Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

A robust and facile method for desulfonation to amines

Chen Li, [1,#] Yilei Huang, [1,#] Sheng Cao, [1,#] Yunhao Luo, [1] Ying Zhang, [1] Guang Yang [1,*]

1 The State Key Laboratory of Medicinal Chemical Biology, College of Pharmacy, Nankai University, Tianjin, 300071, P. R. China.

# These authors contributed equally to this work

Contents of supporting information

1. General Information....3
2. List of Abbreviations....4
3. General Procedure for Synthesis of Sulfamides....5
4. General Procedure for Eliminating the Sulfamides....6
5. Synthesis of Substrates....7
6. Mass analysis of intermediates....33
7. NMR Spectrums of Compounds....34
8. Deprotection of N-Ts-L-Proline causes racemization of product.....139
9. Controlled reactions for mechanism study.....140

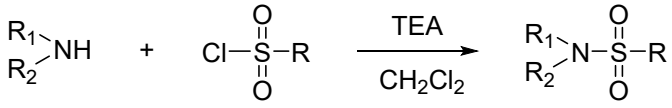
1. General Information

All reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions, unless otherwise noted. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. The used solvents were purified and dried according to common procedures. Other chemicals and solvents were commercially available. High-resolution mass spectra (HRMS) were obtained with a FTICR-MS (Ion spec 7.0T) spectrometer. ^{1}H NMR spectra were obtained by using a Bruker AV 400 or AV 600. Chemical shifts are reported in parts per million (ppm) relative to either a tetramethylsilane internal standard or solvent signals. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants and integration. ^{13}C NMR spectra were recorded using a Bruker AV 400 spectrometer (100 MHz) using $CDCl_3$ as the solvent. Chemical shifts (δ) are reported in parts per million measured relative to the solvent peak. IR spectra were recorded with a Bio-Rad FTS 6000 Fourier infrared spectrometer.

2. List of Abbreviations

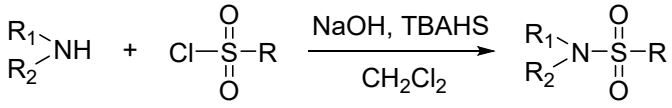
TEA - triethylamine
TBAHS - tetra(n-butyl)ammonium hydrogensulfate
$HPPh_2$ - diphenylphosphane
Ts - P-toluenesulfonyl

3. General Procedure for Synthesis of Sulfamides



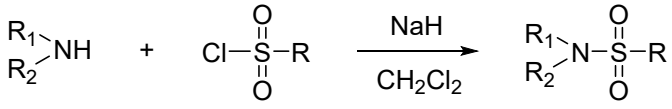
1 **2**

General Procedure A: A secondary amine (**1**, 5 mmol, 1.0 eq) in 25 mL round bottom flask equipped with a magnetic stir bar is dissolved in 10 mL CH_2Cl_2. A CH_2Cl_2 solution (2 mL) of sulfonyl chloride (**2**, 5 mmol, 1.0 eq) is then added at 0°C, followed by a slight excess of TEA (1 mL, 1.4 eq) and the reaction is stirred 4h at room temperature. The solvent is evaporated off and the reaction mixture is extracted with 1 N HCl solution and ethyl acetate. The combined organic phase was dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel to afford the corresponding sulfonamide.



1 **2**

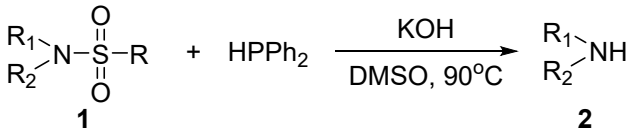
General Procedure B: A secondary amine (**1**, 5 mmol, 1.0 eq) in 25 mL round bottom flask equipped with a magnetic stir bar is dissolved in 10 mL CH_2Cl_2, sodium hydroxide (5 mmol, 1.0 eq) was added followed by TBAHS (0.25 mmol, 0.05 eq). A CH_2Cl_2 solution (2 mL) of sulfonyl chloride (**2**, 5 mmol, 1.0 eq) is then added dropwise at 0°C. After that the mixture was stirred at room temperature for further 4h, the solvent is evaporated off and the reaction mixture is extracted with 1 N HCl solution and ethyl acetate. The combined organic phase was dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel to afford the the desired product.



1 **2**

General Procedure C: To a suspension of sodium hydride (60% dispersion in mineral oil, 6 mmol, 1.2 eq) in anhydrous CH_2Cl_2 (5 mL), a solution of the secondary amine (**1**, 5 mmol, 1.0 eq) was added and the mixture was stirred at 0°C for 1h. To the mixture was added a solution of sulfonyl chloride (**2**, 5 mmol, 1.0 eq) in anhydrous CH_2Cl_2 (3 mL) and the mixture was stirred at room temperature for 6h. The reaction was quenched with water (10 mL) and the resulting precipitate was collected by suction filtration, washed with 1 N HCl solution, the combined organic phase was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel to afford the the desired product.

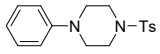
4. General Procedure for Eliminating the Sulfamides



1 **2**

To a solution of sulfamide (**1**, 1 mmol, 1.0 eq) in DMSO (8 mL), potassium hydroxide (2.5 mmol, 2.5 eq) was added and the mixture was sealed under an argon atmosphere. After that $HPPh_2$ (1.1 mmol, 1.1 eq) was injected into the system, and the mixture was stirred at 90°C for 1h. At first, with the addition of $HPPh_2$ the KOH solid became yellow from white, during the process, the system became yellow gradually and finally red. The reaction was quenched with water (10 mL) and the resulting precipitate was extracted with water and ethyl acetate, the combined organic phase was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by neutral alumina column to afford the amine.

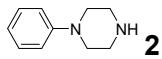
5. Synthesis of Substrates



1

1-phenyl-4-tosylpiperazine **1**

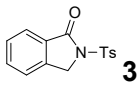
1 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to furnish the desired compound **1** (89 % yield) as a white solid. m. p. 195.5-197.1 °C; IR (KBr) ν_{max}: 2888, 2361, 1597, 1347, 1170, 963, 734, 544 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.61 (m, 2H), 7.41 – 7.29 (m, 2H), 7.26 – 7.22 (m, 2H), 7.03 – 6.65 (m, 3H), 3.23 (dd, *J* = 6.3, 3.4 Hz, 4H), 3.15 (dd, *J* = 6.3, 3.3 Hz, 4H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.7, 143.8, 132.5, 129.8, 129.2, 127.9, 120.8, 116.9, 49.2, 46.1, 21.5. HRMS (ESI) calculated for $C_{17}H_{20}N_2NaO_2S^+$ $[M+Na]^+$: 339.1138, found 339.1141.



2

1-phenylpiperazine **2**

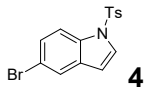
2 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 20:1) to furnish the desired compound **2** as colorless oil. IR (KBr) ν_{max}: 3272, 3061, 3025, 2944, 2910, 2881, 2823, 1596, 1497, 1451, 1322, 1235, 1146, 1127, 990, 761, 692 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.19 (m, 2H), 6.92 – 6.72 (m, 3H), 3.10 – 3.02 (m, 4H), 3.00 – 2.86 (m, 4H), 1.68 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.9, 129.1, 119.6, 116.1, 50.4, 46.2. HRMS (ESI) calculated for $C_{10}H_{14}N_2Na^+$ $[M+Na]^+$: 185.1049, found 185.1051.



3

2-tosylisoindolin-1-one **3**

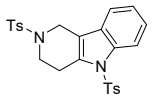
3 was prepared according to the general procedure **C**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 4:1) to furnish the desired compound **3** (71 % yield) as a white solid. m. p. 216.2-218.1 °C; IR (KBr) ν_{max}: 2932, 1924, 1724, 1655, 1594, 1509, 1469, 1450, 1363, 1289, 1220, 1130, 1019, 891, 817, 751, 702, 664 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 7.99 (m, 2H), 7.87 – 7.77 (m, 1H), 7.64 (td, *J* = 7.6, 1.2 Hz, 1H), 7.54 – 7.43 (m, 2H), 7.39 – 7.29 (m, 2H), 4.92 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.1, 145.2, 141.0, 135.4, 133.9, 130.2, 129.8, 128.8, 128.2, 125.1, 123.4, 49.9, 21.7. HRMS (ESI) calculated for $C_{15}H_{13}NNaO_3S^+$ $[M+Na]^+$: 310.0508, found 310.0506.



4

5-bromo-1-tosyl-1H-indole **4**

4 was prepared according to the general procedure **B**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to furnish the desired compound **4** (89 % yield) as a pink solid. m. p. 136.3-138.4 °C; IR (KBr) ν_{max}: 1438, 1373, 1168, 1129 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.72 (dd, *J* = 8.4, 2.2 Hz, 2H), 7.64 (d, *J* = 2.1 Hz, 1H), 7.55 (dd, *J* = 3.8, 2.2 Hz, 1H), 7.38 (dt, *J* = 8.8, 2.1 Hz, 1H), 7.20 (dd, *J* = 8.4, 2.1 Hz, 2H), 6.57 (t, *J* = 2.9 Hz, 1H), 2.32 (d, *J* = 2.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.3, 135.0, 133.6, 132.5, 130.0, 127.6, 127.5, 126.8, 124.1, 116.8, 115.0, 108.3, 21.6. HRMS (ESI) calculated for $C_{15}H_{12}BrNNaO_2S^+$ $[M+Na]^+$: 371.9664, found 371.9663.



5

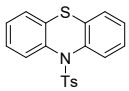
2,3,4,5-tetrahydro-1H-pyrido[4,3-b]indole **5**

5 was prepared according to the general procedure **B** with 2.2 eq TsCl, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to furnish the desired compound **5** (82 % yield) as awhite solid. m. p. 159.7-161.1 °C; IR (KBr) ν_{max}: 2914, 2844, 2361, 1596, 1381, 1151, 1098, 756, 657, 542 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 8.04 (m, 1H), 7.70 (dd, *J* = 13.0, 8.2 Hz, 4H), 7.30 (dd, *J* = 7.9, 5.9 Hz, 4H), 7.22 (dd, *J* = 7.9, 3.5 Hz, 3H), 4.65 (d, *J* = 1.9 Hz, 2H), 3.46 (t, *J* = 5.7 Hz, 2H), 2.73 (td, *J* = 5.5, 2.8 Hz, 2H), 2.41 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.1, 143.8, 136.0, 135.4, 134.4, 130.1, 129.8, 129.1, 127.5, 126.5, 124.8, 123.6, 118.4, 116.7, 114.3, 44.8, 42.9, 21.6, 21.5, 21.4. HRMS (ESI) calculated for $C_{25}H_{24}N_2NaO_4S_2^+$ $[M+Na]^+$: 503.1070, found 503.1073.

6

1-tosylindoline **6**

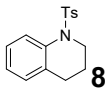
6 was prepared according to the general procedure **B**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 6:1) to furnish the desired compound **6** (93 % yield) as a white solid. m. p. 99.5-101.2 °C; IR (KBr) ν_{max}: 3392, 3031, 2936, 2874, 2853, 1601, 1508, 1460, 1308, 1237, 1153, 1090, 975, 754, 711, 659 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.65 (dd, *J* = 11.5, 8.1 Hz, 3H), 7.30 – 7.13 (m, 3H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 3.89 (t, *J* = 8.4 Hz, 2H), 2.86 (t, *J* = 8.4 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.1, 142.0, 133.9, 131.8, 129.7, 127.7, 127.3, 125.2, 123.7, 115.0, 50.0, 27.9, 21.6. HRMS (ESI) calculated for $C_{15}H_{15}NNaO_2S^+$ $[M+Na]^+$: 296.0716, found 296.0715.



7

10-tosyl-10H-phenothiazine **7**

7 was prepared according to the general procedure **C**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 25:1) to furnish the desired compound **7** (81 % yield) as a yellow solid. m. p. 120.7-122.5 °C; IR (KBr) ν_{max}: 3448, 1637, 1462, 1359, 1307, 1185, 735, 576 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 7.74 (dd, J = 8.0, 1.4 Hz, 2H), 7.33 (td, J = 7.7, 1.5 Hz, 2H), 7.22 (td, J = 7.6, 1.4 Hz, 2H), 7.18 – 7.08 (m, 4H), 7.05 (d, J = 8.1 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 144.1, 136.1, 135.9, 133.1, 130.0, 129.3, 127.7, 127.6, 127.2, 126.9, 21.7. HRMS (ESI) calculated for $C_{19}H_{15}NNaO_2S_2^+$ $[M+Na]^+$: 376.0442, found 376.0440.



8

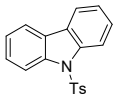
1-tosyl-1,2,3,4-tetrahydroquinoline **8**

8 was prepared according to the general procedure **B**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 6:1) to furnish the desired compound **8** (82 % yield) as a white solid. m. p. 94.8-96.2 °C; IR (KBr) ν_{max}: 3000, 2900, 2850, 1580,1480, 1330 cm^{-1}. ^1H NMR (400 MHz, Chloroform-d) δ 7.79 (dd, J = 8.3, 1.2 Hz, 1H), 7.53 – 7.42 (m, 2H), 7.18 (dd, J = 7.2, 4.8 Hz, 3H), 7.07 (td, J = 7.4, 1.3 Hz, 1H), 7.00 (dd, J = 7.6, 1.6 Hz, 1H), 3.86 – 3.73 (m, 2H), 2.44 (t, J = 6.6 Hz, 2H), 2.37 (s, 3H), 1.66 – 1.60 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.5, 136.9, 136.8, 130.7, 129.6, 129.1, 127.1, 126.5, 125.0, 124.9, 46.5, 29.7, 26.6, 21.6. HRMS (ESI) calculated for $C_{16}H_{17}NNaO_2S^+$ $[M+Na]^+$: 310.0872, found 310.0869.

9

1-tosyl-1H-imidazole **9**

9 was prepared according to the general procedure **C**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 1:1) to furnish the desired compound **9** (61 % yield) as a white solid. m. p. 76.1-78.3 °C; IR (KBr) ν_{max}: 1385, 1198, 1181, 1065 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 7.39 (d, J = 1.3 Hz, 1H), 7.05 (d, J = 8.1 Hz, 2H), 6.68 (t, J = 1.5 Hz, 1H), 6.53 (d, J = 8.2 Hz, 2H), 6.21 (d, J = 1.6 Hz, 1H), 1.51 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 146.0, 136.3, 133.9, 129.5, 129.4, 126.5, 117.1, 19.5. HRMS (ESI) calculated for $C_{10}H_{10}N_2NaO_2S^+$ $[M+Na]^+$: 245.0355, found 245.0357.



10

9-tosyl-9H-carbazole **10**

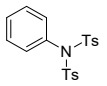
10 was prepared according to the general procedure **C**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 8:1) to furnish the desired compound **10** (54 % yield) as a white solid. m. p. 128.9-130.1 °C; IR (KBr) ν_{max}: 3401, 2919, 1591, 1431, 1371 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 7.51 (dt, J = 8.5, 0.9 Hz, 2H), 7.18 (dt, J = 7.7, 1.0 Hz, 2H), 6.89 – 6.83 (m, 2H), 6.71 (ddd, J = 8.5, 7.3, 1.3 Hz, 2H), 6.58 (td, J = 7.5, 1.0 Hz, 2H), 6.38 – 6.33 (m, 2H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 144.6, 137.6, 133.7,

128.5, 126.3, 125.7, 125.3, 123.1, 119.0, 114.1, 19.2. HRMS (ESI) calculated for $C_{19}H_{15}NNaO_2S^+$ [M+Na]$^+$: 344.0716, found 344.0716.

11

1-tosyl-1H-benzo[d][1,2,3]triazole **11**

11 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 4:1) to furnish the desired compound **11** (75 % yield) as a white solid. m. p. 129.2-131.0 ^{o}C; IR (KBr) ν_{max}: 3061, 2593, 2277, 1967, 1791, 1653, 1510, 1452, 1444, 1392, 1137, 1093, 960, 905, 771, 677, 585 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 8.03 – 7.92 (m, 2H), 7.65 (ddd, *J* = 8.3, 7.0, 1.0 Hz, 1H), 7.46 (td, *J* = 7.6, 1.0 Hz, 1H), 7.32 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.8, 145.4, 134.0, 131.6, 130.3, 130.3, 127.9, 125.9, 120.5, 112.0, 21.7. HRMS (ESI) calculated for $C_{13}H_{11}N_3NaO_2S^+$ [M+Na]$^+$: 296.0464, found 296.0466.



12

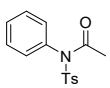
4-methyl-*N*-phenyl-*N*-tosylbenzenesulfonamide **12**

12 was prepared according to the general procedure **A** with 2.2 eq TsCl, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **12** (81 % yield) as a white solid. m. p. 167.6-168.3 ^{o}C; IR (KBr) ν_{max}: 3394, 3066, 1487, 1381 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.3 Hz, 4H), 7.45 – 7.41 (m, 1H), 7.34 (dd, *J* = 11.4, 7.9 Hz, 6H), 7.03 (dd, *J* = 7.5, 1.7 Hz, 2H), 2.46 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.0, 136.7, 134.4, 131.6, 130.2, 129.6, 129.2, 128.6, 21.7. HRMS (ESI) calculated for $C_{20}H_{19}NNaO_4S_2^+$ [M+Na]$^+$: 424.0648, found 424.0645.

13

N,4-dimethyl-*N*-phenylbenzenesulfonamide **13**

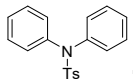
13 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **13** (89 % yield) as a white solid. m. p. 91.2-93.2 ^{o}C; IR (KBr) ν_{max}: 3130, 2915, 1595, 1491, 1341, 1170, 1063, 868 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.9 Hz, 2H), 7.27 (dt, *J* = 17.8, 7.4 Hz, 5H), 7.15 – 6.98 (m, 2H), 3.16 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.6, 141.6, 133.4, 129.4, 128.8, 127.9, 127.3, 126.6, 38.1, 21.6. HRMS (ESI) calculated for $C_{14}H_{15}NNaO_2S^+$ [M+Na]$^+$: 284.0716, found 284.0719.



14

N-phenyl-N-tosylacetamide **14**

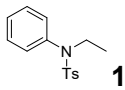
14 was prepared according to the general procedure **C**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to furnish the desired compound **14** (44 % yield) as a white solid. m. p. 139.2-141.0 °C; IR (KBr) ν_{max}: 3393, 2918, 1703, 1593, 1491, 1360, 1163 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.76 (m, 2H), 7.55 – 7.42 (m, 3H), 7.37 – 7.31 (m, 2H), 7.29 – 7.25 (m, 2H), 2.45 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.1, 145.0, 137.0, 136.2, 130.0, 129.9, 129.9, 129.4, 129.2, 25.1, 21.7. HRMS (ESI) calculated for $C_{15}H_{15}NNaO_3S^+$ $[M+Na]^+$: 312.0665, found 312.0662.



15

4-methyl-*N*,*N*-diphenylbenzenesulfonamide **15**

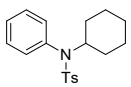
15 was prepared according to the general procedure **B**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 15:1) to furnish the desired compound **15** (83 % yield) as a white solid. m. p. 142.4-143.1 °C; IR (KBr) ν_{max}: 2920, 2361, 1592, 1488, 1351, 1160, 713, 580 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.42 – 7.04 (m, 12H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.7, 141.7, 137.7, 129.6, 129.3, 128.4, 127.8, 127.5, 21.6. HRMS (ESI) calculated for $C_{19}H_{17}NNaO_2S^+$ $[M+Na]^+$: 346.0872, found 346.0873.



16

N-ethyl-4-methyl-*N*-phenylbenzenesulfonamide **16**

16 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **16** (91 % yield) as a white solid. m. p. 84.7-85.9 °C; IR (KBr) ν_{max}: 2976, 2873, 2324, 2088, 1752, 1586, 1355, 1231, 1161, 961, 893, 807, 772, 698 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.48 (dd, *J* = 8.3, 2.1 Hz, 2H), 7.35 – 7.18 (m, 5H), 7.13 – 6.99 (m, 2H), 3.60 (qd, *J* = 7.1, 1.9 Hz, 2H), 2.41 (d, *J* = 2.2 Hz, 3H), 1.06 (td, *J* = 7.2, 1.9 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.2, 138.9, 135.5, 129.4, 128.9, 127.8, 127.7, 45.5, 29.7, 21.5, 14.0. HRMS (ESI) calculated for $C_{15}H_{17}NNaO_2S^+$ $[M+Na]^+$: 298.0872, found 298.0874.

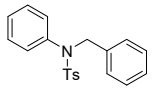


17

N-cyclohexyl-4-methyl-*N*-phenylbenzenesulfonamide **17**

17 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **17** (86 % yield) as a white solid. m. p. 141.3-142.7 °C; IR (KBr) ν_{max}: 3038, 2912, 2243, 2107, 1802, 1589, 1346, 1167, 1071, 912, 876, 822, 759 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.8 Hz, 2H), 7.34 – 7.22 (m, 5H), 7.02 (d, *J* = 7.2 Hz, 2H), 4.15 (tt, *J* = 12.3, 3.9 Hz, 1H), 2.41 (s, 3H), 1.83 (d, *J* = 12.3 Hz, 2H), 1.70 (d, *J* = 13.2 Hz, 2H), 1.52 (d, *J* = 13.7 Hz,

1H), 1.39 – 1.27 (m, 2H), 1.04 (qd, *J* = 12.5, 3.5 Hz, 2H), 0.83 (tdd, *J* = 13.2, 9.3, 3.8 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 142.8, 138.9, 135.8, 132.5, 129.4, 128.6, 128.5, 127.3, 59.1, 32.8, 26.0, 25.1, 21.5. HRMS (ESI) calculated for $C_{19}H_{23}NNaO_2S^+$ [M+Na]$^+$: 352.1342, found 352.1344.



18

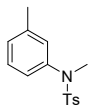
N-benzyl-4-methyl-*N*-phenylbenzenesulfonamide **18**

18 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to furnish the desired compound **18** (81 % yield) as a white solid. m. p. 139.2-140.7 °C; IR (KBr) ν_{max}: 3065, 3033, 2923, 1594, 1457, 1345, 1166 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.53 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.30 – 7.10 (m, 10H), 6.98 (dd, *J* = 6.2, 3.5 Hz, 2H), 4.72 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 143.6, 139.1, 136.1, 135.7, 129.6, 129.0, 128.9, 128.5, 128.4, 127.8, 127.8, 127.6, 54.8, 21.6. HRMS (ESI) calculated for $C_{20}H_{19}NNaO_2S^+$ [M+Na]$^+$: 360.1029, found 369.1026.

19

N,4-dimethyl-*N*-(*o*-tolyl)benzenesulfonamide **19**

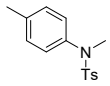
19 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **19** (89 % yield) as a white solid. m. p. 68.8-70.3 °C; IR (KBr) ν_{max}: 2922, 2361, 1493, 1306, 1154, 789, 574 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.63 – 7.41 (m, 2H), 7.33 – 7.25 (m, 3H), 7.19 (td, *J* = 7.5, 1.3 Hz, 1H), 7.04 (td, *J* = 7.5, 1.6 Hz, 1H), 6.60 (dd, *J* = 7.9, 1.3 Hz, 1H), 3.12 (s, 3H), 2.44 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 143.5, 140.5, 139.0, 135.2, 131.4, 129.5, 128.2, 128.1, 127.0, 126.4, 38.9, 21.6, 18.4. HRMS (ESI) calculated for $C_{15}H_{17}NNaO_2S^+$ [M+Na]$^+$: 298.0872, found 298.0871.



20

N,4-dimethyl-*N*-(*m*-tolyl)benzenesulfonamide **20**

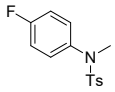
20 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **20** (86 % yield) as a colorless oil. IR (KBr) ν_{max}: 3640, 2923, 2361, 1924, 1602, 1349, 1168, 998, 808, 548 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.44 – 7.36 (m, 2H), 7.17 (s, 2H), 7.09 (t, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.94 (d, *J* = 1.9 Hz, 1H), 6.81 (dt, *J* = 8.0, 1.4 Hz, 1H), 3.09 (s, 3H), 2.33 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 143.6, 141.6, 138.6, 133.6, 129.3, 128.6, 128.0, 127.8, 127.4, 123.2, 38.1, 21.4, 21.2. HRMS (ESI) calculated for $C_{15}H_{17}NNaO_2S^+$ [M+Na]$^+$: 298.0872, found 298.0874.



21

N,4-dimethyl-*N*-(*p*-tolyl)benzenesulfonamide **21**

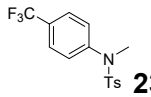
21 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **21** (87 % yield) as a white solid. m. p. 59.7-60.5 °C; IR (KBr) ν_{max}: 2980, 2924, 1343, 1171 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.34 (m, 2H), 7.19 (s, 2H), 7.06 (d, J = 8.2 Hz, 2H), 7.01 – 6.92 (m, 2H), 3.11 (s, 3H), 2.37 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.5, 139.0, 137.2, 133.6, 129.5, 129.4, 127.9, 126.5, 38.2, 21.5, 21.0. HRMS (ESI) calculated for $C_{15}H_{17}NNaO_2S^+$ $[M+Na]^+$: 298.0872, found 298.0872.



22

N-(4-fluorophenyl)-*N*,4-dimethylbenzenesulfonamide **22**

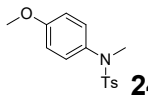
22 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **22** (77 % yield) as a white solid. m. p. 92.6-94.3 °C; IR (KBr) ν_{max}: 1599, 1499, 1344, 1188, 1064, 874 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.34 (m, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.16 – 7.00 (m, 2H), 7.01 – 6.79 (m, 2H), 3.12 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.8, 137.6, 133.2, 129.5, 128.5, 127.8, 115.8, 115.5, 38.2, 21.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.0. HRMS (ESI) calculated for $C_{14}H_{14}FNNaO_2S^+$ $[M+Na]^+$: 302.0621, found 302.0622.



23

N,4-dimethyl-*N*-(4-(trifluoromethyl)phenyl)benzenesulfonamide **23**

23 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **23** (81 % yield) as a white solid. m. p. 70.7-72.1 °C; IR (KBr) ν_{max}: 3068, 2925, 1928, 1615, 1334, 1113, 871, 711, 546 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, J = 8.6 Hz, 2H), 7.49 – 7.34 (m, 2H), 7.34 – 7.07 (m, 4H), 3.18 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.9, 144.1, 133.2, 129.6, 129.0, 128.7, 127.7, 126.2, 125.9 (d, J = 3.4 Hz), 37.7, 21.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.4. HRMS (ESI) calculated for $C_{15}H_{14}F_3NNaO_2S^+$ $[M+Na]^+$: 352.0590, found 352.0593.

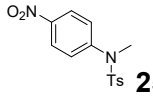


24

N-(4-methoxyphenyl)-*N*,4-dimethylbenzenesulfonamide **24**

24 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **24**

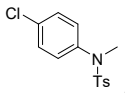
(84 % yield) as a white solid. m. p. 68.6-69.9 °C; IR (KBr) ν_{max}: 1610, 1596, 1587, 1511, 1346, 1247, 1169, 1115 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.33 (m, 2H), 7.20 (s, 2H), 7.04 – 6.90 (m, 2H), 6.86 – 6.67 (m, 2H), 3.71 (d, *J* = 1.4 Hz, 3H), 3.09 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.6, 143.5, 134.2, 133.5, 129.4, 127.9, 127.8, 113.9, 55.3, 38.3, 21.4. HRMS (ESI) calculated for $C_{15}H_{17}NNaO_3S^+$ [M+Na]$^+$: 314.0821, found 314.0825.



25

N,4-dimethyl-*N*-(4-nitrophenyl)benzenesulfonamide **25**

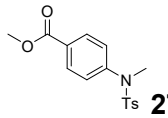
25 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 8:1) to furnish the desired compound **25** (74 % yield) as a yellow solid. m. p. 167.1-168.7 °C; IR (KBr) ν_{max}: 3365, 2998, 2362, 1594, 1447, 1347, 1167, 871, 693, 502 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.23 – 8.11 (m, 2H), 7.48 – 7.39 (m, 2H), 7.39 – 7.31 (m, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 3.22 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.4, 144.4, 133.1, 129.7, 127.6, 125.6, 124.3, 37.5, 29.7, 21.6. HRMS (ESI) calculated for $C_{14}H_{14}N_2NaO_4S^+$ [M+Na]$^+$: 329.0566, found 329.0563.



26

N-(4-chlorophenyl)-*N*,4-dimethylbenzenesulfonamide **26**

26 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **26** (81 % yield) as a white solid. m. p. 89.5-91.2 °C; IR (KBr) ν_{max}: 2978, 1596, 1487, 1343, 1155, 881, 714, 611, 506 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.34 (m, 2H), 7.34 – 7.13 (m, 4H), 7.09 – 6.92 (m, 2H), 3.10 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.9, 140.2, 133.1, 132.7, 129.5, 128.9, 127.8, 37.9, 21.5. HRMS (ESI) calculated for $C_{14}H_{14}ClNNaO_2S^+$ [M+Na]$^+$: 318.0326, found 318.0329.



27

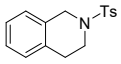
methyl 4-((N,4-dimethylphenyl)sulfonamido)benzoate **27**

27 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **27** (92 % yield) as a white solid. m. p. 105.2-107.1 °C; IR (KBr) ν_{max}: 2955, 1719, 1600, 1152, 1103, 1054, 878, 721, 550 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 7.86 (m, 2H), 7.39 (dt, *J* = 7.7, 2.2 Hz, 2H), 7.30 – 7.13 (m, 4H), 3.91 (q, *J* = 2.2 Hz, 3H), 3.19 (q, *J* = 2.0 Hz, 3H), 2.40 (q, *J* = 2.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.3, 145.7, 144.0, 133.1, 130.2, 129.5, 128.3, 127.7, 125.5, 52.2, 37.6, 21.5. HRMS (ESI) calculated for $C_{16}H_{17}NNaO_4S^+$ [M+Na]$^+$: 342.0776, found 342.0773.

28

4-tosylmorpholine **28**

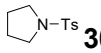
28 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 2:1) to furnish the desired compound **28** (84 % yield) as a white solid. m. p. 148.9-150.7 °C; IR (KBr) ν_{max}: 2853, 1453, 1346, 1165, 1114, 941, 815, 734, 545 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.53 (m, 2H), 7.34 (d, J = 7.9 Hz, 2H), 3.79 – 3.64 (m, 4H), 3.06 – 2.90 (m, 4H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.9, 132.0, 129.7, 127.8, 66.0, 46.0, 21.5. HRMS (ESI) calculated for $C_{11}H_{15}NNaO_3S^+$ $[M+Na]^+$: 264.0665, found 264.0663.



29

2-tosyl-1,2,3,4-tetrahydroisoquinoline **29**

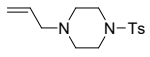
29 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to furnish the desired compound **29** (88 % yield) as a white solid. m. p. 143.7-145.3 °C; IR (KBr) ν_{max}: 2935, 2861, 2822, 2361, 1594, 1339, 1165, 951, 735, 545 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 7.72 (d, J = 7.9 Hz, 2H), 7.43 (d, J = 7.9 Hz, 2H), 7.25 – 6.89 (m, 4H), 4.16 (s, 2H), 3.25 (t, J = 6.0 Hz, 2H), 2.82 (d, J = 6.1 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 144.0, 133.4, 133.4, 132.0, 130.3, 129.1, 127.9, 127.1, 126.8, 126.5, 47.7, 44.0, 28.5, 21.4. HRMS (ESI) calculated for $C_{16}H_{17}NNaO_2S^+$ $[M+Na]^+$: 310.0872, found 310.0875.



30

1-tosylpyrrolidine **30**

30 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 3:1) to furnish the desired compound **30** (88 % yield) as a white solid. m. p. 120.8-121.6 °C; IR (KBr) ν_{max}: 2983, 1468, 1333, 1155, 816, 695, 549 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.65 (m, 2H), 7.32 (d, J = 8.0 Hz, 2H), 3.39 – 3.11 (m, 4H), 2.43 (s, 3H), 1.92 – 1.63 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.3, 133.9, 129.6, 127.6, 47.9, 25.2, 21.5. HRMS (ESI) calculated for $C_{11}H_{15}NNaO_2S^+$ $[M+Na]^+$: 248.0716, found 248.0718.

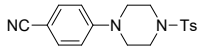


31

1-allyl-4-tosylpiperazine **31**

31 was prepared according to the general procedure A, and purified by chromatography on silica gel (CH_2Cl_2: MeOH = 25:1) to furnish the desired compound **31** (91 % yield) as a white solid. m. p. 164.7-166.3 °C; IR (KBr) ν_{max}: 2924, 2587, 2417, 1455, 1352, 1165, 942, 730, 548 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 7.62 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 6.08 (dt, J = 16.2, 8.1 Hz, 1H), 5.66 – 5.47 (m, 2H), 4.02 – 2.91 (m, 10H), 2.44 (s, 3H).

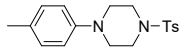
^{13}C NMR (100 MHz, DMSO-d_6) δ 144.8, 132.3, 130.2, 127.4, 126.2, 126.1, 59.4, 50.5, 43.1, 21.6. HRMS (ESI) calculated for $C_{14}H_{20}N_2NaO_2S^+$ [M+Na]$^+$: 303.1143, found 303.1141.



32

4-(4-tosylpiperazin-1-yl)benzonitrile **32**

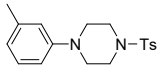
32 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 6:1) to furnish the desired compound **32** (82 % yield) as a white solid. m. p. 156.5-157.8 ^{o}C; IR (KBr) ν_{max}: 2856, 2208, 1601, 1513, 1300, 1174, 1003, 731, 595 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 8.3, 2.3 Hz, 2H), 7.45 (ddd, *J* = 9.0, 4.1, 1.9 Hz, 2H), 7.35 (dd, *J* = 8.4, 2.2 Hz, 2H), 6.96 – 6.70 (m, 2H), 3.39 (dt, *J* = 5.9, 2.6 Hz, 4H), 3.26 – 2.99 (m, 4H), 2.43 (d, *J* = 2.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.8, 133.5, 144.2, 132.2, 129.9, 127.8, 119.7, 114.9, 101.2, 47.0, 45.6, 21.6. HRMS (ESI) calculated for $C_{18}H_{19}N_3NaO_2S^+$ [M+Na]$^+$: 364.1090, found 364.1092.



33

1-(*p*-tolyl)-4-tosylpiperazine **33**

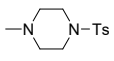
33 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 8:1) to furnish the desired compound **33** (87 % yield) as a white solid. m. p. 212.4-214.0 ^{o}C; IR (KBr) ν_{max}: 2910, 2822, 2361, 1514, 1346, 1162, 948, 730, 548 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.54 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.14 – 6.97 (m, 2H), 6.85 – 6.71 (m, 2H), 3.16 (p, *J* = 4.3, 3.6 Hz, 8H), 2.43 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.6, 143.8, 132.4, 130.4, 129.8, 129.7, 127.9, 117.2, 49.7, 46.2, 21.5, 20.5. HRMS (ESI) calculated for $C_{18}H_{22}N_2NaO_2S^+$ [M+Na]$^+$: 353.1294, found 353.1298.



34

1-(m-tolyl)-4-tosylpiperazine **34**

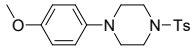
34 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 8:1) to furnish the desired compound **34** (82 % yield) as a white solid. m. p. 129.8-131.1 ^{o}C; IR (KBr) ν_{max}: 2971, 2856, 2361, 1600, 1447, 1345, 1144, 954, 733, 547 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.10 (t, *J* = 7.7 Hz, 1H), 6.72 – 6.58 (m, 3H), 3.21 – 3.15 (m, 4H), 3.15 – 3.01 (m, 4H), 2.40 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.8, 143.9, 139.0, 132.4, 129.8, 129.1, 128.0, 121.6, 117.7, 114.0, 49.2, 46.2, 21.8, 21.6. HRMS (ESI) calculated for $C_{18}H_{22}N_2NaO_2S^+$ [M+Na]$^+$: 353.1294, found 353.1293.



35

1-methyl-4-tosylpiperazine **35**

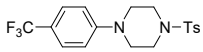
35 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (DCM: MeOH = 15:1) to furnish the desired compound **35** (46 % yield) as a white solid. m. p. 155.6-157.4 °C; IR (KBr) ν_{max}: 2853, 2797, 1345, 1287, 1167, 1151, 943, 921 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.59 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 3.04 (t, *J* = 4.9 Hz, 4H), 2.49 (t, *J* = 5.0 Hz, 4H), 2.42 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.7, 132.4, 129.6, 127.9, 54.0, 45.9, 45.6, 21.5. HRMS (ESI) calculated for $C_{12}H_{18}N_2NaO_2S^+$ $[M+Na]^+$: 277.0981, found 277.0979.



36

1-(4-methoxyphenyl)-4-tosylpiperazine **36**

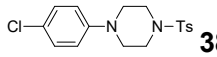
36 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 8:1) to furnish the desired compound **36** (87 % yield) as a white solid. m. p. 177.3-178.5 °C; IR (KBr) ν_{max}: 2825, 2361, 1596, 1513, 1161, 908, 731, 548 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 6.83 (t, *J* = 6.3 Hz, 4H), 3.75 (s, 3H), 3.14 (dq, *J* = 9.5, 4.1 Hz, 8H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 154.6, 145.0, 143.8, 132.4, 129.7, 127.9, 119.1, 114.5, 55.5, 50.6, 46.2, 21.5. HRMS (ESI) calculated for $C_{18}H_{22}N_2NaO_3S^+$ $[M+Na]^+$: 369.1243, found 369.1244.



37

1-tosyl-4-(4-(trifluoromethyl)phenyl)piperazine **37**

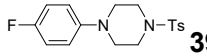
37 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 8:1) to furnish the desired compound **37** (81 % yield) as a white solid. m. p. 219.5-220.8 °C; IR (KBr) ν_{max}: 2835, 1615, 1455, 1331, 1208, 1021, 812, 578 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.56 (m, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.34 (dd, *J* = 6.3, 3.8 Hz, 4H), 3.28 – 3.13 (m, 4H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.7, 144.0, 132.3, 129.8, 127.9, 126.5 (d, *J* = 4.2 Hz), 115.3, 48.0, 45.8, 21.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.6. HRMS (ESI) calculated for $C_{18}H_{19}F_3N_2NaO_2S^+$ $[M+Na]^+$: 407.1012, found 407.1015.



38

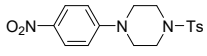
1-(4-chlorophenyl)-4-tosylpiperazine **38**

38 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 8:1) to furnish the desired compound **38** (78% yield) as a white solid. m. p. 205.4-206.9 °C; IR (KBr) ν_{max}: 2831, 2361, 1495, 1349, 1161, 946, 732, 547 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.64 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.15 (m, 2H), 6.81 – 6.74 (m, 2H), 3.22 – 3.18 (m, 4H), 3.15 (d, *J* = 5.6 Hz, 4H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.3, 143.9, 132.4, 129.8, 129.1, 127.9, 125.7, 118.0, 49.14, 45.9, 21.5. HRMS (ESI) calculated for $C_{17}H_{19}ClN_2NaO_2S^+$ $[M+Na]^+$: 373.0748, found 373.0751.


39

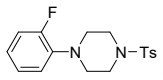
1-(4-fluorophenyl)-4-tosylpiperazine **39**

39 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 8:1) to furnish the desired compound **39** (74 % yield) as a white solid. m. p. 189.1-191.0 °C; IR (KBr) ν_{max}: 2853, 2361, 1512, 1354, 1269, 1121, 901, 650, 516 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 6.93 (t, *J* = 8.5 Hz, 2H), 6.82 (dd, *J* = 9.0, 4.6 Hz, 2H), 3.14 (s, 8H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.9, 156.5, 147.4, 143.9, 132.4, 128.8 (d, *J* = 186.4 Hz), 118.8 (d, *J* = 7.7 Hz), 115.8 (d, *J* = 22.0 Hz), 50.1, 46.1, 21.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -123.0. HRMS (ESI) calculated for $C_{17}H_{19}FN_2NaO_2S^+$ $[M+Na]^+$: 357.1043, found 357.1042.


40

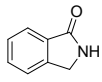
1-(4-nitrophenyl)-4-tosylpiperazine **40**

40 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 6:1) to furnish the desired compound **40** (76 % yield) as a yellow solid. m. p. 201.8-203.0 °C; IR (KBr) ν_{max}: 2844, 2361, 1592, 1499, 1318, 1163, 946, 695 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 – 8.03 (m, 2H), 7.77 – 7.59 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.82 – 6.75 (m, 2H), 3.65 – 3.35 (m, 4H), 3.21 – 3.08 (m, 4H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 154.2, 144.2, 139.3, 132.2, 129.9, 127.8, 125.9, 113.4, 46.9, 45.6, 21.6. HRMS (ESI) calculated for $C_{17}H_{19}N_3NaO_4S^+$ $[M+Na]^+$: 384.0988, found 384.0987.


41

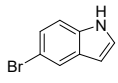
1-(2-fluorophenyl)-4-tosylpiperazine **41**

41 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 8:1) to furnish the desired compound **41** (81 % yield) as a white solid. m. p. 149.9-151.0 °C; IR (KBr) ν_{max}: 3426, 3043, 2983, 2830, 1595, 1345, 1124, 956, 727 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.10 – 6.84 (m, 4H), 3.25 – 3.01 (m, 8H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.7 (d, *J* = 245.3 Hz), 143.9, 139.3 (d, *J* = 8.7 Hz), 132.4, 129.8, 127.9, 124.6 (d, *J* = 3.4 Hz), 123.3 (d, *J* = 7.7 Hz), 119.3, 116.2 (d, *J* = 20.7 Hz), 50.0 (d, *J* = 3.2 Hz), 46.2, 21.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -123.2. HRMS (ESI) calculated for $C_{17}H_{19}FN_2NaO_2S^+$ $[M+Na]^+$: 357.1043, found 357.1041.


42

isoindolin-1-one **42**

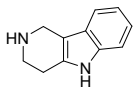
42 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 30:1) to furnish the desired compound **42** as a white solid. m. p. 149.8-151.7 °C; IR (KBr) ν_{max}: 3481, 3209, 3080, 3024, 2928, 2862, 1682 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 13.34 (s, 1H), 12.32 (s, 2H), 12.22 (s, 1H), 9.13 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 175.2, 149.3, 137.8, 136.4, 132.8, 128.9, 128.0, 50.1. HRMS (ESI) calculated for $C_8H_7NNaO^+$ $[M+Na]^+$: 156.0420, found 156.0418.



43

5-bromo-1*H*-indole **43**

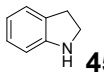
43 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 20:1) to furnish the desired compound **43** as a white solid. m. p. 90.8-92.5 °C; IR (KBr) ν_{max}: 3384, 3102, 3030, 1621, 1563, 1452, 1312, 800 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 11.33 (s, 1H), 7.74 (d, J = 2.0 Hz, 1H), 7.44 – 7.35 (m, 2H), 7.21 (dd, J = 8.5, 2.0 Hz, 1H), 6.44 (d, J = 3.1 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 135.1, 130.0, 127.3, 123.9, 122.7, 113.8, 101.3, 79.7. HRMS (ESI) calculated for $C_8H_6BrNNa^+$ $[M+Na]^+$: 217.9576, found 217.9573.



44

2,3,4,5-tetrahydro-1*H*-pyrido[4,3-*b*]indole **44**

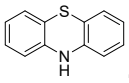
44 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 15:1) to furnish the desired compound **44** as a white solid. m. p. 216.3-218.1 °C; IR (KBr) ν_{max}: 1616, 1579, 1562, 1487, 1345, 1240, 1013, 918 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 10.79 (s, 1H), 7.36 (d, J = 7.7 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.01 (ddd, J = 8.1, 7.0, 1.3 Hz, 1H), 6.94 (td, J = 7.4, 1.1 Hz, 1H), 4.91 (d, J = 7.8 Hz, 1H), 3.97 (s, 2H), 3.08 (t, J = 5.7 Hz, 2H), 2.67 (t, J = 5.5 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 136.1, 132.2, 127.3, 121.0, 118.8, 117.8, 111.4, 106.9, 43.2, 42.3, 21.3. HRMS (ESI) calculated for $C_{11}H_{12}N_2Na^+$ $[M+Na]^+$: 195.0893, found 195.0897.



45

Indoline **45**

45 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 30:1) to furnish the desired compound **45** as a brown oil. IR (KBr) ν_{max}: 3375, 3046, 3029, 2932, 1606, 1486, 1406, 1322,1244, 1167, 1092, 1056, 1022 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.13 – 7.05 (m, 1H), 7.00 (td, J = 7.6, 1.1 Hz, 1H), 6.72 – 6.60 (m, 2H), 3.52 (t, J = 8.4 Hz, 3H), 3.01 (t, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.7, 129.4, 127.3, 124.7, 118.7, 109.5, 47.4, 29.9. HRMS (ESI) calculated for $C_8H_9NNa^+$ $[M+Na]^+$: 142.0627, found 142.0626.



46

10*H*-phenothiazine **46**

46 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 20:1) to furnish the desired compound **46** as a white solid. m. p. 183.8-184.6 °C; IR (KBr) ν_{max}: 3338, 3097, 1596, 1572, 1473, 1444, 1155, 1118, 1034, 856, 682, 655, 493 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 8.60 (s, 1H), 6.99 (td, J = 7.6, 1.5 Hz, 2H), 6.92 (dd, J = 7.7, 1.5 Hz, 2H), 6.80 – 6.67 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 142.6, 128.0, 126.7, 122.2, 116.9, 114.9. HRMS (ESI) calculated for $C_{12}H_9NNaS^+$ $[M+Na]^+$: 222.0348, found 222.0346.

47

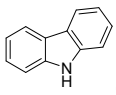
1,2,3,4-tetrahydroquinoline **47**

47 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 20:1) to furnish the desired compound **47** as a yellow oil. IR (KBr) ν_{max}: 3415, 2923, 2835, 1605, 1496, 1311, 743 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.05 – 6.87 (m, 2H), 6.59 (td, J = 7.4, 1.2 Hz, 1H), 6.44 (dd, J = 7.8, 1.2 Hz, 1H), 3.66 (s, 1H), 3.30 – 3.24 (m, 2H), 2.74 (t, J = 6.4 Hz, 2H), 1.96 – 1.88 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.8, 129.6, 126.8, 121.5, 117.0, 114.2, 42.0, 27.0, 22.2. HRMS (ESI) calculated for $C_9H_{11}NNa^+$ $[M+Na]^+$: 156.0784, found 156.0788.

48

1*H*-imidazole **48**

48 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 20:1) to furnish the desired compound **48** as a white solid. m. p. 90.2-91.8 °C; IR (KBr) ν_{max}: 3126, 3032, 2933, 2785, 2691, 1451, 1264, 1058, 935, 841, 762, 661 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 12.17 (s, 1H), 7.68 (t, J = 1.1 Hz, 1H), 7.04 (d, J = 0.9 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 135.6, 122.2. HRMS (ESI) calculated for $C_3H_4N_2Na^+$ $[M+Na]^+$: 91.0627, found 91.0629.



49

9*H*-carbazole **49**

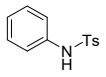
49 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 20:1) to furnish the desired compound **49** as a white solid. m. p. 243.6-245.2 °C; IR (KBr) ν_{max}: 1626, 1602, 1493, 1395, 1337, 1239, 1204, 1108, 927, 857, 748, 573, 508, 439 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 7.24 (d, J = 7.7 Hz, 2H), 6.61 (dd, J = 28.5, 7.8 Hz, 4H), 6.34 (q, J = 6.2, 4.8 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ

140.2, 126.0, 122.9, 120.6, 119.0, 111.4. HRMS (ESI) calculated for $C_{12}H_9NNa^+$ $[M+Na]^+$: 190.0627, found 190.0627.

50

1*H*-benzo[*d*][1,2,3]triazole **50**

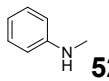
50 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 30:1) to furnish the desired compound **50** as a white solid. m. p. 97.9-99.1 °C; IR (KBr) ν_{max}: 3469, 3085, 2996, 2912, 2850, 2800, 2715, 2519, 1408, 1207, 1008, 870, 741 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 14.19 (s, 1H), 7.96 (dd, *J* = 6.4, 3.1 Hz, 2H), 7.46 – 7.41 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.9, 126.1, 115.0. HRMS (ESI) calculated for $C_6H_5N_3Na^+$ $[M+Na]^+$: 142.0376, found 142.0377.



51

4-methyl-*N*-phenylbenzenesulfonamide **51**

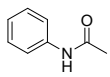
51 was prepared according to the general procedure, and purified by chromatography on silica gel (DCM: MeOH = 20:1) to furnish the desired compound **51** as a white solid. m. p. 104.1-106.4 °C; IR (KBr) ν_{max}: 3291, 3024, 2933, 2865, 1512, 1332, 1157, 981, 812, 511 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.66 (m, 2H), 7.27 (d, *J* = 3.7 Hz, 1H), 7.21 (td, *J* = 4.4, 1.8 Hz, 3H), 7.18 – 7.01 (m, 3H), 2.36 (d, *J* = 3.6 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.0, 136.7, 134.4, 131.6, 130.2, 129.6, 129.2, 128.6, 21.7. HRMS (ESI) calculated for $C_{13}H_{13}NNaO_2S^+$ $[M+Na]^+$: 270.0559, found 270.0557.



52

N-methylaniline **52**

52 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **52** as a colorless oil. IR (KBr) ν_{max}: 3441, 3056, 3023, 2966, 2933, 2912, 2885, 2818, 1606, 1511, 1477, 1423, 1318, 1261, 1160, 692 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.43 (m, 2H), 7.03 (tt, *J* = 7.3, 1.2 Hz, 1H), 6.91 – 6.75 (m, 2H), 3.80 (s, 1H), 3.00 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.8, 129.5, 117.4, 112.7, 30.9. HRMS (ESI) calculated for $C_7H_9NNa^+$ $[M+Na]^+$: 130.0627, found 130.0628.

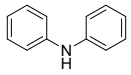


53

N-phenylacetamide **53**

53 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 8:1) to furnish the desired compound **53** as a white solid. m. p. 113.4-115.3 °C; IR (KBr) ν_{max}: 3293, 3262, 3141, 1666, 1621, 1597, 1553, 1501, 1436, 1322, 1264, 762, 755, 609 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 9.92 (s, 1H), 7.65 – 7.58 (m, 2H), 7.32 – 7.26 (m, 2H), 7.02 (tt, *J* = 7.4, 1.2 Hz, 1H), 2.06 (s, 3H). ^{13}C

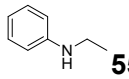
NMR (100 MHz, DMSO-d_6) δ 168.7, 139.8, 129.1, 123.4, 119.5, 24.4. HRMS (ESI) calculated for $C_8H_9NNaO^+$ [M+Na]$^+$: 158.0576, found 158.0574.



54

Diphenylamine **54**

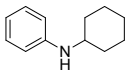
54 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 6:1) to furnish the desired compound **54** as a white solid. m. p. 52.8-53.4 °C; IR (KBr) ν_{max}: 3385, 3052, 1596, 1522, 1493, 1318, 1311, 1172, 758, 744, 692 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.22 (m, 4H), 7.05 (d, *J* = 7.9 Hz, 4H), 6.91 (t, *J* = 7.4 Hz, 2H), 5.66 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.2, 129.4, 121.0, 117.9. HRMS (ESI) calculated for $C_{12}H_{11}NNa^+$ [M+Na]$^+$: 192.0784, found 192.0788.



55

N-ethylaniline **55**

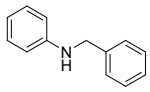
55 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **55** as a brown oil. IR (KBr) ν_{max}: 3422, 3054, 3023, 2972, 2928, 2876, 1605, 1506, 1481, 1317, 1259, 1176, 1148, 691, 618 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.30 (m, 2H), 7.02 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.95 – 6.81 (m, 2H), 3.73 (s, 1H), 3.38 (q, *J* = 7.2 Hz, 2H), 1.48 (d, *J* = 14.4 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.8, 129.5, 117.4, 113.0, 38.6, 15.1. HRMS (ESI) calculated for $C_8H_{11}NNa^+$ [M+Na]$^+$: 144.0784, found 144.0786.



56

N-cyclohexylaniline **56**

56 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 12:1) to furnish the desired compound **56** as a colorless oil. IR (KBr) ν_{max}: 3402, 3198, 2927, 2333, 2087, 1814, 1598, 1501, 1313, 1153, 994, 884, 747, 688 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 (t, *J* = 7.8 Hz, 2H), 6.61 (dd, *J* = 31.6, 7.8 Hz, 3H), 3.24 (ddd, *J* = 13.2, 6.9, 3.1 Hz, 2H), 2.05 (d, *J* = 12.6 Hz, 2H), 1.90 – 1.70 (m, 2H), 1.70 – 1.59 (m, 1H), 1.36 (q, *J* = 12.1 Hz, 2H), 1.28 – 1.00 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.4, 129.3, 116.8, 113.2, 51.7, 33.5, 26.0, 25.0. HRMS (ESI) calculated for $C_{12}H_{17}NNa^+$ [M+Na]$^+$: 198.1253, found 198.1255.



57

N-benzylaniline **57**

57 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to furnish the desired compound **57** as a white solid. m. p.36.9-38.1 °C; IR (KBr) ν_{max}: 3419, 3052, 3025, 2926, 1604, 1517, 1496,

1455, 1331, 1303, 1282, 1182, 985, 751, 744, 739, 695, 689 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 4H), 7.25 – 7.20 (m, 1H), 7.16 – 7.11 (m, 2H), 6.68 (td, *J* = 7.3, 1.1 Hz, 1H), 6.59 – 6.55 (m, 2H), 4.24 (s, 2H), 3.91 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.7, 129.4, 127.7, 127.4, 117.7, 113.0, 48.4. HRMS (ESI) calculated for $C_{13}H_{13}NNa^+$ $[M+Na]^+$: 206.0940, found 206.0944.

58

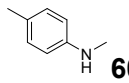
N,2-dimethylaniline **58**

58 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **58** as a yellow oil. IR (KBr) ν_{max}: 3464, 3056, 2931, 2914, 2856, 1879, 1611, 1586, 1516, 1474, 1303, 1253, 1162, 1045, 966, 544 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.52 (td, *J* = 7.7, 1.6 Hz, 1H), 7.40 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.22 – 7.01 (m, 1H), 6.95 (dd, *J* = 8.1, 1.2 Hz, 1H), 3.80 (s, 1H), 3.16 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.6, 130.2, 127.5, 122.2, 117.1, 109.4, 31.0, 17.6. HRMS (ESI) calculated for $C_8H_{11}NNa^+$ $[M+Na]^+$: 144.0784, found 144.0785.

59

N,3-dimethylaniline **59**

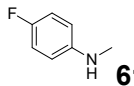
59 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **59** as a yellow oil. IR (KBr) ν_{max}: 3414, 3046, 2983, 2919, 2887, 1607, 1593, 1513, 1495, 1331, 1270, 992, 693 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.31 (m, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.70 (dq, *J* = 5.5, 2.5 Hz, 2H), 3.78 (s, 1H), 3.04 (s, 3H), 2.62 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.8, 139.1, 129.4, 118.4, 113.5, 109.9, 30.9, 21.9. HRMS (ESI) calculated for $C_8H_{11}NNa^+$ $[M+Na]^+$: 144.0784, found 144.0781.



60

N,4-dimethylaniline **60**

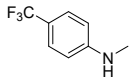
60 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **60** as a yellow oil. IR (KBr) ν_{max}: 3411, 3018, 2981, 2920, 2867, 1619, 1526, 1488, 1317, 1261, 1183, 809 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 8.3 Hz, 2H), 6.88 – 6.55 (m, 2H), 3.61 (s, 1H), 2.97 (s, 3H), 2.48 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.4, 129.9, 126.5, 112.8, 31.2, 20.6. HRMS (ESI) calculated for $C_8H_{11}NNa^+$ $[M+Na]^+$: 144.0784, found 144.0788.



61

4-fluoro-*N*-methylaniline **61**

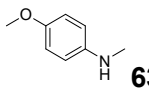
61was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **61** as a black oil. IR (KBr) v_{max}: 3422, 3060, 2914, 1615, 1473, 1512, 1320, 1221, 823 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.91 – 6.83 (m, 2H), 6.51 – 6.44 (m, 2H), 3.66 – 3.32 (m, 1H), 2.73 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.8 (d, J = 234.3 Hz), 145.9, 115.6 (d, J = 21.9 Hz), 113.2 (d, J = 7.3 Hz), 31.2. HRMS (ESI) calculated for $C_7H_8FNNa^+$ $[M+Na]^+$: 148.0533, found 148.0535.



62

N-methyl-4-(trifluoromethyl)aniline **62**

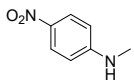
62 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **62** as a brown oil. IR (KBr) v_{max}: 3456, 2933, 2254, 1795, 1652, 1536, 1478, 1381, 1325, 1274, 1188, 1106, 1074 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.31 (m, 2H), 6.54 (d, J = 8.5 Hz, 2H), 4.26 – 3.78 (m, 1H), 2.80 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.8, 126.5 (d, J = 3.3 Hz), 123.9, 118.4 (d, J = 32.7 Hz), 111.4, 30.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -60.8. HRMS (ESI) calculated for $C_8H_8F_3NNa^+$ $[M+Na]^+$: 198.0501, found 198.0500.



63

4-methoxy-*N*-methylaniline **63**

63 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **63** as a brown oil. m. p. 33.9-35.8 °C; IR (KBr) v_{max}: 3428, 3048, 2933, 2828, 1617, 1606, 1511, 1467, 1323, 1243, 1163 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.83 – 6.70 (m, 2H), 6.56 – 6.45 (m, 2H), 3.71 – 3.65 (m, 3H), 3.37 (s, 1H), 2.70 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.1, 144.0, 115.0, 113.7, 55.8, 31.6. HRMS (ESI) calculated for $C_8H_{11}NNaO^+$ $[M+Na]^+$: 160.0733, found 160.0738.

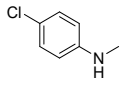


64

N-methyl-4-nitroaniline **64**

64 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **64** as a brown solid. m. p. 149.6-151.4 °C; IR (KBr) v_{max}: 3368, 3011, 2915, 2828, 1602, 1548, 1462, 1362, 1320, 1309, 1289, 1113, 998, 834, 623 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.26 – 7.76 (m, 2H), 7.31 (q, J = 5.0 Hz, 1H), 6.76 – 6.53 (m, 2H), 2.83 (d, J = 5.1 Hz, 3H).

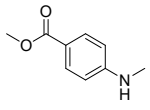
^{13}C NMR (100 MHz, DMSO-d_6) δ 155.7, 136.1, 126.6, 110.8, 29.6. HRMS (ESI) calculated for $C_7H_8N_2NaO_2^+$ [M+Na]$^+$: 175.0478, found 175.0474.



65

4-chloro-*N*-methylaniline **65**

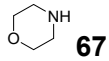
65 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **65** as a yellow oil. IR (KBr) ν_{max}: 3428, 3056, 2933, 2814, 1866, 1606, 1504, 1468, 1447, 1316, 1260, 1179, 1095, 815 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.15 – 7.02 (m, 2H), 6.54 – 6.34 (m, 2H), 3.57 (s, 1H), 2.69 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.1, 129.0, 121.6, 113.5, 30.8. HRMS (ESI) calculated for $C_7H_8ClNNa^+$ [M+Na]$^+$: 164.0237, found 164.0233.



66

methyl 4-(methylamino)benzoate **66**

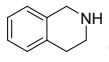
66 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **66** as a white solid. m. p. 93.8-95.4 ^{o}C; IR (KBr) ν_{max}: 3395, 3072, 2948, 1693, 1608, 1584, 1518, 1446, 1264, 1245, 1173 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (ddd, *J* = 8.7, 4.1, 1.8 Hz, 2H), 6.52 (ddd, *J* = 8.7, 4.1, 1.9 Hz, 2H), 4.32 (s, 1H), 3.92 – 3.80 (m, 3H), 2.84 (d, *J* = 5.3 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.5, 153.0, 131.5, 118.0, 111.1, 51.5, 30.1. HRMS (ESI) calculated for $C_9H_{11}NNaO_2^+$ [M+Na]$^+$: 188.0687, found 188.0684.



67

Morpholine **67**

67 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 15:1) to furnish the desired compound **67** as a colorless oil. IR (KBr) ν_{max}: 3334, 3304, 3288, 2951, 2933, 2911, 2849, 2830, 1466, 1321, 1143, 1096, 890, 863, 836, 808 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.68 (t, *J* = 4.6 Hz, 4H), 2.88 (t, *J* = 4.6 Hz, 4H), 1.72 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 68.1, 46.5. HRMS (ESI) calculated for $C_4H_9NNaO^+$ [M+Na]$^+$: 110.0576, found 110.0573.



68

1,2,3,4-tetrahydroisoquinoline **68**

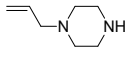
68 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 20:1) to furnish the desired compound **68** as yellow oil. IR (KBr) ν_{max}: 3264, 3043, 2922, 2936, 2810, 1497, 1455, 1424, 1321, 1122, 943, 623, 792, 743 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 (dq, *J* = 13.3, 3.9 Hz, 3H), 7.03 – 6.92 (m, 1H),

3.99 (s, 2H), 3.12 (td, *J* = 6.0, 2.5 Hz, 2H), 2.78 (d, *J* = 6.5 Hz, 2H), 1.80 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 136.0, 134.8, 129.3, 126.2, 126.0, 125.7, 48.4, 44.0, 29.2. HRMS (ESI) calculated for $C_9H_{11}NNa^+$ [M+Na]$^+$: 156.0784, found 156.0788.


69

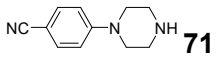
Pyrrolidine **69**

69 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 10:1) to furnish the desired compound **69** as a yellow oil. IR (KBr) ν_{max}: 3264, 2957, 2910, 2866, 1486, 1400, 1298, 1168, 1110, 1023, 799 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) *δ* 2.89 – 2.46 (m, 4H), 2.09 (s, 1H), 1.73 – 1.36 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) *δ* 47.0, 25.7. HRMS (ESI) calculated for $C_4H_9NNa^+$ [M+Na]$^+$: 94.0627, found 94.0629.


70

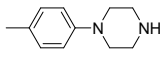
1-allylpiperazine **70**

70 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 20:1) to furnish the desired compound **70** as colorless oil. IR (KBr) ν_{max}: 2941, 2801, 1661, 1449, 1050, 998 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 5.86 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 5.22 – 5.12 (m, 2H), 2.98 (dt, *J* = 6.6, 1.4 Hz, 2H), 2.89 (t, *J* = 4.9 Hz, 4H), 2.41 (s, 4H), 1.62 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 134.9, 117.8, 62.3, 54.4, 46.0. HRMS (ESI) calculated for $C_7H_{14}N_2Na^+$ [M+Na]$^+$: 149.1049, found 149.1045.


71

4-(piperazin-1-yl)benzonitrile **71**

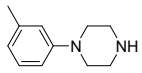
71 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 20:1) to furnish the desired compound **71** as white solid. m. p. 81.8-83.6 ^{o}C; IR (KBr) ν_{max}: 3325, 2215,1606 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.73 – 7.41 (m, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 3.31 (t, *J* = 5.2 Hz, 4H), 3.19 – 2.84 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 153.8, 133.5, 120.0, 114.2, 100.2, 48.2, 45.7. HRMS (ESI) calculated for $C_{11}H_{13}N_3Na^+$ [M+Na]$^+$: 210.1002, found 210.1005.


72

1-(*p*-tolyl)piperazine **72**

72 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 20:1) to furnish the desired compound **72** as white solid. m. p. 32.1-34.0 ^{o}C; IR (KBr) ν_{max}: 3402, 3033, 2928, 2894, 2811, 1606, 1583, 1499, 1448, 1236, 1143, 943, 769, 696 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) *δ* 7.05 – 6.94 (m, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 2.99 – 2.90 (m, 4H), 2.87 – 2.72 (m, 4H), 2.19 (s, 3H). ^{13}C NMR (100 MHz,

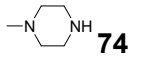
DMSO-d_6) δ 150.2, 129.8, 127.8, 116.0, 50.4, 46.2, 20.5. HRMS (ESI) calculated for $C_{11}H_{16}N_2Na^+$ [M+Na]$^+$: 199.1206, found 199.1203.



73

1-(*m*-tolyl)piperazine **73**

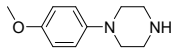
73 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 20:1) to furnish the desired compound **73** as white solid. m. p. 125.6-127.5 ^{o}C; IR (KBr) ν_{max}: 3293, 3037, 2943, 2911, 2821, 1604, 1581, 1496, 1448, 1247, 1147, 954, 775, 694 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.07 (t, J = 7.8 Hz, 1H), 6.74 – 6.65 (m, 2H), 6.58 (dd, J = 7.4, 1.4 Hz, 1H), 3.03 – 2.96 (m, 4H), 2.81 (dd, J = 6.3, 3.7 Hz, 4H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.3, 138.3, 129.1, 119.9, 116.5, 113.0, 50.0, 46.2, 21.9. HRMS (ESI) calculated for $C_{11}H_{16}N_2Na^+$ [M+Na]$^+$: 199.1206, found 199.1207.



74

1-methylpiperazine **74**

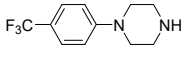
74 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 15:1) to furnish the desired compound **74** as colorless oil. IR (KBr) ν_{max}: 2941, 2913, 2844, 2796, 2766, 1455, 1443, 1317, 1285, 1156, 1147, 1122, 1013, 999, 587 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.94 – 1.87 (m, 4H), 1.52 – 1.33 (m, 4H), 1.29 (s, 3H), 0.73 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 55.8, 46.0, 45.4. HRMS (ESI) calculated for $C_5H_{12}N_2Na^+$ [M+Na]$^+$: 123.0893, found 123.0896.



75

1-(4-methoxyphenyl)piperazine **75**

75 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 20:1) to furnish the desired compound **75** as white solid. m. p. 203.7-205.5 ^{o}C; IR (KBr) ν_{max}: 3377, 3000, 2933, 1644, 1603, 1513, 1468, 1249, 1027 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.95 – 6.74 (m, 4H), 3.68 (s, 3H), 2.90 (dd, J = 6.4, 3.4 Hz, 4H), 2.82 (dd, J = 6.4, 3.3 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.3, 146.7, 117.7, 114.7, 55.6, 51.4, 46.2. HRMS (ESI) calculated for $C_{11}H_{16}N_2NaO^+$ [M+Na]$^+$: 215.1155, found 215.1157.

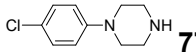


76

1-(4-(trifluoromethyl)phenyl)piperazine **76**

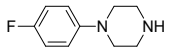
76 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 20:1) to furnish the desired compound **76** as white solid. m. p. 89.2-91.1 ^{o}C; IR (KBr) ν_{max}: 3259, 2834, 1669, 1613, 1325, 1099,1067 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.48 (d, J = 8.7 Hz, 2H), 7.03 (d, J = 8.7 Hz, 2H), 3.29 – 3.09 (m, 4H), 2.82 (t, J = 5.0 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.3, 126.6 (q, J = 3.3 Hz), 124.2,

118.2, 114.4, 48.6, 45.8. ^{19}F NMR (376 MHz, DMSO-d_6) δ -59.4. HRMS (ESI) calculated for $C_{11}H_{13}F_3N_2Na^+$ [M+Na]$^+$: 253.0923, found 253.0924.


77

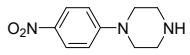
1-(4-chlorophenyl)piperazine **77**

77 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 20:1) to furnish the desired compound **77** as white solid. m. p. 76.6-78.3 ^{o}C; IR (KBr) ν_{max}: 3348, 3062, 2934, 2819, 1514, 1477, 1268, 1142, 836, 722 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.26 – 7.17 (m, 2H), 6.96 – 6.88 (m, 2H), 3.02 (d, J = 7.1 Hz, 4H), 2.81 (t, J = 5.1 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.9, 129.0, 122.5, 117.2, 49.6, 46.0. HRMS (ESI) calculated for $C_{10}H_{13}ClN_2Na^+$ [M+Na]$^+$: 219.0659, found 219.0657.


78

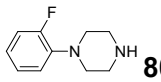
1-(4-fluorophenyl)piperazine **78**

78 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 20:1) to furnish the desired compound **78** as white solid. m. p. 30.9-32.8 ^{o}C; IR (KBr) ν_{max}: 3269, 3051, 2948, 2826, 2802, 1509,1452, 1237, 1144, 823, 818, 715 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.03 (t, J = 8.9 Hz, 2H), 6.96 – 6.71 (m, 2H), 2.97 (d, J = 7.2 Hz, 4H), 2.83 (dd, J = 6.3, 3.7 Hz, 4H), 2.43 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.4 (d, J = 235.4 Hz), 149.1, 117.4 (d, J = 6.8 Hz), 115.6 (d, J = 21.8 Hz), 50.7, 46.1. ^{19}F NMR (376 MHz, DMSO-d_6) δ -125.9. HRMS (ESI) calculated for $C_{10}H_{13}FN_2Na^+$ [M+Na]$^+$: 203.0955, found 203.0959.


79

1-(4-nitrophenyl)piperazine **79**

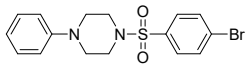
79 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 20:1) to furnish the desired compound **79** as yellow solid. m. p. 131.1-133.0 ^{o}C; IR (KBr) ν_{max}: 3338, 2921, 1601, 1456, 1314, 1251,1104, 841, 667 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30 – 7.70 (m, 2H), 7.08 – 6.91 (m, 2H), 3.43 – 3.32 (m, 4H), 2.86 – 2.76 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.5, 137.0, 126.2, 112.8, 48.0, 45.8. HRMS (ESI) calculated for $C_{10}H_{13}N_3NaO_2^+$ [M+Na]$^+$: 230.0900, found 230,0902.


80

1-(2-fluorophenyl)piperazine **80**

80 was prepared according to the general procedure, and purified by neutral alumina column (CH_2Cl_2: MeOH = 20:1) to furnish the desired compound **80** as white solid. m. p. 45.4-47.2 ^{o}C; IR (KBr) ν_{max}: 3273, 3059, 2977, 2842, 2799, 1523,1474, 1239, 1143, 845, 812, 718 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.22 – 7.04 (m, 2H), 7.05 – 6.91 (m, 2H),

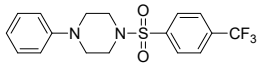
2.97 – 2.78 (m, 8H), 2.52 – 2.14 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.5 (d, J = 244.1 Hz), 141.1 (d, J = 7.7 Hz), 125.2 (d, J = 3.3 Hz), 122.5 (d, J = 8.5 Hz), 119.5, 116.3 (d, J = 20.7 Hz), 52.0 (d, J = 3.1 Hz), 46.2. ^{19}F NMR (376 MHz, DMSO-d_6) δ -122.9. HRMS (ESI) calculated for $C_{10}H_{13}FN_2Na^+$ [M+Na]$^+$: 203.0955, found 203.0952.



81

1-((4-bromophenyl)sulfonyl)-4-phenylpiperazine **81**

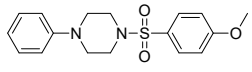
81 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **81** as a white solid. m. p. 181.7-183.4 ^{o}C; IR (KBr) ν_{max}: 2887, 2361, 1599, 1389, 1172, 954, 754, 565 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.73 – 7.61 (m, 4H), 7.28 – 7.23 (m, 2H), 6.94 – 6.83 (m, 3H), 3.24 (dd, J = 6.2, 3.3 Hz, 4H), 3.20 – 3.14 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-d) δ 150.6, 134.6, 132.5, 129.3 (d, J = 4.3 Hz), 128.2, 121.0, 117.0, 49.2, 46.1, 29.7. HRMS (ESI) calculated for $C_{16}H_{17}BrN_2NaO_2S^+$ [M+Na]$^+$: 403.0086, found 403.0084.



82

1-phenyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)piperazine **82**

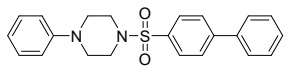
82 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 8:1) to furnish the desired compound **82** as a white solid. m. p. 171.1-172.8 ^{o}C; IR (KBr) ν_{max}: 3018, 2829, 1598, 1394, 1197, 946, 767, 550 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.92 (d, J = 8.2 Hz, 2H), 7.81 (d, J = 8.3 Hz, 2H), 7.32 – 7.15 (m, 2H), 7.04 – 6.70 (m, 3H), 3.35 – 3.11 (m, 8H). ^{13}C NMR (100 MHz, Chloroform-d) δ 150.6, 139.3, 134.7 (q, J = 33.2 Hz), 128.8 (d, J = 95.8 Hz), 126.8 – 125.6 (m), 124.6, 121.9, 121.0, 117.0, 49.2, 46.1. ^{19}F NMR (376 MHz, Chloroform-d) δ -63.1. HRMS (ESI) calculated for $C_{17}H_{17}F_3N_2NaO_2S^+$ [M+Na]$^+$: 393.0855, found 393.0852.



83

1-((4-methoxyphenyl)sulfonyl)-4-phenylpiperazine **83**

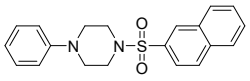
83 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **83** as a white solid. m. p. 167.4-169.1 ^{o}C; IR (KBr) ν_{max}: 2886, 2301, 1596, 1499, 1309, 1160, 949, 695, 559 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.73 – 7.68 (m, 2H), 7.24 – 7.14 (m, 4H), 6.96 – 6.84 (m, 2H), 6.84 – 6.74 (m, 1H), 3.86 (s, 3H), 3.26 – 3.15 (m, 4H), 2.98 (dd, J = 6.2, 3.8 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.4, 150.8, 130.4, 129.4, 126.6, 120.1, 116.6, 115.1, 56.2, 48.4, 46.3. HRMS (ESI) calculated for $C_{17}H_{20}N_2NaO_3S^+$ [M+Na]$^+$: 355.1087, found 355.1084.



84

1-([1,1'-biphenyl]-4-ylsulfonyl)-4-phenylpiperazine **84**

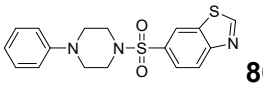
84 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to furnish the desired compound **84** as a white solid. m. p. 209.7-211.3 °C; IR (KBr) ν_{max}: 2830, 2361, 1596, 1393, 1165, 946, 767, 580 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.52 – 7.41 (m, 3H), 7.26 (s, 2H), 6.88 (d, *J* = 8.4 Hz, 3H), 3.25 (dq, *J* = 9.7, 4.2 Hz, 8H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.0, 139.2, 134.0, 129.2, 129.1, 128.6, 128.4, 127.8, 127.4, 120.9, 116.9, 100.0, 49.2, 46.1. HRMS (ESI) calculated for $C_{22}H_{22}N_2NaO_2S^+$ $[M+Na]^+$: 401.1294, found 401.1299.



85

1-(naphthalen-2-ylsulfonyl)-4-phenylpiperazine **85**

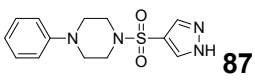
85 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **85** as a pink solid. m. p. 136.3-138.1 °C; IR (KBr) ν_{max}: 2888, 2361, 1597, 1345, 1233, 954, 766, 548 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.36 (d, *J* = 1.8 Hz, 1H), 7.94 (dd, *J* = 8.2, 3.3 Hz, 2H), 7.87 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.76 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.59 (pd, *J* = 6.9, 1.5 Hz, 2H), 7.24 – 7.16 (m, 2H), 6.94 – 6.71 (m, 3H), 3.29 – 3.08 (m, 8H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.7, 132.6, 129.4, 129.3, 129.3, 129.0, 128.0, 123.1, 120.8, 116.9, 49.2, 46.2. HRMS (ESI) calculated for $C_{20}H_{20}N_2NaO_2S^+$ $[M+Na]^+$: 375.1138, found 375.1134.



86

6-((4-phenylpiperazin-1-yl)sulfonyl)benzo[d]thiazole **86**

86 was prepared according to the general procedure A, and purified by chromatography on silica gel (CH_2Cl_2) to furnish the desired compound **86** as a white solid. m. p. 195.5-196.9 °C; IR (KBr) ν_{max}: 2826, 1598, 1503, 1241, 1119, 1101, 951, 685, 527 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 9.69 (d, *J* = 4.2 Hz, 1H), 8.78 (d, *J* = 4.0 Hz, 1H), 8.34 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.91 (dd, *J* = 9.4, 3.8 Hz, 1H), 7.19 (q, *J* = 6.7, 5.9 Hz, 2H), 6.89 (dd, *J* = 8.1, 4.0 Hz, 2H), 6.80 (t, *J* = 6.2 Hz, 1H), 3.21 (d, *J* = 5.5 Hz, 4H), 3.08 (d, *J* = 5.8 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.8, 156.0, 150.8, 135.1, 132.0, 129.4, 125.6, 124.2, 124.0, 120.2, 116.6, 48.4, 46.4. HRMS (ESI) calculated for $C_{17}H_{17}N_3NaO_2S_2^+$ $[M+Na]^+$: 382.0660, found 382.0656.

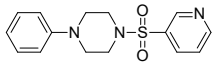


87

1-((1H-pyrazol-4-yl)sulfonyl)-4-phenylpiperazine **87**

87 was prepared according to the general procedure A, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **87** as a white solid. m. p. 259.1-260.3 °C; IR (KBr) ν_{max}: 3137, 3121, 2834, 1600, 1502, 1393, 1241, 1143, 944, 751, 612 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 13.83 (s, 1H), 8.42 (s, 1H), 7.88 (s, 1H), 7.21 (q, *J* = 6.6, 6.0 Hz, 2H), 6.92 (t, *J* = 6.0 Hz, 2H), 6.81 (t, *J* = 6.7 Hz, 1H),

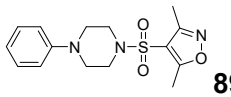
3.22 (d, *J* = 6.4 Hz, 4H), 2.96 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.8, 139.1, 132.1, 129.5, 120.1, 116.6, 115.6, 48.2, 46.1. HRMS (ESI) calculated for $C_{13}H_{16}N_4NaO_2S^+$ [M+Na]$^+$: 315.0892, found 315.0899.



88

1-phenyl-4-(pyridin-3-ylsulfonyl)piperazine **88**

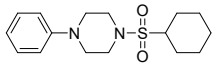
88 was prepared according to the general procedure A, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 1:1) to furnish the desired compound **88** as a white solid. m. p. 182.1-184.0 ^{o}C; IR (KBr) ν_{max}: 3041, 2855, 1599, 1392, 1180, 946, 759, 579 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.03 (d, *J* = 2.2 Hz, 1H), 8.85 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.08 (dt, *J* = 8.1, 1.8 Hz, 1H), 7.52 (dd, *J* = 8.1, 4.8 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.03 – 6.75 (m, 3H), 3.25 (h, *J* = 4.3 Hz, 8H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.6, 150.5, 148.6, 135.4, 132.4, 129.3, 123.8, 121.1, 117.1, 49.2, 46.0. HRMS (ESI) calculated for $C_{15}H_{17}N_3NaO_2S^+$ [M+Na]$^+$: 326.0934, found 326.0937.



89

3,5-dimethyl-4-((4-phenylpiperazin-1-yl)sulfonyl)isoxazole **89**

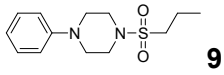
89 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to furnish the desired compound **89** as a white solid. m. p. 156.7-158.5 ^{o}C; IR (KBr) ν_{max}: 2924, 2826, 1598, 1372, 1180, 946, 690, 533 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.1 Hz, 2H), 6.92 (t, *J* = 6.6 Hz, 3H), 3.28 (d, *J* = 3.0 Hz, 8H), 2.68 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.9, 158.0, 150.5, 129.3, 121.2, 117.1, 113.1, 49.2, 45.5, 13.0, 11.4. HRMS (ESI) calculated for $C_{15}H_{19}N_3NaO_3S^+$ [M+Na]$^+$: 344.1039, found 344.1037.



90

1-(cyclohexylsulfonyl)-4-phenylpiperazine **90**

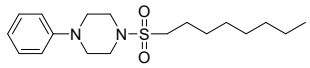
90 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 8:1) to furnish the desired compound **90** as a white solid. m. p. 121.0-122.7 ^{o}C; IR (KBr) ν_{max}: 2935, 2766, 2360, 1599, 1318, 1144, 971, 771, 582 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (dd, *J* = 8.8, 7.0 Hz, 2H), 6.86 (dd, *J* = 8.2, 6.6 Hz, 3H), 3.58 – 3.39 (m, 4H), 3.24 – 3.07 (m, 4H), 2.92 (tt, *J* = 12.0, 3.5 Hz, 1H), 2.11 (dd, *J* = 12.6, 3.7 Hz, 2H), 1.82 (d, *J* = 2.9 Hz, 2H), 1.66 (dt, *J* = 12.5, 3.2 Hz, 1H), 1.49 (qd, *J* = 12.4, 3.5 Hz, 2H), 1.21 (ddtd, *J* = 25.5, 15.9, 12.7, 3.4 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.0, 129.2, 120.5, 116.9, 61.3, 50.0, 46.2, 26.7, 25.2. HRMS (ESI) calculated for $C_{16}H_{24}N_2NaO_2S^+$ [M+Na]$^+$: 331.1451, found 331.1450.



91

1-phenyl-4-(propylsulfonyl)piperazine **91**

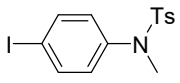
91 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 6:1) to furnish the desired compound **91** as a white solid. m. p. 107.8-109.5 °C; IR (KBr) ν_{max}: 2971, 2825, 2361, 1601, 1333, 1154, 908, 722, 574 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.23 (m, 2H), 6.92 (t, *J* = 6.6 Hz, 3H), 3.42 (q, *J* = 5.2 Hz, 4H), 3.24 (t, *J* = 5.2 Hz, 4H), 2.91 (dt, *J* = 10.7, 5.7 Hz, 2H), 1.98 – 1.80 (m, 2H), 1.07 (q, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.8, 129.3, 120.8, 117.0, 50.9, 49.7, 45.8, 16.9, 13.2. HRMS (ESI) calculated for $C_{13}H_{20}N_2NaO_2S^+$ $[M+Na]^+$: 291.1138, found 291.1136.



92

1-(octylsulfonyl)-4-phenylpiperazine **92**

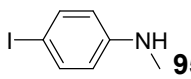
92 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to furnish the desired compound **92** as a white solid. m. p. 102.1-103.7 °C; IR (KBr) ν_{max}: 2920, 2851, 2361, 1601, 1383, 872, 721, 537 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 7.7 Hz, 2H), 6.94 (d, *J* = 8.1 Hz, 3H), 3.44 (t, *J* = 4.8 Hz, 4H), 3.25 (t, *J* = 4.9 Hz, 4H), 3.04 – 2.84 (m, 2H), 1.84 (p, *J* = 7.7 Hz, 2H), 1.49 – 1.23 (m, 11H), 0.88 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.8, 129.3, 120.9, 117.0, 49.7, 49.3, 45.8, 31.7, 29.1, 29.0, 28.5, 23.0, 22.6, 14.1. HRMS (ESI) calculated for $C_{18}H_{30}N_2NaO_2S^+$ $[M+Na]^+$: 361.1920, found 361.1921.



