Supporting Information

Aromatic Substituent Effects on the Flexibility of Metal-Organic Frameworks

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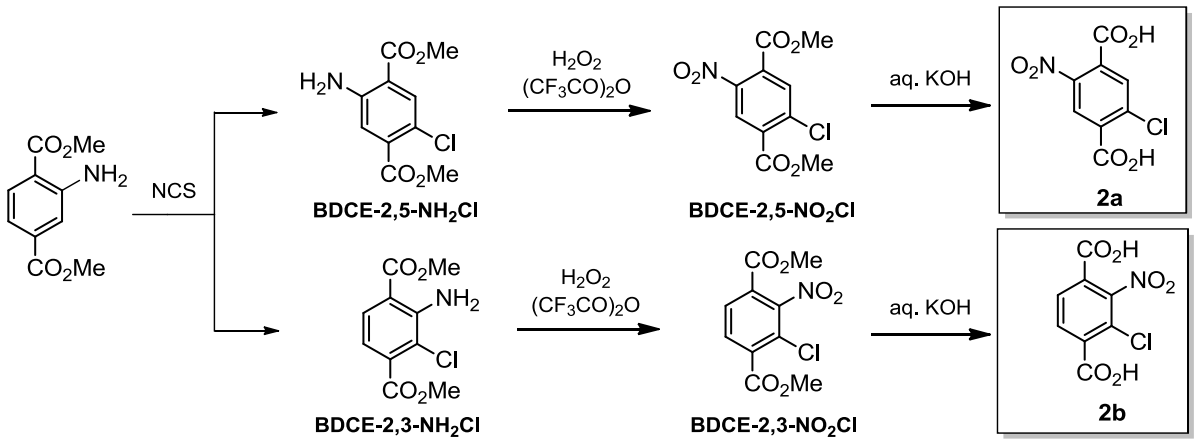
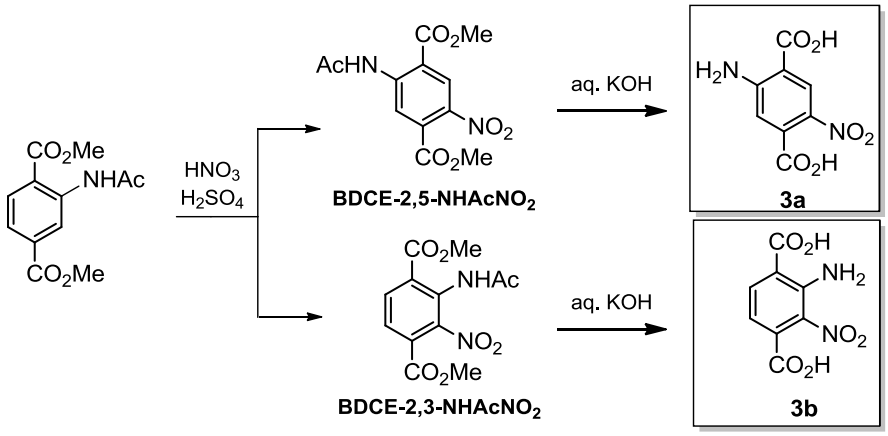
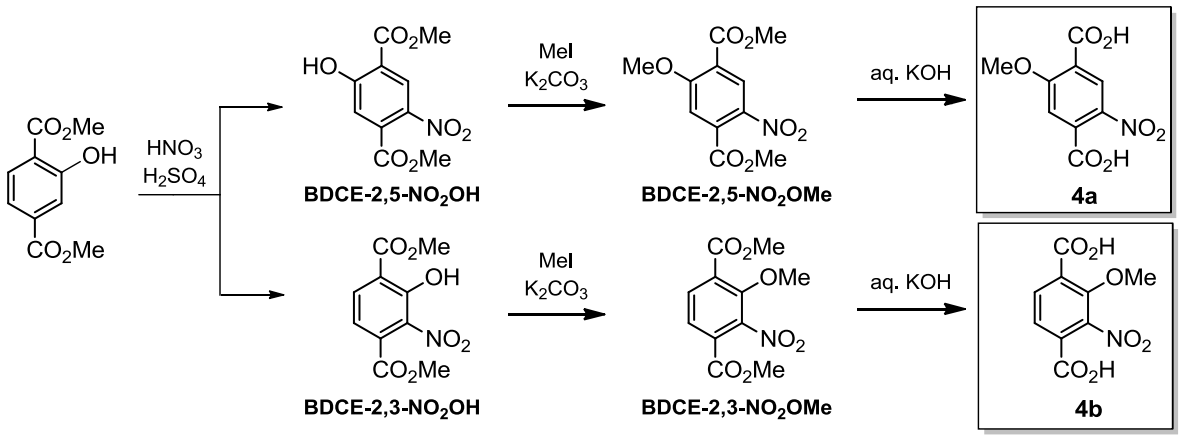
Overall Schemes for Ligand Synthesis



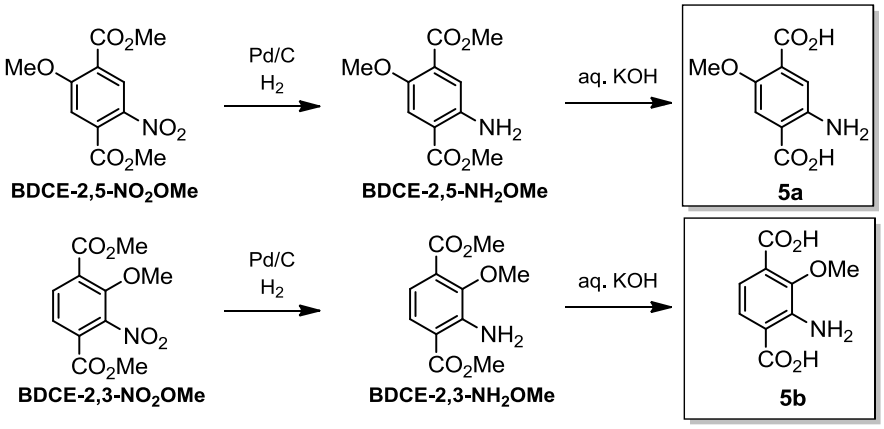
Scheme S1. Synthesis of BDC-2,5/2,3-NO_2Cl (**2a** and **2b**).



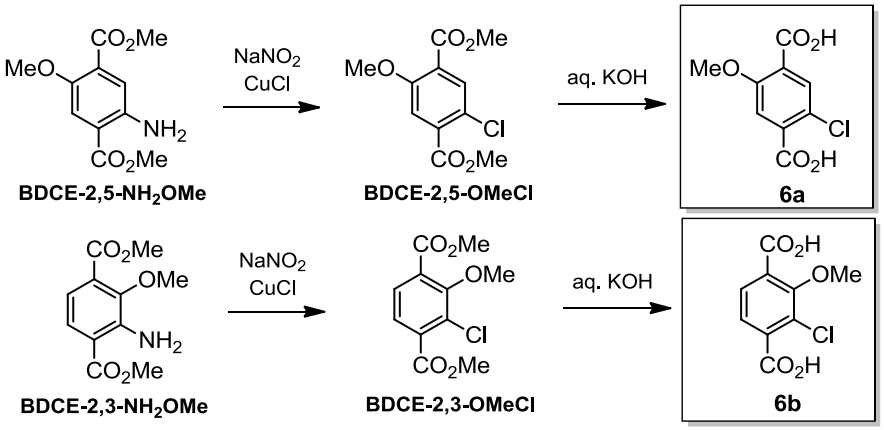
Scheme S2. Synthesis of BDC-2,5/2,3-NO_2NH_2 (**3a** and **3b**).



Scheme S3. Synthesis of BDC-2,5/2,3-NO_2OMe (**4a** and **4b**).

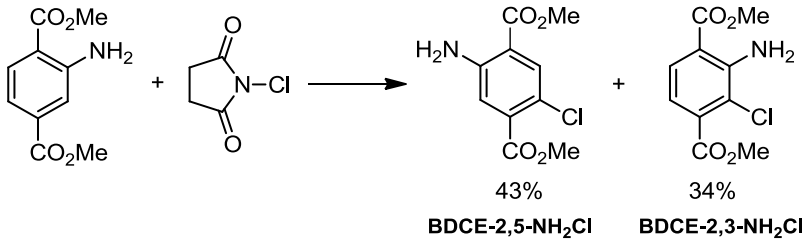


Scheme S4. Synthesis of BDC-2,5/2,3-NH_2OMe (**5a** and **5b**).



Scheme S5. Synthesis of BDC-2,5/2,3-OMeCl (**6a** and **6b**).

Detailed Procedures of Ligand Synthesis

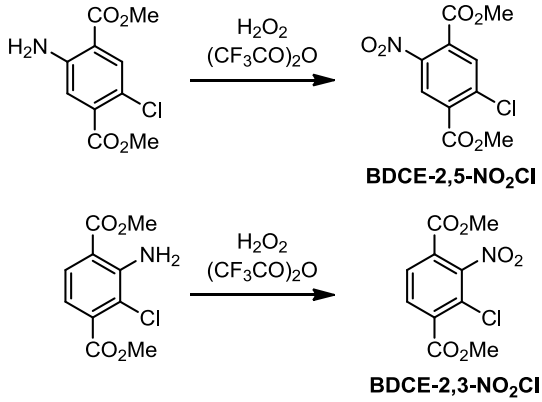


Dimethyl-2-amino-5-chloroterephthalate and Dimethyl-2-amino-3-chloroterephthalate.[S1]

Dimethyl-2-aminoterephtalate (2.0 g, 10 mmol) and *N*-chlorosuccinimide (1.4 g, 10.5 mmol) were dissolved in isopropanol (200 mL). The mixture was stirred at 60 ^{o}C for 24 h. Once conversion was complete (by TLC), the, solvent was evaporated. The solid mixture was separated by silica gel column chromatography (10% EtOAc/*n*-Hexane) and the desired compounds, dimethyl-2-amino-5-chloroterephthalate (1.05 g, 43%) and dimethyl-2-amino-3-chloroterephthalate (827 mg, 34%), were obtained

Dimethyl-2-amino-5-chloroterephthalate: ^{1}H NMR ($CDCl_3$, 400MHz, ppm.): δ 7.89 (1H, s), 7.07 (1H, s), 5.79 (2H, br), 3.91 (3H, s), 3.88 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.1, 165.9, 148.5, 135.0, 133.1, 119.4, 119.0, 113.6, 52.7, 52.2.

Dimethyl-2-amino-3-chloroterephthalate: ^{1}H NMR ($CDCl_3$, 400 MHz, ppm.): δ 7.84 (1H, d, *J* = 8.4 Hz), 6.94 (1H, d, *J* = 8.4 Hz), 3.93 (3H, s), 3.90 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.8, 166.6, 147.4, 135.3, 129.5, 118.7, 116.2, 113.3, 52.8, 52.3.



Dimethyl-2-chloro-5-nitroterephthalate and Dimethyl-2-chloro-3-nitroterephthalate.

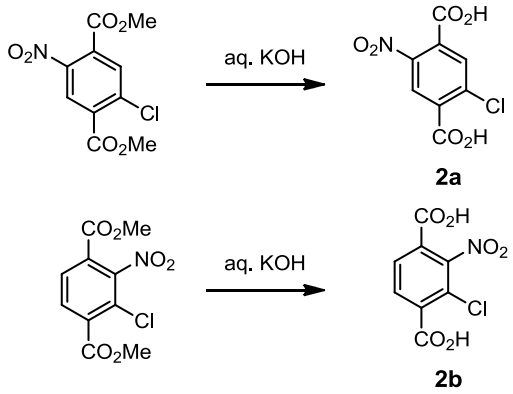
To a solution of 30% H_2O_2 (1.2 mL, 11.7 mmol) in CH_2Cl_2 (6.6 mL) at 0 ^{o}C was added drop-wise trifluoroacetic anhydride (1.9 mL, 13.7 mmol). The solution was warmed to room temperature and dimethyl-2-chloro-5-nitroterephthalate (428 mg, 1.76 mmol) dissolved in CH_2Cl_2 (2 mL) was added drop-wise. After stirring for 3 h at 45 ^{o}C, the mixture was cooled to 0 ^{o}C and Na_2SO_3 was added slowly. The resulting mixture was extracted with EtOAc. The organic phase was washed with brine. The solution was then dried using $MgSO_4$, filtered, and evaporated of ethyl acetate. The solid mixture was separated by silica gel column chromatography (10% MC/*n*-Hexane) and the desired compound, dimethyl-2-chloro-5-nitroterephthalate (397 mg, 83%), was obtained as a yellow solid.

Dimethyl-2-chloro-5-nitroterephthalate: ^{1}H NMR ($CDCl_3$, 400 MHz, ppm.): δ 8.45 (1H, s), 7.78 (1H, s), 3.99 (3H, s), 3.95 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 164.1, 163.2, 145.5, 139.3, 132.5, 132.4, 131.1,

127.3, 53.8, 53.3. ESI-MS(+) *m/z* calcd. For $C_{10}H_8NNaO_6$ $[M+Na]^+$: 295.9932, found $[M+Na]^+$: 295.9932.

Dimethyl-2-chloro-3-nitroterephthalate was obtained in comparable yield from a similar procedure using dimethyl-2-amino-3-chloroterephthalate as a starting material.

Dimethyl-2-chloro-3-nitroterephthalate: ^{1}H NMR ($CDCl_3$, 400 MHz, ppm.): δ 8.03 (1H, d, *J* = 8.2 Hz), 7.96 (1H, d, *J* = 8.2 Hz), 3.98 (3H, s), 3.93 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 164.1, 162.0, 150.1, 135.9, 131.8, 129.4, 126.2, 126.0, 53.7, 53.4. ESI-MS(+) *m/z* calcd. For $C_{10}H_8NNaO_6$ $[M+Na]^+$: 295.9932, found $[M+Na]^+$: 295.9932.



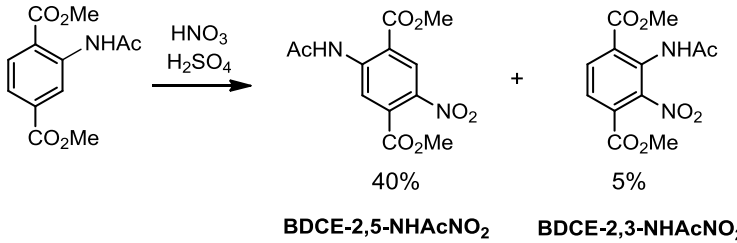
*2-Chloro-5-nitroterephthalic acid (**2a**) and 2-Chloro-3-nitroterephthalic acid (**2b**).*

Dimethyl-2-chloro-5-nitroterephthalate (480 mg, 1.8 mmol) was dissolved in 7 mL of THF. To this, 7 mL of a 4% KOH aqueous solution was added drop-wise. The mixture was stirred under reflux condition (66 ^{o}C) for overnight. Once conversion was complete (by TLC), THF was removed by evaporation and the mixture was acidified with a 1.0 M HCl aqueous solution. The solution was stored overnight in a refrigerator. The precipitate was collected by filtration, and washed with water. The desired compound was obtained by air drying (**2a**, 191 mg, 46%) as a yellow solid.

2-chloro-5-nitroterephthalic acid (**2a**): ^{1}H NMR (DMSO-d_6, 400 MHz, ppm.): δ 8.39 (1H, s), 8.02 (1H, s); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 164.4, 164.4, 145.8, 136.5, 134.3, 131.8, 130.9, 126.3. ESI-MS(-) *m/z* calcd. For $C_8H_3ClNO_6$ $[M-H]^-$: 243.9654, found $[M-H]^-$: 243.9655.

2-chloro-3-nitroterephthalic acid was obtained in comparable yield from a similar procedure using dimethyl-2-chloro-3-nitroterephthalate as a starting material.

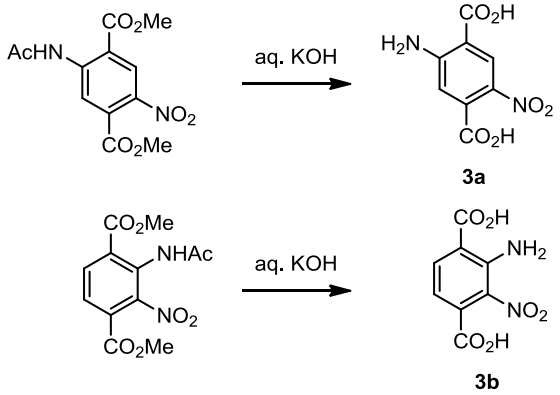
2-chloro-3-nitroterephthalic acid (**2b**): ^{1}H NMR (DMSO-d_6, 400 MHz, ppm.): δ 8.10 (1H, d, *J* = 8.2 Hz), 8.07 (1H, d, *J* = 8.2 Hz); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 165.0, 162.8, 149.1, 137.0, 131.9, 130.3, 126.5, 123.1. ESI-MS(-) *m/z* calcd. For $C_8H_3ClNO_6$ $[M-H]^-$: 243.9654, found $[M-H]^-$: 243.9657.



Dimethyl-2-acetamido-5-nitroterephthalte and Dimethyl-2-acetamido-3-nitroterephthalte.[S2]

Dimethylacetamidoterephthalate (3.8 g, 15 mmol) was dissolved in concentrated sulfuric acid (30 mL) and the mixture was stirred at 0 ^{o}C. Then 60% nitric acid (8.6 mL, 21 mmol) was added drop-wise to cooled mixture and the mixture was continuously stirred for 2 hour at 0 ^{o}C. The reaction was quenched by addition of ice and the resulting yellow solid. The yellow solid mixture was separated by silica gel column chromatography (25% EtOAc/*n*-Hexane) and the desired compound, Dimethyl-2-acetamido-5-nitroterephthalte (1.8g, 40%) and dimethyl-2-acetamido-3-nitroterephthalate (220 mg, 5%), were obtained as a pale yellow solid.
Dimethyl 2-acetamido-5-nitroterephthalate: ^{1}H NMR ($CDCl_3$, 400 MHz, ppm.): δ 11.35 (1H, s, br), 9.03 (1H, s), 8.76 (1H, s), 4.01 (3H, s), 3.96 (3H, s), 2.29 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 169.4, 166.7, 165.7, 145.8, 139.7, 134.6, 127.7, 119.9, 115.2, 53.6, 53.3, 25.6.

Dimethyl 2-acetamido-3-nitroterephthalate: ^{1}H NMR ($CDCl_3$, 400 MHz, ppm.): δ 9.21 (1H, s, br), 8.12 (1H, d, *J* = 8.2), 7.63 (1H, d, *J* = 8.2 Hz), 3.95 (3H, s), 3.91 (3H, s), 2.19 (3H, s); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ 169.2, 165.7, 164.3, 145.0, 133.0, 131.1, 130.7, 128.0, 125.9, 53.7, 53.3, 24.0.



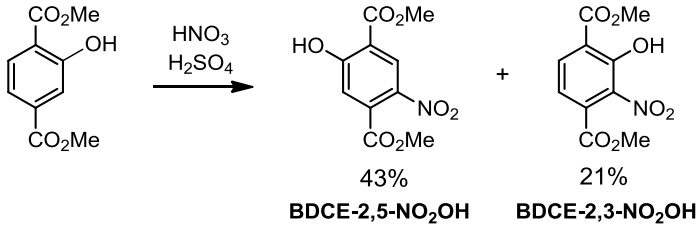
*2-Amino-5-nitroterephthalic acid (**3a**) and 2-Amino-3-nitroterephthalic acid (**3b**).*

Dimethyl-2-acetamido-5-nitroterephthalte (130 mg, 0.43 mmol) was dissolved in 2.5 mL of THF. To this, 2.5 mL of a 4% KOH aqueous solution was added drop-wise. The mixture was stirred under reflux condition (66 ^{o}C) for overnight. Once conversion was complete (by TLC), THF was removed by evaporation and the mixture was acidified with a 1.0 M HCl aqueous solution. The solution was stored overnight in a refrigerator. The precipitate was collected by filtration, and washed with water. The desired compound was obtained by air drying (**3a**, 81 mg, 83%) as a yellow solid.

2-Amino-5-nitroterephthalic acid (**3a**): ^{1}H NMR (DMSO-d_6, 400 MHz, ppm.): δ 13.55 (2H, s, br), 8.48 (1H, s), 7.92 (2H, s, br), 6.88 (1H, s); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 167.6, 167.3, 155.3, 135.8, 132.3, 129.9, 115.3, 108.9. ESI-MS(-) *m/z* calcd. For $C_8H_5NO_6$ [*M-H*]$^{-}$: 225.0153, found [*M-H*]$^{-}$: 225.0154.

2-Amino-3-nitroterephthalic acid was obtained in comparable yield from a similar procedure using dimethyl-2-acetamido-3-nitroterephthalte as a starting material.

2-Amino-3-nitroterephthalic acid (**3b**): ^{1}H NMR (DMSO-d_6, 400MHz, ppm.): δ 13.74 (2H, s, br), 8.10 (1H, d, J = 8.0 Hz), 7.65 (2H, s, br), 6.89 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 168.1, 166.2, 144.2, 136.2, 134.0, 133.9, 115.9, 114.2. ESI-MS(-) *m/z* calcd. For $C_8H_5NO_6$ [*M-H*]$^{-}$: 225.0153, found [*M-H*]$^{-}$: 225.0158.



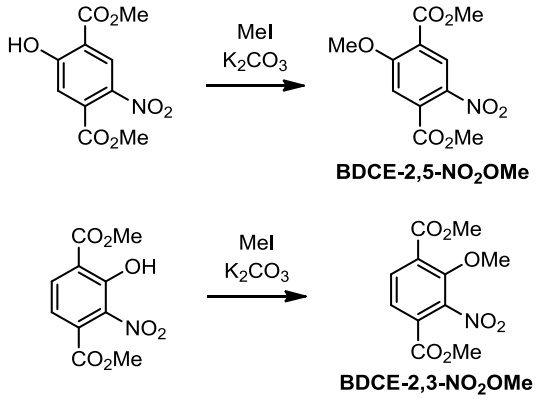
Dimethyl-2-hydroxy-5-nitroterephthalate and Dimethyl-2-hydroxy-3-nitroterephthalate.

The BDCE-2,5-NO_2OH and BDCE-2,3-NO_2OH were prepared using a modified method from what has been previously described.[S2]

Dimethyl-2-hydroxyterephthalate (2.1 g, 10 mmol) was dissolved in concentrated sulfuric acid (30 mL) and the mixture was stirred at 0 ^{o}C. Then 60% nitric acid (0.9 mL, 12 mmol) was added drop-wise to cooled mixture and the mixture was continuously stirred for 30 min at 0 ^{o}C. The reaction was quenched by addition of water and the resulting mixture was extracted with EtOAc. The organic phase was washed with brine. The solution was then dried using $MgSO_4$, filtered, and evaporated of ethyl acetate. The oil mixture was separated by silica gel column chromatography (5% EtOAc/*n*-Hexane) and the desired compound, dimethyl 2-hydroxy-5-nitroterephthalate (1.1 g, 43%) and dimethyl 2-hydroxy-3-nitroterephthalate (536 mg, 21%), were obtained as a colorless solid.

Dimethyl 2-hydroxy-5-nitroterephthalate: ^{1}H NMR ($CDCl_3$, 400 MHz, ppm.): δ 11.39 (1H, s), 8.59 (1H, s), 7.11 (1H, s), 4.02 (3H, s), 3.93 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 168.9, 163.0, 153.2, 140.1, 131.4, 128.7, 120.1, 117.6, 53.6, 53.5. ESI-MS(+) *m/z* calcd. For $C_{10}H_9NNaO_7$ $[M+Na]^+$: 278.0271, found $[M+Na]^+$: 278.0273.

Dimethyl 2-hydroxy-3-nitroterephthalate: ^{1}H NMR ($CDCl_3$, 400 MHz, ppm.): δ 11.32 (1H, s), 8.01 (1H, d, J = 8.3 Hz), 7.48 (1H, d, J = 8.3 Hz), 4.03 (3H, s), 3.90 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 168.7, 165.6, 165.3, 138.3, 135.7, 127.6, 118.7, 113.2, 53.6, 53.5. ESI-MS(+) *m/z* calcd. For $C_{10}H_9NNaO_7$ $[M+Na]^+$: 278.0271, found $[M+Na]^+$: 278.0275.



Dimethyl-2-methoxy-5-nitroterephthalate and Dimethyl-2-methoxy-3-nitroterephthalate.

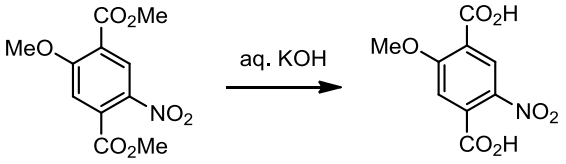
Dimethyl-2-hydroxy-5-nitroterephthalate (230 mg, 0.9 mmol) and potassium carbonate (373 mg, 2.7 mmol), iodomethane (0.17 mL, 2.7 mmol) were dissolved in acetone (15 mL). The mixture was stirred under reflux condition (60^{o}C) for overnight. Once conversion was complete (by TLC), the solvent was evaporated. And then water was added to dissolve all of the inorganic salt. The solution was three times extracted with ethyl acetate. The solution was then dried using $MgSO_4$, filtered, and evaporated of ethyl acetate. Then the desired compound,

dimethyl 2-methoxy-5-nitroterephthalate (220 mg, 91%), were obtained as a colorless solid.

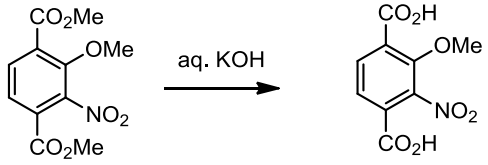
Dimethyl-2-methoxy-5-nitroterephthalate: ^{1}H NMR ($CDCl_3$, 400 MHz, ppm.): δ 8.54 (1H, s), 7.12 (1H, s), 4.02 (3H, s), 3.95 (3H, s), 3.93 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 166.0, 163.9, 162.6, 139.2, 133.9, 128.8, 121.7, 112.4, 57.2, 53.8, 52.9. ESI-MS(+) *m/z* calcd. For $C_{11}H_{11}NNaO_7$ $[M+Na]^+$: 292.0428, found $[M+Na]^+$: 292.0433.

Dimethyl-2-methoxy-3-nitroterephthalate was obtained in comparable yield from a similar procedure using dimethyl-2-hydroxy-3-nitroterephthalate as a starting material.

Dimethyl 2-methoxy-3-nitroterephthalate: ^{1}H NMR ($CDCl_3$, 400 MHz, ppm.): δ 8.00 (1H, d, *J* = 8.3 Hz), 7.81 (1H, d, *J* = 8.3 Hz), 3.97 (3H, s), 3.95 (3H, s), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 164.1, 162.6, 152.1, 146.8, 132.9, 130.0, 126.6, 125.6, 65.0, 53.5, 53.2. ESI-MS(+) *m/z* calcd. For $C_{11}H_{11}NNaO_7$ $[M+Na]^+$: 292.0428, found $[M+Na]^+$: 292.0433.



4a



4b

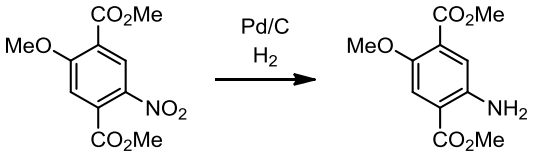
*2-Methoxy-5-nitroterephthalic acid (**4a**) and 2-Methoxy-3-nitroterephthalic acid (**4b**).*

Dimethyl-2-methoxy-5-nitroterephthalate (190 mg, 0.7 mmol) was dissolved in 7 mL of THF. To this, 7 mL of a 4% KOH aqueous solution was added drop-wise. The mixture was stirred under reflux condition (66 ^{o}C) for overnight. Once conversion was complete (by TLC), THF was removed by evaporation and the mixture was acidified with a 1.0 M HCl aqueous solution. The solution was stored overnight in a refrigerator. The precipitate was collected by filtration, and washed with water. The desired compound was obtained by air drying (**4a**, 108 mg, 64%) as a colorless solid.

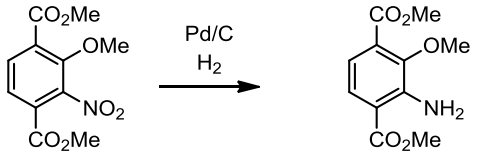
2-methoxy-5-nitroterephthalic acid (**4a**): ^{1}H NMR (DMSO-d_6, 400 MHz, ppm.): δ 8.32 (1H, s), 7.43 (1H, s), 3.99 (3H, s); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 166.2, 164.9, 161.7, 138.3, 134.2, 127.2, 122.6, 112.7, 57.2. ESI-MS(-) *m/z* calcd. For $C_9H_6NO_7$ $[M-H]^-$: 240.0150, found $[M-H]^-$: 240.0150.

2-Methoxy-3-nitroterephthalic acid was obtained in comparable yield from a similar procedure using dimethyl-2-methoxy-3-nitroterephthalate as a starting material.

2-Methoxy-3-nitroterephthalic acid (**4b**): ^{1}H NMR (DMSO-d_6, 400 MHz, ppm.): δ 8.03 (1H, d, *J* = 8.2 Hz), 7.82 (1H, d, *J* = 8.2 Hz), 3.86 (3H, s); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 165.0, 163.3, 150.6, 145.6, 133.0, 130.6, 126.8, 125.7, 64.3. ESI-MS(-) *m/z* calcd. For $C_9H_6NO_7$ $[M-H]^-$: 240.0150, found $[M-H]^-$: 240.0152.



BDCE-2,5-NH_2OMe



BDCE-2,3-NH_2OMe

Dimethyl-2-amino-5-methoxyterephthalate and Dimethyl-2-amino-3-methoxyterephthalate.

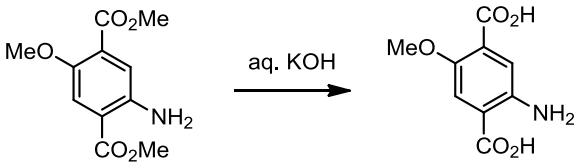
The BDCE-2,5-NH_2OMe and BDCE-2,3-NH_2OMe were prepared using a modified method from what has been previously described.[S3]

Dimethyl-2-methoxy-5-nitroterephthalate (540 mg, 2 mmol) was dissolved in EtOAc (2 mL)/EtOH (8 mL) solution and hydrogenated using 10% Pd/C (54 mg, 10 wt%) under 1 atm hydrogen at 50 ^{o}C for 4 h. The resulting suspension filtered through celite and evaporated of EtOAc/EtOH. The solid mixture was separated by silica gel column chromatography (5% EtOAc/*n*-Hexane) and the desired compound, dimethyl 2-amino-5-methoxyterephthalate (455 mg, 95%), was obtained as a pale yellow solid.

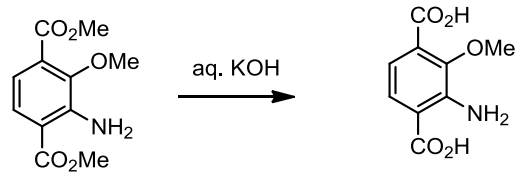
Dimethyl 2-amino-5-methoxyterephthalate: ^{1}H NMR ($CDCl_3$, 400 MHz, ppm.): δ 7.43 (1H, s), 7.10 (1H, s), 5.08 (3H, s, br), 3.90 (3H, s), 3.89 (3H, s), 3.84 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.7, 166.4, 149.4, 143.9, 126.8, 120.1, 114.3, 113.9, 56.9, 52.5, 52.1. ESI-MS(+) *m/z* calcd. For $C_{11}H_{13}NNaO_5$ $[M+Na]^+$: 262.0686, found $[M+Na]^+$: 262.0686.

Dimethyl-2-amino-3-methoxyterephthalate was obtained in comparable yield from a similar procedure using dimethyl-2-methoxy-3-nitroterephthalate as a starting material.

Dimethyl 2-amino-3-methxoyterephthalate: ^{1}H NMR ($CDCl_3$, 400 MHz, ppm.): δ 7.64 (1H, d, J = 8.6 Hz), 7.00 (1H, d, J = 8.6 Hz), 5.85 (2H, s, br), 3.92 (3H, s), 3.89 (3H, s), 3.87 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 168.1, 166.3, 147.7, 144.9, 127.4, 125.9, 116.7, 114.3, 61.4, 52.5, 52.1. ESI-MS(+) *m/z* calcd. For $C_{11}H_{13}NNaO_5$ $[M+Na]^+$: 262.0686, found $[M+Na]^+$: 262.0691.



5a



5b

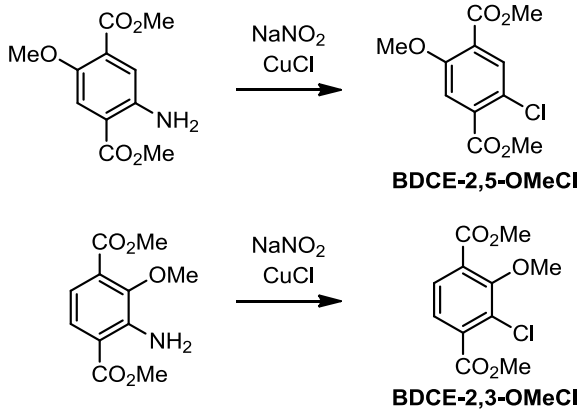
*2-Amino-3-methoxyterephthalic acid (**5a**) and 2-Amino-5-methoxyterephthalic acid (**5b**).*

Dimethyl-2-amino-5-methoxyterephthalate (455 mg, 1.9 mmol) was dissolved in 10 mL of THF. To this, 10 mL of a 4% KOH aqueous solution was added drop-wise. The mixture was stirred under reflux condition (66 ^{o}C) for 3 h. Once conversion was complete (by TLC), THF was removed by evaporation and the mixture was acidified with a 1.0 M HCl aqueous solution. The precipitate was collected by filtration, and washed with water. The desired compound was obtained by air drying (**5a**, 344 mg, 86%) as a colorless solid.

2-Amino-5-methoxyterephthalic acid (**5a**): ^{1}H NMR (DMSO-d$_6$, 400 MHz, ppm.): δ 7.30 (1H, s), 7.02 (1H, s), 3.69 (s, 3H); ^{13}C NMR (DMSO-d$_6$, 100 MHz, ppm): δ 168.8, 167.2, 146.7, 145.4, 128.6, 118.2, 113.8, 111.6, 56.3. ESI-MS(-) *m/z* calcd. For $C_9H_8NO_5$ [*M-H*]$^-$: 210.0408, found [*M-H*]$^-$: 210.0409.

2-Amino-3-methoxyterephthalic acid was obtained in comparable yield from a similar procedure using dimethyl-2-amino-3-methoxyterephthalate as a starting material.

2-Amino-3-methoxyterephthalic acid (**5b**): ^{1}H NMR (DMSO-d$_6$, 400 MHz, ppm.): δ 7.52 (1H, d, *J* = 8.4 Hz), 6.74 (1H, d, J = 8.4 Hz), 3.73 (3H, s); ^{13}C NMR (DMSO-d$_6$, 100 MHz, ppm): δ 169.2, 167.3, 145.9, 145.6, 129.1, 125.9, 114.1, 112.6, 60.6. ESI-MS(-) *m/z* calcd. For $C_9H_8NO_5$ [*M-H*]$^-$: 210.0408, found [*M-H*]$^-$: 210.0408.



Dimethyl-2-chloro-5-methoxyterephthalate and Dimethyl-2-chloro-3-methoxyterephthalate.

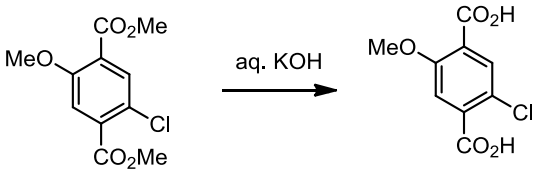
Dimethyl-2-amino-5-methoxyterephthalate (240 mg, 1 mmol) was added by 175 µL of 36% HCl solution in 400 µL of water was stirred at 0 ^{o}C. At the same temperature range, 89.7 mg (1.3 mmol) of $NaNO_2$ solution in 870 µL of water was added drop-wise and the mixture was stirred for 1 hour. At the same temperature range, 120 mg (1.2 mmol) of CuCl was mixed with 175 µL of 36% HCl, and the above solution was slowly added to CuCl/HCl solution. The mixed solution was stirred for 1 hour at 0 ^{o}C and for 2 hours at room temperature. The resultant was extracted with ethyl acetate, the organic layer was dried using $MgSO_4$, and filtered, evaporated of ethyl acetate. The solid mixture was separated by silica gel column chromatography (10% EtOAc/*n*-Hexane) and the desired compound, dimethyl-2-chloro-5-methoxyterephthalate (180 mg, 70%), was obtained as a colorless solid.

Dimethyl-2-chloro-5-methxoyterephthalate: ^{1}H NMR ($CDCl_3$, 400 MHz, ppm.): δ 7.84 (1H, s), 7.39 (1H, s), 3.96 (s, 3H), 3.93 (s, 3H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 165.5, 164.7, 157.1, 133.8, 133.7, 124.5, 124.0, 114.9, 56.7, 52.9, 52.7. ESI-MS(+) *m/z* calcd. For $C_{11}H_{11}ClNaO_5$ [*M+Na*]$^+$: 281.0187, found [*M+Na*]$^+$:281.0191.

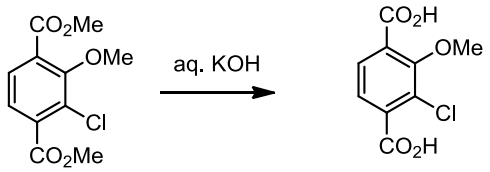
Dimethyl-2-chloro-3-methoxyterephthalate was obtained in comparable yield from a similar procedure using dimethyl-2-amino-3-methoxyterephthalate as a starting material.

Dimethyl 2-chloro-3-methxoyterephthalate: ^{1}H NMR ($CDCl_3$, 400 MHz, ppm.): δ 7.69 (1H, d, *J* = 8.2 Hz), 7.51 (1H, d, *J* = 8.2 Hz), 3.96 (s, 3H), 3.95 (s, 3H), 3.94 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 165.6, 165.3,

156.7, 135.5, 129.3, 129.2, 128.9, 125.4, 62.2, 52.8, 52.7. ESI-MS(+) *m/z* calcd. For $C_{11}H_{11}ClNaO_5$ $[M+Na]^+$: 281.0187, found $[M+Na]^+$:281.0190.



6a



6b

*2-Chloro-3-methoxyterephthalic acid (**6a**) and 2-Chloro-5-methoxyterephthalic acid (**6b**).*

Dimethyl-2-chloro-5-methoxyterephthalate (258 mg, 1 mmol) was dissolved in 5 mL of THF. To this, 5 mL of a 4% KOH aqueous solution was added drop-wise. The mixture was stirred under reflux condition (66 ^oC) for overnight. Once conversion was complete (by TLC), THF was removed by evaporation and the mixture was acidified with a 1.0 M HCl aqueous solution. The solution was stored overnight in a refrigerator. The precipitate was collected by filtration, and washed with water. The desired compound was obtained by air drying (**6a**, 164 mg, 71 %) as a colorless solid.

2-Chloro-5-methoxyterephthalic acid (**6a**): ^1H NMR (DMSO-d_6, 400 MHz, ppm.): δ 7.68 (1H, s), 7.43 (1H, s), 3.85 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 166.1, 165.5, 156.2, 135.0, 131.6, 125.0, 121.8, 114.2, 56.3. ESI-MS(-) *m/z*calcd. For $C_9H_6ClO_5$ $[M-H]^-$: 228.9909, found $[M-H]^-$: 228.9906.

2-Chloro-3-methoxyterephthalic acid was obtained in comparable yield from a similar procedure using dimethyl-2-chloro-3-methoxyterephthalate as a starting material.

2-Chloro-3-methxoyterephthalic acid (**6b**): ^1H NMR (DMSO-d_6, 400 MHz, ppm.): δ 7.70 (1H, d, J = 8.0 Hz), 7.68 (1H, s), 7.53 (1H, dd, J = 8.0, 1.1 Hz), 3.84 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 166.4, 166.1 155.0 136.6, 129.9, 129.0 126.4, 124.8, 61.9. ESI-MS(-) *m/z* calcd. For $C_9H_6ClO_5$ $[M-H]^-$: 228.9909, found $[M-H]^-$: 228.9910.

