Supporting Information

Secondary Sphere Effects on Porous Polymeric Organocatalysts for CO_2 Transformations: Subtle Modifications Resulting in Superior Performance

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Characterization

The gas adsorption isotherms were collected on the surface area analyzer ASAP 2020. The N_2 sorption isotherms were measured at 77 K using a liquid N_2 bath. IR spectra were recorded on a Nicolet Impact 410 Attenuated Total Reflectance-Fourier transform Infrared (ATR-FTIR) spectrometer. X-ray photoelectron spectroscopy (XPS) spectra were performed on a Thermo ESCALAB 250 with Al $K\alpha$ irradiation at θ=90° for X-ray sources, and the binding energies were calibrated using the C1s peak at 284.9 eV. ^{1}H NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts are expressed in ppm downfield from TMS at δ=0 ppm, and *J* values are given in Hz. ^{13}C (100.5 MHz) cross-polarization magic-angle spinning (CP-MAS) NMR experiments were recorded on a Varian infinity plus 400 spectrometer equipped with a magic-angle spin probe in a 4-mm ZrO_2 rotor. The high-resolution mass spectra (HRMS) were collected on an Agilent 6244 Tof-MS spectrometer and were reported for the molecular ion (M^+).

Computational Methods

Quantum chemical calculations were performed with the Gaussian 09 C.01 software.[1] We adopted the density functional theory (DFT) approach for our calculations using the classical B3LYP hybrid density functional[2,3] with the 6-31G(d)[4,5] basis set for all the light atoms. Frequency calculations were performed at the B3LYP/6-31G(d) level to ensure that all the geometries in the gas phase (optimized at the same B3LYP/6-31G(d) level) were minimal. Frequency calculations were performed at the B3LYP/6-31G(d) level to ensure that all the reactants, intermediates and products in the gas phase were minima. The transition state search function was used to explore accurate transition state with a single imaginary frequency. Then the intrinsic reaction coordinate (IRC) theory was used to verify that the given transition states were well connected to the desired adjacent minima.

Table S1. The pseudo-first-order rate constant k values and the apparent activation energies (E_a) of various polymeric pyridinium salts in the cycloaddition of 1,2-epoxy-3-phenoxypropane and CO_2 derived from the slopes in Figure S20.[a]

Catalysts	k (s^{-1})		E_a (kJ mol^{-1})
PQA-Py-Br	35 ºC	0.00090	77.6
	40 ºC	0.00146	
	50 ºC	0.00359	
PQA-*p*NH_2Py-Br	35 ºC	0.00388	55.6
	40 ºC	0.00549	
	50 ºC	0.01168	
PQA-*p*N$(Me)_2$Py-Br	35 ºC	0.00157	68.0
	40 ºC	0.00248	
	50 ºC	0.00557	
PQA-*p*NHCOMePy-Br	35 ºC	0.00276	61.0
	40 ºC	0.00429	
	50 ºC	0.00886	
PQA-*p*ClPy-Br	35 ºC	0.00080	82.6
	40 ºC	0.00135	
	50 ºC	0.00347	
PQA-*o*NH_2Py-Br	35 ºC	0.00646	40.8
	40 ºC	0.00833	
	50 ºC	0.01350	

[a] Reaction conditions: 1,2-epoxy-3-phenoxypropane (1.0 g, 6.7 mmol), catalyst (25 mg), CO_2 (1 atm).

Table S2. Catalytic data over various catalytic materials in the cycloaddition of 1,2-epoxy-3-phenoxypropane and CO_2.

Catalysts (loading)	Temperature (°C)	Time (h)	Yield (%)	TON
PIP-Bn-Cl[1] (0.75 mmol %)	80	48	89.6	120
COP-222[2] (1.8 mol %)	100	36	91	50
PGDBr-5-2OH[3] (1.9 mol %)	70	8	93	49
Si-PMS[4] (0.9 mol%)	110	2	95	106
POM3-IM[5] (5 mol%)	120	12	91	182
F-PIL-Br[6] (1 mol%)	120	9	97	97
MOP-0[7] (3 mol %)	100	24	87	29
This work (0.1 mol %)	120	12	99	990

1. Sun, Q.; Jin, Y.; Aguila, B.; Meng, X.; Ma, S.; Xiao, F.-S. Porous Ionic Polymers as A Robust and Efficient Platform for Capture and Chemical Fixation of Atmospheric CO_2. *ChemSusChem* **2017**, *10*, 1160-1165.
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3. Guo, Z. J.; Jiang, Q.W.; Shi, Y. M.; Li, J.; Yang, X. N.; Hou, W.; Zhou, Y.; Wang, J. Tethering Dual Hydroxyls into Mesoporous Poly(ionic liquid)s for Chemical Fixation of CO_2 at Ambient Conditions: A Combined Experimental and Theoretical Study. *Acs Catal.*, **2017**, *7*, 6770-6780.
4. Wang, J.; Leong, J.; Zhang, Y. Efficient Fixation of CO_2 into Cyclic Carbonates Catalysed by Silicon-Based Main Chain Poly-Imidazolium Salts. *Green Chem*., **2014**, *16*, 4515-4519.
5. Wang, J.; Sng, W.; Yi, G.; Zhang, Y. Imidazolium Salt-Modified Porous Hypercrosslinked Polymers for Synergistic CO_2 Capture and Conversion. *Chem. Commun.,* **2015**, *51*, 12076-12079.
6. Yang, Z.-Z.; Zhao, Y.; Ji, G.; Zhang, H.; Yu, B.; Gao, X.; Liu, Z. Fluoro-Functionalized Polymeric Ionic Liquids: Highly Efficient Catalysts for CO_2 Cycloaddition to Cyclic Carbonates under Mild Conditions. *Green Chem*., **2014**, *16*, 3724-3728.
7. Zhang, N.; Zou, B.; Yang, G.-P.; Yu, B.; Hu, C.-W. Melamine-Based Mesoporous Organic Polymers as Metal-Free Heterogeneous Catalyst: Effect of Hydroxyl on CO_2 Capture and Conversion. *J. CO_2 Util.,* **2017**, *22*, 9-14.

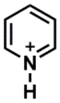
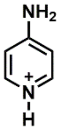
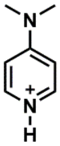
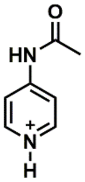
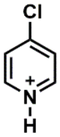
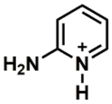
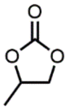
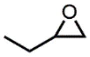
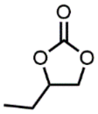
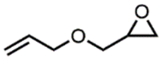
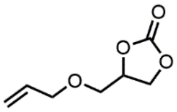
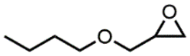
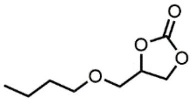
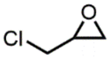
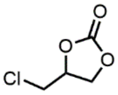
Pyridinium acids	pK_a values
	5.25
	9.11
	9.60
	13.82
	3.18
	6.82

Table S3. pK_a values of various pyridinium acids.

Table S4. PQA-*o*NH$_2$Py-Br catalyzed cycloaddition reactions of epoxides with CO$_2$.[a]

Entry	Epoxides	Products	T (ºC)	Time (h)	Yields (%)[b]
1			25	72	99
2			50	24	99
3			50	96	84
4			50	120	90
5[b]			70	72	99

[a] Reaction conditions: epoxide (1.0 g), PQA-*o*NH$_2$Py-Br (50 mg), CO$_2$ (1 atm). [b] 25 mg of PQA-*o*NH$_2$Py-Br was used. [c] The yields were determined by ^{1}H NMR.

Recycle times	1	2	3	4	5	6	7	8	9	10
Yield (%)	99	99	99	99	99	98	99	99	98	97

Table S5. Recycling test of PQA-*o*NH$_2$Py-Br.[a]

[a] Reaction conditions: 1,2-epoxy-3-phenoxypropane (1.0 g, 6.7 mmol), PQA-*o*NH$_2$Py-Br (25 mg), CO$_2$ (1 atm), 75 °C, and 72 h. The yields were determined by ^{1}H NMR.

Table S6. The pseudo-first-order rate constant k values and the apparent activation energies (E_a) of various polymeric pyridinium salts in the cycloaddition of 1-butyl-2-phenyl aziridine and CO_2 derived from the slopes in Figure S26.[a]

Catalysts	k (s^{-1})		E_a (kJ mol^{-1})
PQA-Py-Br	40 ºC	0.01037	37.8
	50 ºC	0.01599	
	60 ºC	0.02439	
PQA-*p*NH$_2$Py-Br	40 ºC	0.02422	31.6
	50 ºC	0.03592	
	60 ºC	0.05020	
PQA-*p*N(Me)$_2$Py-Br	40 ºC	0.01381	35.4
	50 ºC	0.02106	
	60 ºC	0.03130	
PQA-*p*NHCOMePy-Br	40 ºC	0.01845	33.5
	50 ºC	0.02797	
	60 ºC	0.04066	
PQA-*p*ClPy-Br	40 ºC	0.00852	40.1
	50 ºC	0.01340	
	60 ºC	0.02098	
PQA-*o*NH$_2$Py-Br	40 ºC	0.02823	27.6
	50 ºC	0.04095	
	60 ºC	0.05573	

[a] Reaction conditions: 1-butyl-2-phenyl aziridine (174.0 mg, 1 mmol), catalyst (25 mg), CO_2 (1 MPa).

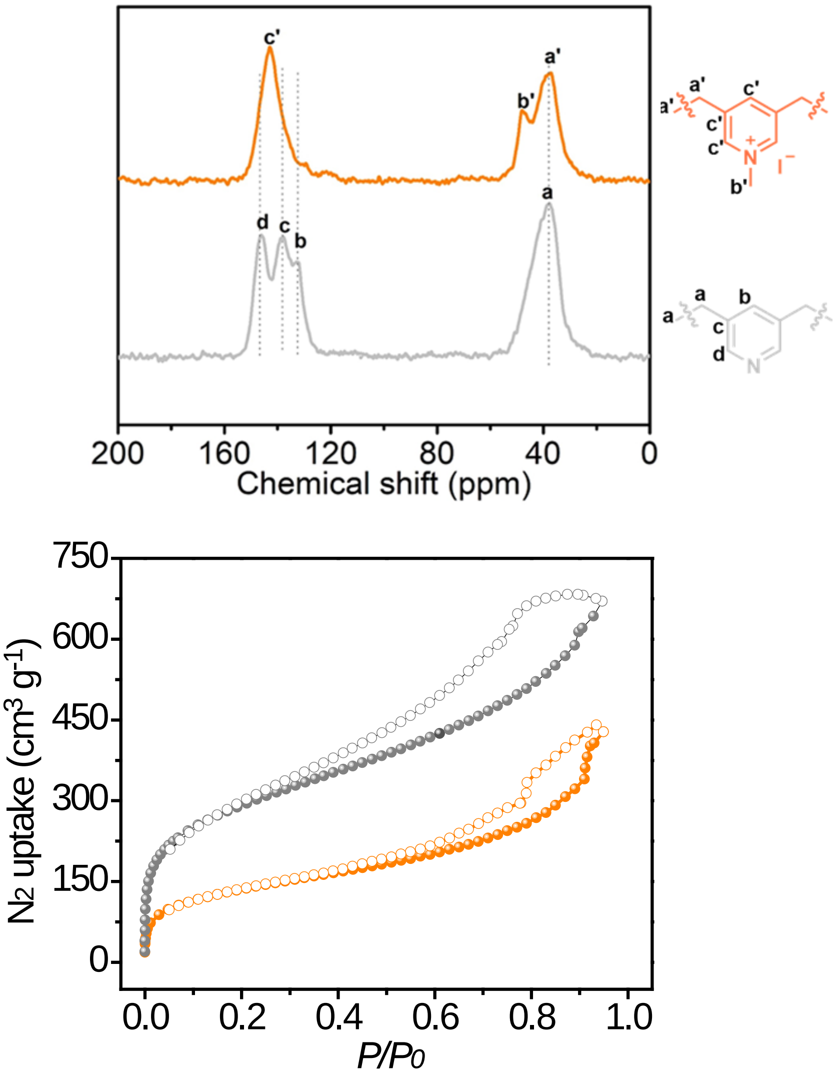


Figure S1. Solid-state ^{13}C NMR spectra (top) and N_2 sorption isotherms collected at 77 K (bottom) of PQA-Py-Br (orange) and its corresponding pyridine-based polymer (light gray) with a BET surface area of 447 m^2 g^{-1} and 979 m^2 g^{-1}, respectively.

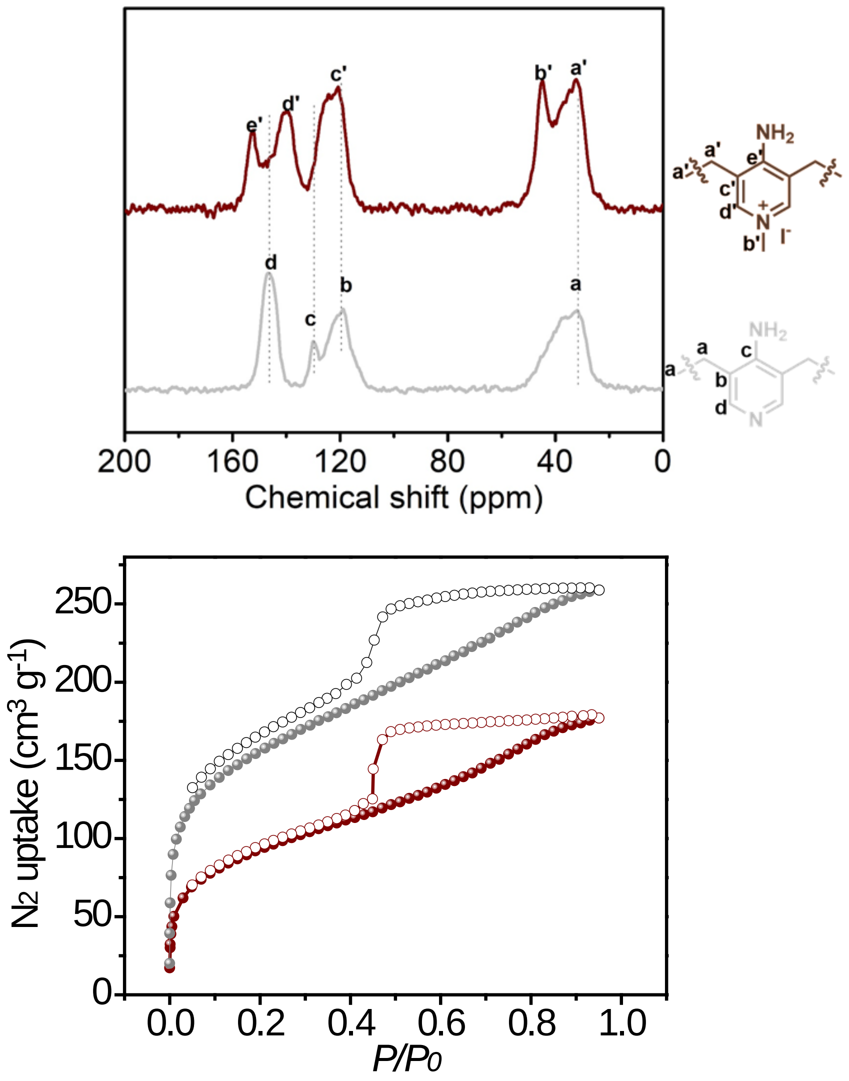


Figure S2. Solid-state ^{13}C NMR spectra (top) and N_2 sorption isotherms collected at 77 K (bottom) of PQA-*p*NH_2Py-Br (brown) and its corresponding pyridine-based polymer (light gray) with a BET surface area of 311 m^2 g^{-1} and 536 m^2 g^{-1}, respectively.

