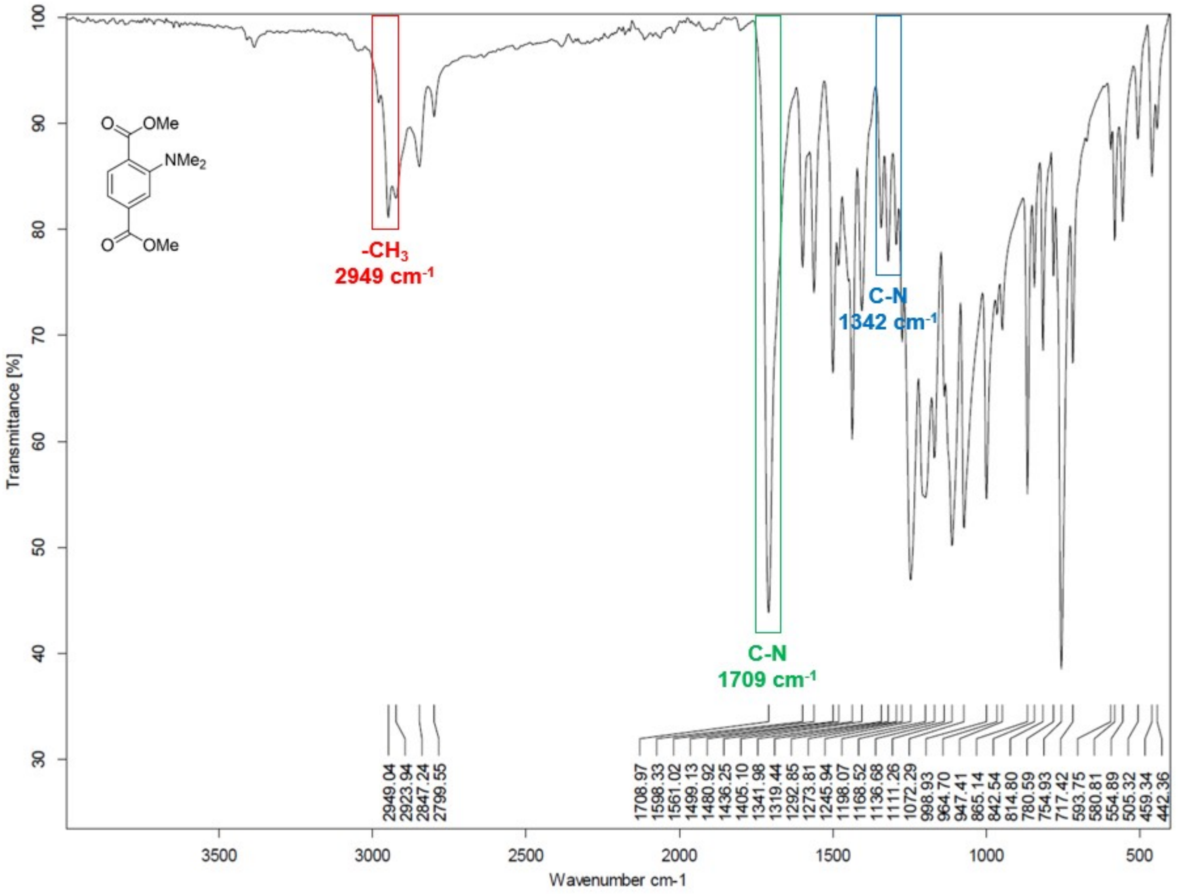
Chemical Formula: $C_{11}H_{13}NO_4$
Exact Mass: 223



Dimethyl-2-(dimethylamino)terephtahalate (BDCE-NMe$_2$)







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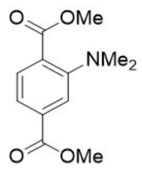
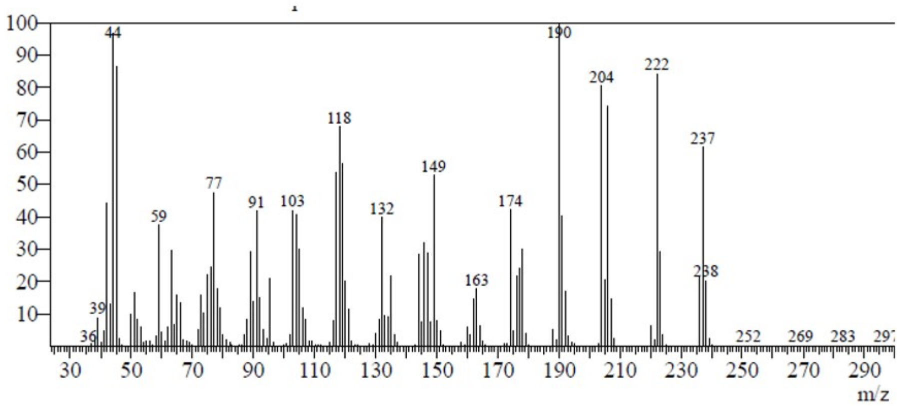
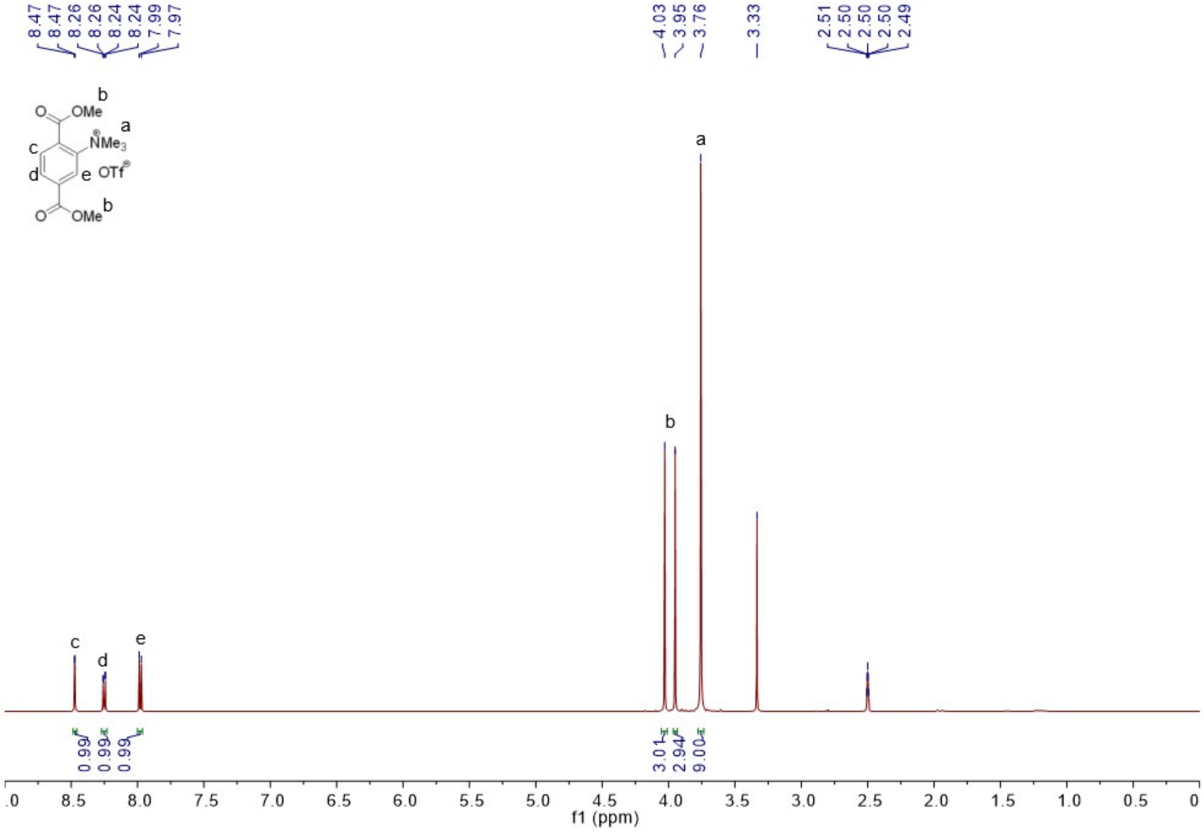


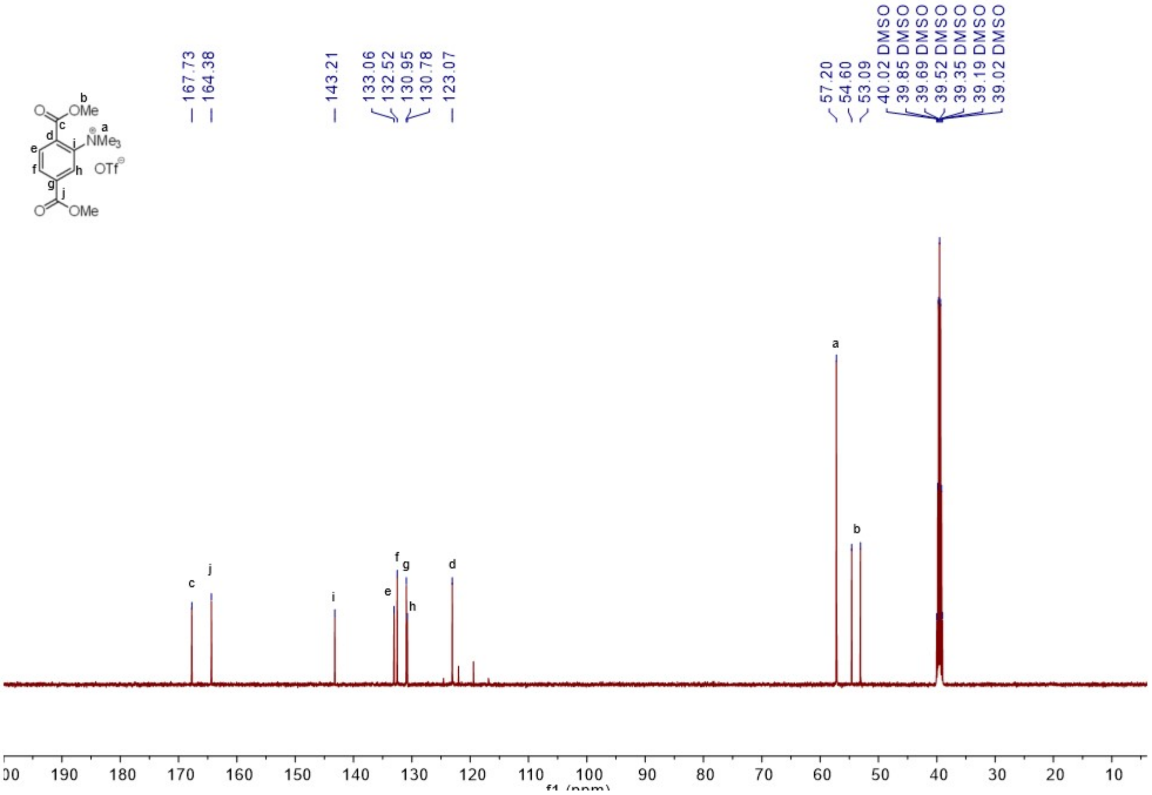
Chemical Formula: $C_{12}H_{15}NO_4$

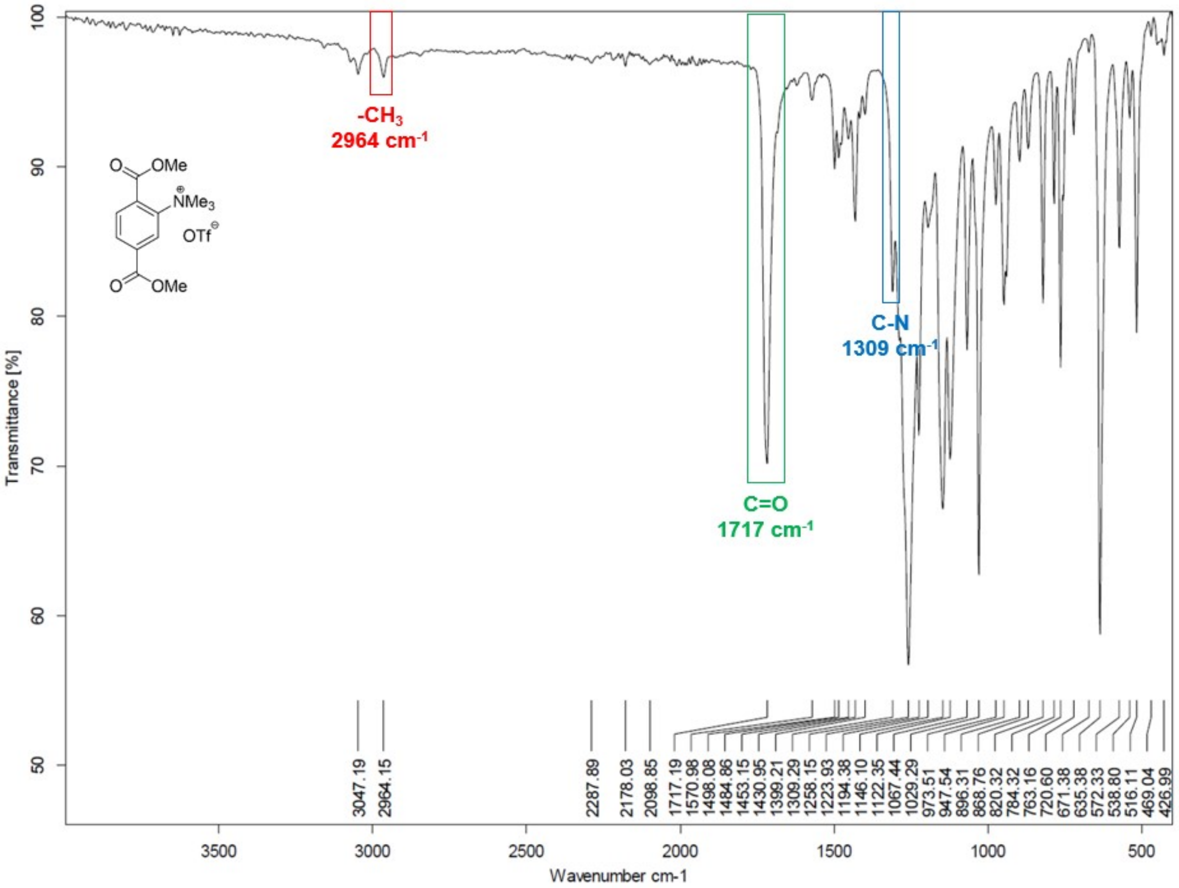
Exact Mass: 237



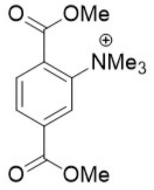
2,5-Bis(methoxycarbonyl)-*N,N,N*-trimethylbenzenaminium trifluoromethanesulfonate (BDCE-NMe$_3$OTf)