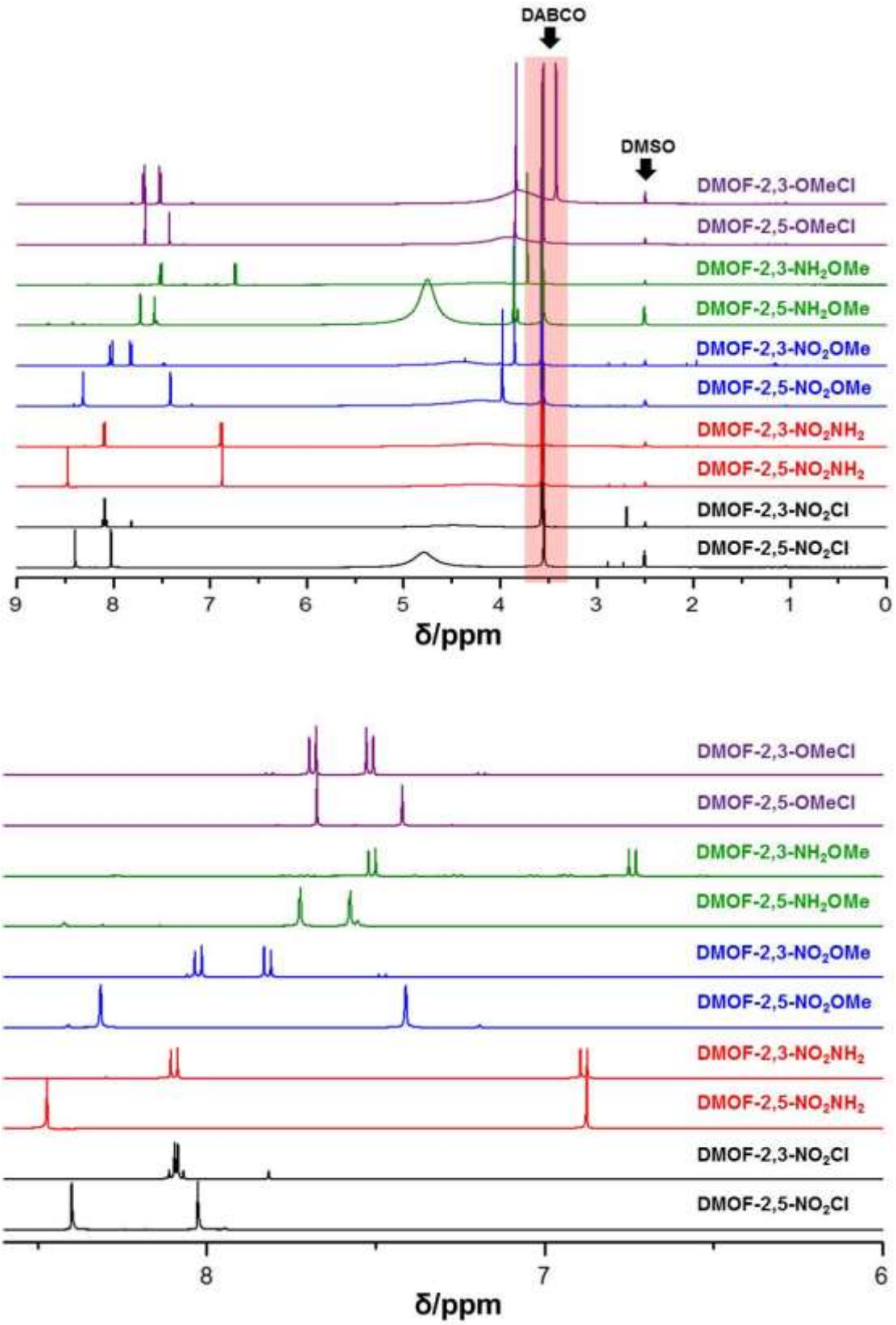


Figure S1. ^{1}H NMR of regioisomeric DMOFs after acid digestion; full range (top) and aromatic range (bottom).

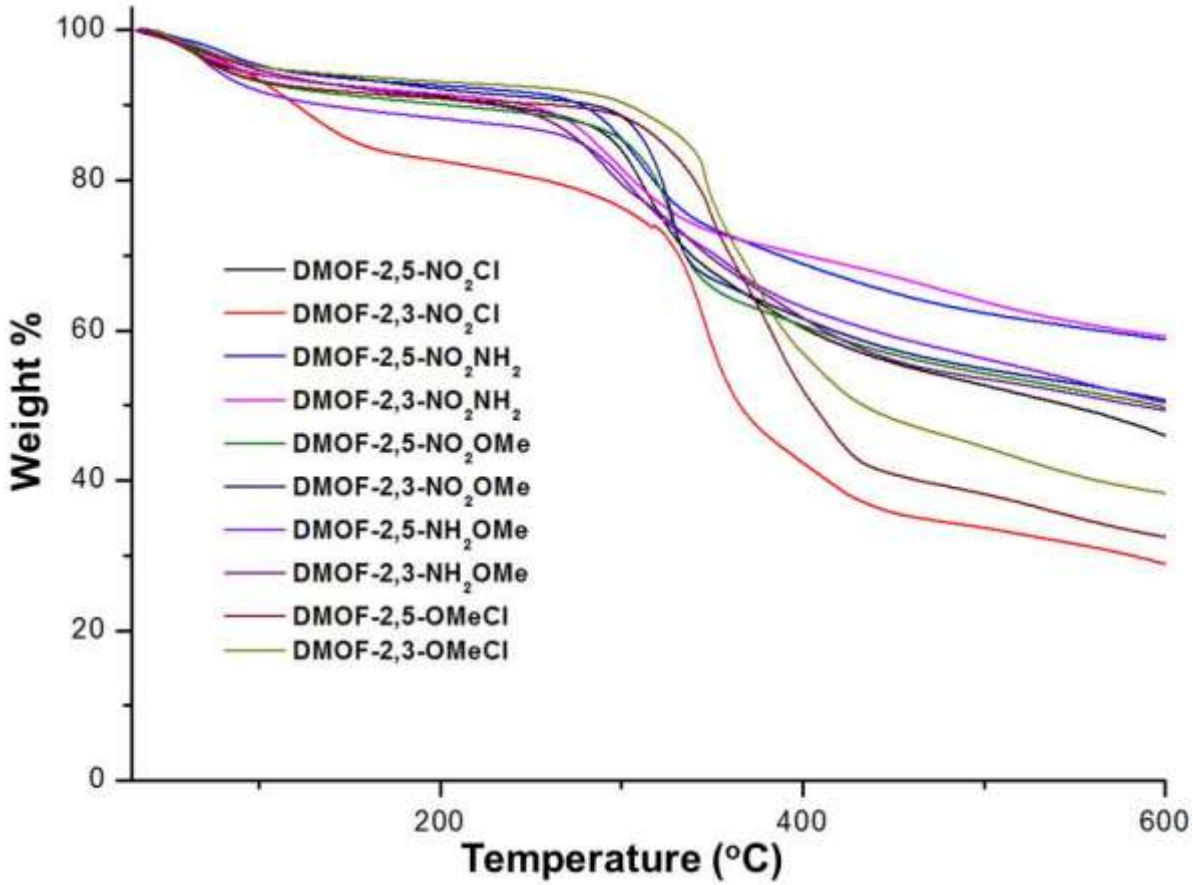


Figure S2. TGA of regioisomeric DMOFs.

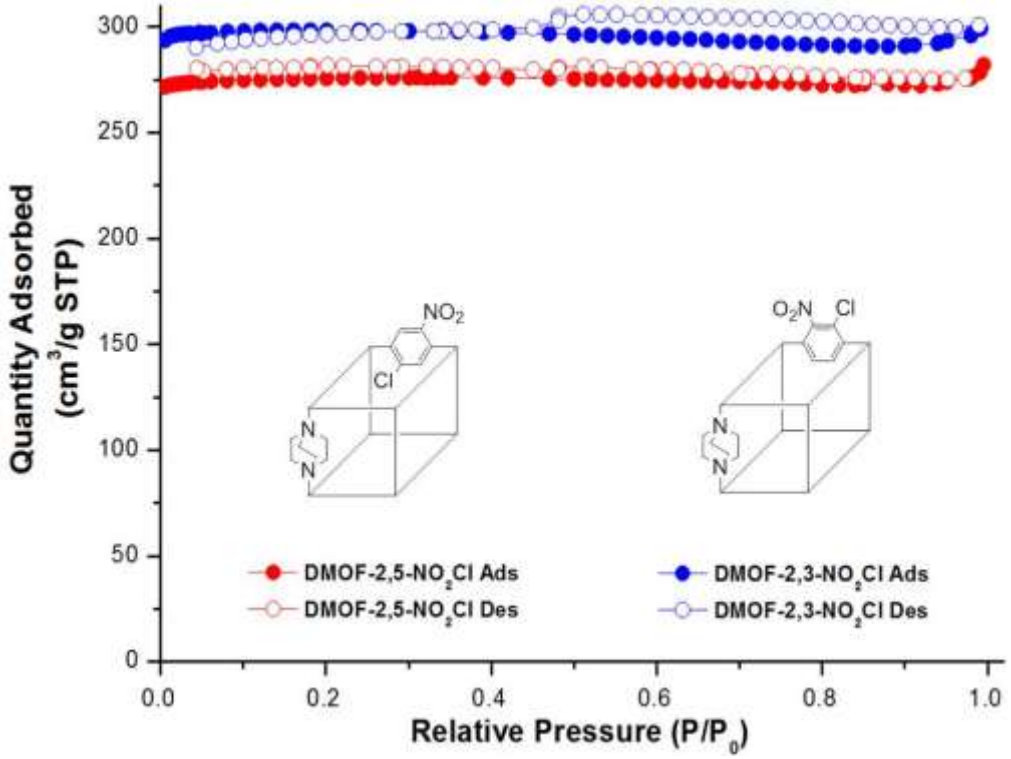


Figure S3. N_2 isotherm (77 K) of DMOF-2,5-NO_2Cl and DMOF-2,3-NO_2Cl. Adsorption and desorption traces are indicated by filled and open symbols, respectively.

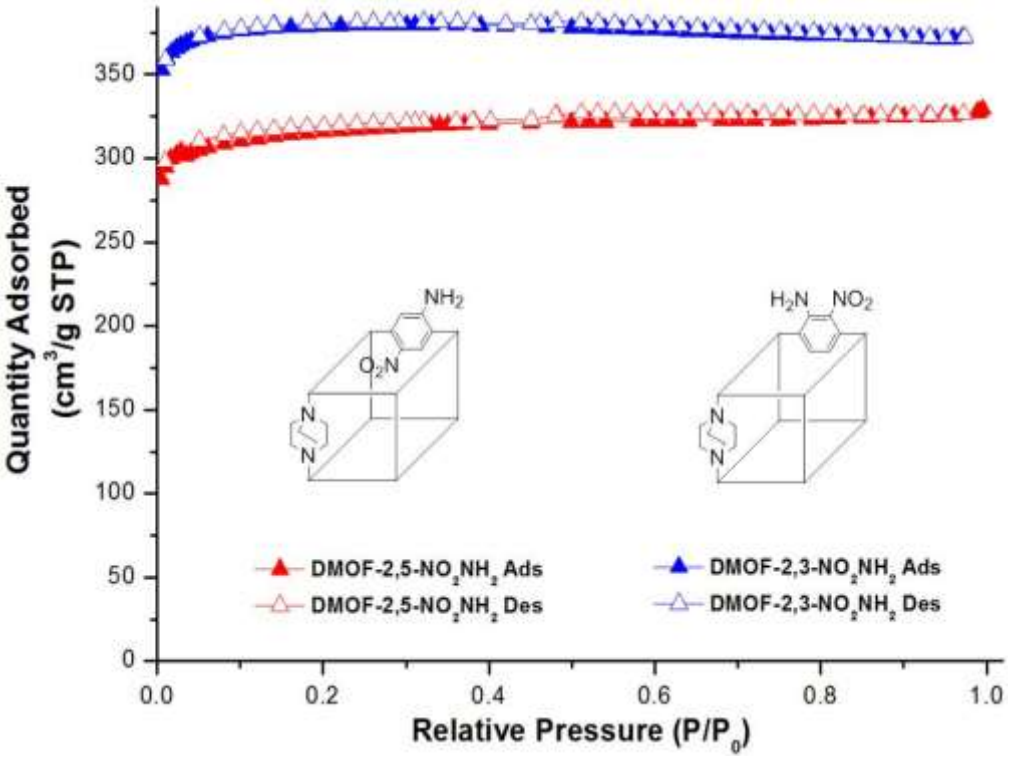


Figure S4. N_2 isotherm (77 K) of DMOF-2,5-NO_2NH_2 and DMOF-2,3-NO_2NH_2. Adsorption and desorption traces are indicated by filled and open symbols, respectively.

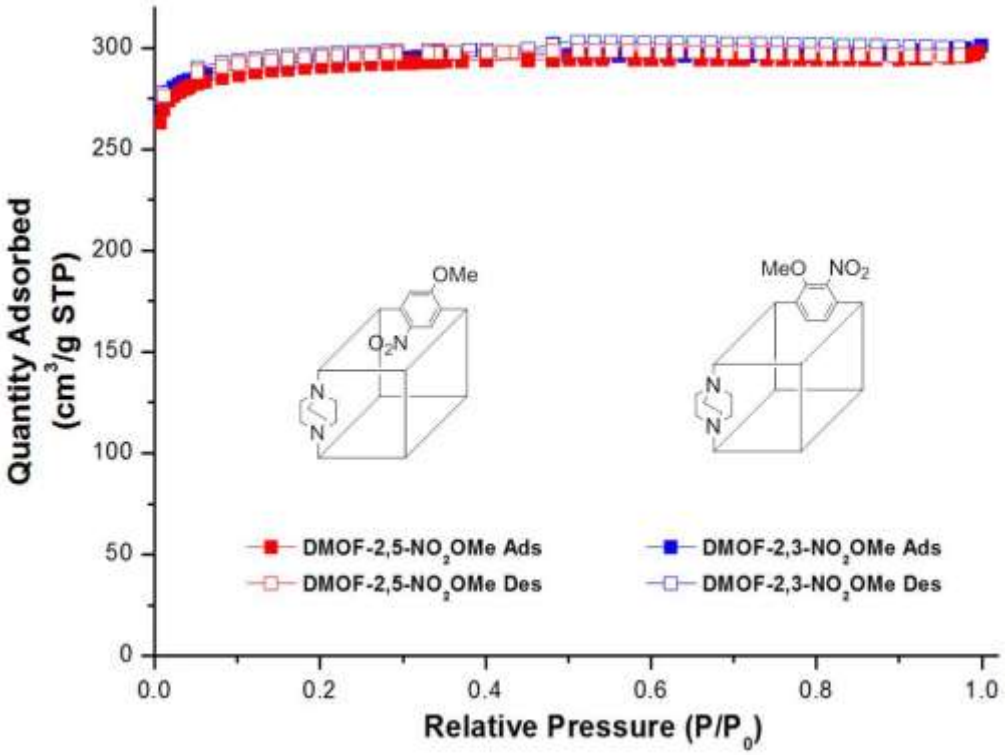


Figure S5. N_2 isotherm (77 K) of DMOF-2,5-NO_2OMe and DMOF-2,3-NO_2OMe. Adsorption and desorption traces are indicated by filled and open symbols, respectively.

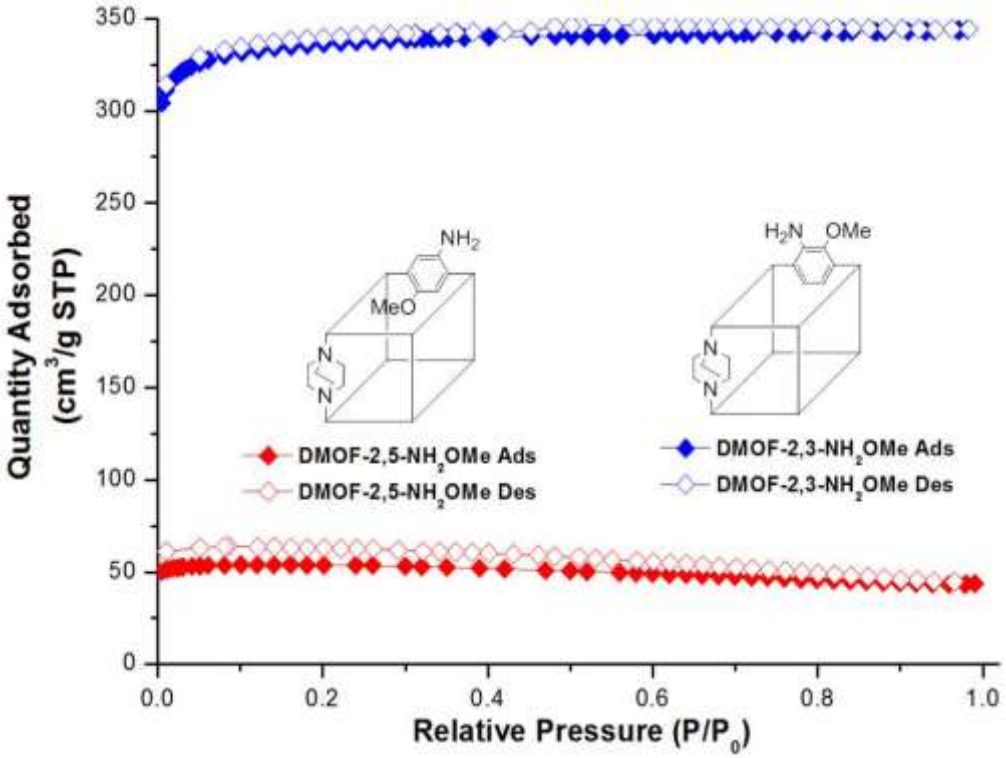


Figure S6. N_2 isotherm (77 K) of DMOF-2,5-NH_2OMe and DMOF-2,3-NH_2OMe. Adsorption and desorption traces are indicated by filled and open symbols, respectively.

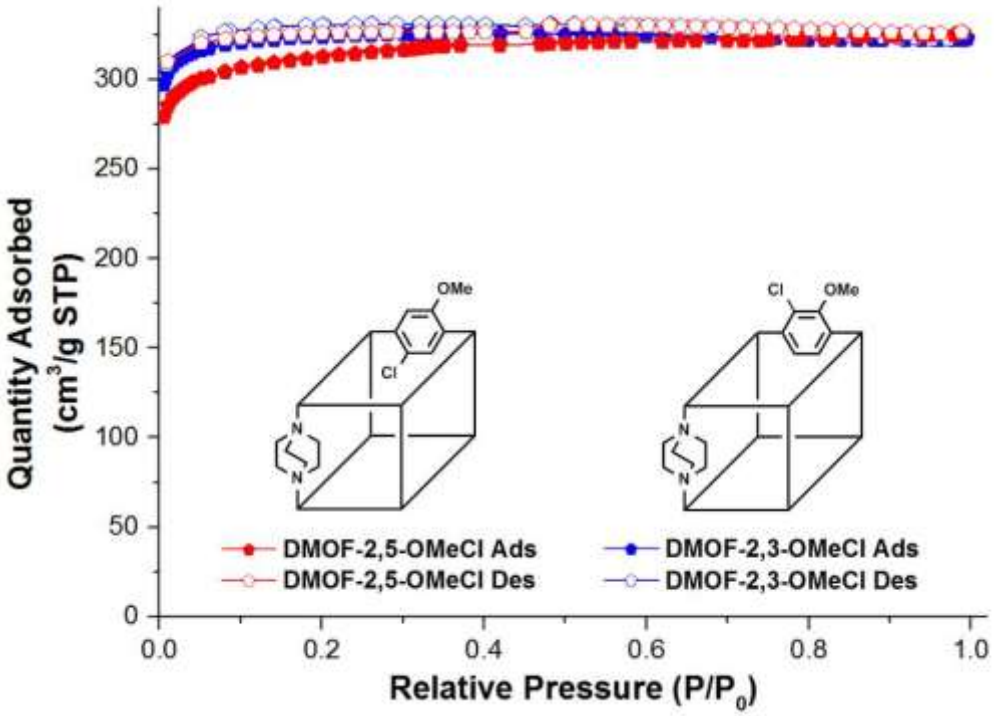


Figure S7. N_2 isotherm (77 K) of DMOF-2,5-OMeCl and DMOF-2,3-OMeCl. Adsorption and desorption traces are indicated by filled and open symbols, respectively.

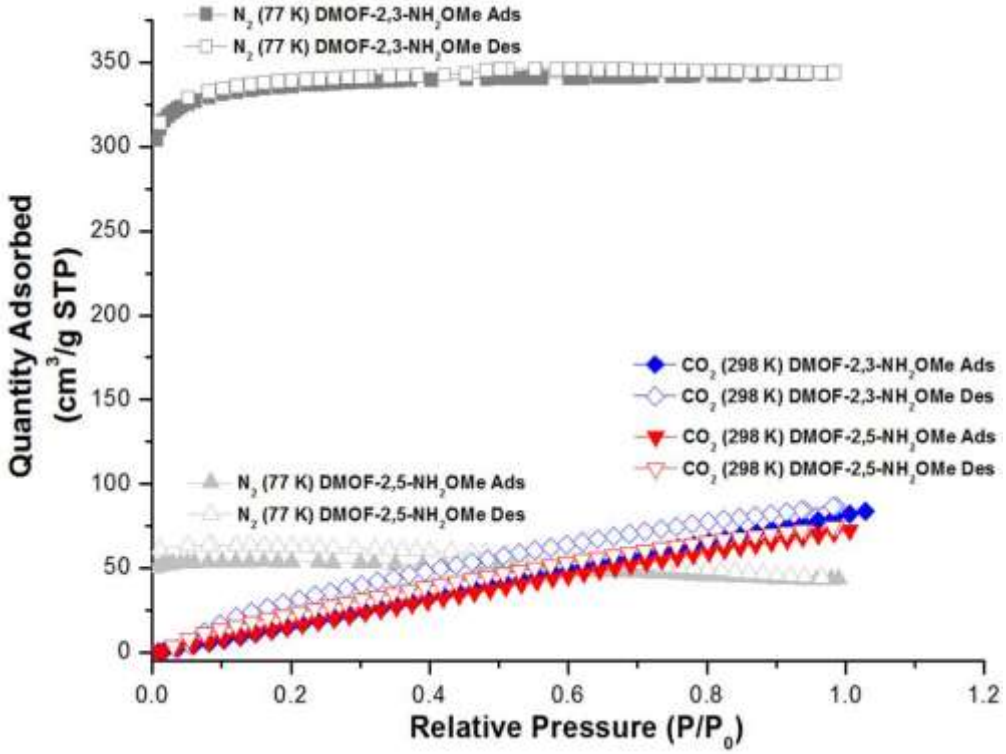


Figure S8. N_2 (77 K) and CO_2 (298 K) sorption isotherms of DMOF-2,5-NH_2OMe. Adsorption and desorption traces are indicated by filled and open symbols, respectively.

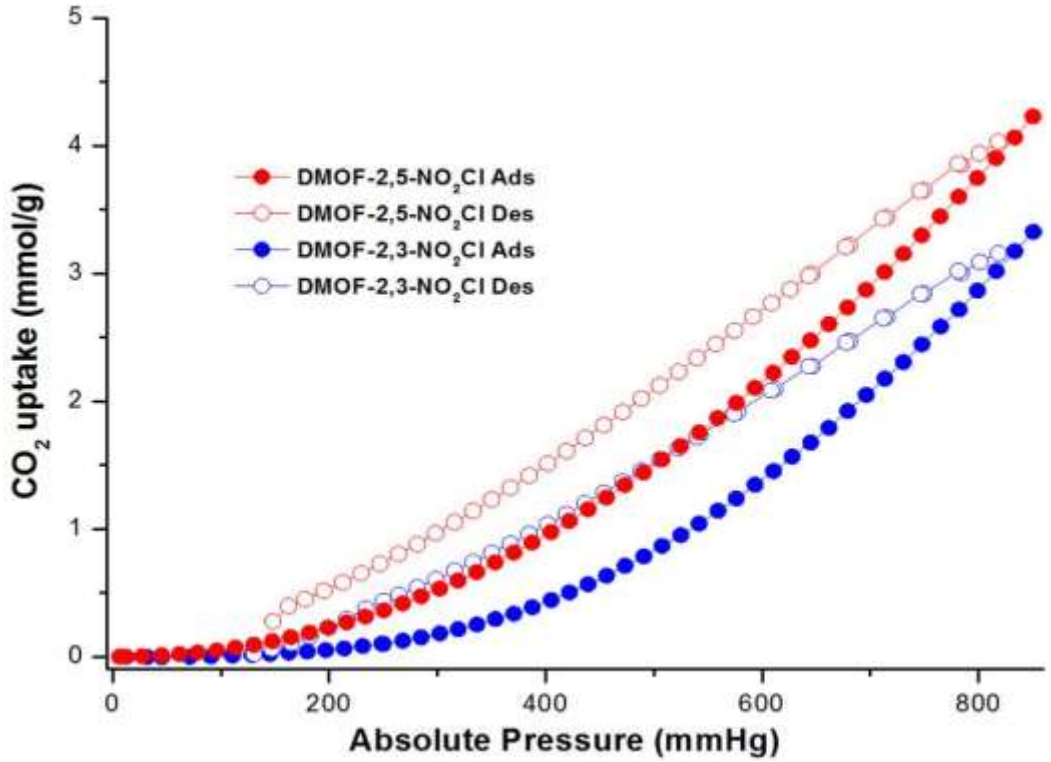


Figure S9. CO_2 isotherm (298 K) of DMOF-2,5-NO_2Cl and DMOF-2,3-NO_2Cl. Adsorption and desorption traces are indicated by filled and open symbols, respectively.

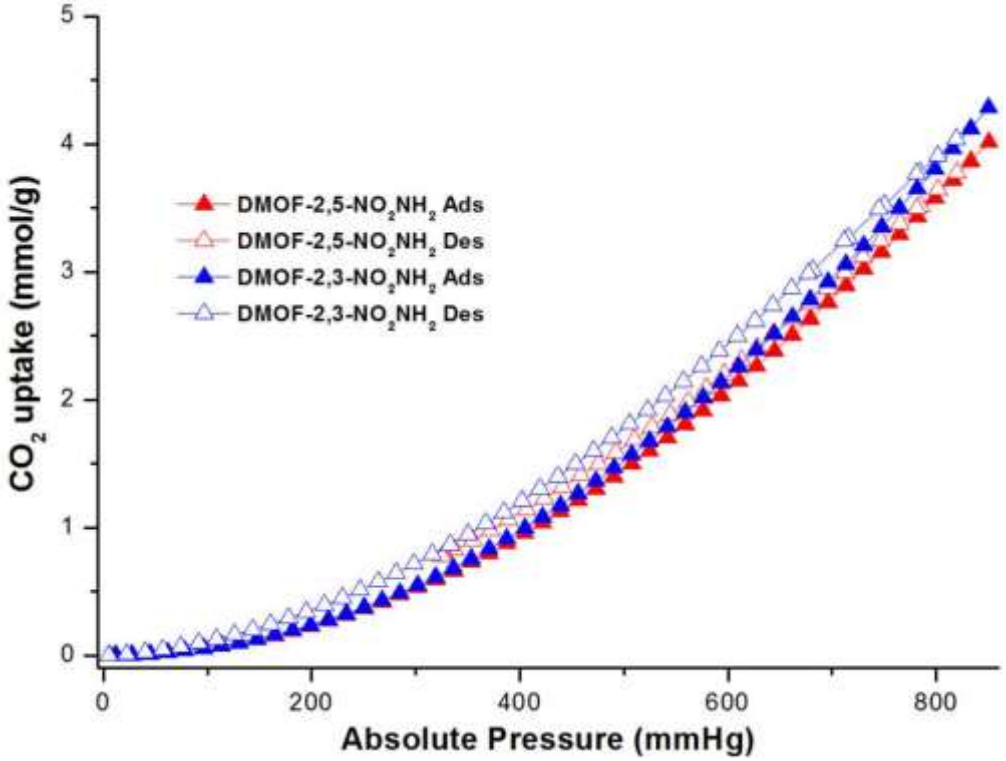


Figure S10. CO_2 isotherm (298 K) of DMOF-2,5-NO_2NH_2 and DMOF-2,3-NO_2NH_2. Adsorption and desorption traces are indicated by filled and open symbols, respectively.

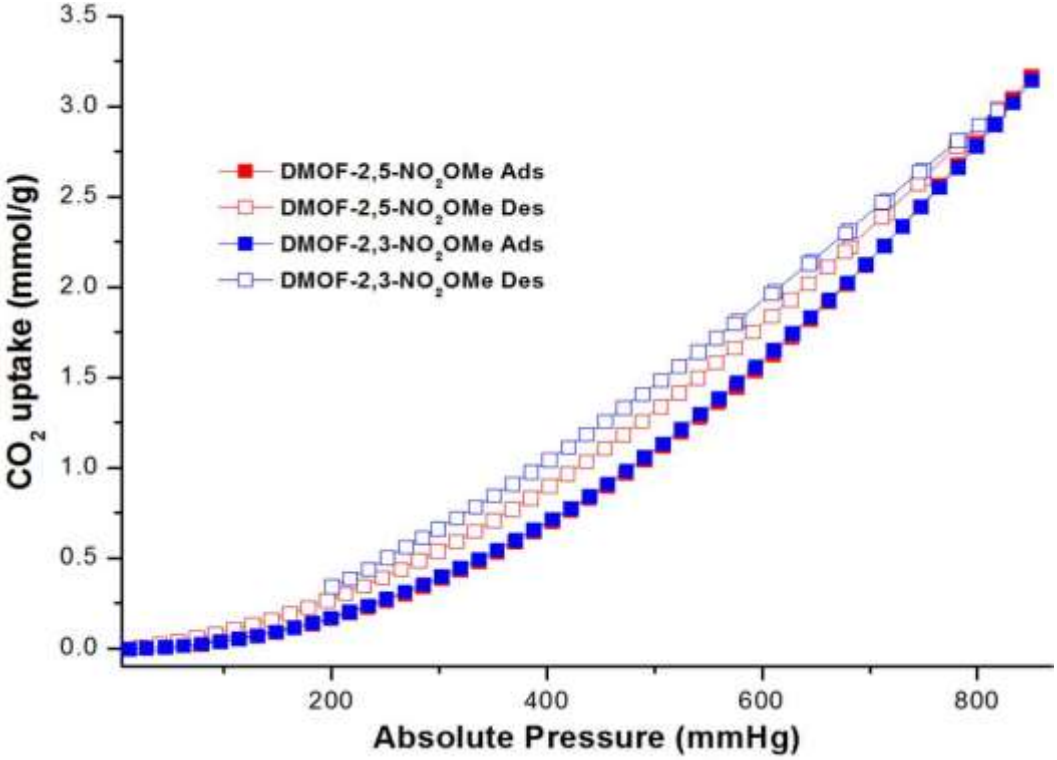


Figure S11. CO_2 isotherm (298 K) of DMOF-2,5-NO_2OMe and DMOF-2,3-NO_2OMe. Adsorption and desorption traces are indicated by filled and open symbols, respectively.

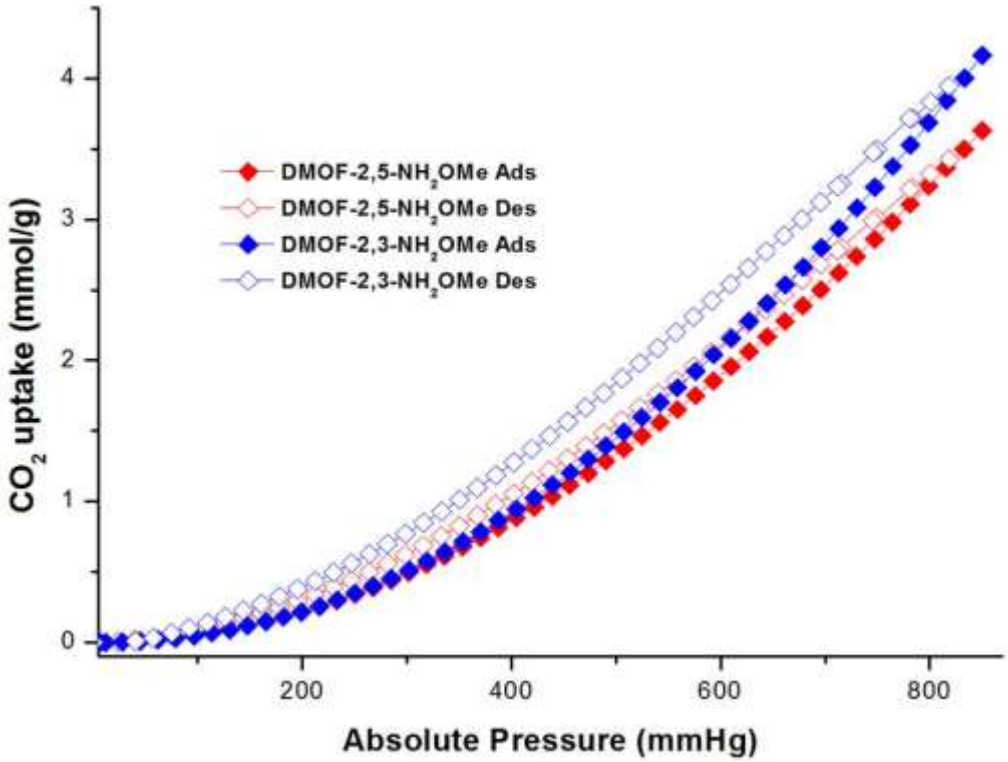


Figure S12. CO_2 isotherm (298 K) of DMOF-2,5-NH_2OMe and DMOF-2,3-NH_2OMe. Adsorption and desorption traces are indicated by filled and open symbols, respectively.

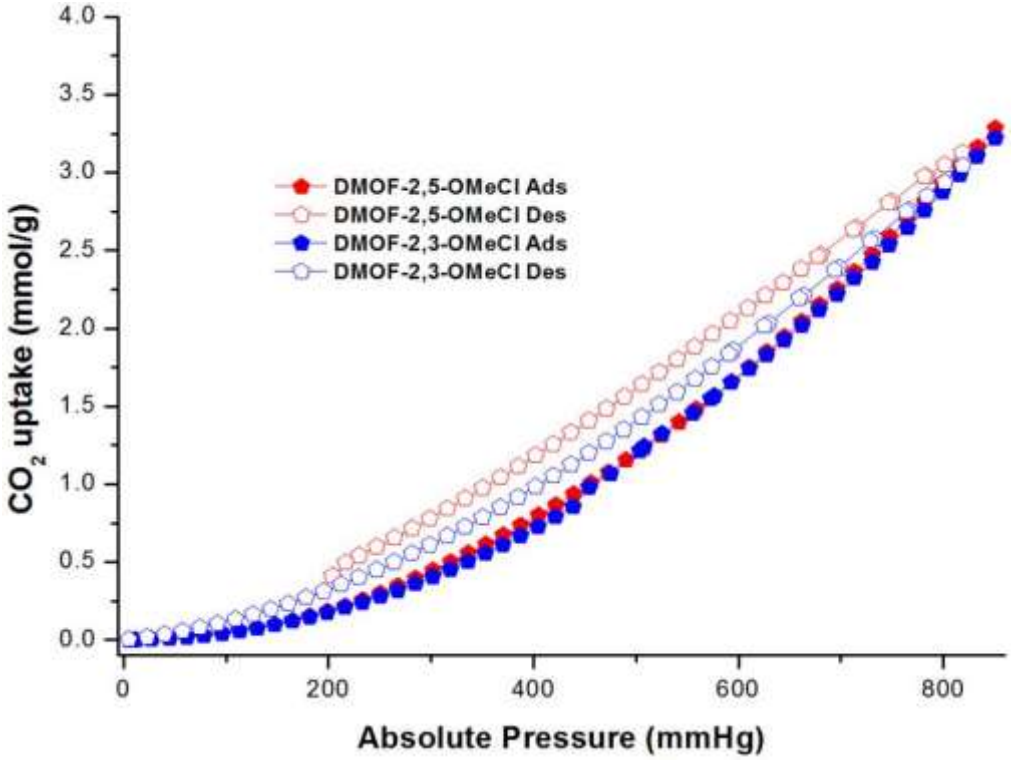


Figure S13. CO_2 isotherm (298 K) of DMOF-2,5-OMeCl and DMOF-2,3-OMeCl. Adsorption and desorption traces are indicated by filled and open symbols, respectively.

Table S1. CO_2 uptake (mmol/g, 298 K) for regioisomeric DMOFs at near 760 torr and 850 torr.

