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Efficient Ullmann C-X coupling reaction catalyzed by a recoverable functionalized-chitosan supported copper complex

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1 Experiment

1.1 General

Chitosan powder (MW: 10,000-50,000, deacetylation degree 95%, purchased from Aladdin reagent (Shanghai) Co., Ltd.) was used without further purification. Pyridine-2-carboxaldehyde, 2-hydroxybenzaldehyde and N,N'-carbonyldiimidazole were purchased from Damas-beta, 2-Pyridinecarboxylic acid was purchased from Sinopharm Chemical Reagent Co. Ltd. Aryl halides, imidazole and sulfinate salts were purchased from Alfa Aesar. Melting points were determined on an X4-Data microscopic melting point apparatus and were uncorrected. Nuclear magnetic resonance (NMR) spectra were measured at 400 MHz (^{1}H) or at 100 MHz (^{13}C) with $CDCl_3$ as solvent on a Bruker Avance DRX-400 spectrometer. All reactions were monitored by analytical thin-layer chromatography (TLC) from Merck with detection by UV. The products were purified by column chromatography through silica gel (300-400 mesh). All reagents and solvents were general reagent grade unless otherwise stated.

1.2 Preparation of Functional Chitosan.

The preparation of PCCS. Chitosan (2.0 g, equivalent to 12.4 mmol NH_2 group), pyridine-2-carboxaldehyde (4.72 mL, 49.6 mmol) and acetic acid (10 mL) were added to methanol (75 mL). Then the mixture was refluxed for 12 h at 65 ^{o}C. After the resultant mixture was cooled to 0 ^{o}C, the solid was separated by filtration, washed with ethanol and then dried under vacuum at 50 ^{o}C for 12 h.

The preparation of HBCS. Chitosan (2.0 g, equivalent to 12.4 mmol NH_2 group) and 2-hydroxybenzaldehyde (7.58 g, 62.1 mmol) were added to ethanol (100 mL), meanwhile 10 mL acetic acid was added. The mixture was refluxed for 12 h at 70 ^{o}C, then cooled with ice water to 0 ^{o}C. The solid was separated by filtration, and finally dried under vacuum at 50 ^{o}C for 12 h.

The preparation of PACS. *N,N'*-Carbonyldiimidazole (3.24 g, 20 mmol) and 2-Pyridinecarboxylic acid (1.85 g, 15 mmol) were heated to 60 °C in THF (100 mL) with stirring. After adding chitosan (1.61 g, 10 mmol), the mixture was stirred at 60 °C for 12 h. The product was crystallized by adding ice water and dried under vacuum at 50 ^{o}C for 12 h.

1.3 The preparation of functionalized-chitosan supported copper complex

Three modified chitosan supported copper salt was synthesized according to the following procedure: the catalyst was prepared by suspending modified chitosan in a solution of copper salt for 3 h under neutral conditions at 50 °C (For CuI, the solvent was acetonitrile. For $CuSO_4$ and $Cu(OAc)_2$, water was used as solvent). After adsorption of the copper, the solid was preconditioned by washing thoroughly to remove any loose Cu compounds and dried under vacuum at 50 °C overnight to give the catalyst. After complexation with CuI, $CuSO_4$ and $Cu(OAc)_2$, the colors of thess catalyst are as follows: PCCS@CuI is reddish brown, PCCS@ $CuSO_4$ is green, PCCS@$Cu(OAc)_2$ is green, HBCS@CuI is yellow, HBCS@$CuSO_4$ is yellow, HBCS@$Cu(OAc)_2$ is yellow, PACS@ CuI is green, PACS@$CuSO_4$ is blue, PACS@$Cu(OAc)_2$ is blue.

1.4 General procedure for Ullmann reaction catalyzed by the PCCS@CuI

To a stirred solution of DMSO (3 mL) were added aryl halide (1.0 mmol), nucleophile (1.2 mmol), PCCS@CuI and Cs_2CO_3 (2 mmol) at room temperature. Then the reaction mixture was heated to 110 ^oC under air and stirred for 24 h. After cooling to room temperature, the catalyst PCCS@CuI was separated by centrifugation. The reaction mixture was partitioned by adding the ethyl acetate (20 mL) and water (20 mL). Subsequently, the organic phase was separated and the aqueous phase was extracted with ethyl acetate (20 mL) twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Then the crude product was purified by column chromatography through silica gel, eluting with petroleum ether/ethyl acetate solvent mixture, to give the pure product.

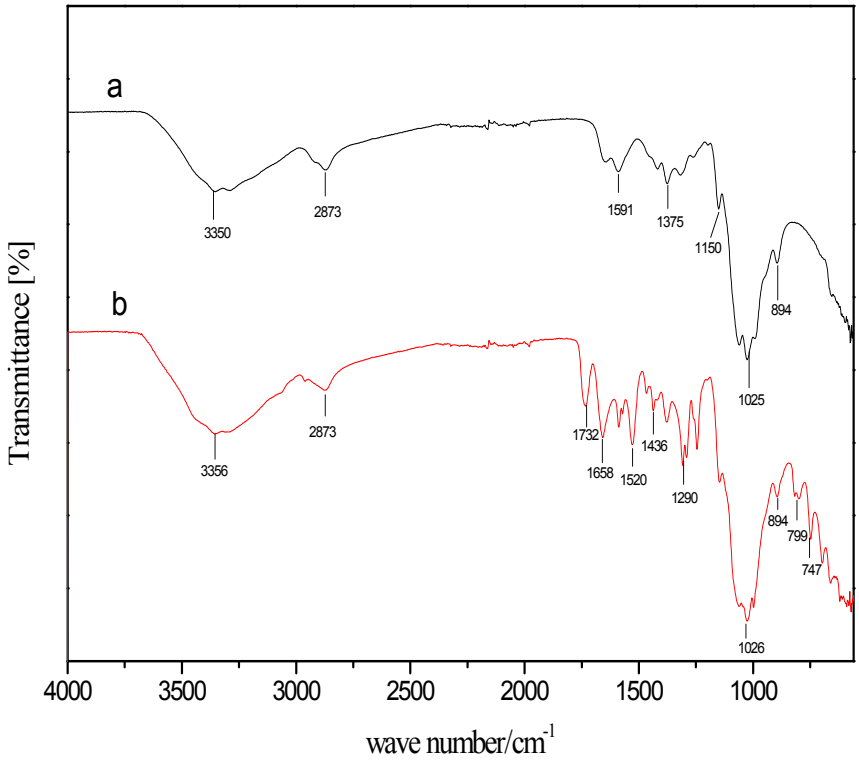


Figure S1. FTIR spectra of (a) CS (b) PACS

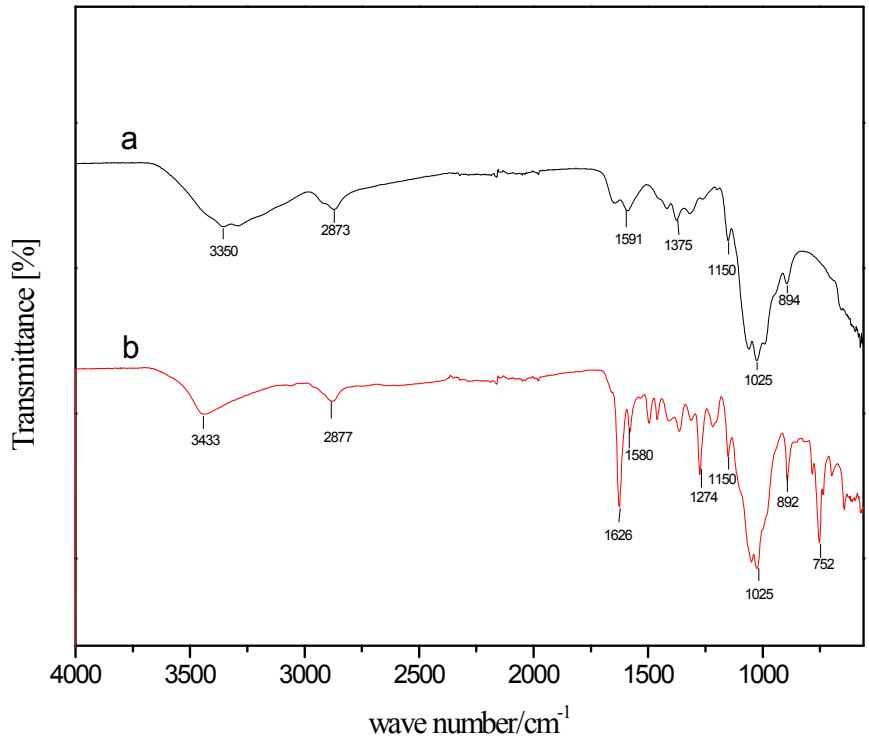


Figure S2. FTIR spectra of (a) CS (b) HBCS

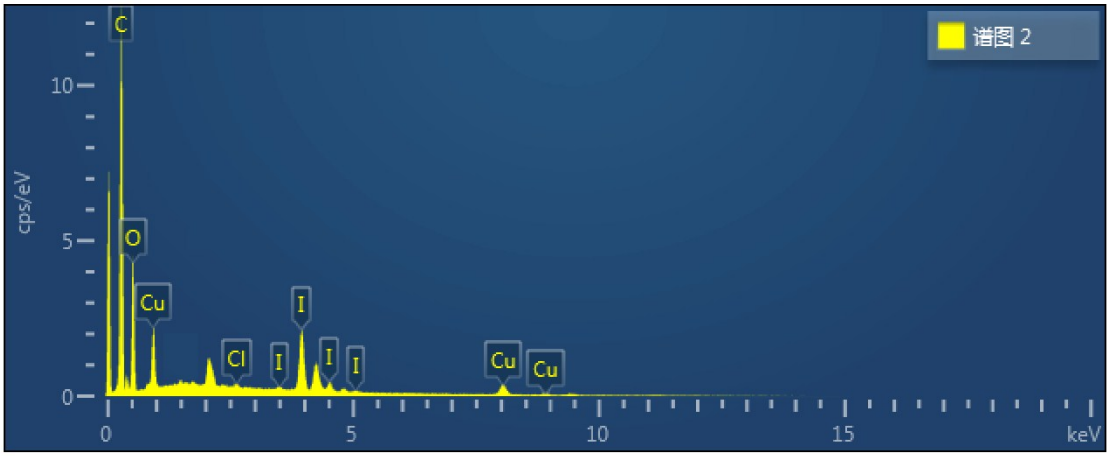


Figure S3. EDS of recovered PCCS@CuI after the fifth run.

2. The spectral data of the products

1-Phenyl-1*H*-imidazole 3a. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.42 – 7.35 (m, 3H), 7.29 (s, 1H), 7.21 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 135.6, 130.4, 129.8, 127.5, 121.5, 118.2. MS (EI): *m/z* = 144 $[M]^+$.

1-(4-Methoxyphenyl)-1*H*-imidazole 3b. Pale yellow solid, m.p.: 60-61 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.30 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 6.6 Hz, 2H), 6.99 (d, J = 12.0 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 135.8, 130.7, 129.9, 123.3, 118.8, 114.9, 55.6. MS (EI): m/z = 174 $[M]^+$.

1-(p-tolyl)-*1H*-imidazole 3c. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.24 (d, J = 8.0 Hz, 5H), 7.17 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 135.6, 135.0, 130.4, 130.2, 121.4, 118.4, 20.9.

1-(4-Ethoxyphenyl)-*1H*-imidazole 3d. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.30 – 7.20 (m, 2H), 7.16 (d, *J* = 9.0 Hz, 2H), 7.00 – 6.84 (m, 2H), 4.03 (qd, *J* = 6.8, 2.6 Hz, 2H), 1.41 (td, *J* = 7.0, 2.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.3, 135.9, 130.6, 130.0, 123.2, 118.8, 115.4, 63.9, 14.8.

1-(2-methoxyphenyl)-*1H*-imidazole 3e. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.36 – 7.27 (m, 1H), 7.27 – 7.20 (m, 1H), 7.15 (d, J = 15.4 Hz, 2H), 7.01 (dd, J = 13.4, 7.6 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 137.8, 128.9, 128.7, 126.5, 125.5, 121.0, 120.3, 112.4, 55.8.

1-(o-tolyl)-*1H*-imidazole 3f. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.34 (t, J = 8.0 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.23 – 7.19 (m, 2H), 7.05 (t, J = 1.0 Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.5, 136.7, 133.9, 131.3, 129.3, 128.8, 126.9, 126.6, 120.5, 17.6.

1-(4-(Trifluoromethoxy)phenyl)-1*H*-imidazole 3g. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.44 (d, J = 12.0 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 7.27 (s, 1H), 7.22 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1 (J = 1 Hz), 135.7 (J = 27 Hz), 130.8, 122.9, 122.6, 121.7, 119.1, 118.3. MS (EI): m/z = 228 [M]+. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.85.

1-(4-Fluorophenyl)-1*H*-imidazole 3h. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 15.0 Hz, 1H), 7.42 – 7.32 (m, 2H), 7.26 – 7.11 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 160.5, 134.8 (*J* = 194.4 Hz), 130.4, 123.5 (J = 8.5 Hz), 118.6, 116.8 (J = 23.0 Hz). MS (EI): m/z =

162 $[M]^+$.^{19}F NMR (376 MHz, $CDCl_3$) δ -58.08.

1-(4-Chlorophenyl)-1*H*-imidazole 3i. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.52 – 7.42 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.27 (s, 1H), 7.21 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 135.5, 133.2, 130.7, 130.0, 122.7, 118.2. MS (EI): *m/z* = 178 $[M]^+$.

1-(4-Nitrophenyl)-1*H*-imidazole 3j. Yellow solid. m.p.: 208-209 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 8.0 Hz, 2H), 8.01 (s, 1H), 7.60 (d, J = 12.0 Hz, 2H), 7.41 (s, 1H), 7.29 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.3, 142.0, 135.4, 131.8, 125.8, 121.1, 117.7. MS (EI): *m/z* = 189 $[M]^+$.

1-(4-(*1H*-Imidazol-1-yl)phenyl)ethanone 3k. White solid. m.p.: 112-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, J = 8.6, 2.2 Hz, 2H), 7.99 (s, 1H), 7.53 – 7.50 (m, 2H), 7.38 (s, 1H), 7.27 (s, 1H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 140.7, 135.9, 135.4, 131.1, 130.3, 120.8, 117.8, 26.6. MS (EI): *m/z* = 186 $[M]^+$.

1-(4-Methoxyphenyl)pyrrolidine 3l. Yellow solid. m.p.: 45-46 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (d, J = 8.0 Hz, 2H), 6.45 (d, J = 8.0 Hz, 2H), 3.67 (s, 3H), 3.14 (t, J = 6.4 Hz, 4H), 1.99 – 1.79 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 142.2, 114.0, 111.6, 54.9, 47.2, 24.4. MS (EI): *m/z* = 177 $[M]^+$.

***N*-butyl-4-methoxyaniline 3m**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.81 – 6.76 (m, 2H), 6.61 – 6.57 (m, 2H), 3.75 (s, 3H), 3.08 – 3.05 (m, 2H), 1.60 (dt, J = 20.0, 7.2 Hz, 2H), 1.43 (dt, J = 14.8, 7.4 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.0, 142.8, 114.9, 114.1, 55.9, 44.8, 31.8, 20.3, 13.9.

***N*-(4-methoxyphenyl)-2-pyrrolidinone 3n.** White solid. m.p.: 111-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 9.0 Hz, 2H), 6.91 (d, J = 9.0 Hz, 2H), 3.98 – 3.63 (m, 5H), 2.60 (t, J = 12.4 Hz, 2H), 2.24 – 2.09 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 156.6, 132.7, 121.8, 114.1, 55.5, 49.2, 32.5, 18.0. MS (EI): *m/z* = 191 $[M]^+$.

1-(4-Methoxyphenyl)-1*H*-benz[d]imidazole 3o. Yellow solid, m.p.: 96-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.87 – 7.73 (m, 1H), 7.43 – 7.36 (m, 1H), 7.33 (d, J = 8.8 Hz, 2H), 7.24 (p, J = 7.2 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 143.8, 142.6, 134.3, 129.2, 125.8, 123.6, 122.6, 120.5, 115.1, 110.4, 55.7. MS (EI): *m/z* = 224 $[M]^+$.

1-(4-methoxyphenyl)-4-methyl-1*H*-imidazole 3p. White solid, m.p.: 79-80 °C. ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.19 (d, J = 8.4 Hz, 2H), 6.94 – 6.80 (m, 3H), 3.76 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 138.7, 135.5, 130.4, 123.0, 115.7, 114.9, 55.6, 13.7.MS (EI): *m/z* = 188 $[M]^+$.

1-(4-methoxyphenyl)-5-nitro-1*H*-indole 3q. White solid ^1H NMR (600 MHz, $CDCl_3$) δ 8.64 (d, J = 2.2 Hz, 1H), 8.09 (dd, J = 9.0, 2.2 Hz, 1H), 7.43 – 7.37 (m, 4H), 7.10 – 7.04 (m, 2H), 6.82 (dd, J = 3.2, 0.4 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.1, 142.1, 139.2, 131.7, 131.5, 128.1, 126.3, 118.3, 117.8, 115.0, 110.4, 105.1, 55.7.

Diphenyl sulphone 5a. White solid, m.p.: 123-124 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.6 Hz, 4H), 7.58 (t, J = 7.4 Hz, 2H), 7.52 (t, J = 7.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 133.2, 129.3, 127.7. MS (EI): m/z = 218 $[M]^+$.

4-Methoxyphenyl phenyl sulfone 5b. White solid, m.p.: 91-92 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 14.2, 7.6 Hz, 4H), 7.44 (dd, J = 14.8, 7.0 Hz, 3H), 6.89 (d, J = 7.6 Hz, 2H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 141.4, 132.1, 131.8, 128.9, 128.2, 126.3, 113.5, 54.6. MS (EI): m/z = 248 $[M]^+$.

Phenyltolyl sulfone 5c. White solid, m.p.: 125-126 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 7.0 Hz, 1H), 7.43 (d, J = 7.6 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 140.9, 137.6, 131.9, 128.9, 128.2, 126.7, 126.5, 20.6. MS (EI): m/z = 232 $[M]^+$.

1-methoxy-2-(phenylsulfonyl)benzene 5d. White solid, m.p.: 74-76 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, J = 7.8, 1.2 Hz, 1H), 7.93 – 7.86 (m, 2H), 7.59 (ddd, J = 6.6, 3.8, 1.2 Hz, 1H), 7.55 – 7.48 (m, 3H), 7.42 (t, J = 7.4 Hz, 1H), 7.26 (d, J = 7.6 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 138.9, 138.0, 133.6, 132.9, 132.7, 129.5, 129.0, 127.7, 126.5, 20.2. MS (EI): m/z = 156 $[M]^+$.

1-(Phenylsulfonyl)-4-(trifluoromethyl)benzene 5e. White solid, m.p.: 91-92 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.2 Hz, 2H), 8.04 – 7.94 (m, 2H), 7.79 (d, J = 8.2 Hz, 2H), 7.69 – 7.60 (m, 1H), 7.56 (dd, J = 10.4, 4.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 140.6, 134.6 (J = 160 Hz), 129.6, 128.2, 127.9, 126.5 (J = 8.5 Hz), 124.5, 121.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.21. MS (EI): m/z = 286 $[M]^+$.

4-Chlorophenyl phenyl sulfone 5f. White solid, m.p.: 93-95 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.4 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 7.2 Hz, 1H), 7.55 – 7.44 (m, 4H).

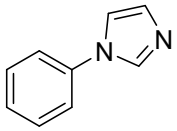
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 140.1, 139.9, 133.5, 129.6, 129.4, 129.1, 127.6. MS (EI): m/z = 252 $[M]^+$.

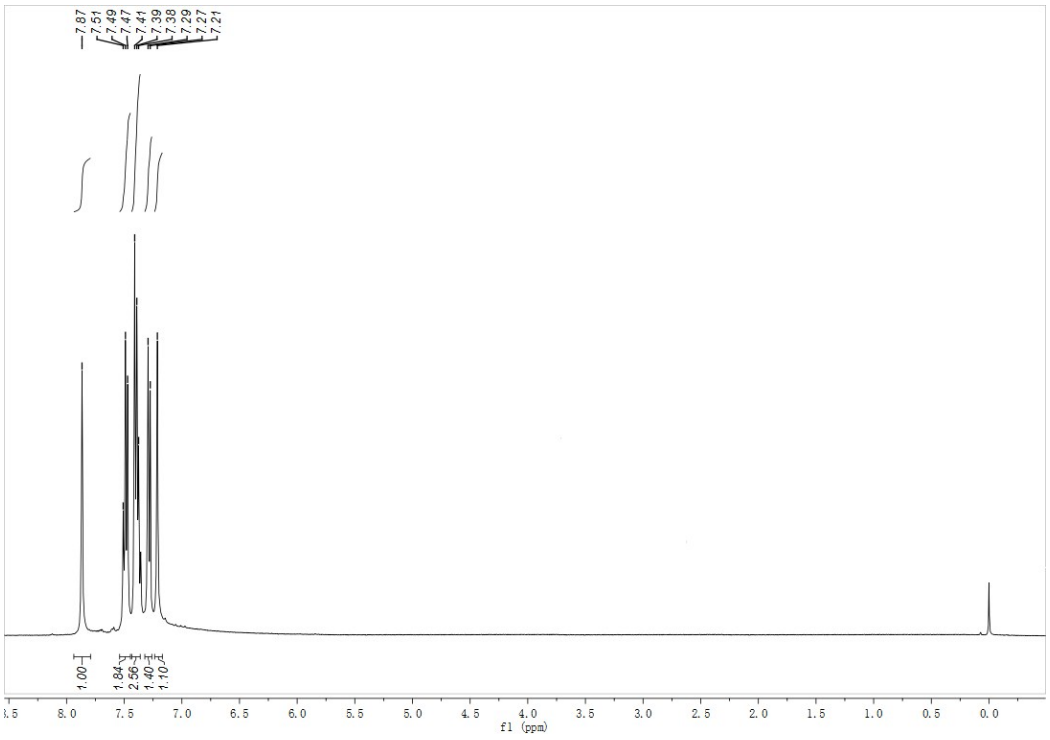
4-Nitrophenyl phenyl sulfone 5g. Yellow solid, m.p.: 141-143 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.8 Hz, 2H), 8.14 (d, J = 8.8 Hz, 2H), 7.98 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 147.4, 140.0, 134.2, 129.7, 128.9, 128.0, 124.5. MS (EI): m/z = 263 $[M]^+$.

