Supporting Information

Direct Reductive Amination of Ketones with Ammonium Salt Catalysed by Cp*Ir(III) Complexes Bearing an Amidato Ligand

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1. General Information

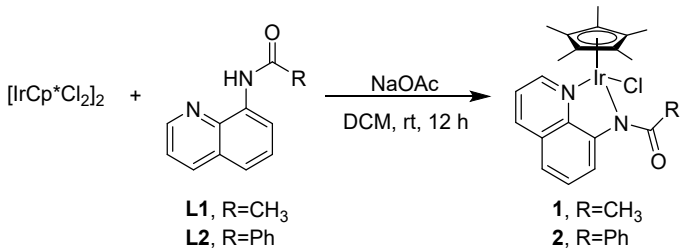
All reactions were carried out under an atmosphere of argon in glovebox or using standard Schlenk Techniques, unless otherwise noted. Solvents (TFE, HFIP and MeOH) were purchased from *J & K* or *Energy*. Ammonium formate and formic acid were used as received from the suppliers. Column chromatography was performed with *Silicycle* silica gel (SiliaFlash P60, 230—400 mesh). NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR, 162 MHz for ^{31}P or a Bruker DPX 600 spectrometer at 600 MHz for ^{1}H NMR, 151 MHz for ^{13}C NMR, 376 MHz for ^{19}F. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual chloroform (7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C), benzene (7.16 ppm for ^{1}H and 128.06 ppm for ^{13}C), dichloromethane (5.32 ppm for ^{1}H and 53.84 ppm for ^{13}C) or DMSO-d_6 (2.50 ppm for ^{1}H and 39.5 ppm for ^{13}C). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet, br, broad. HPLC analysis was carried out on Agilent 1260 Series instrument using a chiral stationary phase. High resolution mass spectra (HRMS) were obtained on Thermo Scientific Q Exactive hybrid quadrupole-Orbitrap mass spectrometer.

2. General experimental details

2.1 Synthesis of complexes

Complexes **1** and **2** were prepared according to a reported method.[1] Complexes **3** and **4** were generously provided by Prof. Gong Chen.[2]

2.1.1 Synthesis of complexes **1** and **2**



L1, R=CH_3
L2, R=Ph

1, R=CH_3
2, R=Ph

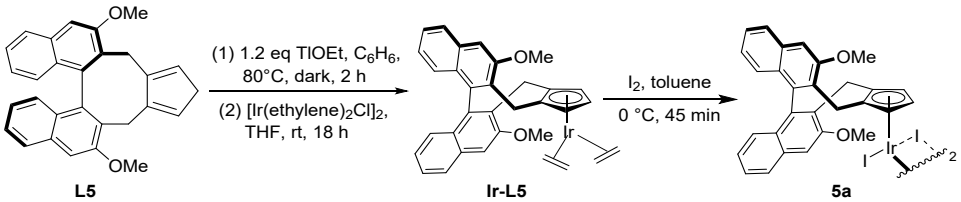
In a glovebox, $[IrCp^*Cl_2]_2$ (100.0 mg, 0.126 mmol), ligand **L** (0.251 mmol) and NaOAc (62.0 mg, 0.756 mmol) were charged into a Schlenk tube contain a magnetic stirring bar, followed by addition of DCM (5 mL). The reaction mixture was stirred at room temperature for 12 h. After completion of the reaction, the reaction mixture was directly evaporated to dryness. The product was finally purified by column chromatography on silica gel (eluent: DCM: EtOAc=1:1).

Complex **1**: Yellow solid, 110.0 mg (78%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.85 (d, *J* = 8.0 Hz, 1H), 8.62 (d, *J* = 5.0 Hz, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 7.52 (t, *J* = 7.9 Hz, 1H), 7.41 (dd, *J* = 8.3, 5.1 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 2.60 (s, 3H), 1.52 (s, 15H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.3, 150.3, 149.8, 146.5, 138.2, 130.0, 129.0, 123.5, 122.1, 118.6, 86.8, 29.0, 8.8.

Complex **2**: Red solid, 117.0 mg (73%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.71 (d, *J* = 5.0 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.98 – 7.87 (m, 2H), 7.43-7.41 (m, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.32-7.27 (m, 3H), 7.24-7.21 (m, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 1.49 (s, 15H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.8, 151.9, 148.9, 146.0, 140.3, 130.0, 130.1, 129.9, 129.6, 129.0, 127.9, 122.7, 122.2, 117.3, 87.1, 9.0.

2.1.2 Synthesis of complex **5a** and **5**

Complex **5a** was prepared according to a reported procedure.[3]



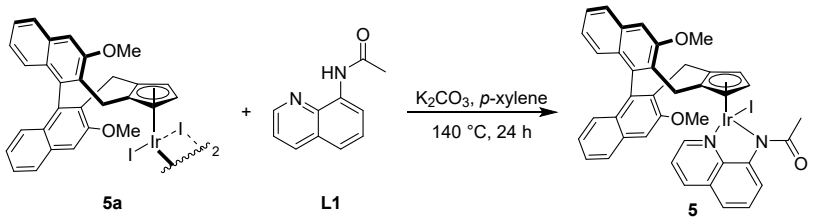
L5 **Ir-L5** **5a**

In glovebox, ligand **L5** (100.0 mg, 0.247 mmol) was dissolved in benzene (2.0 mL) in a sealed

tube, followed by addition of a solution of TlOEt (74.3 mg, 0.297 mmol) in benzene (1.0 mL) in the absence of light. The mixture was heated at 80 °C for 2 h before cooling to room temperature. In parallel, ethylene gas was bubbled through a suspension of $[Ir(COE)_2Cl_2]_2$ (132.8 mg, 0.148 mmol) in THF (2.0 mL) at 0 °C until a clear yellow-brown solution formed. This solution was added to the above prepared reaction mixture at room temperature under argon and was stirred for 18 h. After completion of the reaction, the mixture was passed through a short column of silica gel and washed with toluene (ca. 30 mL, monitored by TLC). The filtrate was evaporated to dryness under reduced pressure, affording 128.0 mg of colorless solid & red gum as product, typically as a mixture of complex **Ir-L5**, unreacted ligand **L5** (mole ratio: 2.1:1) and a small amount of toluene. This product was directly used for the next step without further purification.

Under argon, a solution of I_2 (40.6 mg, 0.16 mmol) in toluene (1.0 mL) was added to a solution of **Ir-L5** [128.0 mg, n(**Ir-L5**): n(**L5**) ≈2.1:1, ca. 0.15 mmol] in toluene (2.0 mL) in the absence of light. The reaction mixture was stirred at 0 °C for 45 min. After this, 30 mL of hexane was added to the reaction mixture under stirring. The formed brown precipitate was collected by filtration, washed with hexane (3 mL*3) and dried under reduced pressure. The brown solid was re-dissolved in DCM, and then evaporated to dryness, affording 130.0 mg of dark red-brown shinny solid as product. Overall yield of two steps: 61%. The unreacted ligand could be recycled. The spectra are consistent with the reported literature.[3]

Complex **5a**: **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 8.25 (d, *J* = 7.8 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 2H), 7.41–7.38 (m, 3H), 7.31 (s, 2H), 7.22 (s, 2H), 7.10 (m, 5H), 6.97 (dd, *J* = 8.3, 3.7 Hz, 4H), 5.76 (s, 2H), 5.48 (s, 2H), 4.91 (s, 2H), 4.02 (s, 6H), 3.98 (d, *J* = 14.0 Hz, 2H), 3.63 (d, *J* = 15.5 Hz, 2H), 3.36 (d, *J* = 16.0 Hz, 2H) 3.32 (s, 6H), 2.78 (d, *J* = 15.5 Hz, 2H). **^{13}C NMR** (151 MHz, CD_2Cl_2) δ 156.6, 155.9, 138.5, 137.0, 134.5, 134.0, 128.3, 127.7, 127.5, 127.4, 127.2, 127.1, 126.9, 124.8, 124.6, 124.3, 106.5, 106.2, 97.8, 90.0, 84.1, 81.8, 68.8, 56.3, 55.4, 27.2, 24.5.



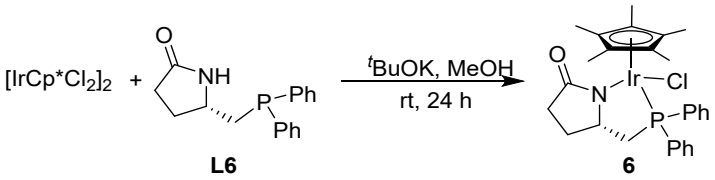
In glovebox, the Ir dimer **5a** (17.0 mg, 0.01 mmol), ligand **L1** (3.7 mg, 0.02 mmol) and K_2CO_3 (13.8 mg, 0.1 mmol) were charged into a Schlenk tube contain a magnetic stirring bar, followed by addition of *p*-xylene (1.0 mL). The reaction mixture was stirred at 140°C for 24 h. After cooling to room temperature, the volatile was evaporated to dryness under reduced pressure. The residue was dissolved by DCM, filtered through a celite pad, and then washed with DCM (2 mL*3). The combined filtrate was evaporated to dryness and the product was purified by column chromatography on silica gel (eluent: DCM/MeOH=100:1 to 50:1). Complex **5** was obtained as

yellow solid. Yield: 10.0 mg (55.6%).

Complex **5**: **^{1}H NMR** (600 MHz, $CDCl_3$) (4:1 mixture of diastereoisomers; the peaks correspond to major diastereoisomer) δ 9.15 (d, *J* = 8.1 Hz, 1H), 8.28 (d, *J* = 4.9 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.62 (t, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.38 (t, *J* = 6.0 Hz, 1H), 7.34 (t, *J* = 6.0 Hz, 1H), 7.27 (s, 1H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.06-7.02 (m, 2H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 1H), 6.57 (dd, *J* = 8.2, 5.2 Hz, 1H), 6.20 (s, 1H), 5.74 (s, 1H), 5.61 (s, 1H), 5.14 (s, 1H), 4.04 (s, 3H), 3.82 (m, 1H), 3.80 (m, 1H), 2.99 (s, 3H), 2.75 (d, *J* = 12.0 Hz, 1H), 2.66 (s, 3H), 2.49 (d, *J* = 12.0 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 178.5, 155.3, 154.4, 150.9, 150.4, 146.5, 137.7, 137.0, 136.9, 134.0, 133.5, 130.2, 129.7, 127.3, 127.0, 126.8, 126.7, 126.5, 126.4, 126.3, 125.1, 125.0, 124.4, 124.0, 123.8, 121.3, 118.2, 106.1, 105.4, 94.7, 90.7, 87.4, 80.1, 66.8, 55.9, 55.3, 32.3, 24.3, 23.4. **HRMS (ESI)**: calcd. for $C_{40}H_{33}IIrN_2O_3^+$, $[M+H]^+$ = 909.1165, found: 909.1158; $C_{40}H_{32}IrN_2O_3^+$, $[M-I]^+$ = 781.2042, found: 781.2036.

2.1.3 Synthesis of complex **6**

Ligand **L6** was prepared by a reported method.[4]



In glovebox, $[IrCp^*Cl_2]_2$ (40.0 mg, 0.05 mmol), **L6** (28.3 mg, 0.1 mmol) and ^{t}BuOK (11.8 mg, 0.11 mmol) were charged into a Schlenk tube contain a magnetic stirring bar, followed by addition of MeOH (1.0 mL). The reaction mixture was stirred at room temperature for 24 h, and then evaporated to dryness. The resulting residue was dissolved by DCM, filtered through a celite pad, and the filtrate was evaporated to dryness. The crude product was dissolved with 1.0 mL of DCM, layered with 5.0 mL of hexane, and then stored in freezer (-20 °C) overnight. The formed yellow crystalline solid was collected by filtration, washed with hexane (1 mL*2), and then dried under vacuum to afford the desired product **6**. Yield: 38.6 mg, 60%.

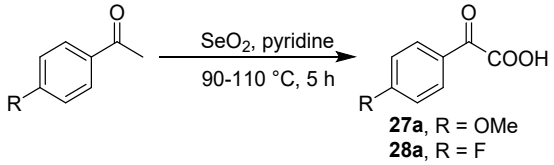
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.58-7.36 (m, 8H), 7.17-7.13 (m, 2H), 4.04 (d, *J* = 6.4 Hz, 1H), 2.76 – 2.63 (m, 2H), 2.52-2.45 (m, 1H), 2.38-2.32 (m, 1H), 2.02-1.93 (m, 1H), 1.72-1.71 (m, 1H), 1.61 (d, *J* = 2.3 Hz, 15H). **^{13}C NMR** (151 MHz, CD_2Cl_2) δ 178.0, 135.1 (d, *J* = 10.5 Hz), 132.1 (d, *J* = 9.0 Hz), 131.5, 131.0, 129.0 (d, *J* = 10.5 Hz), 93.1 (d, *J*=3.0 Hz), 70.7, 39.7 (d, *J* = 33.0 Hz), 36.6, 31.0 (d, *J* = 15.0 Hz), 9.5. **^{31}P NMR** (162 MHz, CD_2Cl_2) δ 29.56 (s). **HRMS (ESI)**: calcd. for $C_{27}H_{33}ClIrNOP^+$, $[M+H]^+$ = 646.1618, found: 646.1603.

Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a wet acetone solution of complex **6**. Selected relevant metric parameters is listed in **Figure S1** and

the crystal data is shown in **Table S1**.

2.1.4 Synthesis of substrates

2-(4-methoxyphenyl)-2-oxoacetic acid (**27a**) and 2-(4-fluorophenyl)-2-oxoacetic acid (**28a**) were prepared by a known method.[5] Other substrates are commercially available.



Under argon, the ketone (10 mmol) and SeO_2 (1.66 g, 15 mmol) were added to a Schlenk flask, followed by addition of pyridine (30 mL). The reaction mixture was stirred at 110°C for 1 h, then 90°C for 4 h. After cooling to room temperature, the mixture was filtered through a celite pad, washed with EtOAc, and then the filtrate was evaporated to dryness. The residue was dissolved in EtOAc (30 mL), washed with 1 M HCl (30 mL) and brine (20 mL), and then dried over anhydrous Na_2SO_4 before evaporation to dryness. The product was then purified by column chromatography on silica gel (eluent: EtOAc: Petroleum ester = 9:1). The spectra are consistent with the reported literarure.[6]

2-(4-methoxyphenyl)-2-oxoacetic acid (**27a**): White solid, 1.3 g (72%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 9.0 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 3.92 (s, 3H). **^{13}C** NMR (151 MHz, $CDCl_3$) δ 182.1, 166.0, 161.2, 134.6, 124.8, 114.6, 55.9.

2-(4-fluorophenyl)-2-oxoacetic acid (**28a**): White solid, 1.4 g (83%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.92 (br s, 1H), 8.42 – 8.33 (m, 2H), 7.21 (t, *J* = 8.3 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 183.02, 168.32, 166.59, 162.50, 134.4 (d, *J* = 10.5 Hz), 128.40, 116.6 (d, *J* = 22.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -99.26.

2.2 General procedure for the reaction condition optimization

Under argon, 2-acetonaphthone (340.5 mg, 2.0 mmol), catalyst (2.0 μmol) and $HCOONH_4$ (4-10 mmol) were charged into a Schlenk tube contain a magnetic stirring bar, followed by addition of solvent (3.0 mL) and acid (2-10 mmol). The reaction mixture was refluxed for 8 h. After cooling to room temperature, 1,3,5-trimethoxybenzene (1.0 mmol, 168.2 mg) was dissolved into the reaction mixture as internal standard sample. Part of the resulting solution (ca. 0.1 mL) was taken out, dissolved in MeOH-d_4 (0.5 mL), and then analyzed by ^{1}H NMR.

2.3 Typical procedure for complex 1-catalyzed DRA

Under argon, ketone (2.0 mmol), complex **1** (1.1 mg, 2 μmol) and $HCOONH_4$ (378.4 mg, 6.0 mmol) were charged into a Schlenk tube containing a magnetic stirring bar, followed by addition of MeOH (3.0 mL) and HCOOH (276.2 mg, 6.0 mmol). The reaction mixture was refluxed for 8 h. After cooling to room temperature, the product amine was isolated depend on the quality of reaction and the property of the product amine, generally through methods A-D as given below.

Method A: After cooling, the volatile was evaporated to dryness. 1 M HCl solution was added to the resulting residue, and the mixture was extracted with EtOAc (10 mL*3) to remove neutral compounds. The aqueous phase was basified with NaOH till pH = 10-11, then extracted with DCM or EtOAc (20 mL*5). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. Method A was applied for purify compounds **8b**-**11b**, **13b**-**16b**, **18b**-**23b** and **30b**.

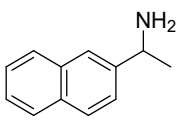
Method B: After cooling, the volatile was evaporated to dryness. Water and NaOH was added to the residue under stirring till pH = 11. The mixture was extracted with DCM (20 mL*5), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The crude product was purified by column chromatography on silica gel (eluent: DCM/methanol=40:1 to 20:1, with 0.5% triethylamine). Method B was applied for purify compounds **17b**, **24b, 25b** and **31b**.

Method C: After cooling, excess of $NaHCO_3$ was added. The mixture was stirred at room temperature for 0.5 h, then filtered, washed with MeOH (3 mL*3), and then evaporated to dryness. The crude product was purified by column chromatography on silica gel (eluent: DCM/methanol=40:1 to 20:1, with 0.5% triethylamine). Method C was applied for purify compound **12b**. Compound **12b** is sparely dissolved in DCM or EtOAc while has a good solubility in basic aqueous solution (pH=8).

Method D: After cooling, the product was directly precipitated from the solution. The product was collected by filtration, washed with MeOH (2 mL*2), and then dried under vacuum. Method D was applied for purify compounds **26b**-**29b**.

2.4 Characterization of amine products

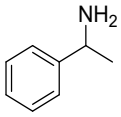
All isolated primary amine products are known compounds.



8b

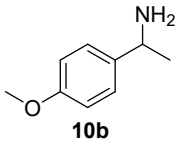
1-(naphthalen-2-yl)ethan-1-amine (**8b**)[6]: white solid; 290.0 mg, 85% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 3H), 7.77 (s, 1H), 7.51 – 7.42 (m, 3H), 4.28 (q, *J* = 6.6 Hz, 1H), 2.17

(br s, 2H), 1.48 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.7, 133.6, 132.8, 128.4, 128.0, 127.7, 126.2, 125.7, 124.6, 124.0, 51.6, 25.4.



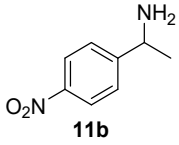
9b

1-phenylethan-1-amine (**9b**)[7]: light yellow oil; 208.0 mg, 86% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 7.24-7.21 (m, 1H), 4.10 (q, J = 6.6 Hz, 1H), 1.71 (br s, 2H), 1.39 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.8, 128.6, 127.0, 125.8, 51.4, 25.7.



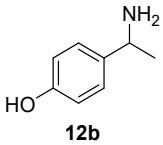
10b

1-(4-methoxyphenyl)ethan-1-amine (**10b**)[6]: light yellow oil; 269.0 mg, 89% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (d, J = 8.7 Hz, 2H), 6.95 – 6.76 (m, 2H), 4.79 (br s, 1H), 4.07 (q, J = 6.6 Hz, 1H), 3.79 (s, 3H), 1.82 (br s, 1H), 1.36 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.5, 140.0, 126.8, 113.9, 55.4, 50.8, 25.7.



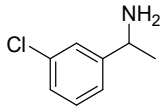
11b

1-(4-nitrophenyl)ethan-1-amine (**11b**)[6]: red oil; 260.0 mg, 79% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.17 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.3 Hz, 2H), 4.25 (q, J = 6.6 Hz, 1H), 1.61 (br s, 2H), 1.39 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 155.2, 147.0, 126.8, 123.9, 51.0, 25.9.



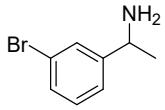
12b

4-(1-aminoethyl)phenol (**12b**): white solid; 253.0 mg, 93% yield. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 9.15 (br s, 1H), 7.13 (d, J = 8.1 Hz, 2H), 6.66 (d, J = 8.0 Hz, 2H), 3.87 (q, J = 6.5 Hz, 1H), 1.18 (d, J = 6.5 Hz, 3H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 155.7, 139.0, 126.7, 114.7, 50.1, 26.3. **HRMS (ESI)**: calcd. for $C_8H_{12}NO^+$, $[M+H]^+$ = 138.0919, found: 138.0913.



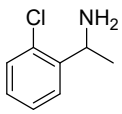
13b

1-(3-chlorophenyl)ethan-1-amine (**13b**)[6]: light yellow oil; 264.0 mg, 85% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.26-7.20 (m, 3H), 4.09 (q, *J* = 6.6 Hz, 1H), 1.58 (br s, 2H), 1.36 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.9, 134.4, 129.9, 127.0, 126.1, 124.1, 51.1, 25.7.



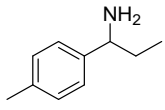
14b

1-(3-bromophenyl)ethan-1-amine (**14b**)[7]: yellow oil; 348.0 mg, 87% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 7.2 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 4.08 (q, *J* = 6.6 Hz, 1H), 1.58 (br s, 2H), 1.36 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.2, 130.2, 130.0, 129.1, 124.6, 122.7, 51.1, 25.8.



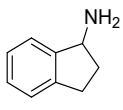
15b

1-(2-chlorophenyl)ethan-1-amine (**15b**)[6]: yellow oil; 192.0 mg, 62% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 4.54 (q, *J* = 6.6 Hz, 1H), 1.67 (br s, 2H), 1.39 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.7, 132.7, 129.7, 127.9, 127.3, 126.4, 47.7, 23.7.



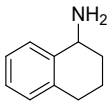
16b

1-(p-tolyl)propan-1-amine (**16b**): light yellow oil; 283.0 mg, 95% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.20 (d, *J* = 7.4 Hz, 2H), 7.14 (d, *J* = 7.5 Hz, 2H), 3.76 (t, *J* = 6.8 Hz, 1H), 2.34 (s, 3H), 1.72-1.65 (m, 2H), 1.64 (br s, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.6, 136.5, 129.2, 126.4, 57.6, 32.5, 21.1, 11.1. **HRMS (ESI)**: calcd. for $C_{10}H_{16}N^+$, $[M+H]^+$ = 150.1283, found: 150.1276.



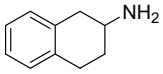
17b

2,3-dihydro-*1H*-inden-1-amine (**17b**)[7]: white solid, 192.0 mg, 73% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 5.4 Hz, 1H), 7.22-7.20 (m, 3H), 4.44 (t, *J* = 7.0 Hz, 1H), 3.79 (br s, 2H), 3.05-3.01 (m, 1H), 2.85-2.79 (m, 1H), 2.50 – 2.45 (m, 1H), 1.85-1.79 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.6, 143.5, 128.0, 126.8, 124.9, 124.1, 57.0, 35.4, 30.3.



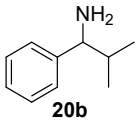
18b

1,2,3,4-tetrahydronaphthalen-1-amine (**18b**)[6]: yellow oil; 245.0 mg, 84% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.2 Hz, 1H), 7.20 – 7.12 (m, 2H), 7.09-7.07 (m, 1H), 3.98 (t, *J* = 5.6 Hz, 1H), 2.85-2.70 (m, 2H), 2.07 – 2.00 (m, 1H), 1.98 – 1.88 (m, 1H), 1.82-1.75 (m, 1H), 1.74 – 1.67 (m, 1H), 1.65 (br s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.3, 136.8, 129.1, 128.1, 126.7, 126.1, 49.5, 33.6, 29.7, 19.7.



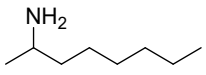
19b

1,2,3,4-tetrahydronaphthalen-2-amine (**19b**)[7]: green oil, 120.0 mg, 41% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.11 – 7.07 (m, 4H), 3.20-3.17 (m, 1H), 3.02-2.98 (m, 1H), 2.92-2.83 (m, 2H), 2.59-2.54 (m, 1H), 2.02 – 1.99 (m, 1H), 1.75 (br s, 2H), 1.63-1.57 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 135.9, 135.3, 129.4, 128.8, 125.9, 125.8, 47.4, 39.5, 33.0, 28.2.



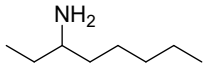
20b

2-methyl-1-phenylpropan-1-amine (**20b**)[6]: yellow oil; 243.0 mg, 82% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.32-7.28 (m, 4H), 7.23 (t, *J* = 6.9 Hz, 1H), 3.60 (d, *J* = 7.2 Hz, 1H), 1.88-1.83 (m, 1H), 1.57 (br s, 2H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.77 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 145.6, 128.3, 127.1, 126.9, 62.6, 35.6, 19.9, 19.0.



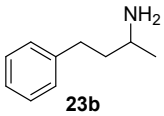
21b

octan-2-amine (**21b**)[7]: yellow oil; 207.0 mg, 81% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.84 (q, *J* = 5.3 Hz, 1H), 1.55 (br s, 2H), 1.38 – 1.25 (m, 10H), 1.03 (d, *J* = 6.2 Hz, 3H), 0.85 (t, *J* = 6.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 47.0, 40.3, 32.0, 29.5, 26.5, 24.0, 22.7, 14.2.



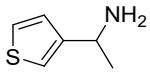
22b

octan-3-amine (**22b**)[7]: yellow oil; 226.0 mg, 88% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.60 (dd, *J* = 7.1, 4.9 Hz, 1H), 1.48 – 1.38 (m, 5H), 1.33 – 1.21 (m, 7H), 0.93-0.87 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 52.8, 37.7, 32.2, 30.8, 26.0, 22.8, 14.2, 10.5.



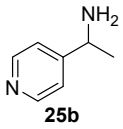
23b

4-phenylbutan-2-amine (**23b**)[6]: yellow oil; 278.0 mg, 94% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.4 Hz, 2H), 7.19-7.16 (m, 3H), 2.91 (q, *J* = 6.3 Hz, 1H), 2.71-2.60 (m, 2H), 1.70-1.60 (m, 2H), 1.4 (br s, 2H), 1.10 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.4, 128.5, 128.4, 125.8, 46.7, 41.9, 32.9, 24.1.



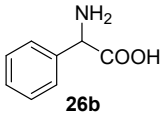
24b

1-(thiophen-3-yl)ethan-1-amine (**24b**)[6]: yellow oil; 213.0 mg, 84% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 – 7.26 (m, 1H), 7.10 (s, 1H), 7.06 (d, *J* = 4.9 Hz, 1H), 4.19 (q, *J* = 6.6 Hz, 1H), 1.63 (br s, 2H), 1.41 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.3, 126.1, 126.0, 119.2, 47.3, 25.4.



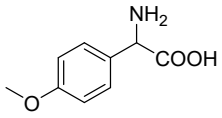
25b

1-(pyridin-4-yl)ethan-1-amine (**25b**)[6]: yellow oil; 194.0 mg, 80% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.6 Hz, 2H), 7.28 (d, *J* = 4.9 Hz, 2H), 4.11 (q, *J* = 6.5 Hz, 1H), 2.14 (br s, 2H), 1.38 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.2, 150.1, 121.2, 50.5, 25.3.



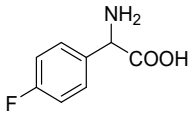
26b

2-amino-2-phenylacetic acid (**26b**)[6]: white solid; 222.0 mg, 74% yield. ^{1}H NMR (600 MHz, DMSO-d_6 + 1 drop of 12 M HCl aq.) δ 8.95 (br s, 3H), 7.50-7.48 (m, 2H), 7.44 – 7.39 (m, 3H), 5.02 (q, *J* = 5.4 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6 + 1 drop of 12 M HCl aq.) δ 169.8, 133.4, 129.5, 129.1, 128.4, 55.8.



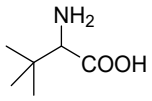
27b

2-amino-2-(4-methoxyphenyl)acetic acid (**27b**)[6]: white solid, 320.0 mg, 89% yield. **^{1}H NMR** (600 MHz, DMSO-d_6 + 1 drop of 12 M HCl aq.) δ 8.85 (*d*, *J* = 4.6 Hz, 3H), 7.41 – 7.39 (m, 2H), 6.98 – 6.96 (m, 2H), 4.95 (q, *J* = 5.5 Hz, 1H), 3.74 (s, 3H). **^{13}C NMR** (151 MHz, DMSO-d_6 + 1 drop of 12 M HCl aq.) δ 170.1, 160.1, 129.8, 125.3, 114.5, 55.5, 55.2.



