Electronic supplementary information for

Tri-Coordinated PdNP Architecture for Simultaneous Capture, Activation, and Catalytic Conversion of Dilute CO_2 via Multisite Synergy

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1. Experimental Section

1.1 General

All starting materials, reagents and solvents were supplied commercially from Sigma Aldrich, Alfa Aesar, and/or Sinopharm Chemical Reagent Limited Corporation. All nuclear magnetic resonance spectroscopy (NMR) were tested with Bruker Avance III 400 NMR spectrometer. Fourier-transform infrared spectroscopy (FT-IR) were tested on an Avatar Nicholet FT-IR spectrometer in neat with the smart OMNI-transmission accessories or KBr pellets by standard method, and frequencies were reported as cm^{-1}. High performance liquid chromatography coupled with high resolution mass spectrometry (HPLC–HR–MS) were obtained using a Waters G2-XS QTOF mass spectrometer, with samples dissolved in methanol. X-ray diffraction (XRD) pattern were recorded with Bruker D8 advanced X-ray diffraction measurement system, with Cu Kα source (λ=1.54 Å). Transmission electron microscope (TEM) observations were conducted by JEM-2000EX at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher) using an Al Ka source (15 kV, 10 mA) with Ar etching for 30 min (the charge of C-C carbon species here was corrected to 284.8 eV). Solution-state ultraviolet–visible (UV–Vis) spectra were measured on JASCO V-770 spectrometer with a 1 cm quartz cell at room temperature (RT. around 25 °C). Inductively coupled plasma–optical emission spectroscopy (ICP–OES) analyses were conducted by Shimadzu ICPS-8100. The AcGlu-MeIm-PdNPs **1c-4c** were further characterized by ICP–OES, thermogravimetric analysis (TGA) and high-resolution TEM (HR-TEM). The gas proportioner was model KT-C3ZS, produced by Zhengzhou Ketan Instrument Equipment Co., Ltd was used to delivers a continuous and stable source of CO_2 (flow rate is set at 40 sccm).

1.2 Synthesis of *N*-substituted imidazoles

1.2.1 Synthesis of 1-butyl-2-methyl-1H-imidazole

Sodium hydride (60% in oil, 0.92 g, 23.0 mmol) was added to a redistilled tetrahydrofuran solution of 2-methylimidazole (1.64 g, 17.0 mmol) in a 250 mL round-bottom flask. The mixture was stirred at 0 °C for 2.0 h, after which 1-bromobutane (3.7 mL, 34.0 mmol) and tetraoctylammonium bromide (0.02 g, catalytic) were sequentially added. Stirring was continued at room temperature for an additional 4.0 h, yielding a yellow suspension. Volatiles were removed by rotary evaporation to afford a yellow solid. Dichloromethane was added, and the mixture was filtered through a sand core funnel under suction to yield a colorless filtrate. After solvent removal by rotary evaporation, the product was purified by column chromatography on silica (mesh 200–300 μm) using dichloromethane/methanol (20:1) as the mobile phase. This yielded 1-butyl-2-methyl-1H-imidazole (2.04 g, 87%) as a pale yellow viscous liquid. Other *N*-substituted imidazoles were prepared using an analogous procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H), 6.76 (d, J = 1.1 Hz, 1H), 3.77 (td, J = 7.3, 1.9 Hz, 2H), 2.32 (d, J = 2.1 Hz, 3H), 1.74 – 1.56 (m, 2H), 1.40 – 1.17 (m, 3H), 0.90 (td, J = 7.3, 1.9 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 126.8, 119.0, 77.5, 77.2, 76.8, 45.8, 32.7, 19.7, 13.6, 12.9 ppm.

1.2.2 Synthesis of 2-methyl-1-((perfluorophenyl)methyl)-1H-imidazole

Sodium hydride (60% in oil, 0.88 g, 12.0 mmol) was added to a redistilling tetrahydrofuran solution of 2-methylimidazole (0.82 g, 10.0 mmol) in a 250 mL round-bottom flask, and the resulting suspension was stirred at the ice-bath for around 2.0 h. 1-(bromomethyl)-2,3,4,5,6-pentafluorobenzene (2.61 g, 10 mmol) and tetraoctyl ammonium bromide (0.01 g) for catalytic quantities was then added in the flask and the mixture was stirred at RT for another 4.0 h. The volatiles were removed by rotary evaporation to get a black solid. Dichloromethane was added and the mixture was filtered by suction through a sand core funnel. The filtrate was collected and solvent was removed by rotary evaporation. Purification by column chromatography on silica (mesh 200-300 μm) with dichloromethane/methanol (20:1)

gave the product (1.91 g, 73%) as a pale yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (d, J = 1.0 Hz, 1H), 6.68 (d, J = 1.4 Hz, 1H), 5.00 (s, 2H), 2.30 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 146.4, 146.3, 146.2, 144.6, 144.0, 143.9, 143.9, 142.7, 140.2, 138.9, 138.8, 138.7, 136.4, 136.3, 136.1, 110.0, 109.9, 109.8, 109.7, 36.8, 12.4 ppm.

1.3 General procedure for the synthesis of AcGlu-MeIm-Br (1a–4a)

Compound 1,2-dimethyl-1H-imidazole (0.48 g, 5.0 mmol) and 2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyloxy)-ethyl bromide (2.39 g, 5.25 mmol) were dissolved in dry acetonitrile and heated at 120 °C in a sealed high-pressure reactor for 48 h.[1] After cooling, the solvent was decanted, then the volatiles were removed by rotary evaporation. Purification by column chromatography on silica (mesh 200-300 μm) with dichloromethane/methanol (20:1) gave the product **1a** (2.62 g, 95%) as a pale yellow viscous liquid. AcGlu-MeIm-Br **2a**–**4a** was prepared in a similar method.

1a, a pale yellow viscous liquid, 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 1.9 Hz, 1H), 7.55 (d, J = 1.9 Hz, 1H), 5.13 (dd, J = 11.0, 8.0 Hz, 1H), 4.98 (t, J = 9.7 Hz, 1H), 4.83 (dd, J = 9.5, 8.1 Hz, 1H), 4.68 (dd, J = 15.0, 3.0 Hz, 1H), 4.52 (d, J = 8.0 Hz, 2H), 4.22 (dd, J = 12.4, 4.8 Hz, 2H), 4.14 – 4.00 (m, 2H), 3.91 (s, 3H), 3.72 (ddd, J = 10.1, 4.7, 2.0 Hz, 1H), 2.70 (s, 3H), 2.07 (s, 3H), 2.01 – 1.88 (m, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 169.8, 169.4, 169.3, 145.0, 122.5, 121.4, 100.0, 72.3, 71.3, 70.9, 68.1, 68.0, 61.5, 53.7, 48.3, 35.8, 20.7, 20.7, 20.4, 20.4, 10.6 ppm. HR-MS m/z: $[M\text{-}Br]^+$ calcd for $C_{21}H_{31}N_2O_{10}$ 471.19732; found 471.19785.

2a, a pale yellow solid, 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 2.1 Hz, 1H), 7.43 (d, J = 2.1 Hz, 1H), 5.09 (t, J = 9.5 Hz, 1H), 4.92 (t, J = 9.7 Hz, 1H), 4.78 (dd, J = 9.7, 8.0 Hz, 1H), 4.66 (ddd, J = 14.6, 5.3, 2.9 Hz, 1H), 4.55 (dd, J = 7.8, 3.1 Hz, 1H), 4.51 (d, J = 8.0 Hz, 1H), 4.19 (ddd, J = 12.3, 7.0, 4.1 Hz, 2H), 4.14 – 4.04 (m, 3H), 4.01 (dd, J = 12.4, 2.2 Hz, 1H), 3.70 (ddd, J = 10.1, 4.9, 2.2 Hz, 1H), 2.67 (s, 3H), 2.02 (s, 3H), 1.94 (s, 3H), 1.89 (d, J = 6.6 Hz, 6H), 1.76 (dt, J = 20.9, 7.5 Hz, 2H), 1.43 – 1.27 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$)

δ 170.6, 169.9, 169.6, 169.5, 144.4, 122.7, 121.9, 100.3, 72.6, 71.9, 71.1, 68.2, 67.8, 61.7, 53.5, 49.5, 49.4, 31.5, 21.0, 20.6, 20.5, 19.8, 13.6, 11.6 ppm. HR-MS m/z: $[M\text{-}Br]^+$ calcd for $C_{24}H_{37}N_2O_{10}$, 513.24427; found, 513.24497.

3a, a pale yellow viscous liquid, 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.88 (m, 1H), 7.38 (td, J = 7.6, 3.3 Hz, 4H), 7.30 – 7.26 (m, 2H), 5.40 (q, J = 15.2 Hz, 2H), 5.14 (td, J = 9.5, 1.5 Hz, 1H), 4.97 (dd, J = 14.2, 5.2 Hz, 1H), 4.85 – 4.75 (m, 1H), 4.66 (d, J = 12.3 Hz, 1H), 4.55 (d, J = 8.0 Hz, 2H), 4.30 – 3.99 (m, 4H), 3.73 (ddd, J = 10.1, 4.9, 2.2 Hz, 1H), 2.71 (d, J = 2.6 Hz, 3H), 2.05 (d, J = 2.1 Hz, 3H), 2.01 – 1.89 (m, 9) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 169.9, 169.6, 145.0, 129.6, 129.4, 128.1, 122.5, 121.3, 100.3, 72.4, 71.9, 71.1, 68.2, 68.1, 61.7, 52.4, 48.7, 20.8, 20.8, 20.6, 20.5, 11.1 ppm. HR-MS m/z: $[M\text{-}Br]^+$ calcd for $C_{27}H_{35}N_2O_{10}$, 547.22862; found, 547.22890.

4a, a pale yellow viscous liquid, 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 2.1 Hz, 1H), 7.47 (d, J = 1.5 Hz, 1H), 5.70 – 5.53 (m, 2H), 5.09 (t, J = 9.5 Hz, 1H), 4.91 (t, J = 9.7 Hz, 1H), 4.72 (dd, J = 9.6, 8.0 Hz, 1H), 4.60 (ddd, J = 14.4, 5.0, 3.0 Hz, 1H), 4.56 – 4.46 (m, 2H), 4.15 (dd, J = 12.4, 4.8 Hz, 2H), 4.09 – 3.94 (m, 2H), 3.71 (ddd, J = 10.0, 4.7, 2.2 Hz, 1H), 2.76 (s, 3H), 2.01 (s, 3H), 1.94 (s, 3H), 1.91 (s, 3H), 1.87 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 169.9, 169.5, 169.5, 145.7, 122.7, 121.5, 100.2, 72.3, 71.8, 71.1, 68.1, 67.8, 61.6, 49.0, 40.3, 20.8, 20.7, 20.5, 20.5, 10.9 ppm. HR-MS m/z: $[M\text{-}Br]^+$ calcd for $C_{27}H_{30}N_2O_{10}F_5$, 637.18151; found, 637.18200.

1.4 General procedure for the synthesis of AcGlu-MeIm-Pd (1b-4b)

AcGlu-based 2-methylimidazolium halopalladate salt **1b** was prepared as follows: in a 100.0 mL round-bottom flask, **1a** (0.17 g, 0.3 mmol) were dissolved in 50.0 mL of DCM, and aqueous solution of Na_2PdCl_4 (1.0 g·100.0 mL^{-1}, 7.6 mL) was added in the flask and the mixture was stirred at RT overnight.[2] The two-phase mixture was vigorously stirred until all the Na_2PdCl_4 was transferred into the organic layer, followed by a phase-separation to yield the organic layer. The organic layer was washed twice with ultrapure water, then removed by rotary evaporation and dried

under vacuum to get the product **1b** (0.17 g, 96%) as a reddish brown solid. AcGlu-MeIm-Pd **2b**–**4b** was prepared in similar processes.

1b, a reddish brown solid, 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 2.1 Hz, 1H), 7.57 (d, J = 2.0 Hz, 1H), 5.19 (t, J = 9.5 Hz, 1H), 5.03 (t, J = 9.7 Hz, 1H), 4.92 (dd, J = 9.6, 8.0 Hz, 1H), 4.81 – 4.64 (m, 3H), 4.37 (dt, J = 8.7, 4.2 Hz, 1H), 4.27 (dd, J = 12.5, 4.6 Hz, 1H), 4.22 – 4.10 (m, 2H), 4.06 (s, 3H), 3.80 (ddd, J = 10.0, 4.5, 2.2 Hz, 1H), 2.93 (s, 3H), 2.10 (s, 3H), 2.02 – 1.96 (m, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 169.8, 169.4, 169.4, 145.1, 123.1, 122.1, 100.1, 72.4, 71.6, 71.0, 68.0, 67.8, 61.6, 49.1, 36.4, 20.9, 20.8, 20.5, 20.4, 11.4 ppm. FT-IR (cm^{-1}): 3436, 3139, 2961, 2360, 1747, 1589, 1537, 1513, 1429, 1369, 1223, 1169, 1120, 1037, 957, 800, 748, 697. HR-MS m/z: $[M\text{-}PdCl_4]^+$ calcd for $C_{21}H_{31}N_2O_{10}$, 471.1979; found, 471.1980.

2b, a reddish brown solid, 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 2.0 Hz, 1H), 7.52 (d, J = 2.0 Hz, 1H), 5.16 (d, J = 9.5 Hz, 1H), 5.00 (t, J = 9.7 Hz, 1H), 4.89 (dd, J = 9.5, 8.1 Hz, 1H), 4.73 (dd, J = 18.8, 5.8 Hz, 3H), 4.39 (s, 1H), 4.34 – 4.28 (m, 2H), 4.28 – 4.22 (m, 2H), 4.12 (dd, J = 12.4, 1.9 Hz, 1H), 3.81 (dd, J = 10.1, 2.3 Hz, 1H), 2.91 (s, 3H), 2.07 (s, 3H), 2.00 – 1.94 (m, 9H), 1.93 – 1.87 (m, 2H), 1.45 (dq, J = 14.7, 7.3 Hz, 2H), 1.45 (dq, J = 14.7, 7.3 Hz, 2H), 0.99 (t, J = 7.3 Hz, 3H), 0.99 (t, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 169.9, 169.5, 144.4, 122.7, 121.9, 100.3, 72.5, 71.9, 71.1, 68.1, 67.6, 61.7, 49.6, 49.4, 31.5, 20.9, 20.5, 20.5, 19.8, 13.6, 11.5 ppm. FT-IR (cm^{-1}): 3597, 3513, 3177, 3134, 2960, 2936, 2874, 1753, 1626, 1585, 1530, 1433, 1375, 1227, 1169, 1126, 1037, 908, 749, 698. HR-MS m/z: $[M\text{-}PdCl_4]^+$ calcd for $C_{24}H_{37}N_2O_{10}$, 513.2448; found, 513.2446.

3b, a reddish brown solid, 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.51 – 7.32 (m, 6H), 5.59 (s, 2H), 5.20 (t, J = 9.5 Hz, 1H), 5.02 (t, J = 9.7 Hz, 1H), 4.91 (dd, J = 11.8, 5.8 Hz, 1H), 4.80 (s, 2H), 4.70 (d, J = 8.0 Hz, 1H), 4.41 (d, J = 10.7 Hz, 1H), 4.32 – 4.19 (m, 2H), 4.14 (d, J = 12.4 Hz, 1H), 3.84 – 3.73 (m, 1H), 2.99 (s, 3H), 2.07 (s, 3H), 1.98 (dd, J = 13.0, 5.8 Hz, 9H) ppm;^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 170.1, 169.4, 169.3, 144.8, 126.9, 119.4, 100.5, 72.5, 71.9, 70.7, 68.7, 68.2, 61.7, 45.5,

20.7, 20.5, 12.83 ppm. HR-MS m/z: $[M\text{-}PdCl_4]^+$ calcd for $C_{27}H_{35}N_2O_{10}$, 547.22862; found, 547.22926.

4b, a reddish brown solid, 98%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 2.0 Hz, 1H), 7.65 (s, 1H), 5.71 (s, 2H), 5.19 (t, J = 9.5 Hz, 1H), 5.01 (t, J = 9.7 Hz, 1H), 4.88 – 4.81 (m, 1H), 4.76 (s, 2H), 4.70 (d, J = 8.0 Hz, 1H), 4.39 (dd, J = 11.2, 4.2 Hz, 1H), 4.20 (ddd, J = 36.4, 12.3, 3.2 Hz, 3H), 3.81 (ddd, J = 10.0, 4.2, 2.2 Hz, 1H), 3.00 (s, 3H), 2.09 (s, 3H), 2.03 – 1.96 (m, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 170.0, 169.5, 169.5, 145.7, 123.2, 122.6, 100.3, 72.4, 71.9, 71.1, 68.2, 67.4, 61.6, 49.8, 40.8, 20.9, 20.8, 20.6, 20.5, 11.4 ppm. HR-MS m/z: $[M\text{-}PdCl_4]^+$ calcd for $C_{27}H_{30}N_2O_{10}F_5$, 637.18151; found, 637.18163.

1.5 General procedure for the synthesis of AcGlu-MeIm-PdNPs 1c–4c

AcGlu-MeIm-PdNP **1c** was prepared as follows: in a 100.0 mL round-bottom flask, **1b** (0.18 mg, 0.3 mmol) were dissolved in 50.0 mL of dichloromethane, and freshly prepared ice aqueous solution of $NaBH_4$ (3.0 mmol) was slowly added in the flask and the mixture was stirred at an ice-salt bath for 1-2 h.[3] The solution was washed twice with ultrapure water, then removed by rotary evaporation and dried under vacuum to obtained the product **1c** (0.15 g, 95%) as a black solid. AcGlu-MeIm-PdNPs **2c**–**4c** was prepared in similar processes.

1c, a black solid, 96%. ^{1}H NMR (400 MHz, DMSO) δ 7.84 (s, 1H), 7.68 (s, 1H), 5.48 (s, 2H), 5.23 (s, 1H), 4.86 (s, 2H), 4.71 (s, 1H), 4.38 (s, 2H), 4.05 (d, J = 45.6 Hz, 5H), 2.61 (s, 3H), 1.97 (s, 9H) ppm, ^{13}C NMR (101 MHz, DMSO) δ 170.4, 169.9, 169.7, 169.5, 145.4, 134.9, 129.4, 128.9, 128.1, 122.3, 122.0, 99.4, 72.3, 71.1, 68.5, 67.4, 62.1, 51.1, 48.1, 20.9, 20.8, 20.6, 10.2 ppm. FT-IR (cm^{-1}): 3460, 2959, 2926, 2854, 1752, 1626, 1572, 1515, 1429, 1369, 1255, 1226, 1166, 1035, 903, 803, 698, 601, 529. HR-MS m/z: $[M\text{-}Pd]^+$ calcd for $C_{21}H_{31}N_2O_{10}$, 471.19732; found, 471.19767.

2c, a black solid, 99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.37 (s, 1H), 5.09 (s, 1H), 4.95 (s, 3H), 4.80 (s, 2H), 4.60 (s, 1H), 4.23 (s, 1H), 4.20 (s, 2H), 4.10 (s, 2H), 3.76 (s, 1H), 2.70 (s, 3H), 2.36 (s, 3H), 2.04 (s, 3H), 1.94 (s, 9H), 1.81 – 1.78 (m, 2H), 1.38 – 1.35 (m, 2H), 0.93 (s, 3H) ppm, ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 169.8,

169.5, 169.5, 144.2, 100.2, 72.5, 71.6, 71.4, 71.0, 68.1, 61.7, 31.6, 29.5, 20.8, 20.7, 20.4, 19.6, 13.4, 10.2 ppm .FT-IR (cm^{-1}): 3450, 2961, 2928, 2872, 1752, 1637, 1511, 1431, 1369, 1257, 1257, 1226, 1167, 1038, 909, 803, 700, 596. HR-MS m/z: $[M-Pd]^+$ calcd for $C_{24}H_{37}N_2O_{10}$, 513.24427; found, 513.24436.

3c, a black solid, 98%. ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.43 (d, J = 6.9 Hz, 3H), 7.31 (d, J = 5.8 Hz, 3H), 5.49 – 5.30 (m, 2H), 5.18 (t, J = 9.6 Hz, 1H), 4.99 (t, J = 9.7 Hz, 1H), 4.85 (t, J = 8.8 Hz, 1H), 4.71 (s, 1H), 4.58 (t, J = 12.7 Hz, 2H), 4.34 – 4.13 (m, 3H), 4.09 (d, J = 12.4 Hz, 1H), 3.75 (dd, J = 10.9, 4.8 Hz, 1H), 2.75 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 1.99 (s, 9H) ppm, ^{13}C NMR (101 MHz, DMSO) δ 170.5, 170.0, 169.8, 169.5, 145.5, 135.0, 129.5, 129.0, 128.2, 122.4, 122.1, 99.5, 72.4, 71.2, 68.6, 67.5, 62.1, 51.1, 48.2, 21.0, 20.8, 20.7, 10.2 ppm, FT-IR (cm^{-1}): 3450, 2961, 2928, 2872, 1752, 1637, 1511, 1432, 1369, 1257, 1225, 1167, 1038, 909, 803, 701, 596. HR-MS m/z: $[M-Pd]^+$ calcd for $C_{27}H_{35}N_2O_{10}$, 547.22862; found, 547.22926.

4c, a black solid, 99%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.61 – 7.36 (m, 1H), 5.62 (s, 2H), 5.22 – 5.16 (m, 1H), 5.05 – 4.98 (m, 1H), 4.77 (s, 1H), 4.58 (d, J = 47.6 Hz, 3H), 4.17 (d, J = 52.8 Hz, 4H), 3.80 (s, 1H), 2.08 (d, J = 7.8 Hz, 3H), 1.99 (d, J = 14.2 Hz, 9H), 1.25 (s, 3H) ppm, ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 169.9, 169.5, 123.6, 100.5, 72.5, 72.0, 71.2, 68.2, 61.9, 29.7, 21.0, 20.6 ppm. FT-IR (cm^{-1}): 3449, 2961, 2923, 2852, 1753, 1657, 1524, 1509, 1429, 1369, 1225, 1170, 1037, 964, 910, 799, 684, 596. HR-MS m/z: $[M-Pd]^+$ calcd for $C_{27}H_{30}N_2O_{10}F_5$, 637.18151; found, 547.22853.

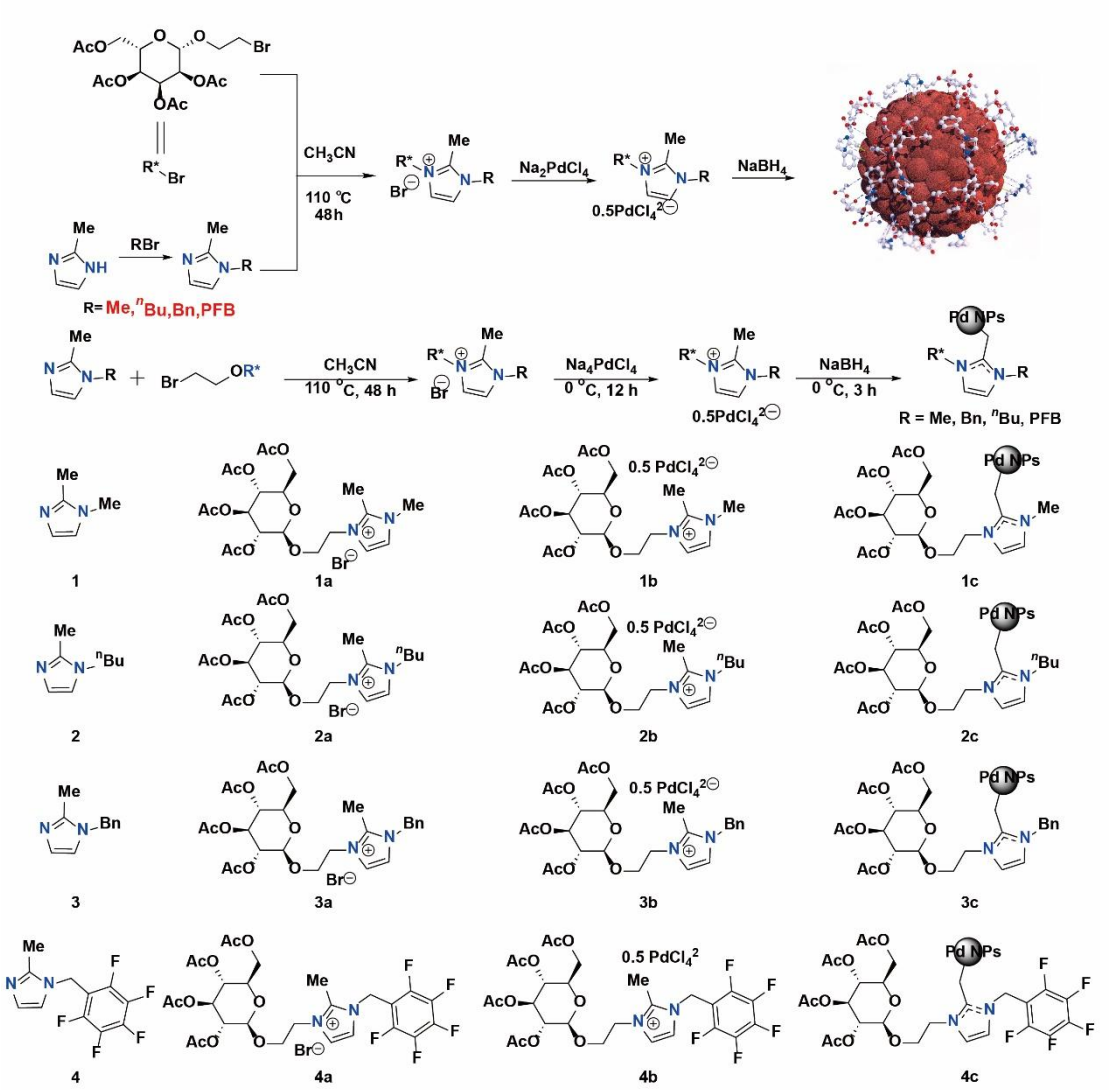


Fig. S1. Synthetic route and chemical structures of PdNPs **1c**–**4c**.

1.6 Structural analysis of selected AcGlu-MeIm salts and PdNPs.

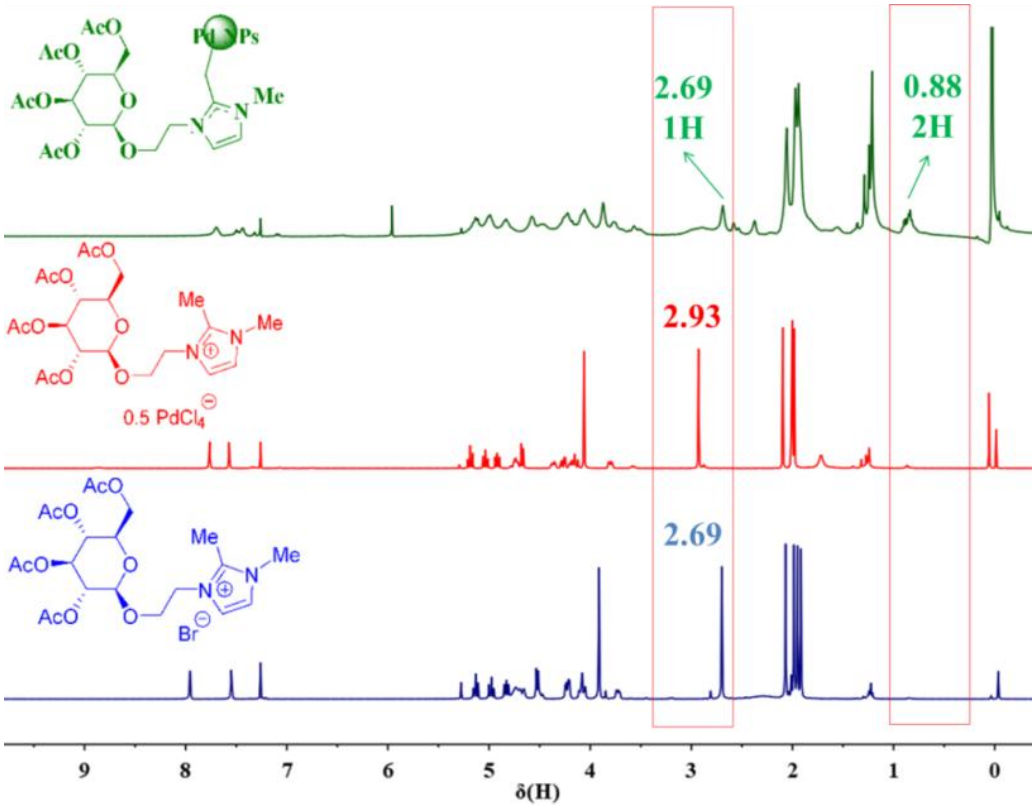


Fig. S2. ^{1}H NMR spectra of AcGlu-MeIm salts and PdNPs (**1a**–**1c**).

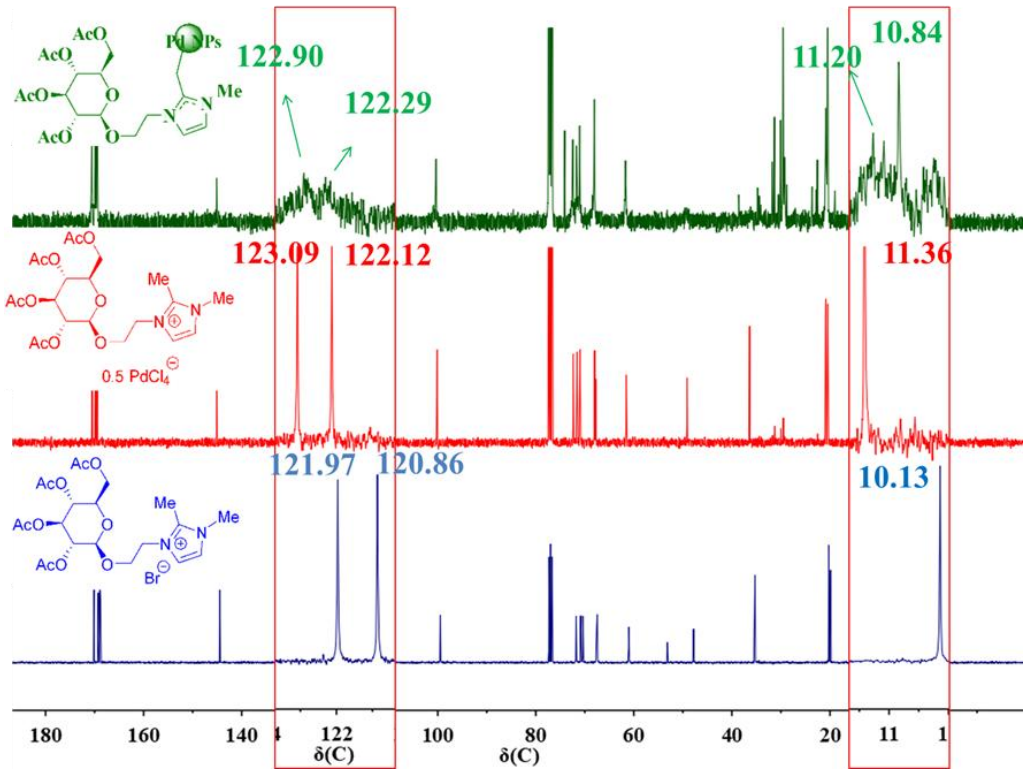


Fig. S3. ^{13}C NMR spectra of AcGlu-MeIm salts and PdNPs (**1a**–**1c**).

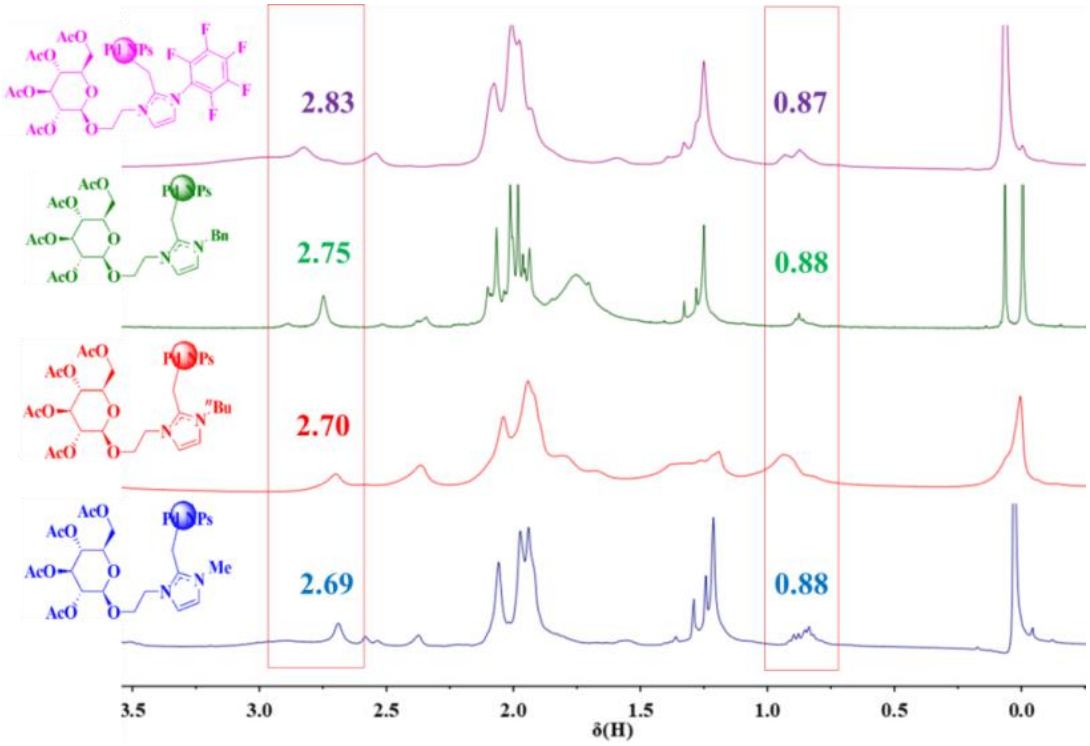


Fig. S4. ^{1}H NMR spectra of PdNPs **1c**–**4c**.

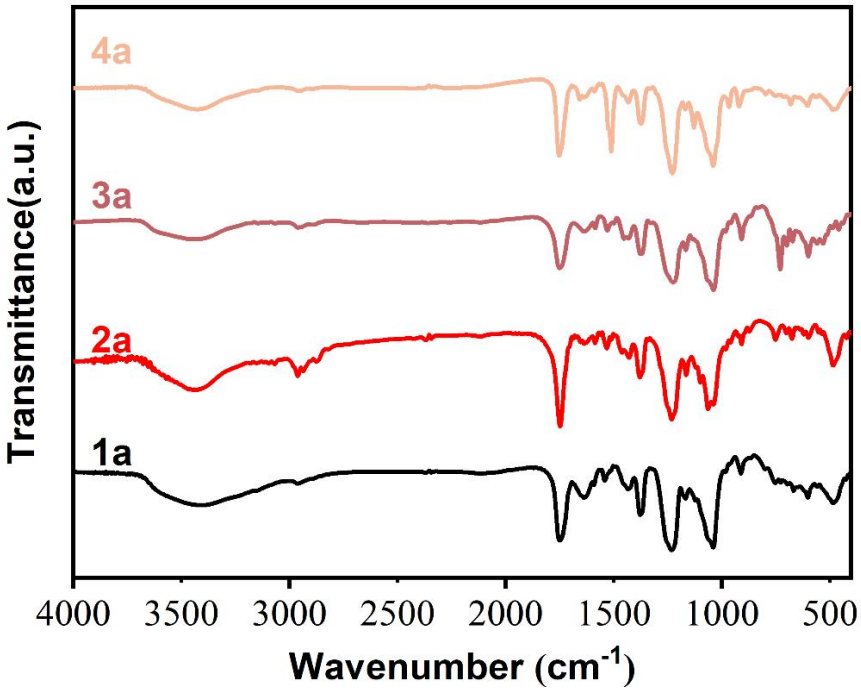


Fig. S5. FT-IR spectra of AcGlu-MeIm-Br **1a**–**4a**.

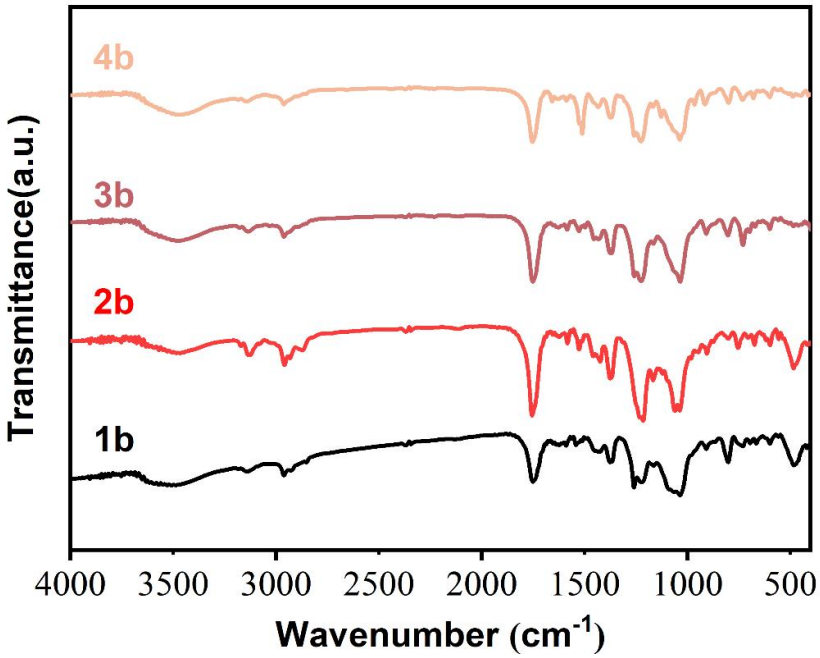


Fig. S6. FT-IR spectra of AcGlu-MeIm-Pd **1b**–**4b**.

