Solvent-Controlled Two-Step One-Pot Syntheses of α-X (X= Br or Cl) Enamino ketones/ esters and 3-(2, 5-dioxopyrrolidin-1-yl)acrylate by Terminal Carbonyl Alkynes

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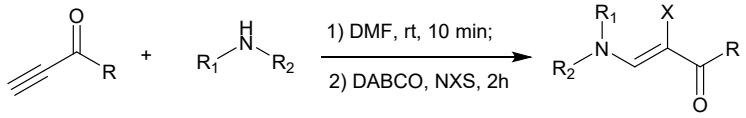
1 General Information

All reagents were obtained from commercial sources (Energy Chemical and Titan) with >99% purity and used without further purification unless otherwise noted. Some reactions have been performed in a dry 10 mL Schlenk tube under N_2. Analytical thin layer chromatography (TLC) was carried out with silica gel GF 254. Visualization was accomplished with a UV lamp. ^1H and ^{13}C NMR spectra were recorded on BRUKER DRX-400 spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. Mass spectra (API) were tested on Agilent 6100 Liquid Chromatography-Mass Spectrum. The single-crystal X-ray diffraction was conducted on BRUKER AXS Smart APEX II X-Ray Single Crystal Diffractometer at Zhejiang University, China.

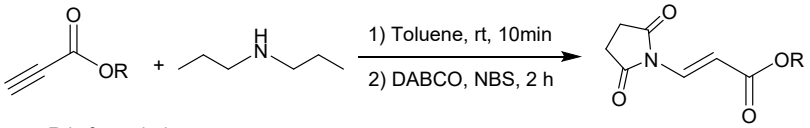
2.1 General Procedure for (*Z*)- 2-X (X= Cl or Br)-3-(di-amino)acrylate(3a/b/c)[1]



X = Cl or Br

A solution of terminal carbonyl alkynes (0.5 mmol, 1.0 equiv) and amines (0.75 mmol, 1.5 equiv) in 1 mL DMF in a dry pressure tube was allowed to stir at room temperature for 10 min. Then DABCO (1 mmol, 2 equiv) and NXS (1 mmol, 2 equiv) were added to above reaction mixture at room temperature with stirring. The finally reaction mixture was stirred for another 2h at room temperature. The residue was purified by neutral alumina column chromatography ($V_{petroleum\ ether}$ /V_{EtOAc}) without further work-up to provide corresponding products in moderate to good yields.

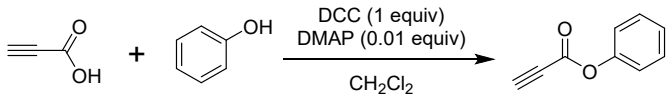
2.2 General Procedure for ethyl (*E*)-3-(2, 5-dioxopyrrolidin-1-yl) acrylate (3d)



R is fatty chain.

A solution of aliphatic propiolate (0.5 mmol 1.0 equiv) and dipropylamine (0.75 mmol 1.5 equiv) in 1 mL toluene was stirred 10 min at room temperature in a dry pressure tube. Then DABCO (1 mmol, 2 equiv) and NBS (1 mmol, 2 equiv) were allowed to add in the above reaction mixture at room temperature and the finally reaction mixture was continued to stir for another 2 h. The reaction residue was purified by silica gel chromatography ($V_{petroleum\ ether}$ /V_{EtOAc} = 3:1) without further work-up to provide corresponding products in moderate yields.

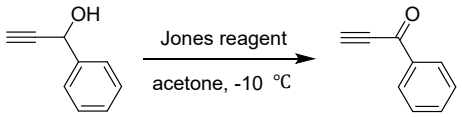
2.3 General procedure for Synthesis of phenyl propiolate[2]



A solution of DMAP (0.012 g, 0.010 mmol) and DCC (2.06 g, 10 mmol) in

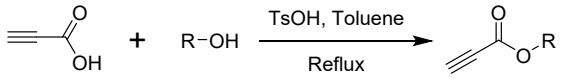
CH_2Cl_2 (15 mL) was added slowly over 1 h to a solution of propiolic acid (10 mmol) and phenol (11 mmol) in CH_2Cl_2 (15 mL) at 0 °C. The mixture was allowed to stir at room temperature until the acid was consumed (determined by TLC). Upon completion, the mixture was filtered through a layer of Celite 545, the filtrate was concentrated by rotary evaporation, and the residue was purified by silica gel column chromatography to afford corresponding propiolates in 83% yields.