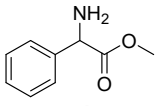
28b

2-amino-2-(4-fluorophenyl)acetic acid (**28b**)[6]: white solid, 270.0 mg, 80% yield. **^{1}H NMR** (600 MHz, DMSO-d_6 + 1 drop of 12 M HCl aq.) δ 8.98 (br, 3H), 7.57 – 7.54 (m, 2H), 7.29-7.26 (m, 2H), 5.09 – 5.07 (m, 1H). **^{13}C NMR** (151 MHz, DMSO-d_6 + 1 drop of 12 M HCl aq.) δ 169.7, 162.7 (d, *J* = 244.5 Hz), 130.8 (d, *J* = 7.5 Hz), 129.74 (d, *J* = 3.0 Hz), 116.0 (d, *J* = 22.5 Hz), 55.0. **^{19}F NMR** (376 MHz, DMSO-d_6 + 1 drop of 12 M HCl aq.) δ -112.3.



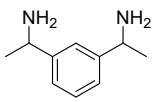
29b

2-amino-3,3-dimethylbutanoic acid (**29b**)[6]: white solid, 157.0 mg, 60% yield. **^{1}H NMR** (600 MHz, D_2O) δ 3.46 (s, 1H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, D_2O + 1 drop of methanol as reference) δ 174.2, 64.7, 32.6, 26.5.



30b

Methyl 2-amino-2-phenylacetate (**30b**)[7]: yellow oil, 136.0 mg, 40% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5H), 4.61 (s, 1H), 3.69 (s, 3H), 1.92 (br s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.5, 140.3, 128.9, 128.1, 126.9, 58.8, 52.5.



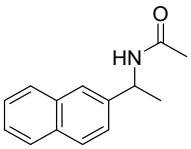
31b

1,1'-(1,3-phenylene)bis(ethan-1-amine) (**31b**)[8]: light yellow oil, 246.0 mg, 75% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 2H), 4.12 (q, *J* = 6.6 Hz, 2H), 1.77 (br s, 4H), 1.40 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.0, 128.8, 124.4, 123.2, 51.5, 25.8.

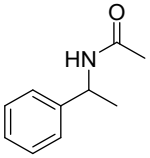
2.5 General procedure for asymmetric reductive amination

Under argon, ketone (0.2 mmol), catalyst (2.0 μmol) and $HCOONH_4$ (37.8 mg, 0.6 mmol) were charged into a Schlenk tube containing a magnetic stirring bar, followed by addition of solvent (1.0 mL) and acid (0.6 mmol). The reaction mixture was refluxed for the indicated reaction time. After cooling to room temperature, 1,3,5-trimethoxybenzene (0.1 mmol, 16.8 mg) was dissolved into the reaction mixture as internal standard sample, and 0.1 mL of this solution was taken out and dissolved in 0.5 mL of MeOH-*d*$_4$ before analysis by ^{1}H NMR to determine the yield of product. The volatiles of the rest reaction mixture were evaporated to dryness. 1 M HCl solution was added to the resulting residue, and the mixture was extracted with EtOAc (3 mL*3) to remove neutral compounds. The aqueous phase was basified with $NaHCO_3$ till pH = 8, then extracted with DCM (3 mL*3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated to dryness.

The obtained product was dissolved in DCM (1 mL), Ac_2O (2 equiv.) was then added and the mixture was stirred at room temperature overnight. The acylation product was isolated by column chromatography on silica gel. The ee values were determined by HPLC on a chiral stationary phase.



16% ee, HPLC method: Chiralpak AD-H column, hexane/isopropanol = 95/5; flow rate = 1.0 mL/min; UV detection at 220 nm. Retention time: t_{major} = 14.8 min, t_{minor} = 23.4 min.



0% ee, HPLC method: Chiralpak AD-3 column, hexane/isopropanol = 90/5; flow rate = 1.0 mL/min; UV detection at 210 nm. Retention time: t_1 = 11.4 min, t_2 = 14.7 min.

2.6 Cp*Ir(III)–H species detection

In glovebox, complex **1** (5.5 mg, 0.01 mmol) was added to an NMR tube, then MeOH-*d*$_4$ (0.6 mL) and formic acid/triethylamine azeotrope (5:2, 4.3 mg) were injected. The mixture was shaken gently and placed at room temperature for 1 h. After this, this sample was subjected to ^{1}H NMR analysis, a new Ir–H species with 1H intensity was observed at -9.56 ppm.

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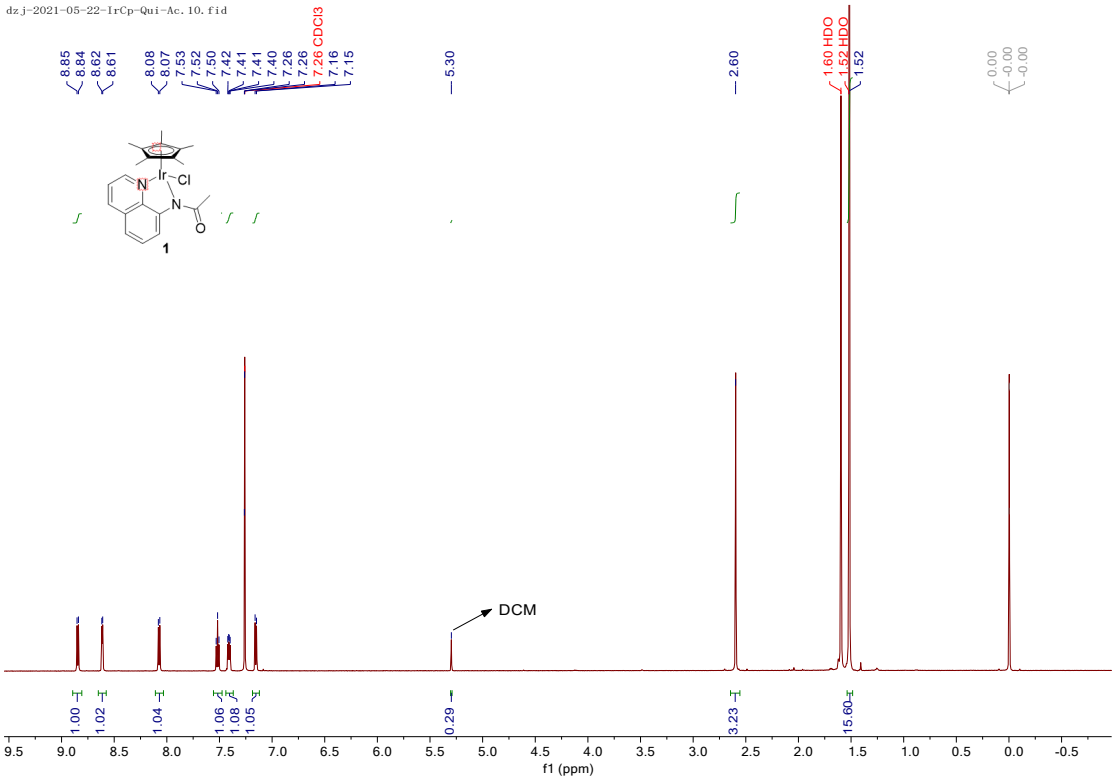
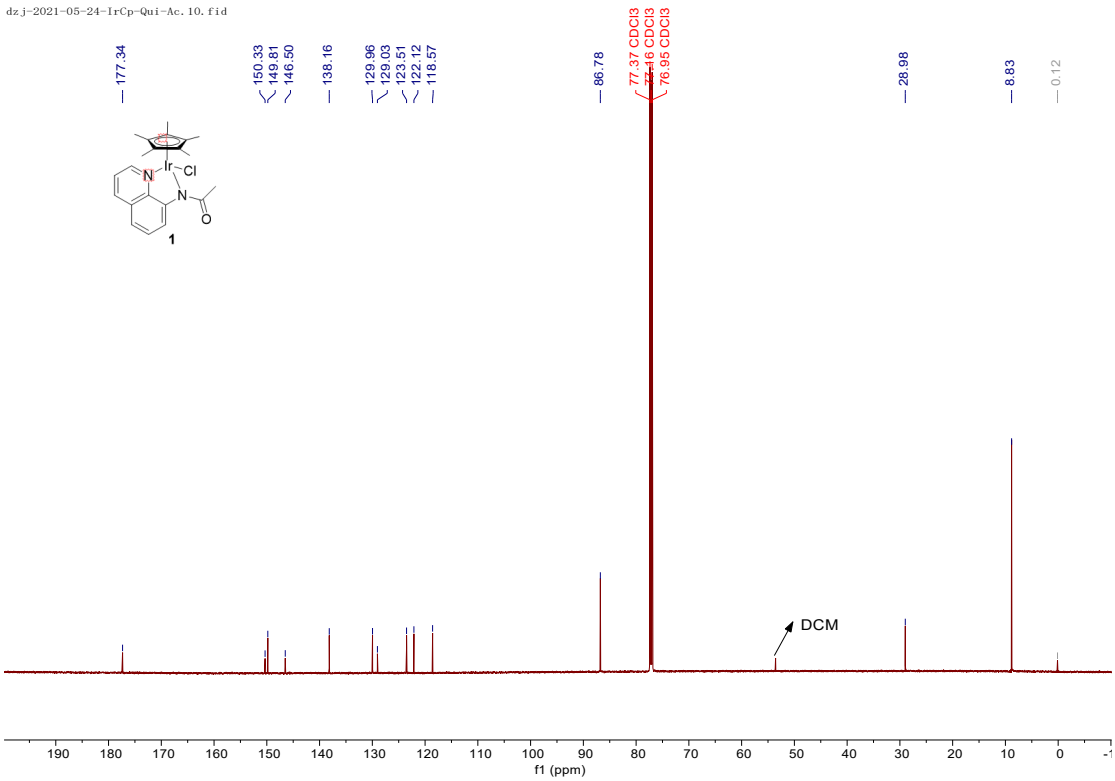
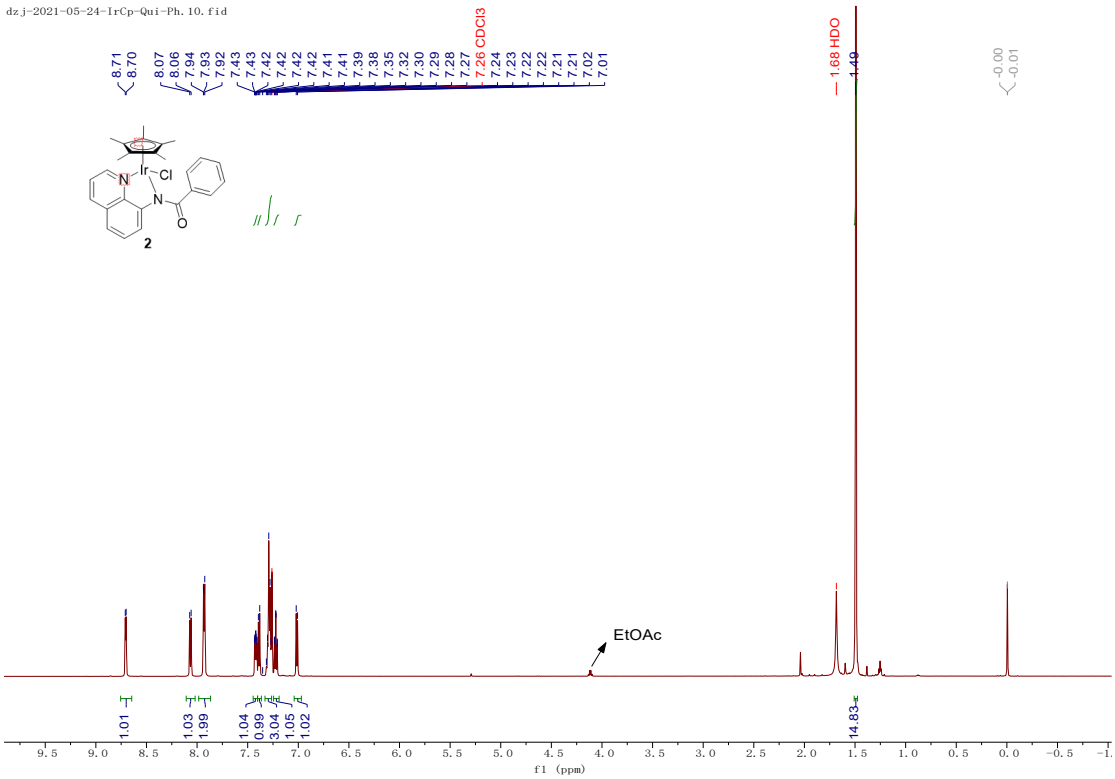
3. NMR Spectra



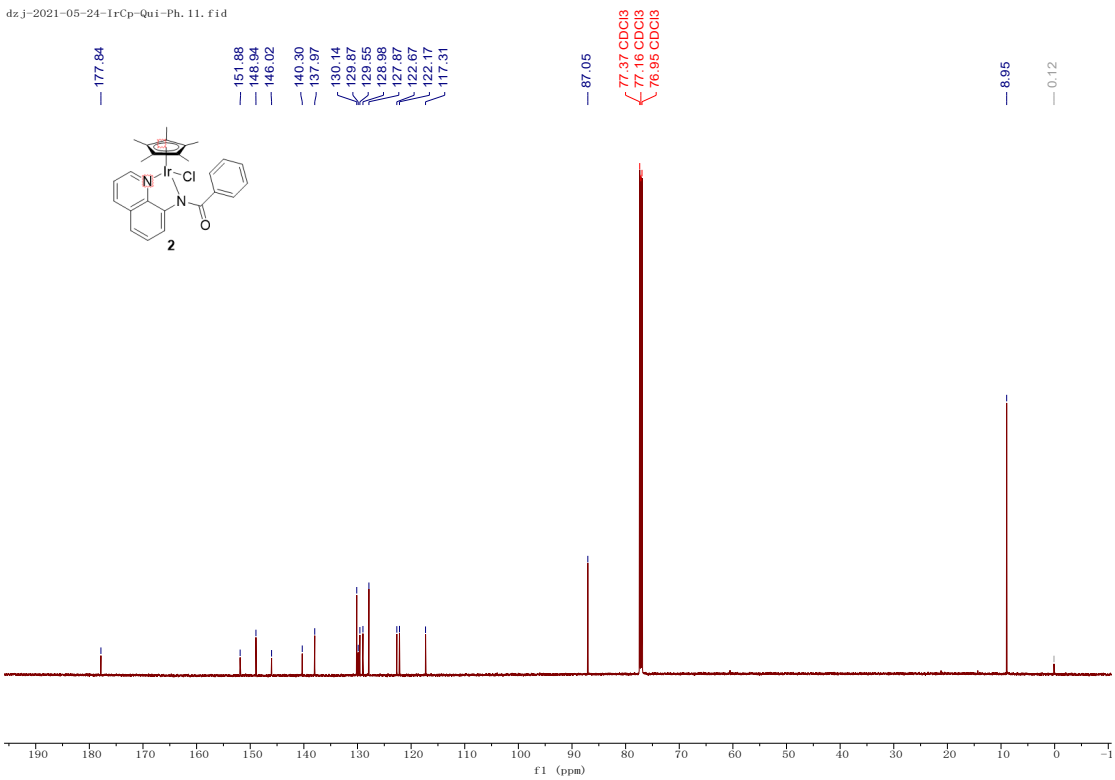
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of complex **1**



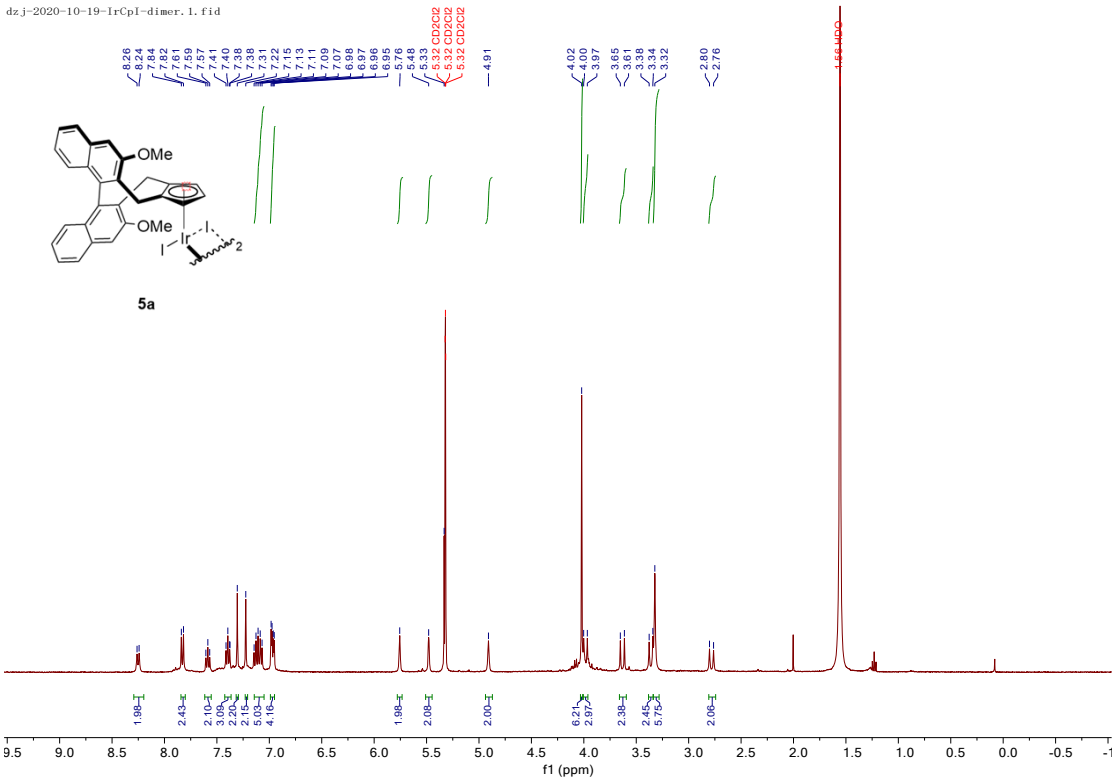
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of complex **1**



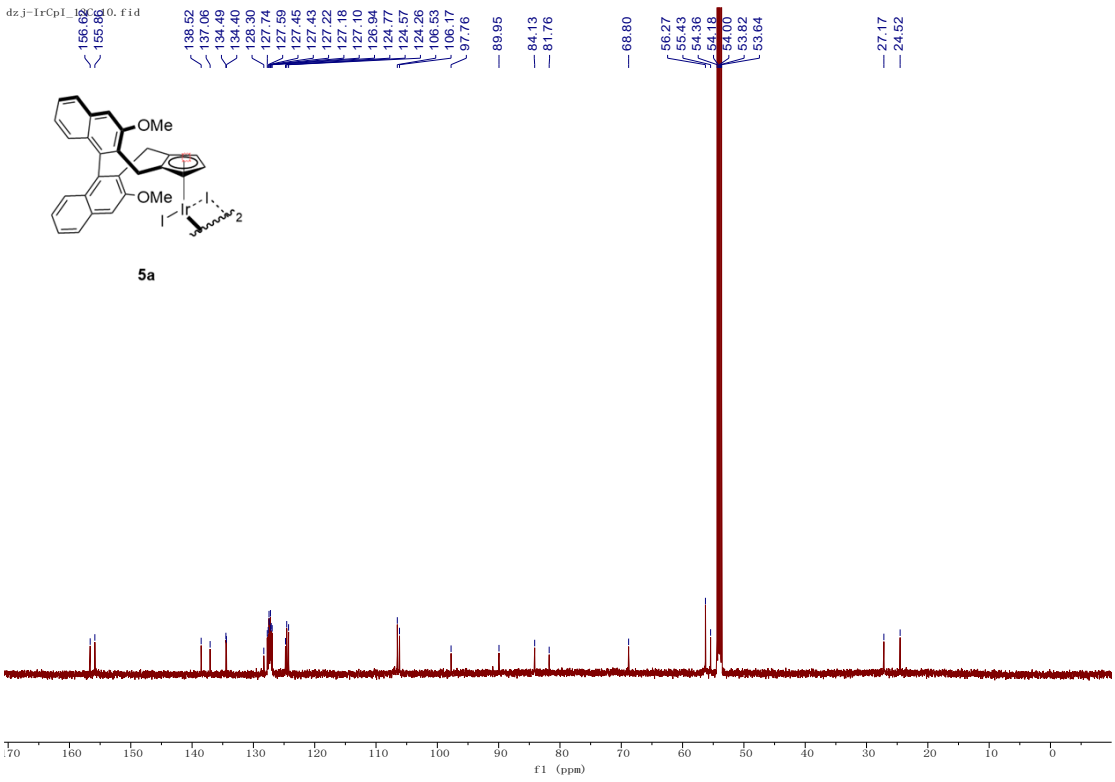
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of complex **2**



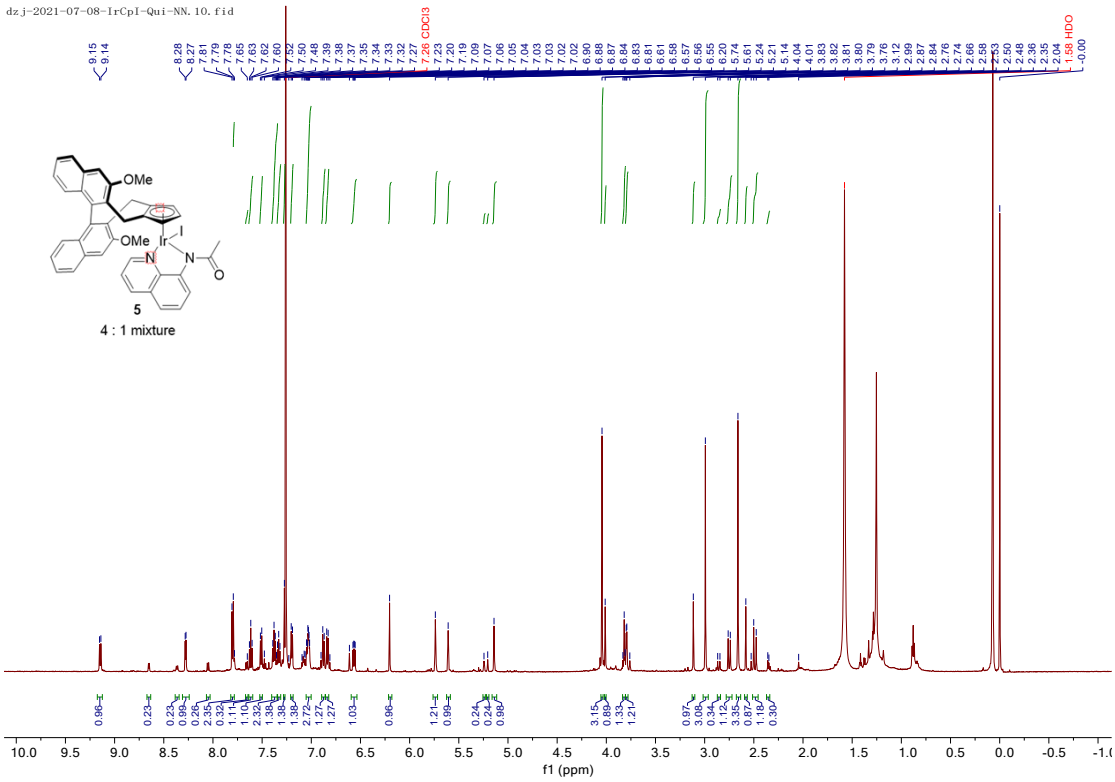
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of complex **2**



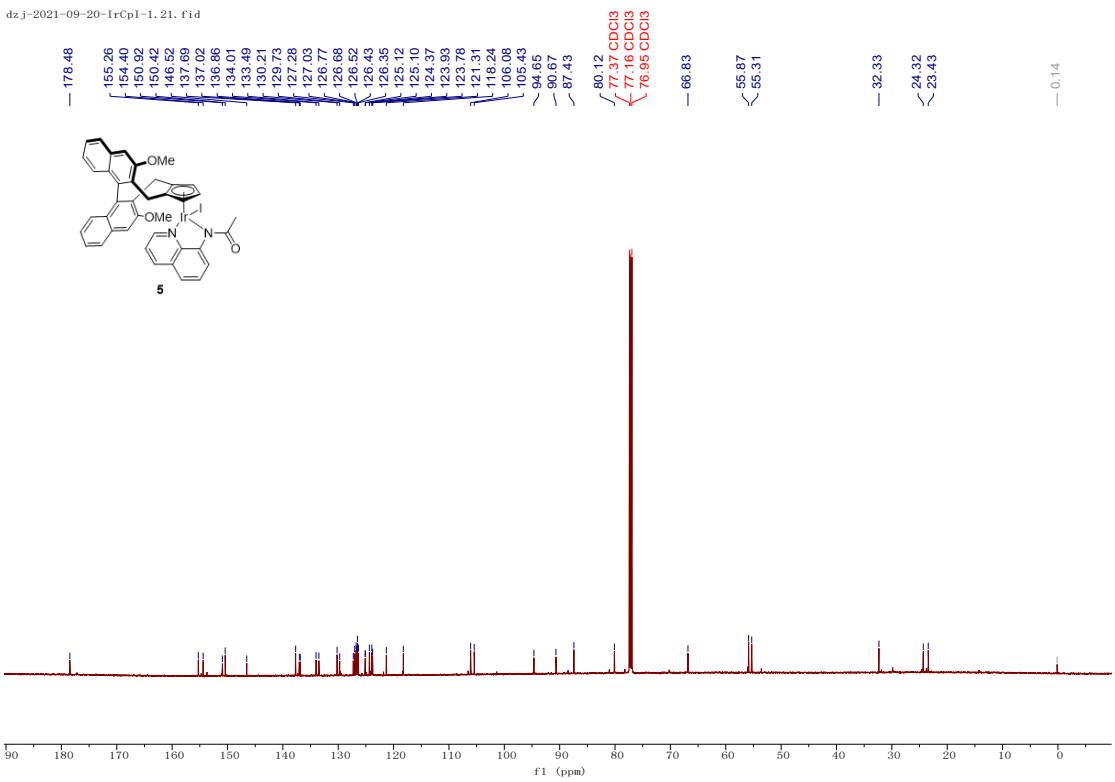
^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of complex **5a**



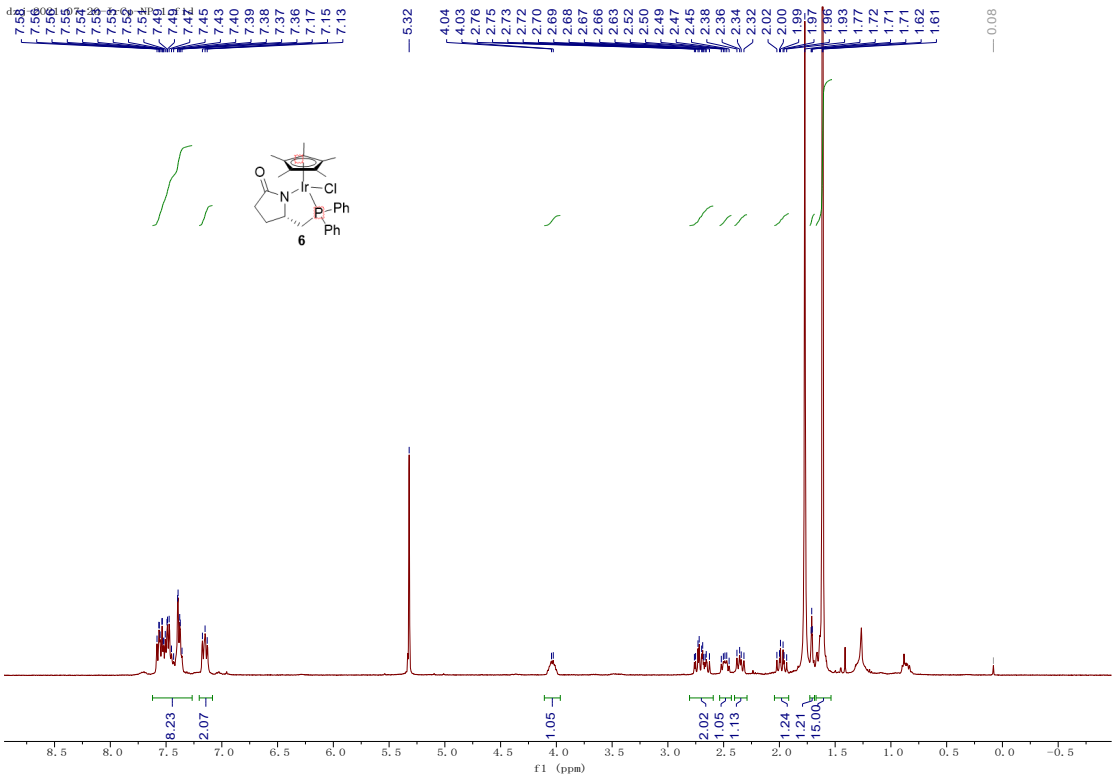
^{13}C NMR spectrum (151 MHz, CD_2Cl_2) of complex **5a**



