Enhanced CO_2 uptake by intramolecular proton transfer reactions in amino-functionalized pyridine-based ILs

Mingguang Pan,[ab] R. Vijayaraghavan,[b] Fengling Zhou,[b] Mega Kar,[b] Haoran Li,[a] Congmin Wang*[a] and Douglas R. MacFarlane*[b]

[a]*Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China. E-mail: chewcm@zju.edu.cn*

[b]*Department of Chemistry, Monash University, Clayton VIC 3800, Australia. E-mail: Doug.MacFarlane@monash.edu*

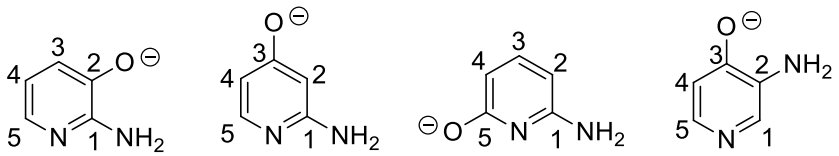
1. General procedures

2-amino-3-hydroxypyridine (2-NH_2-3-OH-Py), 2-amino-4-hydroxypridine (2-NH_2-4-OH-Py), 2-amino-6-hydroxypyridine (2-NH_2-6-OH-Py), 3-amino-4-hydroxypyridine (3-NH_2-4-OH-Py) were purchased from J&K Scientific and Sigma-Aldrich. Trihexyl(tetradecyl)phosphonium chloride ([P_{66614}][Cl]), tri-*n*-butylphosphine, bromoethane were obtained from Sigma-Aldrich. Amberlite IRA-402(OH) (an anion-exchange resin) was obtained from Alfa. All chemicals were obtained in the highest purity grade possible, and were used as received unless otherwise stated. All ionic liquids (ILs) samples were dried under vacuum at 60^{o}C for 24 h. CO_2 gas in ultra high purity grade was passed through a drying column to avoid moisture contamination before use. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DMX-400 spectometer in DMSO-d_6 with tetramethylsilane as the standard. FT-IR spectra were obtained using a Cary 630 FT-IR spectrometer (Agilent Technologies). Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. The water contents of these ILs were determined through Karl Fisher titrations (Metrohm Ltd.).

2. Synthesis of ILs

These anion-functionalized ILs were prepared by neutralizing [P_{66614}]OH (or

[P_{4444}]OH) and weak proton donors such as 2-amino-3-hydroxypyridine (2-NH_2-3-OH-Py) according to the literature method.[S1] For example, a solution of [P_{66614}]OH in ethanol was prepared from [P_{66614}]Cl by using an anion-exchange resin such as Amberlite IRA-402(OH), and then equimolar 2-NH_2-3-OH-Py was added to the [P_{66614}]OH solution in ethanol. The mixture was stirred at room temperature for 3 h. Subsequently, the ethanol and water was removed by distillation at 40 ˚C under reduced pressure. The product thus obtained was dried in high vacuum for 24 h at 50 ˚C.



Scheme S1. The anions used in this work.

[P_{66614}][2-NH_2-3-O-Py]: ^{1}H NMR (DMSO-d_6): δ = 0.84–0.89 (m, 12 H, CH_3), 1.25–1.57 (m, 48 H, CH_2), 2.15–2.22 (m, 8 H, PCH_2), 4.70 (s, 2H, NH_2), 5.89 (dd, 1H, pyridyl-C3), 6.08–6.11 (q, 1H, pyridyl-C4), 6.56 (dd, 1H, pyridyl-C5); ^{13}C NMR (DMSO-d_6): δ = 13.7, 13.8, 17.3, 17.8, 20.6, 21.8, 22.1, 28.2, 28.7, 29.0, 29.1, 29.7, 29.8, 29.9, 30.1, 30.4, 30.9, 31.3, 114.0, 114.3, 124.3, 154.2, 154.6; LR-ESI-MS: *m/z* = 483.4 $[M]^+$ (100%), 109.0 $[M]^-$ (100%); HR-ESI-MS: *m/z* cacld for $[M]^+$ $C_{32}H_{68}P$ 483.5053, found 483.5057, error 0.8 ppm, *m/z* cacld for $[M]^-$ $C_5H_5N_2O$ 109.0407, found 109.0408, error 0.9 ppm; IR: 3026, 2954, 2923, 2854, 1636, 1570, 1523, 1457, 1444, 1377, 1351, 1304, 1254, 1215, 1174, 1111, 1055, 986, 912, 882, 855, 810, 778, 749, 720.

[P_{66614}][2-NH_2-4-O-Py]: ^{1}H NMR (DMSO-d_6): δ = 0.84–0.89 (m, 12 H, CH_3), 1.24–1.60 (m, 48 H, CH_2), 2.15–2.22 (m, 8 H, PCH_2), 4.12 (s, 2H, NH_2), 5.11 (d, 1H, pyridyl-C5), 5.33–5.35 (dd, 1H, pyridyl-C4), 7.08 (d, 1H, pyridyl-C2); ^{13}C NMR (DMSO-d_6): δ = 13.7, 13.8, 17.2, 17.3, 17.7, 17.8, 20.6, 21.2, 21.8, 21.9, 22.1, 27.1, 27.7, 28.2, 28.7, 29.0, 29.1, 29.7, 29.8, 30.1, 30.2, 30.4, 30.8, 31.3, 97.2, 109.9, 146.2, 160.4, 176.8; LR-ESI-MS: *m/z* = 483.4 $[M]^+$ (100%), 109.0 $[M]^-$ (100%); HR-ESI-MS: *m/z* cacld for $[M]^+$ $C_{32}H_{68}P$ 483.5053, found 483.5061, error 1.7 ppm, *m/z* cacld for $[M]^-$ $C_5H_5N_2O$ 109.0407, found 109.0407, error 0.0 ppm; IR: 2954,

2922, 2853, 1583, 1492, 1458, 1412, 1375, 1291, 1242, 1206, 1162, 1109, 973, 823, 784, 720.

[P_{66614}][2-NH_2-6-O-Py]: ^{1}H NMR (DMSO-d_6): δ = 0.84–0.89 (m, 12 H, CH_3), 1.24–1.60 (m, 48 H, CH_2), 2.13–2.20 (m, 8 H, PCH_2), 5.08–5.12 (m, 2 H, pyridyl-C2 and -C4), 6.47 (br, 2H, NH_2), 6.81 (t, 1H, pyridyl-C3); ^{13}C NMR (DMSO-d_6): δ = 13.7, 17.2, 17.3, 17.7, 17.8, 20.7, 21.2, 21.8, 21.9, 22.1, 27.1, 27.7, 28.2, 28.7, 29.0, 29.1, 29.7, 29.9, 30.1, 30.3, 30.4, 30.5, 30.9, 31.3, 86.9, 101.4, 137.6, 158.3, 171.0; LR-ESI-MS: *m/z* = 483.4 $[M]^+$ (100%), 109.0 $[M]^-$ (100%); HR-ESI-MS: *m/z* cacld for $[M]^+$ $C_{32}H_{68}P$ 483.5053, found 483.5054, error 0.2 ppm, *m/z* cacld for $[M]^-$ $C_5H_5N_2O$ 109.0407, found 109.0403, error 3.7 ppm; IR: 2954, 2922, 2853, 1626, 1578, 1546, 1458, 1427, 1376, 1302, 1262, 1215, 1147, 1112, 1066, 988, 816, 772, 713.

