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Fluorinated microporous organic polymers: Design and applications in CO_2 adsorption and conversion

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1. General experimental methods

Materials

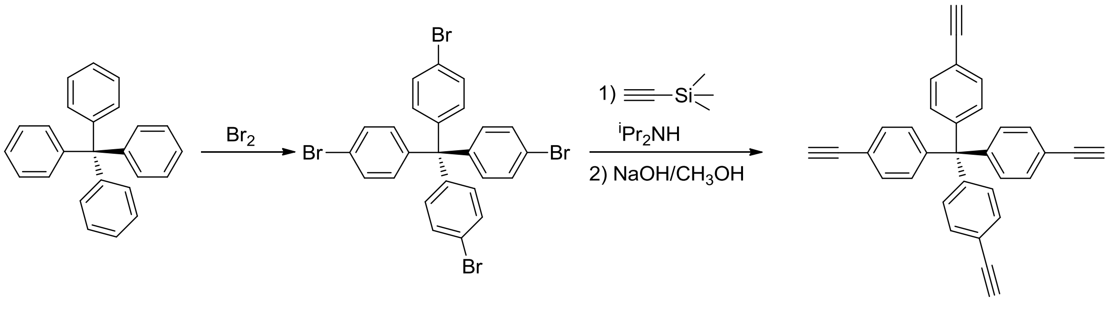
All reagents and solvents were purchased from commercial sources and were used without further purification, unless indicated otherwise. Tetrakis(4-ethynylphenyl)methane (**A**),[1] MOPs shown in Scheme 1 in the text,[2] propargyl alcohols,[3] coordination of $AgBF_4$ with polymers and 1,10-phenanthroline,[4] complex from $AgBF_4$, 1,10-phenanthroline and deep,**[5]** **F-NHC-Ag**[6] were prepared following procedures reported in the literature and some with modifications.

Instrumentation

Liquid ^1H NMR spectra was recorded in $CDCl_3$ using residual $CHCl_3$ as internal reference (7.26 ppm) on Bruck 400 spectrometer. Liquid ^{13}C NMR was recorded at 100.6 MHz in $CDCl_3$ using residual $CHCl_3$ as internal reference (77.0 ppm). Solid-state NMR experiments were performed on a Bruker WB Avance II 400 MHz spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with a 4-mm double-resonance MAS probe and with a sample spinning rate of 10.0 kHz; a contact time of 2 ms (ramp 100) and pulse delay of 3 s were applied. FTIR spectra of the samples were collected on a TENSOR 27 FTIR at a resolution of 2 cm^{-1}. The elemental analysis of the polymer was determined using a Flash EA1112 analyzer. The nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020M system. The samples were outgassed at 120 ^oC for 8 h before the measurements. Surface areas were calculated from the adsorption data using Langmuir and Brunauer-Emmett-Teller (BET) methods. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDFT) method. Field emission scanning electron microscopy (SEM) observations were performed on a Hitachi S-4800 microscope operated at an accelerating voltage of 10.0 kV. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-1011 instrument operated at 200 kV. The thermal properties of the materials were evaluated using a thermogravimetric analysis (TGA) instrument (STA PT1600 Linseis) over the temperature range of 25 to 800 ℃ under air atmosphere with a heating rate of 10 ℃/min. X-ray photoelectron spectroscopy (XPS) was performed on an ESCAL Lab 220i-XL spectrometer at a pressure of $\sim 3 \times 10^{-9}$ mbar (1 mbar = 100 Pa) using Al Ka as the excitation source (hn=1486.6 eV) and operated at 15 kV and 20 mA. The binding energies were referenced to the C_{1s} line at 284.8 eV from adventitious carbon. The loading content of Ag in the catalysts was determined by ICP-AES (VISTA-MPX).

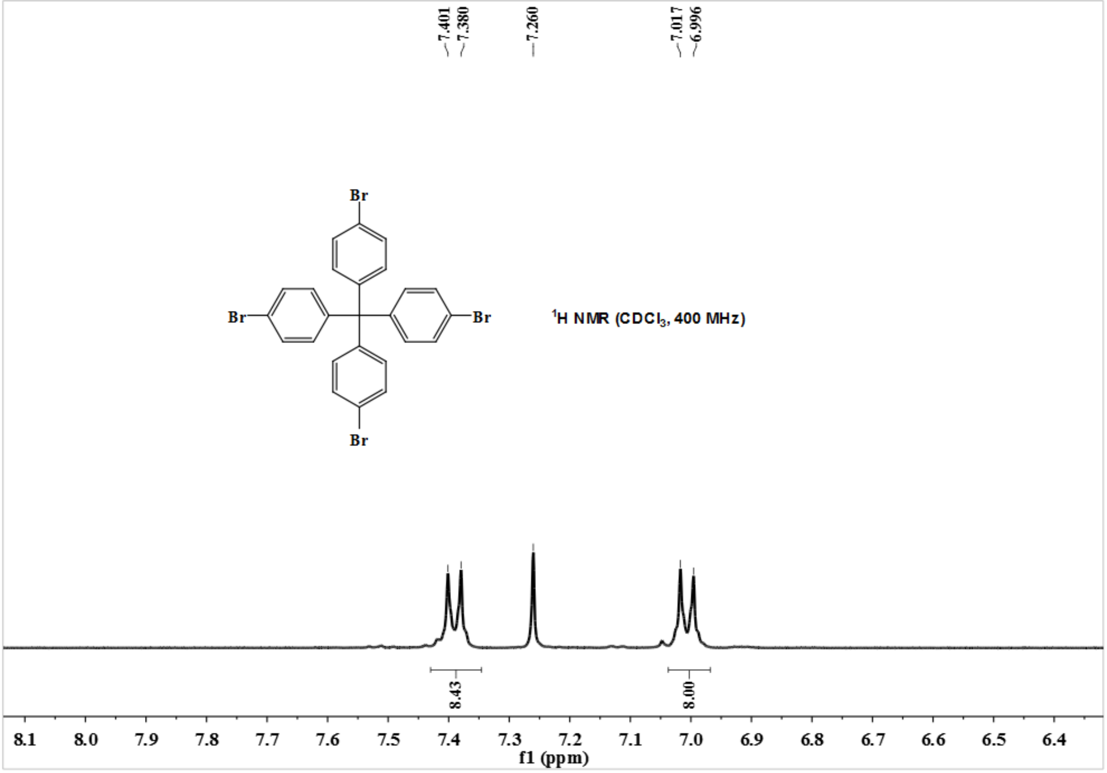
2. Synthetic procedures

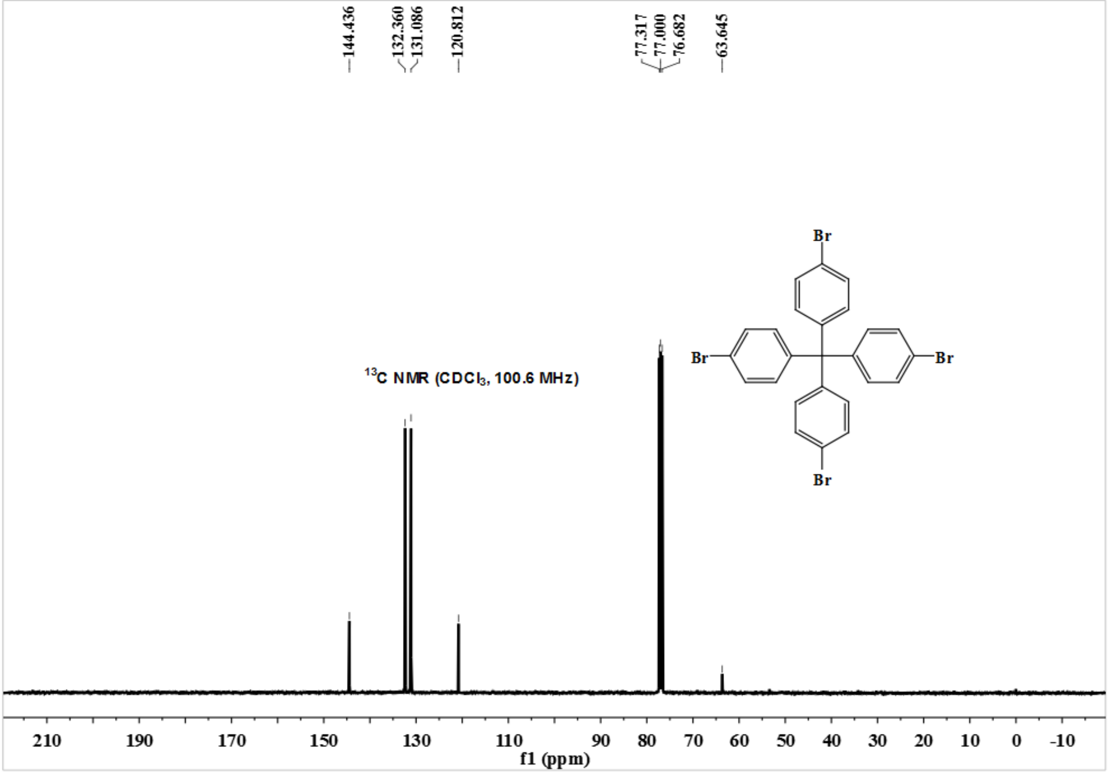
(1) Synthesis of tetrakis(4-ethynylphenyl)methane (A)[1]



Bromine (10.00 mL, 194.61 mmol) was added slowly to tetraphenylmethane (9.00 g, 28.09 mmol) with continuous stirring. The resulting slurry was stirred for an additional 10 h and then poured into ethanol (200 mL) which was cooled to -78 °C. The precipitated solid was filtered, washed with saturated aqueous $NaHSO_3$ solution (100 mL) and dried at 60 °C under vacuum to give tetra(4-bromophenyl)methane as a white solid in 81% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.00 (d, ^3J = 8.4 Hz, 8H), 7.39 (d, ^3J = 8.4 Hz, 8H); ^{13}C NMR (CDCl3, 100.6 MHz) δ63.6, 120.8, 131.1, 132.4, 144.4; EI-MS calculated for [M]: $C_{25}H_{16}Br_4$ (636.01), found [M] (632, 632,633, 634,635, 636, 637, 638, 639, 640), [M-Br] (553-561), [M-2Br] (476-484), [M-3Br] (397-402), [M-4Br] (319-322), [M-$C_6H_4Br_4$] (239).

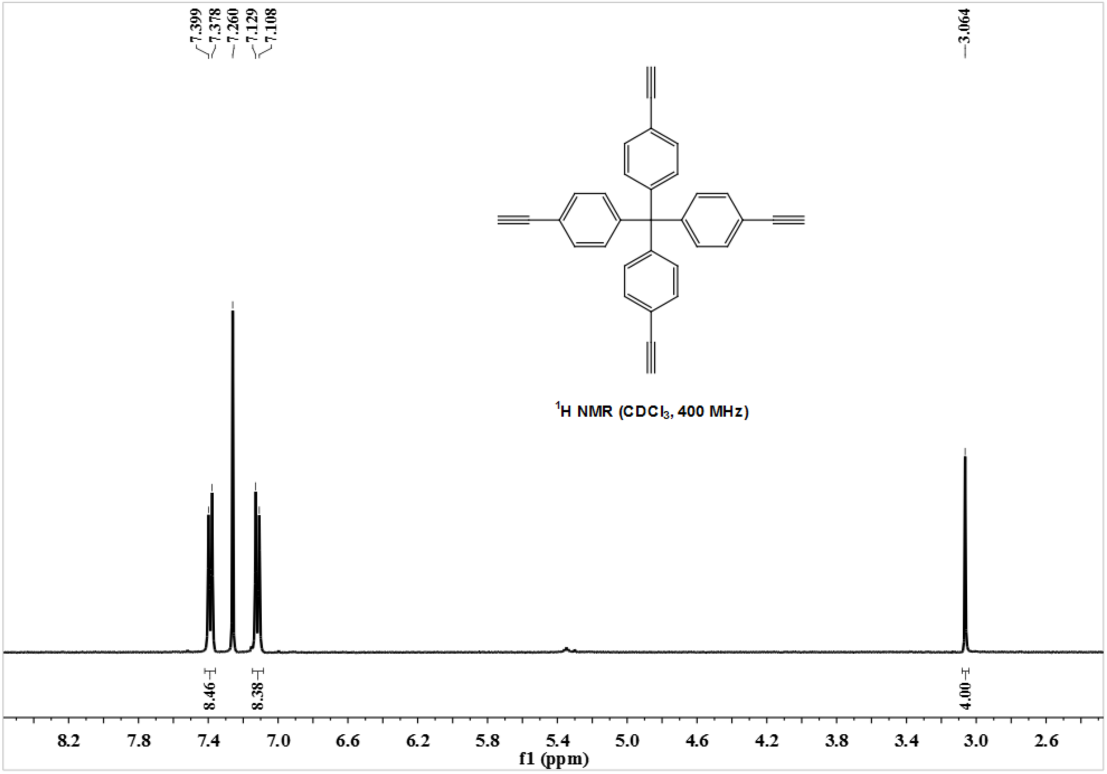


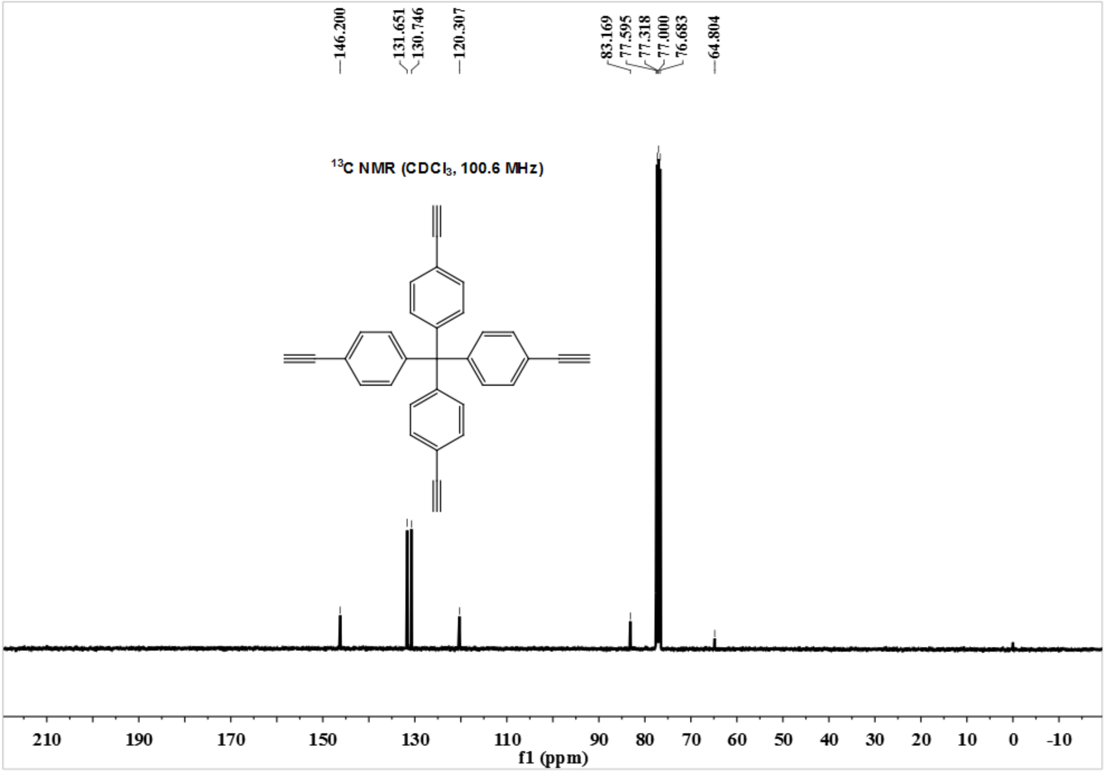


Tetra(4-bromophenyl)methane (4.02 g, 6.33 mmol), $PdCl_2(PPh_3)_2$ (0.266 g, 0.37 mmol), CuI (0.048 g, 0.25 mmol), and PPh_3(0.2 g, 0.76 mmol) were placed in a round-bottom flask; anhydrous $^{i}Pr_2NH$ (50 mL) and trimethylsilylacetylene (4.3 mL, 30.36 mmol) was added via a syringe. The reaction mixture was brought to reflux (90 ^{o}C) for 24 h and then cooled down to room temperature. Solvent was removed in vacuum, and $CHCl_3$ was added to dissolve the residue and filtered through a pad of Celite. The filtrate was washed with dilute Na_2EDTA solution and then dried over anhydrous Na_2SO_4; the solution was concentrated, and ethanol was added to obtain tetra(4-trimethylsilyacetylenephenyl)methane as a white solid product (89% yield).