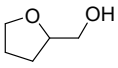
2.4 General procedure for Synthesis of 1-phenylprop-2-yn-1-one[3]



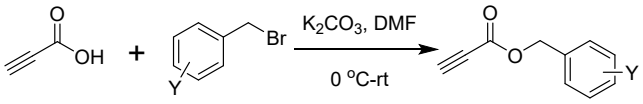
Jones reagent (0.75 mL, 1.2 equiv) was added to a solution of 1-Phenyl-2-propyn-1-ol (0.68g, 5.09 mmol) in acetone at -10 °C by dropwise, which left a persistent yellow tint after 30 min. Excess Jones reagent was quenched by the addition of 2-propanol (0.10 mL), and continued to stir for another 15 min at the same temperature. The reaction mixture was filtered through Celite 545 and dried by $MgSO_4$, subsequently the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (10% ethyl acetate in petroleum ether) to give the product as a volatile colorless liquid (401.8 mg, 3.72 mmol, 73%).

2.5 Synthesis of aliphatic or benzyl propiolate



R = $CH_3(CH_2)_5$, $CH_3(CH_2)_7$, $CH_3(CH_2)_8$ and 

A mixture of propionic acid (6.69 g, 95.5 mmol, 1.0 equiv), 1-hexanol (13.2 mL, 105.1 mmol, 1.1 equiv) and ρ-toluenesulfonic acid monohydrate (1.82 g, 9.6 mmol, 0.1 equiv) in toluene (275 mL) were refluxed for 18 h with a Dean-Stark apparatus. The solvent was removed in vacuo and the resultant yellow residue was purified by flash chromatography to yield the title compound as colourless oil.

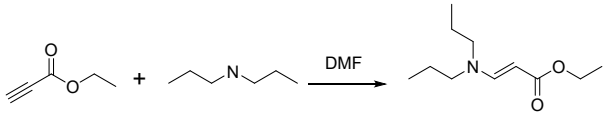


Y = CH_3, F, CF_3

A propionic acid (0.70 g, 10 mmol) in DMF (8 mL) was added to a suspension of K_2CO_3 (1.38 g, 10 mmol) in DMF (15 mL) and the reaction mixture was stirred at 0 ℃ for 10 min. Following by, benzyl bromide (1.45 g, 8.5 mmol) was added to the above mixture at room temperature, and the resulting solution was continued to stir for another 2 h and then the reaction was quenched with 25 mL water. The resulting solution was extracted with EtOAc (3×15 mL). The combined organic layers were washed with brine and then dried by Na_2SO_4. After evaporation of the solvent under reduced pressure, the crude product was purified by flash chromatography on silica

gel to give a series of colorless oil.

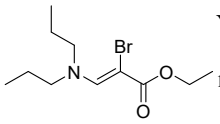
2.6 General Procedure for (*E*)-3-aminoacrylates[4]



Ethyl propiolate (0.5 mmol) was slowly added to the solution of Di-*n*-propylamine (0.75 mmol) in 1 mL DMF in a 1mL Pressure tube, and then the reaction mixture was continued to stir for another 10 min. The reaction was quenched with saturated aqueous $NaHCO_3$ (1 mL), and resulting solution was extracted by AcOEt (3×5 mL) . The combined organic layers was washed by saturated brine (3×5mL) and dried by Na_2SO_4.The filtrate was concentrated under reduced pressure after filtering. The residue was purified by column chromatography on silica gel (Petroleum ether /EtOAc) to afford desired product (*E*)-3-aminoacrylates.

3. Characterization of the products

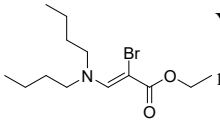
Ethyl (Z)-2-bromo-3-(dipropylamino)acrylate (3aa)



Yield: 81%, V_{PE} : V_{EA} = 10:1, light yellow oily liquid, 112.8 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 4.17 (*q*, *J* = 7.1 Hz, 2H), 3.32 (*t,* *J* = 7.9 Hz, 4H), 1.67-1.57 (m, 4H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 146.6, 75.1, 61.1, 22.9, 14.7, 10.9. HR-MS(ESI), m/z (%): Calcd for $C_{11}H_{20}BrNNaO_2$ ([M+Na]$^+$): 300.0570, Found: 300.0571.

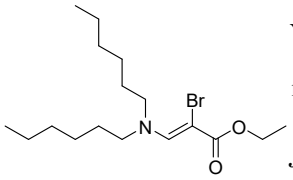
Ethyl (Z)-2-bromo-3-(dibutylamino)acrylate (3ab)



Yield: 70%, V_{PE} : V_{EA} = 10:1, yellow oily liquid, 107.3 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (*s*, 1H), 4.20 (*q*, *J* = 7.1 Hz, 2H), 3.44-3.33 (*t*, *J* = 7.4 Hz, 4H), 1.65-1.55 (m, 4H), 1.39-1.27 (m, 7H), 0.95 (*t*, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 146.6, 75.2, 61.0, 53.5, 31.7, 19.8, 14.7, 13.9. HR-MS(ESI), m/z (%): Calcd for $C_{13}H_{24}BrNNaO_2$ ([M+Na]$^+$): 328.0883, Found: 328.0887.