[P_{66614}][3-NH_2-4-O-Py]: ^{1}H NMR (DMSO-d_6): δ = 0.84–0.90 (m, 12 H, CH_3), 1.25–1.60 (m, 48 H, CH_2), 2.15–2.22 (m, 8 H, PCH_2), 5.76 (d, 1 H, pyridyl-C4), 7.18 (d, 1 H, pyridyl-C5), 7.28 (s, 1H, pyridyl-C1); ^{13}C NMR (DMSO-d_6): δ = 13.7, 13.8, 17.2, 17.3, 17.6, 17.7, 20.6, 21.8, 22.1, 28.2, 28.7, 29.0, 29.1, 29.7, 29.8, 29.9, 30.1, 30.4, 30.9, 31.3, 111.1, 131.4, 136.8, 141.0, 166.0; LR-ESI-MS: *m/z* = 483.1 $[M]^+$ (100%), 108.9 $[M]^-$ (100%); HR-ESI-MS: *m/z* cacld for $[M]^+$ $C_{32}H_{68}P$ 483.5053, found 483.5060, error 1.4 ppm, *m/z* cacld for $[M]^-$ $C_5H_5N_2O$ 109.0407, found 109.0406, error 0.9 ppm; IR: 2954, 2922, 2853, 1590, 1577, 1502, 1458, 1420, 1368, 1314, 1249, 1213, 1168, 1111, 1034, 993, 877, 817, 720.

[P_{4444}][2-NH_2-3-O-Py]: ^{1}H NMR (DMSO-d_6): δ = 0.89–0.92 (m, 12 H, CH_3), 1.35–1.49 (m, 16 H, CH_2), 2.15–2.22 (m, 8 H, 4 CH_2), 4.72 (s, 2 H, NH_2), 5.89 (dd, 1 H, pyridyl-C3), 6.09–6.12 (q, 1 H, pyridyl-C4), 6.57 (dd, 1 H, pyridyl-C5); ^{13}C NMR (DMSO-d_6): δ = 13.2, 17.1, 17.5, 22.6, 22.7, 23.2, 23.4, 113.5, 114.6, 123.3, 154.9, 155.3; LR-ESI-MS: *m/z* = 259.2 $[M]^+$ (100%), 108.9 $[M]^-$ (100%); HR-ESI-MS: *m/z* cacld for $[M]^+$ $C_{16}H_{36}P$ 259.2549, found 259.2551, error 0.8 ppm, *m/z* cacld for $[M]^-$ $C_5H_5N_2O$ 109.0407, found 109.0402, error 4.6 ppm; IR: 3025, 2957, 2930, 2870, 1571, 1522, 1465, 1441, 1379, 1350, 1305, 1252, 1215, 1121, 1096, 1054, 1004, 967,

915, 882, 809, 776, 747, 721.

3. CO_2 absorption results and analysis data based on FT-IR and NMR spectra

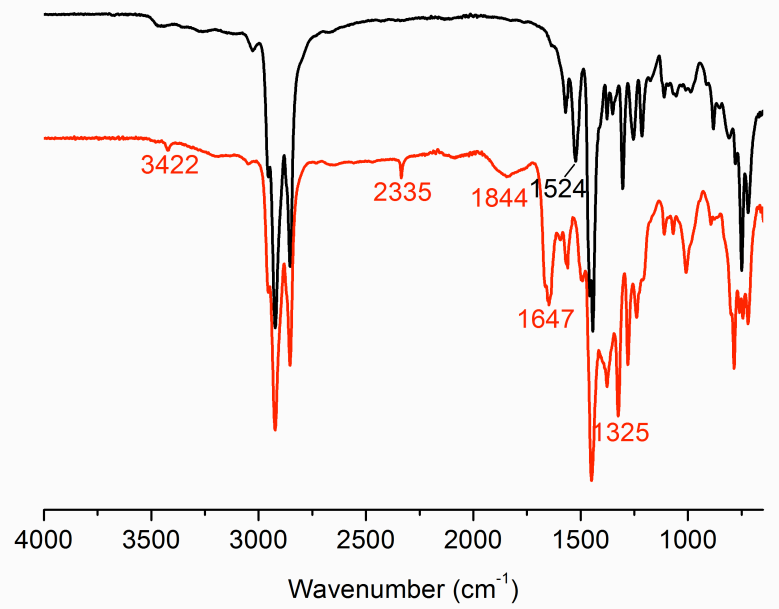


Figure S1. FT-IR spectra of [P_{66614}][2-NH_2-3-O-Py] before (black) and after (red) CO_2 uptake.

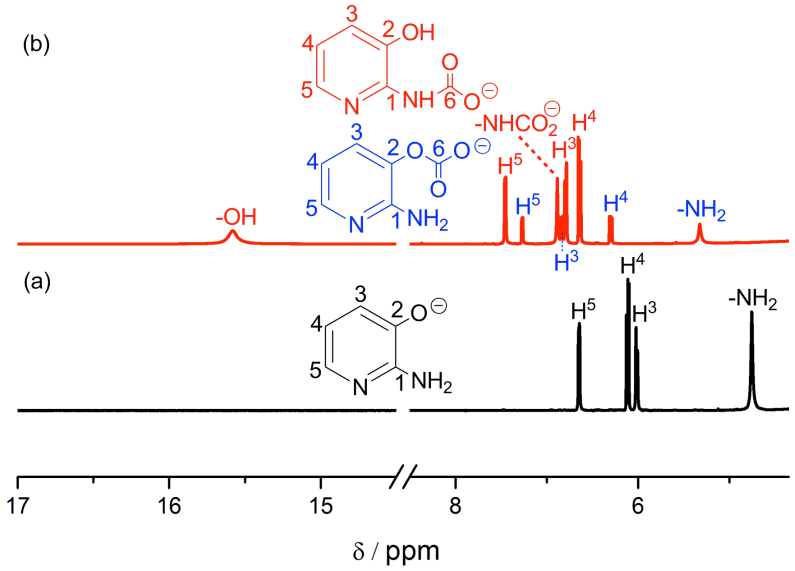


Figure S2. Partial ^{1}H NMR spectra (400 MHz, room temperature, DMSO-d_6) of [P_{66614}][2-NH_2-3-O-Py] before (a) and after (b) CO_2 uptake. The hydroxyl group shifted to 15.58 ppm may due to the formation of strong intramolecular hydrogen bonding.

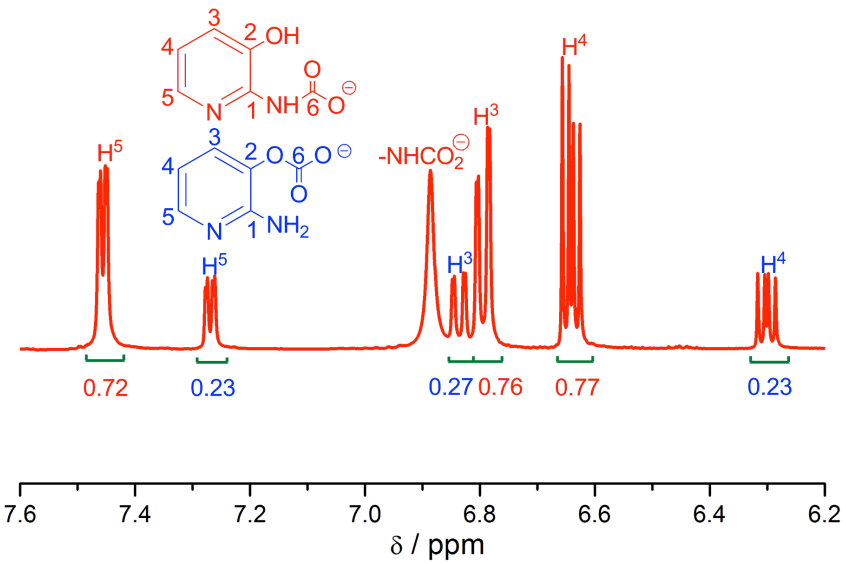


Figure S3. Partial NMR integral area (400 MHz, room temperature, DMSO-d_6) of [P_{66614}][2-NH_2-3-O-Py] after CO_2 uptake.