94

N-(4-iodophenyl)-N,4-dimethylbenzenesulfonamide **94**

94 was prepared according to the general procedure **A**, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 12:1) to furnish the desired compound **94** (74 % yield) as a yellow solid. m. p. 92.5-94.1 °C; IR (KBr) ν_{max}: 3032, 2874, 1592, 1484, 1261, 1153, 1066, 1001, 864, 722, 701, 663 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.57 (m, 2H), 7.43 – 7.40 (m, 2H), 7.27 – 7.24 (m, 2H), 6.91 – 6.78 (m, 2H), 3.12 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 141.9, 141.5, 138.0, 133.1, 129.5, 128.4, 127.8, 92.3, 37.8, 21.6. HRMS (ESI) calculated for $C_{14}H_{14}INNaO_2S^+$ $[M+Na]^+$: 409.9688, found 409.9691.

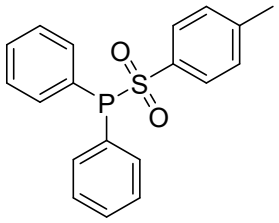


95

4-iodo-N-methylaniline **95**

95 was prepared according to the general procedure, and purified by chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to furnish the desired compound **95** as a yellow oil; IR (KBr) ν_{max}: 3416, 3185, 2980, 2879, 2571, 2385, 2118, 1872, 1590, 1432, 1389, 1314, 1292, 1180, 1100, 993, 807, 743, 686 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.31 (m, 2H), 6.42 – 6.30 (m, 2H), 3.46 (s, 1H), 2.78 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.9, 137.7, 114.6, 77.7, 30.6. HRMS (ESI) calculated for $C_7H_8INNa^+$ $[M+Na]^+$: 255.9599, found 255.9597.

6. Mass analysis of intermediates



diphenyl(tosyl)phosphane

According to the general procedure can find Ph_2PTs as the side product in the reaction.

HRMS (ESI) calculated for $C_{19}H_{17}NaO_2PS^+$ [M+Na]$^+$: 363.0585, found 363.1631.

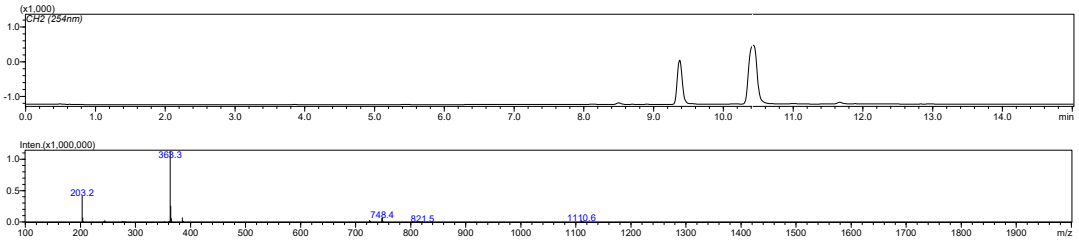


Figure S1. LC-MS of ***Ph2PTs***

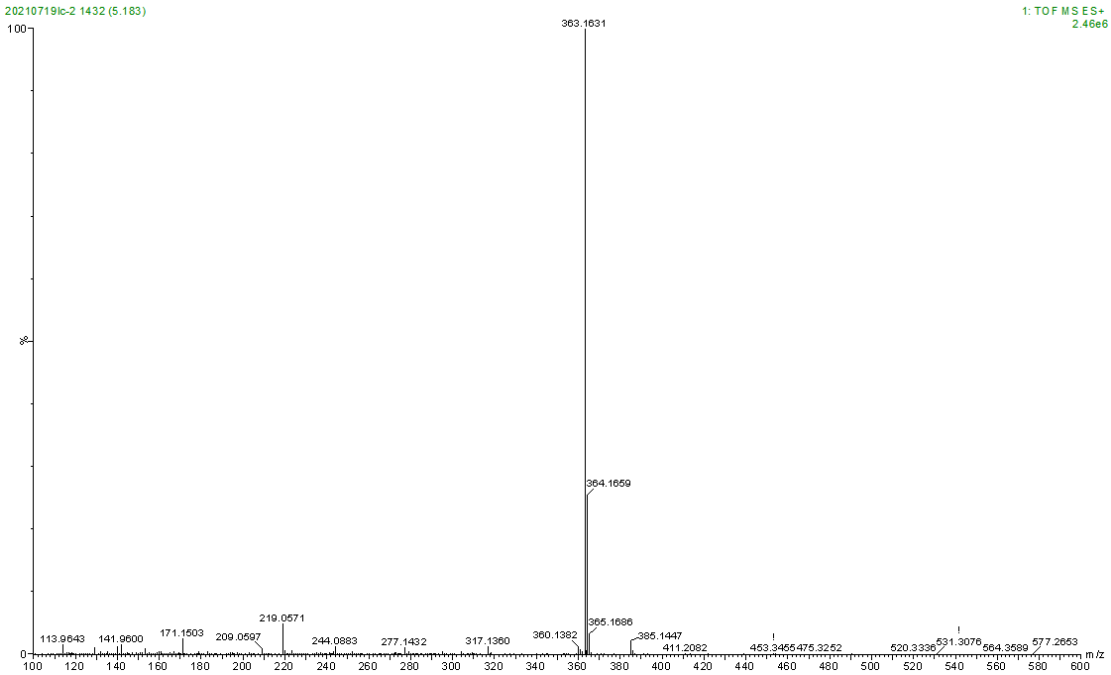
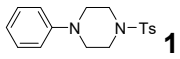
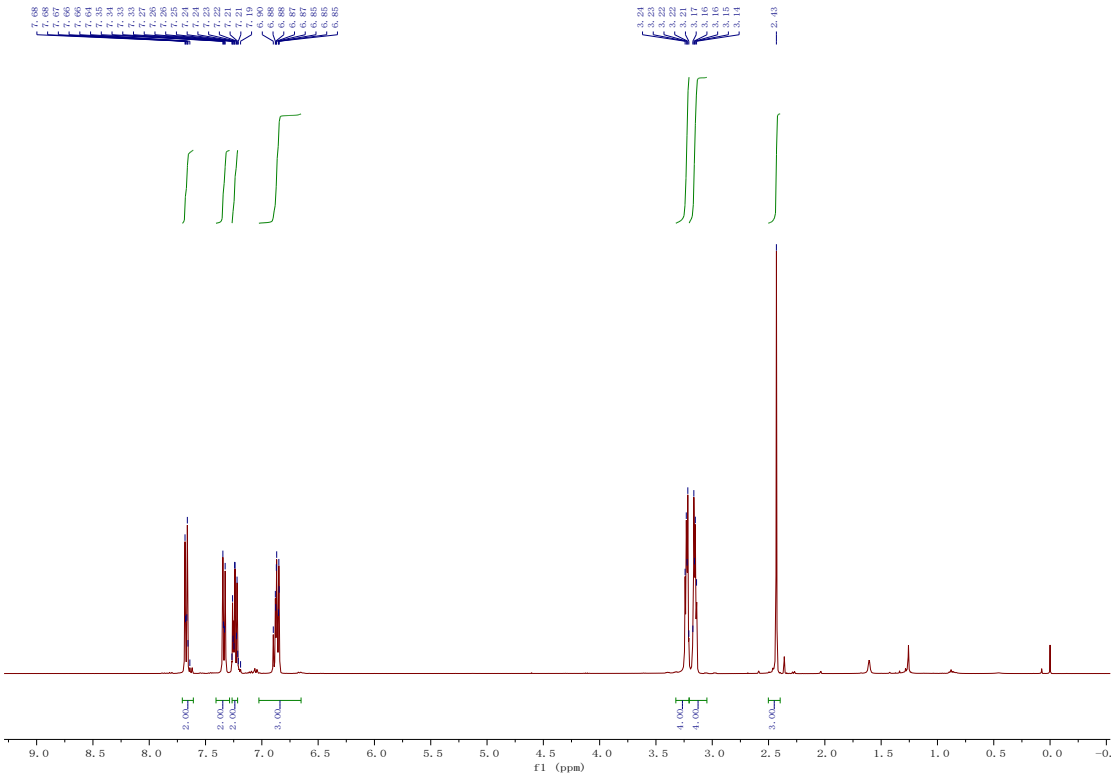


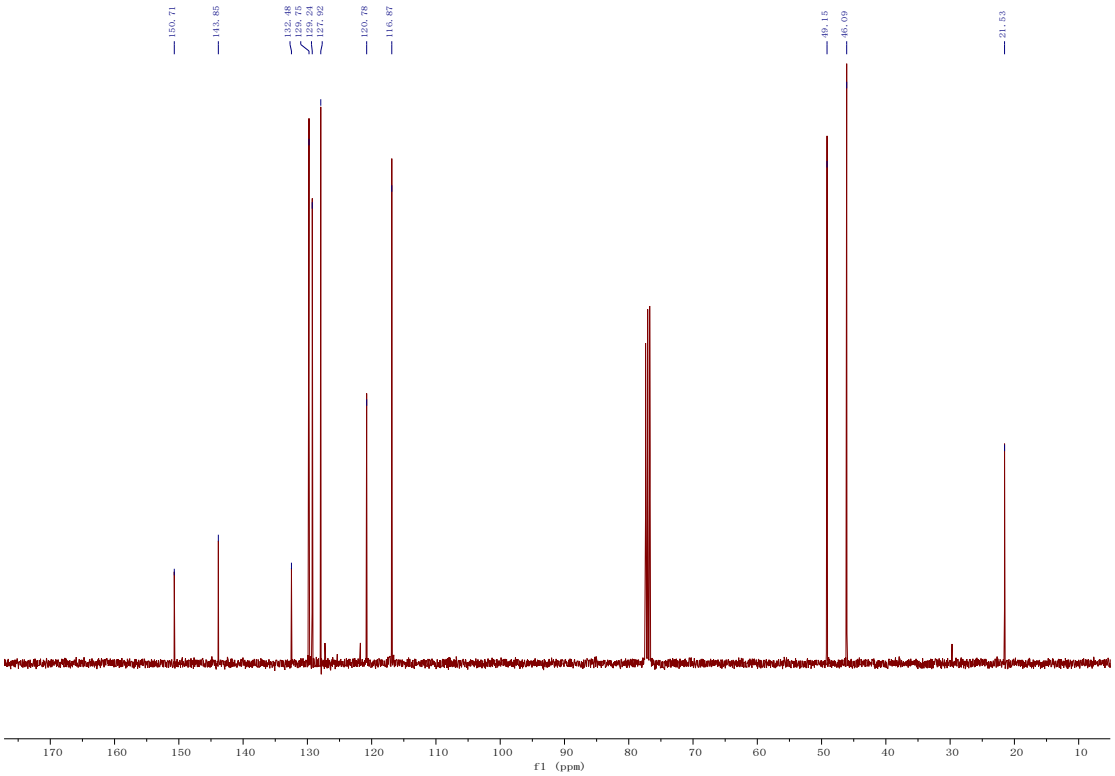
Figure S2. HR-MS of ***Ph2PTs***

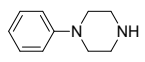
7. NMR Spectrums of Compounds



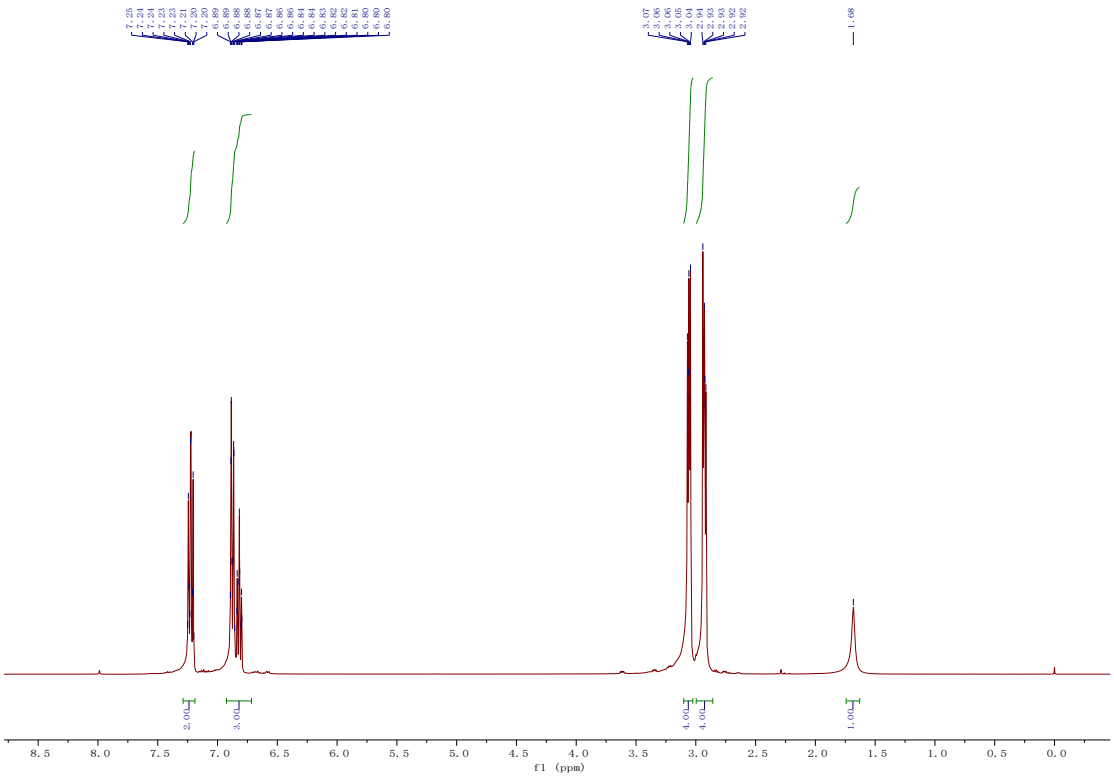
1

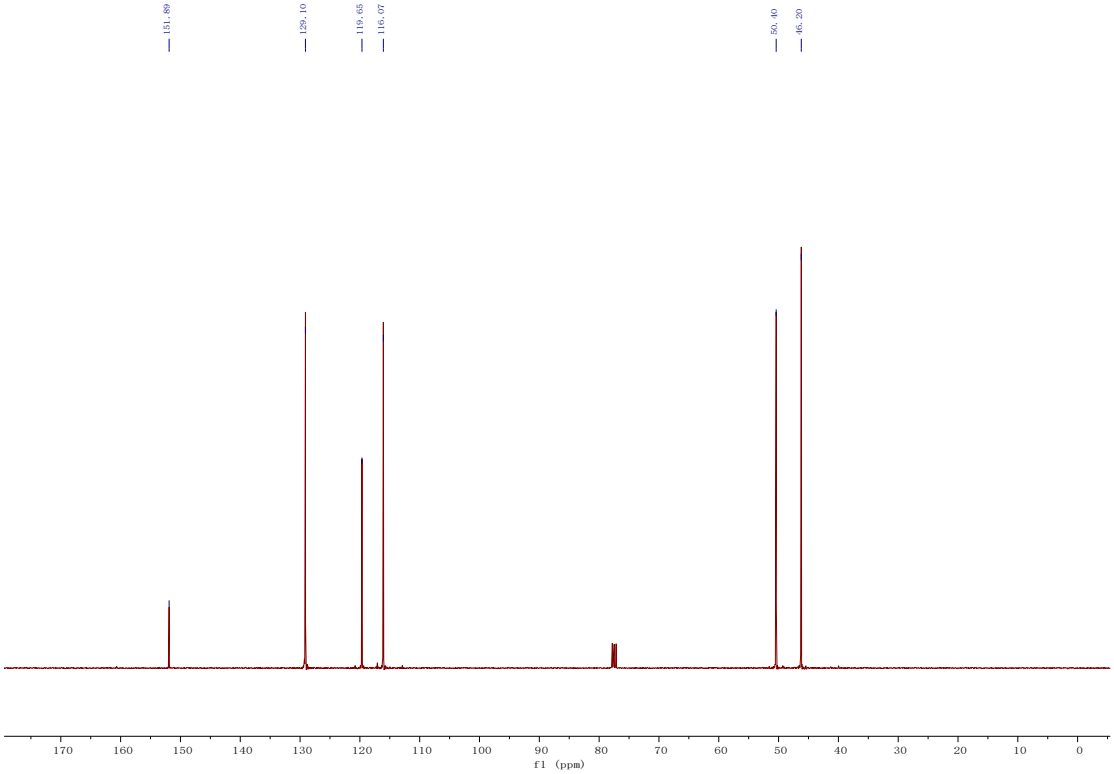





N
NH

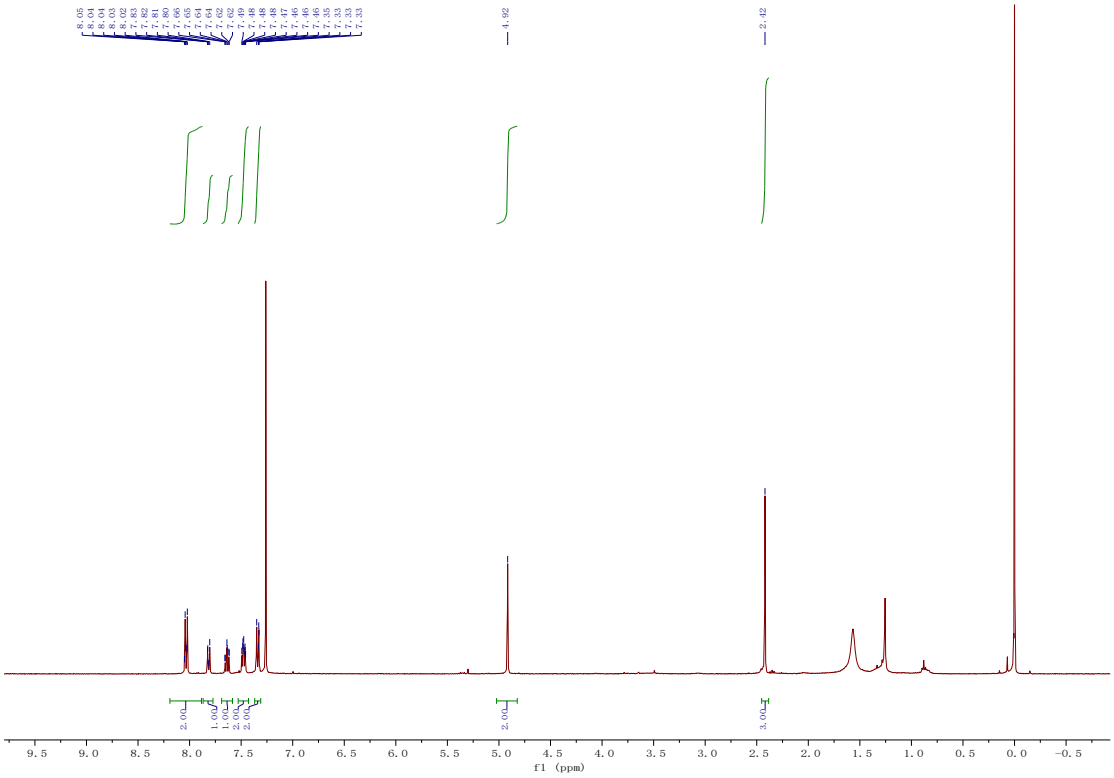
2

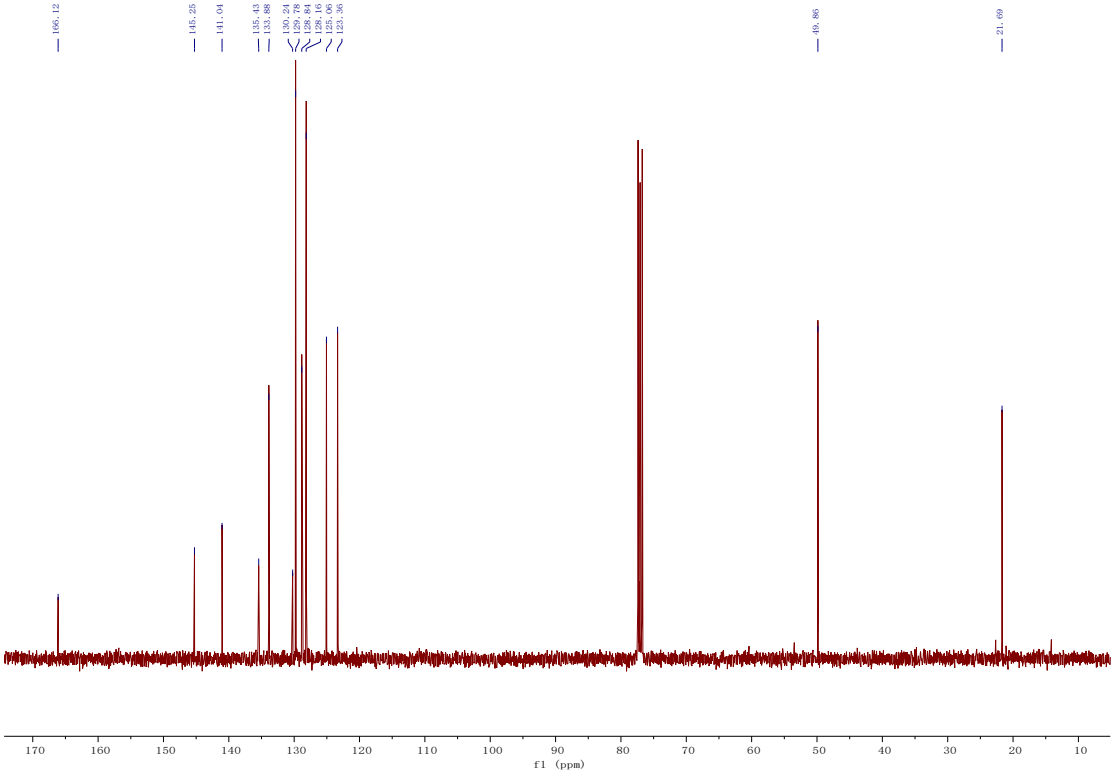

7.25
7.24
7.24
7.24
7.23
7.23
7.21
7.21
7.20
7.20
6.89
6.89
6.88
6.88
6.87
6.87
6.86
6.86
6.84
6.84
6.83
6.82
6.82
6.81
6.81
6.80
6.80
3.07
3.06
3.06
3.05
3.05
2.94
2.94
2.93
2.93
2.92
2.92
1.68
2.00
3.00
4.00
4.00
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

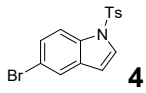

151.89
129.10
119.65
116.07
50.40
46.20
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N–Ts

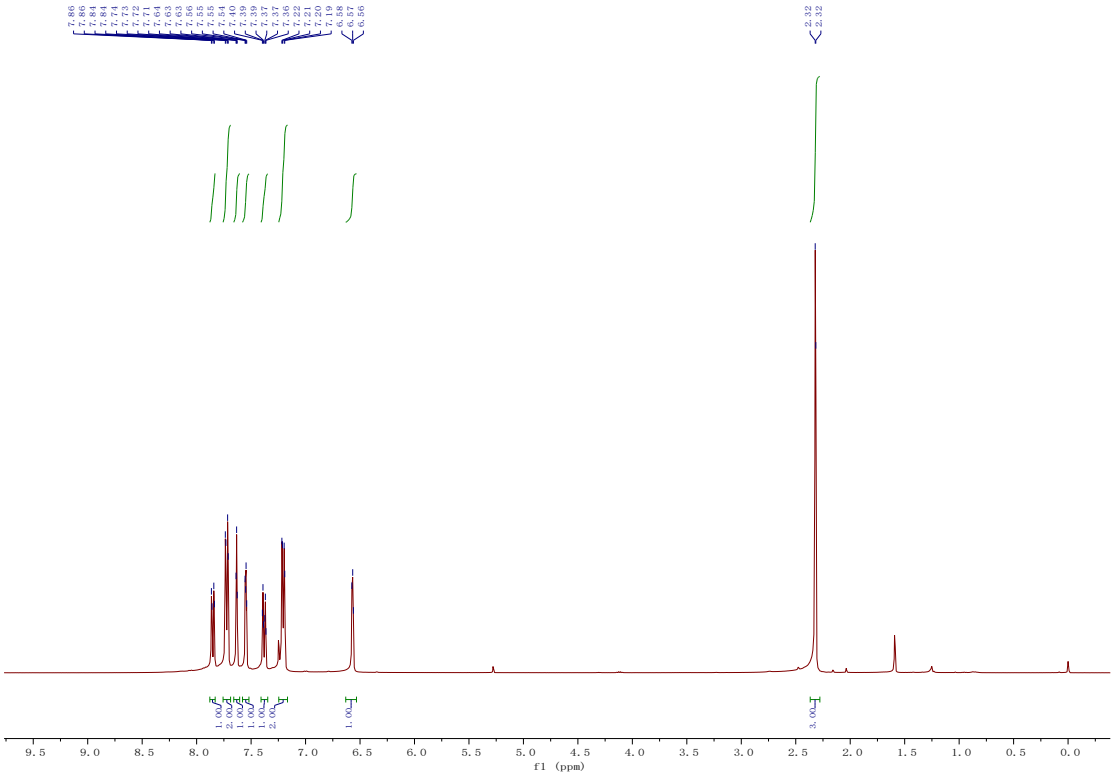
3

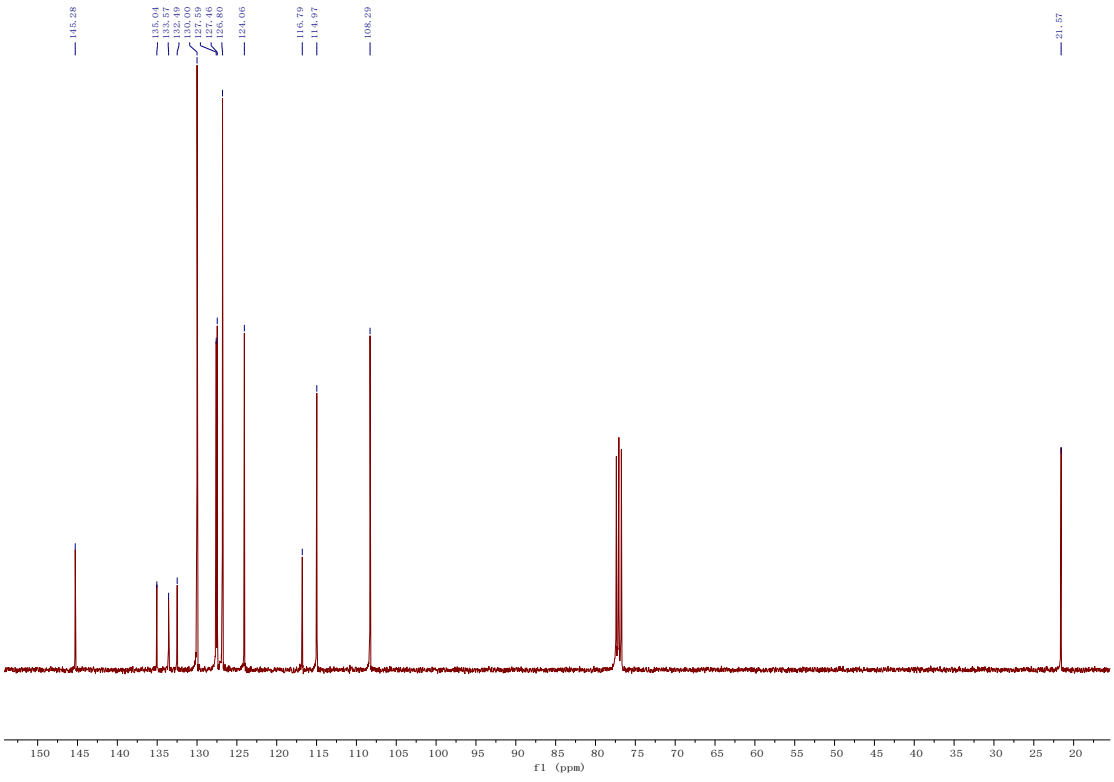

8.05
8.04
8.04
8.03
8.02
7.83
7.82
7.81
7.80
7.65
7.64
7.64
7.62
7.49
7.48
7.48
7.47
7.46
7.46
7.35
7.33
7.33
4.92
2.42
2.00
1.00
1.03
2.04
2.05
2.00
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

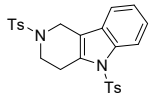

166.12
145.25
141.04
135.43
133.86
130.24
129.78
128.84
128.16
125.06
123.36
49.86
21.69
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Ts
N
Br

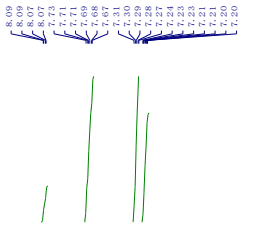
4

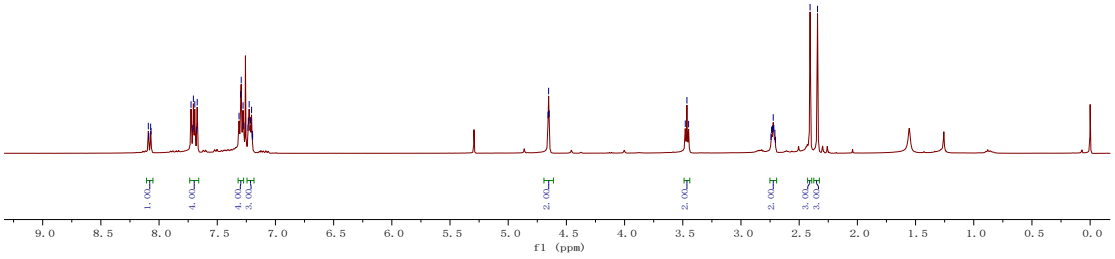

7.86
7.85
7.84
7.84
7.74
7.73
7.72
7.71
7.64
7.63
7.63
7.56
7.55
7.55
7.54
7.40
7.39
7.39
7.37
7.37
7.36
7.22
7.21
7.20
7.19
6.58
6.57
6.56
2.32
2.32
1.00
2.00
1.00
1.00
1.00
2.06
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

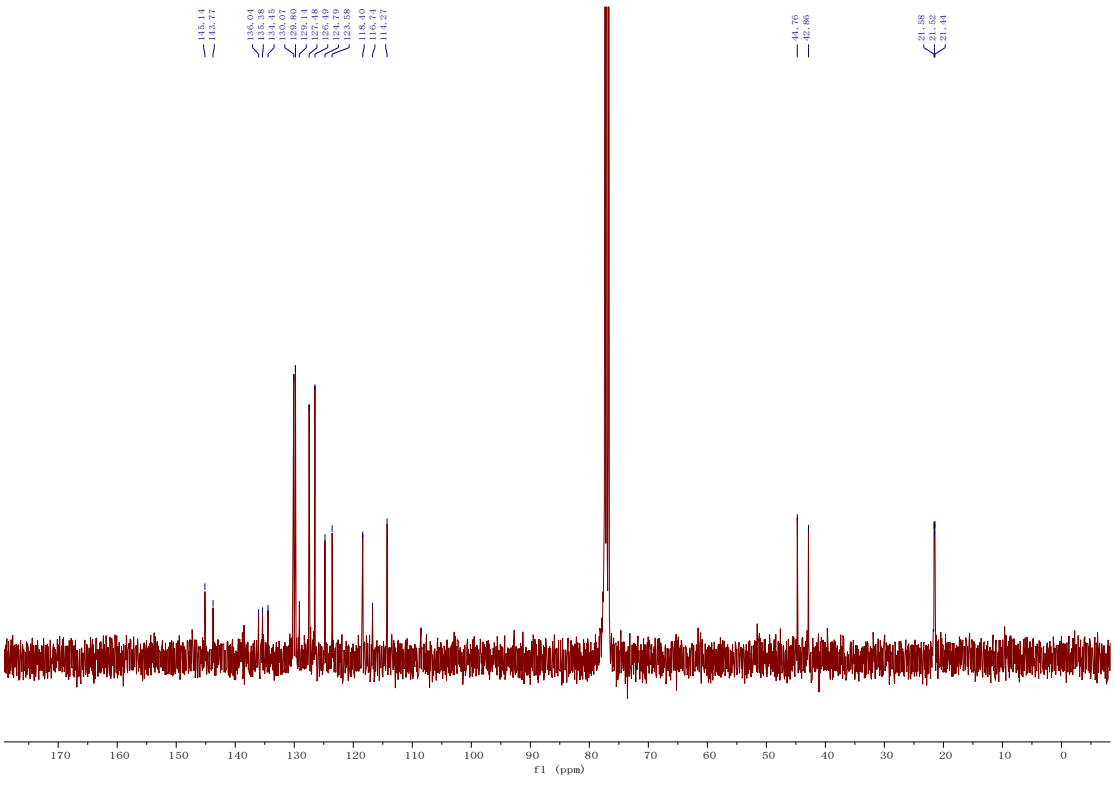

145.28
135.04
133.57
132.49
130.00
127.58
127.46
126.80
124.06
116.79
114.97
108.29
21.57
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

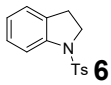

Ts
N
N
Ts

5

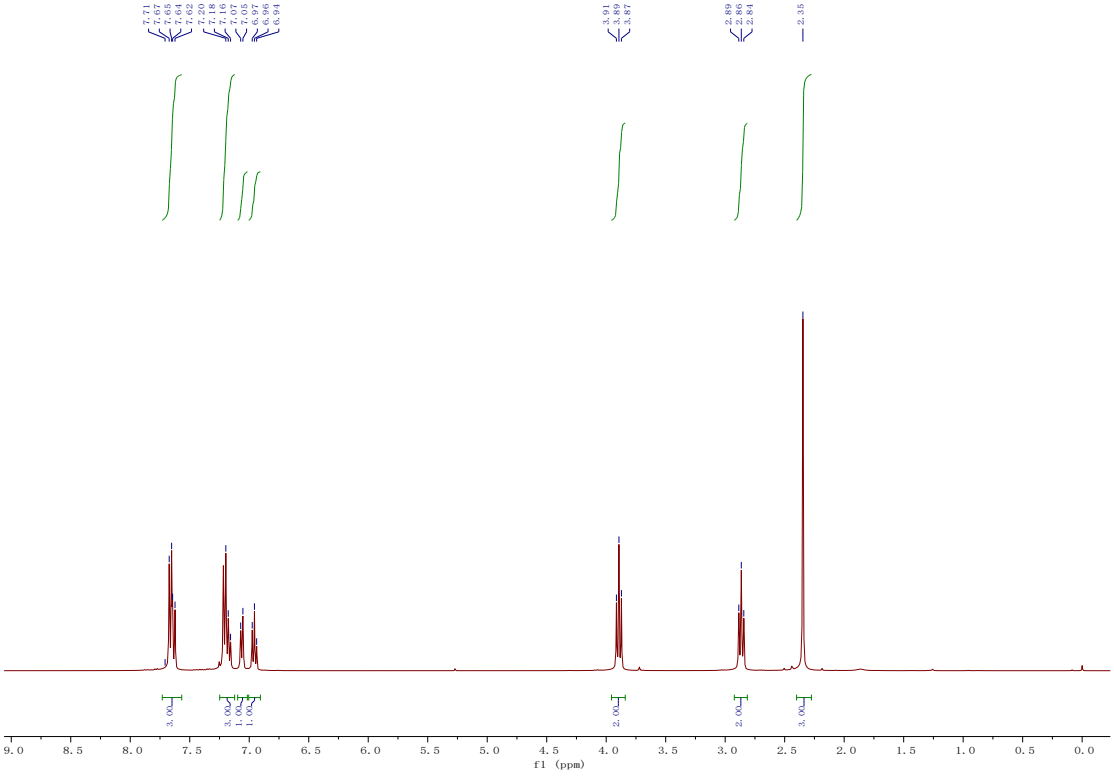

8.09
8.09
8.07
8.07
7.73
7.71
7.71
7.69
7.68
7.67
7.31
7.30
7.29
7.28
7.27
7.24
7.23
7.21
7.21
7.20
7.20
4.66
4.65
4.65
3.48
3.46
3.45
2.74
2.74
2.73
2.72
2.72
2.71
2.70
2.41
2.34

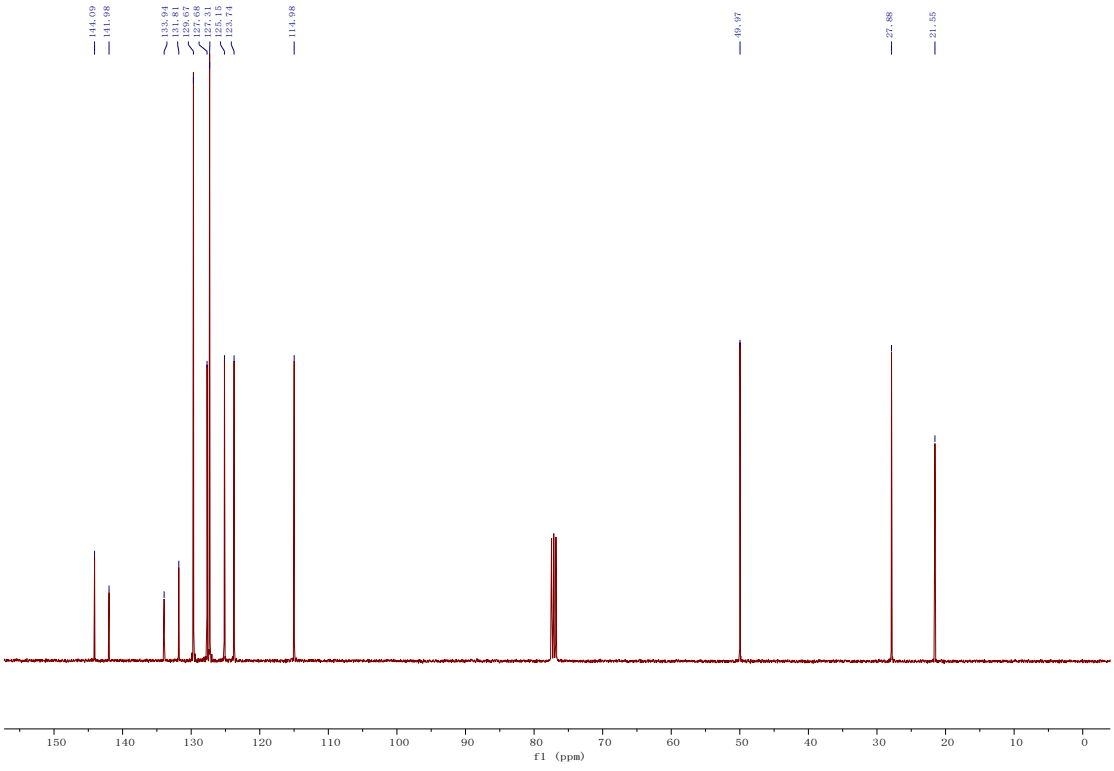

1.00
4.00
4.00
3.00
2.00
2.00
2.00
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

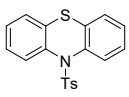

145.14
143.77
136.04
135.38
134.45
130.07
129.80
129.14
127.48
126.49
124.79
123.58
118.40
116.74
114.27
44.76
42.86
21.58
21.52
21.44
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
Ts

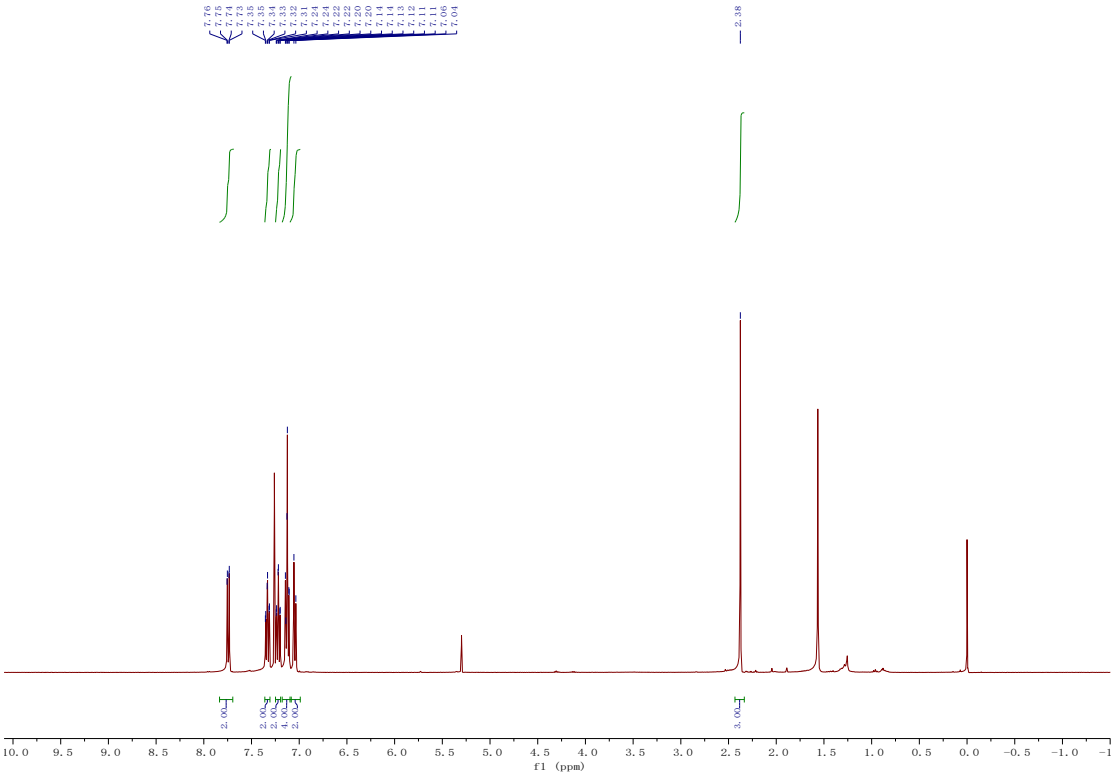
6

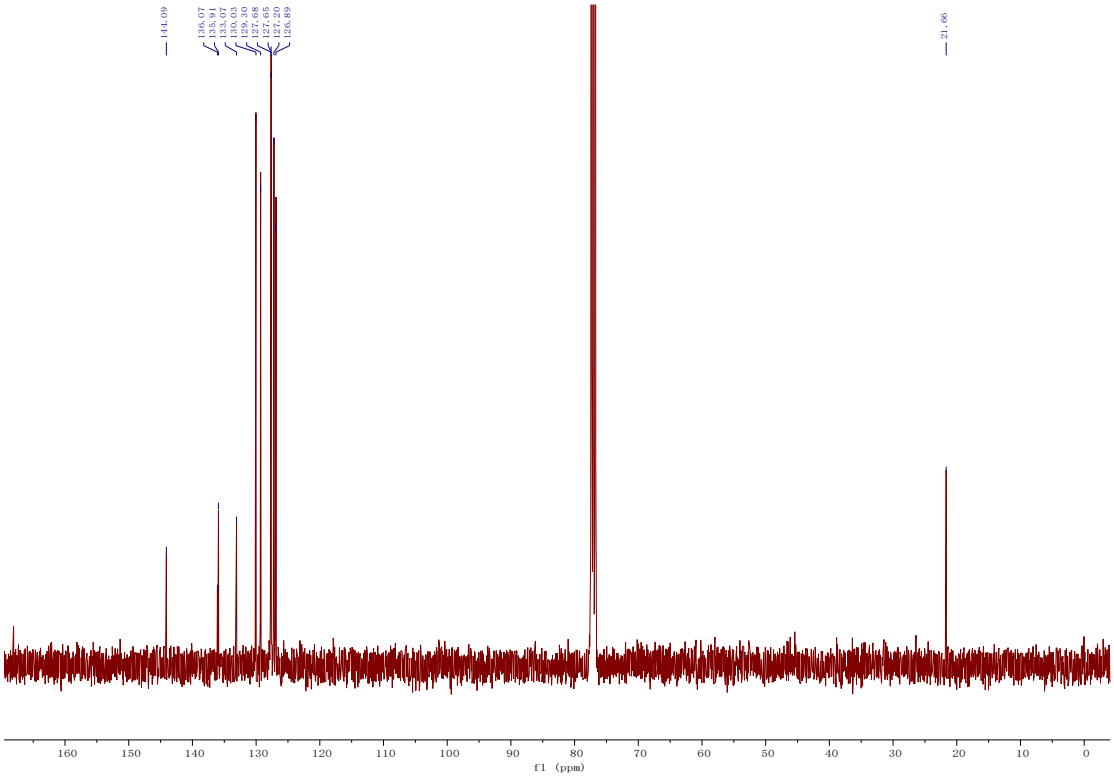

7.71
7.67
7.65
7.64
7.62
7.20
7.18
7.16
7.07
7.05
6.97
6.96
6.94
3.91
3.89
3.87
2.89
2.86
2.84
2.35
3.00
3.00
1.05
1.00
2.00
2.00
3.00
f1 (ppm)

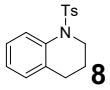

144.09
141.98
133.94
131.81
129.67
127.68
127.31
126.15
125.74
114.98
49.97
27.88
21.55
f1 (ppm)


S
N
Ts

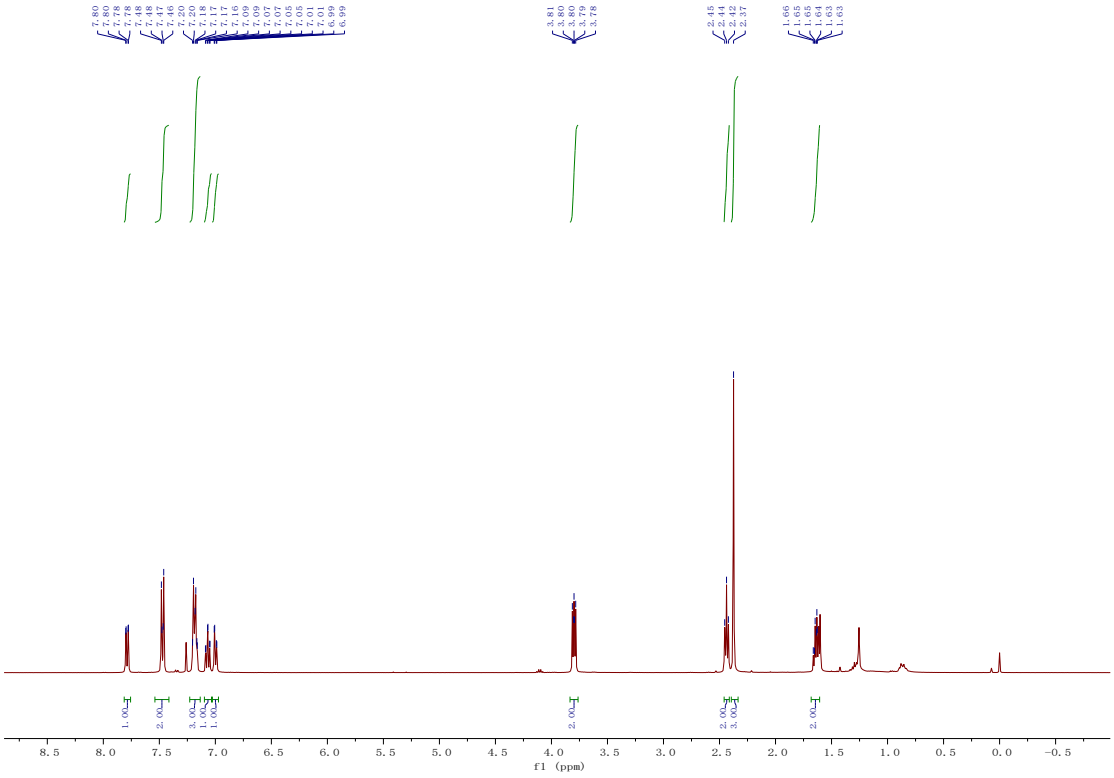
7

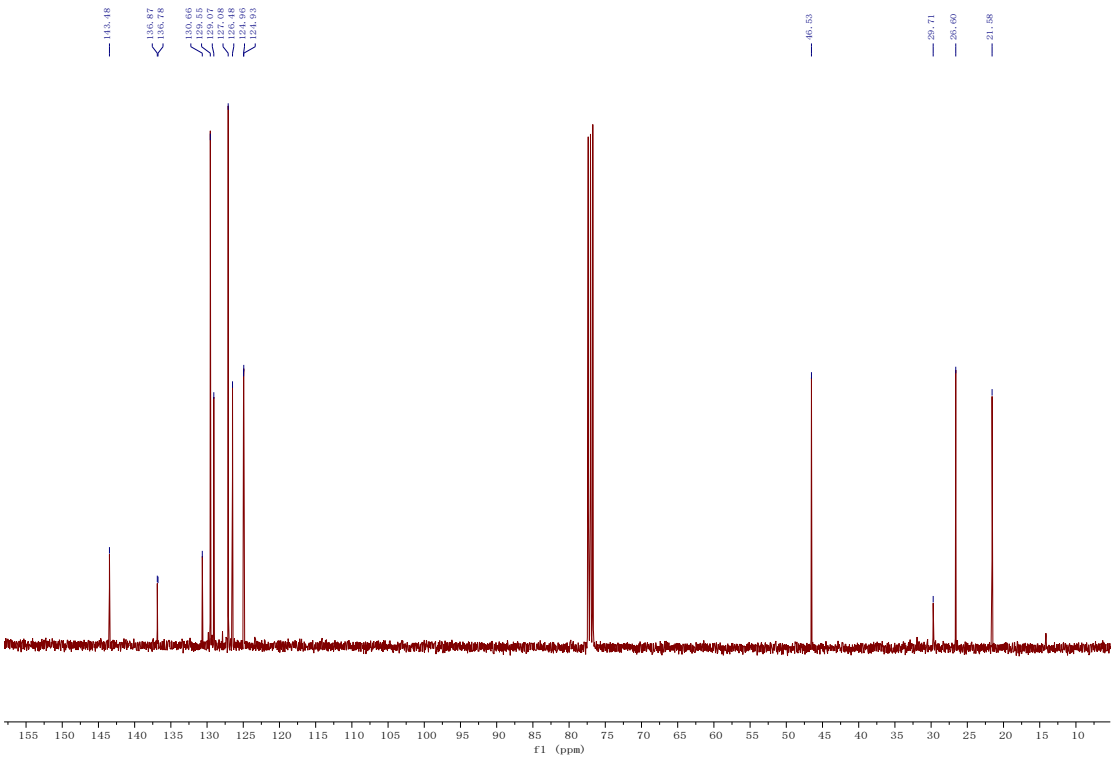

7.76
7.75
7.74
7.73
7.35
7.34
7.33
7.32
7.31
7.24
7.24
7.22
7.22
7.20
7.14
7.14
7.13
7.12
7.11
7.11
7.06
7.04
2.38
2.00
2.00
2.00
4.00
2.02
3.00
f1 (ppm)


144.09
136.07
135.91
133.97
130.03
129.30
127.68
127.65
127.20
126.89
21.66
f1 (ppm)


Ts
N

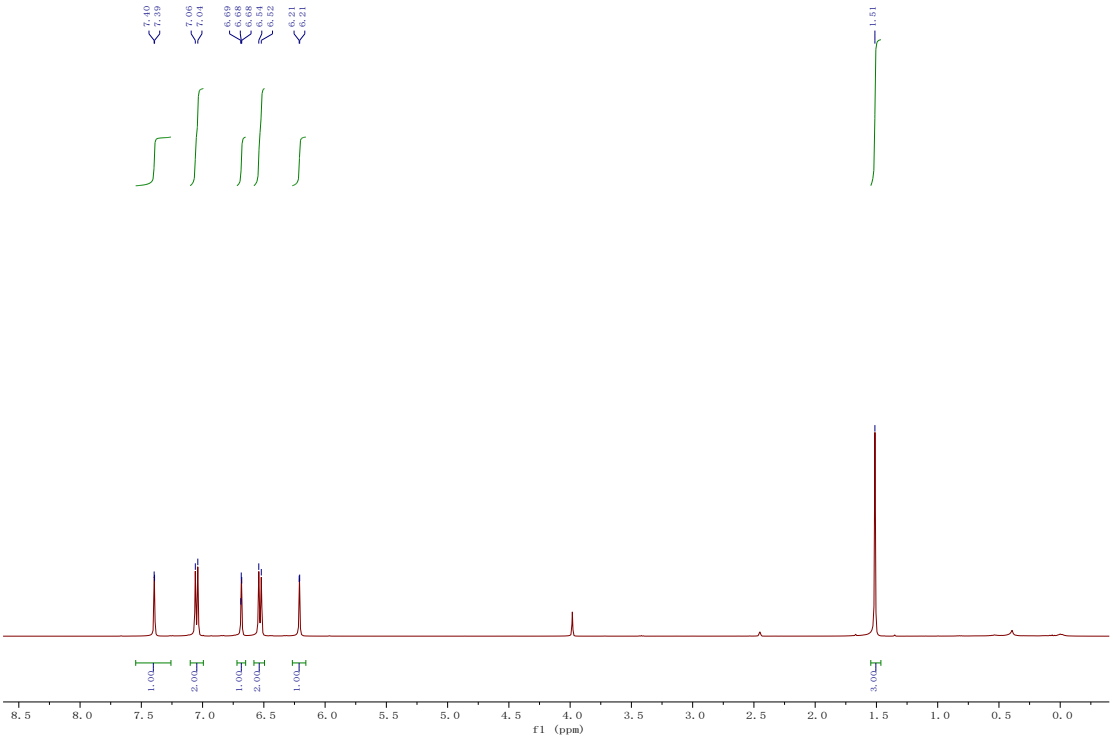
8

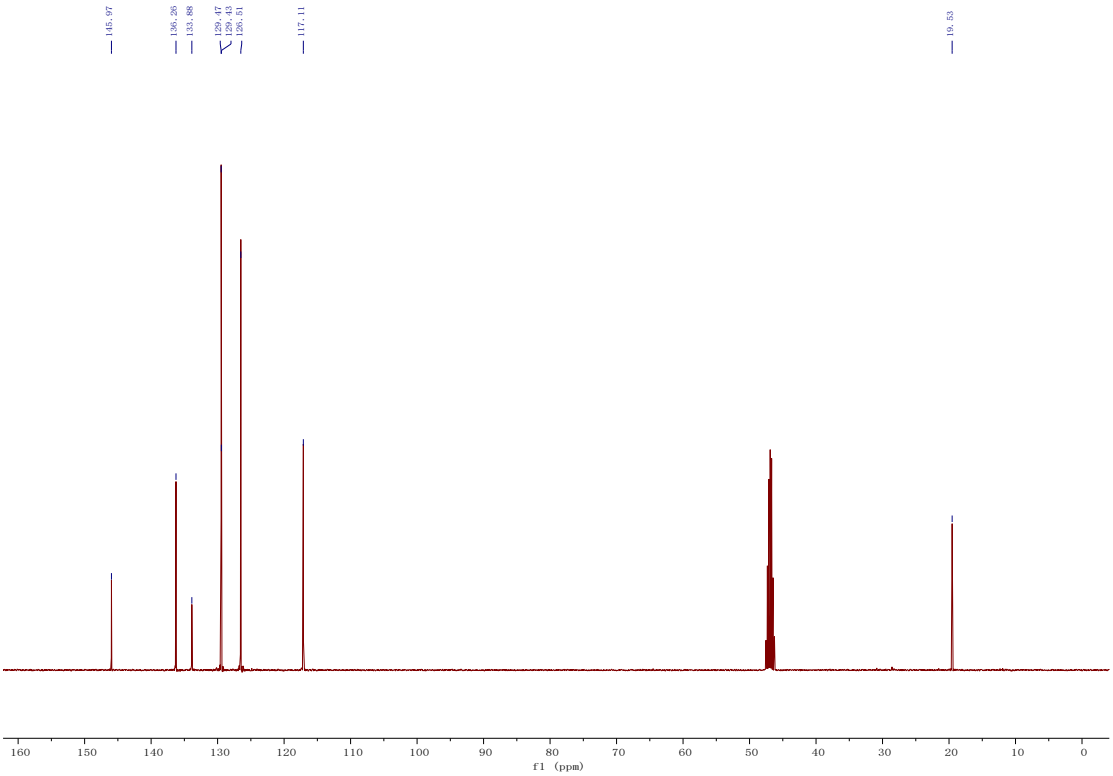

7.80
7.80
7.78
7.78
7.48
7.48
7.47
7.46
7.20
7.18
7.17
7.17
7.16
7.09
7.09
7.07
7.07
7.05
7.05
7.01
7.01
6.99
6.99
3.81
3.80
3.80
3.79
3.78
2.45
2.14
2.42
2.37
1.66
1.65
1.65
1.64
1.63
1.63
1.00
2.00
3.00
1.00
1.00
2.00
2.00
3.00
2.00
f1 (ppm)

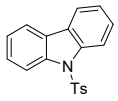

143.48
136.87
136.78
130.66
129.15
128.57
127.08
126.48
124.96
124.93
46.53
29.71
26.60
21.58
f1 (ppm)


N
N
Ts

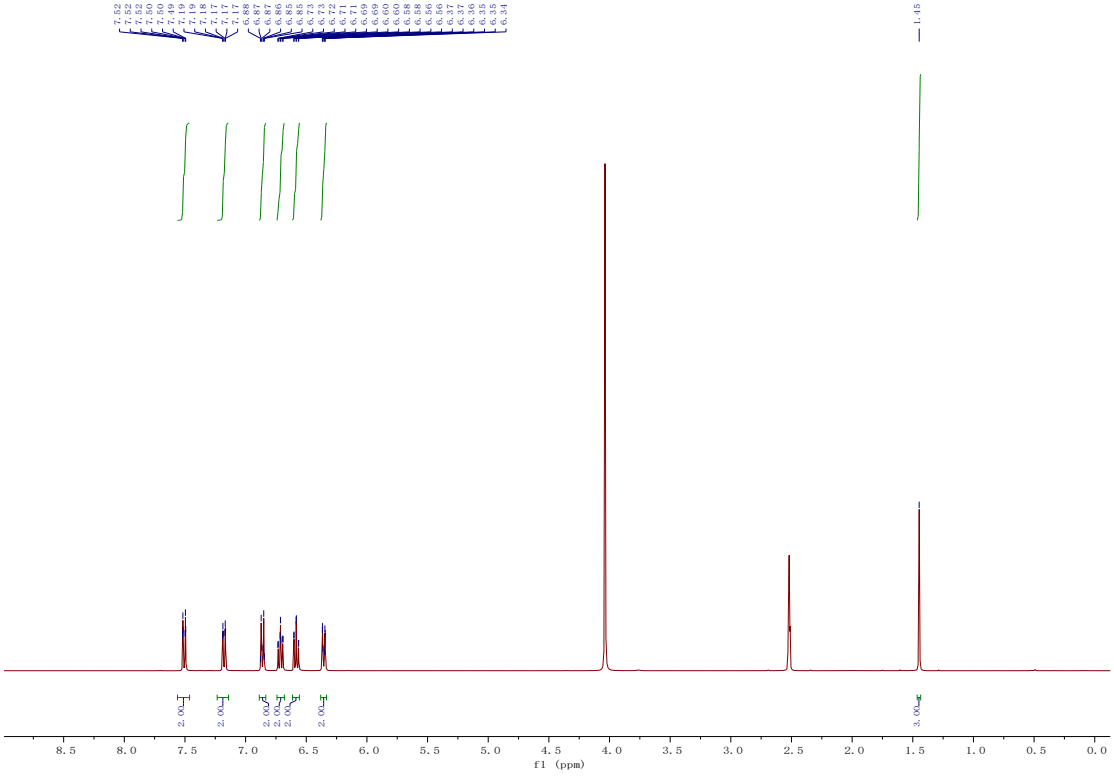
9

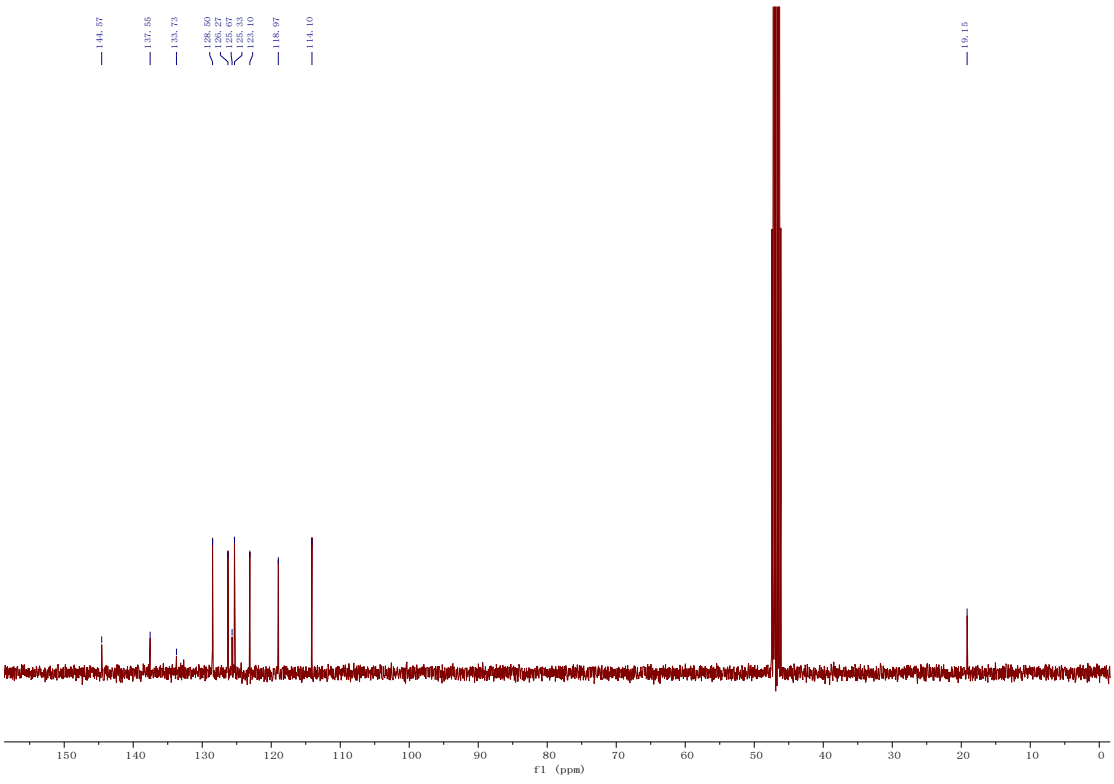

7.40
7.39
7.06
7.04
6.69
6.68
6.68
6.54
6.52
6.21
6.21
1.51
1.00
2.00
1.00
2.00
1.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

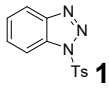

145.97
136.26
133.88
129.47
129.43
126.91
117.11
19.53
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
Ts

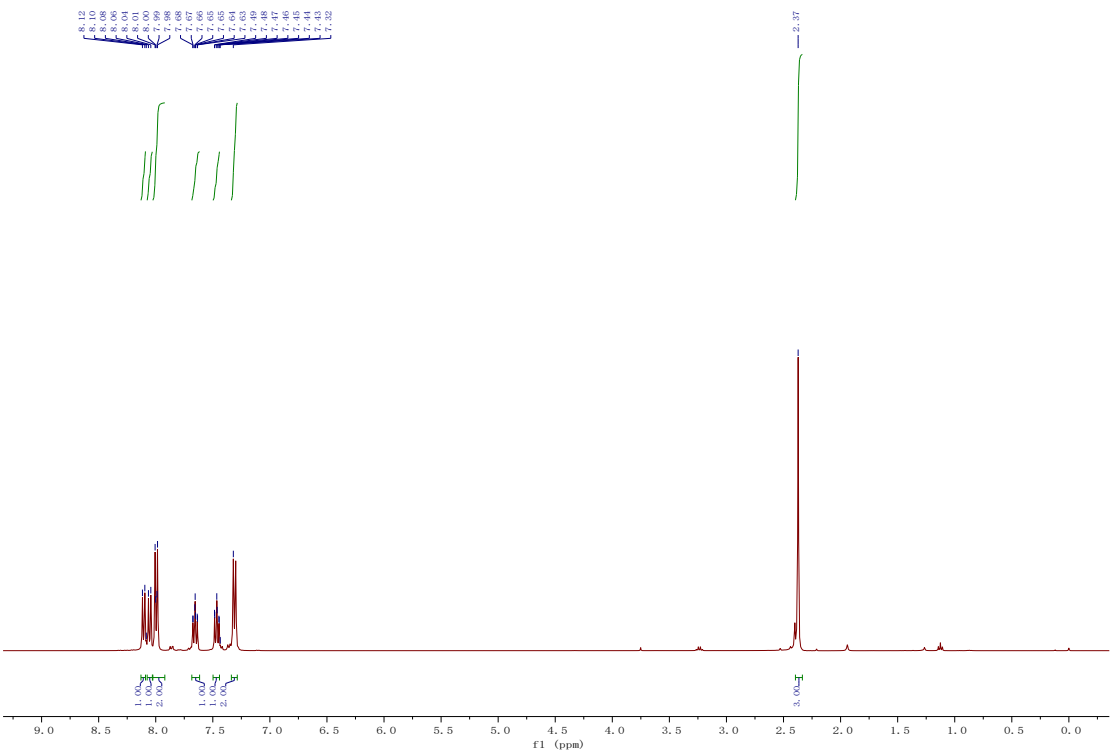
10

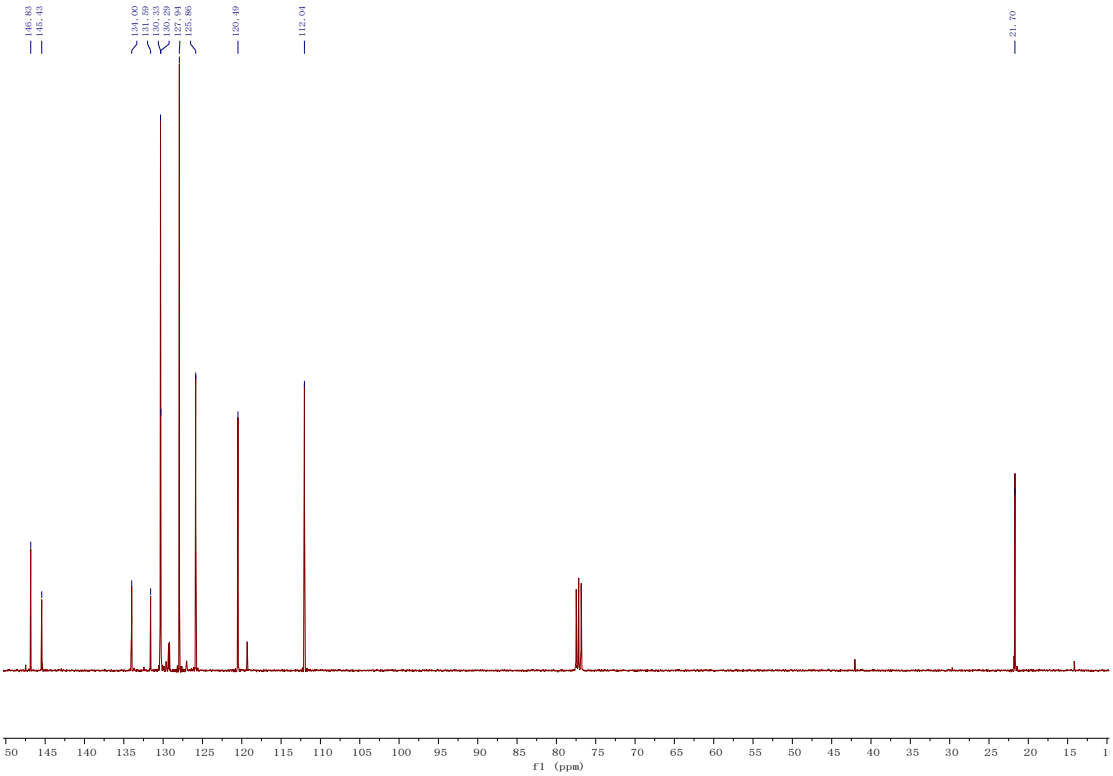

7.52
7.52
7.52
7.50
7.50
7.49
7.19
7.19
7.18
7.17
7.17
7.17
6.88
6.87
6.87
6.86
6.85
6.85
6.73
6.73
6.72
6.71
6.71
6.69
6.69
6.60
6.60
6.58
6.58
6.56
6.56
6.37
6.37
6.36
6.35
6.35
6.34
1.45
2.00
2.00
2.00
2.00
2.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

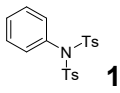

144.57
137.65
133.73
128.50
126.27
125.67
125.33
123.10
118.97
114.10
19.15
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
N
N
Ts

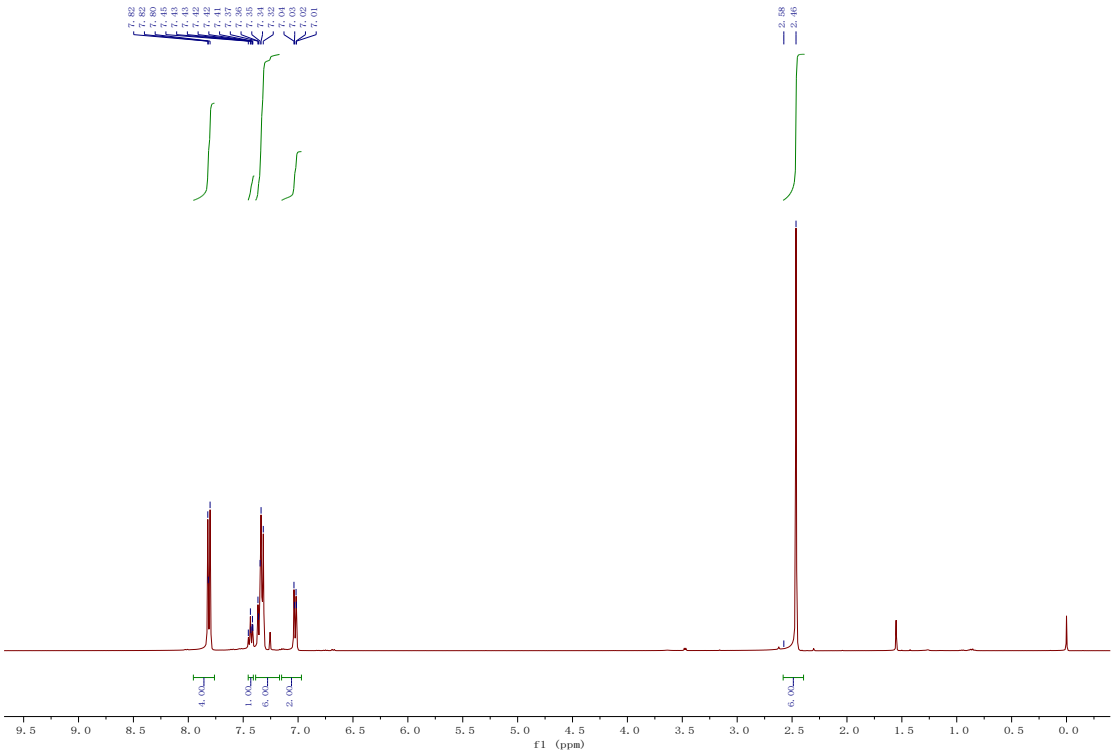
11

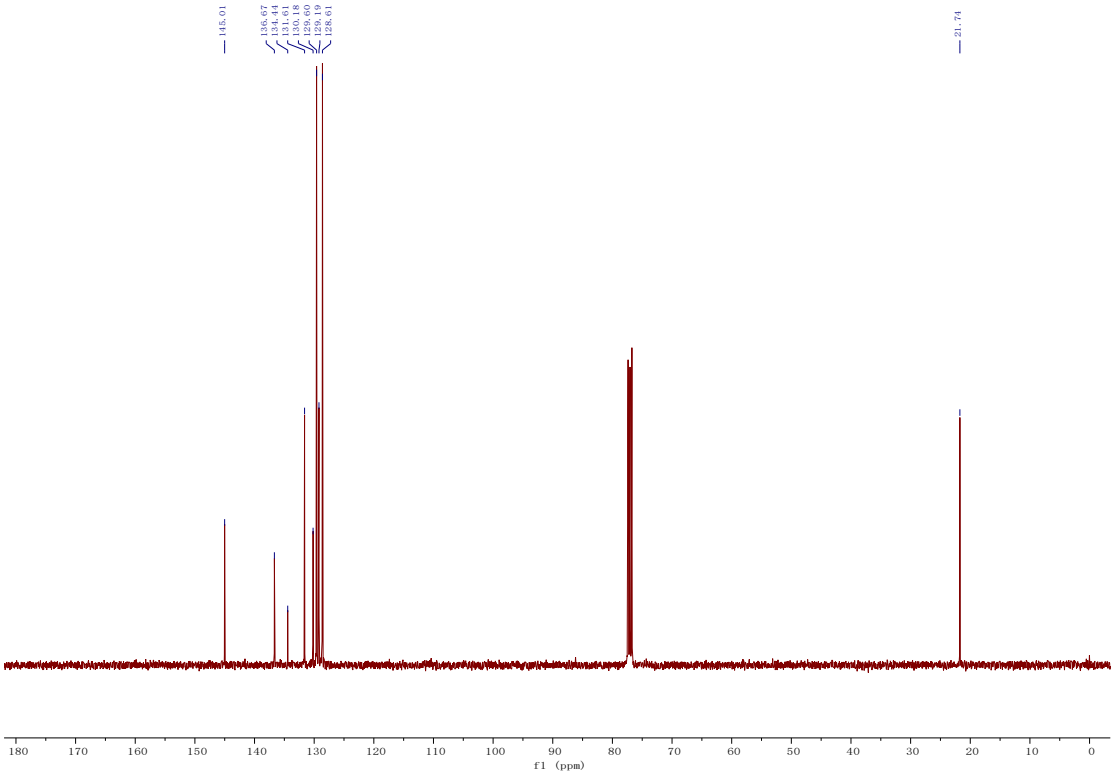

8.12
8.10
8.08
8.06
8.04
8.01
8.00
7.99
7.98
7.68
7.67
7.66
7.65
7.64
7.63
7.49
7.48
7.47
7.46
7.45
7.44
7.43
7.32
2.37
1.00
1.00
2.00
1.00
1.00
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


146.83
145.43
134.00
131.59
130.33
130.29
127.94
125.86
120.49
112.04
21.70
50
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)


Ts
N
Ts

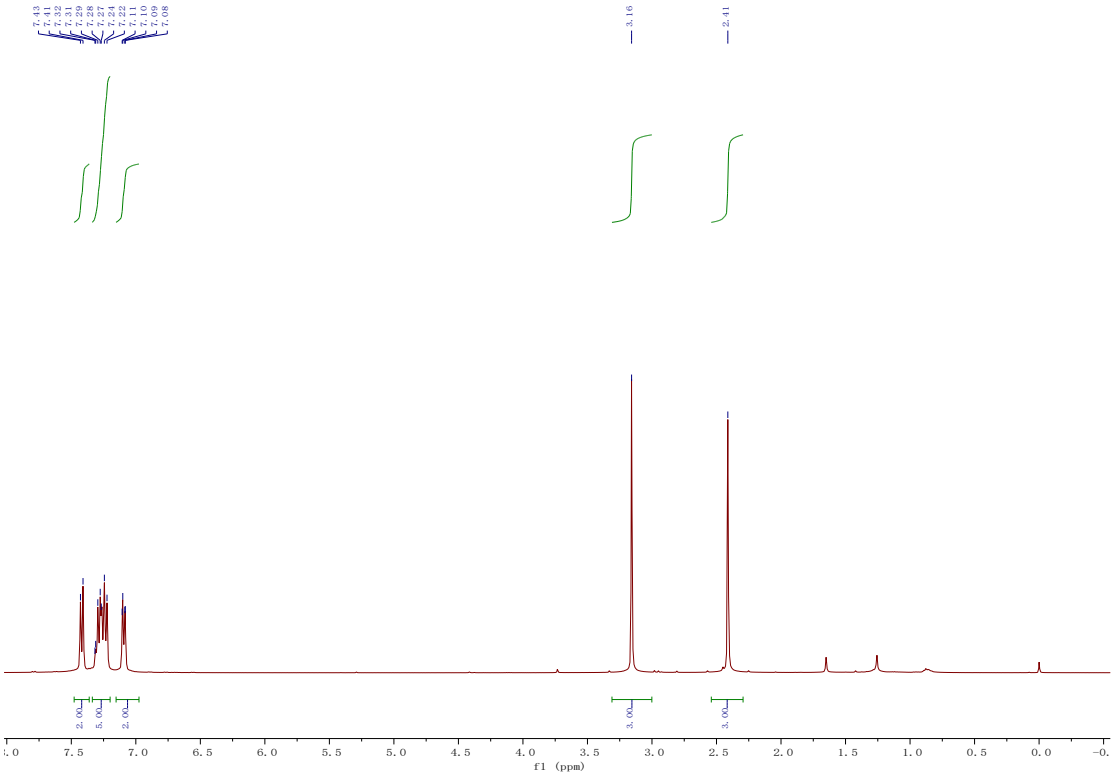
12

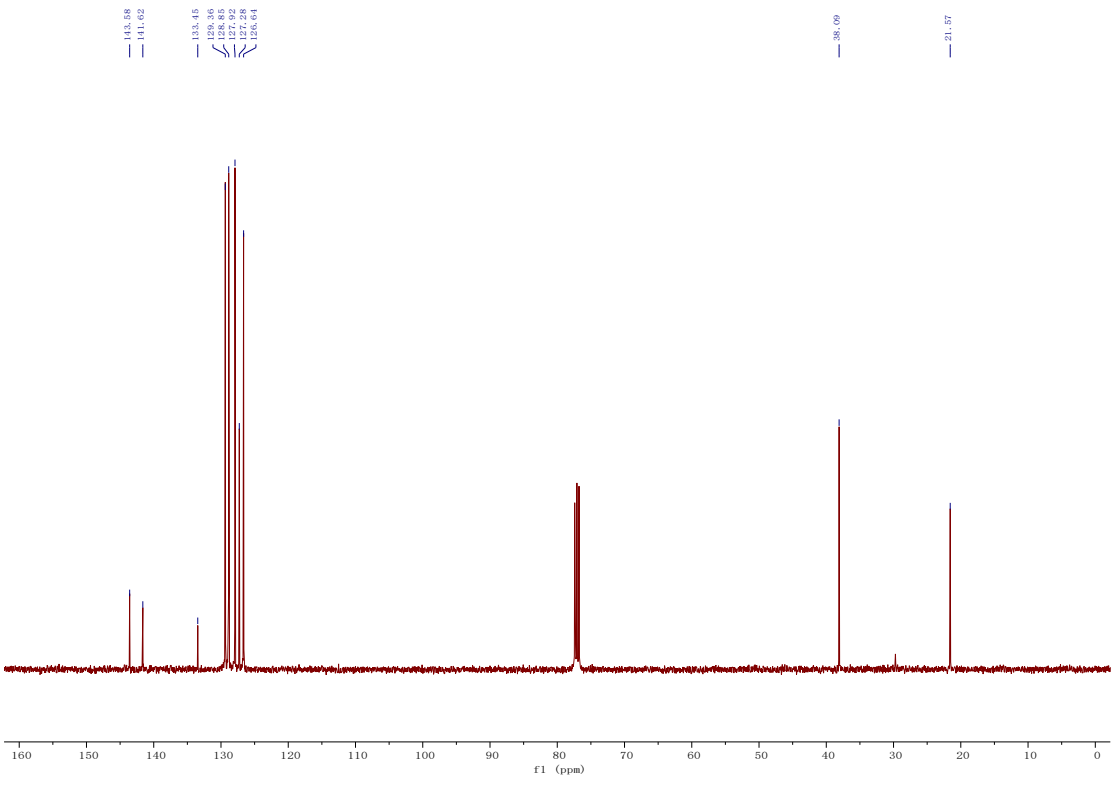

7.82
7.82
7.80
7.45
7.43
7.43
7.42
7.42
7.41
7.37
7.36
7.35
7.34
7.32
7.04
7.03
7.02
7.01
2.58
2.46
4.00
1.00
6.06
2.06
6.00
f1 (ppm)

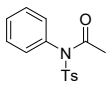

145.01
136.67
134.44
131.61
130.18
129.60
129.19
128.61
21.74
f1 (ppm)


N
Ts

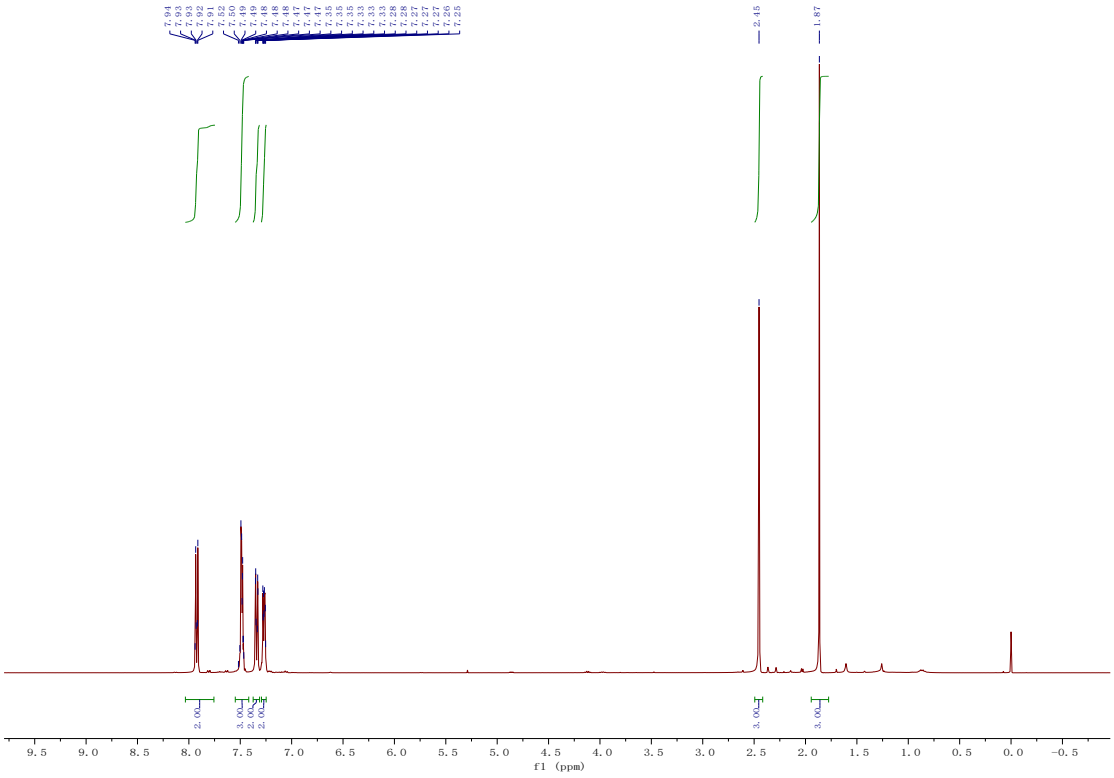
13

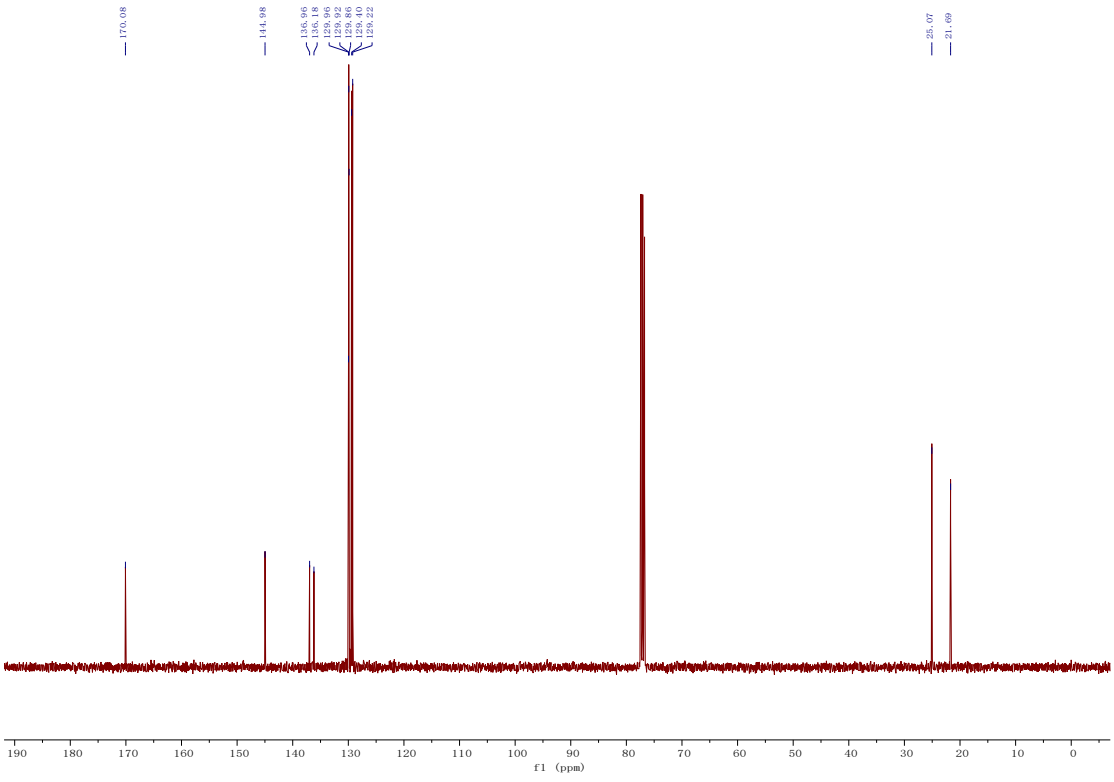

7.43
7.41
7.32
7.31
7.29
7.28
7.27
7.24
7.22
7.11
7.10
7.09
7.08
3.16
2.41
2.00
5.08
2.00
3.00
3.00
f1 (ppm)