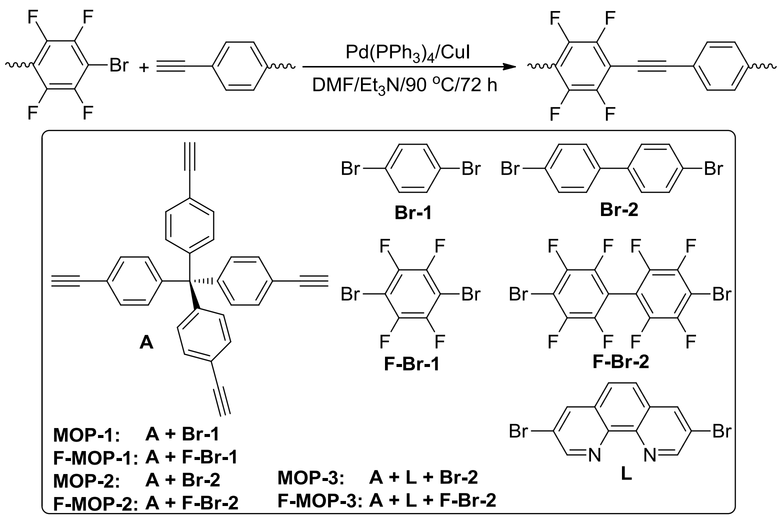
NaOH (0.164 g, 4.1 mmol) was dissolved in 5 mL of CH_3OH, then added to a solution of tetra(4-trimethylsilyacetylenephenyl)methane (0.2919 g, 0.41 mmol) in 20 mL of CH_2Cl_2, and then stirred for 6 h at room temperature. The reaction mixture was washed with water, and the aqueous phase was extracted with CH_2Cl_2 and the combined organic phases were washed with brine, and then dried over anhydrous Na_2SO_4. The solution was concentrated, and ethanol was added to the solution. Tetrakis(4-ethynylphenyl)methane (**A**) was obtained as light yellow solid (75% yield).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.06 (s, 4H), 7.12 (d, ^{3}J = 8.4 Hz, 8H), 7.39 (d, ^{3}J = 8.4 Hz, 8H); ^{13}C NMR (CDCl3, 100.6 MHz) δ 64.8, 77.6, 83.2, 120.3, 130.7, 131.7, 146.2; EI-MS calculated for [M]: $C_{33}H_{20}$ (416.51), found [M] (416), [M-C_8H_5] (315), [M-$C_{16}H_{10}$] (214).



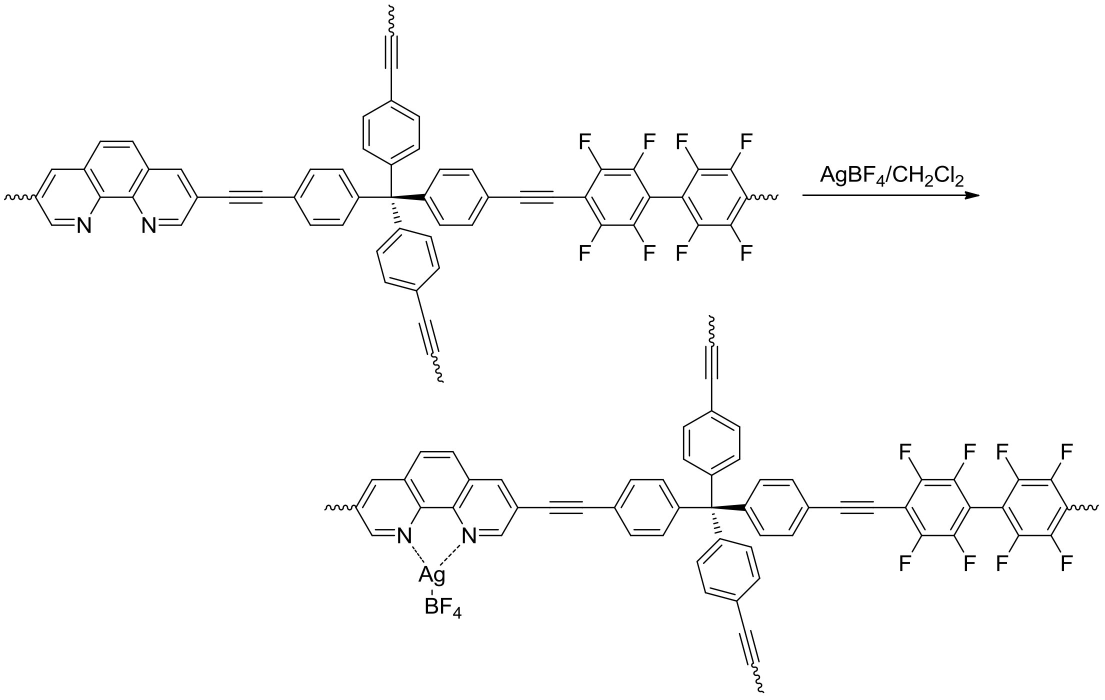


(2) Synthesis of the polymers in this study (Scheme 1 in the text)[2]



Tetrakis(4-ethynylphenyl)methane (**A**) (208.3 mg, 0.5 mmol), aromatic bromide monomers (**Br-1**, **F-Br-1**, **Br-2** or **F-Br-2**) (1 mmol) or mixture of aromatic bromide monomers (**Br-2** or **F-Br-2**)/L (molar ratio: 1.5:1) (1 mmol), tetrakis-(triphenylphosphine)palladium (20 mg), and copper iodide (10 mg) were dissolved in the mixture of DMF (4 mL) and Et_3N (4 mL). The reaction mixture was heated to 90 °C, stirred for 72 h under a nitrogen atmosphere, and then cooled to room temperature. The precipitated network polymer was filtered and washed several times with chloroform, water, methanol, acetone and THF to remove any unreacted monomer or catalyst residues. Further purification of the polymer was carried out by Soxhlet extraction with THF for 24 h. The product was dried in vacuum for 24 h at 100 °C as brown powders, with yield of 63% (**MOP-1**), 70% (**F-MOP-1**), 67% (**MOP-2**), 79% (**F-MOP-2**), 62% (**MOP-3**), 72% (**F-MOP-3**).

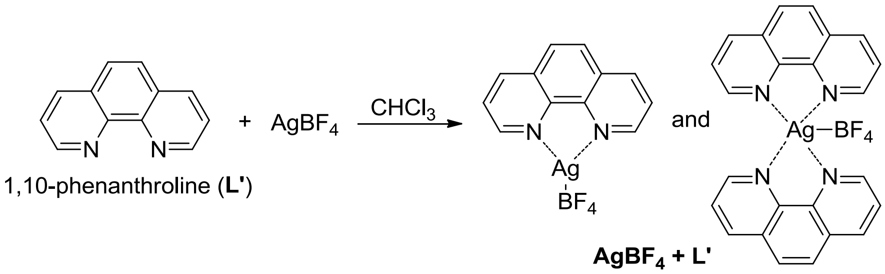
(3) Synthesis of F-MOP-3-Ag and MOP-3-Ag[4]



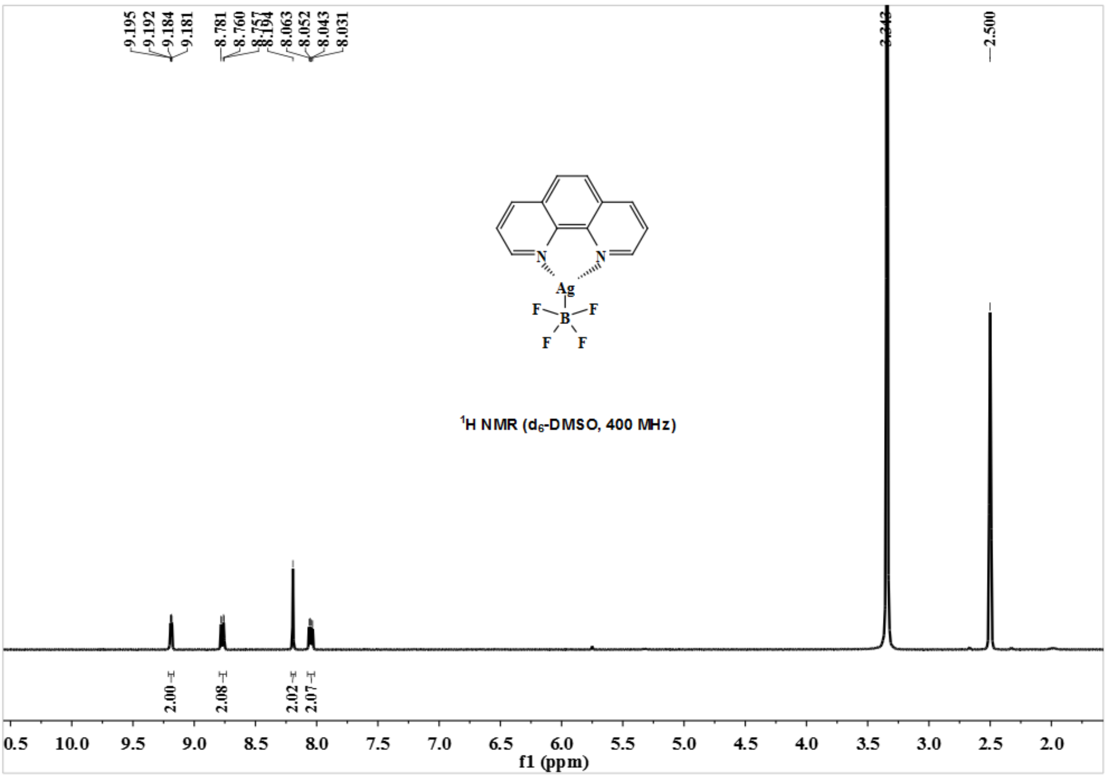
$AgBF_4$ (144.1 mg) was dissolved in 100 mL of dichloromethane, and then **F-MOP-3** or **MOP-3** (676.3 mg) was added. The mixture was kept stirring under exclusion of light for 24 h at room temperature. The resulting solid was isolated by filtration and washed with dichloromethane using

Soxhlet extraction for 48 h, and then dried at 60 °C under vacuum for 12 h to yield **F-MOP-3-Ag** or **MOP-3-Ag** as brown powders. The Ag content was determined by ICP: 6.35 wt% (**MOP-3-Ag**), 5.43 wt% (**F-MOP-3-Ag**).

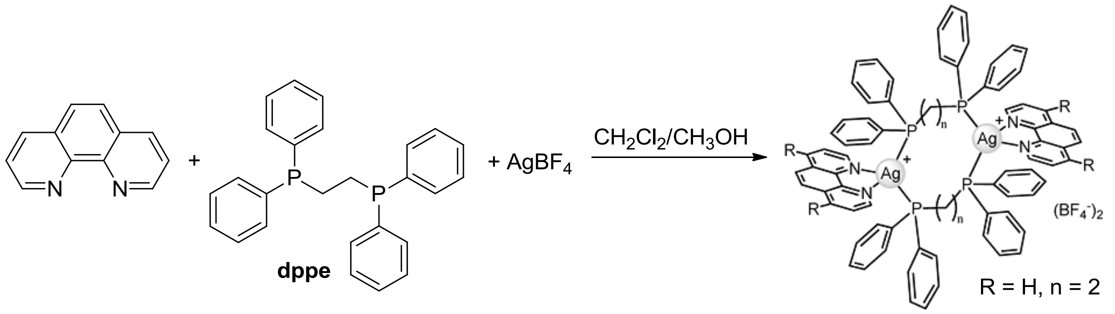
(4) Synthesis of complex $AgBF_4$ + L'[4]



To a solution of 1,10-phenanthroline (**L'**) (18.0 mg, 0.1 mmol) in $CHCl_3$ (3 mL) was dropped a solution of $AgBF_4$ (19.5 mg, 0.1 mmol) in $CHCl_3$ (3 mL). The mixture was stirred under exclusion of light for 1 h and the precipitate was isolated by centrifugation and the white solid was dried under vacuum at 40 °C for 24 h. ^1H NMR (d_6-DMSO, 400 MHz) δ 8.03-8.06 (m, 2H), 8.19 (s, 2H), 8.76-8.78 (m, 2H), 9.18-9.20 (m, 2H). ESI-MS found [**L'** + Ag + CH_3CN]$^+$ (318.9, 320.8) (7%), [L' + Ag + $CH_3S(O)CH_3$]$^+$ (366.8, 364.9) (13%), [2L' + Ag]$^+$ (466.7, 468.7) (80%).

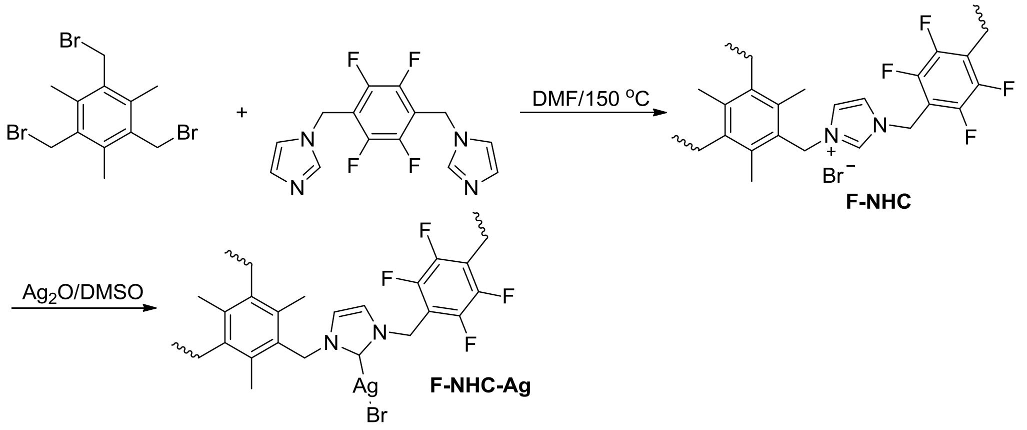


(5) Synthesis of complex prepared from $AgBF_4$, dppe and phenanthroline[5]



A solution of dppe (1 mmol) and $AgBF_4$ (1 mmol) in a 5:1 CH_2Cl_2/MeOH mixture was stirred for 1 h, and then 1,10-phenanthroline (1 mmol) was added. after stirring for 1 h, the solvents were evaporated. The complexes were then obtained pure as light yellow crystalline solids by slow diffusion of Et_2O into a CH_2Cl_2 solution of the crude product.

(6) Synthesis of F-NHC-Ag[6]

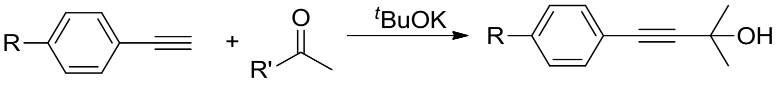


In a stainless steel autoclave, 2,4,6-tris(bromomethyl)mesitylene (399.0 mg, 1 mmol) and $ImCH_2PhF_4CH_2Im$ (465.4 mg, 1.5 mmol) were dissolved in 100 mL of DMF. The autoclave was capped and placed in an oven at 110 ^{o}C for 24 h. A white solid product was precipitated and filtered, washed with DMF and Et_2O, and dried under vacuum at 80 ^{o}C for 24 h. **F-NHC** was obtained as white powder with 80% yield.

Ag_2O (150 mg, 0.65 mmol) was added to a DMSO (15 mL) suspension of **F-NHC** (1 g). The resulting mixture was stirred at room temperature for 2 h, and at 80 ℃ for 10 h. It was poured into 30 ml of CH_2Cl_2, and then 100 ml of Et_2O was added. The white solid obtained was filtered, washed with DMF and CH_2Cl_2, and dried under vacuum. **F-NHC-Ag** was obtained in 95% yield. The Ag content was 5.94 wt% as determined by ICP.