Ethyl (Z)-2-bromo-3-(dihexylamino)acrylate (3ac)

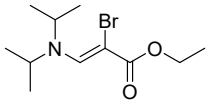


Yield: 75%, V_{PE} : V_{EA} = 10:1, yellow oily liquid, 136.0 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (*s*, 1H), 4.17 (*q*, *J* = 7.1 Hz, 2H), 3.35 (*t*, *J* = 7.6 Hz, 4H), 1.58 (*p*, *J* = 7.3 Hz, 4H), 1.32-1.25 (m, 15H), 0.87 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 146.8, 75.4, 61.3, 48.3, 31.9, 29.9, 26.5, 22.9, 15.0,

14.4. HR-MS(ESI), m/z (%): Calcd for $C_{17}H_{32}BrNNaO_2$ ([M+Na]$^+$): 384.1509, Found: 384.1515.

Ethyl (Z)-2-bromo-3-(diisopropylamino)acrylate (3ad)

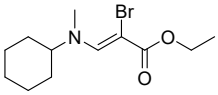


Yield: 58%, V_{PE} : V_{EA} = 10:1, yellow oily liquid, 80.8 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 4.18 (*q*, *J* = 7.1 Hz, 2H), 1.51 (*d*, *J* = 6.5 Hz, 2H), 1.27 (*t*, *J* = 7.1 Hz, 3H), 1.20 (*d, J* = 6.7 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 142.2, 75.1, 60.9, 47.2, 22.2, 14.6. HR-MS(ESI), m/z (%): Calcd for $C_{11}H_{20}BrNNaO_2$ ([M+Na]$^+$): 300.0570, Found: 300.0572.

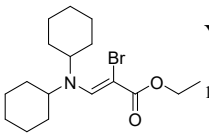
Ethyl (*Z*)-2-bromo-3-(cyclohexyl(methyl)amino)acrylate (3ae)

Yield: 58%, V_{PE}: V_{EA} = 10:1, light yellow oily liquid, 84.0 mg.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.17 (s, 3H), 1.85 – 1.77 (m, 4H), 1.68 – 1.59 (m, 1H), 1.49 – 1.36 (m, 2H), 1.35 – 1.20 (m, 6H), 1.07 (qt, *J* = 13.0, 3.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 146.4, 75.2, 61.0, 31.1, 25.6, 25.3, 14.7. HR-MS(ESI), m/z (%): Calcd for $C_{12}H_{20}BrNNaO_2$ ([M+Na]$^+$): 312.0570, Found: 312.0578.

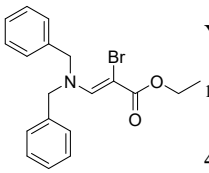
Ethyl (*Z*)-2-bromo-3-(dicyclohexylamino)acrylate (3af)



Yield: 60%, V_{PE}: V_{EA} = 10:1, light yellow oily liquid, 107.6 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (*s*, 1H), 4.15 (*q*, *J* = 7.1 Hz, 2H), 1.85-1.54 (*m*, 11H), 1.47-1.18 (*m*, 12H), 1.07 (*qt*, *J* = 12.7, 3.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 143.1, 74.5, 60.8, 56.2, 33.3, 25.8, 25.3, 14.6. HR-MS (ESI), m/z (%): Calcd for $C_{17}H_{28}BrNNaO_2$ ([M+Na]$^+$): 380.1196, Found: 380.1205.

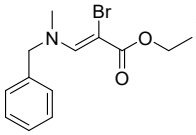
Ethyl (*Z*)-2-bromo-3-(dibenzylamino)acrylate (3ag)



Yield: 48%, V_{PE}: V_{EA}=10:1, light yellow oily liquid, 90.1 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (*s*, 1H), 7.43-7.33 (*m*, 6H), 7.29-7.24 (*m*, 4H), 4.65 (*s*, 4H), 4.27 (*q*, *J* = 7.1 Hz, 2H), 1.34 (*t*, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 147.2, 136.5, 128.9, 127.9, 127.7, 61.3, 14.6. HR-MS (ESI), m/z (%): Calcd for $C_{19}H_{20}BrNNaO_2$ ([M+Na]$^+$): 396.0570, Found: 396.0587.