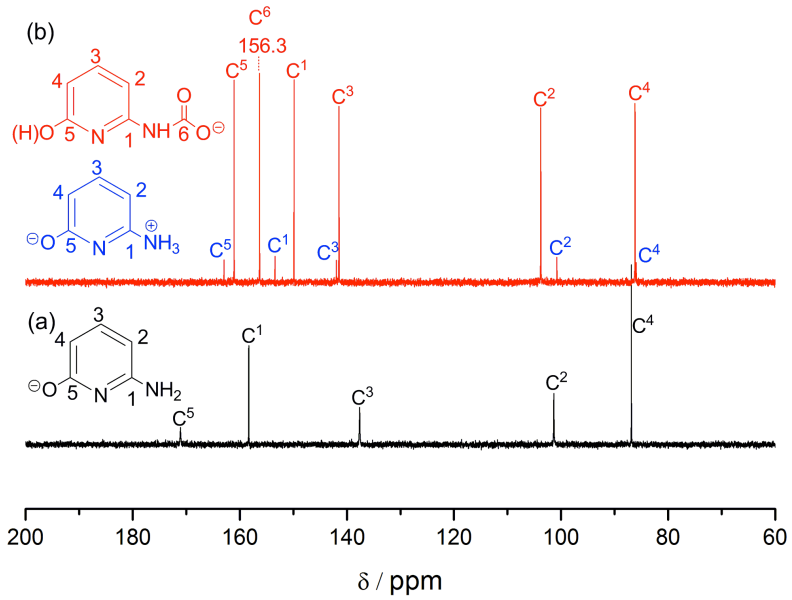


Figure S4. Partial ^{13}C NMR spectra (100 MHz, room temperature, DMSO-d_6) of [P_{66614}][2-NH_2-6-O-Py] before (a) and after (b) CO_2 uptake.

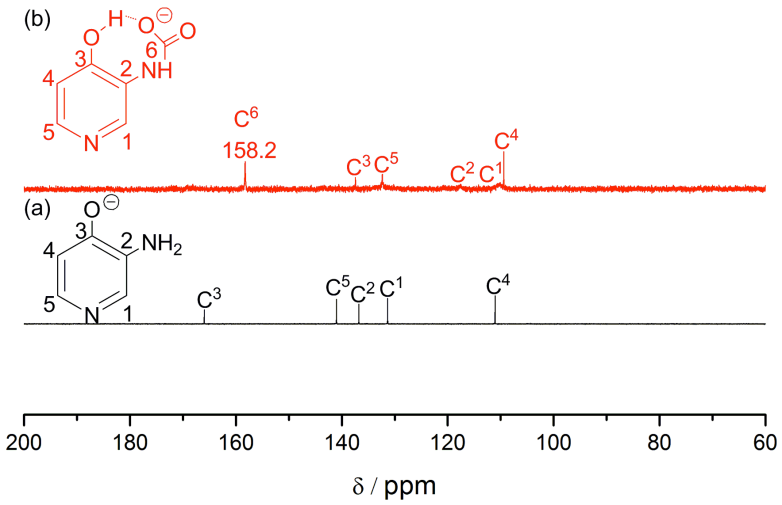


Figure S5. Partial ^{13}C NMR spectra (100 MHz, room temperature, DMSO-d_6) of [P_{66614}][3-NH_2-4-O-Py] before (a) and after (b) CO_2 uptake.

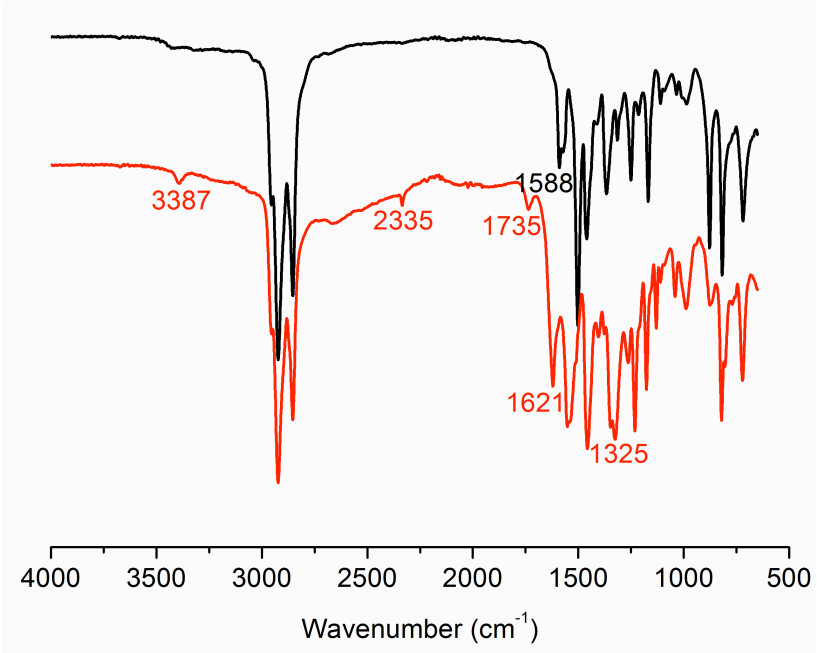


Figure S6. FT-IR spectra of [P_{66614}][3-NH_2-4-O-Py] before (black) and after (red) CO_2 uptake.

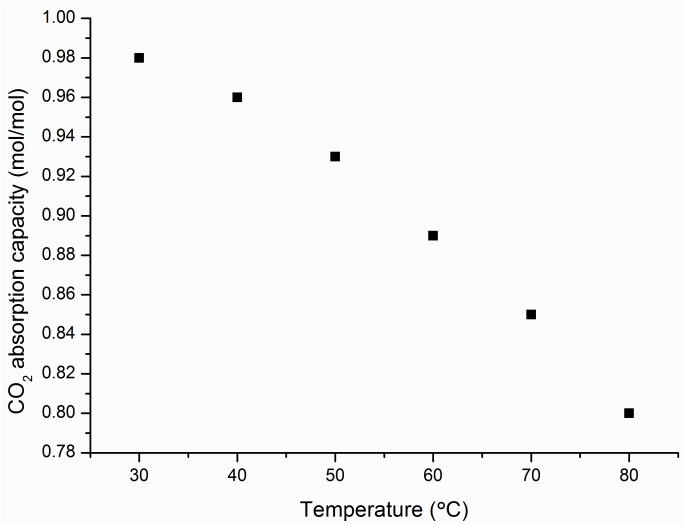


Figure S7. The effect of temperature on CO_2 absorption by $[P_{66614}][2\text{-}NH_2\text{-}3\text{-}O\text{-}Py]$.

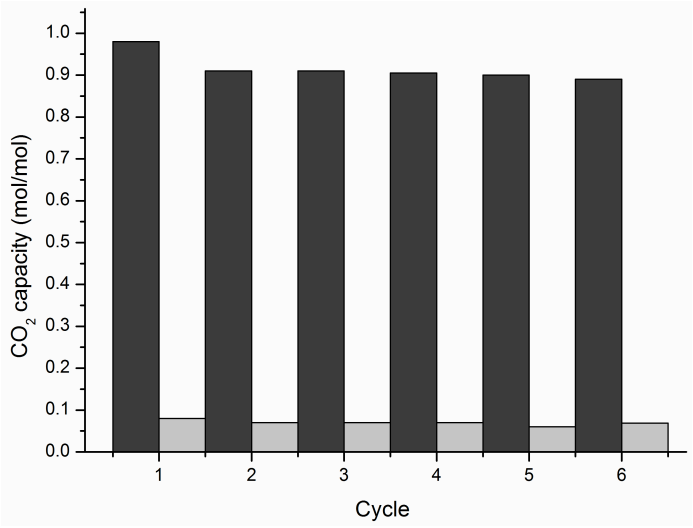


Figure S8. Cycles of CO_2 absorption and desorption by $[P_{66614}][2\text{-}NH_2\text{-}3\text{-}O\text{-}Py]$. Dark gray, CO_2 absorption capacity; light gray, CO_2 desorption capacity.