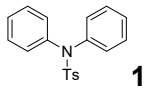

143.58
141.62
133.45
129.36
128.85
127.92
127.28
126.64
38.09
21.57
f1 (ppm)


O
N
Ts

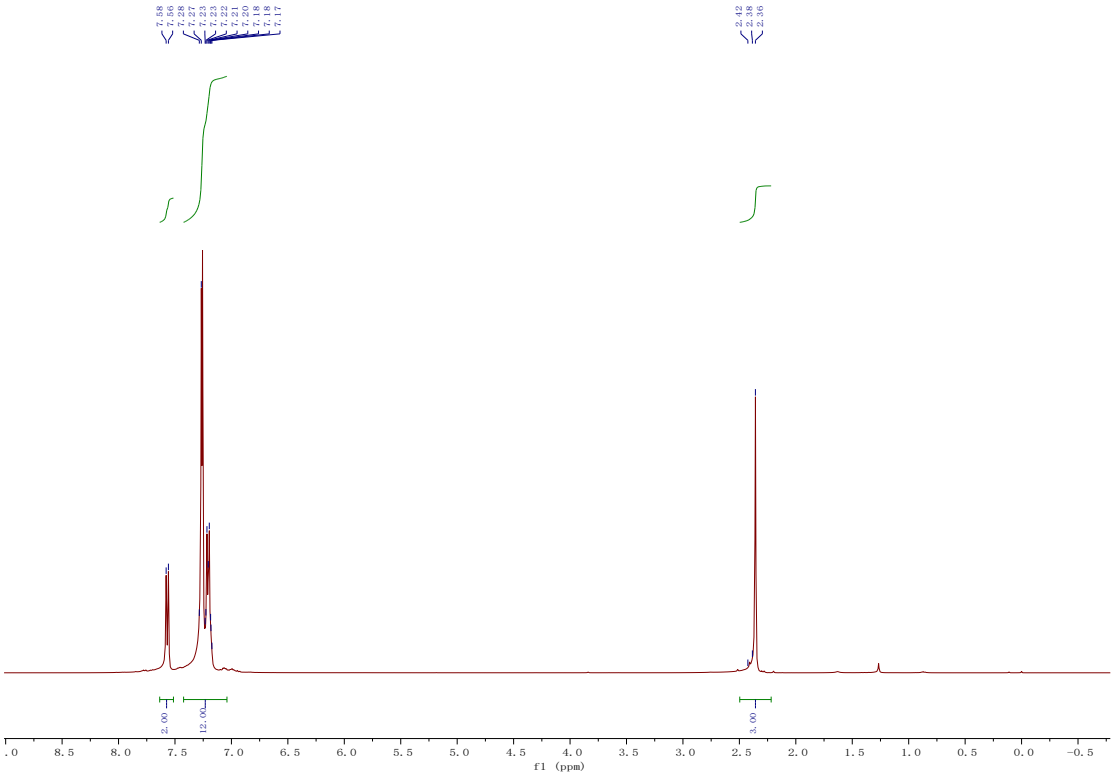
14

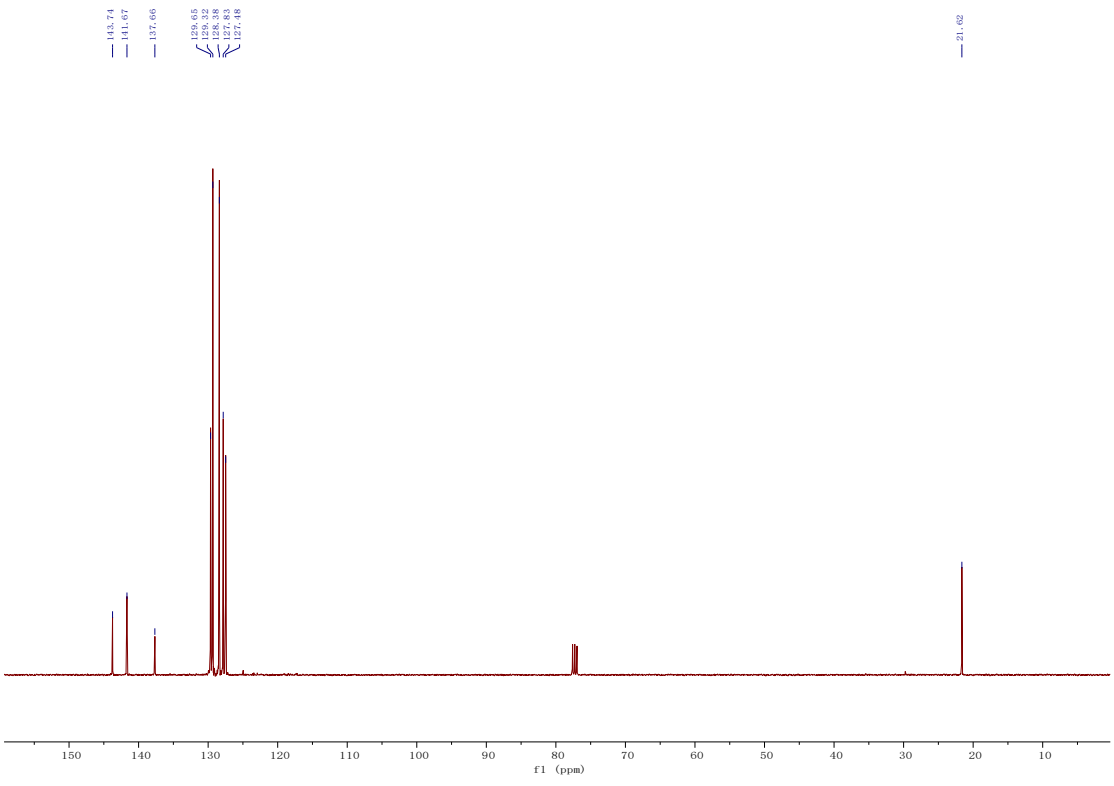

7.94
7.93
7.93
7.92
7.91
7.91
7.52
7.50
7.49
7.49
7.48
7.48
7.48
7.47
7.47
7.47
7.35
7.35
7.35
7.33
7.33
7.28
7.28
7.27
7.27
7.27
7.26
7.25
2.45
1.87
2.00
3.00
2.00
2.00
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

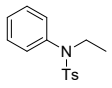

170.08
144.98
136.96
136.18
129.96
129.92
129.86
129.40
129.22
25.07
21.69
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


N
Ts

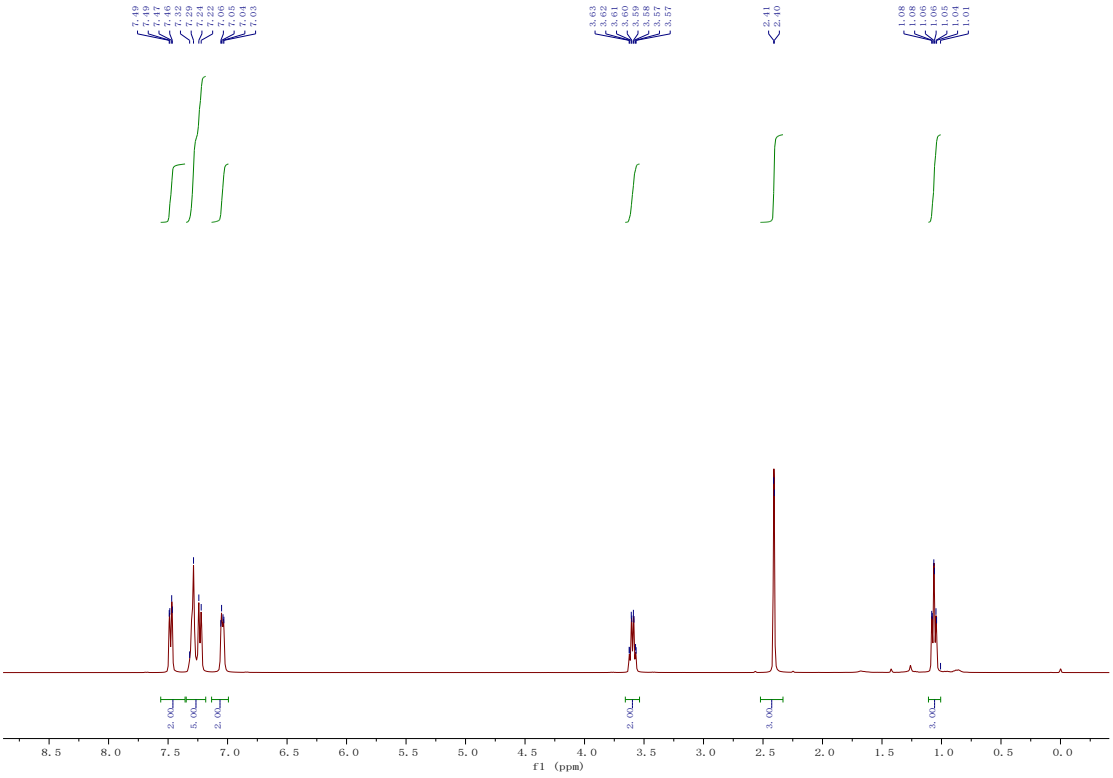
15

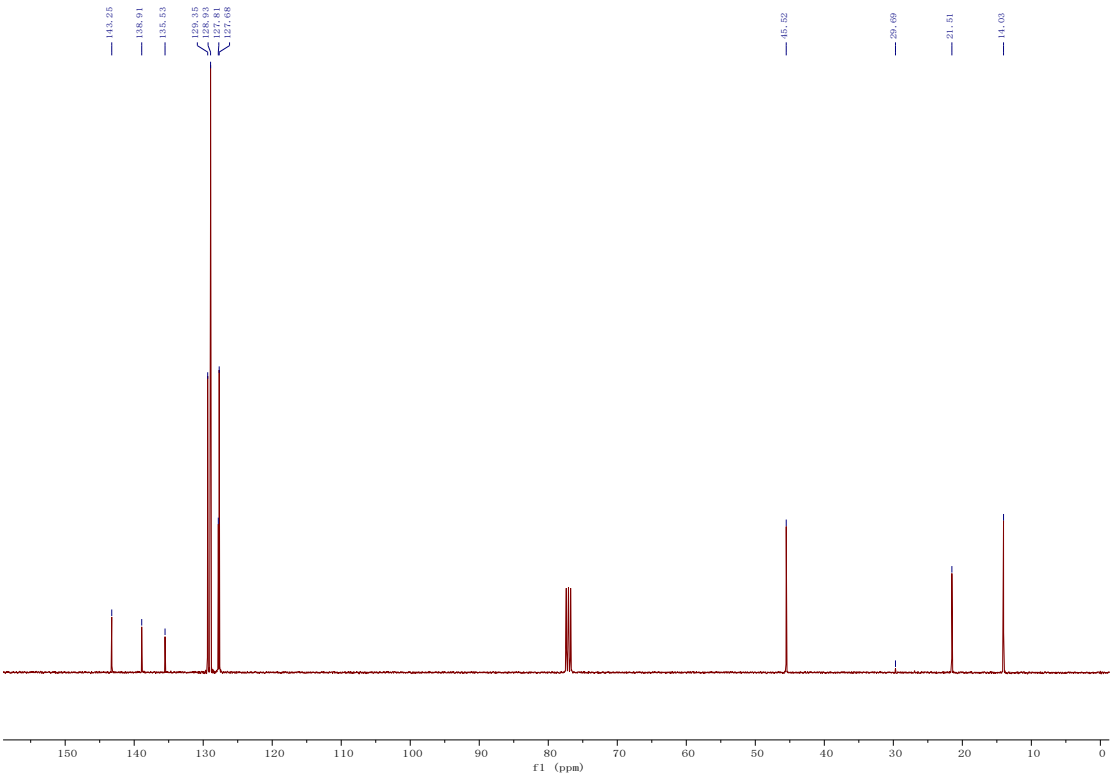

7.58
7.56
7.28
7.27
7.23
7.22
7.21
7.20
7.18
7.18
7.17
2.42
2.38
2.36
2.00
12.00
3.00
f1 (ppm)

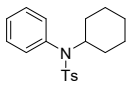

143.74
141.67
137.66
129.65
129.32
128.38
127.83
127.48
21.62
f1 (ppm)


N
Ts

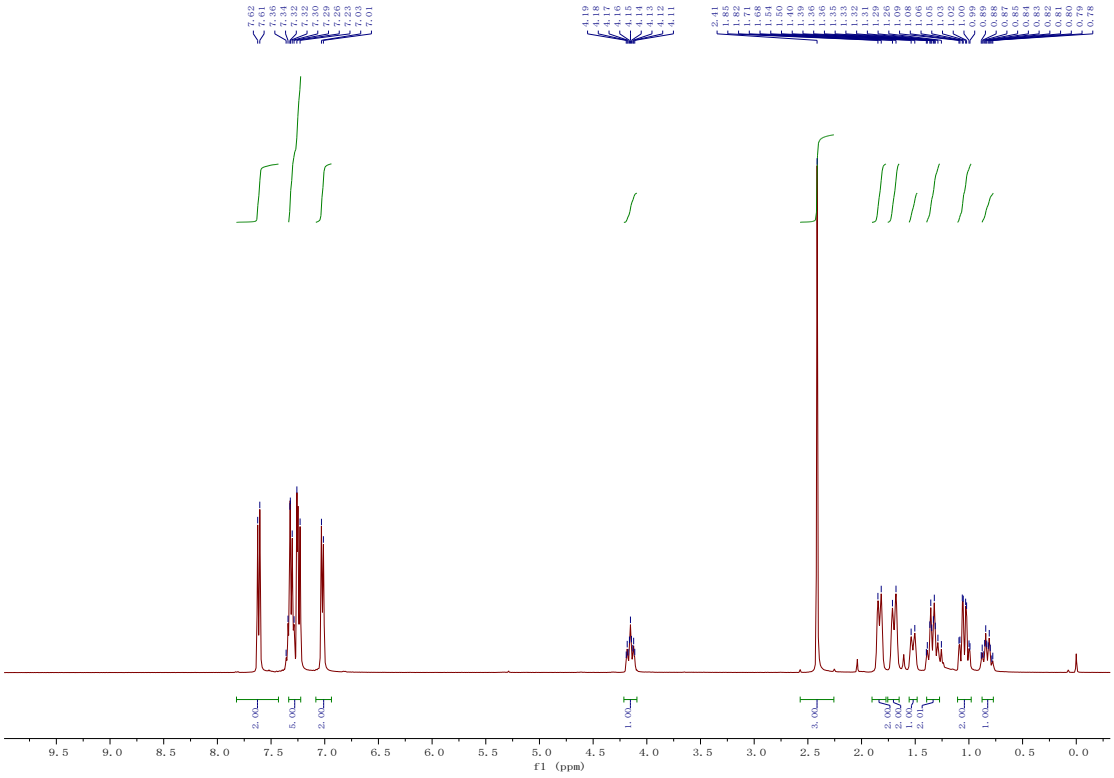
16

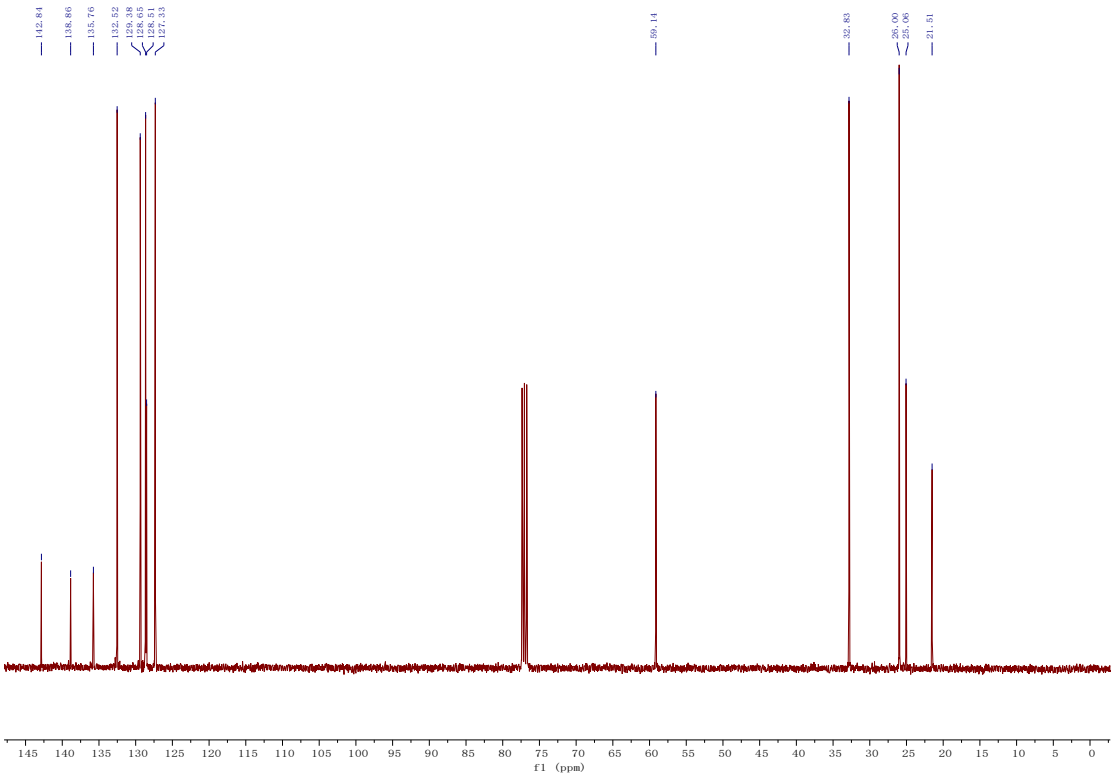

7.49
7.49
7.47
7.46
7.32
7.29
7.24
7.22
7.05
7.04
7.03
3.63
3.62
3.61
3.60
3.59
3.58
3.57
3.57
2.41
2.40
1.08
1.08
1.06
1.06
1.05
1.04
1.01
2.00
5.00
2.00
2.00
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

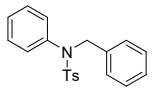

143.25
138.91
135.53
129.35
128.93
127.81
127.68
45.52
29.69
21.51
14.03
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
Ts

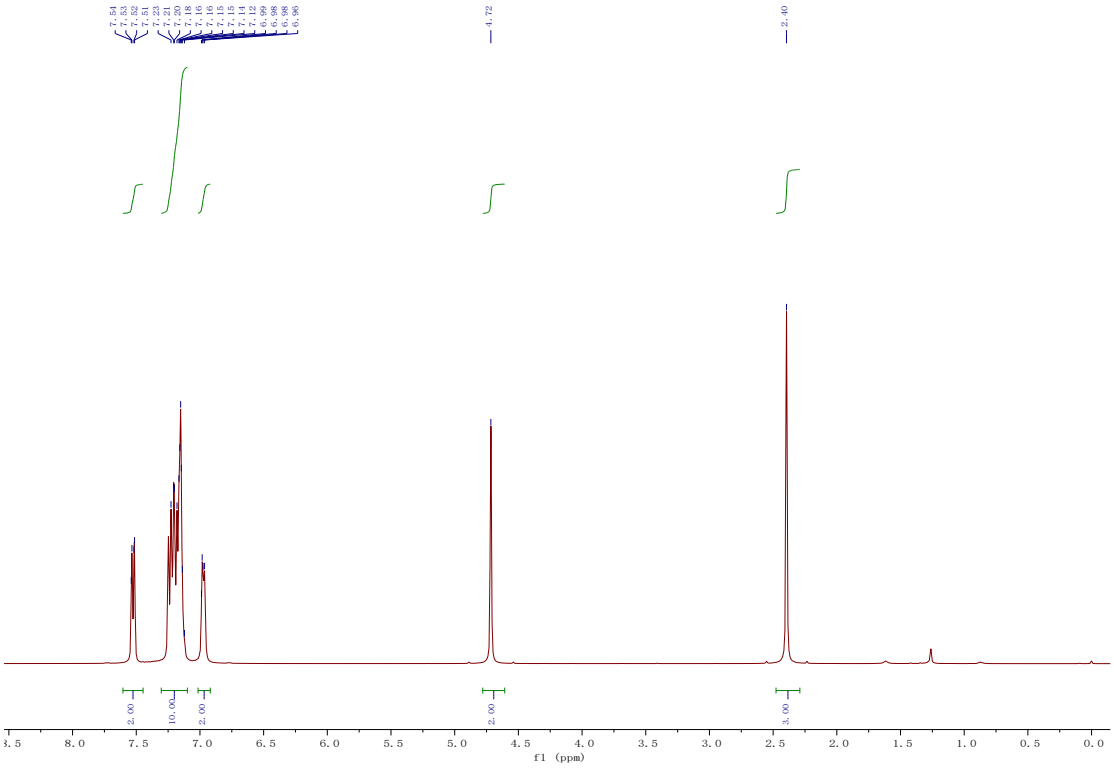
17

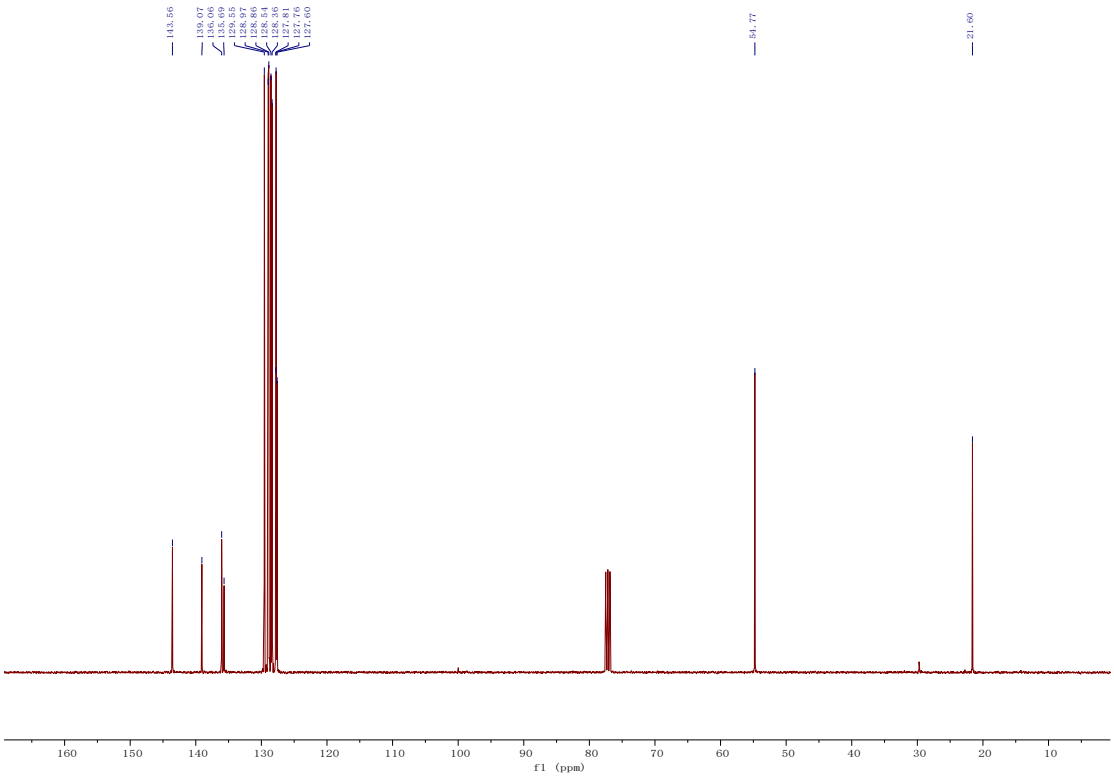

7.62
7.61
7.36
7.34
7.32
7.32
7.30
7.29
7.25
7.23
7.03
7.01
4.19
4.18
4.17
4.16
4.15
4.14
4.13
4.12
4.11
2.41
1.85
1.82
1.71
1.68
1.54
1.50
1.40
1.39
1.36
1.35
1.33
1.32
1.31
1.29
1.26
1.09
1.08
1.06
1.05
1.03
1.02
1.00
0.99
0.89
0.88
0.87
0.85
0.84
0.83
0.82
0.81
0.80
0.79
0.78
2.00
5.00
2.00
1.00
3.00
2.00
2.00
1.00
2.01
2.00
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

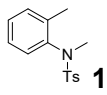

142.84
138.86
135.76
132.52
129.38
128.65
128.51
127.33
89.14
32.83
26.00
25.06
21.51
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


N
Ts

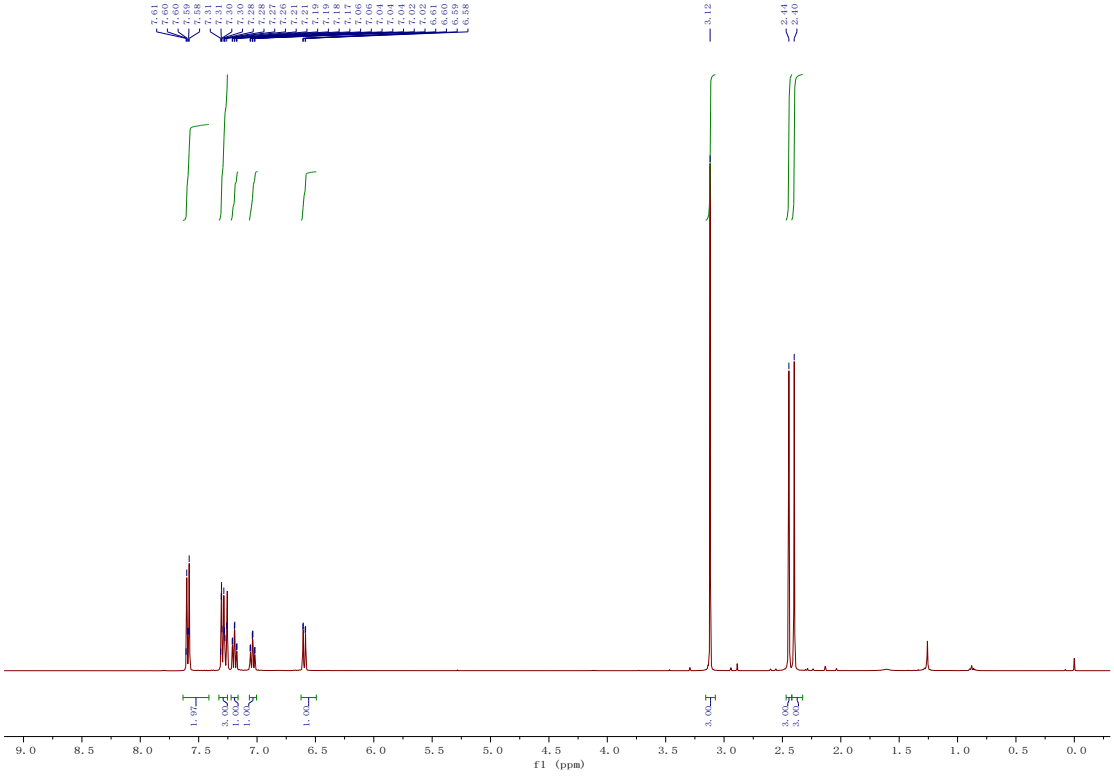
18

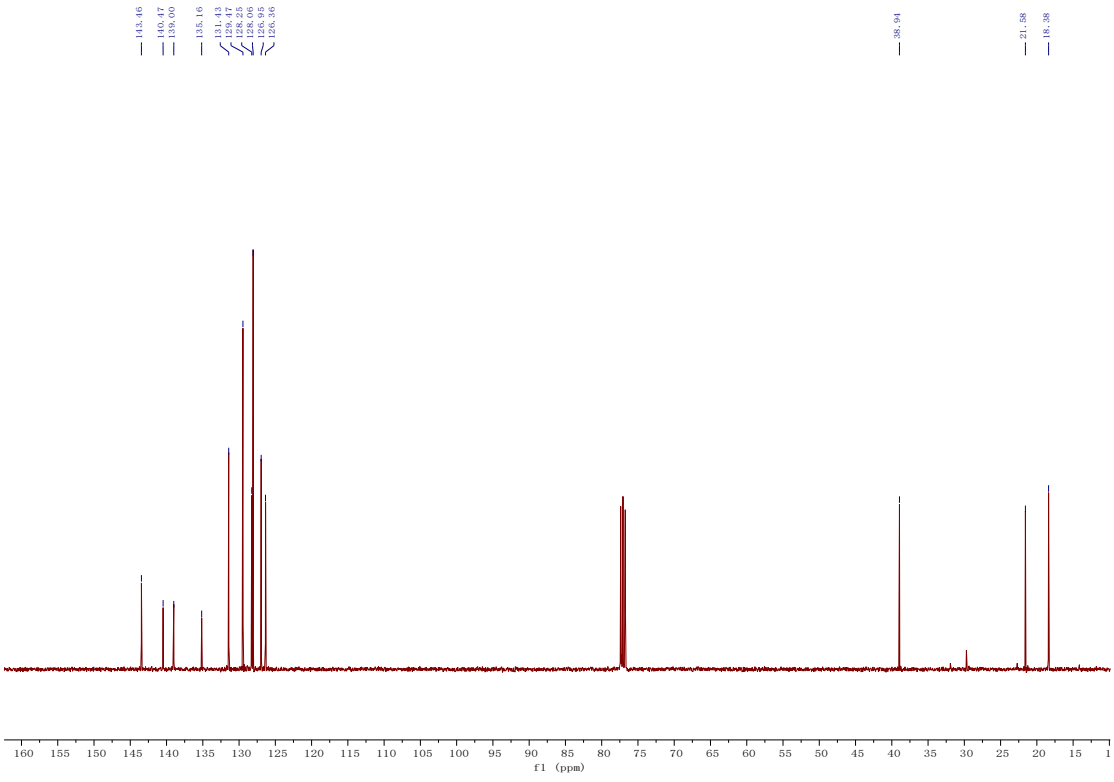

7.54
7.53
7.52
7.51
7.23
7.21
7.20
7.18
7.16
7.15
7.15
7.14
7.12
6.99
6.98
6.98
6.96
4.72
2.40
2.00
10.00
2.00
2.00
3.00
f1 (ppm)

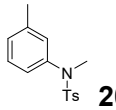

143.56
139.07
135.66
135.69
129.55
128.97
128.86
128.54
128.36
127.81
127.75
127.60
54.77
21.60
f1 (ppm)


N
Ts

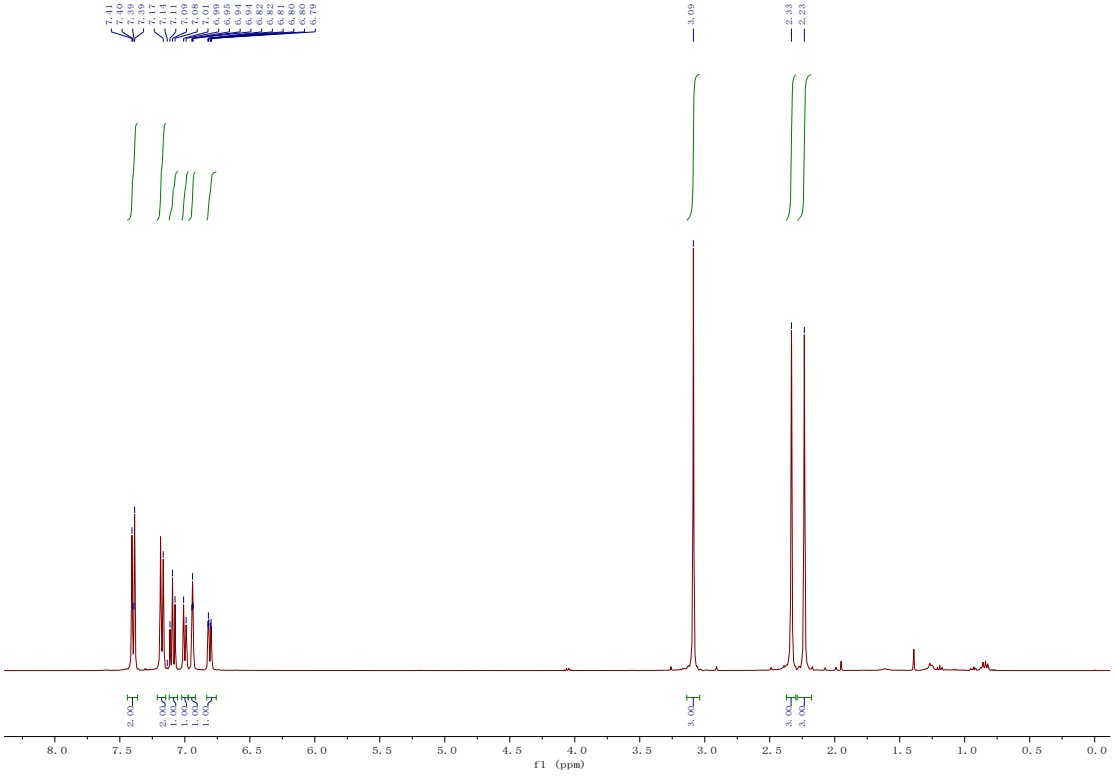
19

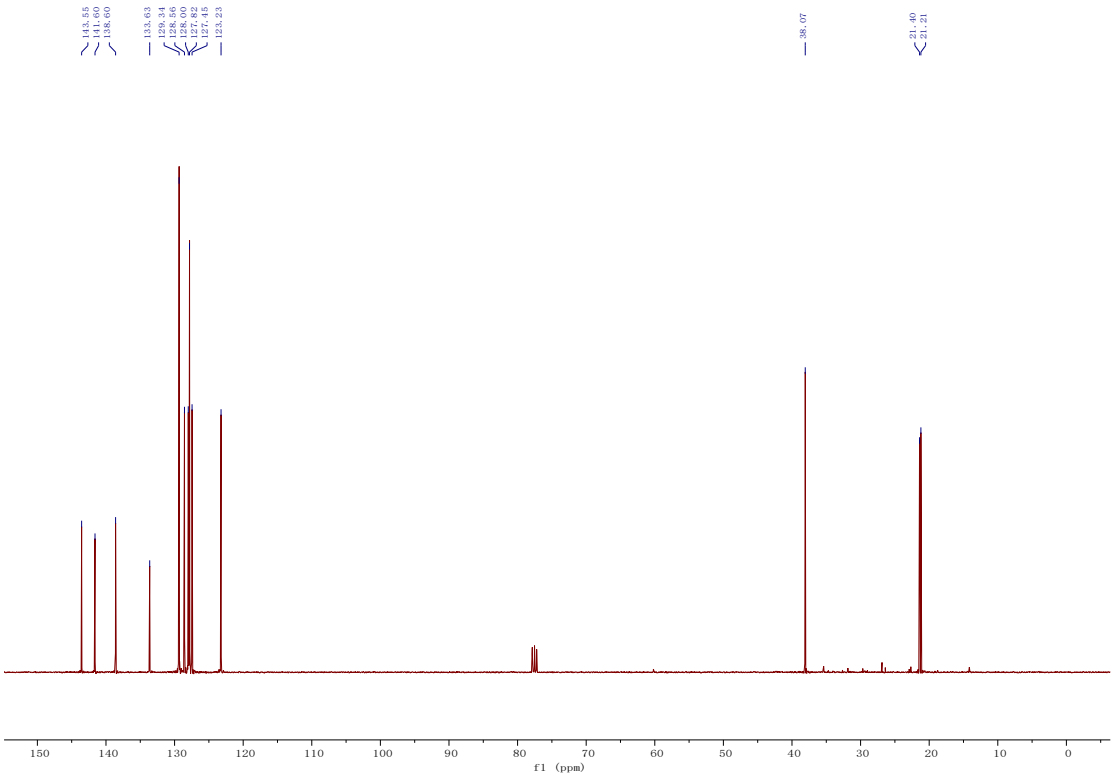

7.61
7.60
7.60
7.59
7.58
7.58
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.26
7.21
7.21
7.19
7.19
7.18
7.18
7.17
7.06
7.06
7.04
7.04
7.04
7.02
7.02
6.61
6.60
6.59
6.58
3.12
2.44
2.40
1.97
3.00
1.00
1.00
1.00
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

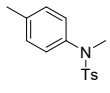

143.46
140.47
139.00
135.16
131.43
129.47
128.55
128.06
126.95
126.36
38.94
21.58
18.38
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
1
f1 (ppm)


N
Ts

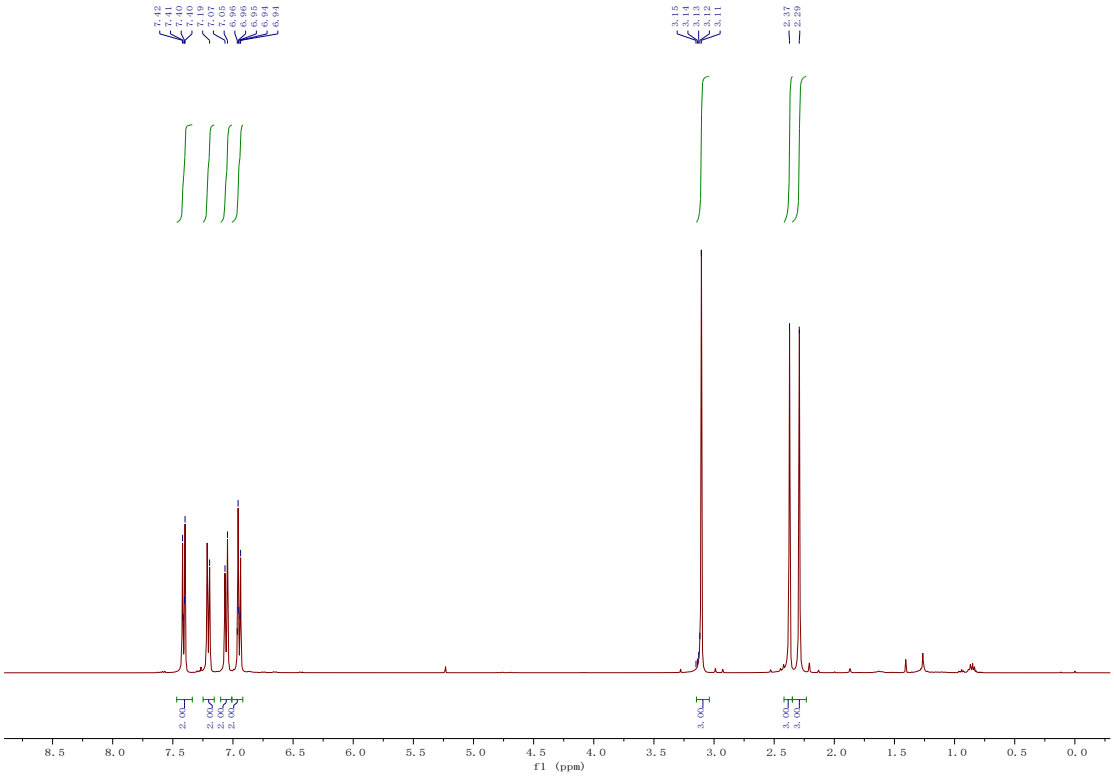
20

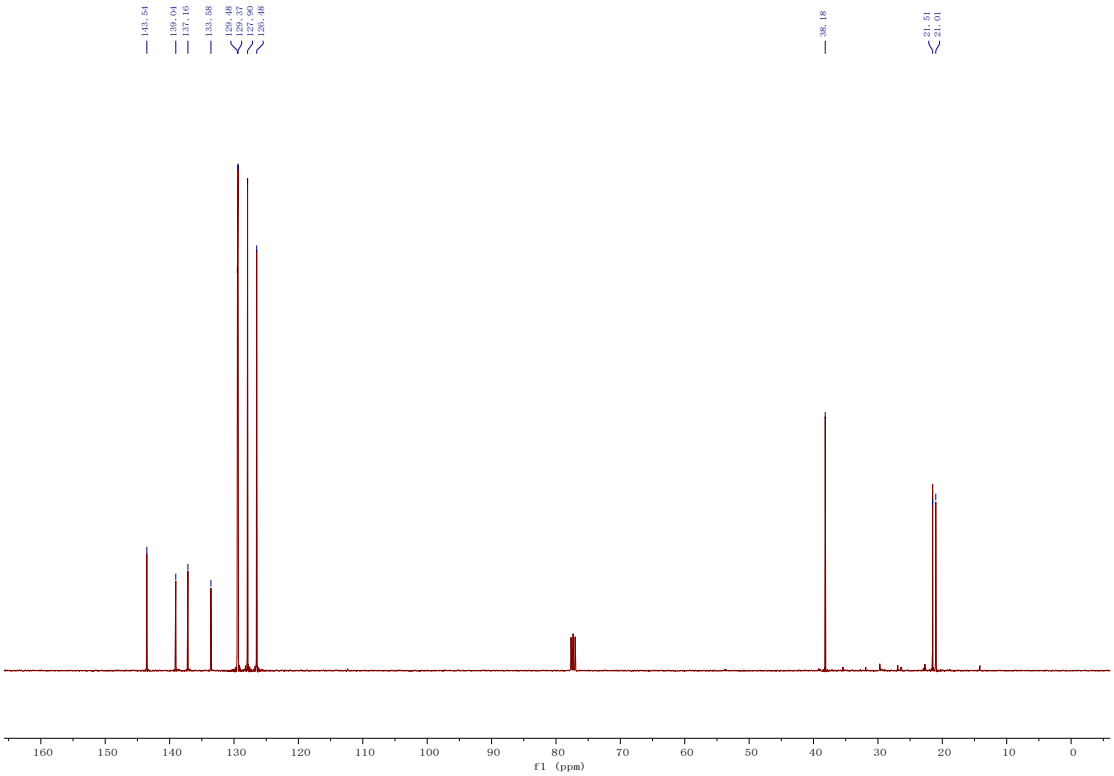

7.41
7.40
7.39
7.39
7.17
7.14
7.11
7.09
7.08
7.01
6.99
6.95
6.94
6.82
6.82
6.81
6.80
6.80
6.79
3.09
2.33
2.23
2.00
2.00
1.00
1.00
1.00
1.00
3.00
3.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

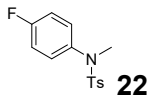

143.55
141.60
138.60
133.63
129.34
128.56
128.00
127.82
127.45
123.23
38.07
21.40
21.21
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
Ts

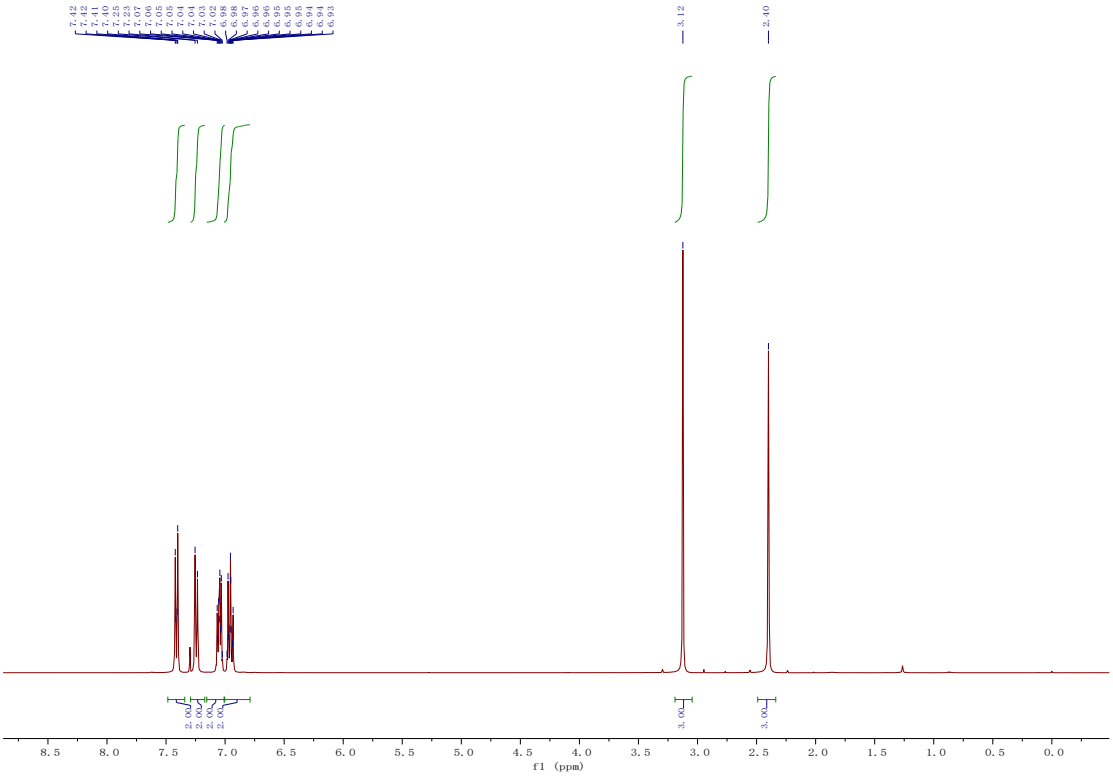
21

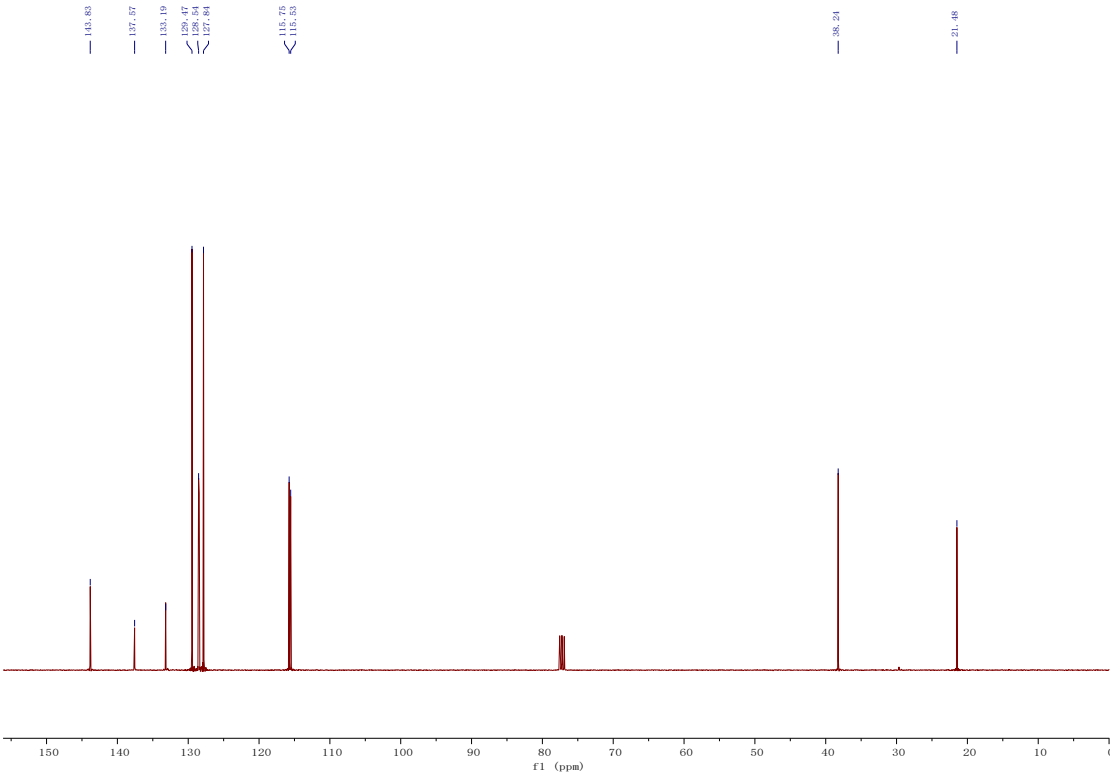

7.42
7.41
7.40
7.19
7.07
7.05
6.96
6.95
6.94
6.94
3.15
3.14
3.13
3.12
3.11
2.37
2.29
2.00
2.00
2.00
2.04
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

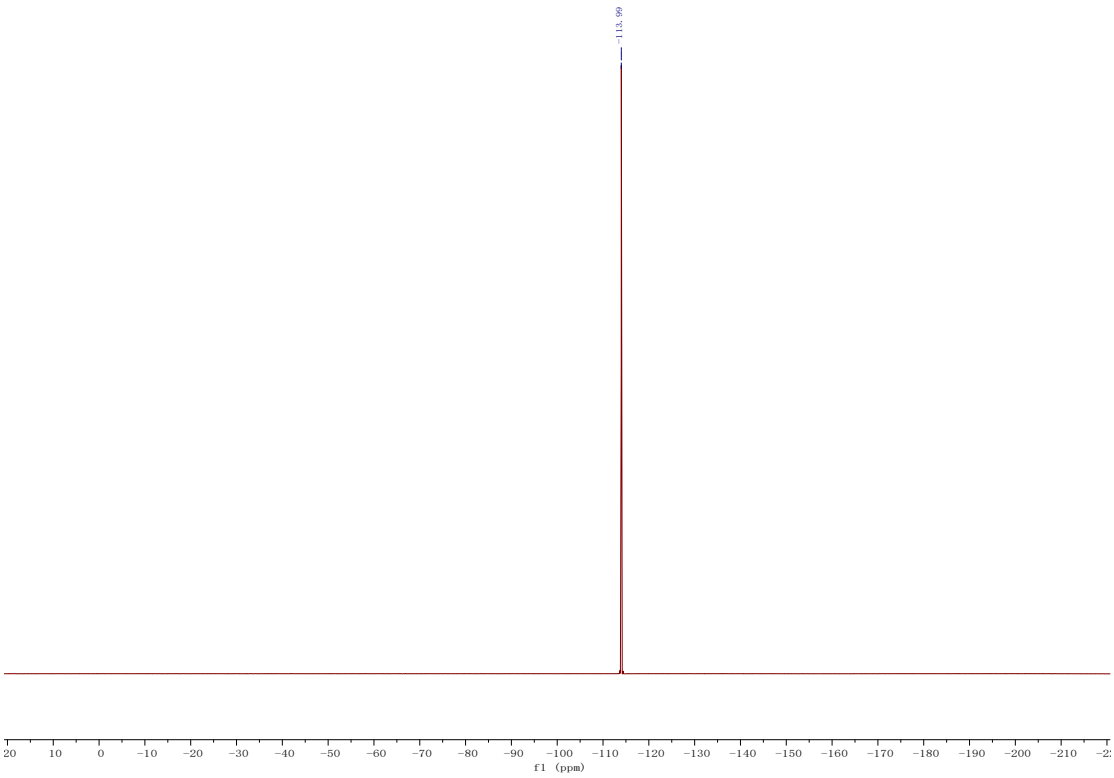

143.54
139.04
137.16
133.58
129.48
128.37
127.90
125.48
38.18
21.51
21.01
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

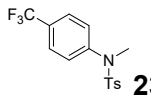

F
N
Ts

22

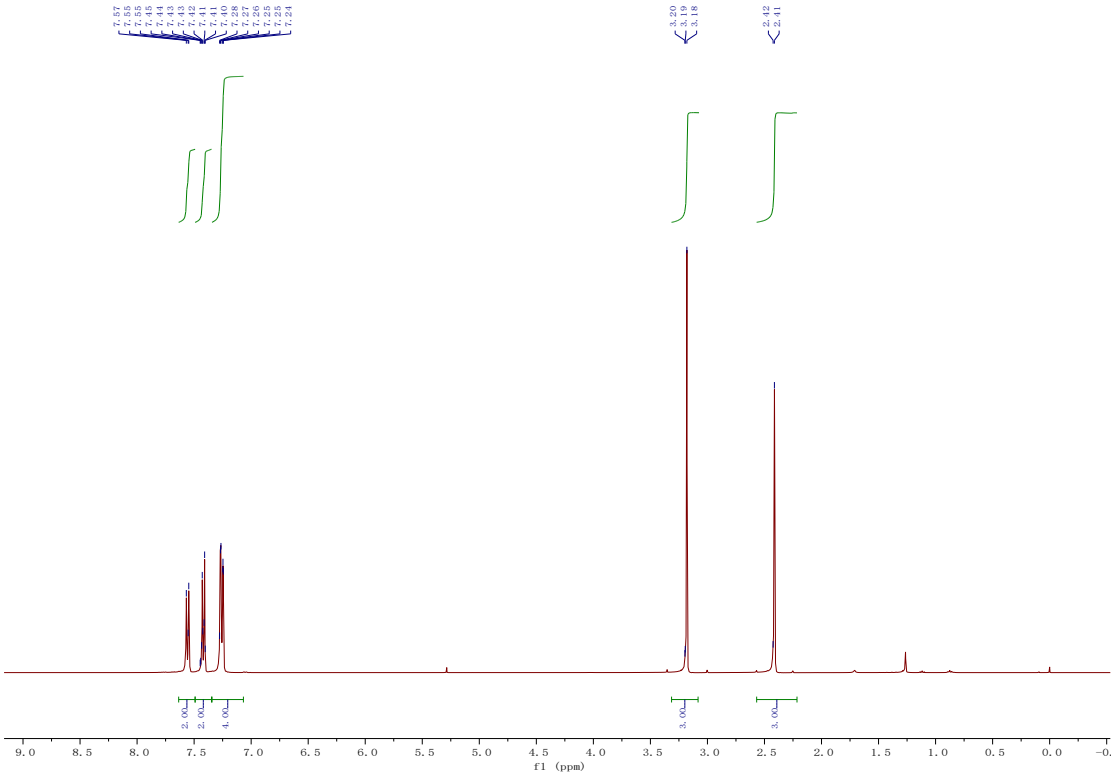

7.42
7.42
7.41
7.40
7.25
7.23
7.07
7.06
7.05
7.05
7.04
7.04
7.03
7.02
7.02
6.98
6.97
6.96
6.96
6.95
6.95
6.94
6.94
6.93
3.12
2.40
2.00
2.00
2.00
2.00
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

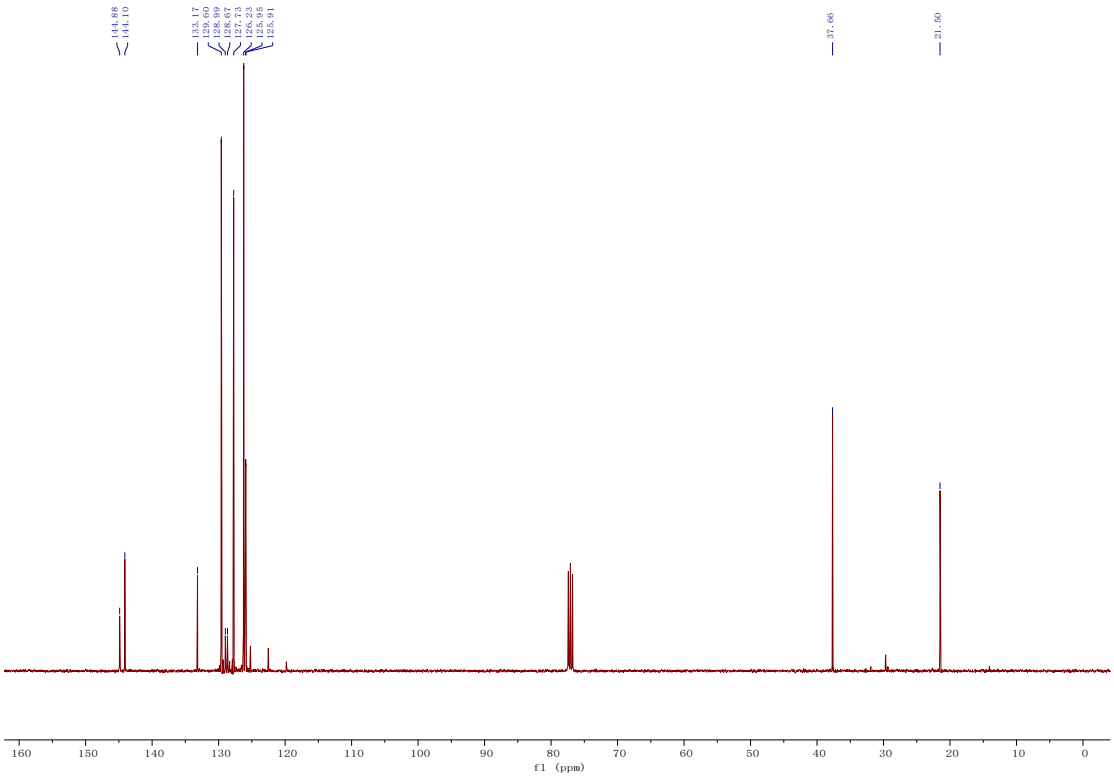

143.83
137.57
133.19
129.47
128.84
127.84
115.75
115.53
38.24
21.48
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

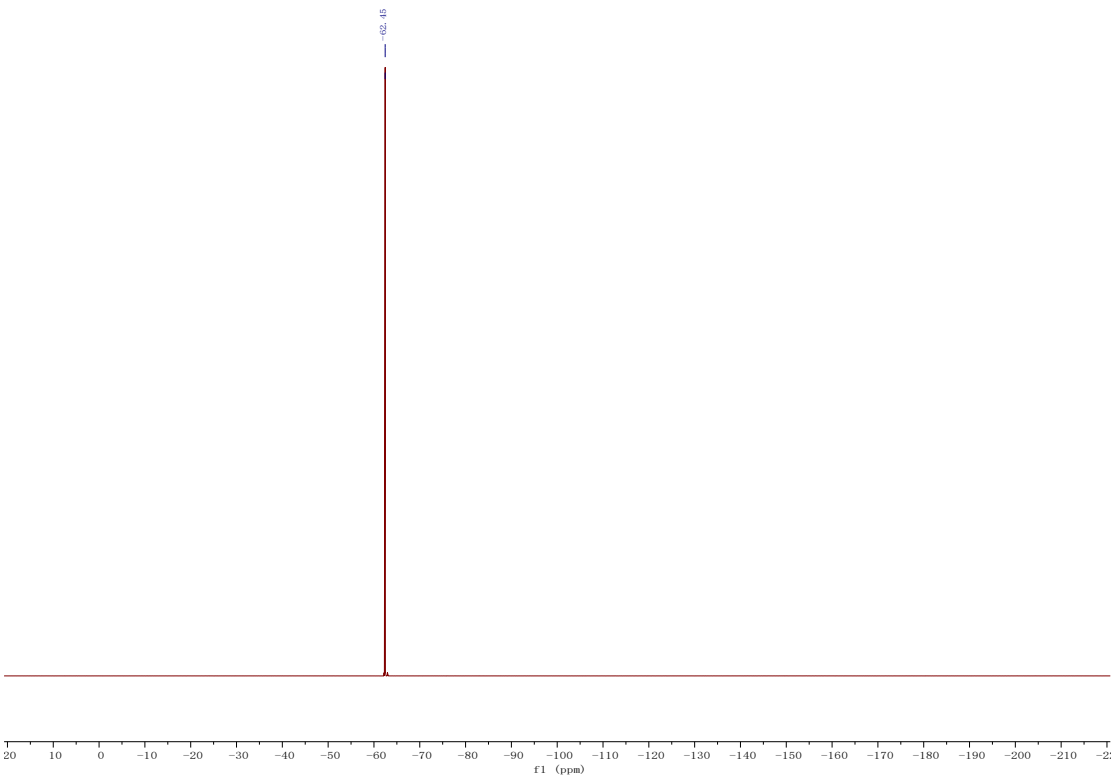

-113.99
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

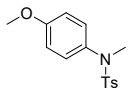

F3C
N
Ts

23


7.57
7.55
7.55
7.45
7.44
7.43
7.43
7.42
7.41
7.41
7.40
7.28
7.27
7.26
7.25
7.25
7.24
3.20
3.19
3.18
2.42
2.41
2.00
2.00
4.00
3.00
3.00
f1 (ppm)


144.88
144.10
133.17
129.60
128.99
128.67
127.32
127.32
126.23
125.95
125.91
37.66
21.50
f1 (ppm)

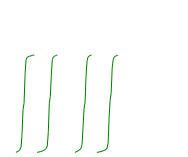

-62.45
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

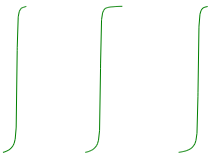

O
N
Ts

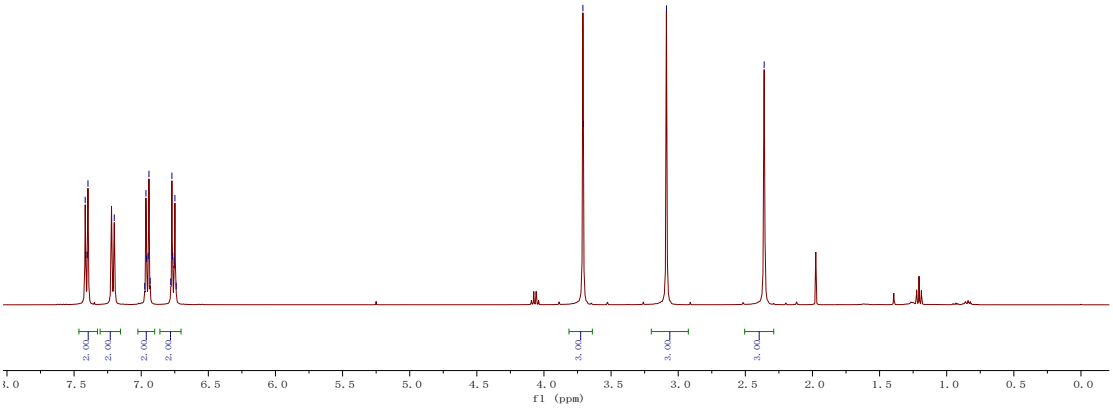
24


7.42
7.41
7.40
7.40
7.39
6.97
6.96
6.96
6.95
6.94
6.93
6.78
6.77
6.77
6.75
6.75
6.74


3.71
3.71
3.09
2.36

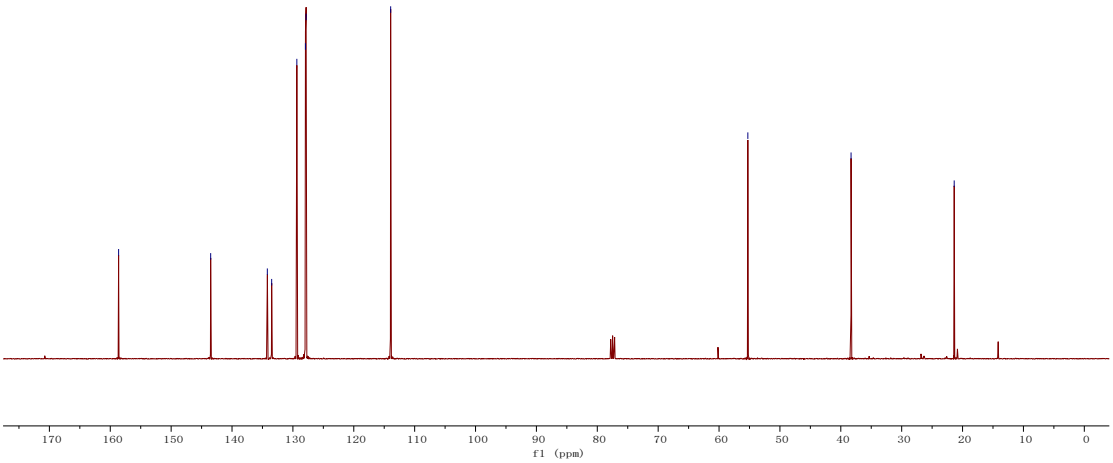


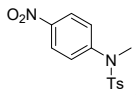



2.00
2.00
2.00
2.00
3.00
3.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

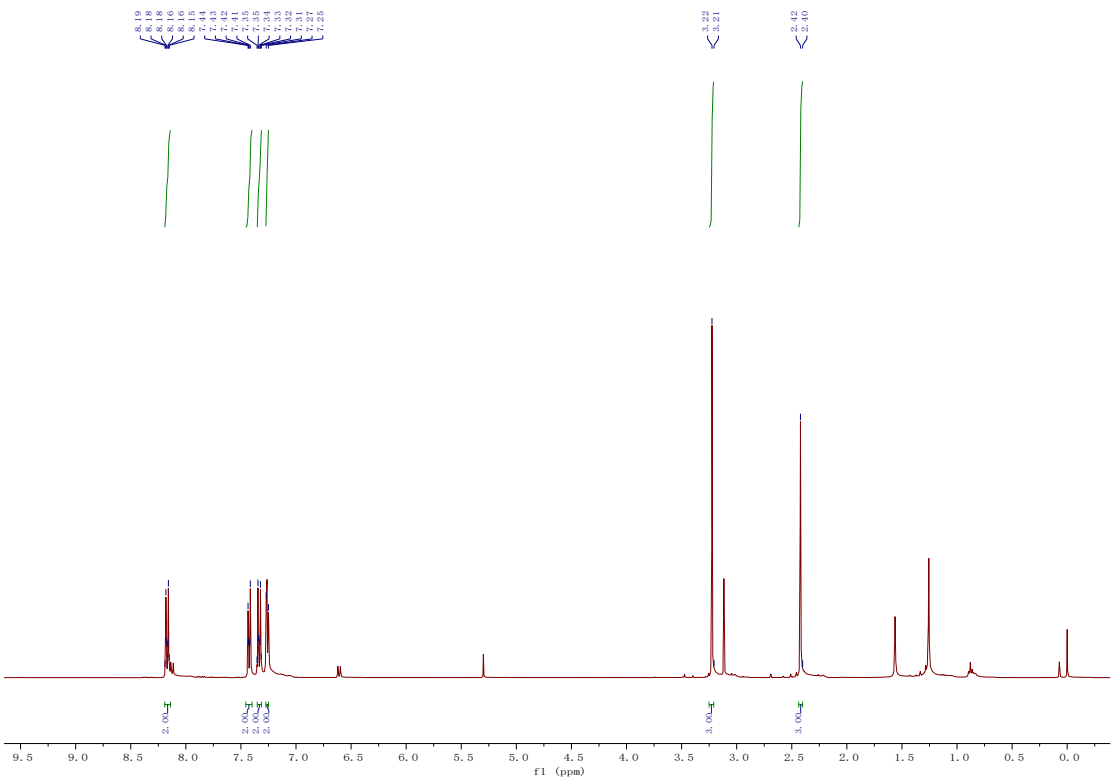

158.63
143.51
134.20
133.49
129.35
127.94
127.83
113.94

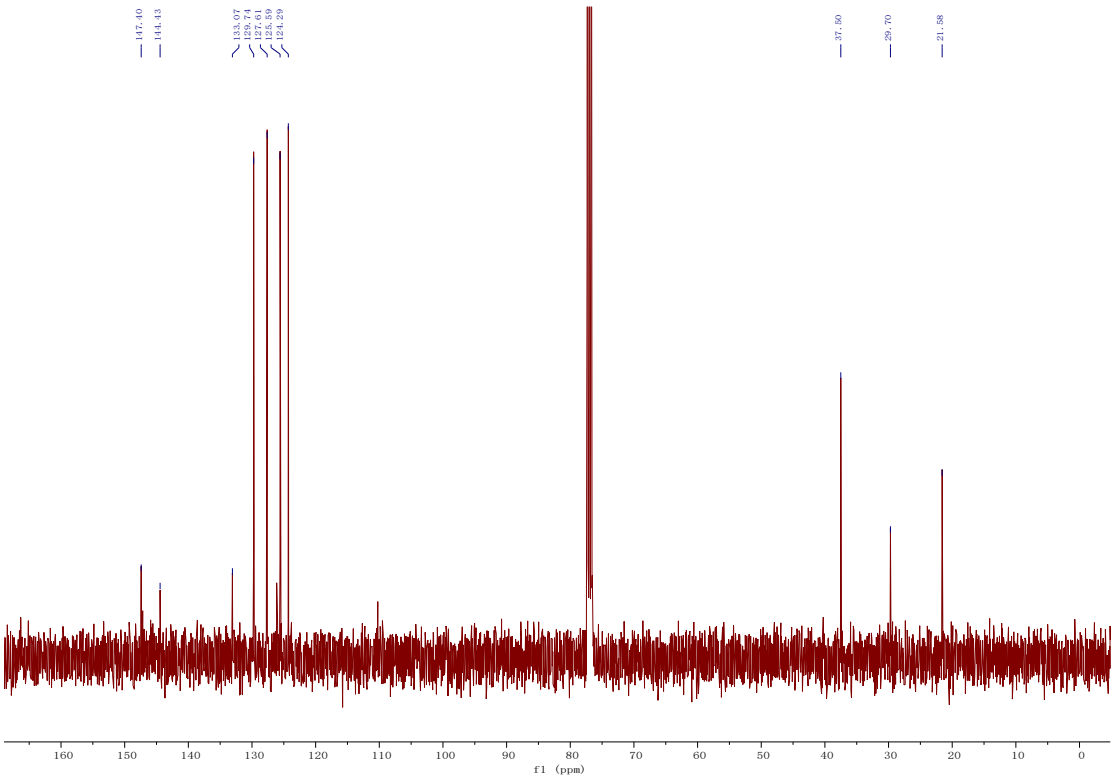

55.27
38.31
21.37

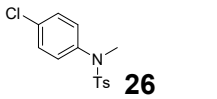

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O2N
N
Ts

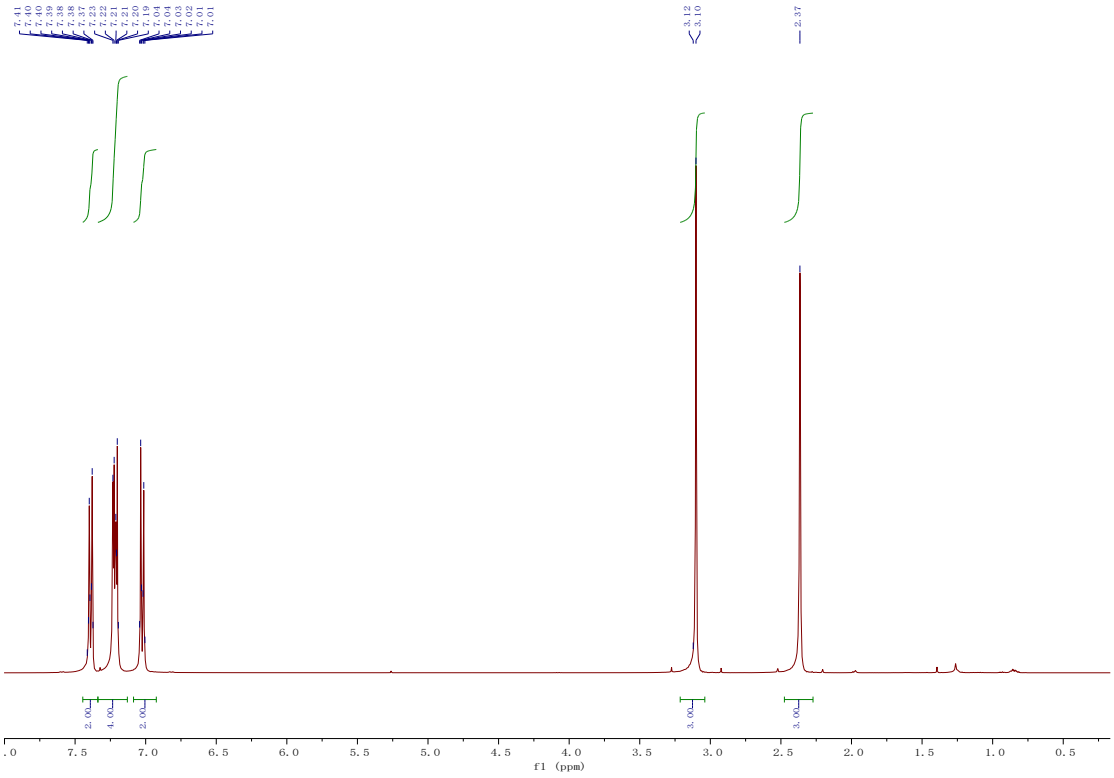
25

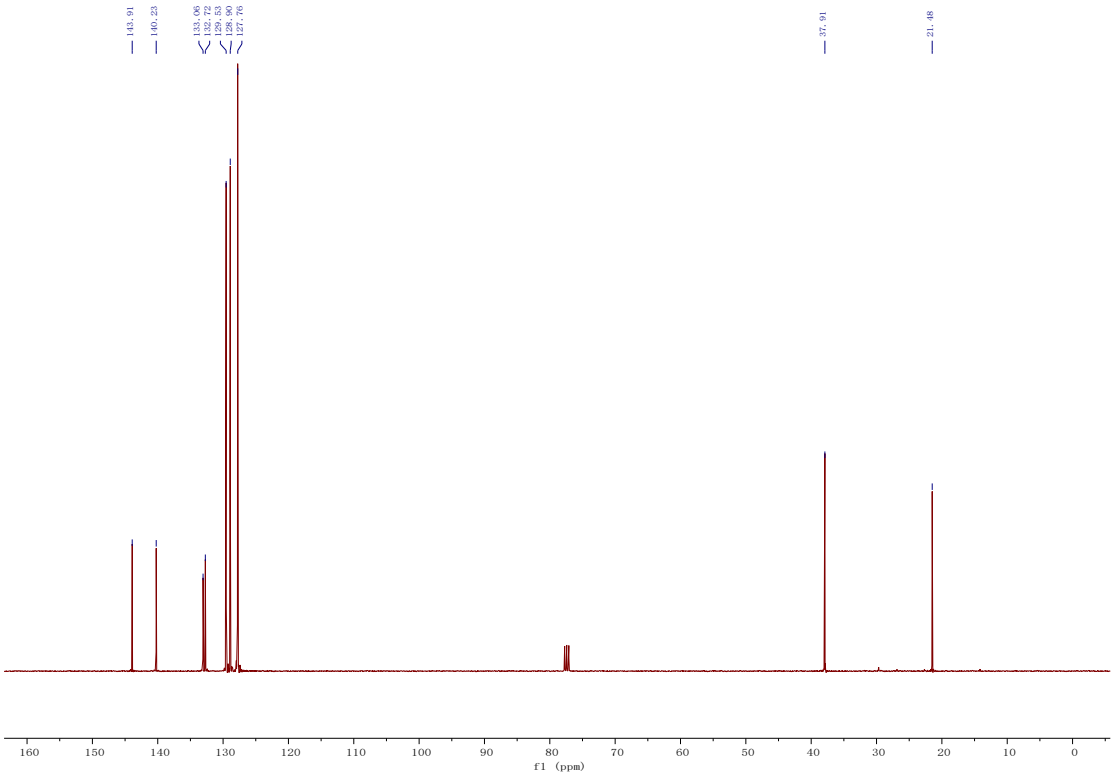

8.19
8.18
8.18
8.16
8.16
8.15
7.44
7.43
7.42
7.41
7.35
7.35
7.34
7.33
7.32
7.31
7.27
7.25
3.22
3.21
2.42
2.40
2.00
2.00
2.00
2.04
3.00
3.00
f1 (ppm)

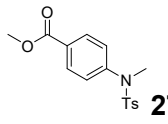

147.40
144.43
133.07
129.74
127.61
125.99
124.29
37.50
29.70
21.58
f1 (ppm)


Cl
N
Ts

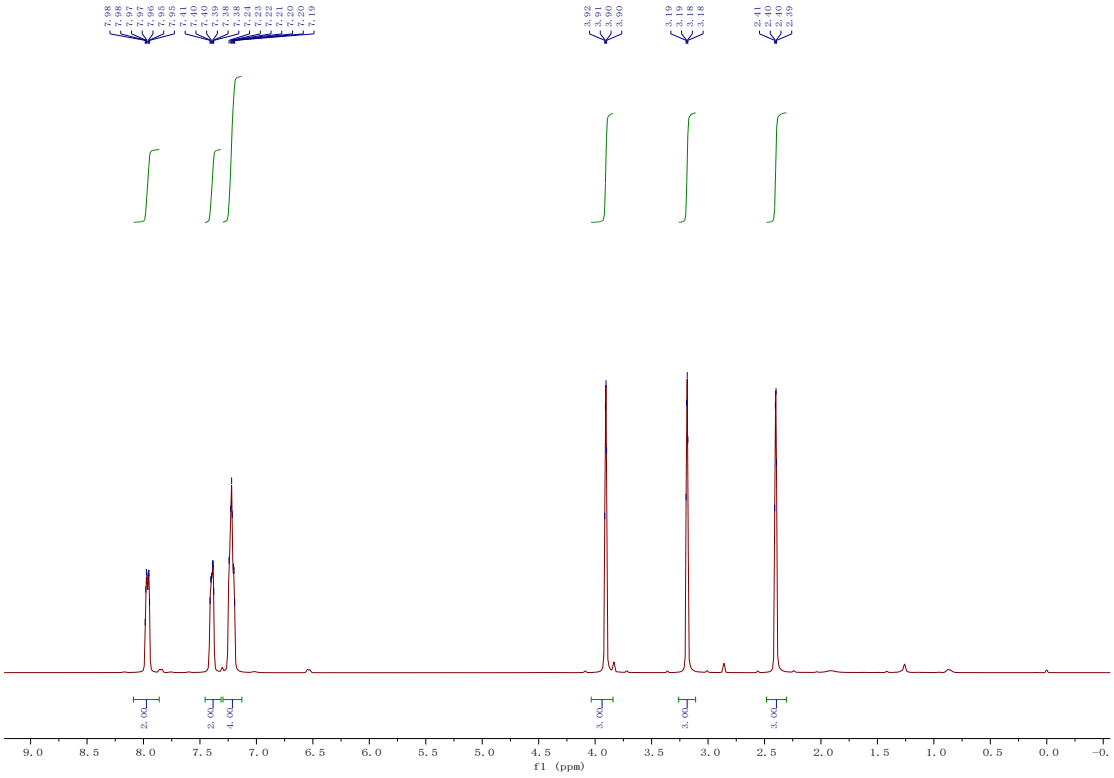
26

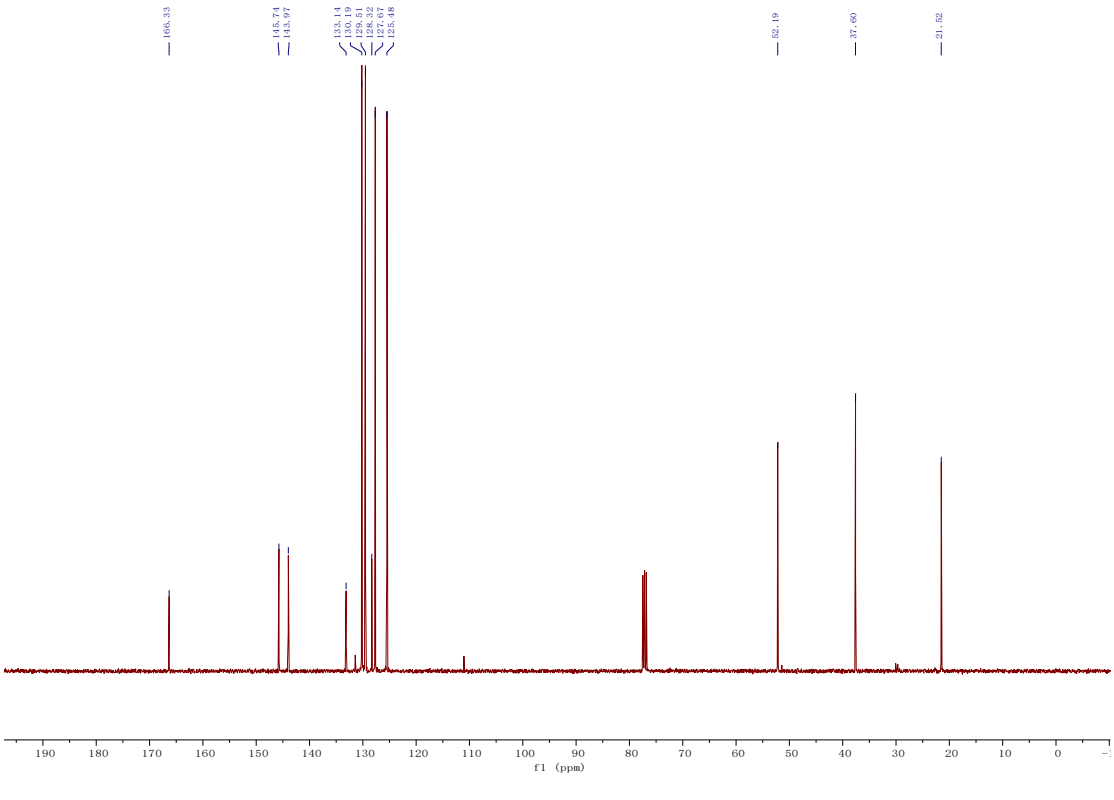

7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.23
7.22
7.21
7.21
7.20
7.19
7.04
7.04
7.03
7.02
7.01
7.01
3.12
3.10
2.37
2.00
4.00
2.00
3.00
3.00
f1 (ppm)


143.91
140.23
133.06
132.72
129.53
128.90
127.76
37.91
21.48
f1 (ppm)