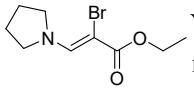
Ethyl (*Z*)-3-(benzyl(methyl)amino)-2-bromoacrylate (3ah)



Yield: 52%, V_{PE}: V_{EA}= 10:1, light yellow oily liquid, 77.7 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (*s*, 1H), 7.42-7.32 (*m*, 3H), 7.30-7.24 (*m*, 2H), 4.61 (*s*, 2H), 4.24 (*q*, *J* = 7.1 Hz, 2H), 3.16 (*s*, 3H), 1.31 (*d*, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 147.5, 136.4, 128.8, 127.9, 127.4, 77.3, 61.2, 59.7, 39.8, 14.6. HR-MS(ESI), m/z (%): Calcd for $C_{13}H_{16}BrNNaO_2$ ([M+Na]$^+$): 320.0257, Found: 320.0262.

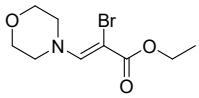
Ethyl (Z)-2-bromo-3-(pyrrolidin-1-yl)acrylate (3ai)



Yield: 65%, V_{PE}: V_{EA}= 10:1, yellow oily liquid, 80.7 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (*s*, 1H), 4.16 (*q*, *J* = 7.1 Hz, 2H), 3.66 (*s*, 4H), 1.88-1.83 (m, 4H), 1.25 (*t*, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 145.0, 76.6, 60.9, 51.3, 25.1, 14.6. HR-MS (ESI), m/z (%): Calcd for $C_9H_{14}BrNNaO_2$ ([M+Na]$^+$): 270.0100, Found:270.0101.

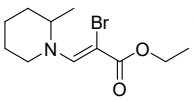
Ethyl (Z)-2-bromo-3-morpholinoacrylate (3aj)



Yield: 68%, V_{PE}: V_{EA}= 4:1, white solid, 90.4 mg, m.p. : 62.7-64.5 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 4.20 (*q*, *J* = 7.1 Hz, 2H), 3.74-3.68 (m, 8H), 1.28 (*t*, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 145.9, 77.7, 66.7, 61.3, 50.7, 14.5. HR-MS(ESI), m/z (%): Calcd for $C_9H_{14}BrNNaO_3$ ([M+Na]$^+$): 286.0049, Found:286.0050.

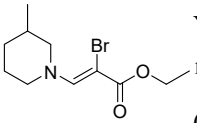
Ethyl (Z)-2-bromo-3-(2-methylpiperidin-1-yl)acrylate (3ak)



Yield: 55%, V_{PE}: V_{EA}= 10:1, light yellow oily liquid, 76.1 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.80-3.59 (m, 2H), 1.79-1.41 (m, 7H), 1.30-1.23 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 145.4, 75.3, 60.9, 31.4, 26.1, 19.8, 17.3, 14.6. HR-MS(ESI), m/z (%): Calcd for $C_{11}H_{18}BrNNaO_2$ ([M+Na]$^+$): 298.0413, Found: 298.0443.

Ethyl (Z)-2-bromo-3-(3-methylpiperidin-1-yl)acrylate (3al)

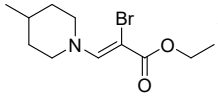


Yield: 45%, V_{PE}: V_{EA}= 10:1, light yellow oily liquid, 62.6 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 4.22 – 4.04 (m, 4H), 3.03 (m, 1H), 2.72 (dd, *J* = 13.0, 10.5 Hz, 1H), 1.91 – 1.81 (m, 1H), 1.71 m, 2H), 1.60 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.14 (m, 1H), 0.90 (d, *J* = 6.7 Hz, 3H. ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 146.2, 75.7,

61.1, 58.4, 51.5, 32.9, 31.8, 25.7, 18.8, 14.7. HR-MS(ESI), m/z (%): Calcd for $C_{11}H_{19}BrNO_2$ ($[M+H]^+$): 276.0594, Found:276.0603.

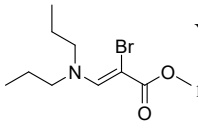
Ethyl (Z)-2-bromo-3-(4-methylpiperidin-1-yl)acrylate (3am)



Yield: 46%, V_{PE}: V_{EA}= 10:1, light yellow oily liquid, 63.8 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 4.27-4.14 (m, 4H), 3.02 (*ddd*, *J* = 13.2, 12.3, 2.6 Hz, 2H), 1.72-1.64 (*m*, 2H), 1.63-1.53 (*m*, 1H), 1.29-1.19 (*m*, 5H), 0.94 (*d*, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 146.2, 75.9, 61.1, 51.3, 34.5, 31.0, 21.8, 14.7. HR-MS(ESI), m/z (%): Calcd for $C_{11}H_{18}BrNNaO_2$ ($[M+Na]^+$): 298.0413, Found: 298.0437.