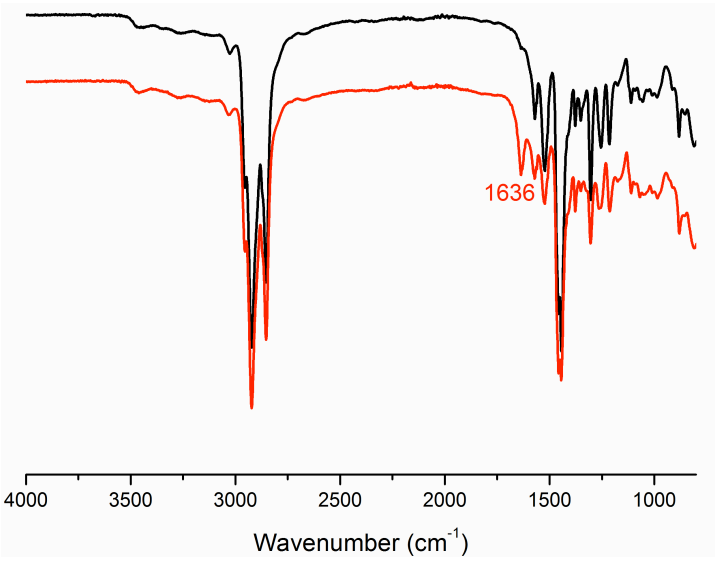


Figure S9. FT-TR spectra of $[P_{66614}][2\text{-}NH_2\text{-}3\text{-}O\text{-}Py]$. Black, the fresh IL; red, the IL after CO_2 desorption (under N_2 bubbling at 80 ˚C for one hour).

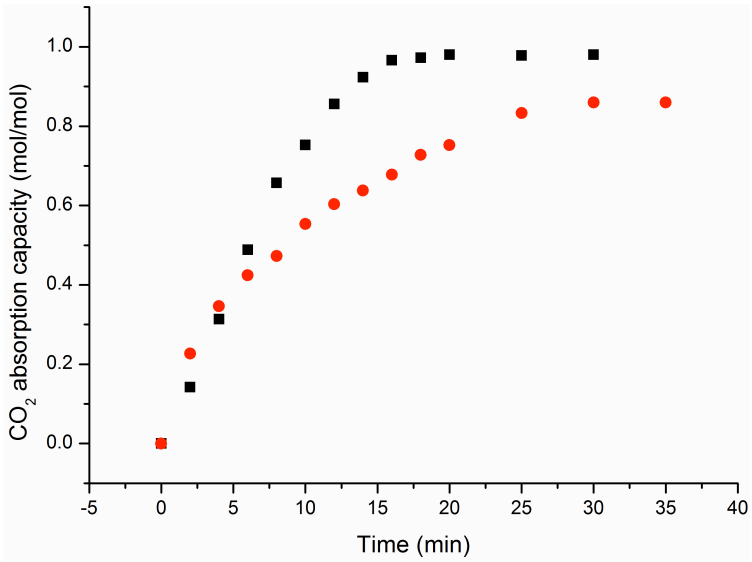


Figure S10. CO_2 absorption by $[P_{66614}][2\text{-}NH_2\text{-}3\text{-}O\text{-}Py]$ with (red) and without (black) ~2.0 wt.% H_2O.

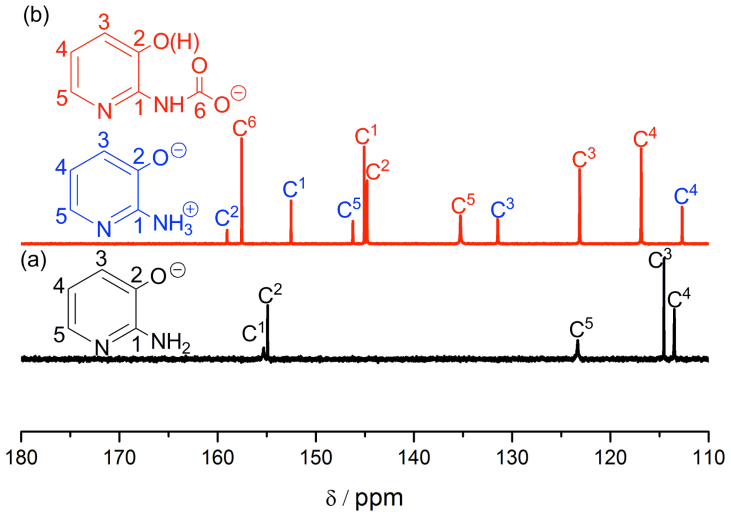


Figure S11. Partial ^{13}C NMR spectra (100 MHz, room temperature, DMSO-d_6) of $[P_{4444}][2\text{-}NH_2\text{-}3\text{-}O\text{-}Py]$ before (a) and after (b) CO_2 uptake.

4. Orignal NMR spectra

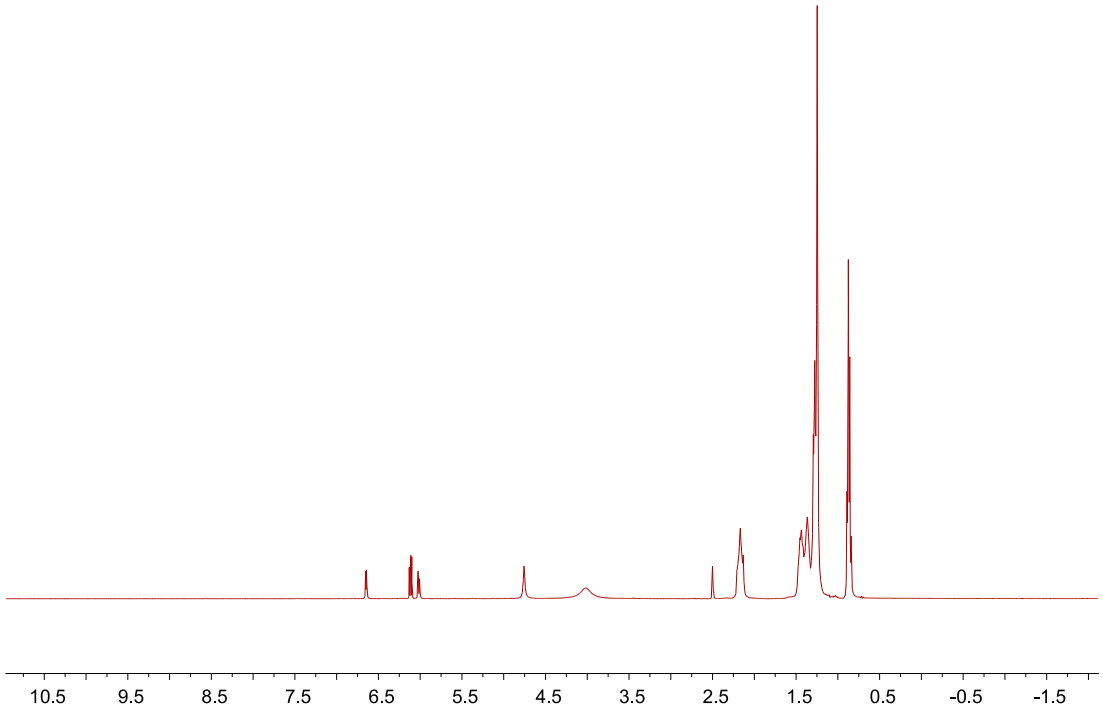


Figure S12. ^{1}H NMR spectrum (400 MHz, room temperature, DMSO-d_6) of [P_{66614}][2-NH_2-3-O-Py].

