Supporting Information

Transition-Metal-Free Lactonization of sp^2 C–H Bonds with CO_2

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General Considerations

All reactions were set up with glovebox and carried out under a carbon dioxide atmosphere in Schlenk tubes. Reaction temperatures were reported as the temperature of the heat transfer medium surrounding the vessel unless otherwise stated.Anhydrous solvent (including diglyme and DMF, 99.8%, Water< 0.005%) were purchased from J&K Scientific Ltd., and used as received Commercially available chemicals were obtained from J&K Scientific Ltd., Acros Organics, Aldrich Chemical Co., Alfa Aesar, ABCR and TCI and used as received unless otherwise stated. KO^{t}Bu (98%, 100 g) was obtained from J&K Scientific Ltd..

^{1}H and ^{13}C NMR spectra were recorded on a Brüker Advance 400 and 600 spectrometer (^{1}H: 400 MHz, ^{13}C: 101 MHz and 151 MHz). Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are given in ppm relative to TMS, The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm; CD_2Cl_2: δH = 5.32 ppm, δC = 53.84 ppm; CD_3OD: δH = 3.31 ppm, δC = 49.00 ppm; $(CD_3)_2SO$: δH = 2.50 ppm, δC = 39.52 ppm).

GC-MS was obtained using electron ionization (Agilent Technologies 7890B/GC-System and 5977A/MSD). GC-MS was obtained on a Agilent Technologies 7890B/GC-System. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm. Exact ESI mass spectras are recorded on a SHIMADZU LCMS-IT-TOF. ESI-MS are obtained on a Thermo-ITQ. Metal element contents were obtained on a thermo ICP-AES (IRIS Adv.)

Synthesis of Substrates

The substrates in **Table1 and Table 2** were prepared according to procedures described in the literature[S1] reported before.

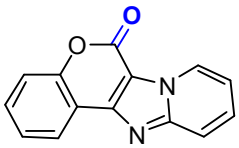
The substrates in **Table 3** were prepared according to procedures described in the literature reported before.[S2]

All the protocols were employed without any optimization of the reaction conditions.

Synthesis and Characterization of Products

An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the substrate (0.2 mmol). The Schlenk tube was then introduced in a glovebox where it was charged with KO^{t}Bu (101 mg, 0.9 mmol, 4.5 eq.). The tube was taken out of the glovebox and connected to a vacuum line where it was evacuated and back-filled under CO_2 flow for at least 3 times. The diglyme (2 mL) were added under CO_2 flow. Once added, the tube was closed at atmospheric pressure of CO_2 (1 atm) and stirred for 24 hours at 140 °C. Then, the mixture was cooled to room temperature, quenched with 2 mL water and 2 mL AcOEt, then concentrated in vacuo. The residue was purified by silica gel flash chromatography (petroleum ether/AcOEt 2/1) to give the pure desired product.

6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2a) [S3]



42.5 mg, 0.180 mmol, 90 %;

Whitesolid;

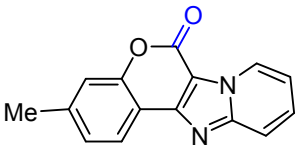
R$_f$(PE/EA 1/1): 0.18;

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (d, *J* = 6.7 Hz, 1H), 8.32 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.89 (d, *J* = 9.1 Hz, 1H), 7.72 – 7.41 (m, 4H), 7.20 (t, *J* = 6.8 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$):δ 154.82, 153.24, 150.43, 149.91,130.88, 130.72, 128.09, 124.77, 123.49, 117.50, 117.48, 116.69, 114.66,109.70;

Exact Mass ESI-MS: calculated m/z for $[C_{14}H_9N_2O_2H]^+$: 237.0659, found: 237.0655.

3-methyl-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2b)



43.0 mg, 0.172 mmol, yield 86%;

White solid;

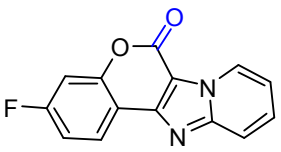
R$_f$ (PE/EA 3/1): 0.12 ;

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, J = 6.7 Hz, 1H), 8.16 (d, J = 7.9 Hz, 1H), 7.86 (d, J = 9.1 Hz, 1H), 7.68 – 7.59 (m, 1H), 7.30 (s, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.17 (t, J = 6.8 Hz, 1H), 2.50 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$)δ 154.99 , 153.36 , 150.44 , 150.15 , 141.89 , 130.60 , 128.08 , 125.96 , 123.16 , 117.66 , 117.36 , 114.49 , 114.06 , 109.33, 21.79;

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{10}N_2O_2H]^+$: 251.0815, found: 251.0811.

3-fluoro-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2c)



38.0 mg, 0.15 mmol, yield 75%;

White solid;

R$_f$ (PE/EA 3/1): 0.15 ;

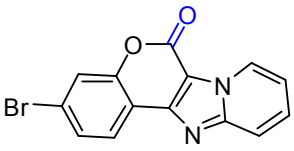
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, J = 6.7 Hz, 1H), 8.30 (dd, J = 8.7, 6.1 Hz, 1H), 7.88 (d, J = 9.1 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.26 – 7.15 (m, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.20, 161.69, 153.49, 149.52, 148.60, 129.94, 127.08,123.98 (d, *J* = 9.5 Hz), 116.46, 113.79, 112.31, 111.97, 111.75, 104.12(d, *J* = 25.8 Hz)

^{19}F NMR (376 MHz, $CDCl_3$) δ -106.95;

Exact Mass ESI-MS: calculated m/z for $[C_{14}H_7FN_2O_2Na]^+$: 277.0384, found: 277.0384.

3-bromo-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2d)



48.3 mg, 0.154 mmol, yield 77%;

White solid;

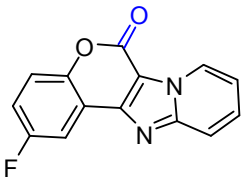
R$_f$ (PE/EA 3/1): 0.10;

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (dt, J = 6.7, 1.2 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.88 (dt, J = 9.1, 1.1 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.56 (dd, J = 8.3, 1.8 Hz, 1H), 7.22 (td, J = 6.8, 1.2 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.13, 153.34, 150.53, 149.33, 130.99, 128.16, 128.08, 124.54, 124.49, 120.74, 117.58, 115.73, 114.91, 109.56;

Exact Mass ESI-MS: calculated m/z for $[C_{14}H_7BrN_2O_2H]^+$: 314.9764, found: 314.9764.

2-fluoro-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2e)



33.9 mg, 0.133 mmol, yield 67%;

White solid;

R$_f$(PE/EA 3/1): 0.22;

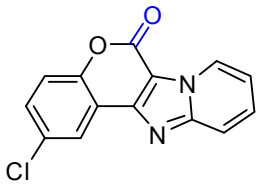
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (d, J = 6.8 Hz, 1H), 7.97 (dd, J = 8.0, 3.2 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.68 (dd, J = 8.0, 7.0, 1H), 7.49 (dd, J = 9.1, 4.3 Hz, 1H), 7.33 – 7.25 (m, 1H), 7.22 (dd, J =7.2, 6.8 Hz, 1H);

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.47;

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.28 (d, *J* = 244.7 Hz), 154.49 , 150.46 , 149.35 (d, *J* = 2.1 Hz), 149.22 (d, *J* = 2.8 Hz), 130.94, 128.12, 119.14 (d, *J* = 8.6 Hz), 118.25 (d, *J* = 24.6 Hz), 117.87 (d, *J* = 9.4 Hz), 117.67, 114.94 , 109.93, 109.33 (d, *J* = 25.0 Hz);

Exact Mass ESI-MS: calculated m/z for $[C_{14}H_7FN_2O_2Na]^+$: 277.0384, found: 277.0384.

2-chloro-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2f)



43.6 mg, 0.162mmol, yield 81%;

White solid;

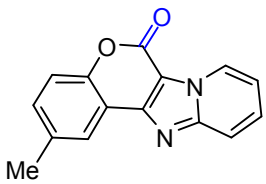
R$_f$(PE/EA 3/1): 0.32;

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (d, J = 6.8 Hz, 1H), 8.29 (d, J = 2.5 Hz, 1H), 7.88 (s, 1H), 7.73 – 7.64 (m, 1H), 7.52 (dd, J = 8.9, 2.5 Hz, 1H), 7.45 (d, J = 8.8 Hz, 1H), 7.23 (t, J = 6.9 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.29, 151.57, 150.51, 148.87, 130.96, 130.82, 130.37, 128.09, 123.15, 118.91, 117.97, 117.69, 114.95, 109.90;

Exact Mass ESI-MS: calculated m/z for $[C_{14}H_7ClN_2O_2H]^+$: 271.0269, found: 271.0262.

2-methyl-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2g)



46.5 mg, 0.186mmol, yield 93%;

White solid;

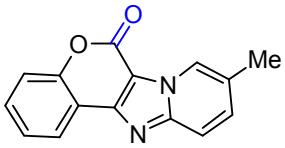
R_f(PE/EA 3/1): 0.22;

^{1}H NMR (400 MHz, $CDCl_3$)δ 9.20 (d, J = 6.7 Hz, 1H), 8.08 (s, 1H), 7.86 (d, J = 9.0 Hz, 1H), 7.69 – 7.60 (dd, 1H), 7.37 (m, 2H), 7.18 (dd, J = 6.8 Hz, 1H), 2.49 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.99, 151.38, 150.39, 149.95, 134.58, 131.83, 130.60, 128.09, 123.30, 117.43, 117.19, 116.28, 114.54, 109.74, 20.90;

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{10}N_2O_2H]^+$: 251.0815, found: 251.0812.

9-methyl-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2h)[S3]



43.2mg, 0.172mmol, yield 86%;

White solid;

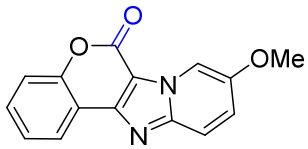
R_f(PE/EA 3/1): 0.39;

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (dt, *J* = 1.9, 1.0 Hz, 1H), 8.30 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.79 (d, *J* = 9.2 Hz, 1H), 7.63 – 7.36 (m, 4H), 2.49 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.95, 153.19 , 149.73, 149.45, 133.70, 130.70, 126.06, 124.94, 124.73, 123.42, 117.49, 116.88, 116.73, 109.46, 18.22;

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{10}N_2O_2H]^+$: 251.0815, found: 251.0811.

9-methoxy-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2i)



49.5mg, 0.186mmol, 93%;

White solid;

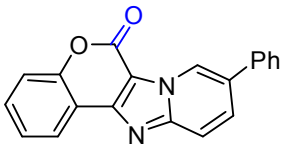
R_f(PE/EA 3/1): 0.23;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, J = 2.4 Hz, 1H), 8.27 (d, J = 7.8 Hz, 1H), 7.76 (d, J = 9.7 Hz, 1H), 7.61 – 7.47 (m, 2H), 7.47 – 7.35 (m, 2H), 3.97 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.01, 151.99, 149.67, 148.40, 146.13, 129.49, 124.43, 123.72, 122.19, 116.45, 115.94, 109.45, 108.76, 55.55;

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{10}N_2O_3Na]^+$: 289.0584, found: 289.0580.

9-phenyl-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2j)



47.4 mg, 0.152 mmol, yield 76%;

White solid;

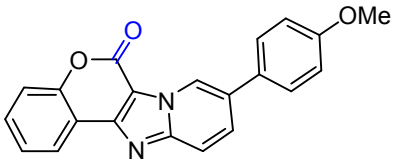
R$_f$(PE/EA 3/1): 0.32;

^{1}H NMR (400 MHz, $CDCl_3$)δ 9.36 (s, 1H), 8.29 (d, J = 7.8 Hz, 1H), 7.94 – 7.86 (m, 2H), 7.68 – 7.62 (m, 2H), 7.60 – 7.40 (m, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.82, 153.26, 150.19, 149.62, 135.93, 131.11, 130.87, 129.31, 129.30, 128.61, 127.16, 125.18, 124.78, 123.49, 117.51, 117.22, 116.76;

Exact Mass ESI-MS: calculated m/z for $[C_{20}H_{12}N_2O_2H]^+$: 313.0972, found: 313.0970.

9-(4-methoxyphenyl)-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2k)



54.7 mg, 0.160 mmol, yield 80%;

White solid;

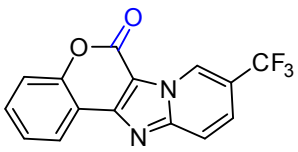
R$_f$(PE/EA 3/1): 0.23;

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.28 (d, J = 7.8 Hz, 1H), 7.90 – 7.83 (m, 2H), 7.59 – 7.54 (m, 3H), 7.49 (d, J = 8.3 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.02 (d, J = 8.2 Hz, 2H), 3.87 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.08, 154.84, 153.24, 150.04, 149.43, 131.01, 130.79, 128.99, 128.26, 128.23, 124.74, 124.47, 123.45, 117.49, 117.09, 116.80, 114.73, 109.86, 55.42;

Exact Mass ESI-MS: calculated m/z for $[C_{21}H_{14}N_2O_3Na]^+$: 365.0897, found: 365.0895.

9-(trifluoromethyl)-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2l) [S3]



34.1 mg, 0.112 mmol, yield 56 %;

White solid;

R$_f$(PE/EA 3/1): 0.33;

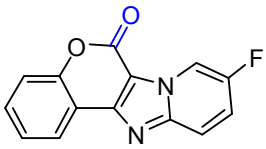
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.30 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.98 (d, *J* = 9.5 Hz, 1H), 7.80 (dd, *J* = 9.5, 1.8 Hz, 1H), 7.68 – 7.39 (m, 3H);

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.88;

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.52, 153.37, 151.19, 150.22, 131.58, 126.87 (q, *J* = 5.3 Hz), 126.62 (q, *J* = 2.5 Hz), 125.11, 123.71, 122.94 (q, *J* = 270.2 Hz), 119.08 (q, *J* = 34.8 Hz), 118.16, 117.67, 116.23, 110.48;

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_7F3N_2O_2H]^+$: 305.0532, found: 305.0530.

9-fluoro-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one(2m) [S3]



34.6 mg, 0.136 mmol, yield 68%;

White solid;

R$_f$(PE/EA 3/1): 0.21;

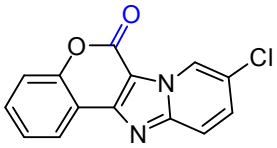
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (t, J = 2.7 Hz, 1H), 8.27 (dd, J = 7.8 Hz, 1.6 Hz, 1H), 7.85 (dd, J = 9.8, 4.7 Hz, 1H), 7.58 (m, 2H), 7.50 (m, 1H), 7.44 (m, 1H);

^{19}F NMR (376 MHz, $CDCl_3$) δ -135.32;

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.15, 154.68, 153.19, 152.75, 150.46, 147.91, 131.04, 124.92, 123.42, 122.44, 122.19, 117.92, 117.83, 117.60, 116.61, 115.62, 115.20, 110.78;

Exact Mass ESI-MS: calculated m/z for $[C_{14}H_7FN_2O_2Na]^+$: 277.0384, found: 277.0384.

9-chloro-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2n) [S3]



36.7 mg, 0.136mmol, yield 68%;

White solid;

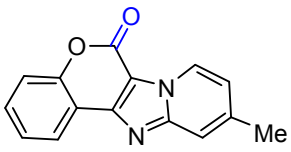
R$_f$(PE/EA 3/1): 0.2 ;

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (d, J = 2.1 Hz, 1H), 8.27 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 9.5 Hz, 1H), 7.65 – 7.54 (m, 2H), 7.50 (d, J = 8.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.61, 153.22, 150.21, 148.70, 131.99, 131.16, 126.03, 124.95, 123.53, 122.98, 117.72, 117.60, 116.47, 109.94;

Exact Mass ESI-MS: calculated m/z for $[C_{14}H_7ClN_2O_2H]^+$: 271.0269, found: 271.0272.

10-methyl-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2o) [S3]



45.0mg, 0.180mmol, yield 90%;

White solid;

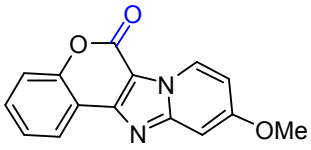
R$_f$(PE/EA 3/1): 0.29;

^{1}H NMR(400 MHz, $CDCl_3$) δ 9.06 (d, *J* = 6.9 Hz, 1H), 8.29 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.67 – 7.37 (m, 4H), 7.02 (dd, J = 6.9, 1.5 Hz, 1H), 2.56 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.8, 153.3, 150.9, 150.2, 142.6, 130.7, 127.1, 124.7, 123.5, 117.5, 117.2, 116.9, 116.2, 109.4, 21.9;

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{10}N_2O_2H]^+$: 251.0815, found:251.0812.

10-methoxy-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2p) [S3]



48.9 mg, 0.184mmol, yield 92%;

White solid;

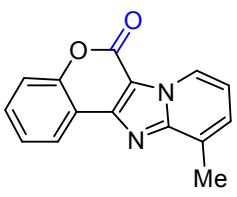
R$_f$(PE/EA 3/1): 0.15;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, *J* = 7.7 Hz, 1H), 8.25 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.60 – 7.38 (m, 3H), 7.12 (d, *J* = 2.3 Hz, 1H), 6.84 (dd, *J* = 7.4, 2.5 Hz, 1H), 3.97 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 154.7, 153.3, 152.8, 150.6, 130.6, 128.3, 124.6, 123.3, 117.5, 116.8, 109.0, 95.5, 56.0;

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{10}N_2O_3H]^+$: 267.0764, found:267.0763.