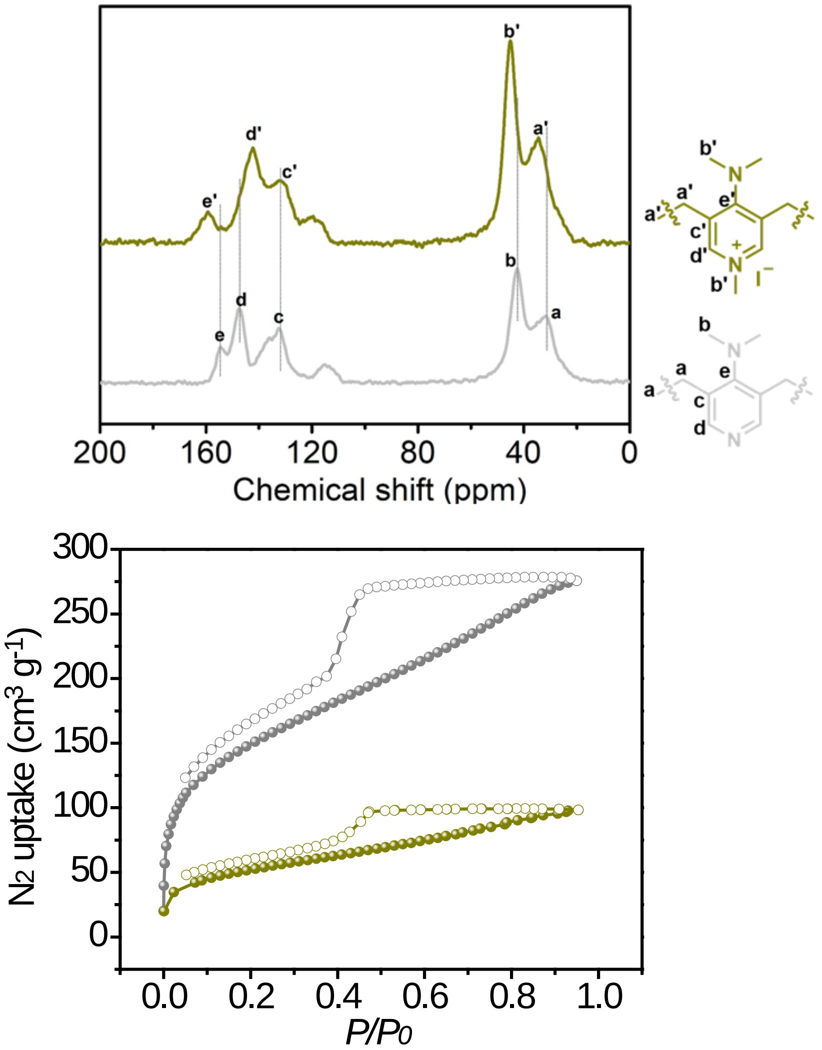


Figure S3. Solid-state ^{13}C NMR spectra (top) and N_2 sorption isotherms collected at 77 K (bottom) of PQA-*p*N(Me)$_2$Py-Br (dark yellow) and its corresponding pyridine-based polymer (light gray) with a BET surface area of 223 m^2 g^{-1} and 535 m^2 g^{-1}, respectively.

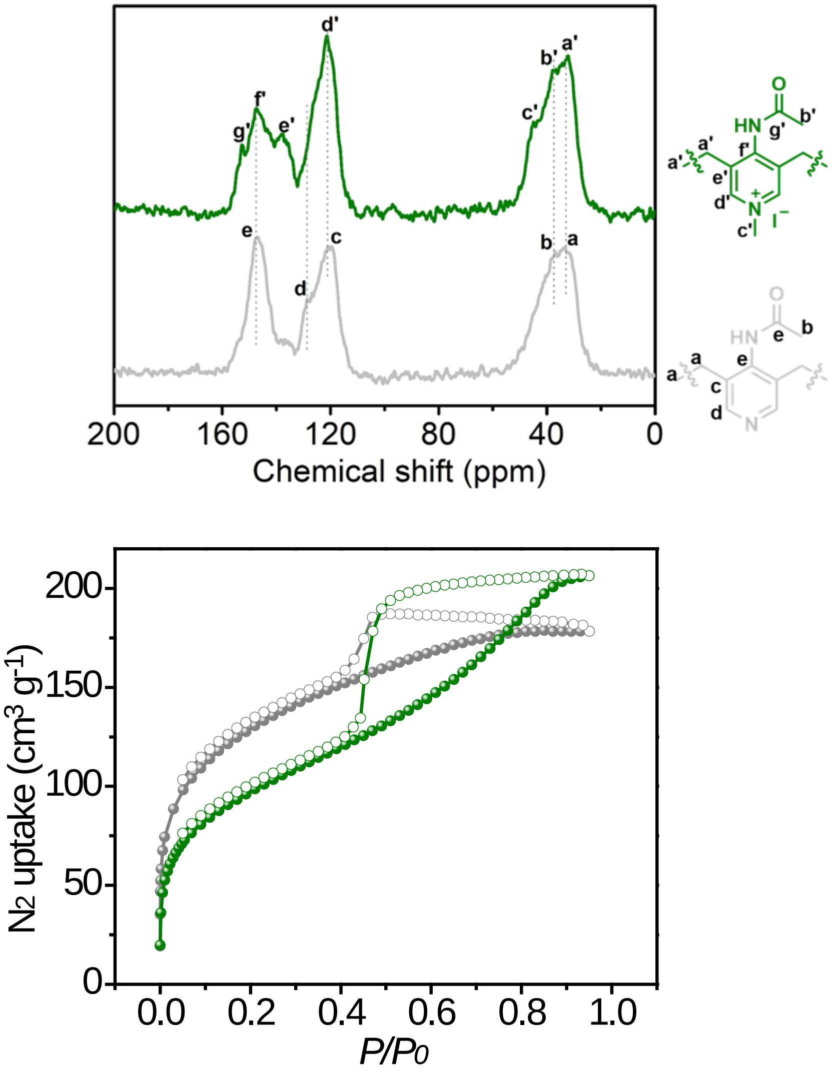


Figure S4. Solid-state ^{13}C NMR spectra (top) and N_2 sorption isotherms collected at 77 K (bottom) of PQA-*p*NHCOMePy-Br (green) and its corresponding pyridine-based polymer (light gray) with a BET surface area of 323 m^2 g^{-1} and 436 m^2 g^{-1}, respectively.

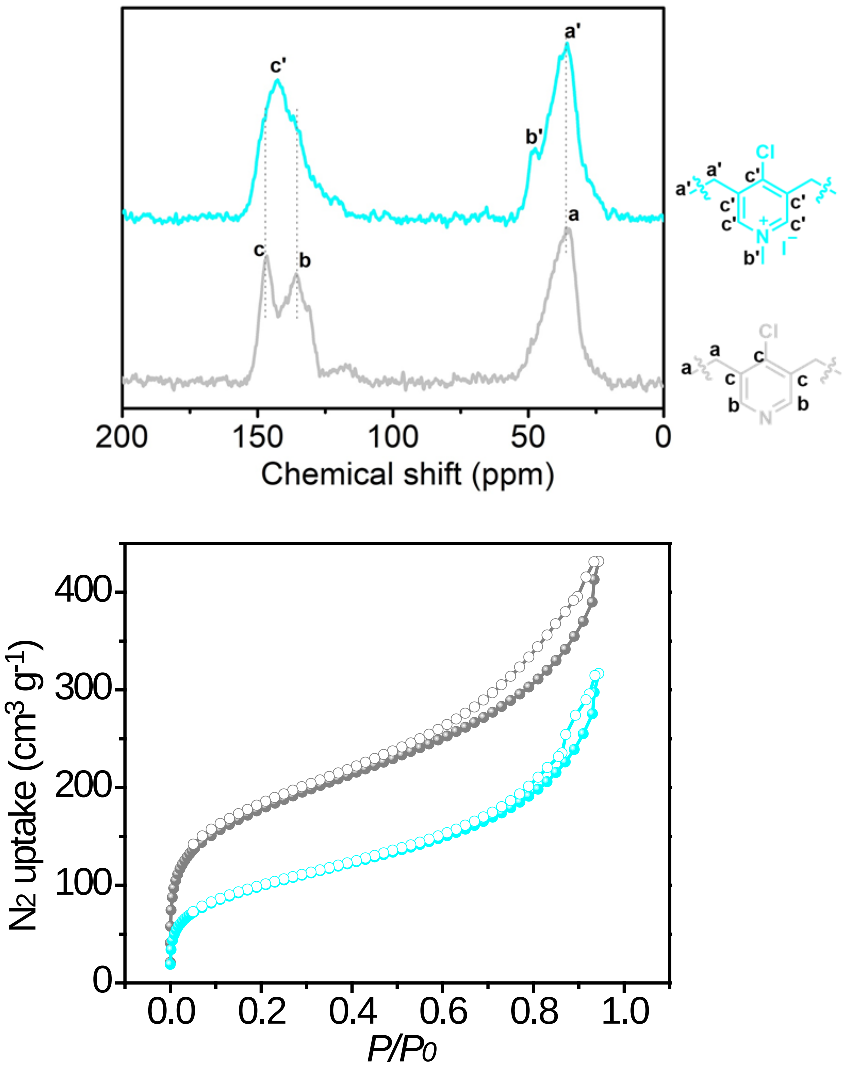


Figure S5. Solid-state ^{13}C NMR spectra (top) and N_2 sorption isotherms collected at 77 K (bottom) of PQA-*p*ClPy-Br (cyan) and its corresponding pyridine-based polymer (light gray) with a BET surface area of 327 m^2 g^{-1} and 602 m^2 g^{-1}, respectively.

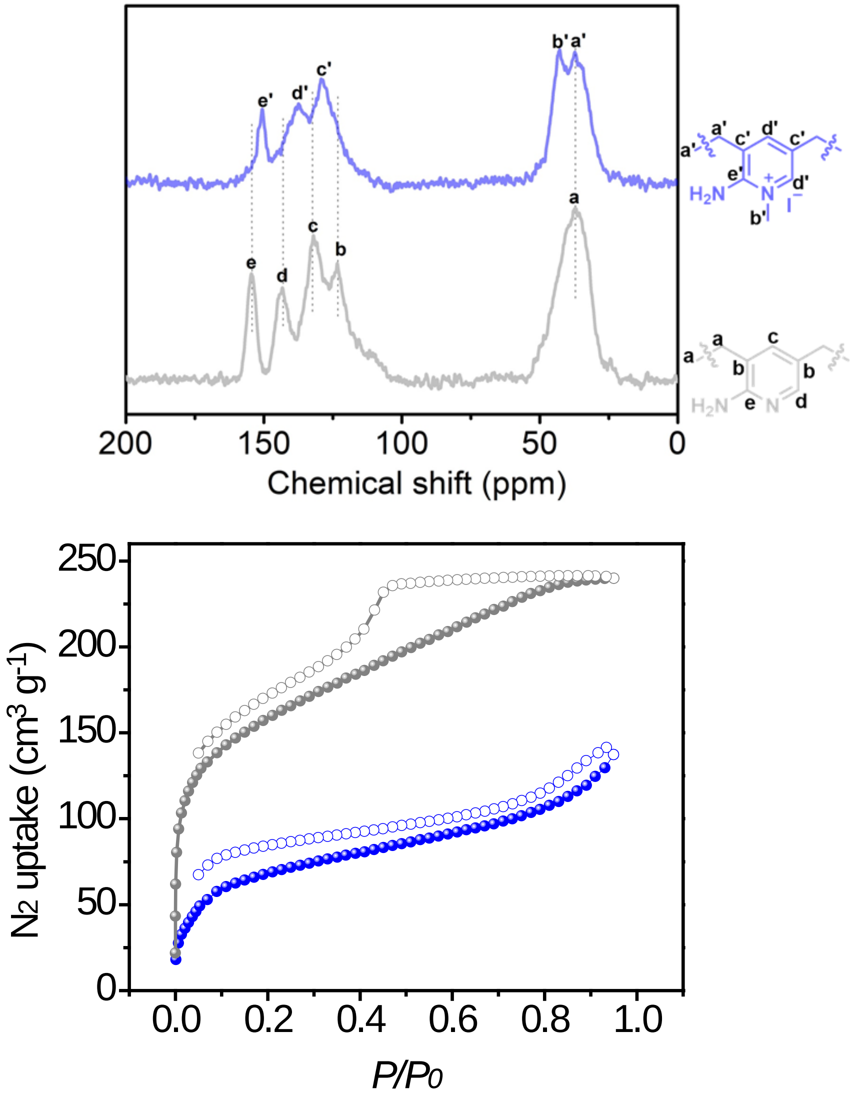


Figure S6. Solid-state ^{13}C NMR spectra (top) and N_2 sorption isotherms collected at 77 K (bottom) of PQA-*o*NH_2Py-Br (blue) and its corresponding pyridine-based polymer (light gray) with a BET surface area of 315 m^2 g^{-1} and 555 m^2 g^{-1}, respectively.

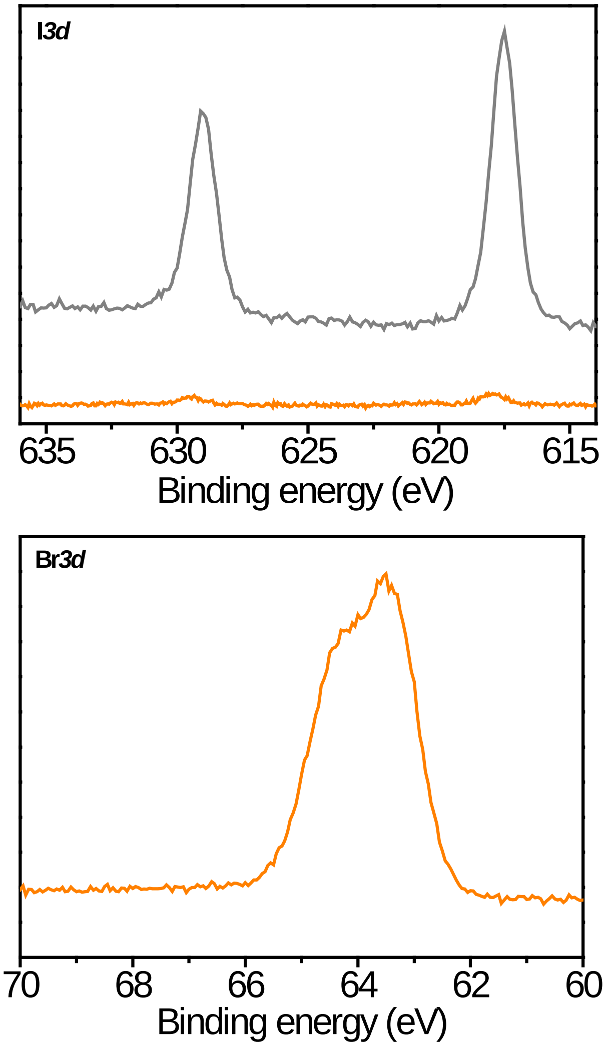


Figure S7. XPS spectra of PQA-Py-I (light gray) and PQA-Py-Br (orange)

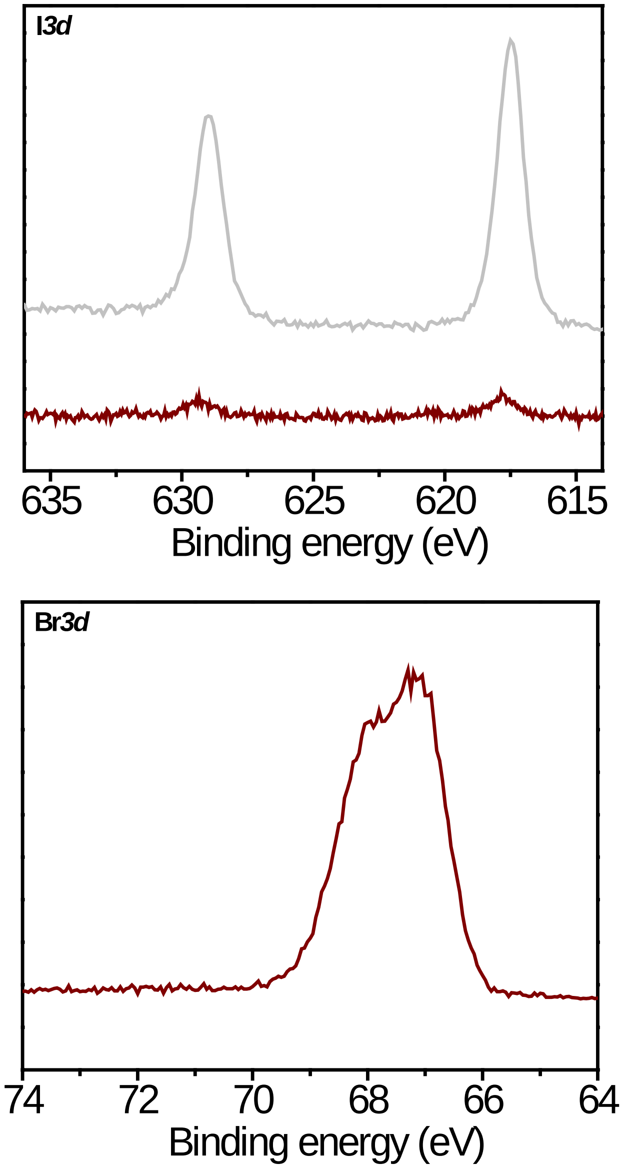


Figure S8. XPS spectra of PQA-*p*NH$_2$Py-I (light gray) and PQA-*p*NH$_2$Py-Br (brown)