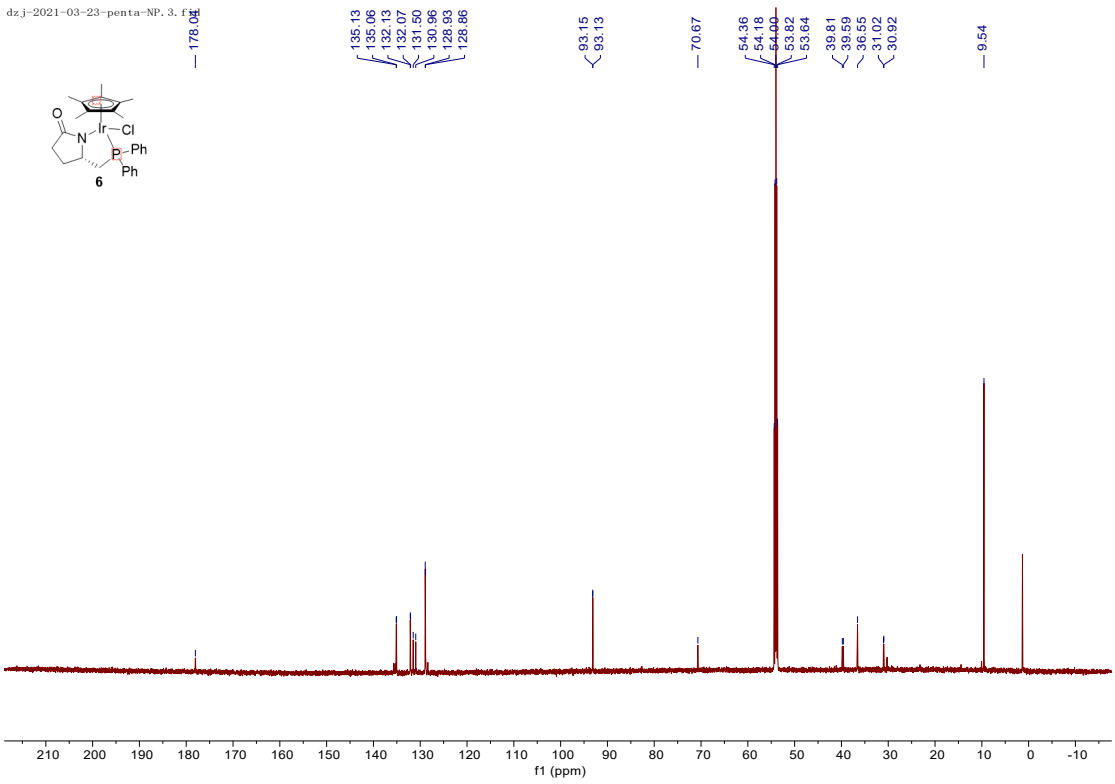
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of complex **5**



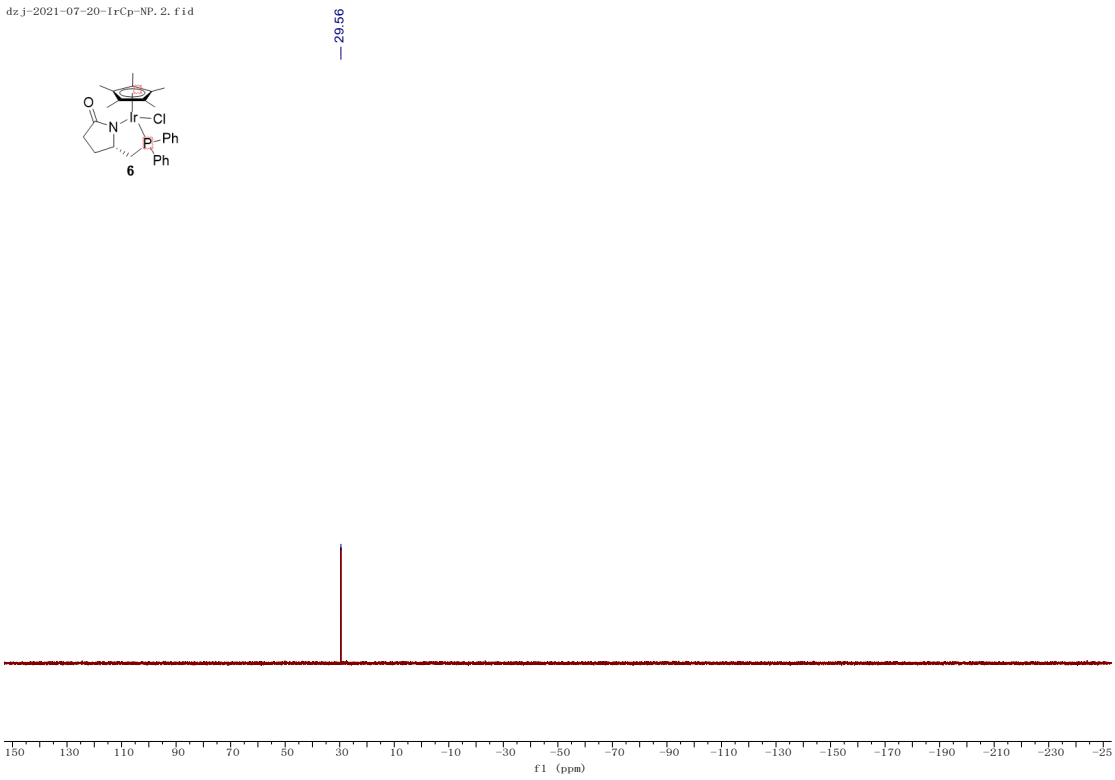
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of complex **5**



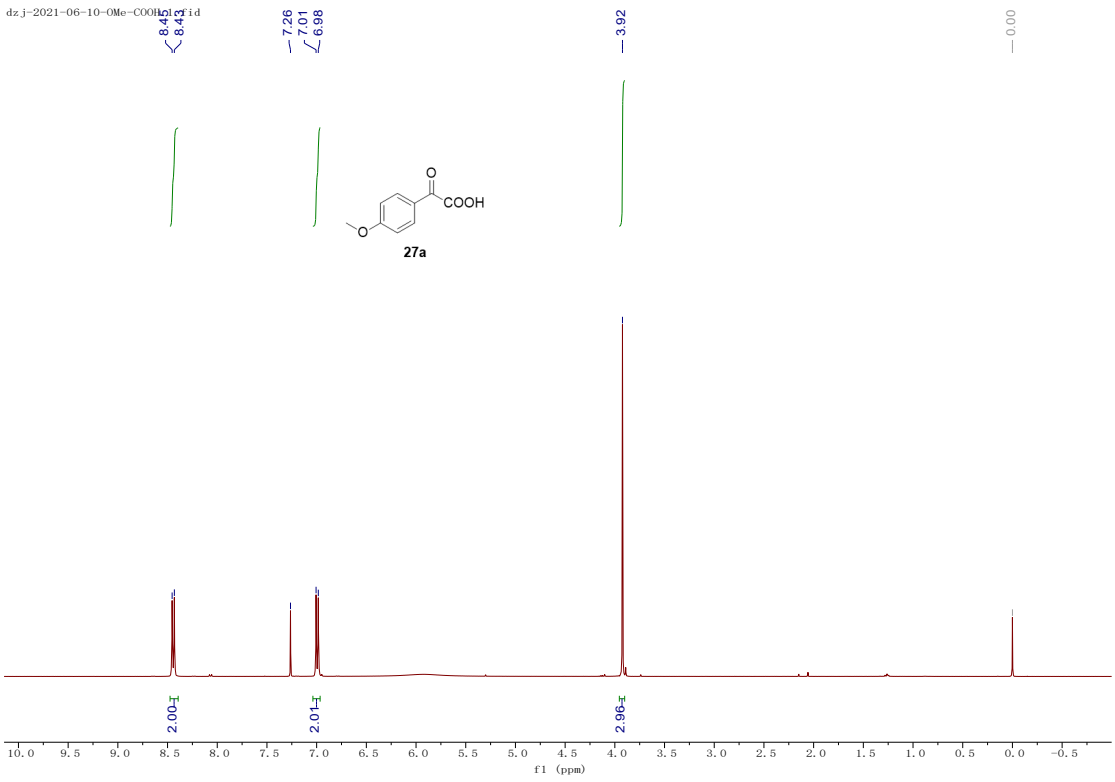
^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of complex **6**



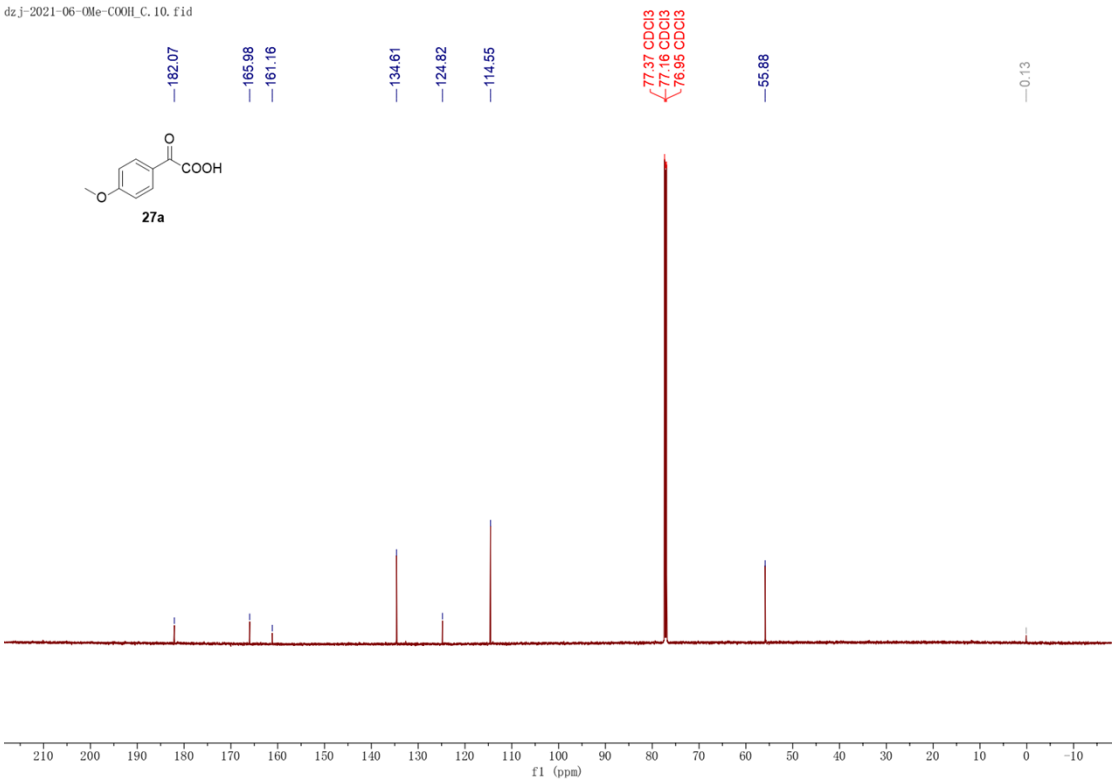
^{13}C NMR spectrum (151 MHz, CD_2Cl_2) of complex **6**



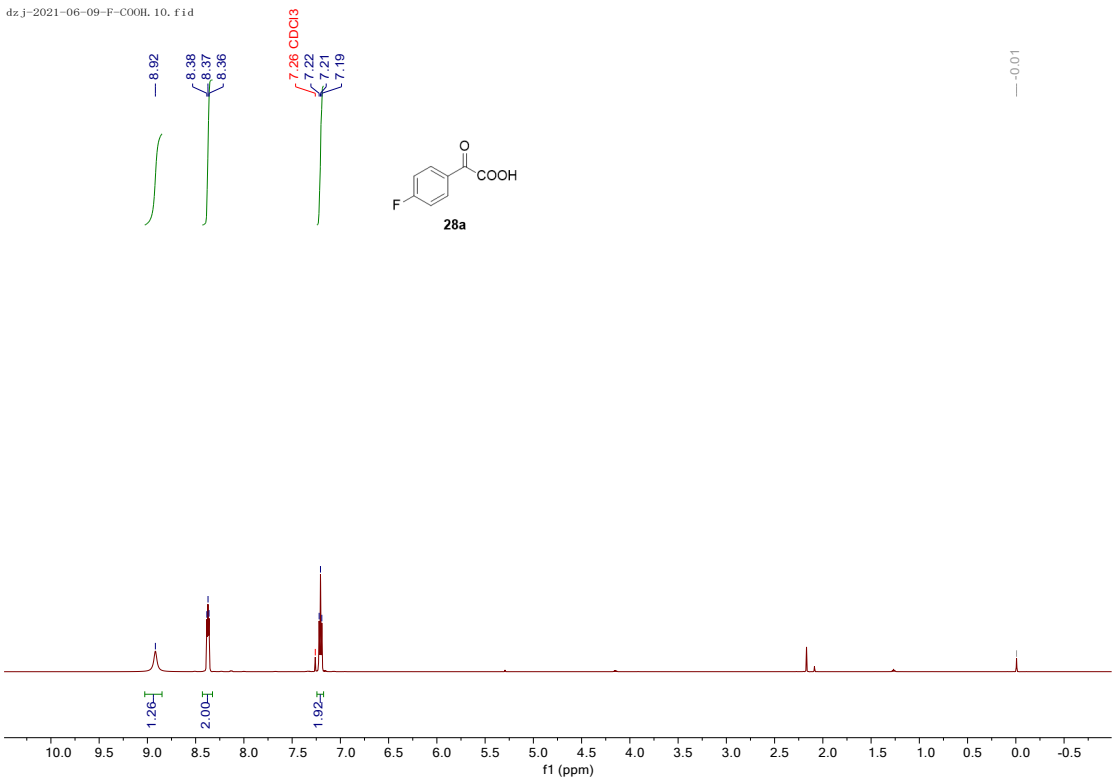
^{31}P NMR spectrum (162 MHz, CD_2Cl_2) of complex **6**



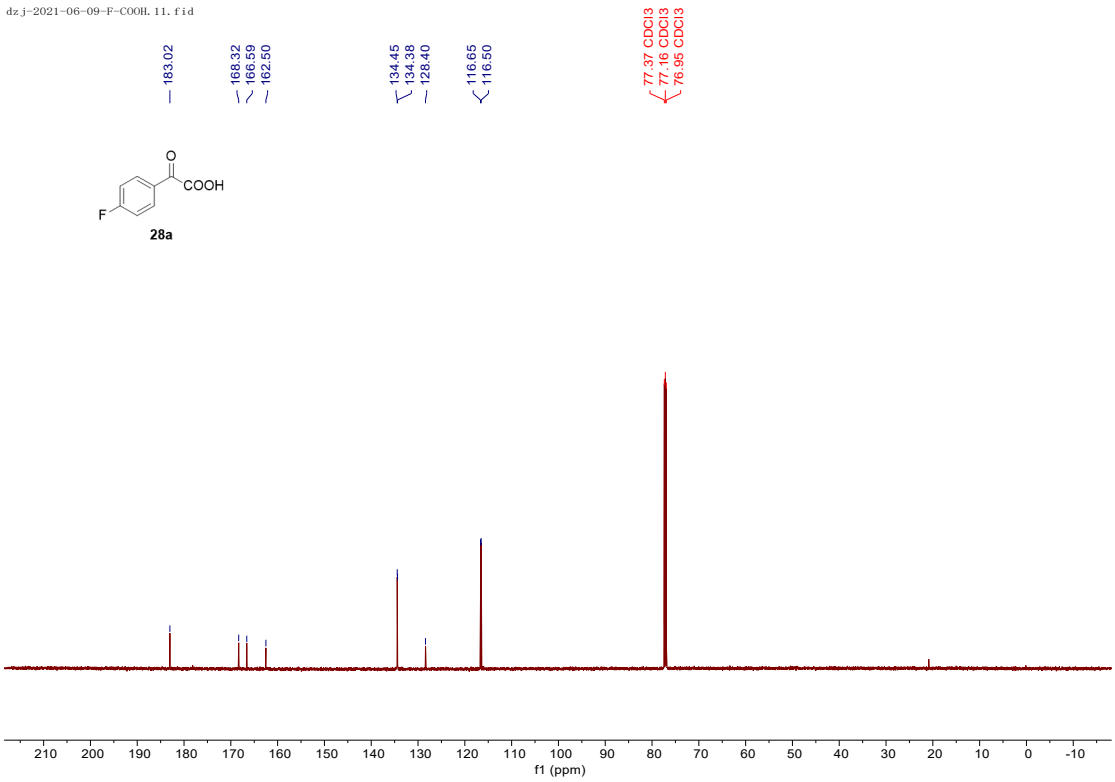
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2-(4-methoxyphenyl)-2-oxoacetic acid** (**27a**)



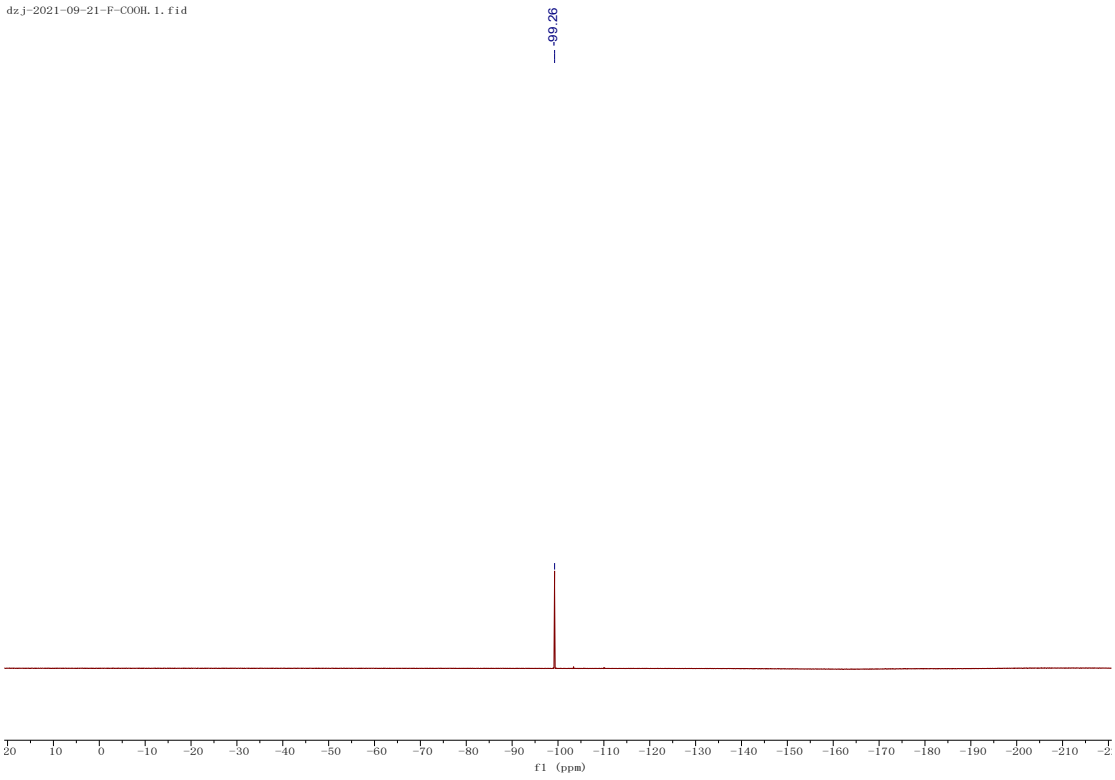
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2-(4-methoxyphenyl)-2-oxoacetic acid** (**27a**)



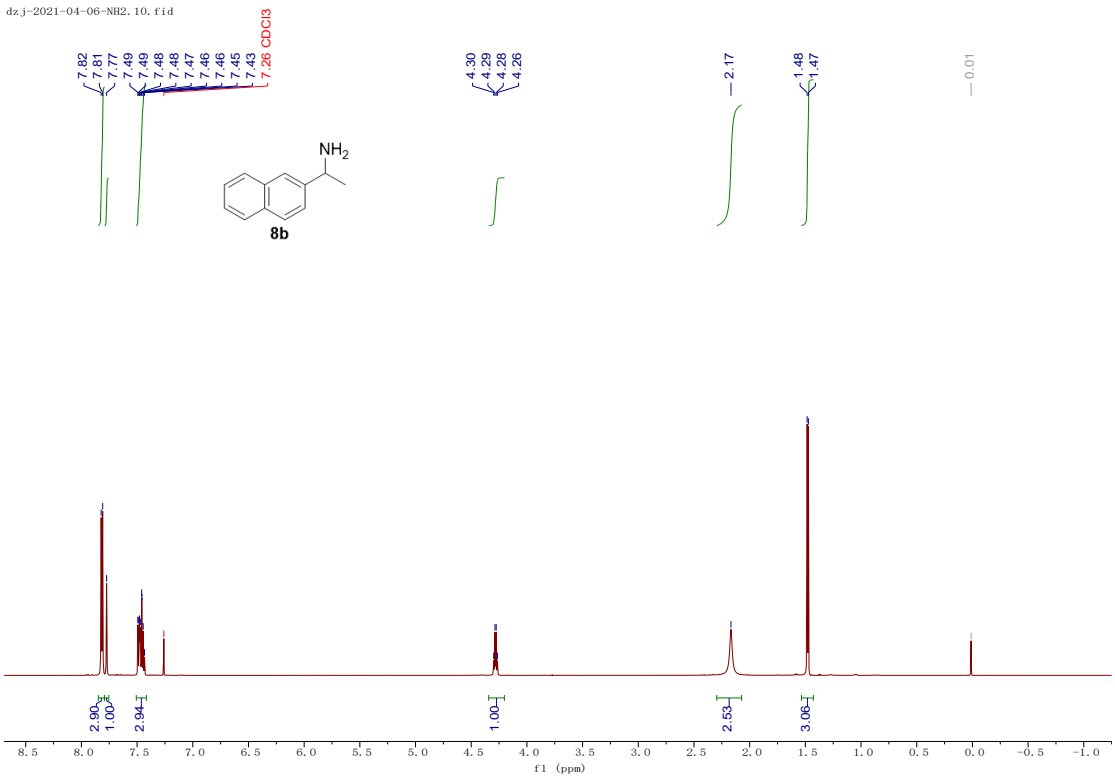
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2-(4-fluorophenyl)-2-oxoacetic acid** (**28a**)



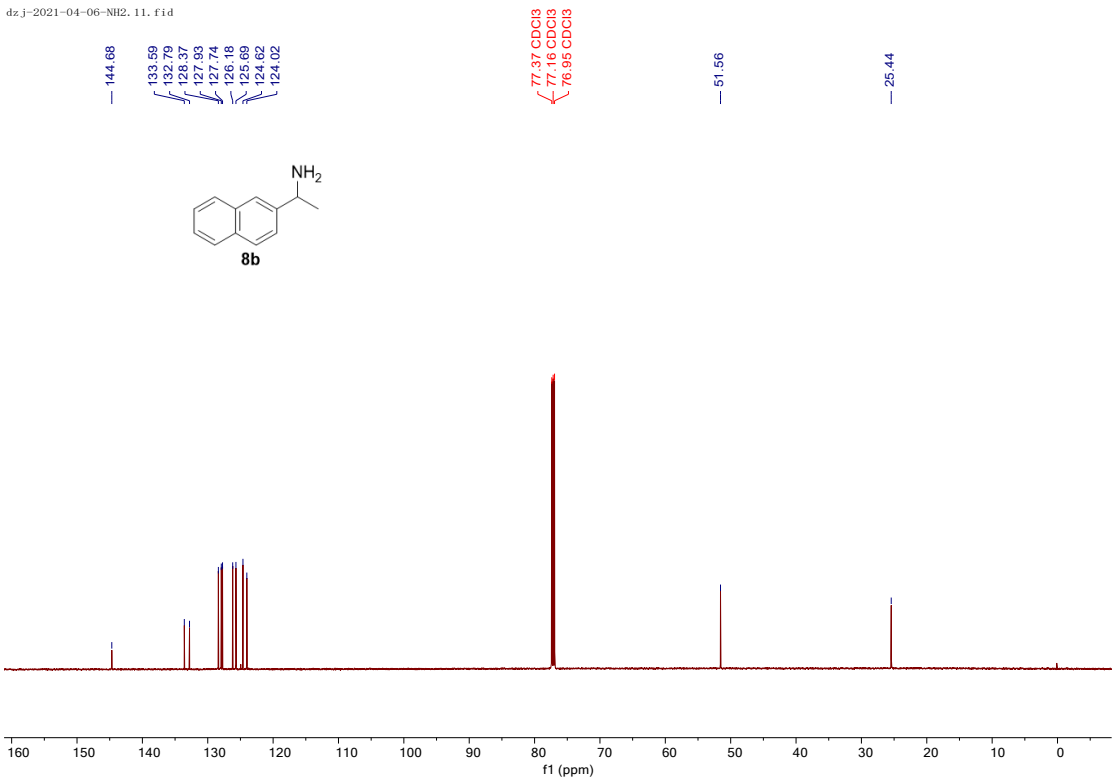
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2-(4-fluorophenyl)-2-oxoacetic acid** (**28a**)



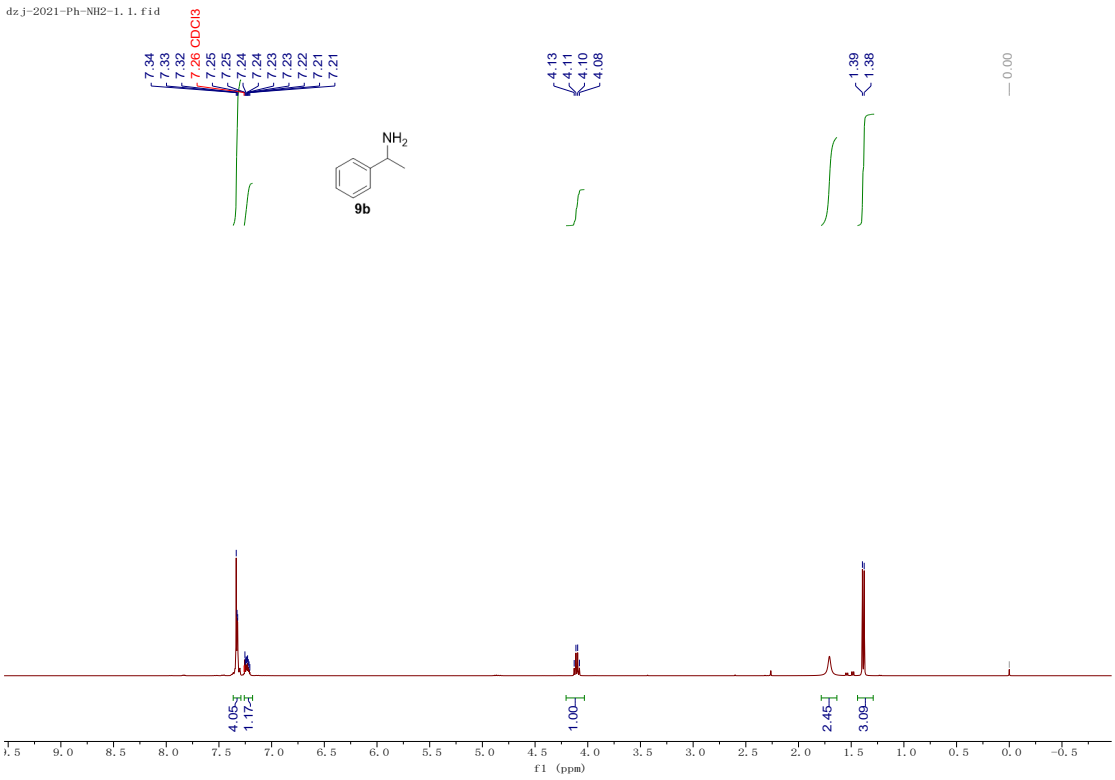
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **2-(4-fluorophenyl)-2-oxoacetic acid** (**28a**)



