Photoinduced $FeCl_3$-catalyzed α-C(sp^3)−H azolation of Primary Aliphatic alcohols via LMCT-driven HAT

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Supporting Information

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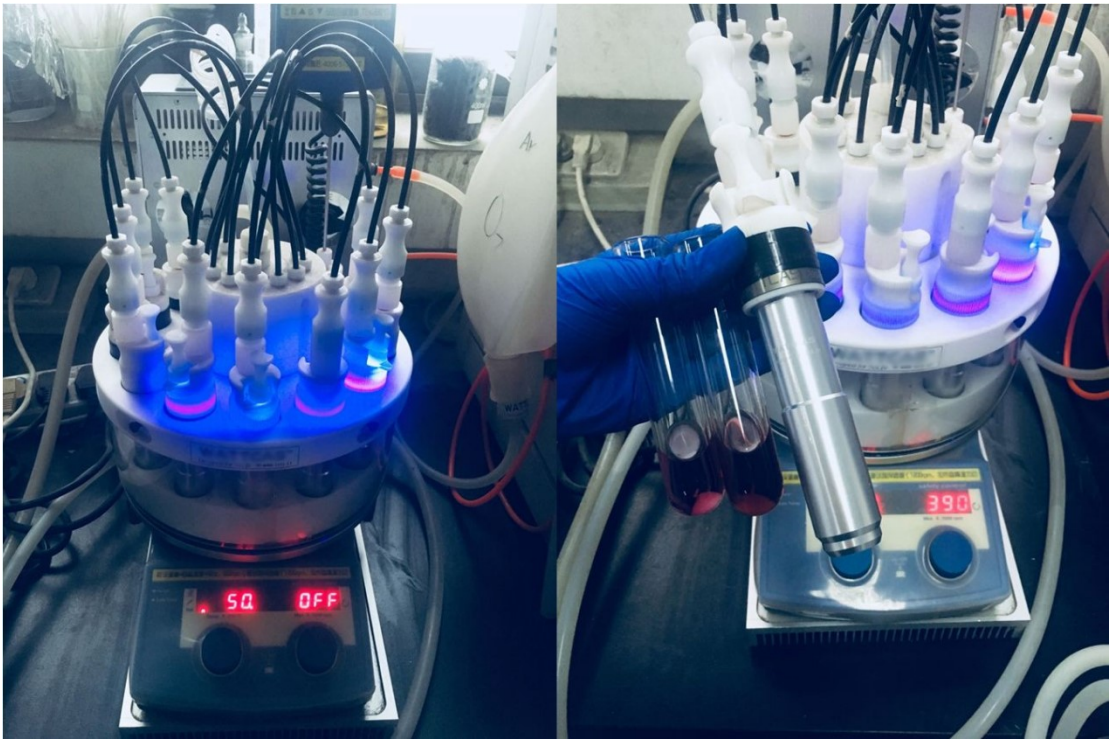


Figure S1. Details for the photochemical reaction setup.

The light Source and the Material of the Irradiation Vessel

Manufacturer: Xi'an WATTECS experimental equipment Co. Ltd

Model: WP-TEC-1020SL

Broadband source: X = 390 nm (light power: 16 W).

Material of the irradiation vessel: borosilicate reaction tube (20 ml)

Distance from the light source to the irradiation vessel: 2.0 cm

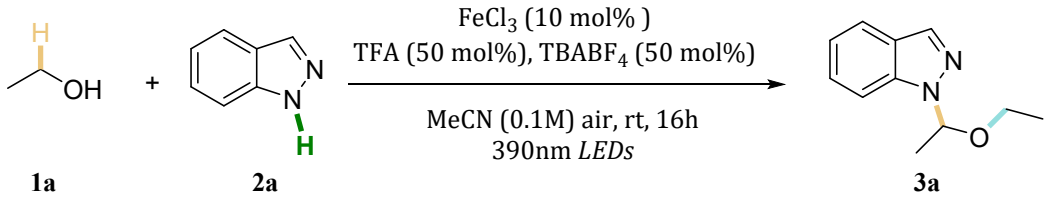
Not use any filters

I. General methods and materials

All chemicals and reagents were used of commercial grade and were used without further purification. The reactions were monitored by thin-layer chromatography (TLC) using silica gel GF254. Column chromatography was performed with 200–300 mesh silica gel. All yields refer to isolated products after purification. The intermediates and the products synthesized were fully characterized by spectroscopic data. The NMR spectra were recorded on Bruker DRX-400 (^{1}H: 400 MHz, ^{13}C: 101MHz) using $CDCl_3$ and DMSO-d6 as solvents. The following abbreviation were used to explain the multiplicities: (s) = singlet, (d) = doublet, (t) = triplet, (q) = quartet, (sept) = septuplet, (dd) = double doublet, (dt) = double triplet, (dq) = double quartet, (ddd) = double-

double doublet, (m) = multiplet; Chemical shifts (δ) are expressed in parts per million (ppm) and J values are given in hertz (Hz). IR spectra were recorded on an FT-IR Thermo Nicolet Avatar 360 using a KBr pellet. HRMS was performed on an Agilent LC/MSD TOF instrument. The melting points were measured by the XT-4A melting point apparatus without correction.

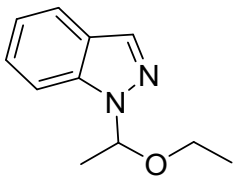
II. Synthesis of hemiacetal azole ether



1a **2a** **3a**

***General Procedure*:** To a Schlenk flask fitted with a magnetic stir bar add **1a** (0.6 mmol, 3 equiv.), **2a** (0.2 mmol, 1 equiv.), $FeCl_3$ (3.24 mg, 10 mol%), TFA (11.40 mg, 50 mol%), $TBABF_4$ (32.93 mg, 50 mol%) and 2 mL MeCN. Stir the mixture at room temperature under air while irradiating with a 390 nm (16 W) *LEDs* for 16 hours. After completion, dilute the reaction with ethyl acetate (20 mL), wash with water (20mL), and dry the organic layer over brine and sodium sulfate. Purify the crude product by flash column chromatography on silica gel (200–300 mesh) using petroleum ether and ethyl acetate (15:1) as eluent to afford the product in 86% yield[1].

III. Characterization of the products



1-(1-ethoxyethyl)-1*H*-indazole (3a)

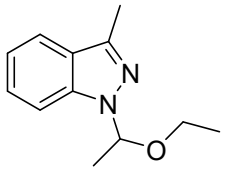
The crude product was separated and purified via silica gel on column chromatography, eluting with petroleum ether/ethyl acetate (15:1) to obtain colorless oily liquid 3a (32.70 mg) with a reaction yield of 86%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.74 (d, *J* = 8.08 Hz, 1H), 7.70 (d, *J* = 8.52 Hz, 1H), 7.38 (t, *J* = 7.71 Hz, 1H), 7.17 (t, *J* = 7.50 Hz, 1H), 5.91 (q, *J* = 6.09 Hz, 1H), 3.52 – 3.41 (m, 1H), 3.30 – 3.18 (m, 1H), 1.80 (d, *J* = 6.07 Hz, 3H), 1.13 (t, *J*

= 7.03 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 133.5, 126.5, 125.1, 121.3, 121.1, 110.6, 86.8, 63.8, 21.0, 15.0.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{15}N_2O^+$ 191.1179; Found 191.1175.



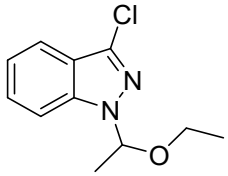
1-(1-ethoxyethyl)-3-methyl-1*H*-indazole (**3b**)

The crude product was separated and purified via silica gel on column chromatography, eluting with petroleum ether/ethyl acetate (15:1) to obtain colorless oily liquid 3b (31.43 mg) with a reaction yield of 77%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.10 Hz, 1H), 7.62 (d, *J* = 8.48 Hz, 1H), 7.36 (t, *J* = 7.12 Hz, 1H), 7.15 (t, *J* = 7.93 Hz, 1H), 5.81 (q, *J* = 6.07 Hz, 1H), 3.48 – 3.39 (m, 1H), 3.30 – 3.22 (m, 1H), 2.57 (s, 3H), 1.77 (d, *J* = 6.06 Hz, 3H), 1.13 (t, *J* = 7.04 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 139.6, 126.5, 124.5, 120.6, 120.4, 110.5, 86.3, 63.8, 21.0, 15.0, 12.1.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{17}N_2O^+$ 205.1336; Found 205.1331.



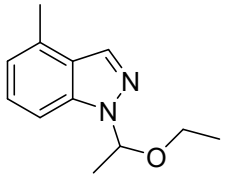
3-chloro-1-(1-ethoxyethyl)-1*H*-indazole (**3c**)

The crude product was separated and purified via silica gel on column chromatography, eluting with petroleum ether/ethyl acetate (15:1) to obtain colorless oily liquid 3c (32.27 mg) with a reaction yield of 72%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.55 (m, 2H), 7.42 (t, *J* = 6.99 Hz, 1H), 7.27 – 7.18 (m, 1H), 5.81 (q, *J* = 6.07 Hz, 1H), 3.51 – 3.42 (m, 1H), 3.35 – 3.26 (m, 1H), 1.77 (d, *J* = 6.09 Hz, 3H), 1.14 (t, *J* = 7.04 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 133.5, 127.7, 122.1, 121.8, 120.0, 111.0, 87.4, 64.0, 21.0, 14.9.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{14}ClN_2O^+$ 225.0790; Found 225.0790.



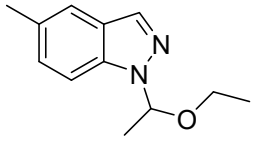
1-(1-ethoxyethyl)-4-methyl-1*H*-indazole (**3d**)

The crude product was separated and purified via silica gel on column chromatography, eluting with petroleum ether/ethyl acetate (15:1) to obtain colorless oily liquid 3d (31.84 mg) with a reaction yield of 78%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.52 (d, *J* = 8.48 Hz, 1H), 7.29 – 7.25 (m, 1H), 6.94 (d, *J* = 6.97 Hz, 1H), 5.89 (q, *J* = 6.08 Hz, 1H), 3.49 – 3.40 (m, 1H), 3.28 – 3.19 (m, 1H), 2.60 (s, 3H), 1.79 (d, *J* = 6.08 Hz, 3H), 1.13 (t, *J* = 7.03 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 132.4, 131.7, 126.7, 125.5, 121.1, 108.0, 86.8, 63.8, 21.0, 18.8, 15.0.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{17}N_2O^+$ 205.1336; Found 205.1333.



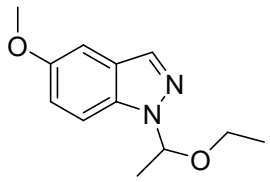
1-(1-ethoxyethyl)-5-methyl-1*H*-indazole (**3e**)

The crude product was separated and purified via silica gel on column chromatography, eluting with petroleum ether/ethyl acetate (15:1) to obtain colorless oily liquid 3e (32.25 mg) with a reaction yield of 79%.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.91 (s, 1H), 7.60 (d, *J* = 8.58 Hz, 1H), 7.50 (s, 1H), 7.22 (d, *J* = 8.63 Hz, 1H), 5.87 (q, *J* = 6.08 Hz, 1H), 3.50 – 3.39 (m, 1H), 3.29 – 3.18 (m, 1H), 2.46 (s, 3H), 1.79 (d, *J* = 6.06 Hz, 3H), 1.13 (t, *J* = 7.04 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 132.9, 130.6, 128.5, 125.5, 120.3, 110.3, 86.8, 63.7, 21.4, 21.0, 15.0.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{17}N_2O^+$ 205.1336; Found 205.1335.



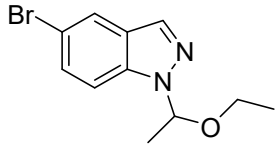
1-(1-ethoxyethyl)-5-methoxy-1*H*-indazole (**3f**)

The crude product was separated and purified via silica gel on column chromatography, eluting with petroleum ether/ethyl acetate (15:1) to obtain colorless oily liquid 3f (36.98 mg) with a reaction yield of 84%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.60 (d, *J* = 8.83 Hz, 1H), 7.11 – 7.03 (m, 2H), 5.84 (q, *J* = 6.07 Hz, 1H), 3.84 (s, 3H), 3.50 – 3.38 (m, 1H), 3.30 – 3.17 (m, 1H), 1.77 (d, *J* = 6.10 Hz, 3H), 1.12 (t, *J* = 7.04 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 134.4, 132.7, 125.4, 118.7, 111.6, 100.3, 87.0, 63.7, 55.7, 21.0, 15.0.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{17}N_2O_2^+$ 221.1285; Found 221.1283.



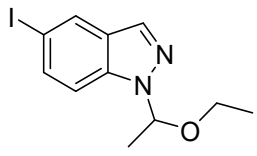
5-bromo-1-(1-ethoxyethyl)-1*H*-indazole (**3g**)

The crude product was separated and purified via silica gel on column chromatography, eluting with petroleum ether/ethyl acetate (15:1) to obtain colorless oily liquid 3g (41.27 mg) with a reaction yield of 77%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.86 (d, *J* = 1.14 Hz, 1H), 7.59 (d, *J* = 8.91 Hz, 1H), 7.43 (dd, *J* = 8.92, 1.83 Hz, 1H), 5.86 (q, *J* = 6.07 Hz, 1H), 3.48 – 3.38 (m, 1H), 3.27 – 3.15 (m, 1H), 1.76 (d, *J* = 6.07 Hz, 3H), 1.11 (t, *J* = 7.04 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 132.6, 129.5, 126.6, 123.7, 114.2, 112.1, 87.3, 63.9, 21.0, 14.9.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{14}BrN_2O^+$ 269.0285; Found 269.0283.



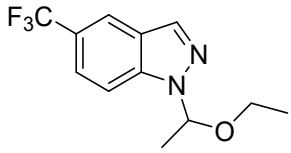
1-(1-ethoxyethyl)-5-iodo-1*H*-indazole (**3h**)

The crude product was separated and purified via silica gel on column chromatography, eluting with petroleum ether/ethyl acetate (15:1) to obtain colorless oily liquid 3h (45.50 mg) with a reaction yield of 72%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 7.89 (s, 1H), 7.59 (dd, *J* = 8.83, 1.59 Hz, 1H), 7.50 (d, *J* = 8.86 Hz, 1H), 5.85 (q, *J* = 6.07 Hz, 1H), 3.48 – 3.39 (m, 1H), 3.25 – 3.15 (m, 1H), 1.75 (d, *J* = 6.10 Hz, 3H), 1.11 (t, *J* = 7.05 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 134.7, 132.3, 130.2, 127.5, 112.5, 87.3, 84.5, 63.9, 21.0, 14.9.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{14}IN_2O^+$ 317.0146; Found 317.0144.



1-(1-ethoxyethyl)-5-(trifluoromethyl)-1*H*-indazole (**3i**)

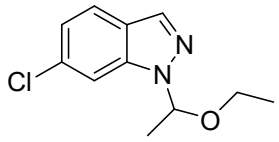
The crude product was separated and purified via silica gel on column chromatography, eluting with petroleum ether/ethyl acetate (15:1) to obtain colorless oily liquid 3i (32.52 mg) with a reaction yield of 63%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (s, 1H), 7.72 (s, 1H), 7.64 (d, *J* = 8.56 Hz, 1H), 7.13 (dd, *J* = 8.59, 1.73 Hz, 1H), 5.84 (q, *J* = 6.07 Hz, 1H), 3.51 – 3.40 (m, 1H), 3.30 – 3.18 (m, 1H), 1.76 (d, *J* = 6.08 Hz, 3H), 1.14 (t, *J* = 7.04 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 134.4, 126.1, 124.8 (q, *J* =272.70 Hz), 123.8 (q, *J* =32.32 Hz), 123.1 (q, *J* =3.37 Hz), 119.5 (q, *J* =4.71 Hz), 111.4, 87.6, 64.1, 21.1, 14.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{14}F_3N_2O^+$ 259.1053; Found 259.1050.



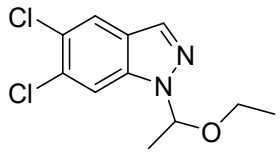
6-chloro-1-(1-ethoxyethyl)-1*H*-indazole (**3j**)

The crude product was separated and purified via silica gel on column chromatography, eluting with petroleum ether/ethyl acetate (15:1) to obtain colorless oily liquid 3j (34.06 mg) with a reaction yield of 76%.

^{1}HNMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.65 (s, 1H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.07 (dd, *J* = 8.6, 1.7 Hz, 1H), 5.77 (q, *J* = 6.1 Hz, 1H), 3.42 – 3.15 (m, 2H), 1.69 (d, *J* = 6.1 Hz, 3H), 1.08 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 133.5, 132.9, 123.6, 122.3, 122.2, 110.5, 87.3, 64.0, 21.0, 15.0.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{14}ClN_2O^+$ 225.0790; Found 225.0793.



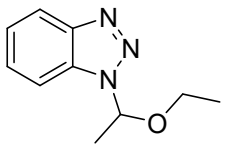
5,6-dichloro-1-(1-ethoxyethyl)-1*H*-indazole (**3k**)

The crude product was separated and purified via silica gel on column chromatography, eluting with petroleum ether/ethyl acetate (15:1) to obtain colorless oily liquid 3k (36.64 mg) with a reaction yield of 71%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.87 (s, 1H), 7.83 (s, 1H), 5.83 (q, *J* = 6.08 Hz, 1H), 3.50 – 3.41 (m, 1H), 3.33 – 3.20 (m, 1H), 1.75 (d, *J* = 6.07 Hz, 3H), 1.15 (t, *J* = 7.05 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 132.8, 131.2, 125.7, 124.5, 122.0, 112.2, 87.7, 64.2, 21.1, 15.0.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{13}Cl_2N_2O^+$ 259.0400; Found 259.0399.



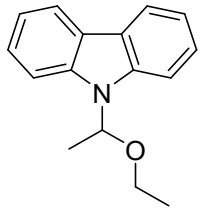
1-(1-ethoxyethyl)-1*H*-benzo[*d*][1,2,3]triazole (**3l**)

The crude product was separated and purified via silica gel on column chromatography, eluting with petroleum ether/ethyl acetate (15:1) to obtain colorless oily liquid 3l (32.49 mg) with a reaction yield of 85%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.39 Hz, 1H), 7.71 (d, *J* = 8.31 Hz, 1H), 7.38 (t, *J* = 8.18 Hz, 1H), 7.28 (t, *J* = 7.15 Hz, 1H), 6.17 (q, *J* = 6.13 Hz, 1H), 3.48 – 3.36 (m, 1H), 3.20 – 3.09 (m, 1H), 1.77 (d, *J* = 6.16 Hz, 3H), 1.03 (t, *J* = 7.04 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 131.1, 127.4, 124.2, 120.0, 111.2, 87.0, 64.3, 21.2, 14.7.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{14}N_3O^+$ 192.1132; Found 192.1132.



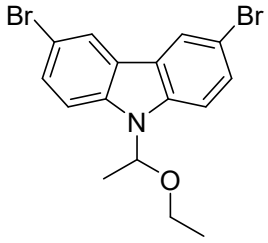
9-(1-ethoxyethyl)-9*H*-carbazole (**3m**)

The crude product was separated and purified via silica gel on column chromatography, eluting with petroleum ether/ethyl acetate (15:1) to obtain brown oily liquid 3m (29.65 mg) with a reaction yield of 62%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 7.76 Hz, 2H), 7.67 (d, *J* = 8.25 Hz, 2H), 7.46 (t, *J* = 7.74 Hz, 2H), 7.27 (t, *J* = 7.47 Hz, 2H), 6.02 (q, *J* = 6.07 Hz, 1H), 3.49 – 3.40 (m, 1H), 3.39 – 3.31 (m, 1H), 1.81 (d, *J* = 6.09 Hz, 3H), 1.18 (t, *J* = 7.04 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3 (2C), 125.8 (2C), 123.7 (2C), 120.4 (2C), 119.5 (2C), 110.6 (2C), 82.4, 63.6, 20.3, 15.0.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{18}NO^+$ 240.1383; Found 240.1385.



3,6-dibromo-9-(1-ethoxyethyl)-9*H*-carbazole (**3n**)

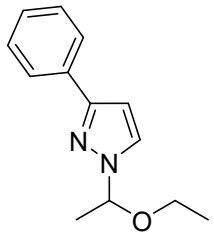
The crude product was separated and purified via silica gel on column chromatography, eluting with petroleum ether/ethyl acetate (15:1) to obtain brown oily liquid 3n (41.86 mg) with a reaction yield of 53%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 – 8.12 (m, 2H), 7.57 – 7.49 (m, 4H), 5.90 (q, *J* = 6.07 Hz, 1H), 3.45 – 3.36 (m, 1H), 3.31 – 3.21 (m, 1H), 1.74 (d, *J* = 6.06 Hz, 3H), 1.15 (t, *J* = 7.04 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2 (2C), 129.3 (2C), 124.4 (2C), 123.4 (2C), 112.8

(2C), 112.3 (2C), 82.7, 63.9, 20.4, 15.0.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{16}Br_2NO^+$ 397.9573 ; Found 397.9577.



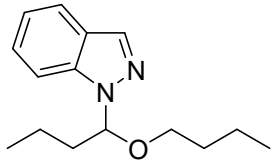
1-(1-ethoxyethyl)-3-phenyl-1*H*-pyrazole (**3o**)

The crude product was separated and purified via silica gel on column chromatography, eluting with petroleum ether/ethyl acetate (15:1) to obtain colorless oily liquid 3o (32.42 mg) with a reaction yield of 75%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.74 (m, 2H), 7.58 (d, *J* = 2.44 Hz, 1H), 7.36 (t, *J* = 7.53 Hz, 2H), 7.29 – 7.23 (m, 1H), 6.60 (d, *J* = 2.45 Hz, 1H), 5.54 (q, *J* = 6.02 Hz, 1H), 3.51 – 3.43 (m, 1H), 3.40 – 3.31 (m, 1H), 1.66 (d, *J* = 6.04 Hz, 3H), 1.12 (t, *J* = 7.05 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 133.6, 128.7 (2C), 127.7, 127.3, 125.8 (2C), 103.8, 87.7, 64.2, 22.3, 15.0.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{17}N_2O^+$ 217.1336; Found 217.1336.



