Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Low-melting Multicharge Ionic Liquids with $[Ln(NO_3)_5]^{2-}$ (*Ln* = Ho–Lu): Structural, Electrostatic, Thermochemical, and Fluorescence Properties

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Contents

Experimental Section

Chemicals and Materials. All chemicals and solvents were commercial and of reagent grade purity or higher. Solvents were dried by standard procedures. 1,2,3-trimethylimidazolium iodide ([MC_1mim]I), 1,2,3-trimethylimidazolium nitrate ([MC_1mim]NO_3), 1-alkyl-3-methylimidazolium bromides ([$C_n$mim]Br, n = 2, 4, 6, 8), and 1-alkyl-3-methylimidazolium nitrates ([$C_n$mim]NO_3, n = 2, 4, 6, 8) were synthesized according to the literature procedures.

General Methods. All the last products were synthesized by mixing above-mentioned imidazolium nitrate precursors (10 mmol) and lanthanide(III) (Ho, Er, Tm, Yb, Lu) nitrate (5 mmol) hexahydrate with a molar ratio of 2:1 in acetonitrile (10 mL) in a round flask. The reaction mixture was stirred at 60 °C for 72 hours. The mixture was dried to yield complex **1a** as yellowish solid, complex **2a** as pink solid and complex **3a**, **4a**, **5a** as white solid. Recrystallization from acetonitrile/ethyl acetate yielded transparent prisms crystals suitable for X-ray diffraction determination.

Infrared spectra (IR) were recorded on a NEXUS 670 FT-IR spectrometer using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz nuclear magnetic resonance spectrometer operating at 400 and 100 MHz, respectively, with DMSO-d_6 as locking solvent unless otherwise stated. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to TMS. Differential scanning calorimetry (DSC) measurements were performed on a TA Q20 calorimeter equipped with a cool accessory and calibrated using standard pure indium, which was gently flooded with N_2 with flow rate of 20 mL min^{-1}. Measurements were carried out by heating from −80 °C to 180 °C with a heating rate of 10 °C min^{-1}. Thermogravimetric analysis (TGA) measurements were accomplished on a NETZSCH TG 209F1 thermogravimetric analyzer by heating samples at 10 °C min^{-1} from 25 to 600 °C. Elemental analyses

(H, C and N) were performed on an Elementar Vario MICRO CUBE elemental analyzer. Related characterization data can be found in the Supporting Information.

Crystal Structure Determination. Single crystals of a were removed from the test tube; a suitable crystal was selected, attached to a glass fiber; and the data were collected at 143 K using a Xcalibur, Eos diffractometer. Using Olex2, the structure was solved with the olex2. solve structure solution program using charge flipping and refined with the ShelXL-2012 refinement package using least squares minimisation. The structure was solved in the space group C2/c by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp3 carbon atoms and 1.2 times for all other carbon atoms. All data were integrated with Crysalispro and an analytical absorption correction using SCALE3 ABSPACK was applied. For **1a,** R(int) was 0.0489 after correction. For **2a,** R(int) was 0.0454 after correction. For **3a,** R(int) was 0.0654 after correction. For **4a,** R(int) was 0.0469 after correction. For **5a,** R(int) was 0.0948 after correction. No decomposition was observed during data collection. More details concerning the crystallographic data can be requested from the Cambridge Crystallographic Data Center [www.ccdc.cam.ac.uk/data_request/cif] with the deposition numbers CCDC-2237582 (**1a**), CCDC-2237584(**2a**), CCDC-2237585 (**3a**), CCDC-2237588 (**4a**) and CCDC-2237590 (**5a**).

Photophysical Measurements. Luminescence spectra were recorded using a NanoLog infrared fluorescence spectrometer (Nanolog FL3-2iHR) with a xenon lamp (Xe900) as the excitation source, a photomultiplier tube for detection. Excitation and emission spectra were collected at 0.5 nm band pass at 293 K. Luminescence data were collected on samples placed into 2.4 mm quartz capillaries or quartz Suprasil cells. Emission and excitation spectra were measured on a NanoLog infrared fluorescence

spectrometer equipped with either a visible photomultiplier tube (PMT) (200−900 nm, R920), a NIR solid-state InGaAs detector (800−1700 nm, DSS-IGA020L). All spectra were corrected for instrumental functions. Luminescence lifetimes were determined under maximal excitation of samples. The output signal of the luminescence lifetimes are averages of at least three independent measurements. Quantum yields in the NIR were determined according to an absolute method.

Characterization Data

All the complexes were obtained from analogue routes yielded transparent liquid products. The details of data are summarized below:

$[MC_1mim]_2[Ho(NO_3)_5]$ (**1a**): 1,2,3-Trimethylimidazolium nitrate (1.7317 g, 10 mmol) and holmium(III) nitrate pentahydrate (2.2051 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 72 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a yellowish solid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 7.58 (s, 2H), 3.75 (s, 6H), 2.55 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, TMS): δ = 144.78, 122.98, 34.70, 9.13 ppm; IR (KBr): v = 3147, 2970, 2472, 1782, 1736, 1591, 1491, 1319, 1244, 1126, 1032, 814, 744, 658 cm^{-1}; Anal. calcd for **1a** $C_{12}H_{22}HoN_9O_{15}$ (697.28): C 20.67, H 3.18, N 18.08; found: C 20.68, H 3.52, N 18.52.

$[C_2mim]_2[Ho(NO_3)_5]$ (**1b**): 1-Ethyl-3-methylimidazolium nitrate (1.7317 g, 10 mmol) and holmium(III) nitrate pentahydrate (2.2051 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 72 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a yellowish liquid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.15 (s, 1H), 7.79 (s, 1H), 7.70 (s, 1H), 4.20 (q, J = 7.2 Hz, 2H; CH_2), 3.84 (s, 3H), 1.41 (t, J = 7.2 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, TMS): δ = 136.37, 123.66, 122.06, 44.20, 35.74, 15.18 ppm; IR (KBr): v = 3157, 3116, 2989, 1572, 1491, 1315, 1169, 1030, 841, 818, 746, 648, 623 cm^{-1};

Anal. calcd for **1b** $C_{12}H_{22}HoN_9O_{15}$ (697.28): C 20.67, H 3.18, N 18.08; found: C 20.22, H 3.54, N 17.80.

$[C_4mim]_2[Ho(NO_3)_5]$ (**1c**): 1-Butyl-3-methylimidazolium nitrate (2.0123 g, 10 mmol) and holmium(III) nitrate pentahydrate (2.2051 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 72 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a yellowish liquid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.16 (s, 1H), 7.78(s, 1H), 7.71 (s, 1H), 4.16 (t, J = 7.2 Hz, 2H; CH_2), 3.84 (s, 3H), 1.75 (m, 2H; CH_2), 1.23 (m, 2H; CH_2), 0.87 (t, J = 7.2 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, TMS): δ = 136.74, 123.76, 122.40, 48.60, 35.81, 31.74, 18.88, 13.37 ppm; IR (KBr): v = 3155, 3116, 2964, 2875, 1570, 1495, 1313, 1167, 1030, 843, 818, 746, 652, 623 cm^{-1}; Anal. calcd for **1c** $C_{16}H_{30}HoN_9O_{15}$ (753.39): C 25.51, H 4.01, N 16.73; found: C 25.72, H 4.20, N 16.84.

$[C_6mim]_2[Ho(NO_3)_5]$ (**1d**): 1-Hexyl-3-methylimidazolium nitrate (2.2928 g, 10 mmol) and holmium(III) nitrate pentahydrate (2.2051 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 84 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a yellowish liquid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.15 (s, 1H), 7.79 (s, 1H), 7.71 (s, 1H), 4.16 (t, J = 7.2 Hz, 2H; CH_2), 3.85 (s, 3H), 1.77 (m, 2H; CH_2), 1.26 (m, 6H; CH_2), 0.85 (t, J = 7.2 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, DMSO- d_6, 25 °C, TMS): δ = 136.63, 123.69, 122.35, 48.83, 35.79, 30.61, 29.41, 25.21, 21.94, 13.91 ppm; IR (KBr): v = 3153, 3115, 2956, 2931, 2864, 1570, 1498, 1313, 1165, 1030, 835, 818, 746, 654, 623 cm^{-1}; Anal. calcd for **1d** $C_{20}H_{38}HoN_9O_{15}$ (809.50): C 29.67, H 4.73, N 15.57; found: C 30.05, H 4.92, N 15.43.

$[C_8mim]_2[Ho(NO_3)_5]$ (**1e**): 1-Methyl-3-octylimidazolium nitrate (2.5733 g, 10 mmol) and holmium(III) nitrate pentahydrate (2.2051 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 84 h. After

reaction, the by-product water and the solvent were removed by distillation in vacuum to give a yellowish liquid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.16 (s, 1H), 7.79 (s, 1H), 7.71 (s, 1H), 4.15 (t, J = 7.2 Hz, 2H; CH_2), 3.85 (s, 3H), 1.77 (m, 2H; CH_2), 1.23 (m, 10H; CH_2), 0.83(t, J = 7.2 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, TMS): δ = 136.67, 123.71, 122.38, 48.86, 35.80, 31.26, 29.49, 28.57, 28.43, 25.59, 22.15, 14.03 ppm; IR (KBr): v = 3155, 3115, 2929, 2858, 1570, 1491, 1313, 1165,1030, 843, 818, 746, 654, 623 cm^{-1}; Anal. calcd for **1e** $C_{24}H_{46}HoN_9O_{15}$ (865.60): C 33.30, H 5.36, N 14.56; found: C 33.67, H 5.61, N 14.70.

$[MC_1mim]_2[Er(NO_3)_5]$ (**2a**): 1,2,3-Trimethylimidazolium nitrate (1.7317 g, 10 mmol) and erbium(III) nitrate pentahydrate (2.2168 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 72 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a light red solid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 7.58 (s, 2H), 3.75 (s, 6H), 2.55 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, TMS): δ = 144.88, 122.08, 34.80, 9.23 ppm; IR (KBr): v = 3151, 2968, 2405, 1770, 1736, 1595, 1483, 1311, 1128, 1093, 1032, 862, 814, 742, 647 cm^{-1}; Anal. calcd for **2a** $C_{12}H_{22}ErN_9O_{15}$ (699.61): C 20.60, H 3.17, N 18.02; found: C 20.36, H 3.23, N 18.38.

$[C_2mim]_2[Er(NO_3)_5]$ (**2b**): 1-Ethyl-3-methylimidazolium nitrate (1.7317 g, 10 mmol) and erbium(III) nitrate pentahydrate (2.2168 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 72 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a light red liquid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.14 (s, 1H), 7.79 (s, 1H), 7.70 (s, 1H), 4.19 (q, J = 7.2 Hz, 2H; CH_2), 3.84 (s, 3H), 1.41 (t, J = 7.2 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, TMS): δ = 136.70, 123.94, 122.36, 44.50, 36.03, 15.50 ppm; IR

(KBr): v = 3159, 3120, 2989, 1572, 1495, 1315, 1167, 1030, 843, 816, 746, 646, 623 cm^{-1}; Anal. calcd for **2b** $C_{12}H_{22}ErN_9O_{15}$ (699.61): C 20.60, H 3.17, N 18.02; found: C 20.18, H 3.37, N 18.10.

$[C_4mim]_2[Er(NO_3)_5]$ (**2c**): 1-Butyl-3-methylimidazolium nitrate (2.0123 g, 10 mmol) and erbium(III) nitrate pentahydrate (2.2168 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 72 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a light red liquid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.14 (s, 1H), 7.78(s, 1H), 7.71 (s, 1H), 4.16 (t, J = 7.2 Hz, 2H; CH_2), 3.85 (s, 3H), 1.76 (m, 2H; CH_2), 1.26 (m, 2H; CH_2), 0.90 (t, J = 7.2 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, TMS): δ = 136.86, 123.88, 122.54, 48.76, 35.97, 31.64, 19.06, 13.56 ppm; IR (KBr): v = 3157, 3118, 2964, 2875, 1570, 1498, 1315, 1167, 1030, 843, 816, 746, 652, 623 cm^{-1}; Anal. calcd for **2c** $C_{16}H_{30}ErN_9O_{15}$ (755.72): C 25.43, H 4.00, N 16.68; found: C 24.97, H 4.16, N 16.77.

$[C_6mim]_2[Er(NO_3)_5]$ (**2d**): 1-Hexyl-3-methylimidazolium nitrate (2.2928 g, 10 mmol) and erbium(III) nitrate pentahydrate (2.2168 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 84 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a light red liquid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.17 (s, 1H), 7.79 (s, 1H), 7.72 (s, 1H), 4.17 (t, J = 7.2 Hz, 2H; CH_2), 3.87 (s, 3H), 1.78 (m, 2H; CH_2), 1.28 (m, 6H; CH_2), 0.88 (t, J = 7.2 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, DMSO- d_6, 25 °C, TMS): δ = 136.67, 123.74, 122.40, 48.88, 35.85, 30.67, 29.46, 25.26, 22.00, 13.98 ppm; IR (KBr): v = 3155, 3118, 2958, 2933, 2864, 1570, 1498, 1315, 1165, 1030, 843, 816, 746, 652, 623 cm^{-1}; Anal. calcd for **2d** $C_{20}H_{38}ErN_9O_{15}$ (811.83): C 29.59, H 4.72, N 15.53; found: C 29.29, H 4.85, N 15.98.

$[C_8mim]_2[Er(NO_3)_5]$ (**2e**): 1-Methyl-3-octylimidazolium nitrate (2.5733 g, 10 mmol) and erbium(III) nitrate pentahydrate (2.2168 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 84 h. After

reaction, the by-product water and the solvent were removed by distillation in vacuum to give a light red liquid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.11 (s, 1H), 7.779 (s, 1H), 7.70 (s, 1H), 4.14 (t, J = 7.2 Hz, 2H; CH_2), 3.84 (s, 3H), 1.77 (m, 2H; CH_2), 1.25 (m, 10H; CH_2), 0.85(t, J = 7.2 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, TMS): δ = 136.60, 123.69, 122.35, 48.84, 35.81, 31.28, 29.45, 28.55, 28.40, 25.57, 22.13, 14.03 ppm; IR (KBr): v = 3155, 3118, 2929, 2858, 1570, 1491, 1310, 1165, 1030, 845, 816, 746, 652, 623 cm^{-1}; Anal. calcd for **2e** $C_{24}H_{46}ErN_9O_{15}$ (867.93): C 33.21, H 5.34, N 14.52; found: C 33.65, H 5.23, N 14.66.

$[MC_1mim]_2[Tm(NO_3)_5]$ (**3a**): 1,2,3-Trimethylimidazolium nitrate (1.7317 g, 10 mmol) and thulium(III) nitrate pentahydrate (2.2252 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 72 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a light green solid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 7.578 (s, 2H), 3.74 (s, 6H), 2.54 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, TMS): δ = 144.94, 122.05, 34.76, 9.28 ppm; IR (KBr): v = 3151, 2968, 2405, 1770, 1736, 1595, 1483, 1311, 1128, 1093, 1032, 862, 814, 742, 647 cm^{-1}; Anal. calcd for **3a** $C_{12}H_{22}TmN_9O_{15}$ (701.29): C 20.55, H 3.16, N 17.98; found: C 20.13, H 3.17, N 18.08.

$[C_2mim]_2[Tm(NO_3)_5]$ (**3b**): 1-Ethyl-3-methylimidazolium nitrate (1.7317 g, 10 mmol) and thulium(III) nitrate pentahydrate (2.2252 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 72 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a light green liquid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.12 (s, 1H), 7.77 (s, 1H), 7.69 (s, 1H), 4.18 (q, J = 7.2 Hz, 2H; CH_2), 3.83 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, TMS): δ = 136.37, 123.66, 122.06, 44.20, 3521.74, 15.18 ppm;

IR (KBr): v = 3159, 3120, 2989, 1572, 1498, 1317, 1167, 1030, 843, 816, 748, 646, 623 cm^{-1}; Anal. calcd for **3b** $C_{12}H_{22}TmN_9O_{15}$ (701.29): C 20.55, H 3.16, N 17.98; found: C 20.28, H 3.41, N 18.08.

$[C_4mim]_2[Tm(NO_3)_5]$ (**3c**): 1-Butyl-3-methylimidazolium nitrate (2.0123 g, 10 mmol) and thulium(III) nitrate pentahydrate (2.2252 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 72 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a light green liquid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.13 (s, 1H), 7.77(s, 1H), 7.70 (s, 1H), 4.15 (t, J = 7.2 Hz, 2H; CH_2), 3.84 (s, 3H), 1.75 (m, 2H; CH_2), 1.25 (m, 2H; CH_2), 0.90 (t, J = 7.2 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, TMS): δ = 136.74, 123.76, 122.40, 48.60, 35.81, 31.74, 18.88, 13.37 ppm; IR (KBr): v = 3157, 3118, 2964, 2875, 1570, 1491, 1317, 1167, 1030, 843, 818, 748, 652, 623 cm^{-1}; Anal. calcd for **3c** $C_{16}H_{30}TmN_9O_{15}$ (757.39): C 25.37, H 3.99, N 16.64; found: C 24.88, H 4.06, N 17.07.

$[C_6mim]_2[Tm(NO_3)_5]$ (**3d**): 1-Hexyl-3-methylimidazolium nitrate (2.2928 g, 10 mmol) and thulium(III) nitrate pentahydrate (2.2252 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 84 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a light green liquid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.11 (s, 1H), 7.76 (s, 1H), 7.69 (s, 1H), 4.14 (t, J = 7.2 Hz, 2H; CH_2), 3.84 (s, 3H), 1.76 (m, 2H; CH_2), 1.265 (m, 6H; CH_2), 0.86 (t, J = 7.2 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, DMSO- d_6, 25 °C, TMS): δ = 136.63, 123.69, 122.35, 48.83, 35.79, 30.61, 29.41, 25.21, 21.94, 13.91 ppm; IR (KBr): v = 3155, 3116, 2958, 2931, 2864, 1570, 1498, 1315, 1165, 1030, 843, 816, 746, 652, 623 cm^{-1}; Anal. calcd for **3d** $C_{20}H_{38}TmN_9O_{15}$ (813.50): C 29.53, H 4.71, N 15.50; found: C 29.24, H 4.77, N 15.72.

$[C_8mim]_2[Tm(NO_3)_5]$ (**3e**): 1-Methyl-3-octylimidazolium nitrate (2.5733 g, 10 mmol) and thulium(III) nitrate pentahydrate (2.2252 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 84 h. After

reaction, the by-product water and the solvent were removed by distillation in vacuum to give a light green liquid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.156 (s, 1H), 7.779 (s, 1H), 7.70 (s, 1H), 4.14 (t, J = 7.2 Hz, 2H; CH_2), 3.85 (s, 3H), 1.76 (m, 2H; CH_2), 1.25 (m, 10H; CH_2), 0.89(t, J = 7.2 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, TMS): δ = 136.87, 123.89, 122.56, 49.06, 36.00, 31.49, 29.68, 28.79, 28.64, 25.759, 22.39, 14.29 ppm; IR (KBr): ν = 3155, 3116, 2929, 2858, 1570, 1498, 1313, 1165, 1028, 845, 816, 748, 652, 623 cm^{-1}; Anal. calcd for **3e** $C_{24}H_{46}TmN_9O_{15}$ (869.61): C 33.15, H 5.33, N 14.50; found: C 32.72, H 5.55, N 14.34.

$[MC_1mim]_2[Yb(NO_3)_5]$ (**4a**): 1,2,3-Trimethylimidazolium nitrate (1.7317 g, 10 mmol) and ytterbium(III) nitrate pentahydrate (2.2456 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 72 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a white solid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 7.60 (s, 2H), 3.77 (s, 6H), 2.57 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d6, 25 °C, TMS): δ = 144.86, 122.05, 34.76, 9.19 ppm. ATR-IR (25 °C): υ = 3146, 1782, 1739, 1589, 1474, 1310, 1242, 1126, 1093, 1032, 864, 815, 810, 761, 747, 734, 707, 658, 621, 584, 478 cm^{-1}; elemental analysis: calcd(%)for **4a** ($C_{12}H_{22}YbN_9O_{15}$, 705.41): C 20.43, H 3.14, N 17.87; found: C 20.84, H 2.98, N 16.86.

$[C_2mim]_2[Yb(NO_3)_5]$ (**4b**): 1-Ethyl-3-methylimidazolium nitrate (1.7317 g, 10 mmol) and ytterbium(III) nitrate pentahydrate (2.2456 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 72 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a white solid in quantitative yield. ^{1}H NMR(400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.18 (s, 1H), 7.81 (s,1H), 7.72 (s, 1H), 4.22 (q, 3J(H,H) = 7.2 Hz, 2H; CH_2), 3.86 (s,3H), 1.42 (t, 3J(H,H) = 7.2 Hz, 3H; CH_3) ppm; ^{13}C NMR(100 MHz, DMSO-d_6, 25 °C, TMS): δ = 136.44,

123.71, 122.12, 44.26, 35.80, 15.25 ppm; ATR-IR (25 °C): υ = 3157, 3117, 2986, 2947, 2530, 1777, 1733, 1572, 1479, 1302, 1164, 1027, 840, 814, 746, 647, 621 cm^{-1}; elemental analysis: calcd(%) for **4b** ($C_{12}H_{22}YbN_9O_{15}$, 705.41): C 20.43, H 3.14, N 17.87; found: C 20.30, H 3.28,N 17.36.

$[C_4mim]_2[Yb(NO_3)_5]$ (**4c**): 1-Butyl-3-methylimidazolium nitrate (2.0123 g, 10 mmol) and ytterbium(III) nitrate pentahydrate (2.2456 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 72 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a colorless liquid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.16 (s, 1H), 7.79 (s, 1H), 7.72 (s, 1H), 4.17 (t, 3J(H,H) = 7.2 Hz, 2H; CH_2), 3.86 (s,3H), 1.75 (m, 2H; CH_2), 1.25 (m, 2H; CH_2), 0.91 (t, 3J(H,H) = 7.4 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C,TMS): δ = 136.68, 123.73, 122.39, 48.58, 35.82, 31.46, 18.88,13.38 ppm; ATR-IR (25 °C): υ = 3153, 3117, 2963,2939, 2874, 1569,1481, 1302, 1163, 1027, 841, 814, 748, 650, 621 cm^{-1}; elemen-tal analysis: calcd(%) for **4c** ($C_{16}H_{30}YbN_9O_{15}$, 761.51): C 25.24, H 3.97, N 16.55; found: C 25.01, H 4.15, N 16.48.

$[C_6mim]_2[Yb(NO_3)_5]$ (**4d**): 1-Hexyl-3-methylimidazolium nitrate (2.2928 g, 10 mmol) and ytterbium(III) nitrate pentahydrate (2.2456 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 84 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a colorless liquid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.15 (s, 1H), 7.78 (s, 1H), 7.72 (s, 1H), 4.16 (t, 3J(H,H) = 7.2 Hz, 2H; CH_2), 3.86 (s,3H), 1.76 (m, 2H; CH_2), 1.27 (m, 6H; CH_2), 0.87 (t, 3J(H,H) = 6.9 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C,TMS): δ = 136.65, 123.72, 122.37, 48.85, 35.81, 30.64, 29.43, 25.24, 21.98, 13.95 ppm; ATR-IR (25 °C): υ = 3152 3116, 2958, 2930, 2862, 1570, 1482, 1303,

1162, 1027, 844, 814, 748, 650, 622cm^{-1}; elemental analysis: calcd(%) for **4d** ($C_{20}H_{38}YbN_9O_{15}$, 817.62): C 29.38, H 4.68, N 15.42; found: C 29.42, H 4.70, N 15.40.

$[C_8mim]_2[Yb(NO_3)_5]$ (**4e**): 1-Methyl-3-octylimidazolium nitrate (2.5733 g, 10 mmol) and ytterbium(III) nitrate pentahydrate (2.2456 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 84 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a colorless liquid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.15 (s, 1H), 7.78 (s, 1H), 7.71 (s, 1H), 4.15 (t, 3J(H,H) = 7.2 Hz, 2H; CH_2), 3.85 (s, 3H), 1.77 (m, 2H; CH_2), 1.25 (m, 10H; CH_2), 0.86 (t, 3J(H,H) = 6.8 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6,25 °C, TMS): δ = 136.59, 123.68, 122.33, 48.73, 35.79, 31.23, 29.44, 28.54, 28.39, 25.55, 22.12, 14.02 ppm; ATR-IR (25 °C): υ = 3158, 3122, 2954, 2929, 2857, 1571, 1483, 1304, 1163, 1027, 845, 814, 747, 650, 622 cm^{-1}; elemental analysis: calcd(%) for **4e** ($C_{24}H_{46}YbN_9O_{15}$, 873.73): C 32.99, H 5.52, N 14.43; found: C 32.90, H 5.52, N 14.31.

$[MC_1mim]_2[Lu(NO_3)_5]$ (**5a**): 1,2,3-Trimethylimidazolium nitrate (1.7317 g, 10 mmol) and lutetium(III) nitrate hexahydrate (2.3454 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 72 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a white solid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 7.58 (s, 2H), 3.74 (s, 6H), 2.54 (s, 3H) ppm. ^{13}C NMR(100 MHz, DMSO-d_6, 25 °C, TMS): δ = 144.87, 122.05, 34.14, 9.17 ppm. ATR-IR (25 °C): υ = 3145, 1782, 1738, 1589, 1474, 1293, 1242, 1126, 1093, 1032, 865, 815, 810, 760, 748, 733, 707, 658, 621, 583, 477 cm^{-1}; elemental analysis: calcd(%)for **5a** ($C_{12}H_{22}LuN_9O_{15}$, 707.32): C 20.38, H 3.14, N 17.82; found: C 20.08, H 2.93, N 17.59.

$[C_2mim]_2[Lu(NO_3)_5]$ (**5b**): 1-Ethyl-3-methylimidazolium nitrate (1.7317 g, 10 mmol) and lutetium(III) nitrate hexahydrate (2. 3454 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 72 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a white solid in quantitative yield. ^{1}H NMR(400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.17 (s, 1H), 7.78 (s,1H), 7.69 (s, 1H), 4.17 (q, 3J(H,H) = 7.2 Hz, 2H; CH_2), 3.83 (s,3H), 1.38 (t, 3J(H,H) = 7.2 Hz, 3H; CH3) ppm; ^{13}C NMR(100 MHz, DMSO-d_6, 25 °C, TMS): δ = 136.54, 123.75, 123.16, 44.31, 35.81, 15.29 ppm; ATR-IR (25 °C): υ = 3158, 3117, 2992,2522, 1734, 1570, 1479, 1304, 1164, 1027, 840, 814, 747, 647, 621 cm^{-1}; elemental analysis: calcd(%) for **5b** ($C_{12}H_{22}LuN_9O_{15}$,707.32): C 20.38, H 3.14, N 17.82; found: C 20.39, H 3.20, N 17.80.

$[C_4mim]_2[Lu(NO_3)_5]$ (**5c**): 1-Butyl-3-methylimidazolium nitrate (2.0123 g, 10 mmol) and lutetium(III) nitrate hexahydrate (2. 3454 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 72 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a colorless liquid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.15 (s, 1H), 7.77(s, 1H), 7.70 (s, 1H), 4.15 (t, 3J(H,H) = 7.2 Hz, 2H; CH_2), 3.84 (s,3H), 1.75 (m, 2H; CH_2), 1.23 (m, 2H; CH_2), 0.88 (t, 3J(H,H) = 7.4 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C,TMS): δ = 136.65, 123.69, 122.35, 48.56, 35.78, 31.43, 18.84, 13.34 ppm; ATR-IR (25 °C): υ = 3153, 3117, 2963, 2939, 2874, 1569, 1481, 1302, 1163, 1027, 841, 814, 748, 650, 621 cm^{-1}; elemen-tal analysis: calcd(%) for **5c** ($C_{16}H_{30}LuN_9O_{15}$, 763.43): C 25.17, H 3.96, N 16.51; found: C 25.20,H 3.90, N 16.61.

$[C_6mim]_2[Lu(NO_3)_5]$ (**5d**): 1-Hexyl-3-methylimidazolium nitrate (2.2928 g, 10 mmol) and lutetium(III) nitrate hexahydrate (2. 3454 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 84 h. After reaction, the by-product water and the solvent were removed by distillation in

vacuum to give a colorless liquid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.19 (s, 1H), 7.78(s, 1H), 7.70 (s, 1H), 4.13 (t, 3J(H,H) = 7.2 Hz, 2H; CH_2), 3.83 (s,3H), 1.74 (m, 2H; CH_2), 1.22 (m, 6H; CH_2), 0.81 (t, 3J(H,H) = 6.9 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C,TMS): δ = 136.92, 123.85, 122.54, 49.02, 35.90, 30.79, 30.62,25.39, 22.14, 14.08 ppm; ATR-IR (25 °C): υ = 3156, 3116, 2958,2931, 2873, 2863, 1570, 1482, 1305, 1163, 1027, 844, 814, 748, 650,622cm−1; elemental analysis: calcd(%) for **5d** ($C_{20}H_{38}LuN_9O_{15}$, 819.53): C 29.31, H 4.67, N 15.38; found: C 29.41, H 4.69, N 15.39.

$[C_8mim]_2[Lu(NO_3)_5]$ (**5e**): 1-Methyl-3-octylimidazolium nitrate (2.5733 g, 10 mmol) and lutetium(III) nitrate hexahydrate (2. 3454 g, 5 mmol) were reacted in acetonitrile (10 mL) at 60 °C for 84 h. After reaction, the by-product water and the solvent were removed by distillation in vacuum to give a colorless liquid in quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.17 (s, 1H), 7.77 (s, 1H), 7.70 (s, 1H), 4.14 (t, 3J(H, H) = 7.2 Hz, 2H; CH_2), 3.84 (s, 3H), 1.75 (m, 2H; CH_2), 1.22 (m, 10H; CH_2), 0.83 (t, 3J(H,H) = 6.8 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, TMS): δ = 136.75, 123.74, 122.42, 48.90, 35.82, 31.30,29.54, 28.62, 28.47, 25.64, 22.20, 14.08 ppm; ATR-IR (25 °C): υ = 3156, 3152, 3116, 2956, 2929, 2857, 1570, 1484, 1305, 1162, 1027, 845, 814, 748, 651, 622 cm^{-1}; elemental analysis: calcd(%) for **5e**($C_{24}H_{46}LuN_9O_{15}$, 875.64): C 32.92, H 5.3, N 14.40; found: C 32.81, H 5.31, N 14.44.

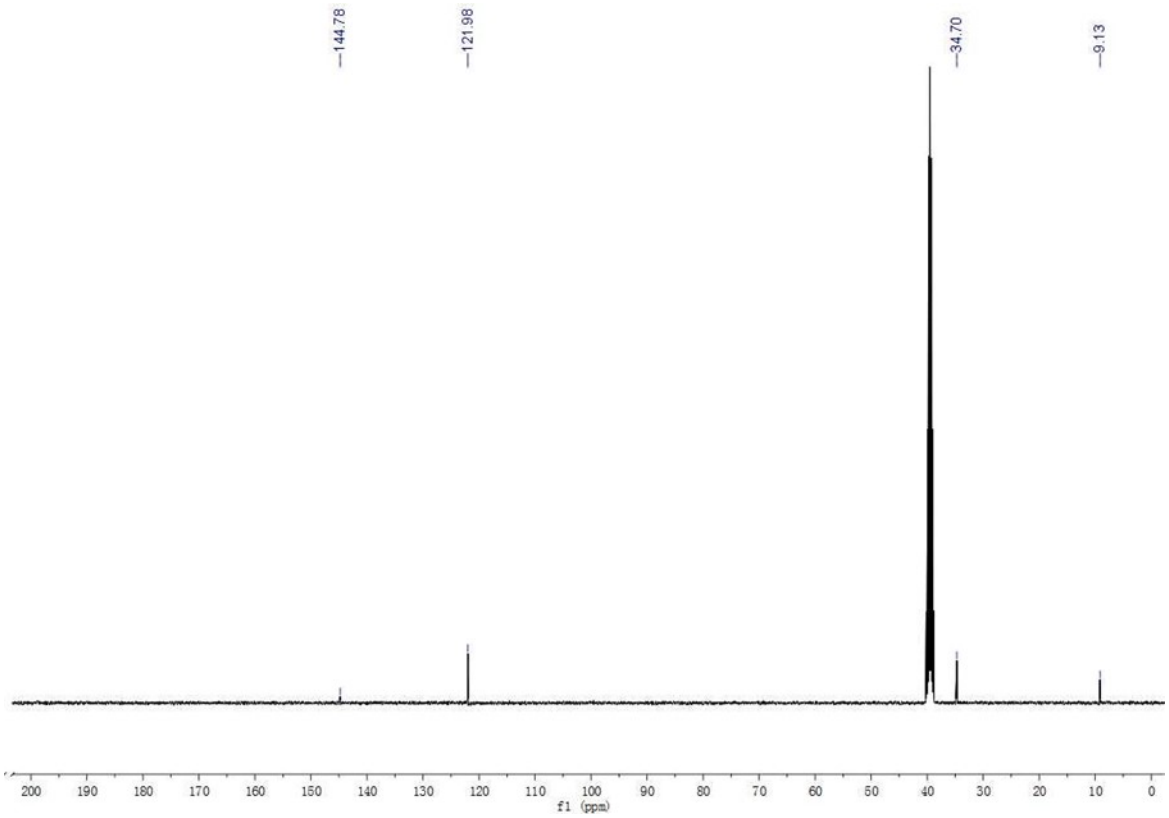

Figure S1. The ^{13}C NMR spectrum of **1a**.

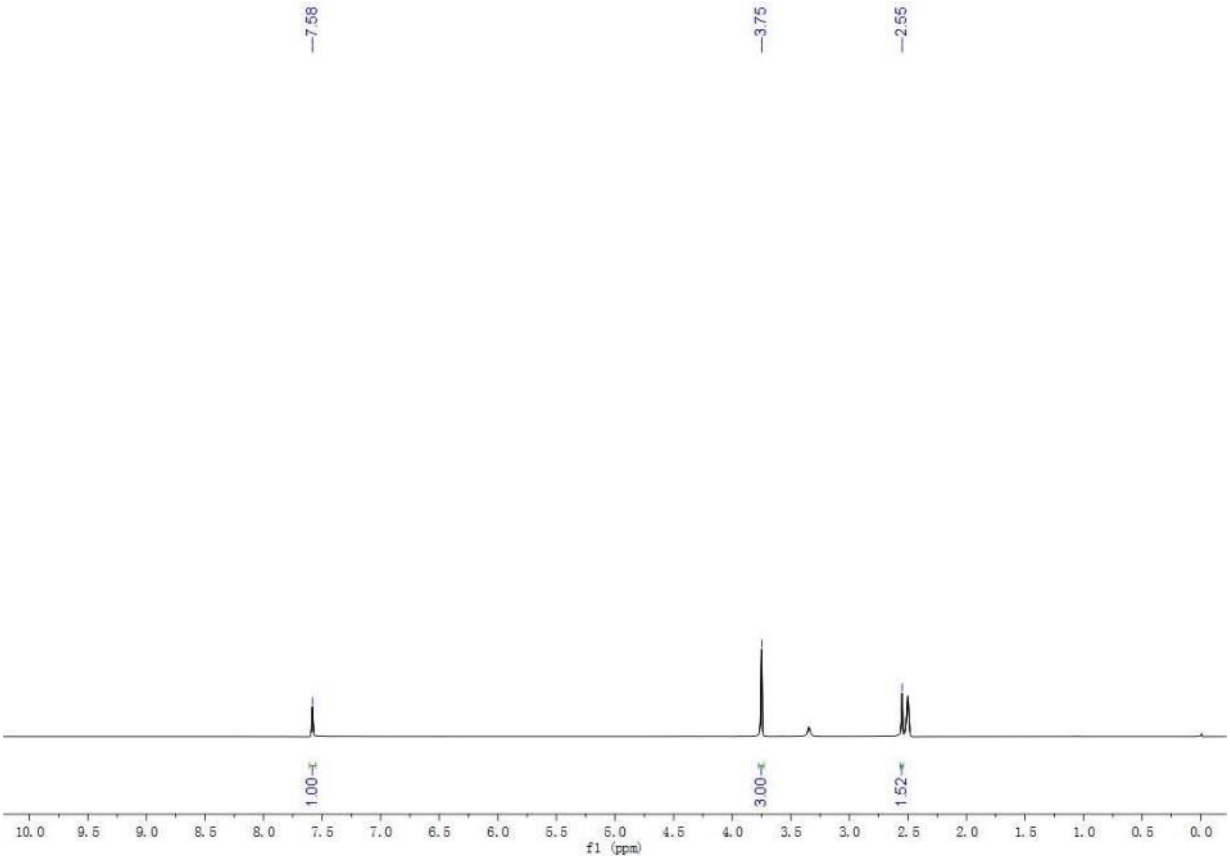

Figure S2. The ^{1}H NMR spectrum of **1a**.