11-methyl-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2q)



48.0mg, 0.192mmol, yield 96%;

White solid;

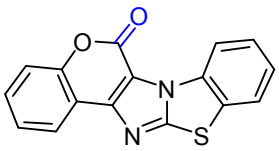
R_f (PE/EA 3/1): 0.44;

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, *J* = 6.7 Hz, 1H), 8.35 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.60 – 7.47 (m, 2H), 7.45 – 7.39 (m, 2H), 7.08 (t, *J* = 6.9 Hz, 1H), 2.77 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.03, 153.21, 150.81, 149.46, 130.65, 129.48, 127.81, 125.74, 124.58, 123.66, 117.44, 116.97, 114.59, 110.09, 17.16;

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{10}N_2O_2Na]^+$: 273.0634, found: 273.0634.

6H-benzo[d]chromeno[4',3':4,5]imidazo[2,1-b]thiazol-6-one (2r)



31.0 mg, 0.106mmol, yield 53%;

White solid;

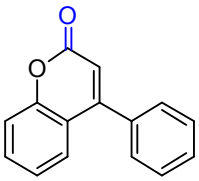
R_f (PE/EA 10/1): 0.21;

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (d, J = 8.3 Hz, 1H), 8.20 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.64 – 7.39 (m, 5H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.43, 153.77, 152.75, 152.67, 132.67, 130.31, 129.30, 127.28, 125.98, 124.78, 123.74, 122.96, 117.50, 117.21, 116.54, 114.12;

Exact Mass ESI-MS: calculated m/z for $[C_{16}H_8N_2O_2SH]^+$: 293.0379, found: 293.0376.

4-phenyl-2H-chromen-2-one (2s) [S2]



16.9 mg, 0.076 mmol, yield 38%;

White solid;

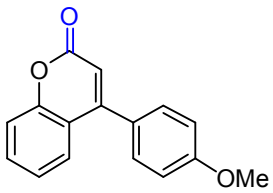
R_f (PE/EA 40/1): 0.15;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.37 (m, 8H), 7.29 – 7.19 (m, 1H), 6.38 (s, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.77, 155.68, 154.19, 135.20, 131.94, 129.70, 128.88, 128.45, 127.02, 124.18, 119.00, 117.34, 115.19;

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{10}O_2Na]^+$: 245.0573, found: 245.0564.

4-(4-methoxyphenyl)-2H-chromen-2-one (2t) [S2]



19.7 mg, 0.078mmol, yield 39%;

White solid;

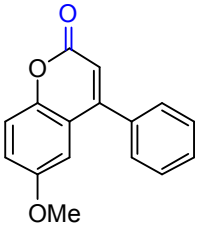
R$_f$(PE/EA 10/1): 0.21;

^{1}H NMR(400 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 2H), 7.39 – 7.29 (m, 3H), 7.16 (d, J = 7.5 Hz, 1H), 6.98 (d, J = 8.7 Hz, 2H), 6.29 (s, 1H), 3.82 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.96, 160.83, 155.35, 154.24, 131.82, 129.97, 127.46, 127.03, 124.09, 119.15, 117.37, 114.64, 114.34, 55.47;

Exact Mass ESI-MS: calculated m/z for $[C_{16}H_{12}O_3Na]^+$: 275.0679, found: 275.0671.

6-methoxy-4-phenyl-2H-chromen-2-one (2u) [S2]



25.2 mg, 0.100mmol, yield 50%;

White solid;

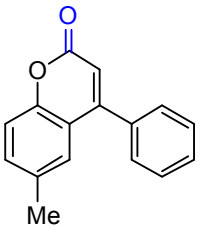
R$_f$(PE/EA 10/1): 0.19;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 3H), 7.50 – 7.42 (m, 2H), 7.35 (d, J = 9.0 Hz, 1H), 7.13 (dd, J = 9.0, 3.0 Hz, 1H), 6.93 (d, J = 2.9 Hz, 1H), 6.38 (s, 1H), 3.75 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.96, 155.87, 155.35, 148.57, 135.27, 129.71, 128.93, 128.33, 119.44, 118.99, 118.23, 115.63, 109.98, 55.79;

Exact Mass ESI-MS: calculated m/z for $[C_{16}H_{12}O_3Na]^+$: 275.0679, found: 275.0673.

6-methyl-4-phenyl-2H-chromen-2-one (2v)[S2]



33.5 mg, 0.142mmol, yield 71%;

White solid;

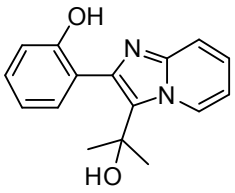
R$_f$(PE/EA 40/1): 0.13;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 3H), 7.45 (m, 2H), 7.36 (m, 1H), 7.30 (m, 1H), 7.25 (s, 1H), 6.35 (s, 1H), 2.34 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.63, 152.33, 135.39, 133.88, 132.92, 129.60, 128.86, 128.42, 126.71, 118.69, 117.06, 115.18, 20.94;

ESI-MS: calculated m/z for $[C_{16}H_{12}O_2H]^+$: 237.09, found: 237.09.

2-(3-(2-hydroxypropan-2-yl)imidazo[1,2-a]pyridin-2-yl)phenol (3)



44.5 mg, 0.166 mmol, yield 83%;

White solid;

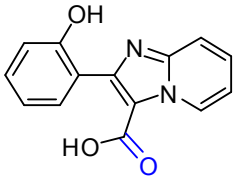
$\mathbf{R}_f$(PE/EA 1/1): 0.23;

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.33 (s, 1H), 8.93 (d, J = 7.1 Hz, 1H), 7.48 (d, J = 9.0 Hz, 1H), 7.30 – 7.10 (m, 3H), 6.97 – 6.77 (m, 3H), 5.34 (s, 1H), 1.42 (s, 6H);

^{13}C NMR (101 MHz, DMSO-d_6) δ 155.89, 143.89, 138.45, 132.01, 129.43, 128.32, 127.20, 125.19, 123.85, 118.78, 117.03, 115.59, 111.33, 69.12, 29.34;

Exact Mass ESI-MS: calculated m/z for $[C_{16}H_{16}N_2O_2H]^+$: 269.1285,found: 269.1273.

2-(2-hydroxyphenyl)imidazo[1,2-a]pyridine-3-carboxylic acid (4)



40.1 mg, 0.158 mmol, yield 79%;

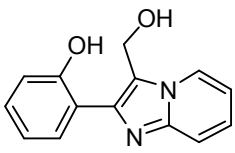
White solid;

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.35 (d, J = 7.0 Hz, 1H), 7.78 .(d, J = 8.9 Hz, 1H), 7.64 – 7.52 (m, 1H), 7.47 (dd, J = 7.6, 1.7 Hz, 1H), 7.34 – 7.16 (m, 2H), 6.95 – 6.79 (m, 2H);

^{13}C NMR (101 MHz, DMSO-d_6) δ 162.53 , 156.24 , 149.25 , 145.93 , 131.51 , 130.27 , 128.63 , 128.35 , 121.61 , 118.77 , 117.01 , 116.31 , 114.84 , 114.02 ;

Exact Mass ESI-MS: calculated m/z for $[C_{14}H_{10}N_2O_3H]^+$: 255.0764, found: 255.0770.

2-(3-(hydroxymethyl)imidazo[1,2-a]pyridin-2-yl)phenol（5）



41.3 mg, 0.172 mmol, yield 86%;

White solid;

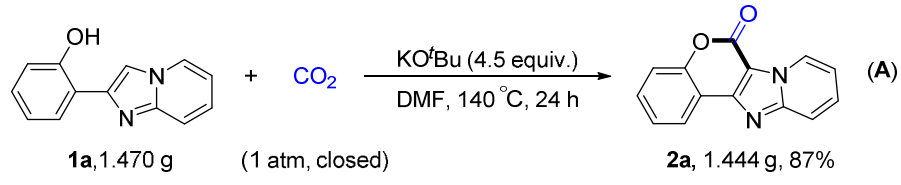
$\mathbf{R}_f$(PE/EA 1/1): 0.2;

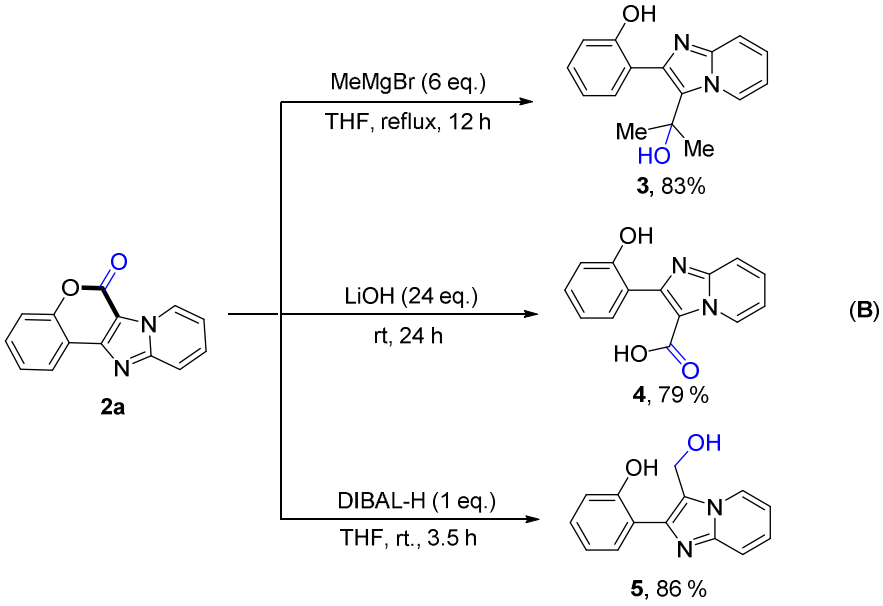
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 6.8 Hz, 1H), 7.50 (d, J = 9.4 Hz, 2H), 7.30 – 7.23 (m, 1H), 7.16 (t, J = 7.7 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 6.89 (t, J = 6.8 Hz, 1H), 6.84 (t, J = 7.5 Hz, 1H), 5.11 (s, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.99 , 143.26 , 142.31 , 129.73 , 127.55 , 125.91 , 124.08 , 119.24 , 118.43 , 117.40 , 116.90 , 116.62 , 113.14 , 54.37;

Exact Mass ESI-MS: calculated m/z for $[C_{21}H_{14}N_2O_3Na]^+$: 365.0897, found: 365.0895.

The Application of the Reaction





Synthesis of 3[S4]

The lactone **2a** (47.2 mg, 0.2 mmol) was dissolved in 15 mL THF. A solution of methyl magnesium bromide reagent (3M in diethy ether, 0.4 mL, 1.2 mmol) in 10 mL THF was added to the reaction dropwise. Then the combined solution was refluxed and the reaction was monitored by TLC. Workup entailed an extraction with brine and methylene chloride. The organic layer was dried with anhydrous magnesium sulfate. The solution was concentrated and furtherpurified by flash chromatography on silica gel, producing the 2-(3-(2-hydroxypropan-2-yl)imidazo[1,2-a]pyridin-2-yl)phenol (**3**) as a white solid(44.5 mg, 83%).

Synthesis of 4[S5]

To a 50 mL flask were added the lactone **2a** (47.2 mg, 0.20 mmol) and LiOH (115.2 mg, 4.8 mmol, 24 equiv). Then the mixture was added MeOH (16 mL), THF (8 mL), and H_2O (4 mL). The reaction mixture was then stirred for 24 h at room temperature, and the course of the reaction was followed by TLC until completion. The MeOH and

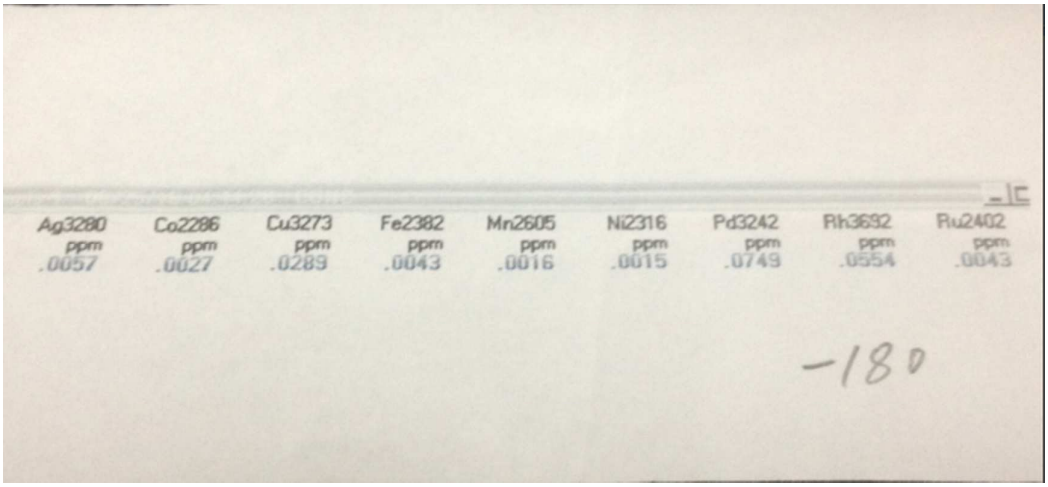
THF were then removed in vacuo, and the resulting residue was diluted with ice water (15 mL), and EtOAc (20 mL). After acidification with 2 M HCl (pH 4−5), the solution was extracted with EtOAc three times. The combined organic extract was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The crude product was washed with EtOAc furnishing the final hydroxyacids **4** as a white solid (40.1 mg, 79 % yield).

Synthesis of 5[S6]

The lactone **2a** (47.2 mg, 0.2 mmol) was dissolved in DCM (6 mL) and cooled in a round bottom flask to −78 ℃ in a dry ice/acetone bath. Diisobutylaluminiumhydride (DIBAL-H) (1.0 M in toluene 0.2 mL, 0.2 mmol) was added to the reaction dropwise. The reaction was monitored by TLC. Work up entailed an extraction with brine and methylene chloride. The organic layer was dried with anhydrous magnesium sulfate. The solution was concentrated and further purified by flash chromatography on silica gel, producing the 2-(3-(hydroxymethyl)imidazo[1,2-a]pyridin-2-yl)phenol **5** as a white solid (41.3 mg, 86%).

Determination of Metal Element Contents.

Element	Ag3280	Co2286	Cu3273	Fe2382	Mn2605
Units	ppm	ppm	ppm	ppm	ppm
Avg	0.0057	0.0027	0.0289	0.0043	0.0016
Element	Ni2316	Pd3242	Rh3692	Ru2402	
Units	ppm	ppm	ppm	ppm	
Avg	0.0015	0.0749	0.0554	0.0043	



References

[S1] Mutai, T.; Sawatani, H.; Shida, T.; Shono, H.; Araki, K. *J. Org. Chem.* **2013**, *78*, 2482.

[S2] Sasano,K.; Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2013**, *135*, 10954.

[S3] Zhang, J.; Zhang, X.; Fan, X. *J. Org. Chem.* **2016**, 81, 3206.

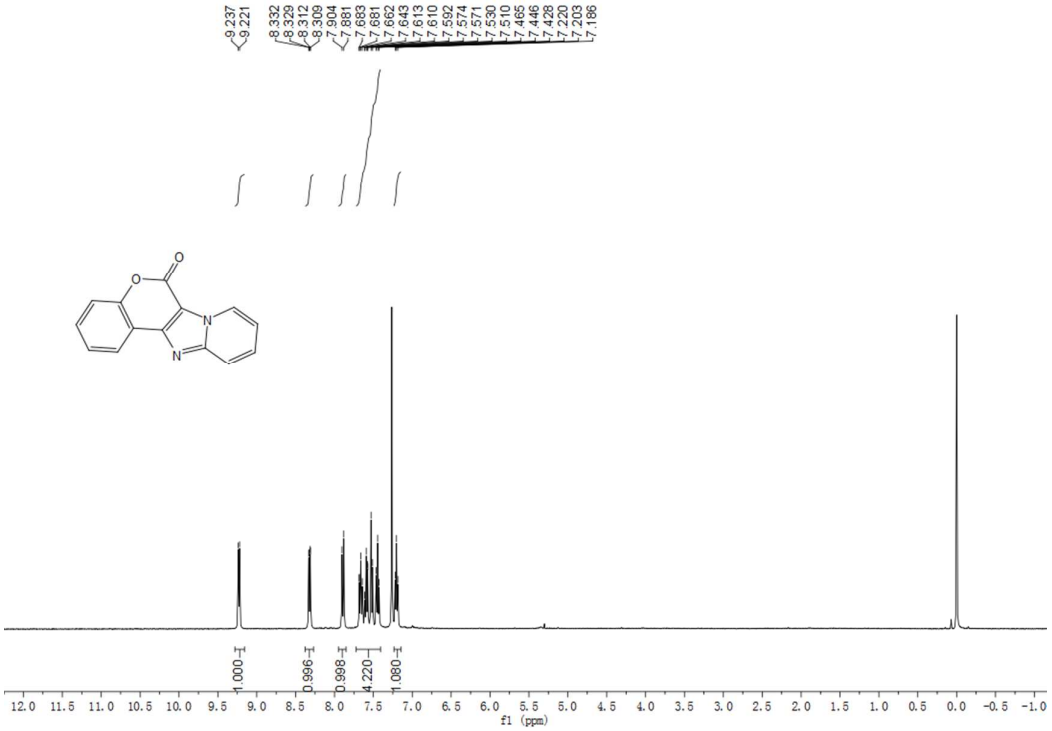
[S4] Huang, C.G.; Beveridge, K. A.; Wan, P. *J. Am. Chem. Soc.***1991**, *113*, 7676.