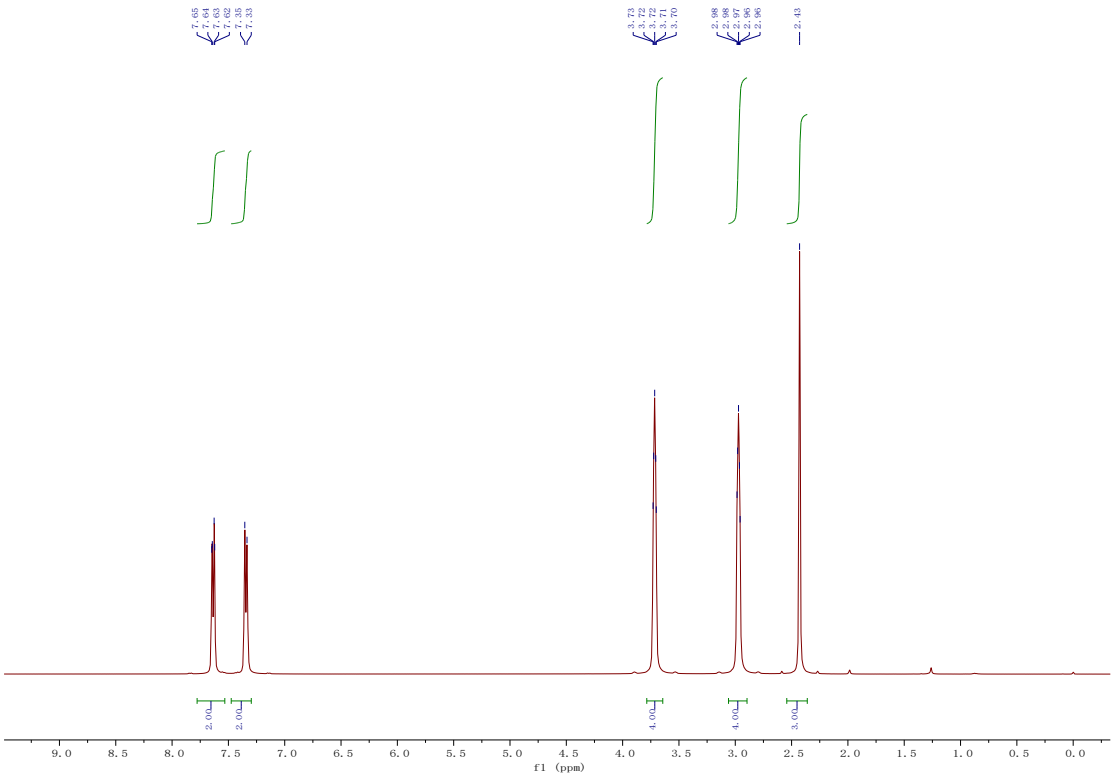
27

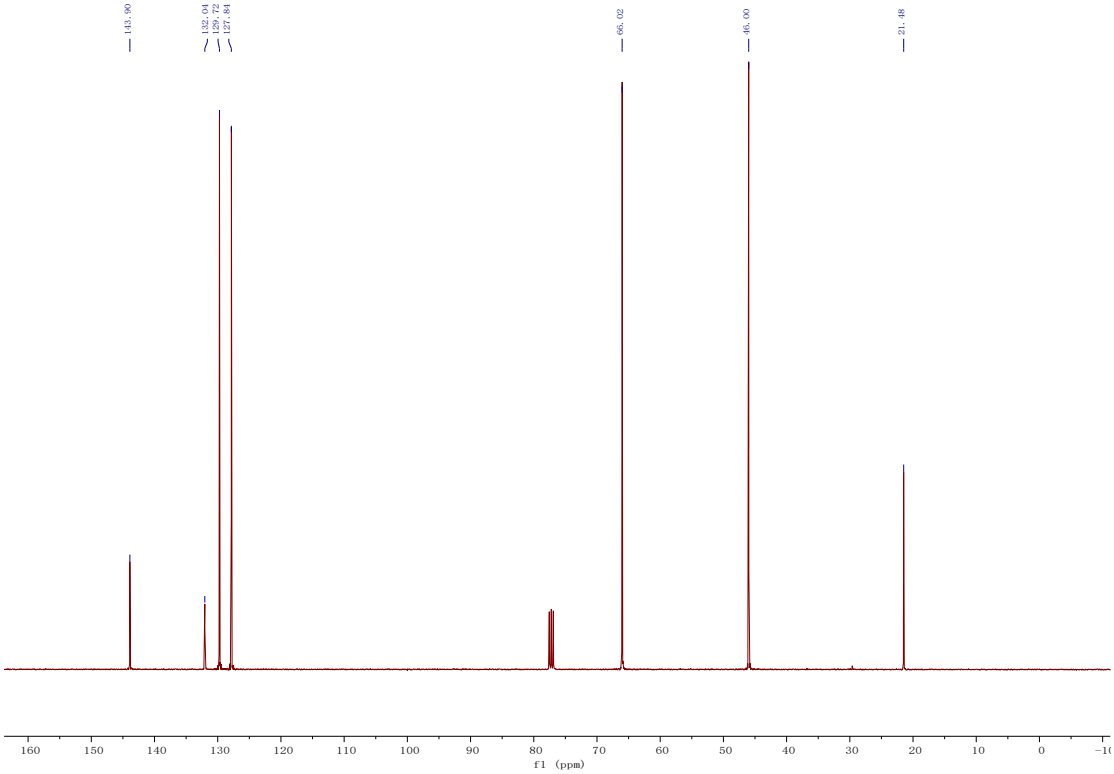

7.98
7.98
7.97
7.97
7.96
7.95
7.95
7.41
7.40
7.40
7.39
7.38
7.38
7.24
7.23
7.22
7.21
7.20
7.20
7.19
3.92
3.91
3.90
3.90
3.19
3.19
3.18
3.18
2.41
2.40
2.40
2.39
2.00
2.00
4.00
3.00
3.00
3.00
f1 (ppm)

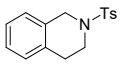

166.33
145.74
143.97
133.14
130.19
129.51
128.32
127.67
125.48
82.19
37.60
21.52
f1 (ppm)


Ts
N
O

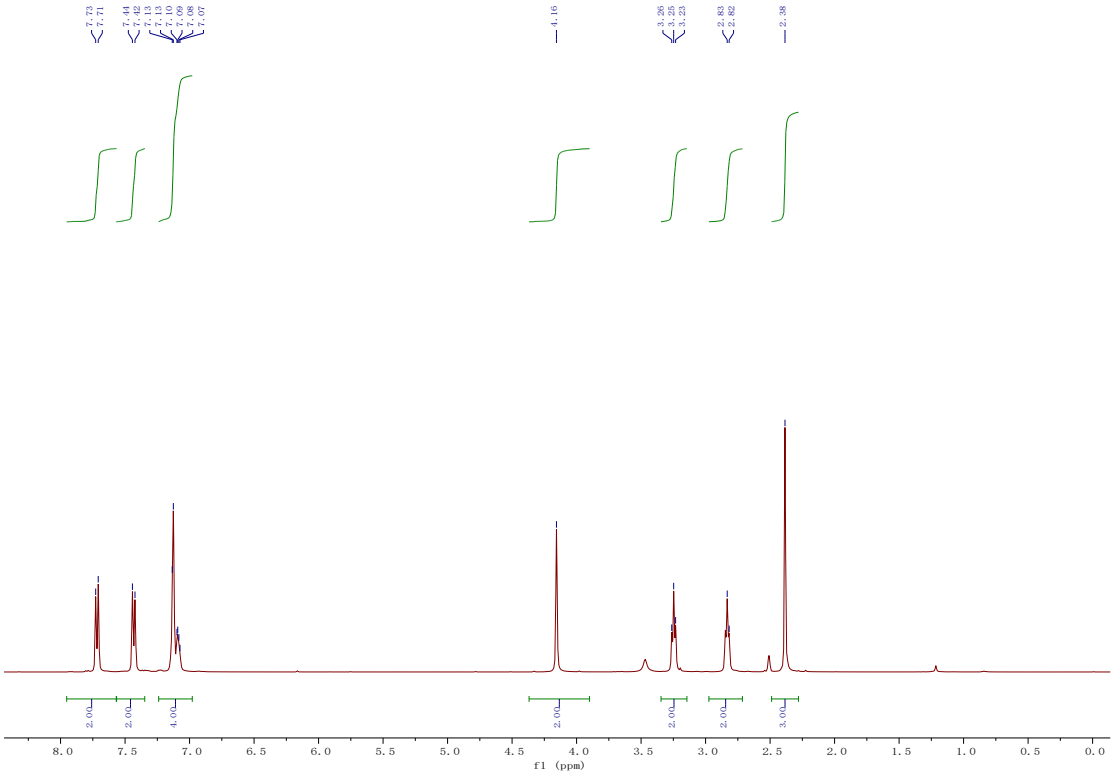
28

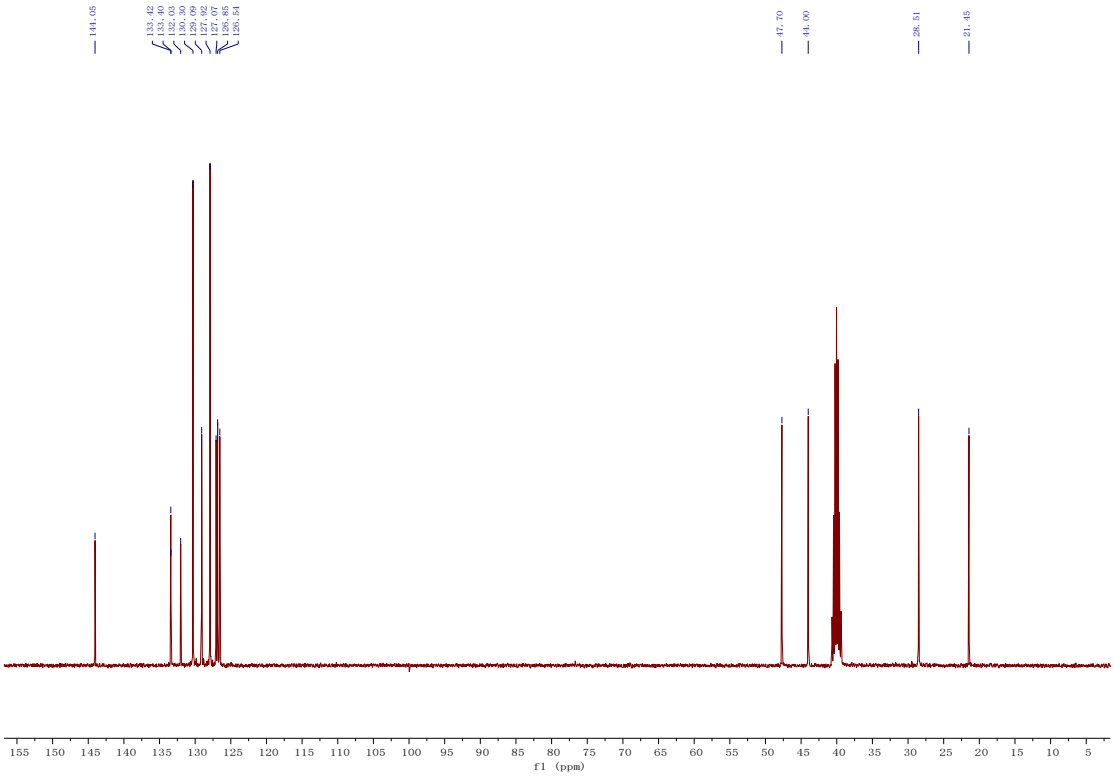

7.65
7.64
7.63
7.62
7.35
7.33
3.73
3.72
3.72
3.71
3.70
2.98
2.98
2.97
2.96
2.96
2.43
2.00
2.00
4.00
4.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

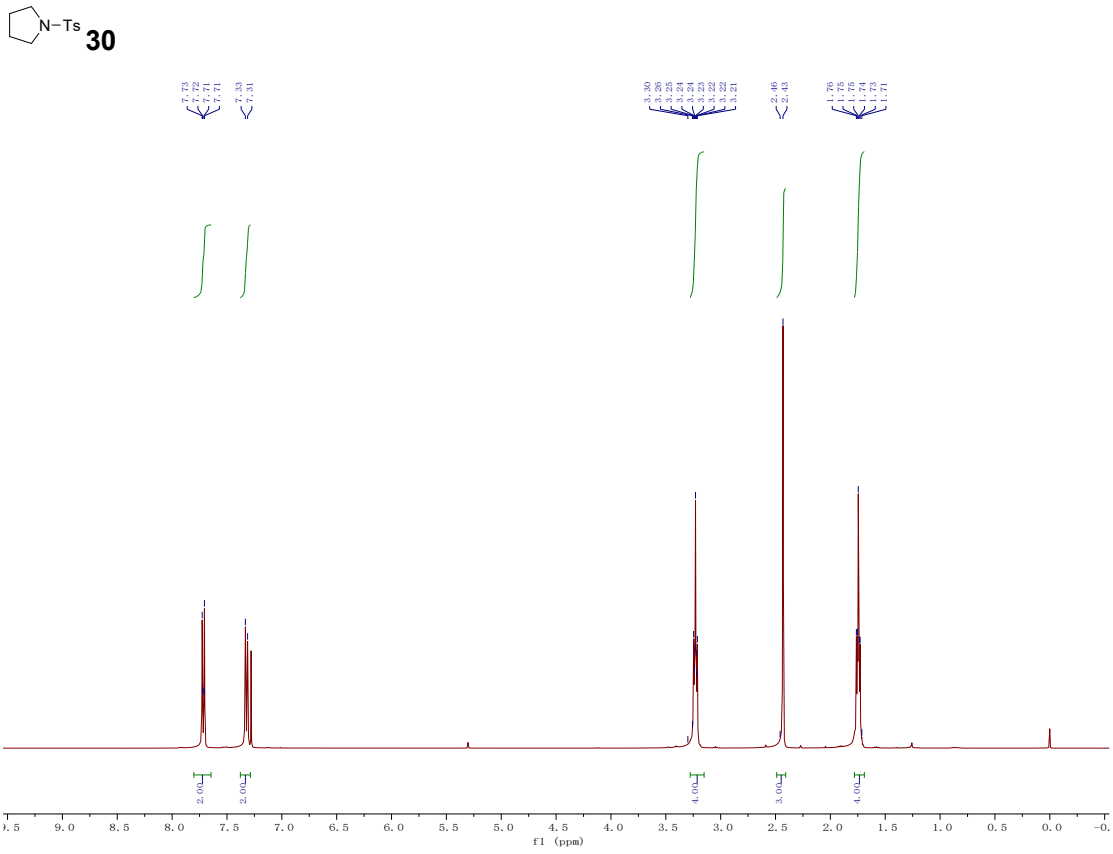

143.90
132.04
129.72
127.84
66.02
46.00
21.48
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

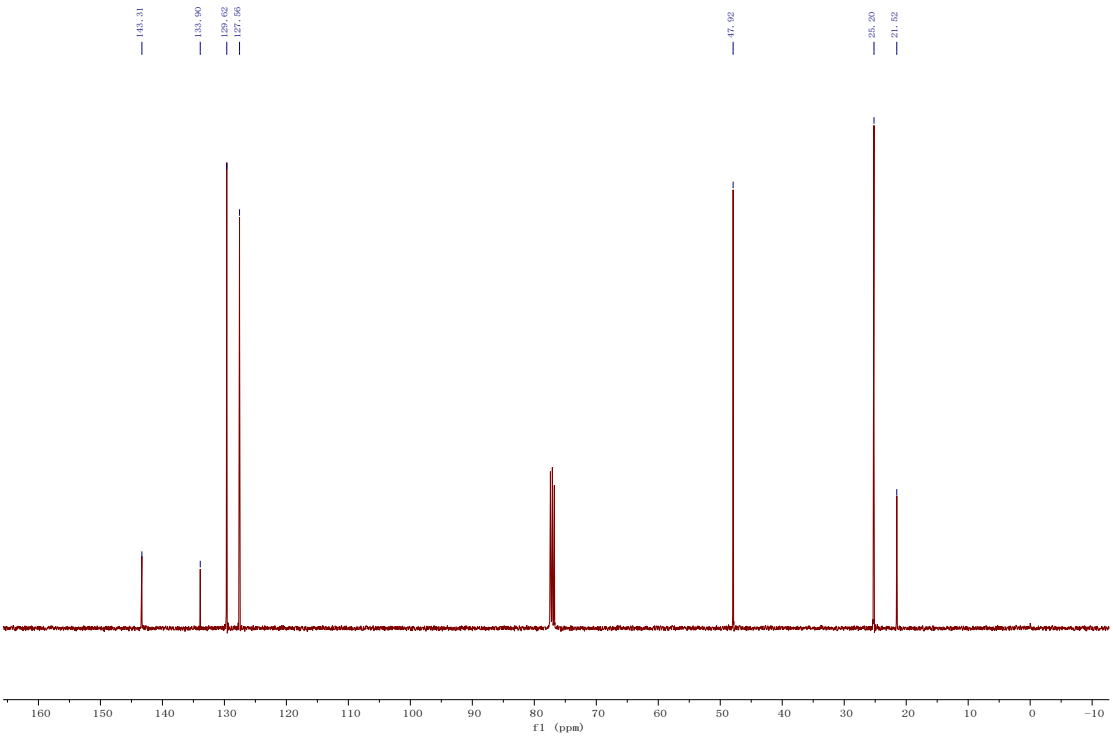

Ts
N

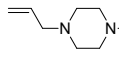
29


7.73
7.71
7.44
7.42
7.13
7.10
7.09
7.08
7.07
4.16
3.26
3.25
3.23
2.83
2.82
2.38
2.00
2.00
4.00
2.00
2.00
2.00
3.00
f1 (ppm)

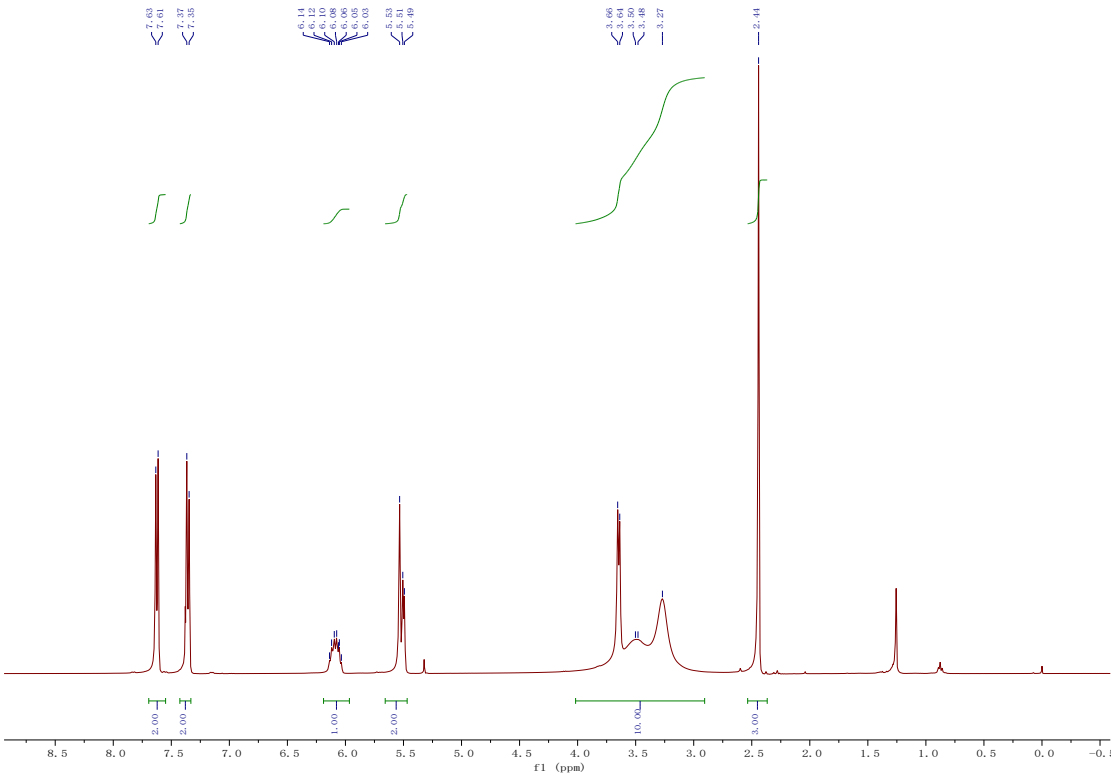

144.05
133.42
133.40
132.03
130.30
129.09
127.92
127.07
126.85
126.54
47.70
44.00
28.51
21.45
f1 (ppm)

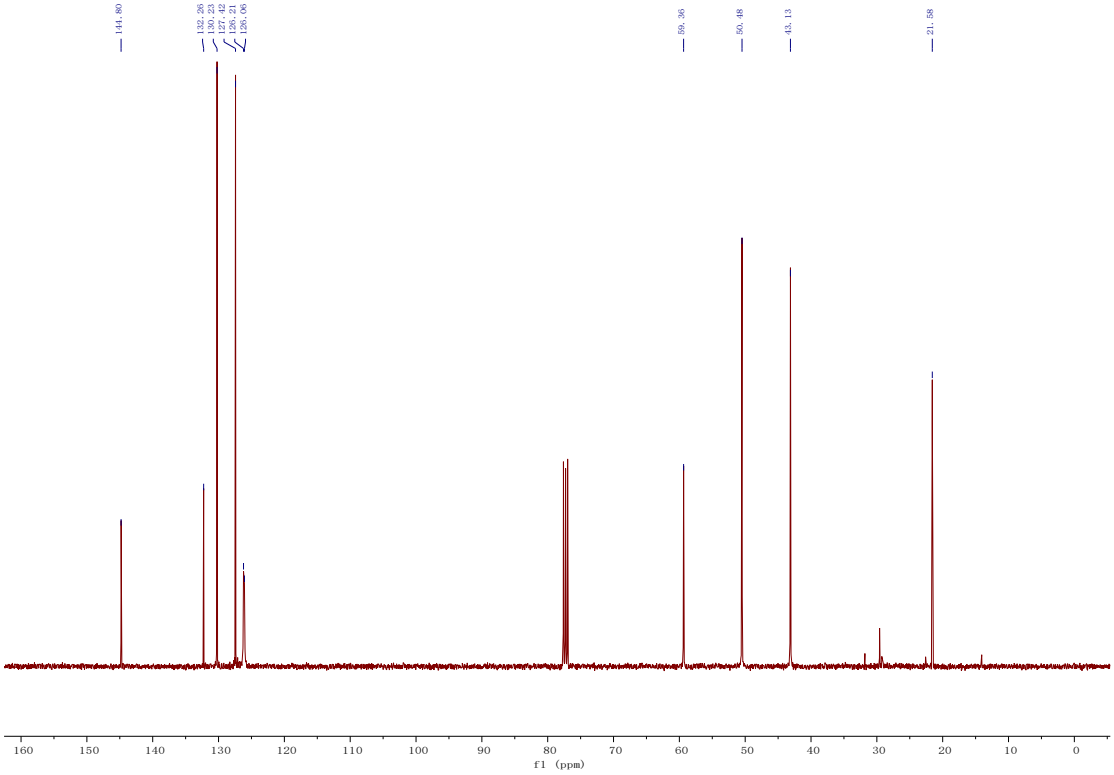

N–Ts
30
7.73
7.72
7.71
7.71
7.33
7.31
3.30
3.26
3.25
3.24
3.23
3.22
3.22
3.21
2.46
2.43
1.76
1.75
1.75
1.75
1.74
1.73
1.71
2.00
2.00
4.00
3.00
4.00
f1 (ppm)

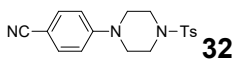

143.31
133.90
129.62
127.56
47.92
25.20
21.52
f1 (ppm)


N
N–Ts

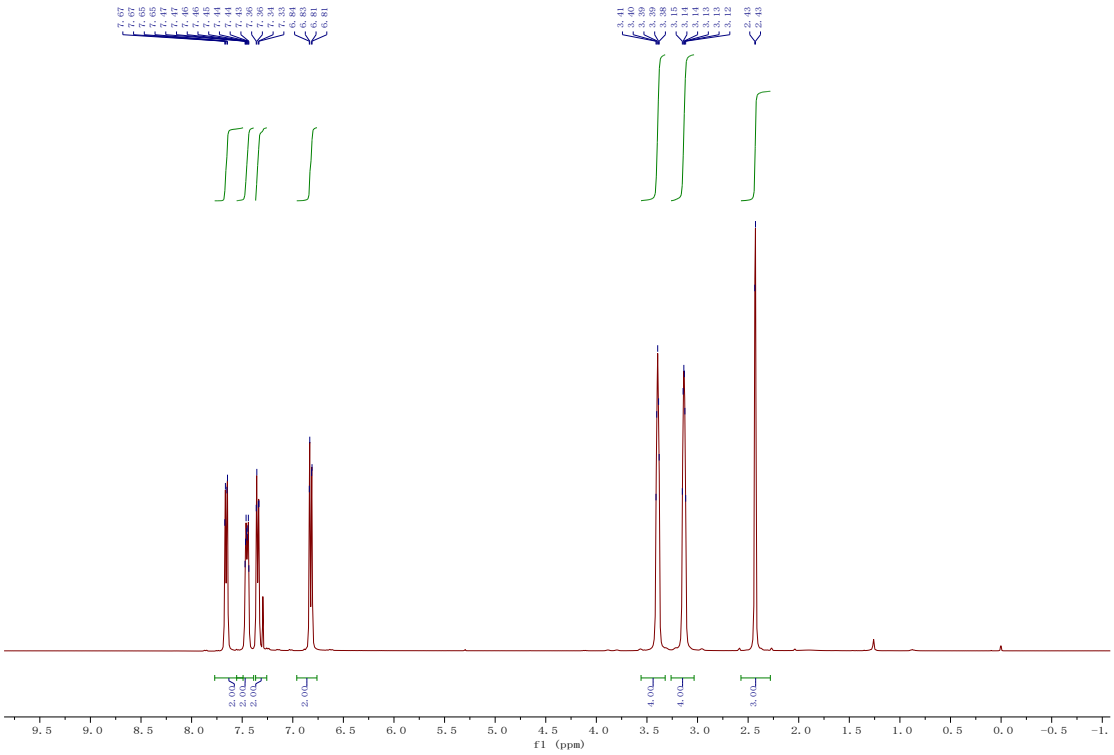
31

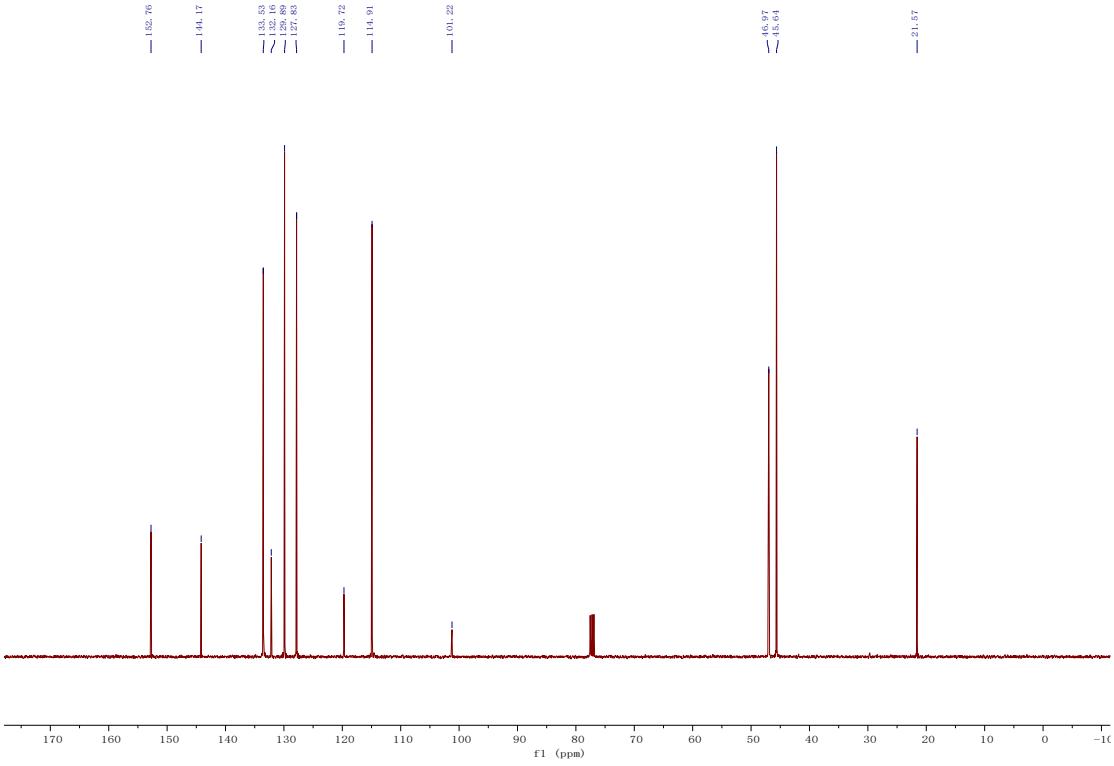

7.63
7.61
7.37
7.35
6.14
6.12
6.10
6.08
6.06
6.05
6.03
5.53
5.51
5.49
3.66
3.64
3.50
3.48
3.27
2.44
2.00
2.00
1.00
2.00
10.06
3.00
f1 (ppm)

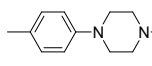

144.80
132.26
130.23
127.42
126.21
126.06
89.36
50.48
43.13
21.58
f1 (ppm)


NC
N
N
Ts

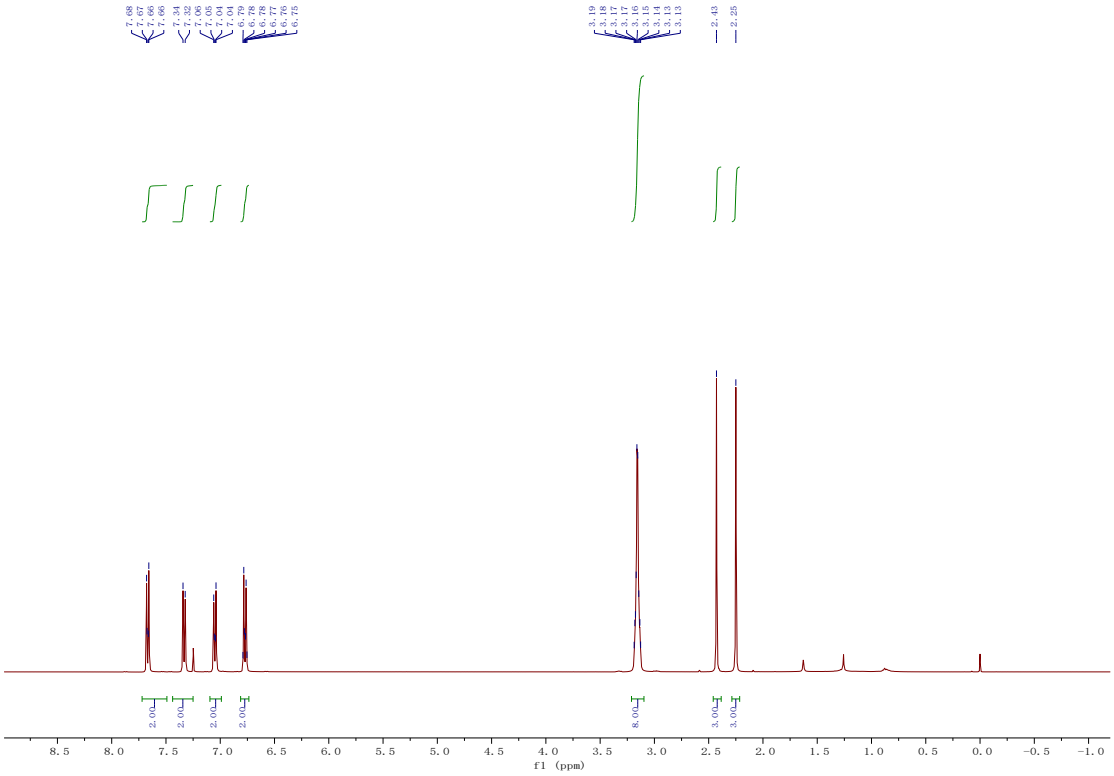
32

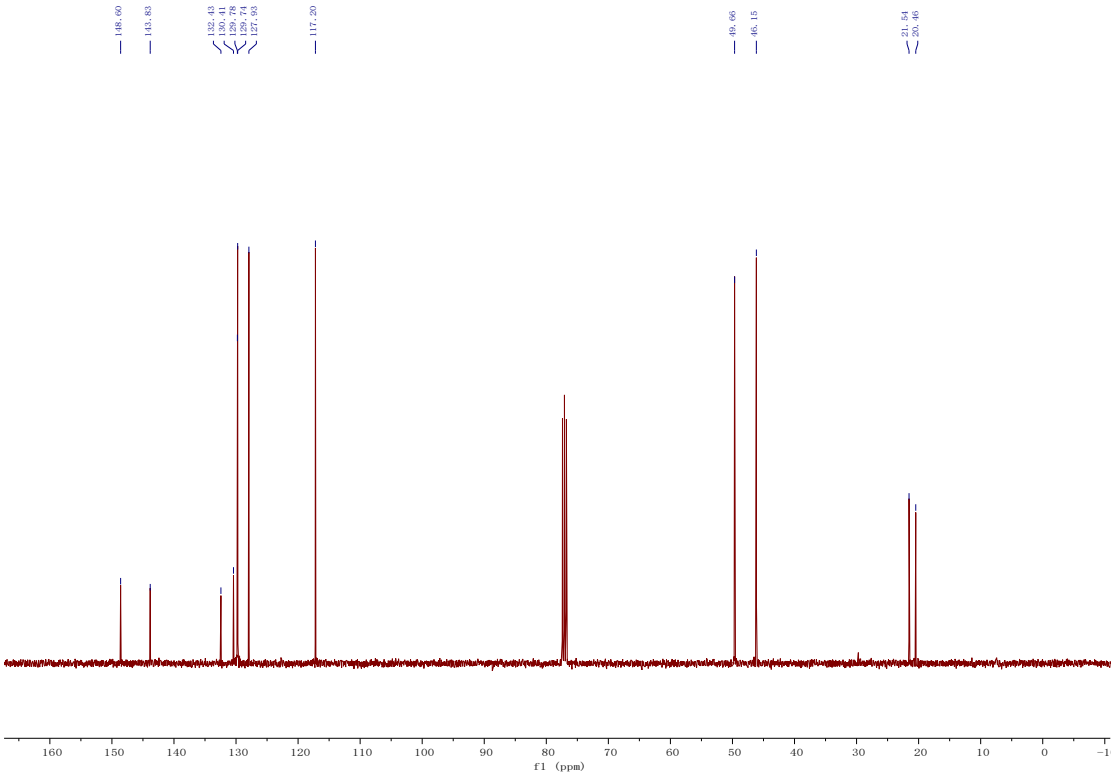

7.67
7.67
7.65
7.65
7.47
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.36
7.34
7.33
6.84
6.83
6.81
6.81
3.41
3.40
3.39
3.38
3.15
3.14
3.14
3.13
3.13
3.12
2.43
2.43
2.00
2.00
2.00
2.00
4.00
4.00
3.00
f1 (ppm)

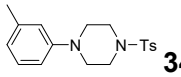

182.76
144.17
133.53
132.16
129.89
127.83
119.72
114.91
101.22
46.97
45.64
21.57
f1 (ppm)


N
N–Ts

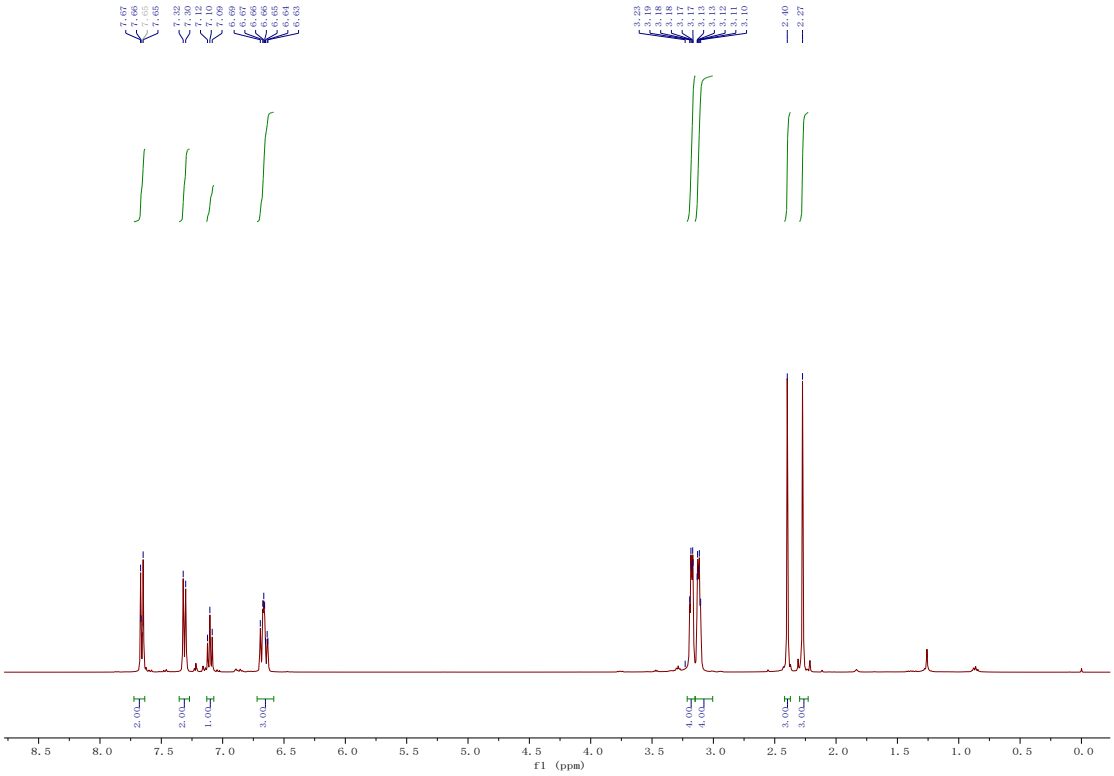
33

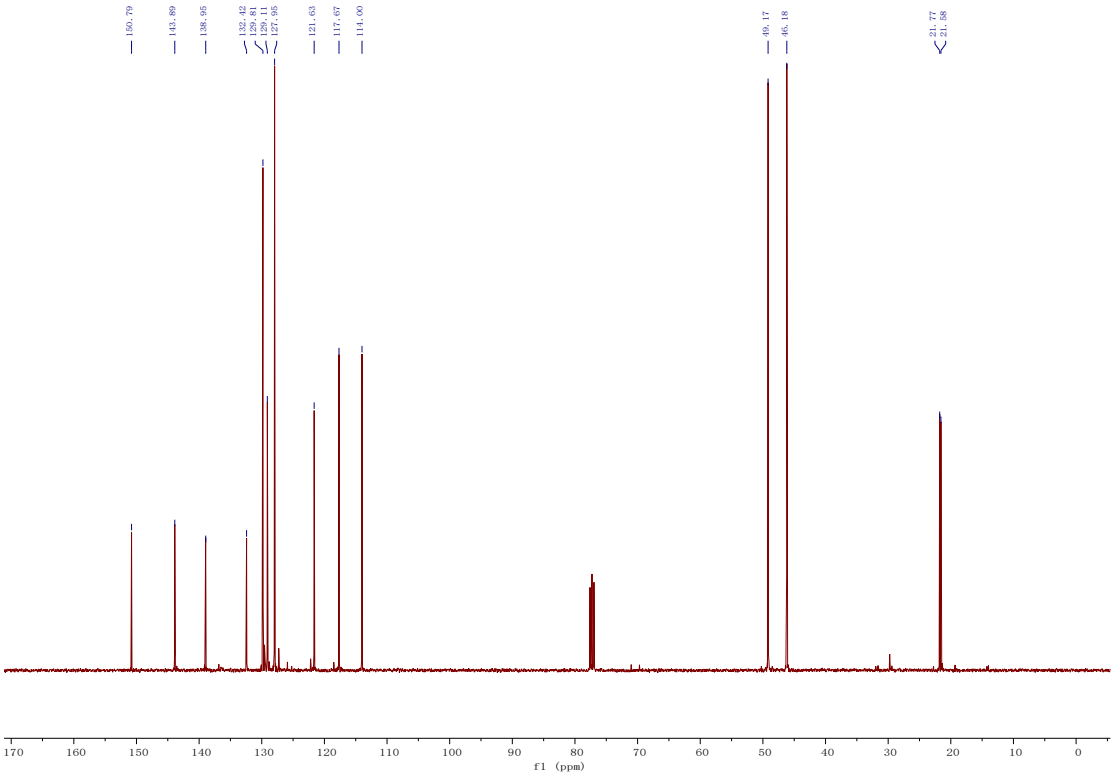

7.68
7.67
7.65
7.66
7.34
7.32
7.06
7.05
7.04
7.04
6.79
6.78
6.78
6.77
6.76
6.75
3.19
3.18
3.17
3.17
3.16
3.15
3.14
3.13
3.13
2.43
2.25
2.00
2.00
2.00
2.00
8.00
3.00
3.00
f1 (ppm)

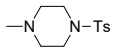

148.60
143.83
132.43
130.41
129.78
129.74
127.93
117.20
49.66
45.15
21.54
20.46
f1 (ppm)


N
N−Ts

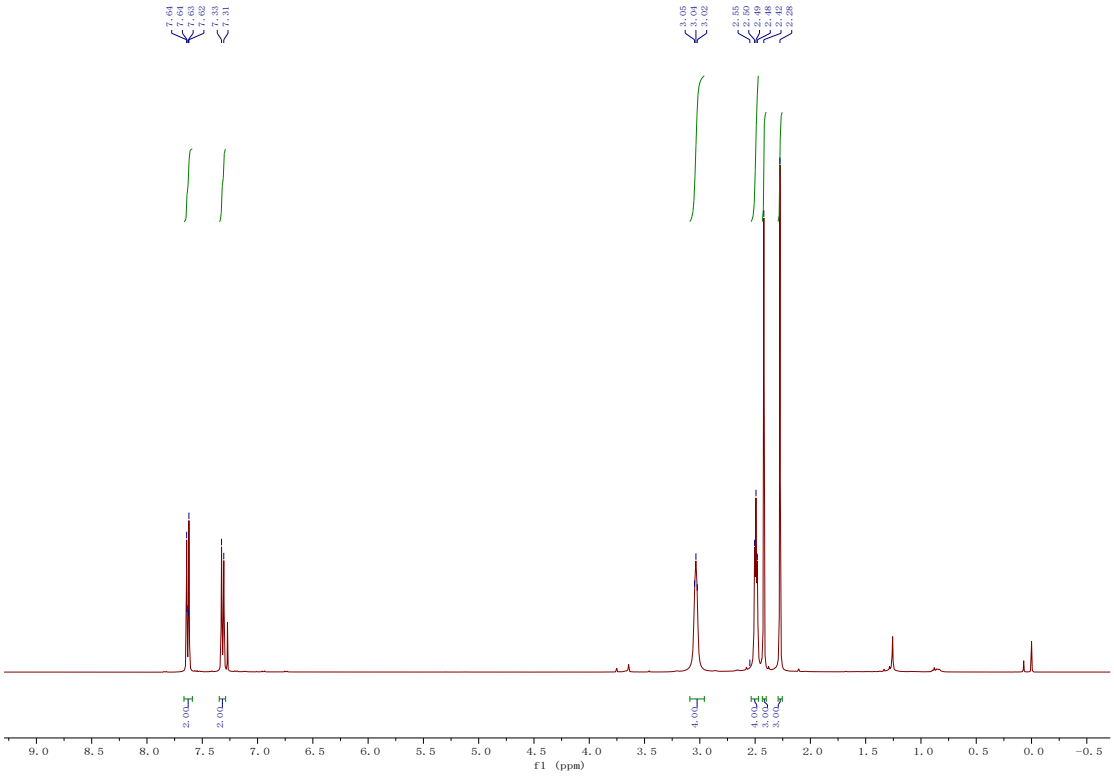
34

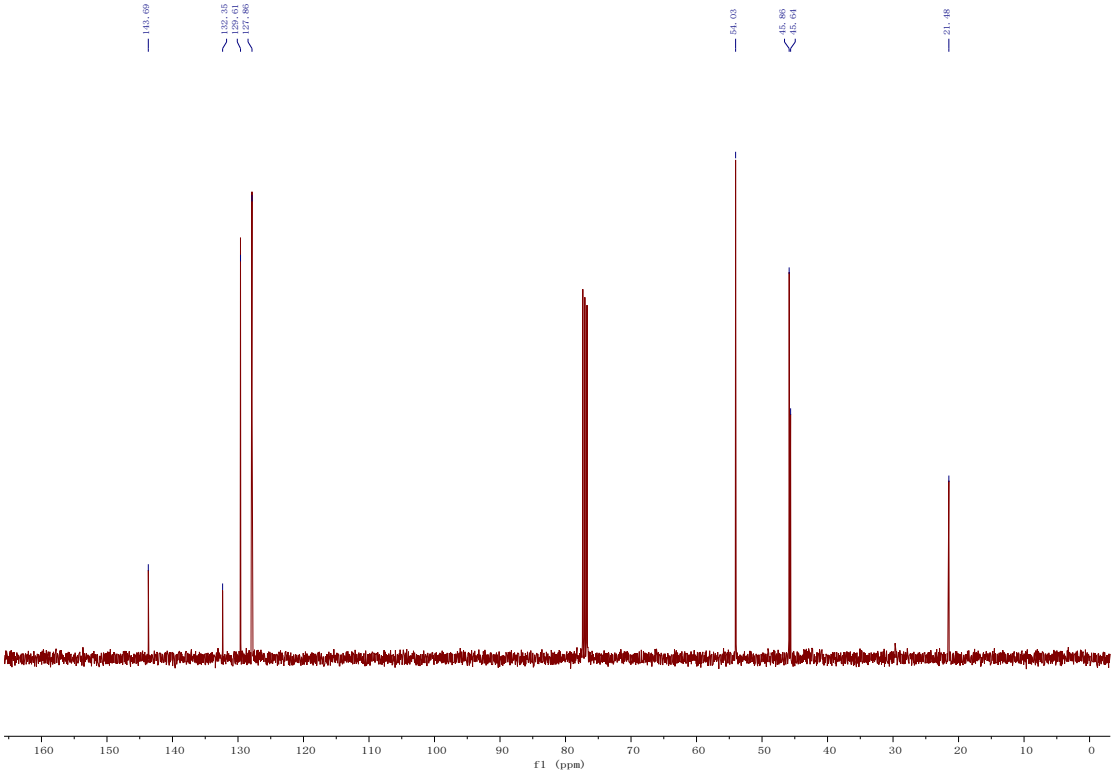

7.67
7.66
7.65
7.32
7.30
7.12
7.10
7.09
6.69
6.67
6.66
6.65
6.64
6.63
3.23
3.19
3.18
3.18
3.17
3.17
3.13
3.13
3.12
3.11
3.10
2.40
2.27
2.00
2.00
1.00
3.00
4.00
4.00
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

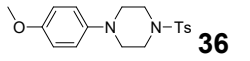

150.79
143.89
138.95
132.42
129.81
129.11
127.95
121.63
117.67
114.00
49.17
46.18
21.77
21.58
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


—N
N—Ts

35

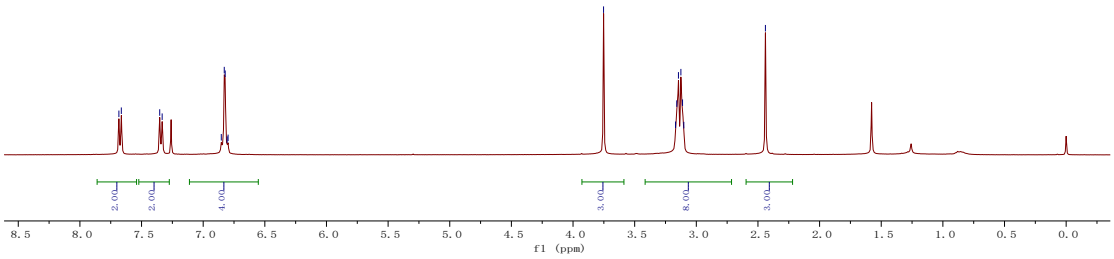

7.64
7.64
7.63
7.62
7.33
7.31
3.05
3.04
3.02
2.55
2.50
2.49
2.48
2.42
2.28
2.00
2.00
4.00
4.00
3.02
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

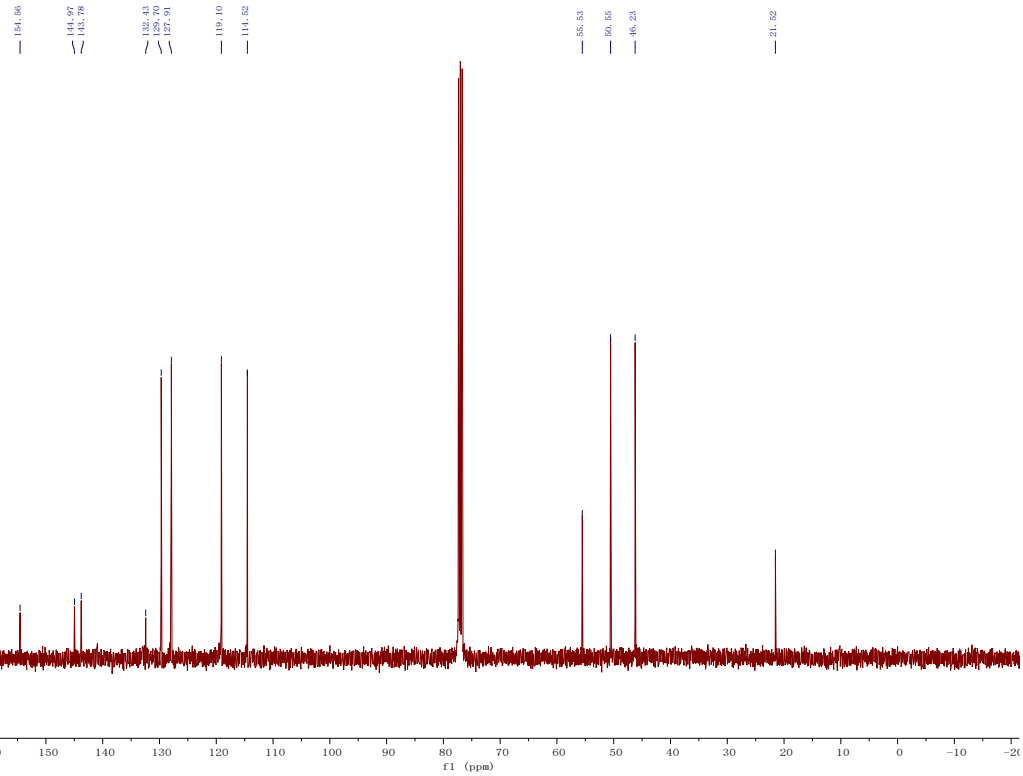

143.69
132.35
129.61
127.86
54.03
45.86
45.64
21.48
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

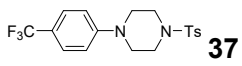

O
N
N–Ts

36

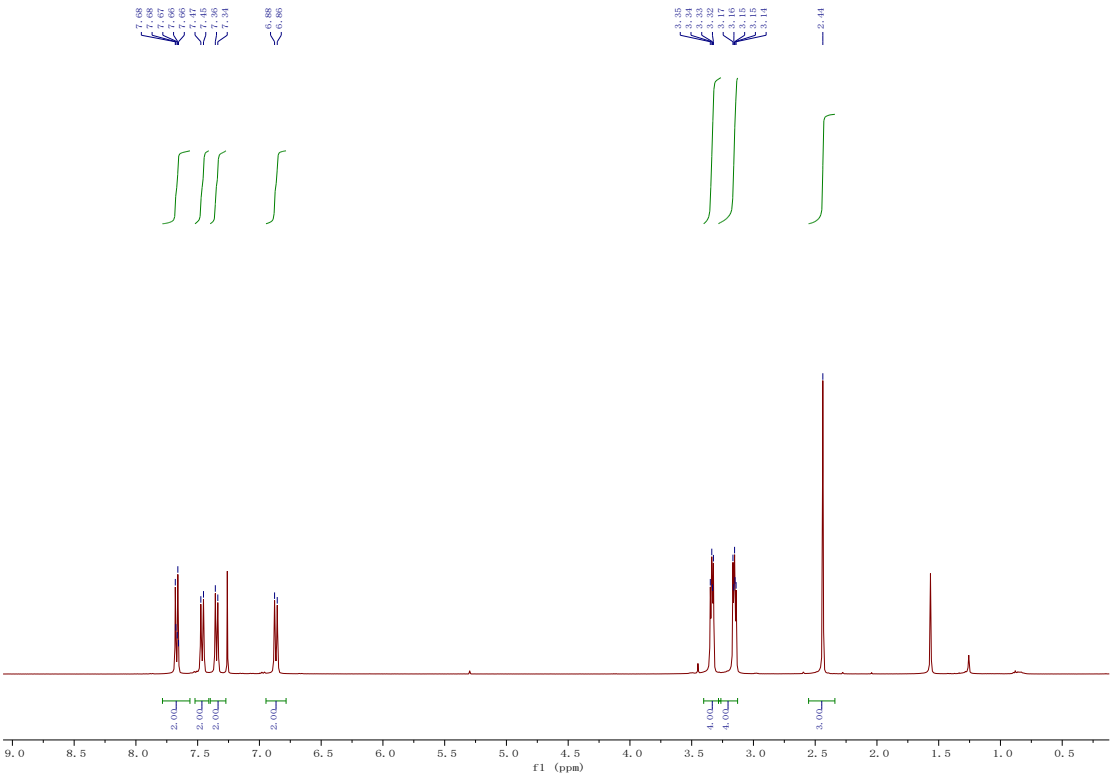

7.68
7.66
7.35
7.33
6.85
6.83
6.82
6.81
6.80
3.75
3.17
3.16
3.14
3.13
3.11
3.10
2.44

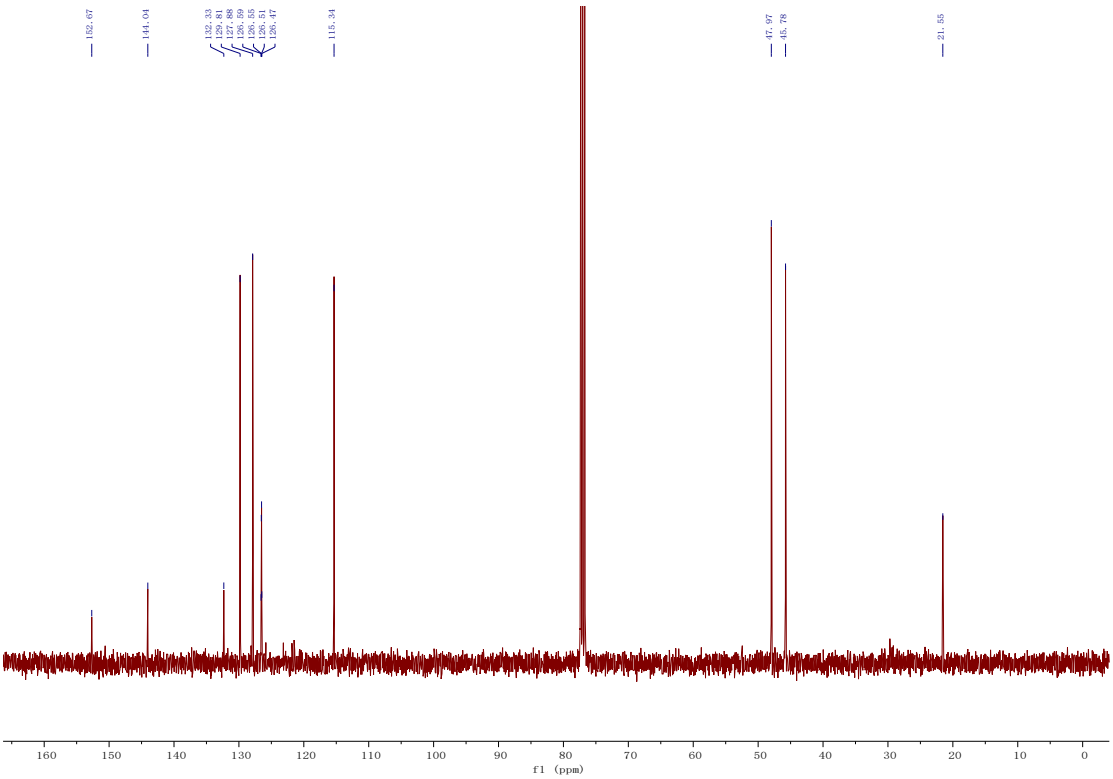

2.00
2.00
4.00
3.00
8.00
3.00
f1 (ppm)

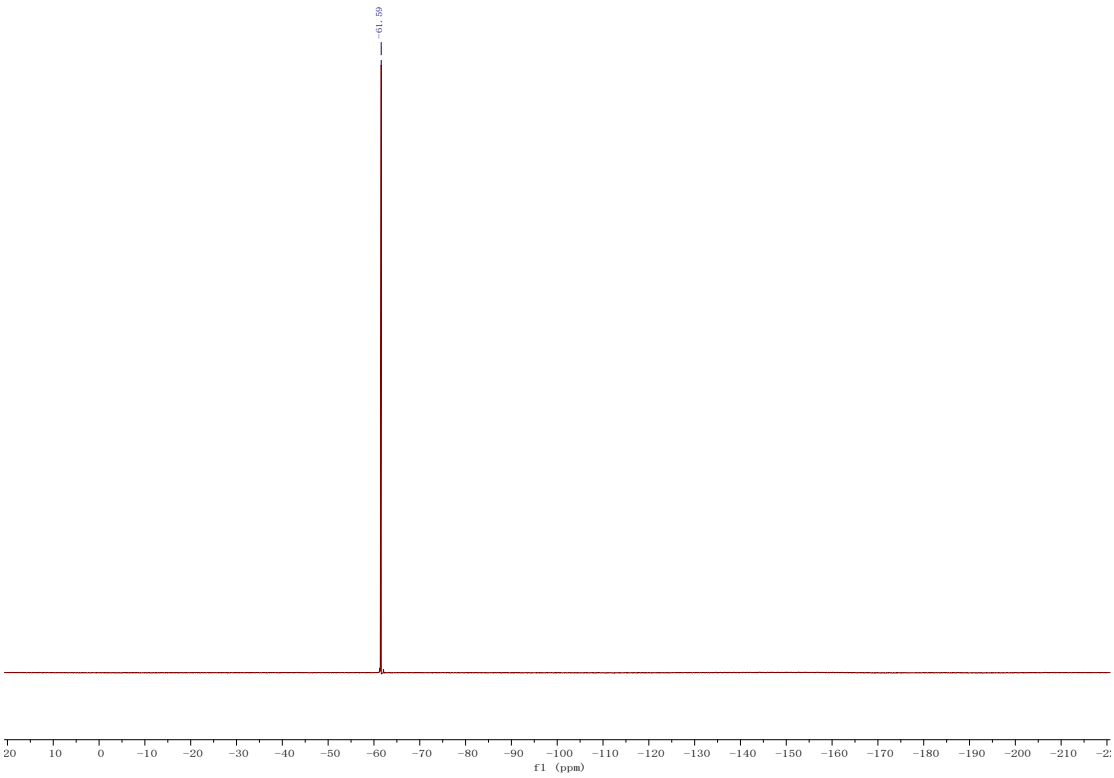

154.56
144.97
143.78
132.43
129.70
127.91
119.10
114.52
55.53
50.55
46.23
21.52
f1 (ppm)

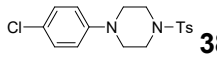

F3C
N
N–Ts

37

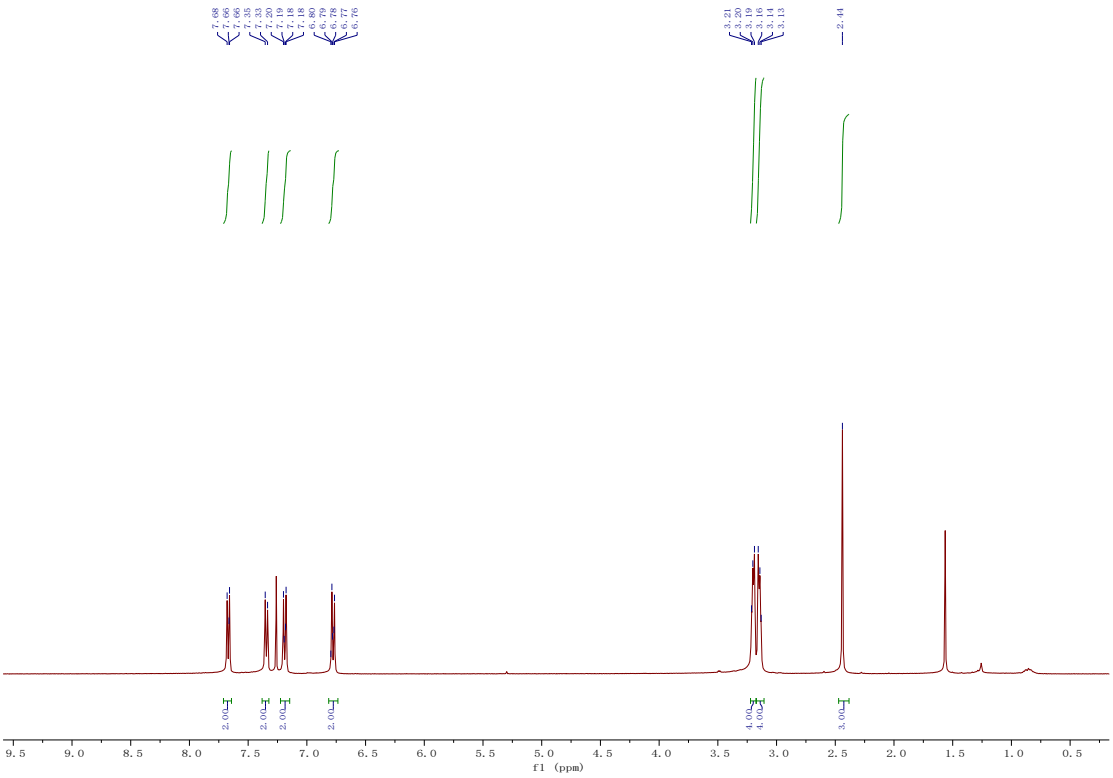

7.68
7.68
7.67
7.66
7.66
7.47
7.45
7.36
7.34
6.88
6.86
3.35
3.34
3.33
3.32
3.17
3.16
3.15
3.15
3.14
2.44
2.00
2.00
2.00
2.00
4.00
4.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

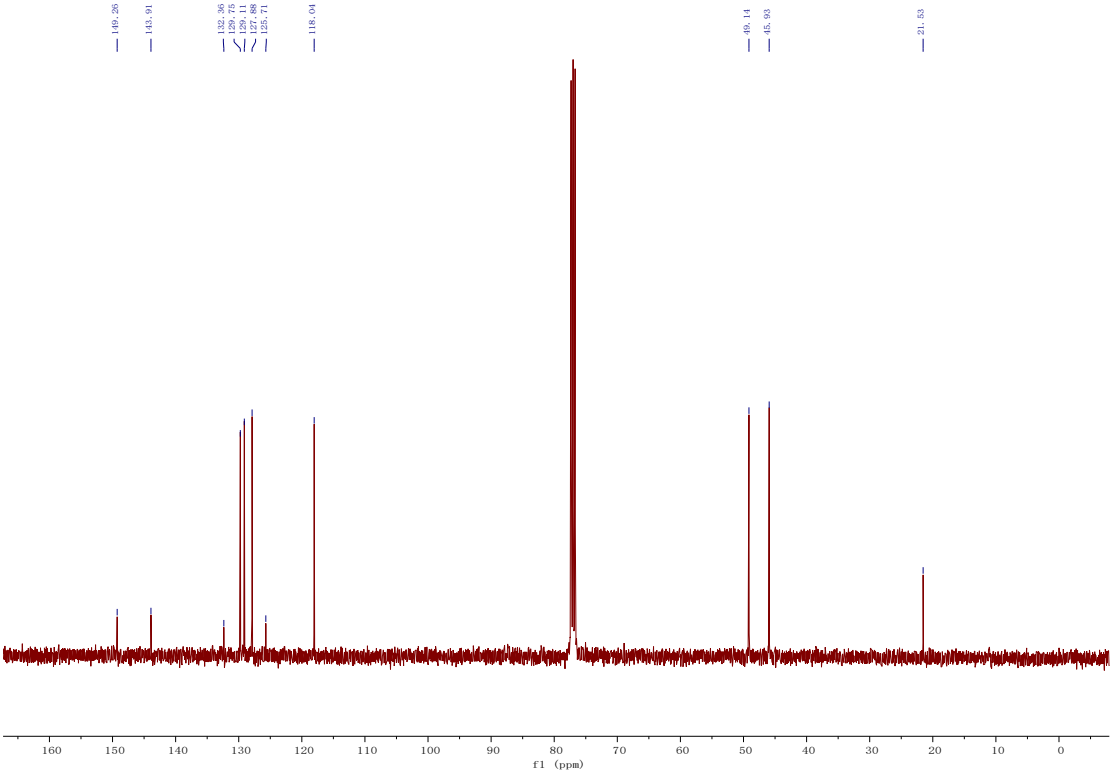

152.67
144.04
132.33
129.81
127.88
126.89
126.55
126.51
126.47
115.34
47.97
45.78
21.55
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

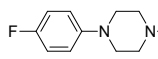

-61.59
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


Cl
N
N
Ts

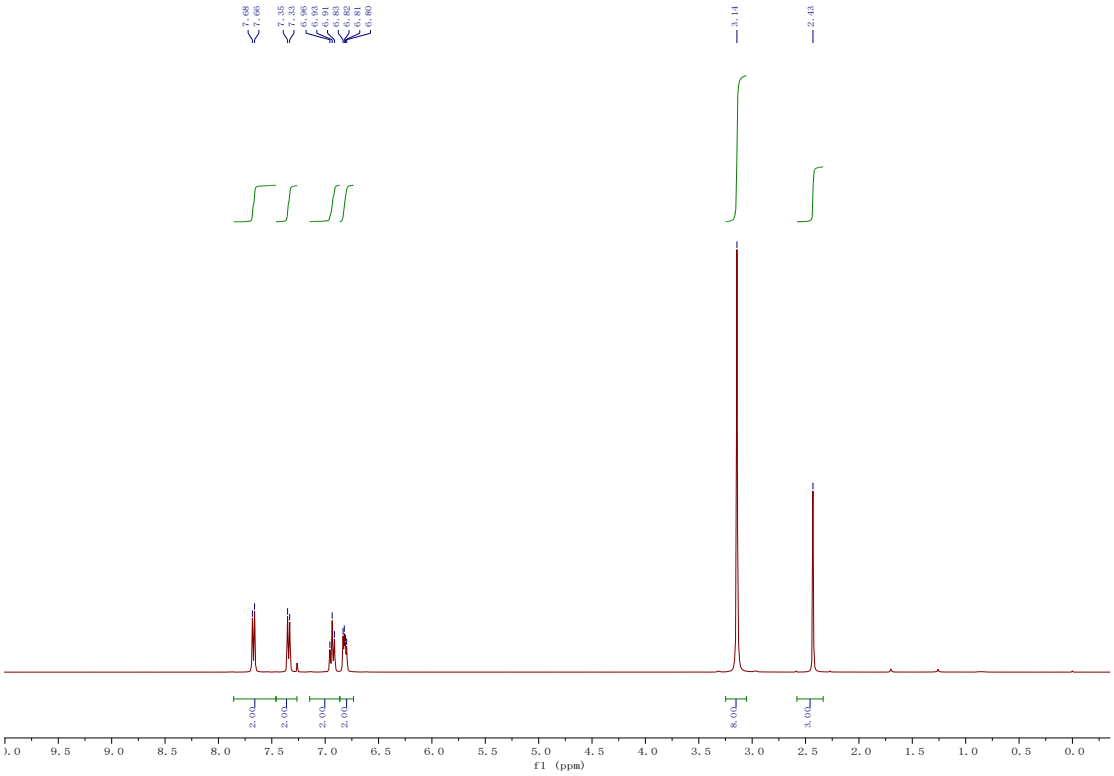
38

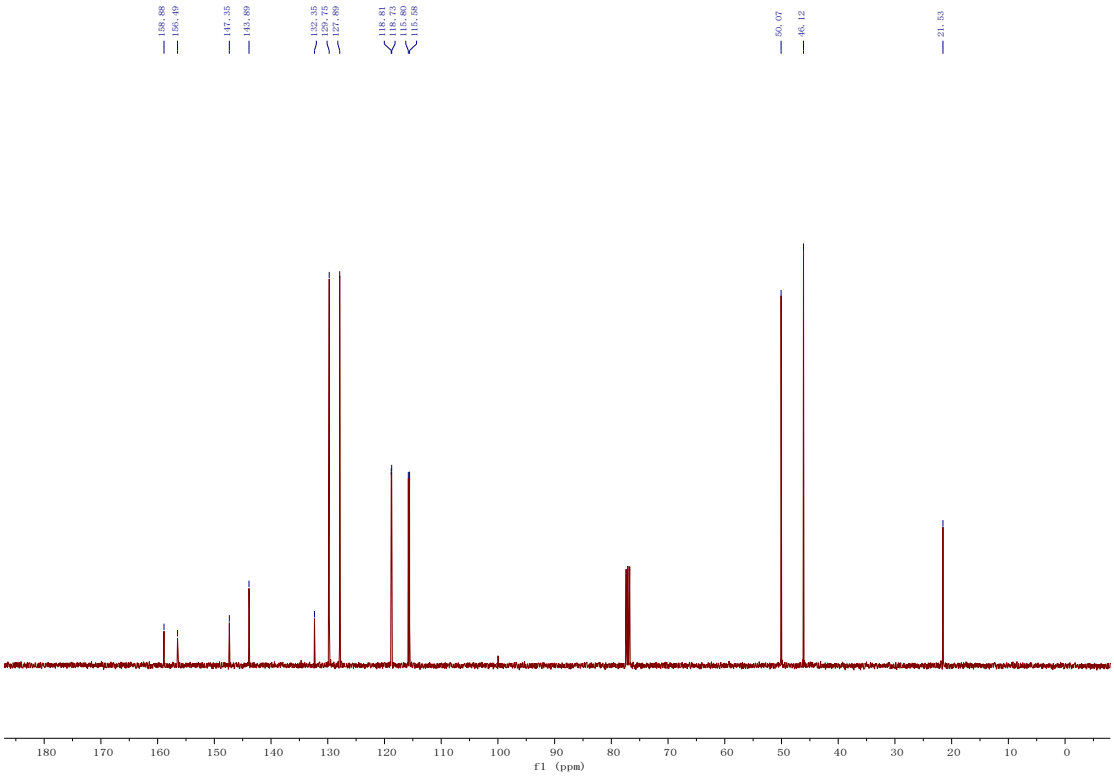

7.68
7.66
7.36
7.35
7.33
7.20
7.19
7.18
7.18
6.80
6.79
6.78
6.77
6.76
3.21
3.20
3.19
3.16
3.14
3.13
2.44
2.00
2.00
2.00
2.00
4.00
4.00
3.00
f1 (ppm)

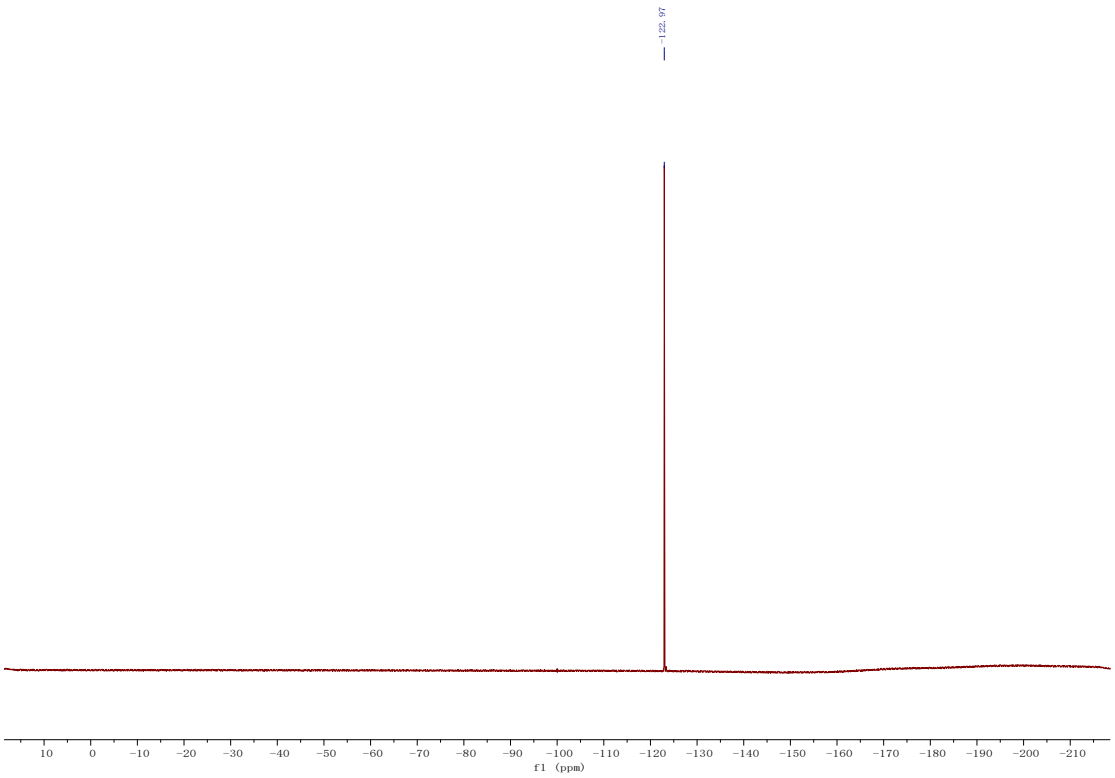

149.26
143.91
132.36
129.75
129.11
127.98
125.71
118.04
49.14
45.93
21.53
f1 (ppm)

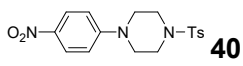

F
N
N–Ts

39

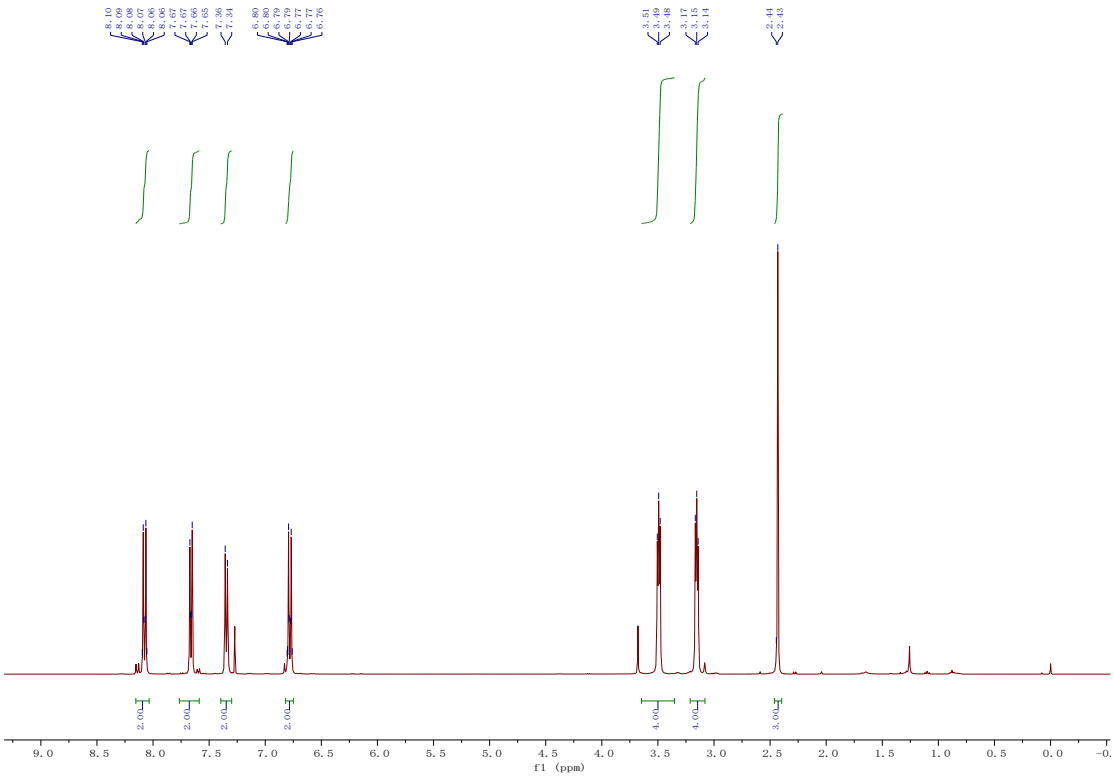

7.68
7.66
7.35
7.33
6.96
6.93
6.91
6.85
6.82
6.81
6.80
3.14
2.43
2.00
2.00
2.00
2.00
8.00
3.00
f1 (ppm)

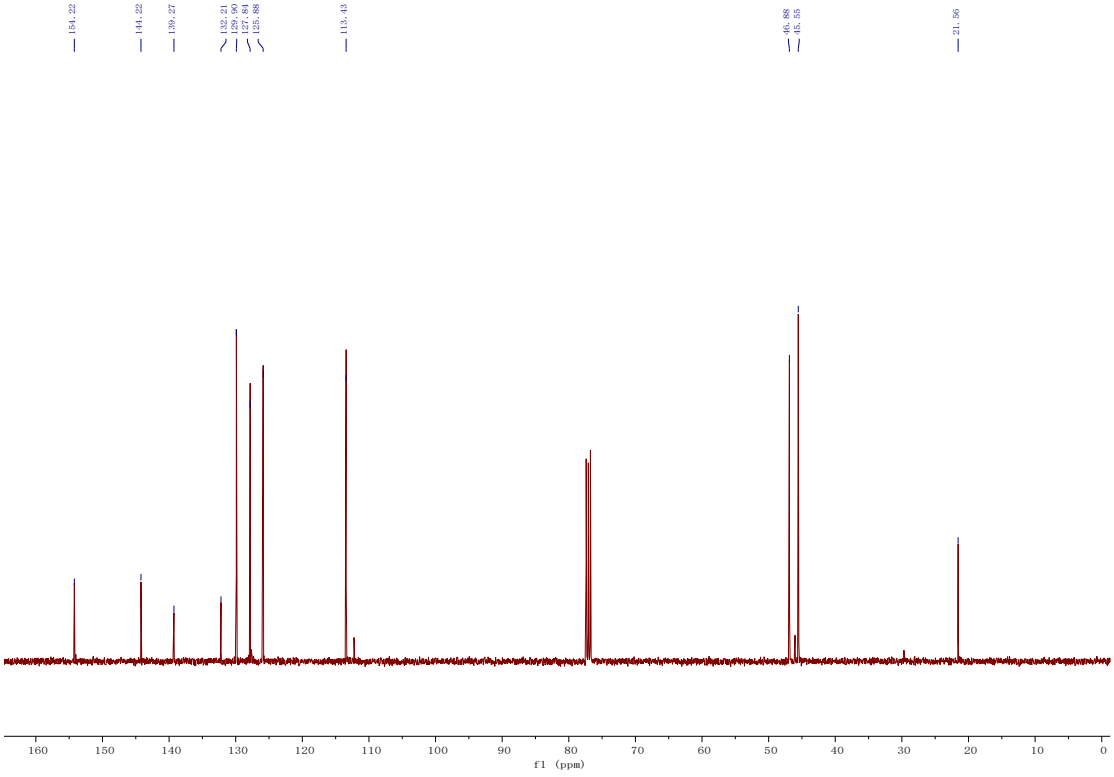

158.88
156.49
147.35
143.89
132.35
129.75
127.89
118.81
118.73
115.80
115.58
50.07
46.12
21.53
f1 (ppm)


-122.97
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


O2N
N
N
Ts

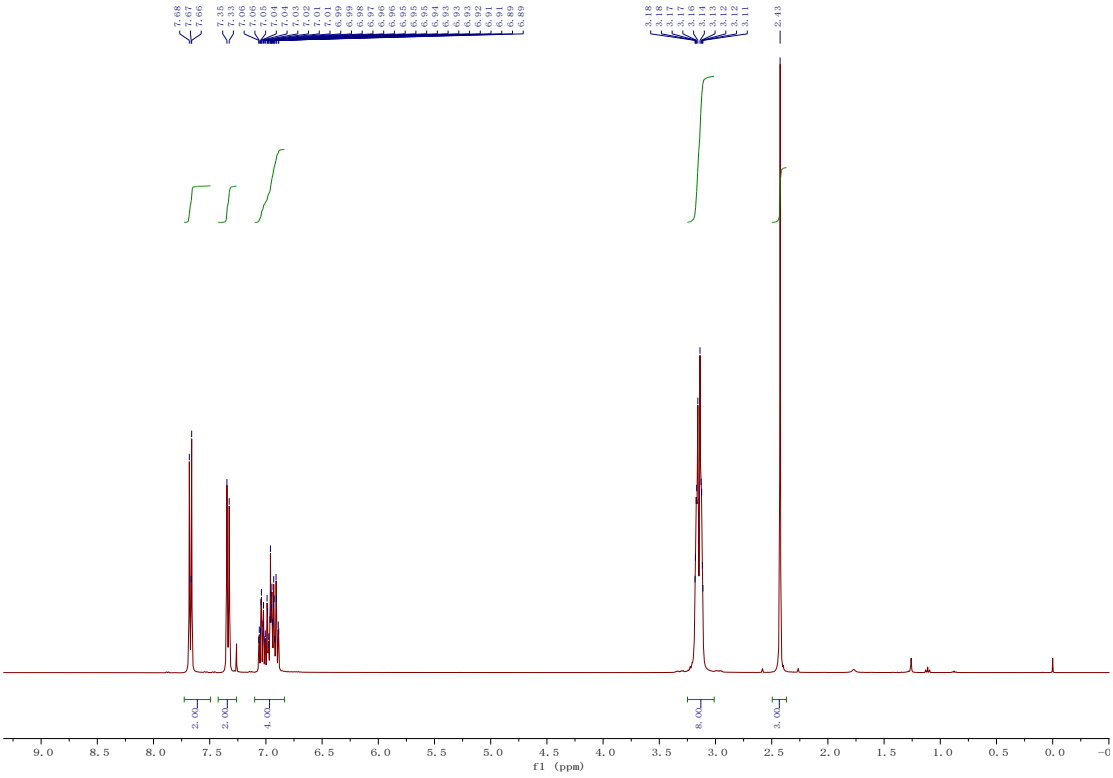
40

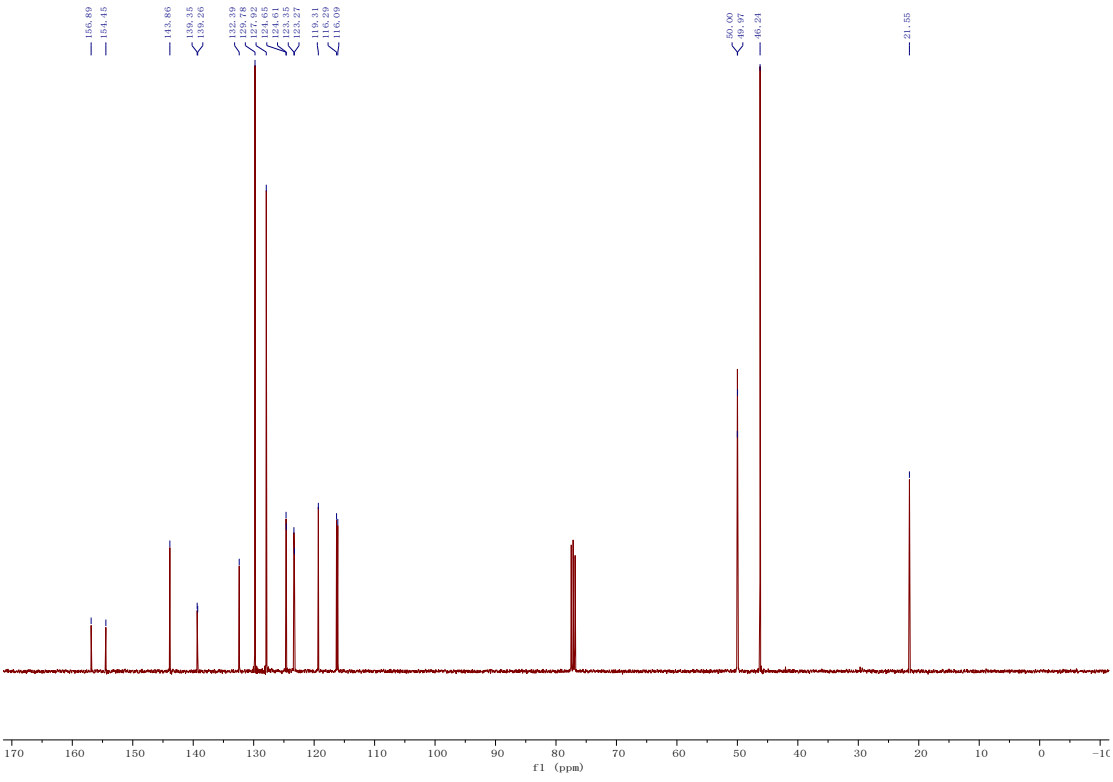

8.10
8.09
8.08
8.07
8.06
8.05
7.67
7.67
7.66
7.65
7.35
7.34
6.80
6.80
6.79
6.79
6.77
6.77
6.76
3.51
3.49
3.48
3.17
3.15
3.14
2.44
2.43
2.00
2.00
2.00
2.00
4.00
4.00
3.00
f1 (ppm)

