Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information for:

Copper-Catalyzed N-Formylation of Amines with CO_2 under Ambient Condition

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1. General information

2. Mass spectra of formoxysilane

3. NMR data

4. Spectrum

1 General information

1.1 Materials and Equipment information

All the reagents with purities of more than 99% were purchased and used as received from Energy Chemical and Beijing innoChem Science & Technology Co., Ltd. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) were recorded on a Bruker Avance III HD 400 MHz NMR spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) at ambient temperature in deuterated DMSO. The HRMS spectra were recorded on GTC Premier Spectrometer (WATERS) using EI ionization method. GC/MS analysis was conducted on Agilent 7890B GC + 5977 MSD.

1.2 Experiment Procedure

The preparation of the solution of catalyst: $Cu(OAc)_2 \cdot 2H_2O$ （20.0 mg, 0.1 mmol）and dppe (47.8 mg, 1.2 mmol) were dissolved in 50 mL acetonitrile in avolumetric flask. The concentration of the catalyst was 2 mmol/L.

General reaction procedure: 500 μmL catalyst solution prepared above which contained 1 μmol $Cu(OAc)_2 \cdot 2H_2O$ and 1.2 μmol dppe, was transferred to a 25 mL flask using a pipette. Acetonitrile was removed under vacuum. Then 1 mmol of substrate and 2 mL solvent (e.g. toluene) was added. The flask was connected with a balloon filled with CO_2 gas. The reaction was conducted under 25℃ with stirring 700 rpm. The reaction mixture was analyzed by GC-MS and GC with biphenyl as an internal standard, or purified by flash column chromatography on silica gel to afford the desired product. The products were analyzed by ^{1}H NMR, ^{13}C NMR spectra and high resolution mass spectrometry (HRMS).

2 Mass spectra of formoxysilane

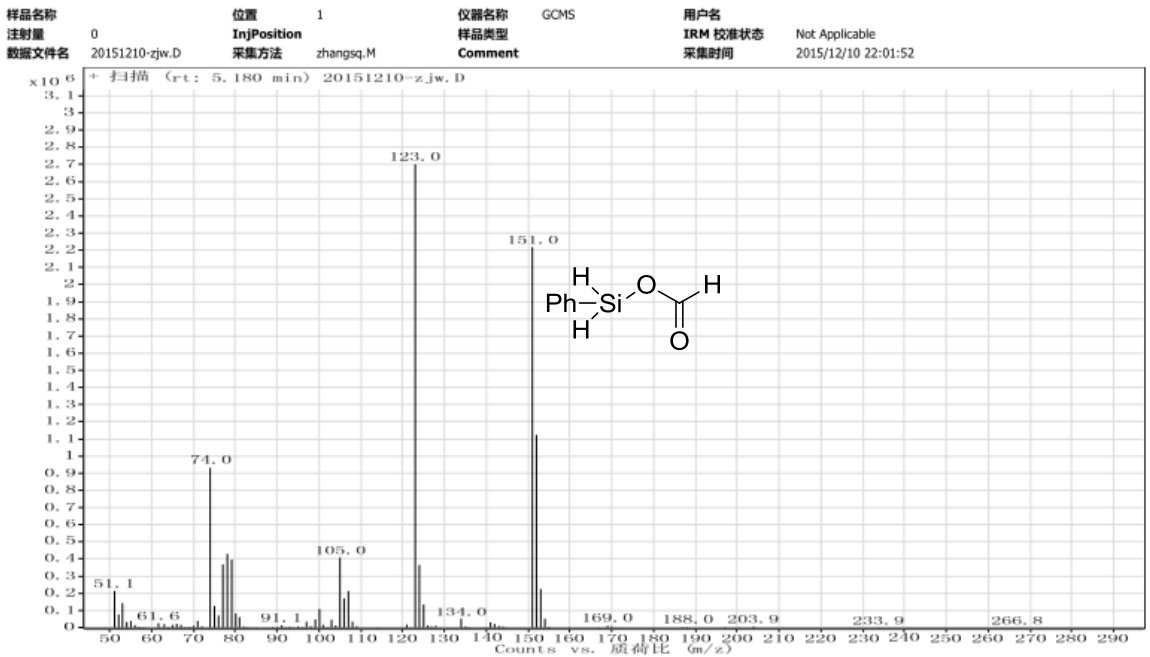
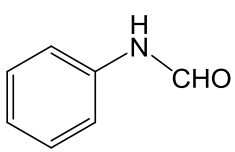
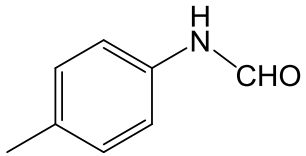


Figure S1 Mass spectra of formoxysilane.

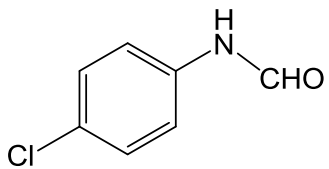
3 NMR data



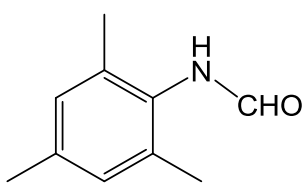
N-Phenylformamide. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.16 (s, 1H), 8.78 (d, J = 11.0 Hz, 0.26H), 8.28 (d, J = 2.7 Hz, 0.73H), 7.59 (d, J = 7.7 Hz, 1.49H), 7.31 (t, J = 7.9 Hz, 2.04H), 7.19 (d, J = 7.7 Hz, 0.53H), 7.09-7.05 (m, 1.02H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.93, 159.99, 138.80, 138.70, 129.83, 129.29, 124.08, 124.03, 119.62, 118.00. HRMS (EI): calculated for C_7H_7NO (M^+), 121.0528; found 121.0529.



N-*p*-Tolylformamide. ^{1}H NMR (400 MHz, DMSO- d_6) δ 10.03 (d, J = 23.3 Hz, 1.03H), 8.70 (d, J = 11.1 Hz, 0.26H), 8.22 (s, 0.74H), 7.46 (d, J = 8.3 Hz, 1.67H), 7.12-7.06 (m, 2.72H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.87, 159.75, 136.21, 133.17, 132.98, 130.22, 129.65, 128.09, 119.59, 118.19, 20.90, 20.76. HRMS (EI): calculated for C_8H_9NO (M^+), 135.0684; found 135.0686.

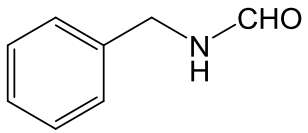


N-(4-Chlorophenyl)formamide. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.31 (m, 0.74H), 10.20 (d, J = 10.5 Hz, 0.22H), 8.78 (d, J = 10.9 Hz, 0.2H), 8.29 (s, 0.75H), 7.61 (d, J = 8.8 Hz, 1.69H), 7.36 (d, J = 8.8 Hz, 2.01H), 7.23-7.17(m, 0.54H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.95, 160.15, 137.88, 137.61, 129.68, 129.21, 127.95, 127.63, 121.19, 119.48. HRMS (EI): calculated for C_7H_6NOCl (M^+), 155.0138; found 155.0137.



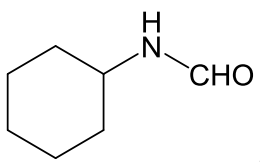
N-Mesitylformamide. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.32 (s, 0.82H), 9.15 (d, J = 8.6 Hz , 0.19H), 8.22 (s, 0.81H), 7.92 (d, J = 11.6 Hz, 0.18H), 6.92(s, 0.37H), 6.87(s, 1.67H), 2.21 (s, 3.04H), 2.16 (s, 1.16H), 2.10 (s,

5.03H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.13, 159.82, 136.37, 135.9, 135.24, 134.86, 131.83, 129.26, 128.72, 20.91, 19.11, 18.73, 18.62. HRMS (EI): calculated for $C_{10}H_{13}NO$ (M^+), 163.0997; found 163.0999.



N-Benzylformamide. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.50 (s, 1H), 8.15 (s, 1.19H), 7.35–7.26 (m, 5.68H), 4.31 (d, J = 5.8 Hz, 2.29H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.36, 161.50, 140.09, 139.43, 128.89, 128.78,127.75, 127.53 127.50, 127.32, 45.03, 41.22. HRMS (EI): calculated for C_8H_9NO (M^+), 135.0684; found 135.0682.

N-Octylformamide. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97 (s, 1.02H), 7.92 (s, J = 4.9 Hz, 0.72H), 7.65 (s, 0.20H), 3.09–3.03 (m, 2H), 1.37 (d, J = 9.5 Hz, 2.15H), 1.23 (s, 10.28H), 0.93–0.83 (m, 3.04H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.21, 37.51, 31.71, 31.38, 29.48, 29.13, 26.84, 22.54, 14.30. HRMS (EI): calculated for $C_9H_{19}NO$ (M^+), 157.1467; found 157.1464.



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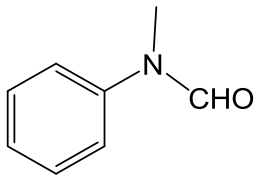
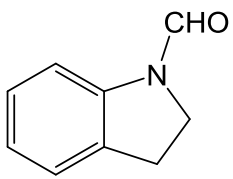
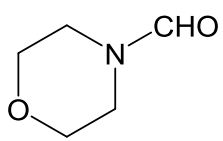
N-Cyclohexylformamide. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97 (d, J = 24.0 Hz, 2H), 3.63-3.56 (m, 0.83), 3.18(m, 0.12H), 1.73–1.62 (m, 4.02H). 1.51 (d, J = 12.4 Hz, 1.01H), 1.30-1.05 (m, 5.07H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.67, 160.28, 50.68, 46.54, 34.62, 32.74, 25.61, 25.28, 25.00, 24.79. HRMS (EI): calculated for $C_7H_{13}NO$ (M^+), 127.0997; found 127.0999.



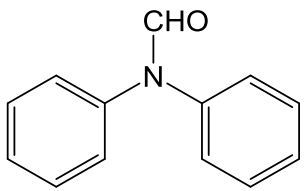
N-Methyl-N-Phenylformamide. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.54 (s, 0.90H), 8.36 (s, 0.09H), 7.51–7.41 (m, 2.34H), 7.34 (d, J = 7.5 Hz, 1.99H), 7.26 (t, J = 7.3 Hz, 0.99H), 3.22 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.99, 162.46, 142.54, 129.86, 129.12, 126.06, 125.84, 123.50, 121.99, 31.48. HRMS (EI): calculated for C_8H_9NO (M^+), 135.0684; found 135.0685.



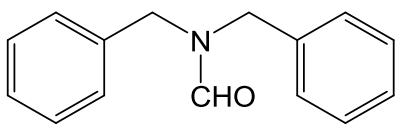
Indoline-1-Carbaldehyde. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.03 (s, 0.70H), 8.47 (s, 0.22H), 7.91 (d, J = 7.9 Hz, 0.24H), 7.40 (d, J = 8.0 Hz, 1.06H), 7.24 (d, J = 7.4 Hz, 1.09H), 7.16 (t, J = 7.6 Hz, 1.11H), 7.00 (t, J = 7.4 Hz, 1.03H), 4.09 (t, J = 8.5 Hz, 0.48H), 3.89 (t, J = 8.5 Hz, 1.50H), 3.08 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.52, 158.77, 141.73, 141.66, 133.08, 132.18, 127.74, 127.46, 126.24, 125.55, 124.49, 124.06, 115.96, 110.28, 46.92, 44.60, 27.66, 27.07. HRMS (EI): calculated for C_9H_9NO (M^+), 147.0684; found 147.0687.



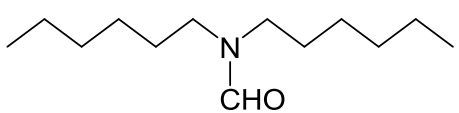
Morpholine-4-Carbaldehyde. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 (s, 1H), 3.58(t, J = 4.6 Hz, 2.20H), 3.53 (t, J = 5.2 Hz, 2.19H), 3.39 (t, J = 5.3 Hz, 3.85H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.39, 67.20, 66.21, 45.56, 40.39.HRMS (EI): calculated for $C_5H_5NO_2$ (M^+), 115.0633; found 115.0635.



N, N-Diphenyl-formamide. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.67 (s, 1H), 7.44 (t, J = 7.7 Hz, 4.25H), 7.32 (t, J = 5.6 Hz, 2.07H), 7.25 (d, J = 7.6 Hz, 4.20H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.22, 140.20, 130.10, 129.63, 127.25, 127.07, 127.03, 125.10. HRMS (EI): calculated for $C_{13}H_{11}NO$ (M^+), 197.0841; found 197.0842.



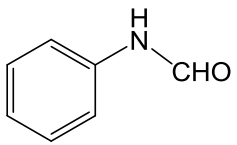
N, N-Dibenzylformamide. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.48 (s, 1H), 7.39-7.31 (m, 5.64H), 7.28 (d, J = 7.1 Hz, 1.28H), 7.23 (d, J = 7.1 Hz, 2.3H), 7.18 (d, J = 7.0 Hz, 2.14H), 4.36 (s, 2.15H), 4.30 (s, 1.99H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.66, 137.13, 137.00, 129.13, 128.96, 128.28, 128.26, 128.15, 127.69, 50.16, 44.69. HRMS (EI): calculated for $C_{15}H_{15}NO$ (M^+), 225.1154; found 225.1155.