1-(1-butoxybutyl)-1*H*-indazole (**3p**)

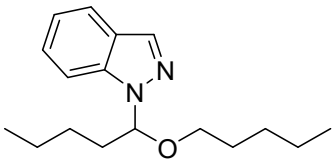
The crude product was separated and purified via silica gel on column chromatography, eluting with petroleum ether/ethyl acetate (15:1) to obtain colorless oily liquid 3p (32.02 mg) with a reaction yield of 65%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 0.94 Hz, 1H), 7.74 (d, *J* = 8.13 Hz, 1H), 7.69 (dd, *J* = 8.52, 0.97 Hz, 1H), 7.36 (t, *J* = 8.27 Hz, 1H), 7.16 (t, *J* = 7.53 Hz, 1H), 5.68 (t, *J* = 6.79 Hz, 1H), 3.41 – 3.34 (m, 1H), 3.24 – 3.16 (m, 1H), 2.23 – 2.07 (m, 2H), 1.53 – 1.24 (m, 6H), 0.90 (t, *J* = 7.38 Hz, 3H), 0.81 (t, *J* = 7.36 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 133.4, 126.4, 125.1, 121.2, 121.1, 110.8, 90.9,

68.3, 36.8, 31.5, 19.4, 18.5, 13.9, 13.8.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{23}N_2O^+$ 247.1805; Found 247.1803.



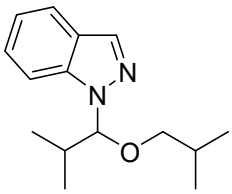
1-(1-(pentyloxy)pentyl)-1*H*-indazole (**3q**)

The crude product was separated and purified via silica gel on column chromatography, eluting with petroleum ether/ethyl acetate (15:1) to obtain colorless oily liquid 3q (37.29 mg) with a reaction yield of 68%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.74 (d, *J* = 8.13 Hz, 1H), 7.69 (d, *J* = 8.48 Hz, 1H), 7.36 (t, *J* = 7.14 Hz, 1H), 7.16 (t, *J* = 7.49 Hz, 1H), 5.66 (t, *J* = 6.86 Hz, 1H), 3.46 – 3.32 (m, 2H), 2.17 (m, 2H), 1.35 – 1.20 (m, 10H), 0.89 (t, *J* = 7.19 Hz, 3H), 0.84 (t, *J* = 7.11 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 133.4, 126.3, 125.1, 121.2, 121.1, 110.8, 91.1, 68.6, 34.5, 29.1, 28.3, 27.3, 22.7, 22.5, 14.2, 14.1.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{27}N_2O^+$ 275.2118; Found 275.2118.



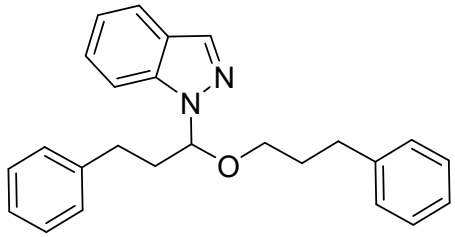
1-(1-isobutoxy-2-methylpropyl)-1*H*-indazole (**3r**)

The crude product was separated and purified via silica gel on column chromatography, eluting with petroleum ether/ethyl acetate (15:1) to obtain colorless oily liquid 3r (32.49 mg) with a reaction yield of 66%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.74 (d, *J* = 8.12 Hz, 1H), 7.69 (d, *J* = 8.49 Hz, 1H), 7.35 (t, *J* = 8.27 Hz, 1H), 7.16 (t, *J* = 7.50 Hz, 1H), 5.21 (d, *J* = 9.09 Hz, 1H), 3.16 – 3.08 (m, 1H), 3.03 – 2.97 (m, 1H), 2.63 – 2.53 (m, 1H), 1.83 (dt, *J* = 13.29, 6.65 Hz, 1H), 1.18 (d, *J* = 6.64 Hz, 3H), 0.87 (d, *J* = 6.68 Hz, 3H), 0.81 (d, *J* = 6.70 Hz, 3H), 0.56 (d, *J* = 6.79 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 133.2, 126.3, 125.1, 121.2, 121.0, 111.1, 96.9, 75.7, 33.4, 28.4, 19.5, 19.4, 19.4, 18.1.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{23}N_2O^+$ 247.1805; Found 247.1807.



1-(3-phenyl-1-(3-phenylpropoxy)propyl)-1*H*-indazole (**3s**)

The crude product was separated and purified via silica gel on column chromatography, eluting with petroleum ether/ethyl acetate (15:1) to obtain colorless oily liquid 3s (45.16 mg) with a reaction yield of 66%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.65 (d, *J* = 8.14 Hz, 1H), 7.51 (d, *J* = 8.55 Hz, 1H), 7.26 (t, *J* = 7.71 Hz, 1H), 7.16 – 7.03 (m, 9H), 6.94 (d, *J* = 7.01 Hz, 2H), 5.53 (t, *J* = 6.34 Hz, 1H), 3.31 – 3.24 (m, 1H), 3.14 – 3.08 (m, 1H), 2.58 – 2.37 (m, 6H), 1.75 – 1.66 (m, 2H).

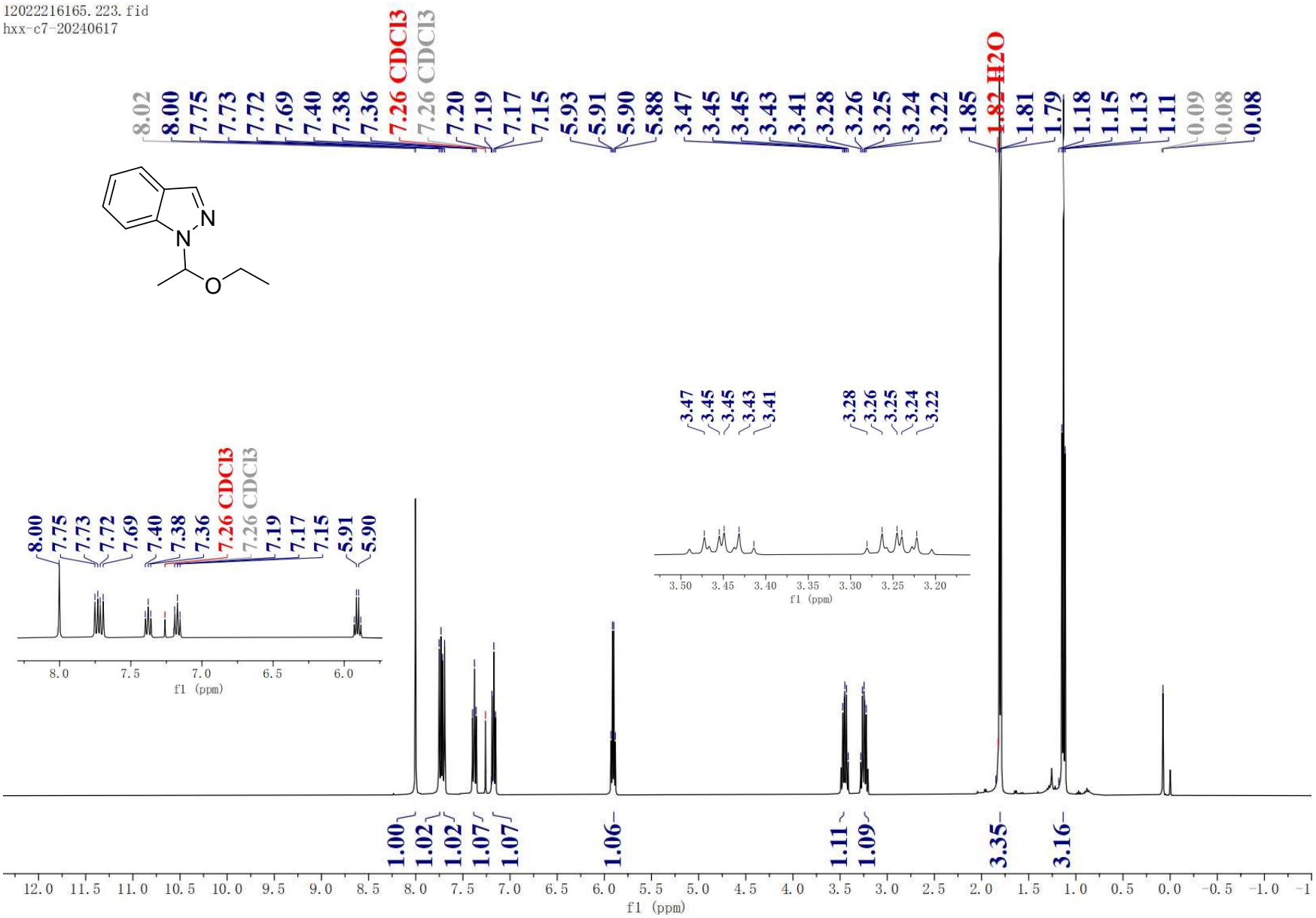
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 140.9, 139.1, 133.8, 128.6 (2C), 128.6 (2C), 128.5 (2C), 128.4 (2C), 126.6, 126.2, 125.9, 125.1, 121.3, 121.2, 110.6, 89.7, 67.8, 36.1, 32.4, 31.4, 31.1.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{27}N_2O^+$ 371.2118; Found 371.2116.

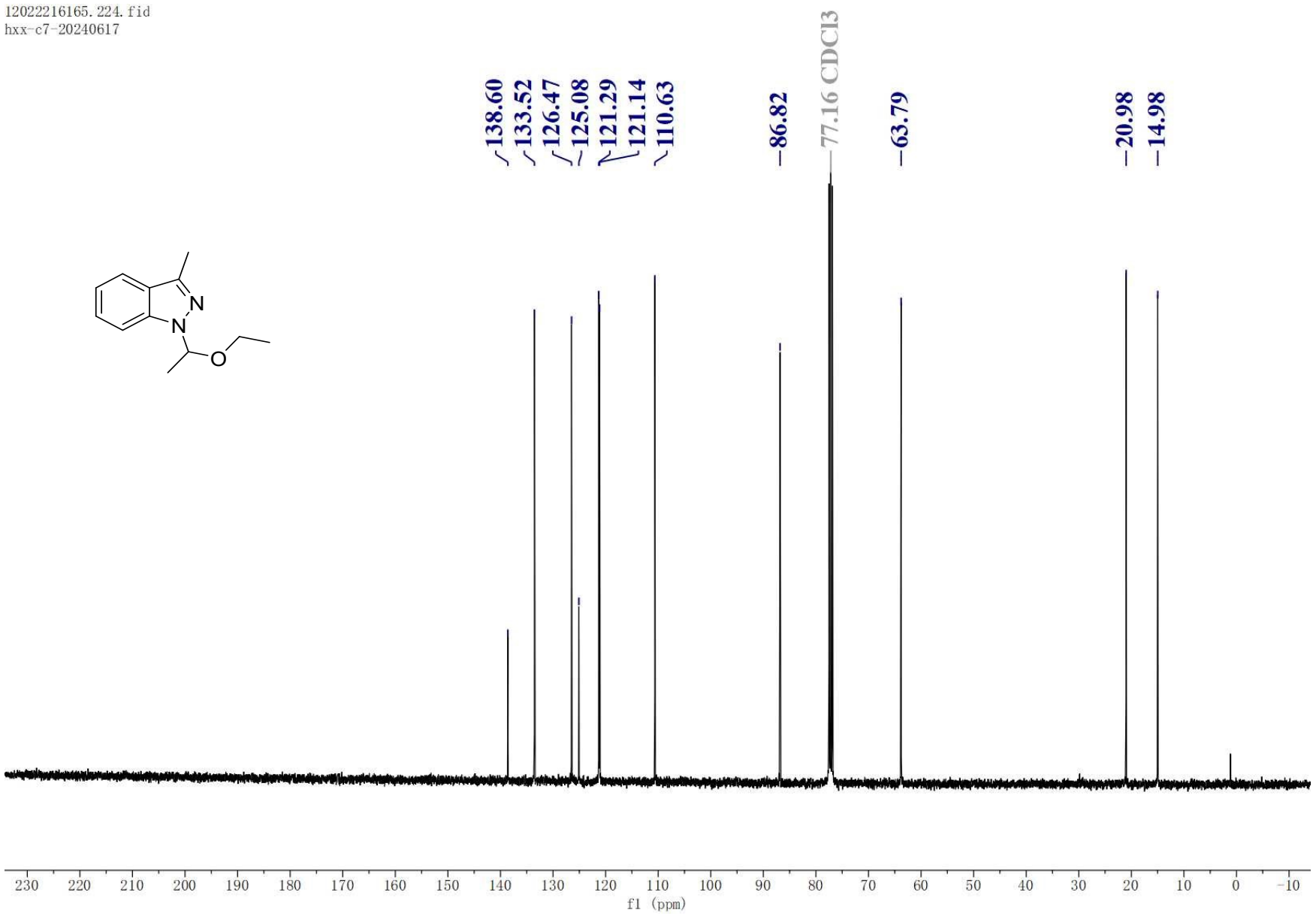
IV. References

1. J. Sun, Y. Zhang, S. Mathan, Y. Wang and Y. Pan, *J. Org. Chem.*, 2016, **81**, 3380-3385.

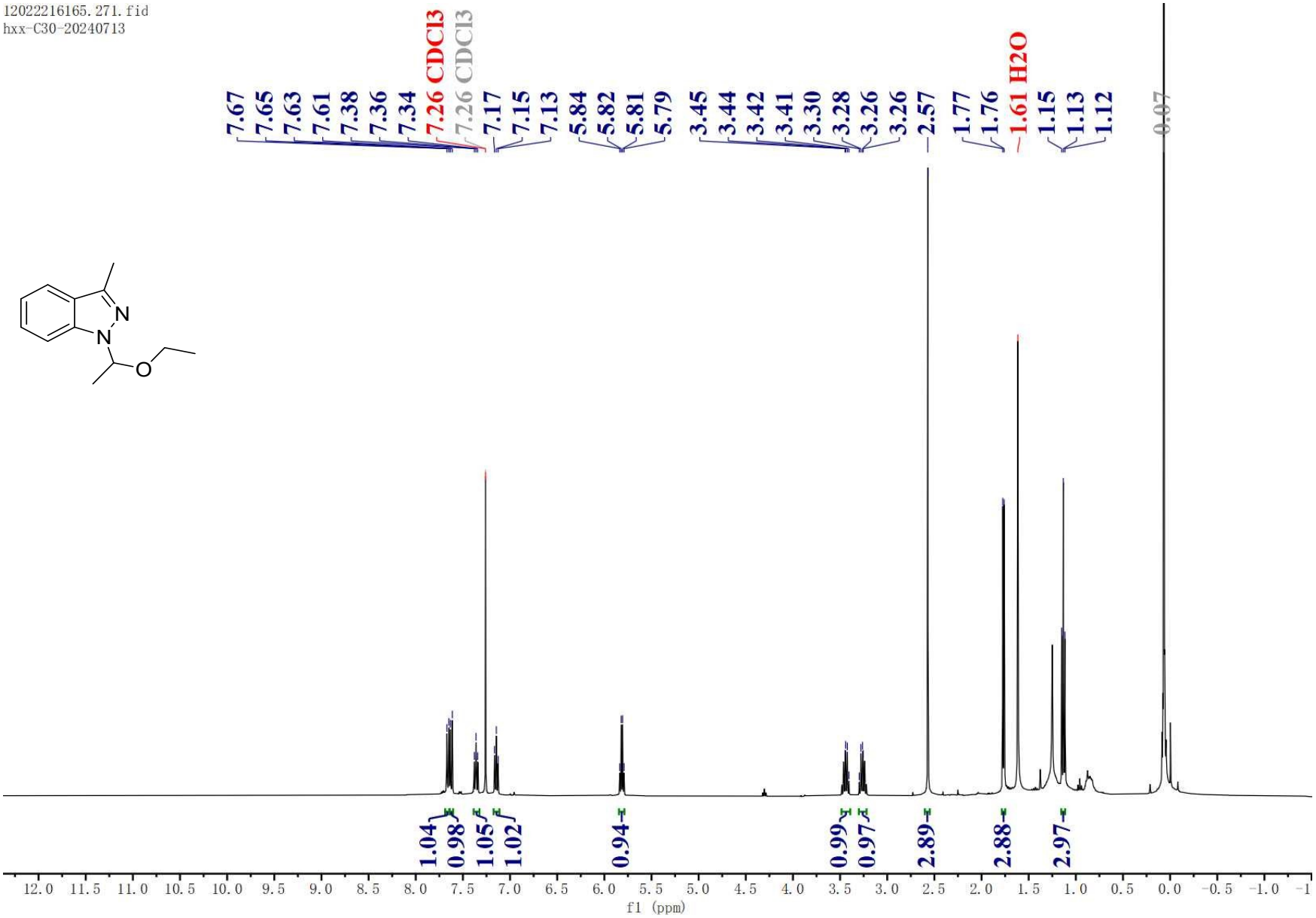
V. NMR Charts



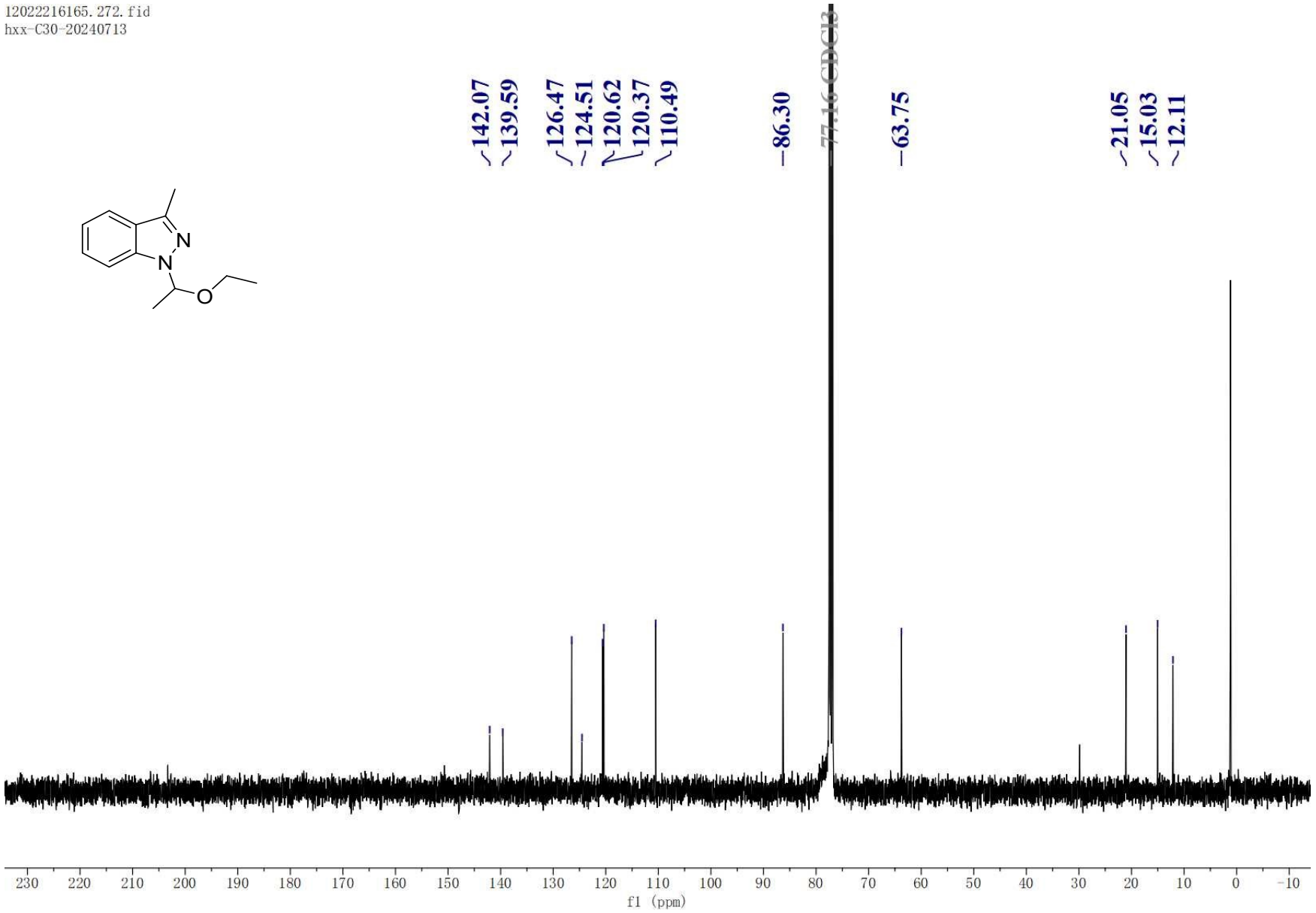
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3a**