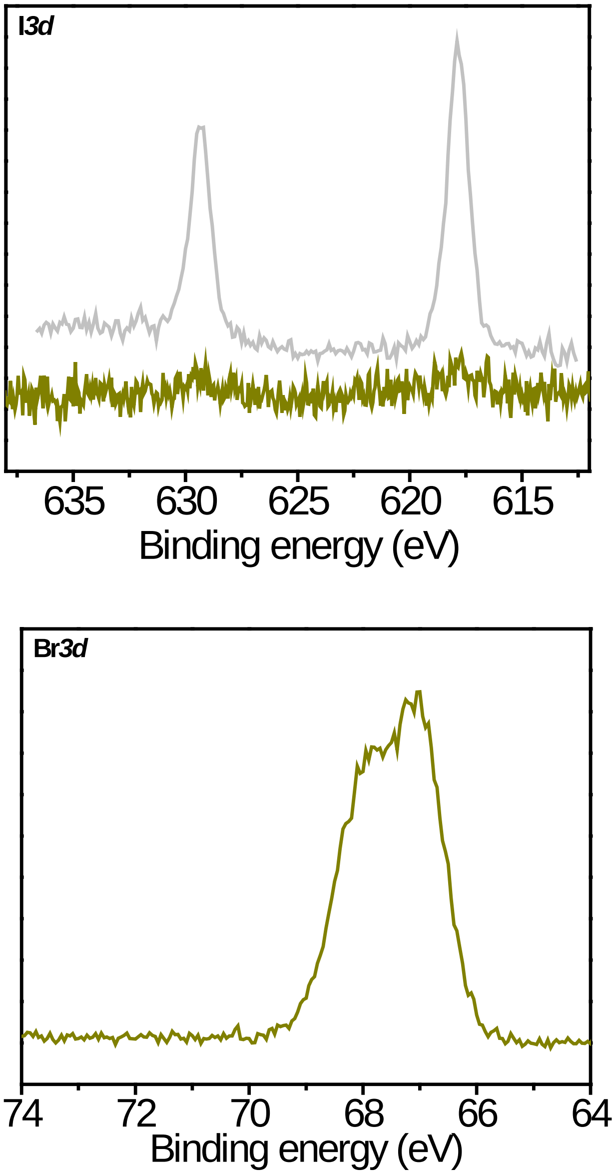


Figure S9. XPS spectra of PQA-*p*N(Me)$_2$Py-I (light gray) and PQA-*p*N(Me)$_2$Py-Br (dark yellow)

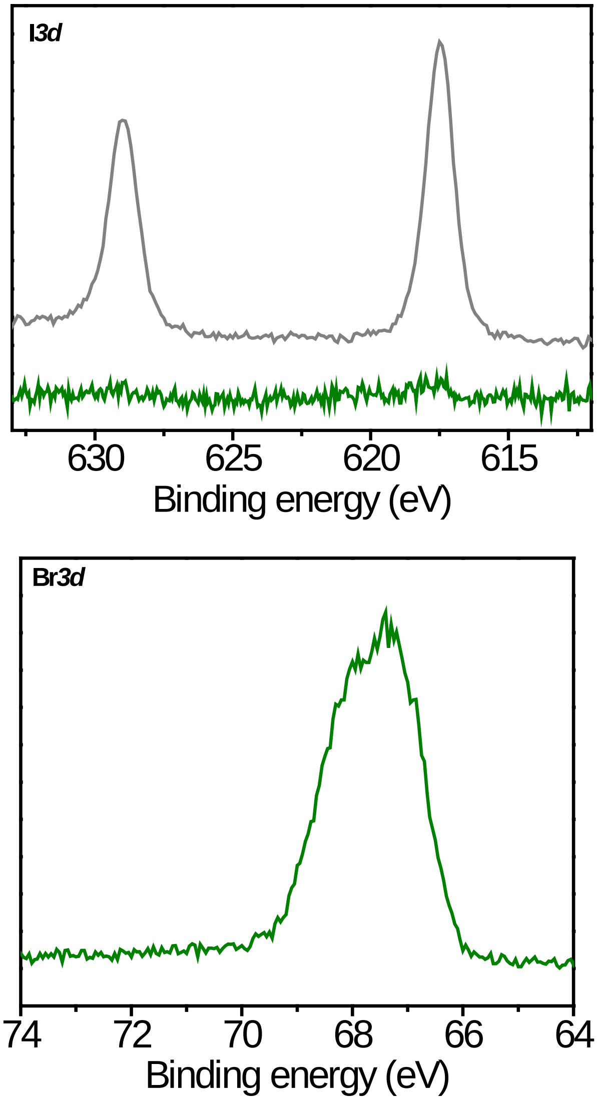


Figure S10. XPS spectra of PQA-*p*NHCOMePy-I (light gray) and PQA-*p*NHCOMePy-Br (green)

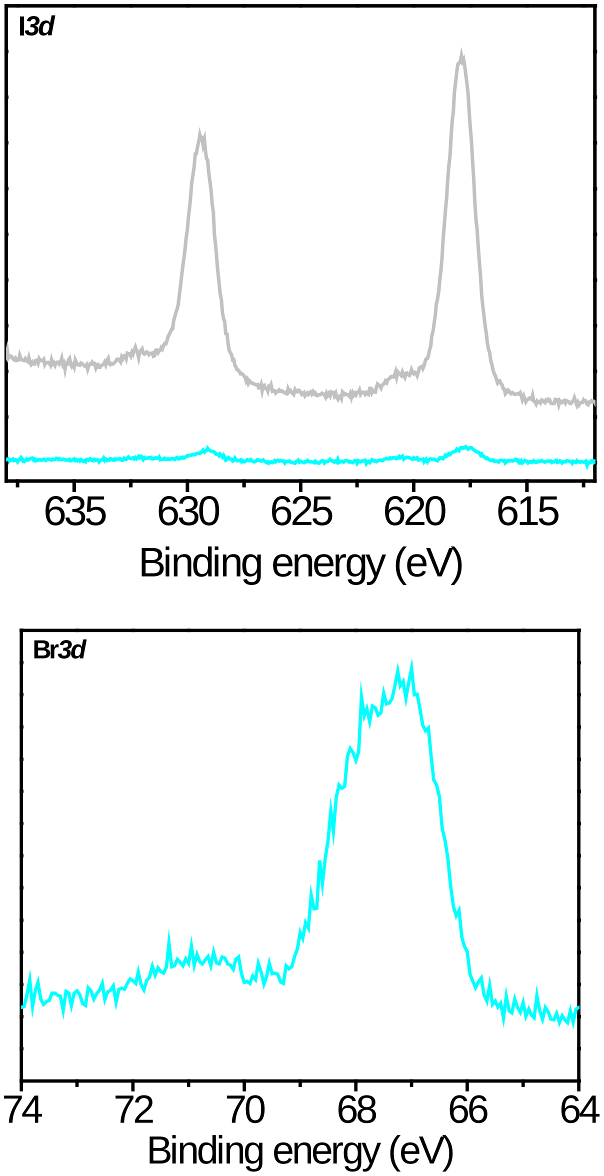


Figure S11. XPS spectra of PQA-*p*ClPy-I (light gray) and PQA-*p*ClPy-Br (cyan)

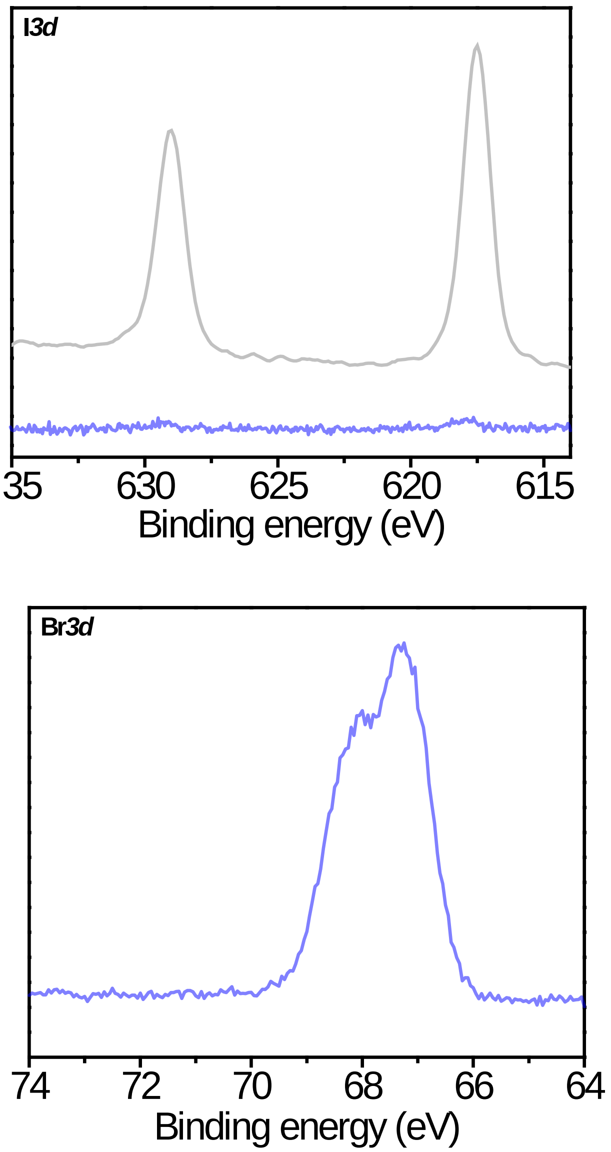


Figure S12. XPS spectra of PQA-*o*NH_2Py-I (light gray) and PQA-*o*NH_2Py-Br (blue).

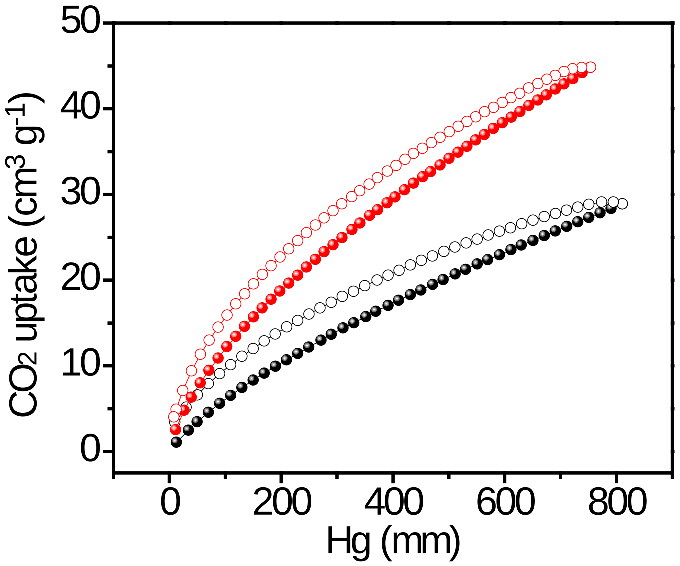


Figure S13. CO_2 sorption isotherms of PQA-Py-Br collected at 0 °C (red) and 25 °C (black), respectively.

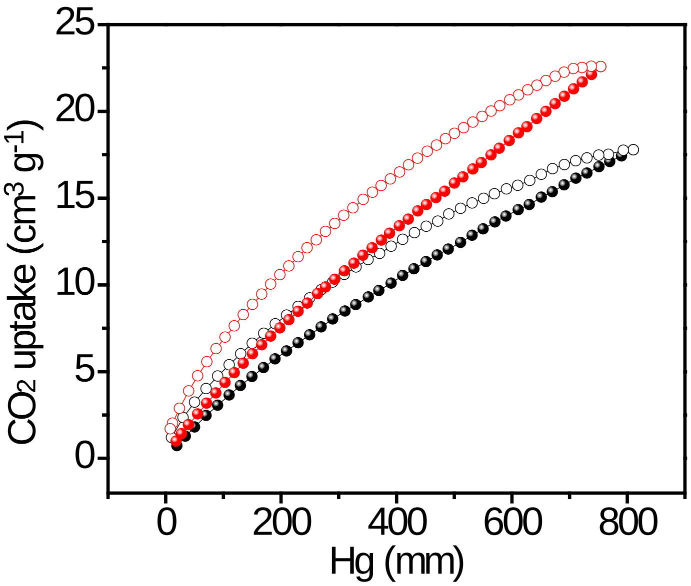


Figure S14. CO_2 sorption isotherms of PQA-*p*NH_2Py-Br collected at 0 °C (red) and 25 °C (black), respectively.

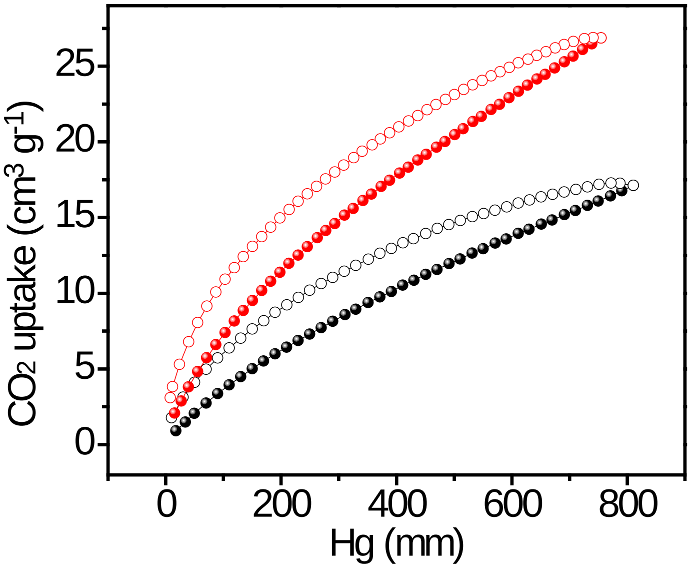


Figure S15. CO_2 sorption isotherms of PQA-*p*N(Me)$_2$Py-Br collected at 0 °C (red) and 25 °C (black), respectively.

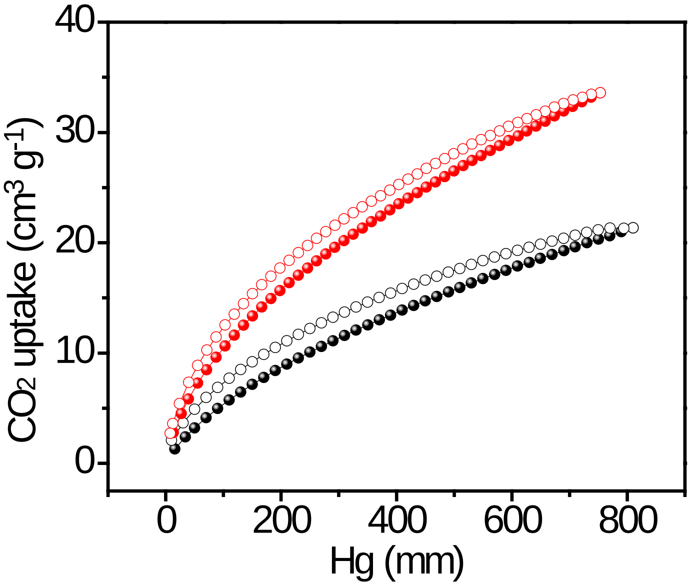


Figure S16. CO$_2$ sorption isotherms of PQA-*p*NHCOMePy-Br collected at 0 °C (red) and 25 °C (black), respectively.