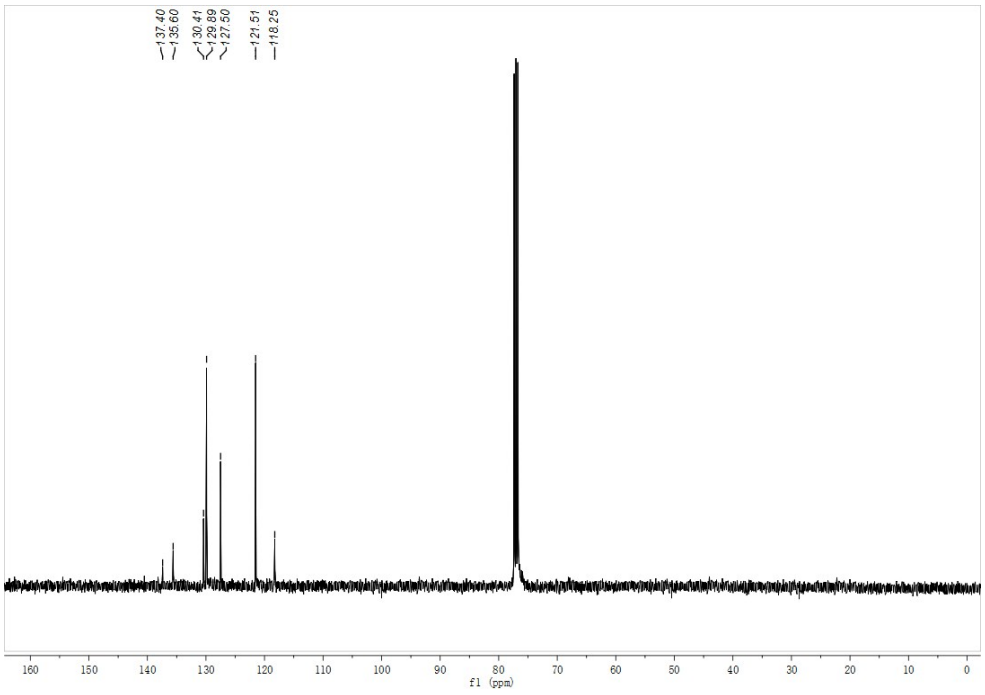
3-Nitro-(phenylsulfonyl)benzene 5h. Yellow solid, m.p.: 78-80 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.35 (d, J = 8.2 Hz, 1H), 8.22 (d, J = 7.6 Hz, 1H), 7.93 (d, J = 7.4 Hz, 2H), 7.67 (t, J = 8.0 Hz, 1H), 7.58 (t, J = 7.4 Hz, 1H), 7.49 (dd, J = 15.2, 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 142.9, 139.1, 133.1, 132.1, 129.7, 128.7, 126.9, 126.7, 121.9. MS (EI): m/z = 263 $[M]^+$.

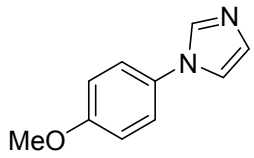
4-Acetylphenyl phenyl sulfone 5i. White solid, m.p.: 130-131 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.03 (m, 4H), 8.01 – 7.94 (m, 2H), 7.62 (dd, J = 8.0, 6.4 Hz, 1H), 7.55 (t, J = 7.6 Hz, 2H), 2.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 145.4, 140.8, 140.4, 133.7, 129.5, 129.1, 127.9, 127.8, 26.9. MS (EI): m/z = 260 $[M]^+$.

3. NMR spectra of products





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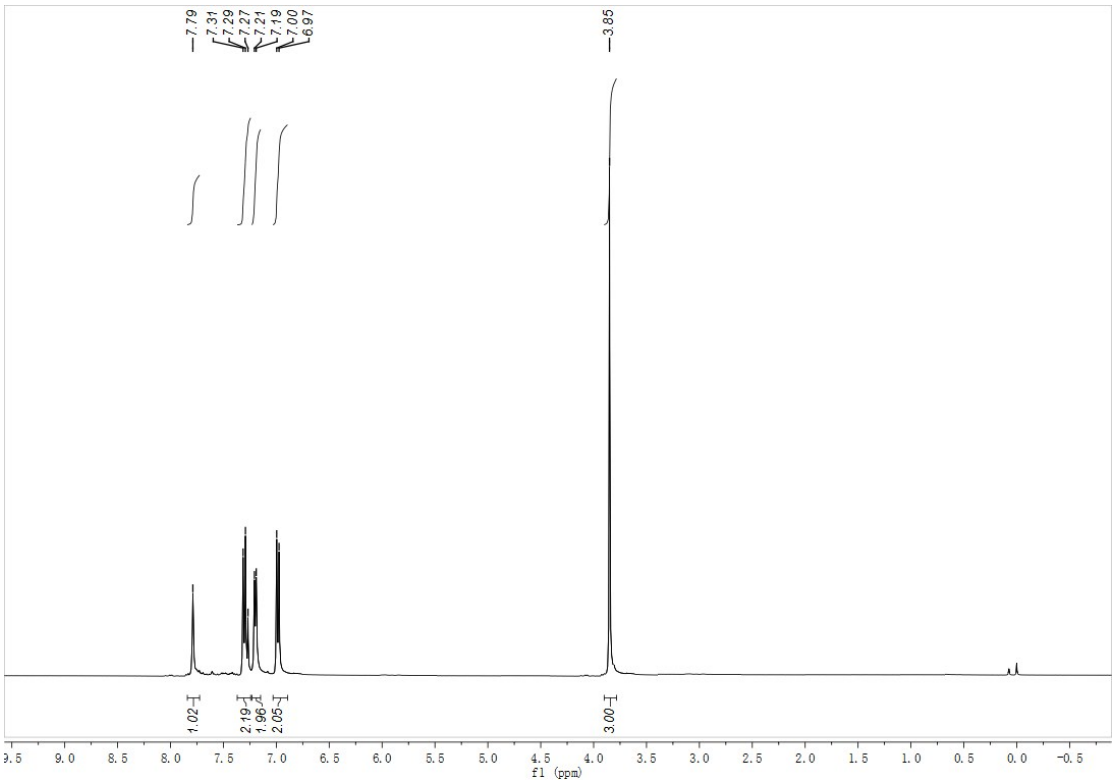
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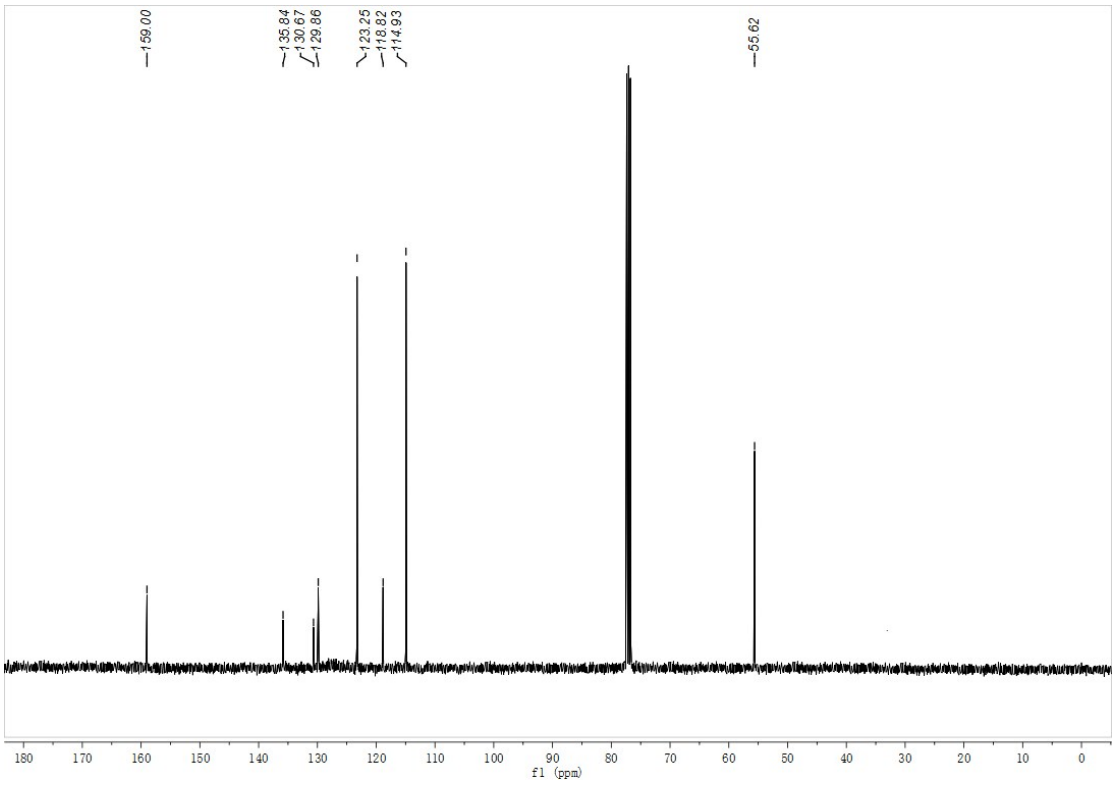
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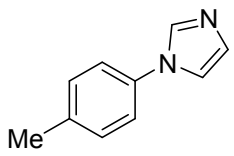
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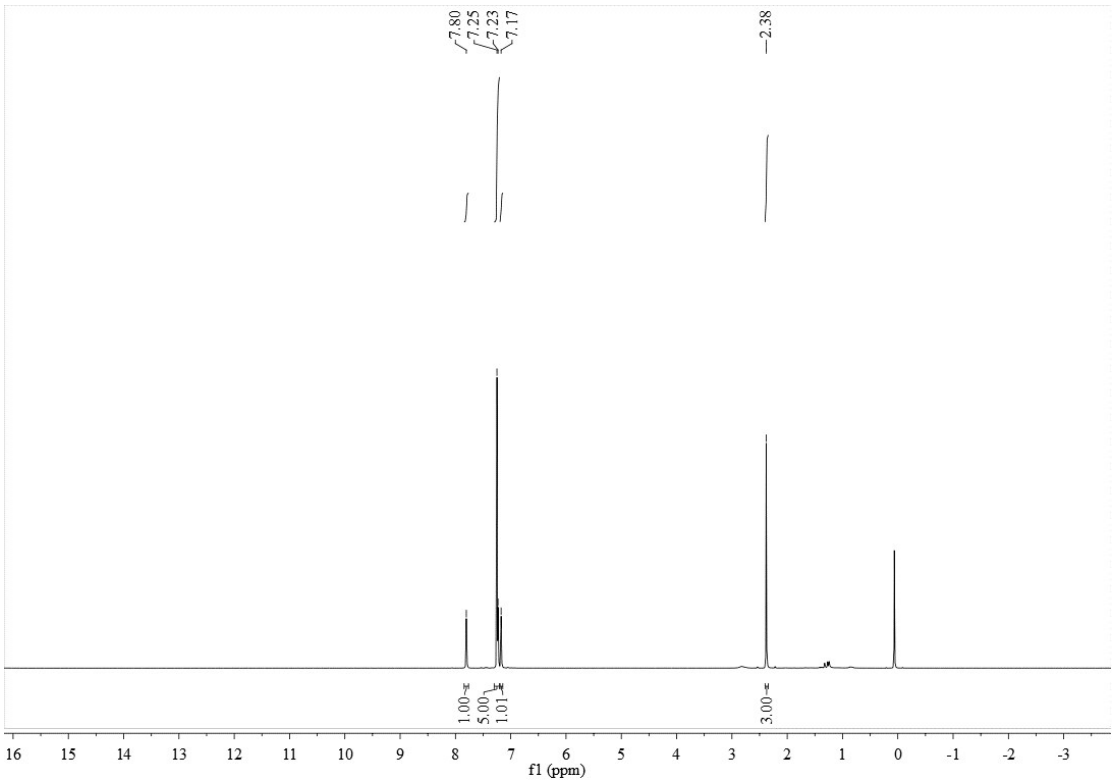
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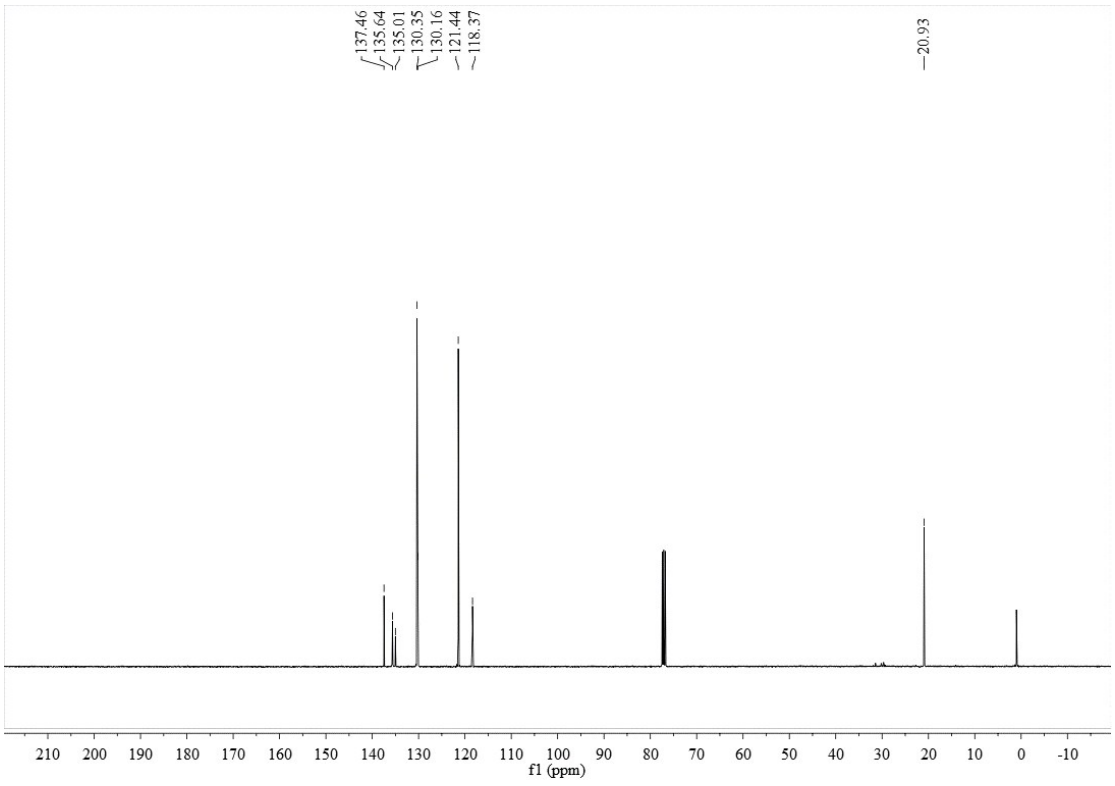
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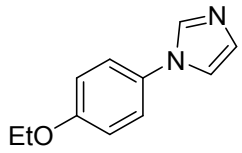
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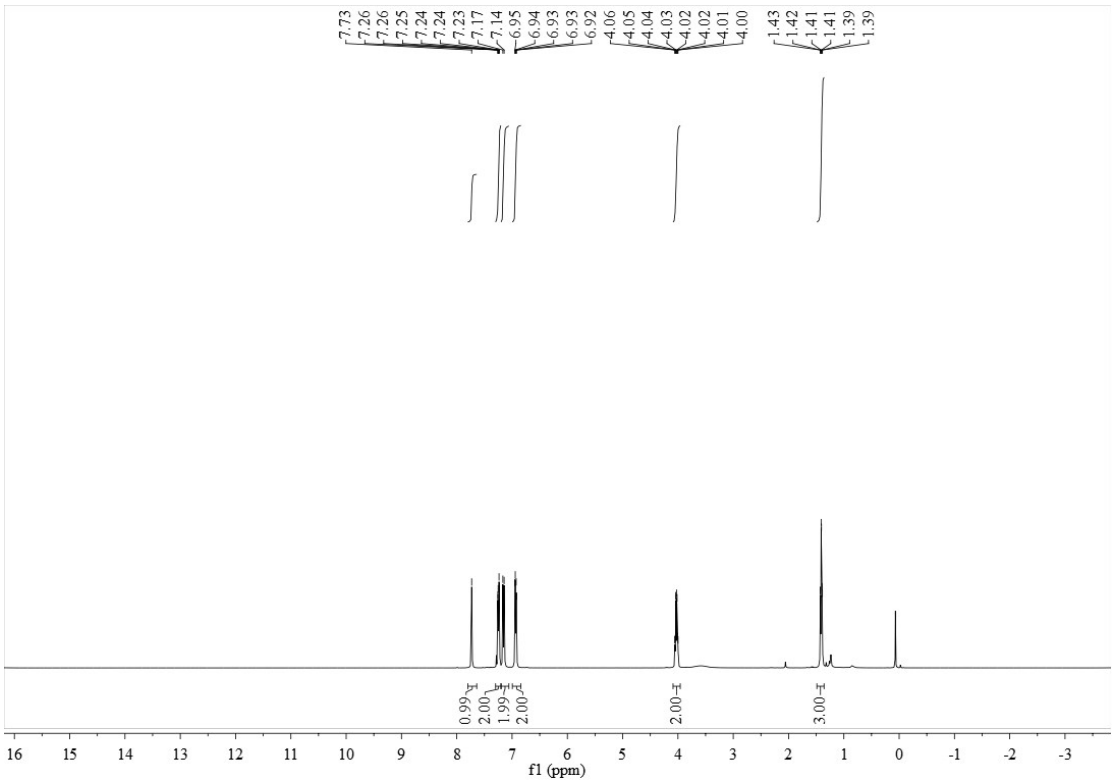
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6.95
6.94
6.93
6.93
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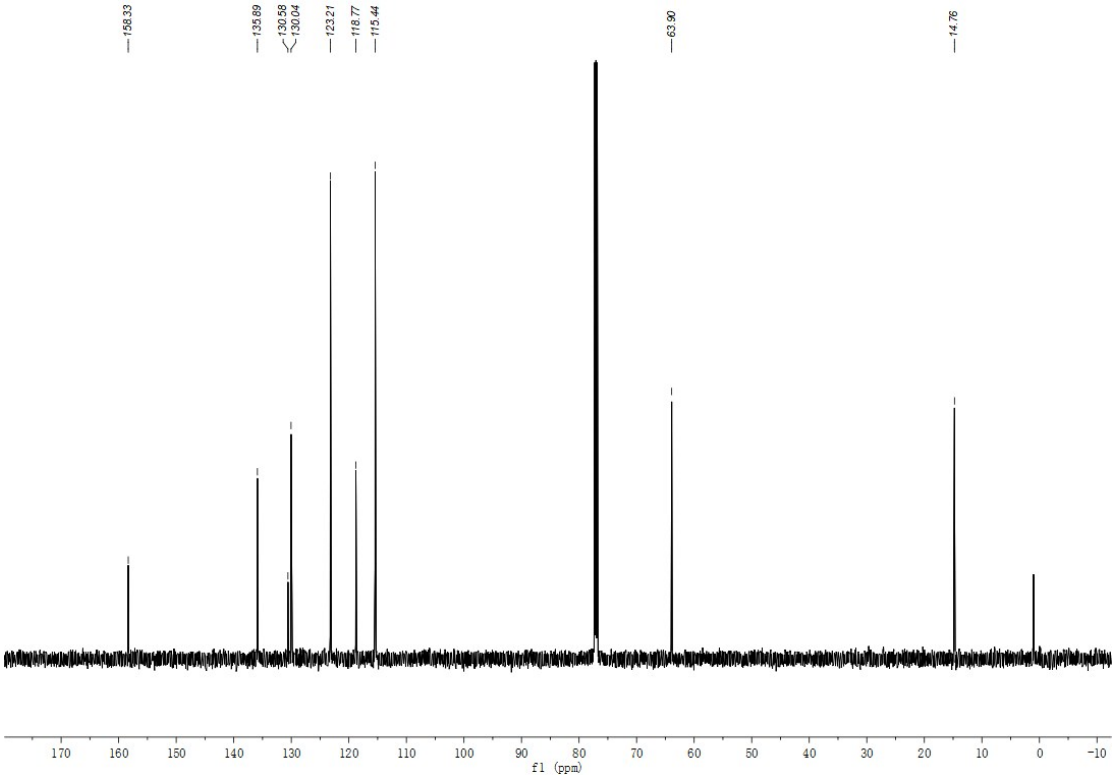
4.06
4.05
4.04
4.03
4.02
4.02
4.01
4.00
1.43
1.42
1.41
1.41
1.39
1.39
0.99
2.00
1.99
2.00
2.00
3.00
f1 (ppm)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130.04
123.21
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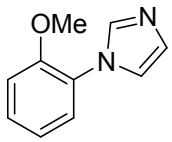
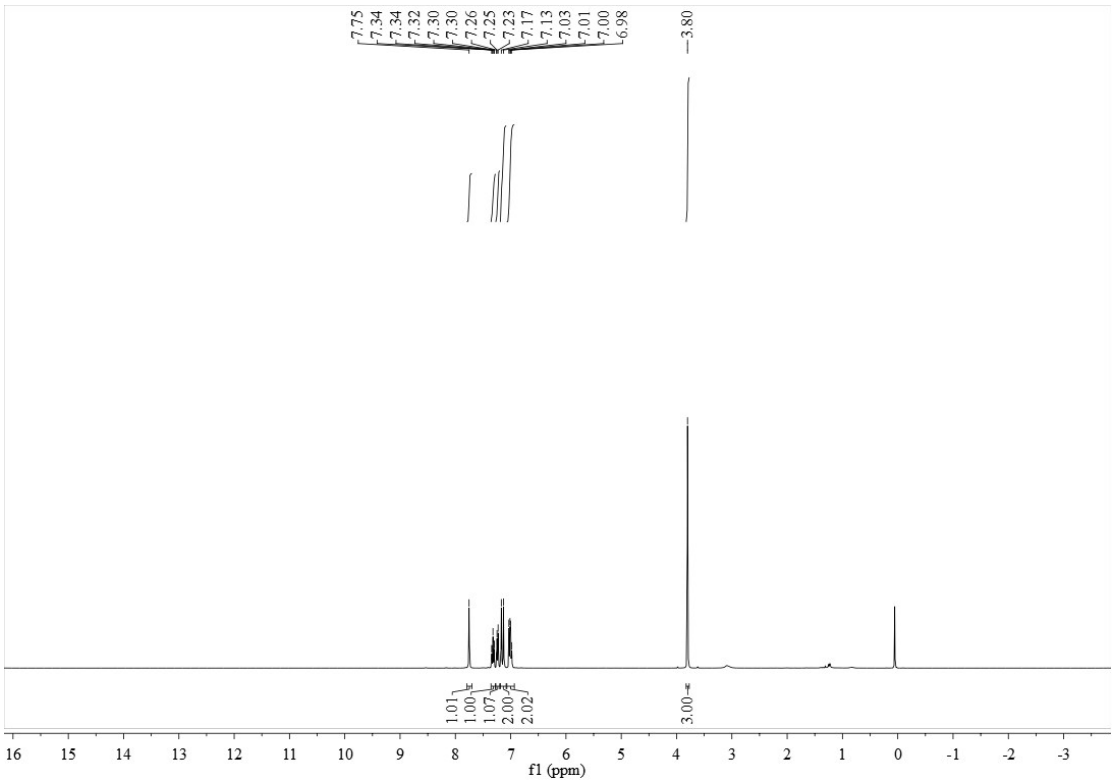
115.44
63.90
14.76
f1 (ppm)