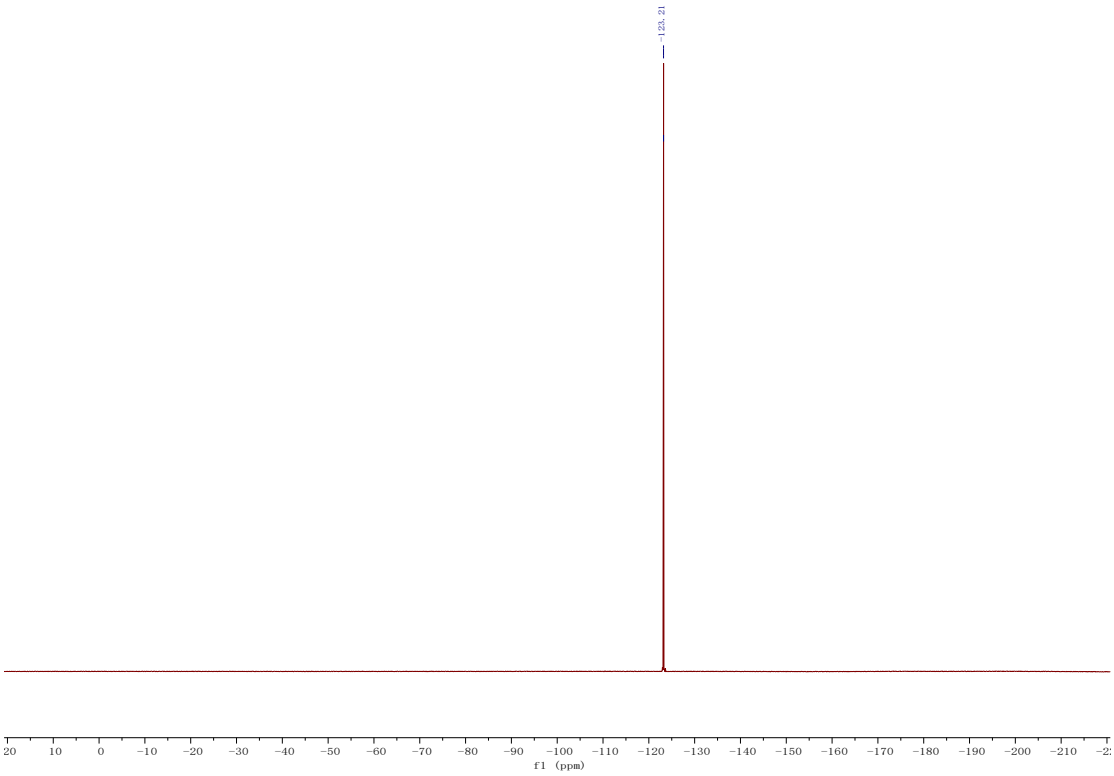

154.22
144.22
139.27
132.21
129.90
127.84
125.88
113.43
46.88
45.55
21.56
f1 (ppm)

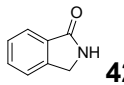

F
N
N−Ts

41

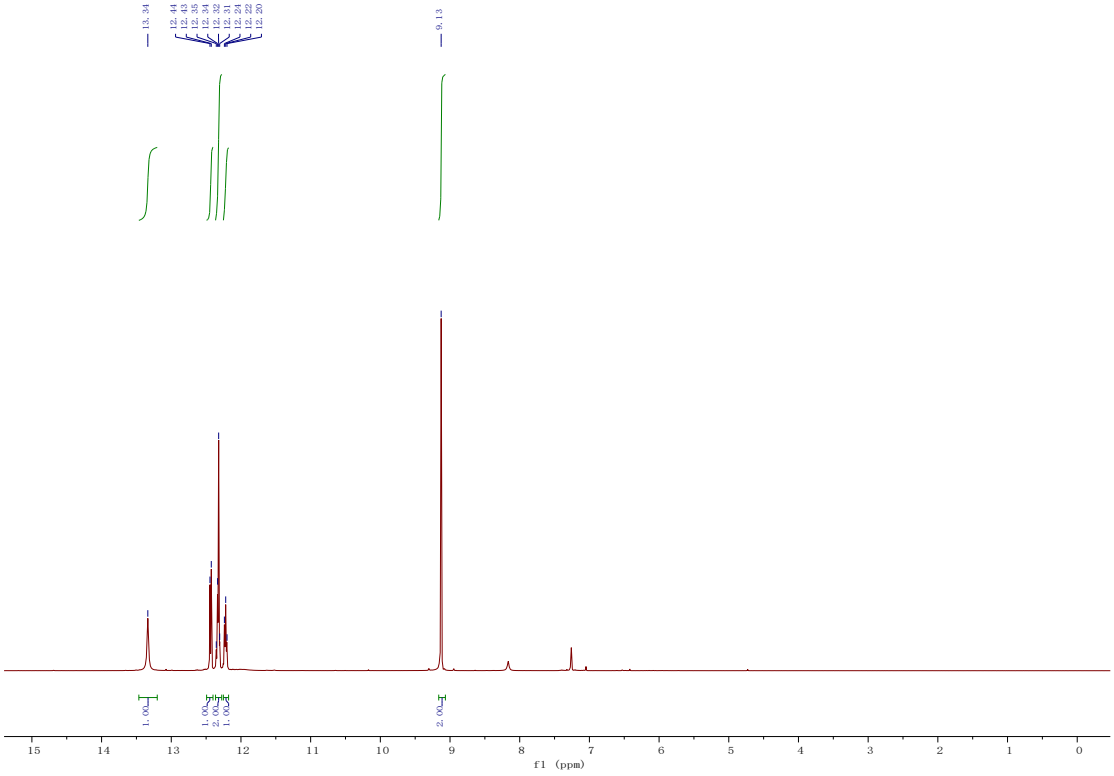

7.68
7.67
7.66
7.35
7.33
7.06
7.05
7.04
7.03
7.02
7.01
6.99
6.99
6.98
6.97
6.96
6.95
6.95
6.95
6.94
6.93
6.93
6.92
6.91
6.91
6.89
6.89
3.18
3.18
3.17
3.17
3.16
3.14
3.13
3.12
3.11
2.43
2.00
2.00
4.00
8.00
3.00
f1 (ppm)

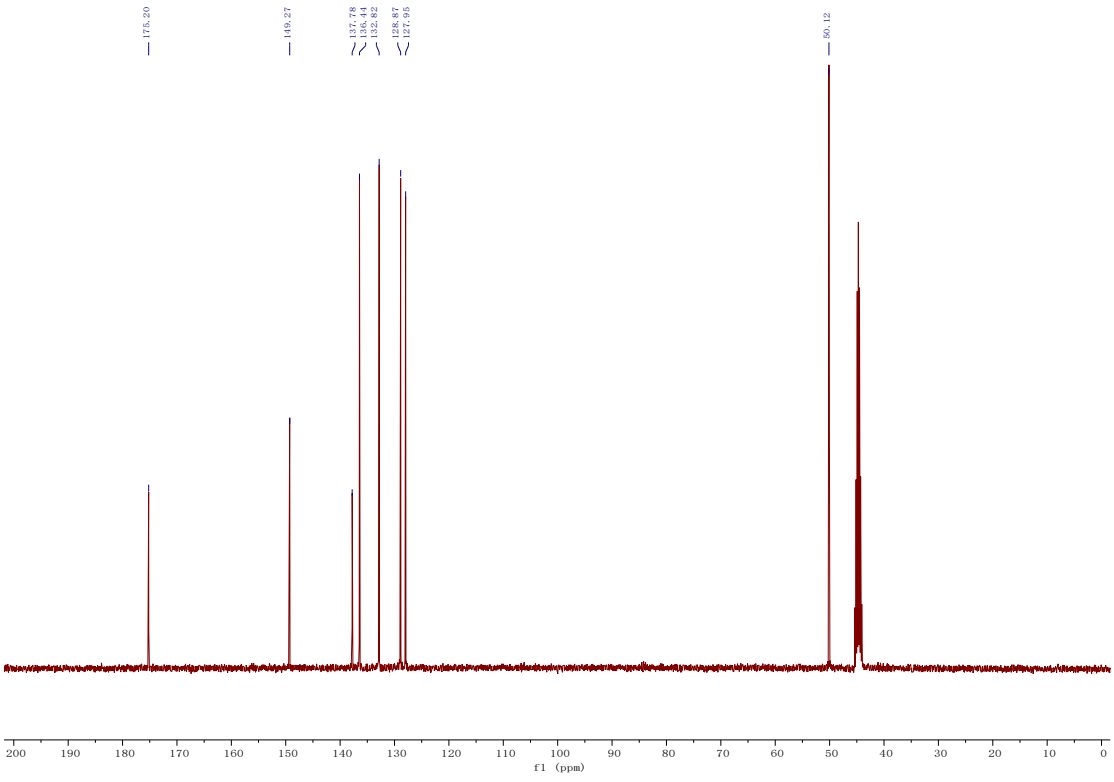

156.89
154.45
143.86
139.35
139.26
132.39
129.78
127.92
124.65
124.61
123.35
123.27
119.31
116.29
116.09
50.99
49.97
46.24
21.55
f1 (ppm)

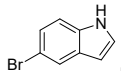

-123.21
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


O
NH

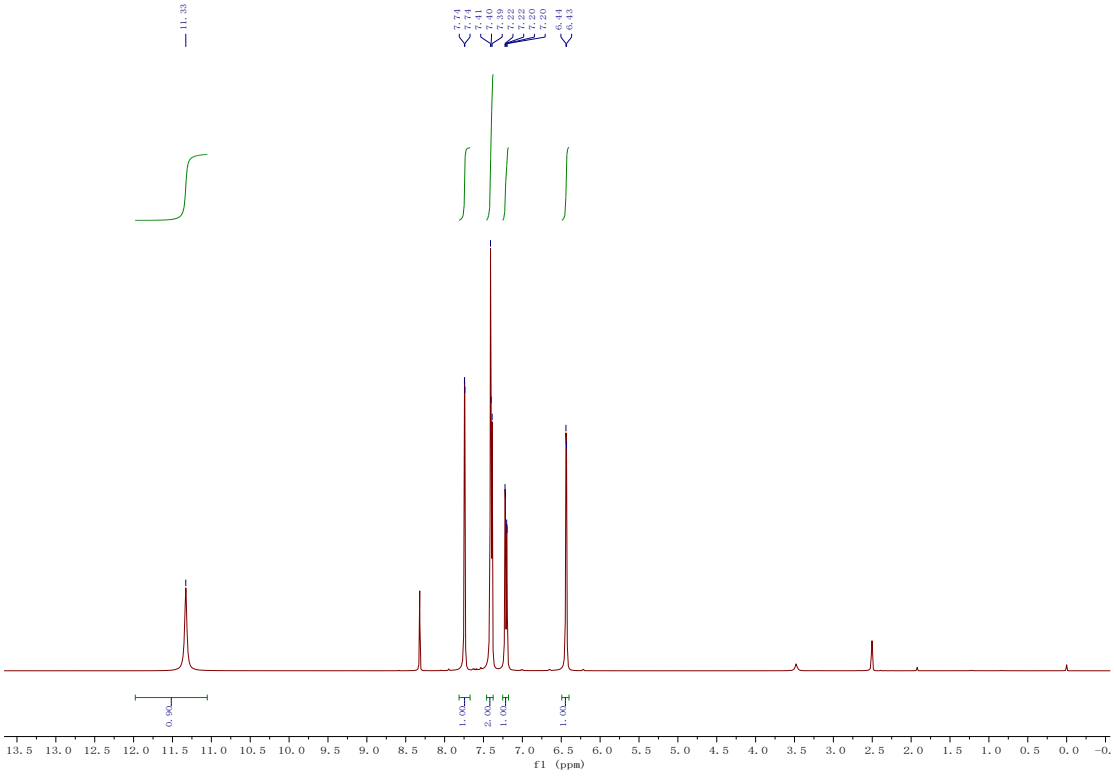
42

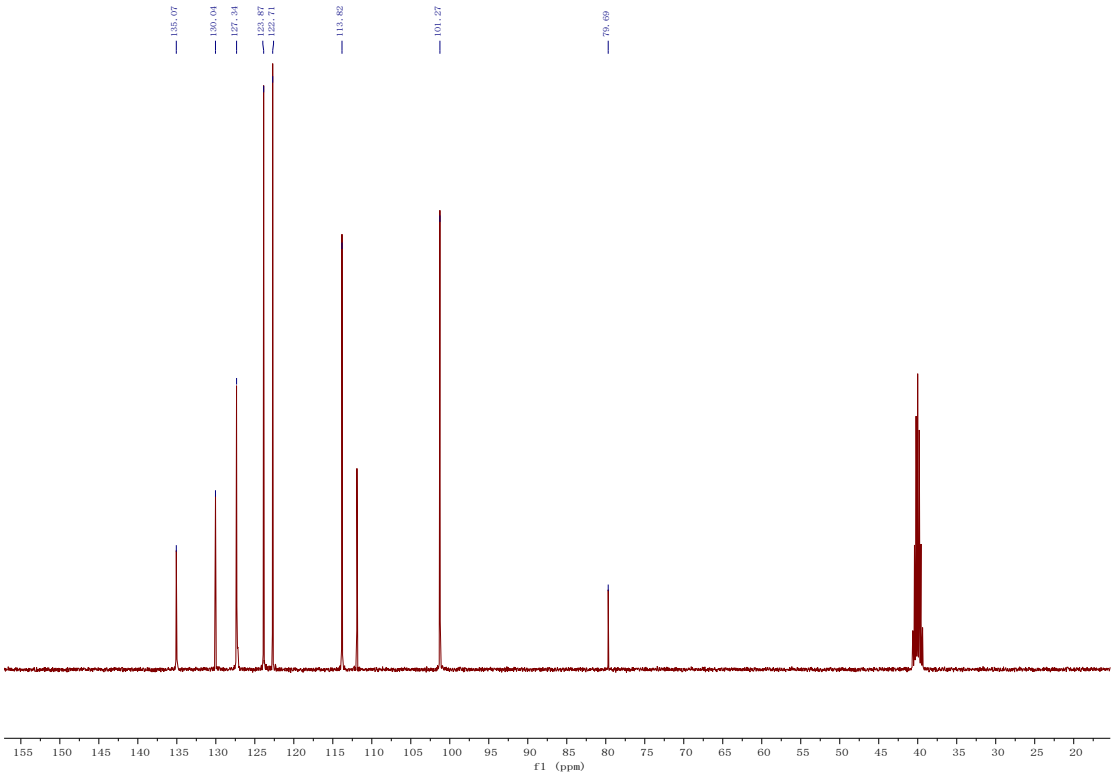

13.34
12.44
12.43
12.35
12.34
12.32
12.31
12.24
12.22
12.20
9.13
1.00
2.00
1.00
2.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

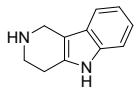

175.20
149.27
137.78
135.44
132.82
128.87
127.98
50.12
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H
N
Br

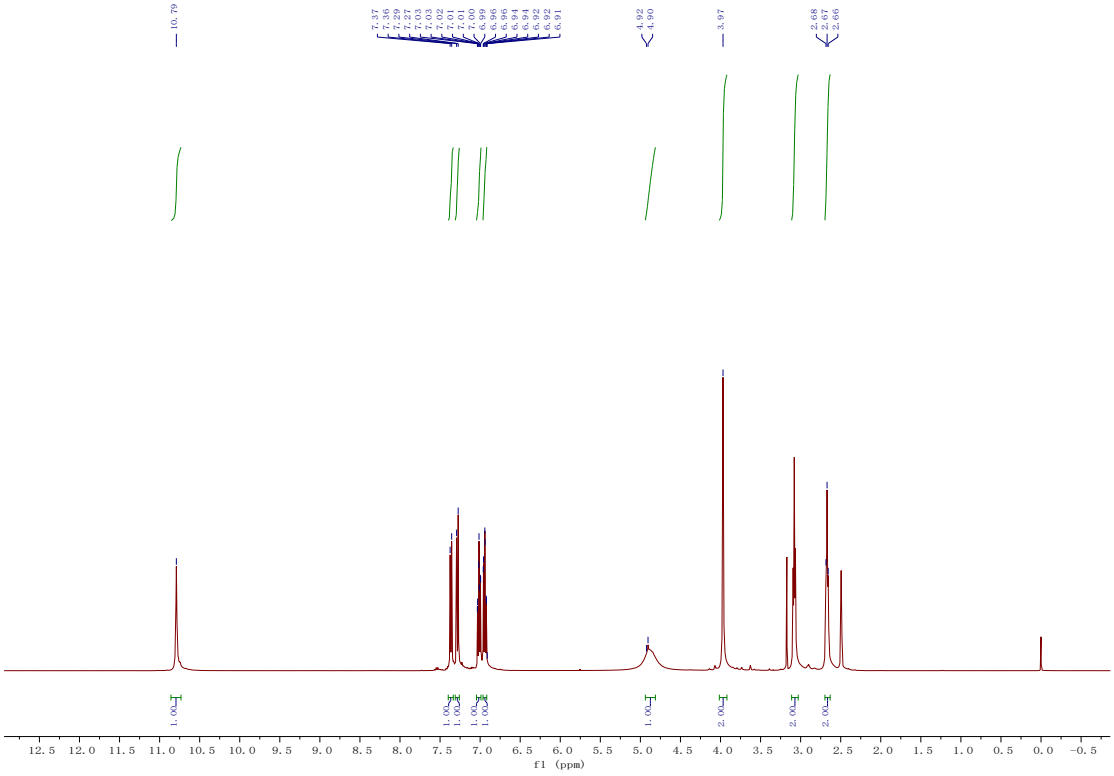
43

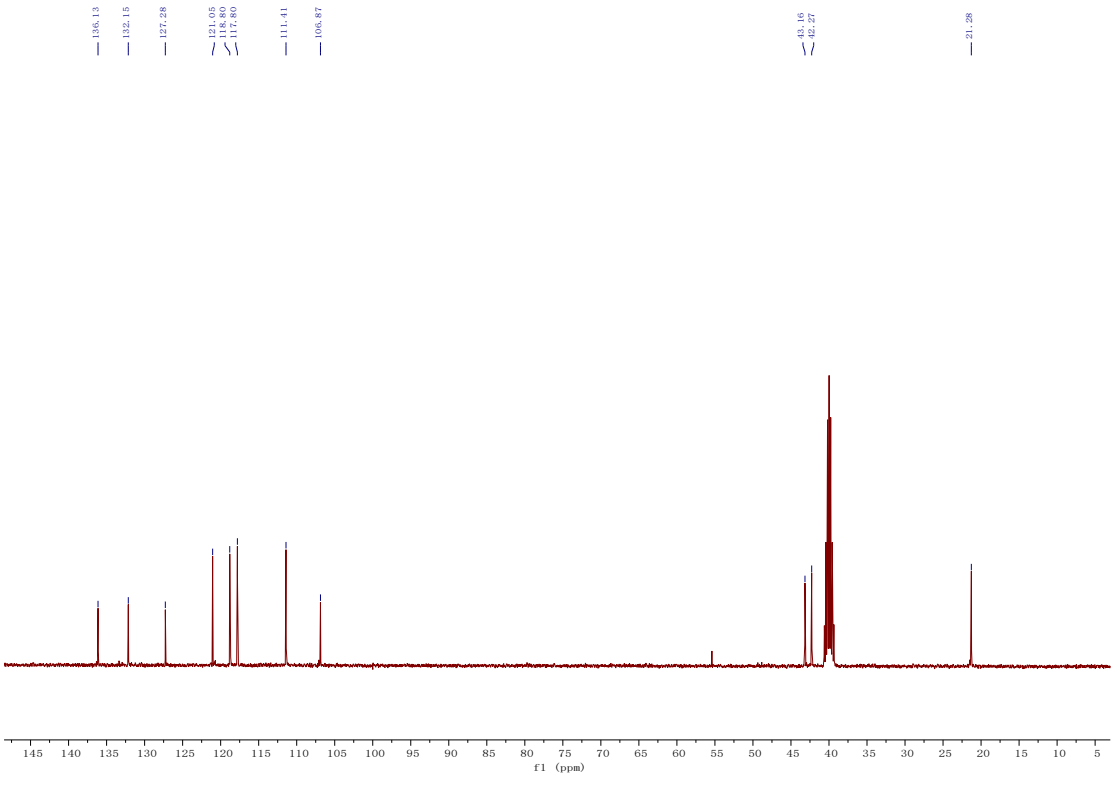

11.33
7.74
7.74
7.41
7.40
7.39
7.22
7.20
7.20
6.44
6.43
0.90
1.00
2.00
1.00
1.00
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

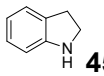

135.07
130.04
127.34
123.87
122.71
113.82
101.27
79.69
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)


HN
N
H

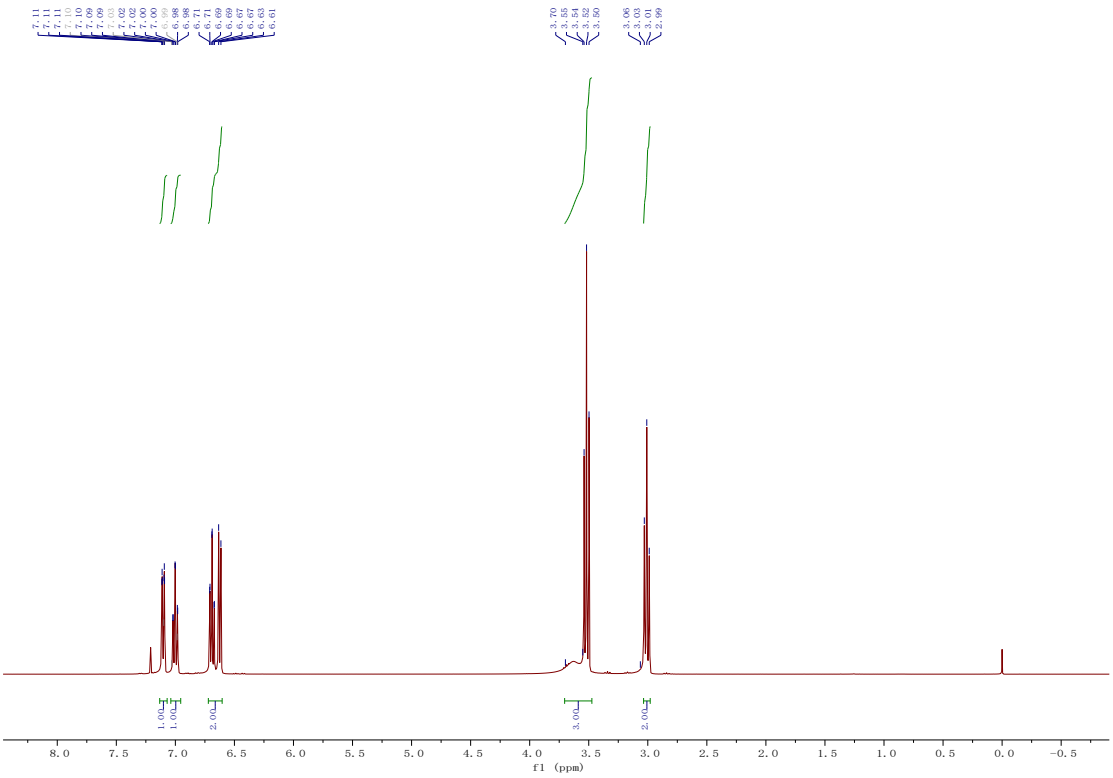
44

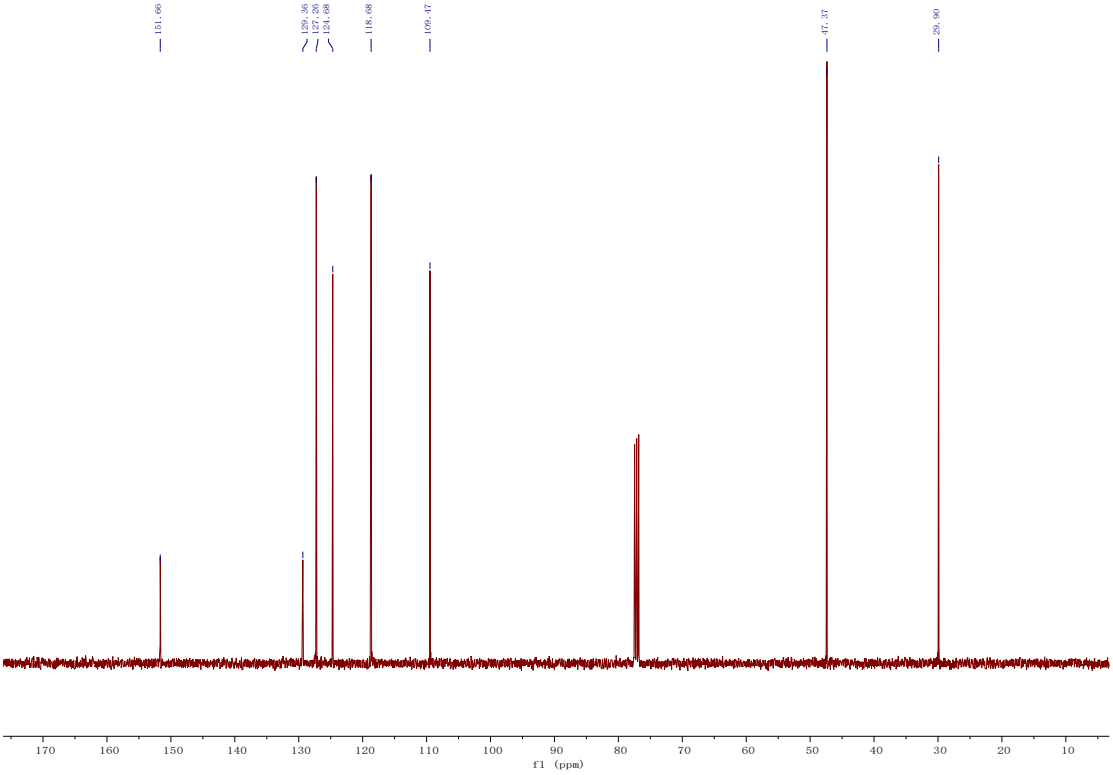

10.79
7.37
7.36
7.29
7.27
7.03
7.02
7.01
7.01
7.00
6.99
6.96
6.95
6.94
6.92
6.92
6.91
4.92
4.90
3.97
2.68
2.67
2.66
1.00
1.00
1.00
1.00
1.00
2.00
2.00
2.00
f1 (ppm)

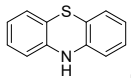

136.13
132.15
127.28
121.05
118.80
117.80
111.41
106.87
43.16
42.27
21.28
f1 (ppm)



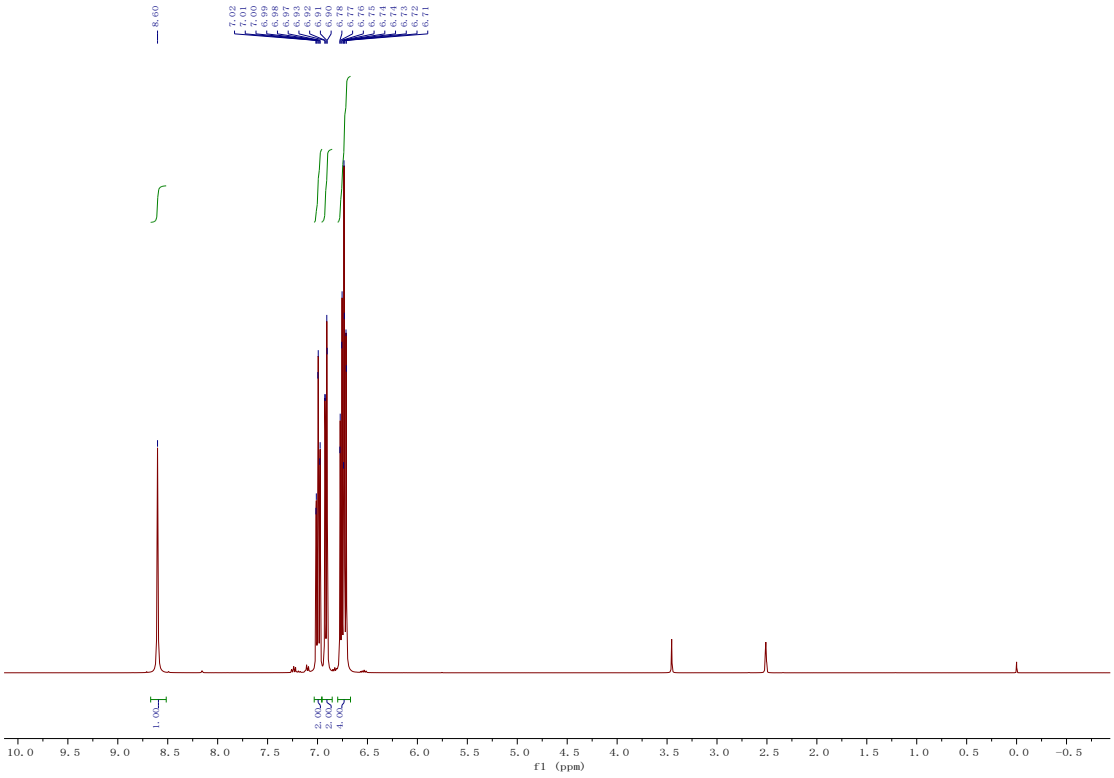
45

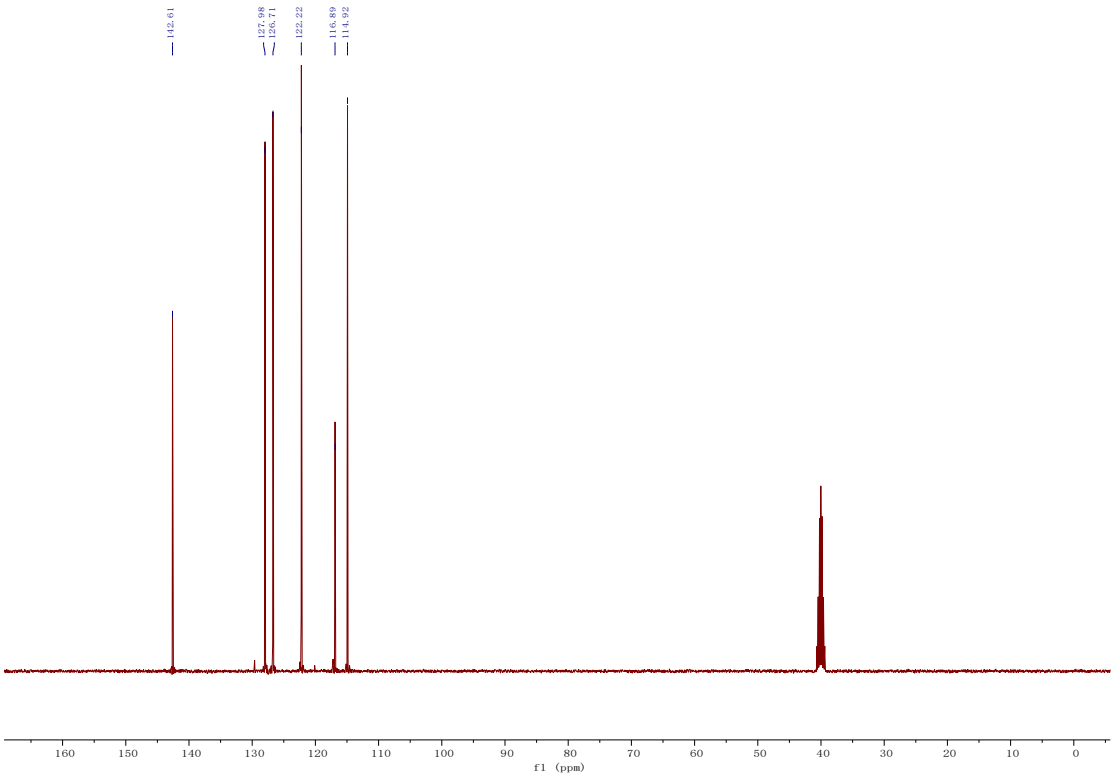

7.11
7.11
7.11
7.10
7.10
7.09
7.09
7.09
7.02
7.02
7.00
7.00
6.98
6.71
6.71
6.69
6.69
6.67
6.67
6.63
6.61
3.70
3.55
3.54
3.52
3.50
3.06
3.03
3.01
2.99
1.00
1.00
2.00
3.00
2.00
f1 (ppm)


151.66
129.35
127.26
124.68
118.68
109.47
47.37
29.90
f1 (ppm)

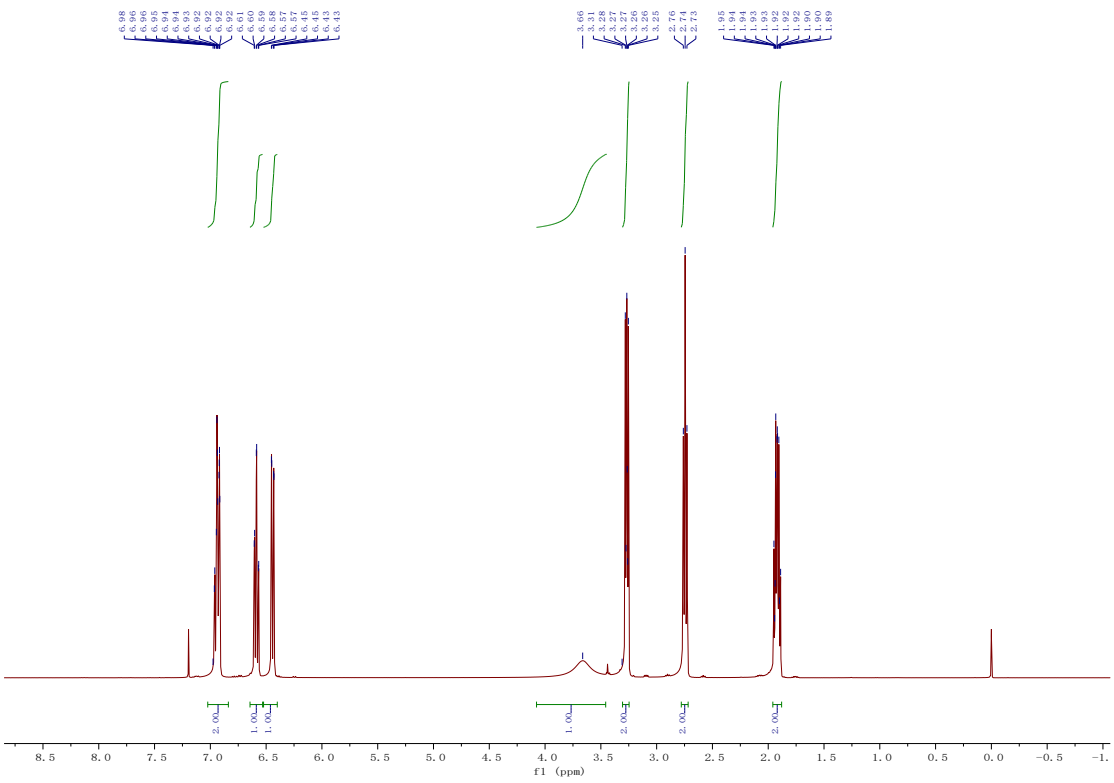

S
N
H

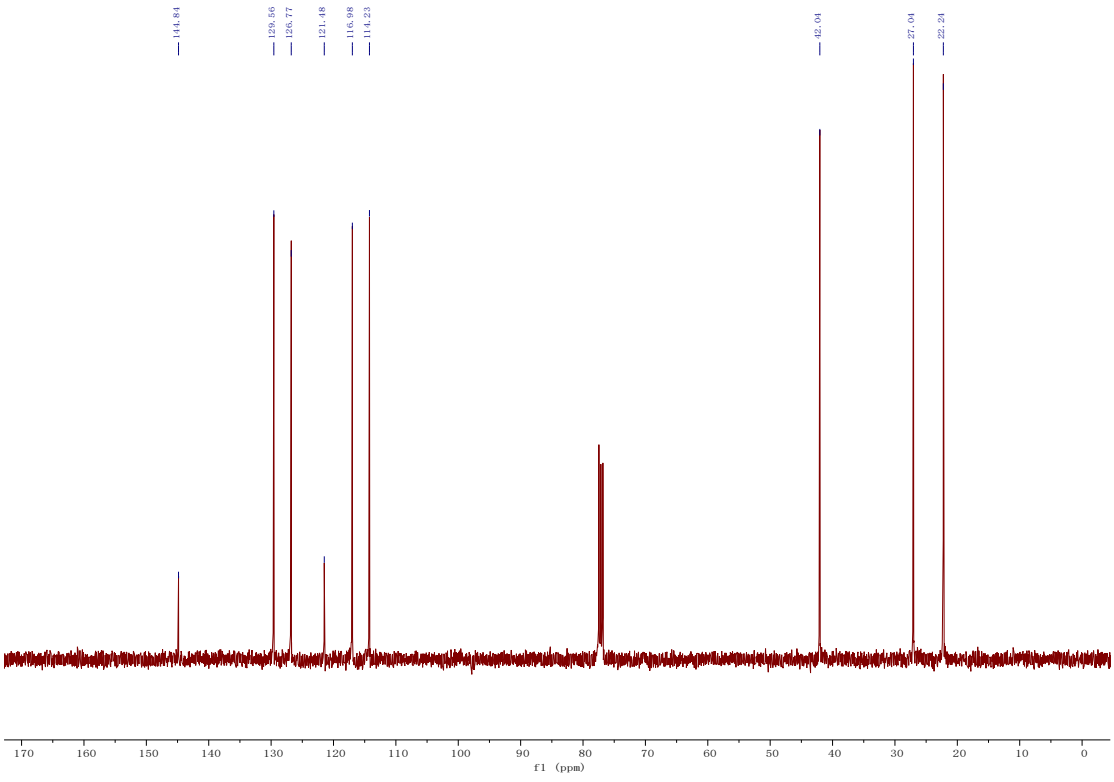
46

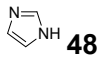

8.60
7.02
7.01
7.00
6.99
6.98
6.97
6.93
6.92
6.91
6.90
6.78
6.77
6.76
6.75
6.74
6.74
6.73
6.72
6.71
1.00
2.00
2.00
4.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


142.61
127.98
126.71
122.22
116.89
114.92
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

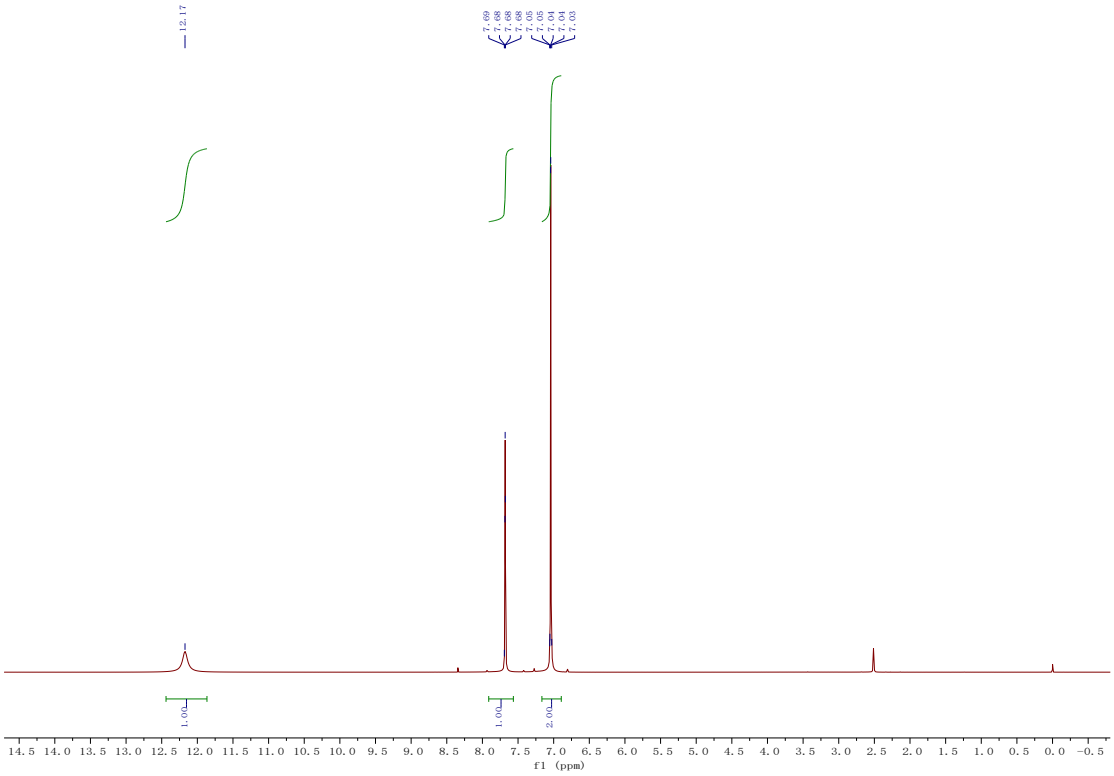
47

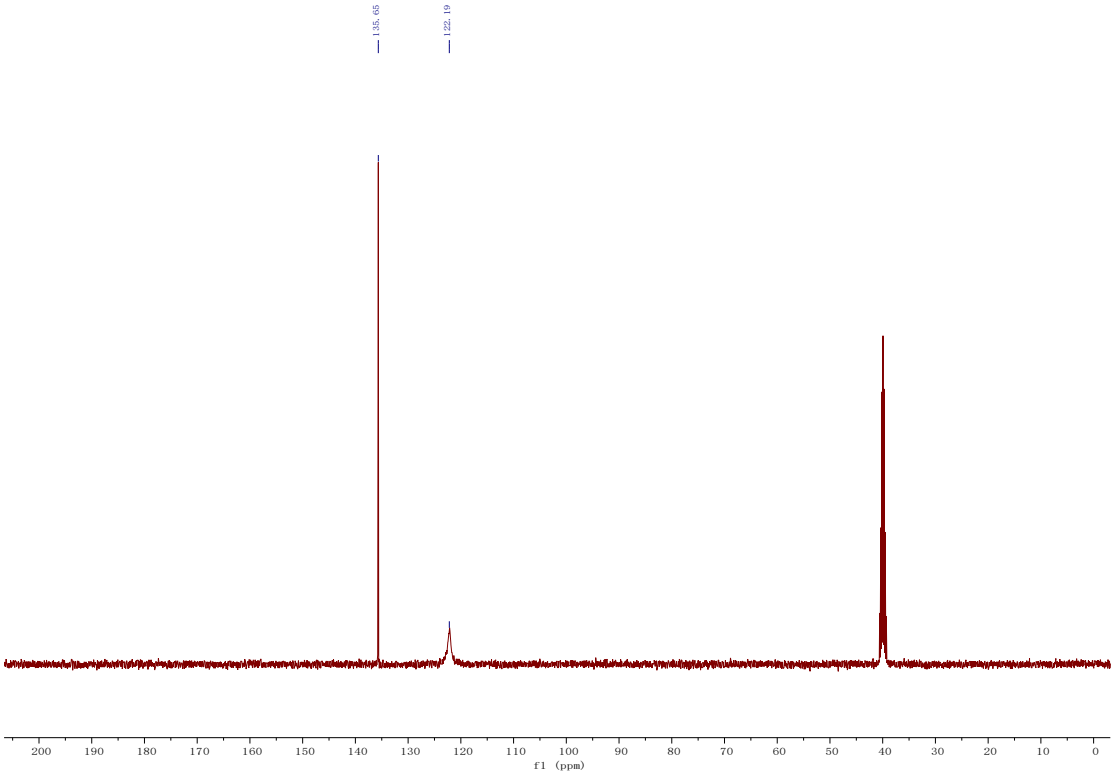

6.98
6.96
6.96
6.95
6.94
6.94
6.93
6.92
6.92
6.92
6.61
6.60
6.59
6.58
6.57
6.57
6.45
6.43
6.43
3.66
3.31
3.28
3.27
3.27
3.26
3.26
3.25
2.76
2.74
2.73
1.95
1.94
1.94
1.93
1.93
1.92
1.92
1.92
1.90
1.90
1.89
2.00
1.00
1.00
1.00
2.00
2.00
2.00
f1 (ppm)

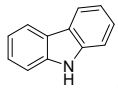

144.84
129.56
126.77
121.48
116.98
114.23
42.04
27.04
22.24
f1 (ppm)


N
NH

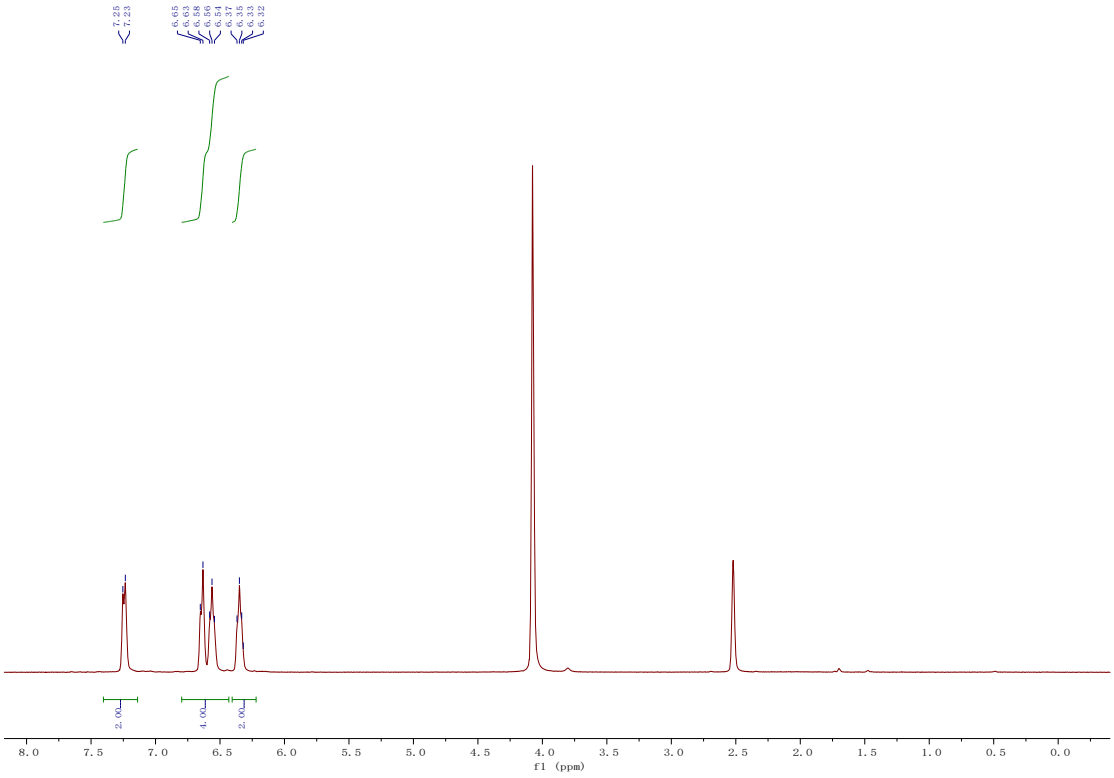
48

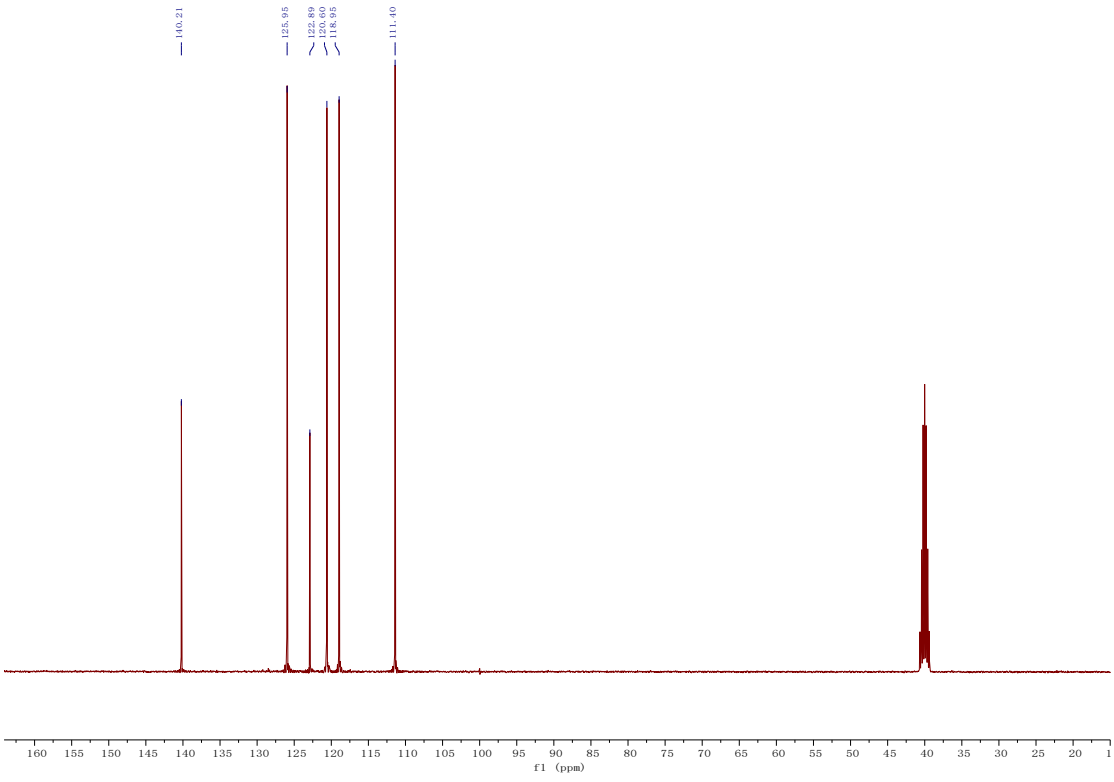

12.17
7.69
7.68
7.68
7.68
7.05
7.04
7.04
7.03
1.00
1.00
2.00
14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


135.65
122.19
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

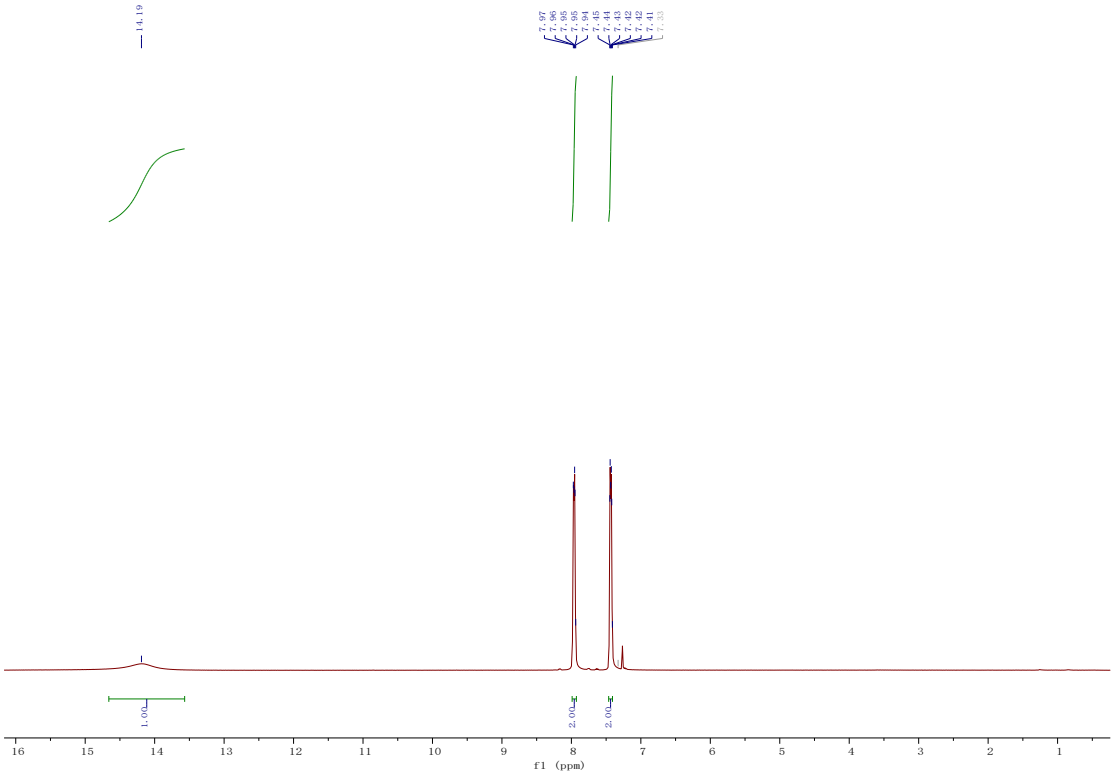


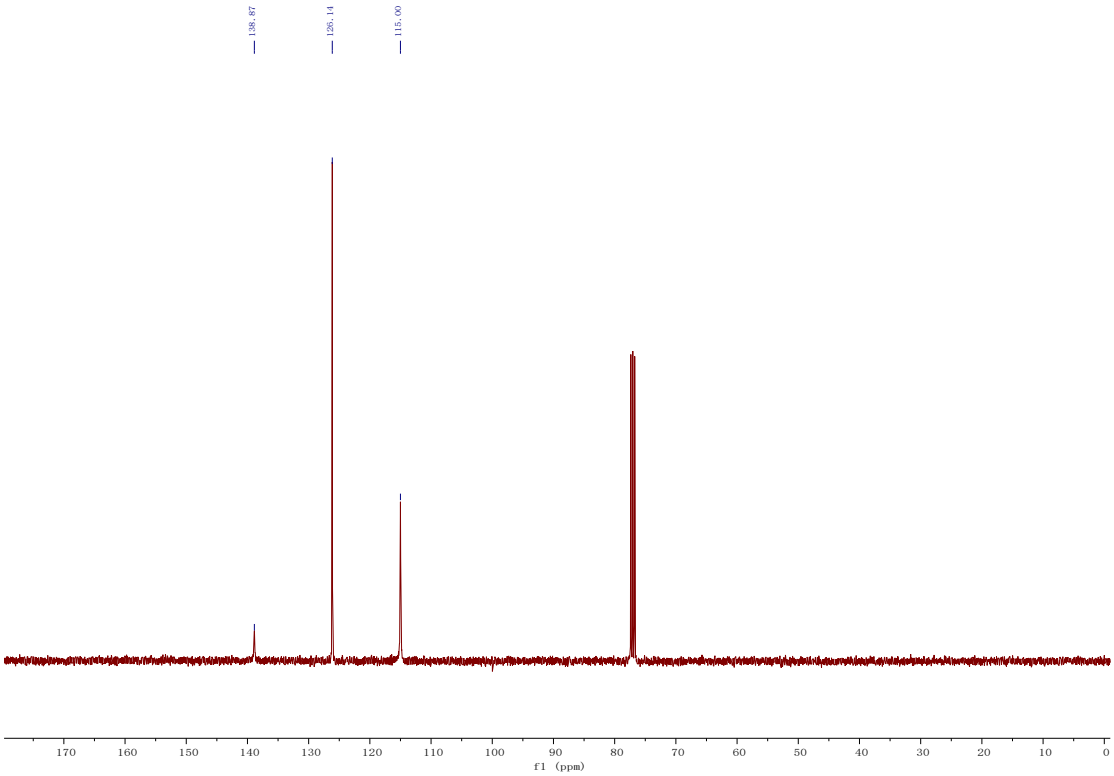
49

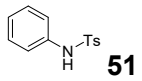

7.25
7.23
6.65
6.63
6.58
6.56
6.54
6.37
6.35
6.33
6.32
2.06
4.06
2.06
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


140.21
125.95
122.89
120.60
118.95
111.40
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 1
f1 (ppm)

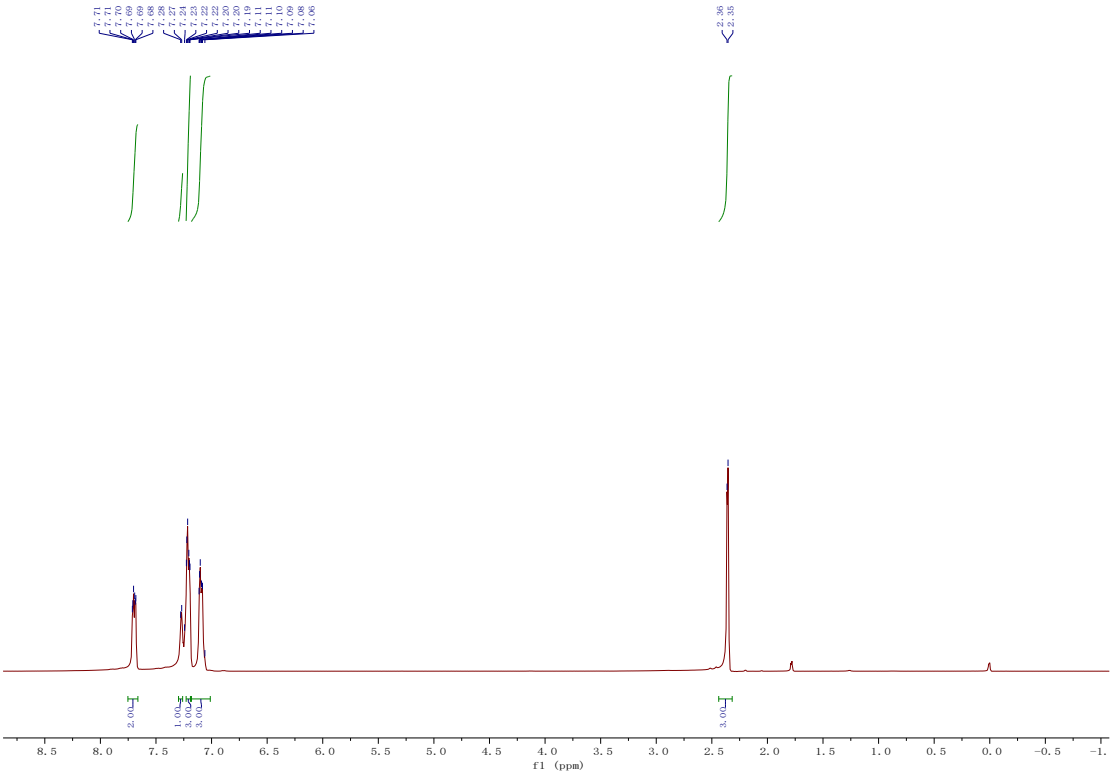
50

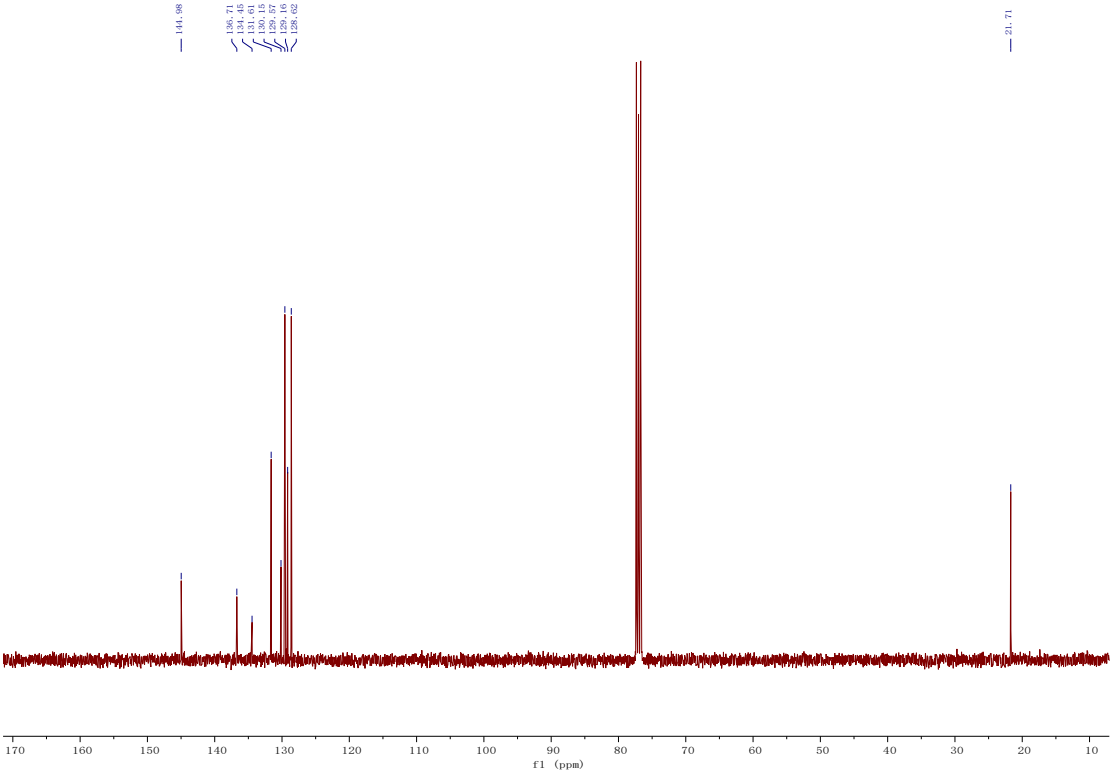

14.19
7.97
7.96
7.96
7.95
7.94
7.45
7.44
7.43
7.42
7.41
7.33
1.00
2.00
2.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
f1 (ppm)

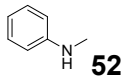

138.87
126.14
115.00
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ts
N
H

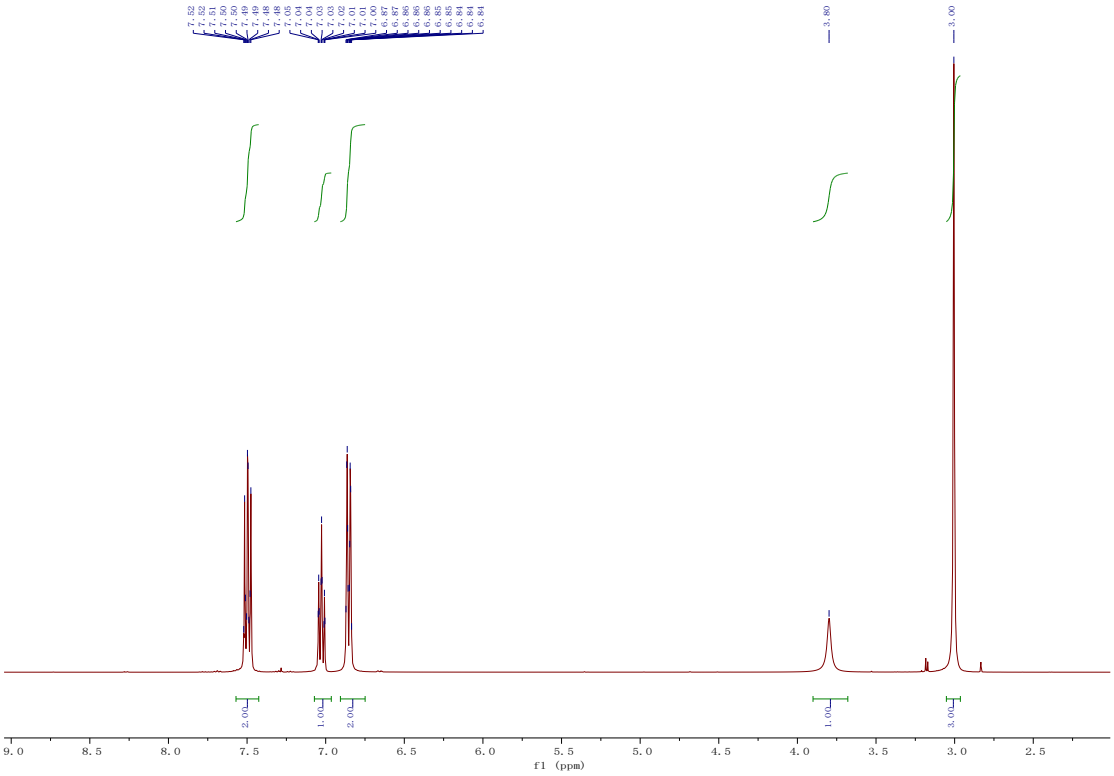
51

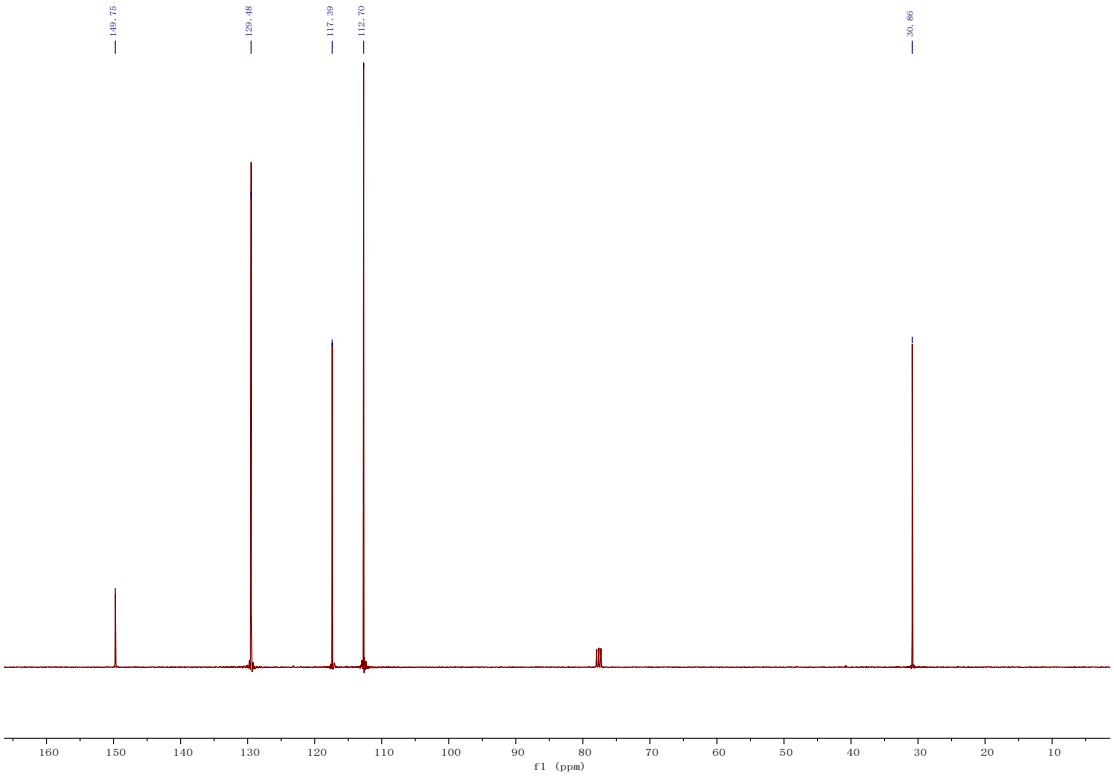

7.71
7.71
7.70
7.69
7.69
7.68
7.28
7.27
7.24
7.23
7.22
7.22
7.20
7.20
7.19
7.11
7.11
7.10
7.09
7.08
7.06
2.36
2.35
2.00
1.00
3.03
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.
f1 (ppm)

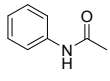

144.98
136.71
134.45
131.61
130.15
129.57
129.16
128.62
21.71
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



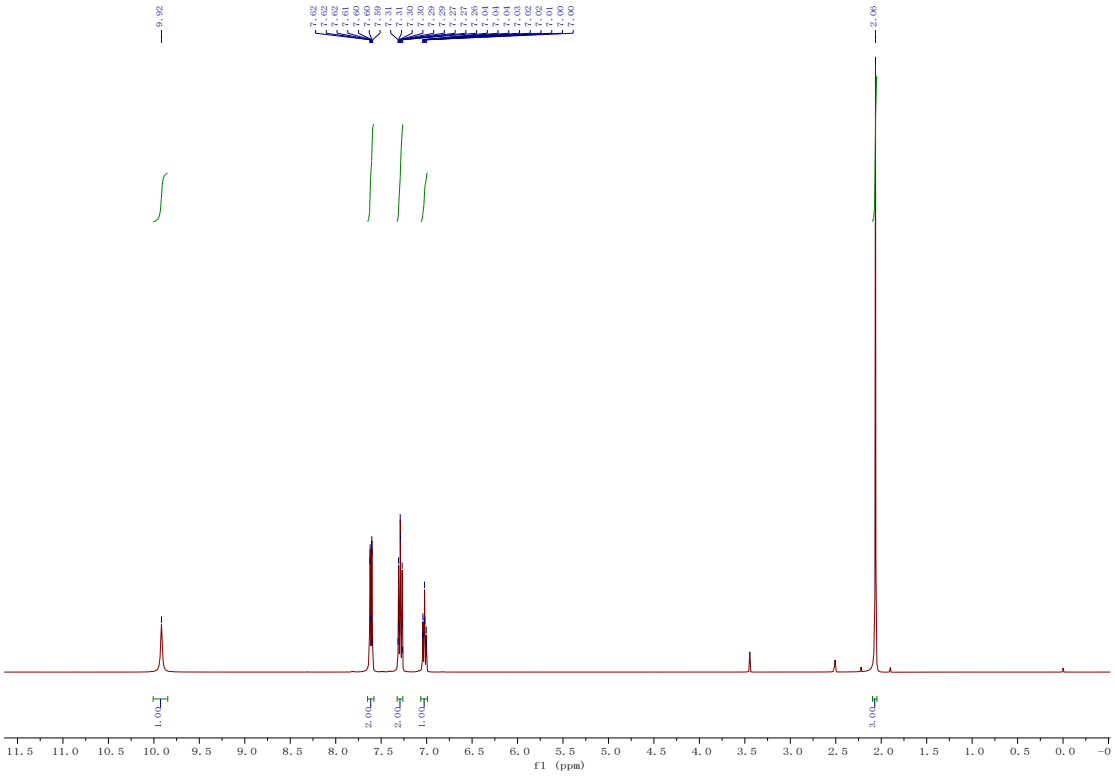
52

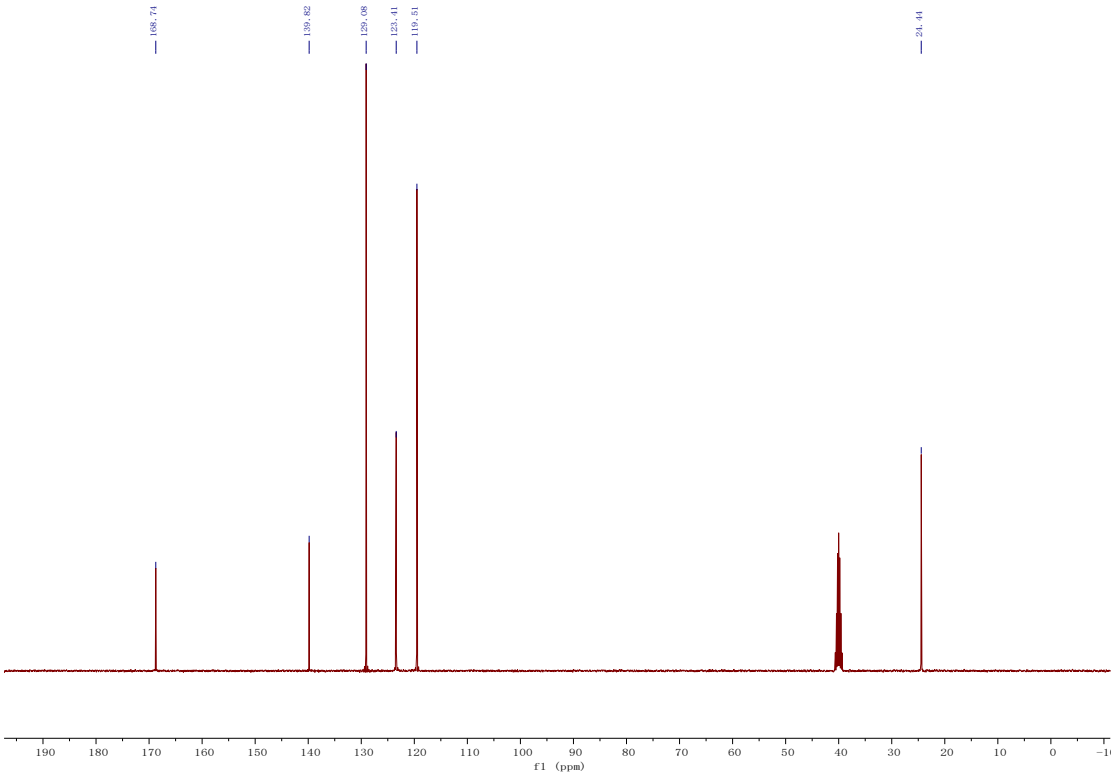

7.52
7.52
7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.05
7.04
7.04
7.03
7.03
7.02
7.01
7.01
7.00
6.87
6.87
6.86
6.86
6.85
6.85
6.84
6.84
3.80
3.00
2.00
1.00
2.00
1.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)

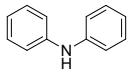

149.75
129.48
117.39
112.70
30.86
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



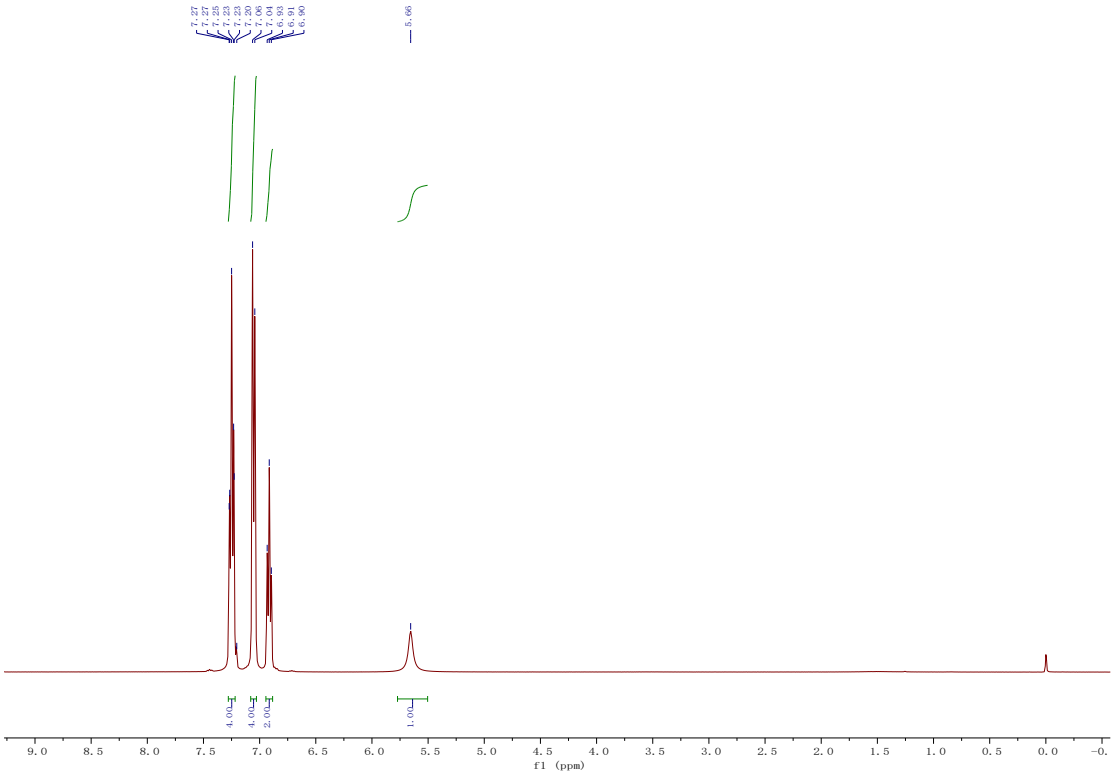
53

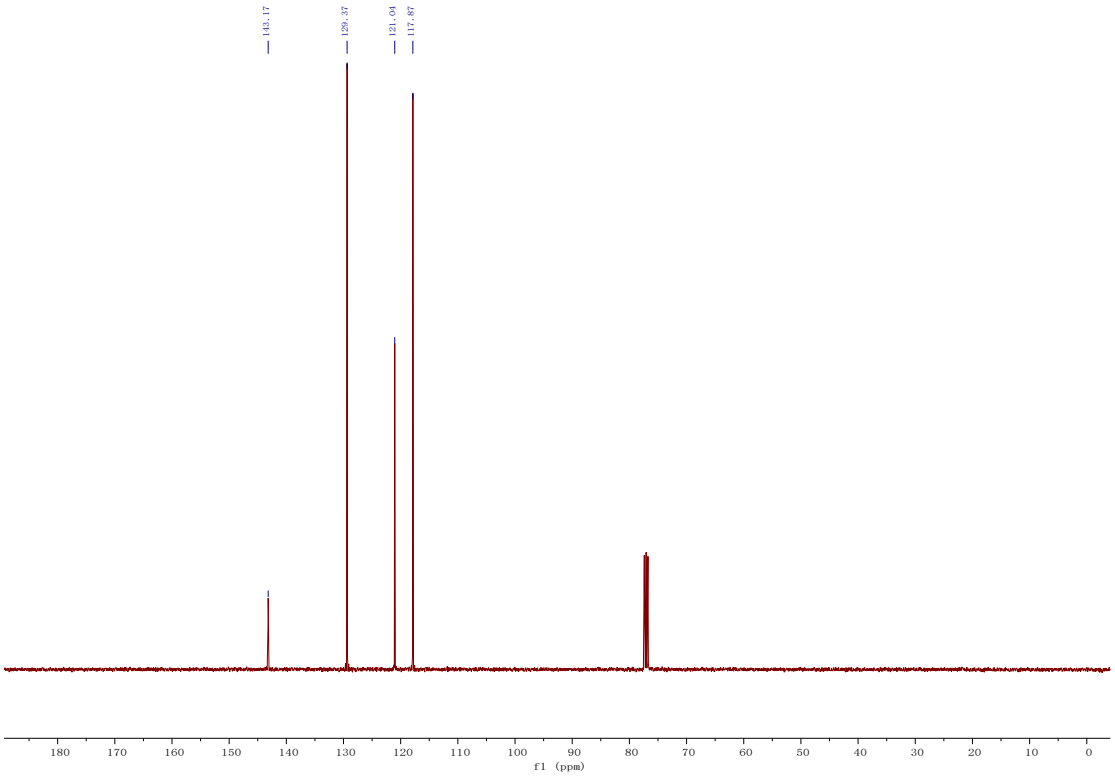

9.92
7.62
7.62
7.62
7.61
7.60
7.59
7.59
7.31
7.31
7.30
7.30
7.29
7.29
7.27
7.27
7.27
7.26
7.04
7.04
7.04
7.03
7.02
7.02
7.01
7.00
7.00
2.06
1.00
2.00
2.00
1.00
3.00
f1 (ppm)

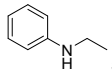

168.74
139.82
129.08
123.41
119.51
24.44
f1 (ppm)



