Supporting Information

Oxygen-implanted MoS_2 nanosheets promoting quinolines synthesis from nitroarenes and aliphatic alcohols via an integrated oxidation-transfer hydrogenation-cyclization mechanism

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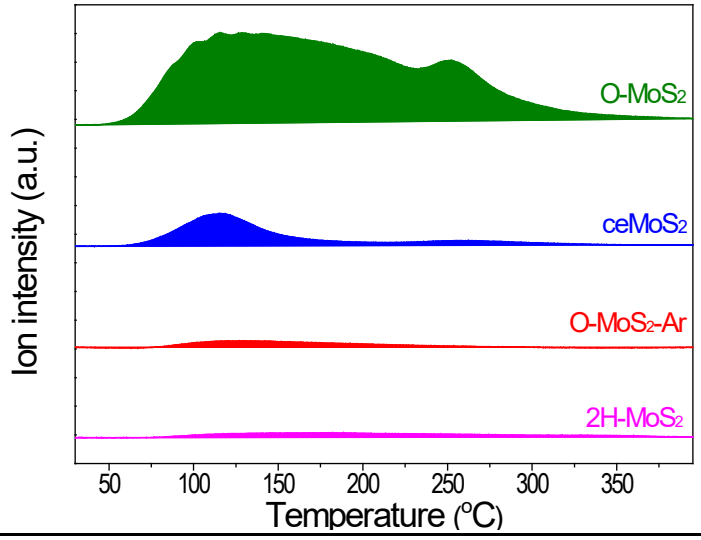
1. NH_3-TPD characterization of the MoS_2 materials

The CUS Mo sites of MoS_2 were probed and quantitatively analyzed by temperature-programmed desorption of ammonia (NH_3-TPD).[1] Milligrams of MoS_2 sample were loaded into a quartz tubular reactor, which was heated in a vertical electronic furnace. The desorption gas mixture was analyzed by an online mass spectrometer (THERMO^{Star} gas analysis system). The sample was initially pretreated at 100 °C under an Ar gas flow (30 mL·min^{-1}) for 1 h to remove the adsorbed impurities and then cool down to room temperature. Then the flowing gas was switched to ammonia gas (99.9%) for 30 min at room temperature, and then back to Ar gas. The reactor temperature was increased to 400 °C at a ramp rate of 10 °C·min^{-1}. The m/z 17 was recorded for NH_3 and HO* from H_2O. The pure NH_3 mass signal was the subtracted value between m/z 17 (NH_3 and HO*) and the HO* mass signal based on the reference mass spectrum of H_2O (m/z 18). The quantification results were calculated by referring to an ammonia standard curve.

Chart S1. NH_3-TPD characterization of the MoS_2 materials



Sample	NH_3 (μmol·g^{-1})	$R_{(CUS\ Mo)}$ (%)[a]
2H-MoS_2	10.7	0.17
ceMoS_2	34.8	0.56
O-MoS_2	226.4	3.63
O-MoS_2-Ar	11.2	0.18

[a] The CUS Mo ratio ($R_{(CUS\ Mo)}$) in MoS_2 catalyst is based on the hypothesis that one CUS Mo site adsorbs one NH_3, which can be regarded as an indicator to describe the trend of CUS Mo sites in MoS_2 catalysts.

Note: The NH_3-desorbing temperature for the MoS_2 catalysts above were all below 350 °C, which could be classified as weak and medium-strong acid sites for heterogeneous catalysts.

2. The lattice structures of the MoO_2 and MoS_2

As shown in Fig. S1a, the MoO_2 is formed with distorted [MoO_6] octahedral with 1.97~2.07 Å Mo−O bonds and 78~97 º O−Mo−O angle, and the Mo···Mo distance ranges from 2.51 to 3.71 Å.[2] Mo in the MoO_2 is six-fold coordinated and the O is three-fold in the bulk and there are two-fold coordinated O species on its surface. In contrast, as shown in Fig. S1b the 2H-MoS_2 is formed with [MoS_3] triangle vertebral pairs sharing the same Mo vertex with 2.41 Å Mo−S bond, 81.1º S−Mo−S angle, and Mo···Mo distance in the 2H-MoS_2 is 3.15 Å. Besides, the MoS_2 consists of six-fold coordinated Mo species and the three-fold coordinated S species. Therefore, the ligand geometries of O ($Mo^{(IV)}$–O) and S ($Mo^{(IV)}$–S), and the lengths of the Mo−O and Mo−S bonds are remarkably different. The obvious differences between Mo(IV)−O and Mo(IV)−S bonds could cause lattice defects in the oxygen-implanted MoS_2.

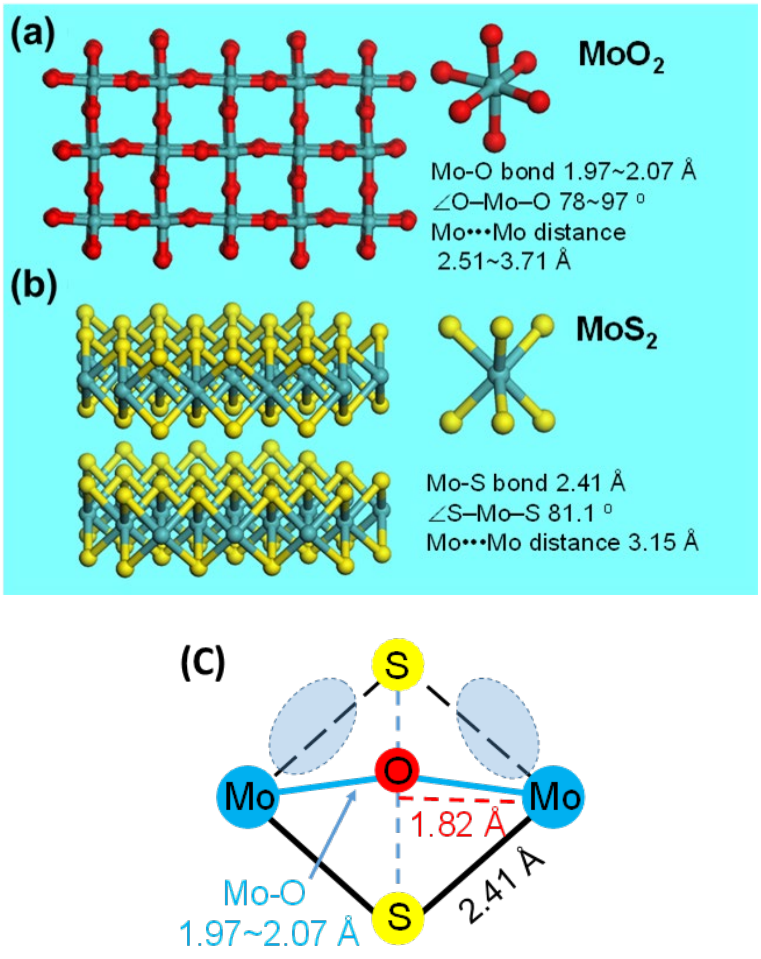


Fig. S1 The lattice structures of the MoO_2 (a), MoS_2 (b), and their difference(c).

3. The transfer hydrogenation mechanism for nitro reduction

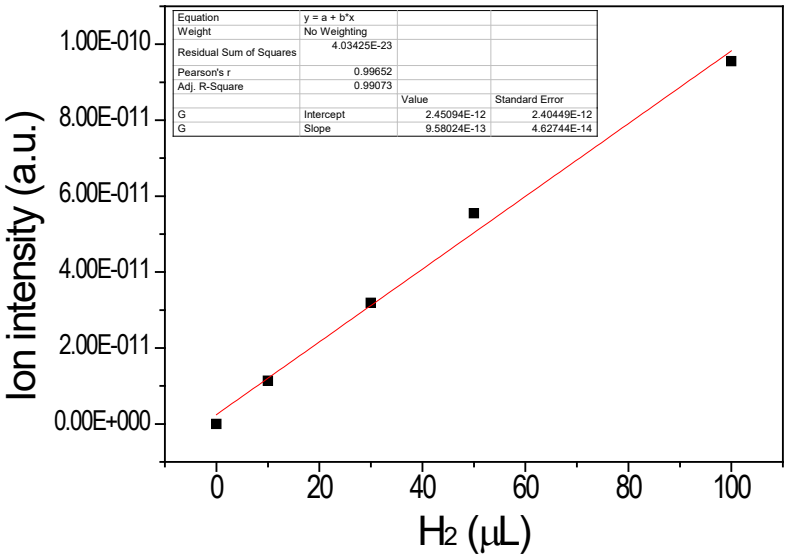


Fig. S2 The standard working curve of the H_2 with a MS detector.

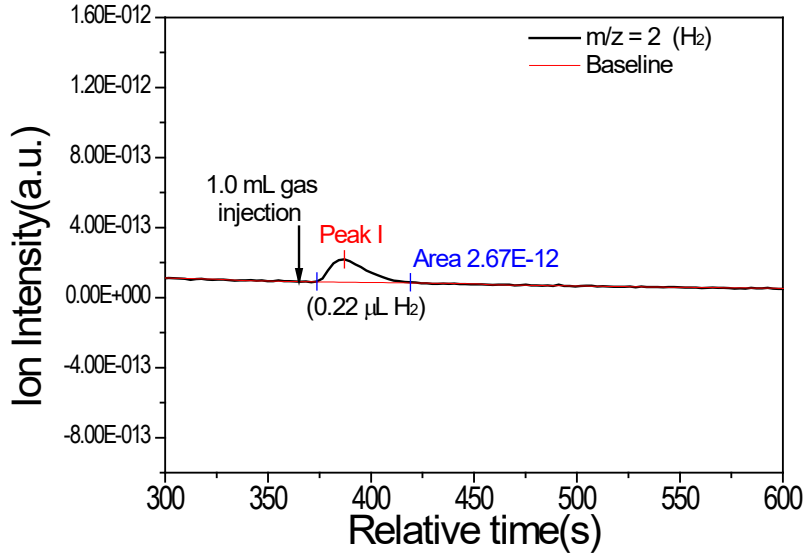


Fig. S3 The gas analysis of the ethanol decomposition. Reaction condition: ethanol 2.5 mL, O-MoS_2 catalyst 100 mg, reactor volume 15 mL, 1.0 MPa Ar, 180 °C, 4 h.

4. The characterizations of other MoS_2 catalysts

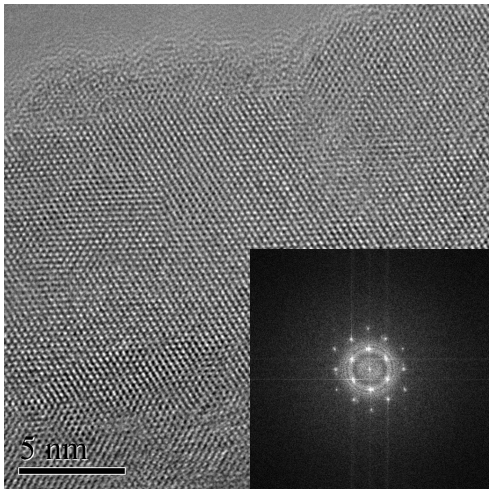


Fig. S4 The HRTEM image of 2H-MoS_2.

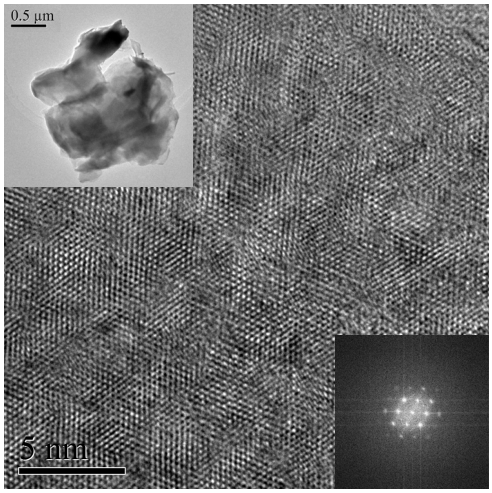


Fig. S5 The HRTEM image of ceMoS_2.

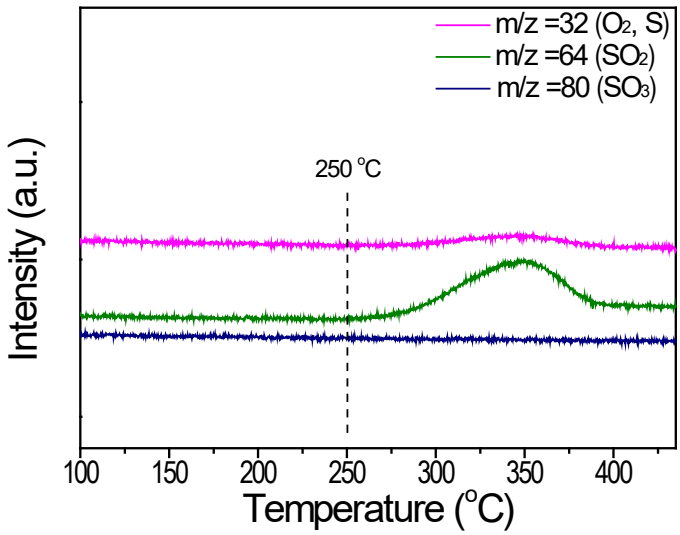


Fig. S6 The TPD profile of the O-MoS_2 in the Ar flow.

As shown in Fig. 1, thermal treatment of O-MoS_2 in Ar gas at 250 °C for 3 h resulted in the material (O-MoS_2-Ar) XRD pattern resembled that of commercial 2H-MoS_2 (JCPDS Card No. 37-1492), signifying that the thermal treatment reformed O-MoS_2. And the TPD-MS results (Fig. S6) showed that there was no lattice oxygen species released from the O-MoS_2 as O_2 or SO_2 below 250 °C in the Ar flow. It could be concluded that the O-MoS_2 and O-MoS_2-Ar had approximate oxygen contents.

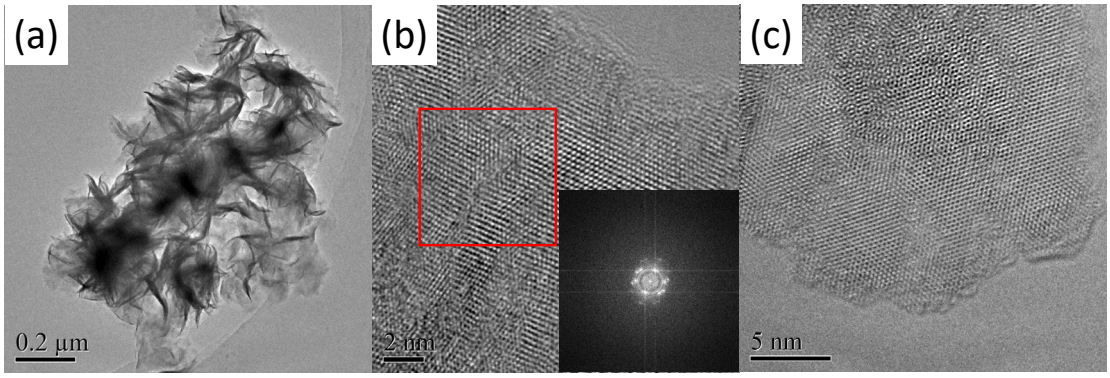


Fig. S7 The HRTEM images of O-MoS_2-Ar.