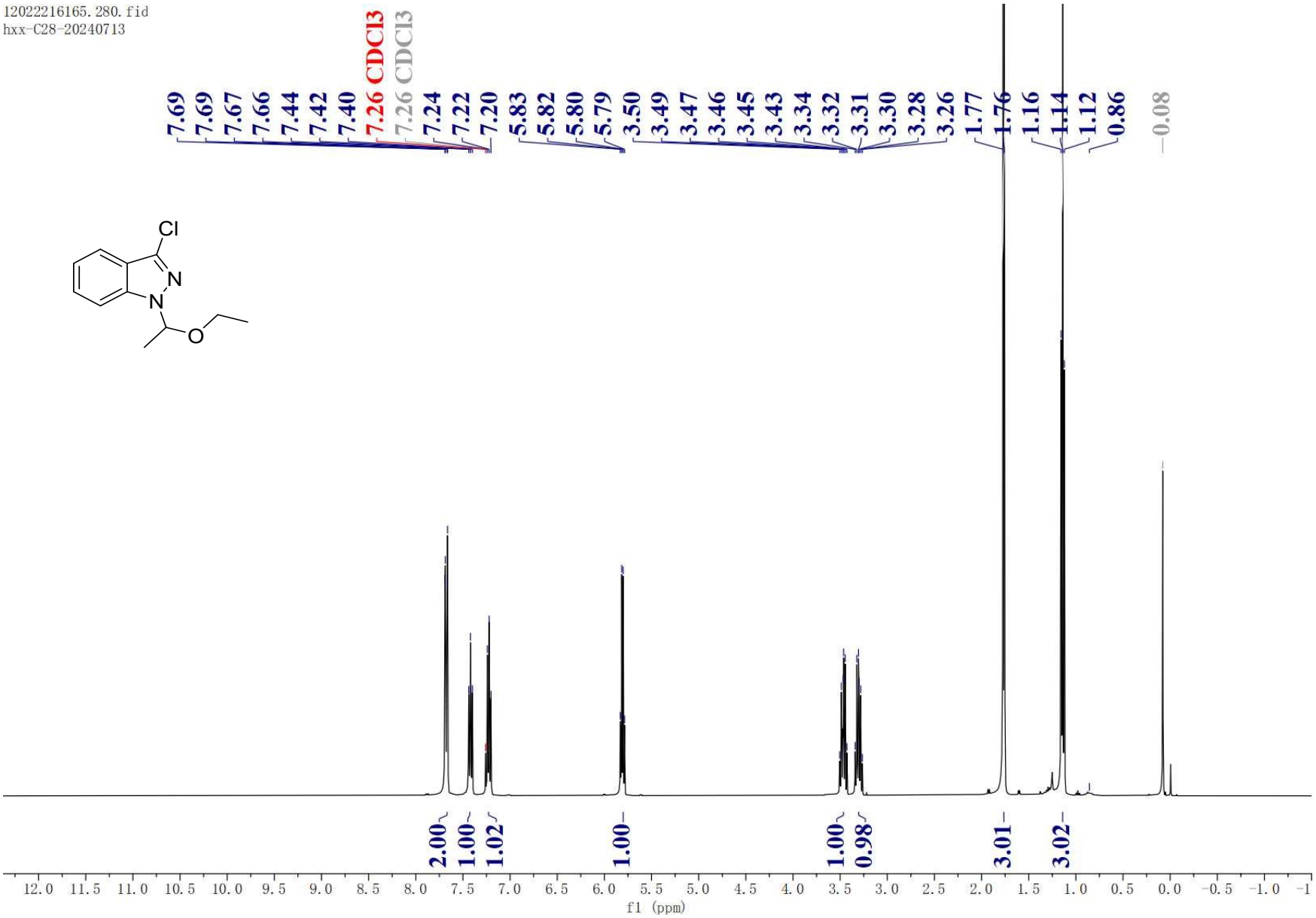
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3a**



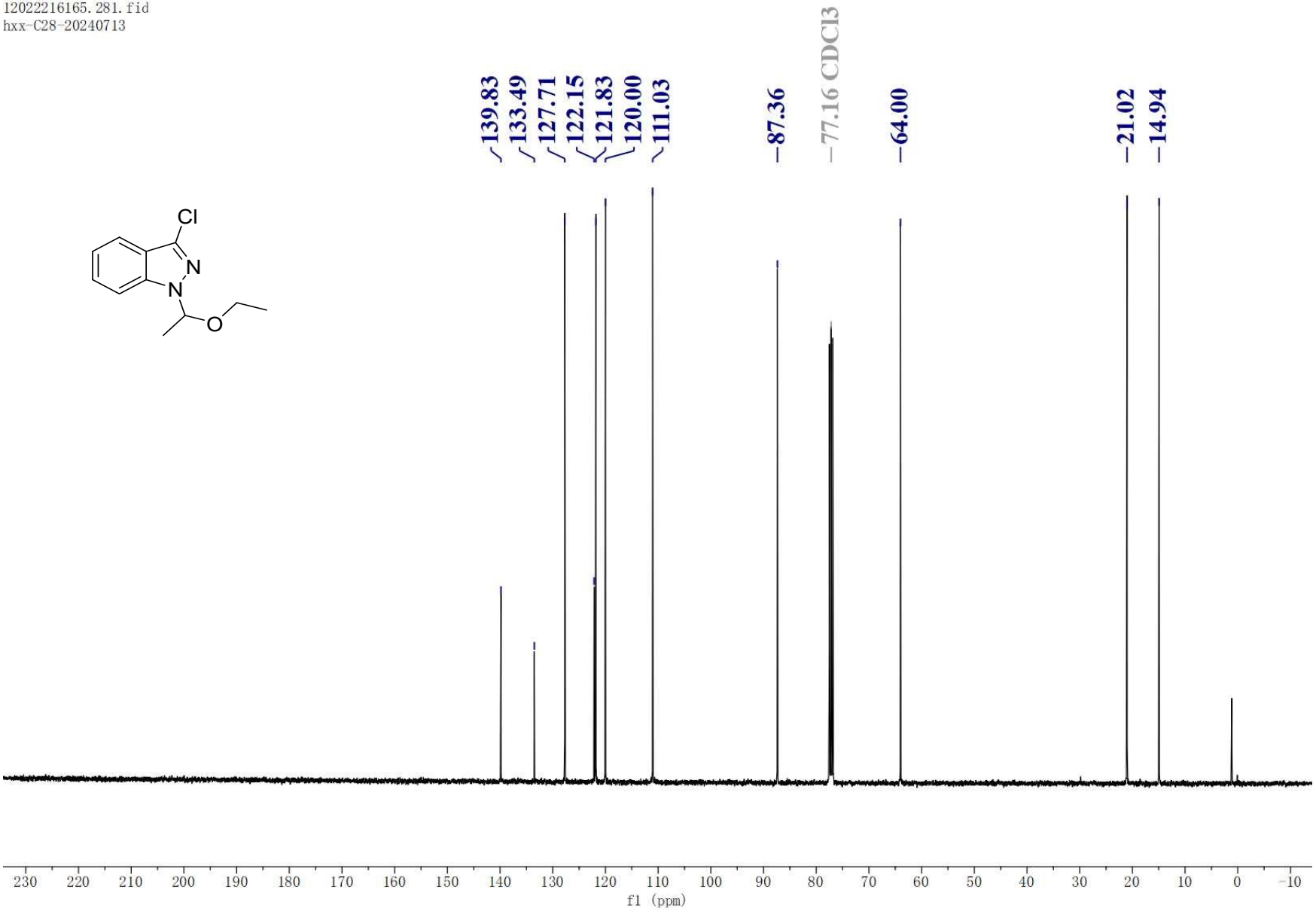
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3b**



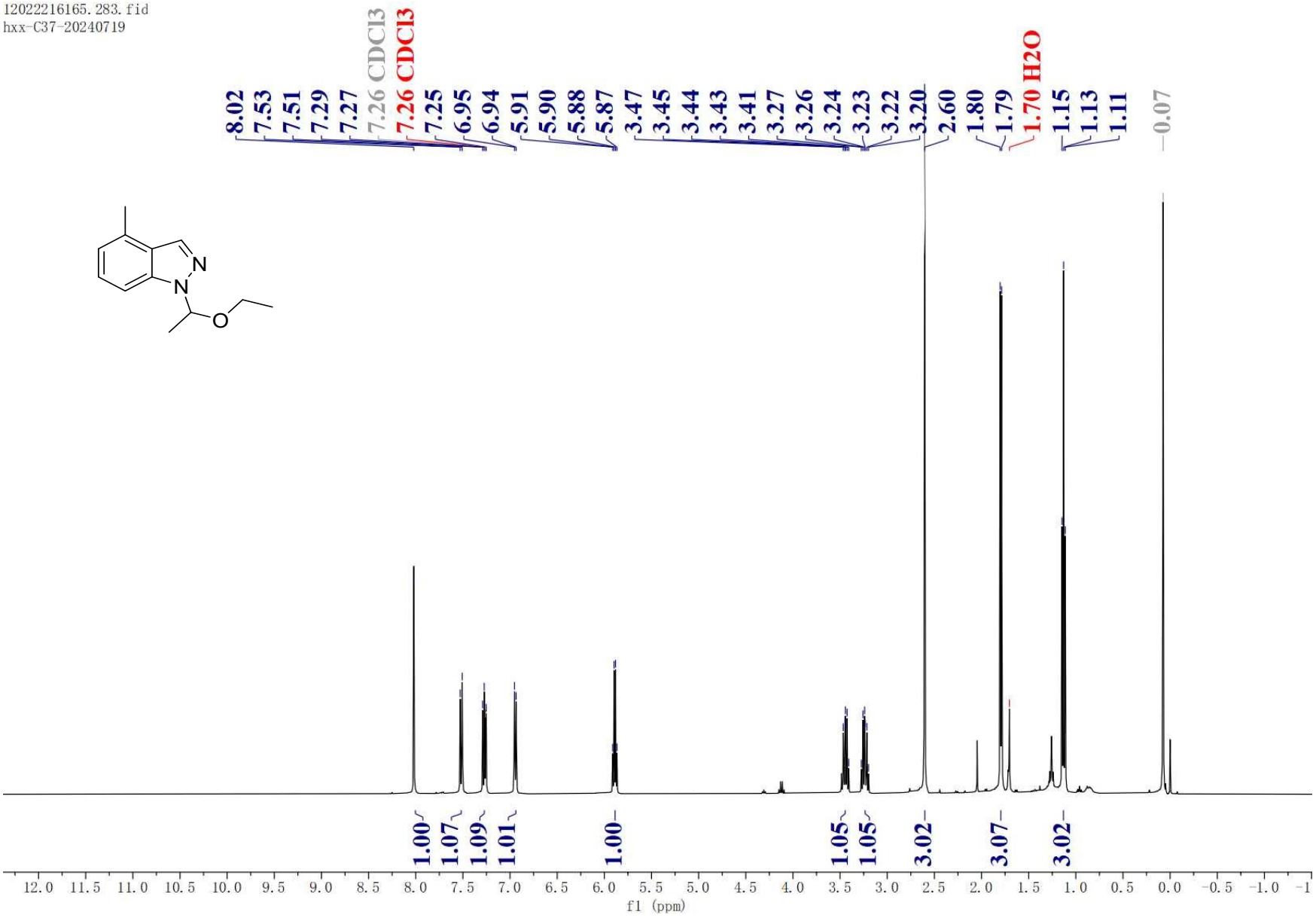
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3b**



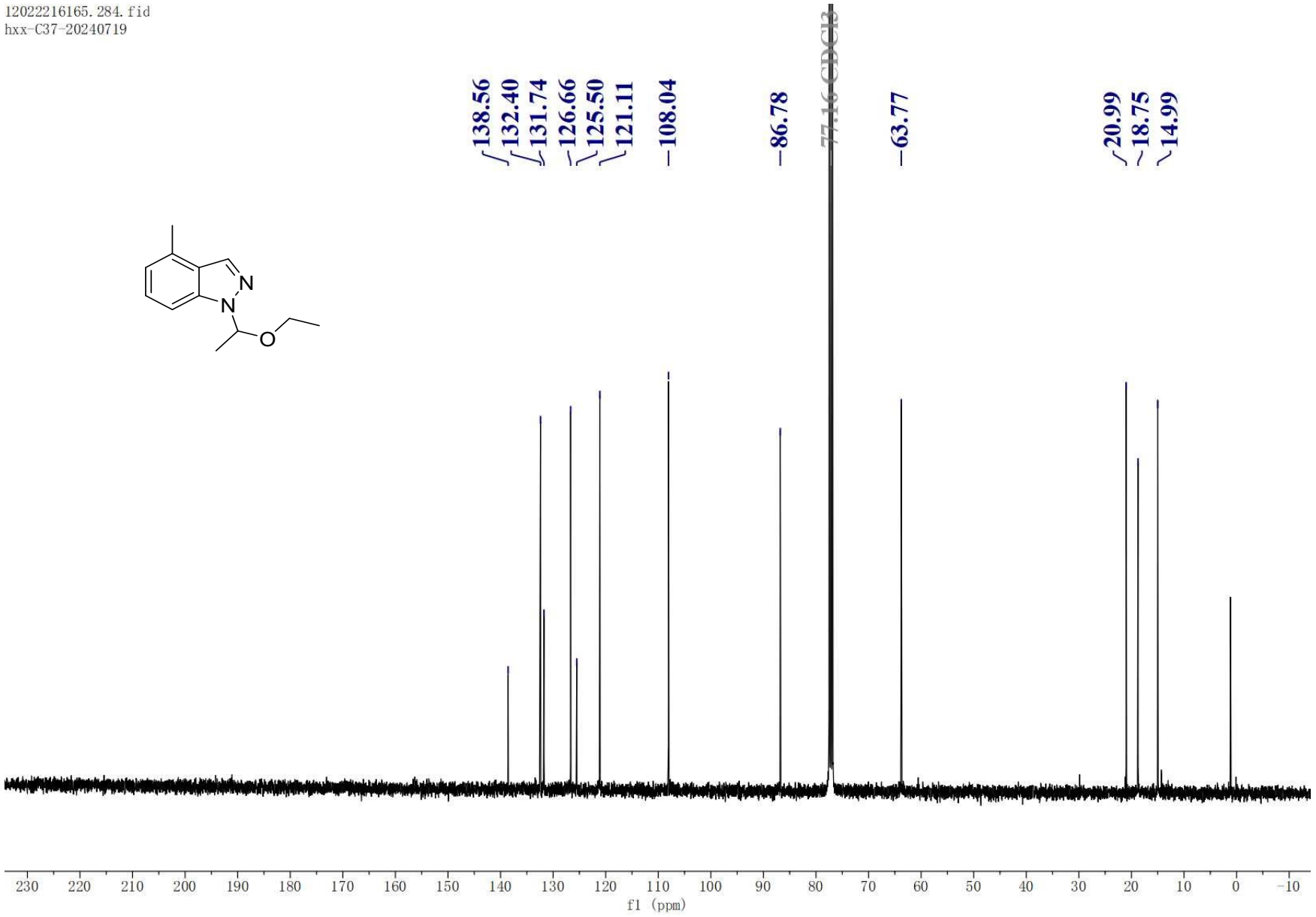
^{1}H-NMR ($CDCl_3$, 400 MHz) **spectrum of 3c**



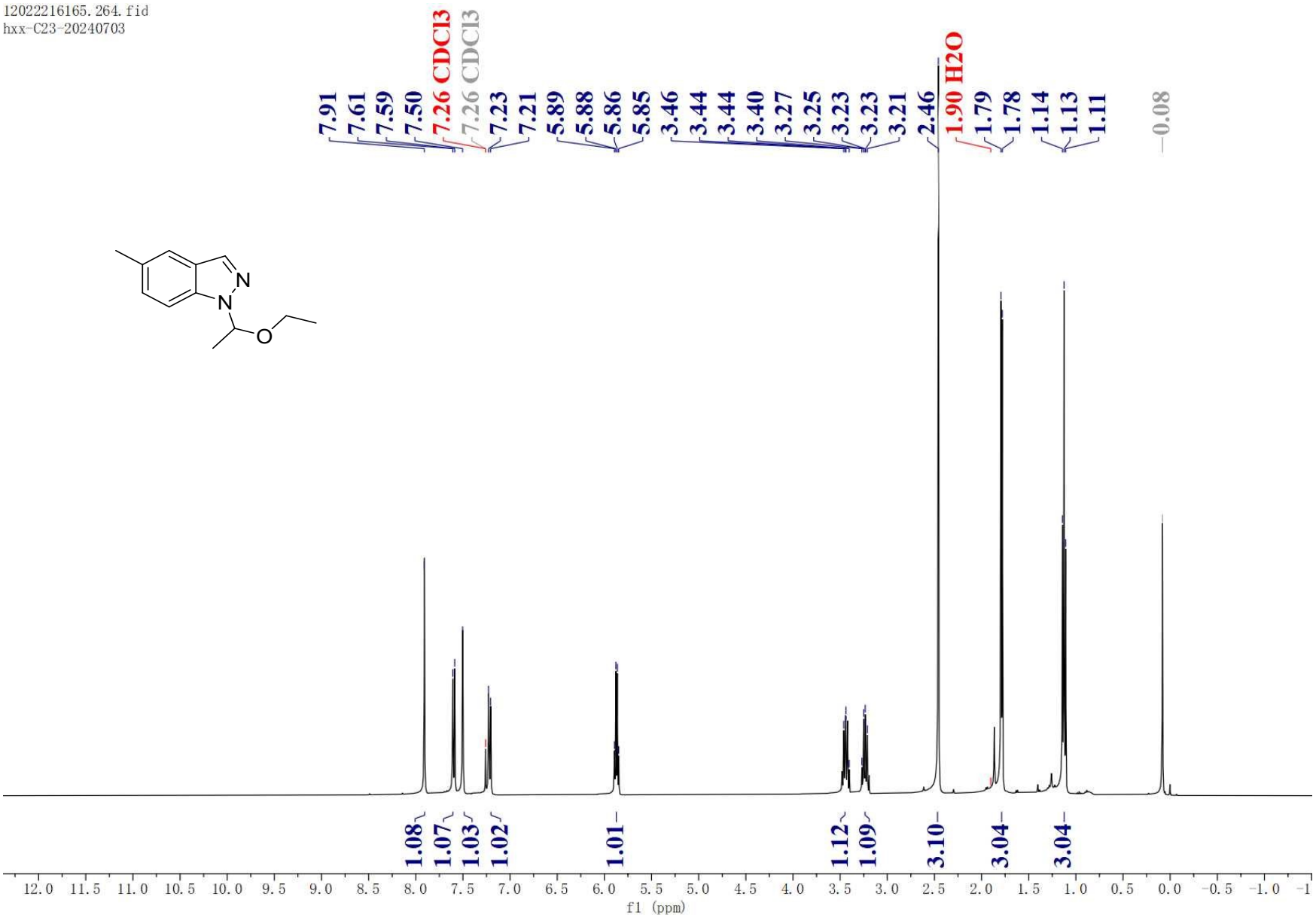
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3c**



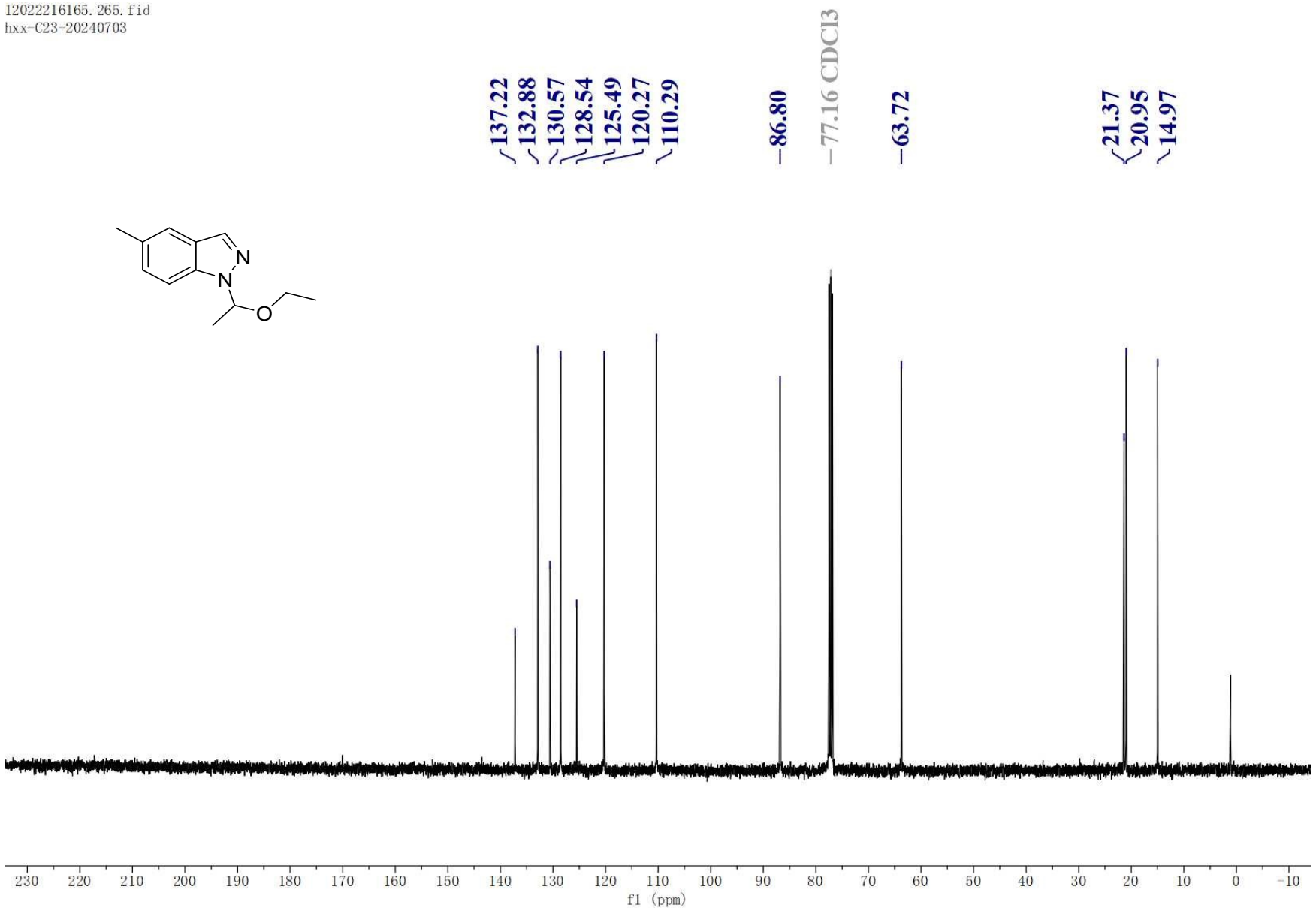
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3d**