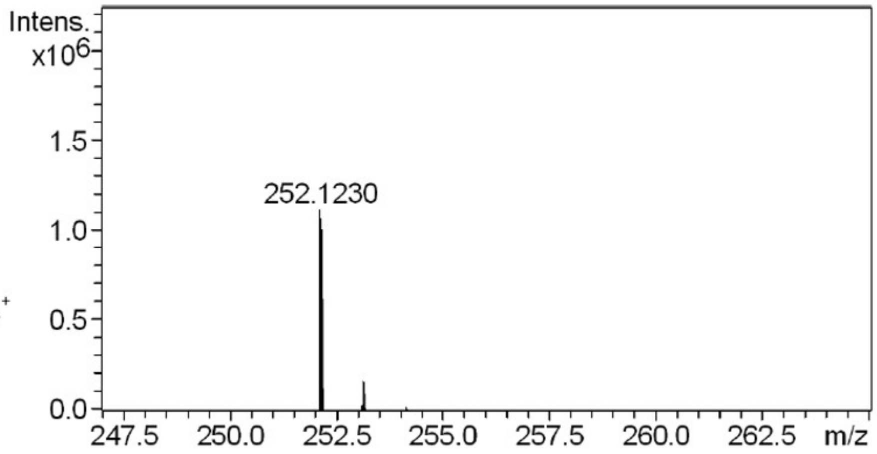




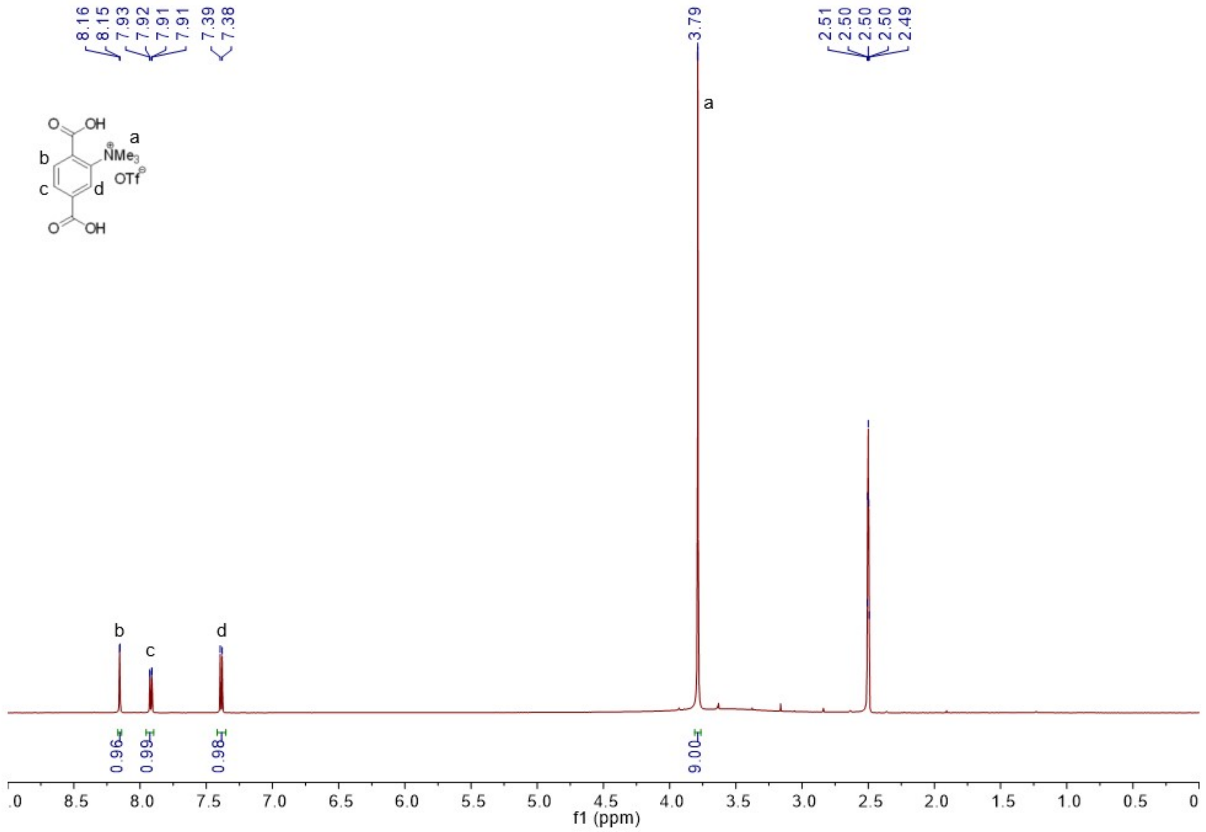
[HR-MS Data for New Compound]

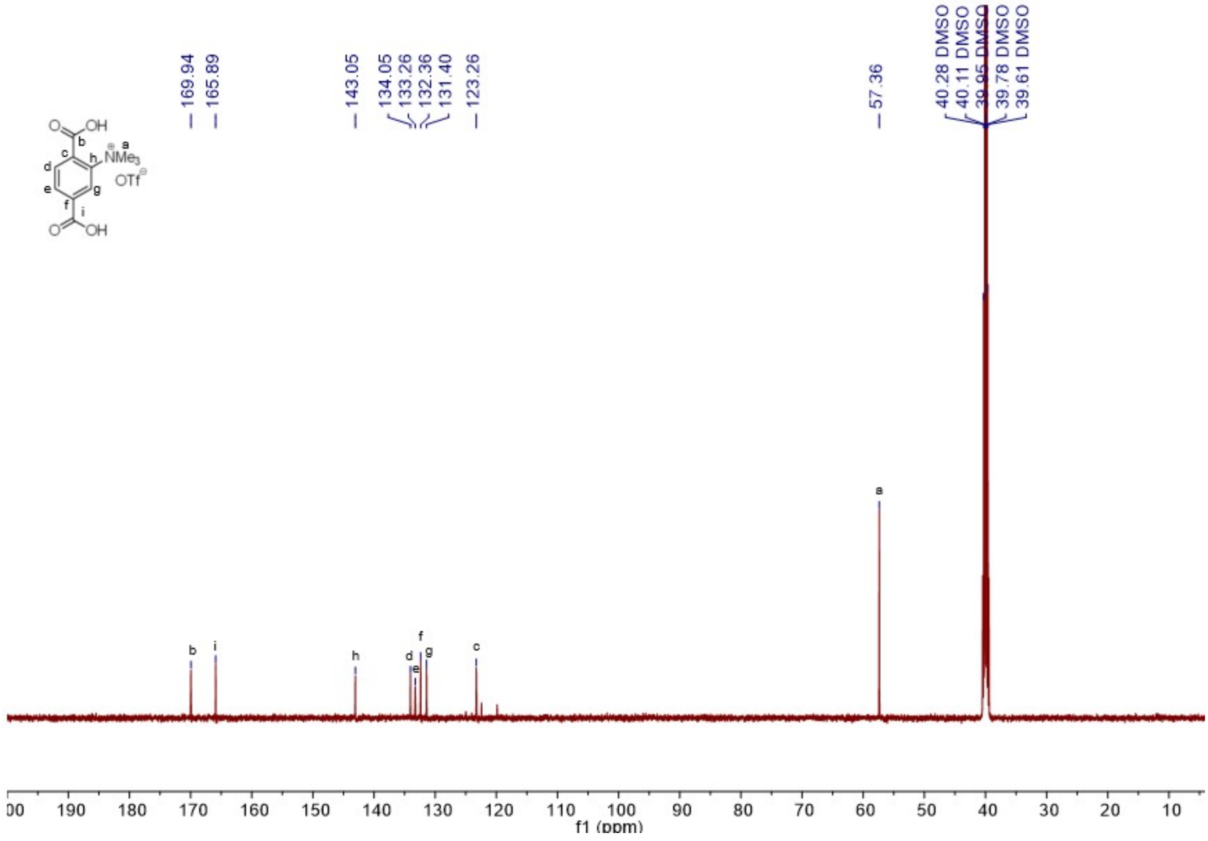


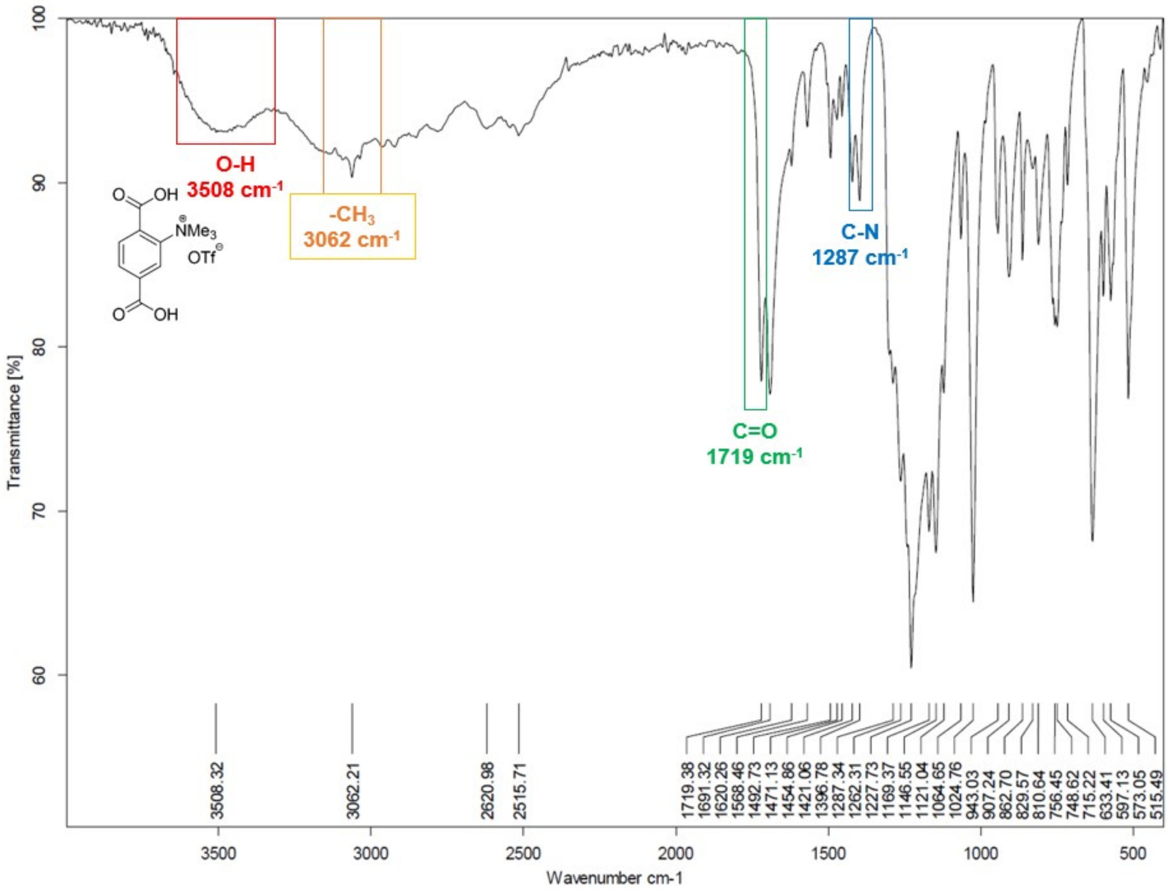
Chemical Formula: $C_{13}H_{18}NO_4^+$
Exact Mass: 252.1230