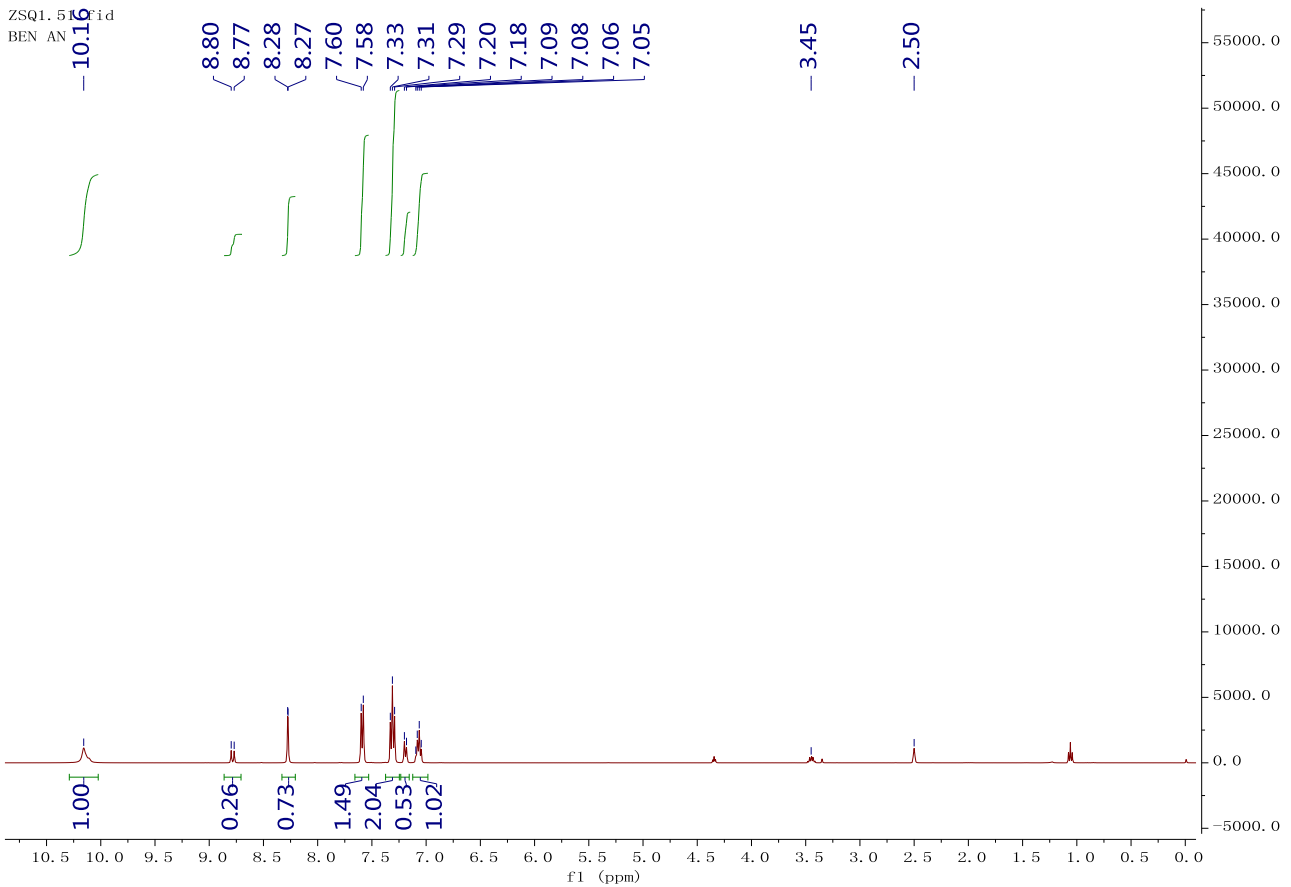
N, N-Dihexylformamide. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99 (s, 1H), 3.17 (m, 4.09H), 1.47–1.41 (m, 4.25H), 1.25-1.15 (m, 12.58H), 0.85 (t, J = 6.7 Hz, 6.37H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.81, 46.81, 41.57, 31.43,

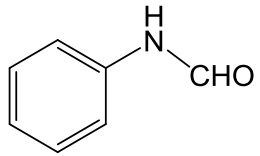
31.32, 28.61, 27.28, 26.50, 26.01, 22.50, 14.24, 14.22. HRMS (EI): calculated for $C_{13}H_{27}NO$ (M^+), 213.2093; found 213.2095.

4. Spectrum

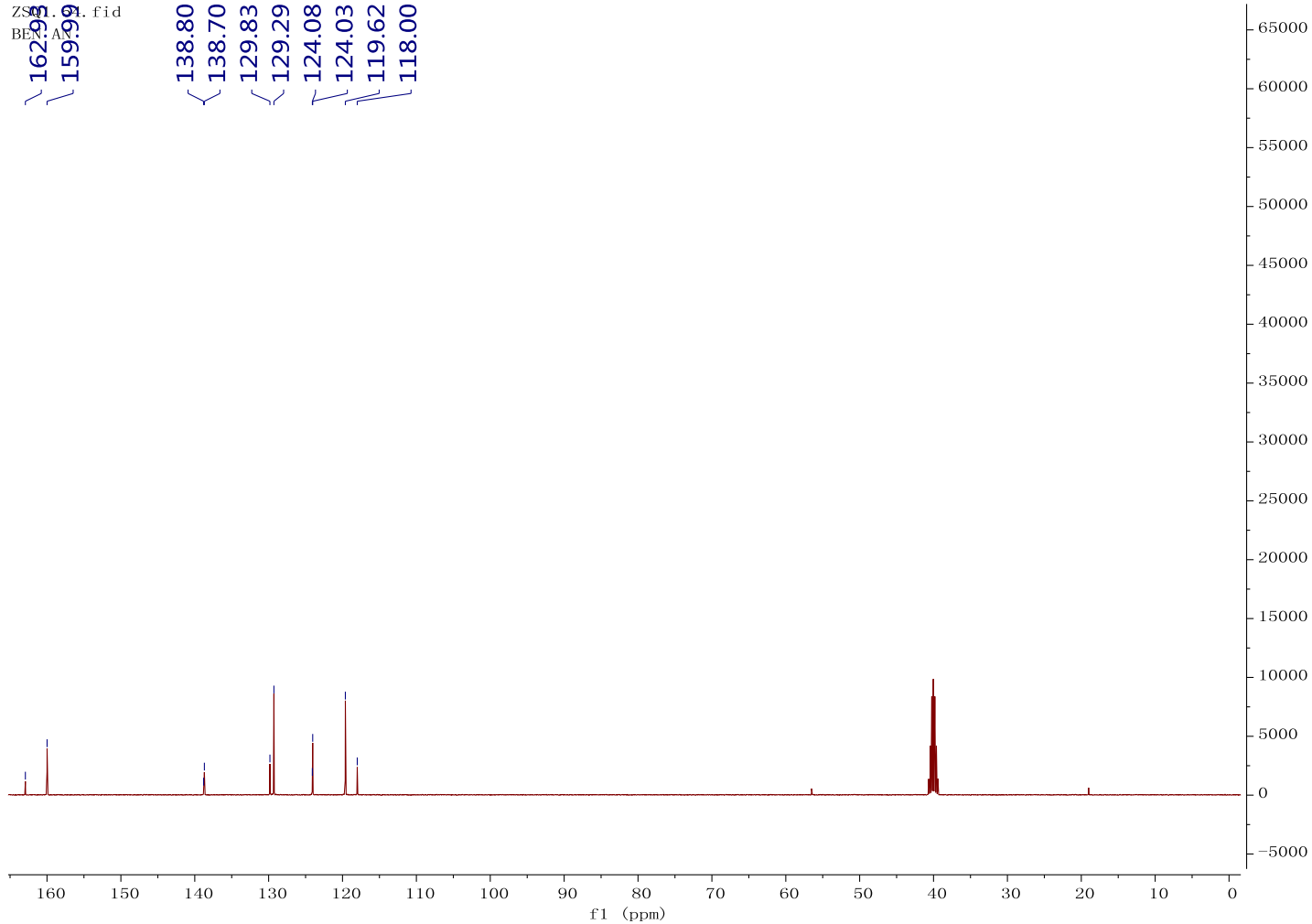


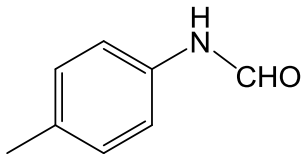
^{1}H NMR (400 MHz, DMSO-d_6)



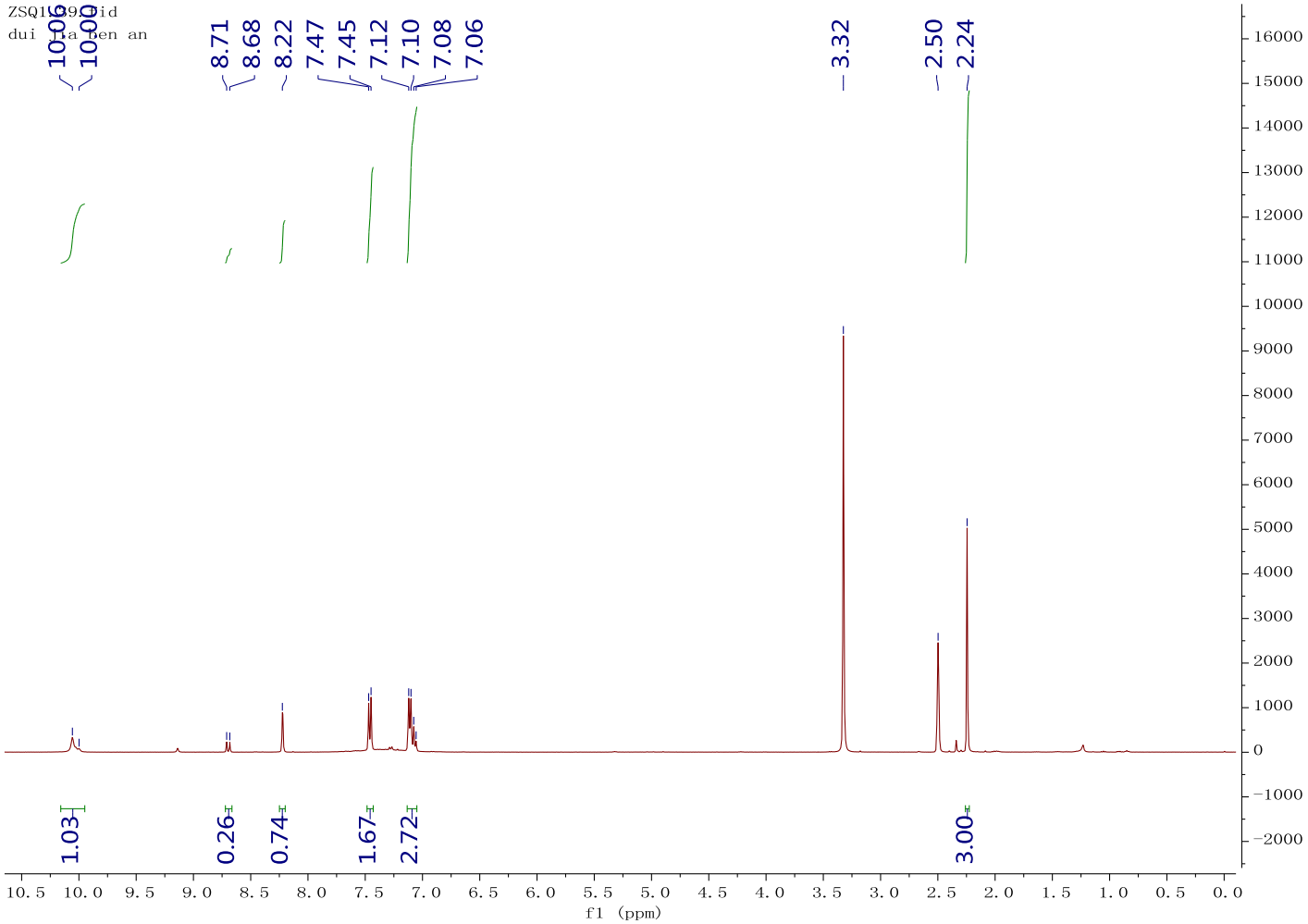


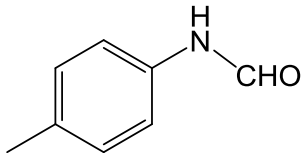
^{13}C NMR (100 MHz, DMSO-d_6)





^{1}H NMR (400 MHz, DMSO-d_6)