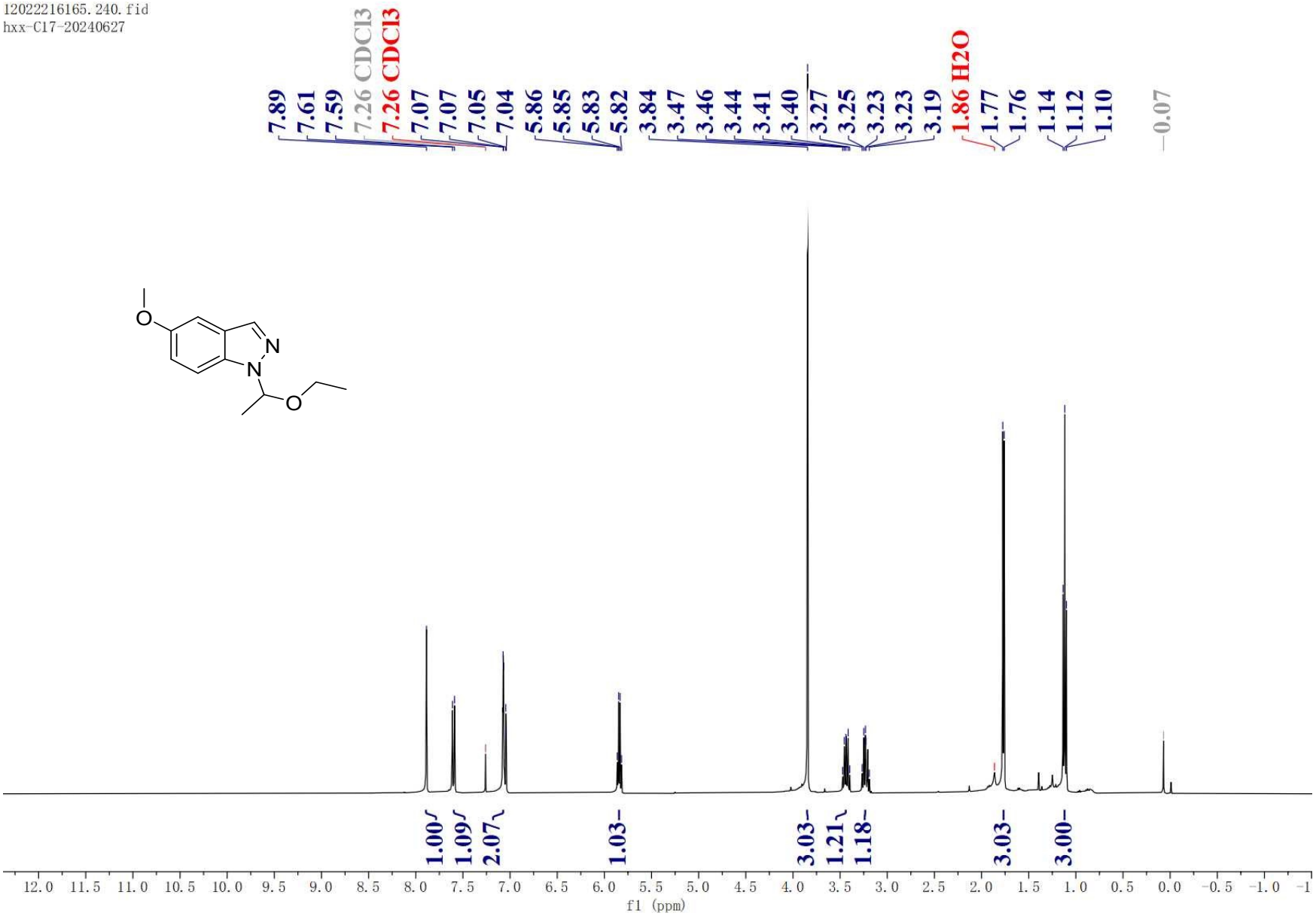
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3d**



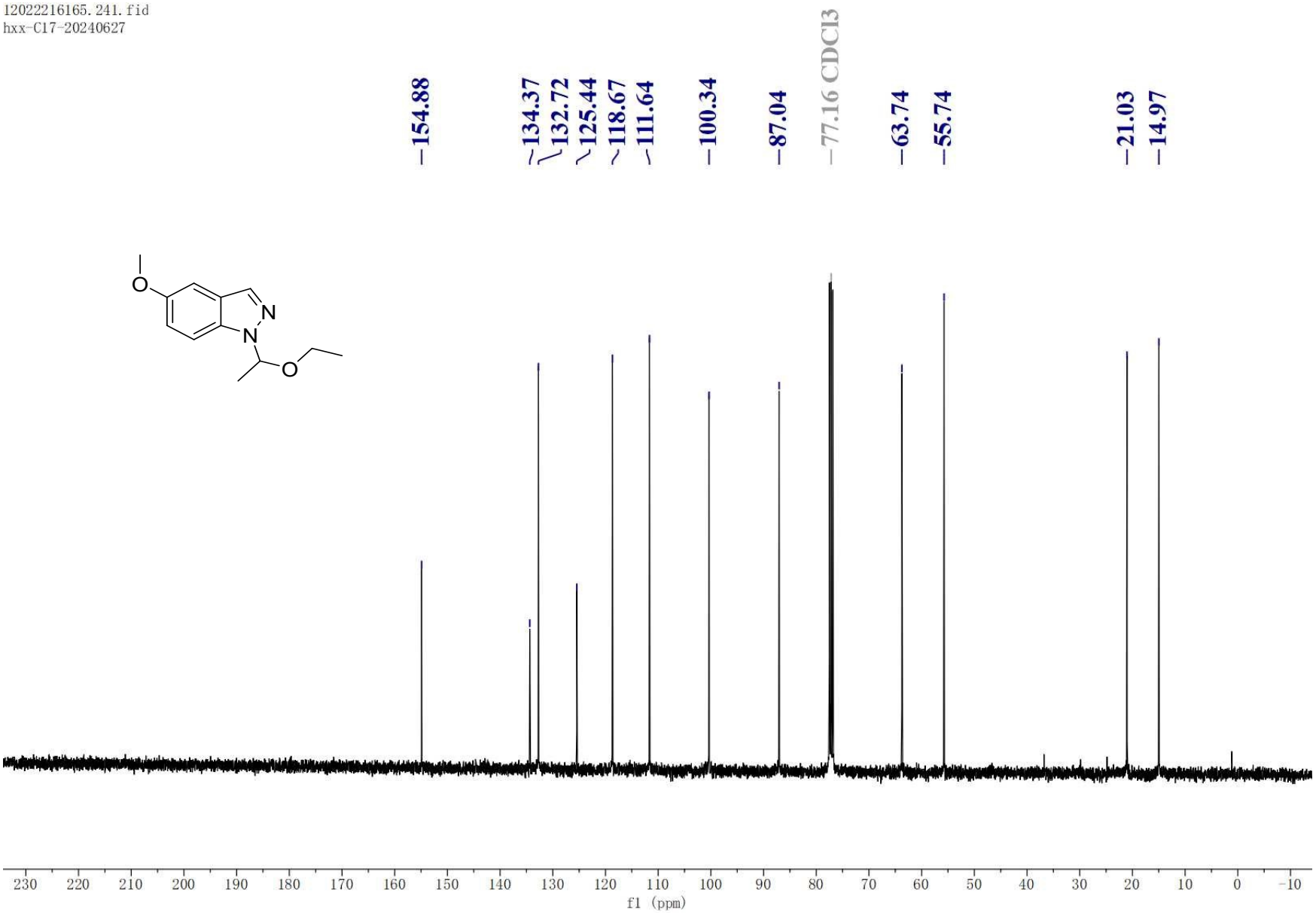
^{1}H-NMR ($CDCl_3$, 400 MHz) **spectrum of 3e**



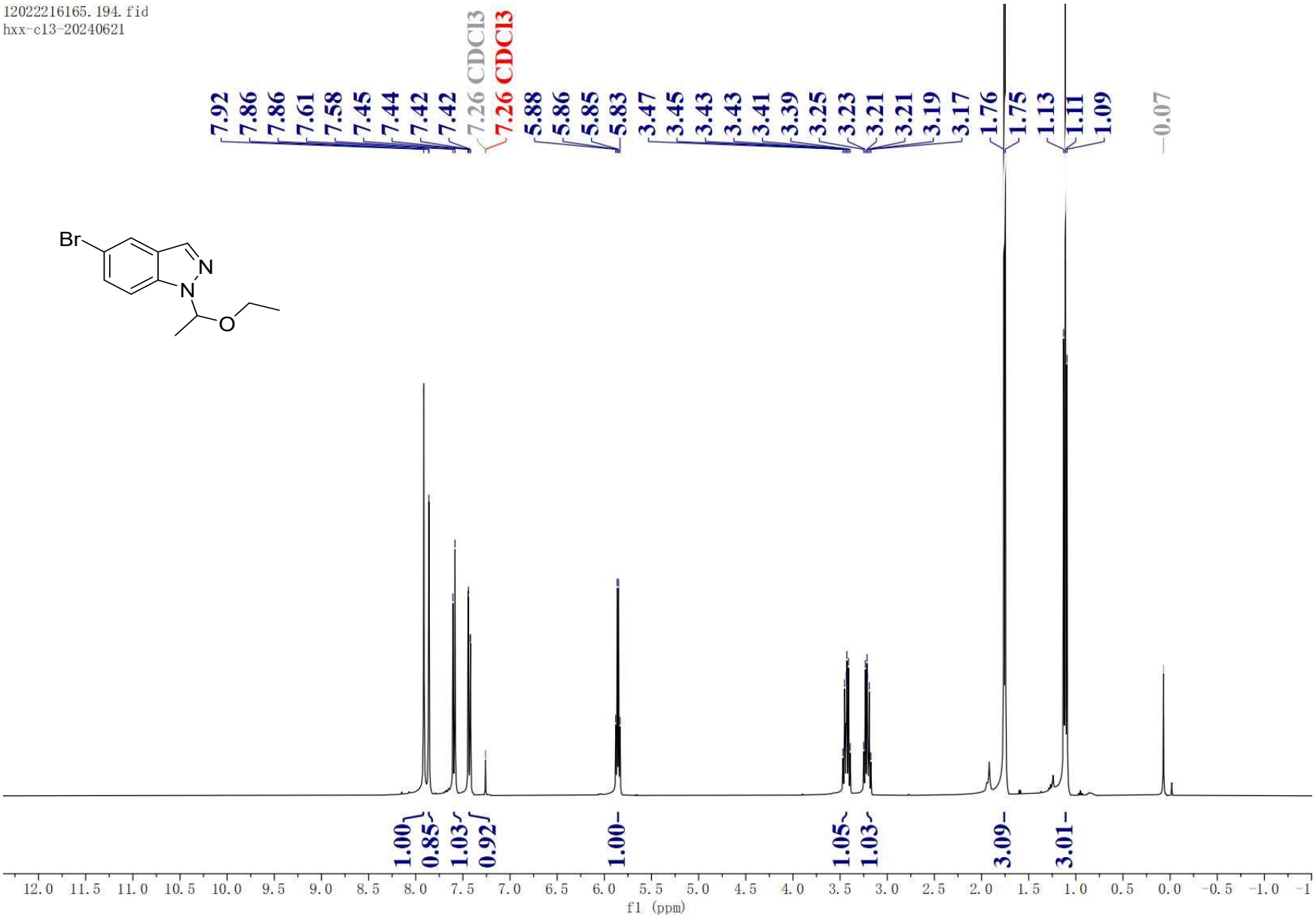
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3e**



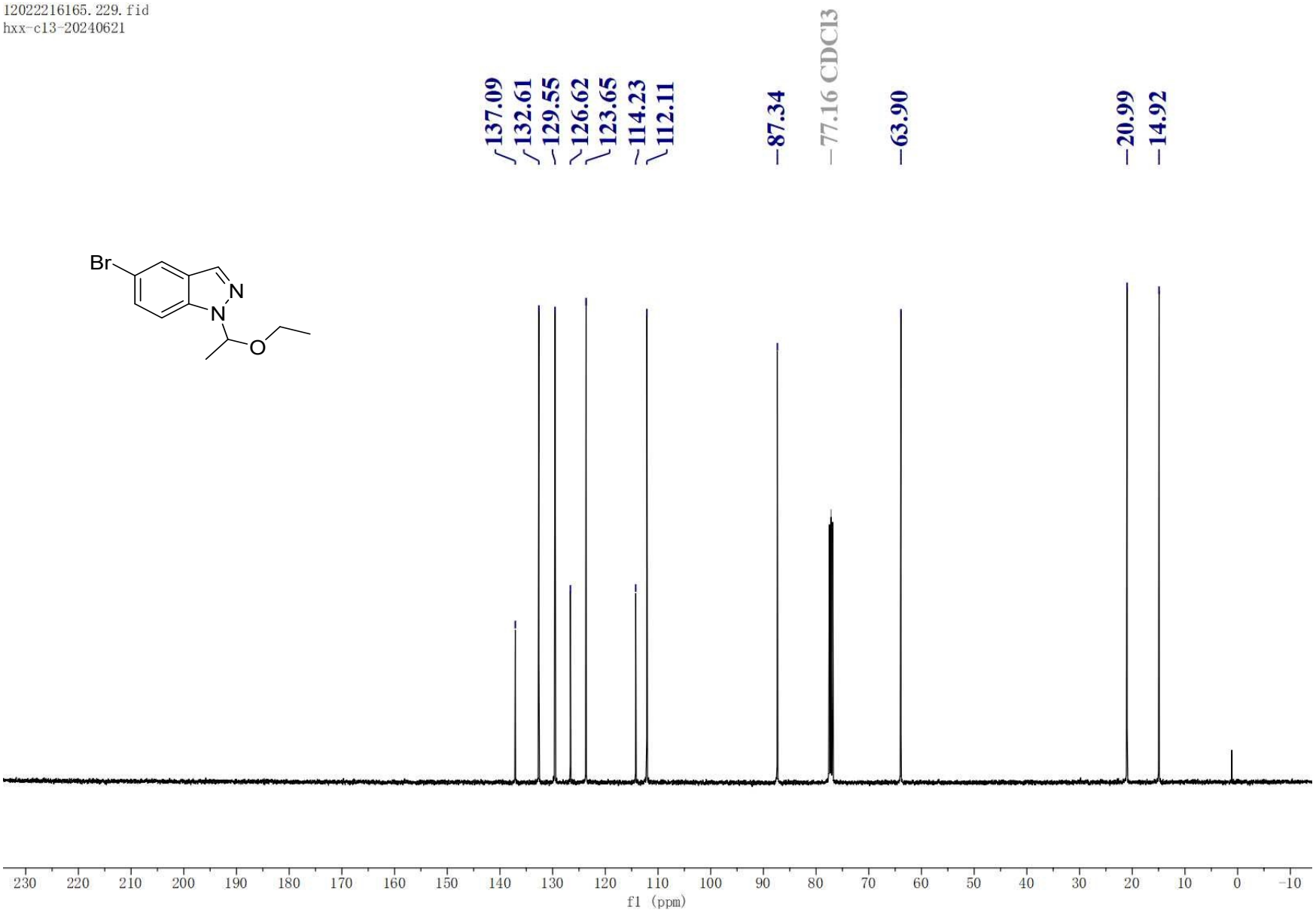
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3f**



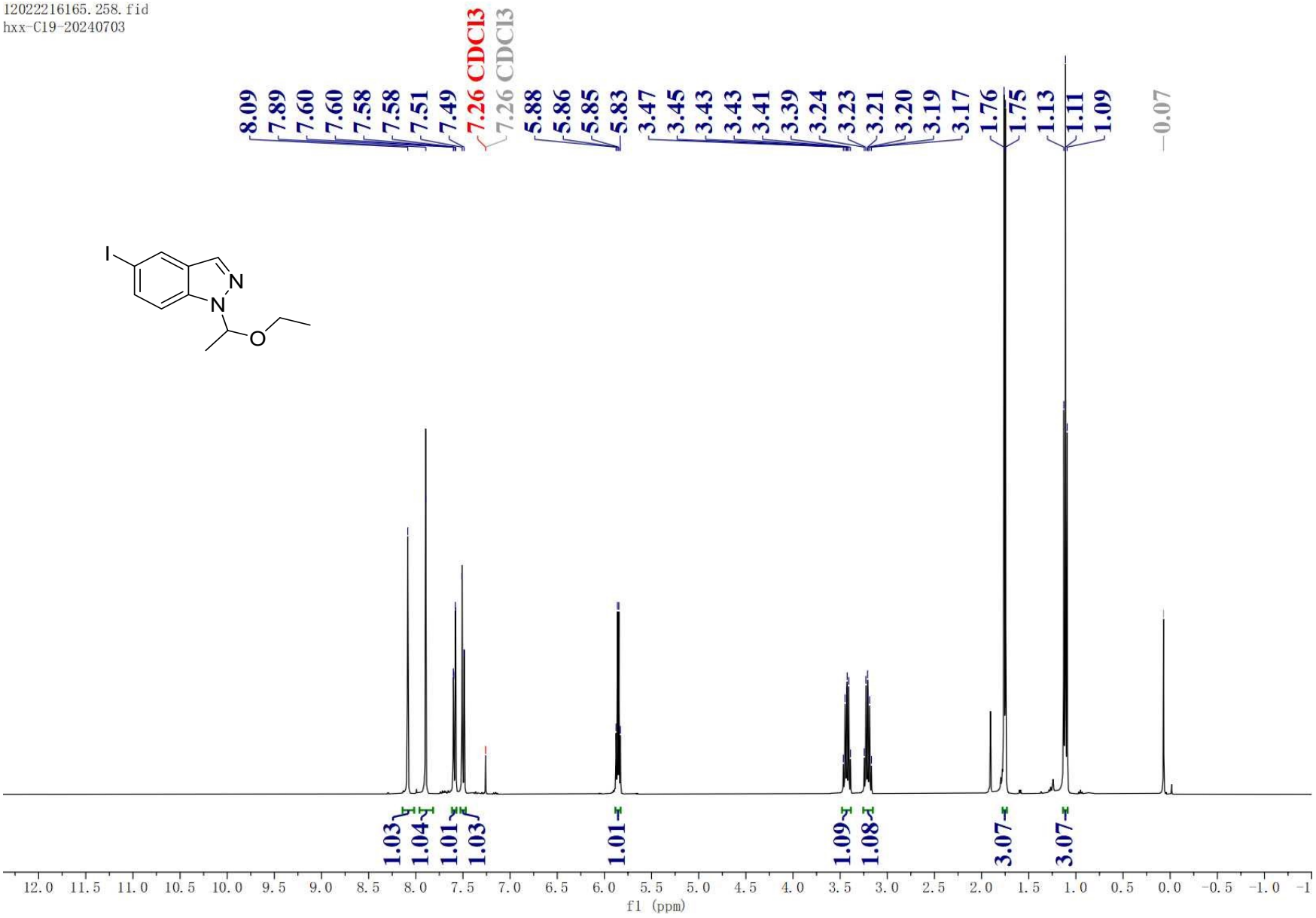
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3f**



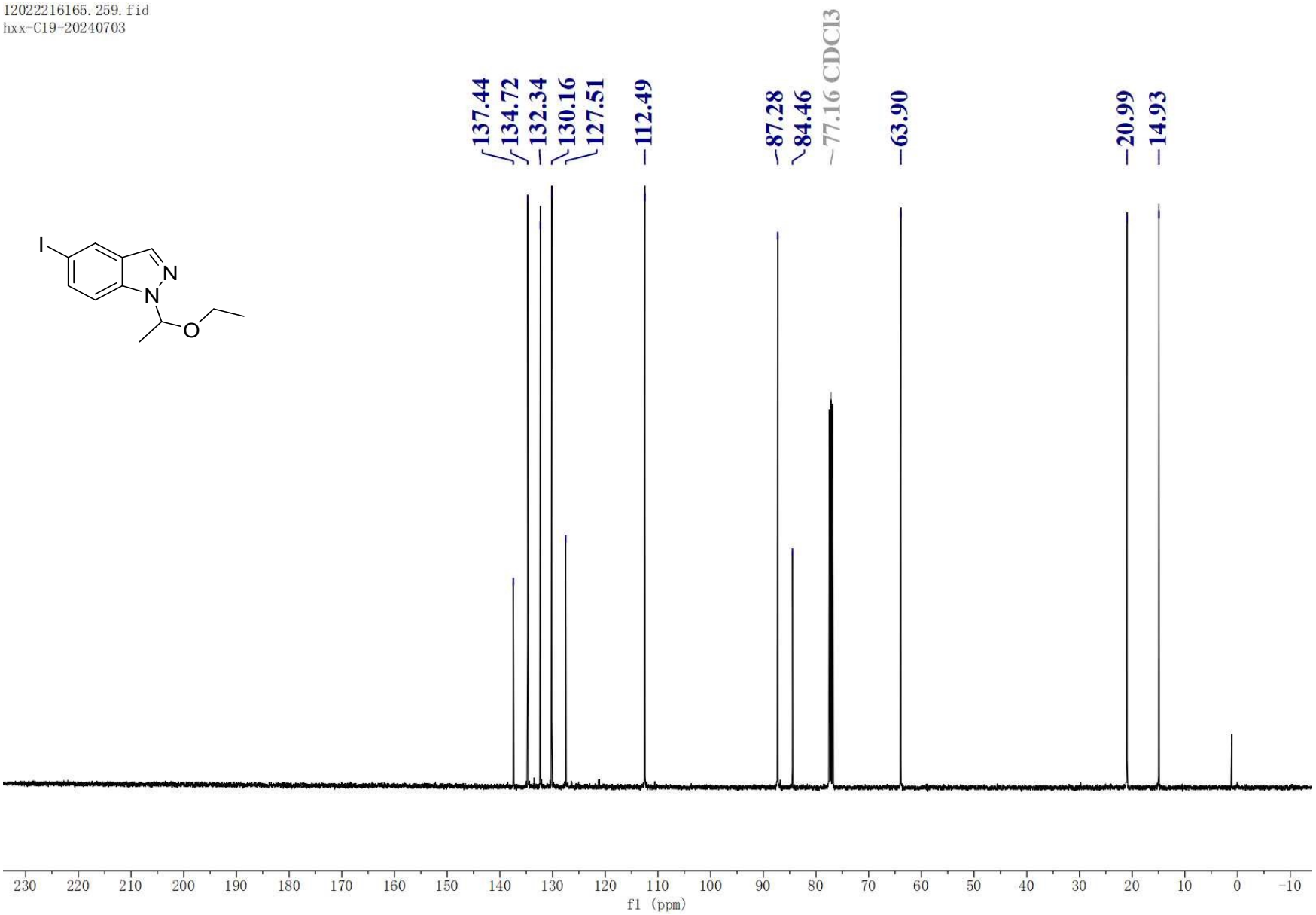
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3g**