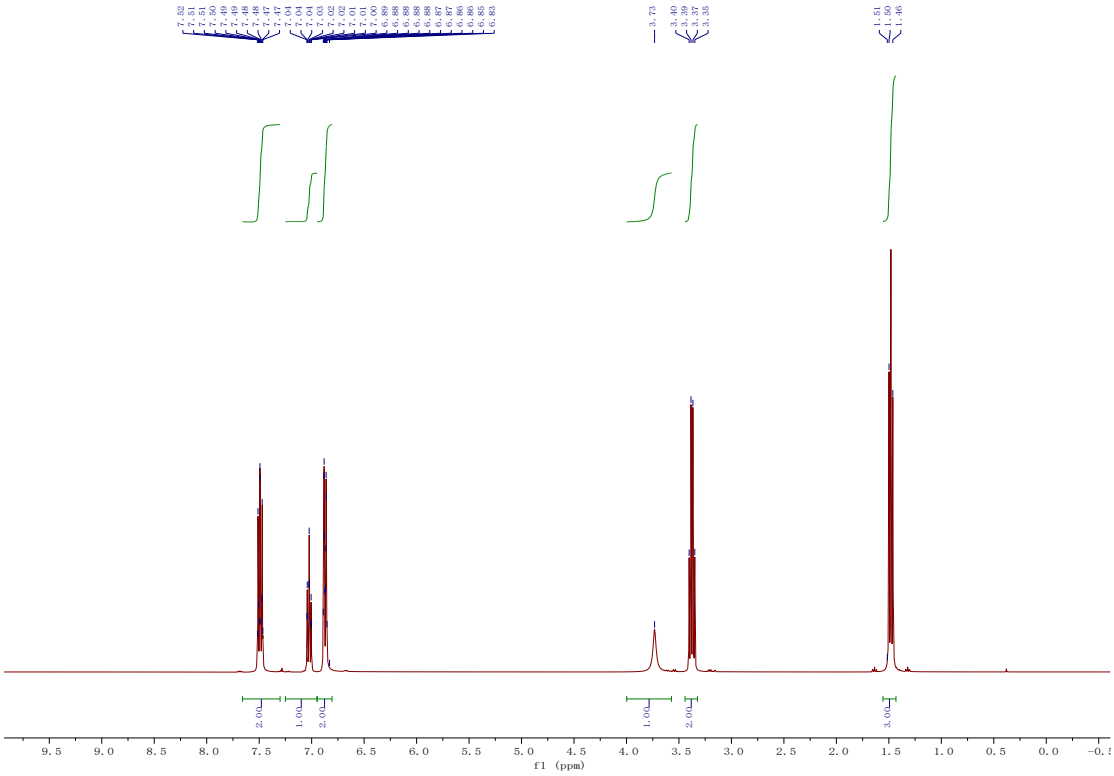
54

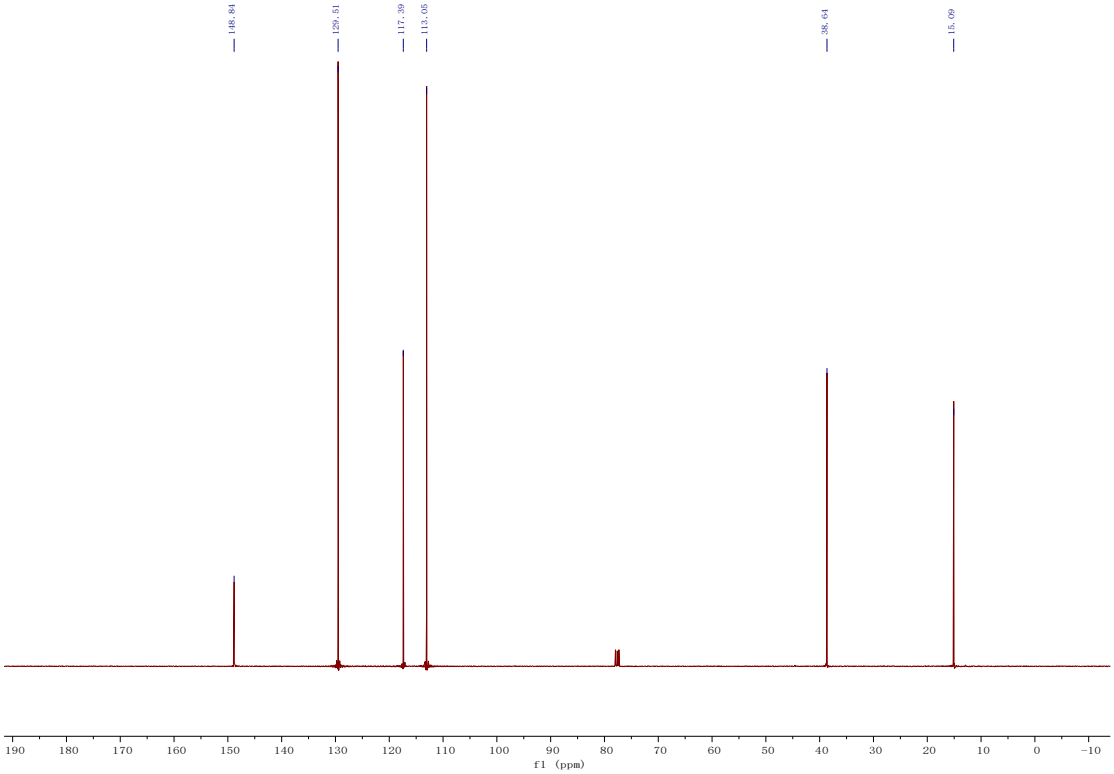

7.27
7.27
7.25
7.23
7.23
7.20
7.06
7.04
6.95
6.91
6.90
5.66
4.00
4.00
2.00
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

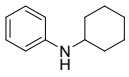

143.17
129.37
121.04
117.87
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



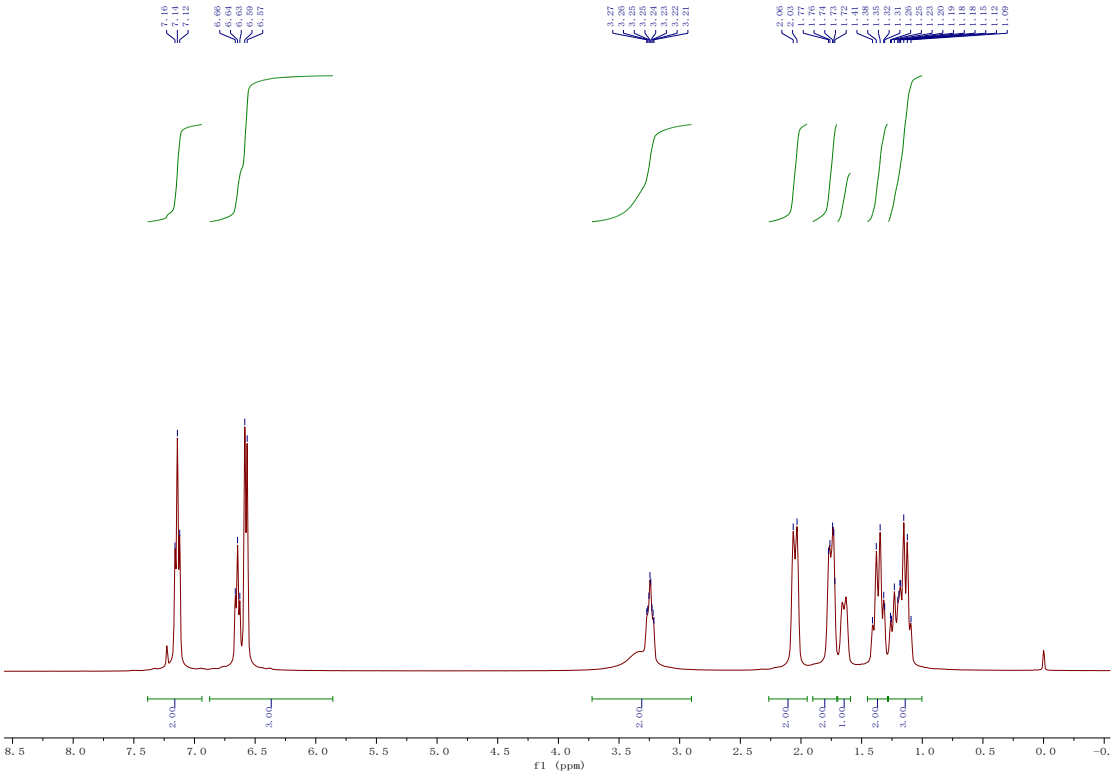
55

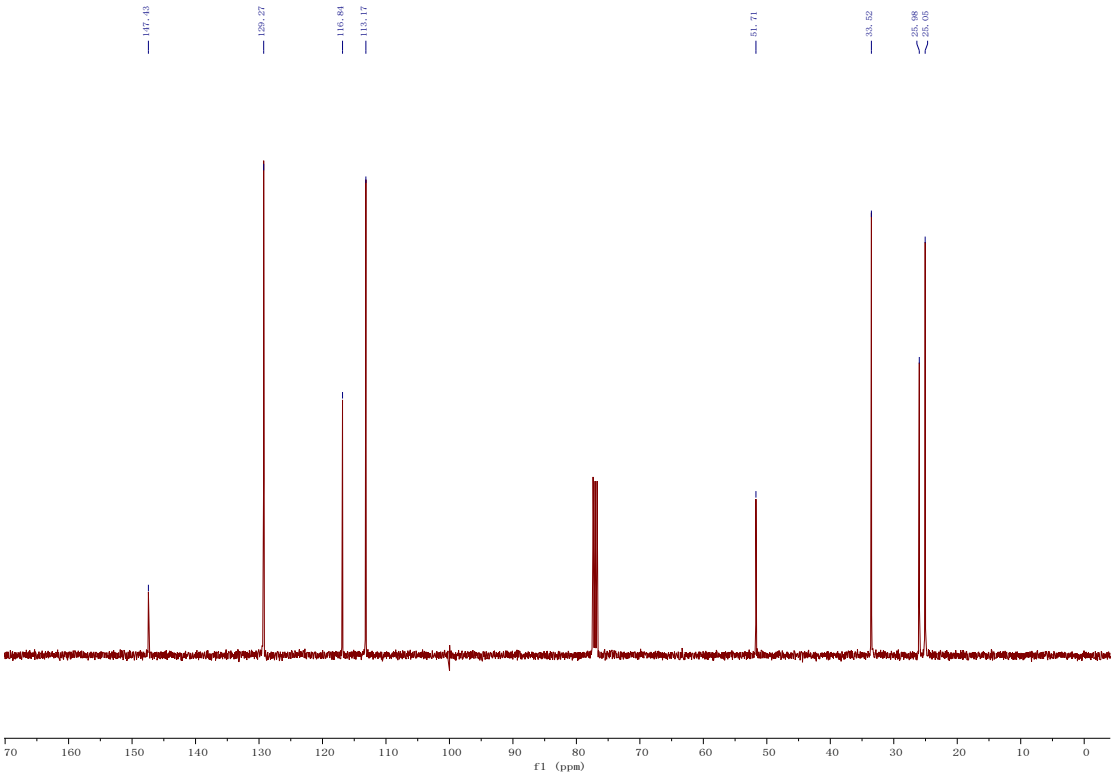

7.52
7.51
7.51
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.04
7.04
7.04
7.03
7.02
7.02
7.01
7.01
7.00
7.00
6.89
6.88
6.88
6.88
6.88
6.87
6.87
6.86
6.86
6.85
6.85
6.83
3.73
3.40
3.39
3.37
3.35
1.51
1.50
1.46
2.00
1.00
2.00
1.00
2.00
3.00
f1 (ppm)

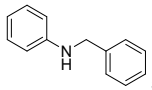

148.84
129.51
117.39
113.05
38.64
15.09
f1 (ppm)



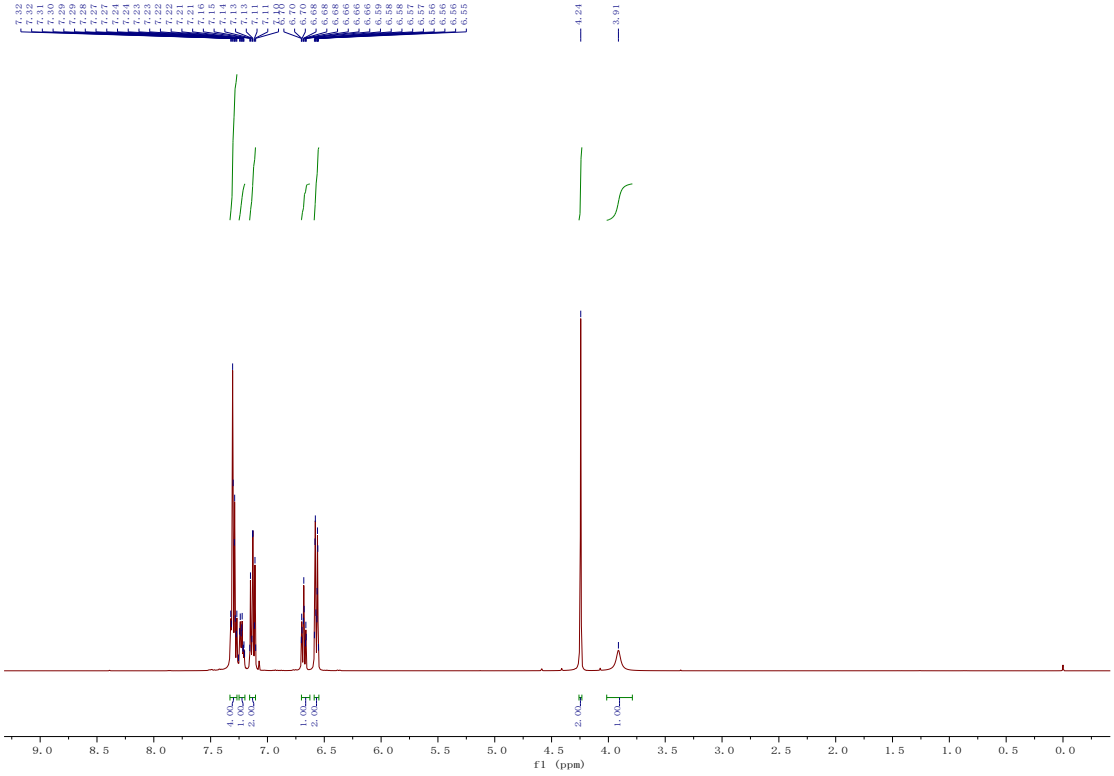
56

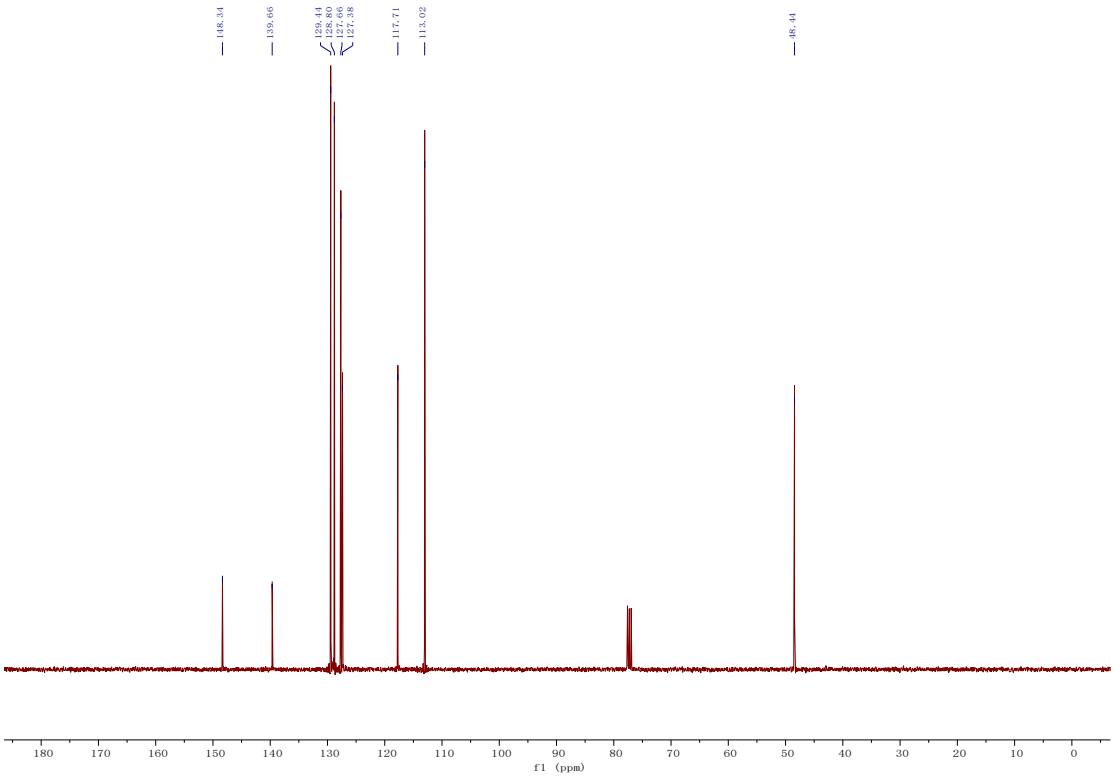

7.16
7.14
7.12
6.66
6.64
6.63
6.59
6.57
3.27
3.26
3.25
3.25
3.24
3.23
3.22
3.21
2.06
2.03
1.77
1.76
1.74
1.73
1.72
1.41
1.38
1.35
1.32
1.31
1.26
1.25
1.23
1.20
1.19
1.18
1.18
1.15
1.13
1.12
1.09
2.00
3.00
2.00
2.00
2.00
1.00
2.00
3.00
f1 (ppm)

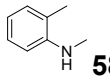

147.43
129.27
116.84
113.17
51.71
33.52
25.98
25.05
f1 (ppm)



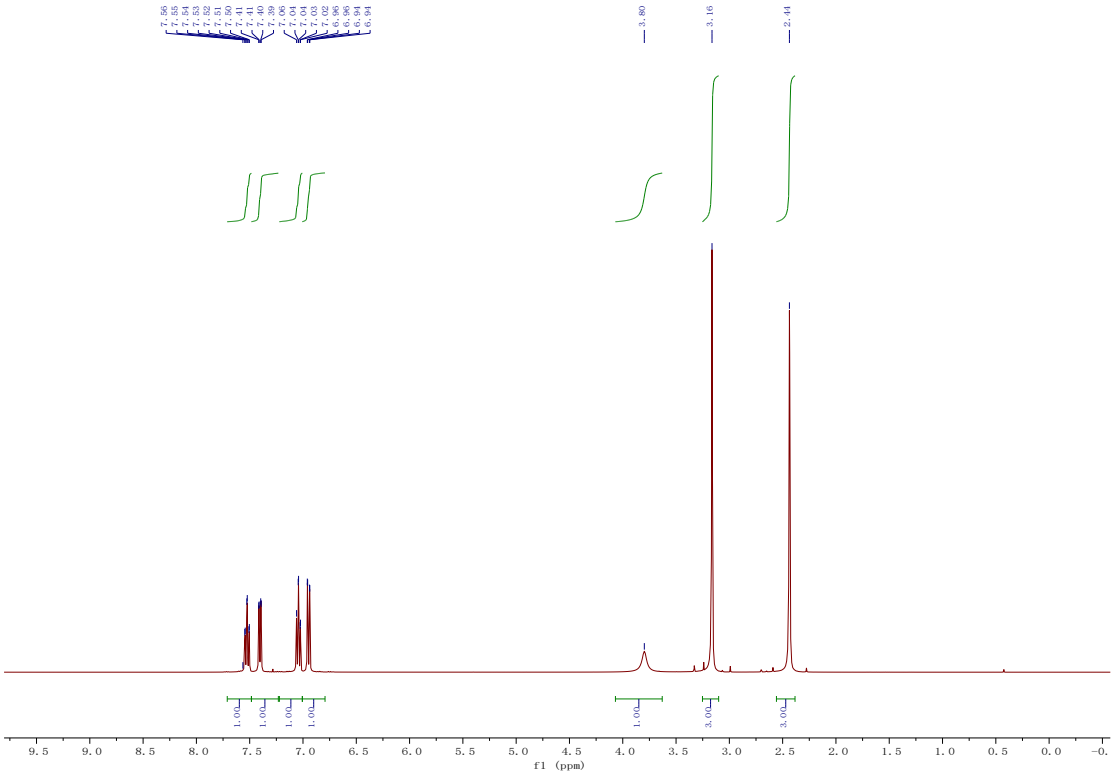
57

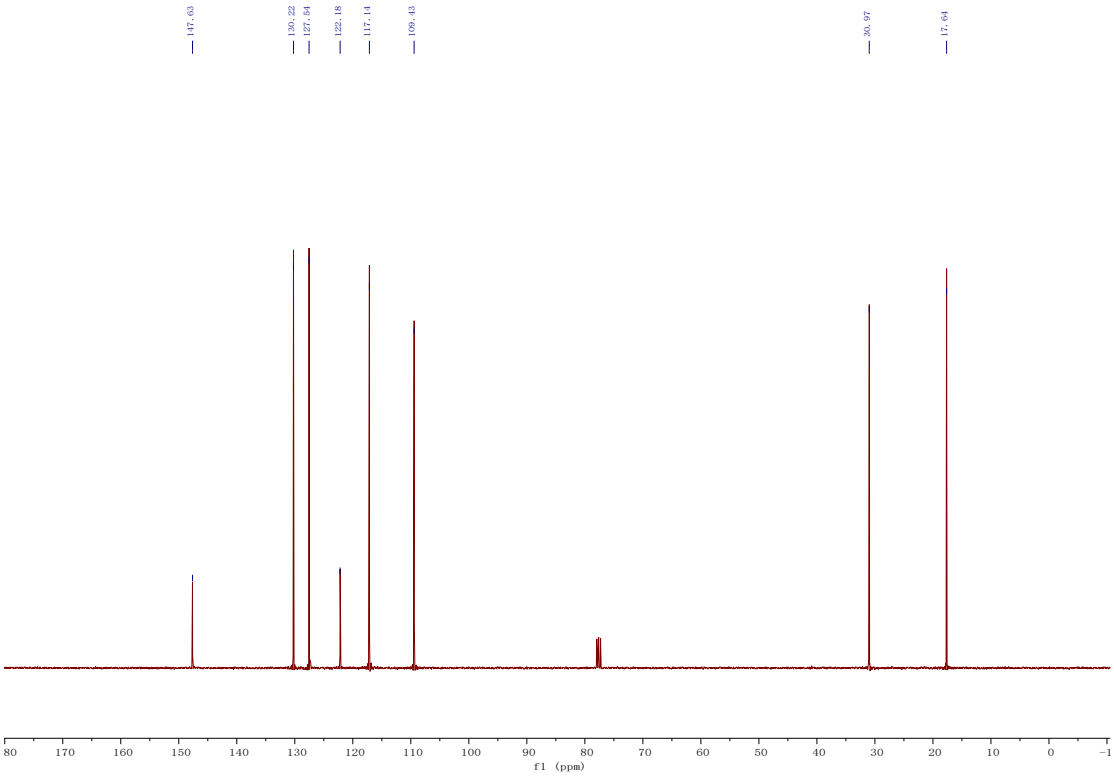

7.32
7.32
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.16
7.15
7.14
7.13
7.11
7.11
7.10
6.70
6.68
6.68
6.68
6.66
6.66
6.66
6.59
6.58
6.58
6.57
6.57
6.56
6.56
6.56
6.55
4.24
3.91
4.00
1.00
2.04
1.00
2.00
2.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

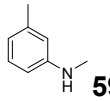

148.34
139.66
129.44
128.80
127.66
127.38
117.71
113.02
48.44
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



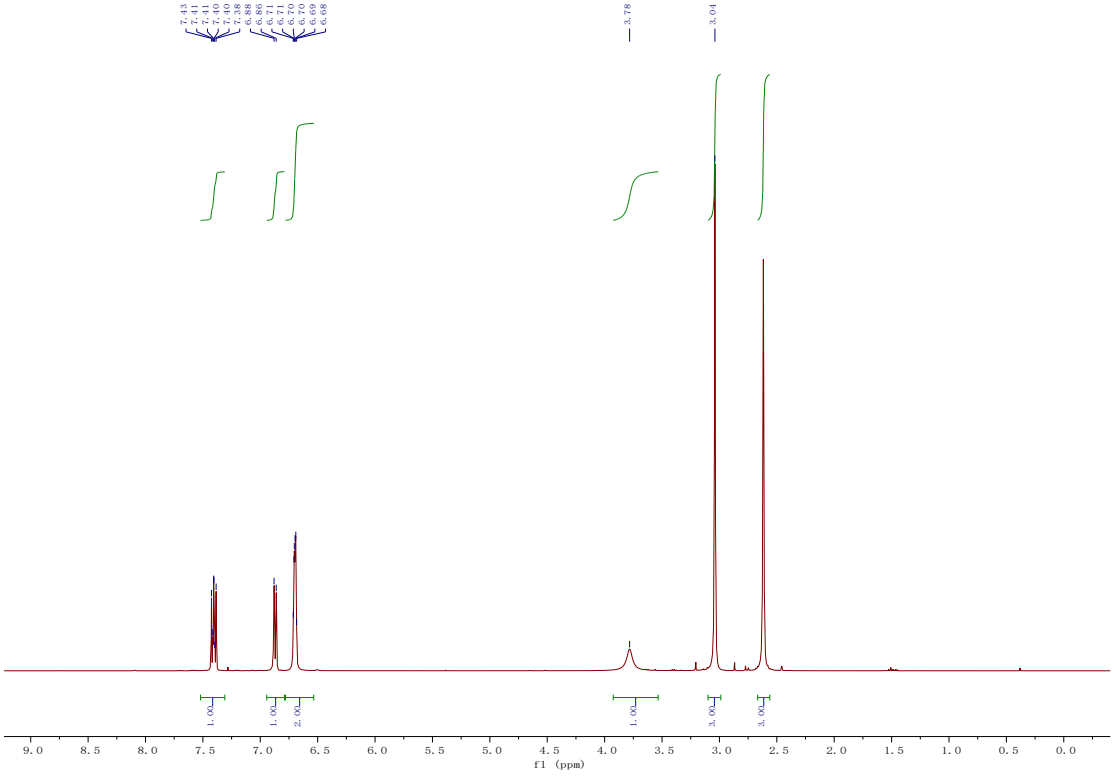
58

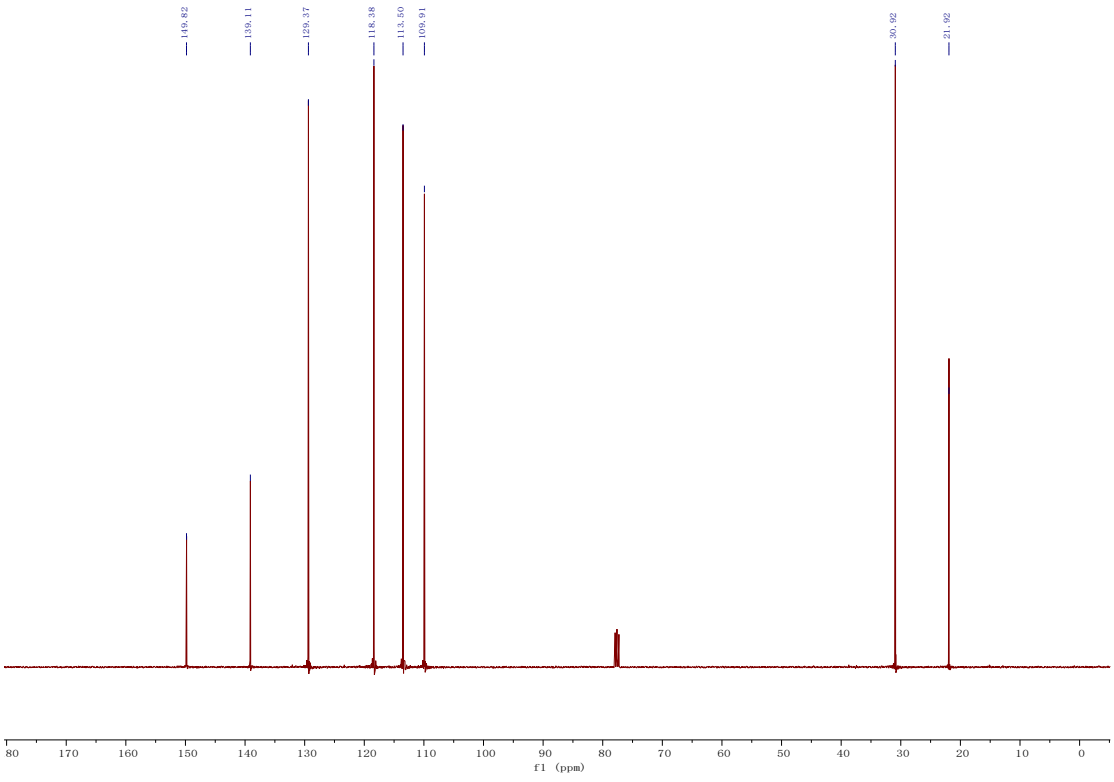

7.56
7.55
7.54
7.53
7.52
7.51
7.50
7.41
7.40
7.39
7.06
7.04
7.03
7.02
6.96
6.94
6.94
3.80
3.16
2.44
1.00
1.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

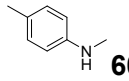

147.63
130.22
127.54
122.18
117.14
109.43
30.97
17.64
f1 (ppm)



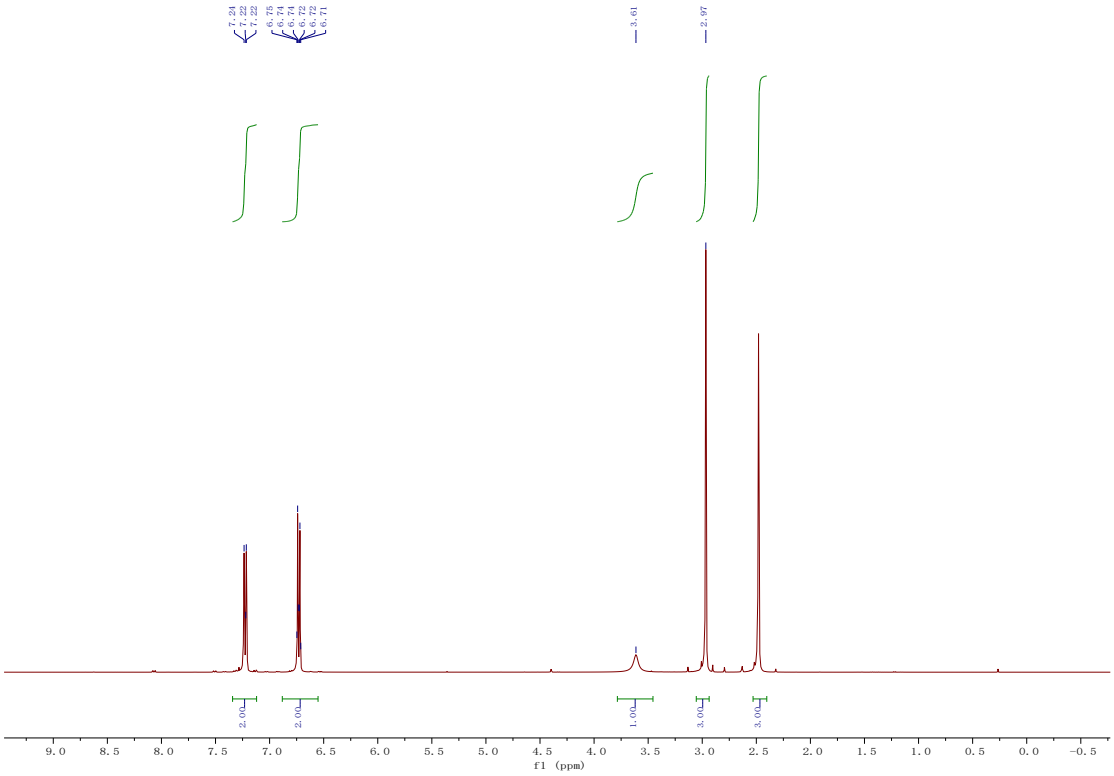
59

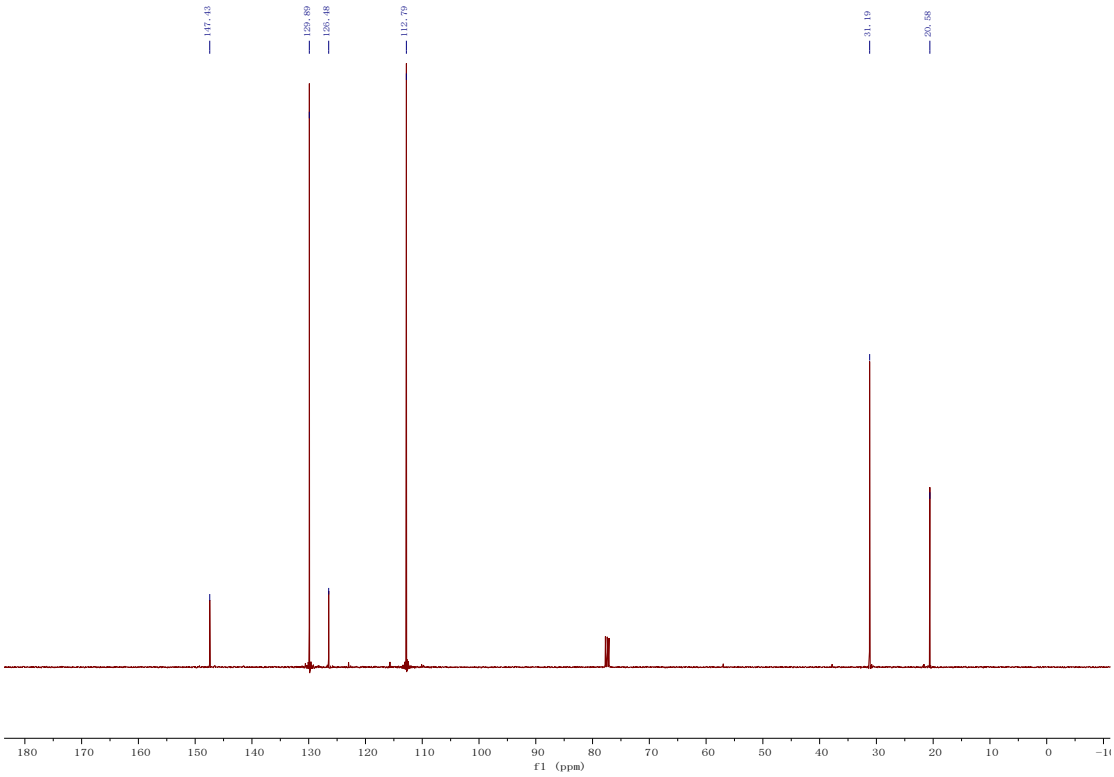

7.43
7.41
7.41
7.40
7.40
7.38
6.88
6.86
6.71
6.71
6.70
6.70
6.69
6.68
3.78
3.04
1.00
1.00
2.00
1.00
3.00
3.00
f1 (ppm)

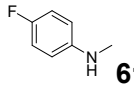

149.82
139.11
129.37
118.38
113.50
109.91
30.92
21.92
f1 (ppm)



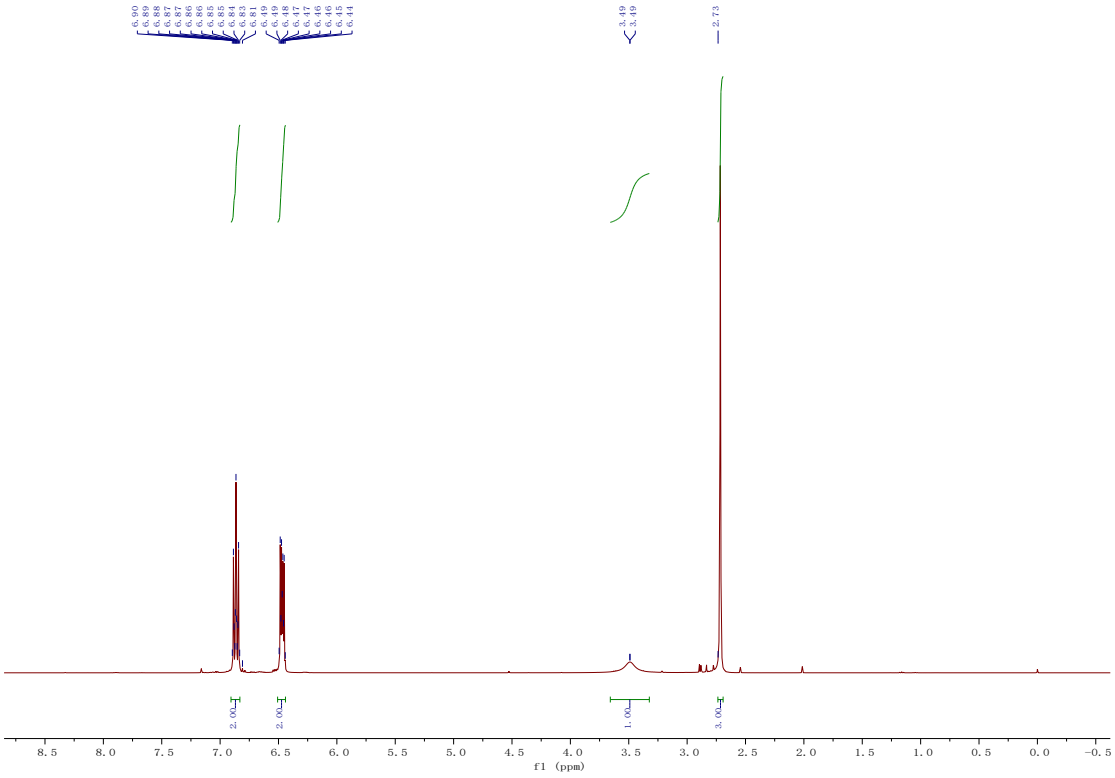
60

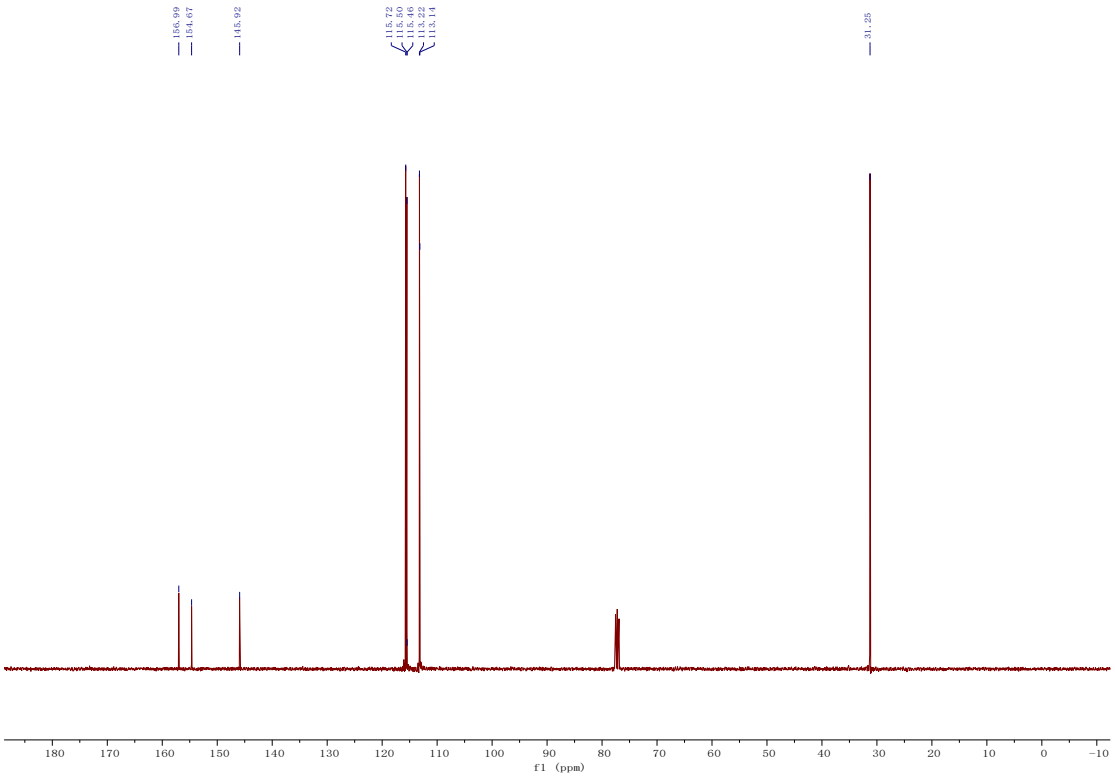

7.24
7.22
7.22
6.75
6.74
6.74
6.72
6.72
6.71
3.61
2.97
2.00
2.00
1.00
3.00
3.00
f1 (ppm)

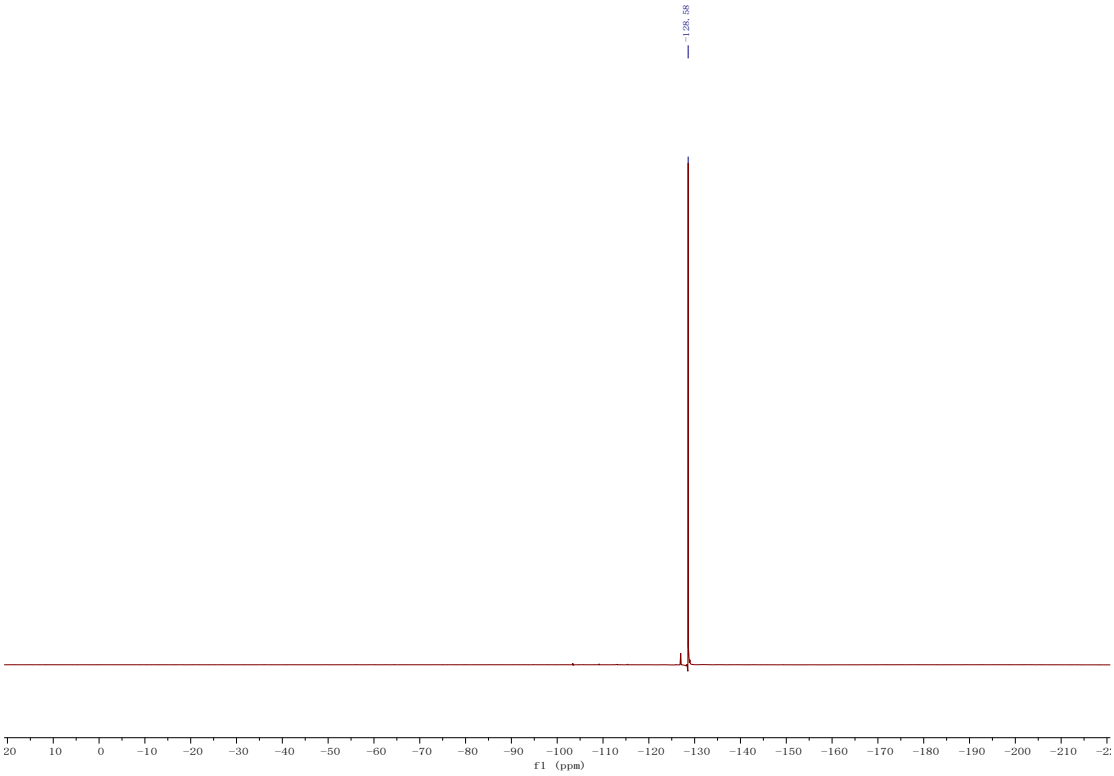

147.43
129.89
126.48
112.79
31.19
20.58
f1 (ppm)

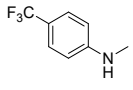

F
N
H

61

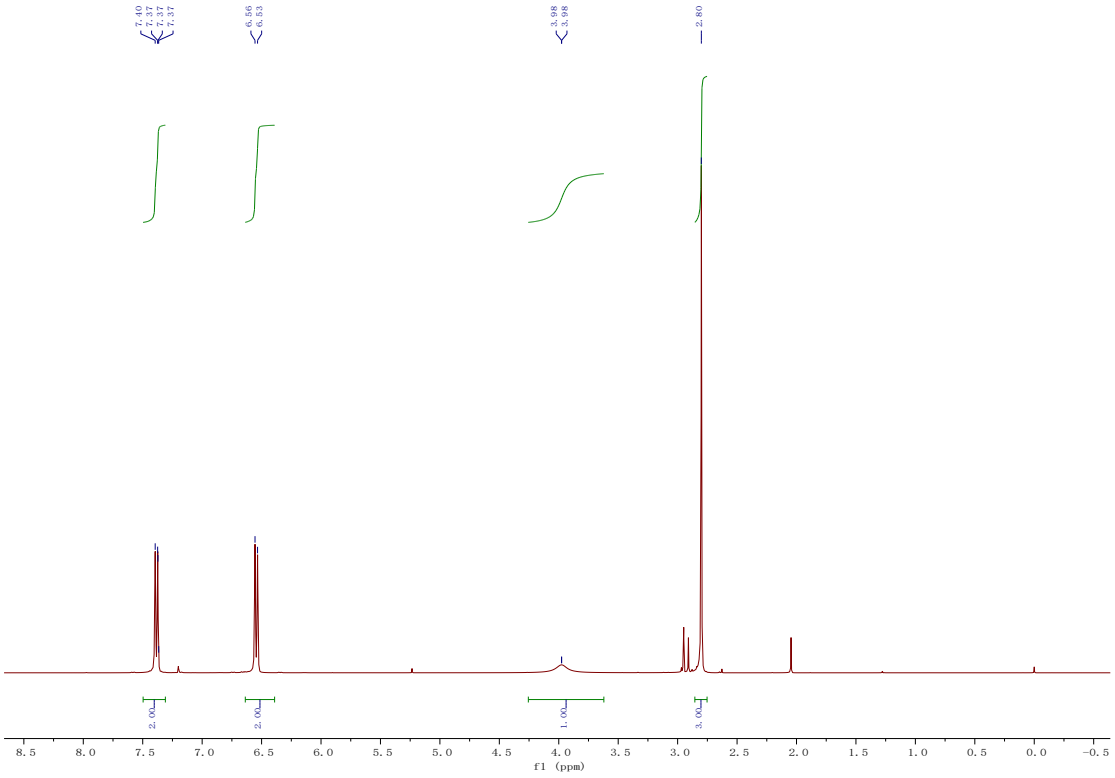

6.90
6.89
6.88
6.87
6.87
6.86
6.86
6.85
6.85
6.84
6.83
6.51
6.49
6.49
6.48
6.47
6.47
6.46
6.46
6.45
6.44
3.49
3.49
2.73
2.00
2.00
1.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

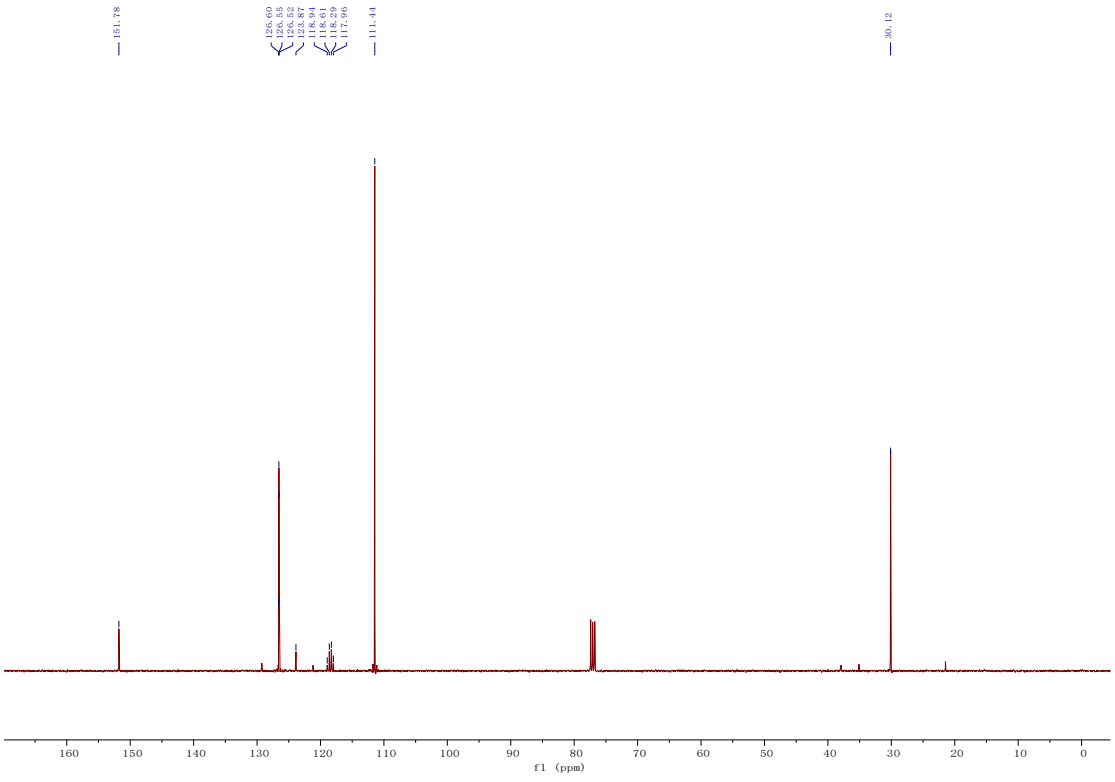

166.99
164.67
145.92
115.72
115.50
115.46
115.22
113.14
31.25
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

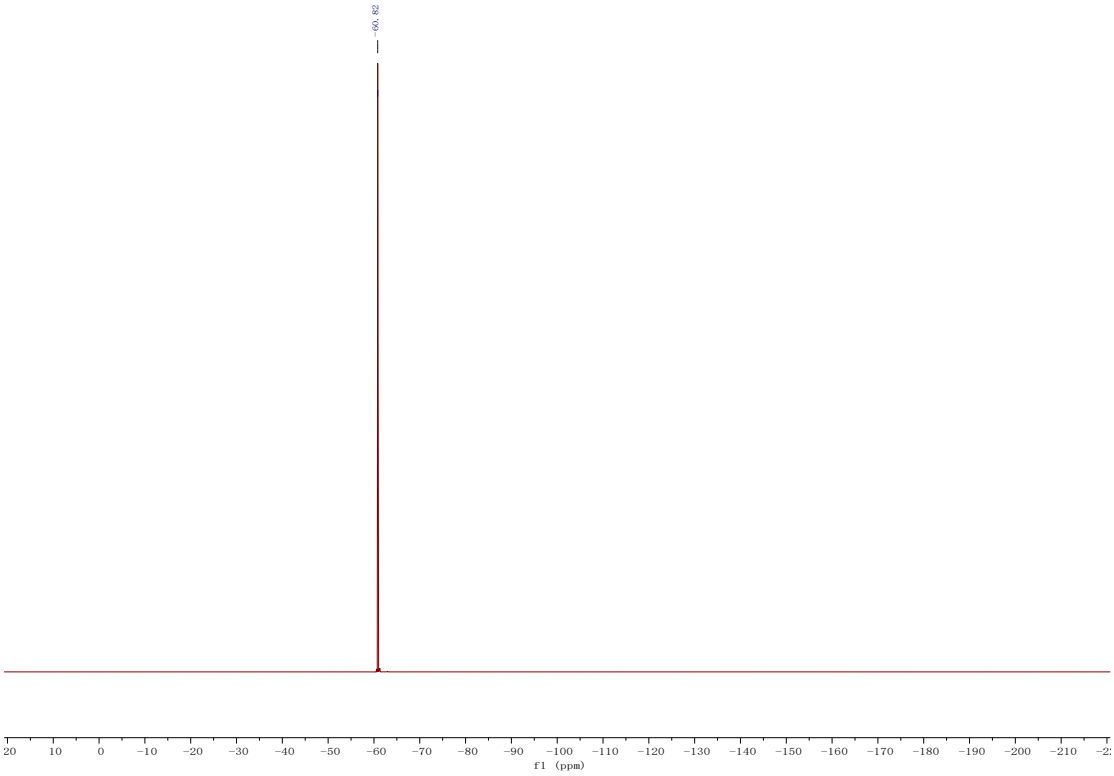

-128.58
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

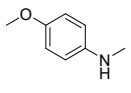


62

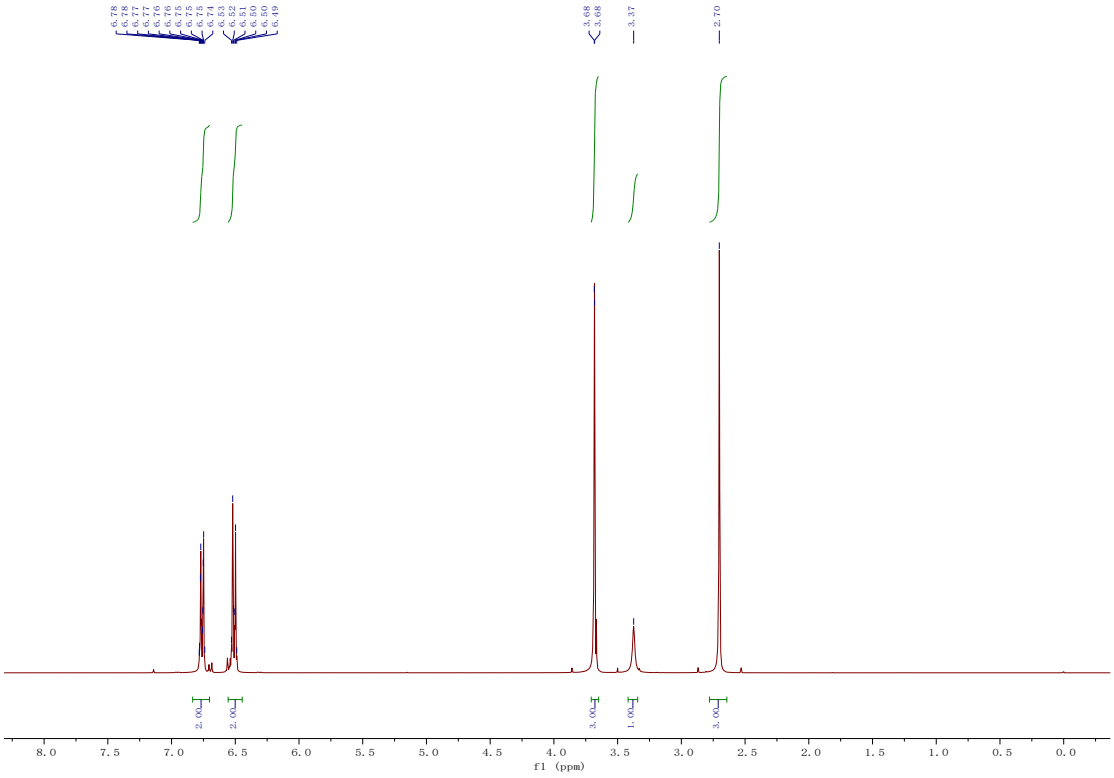

7.40
7.37
7.37
7.37
6.56
6.53
3.98
3.98
2.80
2.00
2.00
1.00
3.00
f1 (ppm)

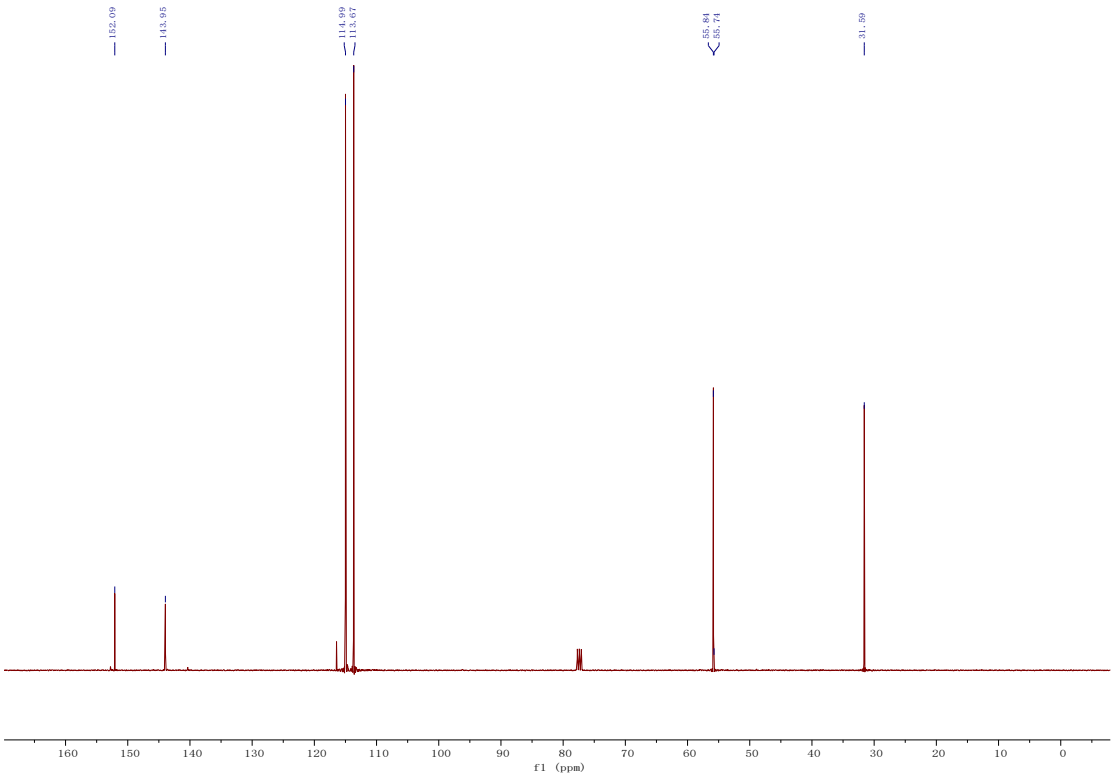

151.78
126.60
126.55
126.52
123.87
118.94
118.90
118.29
117.96
111.44
30.12
f1 (ppm)

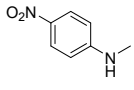

-60.82
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)



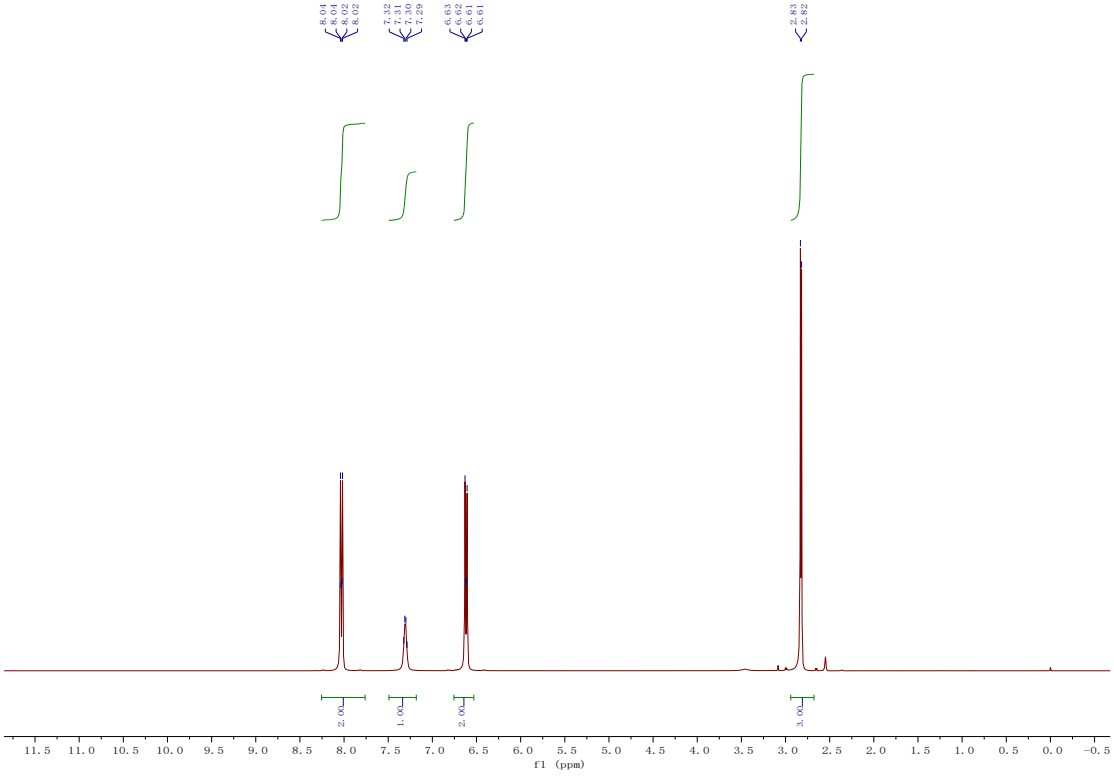
63

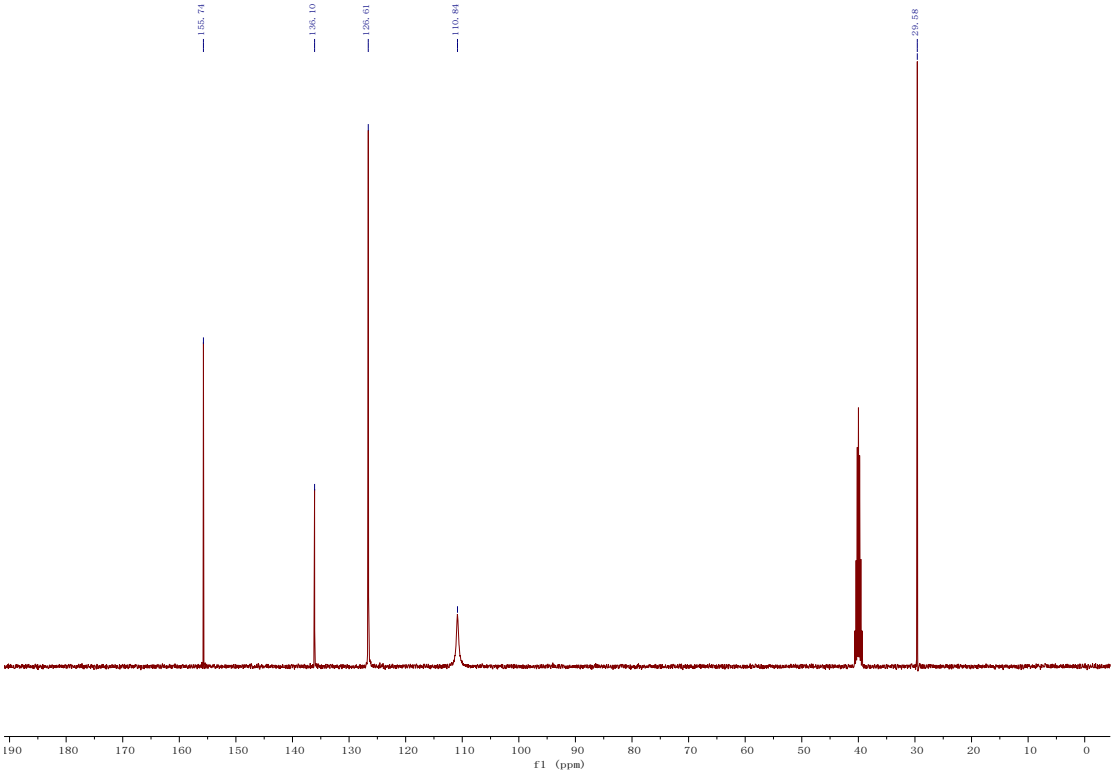

6.78
6.78
6.77
6.77
6.76
6.76
6.75
6.75
6.75
6.74
6.53
6.52
6.51
6.50
6.50
6.49
3.68
3.68
3.37
2.70
2.00
2.00
3.00
1.00
3.00
f1 (ppm)

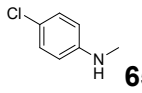

152.09
143.95
114.99
113.67
55.84
55.74
31.59
f1 (ppm)



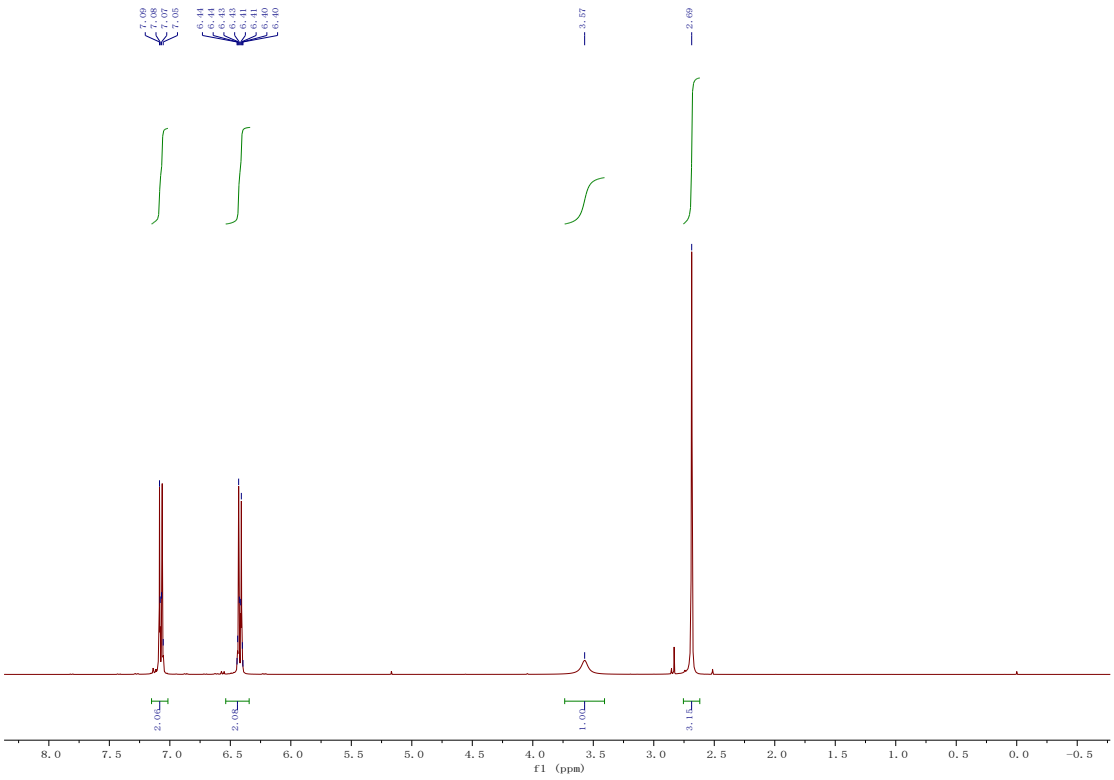
64

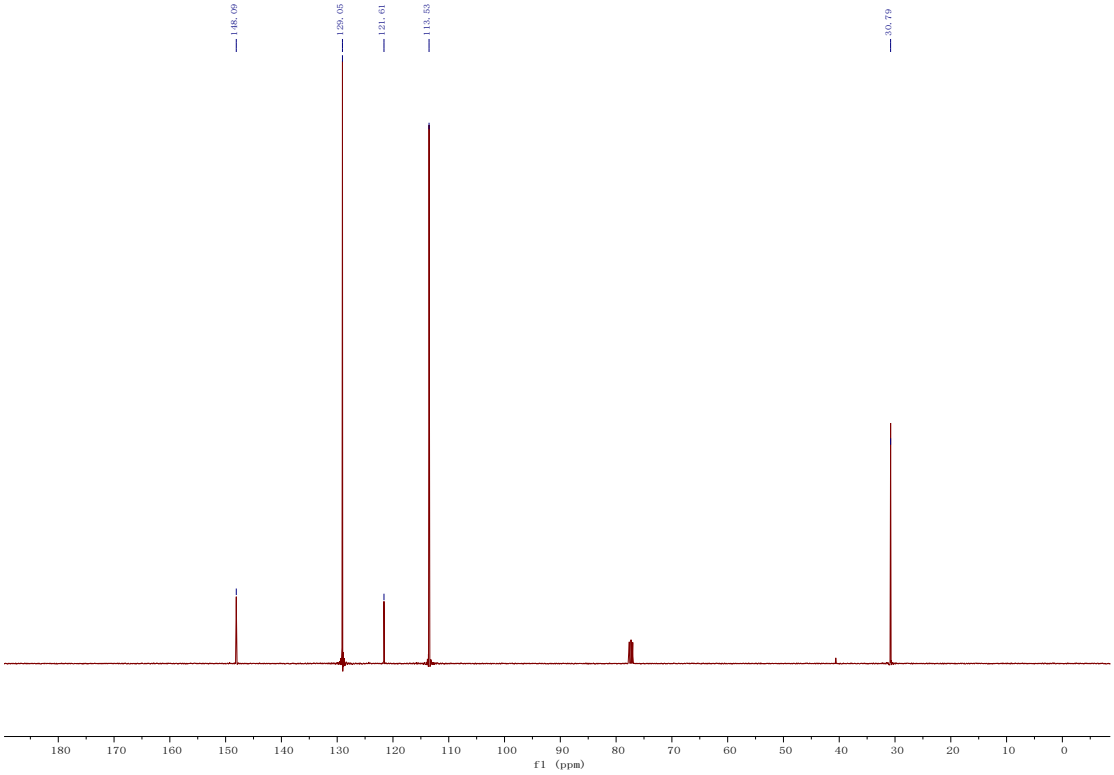

8.04
8.04
8.02
8.02
7.32
7.31
7.30
7.29
6.63
6.62
6.61
6.61
2.83
2.82
2.00
1.00
2.00
3.00
f1 (ppm)

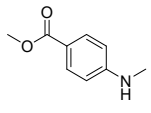

155.74
136.10
126.61
110.84
29.58
f1 (ppm)


Cl
N
H

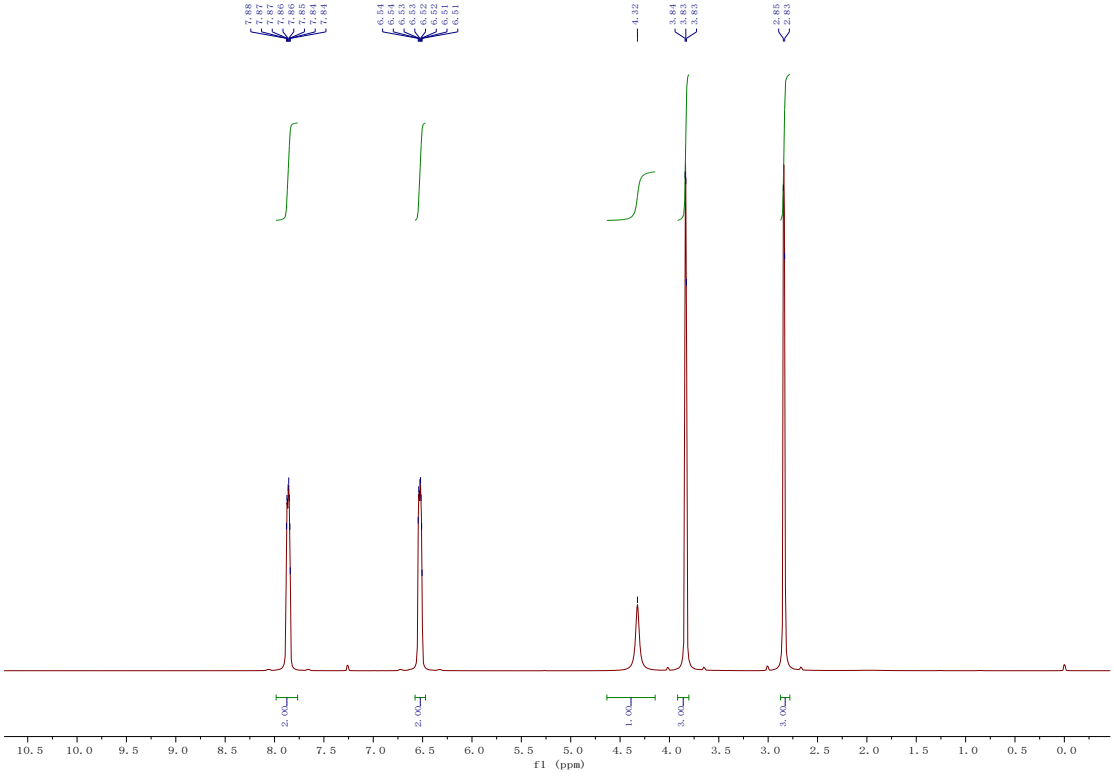
65

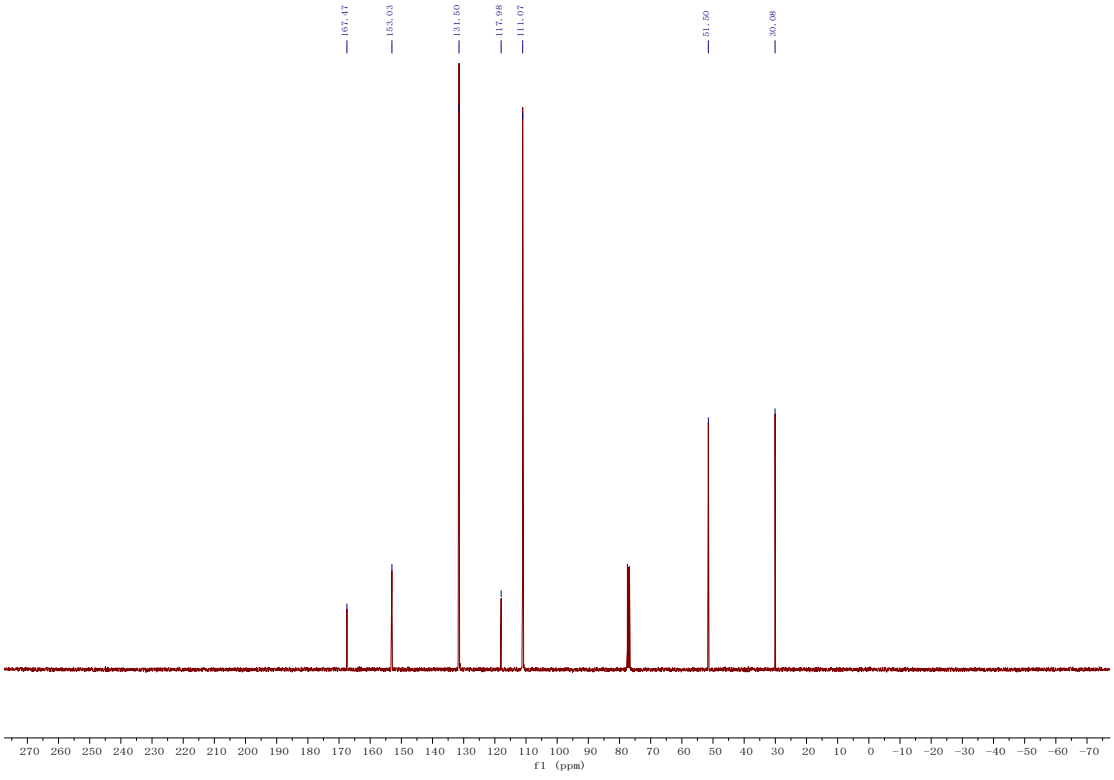

7.09
7.08
7.07
7.05
6.44
6.44
6.43
6.43
6.41
6.41
6.40
6.40
3.57
2.69
2.00
2.08
1.00
3.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

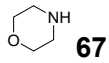

148.09
129.05
121.61
113.53
30.79
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



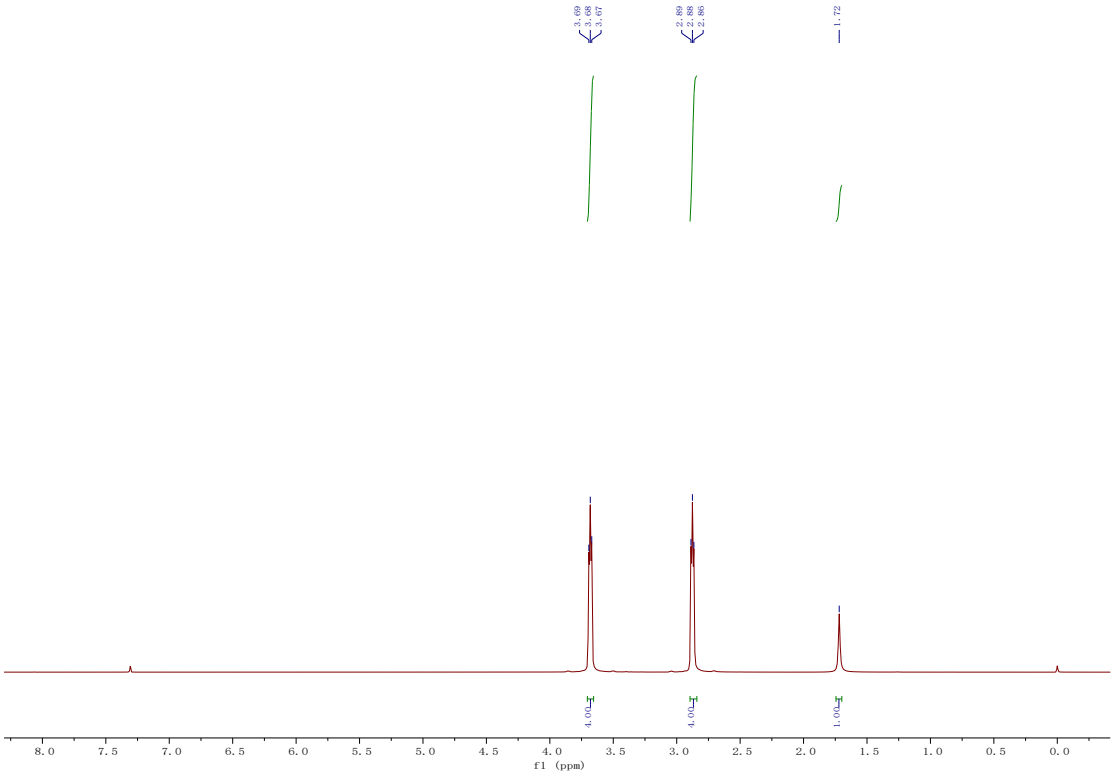
66

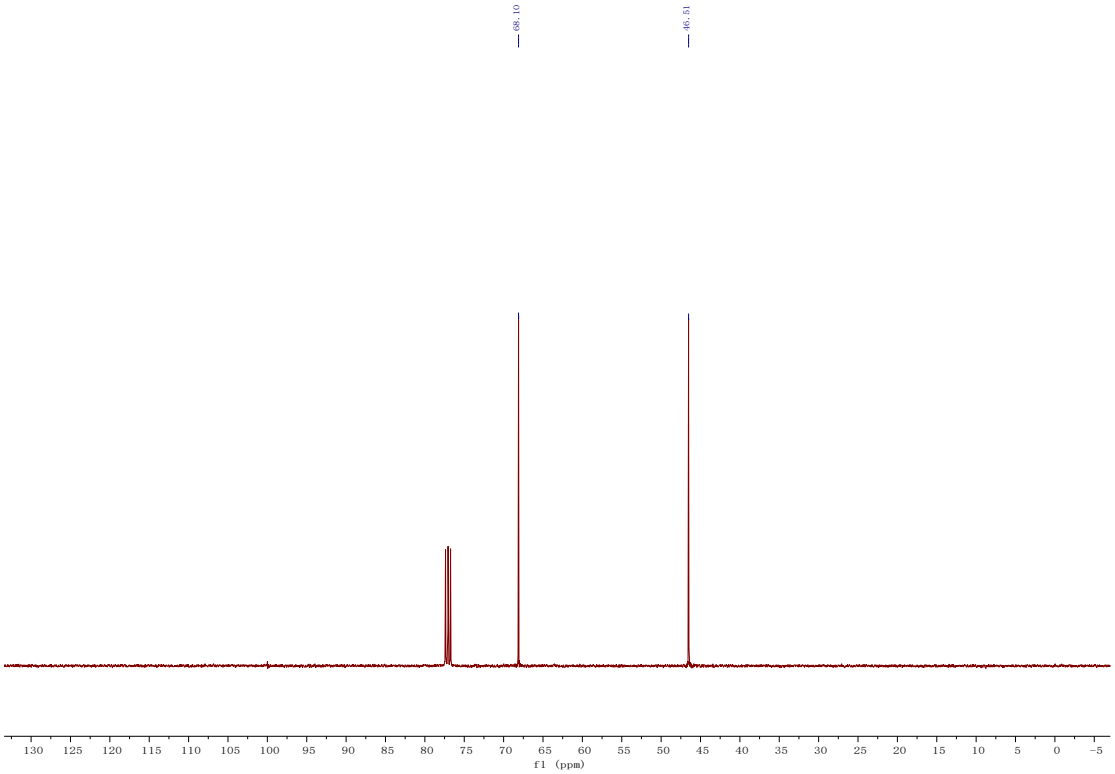

7.88
7.87
7.87
7.86
7.86
7.85
7.84
7.84
6.54
6.54
6.53
6.53
6.52
6.52
6.51
6.51
4.32
3.84
3.83
3.83
2.85
2.83
2.00
2.00
1.00
3.00
3.00
f1 (ppm)

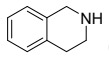

167.47
153.03
131.50
117.98
111.07
51.50
30.08
f1 (ppm)


NH
O

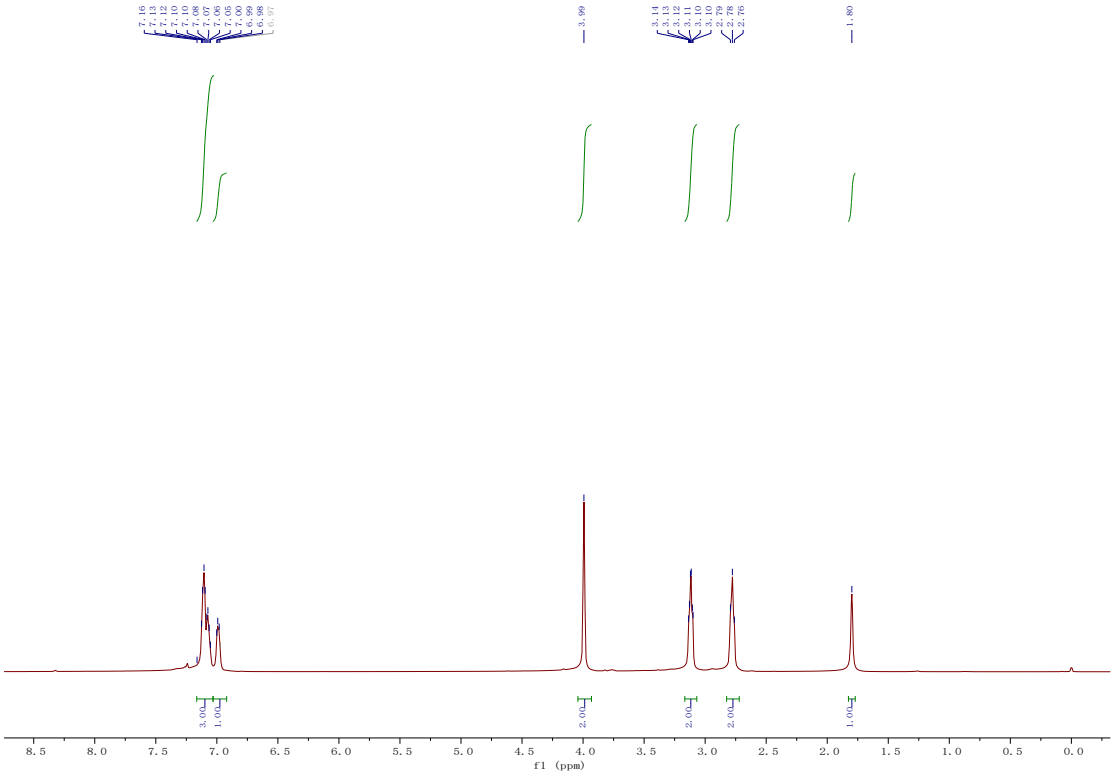
67

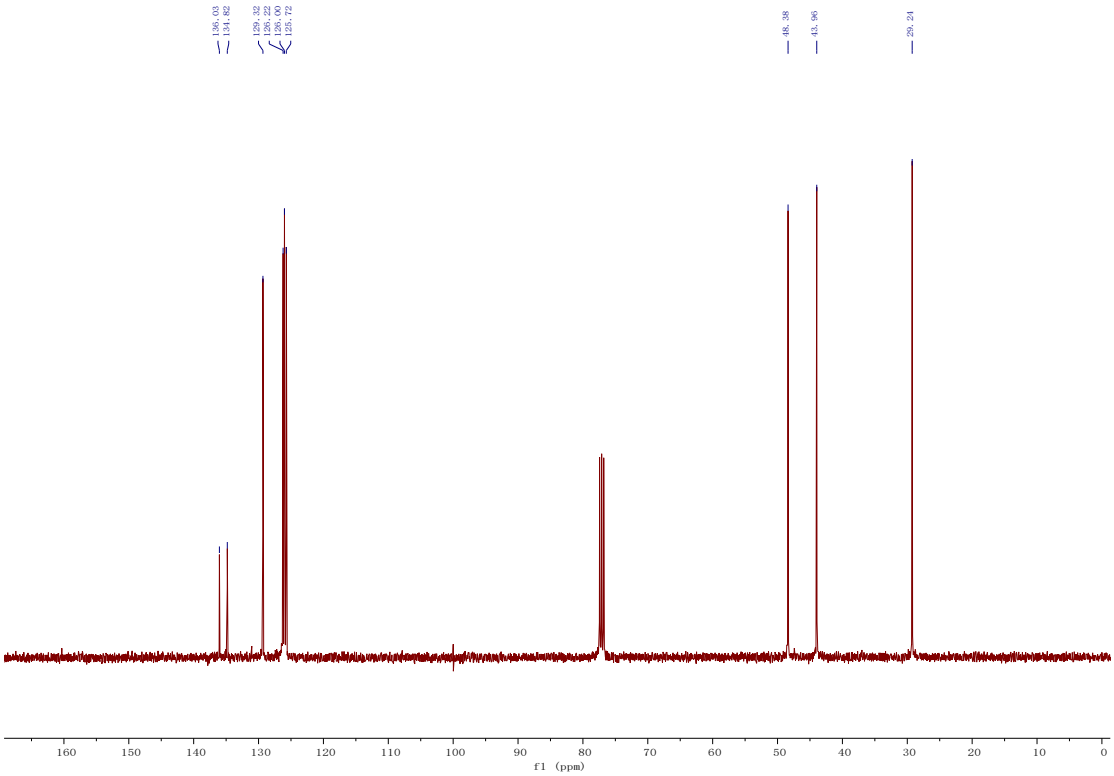

3.69
3.68
3.67
2.89
2.88
2.86
1.72
4.00
4.00
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