2,5-Dicarboxy-*N*,*N*,*N*-trimethylbenzenaminium cation (BDC-NMe_3X, **A**)







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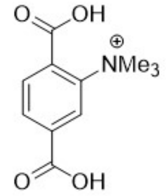
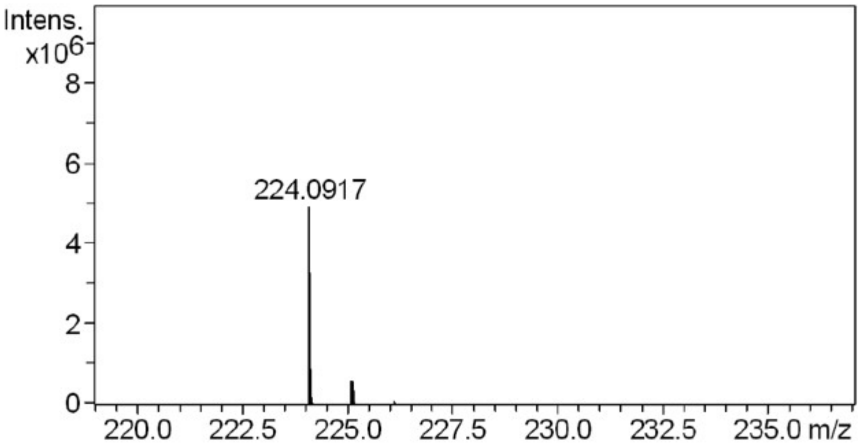
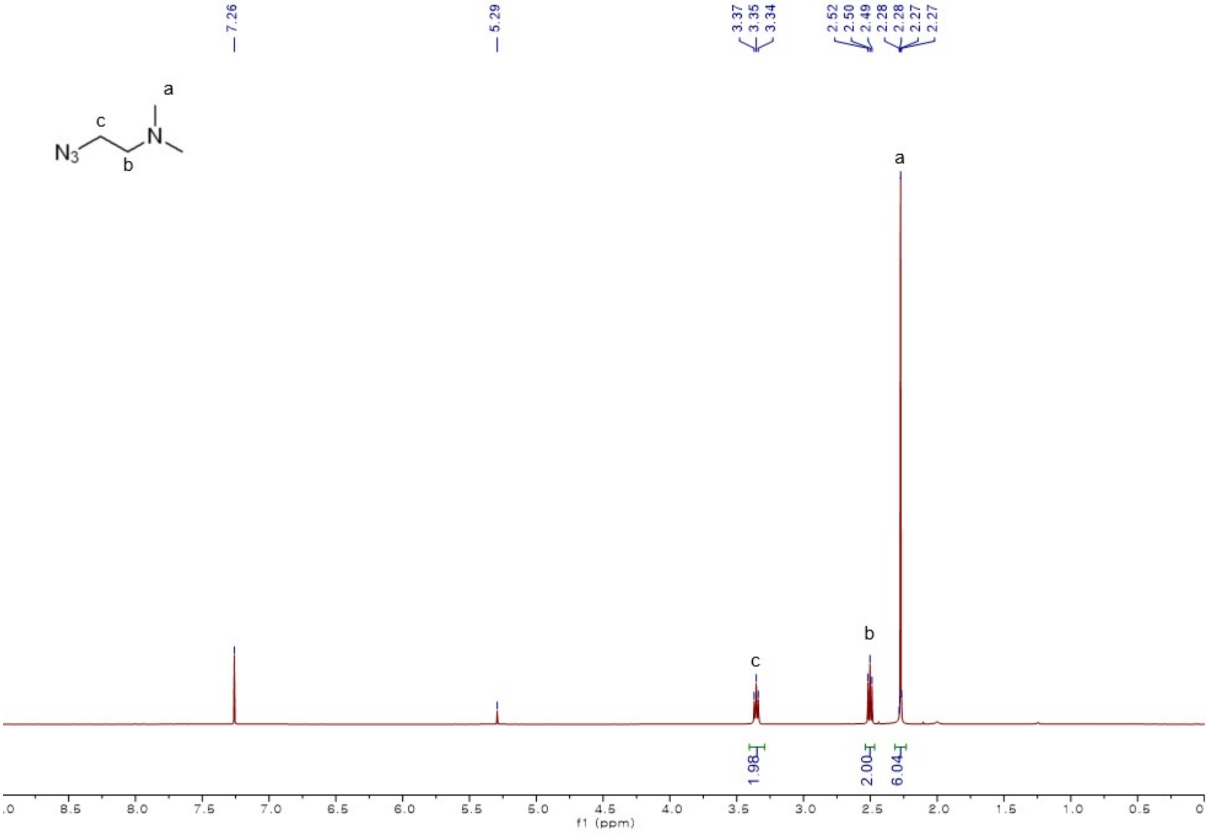
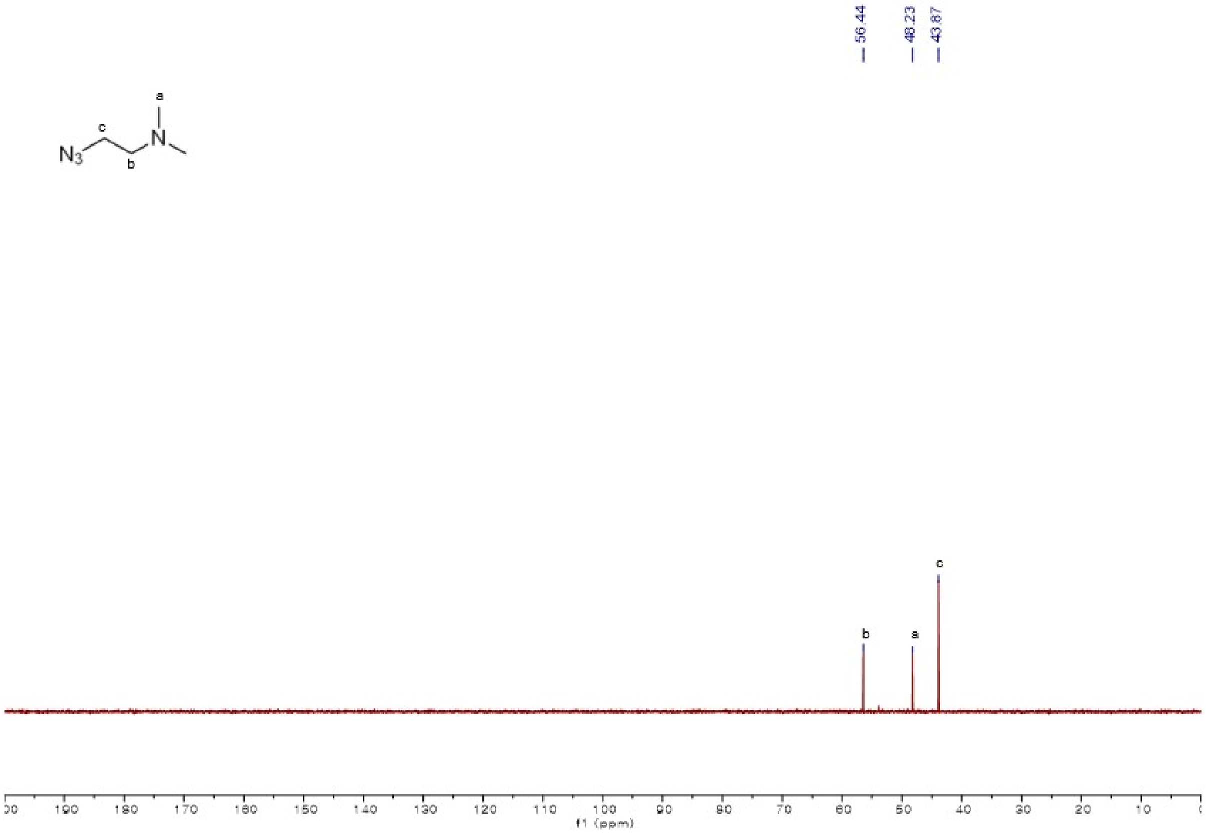


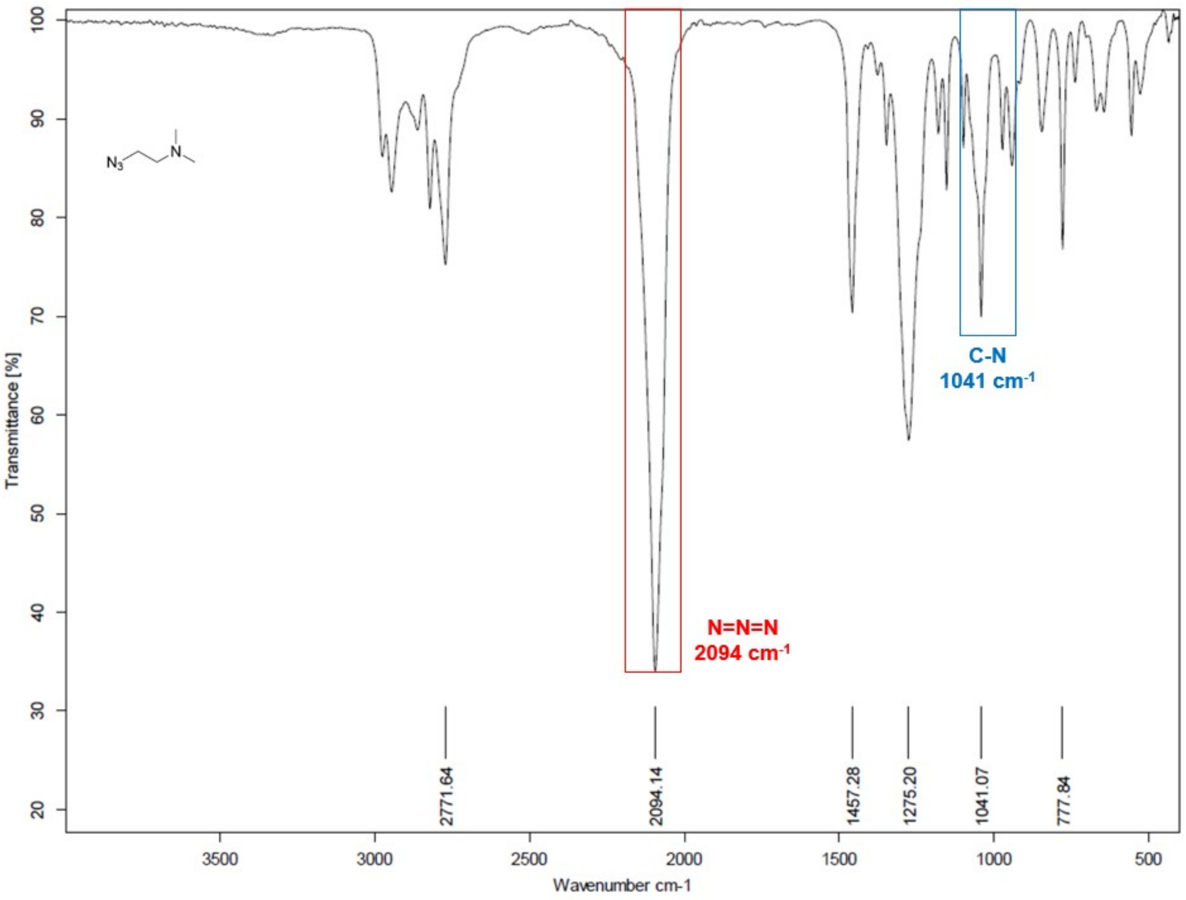
Chemical Formula: $C_{11}H_{14}NO_4$
Exact Mass: 224.0917



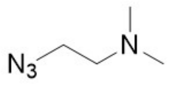
2-Azido-*N,N*-dimethylethanamine (**DMAZ**)