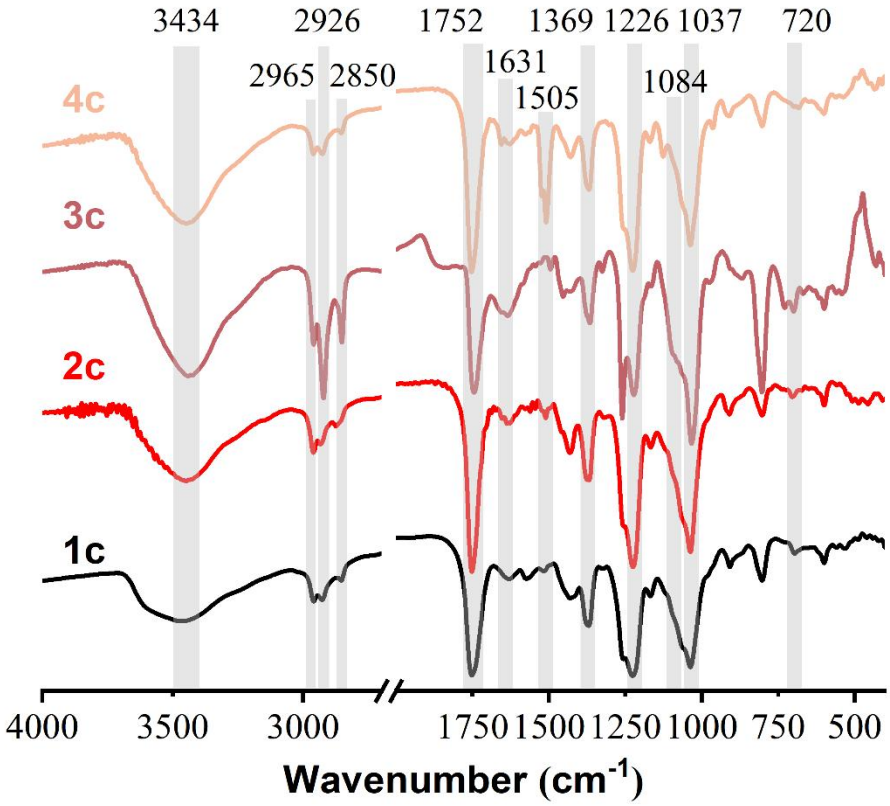


Fig. S7. FT-IR spectra of AcGlu-MeIm-PdNPs **1c**–**4c**.

Table S1. HR-MS analysis results of AcGlu-MeIm salts and PdNPs.

Entry	Predicted $[M]^+$ of L (m/z)	Measured $[M]^+$ of L (m/z)	Molecular formula of L [M]
1a	471.19732	471.19785	$C_{21}H_{31}N_2O_{10}$
1b	471.19732	471.19765	$C_{21}H_{31}N_2O_{10}$
1c	471.19732	471.19767	$C_{21}H_{31}N_2O_{10}$
2a	513.24427	513.24497	$C_{24}H_{37}N_2O_{10}$
2b	513.24427	513.24452	$C_{24}H_{37}N_2O_{10}$
2c	513.24427	513.24436	$C_{24}H_{37}N_2O_{10}$
3a	547.22862	547.22890	$C_{27}H_{35}N_2O_{10}$
3b	547.22862	547.22926	$C_{27}H_{35}N_2O_{10}$
3c	547.22862	547.22853	$C_{27}H_{35}N_2O_{10}$
4a	637.18151	637.18200	$C_{27}H_{30}N_2O_{10}F_5$
4b	637.18151	637.18163	$C_{27}H_{30}N_2O_{10}F_5$
4c	637.18151	637.18173	$C_{27}H_{30}N_2O_{10}F_5$

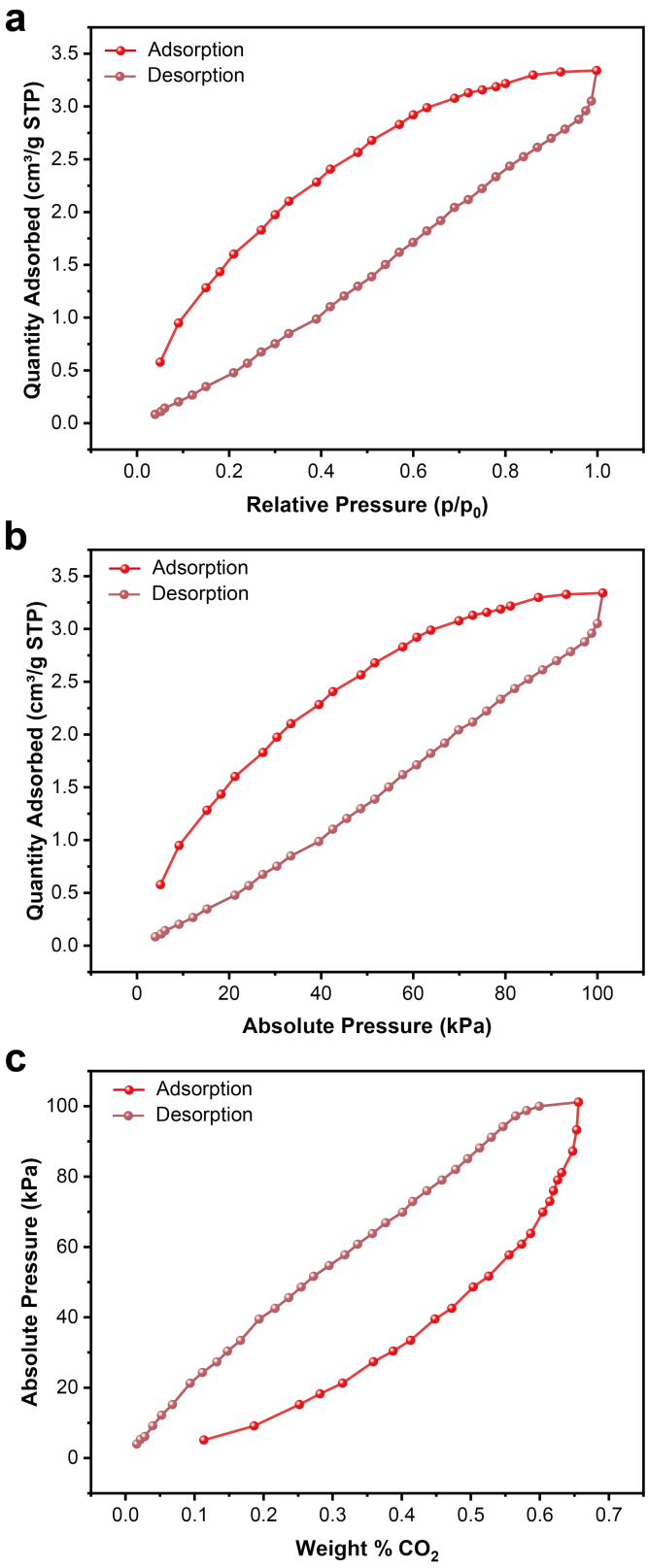


Fig. S8. CO_2 adsorption desorption curve of PdNP **3c**. (a) Isotherm linear plot. (b) Isotherm linear absolute plot. (c) Isotherm pressure composition.

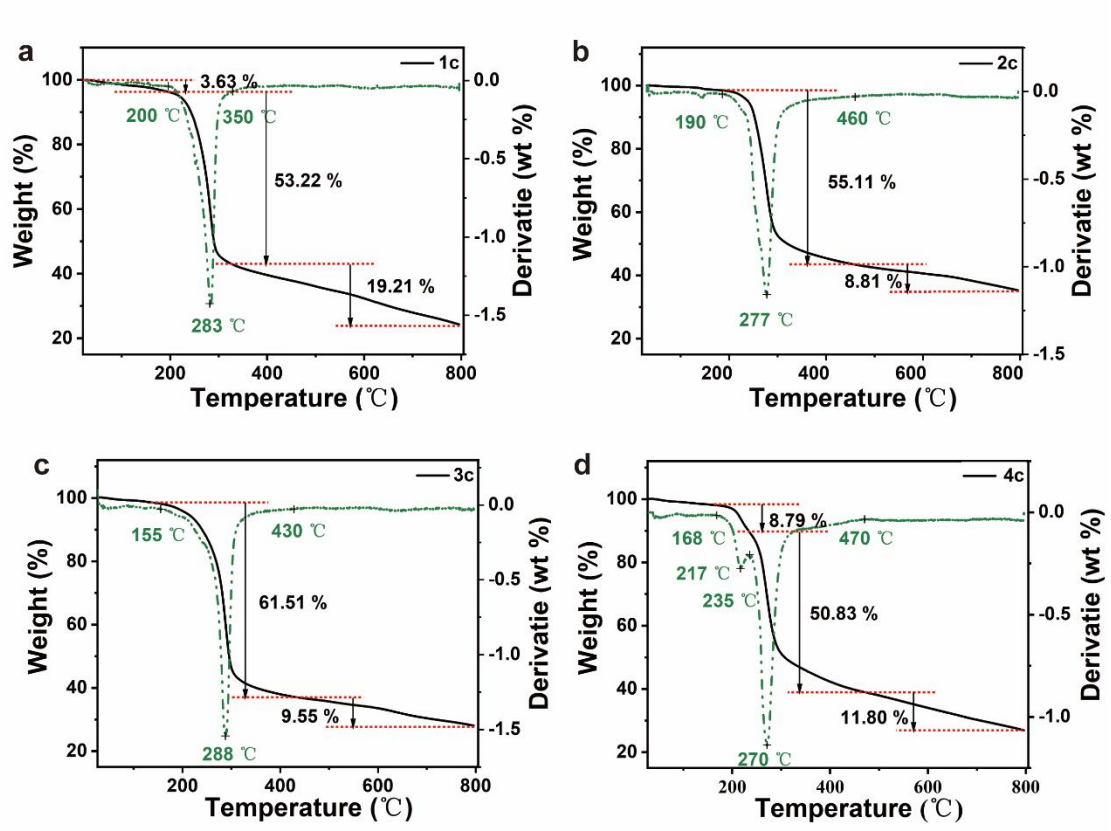


Fig. S9. TGA curve and first-order derivative curve of PdNPs **1c**–**4c**.

Table S2. ICP analytical data for the PdNPs **1c**–**4c**.

Entry	PdNPs	Pd content (%)	metal-to-ligand ratio
1	**1c**	22.95	1.35:1
2	**2c**	18.60	1.11:1
3	**3c**	18.14	1.14:1
4	**4c**	18.82	1.39:1

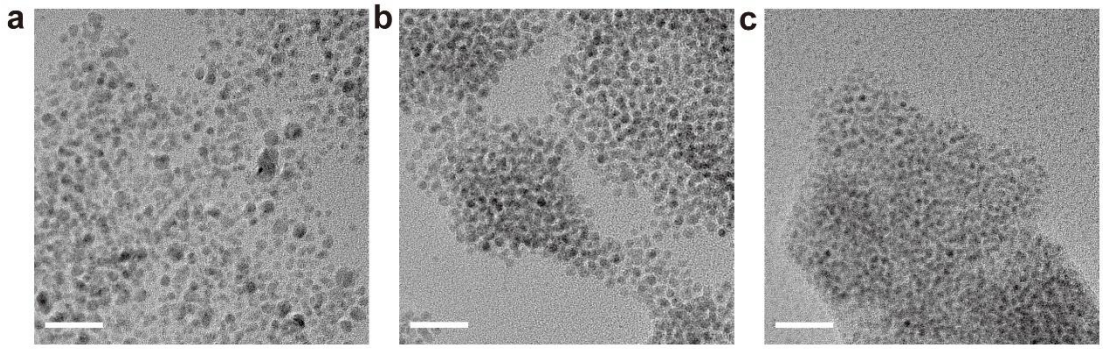


Fig. S10. HR-TEM images of PdNPs **1c** (a), **2c** (b), and **4c** (c). Scale bar: 20 nm.

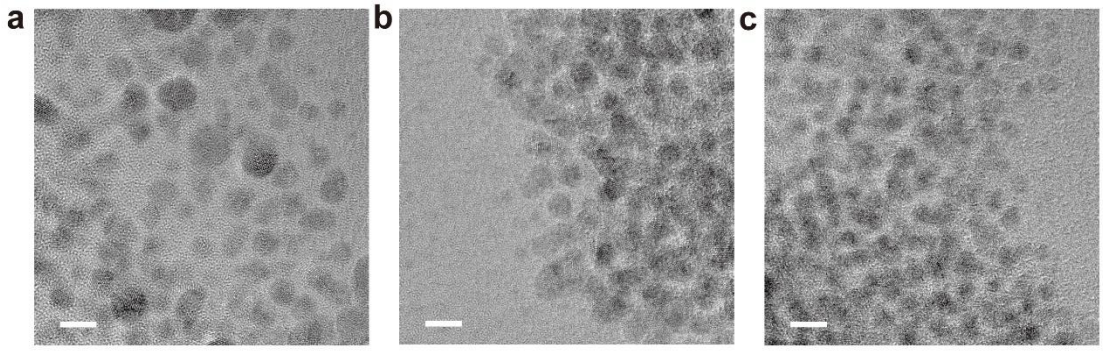


Fig. S11. HR-TEM images of PdNPs **1c** (a), **2c** (b), and **4c** (c). Scale bar: 5 nm

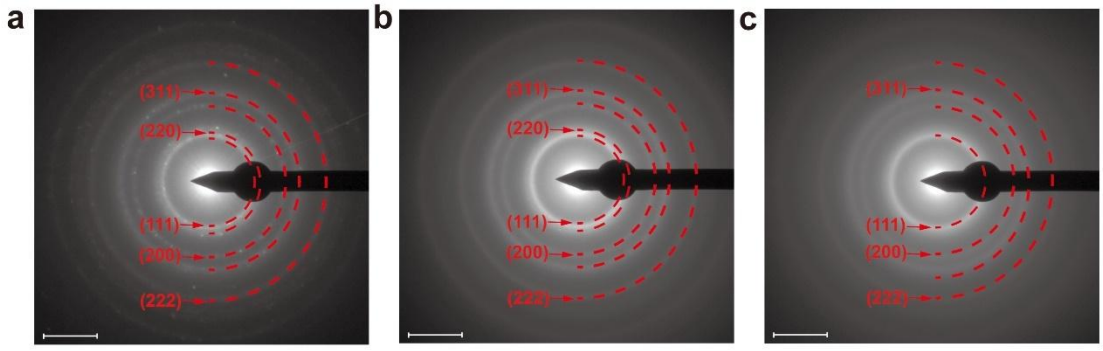


Fig. S12. SAED of PdNPs **1c** (a), **2c** (b), and **4c** (c). Scale bar: 5.00 nm^{-1}.

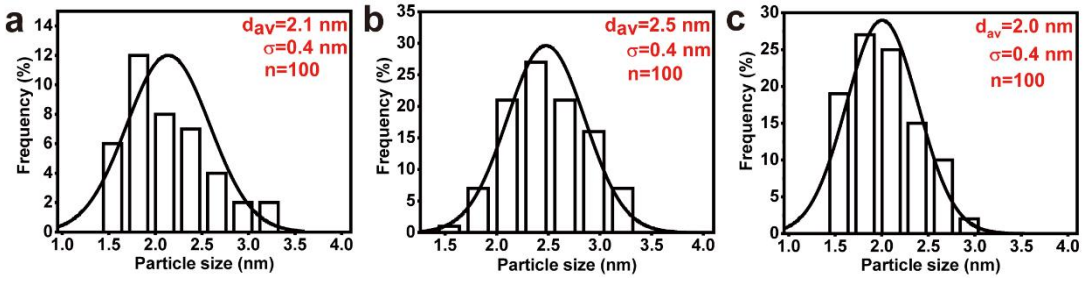


Fig. S13. Size distribution histograms of PdNPs **1c** (a), **2c** (b), and **4c** (c)

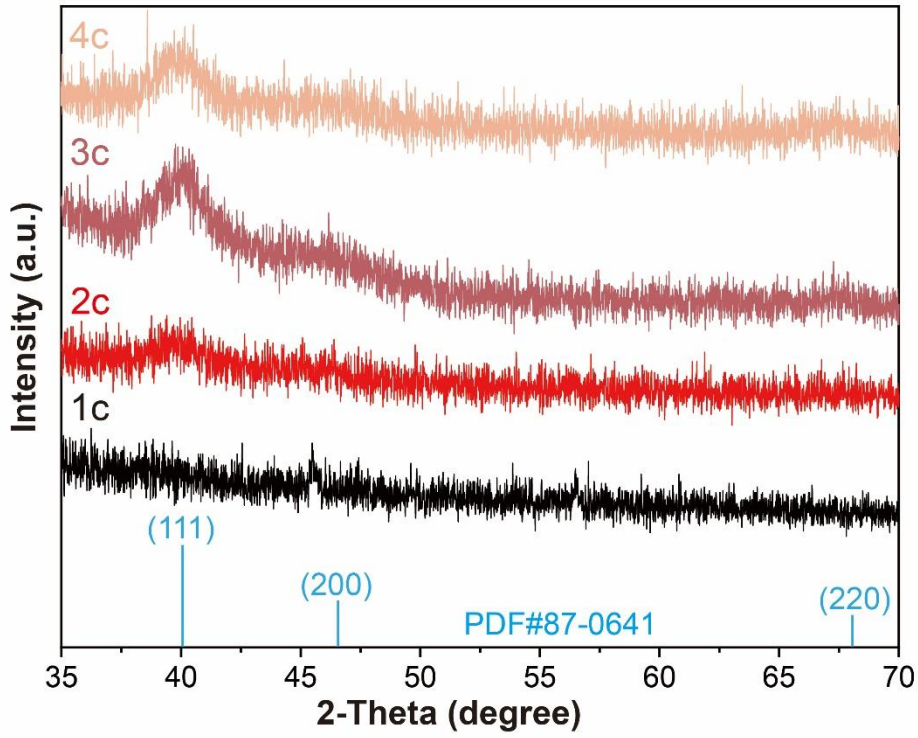


Fig. S14. XRD of PdNPs **1c**–**4c**.

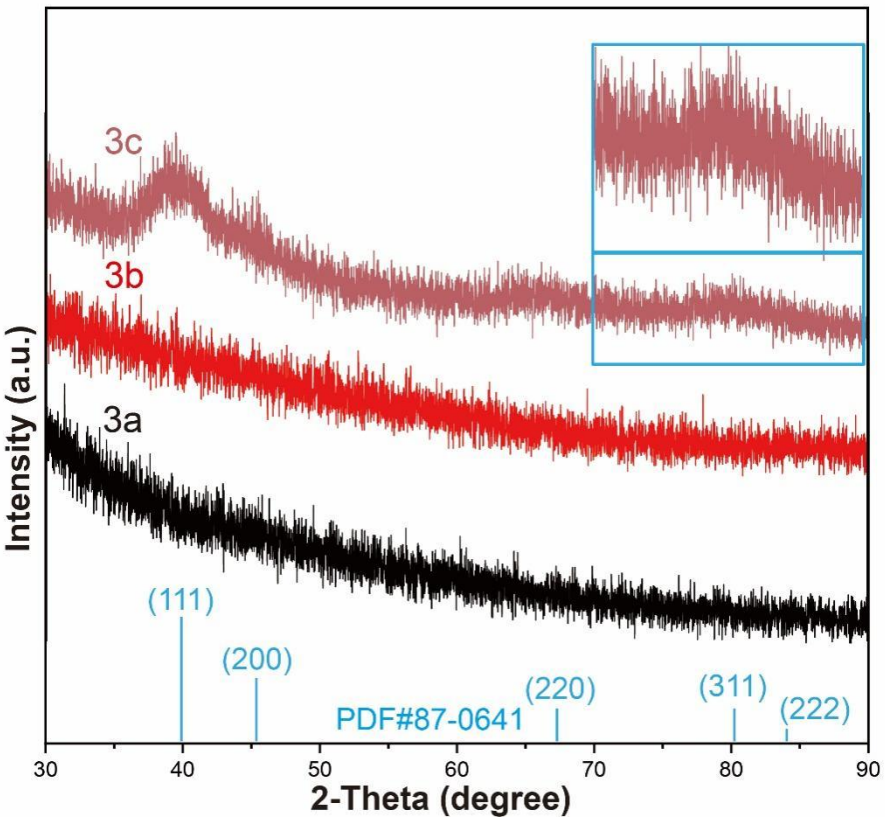


Fig. S15. XRD of **3a**–**3c**.

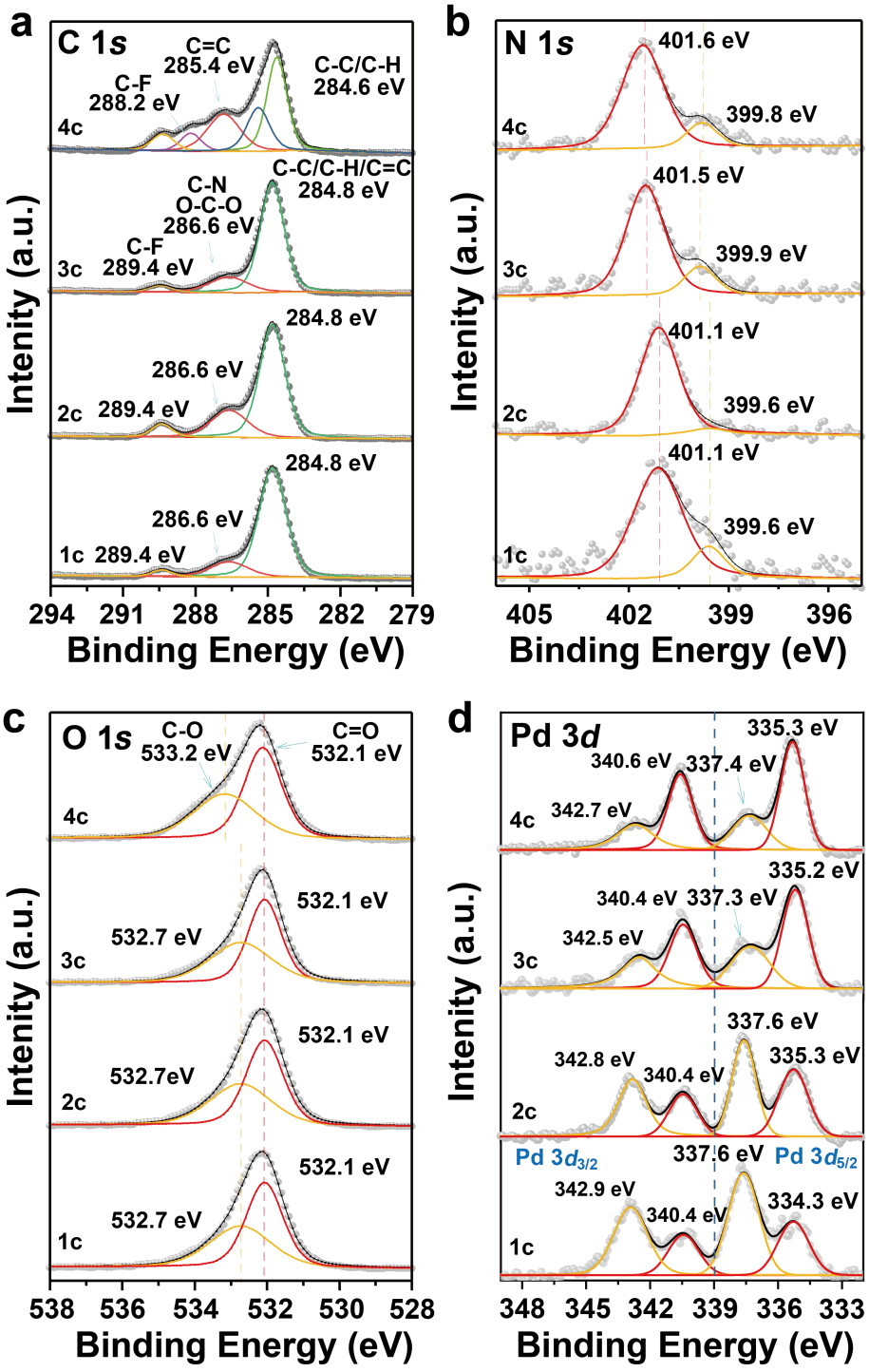


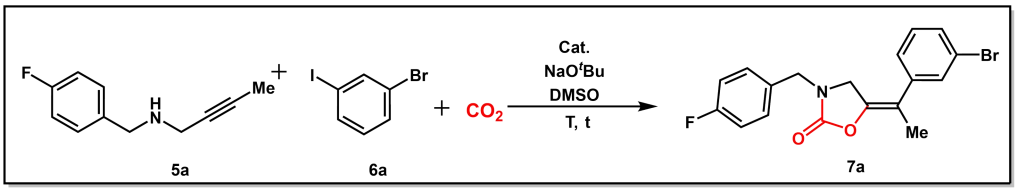
Fig. S16. XPS spectra of PdNPs **1c**–**4c**. **a** XPS spectra of C 1*s*. **b** XPS spectra of N 1*s*. **c** XPS spectra of O 1*s*. **d** XPS spectra of Pd 3*d*.

2. Catalytic evaluation

2.1 General procedures for the AcGlu-MeIm-PdNP-catalyzed 4C-TCRs of CO_2, propargylic amines, and aryl iodides.[4]

The Pd-catalyzed 4C-TCR was conducted as follows: the appropriate amounts of AcGlu-MeIm-PdNP catalyst, propargylic amine, aryl iodide, and base were added to the solvent, then the reaction solution was stirred under RT-80°C for suitable time. After completion of the reaction, the substrate conversions and product yields were determined via ^{1}H NMR analysis. The reactions were monitored by ^{1}H NMR, and the yields were calculated against 1,2,4,5-tetramethylbenzene.

a



b

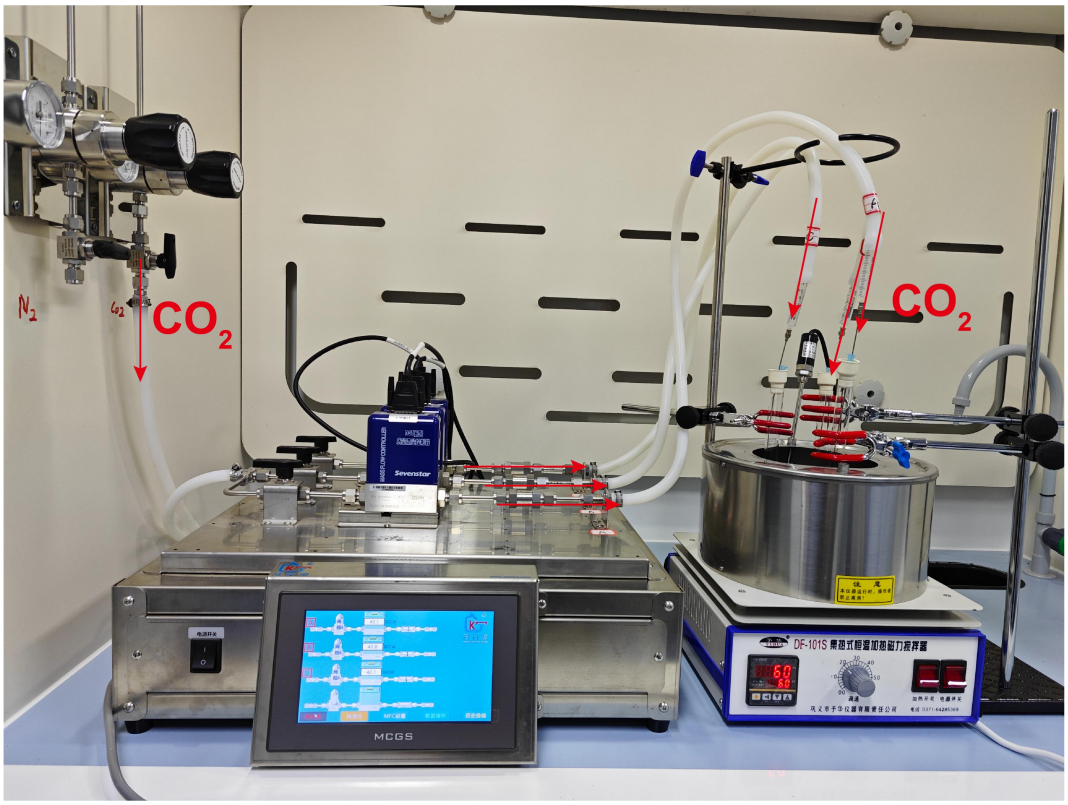


Fig. S17. a AcGlu-MeIm-PdNPs-catalyzed 4C-TCR of CO_2, propargylic amine, and aryl iodide. b The gas proportioner, model KT-C3ZS, produced by Zhengzhou Ketan Instrument Equipment Co., Ltd..

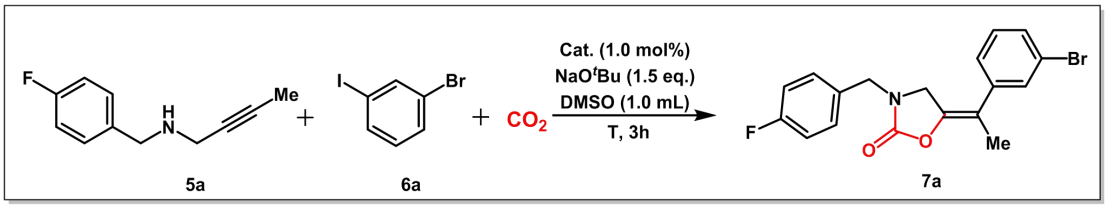
2.1.1 Initial optimization of AcGlu-MeIm-PdNP 4c-catalyzed reaction of CO_2, propargylic amine, and aryl iodide.

Table S3. Optimization of the bases and solvents for benchmark reaction of CO_2, 3-bromoiodobenzene, and *N*-(4-fluorobenzyl)but-2-yn-1-amine.[a]

Entry	Base	Solvent	Yield (%)[b]
1	NaOH	DMSO	68
2	NaOAc	DMSO	57
3	K_2CO_3	DMSO	80
4	$Na_3PO_4 \cdot 12H_2O$	DMSO	79
5	Na_2CO_3	DMSO	66
6	$NaHCO_3$	DMSO	70
7	**NaO^{t}Bu**	**DMSO**	**87**
8	Et_3N	DMSO	2
9	Base-free	DMSO	0
10	NaO^{t}Bu	MeOH	1
11	NaO^{t}Bu	Toluene	0
12	NaO^{t}Bu	MeCN	0
13	NaO^{t}Bu	THF	0
14	NaO^{t}Bu	EtOH	3
15	NaO^{t}Bu	Diox	0
16	NaO^{t}Bu	DMAc	15
17	NaO^{t}Bu	NMP	7
18	NaO^{t}Bu	DEF	0
19	NaO^{t}Bu	DMF	0

[a]Reaction conditions: catalyst (PdNP **4c**, 1.0 mol%, 0.69 mg), 3-bromoiodobenzene (0.2 mmol), *N*-(4-fluorobenzyl)but-2-yn-1-amine (0.1 mmol), solvent (1.0 mL), and base (0.15 mmol) were placed in a Schlenk tube connected to a bottle of CO_2 through a gas proportioner with 40 sccm flow rate, and then stirred at 60^{o}C for 3.0 h. [b]Yields were determined by ^{1}H NMR. (DEF = N,N-Diethylformamide).

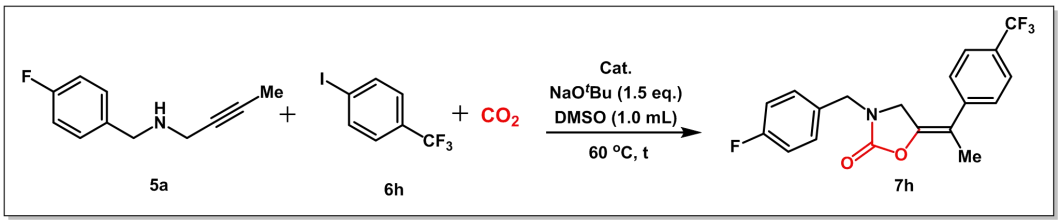
Table S4. Optimization of the react temperatures for benchmark reaction of CO_2, *N*-(4-fluorobenzyl)but-2-yn-1-amine, and 3-bromoiodobenzene.[a]



Entry	Catalyst	Temperature (℃)	Yield (%)[b]
1	**4c**	80	81
2	**4c**	60	87
3	**4c**	40	90
4[c]	**4c**	25	25
5	**3c**	80	83
6	**3c**	**60**	**88**
7	**3c**	30	90
8	**3c**	25	27

[a]Reaction conditions: AcGlu-MeIm-PdNP (1.0 mol%, **3c,** 0.59 mg, **4c,** 0.69 mg), 3-bromoiodobenzene (0.1 mmol), *N*-(4-fluorobenzyl)but-2-yn-1-amine (0.1 mmol), and NaO^{t}Bu (0.15 mmol) were placed in DMSO (1.0 mL) using a Schlenk tube directly connected to a bottle of CO_2 through a gas proportioner with 40 sccm flow rate and then stirred for 3.0 h. [b]Yields were determined by ^{1}H NMR.

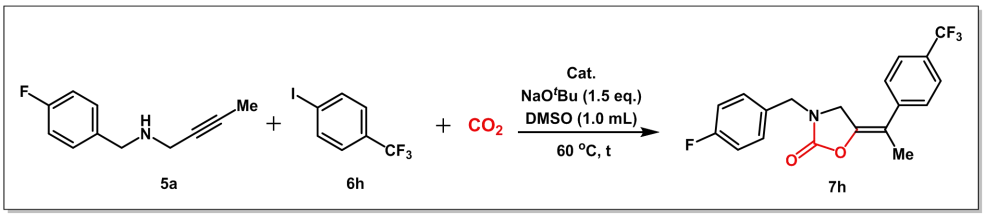
Table S5. Optimization of the AcGlu-MeIm-PdNPs catalyst **1c**–**4c** for benchmark cyclization of CO_2, 3-bromoiodobenzene, and propargylic amine.[a]



Entry	Catalyst (mol%, mg)	Yield (%)[b]
1	**1c** (1.0, 0.51)	75
2	**2c** (1.0, 0.55)	78
3	**3c (1.0, 0.59)**	**88**
4	**4c** (1.0, 0.69)	87
7	**4c** (0.5, 0.35)	17
8	**4c** (0.3, 0.21)	11
9	**4c** (0, 0)	0
10	**3b** (1.0, 0.59)	55
11	**4b** (1.0, 0.69)	50
12[c]	**3c (1.0, 0.59)**	**88**
13[c]	**4c** (1.0, 0.69)	87

[a]Reaction conditions: *N*-(4-fluorobenzyl)but-2-yn-1-amine (0.2 mmol), 3-bromoiodobenzene (0.4 mmol), NaO^{t}Bu (0.3 mmol), DMSO (1.0 mL) were placed in a Schlenk tube directly connected to a bottle of simulated flue gas through a gas proportioner with 40 sccm flow rate then stirred at 60^{o}C for 3.0 h. [b]Yields were determined by ^{1}H NMR. [c]Reaction were placed in a Schlenk tube directly connected to a bottle of simulated flue gas (CO_2/N_2, Vol/Vol = 15:85).

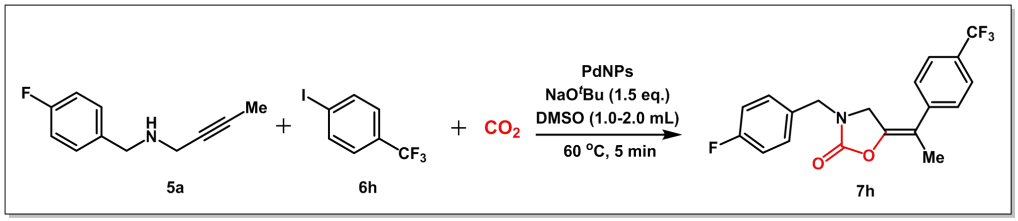
Table S6. Optimization of times and the amount of PdNP **3c** for benchmark reaction of CO_2, 4-trifluoromethyl-iodobenzene, and *N*-(4-fluorobenzyl)but-2-yn-1-amine.[a]



Entry	Catalyst (mol%, mg)	T (℃)/t (min)	Yield (%)[b]
1	**3c** (1.0, 0.59)	60/10	29
2	**3c** (2.0, 1.18)	60/5	67
3	**3c** (2.0, 1.18)	60/10	77
4	**3c (2.0, 1.18)**	**60/20**	**100**
5	**3c** (3.0, 1.77)	60/5	67
6	**3c** (3.0, 1.77)	60/10	100
7	**3c** (5.0, 2.95)	60/10	100

[a]Reaction conditions: *N*-(4-fluorobenzyl)but-2-yn-1-amine (0.1 mmol), 4-trifluoromethyl-iodobenzene (0.2 mmol), NaO^{t}Bu (0.15 mmol), the different amount of PdNP **3c**, and DMSO (1.0 mL) were placed in a Schlenk tube directly connected to a bottle of CO_2 then stirred at 60°C. [b]Yields were determined by ^{1}H NMR.

