Electronic Supplementary Material (ESI) for Chemical Communications.

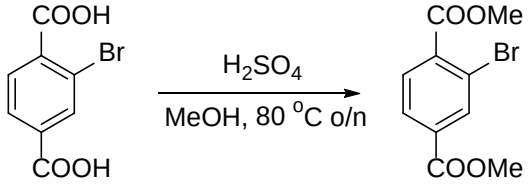
Electronic Supporting Information

General methods

Organic solvents were evaporated using a rotary evaporator with an aspirator or diaphragm, and residual solvents were removed on a vacuum line held at 0.1–1 torr. Analytical thin-layer chromatography (TLC) separations were performed on precoated silica gel 60 F254 plates. TLC plates were visualized with UV light (254 nm). Flash column chromatography separations were performed on silica gel (400-630 mesh). Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on FT AM 400 or 500 instruments (400 MHz or 500 MHz). Chemical shifts are reported in parts per million (ppm) and referenced to the appropriate solvent peak or 0 ppm for TMS. The following abbreviations are used to describe peak multiplicities when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Coupling constants, J, are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded on FT AM 400 or 500 instruments (100 MHz or 125 MHz) and were fully decoupled by broad-band decoupling. Chemical shifts are reported in ppm and referenced to the center line of the triplet of chloroform-*d* at 77.0 ppm or the septet of DMSO-d_6 at 39.52 ppm.

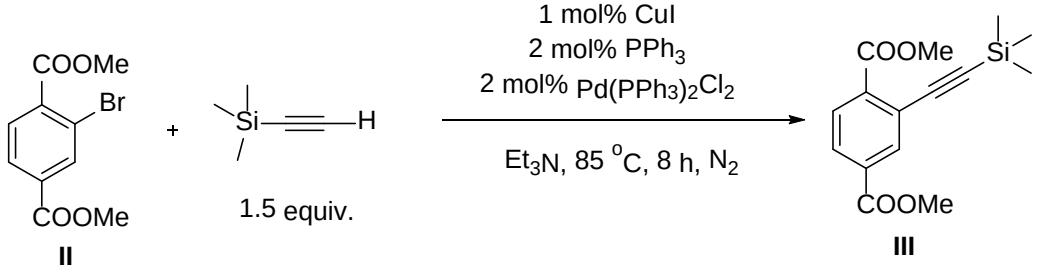
Synthesis of BDC-CB

Synthesis of dimethyl 2-bromoterephtalate (II)



To 2-bromoterephthalic acid (**I**, 4.9 g, 20 mmol) suspended in MeOH (200 mL) was added H_2SO_4 (10 mL, 98%) was slowly at room temperature. After refluxing the reaction mixture overnight, the mixture was cooled to room temperature, and 1.0 M aqueous K_2CO_3 was added to adjust the pH to 8. The solution was extracted with ethyl acetate. The combined organic layers were dried over $MgSO_4$, and the solvent was removed in vacuo. Then, the desired compound, dimethyl 2-bromoterephthalate (**II**, 4.91 g, 18 mmol, 90%), was obtained as a colorless solid. ^{1}H NMR (500 MHz, chloroform-*d*): δ 3.95 (3H, s), 3.96 (3H, s), 7.81-7.82 (1H, d, J = 8.1 Hz), 8.00-8.02 (1H, dd, J = 1.6 Hz, J = 8.1 Hz), 8.32 (1H, d, J = 1.6 Hz). ^{13}C NMR (125 MHz, chloroform-*d*): δ 52.85, 52.94, 121.60, 128.24, 131.16, 133.83, 135.34, 136.24, 165.14, 166.28.

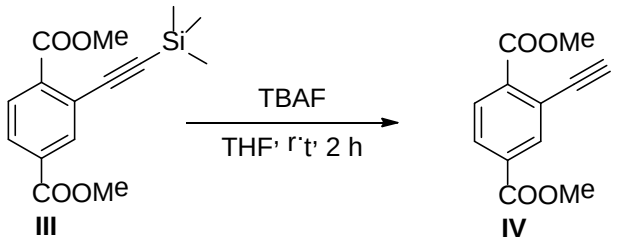
Synthesis of dimethyl 2-((trimethylsilyl)ethynyl)terephthalate (III)



To a two-necked flask was added dimethyl 2-bromoterephthalate (**II**, 4.91 g, 18 mmol), 1 mol% CuI

(34 mg, 0.18 mmol), 2 mol% PPh_3 (94 mg, 0.18 mmol), and 2 mol% $Pd(PPh_3)_2Cl_2$ (252 mg, 0.36 mmol). The flask was evacuated and backfilled with N_2 (3×). Et_3N (90 mL) containing Me_3SiEt (3.78 mL) was added, and the reaction mixture was stirred at 85 °C for 8 h. The reaction was monitored by TLC. After cooling to room temperature, the mixture was filtered by passage through Celite and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc:hexane = 1:30), and an ivory solid was obtained. (**III**, 3.13 g, 10.7 mmol, 60%). ^{1}H NMR (500 MHz, chloroform-*d*): δ 0.27 (9H, s), 3.93 (6H, s), 7.92-7.94 (1H, d, J = 8.7 Hz), 7.96-7.98 (1H, dd, J = 2.1 Hz, J = 8.7 Hz), 8.213-8.214 (1H, d, J = 2.1 Hz). ^{13}C NMR (125 MHz, chloroform-*d*): δ -0.09, 52.41, 52.67, 101.10, 102.28, 123.62, 128.96, 130.42, 132.89, 135.61, 136.20, 165.70, 166.33.

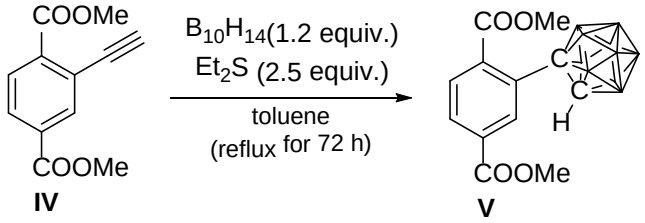
Synthesis of dimethyl 2-ethynylterephthalate (IV)



III **IV**

A round bottom flask was charged with dimethyl 2-((trimethylsilyl)ethynyl)terephthalate (**III**, 2.9 g, 10.0 mmol) dissolved in THF (50 mL). Then, 1.0 M TBAF in THF (12.0 mL, 12.0 mmol) was slowly added. The reaction mixture was stirred at room temperature for 2 h. The reaction was monitored by TLC. After the indicated time, the reaction mixture was slowly quenched by the addition of deionized water and then extracted with DCM. The organic layer was dried and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc:hexane = 1:15), and a reddish solid was obtained (**IV**, 1.42 g, 6.5 mmol, 65%). ^{1}H NMR (500 MHz, chloroform-*d*): δ 3.44 (1H, s), 3.94 (3H, s), 3.95 (3H, s), 7.97-7.99 (1H, d, J = 8.2 Hz), 8.02-8.04 (1H, dd, J = 1.6 Hz, J = 8.2 Hz), 8.275-8.278 (1H, d, J = 1.6 Hz). ^{13}C NMR (125 MHz, chloroform-*d*): δ 52.65, 52.77, 81.20, 83.35, 123.06, 129.40, 130.50, 133.17, 136.06, 136.21, 165.62, 165.97.

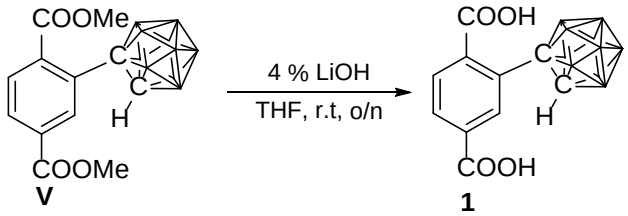
Synthesis of dimethyl 2-o-carboraneterephtalate (V, BDCE-CB)



IV **V**

To a toluene solution (50 mL) of decaborane (0.88 g, 7.2 mmol) and dimethyl 2-ethylnylterephthalate (**IV**, 1.3 g, 6.0 mmol) was slowly added excess diethyl sulfide (2.5 equiv. relative to decaborane) at room temperature. The reaction mixture was stirred at 120 °C for 3 days. After the reaction, the toluene was removed by evaporation. The crude product was purified by passage through an alumina column using toluene as the eluent. A white solid was obtained in 30% yield (**V**, 0.6 g, 1.8 mmol). ^{1}H NMR (500 MHz, chloroform-*d*): δ 1.5-3.5 (10H, br), 3.96 (3H, s), 3.97 (3H, s), 4.81 (1H, s), 7.41-7.43 (1H, d, J = 8.0 Hz), 8.05-8.07 (1H, dd, J = 1.4 Hz, J = 8.0 Hz), 8.52-8.53 (1H, d, J = 1.4 Hz). ^{13}C NMR (125 MHz, chloroform-*d*): δ 52.80, 53.52, 62.05, 70.41, 129.94, 130.31, 130.46, 132.10, 132.95, 136.56, 165.02, 169.40.

Synthesis of dimethyl 2-o-carboraneterephtalic acid (1, BDC-CB)



To a THF solution (10 mL) of dimethyl 2-*o*-carboraneterephtalate (**V**, 338 mg, 1.0 mmol) was added 4% LiOH aqueous solution (10 mL) at room temperature. The reaction mixture was stirred at room temperature overnight. After evaporation of the THF, the remaining aqueous phase was adjusted to pH 2 with 1.0 M aqueous HCl. The ivory precipitate was collected by filtration, washed with water and dried under vacuum to afford BDC-CB (**1**, 217 mg, 0.7 mmol). ^{1}H NMR (500 MHz, dimethyl sulfoxide-d_6): δ 1.5-3.5 (10H, br), 5.73 (1H, s), 7.55-7.57 (1H, d, J = 7.8 Hz), 8.02-8.04 (1H, dd, J = 1.4 Hz, J = 7.8 Hz), 8.231-8.234 (1H, d, J= 1.4 Hz). ^{13}C NMR (125 MHz, dimethyl sulfoxide-d_6): δ 63.56, 75.11, 127.87, 129.57, 130.64, 131.59, 132.02, 138.80, 165.72, 170.02.

Preparation of the MOFs

The UiO-66 series and IRMOF were prepared and activated using previously described methods with slight modifications.

UiO-66

Terephthalic acid (125 mg, 0.75 mmol), $ZrCl_4$ (126 mg, 0.54 mmol), HCl (1 mL) and DMF (*N,N*-dimethylformamide, 15 mL) were placed in a vial, and the mixture was heated in a conventional oven at 80 °C for 12 h and then cooled to room temperature. The microcrystalline powder was then isolated by centrifugation. The solids were washed three times with 12 mL of DMF and then with 12 mL of MeOH three times. The solid material was then rinsed with 12 mL of MeOH and left to soak for 3 days with fresh MeOH exchanged every 24 h. After 3 days of soaking, the solids were centrifuged and dried under vacuum.

IRMOF

Terephthalic acid (68 mg, 0.41 mmol), zinc nitrate hexahydrate (327 mg, 1.1 mmol) and DEF (*N,N*-diethylformamide, 10 mL) were placed in a vial, and the mixture was heated in a conventional oven at 100 °C for 18 h and then cooled to room temperature. The clear crystals were washed with 10 mL of DMF three times.

UiO-66-Br

2-Bromoterephthalic acid (184 mg, 0.75 mmol), $ZrCl_4$ (126 mg, 0.54 mmol), HCl (1 mL) and DMF (15 mL) were placed in a vial, and the mixture was heated in a conventional oven at 80 °C for 12 h and then cooled to room temperature. The microcrystalline powder was then isolated by centrifugation. The solids were washed three times with 12 mL of DMF and then three times with 12 mL of MeOH.

The solid material was then rinsed with 12 mL of MeOH and left to soak for 3 days with fresh MeOH exchanged every 24 h. After 3 days of soaking, the solids were centrifuged and dried under vacuum.

UiO-66-NO_2

2-Nitroterephthalic acid (158 mg, 0.75 mmol), $ZrCl_4$ (126 mg, 0.54 mmol), HCl (1 mL) and DMF (15 mL) were placed in a vial, and the mixture was heated in a conventional oven at 80 °C for 12 h and then cooled to room temperature. The microcrystalline powder was then isolated by centrifugation. The solids were washed three times with 12 mL of DMF and then three times with 12 mL of MeOH. The solid material was then rinsed with 12 mL of MeOH and left to soak for 3 days with fresh MeOH exchanged every 24 h. After 3 days of soaking, the solids were centrifuged and dried under vacuum.

UiO-66-$(H)_{0.75}(NDC)_{0.25}$

Terephthalic acid (100 mg, 0.6 mmol), 1,4-naphthalenedicarboxylic acid (32 mg, 0.15 mmol), $ZrCl_4$ (126 mg, 0.54 mmol), HCl (1 mL) and DMF (15 mL) were placed in a vial, and the mixture was heated in a conventional oven at 80 °C for 12 h and then cooled to room temperature. The microcrystalline powder was then isolated by centrifugation. The solids were washed three times with 12 mL of DMF and then three times with 12 mL of MeOH. The solid material was then rinsed with 12 mL of MeOH and left to soak for 3 days with fresh MeOH exchanged every 24 h. After 3 days of soaking, the solids were centrifuged and dried under vacuum.

Postsynthetic ligand exchange (PSE) with BDC-CB

PSE for UiO-66-(H)(CB)

BDCE-CB (**V**, 6 mg, 0.018 mmol) was dissolved in THF (1 mL) and 4% aqueous LiOH (1 mL). The solution was stirred at room temperature for 1 h. The THF was removed by evaporation, and the remaining aqueous phase was neutralized to pH 7 with 1 M HCl solution. The solution was added to fully dried UiO-66 (16.6 mg, 0.01 mmol), and the mixture was incubated at room temperature. Once the exchange was complete, the microcrystalline powder was separated by centrifugation, and the aqueous phase decanted. The solids were washed three times with 5 mL of water and then washed three times with 5 mL of MeOH. Then, the solids were suspended in 5 mL of MeOH. After 24 h, the solids were separated by centrifugation, and MeOH was decanted. This MeOH soaking step was repeated two more times (for 24 h each). After 3 days of soaking, the solids were separated by centrifugation and dried under vacuum.