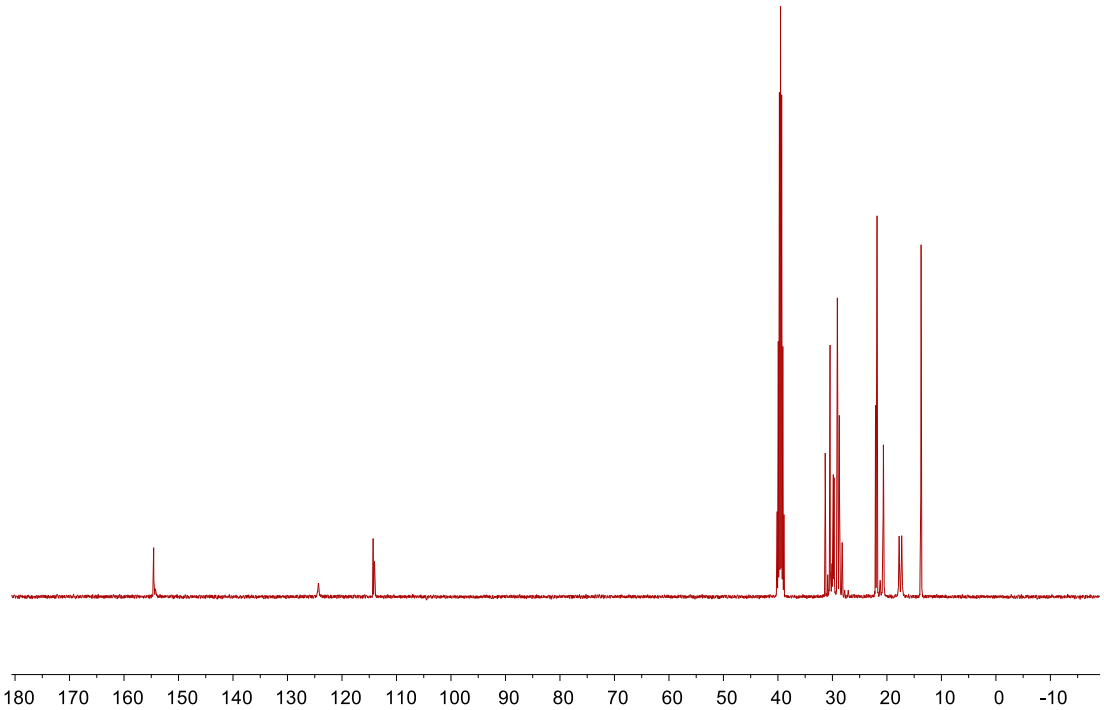


Figure S13. ^{13}C NMR spectrum (100 MHz, room temperature, DMSO-d_6) of [P_{66614}][2-NH_2-3-O-Py].

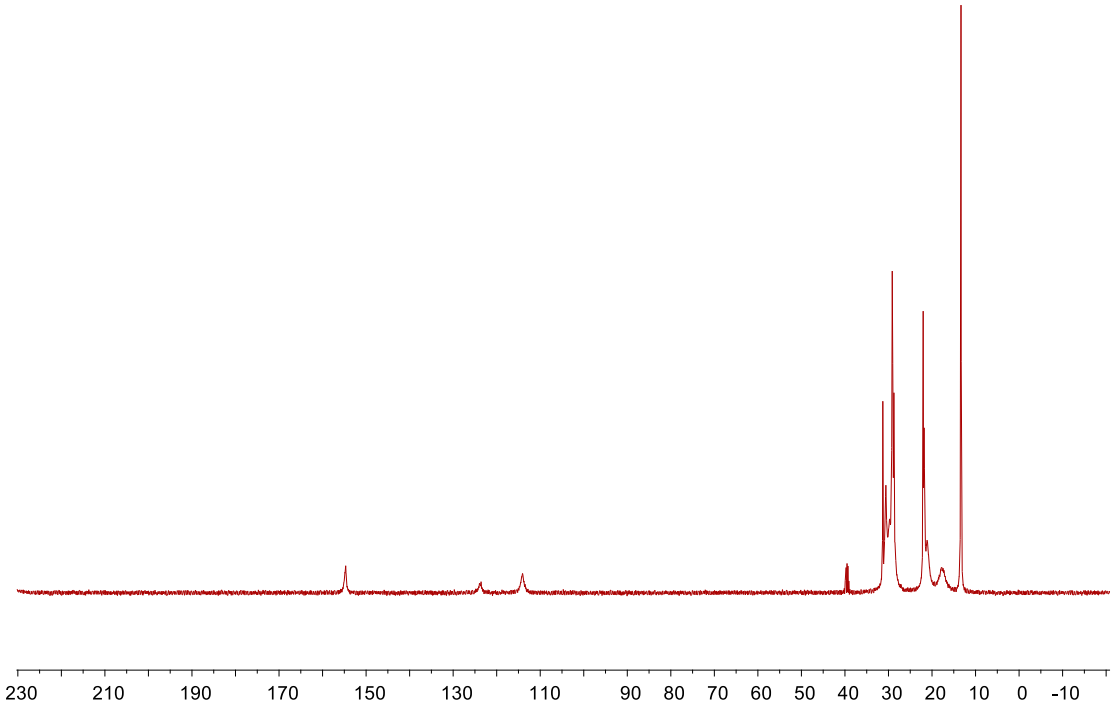


Figure S14. No-deterium ^{13}C NMR spectrum (100 MHz, room temperature, DMSO-d_6) of [P_{66614}][2-NH_2-3-O-Py].

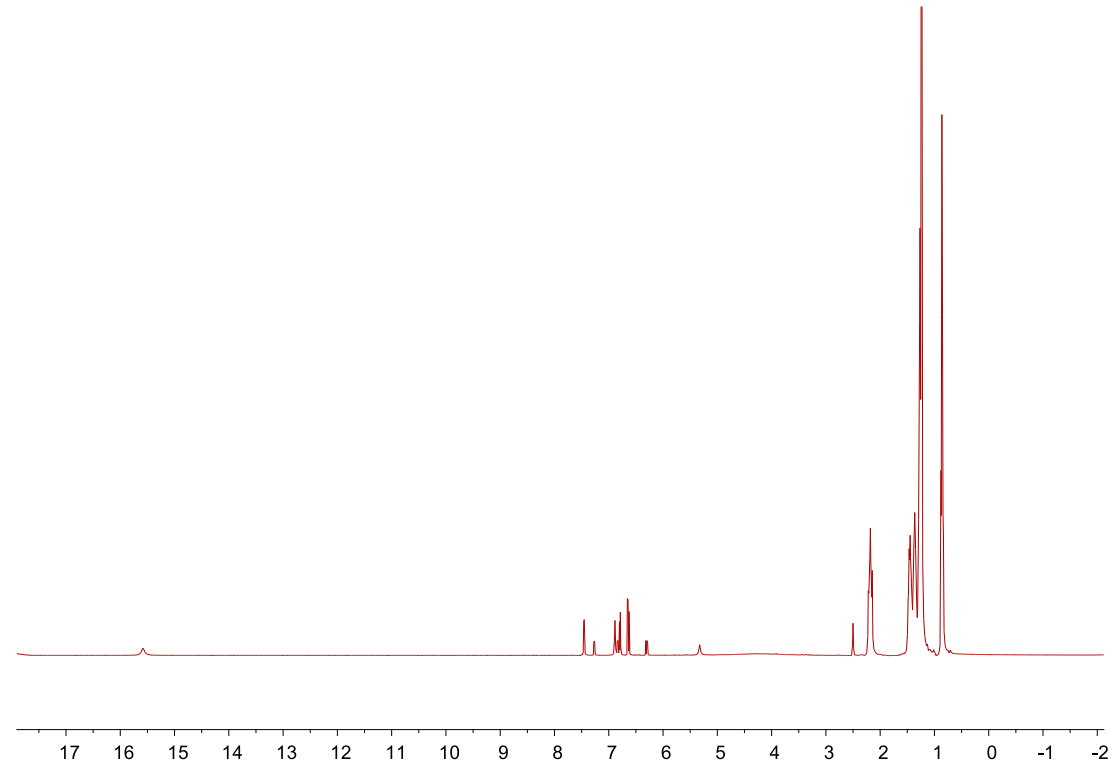


Figure S15. ^{1}H NMR spectrum (400 MHz, room temperature, DMSO-d_6) of [P_{66614}][2-NH_2-3-O-Py] after CO_2 uptake.