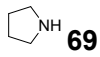

68.10
46.51
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
f1 (ppm)


NH

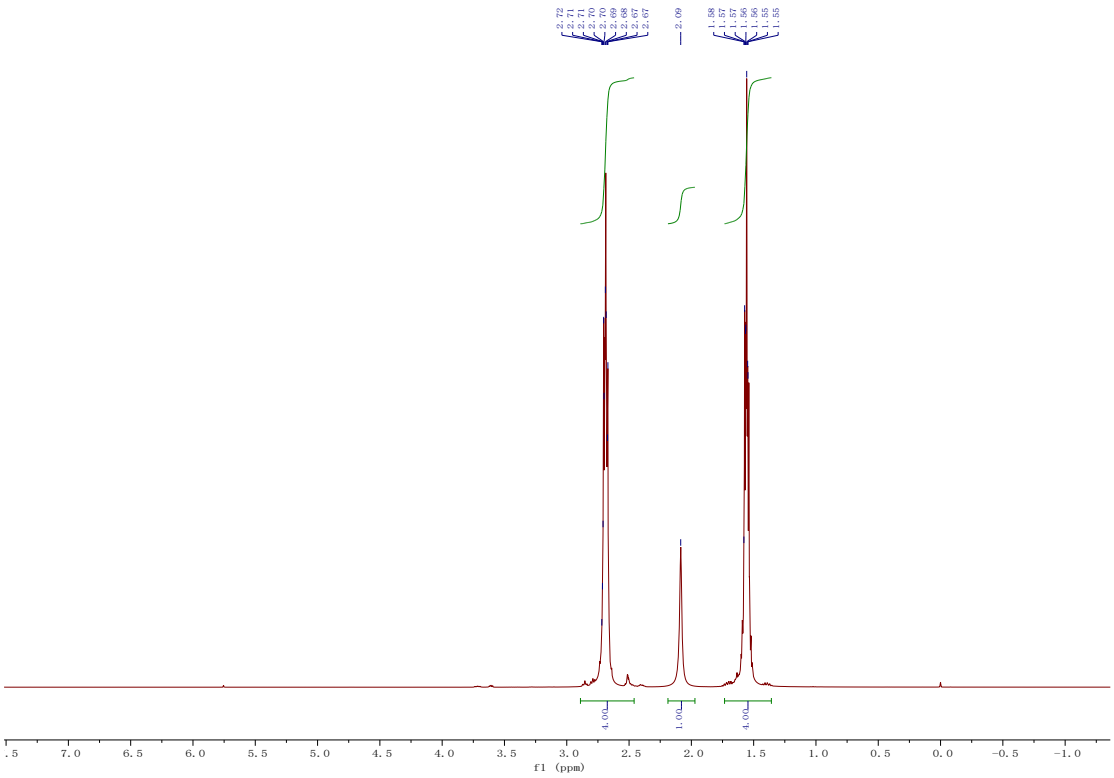
68

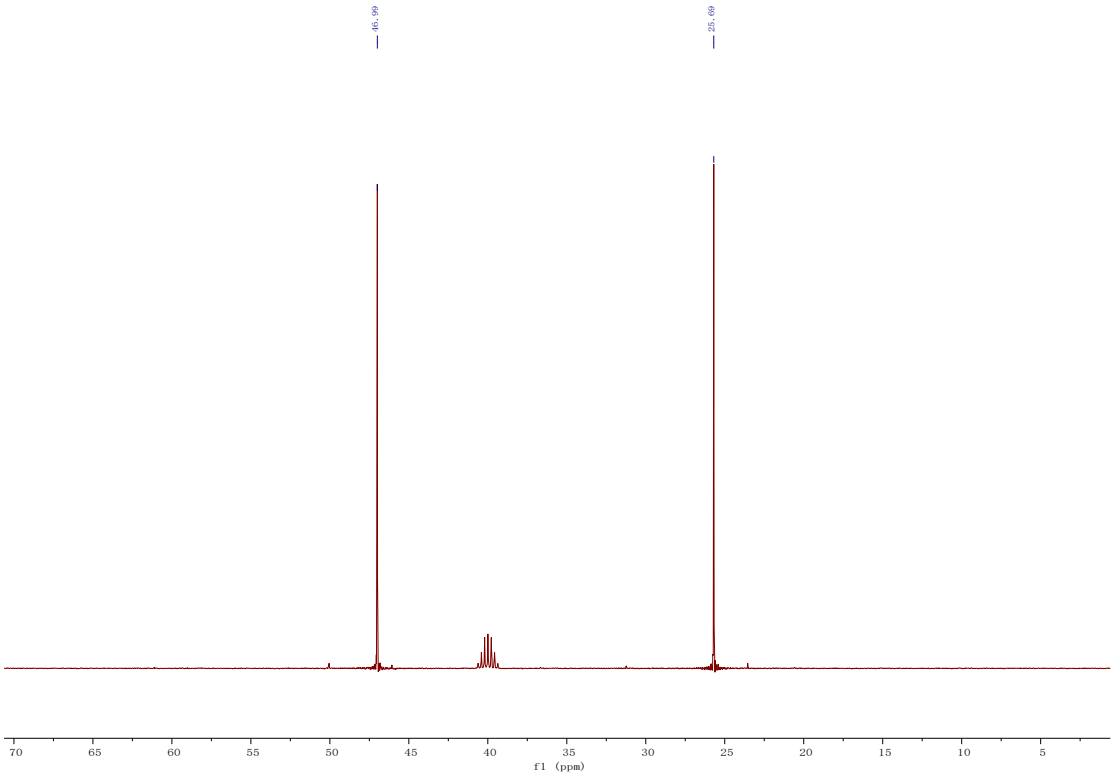

7.16
7.13
7.12
7.10
7.10
7.08
7.07
7.05
7.00
6.99
6.98
6.97
3.99
3.14
3.13
3.12
3.11
3.10
2.79
2.78
2.76
1.80
3.00
1.00
2.00
2.00
2.00
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

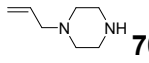

136.03
134.82
129.32
128.22
126.00
125.72
48.38
43.96
29.24
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NH

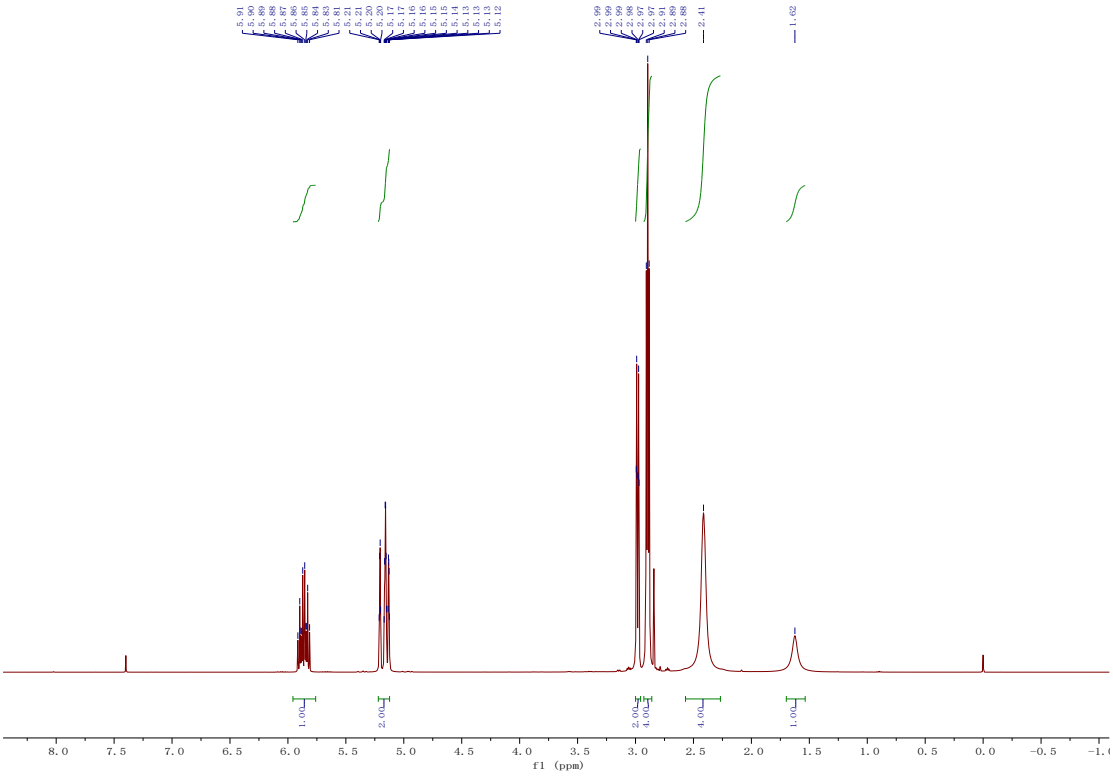
69

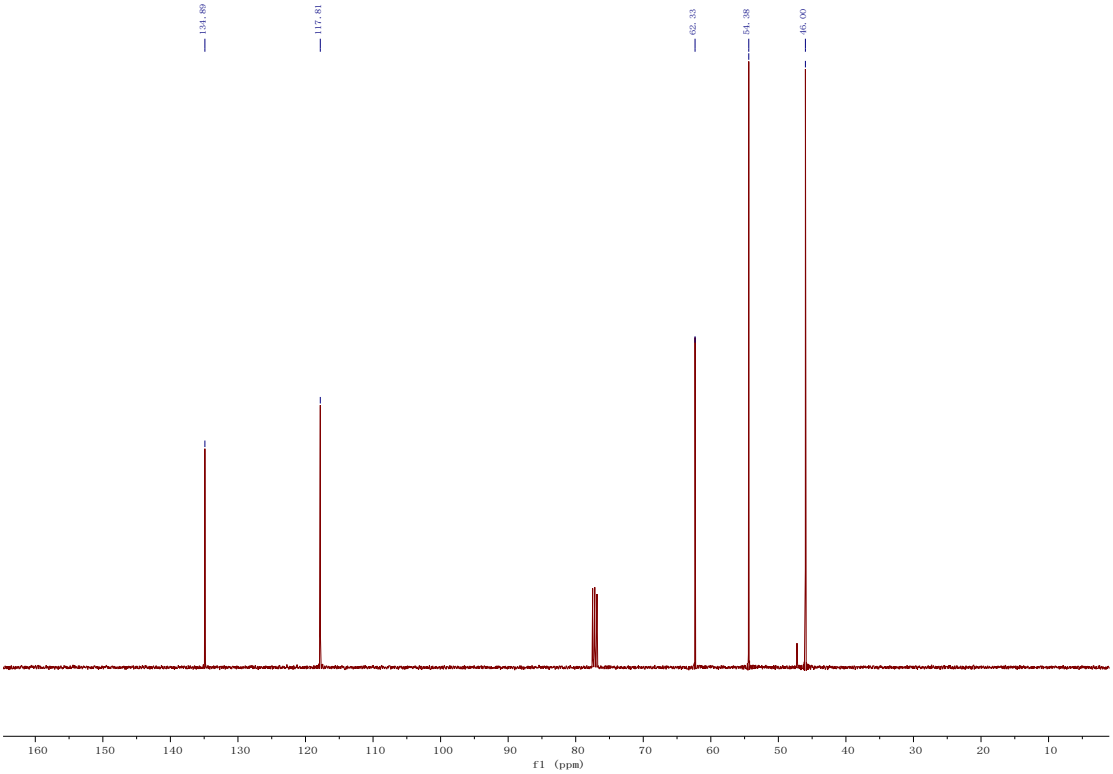

2.72
2.71
2.71
2.70
2.70
2.69
2.68
2.67
2.67
2.09
1.58
1.57
1.57
1.56
1.56
1.55
1.55
4.00
1.00
4.00
f1 (ppm)

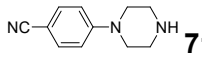

46.99
25.69
f1 (ppm)


N
NH

70

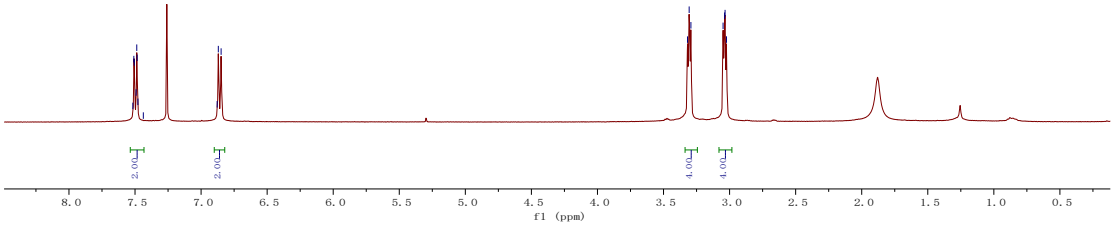

5.91
5.90
5.89
5.88
5.87
5.86
5.85
5.84
5.83
5.81
5.21
5.20
5.20
5.17
5.16
5.16
5.15
5.15
5.14
5.13
5.13
5.13
5.12
2.99
2.99
2.99
2.98
2.97
2.97
2.91
2.89
2.88
2.41
1.62
1.00
2.00
2.00
4.00
4.00
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

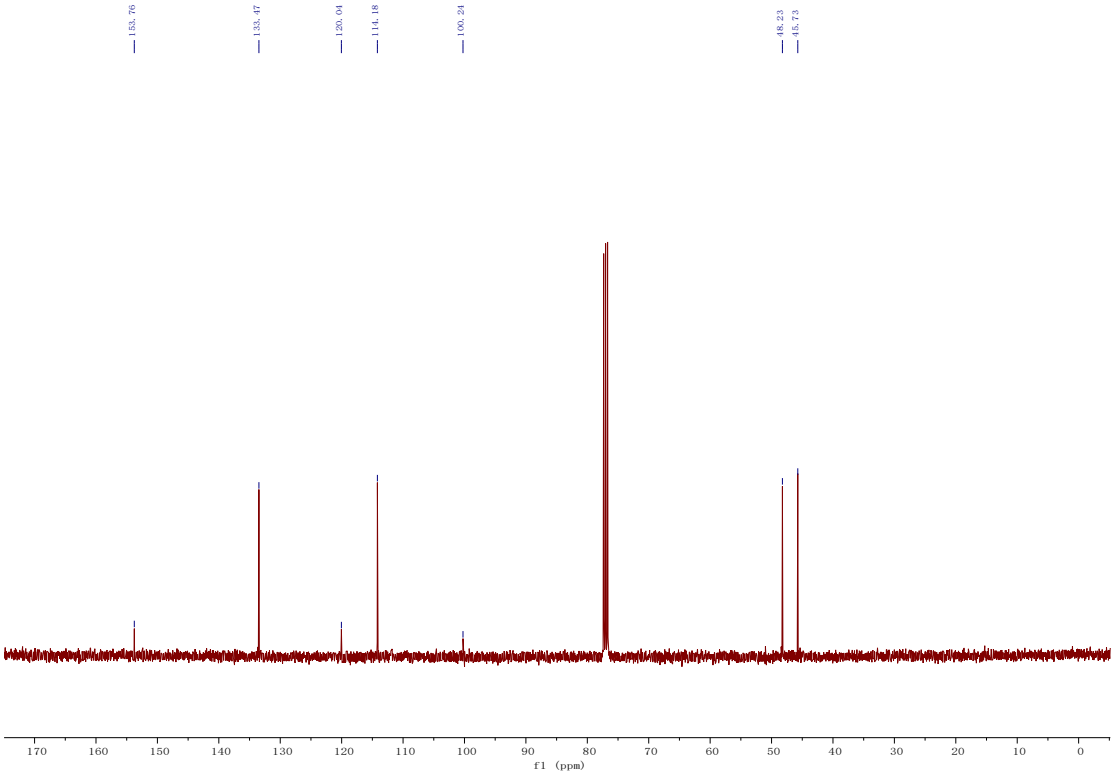

134.89
117.81
62.33
54.38
46.00
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

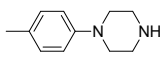

NC
N
NH

71

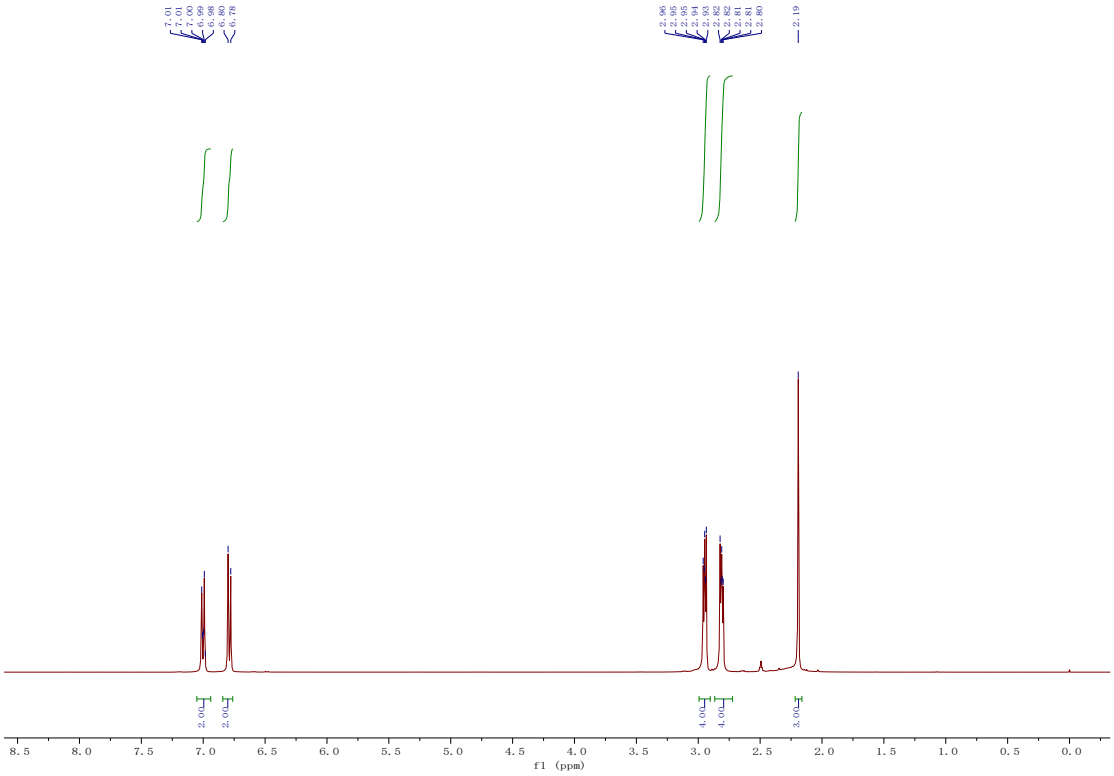

7.52
7.51
7.51
7.49
7.49
7.49
7.48
7.48
7.44
6.88
6.87
6.85
3.32
3.31
3.29
3.05
3.04
3.03
3.02

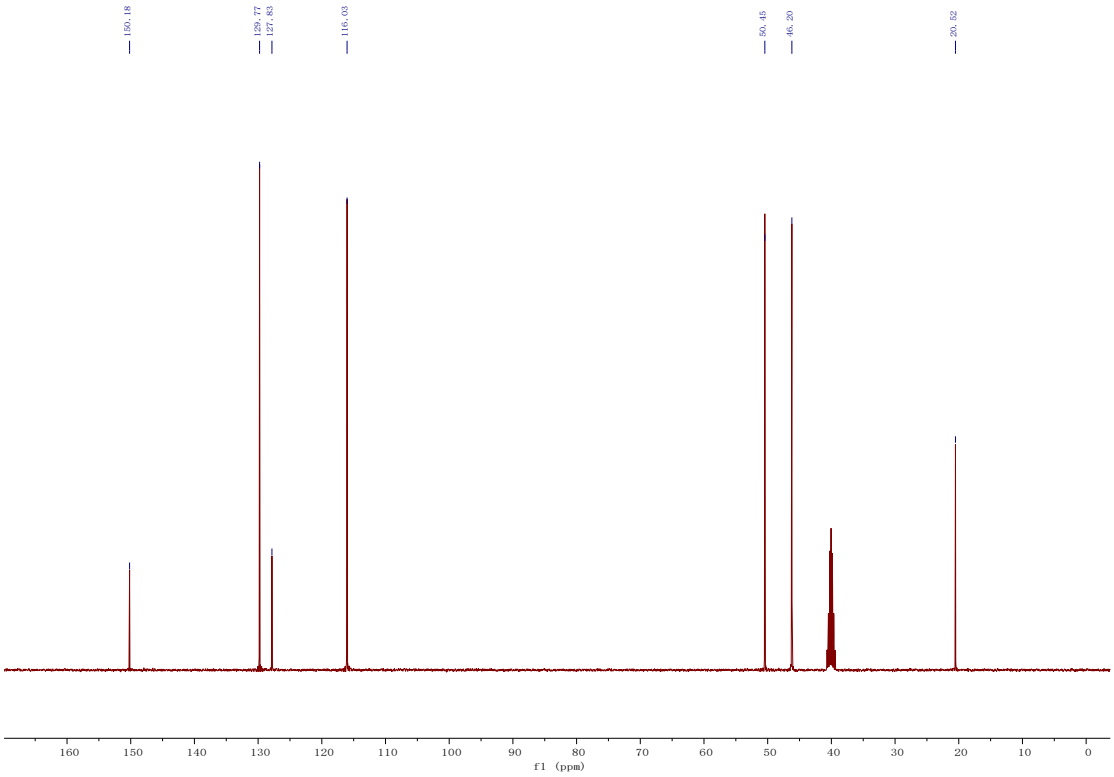

2.00
2.00
4.00
4.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

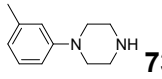

153.76
133.47
120.04
114.18
100.24
48.23
45.73
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
NH

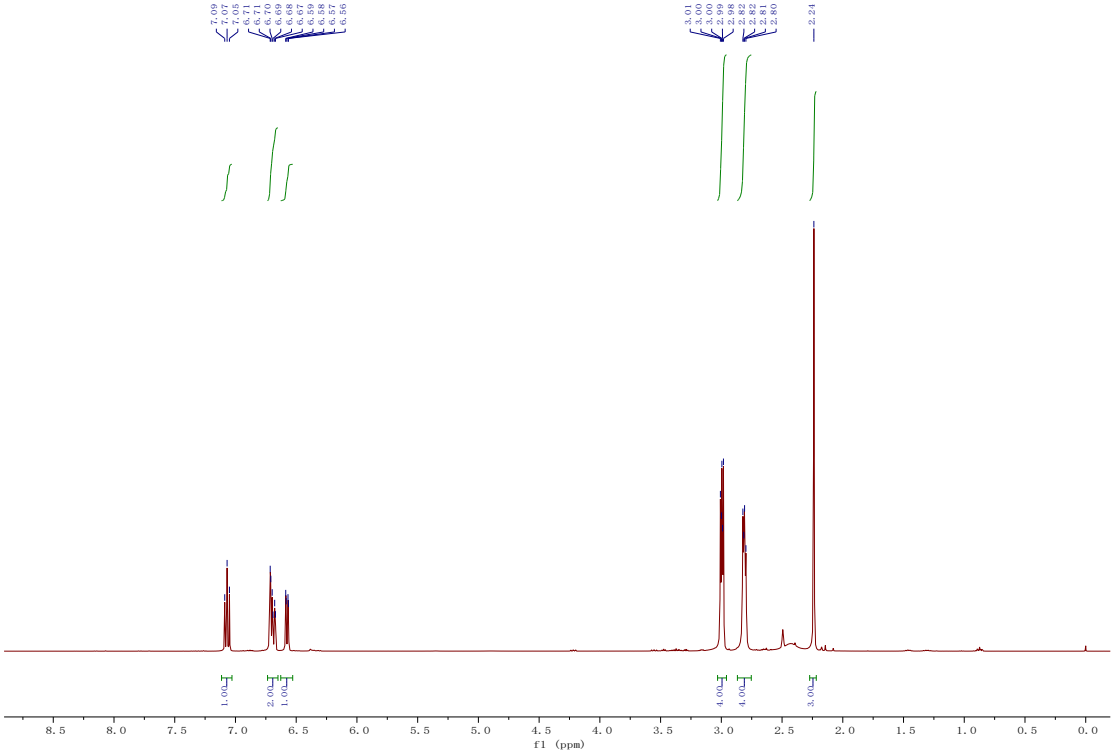
72

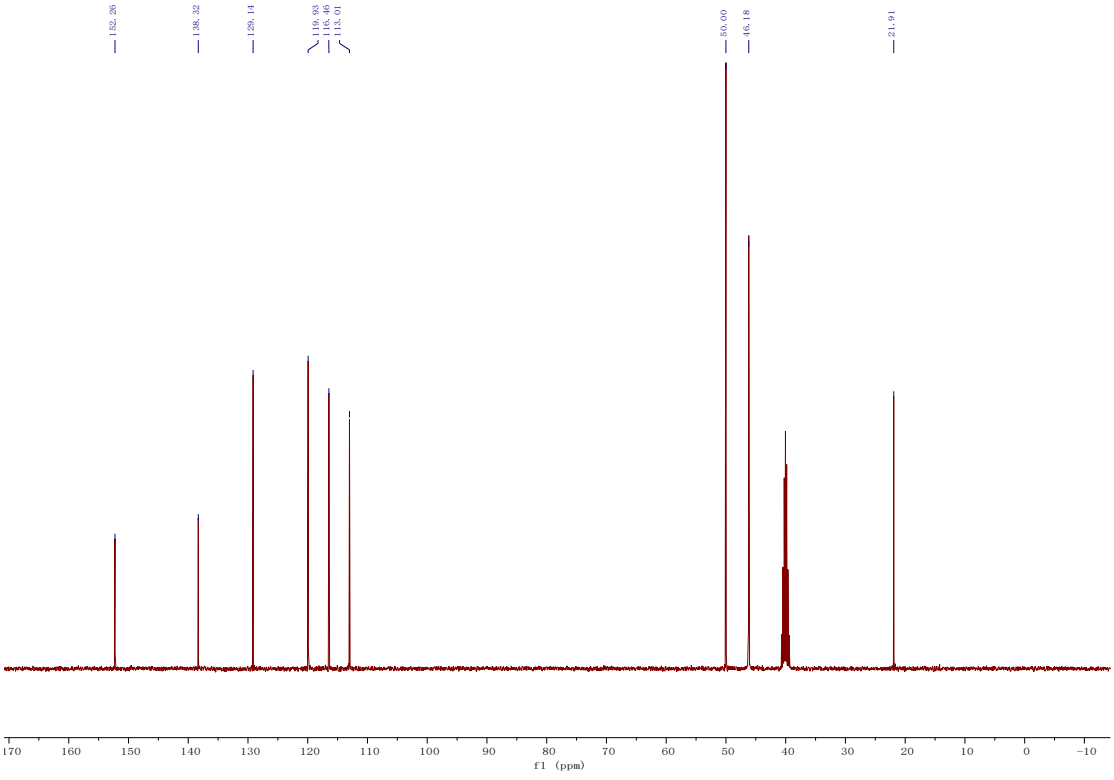

7.01
7.01
7.00
6.99
6.98
6.80
6.78
2.96
2.95
2.95
2.94
2.93
2.82
2.82
2.81
2.81
2.80
2.19
2.00
2.00
4.00
4.00
3.00
f1 (ppm)

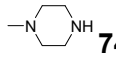

150.18
129.77
127.83
116.03
60.45
46.20
20.52
f1 (ppm)



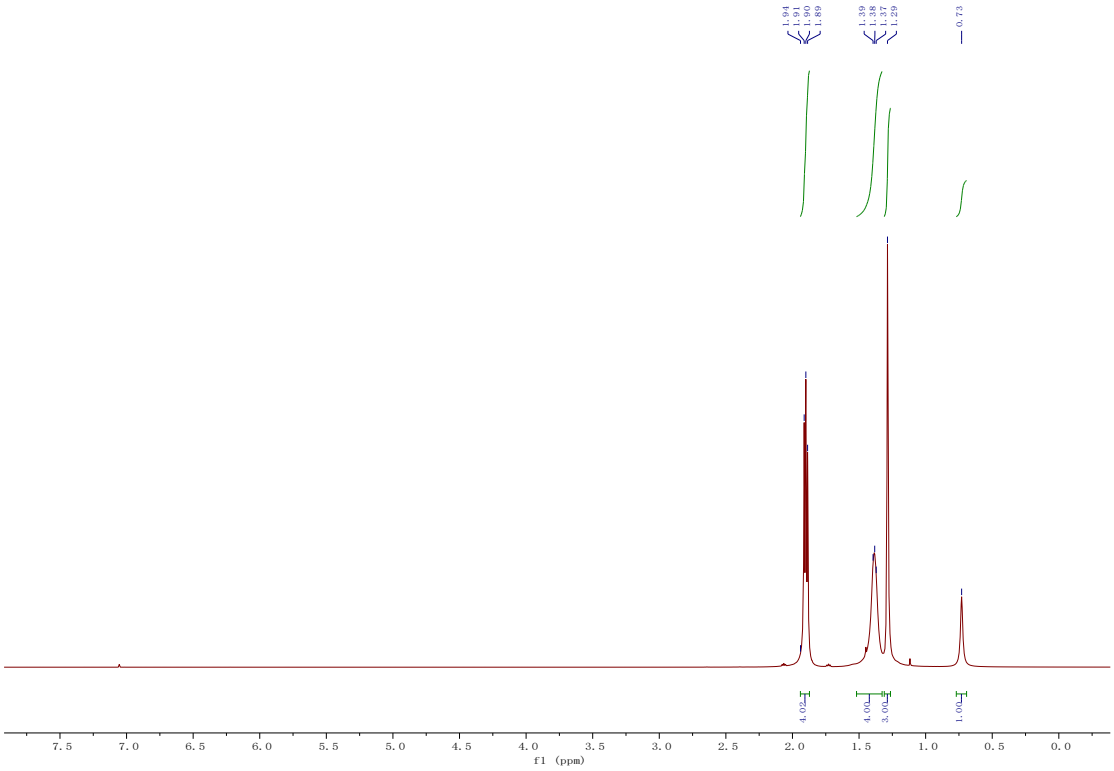
73

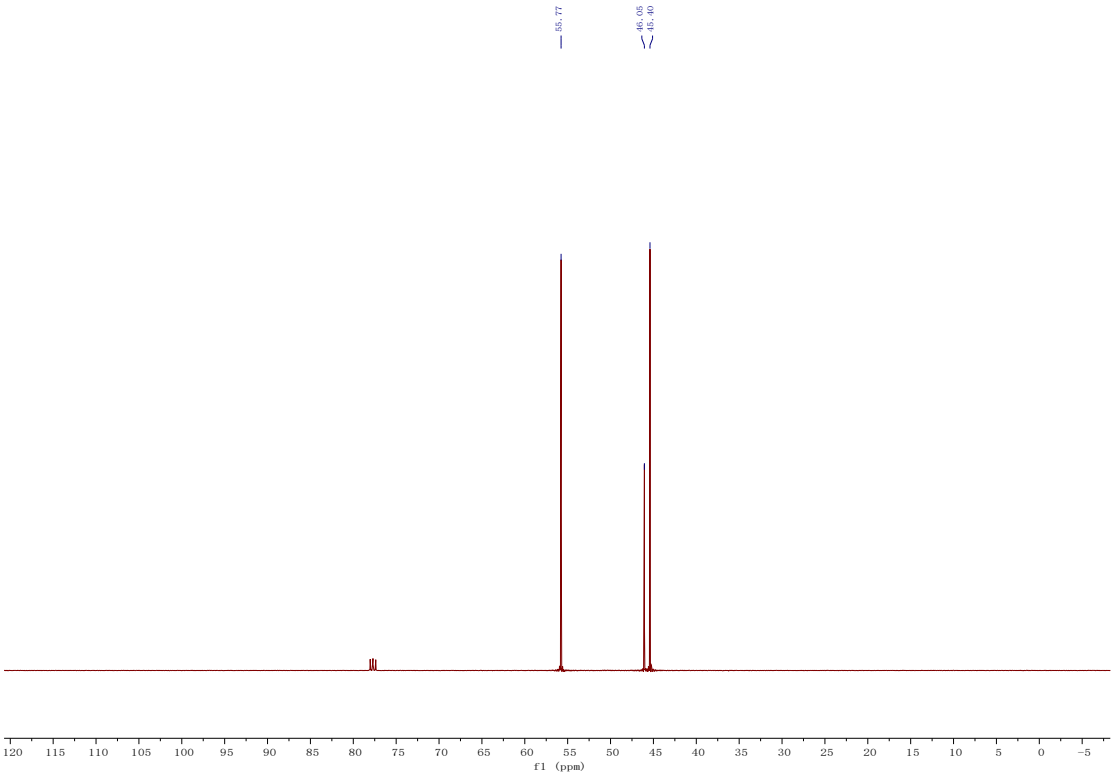

7.09
7.07
7.05
6.71
6.70
6.69
6.68
6.67
6.59
6.58
6.57
6.56
3.01
3.00
3.00
2.99
2.98
2.82
2.82
2.81
2.80
2.24
1.00
2.00
1.00
4.00
4.00
3.00
f1 (ppm)

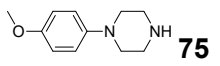

152.26
138.32
129.14
119.93
116.46
113.01
50.00
46.18
21.91
f1 (ppm)



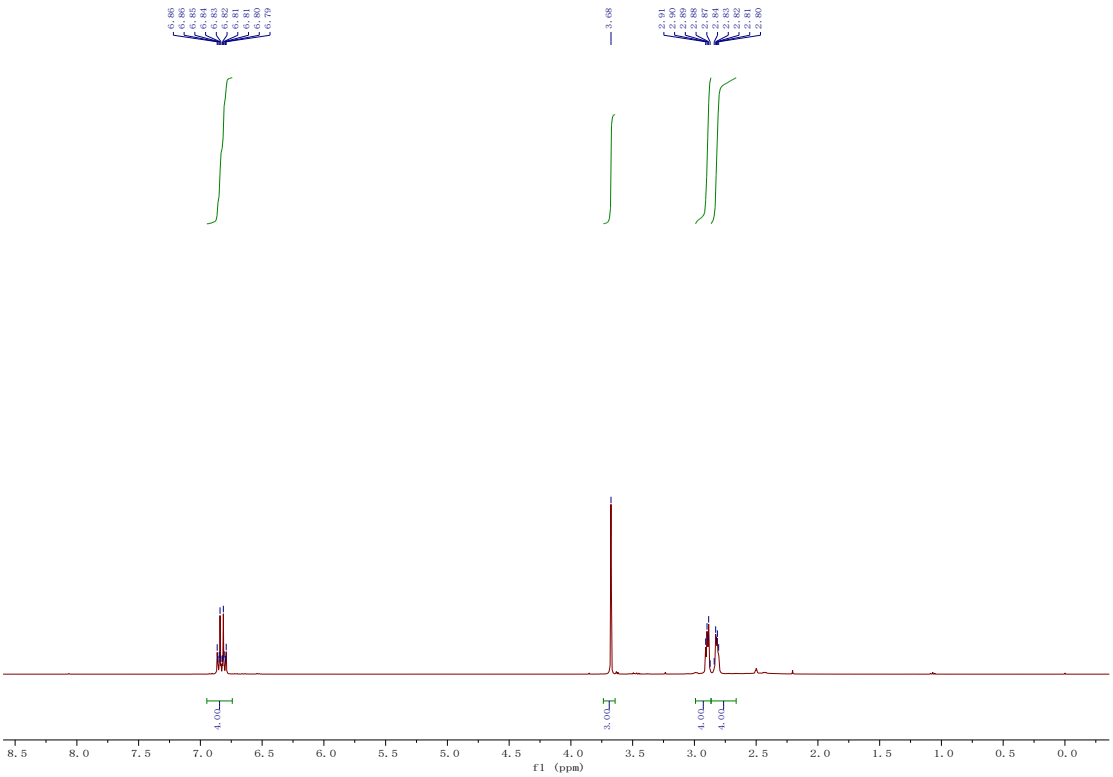
74

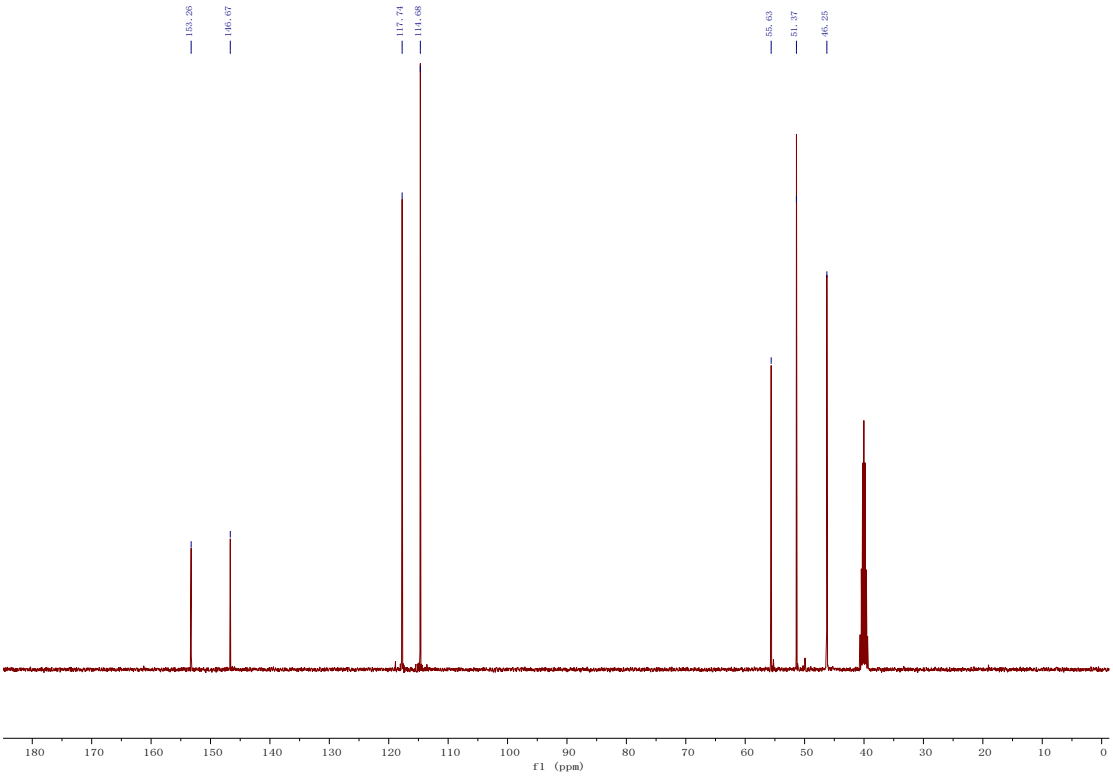

1.94
1.91
1.90
1.89
1.39
1.38
1.37
1.29
0.73
4.03
4.00
3.08
1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

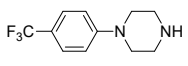

55.77
46.05
45.40
120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5
f1 (ppm)


O
N
NH

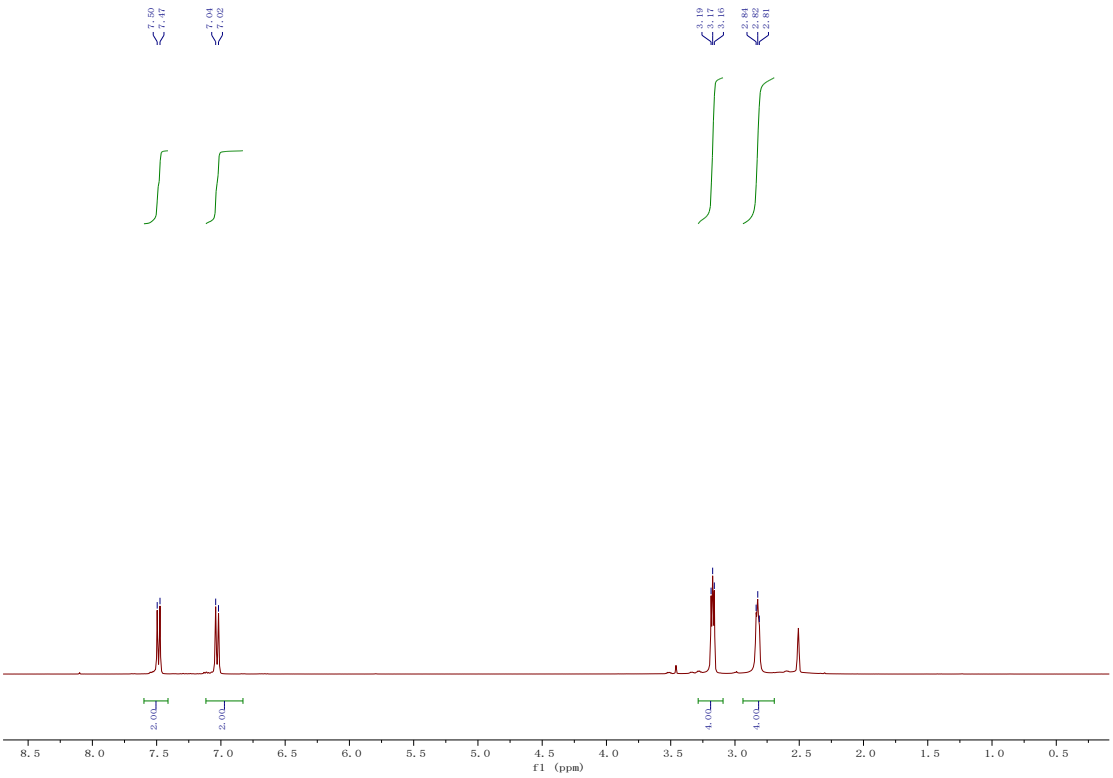
75

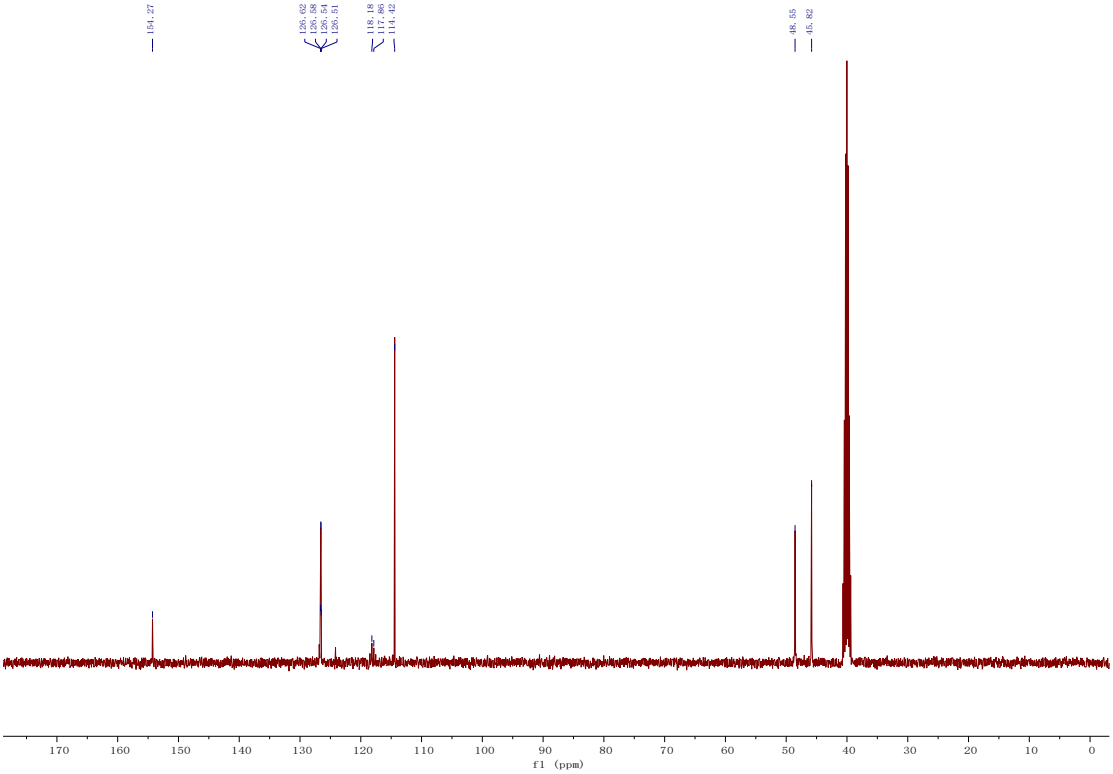

6.85
6.85
6.85
6.84
6.83
6.82
6.81
6.80
6.79
3.68
2.91
2.90
2.89
2.88
2.87
2.84
2.83
2.82
2.81
2.80
4.00
3.04
4.00
4.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

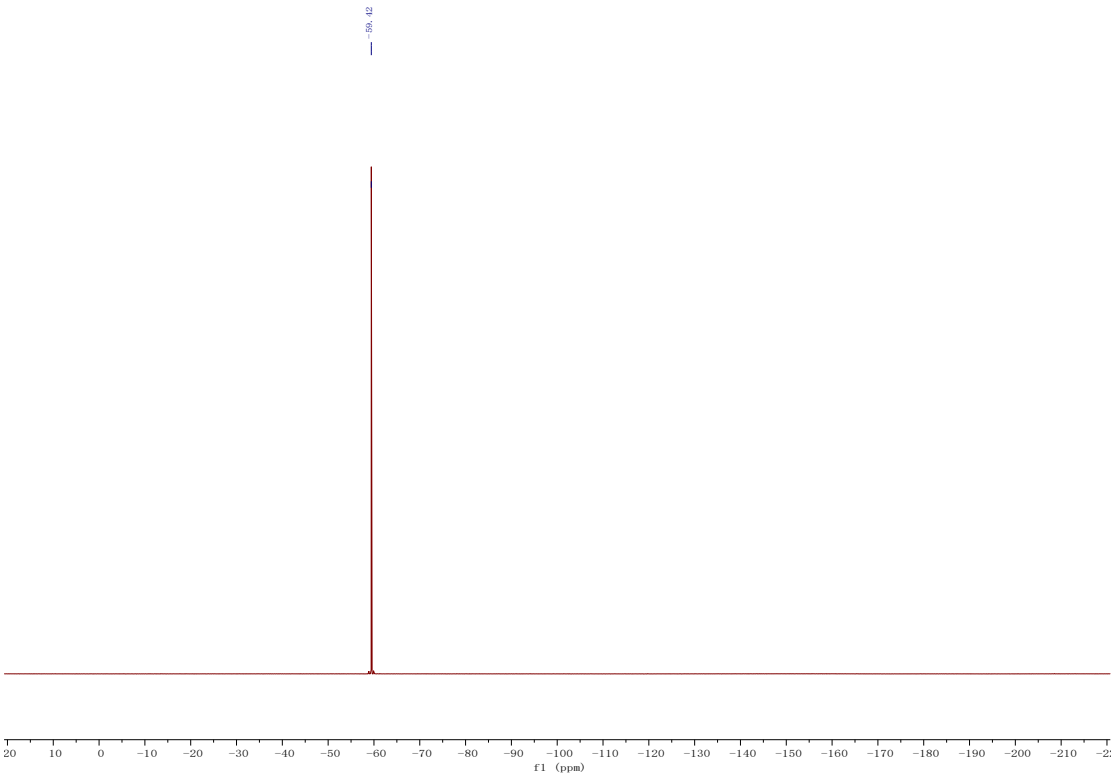

153.26
146.67
117.74
114.68
55.63
51.37
46.25
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

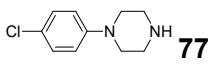

F3C
N
NH

76

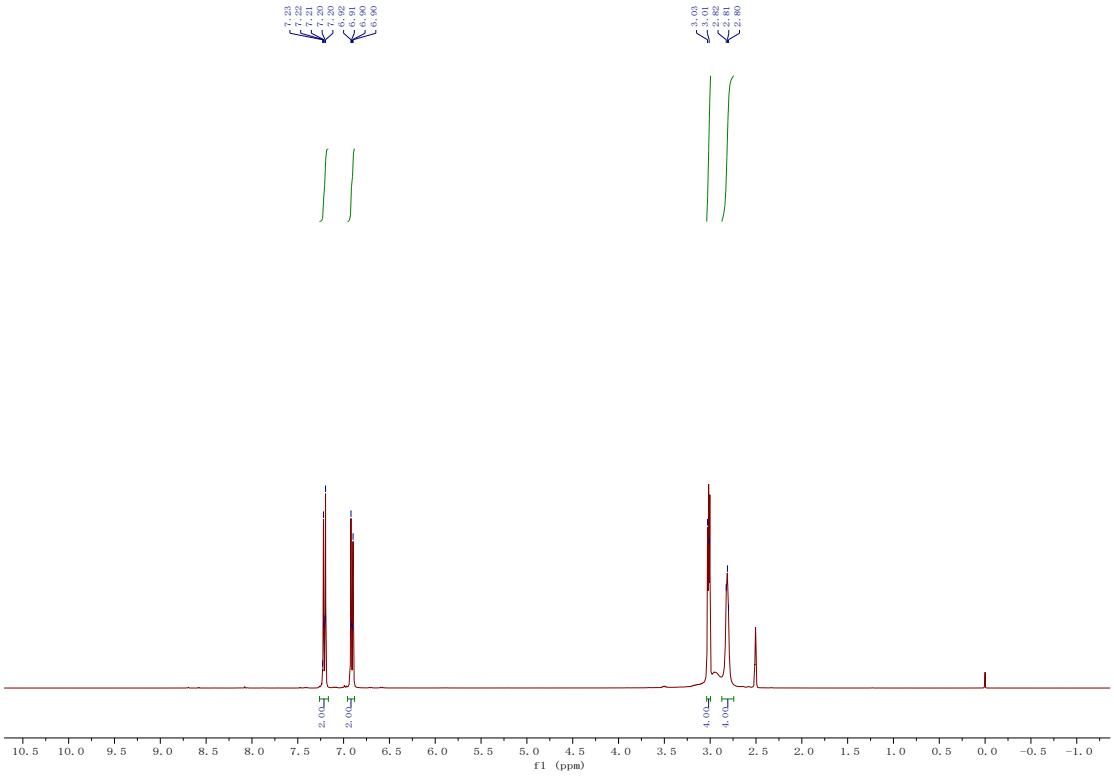

7.50
7.47
7.04
7.02
3.19
3.17
3.16
2.84
2.82
2.81
2.00
2.00
4.00
4.00
f1 (ppm)

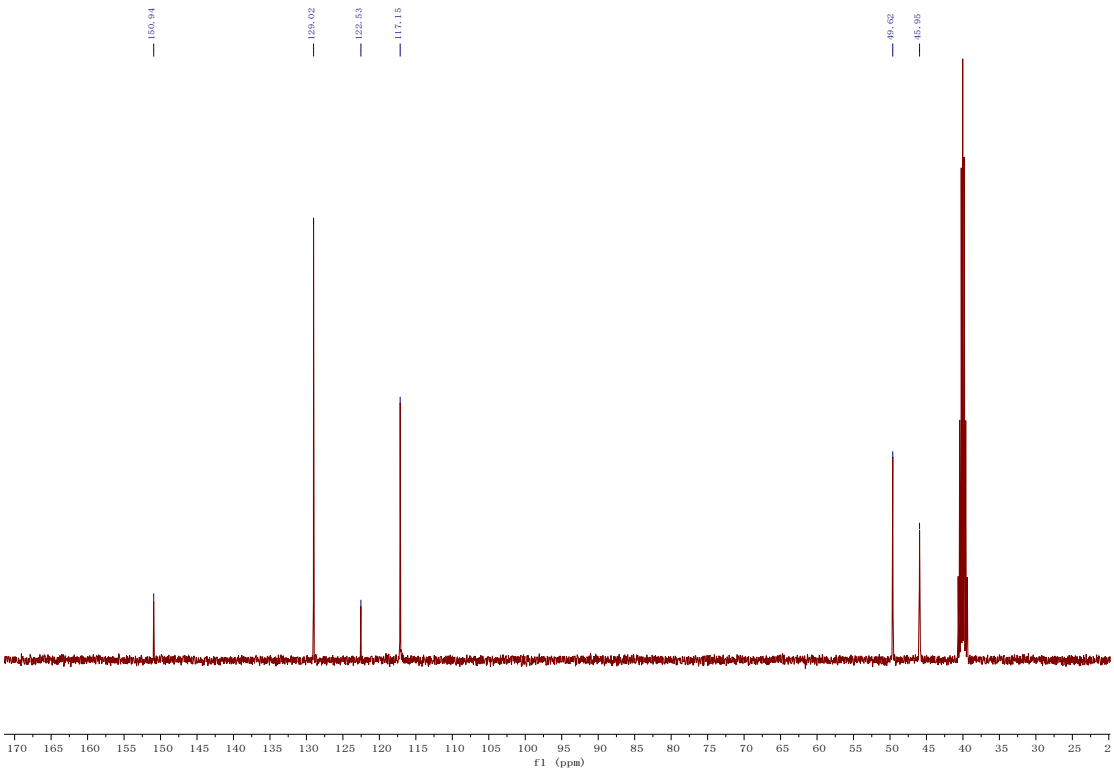

154.27
126.62
126.58
126.54
126.51
118.18
117.95
114.42
48.55
45.82
f1 (ppm)

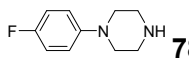

-59.42
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


Cl
N
NH

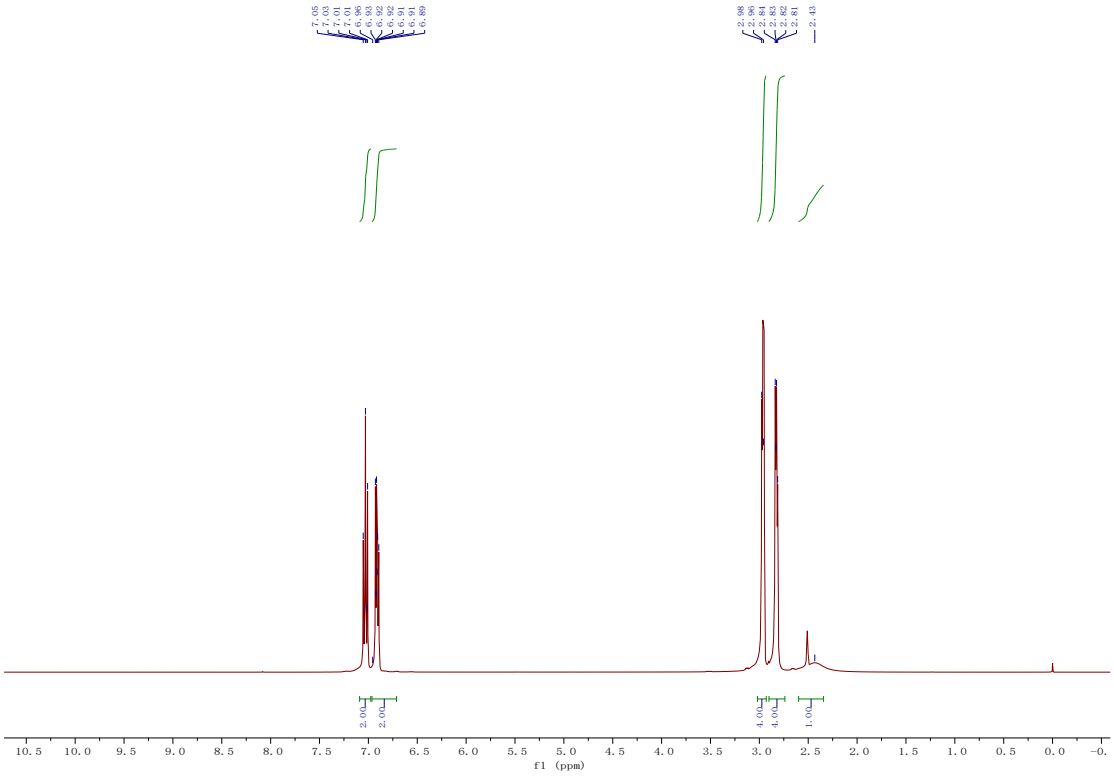
77

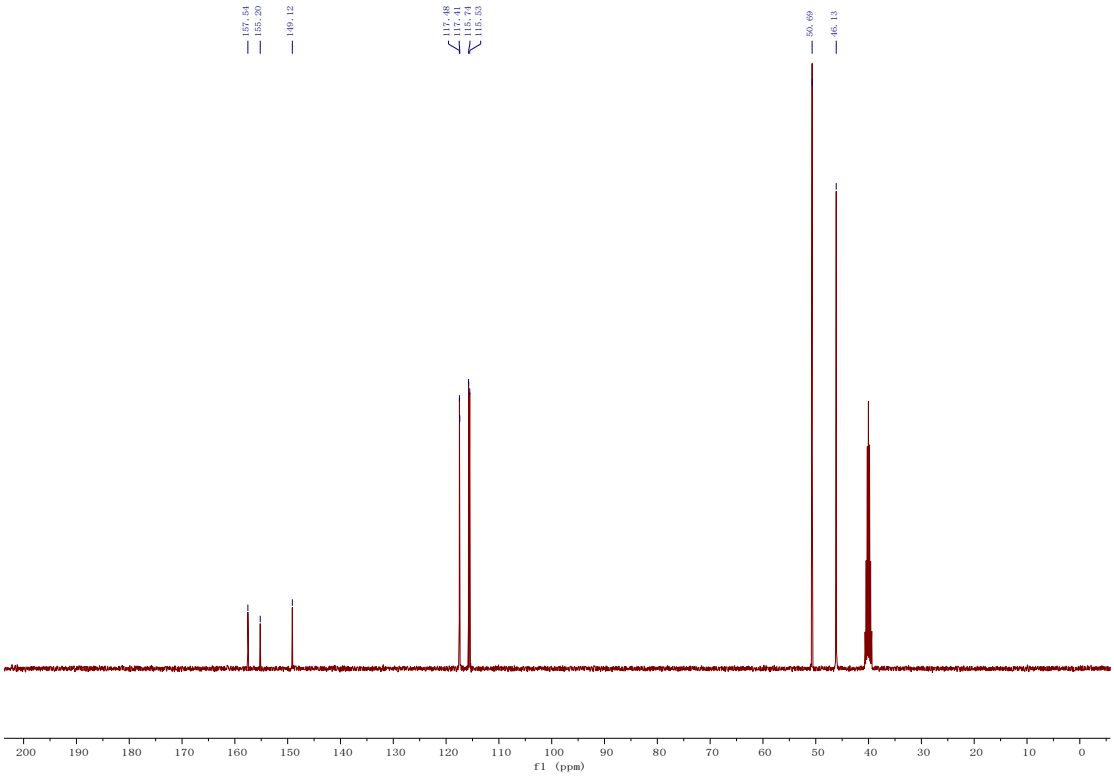

7.23
7.22
7.21
7.20
6.92
6.91
6.90
6.90
3.03
3.01
2.82
2.81
2.80
2.00
2.00
4.00
4.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

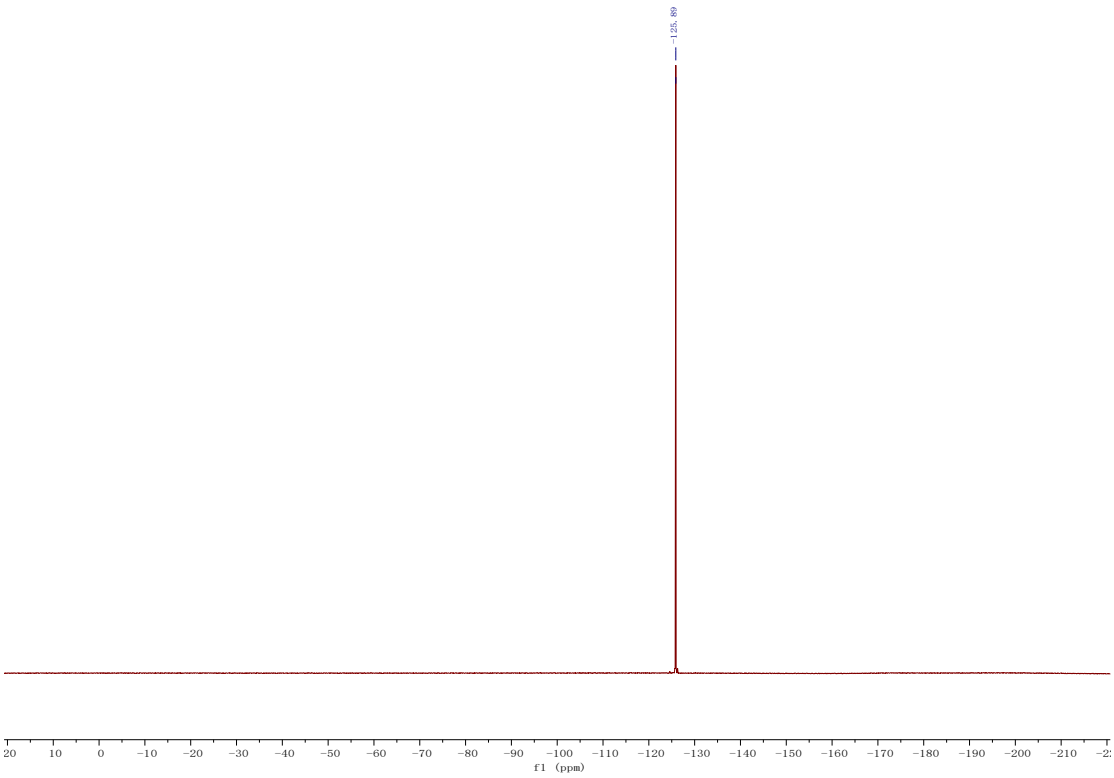

150.94
129.02
122.53
117.15
49.62
45.95
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 2
f1 (ppm)

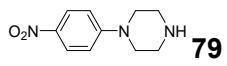

F
N
NH

78

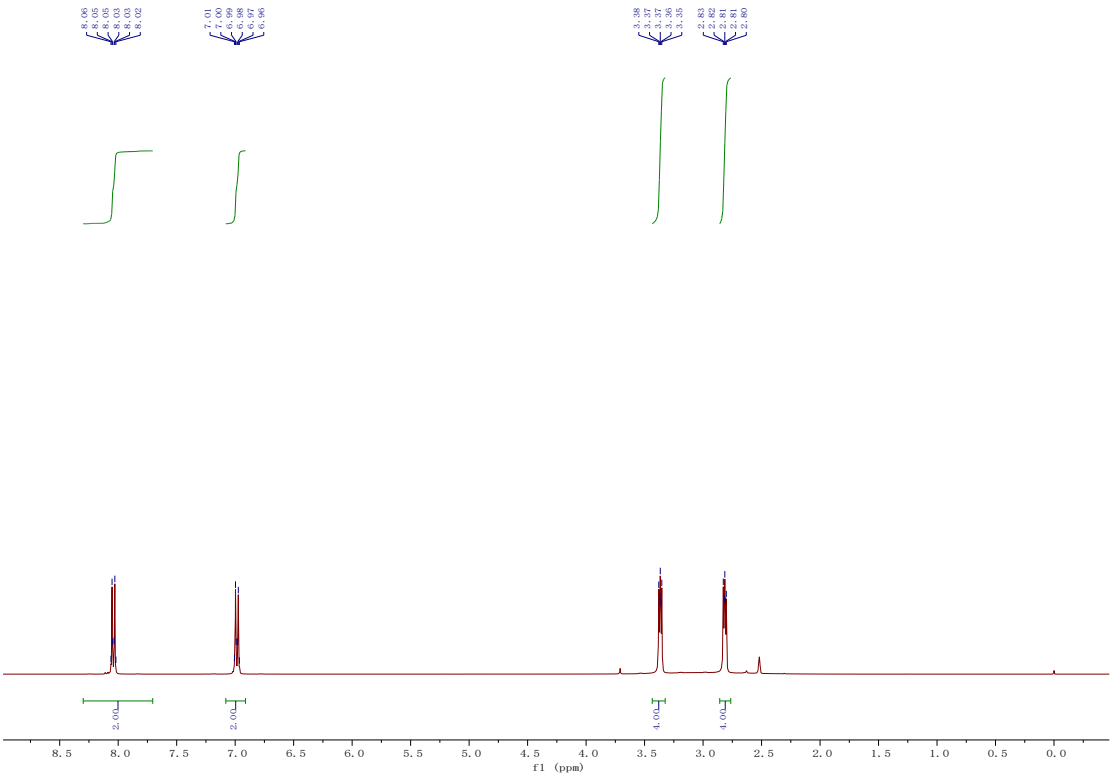

7.05
7.03
7.01
7.01
7.01
6.96
6.93
6.92
6.92
6.91
6.91
6.89
2.98
2.96
2.84
2.83
2.82
2.82
2.81
2.43
2.00
2.00
4.00
4.00
1.00
f1 (ppm)

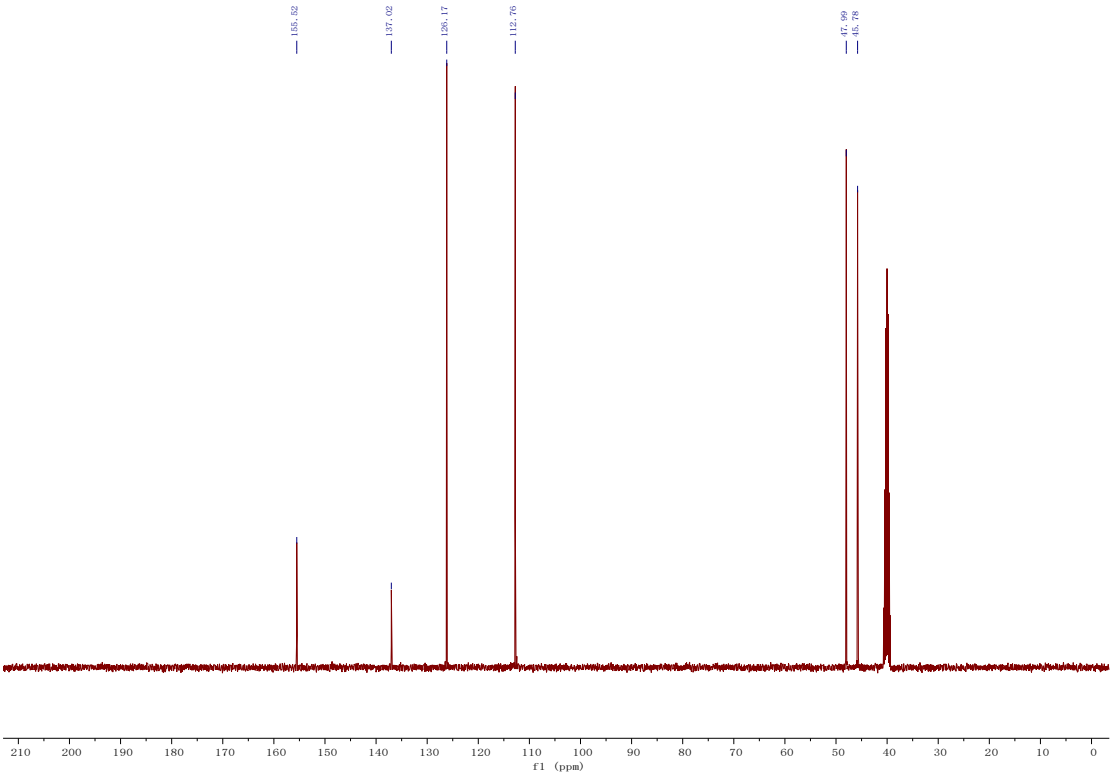

157.54
155.20
149.12
117.48
117.41
115.74
115.53
50.69
46.13
f1 (ppm)

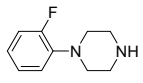

-125.89
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


O2N
N
NH

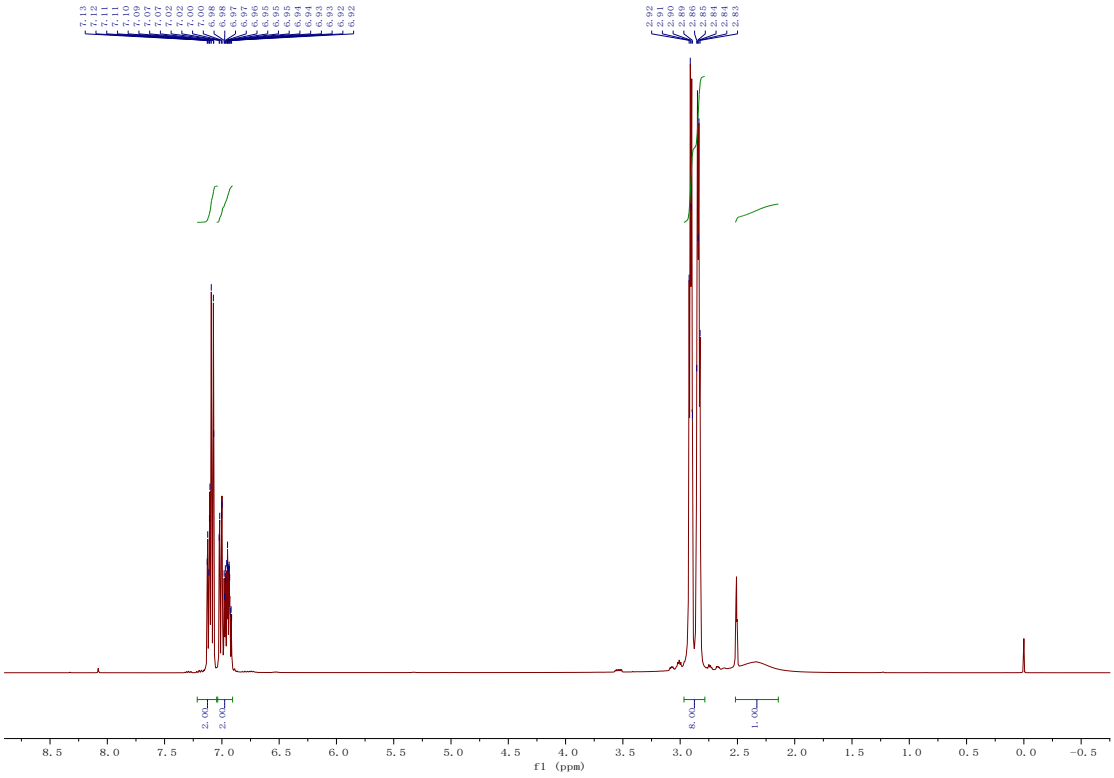
79

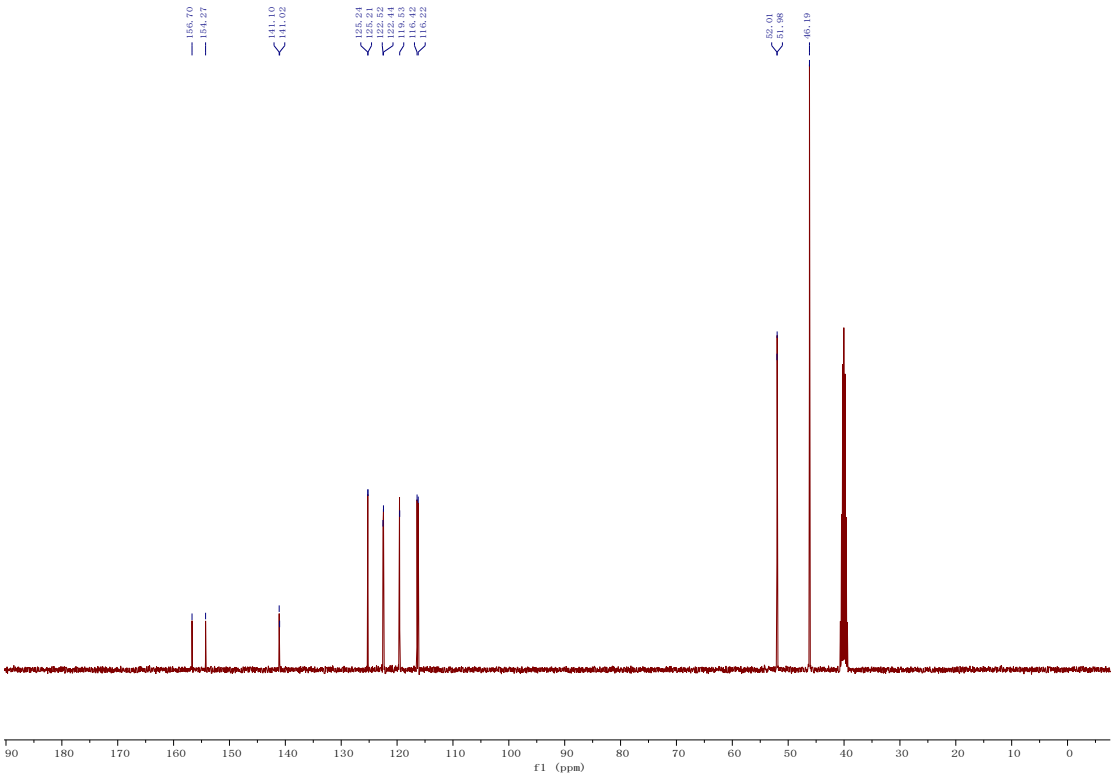

8.06
8.05
8.05
8.03
8.03
8.02
7.01
7.00
6.99
6.98
6.97
6.96
3.38
3.37
3.37
3.36
3.35
2.83
2.82
2.81
2.81
2.80
2.00
2.00
4.00
4.00
f1 (ppm)

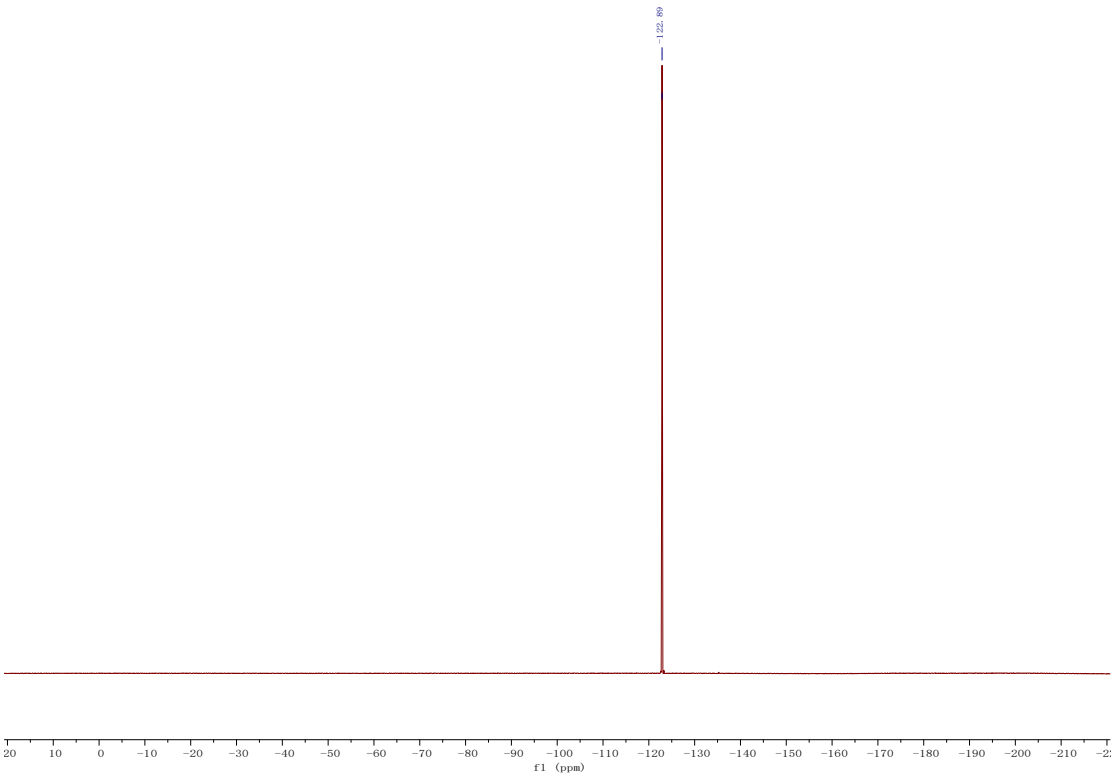

155.52
137.02
126.17
112.76
47.99
45.78
f1 (ppm)

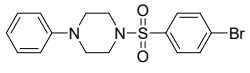

F
N
NH

80

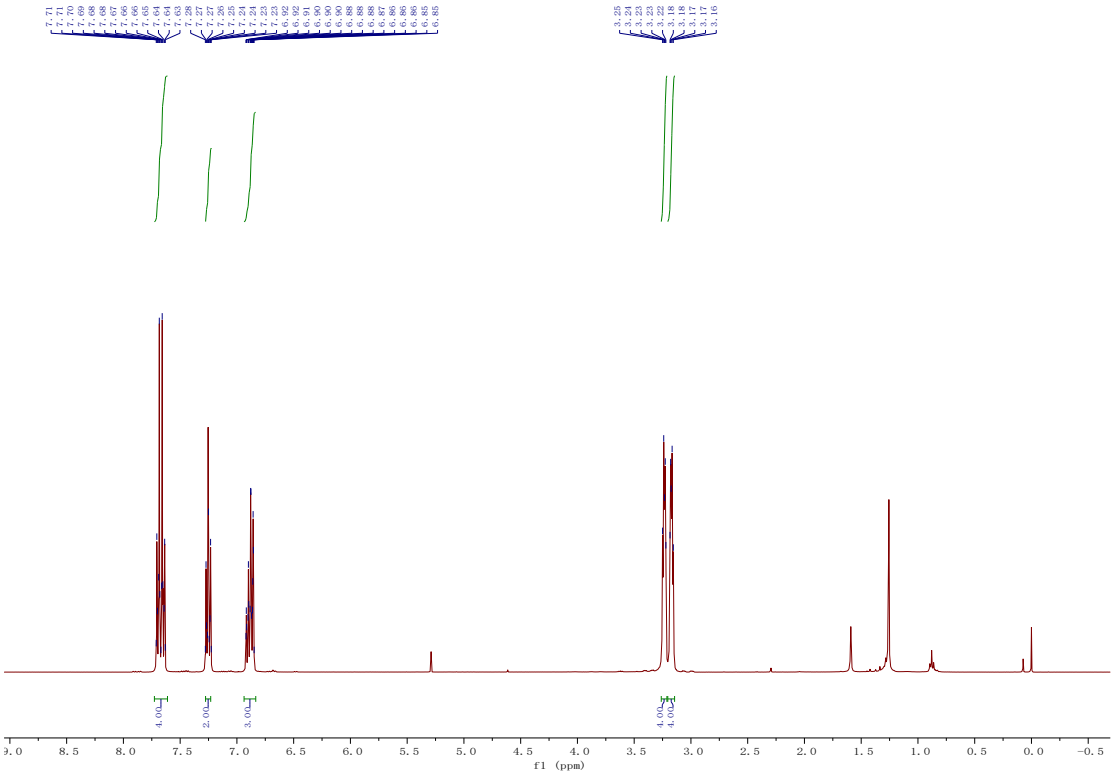

7.13
7.12
7.11
7.11
7.10
7.09
7.07
7.07
7.02
7.02
7.00
7.00
6.98
6.98
6.97
6.97
6.96
6.95
6.95
6.94
6.94
6.93
6.93
6.92
6.92
2.92
2.91
2.90
2.89
2.86
2.85
2.84
2.84
2.83
2.00
2.00
8.00
1.00
f1 (ppm)

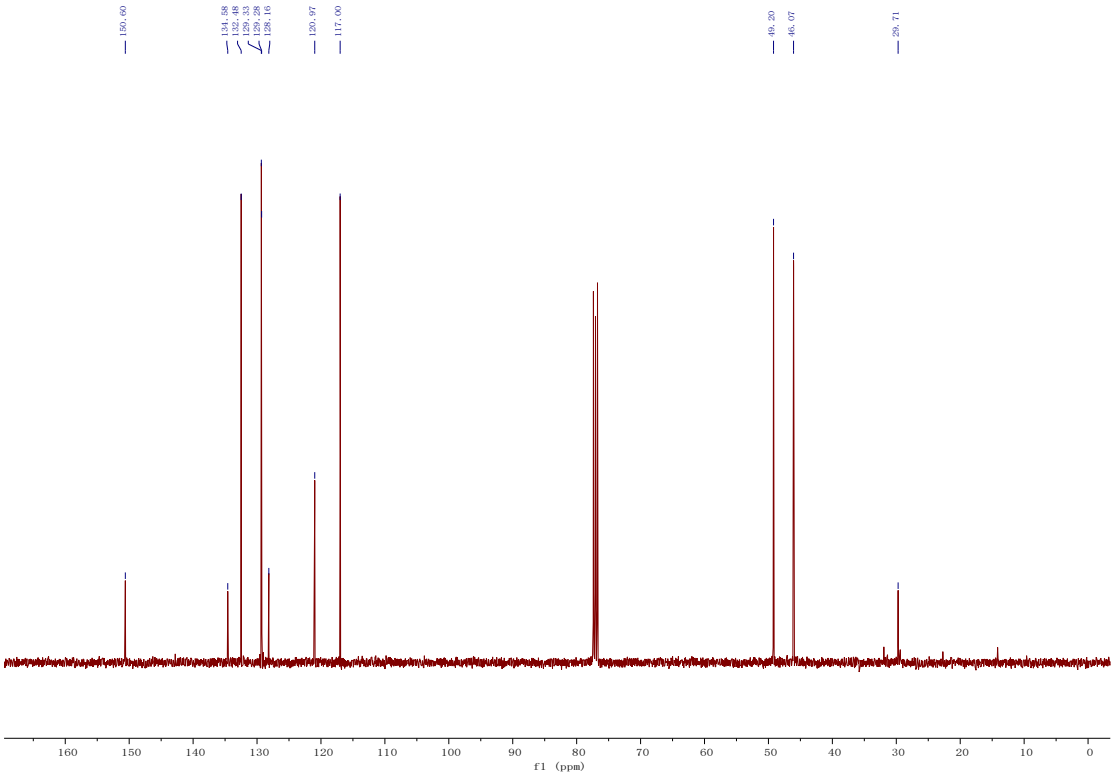

156.70
154.27
141.10
141.02
125.24
125.21
123.52
122.44
119.53
116.42
116.22
52.01
51.98
46.19
f1 (ppm)