OMe
N
N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7.26
7.25
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7.17
7.13
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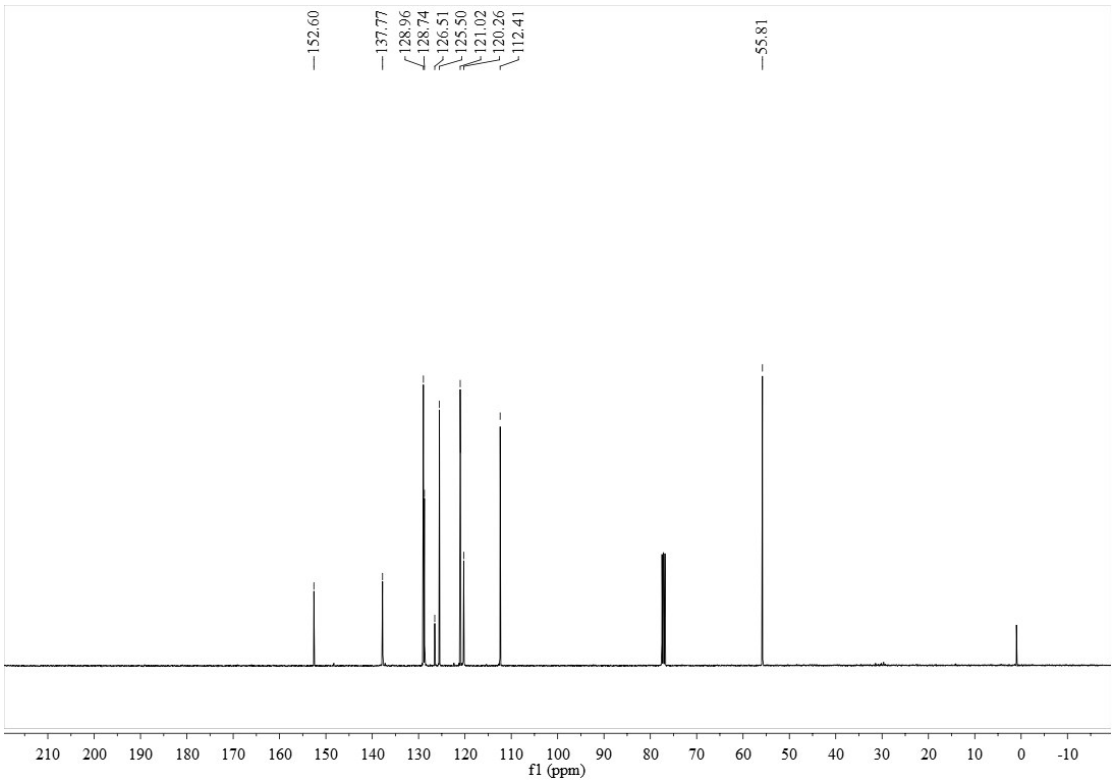
3.80
1.01
1.00
1.07
2.00
2.02
3.00
f1 (ppm)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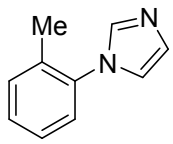
125.50
121.02
120.26
112.41
55.81
f1 (ppm)


Me
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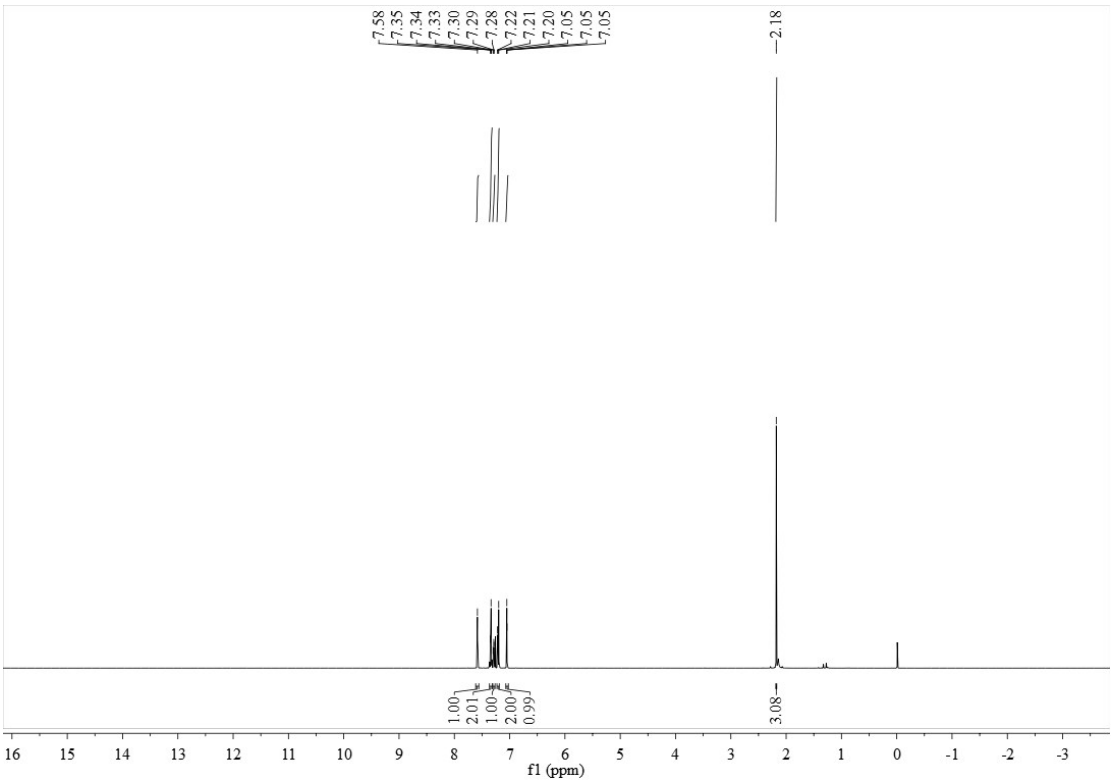
N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7.29
7.28
7.22
7.21
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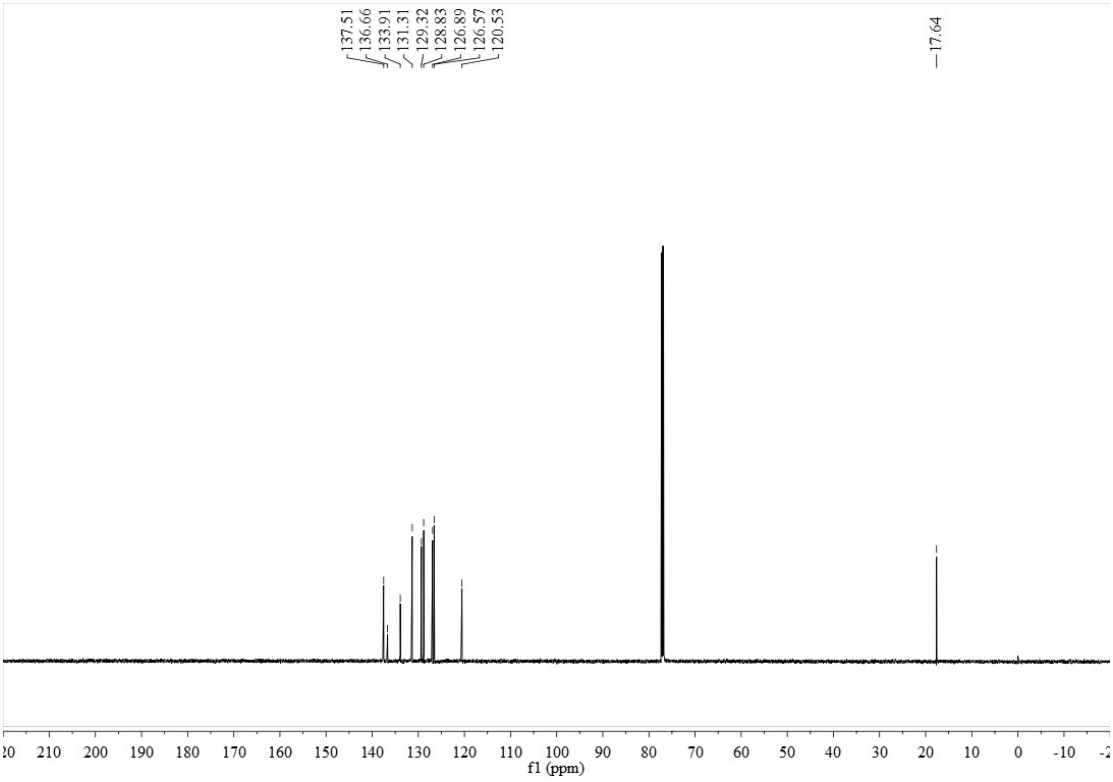
7.05
7.05
7.05
2.18
1.00
2.01
1.00
2.00
0.99
3.08
f1 (ppm)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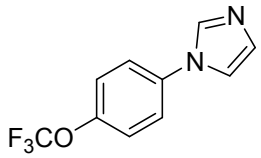
129.32
128.83
126.89
126.57
120.53
17.64
f1 (ppm)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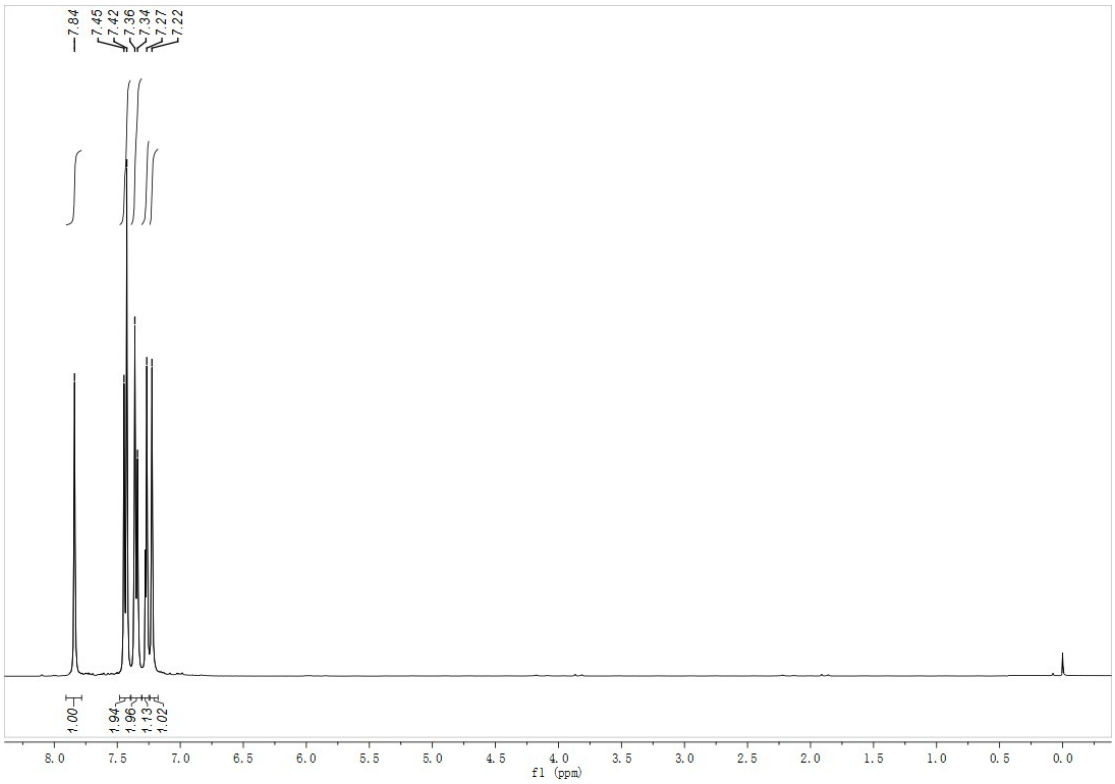
N
F3CO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7.22
1.00
1.94
1.96
1.13
1.02
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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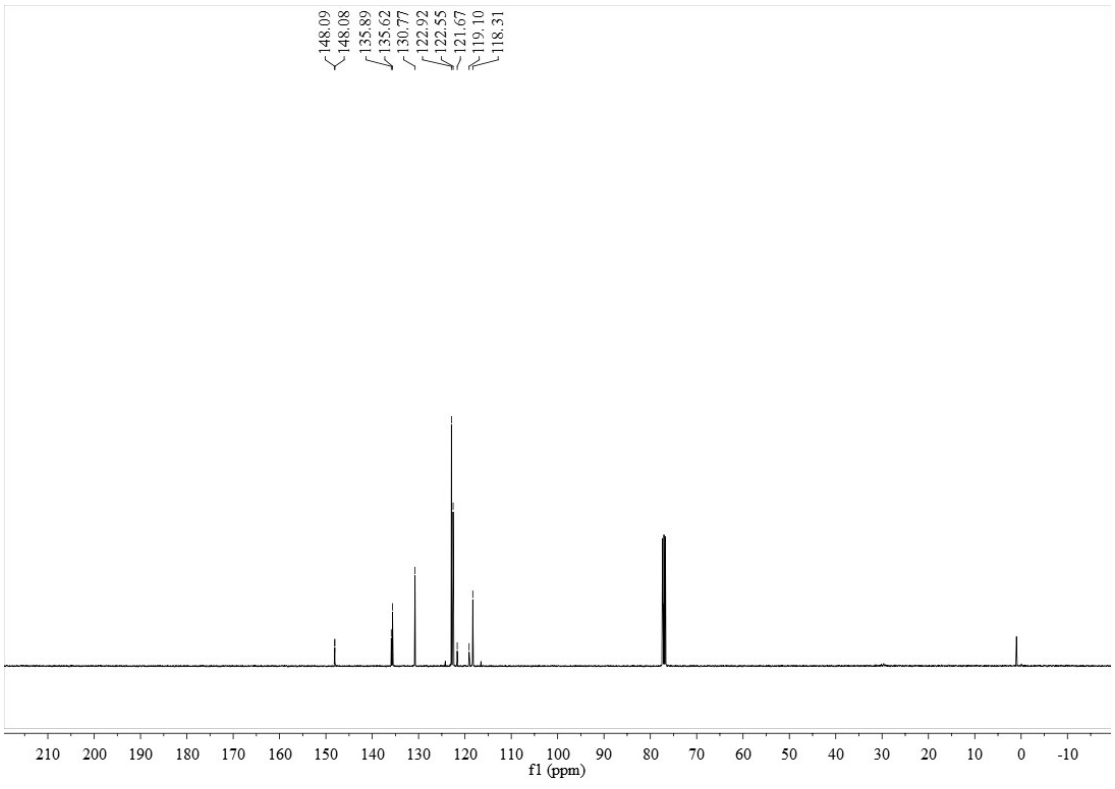
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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148.08
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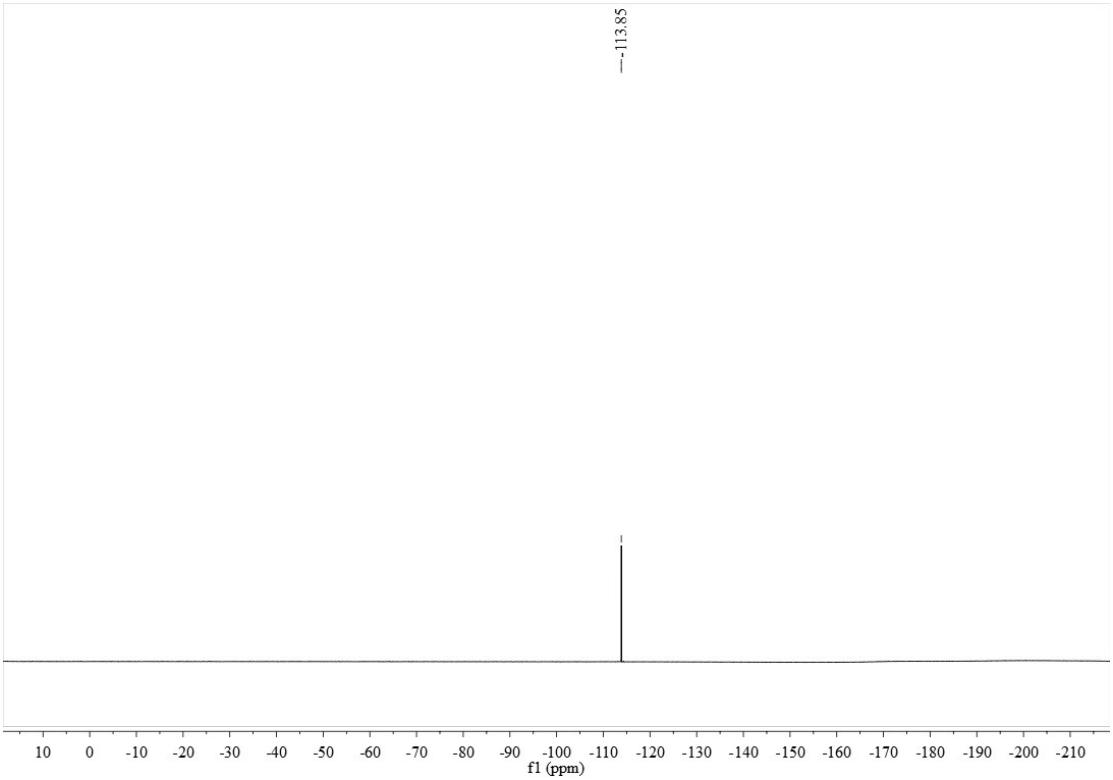
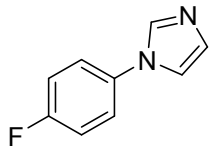
122.92
122.55
121.67
119.10
118.31
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-113.85
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)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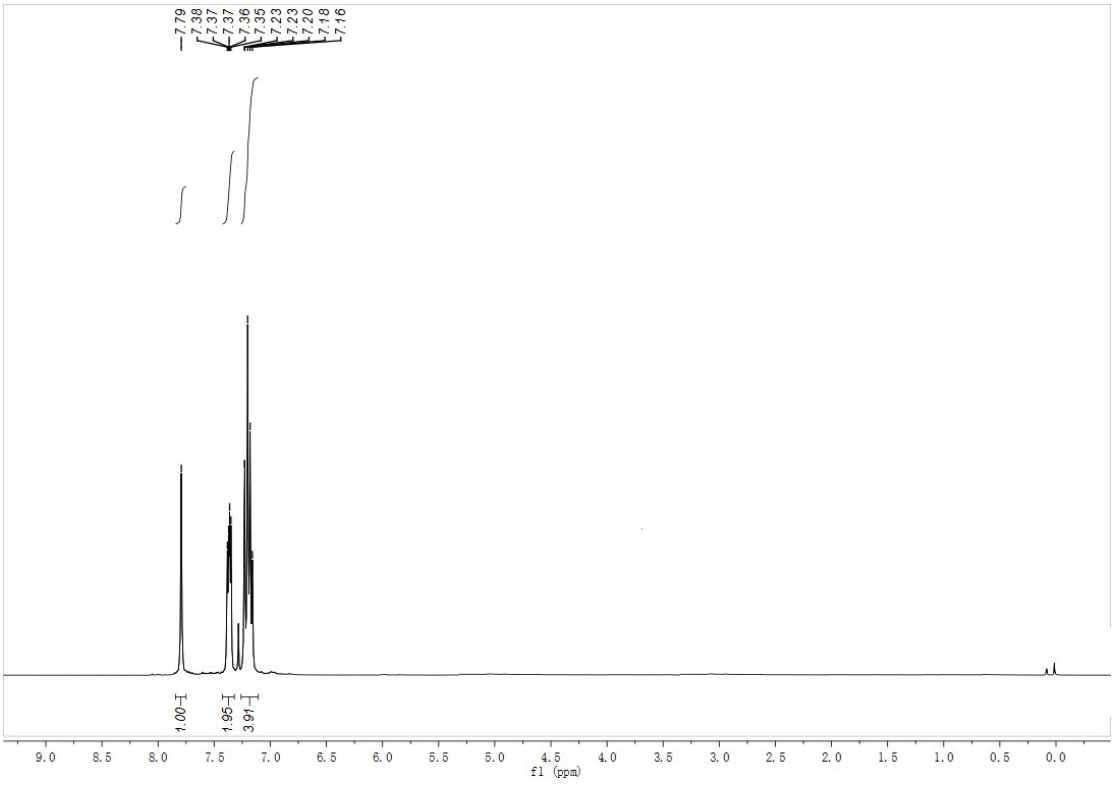
N
F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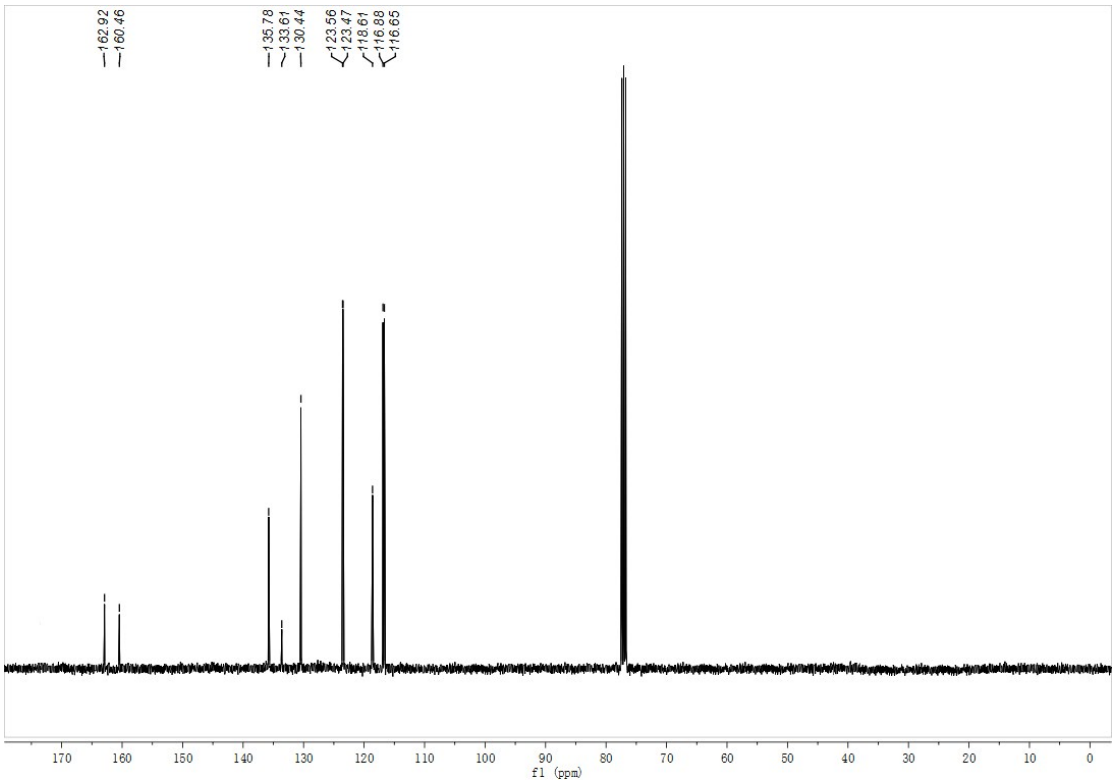
7.35
7.23
7.23
7.20
7.18
7.16
1.00
1.95
3.91
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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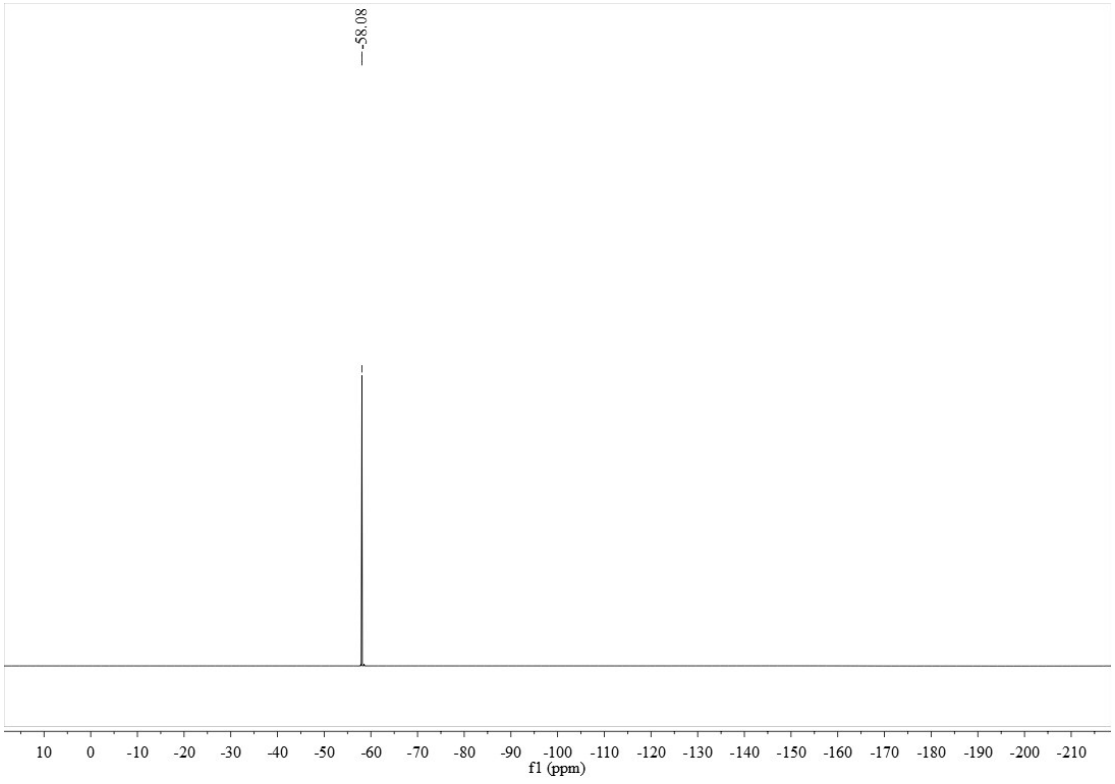
160.46
135.78
133.61
130.44
123.56
123.47
118.61
116.88
116.65
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-58.08
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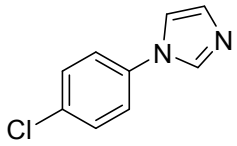
f1 (ppm)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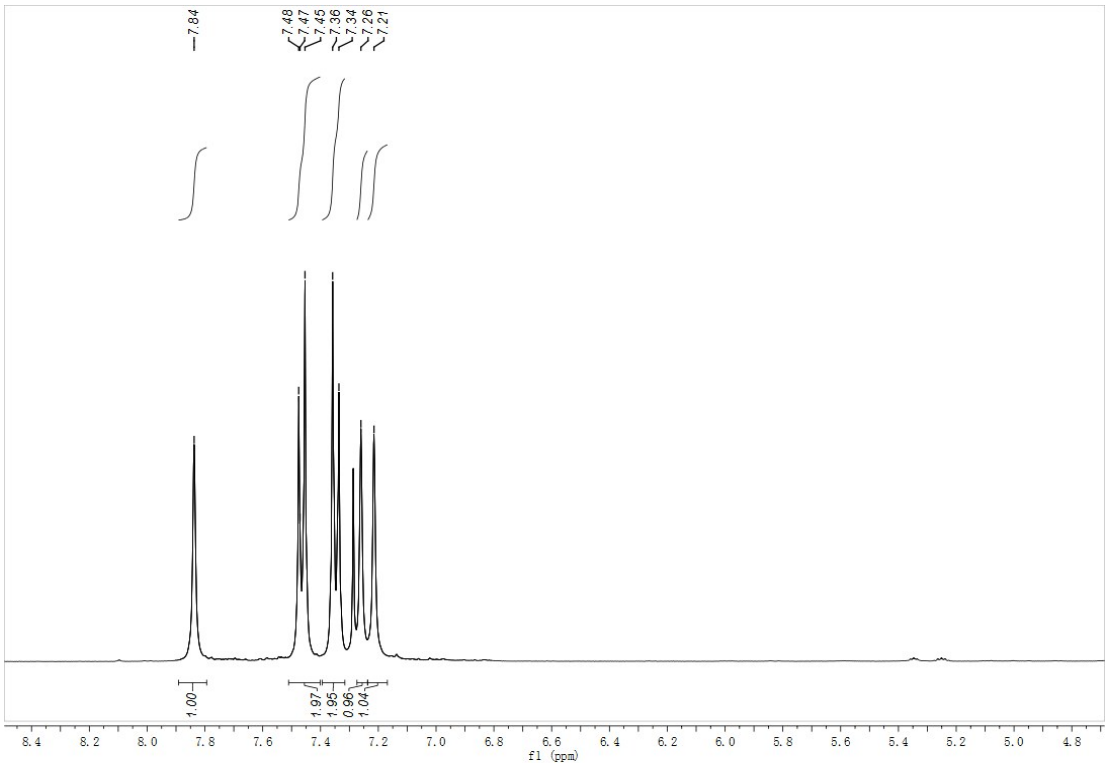
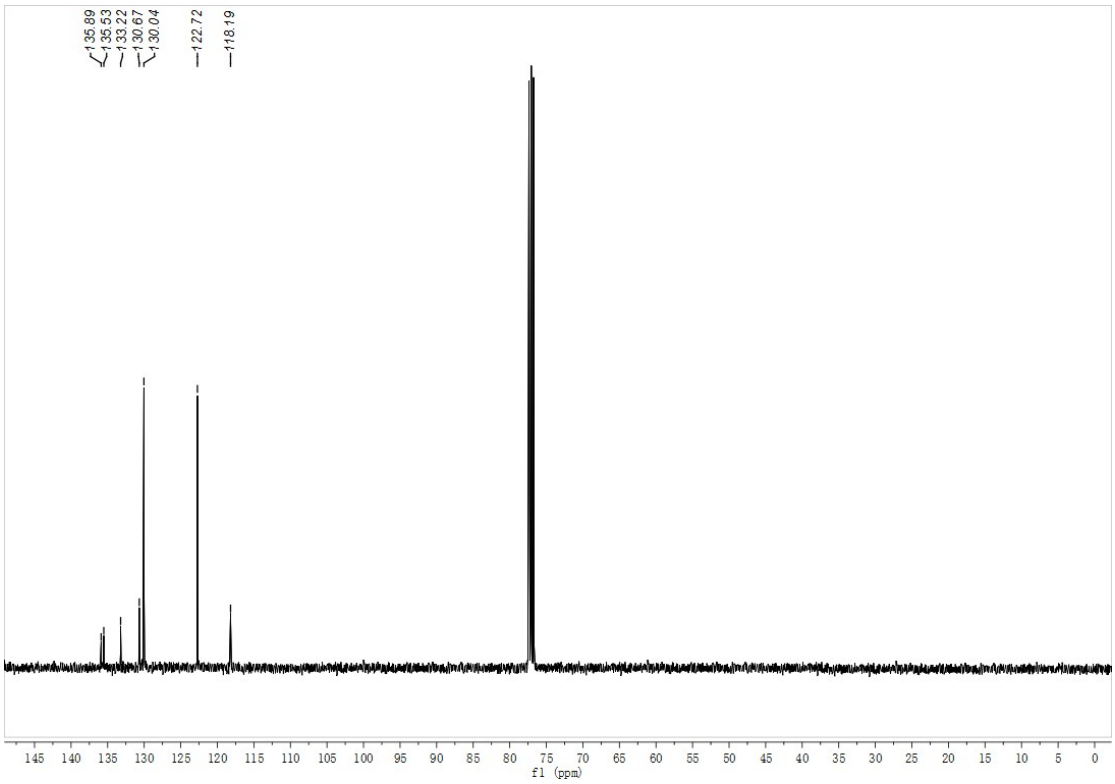
N
Cl


