Supporting information

Correspondance: jsli@csust.edu.cn (Dr J.S. Li)

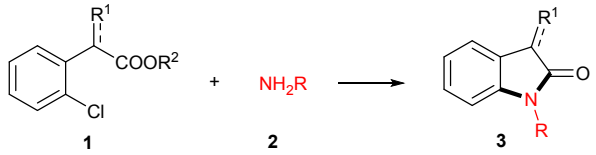
Contents

1. General information

All solvents and reagents were purchased from the suppliers and used without further purification unless otherwise noted. The screwed sealed tube is purchased from Synthware Laboratory Glassware Company. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded in $CDCl_3$ solvent at room temperature on Bruker Avance III 400 spectrometer using TMS as internal standard. MS spectra were performed on an Agilent 6890/5973 GC-MS. IR data of all new indolin-2-ones were recorded on Varian 3100 FT-IR. Elemental analyses were measured on a Perkin Elmer 2400 series analyzer. TLC analyses were performed on silica gel plates and column chromatography was conducted over silica gel (mesh 200-300) at increased pressure.

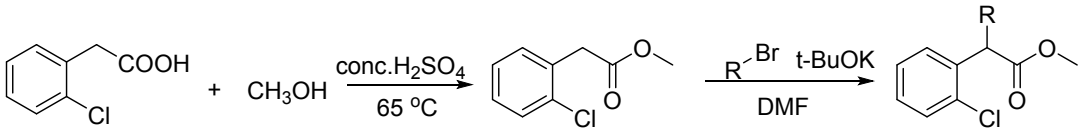
2. Experimental details of the products

1) General procedure for synthesis of 1,3-dihydro-indol-2-ones



2-Chloroarylacetic acid **1** (2 mmol), amine **2** (10 mmol), copper powder (0.013 g, 10 mol%) was combined in a 15 mL screwed sealed tube under atmosphere condition and placed in an oil bath. The reaction mixture was magnetically stirred and heated to 100°C. When the reaction completed or underwent to the time stated in Tables (16 or 24 h), the reaction mixture was cooled to room temperature, and 10% HCl (20 mL) was added to. The organic layer was separated and the aqueous layer was extracted by ethyl acetate (3×10 mL) . The combined extracts were washed with aqueous 5% $NaHCO_3$ (3 × 10 mL), and then dried by anhydrous sodium sulfate. The solvent was removed under reduced pressure to give crude product that was purified by silica gel column chromatography (eluent: petroleum ether /ethyl acetate) to give the pure product **3**.

2) General procedure for synthesis of 2-alkylated 2-Chlorophenylacetic acid methyl ester

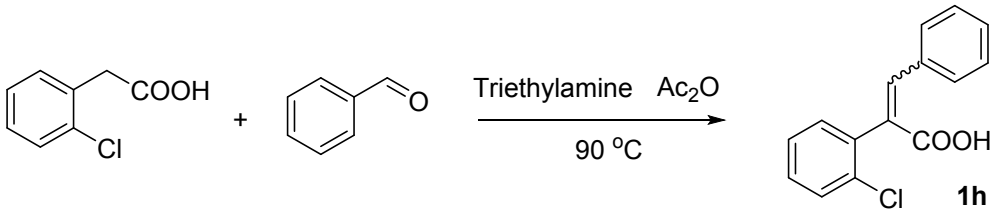


1d R= Et, **1e** R= *n*-Bu

To a stirred solution of 2-chlorophenylacetic acid (10 mmol, 1.7 g) in methanol (20 mL), concentrated sulfuric acid (2 mL) was added. The solution was refluxed for 2 h. After the mixture was cooled to room temperature, the organic layer was separated and the aqueous layer was extracted by ethyl acetate (3 × 20 mL). The combined extracts were dried by anhydrous sodium sulfate and the solvent was removed under reduced pressure to give crude ester.

To a solution of ester (2 mol, 0.369 g), *t*-BuOK (4 mol, 0.448 g) in dry DMF(3 mL) at 0 °C under N_2, then alkyl bromide was added when the solution was stirred for 5 min. The mixture was stirred at room temperature for 12 h, and quenched with water (30 mL). Then the system was extracted by ethyl acetate (3×20 mL). The combined extracts were dried by anhydrous sodium sulfate and the solvent was removed under reduced pressure to give crude **1d** and **1e**, respectively.

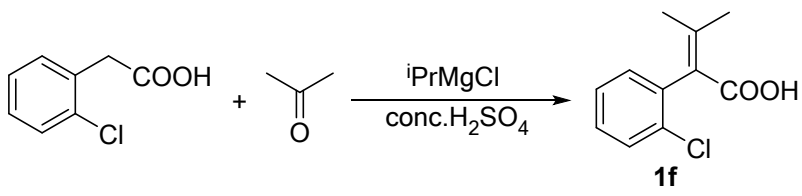
3) General procedure for synthesis of 2-(2-chlorophenyl)-3-monosubstituted acrylic acid



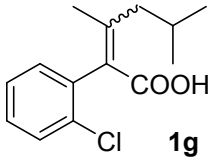
Stirred mixture of 2-Chlorophenylacetic acid (5 mmol, 0.85 g), benzaldehyde (5 mmol, 0.53 g) and triethylamine (5 mmol, 0.51 g) in acetic anhydride (10 mmol, 1.02 g) was refluxed for 5 h. Aqueous 10% $NaHCO_3$ (24 mL) was added to the cooled reaction mixture. The resulted mixture was extracted by ethyl acetate (3 × 20 mL) to remove impurities. Then, the resulted aqueous phase was treated with aqueous HCl (30 mL, 10%), and then extracted by ethyl acetate (3 × 20 mL). The extract was dried by anhydrous sodium sulfate and the solvent was removed under reduced pressure to give crude product, which was purified by flash chromatography.

2-(2-Chlorophenyl)-3-tolylacrylic acid (**1i**) was prepared similarly.

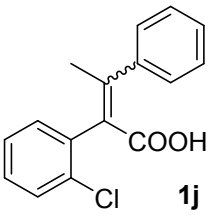
4) General procedure for synthesis of 2-(2-Chlorophenyl)-3,3-disubstituted acrylic acid and its ester



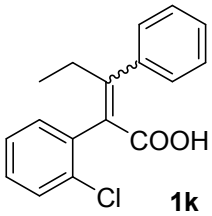
A solution of phenylacetic acid (2 mmol) in dry THF (3 mL) was added to the solution of isopropylmagnesium chloride in THF (4 mmol, 2 M, 2 mL) at room temperature. The resulting thick suspension was stirred at 40°C for 1 h, treated with acetone (3 mmol) at 25°C and stirred at 40°C for another 1 h. Addition of a 14.2% aqueous solution of sulfuric acid (2 mL) under ice cooling, extraction of the aqueous phase with ethyl acetate and evaporation of the organic phase afforded crude hydroxy–acid as a dark oil. To a solution of the hydroxy-acid in CH_2Cl_2 (3 mL) was added under stirring sulfuric acid (1.2 mL) at room temperature. CH_2Cl_2 was evaporated, the yellow solution was stirred for 45 min at room temperature and then poured to ice water. The precipitate was filtered off, washed with water, and dried. **1g**, **1j**, and **1k** were prepared similarly, respectively. The ester of **1f** was prepared according to the H_2SO_4-catalyzed method described above.



1g



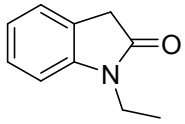
1j



1k

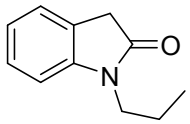
3. Characterization data for the indolin-2-ones and amides

1-Ethyl-1,3-dihydro-indol-2-one(3aa)[1]



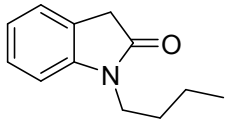
Light yellow solid, m.p. 103-105 °C. (lit.[1] 95-96 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 3.77 (q, *J* = 7.2 Hz, 2H), 3.50 (s, 2H), 1.27 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 144.3, 127.8, 124.8, 124.5, 122.1, 108.2, 35.9, 34.6, 12.7. MS(EI): m/z 161.1 $[M]^+$.

1-Propyl-1,3-dihydro-indol-2-one(3ab)



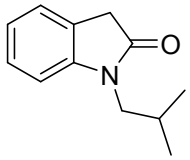
Yellow solid, m.p. 72-74 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.28 – 7.23 (m, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 8 Hz, 1H), 3.67 (t, *J* = 7.4 Hz, 2H), 3.52 (s, 2H), 1.71 (sext, *J* = 7.2 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 144.7, 127.8, 124.7, 124.4, 122.1, 108.4, 41.6, 35.8, 20.8, 11.4. IR (KBr) υ 3057, 2969, 2936, 2880, 2360, 2341, 1705, 1614, 1496, 1466, 1358, 1233, 1203, 1141, 950, 747, 669. MS(EI): m/z 175.1 $[M]^+$. Anal. Calcd for C11H13NO C 75.40, H 7.48, N 7.99%; Found: C 75.22, H 7.30, N 8.13%.

1-Ethyl-1,3-dihydro-indol-2-one(3ac)[1]



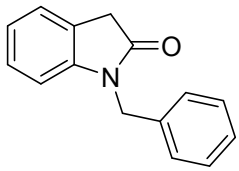
Brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 3.70 (t, *J* = 7.4 Hz, 2H), 3.51 (s, 2H), 1.65 (quint, *J* = 7.5Hz, 2H), 1.40 (sext, *J* = 7.5 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 144.7, 127.8, 124.7, 124.4, 122.1, 108.4, 39.8, 35.8, 29.5, 20.2, 13.8. MS(EI): m/z 189.1 $[M]^+$.

1-Isobutyl-1,3-dihydro-indol-2-one(3ad)[1]



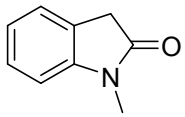
Brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.23 (m, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 3.53 – 3.51 (m, 4H), 2.14 (hept, *J* = 6.8Hz, 1H), 0.96 (d, *J* = 6.4 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 145.1, 127.7, 124.6, 124.4, 122.1, 108.6, 47.5, 35.7, 27.0, 20.2(2 C). MS(EI): m/z 189.1 $[M]^+$.

1-Benzyl-1,3-dihydro-indol-2-one(3ae)[1]



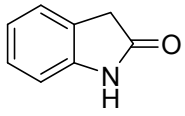
Light yellow solid, m.p. 70-73 °C. (lit.[1] 67-68 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.30 (m, 4H), 7.25- 7.23 (m, 2H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 4.91 (s, 2H), 3.62 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 144.4, 135.9, 128.8(2 C), 127.8, 127.6, 127.4(2 C), 124.5, 124.4, 122.4, 109.1, 43.8, 35.8. MS(EI): m/z 223.1 $[M]^+$.

1-Methyl-1,3-dihydro-indol-2-one(3af)[2]



Light yellow solid, m.p. 97-99 °C. (lit.[2] 91-92 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.23 (m, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 3.51 (s, 2H), 3.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 145.2, 127.9, 124.5, 124.30, 122.33, 108.1, 35.7, 26.1. MS(EI): m/z 147.0 $[M]^+$.

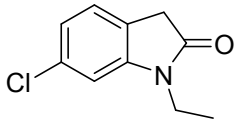
1,3-Dihydro-indol-2-one(3ag)[3]



Yellow solid, m.p. 137-139 °C. (lit.[3] 126-127 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 7.23 – 7.19 (m, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 3.54 (s,

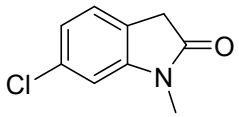
2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 142.7, 127.9, 125.3, 124.6, 122.3, 109.9, 36.4. MS(EI): m/z 133.0 $[M]^+$.

6-Chloro-1-ethyl-1,3-dihydro-indol-2-one(3ba)



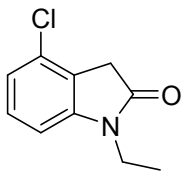
Yellow solid, m.p. 100-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.83 (s, 1H), 3.74 (q, *J* = 7.2 Hz, 2H), 3.48 (s, 2H), 1.26 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 145.5, 133.7, 125.3, 123.0, 121.9, 108.8, 35.4, 34.8, 12.6. IR (KBr) υ 2985, 2939, 2360, 2337, 1721, 1611, 1491, 1367, 1243, 959, 844, 809. MS(EI): m/z 197.0, 195.0 $[M]^+$. Anal. Calcd for C10H10ClNO C 61.39, H 5.15, N 7.16%; Found: C 61.53, H 5.02, N 7.29%.

6-Chloro-1-methyl-1,3-dihydro-indol-2-one(3bf)



Yellow solid, m.p. 124-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.81 (s, 1H), 3.48 (s, 2H), 3.19 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 146.4, 133.7, 125.1, 122.7, 122.1, 108.8, 35.3, 26.3. IR (KBr) υ 3066, 2945, 2359, 2337, 1712, 1614, 1497, 1367, 1093, 931, 804, 640. MS(EI): m/z 183.0, 181.0 $[M]^+$. Anal. Calcd for C9H8ClNO C 59.52, H 4.44, N 7.71%; Found: C 59.66, H 4.60, N 7.53%.

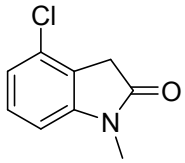
4-Chloro-1-ethyl-1,3-dihydro-indol-2-one(3ca)



Yellow solid, m.p. 87-89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 3.75 (q, *J* = 7.2 Hz, 2H), 3.49 (s, 2H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 145.4, 130.5, 129.2, 123.2, 122.3, 106.5, 35.4, 35.0, 12.7. IR (KBr) υ 3048, 2992, 2938, 2359, 2337, 1706, 1611, 1461,

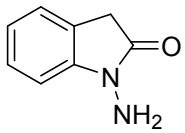
1336, 1264, 1120, 770, 673. MS(EI): m/z 197.0, 195.0 $[M]^+$. Anal. Calcd for C10H10ClNO C 61.39, H 5.15, N 7.16%; Found: C 61.51, H 5.28, N 7.01%.

4-Chloro-1-methyl-1,3-dihydro-indol-2-one(3cf)



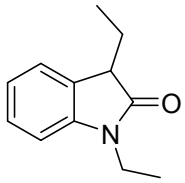
Yellow solid, m.p. 102-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 3.43 (s, 2H), 3.13 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 146.3, 130.4, 129.3, 123.0, 122.5, 106.4, 35.3, 26.5. IR (KBr) υ 3062, 2940, 2359, 2337, 1715, 1613, 1462, 1337, 1300, 1110, 932, 771, 680. MS(EI): m/z 183.0, 181.0 $[M]^+$. Anal. Calcd for C9H8ClNO C 59.52, H 4.44, N 7.71%; Found: C 59.63, H 4.62, N 7.55%.

1-Amino-1,3-dihydro-indol-2-one(3ai)[4]



Yellow solid, m.p. 138-140 °C. (lit.[4] 127.5-128 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 4.25 (br s, 2H), 3.48 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 144.8, 128.1, 124.3, 122.5, 122.0, 108.7, 34.4. MS(EI): m/z 148.0 $[M]^+$.

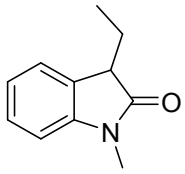
1,3-Diethyl-1,3-dihydro-indol-2-one(3da)



Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19- 7.16 (m, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 3.75 – 3.63 (m, 2H), 3.33 (t, *J* = 6.4 Hz, 1H), 1.94 (quint, *J* = 6.8 Hz, 2H), 1.18 (t, *J* = 7.4 Hz, 3H), 0.79 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 143.7, 129.2, 127.7, 124.0, 122.0, 108.0, 46.6, 34.5, 23.7, 12.7, 9.9. IR (KBr) υ

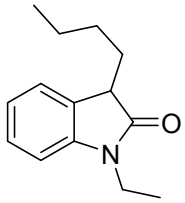
2971, 2934, 2877, 2360, 2341, 1707, 1612, 1466, 1364, 1220, 772. MS(EI): m/z 189.1 $[M]^+$. Anal. Calcd for C12H15NO C 76.16, H 7.99, N 7.40%; Found: C 76.38, H 8.15, N 7.26%.

3-Ethyl-1-methyl-1,3-dihydro-indol-2-one(3df)[5-6]



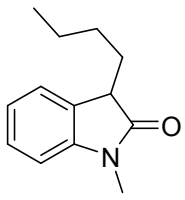
Light yellow solid, m.p. 174-176 ^oC. (lit.[5] 169 ^oC). ^1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 3.40 (t, *J* = 5.8 Hz, 1H), 3.20 (s, 3H), 2.00 (quint, *J* = 6.8 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 144.5, 129.0, 127.8, 123.8, 122.3, 107.9, 46.7, 26.1, 23.7, 10.1. MS(EI): m/z 175.1 $[M]^+$.

3-Butyl-1-ethyl-1,3-dihydro-indol-2-one)(3ea)



Yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.28- 7.24 (m, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8 Hz, 1H), 3.81 – 3.70 (m, 2H), 3.41 (t, *J* = 6.0 Hz, 1H), 1.98 - 1.89 (m, 2H), 1.33 – 1.23 (m, 7H), 0.87 (t, *J* = 6.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 143.5, 129.6, 127.7, 124.0, 122.0, 108.0, 45.6, 34.5, 30.4, 27.8, 22.7, 13.9, 12.7. IR (KBr) υ 2960, 2933, 2360, 2341, 1705, 1614, 1467, 1364, 1220, 772. MS(EI): m/z 217.1 $[M]^+$. Anal. Calcd for C14H19NO C 77.38, H 8.81, N 6.45%; Found: C 77.21, H 8.93, N 6.58%.

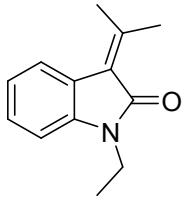
3-Butyl-1-methyl-1,3-dihydro-indol-2-one(3ef)



Yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 3.42 (t, *J* = 6.0 Hz, 1H), 3.20 (s, 3H), 2.00 – 1.89 (m, 2H), 1.34 –

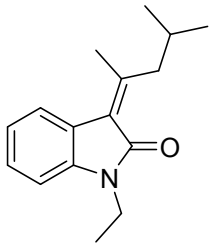
1.29 (m, 4H), 0.87 (t, *J* = 6.6 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 144.4, 129.4, 127.8, 123.8, 122.2, 107.9, 45.6, 30.4, 28.0, 26.1, 22.7, 13.7. IR (KBr) υ 2957, 2932, 2861, 2359, 2341, 1715, 1613, 1494, 1470, 1348, 772. MS(EI): m/z 203.1 $[M]^+$. Anal. Calcd for C13H17NO C 76.81, H 8.43, N 6.89%; Found: C 76.99, H 8.58, N 6.72%.