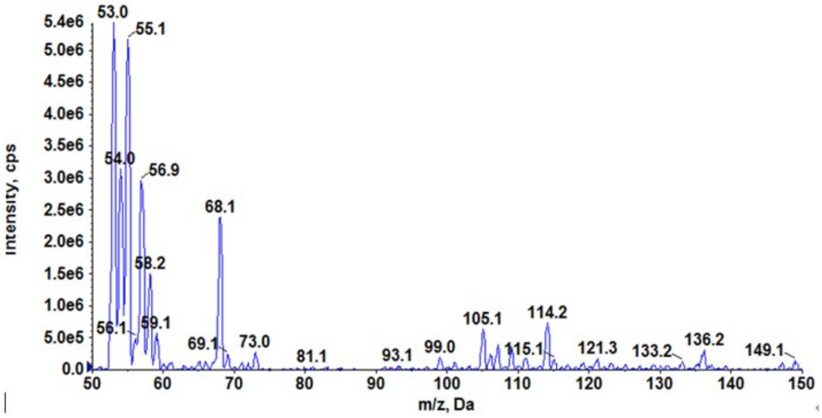




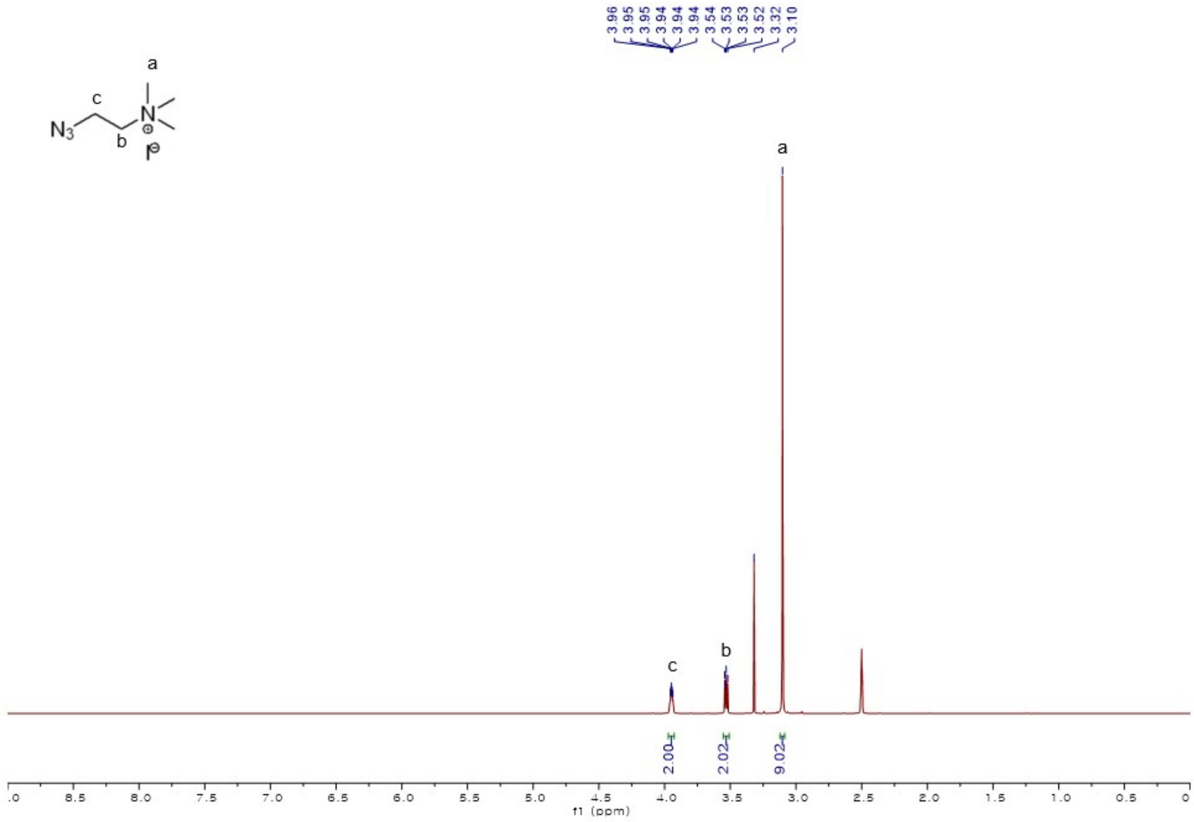
[LC-MS Data]

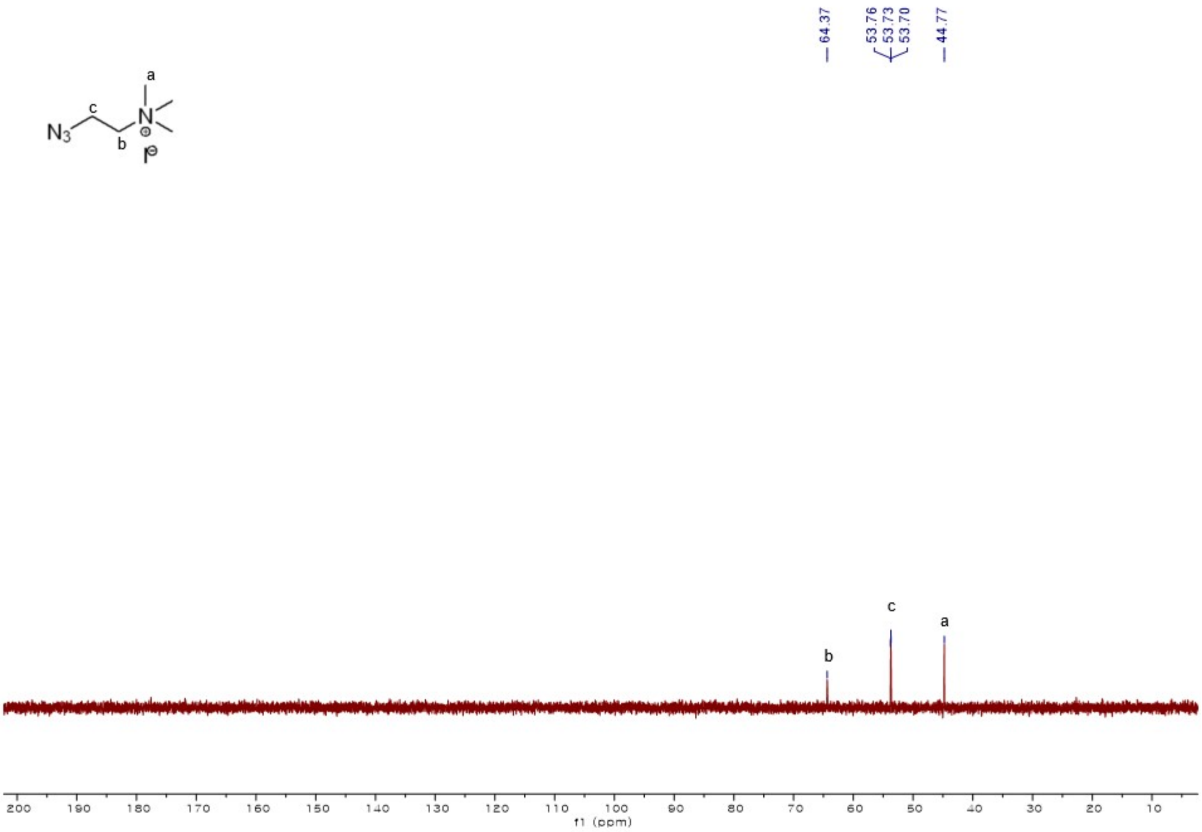


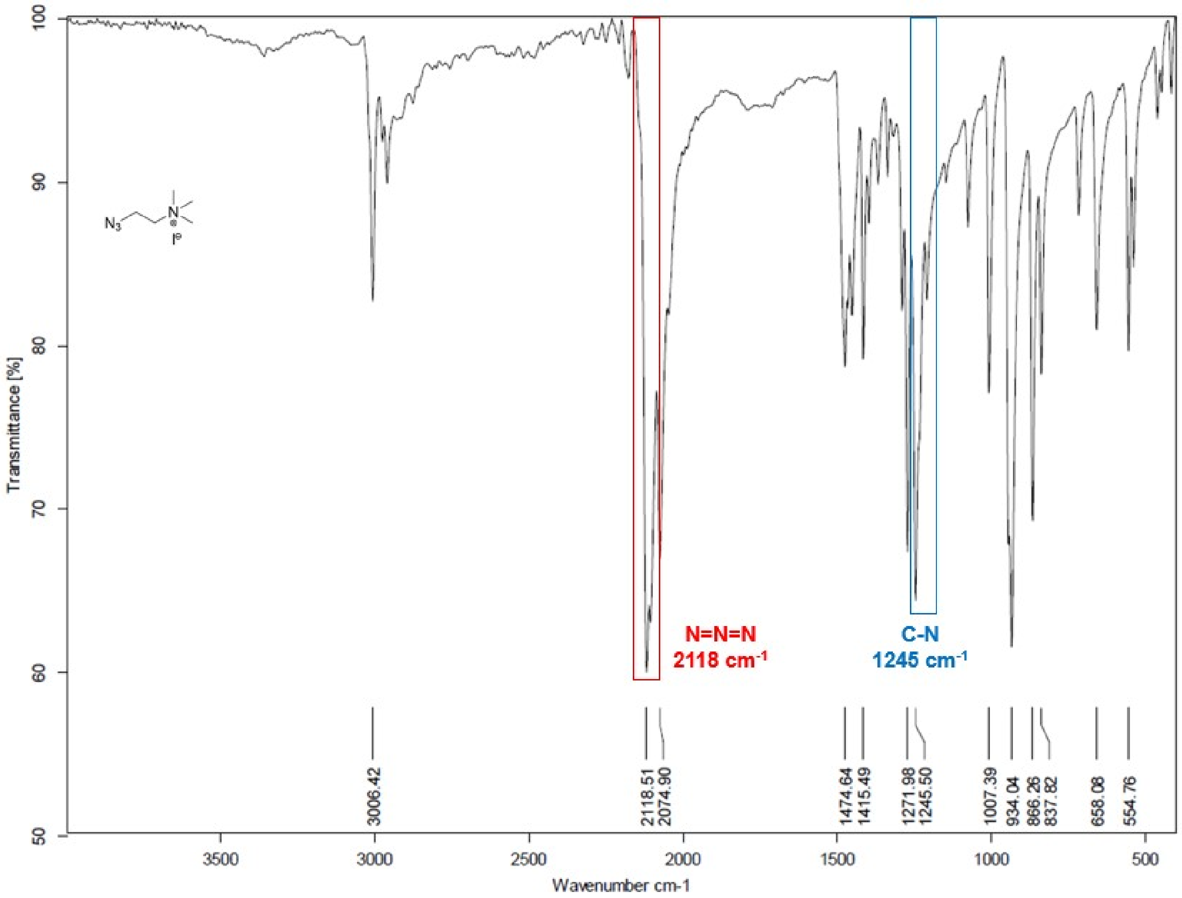
Chemical Formula: $C_4H_{10}N_4$
Exact Mass: 114.1



2-Azido-*N,N,N*-trimethylethanaminium iodide (**TMAZ**)