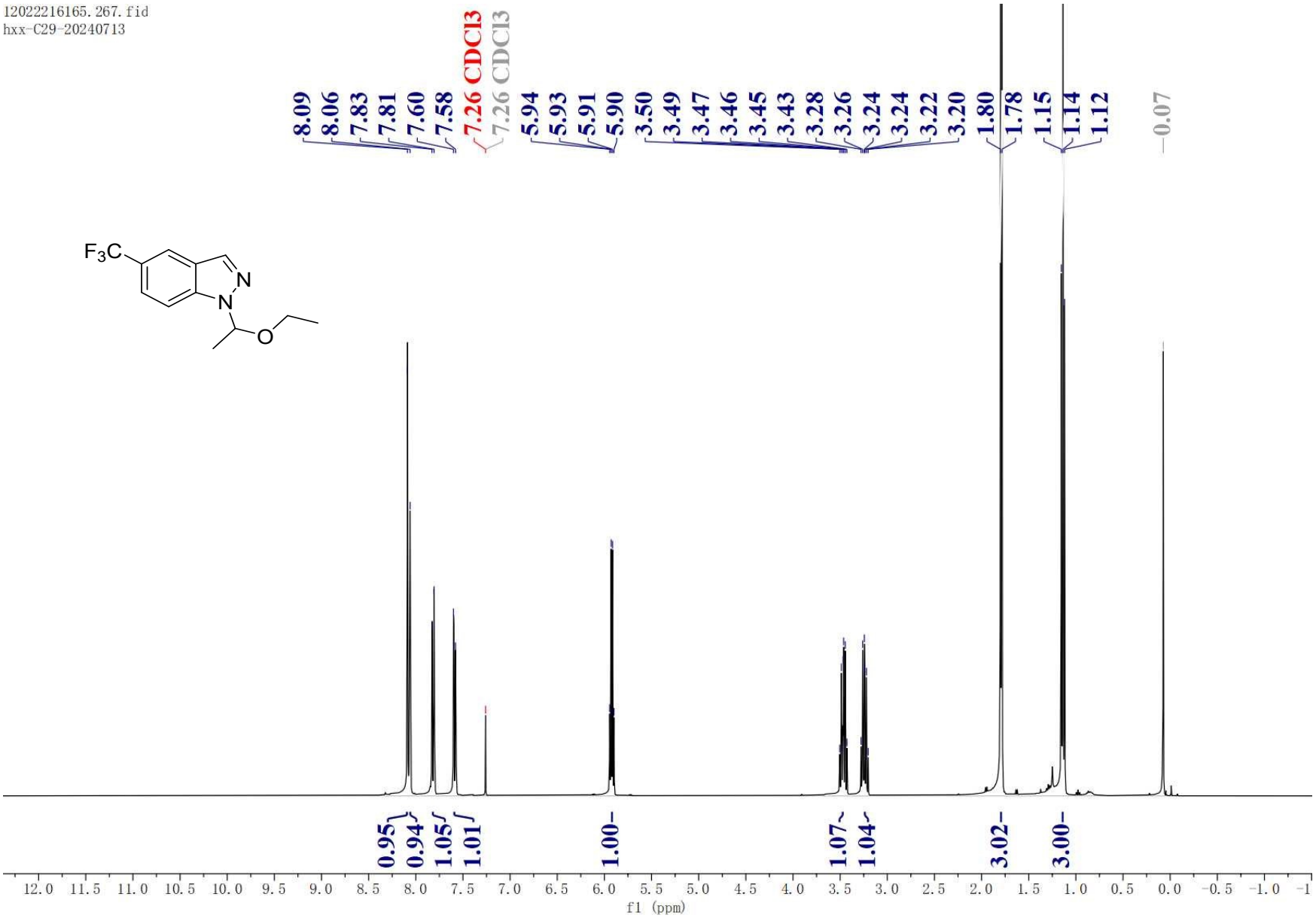
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3g**



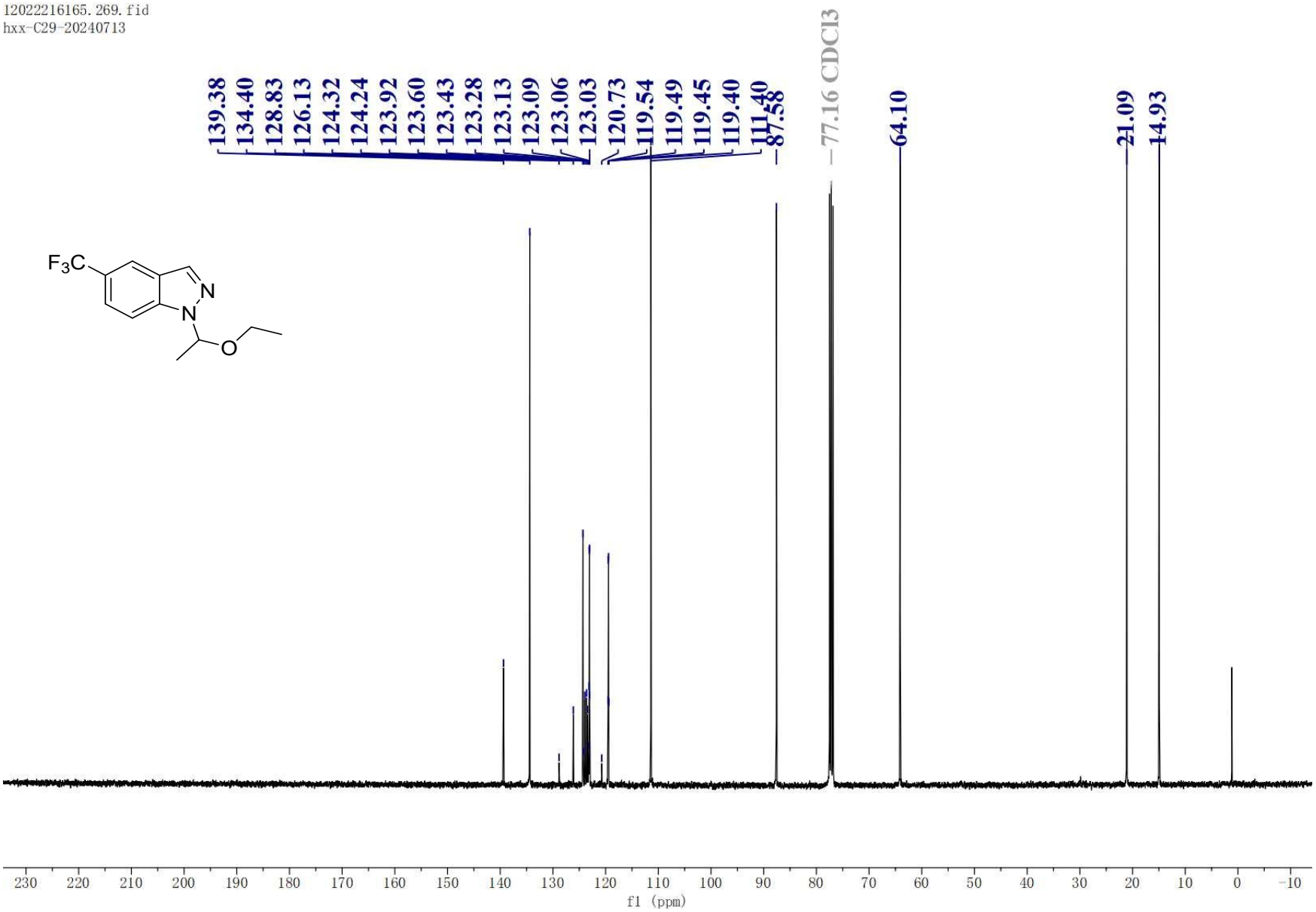
^{1}H-NMR ($CDCl_3$, 400 MHz) **spectrum of 3h**



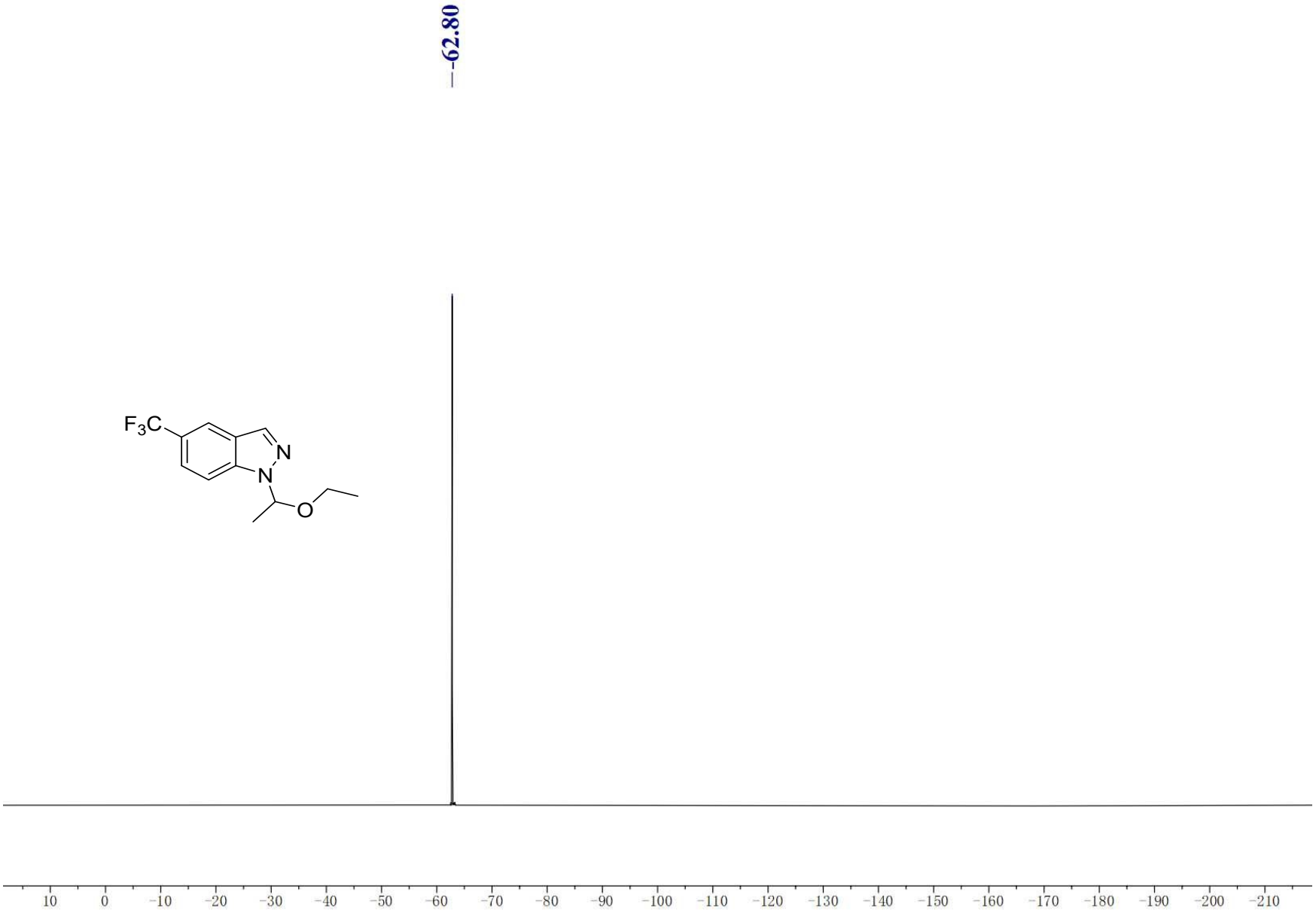
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3h**



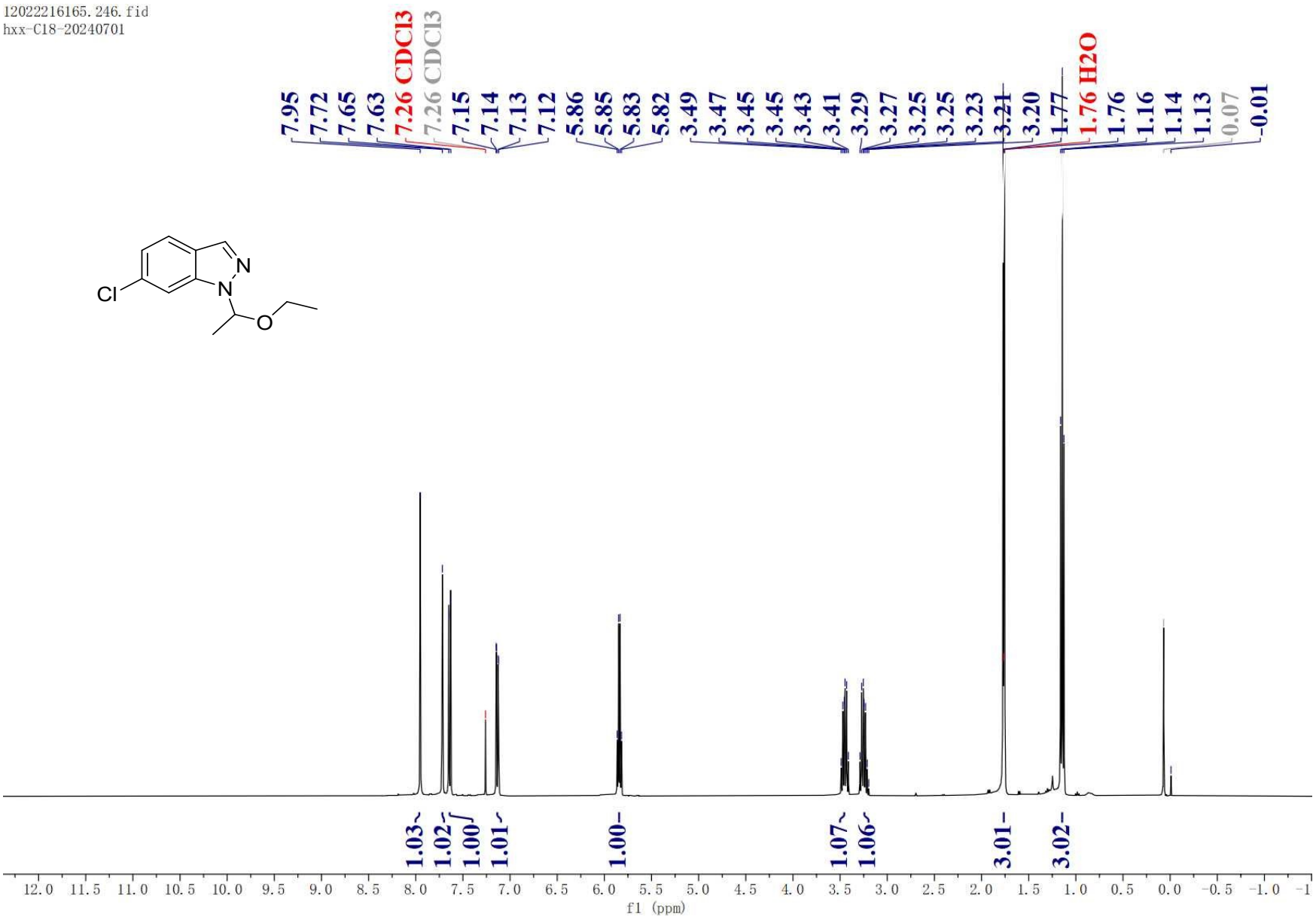
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3i**



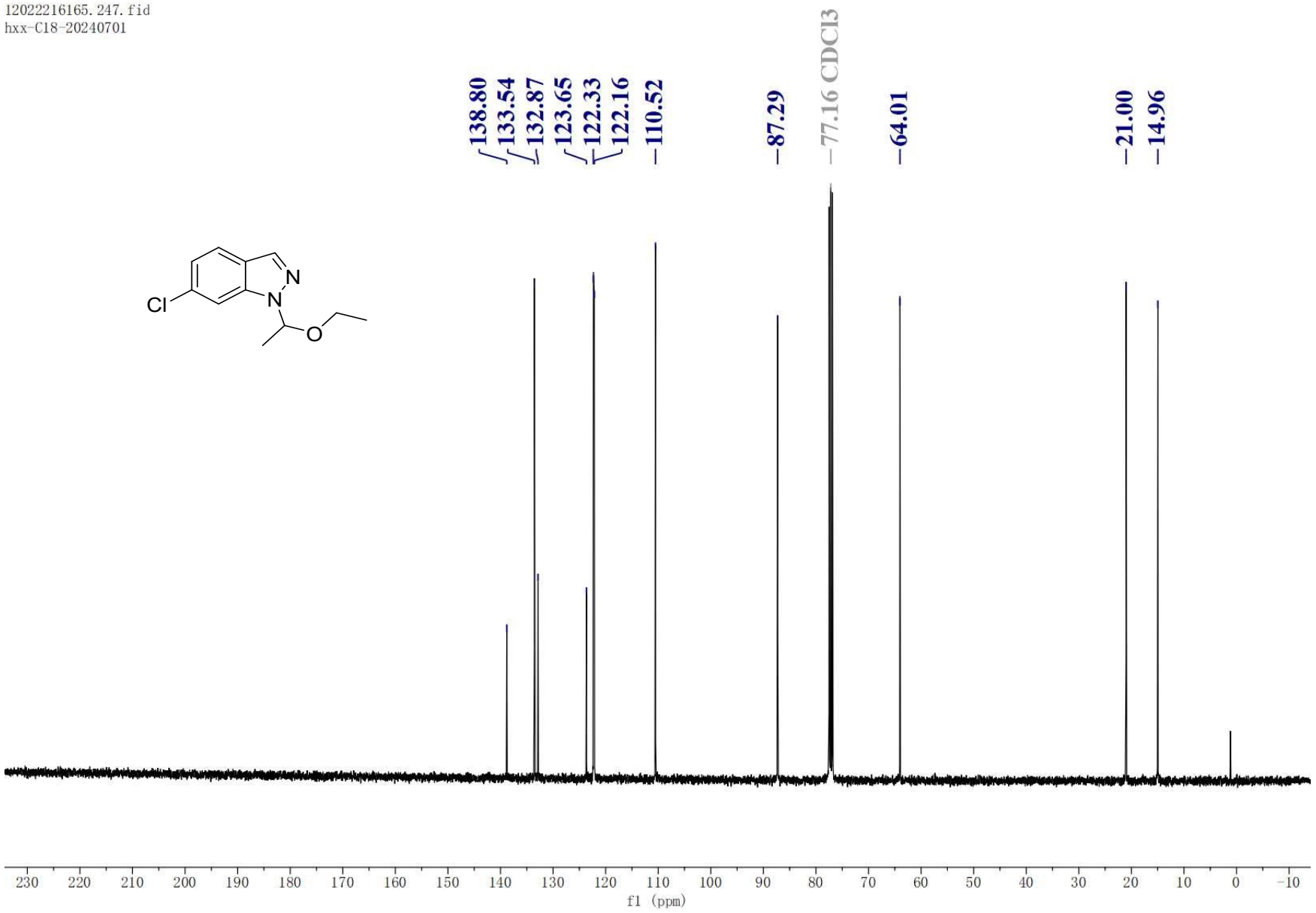
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3i**



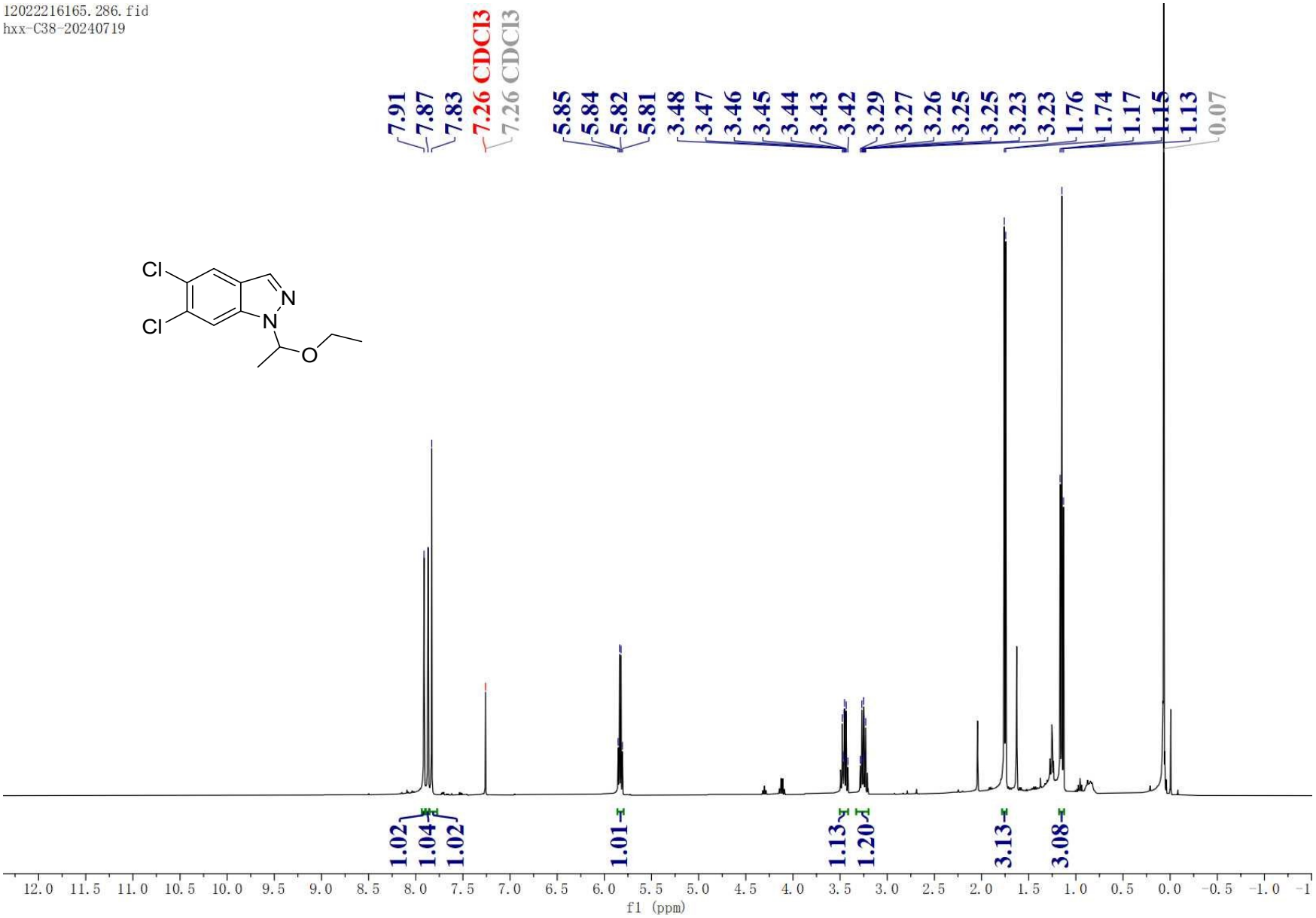
^{19}F NMR (376 MHz, $CDCl_3$**) spectrum of 3i**