HRTEM characterizations showed the most surface of O-MoS_2-Ar became ordered without agglomeration (Fig. S7b). As shown in Fig. S7c, there were still some twisted and disordered lattice structures on the O-MoS_2-Ar surface.

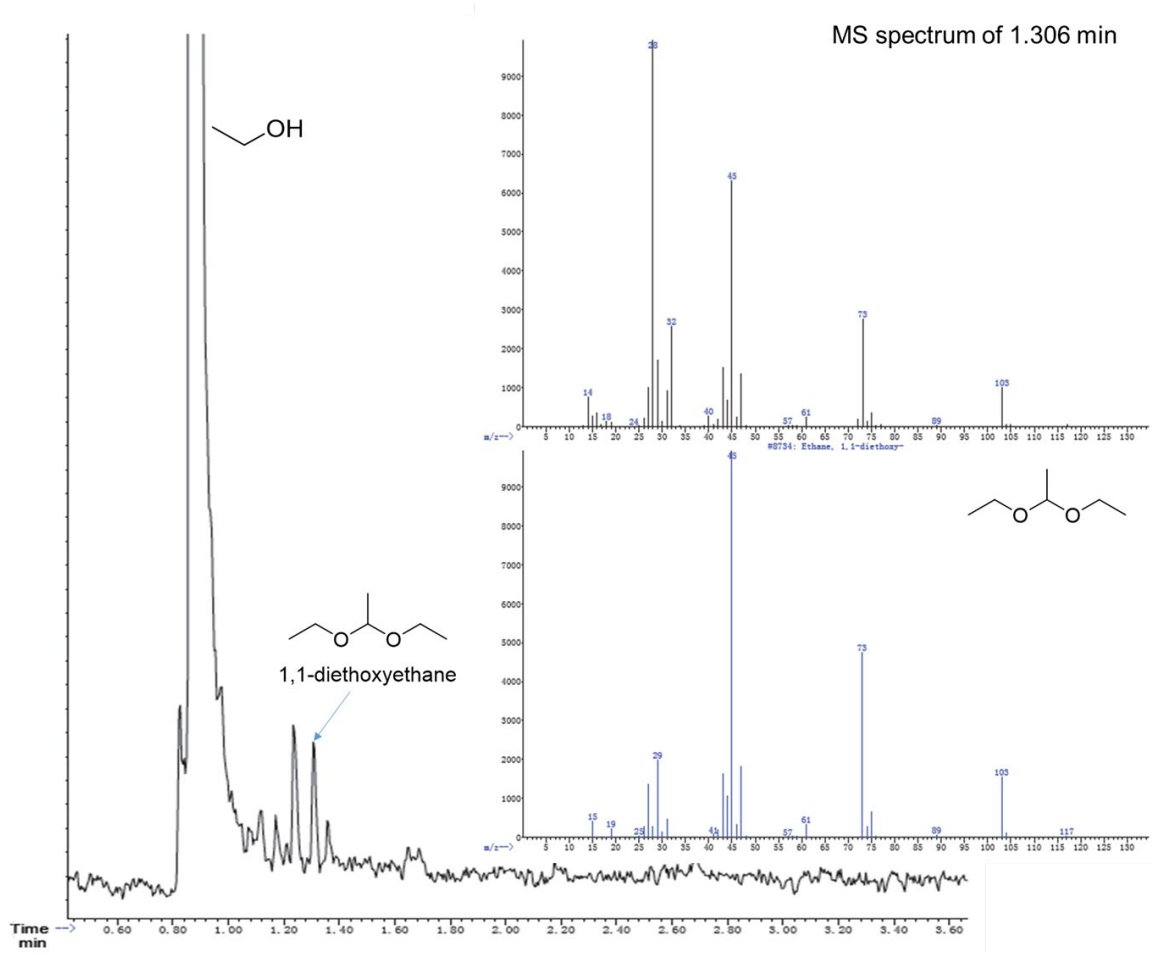


Fig. S8 The GC-MS spectrum of the liquid phase of reaction between O-MoS_2 and ethanol. Reaction condition: O-MoS_2 100 mg, ethanol 5.0 mL, 180 °C, Ar 1 atm, 8 h.

5. The recycling use of the O-MoS_2 for 2-methylquinoline synthesis

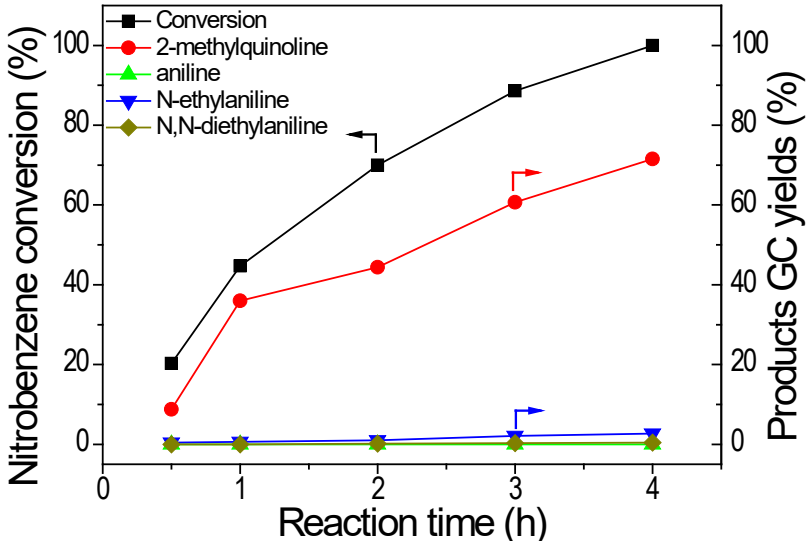


Fig. S9 The synthesis of 2-methylquinoline from nitrobenzene and ethanol over O-MoS_2 under air atmosphere. Reaction condition: nitrobenzene (0.2 mmol), ethanol (2.5 mL), catalyst 25 mg, air 4 atm, 180 °C.

Recovered the O-MoS_2 catalyst after simple washing and vacuum drying treatment can be directly reused at least nine times for the 2-methylquinoline synthesis from nitrobenzene and ethanol, which showed no obvious decline in catalytic ability (Fig. S9).

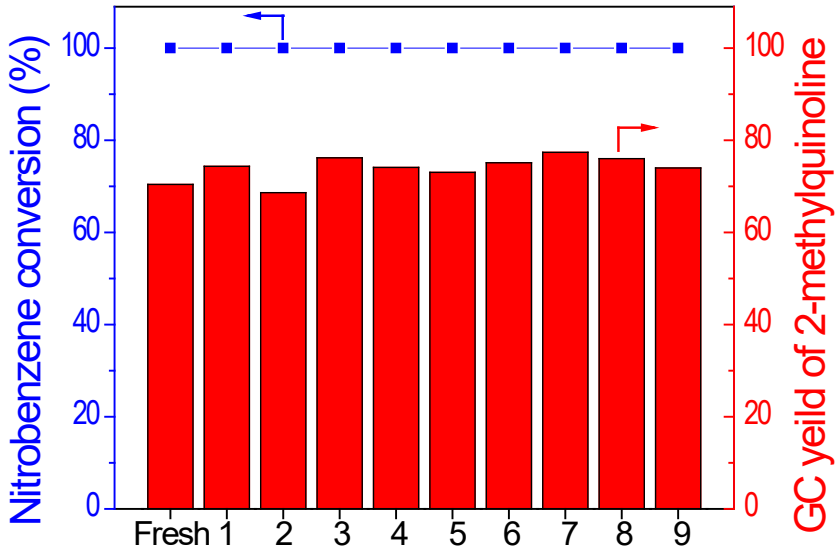


Fig. S10 The recycling use of the O-MoS_2 for 2-methylquinoline synthesis from nitrobenzene and ethanol. Reaction condition: nitrobenzene (0.2 mmol), ethanol (2.5 mL), catalyst 25 mg, air atmosphere 4 atm, 180 °C, 4 h.

6. Controlled experiments

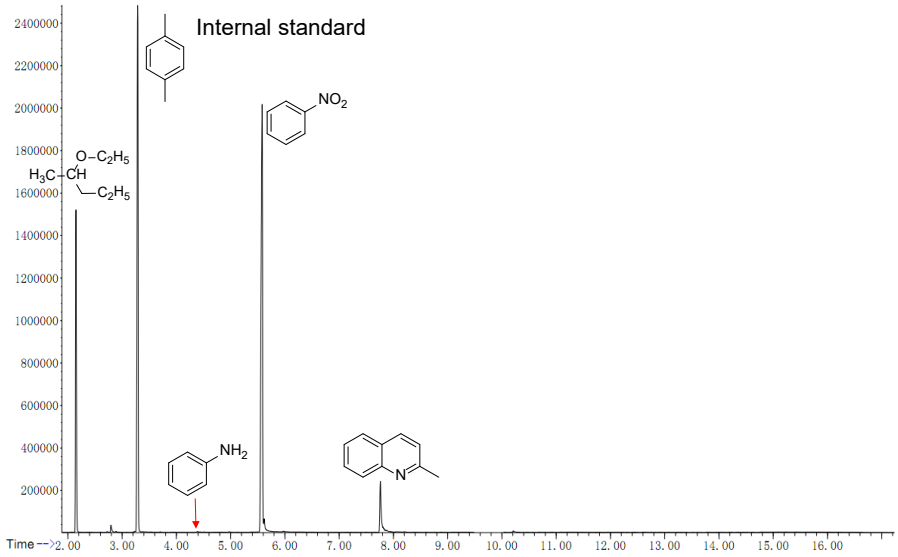
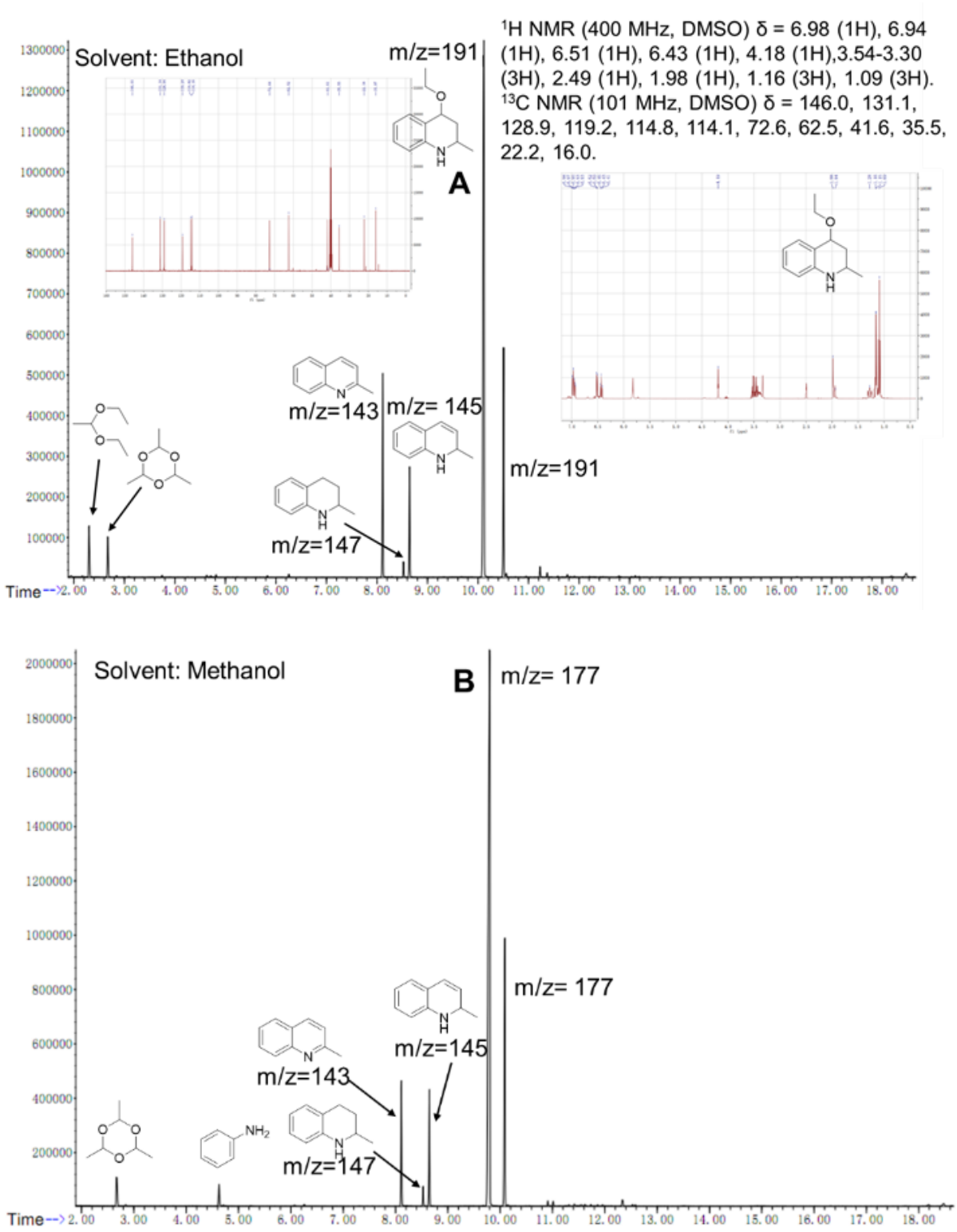


Fig. S11. GC-MS pattern of nitrobenzene conversion. Reaction condition: nitrobenzene 0.2 mmol, ethanol 2.5 mL, O-MoS_2 catalyst 25 mg, air 4 atm, 150 °C, 2 h. Note: Para-xylene is used as the internal standard.