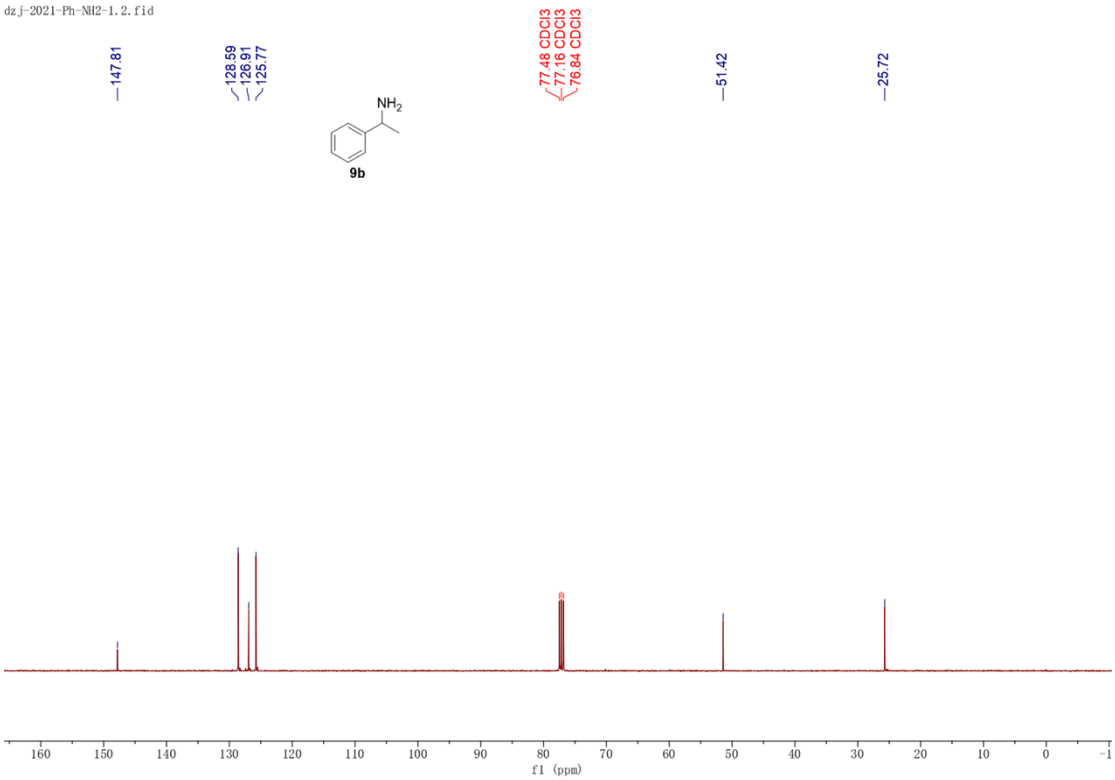
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1-(naphthalen-2-yl)ethan-1-amine** (**8b**)



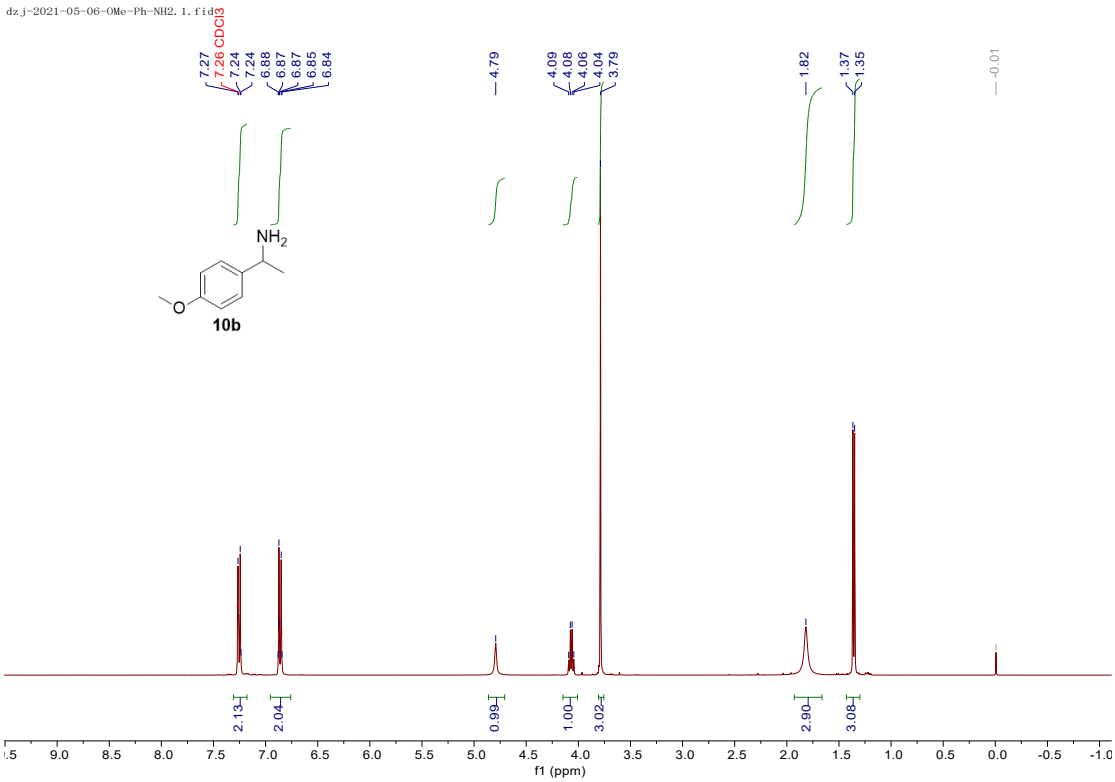
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **1-(naphthalen-2-yl)ethan-1-amine** (**8b**)



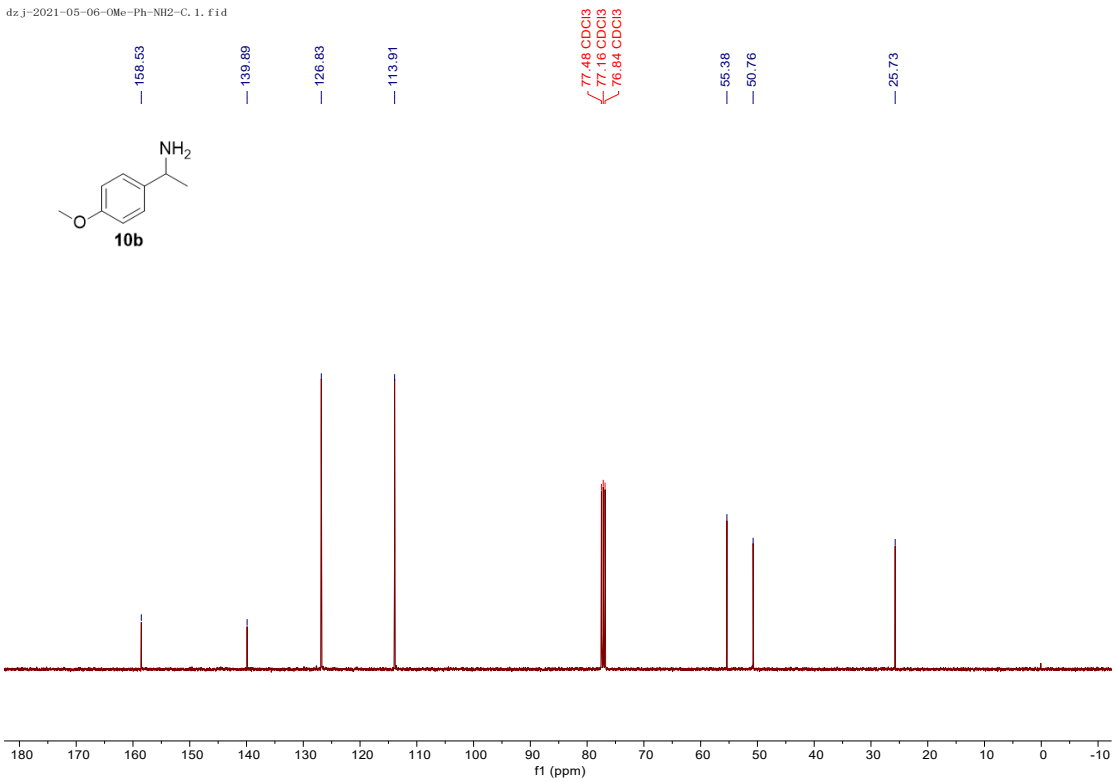
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1-phenylethan-1-amine** (**9b**)



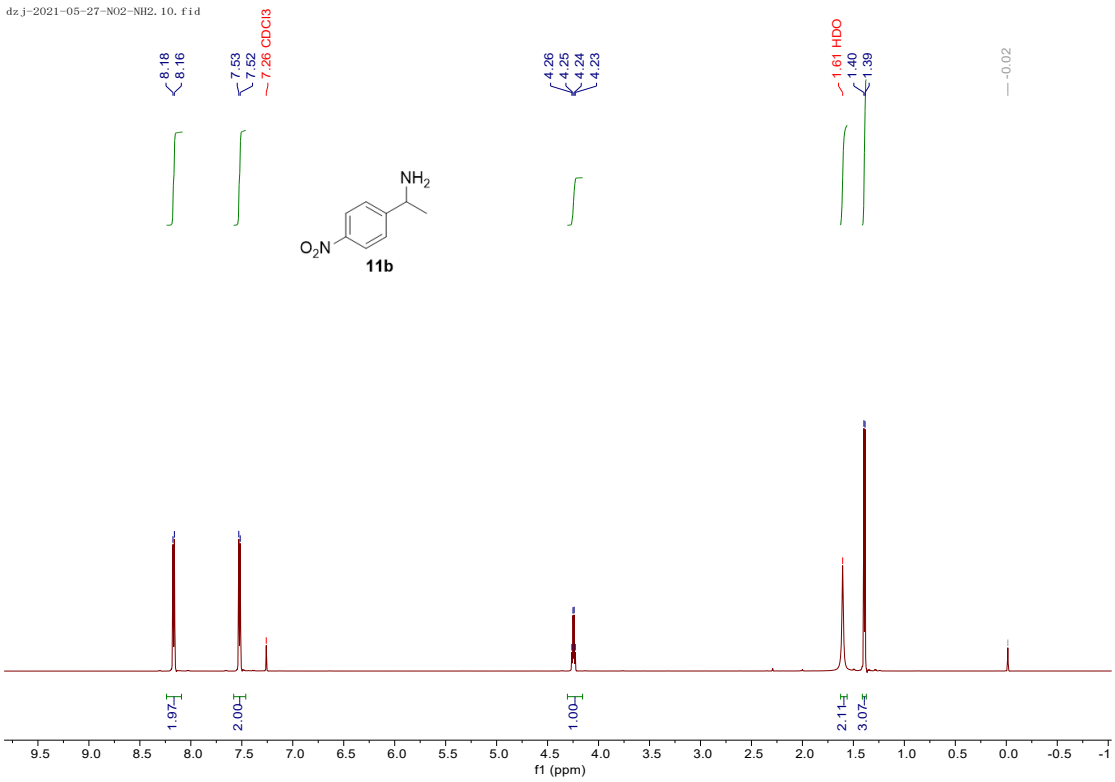
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1-phenylethan-1-amine** (**9b**)



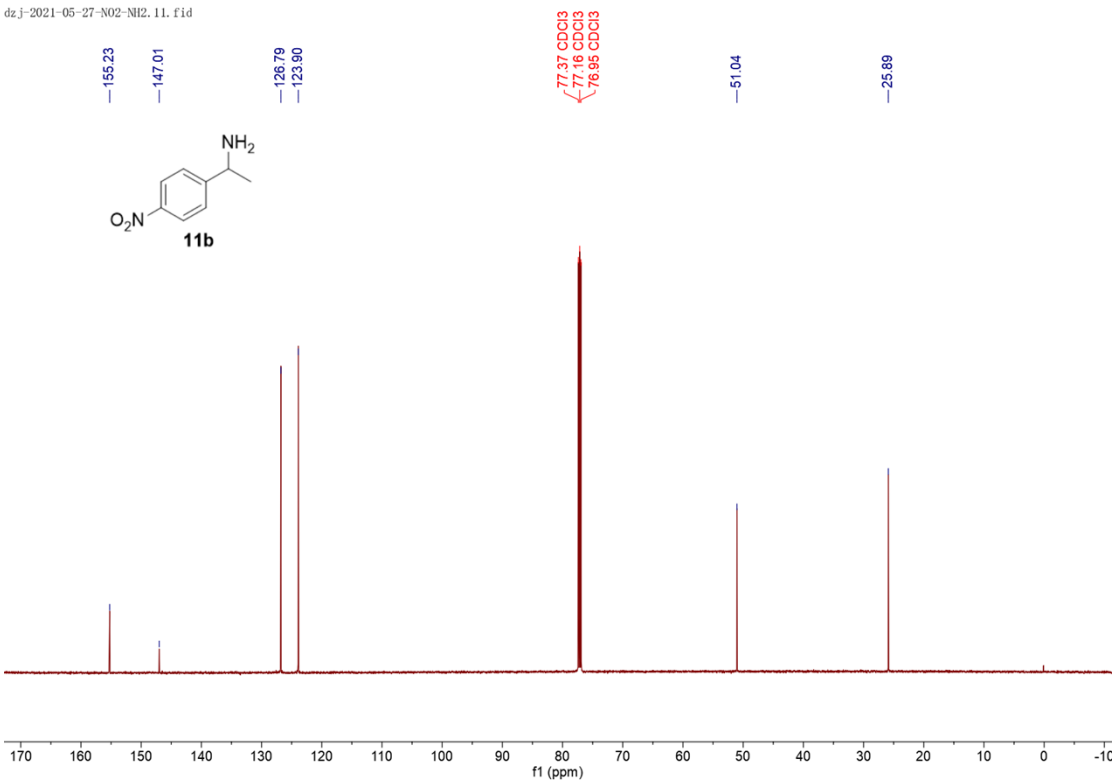
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1-(4-methoxyphenyl)ethan-1-amine** (**10b**)



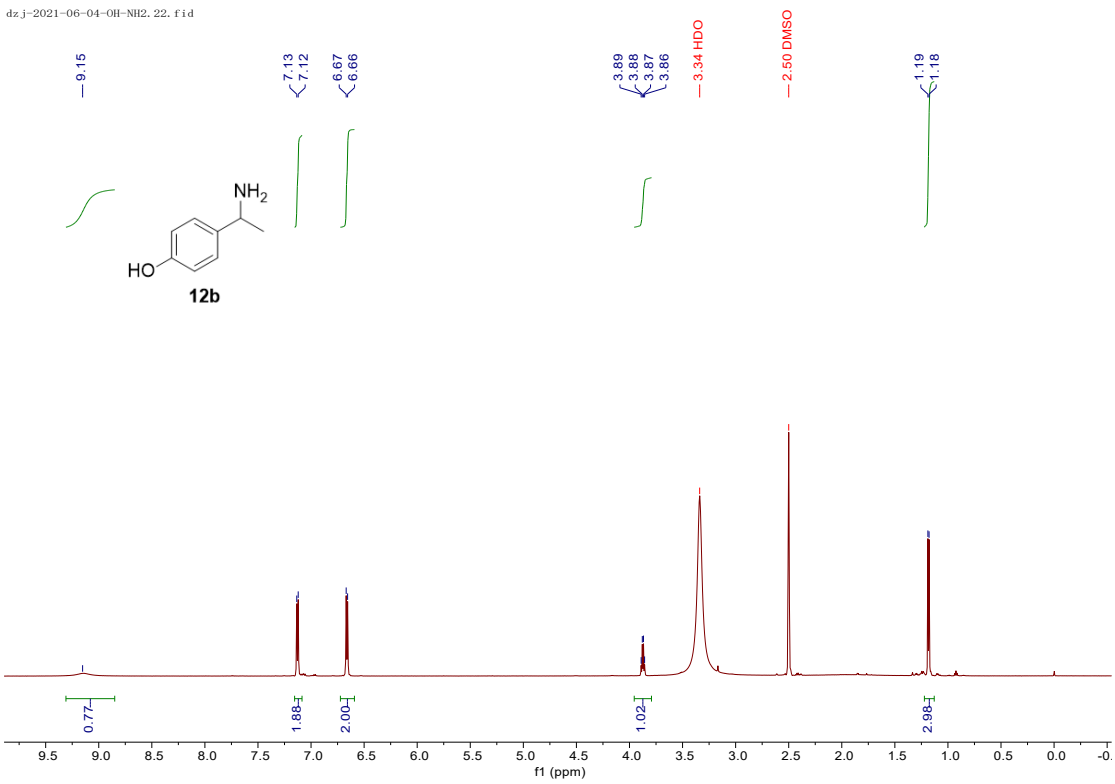
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1-(4-methoxyphenyl)ethan-1-amine** (**10b**)



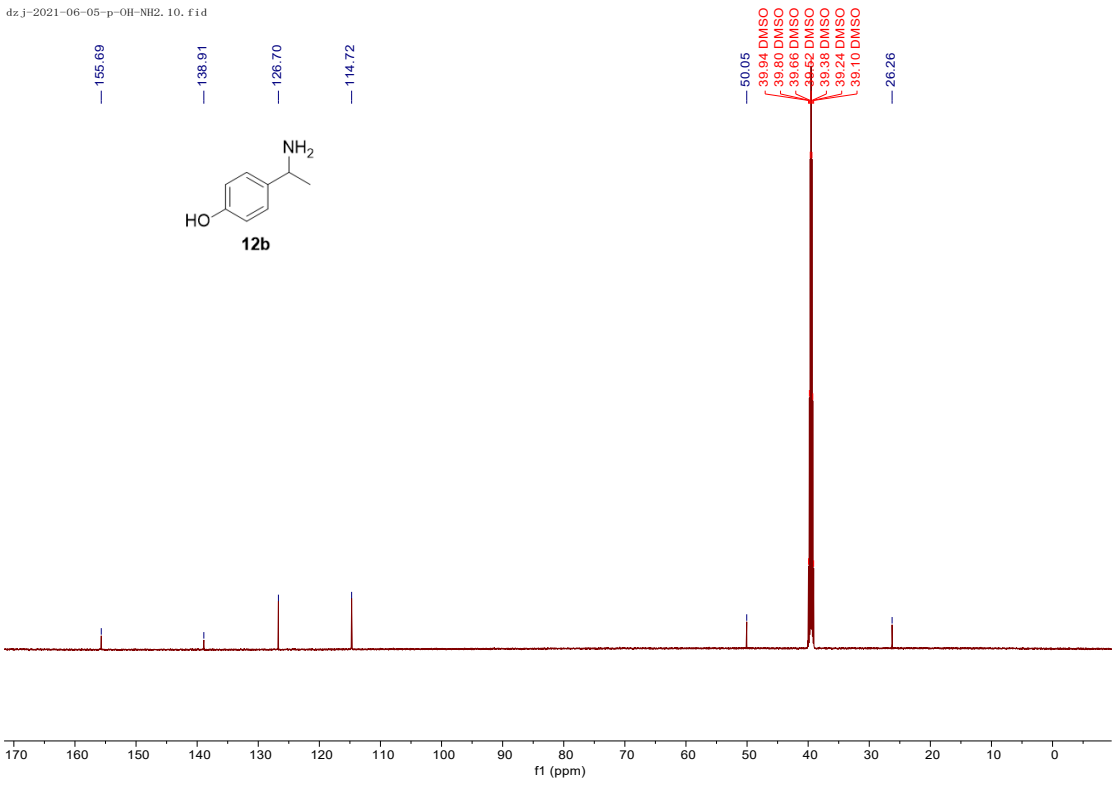
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1-(4-nitrophenyl)ethan-1-amine** (**11b**)



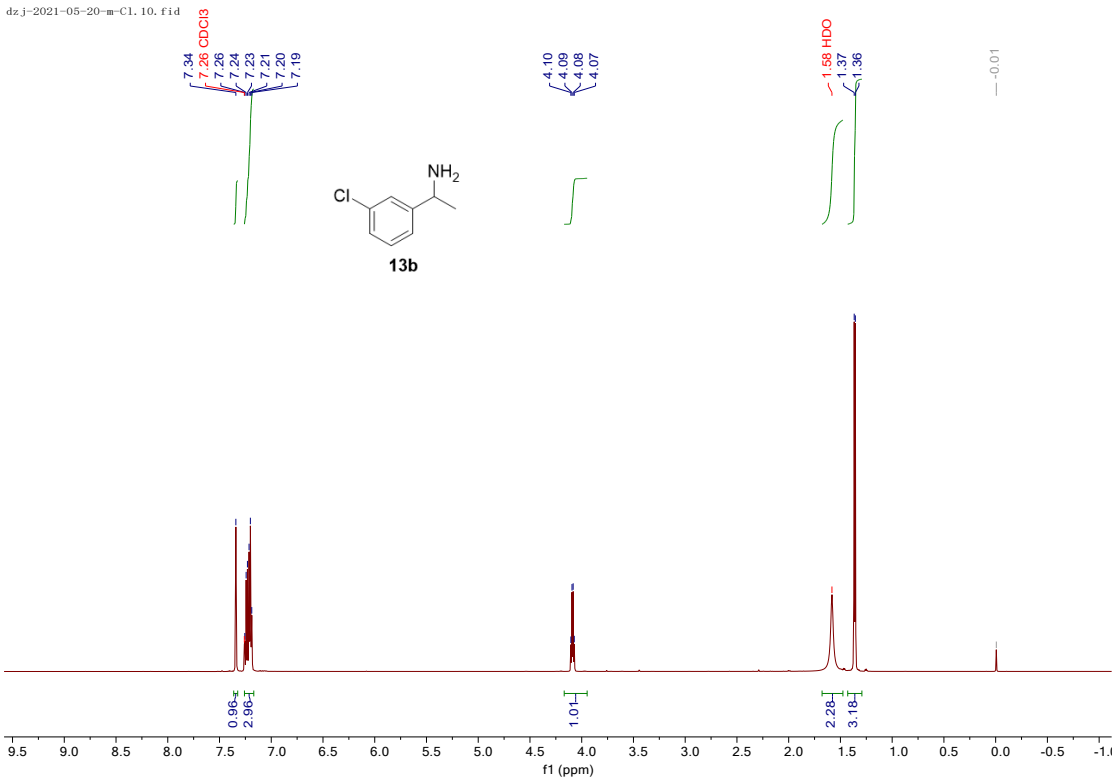
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **1-(4-nitrophenyl)ethan-1-amine** (**11b**)



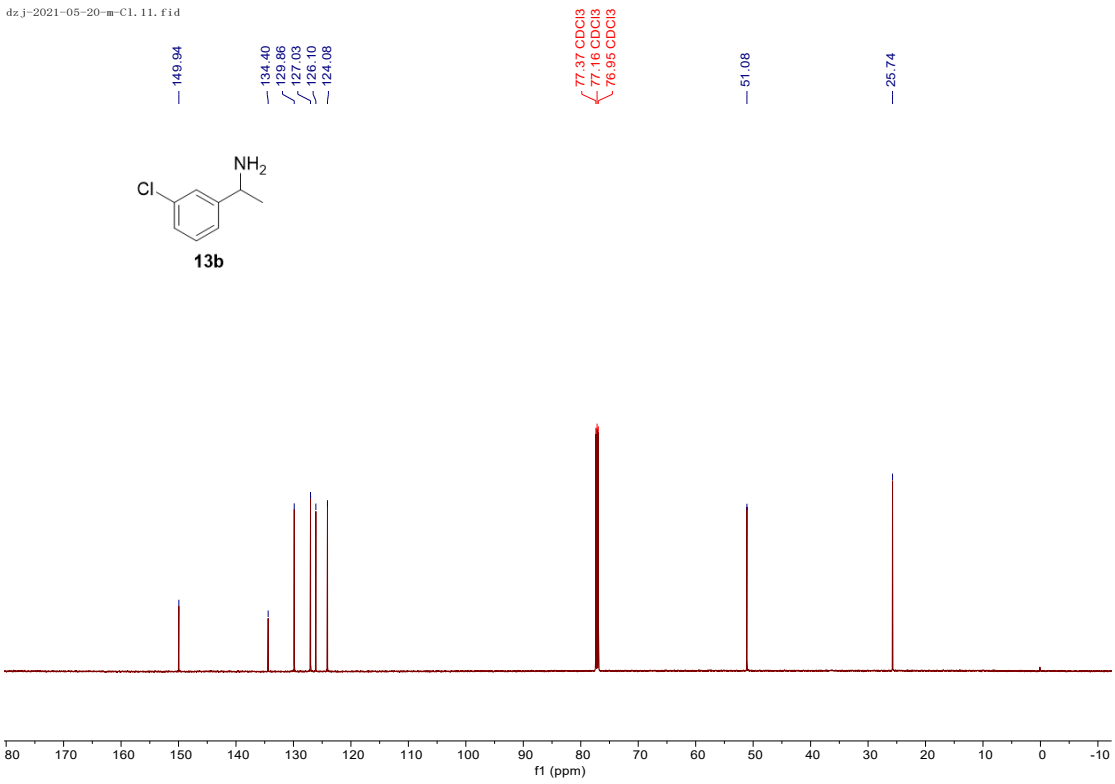
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **4-(1-aminoethyl)phenol** (**12b**)



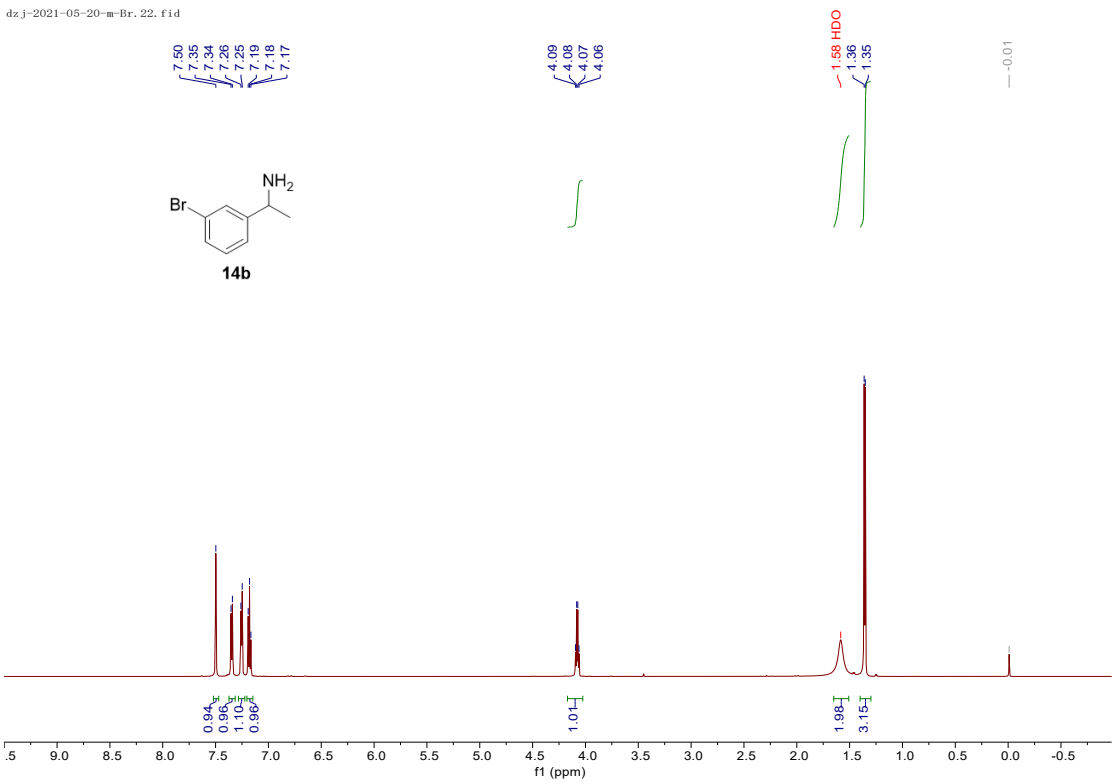
^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **4-(1-aminoethyl)phenol** (**12b**)



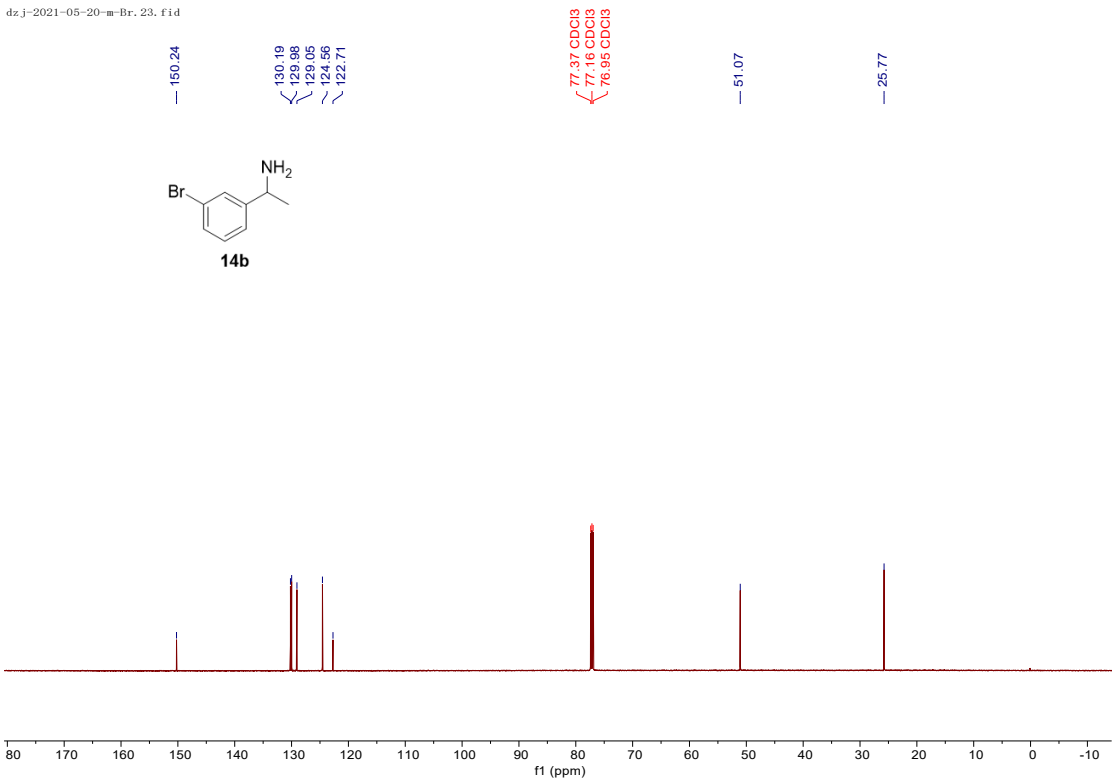
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1-(3-chlorophenyl)ethan-1-amine** (**13b**)