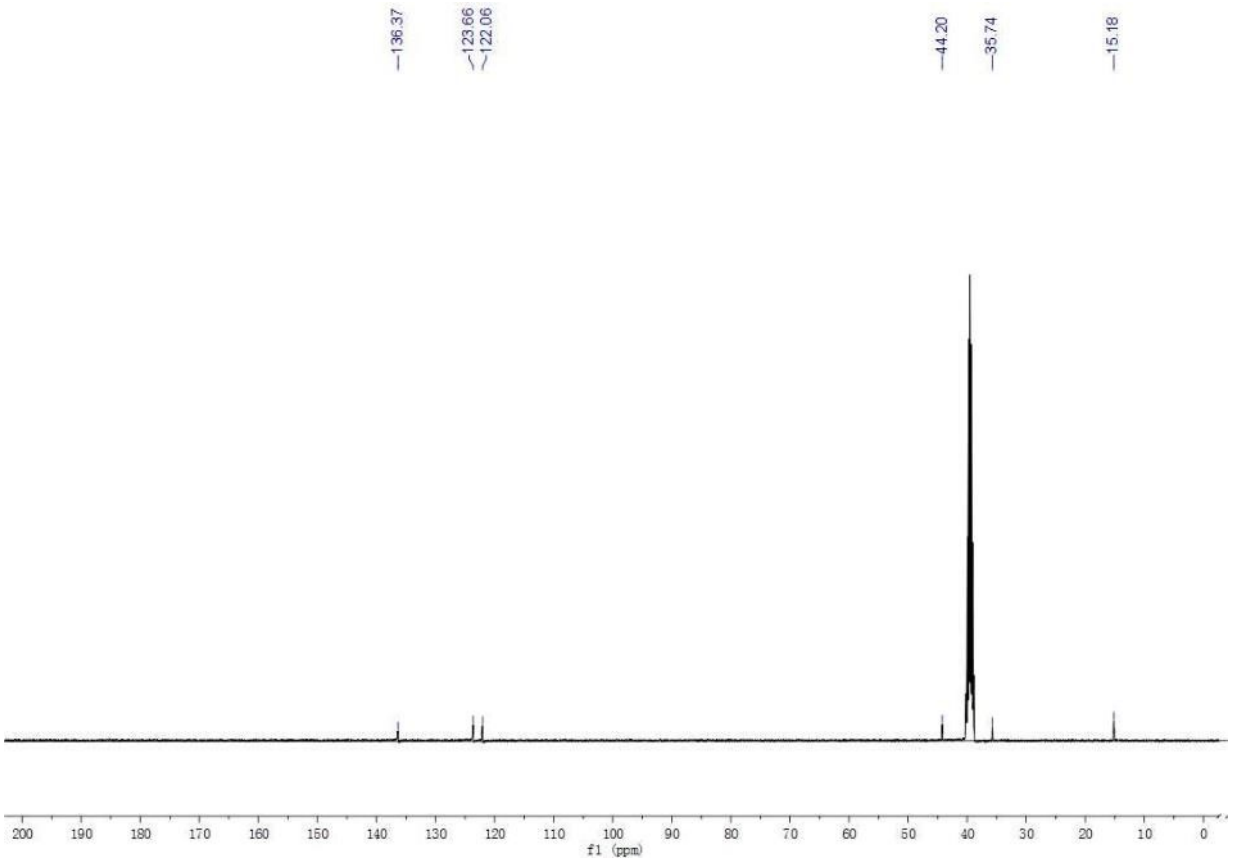

Figure S3. The ^{13}C NMR spectrum of **1b**.

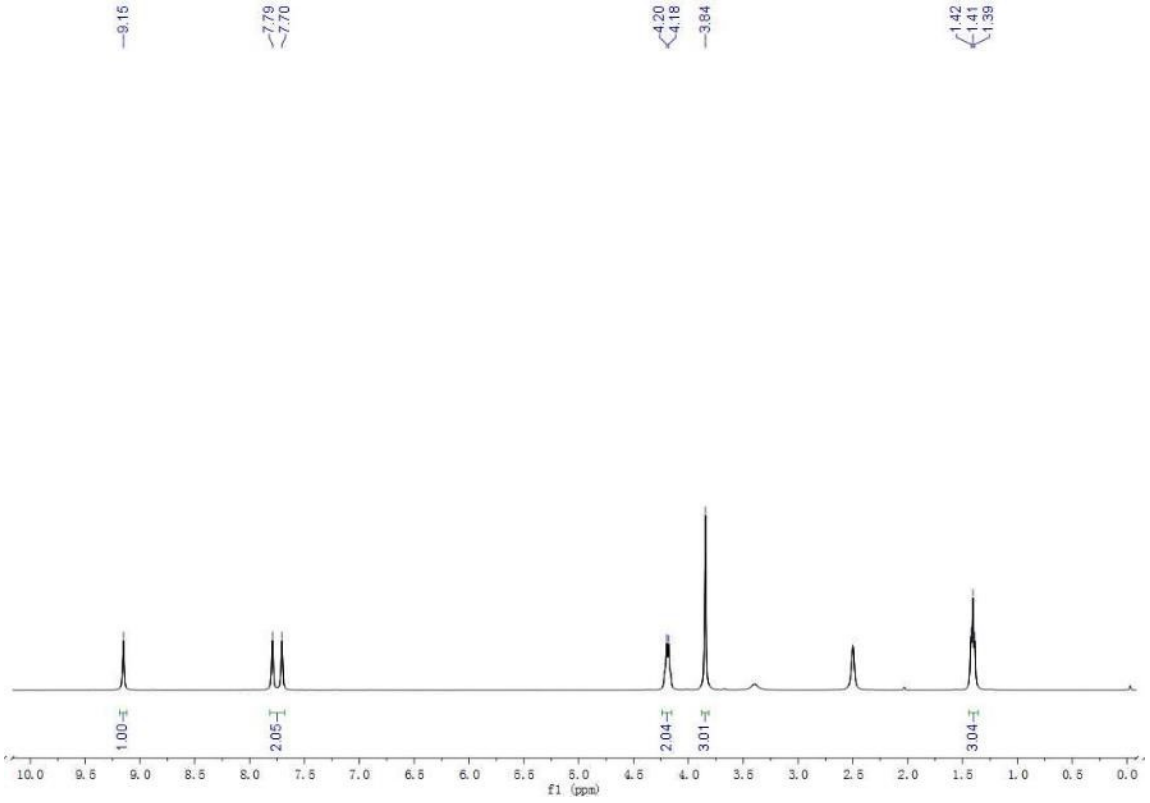

Figure S4. The ^{1}H NMR spectrum of **1b**.

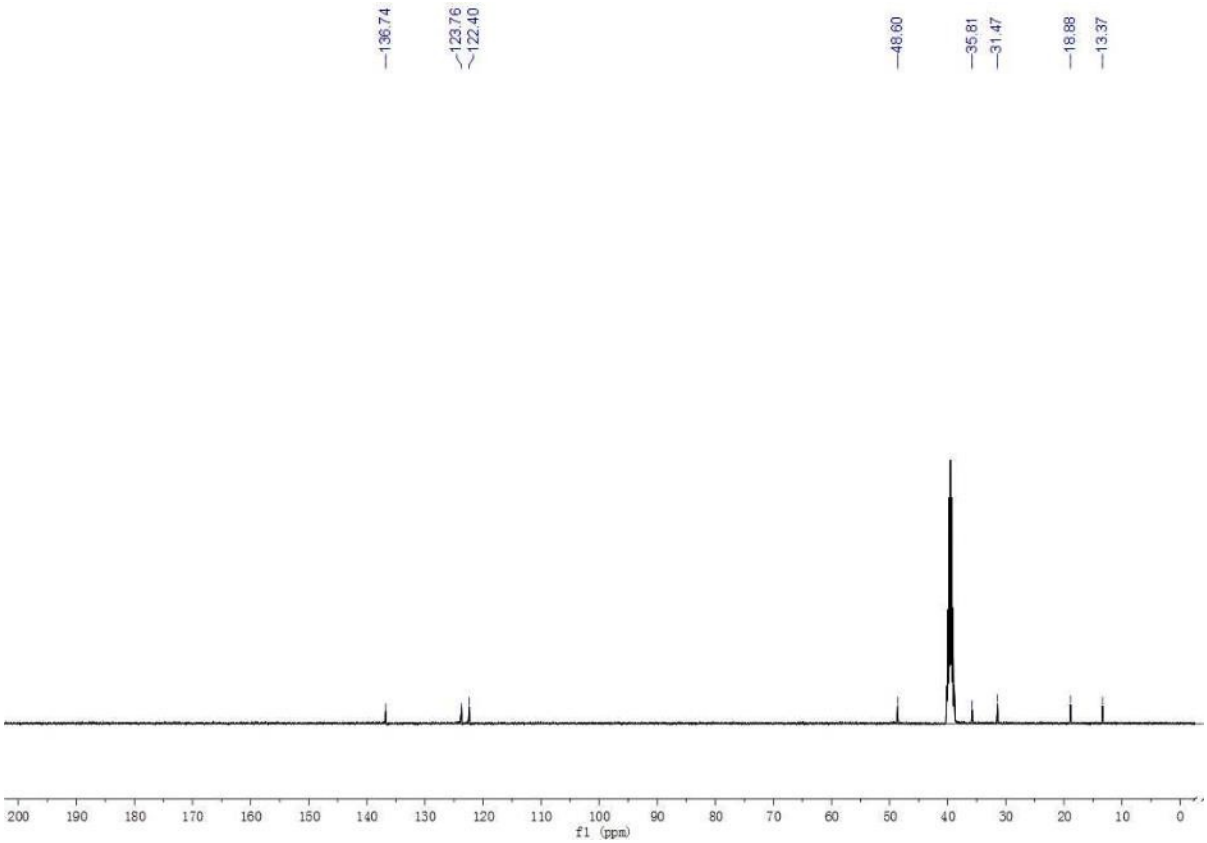

Figure S5. The ^{13}C NMR spectrum of **1c**.

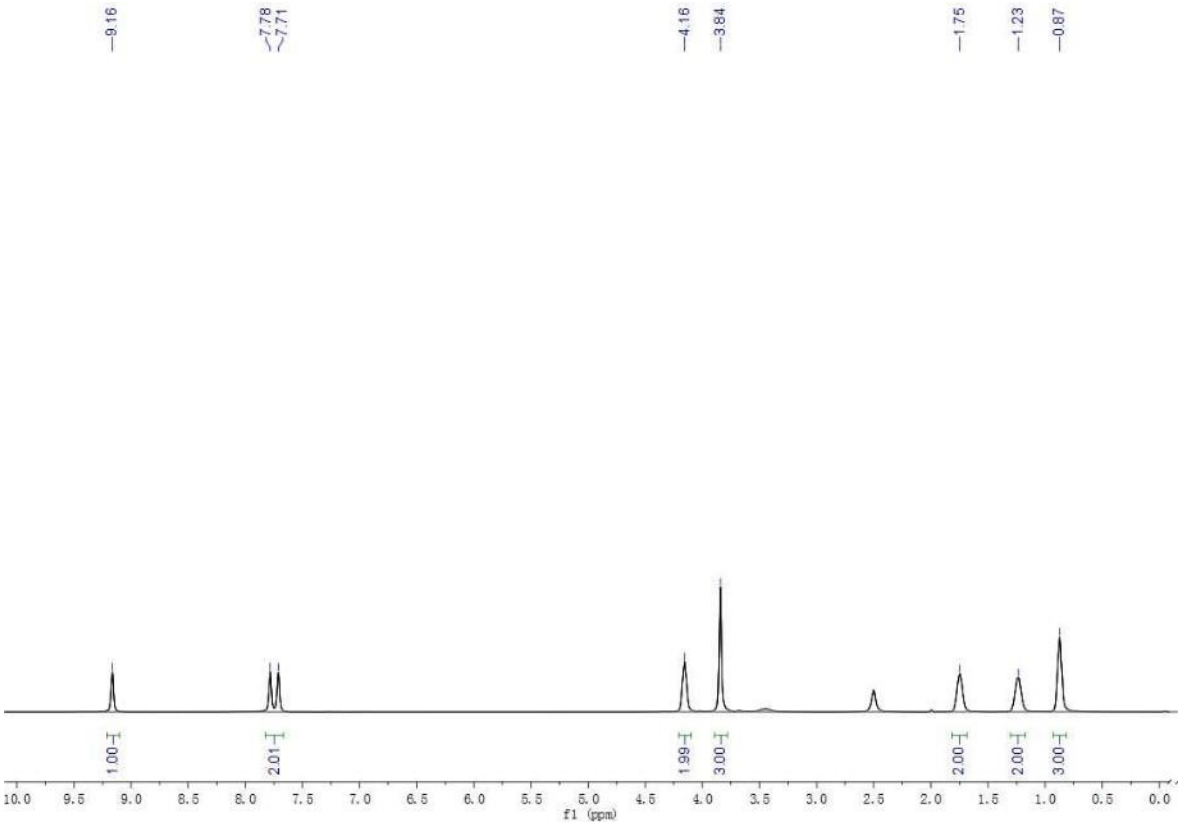

Figure S6. The ^{1}H NMR spectrum of **1c**.

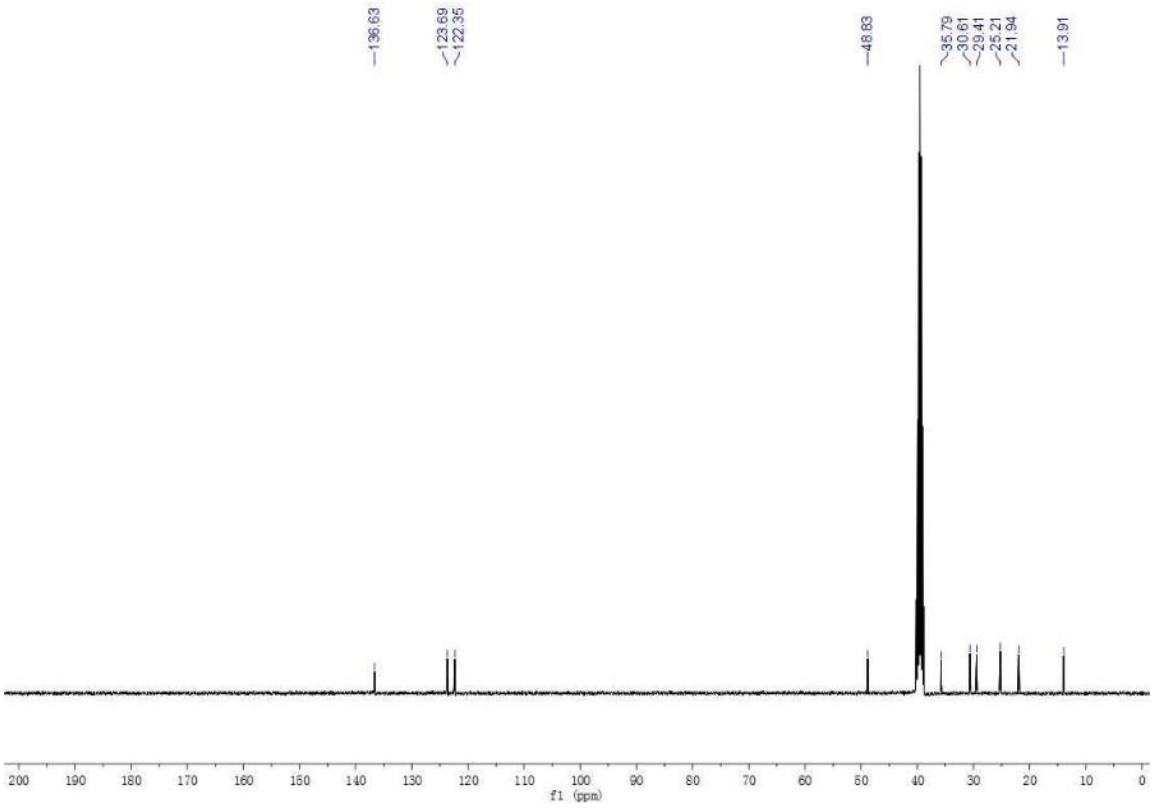

Figure S7. The ^{13}C NMR spectrum of **1d**.

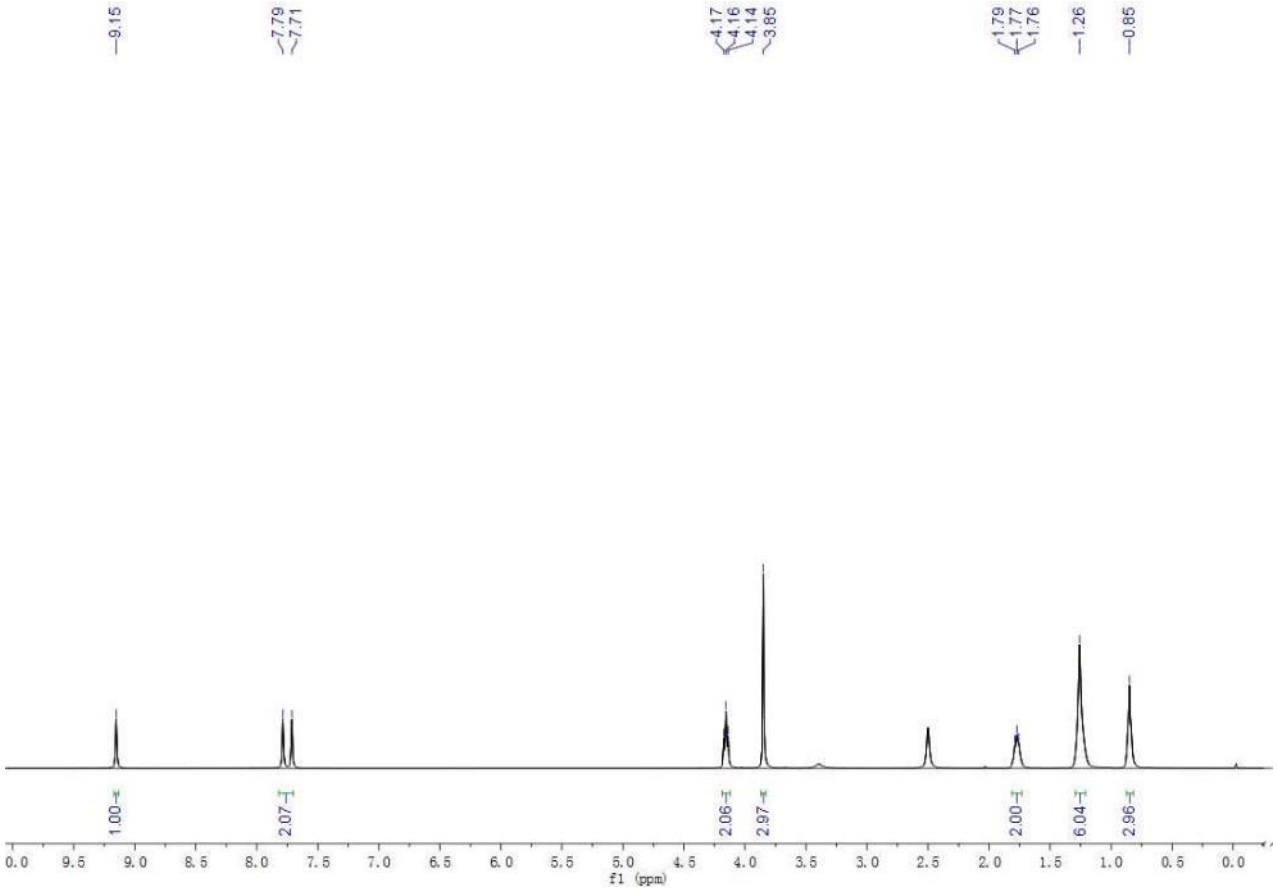

Figure S8. The ^{1}H NMR spectrum of **1d**.

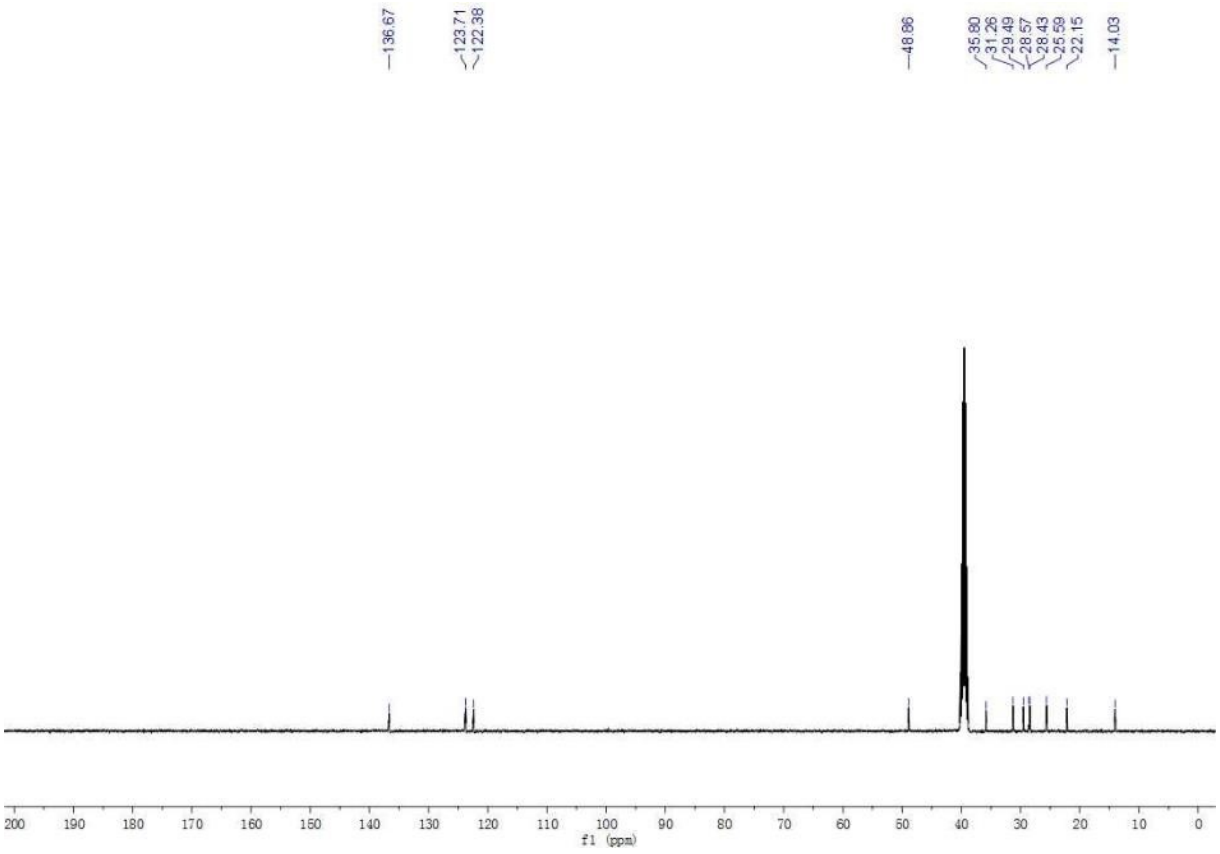

Figure S9. The ^{13}C NMR spectrum of **1e**.

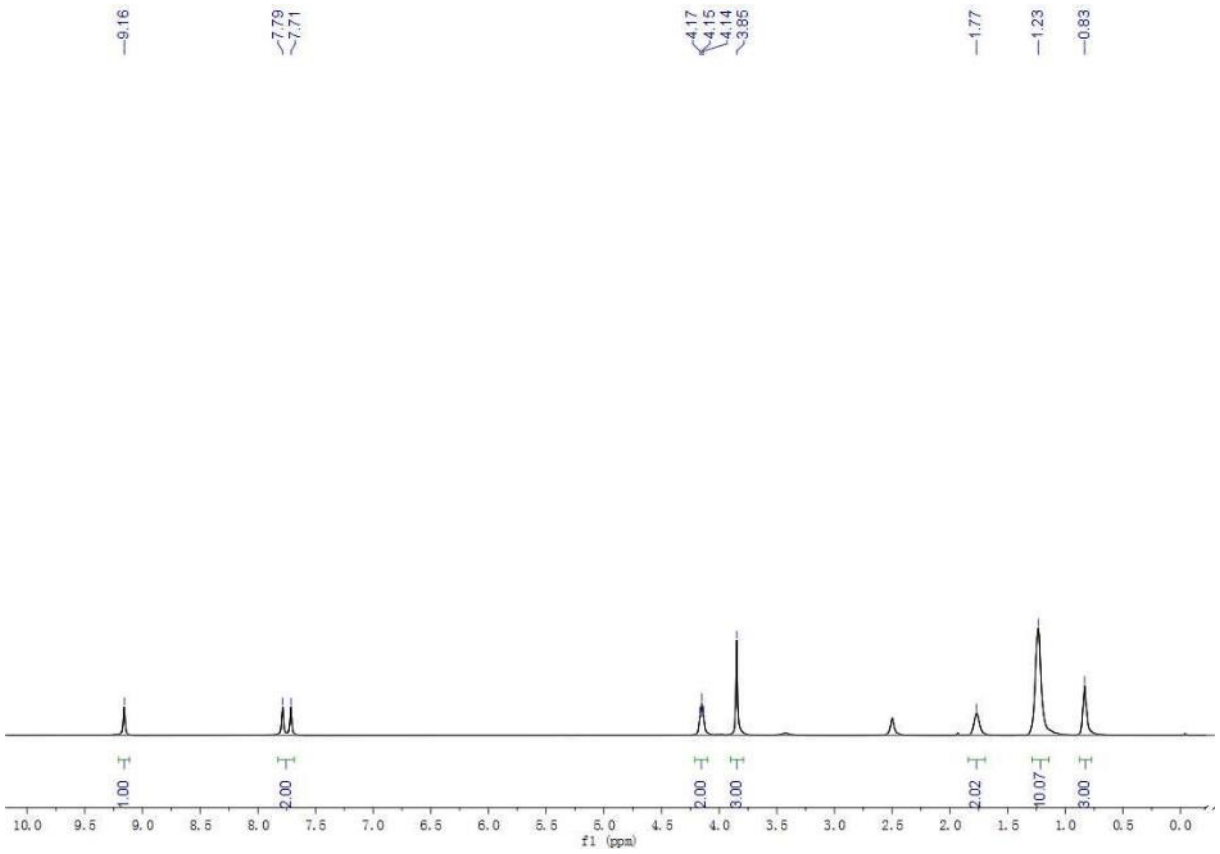

Figure S10. The ^{1}H NMR spectrum of **1e**.

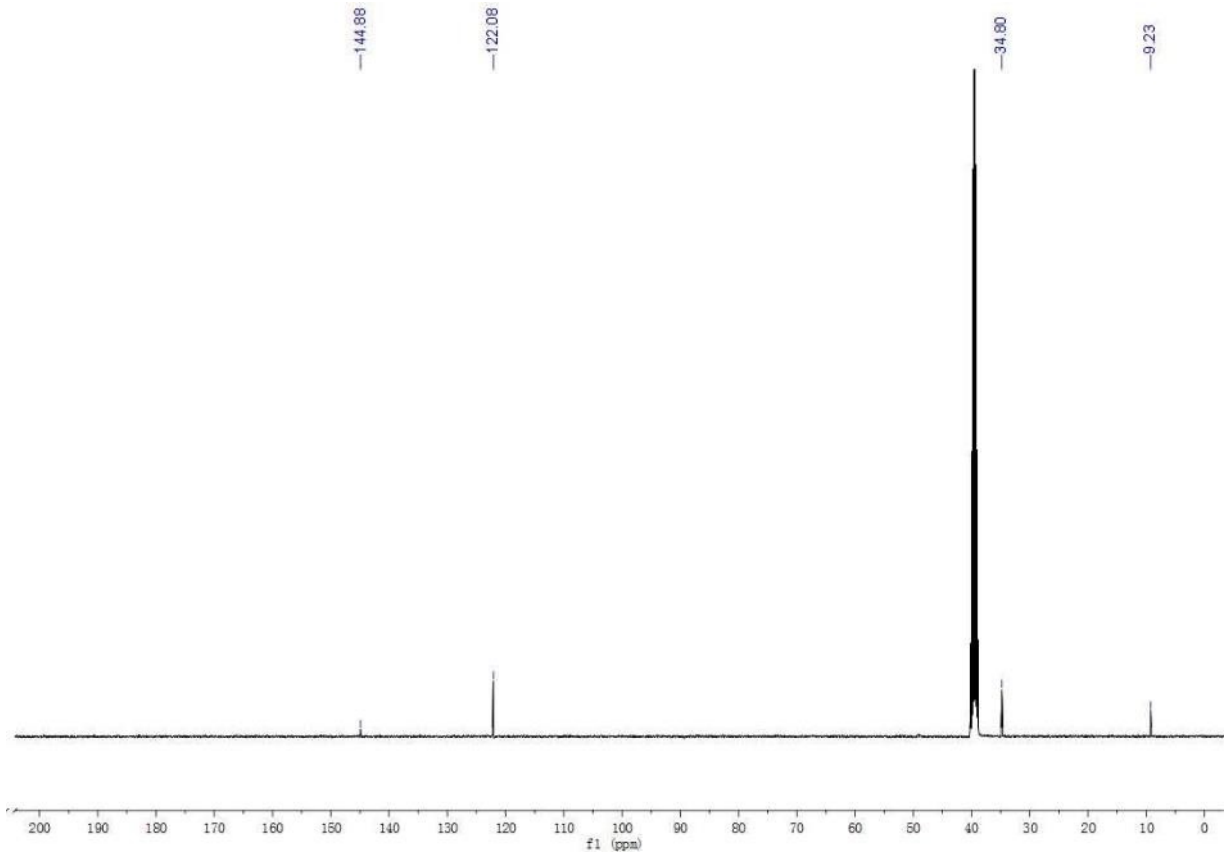

Figure S11. The ^{13}C NMR spectrum of **2a**.

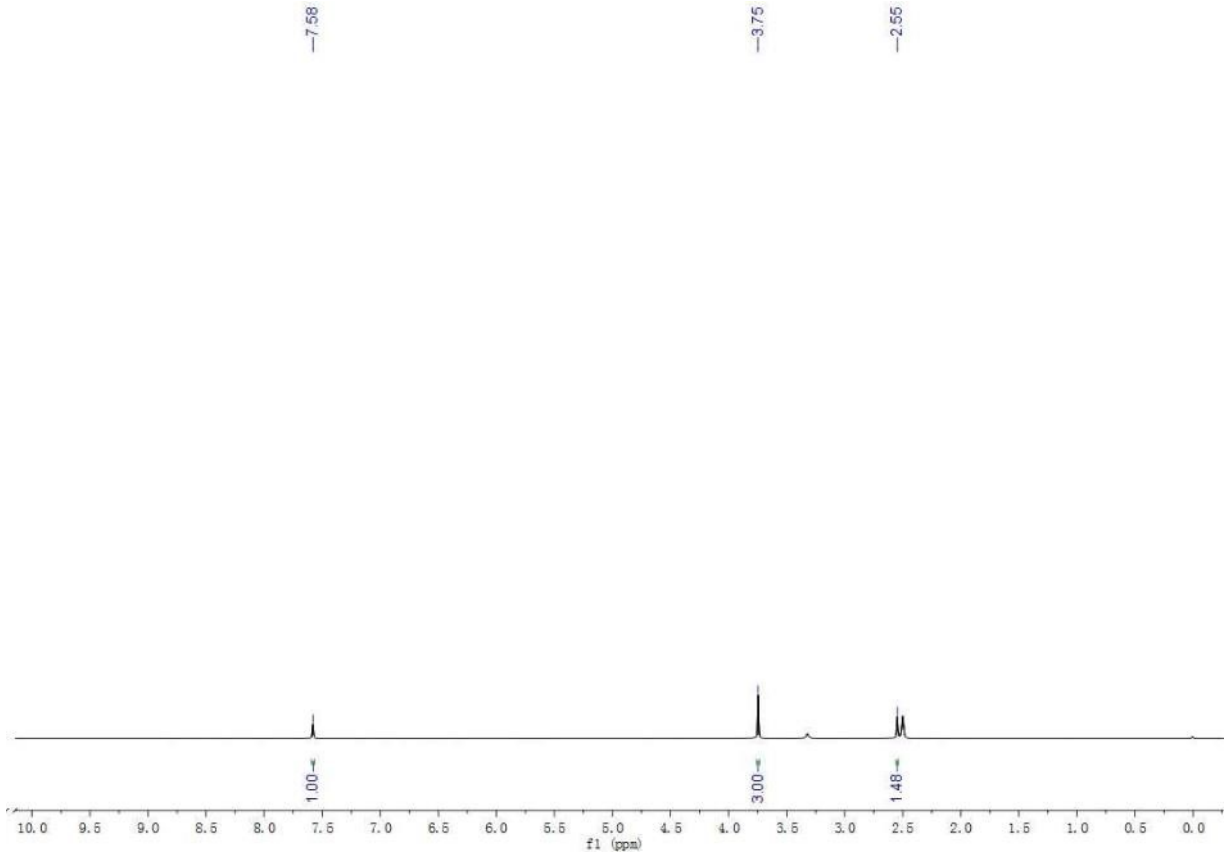

Figure S12. The ^{1}H NMR spectrum of **2a**.