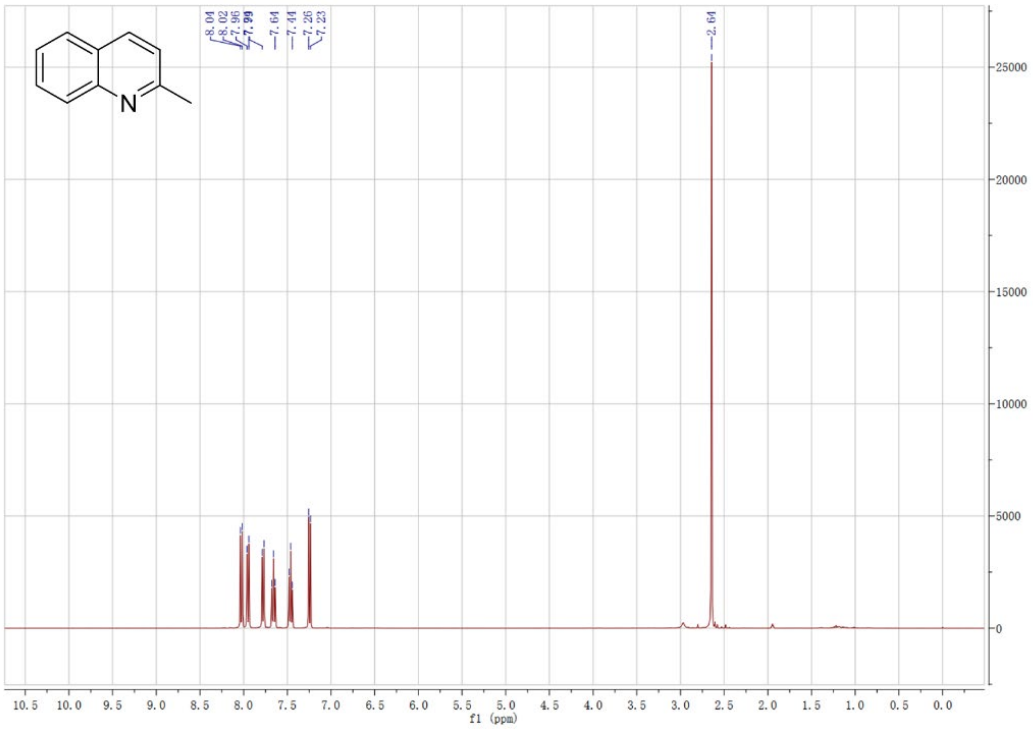
After 2 h reaction at 150 °C, 0.014 mmol nitrobenzene was reduced to 2-methylquinoline, and trace aniline was obtained. At the same time, 0.163 mmol aldehyde acetal was generated. Given the fact that the reduction of one nitrobenzene to aniline needs three ethanol molecules, then two generated acetaldehyde or aldehyde acetal react with the aniline to one 2-methylquinoline molecule. Combining with other reaction rate data (Scheme 2 of the manuscript), it can be confirmed that the transfer hydrogenation of nitro groups is the rate-determining step for the substituted quinolines synthesis.

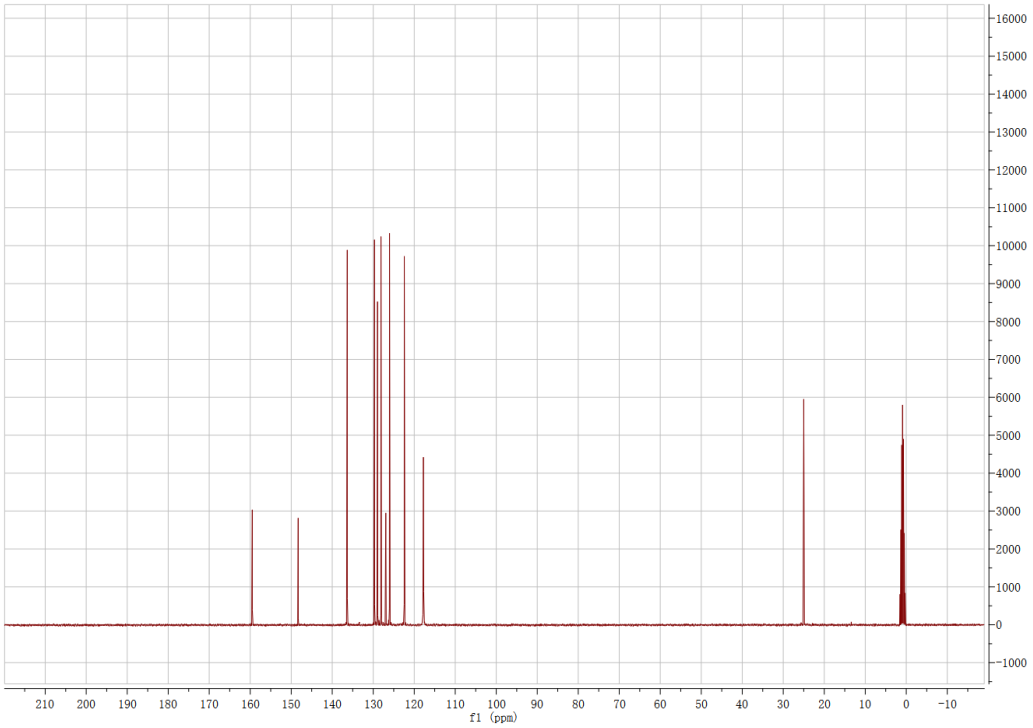


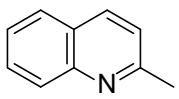
^{1}H NMR (400 MHz, DMSO) δ = 6.98 (1H), 6.94 (1H), 6.51 (1H), 6.43 (1H), 4.18 (1H),3.54-3.30 (3H), 2.49 (1H), 1.98 (1H), 1.16 (3H), 1.09 (3H).
^{13}C NMR (101 MHz, DMSO) δ = 146.0, 131.1, 128.9, 119.2, 114.8, 114.1, 72.6, 62.5, 41.6, 35.5, 22.2, 16.0.

Fig. S12. The GC-MS profile of reaction between aniline and aldehyde in ethanol or methanol at 60 °C.

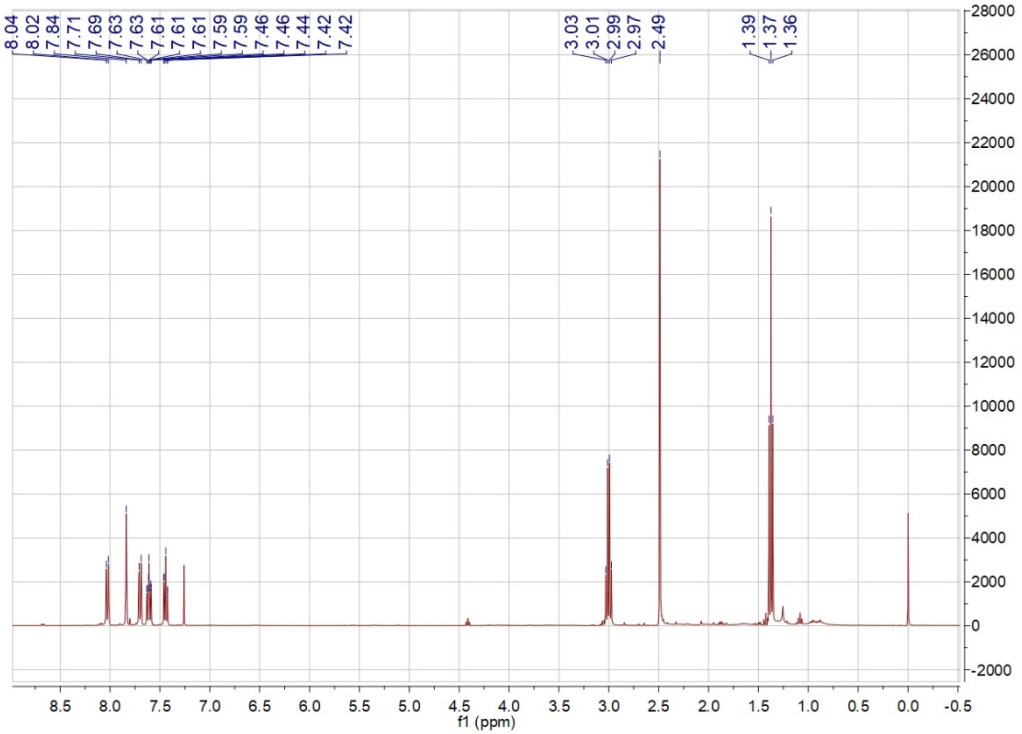
7. Characterization of the quinolines

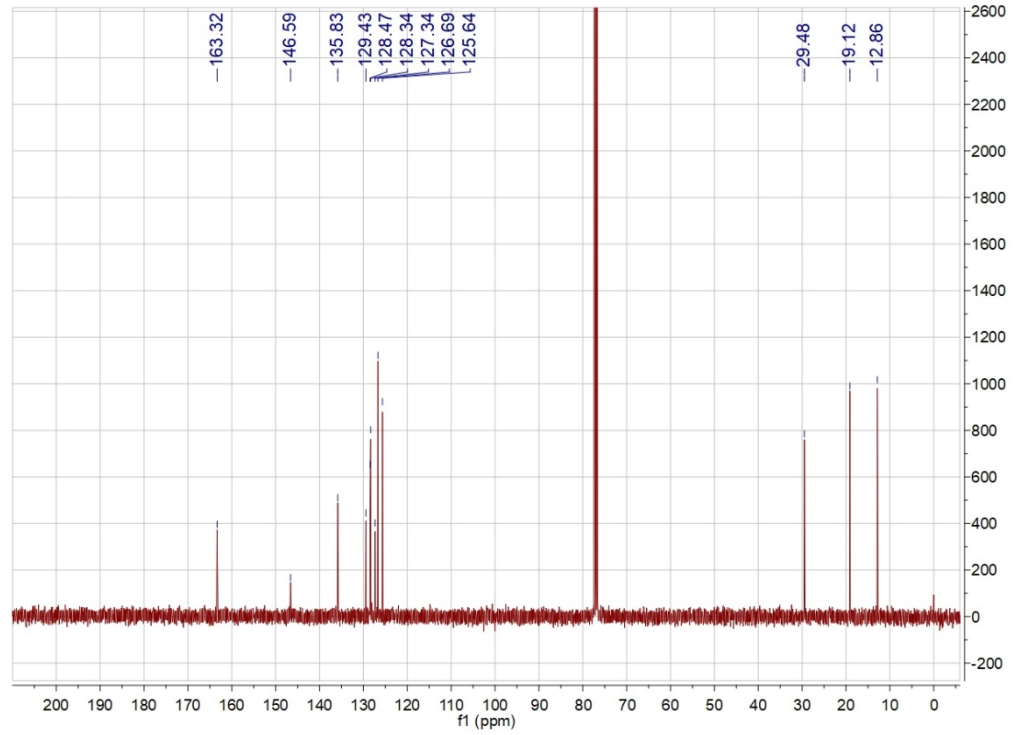


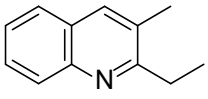




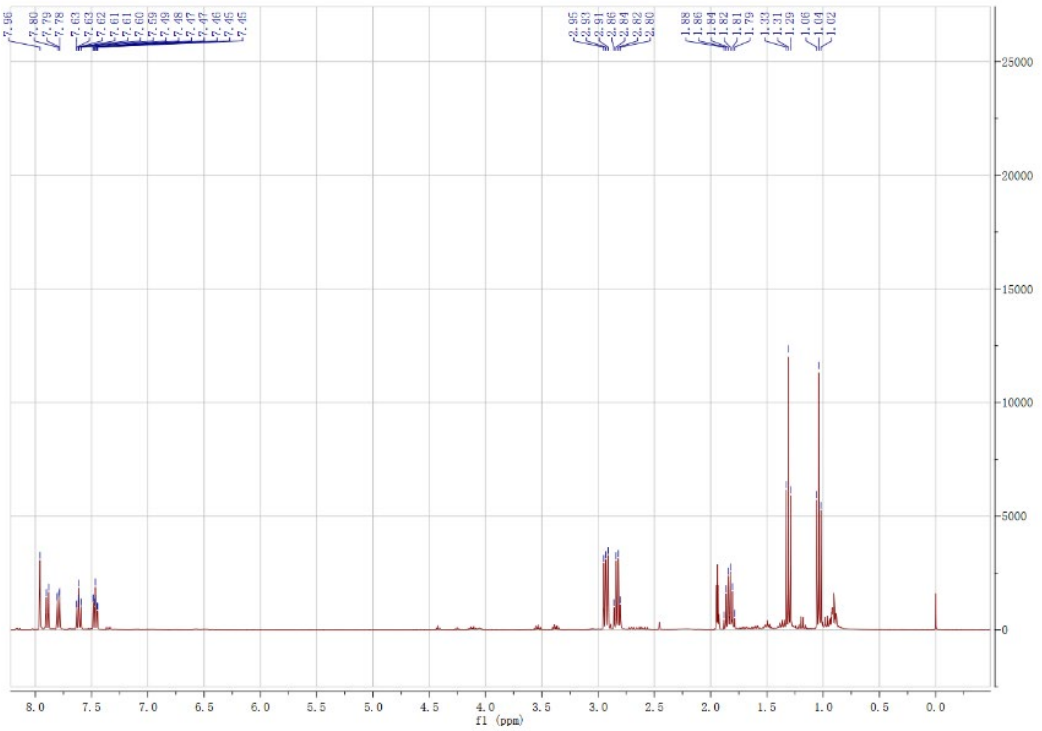
^{1}H NMR (400 MHz, CD_3CN) δ 8.03 (d, J= 8 Hz,1 H), 7.95 (d, J= 8 Hz,1 H), 7.78 (d, J= 8 Hz,1 H), 7.66 (t, J= 8 Hz,1 H), 7.46 (t, J= 8 Hz,1 H), 7.25 (d, J= 12 Hz,1 H), 2.64 (s, 3 H). **^{13}C NMR (101 MHz, CD_3CN)** δ = 159.5, 148.3, 136.3, 129.7, 128.9, 128.1, 126.9, 125.9, 122.4, 24.9.