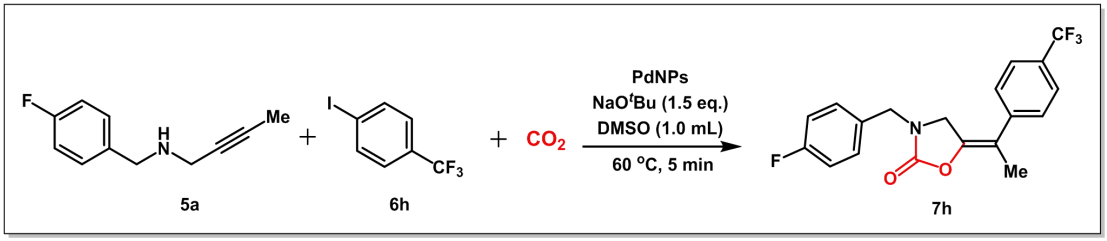
Table S7. Optimization of TOF for CO_2, 4-trifluoromethyl-iodobenzene, and *N*-(4-fluorobenzyl)but-2-yn-1-amine benchmark reaction.[a]



Entry	Catalyst (2.0 mol%)	Solvent (mL)	Yield (%)[b]	TOF (h^{-1})
1	**3c**	DMSO (1.0)	67	402
2	**3c**	DMSO (1.5)	93	561
3	**3c**	**DMSO (2.0)**	**100**	**600**
4	**3c**	DMSO (2.5)	96	576

[a]Reaction conditions: *N*-(4-fluorobenzyl)but-2-yn-1-amine (0.1 mmol), 4-trifluoromethyl-iodobenzene (0.2 mmol), NaO^{t}Bu (0.15 mmol), AcGlu-MeIm-PdNP **3c** (2.0 mol%, 1.18 mg), different volumes of DMSO were placed in a Schlenk tube directly connected to a bottle of CO_2 then stirred at 60°C for 5 min. [b]Yields were determined by ^{1}H NMR.

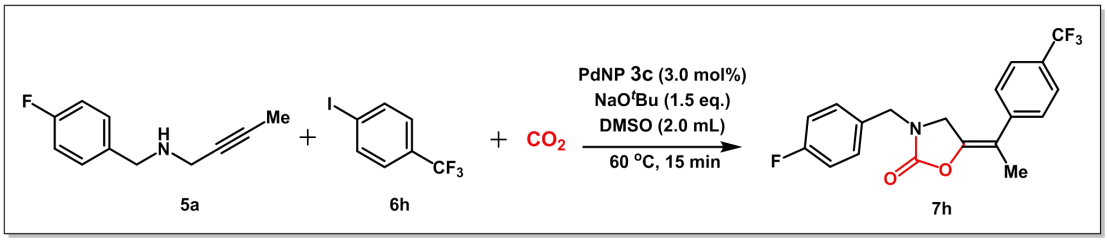
Table S8. Comparison of the catalytic activities of different catalysts for benchmark reaction of CO_2, 4-fluoromethyl-iodobenzene, and *N*-(4-fluorobenzyl)but-2-yn-1-amine.[a]



Entry	Catalyst (2.0 mol%)	m (mg)	t (min)	Yield (%)[b]	TOF (h^{-1})[b]
1	$Pd(OAc)_2$	0.45	180	85	14
2	Na_2PdCl_4	0.61	180	78	13
3	$Pd(PPh_3)_4$	2.31	180	86	14
4	$PdCl_2$	0.35	180	84	14
5	$PdCl_2$(dppf)	1.06	180	47	8
6	Pd/C (10 wt%)	0.21	180	33	3
7	**PdNP 3c**	**1.18**	**5**	**100**	**600**

[a]Reaction conditions: *N*-(4-fluorobenzyl)but-2-yn-1-amine (0.1 mmol), 4-fluoromethyl-iodobenzene (0.2 mmol), NaO^{t}Bu (0.15 mmol), Pd catalyst (2.0 mol%), and DMSO (2.0 mL) were placed in a Schlenk tube directly connected to a bottle of CO_2 then stirred at 60 °C. [b]Yields and TOFs were determined by ^{1}H NMR.

Table S9. Catalytic cycle performance of PdNP **3c** for benchmark reaction of CO_2, 4-trifluoromethyl-iodobenzene, and *N*-(4-fluorobenzyl)but-2-yn-1-amine.[a]



Catalytic cycle	Yield (%)[b]	Conversion (%)[b]
1	100	100
2	99	100
3	99	99
4	99	99
5	99	99
6	99	99
7	95	96

[a]Reaction conditions: *N*-(4-fluorobenzyl)but-2-yn-1-amine (0.1 mmol), 4-trifluoromethyl-iodobenzene (0.2 mmol), NaO^{t}Bu (0.15 mmol), PdNP **3c** (3.0 mol% 1.77 mg), DMSO (2.0 mL) were placed in a Schlenk tube directly connected to a bottle of CO_2 then stirred at 60^{o}C for 15 min. [b]Conversions and yields were determined by ^{1}H NMR.

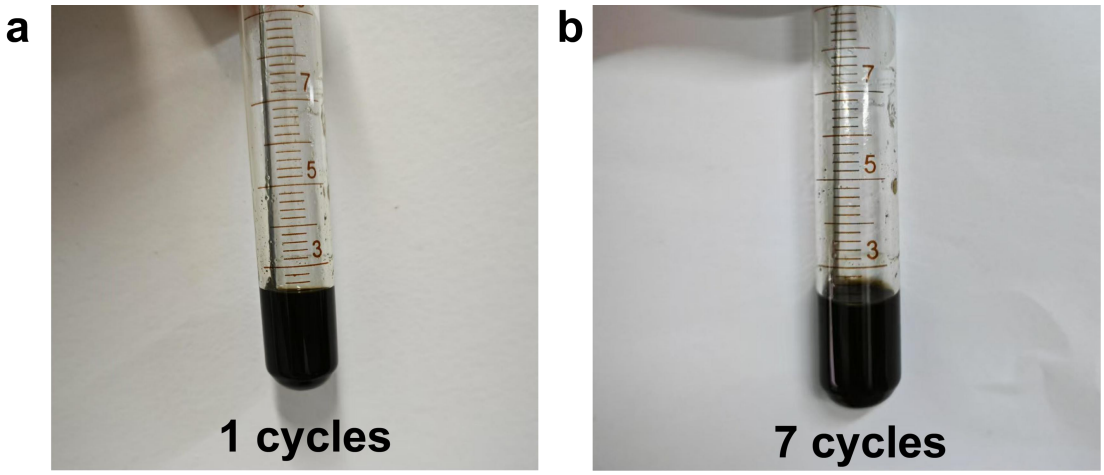


Fig. S18. Photos of catalytic system. (a) The image of catalyst system after 1 cycle. (b) The image of catalyst system after 7 cycles.

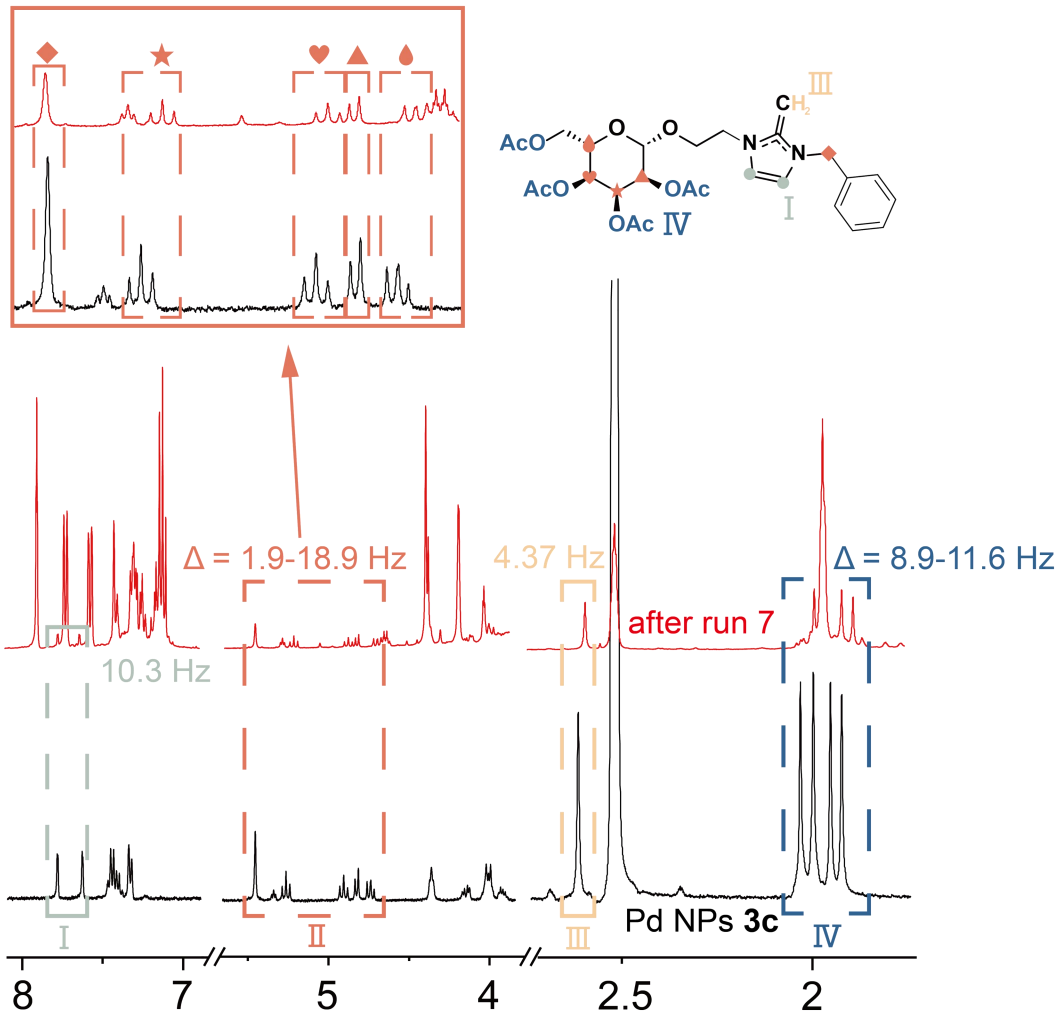


Fig. S19. Comparative ^{1}H NMR of fresh and recycled catalyst after 7 cycles.

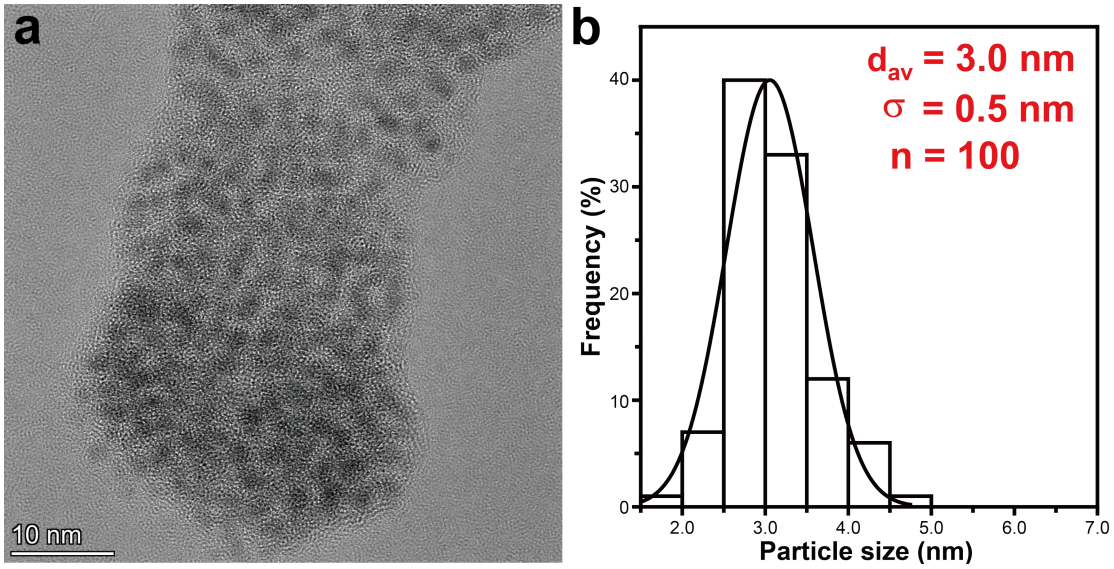


Fig. S20. (a) HR-TEM image of PdNP **3c** after 7 cycles. (b) Size distribution histogram of PdNP **3c** after 7 cycles.

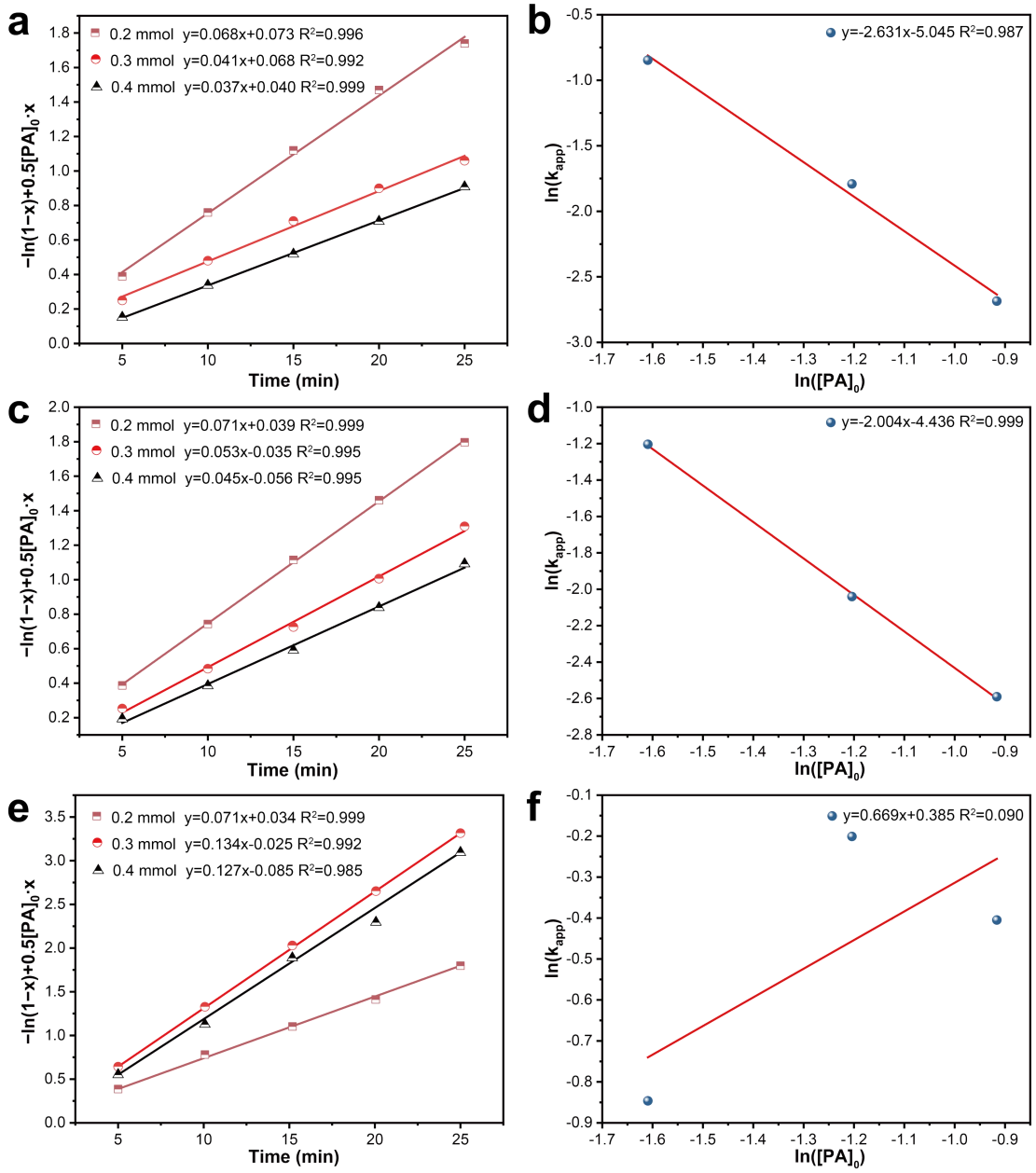
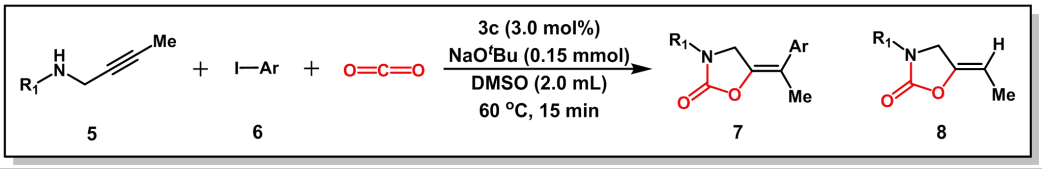


Fig. S21. (a) Pseudo-first order kinetic plots of $[PA]_0$=$[ArI]_0$=0.2, 0.3, 0.4 mmol. (b) Curve fitting of ln(k_{app}) against ln($[PA]_0$) at $[PA]_0$=$[ArI]_0$=0.2, 0.3, 0.4 mmol. (c) Pseudo-first order kinetic plots of $[ArI]_0$=0.2 and $[PA]_0$=0.2, 0.3, 0.4 mmol. (d) Curve fitting of ln(k_{app}) against ln$[PA]_0$ at $[ArI]_0$=0.2 and $[PA]_0$=0.2, 0.3, 0.4 mmol.(e) Pseudo-first order kinetic plots of $[PA]_0$=0.2 and $[ArI]_0$=0.2, 0.3, 0.4 mmol. (f) curve fitting of ln(k_{app}) against ln($[PA]_0$) at $[PA]_0$=0.2 and $[ArI]_0$=0.2, 0.3, 0.4 mmol.

Table S10. The 4C-TCR scope of simulated flue gas, propargylic amines, and aryl iodides.[a]



Entry	Conversion of **5** (%)[b]	Yield (%)[b]	
		7 (%)[b]	**8** (%)[b]
5a	100	88	12
5b	100	91	9
5c	100	91	9
5d	100	83	17
5e	100	88	12
5f	100	92	8
5g	100	95	5
5h	100	100	0
5i	100	100	0
5j	100	97	3
5k	100	81	19
5l	100	81	19
5m	100	95	5
5n	100	89	11
5o	100	99	1
5p	100	100	0

[a]Reaction conditions: propargylic amine (0.1 mmol), aryl iodide (0.2 mmol), NaO^{t}Bu (0.15 mmol), PdNP **3c** (3.0 mol%, 1.77 mg), DMSO (2.0 mL) were placed in a schlenk tube directly connected to a bottle of CO_2 then stirred at 60°C for 15 min. [b]Conversions and yields were determined by ^{1}H NMR.

Table S11. Comparison of catalytic performances of PdNP **3c** with advanced catalysts reported to date in tri-components carboxylative cyclization.

Catalyst	**Dosage (mg)**	**Temp. (°C)**	**P. (bar)**	**t. (h)**	**Yield (%)**	**TOF (h^{-1})**	**Ref.**
PdNP **3c**	1.18	60	1.0	0.83	99	600	herein
PIP-NHO-Pd	0.5	50	1.0	1.0	84	117.7± 1.4	4
PIP-NHO-Pd	2.5	50	1.0	0.5	100	55.6 ± 0.0	4
[a] $Pd(PPh_3)_2Cl_2$	7.0	35	1.0	12	68	/	5
POP-1-Pd	30	RT	1.0	12	96	20	6
[a] $PdCl_2$(dppf)	36.5	40	1.0	22	95	/	7

[a] homogeneous catalyst.

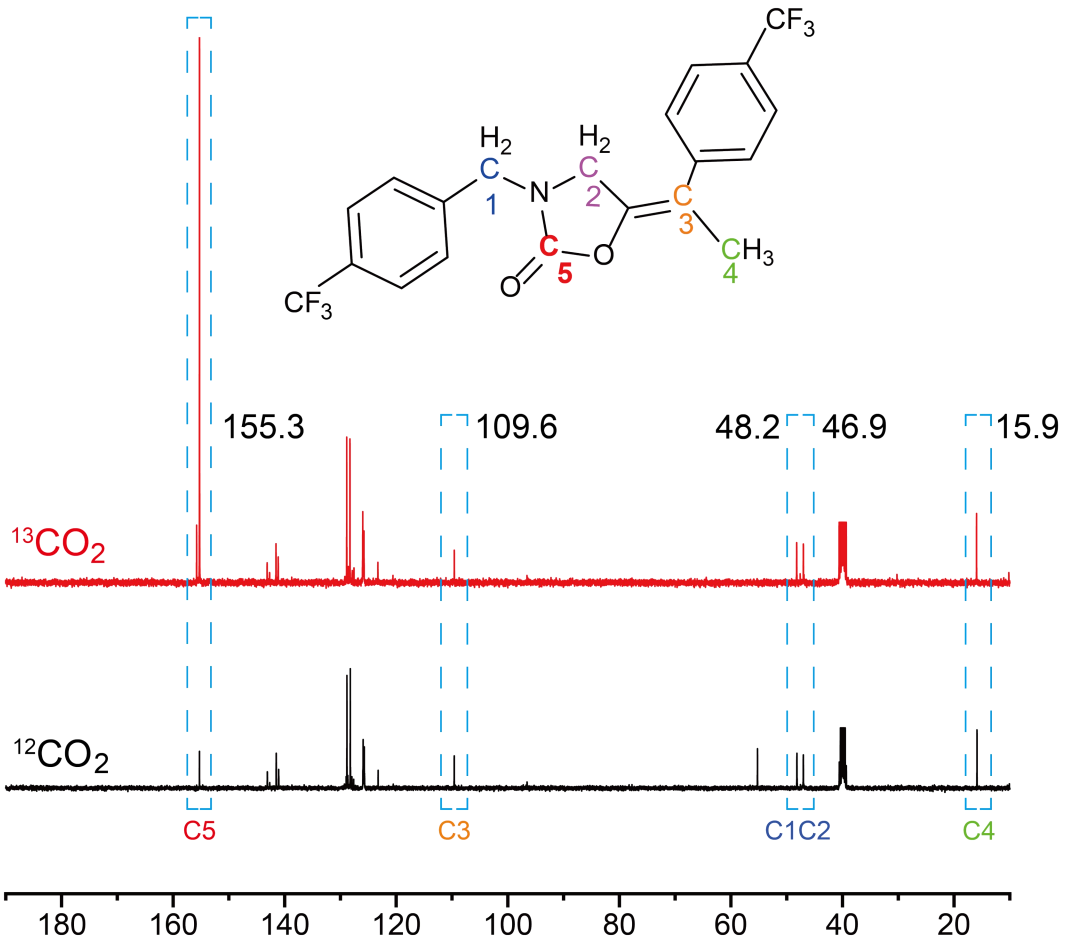


Fig. S22. ^{13}C NMR comparison spectra of ^{13}C-isotope-labeling experiments for **7a**.

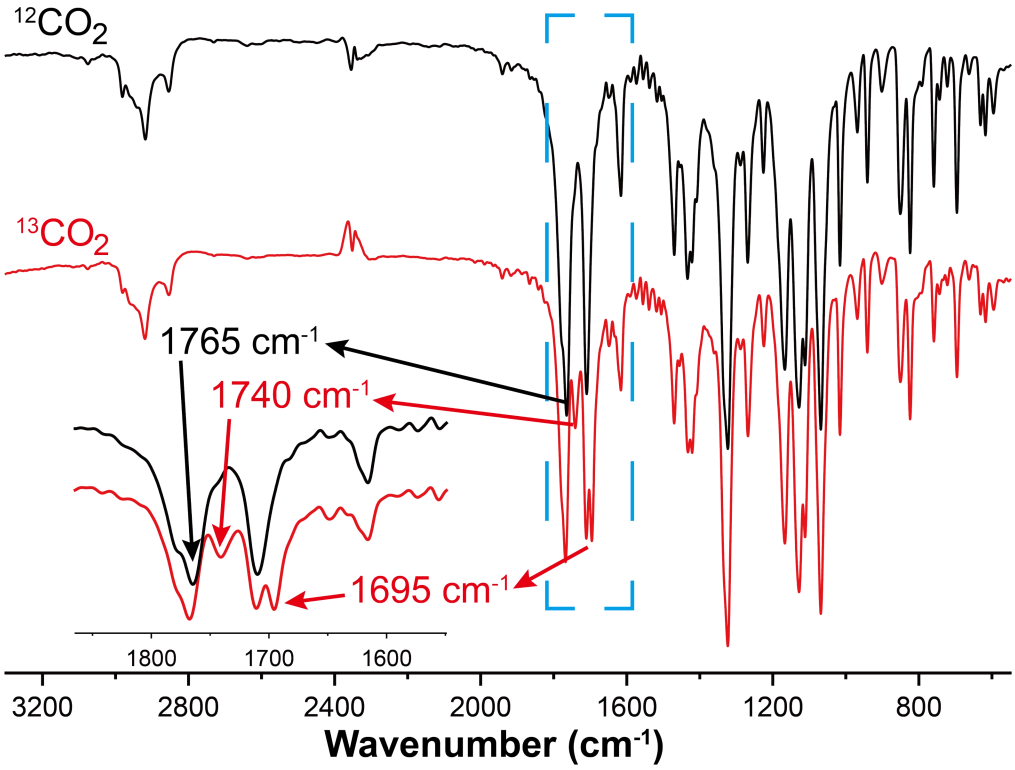


Fig. S23. FT-IR spectra of ^{13}C-isotope-labeling experiments for **7a**.

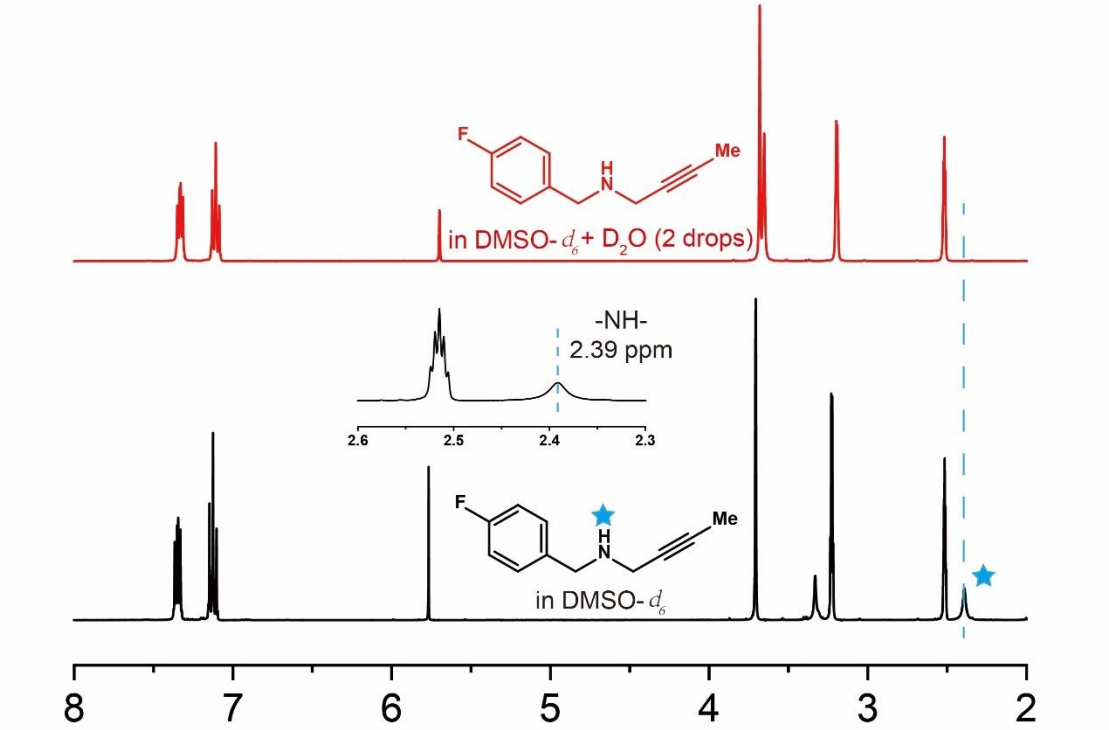


Fig. S24. Hydrogen–deuterium exchange experiment in D_2O/DMSO-d_6.

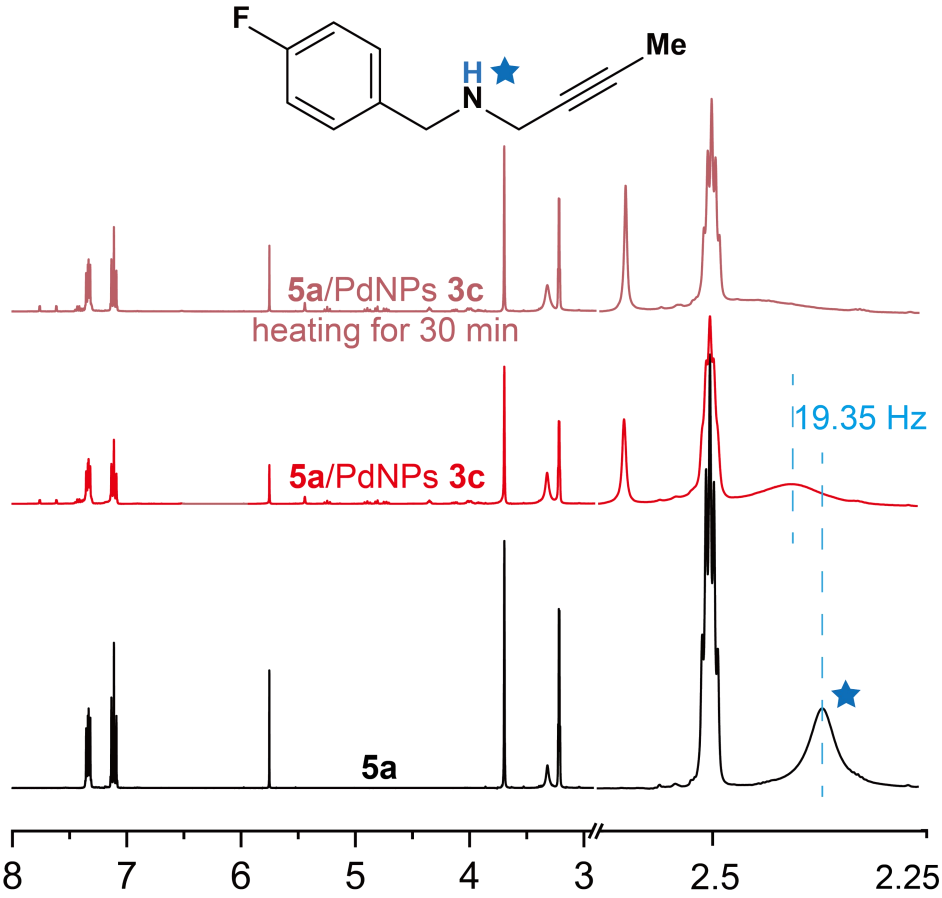


Fig. S25. Partially ^{1}H NMR spectra monitoring of substrate **5a**, **5a**/PdNP **3c**, and **5a**/PdNP **3c**/heating for 30 min at 60℃ in DMSO-d_6.

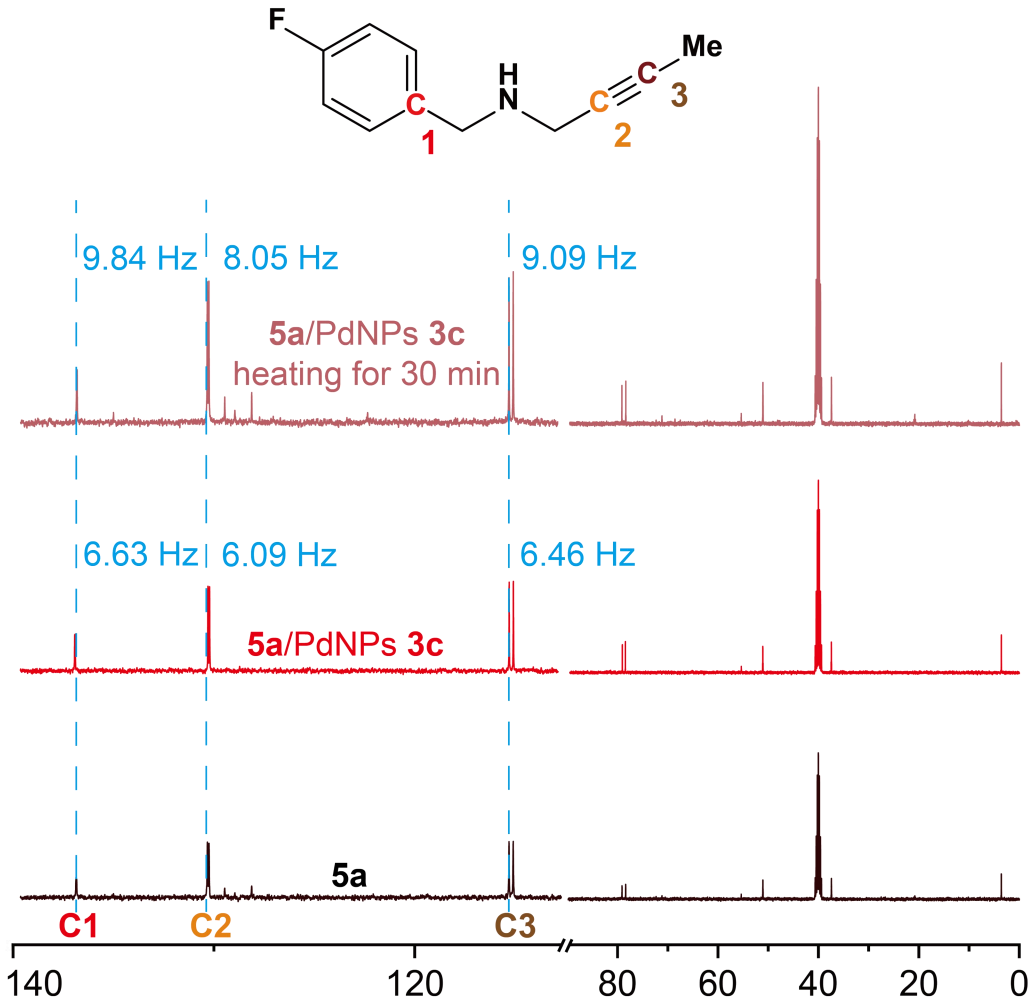


Fig. S26. Partially ^{13}C NMR spectra monitoring of substrate **5a**, **5a**/PdNP **3c**, and **5a**/PdNP **3c**/heating for 30 min at 60℃ in DMSO-d_6.