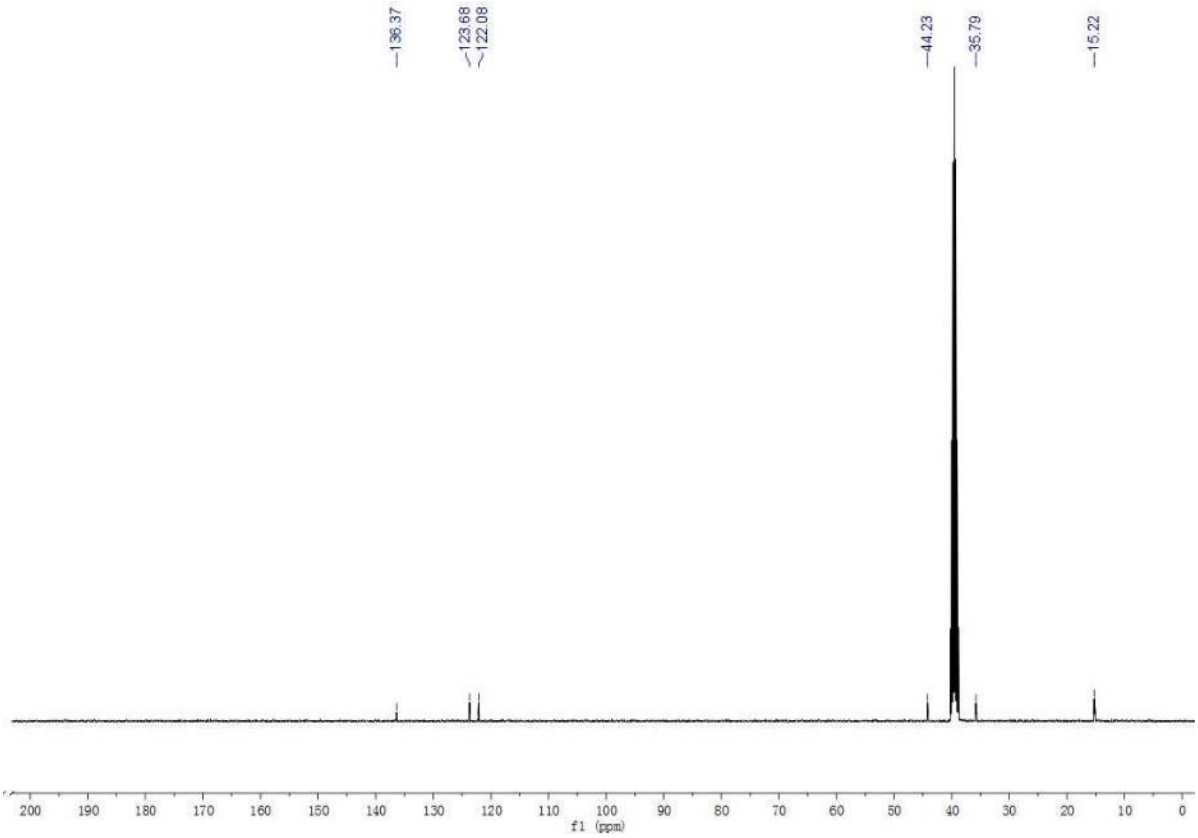

Figure S13. The ^{13}C NMR spectrum of **2b**.

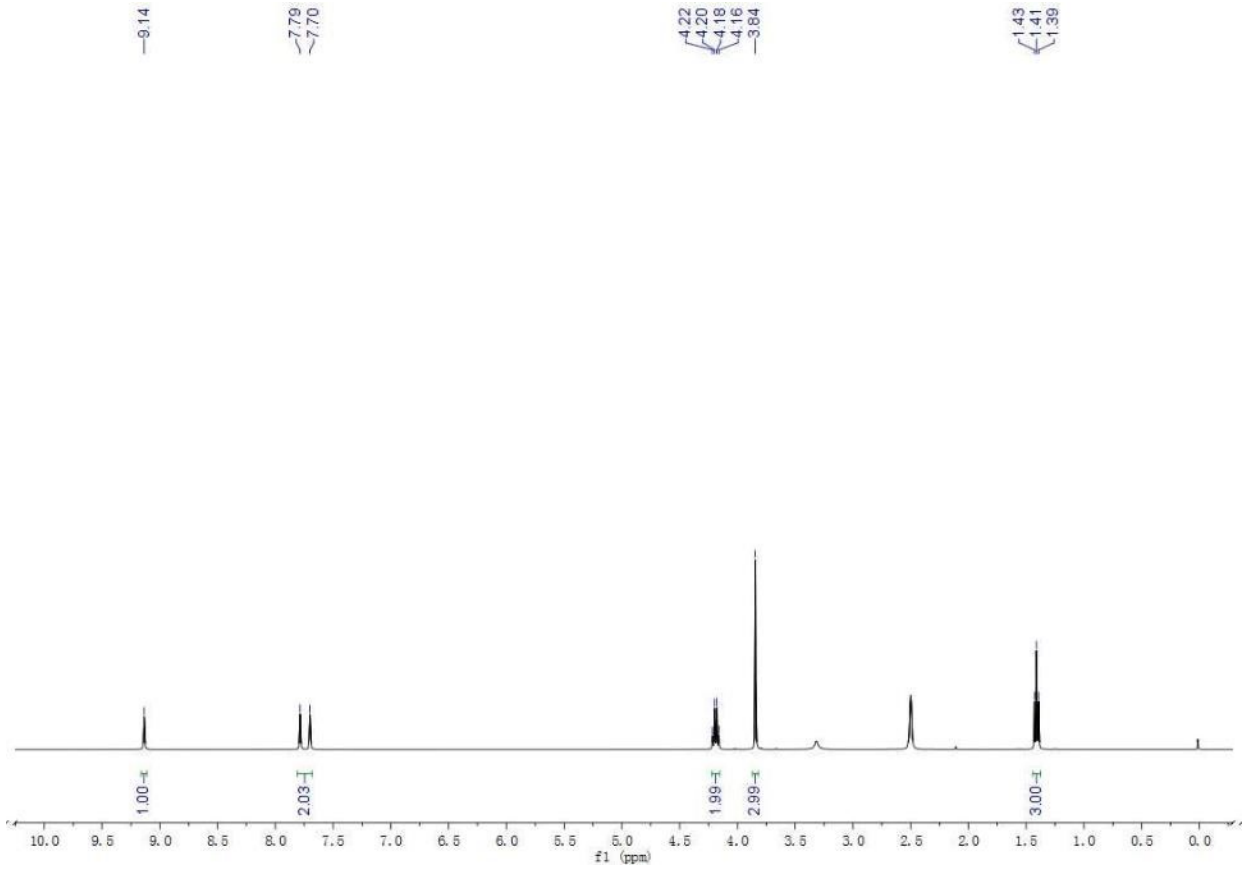

Figure S14. The ^{1}H NMR spectrum of **2b**.

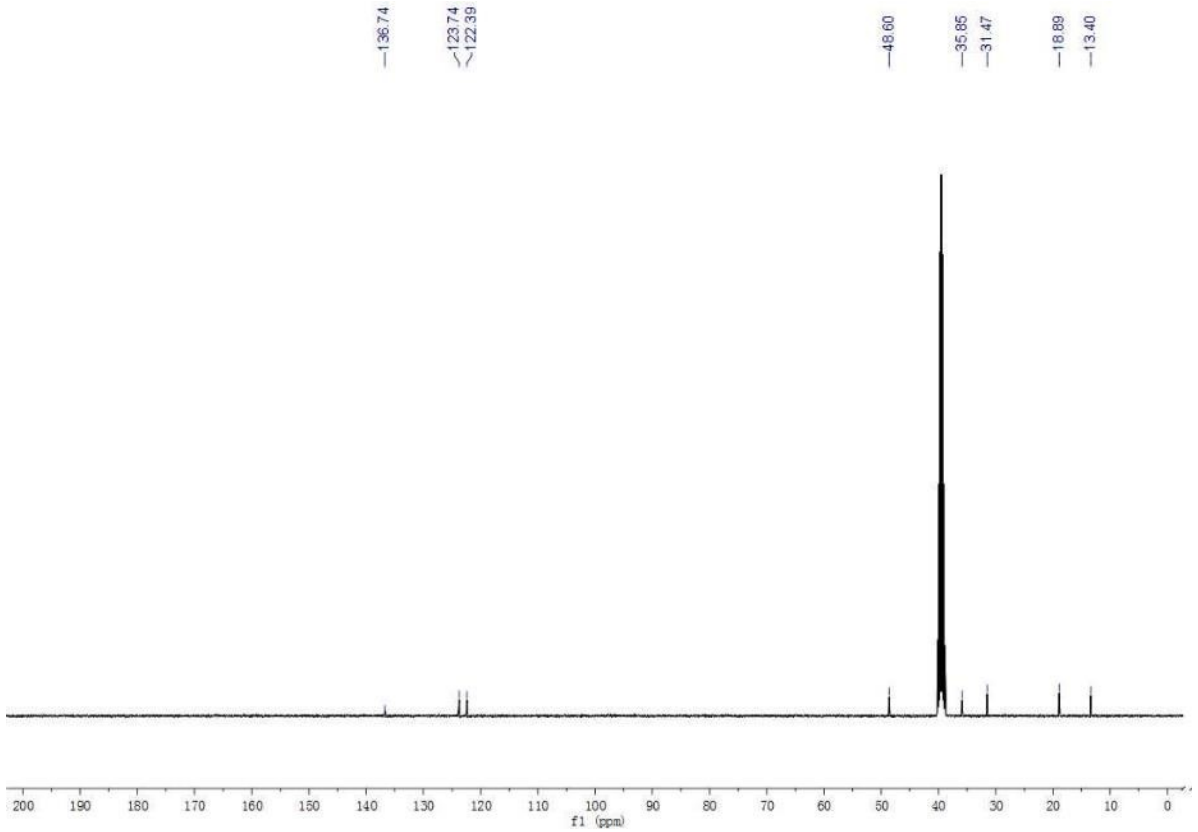

Figure S15. The ^{13}C NMR spectrum of **2c**.

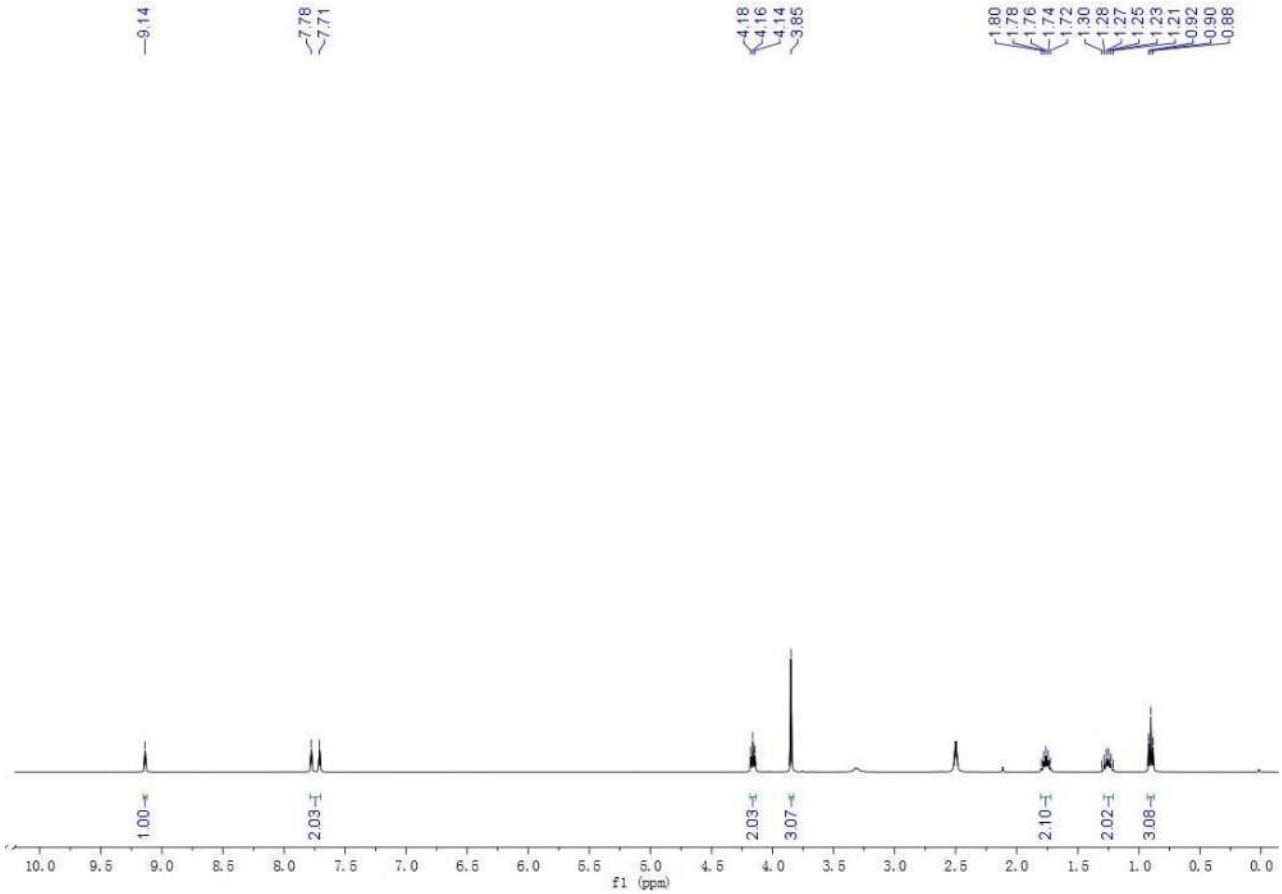

Figure S16. The ^{1}H NMR spectrum of **2c**.

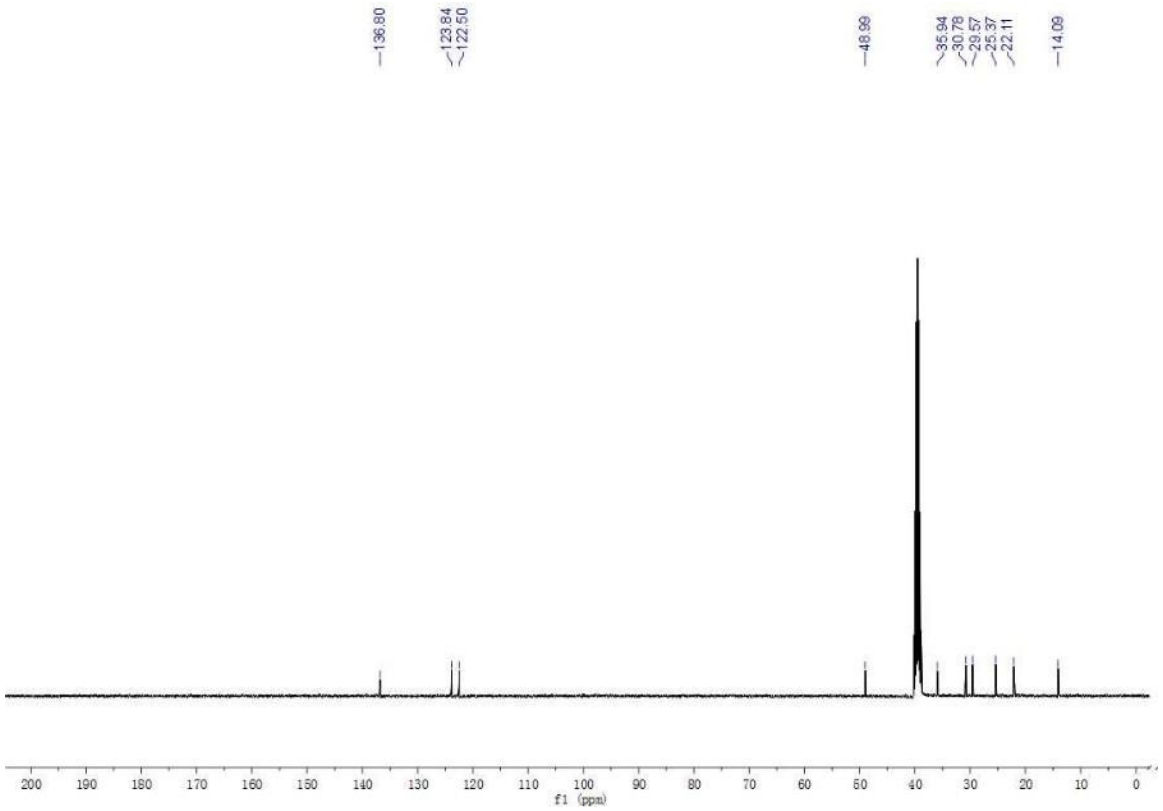

Figure S17. The ^{13}C NMR spectrum of **2d**.

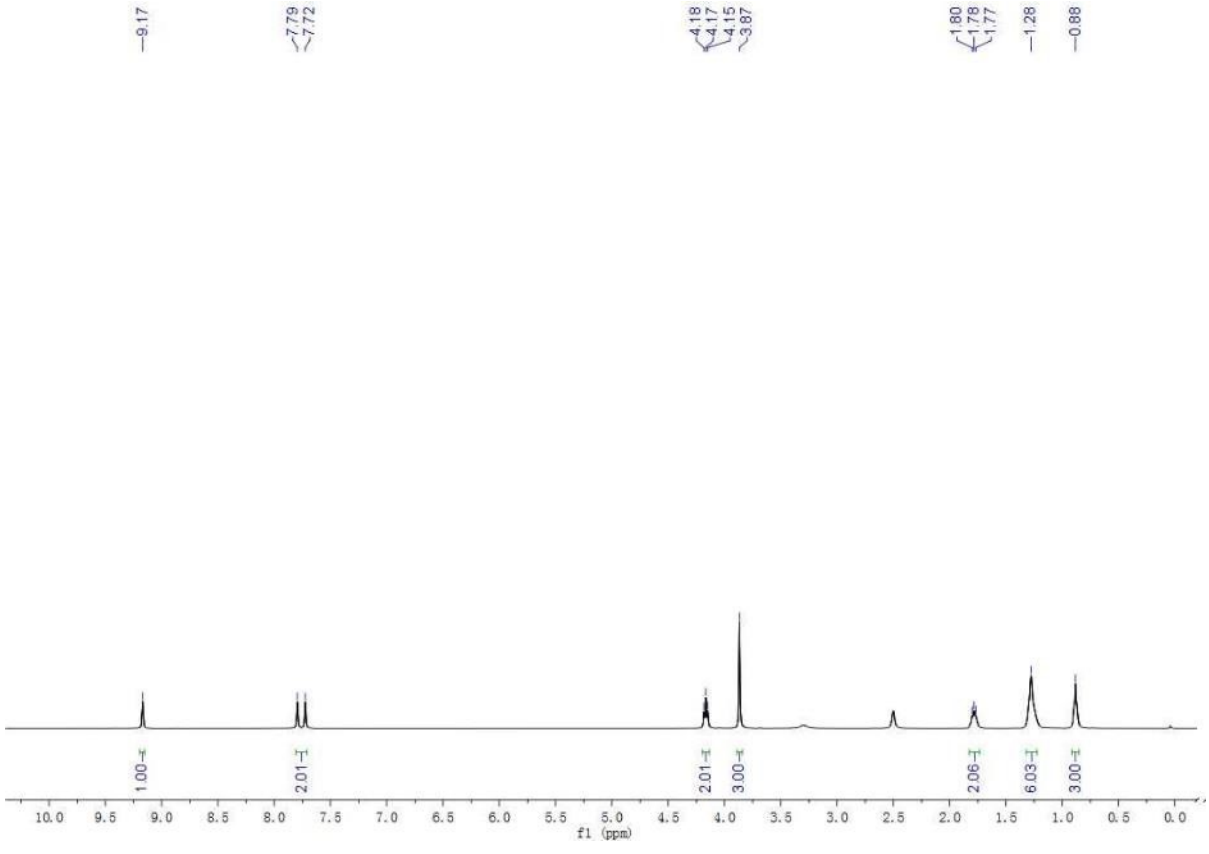

Figure S18. The ^{1}H NMR spectrum of **2d**.

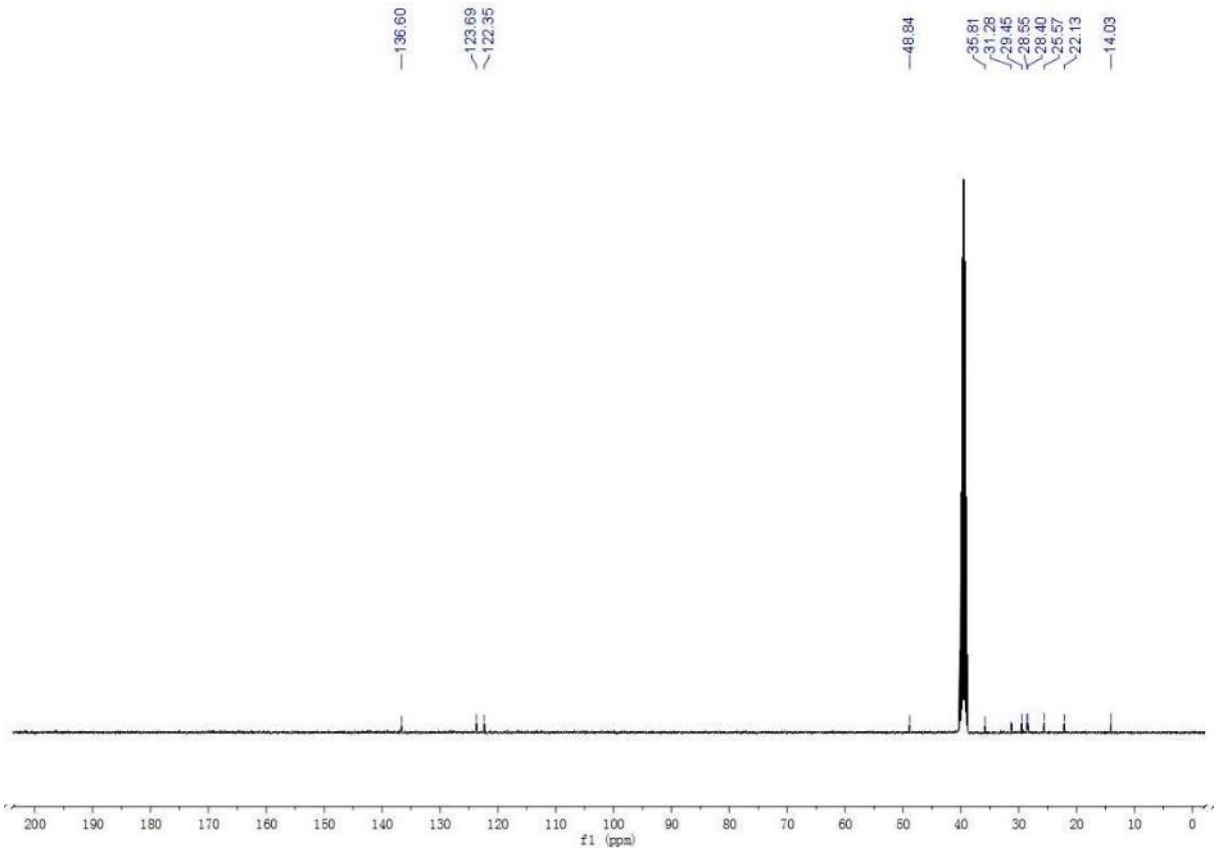

Figure S19. The ^{13}C NMR spectrum of **2e**.

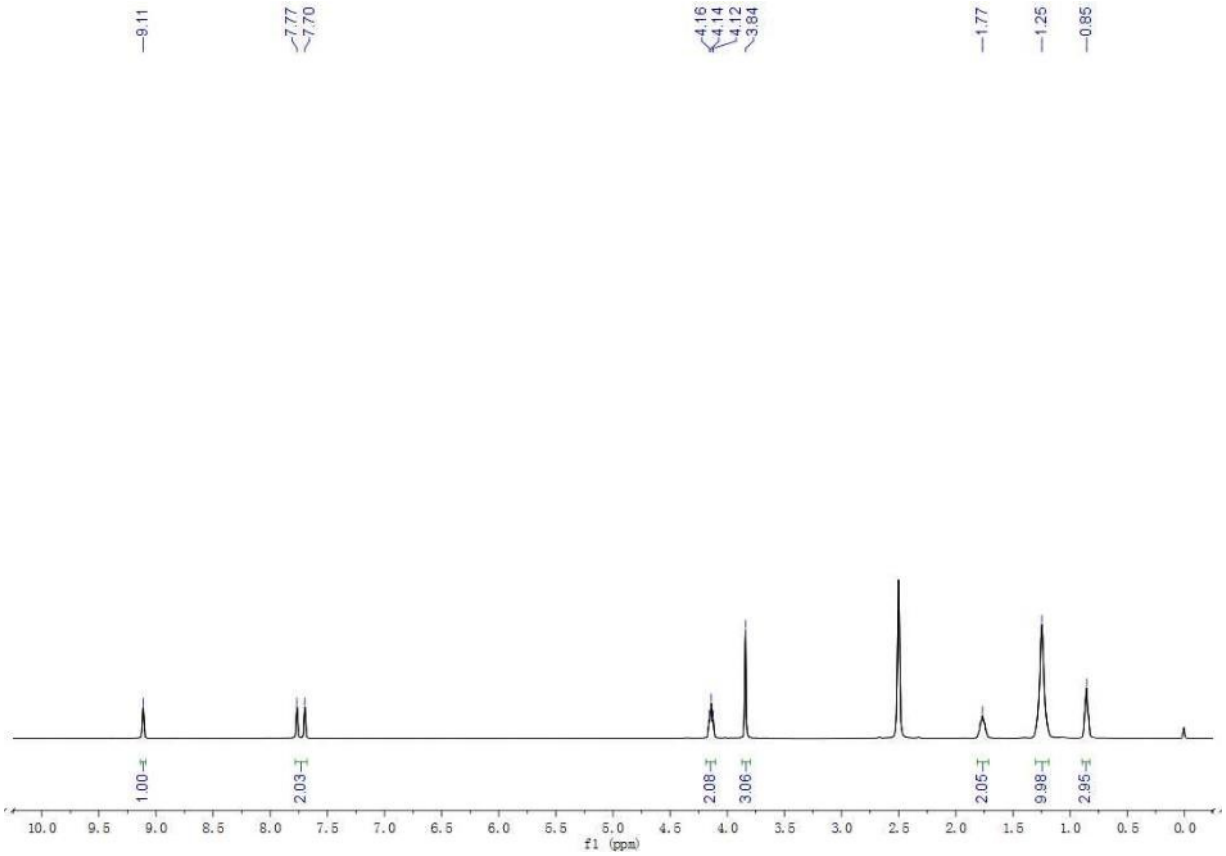

Figure S20. The ^{1}H NMR spectrum of **2e**.

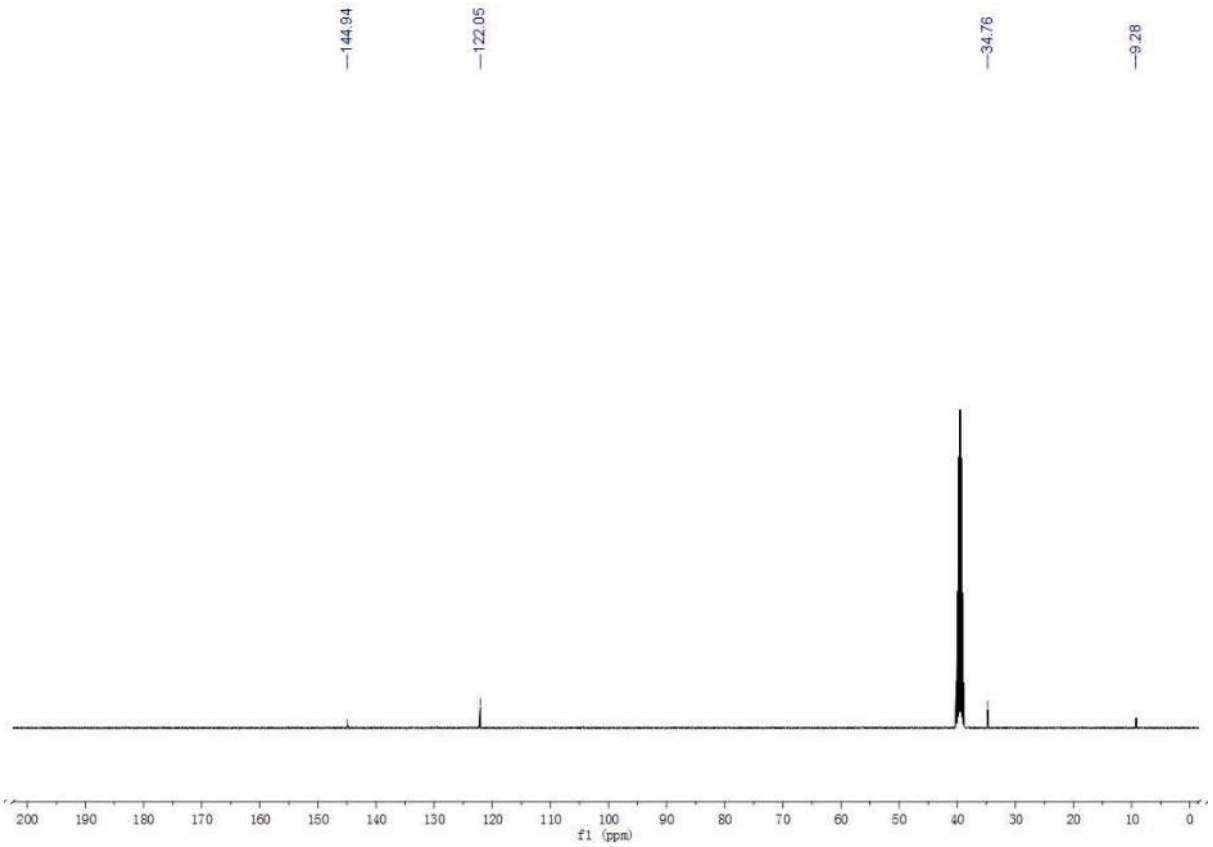

Figure S21. The ^{13}C NMR spectrum of **3a**.

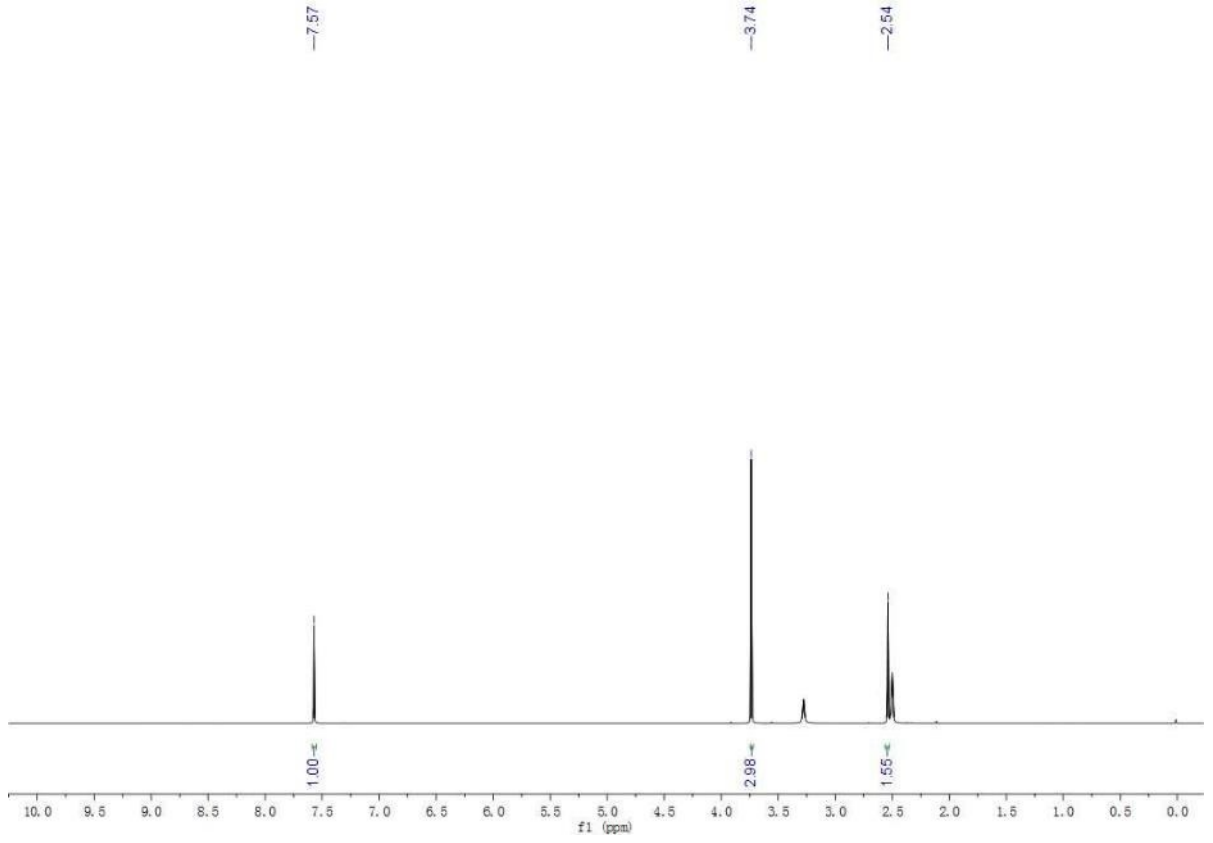

Figure S22. The ^{1}H NMR spectrum of **3a**.

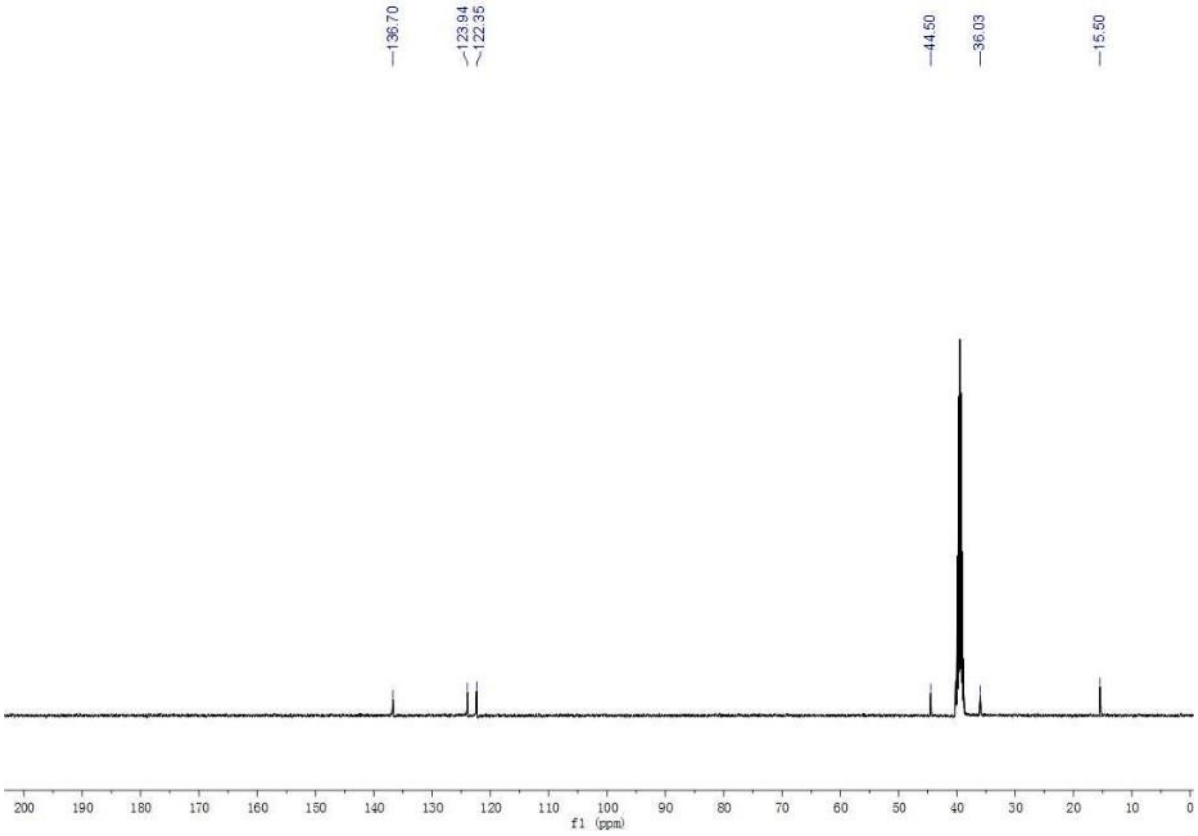

Figure S23. The ^{13}C NMR spectrum of **3b**.