1-Ethyl-3-isopropylidene-1,3-dihydro-indol-2-one(3fa)



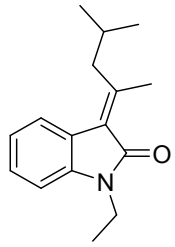
Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 3.81 (q, *J* = 7.2 Hz, 2H), 2.63 (s, 3H), 2.37 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 154.7, 141.1, 127.5, 123.8, 123.5, 122.8, 121.4, 107.6, 34.1, 25.2, 23.1, 12.9. IR (KBr) υ 2932, 2359, 2341, 1732, 1693, 1608, 1354, 1219, 1100, 772. MS(EI): m/z 201.1 $[M]^+$. Anal. Calcd for C13H15NO C 77.58, H 7.51, N 6.96%; Found: C 77.70, H 7.63, N 6.79%.

***Z*-3-(1,3-Dimethyl-butylidene)-1-ethyl-1,3-dihydro-indol-2-one(3ga)**



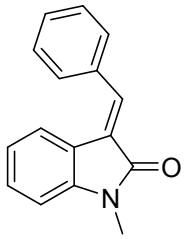
Yellow solid, m.p. 80-81 ^{o}C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 8 Hz, 1H), 3.80 (q, *J* = 7.1 Hz, 2H), 3.07 (d, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 2.06 – 1.99(m, 1H), 1.26 (t, *J* = 7 Hz, 3H), 0.99 (d, *J* = 6.4 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 158.6, 141.2, 127.5, 124.0, 123.8, 123.4, 121.3, 107.5, 44.2, 34.1, 28.4, 24.1, 22.6(2 C), 12.9. IR (KBr) υ 2958, 2866, 2359, 2361, 1682, 1607, 1469, 1356, 1228, 1103, 746. MS(EI): m/z 243.2 $[M]^+$. Anal. Calcd for C16H21NO C 78.97, H 8.70, N 5.76%; Found: C 78.72, H 8.85, N 5.97%.

***E*-3-(1,3-Dimethyl-butylidene)-1-ethyl-1,3-dihydro-indol-2-one(3ga)**



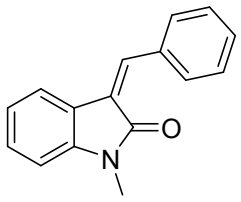
Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 3.82 (q, *J* = 7.2 Hz, 2H), 2.62 – 2.60 (m, 5H), 2.16 – 2.10 (m, 1H), 1.27 (d, *J* = 7.2 Hz, 3H), 1.04 (d, *J* = 6.4 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 159.1, 141.3, 127.5, 123.45, 123.2, 123.0, 121.3, 107.7, 46.7, 34.1, 27.8, 22.81(2 C), 22.76, 12.8. IR (KBr) υ 2959, 2870, 2360, 2337, 1693, 1607, 1467, 1354, 1217, 1102, 772. MS(EI): m/z 243.2 $[M]^+$. Anal. Calcd for C16H21NO C 78.97, H 8.70, N 5.76%; Found: C 78.70, H 8.86, N 5.94%.

***E*-3-Benzylidene-1-methyl-1,3-dihydro-indol-2-one(3ha)[7]**



Deep yellow solid, m.p. 91-93 ^{o}C. (lit.[7] 106 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.63 (t, *J* = 8.0 Hz, 3H), 7.48 – 7.41 (m, 3H), 7.26 (t, *J* = 7.6 Hz, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 3.27 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 144.3, 137.2, 135.0, 129.8, 129.5, 129.3(2 C), 128.6(2 C), 127.3, 122.8, 121.8, 121.2, 108.2, 26.2. MS(EI): m/z 235.0 $[M]^+$.

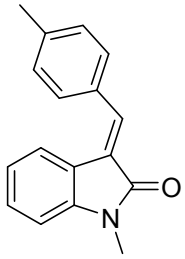
***Z*-3-Benzylidene-1-methyl-1,3-dihydro-indol-2-one(3ha)[8]**



Yellow solid, m.p. 95-97 ^{o}C. (lit.[8] 90-91 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.46 – 7.41 (m, 3H), 7.28 (t, *J* = 7.6Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 8 Hz, 1H), 3.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2,

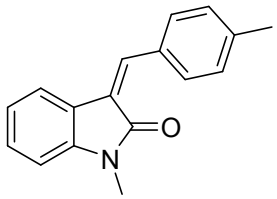
142.4, 137.1, 133.9, 131.9 (2 C), 130.5, 128.9, 128.3(2 C), 126.1, 124.4, 121.9, 119.0, 107.9, 26.0. MS(EI): m/z 235.0 $[M]^+$.

_E_-1-Methyl-3-(4-methyl-benzylidene)-1,3-dihydro-indol-2-one(3ia)[7]



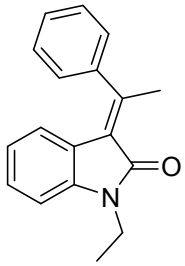
Deep yellow solid, m.p. 74-76 ^oC. (lit.[7] 134 ^oC). ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.27 - 7.23 (m, 3H), 6.88 (t, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.27 (s, 3H), 2.42 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 144.2, 140.0, 137.5, 132.1, 129.6, 129.5(2 C), 129.4(2 C), 126.5, 122.7, 121.7, 121.4, 108.1, 26.2, 21.6. MS(EI): m/z 249.0 $[M]^+$.

_Z_-1-Methyl-3-(4-methyl-benzylidene)-1,3-dihydro-indol-2-one(3ia)[7]



Deep yellow solid, m.p. 124-126 ^oC. (lit.[7] 134 ^oC). ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz,2H), 7.52 -7.51 (m, *2*H), 7.29 - 7.24 (m, *3*H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 3.28 (s, 3H), 2.41 (s, *3*H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 142.2, 141.2, 137.3, 132.2(2 C), 131.3, 129.1(2 C), 128.6, 125.1, 124.6, 121.8, 118.7, 107.8, 26.0, 21.7. MS(EI): m/z 249.0 $[M]^+$.

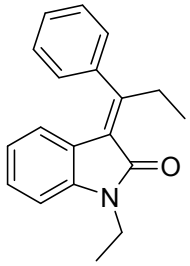
_E_-1-Ethyl-3-(1-phenyl-ethylidene)-1,3-dihydro-indol-2-one(3ja)[9]



Yellow solid, m.p. 94-96 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 3H), 7.27 (d, *J*

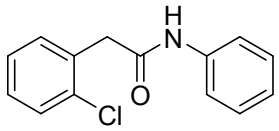
= 6.8 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.61 (t, *J* = 7.6 Hz, 1H), 6.14 (d, *J* = 7.6 Hz, 1H), 3.84 (q, *J* = 7.2 Hz, 2H), 2.81 (s, 3H), 1.29 (t, *J* = 7 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 154.8, 143.1, 141.3, 129.2(2 C), 128.3, 128.0, 126.5(2 C), 123.5, 123.0, 122.9, 121.2, 107.6, 34.2, 22.9, 12.9. MS(EI): m/z 263.1 $[M]^+$.

_E_-1-Ethyl-3-(1-phenyl-propylidene)-1,3-dihydro-indol-2-one(3ka)



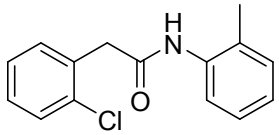
Yellow solid, m.p. 96-98 ^{o}C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 3H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 8 Hz, 1H), 6.59 (t, *J* = 7.6 Hz, 1H), 6.02 (d, *J* = 8.0 Hz, 1H), 3.83 (q, *J* = 7.2 Hz, 2H), 3.34 (q, *J* = 7.3 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 160.6, 141.5, 141.4, 129.1(2 C), 128.2, 128.0, 126.9(2 C), 123.1, 123.0, 123.0, 121.1, 107.5, 34.2, 28.1, 12.8, 12.0. IR (KBr) υ 2974, 2932, 2872, 2359, 2361, 1688, 1607, 1468, 1353, 1224, 752, 702. MS(EI): m/z 277.1 $[M]^+$. Anal. Calcd for C19H19NO C 82.28, H 6.90, N 5.05%; Found: C 82.12, H 7.03, N 5.18%.

2-(2-Chloro-phenyl)-N-phenyl-acetamide(4ah-1)



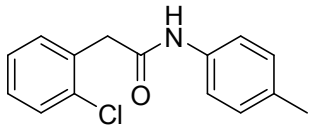
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 4H), 7.28 (m, 4H), 7.08 (t, *J* = 7.4 Hz, 1H), 3.83 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 137.7, 134.4, 132.74, 131.8, 129.9, 129.2, 129.0(2 C), 127.5, 124.5, 120.1(2 C), 77.4, 77.1, 76.7, 42.5. MS(EI): m/z 247.0, 245.0 $[M]^+$.

2-(2-Chloro-phenyl)-N-o-tolyl-acetamide(4ah-2)



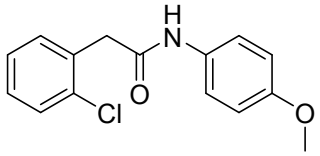
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 4H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.45 (d, *J* = 7.6 Hz, 1H), 3.73 (s, 2H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 145.5, 136.6, 133.3, 131.6, 129.2, 128.2, 127.9, 127. 4, 124.6, 124.5, 122.7, 109.4, 36.0, 17.8. MS(EI): m/z 261.0, 259.0 $[M]^+$.

2-(2-Chloro-phenyl)-N-p-tolyl-acetamide(4ah-3)



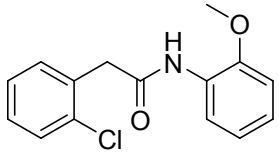
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 5H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H), 3.69 (s, 1H), 2.41 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 145.5, 138.2, 131.9, 130.3(2 C), 127.8, 126.5(2 C), 124.6, 124.4, 122.7, 109.4, 36.1, 21.3. MS(EI): m/z 261.0, 259.0 $[M]^+$.

2-(2-Chloro-phenyl)-N-(4-methoxy-phenyl)-acetamide(4ah-4)



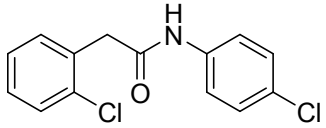
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.28 – 7.26 (m, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 2H), 3.76 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 156.6, 134.4, 132.9, 131.8, 130.7, 129.9, 129.1, 127.5, 122.1(2C), 114.1(2C), 55.5, 42.3. MS(EI): m/z 277.0, 275.0 $[M]^+$.

2-(2-Chloro-phenyl)-*N*-(2-methoxy-phenyl)-acetamide(4ah-5)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.6 Hz, 1H), 7.91 (s, H), 7.44 - 7.41 (m, 2H), 7.31 – 7.25 (m, 2H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.93 (t, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 3.88 (s, 2H), 3.76 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 147.9, 134.5, 132.9, 131.8, 129.8, 129.0, 127.7, 127.4, 123.8, 121.1, 119.7, 110.0, 55.8, 42.8. MS(EI): m/z 277.0, 275.0 $[M]^+$.

2-(2-Chloro-phenyl)-N-(4-chloro-phenyl)-acetamide(4ah-6)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 4H), 7.29 – 7.22 (m, 4H), 3.83 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 136.2, 134.4, 132.5, 131.8, 130.1, 129.5, 129.3, 129.0(2C), 127.6, 121.3(2C), 42.4. MS(EI): m/z 281.0, 279.0 $[M]^+$.