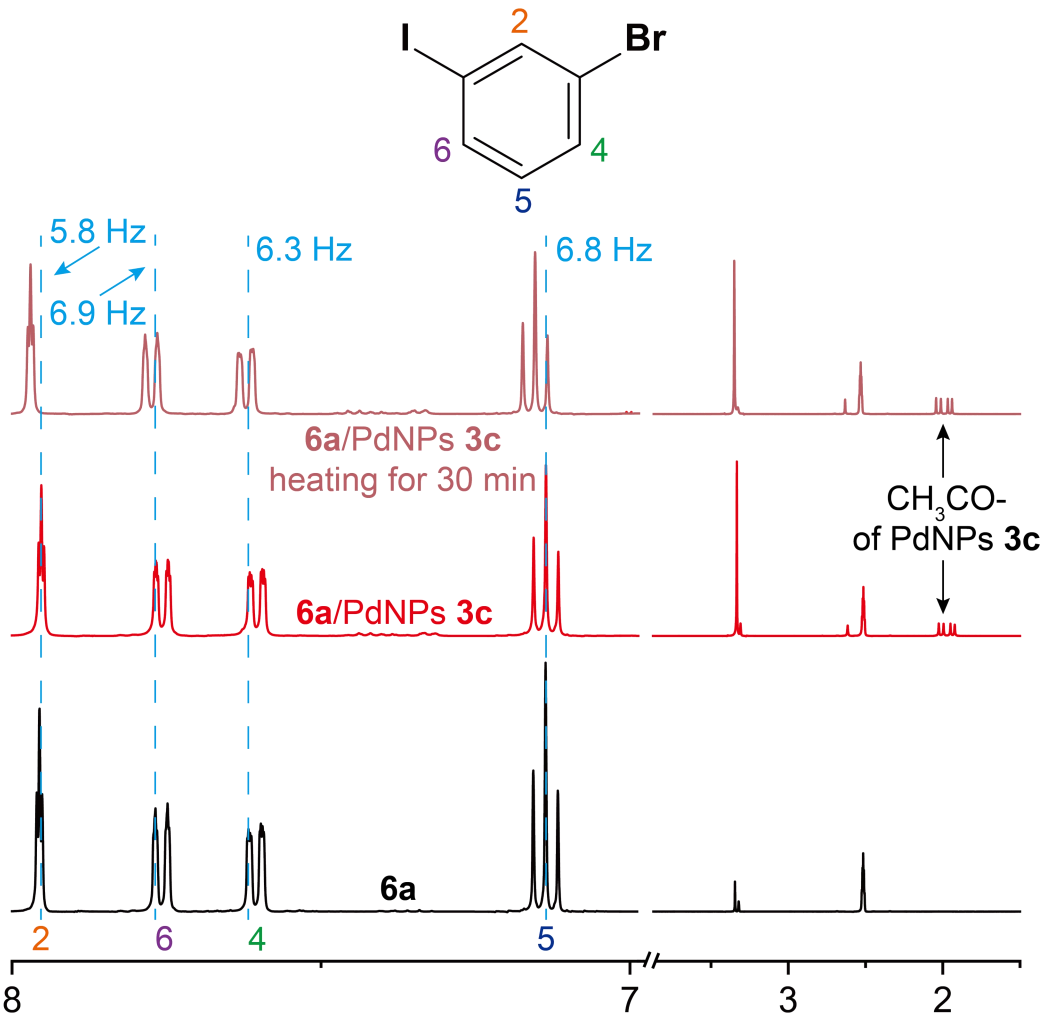


Fig. S27. Partially ^{1}H NMR spectra monitoring of substrate **6a**, **6a**/PdNP **3c**, and **6a**/PdNP **3c**/heating for 30 min at 60°C in DMSO-d_6.

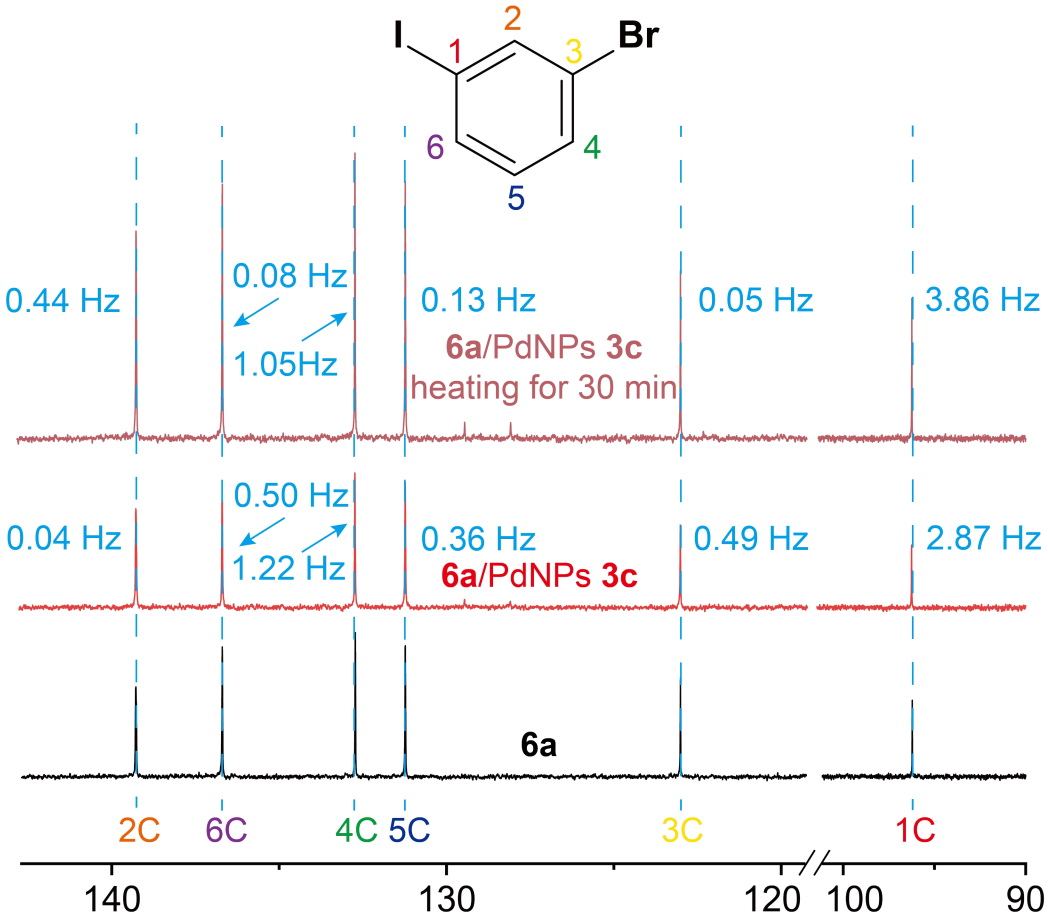


Fig. S28. Partially ^{13}C NMR spectra monitoring of substrate **6a**, **6a**/PdNP **3c**, and **6a**/PdNP **3c**/heating for 30 min at 60℃ in DMSO-d_6.

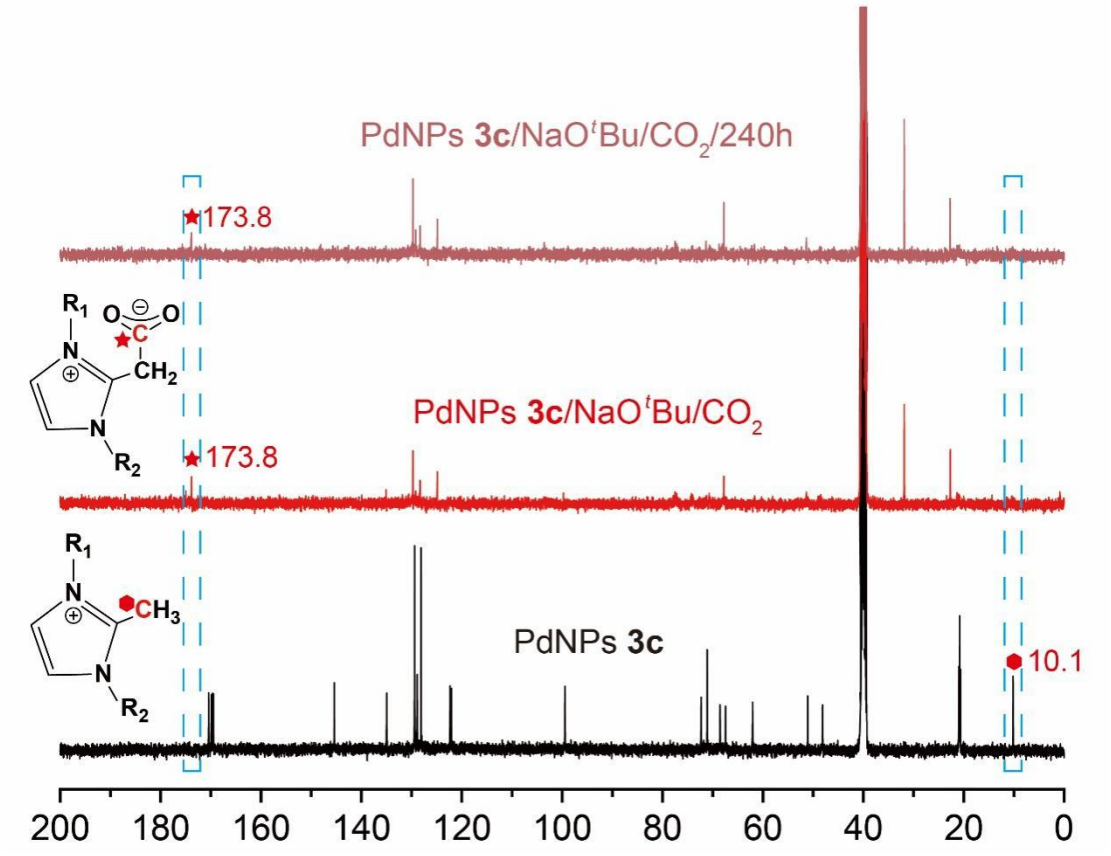


Fig. S29. ^{13}C NMR spectra of PdNP **3c**, PdNP **3c**/NaO^{t}Bu/CO_2, and PdNP **3c**/NaO^{t}Bu/CO_2 at RT.

2.1.2 Products of CO_2 conversion reaction (7a-7p)[4, 7]

(Z)-3-benzyl-5-(1-(3-bromophenyl)ethylidene)oxazolidin-2-one (7a)

92% yield, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 5H), 7.28 – 7.23 (m, 2H), 7.17 (t, J = 7.8 Hz, 1H), 7.08 – 7.03 (m, 1H), 4.46 (s, 2H), 4.02 (dd, J = 4.1, 2.0 Hz, 2H), 2.06 (t, J = 2.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 141.0, 139.3, 135.0, 130.3, 130.2, 128.9, 128.2, 128.1, 128.0, 125.9, 122.7, 111.1, 47.9, 47.2, 16.4 ppm. HR-MS m/z: $[M+H]^+$ calcd for $C_{18}H_{16}NO_2Br$, 357.03644; found, 357.03654.

(Z)-5-(1-(3-bromophenyl)ethylidene)-3-(4-fluorobenzyl)oxazolidin-2-one (7b)

88% yield, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.0 Hz, 1H), 7.29 (t, J = 1.7 Hz, 1H), 7.22 (ddd, J = 21.5, 10.5, 4.9 Hz, 3H), 7.10 – 6.98 (m, 3H), 4.42 (s, 2H), 4.01 (d, J = 2.1 Hz, 2H), 2.05 (t, J = 2.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 161.3, 155.6, 140.9, 139.1, 130.8, 130.8, 130.3, 130.2, 130.2, 129.9, 129.8, 125.9, 122.8, 115.9, 115.8, 111.3, 47.2, 47.2, 16.4 ppm. HR-MS m/z: $[M+Na]^+$ calcd for $C_{18}H_{15}NO_2FBr$, 398.01624; found, 398.01342.

(Z)-5-(1-(3-bromophenyl)ethylidene)-3-(4-(trifluoromethyl)benzyl)oxazolidin-2-one (7c)

91% yield, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 2H), 7.40 – 7.34 (m, 3H), 7.30 (t, J = 1.8 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 7.06 (ddd, J = 7.7, 1.6, 1.1 Hz, 1H), 4.51 (s, 2H), 4.04 (q, J = 2.1 Hz, 2H), 2.06 (t, J = 2.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 140.9, 139.1, 139.1, 138.9, 130.3, 130.3, 130.3, 128.3, 126.0, 126.0, 125.9, 125.9, 122.8, 111.6, 47.5, 47.4, 16.4 ppm. HR-MS m/z: $[M+H]^+$ calcd for $C_{19}H_{15}NO_2Br$, 425.02383; found, 425.02389.

(Z)-5-(1-(3-bromophenyl)ethylidene)-3-(4-methoxybenzyl)oxazolidin-2-one (7d)

91% yield, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 1.5 Hz, 1H), 7.17 (dd, J = 8.2, 6.0 Hz, 3H), 7.05 (d, J = 7.7 Hz, 1H), 6.86 (d, J = 8.6 Hz, 2H), 4.39 (s, 2H), 3.99 (d, J = 2.1 Hz, 2H), 3.79 (s, 3H), 2.05 (t, J = 2.0 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 155.5, 141., 139.4, 130.3, 130.2,

130.2, 129.5, 126.9, 125.9, 122.7, 114.3, 110.9, 55.3, 47.3, 47.1, 16.4 ppm. HR-MS m/z: $[M+Na]^+$ calcd for $C_{19}H_{18}NO_3Br$, 410.03623; found, 410.03705.

(Z)-5-(1-(3-bromophenyl)ethylidene)-3-butyloxazolidin-2-one (7e)

83% yield, pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 5H), 7.28 – 7.23 (m, 2H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.08 – 7.03 (m, 1H), 4.46 (s, 2H), 4.02 (dd, *J* = 4.1, 2.0 Hz, 2H), 2.06 (t, *J* = 2.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 141.0, 139.3, 134.9, 130.3, 130.2, 128.9, 128.2, 128.1, 128.0, 125.9, 122.7, 111.1, 47.9, 47.2, 16.4 ppm. HR-MS m/z: $[M+H]^+$ calcd for $C_{15}H_{18}NO_2Br$, 324.05937; found, 324.05667.

(Z)-5-(1-(3-bromophenyl)ethylidene)-3-(2,6-difluorobenzyl)oxazolidin-2-one (7f)

88% yield, pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.38 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.26 (m, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 6.96 – 6.88 (m, 2H), 4.60 (s, 2H), 4.07 (d, *J* = 2.1 Hz, 2H), 2.04 (t, *J* = 2.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 162.8, 162.7, 160.3, 160.3, 154.8, 141.0, 139.1, 130.6, 130.5, 130.4, 130.3, 130.2, 130.2, 125.8, 122.8, 111.7, 111.7, 111.5, 111.5, 111.1, 110.8, 110.6, 110.4, 47.3, 35.3, 16.4 ppm. HR-MS m/z: $[M+Na]^+$ calcd for $C_{18}H_{14}NO_2F_2Br$, 416.00682; found, 416.00792.

(Z)-3-(4-fluorobenzyl)-5-(1-phenylethylidene)oxazolidin-2-one (7g)

31% yield, pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.34 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.22 (m, 3H), 7.19 – 7.14 (m, 2H), 7.03 (t, *J* = 8.6 Hz, 2H), 4.44 (s, 2H), 4.06 (d, *J* = 2.1 Hz, 2H), 2.10 (t, *J* = 2.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 163.6, 161.2, 155.7, 138.7, 138.3, 130.9, 130.9, 129.8, 129.7, 128.6, 127.1, 127.1, 115.8, 115.6, 112.3, 77.3, 77.0, 76.7, 47.2, 47.1, 16.3 ppm. HR-MS m/z: $[M+H]^+$ calcd for $C_{18}H_{16}NO_2F$, 298.12378; found, 298.12119.

(Z)-5-(1-(4-chlorophenyl)ethylidene)-3-(4-fluorobenzyl)oxazolidin-2-one (7h)

85% yield, pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.28 (d, *J* = 8.4 Hz, 2H), 7.23 (dd, *J* = 8.3, 5.4 Hz, 2H), 7.11 – 6.98 (m, 4H), 4.42 (s, 2H), 4.00 (d, *J* = 1.9 Hz, 2H), 2.06 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 163.8, 161.3, 155.6, 138.7, 137.2, 132.9, 130.8, 130.8, 129.9, 129.8, 128.9, 128.5, 115.9, 115.8, 111.4, 47.2, 47.2,

16.4 ppm. HR-MS m/z: $[M+H]^+$ calcd for $C_{18}H_{15}NO_2FCl$, 332.08481; found, 332.08346.

(Z)-3-(4-fluorobenzyl)-5-(1-(4-(trifluoromethyl)phenyl)ethylidene)oxazolidin-2-one (7i)

100% yield, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.1 Hz, 2H), 7.34 – 7.17 (m, 4H), 7.08 – 6.98 (m, 2H), 4.44 (s, 2H), 4.04 (dd, J = 4.1, 2.0 Hz, 2H), 2.10 (t, J = 2.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 161.3, 155.4, 142.6, 139.5, 130.7, 130.7, 129.9, 129.8, 129.3, 129.0, 127.5, 125.7, 125.6, 125.6, 125.6, 125.3, 122.6, 115.9, 115.8, 111.3, 47.2, 29.6, 16.21 ppm. HR-MS m/z: $[M]^+$ calcd for $C_{19}H_{15}NO_2F_4$, 365.10334; found, 365.10330.

(Z)-4-(1-(3-(4-fluorobenzyl)-2-oxooxazolidin-5-ylidene)ethyl)benzonitrile (7j)

100% yield, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.3 Hz, 2H), 7.25 (dd, J = 11.4, 5.1 Hz, 4H), 7.04 (t, J = 8.6 Hz, 2H), 4.44 (s, 2H), 4.04 (d, J = 2.0 Hz, 2H), 2.10 (t, J = 1.9 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 161.4, 155.2, 143.7, 140.2, 132.5, 130.6, 130.6, 129.9, 129.8, 127.8, 118.5, 116.1, 115.8, 111.1, 110.8, 47.3, 47.2, 16.0 ppm. HR-MS m/z: $[M+H]^+$ calcd for $C_{19}H_{15}N_2O_2F$, 323.11903; found, 323.11791.

(Z)-5-(1-(4-acetylphenyl)ethylidene)-3-(4-fluorobenzyl)oxazolidin-2-one (7k)

97% yield, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.4 Hz, 2H), 7.23 (dd, J = 8.3, 4.9 Hz, 4H), 7.01 (dd, J = 11.8, 5.4 Hz, 2H), 4.42 (s, 2H), 4.04 (d, J = 2.1 Hz, 2H), 2.57 (s, 3H), 2.10 (t, J = 2.0 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 163.8, 161.3, 155.4, 143.8, 139.6, 135.7, 130.7, 130.7, 129.9, 129.8, 128.7, 127.3, 116.0, 115.8, 111.7, 47.3, 47.2, 26.5, 16.1 ppm. HR-MS m/z: $[M+H]^+$ calcd for $C_{20}H_{18}NO_3F$, 340.13435; found, 340.13228.

(Z)-3-(4-fluorobenzyl)-5-(1-(9-oxo-9H-fluoren-3-yl)ethylidene)oxazolidin-2-one (7l)

37% yield, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.4 Hz, 1H), 7.52 – 7.41 (m, 4H), 7.34 – 7.27 (m, 2H), 7.26 – 7.21 (m, 2H), 7.02 (t, J = 8.6 Hz, 2H), 4.44 (s, 2H), 4.07 (d, J = 2.0 Hz, 2H), 2.10 (t, J = 2.0 Hz, 3H) ppm; ^{13}C NMR (101

MHz, $CDCl_3$) δ 193.6, 155.6, 144.0, 143.1, 139.9, 139.2, 134.9, 134.6, 134.2, 133.3, 130.8, 129.9, 129.8, 129.2, 124.5, 122.9, 120.6, 120.3, 116.0, 115.8, 111.7, 47.3, 47.3, 29.7, 16.3 ppm. HR-MS m/z: $[M]^+$ calcd for $C_{25}H_{18}NO_3F$, 399.12652; found, 399.12659.

(Z)-4-(1-(3-benzyl-2-oxooxazolidin-5-ylidene)ethyl)benzonitrile (7m)[7]

95% yield, pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.4 Hz, 2H), 7.39 – 7.29 (m, 3H), 7.28 – 7.23 (m, 4H), 4.47 (s, 2H), 4.07 – 4.04 (m, 2H), 2.10 (t, J = 2.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 143.7, 140.4, 134.8, 132.4, 128.9, 128.3, 128.1, 127.8, 118.5, 110.9, 110.7, 47.9, 47.4, 15.9 ppm. HR-MS m/z: $[M+H]^+$ calcd for $C_{19}H_{16}N_2O_2$, 304.12118; found, 304.12109.

(Z)-5-(1-(4-acetylphenyl)ethylidene)-3-benzyloxazolidin-2-one (7n)

89% yield, pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.37 – 7.30 (m, 3H), 7.27 – 7.22 (m, 4H), 4.47 (s, 2H), 4.07 (d, J = 2.1 Hz, 2H), 2.58 (s, 3H), 2.11 (t, J = 2.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 155.5, 143.8, 139.8, 135.7, 134.9, 128.9, 128.7, 128.2, 128.1, 127.3, 111.5, 47.9, 47.5, 26.5, 16.1 ppm. HR-MS m/z: $[M+H]^+$ calcd for $C_{20}H_{19}NO_3$, 321.13649; found, 321.13643.

(Z)-4-(1-(2-oxo-3-(4-(trifluoromethyl)benzyl)oxazolidin-5-ylidene)ethyl)benzonitrile (7o)

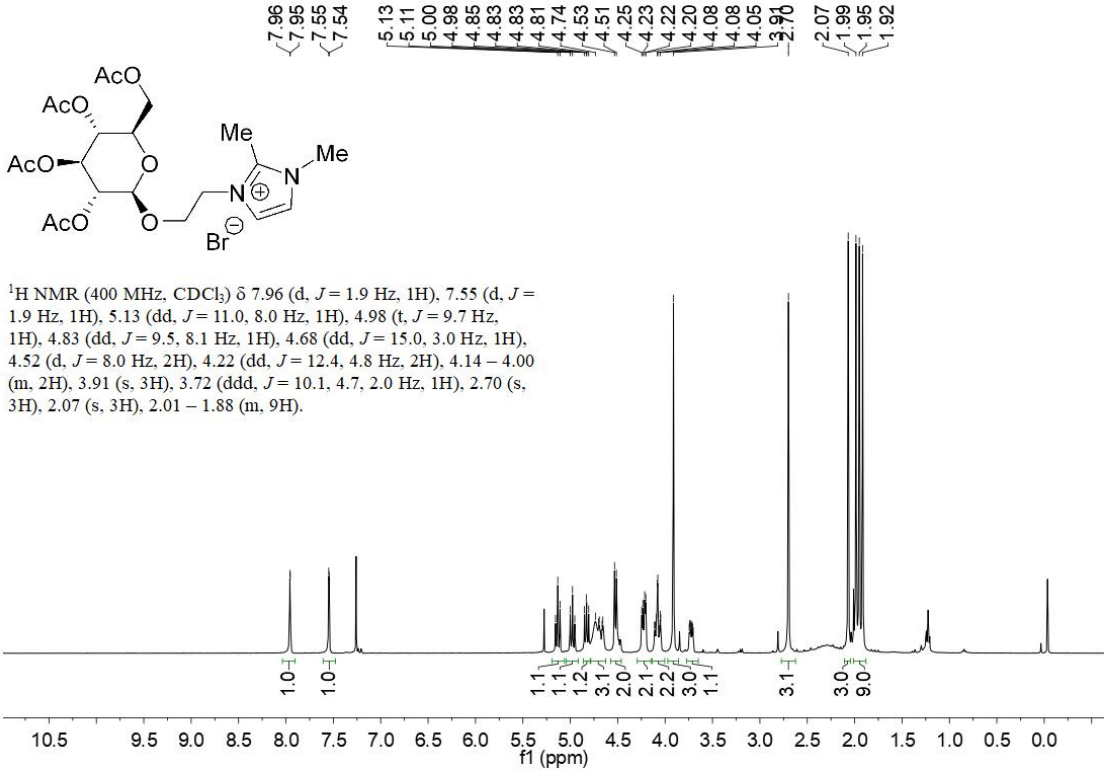
99% yield, pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.55 (m, 4H), 7.38 (d, J = 8.0 Hz, 2H), 7.28 – 7.24 (m, 2H), 4.52 (s, 2H), 4.07 (q, J = 1.9 Hz, 2H), 2.10 (t, J = 2.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 143.5, 139.9, 138.9, 138.9, 138.9, 138.9, 138.9, 138.9, 132.5, 128.3, 128.3, 128.3, 127.8, 127.8, 127.8, 126.0, 125.9, 125.9, 125.9, 125.1, 118.4, 111.4, 110.8, 47.5, 47.5, 16.0 ppm. HR-MS m/z: $[M+H]^+$ calcd for $C_{20}H_{15}N_2O_2F_3$, 372.10856; found, 372.10869.

(Z)-3-(2,6-difluorobenzyl)-5-(1-(3-(trifluoromethyl)phenyl)ethylidene)oxazolidin-2-one (7p)

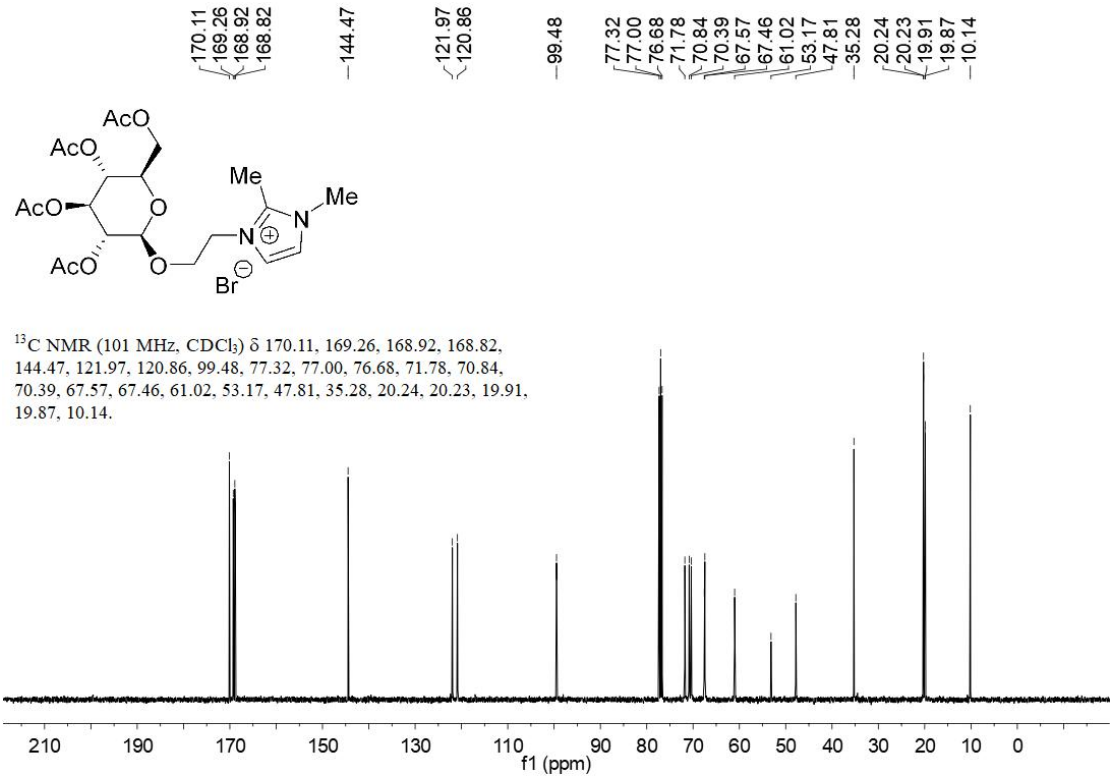
100% yield, pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.1 Hz, 2H), 7.35 – 7.26 (m, 3H), 6.96 – 6.88 (m, 2H), 4.61 (s, 2H), 4.10 (d, J = 2.0 Hz, 2H), 2.09 (t, J = 2.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 162.8, 160.4, 160.3,

154.8, 142.6, 139.5, 130.7, 130.6, 130.5, 129.3, 129.0, 127.5, 125.7, 125.7, 125.6, 125.6, 125.3, 122.6, 111.8, 111.7, 111.6, 111.5, 111.2, 110.8, 110.6, 110.4, 77.3, 77.0, 76.7, 47.3, 35.3, 16.3 ppm. HR-MS m/z: $[M+Na]^+$ calcd for $C_{19}H_{14}NO_2F_5$, 406.08369; found, 406.08442.

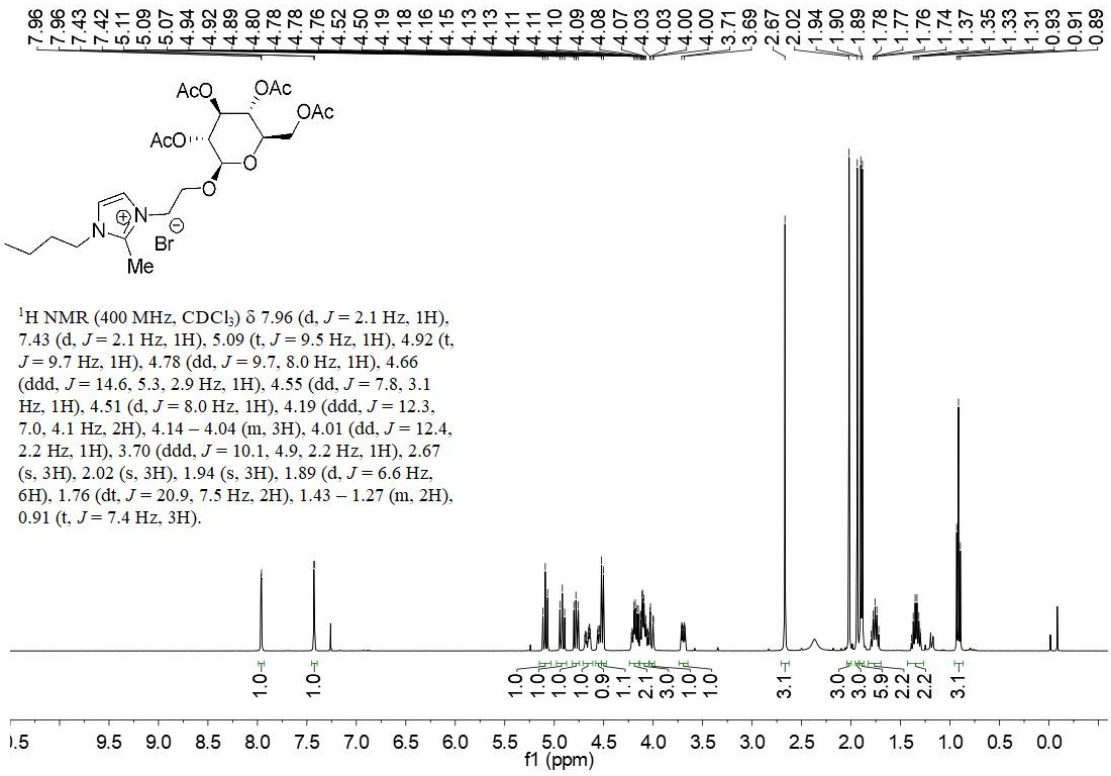
3. Selected Spectral



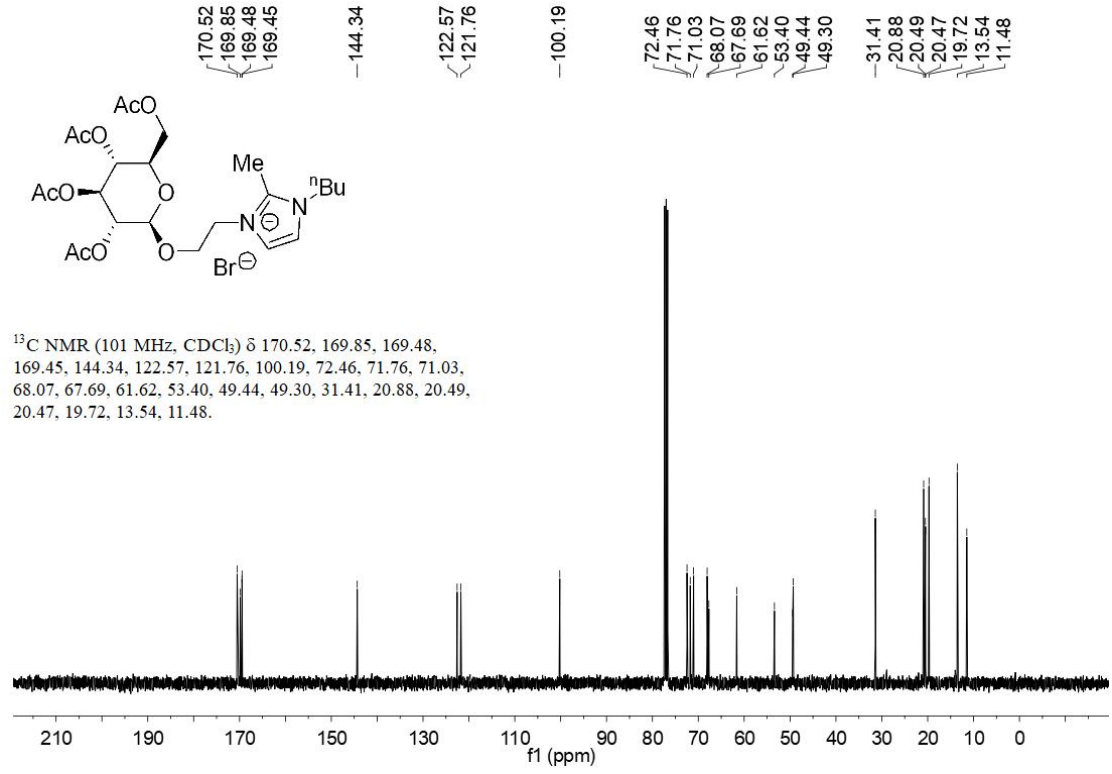
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 1.9 Hz, 1H), 7.55 (d, *J* = 1.9 Hz, 1H), 5.13 (dd, *J* = 11.0, 8.0 Hz, 1H), 4.98 (t, *J* = 9.7 Hz, 1H), 4.83 (dd, *J* = 9.5, 8.1 Hz, 1H), 4.68 (dd, *J* = 15.0, 3.0 Hz, 1H), 4.52 (d, *J* = 8.0 Hz, 2H), 4.22 (dd, *J* = 12.4, 4.8 Hz, 2H), 4.14 – 4.00 (m, 2H), 3.91 (s, 3H), 3.72 (ddd, *J* = 10.1, 4.7, 2.0 Hz, 1H), 2.70 (s, 3H), 2.07 (s, 3H), 2.01 – 1.88 (m, 9H).



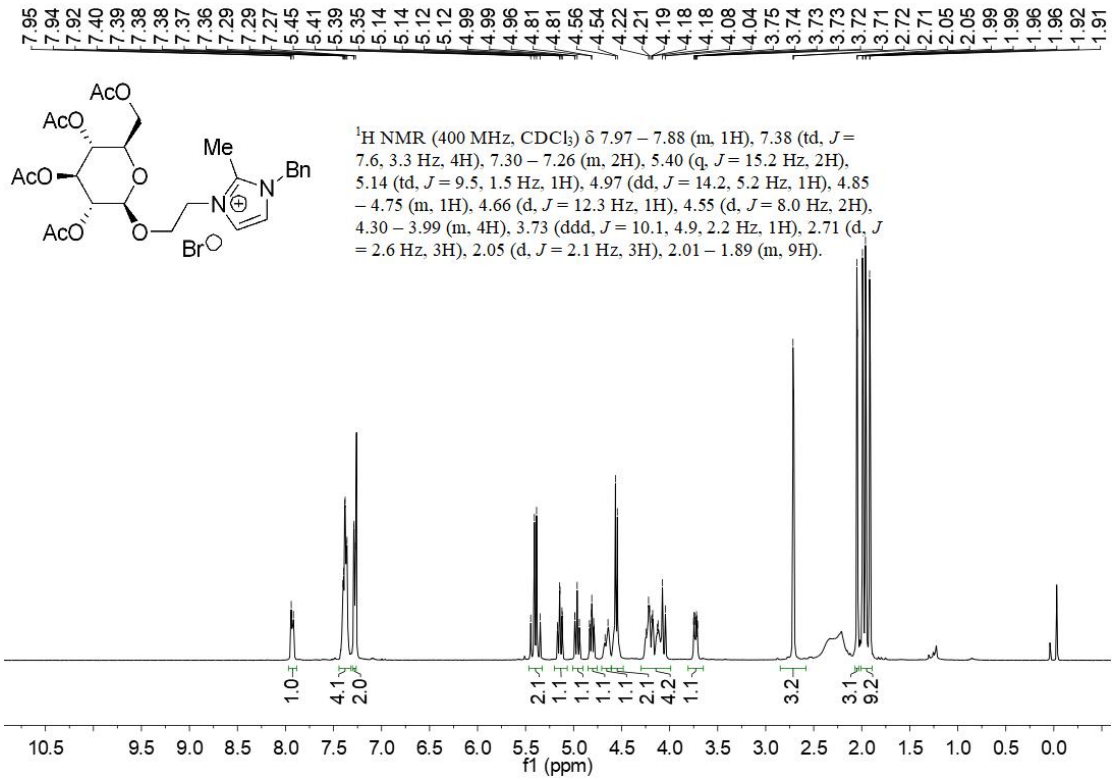
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.11, 169.26, 168.92, 168.82, 144.47, 121.97, 120.86, 99.48, 77.32, 77.00, 76.68, 71.78, 70.84, 70.39, 67.57, 67.46, 61.02, 53.17, 47.81, 35.28, 20.24, 20.23, 19.91, 19.87, 10.14.