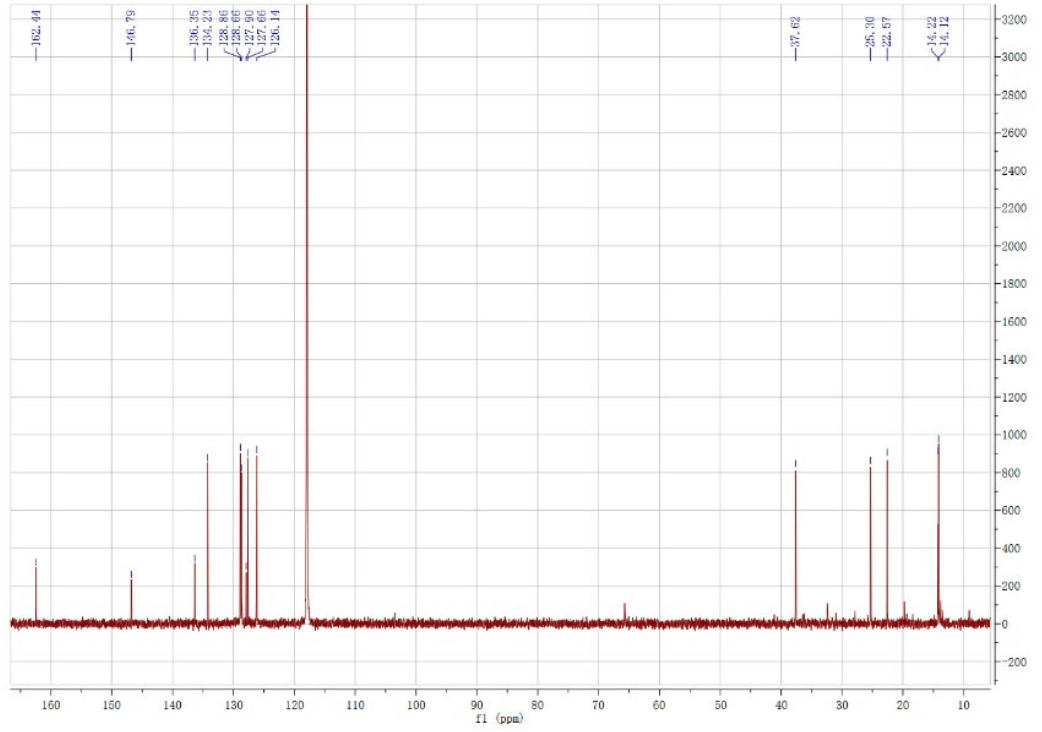


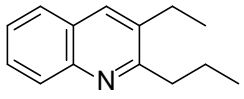




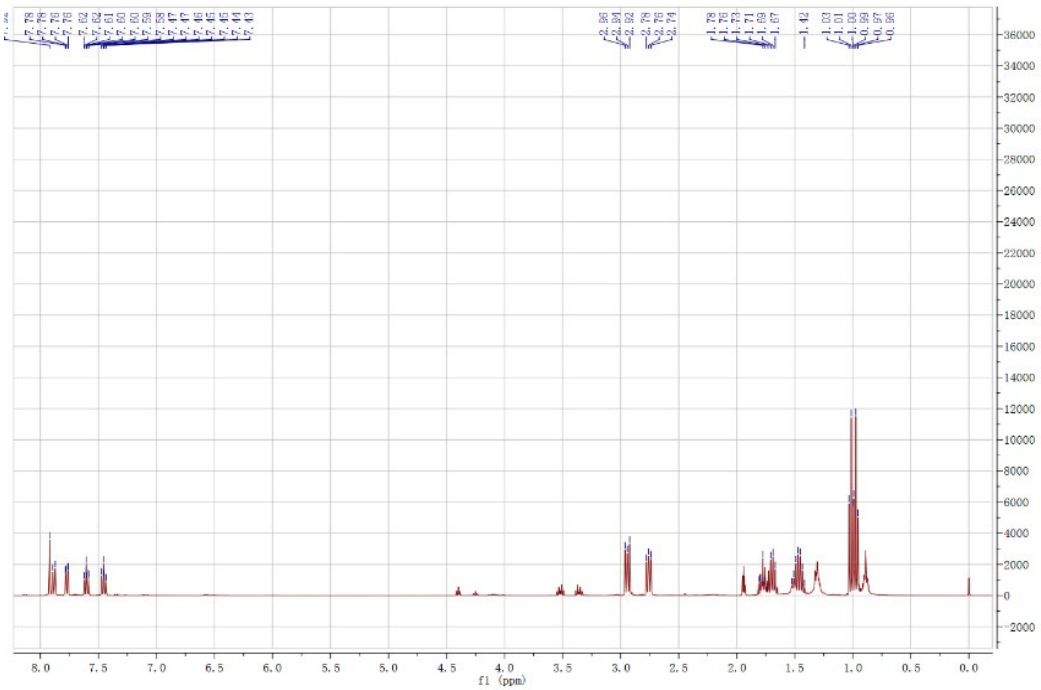
^{1}H NMR (400 MHz, $CDCl_3$) δ=8.03 (d, J= 8.4 Hz, 1H), 7.84 (s, 1H), 7.70 (dd, J_1=8.0 Hz, J_2= 0.8 Hz, 1H), 7.61 (td, J_1=7.6 Hz, J_2= 1.2 Hz, 1H), 7.44 (td, J_1=7.6 Hz, J_2= 1.2 Hz, 1H), 3.00 (q, J= 7.6 Hz, 2H), 2.49 (s, 3H), 1.37 (t, J= 7.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.3, 146.6, 135.8, 129.4, 128.5, 128.3, 127.3, 126.7, 125.6, 29.5, 19.1, 12.9.

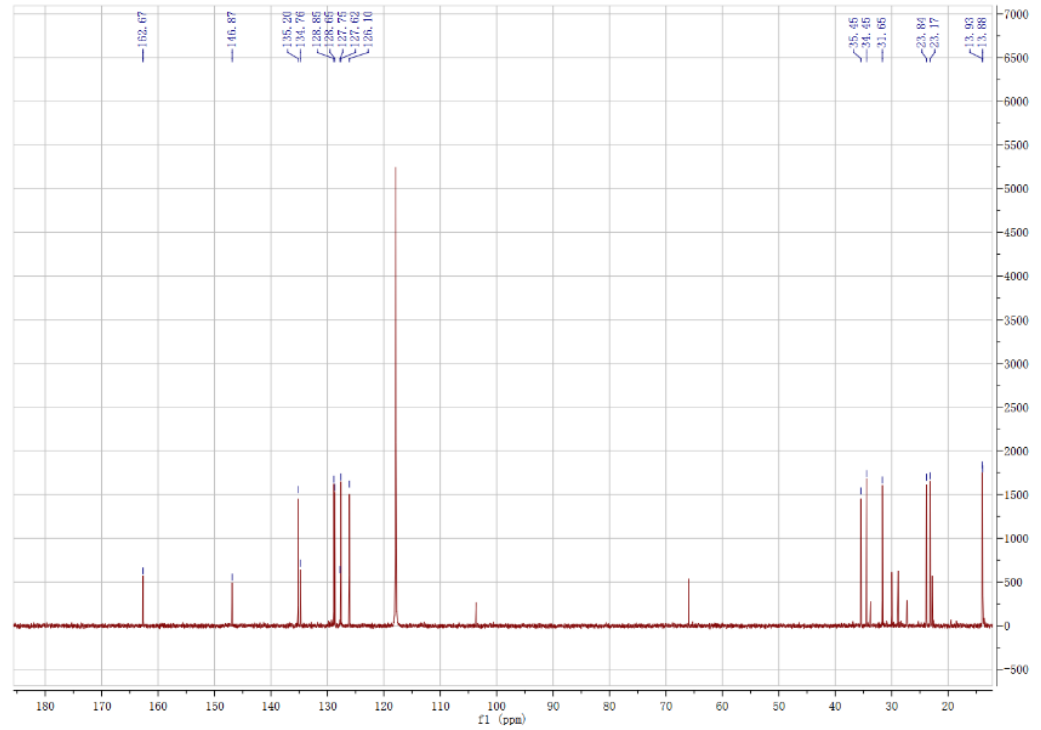


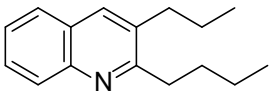




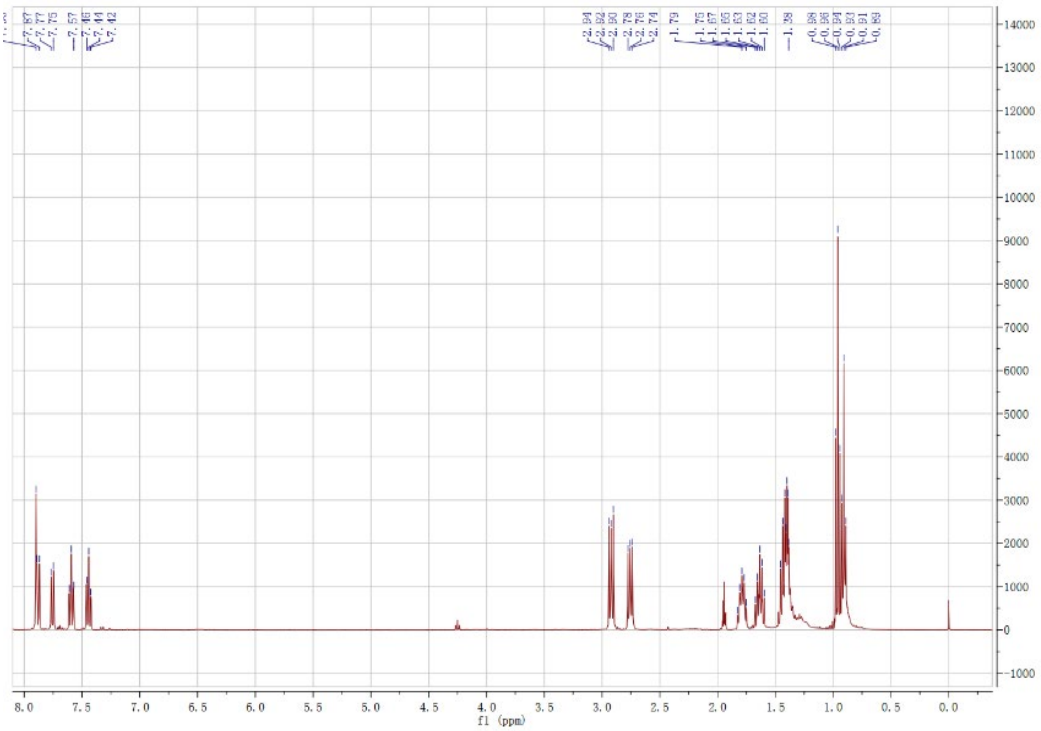
^{1}H NMR (400 MHz, CD_3CN) δ = 7.96 (s, 1H), 7.89 (d, J = 8 Hz, 1H), 7.79 (d, J= 8 Hz,1H), 7.61 (t, J= 8 Hz, 1H), 7.46 (t, J= 8 Hz, 1H), 2.95-2.91 (m, 2H), 2.86-2.80 (2H), 1.88-1.79 (m, J= Hz, 2H), 1.31 (t, J= 8 Hz, 3H), 1.04 (t, J= 8 Hz, 3H). **^{13}C NMR (101 MHz, CD_3CN)** δ = 162.4, 146.8, 136.4, 134.2, 128.8, 128.6, 127.9, 127.6, 126.1, 37.6, 25.3, 22.5, 14.2, 14.1.

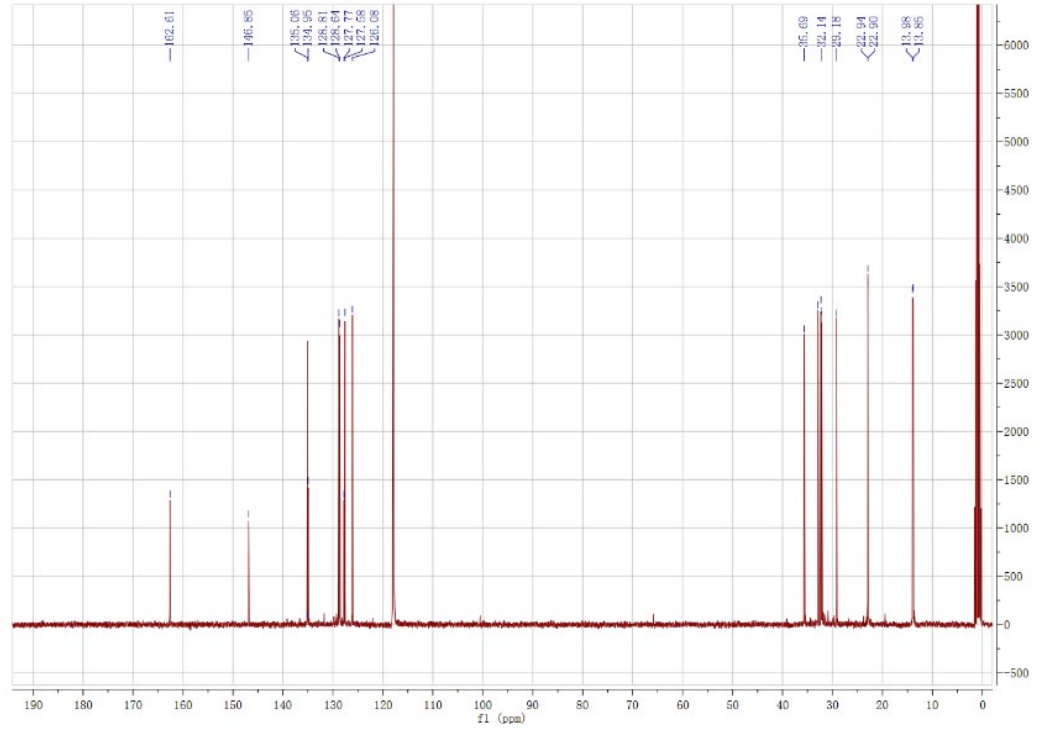


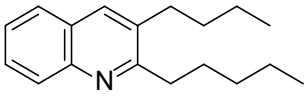




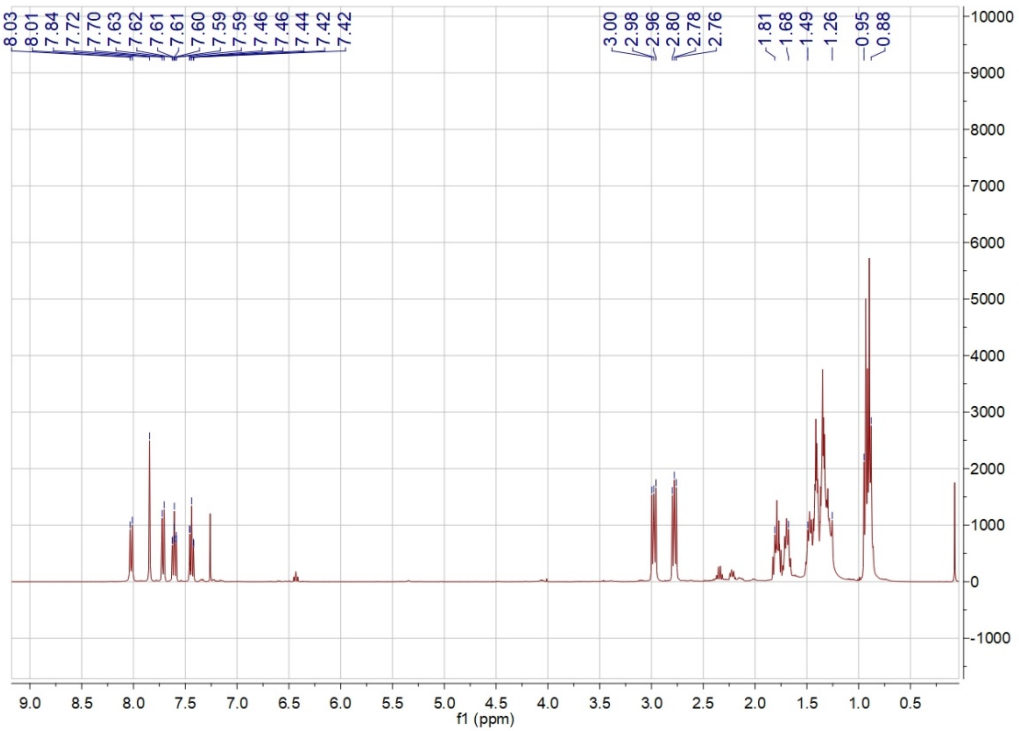
^{1}H NMR (400 MHz, CD_3CN) δ = 7.92 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.77 (dd, J = 8.0,1.2 Hz, 1H), 7.60 (td, J = 7.5,1.2 Hz, 1H), 7.45 (td, J = 7.5, 1.2 Hz, 1H), 2.94 (t, J = 8.0 Hz, 2H), 2.76 (t, J = 8.0 Hz, 2H), 1.81-1.67 (m, 4H), 1.50-1.43 (m, 2H), 1.01 (t, J = 8 Hz, 3H), 0.97 (t, J = 8 Hz, 3H). **^{13}C NMR (101 MHz, CD_3CN)** δ = 162.6, 146.9, 135.2, 134.7, 128.8, 128.6, 127.7, 127.6, 126.1, 35.4, 34.4, 31.6, 23.8, 23.2, 13.9, 13.8.