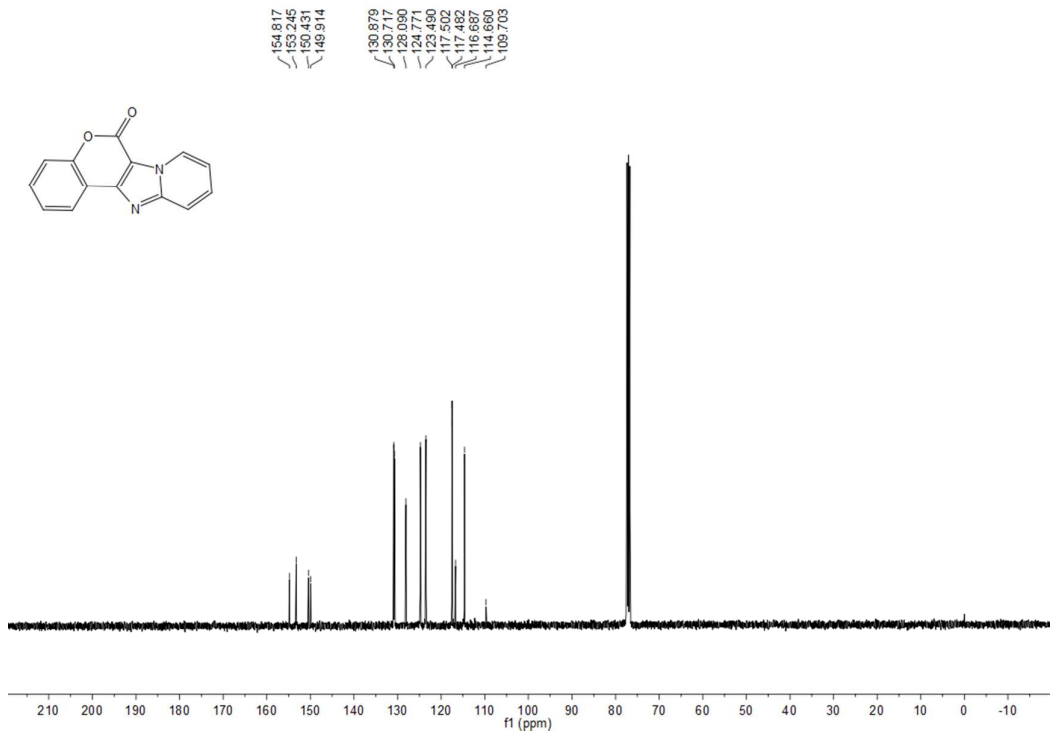
[S5] Dai,J. J.; Xu,W. T.; Wu, Y. D.; Zhang, W. M.; Gong, Y.; He, X. P.; Zhang, X. Q.; Xu, H. J. *J. Org. Chem.* **2015**, *80*, 911.

[S6] Enholm,E. J.; Cottone, J. S.; Allais F. *Org. Lett.* **2001**, *3*, 145.

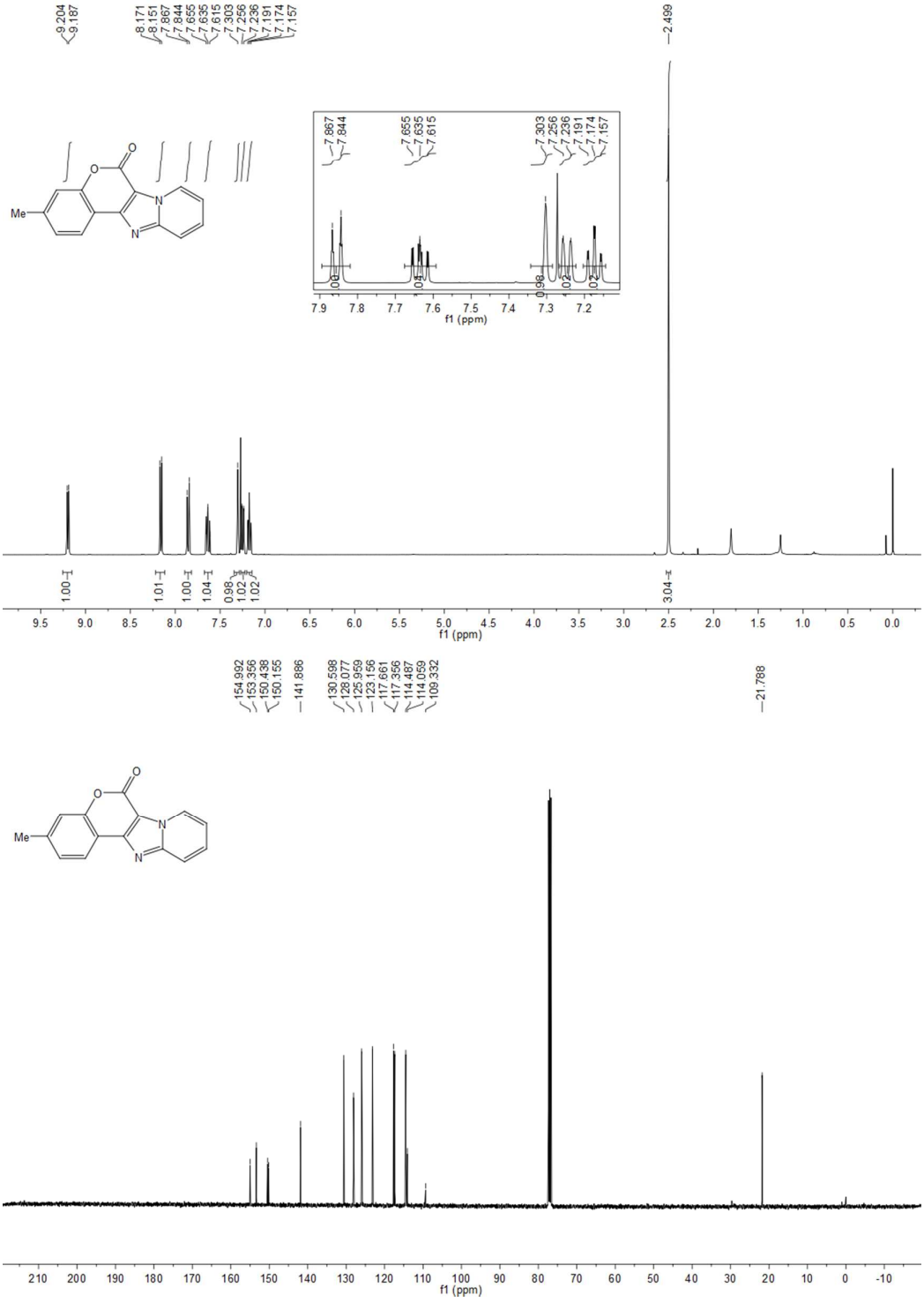
Copies of NMR Spectra

6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2a)

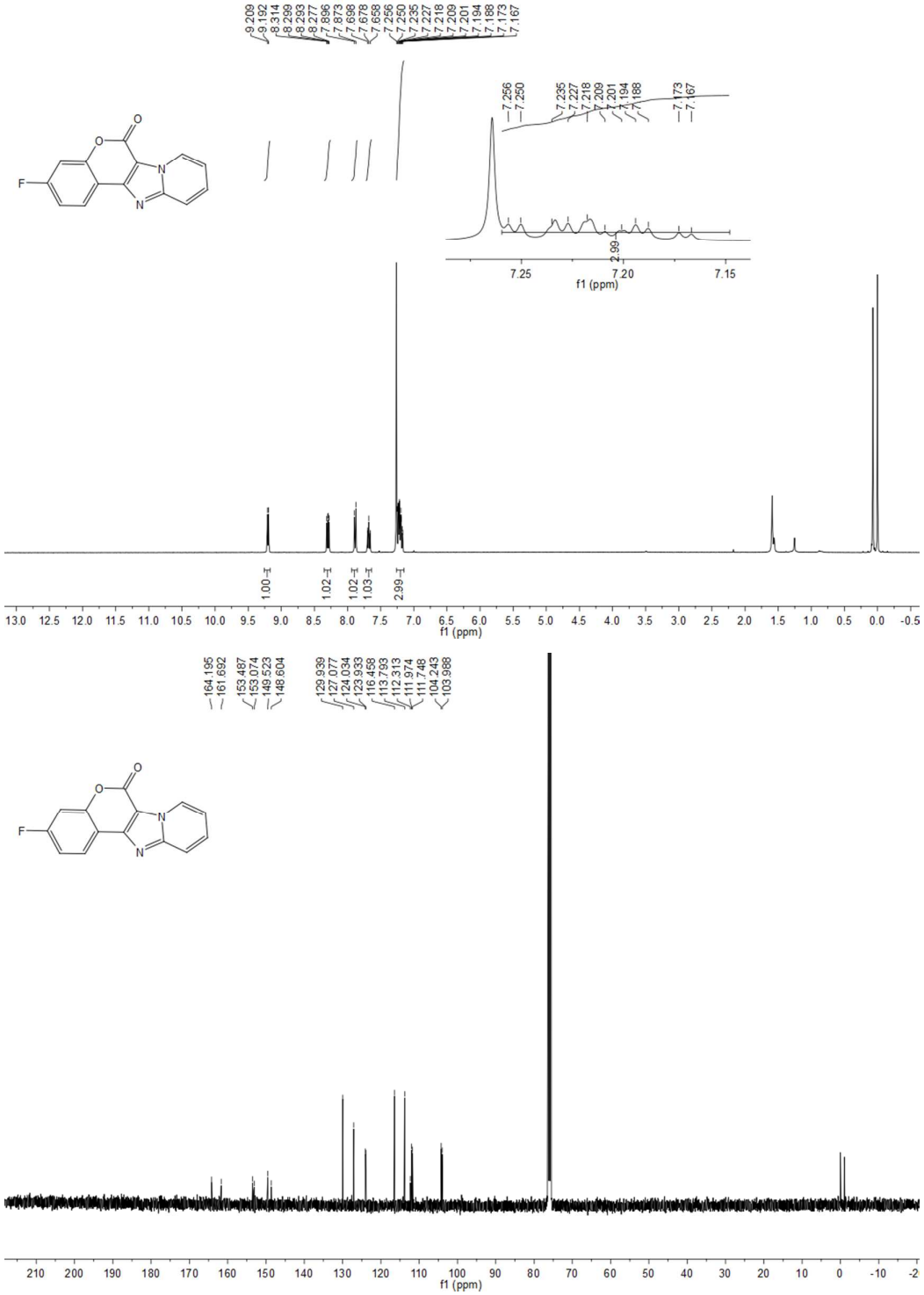


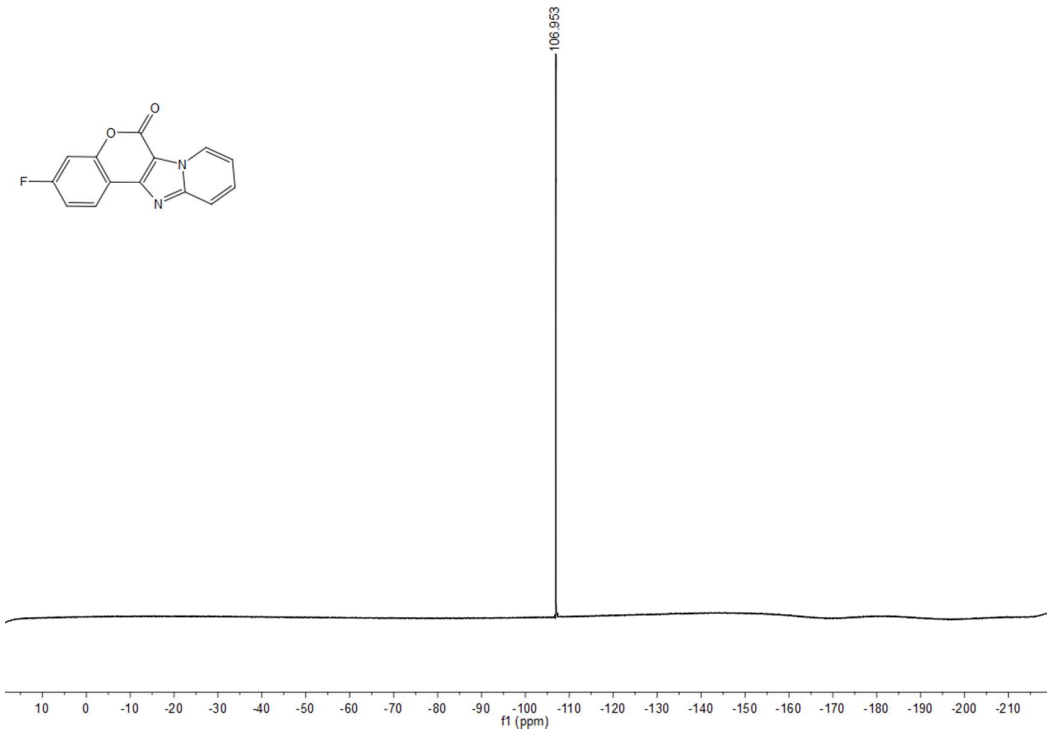


3-methyl-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2b)



3-fluoro-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2c)