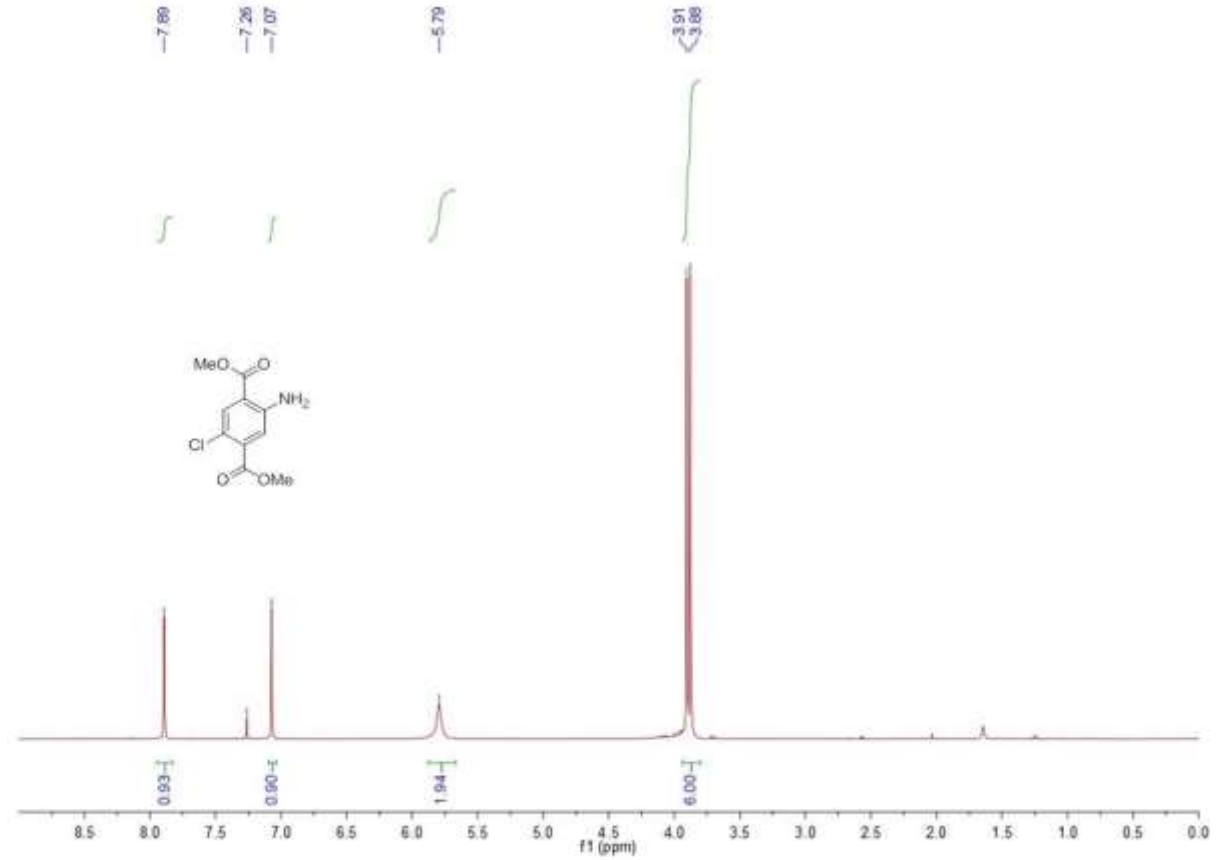
DMOF	CO_2 uptake at 760 torr	CO_2 uptake at 850 torr
DMOF-2,5-NO_2Cl	3.45	4.23
DMOF-2,3-NO_2Cl	2.58	3.33
DMOF-2,5-NO_2NH_2	3.30	4.01
DMOF-2,3-NO_2NH_2	3.50	4.28
DMOF-2,5-NO_2OMe	2.56	3.17
DMOF-2,3-NO_2OMe	2.55	3.14
DMOF-2,5-NH_2OMe	2.98	3.63
DMOF-2,3-NH_2OMe	3.38	4.16
DMOF-2,5-OMeCl	2.70	3.29
DMOF-2,3-OMeCl	2.65	3.22

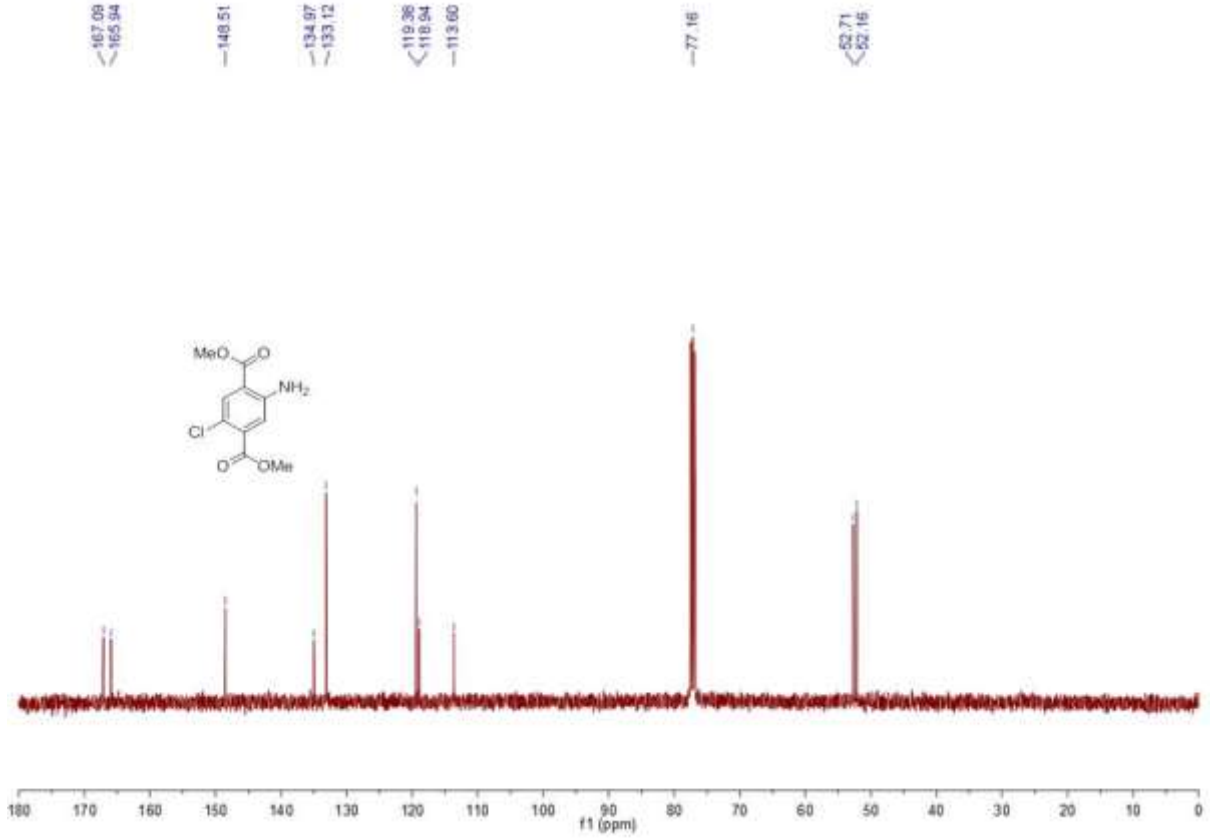
References

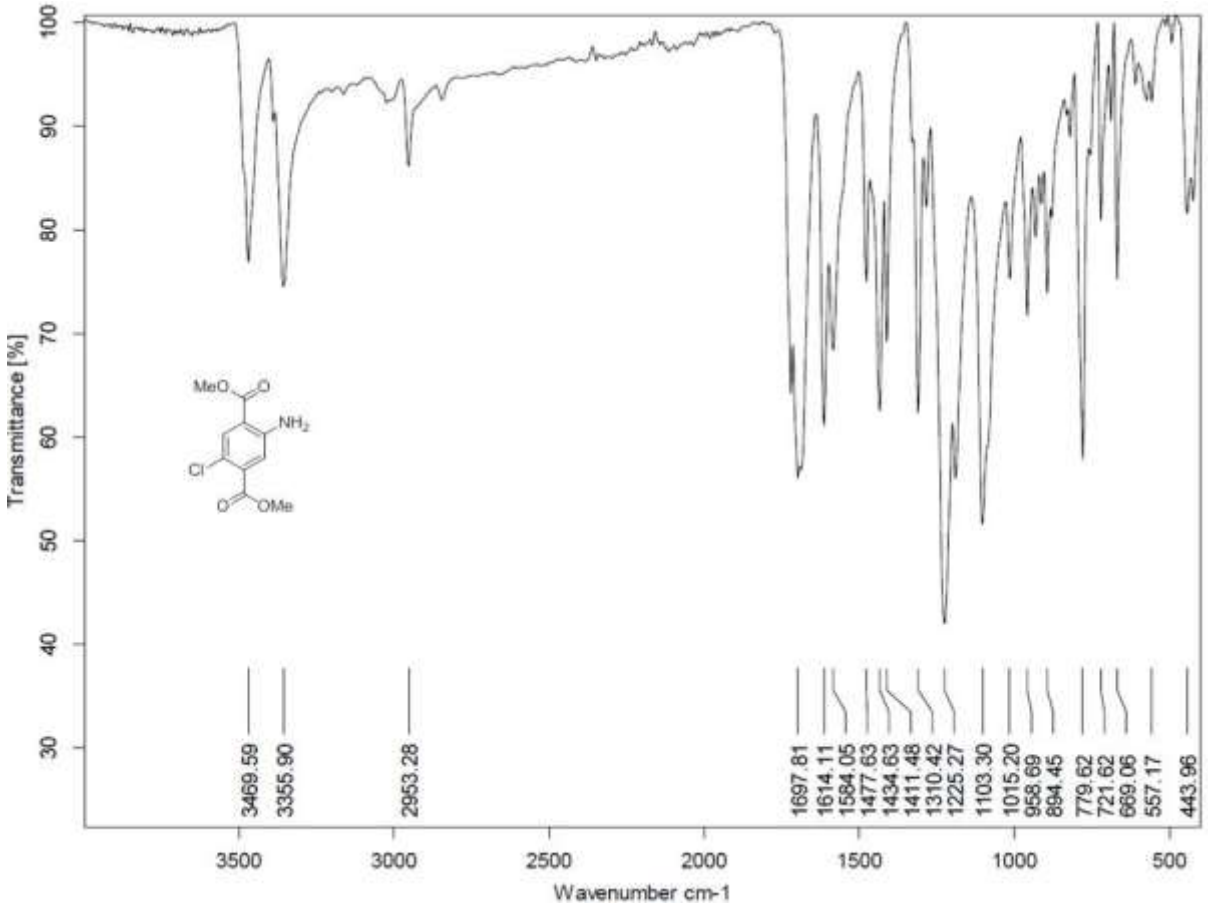
(S1) Kim, M.; Boissonnault, J. A.; Dau, P. V.; Cohen, S. M. *Angew. Chem., Int. Ed*. **2011**, *50*, 12193-12196.
(S2) Heldmann, C.; Shulze, M.; Wegner, G. *Macromolecules*, **1996**, *29*, 4686-4696.
(S3) Pound, G. J.; Pletnev, A. A.; Fanga, X.; Pletneva, E. V. *Chem. Commun*. **2011**, *47*, 5714-5716.

Spectral Copies of ^{1}H, ^{13}C NMR and IR of Obtained Compounds

Dimethyl-2-amino-5-chloroterephthalate (**BDCE-2,5-NH_2Cl**)



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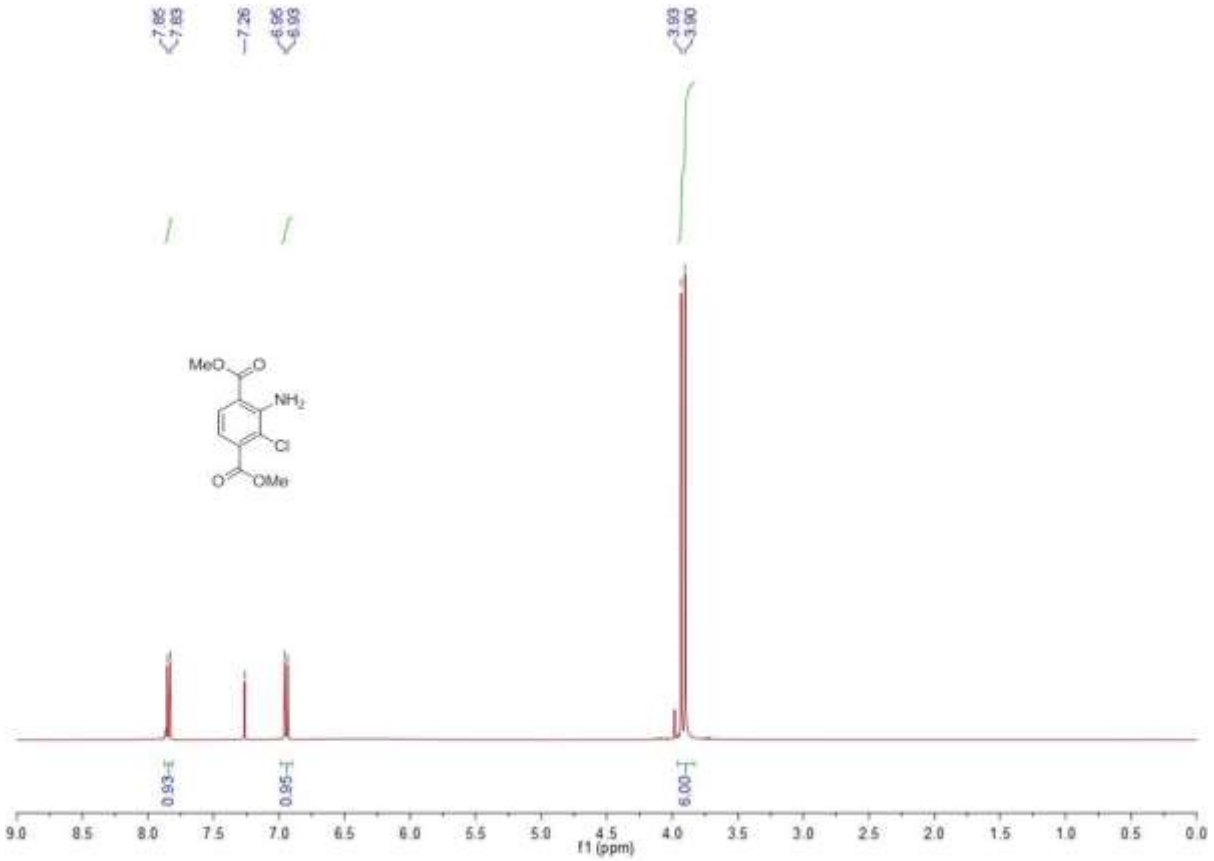
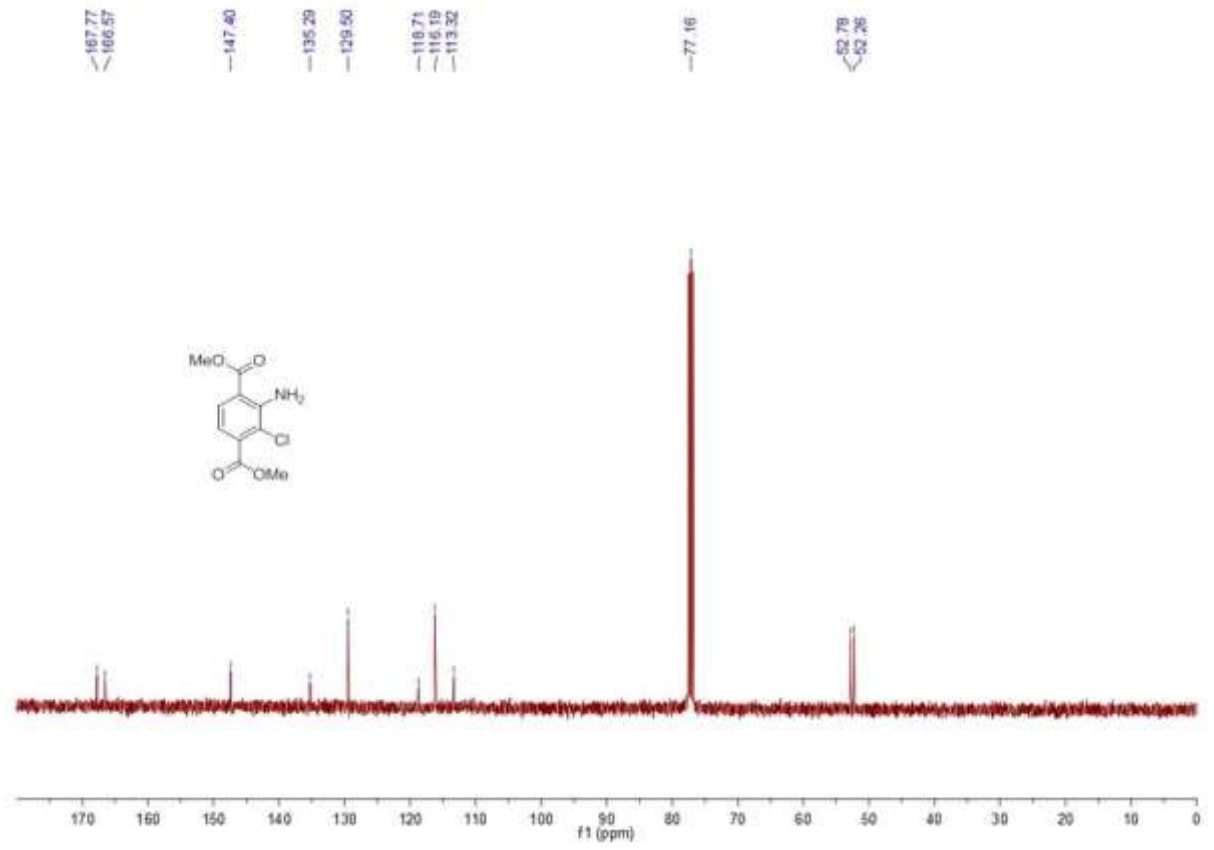
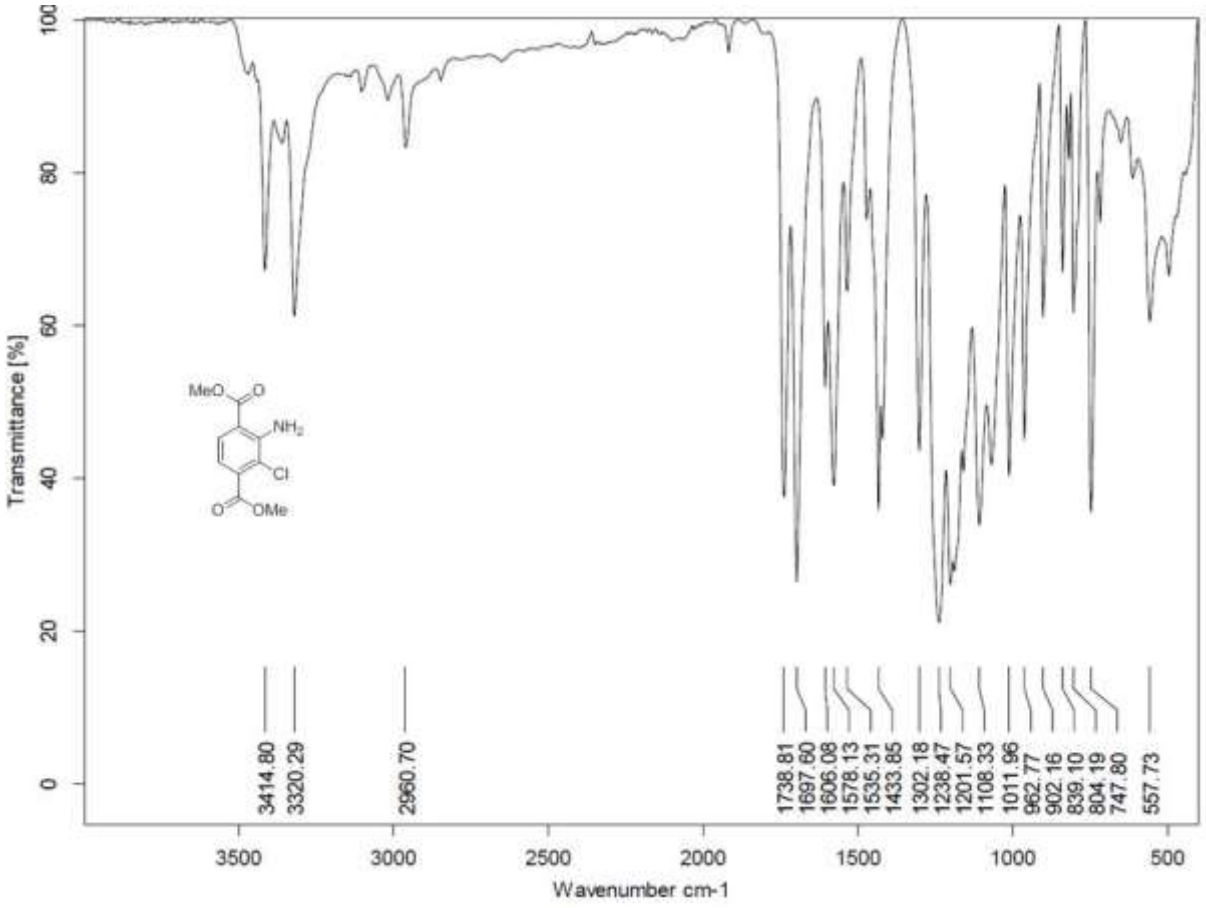
Wavenumber cm-1

Dimethyl-2-amino-3-chloroterephthalate (**BDCE-2,3-NH_2Cl**)



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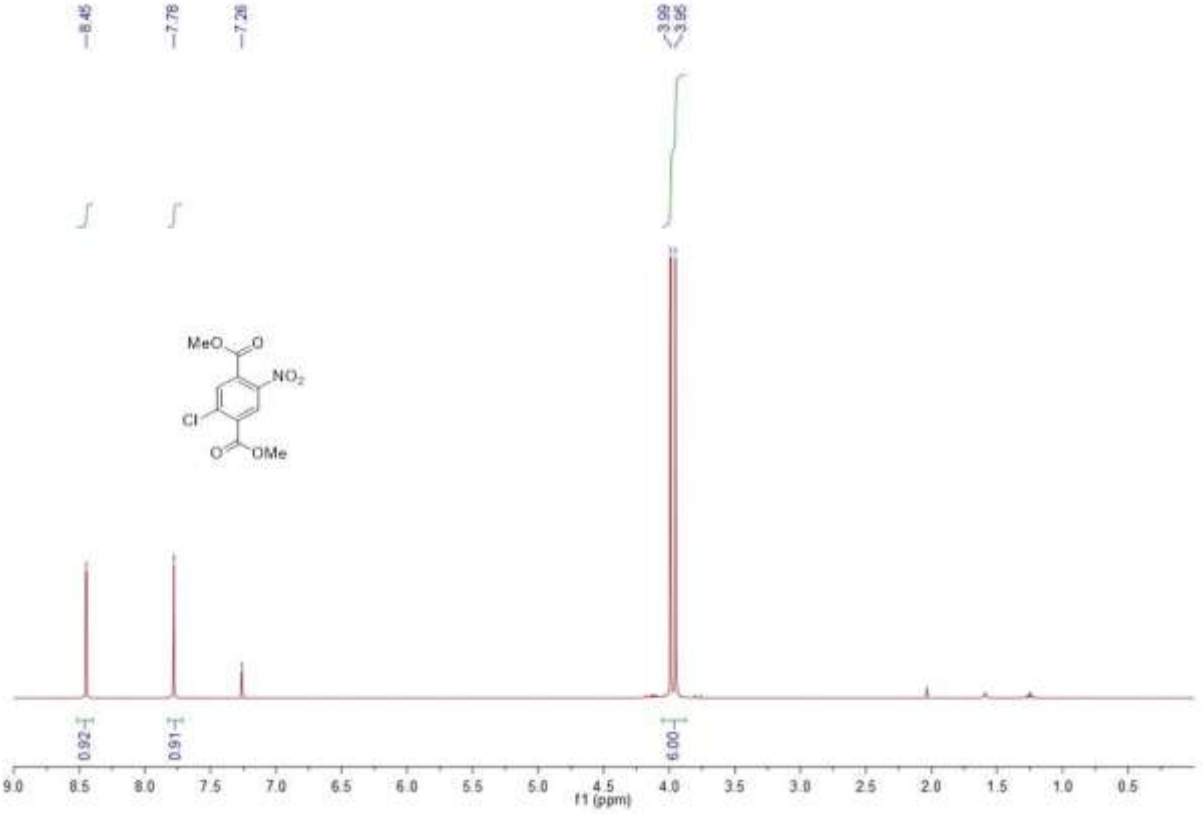
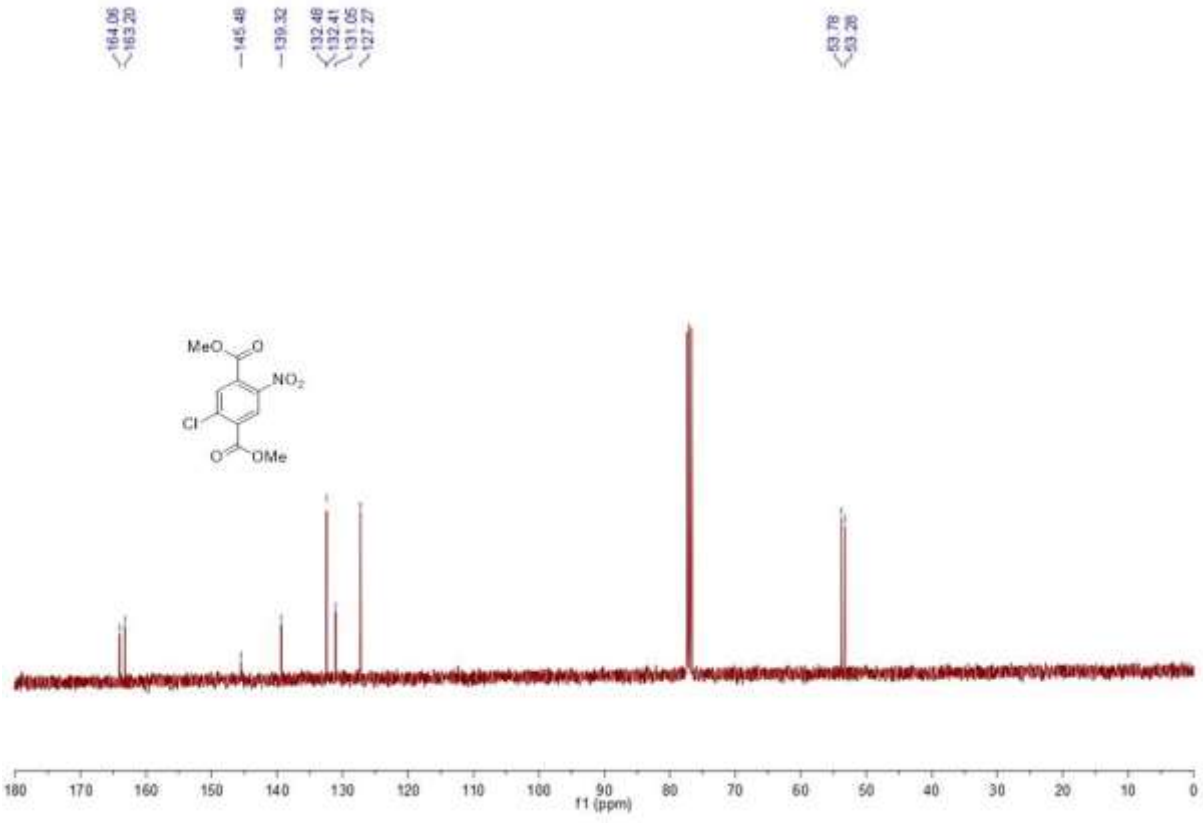
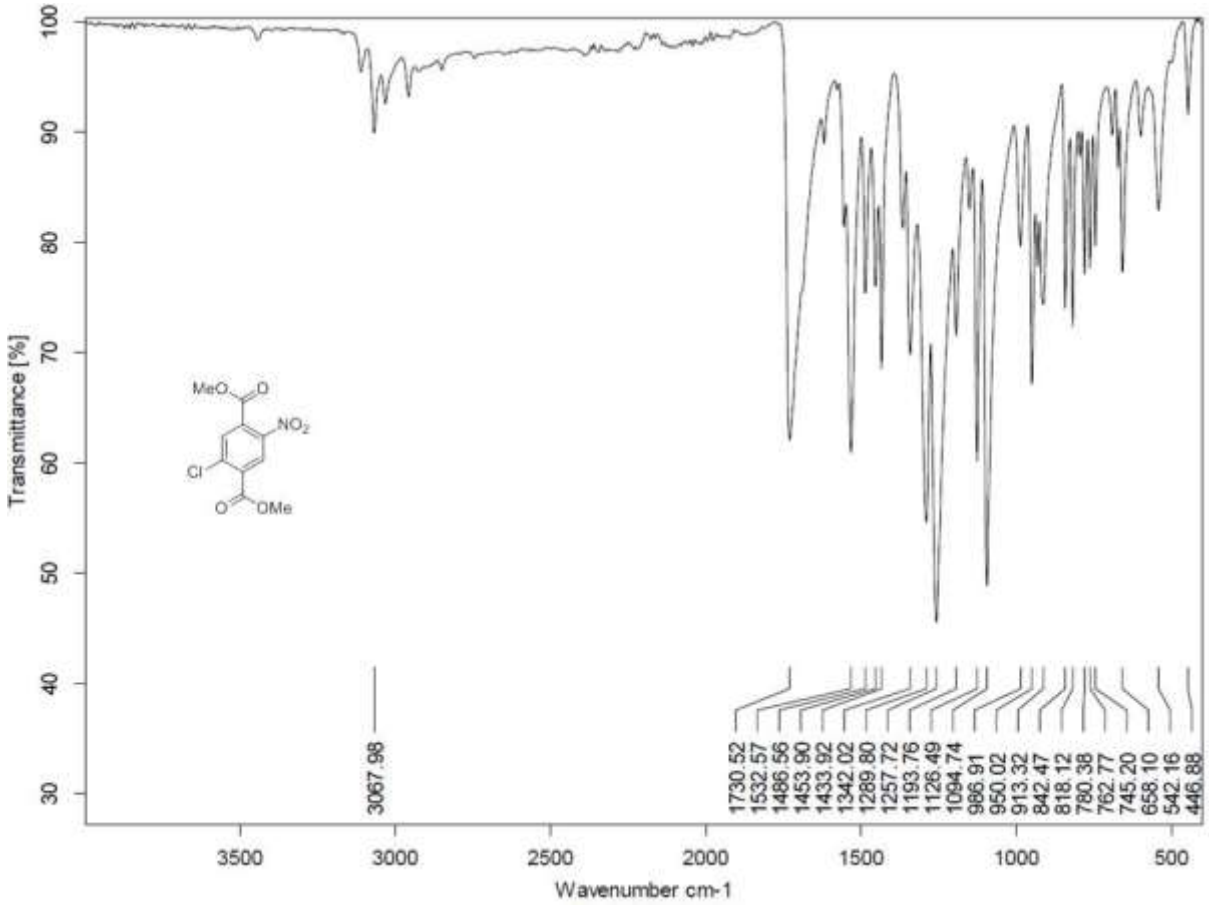
Dimethyl-2-chloro-5-nitroterephthalate (**BDCE-2,5-NO_2Cl**)



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1193.76
1126.49
1094.74
986.91
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842.47
818.12
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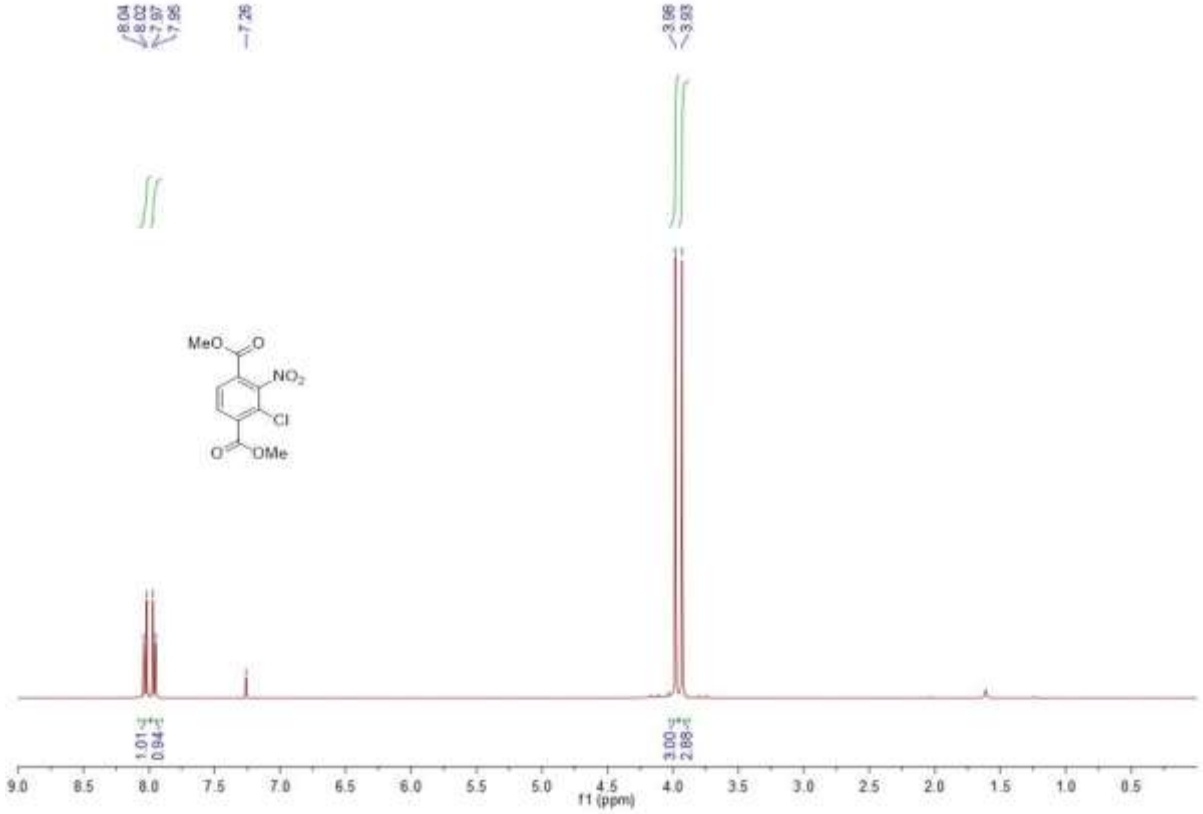
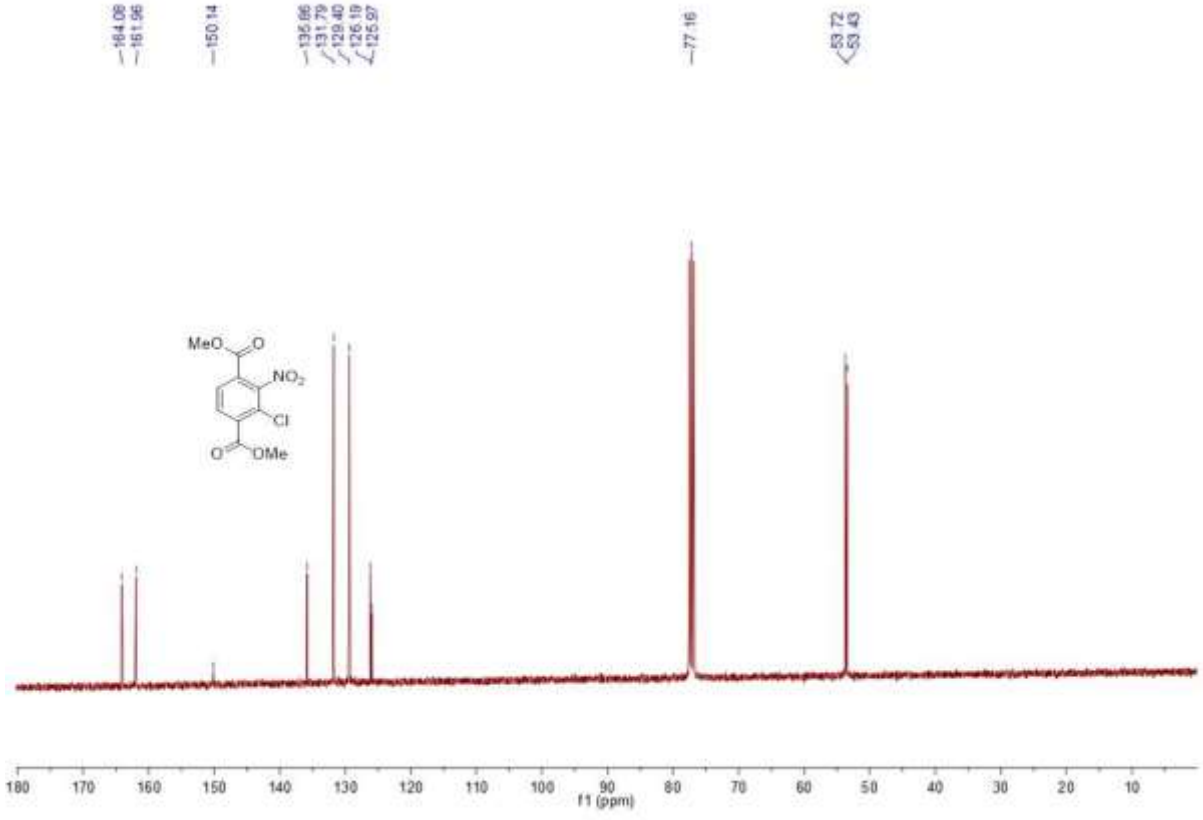
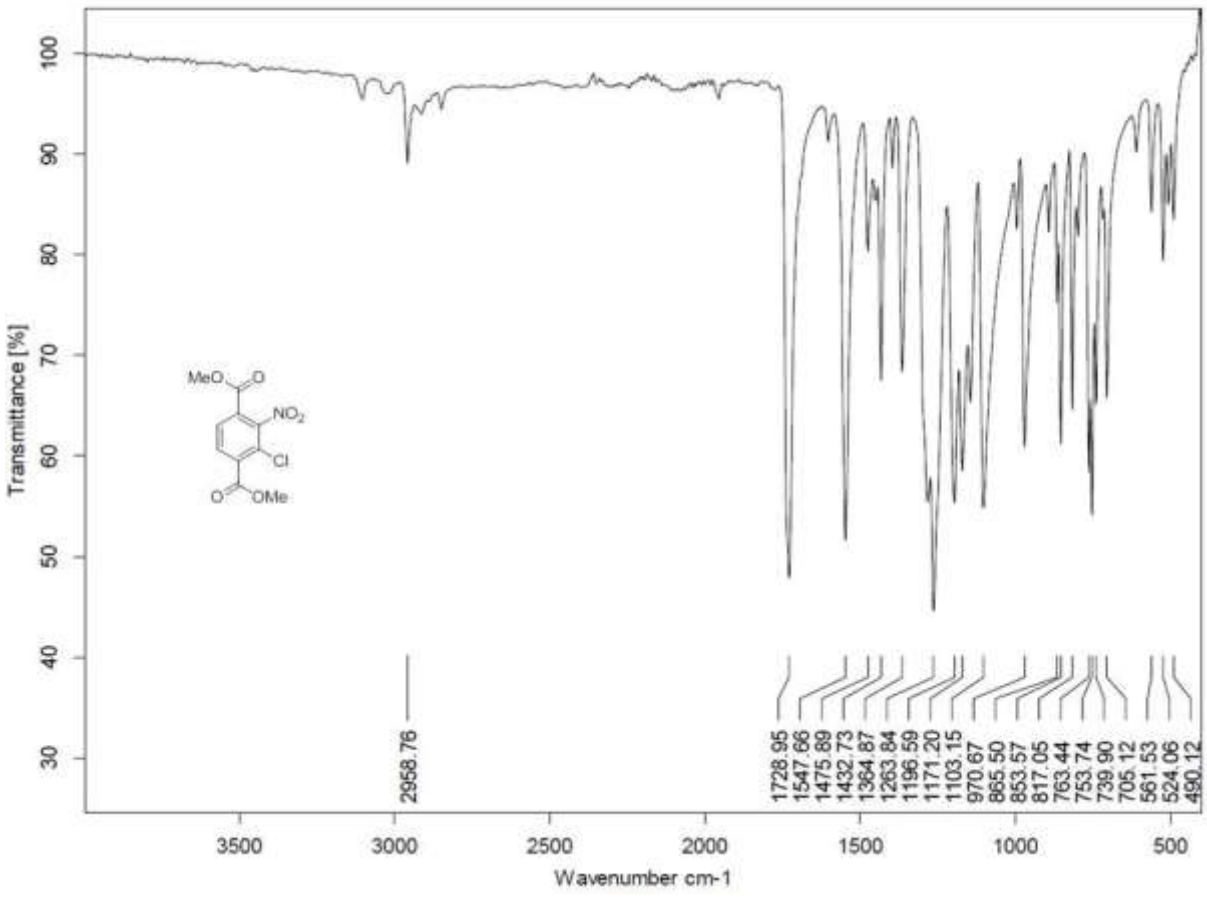
Dimethyl-2-chloro-3-nitroterephthalate (**BDCE-2,3-NO_2Cl**)