100
90
80
70
60
50
Transmittance [%]
N3
N
⊕
I⊖
N=N=N
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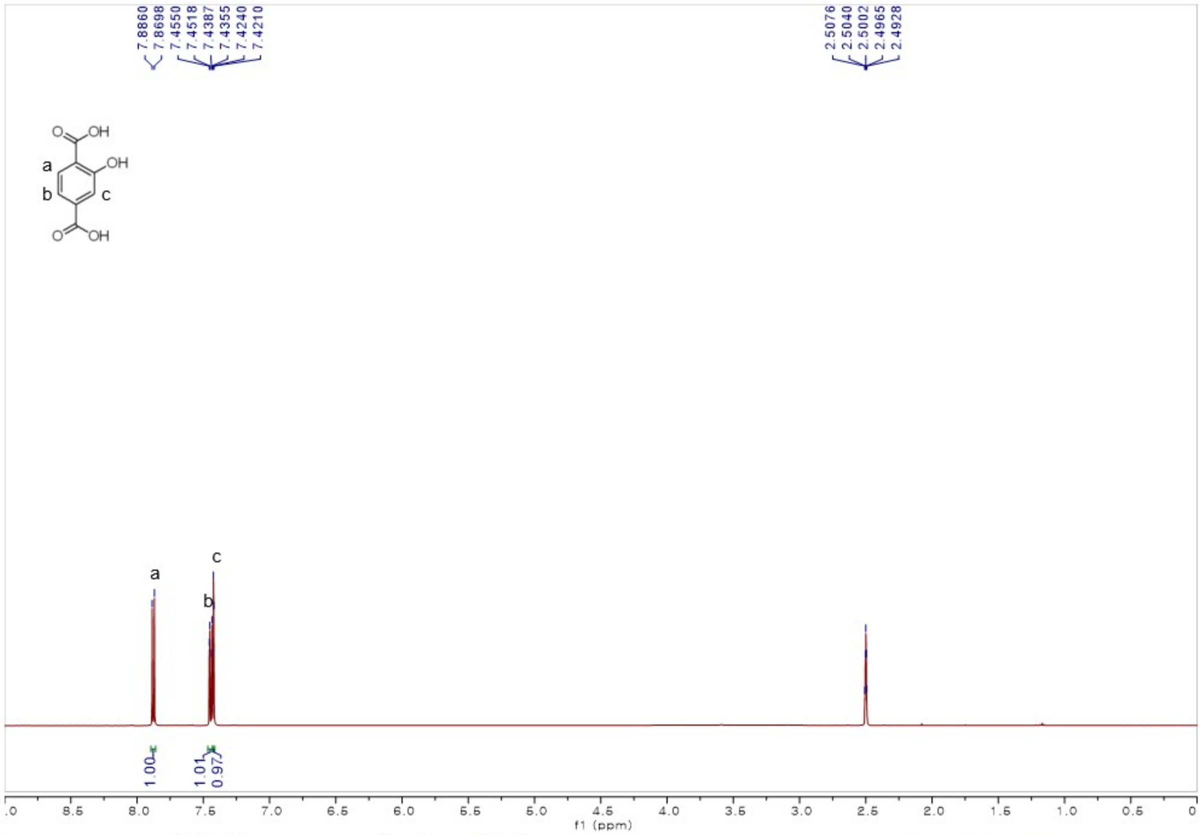
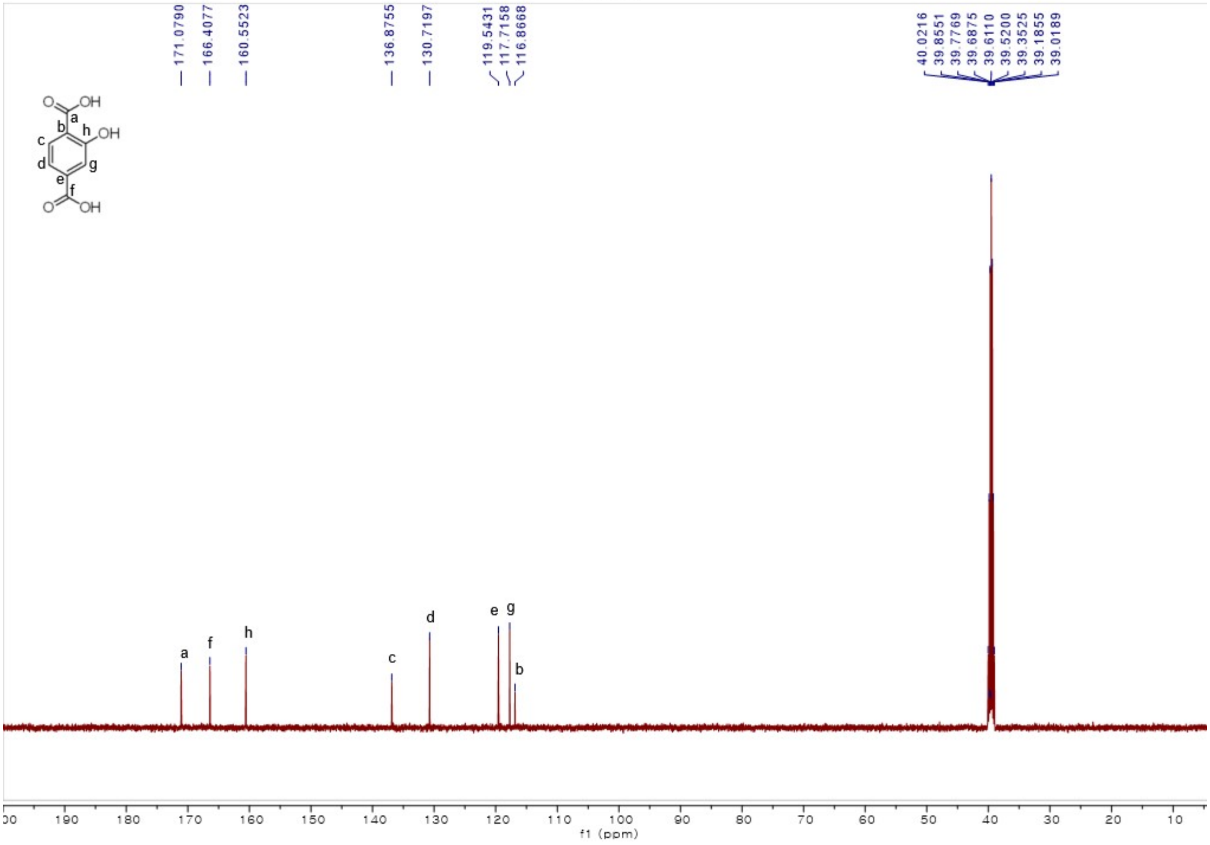
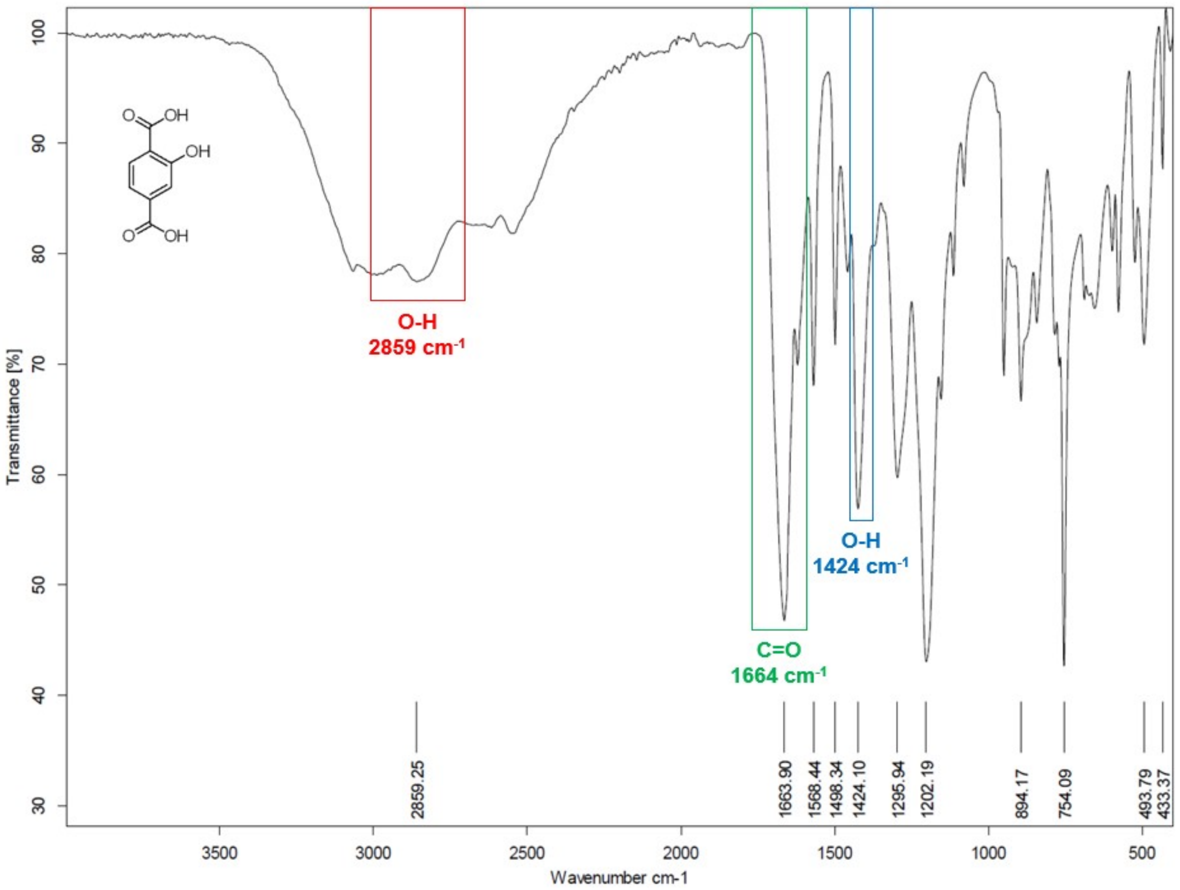
C-N
1245 cm-1
3006.42
2118.51
2074.90
1474.64
1415.49
1271.98
1245.50
1007.39
934.04
866.26
837.82
658.08
554.76
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

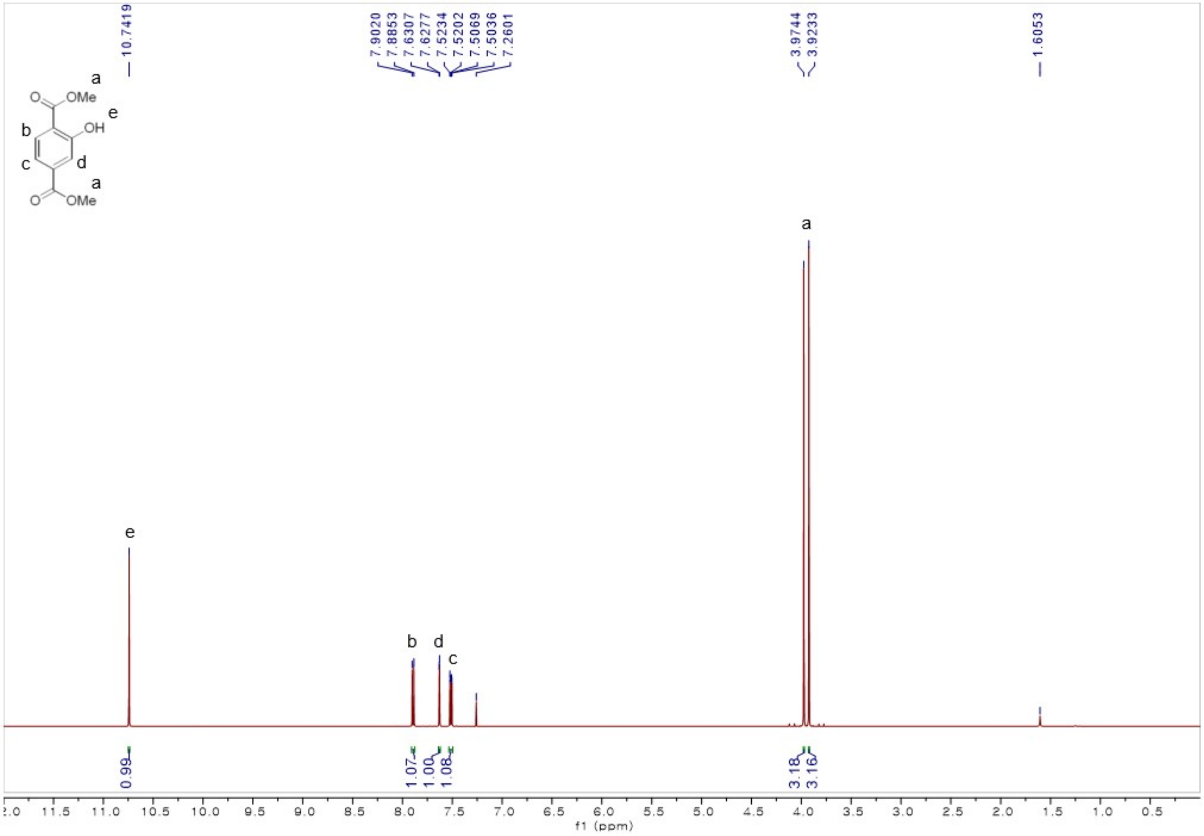
2-Hydroxyterephthalic acid (BDC-OH)