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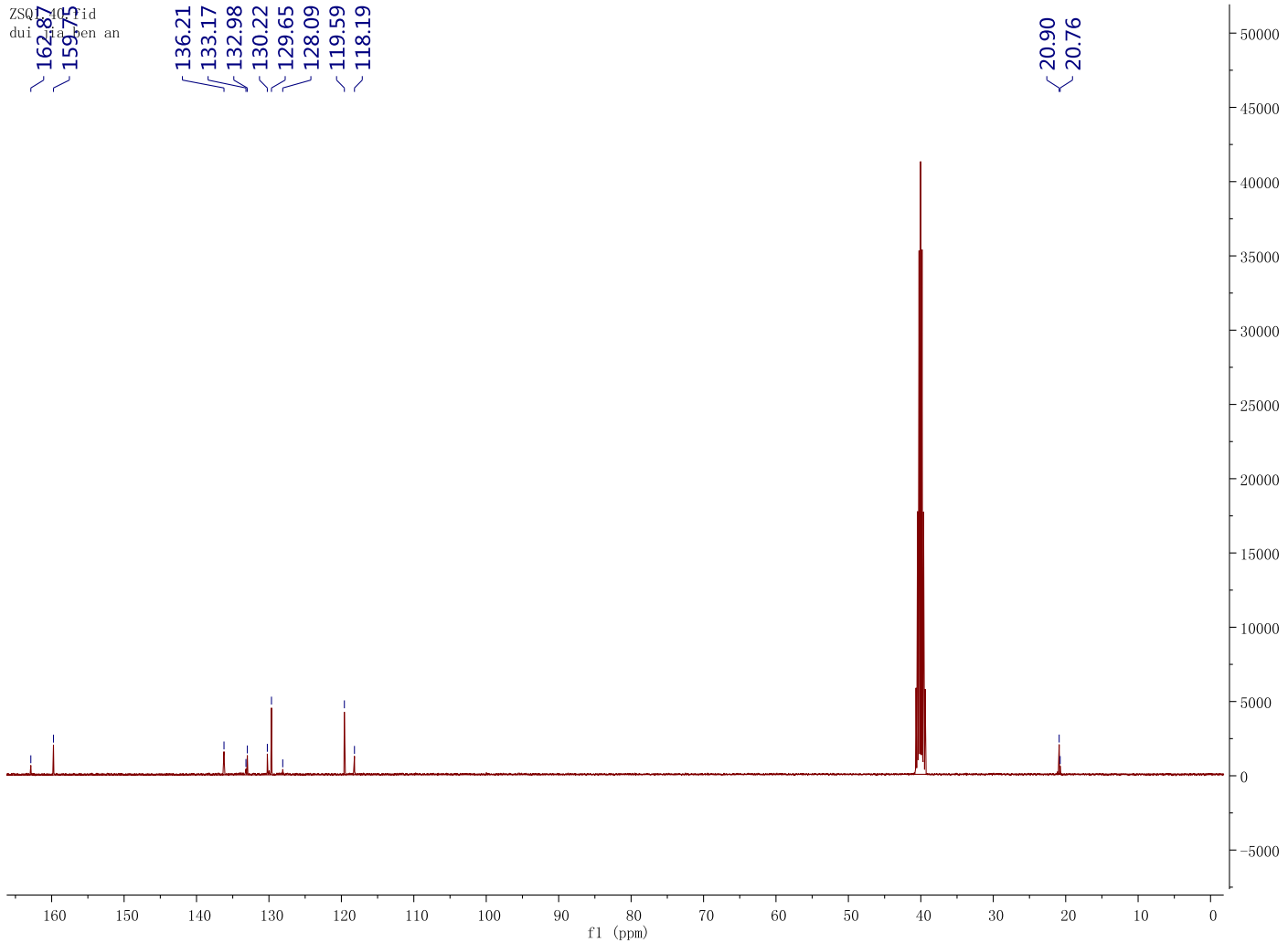
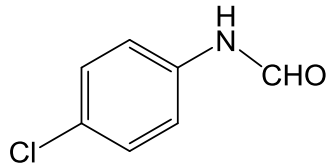
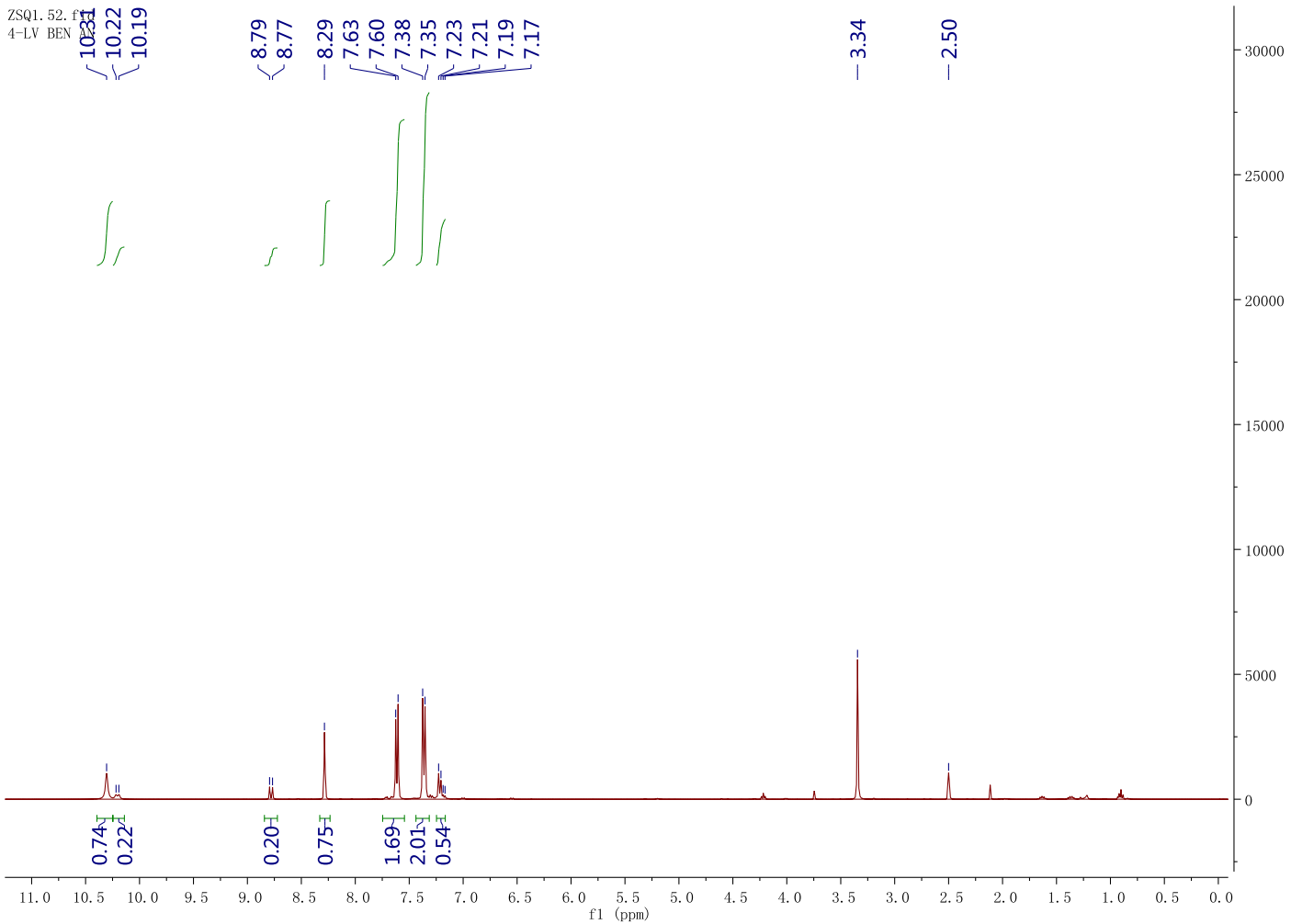
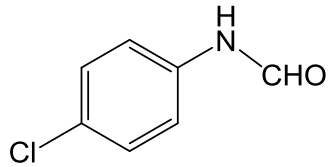


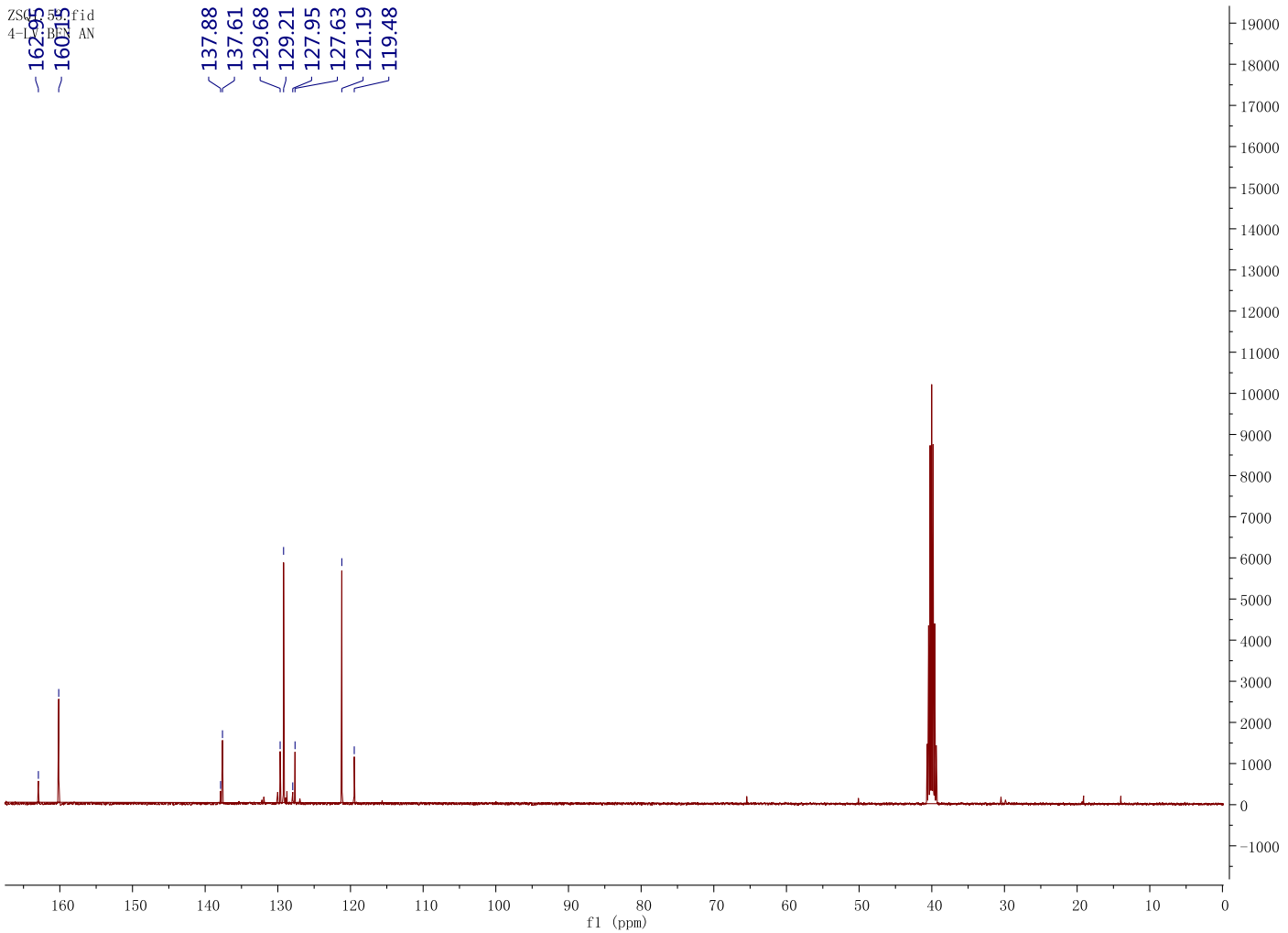


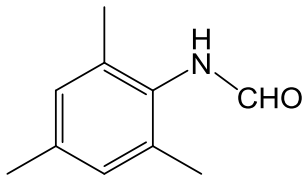
^{1}H NMR (400 MHz, DMSO-d_6)



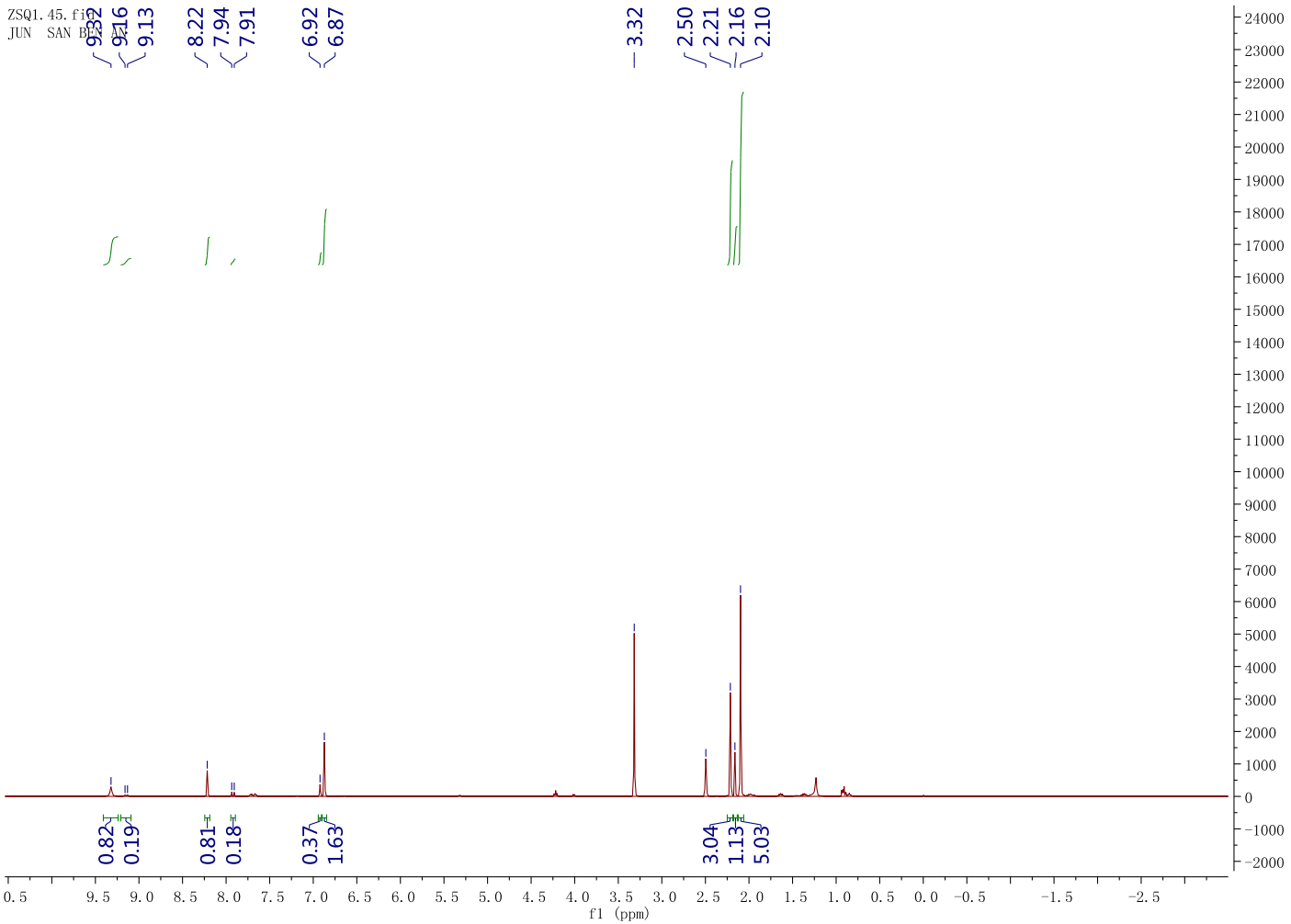


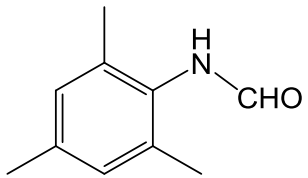
^{13}C NMR (100 MHz, DMSO-d_6)