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3000
2500
2000
1500
1000
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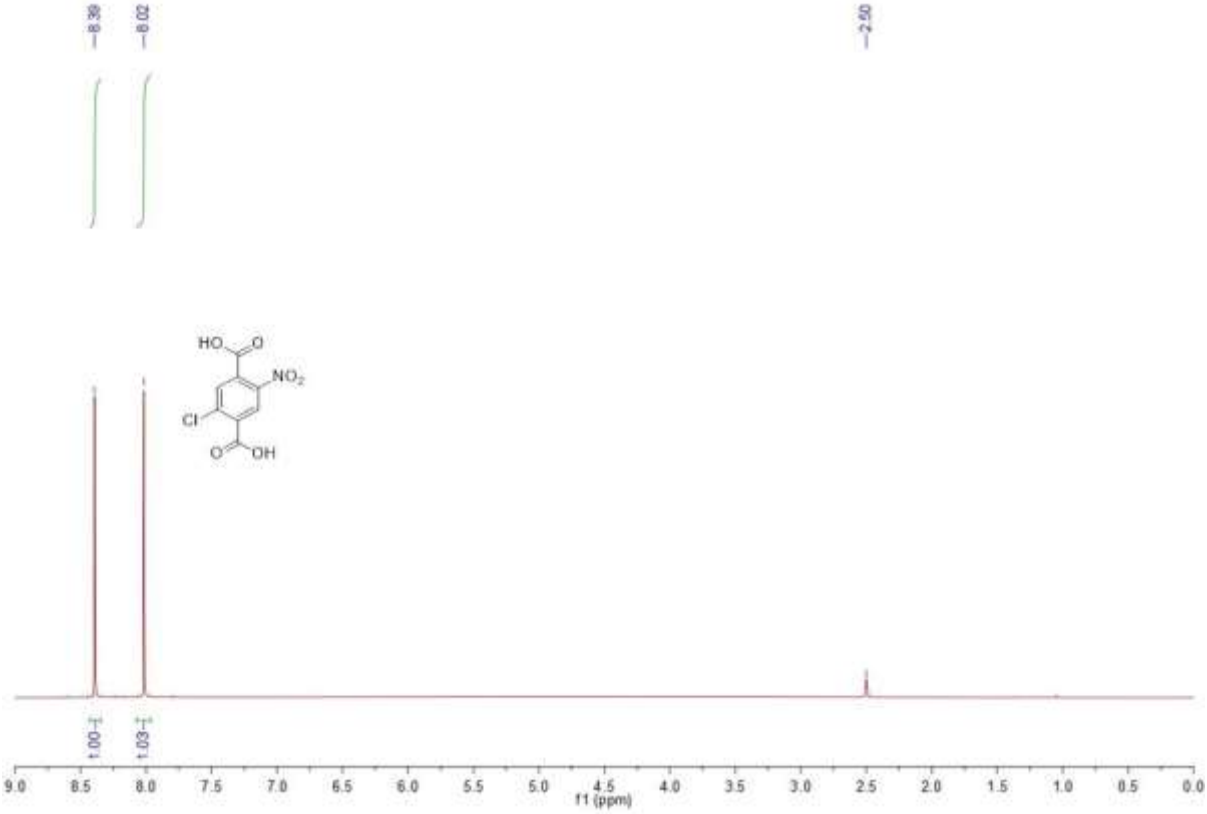
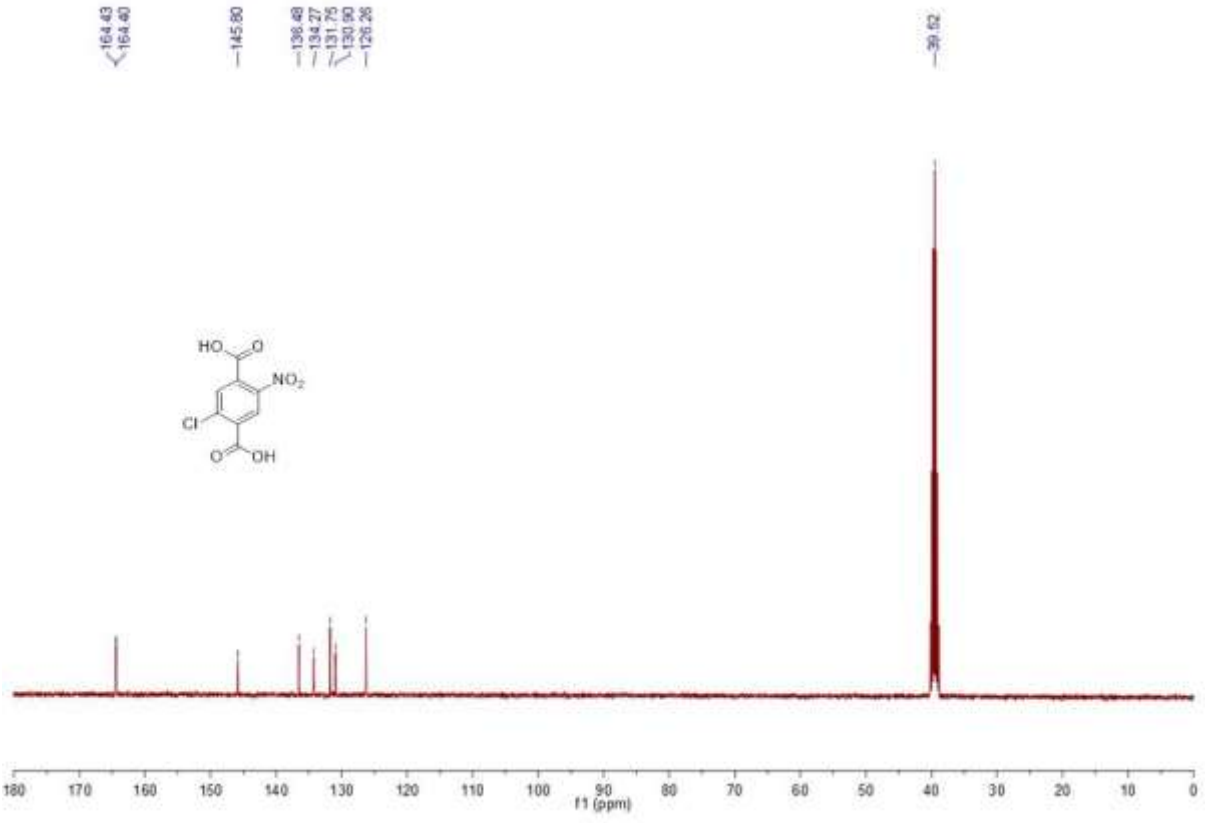
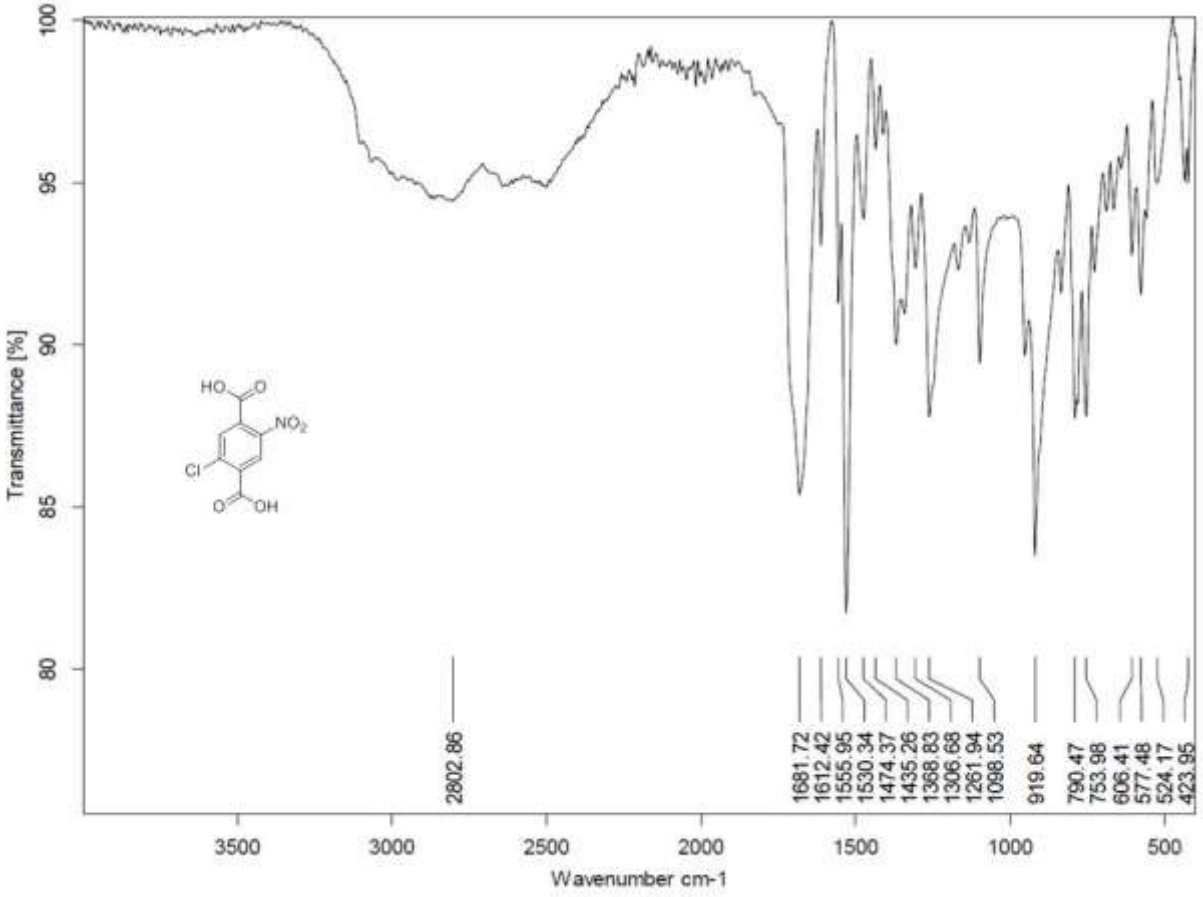
Wavenumber cm-1

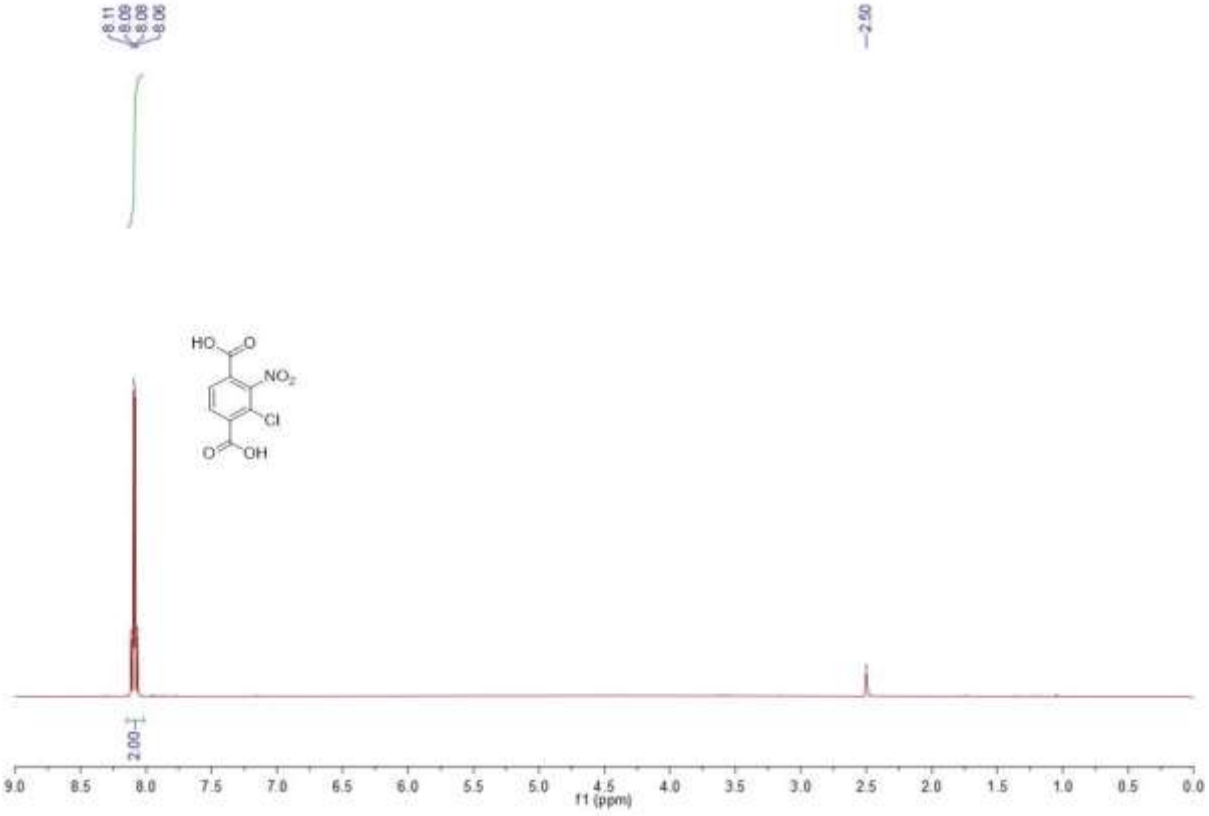
2-Chloro-5-nitroterephthalic acid (**2a**)

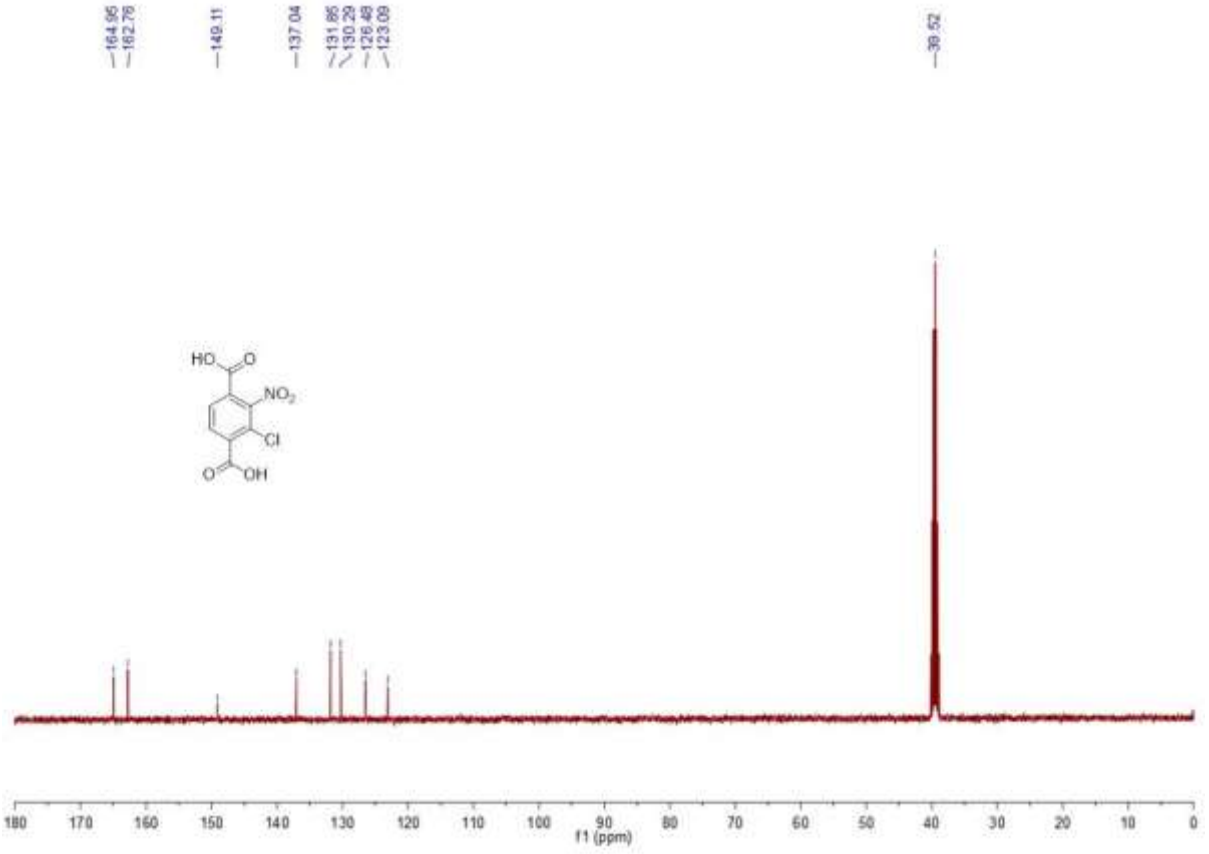


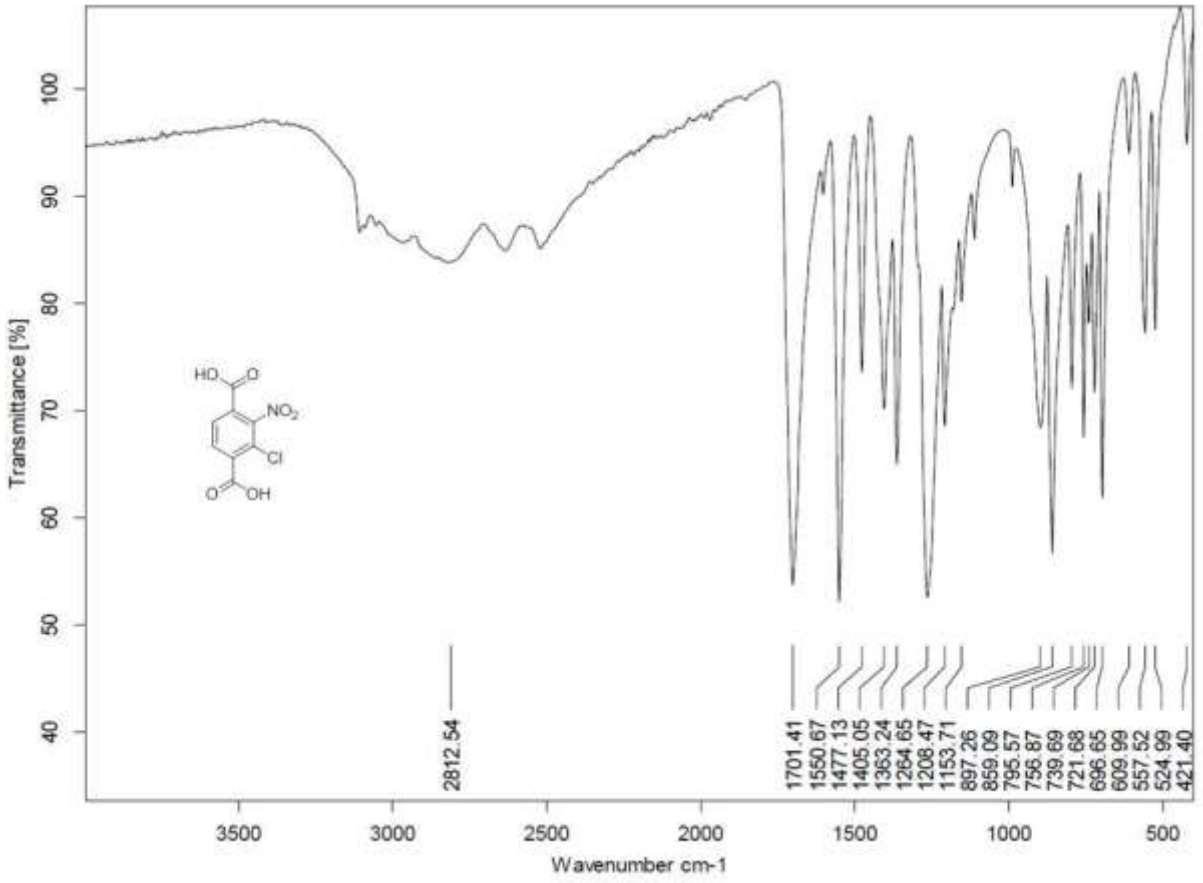



Transmittance [%]
100
95
90
85
80
HO
O
NO2
Cl
O
OH
2802.86
1681.72
1612.42
1555.95
1530.34
1474.37
1435.26
1368.83
1306.68
1261.94
1098.53
919.64
790.47
753.98
606.41
577.48
524.17
423.95
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

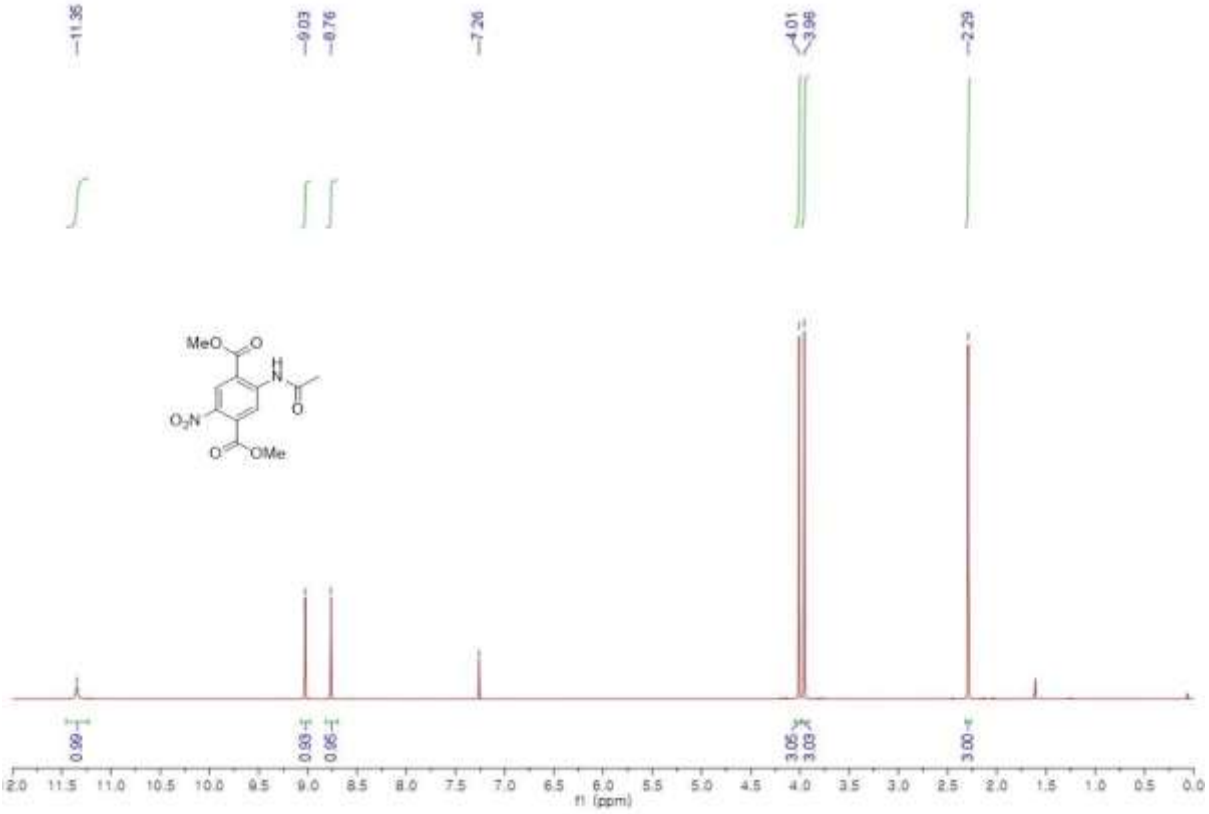
2-Chloro-3-nitroterephthalic acid (**2b**)

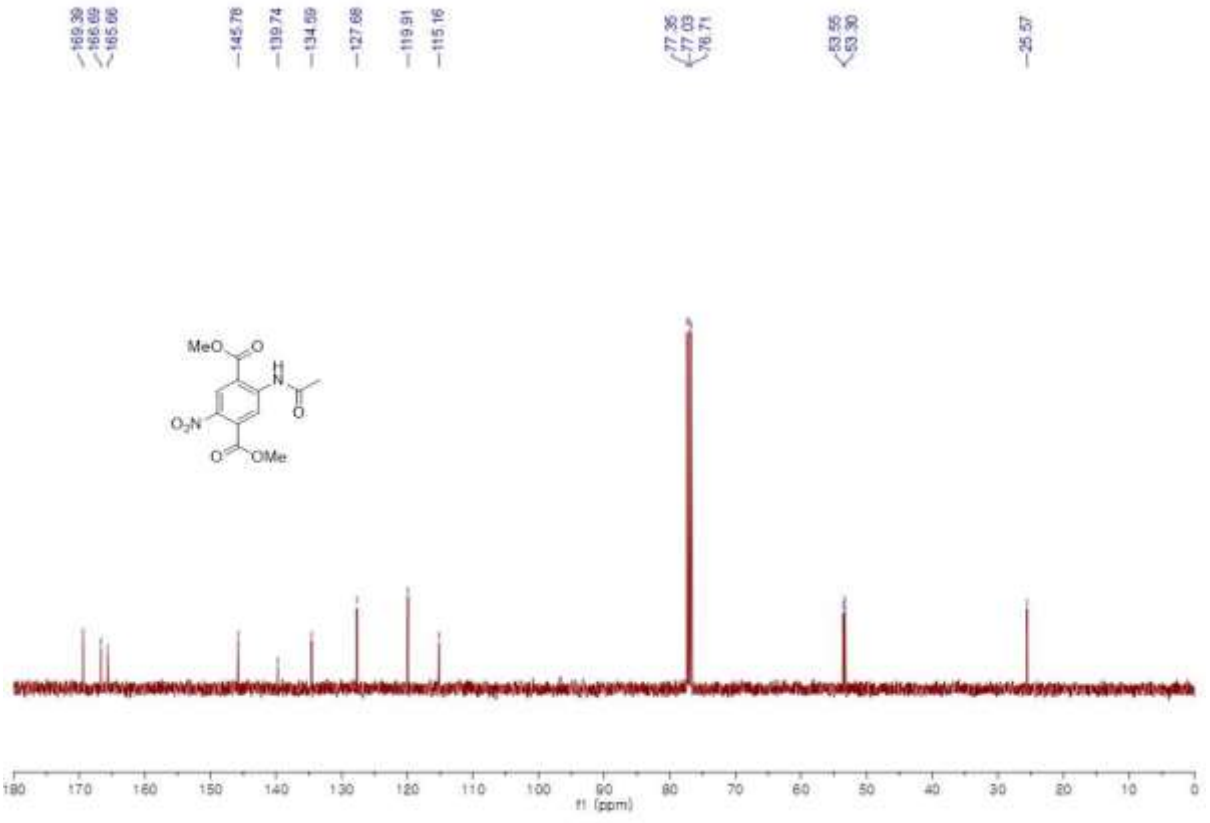


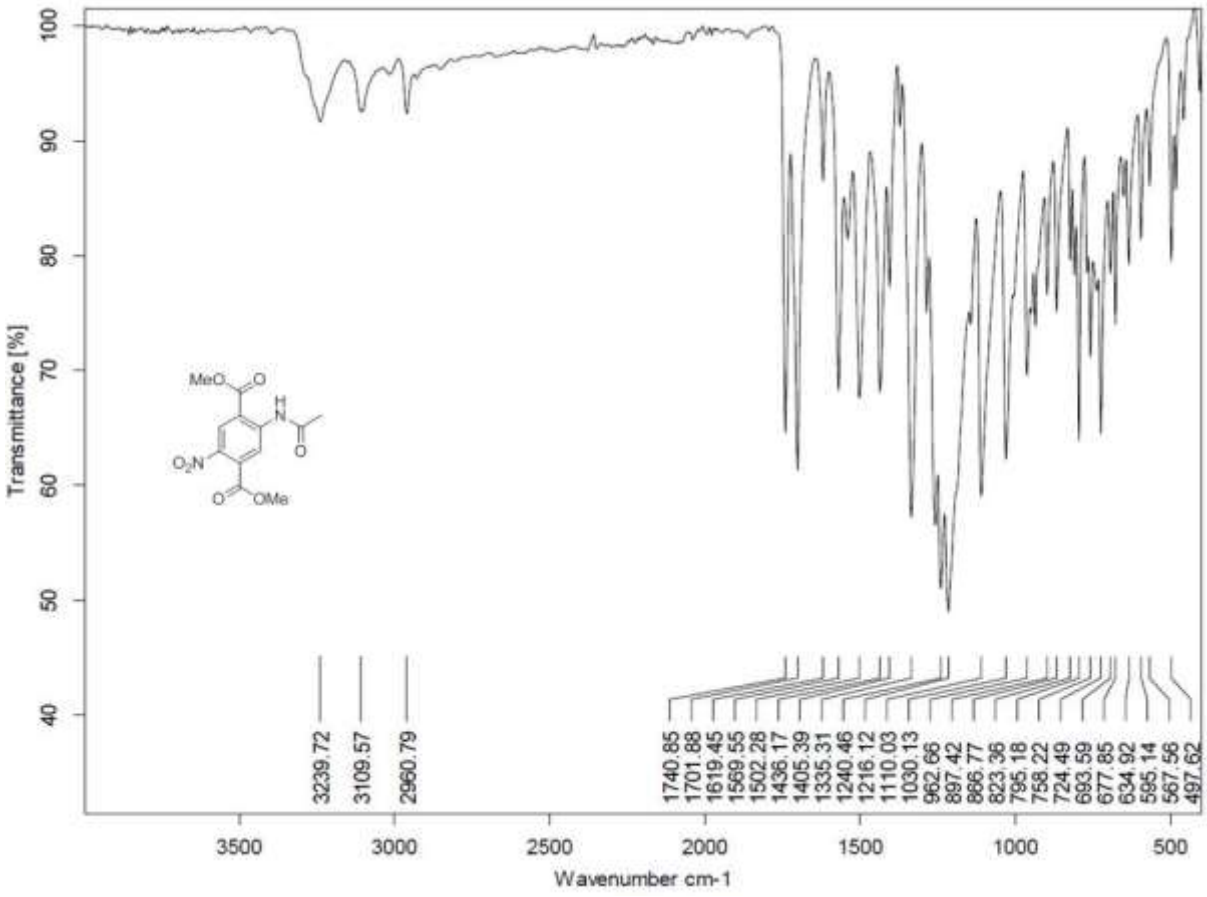



Transmittance [%]
100
90
80
70
60
50
40
HO
O
NO2
Cl
O
OH
2812.54
1701.41
1550.67
1477.13
1405.05
1363.24
1264.65
1208.47
1153.71
897.26
859.09
795.57
756.87
739.69
721.68
696.65
609.99
557.52
524.99
421.40
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

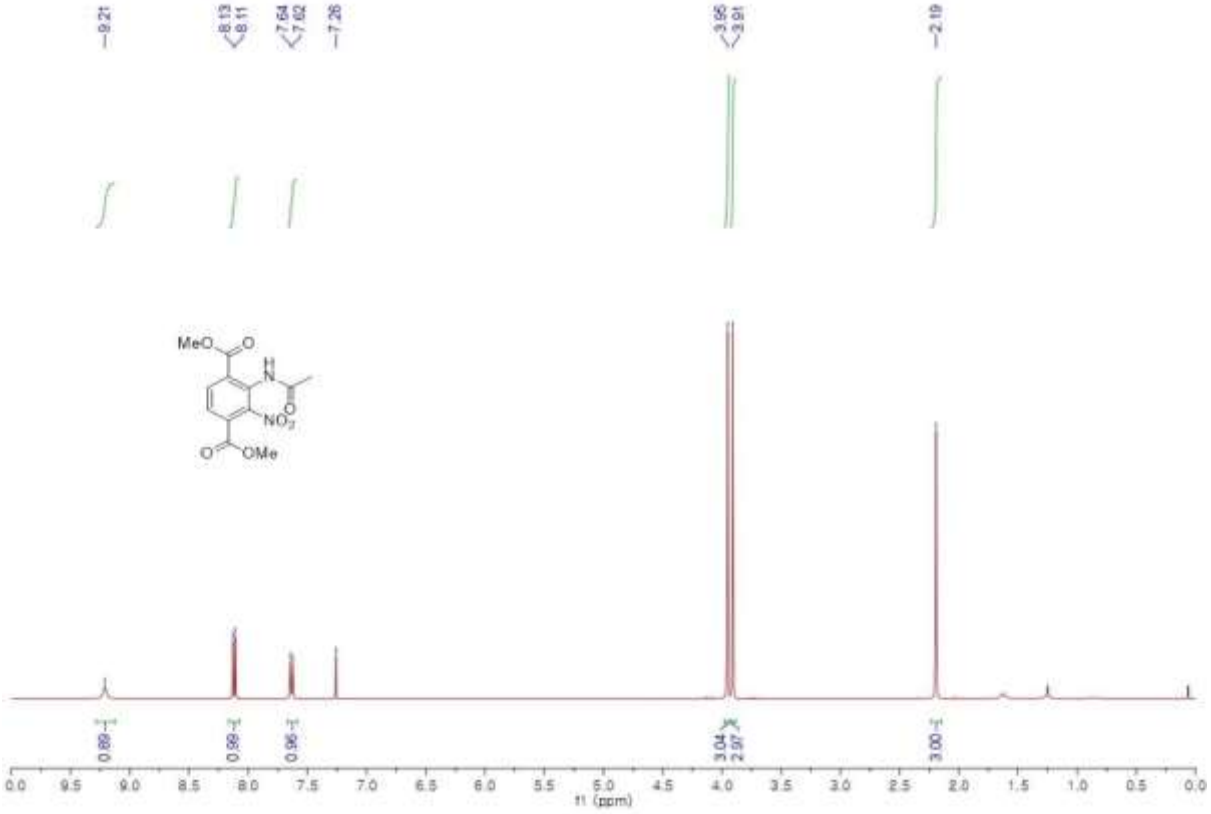
Dimethyl-2-acetamido-5-nitroterephthalate (**BDCE-2,5-NHAcNO$_2$**)

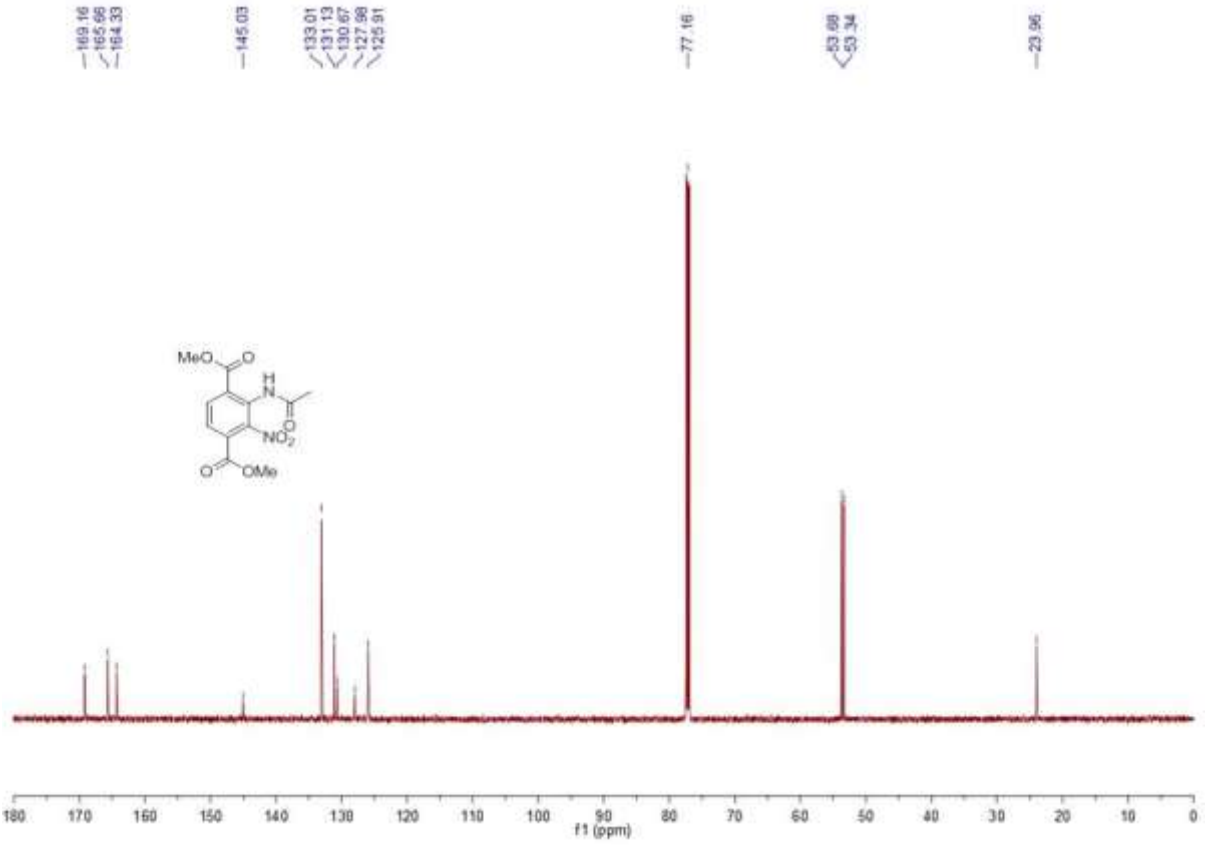


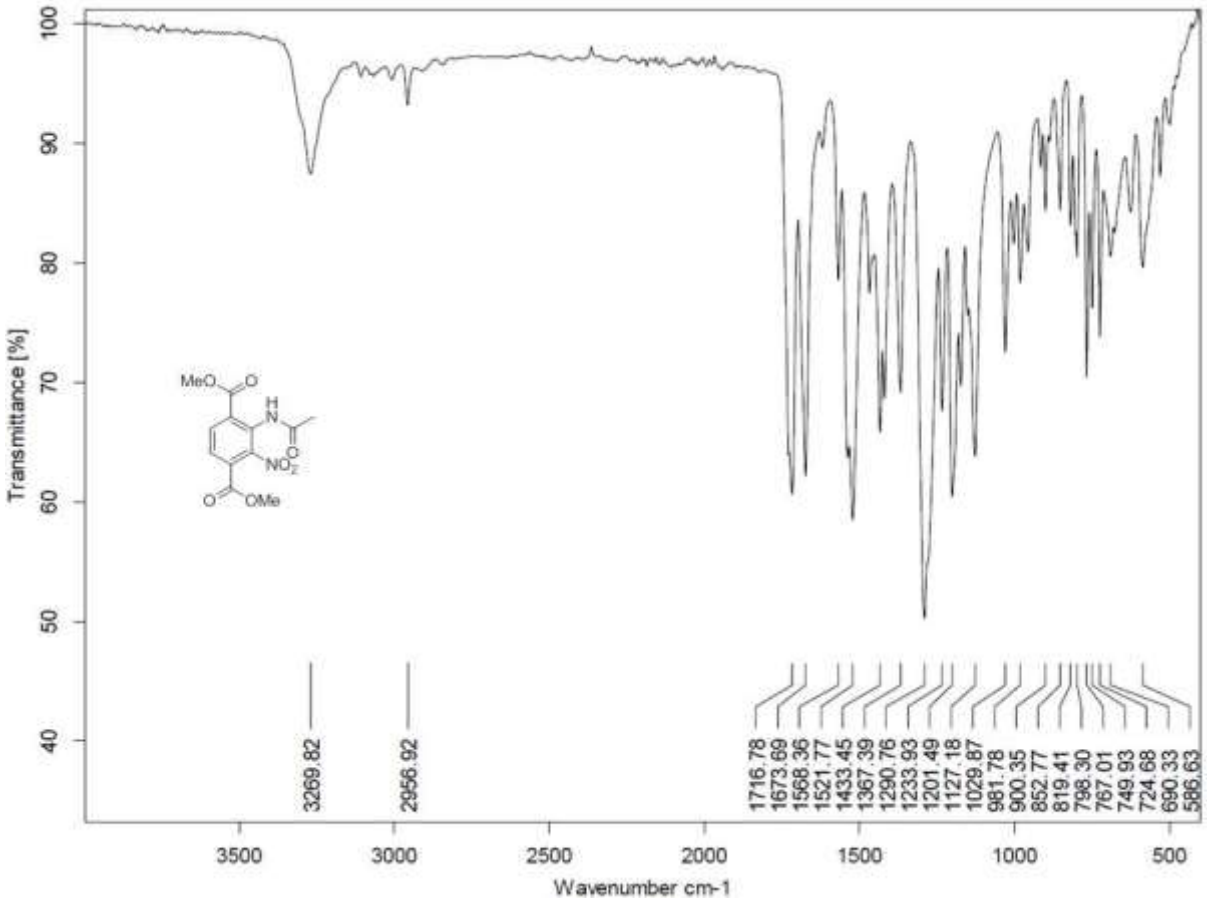



Transmittance [%]
100
90
80
70
60
50
40
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3239.72
3109.57
2960.79
1740.85
1701.88
1619.45
1569.55
1502.28
1436.17
1405.39
1335.31
1240.46
1216.12
1110.03
1030.13
962.66
897.42
866.77
823.36
795.18
758.22
724.49
693.59
677.85
634.92
595.14
567.56
497.62
MeO
O
O2N
OMe

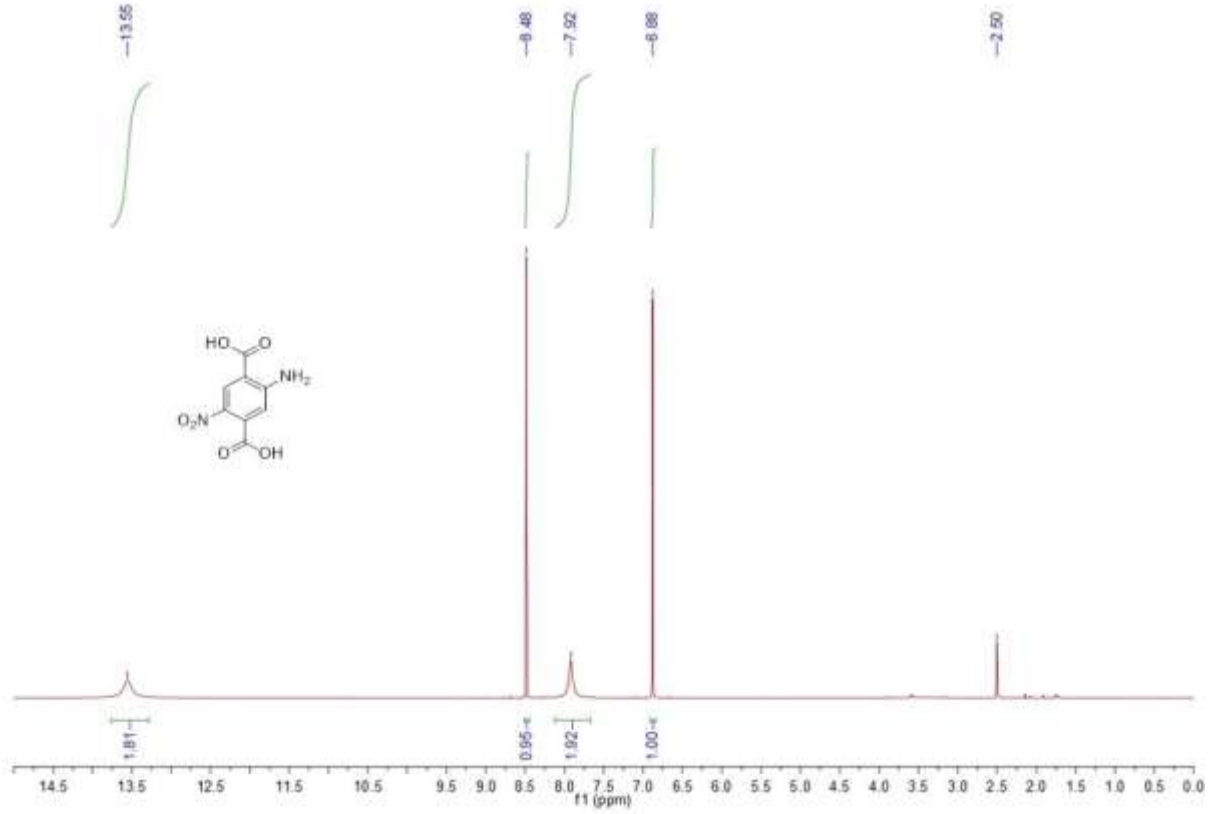
Dimethyl-2-acetamido-3-nitroterephthalate (**BDCE-2,3-NHAcNO$_2$**)