References

1 Poondra, Rajamohan R. *Org. Lett*., 2005, **7**, 863.

2 Qi, Hengzhen. *Synthesis*, 2011, 723.

3 Liu, Bin. *Bioorg. Med. Chem*., 2003, **11**, 3889.

4 Baumgarten, Henry E. *J*. *Am*. *Chem*. *Soc*., 1960, **82**, 3977.

5 Julian, Percy L. *J*. *Am*. *Chem*. *Soc*., 1935, **57**, 2026.

6 Ishikura, Minoru. *Tetrahedron* 2006, **62**, 11580.

7 Teichert, Antje. *Org. Lett*., 2004, **6**, 3477.

8 Ueda, Satoshil. *Chem. Commun*., 2010, **46**, 2462.

9 Tang, Shi; Peng, Peng; Zhong, Ping; Li, Jin-Heng. *J. Org. Chem*., 2008, **73**, 5476.

4. Copies of the NMR spectra of the products

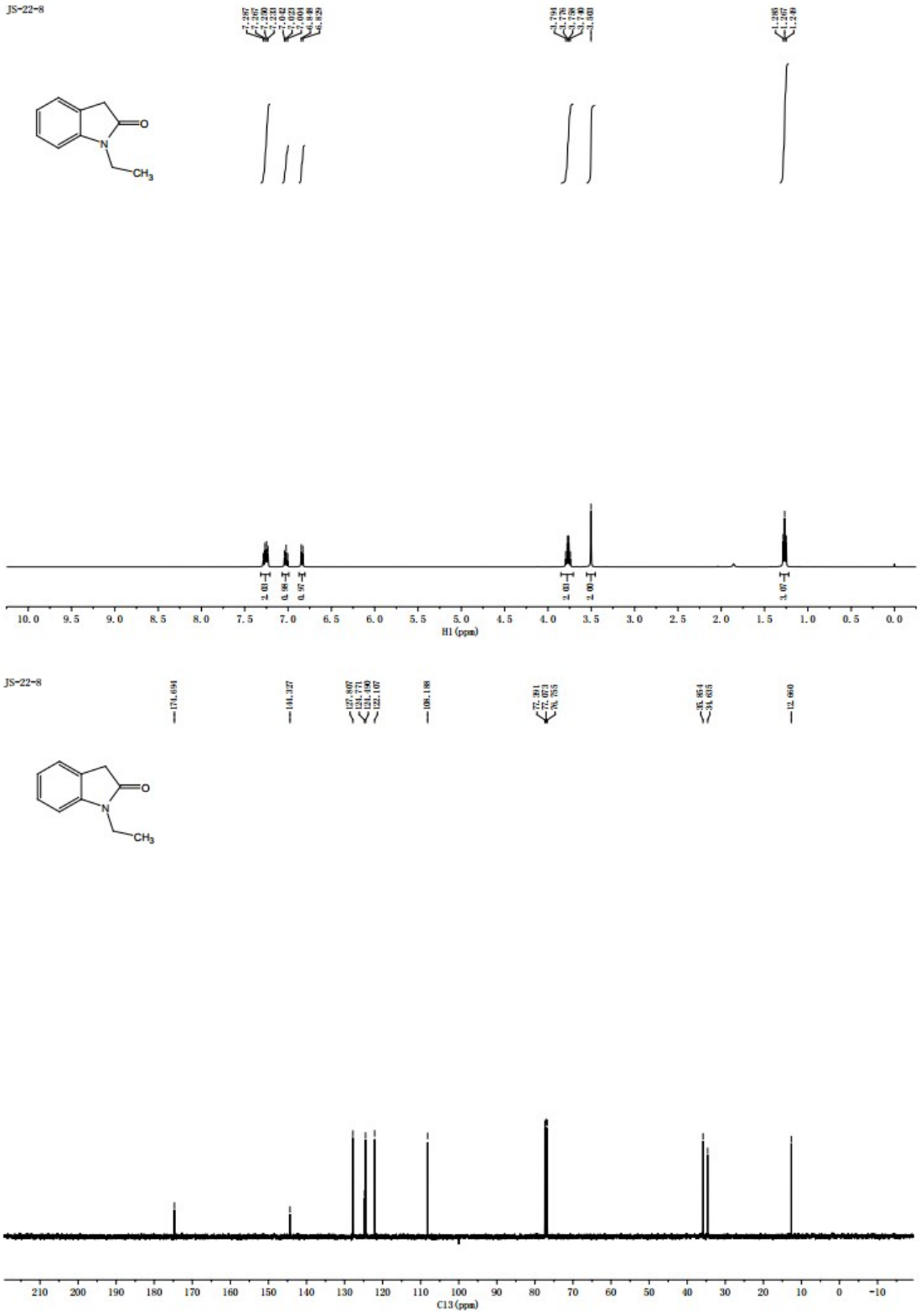


Fig. S1 ^{1}H and ^{13}C NMR copies of oxindole **3aa**

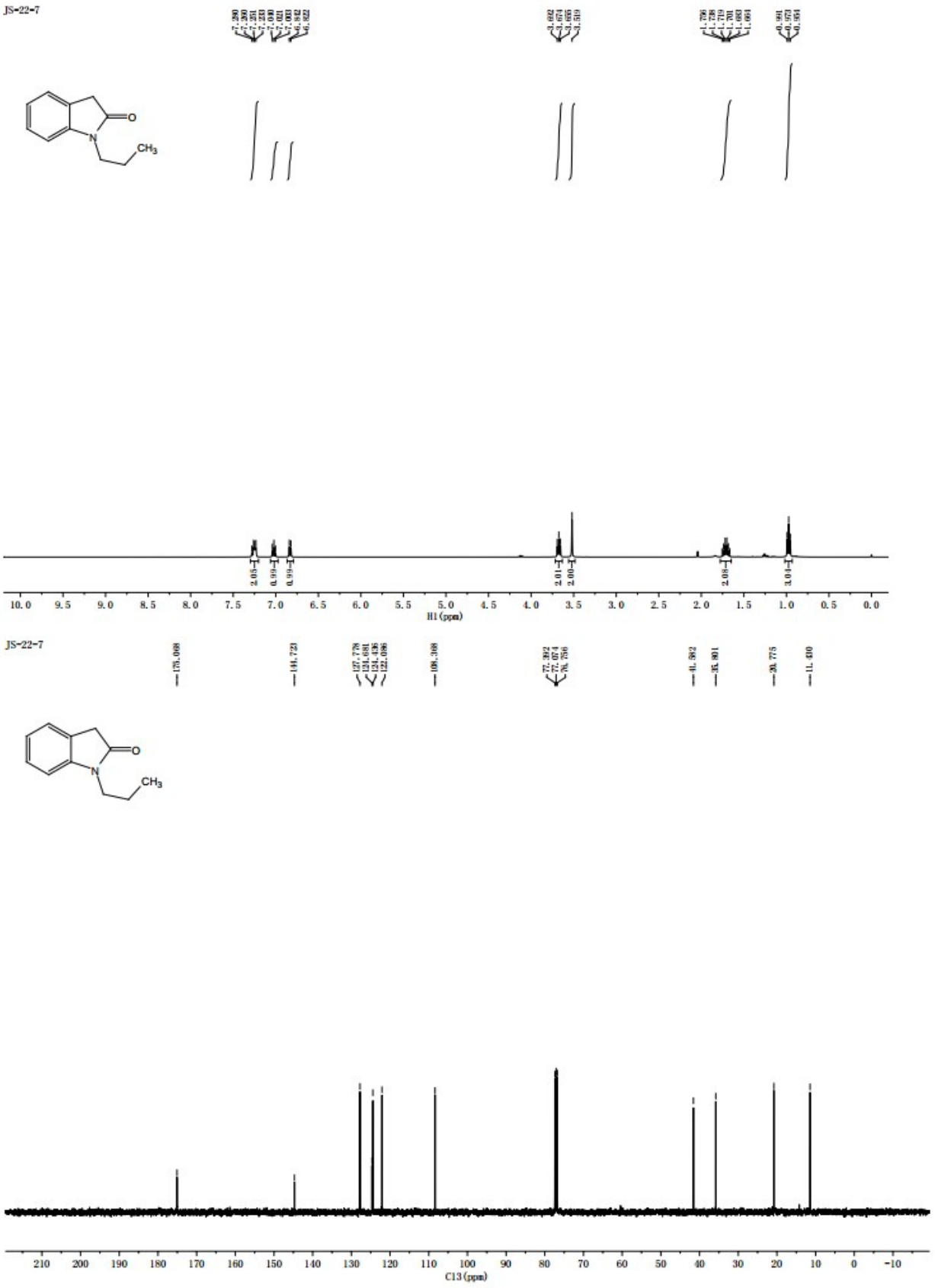


Fig. S2 ^{1}H and ^{13}C NMR copies of oxindole **3ab**

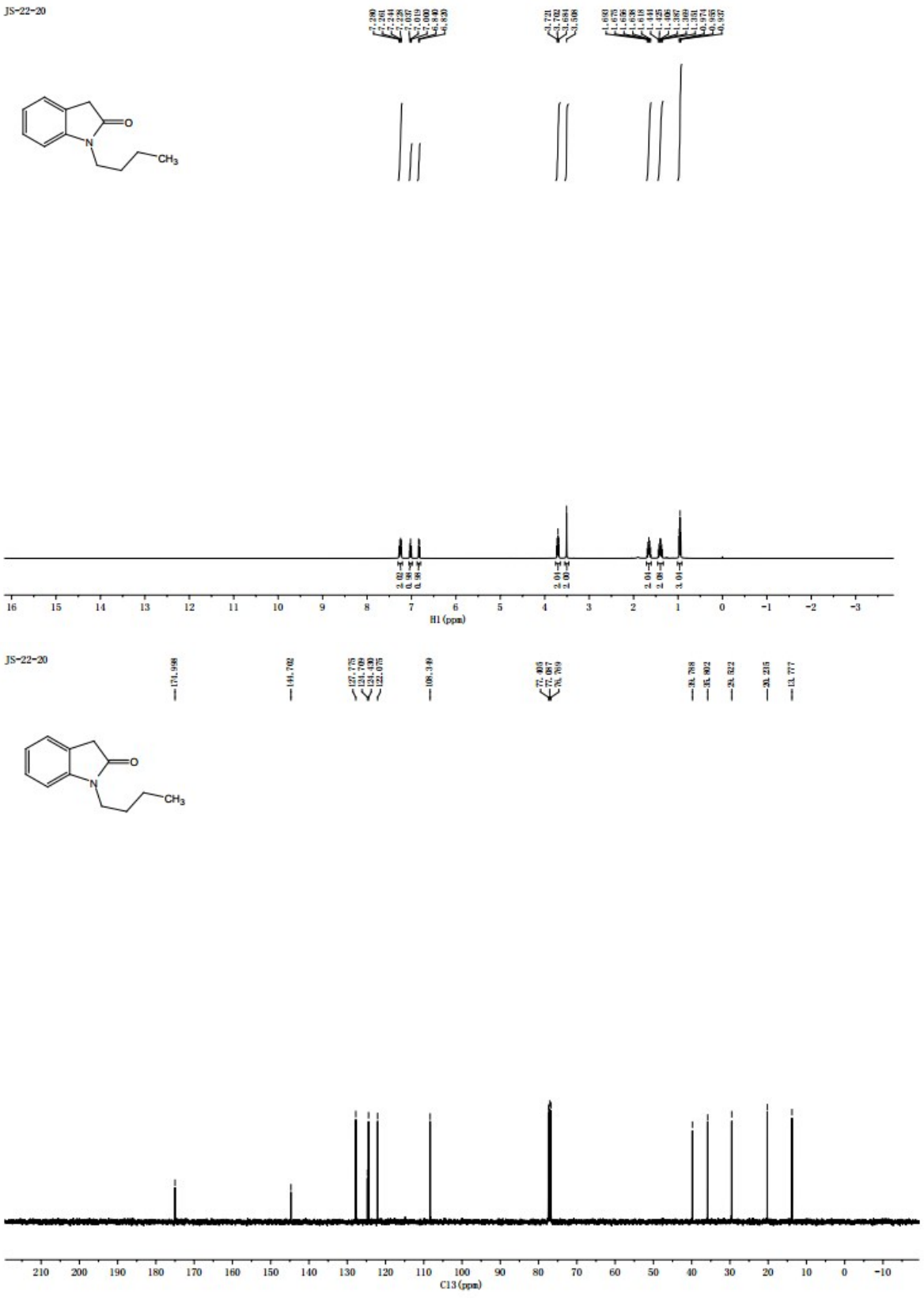


Fig. S3 ^{1}H and ^{13}C NMR copies of oxindole **3ac**

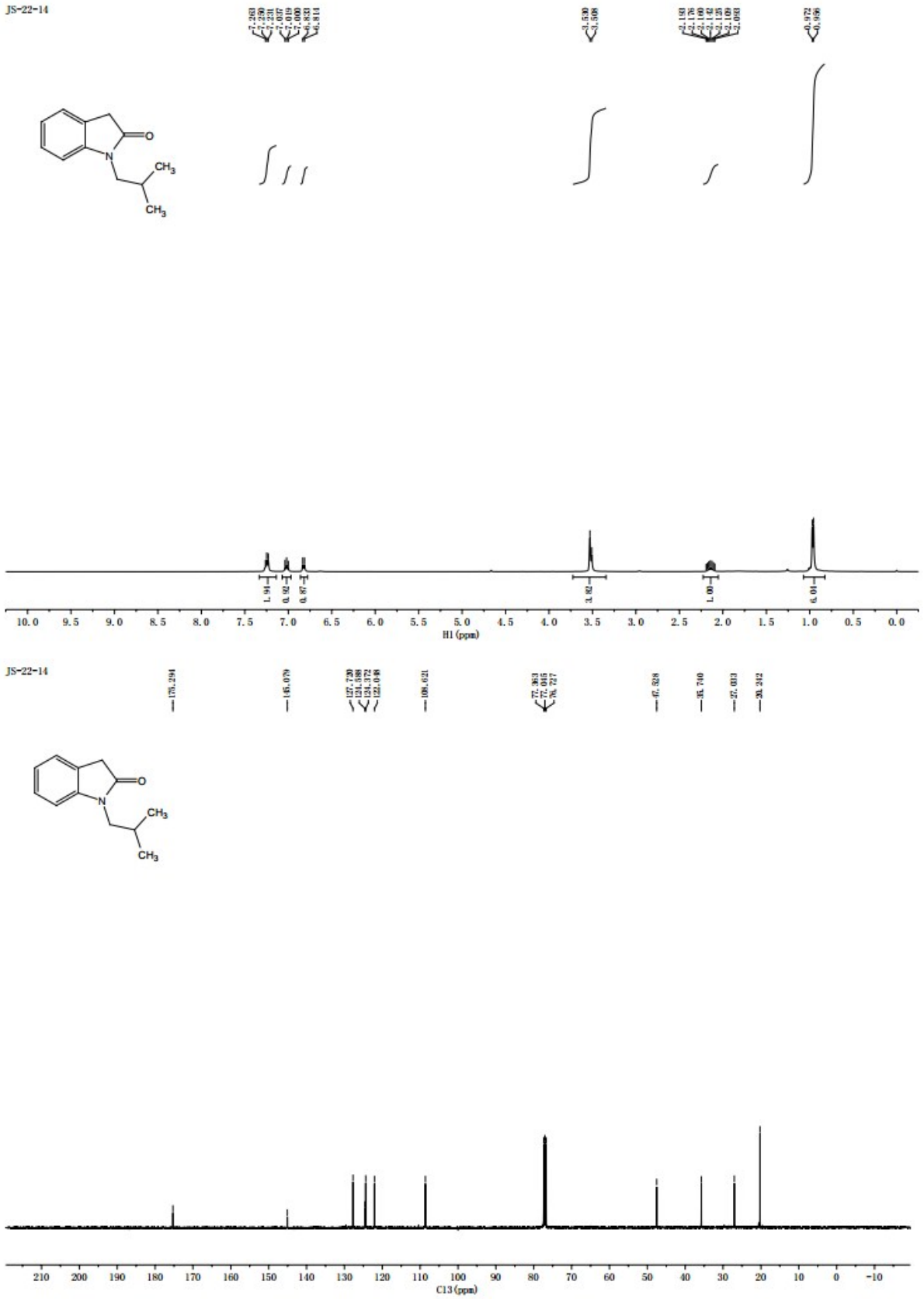


Fig. S4 ^{1}H and ^{13}C NMR copies of oxindole **3ad**

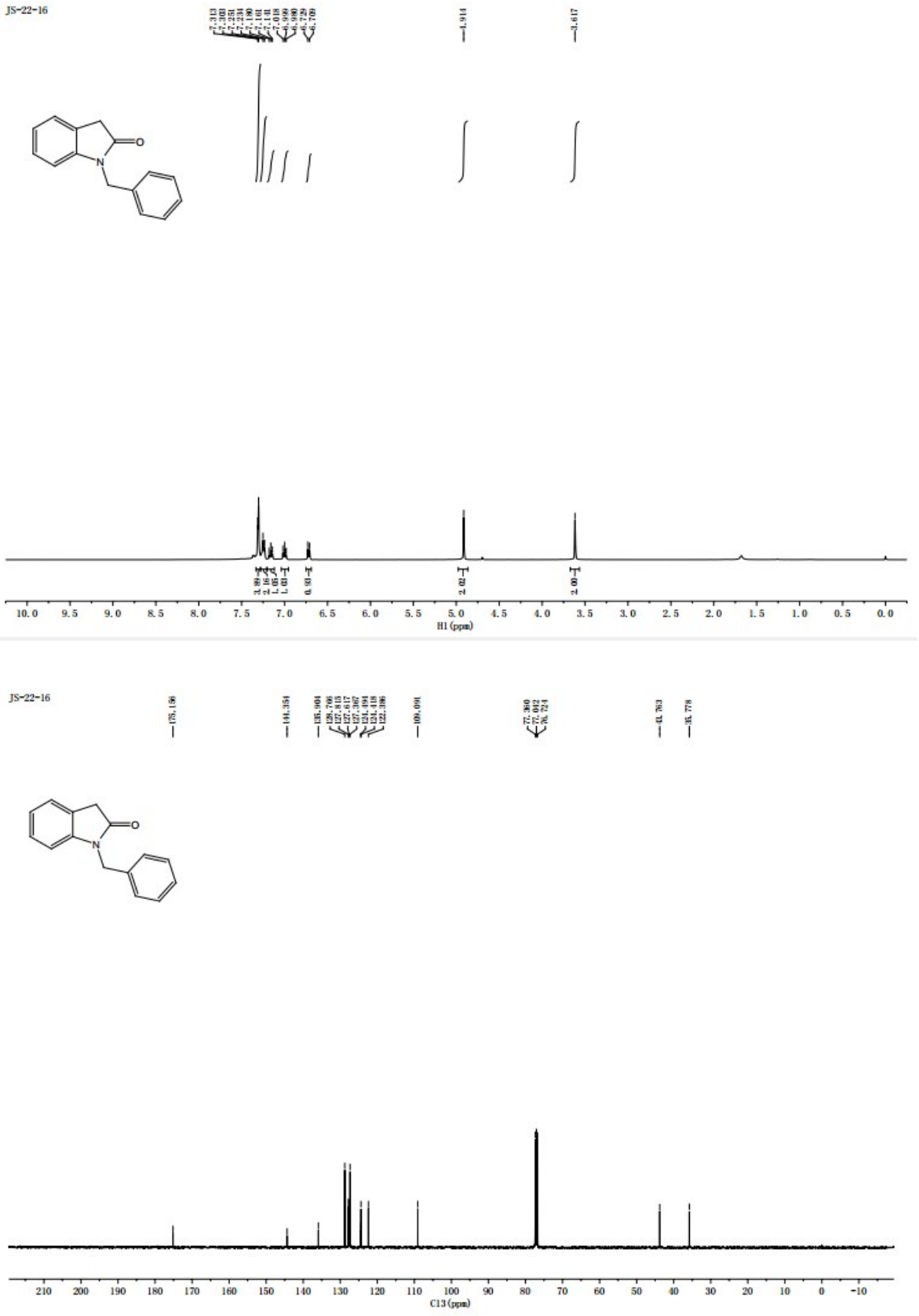


Fig. S5 ^{1}H and ^{13}C NMR copies of oxindole **3ae**

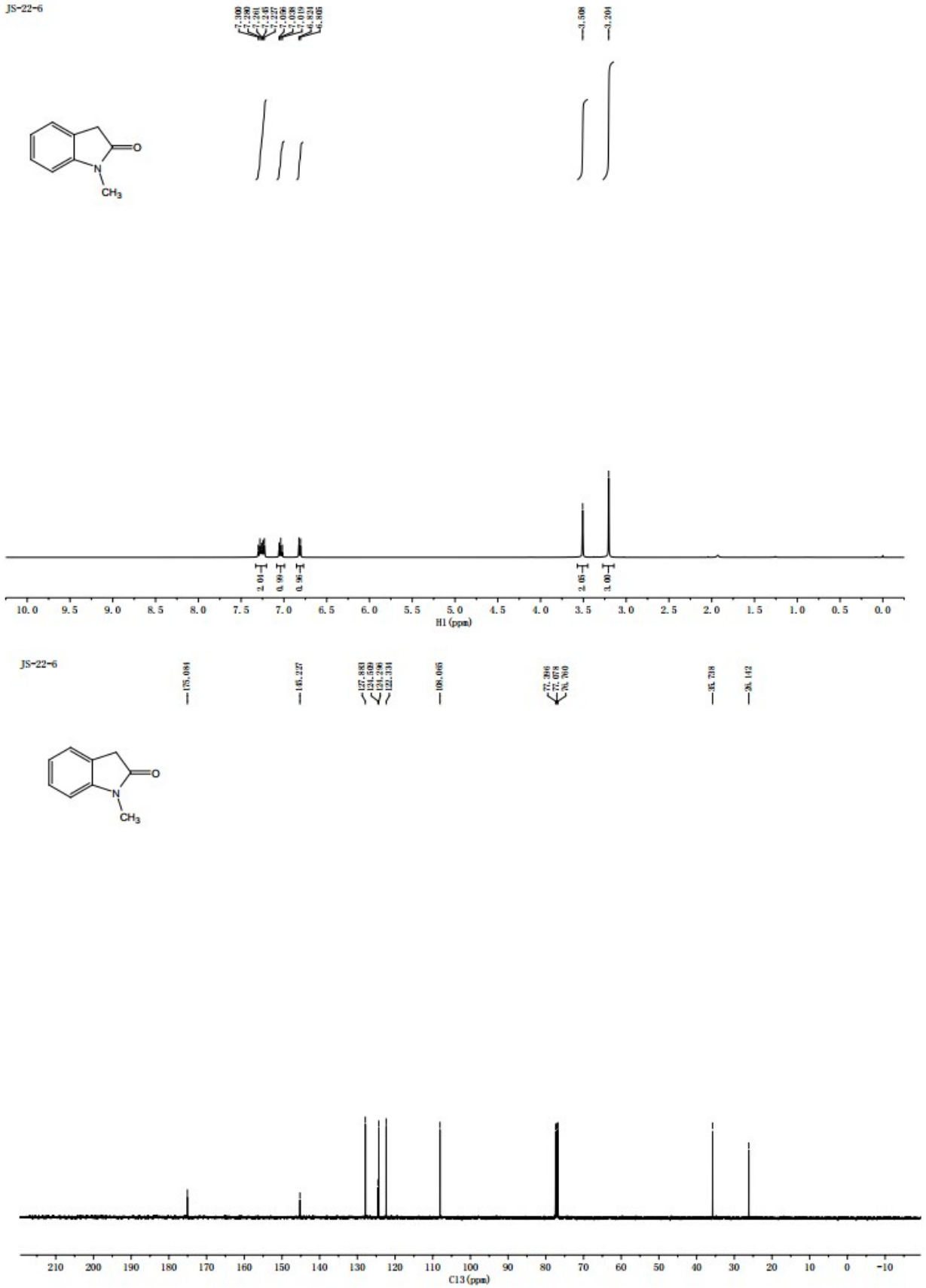


Fig. S6 ^{1}H and ^{13}C NMR copies of oxindole **3af**

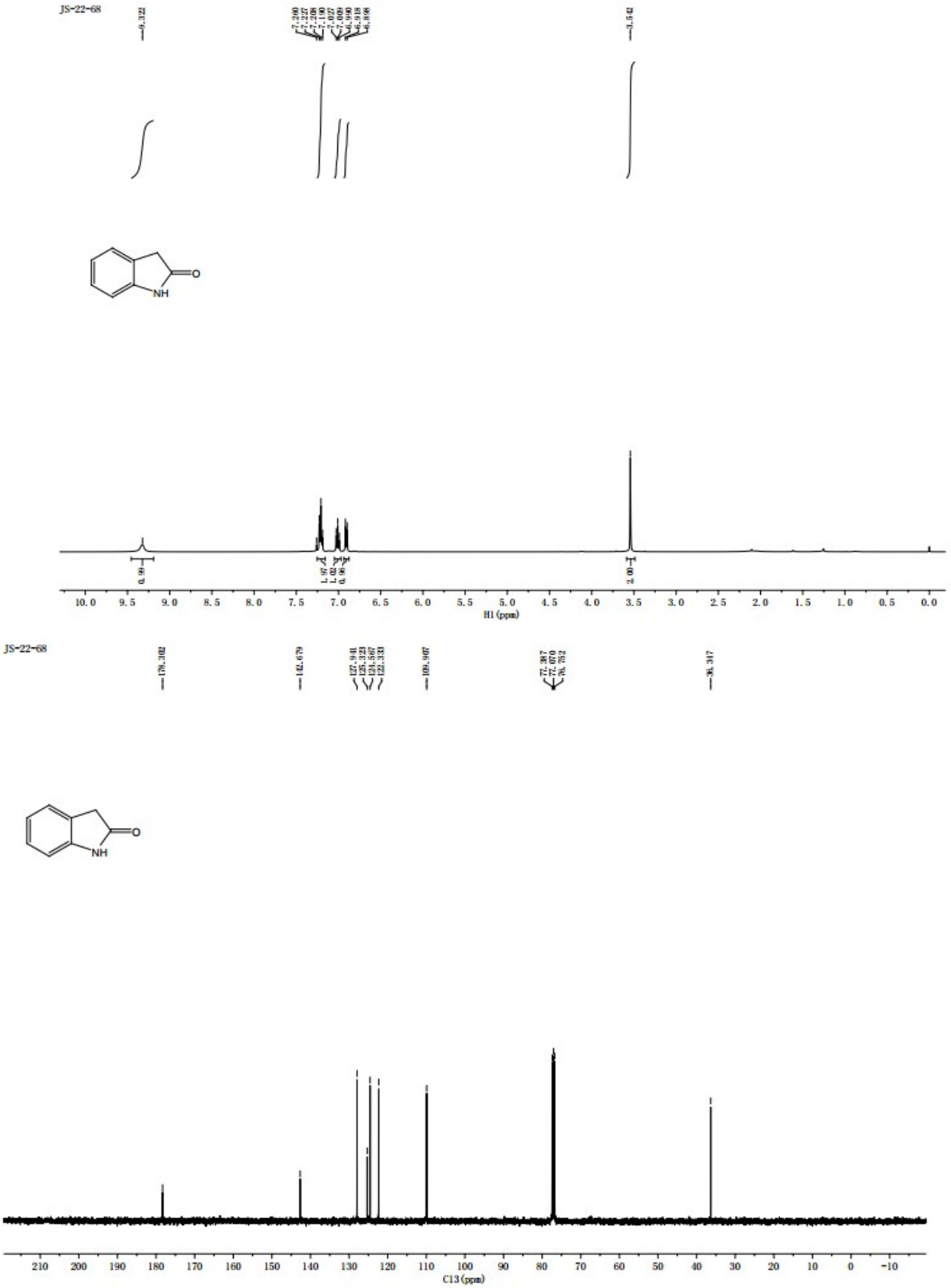