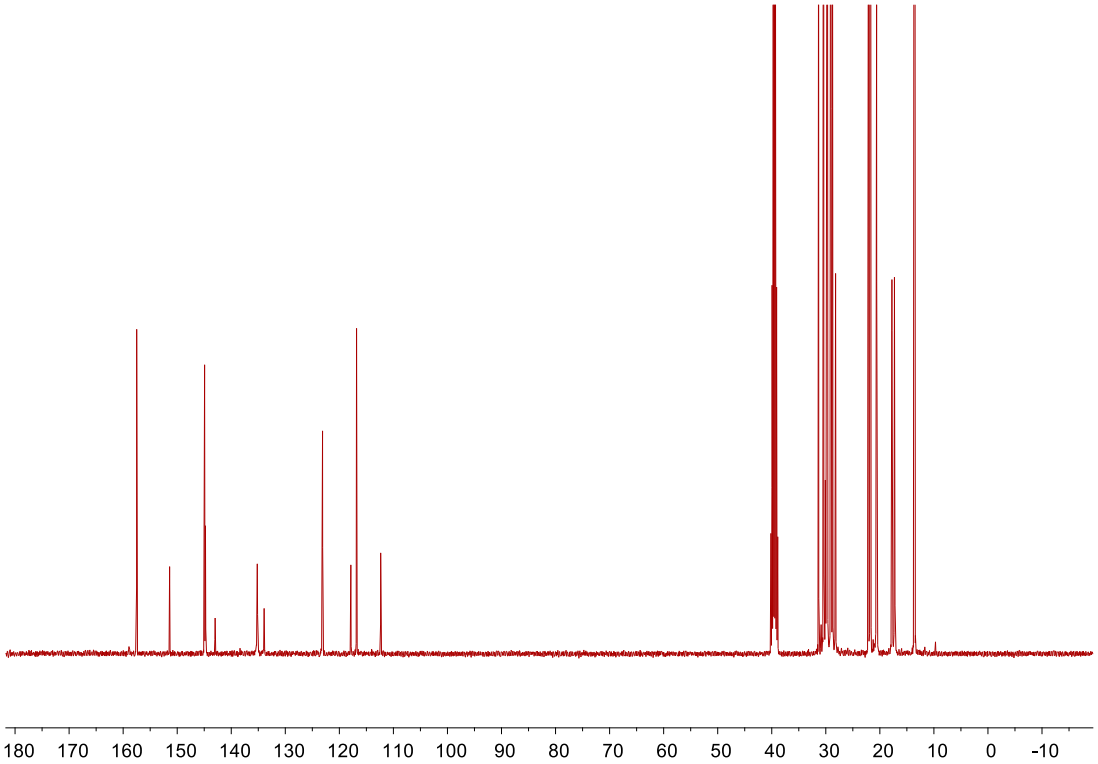


Figure S16. ^{13}C NMR spectrum (100 MHz, room temperature, DMSO-d_6) of [P_{66614}][2-NH_2-3-O-Py] after CO_2 uptake.

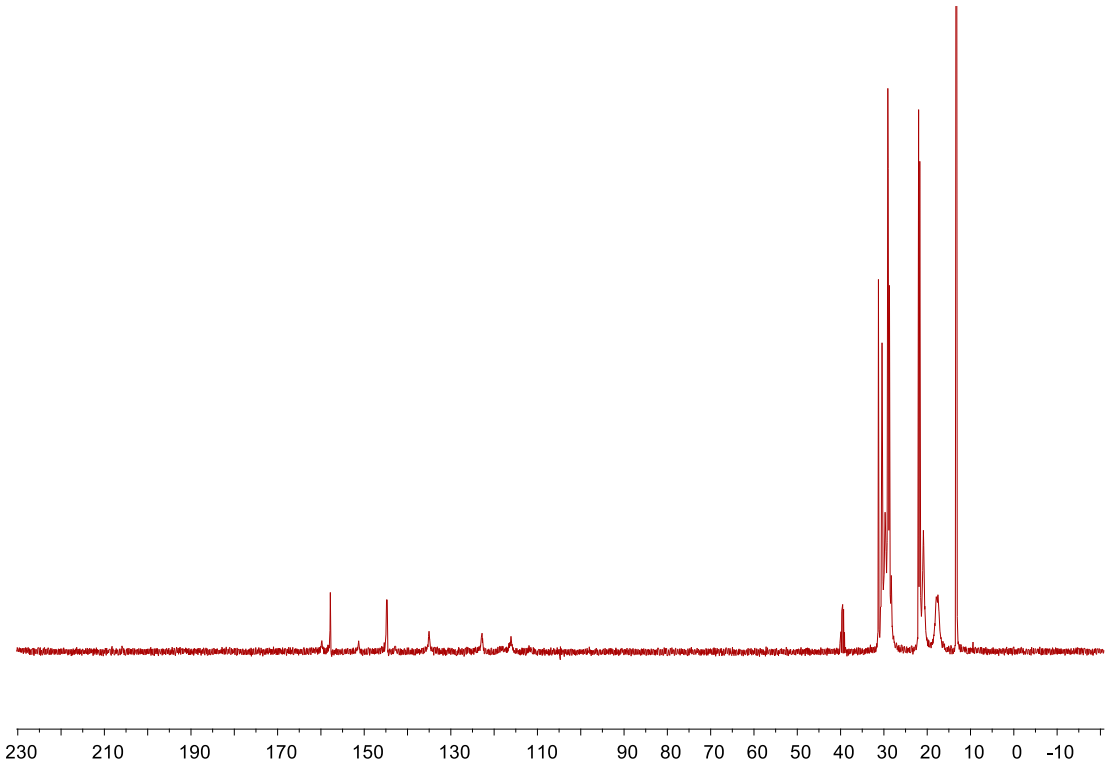


Figure S17. No-deuterium ^{13}C NMR spectrum (100 MHz, room temperature, DMSO-d_6) of [P_{66614}][2-NH_2-3-O-Py].