106.953
O
O
N
N
F
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-10
-20
-30
-40
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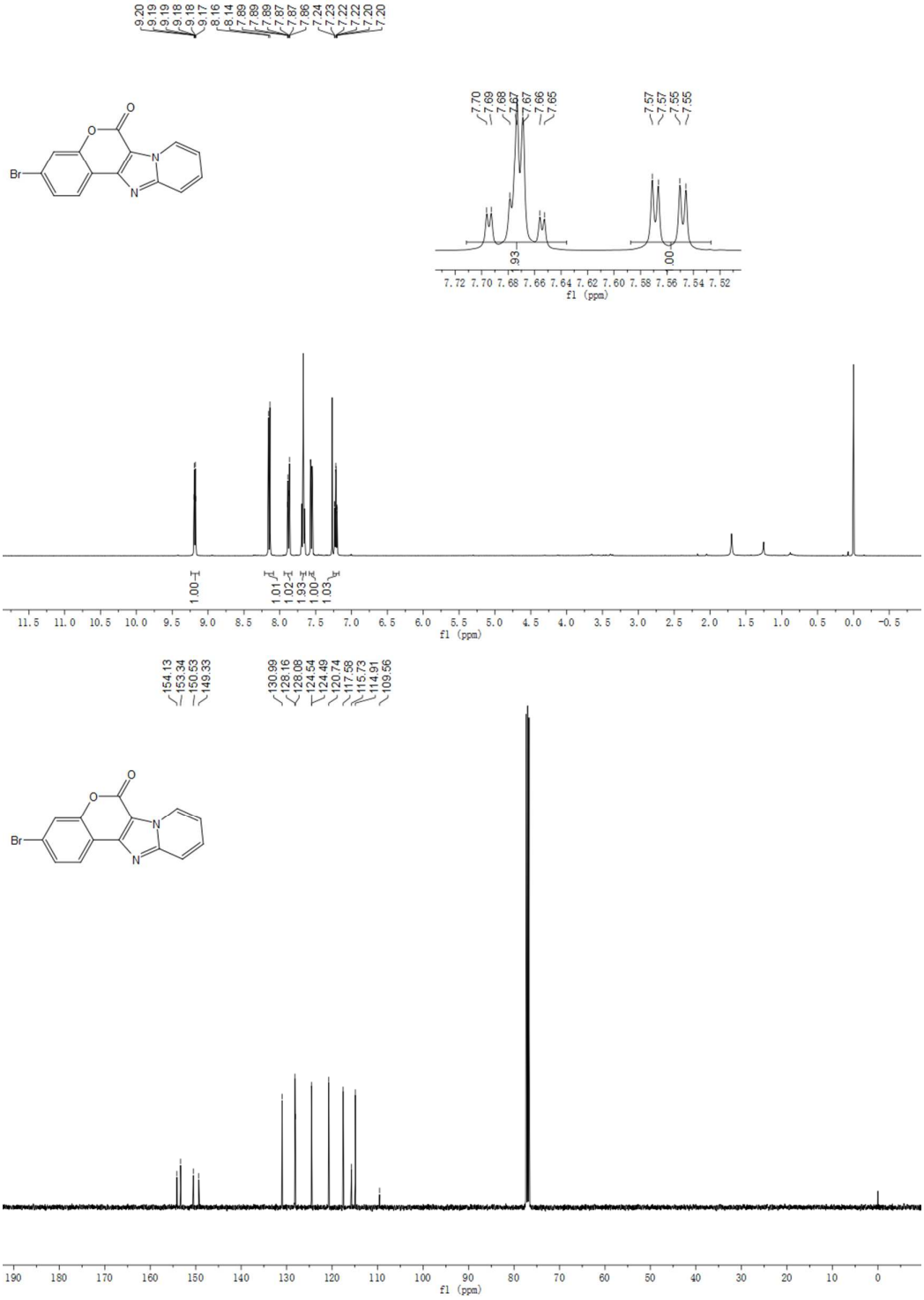
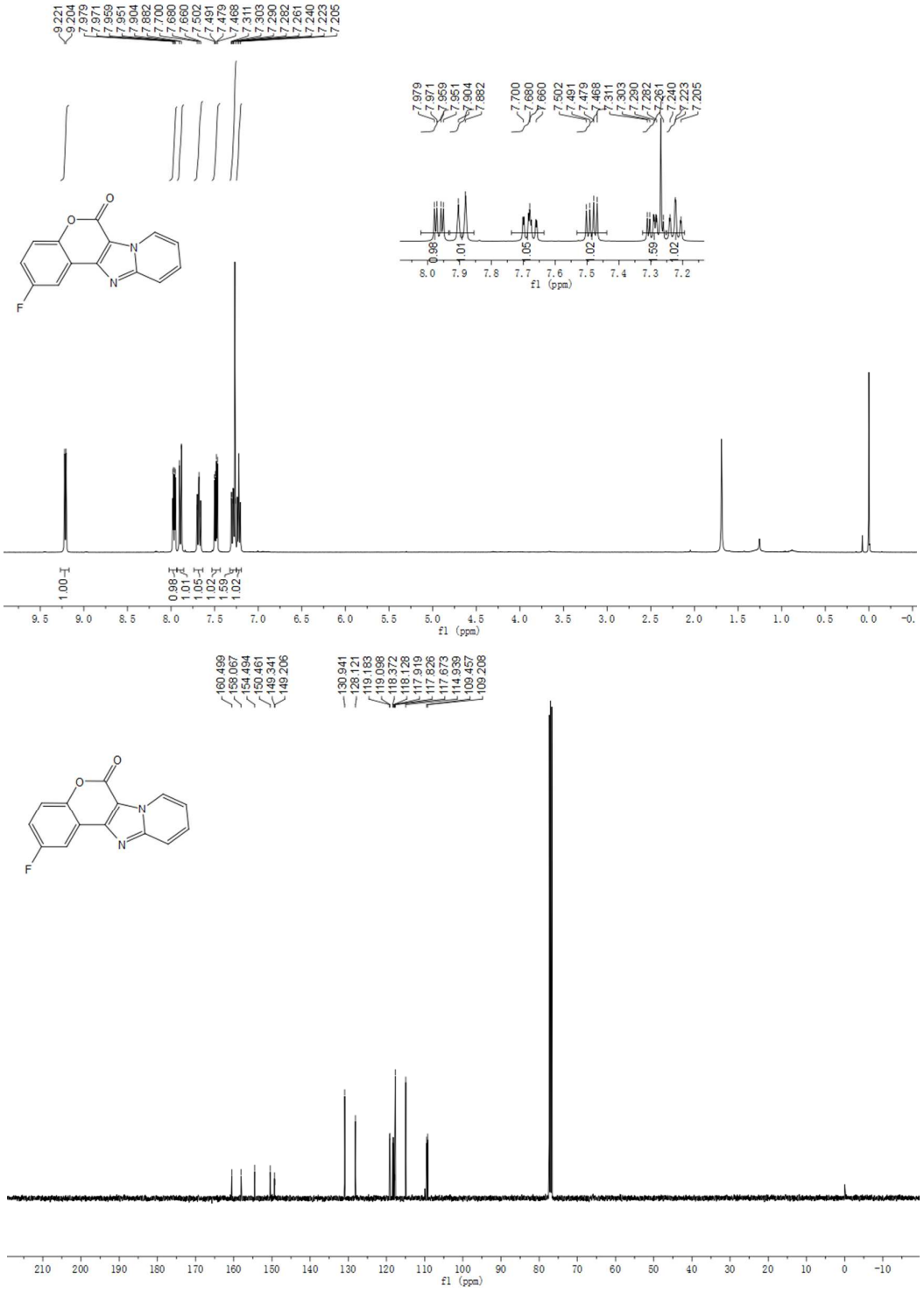
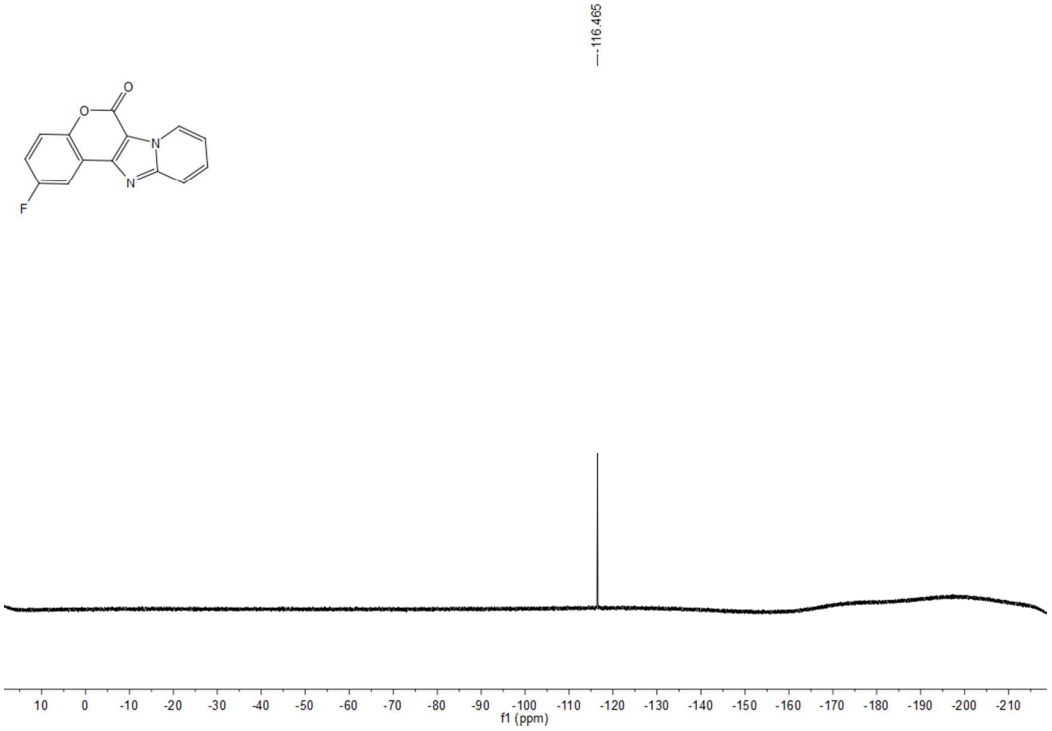
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

3-bromo-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2d)



2-fluoro-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2e)




-116.465
O
O
N
N
F
10
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-10
-20
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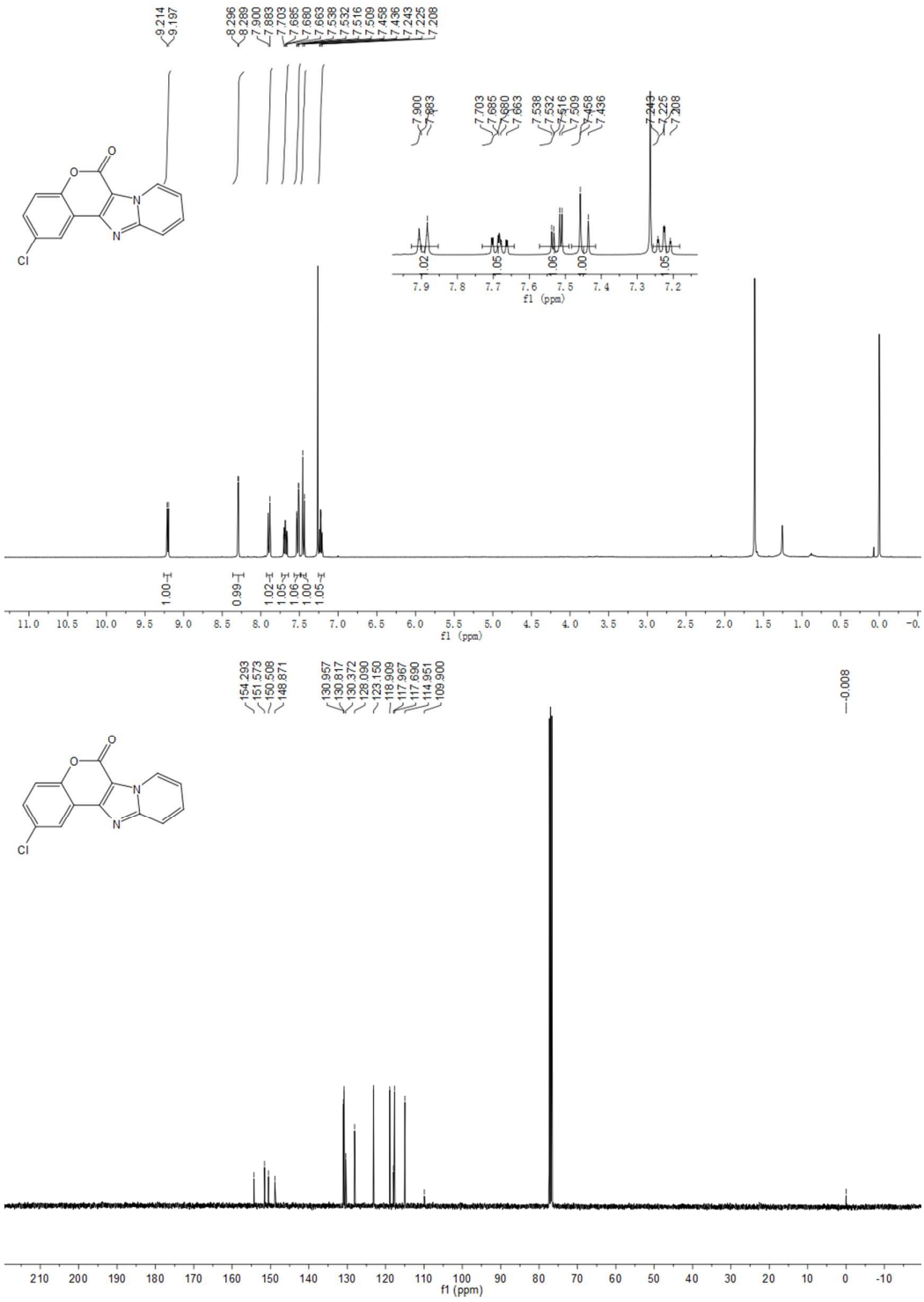
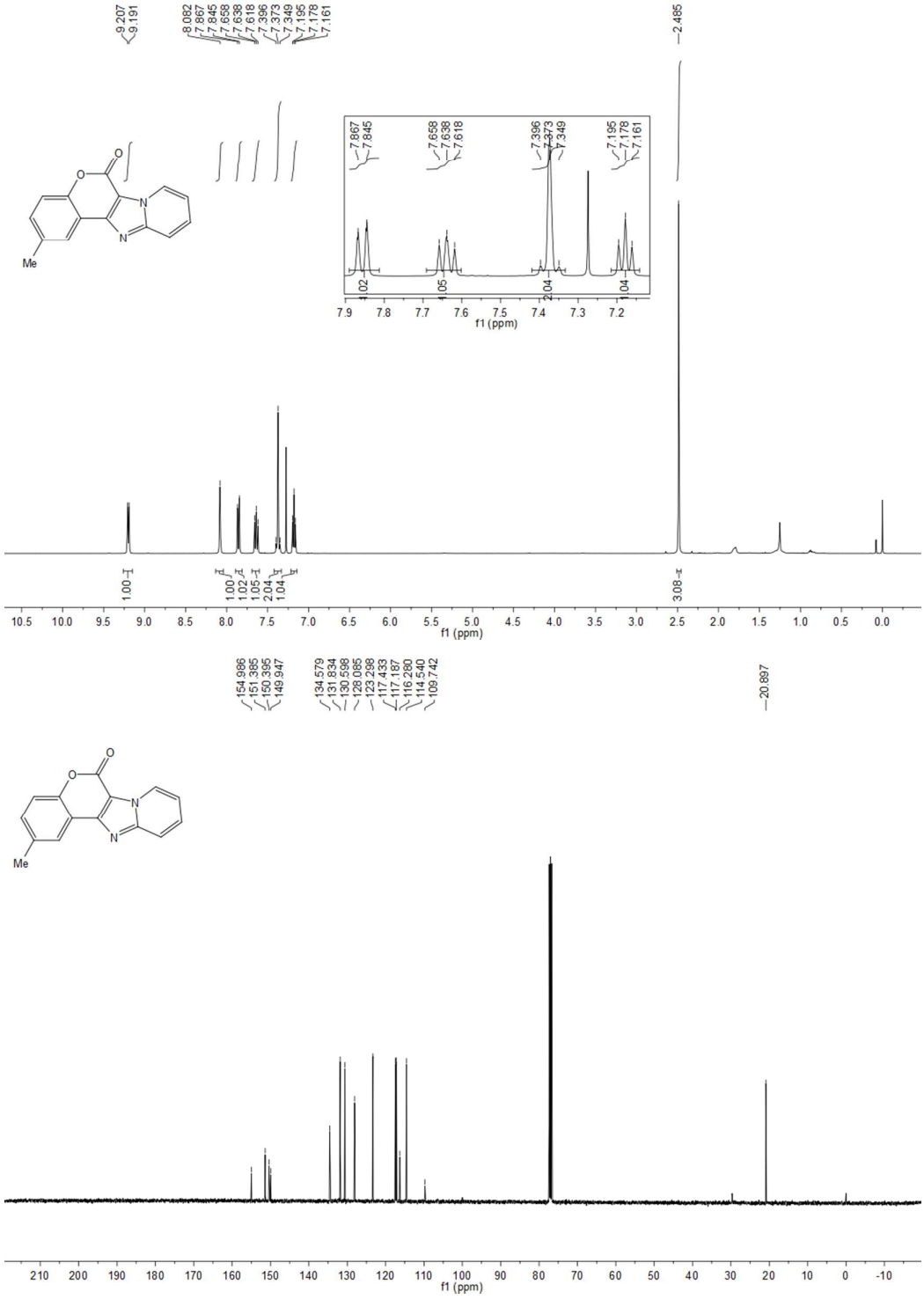
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

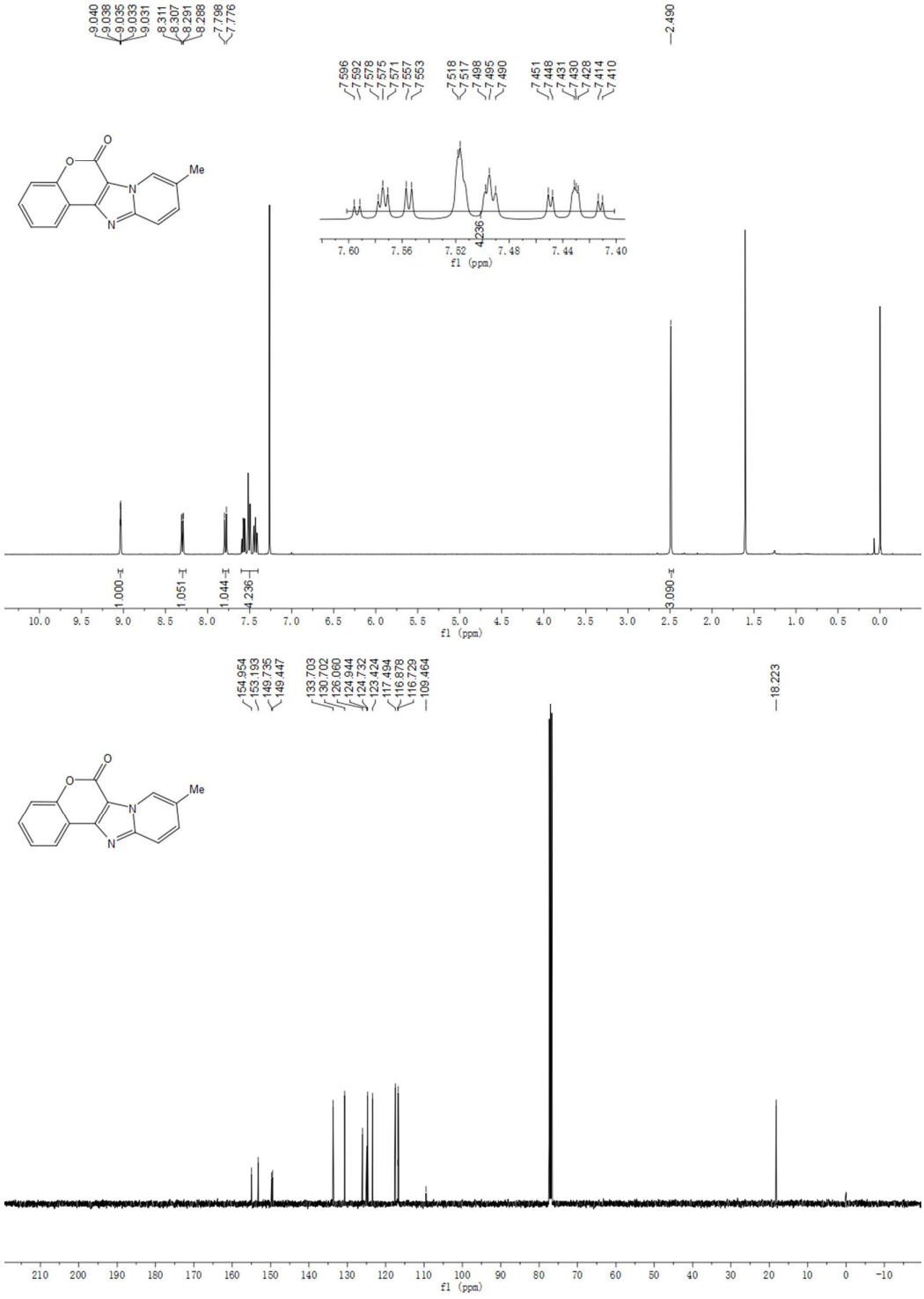
2-chloro-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2f)