Fig. S7 ^{1}H and ^{13}C NMR copies of oxindole **3ag**

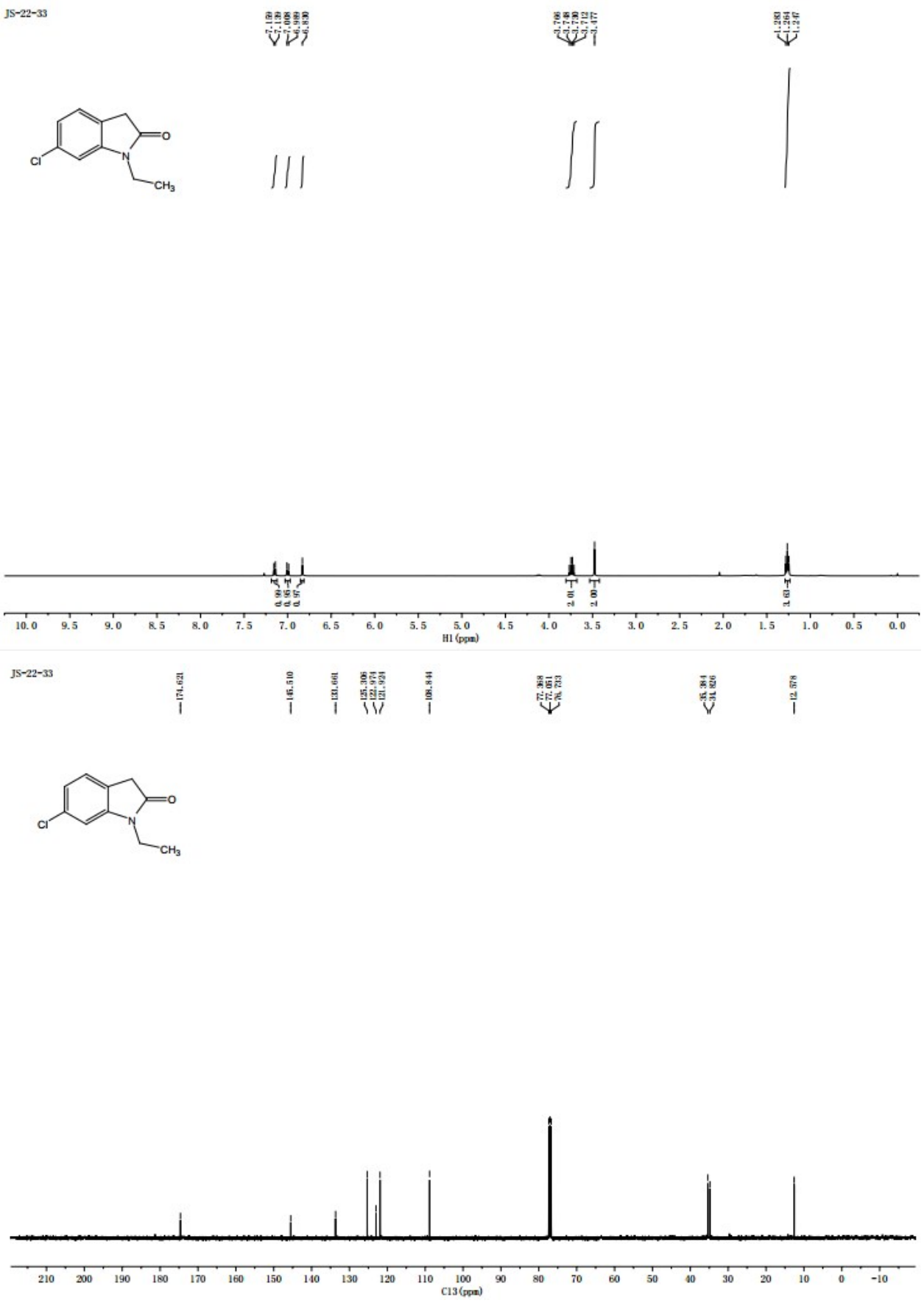


Fig. S8 ^{1}H and ^{13}C NMR copies of oxindole **3ba**

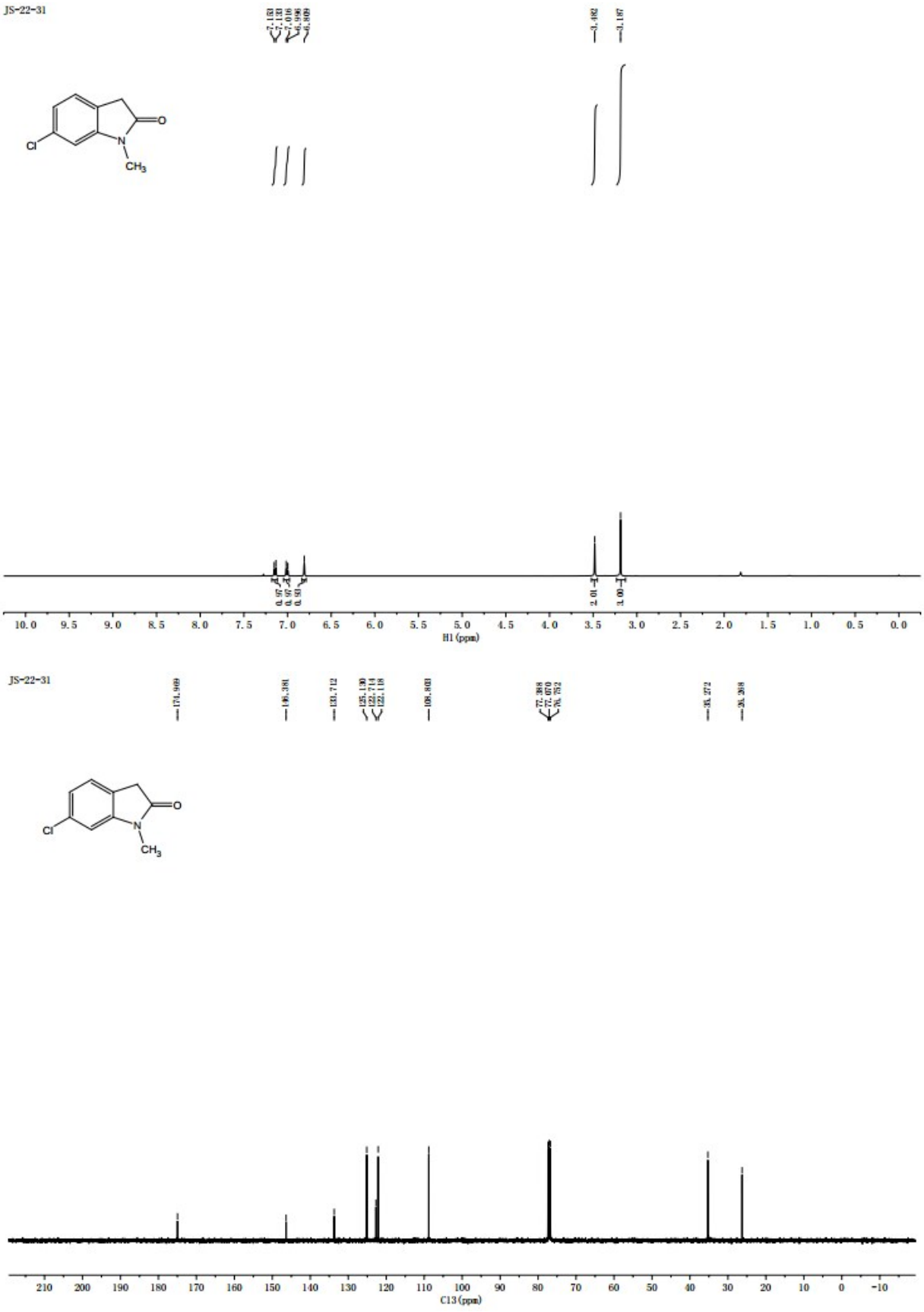


Fig. S9 ^{1}H and ^{13}C NMR copies of oxindole **3bf**

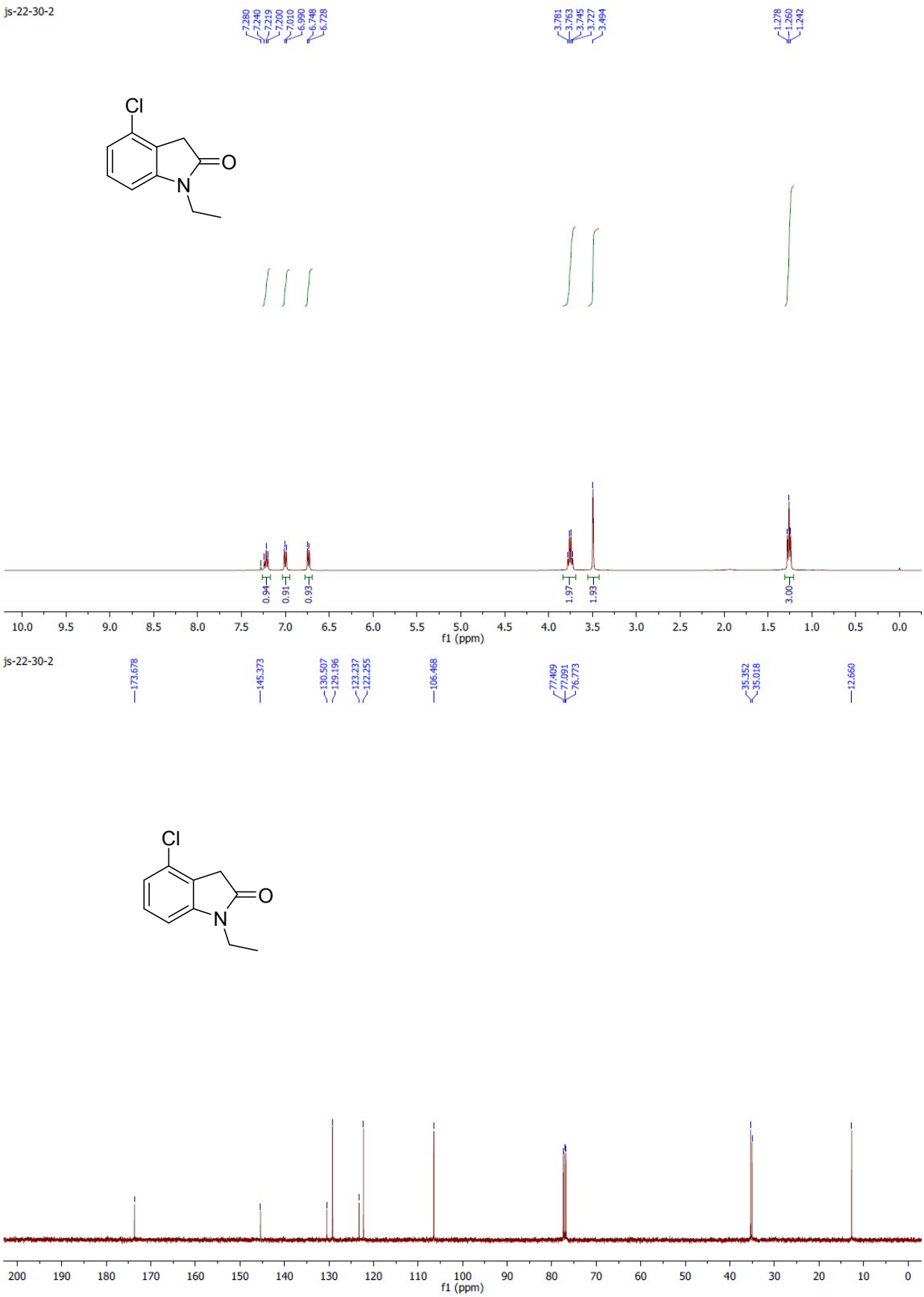


Fig. S10 ^{1}H and ^{13}C NMR copies of oxindole **3ca**

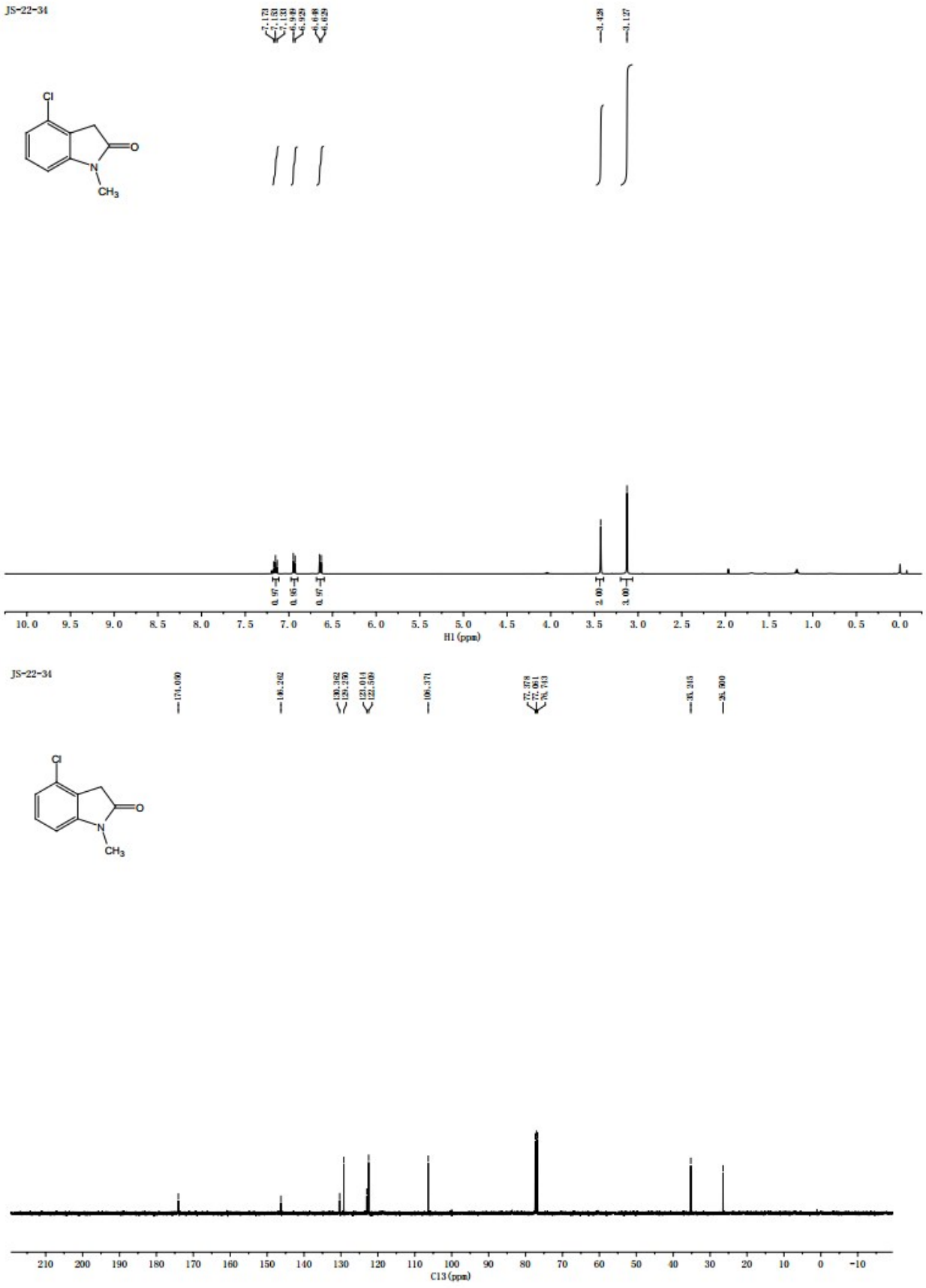


Fig. S11 ^{1}H and ^{13}C NMR copies of oxindole **3cf**

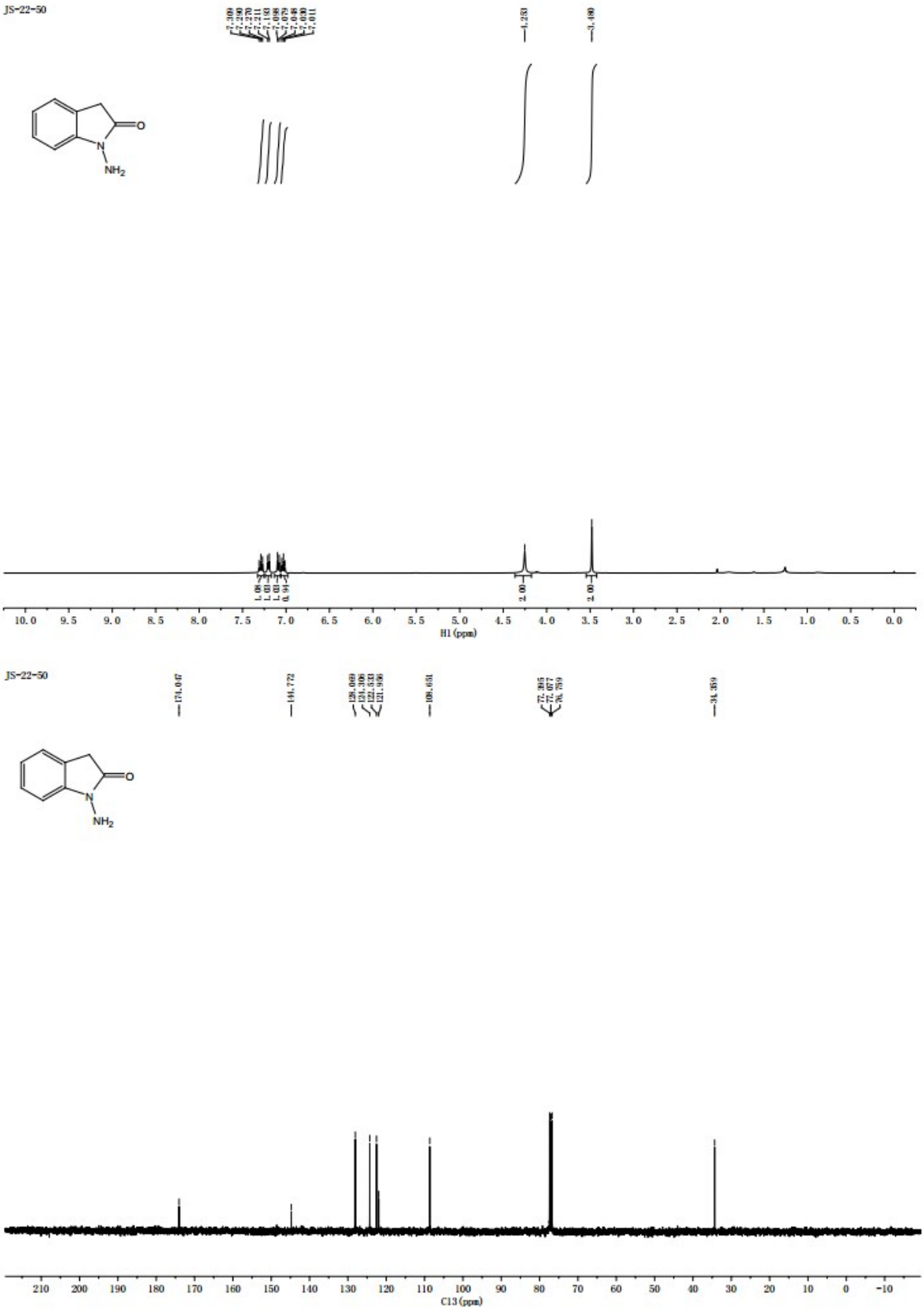


Fig. S12 ^{1}H and ^{13}C NMR copies of oxindole **3ai**

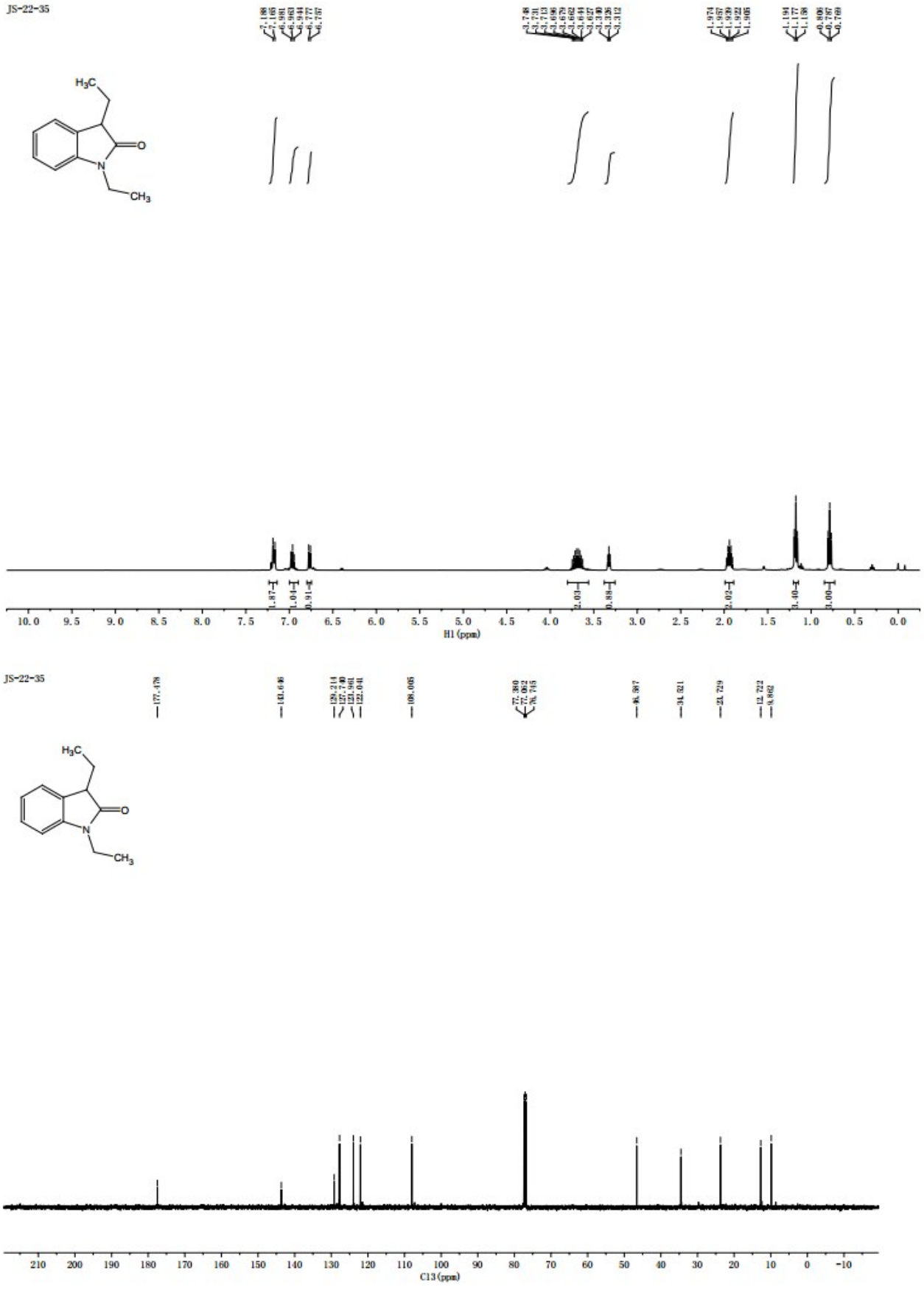