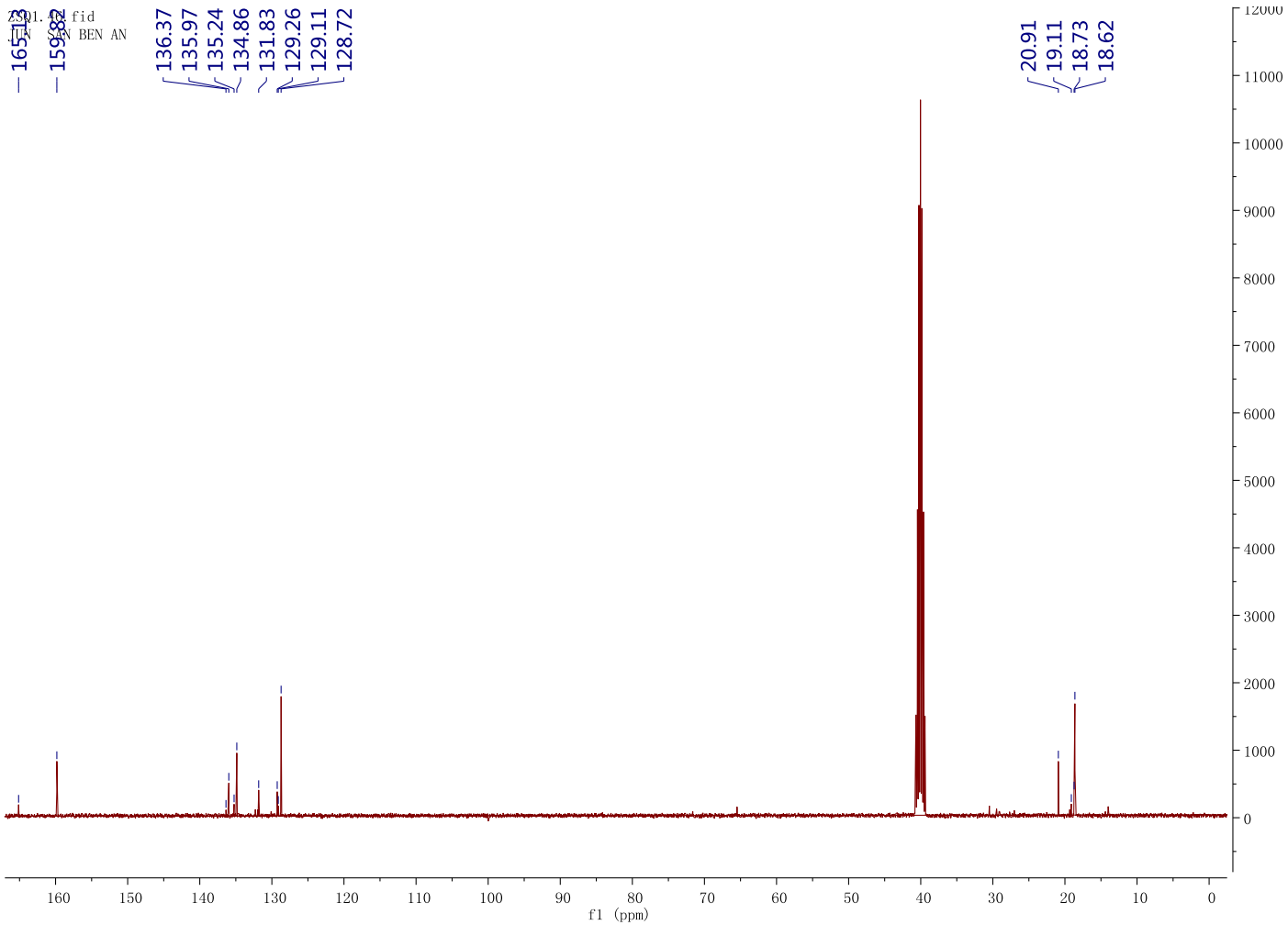


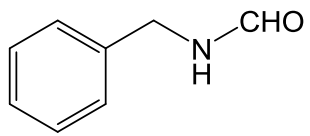
^{1}H NMR (400 MHz, DMSO-d_6)



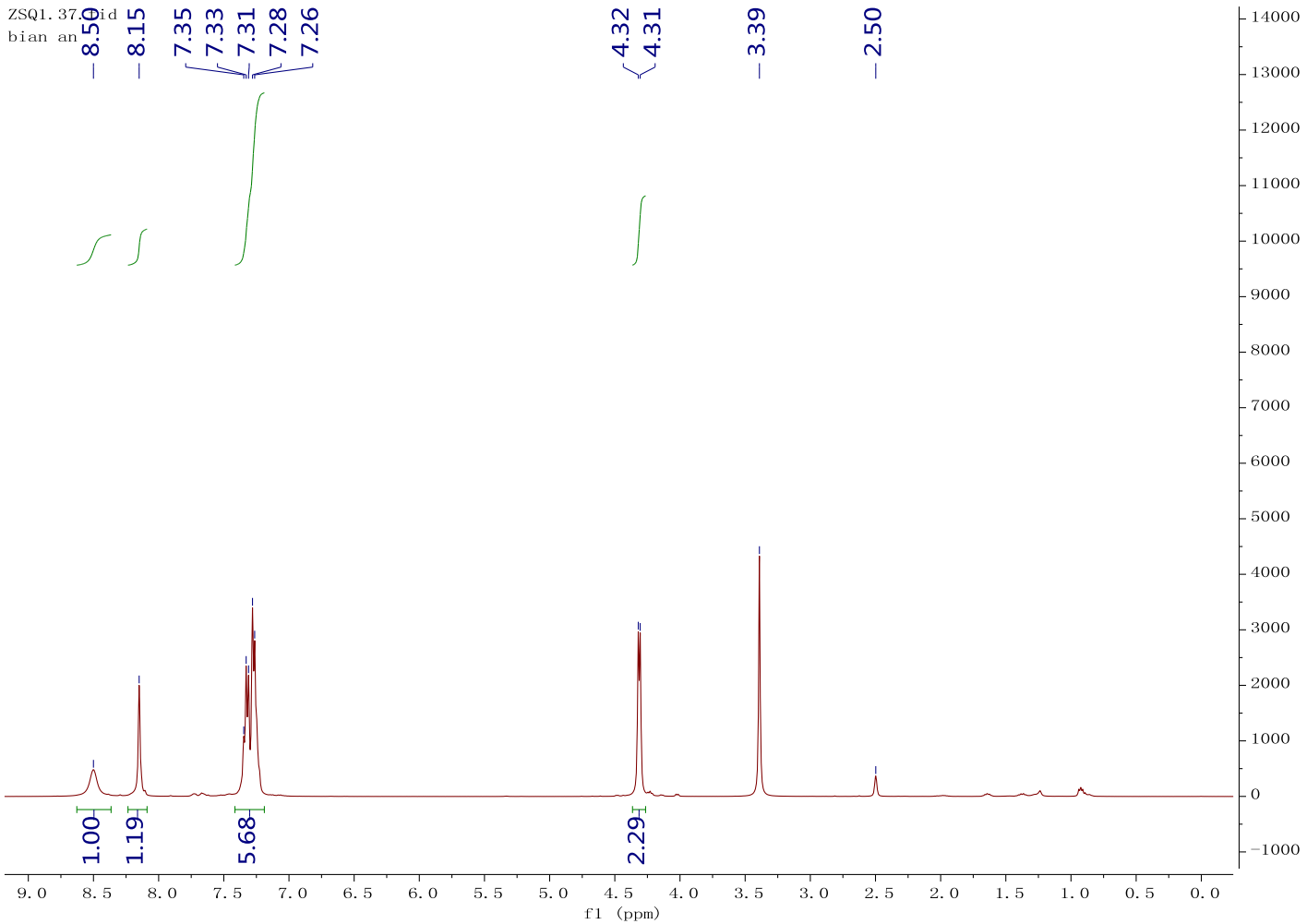


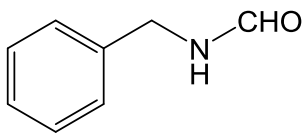
^{13}C NMR (100 MHz, DMSO-d_6)



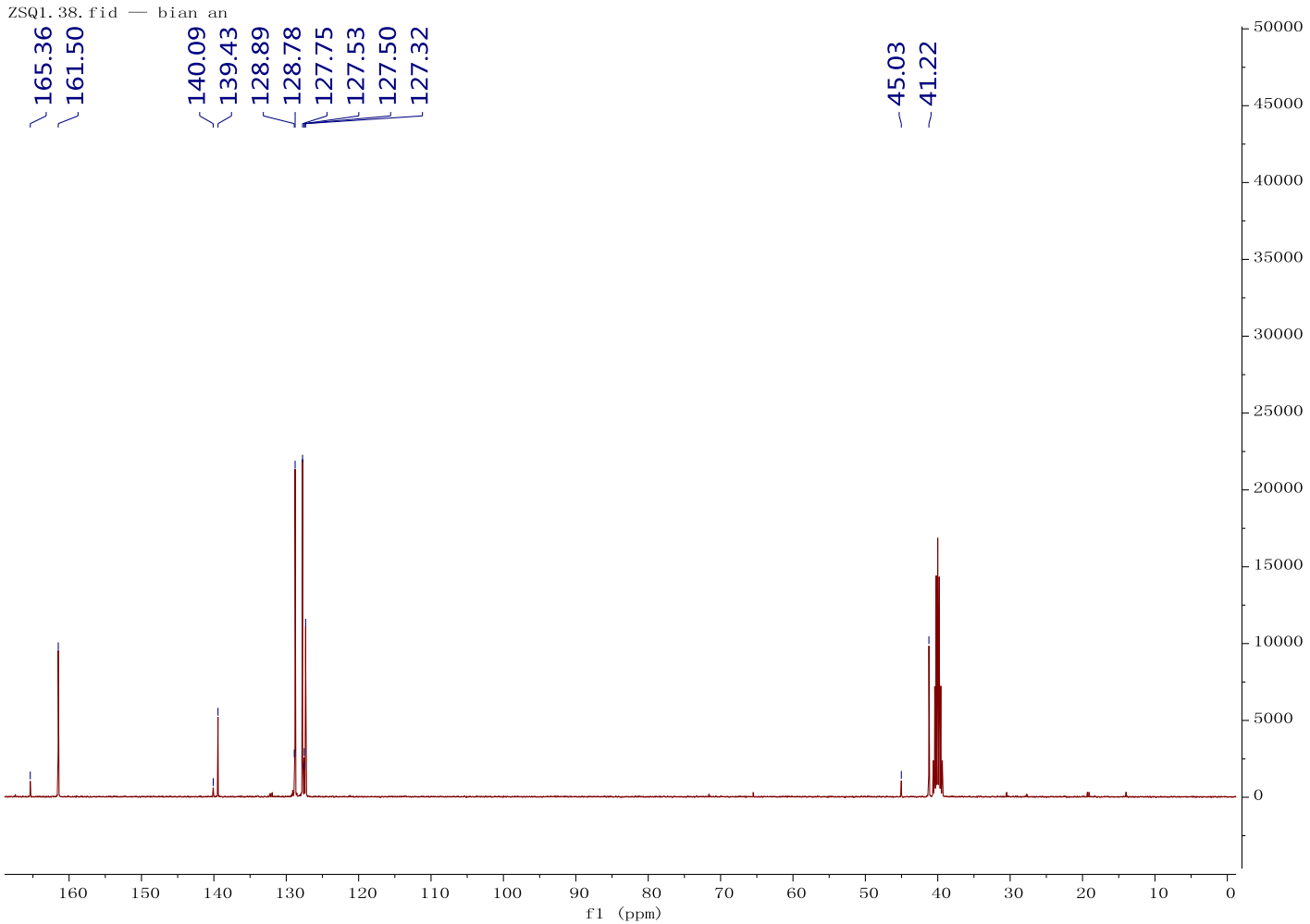


^{1}H NMR (400 MHz, DMSO-d_6)