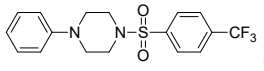

-122.89
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


O
N
N
S
O
Br

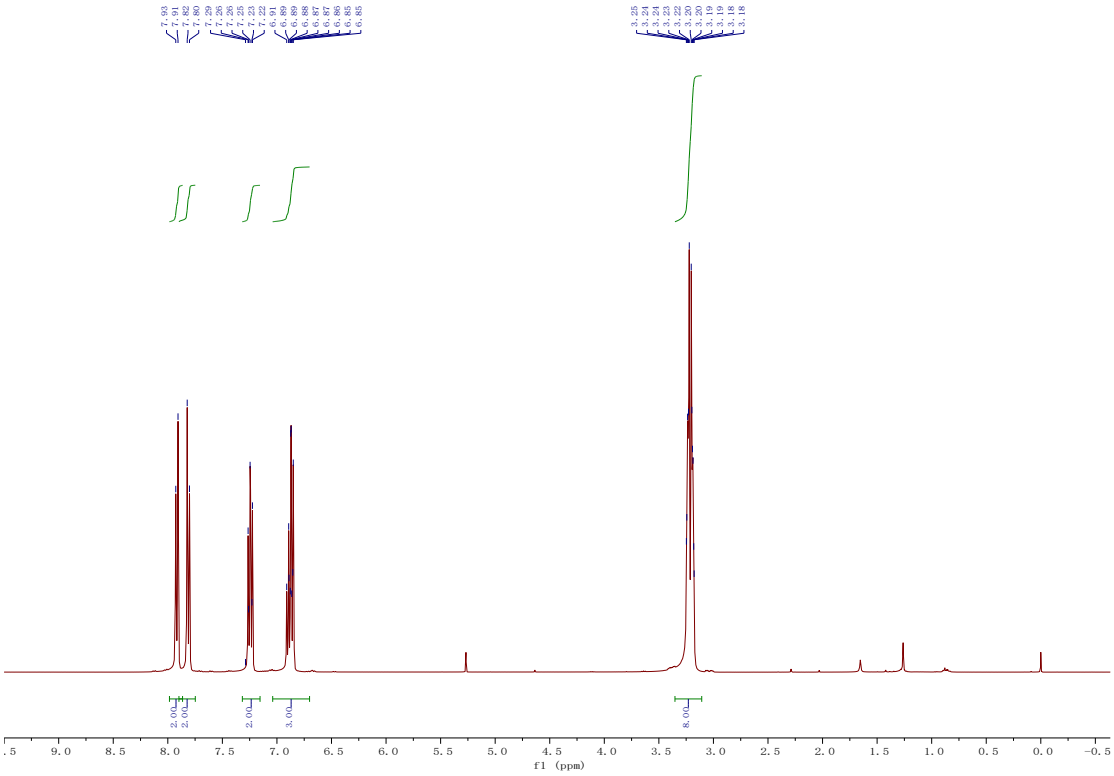
81

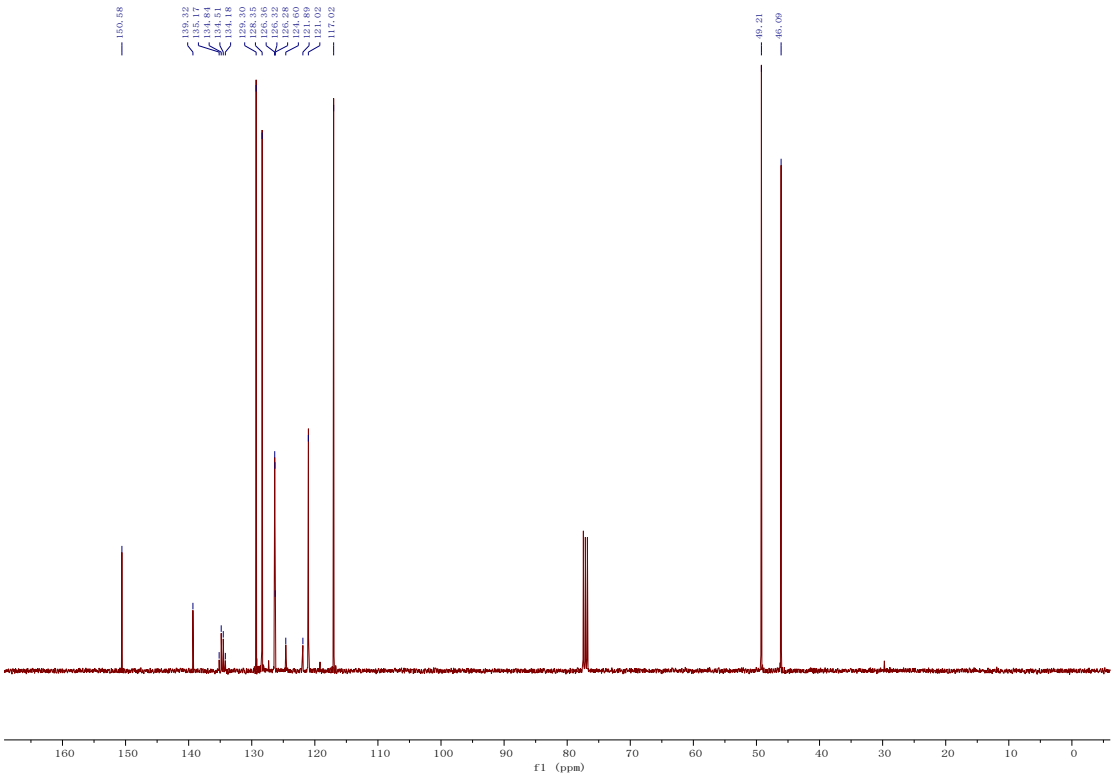

7.71
7.70
7.69
7.68
7.67
7.66
7.65
7.64
7.63
7.28
7.27
7.26
7.25
7.24
7.23
6.92
6.91
6.90
6.89
6.88
6.87
6.86
6.85
3.25
3.24
3.23
3.18
3.17
3.16
4.00
2.00
3.00
4.00
4.00
f1 (ppm)

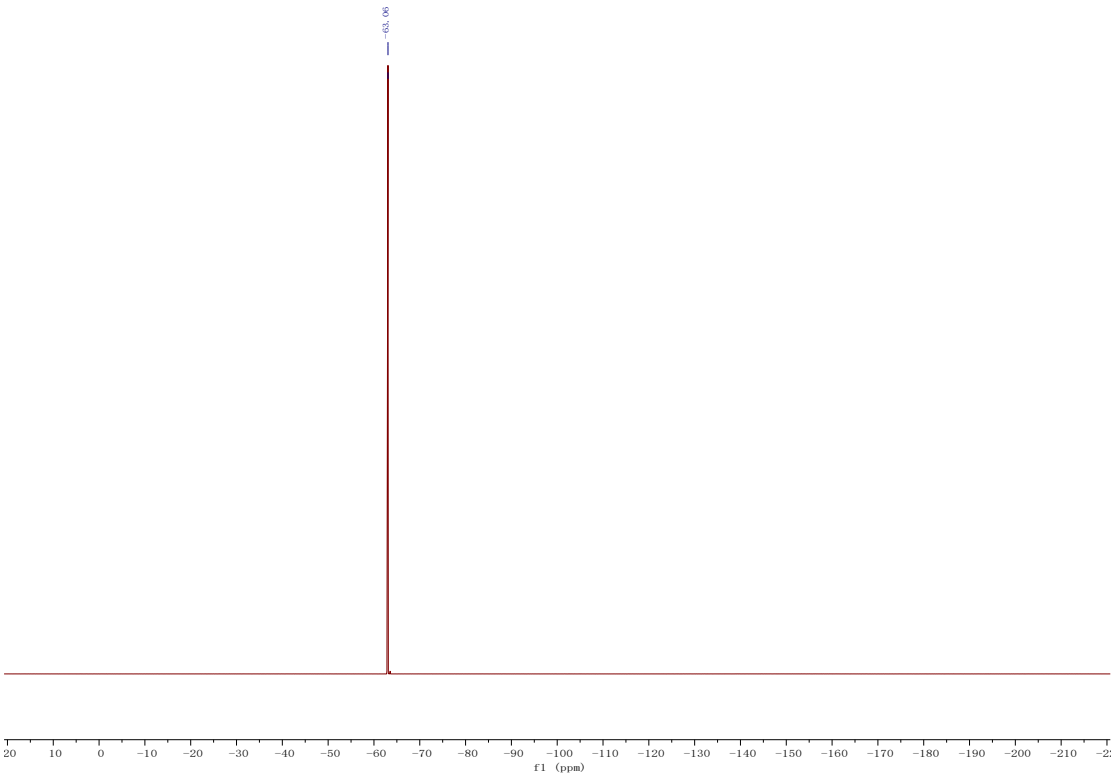

150.60
134.58
132.48
129.33
129.28
126.16
120.97
117.00
49.20
46.07
29.71
f1 (ppm)

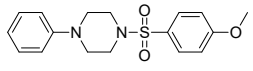


82

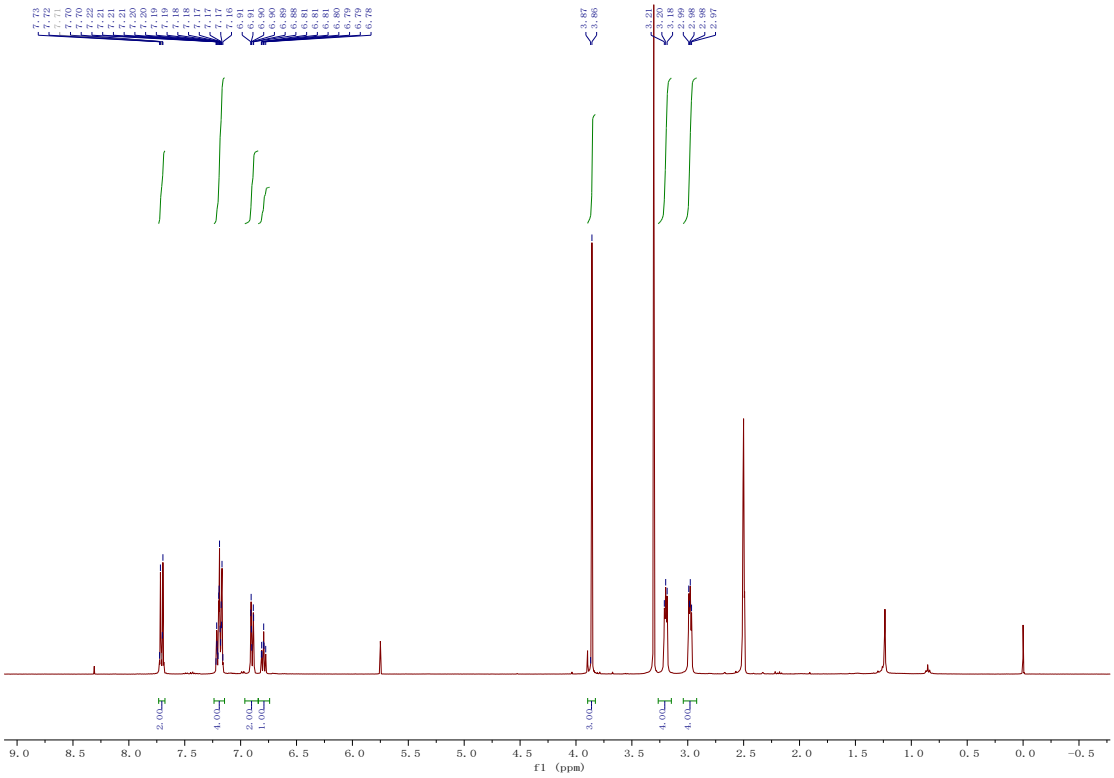

7.93
7.91
7.82
7.80
7.29
7.26
7.25
7.23
7.22
6.91
6.89
6.88
6.87
6.87
6.86
6.85
6.85
3.25
3.24
3.24
3.23
3.22
3.20
3.20
3.19
3.18
3.18
2.00
2.00
2.00
3.00
8.00
f1 (ppm)

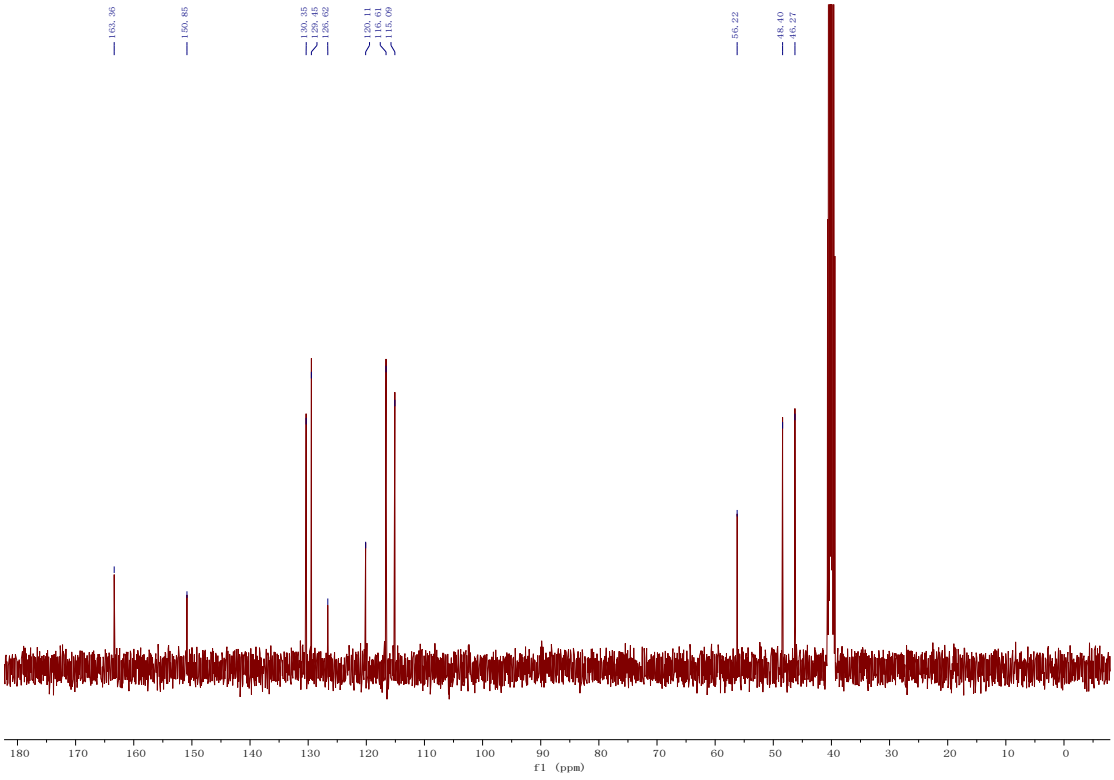

150.68
139.32
135.17
134.84
134.51
134.18
129.30
128.55
126.36
126.32
126.28
124.60
121.89
121.02
117.02
49.21
46.09
f1 (ppm)

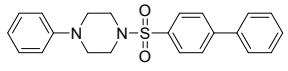

-60.69
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)



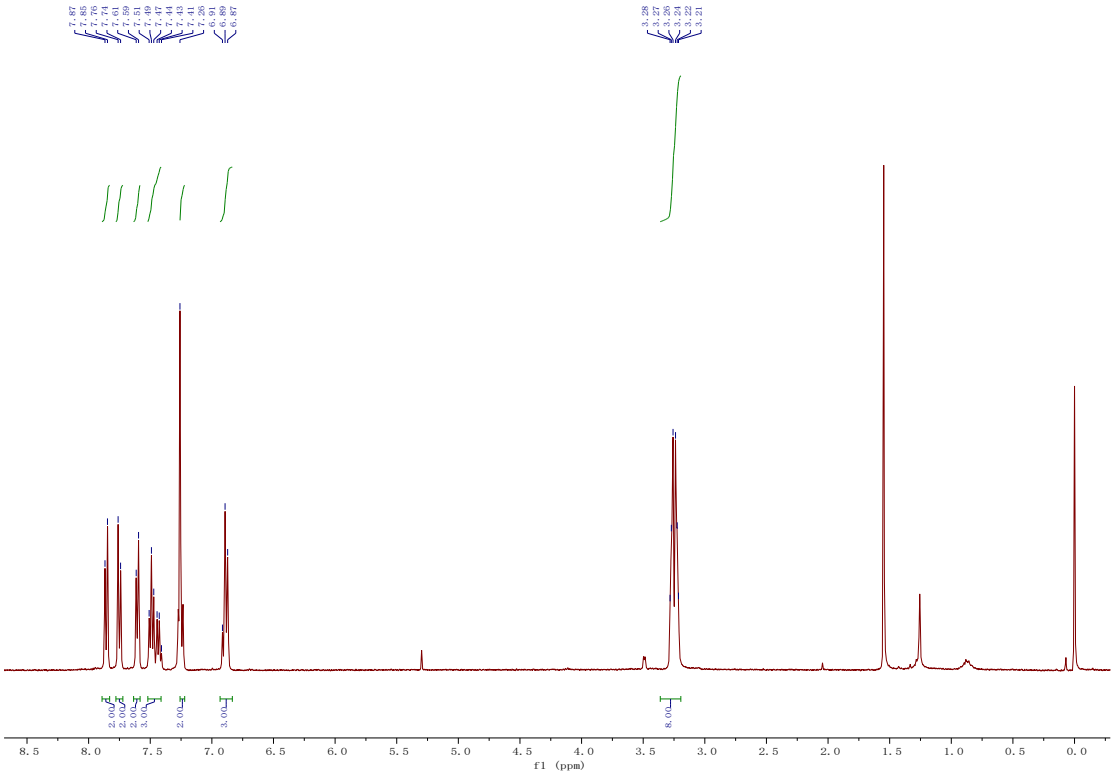
83

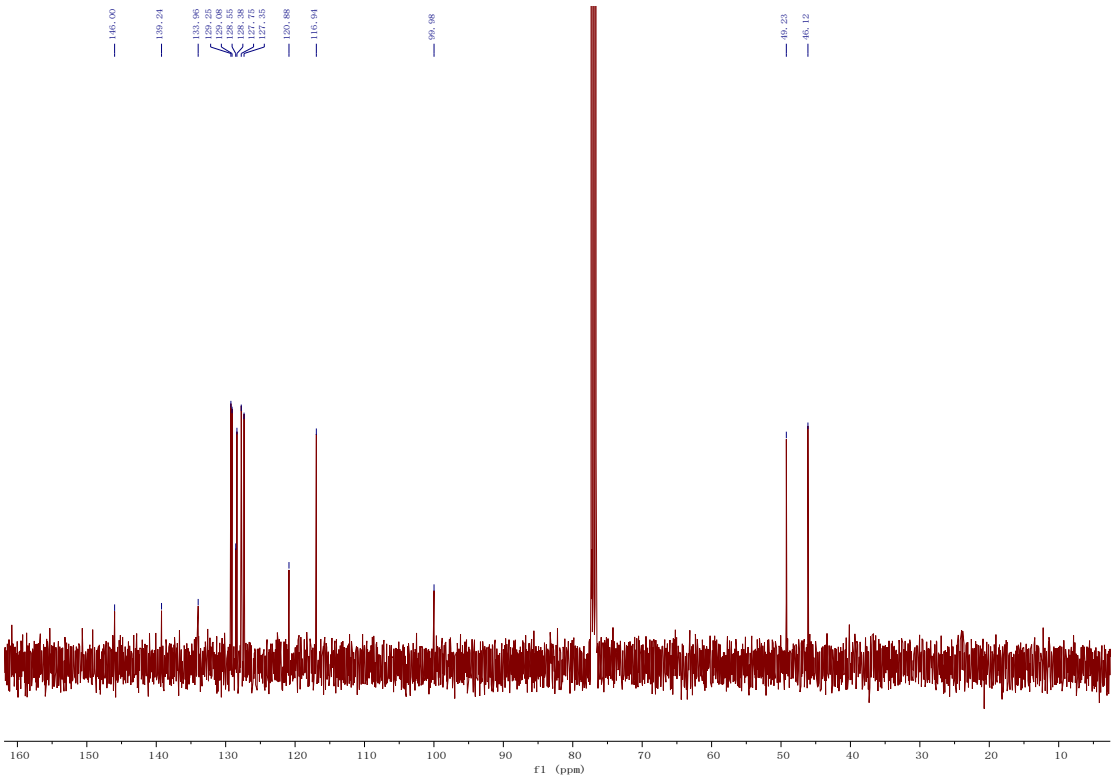

7.73
7.72
7.71
7.70
7.70
7.22
7.21
7.21
7.21
7.20
7.19
7.19
7.18
7.18
7.17
7.17
7.17
7.16
6.91
6.91
6.90
6.89
6.88
6.81
6.81
6.81
6.80
6.79
6.79
6.78
3.87
3.86
3.21
3.20
3.18
2.99
2.98
2.98
2.97
2.00
4.00
2.00
1.00
3.00
4.00
4.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

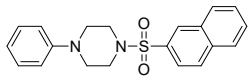

163.36
150.85
130.35
129.45
126.62
120.11
116.61
115.09
56.22
48.40
46.27
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



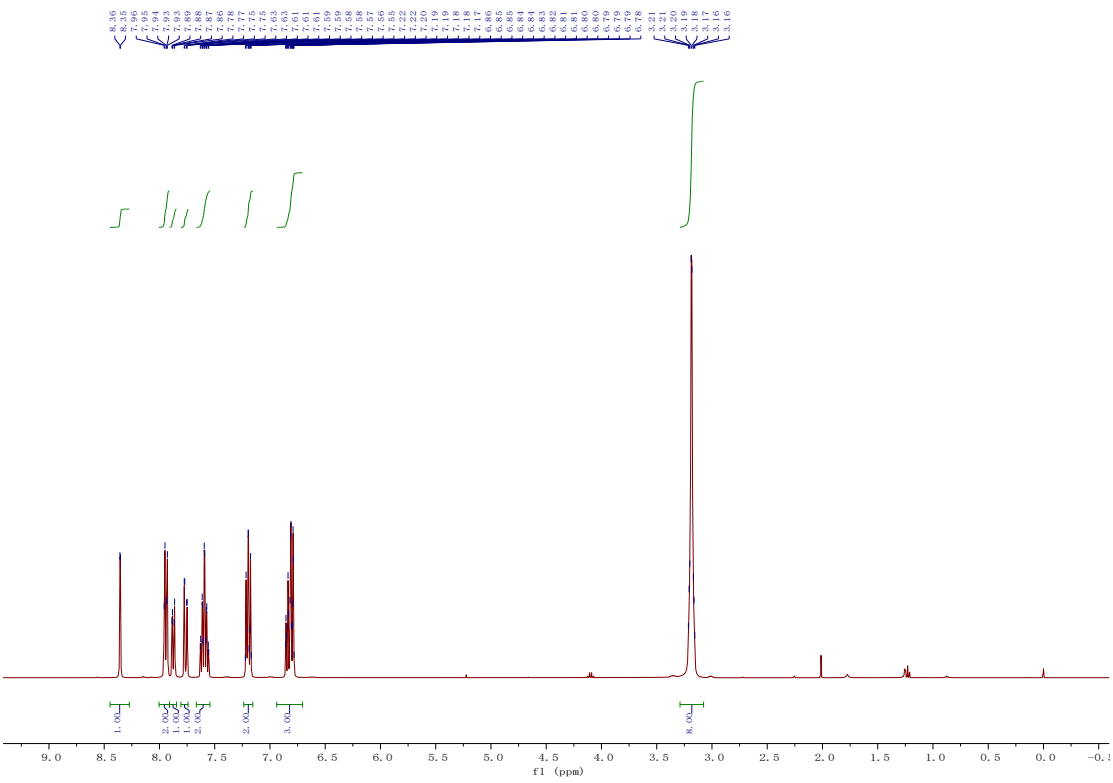
84

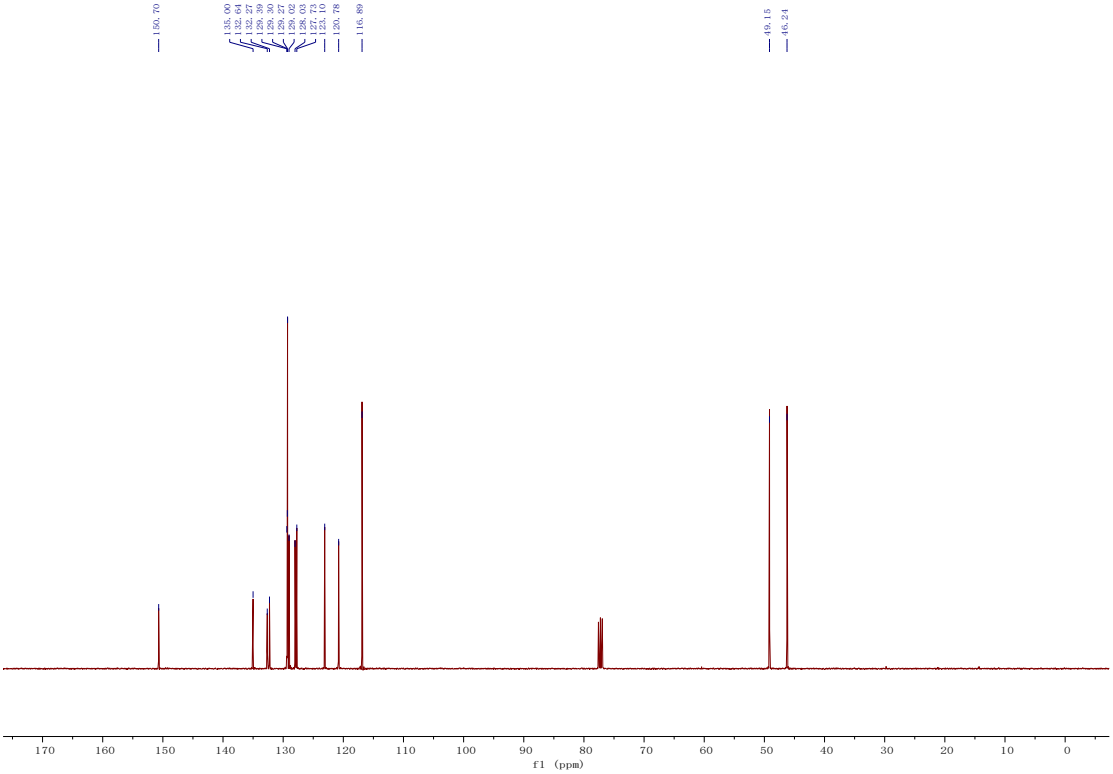

7.87
7.85
7.76
7.74
7.61
7.59
7.51
7.49
7.47
7.44
7.43
7.41
7.26
6.91
6.89
6.87
3.28
3.27
3.25
3.24
3.22
3.22
3.21
2.00
2.00
2.00
3.00
2.00
3.00
8.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

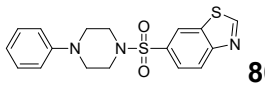

146.00
139.24
133.96
129.25
129.08
128.55
128.38
127.75
127.35
120.88
116.94
99.98
49.23
46.12
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



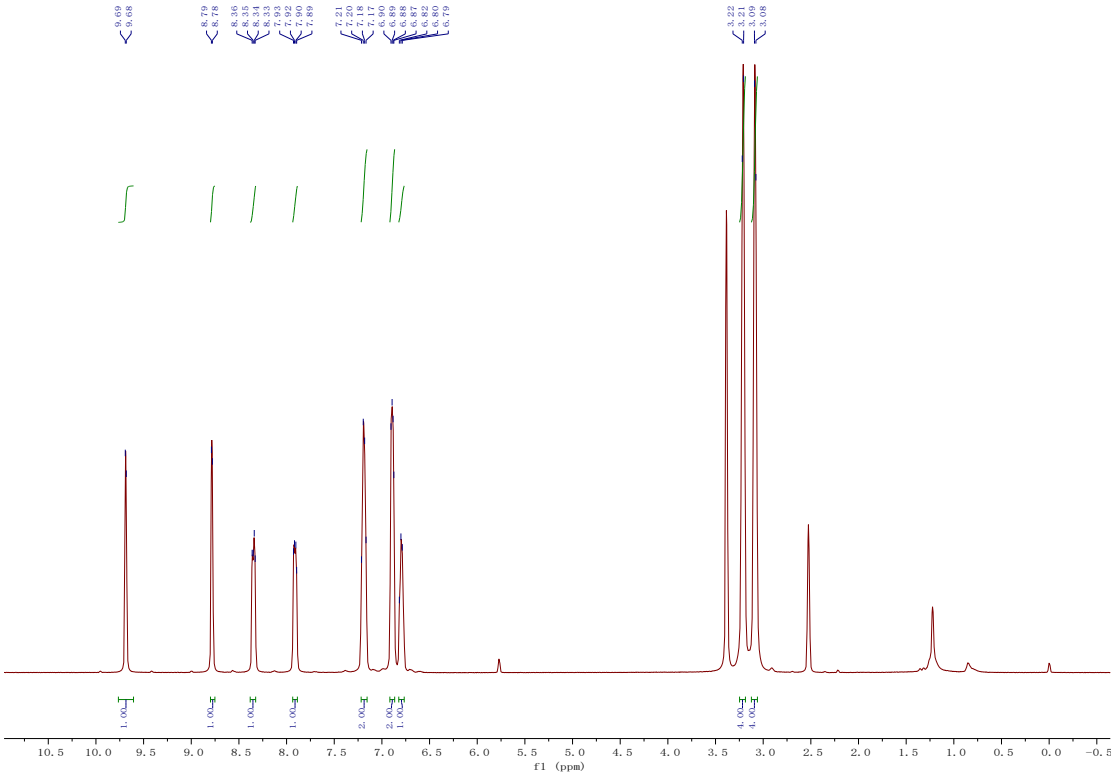
85

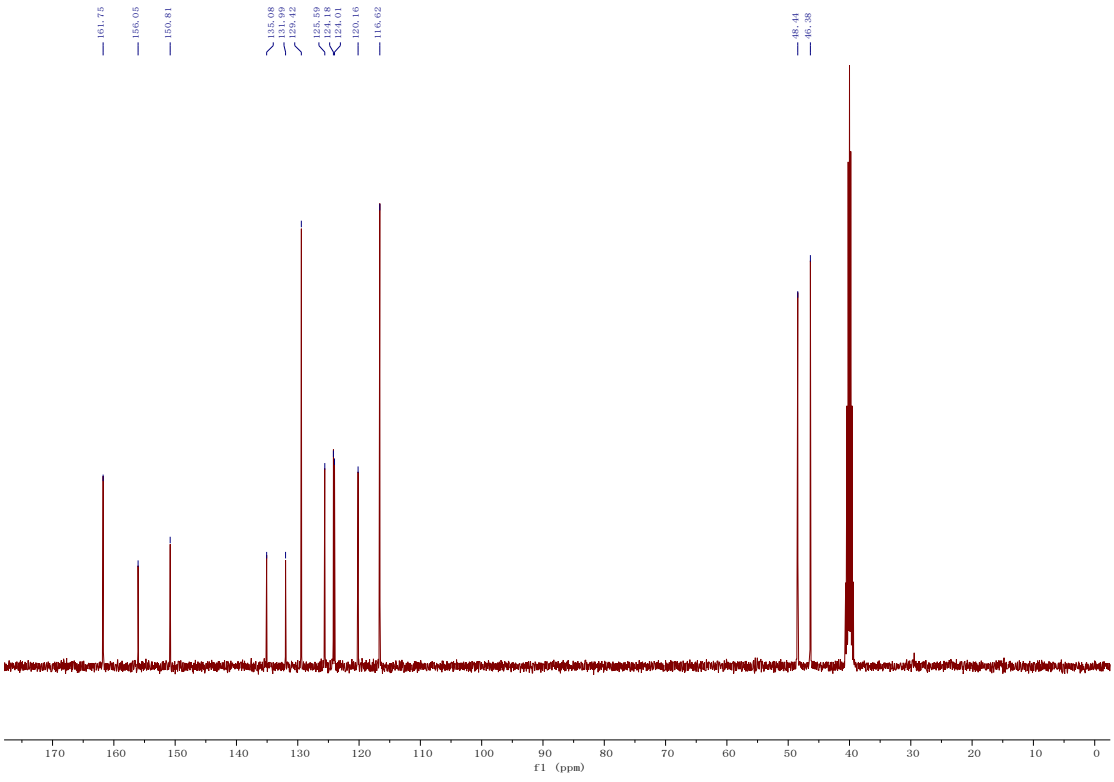

8.36
8.35
7.96
7.95
7.94
7.93
7.89
7.88
7.87
7.86
7.78
7.77
7.76
7.75
7.63
7.62
7.61
7.61
7.59
7.59
7.58
7.57
7.56
7.55
7.22
7.20
7.19
7.19
7.18
7.18
7.17
6.86
6.85
6.85
6.84
6.84
6.83
6.82
6.81
6.81
6.80
6.80
6.79
6.79
6.79
6.78
3.21
3.21
3.20
3.19
3.18
3.17
3.16
3.16
1.00
2.00
1.00
1.00
2.05
2.00
3.06
8.00
f1 (ppm)

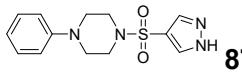

150.70
135.00
132.64
132.27
129.39
129.30
129.27
128.37
128.02
128.03
127.73
124.10
120.78
116.89
49.15
46.24
f1 (ppm)



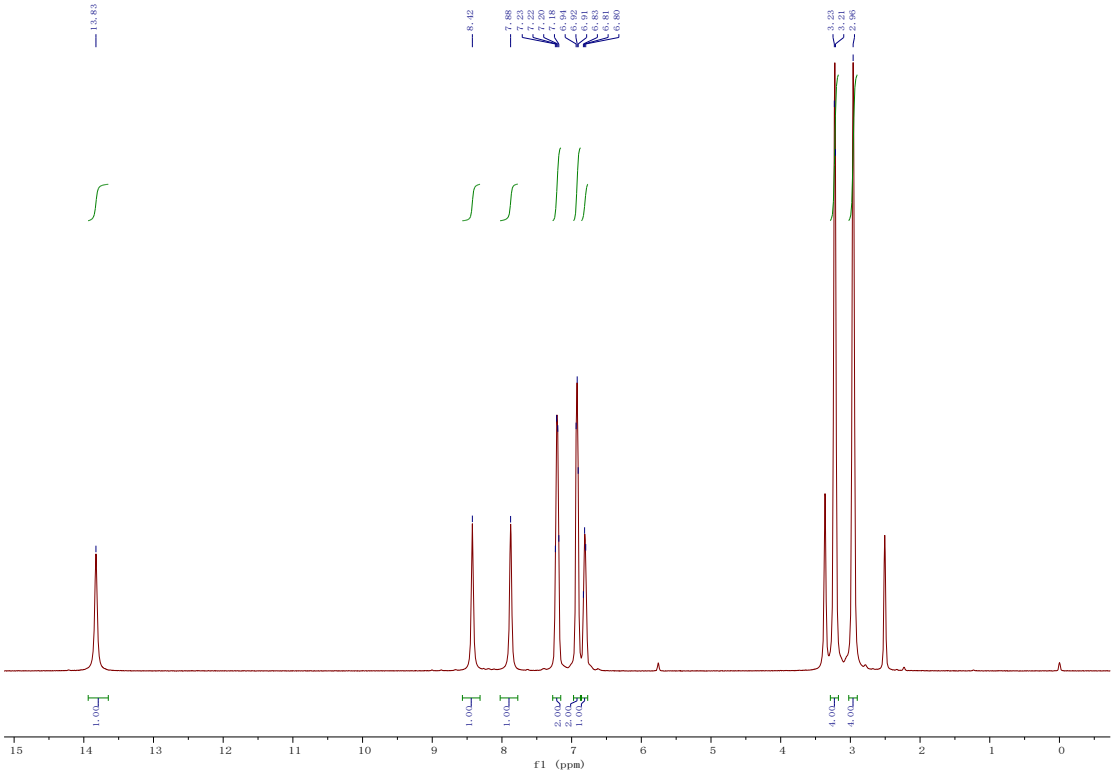
86

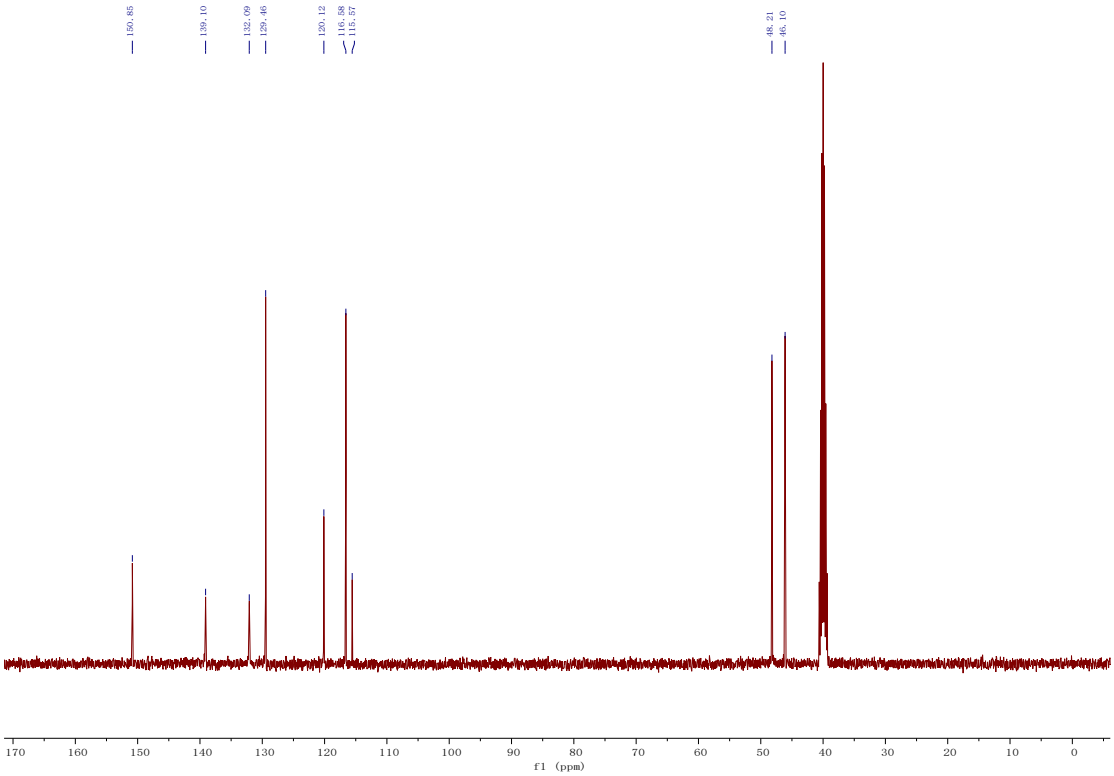

9.69
9.68
8.79
8.78
8.36
8.35
8.34
8.33
7.93
7.92
7.90
7.89
7.21
7.20
7.18
7.17
6.89
6.88
6.87
6.82
6.80
6.79
3.22
3.21
3.09
3.08
1.00
1.00
1.00
1.00
2.00
2.00
1.00
4.00
4.06
f1 (ppm)

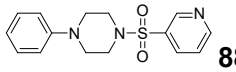

161.75
156.05
150.81
135.08
131.99
129.42
125.59
124.18
124.01
120.16
116.62
48.44
46.38
f1 (ppm)



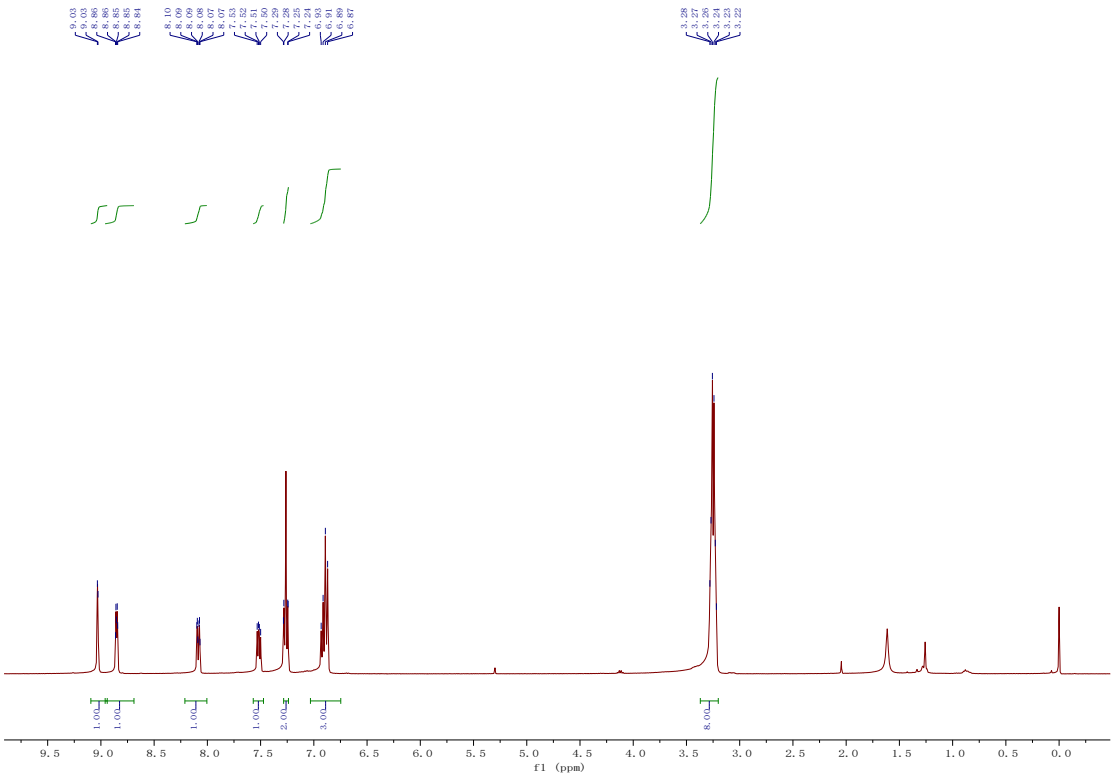
87

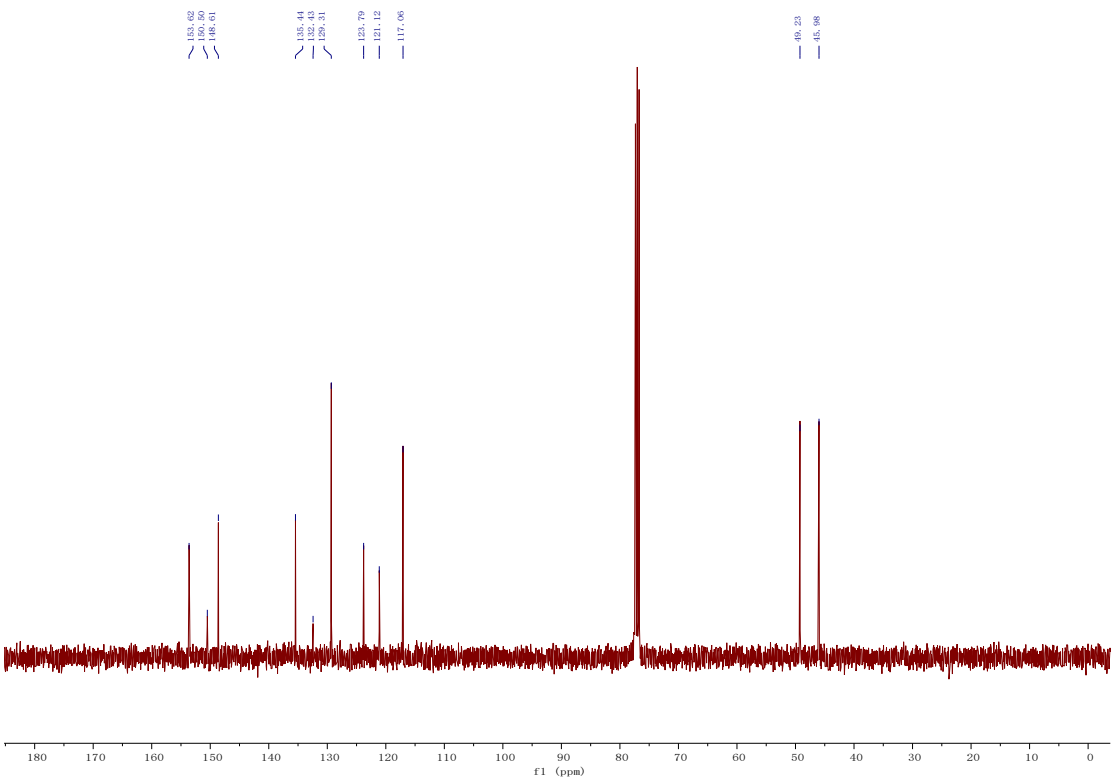

13.83
8.42
7.88
7.23
7.22
7.20
7.18
6.94
6.92
6.91
6.83
6.81
6.80
3.23
3.21
2.96
1.00
1.00
1.00
2.00
2.05
1.00
4.00
4.00
f1 (ppm)

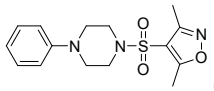

150.85
139.10
132.09
129.46
120.12
116.68
115.57
48.21
46.10
f1 (ppm)



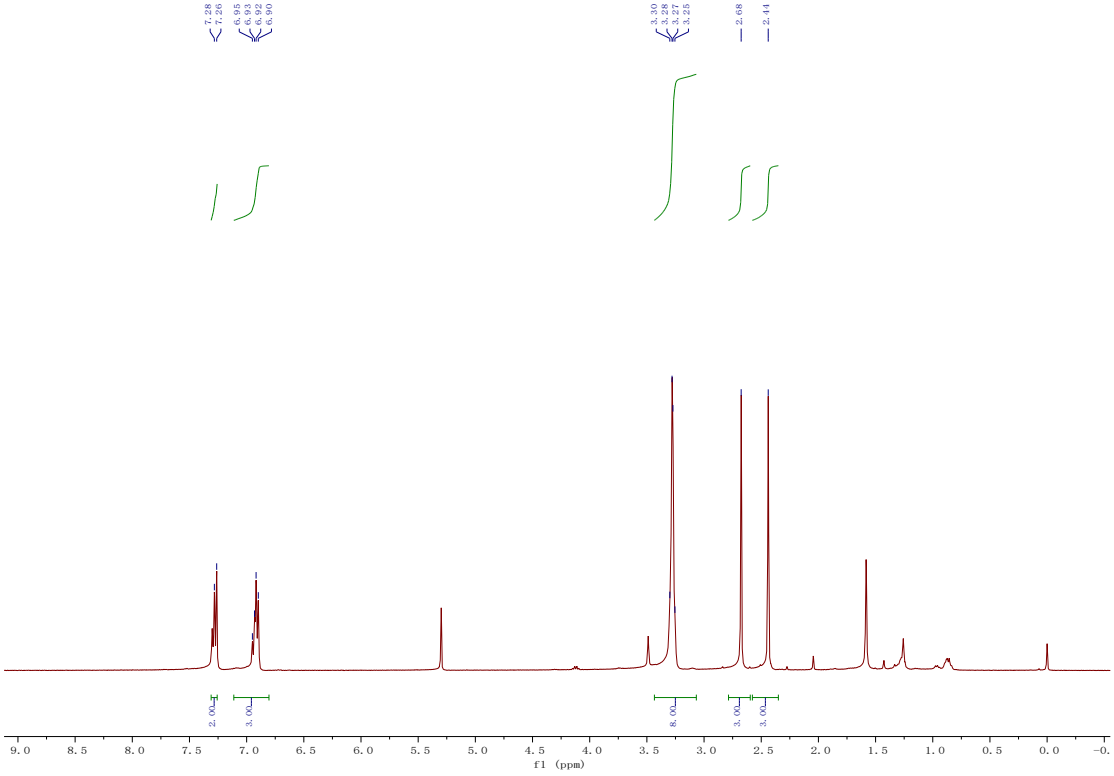
88

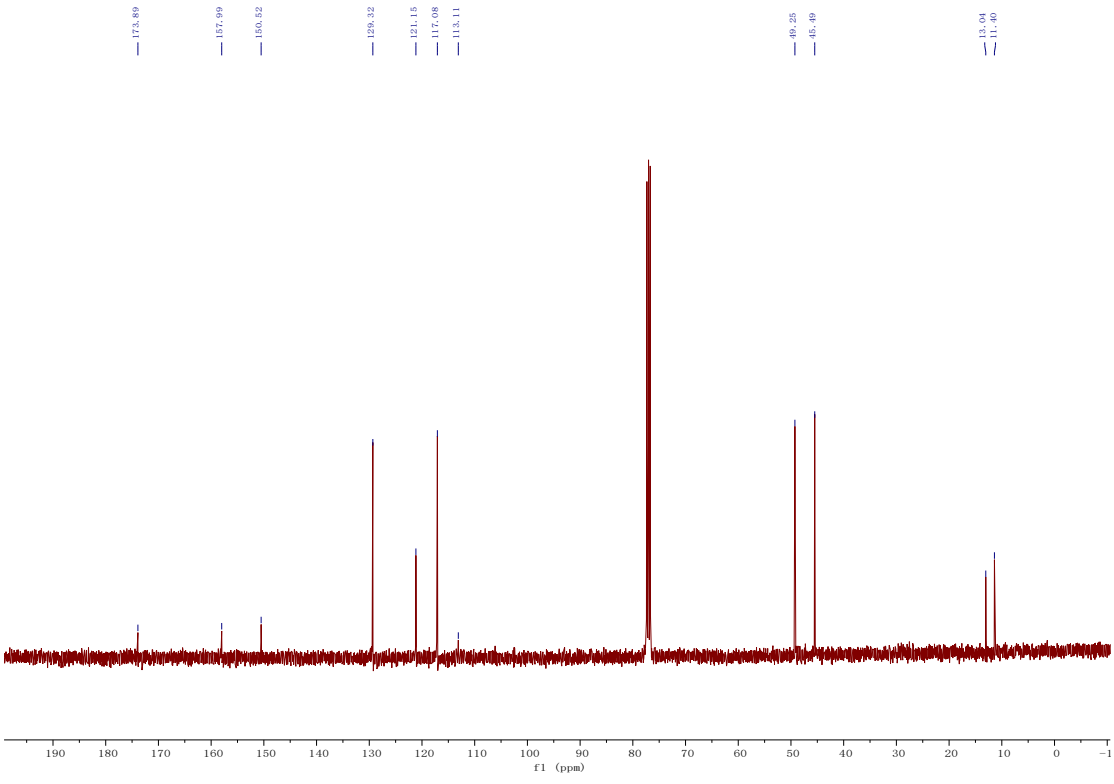

9.03
9.03
8.86
8.86
8.85
8.85
8.84
8.84
8.10
8.09
8.09
8.08
8.07
8.07
7.53
7.52
7.51
7.50
7.29
7.28
7.25
7.24
6.93
6.91
6.89
6.87
3.28
3.27
3.26
3.24
3.23
3.22
1.00
1.00
1.00
1.00
2.00
3.00
8.00
f1 (ppm)

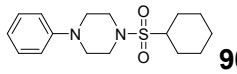

153.62
150.50
148.61
135.44
132.43
129.31
123.79
121.12
117.06
49.23
45.98
f1 (ppm)



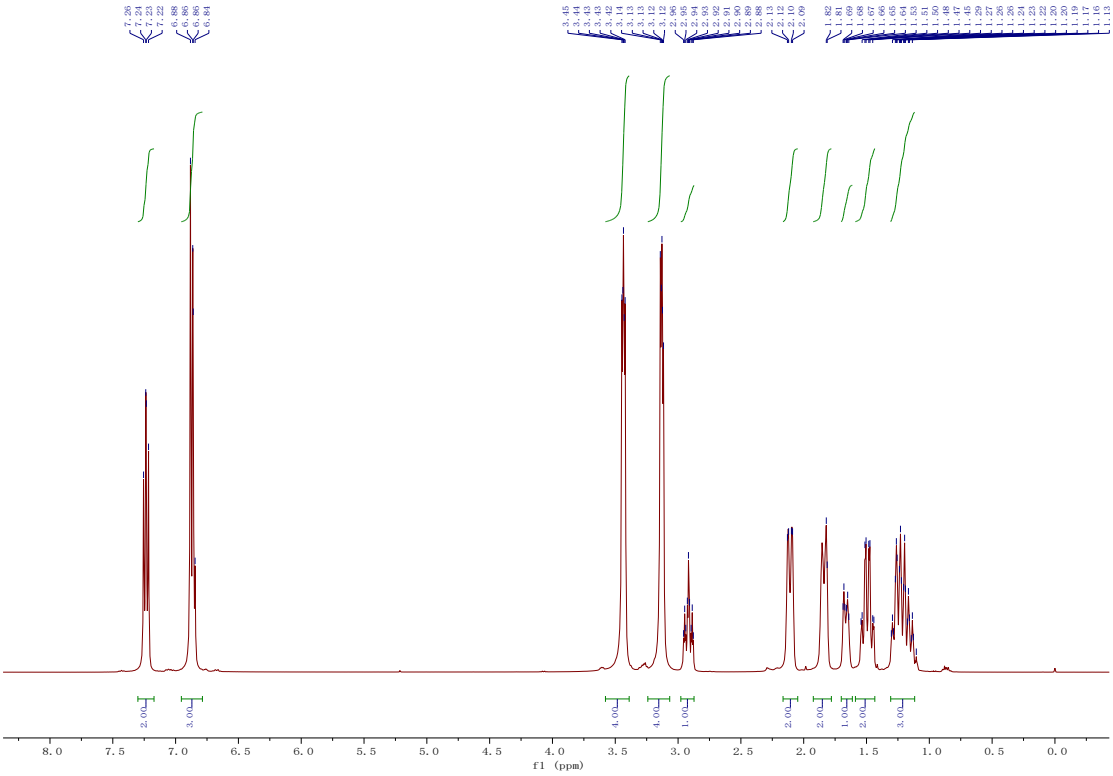
89

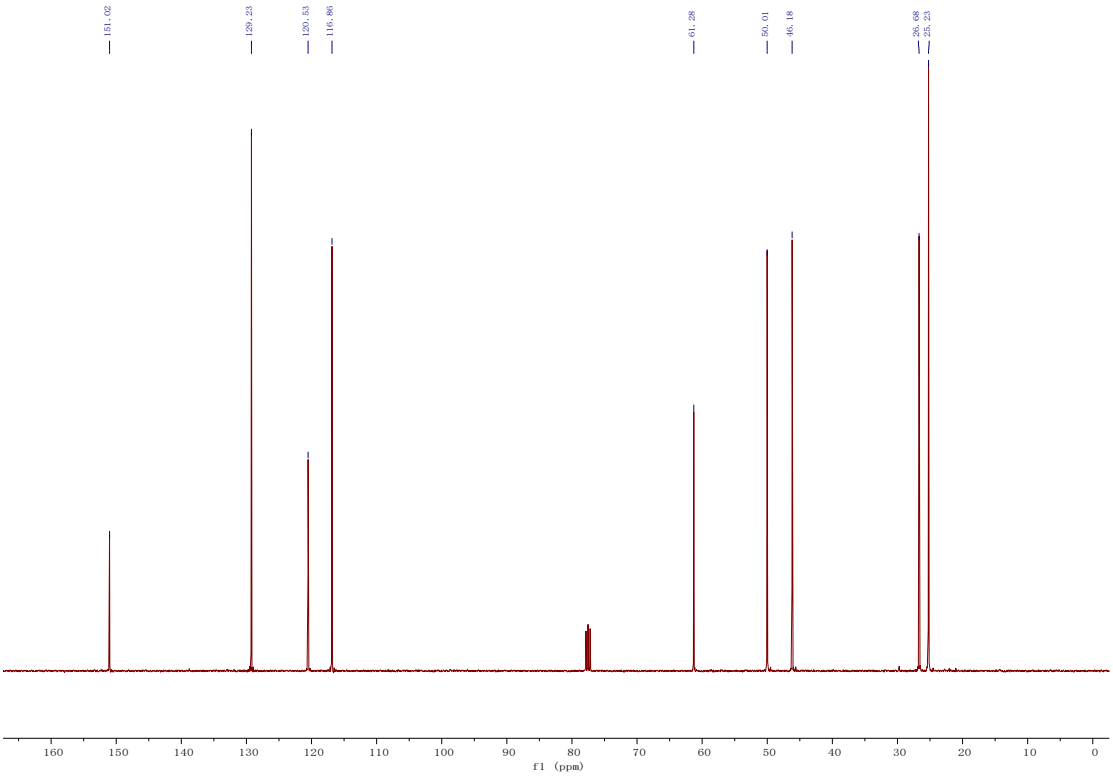

7.28
7.26
6.95
6.93
6.92
6.90
3.30
3.28
3.27
3.25
2.68
2.44
2.00
3.06
8.00
3.06
3.06
f1 (ppm)

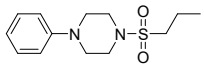

173.89
157.99
150.52
129.32
121.15
117.08
113.11
49.25
45.49
13.04
11.40
f1 (ppm)



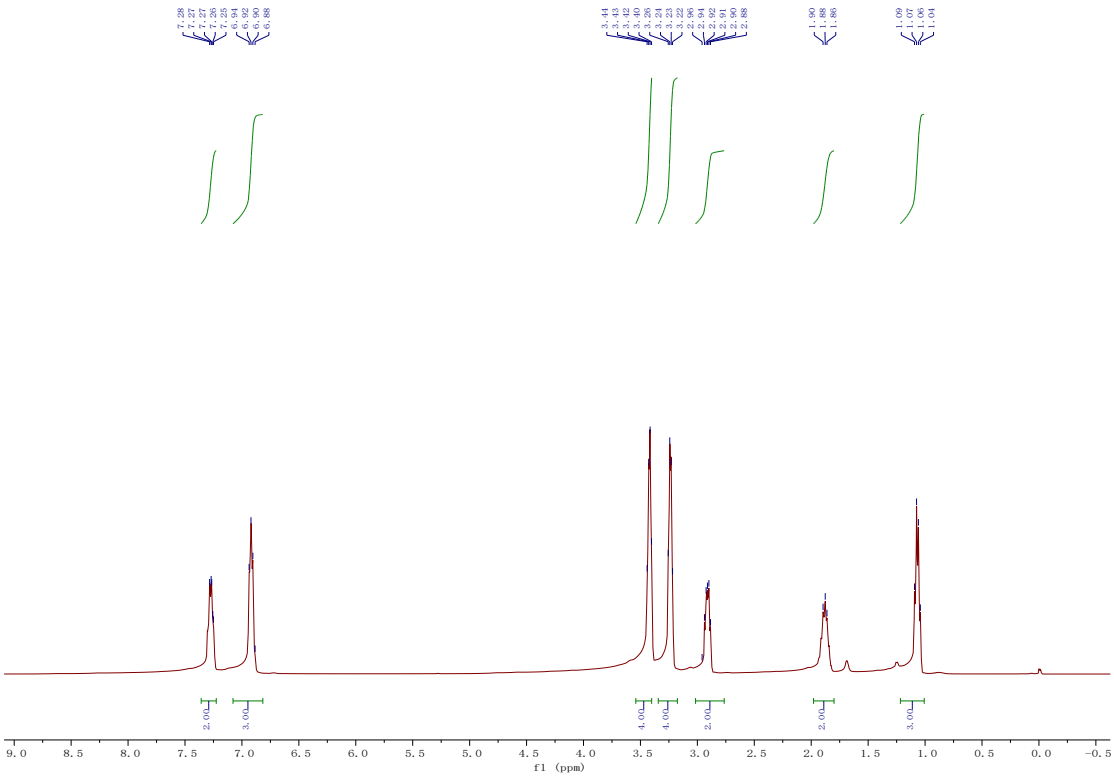
90

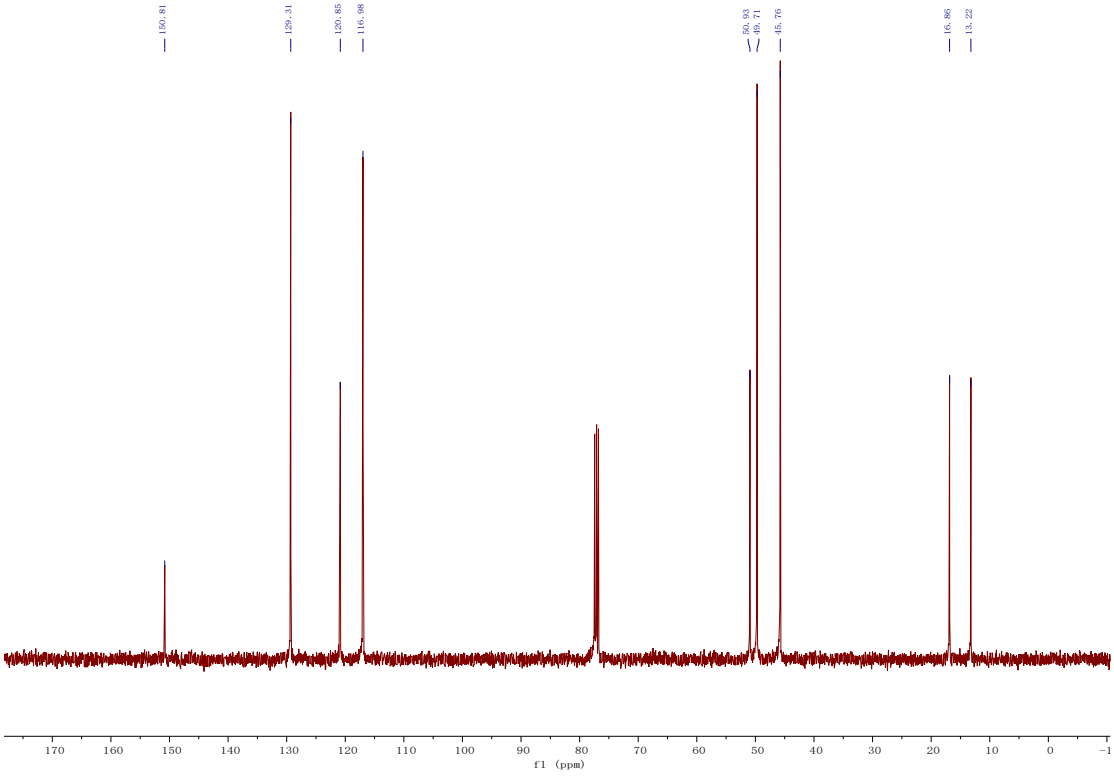


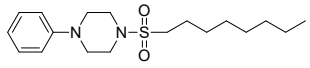




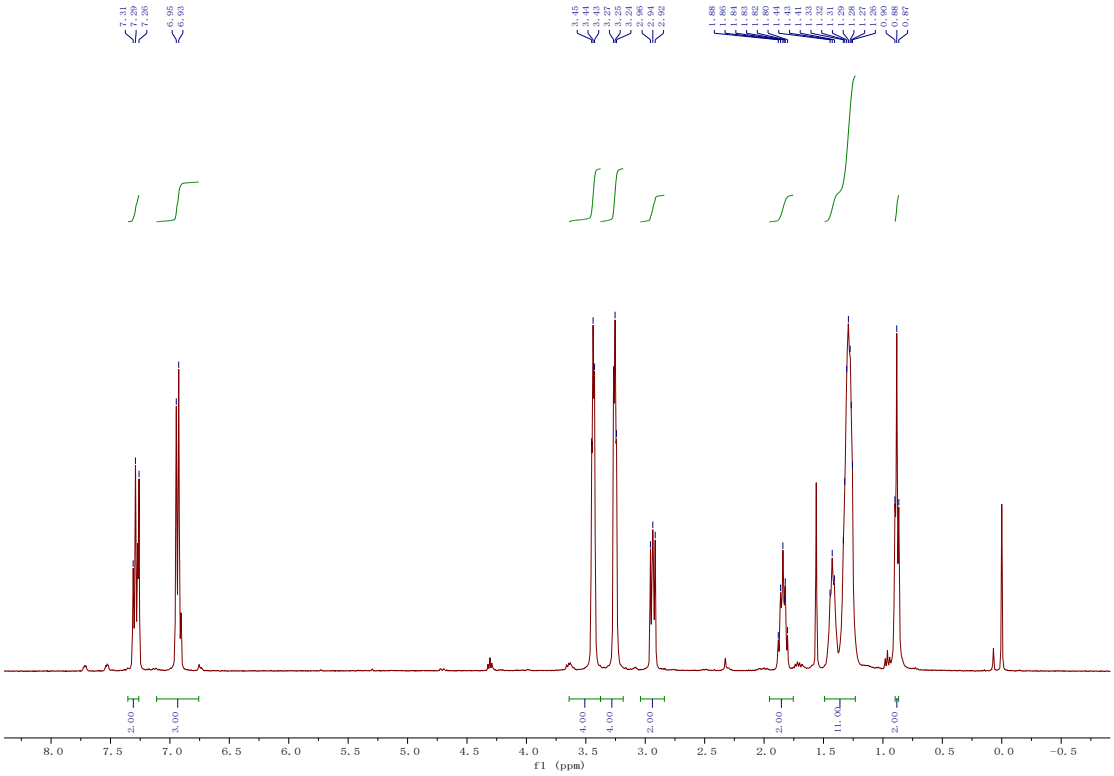
91

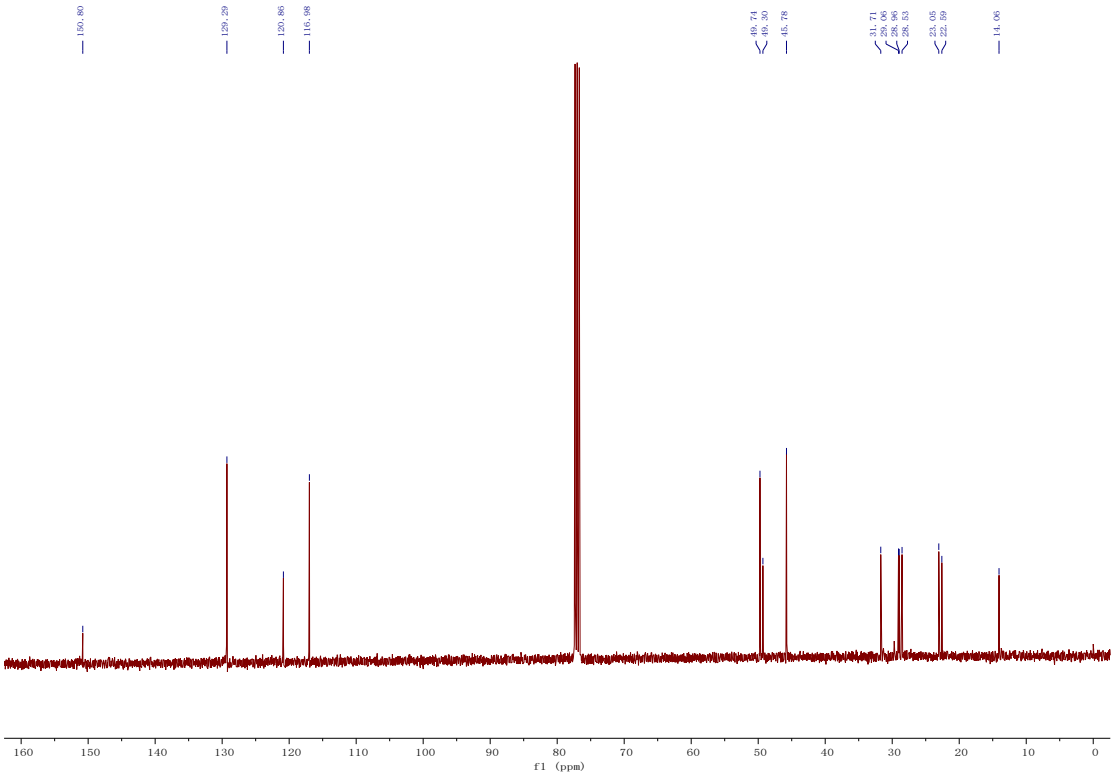

7.28
7.27
7.27
7.26
7.25
6.94
6.92
6.90
6.88
3.44
3.43
3.42
3.40
3.26
3.24
3.23
3.22
2.96
2.94
2.92
2.91
2.90
2.88
1.90
1.88
1.86
1.09
1.07
1.06
1.04
2.00
3.00
4.00
4.00
2.00
2.00
3.00
f1 (ppm)

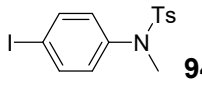

150.81
129.31
120.85
116.98
50.93
49.71
45.76
16.86
13.22
f1 (ppm)



92


7.31
7.29
7.26
6.95
6.93
3.45
3.44
3.43
3.27
3.25
3.24
2.96
2.94
2.92
1.88
1.86
1.84
1.83
1.82
1.80
1.44
1.43
1.41
1.33
1.32
1.31
1.29
1.28
1.27
1.26
0.90
0.88
0.87
2.00
3.00
4.00
4.00
2.00
2.00
11.00
2.00
f1 (ppm)

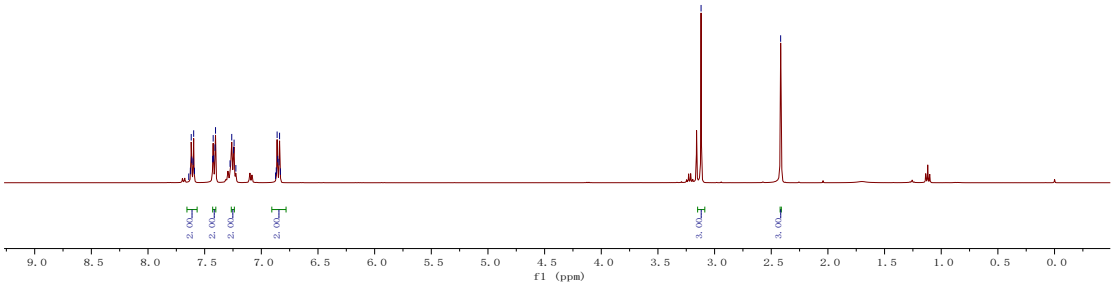

150.80
129.29
120.86
116.98
49.74
49.30
45.78
31.71
29.96
28.96
28.53
23.05
22.99
14.06
f1 (ppm)


Ts
I
N

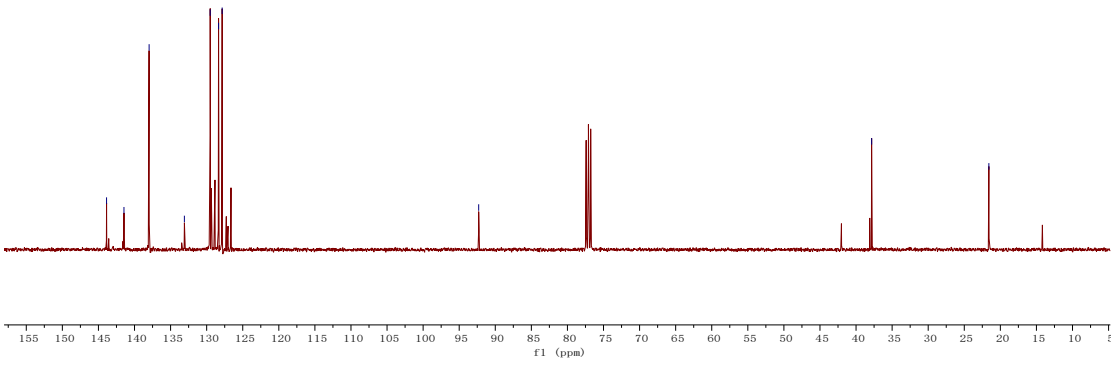
94

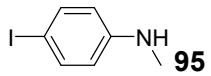

7.64
7.63
7.62
7.61
7.60
7.60
7.59
7.58
7.43
7.42
7.42
7.41
7.40
7.38
7.36
7.24
7.24
7.22
6.87
6.87
6.86
6.86
6.84
6.84
6.83


3.12
2.42

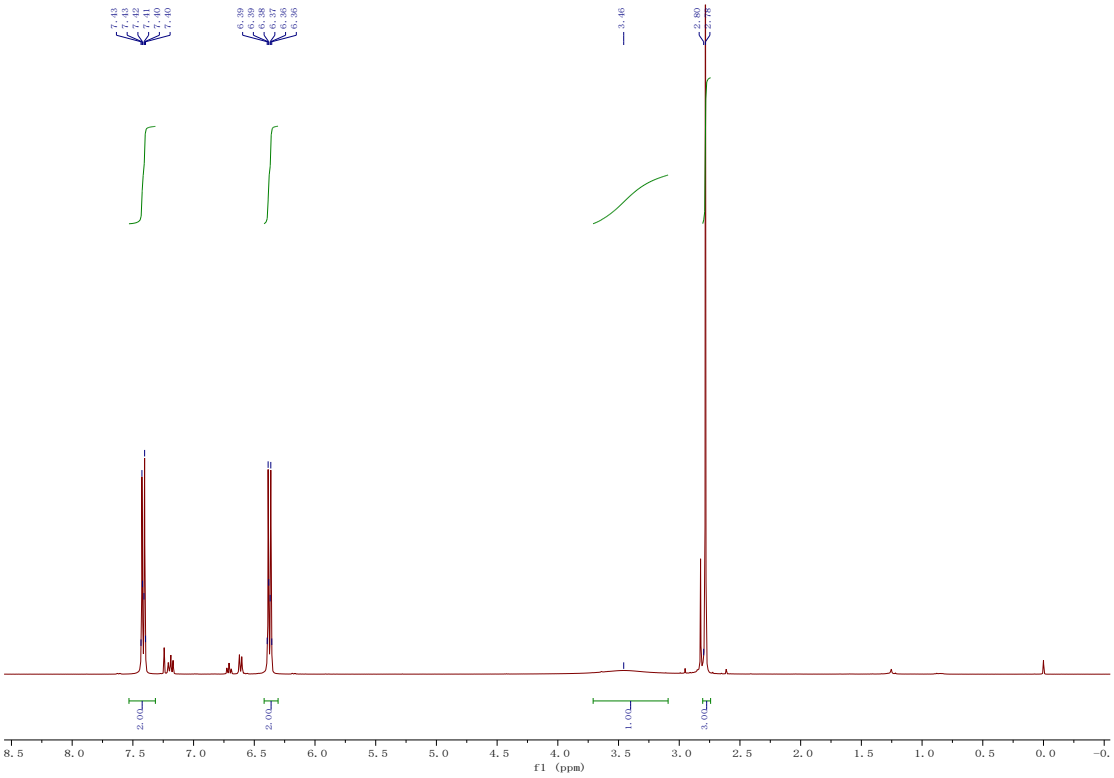

2.00
2.00
2.00
2.00
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

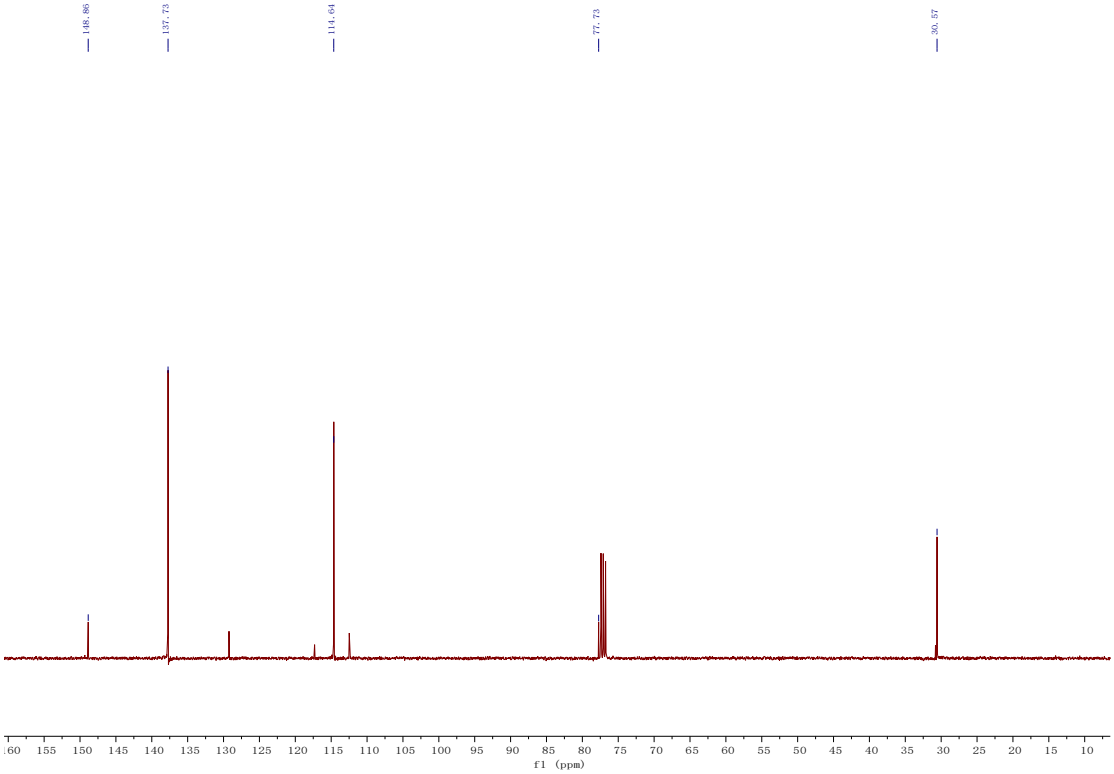

143.88
141.46
137.98
133.09
129.51
128.35
127.88
92.30
37.84
21.59


155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

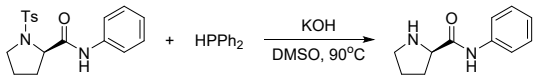

I
NH

95

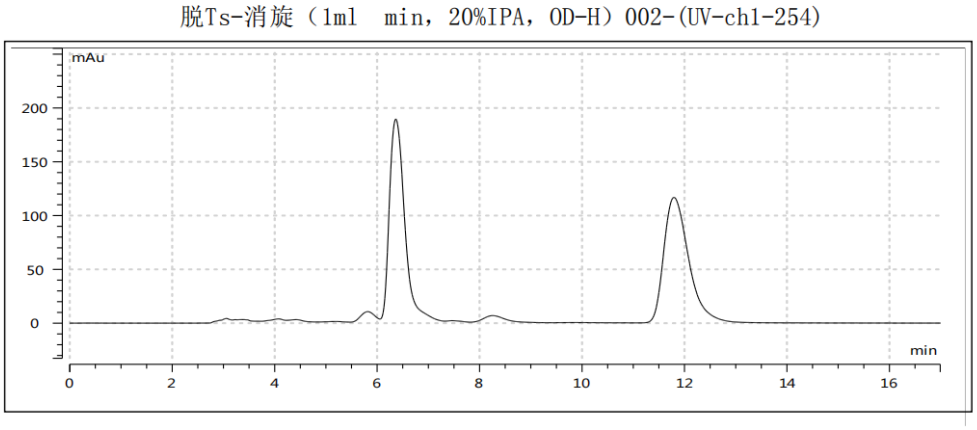

7.43
7.43
7.42
7.41
7.40
7.40
6.39
6.39
6.38
6.37
6.36
6.36
3.46
2.80
2.78
2.00
2.00
1.00
3.00
f1 (ppm)


148.86
137.73
114.64
77.73
30.57
f1 (ppm)

8. Deprotection of N-Ts-L-Proline causes racemization of product.

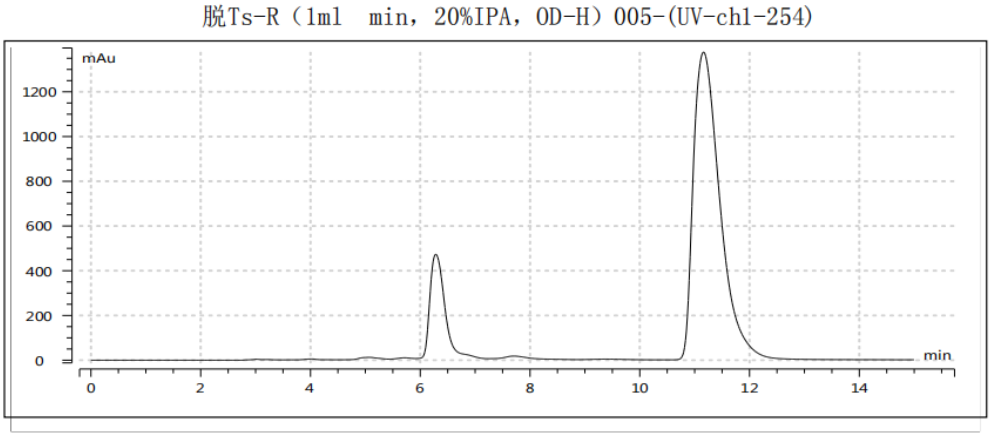


Scheme S1. Deprotection of N-Ts-L-Proline causes racemization of product



峰列表

No	名称	保留时间 (min)	峰面积 (mAu*s)	峰宽 (min)	半峰宽 (min)	峰高 (mAu)	面积百分比 (%)	峰类型
1	N.A.	6.364	3803.60278	0.501	0.310	186.456	49.552	BB
2	N.A.	11.795	3872.33419	0.847	0.507	116.172	50.448	BB
3	总计							



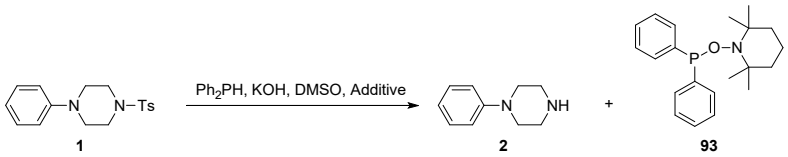
峰列表

No	名称	保留时间 (min)	峰面积 (mAu*s)	峰宽 (min)	半峰宽 (min)	峰高 (mAu)	面积百分比 (%)	峰类型
1	N.A.	6.283	7368.11625	0.434	0.271	443.296	13.690	BB
2	N.A.	11.162	46454.16828	0.839	0.513	1375.966	86.310	BB
3	总计							

Figure S3. Chiral HPLC analysis determines the *ee* value of product.

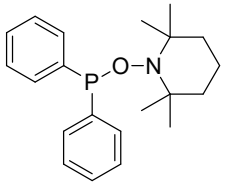
9. Controlled reactions for mechanism study.

Table S1. Controlled reactions for mechanism study.



1 2 93

Entry	Additive	Yield	Compound **93**
1	TEMPO (1.1 eq)	68%	Detected by HRMS
2	TEMPO (4.0 eq)	0%	Detected by HRMS



93

HRMS (ESI) calculated for C11H29NOP+ [M+H]+: 342.1909, found 342.1967.

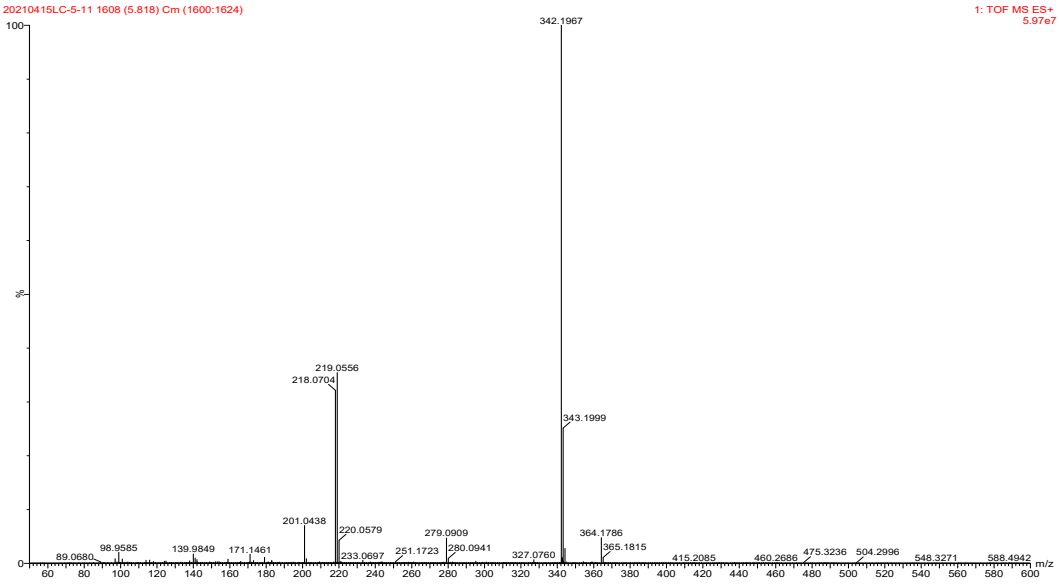


Figure S4. HRMS analysis of TEMPO additive product.