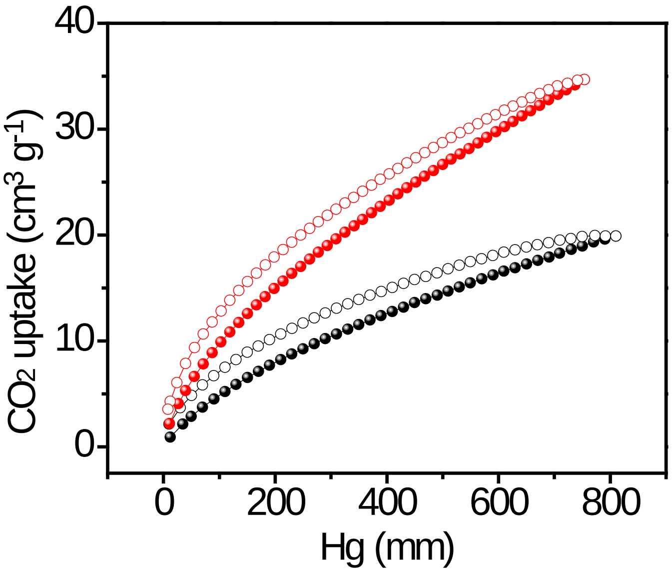


Figure S17. CO_2 sorption isotherms of PQA-*p*ClPy-Br collected at 0 °C (red) and 25 °C (black), respectively.

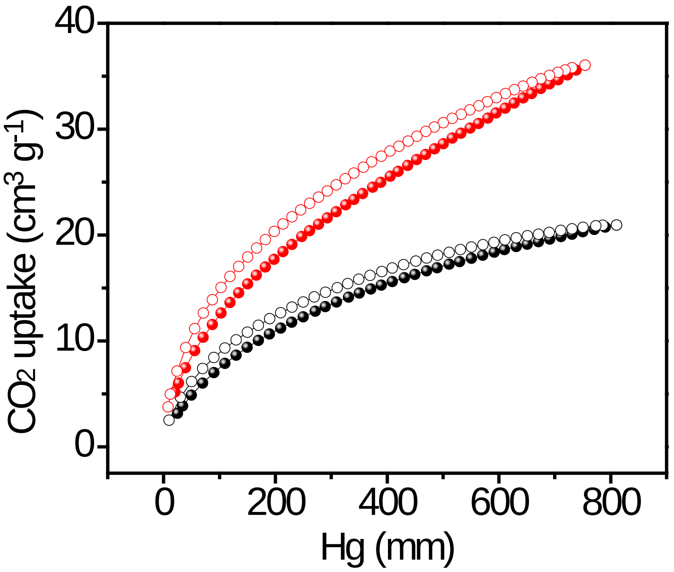


Figure S18. CO_2 sorption isotherms of PQA-*o*NH_2Py-Br collected at 0 °C (red) and 25 °C (black), respectively.

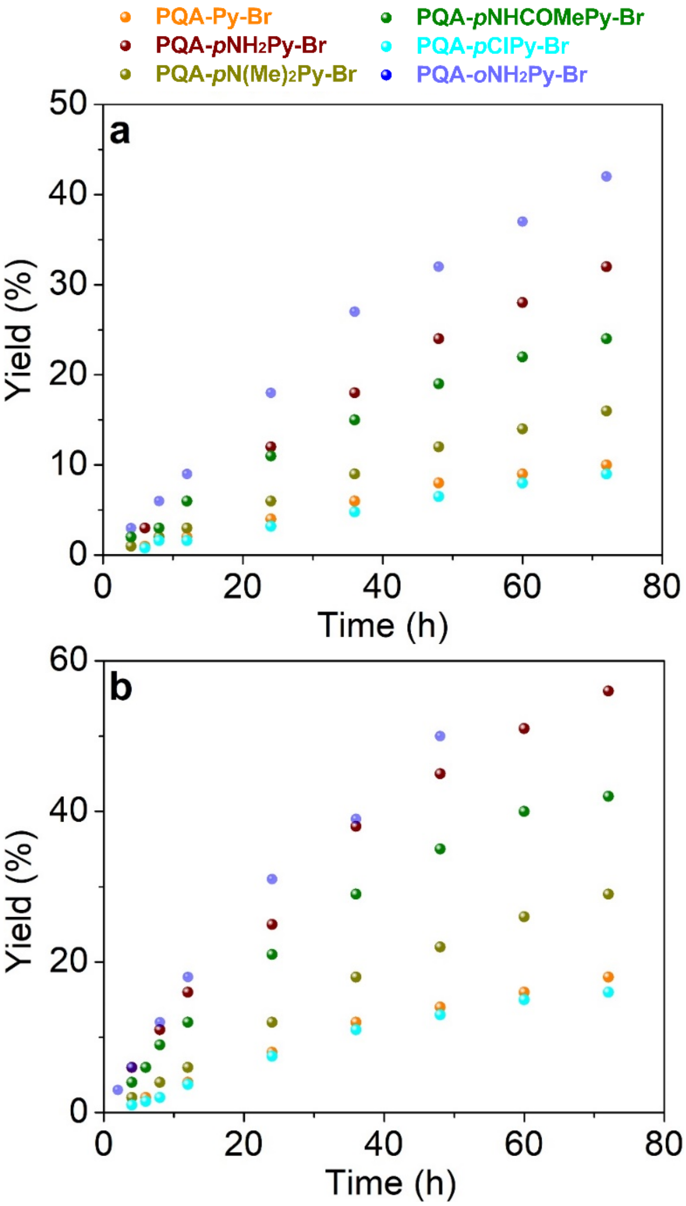


Figure S19. Kinetic rates of carbonate product yields in the cycloaddition of 1,2-epoxy-3-phenoxypropane and CO_2 over various polymeric pyridinium salts at (a) 40 °C and (b) 50 °C.

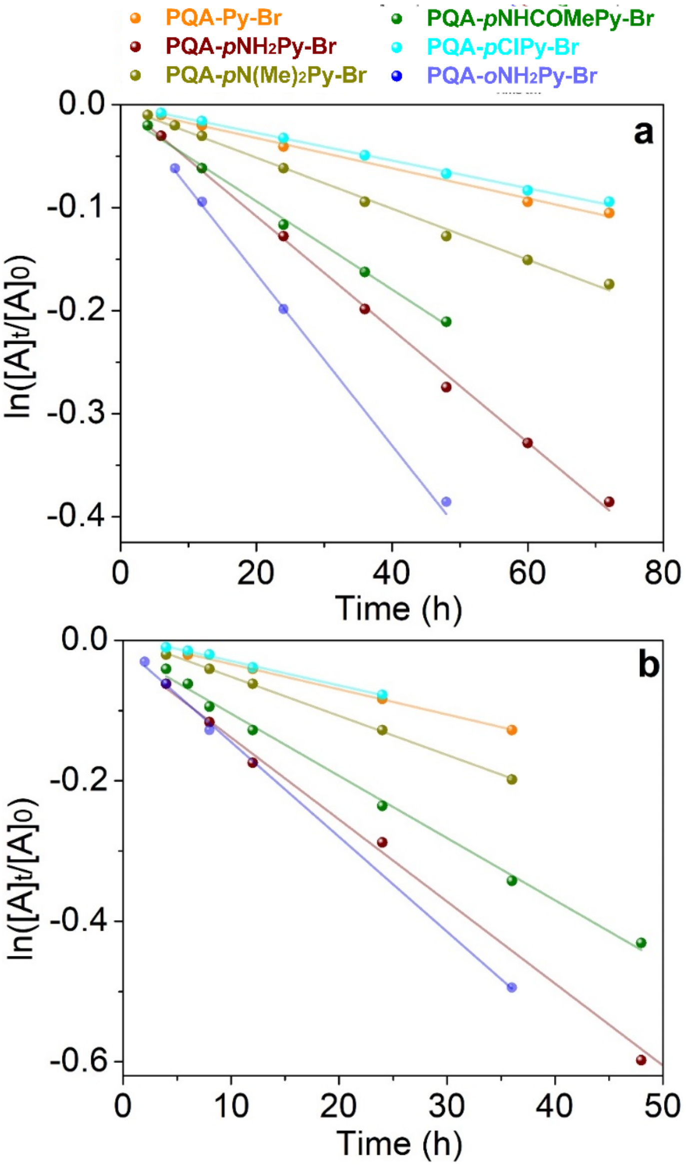


Figure S20. First order reaction rate plots (R^2>0.99 for all) in the cycloaddition of 1,2-epoxy-3-phenoxypropane and CO_2 over various polymeric pyridinium salts at (a) 40 °C and (b) 50 °C.

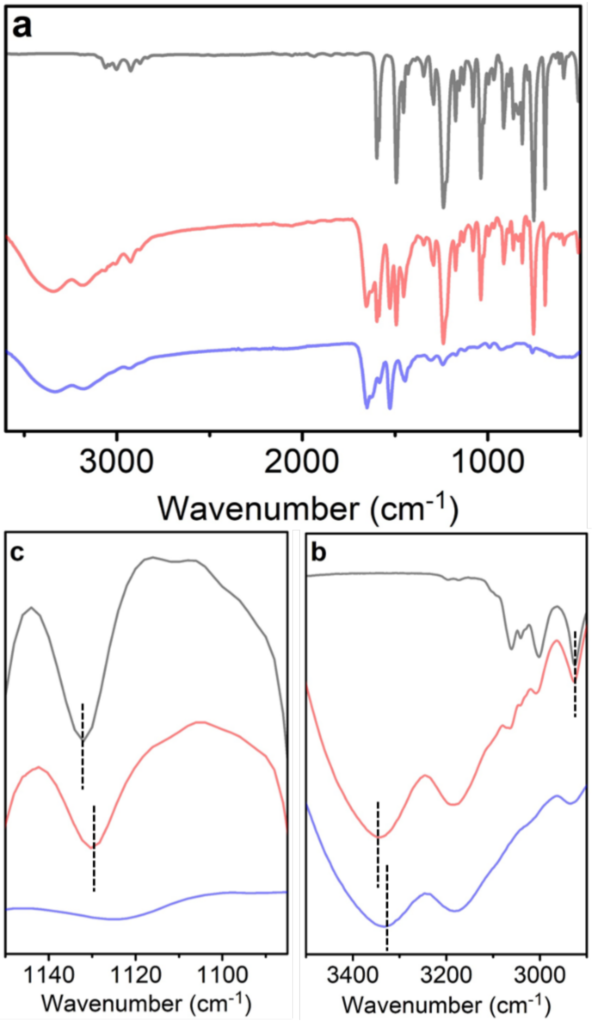


Figure S21. (a) Full scale IR spectra of 1,2-epoxy-3-phenoxypropane (black), PQA-*o*NH$_2$Py-Br (blue), and composite of well mixed PQA-*o*NH$_2$Py-Br (0.1 mmol based on the pyridinium moiety) and 1,2-epoxy-3-phenoxypropane (0.1 mmol, red).

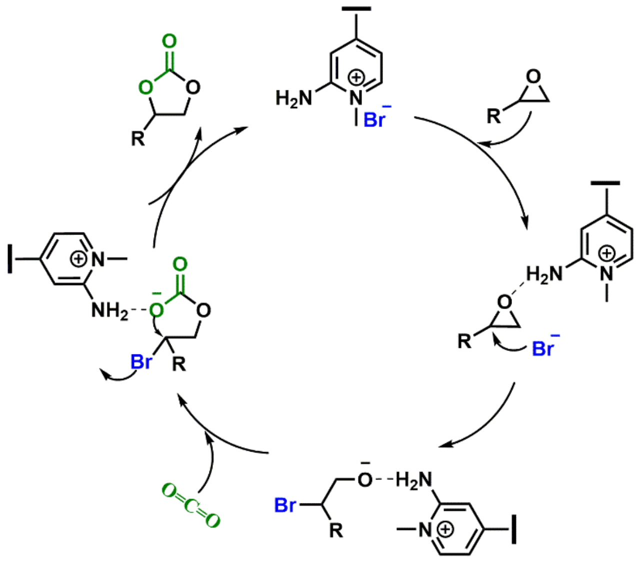


Figure S22. Proposed mechanism for the PQA-NH$_2$Py-Br catalyzed cycloaddition of epoxides with CO$_2$

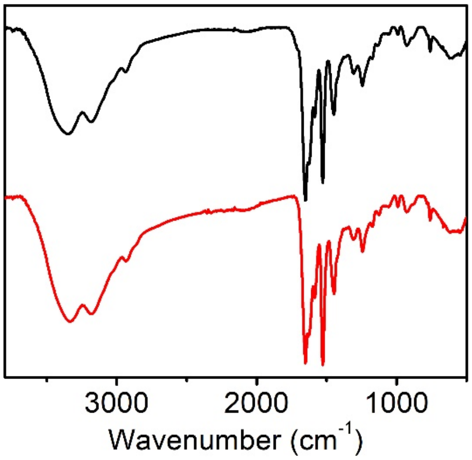


Figure S23. IR spectra of the as-synthesized PQA-*o*NH$_2$Py-Br (black) and the used PQA-*o*NH$_2$Py-Br (red).

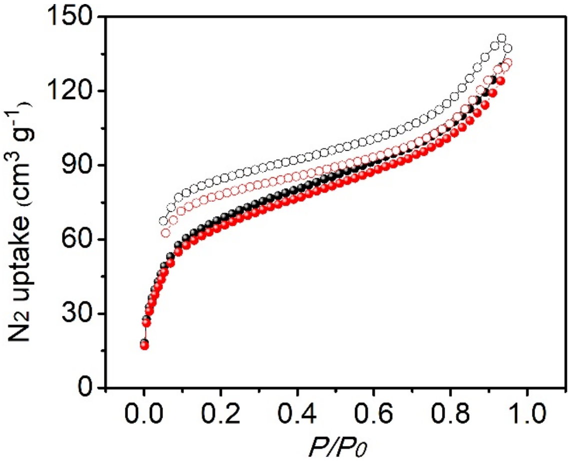


Figure S24. N$_2$ sorption isotherms collected at 77 K of the as-synthesized PQA-*o*NH$_2$Py-Br (black) and the used PQA-*o*NH$_2$Py-Br (red), which validated that the pore structure of PQA-*o*NH$_2$Py-Br was maintained, giving comparable BET surface areas of 315 m^2 g^{-1} and 302 m^2 g^{-1}, respectively.

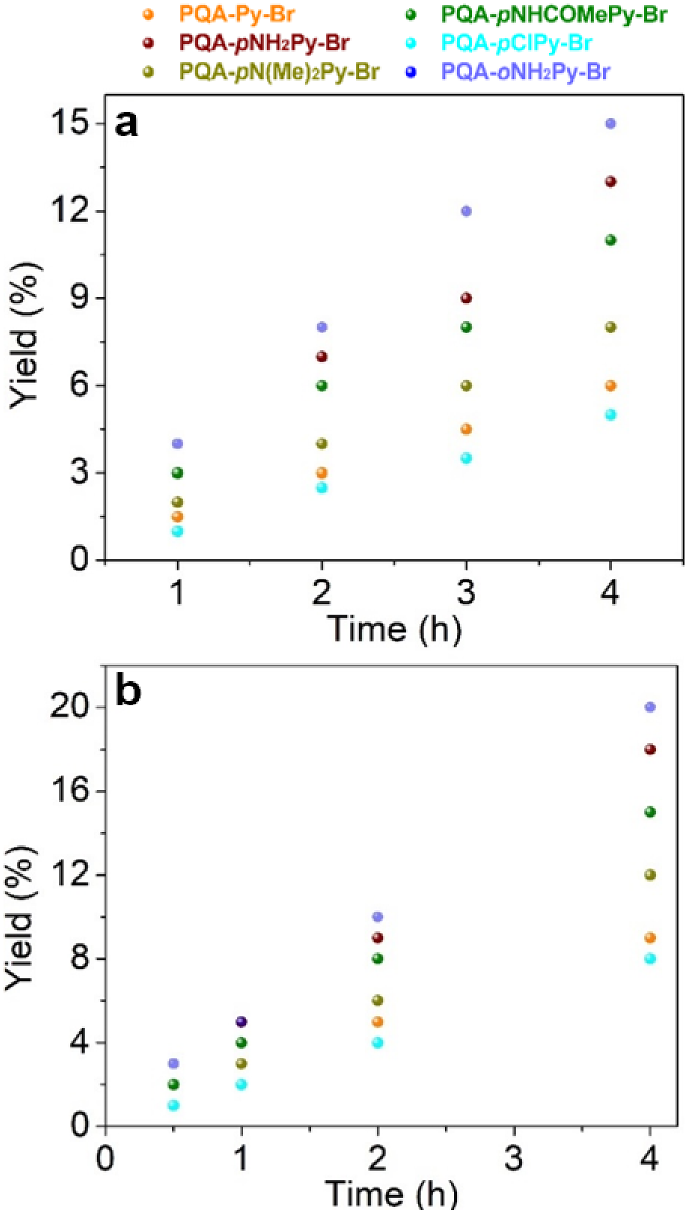


Figure S25. Kinetic rates of oxazolidinone product yields in the cycloaddition of 1-butyl-2-phenyl aziridine and CO_2 over various polymeric pyridinium salts at (a) 50 °C, and (b) 60 °C.