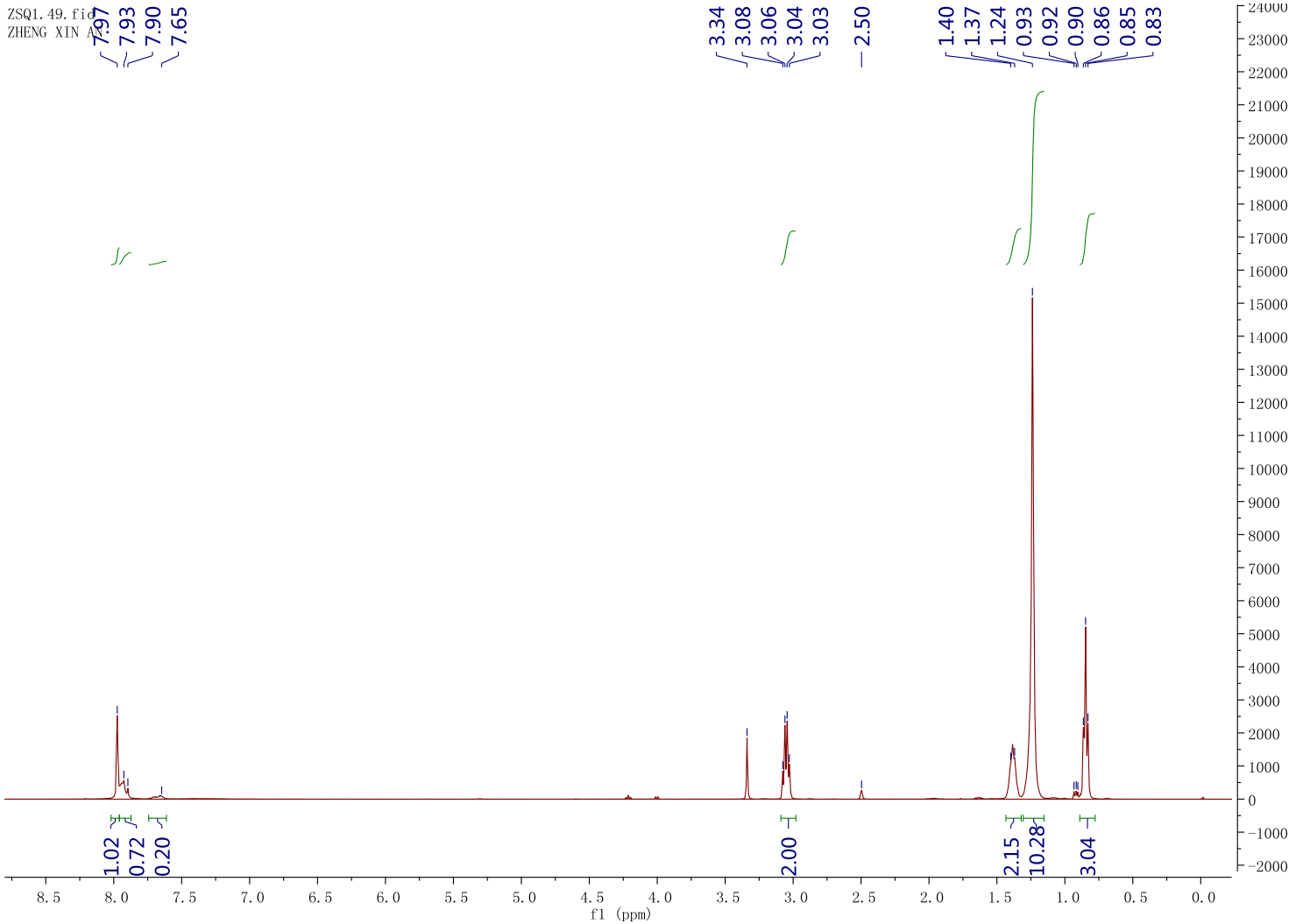




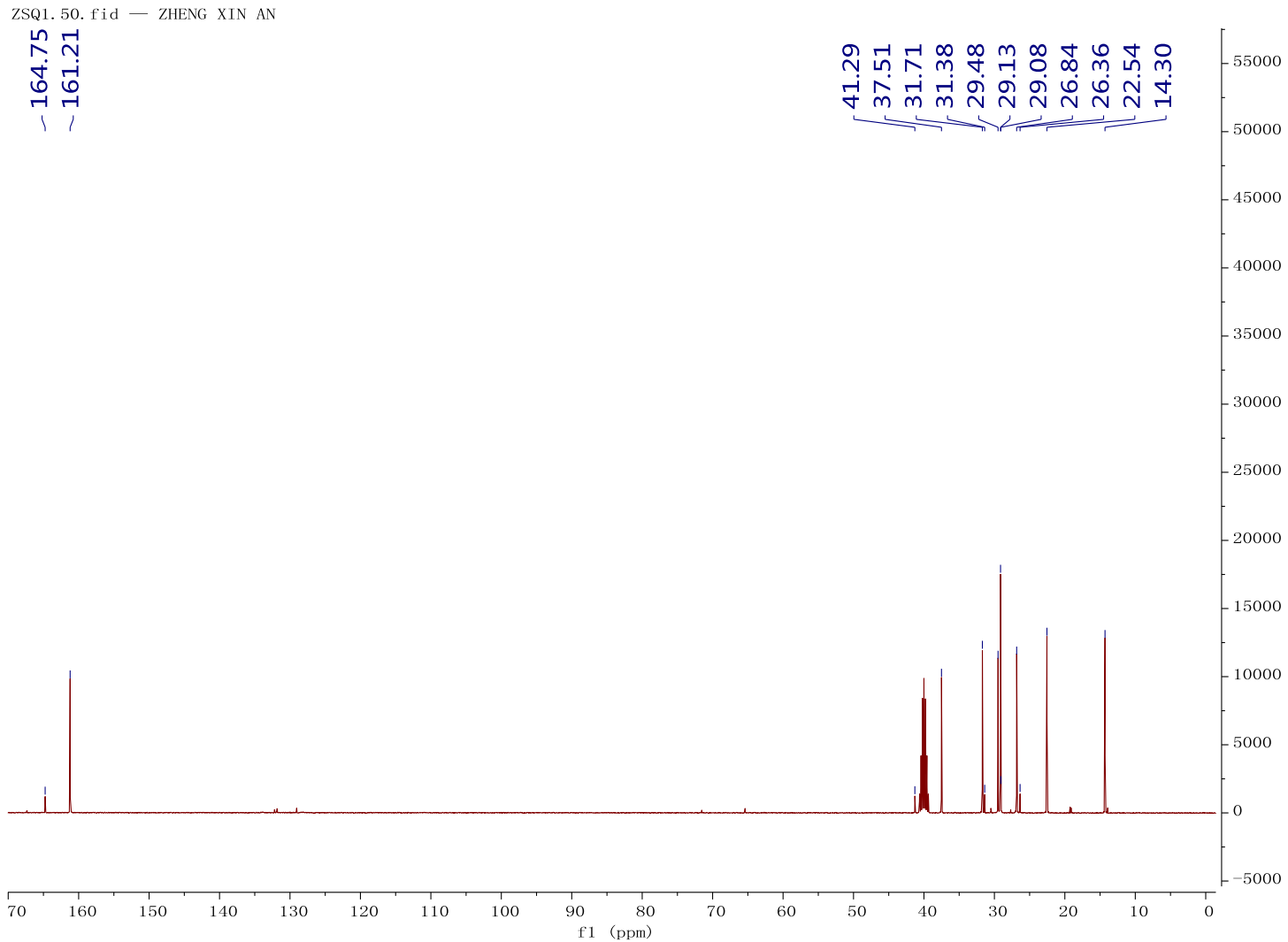
^{13}C NMR (100 MHz, DMSO-d_6)

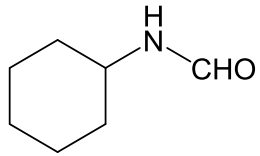


^{1}H NMR (400 MHz, DMSO-d_6)

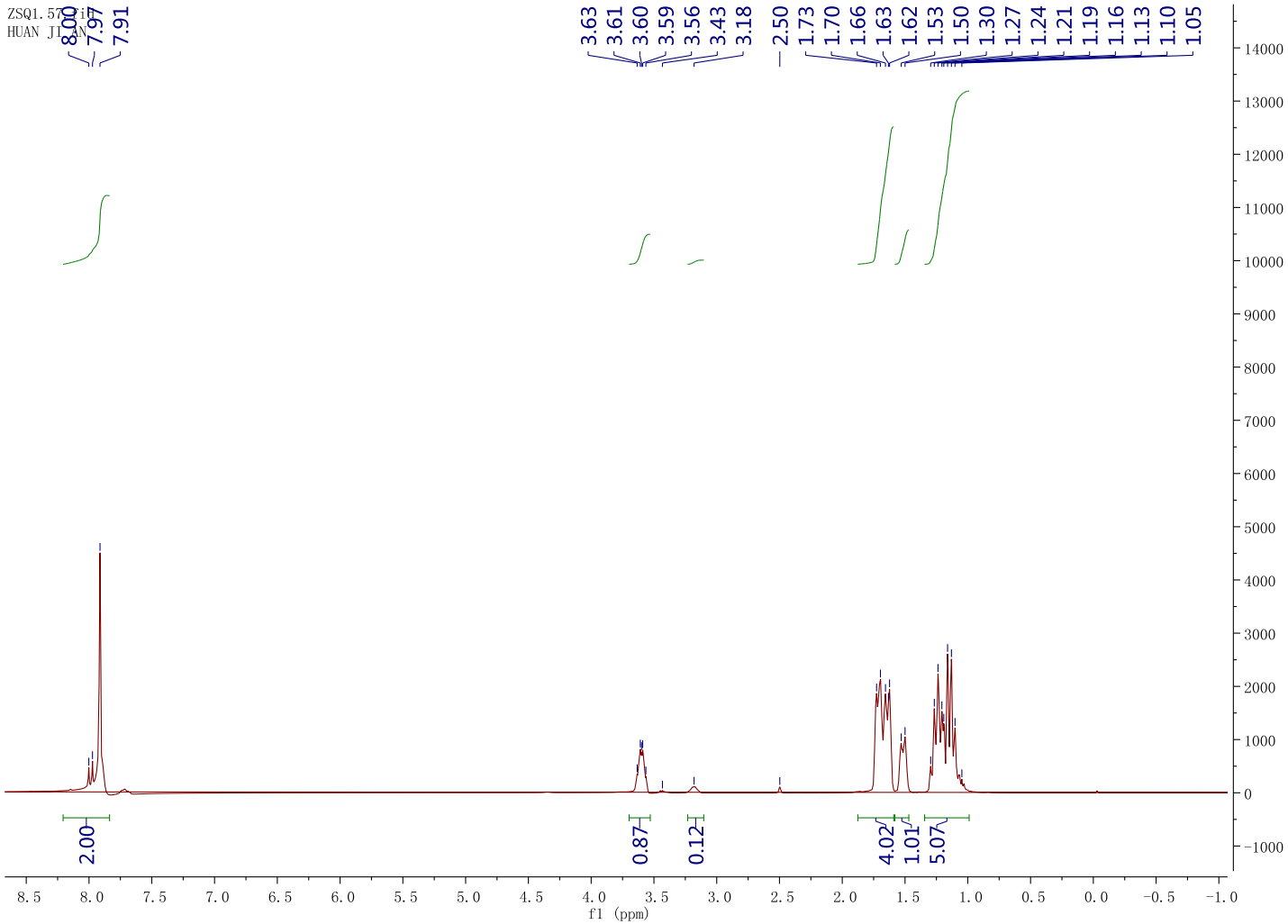


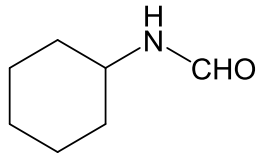
^{13}C NMR (100 MHz, DMSO-d_6)



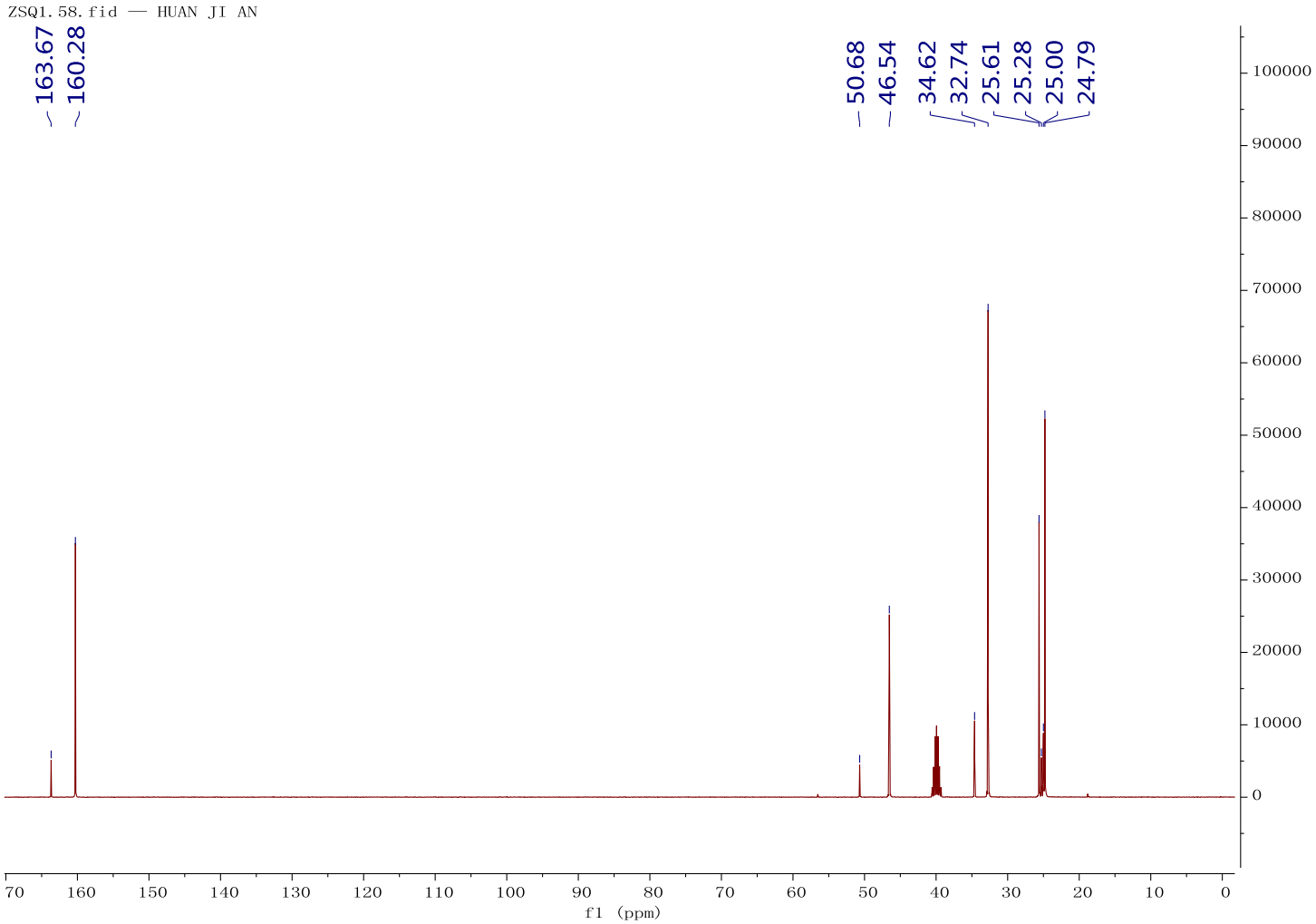


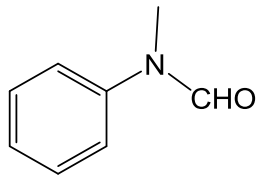
^{1}H NMR (400 MHz, DMSO-d_6)