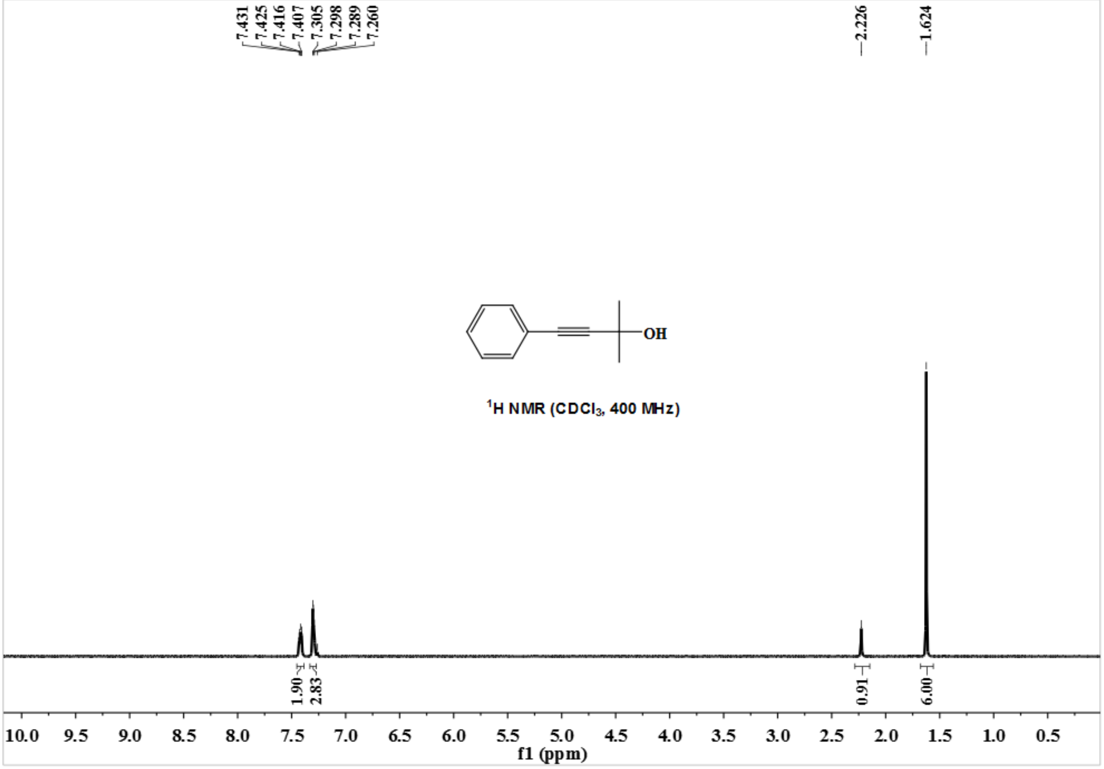
(7) Synthesis of propargyl alcohols[3]

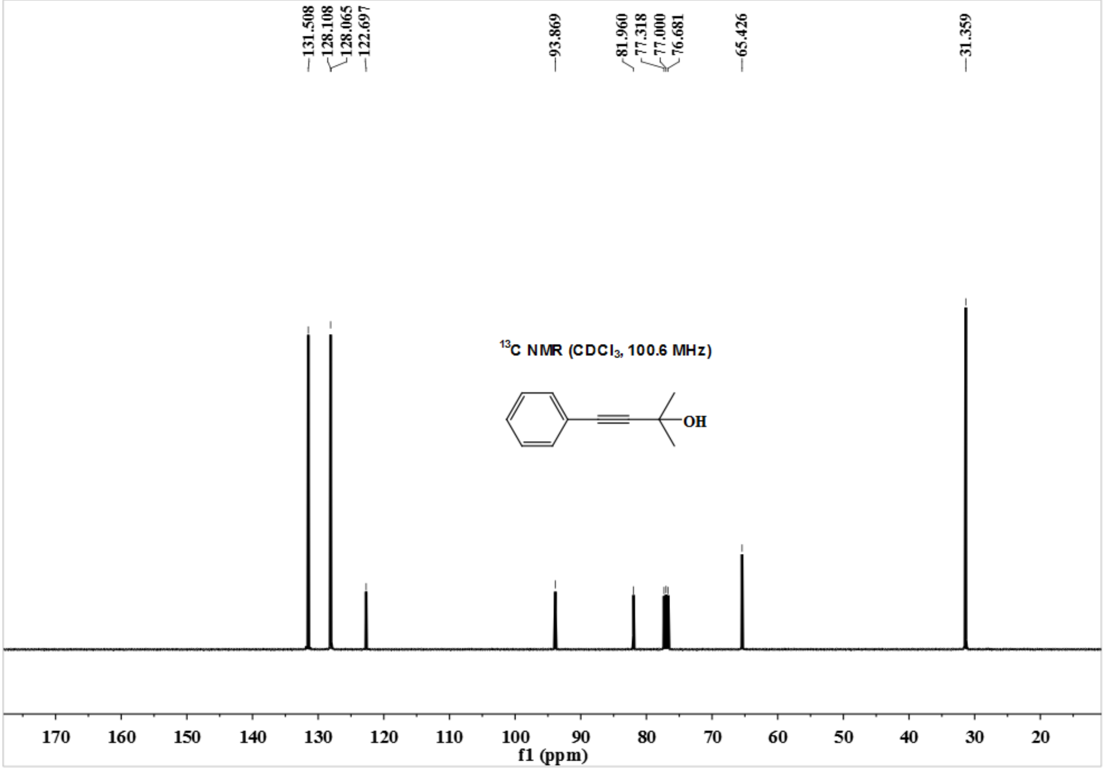
1c (2-phenylbut-3-yn-2-ol) was commercially available.



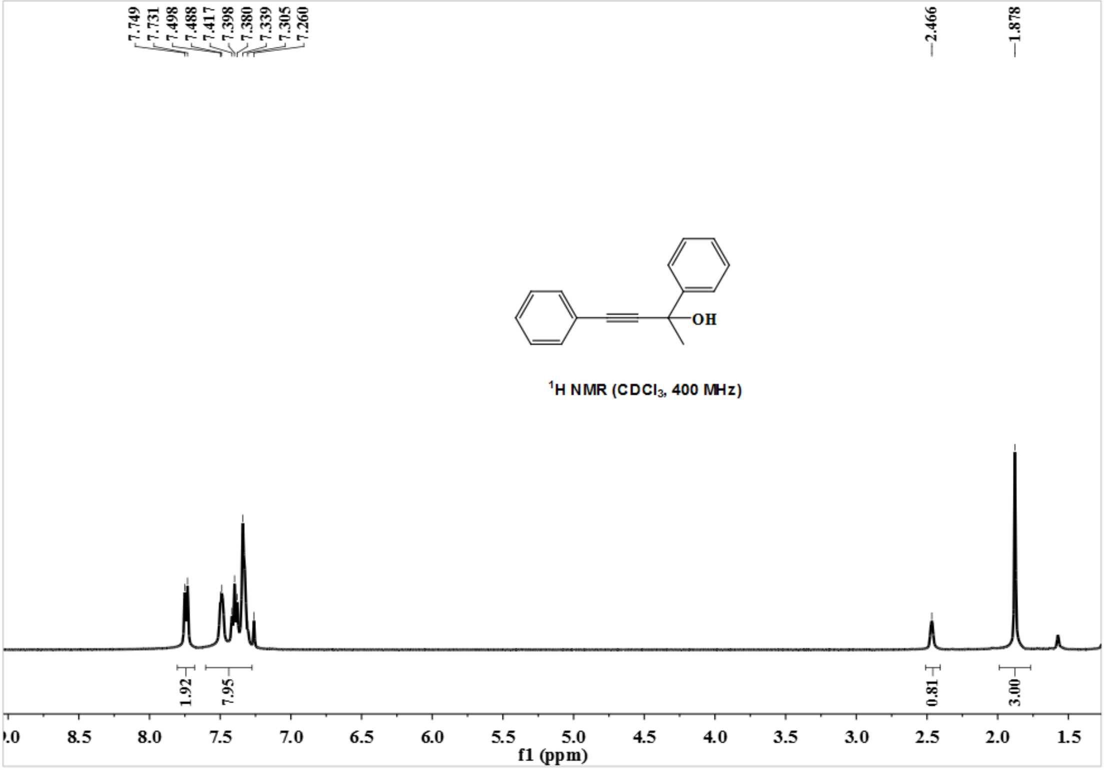
After anhydrous acetone (**1a**, **1d**, **1e**)/acetophenone(**1b**) (10 mmol), phenylacetylene (**1a**, **1b**)/4-fluorophenylacetylene (**1d**)/4-ethynyltoluene (**1e**) (10 mmol) and potassium *t*-butoxide (10 mmol) were well-mixed with agate mortar and pestle, the mixture was kept at room temperature for 4 h. The reaction product was mixed with 10% aqueous sodium chloride, filtered, washed with water and dried to give the propargyl alcohols as colorless or light yellow crystals.

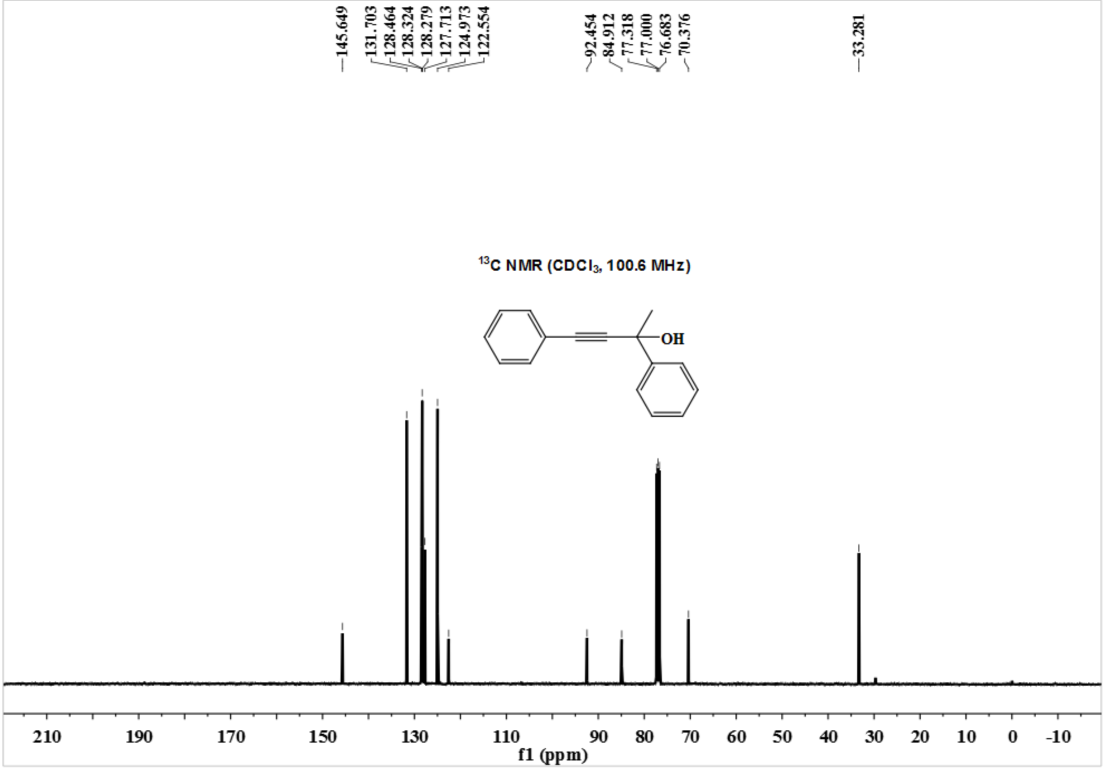
1a: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.62 (s, 6H), 2.23 (s, 1H), 7.29-7.31 (m, 3H), 7.41-7.43 (m, 2H); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 31.4, 65.4, 82.0, 93.9, 122.7, 128.06, 128.11, 131.5; EI-MS calculated for [M]: $C_{11}H_{12}O$ (160.09), found [M] (159, 160), [M-CH$_3$] (145), [M-OH$_2$] (141, 142), [M-C_3H_6O] (102), [M-C_5H_7O] (77).





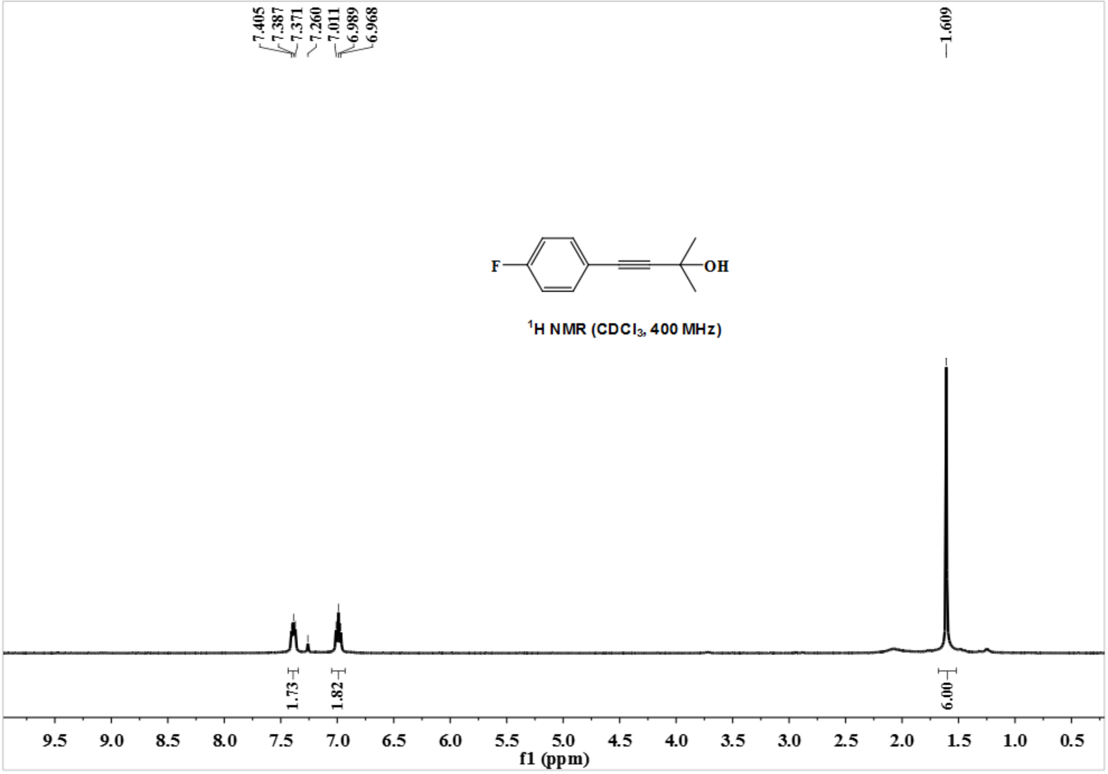
1b: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.88 (s, 3H), 2.47 (s, 1H), 7.31-7.50 (m, 8H), 7.74 (d, ^3J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 33.3, 70.4, 84.9, 92.5, 122.6, 125.0, 127.7, 128.28, 128.32, 128.5, 131.7, 145.6; EI-MS calculated for [M]: $C_{16}H_{14}O$ (222.28), found [M] (221, 222), [M-CH_3] (207), [M-OH_2] (204), [M-C_8H_8O] (102), [M-$C_{10}H_9O$] (77).