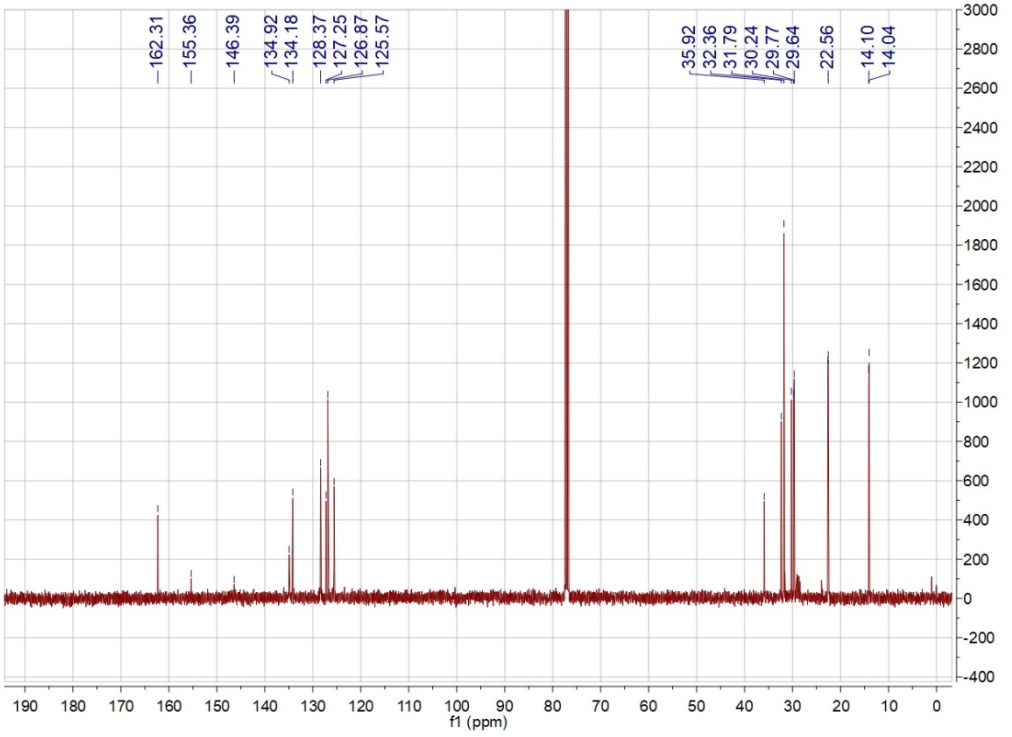


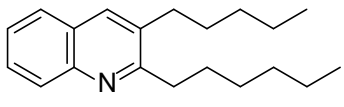




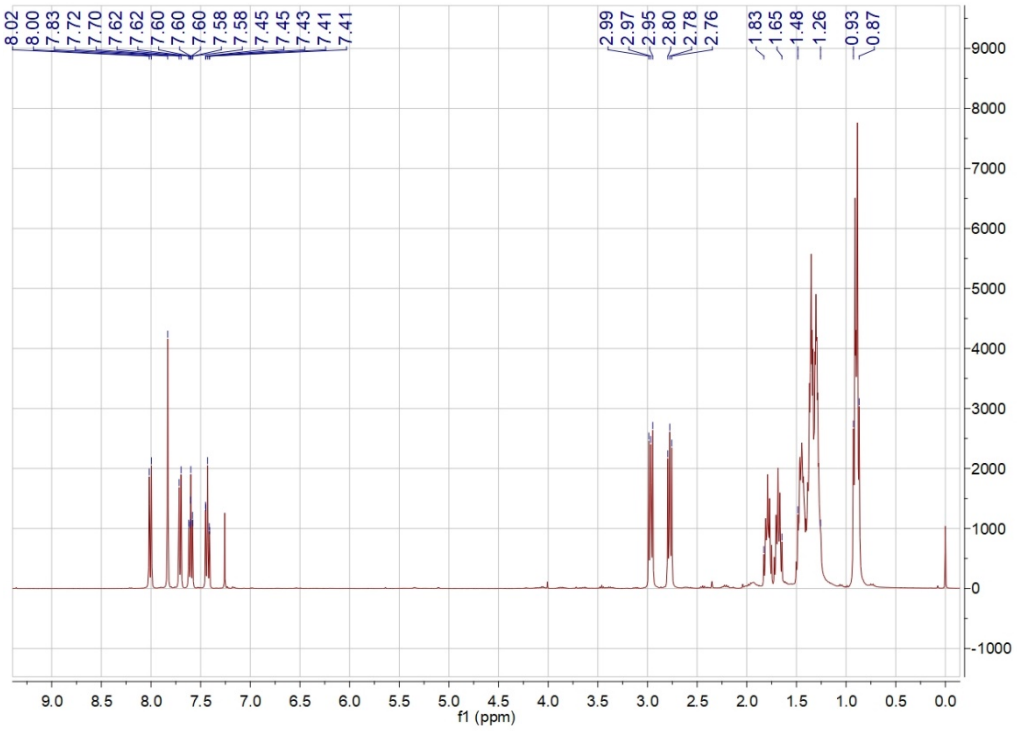
^{1}H NMR (400 MHz, CD_3CN) δ = 7.90 (s, 1H), 7.88 (d, J = 8 Hz,1H), 7.76 (d, J = 8 Hz,1H), 7.59 (t, J = 8 Hz,1H), 7.44 (t, J = 8 Hz,1H), 2.92 (t, J = 8 Hz, 2H), 2.76 (t, J = 8 Hz, 2H), 1.83-1.75(m, 2H), 1.67-1.60 (m, 2H), 1.47-1.35 (6H), 0.96 (t, J = 8 Hz, 3H), 0.91 (t, J = 8 Hz, 3H). **^{13}C NMR (101 MHz, CD_3CN)** δ = 162.6, 146.8, 135.1, 134.9, 128.8, 128.6, 127.8, 127.6, 126.1, 35.7, 32.9, 32.3, 32.1, 29.2, 22.9, 22.9, 13.9, 13.8.

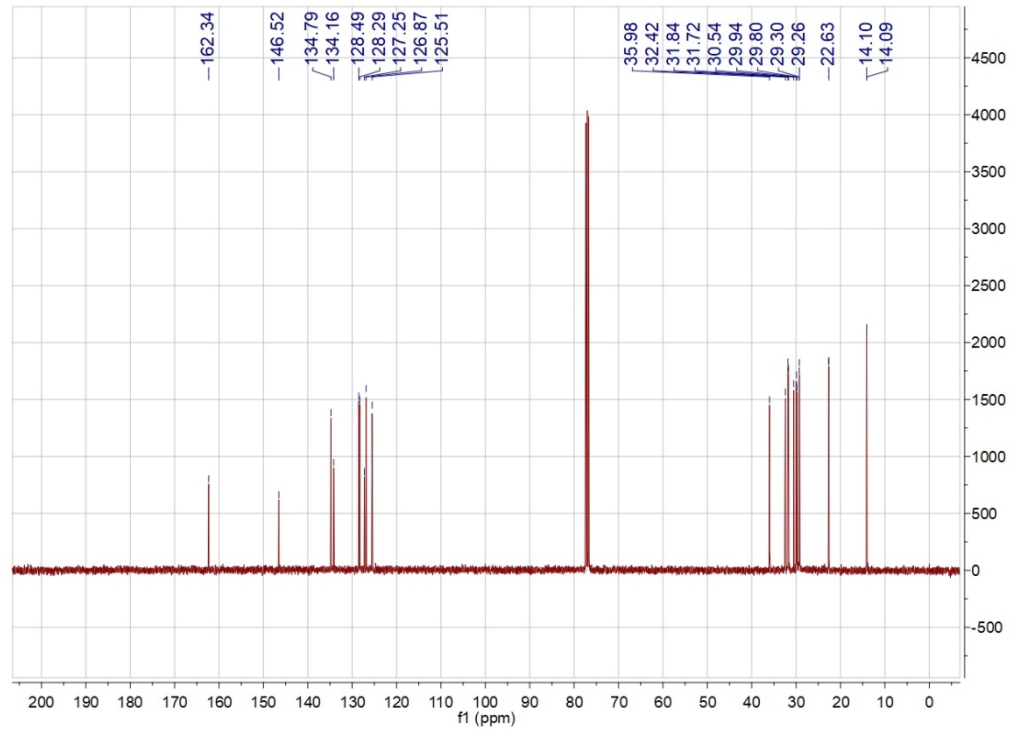


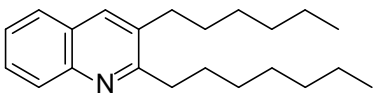




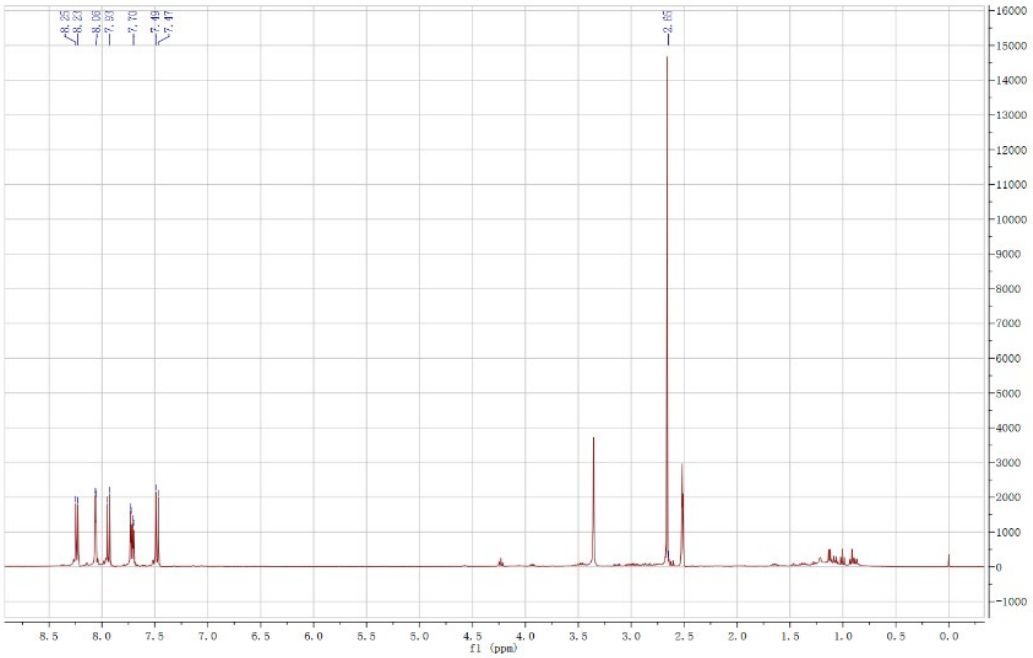
^{1}H NMR (400 MHz, CD_3CN) δ = 8.02 (d, J = 8.4 Hz,1H), 7.84 (s, 1H), 7.71 (d, J = 8.4 Hz,1H), 7.61 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.44 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 2.98(t, J =8.0 Hz, 2H), 2.78(t, J = 8.0 Hz, 2H), 1.81-1.68 (m, 4H), 1.49-1.26 (m, 10H), 0.95-0.88 (m, 6H). **^{13}C NMR (101 MHz, CD_3CN)** δ = 162.3, 155.4, 146.39, 134.9, 134.2, 128.4, 127.3, 126.9, 125.6, 35.9, 32.4, 31.8, 30.2, 29.8, 29.6, 22.6, 22.5, 14.1, 14.0.

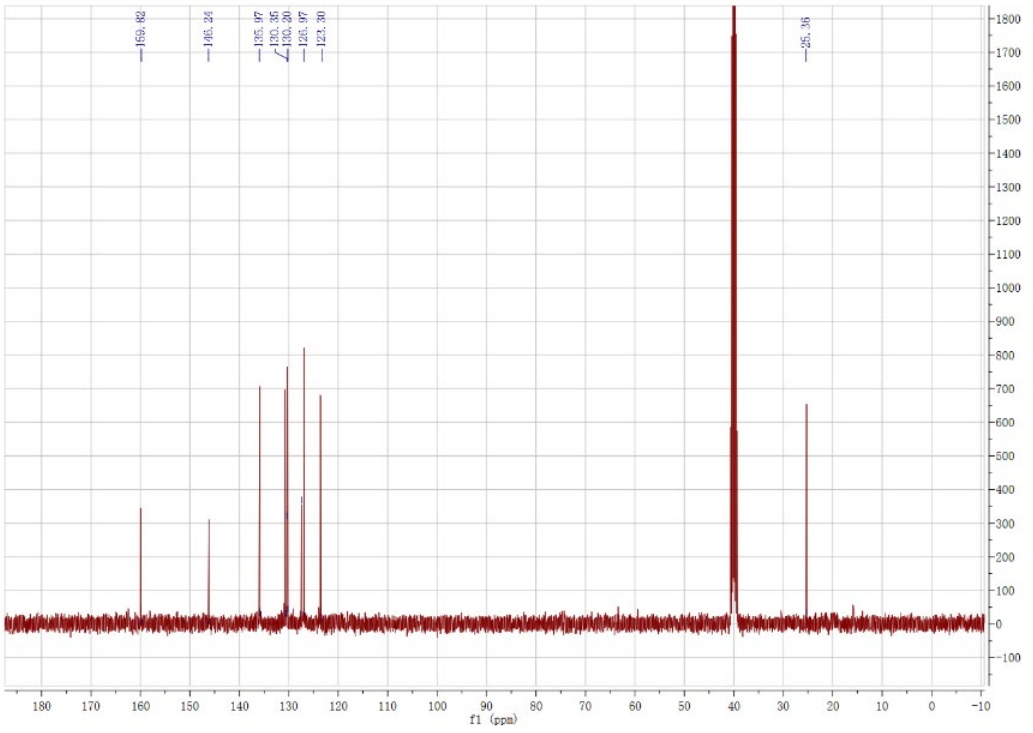


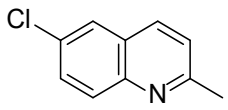




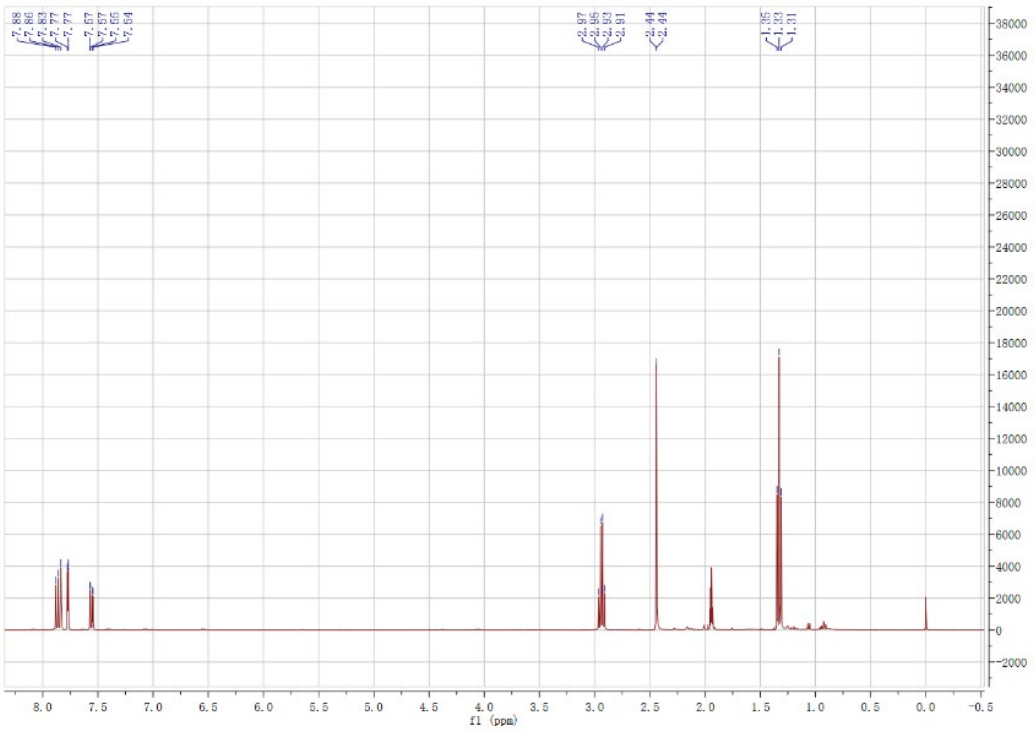
^{1}H NMR (400 MHz, CD_3CN) δ = 8.01 (d, J = 8.4 Hz,1H), 7.83 (s, 1H), 7.71 (d, J = 8.4 Hz,1H), 7.60 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.43 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 2.97(t, J =8.0 Hz, 2H), 2.78(t, J = 8.0 Hz, 2H), 1.83-1.65 (m, 4H), 1.48-1.26 (m, 14H), 0.93-0.87 (m, 6H). **^{13}C NMR (101 MHz, CD_3CN)** δ = 162.3, 146.5, 134.8, 134.2, 128.5, 128.3, 127.3, 126.9, 125.5, 36.0, 32.4, 31.8, 31.7, 30.5, 29.9, 29.8, 29.3, 29.3, 22.7, 22.6, 14.10, 14.09.