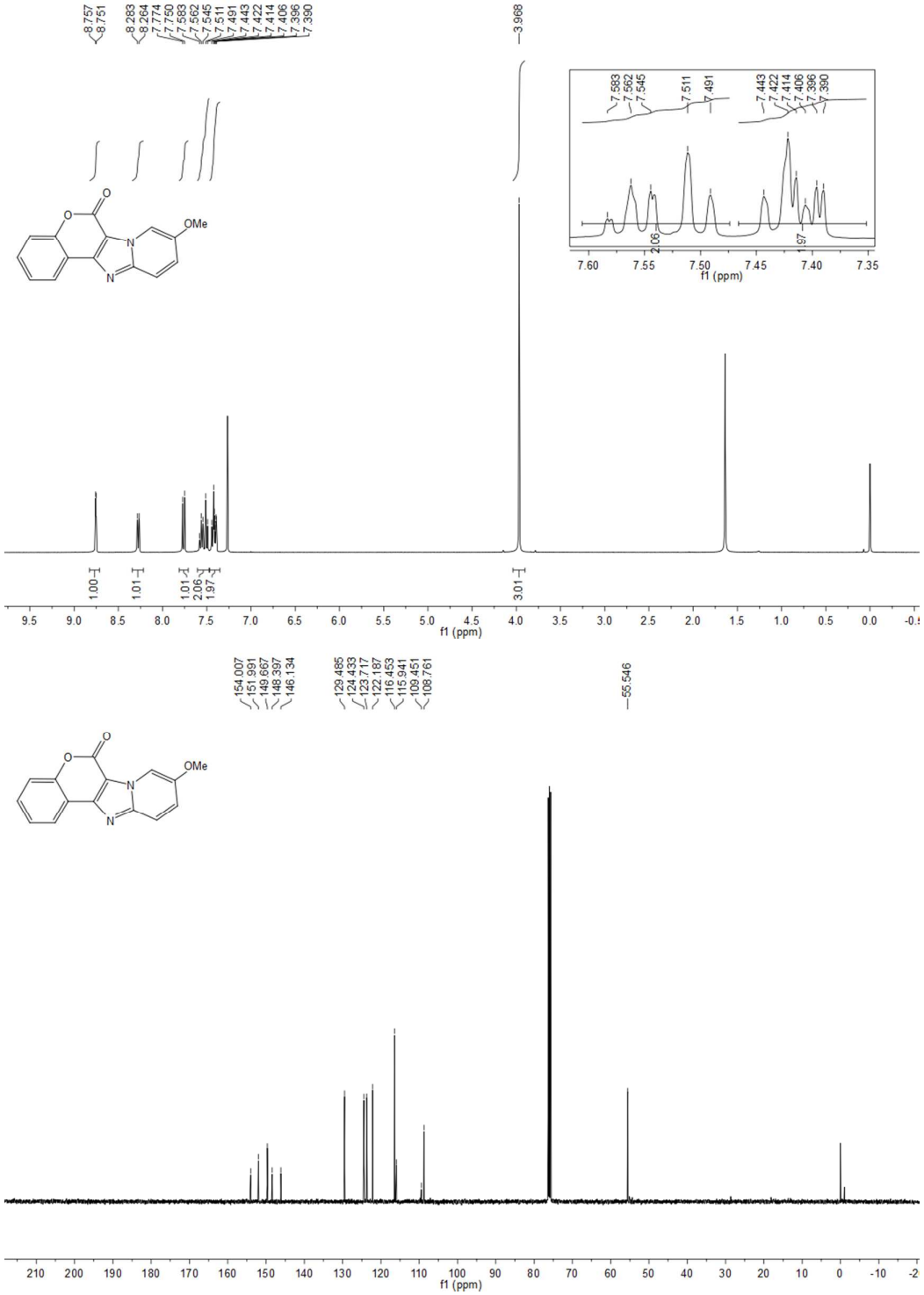
2-methyl-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2g)



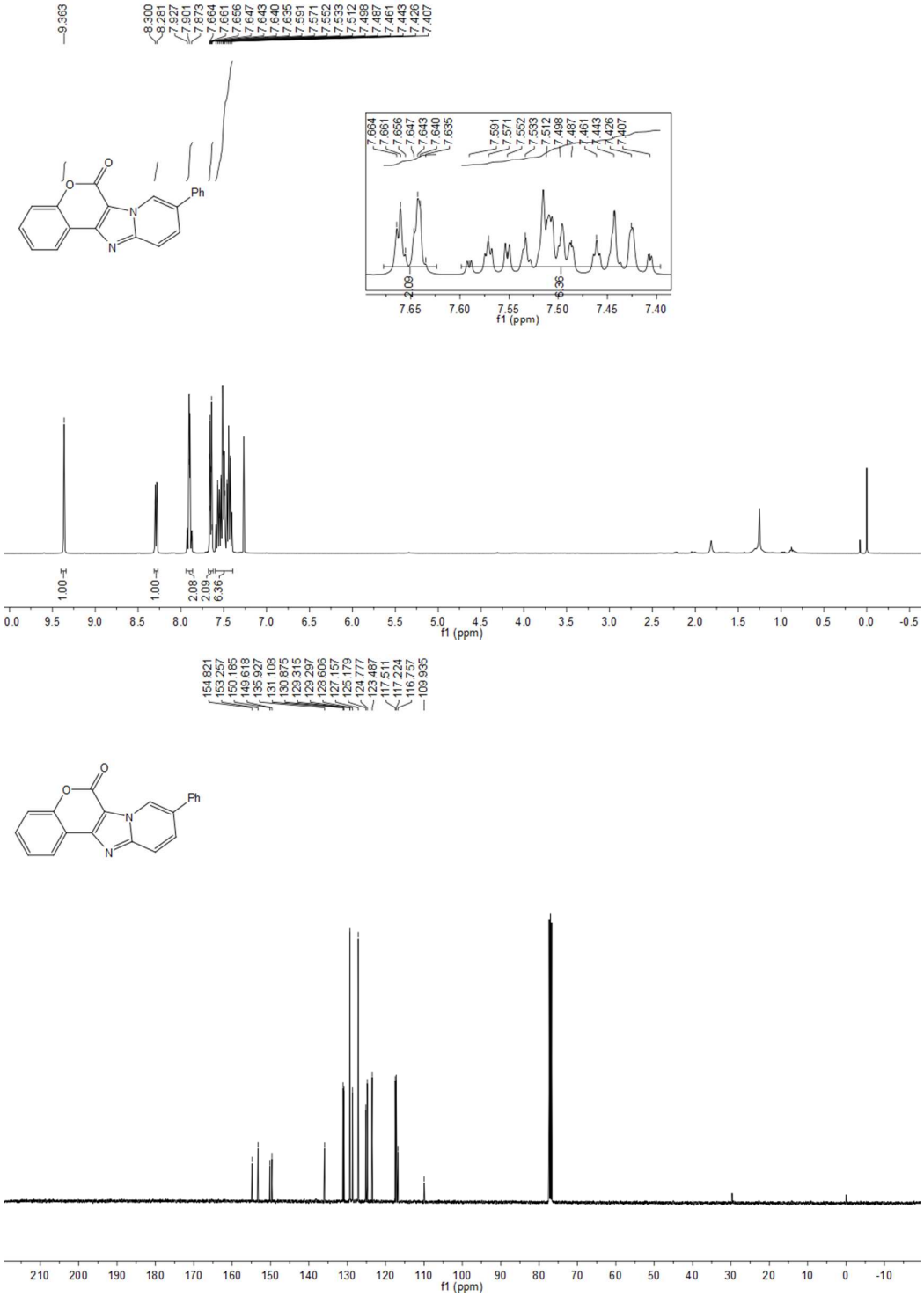
9-methyl-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2h)



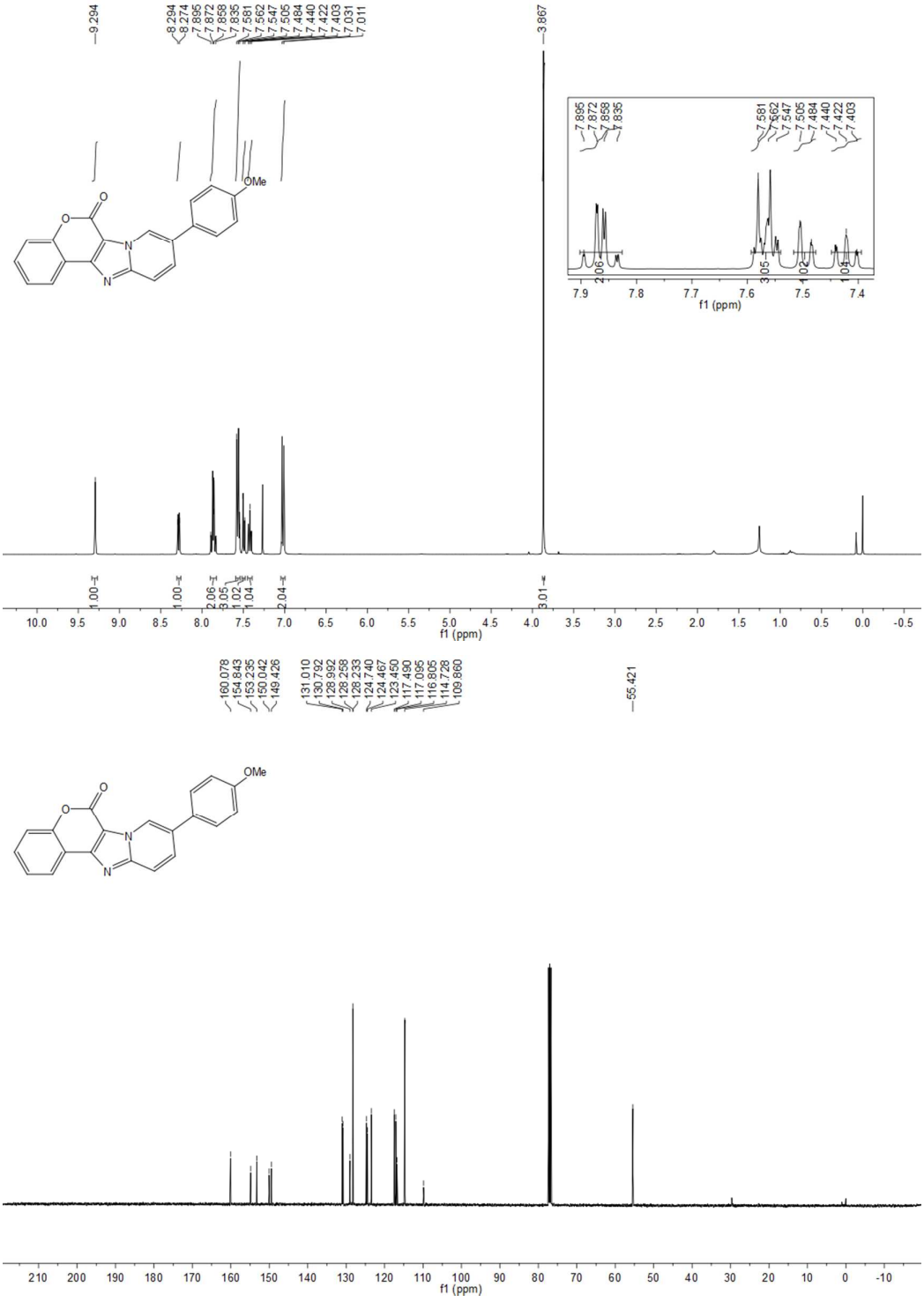
9-methoxy-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2i)



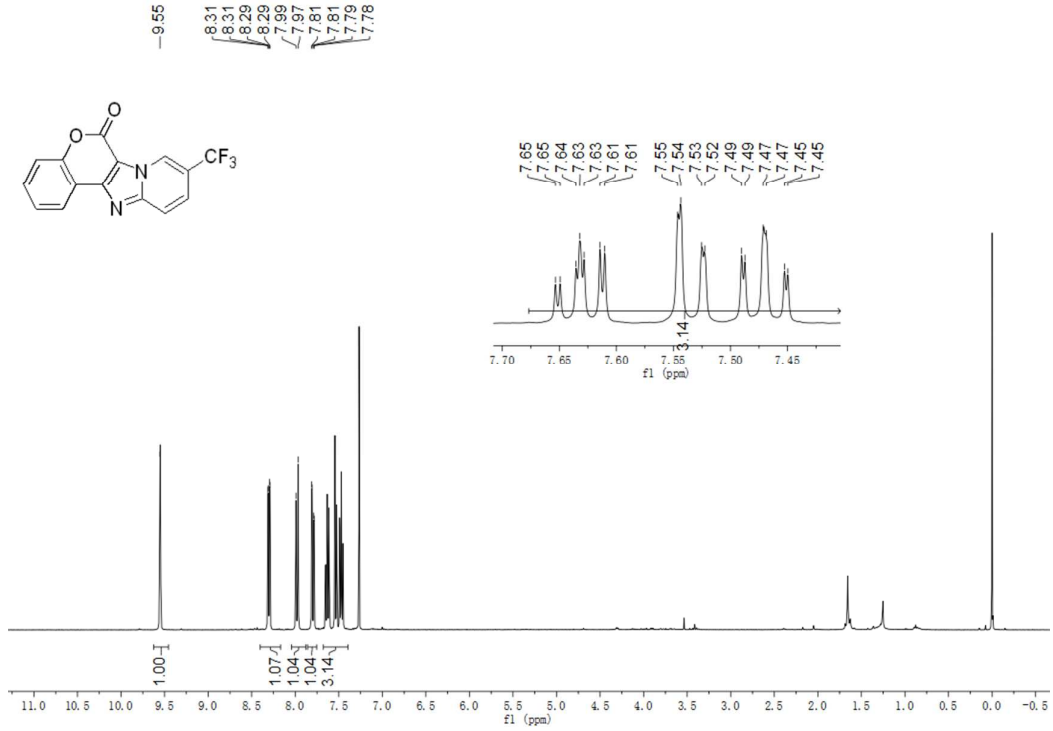
9-phenyl-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2j)

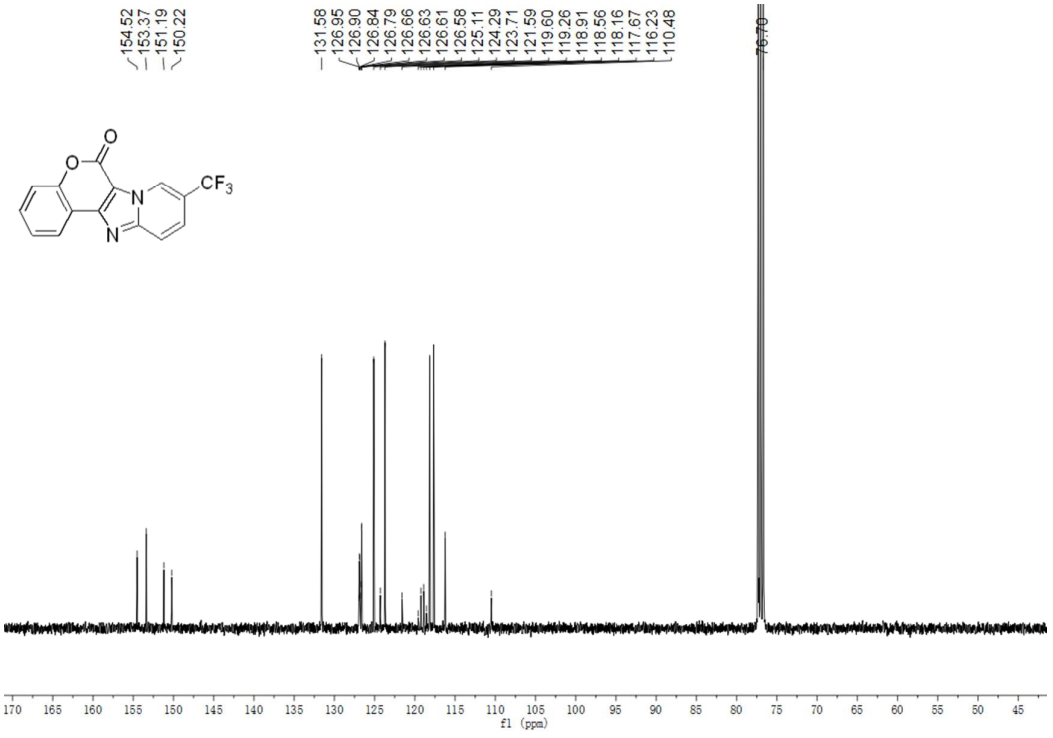


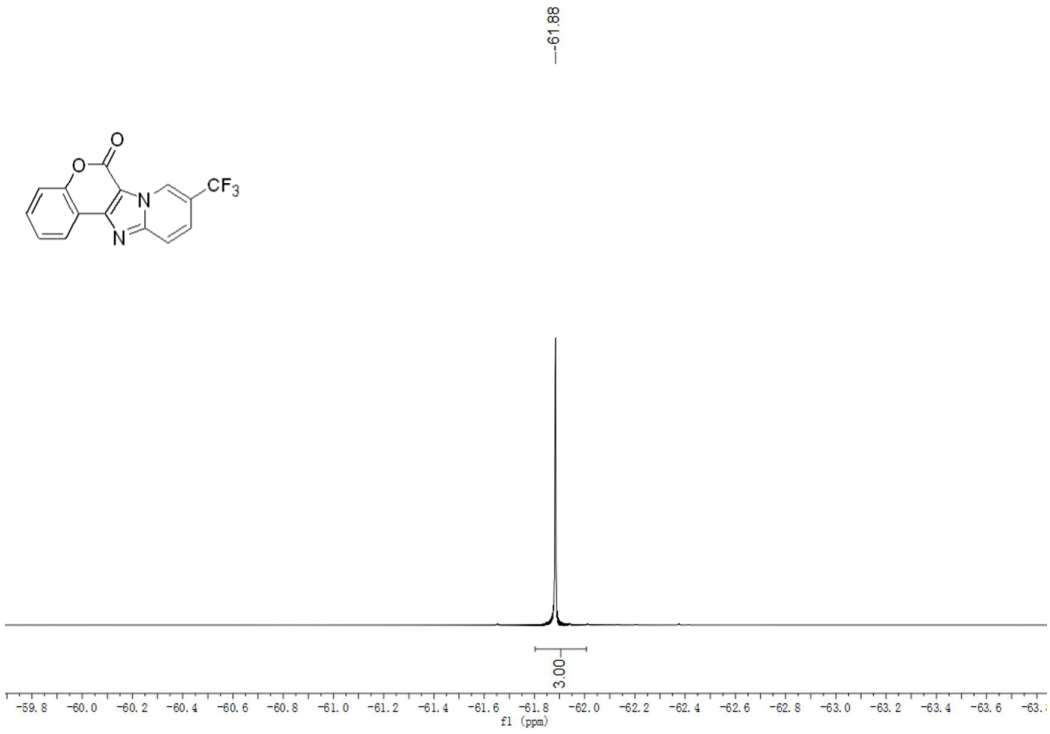
9-(4-methoxyphenyl)-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2k)