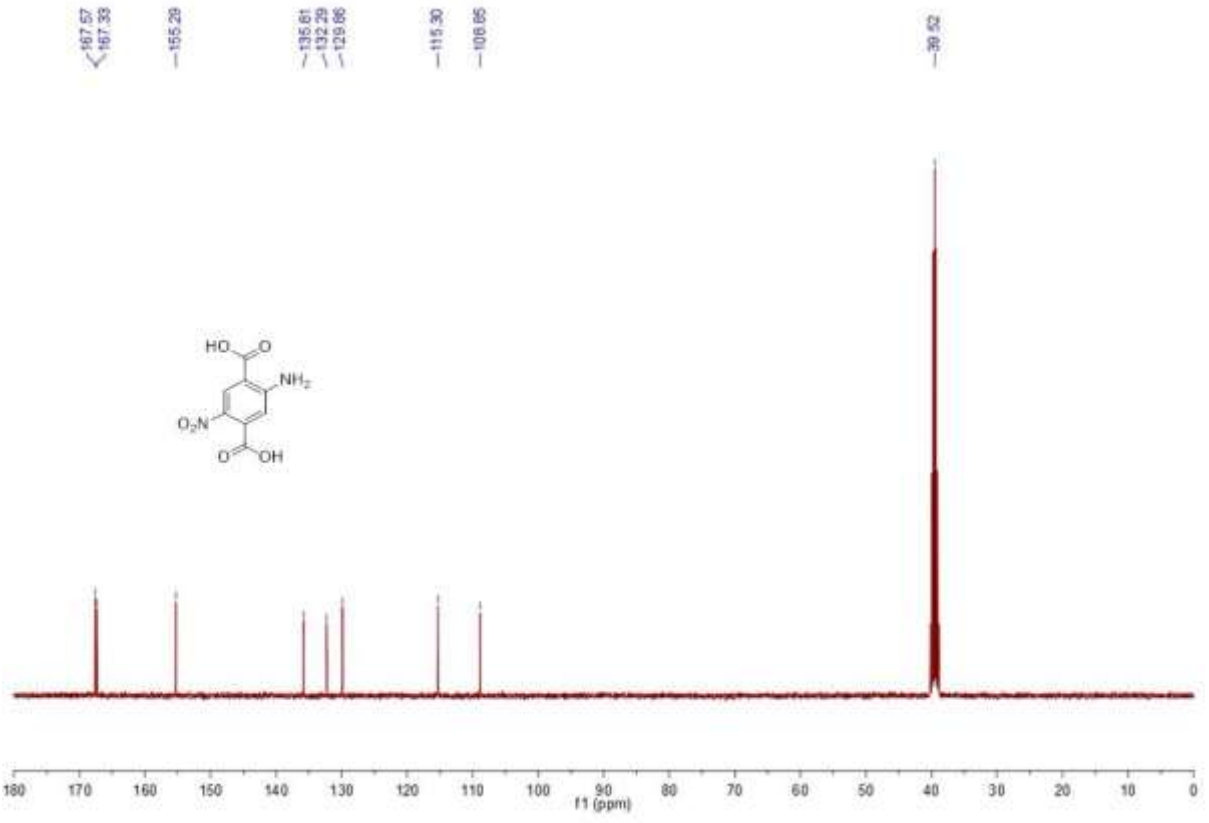


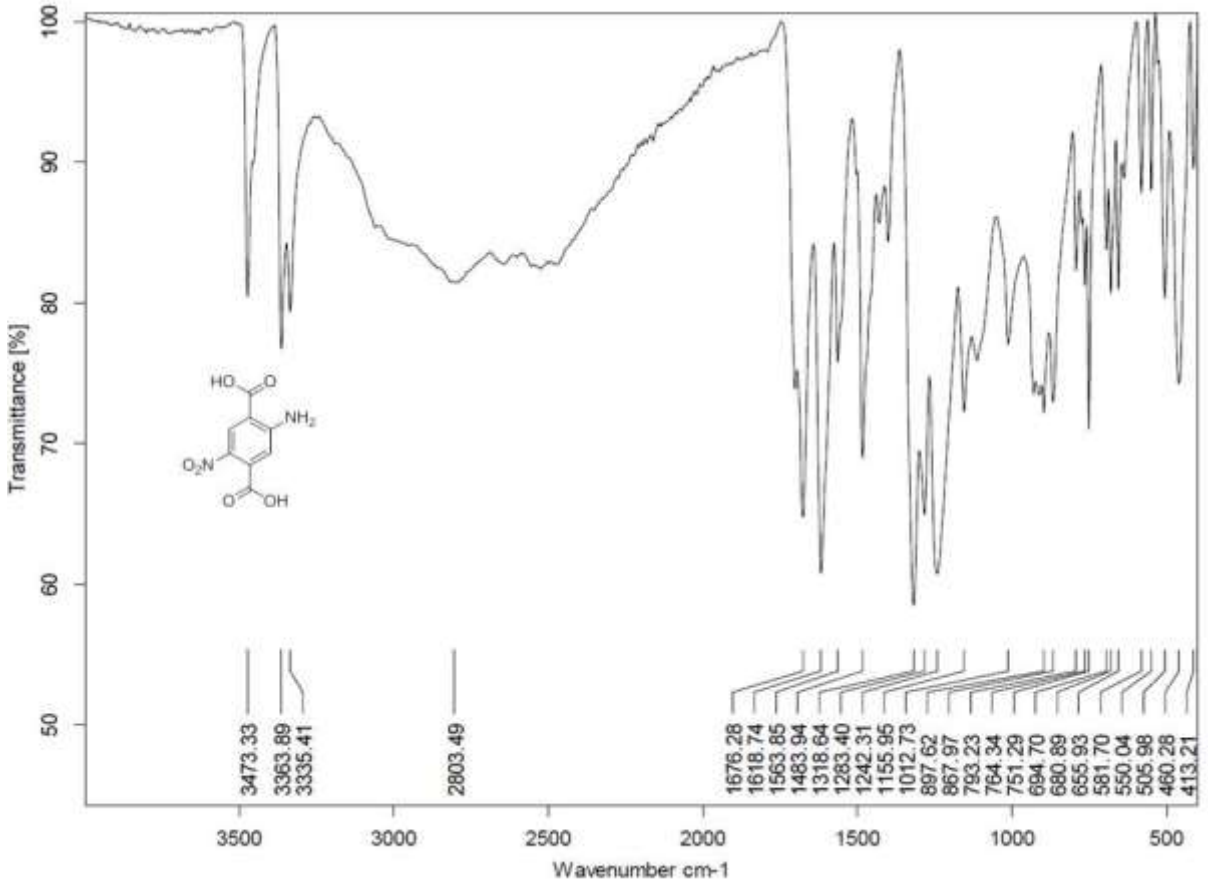



Transmittance [%]
100
90
80
70
60
50
40
3269.82
2956.92
1716.78
1673.69
1568.36
1521.77
1433.45
1367.39
1290.76
1233.93
1201.49
1127.18
1029.87
981.78
900.35
852.77
819.41
798.30
767.01
749.93
724.68
690.33
586.63
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
MeO
O
H
N
O
NO2
O
OMe

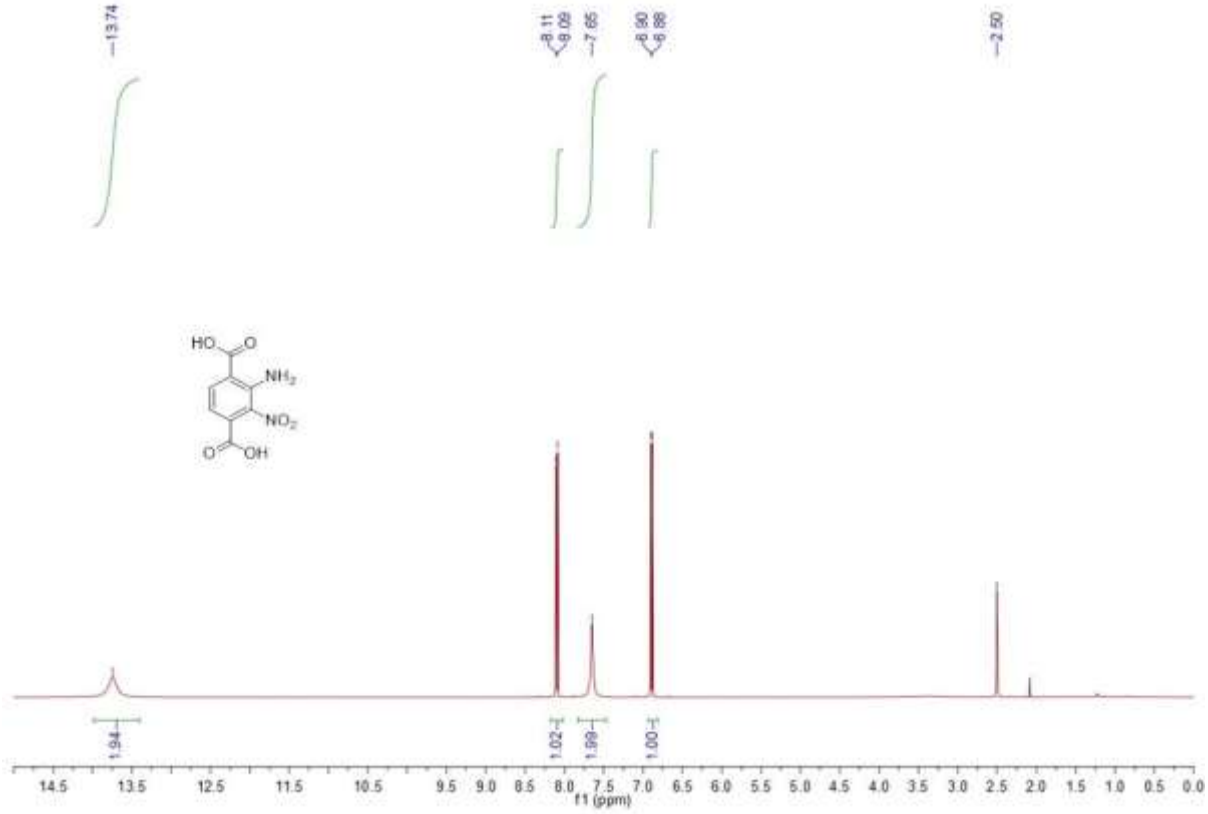
2-Amino-5-nitroterephthalic acid (**3a**)

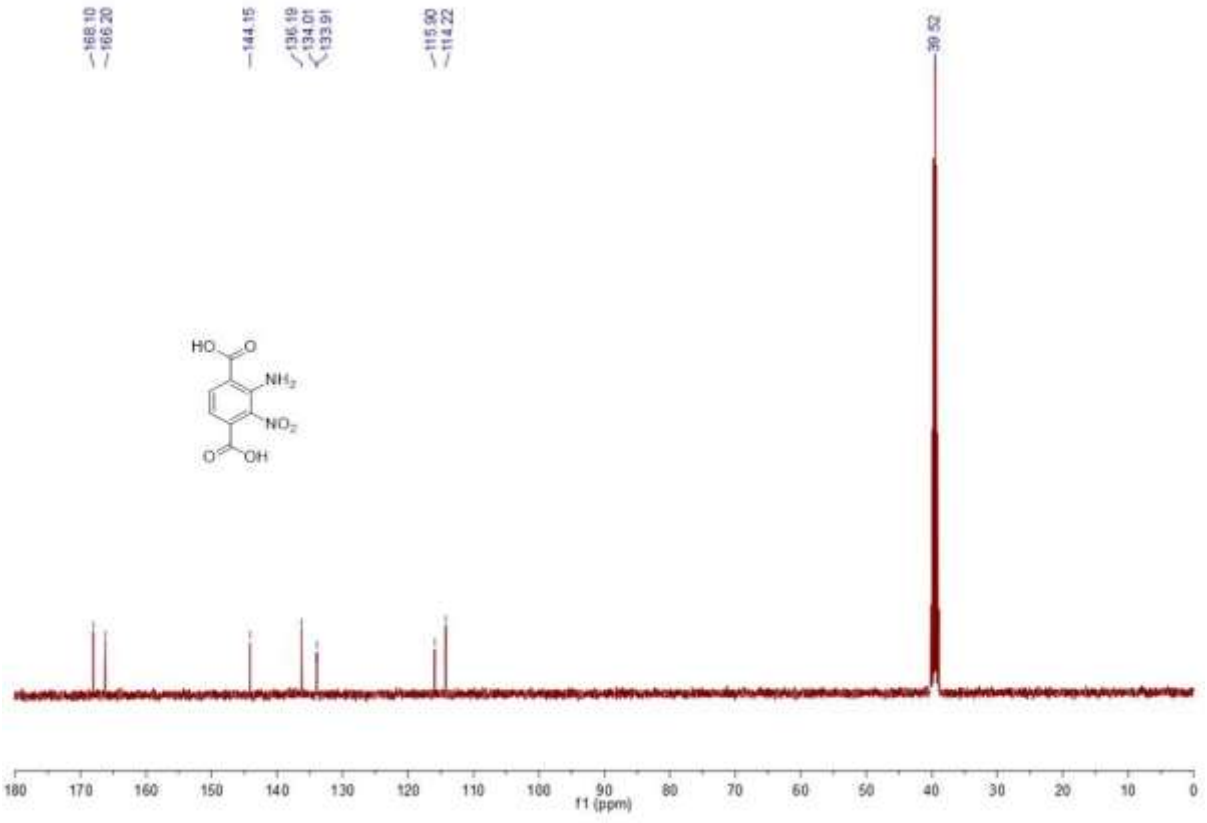


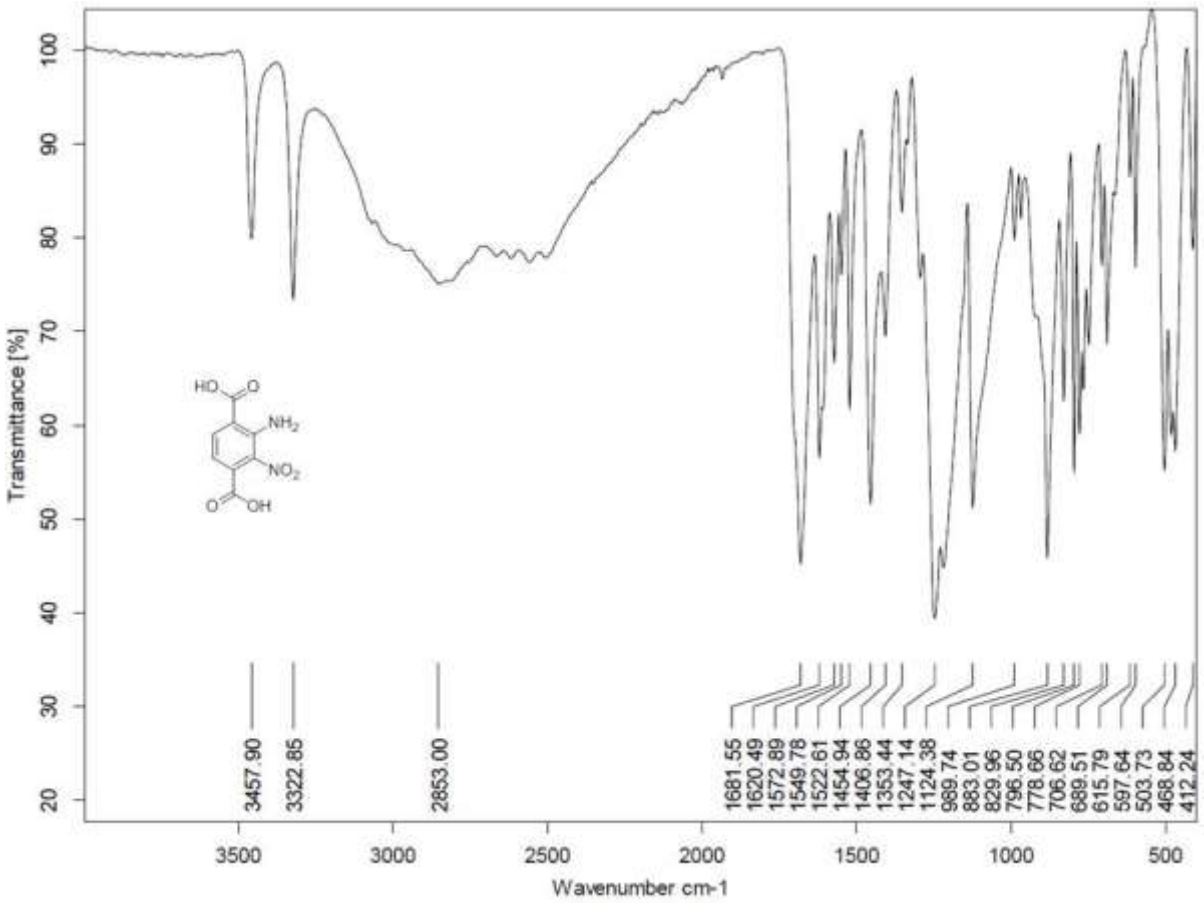



Transmittance [%]
100
90
80
70
60
50
HO
O
NH2
O2N
O
OH
3473.33
3363.89
3335.41
2803.49
1676.28
1618.74
1563.85
1483.94
1318.64
1283.40
1242.31
1155.95
1012.73
897.62
867.97
793.23
764.34
751.29
694.70
680.89
655.93
581.70
550.04
505.98
460.28
413.21
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

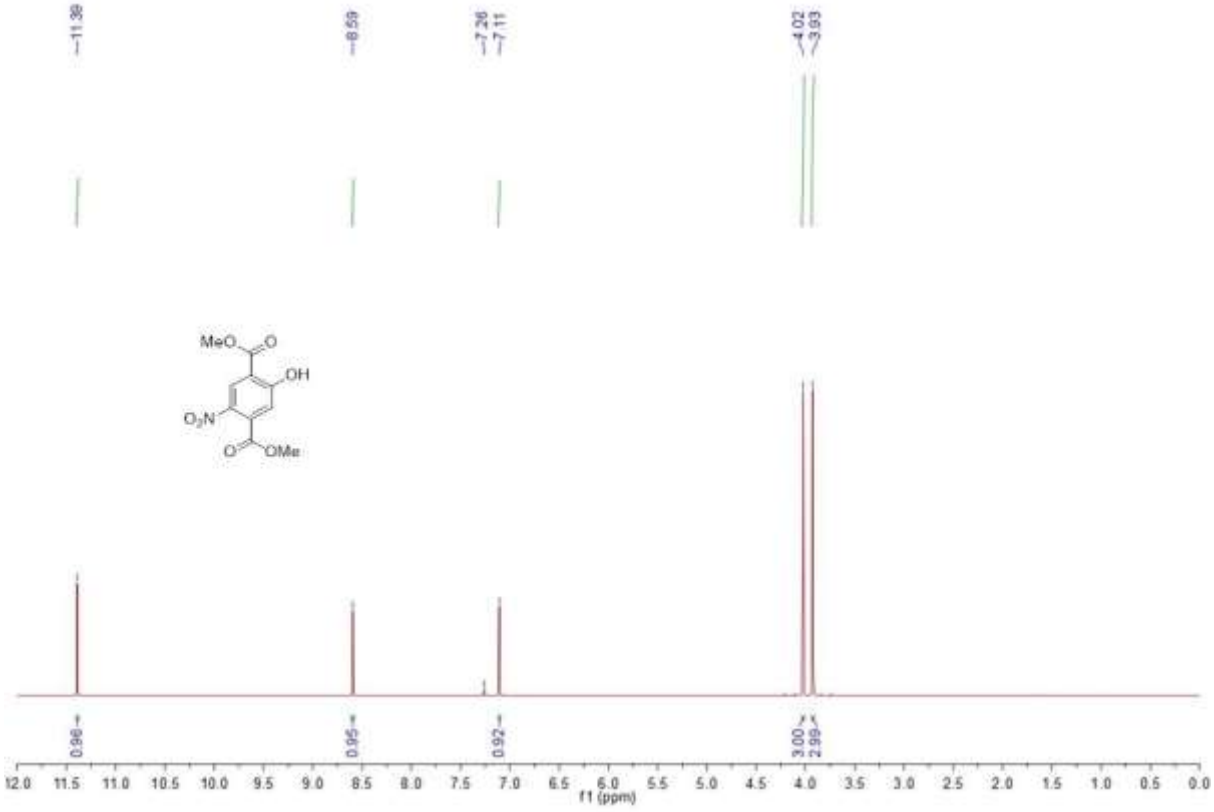
2-Amino-3-nitroterephthalic acid (**3b**)

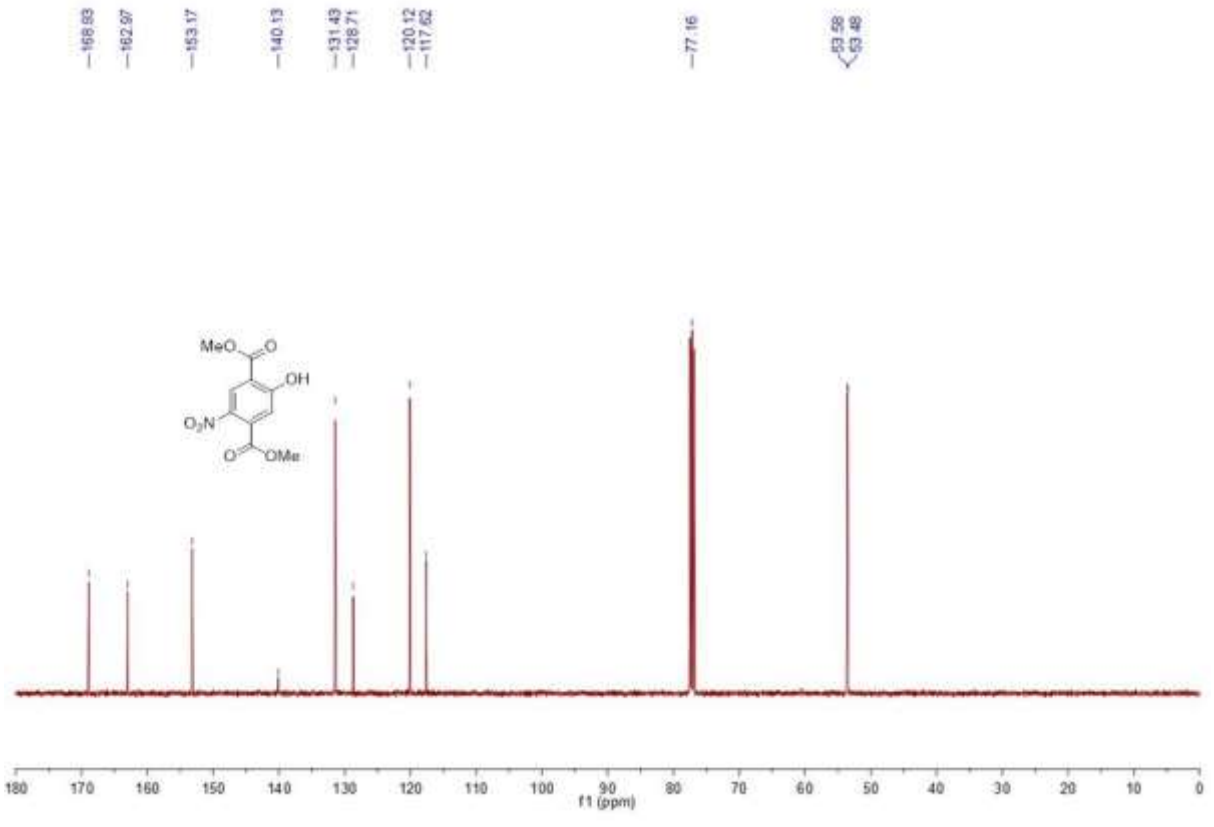


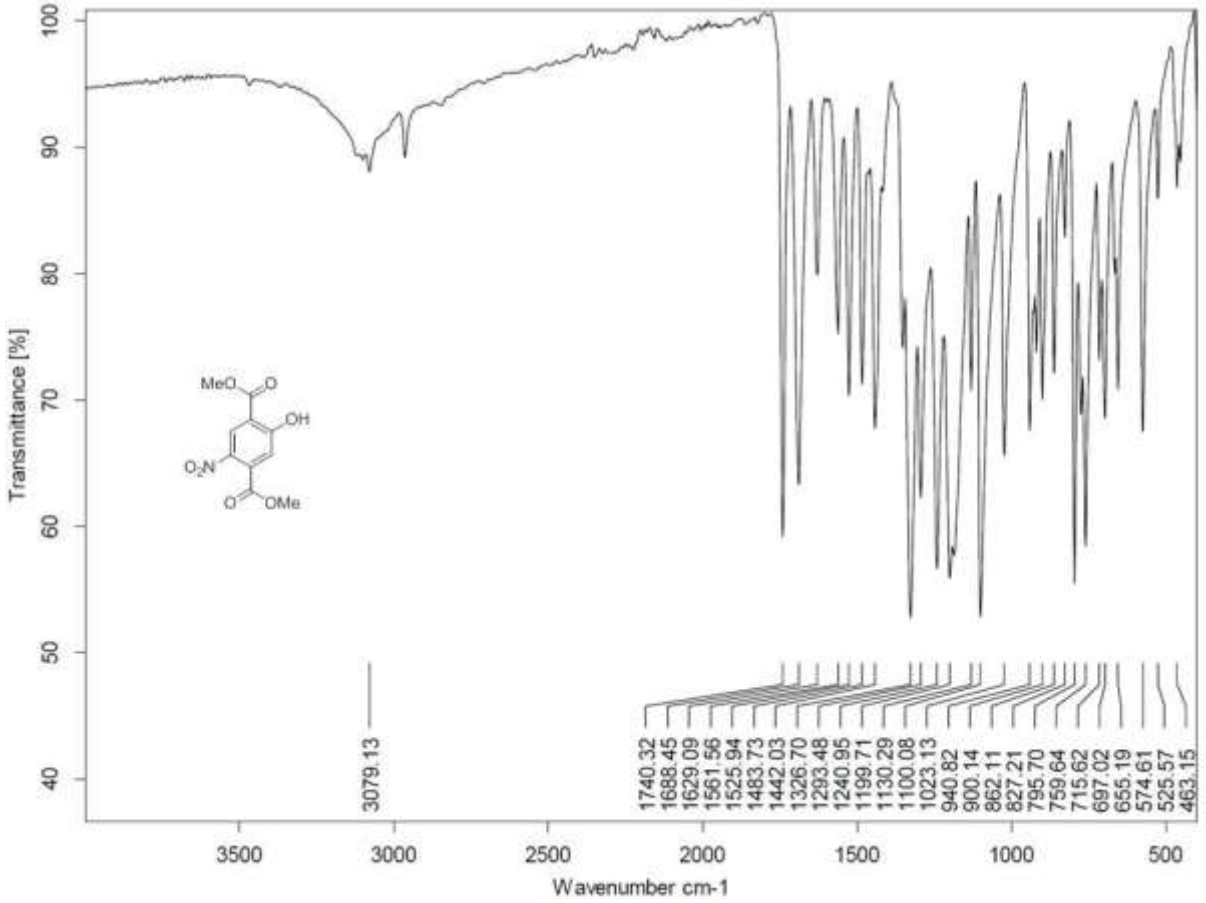



Transmittance [%]
100
90
80
70
60
50
40
30
20
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
HO
O
NH2
NO2
O
OH
3457.90
3322.85
2853.00
1681.55
1620.49
1572.89
1549.78
1522.61
1454.94
1406.86
1353.44
1247.14
1124.38
989.74
883.01
829.96
796.50
778.66
706.62
689.51
615.79
597.64
503.73
468.84
412.24

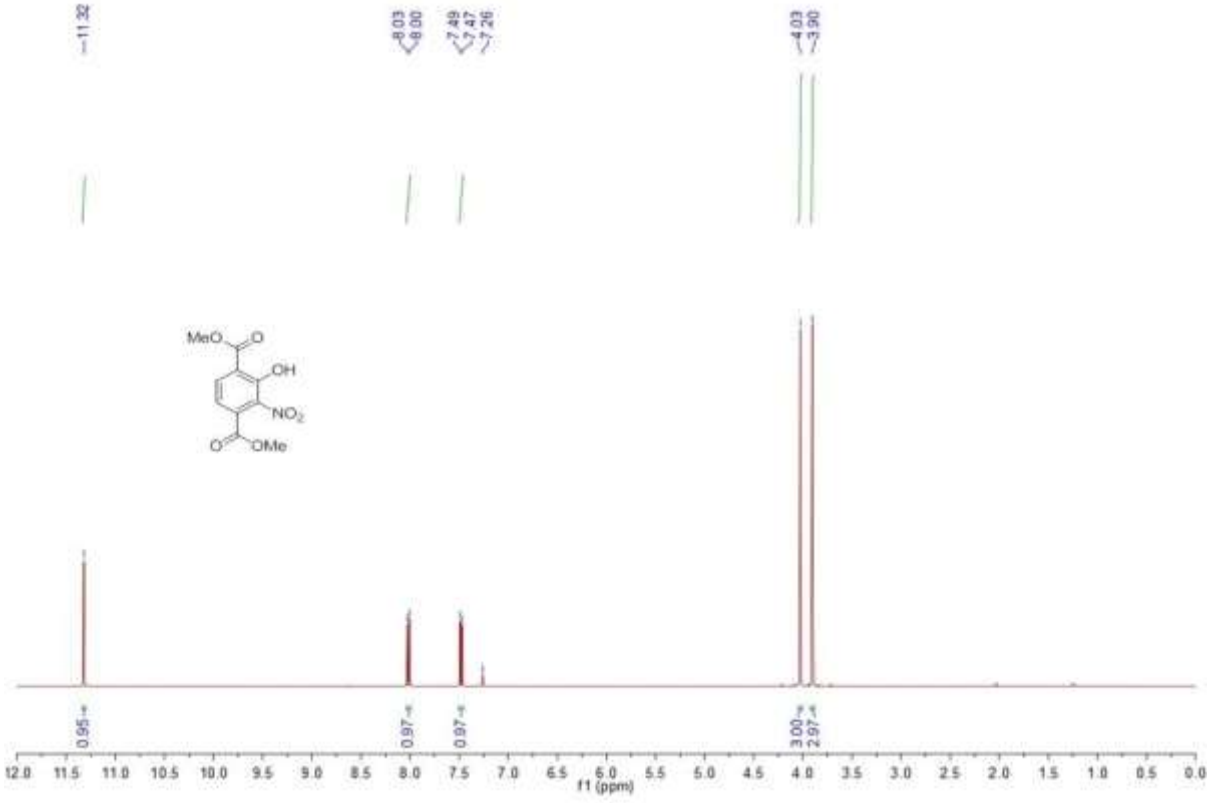
Dimethyl-2-hydroxy-5-nitroterephthalate (**BDCE-2,5-NO_2OH**)

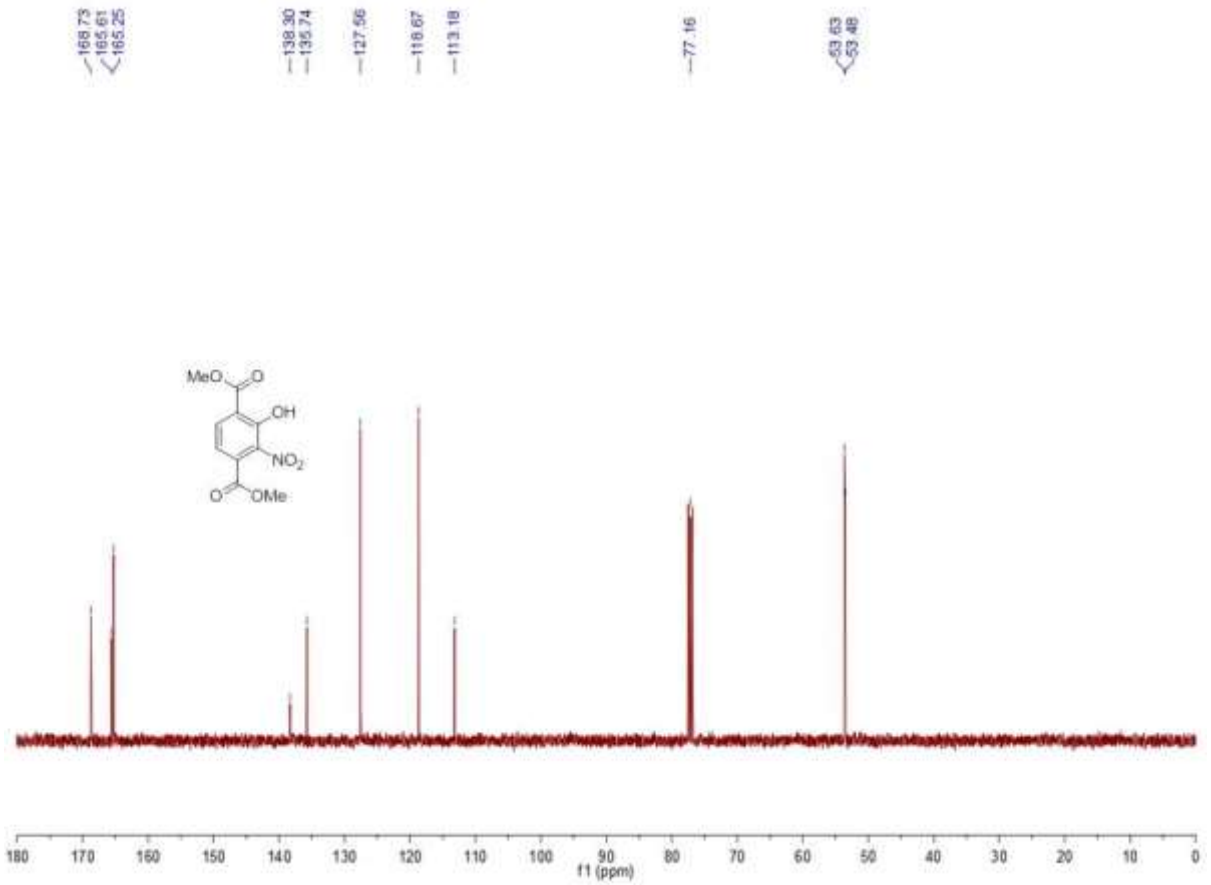


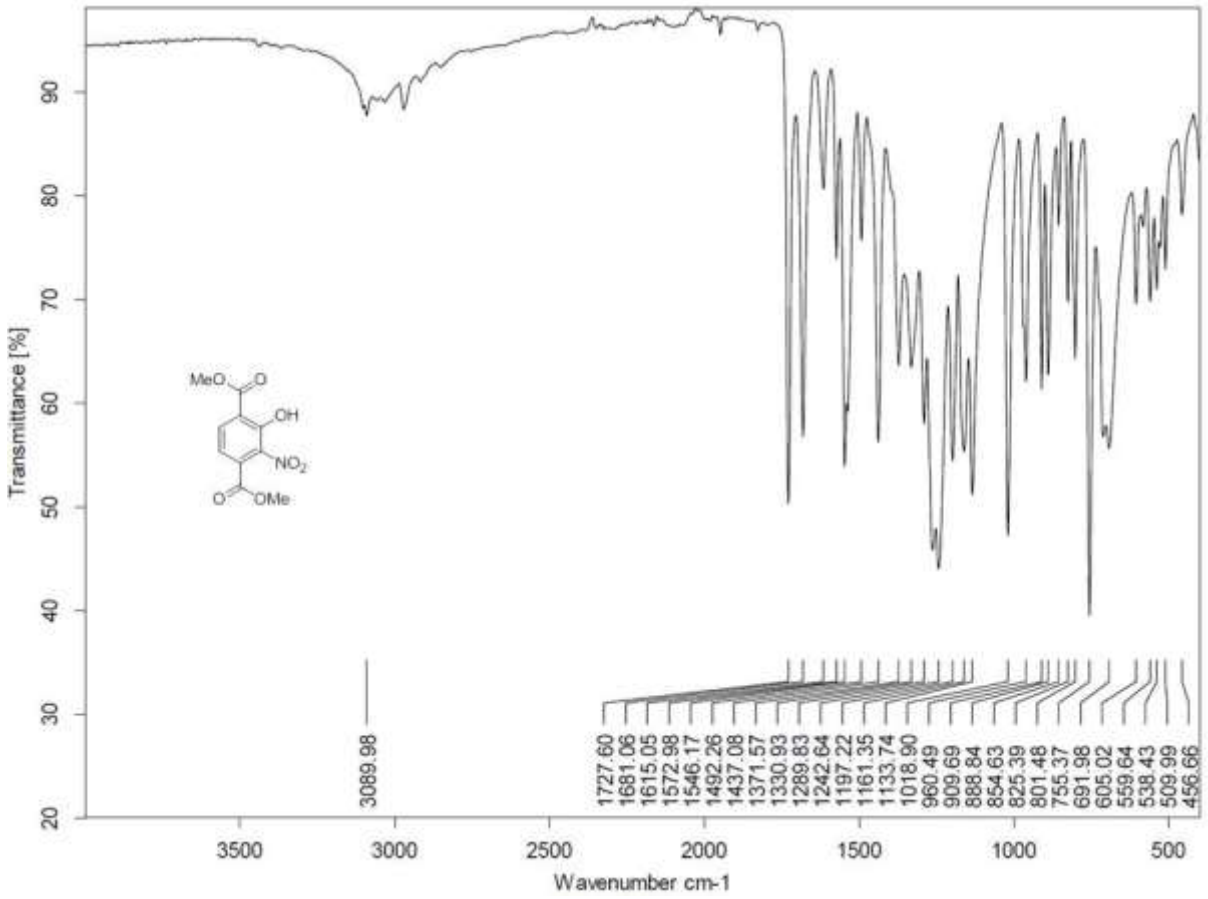



Transmittance [%]
100
90
80
70
60
50
40
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
MeO
O
OH
O2N
O
OMe
3079.13
1740.32
1688.45
1629.09
1561.56
1525.94
1483.73
1442.03
1326.70
1293.48
1240.95
1199.71
1130.29
1100.08
1023.13
940.82
900.14
862.11
827.21
795.70
759.64
715.62
697.02
655.19
574.61
525.57
463.15

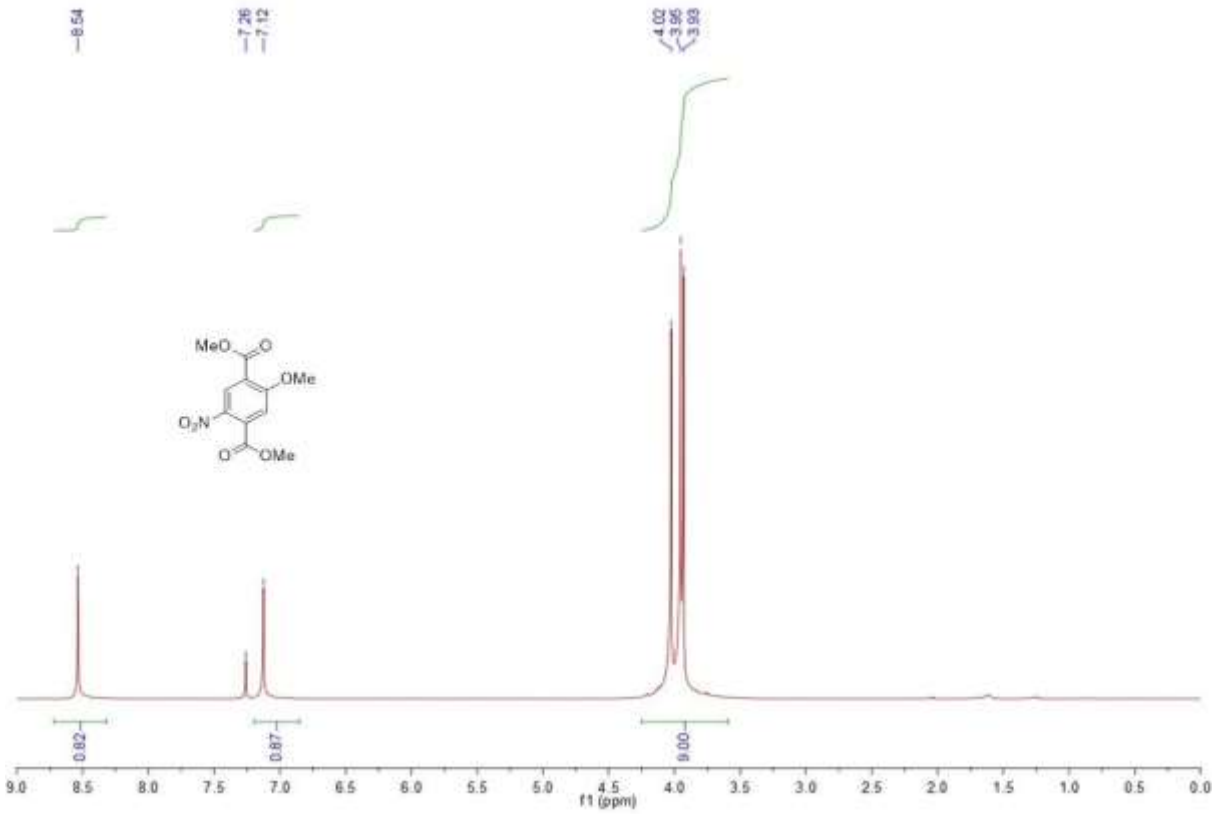
Dimethyl-2-hydroxy-3-nitroterephthalate (**BDCE-2,3-NO_2OH**)