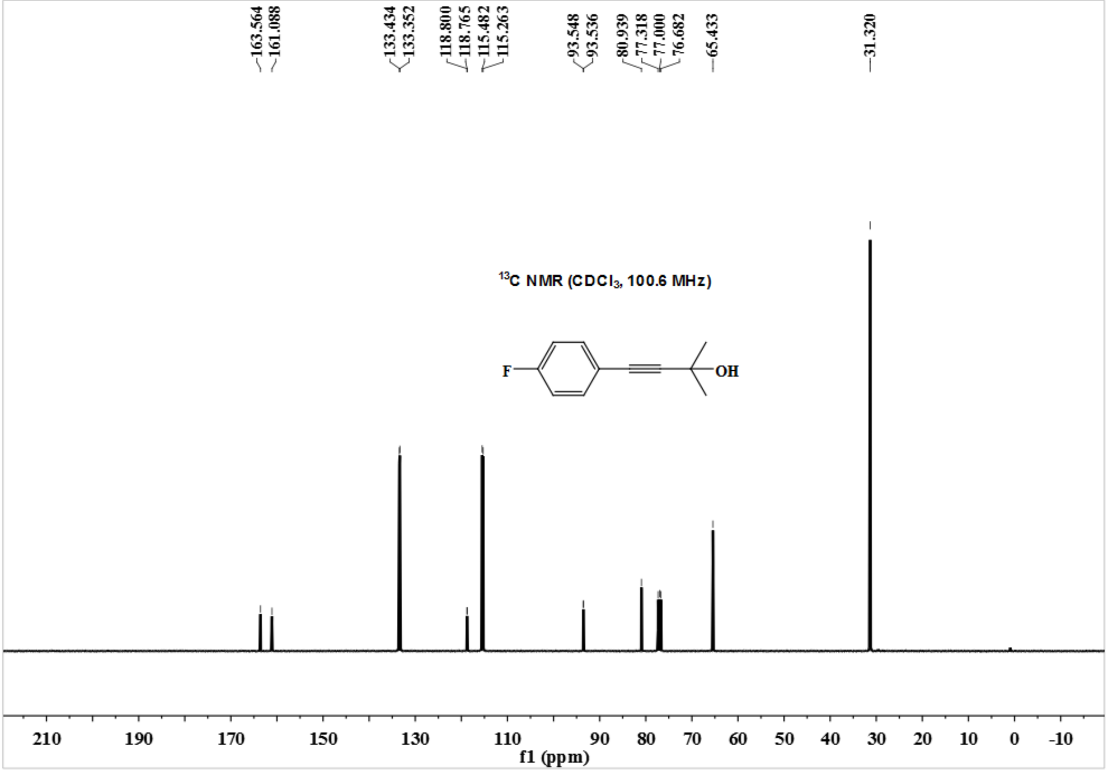




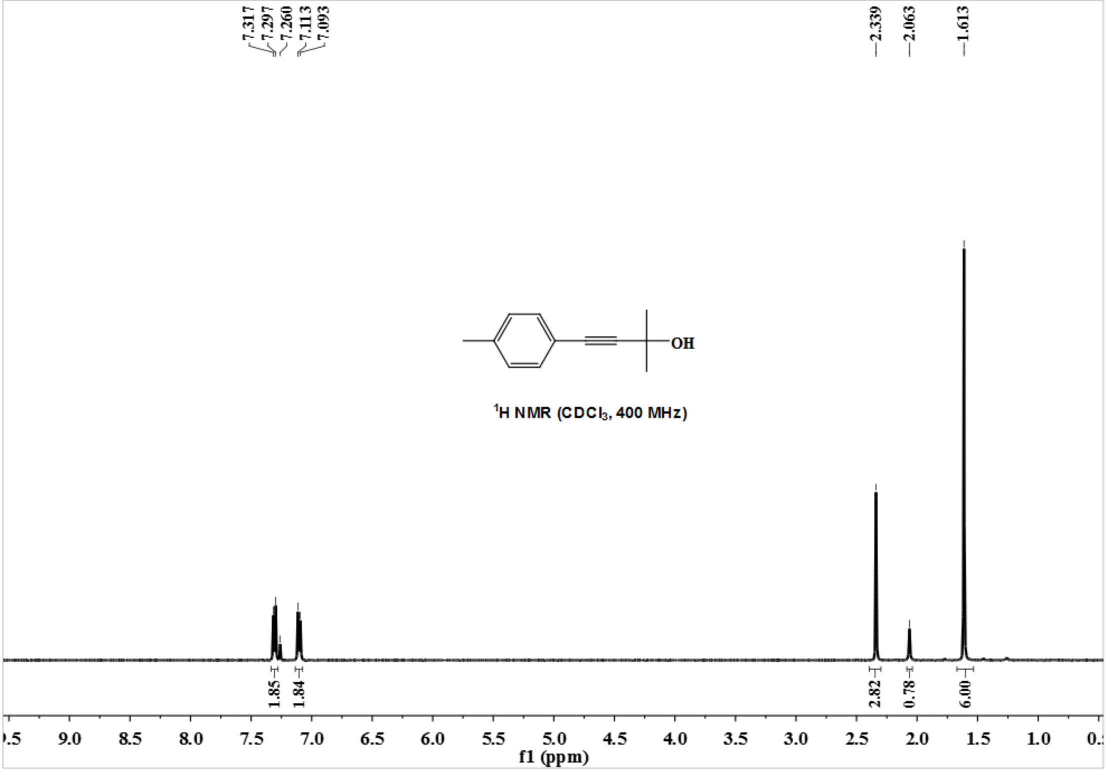
1d: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.61 (s, 6H), 6.99 (t, ^3J = 8.8 Hz, 2H), 7.39 (t, ^3J = 7.2 Hz, 2H);

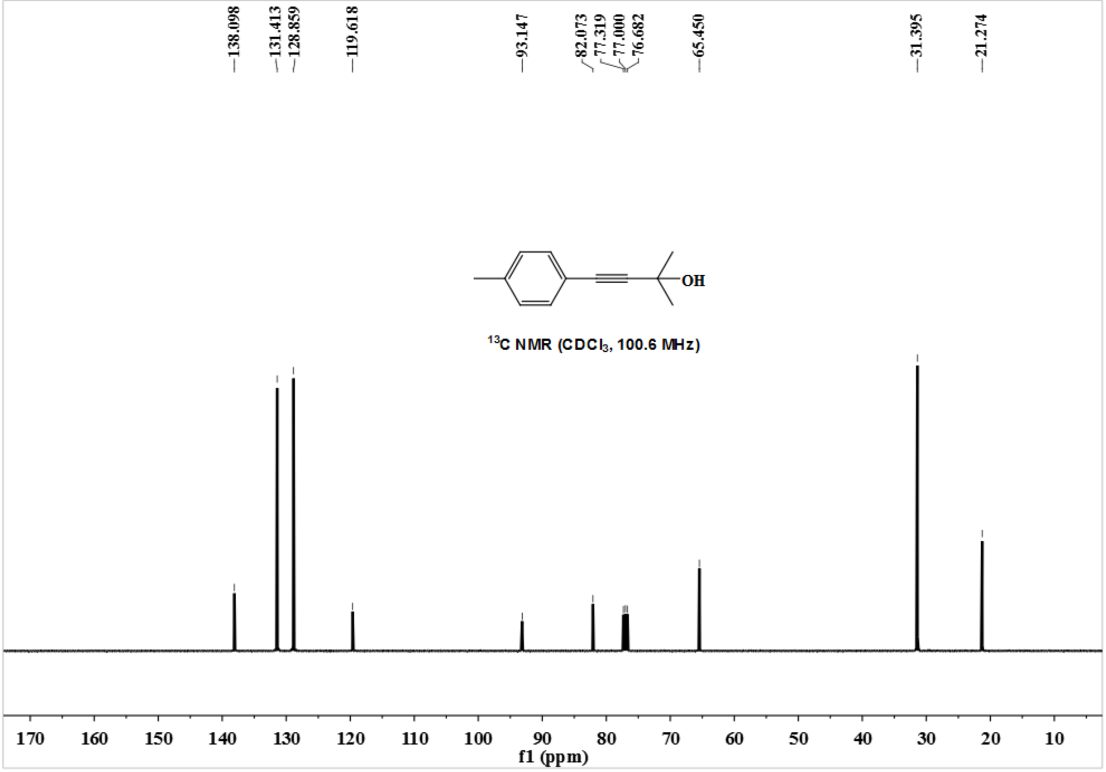
^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 31.3, 65.4, 80.9, 93.53, 93.54, 115.3, 115.5, 118.76, 118.80, 133.35, 133.43, 161.1, 163.6; EI-MS calculated for [M]: $C_{11}H_{11}FO$ (178.20), found [M] (177, 178, 179), [M-CH_3] (163, 164), [M-F] (159, 160), [M-CH_5O] (145), [M-C_3H_6O] (120).





1e: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.61 (s, 6H), 2.06 (s, 1H), 2.34 (s, 3H), 7.10 (d, ^3J = 8 Hz, 2H), 7.31 (d, ^3J = 8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.3, 31.4, 65.5, 82.1, 93.1, 119.6, 128.9, 131.4, 138.1; EI-MS calculated for [M]: $C_{12}H_{14}O$ (174.24), found [M] (173, 174), [M-CH_3] (159, 160), [M-OH_2] (155, 156), [M-CH_5O] (141), [M-C_3H_7O] (115), [M-C_6H_9O] (77).





(7) Typical procedures for the synthesis of α- alkylidene cyclic carbonates from propargyl alcohols and CO_2

A stainless steel autoclave with a Teflon tube (25 mL inner volume) was purged with CO_2 to evacuate air, and then **F-MOP-3-Ag** (10 mol%) (mol% of Ag based on propargyl alcohols), propargyl alcohols (0.25 mmol), DBU (0.25 mmol) and THF (1 mL) were added successively. CO_2 (1 MPa) was charged in the reactor at room temperature. The autoclave was stirred at 25 ^oC for 10 h. After reaction, then the excess of CO_2 was vented. The product yield was determined by ^1H NMR ($CDCl_3$, 400 MHz) using 1,4-bis(chloromethyl)-benzen as an internal standard. The products was also isolated by column chromatography on silica gel and identified by NMR spectra.

For catalyst (**F-MOP-3-Ag**) recycling, the catalyst was recycled by filtration, washed with 50 mL CH_2Cl_2, and then dried under vacuum at 40 ^oC for 24 h. The recycled catalyst was reused for the next run without further purification.

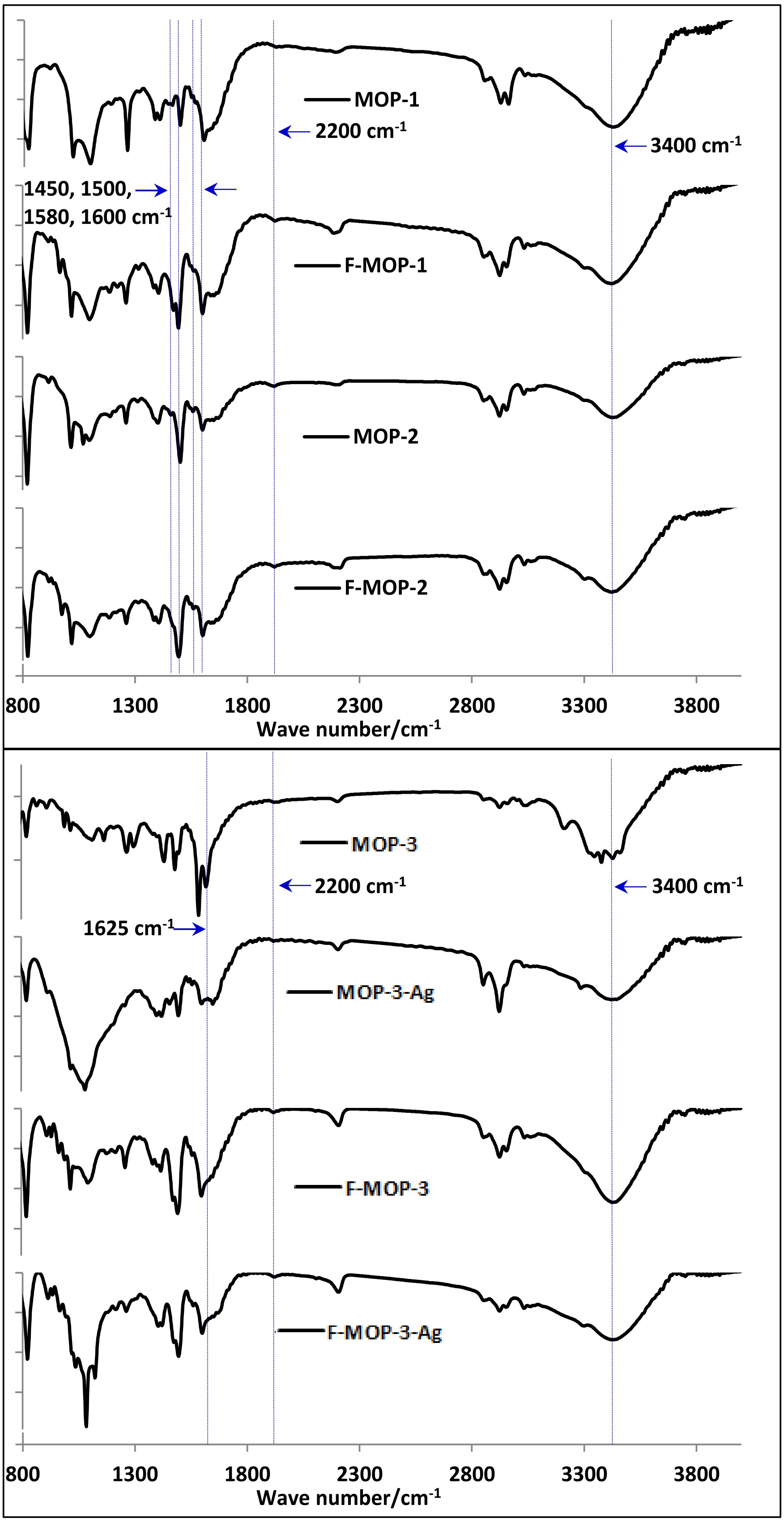


Figure S1. FTIR spectra of the materials in this study. The spectra were recorded as KBr pellets. 2200 and 3400 cm^{-1} (bis-substituted and terminal C-C triple bond respectively), 1450, 1500, 1580 and 1600 cm^{-1} (aromatic rings), 1625 cm^{-1} (C=N stretching).

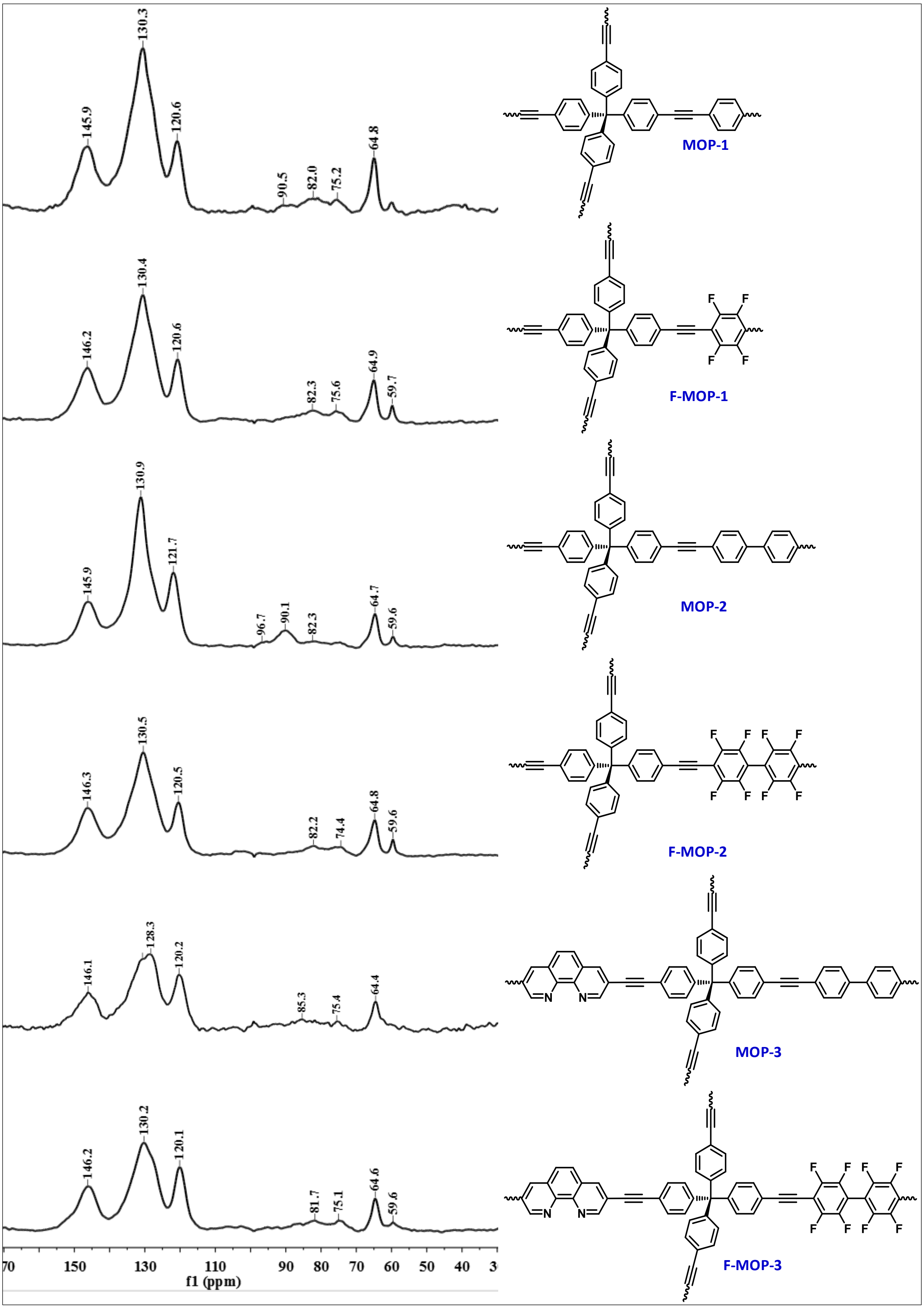


Figure S2. Solid-state ^{13}C CP/MAS NMR spectra for the microporous organic polymers synthesized in this work.