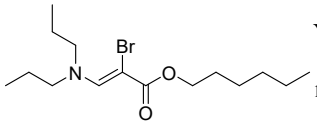
Methyl (Z)-2-bromo-3-(dipropylamino)acrylate (3ba)



Yield: 65%, V_{PE}: V_{EA}= 10:1, light yellow oily liquid, 85.5 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (*s*, 1H), 3.69 (*s*, 3H), 3.31 (*t*, *J* = 7.7 Hz, 4H), 1.66-1.55 (*m*, 4H), 0.87 (*t*, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 146.7, 74.5, 55.2, 52.2, 22.7, 10.8. HR-MS(ESI), m/z (%): Calcd for $C_{10}H_{18}BrNO_2$ ($[M+Na]^+$): 286.0413, Found: 286.0408.

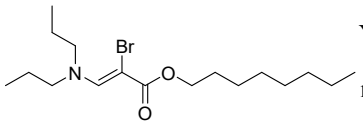
Hexyl (Z)-2-bromo-3-(dipropylamino)acrylate (3bb)



Yield: 65%, V_{PE}: V_{EA}= 20:1, yellow oily liquid, 108.9 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 4.13 (t, *J* = 6.7 Hz, 2H), 3.40-3.31 (m, 4H), 1.65 (m, 6H), 1.42-1.29 (m, 6H), 0.94-0.88 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 146.5, 75.2, 65.2, 54.9, 31.5, 28.8, 25.7, 22.8, 22.5, 14.0, 10.8. HR-MS(ESI), m/z (%): Calcd for $C_{15}H_{28}BrNNaO_2$ ($[M+Na]^+$): 356.1196, Found: 356.1205.

Octyl (Z)-2-bromo-3-(dipropylamino)acrylate (3bc)

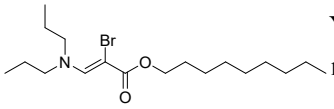


Yield: 67%, V_{PE}: V_{EA} = 20:1, reddish brown oily liquid, 121.6 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 4.09 (t, *J* = 6.7 Hz, 2H), 3.32 (t, *J* = 7.8 Hz, 4H), 1.67-1.56 (m, 6H), 1.35-1.24 (m, 10H), 0.91-0.83 (m, 9H).^{13}C NMR (100

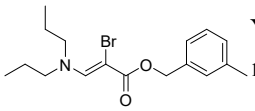
MHz, $CDCl_3$) δ 166.4, 146.5, 75.2, 65.3, 31.9, 29.3 (2C) , 29.0, 26.1, 22.8, 22.7, 14.2, 10.9. HR-MS(ESI), m/z (%): Calcd for $C_{17}H_{32}BrNNaO_2$ ($[M+Na]^+$): 384.1509, Found: 384.1515.

Nonyl (Z)-2-bromo-3-(dipropylamino)acrylate (3bd)



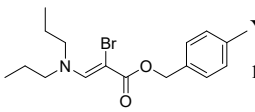
Yield: 68%, V_{PE}: V_{EA} = 20:1, reddish brown oily liquid, 128.1 mg. ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 4.11 (t, J = 6.7 Hz, 2H), 3.39-3.26 (m, 4H), 1.69-1.57 (m, 6H), 1.37-1.24 (m, 12H), 0.93-0.84 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 146.6, 75.3, 65.3, 32.0, 29.6, 29.4 (2C), 29.0, 26.1, 22.9, 22.8, 14.2, 10.9. HR-MS(ESI), m/z (%): Calcd for $C_{18}H_{34}BrNNaO_2$ ($[M+Na]^+$): 398.1665, Found: 398.1668.

3-Methylbenzyl (Z)-2-bromo-3-(dipropylamino)acrylate (3be)



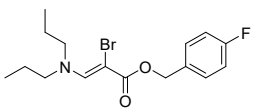
Yield: 51%, V_{PE}: V_{EA} = 20:1, light yellow oily liquid, 90.8 mg. ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.25-7.17 (m, 3H), 7.11 (d, J = 7.3 Hz, 1H), 5.17 (s, 2H), 3.34 (s, 4H), 2.36 (s, 3H), 1.64 (h, J = 7.4 Hz, 4H), 0.91 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 146.9, 138.1, 136.9, 128.6 (2C), 128.4, 124.9, 74.8, 66.7, 22.8, 21.5, 10.9. HR-MS(ESI), m/z (%): Calcd for $C_{17}H_{24}BrNNaO_2$ ($[M+Na]^+$): 376.0883, Found: 376.0879.

4-Methylbenzyl (Z)-2-bromo-3-(dipropylamino)acrylate (3bf)



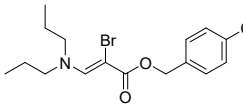
Yield: 48%, V_{PE}: V_{EA} = 20:1, light yellow oily liquid, 85.5 mg. ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 7.8 Hz, 2H), 5.16 (s, 2H), 3.40-3.27 (m, 4H), 2.34 (s, 3H), 1.63 (h, J = 7.4 Hz, 4H), 0.90 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 146.8, 137.6, 134.0, 129.2, 128.1, 75.0, 66.6, 22.8, 21.3, 10.9. HR-MS(ESI), m/z (%): Calcd for $C_{17}H_{24}BrNNaO_2$ ($[M+Na]^+$): 376.0883, Found: 376.0877.