PSE for IRMOF

BDC-CB (**1**, 17.7 mg, 0.057 mmol) was dissolved in THF (1 mL). Then, approximately 5 mg of IRMOF-1 was weighed into a vial, and the BDC-CB/THF solution was added to the IRMOF. The mixture was incubated at 40 °C in an oil bath for 24 h. Once the exchange was complete, the THF was removed by decanting. The crystals were washed with fresh THF (5 mL, 3 times) and then soaked in DCM (dichloromethane, 5 mL). After 24 h, the DCM was decanted off, and this DCM soaking step was repeated two more times.

PSE for UiO-66-(Br)(CB)

BDCE-CB (**5**, 6 mg, 0.018 mmol) was dissolved in THF (1 mL) and 4% aqueous LiOH (1 mL). The

solution was stirred at room temperature for 1 h. The THF was removed by evaporation, and the remaining aqueous phase was neutralized to pH 7 with 1 M HCl solution. The solution was added to fully dried UiO-66-Br (20.9 mg, 0.01 mmol), and the mixture was incubated at room temperature. Once the exchange was complete, the microcrystalline powder was separated by centrifugation, and the aqueous phase was decanted off. The solids were washed three times with 5 mL of water and then three times with 5 mL of MeOH. Then, the solids were suspended in 5 mL of MeOH. After 24 h, the solid was separated by centrifugation, and the MeOH was decanted off. This MeOH soaking step was repeated two more times (for 24 h each). After 3 days of soaking, the solids were isolated by centrifugation and dried under vacuum.

PSE for UiO-66-(NO_2)(CB)

BDCE-CB (**5**, 6 mg, 0.018 mmol) was dissolved in THF (1 mL) and 4% aqueous LiOH (1 mL). The solution was stirred at room temperature for 1 h. The THF was removed by evaporation, and the remaining aqueous phase was neutralized to pH 7 with 1 M HCl solution. The solution was added to fully dried UiO-66-NO_2 (19.3 mg, 0.01 mmol), and the mixture was incubated at room temperature. Once the exchange was complete, the microcrystalline powder was separated by centrifugation, and the aqueous layer was decanted off. The solids were washed three times with 5 mL of water and then three times with 5 mL of MeOH. Then, the solids were suspended in 5 mL of MeOH. After 24 h, the suspension was centrifuged, and the MeOH was decanted off. This MeOH soaking step was repeated two more times (for 24 h each). After 3 days of soaking, the solids were isolated by centrifugation and dried under vacuum.

PSE for UiO-66-(H)(Naph)(CB)

BDCE-CB (**5**, 6 mg, 0.018 mmol) was dissolved in THF (1 mL) and 4% aqueous LiOH (1 mL). The solution was stirred at room temperature for 1 h. The THF was removed by evaporation, and the remaining aqueous phase was neutralized to pH 7 with 1 M HCl solution. The solution was added to fully dried UiO-66-(H)(Naph) (17.3 mg, 0.01 mmol), and the mixture was incubated at room temperature. Once the exchange was complete, the microcrystalline powder was separated by centrifugation, and the aqueous phase decanted off. The solids were washed three times with 5 mL of water and then three times with 5 mL of MeOH. Then, the solids were suspended in 5 mL of MeOH. After 24 h, the suspension was centrifuged, and the MeOH was decanted off. This MeOH soaking step was repeated two more times (for 24 h each). After 3 days of soaking, the solids were isolated by centrifugation and dried under vacuum.

Characterization of MOFs

Digestion and analysis of the MOFs by ^{1}H NMR spectroscopy

Approximately 10 mg of UiO-66 was dried under vacuum at 100 °C and digested with sonication in 590 µL of DMSO and 10 µL of HF (48% aqueous solution). For IRMOF, approximately 10 mg of IRMOF sample was dried under vacuum at 100 °C and digested with sonication in 590 µL of DMSO and 10 µL of DCl (in D_2O) solution.

Powder X-ray diffraction of the MOFs

Approximately 10 mg of the MOF sample was air-dried for 1 min prior to PXRD analysis. PXRD data were collected at ambient temperature on a Rigaku Miniflex at 40 kV, 40 mA for CuKa (λ = 1.5406 Å), with a scan speed of 1 sec/step and a 2θ range of 5-30°.

N_2 full isotherm of the MOFs

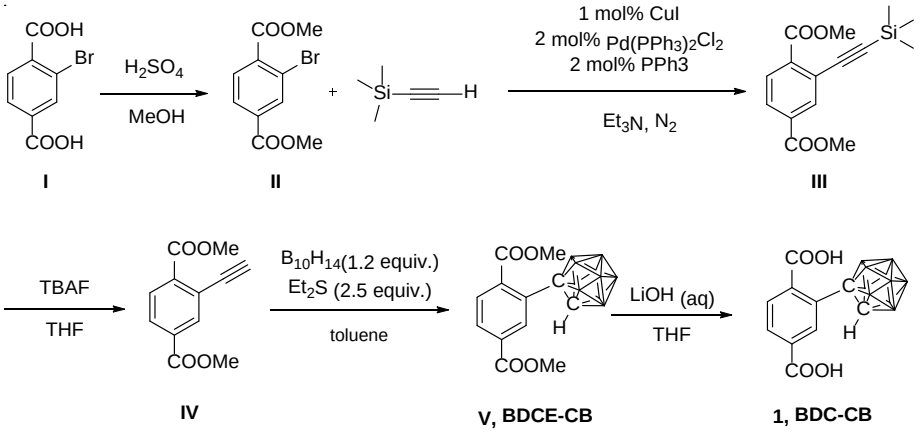
Approximately 50 mg of the MOF sample was evacuated under vacuum for 1 min at room temperature. Samples were then transferred to pre-weighed sample tubes and degassed at 100 °C on a Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 μmHg/min. The sample tube was reweighted to obtain a constant mass of the degassed MOF materials. For the calculation of BET surface area (m^2/g), N_2 nitrogen adsorption isotherms were measured at 77K on a Micromeritics ASAP 2020 Adsorption Analyzer using a volumetric technique.

Thermal analysis of the MOFs

Approximately 10 mg of MOF sample was used for TGA measurements after BET analysis (activated). The sample was analyzed under a stream of N_2 using a TGA (Scinco N-1000); running from room temperature to 800 °C at a scan rate of 10 °C/min.

Photoluminescence (PL) spectroscopy experiments

PL spectroscopic measurements (using a Fluoromax-4P Luminescence Spectrophotometer from HORIBA, λ_{ex} = 395 nm) in the solid state for the carborane-functionalized ligands and MOFs were performed on a 15 × 15 mm quartz plate (thickness = 1 mm).



Scheme S1 Synthesis of BDC-CB (**1**).

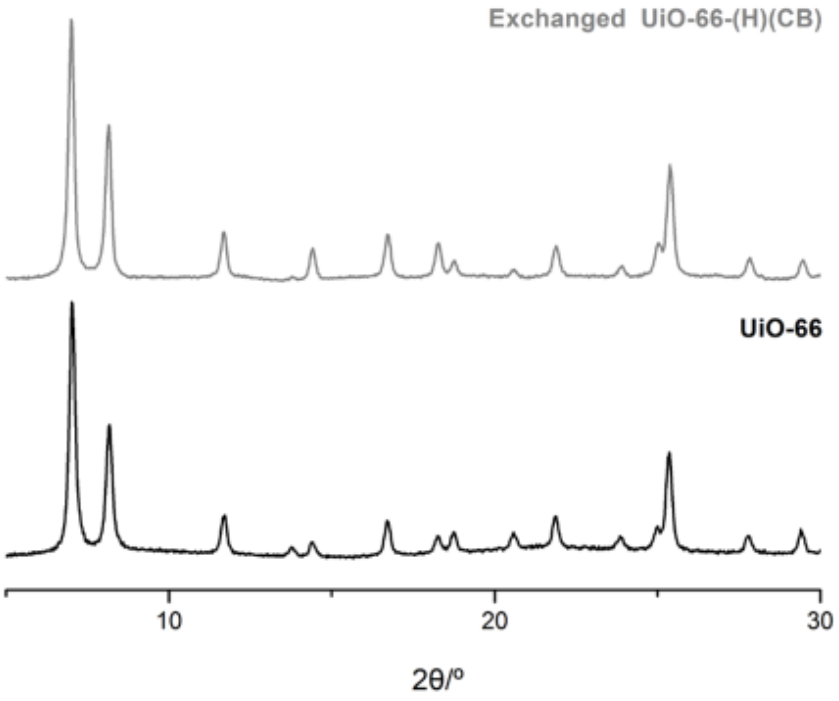


Fig. S1 PXRD patterns of UiO-66- and exchanged UiO-66-(H)(CB).

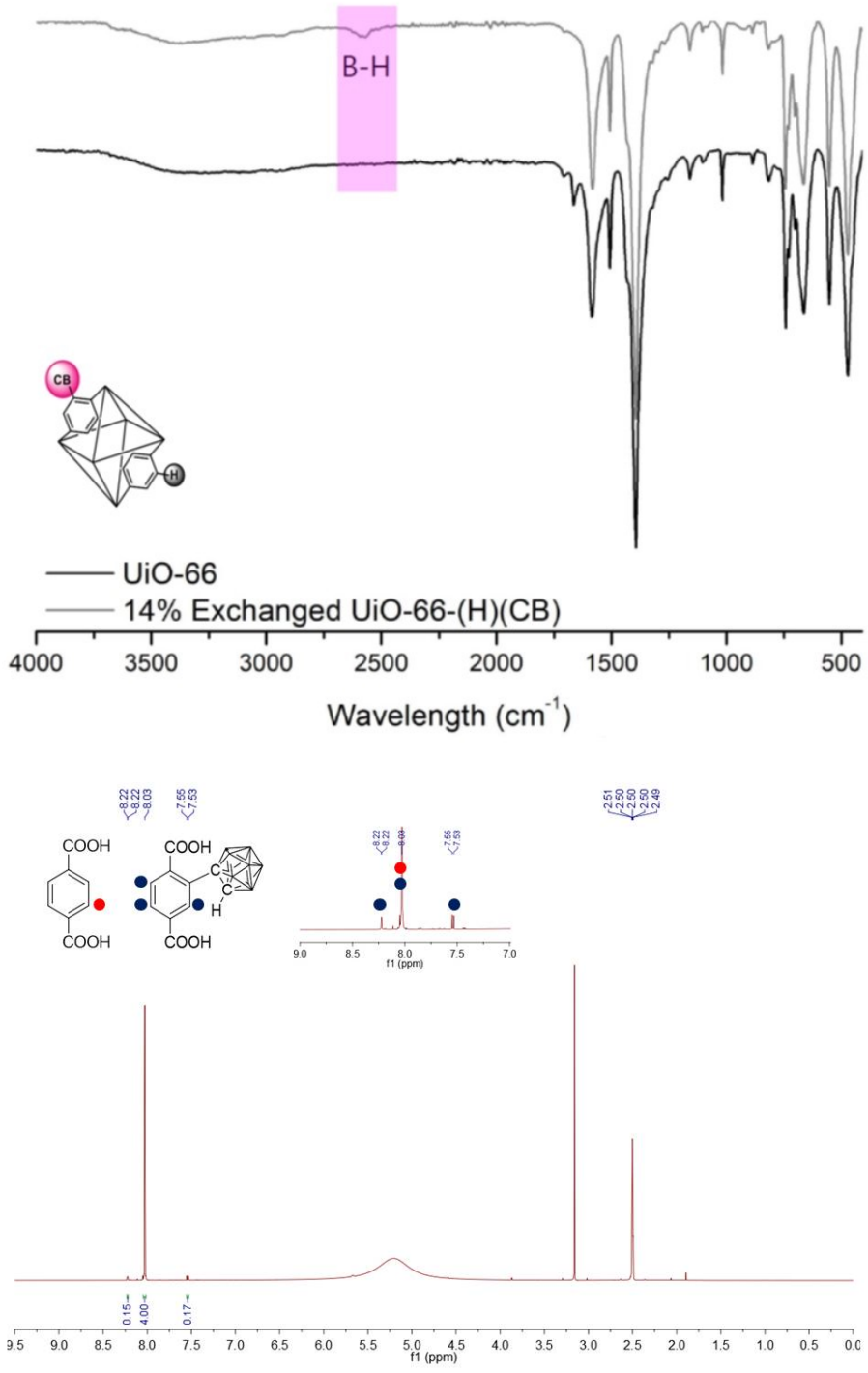


Fig. S2 IR spectra (top) and ^{1}H NMR spectra (bottom) of exchanged UiO-66-(H)(CB).