Table S1 Elemental analysis of the polymers used in this study.

Entry	Polymer	Theoretical value/wt%			Measured value/wt%			
		Molecular formula	C	H	C	H	N	Ag
1	**MOP-1**	$(C_{45}H_{24})_n$	95.72	4.28	76.24	4.80	-	-
2	**F-MOP-1**	$(C_{45}H_{16}F_8)_n$	76.28	2.28	75.46	4.05	-	-
3	**MOP-2**	$(C_{57}H_{32})_n$	95.50	4.50	76.26	4.31	-	-
4	**F-MOP-2**	$(C_{57}H_{16}F_{16})_n$	68.14	1.61	75.45	4.16	-	-
5	**MOP-3**				78.50	4.17	4.05	-
6	**F-MOP-3**				72.6	3.35	2.83	-
7	**MOP-3-Ag**				69.13	4.03	3.12	6.35
8	**F-MOP-3-Ag**				60.08	3.27	2.63	5.43

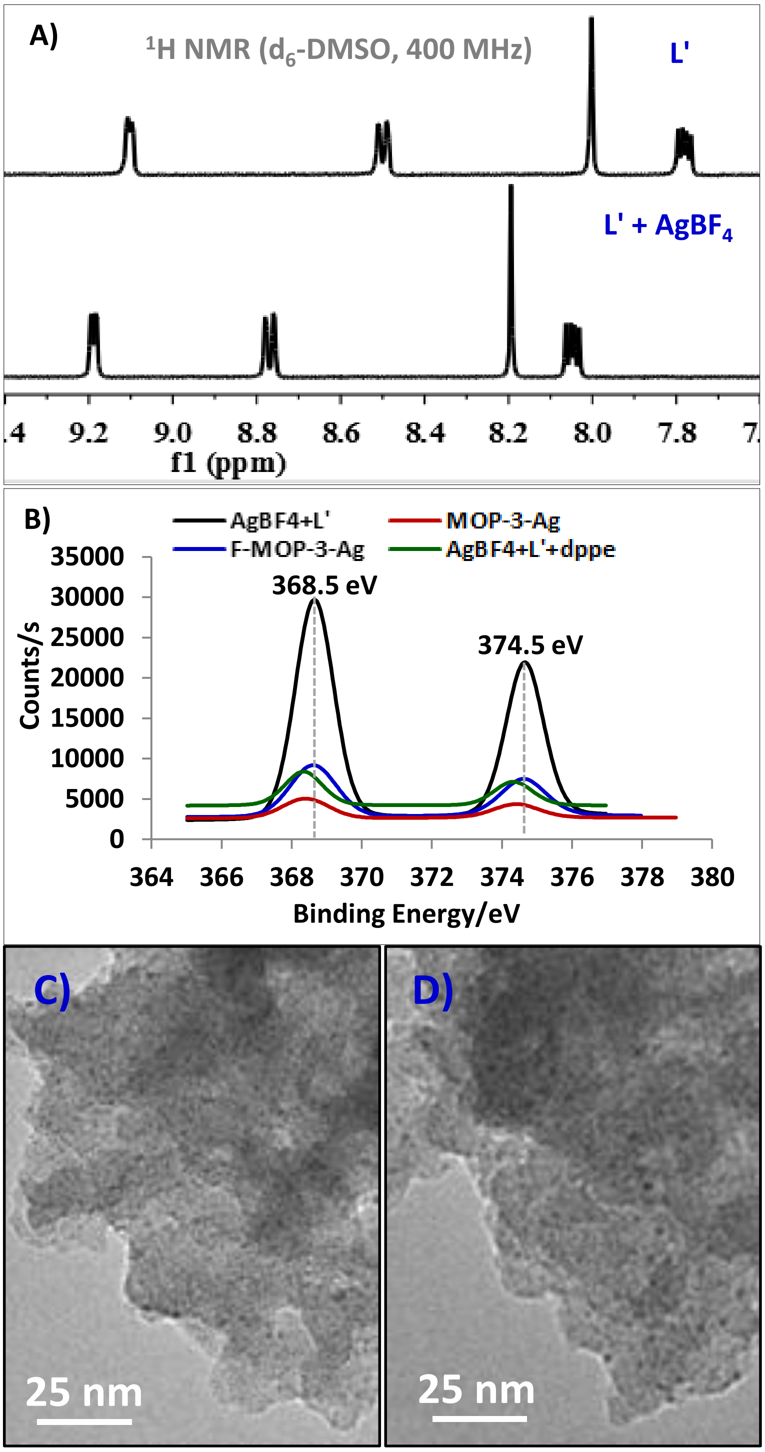


Figure S3. (A) ^{1}H NMR spectra of 1,10-phenanthroline (**L'**) before and after reacting with equimolar AgBF$_4$. (B) XPS spectra (Ag$_{3d5}$) of **MOP-3-Ag**, **F-MOP-3-Ag** and the homogeneous Ag(I) complexes. (C) TEM images of fresh **F-MOP-3-Ag** and (D) after reused for five times.

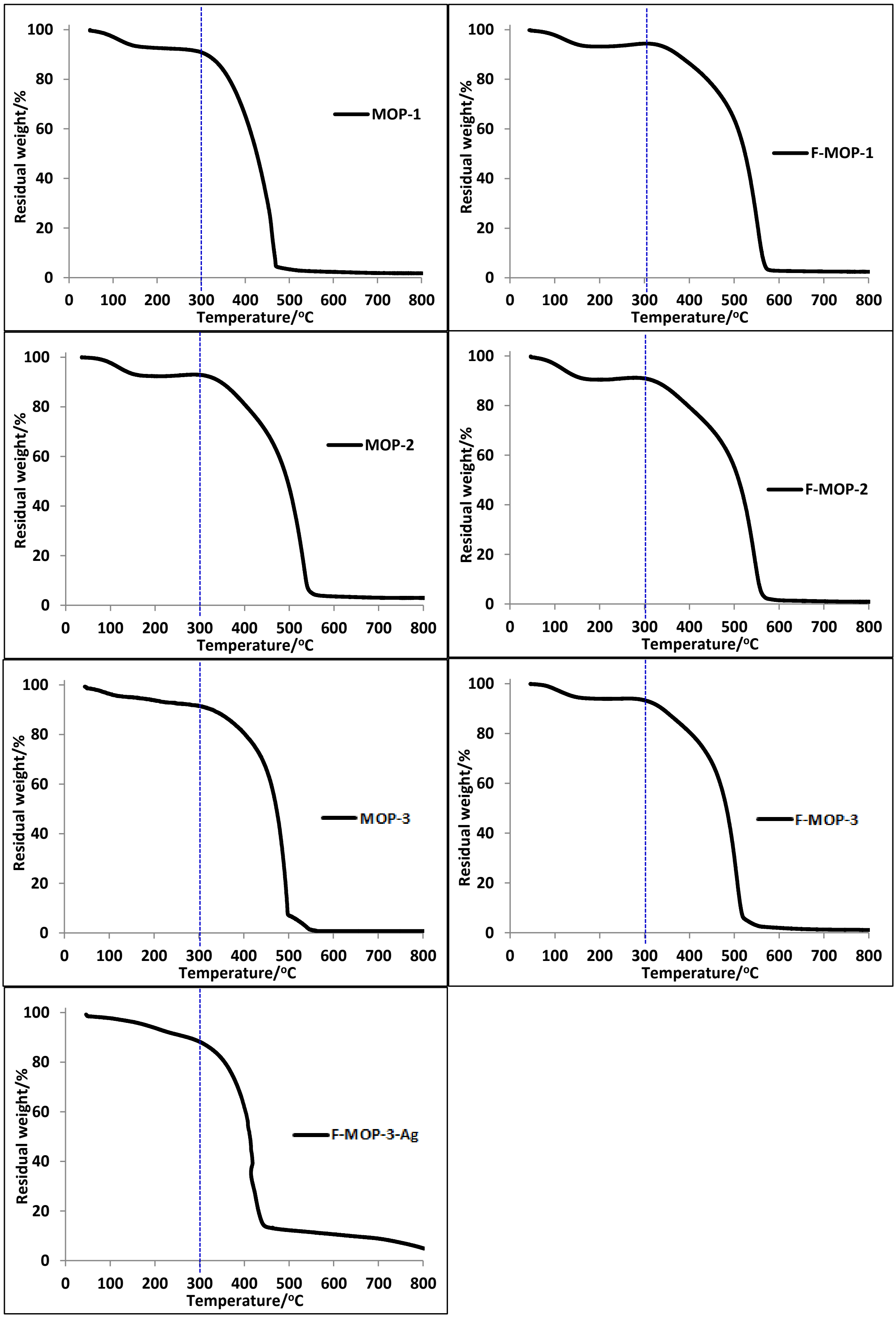
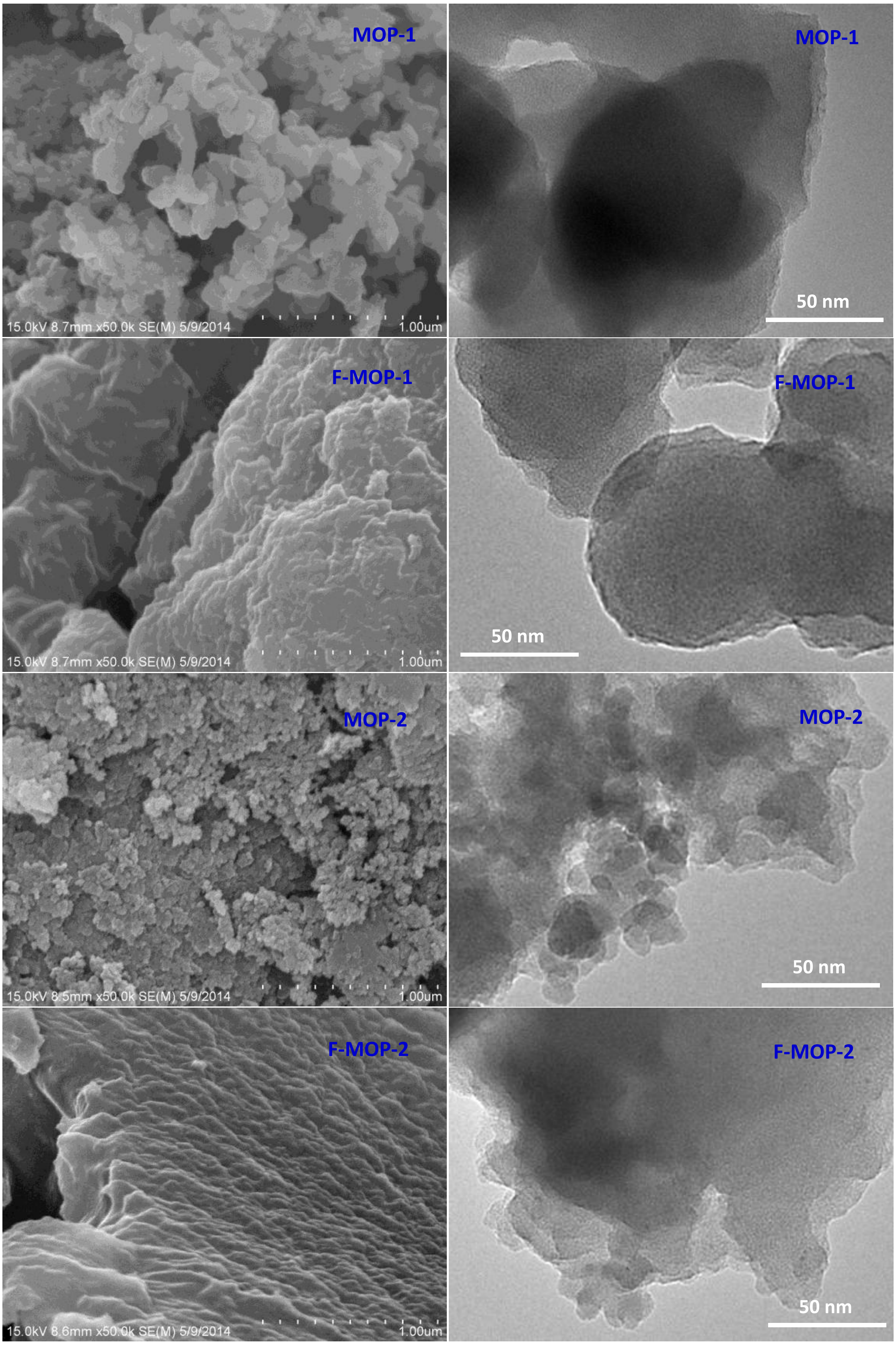


Figure S4. Thermogravimetric analysis (TGA) of the polymers in this study under air from 50 °C up to 800 °C at a heating rate of 10 °C min^{-1}.


MOP-1
15.0kV 8.7mm x50.0k SE(M) 5/9/2014
1.00um
MOP-1
50 nm
F-MOP-1
15.0kV 8.7mm x50.0k SE(M) 5/9/2014
1.00um
F-MOP-1
50 nm
MOP-2
15.0kV 8.5mm x50.0k SE(M) 5/9/2014
1.00um
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F-MOP-2
50 nm

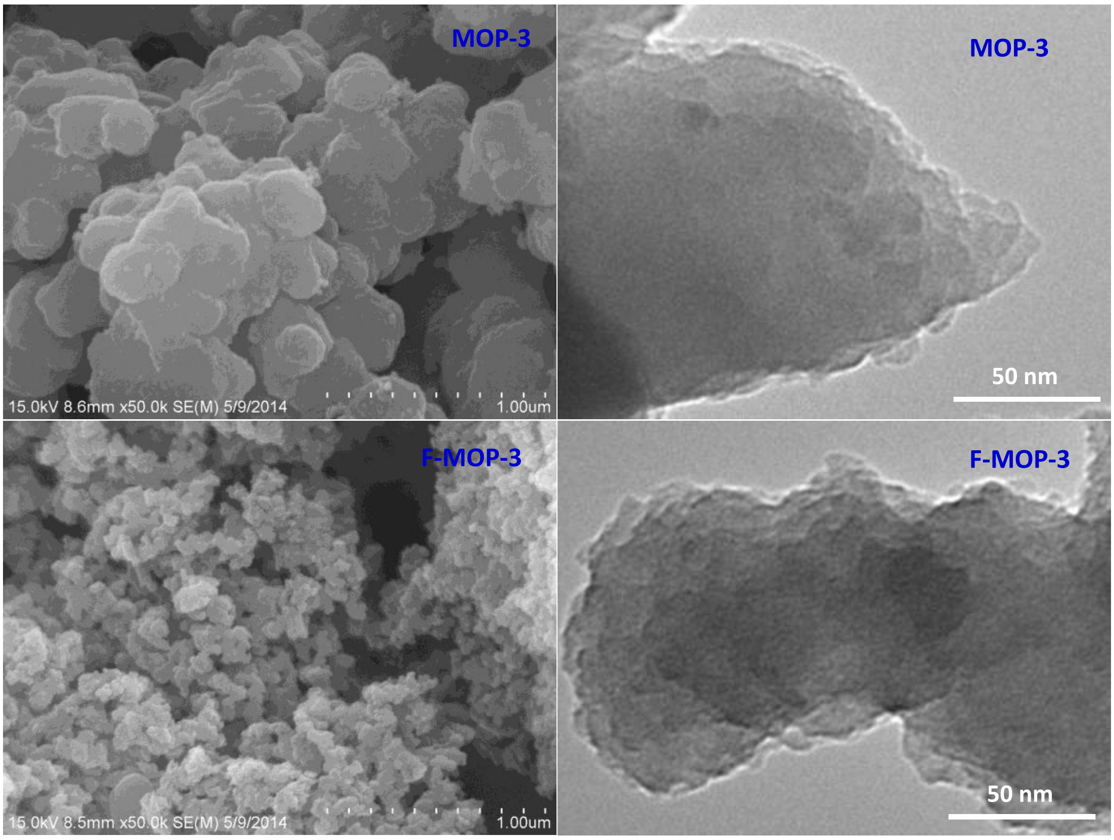


Figure S5. Scanning Electron Microscopy (TEM) (left) and Transmission Electron Microscopy (TEM) (right) images.