4-Fluorobenzyl (Z)-2-bromo-3-(dipropylamino)acrylate (3bg)



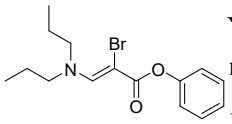
Yield: 54%, V_{PE}: V_{EA} = 20:1, light yellow oily liquid, 97.6 mg. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.39-7.33 (m, 2H), 7.05-6.97 (m, 2H), 5.14 (s, 2H), 3.33 (t, J = 7.7 Hz, 4H), 1.67-1.57 (m, 4H), 0.89 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 162.5 (d, J = 244 Hz), 147.0, 132.8 (d, J = 3 Hz), 129.8 (d, J = 8 Hz), 115.3 (d, J = 22 Hz), 74.5, 65.9, 22.8, 10.8. HR-MS(ESI), m/z (%): Calcd for $C_{16}H_{21}BrFNNaO_2$ ($[M+Na]^+$): 380.0632, Found: 380.0622.

3-(Trifluoromethyl)benzyl (Z)-2-bromo-3-(dipropylamino)acrylate (3bh)



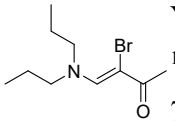
Yield: 67%, V_{PE}: V_{EA} = 20:1, light yellow oily liquid, 136.5 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.60 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 5.24 (s, 2H), 3.45-3.26 (m, 4H), 1.64 (h, J = 7.4 Hz, 4H), 0.91 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 147.3, 141.2 (d, J =1 Hz), 129.8 (q, J = 32 Hz), 127.8, 125.5 (q, J = 4 Hz), 126.5 (q, J = 243 Hz), 74.2, 65.7, 22.9, 10.9. HR-MS(ESI), m/z (%): Calcd for $C_{17}H_{21}BrF_3NNaO_2$ ([M+Na]$^+$): 430.0600, Found: 430.0608.

Phenyl (Z)-2-bromo-3-(dipropylamino)acrylate (3bi)



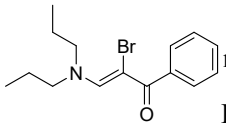
Yield: 55%, V_{PE}: V_{EA} = 10:1, light yellow oily liquid, 90.0 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.41-7.32 (m, 2H), 7.23-7.16 (m, 1H), 7.14-7.08 (m, 2H), 3.41 (s, 4H), 1.69 (h, J = 7.4 Hz, 4H), 0.94 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 151.8, 147.8, 129.2, 125.2, 122.0, 73.9, 22.8, 10.8. HR-MS(ESI), m/z (%): Calcd for $C_{15}H_{20}BrNNaO_2$ ([M+Na]$^+$): 348.0570, Found: 348.0578.

(Z)-3-bromo-4-(dipropylamino)but-3-en-2-one (3bj)



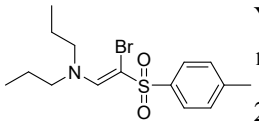
Yield: 65%, V_{PE}: V_{EA} = 8:1, light yellow oily liquid, 80.8 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 3.36 (s, 4H), 2.30 (s, 3H), 1.62 (h, J = 7.4 Hz, 4H), 0.88 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 147.0, 89.0, 27.0, 22.9, 10.8. HR-MS(ESI), m/z (%): Calcd for $C_{10}H_{18}BrNNaO$ ([M+Na]$^+$): 270.0464, Found: 270.0457.

(Z)-2-bromo-3-(dipropylamino)-1-phenylprop-2-en-1-one (3bk)



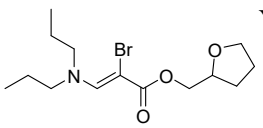
Yield: 69%, V_{PE}: V_{EA} = 8:1, light yellow oily liquid, 107.2 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.32 (m, 6H), 3.33 (s, 4H), 1.60 (q, J = 7.2 Hz, 4H), 0.87 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 152.9, 140.7, 129.8, 128.2, 128.1, 91.6, 22.7, 10.8. HR-MS(ESI), m/z (%): Calcd for $C_{15}H_{20}BrNNaO$ ([M+Na]$^+$): 332.0620, Found: 332.0617.

(Z)-*N*-(2-bromo-2-tosylvinyl)-N-propylpropan-1-amine (3bl)



Yield: 85%, V_{PE}: V_{EA} = 8:1, yellow oily liquid, 153.0 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.77-7.73 (m, 2H), 7.29-7.27 (m, 2H), 3.29 (t, J = 7.7 Hz, 4H), 2.41 (s, 3H), 1.68-1.54 (m, 4H), 0.89 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 143.0, 137.8, 129.3, 127.8, 81.0, 22.6, 21.6, 10.7. HR-MS(ESI), m/z (%): Calcd for $C_{15}H_{22}BrSNNaO_2$ ([M+Na]$^+$): 382.0447, Found: 382.0442.