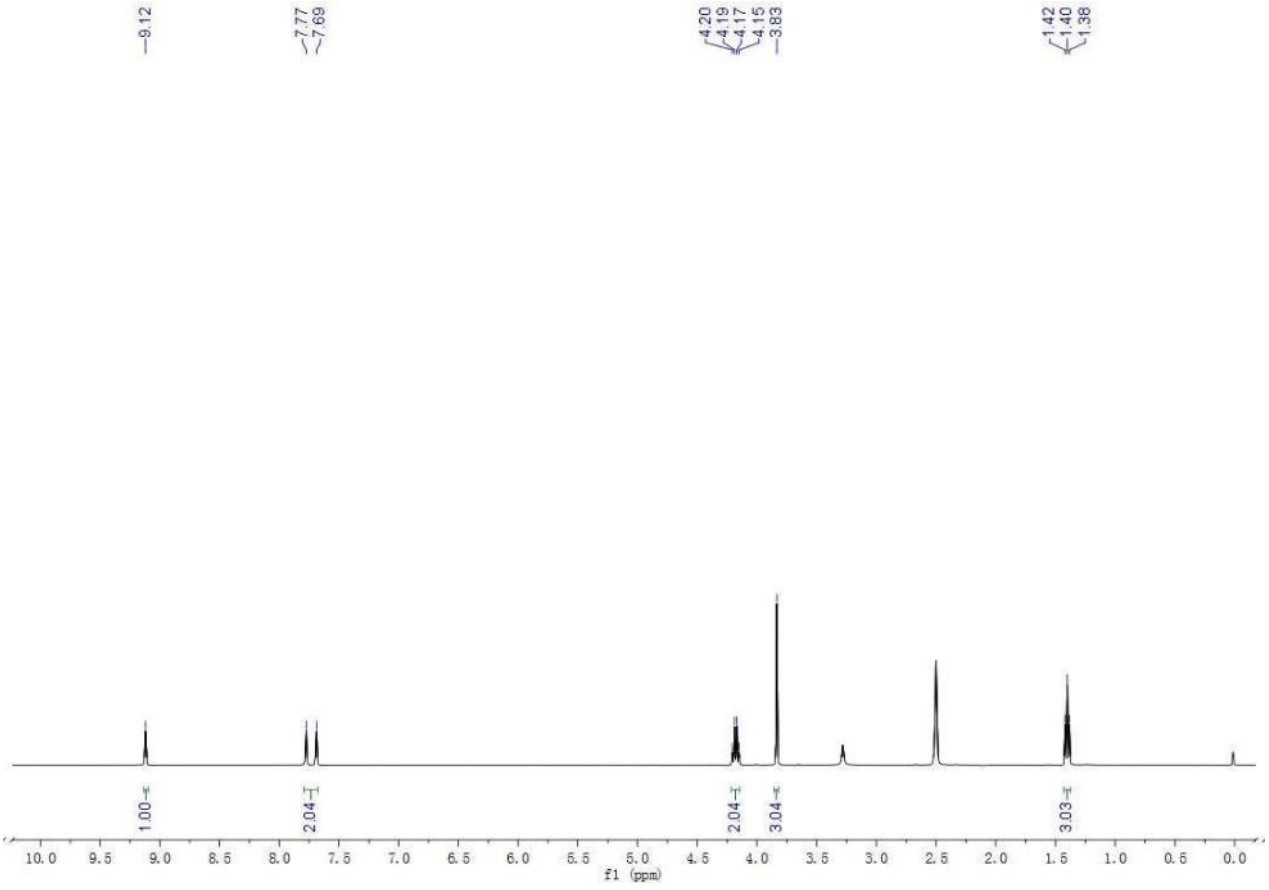

Figure S24. The ^{1}H NMR spectrum of **3b**.

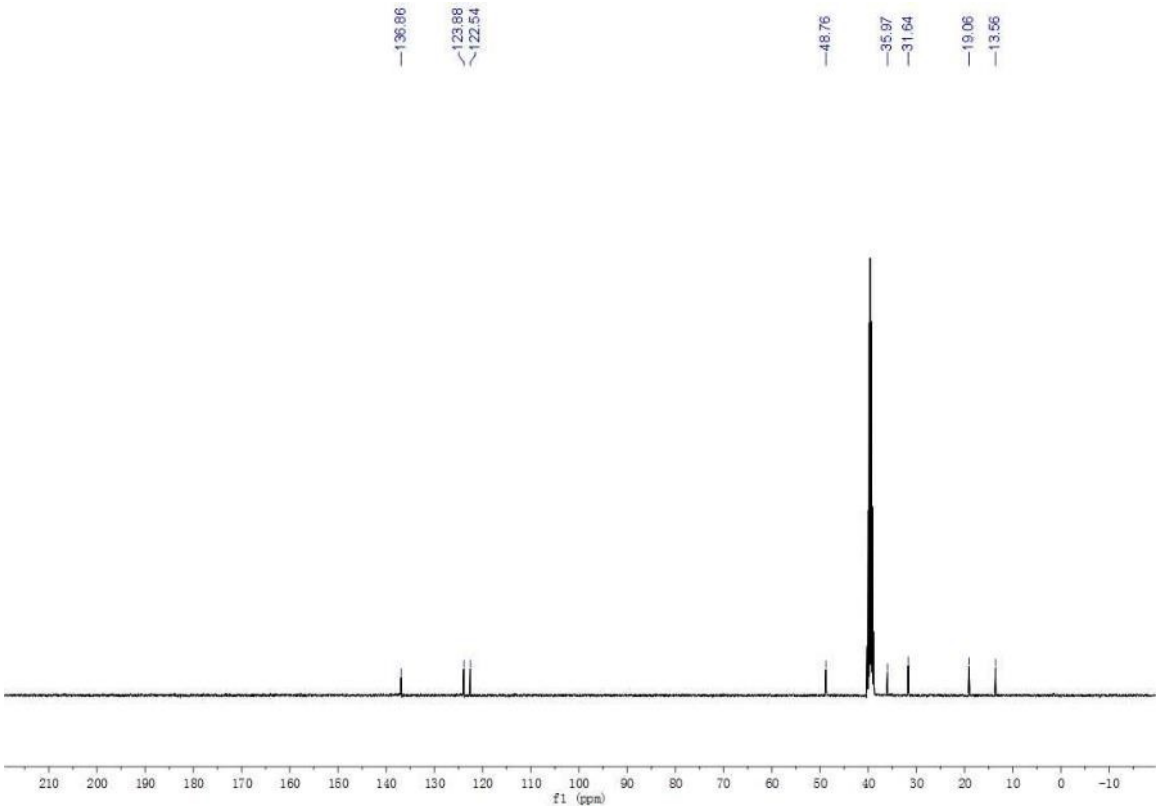

Figure S25. The ^{13}C NMR spectrum of **3c**.

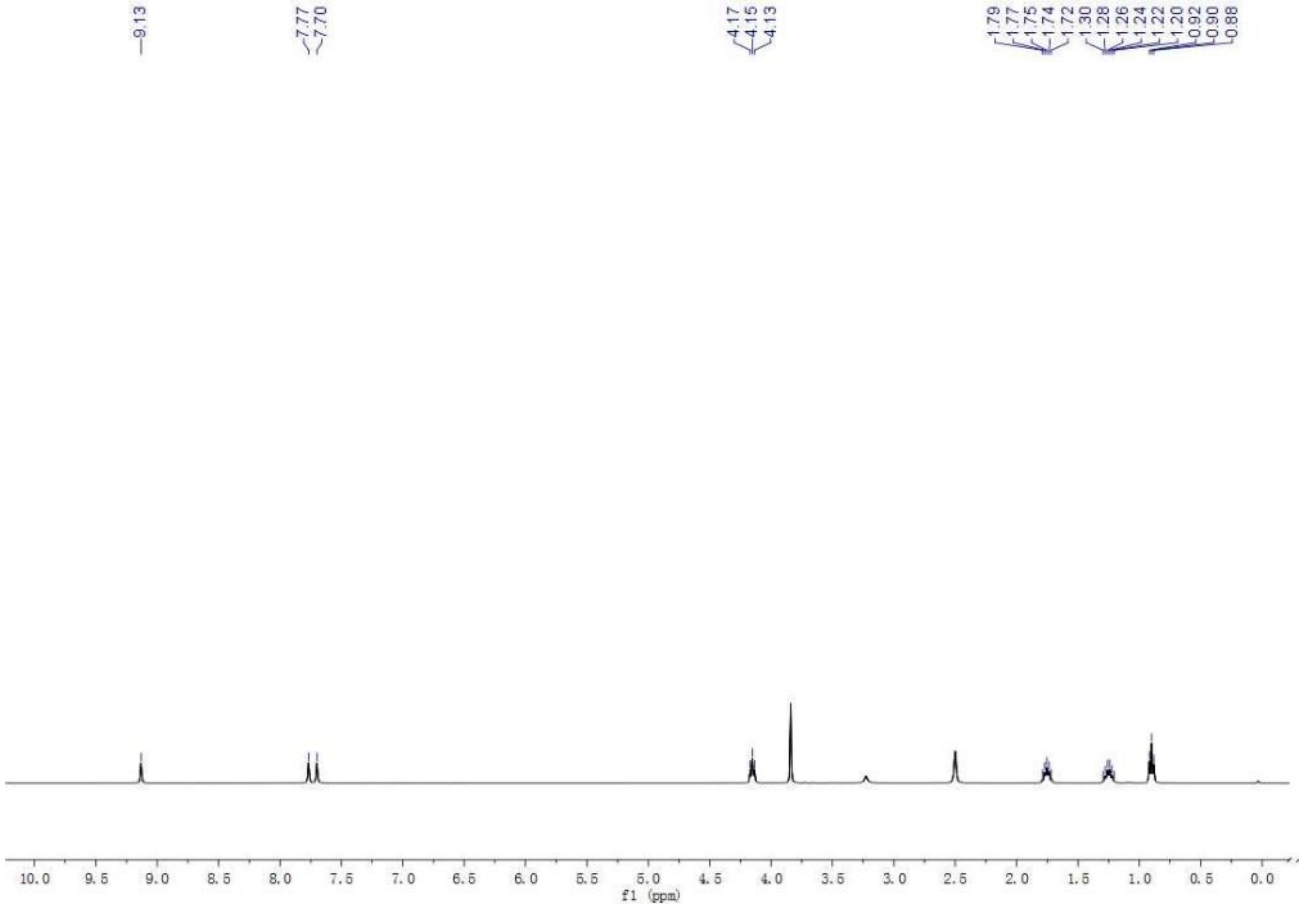

Figure S26. The ^{1}H NMR spectrum of **3c**.

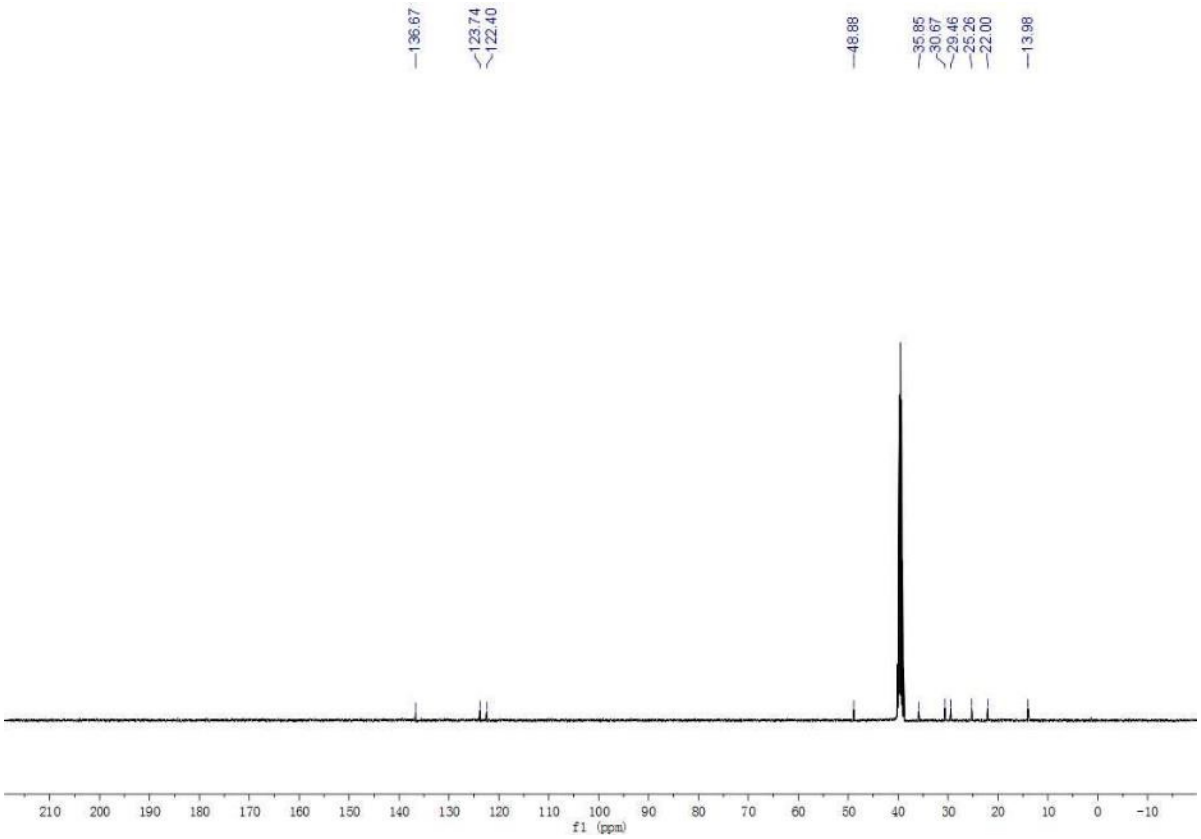

Figure S27. The ^{13}C NMR spectrum of **3d**.

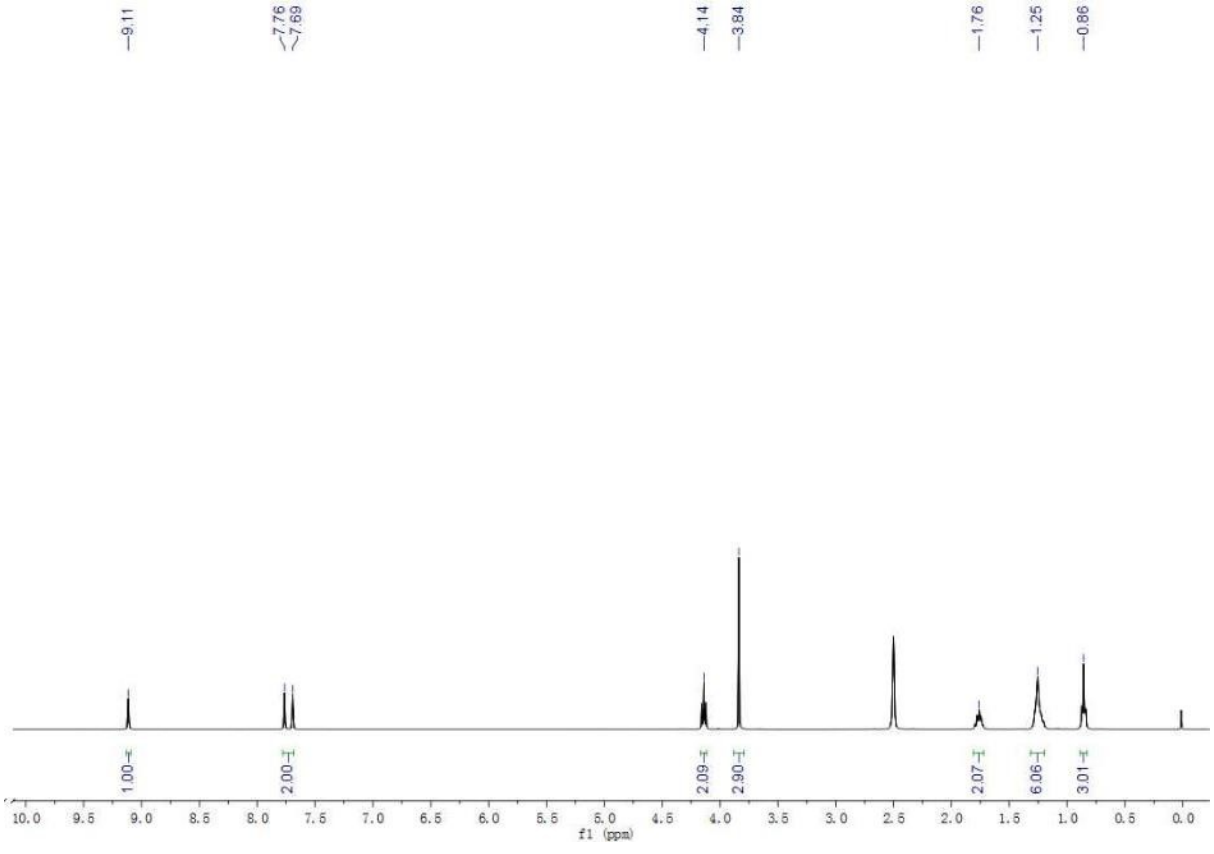

Figure S26. The ^{1}H NMR spectrum of **3d**.

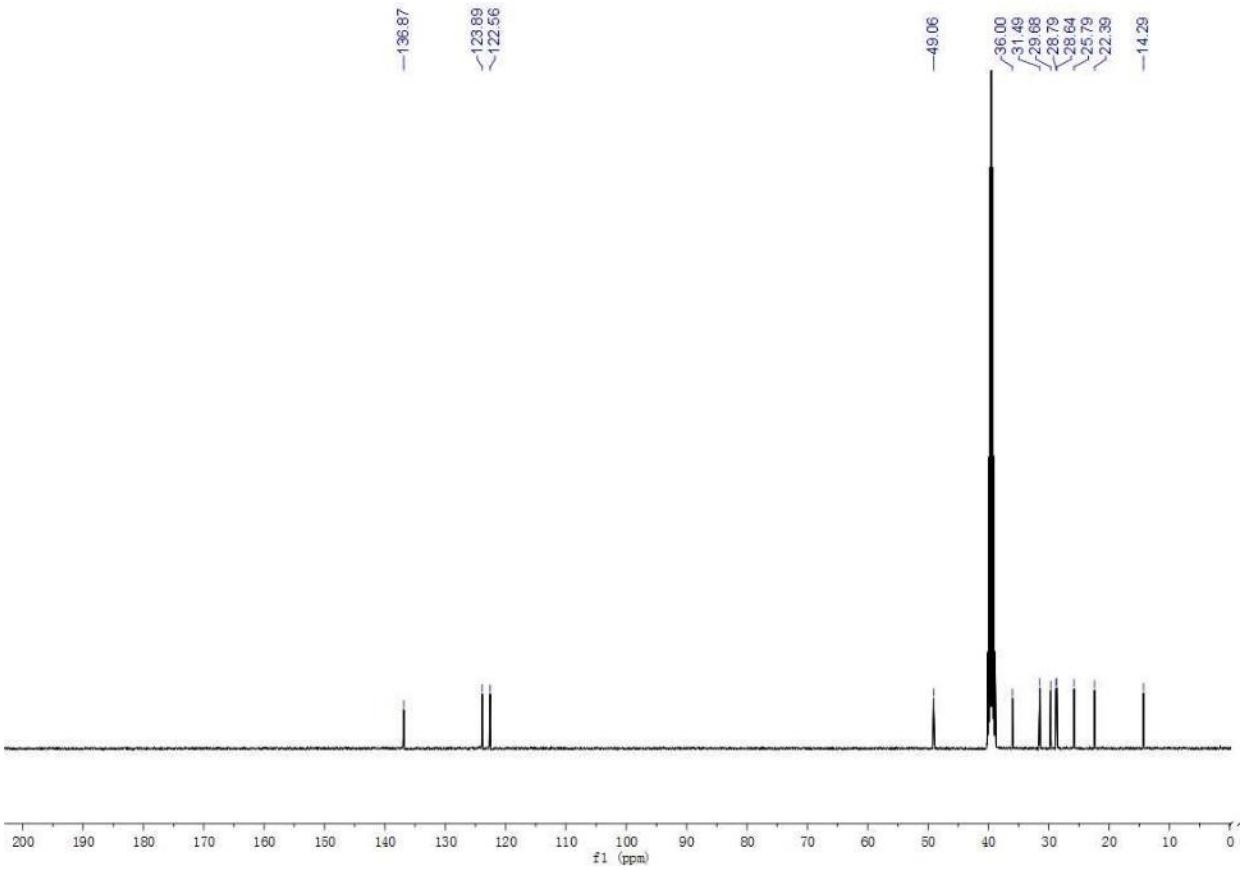

Figure S29. The ^{13}C NMR spectrum of **3e**.

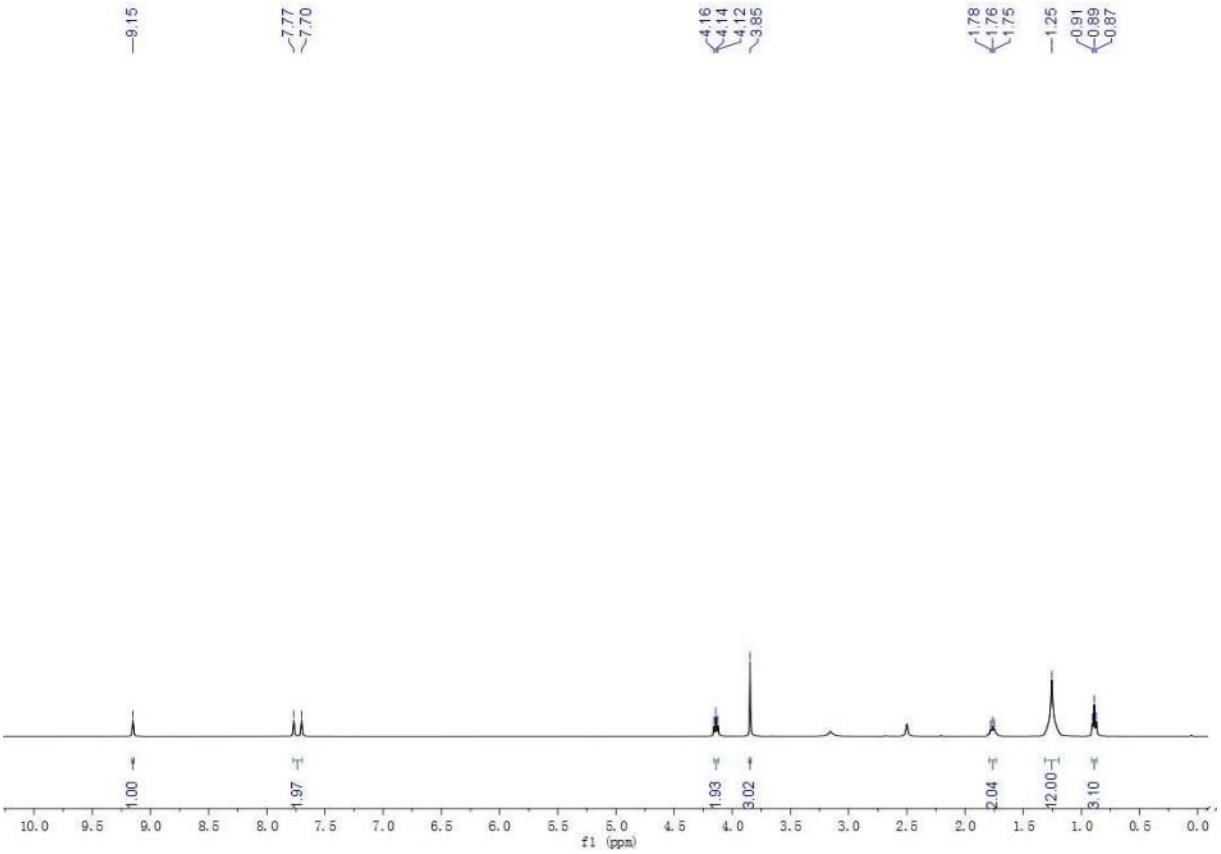

Figure S30. The ^{1}H NMR spectrum of **3e**.

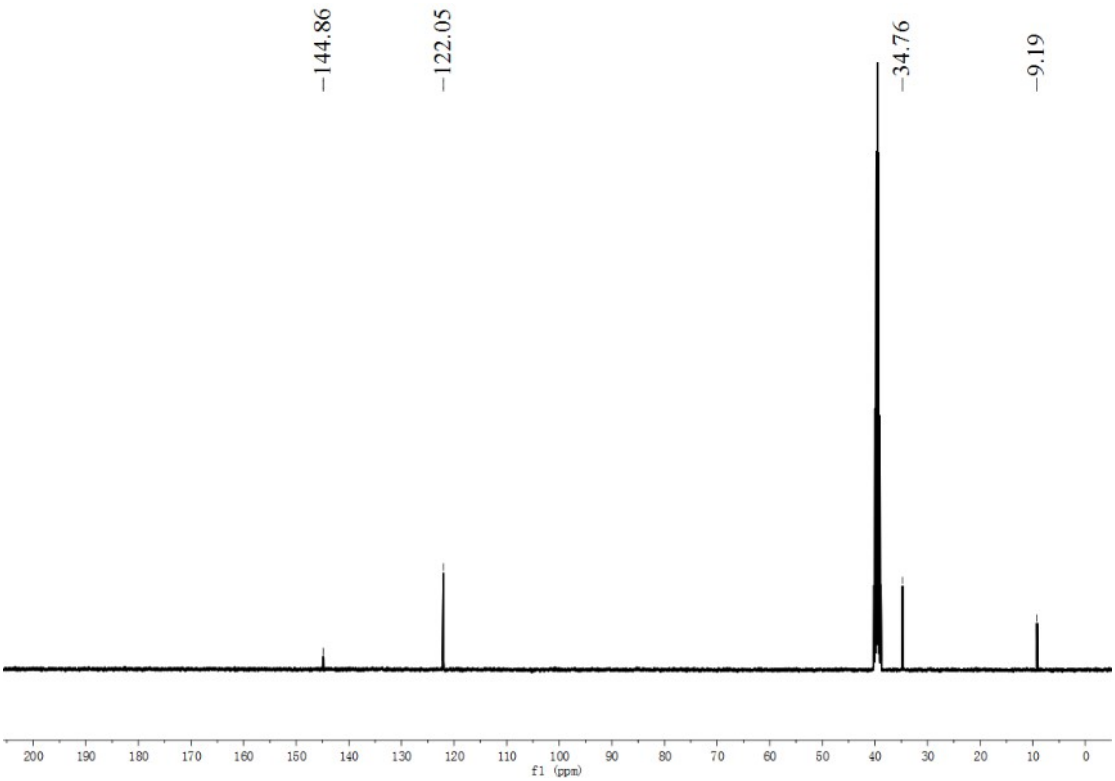

Figure S31. ^{13}C NMR spectrum of complex **4a**.

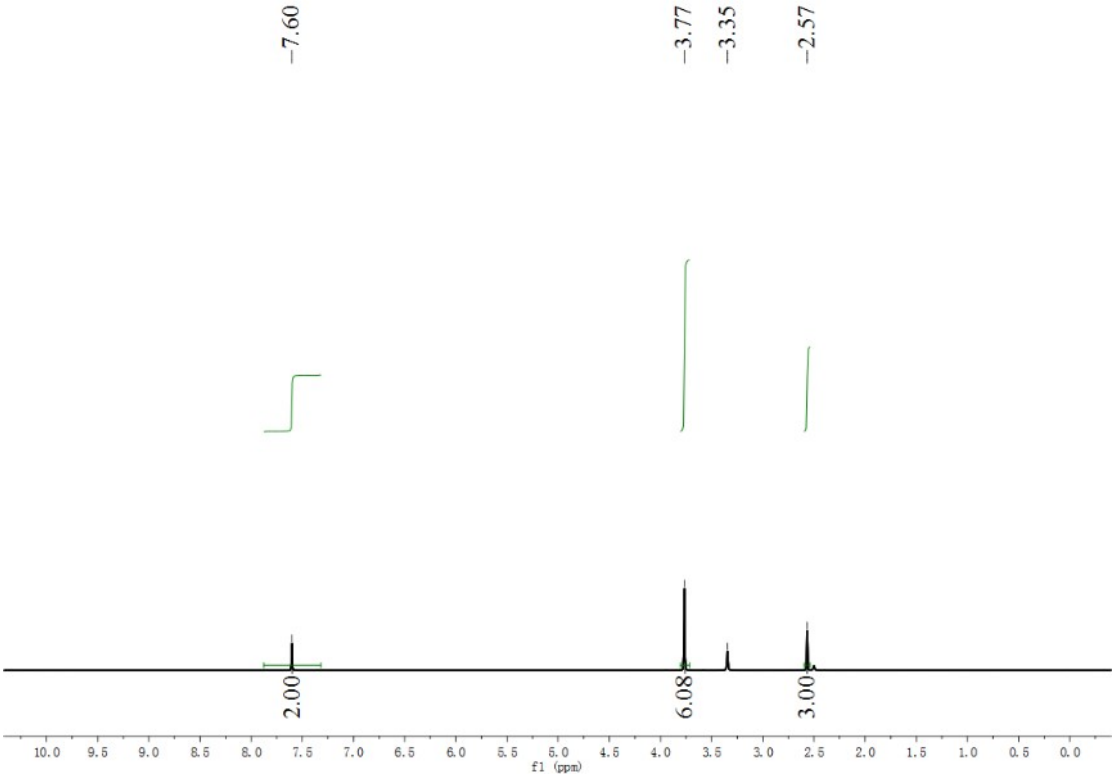

Figure S32. ^{1}H NMR spectrum of complex **4a**.

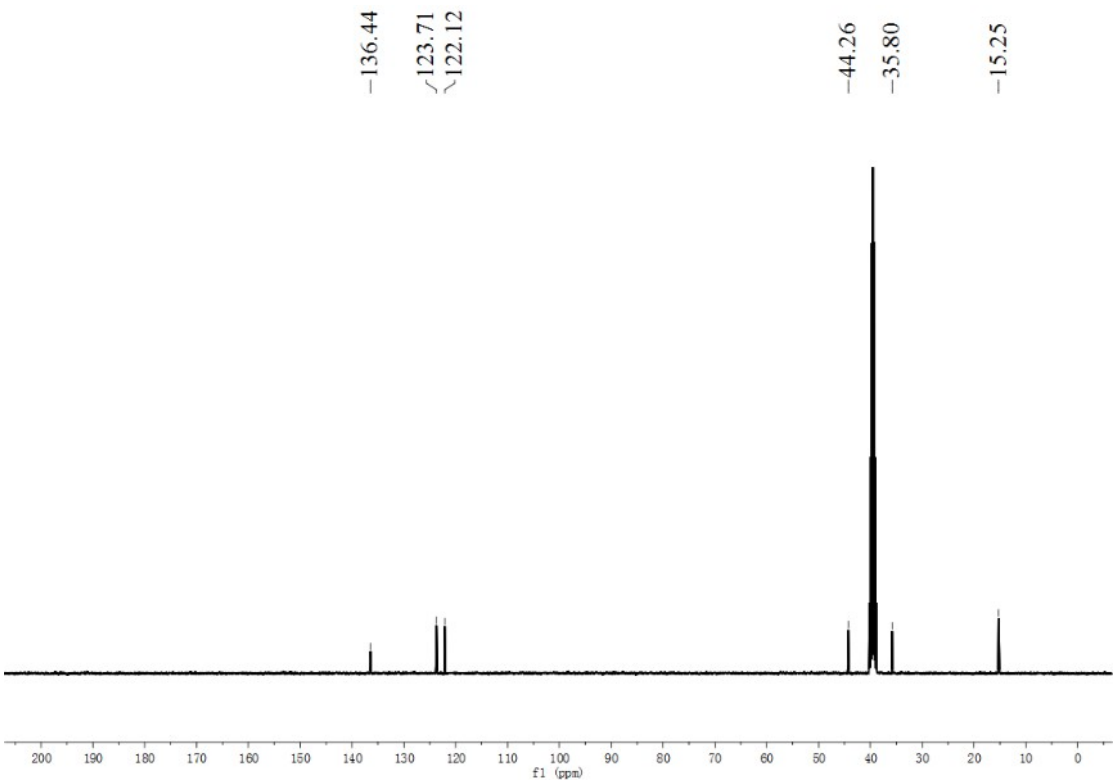

Figure S33. ^{13}C NMR spectrum of complex **4b**.

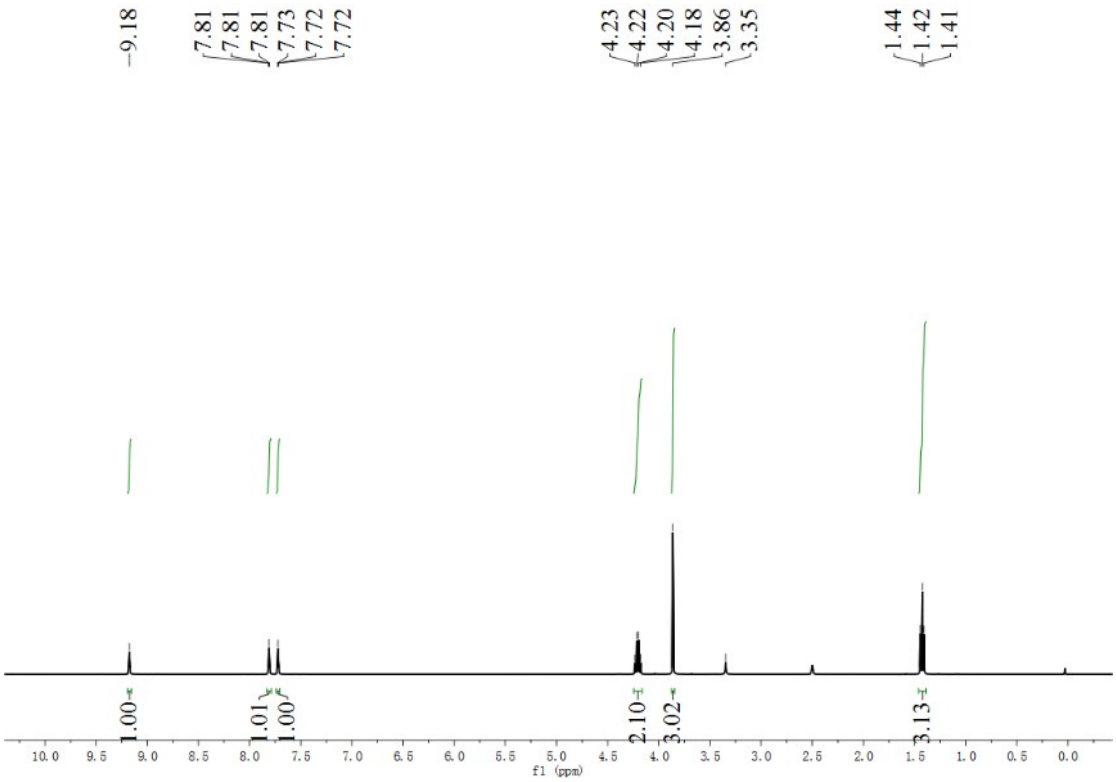

Figure S34. ^{1}H NMR spectrum of complex **4b**.