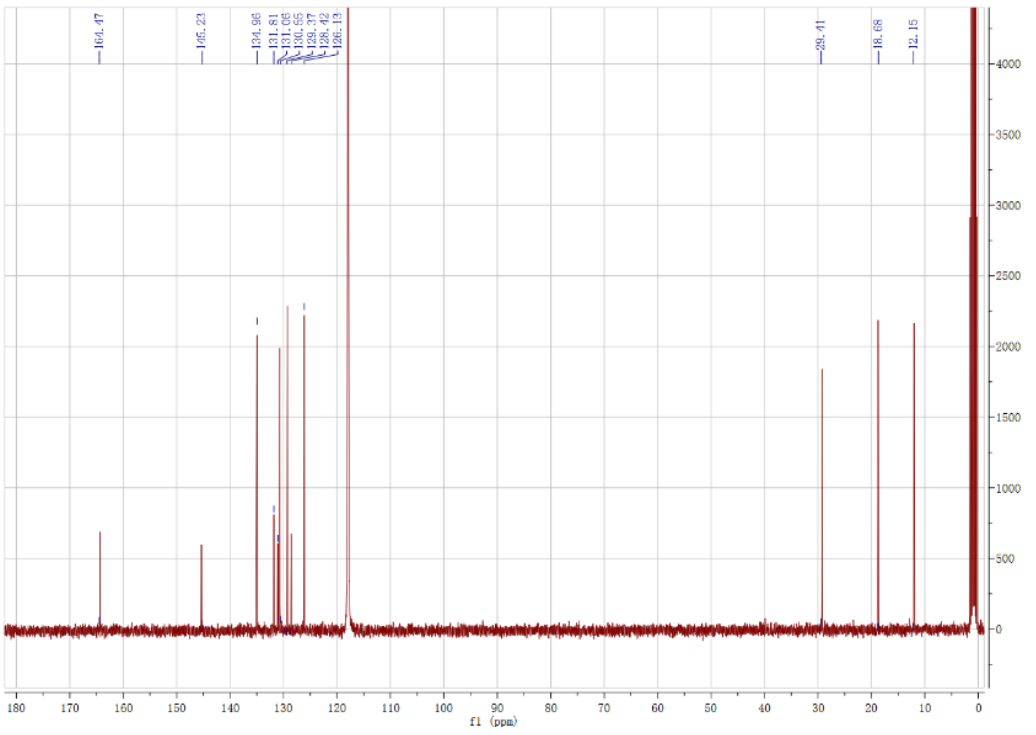


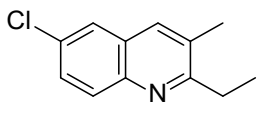




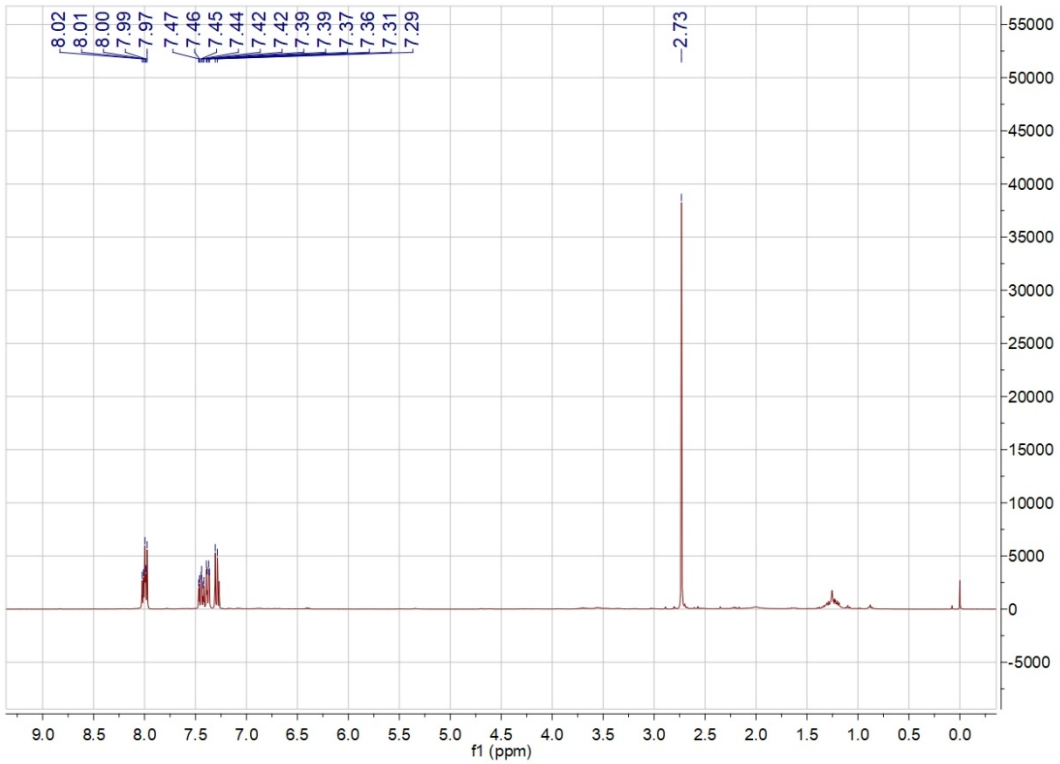
^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 8.24 (d, J = 8 Hz, 1H), 8.06 (d, J = 2.4 Hz,1H), 7.94 (d, J = 8 Hz, 1H), 7.72 (dd, J_1= 9.2 Hz, J_2= 2.4 Hz, 1H), 7.47 (d, J = 8 Hz, 1H), 2.66 (s, 3H). **^{13}C NMR (101 MHz, DMSO)** δ = 159.8, 146.2, 135.9, 130.6, 130.3, 130.2, 127.4, 126.9, 123.3, 25.3.

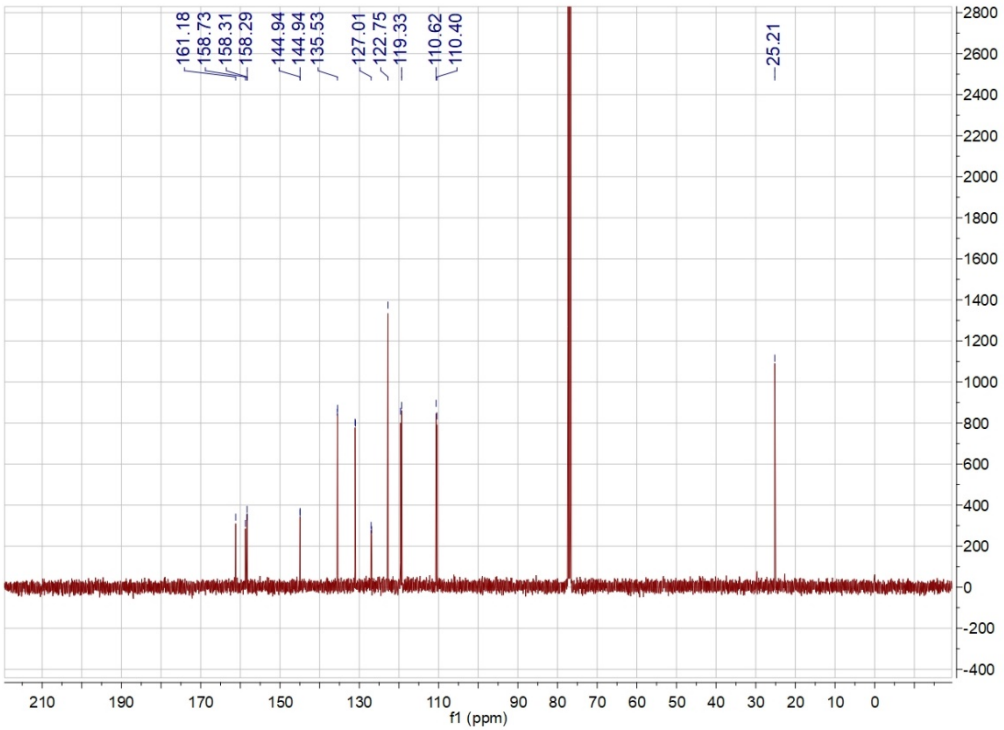


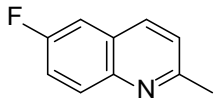




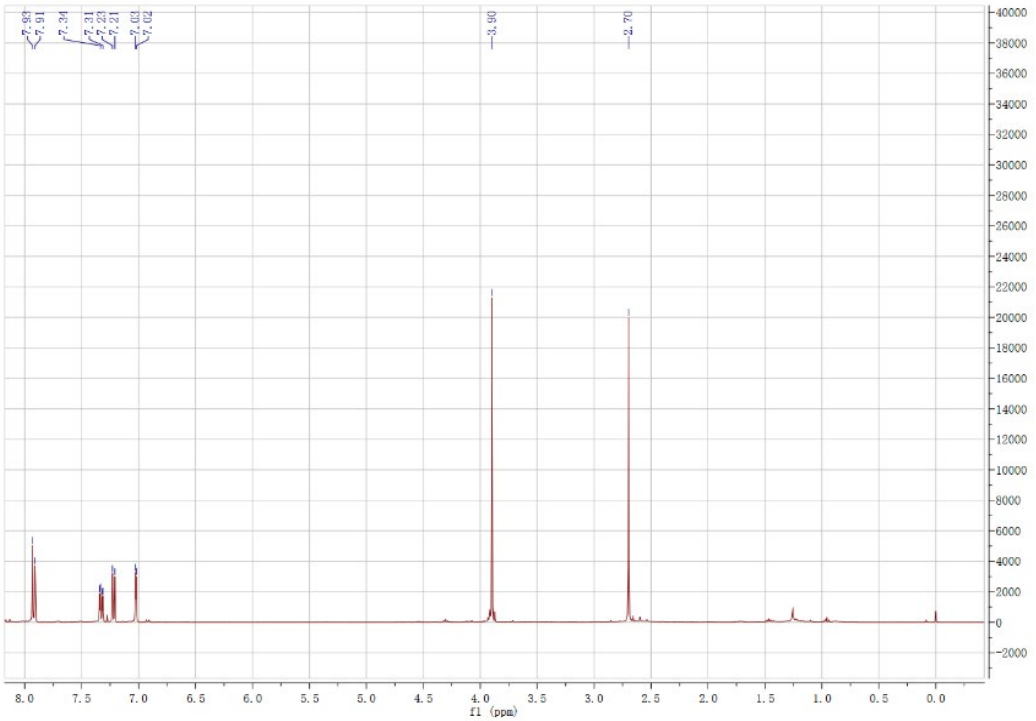
^{1}H NMR (400 MHz, CD_3CN) δ = 7.87 (d, *J*= 8 Hz, 1H), 7.83 (s, 1H), 7.77 (d, *J*= 2.4 Hz, 1H), 7.57, 7.57, 7.55, 7.54 (dd, *J*= 8 Hz, 2.4 Hz, 1H), 2.97-2.91 (q, *J*= 8 Hz, 2H), 2.44 (s, 3H), 1.33 (t, *J*= 8 Hz, 3H). **^{13}C NMR (101 MHz, CD_3CN)** δ = 164.5, 145.2, 134.9, 131.8, 131.1, 130.5, 129.4, 128.4, 126.1, 29.4, 18.7, 12.2.