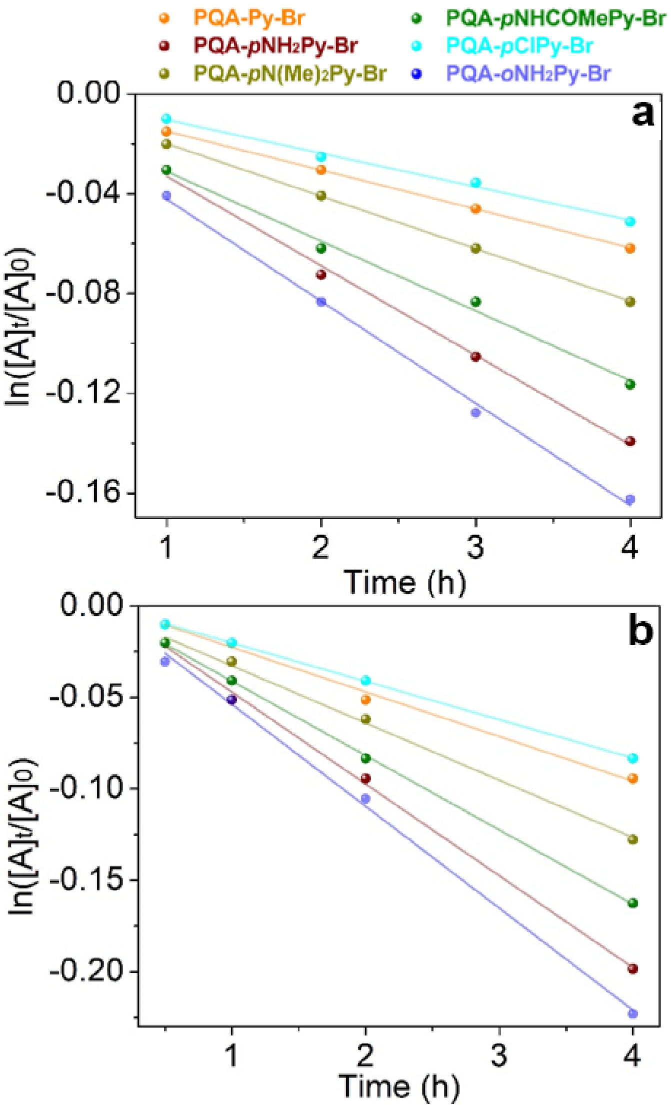


Figure S26. First-order reaction rate plots (R^2>0.99 for all) in the cycloaddition of 1-butyl-2-phenyl aziridine and CO_2 over various polymeric pyridinium salts at (a) 50 °C, and (b) 60 °C.

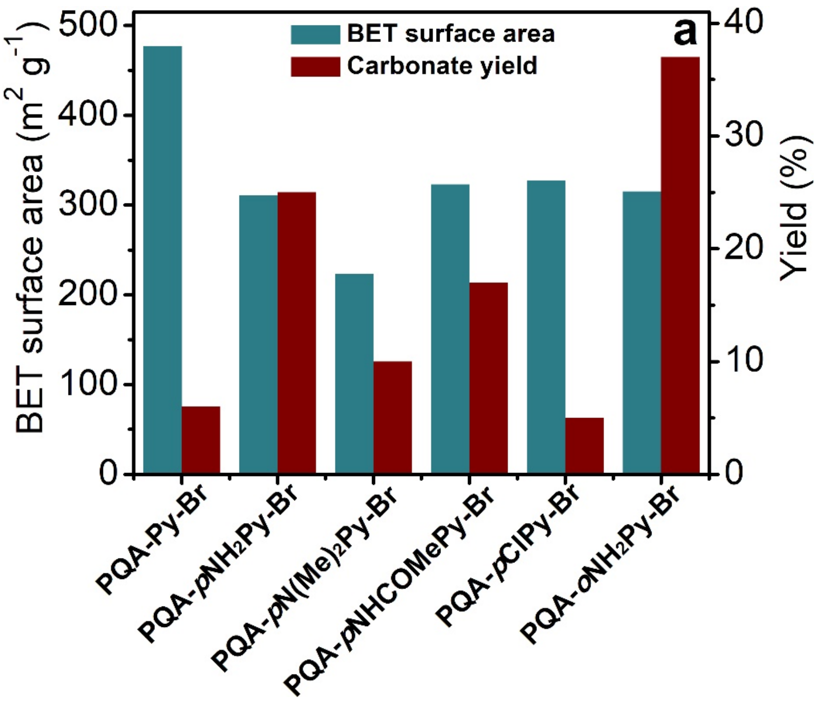


Figure S27. The plot of BET surface area of various pyridinium-based porous polymers versus the corresponding carbonate yield in the cycloaddition of CO_2 and 1,2-epoxy-3-phenoxypropane under the conditions listed in Table 1.

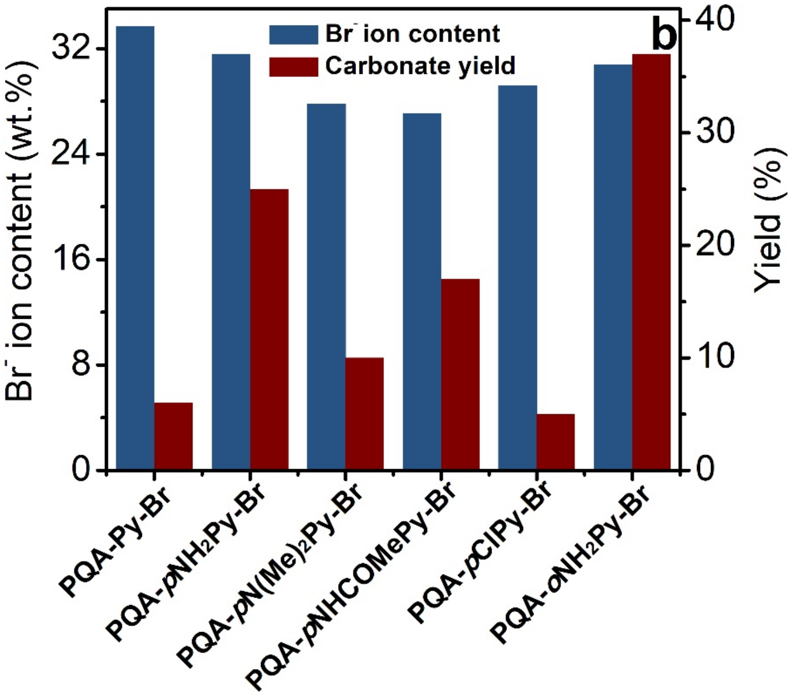


Figure S28. The plot of Br^- ion content of various pyridinium-based porous polymers versus the corresponding carbonate yield in the cycloaddition of CO_2 and 1,2-epoxy-3-phenoxypropane under the conditions listed in Table 1.

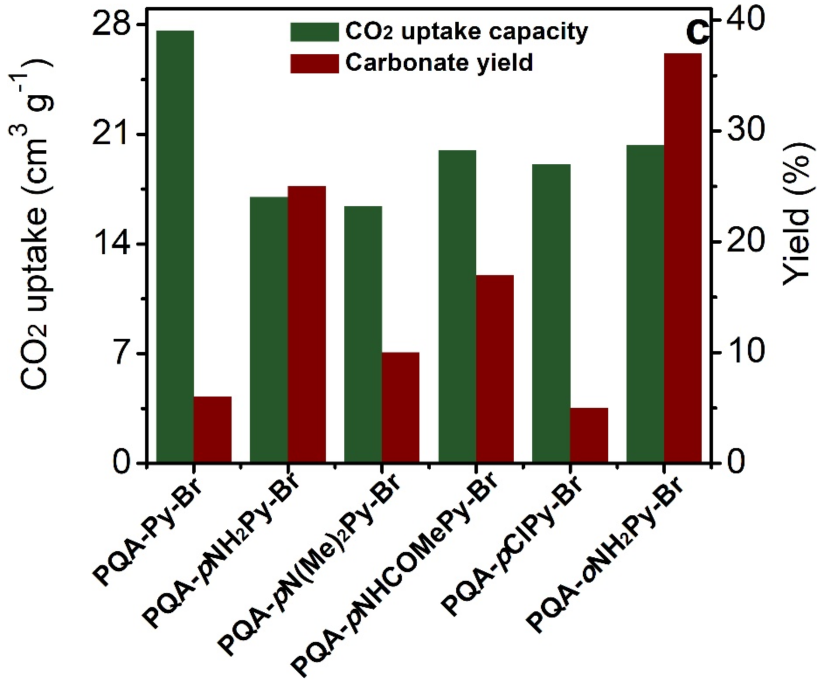
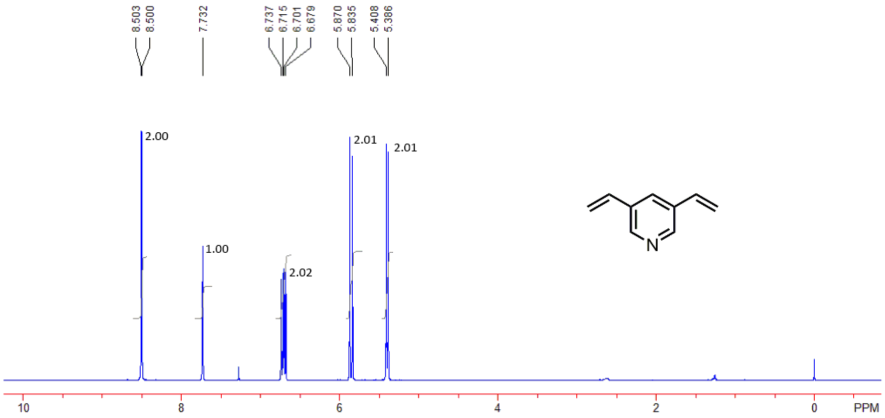
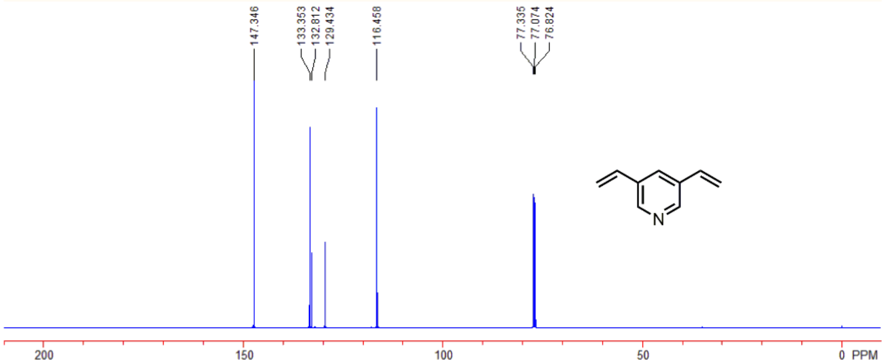
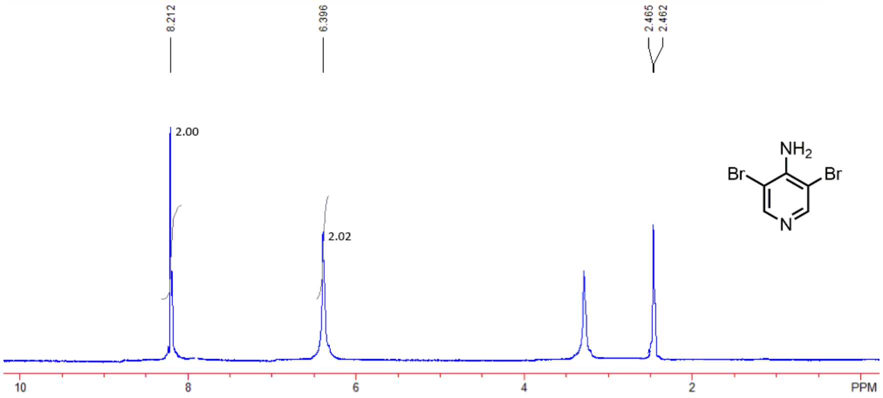
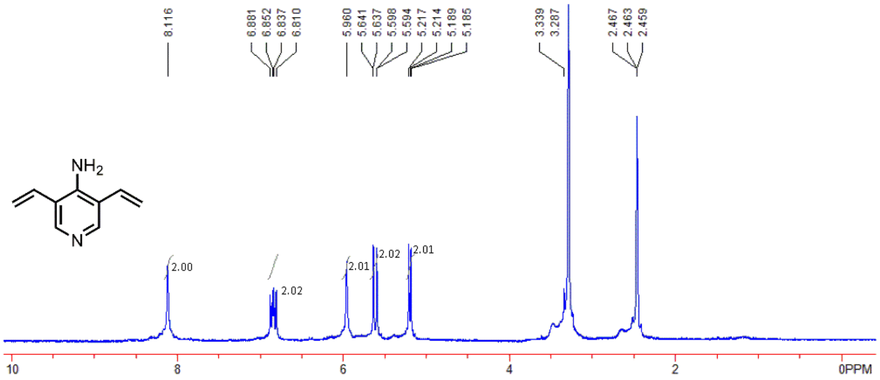


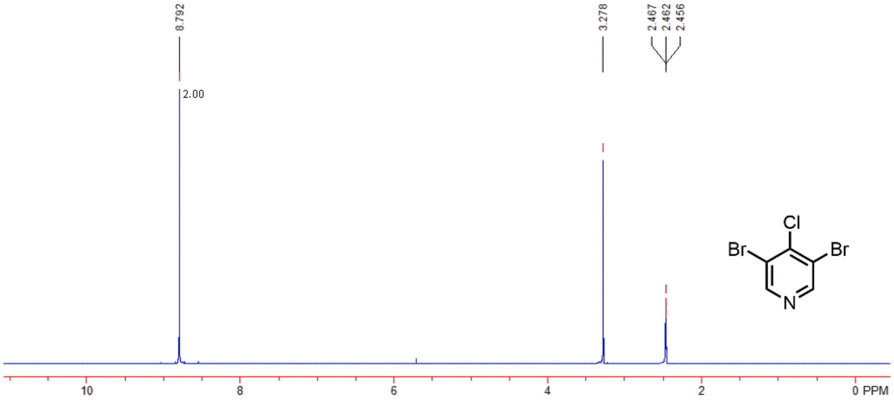
Figure S29. The plot of CO_2 uptake capacity of various pyridinium-based porous polymers versus the corresponding carbonate yield in the cycloaddition of CO_2 and 1,2-epoxy-3-phenoxypropane under the conditions listed in Table 1.


