Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information for

Probing dynamics of carbon dioxides in a metal-organic framework under high pressure by high-resolution solid-state NMR

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Materials

All chemicals employed were obtained from commercial suppliers and used without further purification. MOF-74 was prepared as previously described.[1] $Zn(NO_3)_2 \cdot 6H_2O$ (0.56 g, 1.88 mmol) and H_4DOTP (0.19 g, 0.96 mmol) were dissolved in DMF (20 mL), 2-propanol (1 mL), and water (1 mL) and heated at 105 °C for 20 h. The dark yellow needle crystals thus produced were collected using a centrifuge and washed three times with DMF. The dark yellow needle crystals were then immersed in MeOH for 5 d during. The washing solvent was decanted and freshly replenished three times. Subsequently, the dark yellow needle crystals were immersed in acetone for 1 d. The washing process with acetone was repeated twice and finally immersed in dehydrated chloroform for 2 d. After the washing process, the samples were activated by removing the solvent under vacuum for 12 h at 250 °C after pre-heated at 65 °C for 2h.

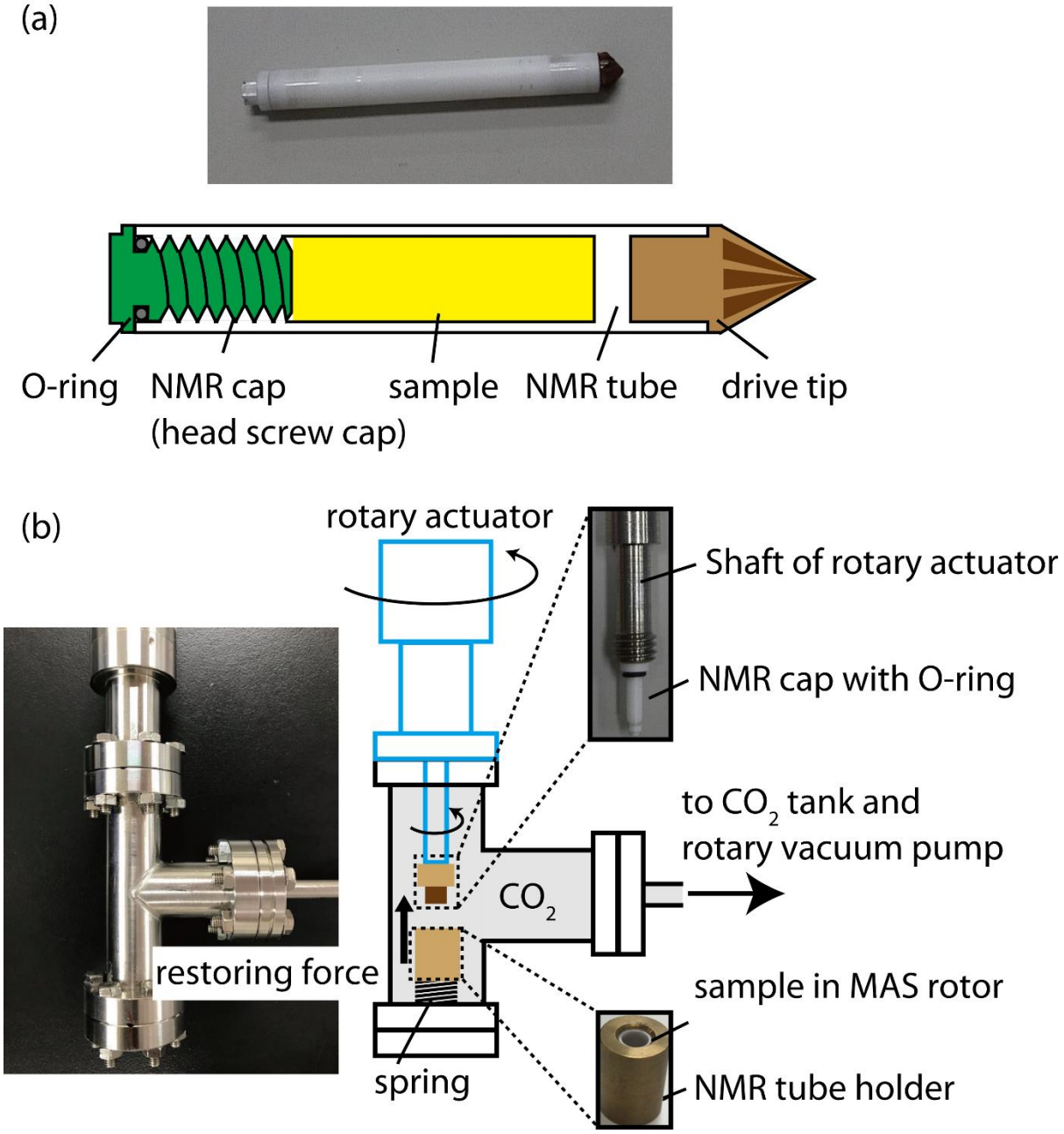

Fig. S1. Photographs and schematic illustrations of (a) MAS NMR rotor for high pressure and (b) instrument for sample packing under CO_2 atmosphere.

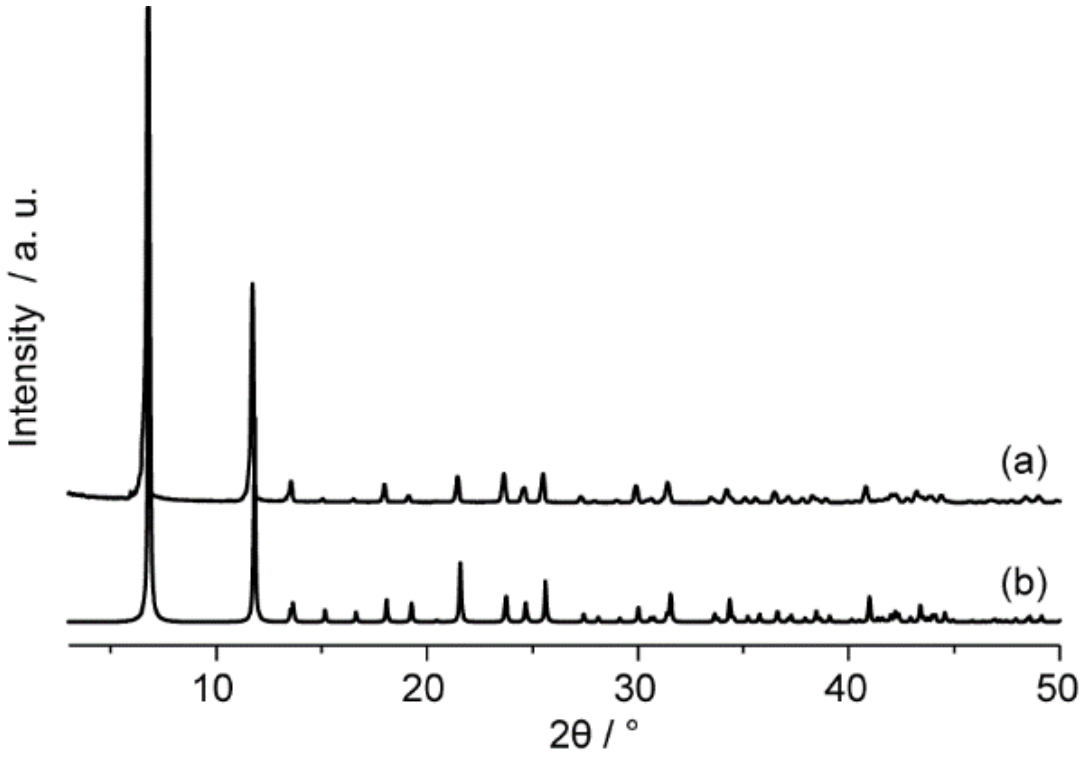

Fig. S2. PXRD patterns of (a) MOF-74 at room temperature and (b) calculation from crystal structure.