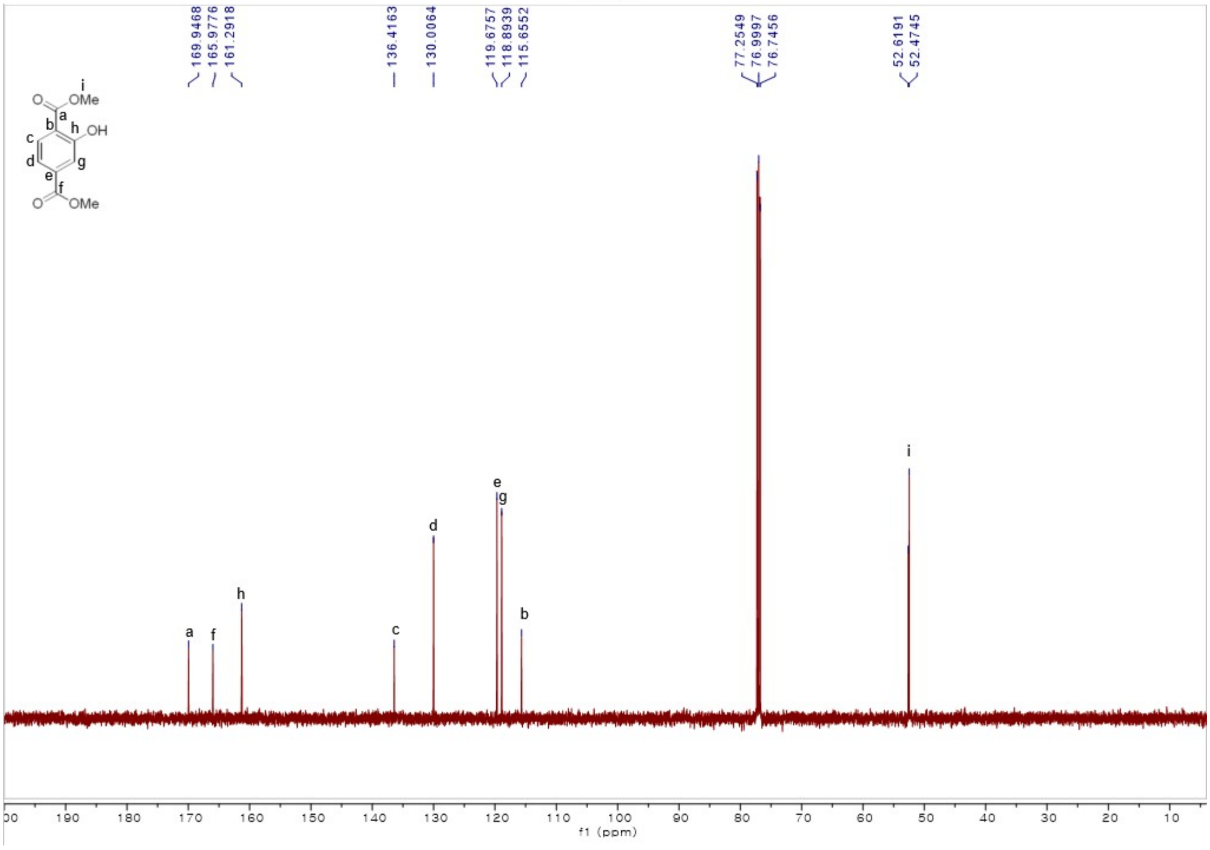


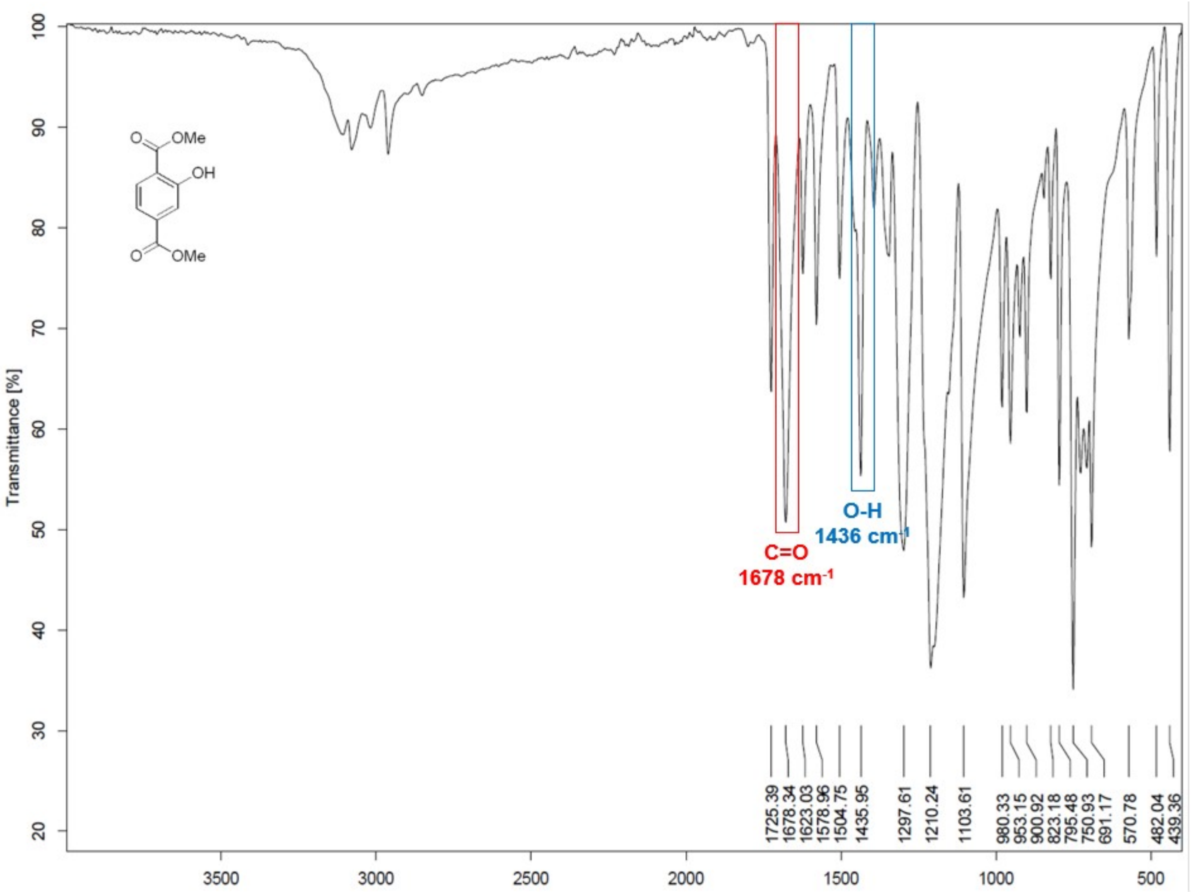



O-H
2859 cm-1
C=O
1664 cm-1
O-H
1424 cm-1
2859.25
1663.90
1568.44
1498.34
1424.10
1295.94
1202.19
894.17
754.09
493.79
433.37
Transmittance [%]
Wavenumber cm-1
100
90
80
70
60
50
40
30
3500
3000
2500
2000
1500
1000
500
OH
OH
OH
O
O

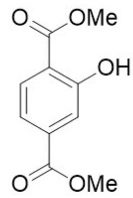
Dimethyl 2-hydroxyterephthalate (BDCE-OH)



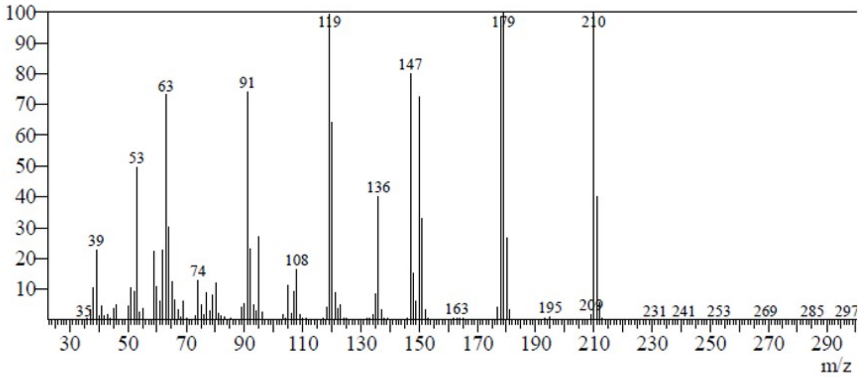




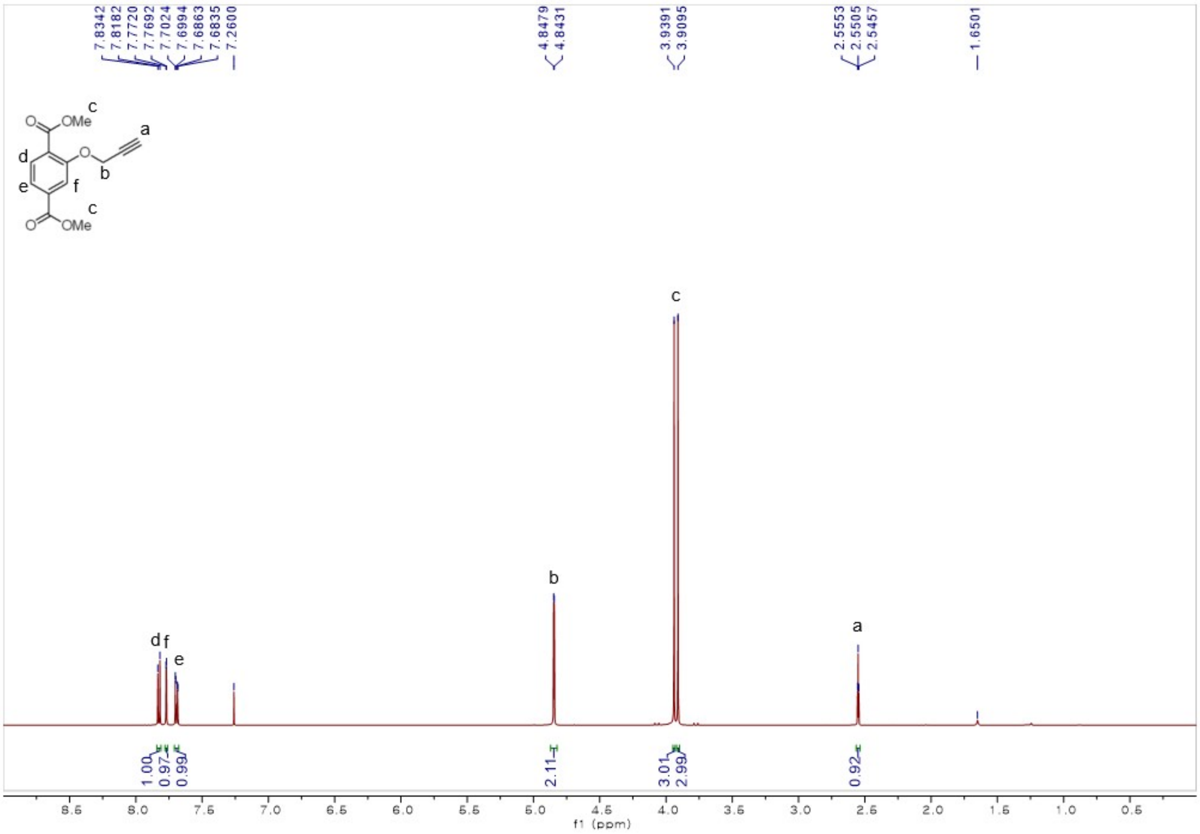
[GC-MS Data]