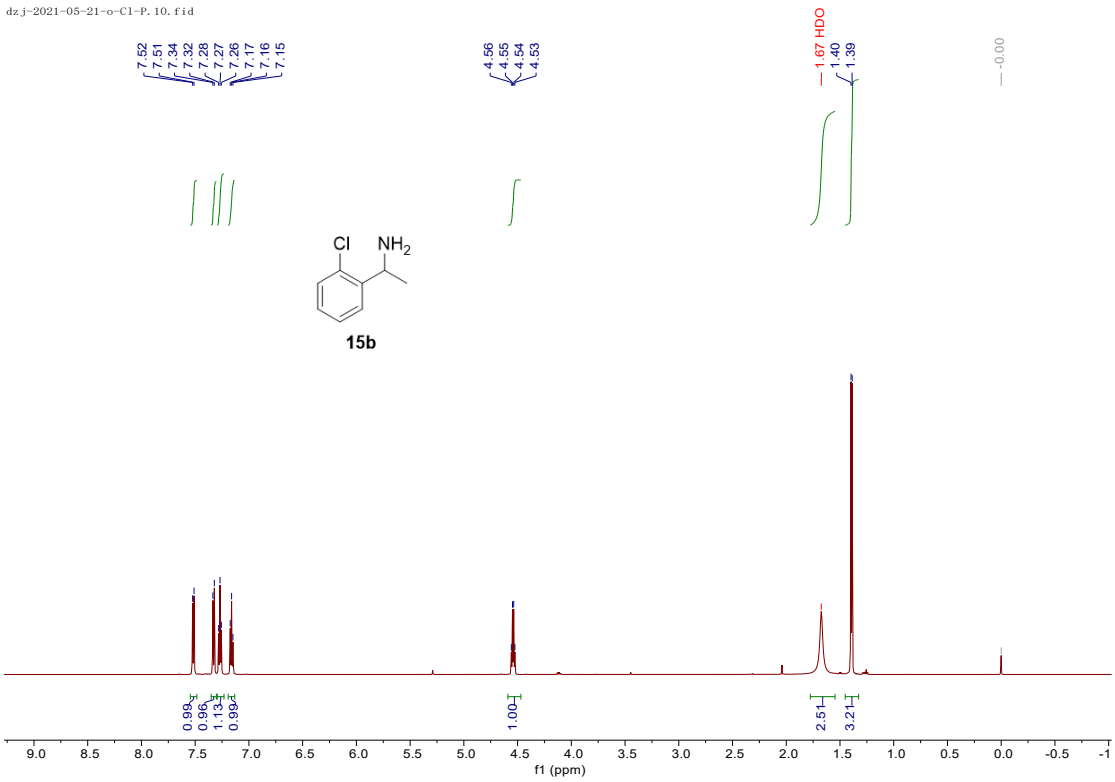
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **1-(3-chlorophenyl)ethan-1-amine** (**13b**)



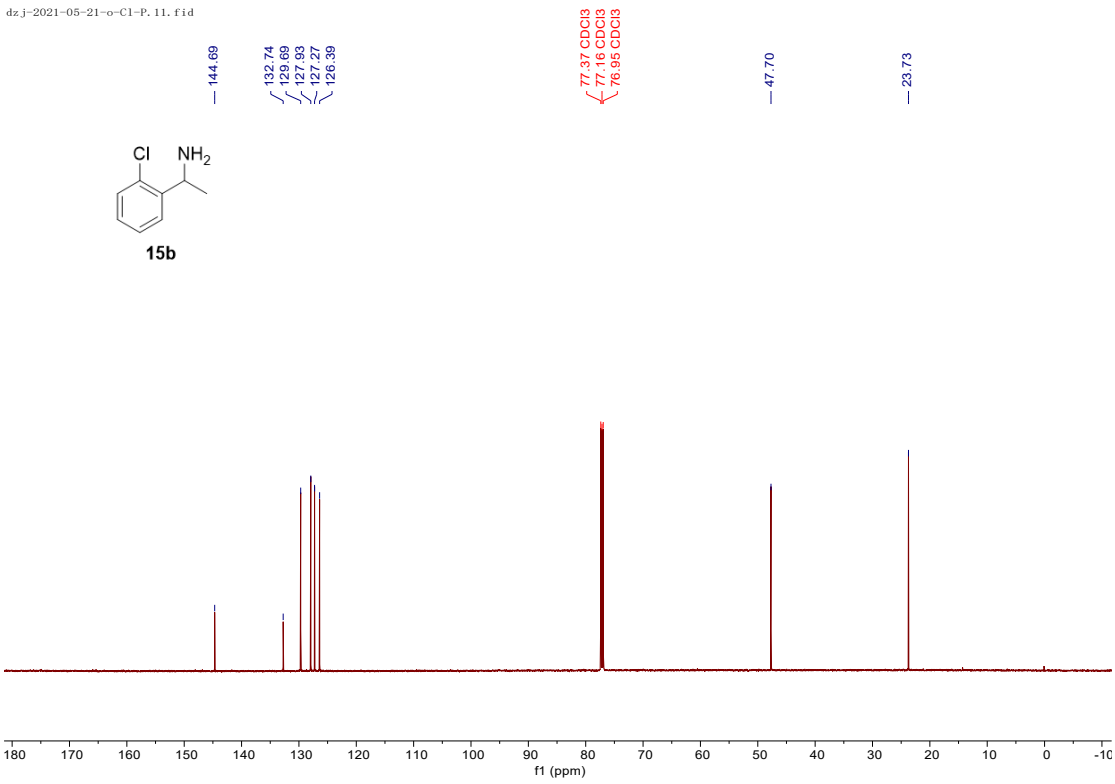
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1-(3-bromophenyl)ethan-1-amine** (**14b**)



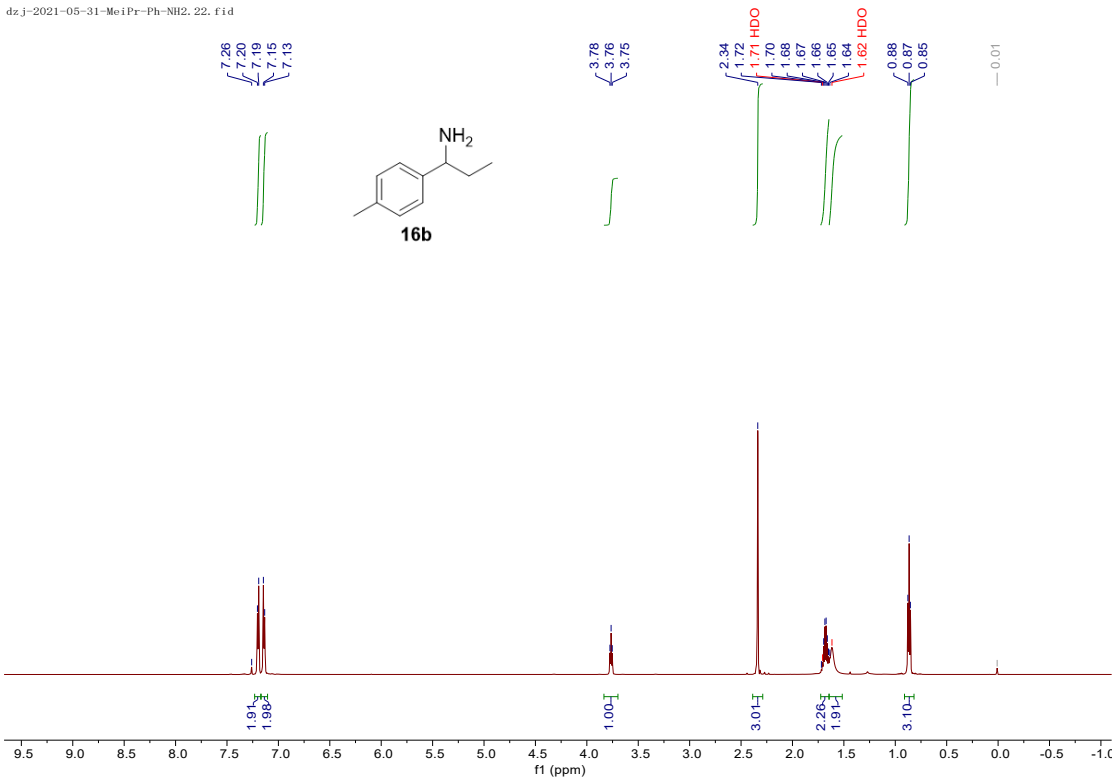
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **1-(3-bromophenyl)ethan-1-amine** (**14b**)



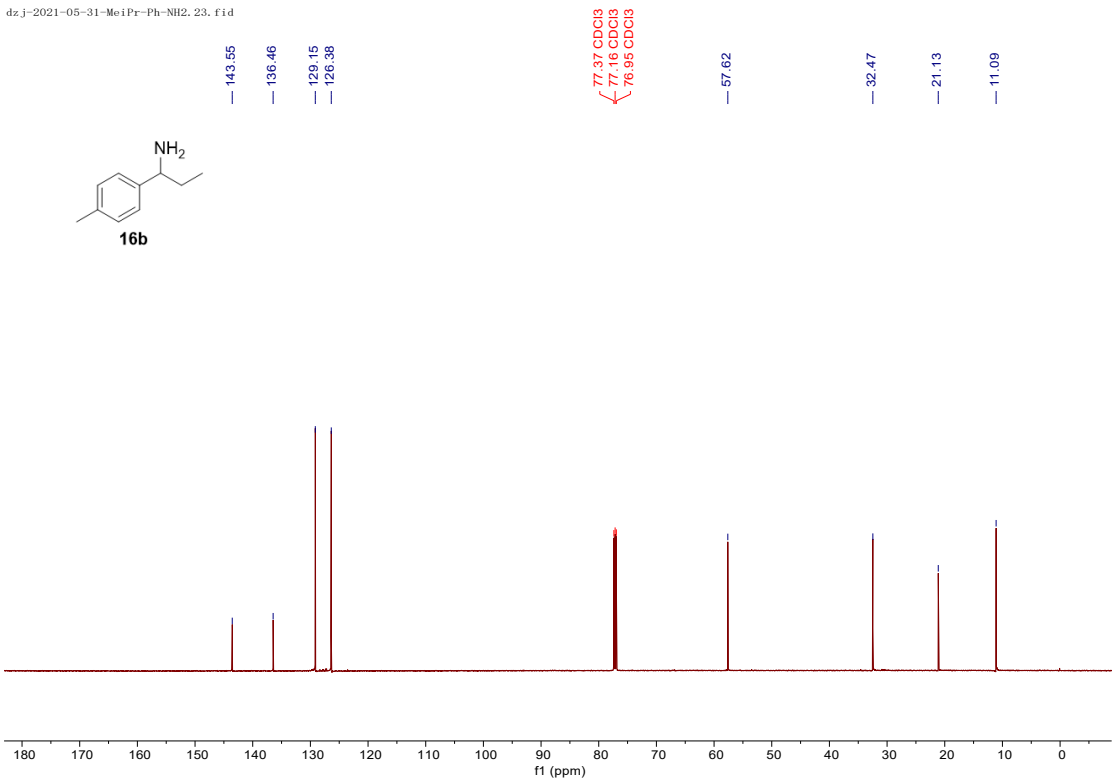
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1-(2-chlorophenyl)ethan-1-amine** (**15b**)



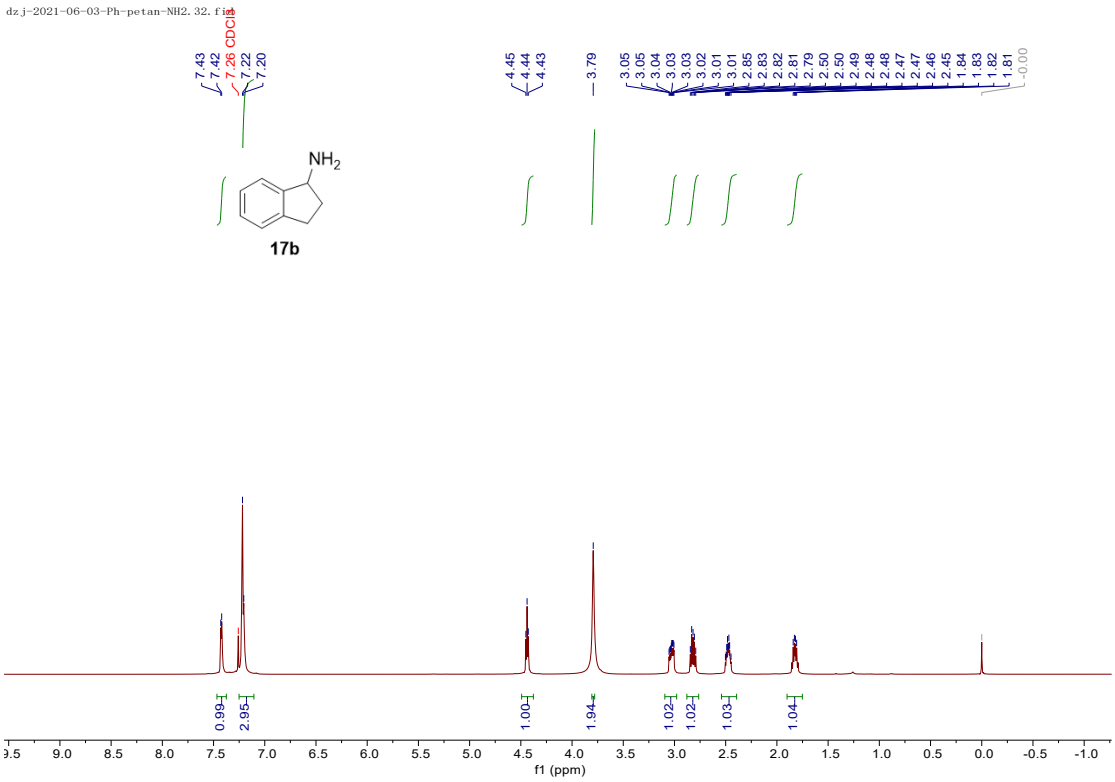
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **1-(2-chlorophenyl)ethan-1-amine** (**15b**)



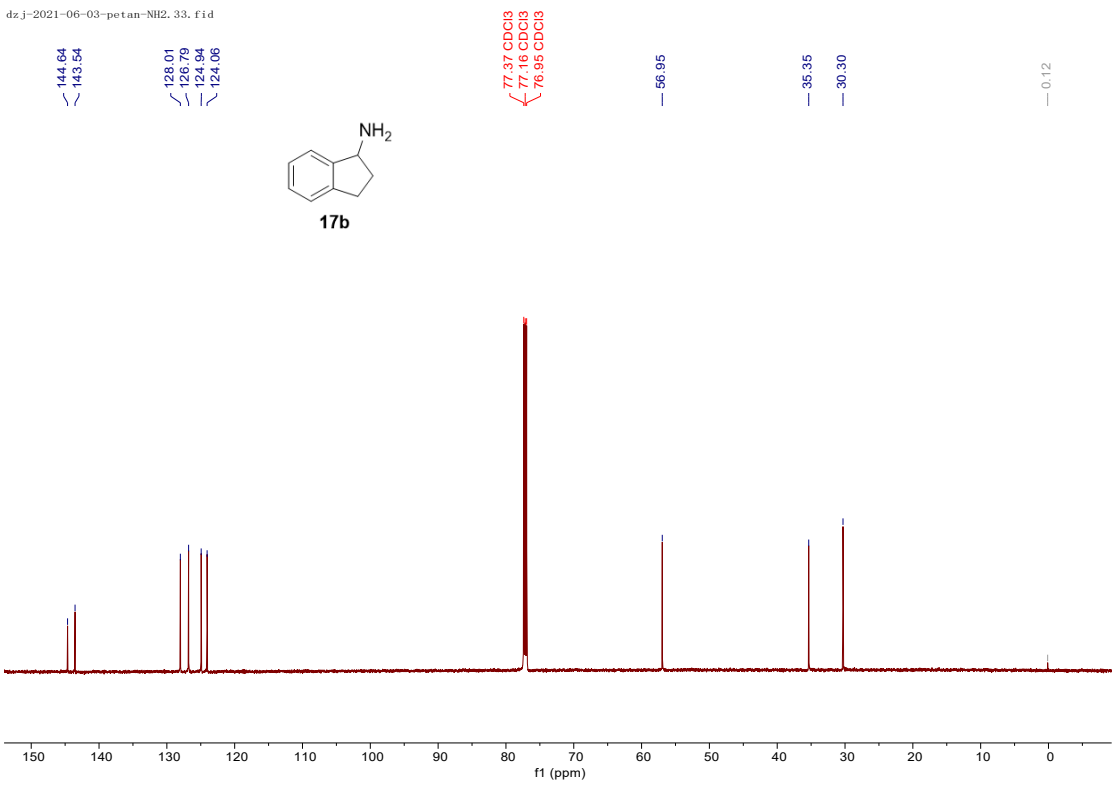
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1-(*p*-tolyl)propan-1-amine** (**16b**)



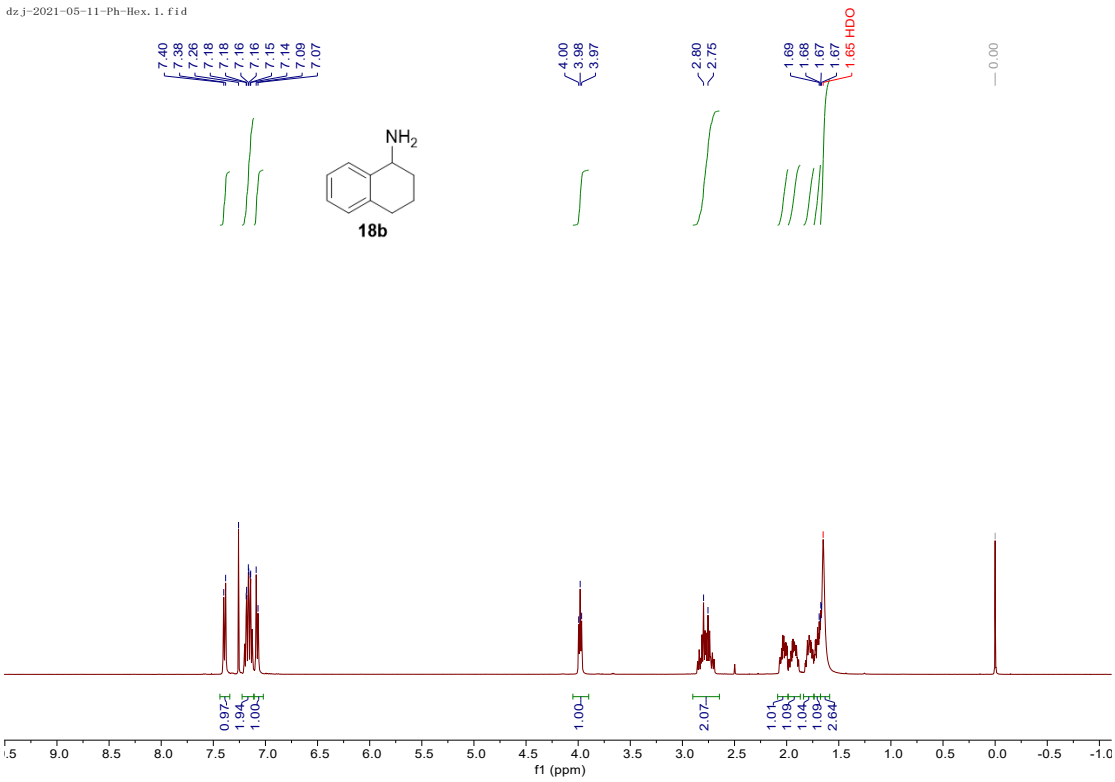
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **1-(*p*-tolyl)propan-1-amine** (**16b**)



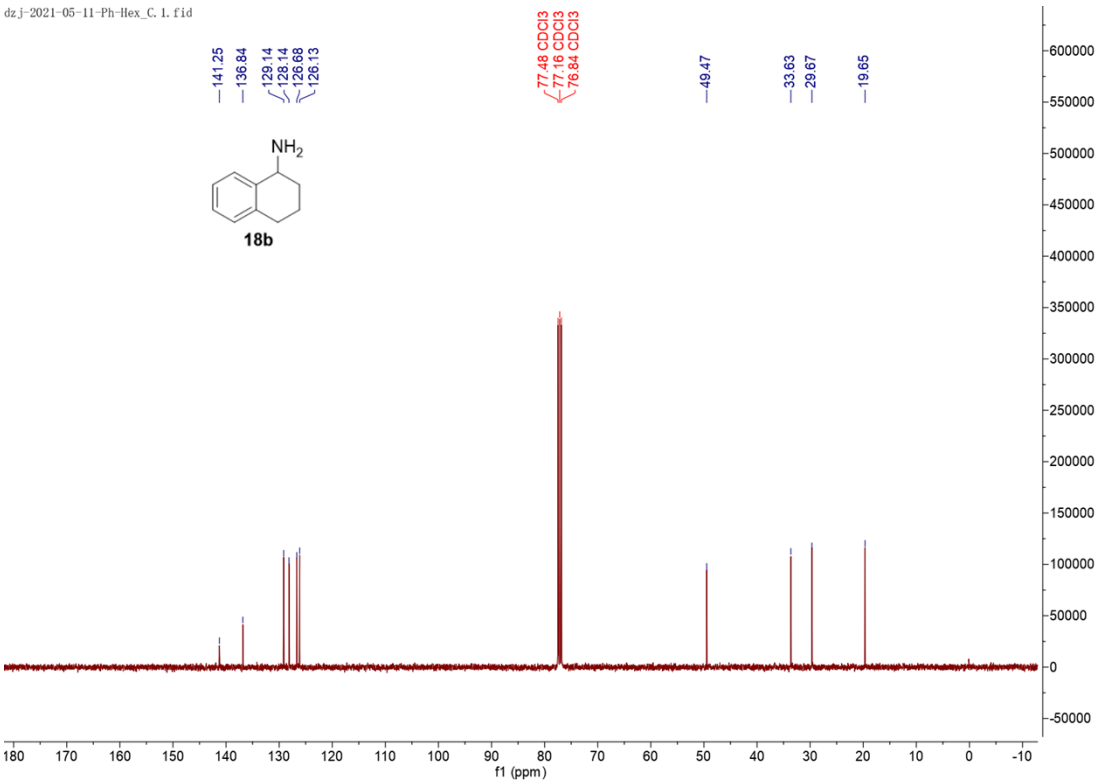
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2,3-dihydro-*1H*-inden-1-amine** (**17b**)



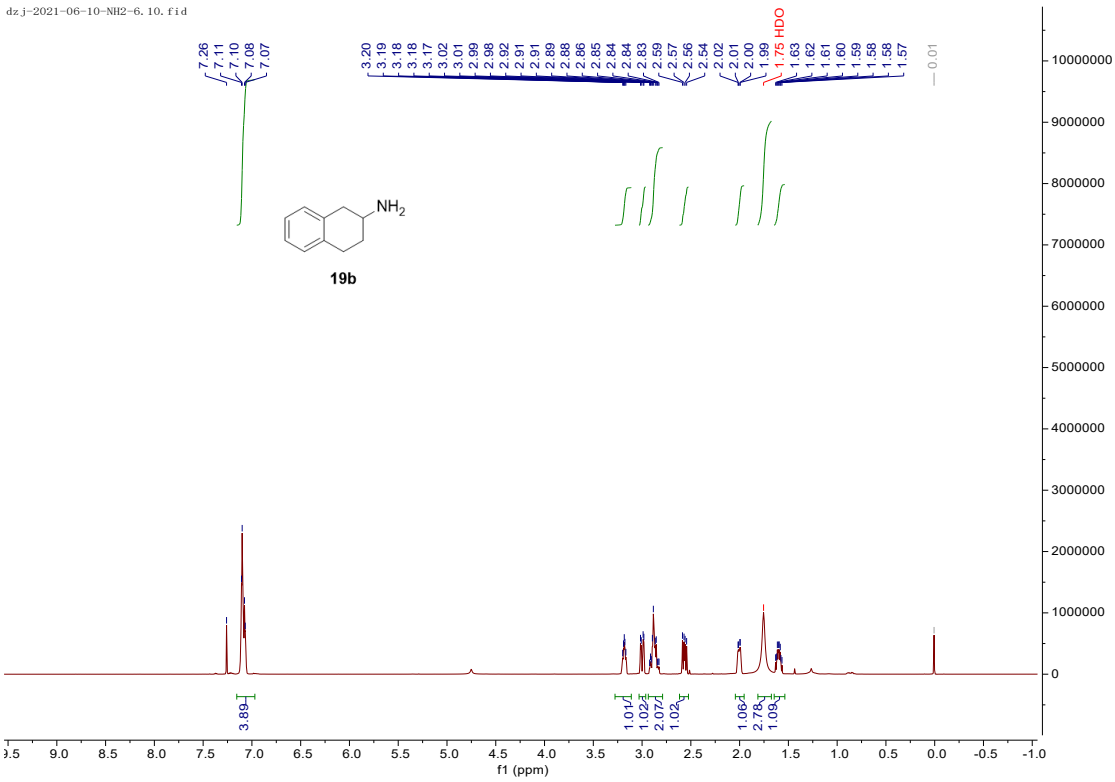
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2,3-dihydro-*1H*-inden-1-amine** (**17b**)



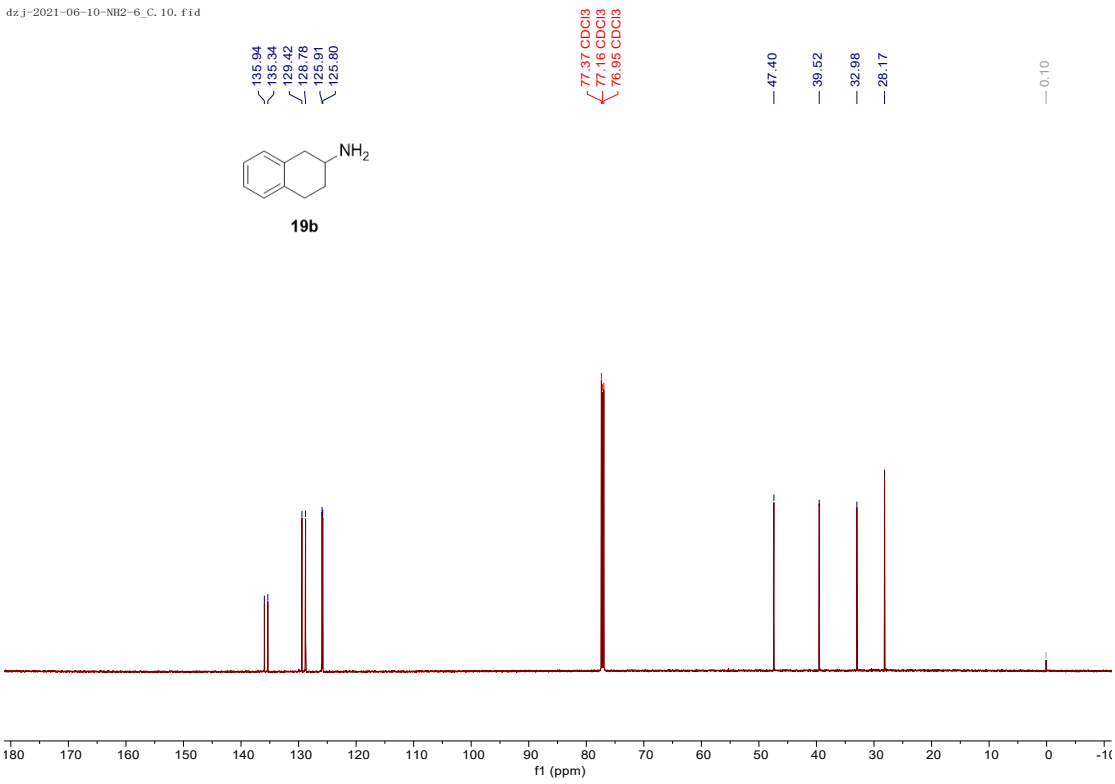
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1,2,3,4-tetrahydronaphthalen-1-amine** (**18b**)