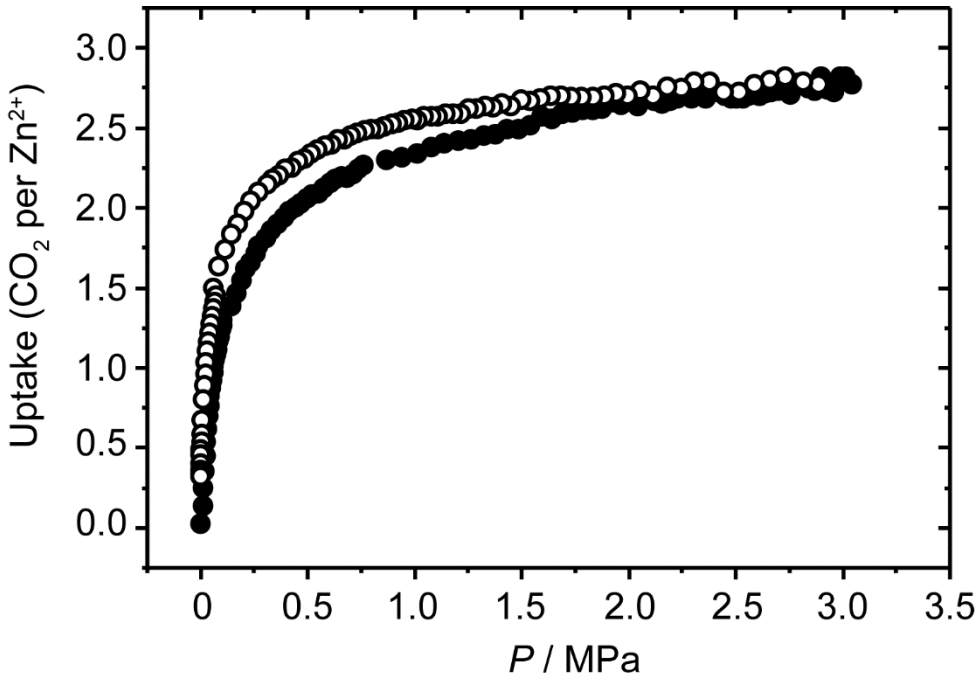

Fig. S3. Adsorption isotherms of CO_2 at 298 K for MOF-74. Closed and open circles represent adsorption and desorption, respectively.