7.84
7.48
7.47
7.45
7.36
7.34
7.26
7.21
1.00
1.97
1.95
0.96
1.04
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8
f1 (ppm)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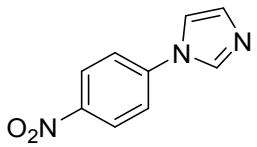
135.53
133.22
130.67
130.04
122.72
118.19
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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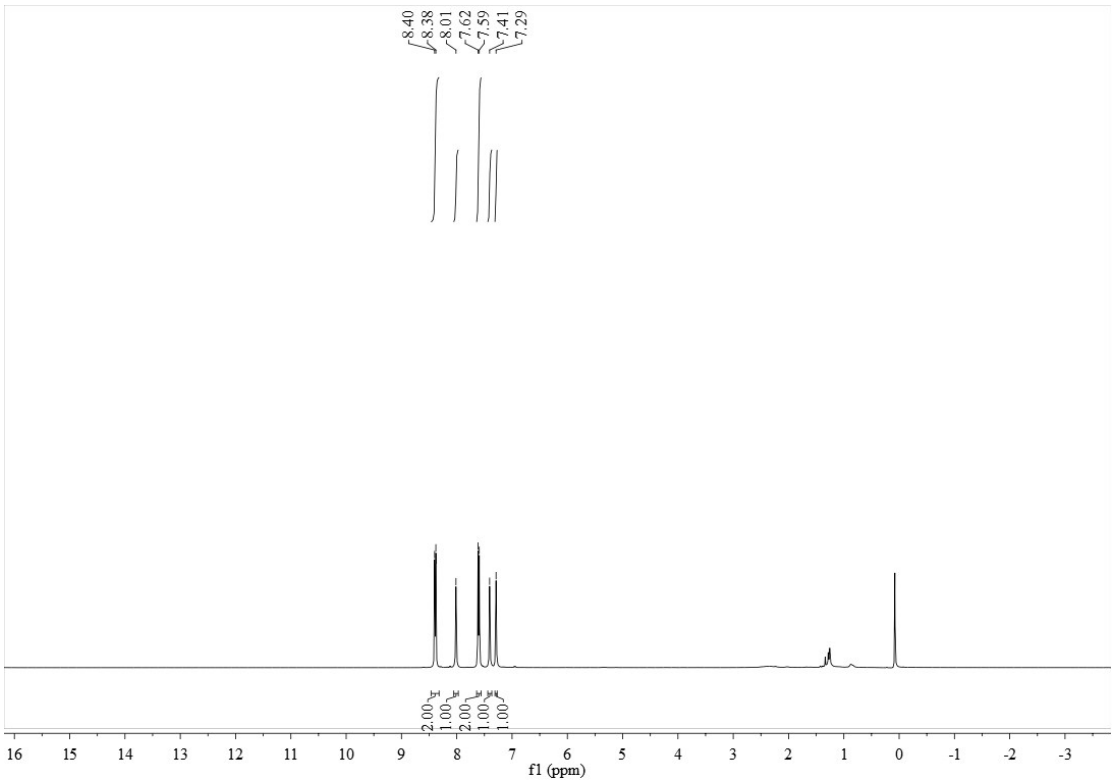
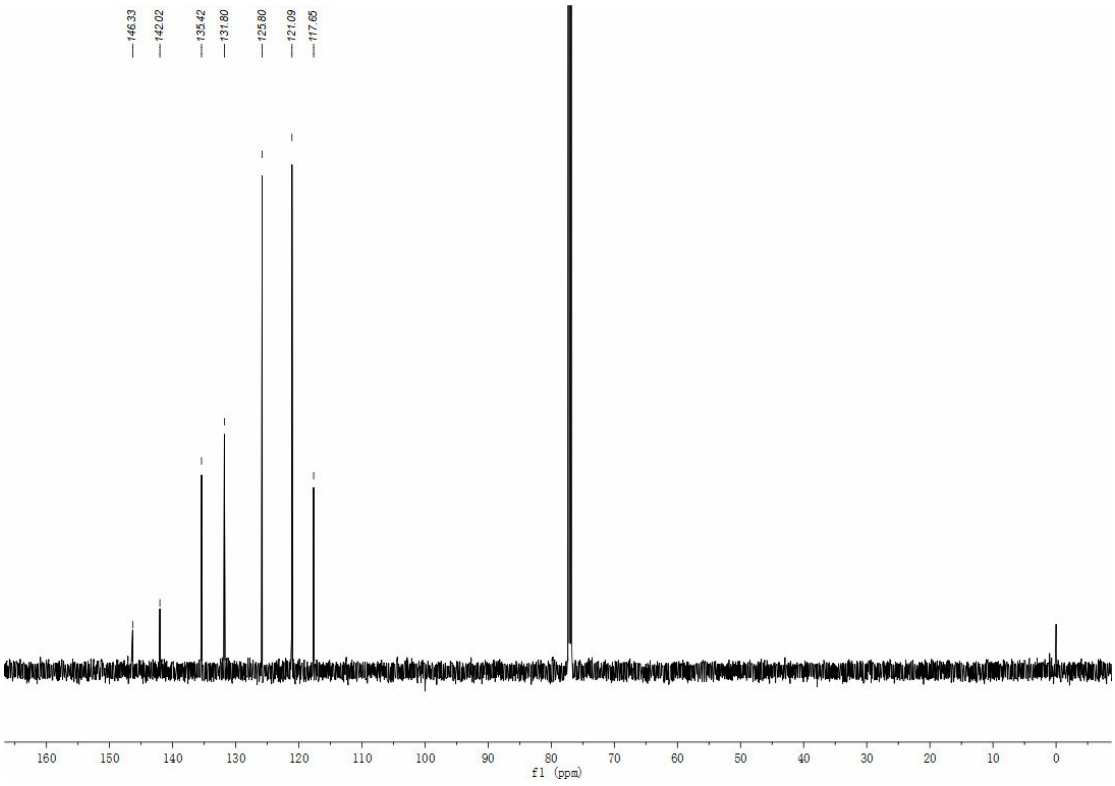
N
O2N


8.40
8.38
8.01
7.62
7.59
7.41
7.29
2.00
1.00
2.00
1.00
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)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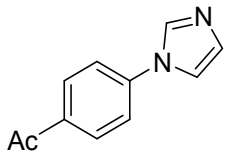
142.02
135.42
131.80
125.80
121.09
117.65
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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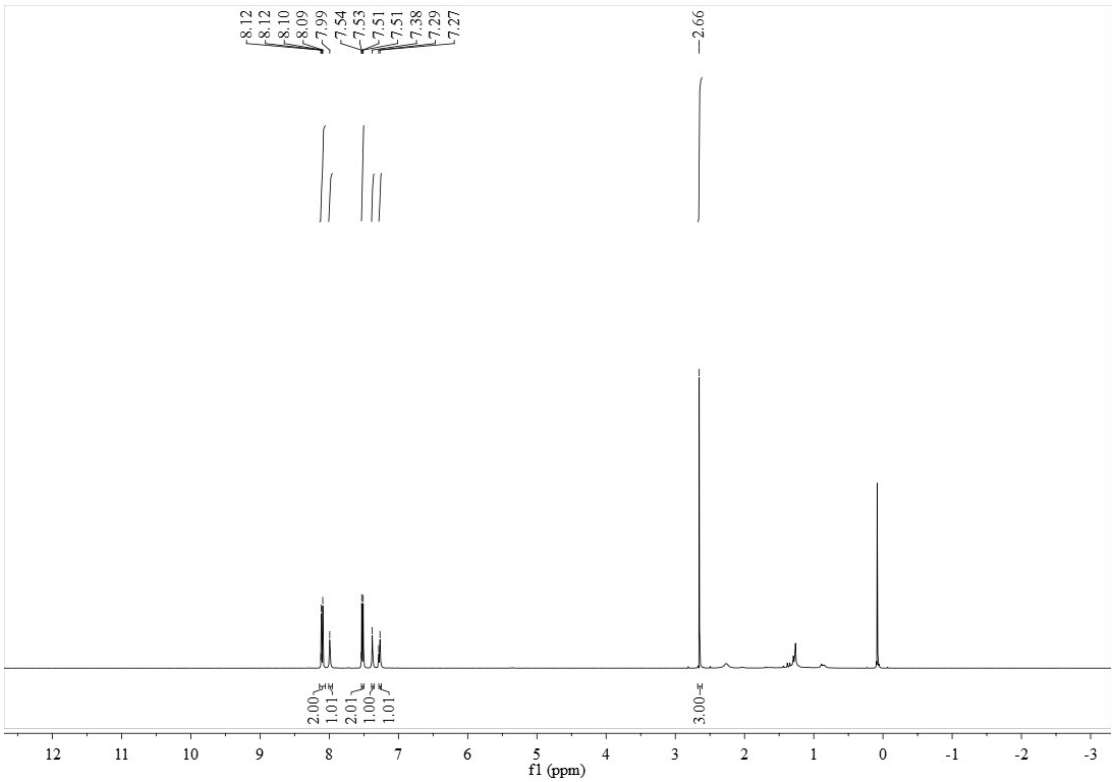
N
Ac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8.12
8.10
8.09
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7.54
7.53
7.51
7.51
7.38
7.29
7.27
2.66
2.00
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2.01
1.00
1.01
3.00
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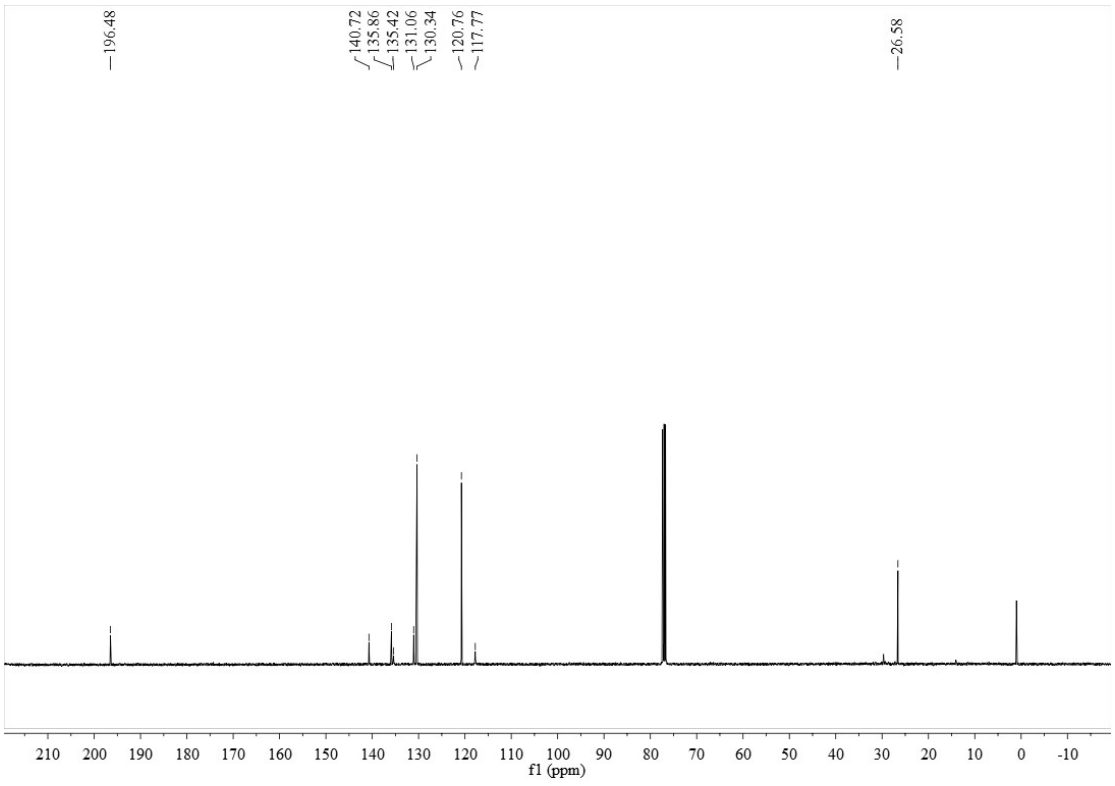
f1 (ppm)