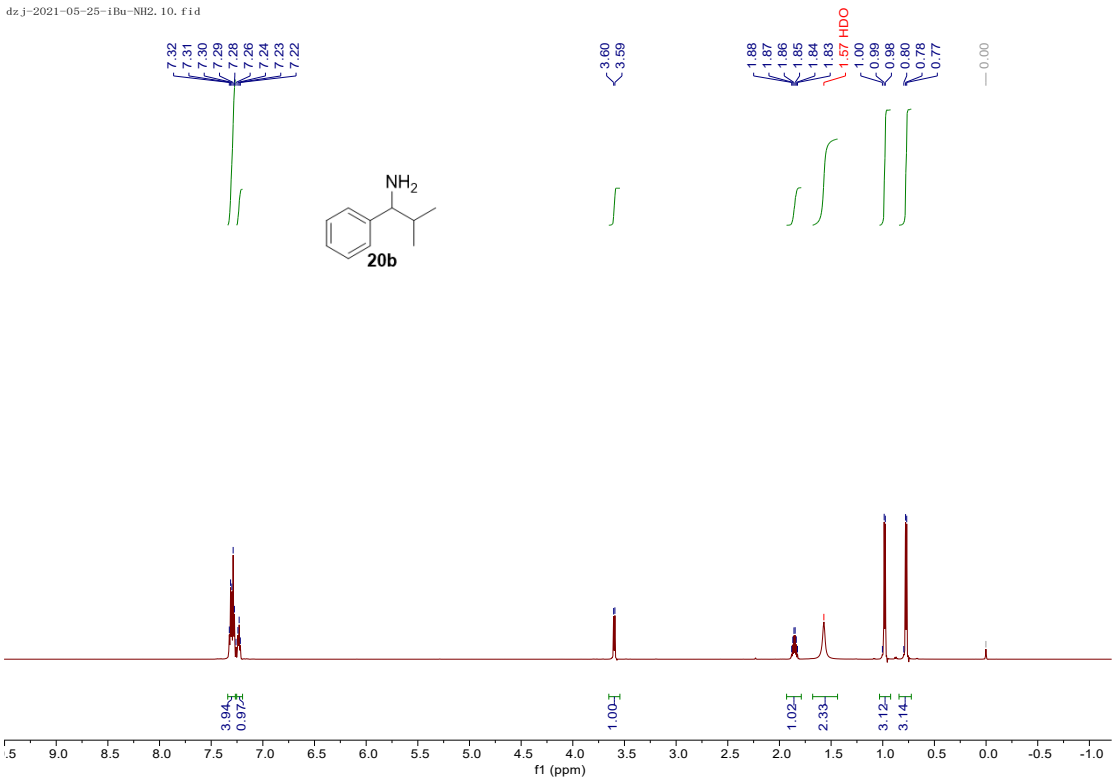
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1,2,3,4-tetrahydronaphthalen-1-amine** (**18b**)



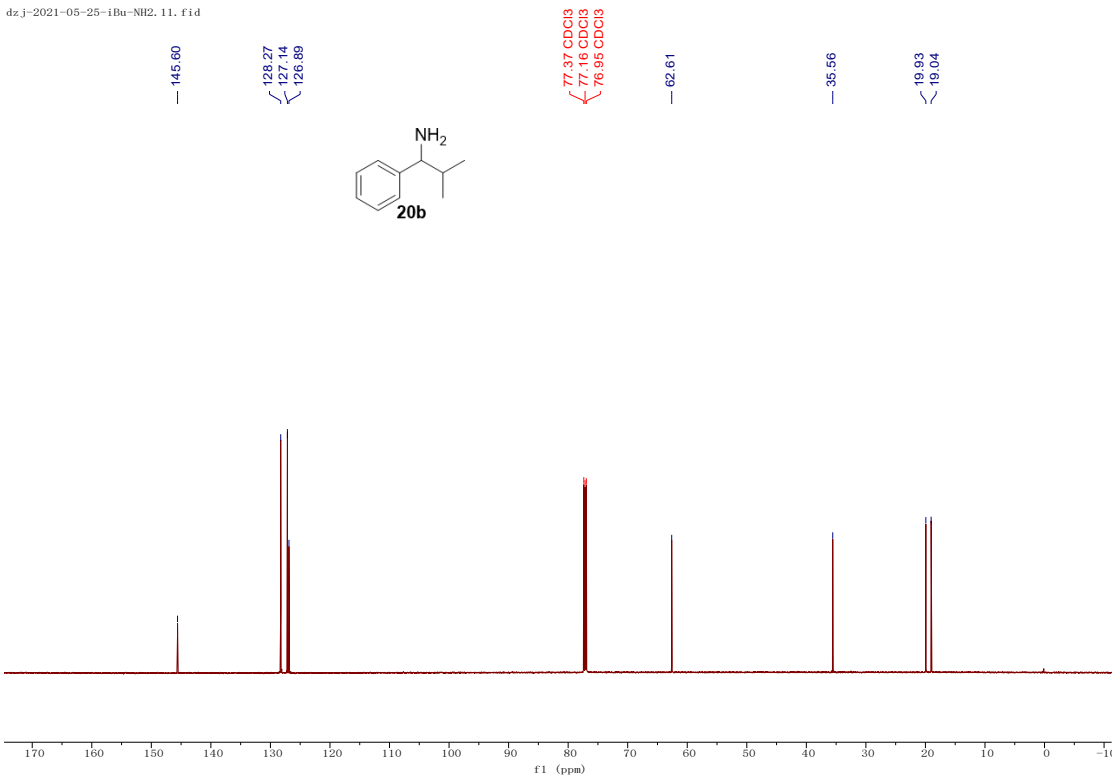
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1,2,3,4-tetrahydronaphthalen-2-amine** (**19b**)



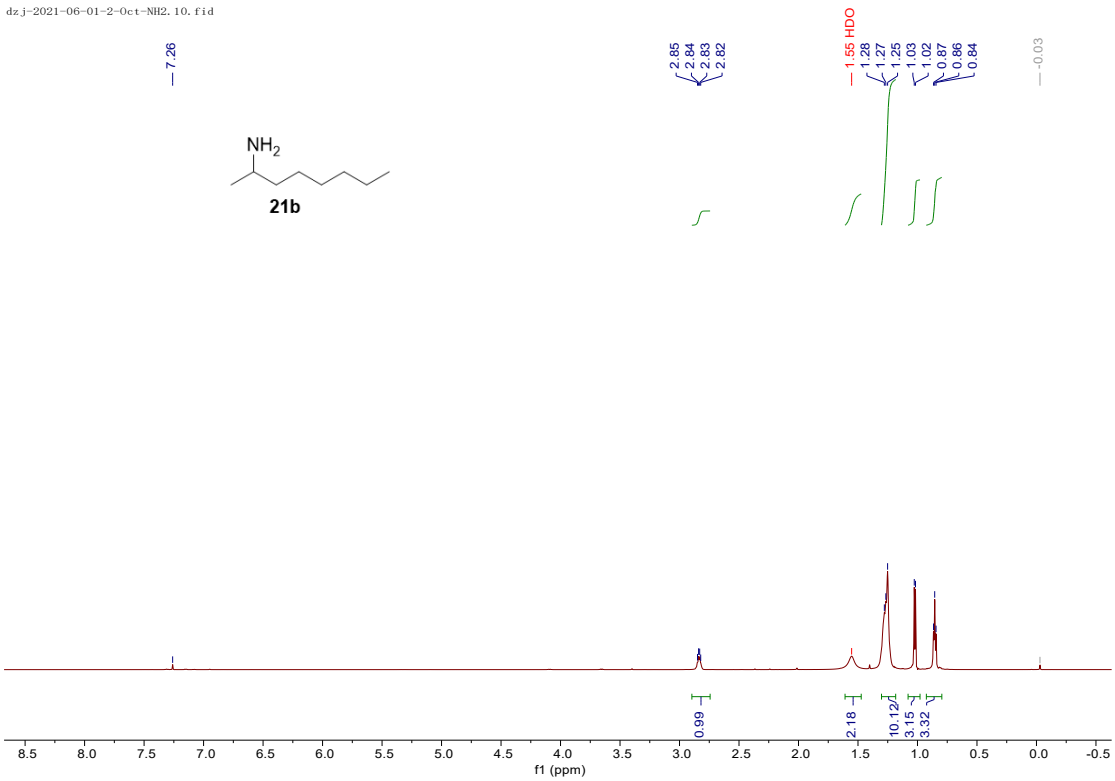
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **1,2,3,4-tetrahydronaphthalen-2-amine** (**19b**)



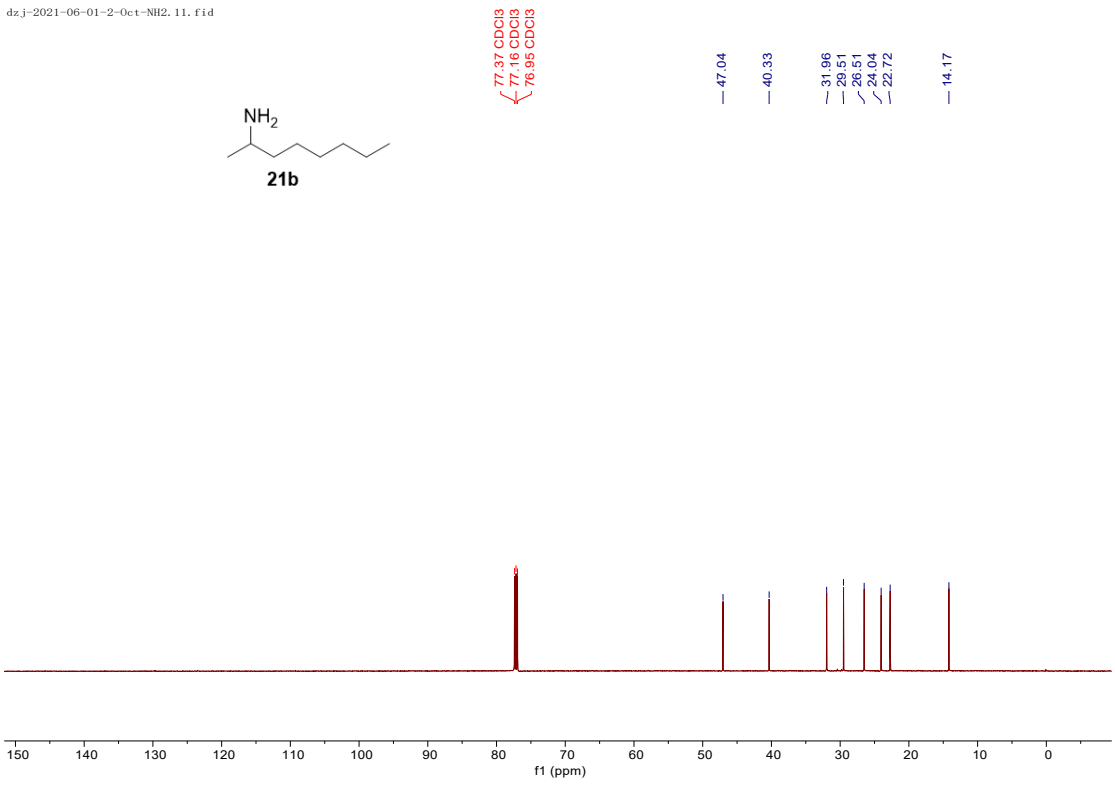
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2-methyl-1-phenylpropan-1-amine** (**20b**)



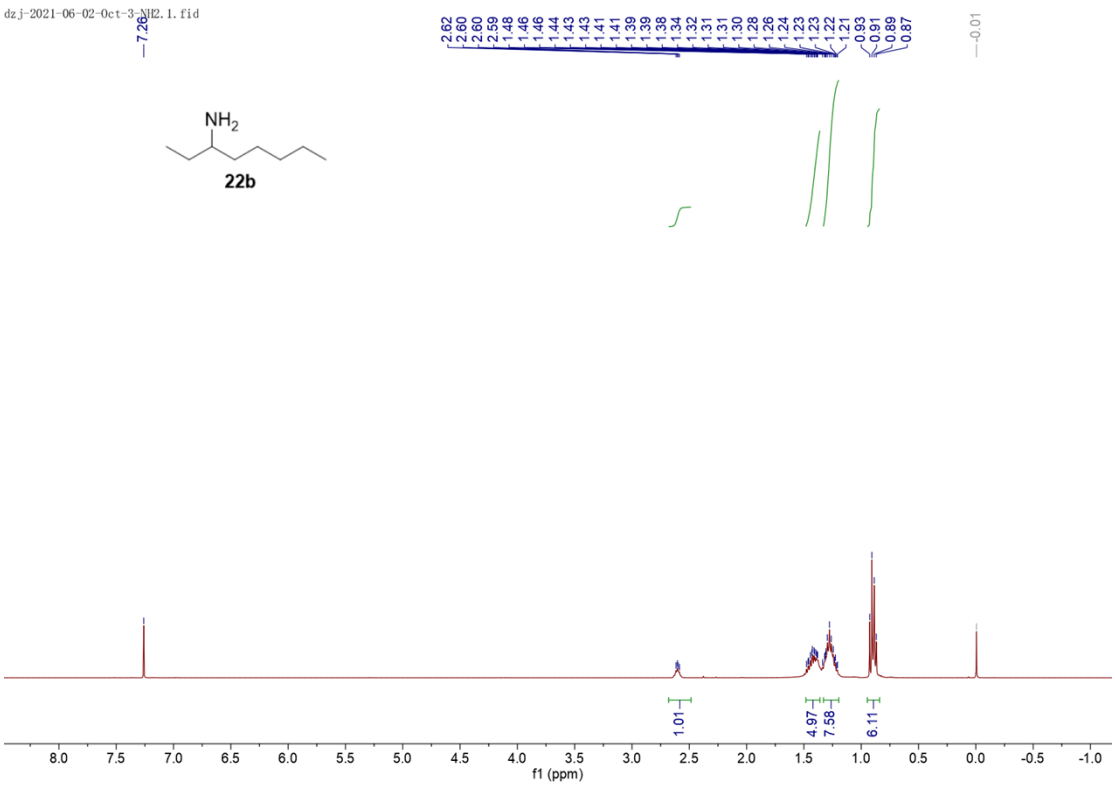
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2-methyl-1-phenylpropan-1-amine** (**20b**)



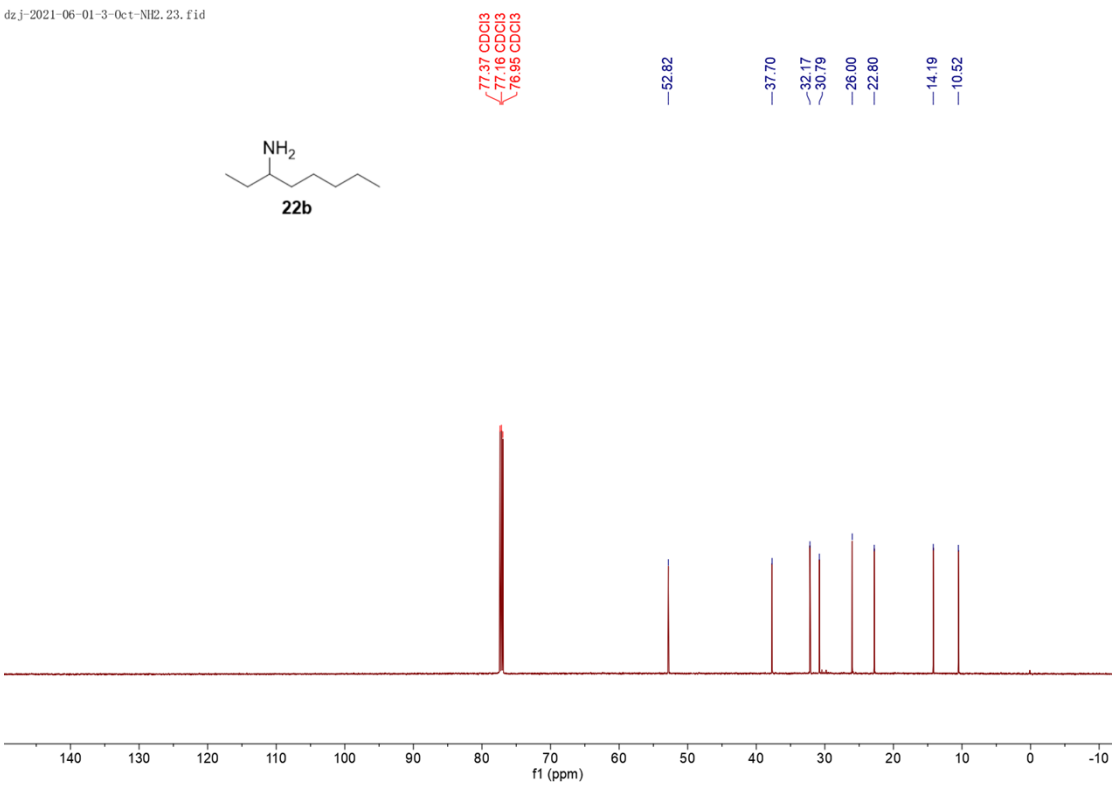
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **octan-2-amine** (**21b**)



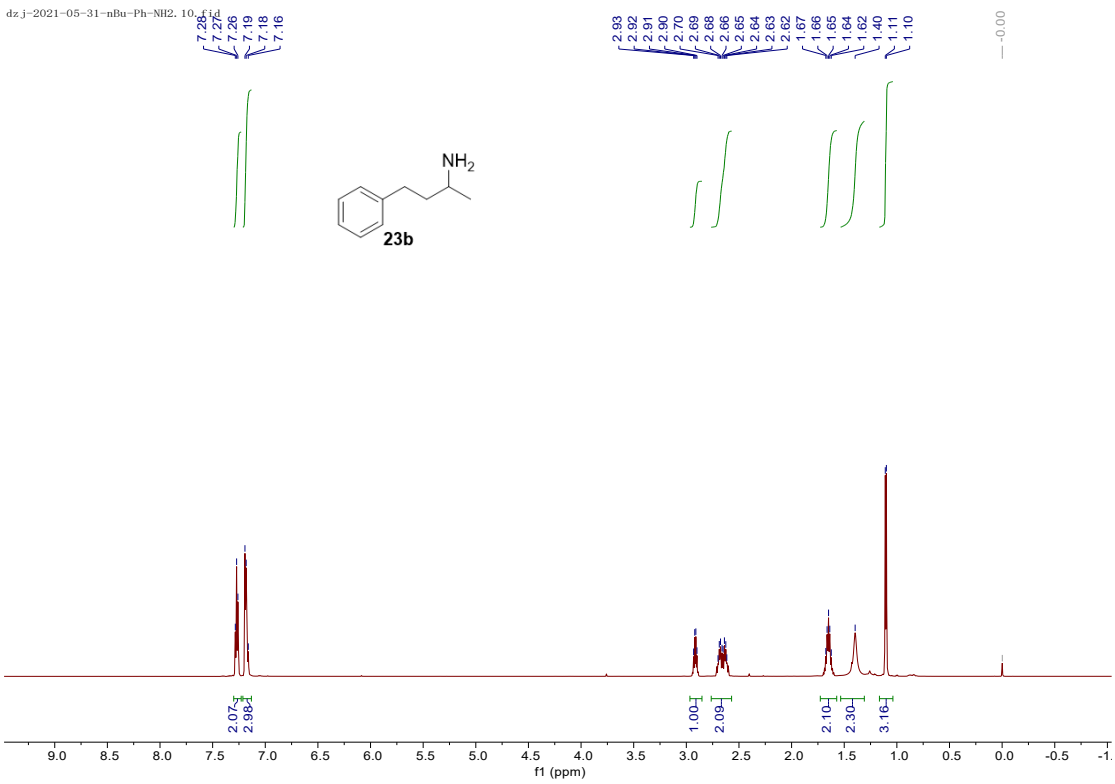
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **octan-2-amine** (**21b**)



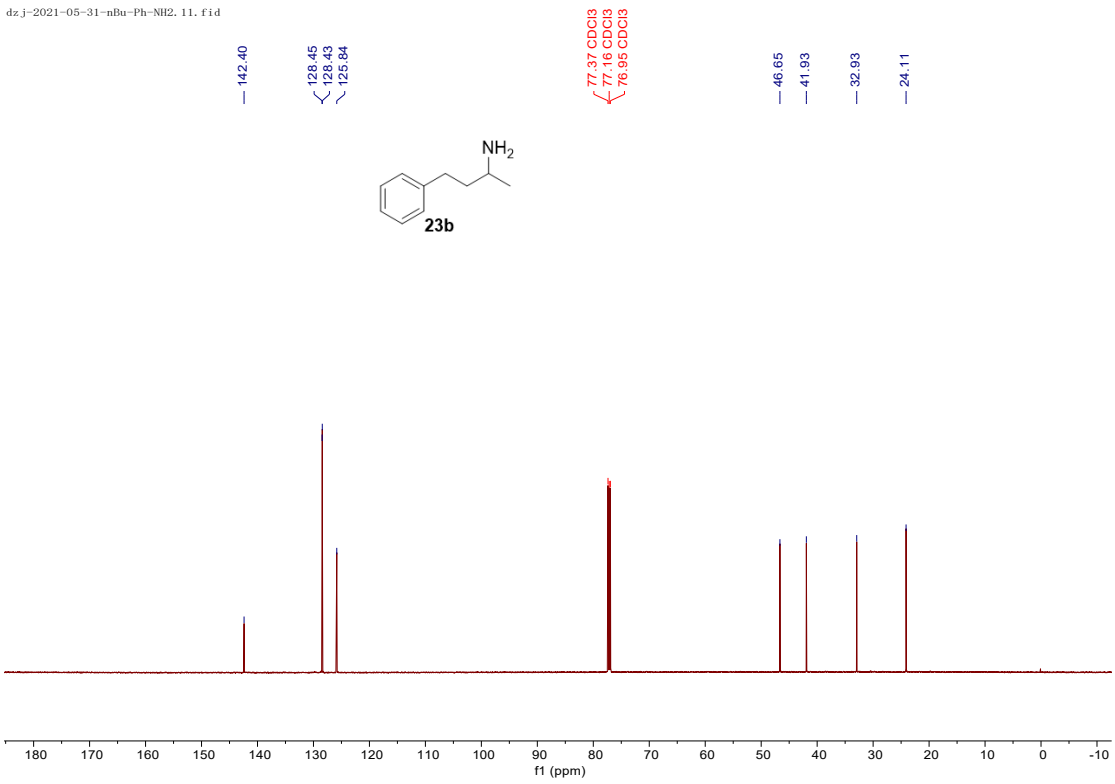
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **octan-3-amine** (**22b**)



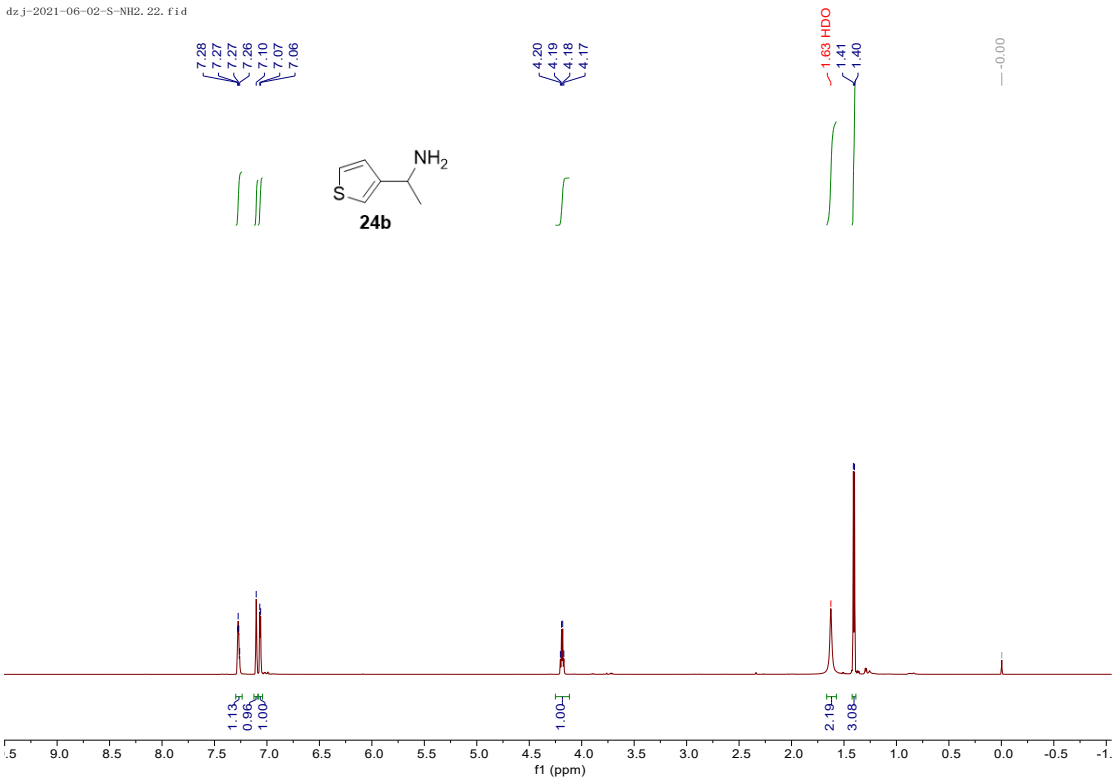
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **octan-3-amine** (**22b**)



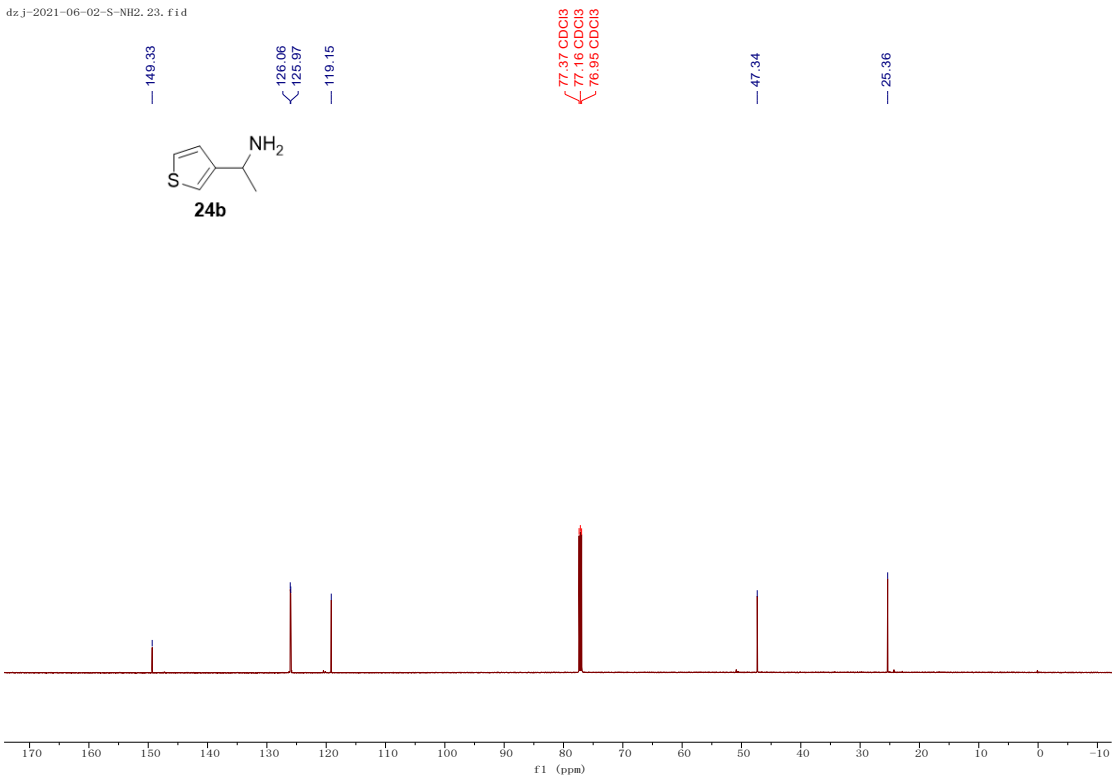
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4-phenylbutan-2-amine** (**23b**)