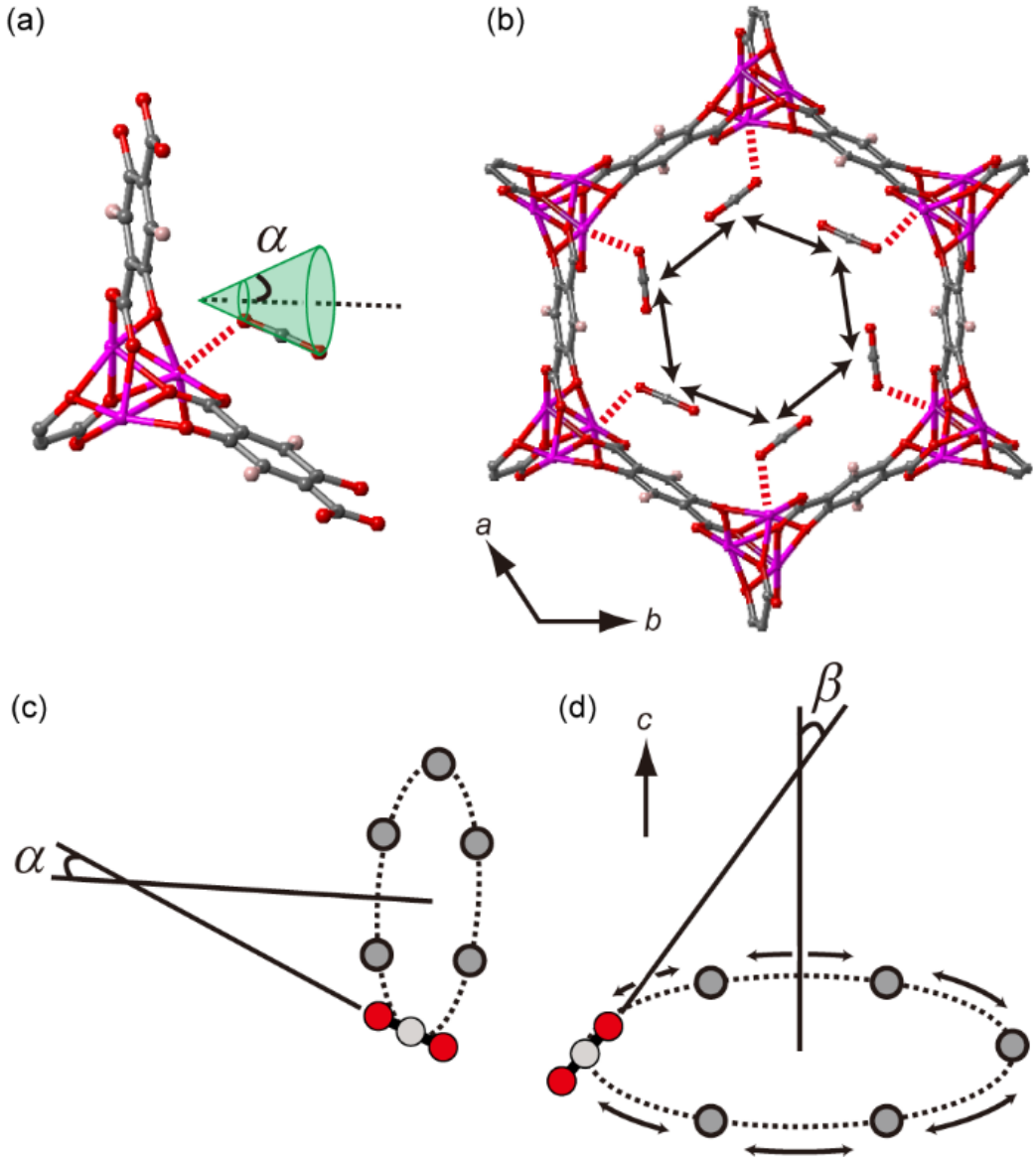

Fig. S4. (a) Localized wobbling around primary site (green circular cone) and (b) 6-hold hopping between primary sites to simulate CSA spectra. In the simulation, we assumed (c) CO_2 jumps to all 6-hold sites with equal probability as wobbling motion and (d) adjacent two sites with equal probability as 6-hold sites hopping.