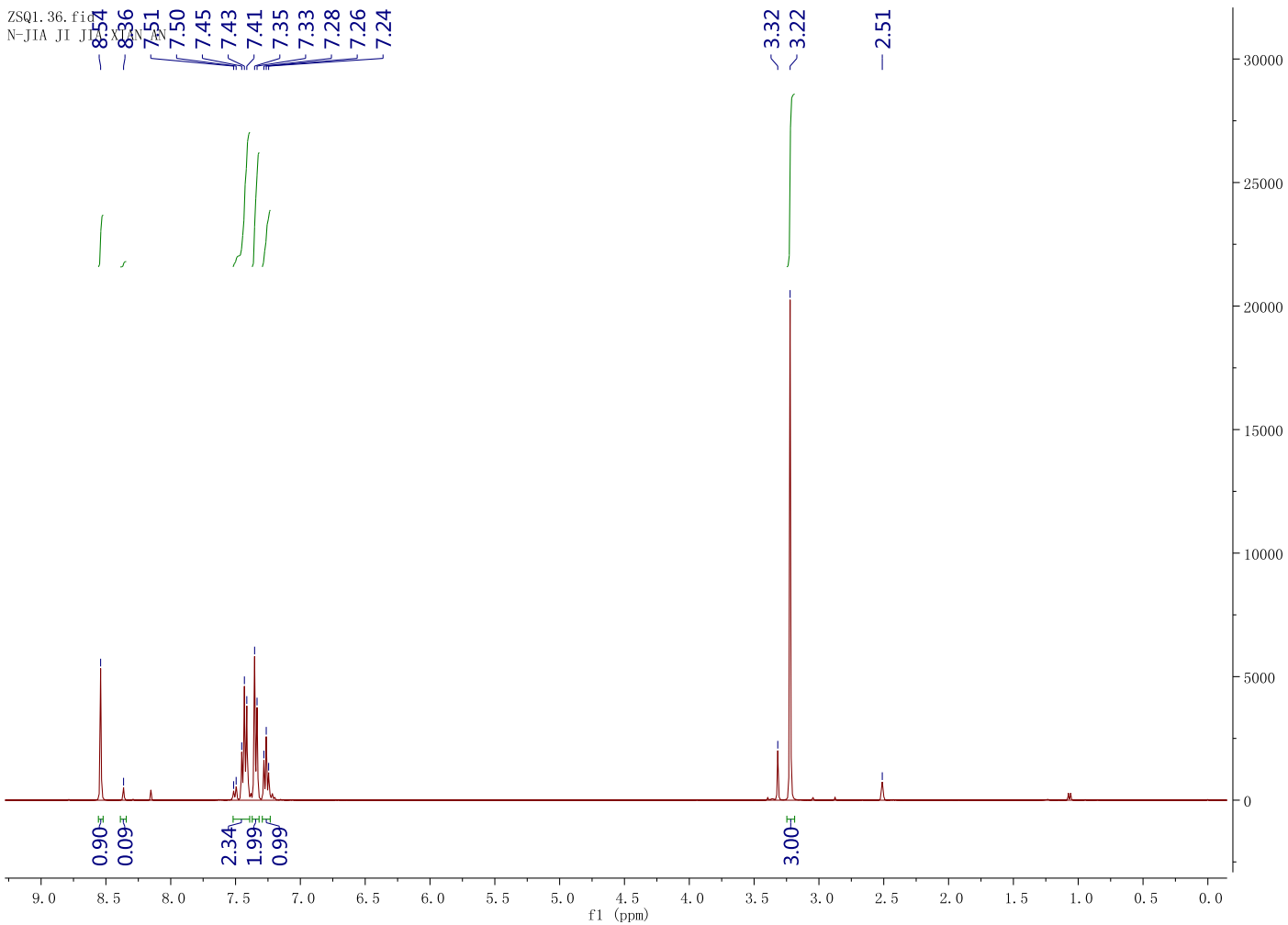


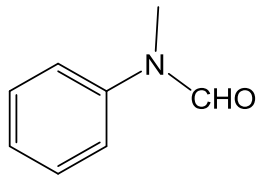
^{13}C NMR (100 MHz, DMSO-d_6)



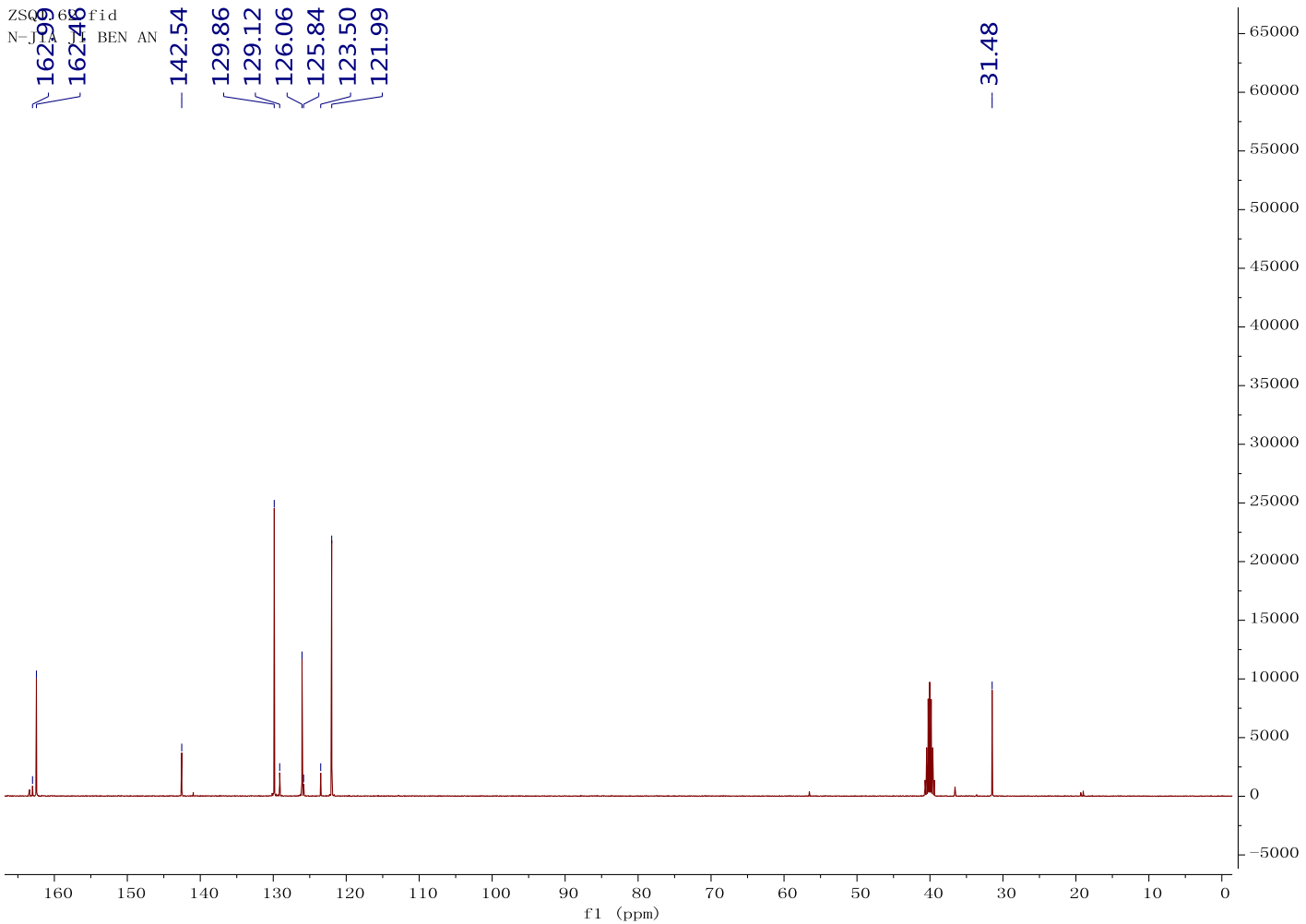


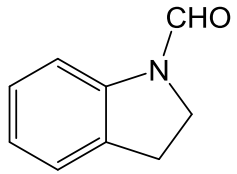
^{1}H NMR (400 MHz, DMSO-d_6)



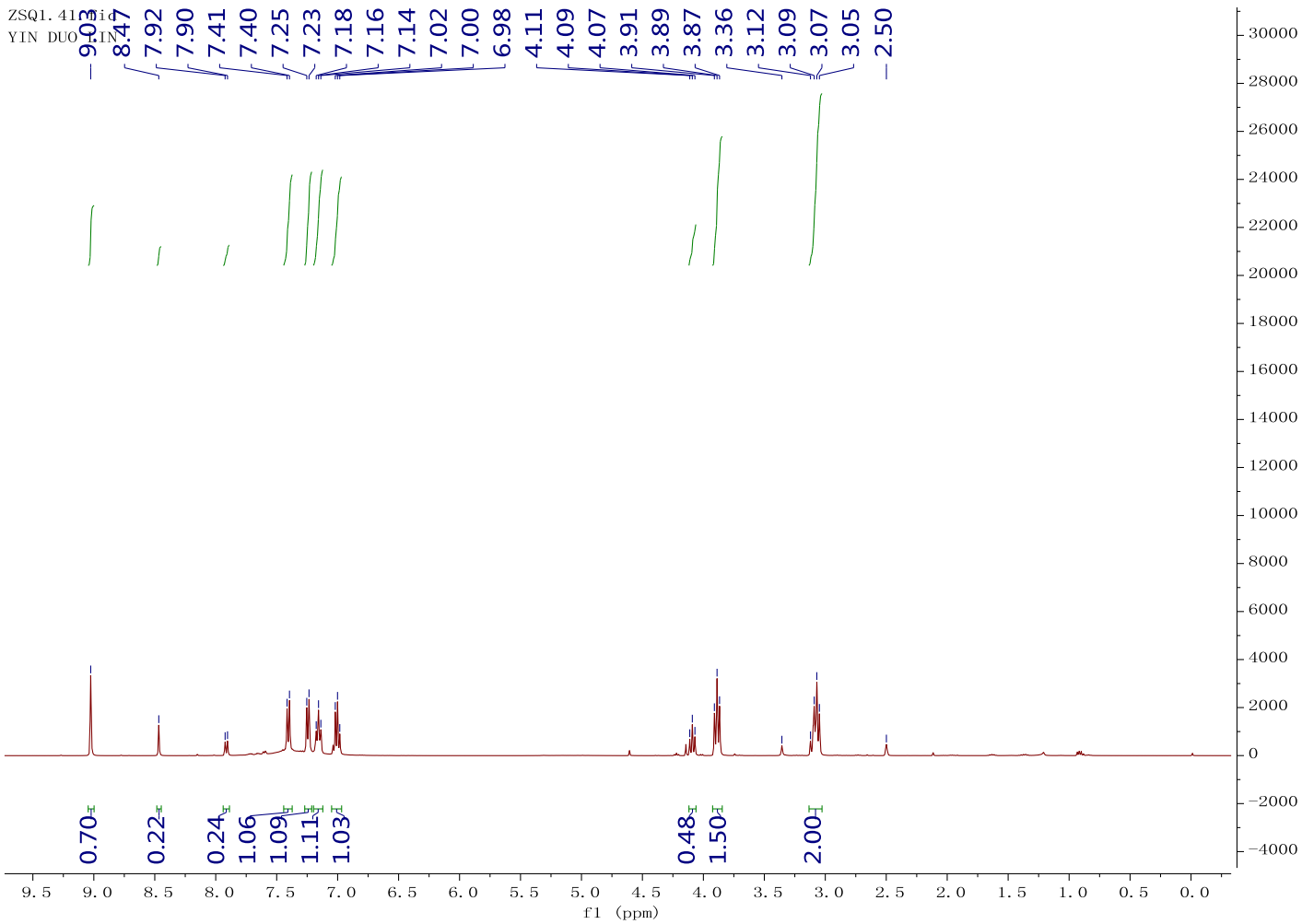


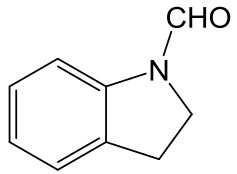
^{13}C NMR (100 MHz, DMSO-d_6)



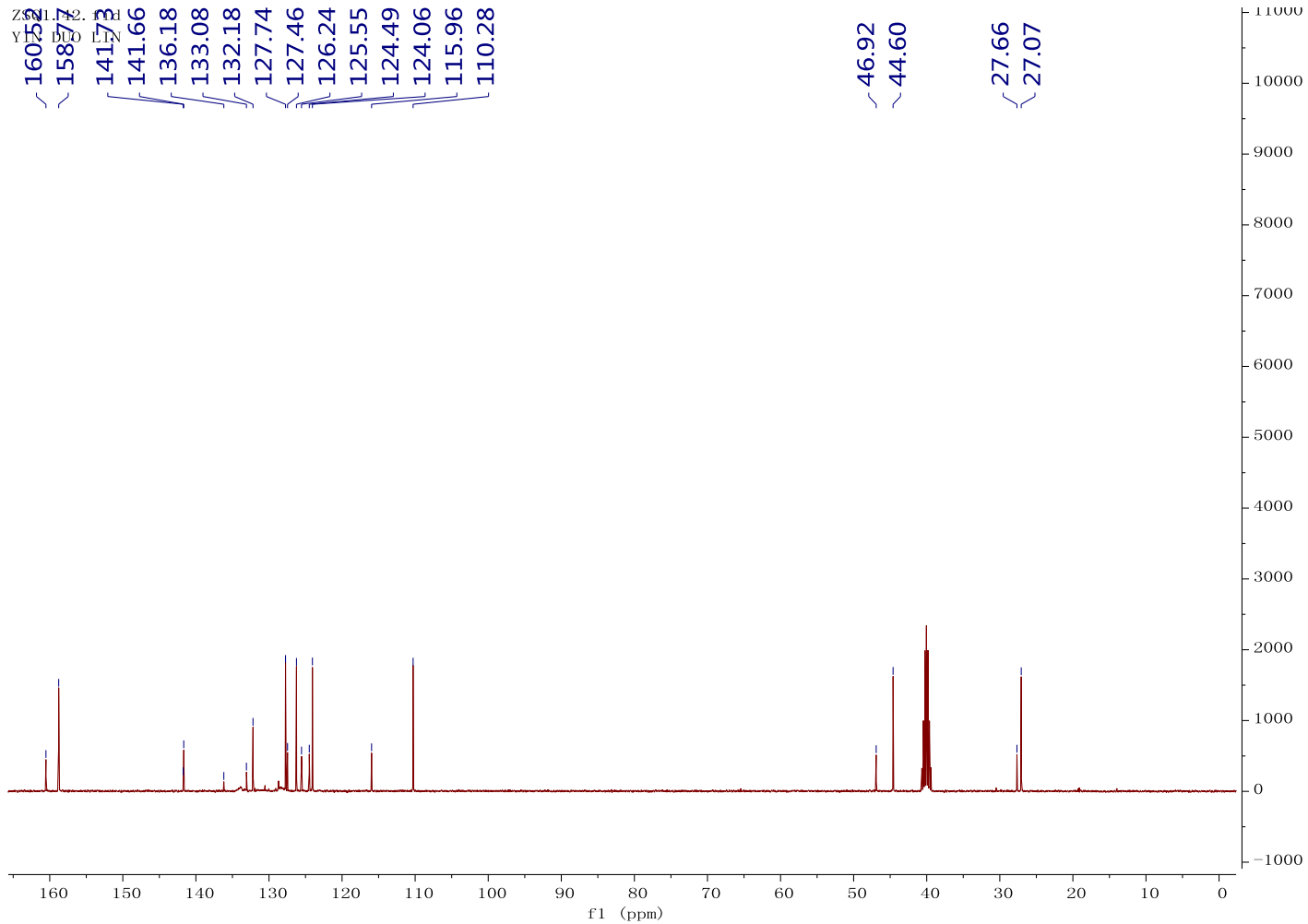


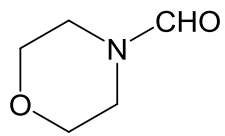
^{1}H NMR (400 MHz, DMSO-d_6)