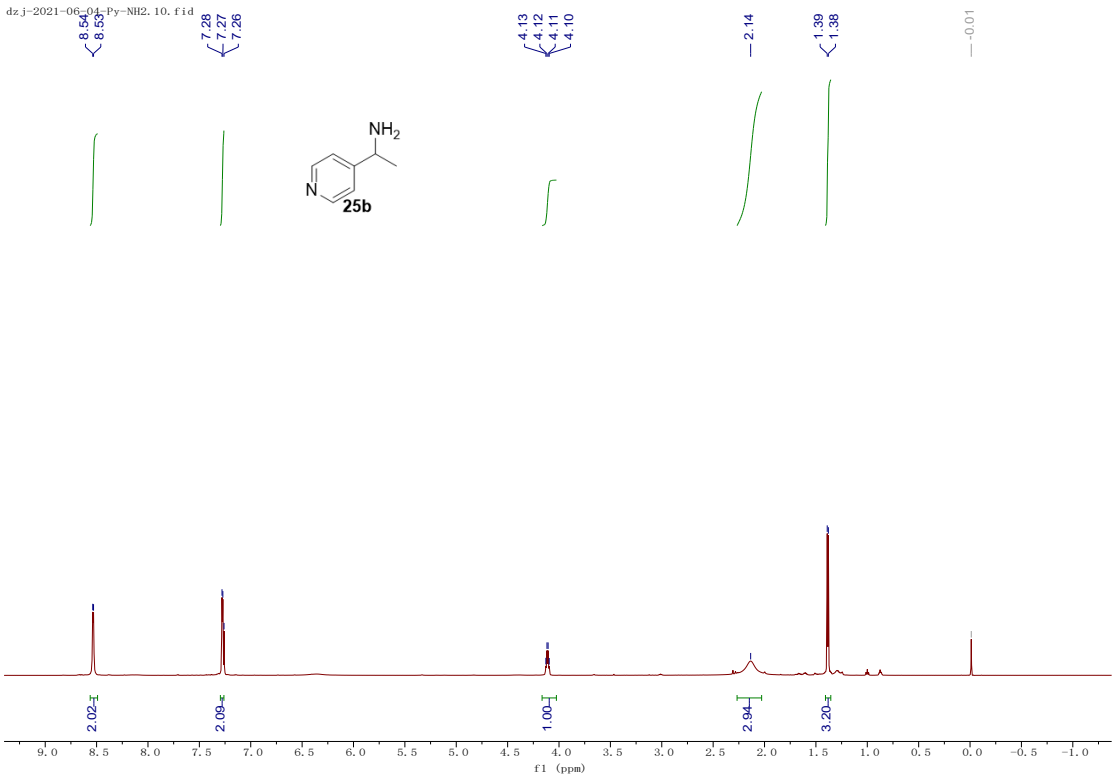
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4-phenylbutan-2-amine** (**23b**)



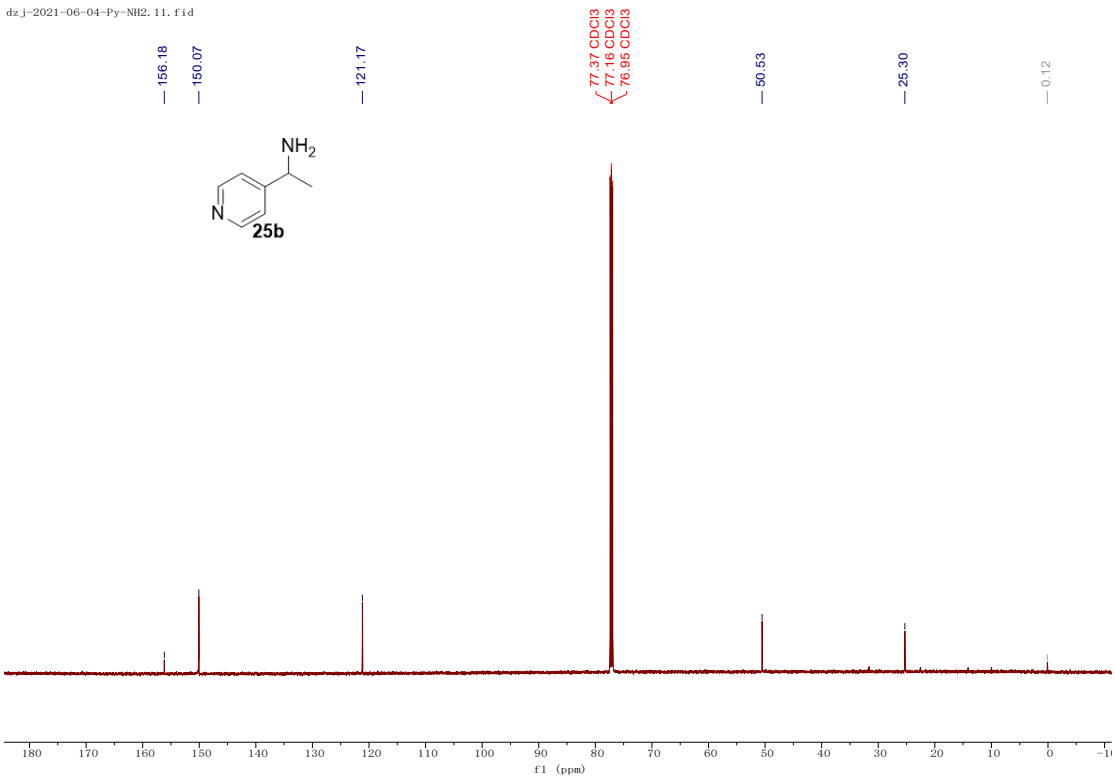
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1-(thiophen-3-yl)ethan-1-amine** (**24b**)



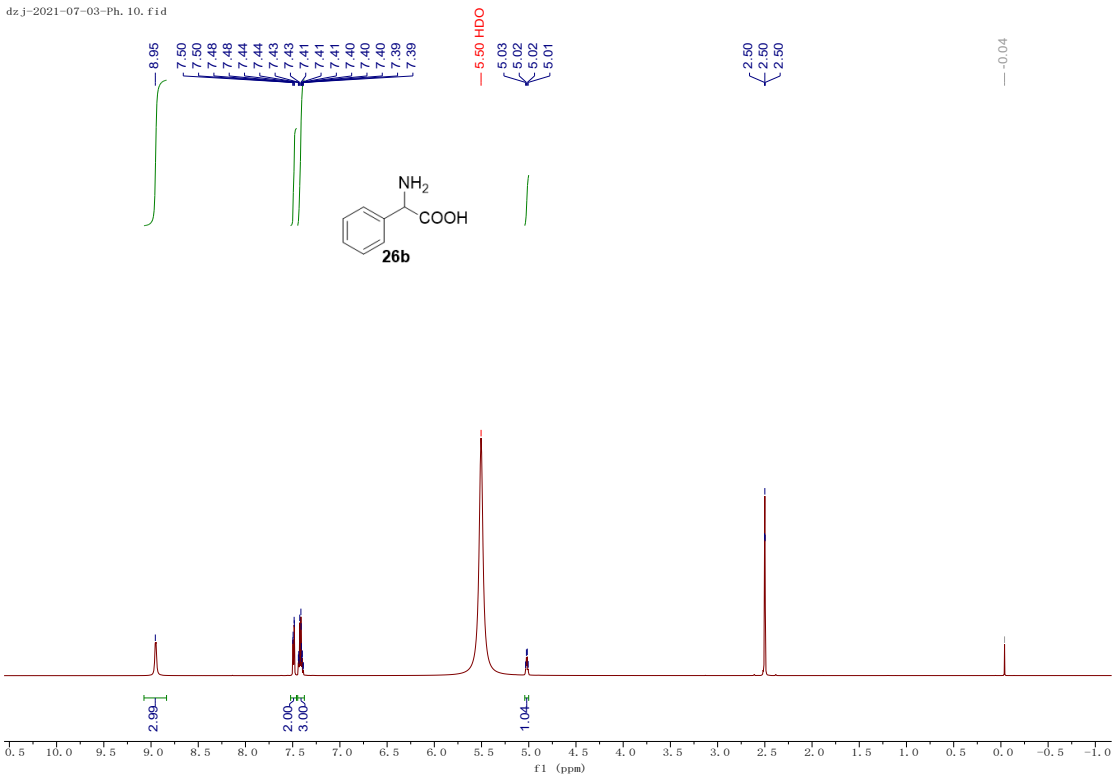
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **1-(thiophen-3-yl)ethan-1-amine** (**24b**)



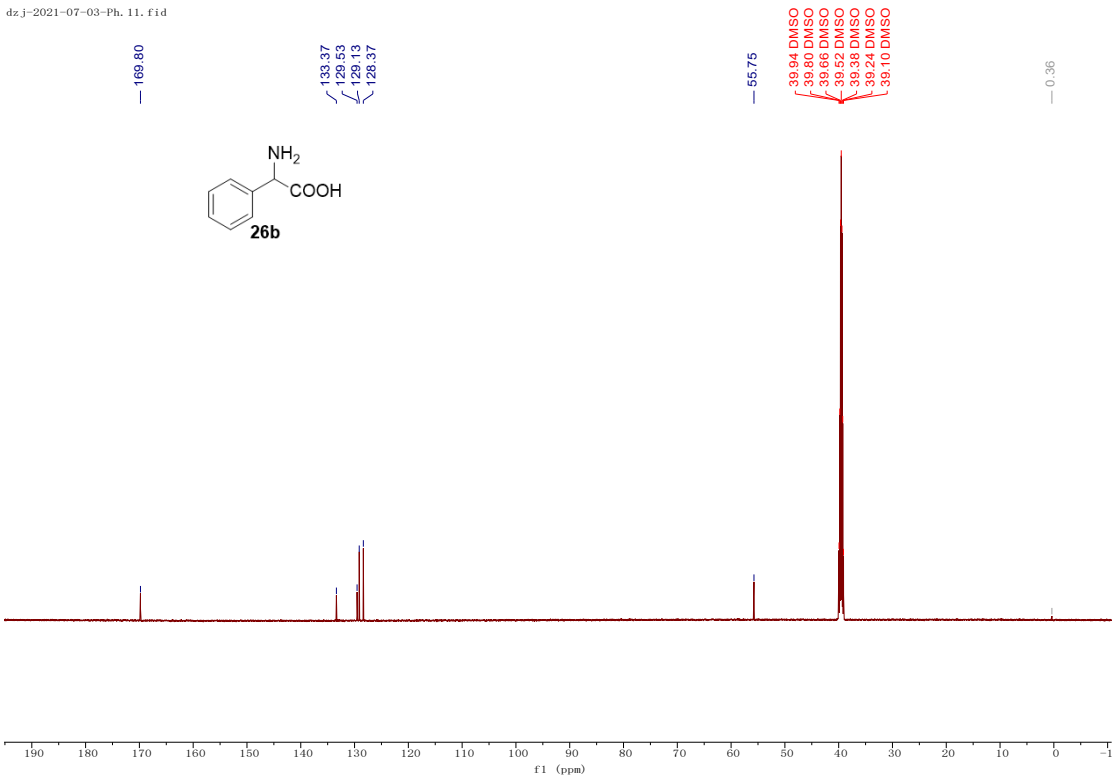
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1-(pyridin-4-yl)ethan-1-amine** (**25b**)



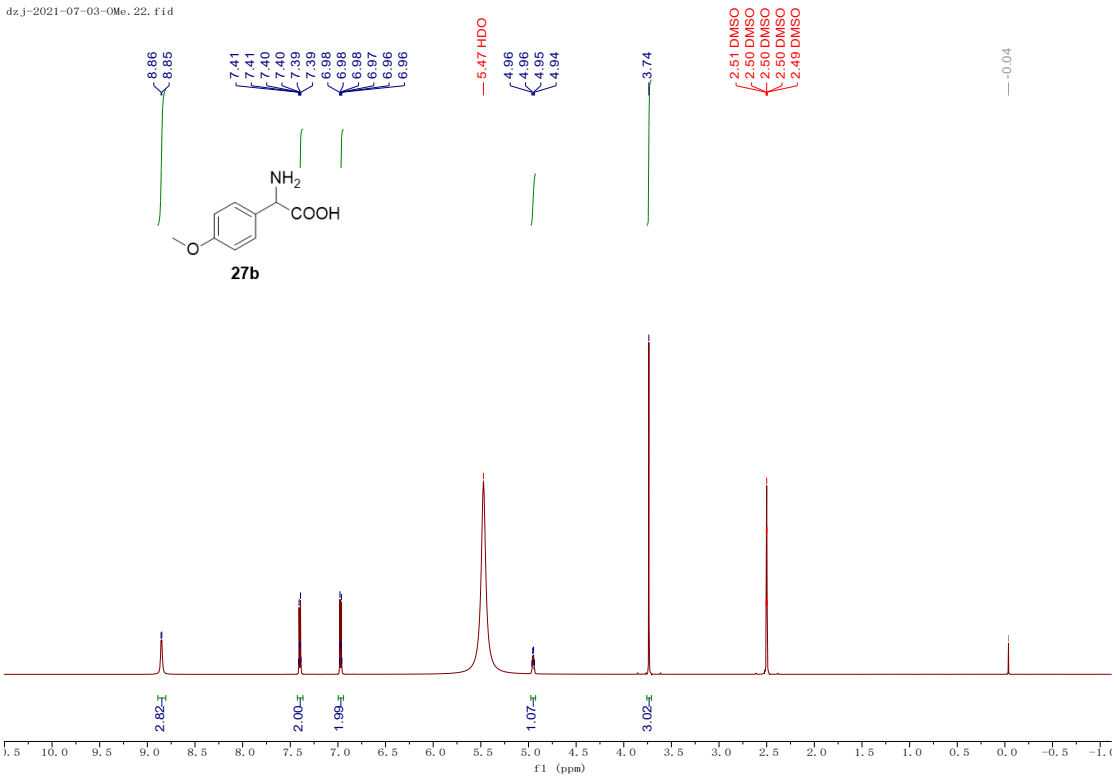
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **1-(pyridin-4-yl)ethan-1-amine** (**25b**)



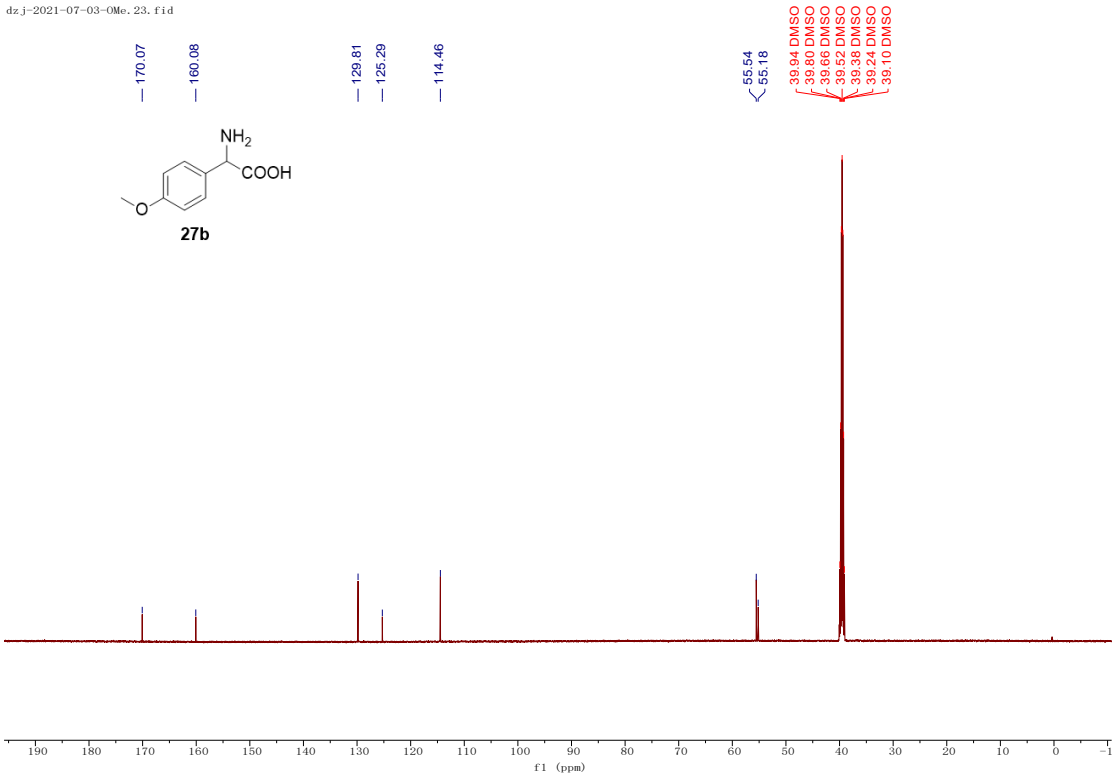
^{1}H NMR spectrum (600 MHz, DMSO-d_6 + HCl) of **2-amino-2-phenylacetic acid** (**26b**)



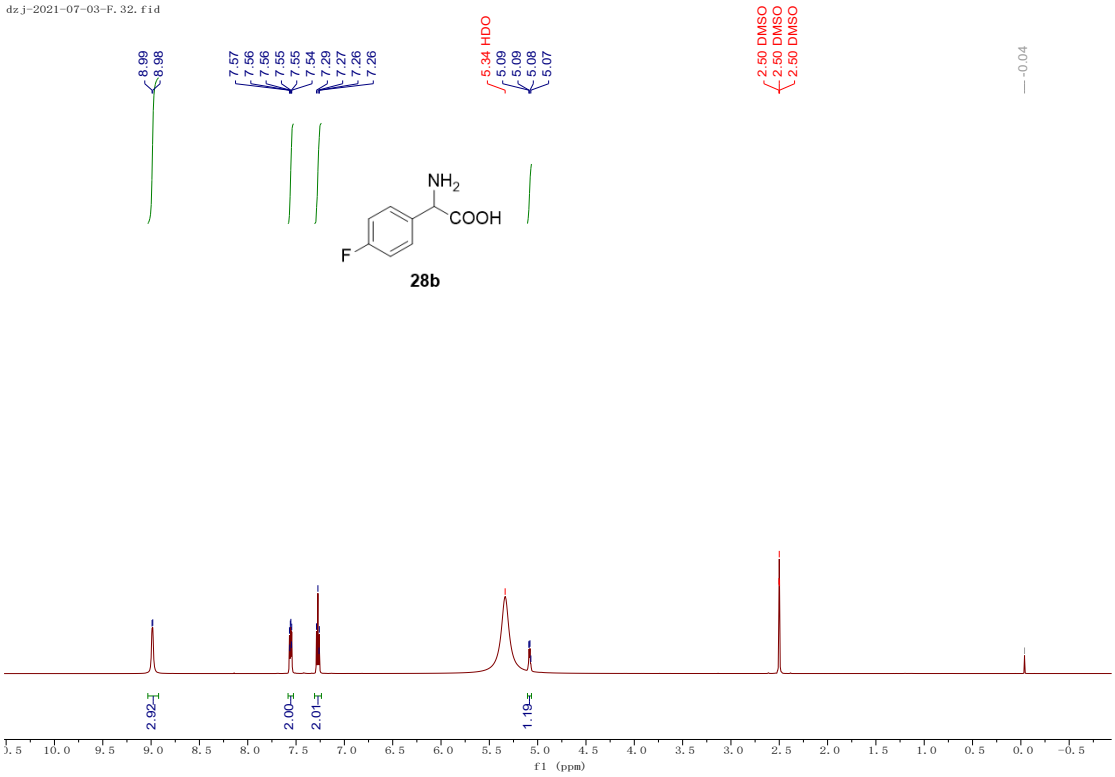
^{13}C NMR spectrum (151 MHz, DMSO-d_6 + HCl) of **2-amino-2-phenylacetic acid** (**26b**)



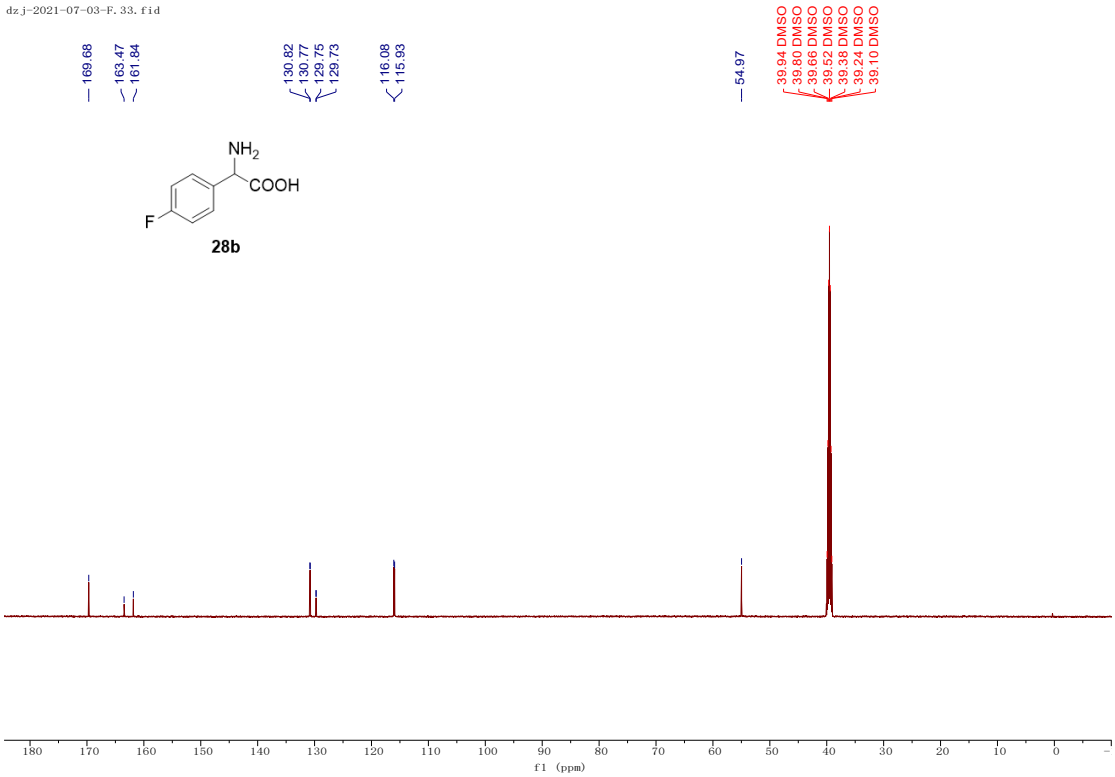
^{1}H NMR spectrum (600 MHz, DMSO-d_6 + HCl) of **2-amino-2-(4-methoxyphenyl)acetic acid (27b)**



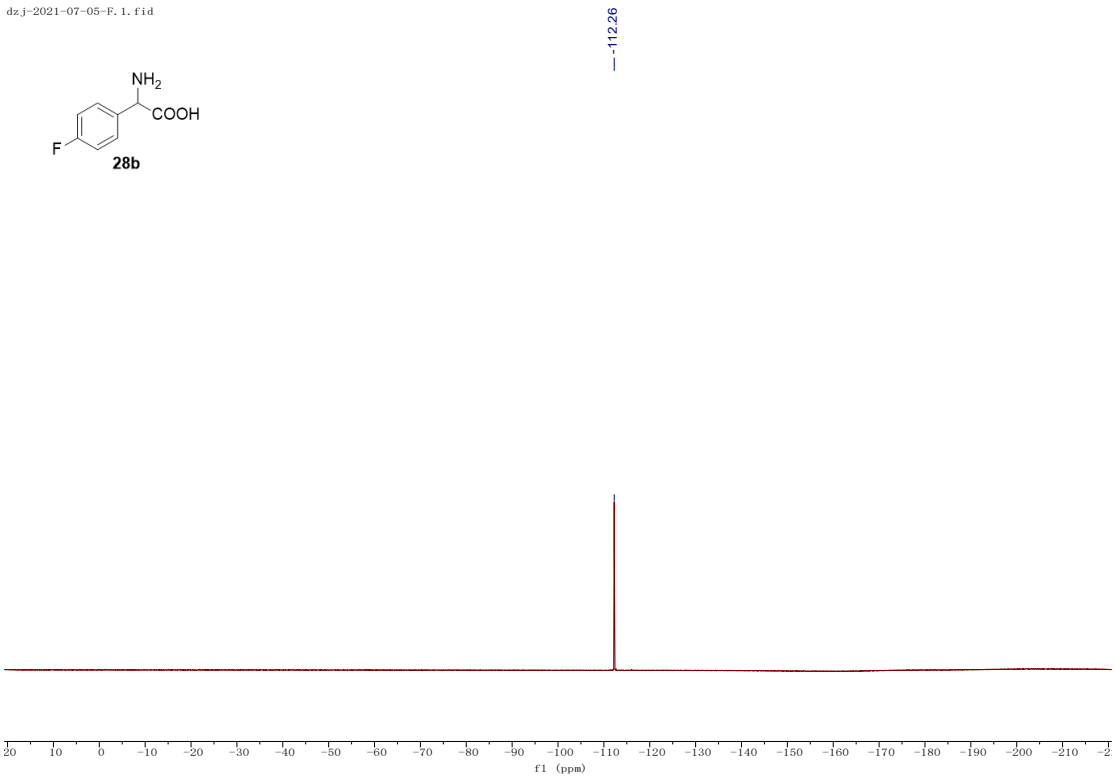
^{13}C NMR spectrum (151 MHz, DMSO-d_6 + HCl) of **2-amino-2-(4-methoxyphenyl)acetic acid (27b)**



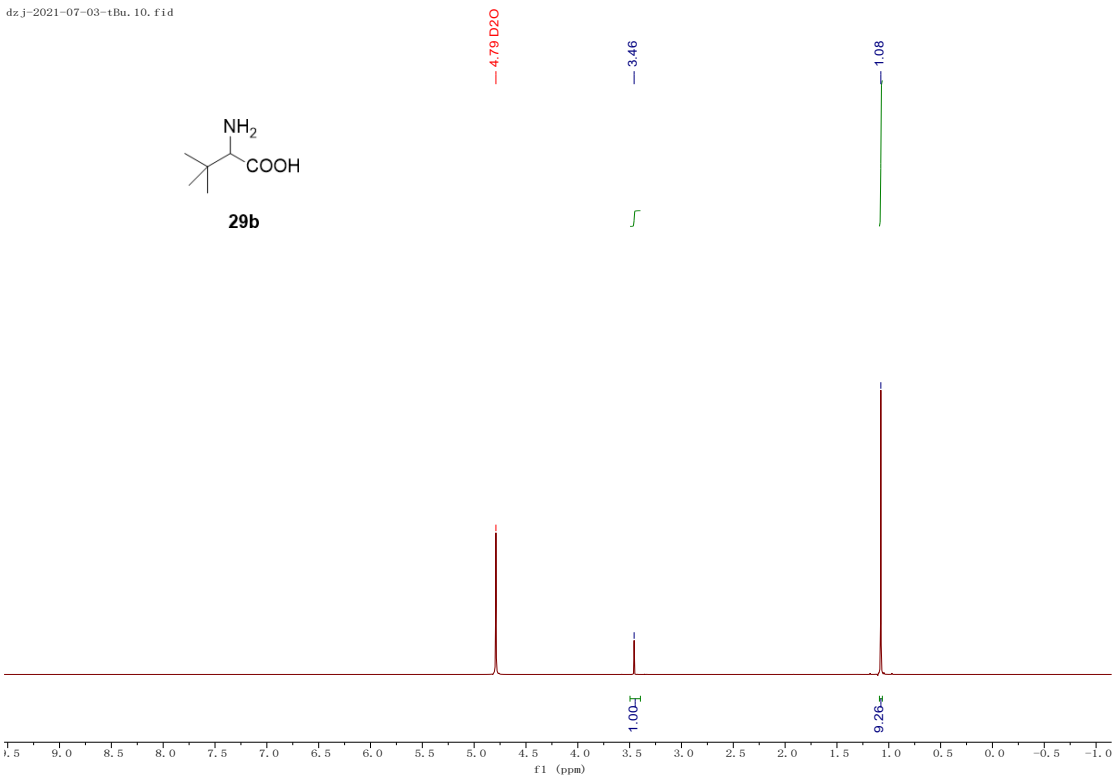
^{1}H NMR spectrum (600 MHz, DMSO-d_6 + HCl) of **2-amino-2-(4-fluorophenyl)acetic acid** (**28b**)