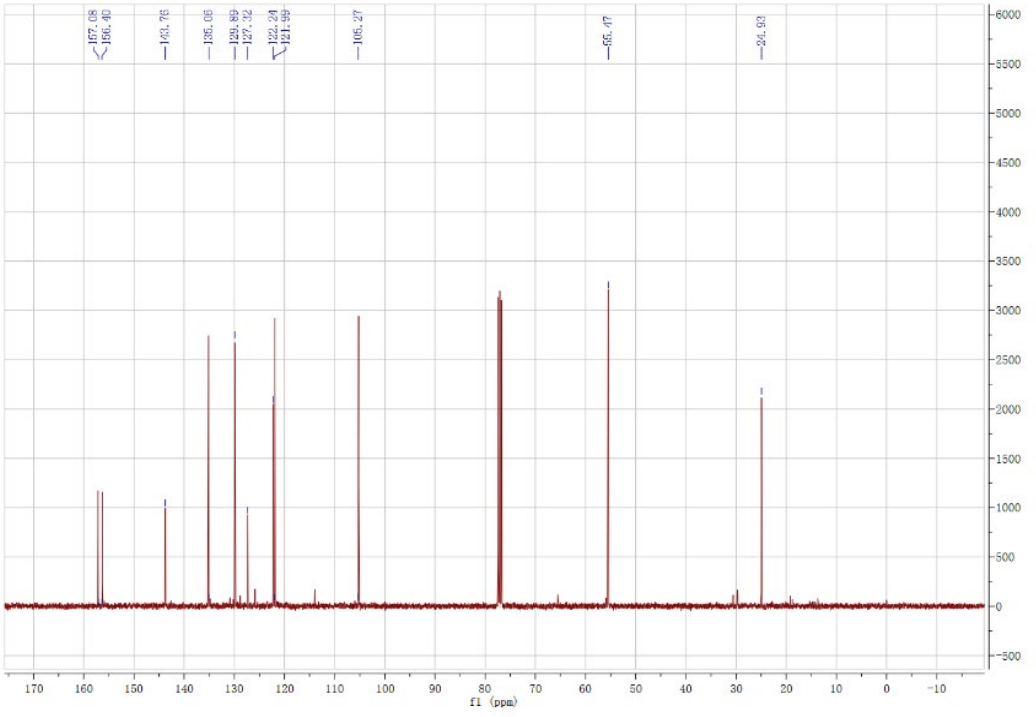


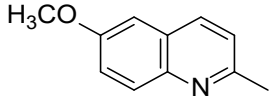




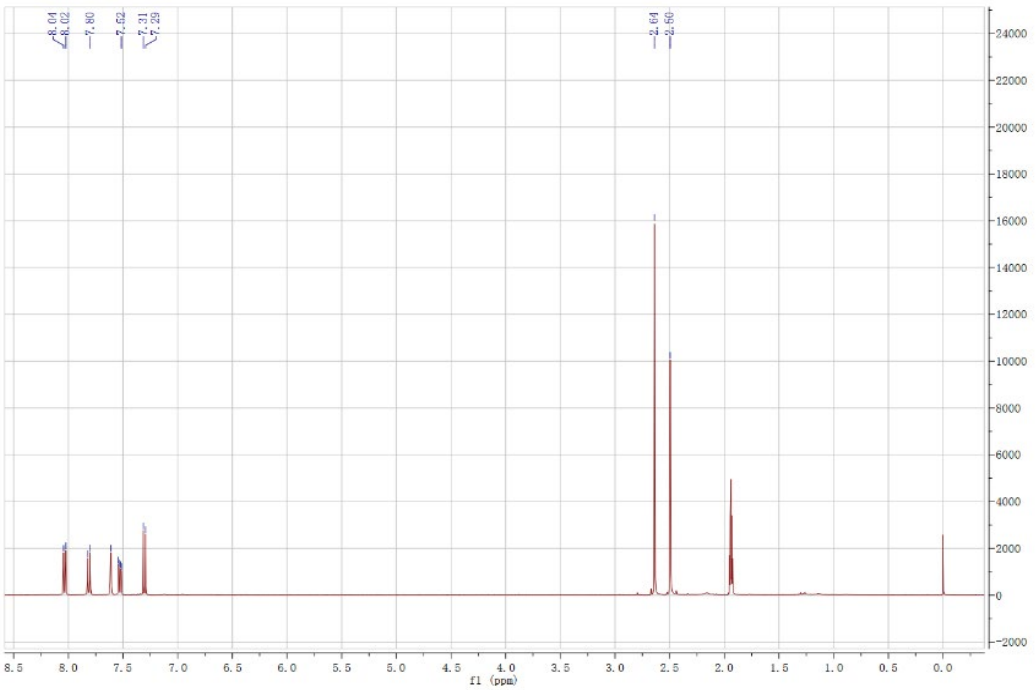
^{1}H NMR (400 MHz, CD_3Cl) δ = 8.02-7.79 (m, 2H), 7.44 (td, J_1= 8.8 Hz, J_2= 2.8 Hz, 1H), 7.38 (dd, J_1= 8.8 Hz, J_2= 2.8 Hz, 1H), 7.30 (d, J= 8.4 Hz1H), 2.73 (s,1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.2, 158.7, 158.3 (d, J=2.7Hz), 144.9 (d, J=0.6Hz), 135.5 (d, J=5.3Hz) 131.0 (d, J=9.1Hz), 127.0 (d, J=9.9Hz), 122.8, 119.4 (d, J=25.6 Hz), 110.5 (d, J=21.6 Hz), 25.2.

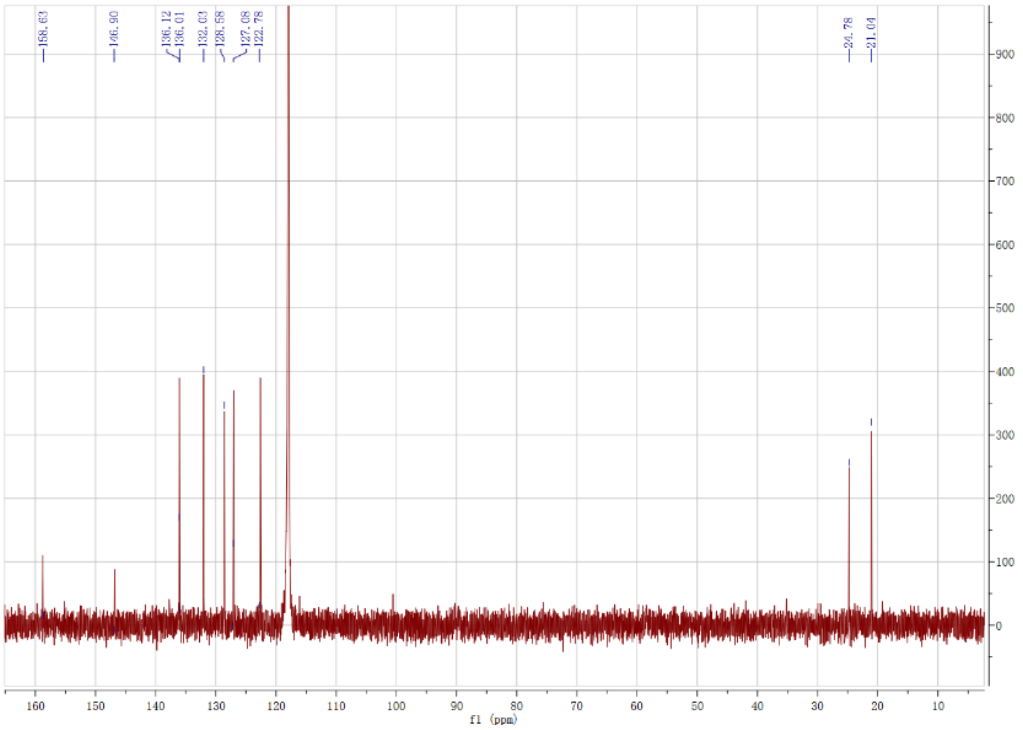


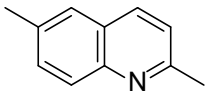




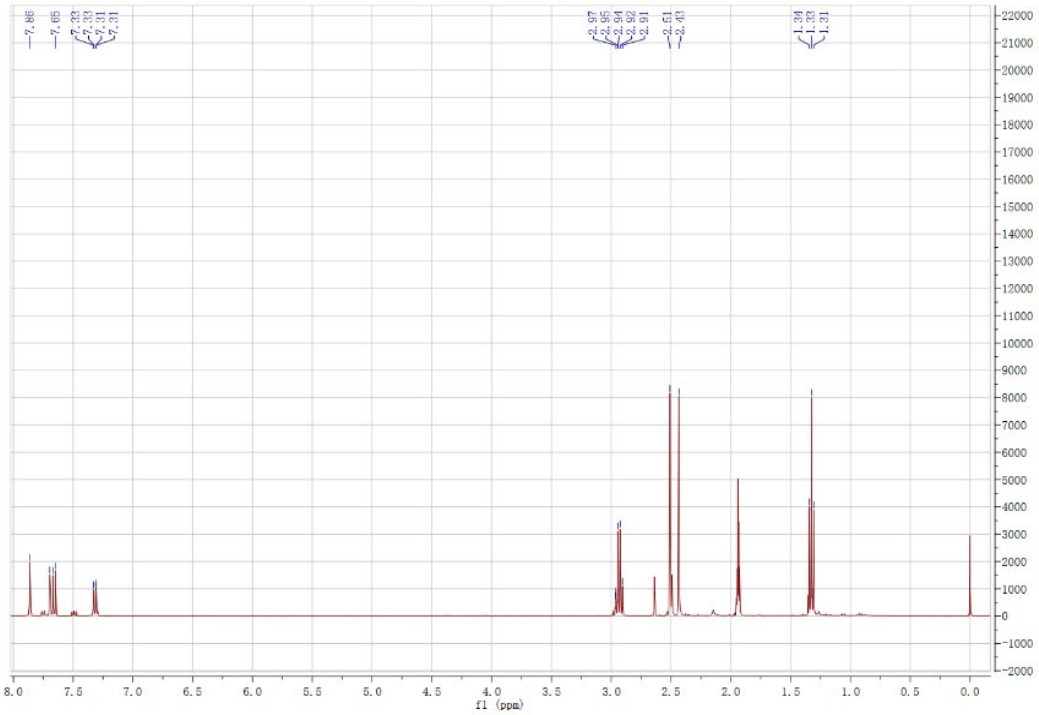
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 (s, 1H), 7.91 (s, 1H), 7.33 (dd, J_1= 4.2 Hz, J_2= 2.8 Hz 1H), 7.22 (d, J= 8.4 Hz, 1H), 7.03 (d, J= 2.8 Hz, 1H), 3.90 (s, 3H), 2.70 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 157.1, 156.4, 143.7, 135.1, 129.9, 127.3, 122.2, 122.0, 105.3, 55.5, 24.9.

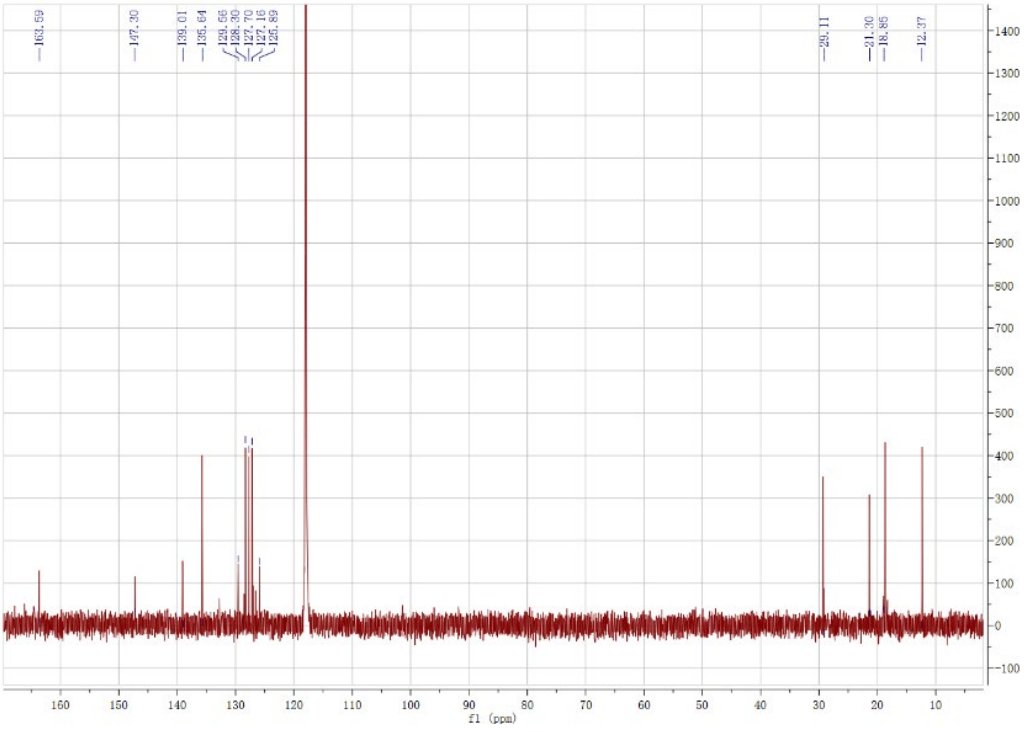


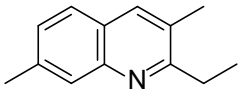




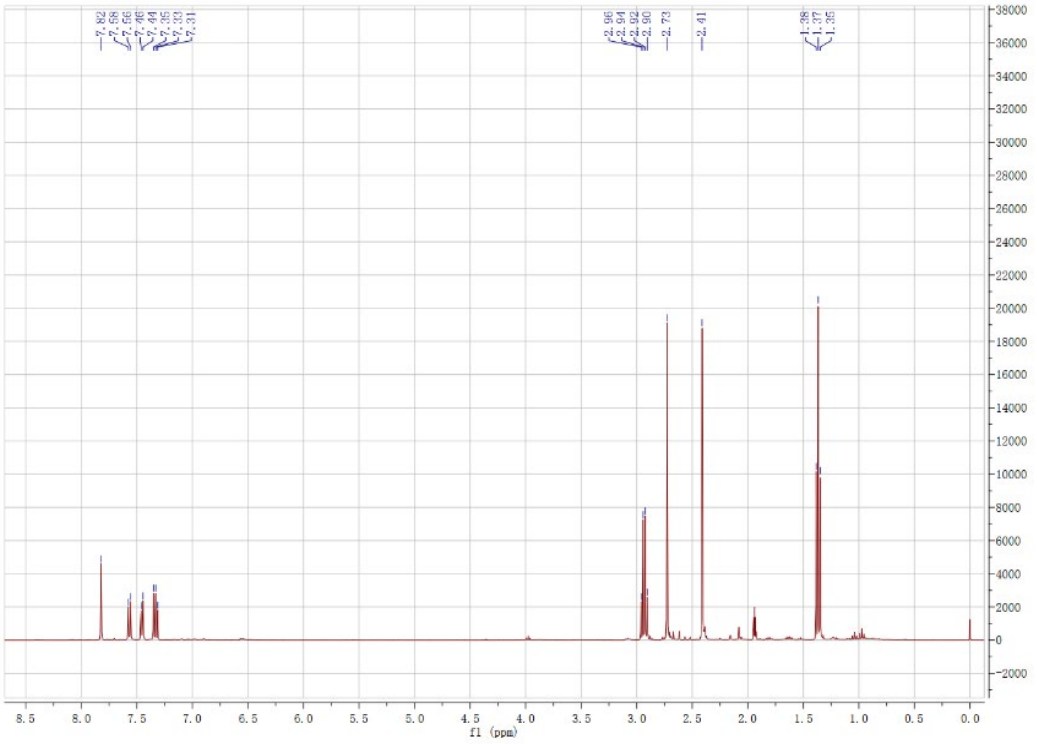
^{1}H NMR (400 MHz, CD_3CN) δ = 8.03 (d, *J*= 8 Hz, 1H), 7.81 (d, *J*= 8 Hz, 1H), 7.61 (s, 1H), 7.53 (d, *J*= 8 Hz, 1H), 7.30 (d, *J*= 8 Hz, 1H), 2.64 (s, 3H), 2.50 (s, 3H). **^{13}C NMR (101 MHz, CD_3CN)** δ = 158.6, 146.9, 136.1, 136.0, 132.0, 128.6, 127.2, 127.1, 122.8, 24.8, 21.0.