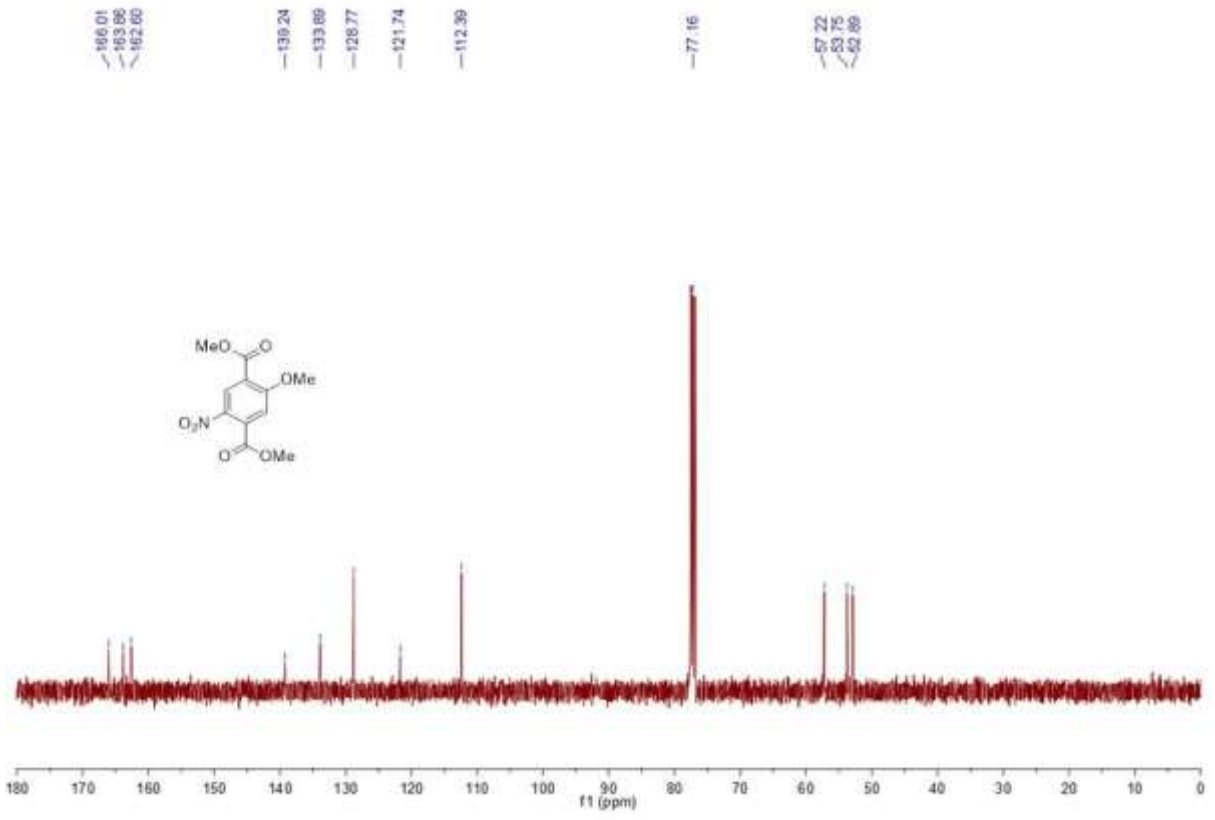


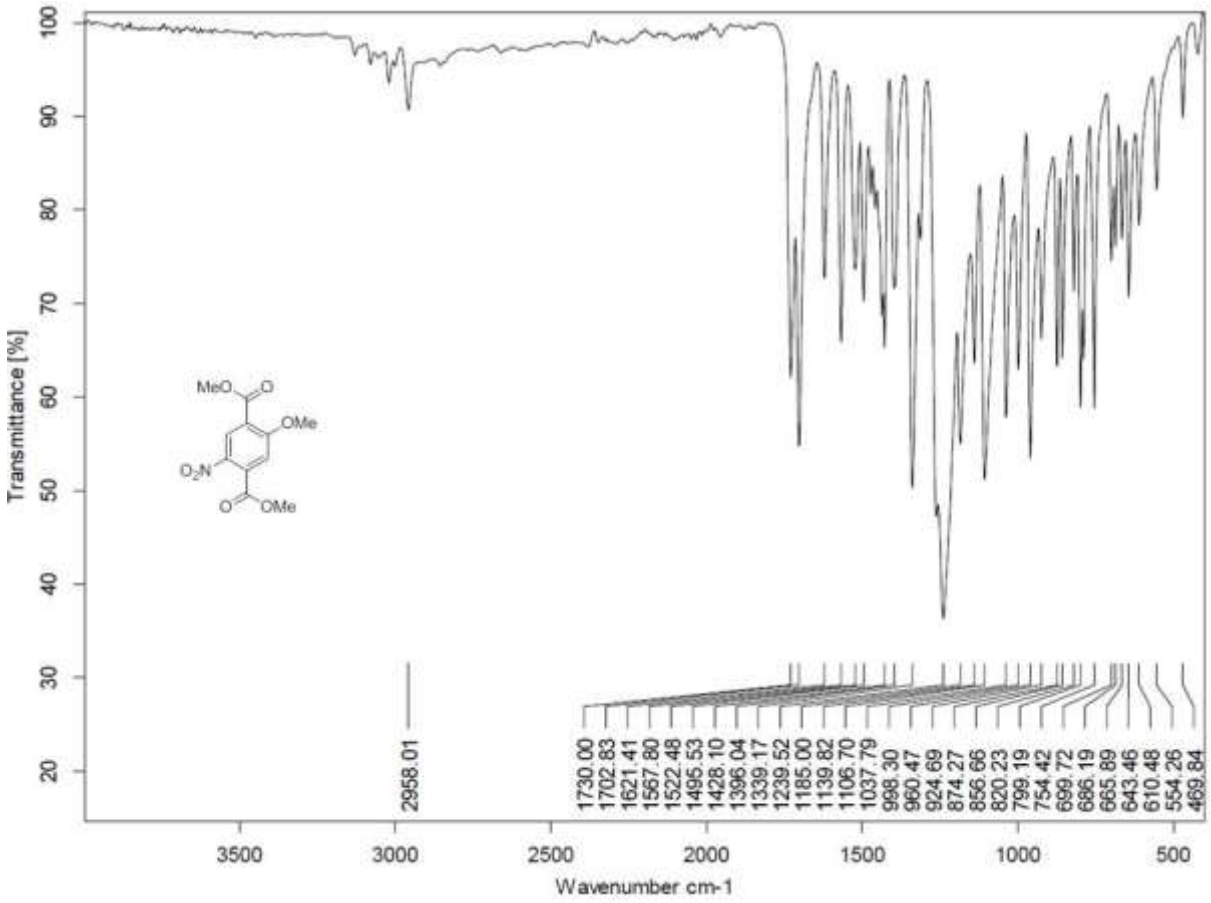



Transmittance [%]
Wavenumber cm-1
3089.98
1727.60
1681.06
1615.05
1572.98
1546.17
1492.26
1437.08
1371.57
1330.93
1289.83
1242.64
1197.22
1161.35
1133.74
1018.90
960.49
909.69
888.84
854.63
825.39
801.48
755.37
691.98
605.02
559.64
538.43
509.99
456.66
MeO
O
OH
NO2
O
OMe

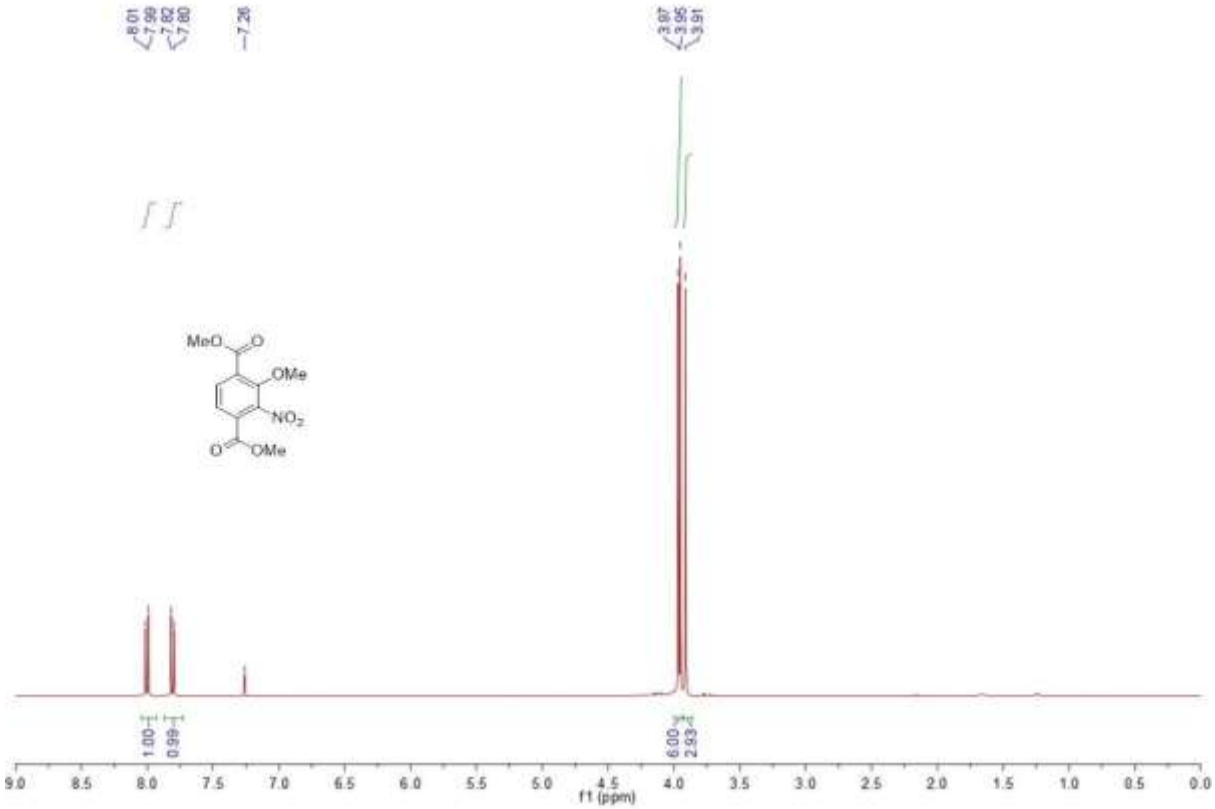
Dimethyl-2-methoxy-5-nitroterephthalate (**BDCE-2,5-NO_2OMe**)

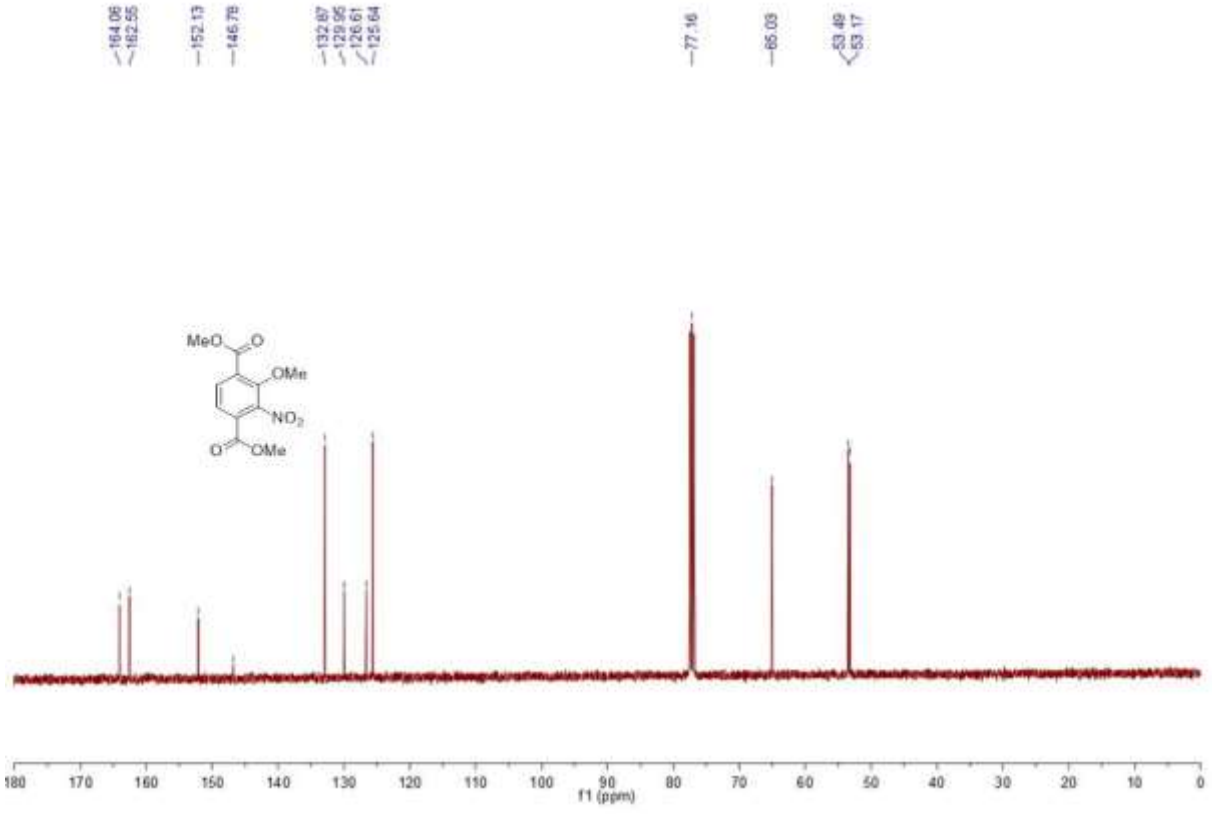


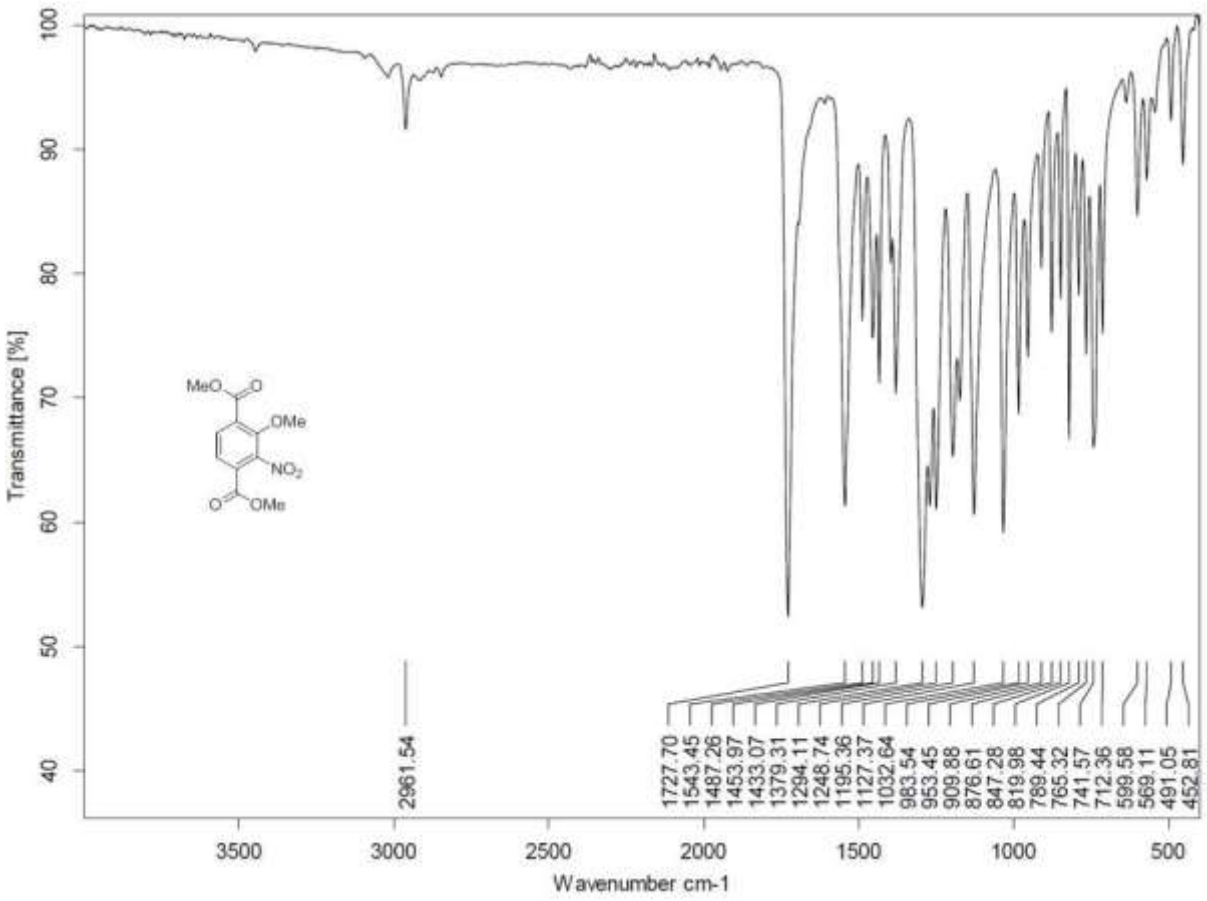



Transmittance [%]
100
90
80
70
60
50
40
30
20
MeO
O
OMe
O2N
O
OMe
2958.01
1730.00
1702.83
1621.41
1567.80
1522.48
1495.53
1428.10
1396.04
1339.17
1239.52
1185.00
1139.82
1106.70
1037.79
998.30
960.47
924.69
874.27
856.66
820.23
799.19
754.42
699.72
686.19
665.89
643.46
610.48
554.26
469.84
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

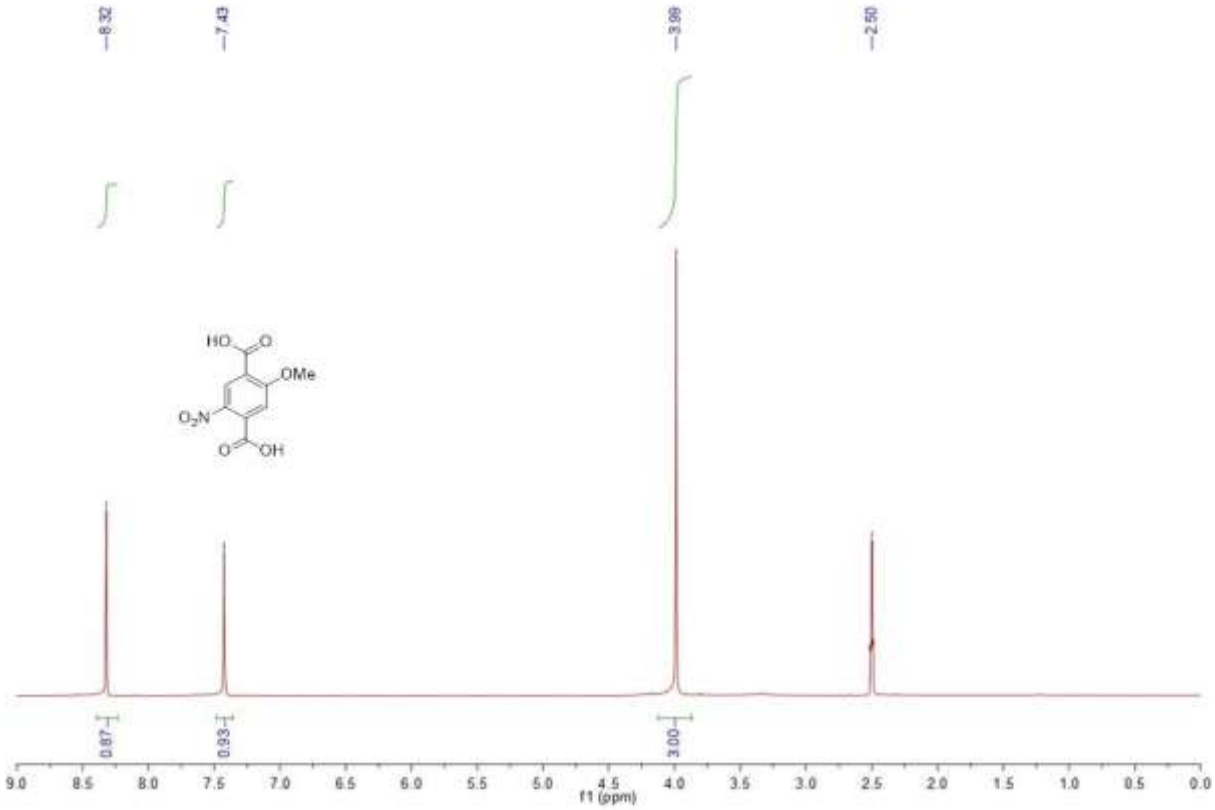
Dimethyl-2-methoxy-3-nitroterephthalate (**BDCE-2,3-NO_2OMe**)

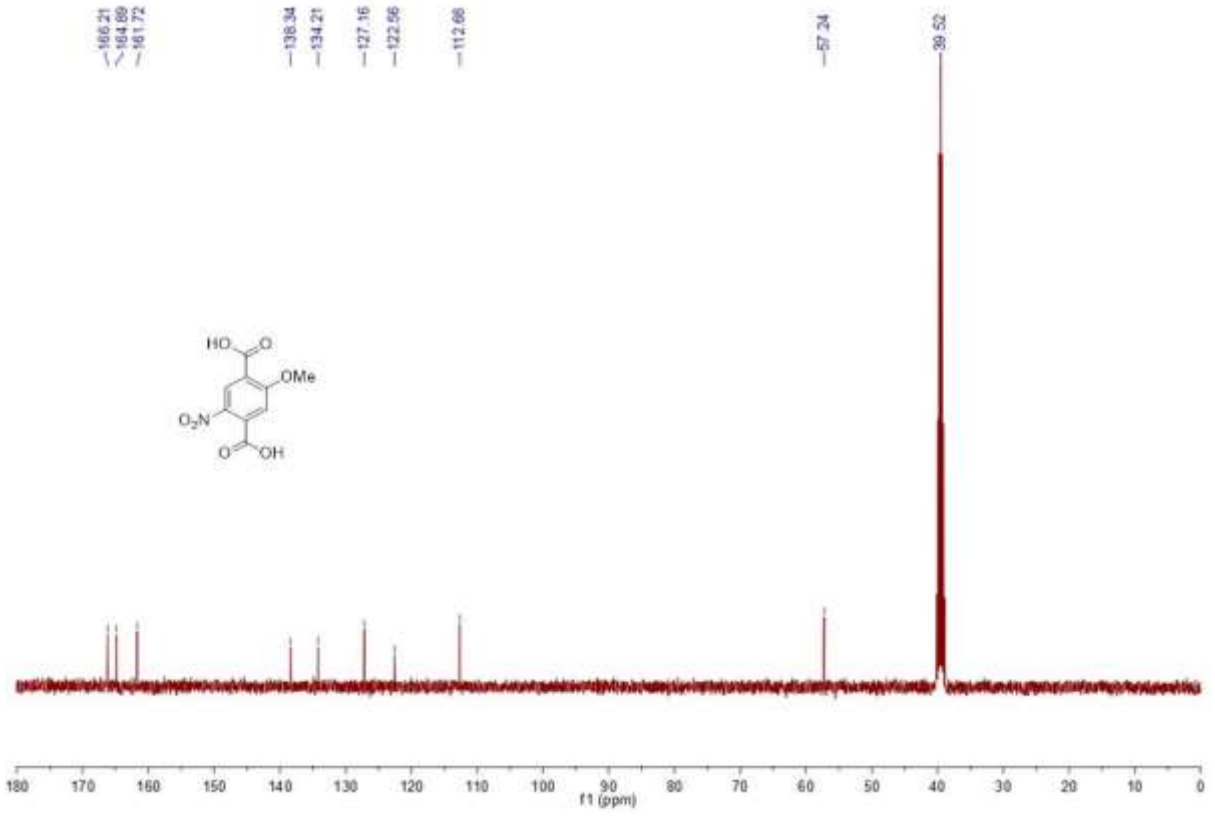


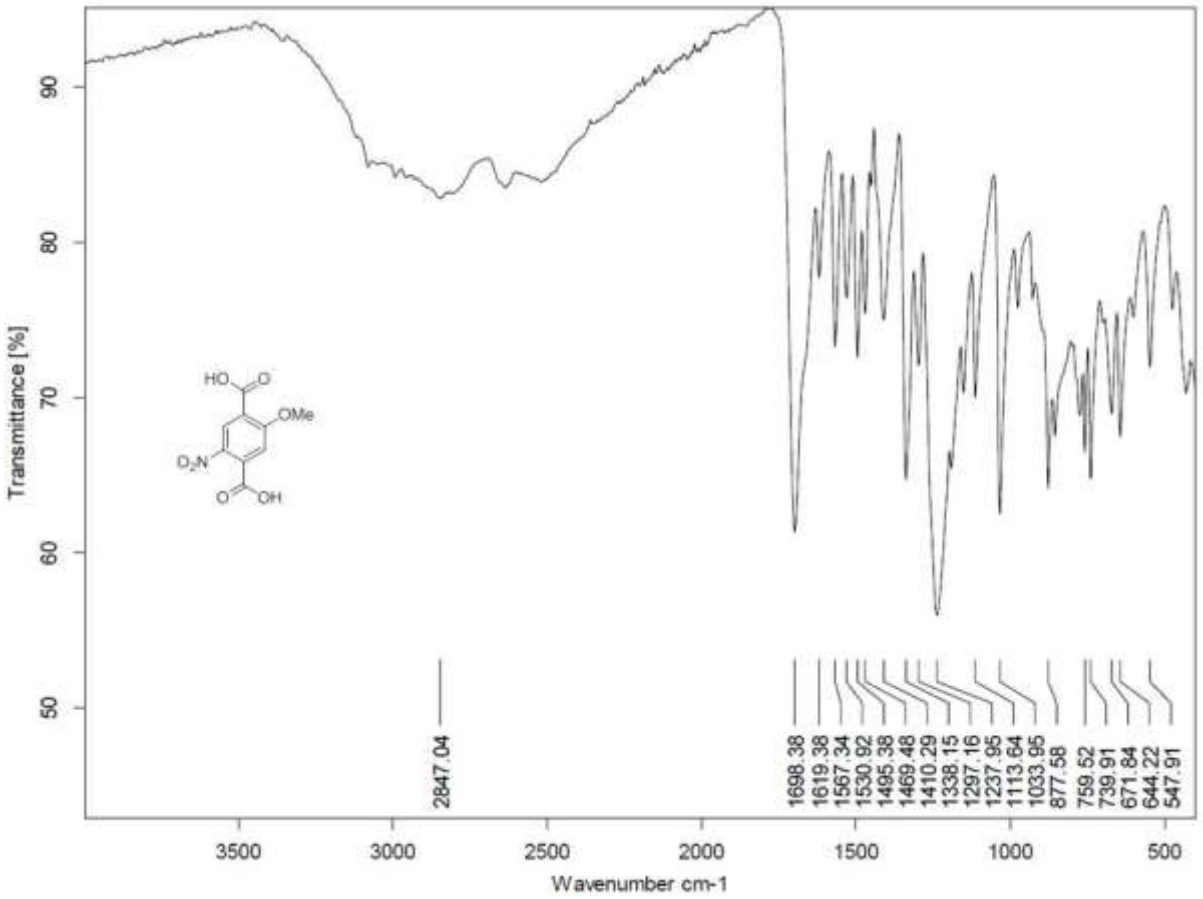



Transmittance [%]
100
90
80
70
60
50
40
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
MeO
O
OMe
NO2
O
OMe
2961.54
1727.70
1543.45
1487.26
1453.97
1433.07
1379.31
1294.11
1248.74
1195.36
1127.37
1032.64
983.54
953.45
909.88
876.61
847.28
819.98
789.44
765.32
741.57
712.36
599.58
569.11
491.05
452.81

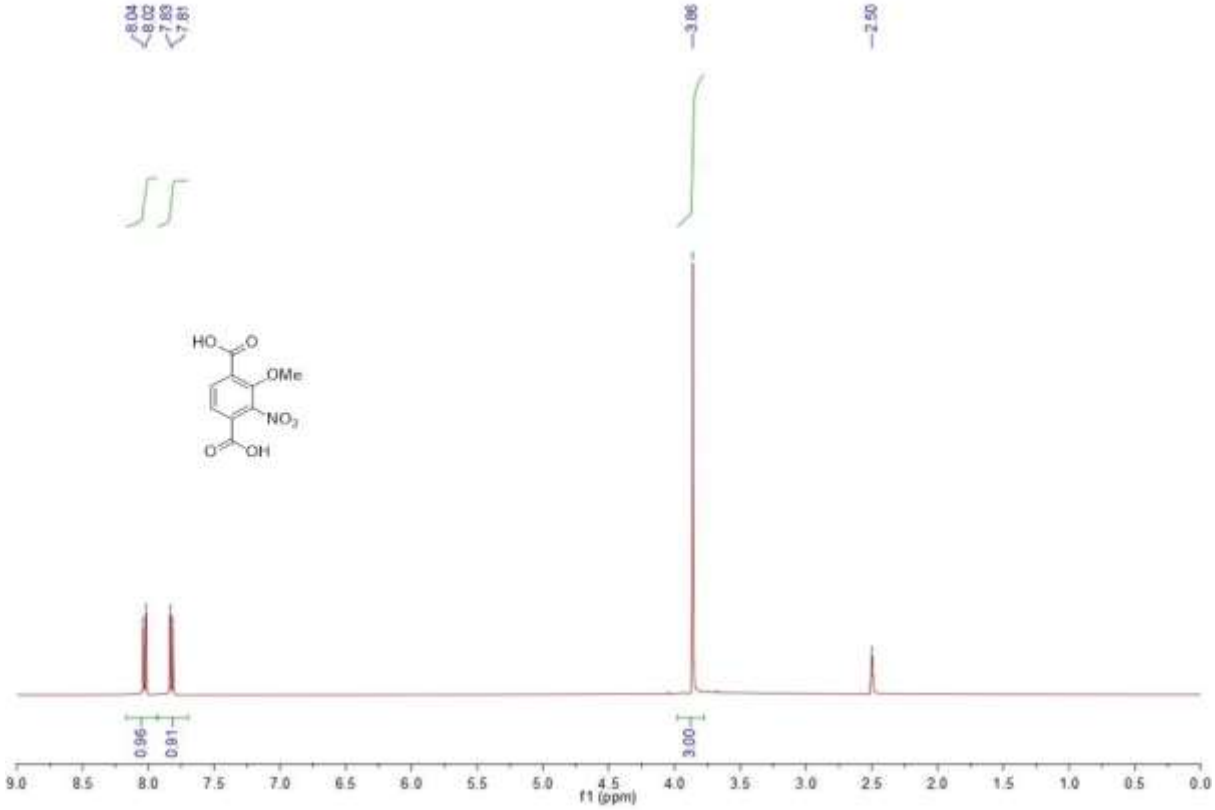
2-Methoxy-5-nitroterephthalic acid (**4a**)

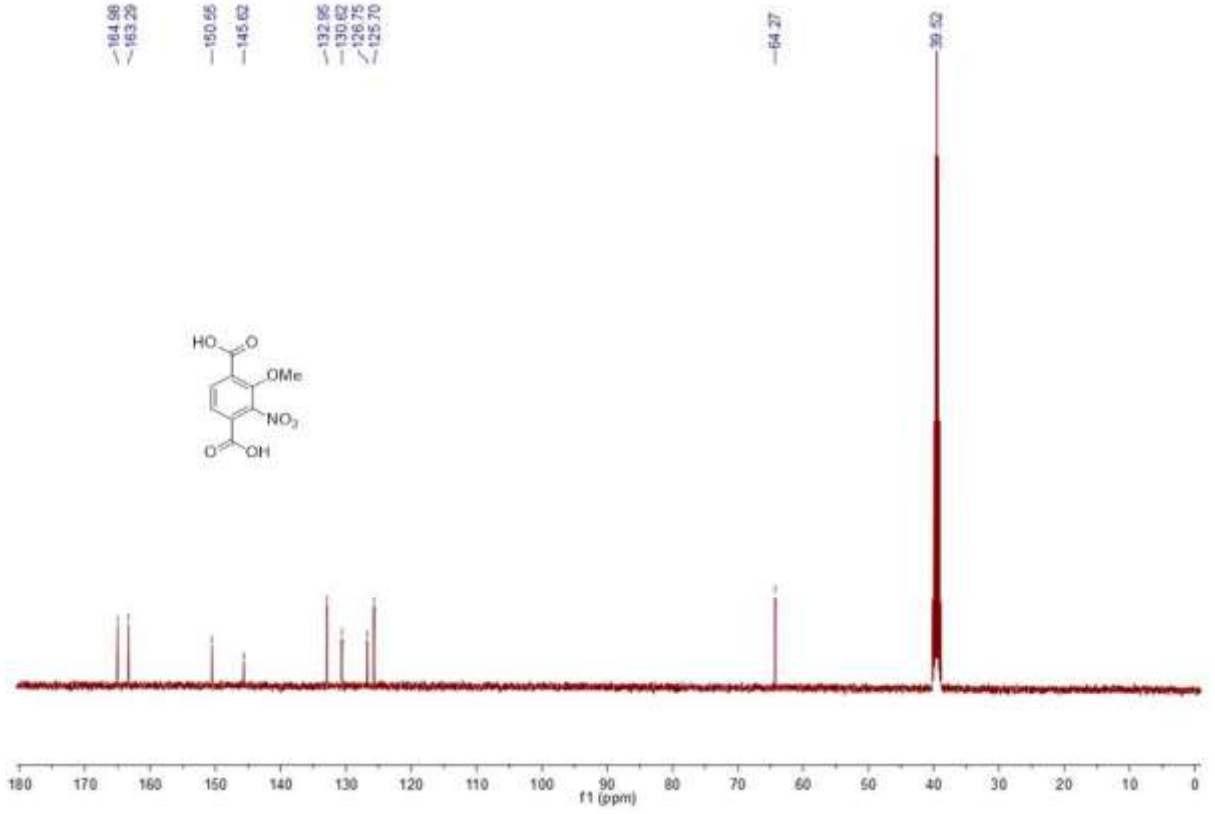


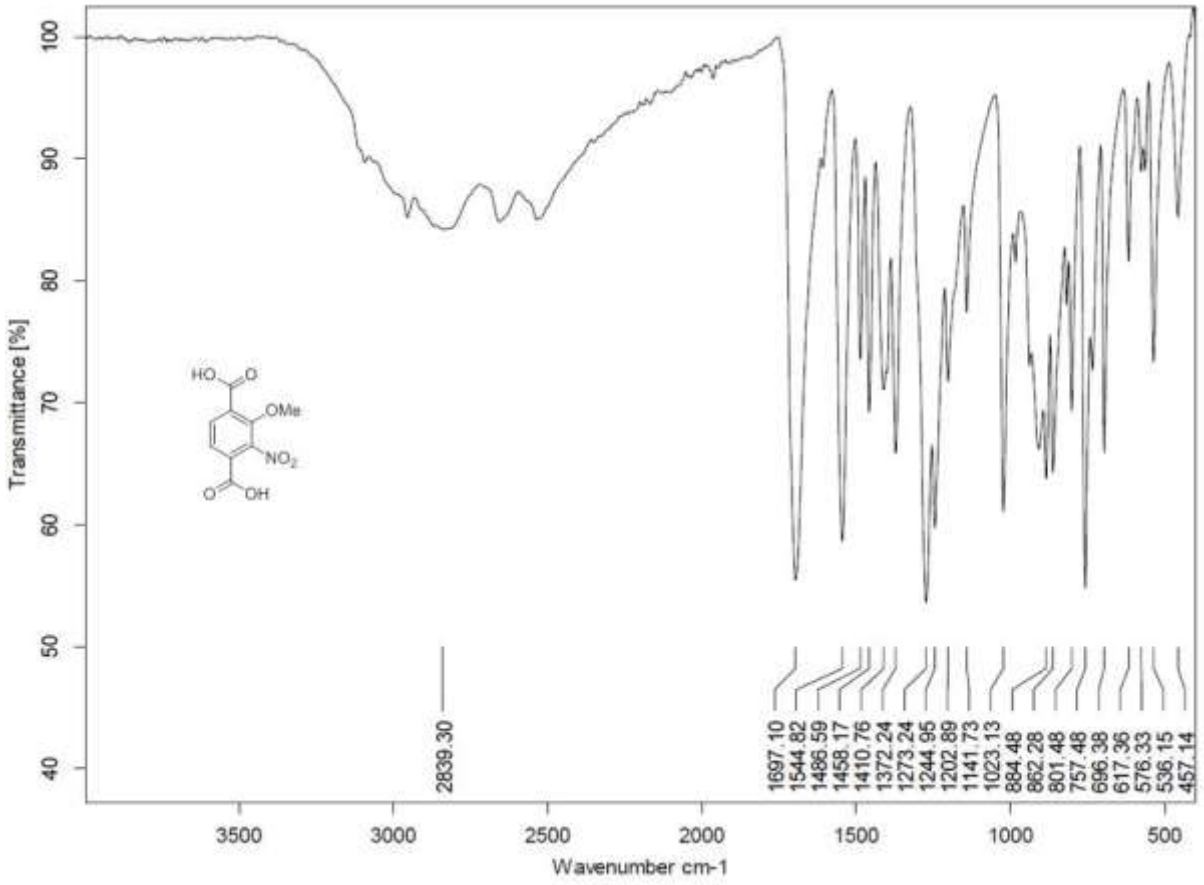



Transmittance [%]
90
80
70
60
50
HO
O
OMe
O2N
O
OH
2847.04
1698.38
1619.38
1567.34
1530.92
1495.38
1469.48
1410.29
1338.15
1297.16
1237.95
1113.64
1033.95
877.58
759.52
739.91
671.84
644.22
547.91
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