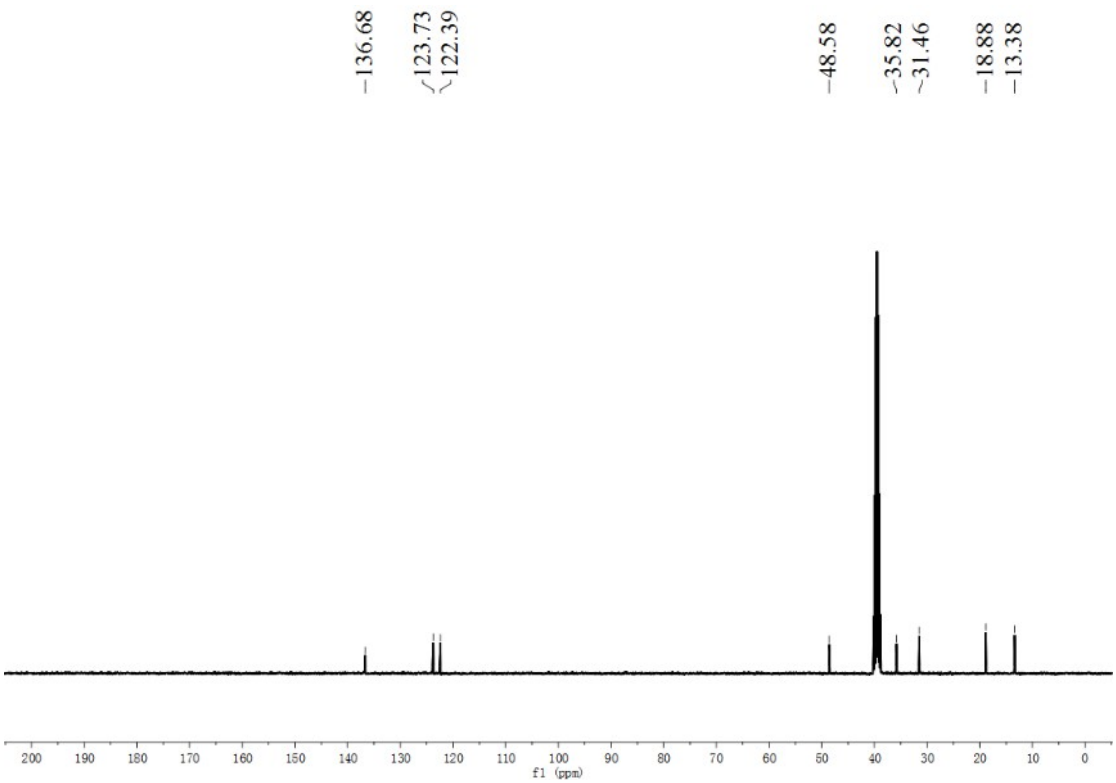

Figure S35. ^{13}C NMR spectrum of complex **4c**.

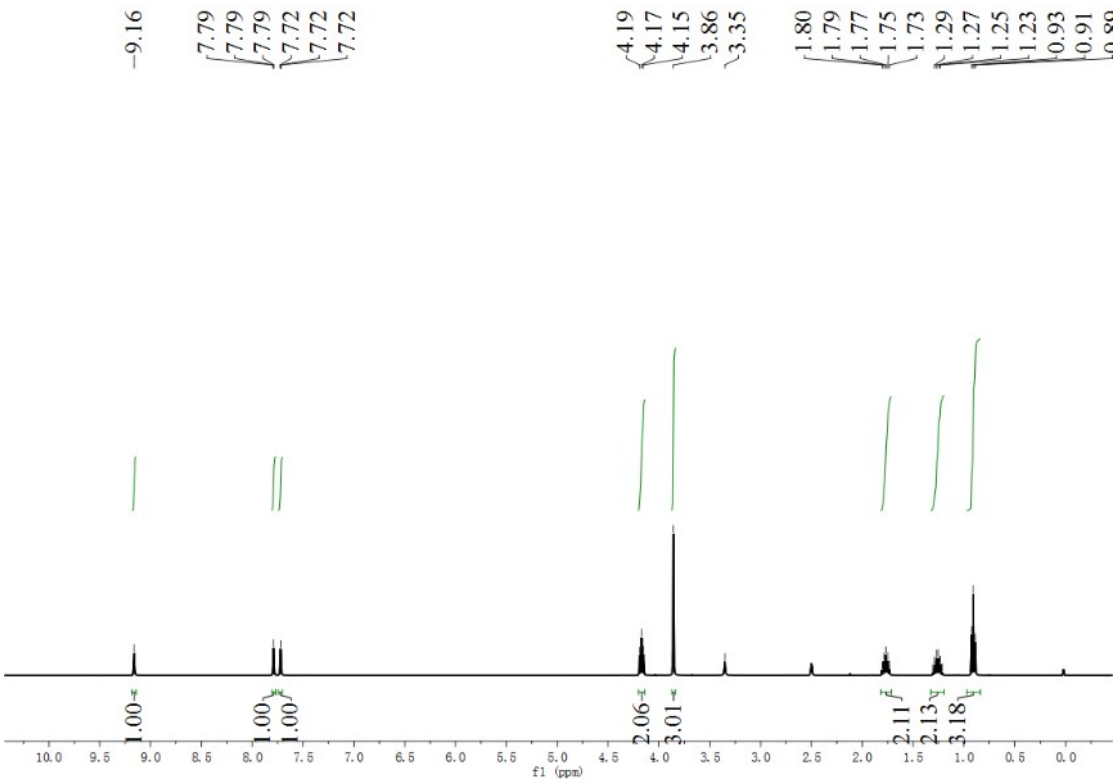

Figure S36. ^{1}H NMR spectrum of complex **4c**.

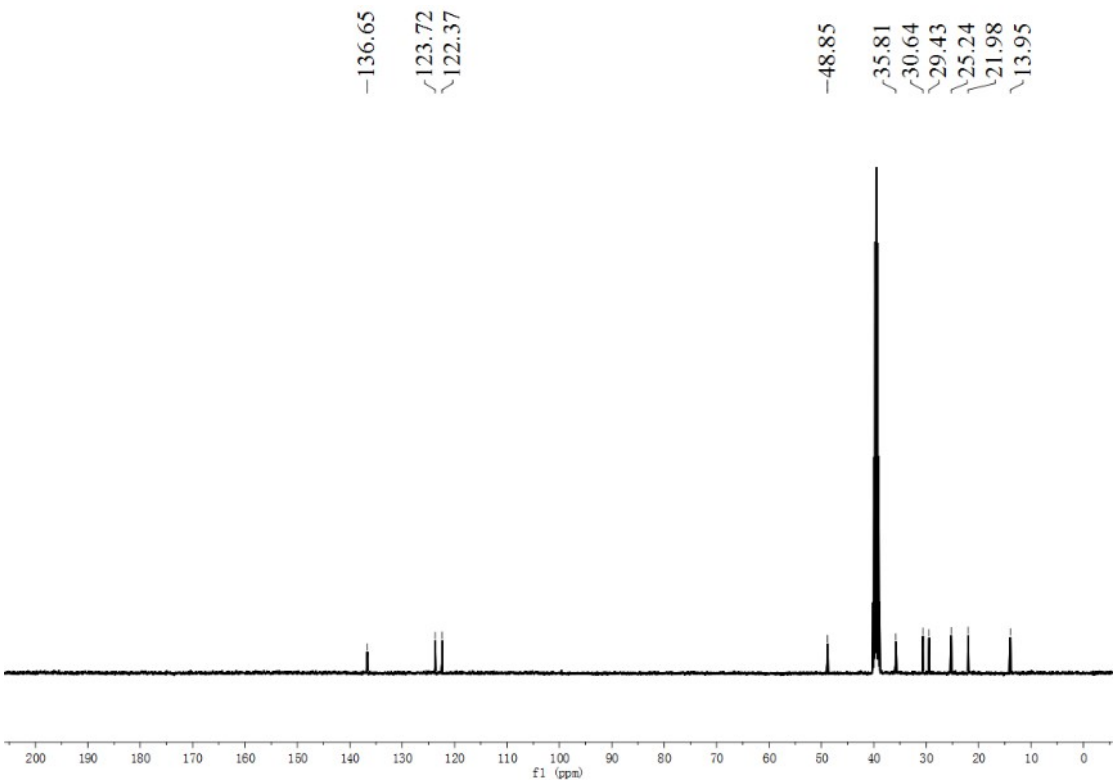

Figure S37. ^{13}C NMR spectrum of complex **4d**.

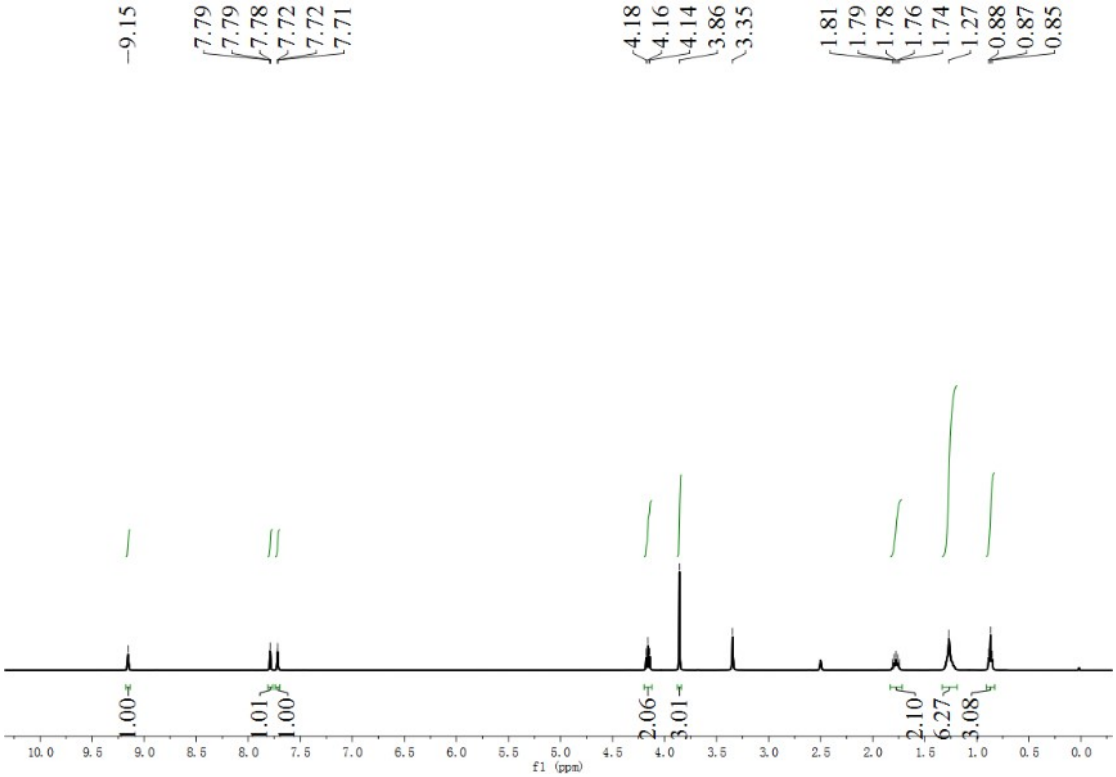

Figure S38. ^{1}H NMR spectrum of complex **4d**.

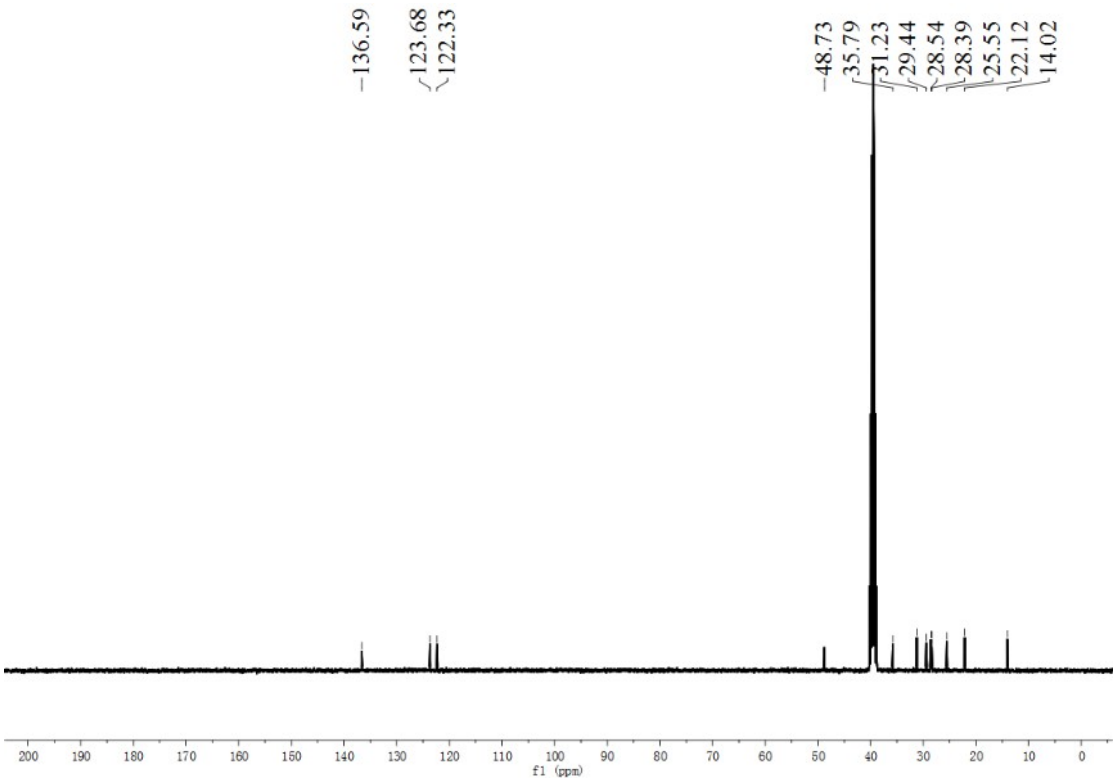

Figure S39. ^{13}C NMR spectrum of complex **4e**.

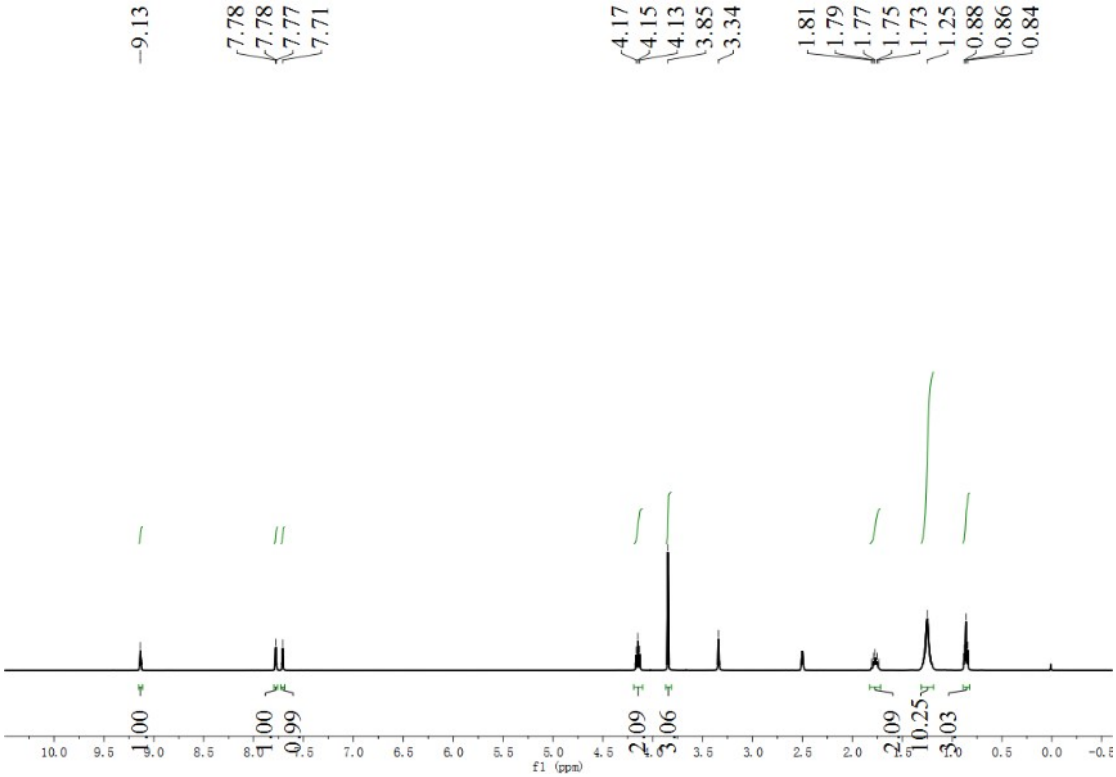

Figure S40. ^{1}H NMR spectrum of complex **4e**.

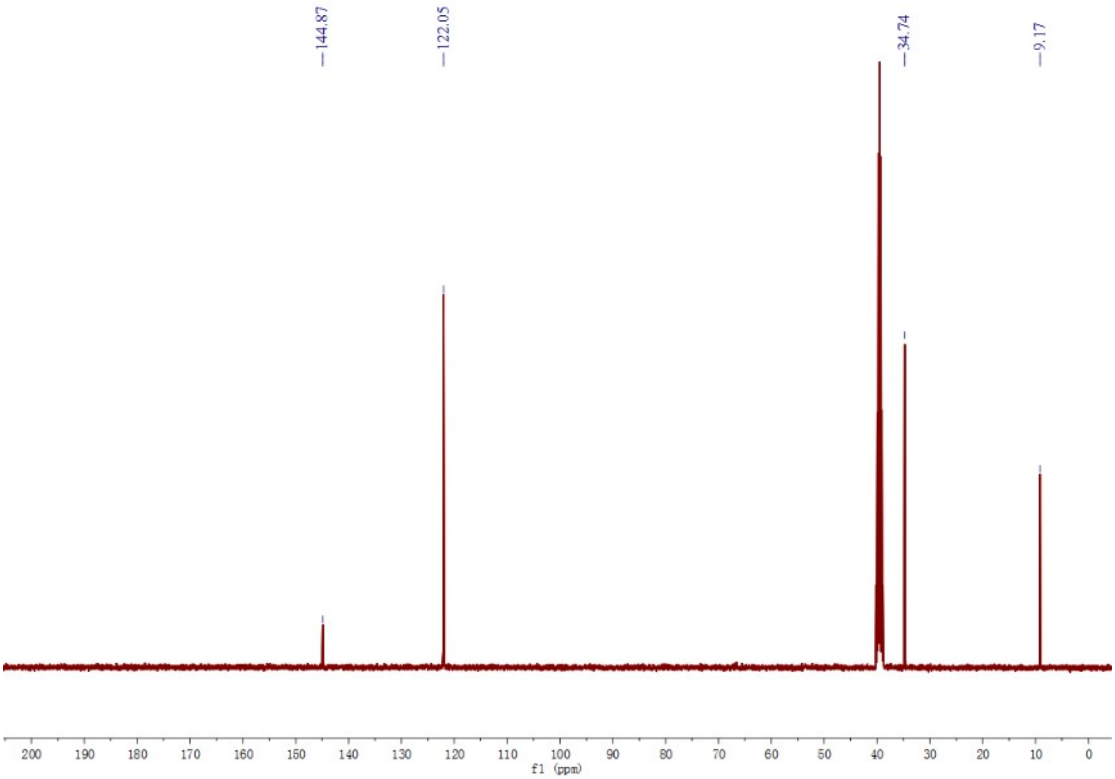

Figure S41. ^{13}C NMR spectrum of complex **5a**.

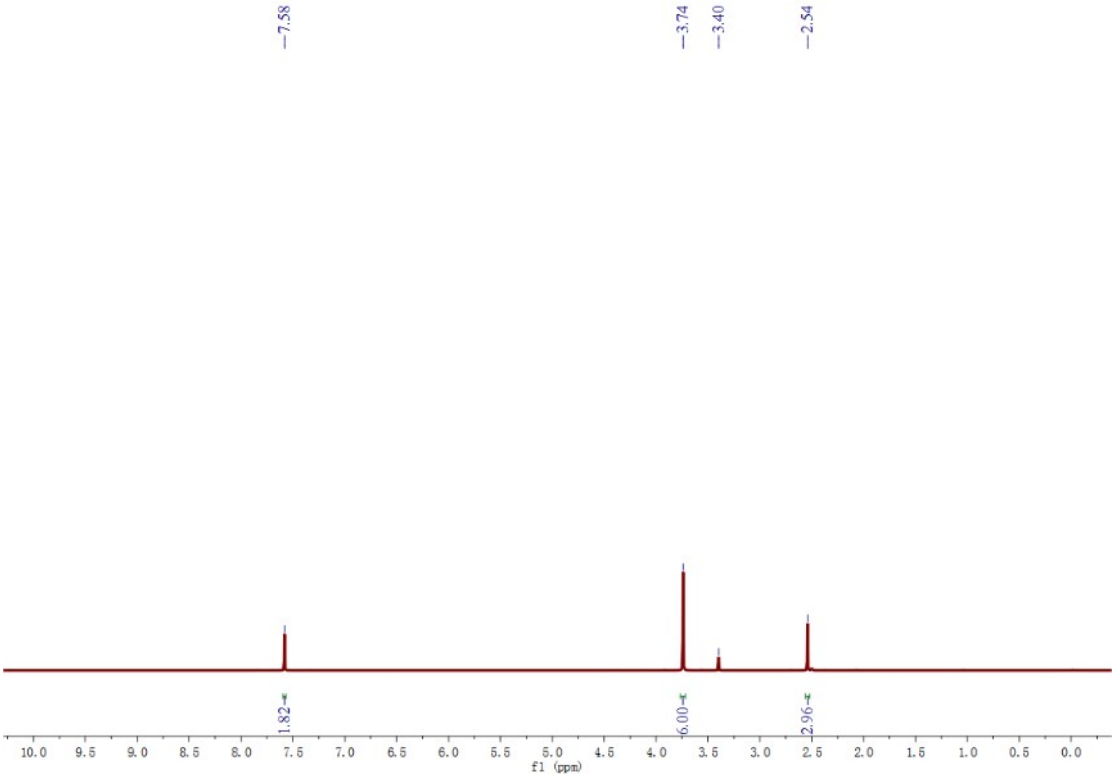

Figure S42. ^{1}H NMR spectrum of complex **5a**.

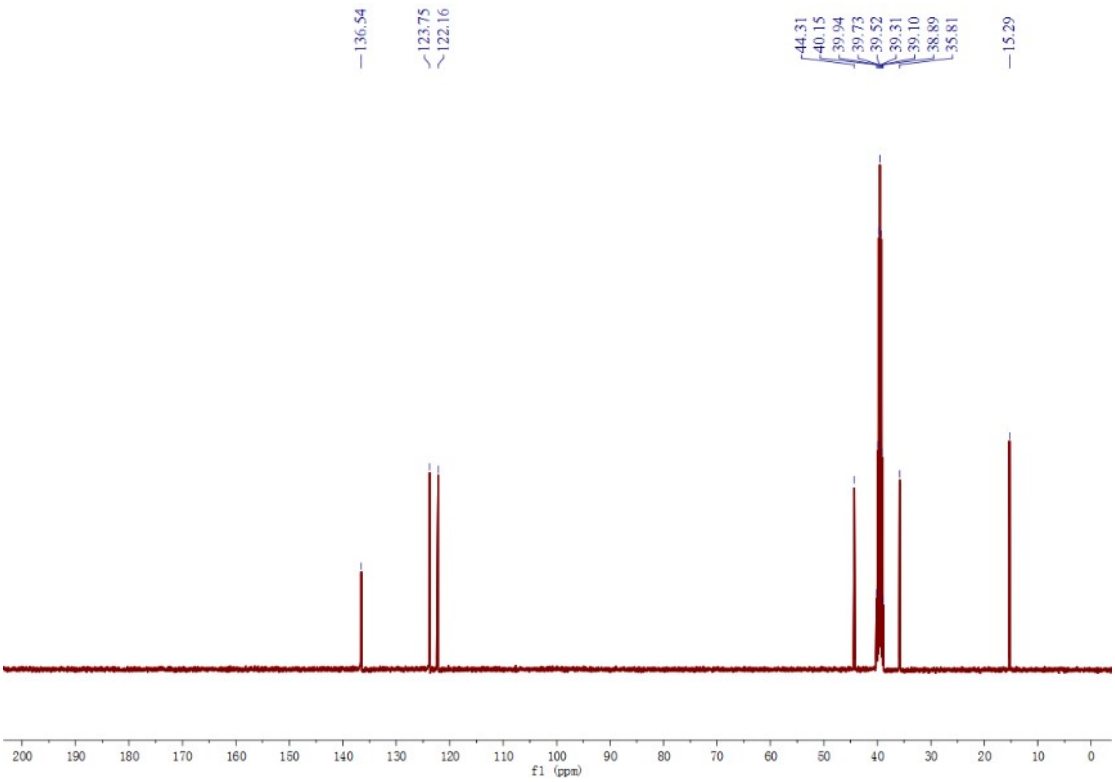

Figure S43. ^{13}C NMR spectrum of complex **5b**.

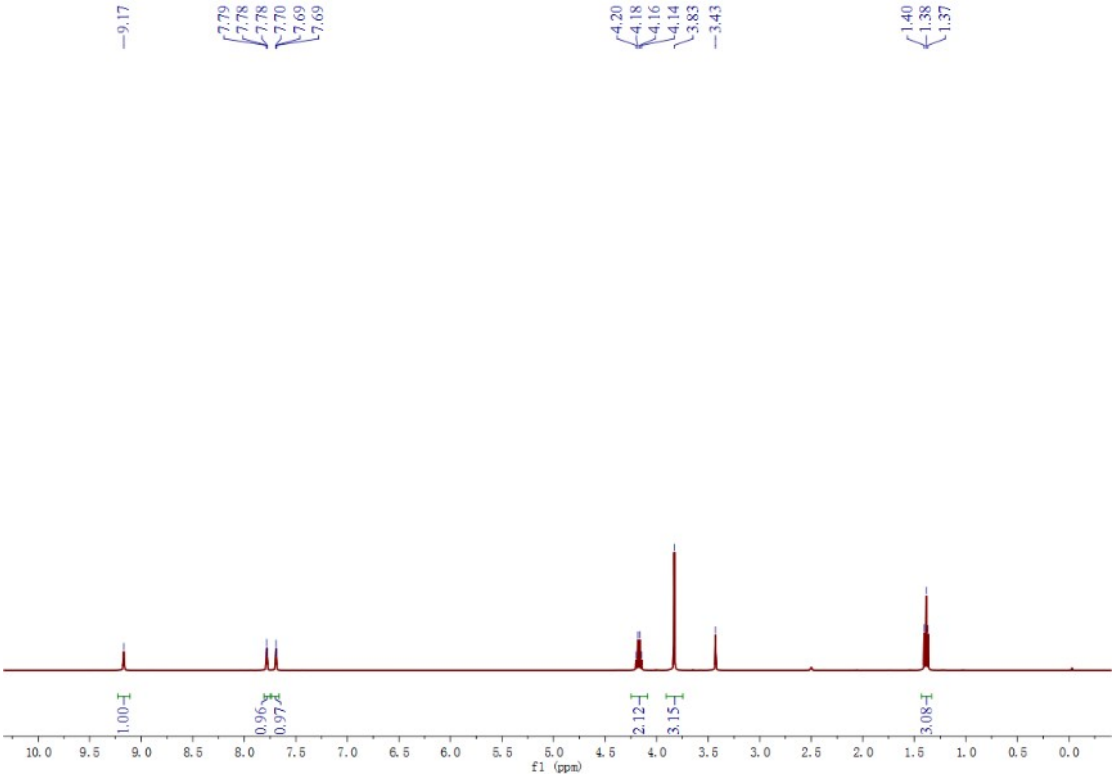

Figure S44. ^{1}H NMR spectrum of complex **5b**.

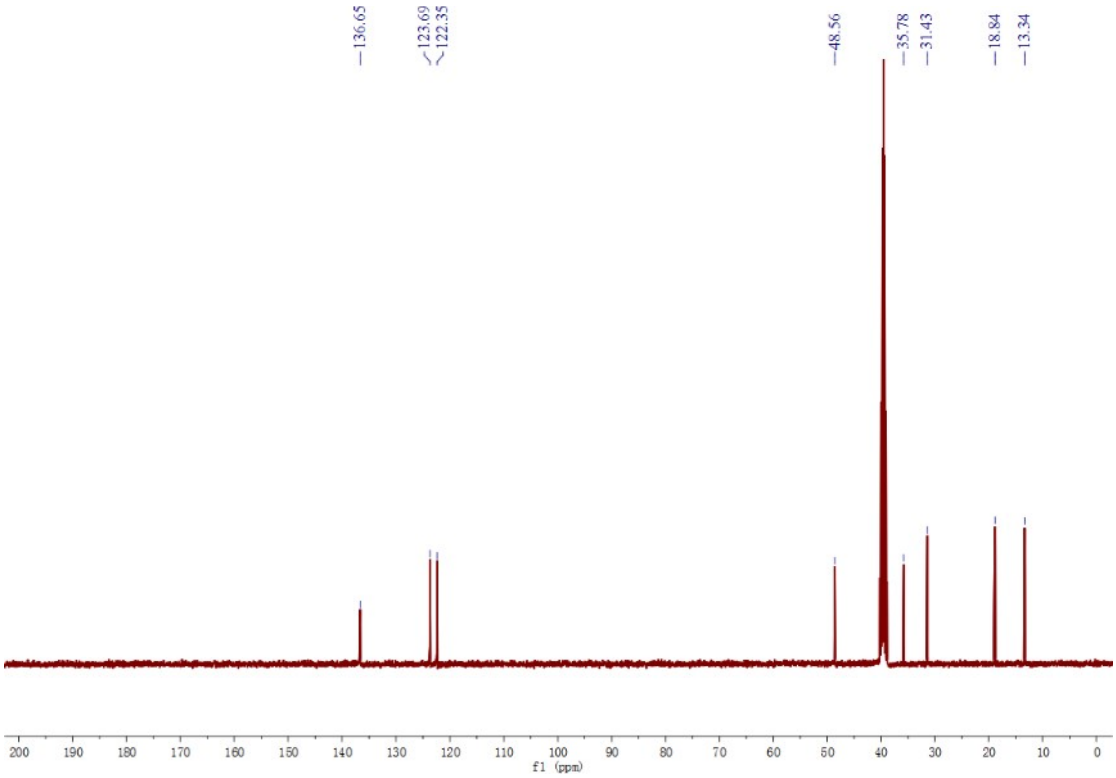

Figure S45. ^{13}C NMR spectrum of complex **5c**.

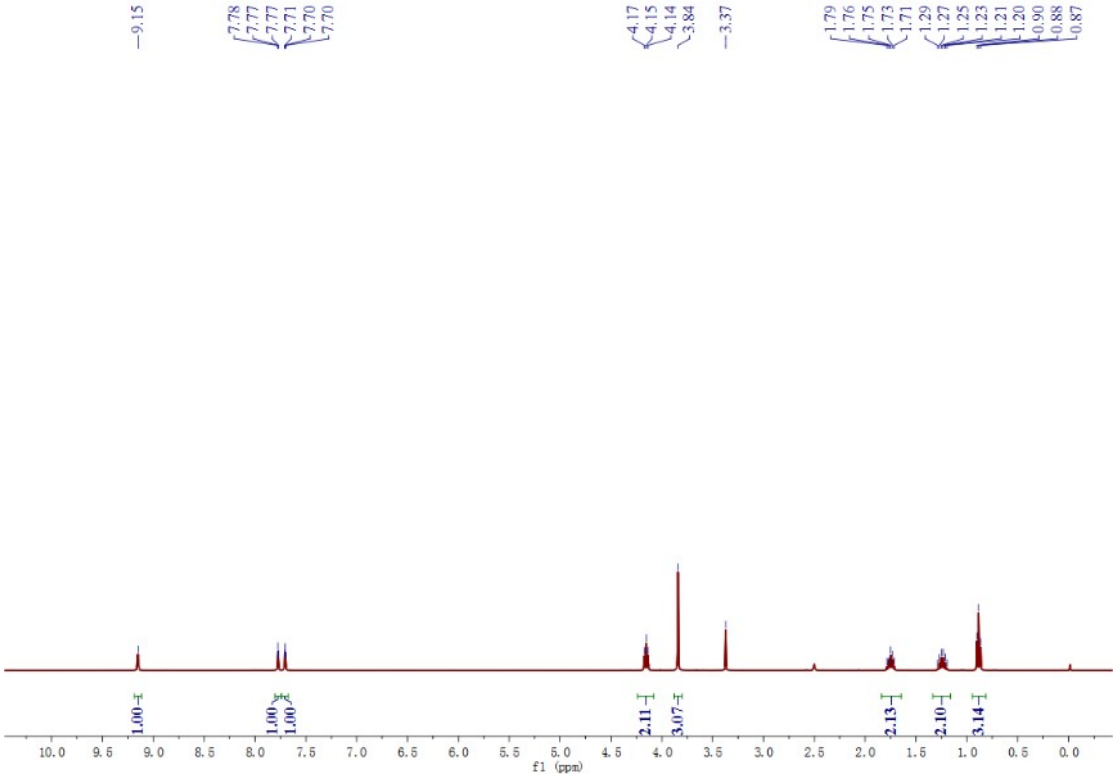

Figure S46. ^{1}H NMR spectrum of complex **5c**.

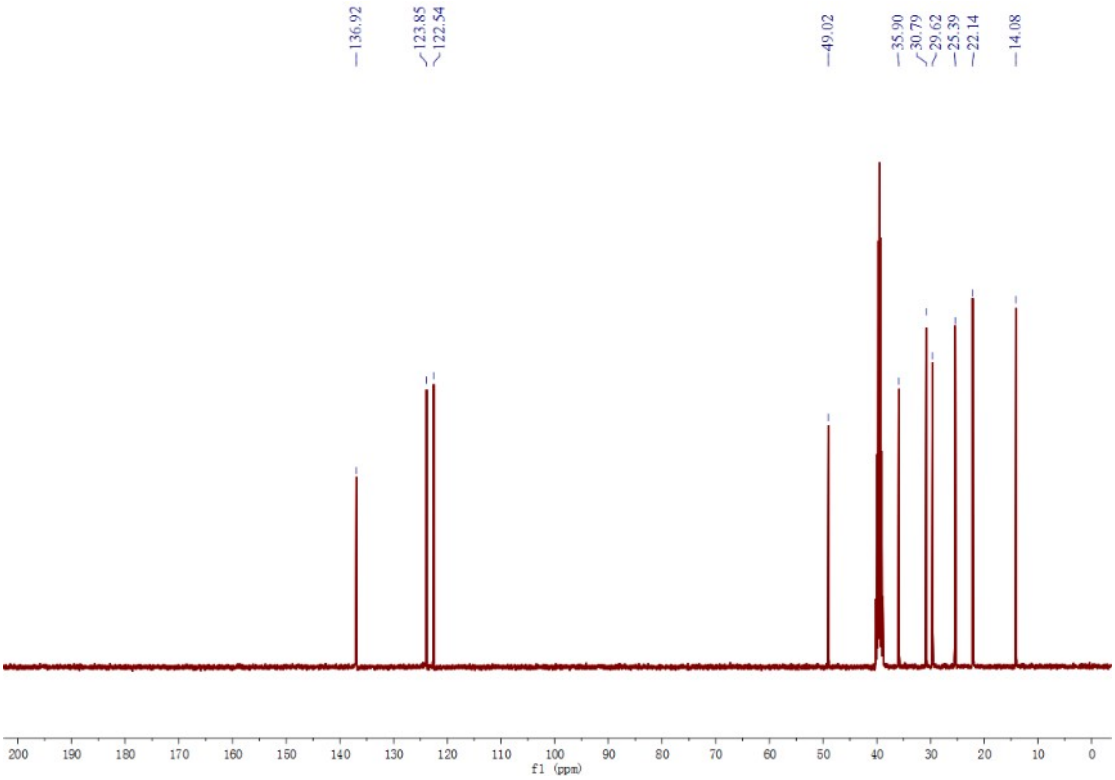

Figure S47. ^{13}C NMR spectrum of complex **5d**.