Fig. S13 ^{1}H and ^{13}C NMR copies of oxindole **3da**

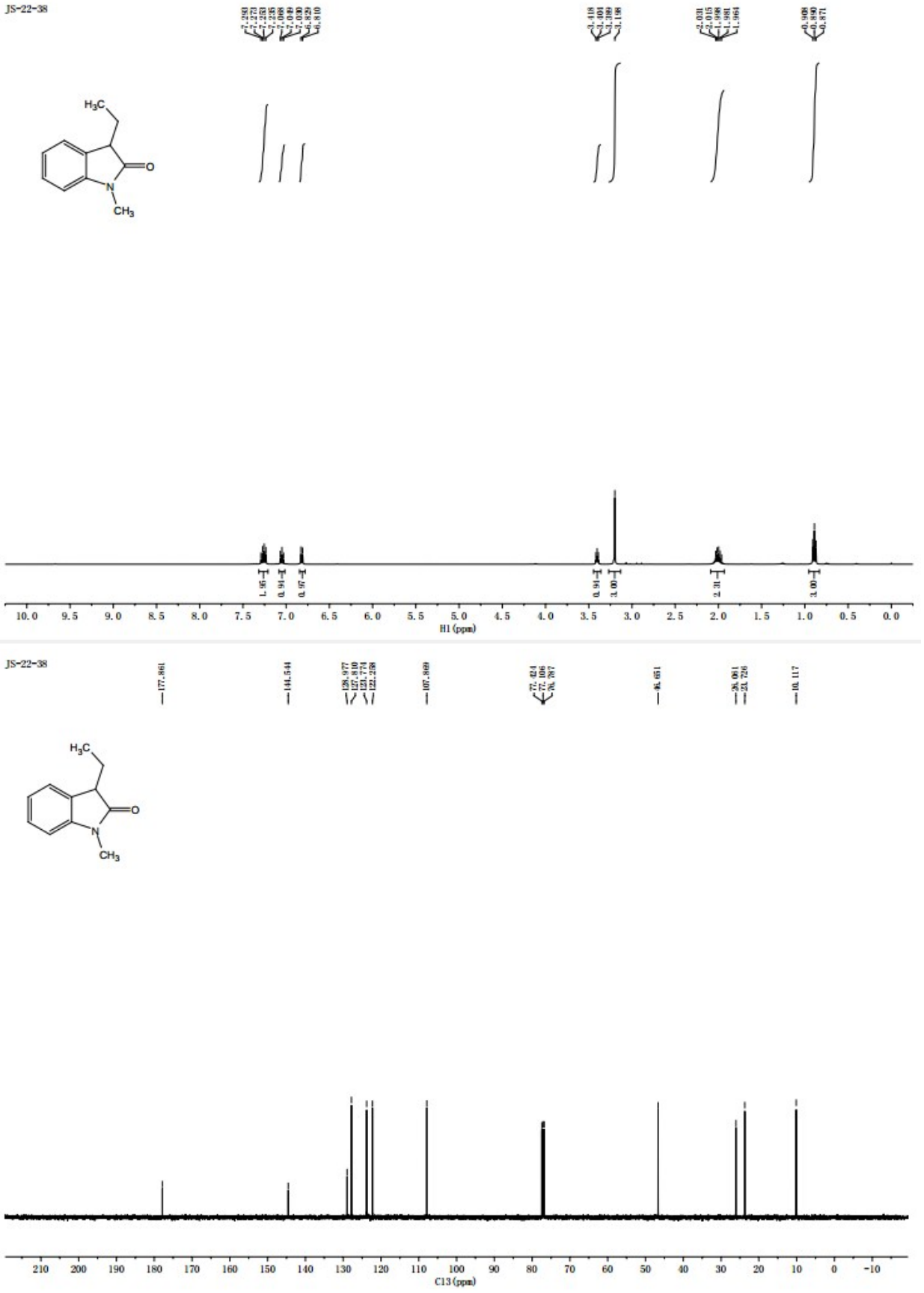


Fig. S14 ^{1}H and ^{13}C NMR copies of oxindole **3df**

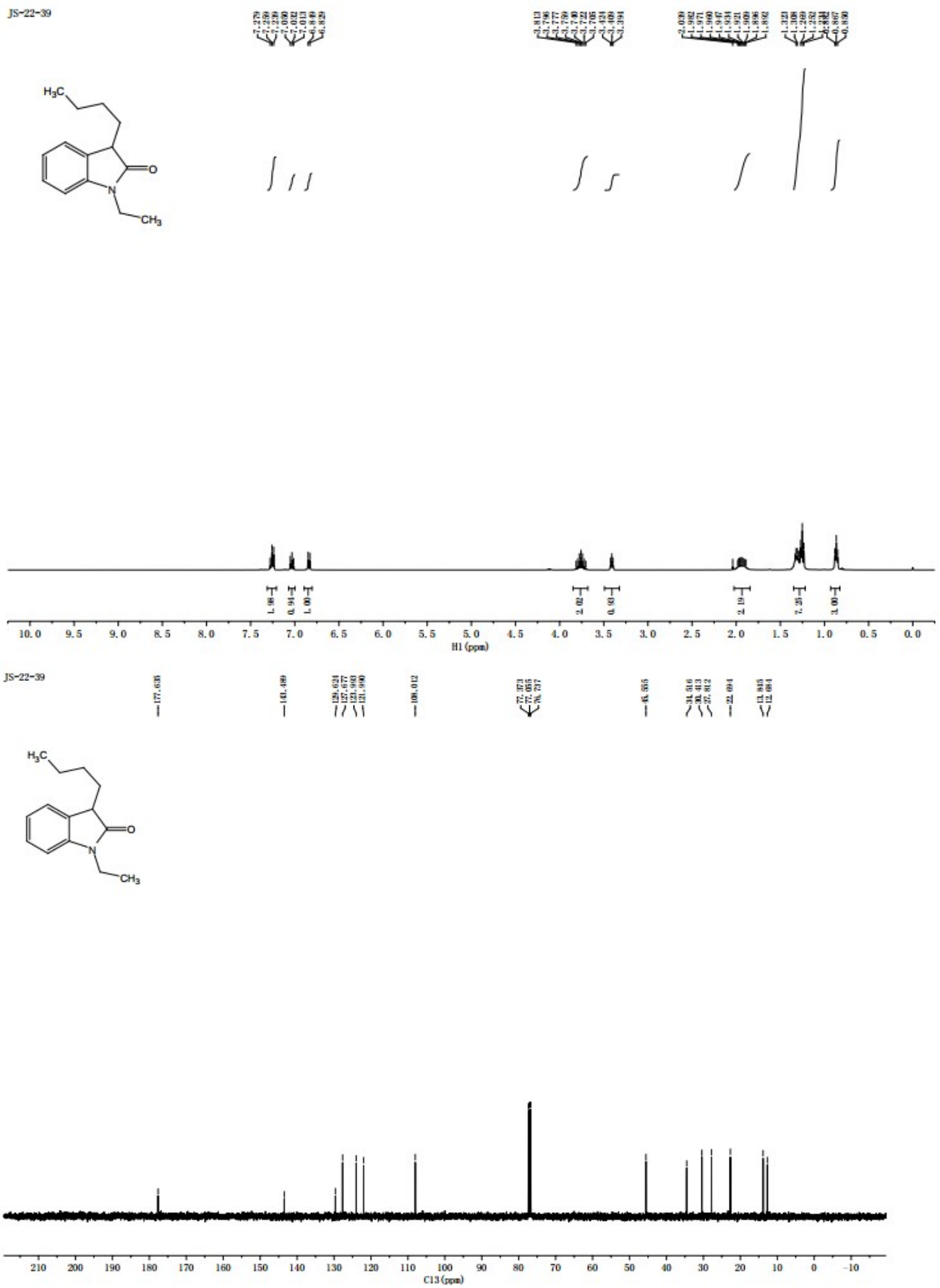


Fig. S15 ^{1}H and ^{13}C NMR copies of oxindole **3ea**

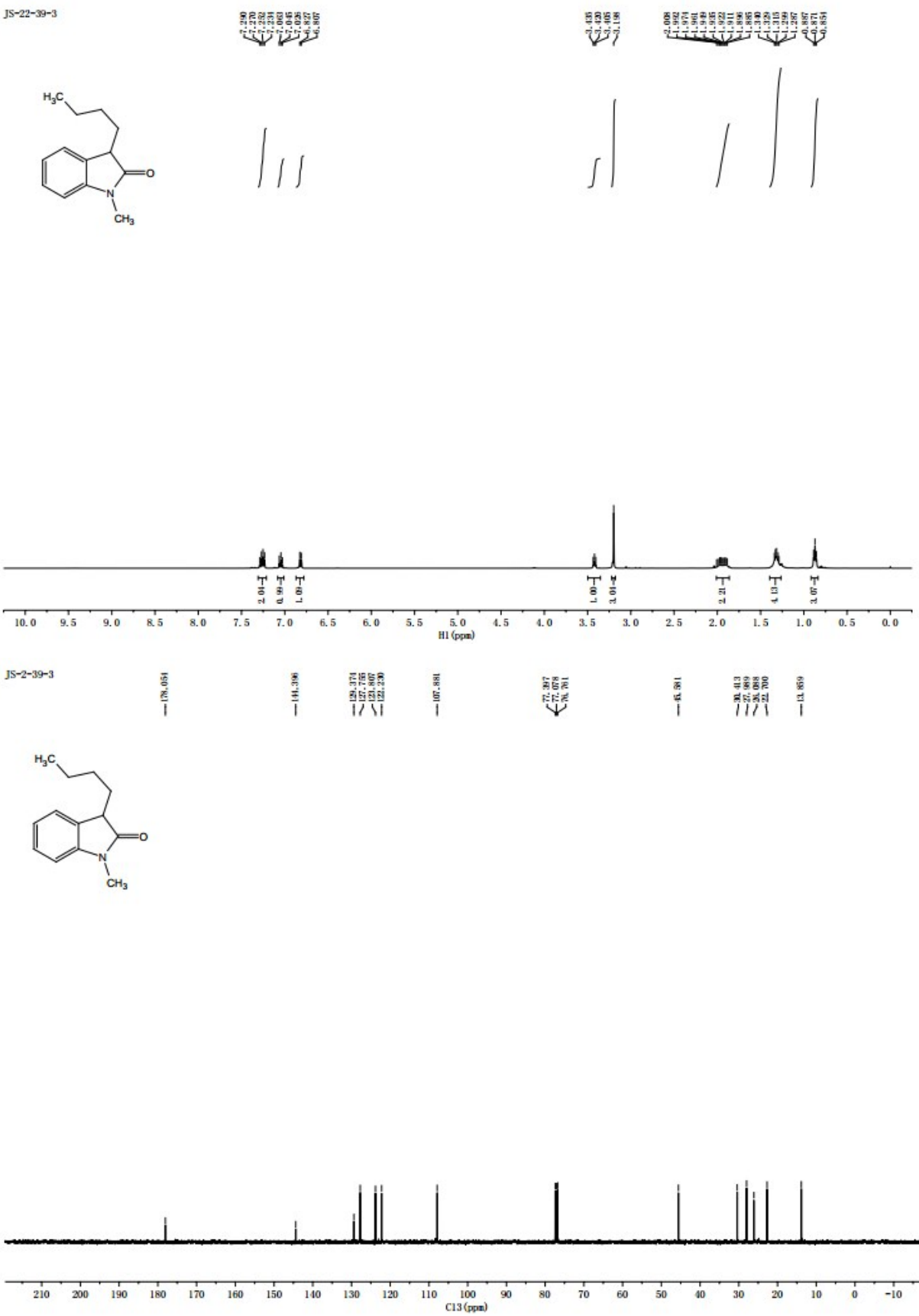


Fig. S16 ^{1}H and ^{13}C NMR copies of oxindole **3ef**

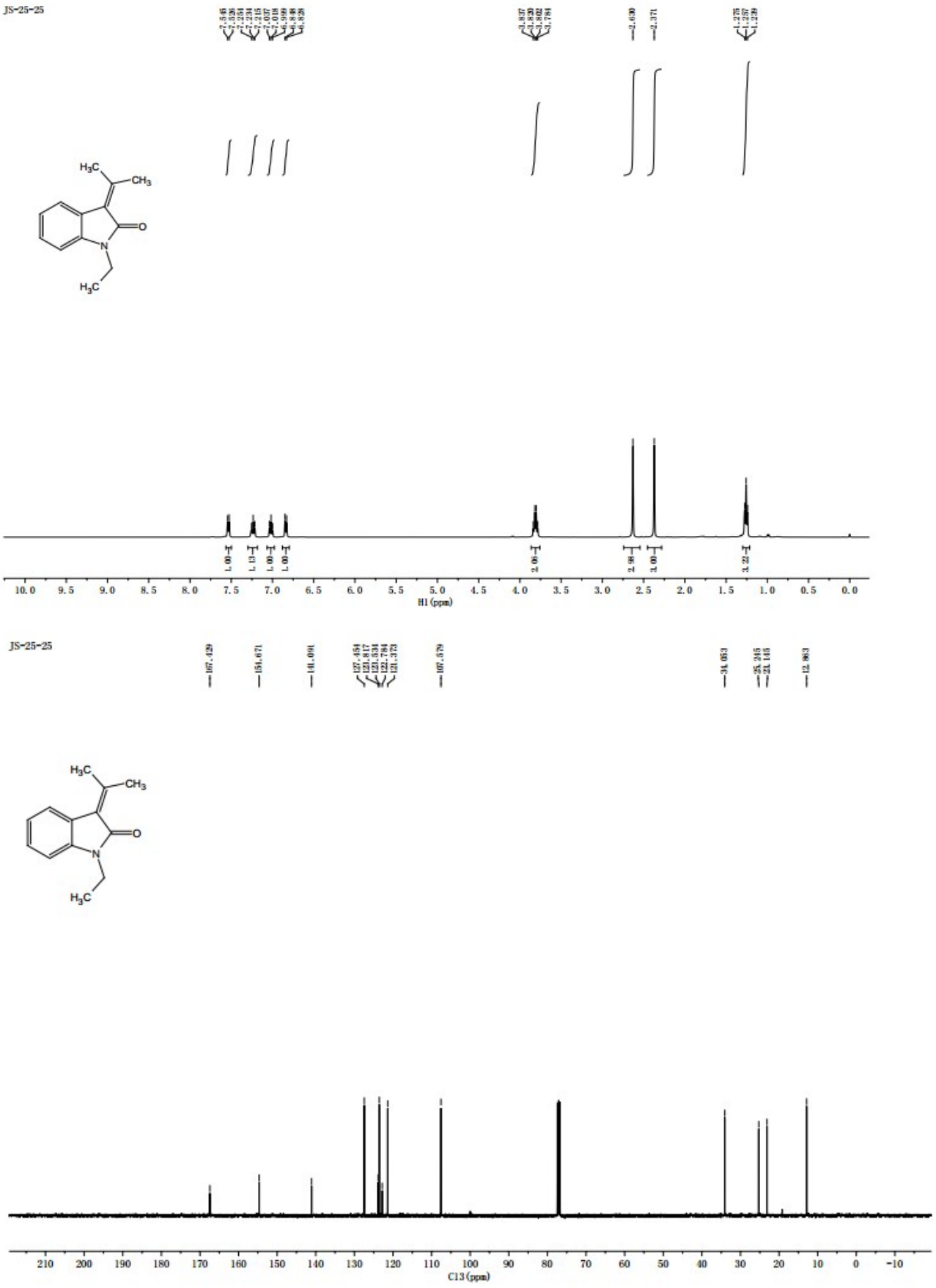


Fig. S17 ^{1}H and ^{13}C NMR copies of oxindole **3fa**

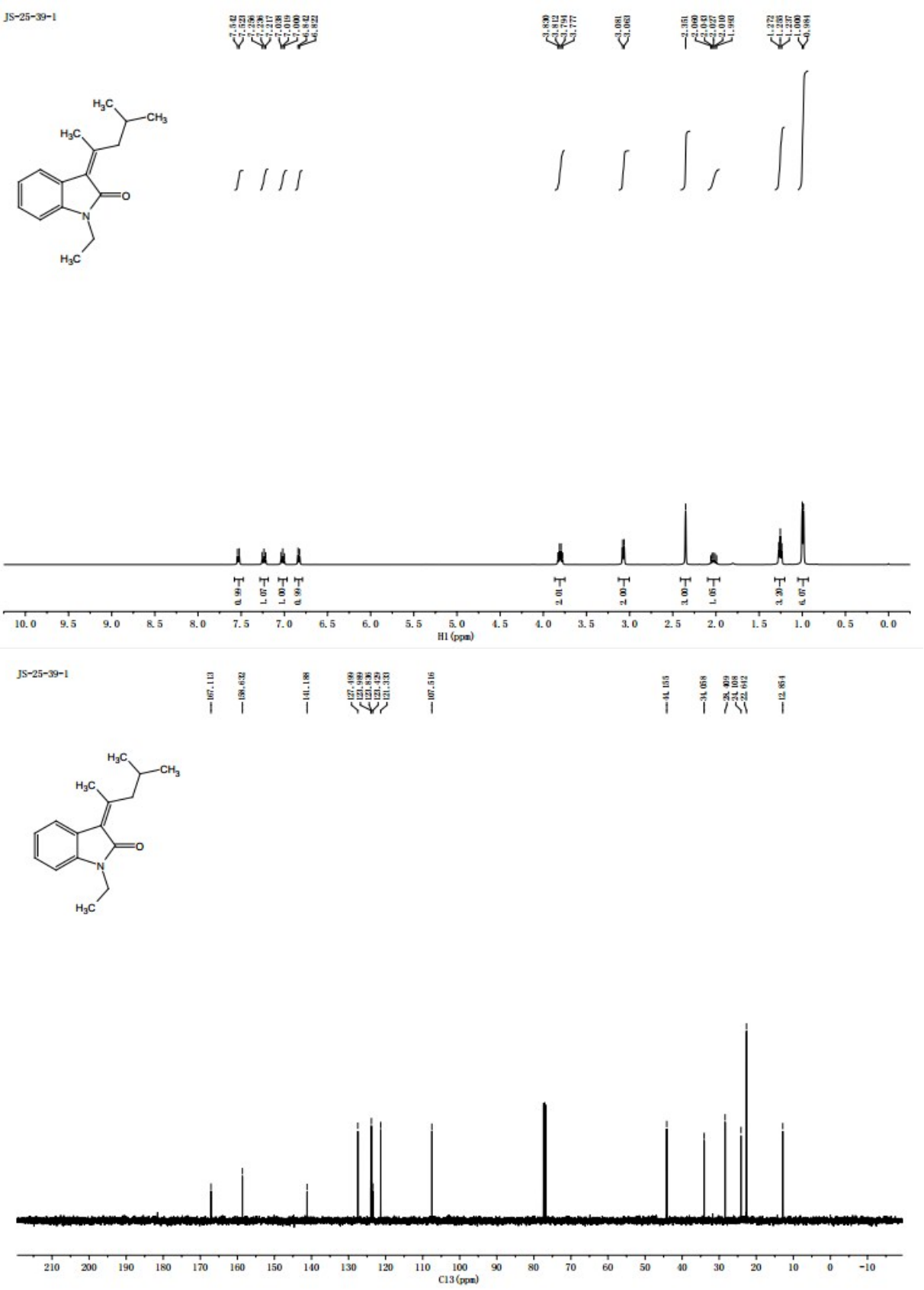


Fig. S18 ^{1}H and ^{13}C NMR copies of oxindole *Z*-**3ga**

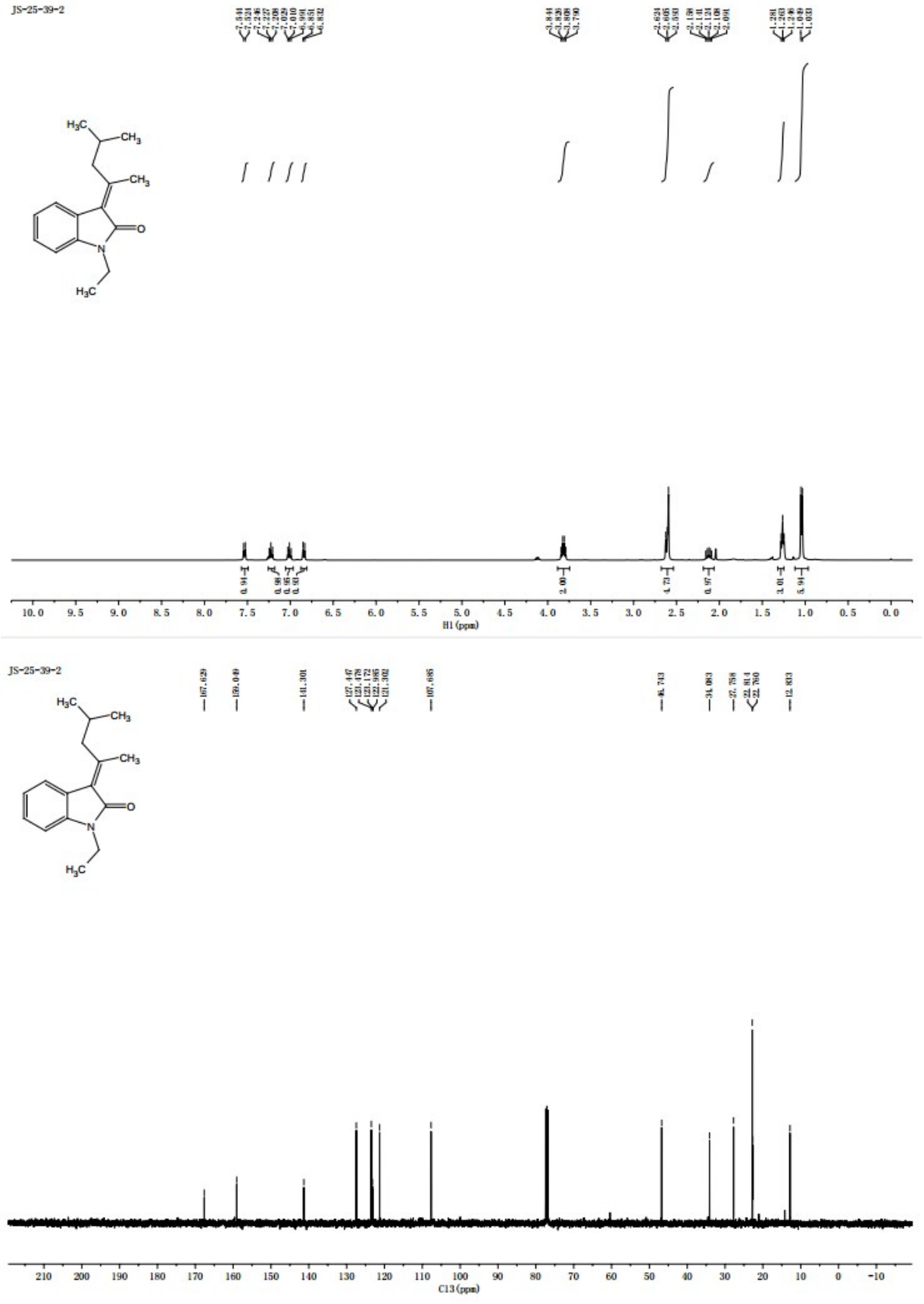