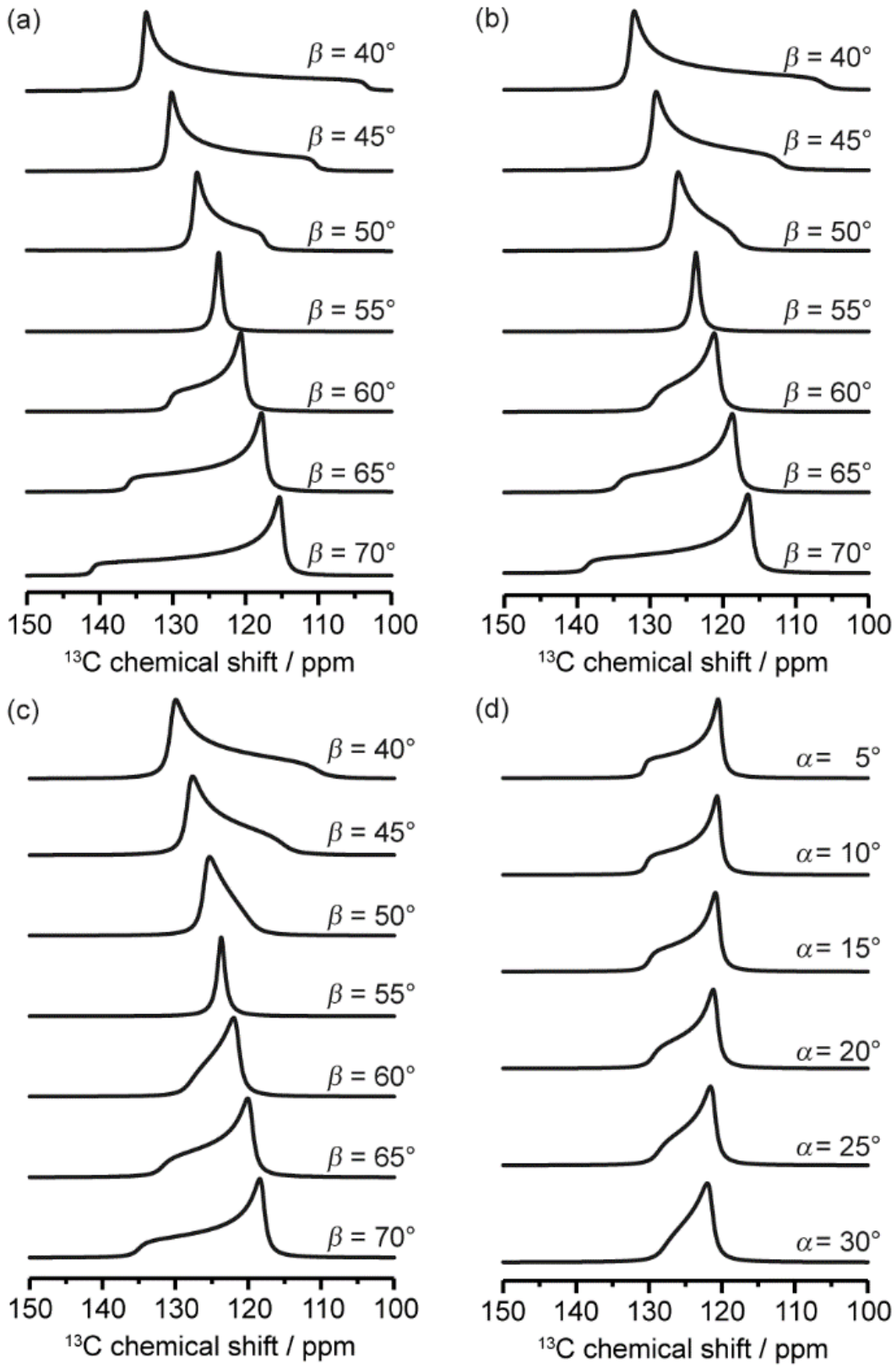

Fig. S5. Simulated ^{13}C CSA NMR spectra using the two types of dynamics (localized wobbling and 6-hold hopping). The α– or β–angles were fixed at (a) α = 10°, (b) α = 20°, (c) α = 30°, and (d) β = 60°, respectively.