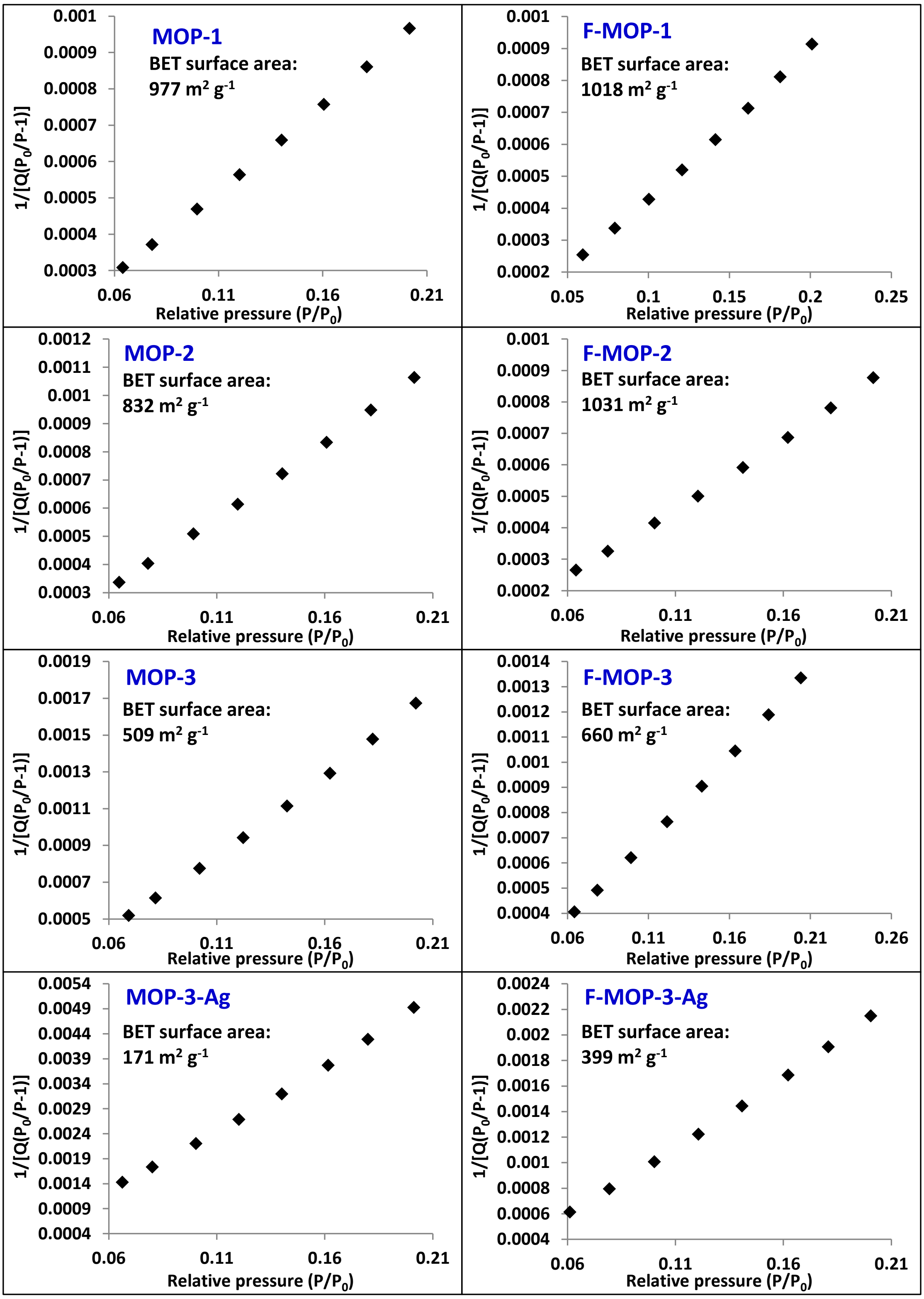


Figure S6. BET plot (P/P0 = 0.06-0.2) from N_2 isotherms at 77 K of the materials in this study.

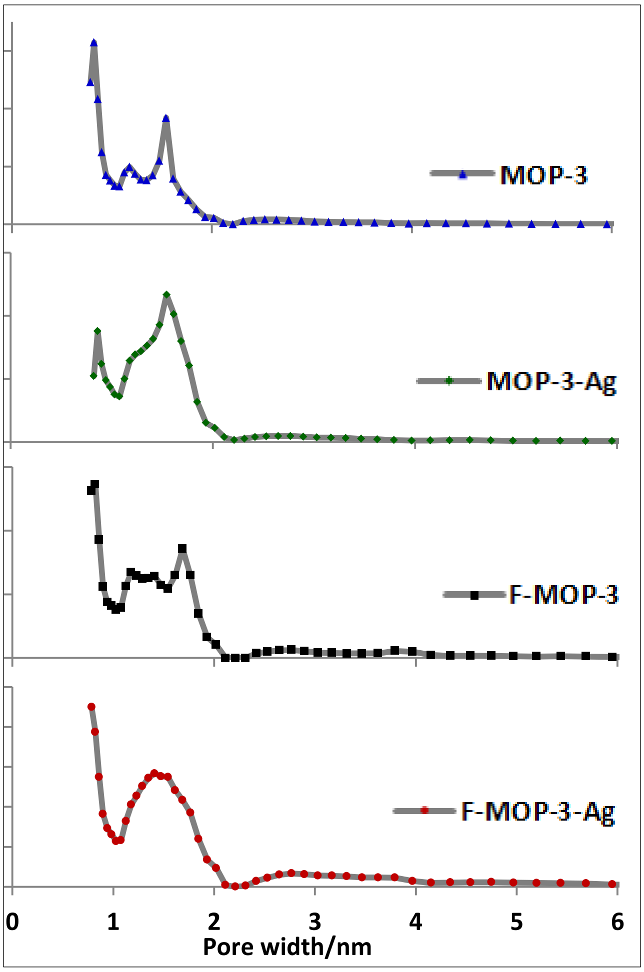


Figure S7. Pore size distributions for **F-MOP-3**, **MOP-3** and the corresponding Ag-coordinated networks from the adsorption branch of the N_2 isotherms by NLDFT method.

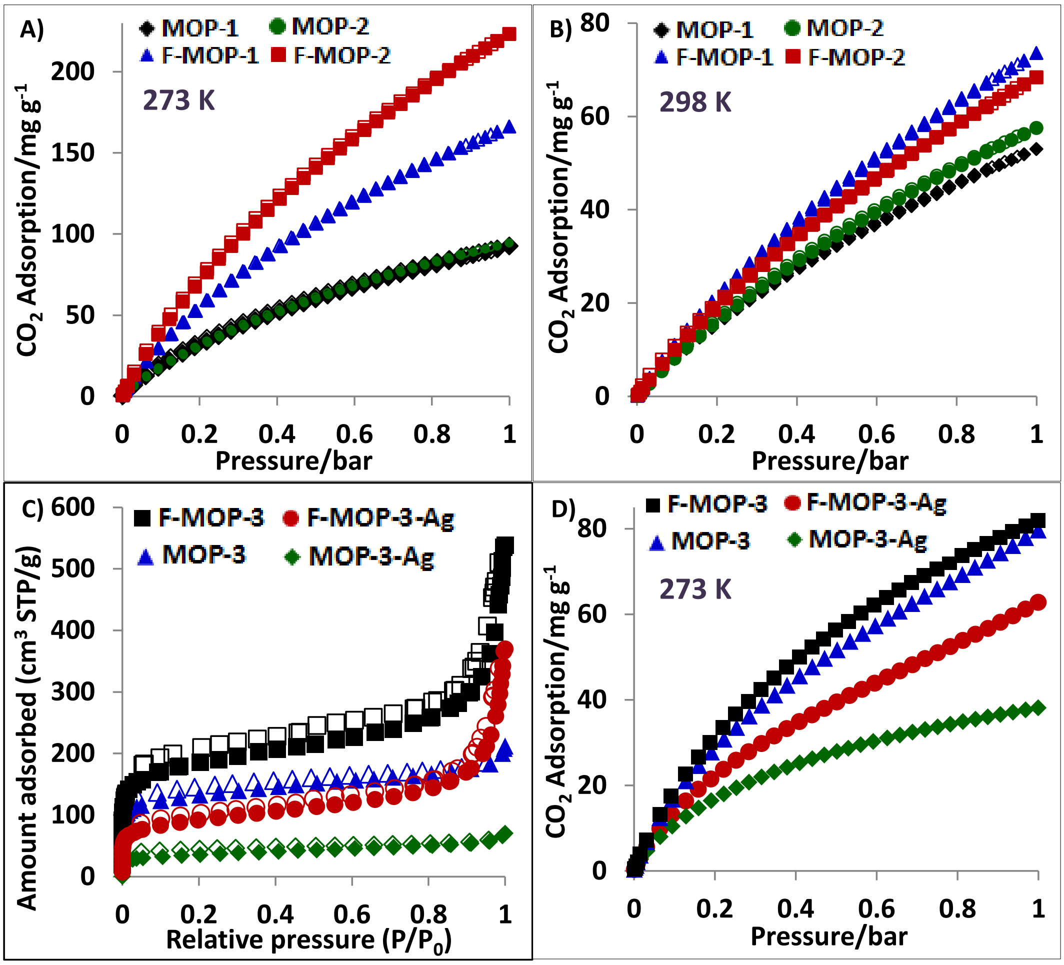


Figure S8 Adsorption (filled) and desorption (empty) isotherms for CO_2 uptake at 273 K (A) and 298 K (B) for **MOP-1**, **F-MOP-1**, **MOP-2** and **F-MOP-2**. Isotherms of N_2 at 77 K (C) and isotherms for CO_2 uptake at 273 K (D) for **F-MOP-3**, **MOP-3** and the corresponding Ag-coordinated networks.

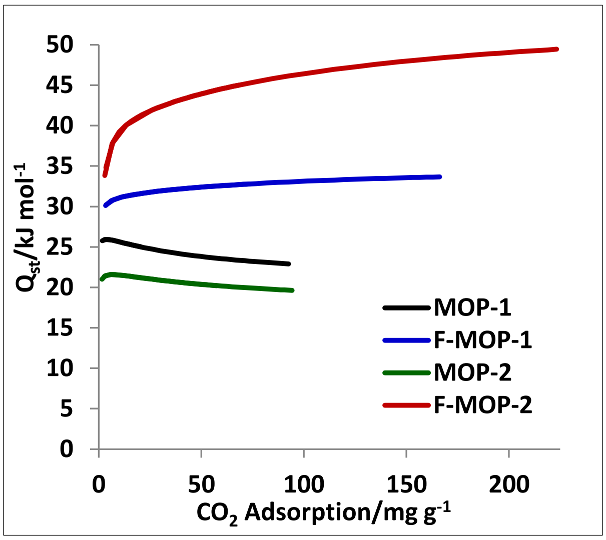
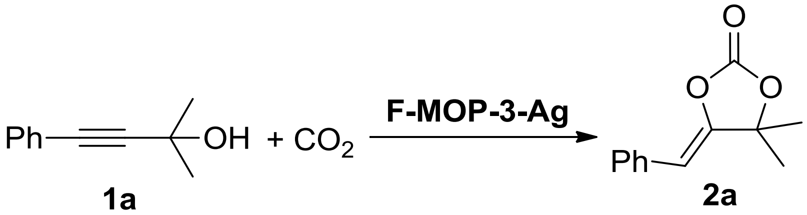


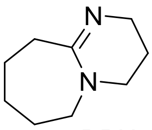
Figure S9. Isosteric heats of adsorption (Qst) for CO_2. Isosteric heats of adsorption were alculated from the adsorption data at 273 and 298 K using Clausius-Clapeyron equation.

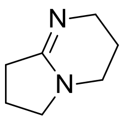
Table S2. Reactions conditions screening for the carboxylative cyclization of propargyl alcohol (**1a**) with CO_2 to produce α-alkylidene cyclic carbonate (**2a**) catalyzed by **F-MOP-3-Ag**[a]

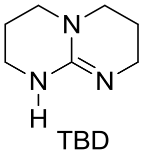


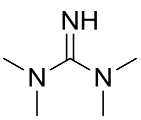
Entry	Solvent	Catalyst loading/mol%[b]	Base[c]	CO_2 pressure/MPa	Time/h	Yield of **2a**/%[d]
1	toluene	5	DBU	1	8	57
2	$CHCl_3$	5	DBU	1	8	26
3	DMF	5	DBU	1	8	10
4	acetyl acetate	5	DBU	1	8	19
5	[BMIm][PF_6][c]	5	DBU	1	8	6
6	PhF_5	5	DBU	1	8	29
7	CF_3CH_2OH	5	DBU	1	8	46
8	$CF_3CH(OH)CF_3$	5	DBU	1	8	26
9	CH_3OH	5	DBU	1	8	0
10	CH_3CN	5	DBU	1	8	0
11	THF	5	DBU	1	8	0
12	DMSO	5	DBU	1	8	0
13	DBU/CF_3CH_2OH[e]	5	-	1	8	0
14	toluene	5	DBN	1	8	31
15	toluene	5	TBD	1	8	55
16	toluene	5	TMG	1	8	18
17	toluene	5	DBU	1	24	81
18	toluene	5	TBD	1	24	79
19	toluene	10	DBU	1	8	88
20	toluene	10	DBU	1	10	100
21	toluene	10	DBU	0.5	10	47

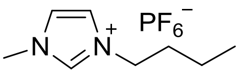
[a] Reaction conditions: **1a** 0.25 mmol, solvent 1 mL, 25 °C. [b] mol% Ag based on **1a**. [c] Structures of the organic bases and [BMIm][PF_6] was shown below. [d] Determined by ^1H NMR ($CDCl_3$, 400 MHz) using 1,4-bis(chloromethyl)-benzene as an internal standard. [e] Prepared through the reaction of equimolar DBU and CF_3CH_2OH as reported in the litereature.[7]