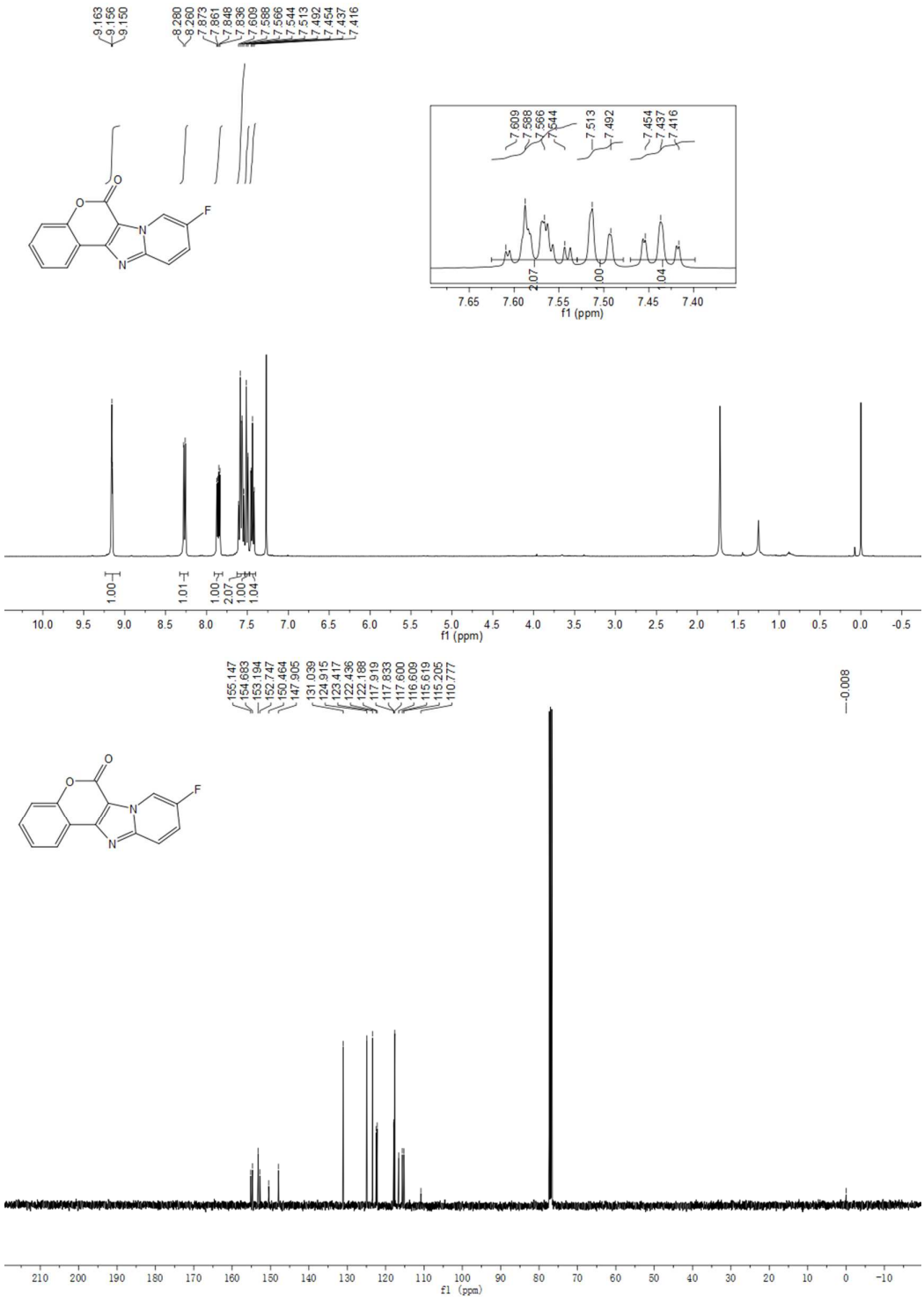
9-(trifluoromethyl)-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2l)





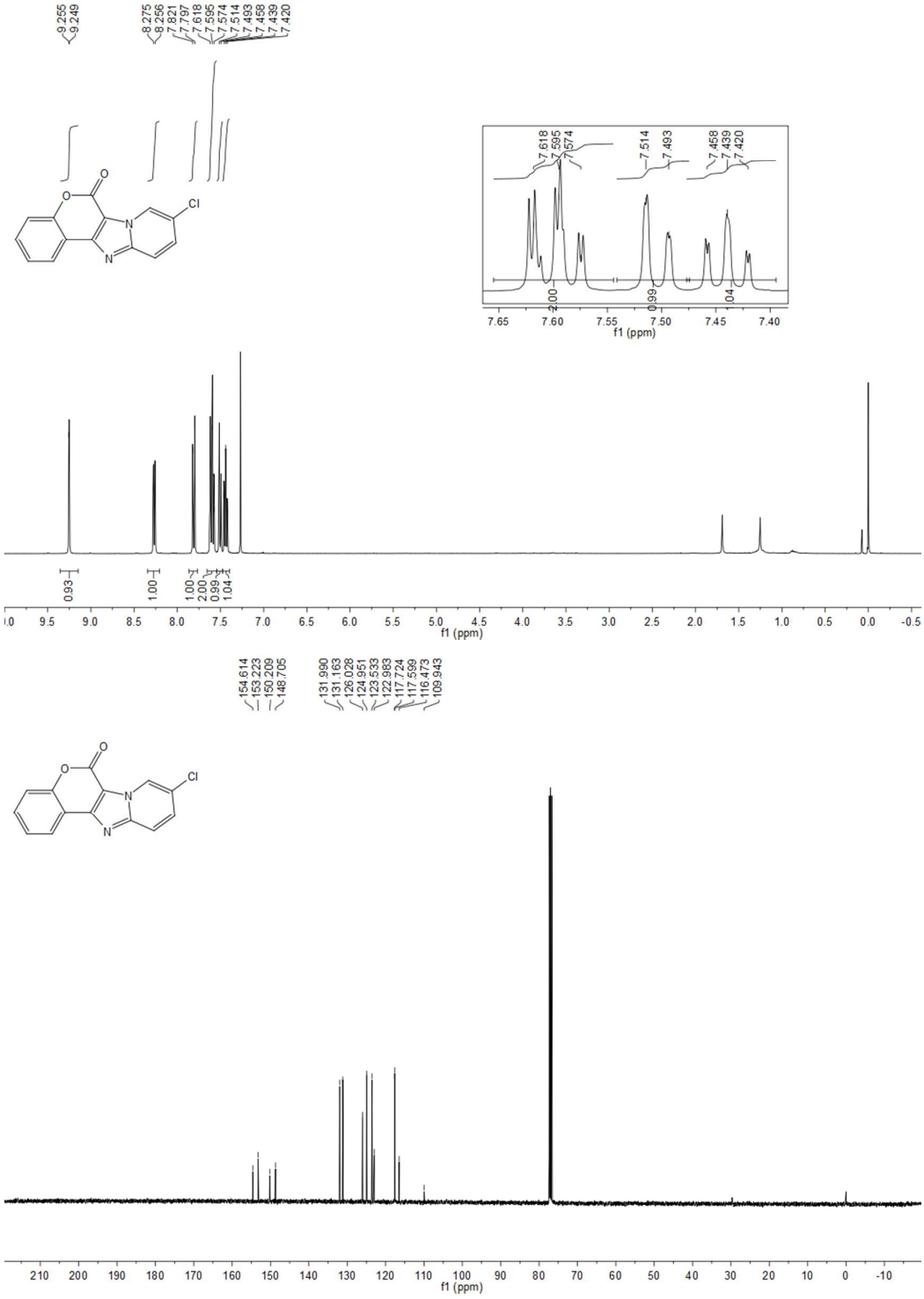

-61.88
O
O
N
N
CF3
3.00
-59.8 -60.0 -60.2 -60.4 -60.6 -60.8 -61.0 -61.2 -61.4 -61.6 -61.8 -62.0 -62.2 -62.4 -62.6 -62.8 -63.0 -63.2 -63.4 -63.6
f1 (ppm)

9-fluoro-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2m)

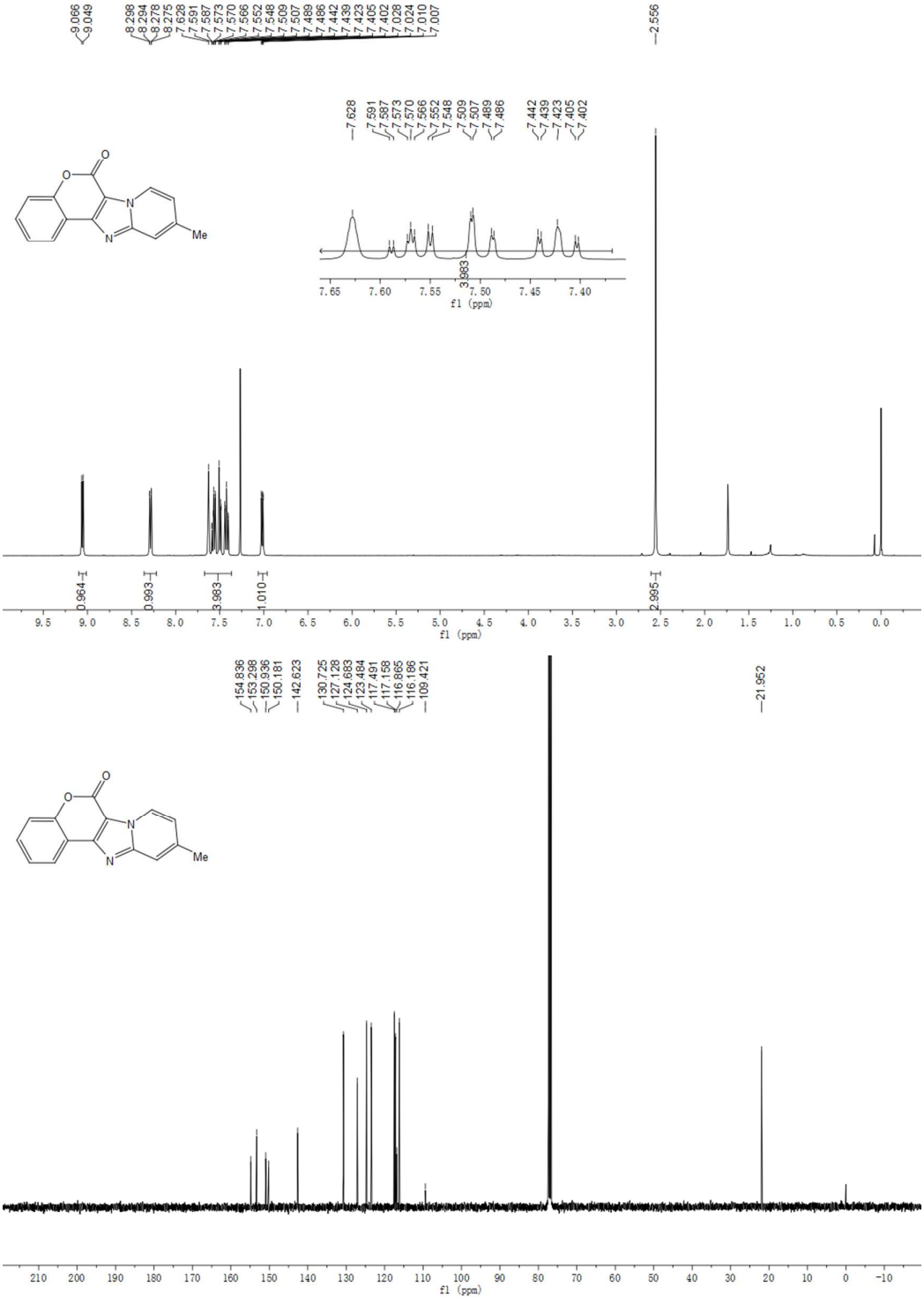



-135.324
O
O
N
N
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

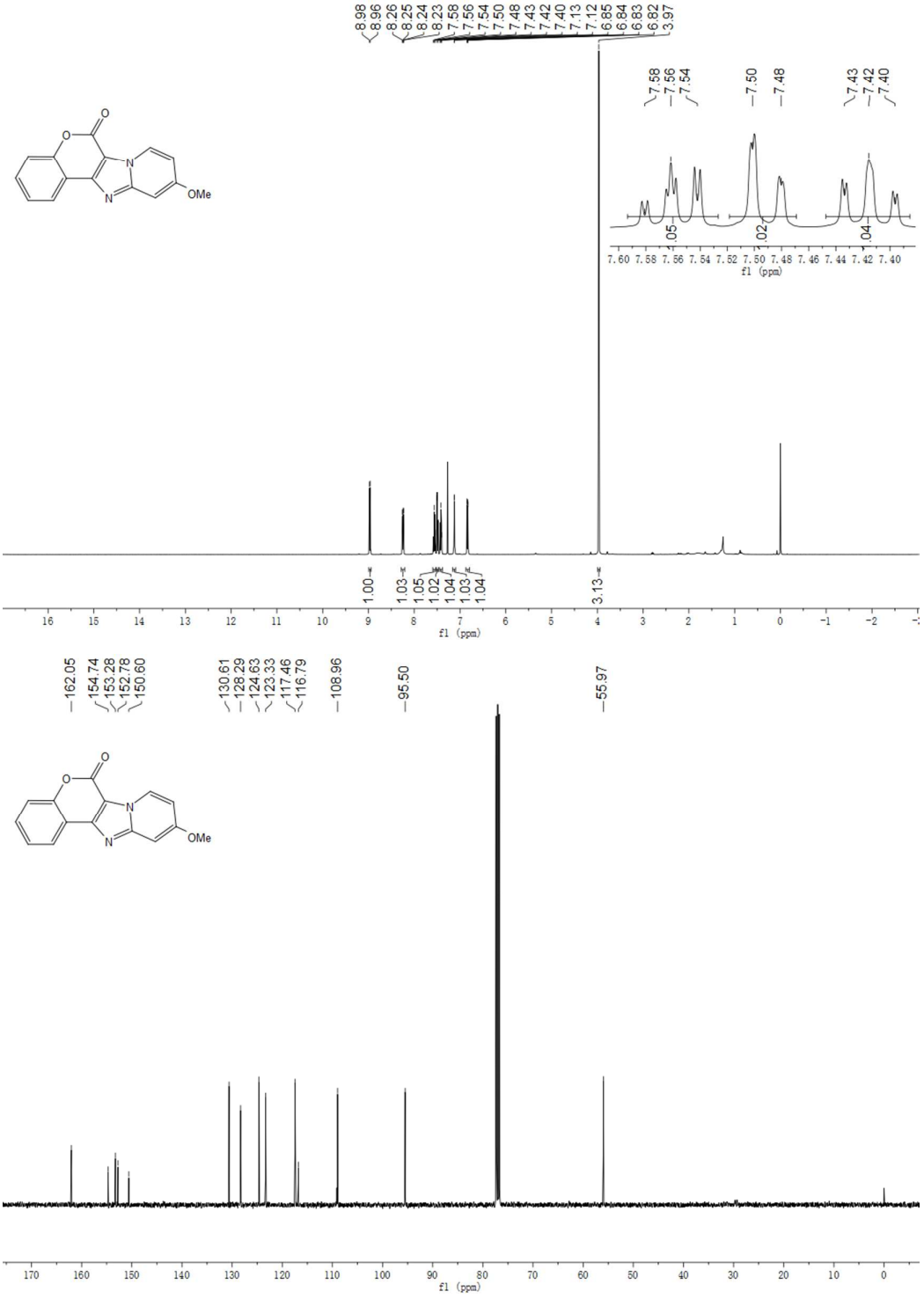
9-chloro-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2n)