196.48
140.72
135.86
135.42
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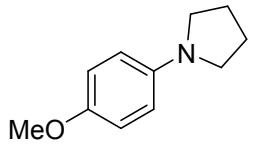
130.34
120.76
117.77
26.58
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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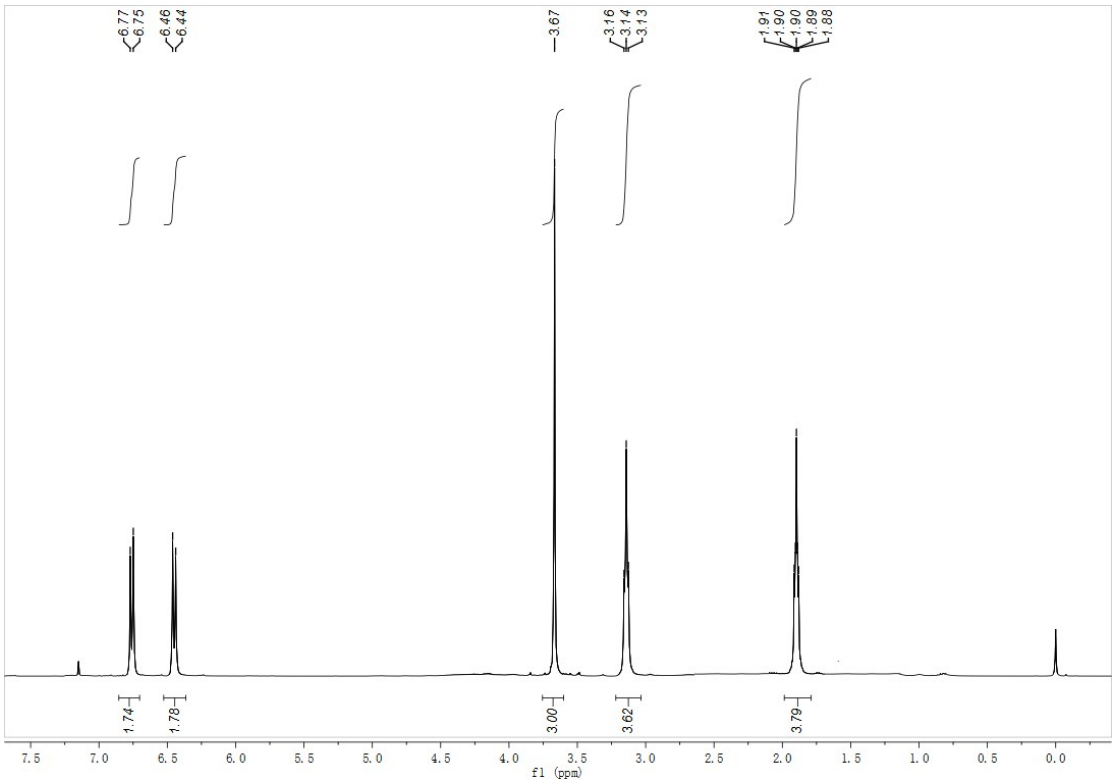
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6.44
3.67
3.16
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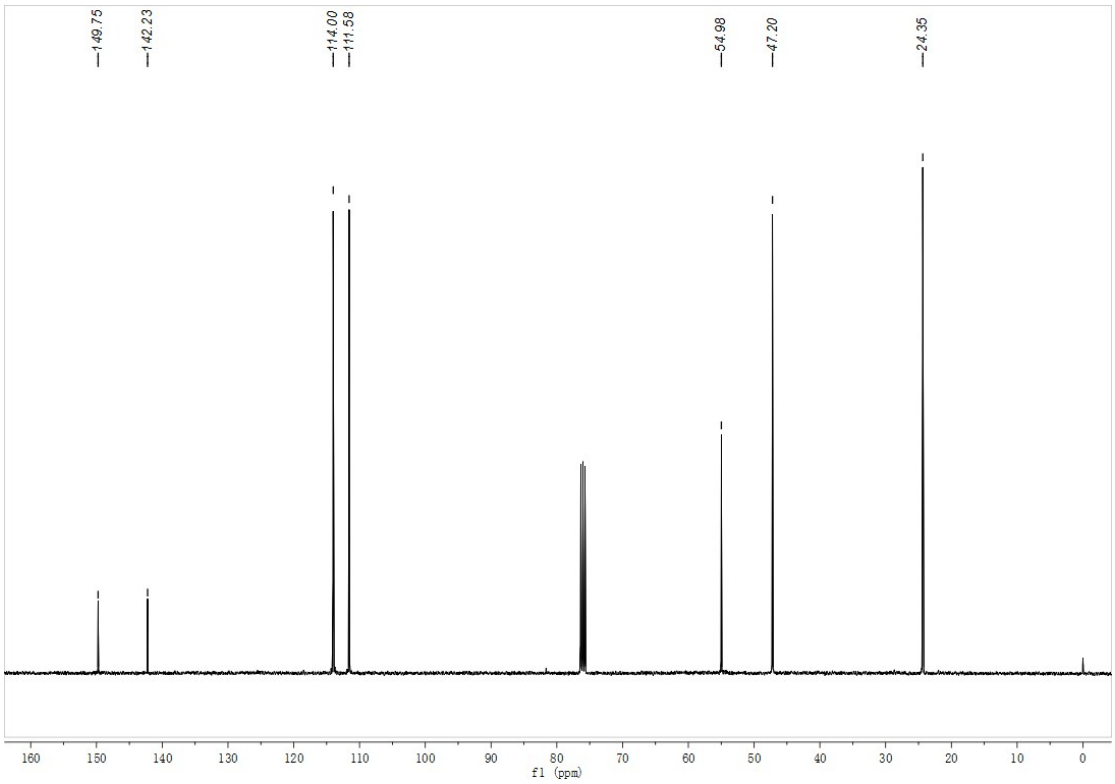
1.91
1.90
1.90
1.89
1.88
1.74
1.78
3.00
3.62
3.79
f1 (ppm)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111.58
54.98
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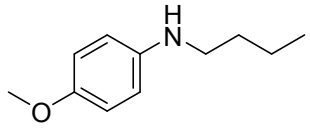
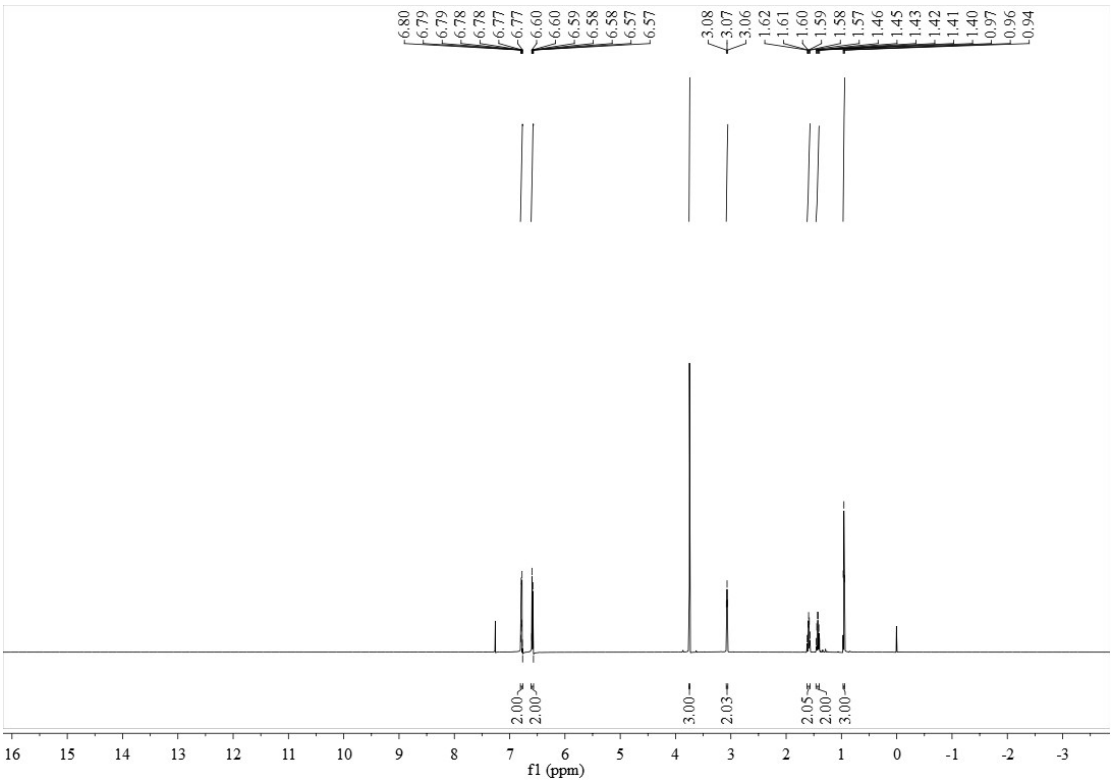
24.35
f1 (ppm)


H
N
O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6.79
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6.78
6.77
6.77
6.60
6.60
6.59
6.58
6.58
6.57
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3.07
3.06
1.62
1.61
1.60
1.59
1.58
1.57
1.46
1.45
1.43
1.42
1.41
1.40
0.97
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0.94
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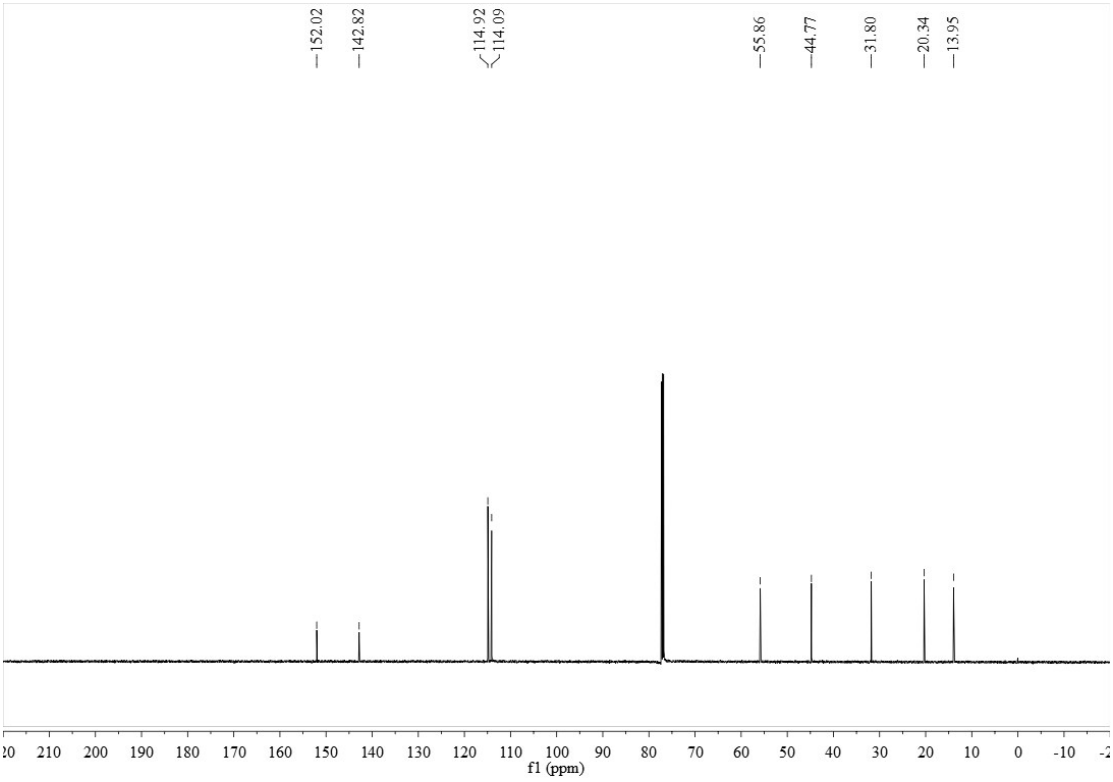
2.00
3.00
2.03
2.05
2.00
3.00
f1 (ppm)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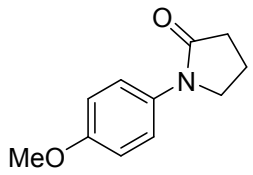
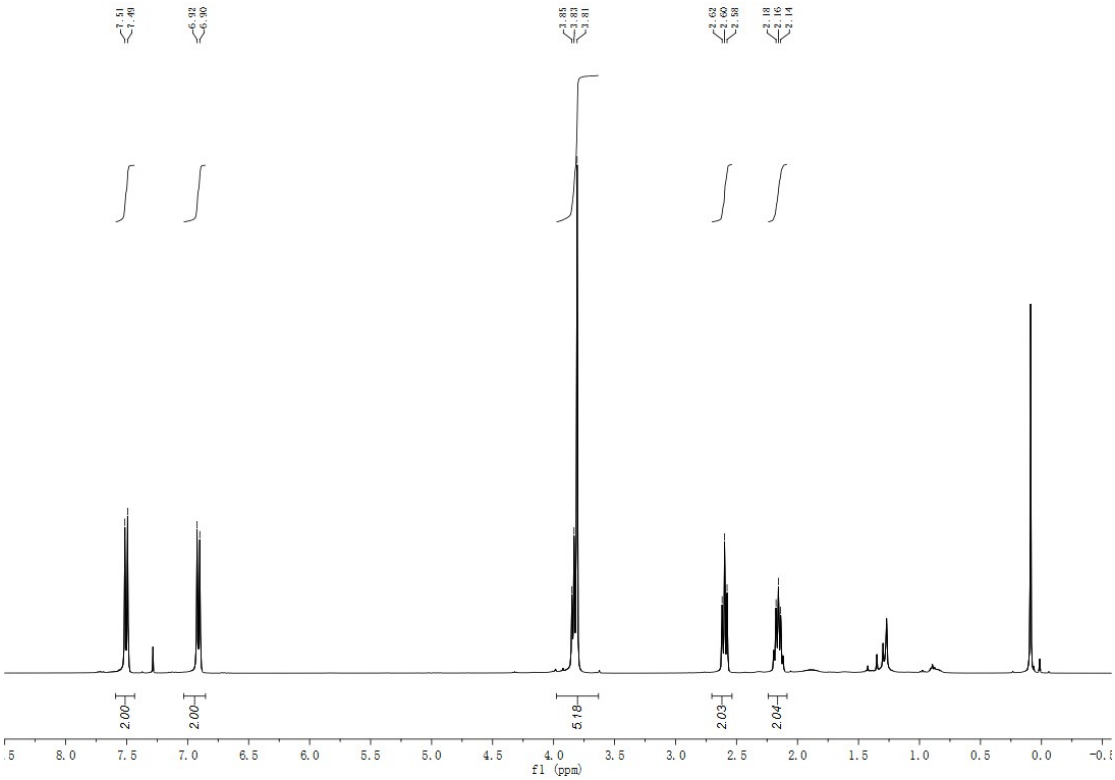
44.77
31.80
20.34
13.95
f1 (ppm)


O
N
MeO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6.90
3.85
3.83
3.81
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2.60
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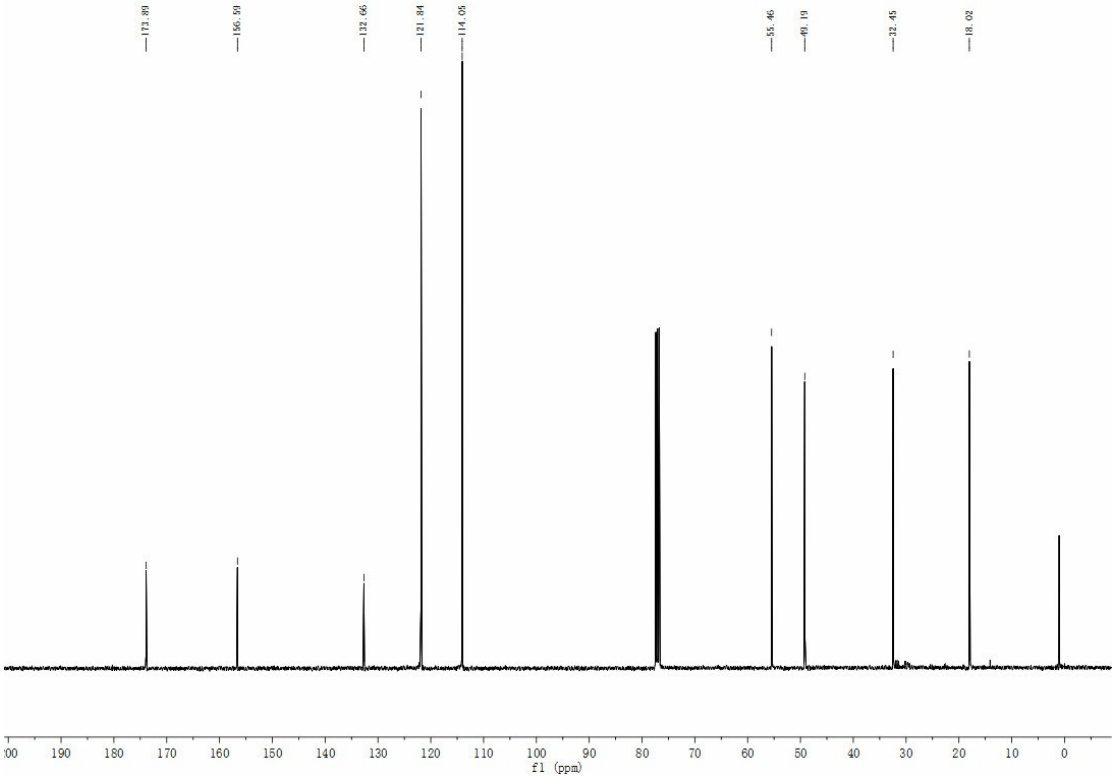
2.18
2.16
2.14
2.00
2.00
5.18
2.03
2.04
f1 (ppm)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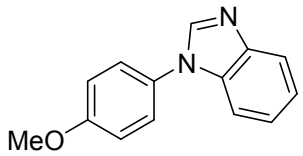
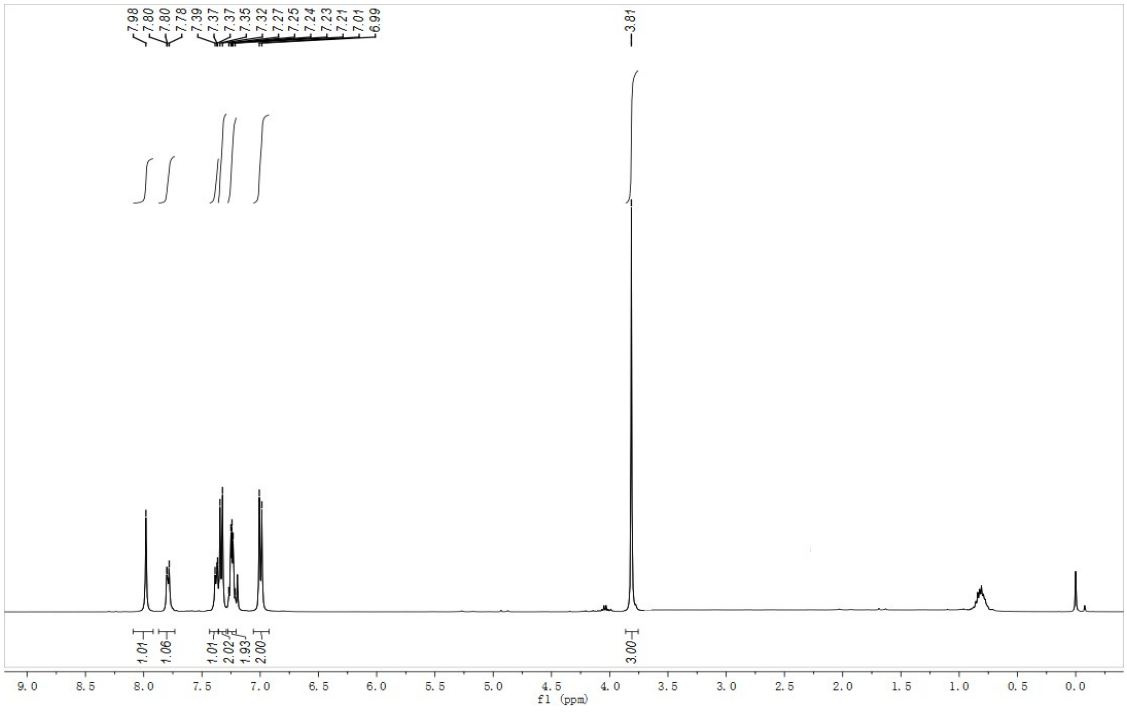
49.19
32.45
18.02
f1 (ppm)