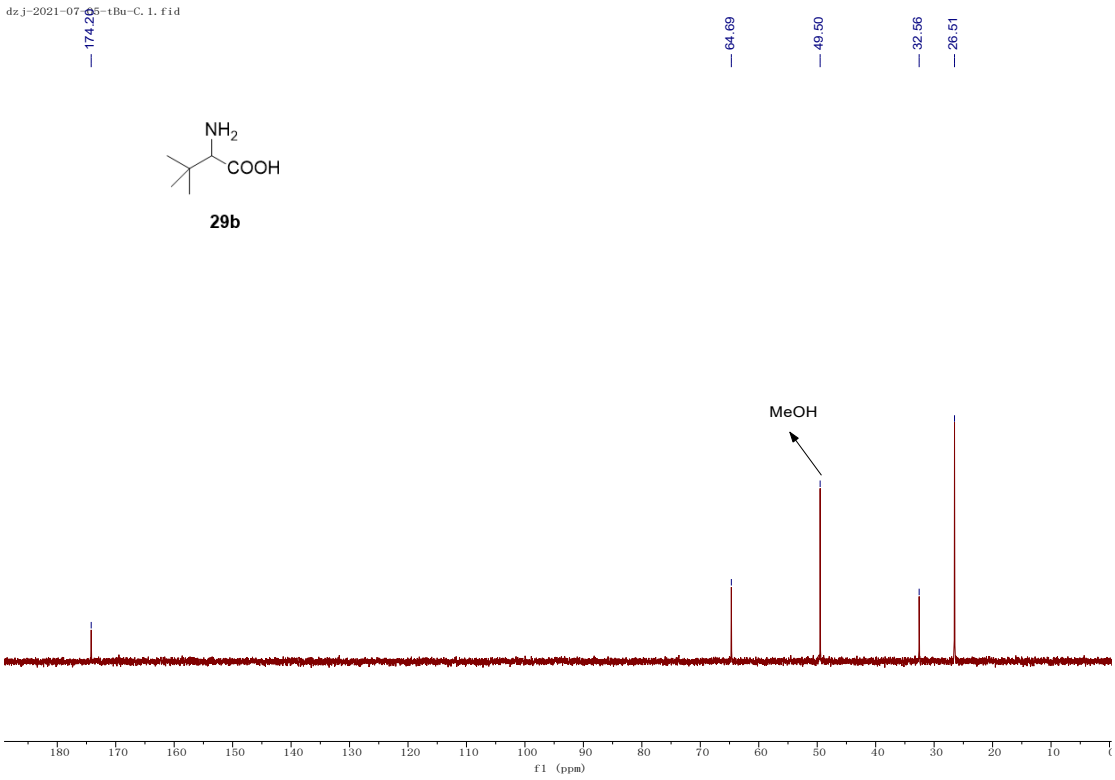
^{13}C NMR spectrum (151 MHz, DMSO-d_6 +HCl) of **2-amino-2-(4-fluorophenyl)acetic acid** (**28b**)



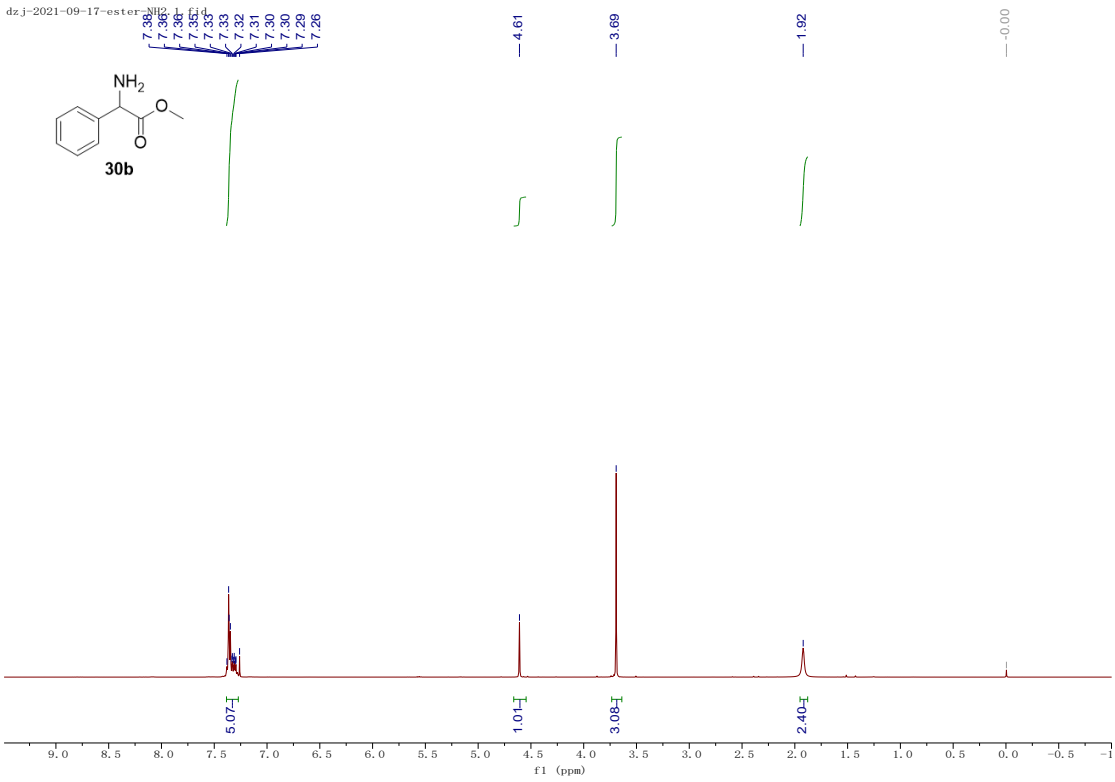
^{19}F NMR spectrum (376 MHz, DMSO-d_6 +HCl) of **2-amino-2-(4-fluorophenyl)acetic acid** (**28b**)



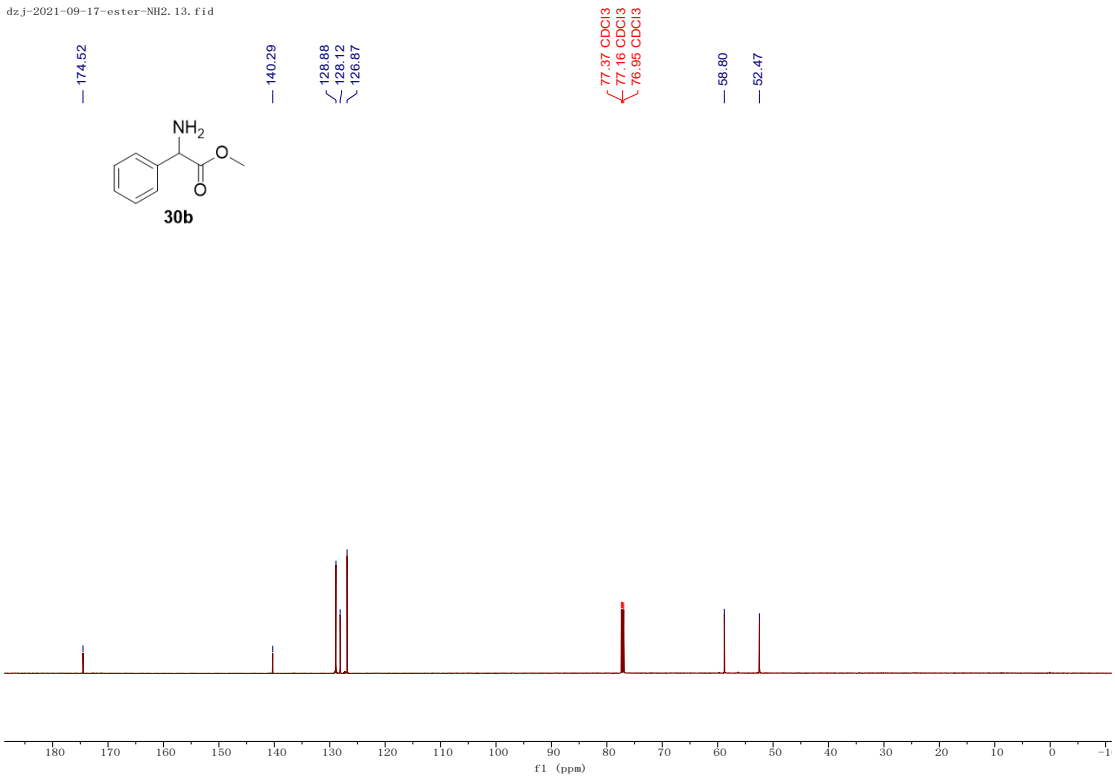
^{1}H NMR spectrum (600 MHz, D_2O) of **2-amino-3,3-dimethylbutanoic acid** (**29b**)



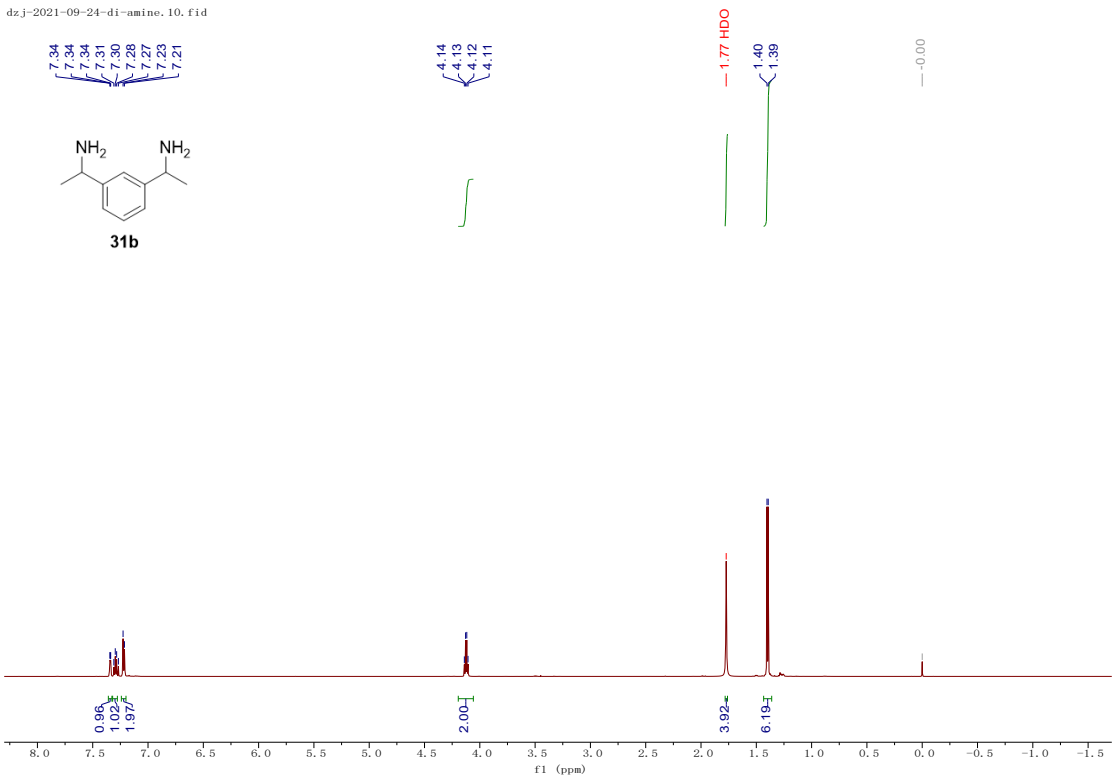
^{13}C NMR spectrum (D_2O + 1 drop of methanol) of **2-amino-3,3-dimethylbutanoic acid** (**29b**)



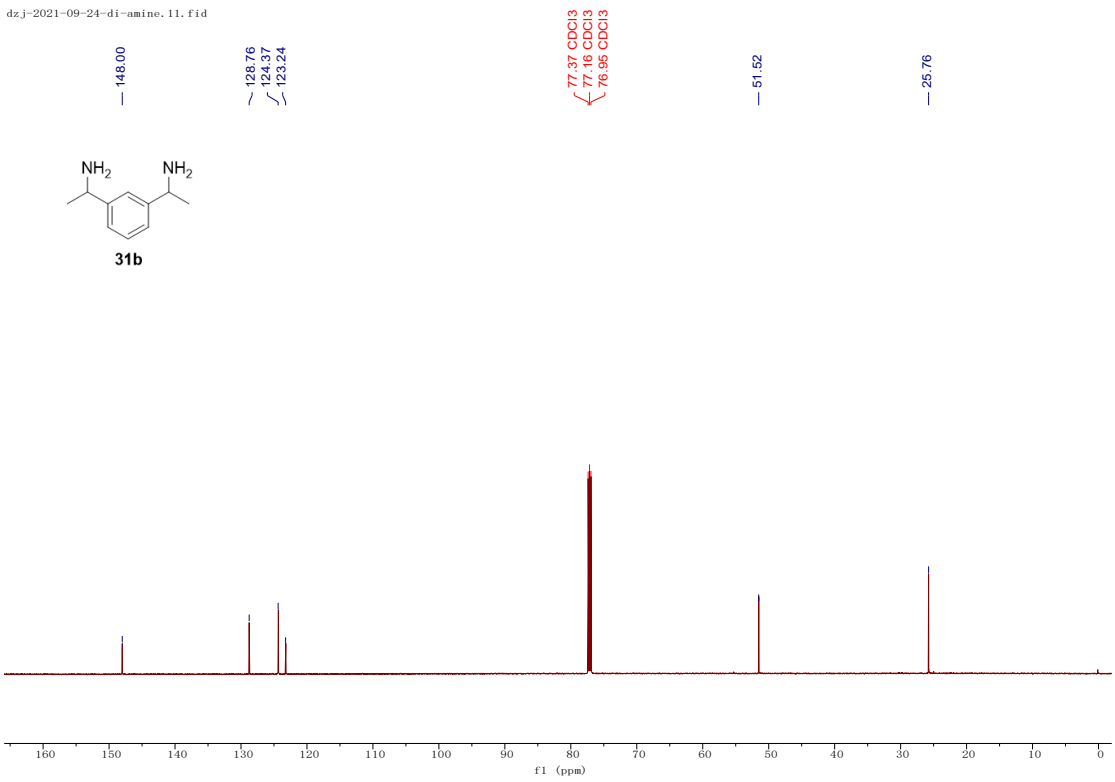
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **Methyl 2-amino-2-phenylacetate** (**30b**)



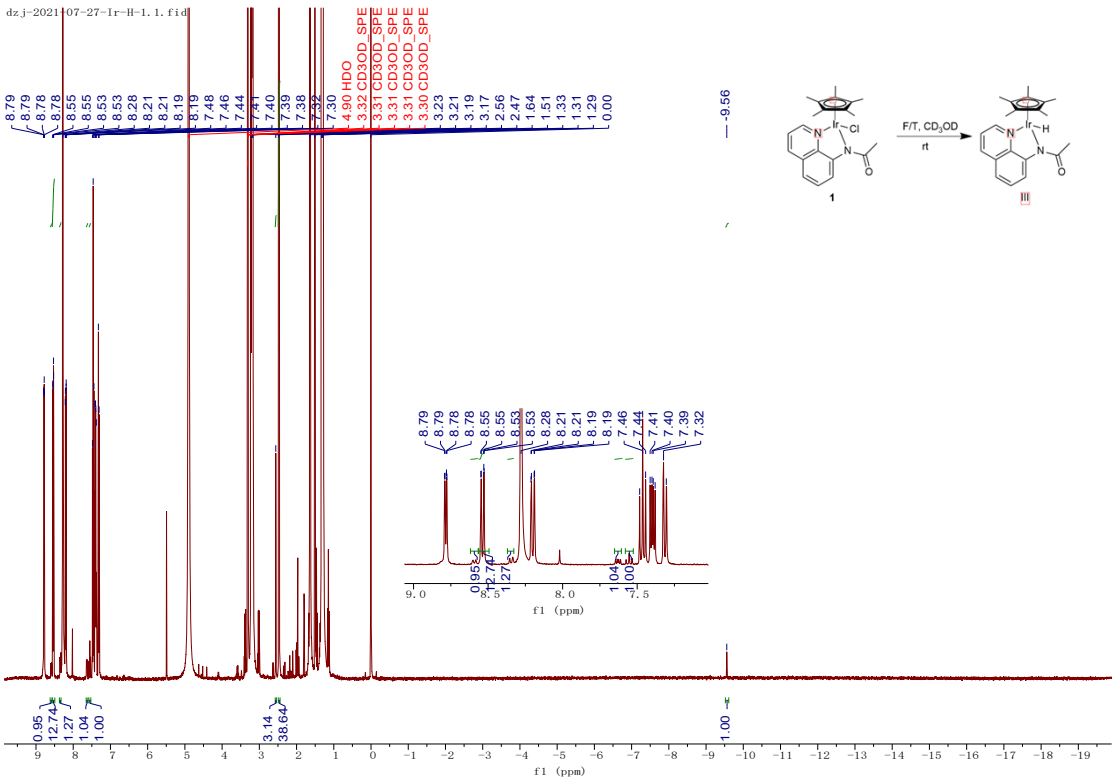
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **Methyl 2-amino-2-phenylacetate** (**30b**)



^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1,1'-(1,3-phenylene)bis(ethan-1-amine)** (**31b**)

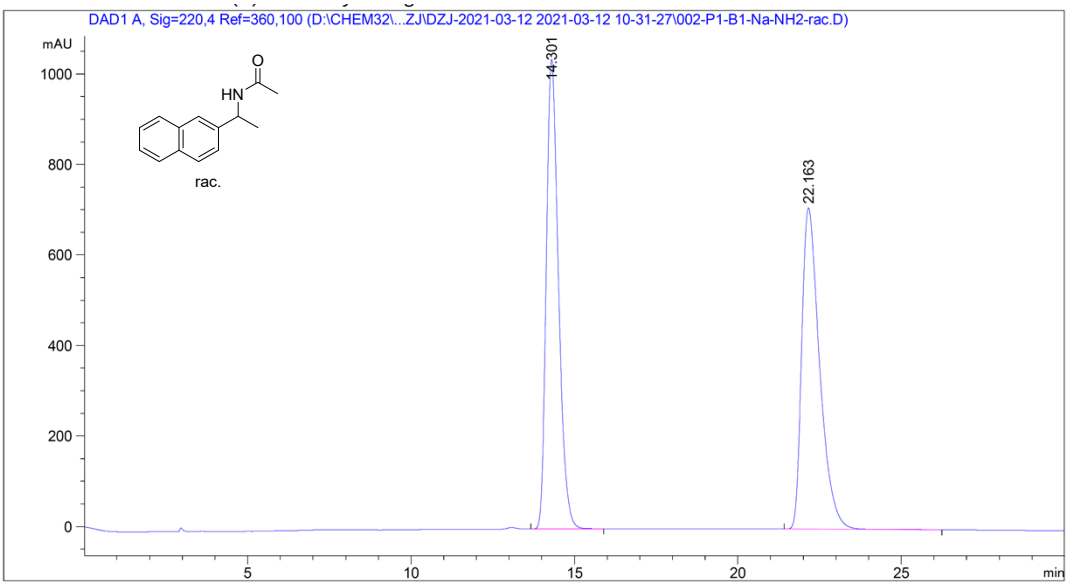


^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **1,1'-(1,3-phenylene)bis(ethan-1-amine)** (**31b**)



^{1}H NMR spectrum (400 MHz, CD_3OD) —detection of active species Cp*Ir(III)-H

4. HPLC spectra

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                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.301 BB    0.3972 2.67957e4  1037.80603  49.8280
   2  22.163 BB    0.5750 2.69807e4   710.56976  50.1720

Totals :                  5.37764e4  1748.37579
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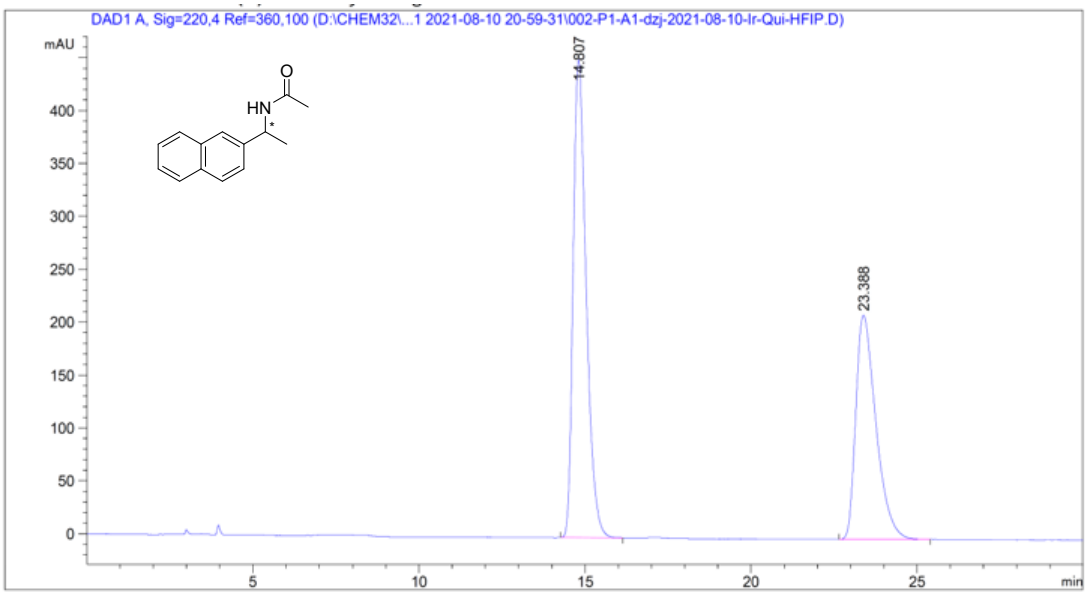


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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.807 BB    0.4150 1.22713e4   451.60181  57.8771
   2  23.388 BB    0.6459 8931.08301  211.81879  42.1229

Totals :                  2.12024e4   663.42059
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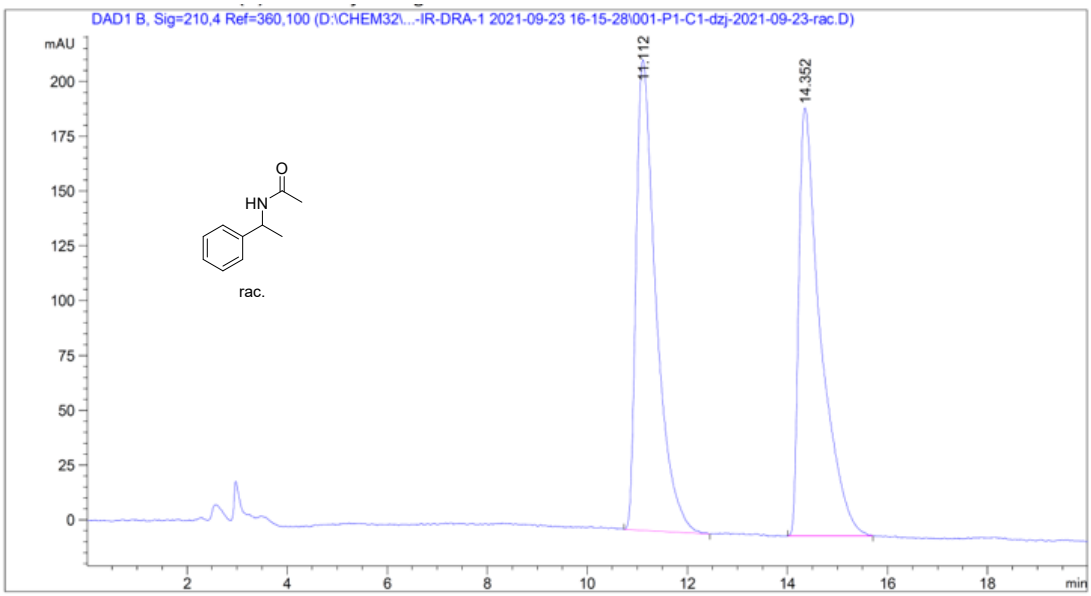


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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.112 BV R  0.4062 5927.40771  214.61528  50.0885
   2  14.352 BV R  0.4209 5906.46875  195.24010  49.9115

Totals :                 1.18339e4   409.85538
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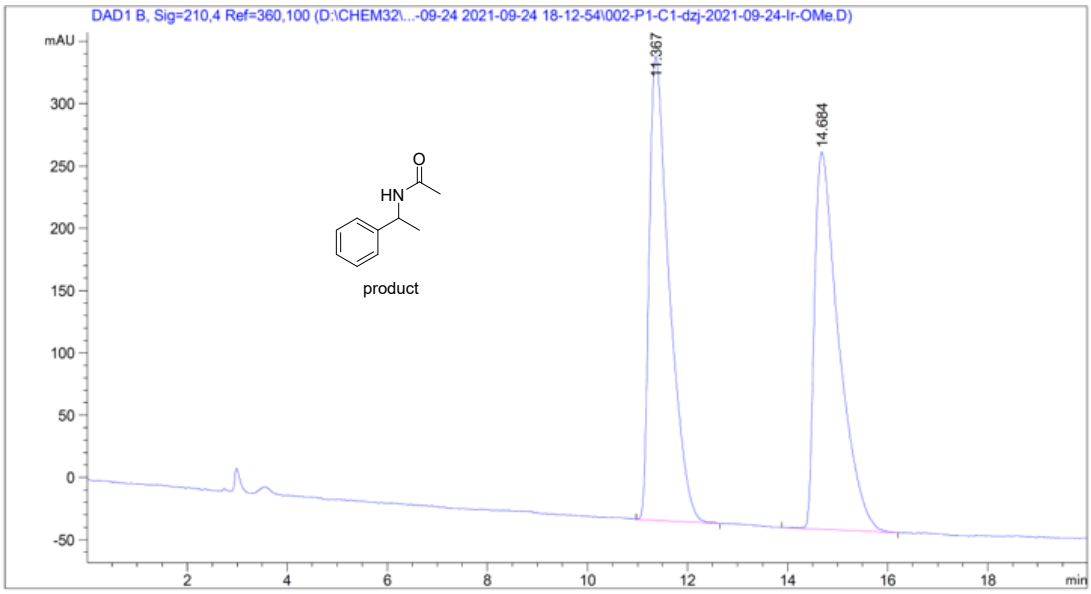


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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.367 BV R  0.4042 1.03435e4   372.24710  50.2702
   2  14.684 VV R  0.4801 1.02323e4   302.91763  49.7298

Totals :                  2.05758e4   675.16473
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5. Crystal date of complex 6 (CCDC 2085717)

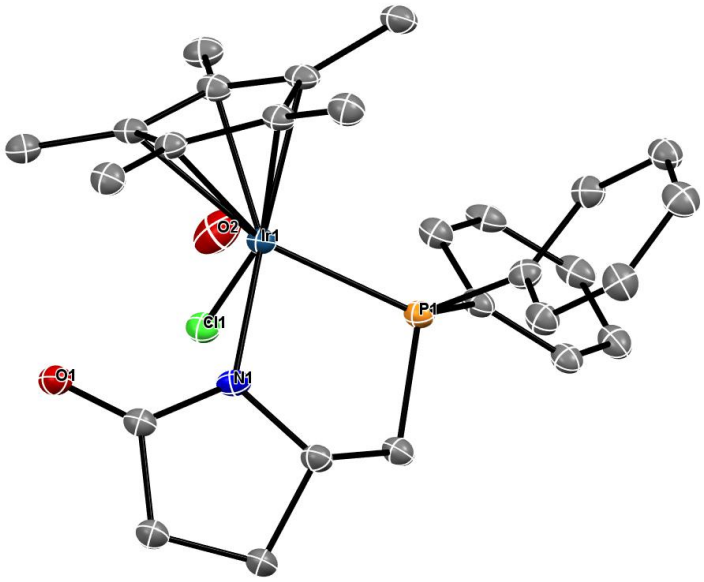

Figure S1. ORTEP plot of complex **6**•0.33H_2O. Ellipsoids are drawn at the 30% probability level. All hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ir1-N1 2.067(5), Ir1-P1 2.2781(15), Ir1-Cl1 2.4258(14); P1-Ir1-Cl1 88.23(5), N1-Ir1-Cl1 83.11(14), N1-Ir1-P1 81.19(15).

Table S1 Crystal data of complex **6**

Formula	$C_{27}H_{32.65}ClIrNO_{1.32}P$
Formula weight	650.96
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	12.8894(7)
b/Å	13.1148(7)
c/Å	14.7203(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2488.3(2)
Z	4
ρ_{calc}g/cm^3	1.738
μ/mm^{-1}	12.144
F(000)	1285.0
Crystal size/mm^3	0.32 × 0.07 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.03 to 136.66
Index ranges	$-15 \le h \le 15$, $-15 \le k \le 15$, $-17 \le l \le 17$
Reflections collected	47540
Independent reflections	4582 [R_{int} = 0.0618, R_{sigma} = 0.0251]
Data/restraints/parameters	4582/0/307
Goodness-of-fit on F^2	1.092
Final R indexes [I>=2σ (I)]	R_1 = 0.0261, wR_2 = 0.0682
Final R indexes [all data]	R_1 = 0.0262, wR_2 = 0.0682
Largest diff. peak/hole / e Å^{-3}	1.79/-0.59
Flack parameter	-0.024(7)