Fig. S19 ^{1}H and ^{13}C NMR copies of oxindole *E*-**3ga**

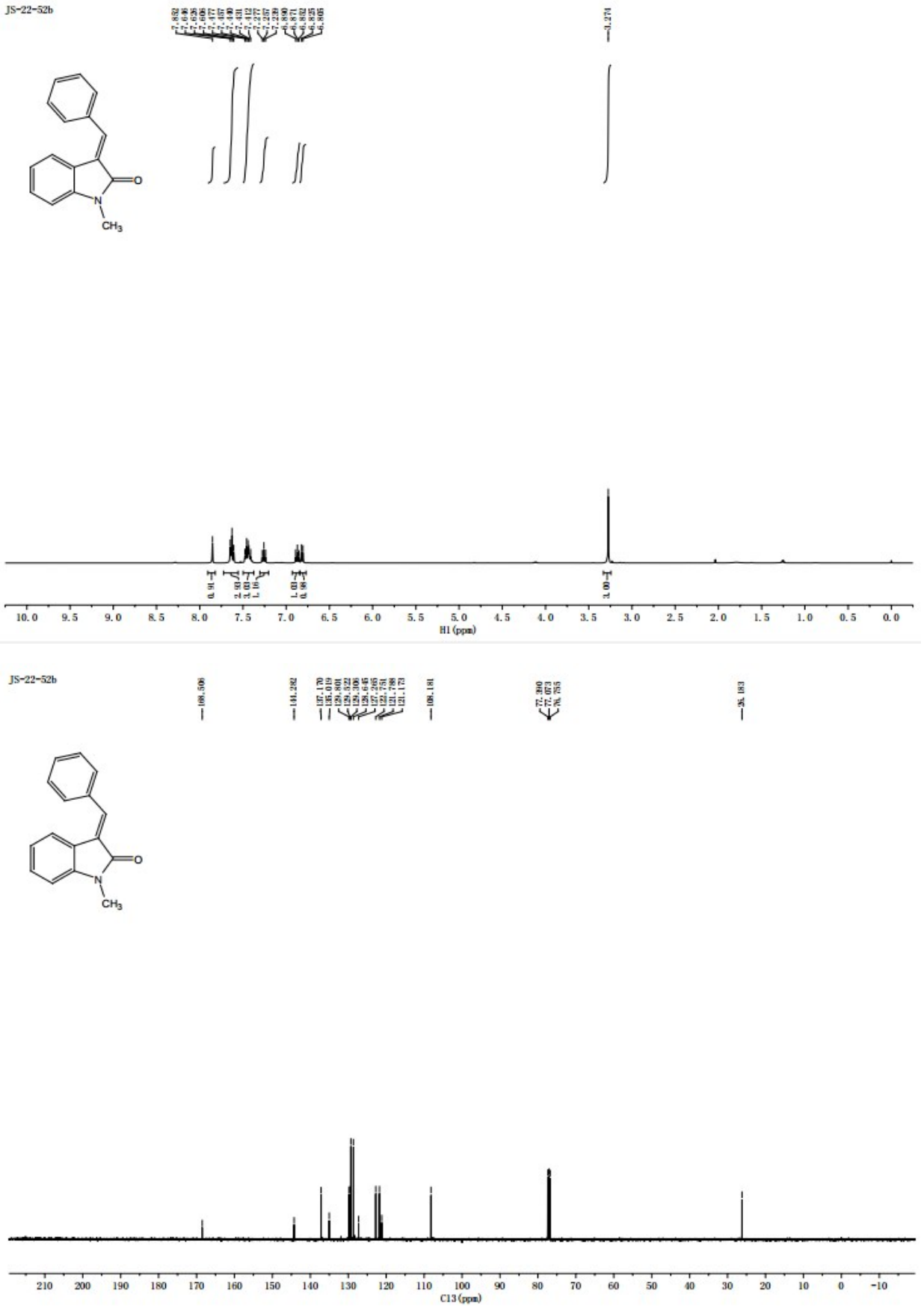


Fig. S20 ^{1}H and ^{13}C NMR copies of oxindole *E*-**3ha**

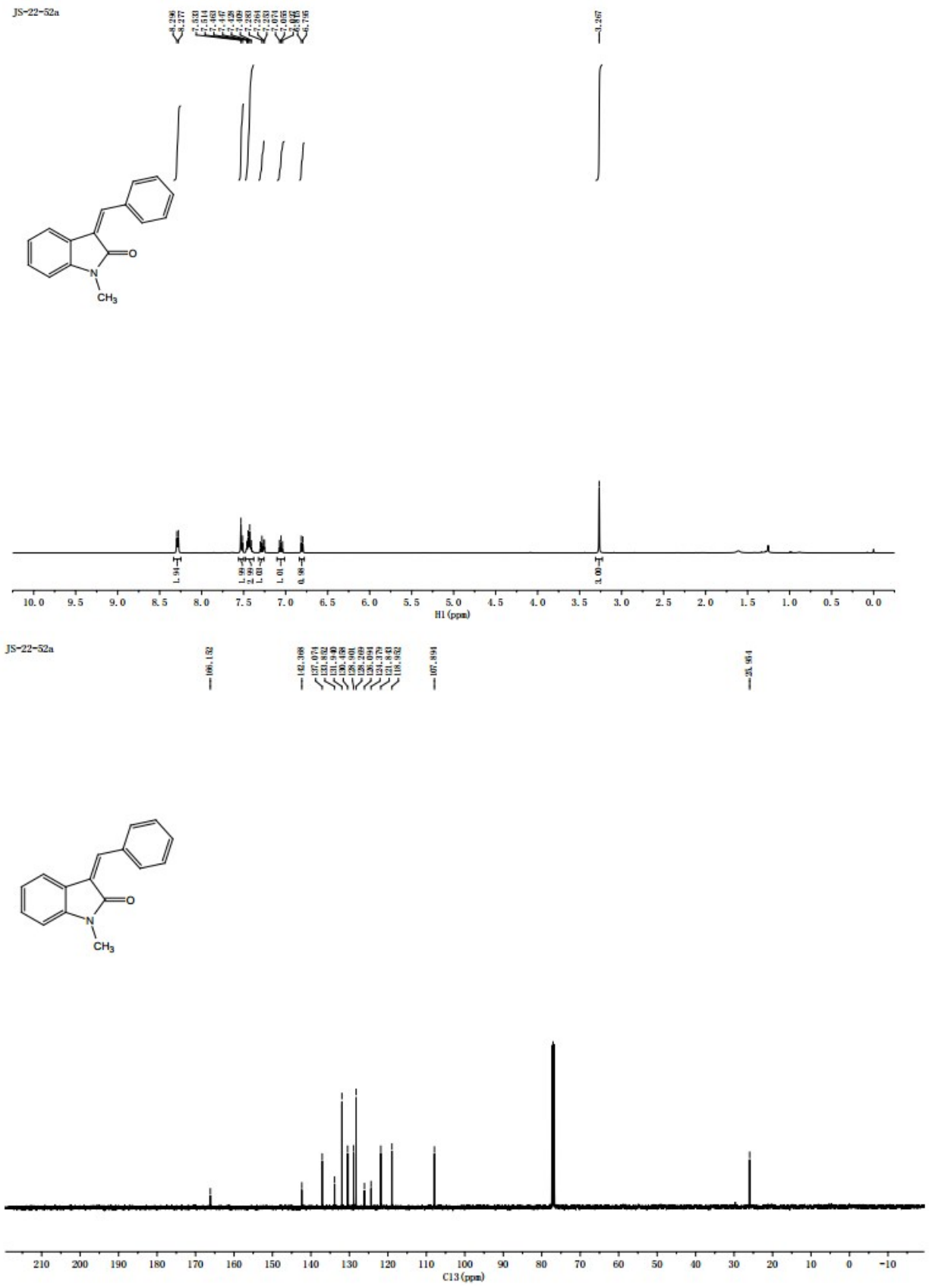


Fig. S21 ^{1}H and ^{13}C NMR copies of oxindole *Z*-**3ha**

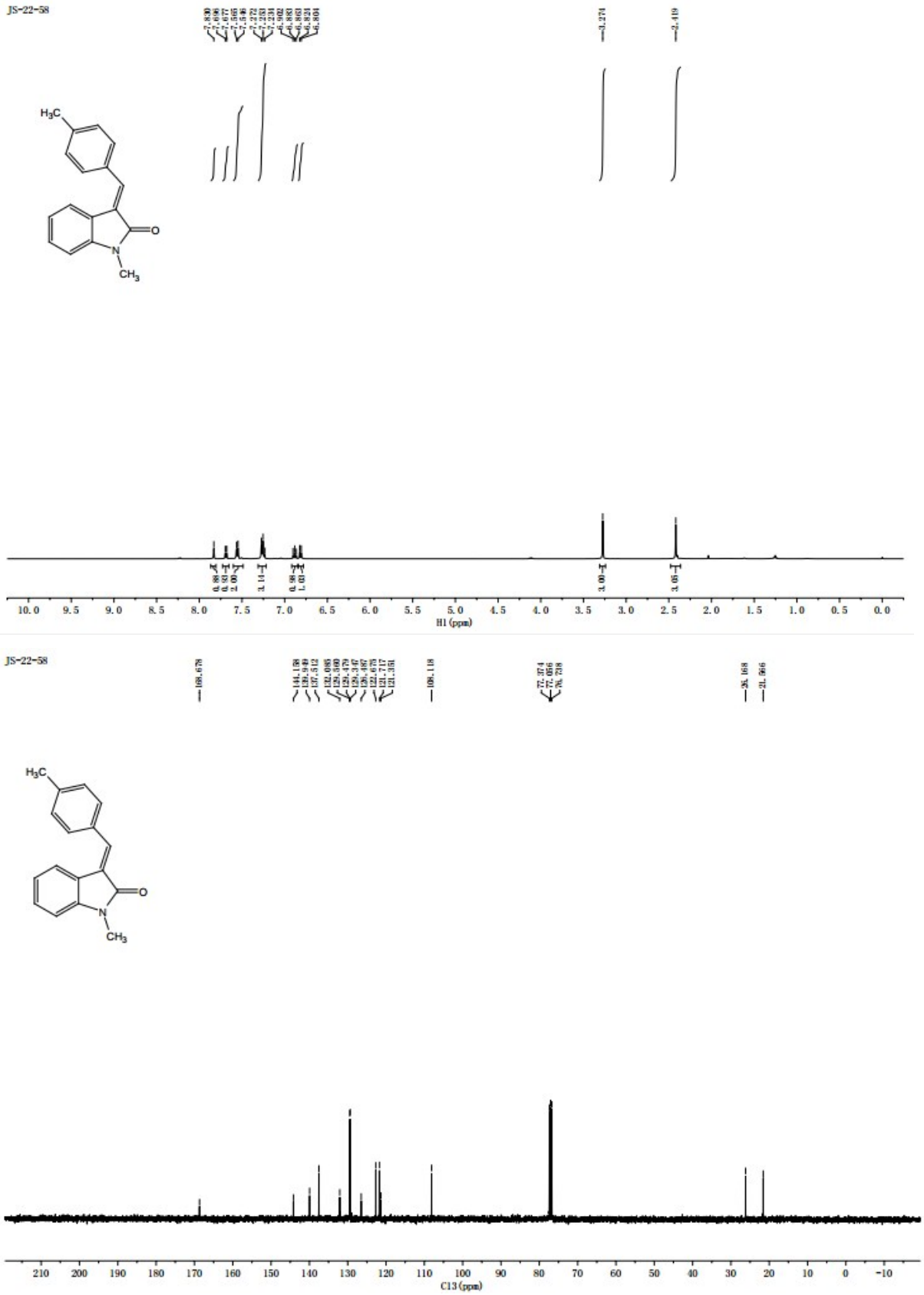


Fig. S22 ^{1}H and ^{13}C NMR copies of oxindole *E*-**3ia**

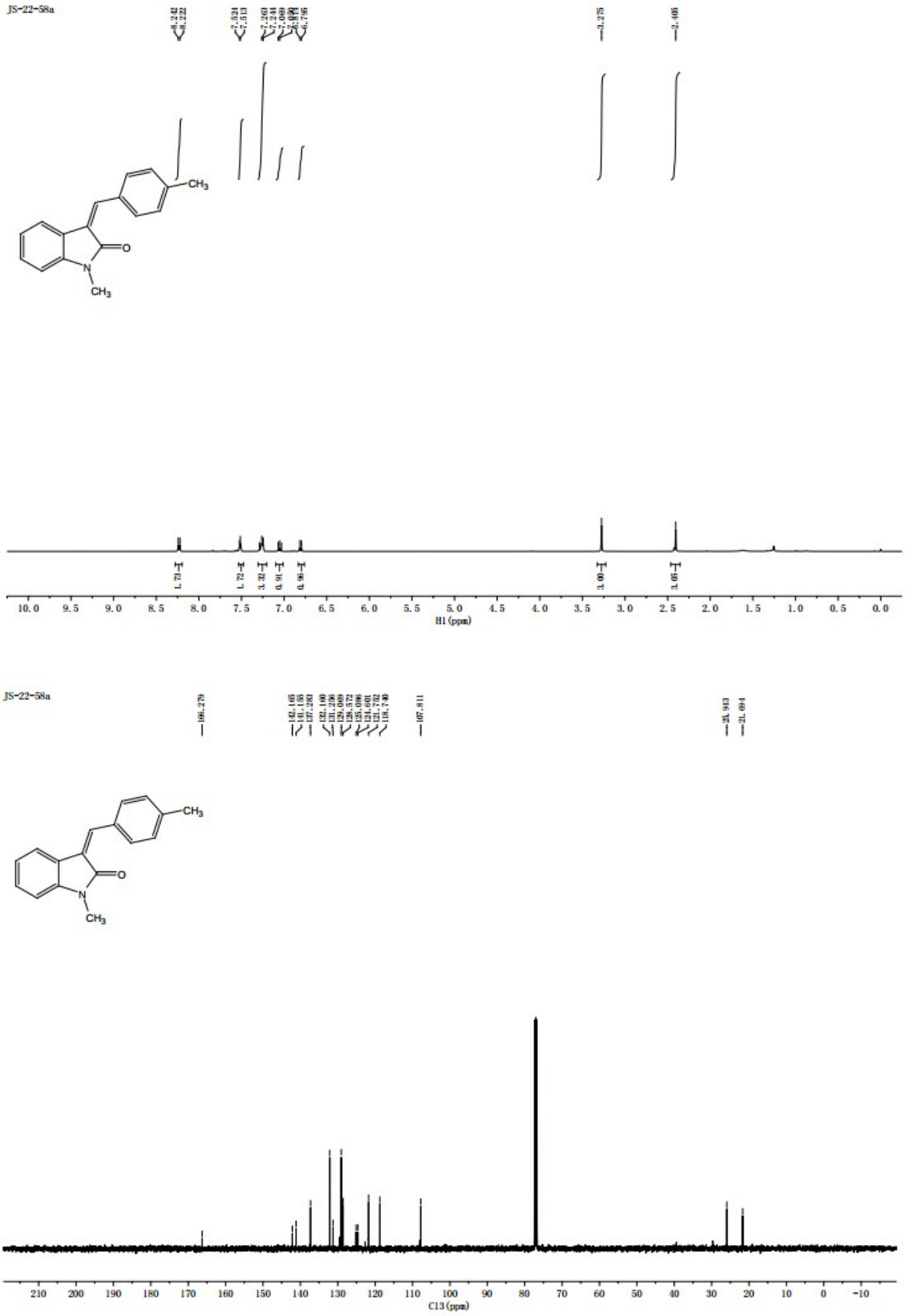


Fig. S23 ^{1}H and ^{13}C NMR copies of oxindole *Z*-**3ia**

Fig. S24 ^{1}H and ^{13}C NMR copies of oxindole *E*-**3ja**

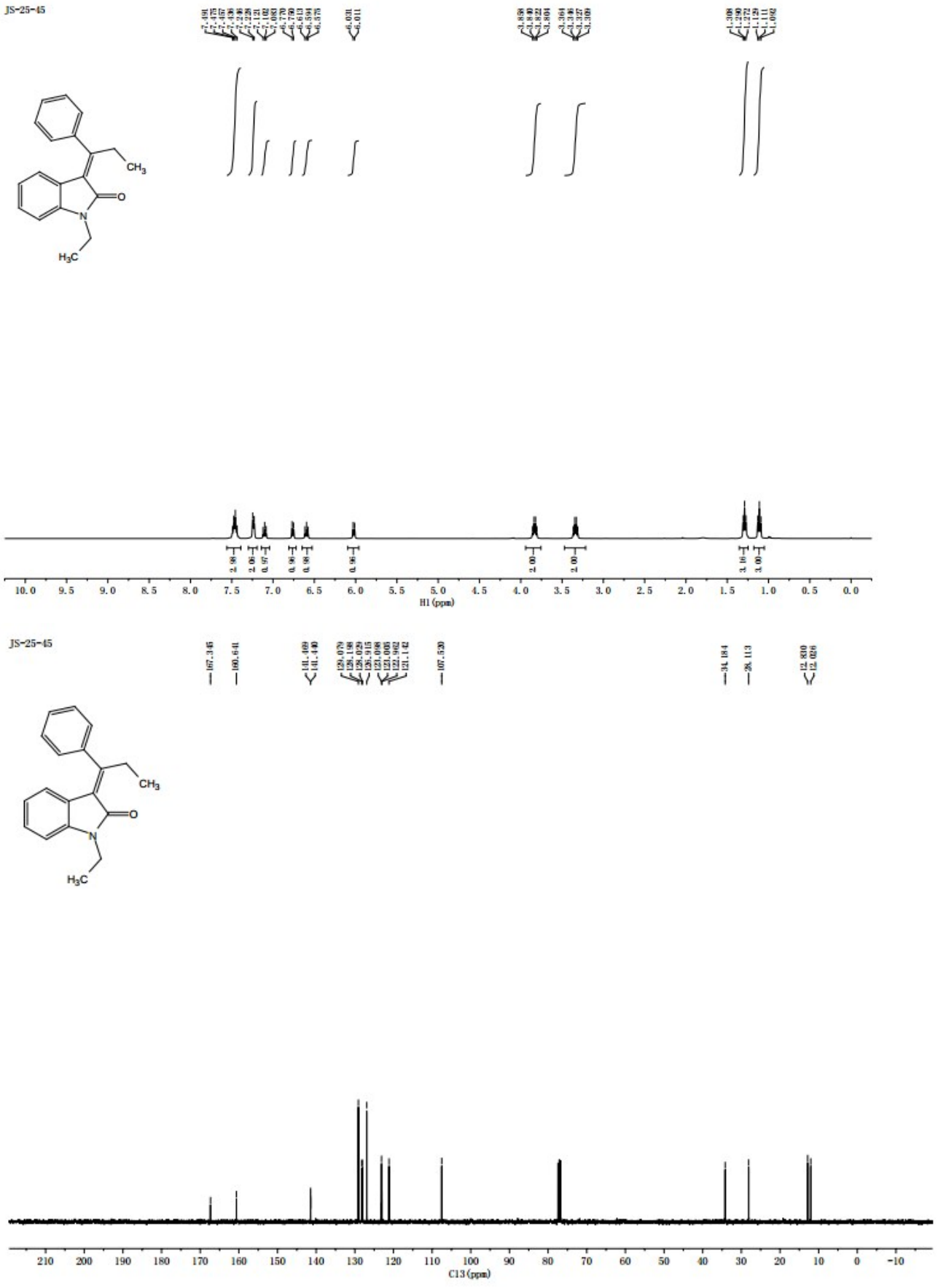


Fig. S25 ^{1}H and ^{13}C NMR copies of oxindole *E*-**3ka**