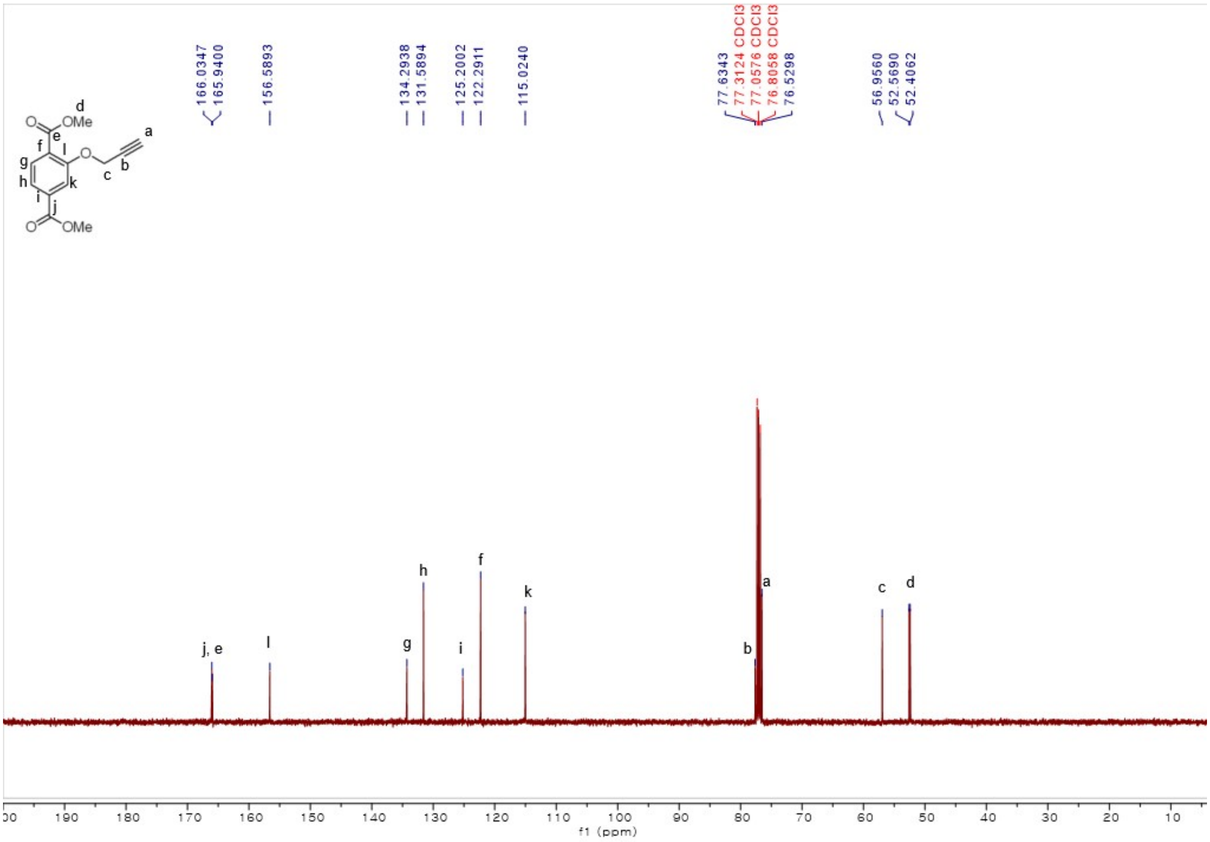


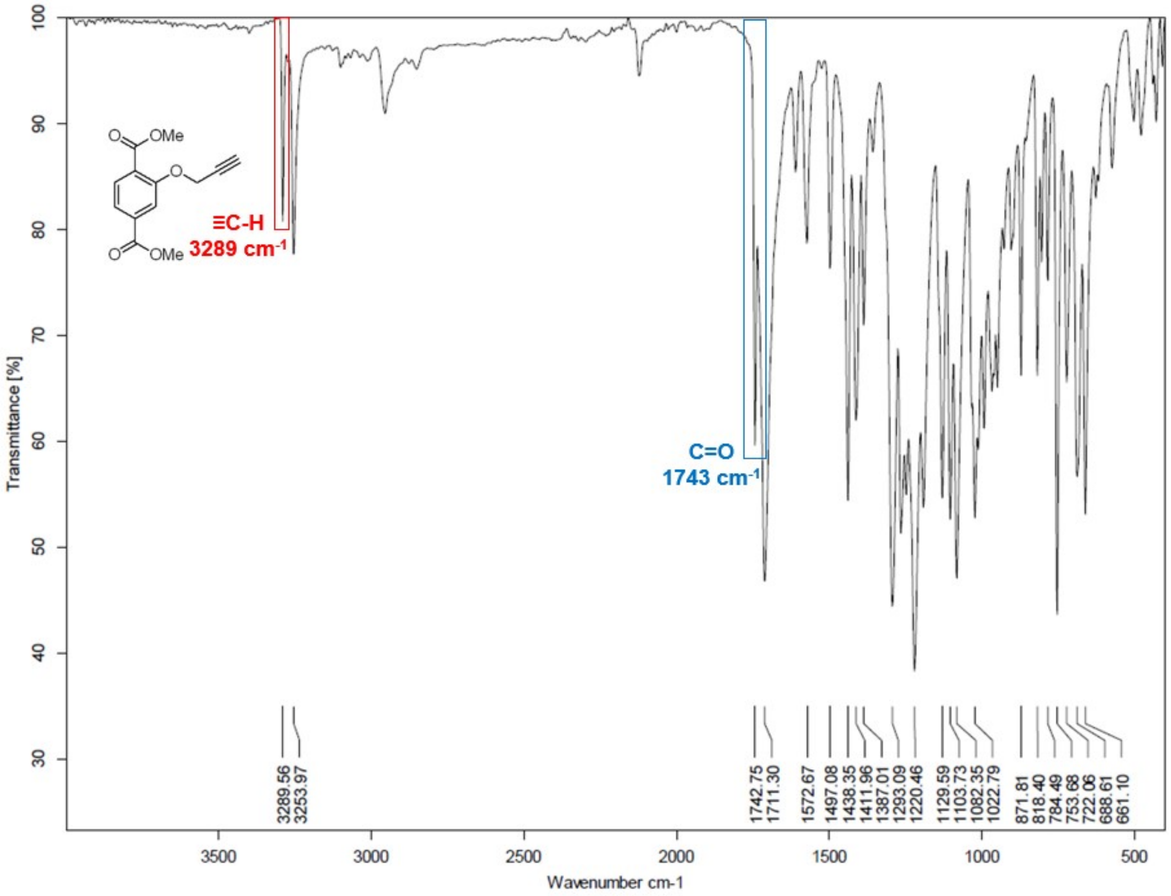
Chemical Formula: $C_{10}H_{10}O_5$
Exact Mass: 210



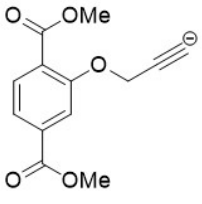
Dimethyl 2-(prop-2-yn-1-yloxy)terephthalate (BDCE-OCH_2CCH)





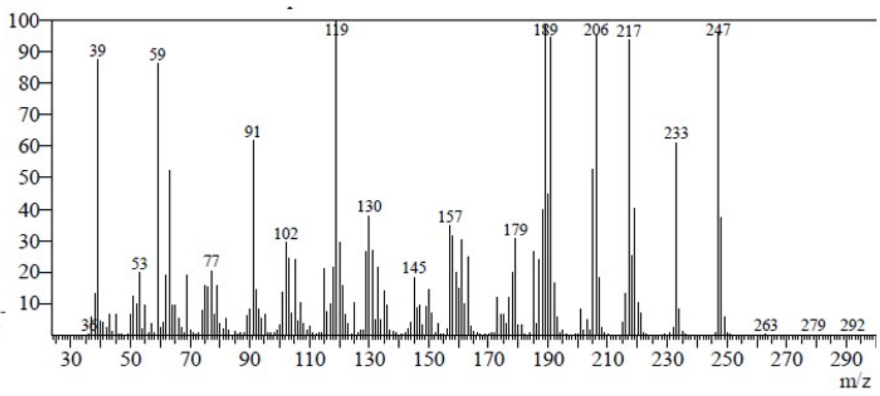


[GC-MS Data]