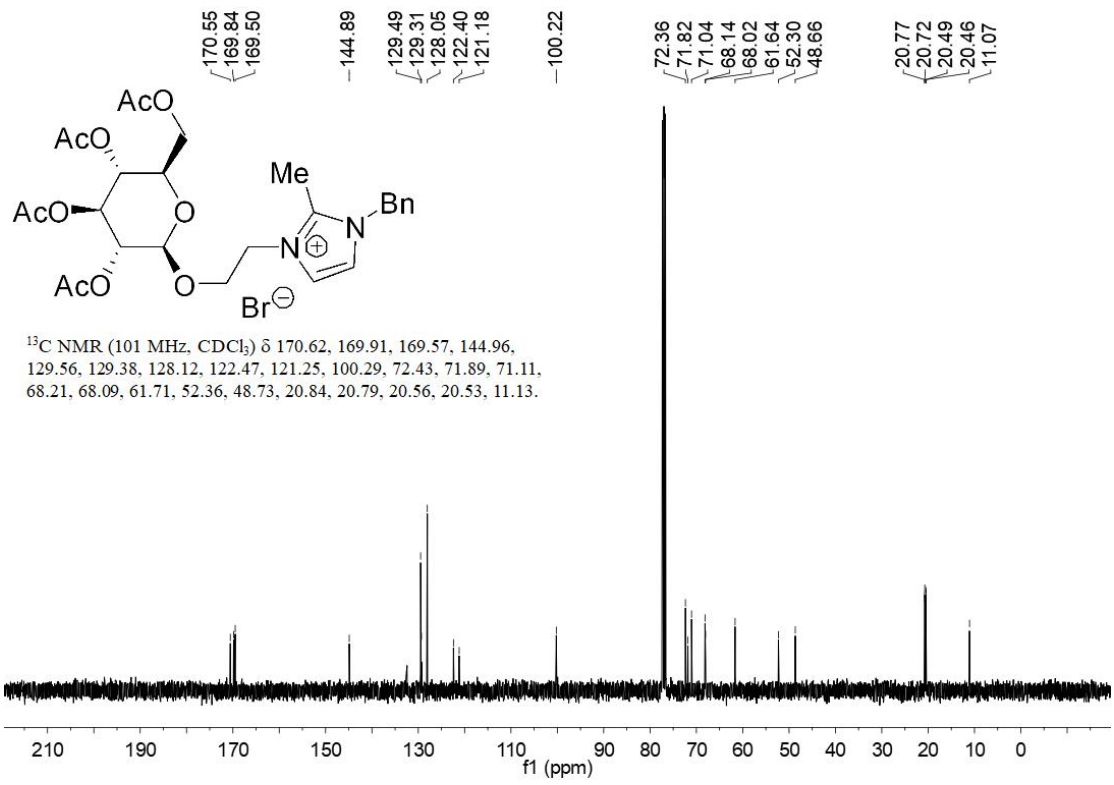
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.1 Hz, 1H), 7.43 (d, *J* = 2.1 Hz, 1H), 5.09 (t, *J* = 9.5 Hz, 1H), 4.92 (t, *J* = 9.7 Hz, 1H), 4.78 (dd, *J* = 9.7, 8.0 Hz, 1H), 4.66 (ddd, *J* = 14.6, 5.3, 2.9 Hz, 1H), 4.55 (dd, *J* = 7.8, 3.1 Hz, 1H), 4.51 (d, *J* = 8.0 Hz, 1H), 4.19 (ddd, *J* = 12.3, 7.0, 4.1 Hz, 2H), 4.14 – 4.04 (m, 3H), 4.01 (dd, *J* = 12.4, 2.2 Hz, 1H), 3.70 (ddd, *J* = 10.1, 4.9, 2.2 Hz, 1H), 2.67 (s, 3H), 2.02 (s, 3H), 1.94 (s, 3H), 1.89 (d, *J* = 6.6 Hz, 6H), 1.76 (dt, *J* = 20.9, 7.5 Hz, 2H), 1.43 – 1.27 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).



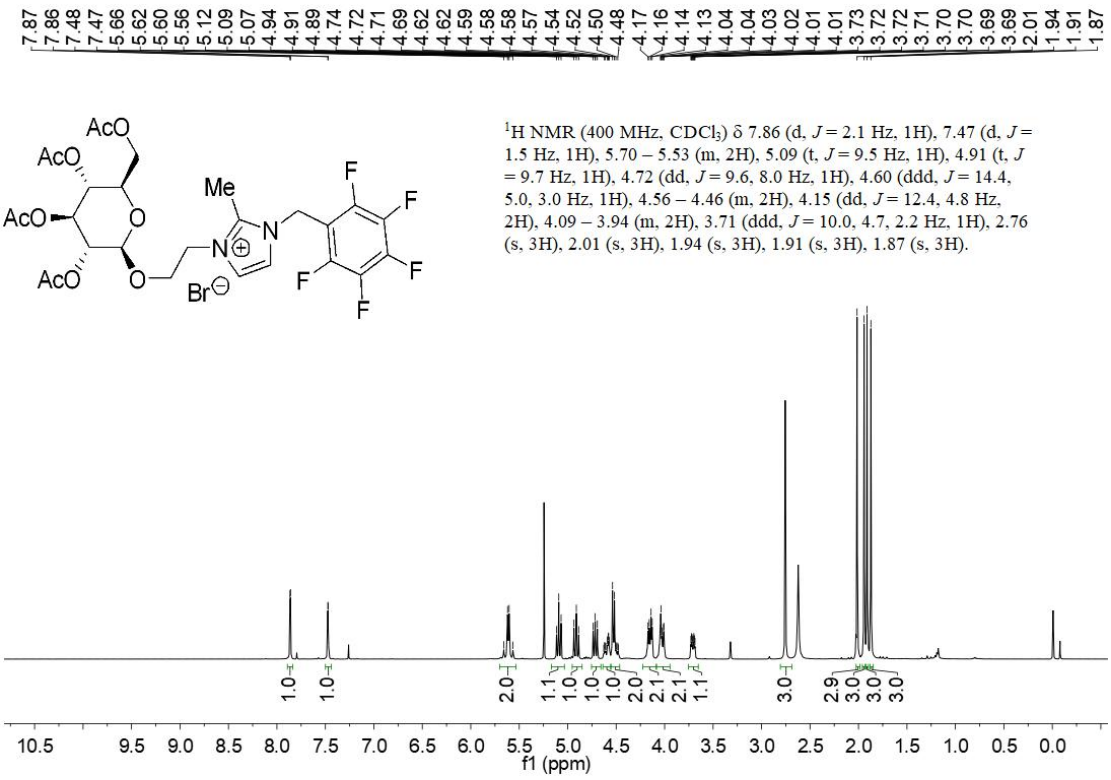
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.52, 169.85, 169.48, 169.45, 144.34, 122.57, 121.76, 100.19, 72.46, 71.76, 71.03, 68.07, 67.69, 61.62, 53.40, 49.44, 49.30, 31.41, 20.88, 20.49, 20.47, 19.72, 13.54, 11.48.



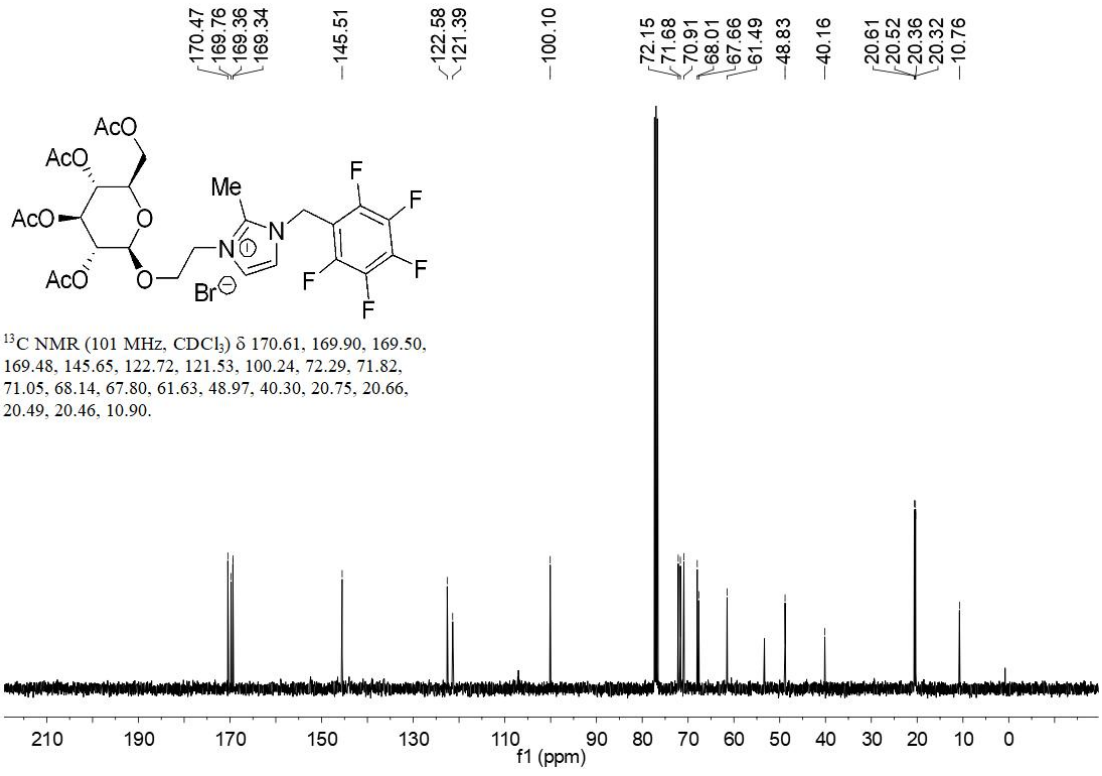
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.88 (m, 1H), 7.38 (td, *J* = 7.6, 3.3 Hz, 4H), 7.30 – 7.26 (m, 2H), 5.40 (q, *J* = 15.2 Hz, 2H), 5.14 (td, *J* = 9.5, 1.5 Hz, 1H), 4.97 (dd, *J* = 14.2, 5.2 Hz, 1H), 4.85 – 4.75 (m, 1H), 4.66 (d, *J* = 12.3 Hz, 1H), 4.55 (d, *J* = 8.0 Hz, 2H), 4.30 – 3.99 (m, 4H), 3.73 (ddd, *J* = 10.1, 4.9, 2.2 Hz, 1H), 2.71 (d, *J* = 2.6 Hz, 3H), 2.05 (d, *J* = 2.1 Hz, 3H), 2.01 – 1.89 (m, 9H).



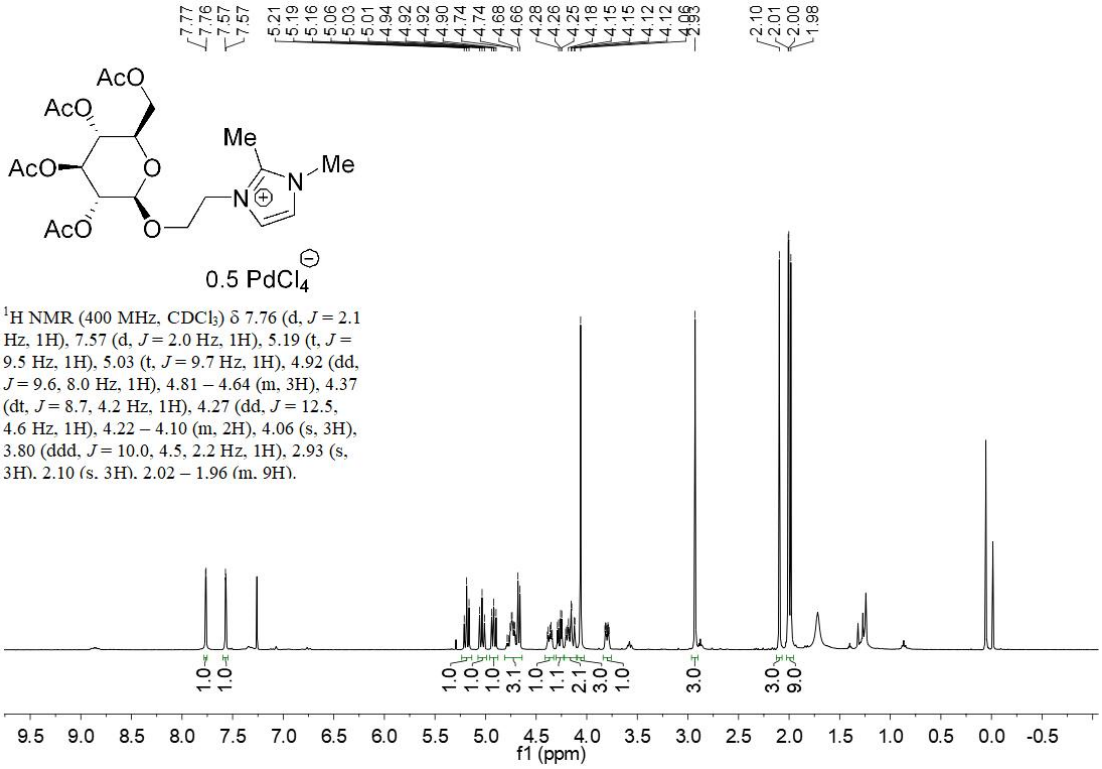
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.62, 169.91, 169.57, 144.96, 129.56, 129.38, 128.12, 122.47, 121.25, 100.29, 72.43, 71.89, 71.11, 68.21, 68.09, 61.71, 52.36, 48.73, 20.84, 20.79, 20.56, 20.53, 11.13.



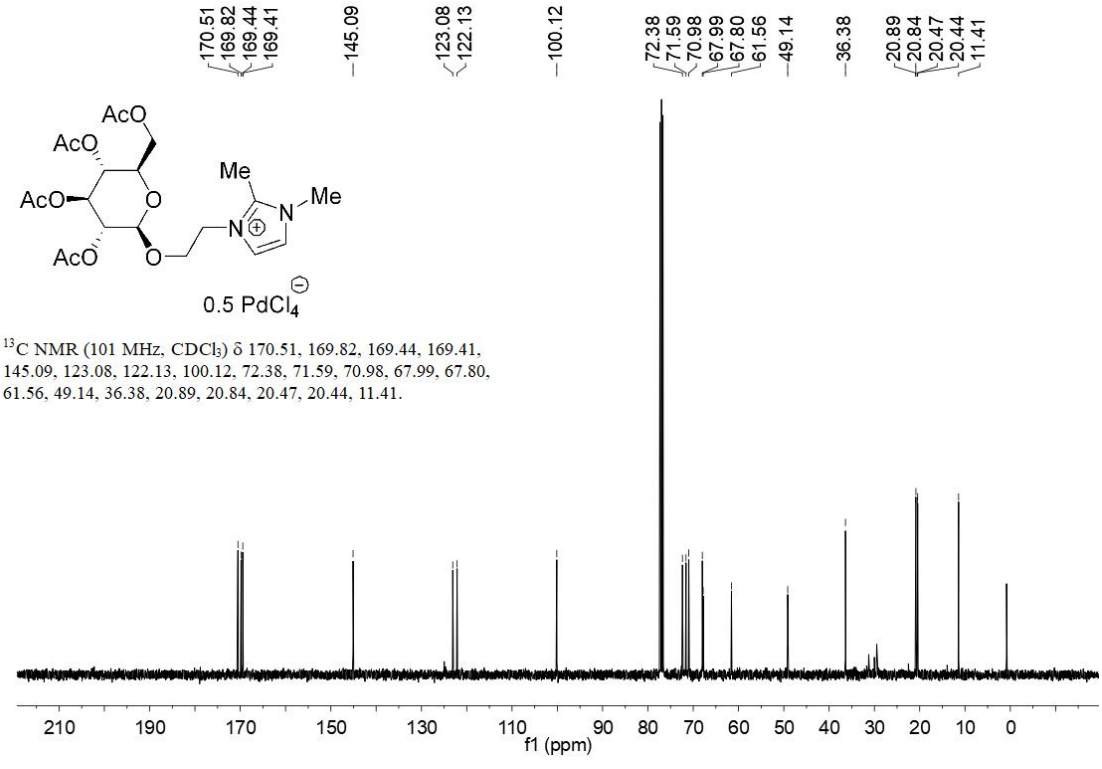
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 2.1 Hz, 1H), 7.47 (d, J = 1.5 Hz, 1H), 5.70 – 5.53 (m, 2H), 5.09 (t, J = 9.5 Hz, 1H), 4.91 (t, J = 9.7 Hz, 1H), 4.72 (dd, J = 9.6, 8.0 Hz, 1H), 4.60 (ddd, J = 14.4, 5.0, 3.0 Hz, 1H), 4.56 – 4.46 (m, 2H), 4.15 (dd, J = 12.4, 4.8 Hz, 2H), 4.09 – 3.94 (m, 2H), 3.71 (ddd, J = 10.0, 4.7, 2.2 Hz, 1H), 2.76 (s, 3H), 2.01 (s, 3H), 1.94 (s, 3H), 1.91 (s, 3H), 1.87 (s, 3H).



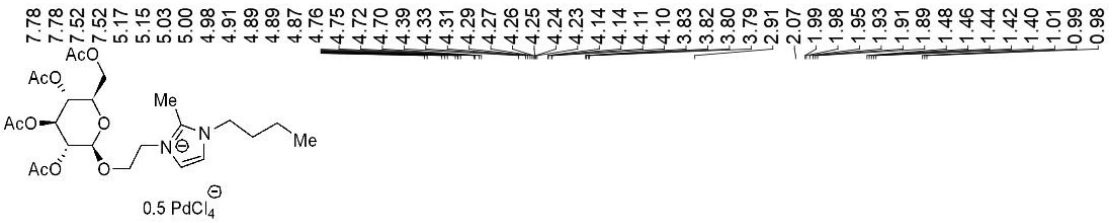
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.61, 169.90, 169.50, 169.48, 145.65, 122.72, 121.53, 100.24, 72.29, 71.82, 71.05, 68.14, 67.80, 61.63, 48.97, 40.30, 20.75, 20.66, 20.49, 20.46, 10.90.



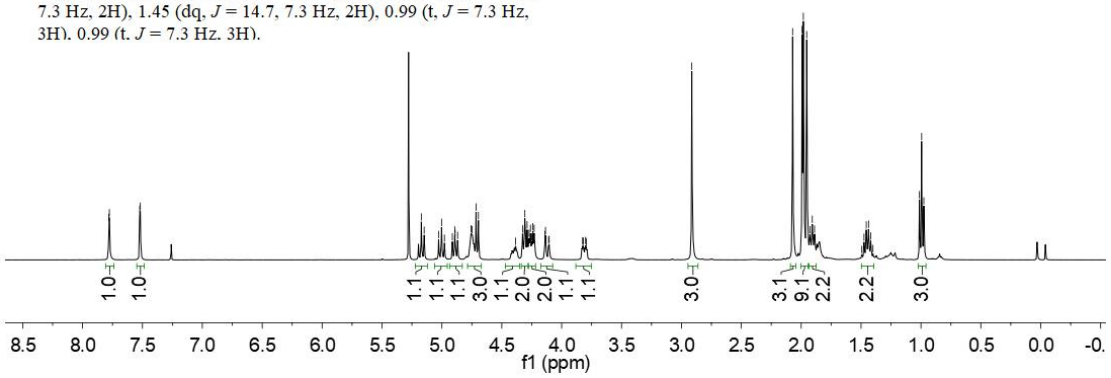
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 2.1 Hz, 1H), 7.57 (d, J = 2.0 Hz, 1H), 5.19 (t, J = 9.5 Hz, 1H), 5.03 (t, J = 9.7 Hz, 1H), 4.92 (dd, J = 9.6, 8.0 Hz, 1H), 4.81 – 4.64 (m, 3H), 4.37 (dt, J = 8.7, 4.2 Hz, 1H), 4.27 (dd, J = 12.5, 4.6 Hz, 1H), 4.22 – 4.10 (m, 2H), 4.06 (s, 3H), 3.80 (ddd, J = 10.0, 4.5, 2.2 Hz, 1H), 2.93 (s, 3H), 2.10 (s, 3H), 2.02 – 1.96 (m, 9H).

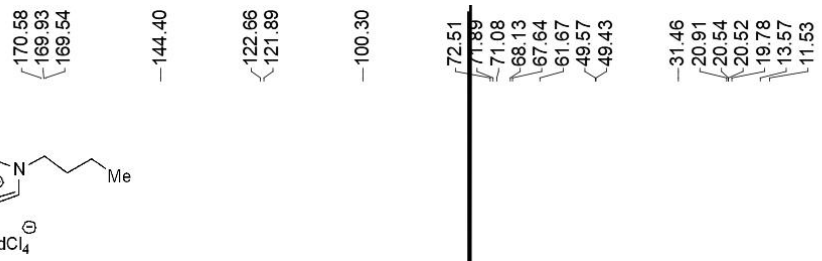


^{13}C NMR (101 MHz, $CDCl_3$) δ 170.51, 169.82, 169.44, 169.41, 145.09, 123.08, 122.13, 100.12, 72.38, 71.59, 70.98, 67.99, 67.80, 61.56, 49.14, 36.38, 20.89, 20.84, 20.47, 20.44, 11.41.

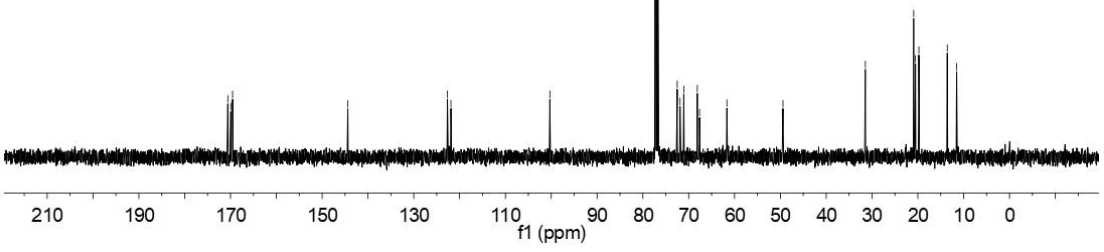


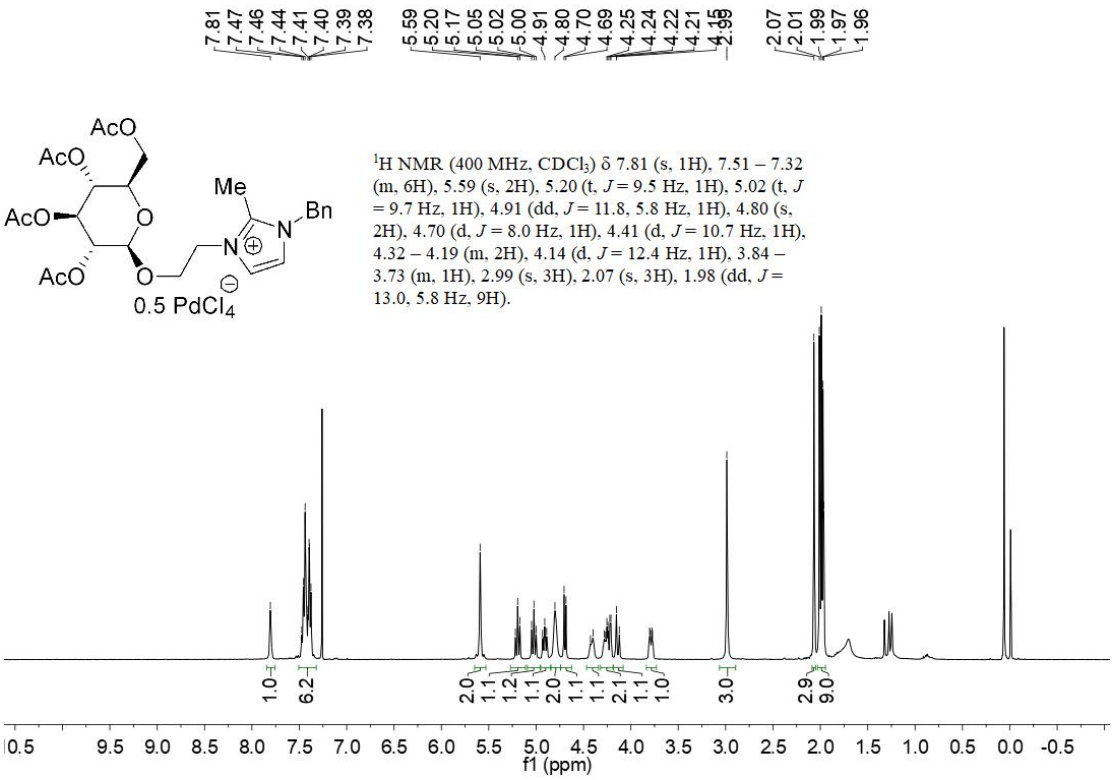
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 2.0 Hz, 1H), 7.52 (d, J = 2.0 Hz, 1H), 5.16 (d, J = 9.5 Hz, 1H), 5.00 (t, J = 9.7 Hz, 1H), 4.89 (dd, J = 9.5, 8.1 Hz, 1H), 4.73 (dd, J = 18.8, 5.8 Hz, 3H), 4.39 (s, 1H), 4.34 – 4.28 (m, 2H), 4.28 – 4.22 (m, 2H), 4.12 (dd, J = 12.4, 1.9 Hz, 1H), 3.81 (dd, J = 10.1, 2.3 Hz, 1H), 2.91 (s, 3H), 2.07 (s, 3H), 2.00 – 1.94 (m, 9H), 1.93 – 1.87 (m, 2H), 1.45 (dq, J = 14.7, 7.3 Hz, 2H), 1.45 (dq, J = 14.7, 7.3 Hz, 2H), 0.99 (t, J = 7.3 Hz, 3H), 0.99 (t, J = 7.3 Hz, 3H).



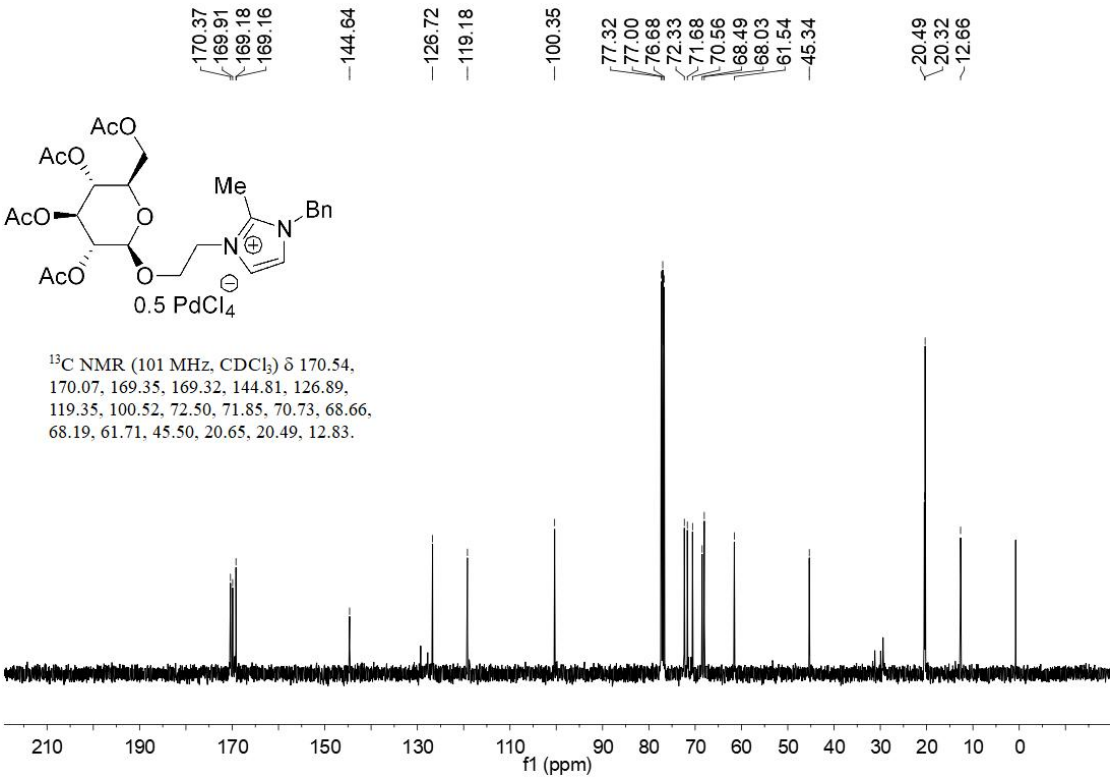


^{13}C NMR (101 MHz, $CDCl_3$) δ 170.58, 169.93, 169.54, 144.40, 122.66, 121.89, 100.30, 72.51, 71.89, 71.08, 68.13, 67.64, 61.67, 49.57, 49.43, 31.46, 20.91, 20.54, 20.52, 19.78, 13.57, 11.53.

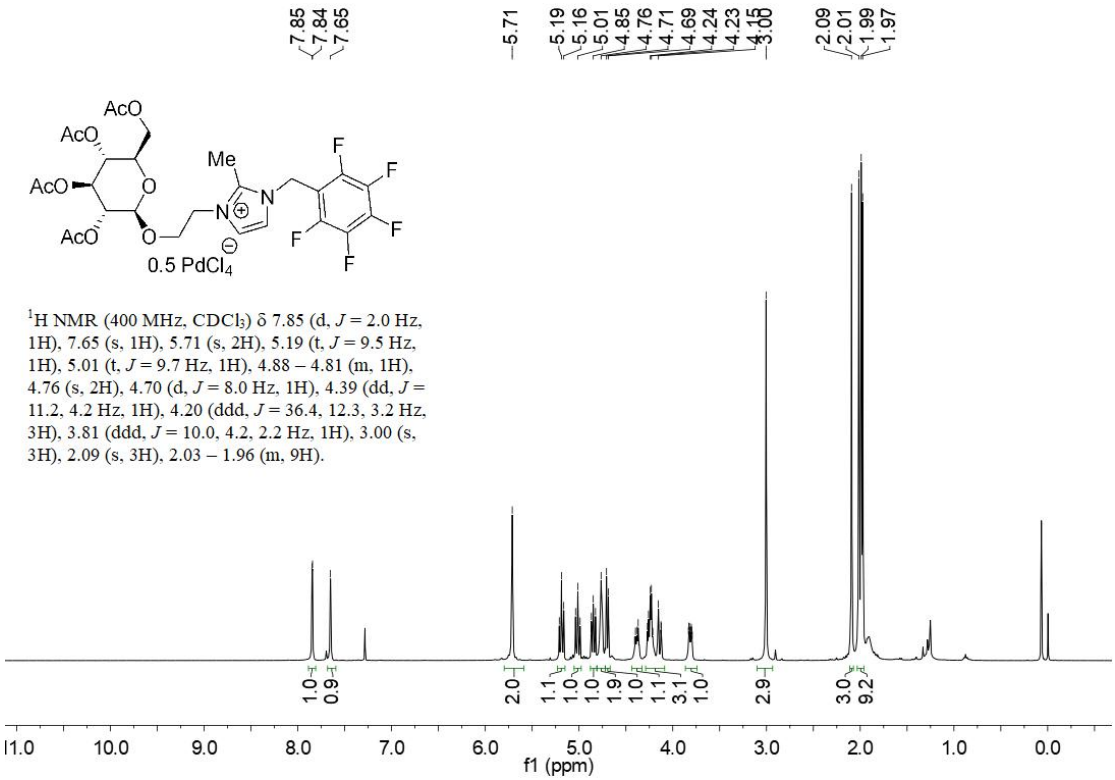




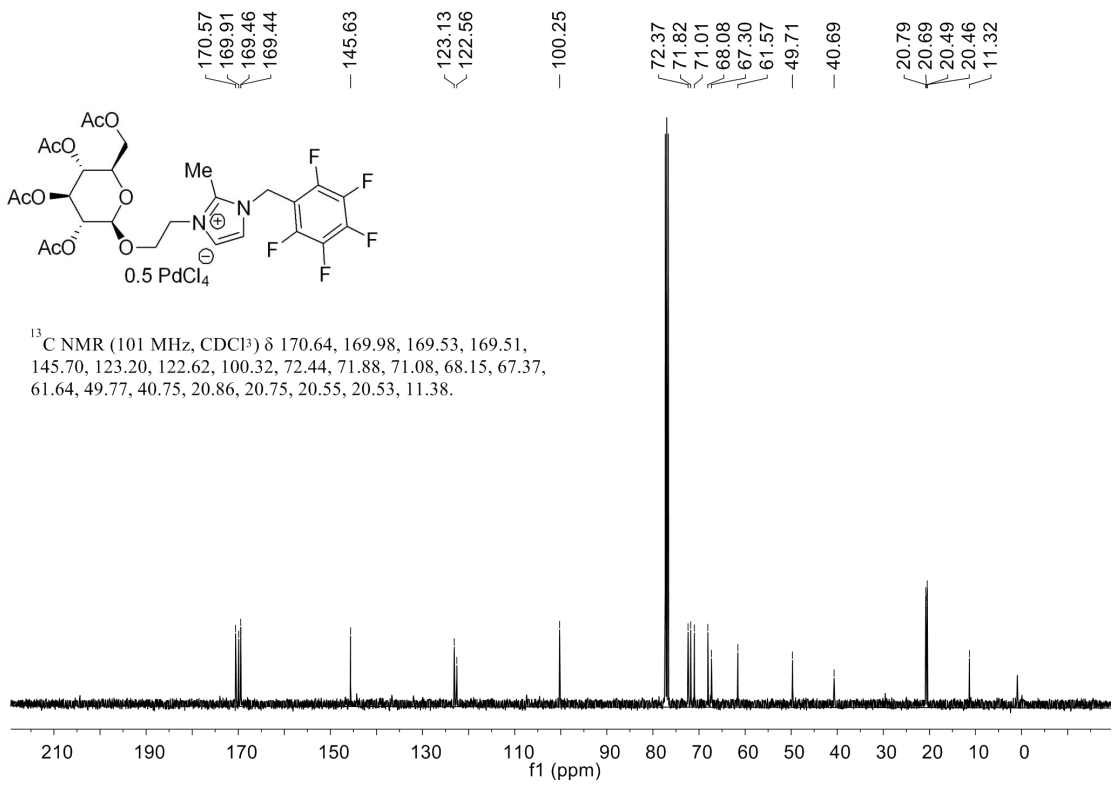
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.51 – 7.32 (m, 6H), 5.59 (s, 2H), 5.20 (t, J = 9.5 Hz, 1H), 5.02 (t, J = 9.7 Hz, 1H), 4.91 (dd, J = 11.8, 5.8 Hz, 1H), 4.80 (s, 2H), 4.70 (d, J = 8.0 Hz, 1H), 4.41 (d, J = 10.7 Hz, 1H), 4.32 – 4.19 (m, 2H), 4.14 (d, J = 12.4 Hz, 1H), 3.84 – 3.73 (m, 1H), 2.99 (s, 3H), 2.07 (s, 3H), 1.98 (dd, J = 13.0, 5.8 Hz, 9H).



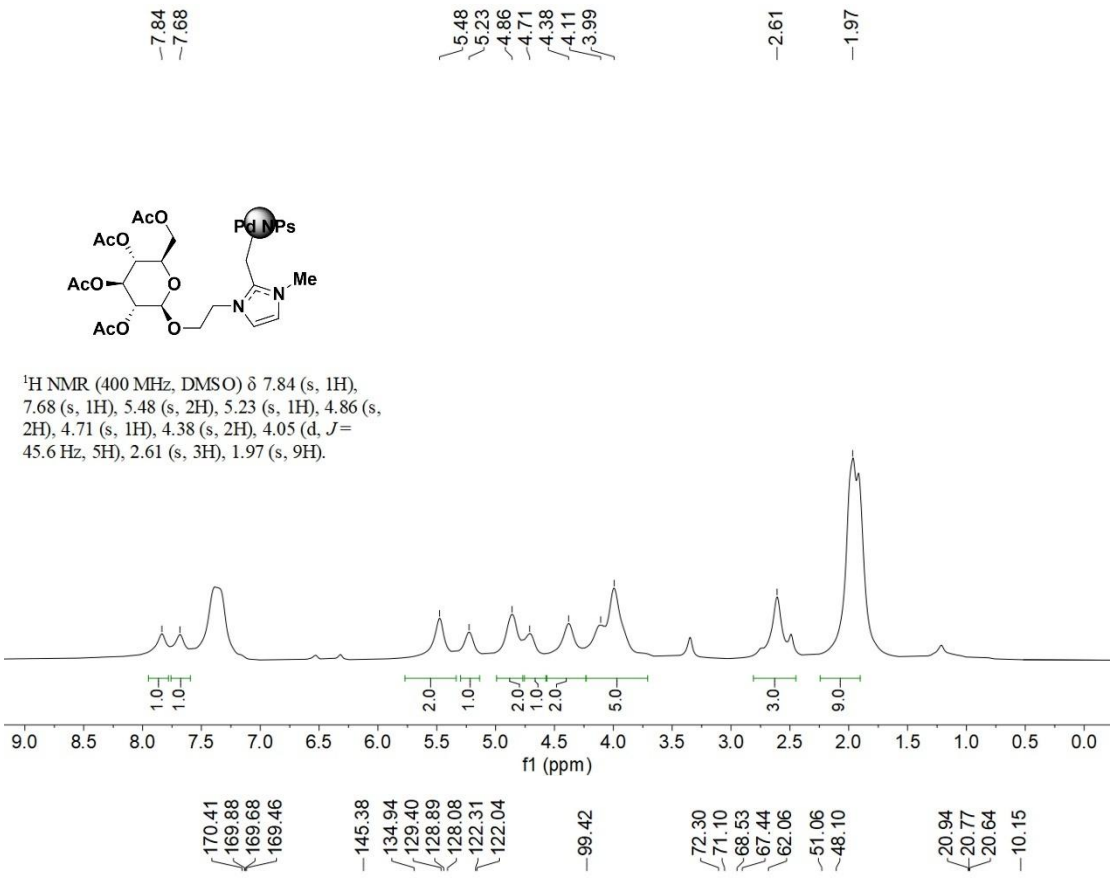
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.54, 170.07, 169.35, 169.32, 144.81, 126.89, 119.35, 100.52, 72.50, 71.85, 70.73, 68.66, 68.19, 61.71, 45.50, 20.65, 20.49, 12.83.