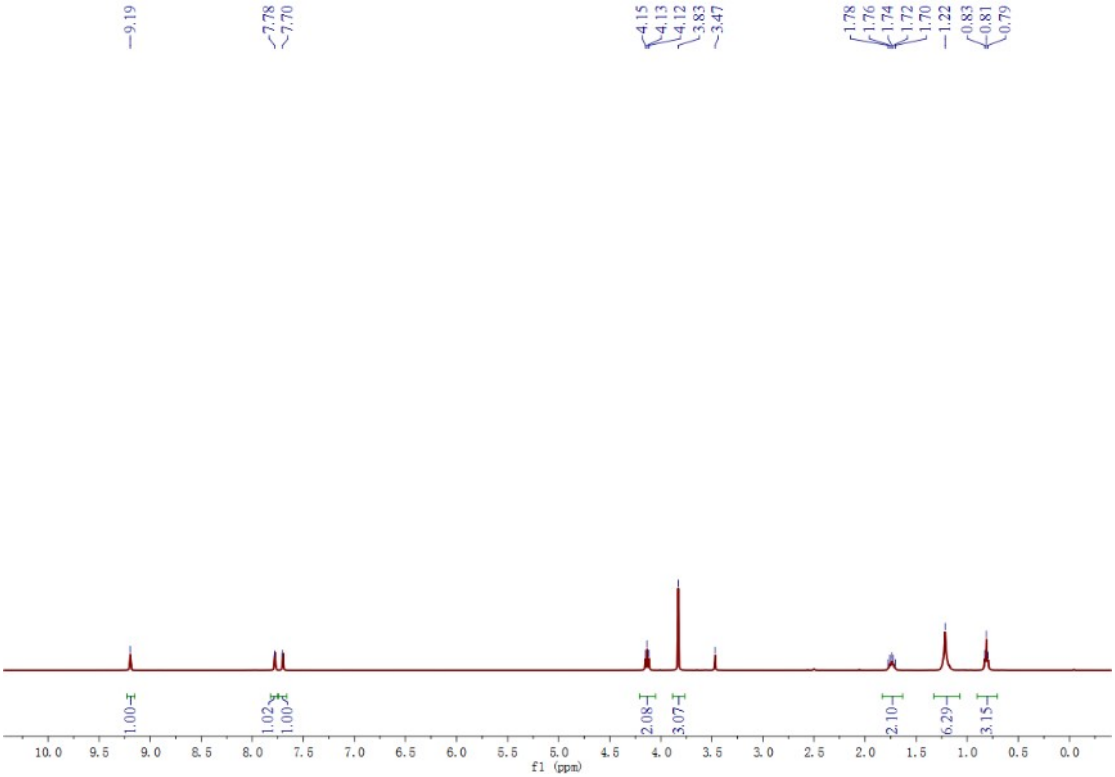

Figure S48. ^{1}H NMR spectrum of complex **5d**.

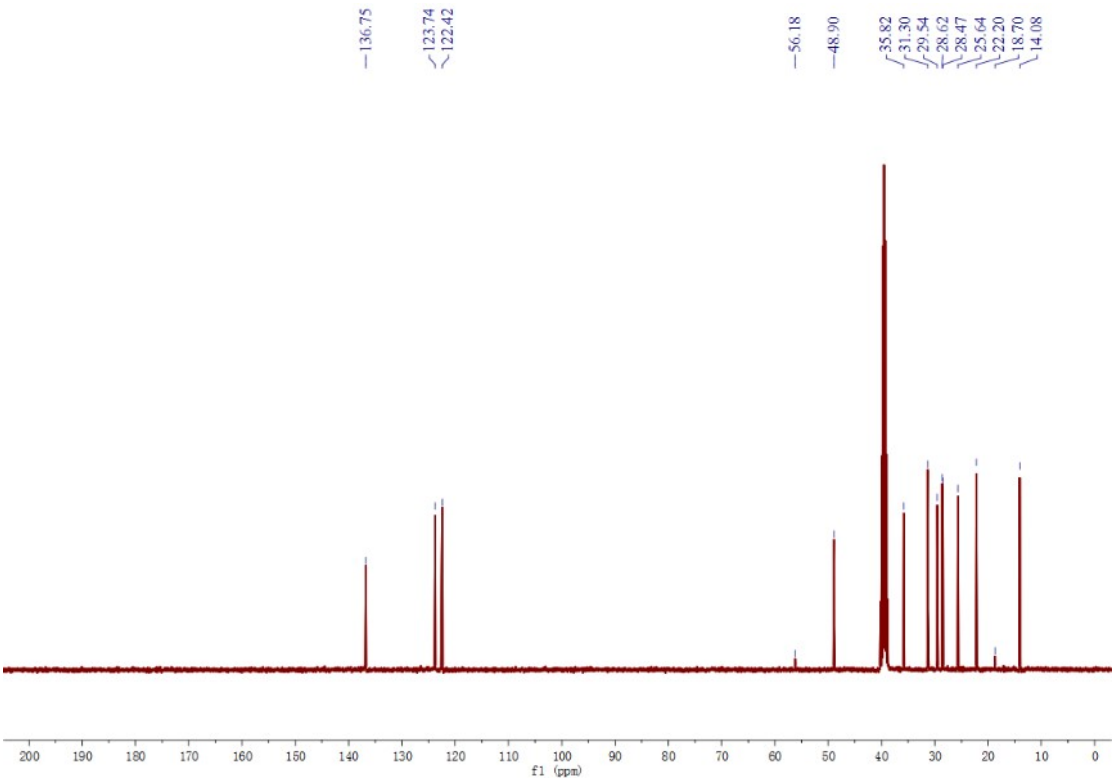

Figure S49. ^{13}C NMR spectrum of complex **5e**.

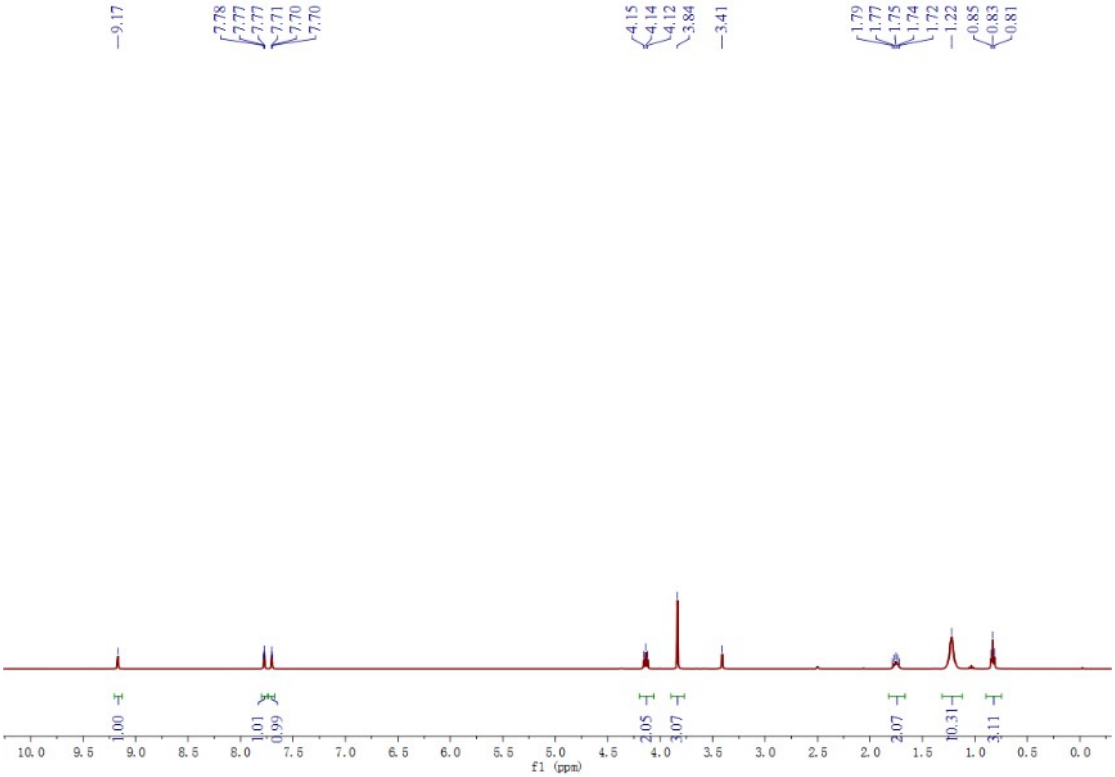

Figure S50. ^{1}H NMR spectrum of complex **5e.**

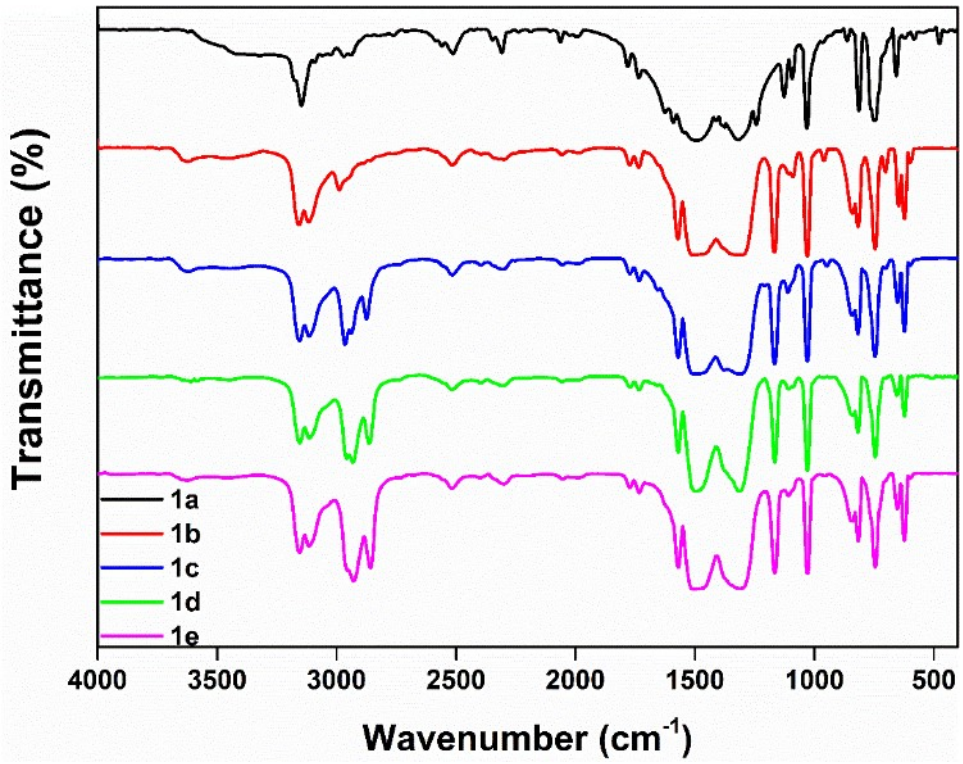

Figure 51. IR spectra of **1a-1e**.

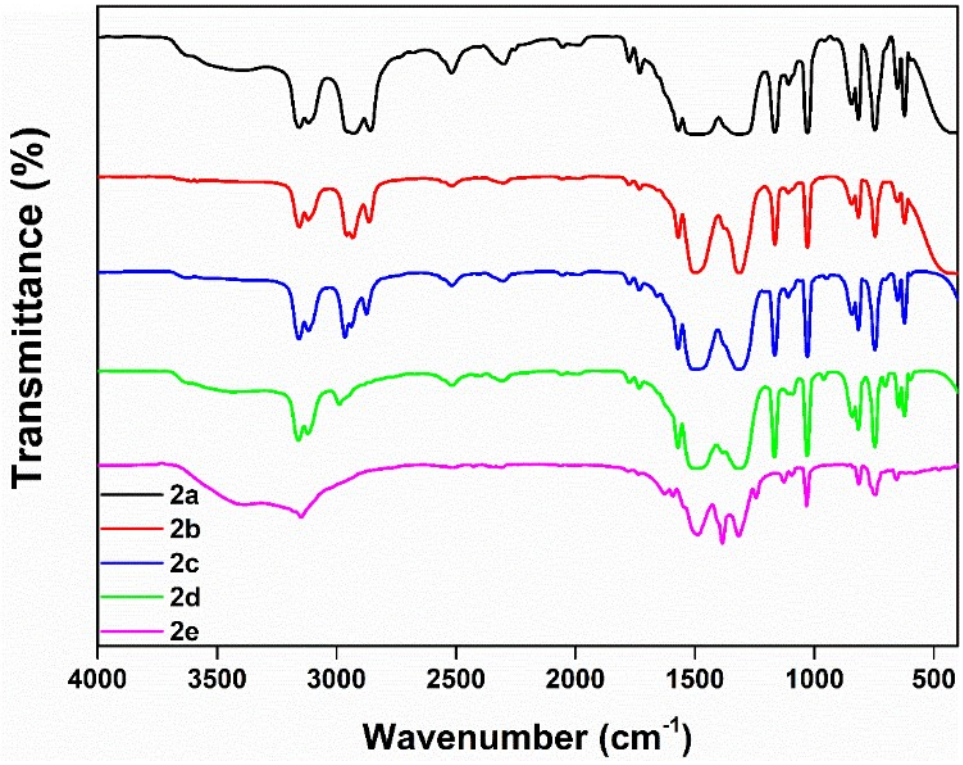

Figure S52. The IR Spectra of **2**.

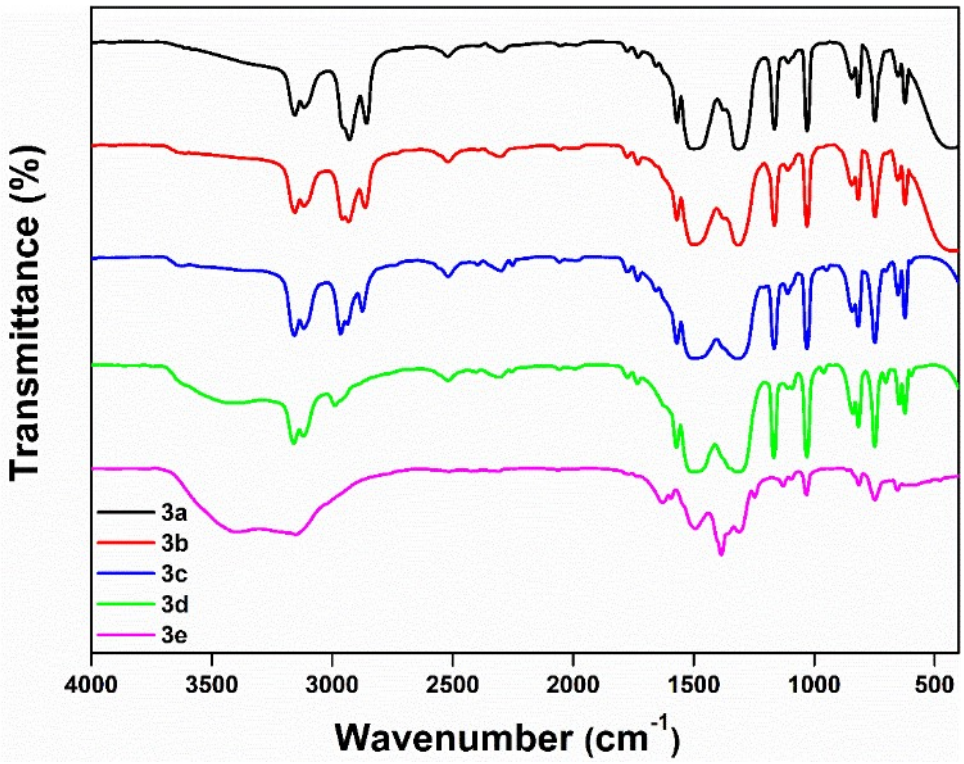

Figure S53. The IR Spectra of **3**.

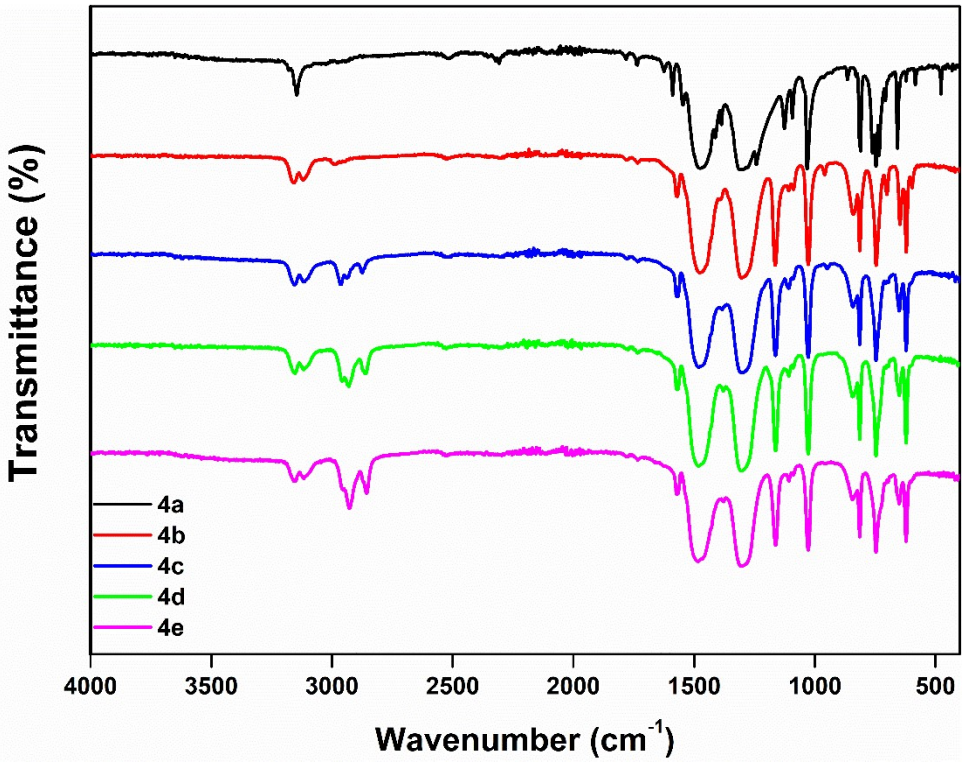

Figure S54. The IR Spectra of **4**.

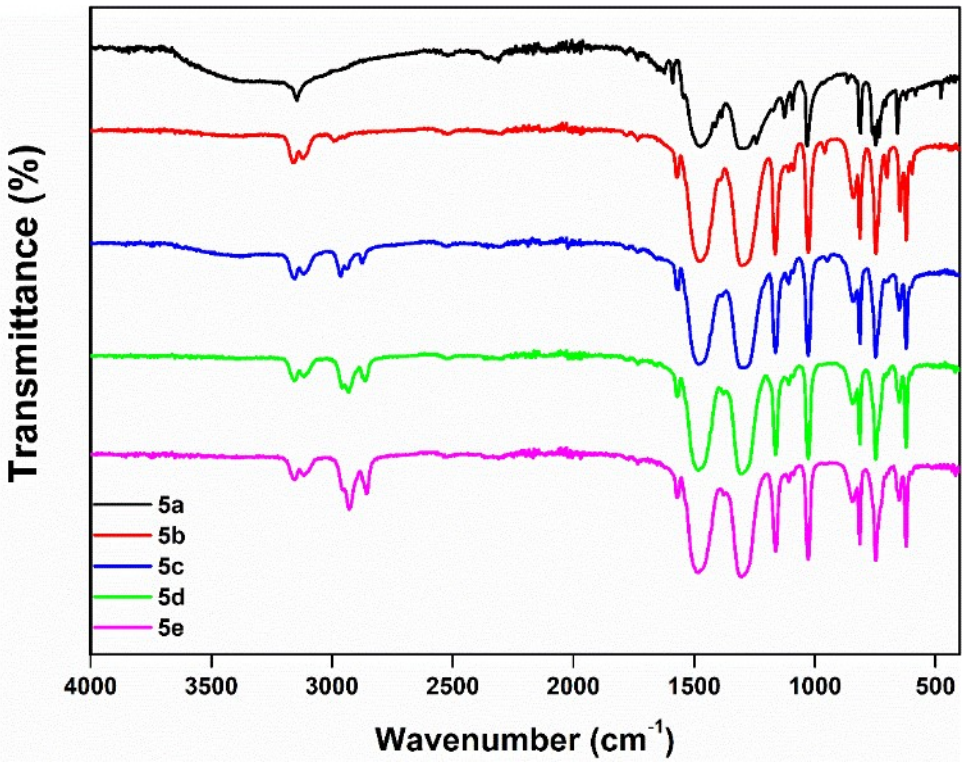

Figure S55. The IR Spectra of **5**.

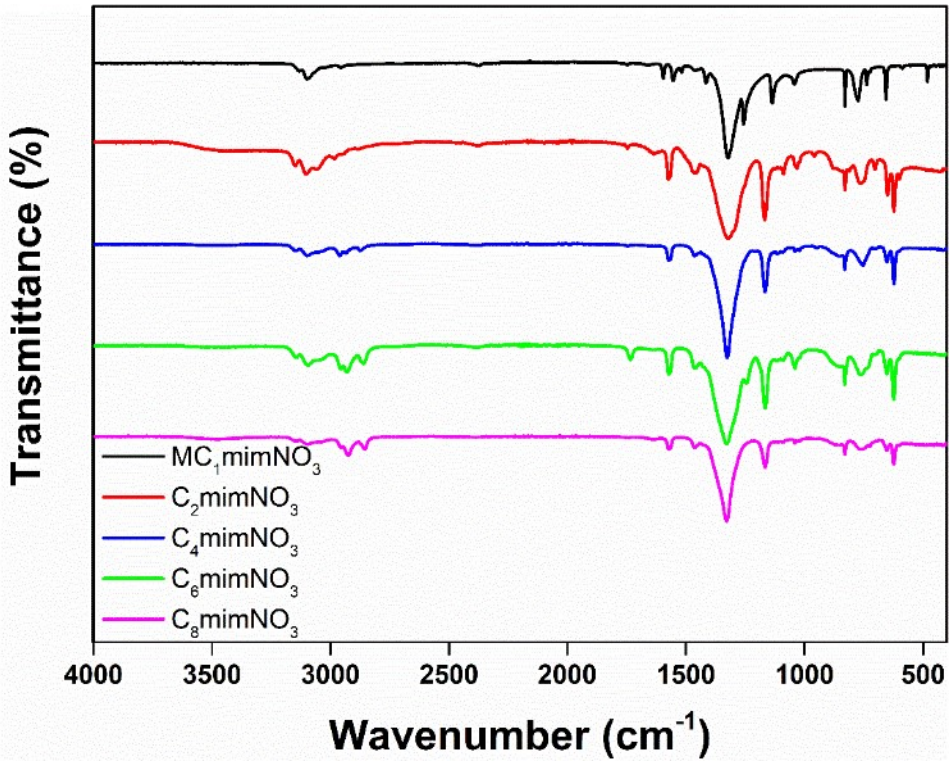

Figure S56. IR spectra of imidazolium nitrates.

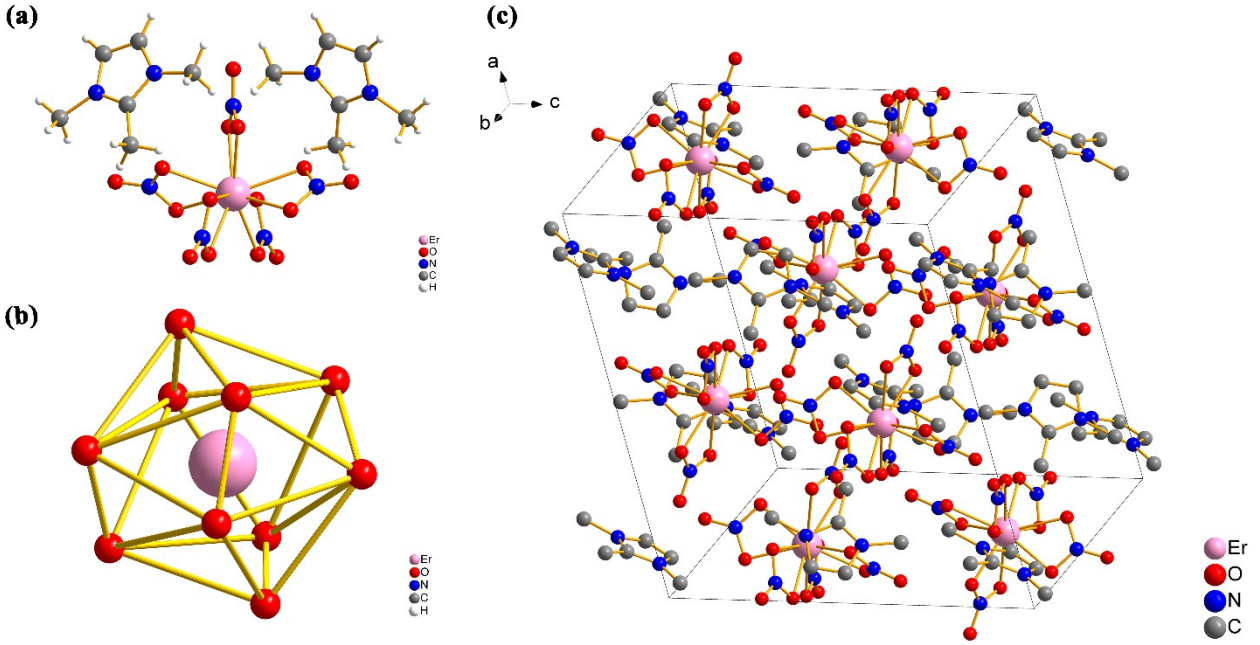

Figure S57. (a, b) Molecular structures and coordinating polyhedrons of **2a**. (c) Unit cells view along the plane (111) direction. H atoms are omitted for clarity.

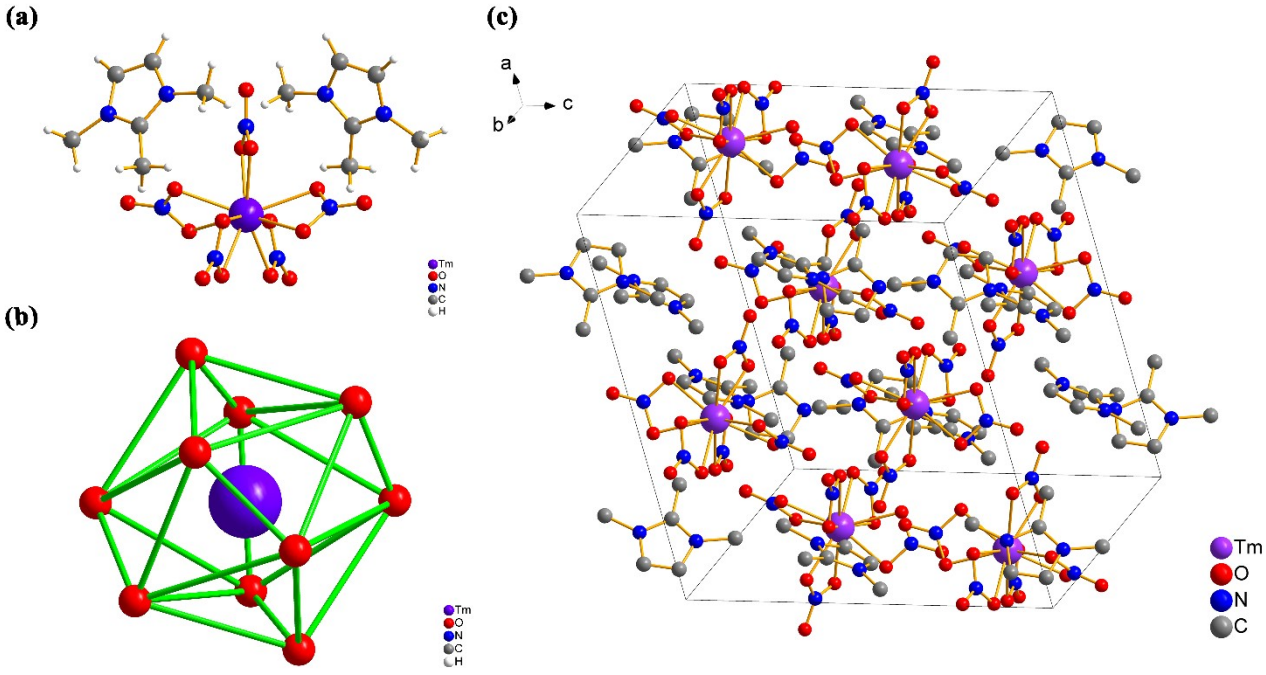

Figure S58. (a, b) Molecular structures and coordinating polyhedrons of **3a**. (c) Unit cells view along the plane (111) direction. H atoms are omitted for clarity.

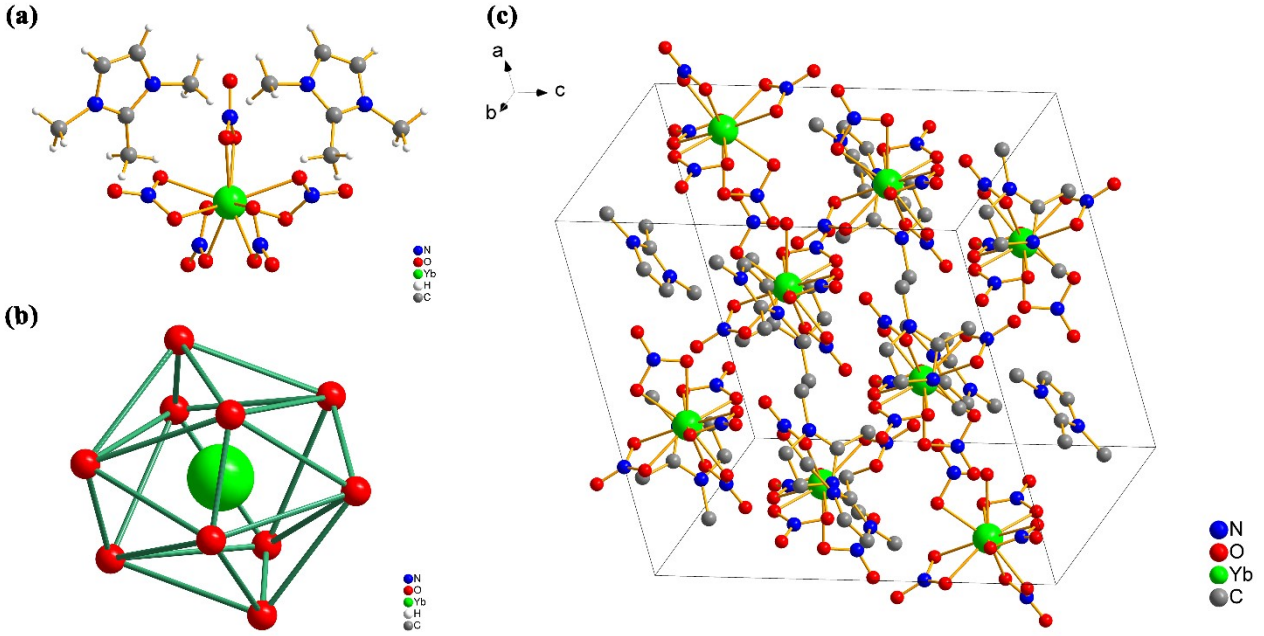

Figure S59. (a, b) Molecular structures and coordinating polyhedrons of **4a**. (c) Unit cells view along the plane (111) direction. H atoms are omitted for clarity.

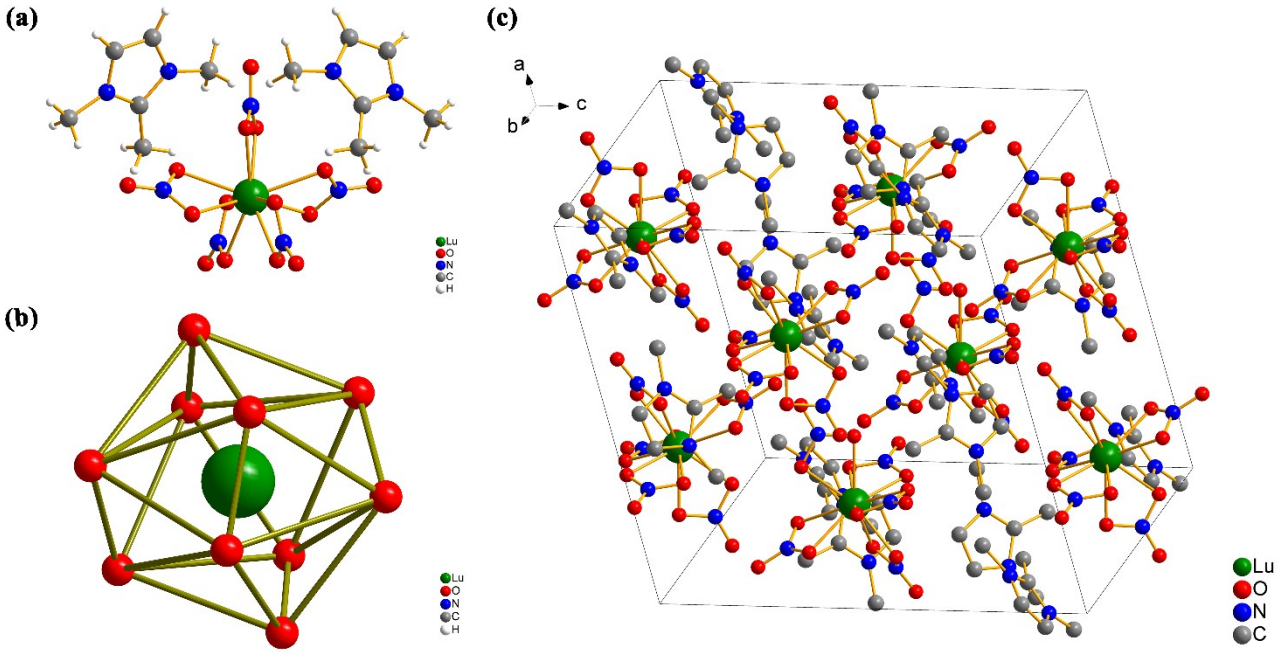

Figure S60. (a, b) Molecular structures and coordinating polyhedrons of **5a**. (c) Unit cells view along the plane (111) direction. H atoms are omitted for clarity.