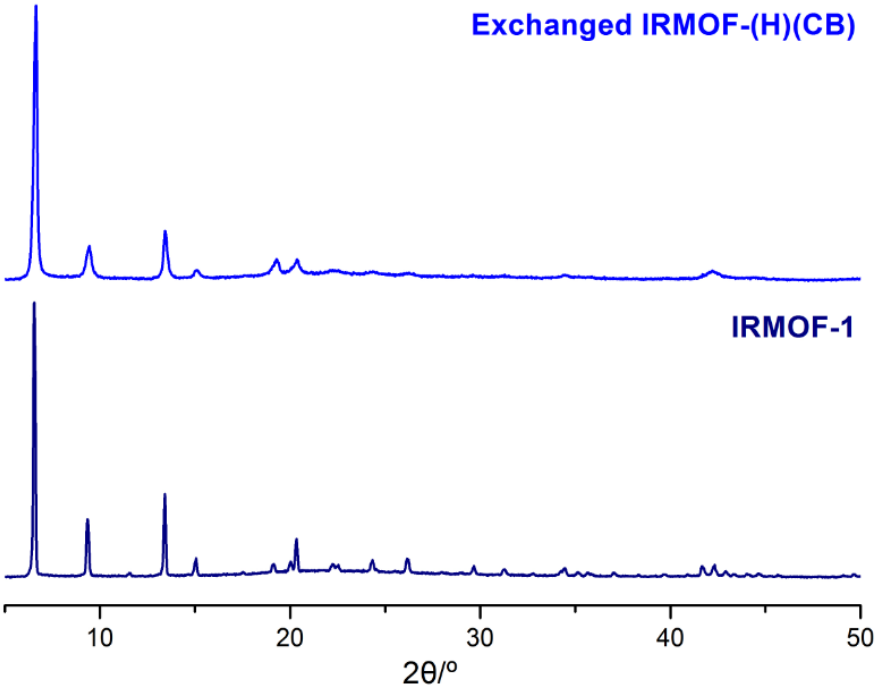


Fig. S3 PXRD of IRMOF and exchanged IRMOF-CB

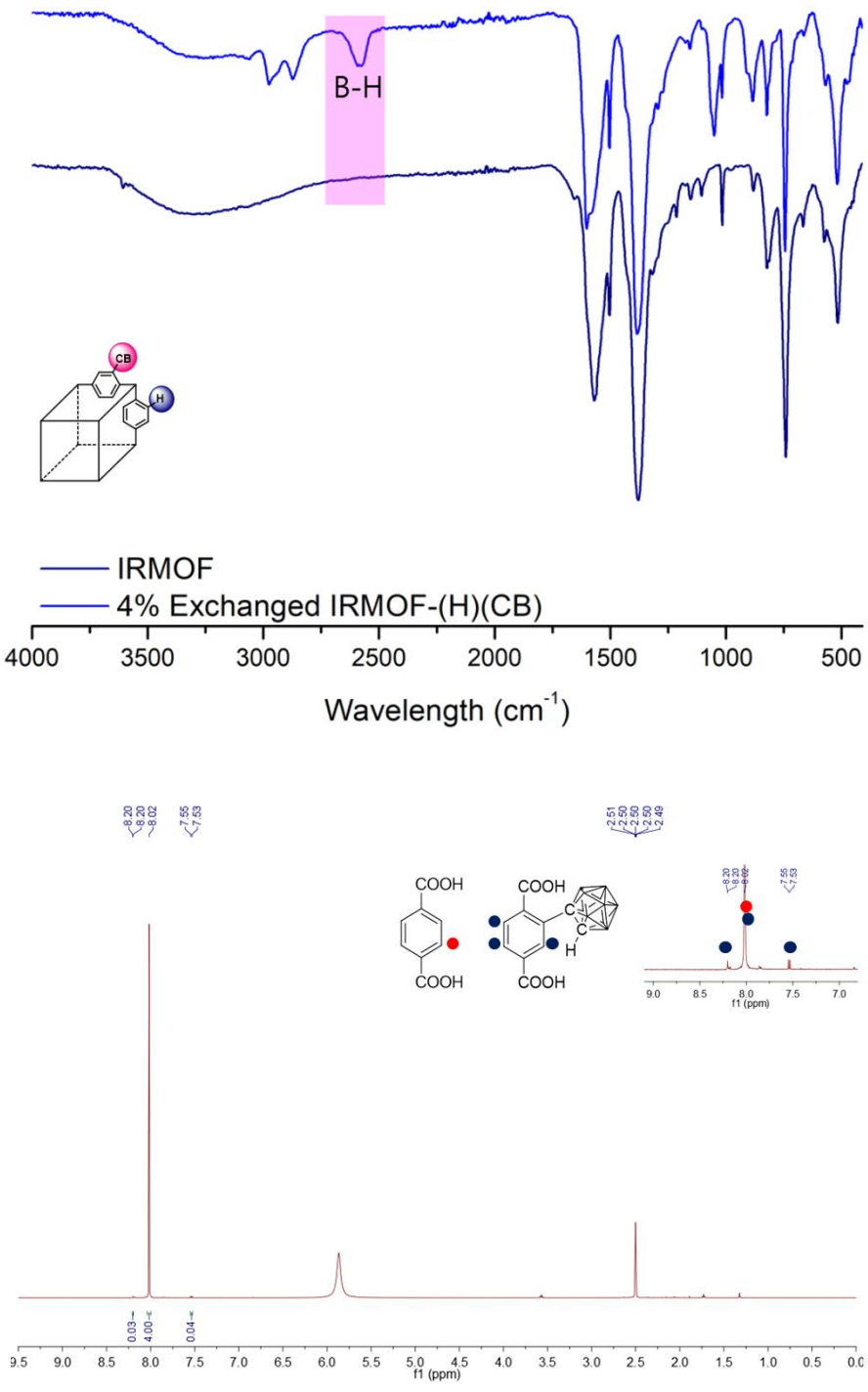


Fig S4 IR spectra (top) and ^{1}H NMR spectra (bottom) of exchanged IRMOF-(H)(CB).

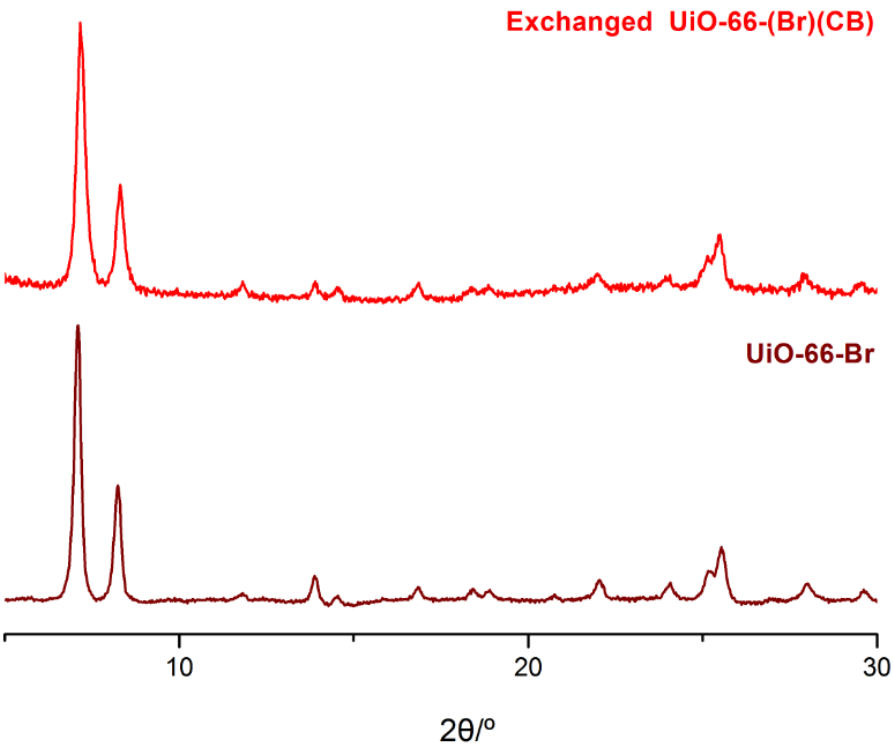


Fig. S5 PXRD of UiO-66-Br and exchanged UiO-66-(Br)(CB).

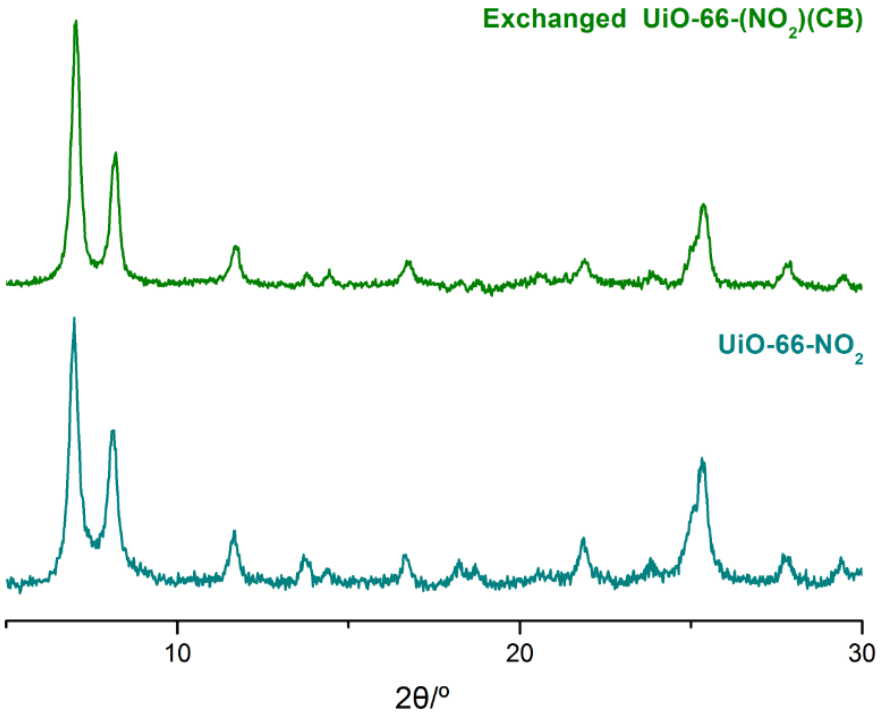


Fig. S6 PXRD of UiO-66-NO_2 and exchanged UiO-66-(NO_2)(CB).

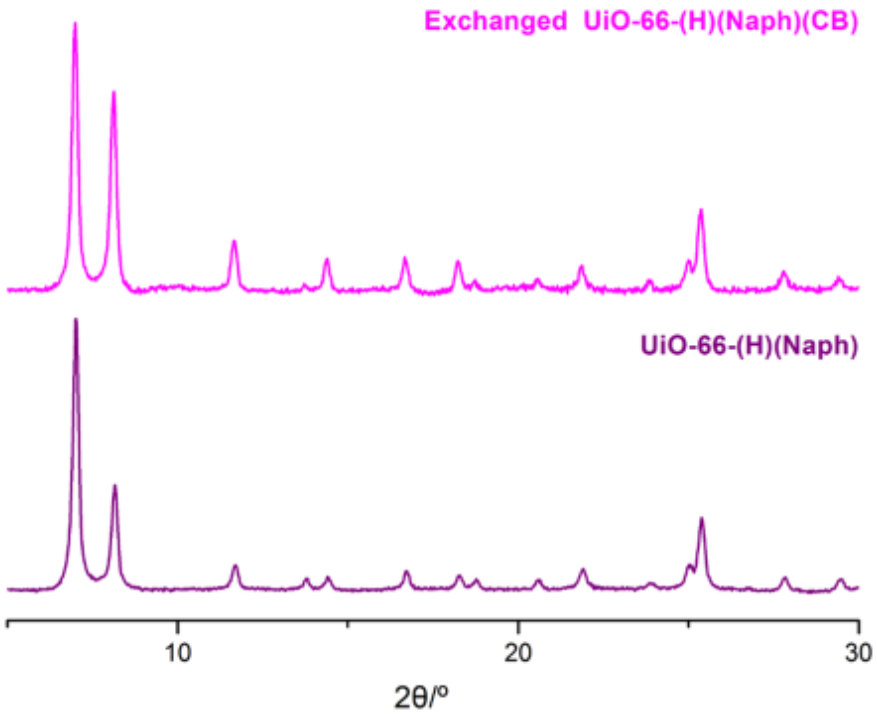


Fig. S7 PXRD of UiO-66-(H)(Naph) and exchanged UiO-66-(H)(Naph)(CB).

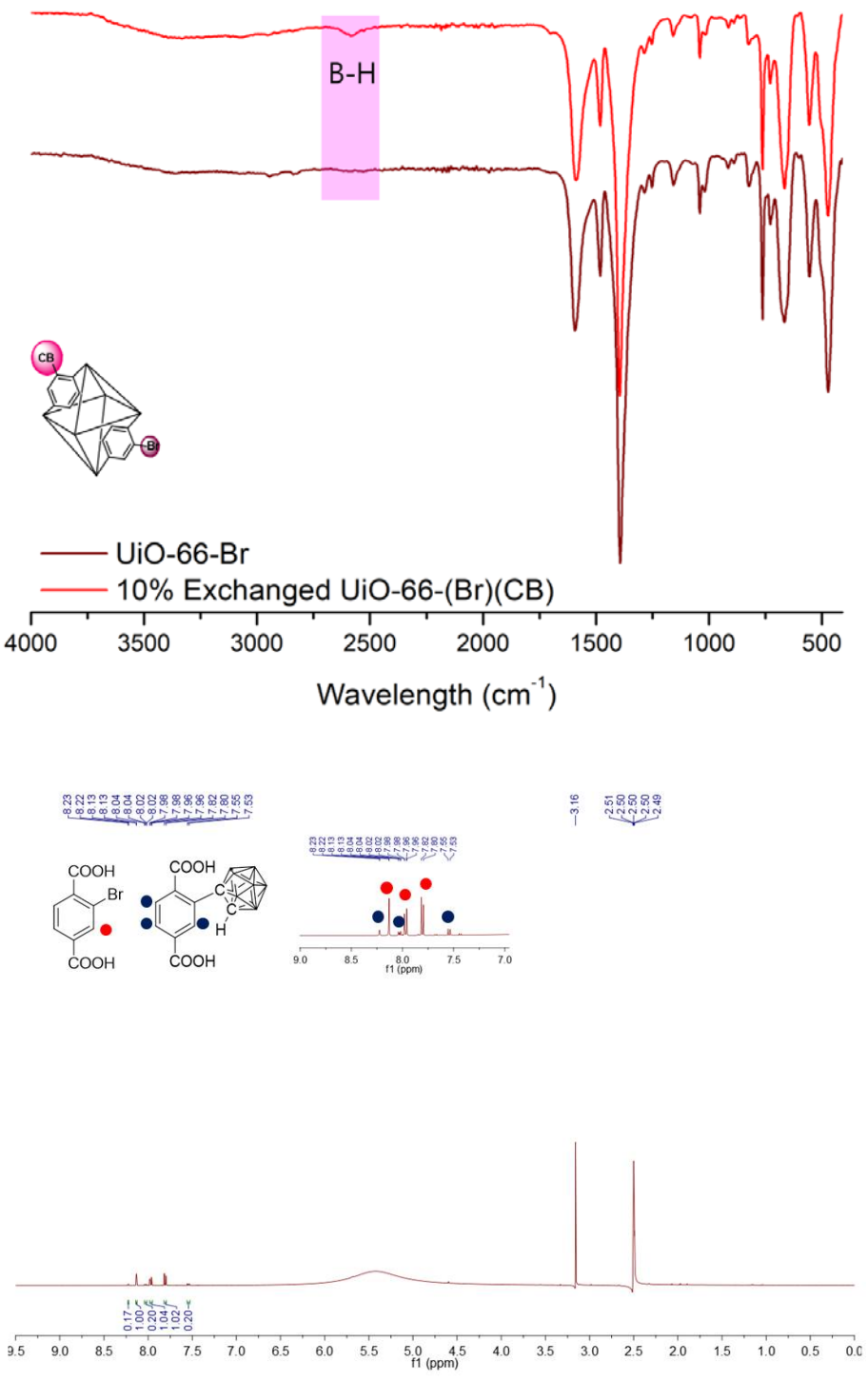


Fig. S8 IR spectra (top) and ^{1}H NMR spectra (bottom) of exchanged UiO-66-(Br)(CB).