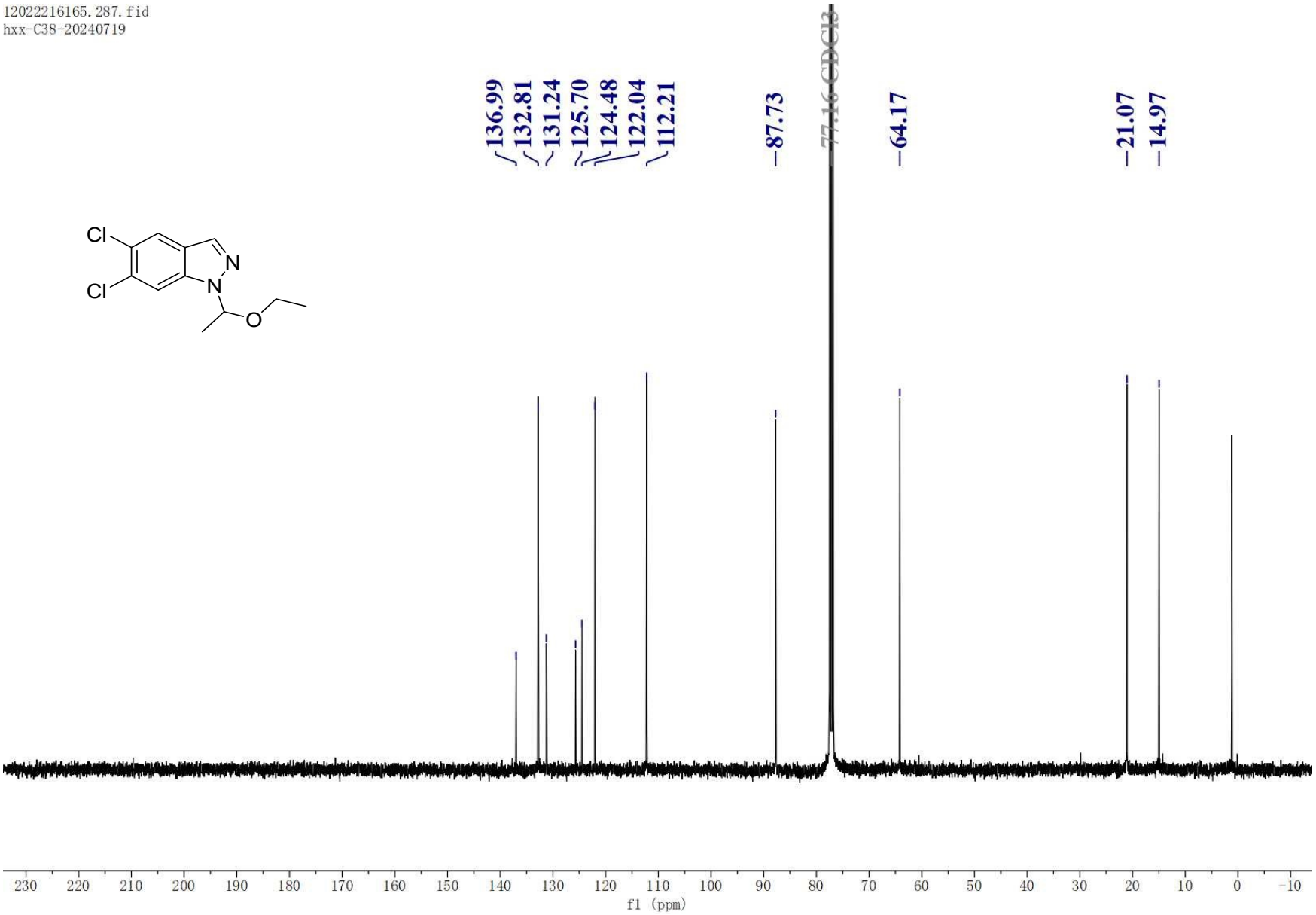
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3j**



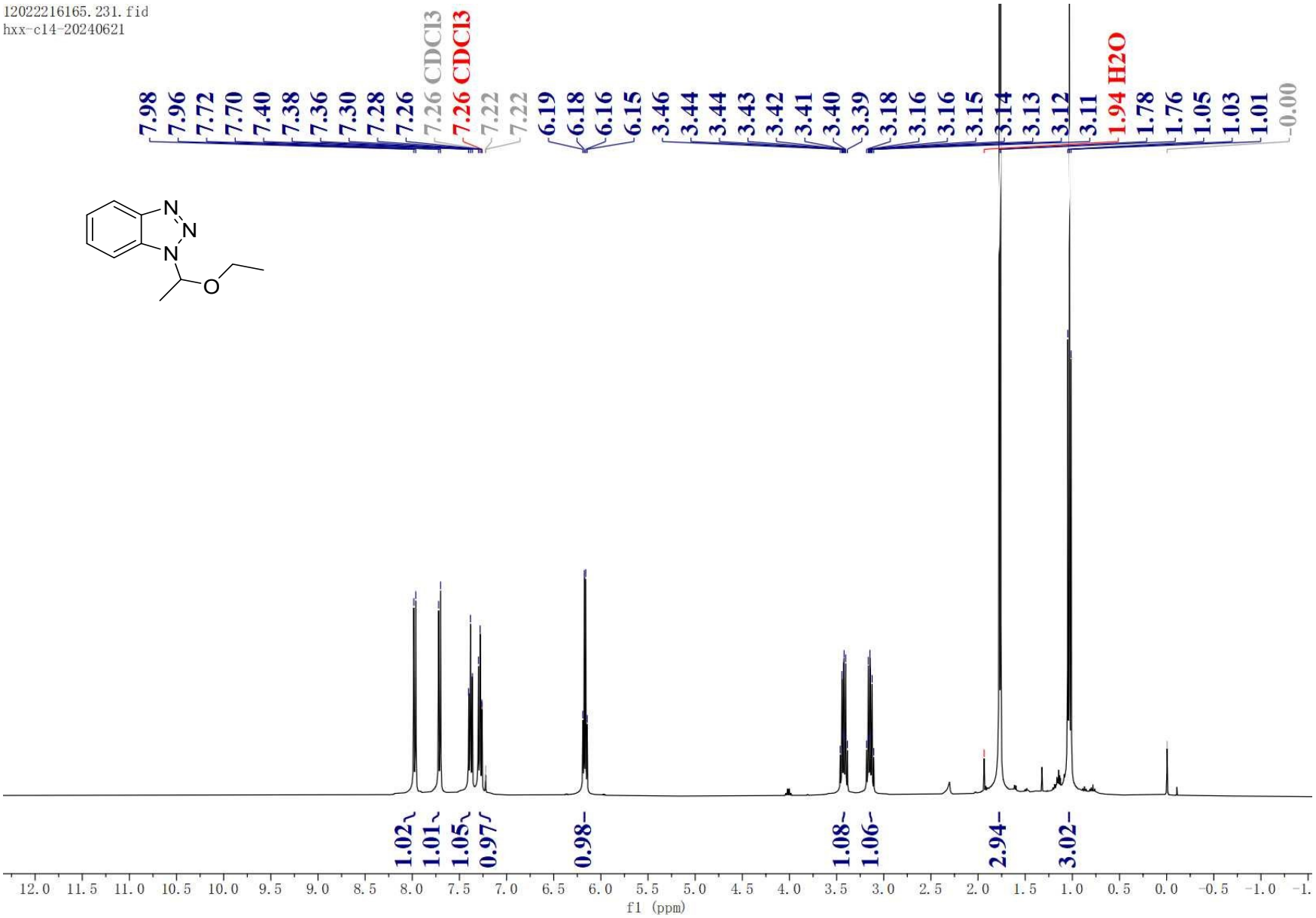
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3j**



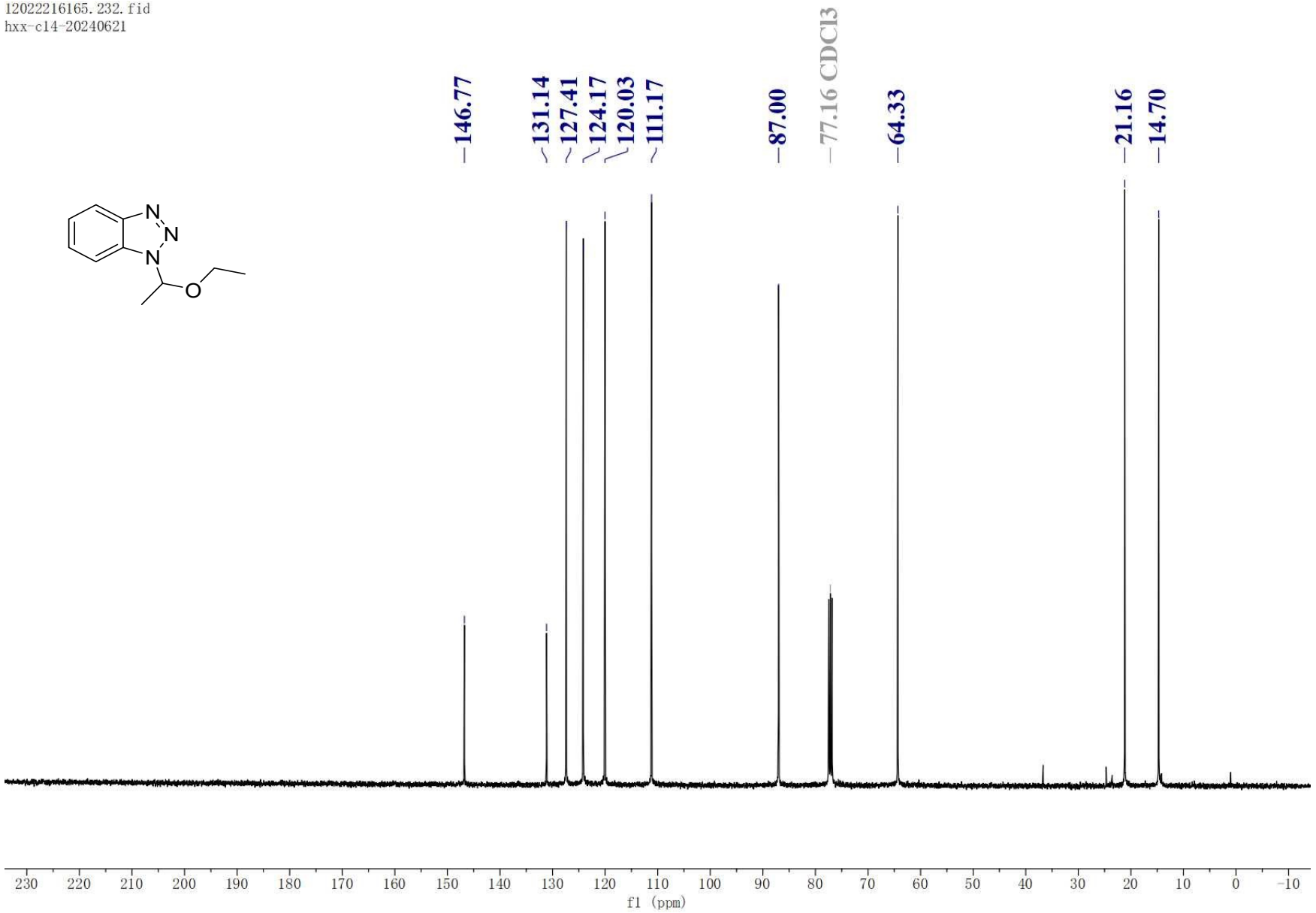
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3k**



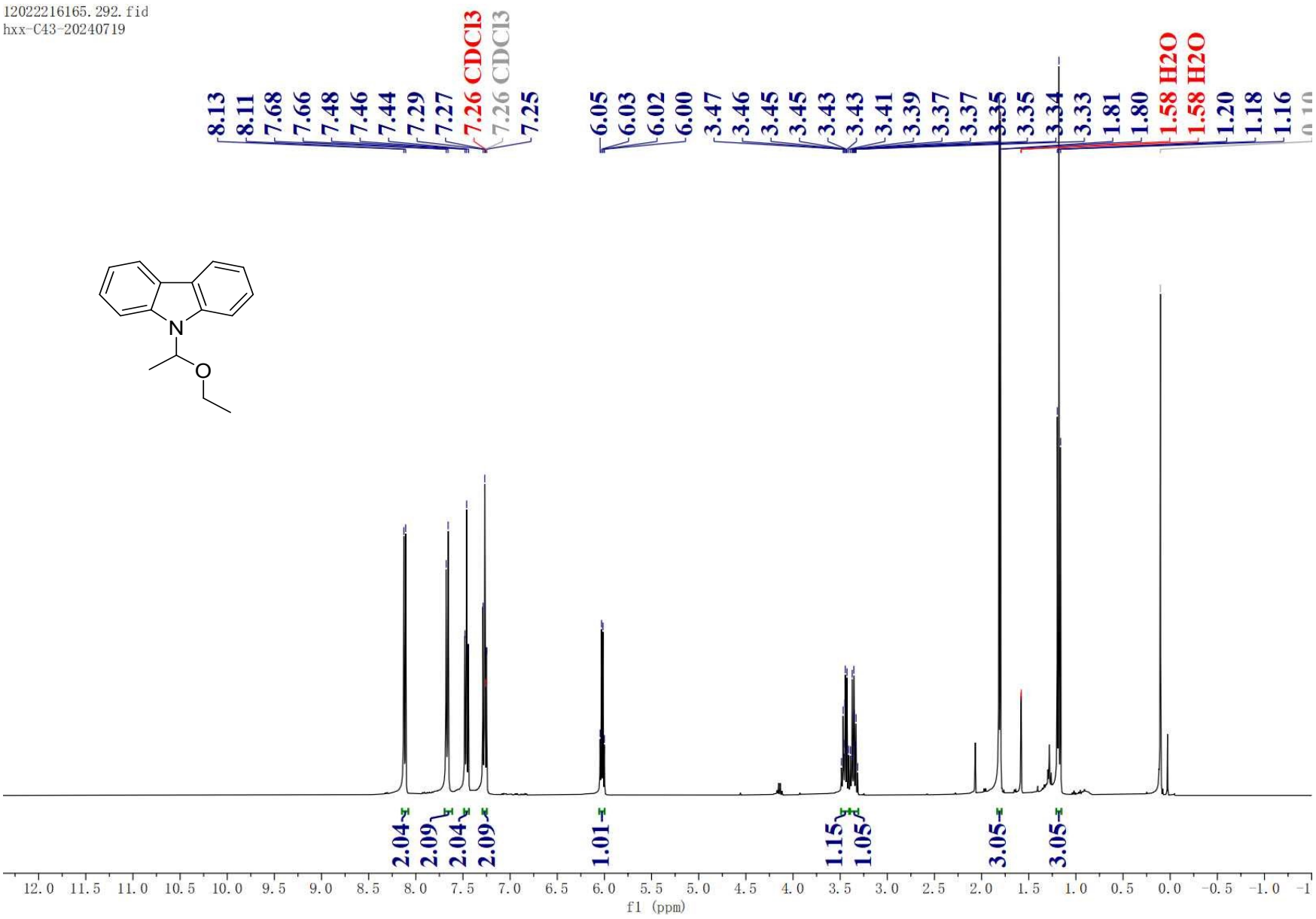
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3k**



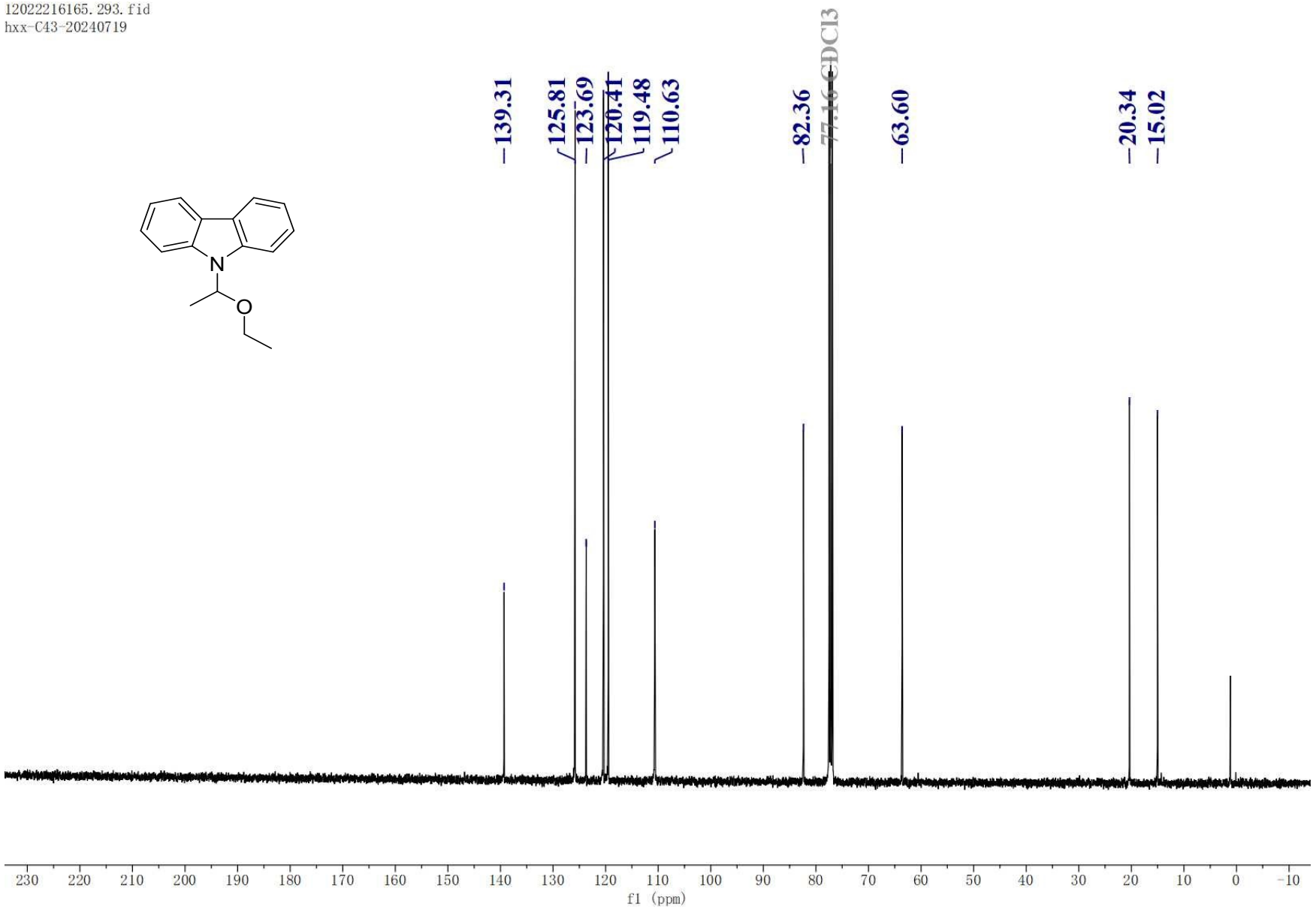
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3l**