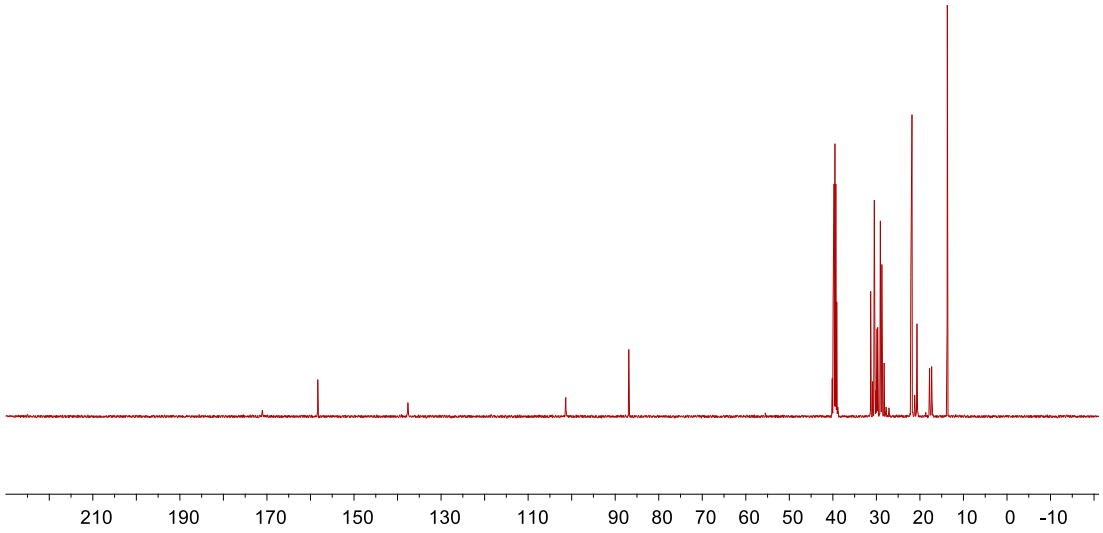


Figure S18. ^{13}C NMR spectrum (100 MHz, room temperature, DMSO-d_6) of [P_{66614}][2-NH_2-6-O-Py].

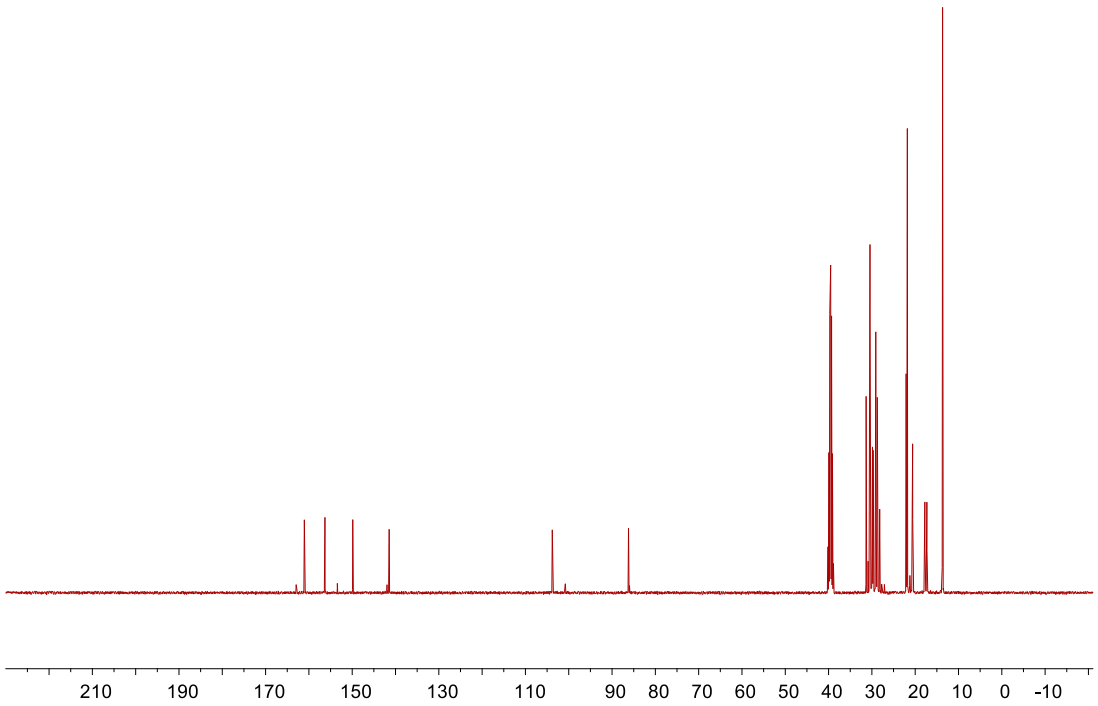


Figure S19. ^{13}C NMR spectrum (100 MHz, room temperature, DMSO-d_6) of [P_{66614}][2-NH_2-6-O-Py] after CO_2 uptake.

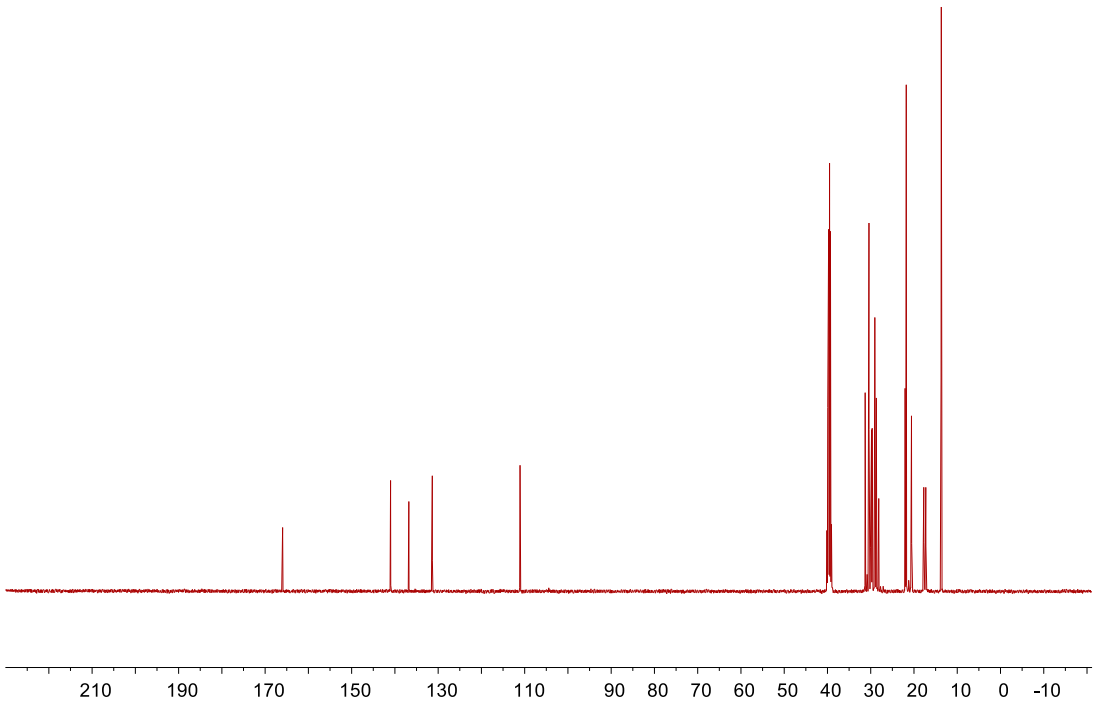


Figure S20. ^{13}C NMR spectrum (100 MHz, room temperature, DMSO-d_6) of [P_{66614}][3-NH_2-4-O-Py].