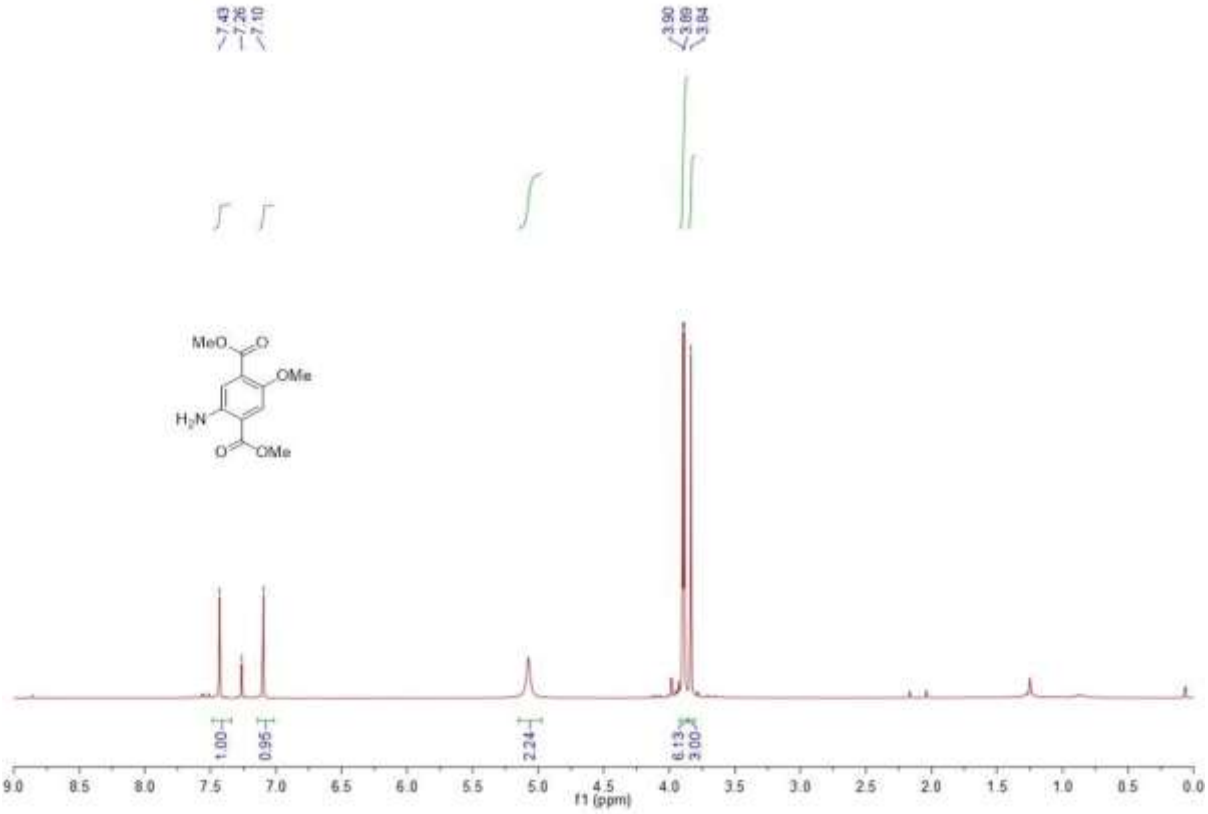
2-Methoxy-3-nitroterephthalic acid (**4b**)

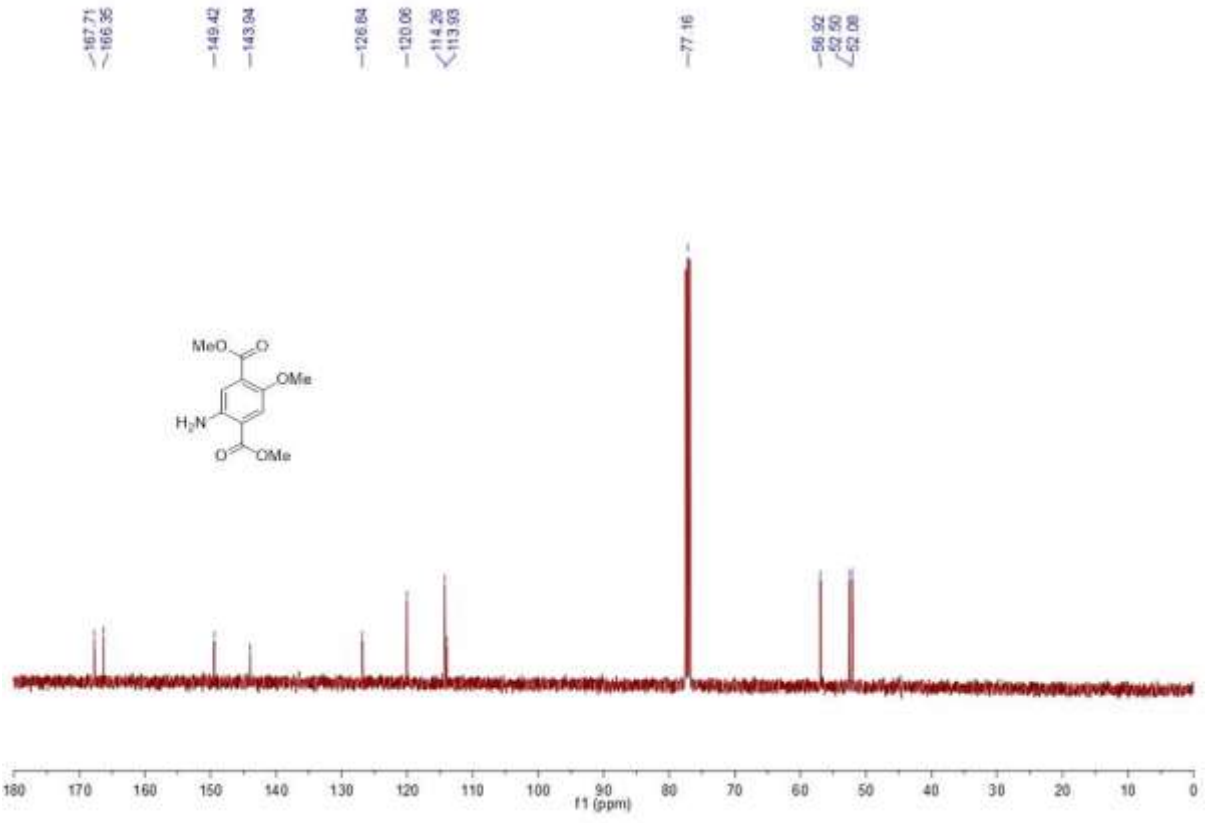


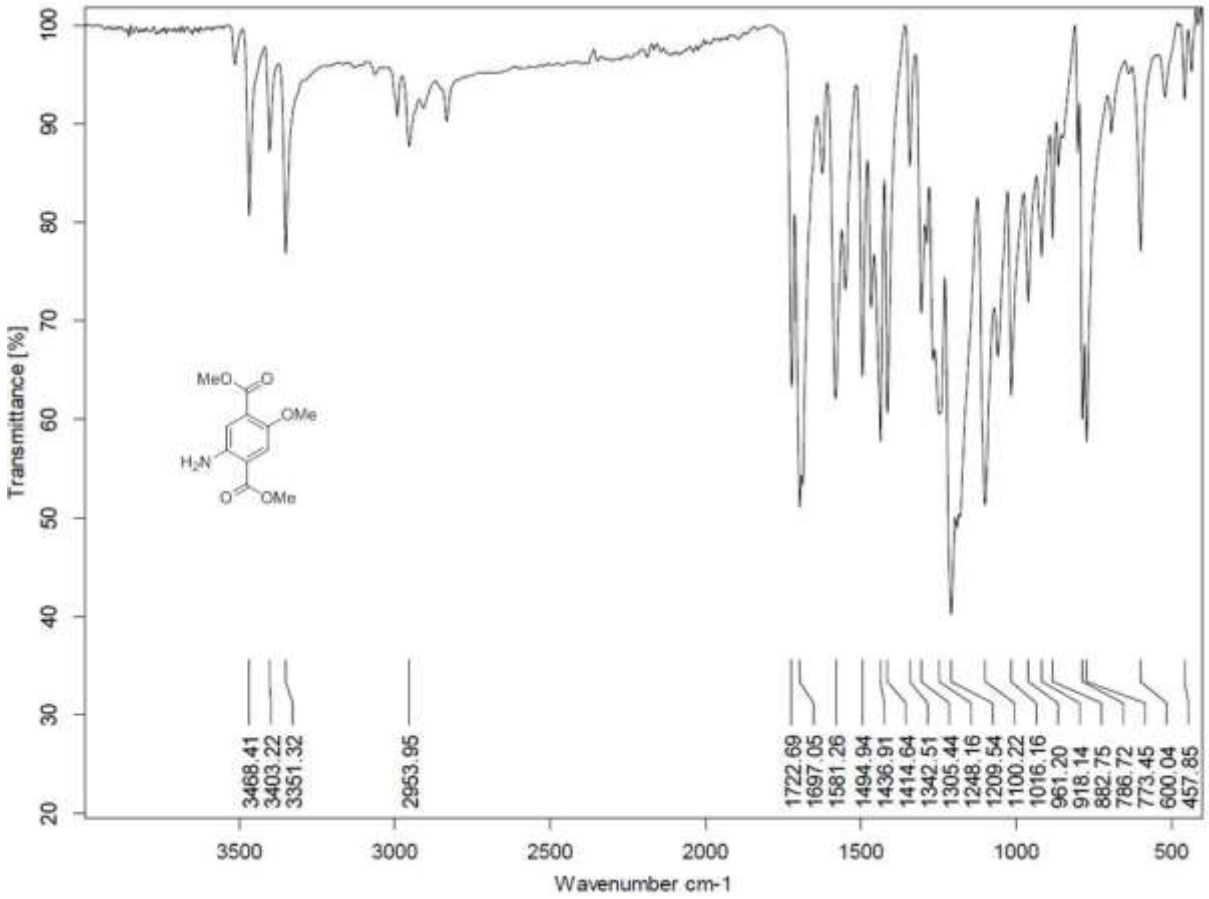



Transmittance [%]
100
90
80
70
60
50
40
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
HO
O
OMe
NO2
O
OH
2839.30
1697.10
1544.82
1486.59
1458.17
1410.76
1372.24
1273.24
1244.95
1202.89
1141.73
1023.13
884.48
862.28
801.48
757.48
696.38
617.36
576.33
536.15
457.14

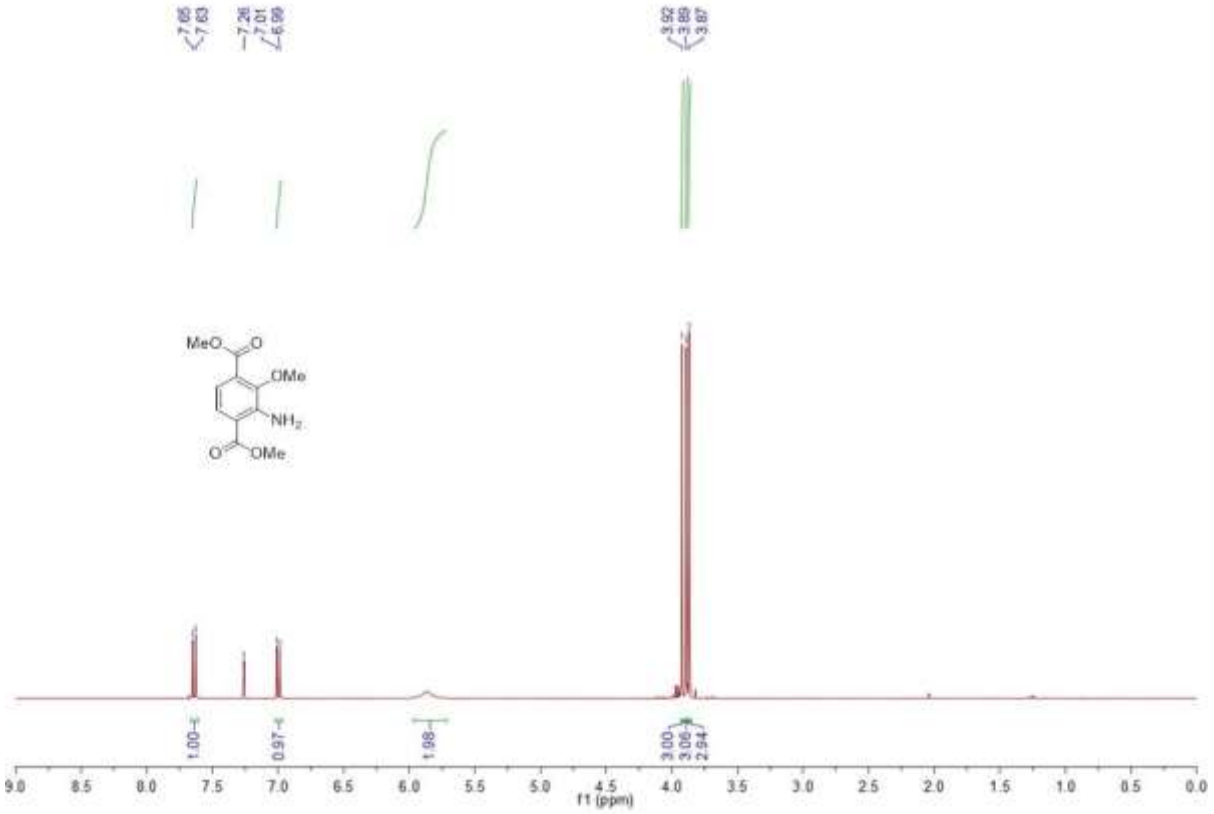
Dimethyl-2-amino-5-methoxyterephthalate (**BDCE-2,5-NH_2OMe**)

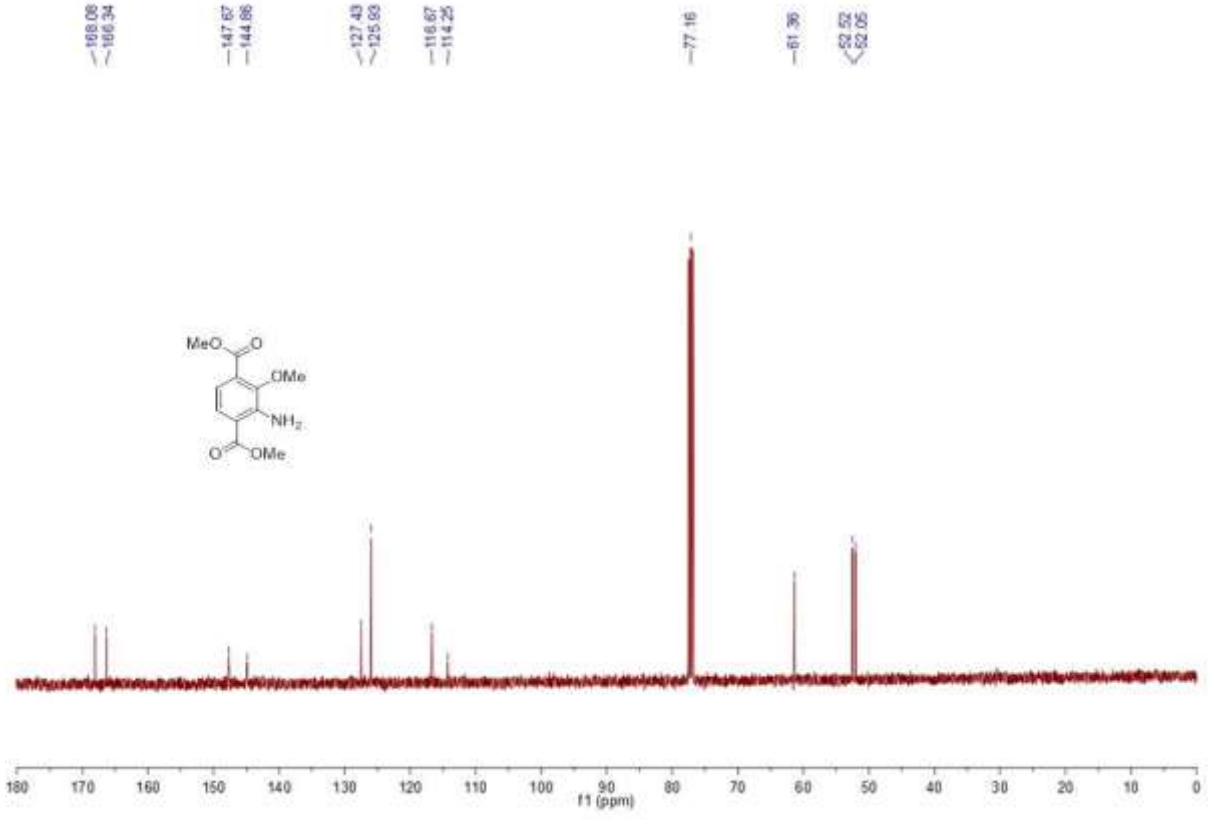


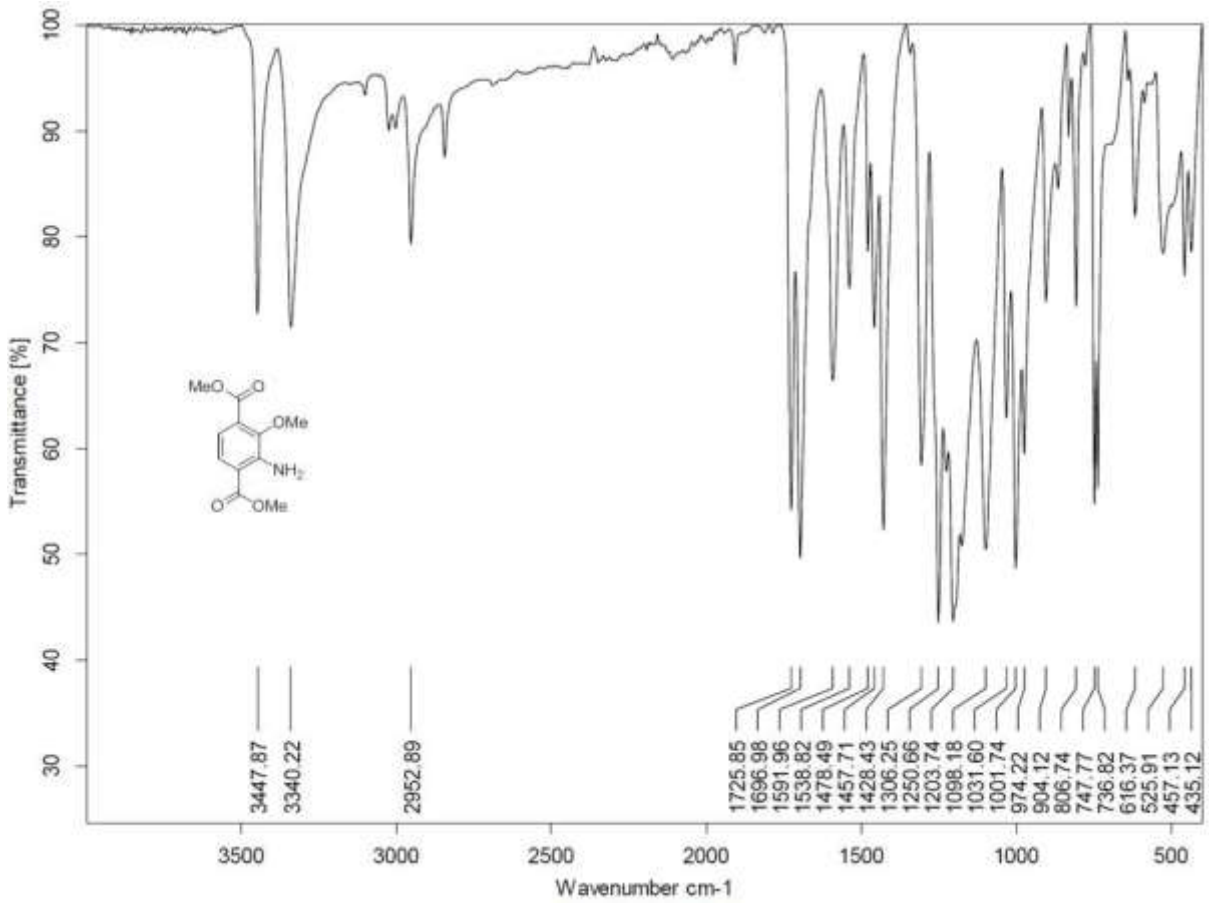



Transmittance [%]
Wavenumber cm-1
3468.41
3403.22
3351.32
2953.95
1722.69
1697.05
1581.26
1494.94
1436.91
1414.64
1342.51
1305.44
1248.16
1209.54
1100.22
1016.16
961.20
918.14
882.75
786.72
773.45
600.04
457.85
MeO
OMe
OMe
H2N

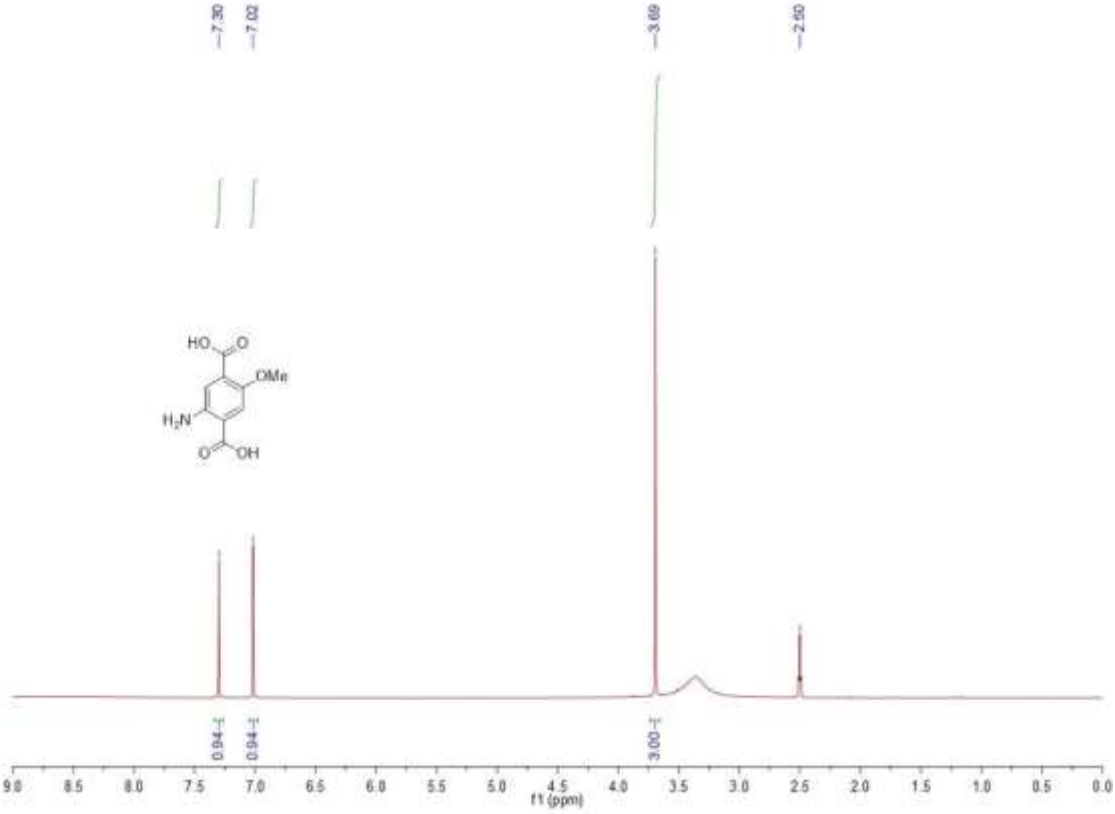
Dimethyl-2-amino-3-methoxyterephthalate (**BDCE-2,3-NH_2OMe**)

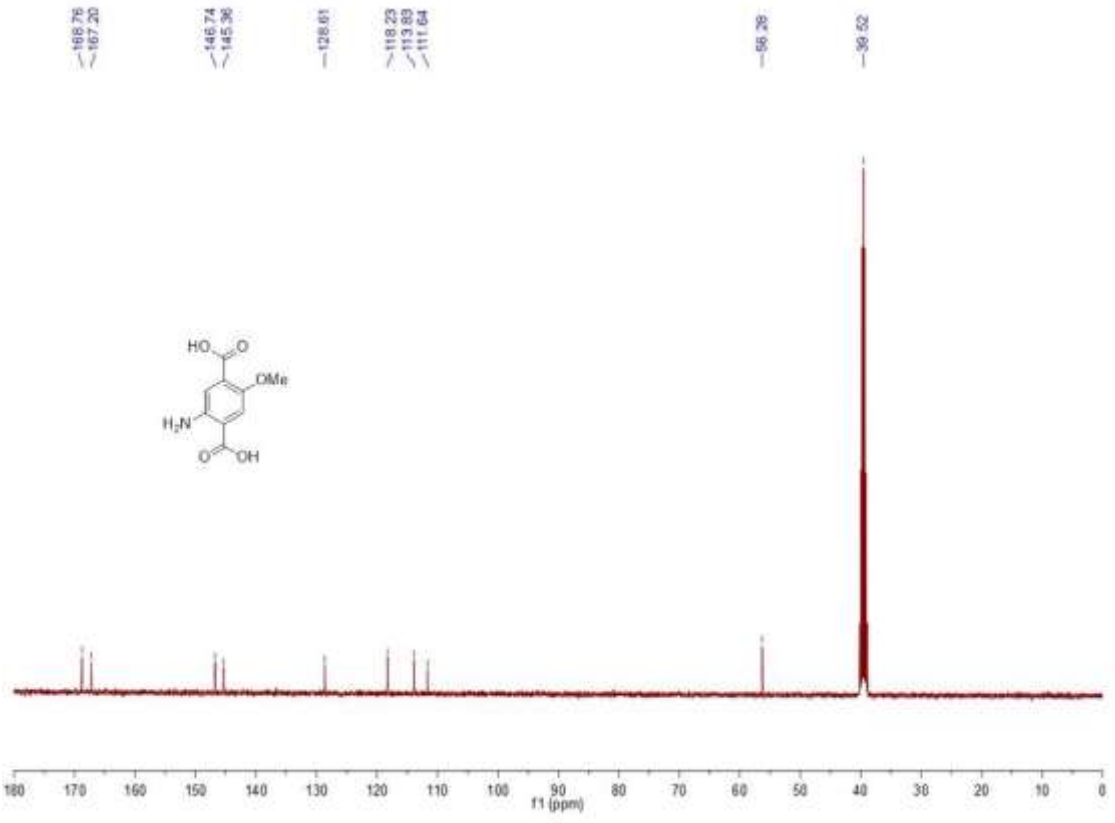


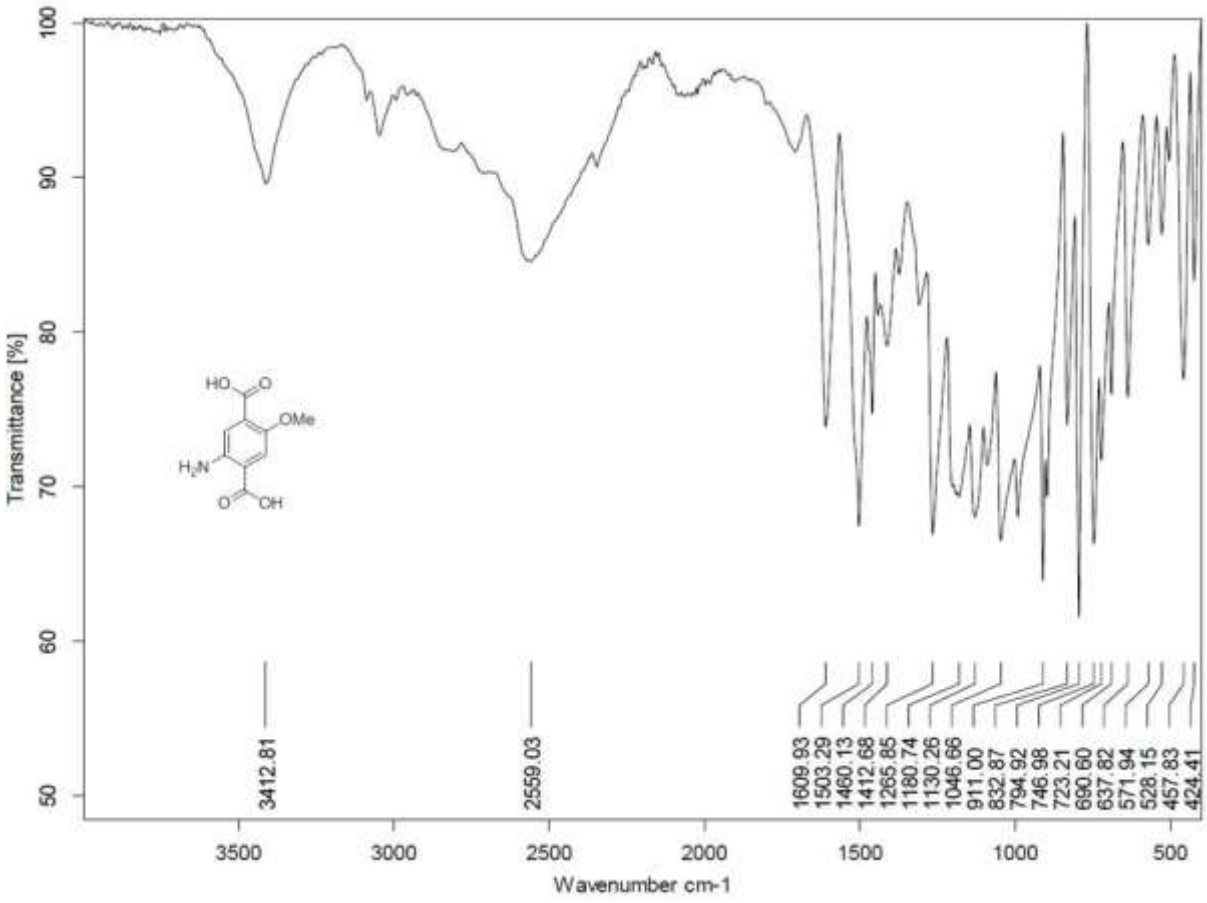



Transmittance [%]
100
90
80
70
60
50
40
30
MeO
O
OMe
NH2
O
OMe
3447.87
3340.22
2952.89
1725.85
1696.98
1591.96
1538.82
1478.49
1457.71
1428.43
1306.25
1250.66
1203.74
1098.18
1031.60
1001.74
974.22
904.12
806.74
747.77
736.82
616.37
525.91
457.13
435.12
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

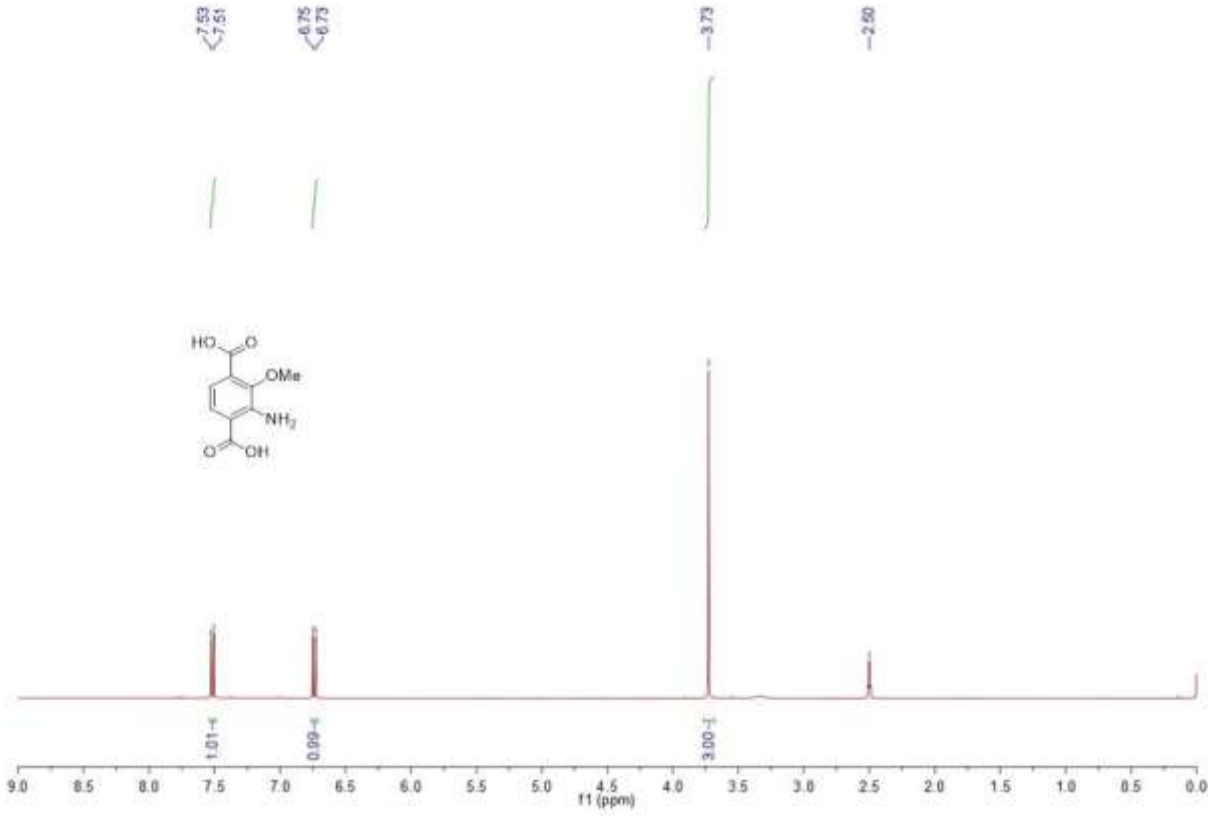
2-Amino-5-methoxyterephthalic acid (**5a**)

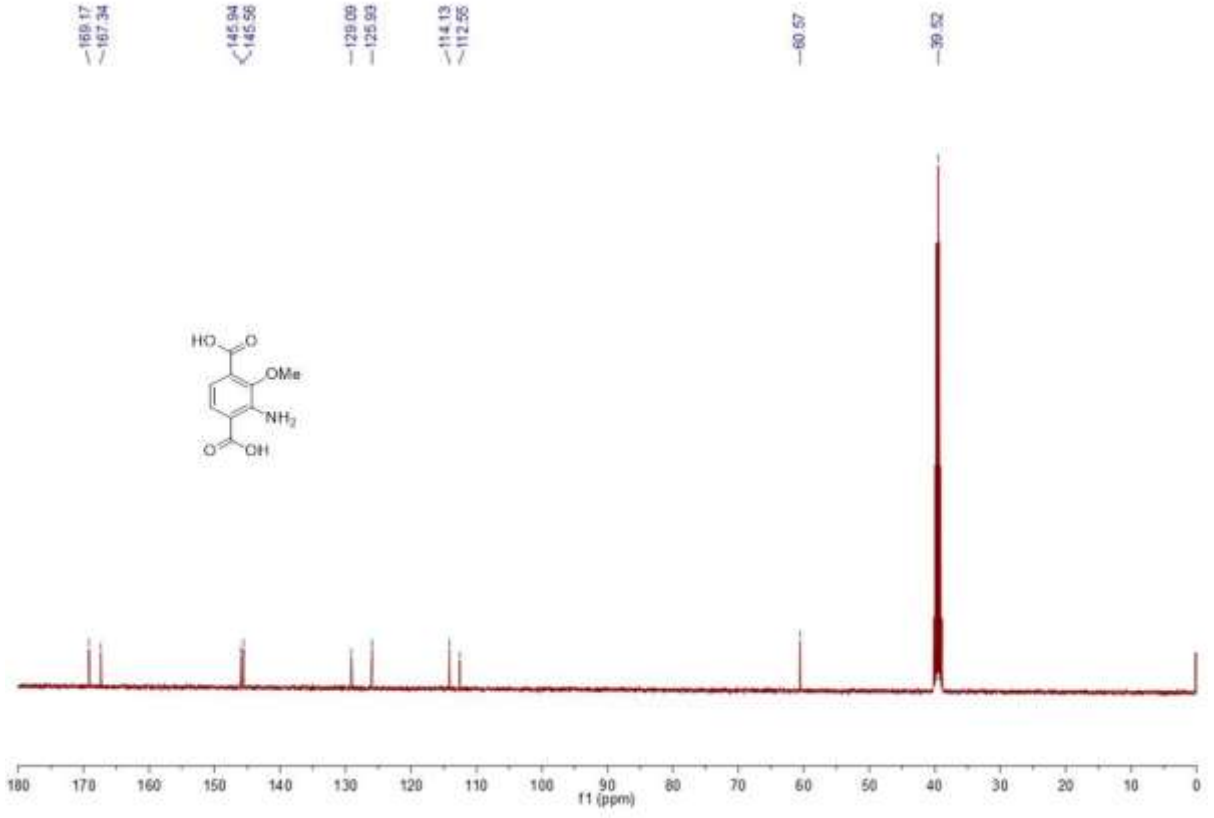


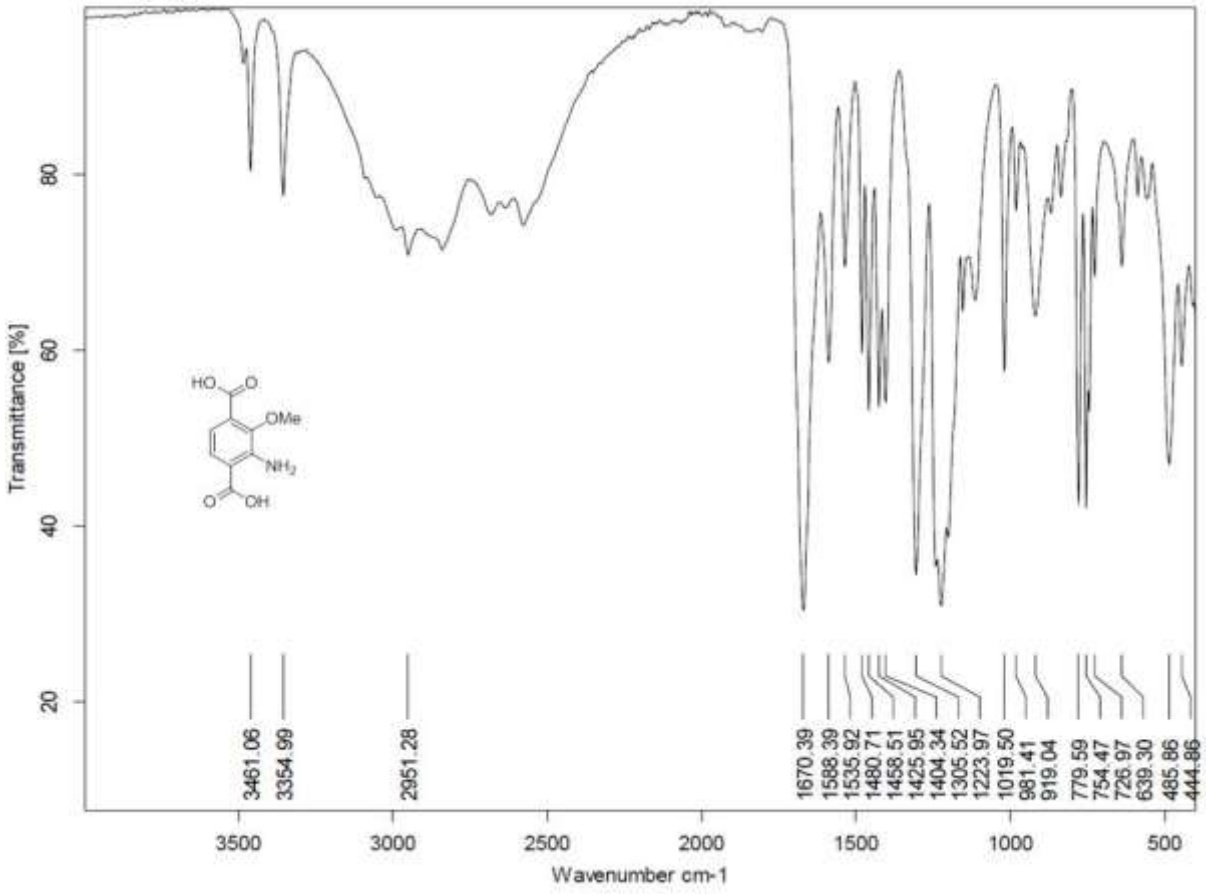



Transmittance [%]
100
90
80
70
60
50
HO
O
OMe
H2N
O
OH
3412.81
2559.03
1609.93
1503.29
1460.13
1412.68
1265.85
1180.74
1130.26
1046.66
911.00
832.87
794.92
746.98
723.21
690.60
637.82
571.94
528.15
457.83
424.41
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