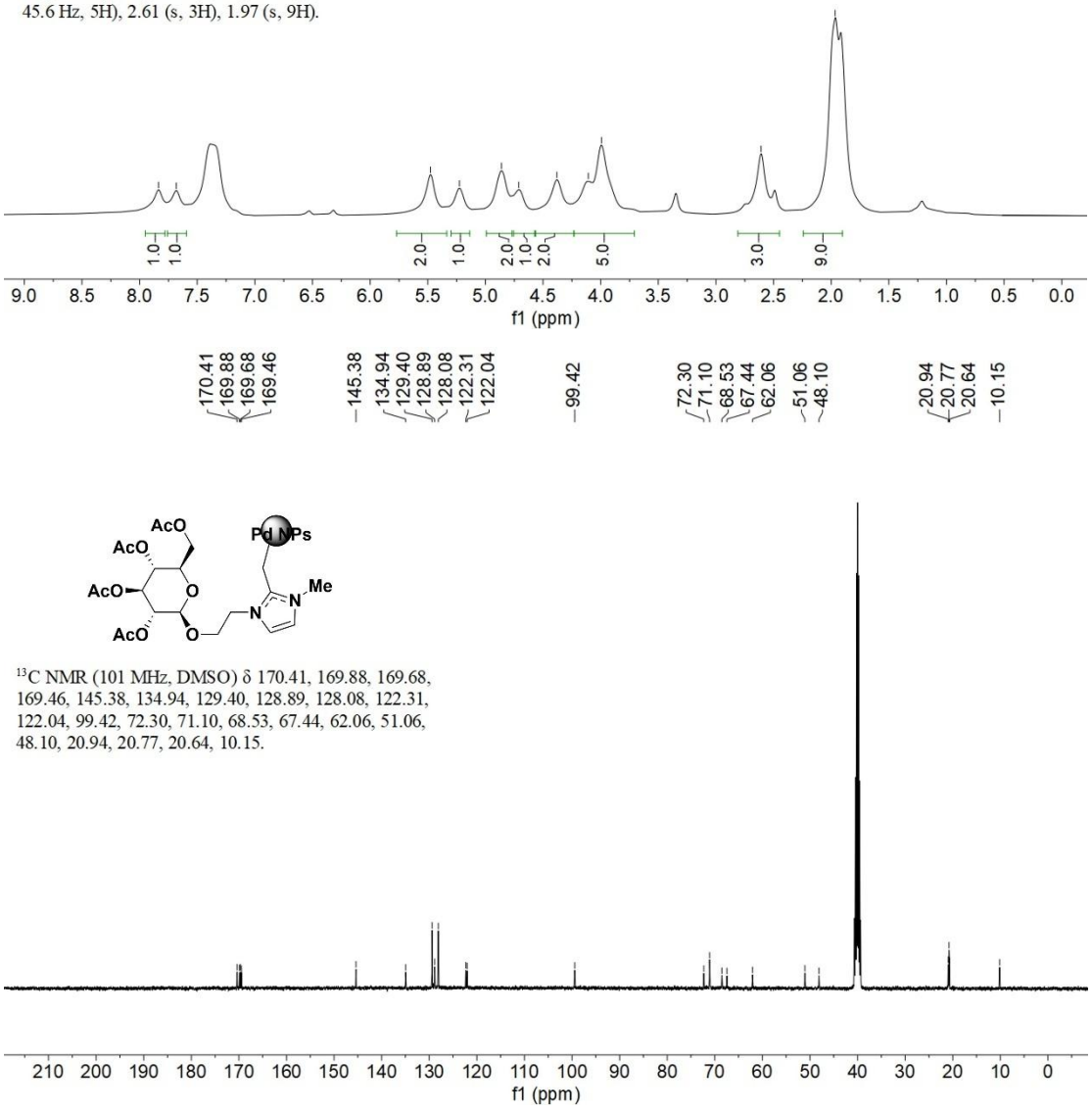
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.0 Hz, 1H), 7.65 (s, 1H), 5.71 (s, 2H), 5.19 (t, *J* = 9.5 Hz, 1H), 5.01 (t, *J* = 9.7 Hz, 1H), 4.88 – 4.81 (m, 1H), 4.76 (s, 2H), 4.70 (d, *J* = 8.0 Hz, 1H), 4.39 (dd, *J* = 11.2, 4.2 Hz, 1H), 4.20 (ddd, *J* = 36.4, 12.3, 3.2 Hz, 3H), 3.81 (ddd, *J* = 10.0, 4.2, 2.2 Hz, 1H), 3.00 (s, 3H), 2.09 (s, 3H), 2.03 – 1.96 (m, 9H).



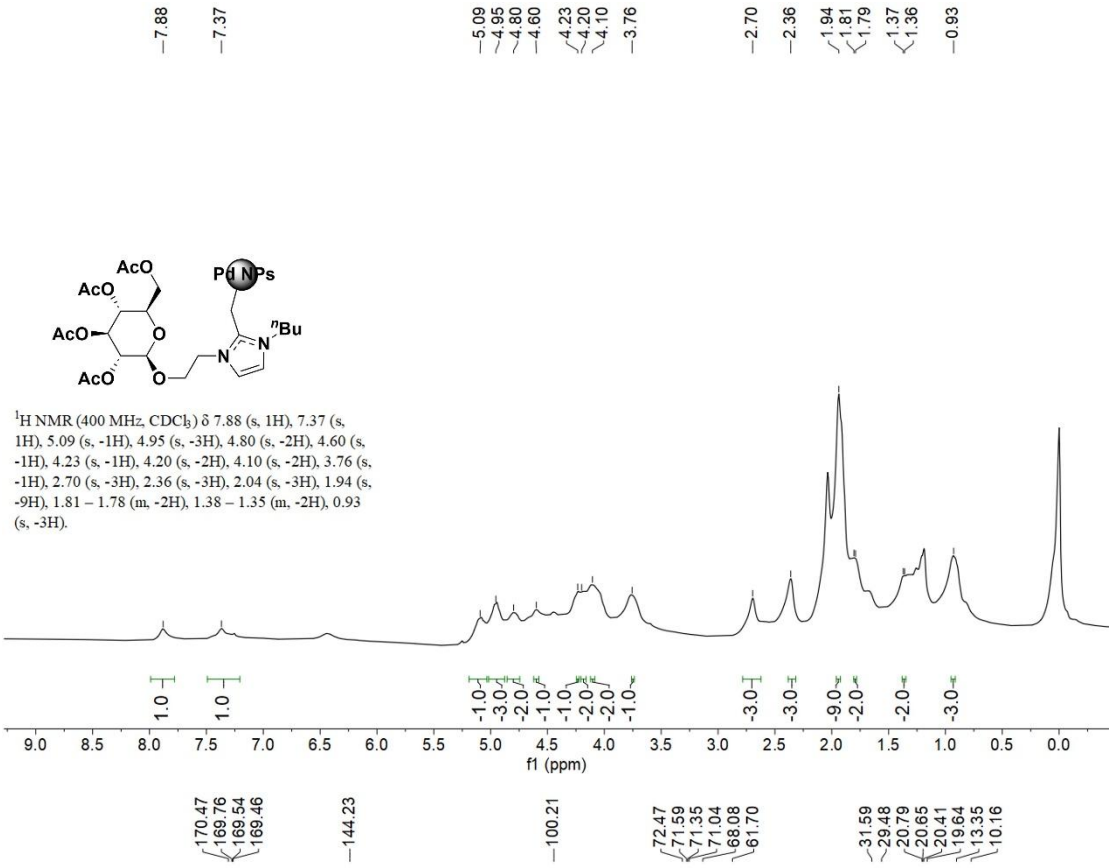
^{13}C NMR (101 MHz, $CDCl^3$) δ 170.64, 169.98, 169.53, 169.51, 145.70, 123.20, 122.62, 100.32, 72.44, 71.88, 71.08, 68.15, 67.37, 61.64, 49.77, 40.75, 20.86, 20.75, 20.55, 20.53, 11.38.



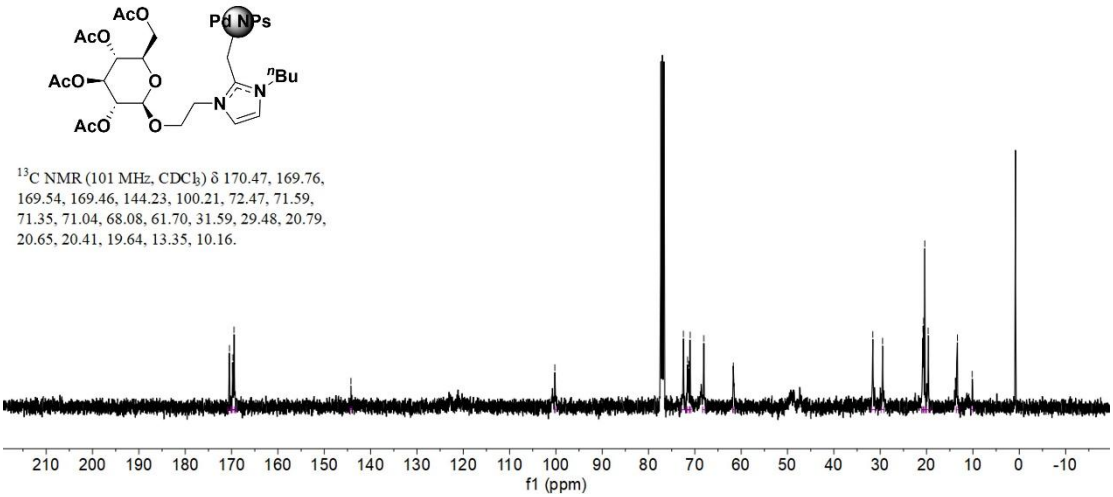
^{1}H NMR (400 MHz, DMSO) δ 7.84 (s, 1H), 7.68 (s, 1H), 5.48 (s, 2H), 5.23 (s, 1H), 4.86 (s, 2H), 4.71 (s, 1H), 4.38 (s, 2H), 4.05 (d, J = 45.6 Hz, 5H), 2.61 (s, 3H), 1.97 (s, 9H).



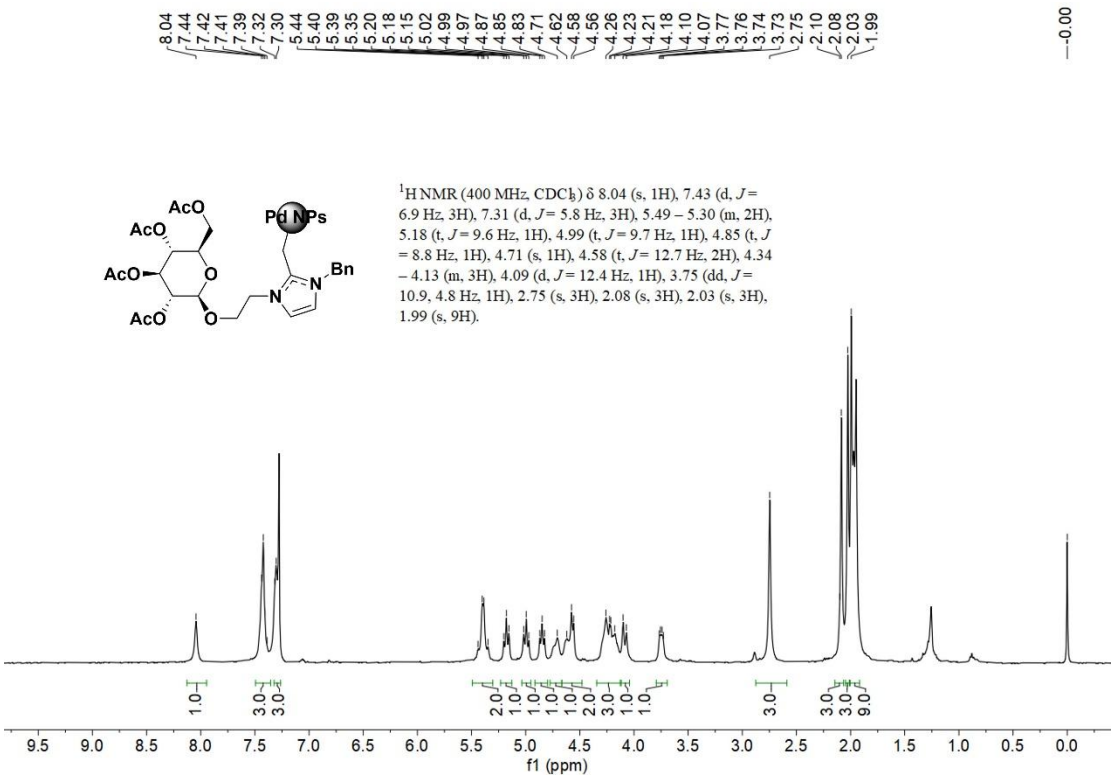
^{13}C NMR (101 MHz, DMSO) δ 170.41, 169.88, 169.68, 169.46, 145.38, 134.94, 129.40, 128.89, 128.08, 122.31, 122.04, 99.42, 72.30, 71.10, 68.53, 67.44, 62.06, 51.06, 48.10, 20.94, 20.77, 20.64, 10.15.



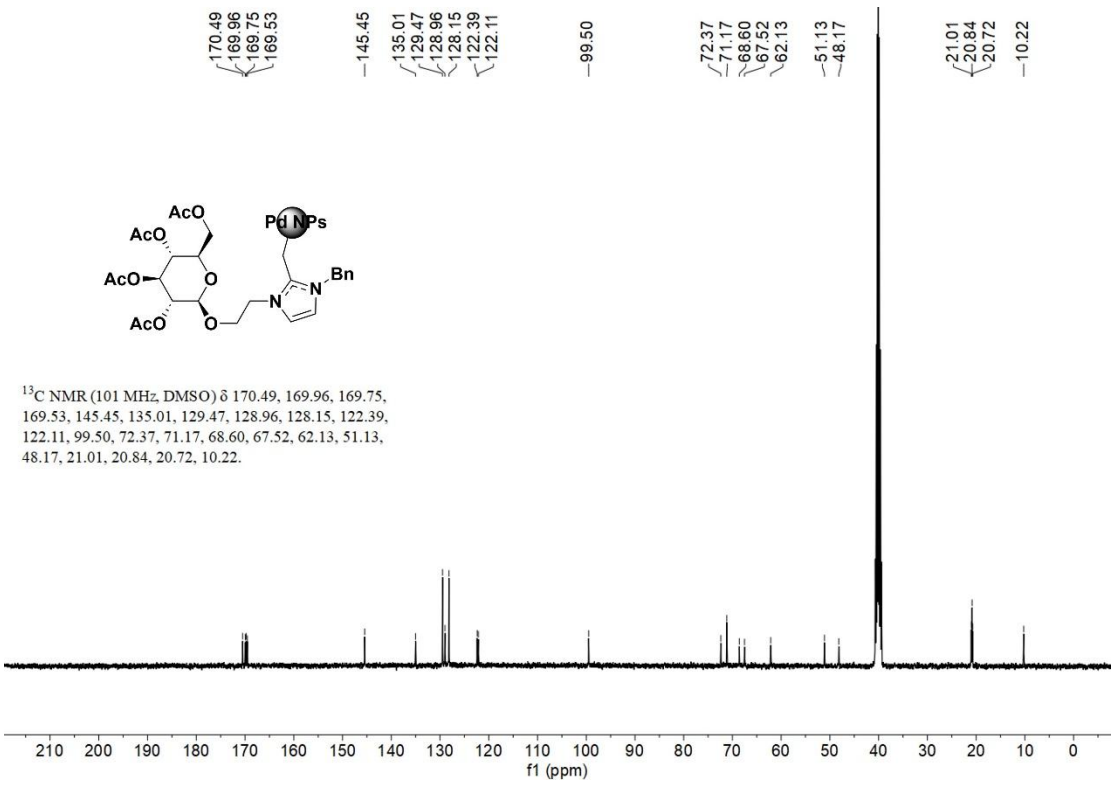
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.37 (s, 1H), 5.09 (s, -1H), 4.95 (s, -3H), 4.80 (s, -2H), 4.60 (s, -1H), 4.23 (s, -1H), 4.20 (s, -2H), 4.10 (s, -2H), 3.76 (s, -1H), 2.70 (s, -3H), 2.36 (s, -3H), 2.04 (s, -3H), 1.94 (s, -9H), 1.81 – 1.78 (m, -2H), 1.38 – 1.35 (m, -2H), 0.93 (s, -3H).



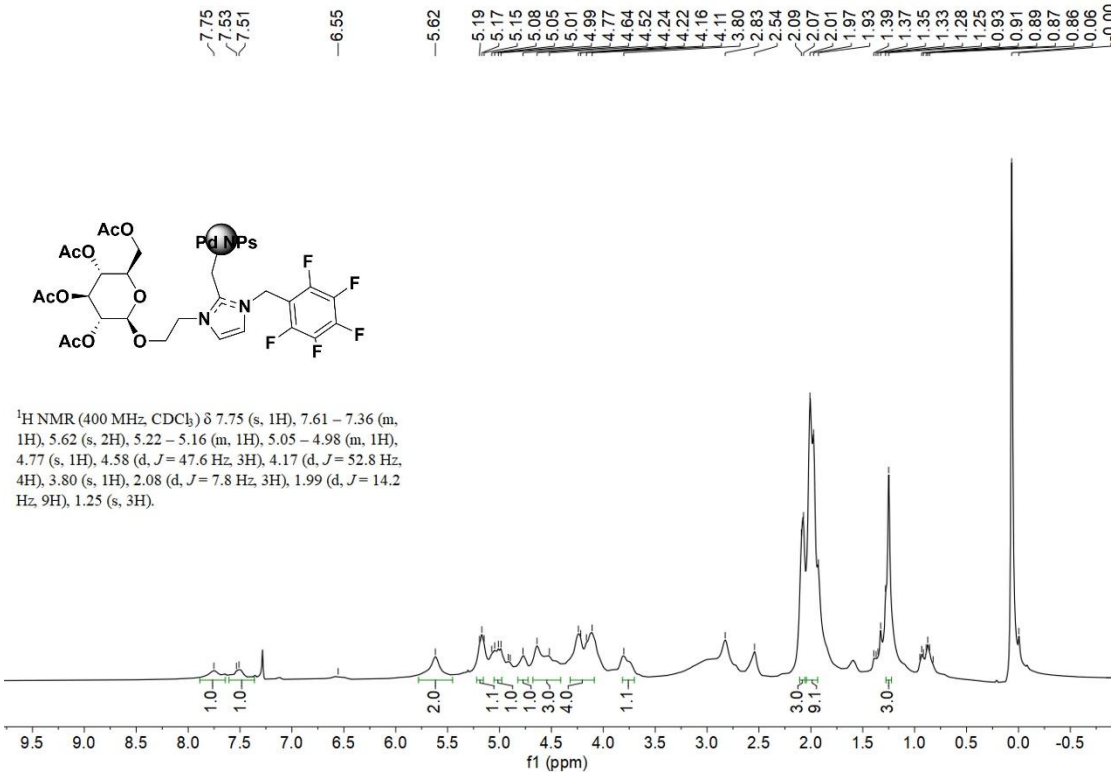
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.47, 169.76, 169.54, 169.46, 144.23, 100.21, 72.47, 71.59, 71.35, 71.04, 68.08, 61.70, 31.59, 29.48, 20.79, 20.65, 20.41, 19.64, 13.35, 10.16.



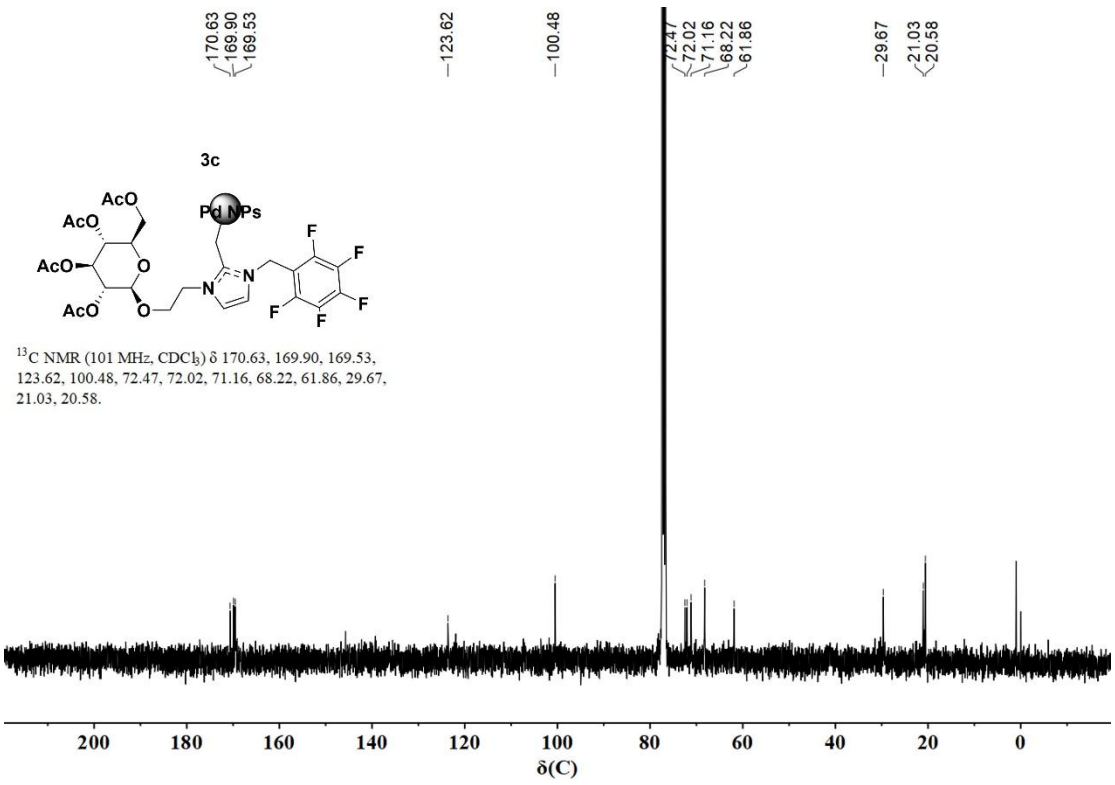
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.43 (d, J = 6.9 Hz, 3H), 7.31 (d, J = 5.8 Hz, 3H), 5.49 – 5.30 (m, 2H), 5.18 (t, J = 9.6 Hz, 1H), 4.99 (t, J = 9.7 Hz, 1H), 4.85 (t, J = 8.8 Hz, 1H), 4.71 (s, 1H), 4.58 (t, J = 12.7 Hz, 2H), 4.34 – 4.13 (m, 3H), 4.09 (d, J = 12.4 Hz, 1H), 3.75 (dd, J = 10.9, 4.8 Hz, 1H), 2.75 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 1.99 (s, 9H).



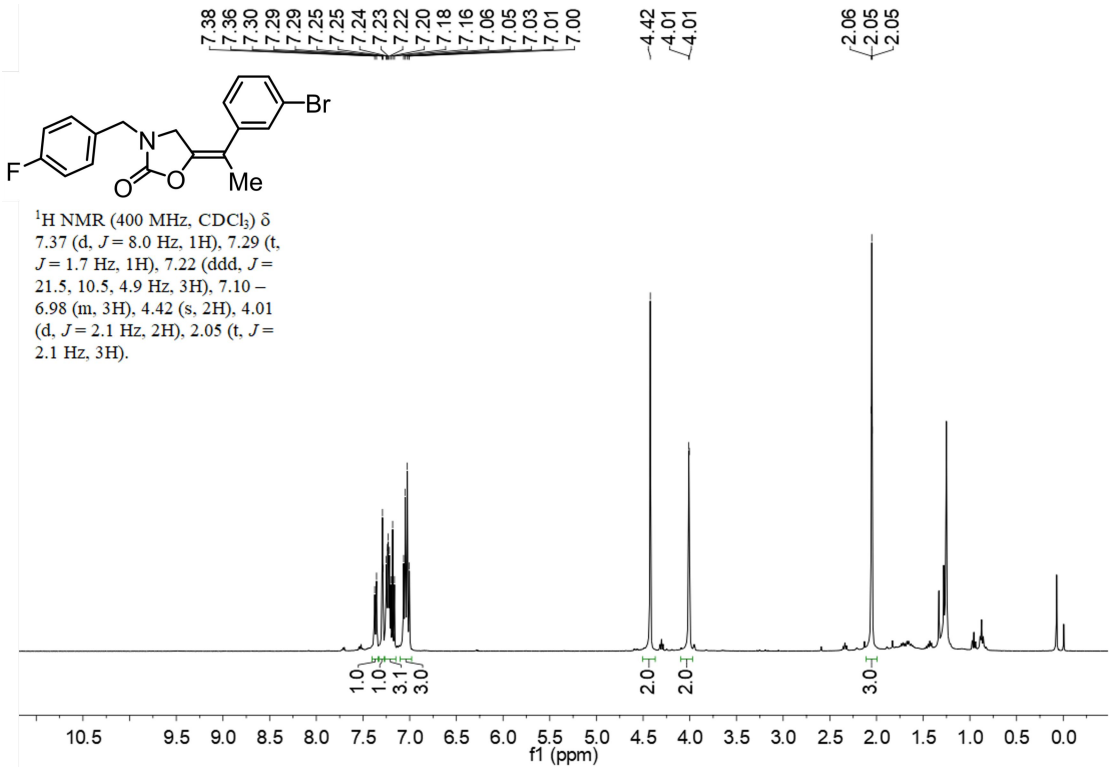
^{13}C NMR (101 MHz, DMSO) δ 170.49, 169.96, 169.75, 169.53, 145.45, 135.01, 129.47, 128.96, 128.15, 122.39, 122.11, 99.50, 72.37, 71.17, 68.60, 67.52, 62.13, 51.13, 48.17, 21.01, 20.84, 20.72, 10.22.



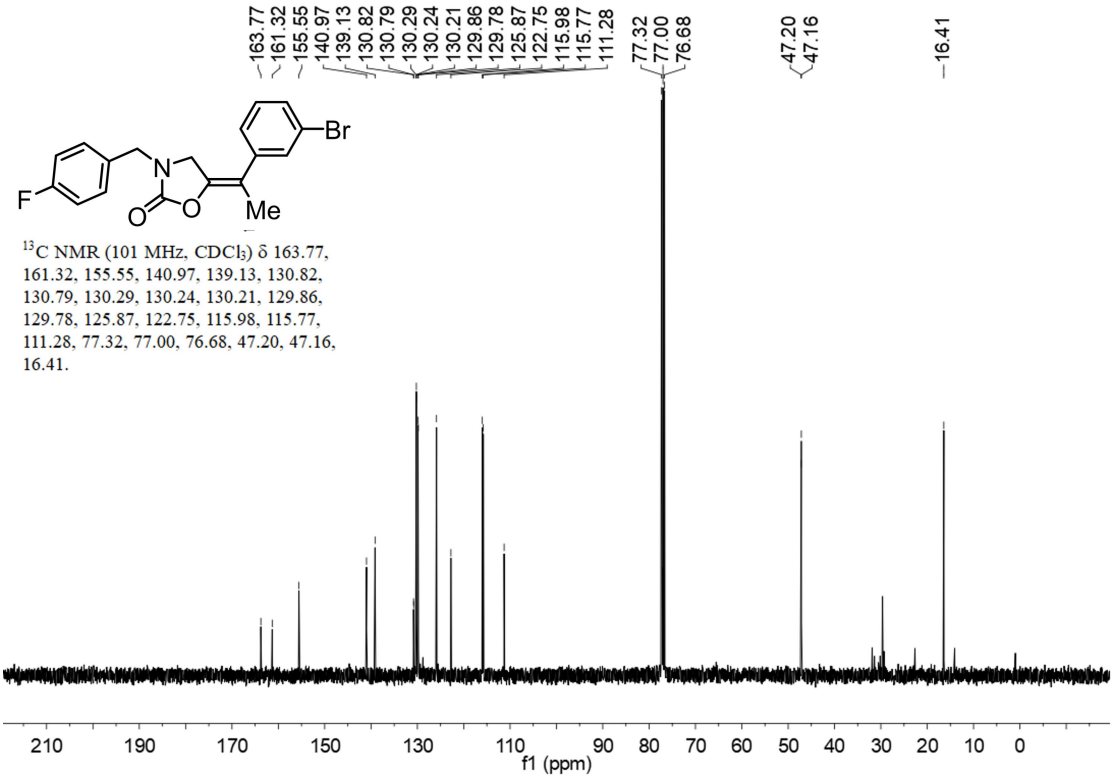
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.61 – 7.36 (m, 1H), 5.62 (s, 2H), 5.22 – 5.16 (m, 1H), 5.05 – 4.98 (m, 1H), 4.77 (s, 1H), 4.58 (d, J = 47.6 Hz, 3H), 4.17 (d, J = 52.8 Hz, 4H), 3.80 (s, 1H), 2.08 (d, J = 7.8 Hz, 3H), 1.99 (d, J = 14.2 Hz, 9H), 1.25 (s, 3H).



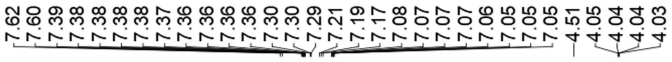
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.63, 169.90, 169.53, 123.62, 100.48, 72.47, 72.02, 71.16, 68.22, 61.86, 29.67, 21.03, 20.58.

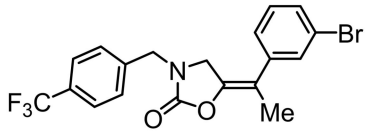


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.0 Hz, 1H), 7.29 (t, J = 1.7 Hz, 1H), 7.22 (ddd, J = 21.5, 10.5, 4.9 Hz, 3H), 7.10 – 6.98 (m, 3H), 4.42 (s, 2H), 4.01 (d, J = 2.1 Hz, 2H), 2.05 (t, J = 2.1 Hz, 3H).

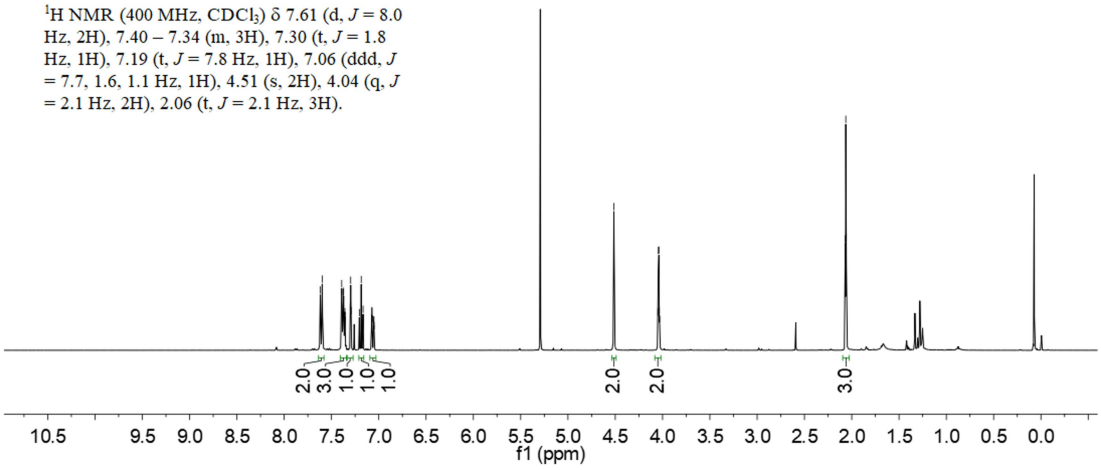


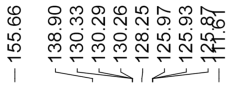
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.77, 161.32, 155.55, 140.97, 139.13, 130.82, 130.79, 130.29, 130.24, 130.21, 129.86, 129.78, 125.87, 122.75, 115.98, 115.77, 111.28, 77.32, 77.00, 76.68, 47.20, 47.16, 16.41.

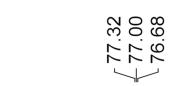


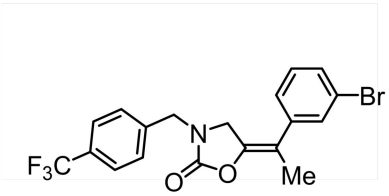


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 2H), 7.40 – 7.34 (m, 3H), 7.30 (t, J = 1.8 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 7.06 (ddd, J = 7.7, 1.6, 1.1 Hz, 1H), 4.51 (s, 2H), 4.04 (q, J = 2.1 Hz, 2H), 2.06 (t, J = 2.1 Hz, 3H).