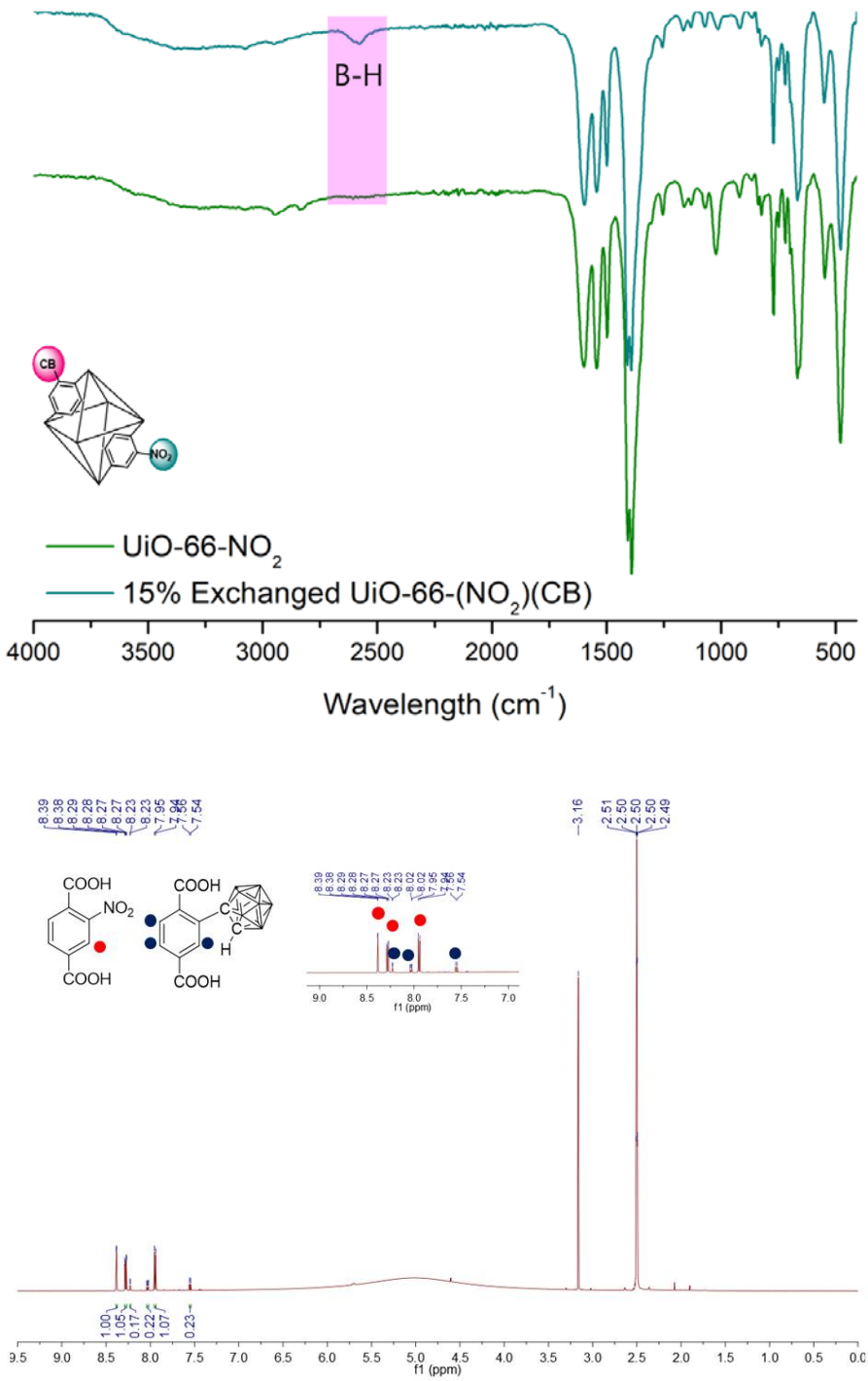


Fig. S9 IR spectra (top) and ^{1}H NMR spectra (bottom) of exchanged UiO-66-(NO_2)(CB).

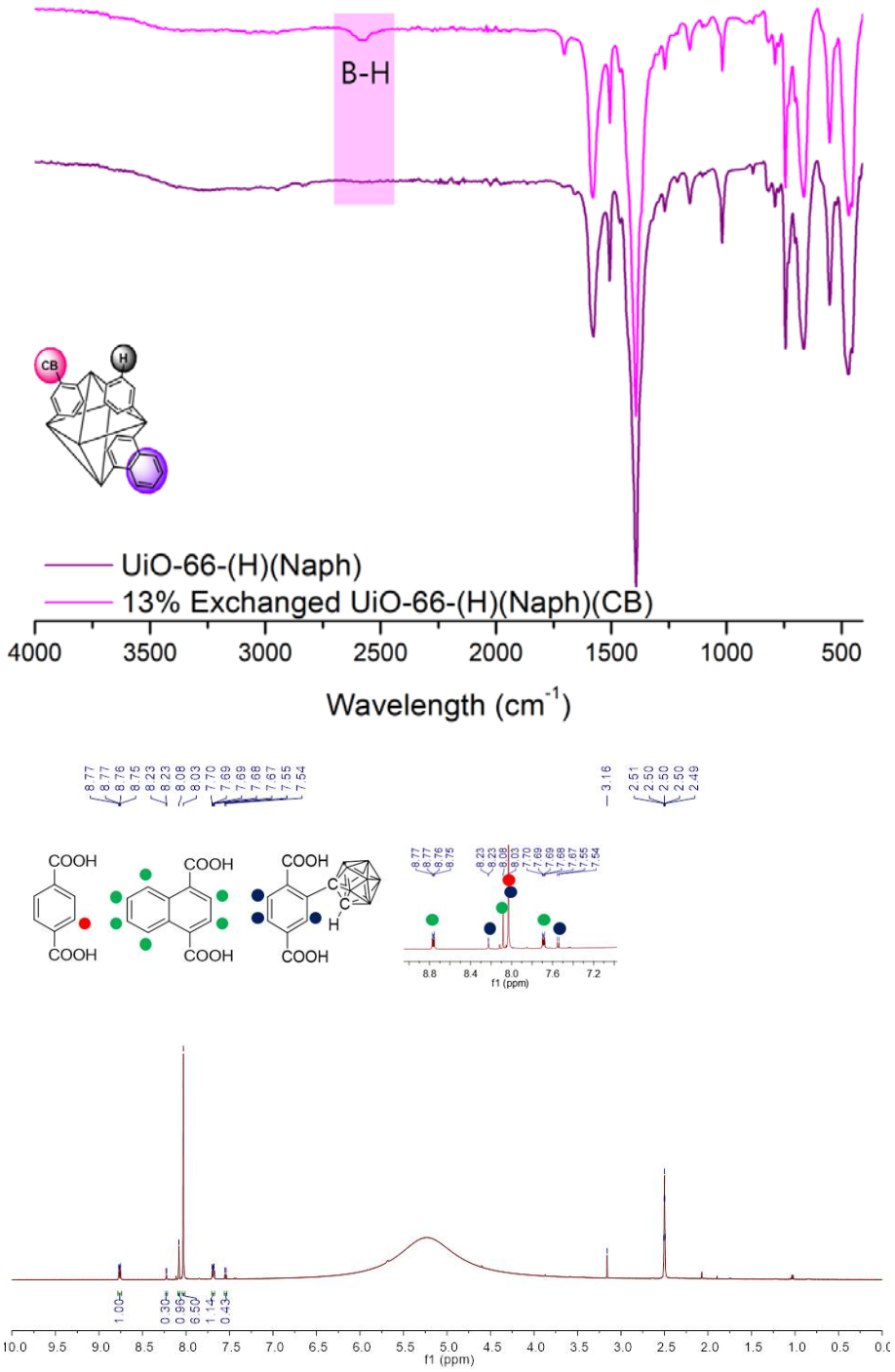


Fig. S10 IR spectra (top) and ^{1}H NMR spectra (bottom) of exchanged UiO-66-(H)(Naph)(CB).

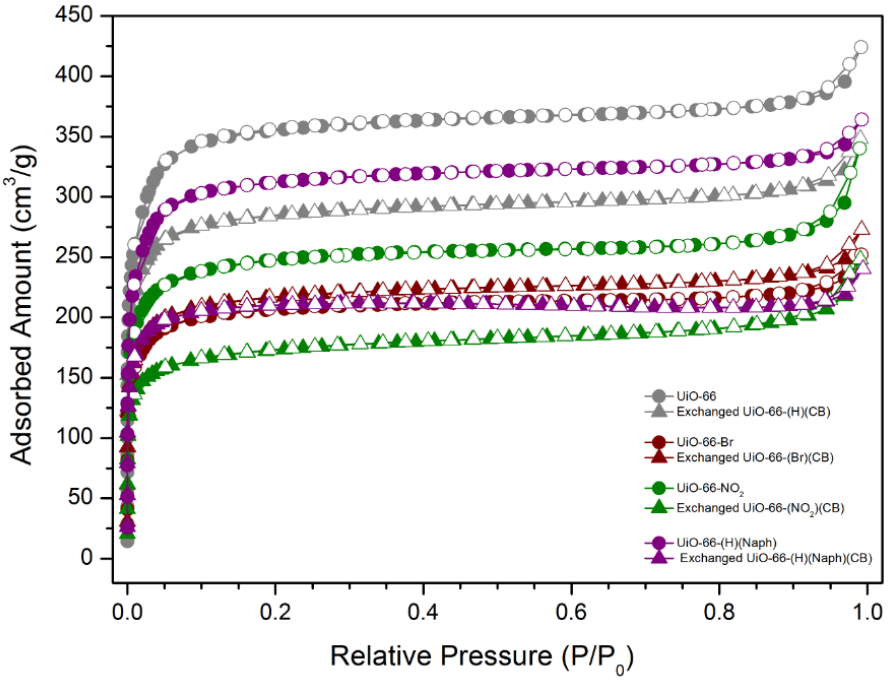


Fig. S11 N_2 full isotherm (at 77K) for UiO-66s and exchanged UiO-66-(R)(CB)s.

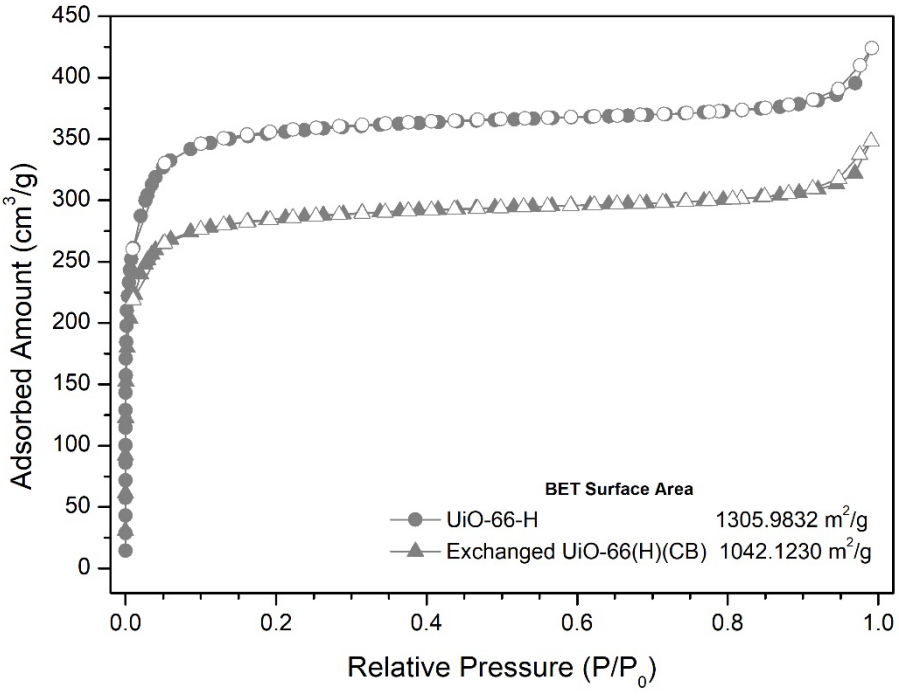


Fig. S12 N_2 full isotherm (at 77K) and BET surface area for UiO-66 and exchanged UiO-66-(H)(CB).