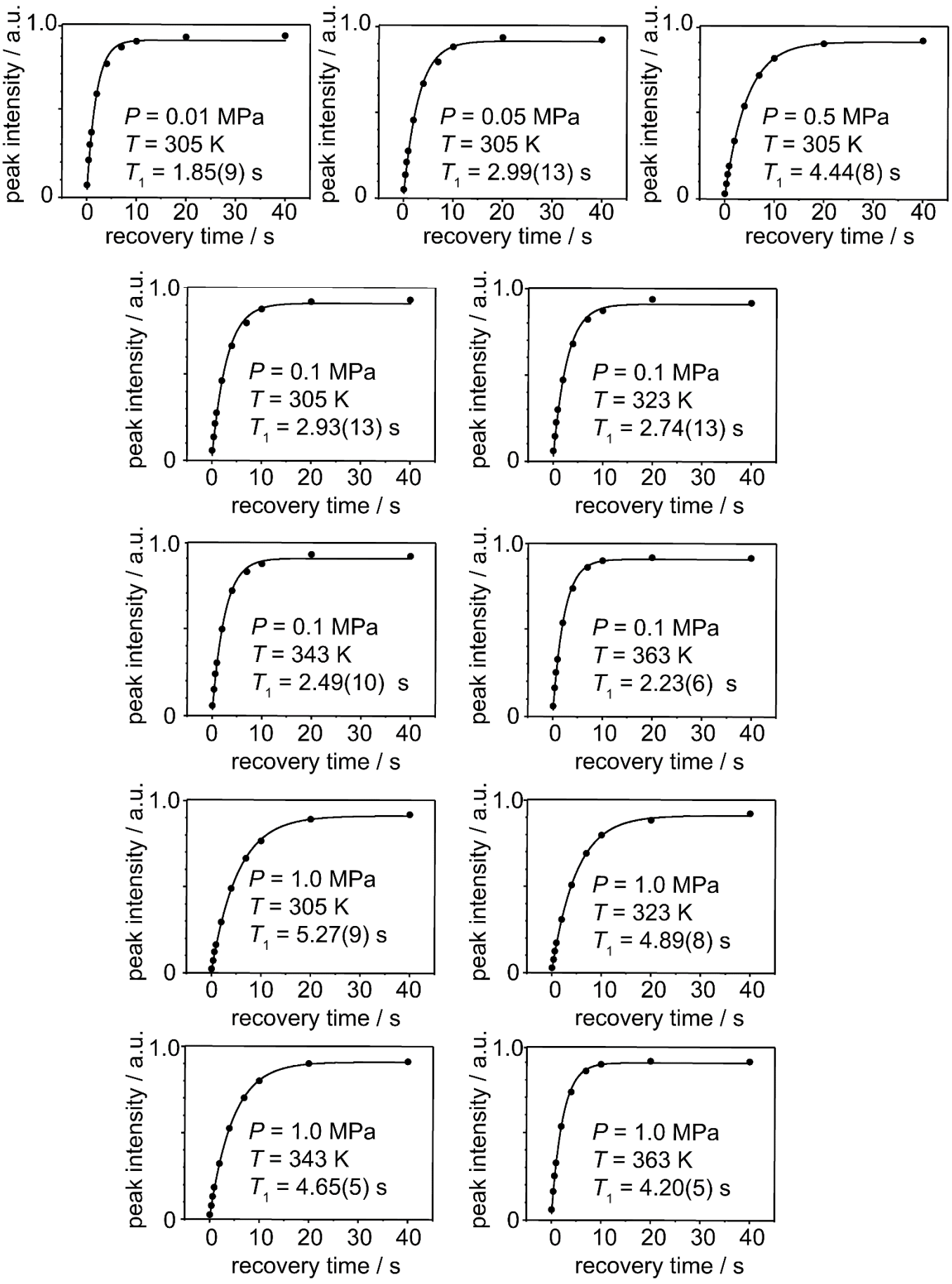

Fig. S6. Saturation recovery curves of T_1 measurements. The values in parentheses are the errors of fit.

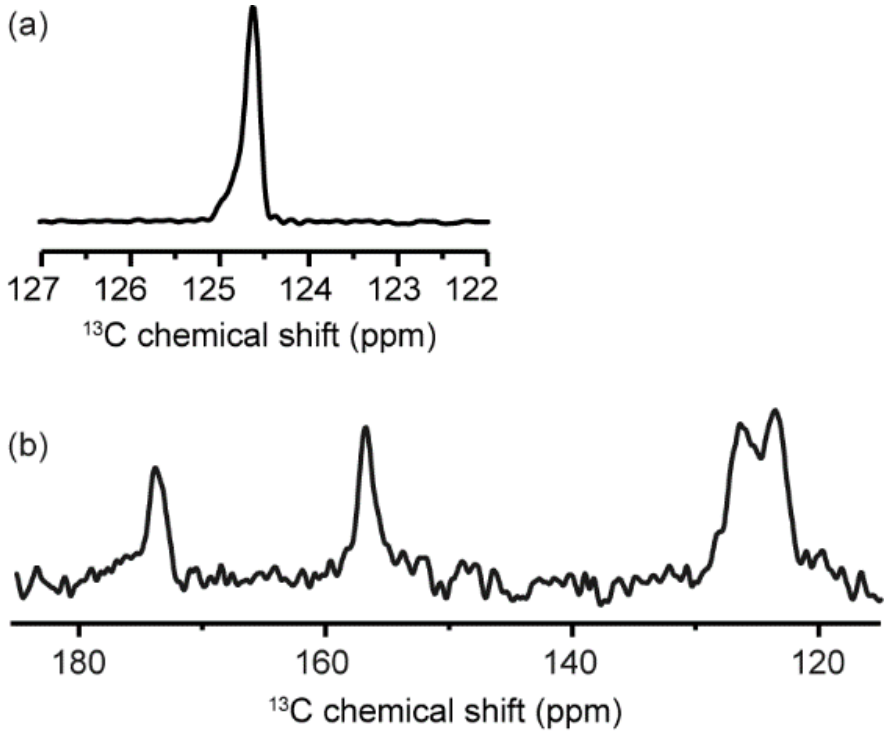

Fig. S7. (a) ^{13}C MAS NMR spectrum of CO_2 at 1 MPa and (b) ^{13}C CP-MAS NMR spectrum of MOF-74 adsorbed natural isotopic abundance CO_2 at 0.1 MPa.