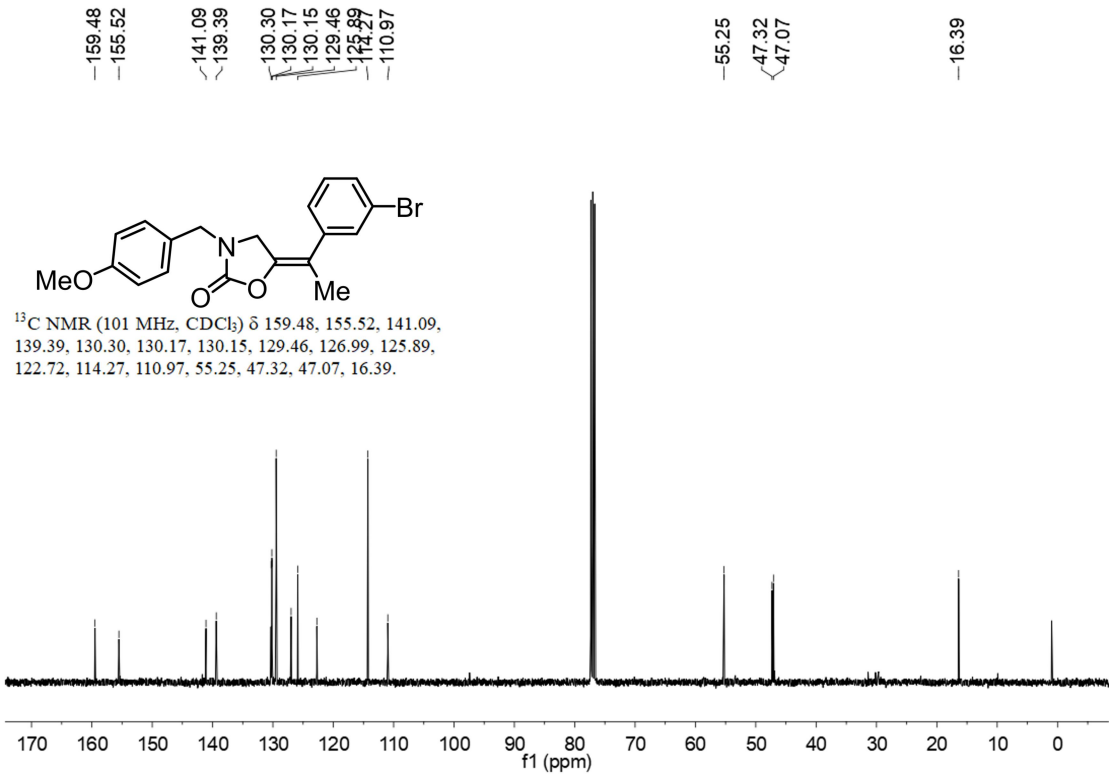




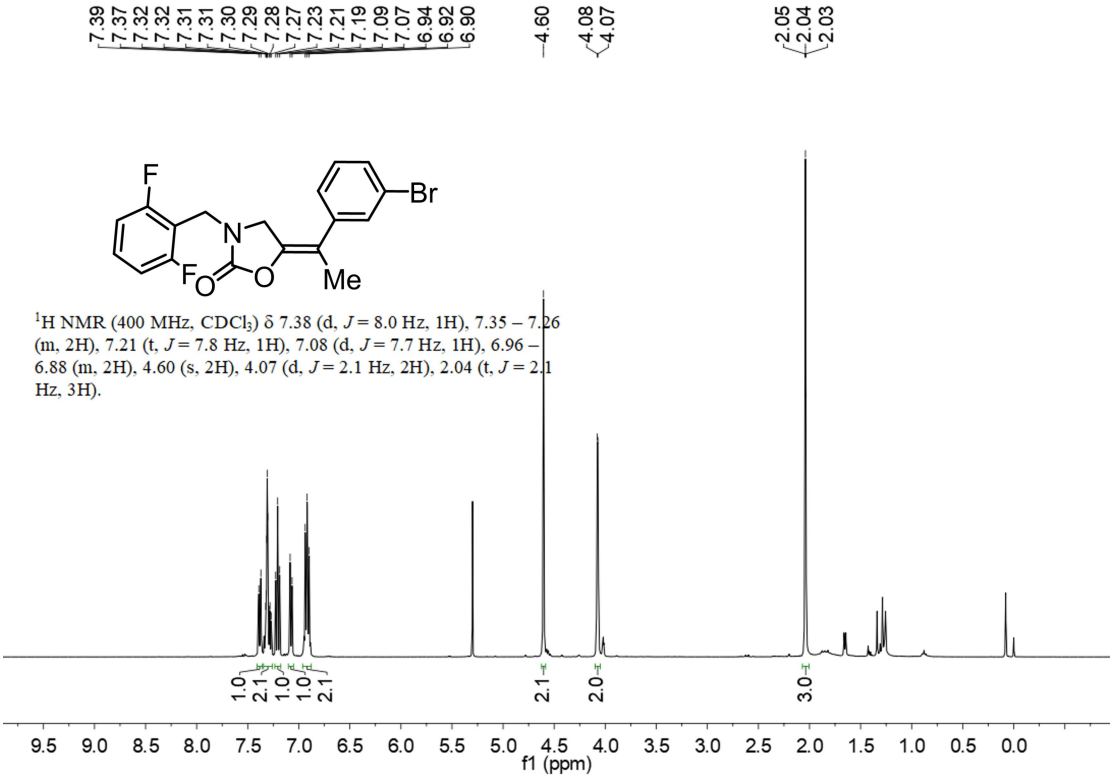




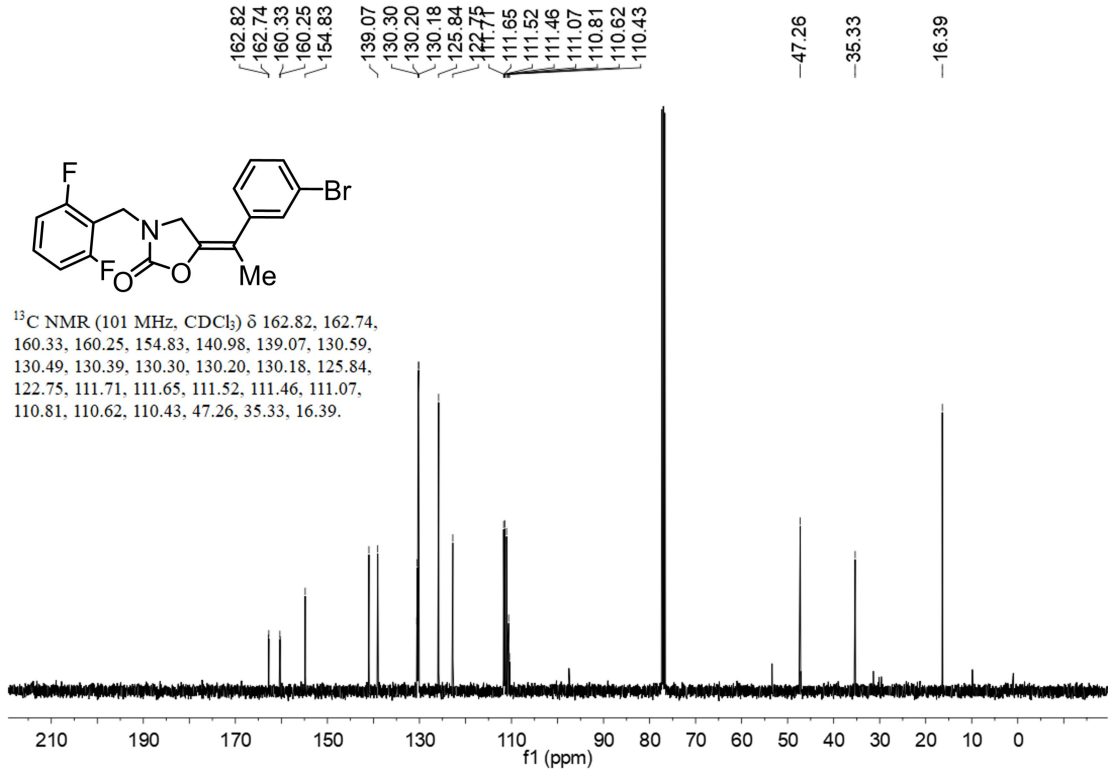
^{13}C NMR (101 MHz, $CDCl^3$) δ 155.66, 140.86, 139.11, 139.10, 138.90, 130.33, 130.29, 130.26, 128.25, 126.00, 125.97, 125.93, 125.87, 122.79, 111.61, 47.49, 47.38, 16.44.



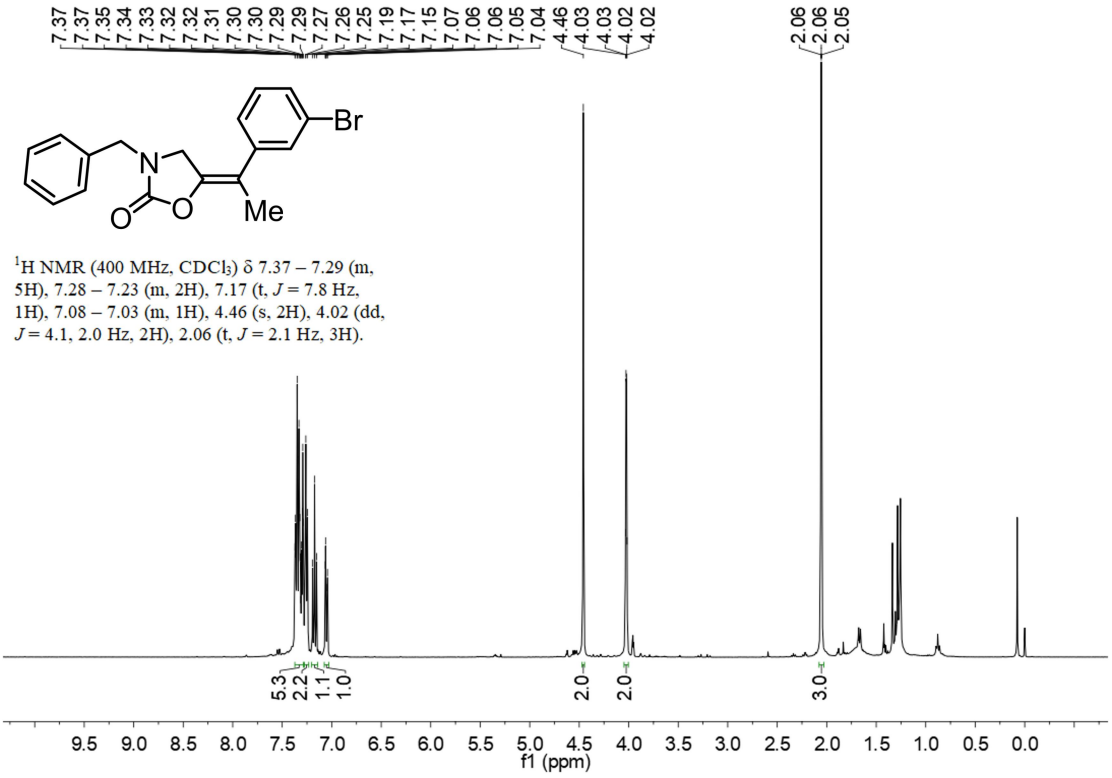
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.48, 155.52, 141.09, 139.39, 130.30, 130.17, 130.15, 129.46, 126.99, 125.89, 122.72, 114.27, 110.97, 55.25, 47.32, 47.07, 16.39.



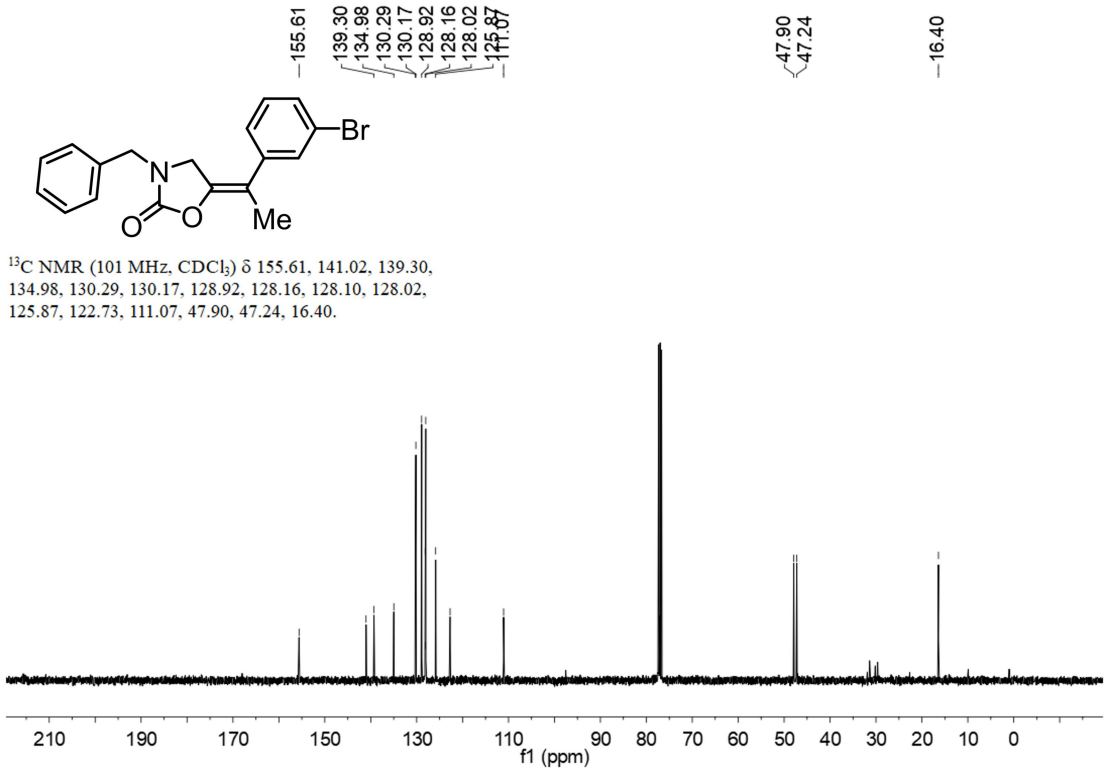
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.0 Hz, 1H), 7.35 – 7.26 (m, 2H), 7.21 (t, J = 7.8 Hz, 1H), 7.08 (d, J = 7.7 Hz, 1H), 6.96 – 6.88 (m, 2H), 4.60 (s, 2H), 4.07 (d, J = 2.1 Hz, 2H), 2.04 (t, J = 2.1 Hz, 3H).



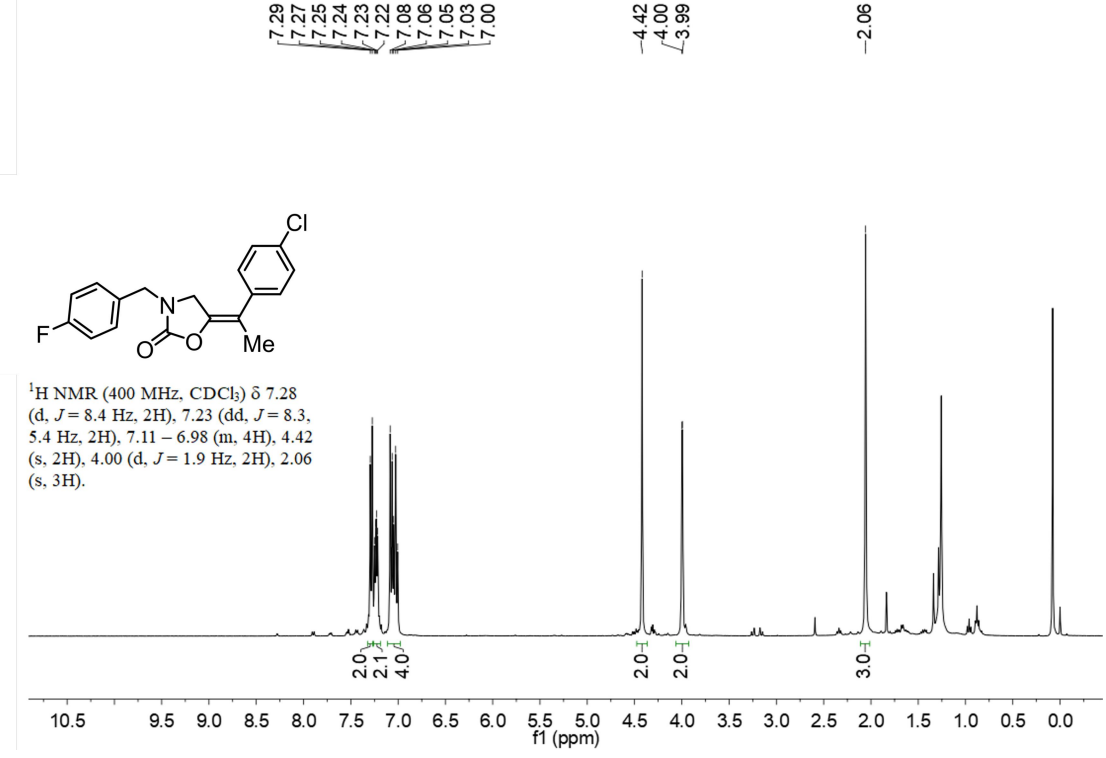
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.82, 162.74, 160.33, 160.25, 154.83, 140.98, 139.07, 130.59, 130.49, 130.39, 130.30, 130.20, 130.18, 125.84, 122.75, 111.71, 111.65, 111.52, 111.46, 111.07, 110.81, 110.62, 110.43, 47.26, 35.33, 16.39.



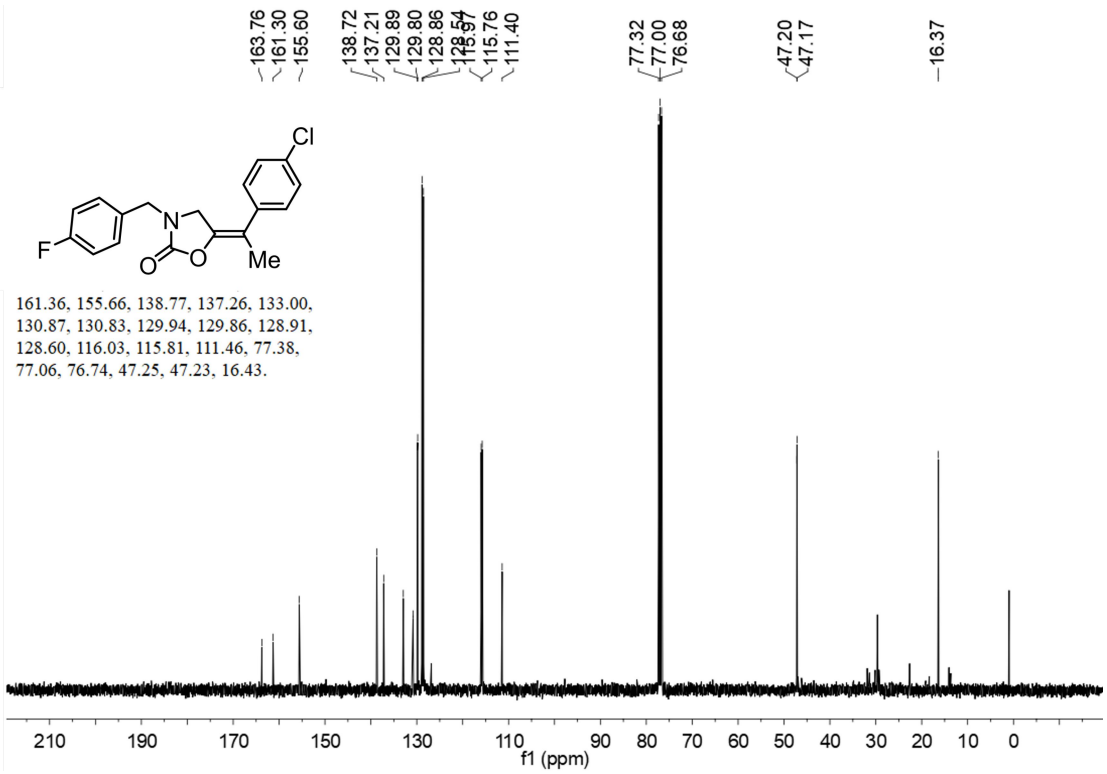
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 5H), 7.28 – 7.23 (m, 2H), 7.17 (t, J = 7.8 Hz, 1H), 7.08 – 7.03 (m, 1H), 4.46 (s, 2H), 4.02 (dd, J = 4.1, 2.0 Hz, 2H), 2.06 (t, J = 2.1 Hz, 3H).

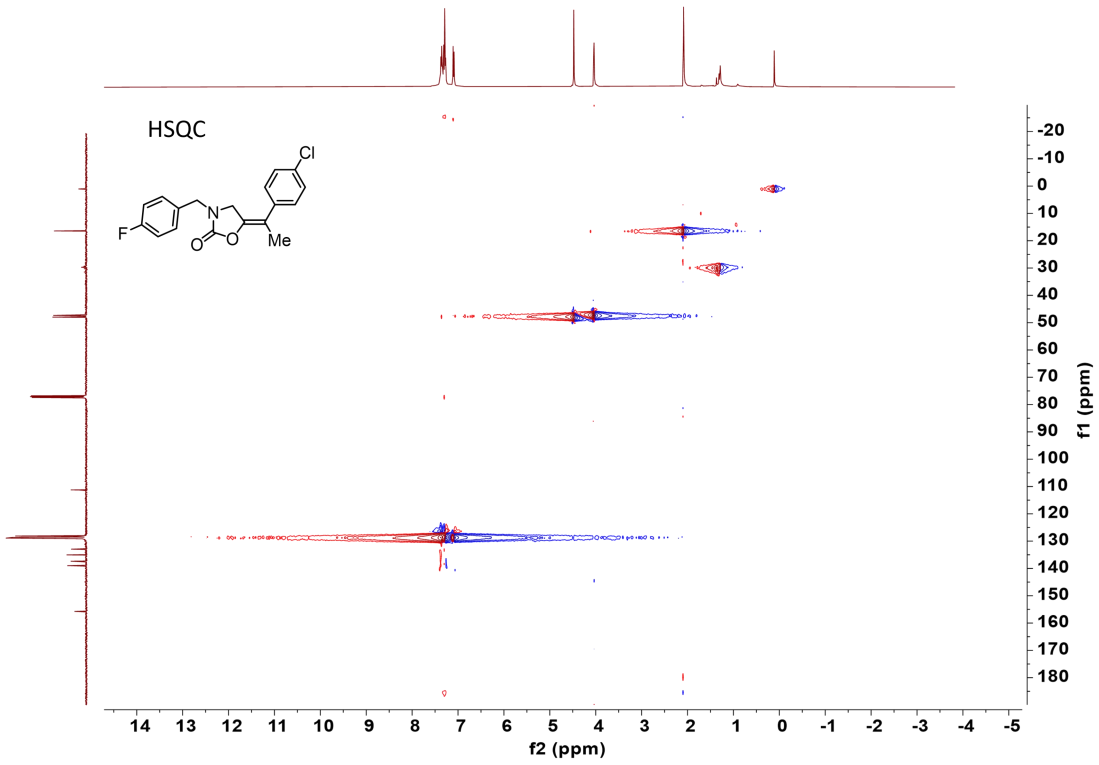


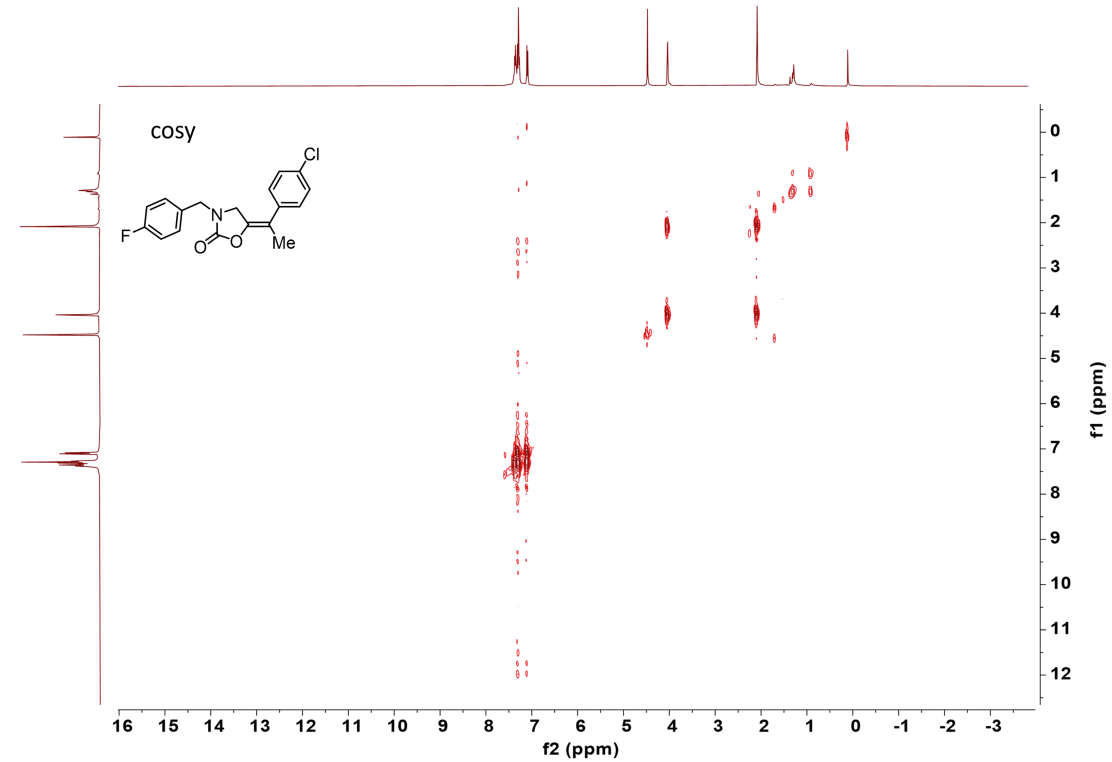
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.61, 141.02, 139.30, 134.98, 130.29, 130.17, 128.92, 128.16, 128.10, 128.02, 125.87, 122.73, 111.07, 47.90, 47.24, 16.40.

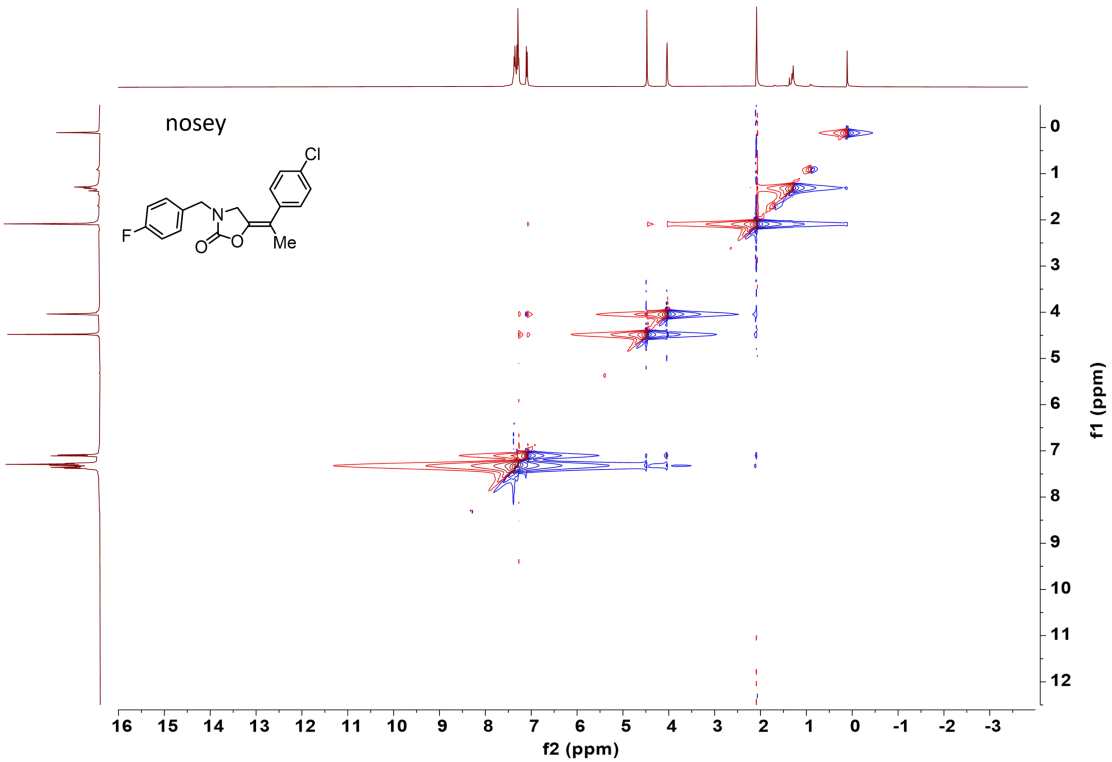


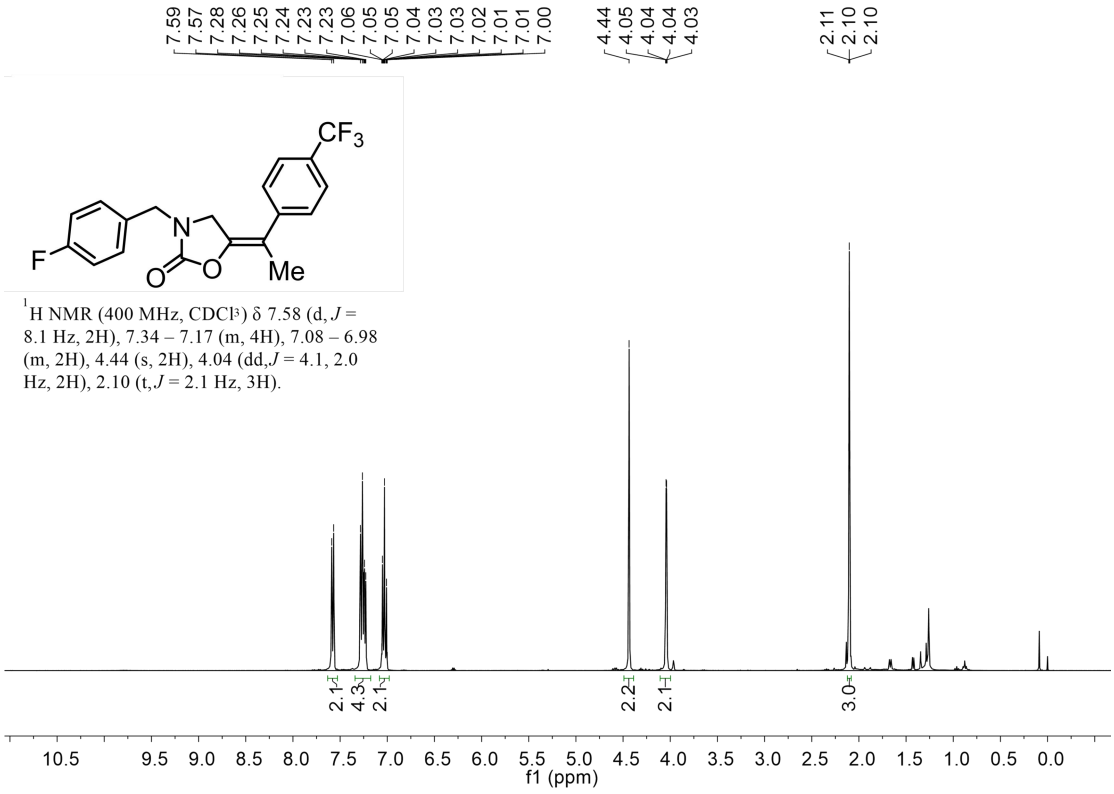
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.4 Hz, 2H), 7.23 (dd, J = 8.3, 5.4 Hz, 2H), 7.11 – 6.98 (m, 4H), 4.42 (s, 2H), 4.00 (d, J = 1.9 Hz, 2H), 2.06 (s, 3H).


163.76
161.30
155.60
138.72
137.21
129.89
129.80
128.86
128.54
115.97
115.76
111.40
77.32
77.00
76.68
47.20
47.17
16.37
Cl
F
N
O
O
Me
161.36, 155.66, 138.77, 137.26, 133.00,
130.87, 130.83, 129.94, 129.86, 128.91,
128.60, 116.03, 115.81, 111.46, 77.38,
77.06, 76.74, 47.25, 47.23, 16.43.
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

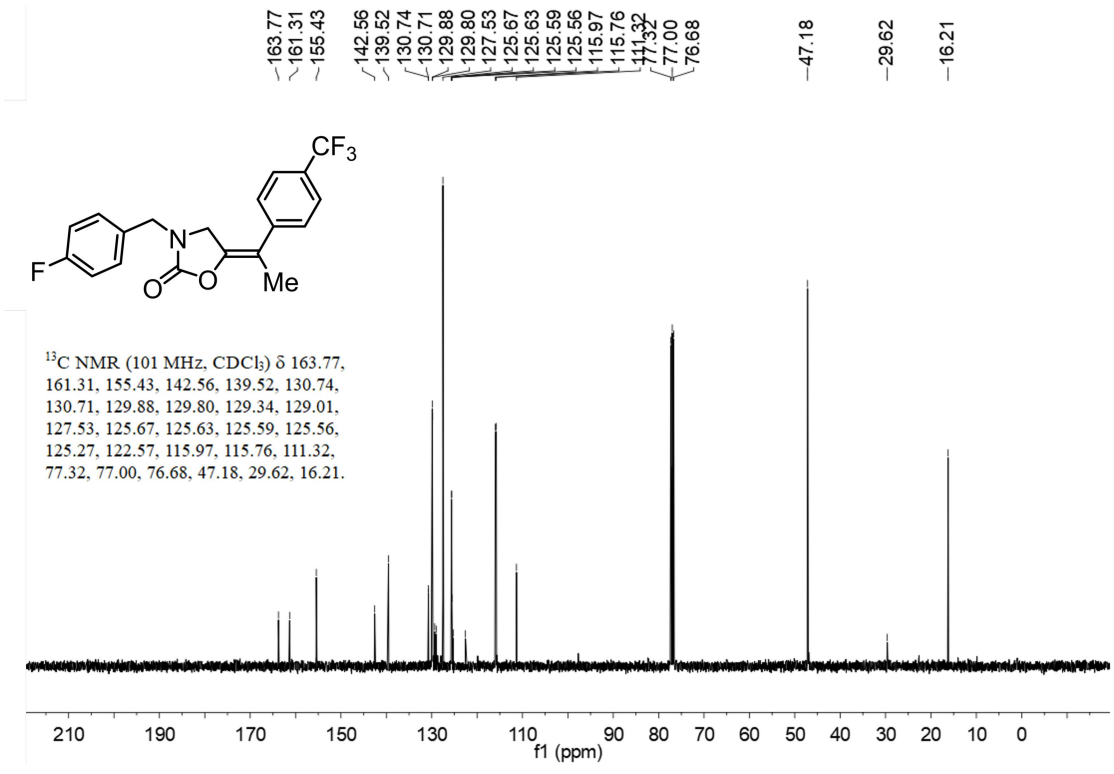

HSQC
Cl
F
N
O
O
Me
-20 -10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180
f1 (ppm)
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5
f2 (ppm)


cosy
Cl
F
N
O
O
Me
f1 (ppm)
f2 (ppm)

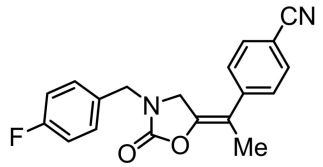

nosey
Cl
F
N
O
O
Me
f1 (ppm)
f2 (ppm)



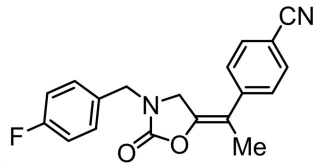
^{1}H NMR (400 MHz, $CDCl^{3}$) δ 7.58 (d, J = 8.1 Hz, 2H), 7.34 – 7.17 (m, 4H), 7.08 – 6.98 (m, 2H), 4.44 (s, 2H), 4.04 (dd,J = 4.1, 2.0 Hz, 2H), 2.10 (t,J = 2.1 Hz, 3H).



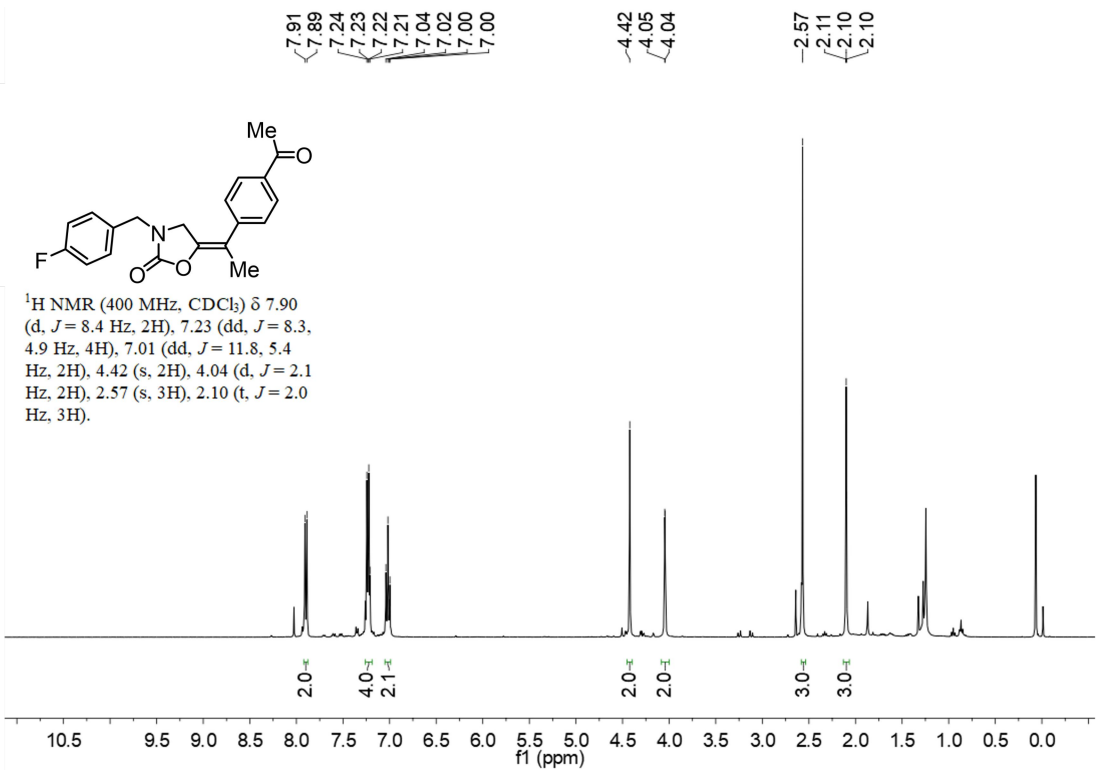
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.77, 161.31, 155.43, 142.56, 139.52, 130.74, 130.71, 129.88, 129.80, 129.34, 129.01, 127.53, 125.67, 125.63, 125.59, 125.56, 125.27, 122.57, 115.97, 115.76, 111.32, 77.32, 77.00, 76.68, 47.18, 29.62, 16.21.



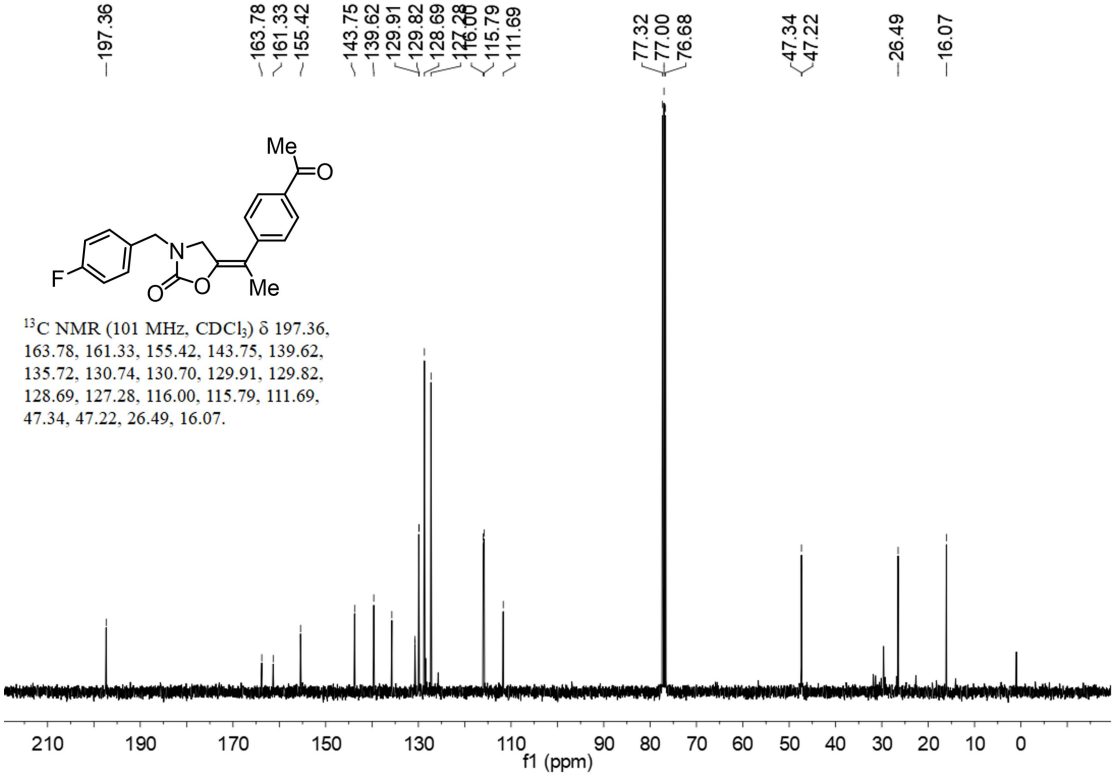
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.25 (dd, *J* = 11.4, 5.1 Hz, 4H), 7.04 (t, *J* = 8.6 Hz, 2H), 4.44 (s, 2H), 4.04 (d, *J* = 2.0 Hz, 2H), 2.10 (t, *J* = 1.9 Hz, 3H).