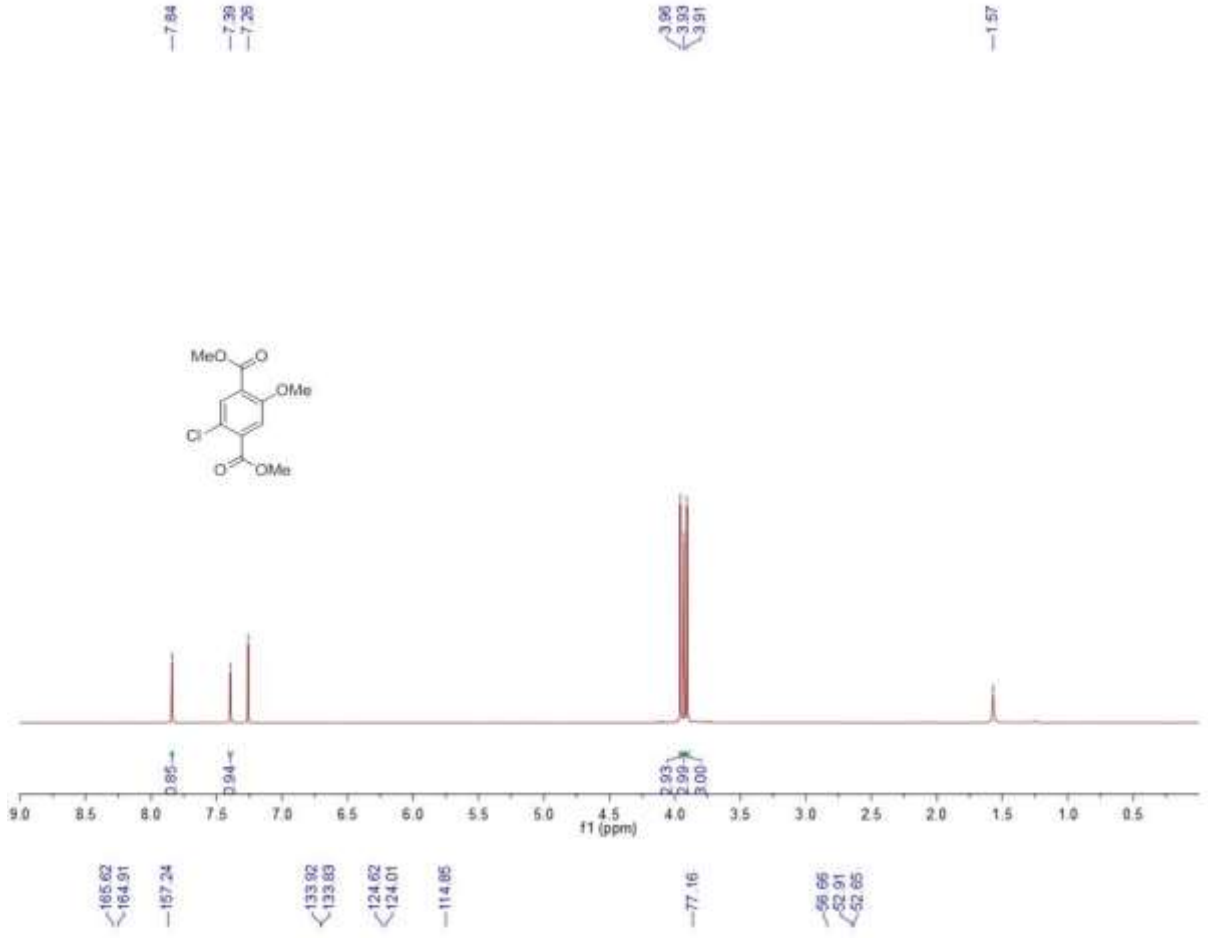
2-Amino-3-methoxyterephthalic acid (**5b**)

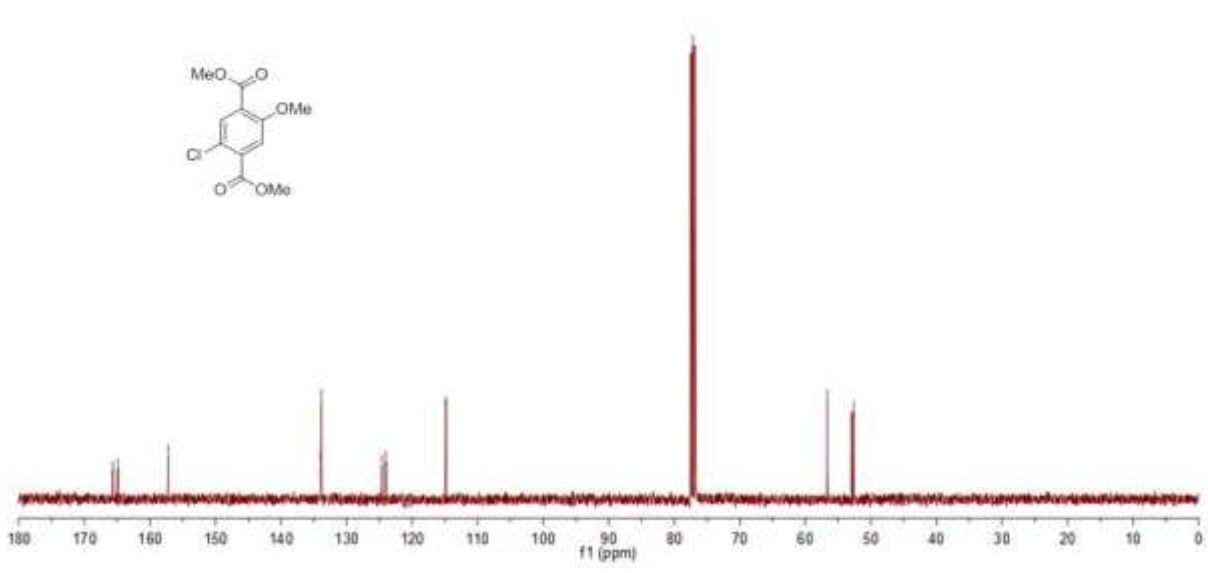


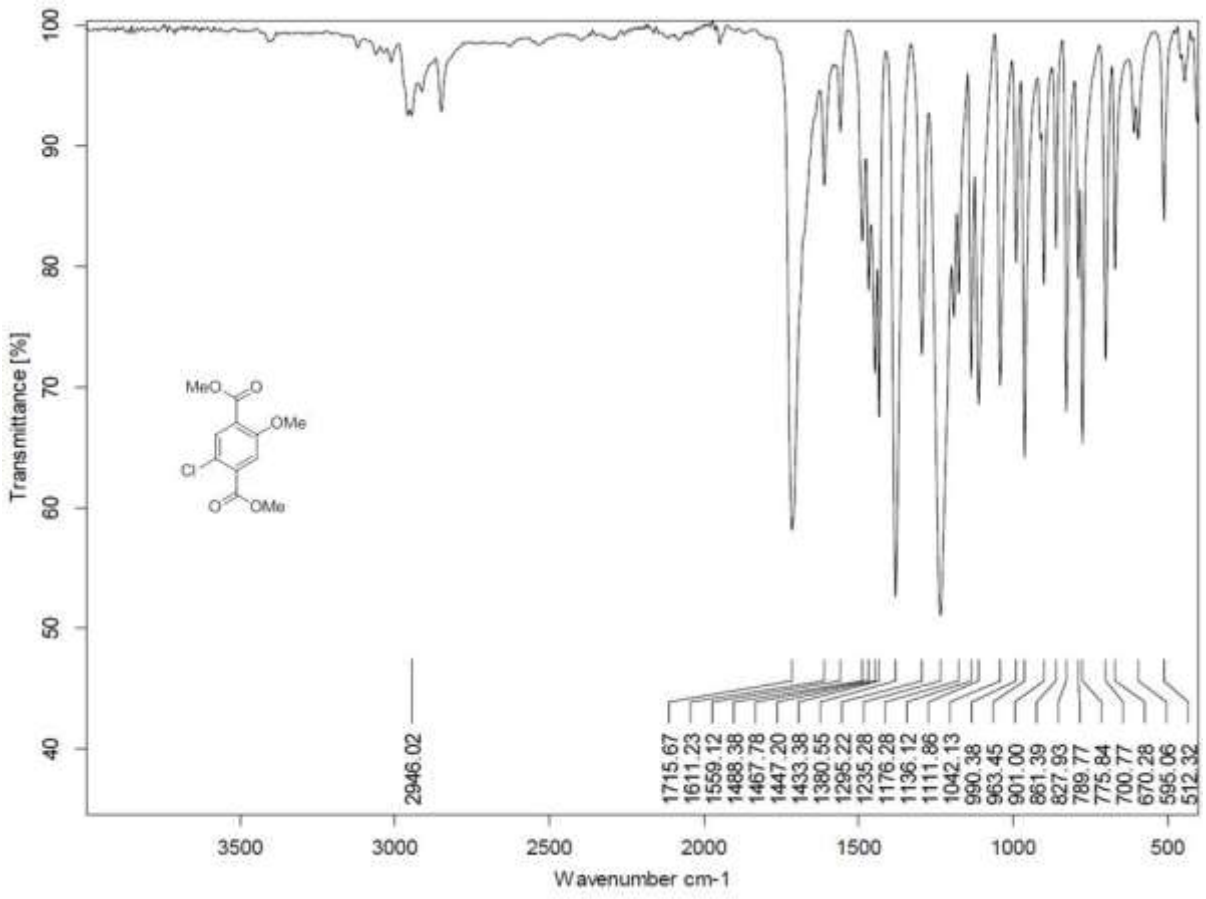



Transmittance [%]
20
40
60
80
HO
O
OMe
NH2
O
OH
3461.06
3354.99
2951.28
1670.39
1588.39
1535.92
1480.71
1458.51
1425.95
1404.34
1305.52
1223.97
1019.50
981.41
919.04
779.59
754.47
726.97
639.30
485.86
444.86
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

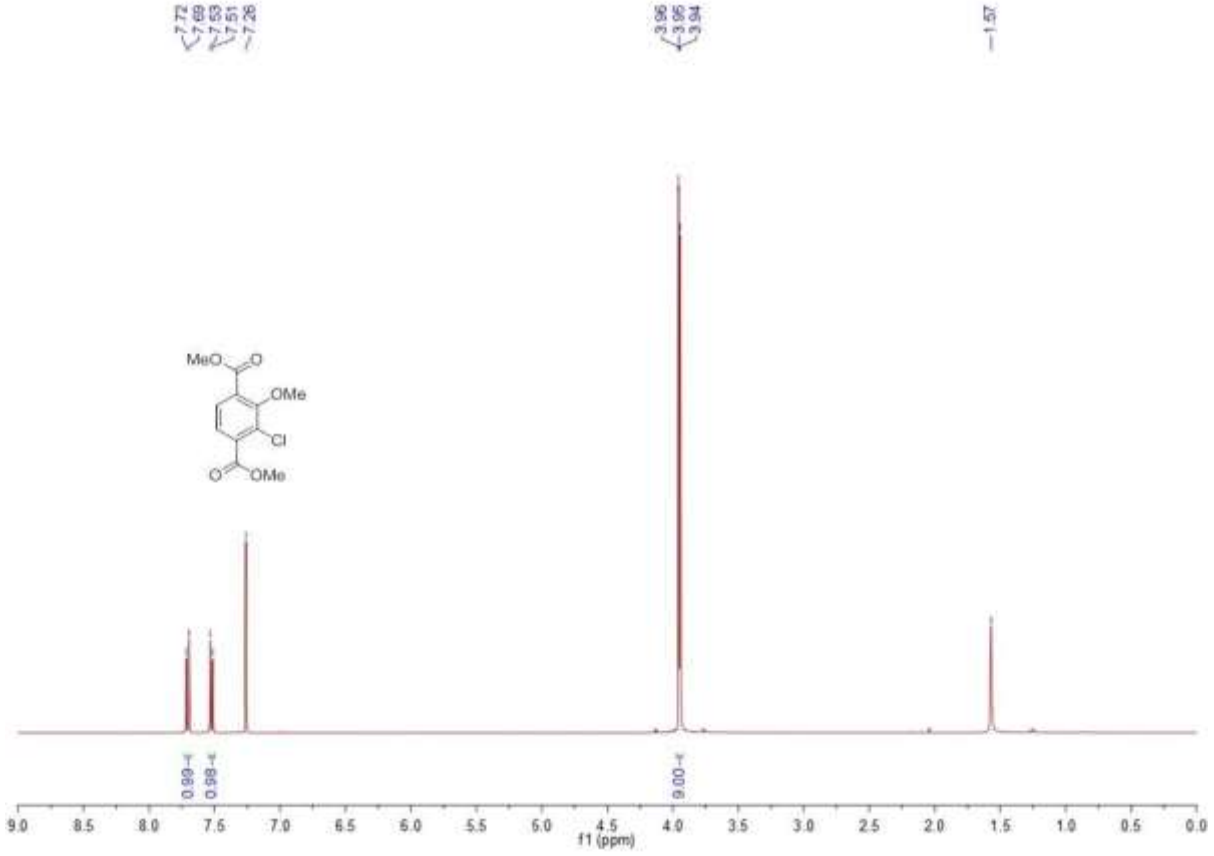
Dimethyl-2-chloro-5-methoxyterephthalate (**BDCE-2,5-OMeCl**)

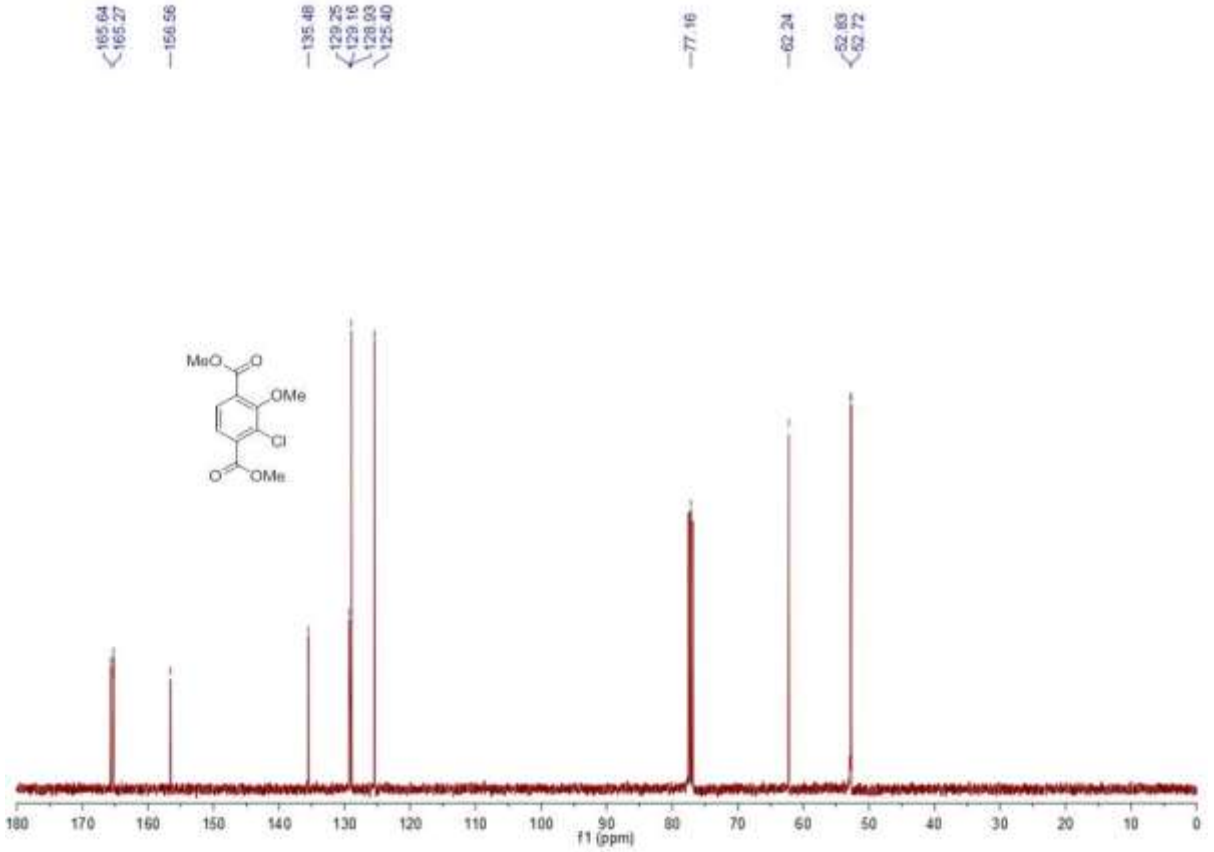


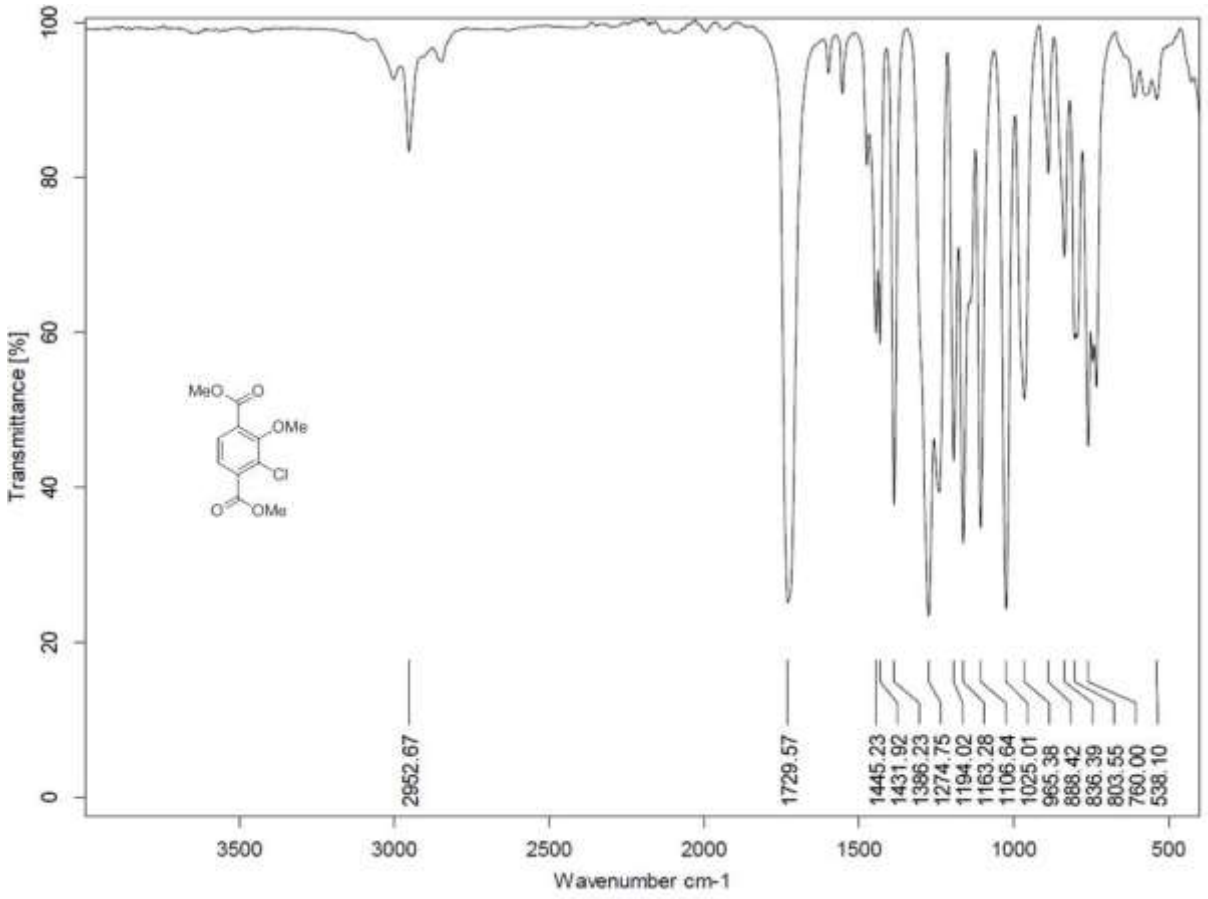



Transmittance [%]
100
90
80
70
60
50
40
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
MeO
O
OMe
Cl
O
OMe
2946.02
1715.67
1611.23
1559.12
1488.38
1467.78
1447.20
1433.38
1380.55
1295.22
1235.28
1176.28
1136.12
1111.86
1042.13
990.38
963.45
901.00
861.39
827.93
789.77
775.84
700.77
670.28
595.06
512.32

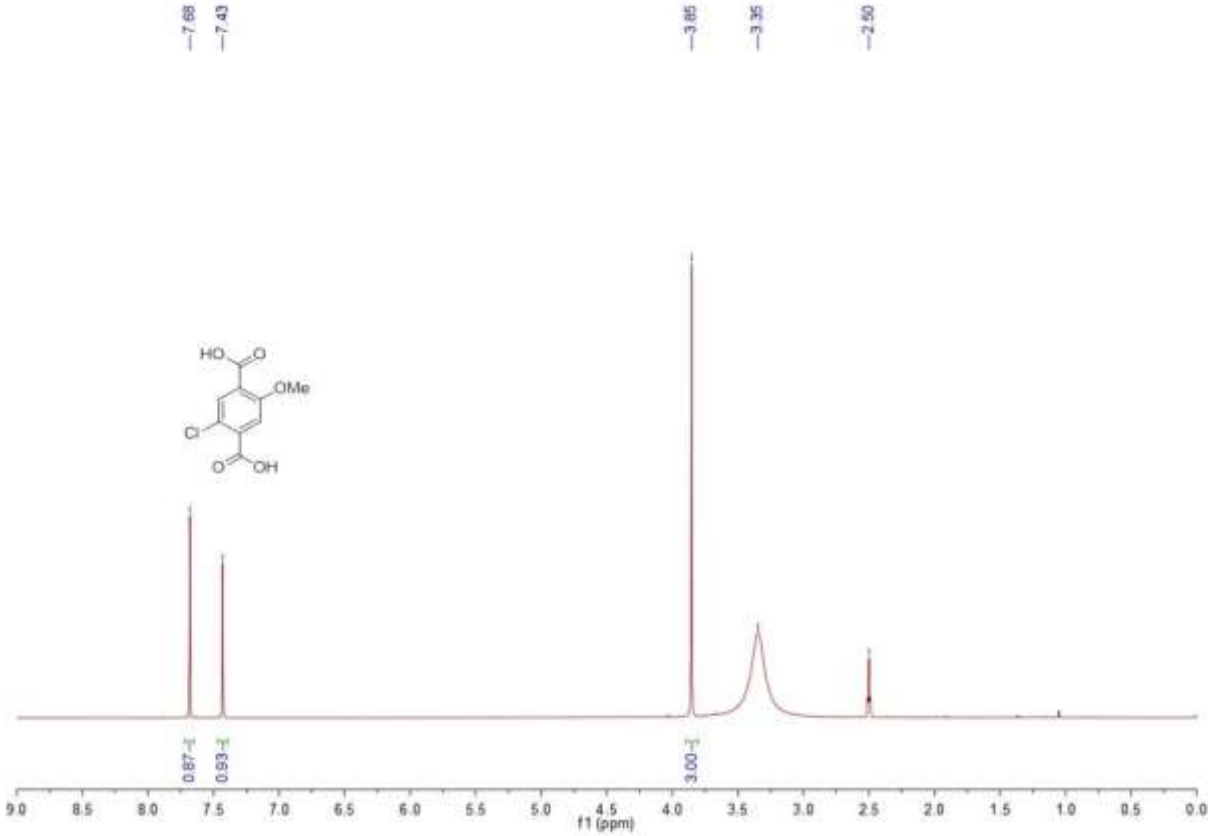
Dimethyl-2-chloro-3-methoxyterephthalate (**BDCE-2,3-OMeCl**)

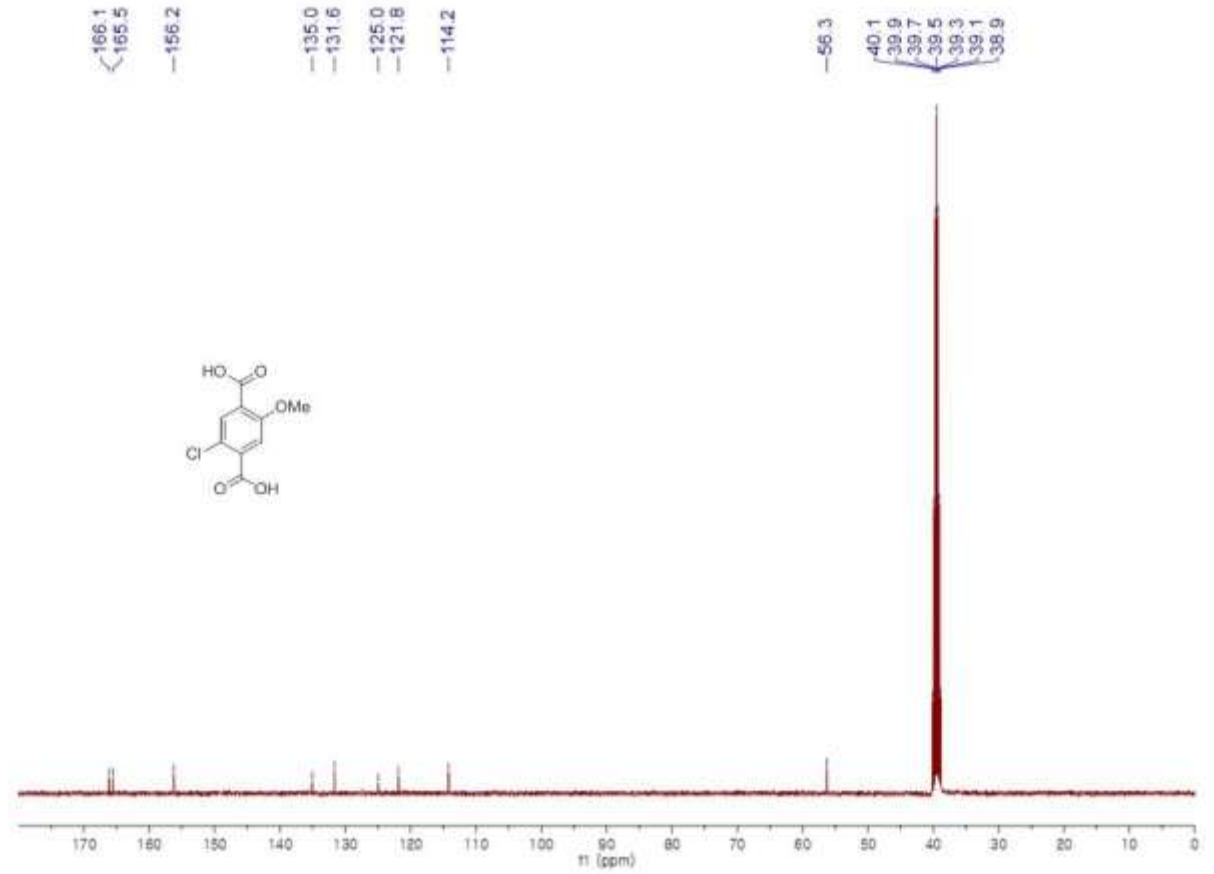


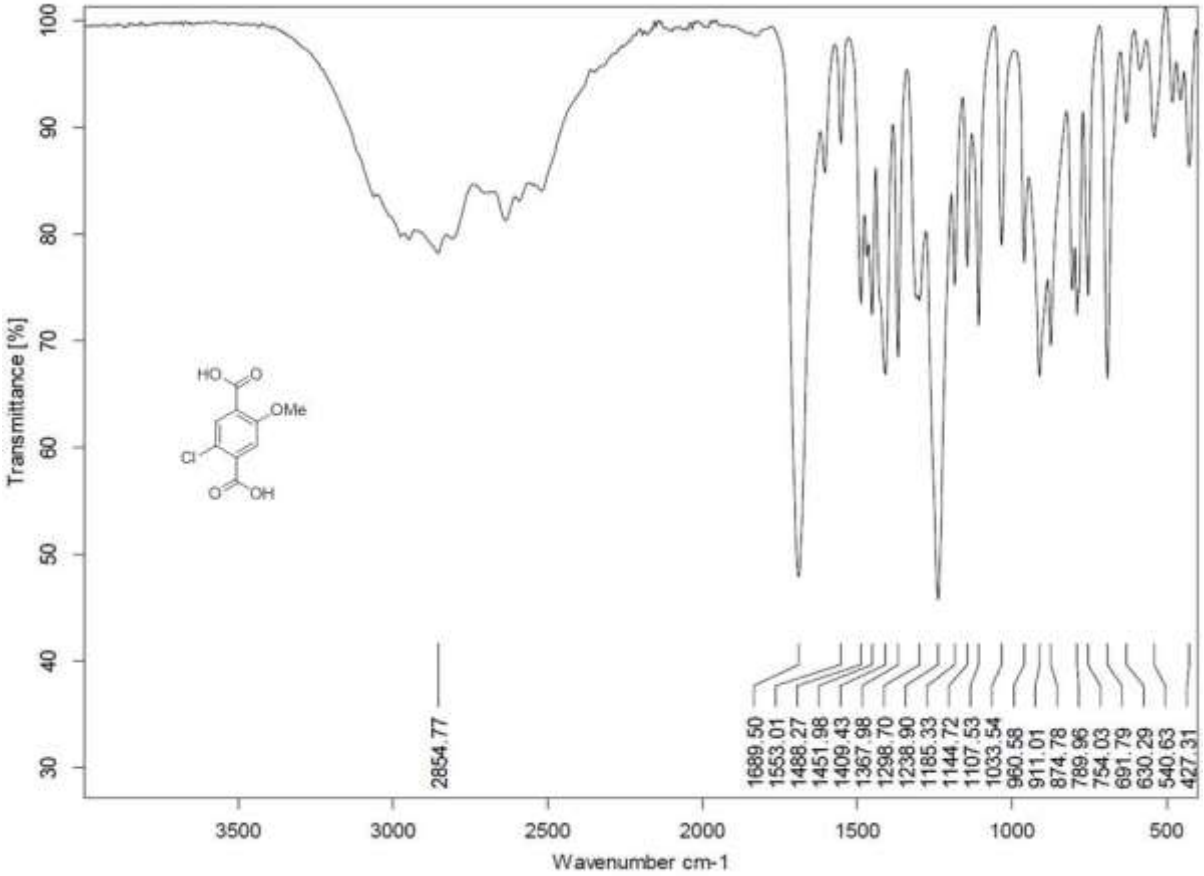



Transmittance [%]
100
80
60
40
20
0
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
MeO
O
OMe
Cl
O
OMe
2952.67
1729.57
1445.23
1431.92
1386.23
1274.75
1194.02
1163.28
1106.64
1025.01
965.38
888.42
836.39
803.55
760.00
538.10

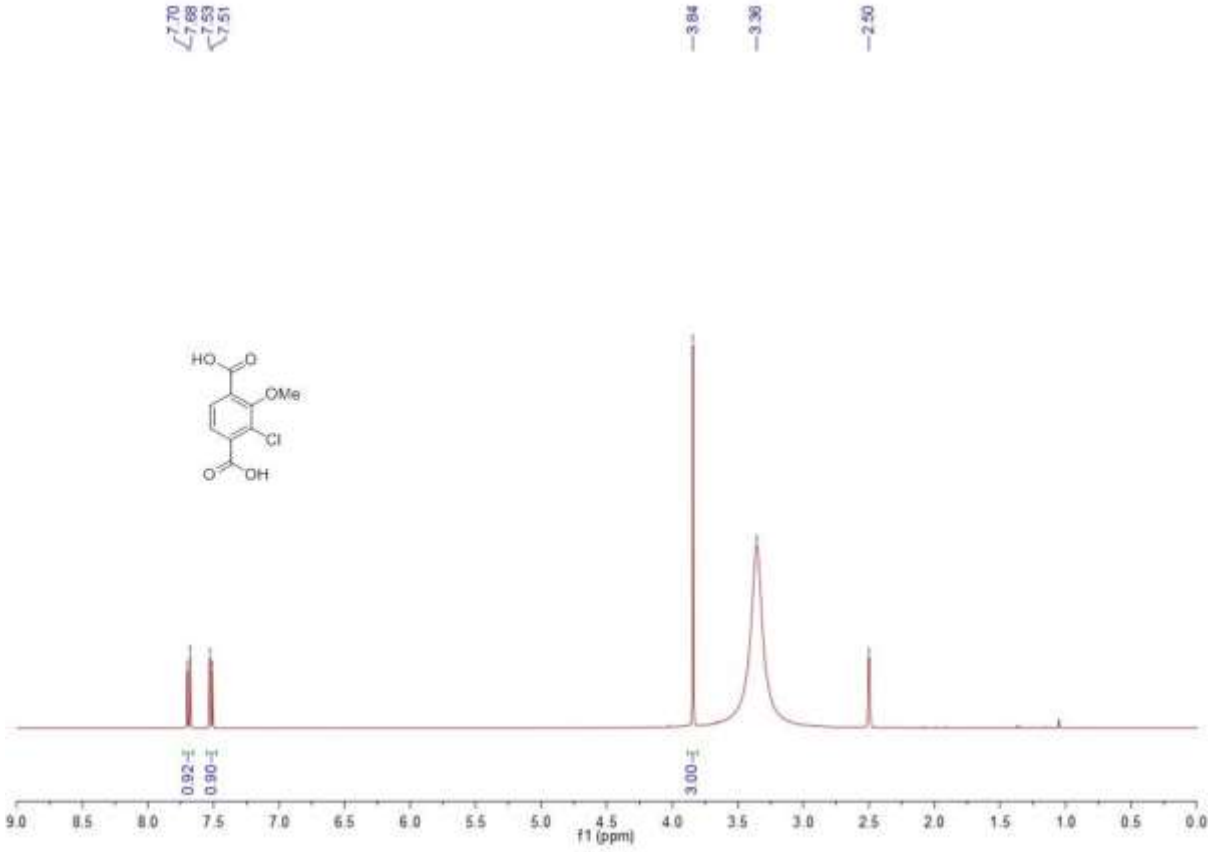
2-Chloro-5-methoxyterephthalic acid (**6a**)

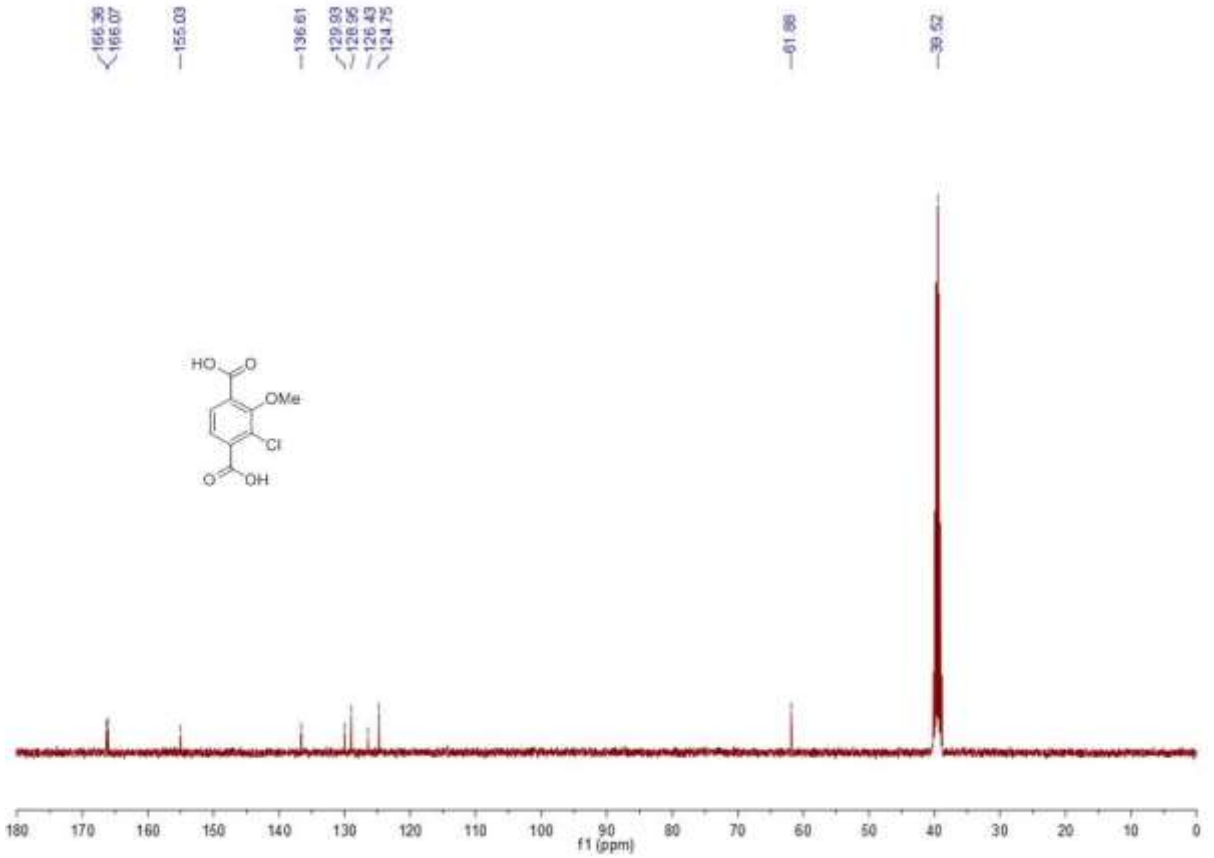


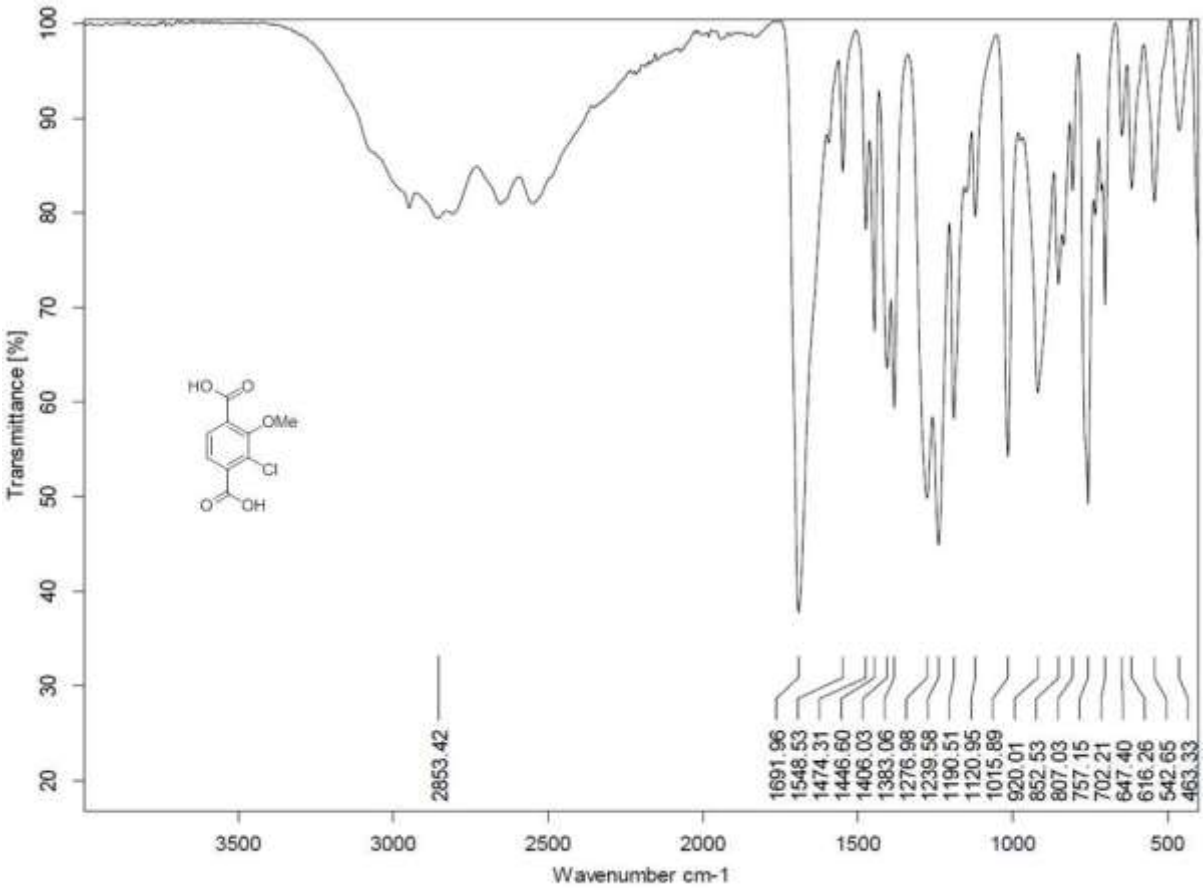



Transmittance [%]
100
90
80
70
60
50
40
30
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
HO
O
OMe
Cl
O
OH
2854.77
1689.50
1553.01
1488.27
1451.98
1409.43
1367.98
1298.70
1238.90
1185.33
1144.72
1107.53
1033.54
960.58
911.01
874.78
789.96
754.03
691.79
630.29
540.63
427.31

2-Chloro-3-methoxyterephthalic acid (**6b**)






Transmittance [%]
Wavenumber cm-1
HO
O
OMe
Cl
O
OH
2853.42
1691.96
1548.53
1474.31
1446.60
1406.03
1383.06
1276.98
1239.58
1190.51
1120.95
1015.89
920.01
852.53
807.03
757.15
702.21
647.40
616.26
542.65
463.33