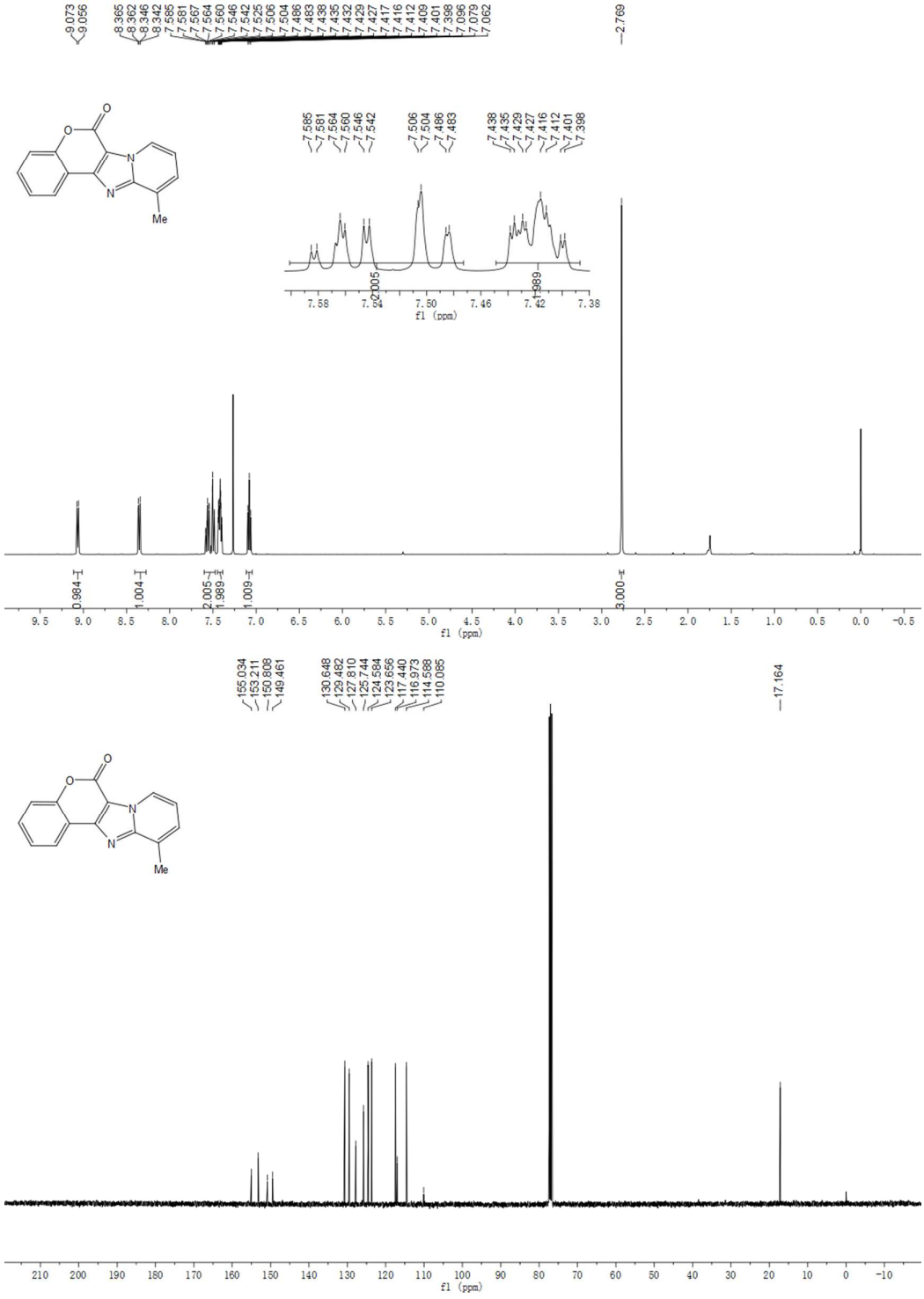
10-methyl-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2o)



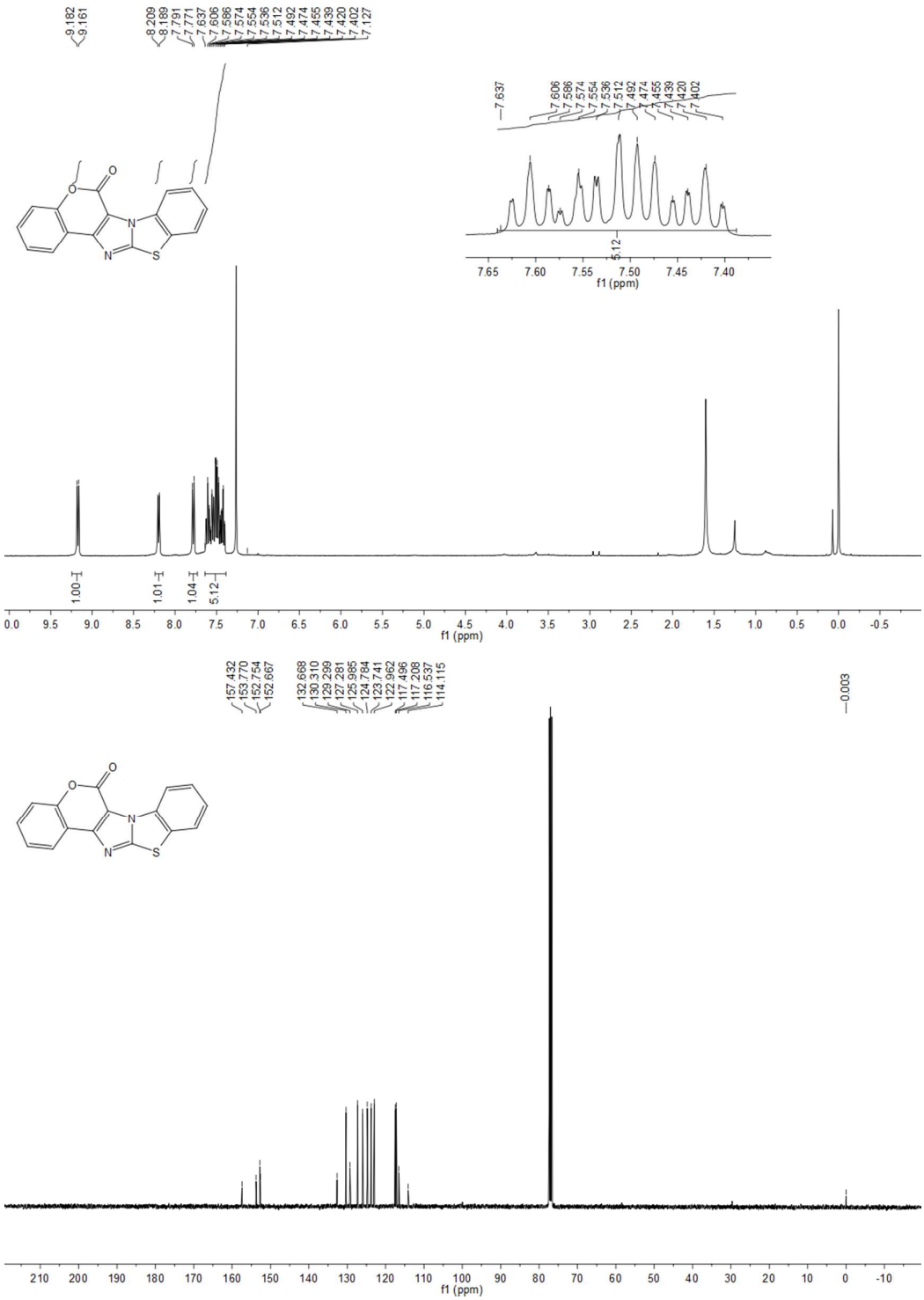
10-methoxy-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2p)



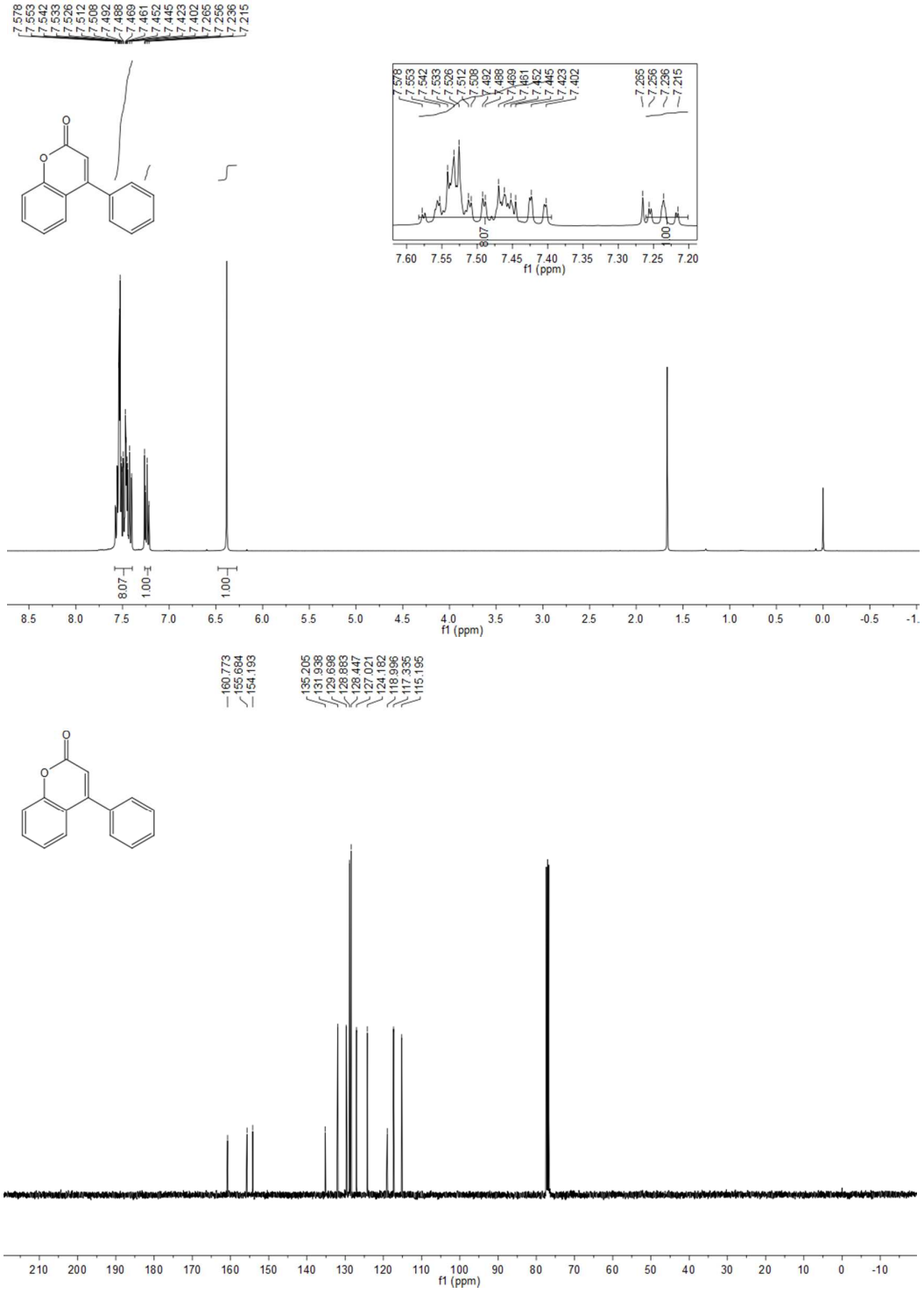
11-methyl-6H-chromeno[4',3':4,5]imidazo[1,2-a]pyridin-6-one (2q)



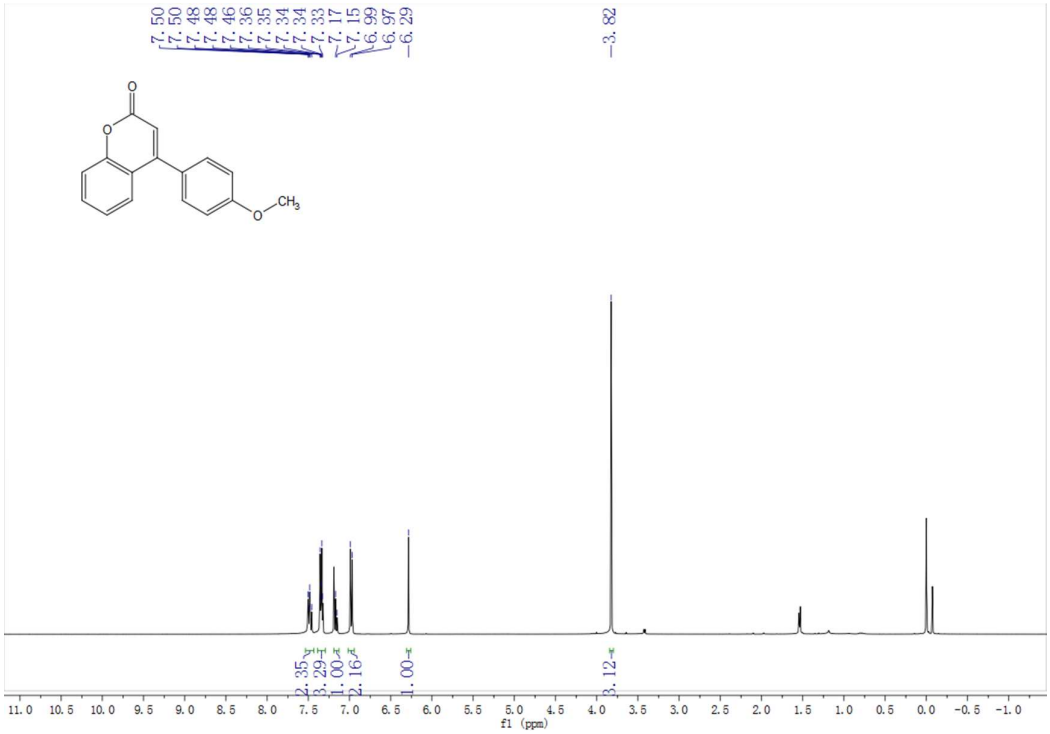
6H-benzo[d]chromeno[4',3':4,5]imidazo[2,1-b]thiazol-6-one (2r)

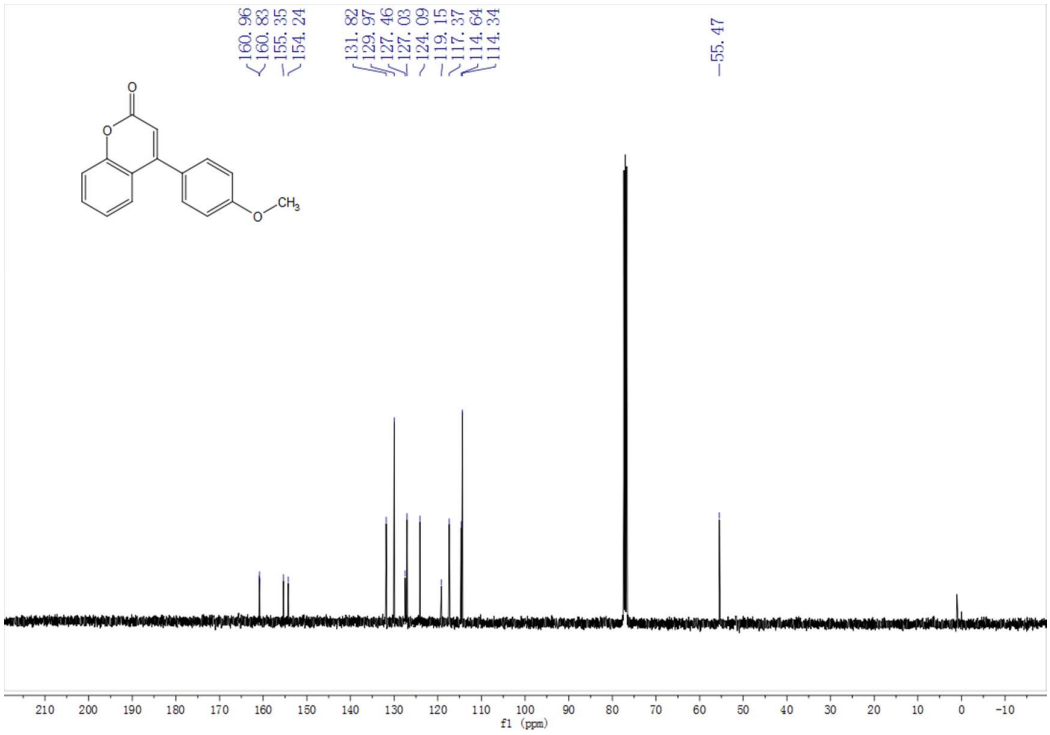


4-phenyl-2H-chromen-2-one (2s)