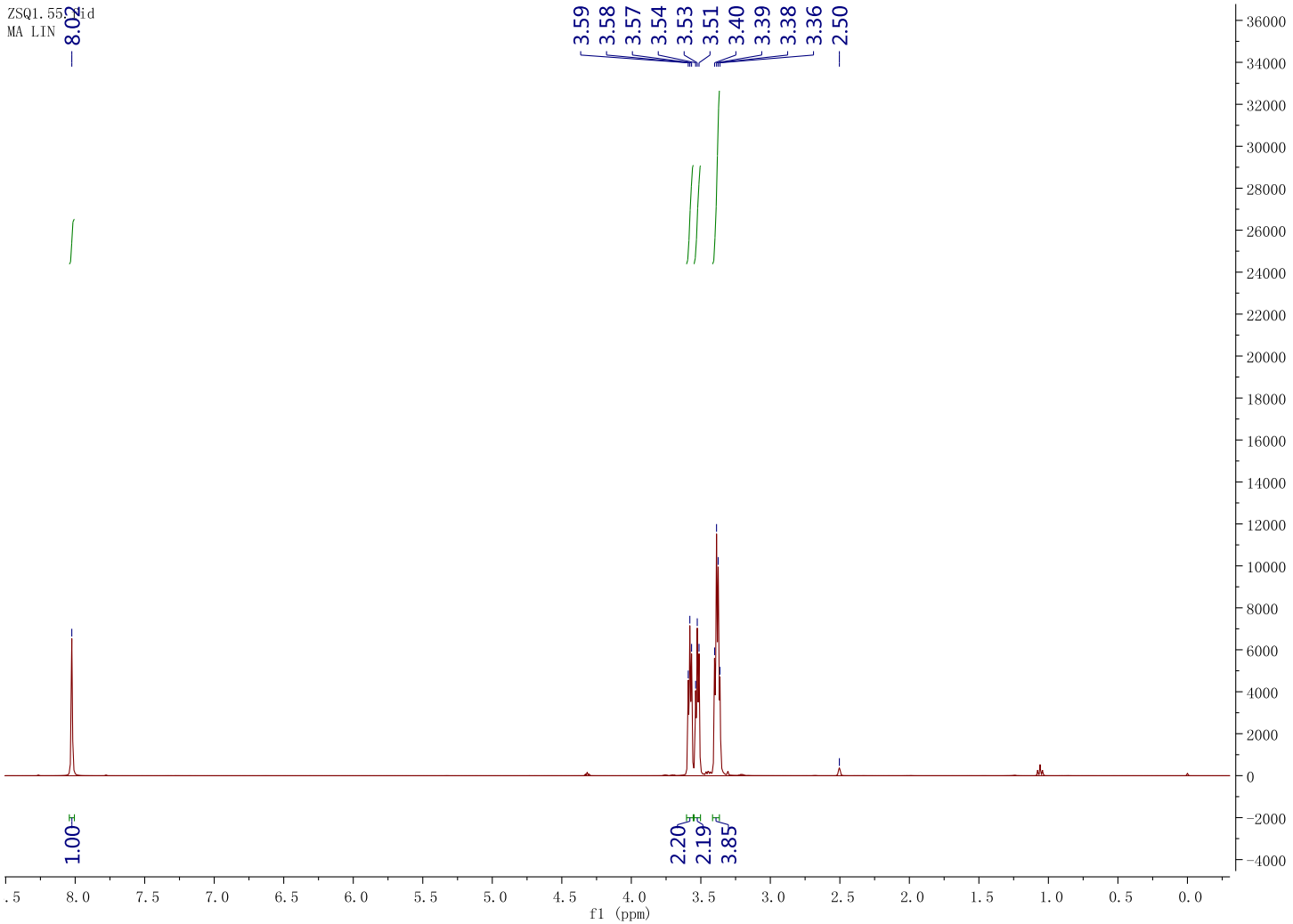


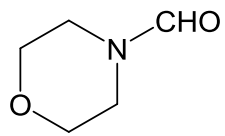
^{13}C NMR (100MHz, DMSO-d_6)



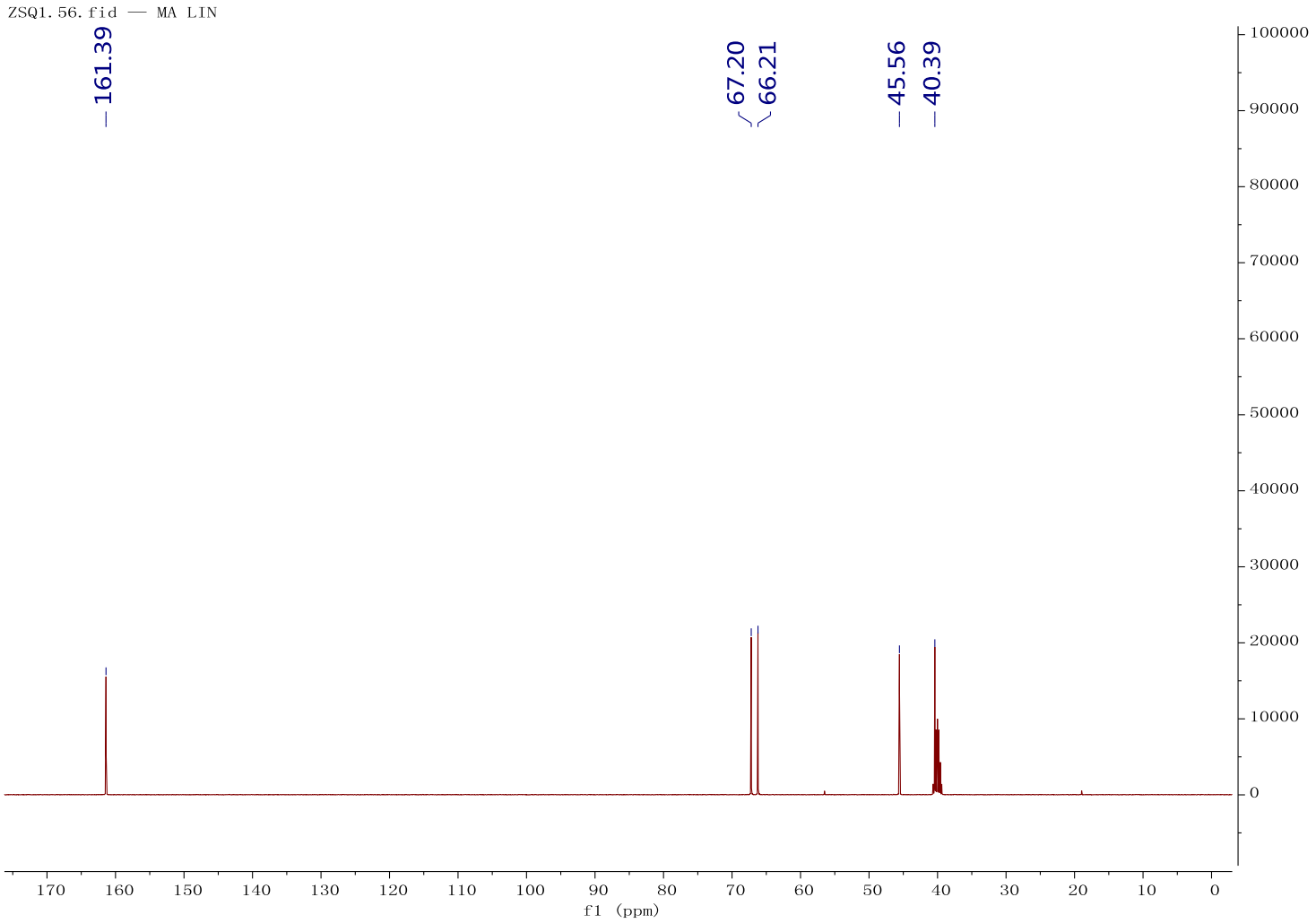


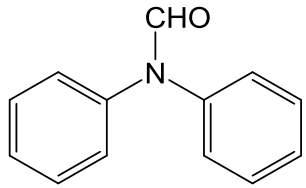
^{1}H NMR (400 MHz, DMSO-d_6)



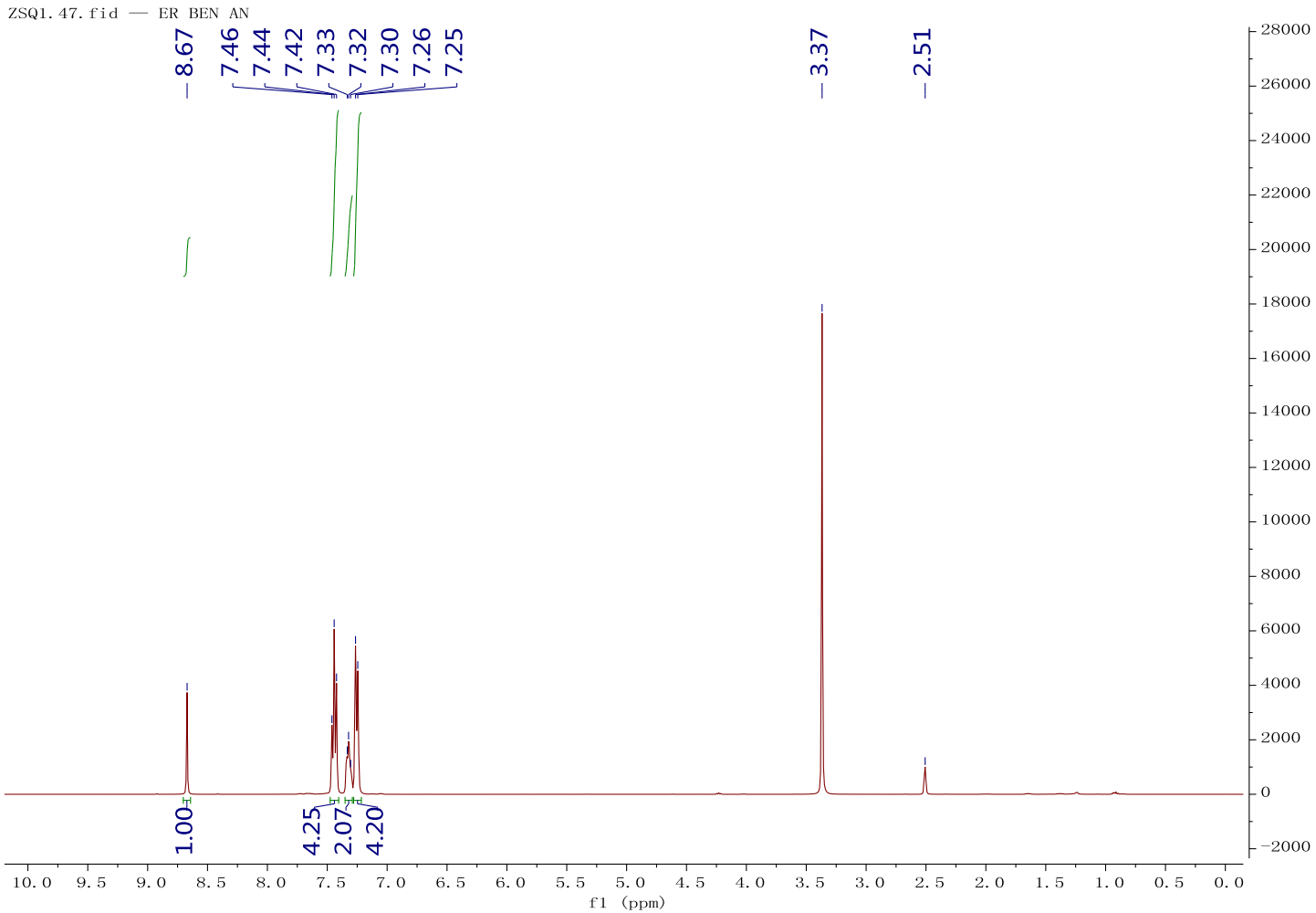


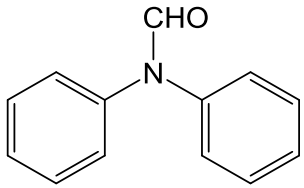
^{13}C NMR (100 MHz, DMSO-d_6)