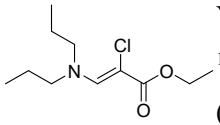
(Tetrahydrofuran-2-yl)methyl (Z)-2-bromo-3-(dipropylamino)acrylate (3bm)



Yield: 66%, V_{PE}: V_{EA} = 20:1, light yellow oily liquid, 110.4 mg.

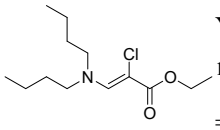
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 4.19-4.03 (m, 3H), 3.91-3.74 (m, 2H), 3.39-3.25 (m, 4H), 2.02-1.81 (m, 3H), 1.71-1.55 (m, 5H), 0.88 (t, J = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 146.9, 76.9, 74.8, 68.6, 67.1, 28.1, 25.9, 22.8, 10.9. HR-MS(ESI), m/z (%): Calcd for $C_{14}H_{24}BrNNaO_3$ ([M+Na]$^+$): 356.0832, Found: 356.0822.

Ethyl (Z)-2-chloro-3-(dipropylamino)acrylate (3ca)



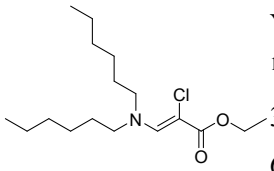
Yield: 65%, V_{PE}: V_{EA} =10:1, light yellow oily liquid, 76.1 mg.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.35-3.24 (m, 4H), 1.60 (h, J = 7.4 Hz, 4H), 1.25 (t, J = 7.1 Hz, 3H), 0.87 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 144.1, 87.8, 60.7, 54.7, 22.8, 14.6, 10.8. HR-MS(ESI), m/z (%): Calcd for $C_{11}H_{20}ClNNaO_2$ ([M+Na]$^+$): 256.1075, Found: 256.1075.

Ethyl (Z)-2-chloro-3-(dibutylamino)acrylate (3cb)



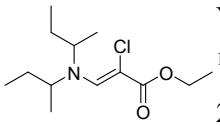
Yield: 48%, V_{PE}: V_{EA} = 8:1, light yellow oily liquid, 62.7 mg.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.34 (t, J = 7.3 Hz, 4H), 1.64-1.51 (m, 4H), 1.36-1.25 (m, 7H), 0.92 (t, J = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 144.1, 87.8, 60.7, 31.7, 19.7, 14.6, 13.8. HR-MS(ESI), m/z (%): Calcd for $C_{15}H_{28}ClNNaO_2$ ([M+Na]$^+$): 284.1393, Found:284.1380.

Ethyl (Z)-2-chloro-3-(dihexylamino)acrylate (3cc)



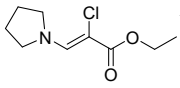
Yield: 55%, V_{PE}: V_{EA} = 10:1, light yellow oily liquid, 87.6 mg.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.40-3.27 (m, 4H), 1.58 (p, J = 7.3 Hz, 4H), 1.31-1.24 (m, 15H), 0.92 – 0.83 (m, 6H).13C NMR (100 MHz, $CDCl_3$) δ 166.4, 144.1, 87.8, 60.7, 31.5, 29.6, 26.2, 22.5, 14.6, 14.0. HR-MS(ESI), m/z (%): Calcd for $C_{17}H_{32}ClNNaO_2$ ([M+Na]$^+$): 340.2014, Found: 340.2009.

Ethyl (Z)-2-chloro-3-(di-sec-butylamino)acrylate (3cd)



Yield: 30%, V_{PE}: V_{EA} = 10:1, light yellow oily liquid, 39.0 mg.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 5.7 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 1.66-1.46 (m, 4H), 1.35-1.23 (m, 5H), 1.20 (d, J = 6.7 Hz, 6H), 0.91 (td, J = 7.4, 5.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 140.6, 87.9, 60.8, 53.6, 14.7, 11.4, 11.3. HR-MS(ESI), m/z (%): Calcd for $C_{13}H_{24}ClNNaO_2$ ([M+Na]$^+$): 284.1388, Found:284.1380.

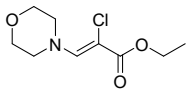
Ethyl (Z)-2-chloro-3-(pyrrolidin-1-yl)acrylate (3ce)



Yield: 43%, V_{PE}: V_{EA} = 10:1, light yellow oily liquid, 43.9 mg.