8.503
8.500
7.732
6.737
6.715
6.701
6.679
5.870
5.835
5.408
5.386
2.00
1.00
2.02
2.01
2.01
N
10
8
6
4
2
0
PPM


147.346
133.353
132.812
129.434
116.458
77.335
77.074
76.824
N
200
150
100
50
0 PPM


8.212
6.396
2.465
2.462
2.00
2.02
NH2
Br
Br
N
10
8
6
4
2
PPM


8.116
6.881
6.852
6.837
6.810
5.960
5.641
5.637
5.598
5.594
5.217
5.214
5.189
5.185
3.339
3.287
2.467
2.463
2.459
NH2
N
2.00
2.02
2.01
2.02
2.01
10
8
6
4
2
0PPM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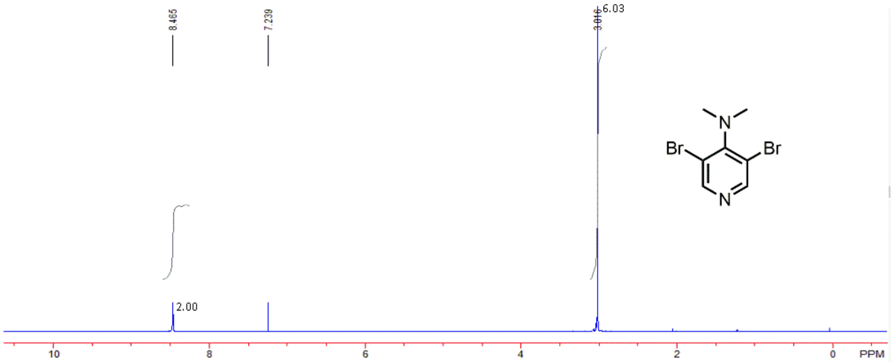
2.462
2.456
2.00
Cl
Br
Br
N
10
8
6
4
2
0 PPM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6.03
N
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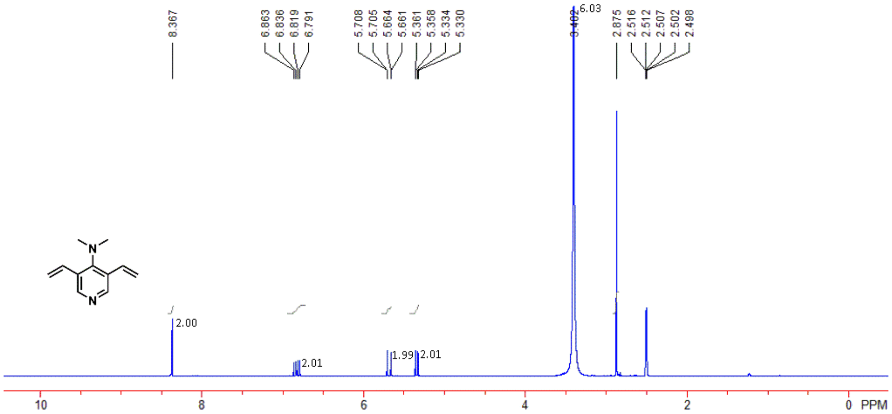
Br
N
2.00
10
8
6
4
2
0
PPM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6.836
6.819
6.791
5.708
5.705
5.664
5.661
5.361
5.358
5.334
5.330
3.402
6.03
2.875
2.516
2.512
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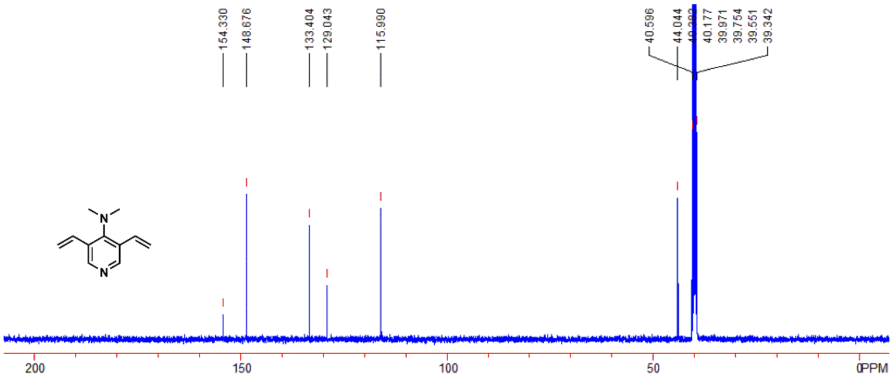
10
8
6
4
2
0 PPM


154.330
148.676
133.404
129.043
115.990
40.596
44.044
40.382
40.177
39.971
39.754
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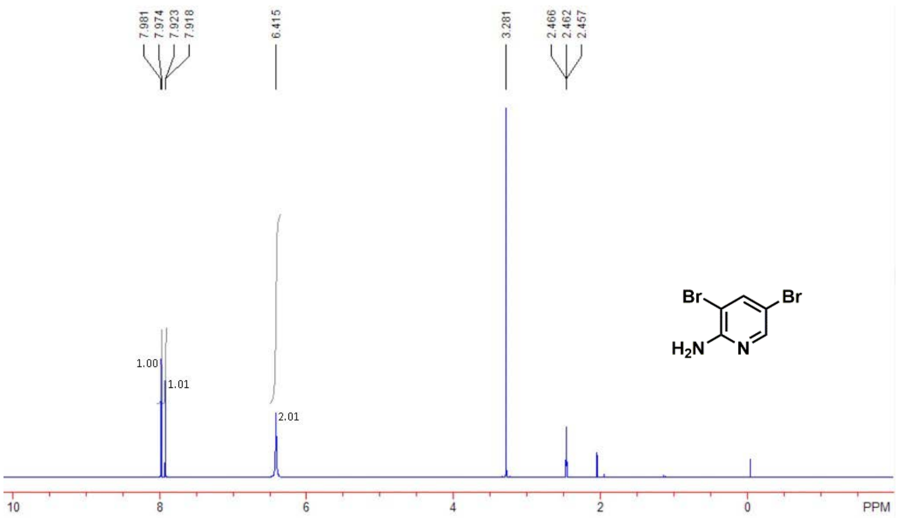
N
200
150
100
50
0PPM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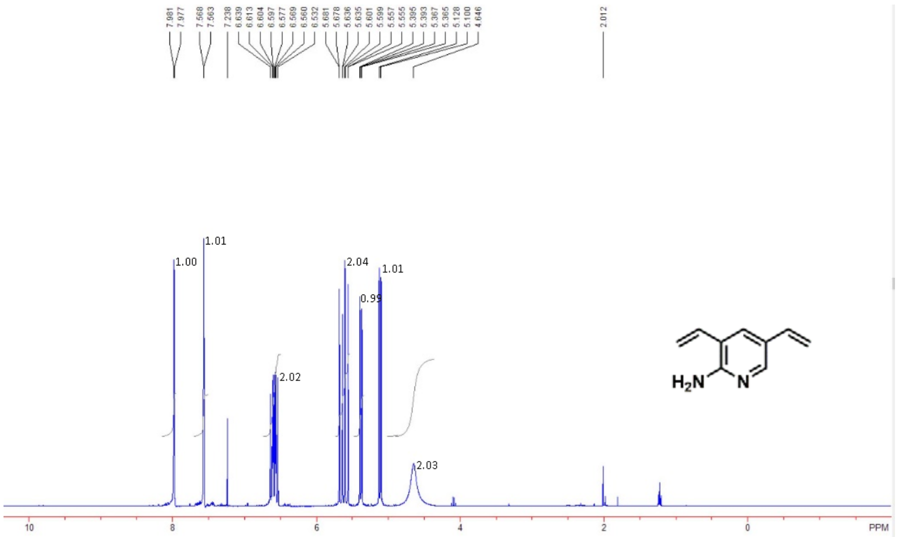
7.974
7.923
7.918
6.415
3.281
2.466
2.462
2.457
1.00
1.01
2.01
Br
Br
H2N
N
10
8
6
4
2
0
PPM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7.568
7.563
7.238
6.639
6.613
6.604
6.597
6.577
6.569
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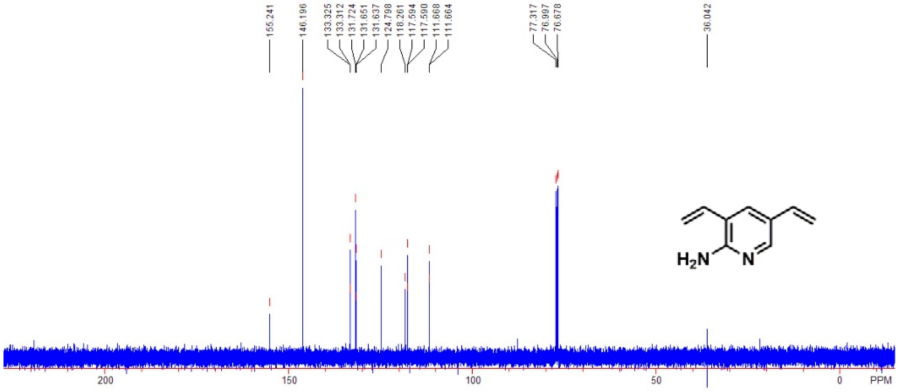
6.532
5.681
5.678
5.636
5.635
5.601
5.599
5.557
5.555
5.395
5.393
5.367
5.365
5.128
5.100
4.646
2.012
1.00
1.01
2.02
2.04
0.99
1.01
2.03
H2N
N
10
8
6
4
2
0
PPM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133.312
131.724
131.651
131.637
124.798
118.261
117.594
117.590
111.668
111.664
77.317
76.997
76.678
36.042
H2N
N
200
150
100
50
0
PPM

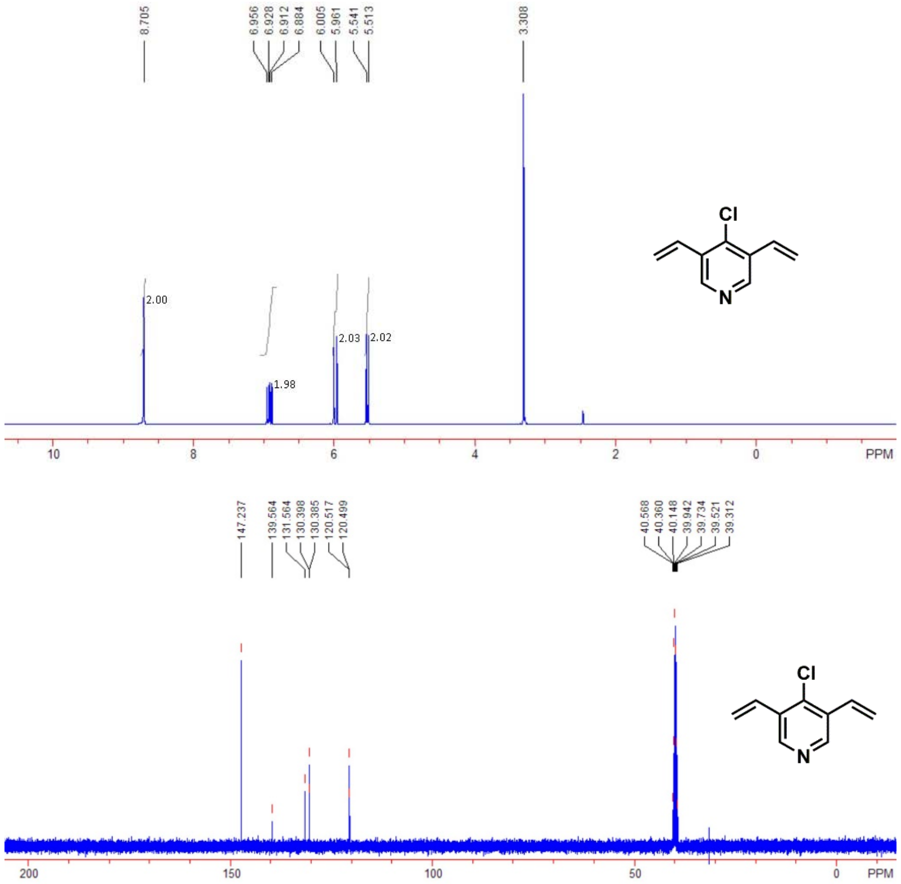
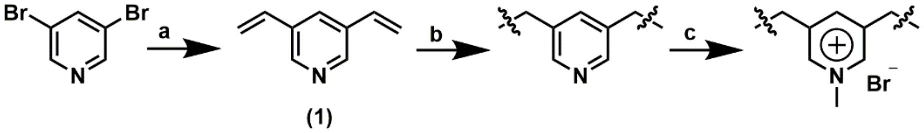


Figure S30. Liquid NMR spectra of various compounds.

Experimental Details

Material synthesis

Synthesis of polymeric pyridinium salt constructed by 1-methylpyridinium bromide moieties (PQA-Py-Br).



Reagents: (a) potassium vinyltrifluoroborate, $Pd(PPh_3)_4$; (b) AIBN; (c) CH_3I, NaBr

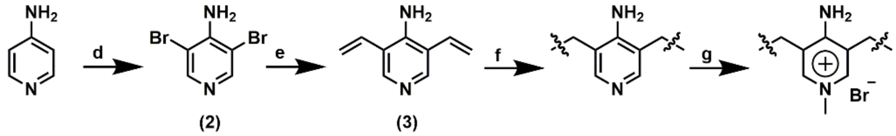
Figure S31. Synthetic scheme of PQA-Py-Br.

3,5-divinylpyridine (1): 3,5-dibromopyridine (2.5 g, 10.6 mmol), potassium vinyltrifluoroborate (3.38 g, 25.4 mmol), K_2CO_3 (4.15 g, 30.2 mmol), and $Pd(PPh_3)_4$ (0.31 g, 0.263 mmol) were introduced into a mixture of toluene (25 mL), THF (25 mL), and H_2O (10 mL), and the resulting mixture was refluxed at 90 °C under N_2 atmosphere for 48 h. The product was extracted with ethyl acetate, washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure, giving the crude compound which was then purified by flash chromatography with hexane/ethyl acetate (5:1) and 1%v/v triethylamine as eluent to afford the title compound as a colorless liquid. Yield: 1.2 g (86%). ^1H NMR (400 MHz, $CDCl_3$, 298K, TMS): 8.50 (d, 2H), 7.73 (s, 1H), 6.68-6.74 (m, 2H), 5.85 (d, 2H), 5.40 (d, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298K, TMS) 147.35, 133.35, 132.81, 129.43, 116.46 ppm. HRMS (EI): calcd for C_9H_9N (M^+) 131.0735, found 131.0734.

Synthesis of pyridine-based porous polymer from 3,5-divinylpyridine: **1** (1.0 g) was dissolved in DMF (10 mL), followed by the addition of free radical initiator azobisisobutyronitrile (AIBN, 25 mg). After being stirred at room temperature to achieve homogeneity, the mixture was transferred into a 20 mL autoclave and maintained at 100 ºC for 24 h. A white solid product (1.0 g, 100% yield) was obtained by extracting the DMF with EtOH and drying in a vacuum at 50 ºC for 12 h. Elemental analysis: calcd for $(C_9H_9N)_n$, C (82.41 %), H (6.92 %), N (10.68 %), found C (79.86 %), H (8.43 %), N (9.27 %).

Synthesis of polymeric pyridinium salt constructed by 1-methylpyridinium bromide moieties. The obtained pyridine-based polymer (0.5 g) was swelled in acetonitrile (40 mL), followed by the addition of iodomethane (1 g). The mixture was then stirred and heated to 80 ºC for 48 h. The resulting powder was washed with ethanol and then exchanged with 2 M NaBr aqueous solution three times under ambient conditions (4 h for each run) to afford the title product as a light yellow powder, denoted as PQA-Py-Br. Elemental analysis: calcd for $(C_{10}H_{12}NBr)_n$, C (53.12 %), H (5.35 %), N (6.19 %), Br (35.34 %), found C (51.31 %), H (7.26 %), N (5.75 %), Br (33.7 %).

Synthesis of polymeric pyridinium salt constructed by 4-amino-1-methylpyridinium bromide moieties (PQA-*p*NH$_2$Py-Br).



Reagents: (d) *N*-bromosuccinimide; (e) potassium vinyltrifluoroborate, Pd(PPh$_3$)$_4$; (f) AIBN; (g) CH$_3$I, NaBr

Figure S32. Synthetic scheme of PQA-*p*NH$_2$Py-Br.