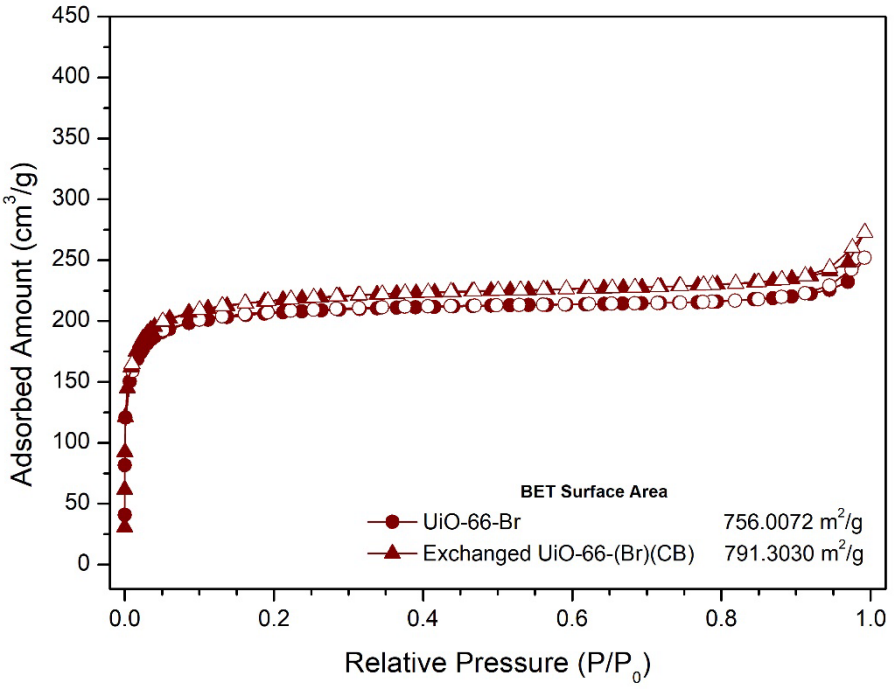


Fig. S13 N_2 full isotherm (at 77K) and BET surface area for UiO-66-Br and exchanged UiO-66-(Br)(CB).

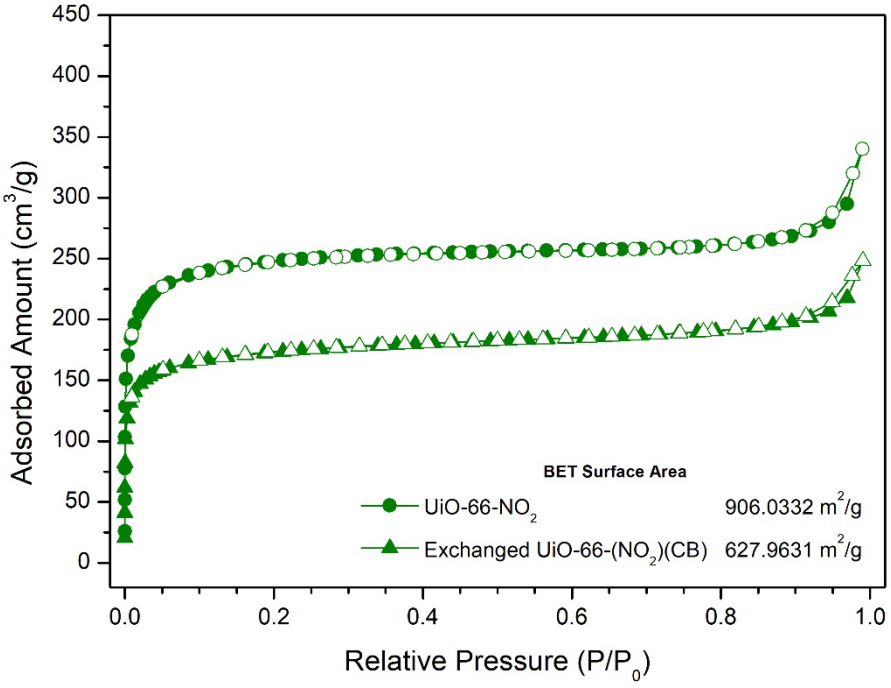


Fig. S14 N_2 full isotherm (at 77K) and BET surface area for UiO-66-NO_2 and exchanged UiO-66-(NO_2)(CB).

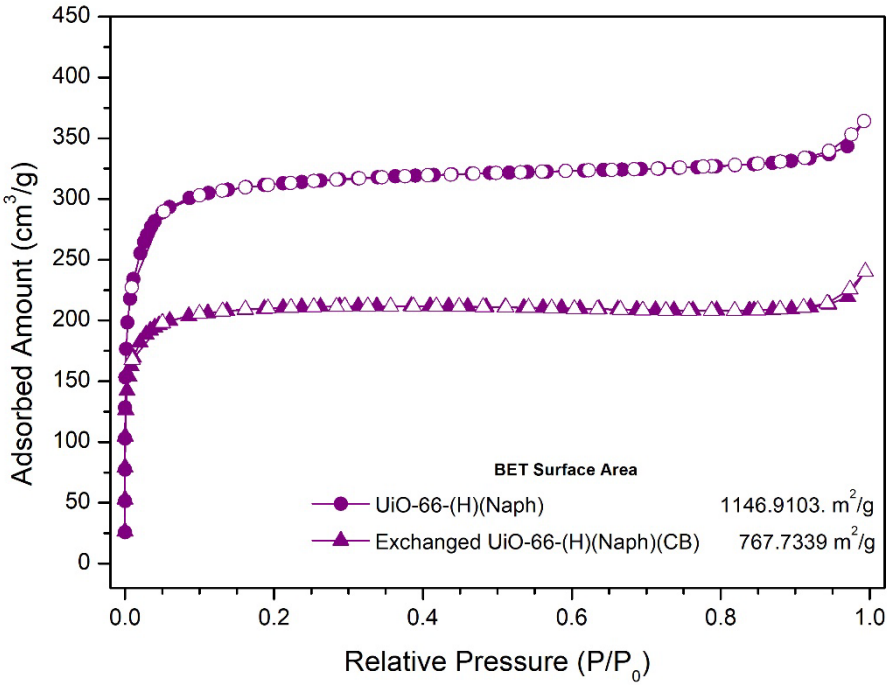


Fig. S15 N_2 full isotherm (at 77K) and BET surface area for UiO-66-(H)(Naph) and exchanged UiO-66-(H)(Naph)(CB).

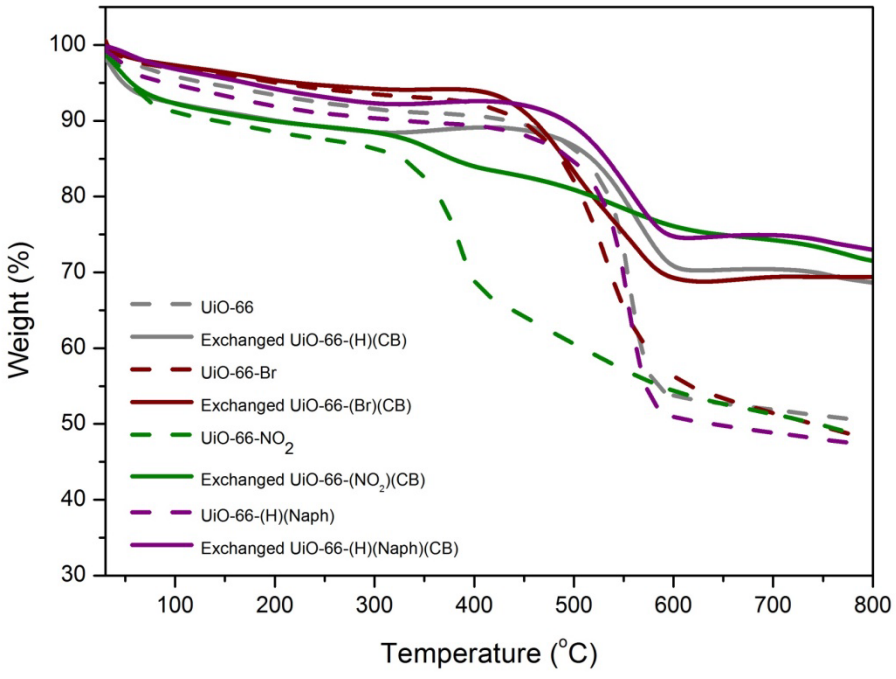


Fig. S16. Thermogravimetric analysis (TGA) of UiO-66 and exchanged UiO-66-Rs with carborane functionalities.

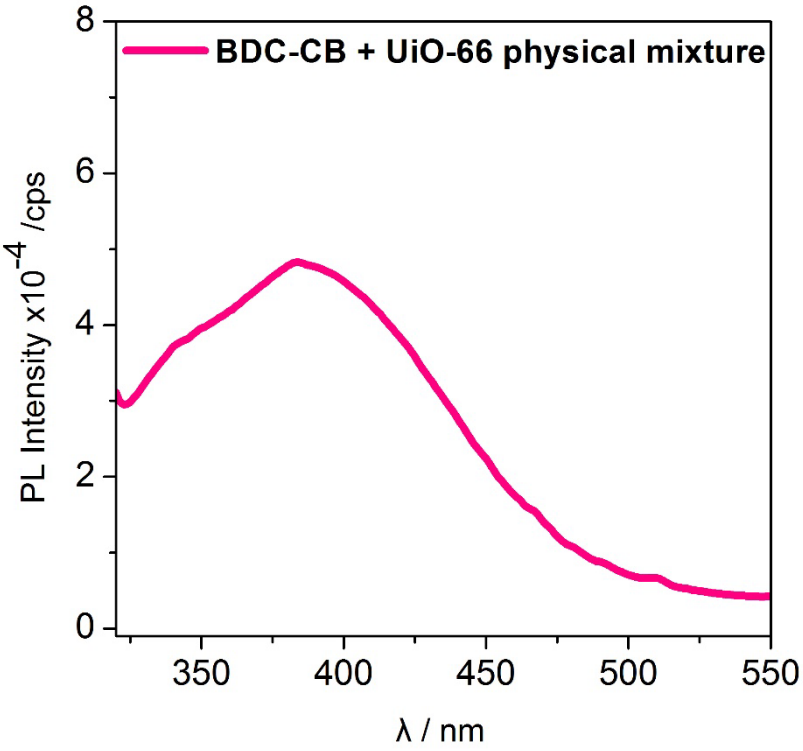


Fig. S17 Photoluminescence (PL) spectra of the physical mixture of BDC-CB and UiO-66 (10 mol% of BDC-CB to UiO-66).

References for Electronic Supporting Information

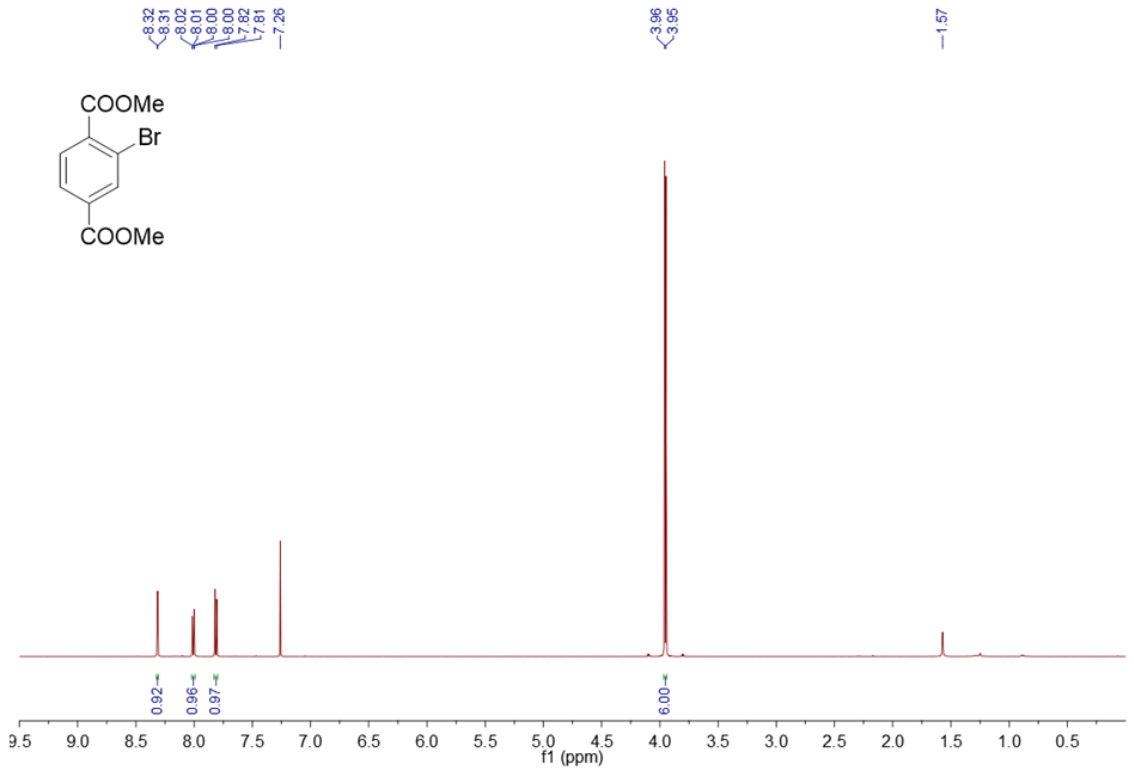
S1 M. J. Katz, Z. J. Brown, Y. J. Colón, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp and O. K. Farha, *Chem. Commun.*, 2013, **49**, 9449–9451.