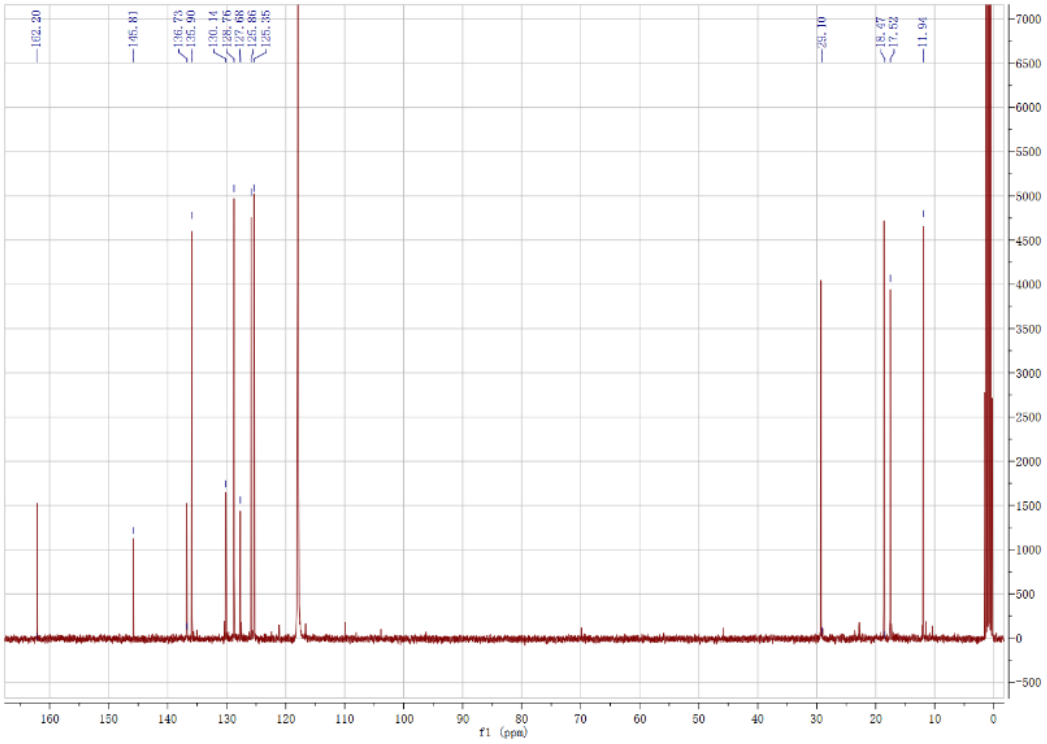


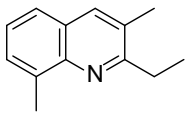




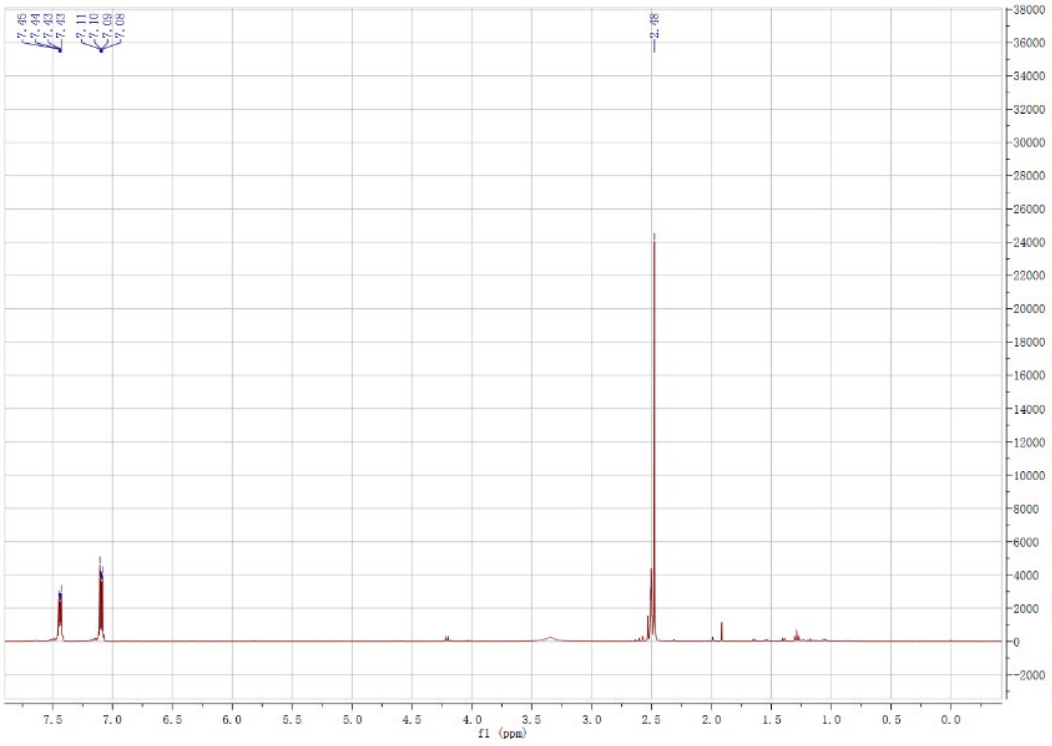
^{1}H NMR (400 MHz, CD_3CN) δ = 7.86 (s, 1H), 7.70 (s, 1H), 7.65 (d, J= 8 Hz, 1 H), 7.32 (dd, J_1= 8 Hz, J_2= 1.6 Hz, 1H), 2.93 (q, J= 7.6 Hz, 2 H), 2.51 (s, 3H), 2.43(s, 3H),1.33 (t, J= 7.6 Hz, 3H). **^{13}C NMR (101 MHz, CD_3CN)** δ = 163.6, 147.3, 139.0, 135.6, 129.6, 128.3, 127.7, 127.1, 125.9, 29.1, 21.3, 18.8, 12.4

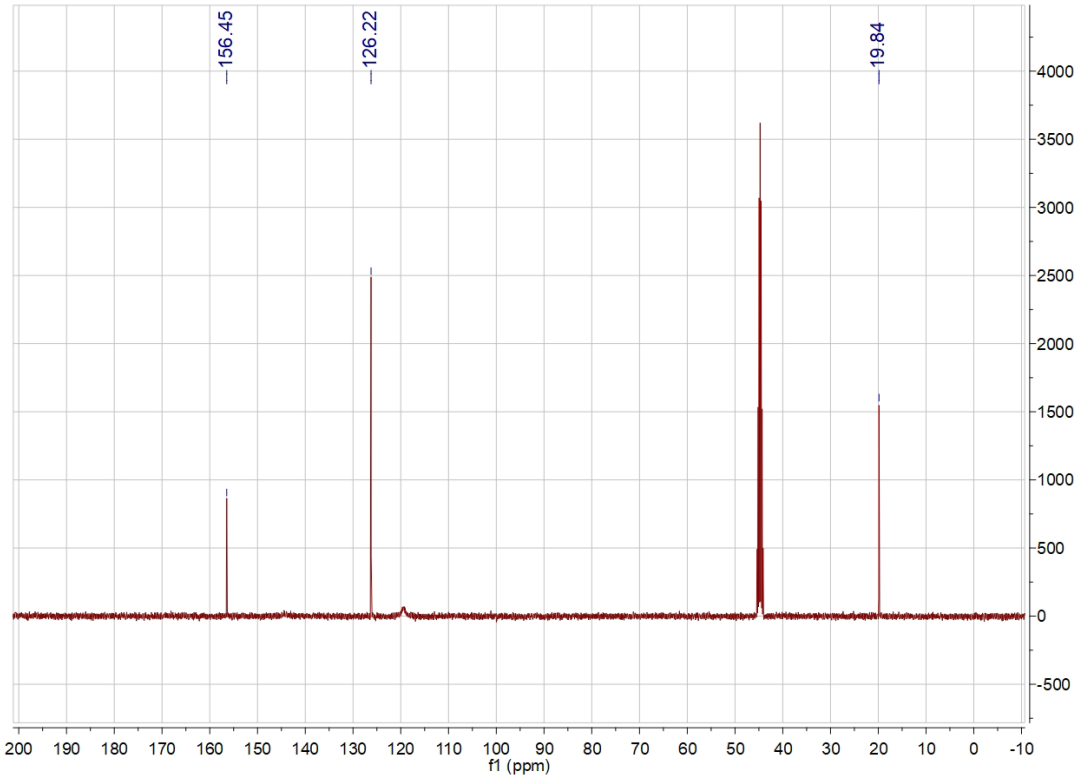


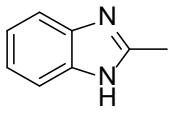




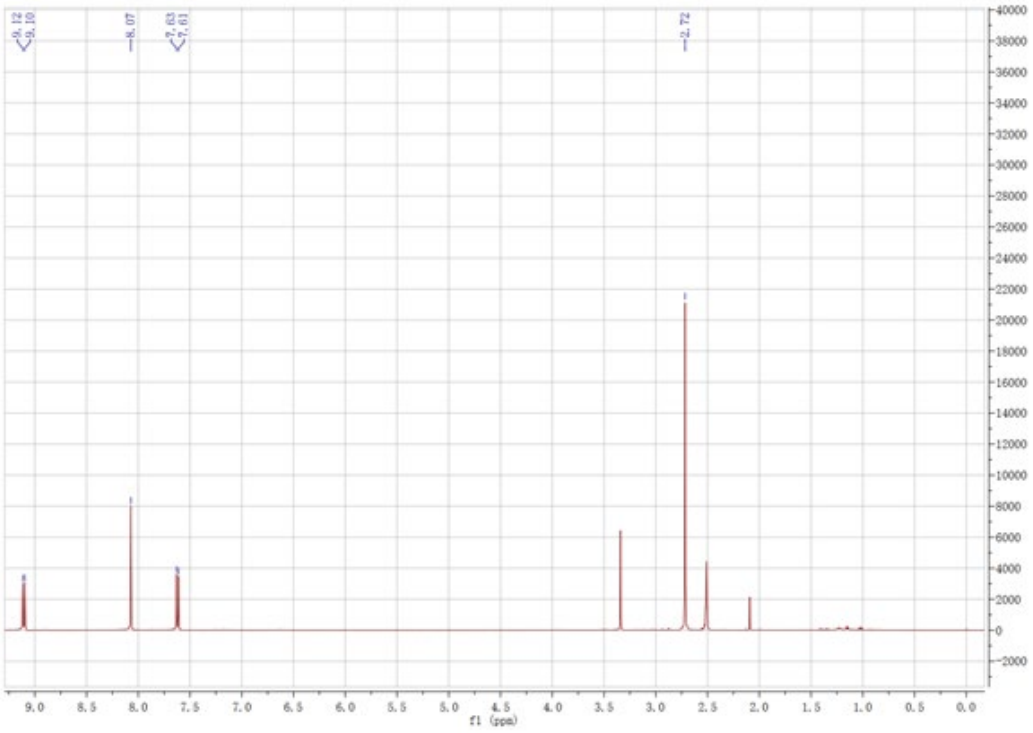
^{1}H NMR (400 MHz, CD_3CN) δ = 7.82 (s, 1H), 7.57 (d, *J*= 8 Hz, 1H), 7.45 (d, *J*= 6.8Hz, 1H), 7.33 (t, *J*= 8 Hz, 1H), 2.92 (q, *J*= 7.5 Hz, 2H), 2.73 (s, 3H), 2.41 (s, 3H), 1.37 (t, J= 7.5 Hz, 3H). **^{13}C NMR (101 MHz, CD_3CN)** δ = 162.2, 145.8, 136.7, 135.9, 130.1, 128.7, 127.7, 125.8, 125.3, 29.1, 18.45, 17.5, 11.9.

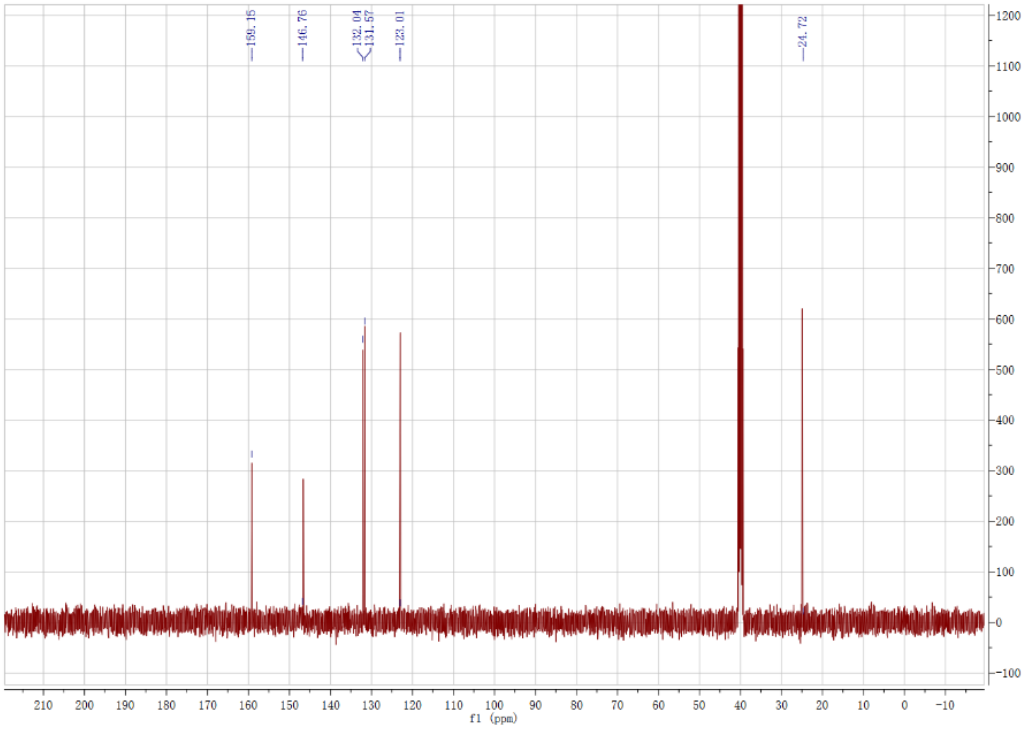


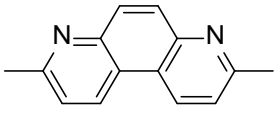




^{1}H NMR (400 MHz, DMSO-d$_6$) δ =7.44 (d, *J*= 3.2 Hz, 1H), 7.43 (d, *J*= 3.2 Hz, 1H), 7.10 (d, *J*= 3.2 Hz, 1H), 7.08 d, (*J*= 2.8 Hz, 1H), 2.48 (s, 3H). **^{13}C NMR (101 MHz, DMSO)** δ = 156.5, 126.2, 19.8.







^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 9.09 (d, *J* = 8.4 Hz, 2H), 8.07 (s, 2H), 7.62 (d, *J* = 8 Hz, 2H), 2.72 (s, 6H). **^{13}C NMR (101 MHz, DMSO-d$_6$)** δ = 159.1, 146.7, 132.0, 131.6, 123.0, 24.7.

References:

1. C. F. Zhang, X. Wang, M. R. Li, Z. X. Zhang, Y. H. Wang, R. Si and F. Wang, *Chin. J. Catal.*, 2016, **37**, 1569-1578.
2. R. Tokarz-Sobieraj, R. Grybos and M. Witko, *Appl. Catal., A*, 2011, **391**, 137-143.