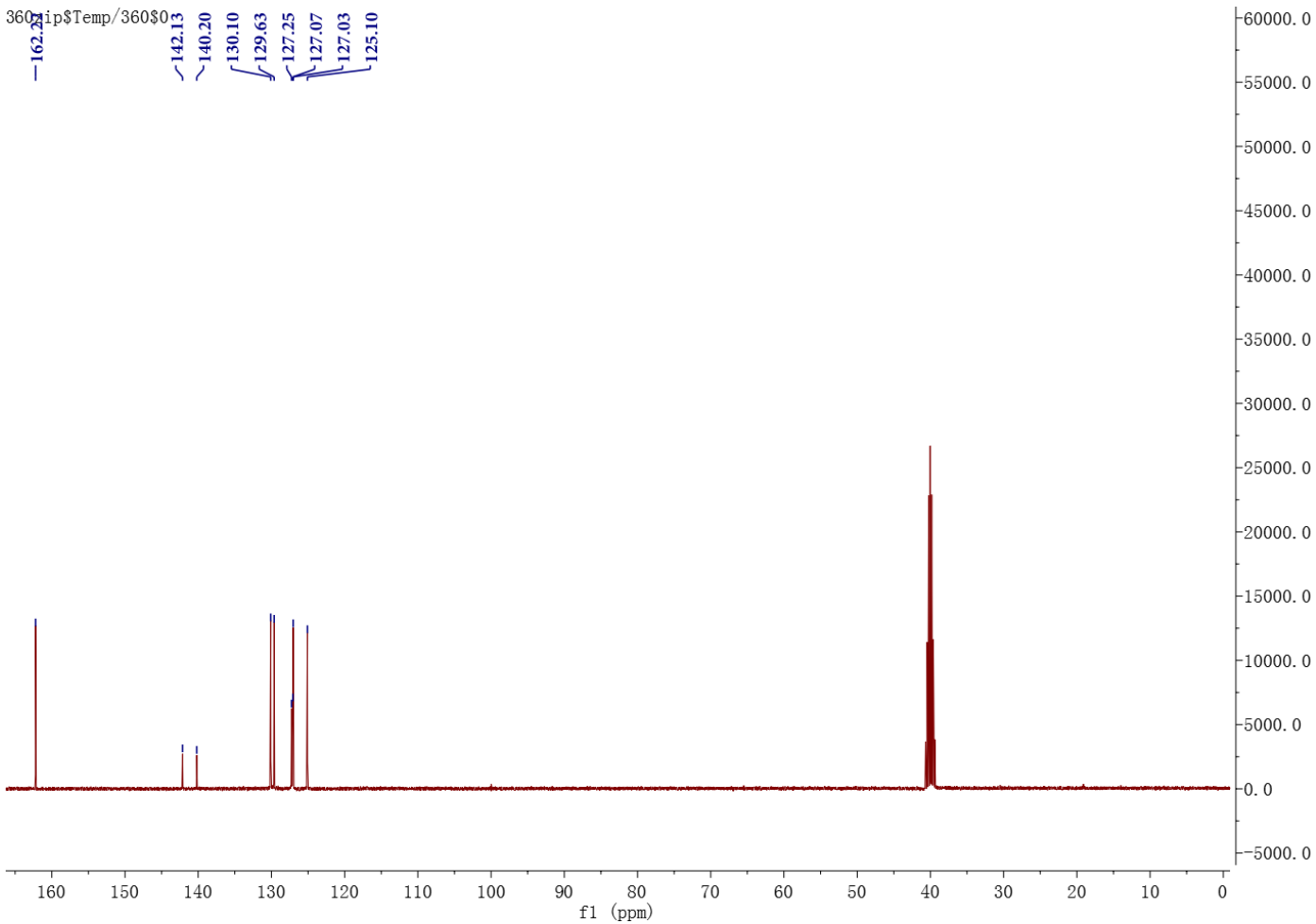


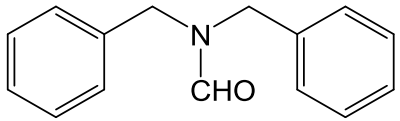
^{1}H NMR (400 MHz, DMSO-d_6)





^{13}C NMR (100 MHz, DMSO-d_6)





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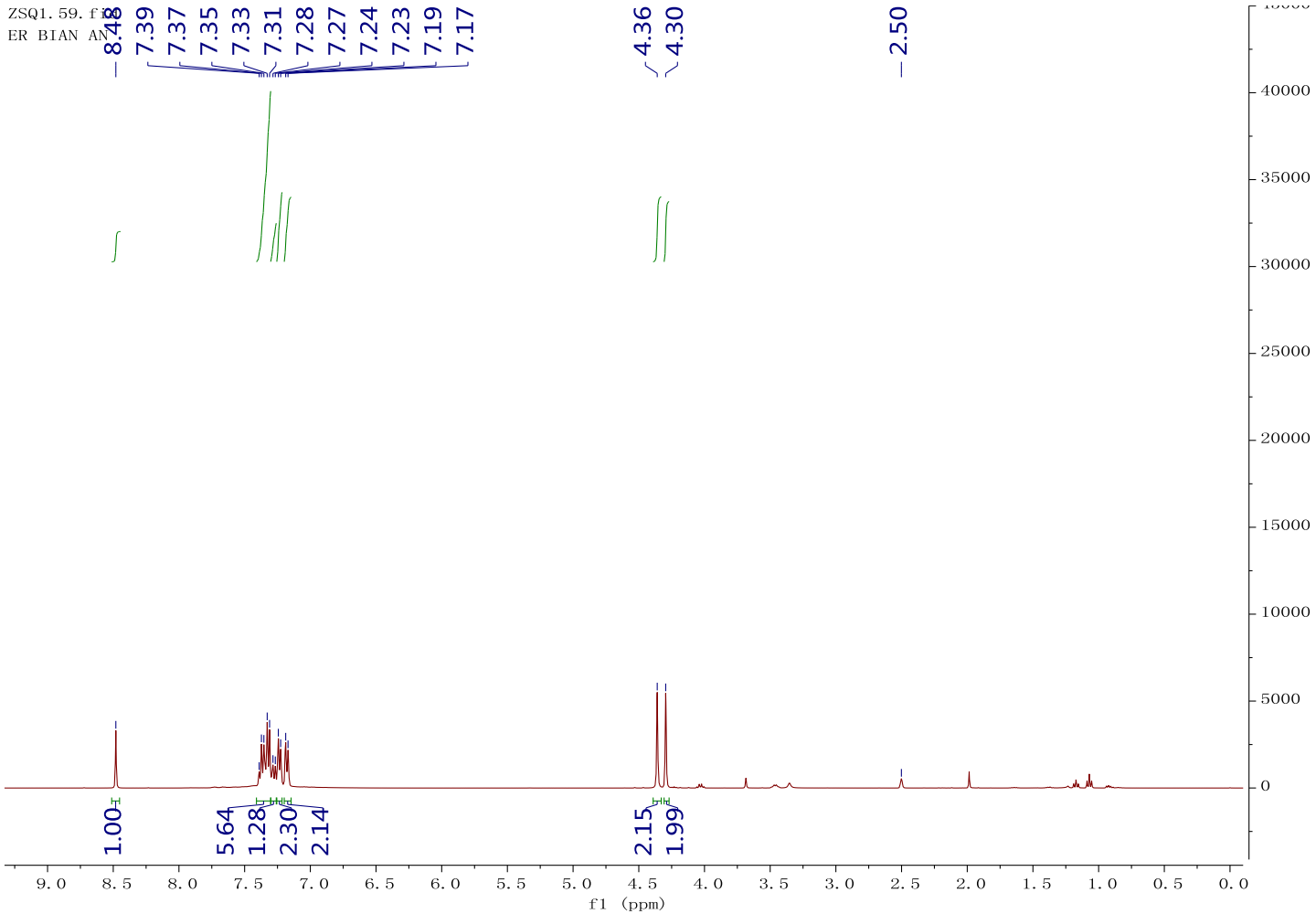
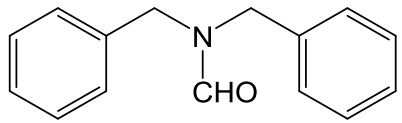
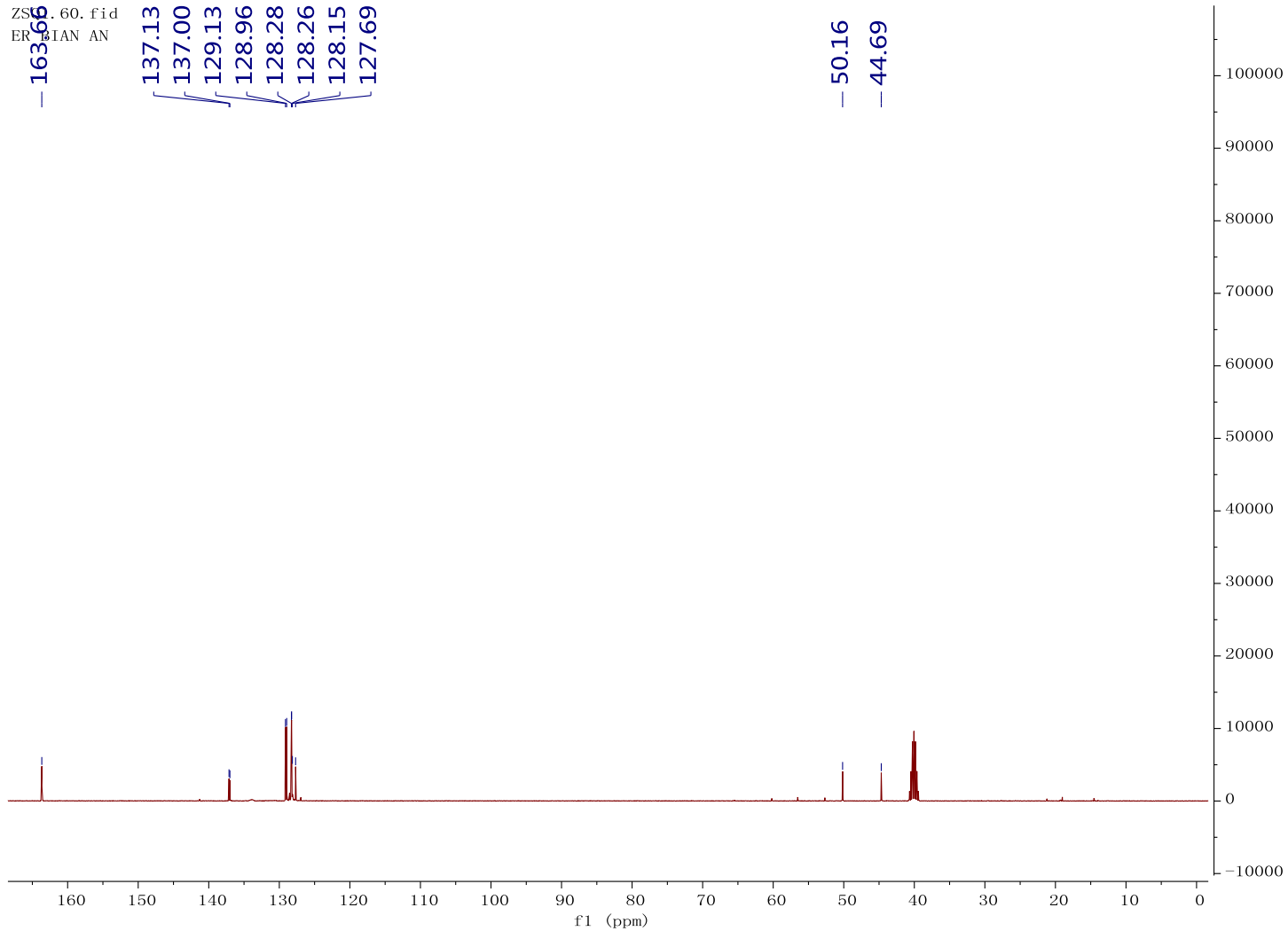
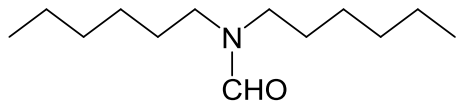




^{13}C NMR (100MHz, DMSO-d_6)





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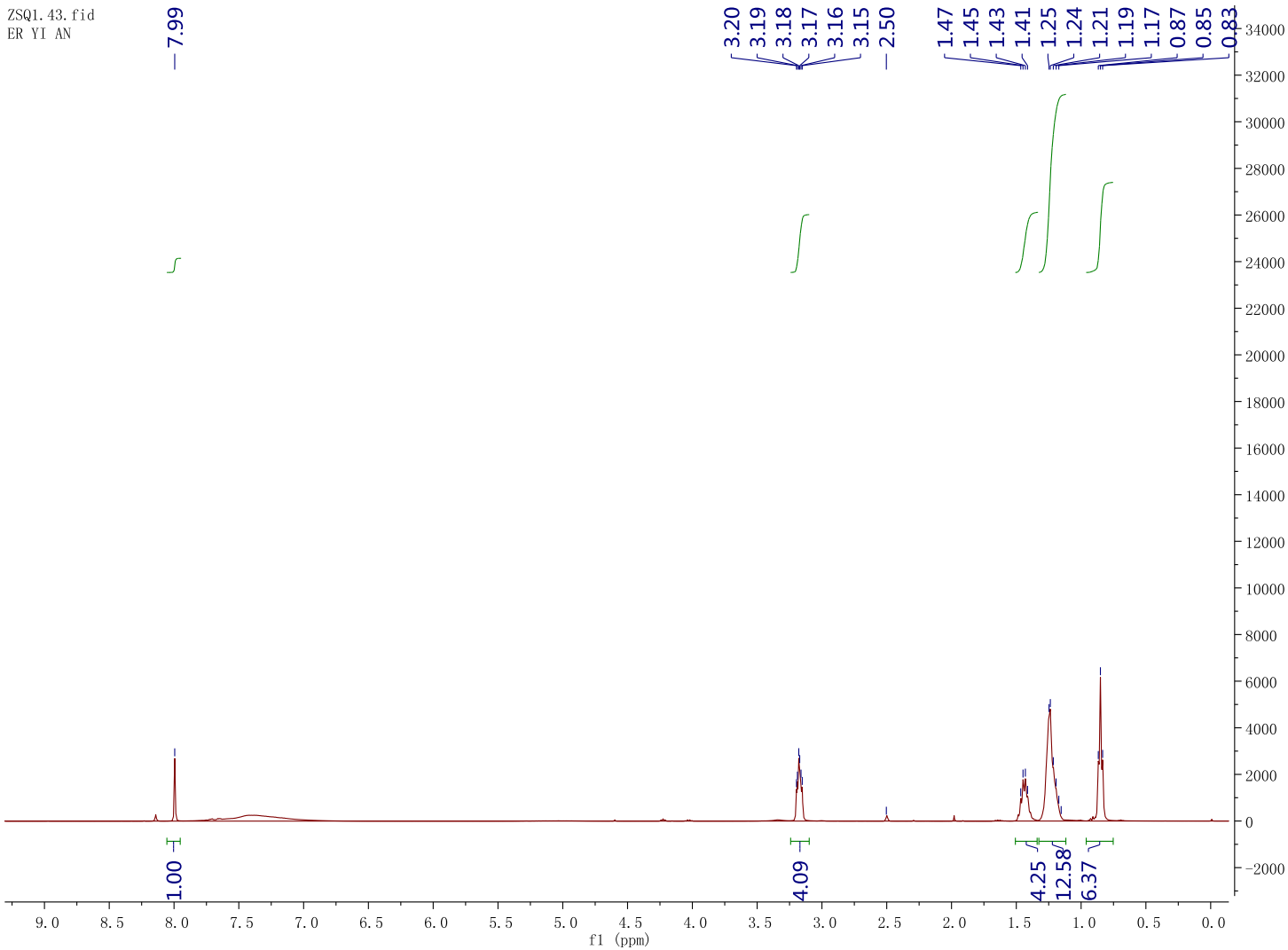

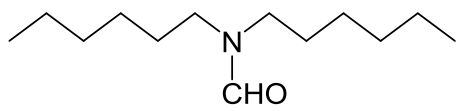

^{13}C NMR (100MHz, DMSO-d_6)