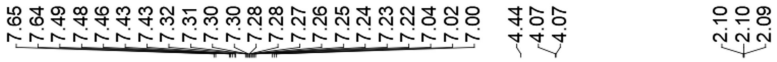
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.83, 161.37, 155.19, 143.67, 140.22, 132.47, 130.63, 130.59, 129.92, 129.84, 127.84, 118.47, 116.06, 115.84, 111.14, 110.80, 77.32, 77.00, 76.68, 47.28, 47.24, 16.01.

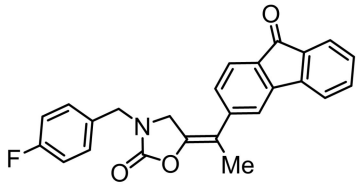


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.4 Hz, 2H), 7.23 (dd, J = 8.3, 4.9 Hz, 4H), 7.01 (dd, J = 11.8, 5.4 Hz, 2H), 4.42 (s, 2H), 4.04 (d, J = 2.1 Hz, 2H), 2.57 (s, 3H), 2.10 (t, J = 2.0 Hz, 3H).

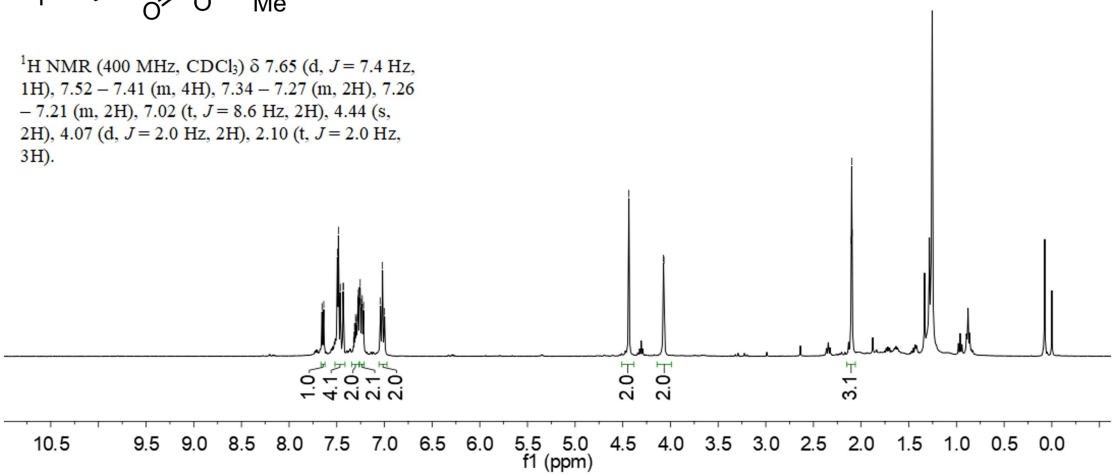


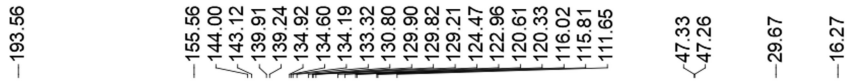
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.36, 163.78, 161.33, 155.42, 143.75, 139.62, 135.72, 130.74, 130.70, 129.91, 129.82, 128.69, 127.28, 116.00, 115.79, 111.69, 47.34, 47.22, 26.49, 16.07.

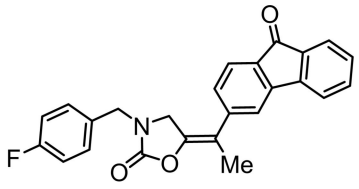




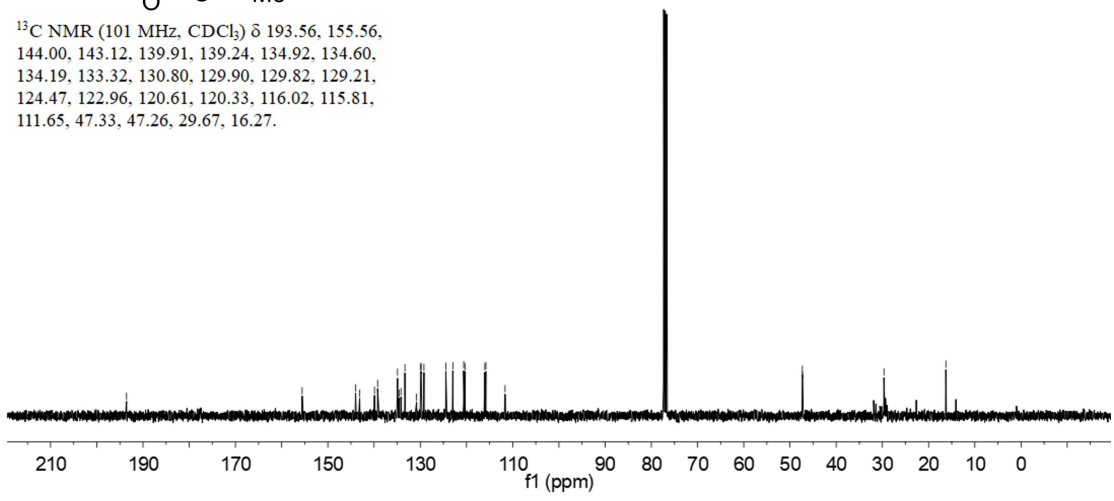
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.4 Hz, 1H), 7.52 – 7.41 (m, 4H), 7.34 – 7.27 (m, 2H), 7.26 – 7.21 (m, 2H), 7.02 (t, J = 8.6 Hz, 2H), 4.44 (s, 2H), 4.07 (d, J = 2.0 Hz, 2H), 2.10 (t, J = 2.0 Hz, 3H).

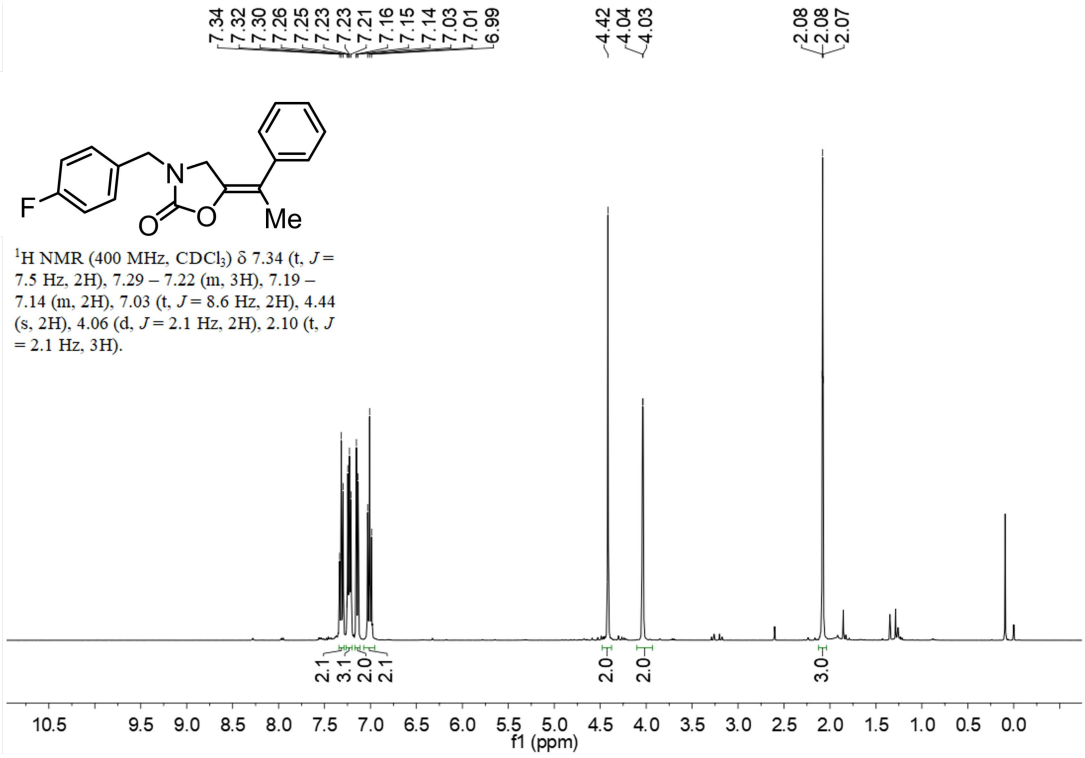




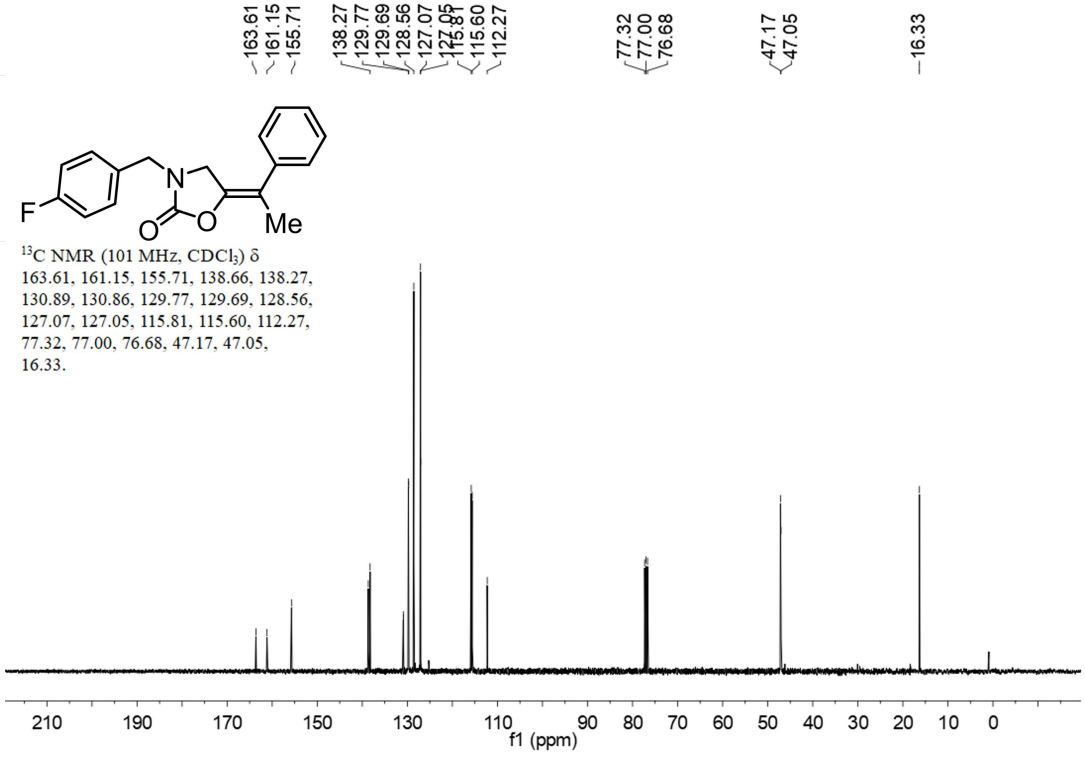


^{13}C NMR (101 MHz, $CDCl_3$) δ 193.56, 155.56, 144.00, 143.12, 139.91, 139.24, 134.92, 134.60, 134.19, 133.32, 130.80, 129.90, 129.82, 129.21, 124.47, 122.96, 120.61, 120.33, 116.02, 115.81, 111.65, 47.33, 47.26, 29.67, 16.27.

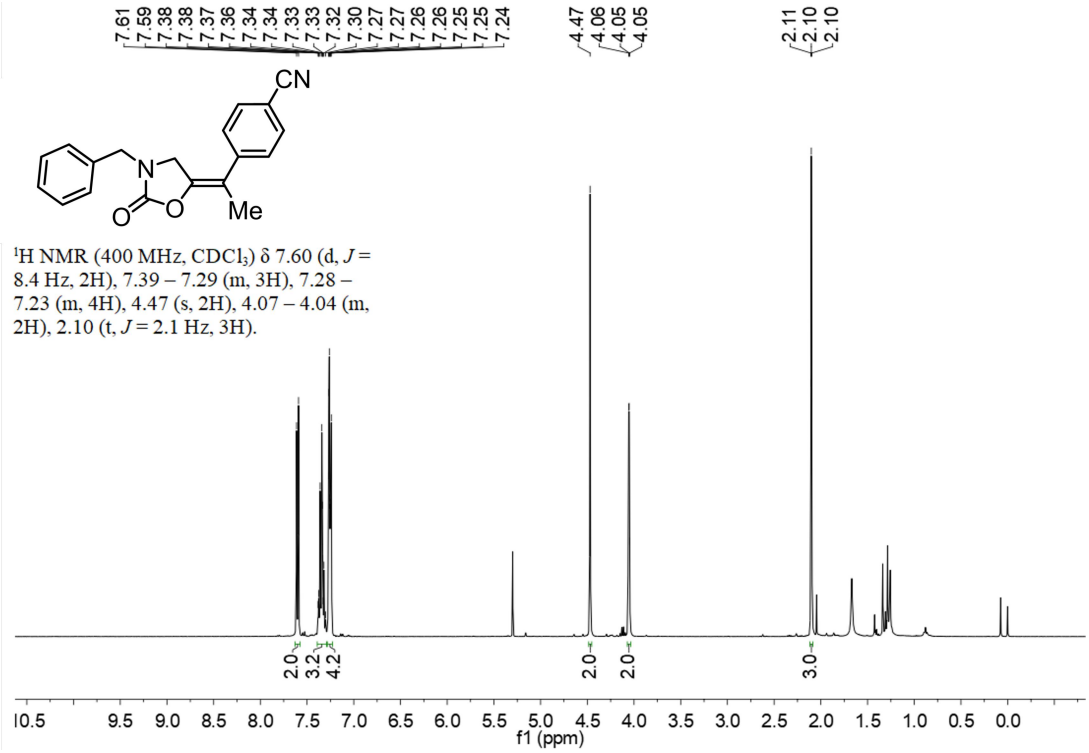




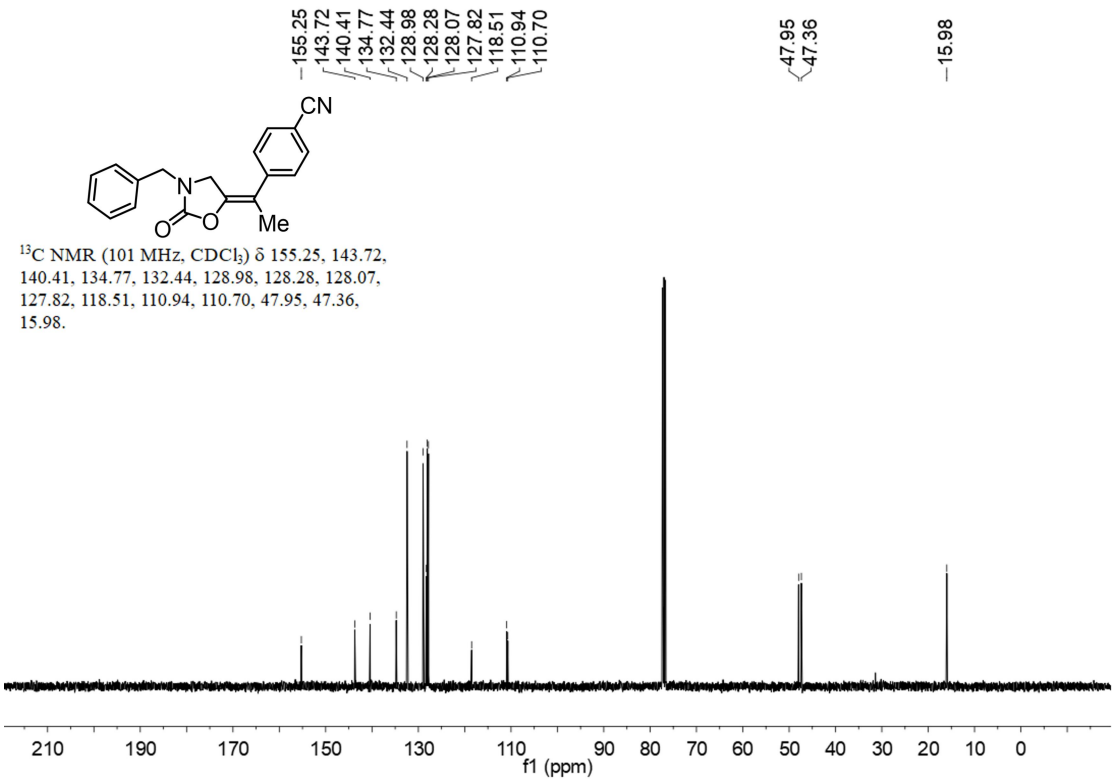
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, J = 7.5 Hz, 2H), 7.29 – 7.22 (m, 3H), 7.19 – 7.14 (m, 2H), 7.03 (t, J = 8.6 Hz, 2H), 4.44 (s, 2H), 4.06 (d, J = 2.1 Hz, 2H), 2.10 (t, J = 2.1 Hz, 3H).



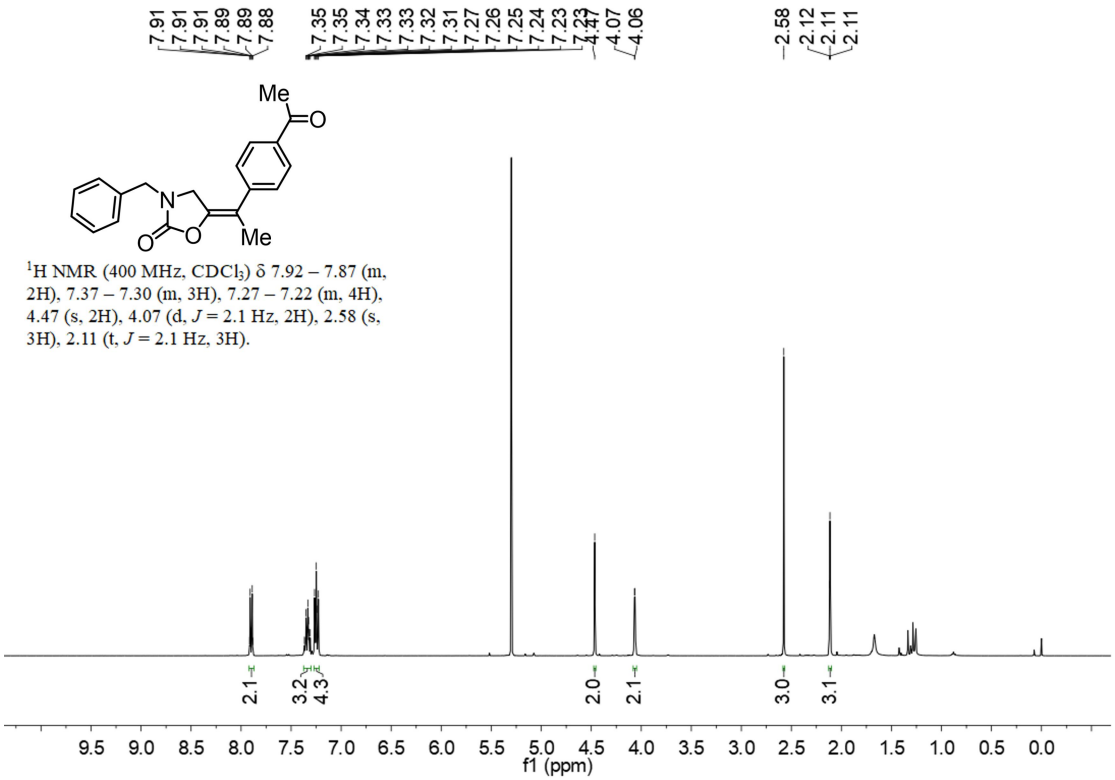
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.61, 161.15, 155.71, 138.66, 138.27, 130.89, 130.86, 129.77, 129.69, 128.56, 127.07, 127.05, 115.81, 115.60, 112.27, 77.32, 77.00, 76.68, 47.17, 47.05, 16.33.



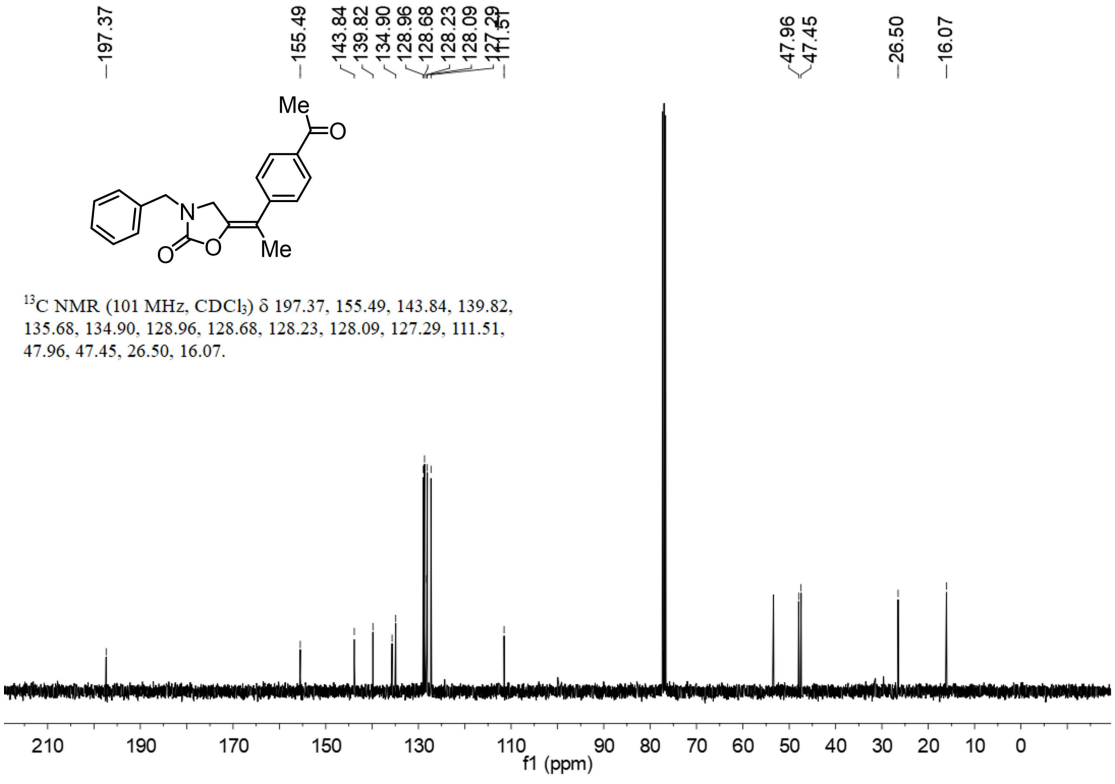
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.4 Hz, 2H), 7.39 – 7.29 (m, 3H), 7.28 – 7.23 (m, 4H), 4.47 (s, 2H), 4.07 – 4.04 (m, 2H), 2.10 (t, J = 2.1 Hz, 3H).



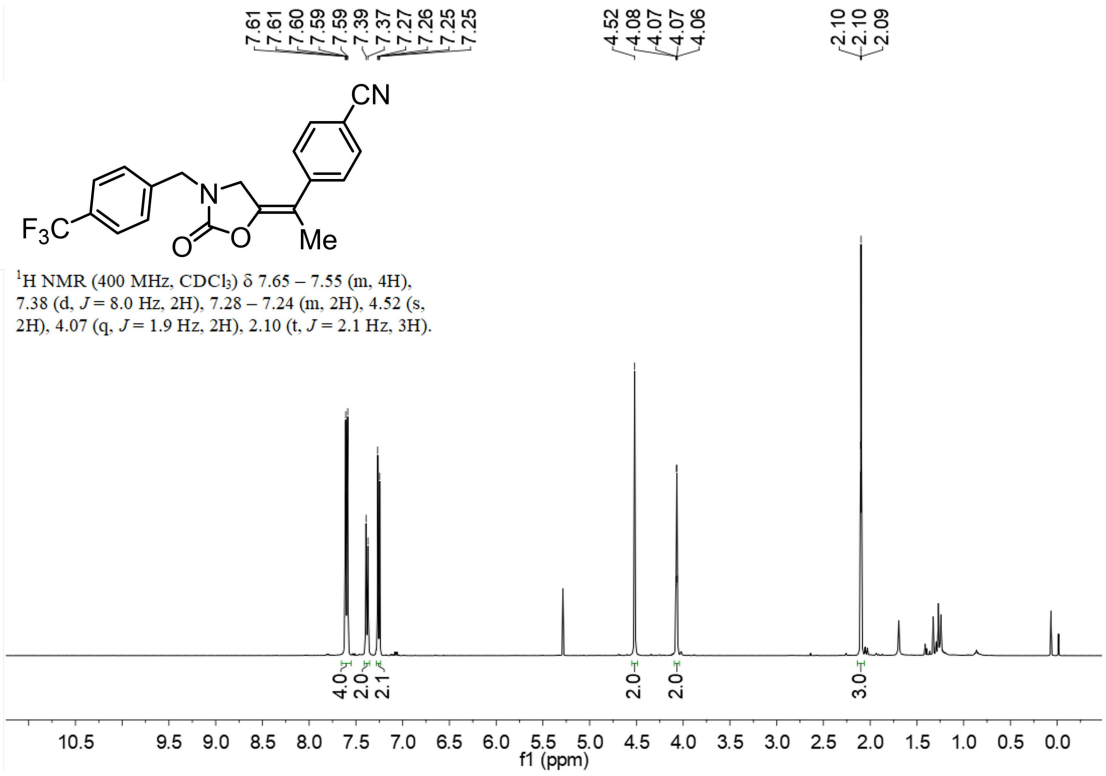
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.25, 143.72, 140.41, 134.77, 132.44, 128.98, 128.28, 128.07, 127.82, 118.51, 110.94, 110.70, 47.95, 47.36, 15.98.



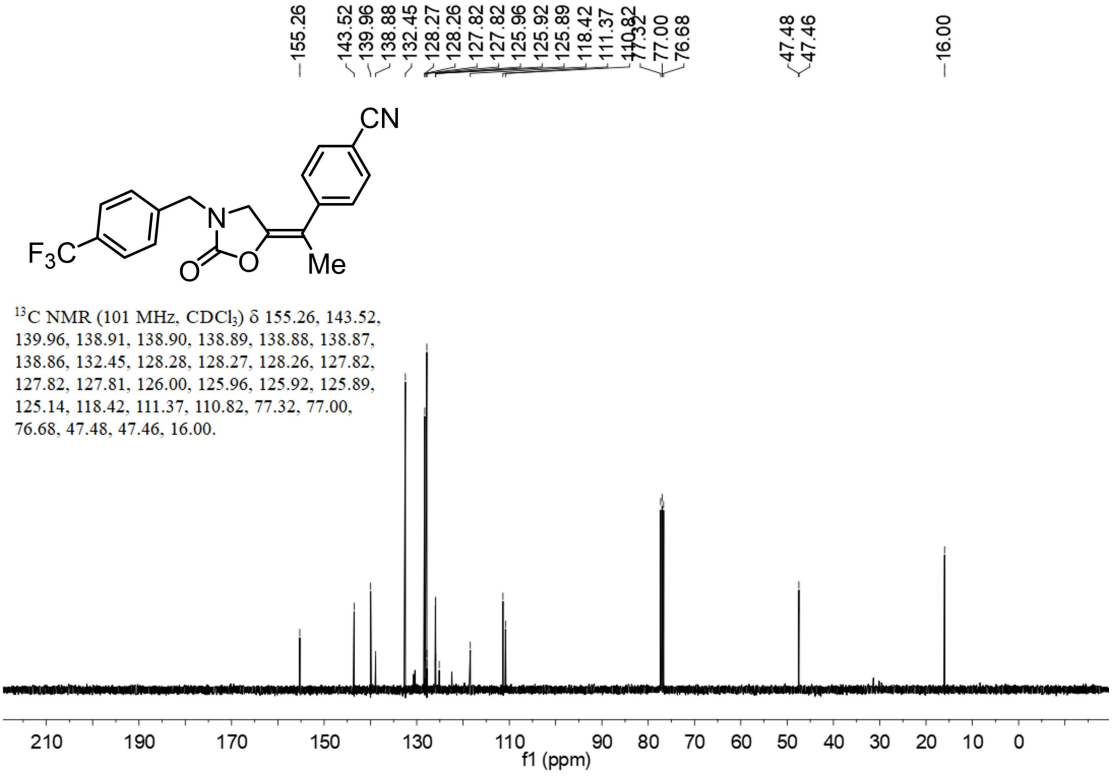
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.37 – 7.30 (m, 3H), 7.27 – 7.22 (m, 4H), 4.47 (s, 2H), 4.07 (d, J = 2.1 Hz, 2H), 2.58 (s, 3H), 2.11 (t, J = 2.1 Hz, 3H).



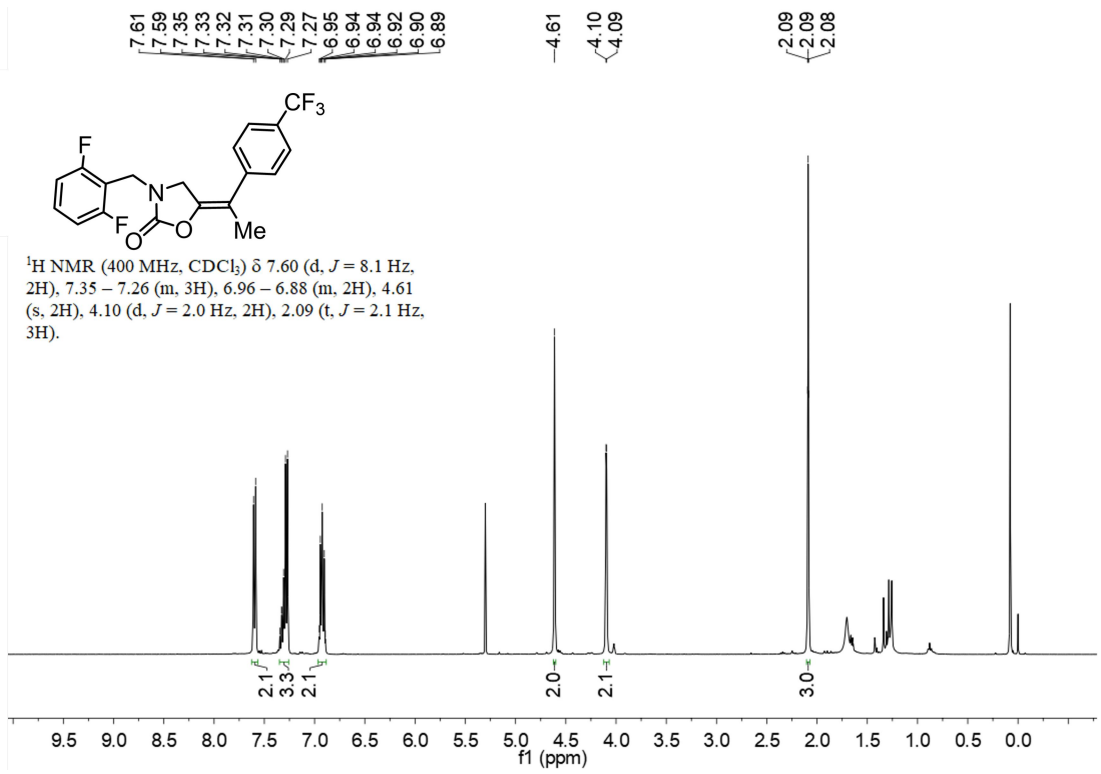
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.37, 155.49, 143.84, 139.82, 135.68, 134.90, 128.96, 128.68, 128.23, 128.09, 127.29, 111.51, 47.96, 47.45, 26.50, 16.07.



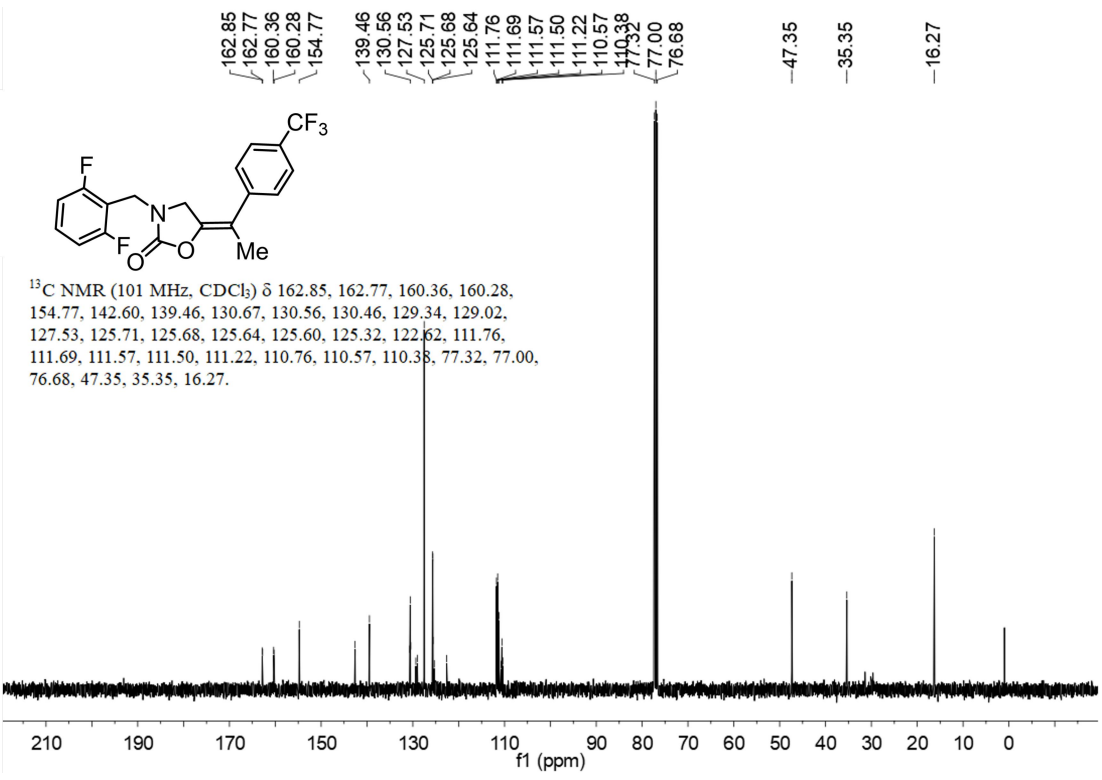
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.55 (m, 4H), 7.38 (d, J = 8.0 Hz, 2H), 7.28 – 7.24 (m, 2H), 4.52 (s, 2H), 4.07 (q, J = 1.9 Hz, 2H), 2.10 (t, J = 2.1 Hz, 3H).



^{13}C NMR (101 MHz, $CDCl_3$) δ 155.26, 143.52, 139.96, 138.91, 138.90, 138.89, 138.88, 138.87, 138.86, 132.45, 128.28, 128.27, 128.26, 127.82, 127.82, 127.81, 126.00, 125.96, 125.92, 125.89, 125.14, 118.42, 111.37, 110.82, 77.32, 77.00, 76.68, 47.48, 47.46, 16.00.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.1 Hz, 2H), 7.35 – 7.26 (m, 3H), 6.96 – 6.88 (m, 2H), 4.61 (s, 2H), 4.10 (d, J = 2.0 Hz, 2H), 2.09 (t, J = 2.1 Hz, 3H).



^{13}C NMR (101 MHz, $CDCl_3$) δ 162.85, 162.77, 160.36, 160.28, 154.77, 142.60, 139.46, 130.67, 130.56, 130.46, 129.34, 129.02, 127.53, 125.71, 125.68, 125.64, 125.60, 125.32, 122.62, 111.76, 111.69, 111.57, 111.50, 111.22, 110.76, 110.57, 110.38, 77.32, 77.00, 76.68, 47.35, 35.35, 16.27.

5. References

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