3,5-dibromopyridin-4-amine (2): To a mixture of 4-aminopyridine (2 g, 21.3 mmol) in carbon tetrachloride (80 mL), *N*-bromosuccinimide (7.57 g, 42.5 mmol) was added in portions. After being stirred at room temperature for 24 h, the product was extracted with chloroform, washed with brine, dried over Na$_2$SO$_4$, and evaporated under reduced pressure, giving the crude compound which was then purified by flash chromatography with hexane/ethyl acetate (2:1) and 1%v/v triethylamine as eluent to afford the title compound as a yellow powder. Yield: 4.9 g (92%). ^{1}H NMR (400 MHz, DMSO-d6, 298K, TMS): 8.21 (s, 2H), 6.40 (s, 2H) ppm. HRMS (EI): calcd for $C_5H_4N_2Br_2$ (M$^+$) 249.8741, found 249.8739.

3,5-divinylpyridin-4-amine (3): **2** (2.5 g, 10 mmol), potassium vinyltrifluoroborate (3.3 g, 24 mmol), K$_2$CO$_3$ (4 g, 30 mmol), and Pd(PPh$_3$)$_4$ (0.29 g, 0.25 mmol) were dissolved in a mixture of toluene (25 mL), THF (25 mL), and H$_2$O (10 mL), and the resulting mixture was refluxed at 90 °C under N$_2$ atmosphere for 48 h. The product was extracted with ethyl acetate, washed with brine, dried over Na$_2$SO$_4$, and evaporated under reduced pressure, giving the crude compound which was then purified by flash chromatography with hexane/ethyl acetate (5:1) and 1%v/v triethylamine as eluent to afford the title compound as a yellow powder. Yield: 1.3 g (89%). ^{1}H NMR (400 MHz, DMSO-d6, 298K, TMS): 8.11 (s, 2H), 6.81-6.88 (m, 2H), 5.96 (s, 2H), 5.59-5.64 (m, 2H), 5.19-5.22 (m, 2H) ppm. HRMS (EI): calcd for $C_9H_{10}N_2$ (M$^+$) 146.0844, found 146.0841.

Synthesis of porous polymer constructed by 4-aminepyridine moieties: **3** (1.0 g) was dissolved in DMF (10 mL), followed by the addition of AIBN (25 mg). After being stirred at room temperature to achieve homogeneity, the mixture was transferred into a 20 mL autoclave and maintained at 100 ºC for 24 h. A yellow solid product was obtained by extracting the DMF solvent with EtOH and drying in a vacuum at 50 ºC for 12 h. Elemental analysis: calcd for $(C_9H_{10}N_2)_n$, C (73.94 %), H (6.89 %), N (19.16 %), found C (71.39 %), H (8.14 %), N (17.87 %).

Synthesis of polymeric pyridinium salt constructed by 4-amino-1-methylpyridinium bromide moieties: The obtained polymeric 4-aminepyridine (0.5 g) was swelled in acetonitrile (40 mL), followed by the addition of iodomethane (1 g). The mixture was then stirred and heated to 80 ºC for 48 h. The resulting powder was washed with ethanol and then exchanged with 2 M aqueous NaBr solution three times under ambient conditions (4 h for each run) to afford the title product as a yellow powder denoted as PQA-*p*NH$_2$Py-Br. Elemental analysis: calcd for $(C_{10}H_{13}N_2Br)_n$, C (49.81 %), H (5.45 %), N (11.62 %), Br (33.14 %), found C (48.53 %), H (6.78 %), N (10.21 %), Br (31.60 %).

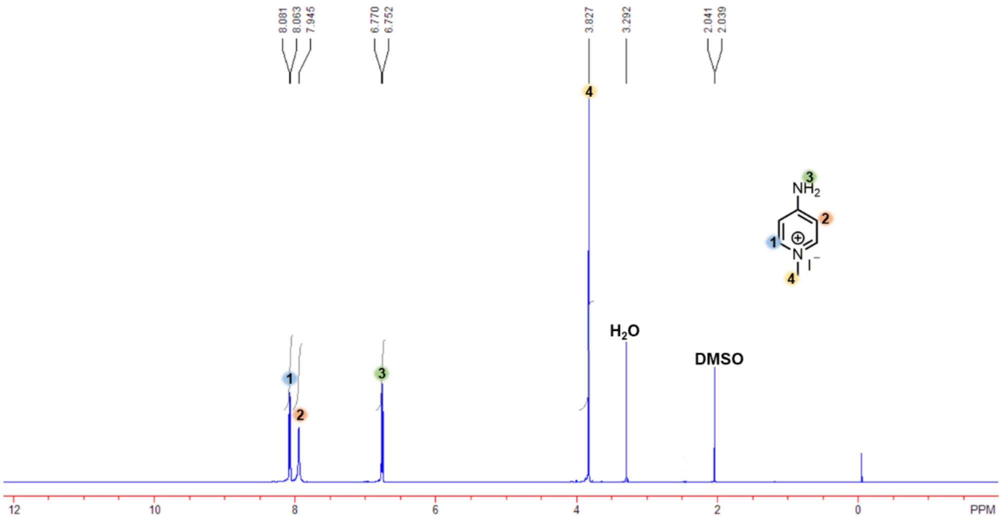
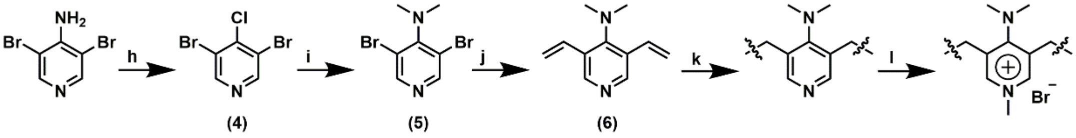


Figure S33. Liquid ^{1}H NMR spectrum of 4-aminopyridine after being treated with an excess of methyl iodide (CH_3I), indicating that the amine groups could survive under the quaternarization conditions.

Synthesis of polymeric pyridinium salt constructed by 4-(dimethylamino)-1-methylpyridinium bromide moieties (PQA-*p*N(Me)$_2$Py-Br).



Reagents: (h) HCl, $NaNO_2$; (i) dimethylamine; (j) potassium vinyltrifluoroborate, $Pd(PPh_3)_4$; (k) AIBN; (l) CH_3I, NaBr

Figure S34. Synthetic scheme of PQA-*p*N(Me)$_2$Py-Br.

3,5-dibromo-4-chloropyridine (4): 3,5-dibromopyridin-4-amine (3 g, 12 mmol) was stirred in concentrated HCl (500 mL) with sodium nitrite (3 g, 43.5 mmol) added in portions at 0-5 ºC. After 1 h, the temperature was increased to room temperature and stirred for 2 h. Following, 40 wt.% sodium hydroxide was added dropwise, with the temperature kept below 50 ºC using an ice bath. After the reaction, the mixture was extracted with ethyl acetate, dried over K_2CO_3, and evaporated under vacuum to give the title product as white needles. Yield: 2.9 g (90%). ^{1}H NMR (400 MHz, DMSO-d6, 298K, TMS): 8.79 (s, 2H) ppm. HRMS (EI): calcd for $C_5H_2Br_2ClN$ (M^+) 268.8243, found 268.8245.

3,5-dibromo(pyridine-4-yl)dimethylamine (5): **4** (2.69 g, 10 mmol) and 33 wt.% aqueous solution of dimethylamine (27 mL, 22 mmol), was heated in a Schlenk tube at 118 °C for 20 h. The reaction mixture was then cooled to room temperature, extracted with ethyl acetate, and washed with 1 M aqueous K_2CO_3 solution and water. The organic layer was dried over $MgSO_4$ and evaporated under vacuum to give a pale yellow product. Yield: 4.37 g (90%). ^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS):

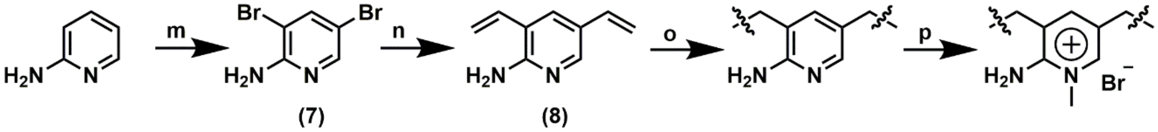
8.47 (s, 2H), 3.02 (s, 6H) ppm. HRMS (EI): calcd for $C_7H_8N_2Br_2$ (M^+) 277.9054, found 277.9052.

3,5-divinyl(pyridine-4-yl)dimethylamine (6): **5** (3.5 g, 13.8 mmol), potassium vinyltrifluoroborate (4.62 g, 33.6 mmol), K_2CO_3 (5.6 g, 42 mmol), and $Pd(PPh_3)_4$ (0.406 g, 0.35 mmol) were dissolved in a mixture of toluene (30 mL), THF (30 mL), and H_2O (10 mL), and the resulting mixture was refluxed at 90 °C under N_2 atmosphere for 48 h. The product was extracted with ethyl acetate, washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure, giving the crude compound which was then purified by flash chromatography with hexane/ethyl acetate (5:1) and 1%v/v triethylamine as eluent to afford the title compound as a yellow powder. Yield: 1.68 g (86%). ^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): 8.36 (s, 2H), 6.79-6.86 (m, 2H), 5.66-5.71 (m, 2H), 5.33-5.36 (m, 2H), 2.88 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298K, TMS) 154.33, 148.68, 133.40, 129.04, 115.99, 44.04 ppm. HRMS (EI): calcd for $C_{11}H_{14}N_2$ (M^+) 174.1157, found 174.1153.

Synthesis of porous polymer constructed by dimethylaminopyridine: **6** (1.0 g) was dissolved in DMF (10 mL), followed by the addition of free radical initiator azobisisobutyronitrile (AIBN, 0.025 g). After being stirred at room temperature to achieve homogeneity, the mixture was transferred into a 20 mL autoclave and maintained at 100 ºC for 24 h. A yellow A typical product was obtained by extracting the DMF solvent with EtOH and drying in a vacuum at 50 ºC for 12 h. Elemental analysis: calcd for $(C_{11}H_{14}N_2)_n$, C (75.82 %), H (8.10 %), N (16.08 %), found C (72.79 %), H (9.58 %), N (14.97 %).

Synthesis of polymeric pyridinium salt constructed by 4-(dimethylamino)-1-methylpyridinium bromide moieties: The obtained polymeric dimethylaminopyridine (0.5 g) was swelled in acetonitrile (40 mL), followed by the addition of iodomethane (1 g). The mixture was then stirred and heated to 80 ºC for 48 h. The resulting powder was washed with ethanol and then exchanged with 2 M aqueous NaBr aqueous solution three times under ambient conditions (4 h for each run) to afford the title product as a yellow powder denoted as PQA-*p*N(Me)$_2$Py-Br. Elemental analysis: calcd for $(C_{12}H_{17}N_2Br)_n$, C (53.54 %), H (5.35 %), N (10.41 %), Br (29.68 %), found C (51.74 %), H (6.86 %), N (9.23 %), Br (27.8 %).

Synthesis of polymeric pyridinium salt constructed by 2-amino-1-methylpyridinium bromide moieties (PQA-*o*NH$_2$Py-Br).



Reagents: (m) *N*-bromosuccinimide; (n) potassium vinyltrifluoroborate, $Pd(PPh_3)_4$; (o) AIBN; (p) CH_3I, NaBr

Figure S35. Synthetic scheme of PQA-*o*NH$_2$Py-Br.

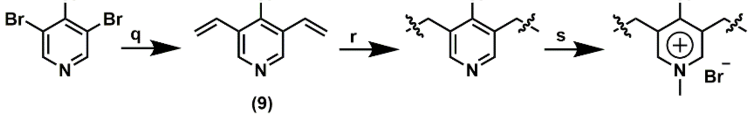
3,5-dibromopyridin-2-amine (7): To a mixture of 2-aminopyridine (2 g, 21.3 mmol) in carbon tetrachloride (80 mL), *N*-bromosuccinimide (7.57 g, 42.5 mmol) was added in portions. After being stirred at room temperature for 24 h, the product was extracted with chloroform, washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure, giving the crude compound which was then purified by flash chromatography with hexane/ethyl acetate (2:1) and 1%v/v triethylamine as eluent to afford the title compound as a yellow powder. Yield: 4.7 g (88%). ^{1}H NMR (400 MHz, DMSO-d6, 298K, TMS): 7.98 (d, 1H), 7.92 (d, 1H), 6.42 (s, 2H) ppm. HRMS (EI): calcd for $C_5H_4N_2Br_2$ (M^+) 249.8741, found 249.8738.

3,5-divinylpyridin-2-amine (8): **7** (2.5 g, 10 mmol), potassium vinyltrifluoroborate (3.3 g, 24 mmol), K_2CO_3 (4 g, 30 mmol), and $Pd(PPh_3)_4$ (0.29 g, 0.25 mmol) were dissolved in a mixture of toluene (25 mL), THF (25 mL), and H_2O (10 mL), and the resulting mixture was refluxed at 90 °C under N_2 atmosphere for 48 h. The product was extracted with ethyl acetate, washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure, giving the crude compound which was then purified by flash chromatography with hexane/ethyl acetate (5:1) and 1%v/v triethylamine as eluent to afford the title compound as a yellow powder. Yield: 1.35 g (92%). ^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): 7.98 (d, 1H), 7.56 (d, 1H), 6.53-6.64 (m, 2H), 5.56-5.68 (m, 2H), 5.10-5.40 (m, 2H), 4.65 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 298K, TMS) 155.24, 146.20, 133.33, 131.72, 131.65, 124.80, 118.26, 117.59, 111.66 ppm. HRMS (EI): calcd for $C_9H_{10}N_2$ (M^+) 146.0844, found 146.0842.

Synthesis of porous polymer constructed by 2-aminepyridine moieties: **8** (1.0 g) was dissolved in DMF (10 mL), followed by the addition of AIBN (25 mg). After being stirred at room temperature to achieve homogeneity, the mixture was transferred into a 20 mL autoclave and maintained at 100 ºC for 24 h. A yellow solid product was obtained by extracting the DMF solvent with EtOH and drying in vacuum at 50 ºC for 12 h. Elemental analysis: calcd for $(C_9H_{10}N_2)_n$, C (73.94 %), H (6.89 %), N (19.16 %), found C (71.47 %), H (8.21 %), N (17.95 %).

Synthesis of polymeric pyridinium salt constructed by 2-amino-1-methylpyridinium bromide moieties: The obtained polymeric 2-aminepyridine (0.5 g) was swelled in acetonitrile (40 mL), followed by the addition of iodomethane (1 g). The mixture was then stirred and heated to 80 ºC for 48 h. The resulting powder was washed with ethanol and then exchanged with 2 M NaBr aqueous solution three times under ambient conditions (4 h for each run) to afford the title product as a light yellow powder denoted as PQA-*o*NH$_2$Py-Br. Elemental analysis: calcd for $(C_{10}H_{13}N_2Br)_n$, C (49.81 %), H (5.45 %), N (11.62 %), Br (33.14 %), found C (48.25 %), H (7.03 %), N (10.53 %), Br (30.8 %).

Synthesis of polymeric pyridinium salt constructed by 4-chloro-1-methylpyridinium bromide moieties (PQA-*p*ClPy-Br).



(9)

Reagents: (q) potassium vinyltrifluoroborate, $Pd(PPh_3)_4$; (r) AIBN; (s) CH_3I, NaBr

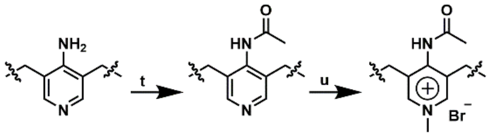
Figure S36. Synthetic scheme of PQA-*p*ClPy-Br.

3,5-divinylpyridin-4-chloro (9): 3,5-dibromo-4-chloropyridine (3.22 g, 12 mmol), potassium vinyltrifluoroborate (3.96 g, 28.8 mmol), K_2CO_3 (4.8 g, 36 mmol), and $Pd(PPh_3)_4$ (0.348 g, 0.3 mmol) were dissolved in a mixture of toluene (25 mL), THF (25 mL), and H_2O (10 mL), and the resulting mixture was refluxed at 90 °C under N_2 atmosphere for 48 h. The product was extracted with ethyl acetate, washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure, giving the crude compound which was then purified by flash chromatography with hexane/ethyl acetate (5:1) and 1%v/v triethylamine as eluent to afford the title compound as a white powder. Yield: 1.8 g (91%). ^1H NMR (400 MHz, DMSO-d6, 298K, TMS): 8.71 (s, 2H), 6.89-6.96 (m, 2H), 5.59-6.01 (m, 2H), 5.51-5.54 (m, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d6, 298K, TMS) 147.24, 139.56, 131.56, 130.39, 120.52 ppm. HRMS (EI): calcd for C_9H_8NCl (M^+) 165.0345, found 165.0342.