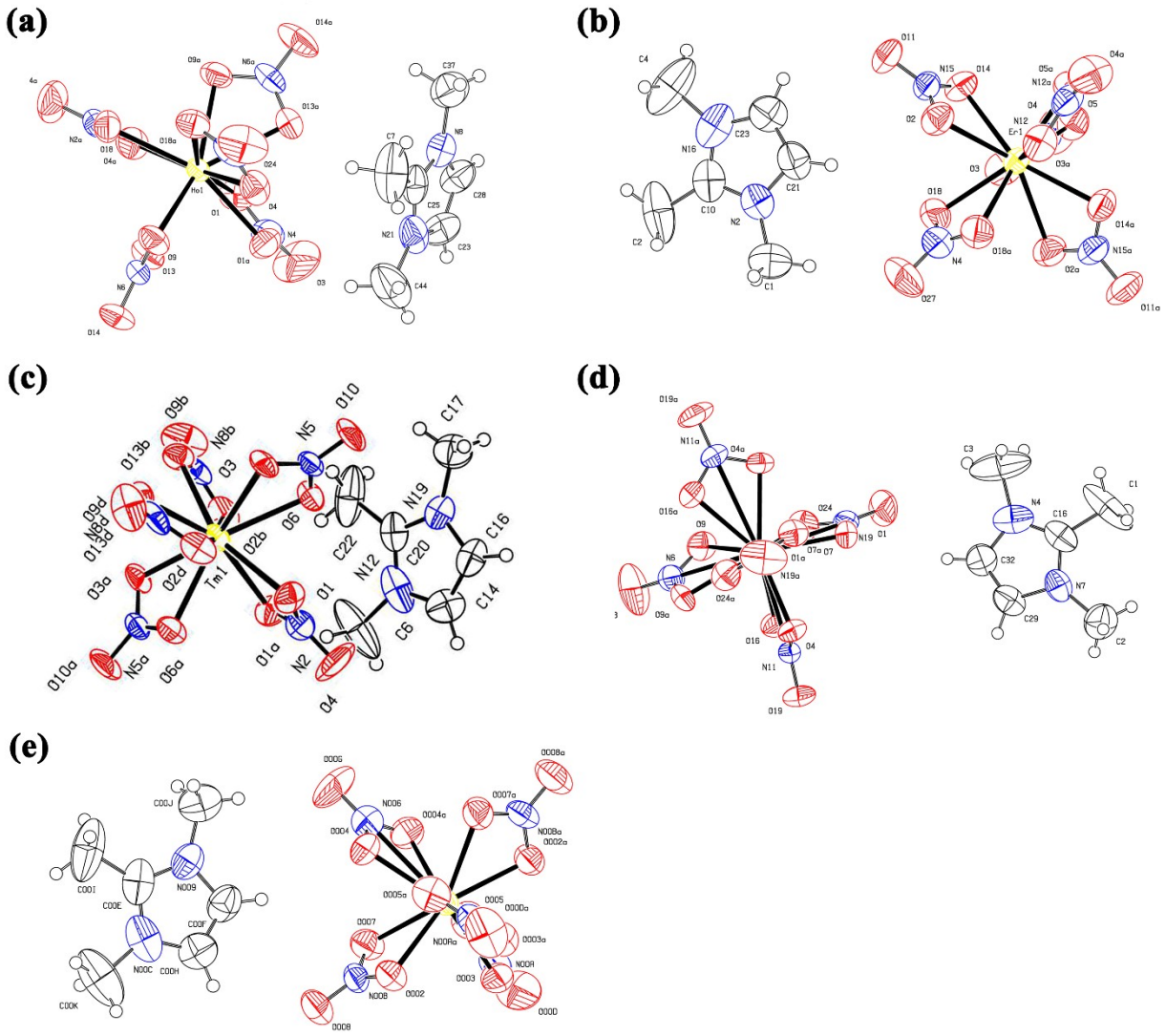

Figure S61. The thermal ellipsoid of **1a**–**5a.**

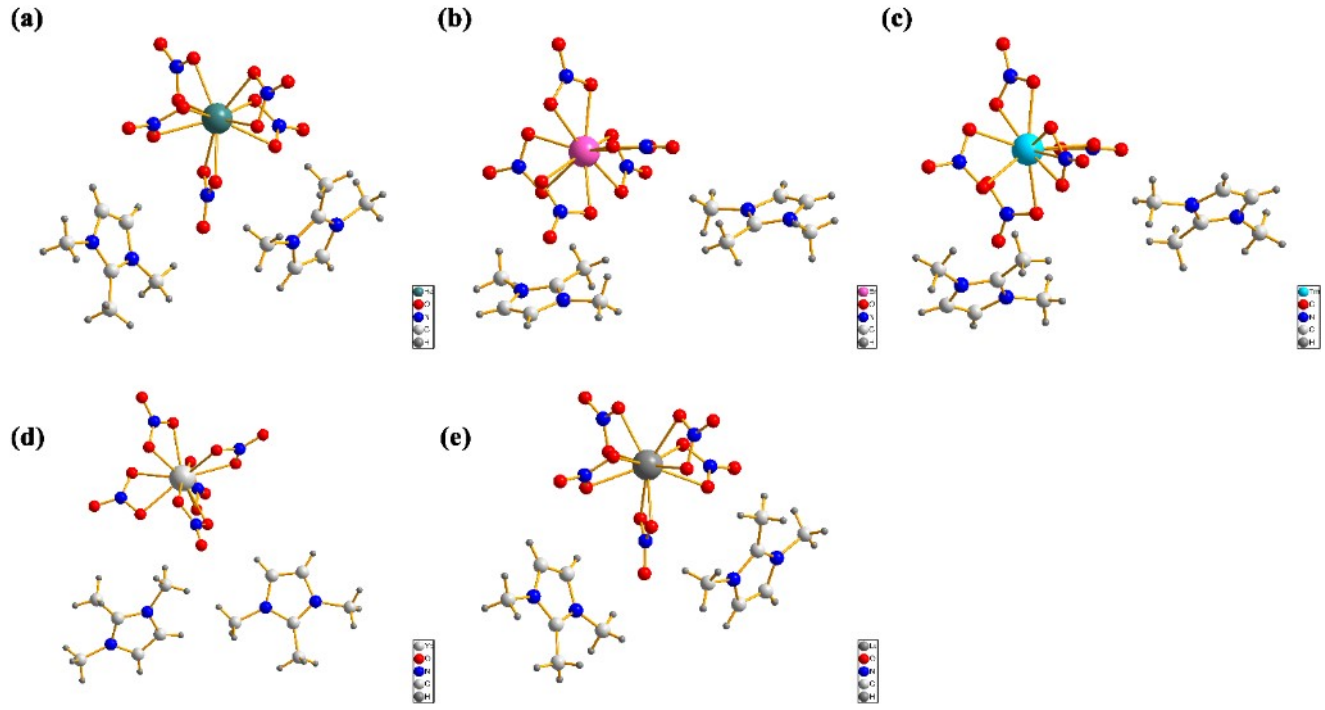

Figure S62. Molecular Structure of **1a**, **2a**, **3a, 4a** and **5a**.

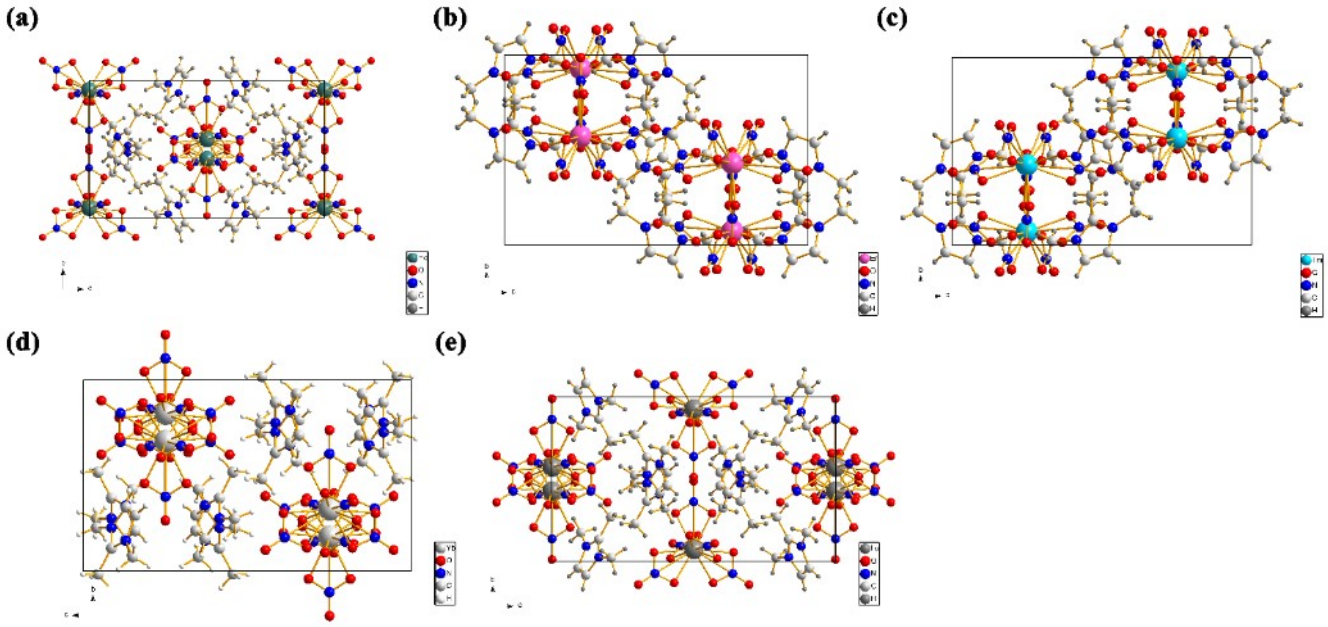

Figure S63. Packing Diagram of **1a**, **2a**, **3a, 4a** and **5a** Viewed down the *a*-axis.

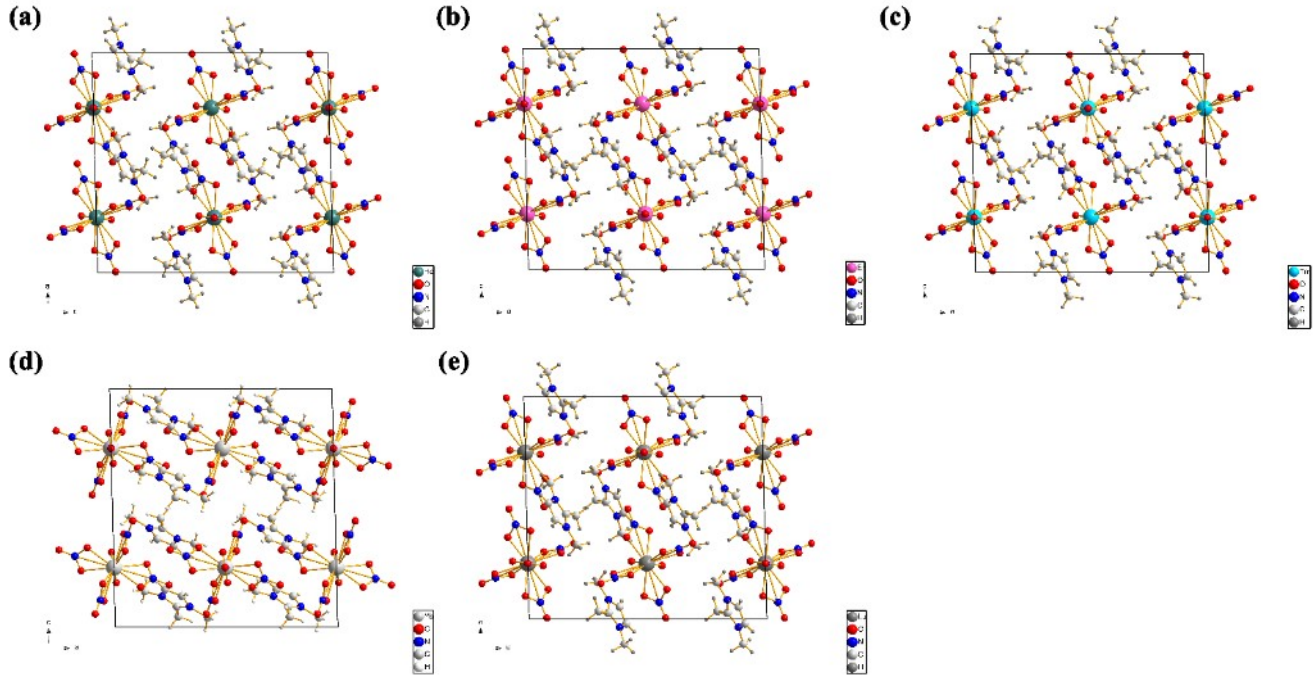

Figure S64. Packing Diagram of **1a**, **2a**, **3a, 4a** and **5a** Viewed down the *b*-axis.

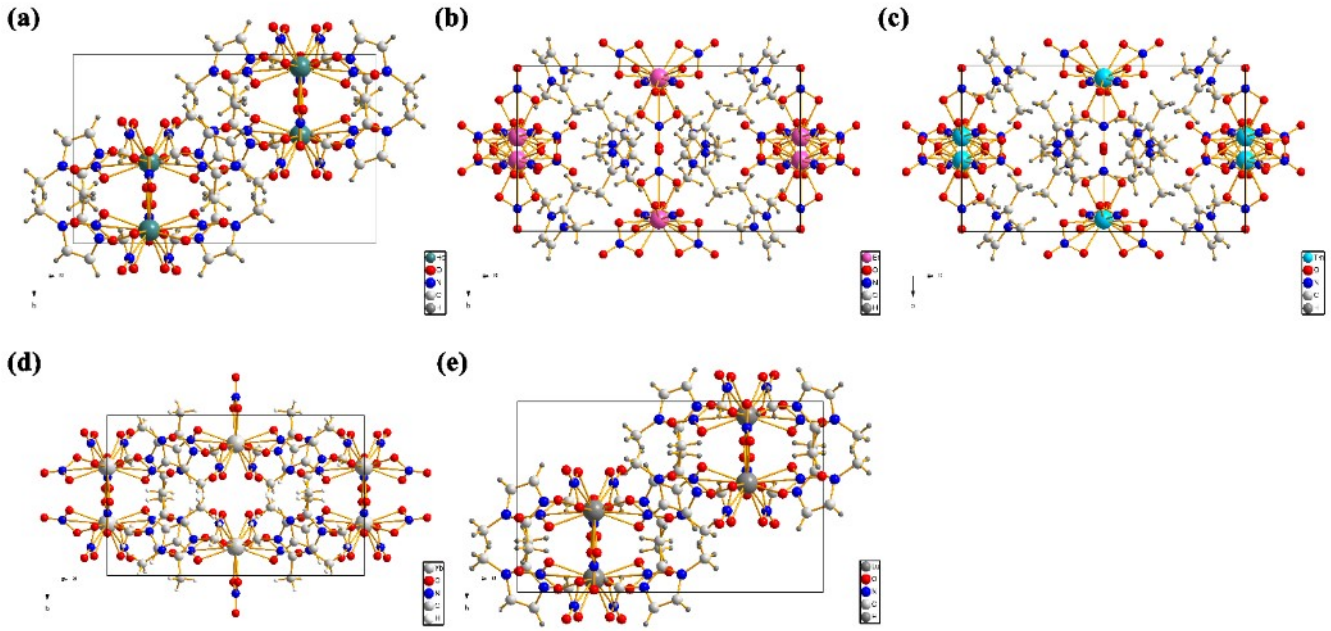

Figure S65. Packing Diagram of **1a**, **2a**, **3a, 4a** and **5a** Viewed down the *c*-axis.

Table S1. Selected bond lengths[Å] and Bond angles[°] in the crystal structure of **1a**.

Bond lengths			
Ho1–O1$^{\#1}$	2.413(3)	Ho1–O8$^{\#1}$	2.424(3)
Ho1–O1	2.413(3)	O1–N1	1.279(6)
Ho1–O2$^{\#1}$	2.452(3)	O2–N1	1.248(5)
Ho1–O2	2.452(3)	O3–N4	1.213(6)
Ho1–O4$^{\#1}$	2.408(3)	O4–N4	1.261(6)
Ho1–O4	2.408(3)	O5–N1	1.200(5)
Ho1–O6$^{\#1}$	2.459(4)	O6–N4	1.262(5)
Ho1–O6	2.459(4)	O7–N3	1.193(10)
Ho1–O8	2.424(3)	O8–N3	1.261(5)
Bond angles			
O1—Ho1—O2	51.93(11)	N9—O13—Ho1	98.1(10)
O4–Ho1–O6	51.77(12)	O2–N1–O1	115.0(3)
O8—Ho1—O8	52.41(17)	O5–N1–O1	120.6(5)
N1–O1–Ho1	96.9(3)	O5–N1–O2	124.4(5)
N1–O2–Ho1	96.0(2)	O7–N3–O8	121.9(3)
N4–O4–Ho1	98.0(3)	O8–N3–O8	116.2(6)
N4–O6–Ho1	95.4(3)	O3–N4–O4	123.0(5)
N3–O8–Ho1	95.7(3)	O3–N4–O6	122.2(5)
N8—O10—Ho1	98.2(10)	O4–N4–O6	114.8(4)

Table S2. Selected bond lengths[Å] and Bond angles[°] in the crystal structure of **2a**[a].

Bond lengths			
Er01–O1$^{\#1}$	2.406(3)	Er01–O8$^{\#1}$	2.447(3)
Er01–O1	2.406(3)	O1–N3	1.264(5)
Er01–O2$^{\#1}$	2.445(3)	O2–N4	1.261(5)
Er01–O2	2.445(3)	O3–N3	1.206(5)
Er01–O4	2.396(3)	O4–N4	1.268(5)
Er01–O4$^{\#1}$	2.396(3)	O5–N4	1.201(5)
Er01–O6$^{\#1}$	2.409(3)	O6–N1	1.265(5)

Er01–O6	2.409(3)	O7–N1	1.200(10)
Er01–O8	2.447(3)	O8–N3	1.260(5)
Bond angles			
O1–Er01–O8	51.94(11)	O6–N1–O6	115.6(5)
O4–Er01–O2	52.07(11)	O7–N1–O6	122.2(3)
O6–Er01–O6	52.76(16)	O3–N3–O1	122.3(5)
N3–O1–Er01	97.6(2)	O3–N3–O8	123.0(5)
N4–O2–Er01	95.6(2)	O8–N3–O1	114.7(4)
N4–O4–Er01	97.8(2)	O2–N4–O4	114.4(3)
N1–O6–Er01	95.8(3)	O5–N4–O2	123.2(4)
N3–O8–Er01	95.7(3)	O5–N4–O4	122.4(4)

[a]Symmetry operation: [i] 1-*x*, +*y*, 1/2-*z*

Table S3. Selected bond lengths[Å] and Bond angles[°] in the crystal structure of **3a**[a].

Bond lengths			
Tm1–O1	2.393(4)	Tm1–O8$^{\#1}$	2.409(4)
Tm1–O1$^{\#1}$	2.393(4)	O1–N5	1.255(8)
Tm1–O2	2.439(4)	O2–N4	1.252(7)
Tm1–O2$^{\#1}$	2.439(4)	O3–N5	1.212(8)
Tm1–O4$^{\#1}$	2.439(5)	O4–N5	1.249(6)
Tm1–O4	2.439(5)	O5–N4	1.214(7)
Tm1–O6	2.383(4)	O6–N4	1.268(7)
Tm1–O6$^{\#1}$	2.383(4)	O7–N1	1.212(14)
Tm1–O8	2.409(4)	O8–N1	1.266(6)
Bond angles			
O1–Tm1–O4	51.85(17)	O7–N1–O8	121.4(4)
O6–Tm1–O2	52.27(15)	O8–N1–O8	117.3(8)
O8–Tm1–O8	53.3(2)	O2–N4–O6	115.0(5)
N5–O1–Tm1	97.5(4)	O5–N4–O2	122.7(6)
N4–O2–Tm1	95.1(3)	O5–N4–O6	122.4(6)
N5–O4–Tm1	95.5(5)	O3–N5–O1	122.0(7)

N4–O6–Tm1	97.4(3)	O3–N5–O4	122.8(8)
N1–O8–Tm1	94.7(4)	O4–N5–O1	115.1(6)

[a]Symmetry operation: [i] +*x*, 1-*y*, 1/2+*z*; [ii]1-*x*, 1-*y*, 1-*z*; [iii]1-*x*, +*y*, 3/2-*z*

Table S4. Selected bond lengths[Å] and Bond angles[°] in the crystal structure of **4a**[a].

Bond lengths			
Yb1–O1	2.379(4)	Yb1–O8	2.435(4)
Yb1–O1$^{\#1}$	2.379(4)	O1–N5	1.250(7)
Yb1–O2	2.436(5)	O2–N5	1.261(5)
Yb1–O2$^{\#1}$	2.436(5)	O3–N5	1.212(7)
Yb1–O4	2.371(4)	O4–N4	1.283(7)
Yb1–O4$^{\#1}$	2.371(4)	O5–N4	1.201(7)
Yb1–O6	2.385(4)	O6–N1	1.263(6)
Yb1–O6$^{\#1}$	2.385(4)	O7–N1	1.196(13)
Yb1–O8$^{\#1}$	2.435(4)	O8–N4	1.254(7)
Bond angles			
O1–Yb1–O2	52.21(15)	O6–N1–O6	115.1(7)
O4–Yb1–O8	52.60(14)	O7–N1–O6	122.4(4)
O6–Yb1–O6	53.1(2)	O5–N4–O4	121.9(6)
N5–O1–Yb1	97.9(3)	O5–N4–O8	124.0(6)
N5–O2–Yb1	94.8(4)	O8–N4–O4	114.1(4)
N4–O4–Yb1	97.6(3)	O1–N5–O2	115.1(5)
N1–O6–Yb1	95.9(4)	O3–N5–O1	122.8(6)
N4–O8–Yb1	95.4(3)	O3–N5–O2	122.1(7)

[a]Symmetry operation: [i]1-*x*, *y*, 3/2-*z*

Table S5. Selected bond lengths[Å] and Bond angles[°] in the crystal structure of **5a**[a].

Bond lengths			
Lu1–O1	2.369(5)	Lu1–O8	2.386(5)
Lu1–O1$^{\#1}$	2.369(5)	O1–N3	1.244(10)
Lu1–O2$^{\#1}$	2.433(6)	O2–N5	1.275(9)
Lu1–O2	2.433(6)	O3–N3	1.221(10)

Lu1–O4[#1]	2.356(5)	O4–N5	1.280(10)
Lu1–O4	2.355(5)	O5–N5	1.196(10)
Lu1–O6	2.427(6)	O6–N3	1.279(8)
Lu1–O6[#1]	2.427(6)	O7–N1	1.212(19)
Lu1–O8[#1]	2.386(5)	O8–N1	1.261(8)
Bond angles			
O1–Lu1–O6	52.6(2)	O7–N1–O8	121.9(5)
O4–Lu1–O2	53.02(19)	O8–N1–O8	116.2(10)
O8–Lu1–O8	53.3(3)	O1–N3–O6	114.9(7)
N3–O1–Lu1	98.1(4)	O3–N3–O1	123.8(9)
N5–O2–Lu1	94.8(4)	O3–N3–O6	121.3(9)
N5–O4–Lu1	98.4(4)	O2–N5–O4	113.7(6)
N3–O6–Lu1	94.3(5)	O5–N5–O2	123.0(9)
N1–O8–Lu1	95.3(5)	O5–N5–O4	123.3(8)

[a]Symmetry operation: [i]3/2-*x*, +*y*, 1-*z*

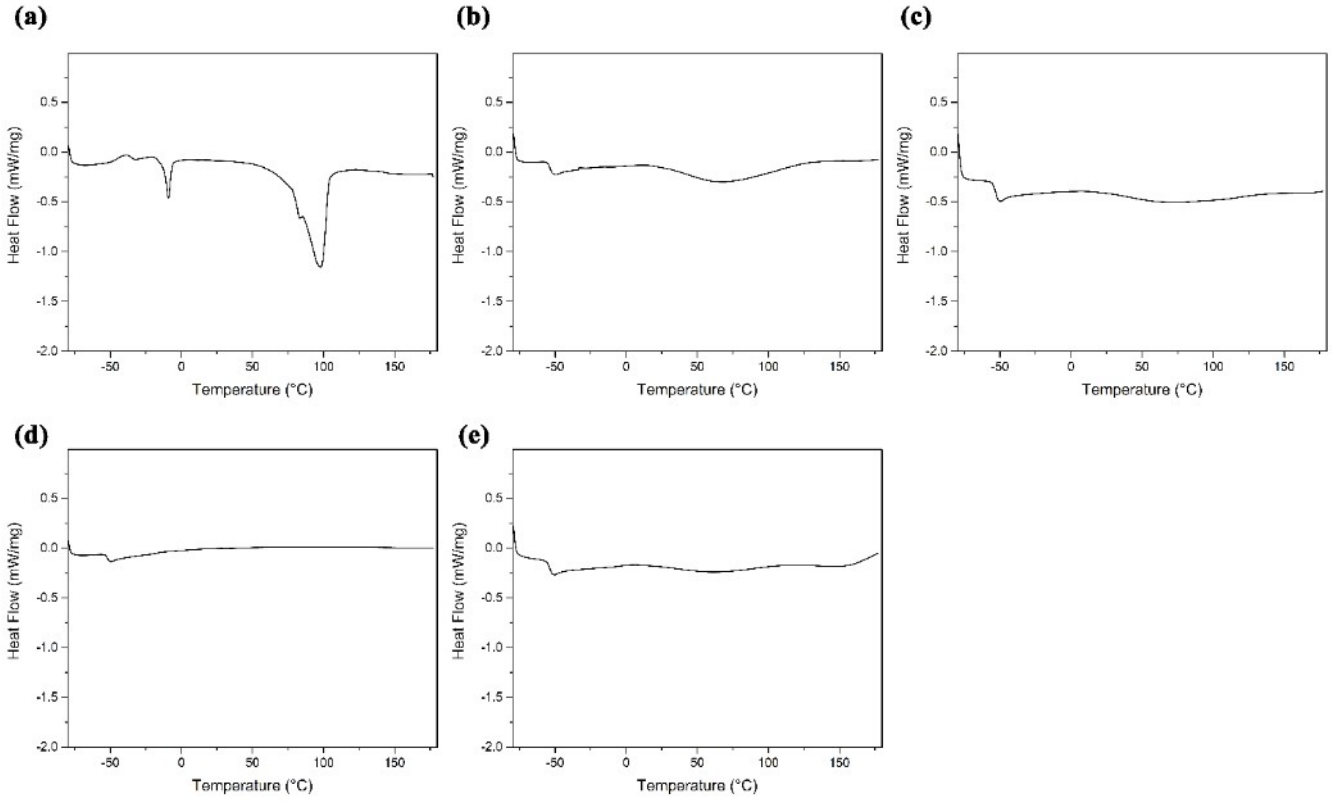

Figure S66. DSC Curves of **1a-1e**.

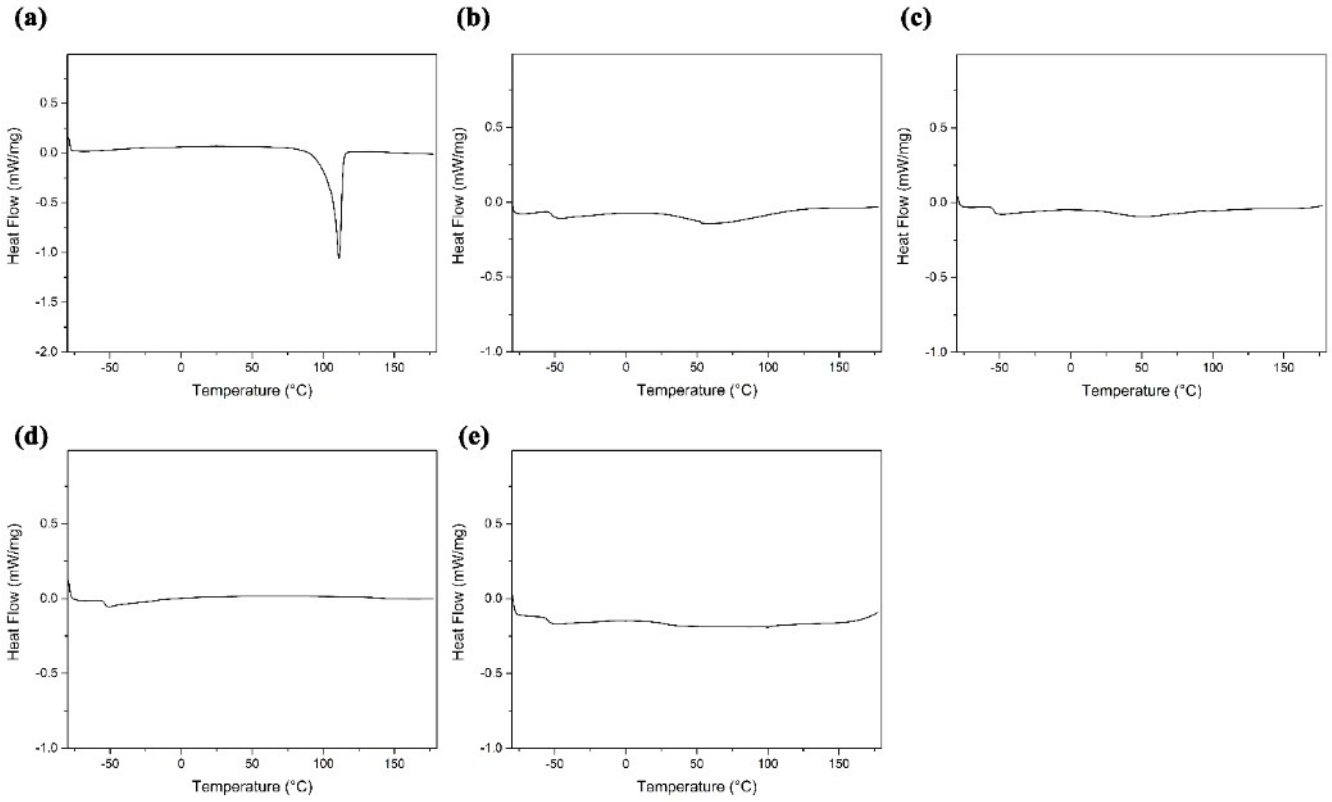

Figure S67. DSC Curves of **2a-2e**.

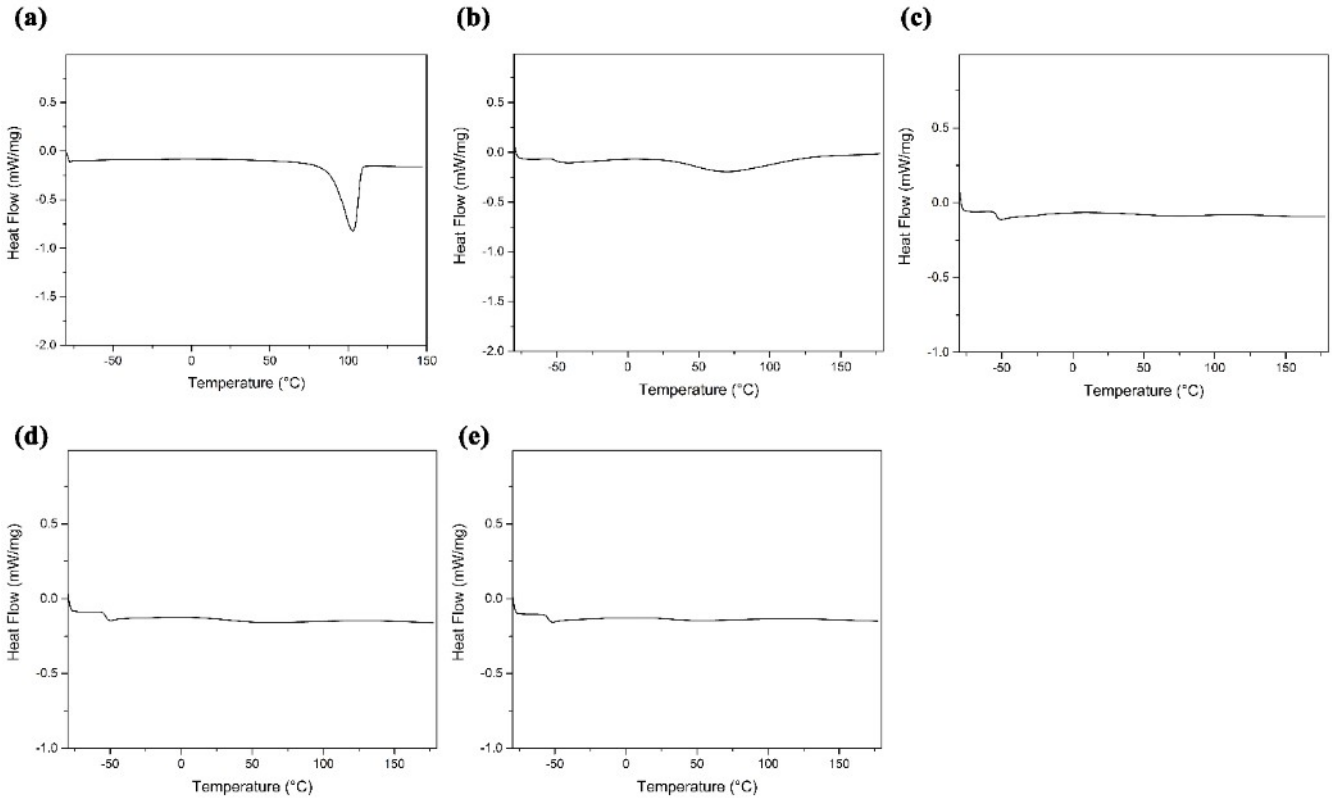

Figure S68. DSC Curves of **3a-3e**.

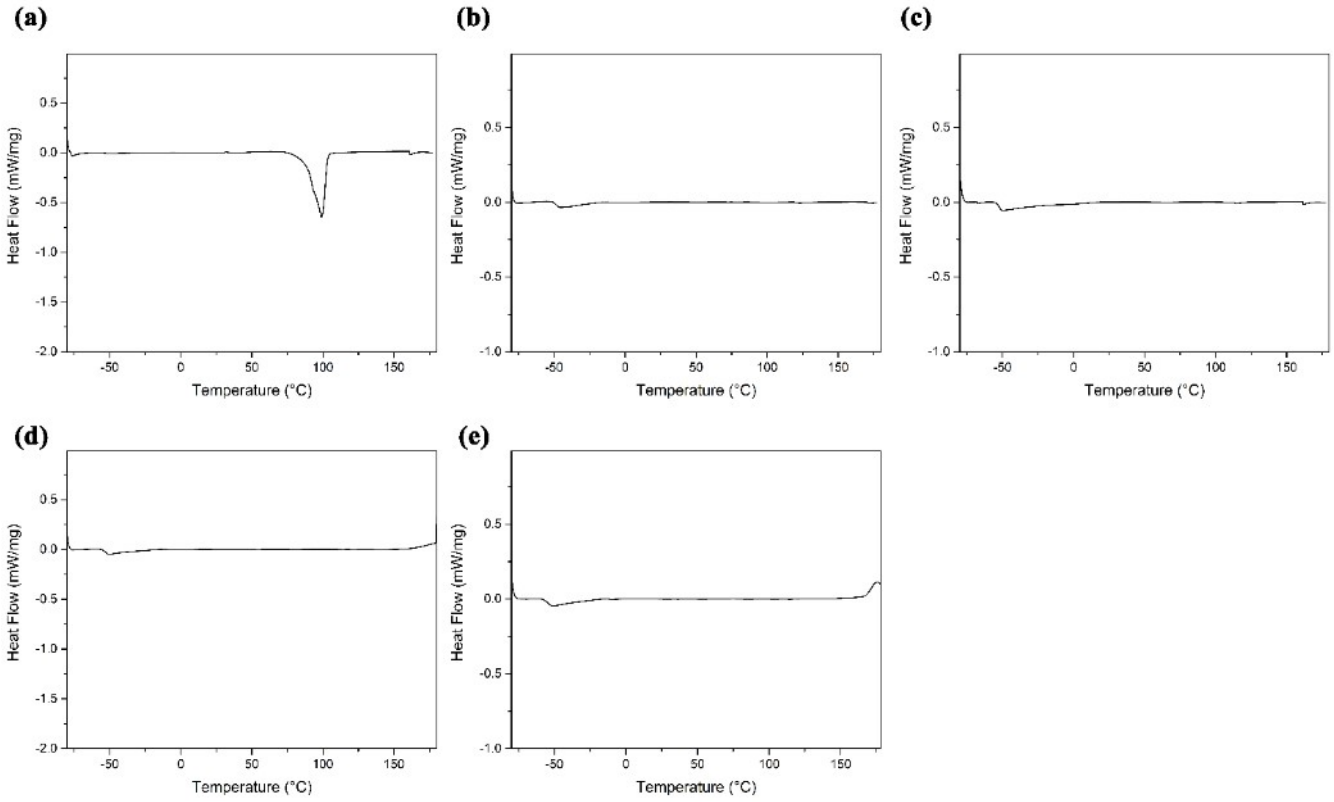

Figure S69. DSC Curves of **4a-4e**.