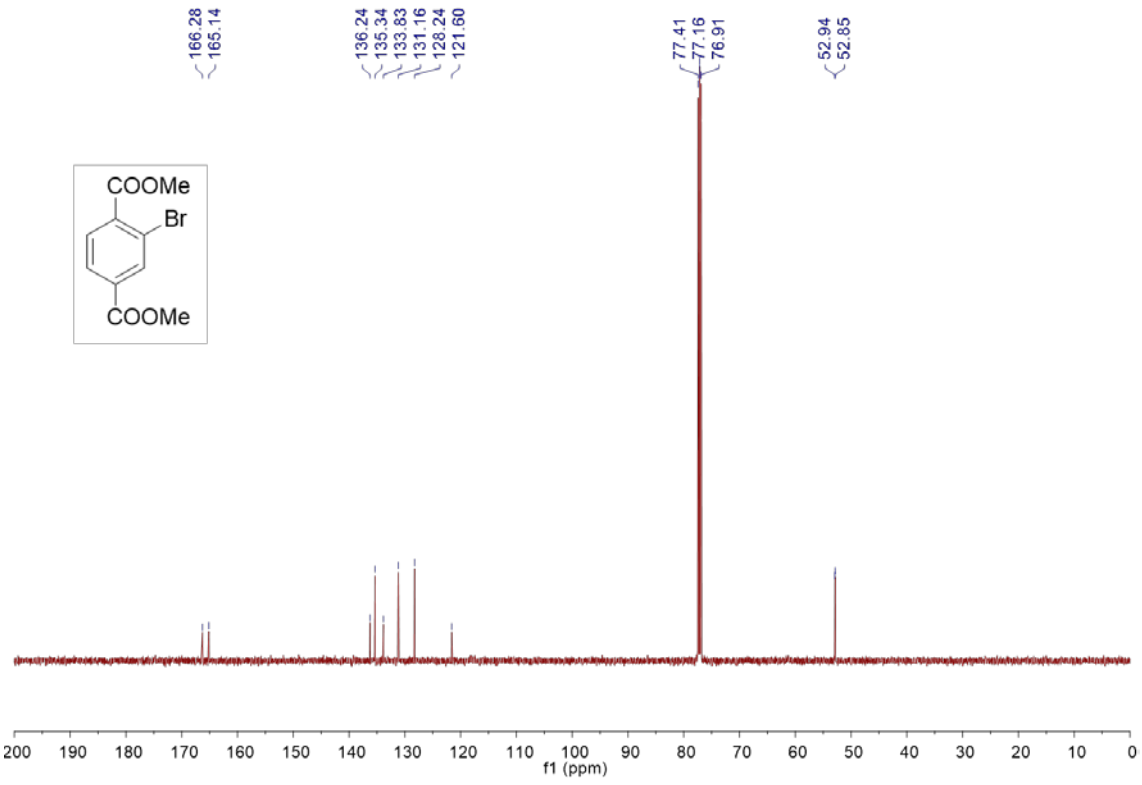
S2 J. L. C. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 1304–1315.

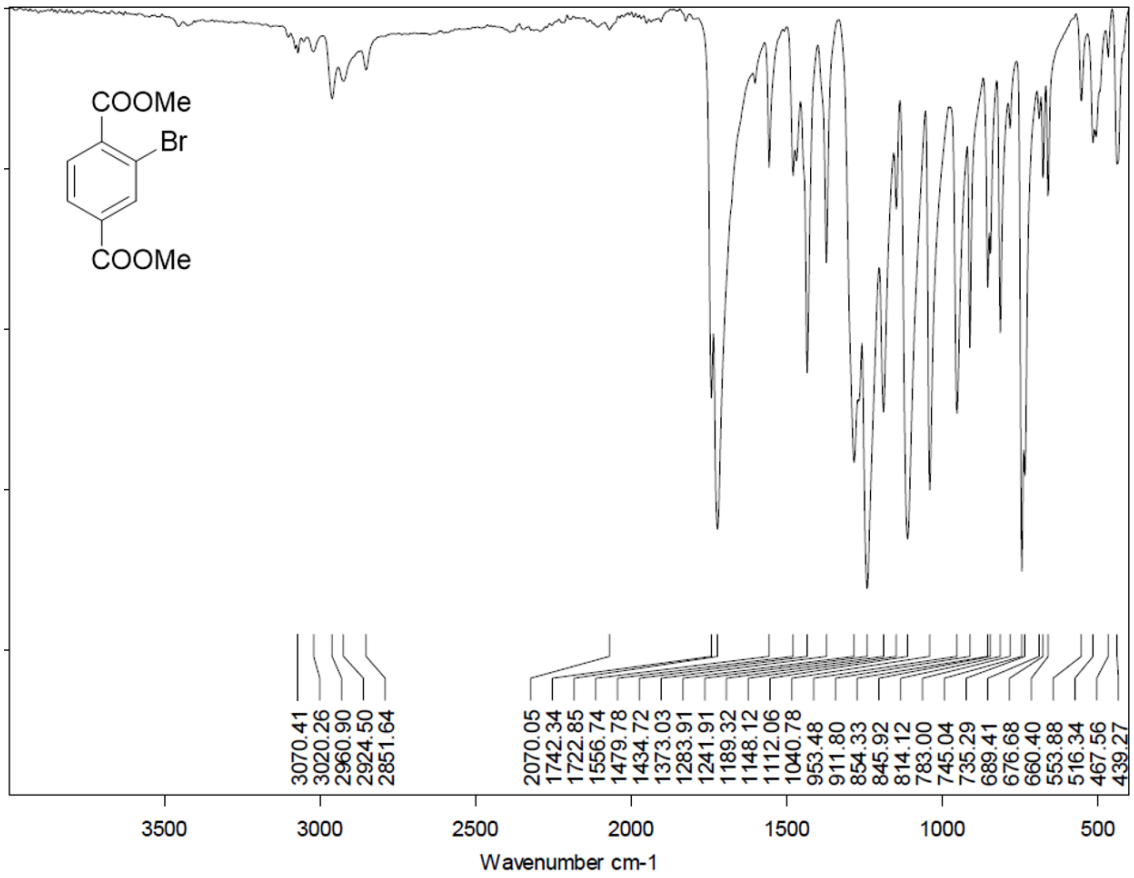
APPENDIX A

^{1}H NMR, ^{13}C NMR, ^{11}B NMR and IR Spectra of the Obtained Compounds

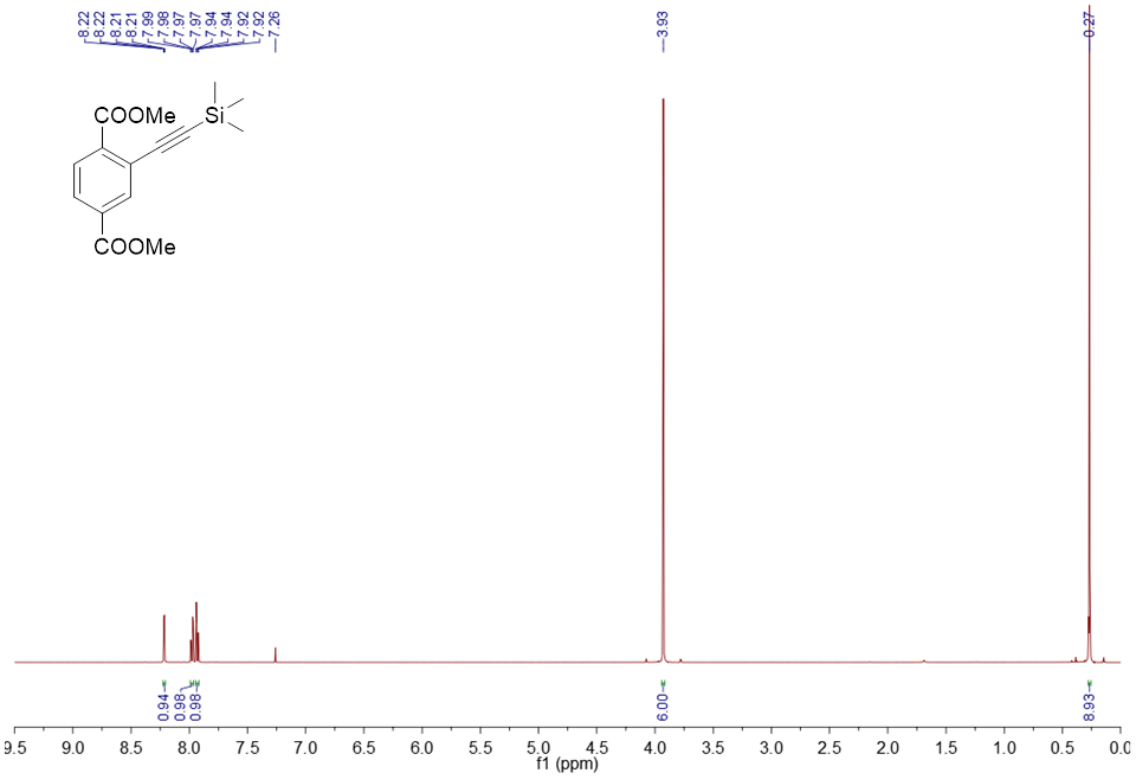
Dimethyl 2-bromoterephthalate (**II**)

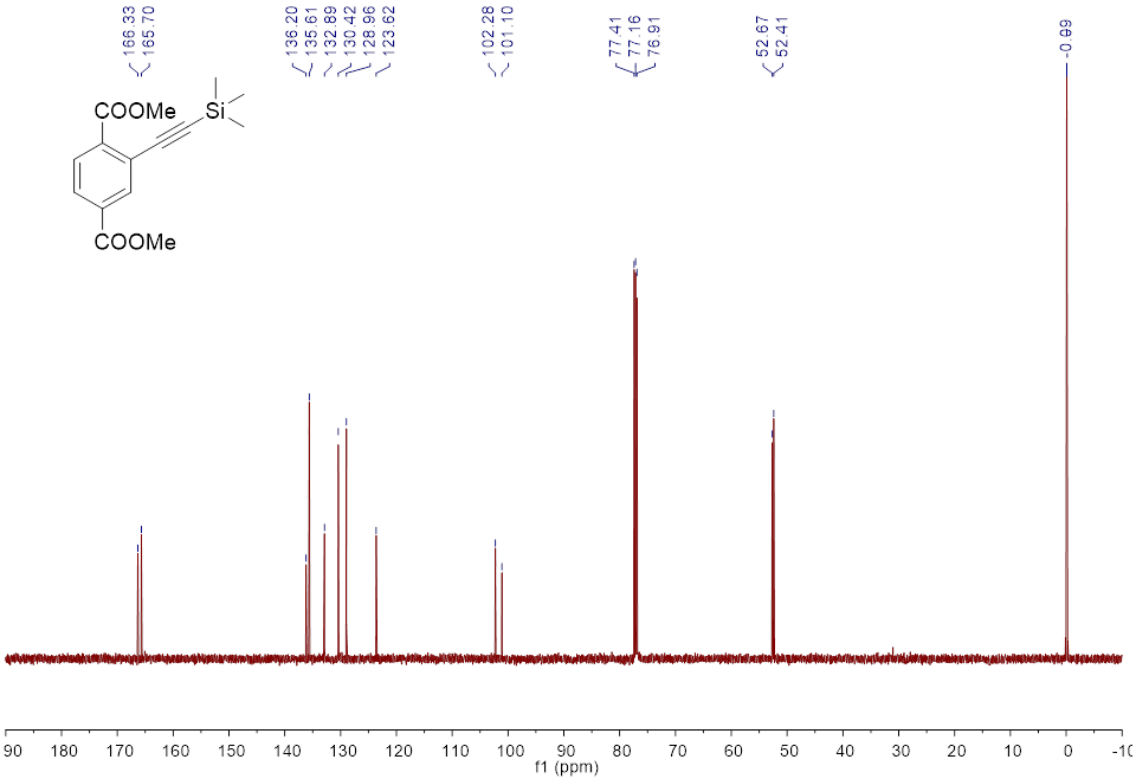


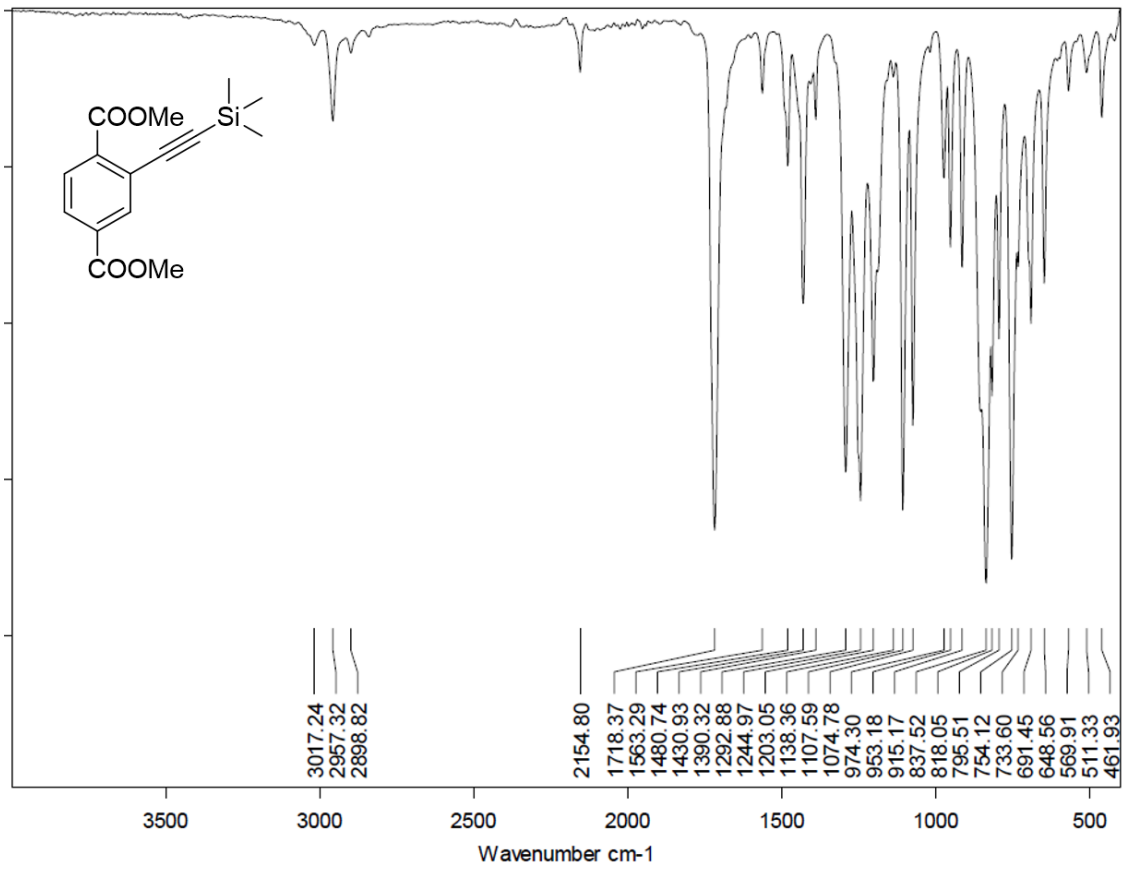



COOMe
Br
COOMe
3070.41
3020.26
2960.90
2924.50
2851.64
2070.05
1742.34
1722.85
1556.74
1479.78
1434.72
1373.03
1283.91
1241.91
1189.32
1148.12
1112.06
1040.78
953.48
911.80
854.33
845.92
814.12
783.00
745.04
735.29
689.41
676.68
660.40
553.88
516.34
467.56
439.27
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