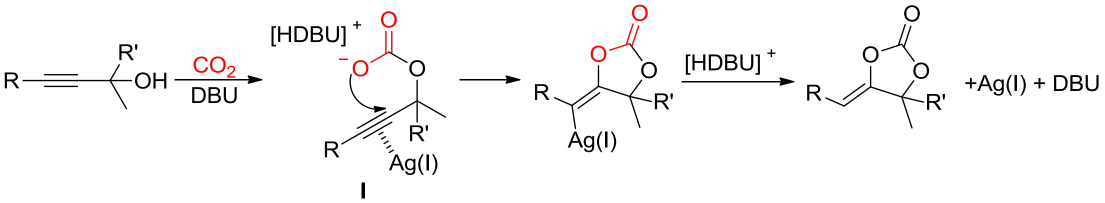

DBU


DBN


TBD


TMG

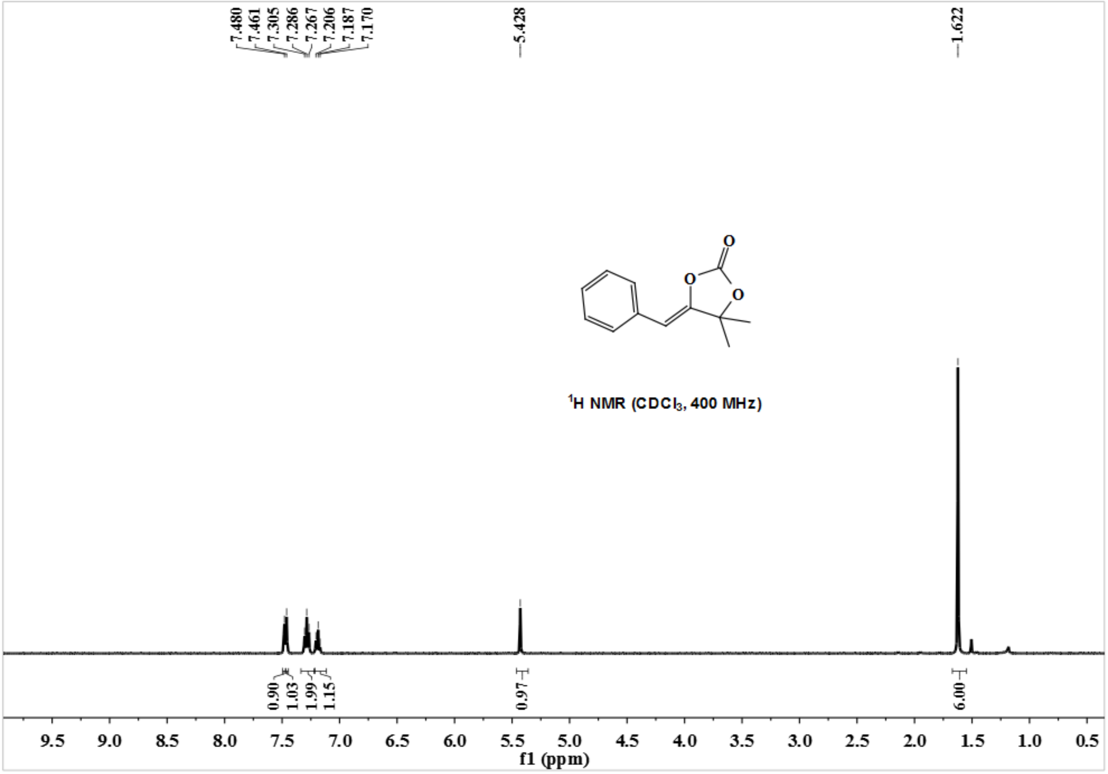

[BMIm][PF_6]

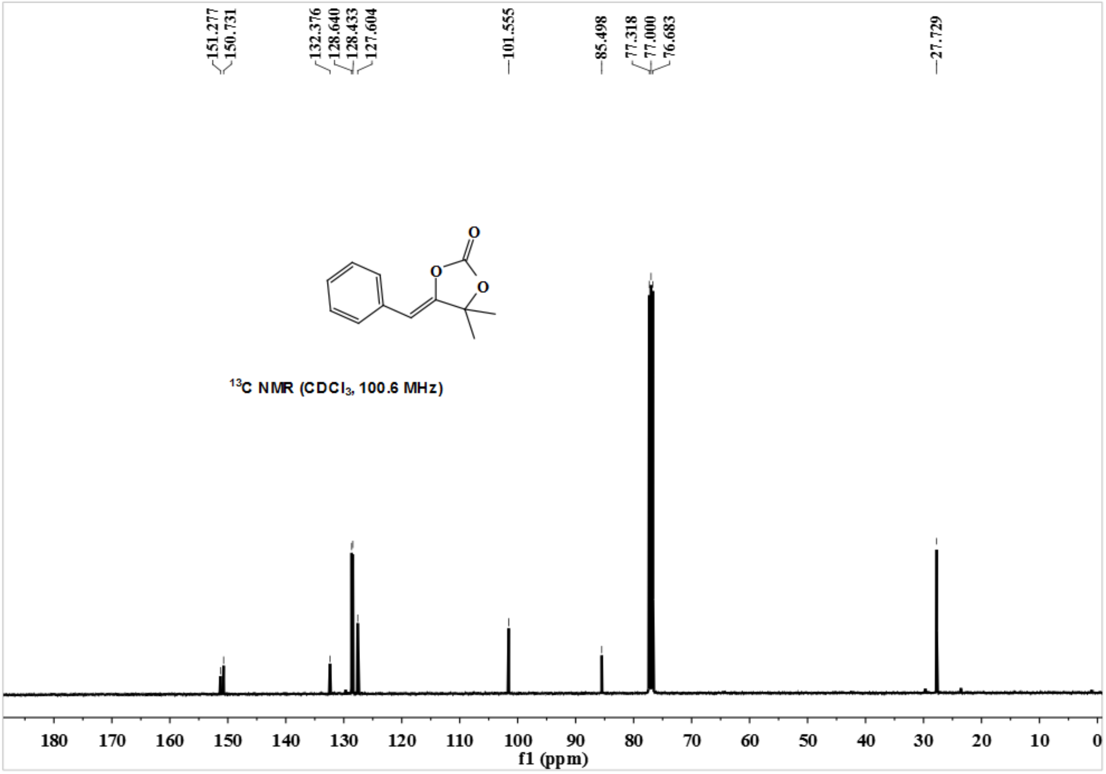


Scheme S1. Proposed mechanism for the reaction of the reaction of propargyl alcohols with CO_2 according to the literature and our experimental results.[8]

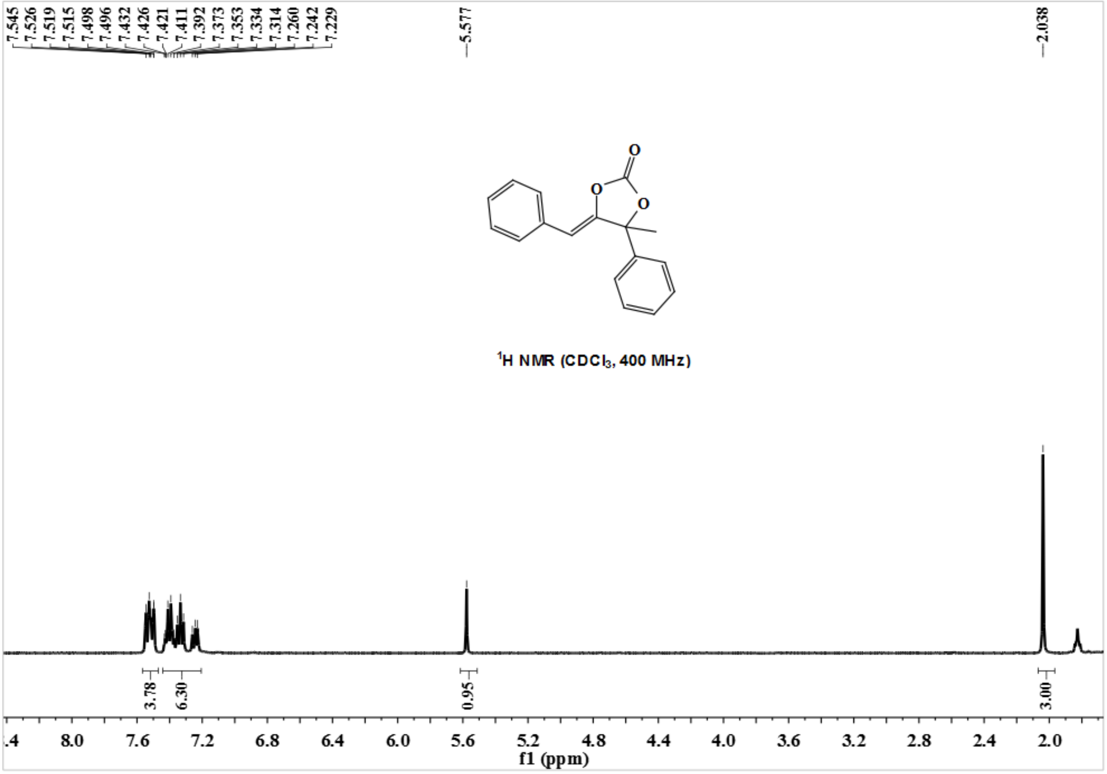
3. NMR characterization and data of the α-alkylidene cyclic carbonates

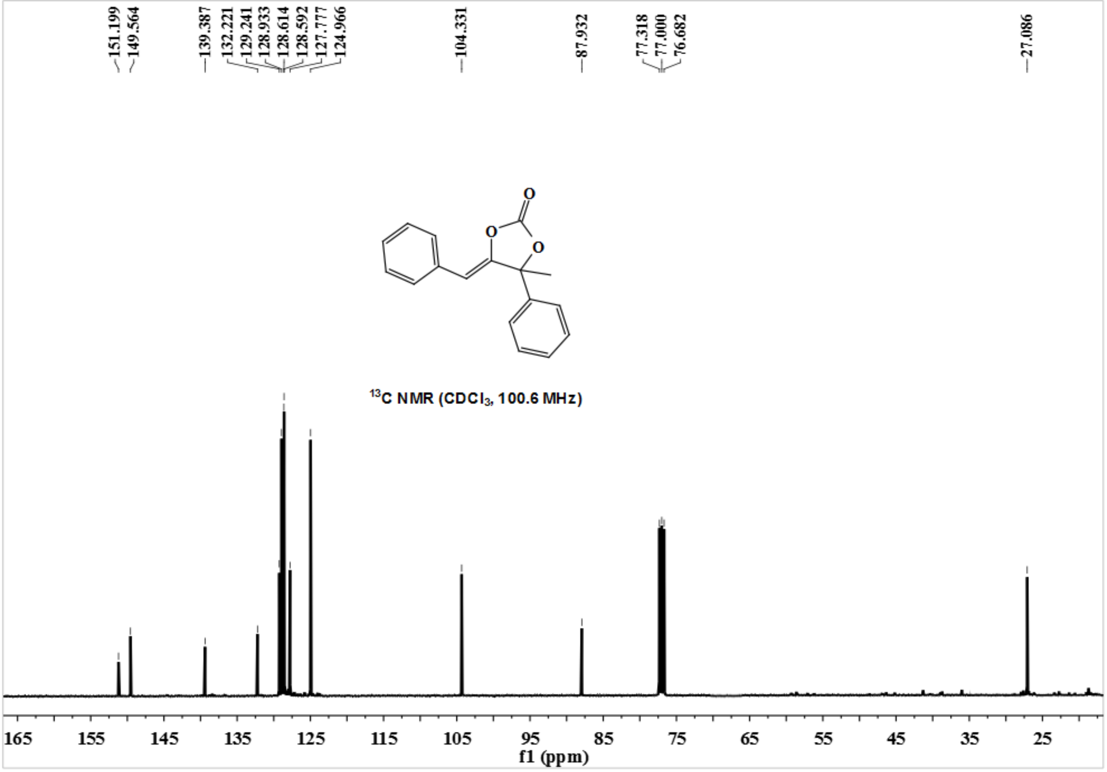
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.62 (s, 6H), 5.43 (s, 1H), 7.19 (t, ^3J = 7.6 Hz, 1H), 7.29 (t, ^3J = 7.6 Hz, 2H), 7.46 (s, 1H), 7.48 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 27.7, 85.5, 101.6, 127.6, 128.4, 128.6, 132.4, 150.7, 151.3; EI-MS calculated for [M]: $C_{12}H_{12}O_3$ (204.22), found [M] (204), [M-CO_2] (160), [M-$C_2O_2H_3$] (145), [M-C_2O_3] (132), [M-$C_3O_3H_3$] (117).



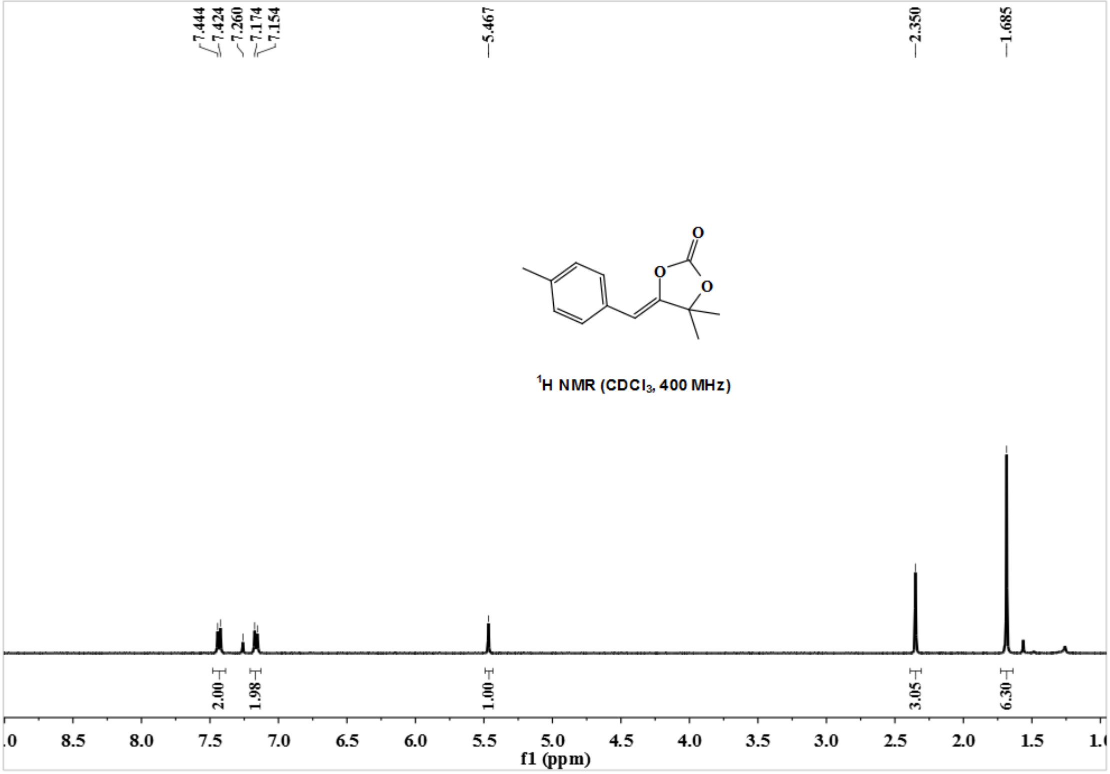


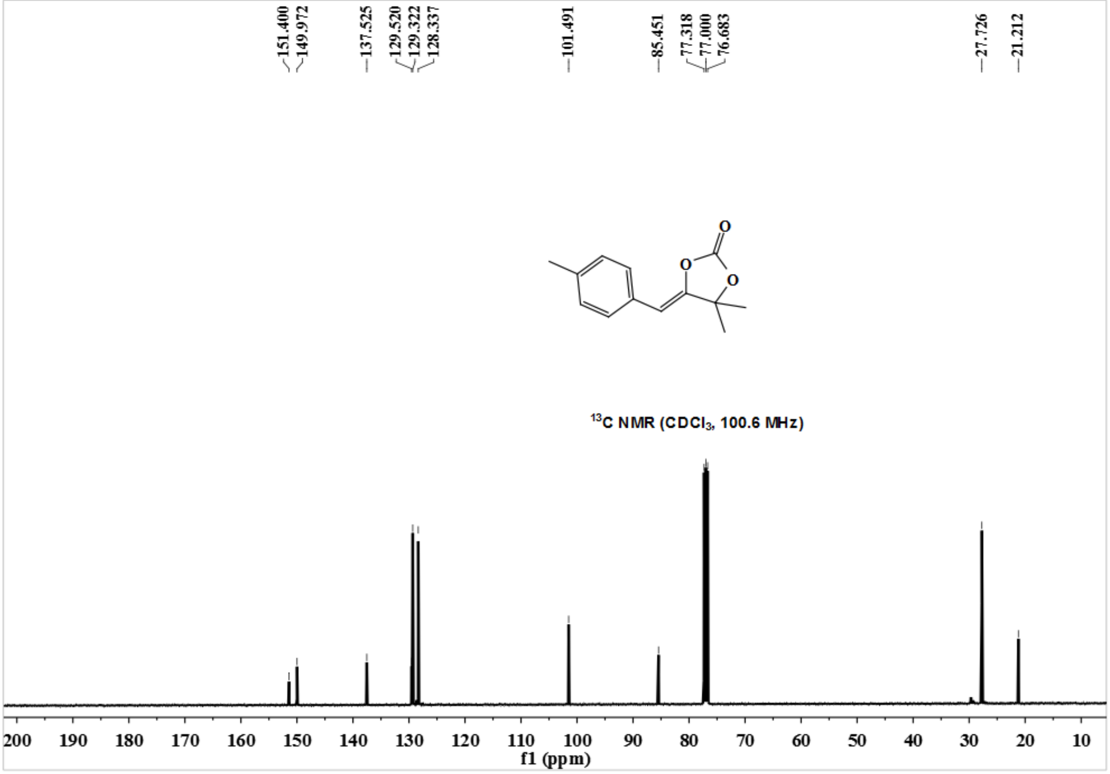
^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.04 (s, 3H), 5.58 (s, 1H), 7.23-7.41 (m, 6H), 7.50-7.55 (m, 4H); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 27.1, 87.9, 104.3, 125.0, 127.8, 128.6, 128.9, 129.2, 132.2, 139.4, 149.6, 151.2; EI-MS calculated for [M]: $C_{17}H_{14}O_3$ (266.09), found [M] (266), [M-CO$_2$] (222), [M-C$_2$O$_3$] (194), [M-C$_6$H$_5$] (189), [M-C$_3$HO$_3$] (179).