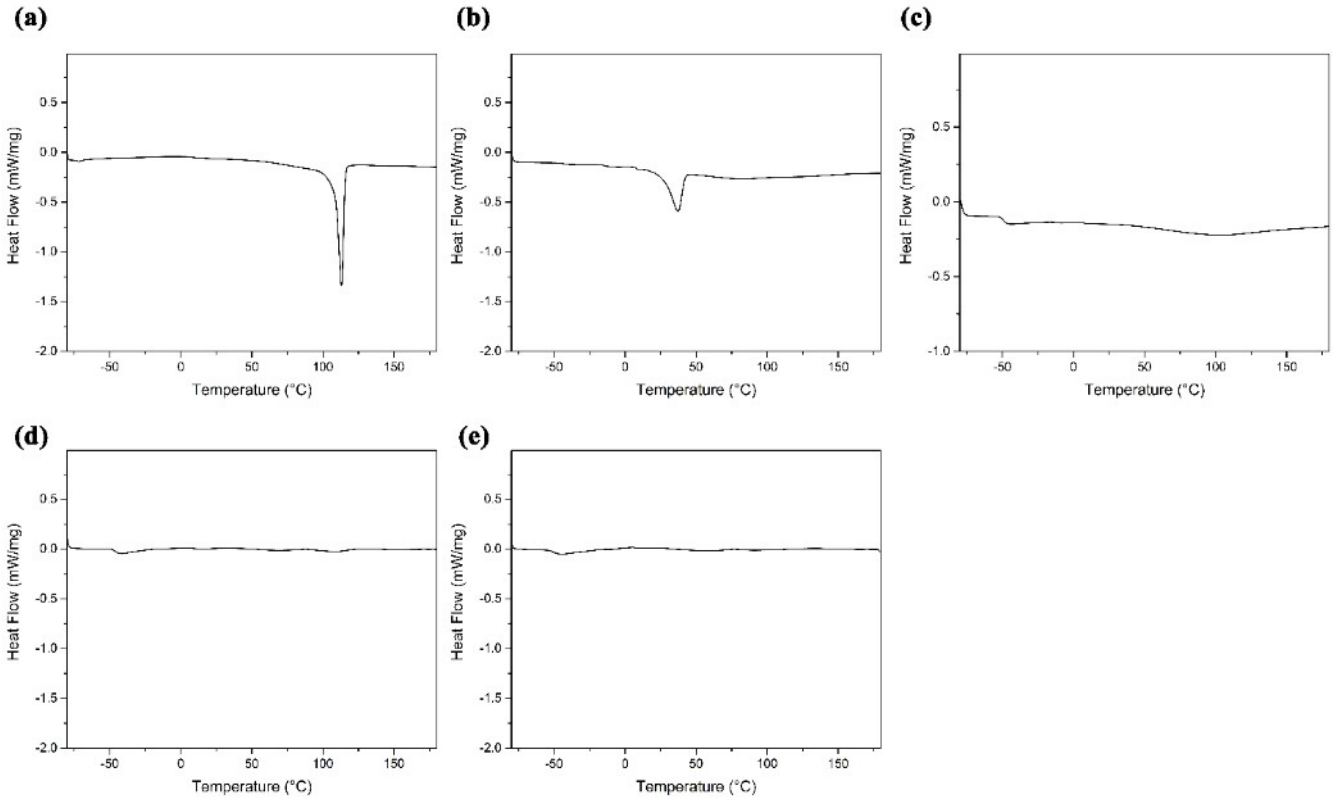

Figure S70. DSC Curves of **5a-5e**.

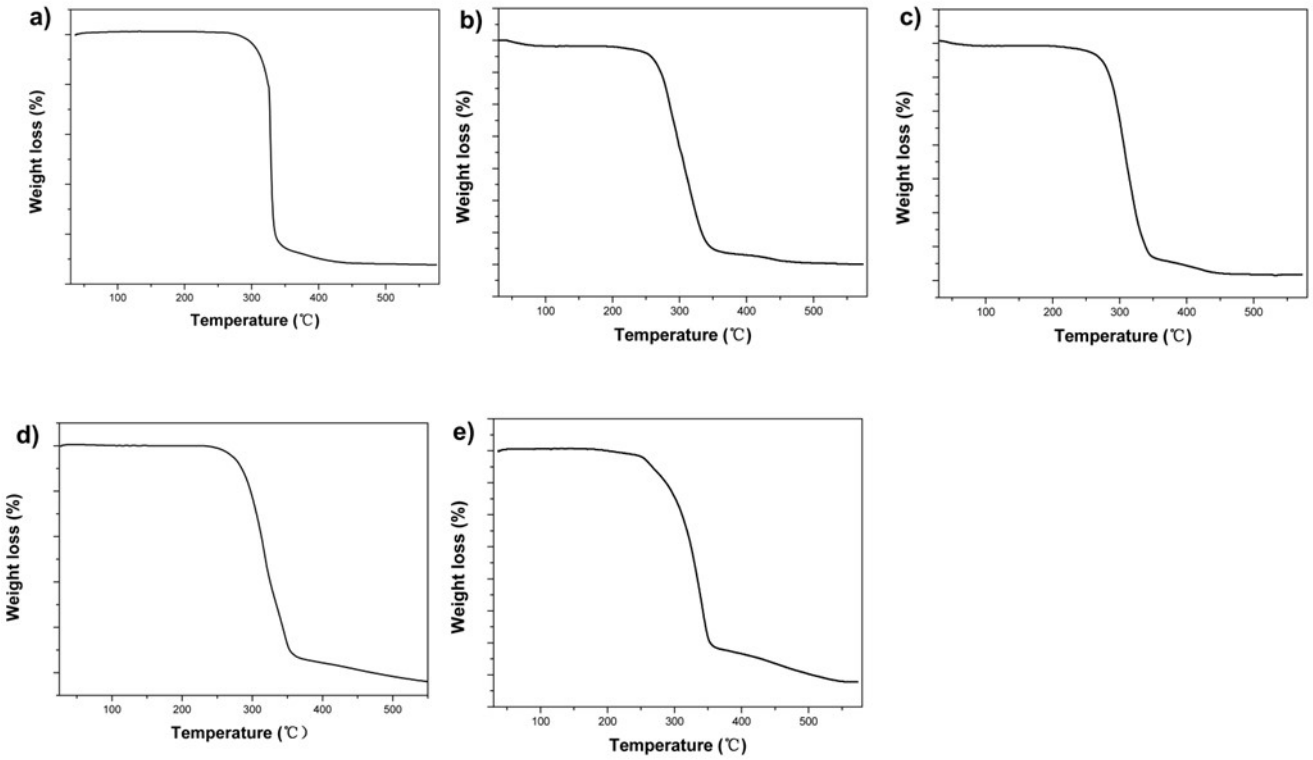

Figure S71. TG Curves of **1a-1e**.

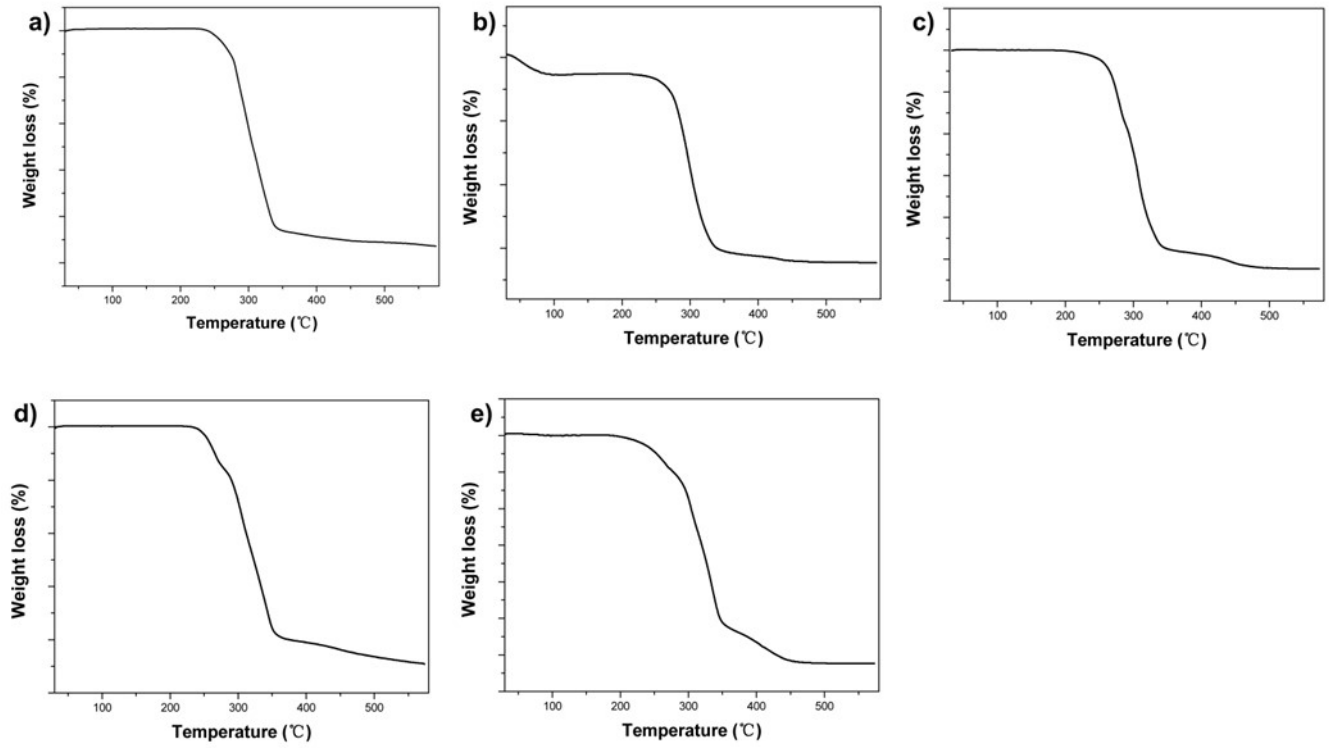

Figure S72. TG Curves of **2a-2e**.

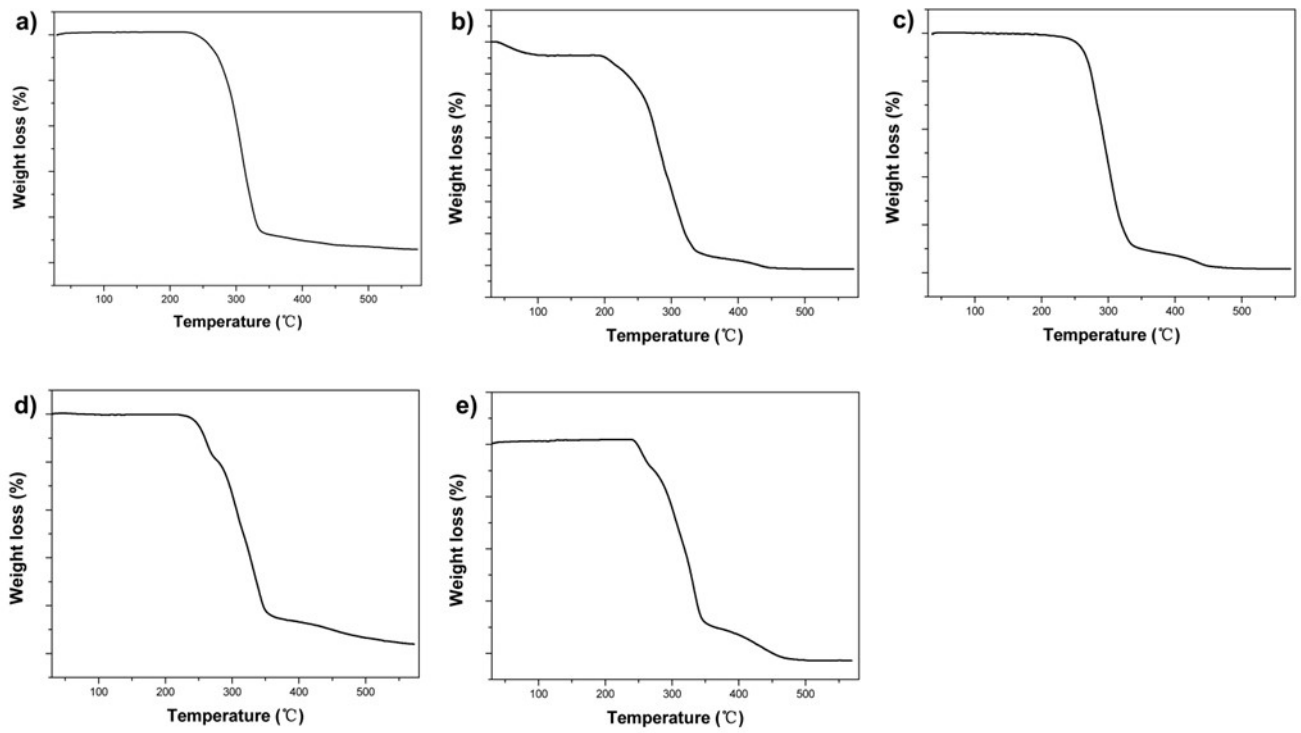

Figure S73. TG Curves of **3a-3e**.

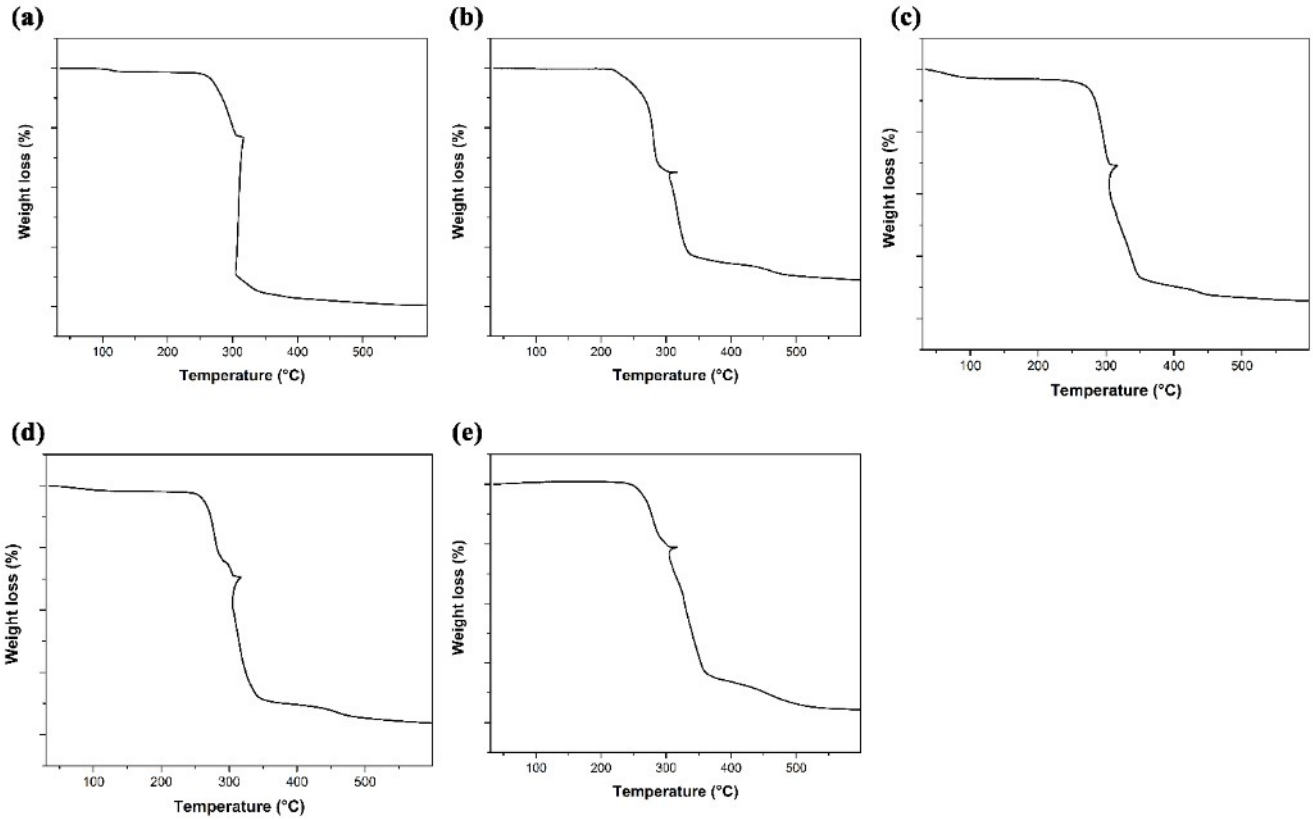

Figure S74. TG Curves of **4a-4e**.

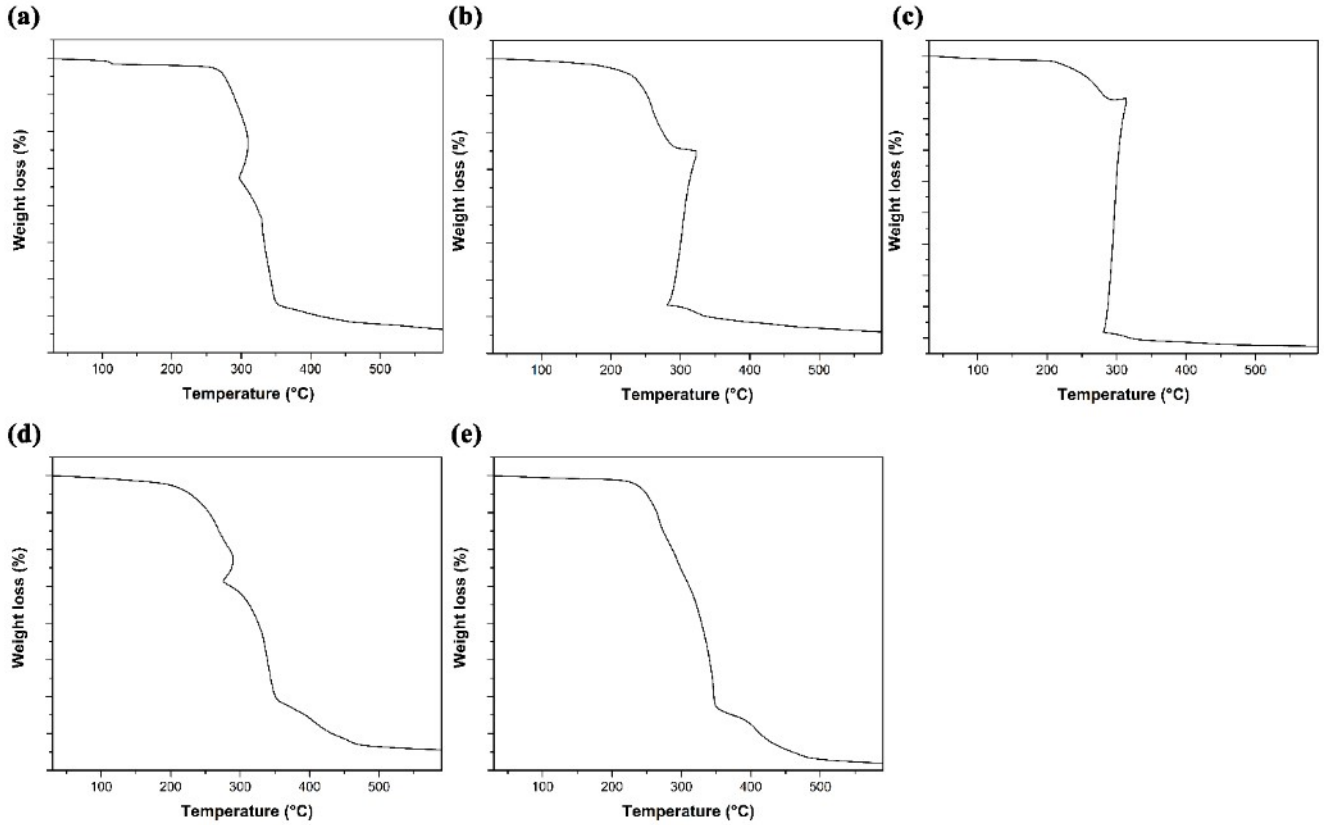

Figure S75. TG Curves of **5a-5e**.

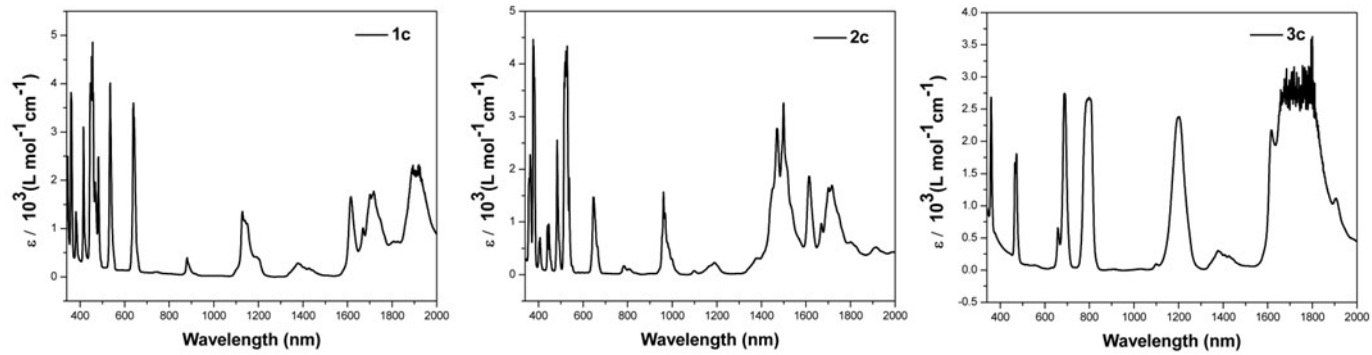

Figure S76. Characteristic 4f-4f Transition from 330 nm to 2000 nm of **1c**, **2c** and **3c**.

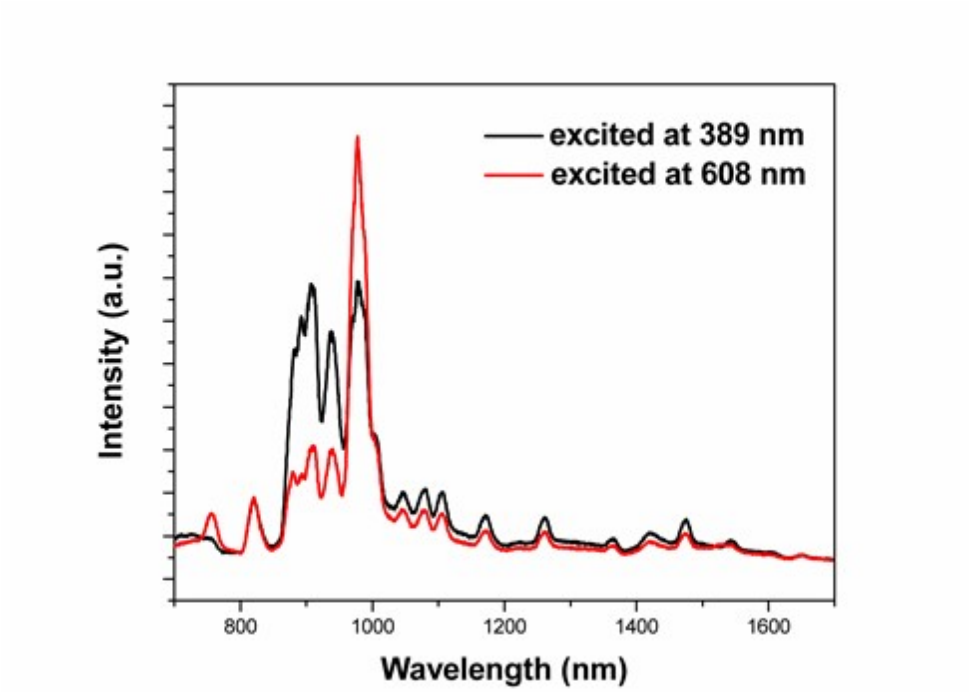

Figure S77. Near-infrared Emission Spectra of **1c** Excitated at 389 nm (black) and 608 nm (red).

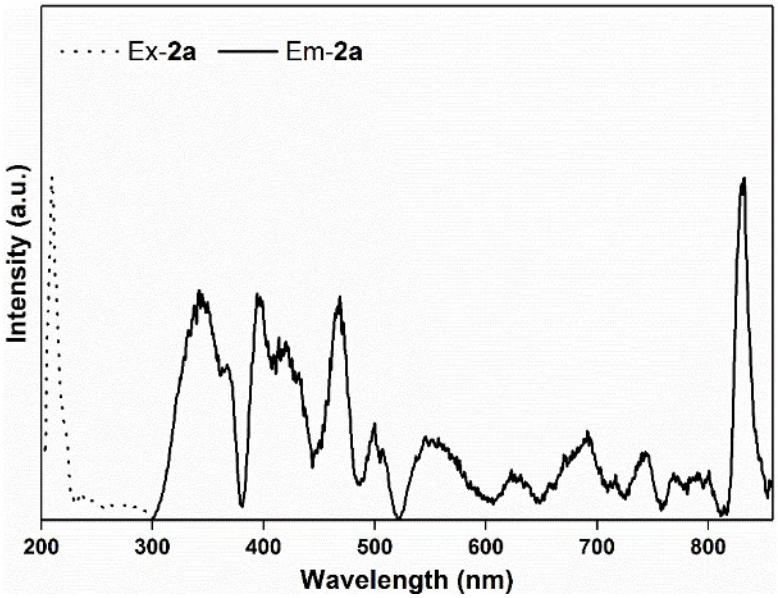

Figure S78. Near-infrared Excitation Spectra and Emission Spectra of **2a**.

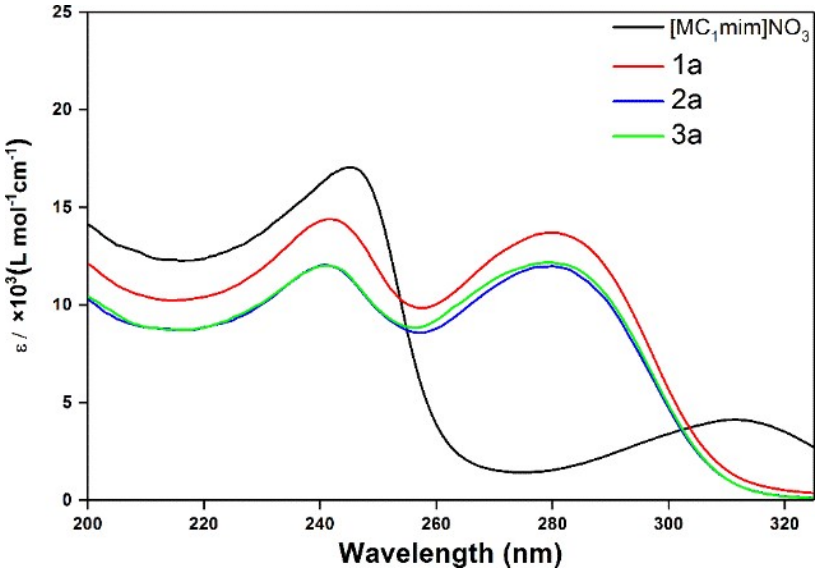

Figure S79. UV absorption spectra of **1a**, **2a**, **3a** and $[MC_1mim]NO_3$ at room temperature

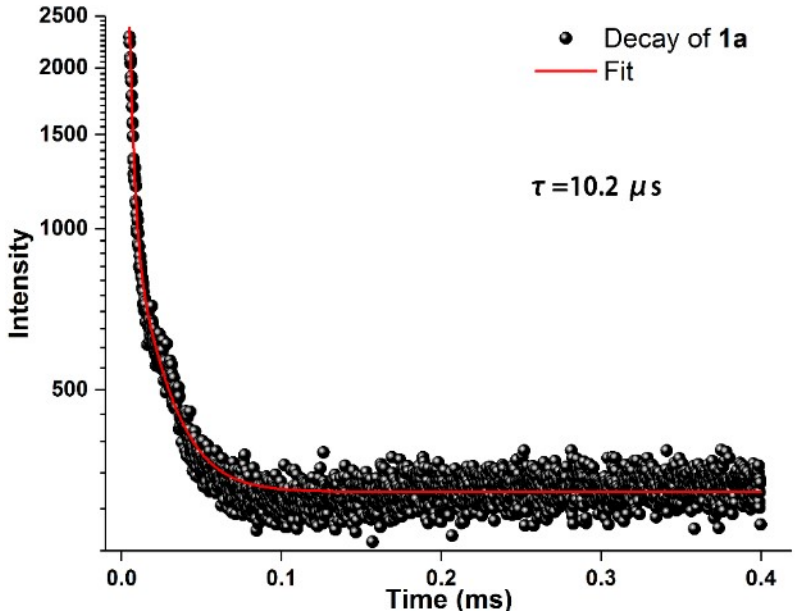

Figure S80. Photoluminescence decay of **1a** liquid recorded under 470 nm diode excitation. The line represents the fitted monoexponential with a decay constant of 10.2 μs.

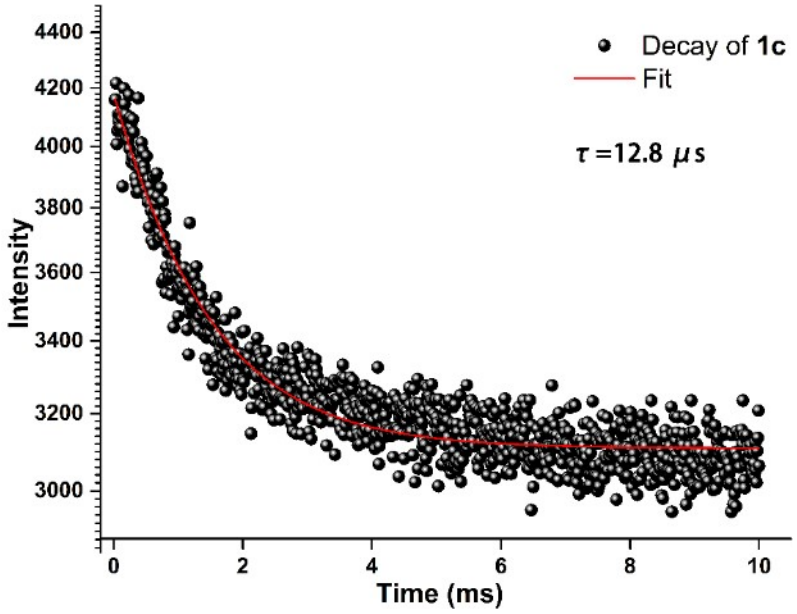

Figure S81. Photoluminescence decay of **1c** liquid recorded under 470 nm diode excitation. The line represents the fitted monoexponential with a decay constant of 12.8 μs.

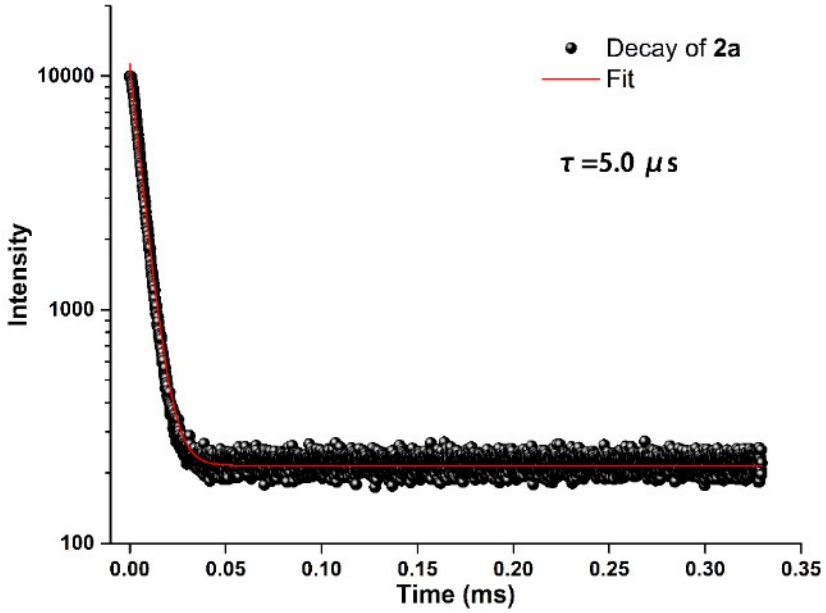

Figure S82. Photoluminescence decay of **2a** liquid recorded under 470 nm diode excitation. The line represents the fitted monoexponential with a decay constant of 5.0 μs.

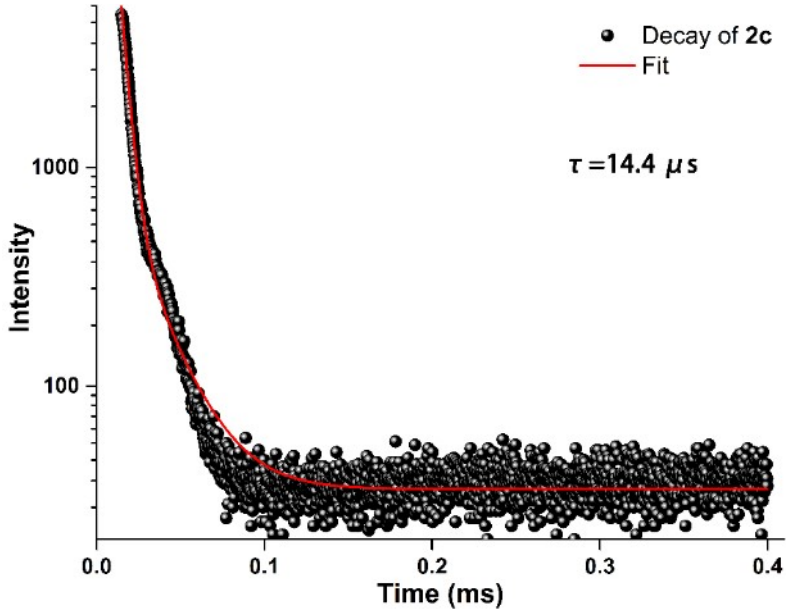

Figure S83. Photoluminescence decay of **2c** liquid recorded under 470 nm diode excitation. The line represents the fitted monoexponential with a decay constant of 14.4 μs.