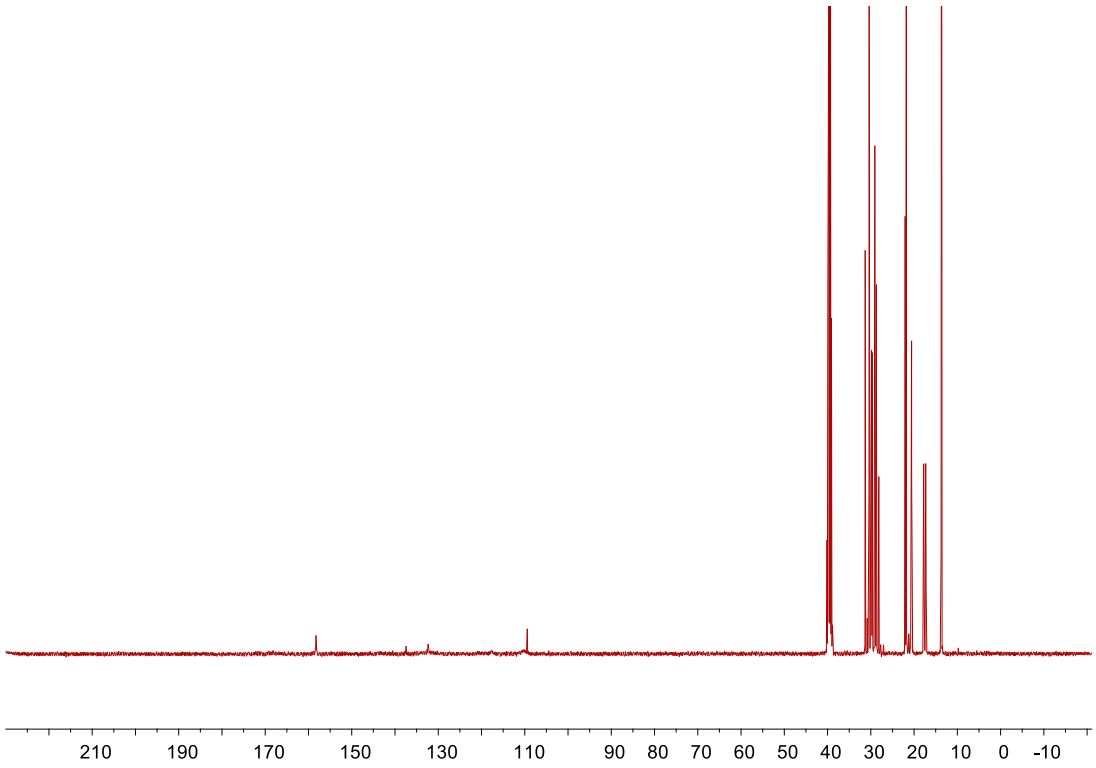


Figure S21. Partial ^{13}C NMR spectrum (100 MHz, room temperature, DMSO-d_6) of [P_{66614}][3-NH_2-4-O-Py] after CO_2 uptake.

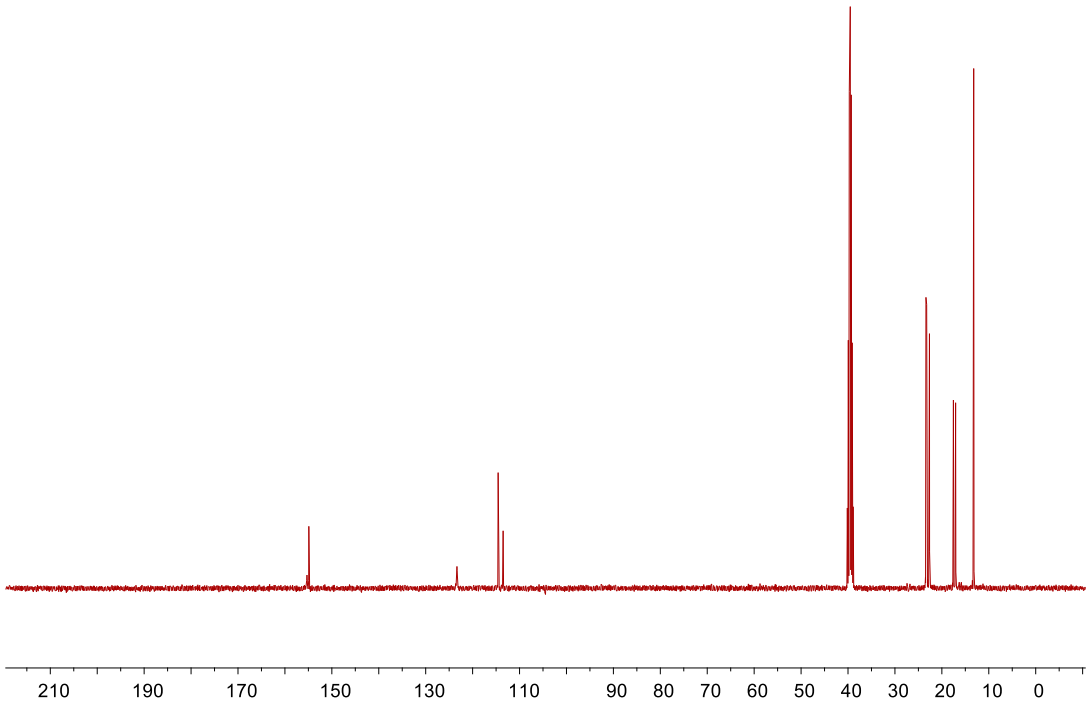


Figure S22. ^{13}C NMR spectrum (100 MHz, room temperature, DMSO-d_6) of [P_{4444}][2-NH_2-3-O-Py].

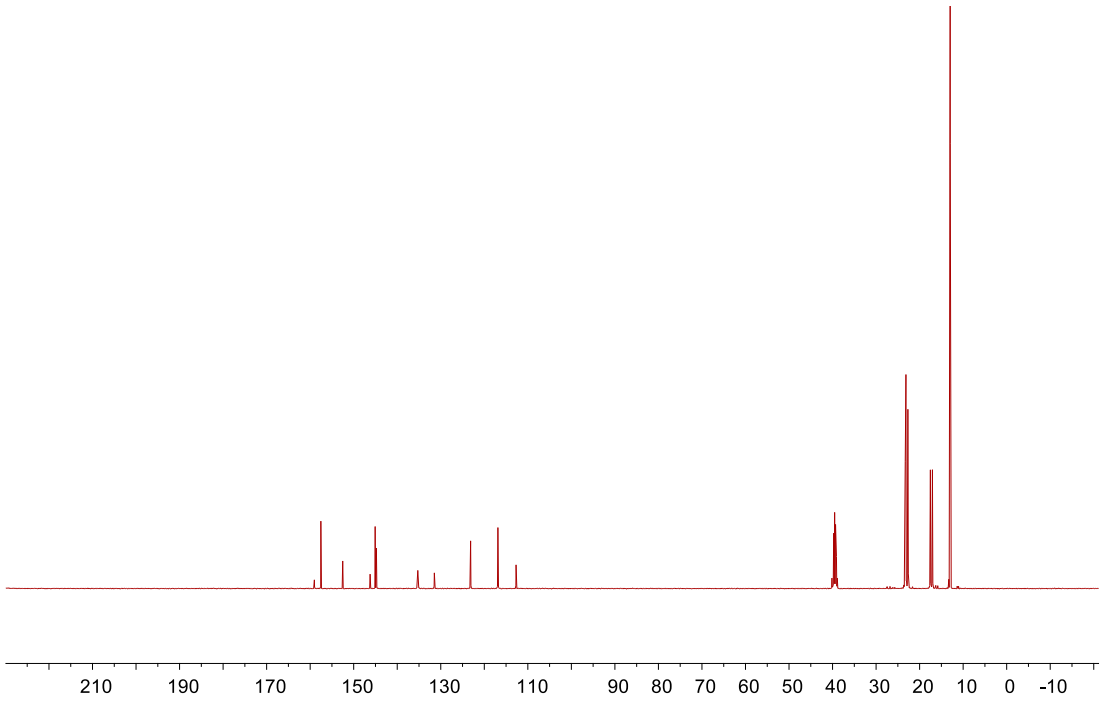


Figure S23. ^{13}C NMR spectrum (100 MHz, room temperature, DMSO-d_6) of [P_{4444}][2-NH_2-3-O-Py] after CO_2 uptake.

References:

S1. (a) K. Fukumoto, Y. Kohno and H. Ohno, *Chem. Lett.*, 2006, **35**, 1252; (b) M. Pan, N. Cao, W. Lin, X. Luo, K. Chen, S. Che, H. Li and C. Wang, *ChemSusChem*, 2016, **9**, 2351.