Synthesis of porous polymer constructed by 4-chloropyridine moieties: **9** (1.0 g) was dissolved in DMF (10 mL), followed by the addition of AIBN (25 mg). After being stirred at room temperature to achieve homogeneity, the mixture was transferred into a 20 mL autoclave and maintained at 100 ºC for 24 h. A white solid product was obtained by extracting the DMF solvent with EtOH and drying in a vacuum at 50 ºC for 12 h. Elemental analysis: calcd for $(C_9H_8NCl)_n$, C (65.27 %), H (4.87 %), N (8.46 %), Cl (21.40 %), found C (63.51 %), H (6.29 %), N (7.14 %), Cl (20.08 %).

Synthesis of polymeric pyridinium salt constructed by 4-chloro-1-methylpyridinium bromide moieties: The obtained polymeric 4-chloropyridine (0.5 g) was swelled in acetonitrile (40 mL), followed by the addition of iodomethane (1 g). The mixture was then stirred and heated to 80 ºC for 48 h. The resulting powder was washed with ethanol and then exchanged with 2 M NaBr aqueous solution three times under ambient conditions (4 h for each run) to afford the title product as a light yellow powder denoted as PQA-*p*ClPy-Br. Elemental analysis: calcd for $(C_{10}H_{11}NBrCl)_n$, C (46.10 %), H (4.26 %), N (5.38 %), Br (30.67 %), Cl (13.61 %), found C (44.76 %), H (6.35 %), N (4.67 %), Br (29.2 %), Cl (12.57 %).

Synthesis of polymeric pyridinium salt constructed by 4-acetamide-1-methylpyridinium bromide moieties (PQA-*p*NHCOMePy-Br).



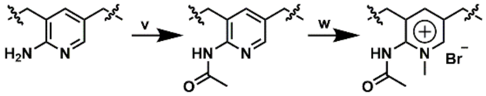
Reagents: (t) acetyl chloride, K_2CO_3; (u) CH_3I, NaBr

Figure S37. Synthetic scheme of PQA-*p*NHCOMePy-Br.

Synthesis of porous polymer constructed by 4-acetamidepyridine moieties: The porous polymer constructed by 4-aminepyridine moieties (0.8 g) was swelled in acetone (10 mL), followed by the addition of K_2CO_3 (3.7 g, 26.8 mmol) and acetyl chloride (1.25 g, 13.8 mmol) in acetone (5 mL) at 0 ºC. The resulting mixture was then stirred for 12 h, after which water (10 mL) was added. A light yellow product was collected and washed with water and acetone and drying in vacuum at 50 ºC for 12 h. Elemental analysis: calcd for $(C_{11}H_{12}N_2O)_n$, C (70.19 %), H (6.43 %), N (14.88 %), O (8.50 %), found C (68.24%), H (8.16 %), N (13.17%), O (7.41 %).

Synthesis of polymeric pyridinium salt constructed by 4-acetamide-1-methylpyridinium bromide moieties: The obtained polymeric 4-acetamidepyridine (0.5 g) was swelled in acetonitrile (40 mL), followed by the addition of iodomethane (1 g). The mixture was then stirred and heated to 80 ºC for 48 h. The resulting powder was washed with ethanol and then exchanged with 2 M NaBr aqueous solution three times under ambient conditions (4 h for each run) to afford the title product as a light yellow powder. Elemental analysis: calcd for $(C_{12}H_{15}N_2OBr)_n$, C (50.90 %), H (5.34 %), N (9.89 %), O (5.65 %), Br (28.22 %), found C (48.86 %), H (7.48 %), N (8.23 %), O (4.97 %), Br (27.1 %).

Synthesis of polymeric pyridinium salt constructed by 2-acetamide-1-methylpyridinium bromide moieties (PQA-*o*NHCOMePy-Br).



Reagents: (v) acetyl chloride, K_2CO_3; (w) CH_3I, NaBr

Figure S38. Synthetic scheme of PQA-*o*NHCOMePy-Br.

Synthesis of porous polymer constructed by 2-acetamidepyridine moieties: The porous polymer constructed by 2-aminepyridine moieties (0.8 g) was swelled in acetone (10 mL), followed by the addition of K_2CO_3 (3.7 g, 26.8 mmol) and acetyl chloride (1.25 g, 13.8 mmol) in acetone (5 mL) at 0 ºC. The resulting mixture was then stirred for 12 h, after which water (10 mL) was added. A light yellow product was collected and washed with water and acetone and drying in vacuum at 50 ºC for 12 h. Elemental analysis: calcd for $(C_{11}H_{12}N_2O)_n$, C (70.19 %), H (6.43 %), N (14.88 %), O (8.50 %), found C (68.32%), H (8.39 %), N (13.14%), O (7.48 %).

Synthesis of polymeric pyridinium salt constructed by 2-acetamide-1-methylpyridinium bromide moieties: The obtained polymeric 2-acetamidepyridine (0.5 g) was swelled in acetonitrile (40 mL), followed by the addition of iodomethane (1 g). The mixture was then stirred and heated to 80 ºC for 48 h. The resulting powder was washed with ethanol and then exchanged with 2 M NaBr aqueous solution three times under ambient conditions (4 h for each run) to afford the title product as a light yellow powder. Elemental analysis: calcd for $(C_{12}H_{15}N_2OBr)_n$, C (50.90 %), H (5.34 %), N (9.89 %), O (5.65 %), Br (28.22 %), found C (48.75 %), H (7.32 %), N (8.58 %), O (4.89 %), Br (27.5 %).

Catalytic Tests

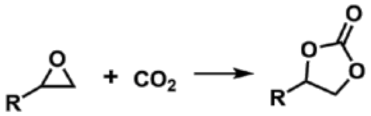


Figure S39. Cycloaddition reactions between epoxides and atmospheric CO_2.

A typical procedure for the cycloaddition reactions between epoxides and atmospheric CO_2: the reactions were carried out in a 10 mL Schlenk flask with a magnetic stirrer. As a typical run, epoxide (1.0 g) and catalyst listed in Table 1 were transferred into the reactor. After sealing and purging with CO_2 using a balloon, the tube was placed in a preheated oil bath and stirred for the desired interval. After the reaction, the catalyst was taken out from the system by centrifugation, and the product was analyzed by ^1H NMR (see Figures S41 and S42). The selectivity of carbonate product is 100%.

A typical procedure for the cycloaddition reactions with high CO_2 pressure: the reactions were carried out in a stainless steel autoclave with a magnetic stirrer. In a typical run, 1,2-epoxy-3-phenoxypropane (3 g, 20 mmol) and PQA-*p*NH_2Py-Br (4.8 mg, 0.02 mmol Br) were transferred into the autoclave. After sealing and purging with CO_2 to 2.0 MPa, the autoclave was placed in a preheated oil bath and stirred for a certain time. After the reaction, the autoclave was cooled using ice water, and CO_2 was released. The product was analyzed by ^1H NMR.

For recycling, the catalyst was separated from the reaction system by centrifugation and washed with excessive $CHCl_3$. The resulting polymer was used directly after drying.

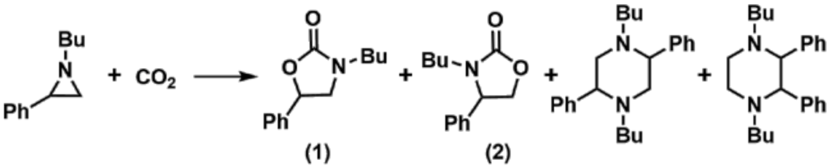


Figure S40. Cycloaddition reactions between aziridines and CO_2.

In a typical experimental procedure for coupling of aziridines with CO_2, 1 mmol of 1-butyl-2-phenyl aziridine and 5 mg of catalyst were added into a 7 mL vial. After that, the vial was transferred into a 100 mL stainless steel autoclave, sealed, and purged with CO_2. Following this, the pressure of CO_2 was adjusted to 1 MPa, and the autoclave was placed in a preheated oil bath with stirring for the mentioned time period. On completion of the reaction, the reactor was cooled to room temperature and CO_2 was ejected slowly. The conversion and selectivity of the reactions were determined by ^1H NMR using terephthalaldehyde as an internal standard (see Figures S43 and S44). 5-Aryl-2-oxazolidinone (1) was preferentially formed with chemoselectivity and regioselectivity close to 100% in all cases.

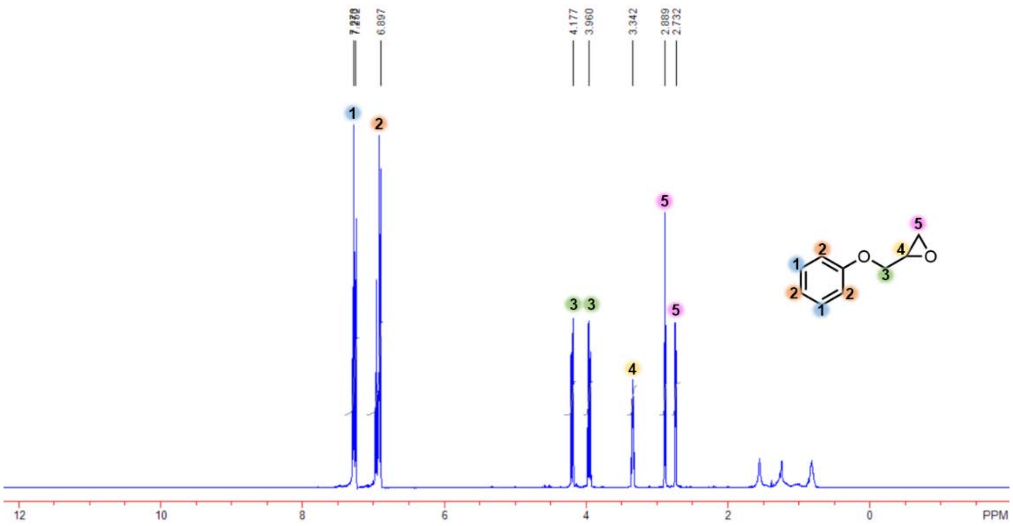


Figure S41. Liquid ^{1}H NMR spectrum of 1,2-epoxy-3-phenoxypropane.

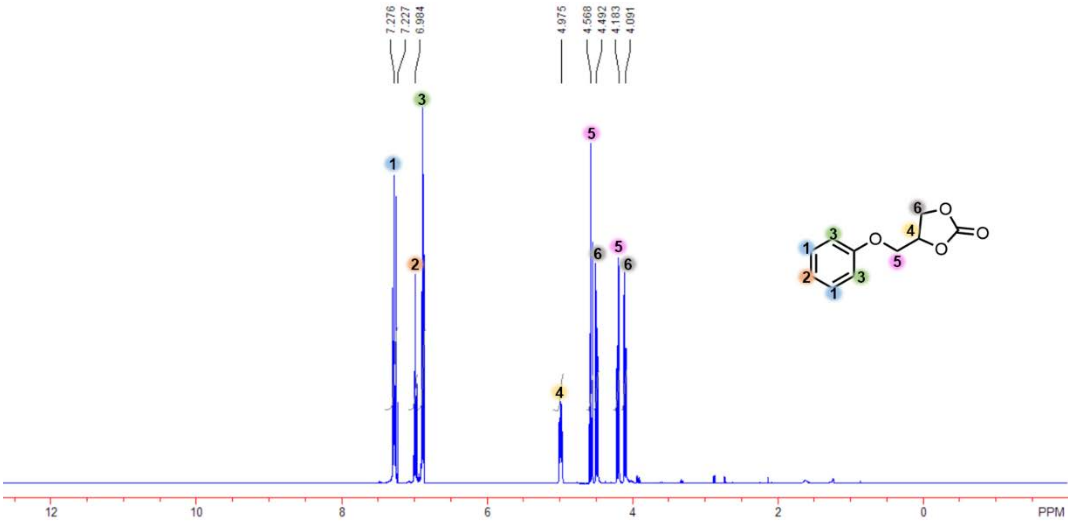


Figure S42. Liquid ^{1}H NMR spectrum of the carbonate product in the cycloaddition between CO_2 and 1,2-epoxy-3-phenoxypropane. The product yield was determined according to the integration of peaks 4 in Figures S41 and S42.

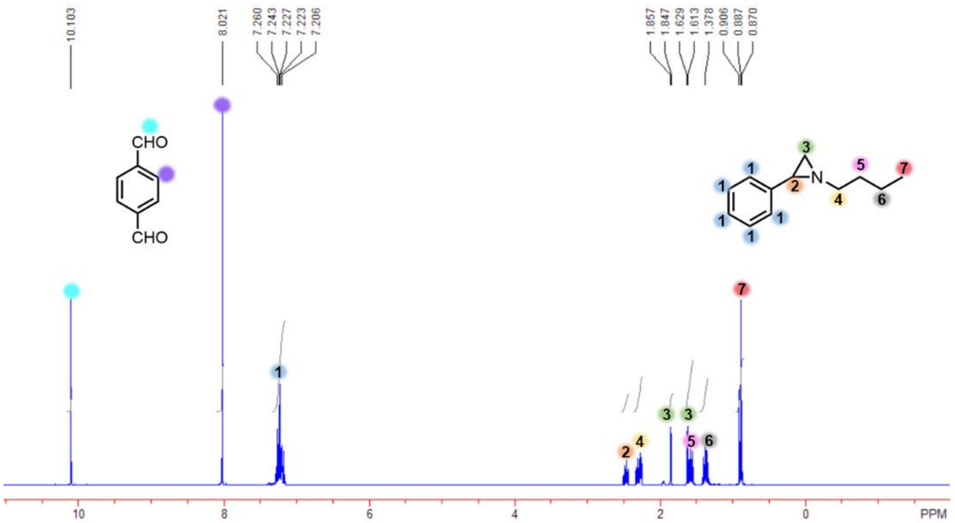


Figure S43. Liquid ^{1}H NMR spectrum of 1-butyl-2-phenyl aziridine. The purity was determined by using terephthalaldehyde as an internal standard.

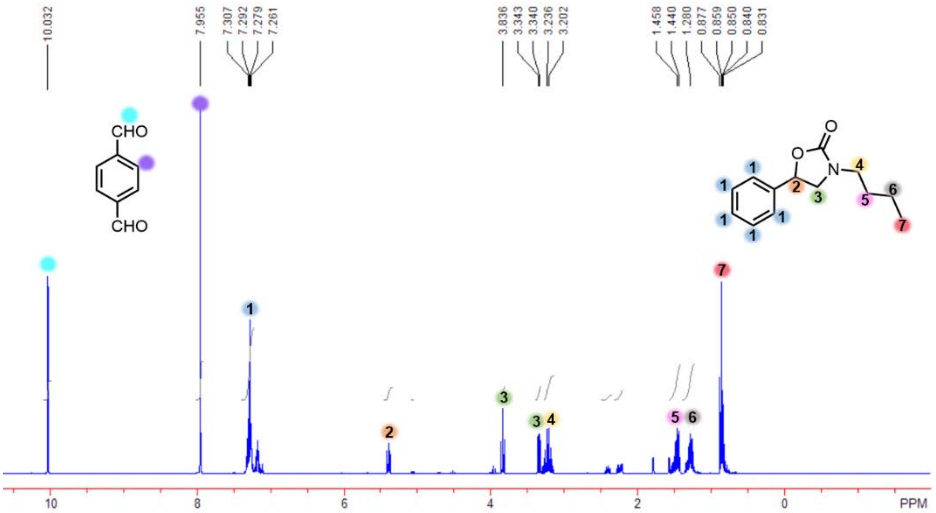


Figure S44. Liquid ^{1}H NMR spectrum of the oxazolidinone product in the transformation of CO_2 to 1-butyl-2-phenyl aziridine. The yield was determined by using terephthalaldehyde as an internal standard, according to the integration of peaks 2 in Figures S43 and S44.

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