N
N
MeO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7.80
7.78
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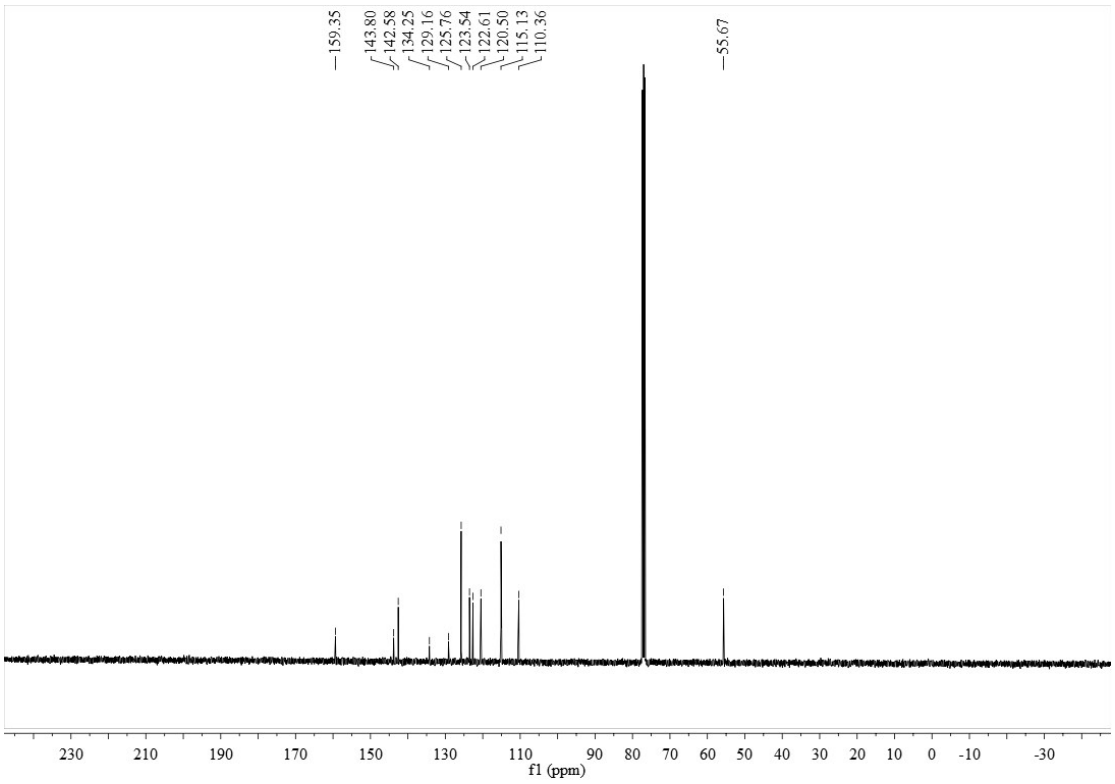
7.37
7.35
7.32
7.27
7.25
7.24
7.23
7.21
7.01
6.99
3.81
1.01
1.06
1.01
2.02
1.93
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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134.25
129.16
125.76
123.54
122.61
120.50
115.13
110.36
55.67
230
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150
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110
90
80
70
60
50
40
30
20
10
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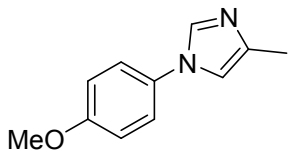
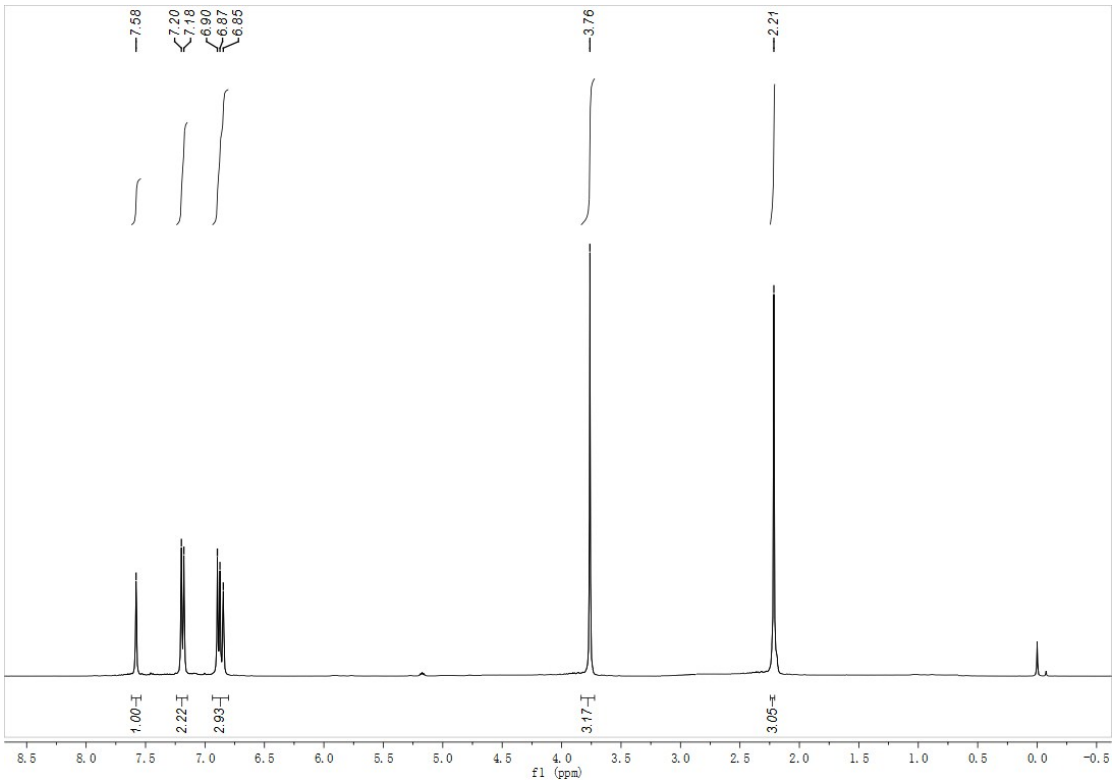
-10
-30
f1 (ppm)


N
N
MeO


7.58
7.20
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6.85
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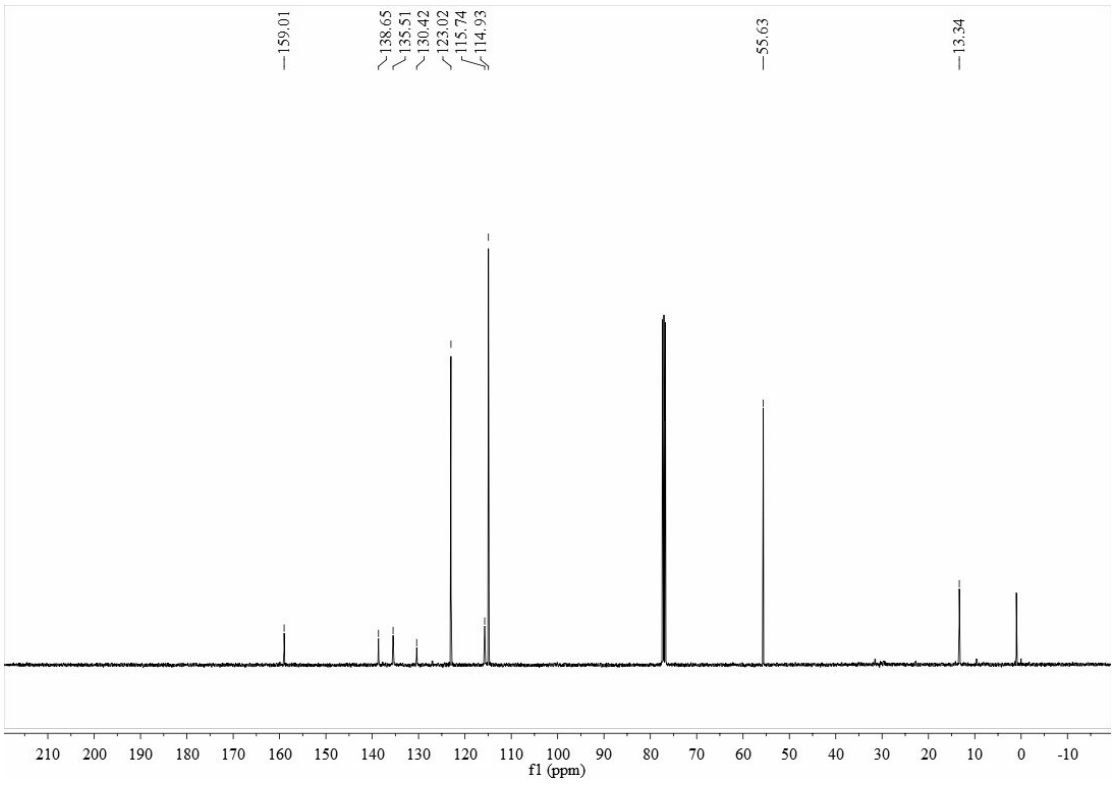
2.21
1.00
2.22
2.93
3.17
3.05
f1 (ppm)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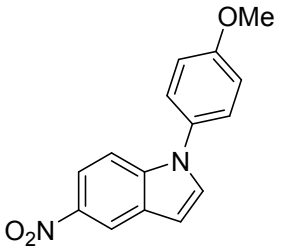
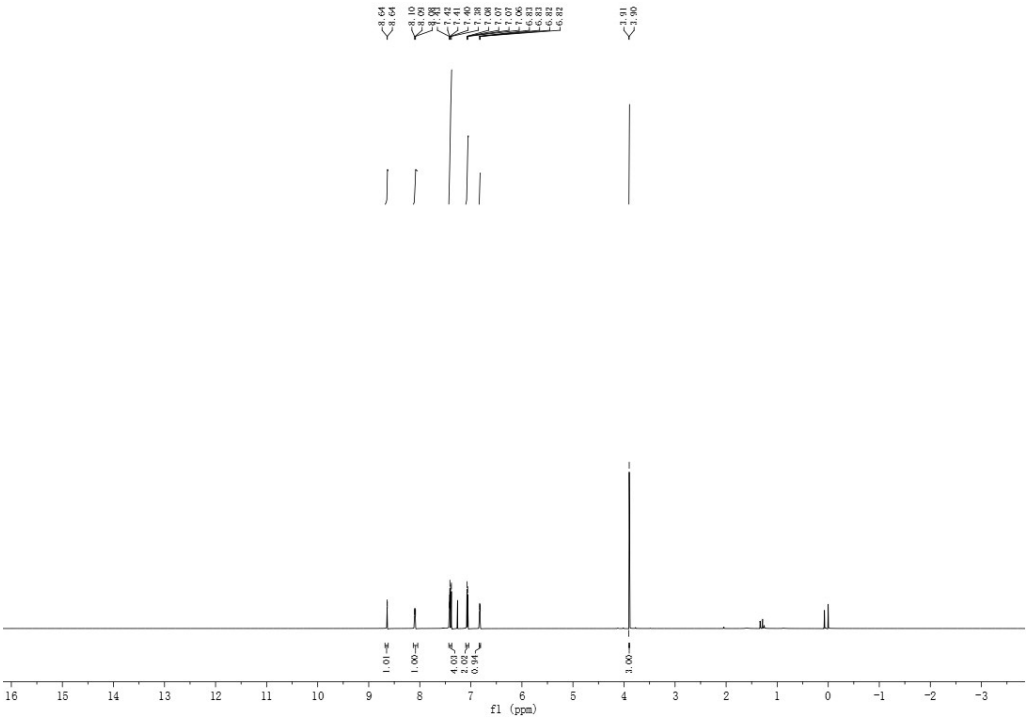
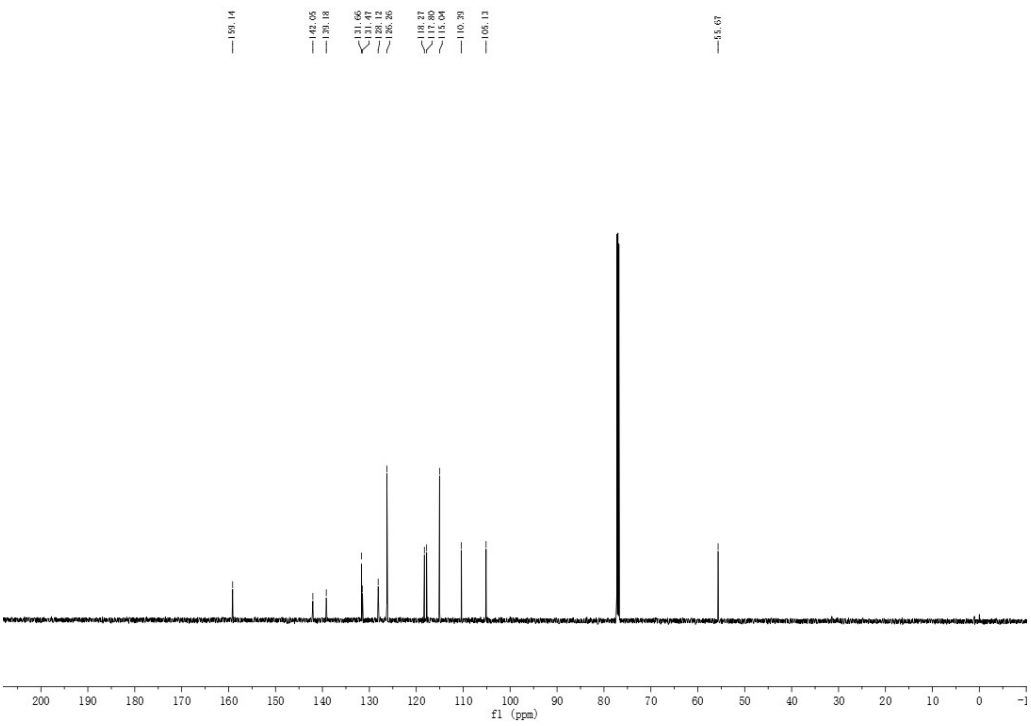
130.42
123.02
115.74
114.93
55.63
13.34
f1 (ppm)


OMe
N
O_2N


8.64
8.64
8.10
8.09
8.08
8.07
7.42
7.41
7.40
7.39
7.38
7.08
7.07
7.06
6.83
6.82
6.82
6.82
3.91
3.90
1.01
1.00
4.03
2.02
0.94
3.00
f1 (ppm)


193.14
142.05
139.18
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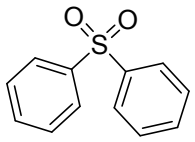
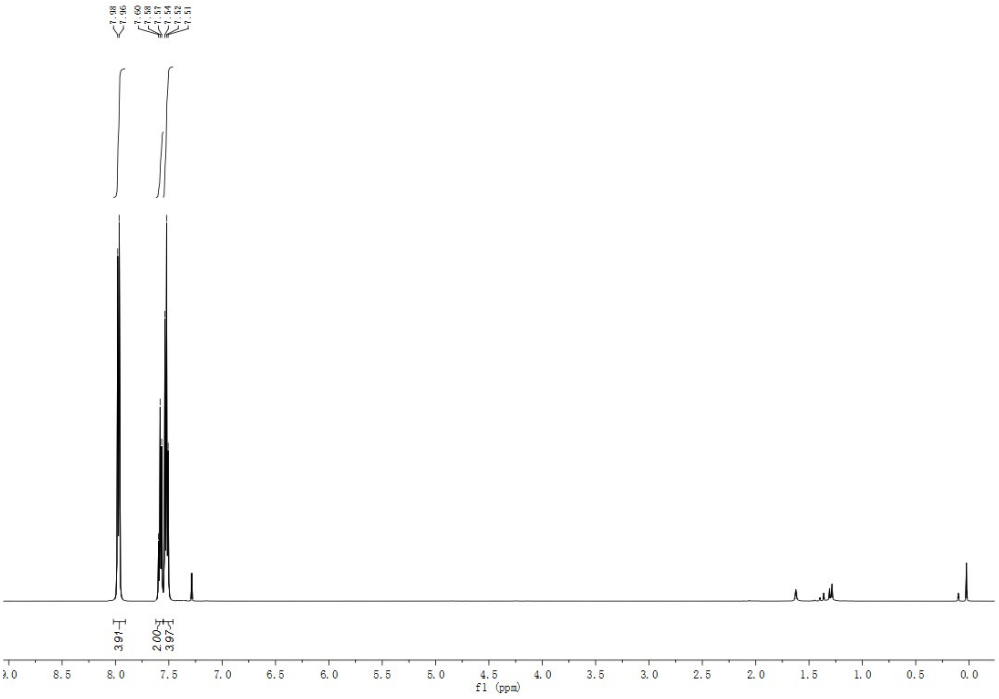
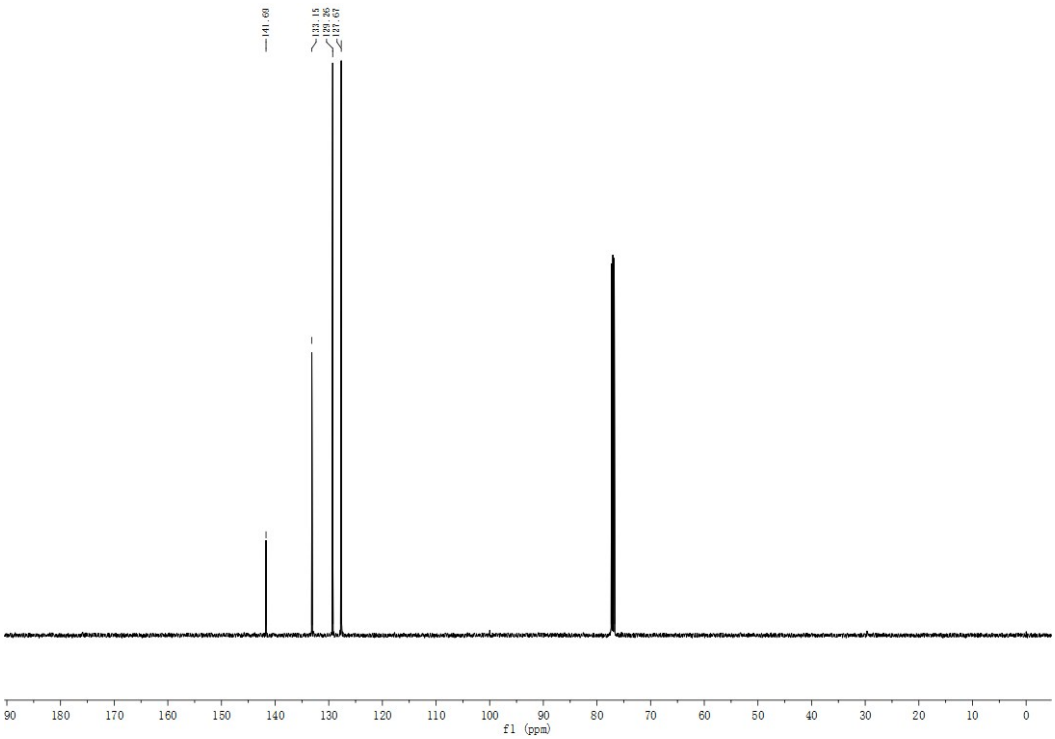
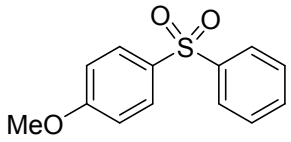
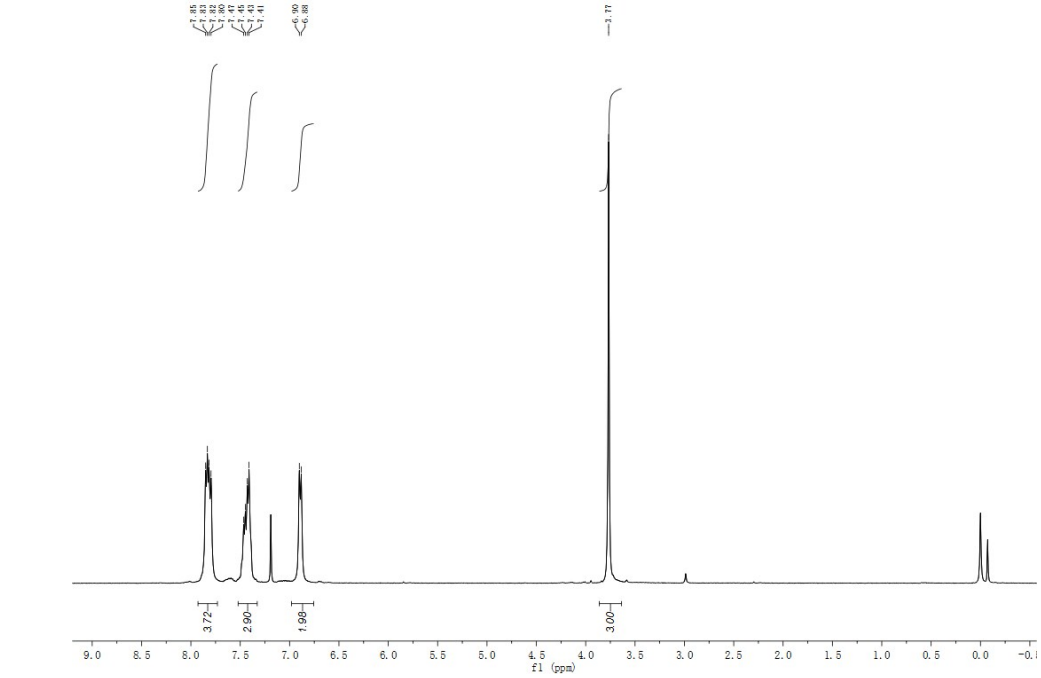
131.47
128.12
126.26
118.27
117.80
115.04
110.39
105.13
55.67
f1 (ppm)

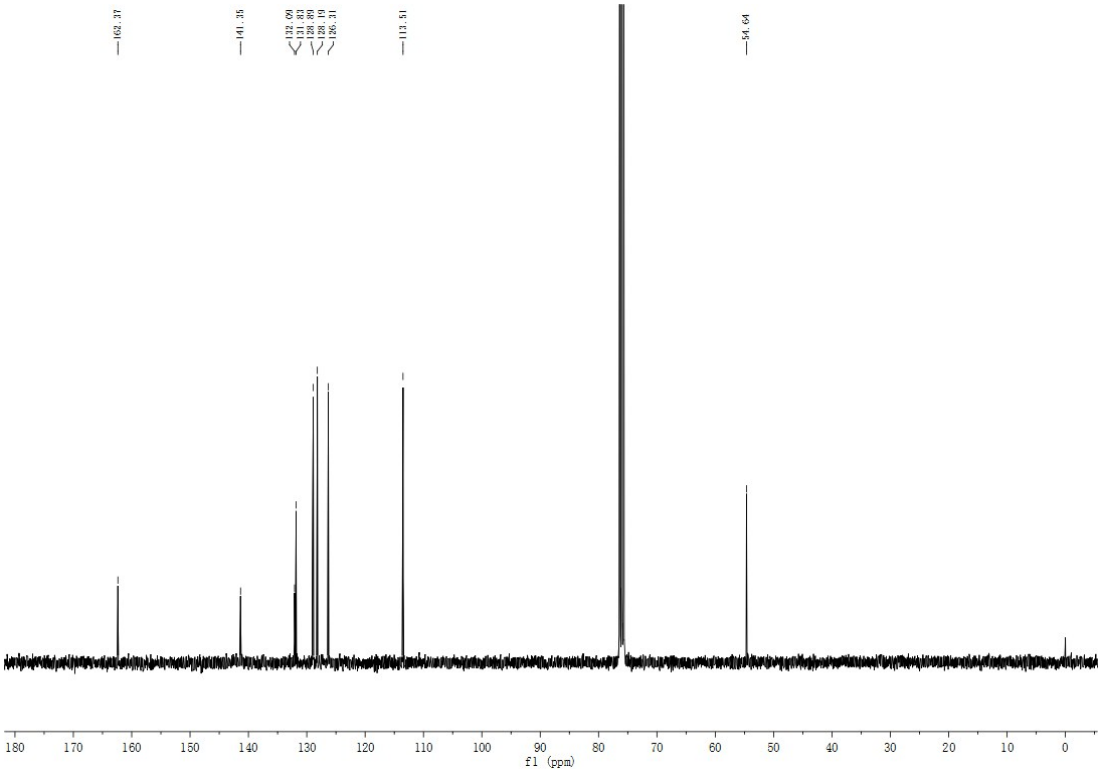


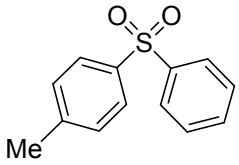

7.98
7.96
7.60
7.58
7.57
7.54
7.53
7.51
3.91
2.00
3.97
f1 (ppm)