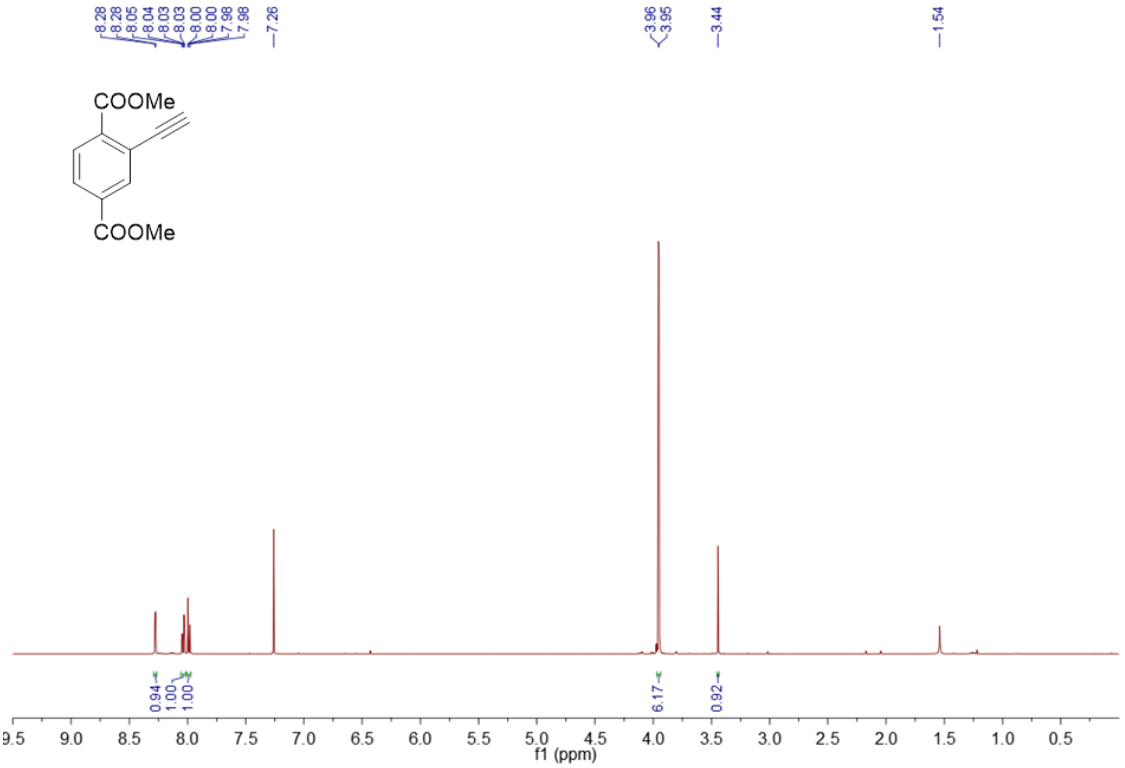
Dimethyl 2-((trimethylsilyl)ethynyl)terephthalate (**III**)

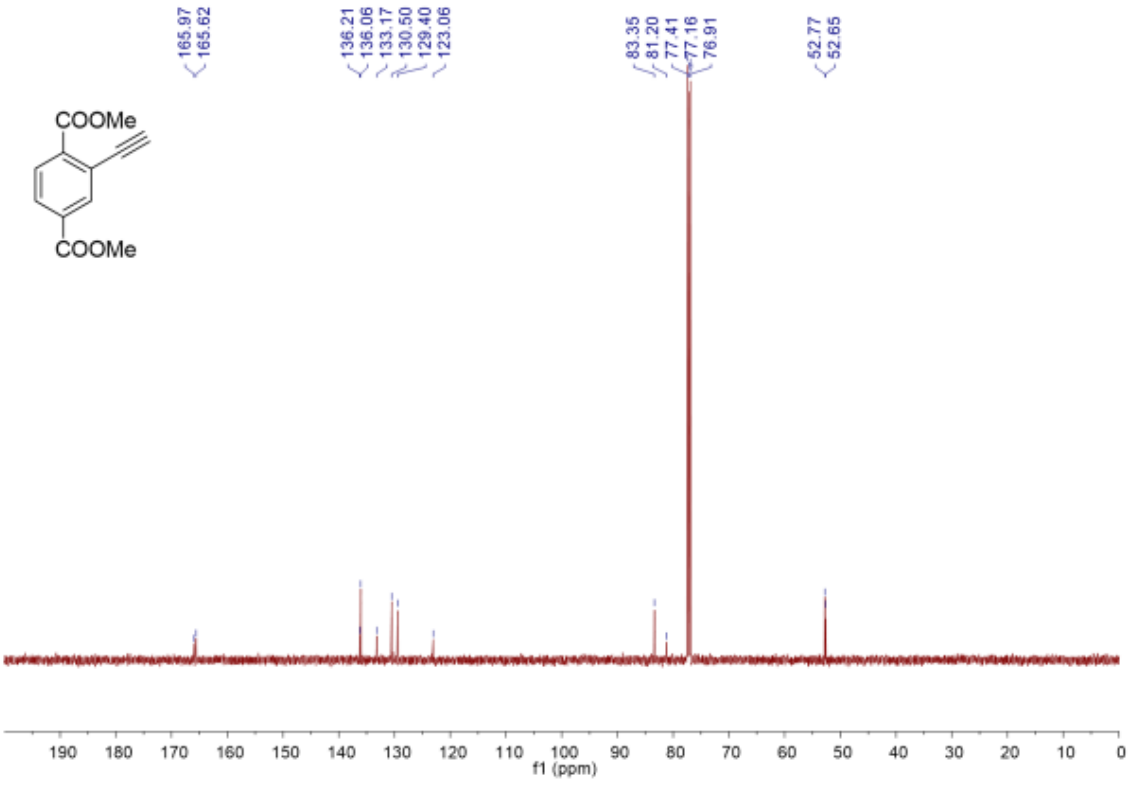


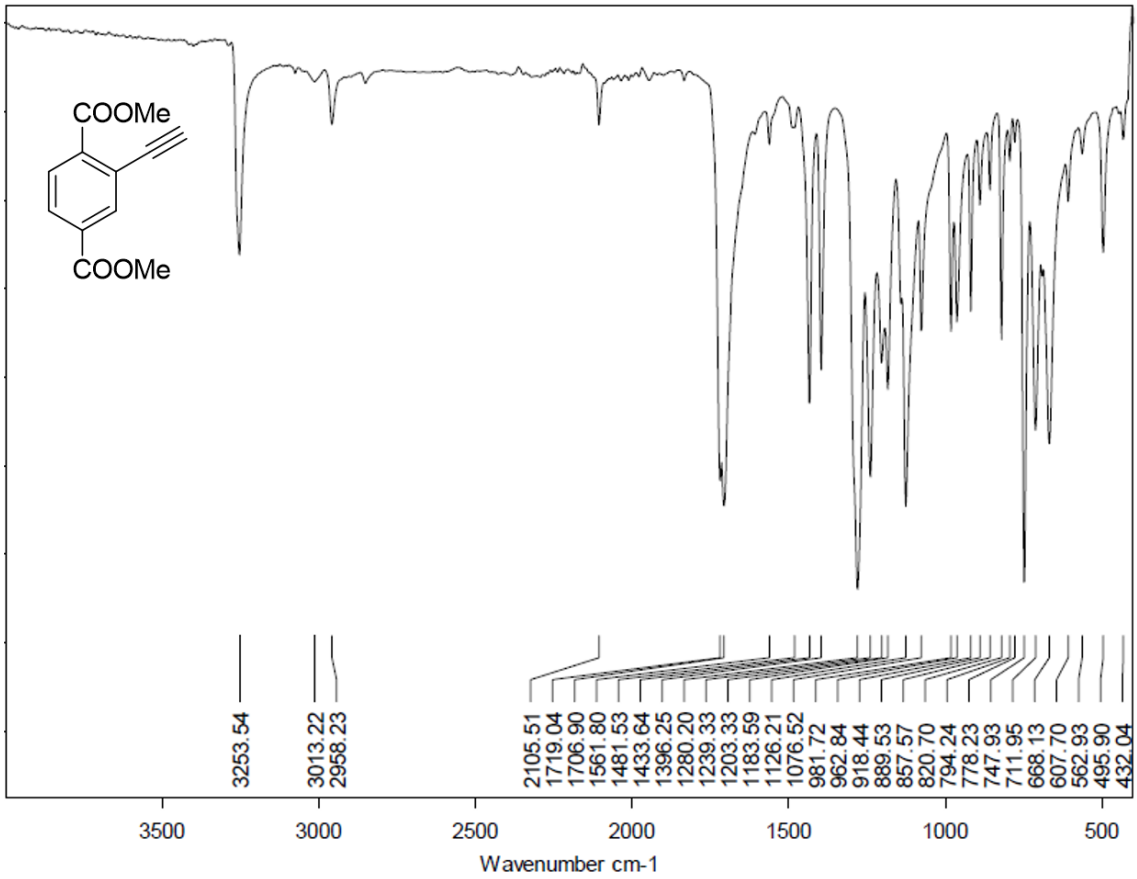



COOMe
Si
COOMe
3017.24
2957.32
2898.82
2154.80
1718.37
1563.29
1480.74
1430.93
1390.32
1292.88
1244.97
1203.05
1138.36
1107.59
1074.78
974.30
953.18
915.17
837.52
818.05
795.51
754.12
733.60
691.45
648.56
569.91
511.33
461.93
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

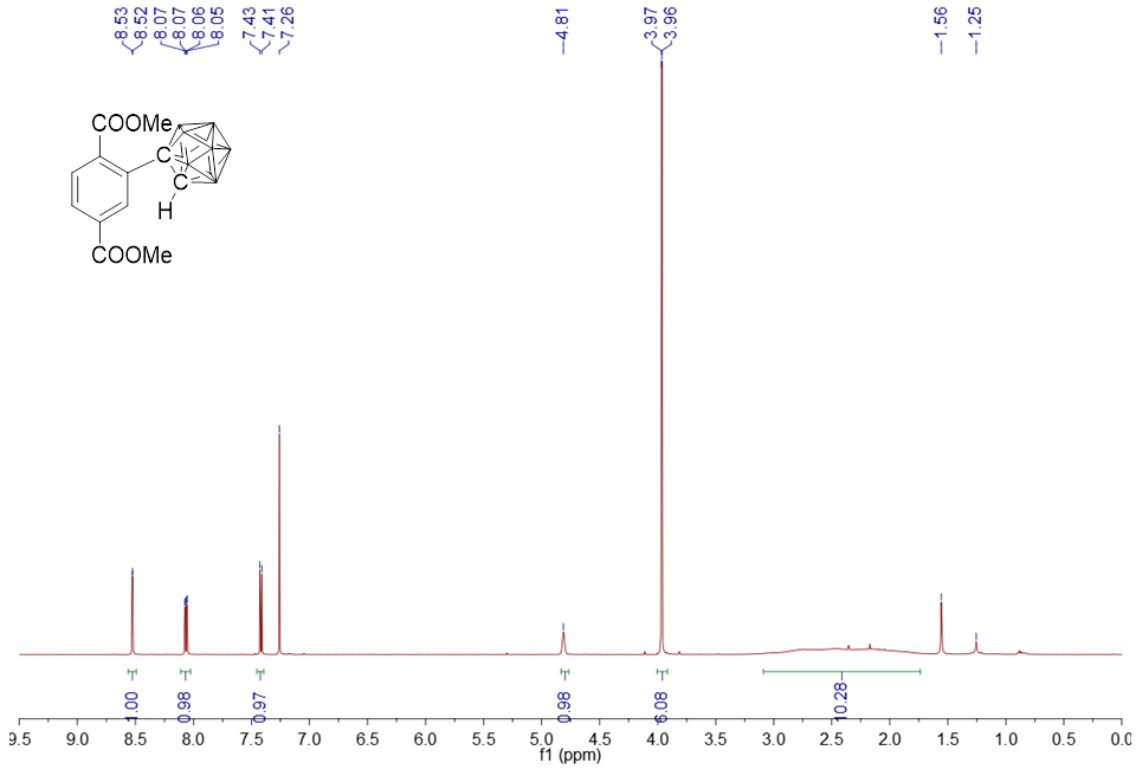
Dimethyl 2-ethynylterephthalate (**IV**)