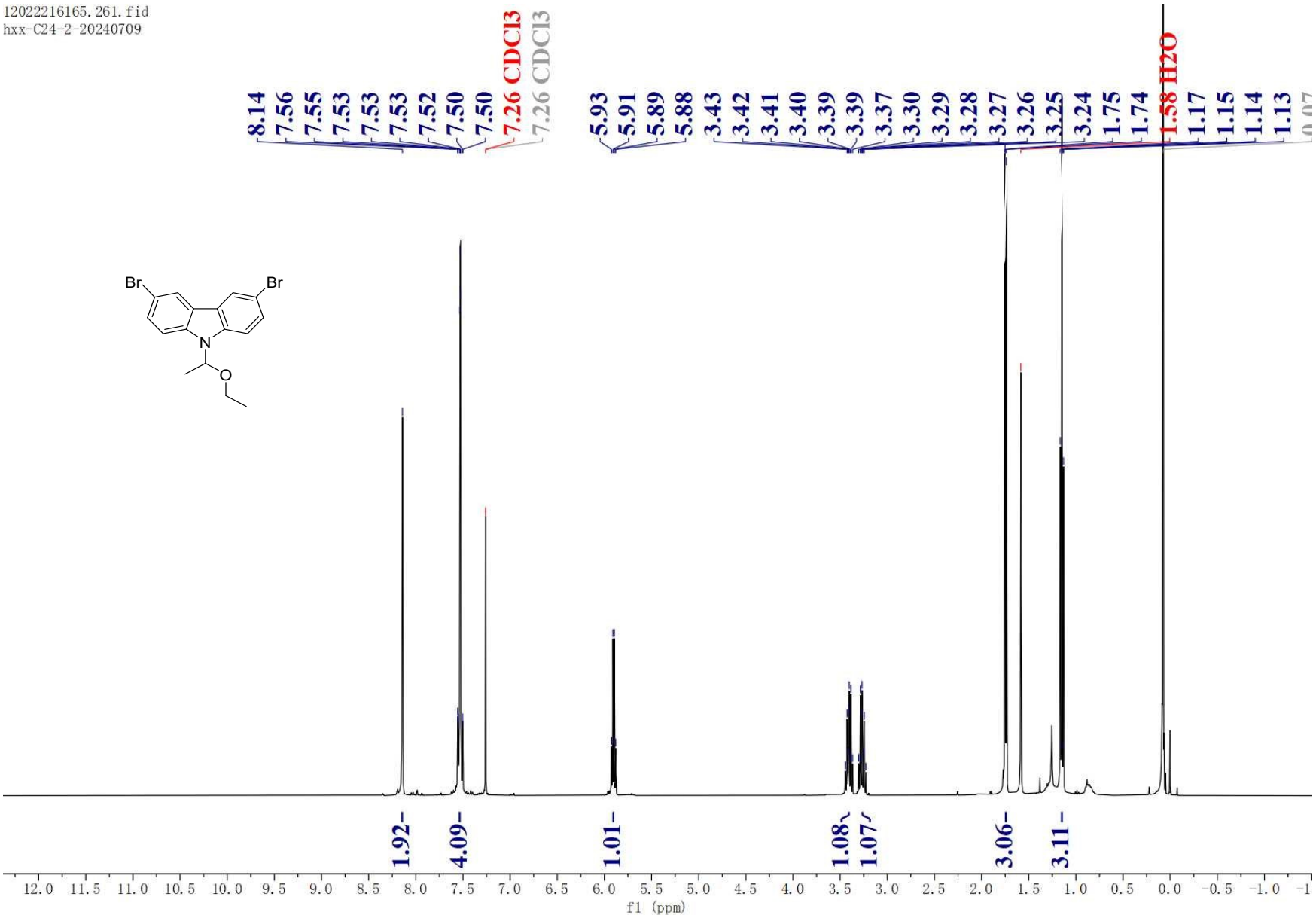
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3l**



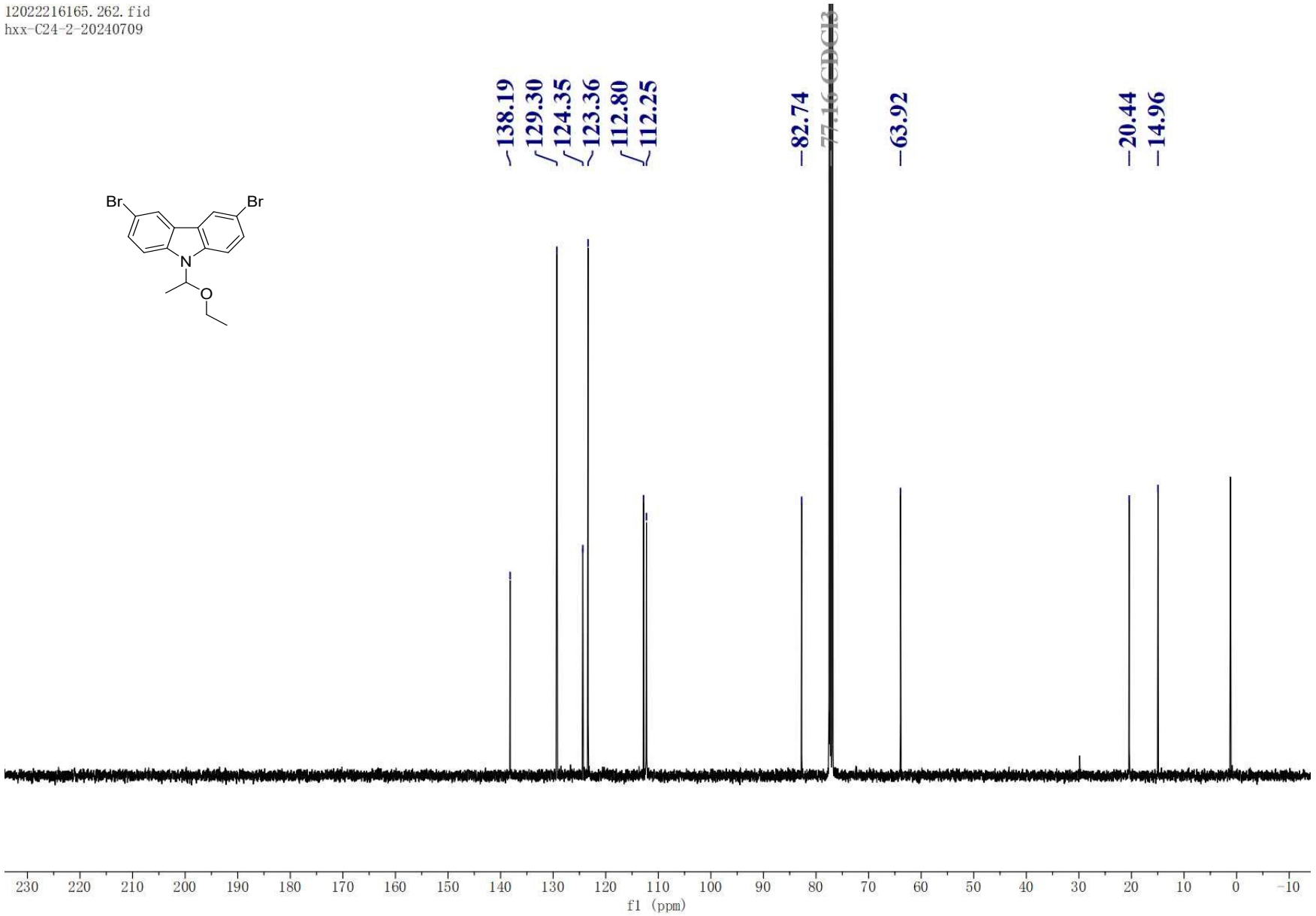
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3m**



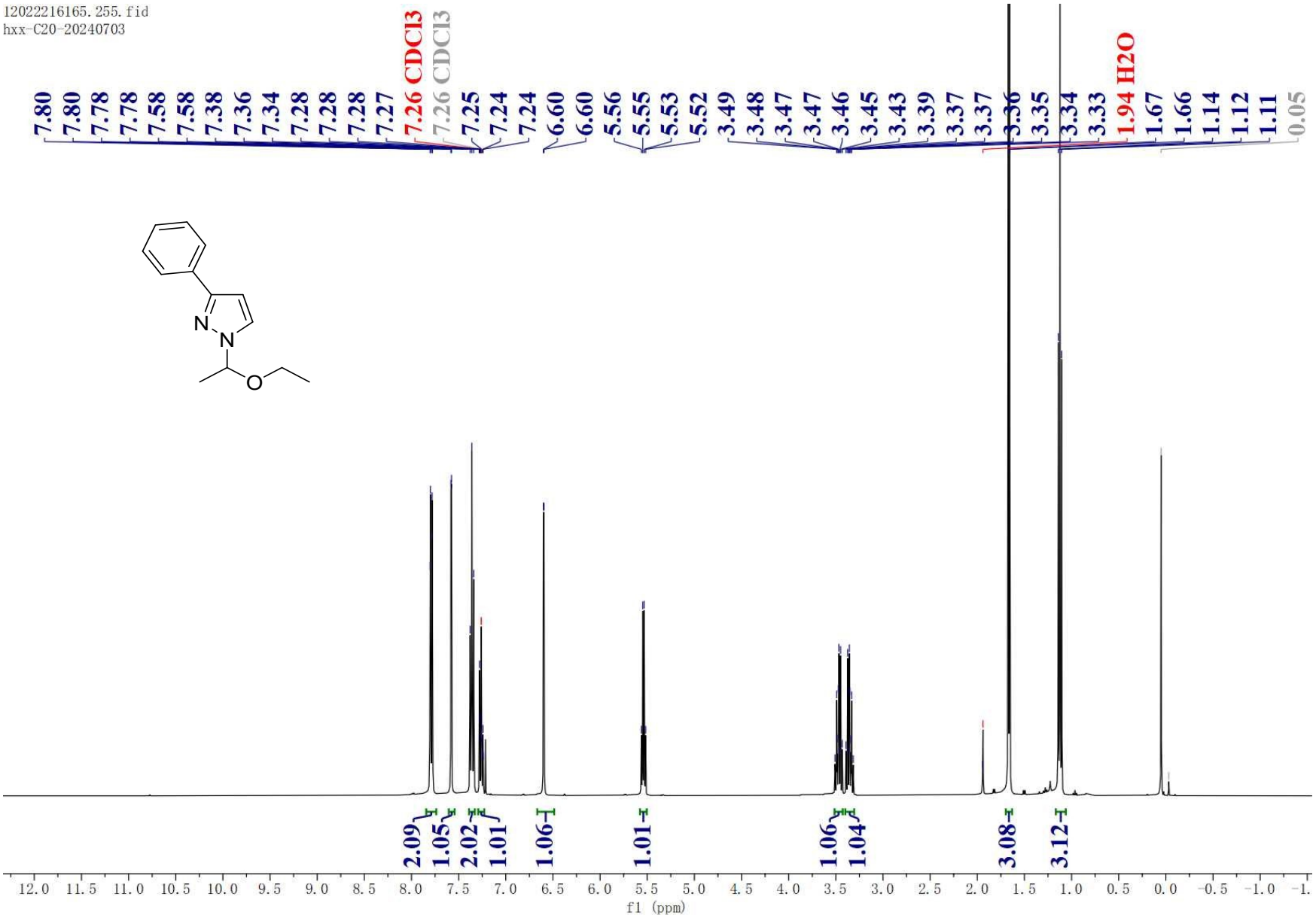
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3m**



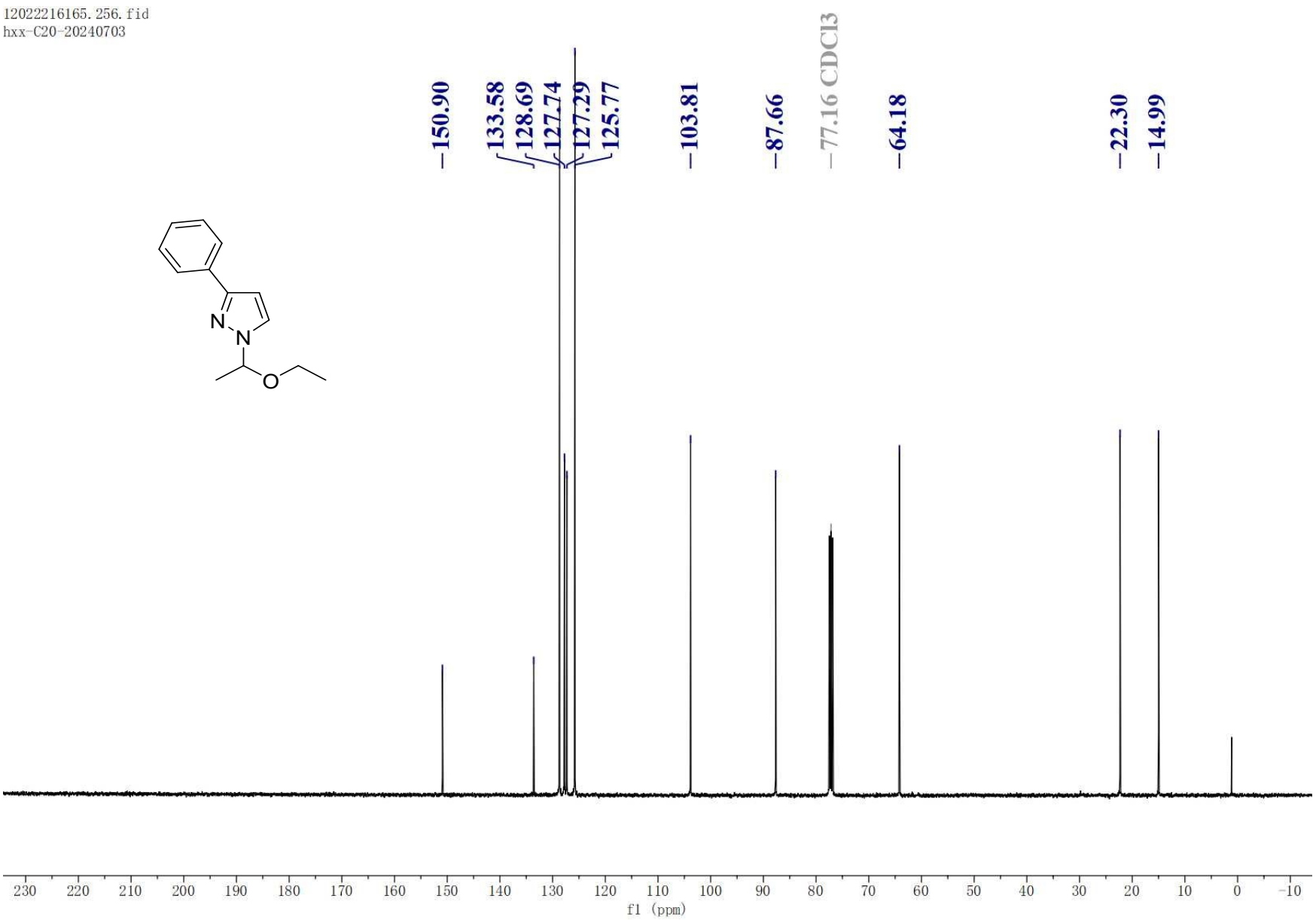
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3n**



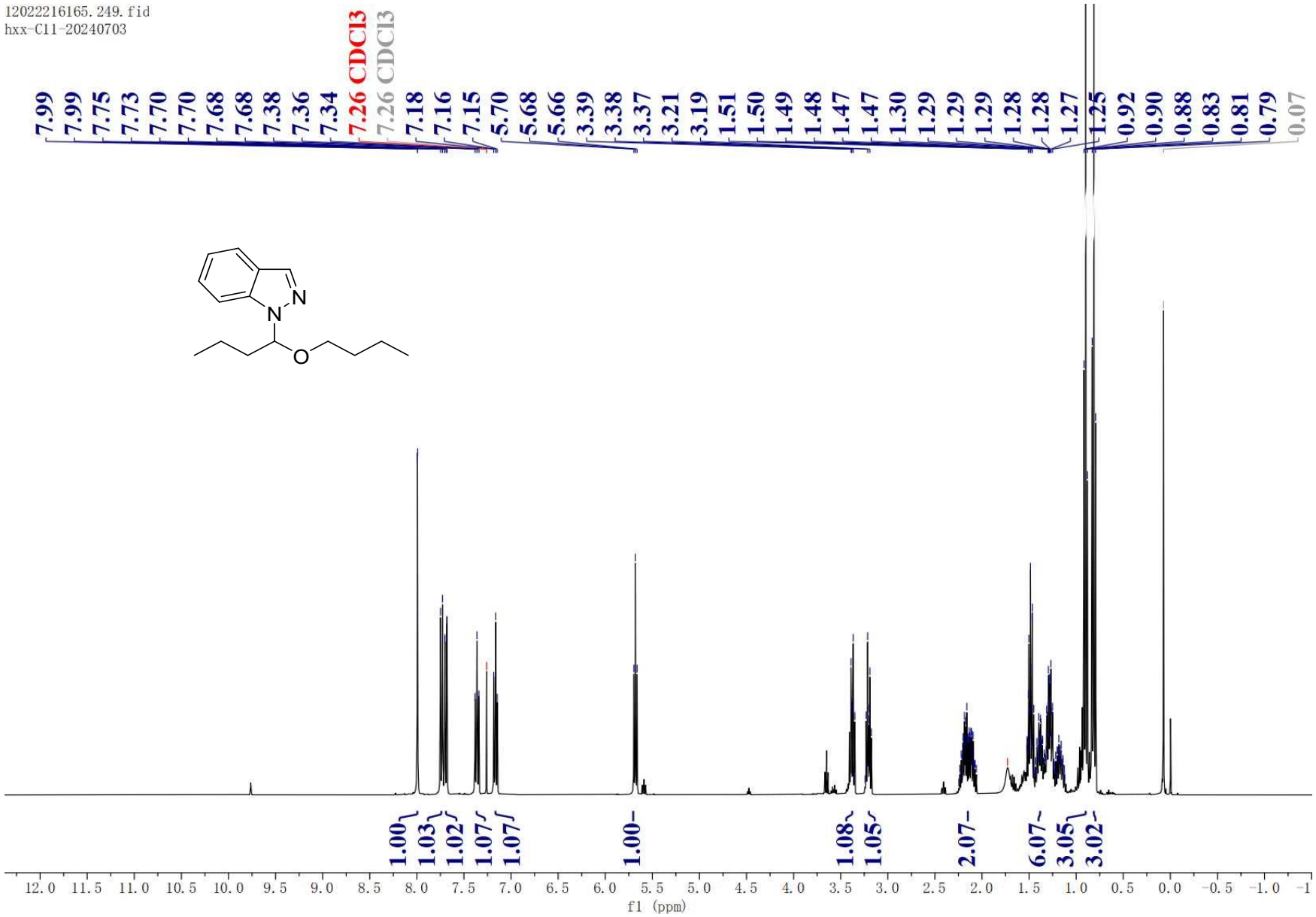
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3n**



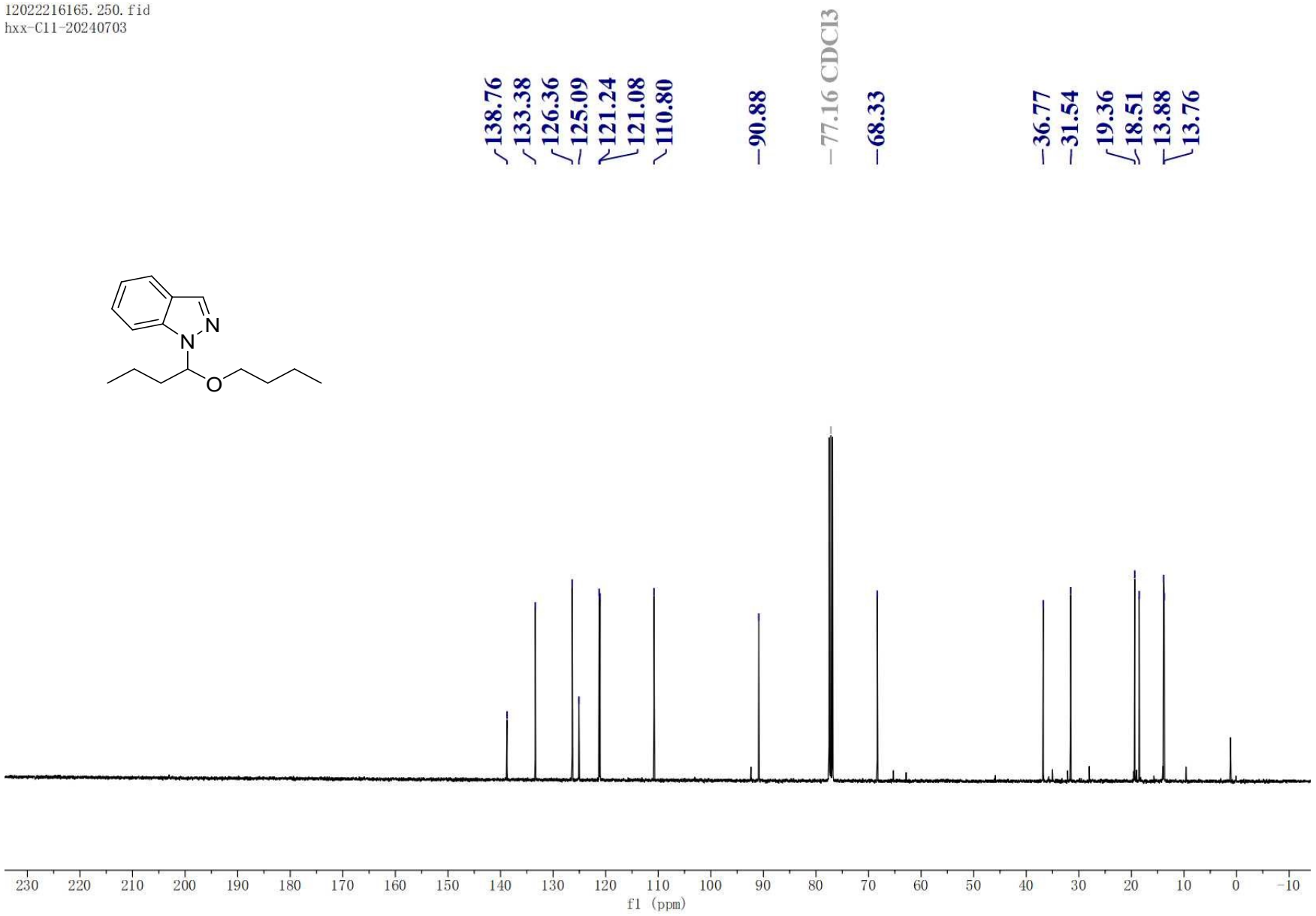
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3o**