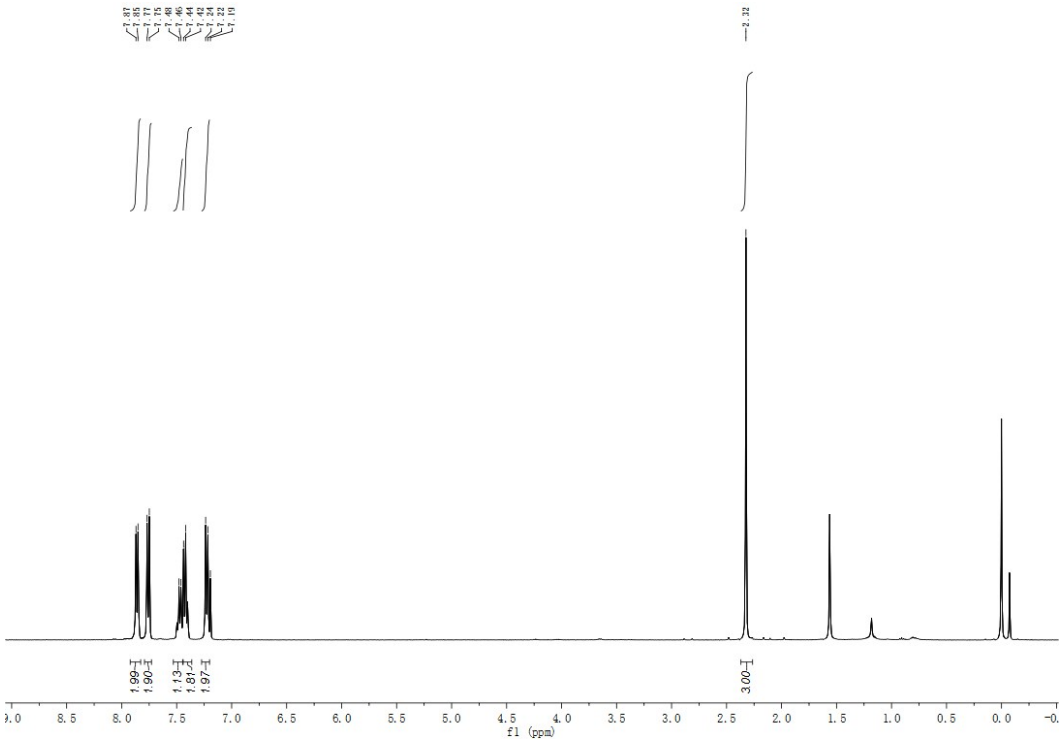

141.69
133.15
129.26
127.61
f1 (ppm)

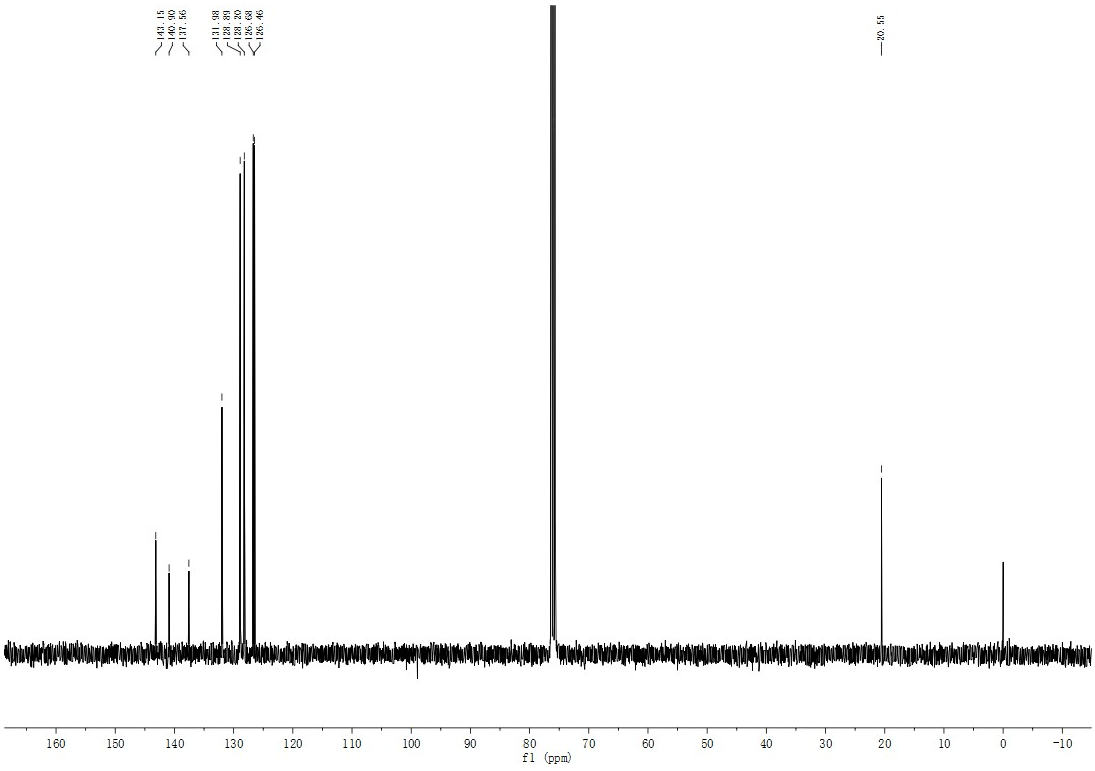

O
O
S
MeO

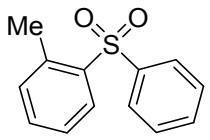

7.85
7.83
7.82
7.80
7.47
7.45
7.43
7.41
6.90
6.88
3.77
3.72
2.90
1.98
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

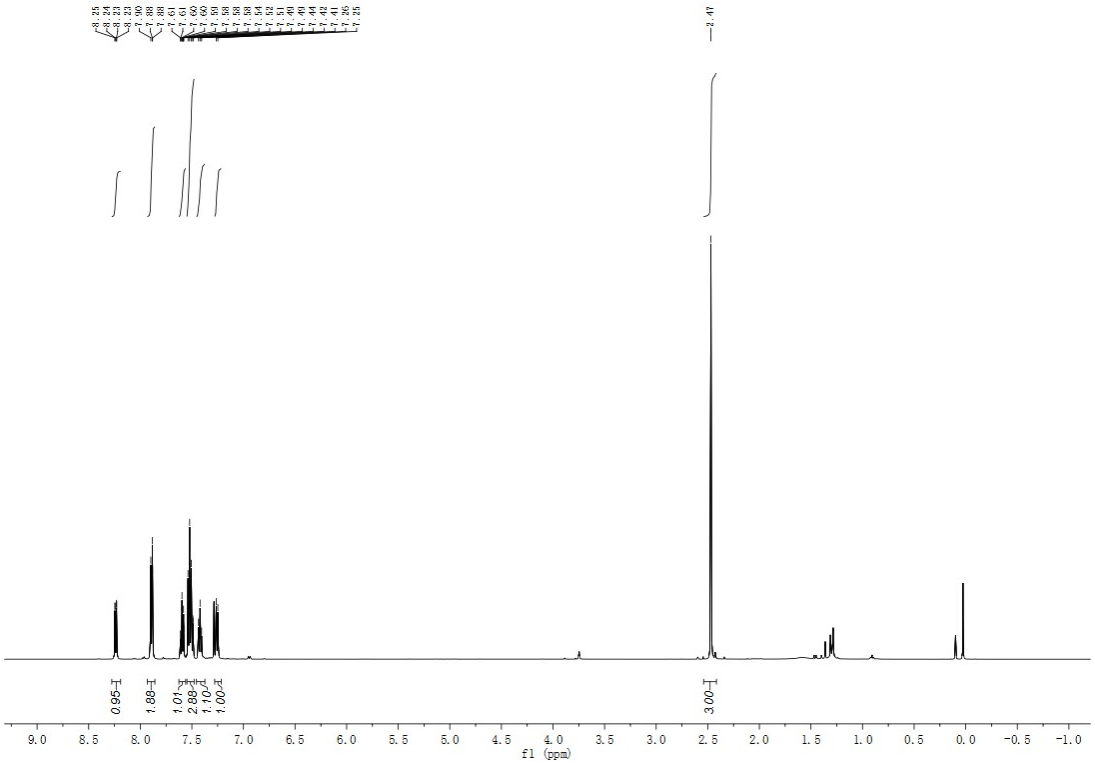

162.37
141.35
132.09
131.83
128.89
128.11
126.31
113.51
54.64
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

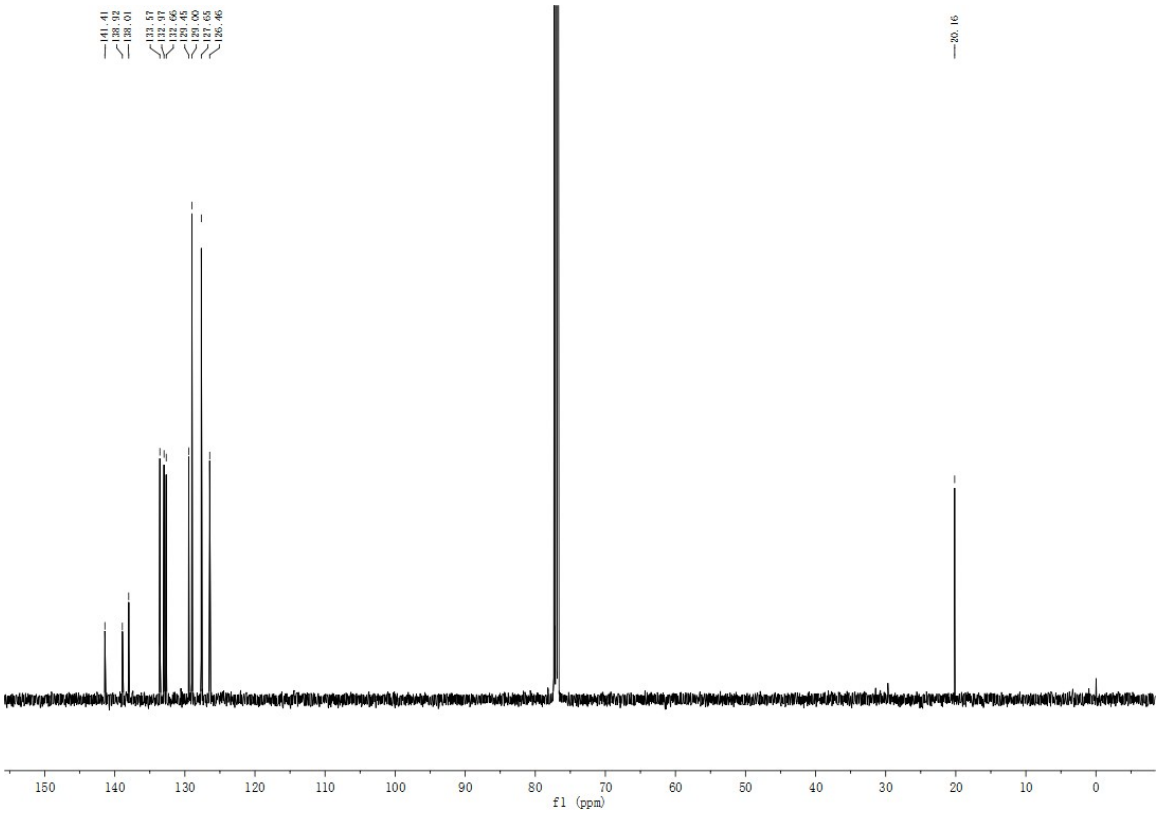

O
O
S
Me


7.87
7.85
7.77
7.75
7.48
7.46
7.44
7.43
7.24
7.22
7.19
2.32
1.99
1.90
1.13
1.81
1.97
3.00
f1 (ppm)


143.15
140.90
137.86
131.88
129.99
129.20
126.68
125.46
20.55
f1 (ppm)


Me
O
O
S


8.25
8.24
8.23
8.23
7.90
7.88
7.88
7.61
7.60
7.60
7.59
7.58
7.58
7.58
7.54
7.52
7.51
7.49
7.49
7.44
7.42
7.41
7.26
7.25
2.47
0.95
1.88
1.01
2.88
1.10
1.00
3.00
f1 (ppm)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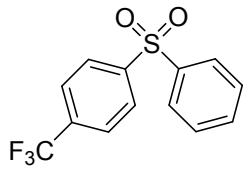
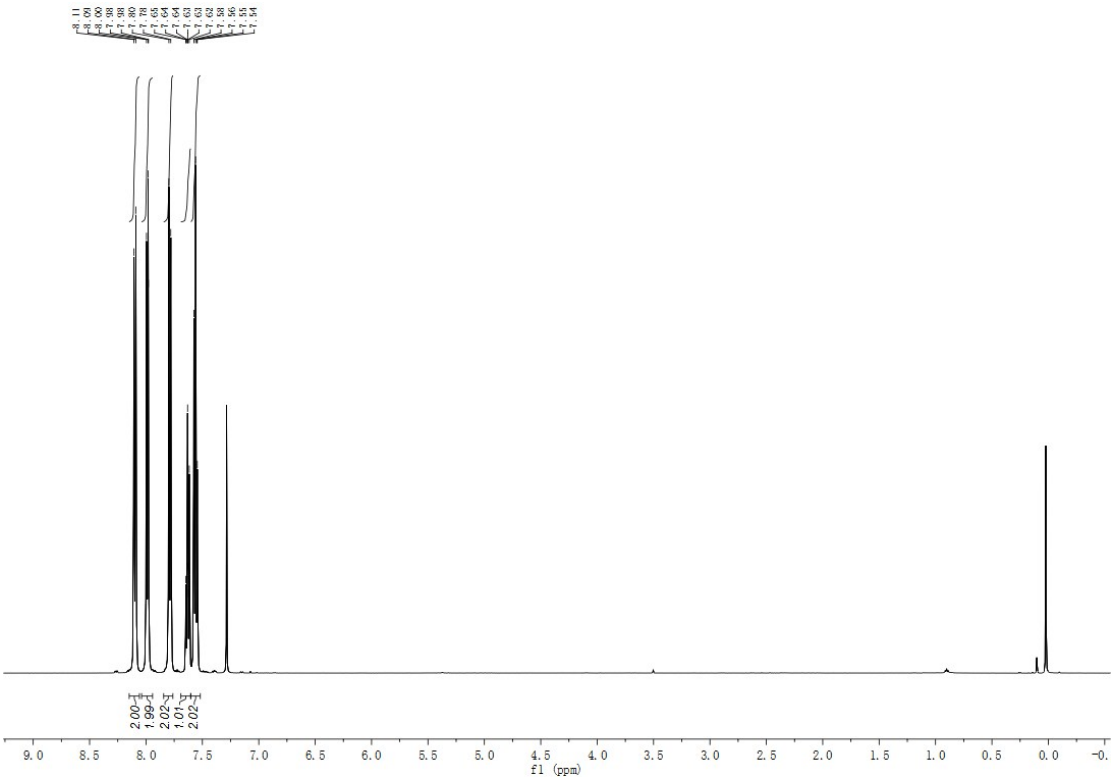
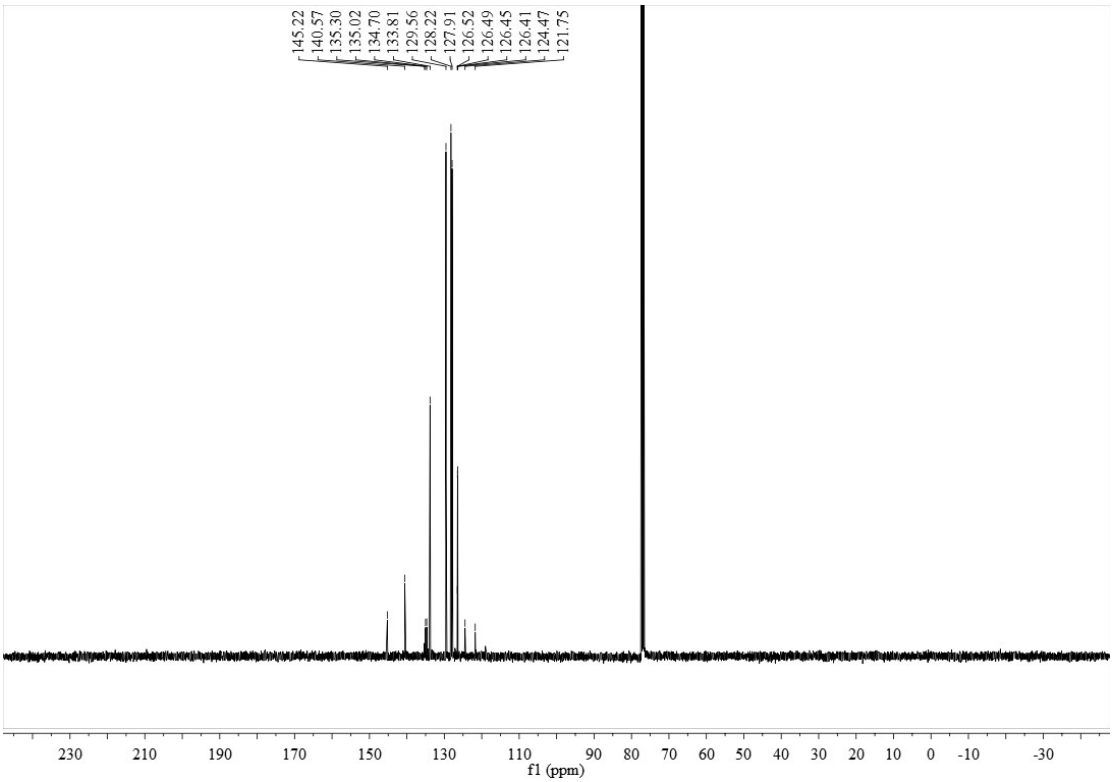
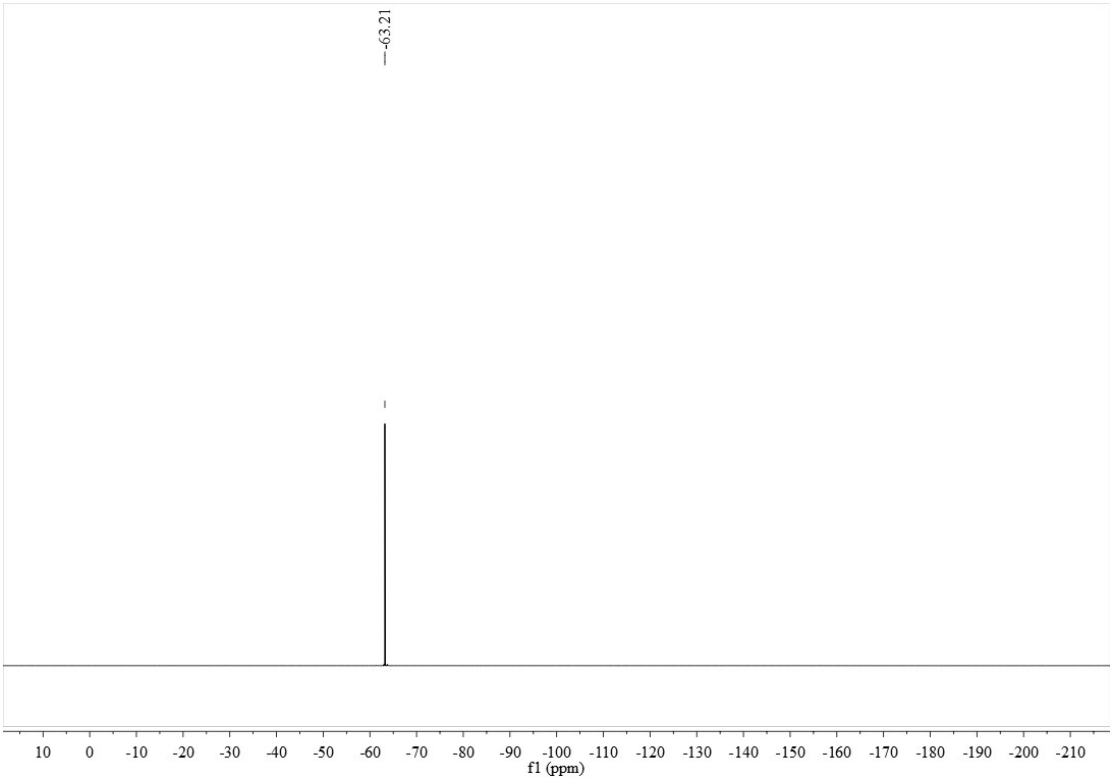
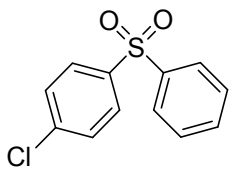
138.32
136.01
133.57
132.97
132.66
131.45
129.00
127.65
126.46
20.16
f1 (ppm)