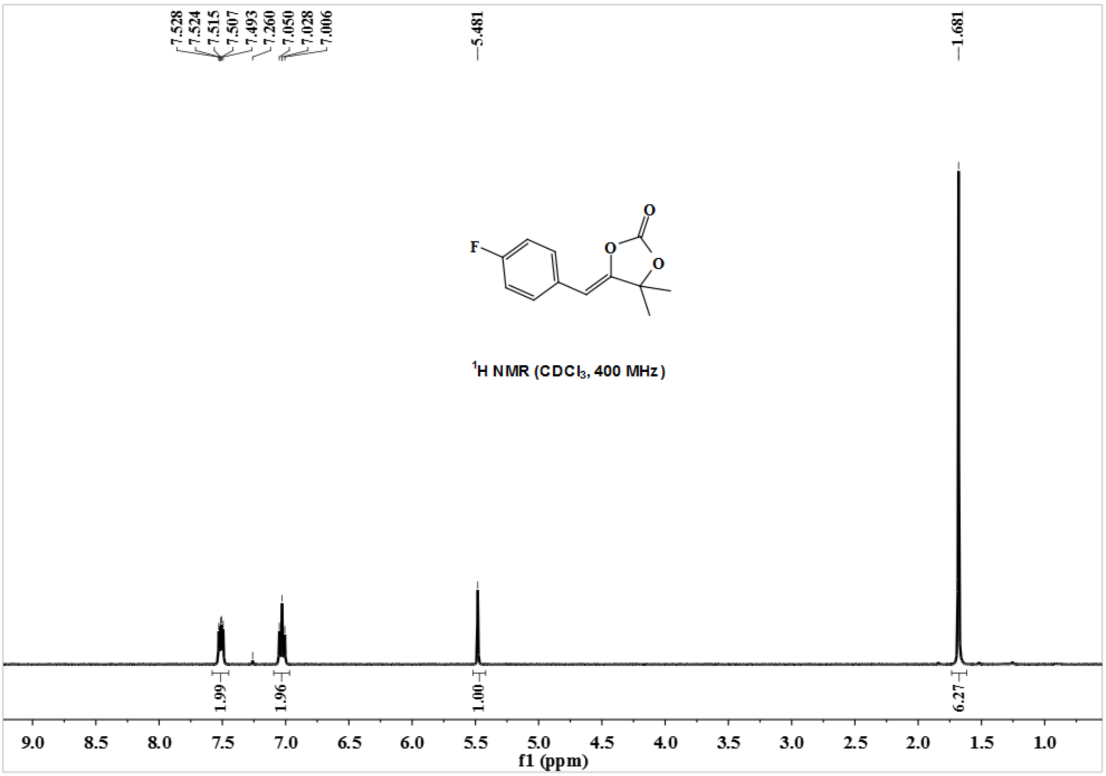


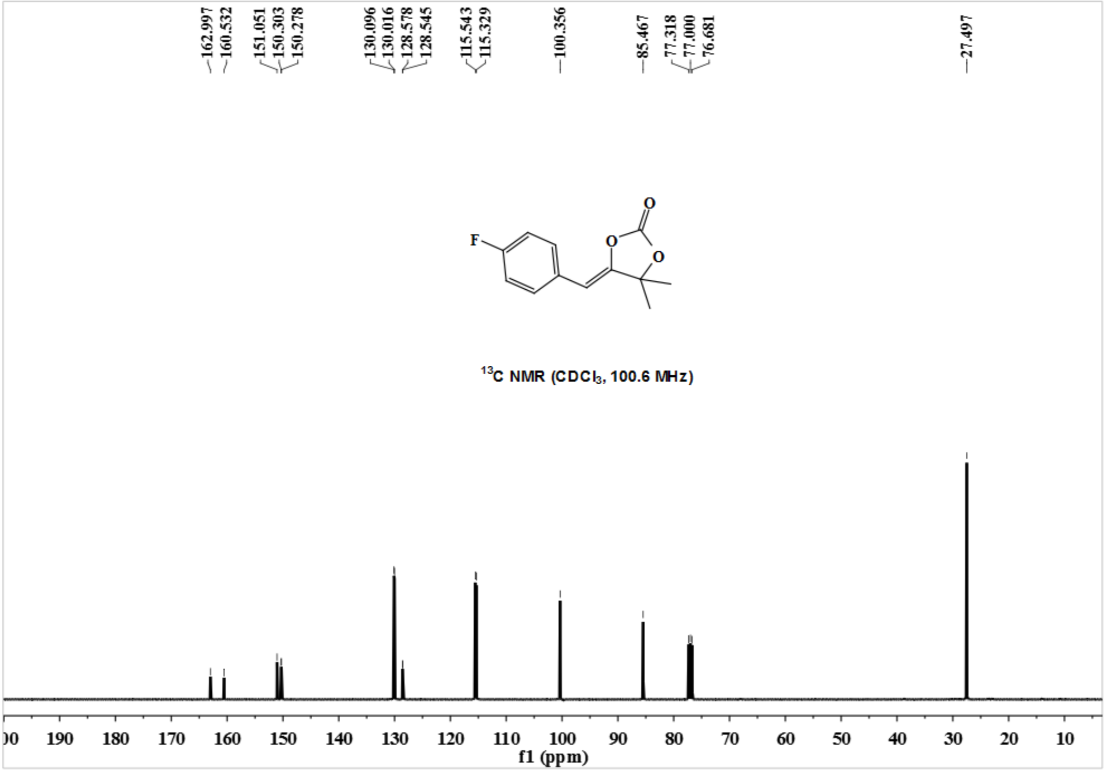
^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.68 (s, 6H), 2.35 (s, 3H), 5.47 (s, 1H), 7.16 (d, ^3J = 8 Hz, 2H), 7.43 (d, ^3J = 8 Hz, 2H); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 21.2, 27.7, 85.4, 101.5, 128.3, 129.3, 129.5, 137.5, 150.0, 151.4; EI-MS calculated for [M]: $C_{13}H_{14}O_3$ (218.09), found [M] (218), [M-CO$_2$] (174), [M-CH$_3$O$_2$] (159), [M-C$_2$O$_3$] (146), [M-C$_3$HO$_3$] (131).



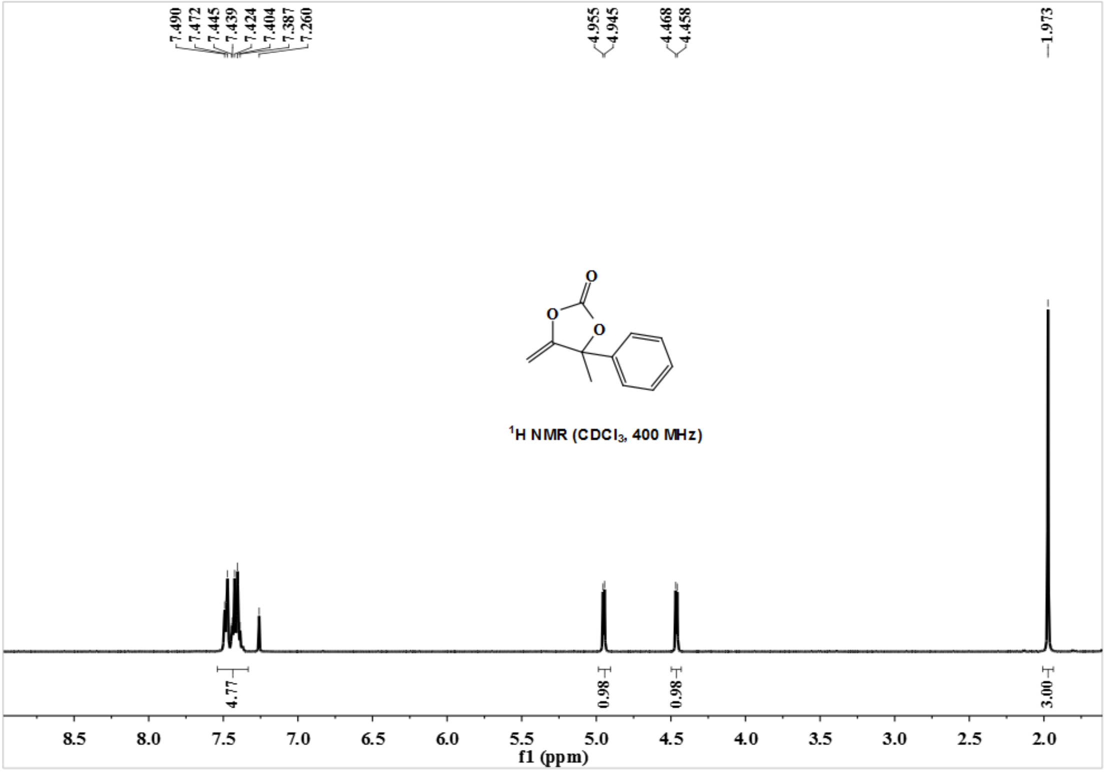


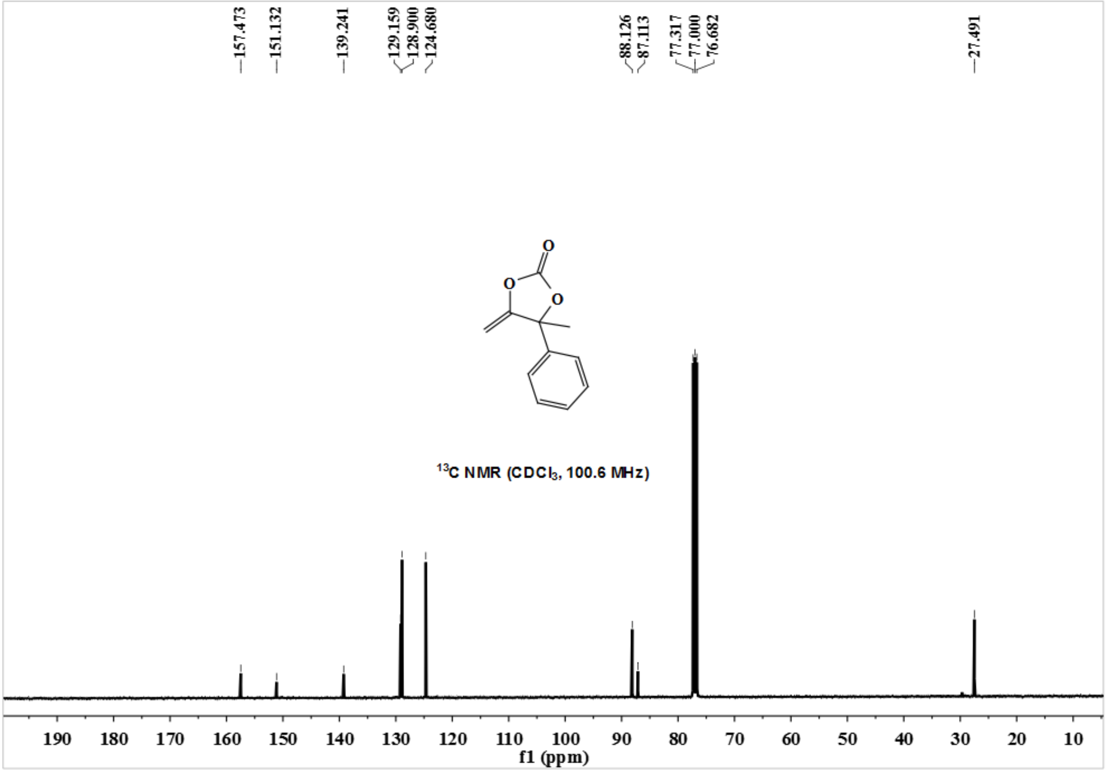
^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.68 (s, 6H), 5.48 (s, 1H), 7.03 (t, ^3J = 8.8 Hz, 2H), 7.49-7.53 (m, 2H); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 27.5, 85.5, 100.4, 115.3, 115.5, 128.5, 128.6, 130.0, 130.1, 150.3, 151.1, 160.5, 163.0; EI-MS calculated for [M]: $C_{12}H_{11}FO_3$ (222.07), found [M] (222), [M-CO_2] (178), [M-$C_2H_3O_2$] (1163), [M-C_2O_3] (150), [M-$C_3H_3O_3$] (135).





^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.97 (s, 3H), 4.46 (d, ^3J = 4 Hz, 1H), 4.95 (d, ^3J = 4 Hz, 1H), 7.39-7.49 (m, 5H); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 27.5, 87.1, 88.1, 124.7, 128.9, 129.2, 139.2, 151.1, 157.5; EI-MS calculated for [M]: $C_{11}H_{10}O_3$ (190.06), found [M] (190), [M-CO_2] (146), [M-$C_2H_3O_2$] (131), [M-C_2O_3] (118), [M-$C_3H_3O_3$] (103), [M-$C_5H_5O_3$] (77).





4. Reference

[1] a) S. Yuan, S. Kirklin, B. Dorney, D.-J. Liu, L. Yu, *Macromolecules* **2009**, *42*, 1554-1559; b) Y. He, S. Xiang, B. Chen, *J. Am. Chem. Soc.* **2011**, *133*, 14570-14573.

[2] J.-X. Jiang, C. Wang, A. Laybourn, T. Hasell, R. Clowes, Y. Z. Khimyak, J. Xiao, S. J. Higgins, D. J. Adams, A. I. Cooper, *Angew. Chem. Int. Ed.* **2011**, *50*, 1072-1075.

[3] Q.-W. Song, B. Yu, X.-D. Li, R. Ma, Z.-F. Diao, R.-G. Li, W. Li, L.-N. He, *Green Chem.* **2013**.

[4] C. Yu, M. G. Cowan, R. D. Noble, W. Zhang, *Chem. Commun.* **2014**, *50*, 5745-5747.

[5] A. Kaeser, B. Delavaux-Nicot, C. Duhayon, Y. Coppel, J.-F. Nierengarten, *Inorg. Chem.* **2013**, *52*, 14343-14354.

[6] a) Z.-Z. Yang, Y. Zhao, G. Ji, H. Zhang, B. Yu, X. Gao, Z. Liu, *Green Chem.* **2014**, DOI: 10.1039/C1034GC00730A; b) Y. Zhang, L. Zhao, P. K. Patra, D. Hu, J. Y. Ying, *Nano Today* **2009**, *4*, 13-20.

[7] C. Wang, H. Luo, D.-e. Jiang, H. Li, S. Dai, *Angew. Chem. Int. Ed.* **2010**, *49*, 5978-5981.

[8] S. Kikuchi, S. Yoshida, Y. Sugawara, W. Yamada, H.-M. Cheng, K. Fukui, K. Sekine, I. Iwakura, T. Ikeno, T. Yamada, *Bull. Chem. Soc. Jpn.* **2011**, *84*, 698-717.