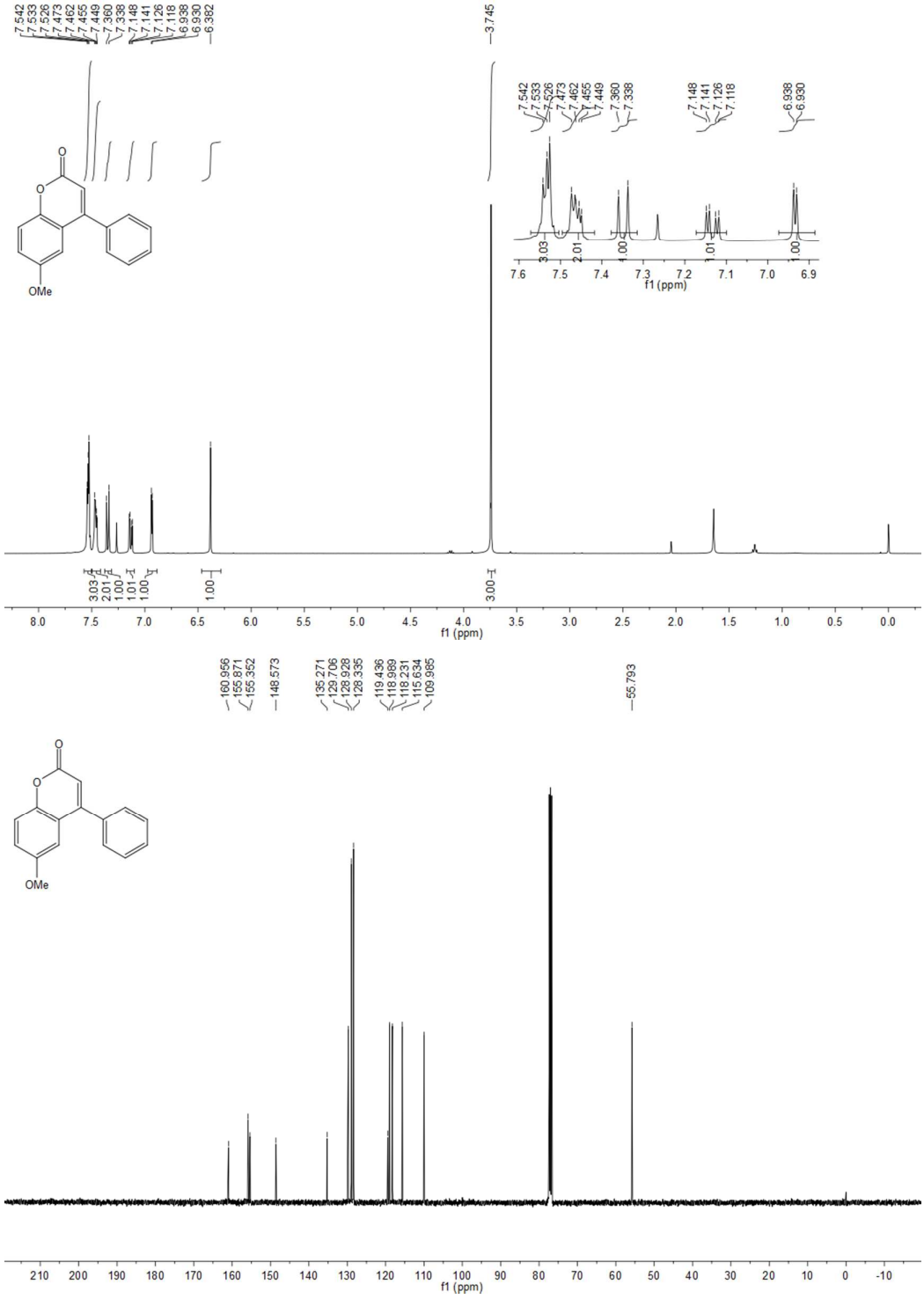


4-(4-methoxyphenyl)-2H-chromen-2-one (2t)

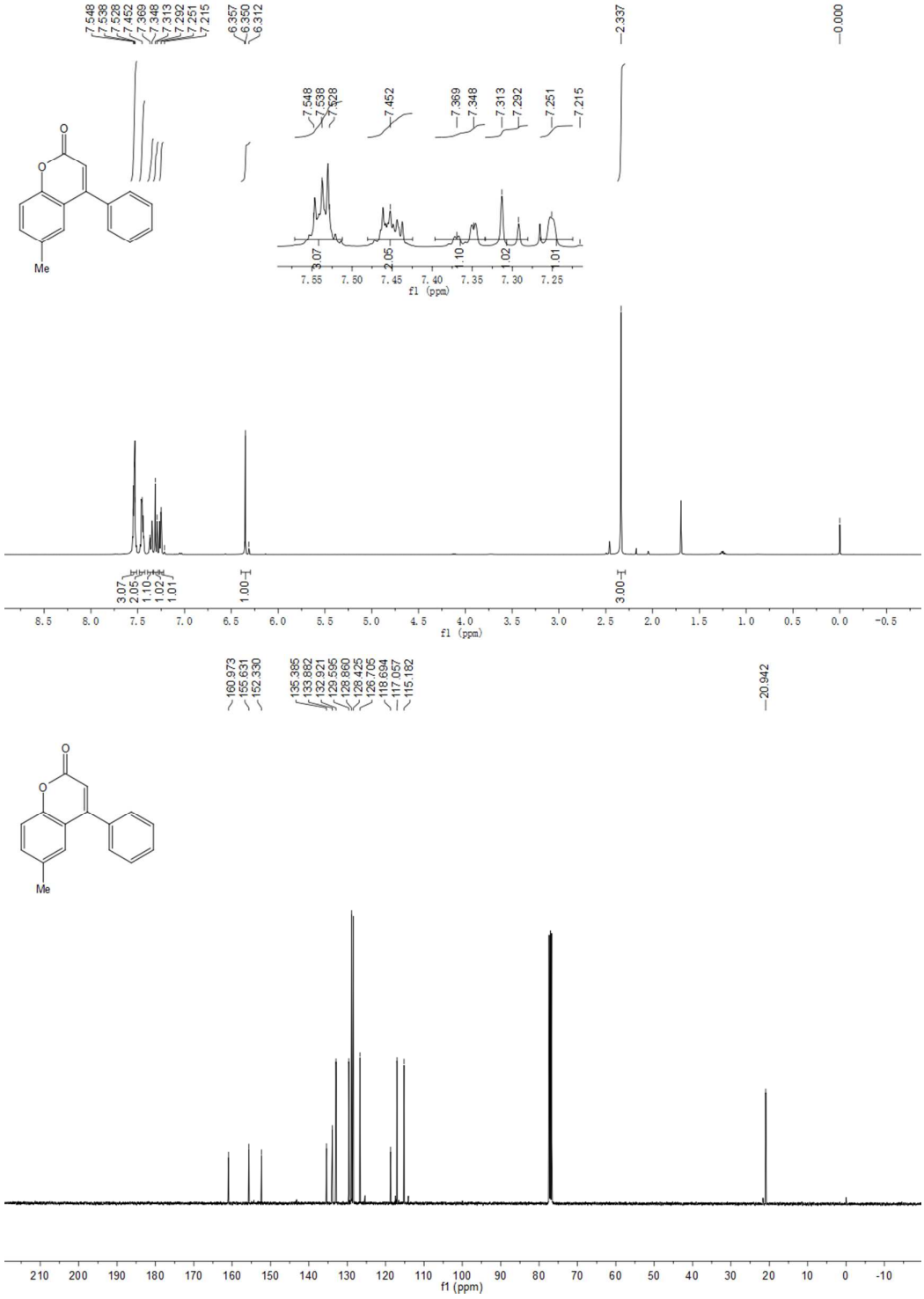




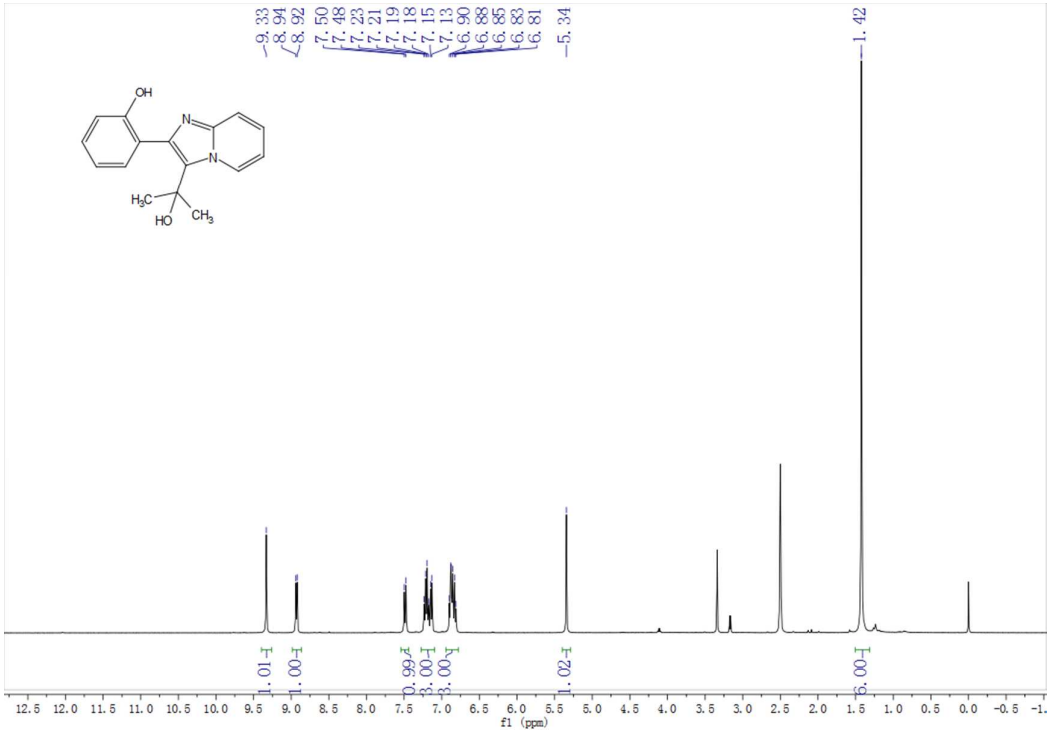
6-methoxy-4-phenyl-2H-chromen-2-one (2u)

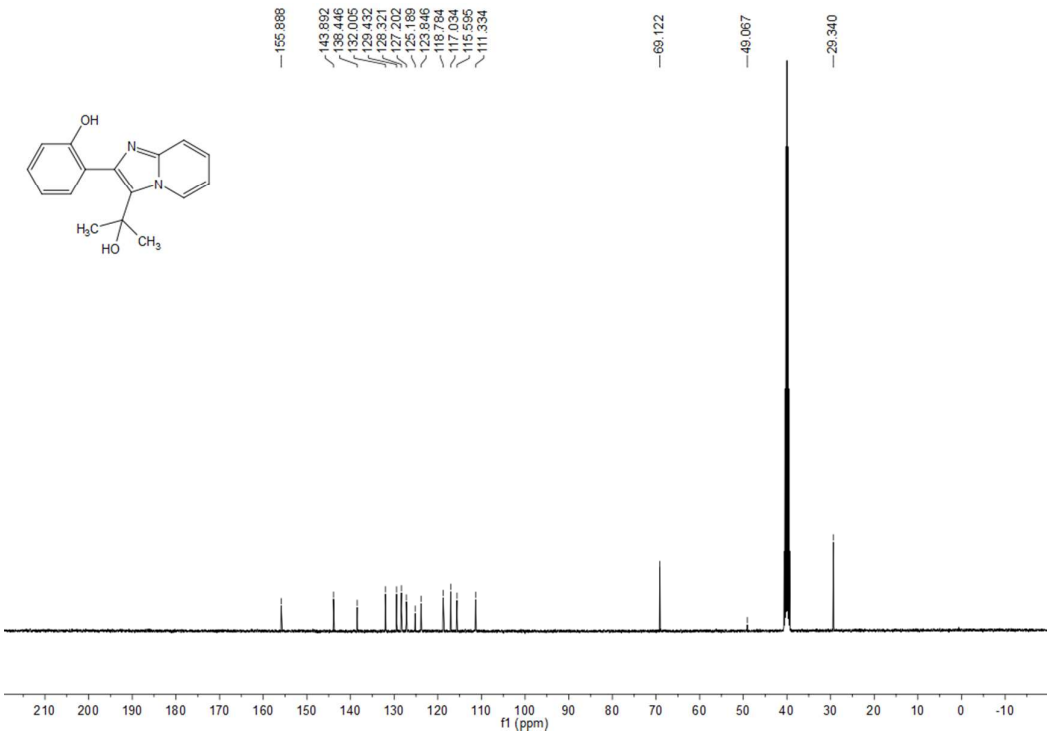


6-methyl-4-phenyl-2H-chromen-2-one (2v)

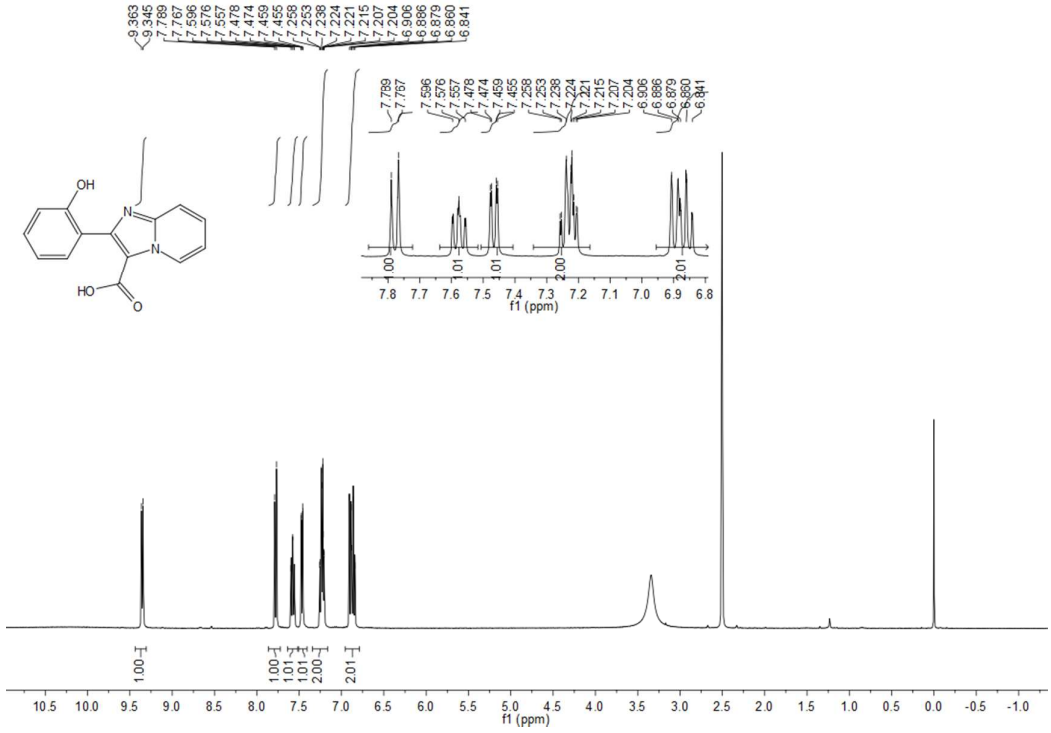


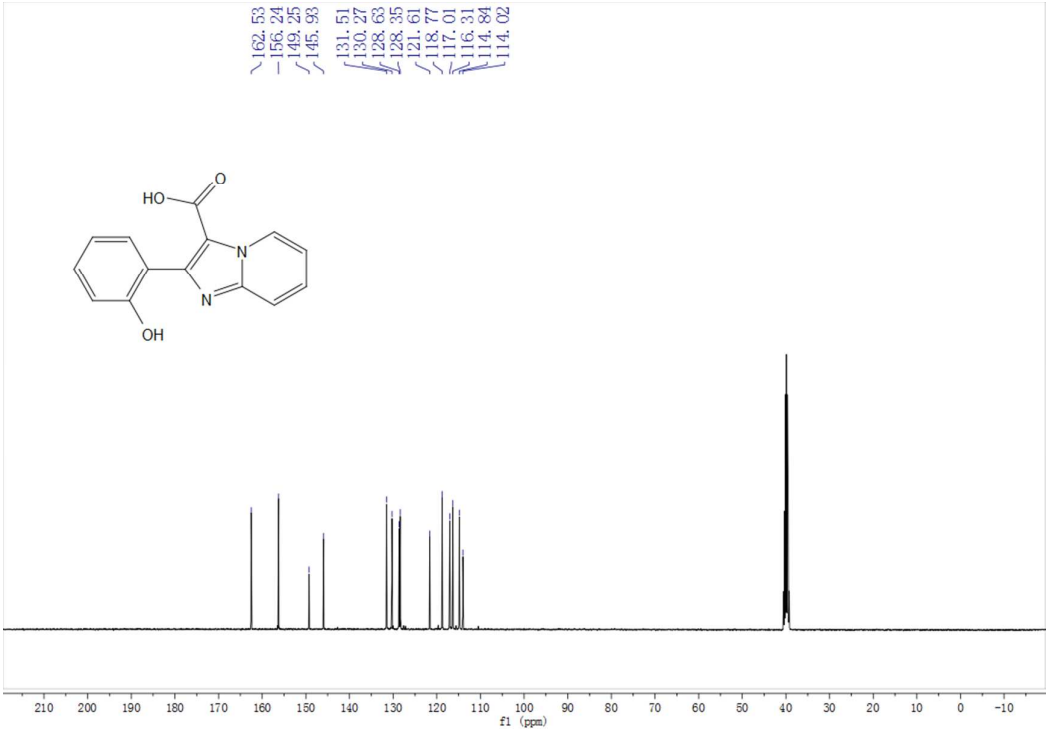
2-(3-(2-hydroxypropan-2-yl)imidazo[1,2-a]pyridin-2-yl)phenol (3)





2-(2-hydroxyphenyl)imidazo[1,2-a]pyridine-3-carboxylic acid (4)





2-(3-(hydroxymethyl)imidazo[1,2-a]pyridin-2-yl)phenol (5)