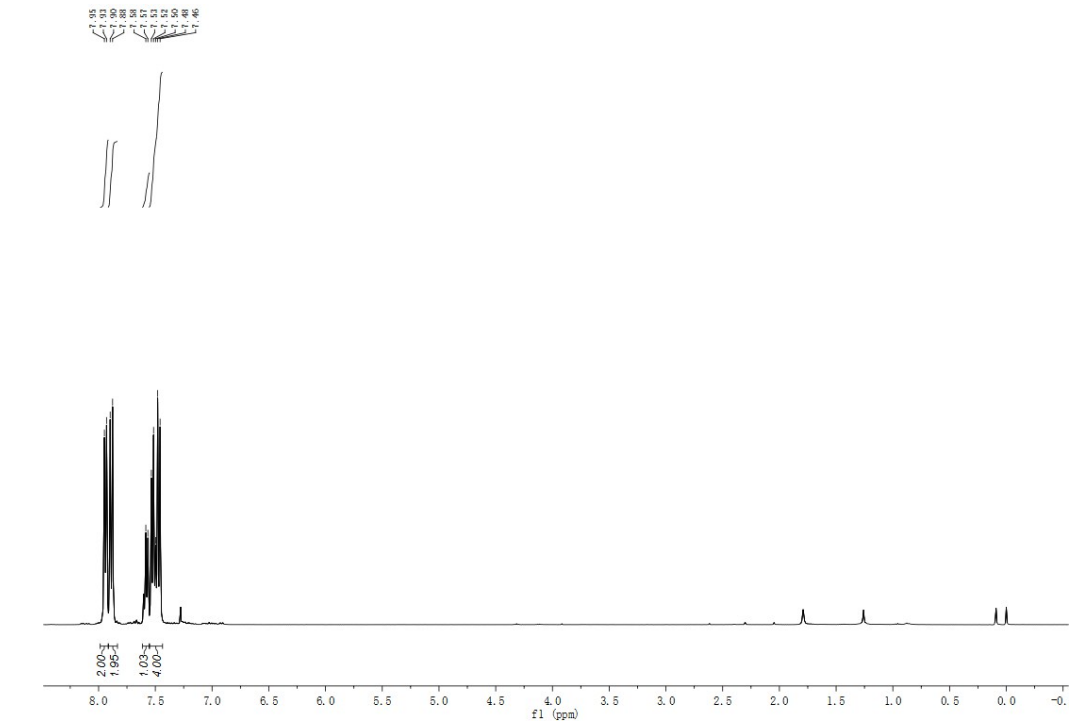

O
S
O
F3C

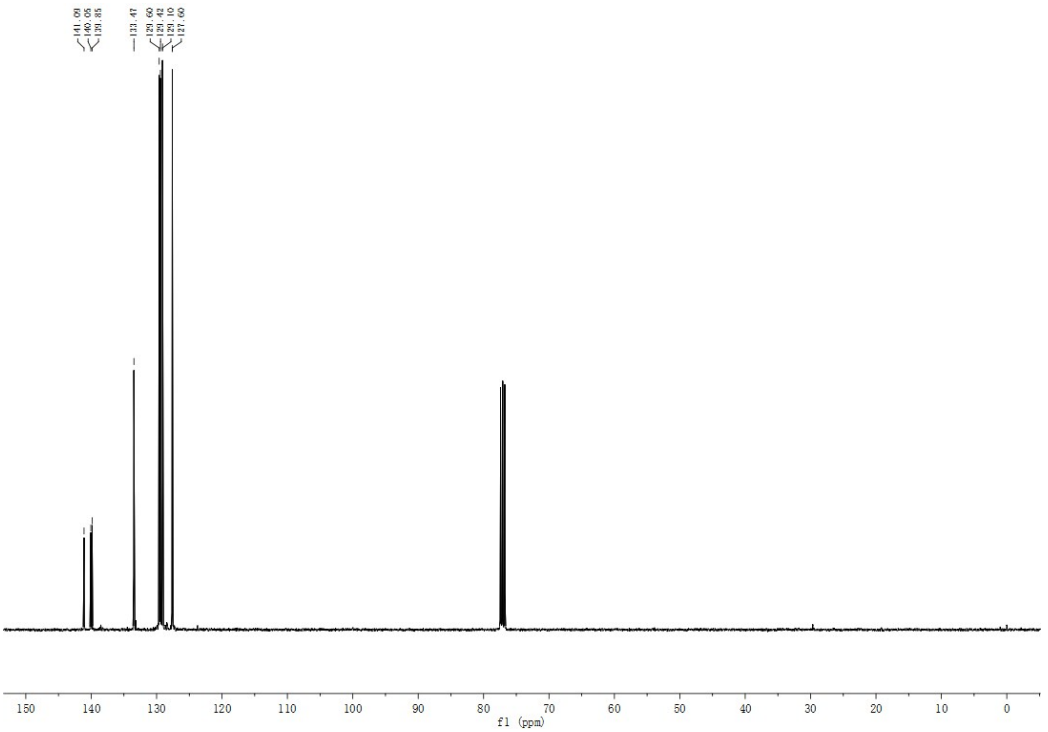

2.00
1.99
2.02
1.01
2.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

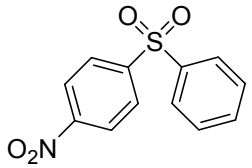

145.22
140.57
135.30
135.02
134.70
133.81
129.56
128.22
127.91
126.52
126.49
126.45
126.41
124.47
121.75
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -30
f1 (ppm)

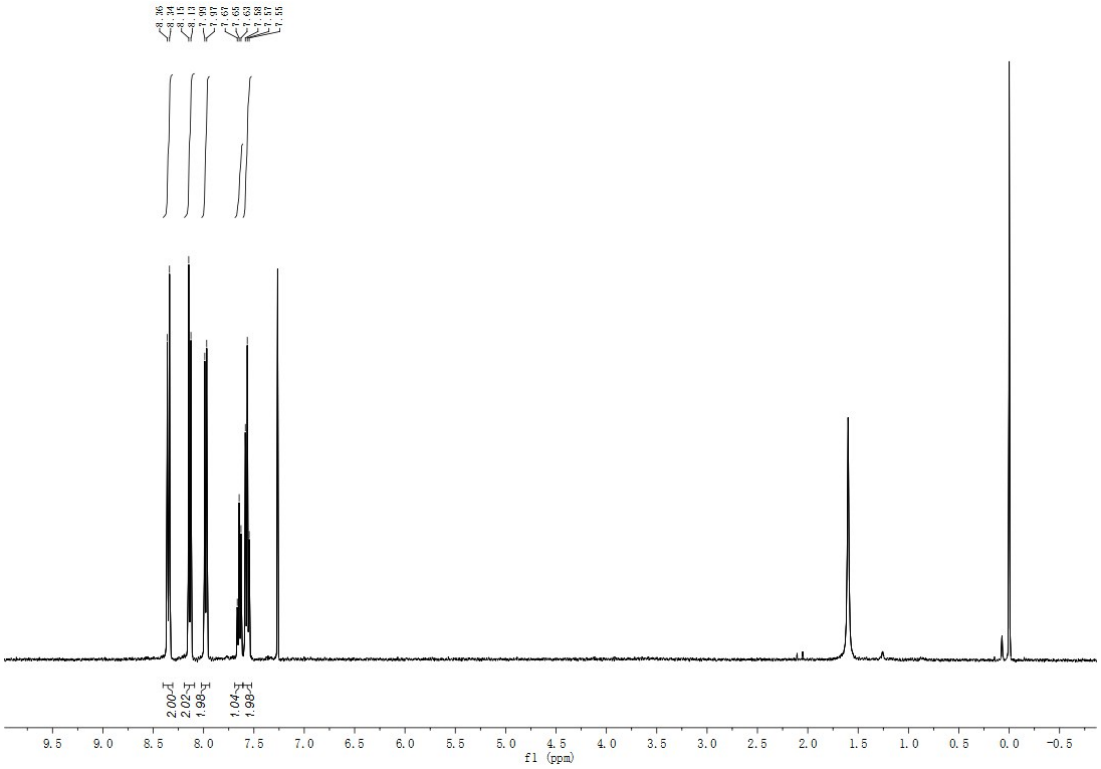

-63.21
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


O
O
S
Cl


7.95
7.93
7.90
7.88
7.58
7.57
7.53
7.52
7.50
7.48
7.46
2.00
1.95
1.03
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
0.0
f1 (ppm)


141.09
140.05
139.86
133.47
129.60
129.42
129.10
127.60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
S
O2N


8.36
8.34
8.15
8.13
7.99
7.97
7.66
7.65
7.63
7.58
7.57
7.55
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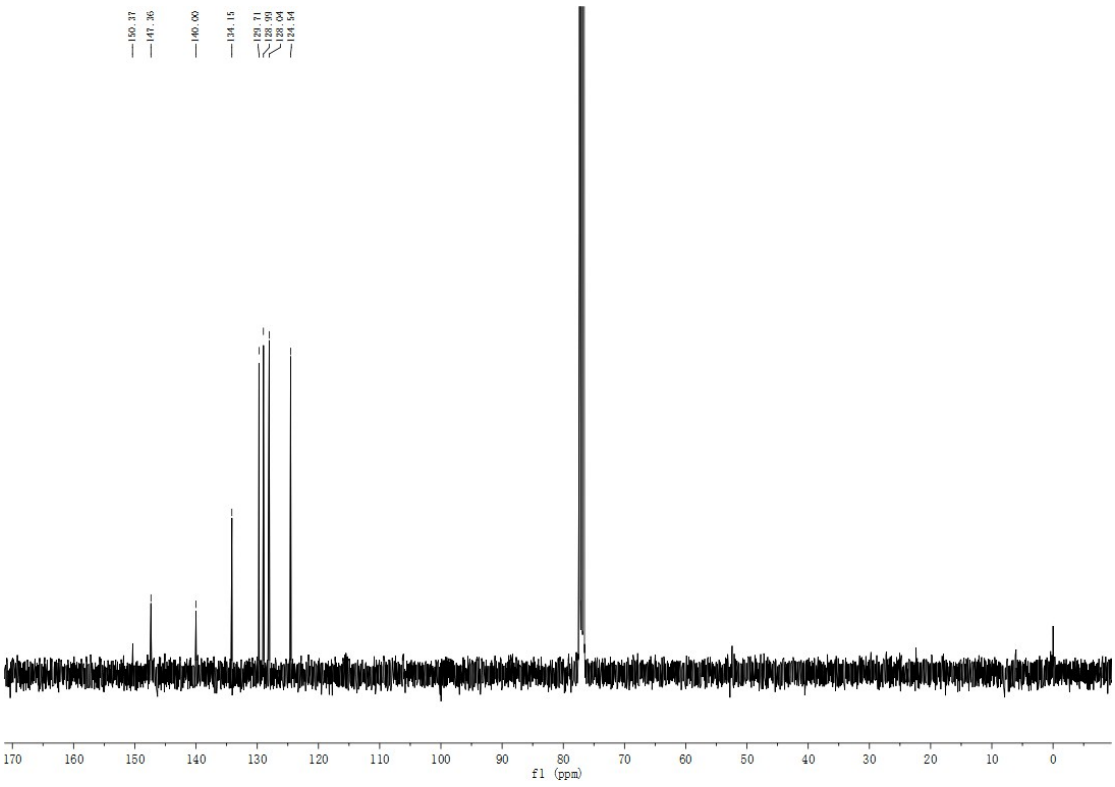
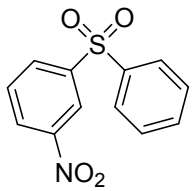
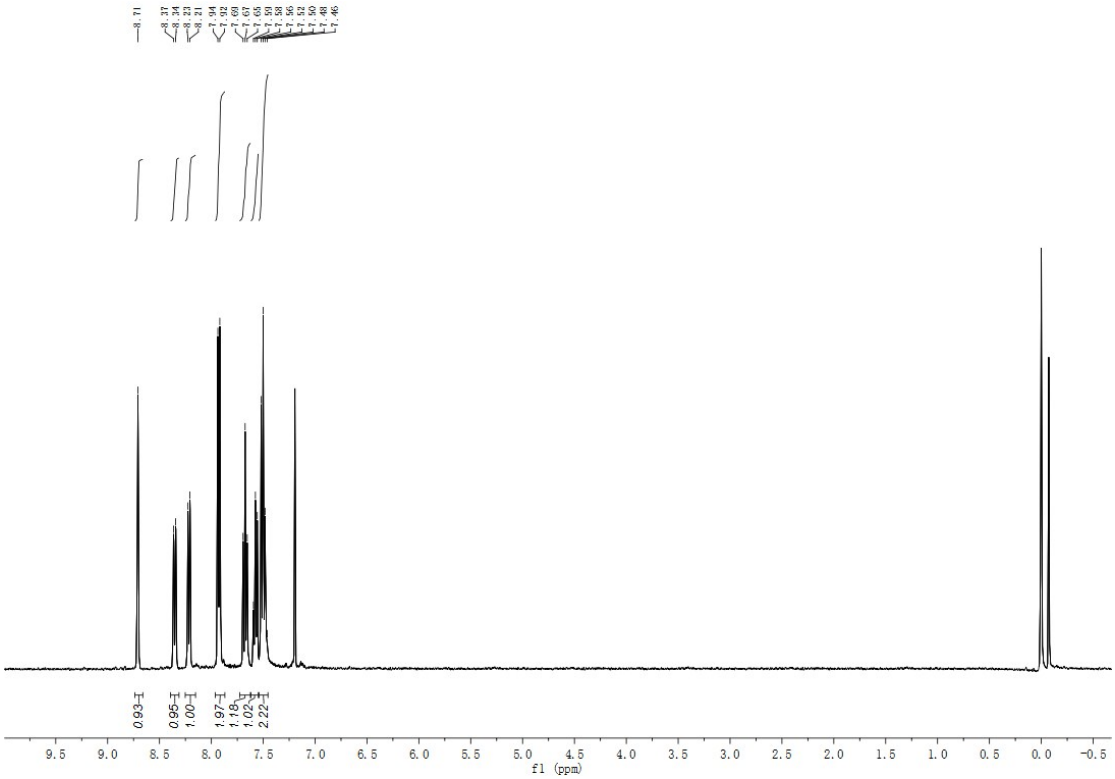
2.02
1.98
1.04
1.98
f1 (ppm)


150.37
147.36
140.00
134.15
129.71
128.98
128.04
124.54
f1 (ppm)


O
O
S
NO2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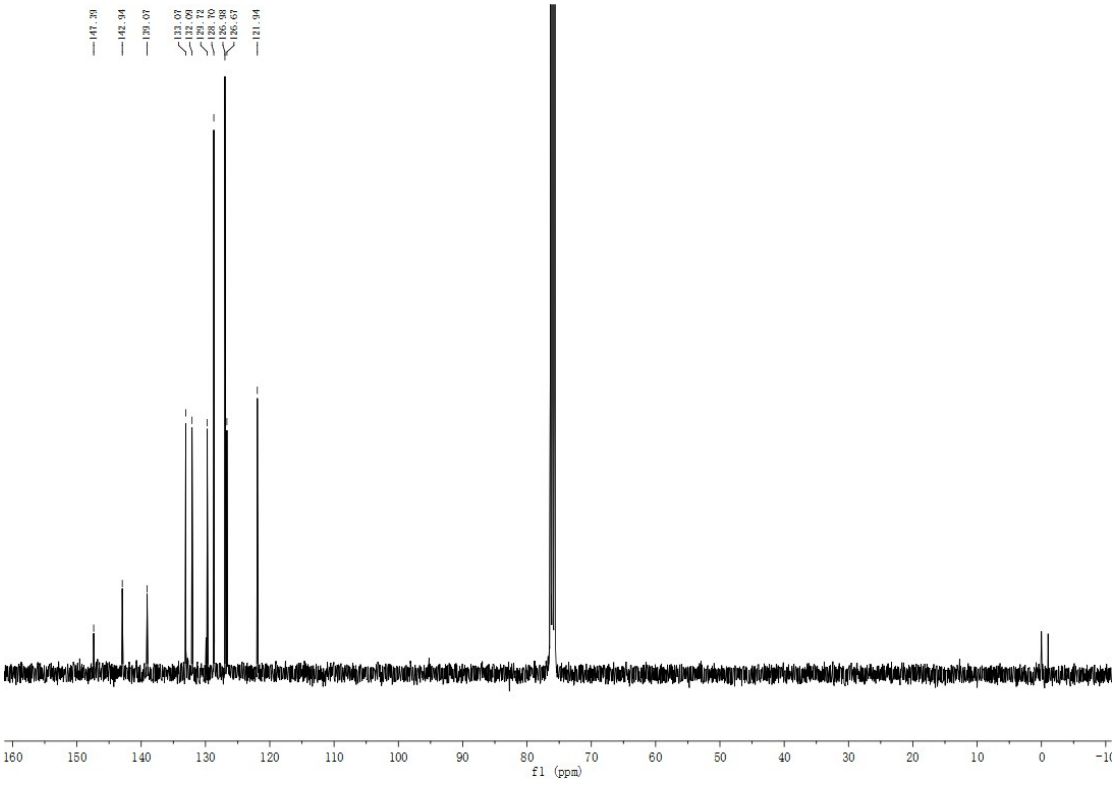
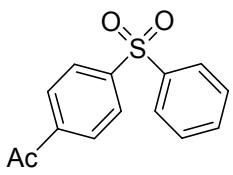
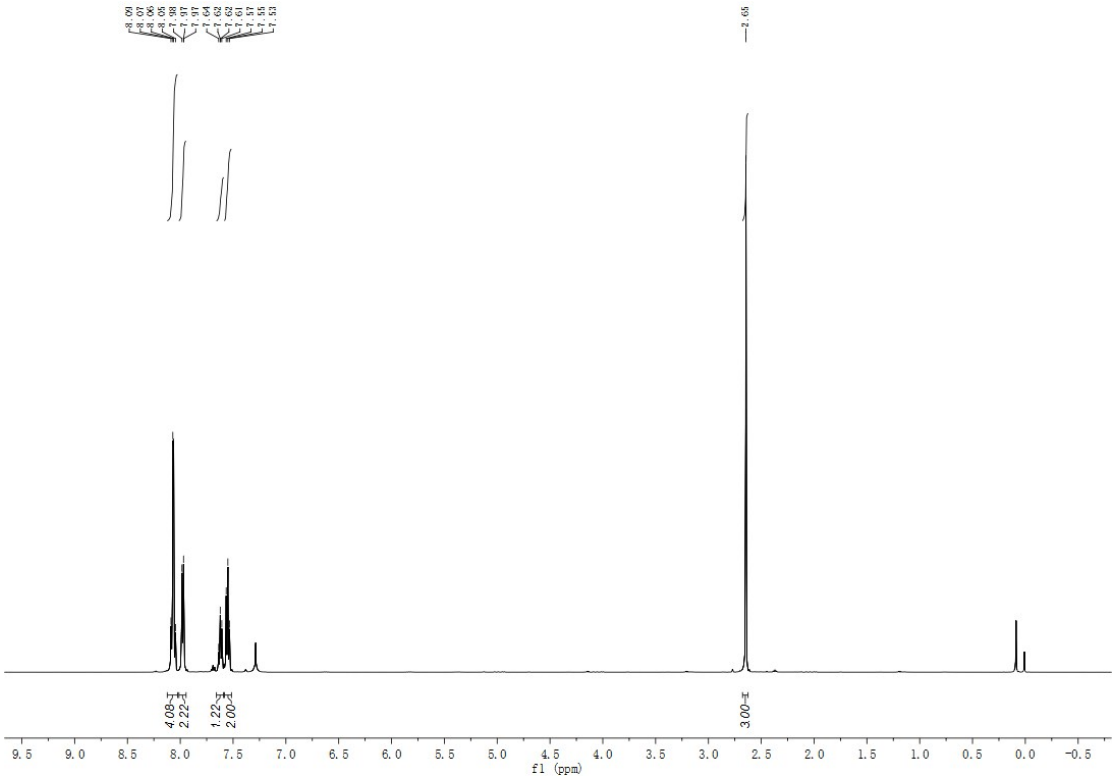
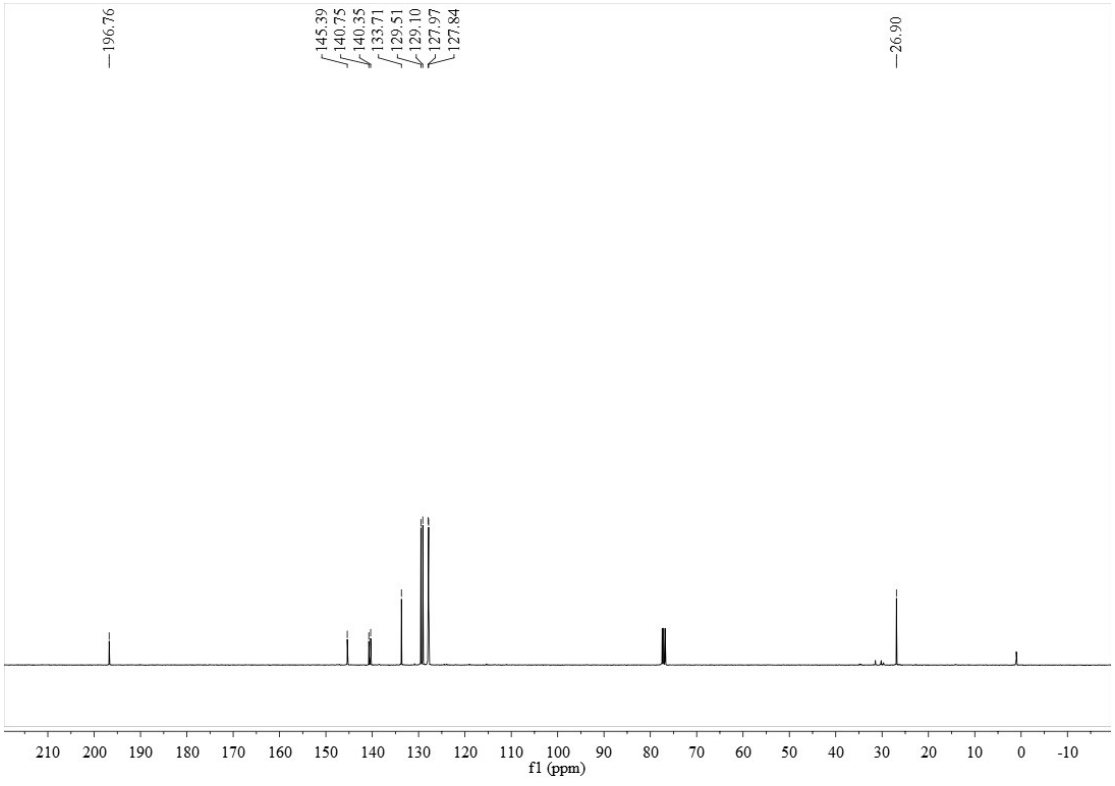
8.37
8.34
8.23
8.21
7.94
7.92
7.69
7.67
7.65
7.58
7.58
7.56
7.52
7.50
7.48
7.46
0.93
0.95
1.00
1.97
1.18
1.02
2.22
f1 (ppm)


147.39
142.94
139.07
133.07
132.09
129.72
128.76
126.98
126.67
121.94
f1 (ppm)


O
O
S
Ac


8.09
8.07
8.06
8.04
8.03
7.98
7.97
7.97
7.64
7.62
7.62
7.61
7.57
7.55
7.53
2.65
4.08
2.22
1.22
2.00
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)


196.76
145.39
140.75
140.35
133.71
129.51
129.10
127.97
127.84
26.90
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)