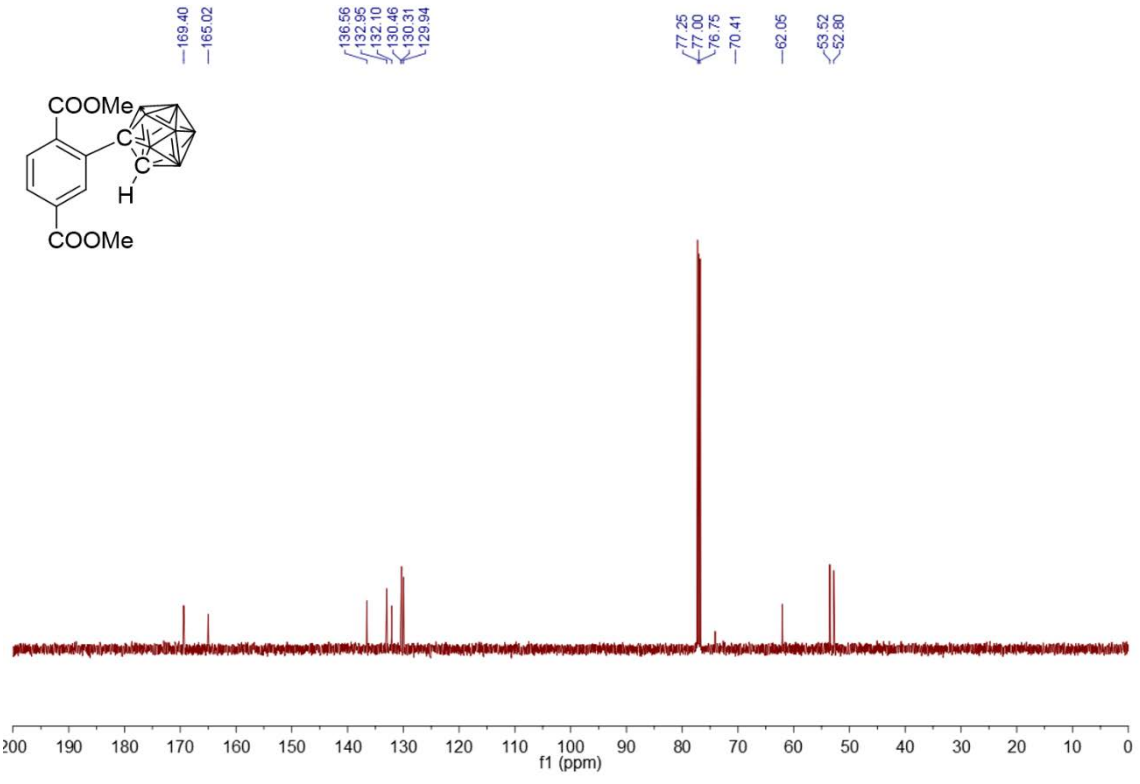


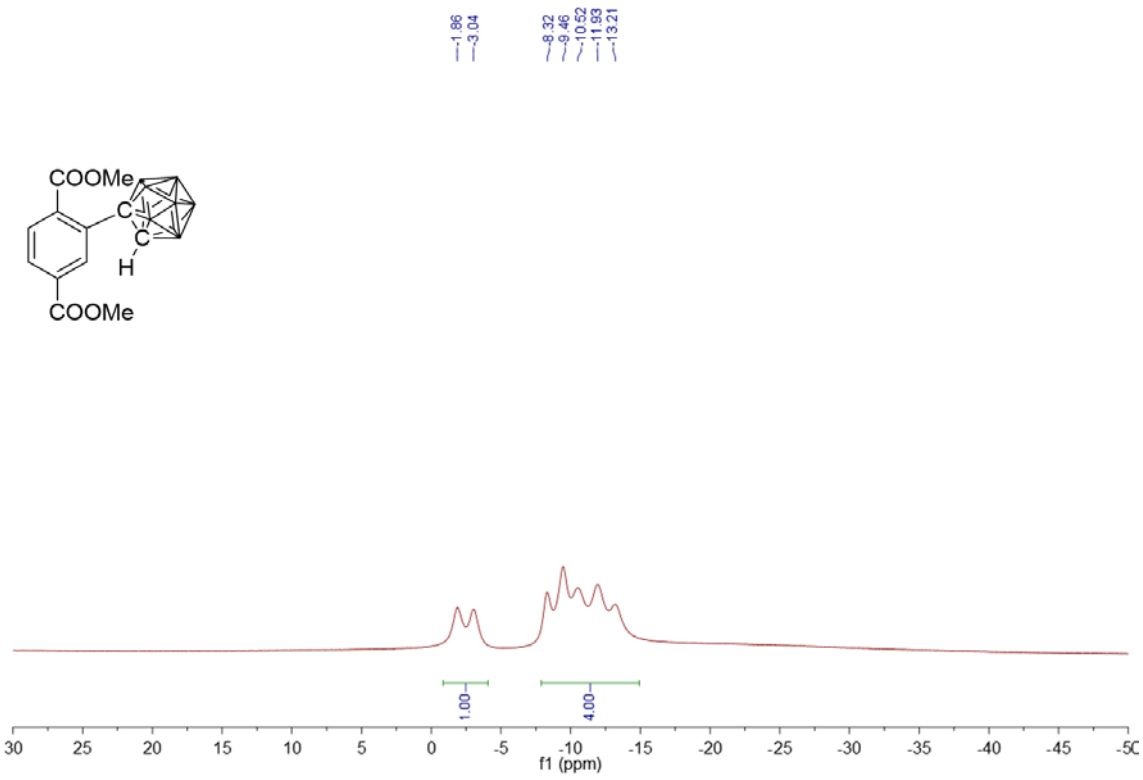



COOMe
COOMe
3253.54
3013.22
2958.23
2105.51
1719.04
1706.90
1561.80
1481.53
1433.64
1396.25
1280.20
1239.33
1203.33
1183.59
1126.21
1076.52
981.72
962.84
918.44
889.53
857.57
820.70
794.24
778.23
747.93
711.95
668.13
607.70
562.93
495.90
432.04
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

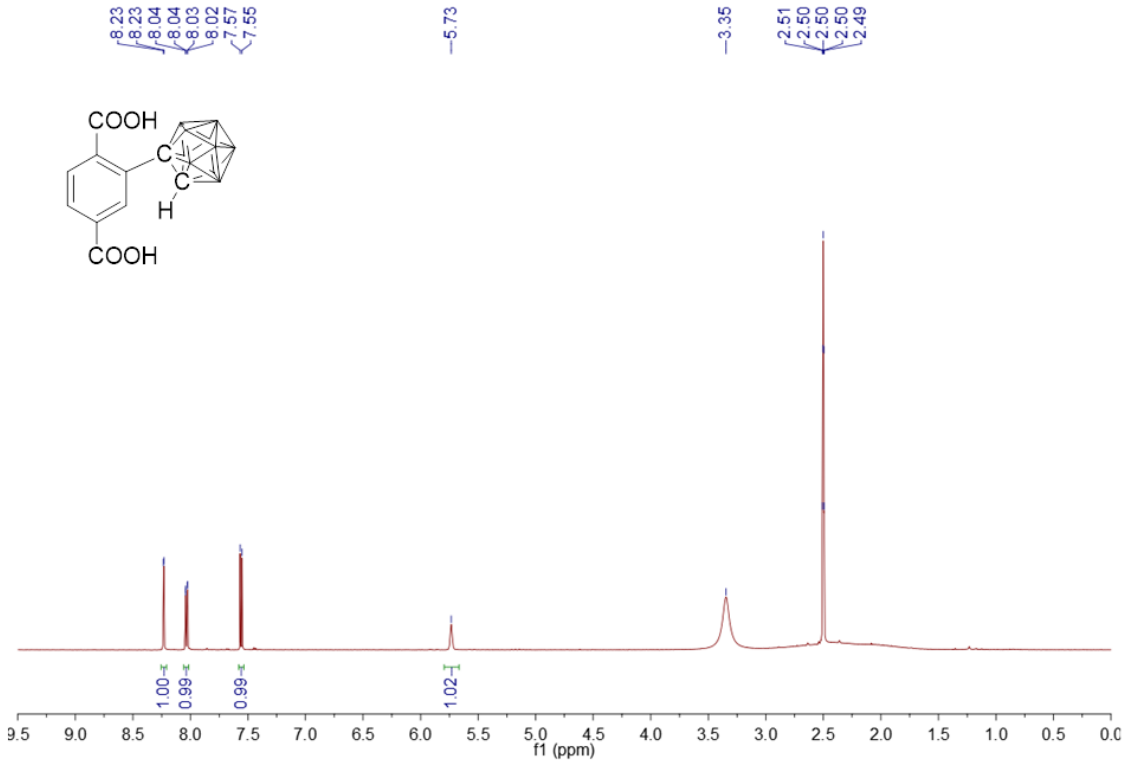
Dimethyl 2-o-carboraneterephtalate (**V**)

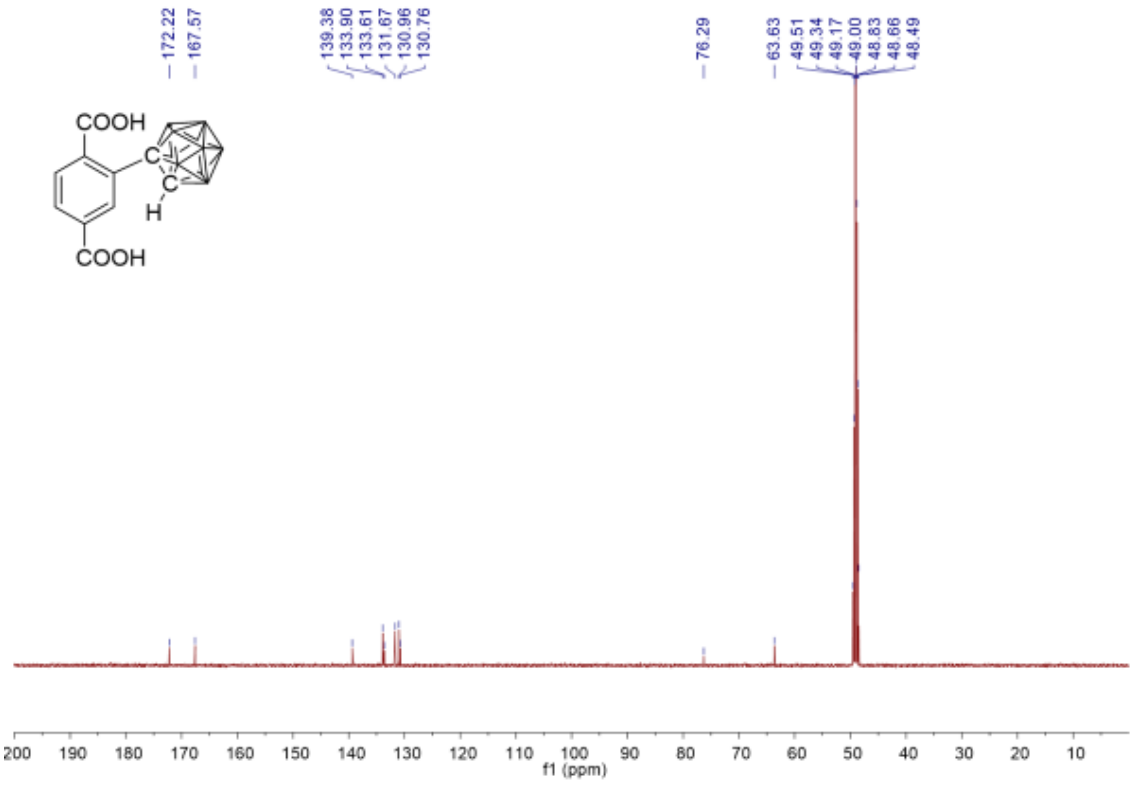


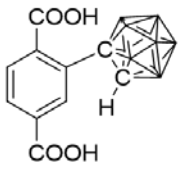



1.86
3.04
8.32
9.46
10.52
11.93
13.21
COOMe
C
C
H
COOMe
1.00
4.00
30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)
COOMe
C
C
H
COOMe
B-H
3066.36
2957.69
2922.96
2851.02
2665.13
2641.12
2597.32
2560.93
2093.28
1946.27
1726.50
1565.95
1491.65
1432.88
1388.81
1296.49
1263.88
1228.61
1194.03
1120.18
1079.49
1029.44
1004.62
973.50
950.58
917.50
859.20
831.87
818.87
800.51
780.95
745.75
731.95
706.21
661.14
612.28
569.94
551.88
534.60
514.49
493.50
448.43
3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1

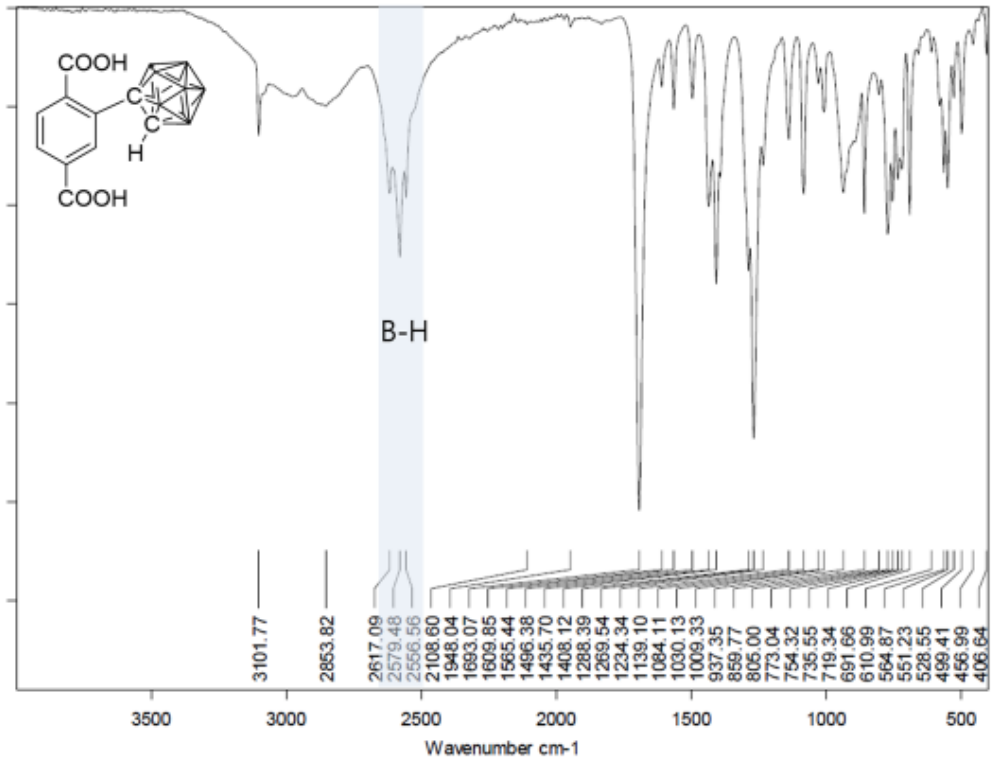
2-*o*-Carboraneterephtalic acid (**1**)






COOH
C
C
H
COOH

-2.34
-3.47
-8.54
-9.69
-11.98
-13.32
1.00
4.57
30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -5
f1 (ppm)


COOH
C
C
H
COOH
B-H
3101.77
2853.82
2617.09
2579.48
2556.56
2108.60
1948.04
1693.07
1609.85
1565.44
1496.38
1435.70
1408.12
1288.39
1269.54
1234.34
1139.10
1084.11
1030.13
1009.33
937.35
859.77
805.00
773.04
754.32
735.55
719.34
691.66
610.99
564.87
551.23
528.55
499.41
456.99
406.64
3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1