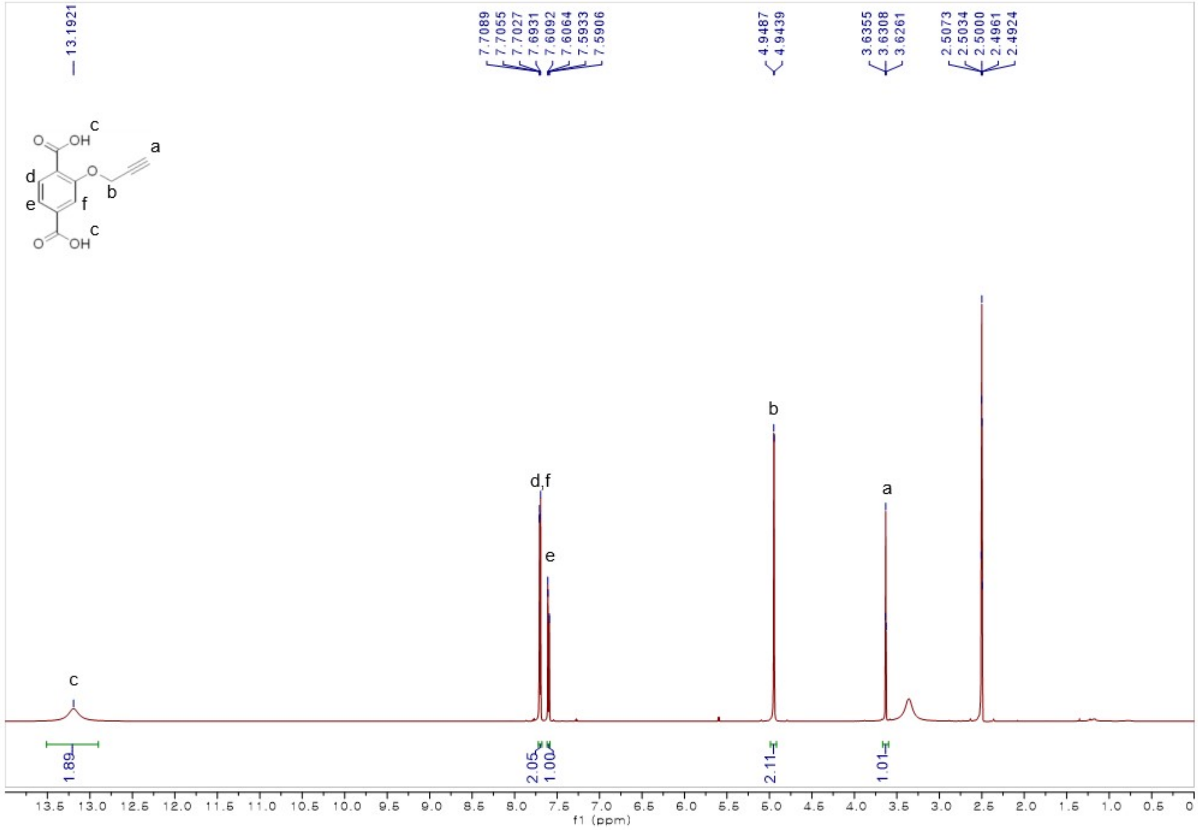


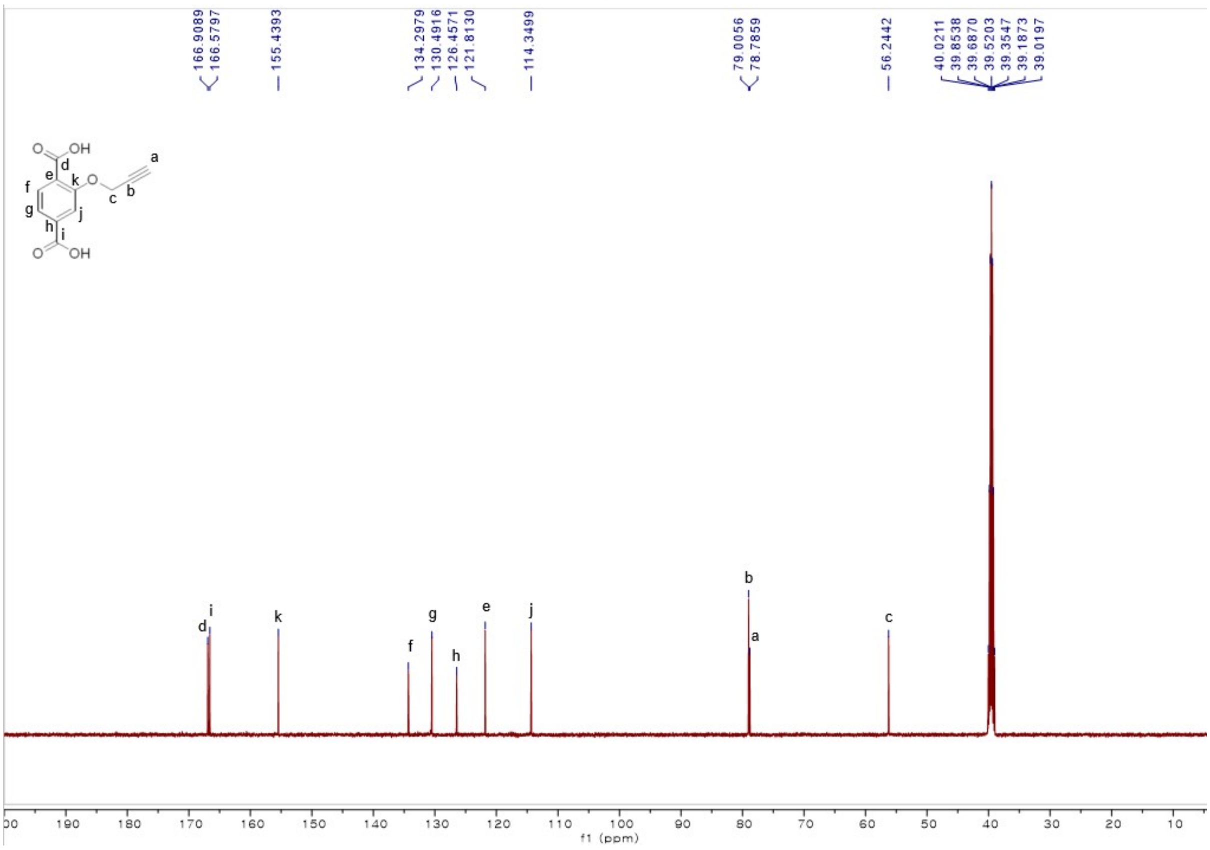
Chemical Formula: $C_{13}H_{11}O_5^-$

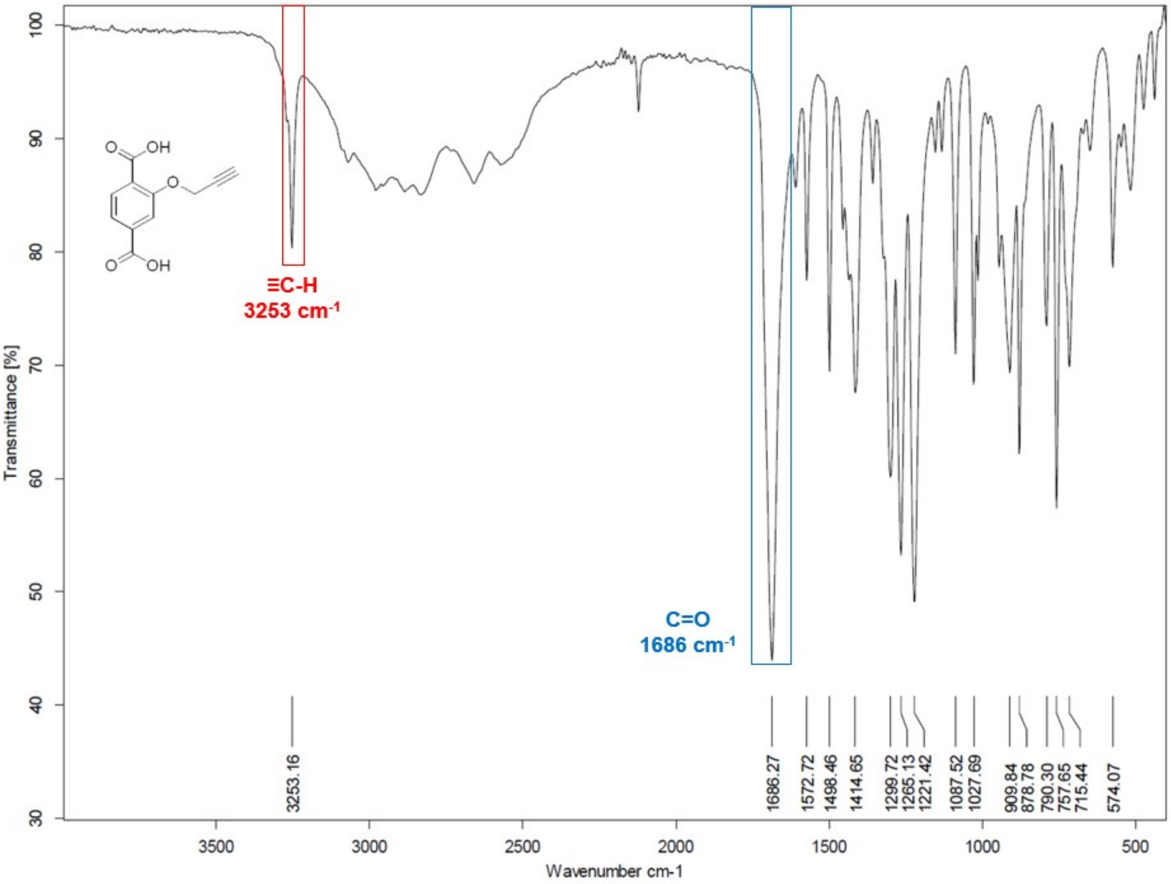
Exact Mass: 247



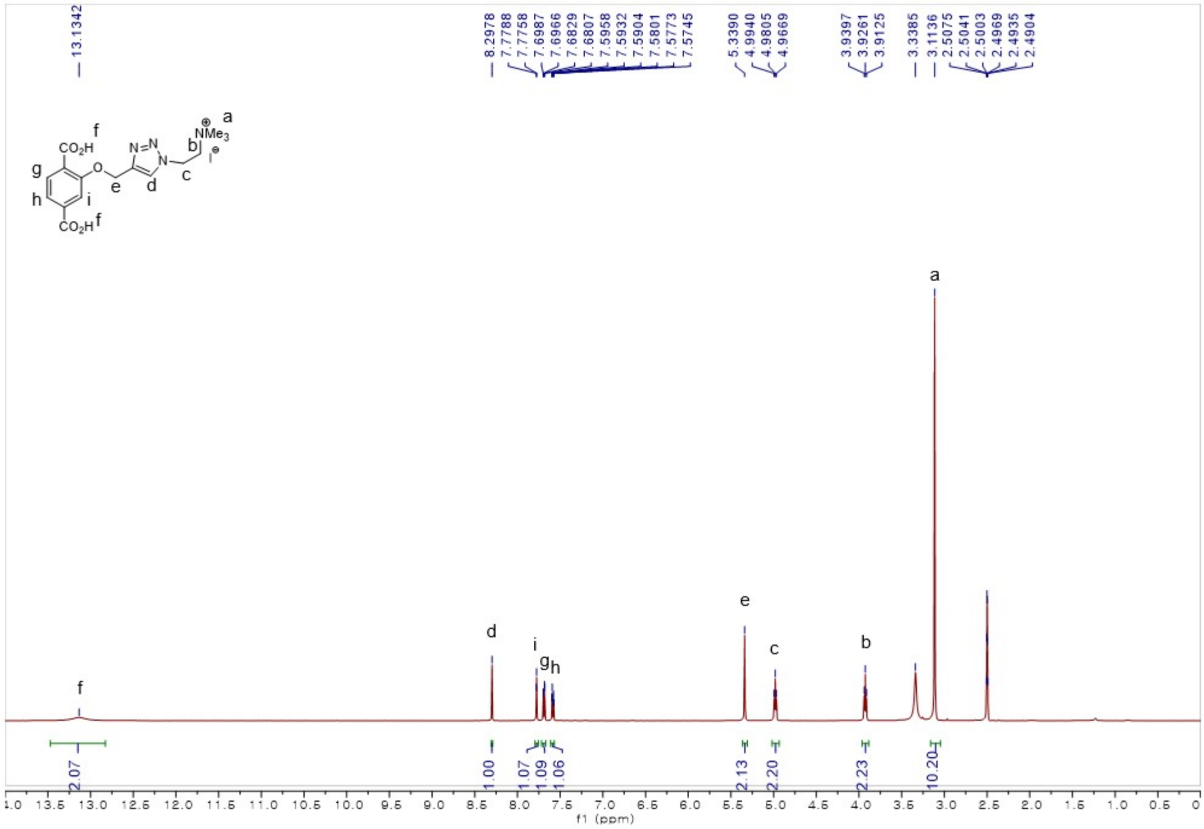
2-(Prop-2-yn-1-yloxy)terephthalic aicd (BDC-OCH$_2$CCH, **B**)

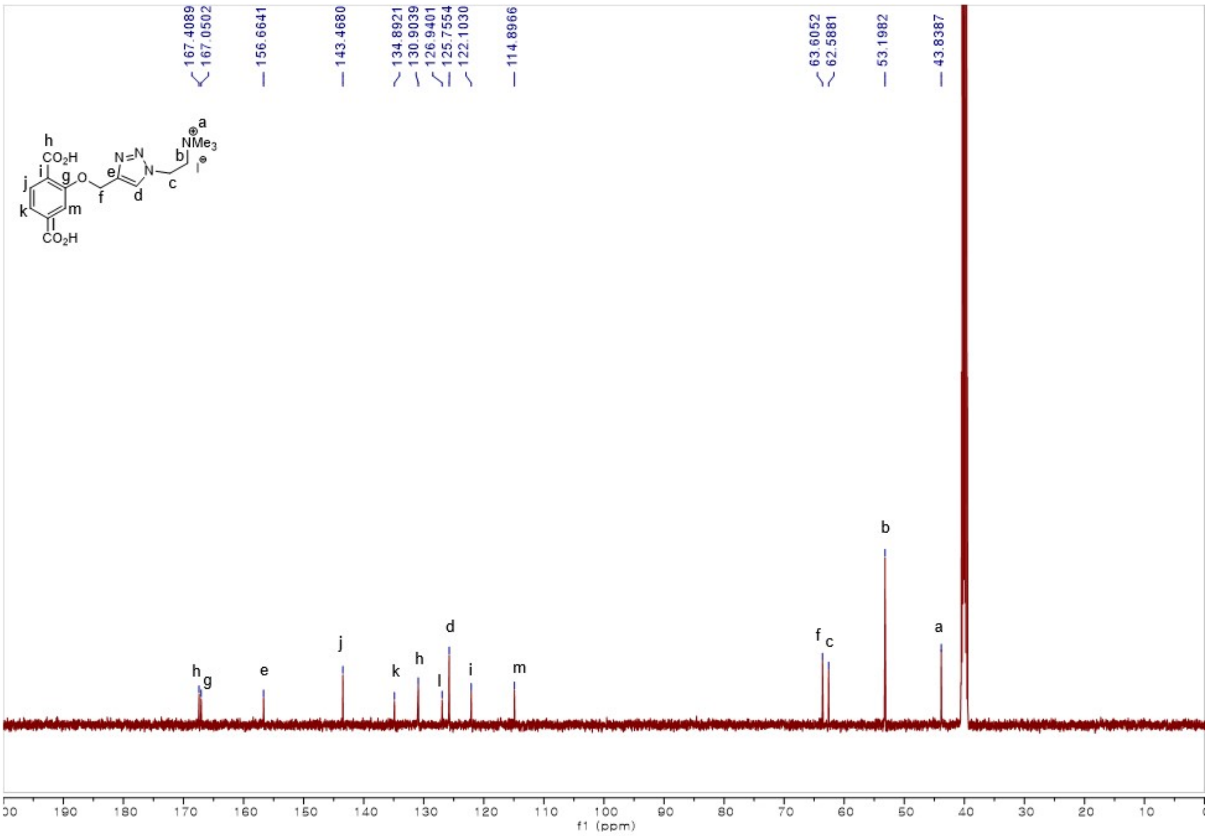


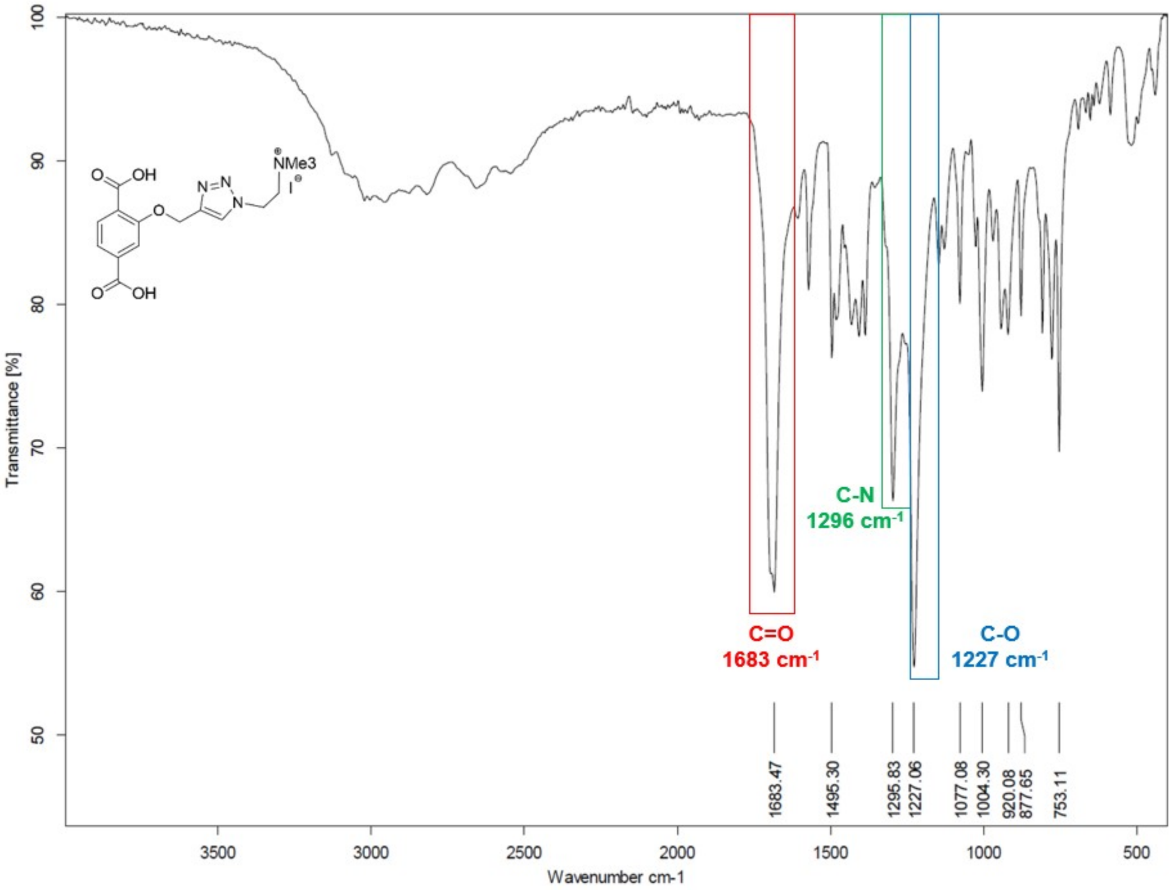



Transmittance [%]
100
90
80
70
60
50
40
30
Wavenumber cm-1
3500
3000
2500
2000
1500
1000
500
O
OH
O
O
OH
≡C-H
3253 cm-1
C=O
1686 cm-1
3253.16
1686.27
1572.72
1498.46
1414.65
1299.72
1265.13
1221.42
1087.52
1027.69
909.84
878.78
790.30
757.65
715.44
574.07

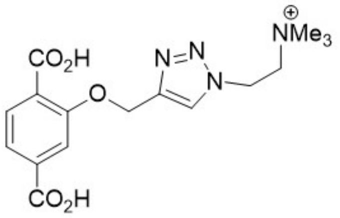
2-(4-((2,5-Dicarboxyphenoxy)methyl)-1H-1,2,3-triazol-1-yl)-N,N,N-trimethylethanaminium iodide (BDC-triazole-NMe_3I, **C**)







[HR-MS Data for New Compound]



Chemical Formula: $C_{16}H_{21}N_4O_5$
Exact Mass: 349.1512