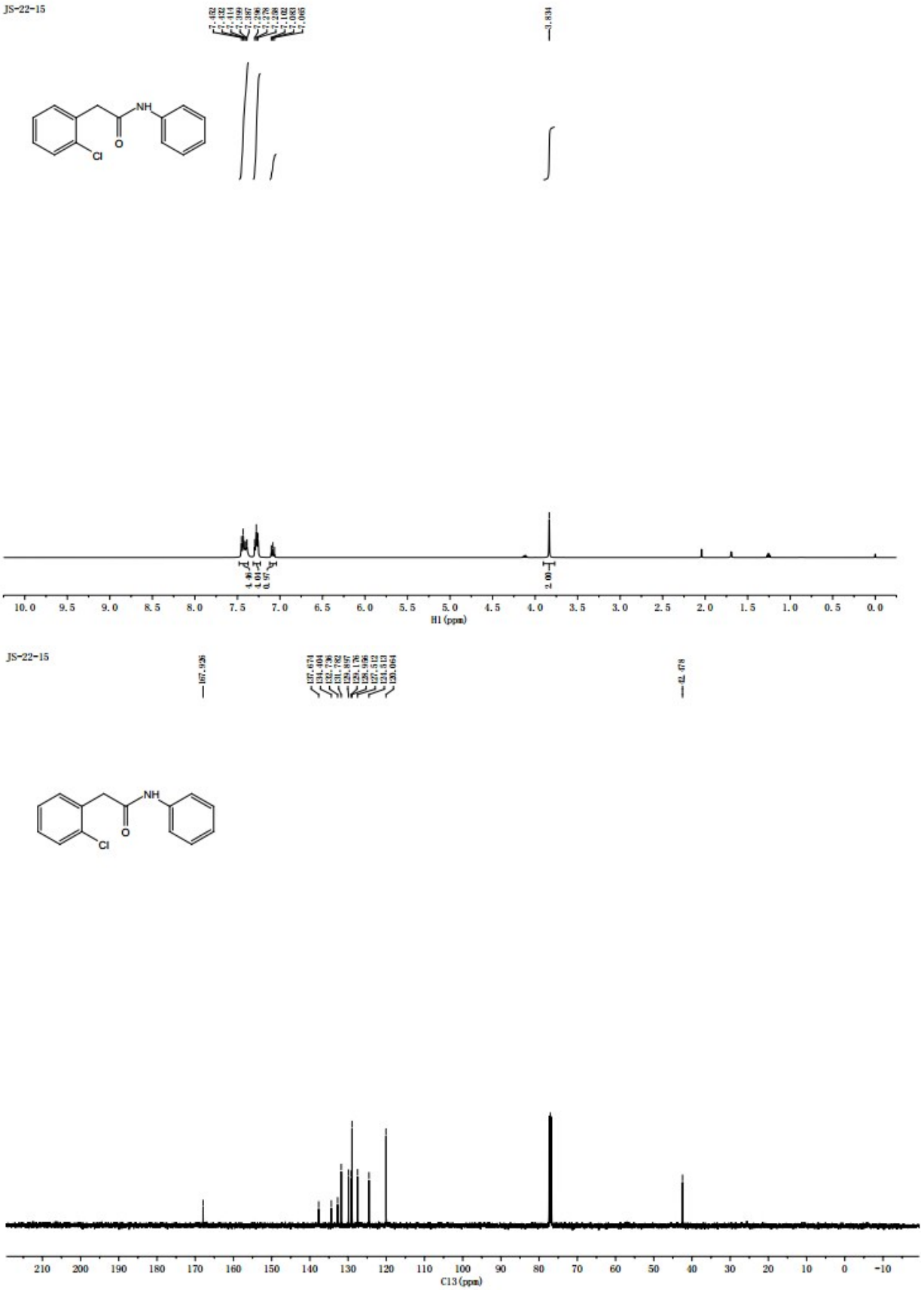


Fig. S26 ^{1}H and ^{13}C NMR copies of amide **4ah-1**

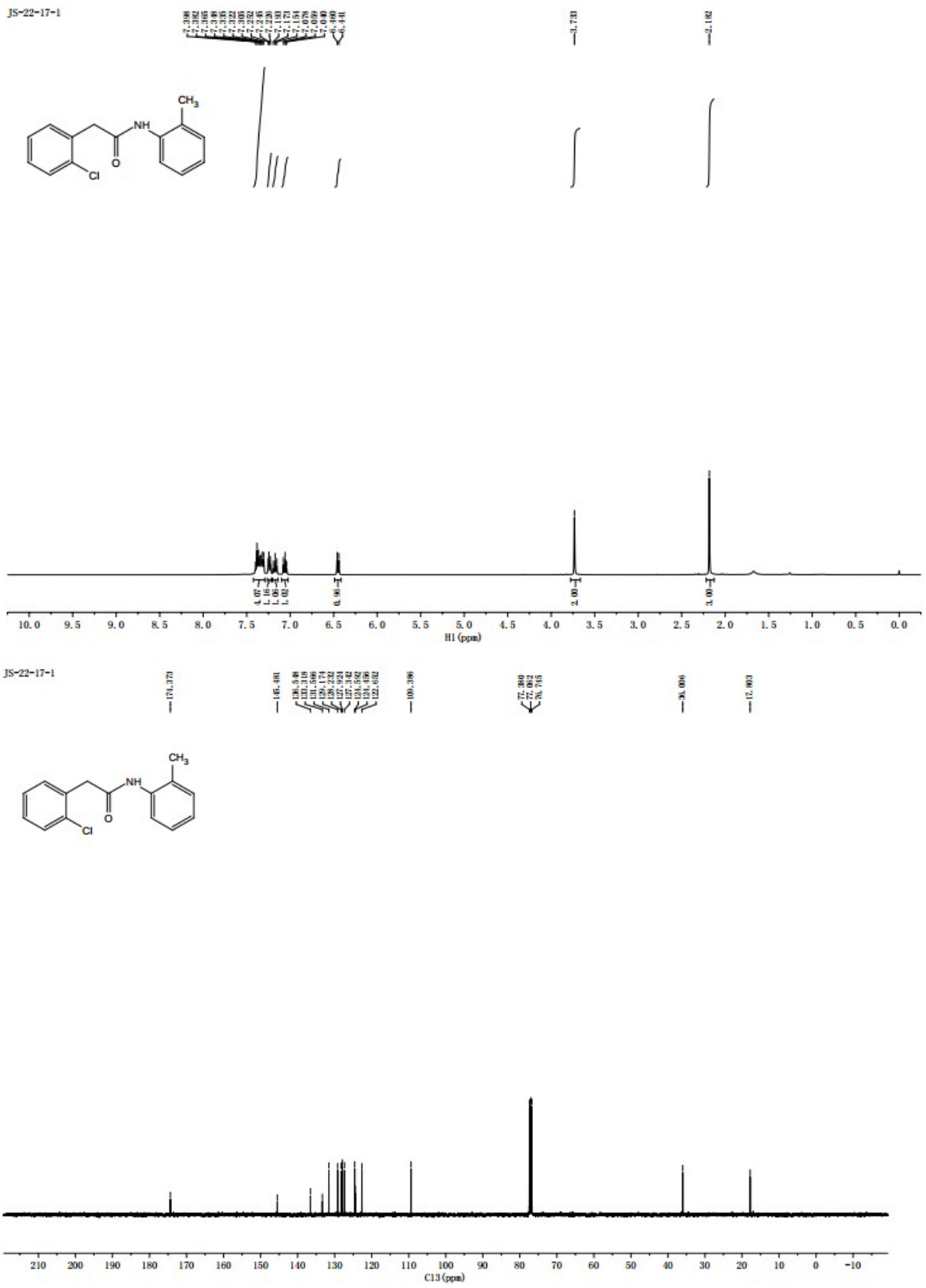


Fig. S27 ^{1}H and ^{13}C NMR copies of amide **4ah-2**

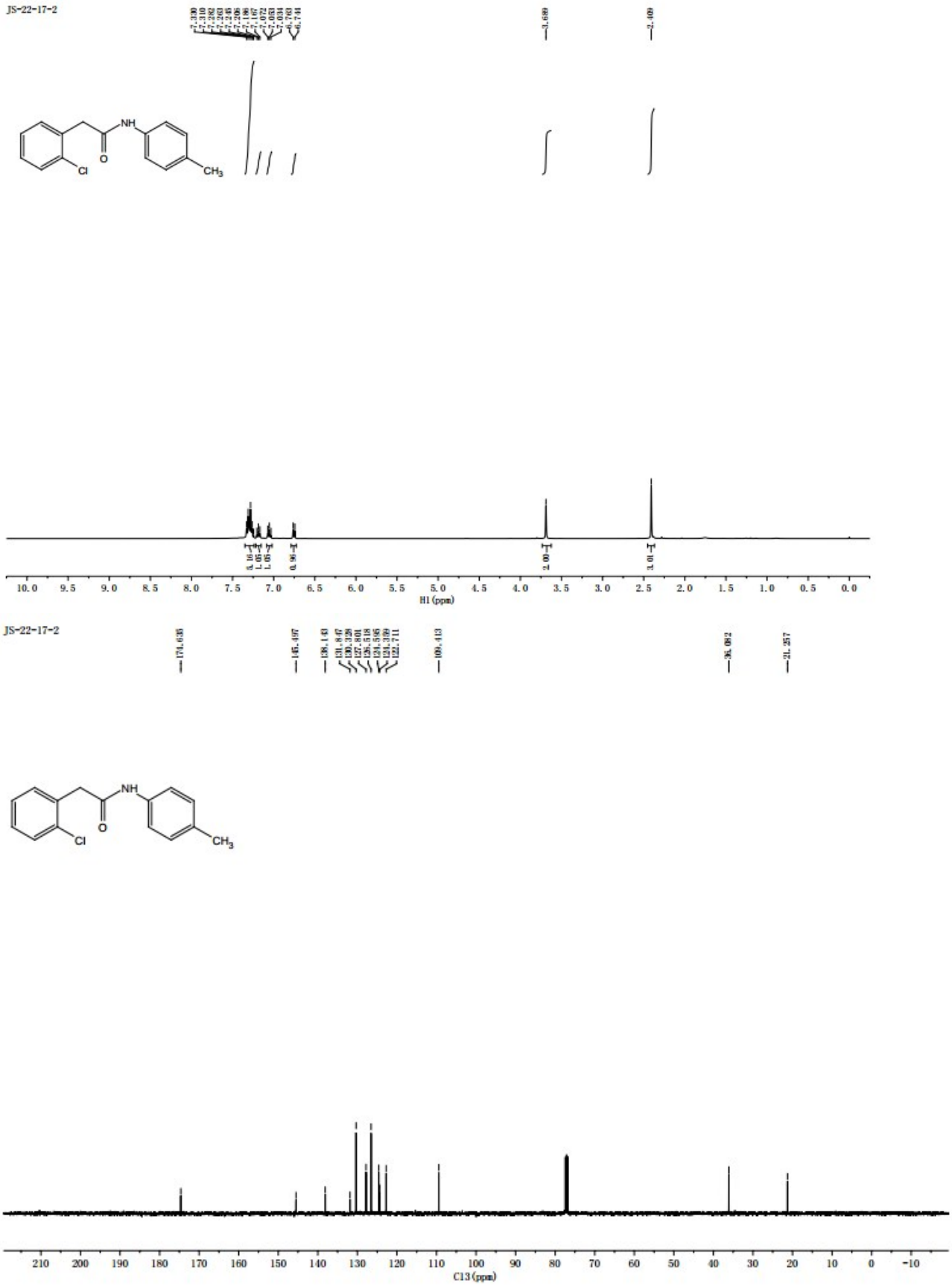


Fig. S28 ^{1}H and ^{13}C NMR copies of amide **4ah-3**

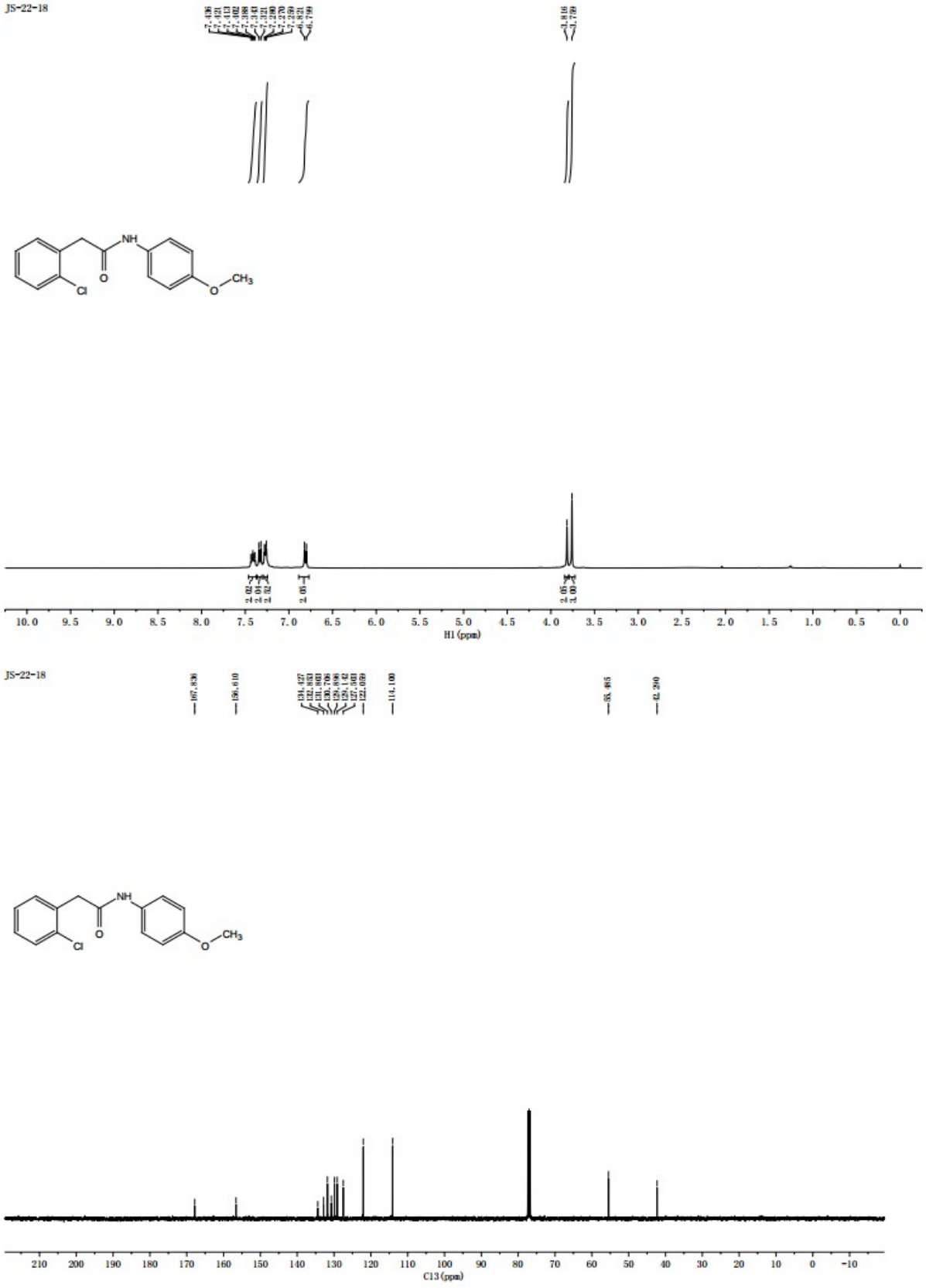


Fig. S29 ^{1}H and ^{13}C NMR copies of amide **4ah-4**

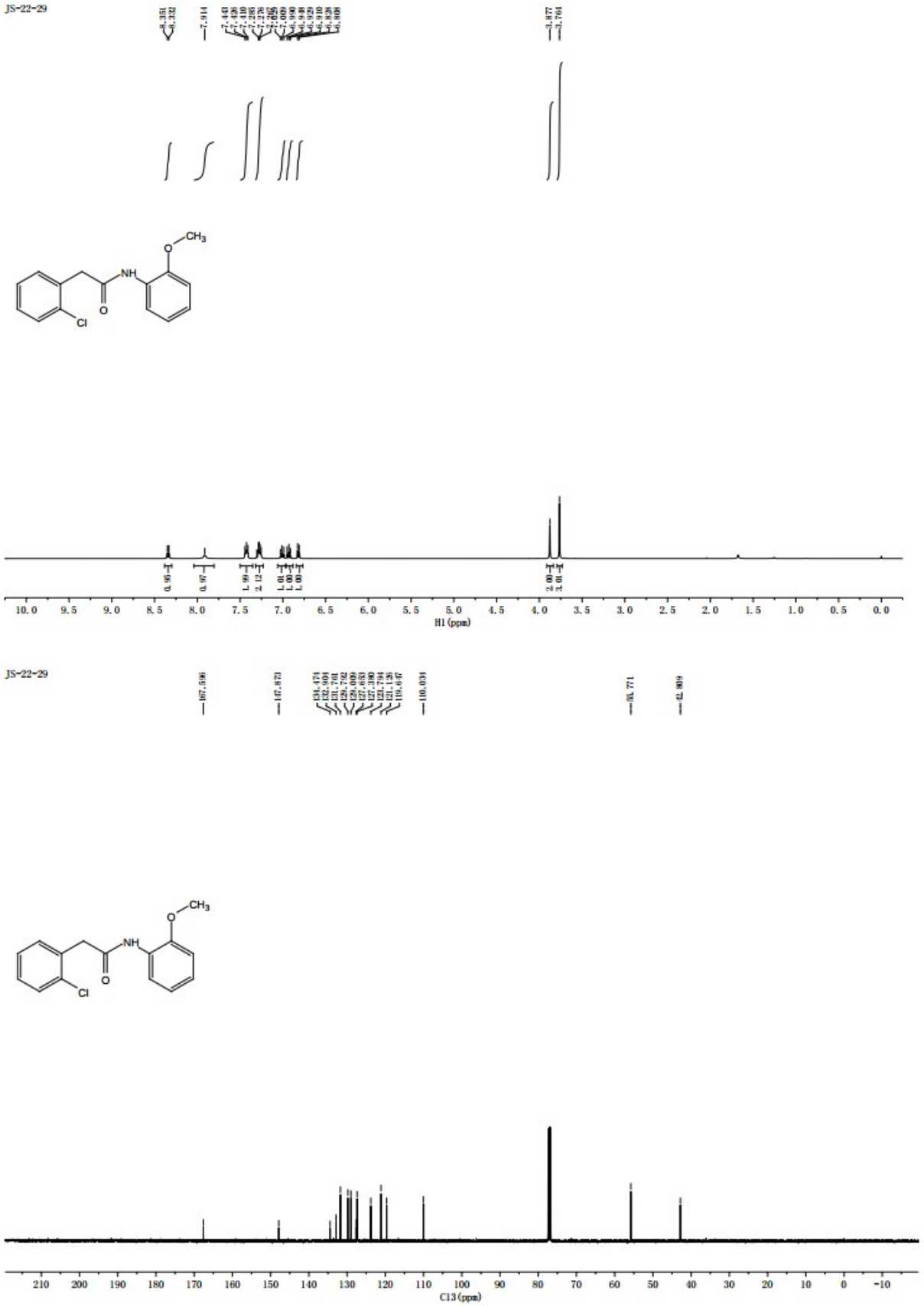


Fig. S30 ^{1}H and ^{13}C NMR copies of amide **4ah-5**

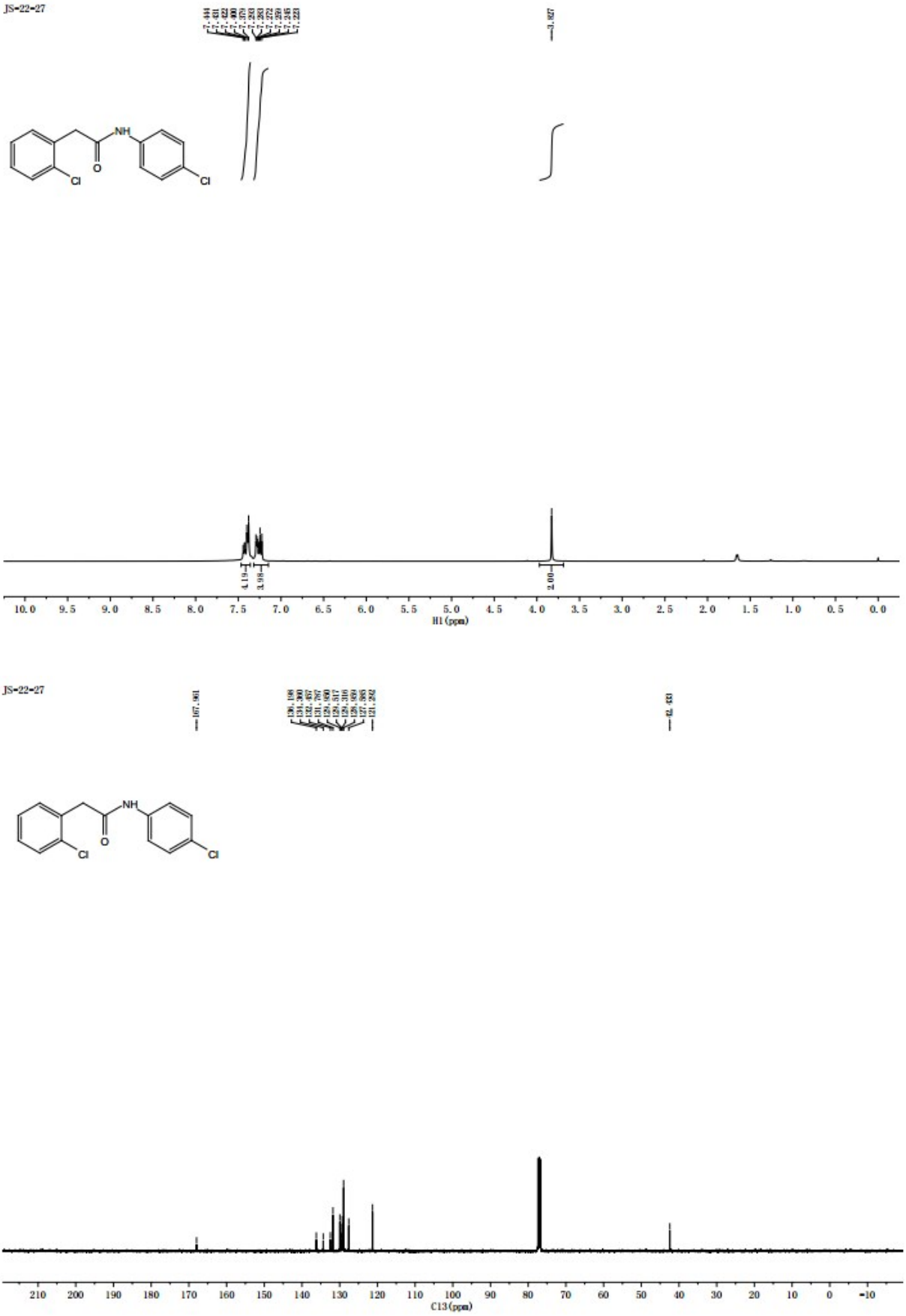


Fig. S31 ^{1}H and ^{13}C NMR copies of amide **4ah-6**