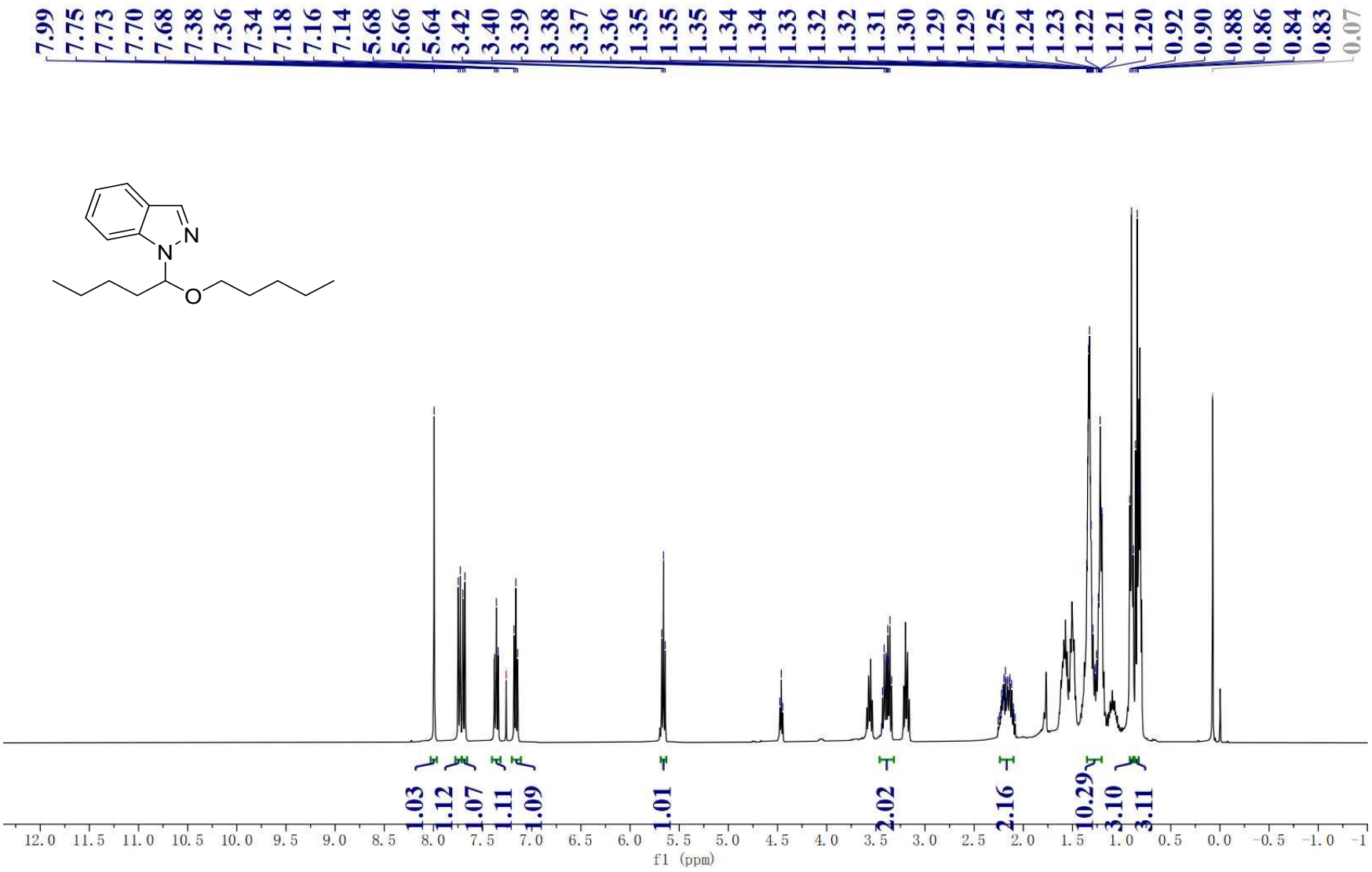
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3o**



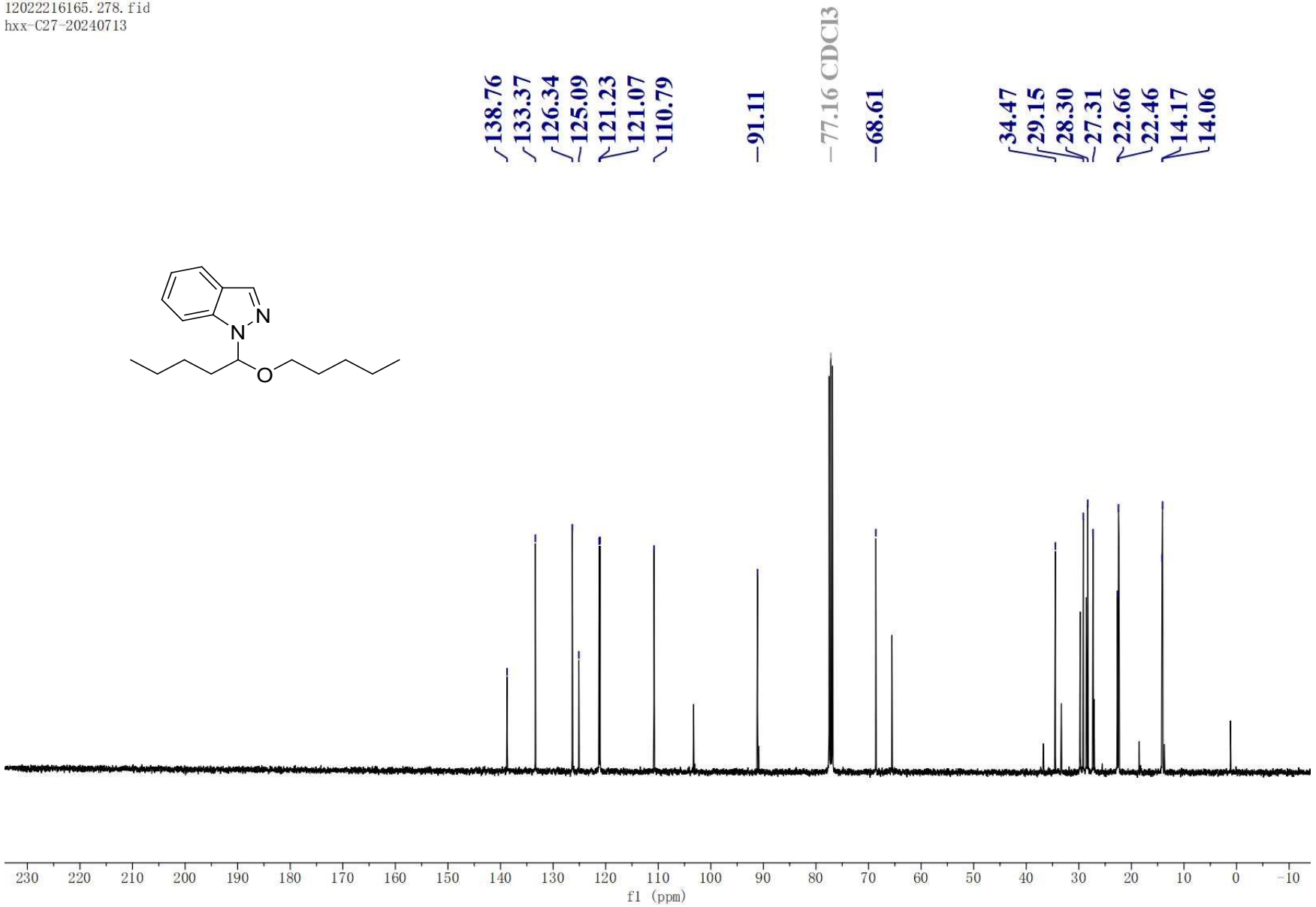
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3p**



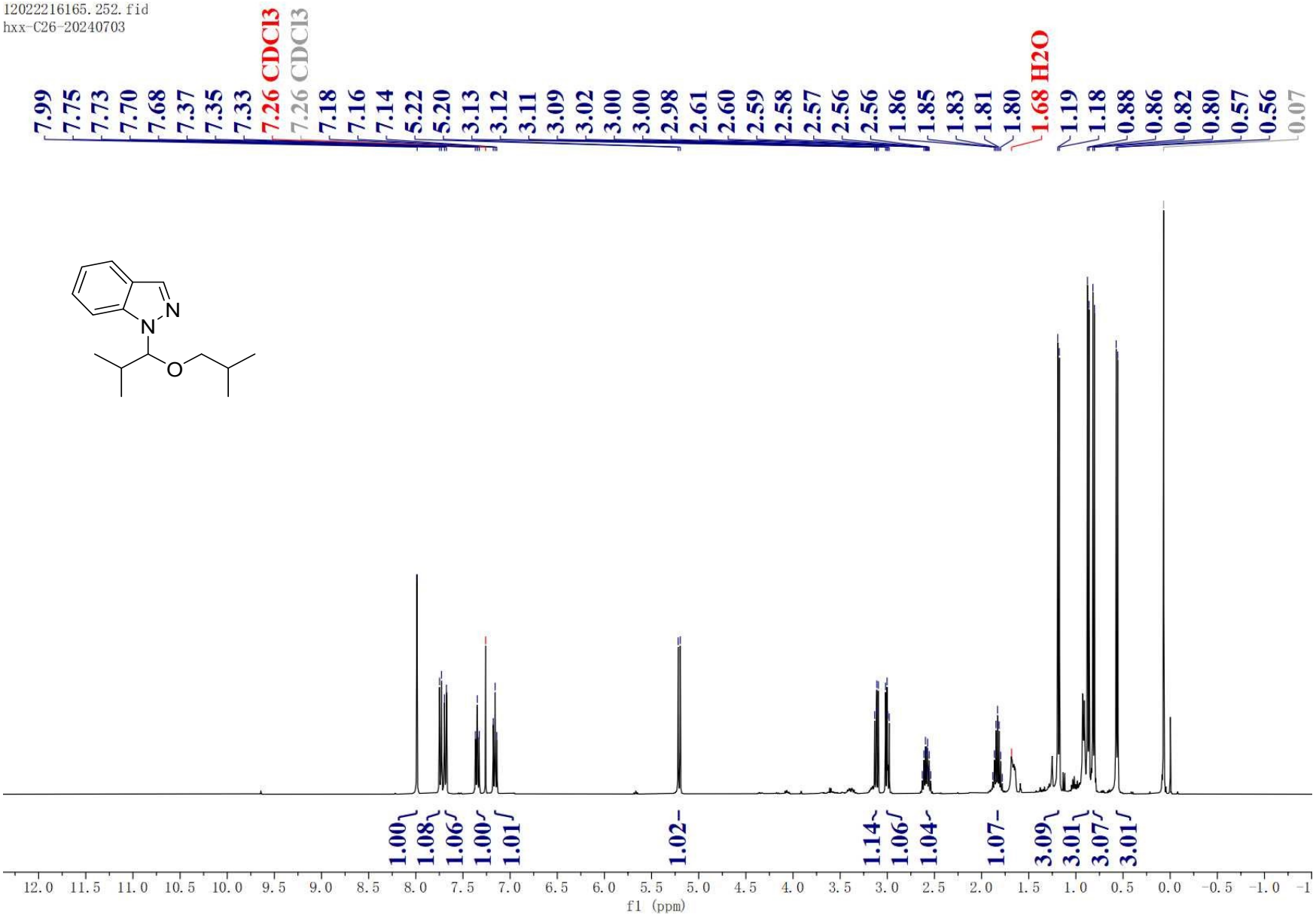
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3p**



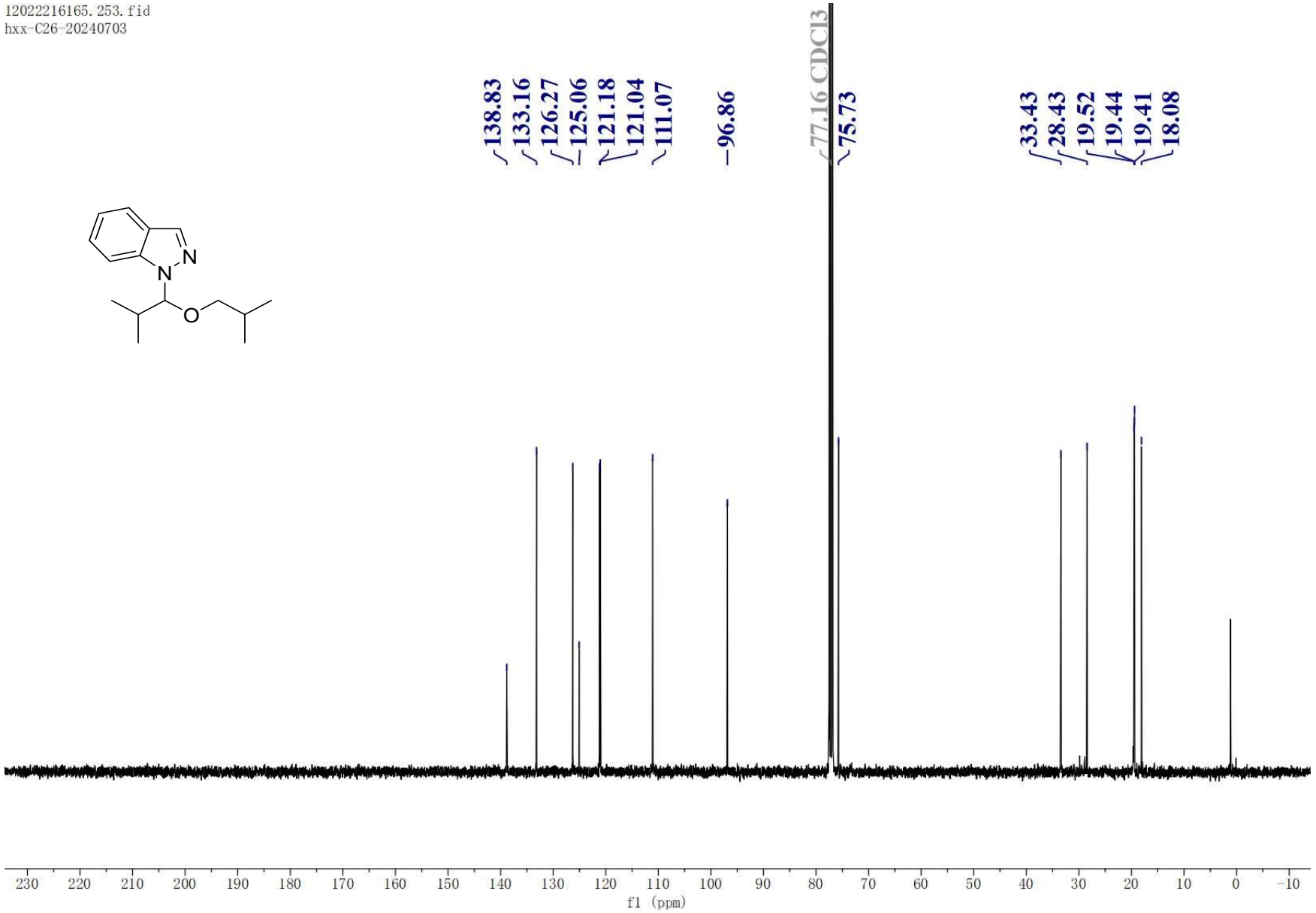
^{1}H-NMR ($CDCl_3$, 400 MHz) **spectrum of 3q**



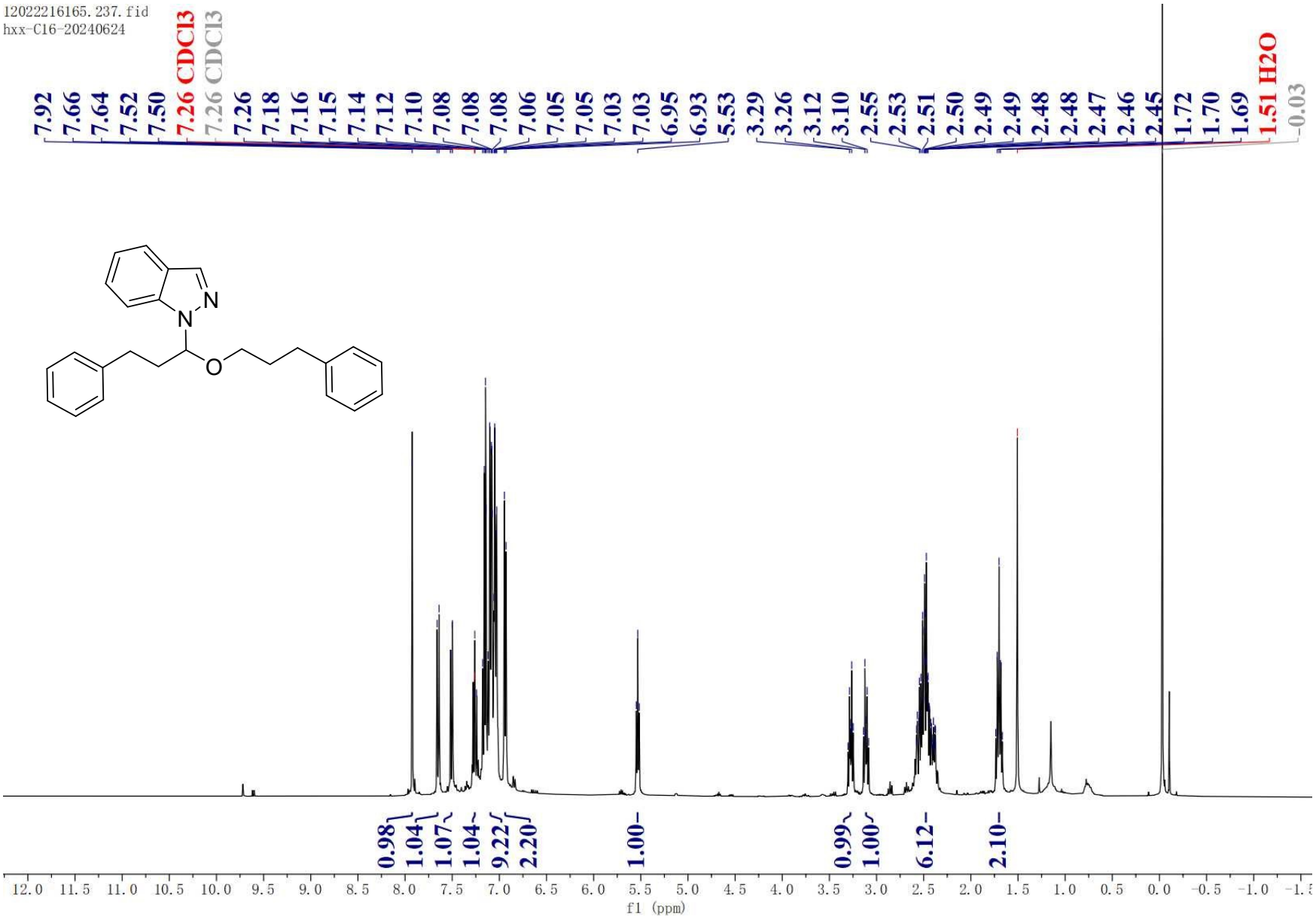
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3q**



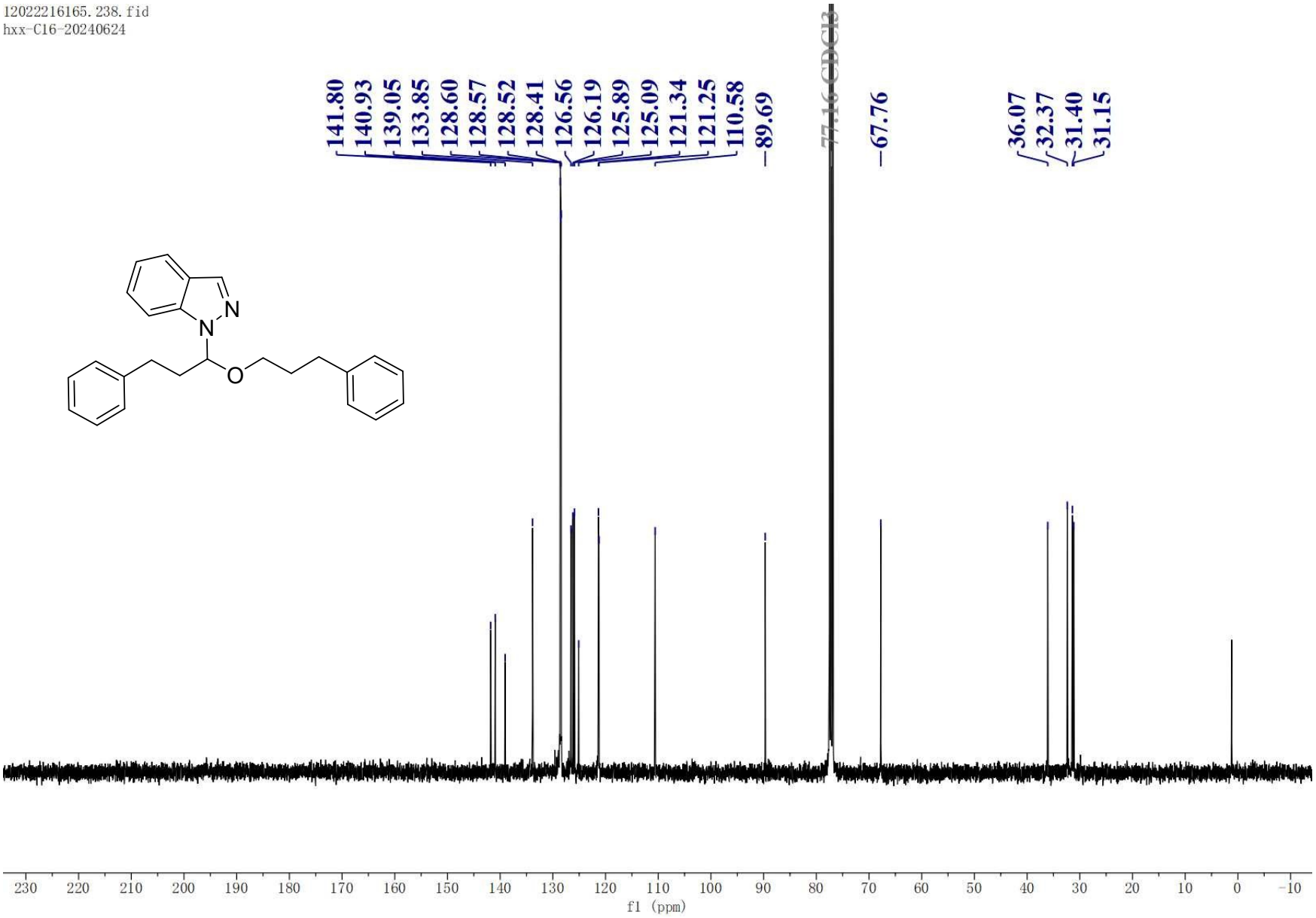
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3r**



^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3r**



^{1}H-NMR ($CDCl_3$) **spectrum of 3s**



^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3s**