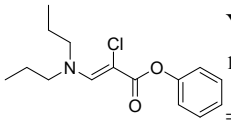
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.64 (s, 4H), 1.89-1.81 (m, 4H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 142.5, 89.3, 60.6, 51.1, 25.2, 14.6. HR-MS(ESI), m/z (%): Calcd for $C_9H_{14}ClNNaO_2$ ([M+Na]$^+$): 226.0605, Found: 226.0600.

Ethyl (Z)-2-chloro-3-morpholinoacrylate (3cf)



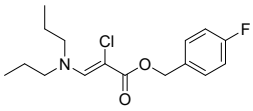
Yield: 43%, V_{PE}: V_{EA} = 10:1, white solid, 47.6 mg, m.p. : 74.3-76.1 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.75-3.65 (m, 8H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 143.6, 90.6, 66.9, 61.2, 50.8, 14.6. HR-MS(ESI), m/z (%): Calcd for $C_9H_{14}ClNNaO_3$ ([M+Na]$^+$): 242.0554, Found: 242.0554.

Phenyl (Z)-2-chloro-3-(dipropylamino)acrylate (3cg)



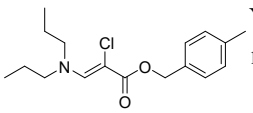
Yield: 58%, V_{PE}: V_{EA} = 20:1, light yellow oily liquid, 81.8 mg.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.38 (d, J = 1.9 Hz, 2H), 7.19 (t, J = 7.4 Hz, 1H), 7.15-7.09 (m, 2H), 3.39 (s, 4H), 1.76-1.62 (m, 4H), 0.94 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 151.7, 145.6, 129.3, 125.3, 122.1, 87.2, 23.0, 11.0. HR-MS(ESI), m/z (%): Calcd for $C_{15}H_{20}ClNNaO_2$ ([M+Na]$^+$): 304.1075, Found: 304.1072.

4-Fluorobenzyl (Z)-2-chloro-3-(dipropylamino)acrylate (3ch)



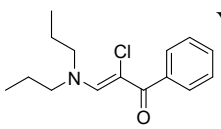
Yield: 53%, V_{PE}: V_{EA} =20:1, light yellow oily liquid, 82.9 mg.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.40-7.33 (m, 2H), 7.06-6.99 (m, 2H), 5.15 (s, 2H), 3.33 (t, J = 7.8 Hz, 4H), 1.68-1.58 (m, 4H), 0.90 (t, J = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 162.4 (d, J = 244 Hz), 144.6, 132.7 (d, J = 3 Hz), 129.8 (d, J = 8 Hz), 115.3 (d, J = 22 Hz), 87.5, 65.6, 22.8, 10.9. HR-MS(ESI), m/z (%): Calcd for $C_{16}H_{21}ClFNNaO_2$ ([M+Na]$^+$): 336.1137, Found: 336.1135.

4-Methylbenzyl (Z)-2-chloro-3-(dipropylamino)acrylate (3ci)



Yield: 35%, V_{PE}: V_{EA} = 10:1, light yellow oily liquid, 54.4 mg.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 7.8 Hz, 2H), 5.16 (s, 2H), 3.38-3.25 (m, 4H), 2.35 (s, 3H), 1.63 (h, J = 7.4 Hz, 4H), 0.90 (t, J = 7.4 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 144.6, 137.7, 134.0, 129.2, 128.2, 87.9, 66.4, 23.0, 21.31, 11.0. HR-MS(ESI), m/z (%): Calcd for $C_{17}H_{24}ClNNaO_2$ ([M+Na]$^+$): 332.1388, Found: 332.1384.

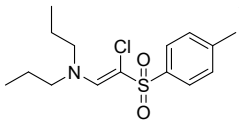
(*Z*)-2-Chloro-3-(dipropylamino)-1-phenylprop-2-en-1-one (3cj)



Yield: 72%, V_{PE}: V_{EA} = 10:1, light yellow oily liquid, 95.8 mg.

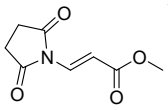
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.43 (m, 2H), 7.41-7.33 (m, 3H), 7.18 (s, 1H), 3.33 (s, 4H), 1.62 (q, J = 7.5 Hz, 4H), 0.89 (t, J = 7.4 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 190.0, 150.5, 140.6, 129.9, 128.3, 128.2, 102.1, 22.9, 11.0. HR-MS(ESI), m/z (%): Calcd for $C_{15}H_{20}ClNNaO$ ($[M+Na]^+$): 288.1126, Found: 288.1118.

(*Z*)-*N*-(2-Chloro-2-tosylvinyl)-N-propylpropan-1-amine (3ck)



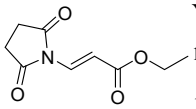
Yield: 80%, V_{PE}: V_{EA} =10:1, light yellow oily liquid, 132.8 mg.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.72 (m, 2H), 7.52 (s, 1H), 7.28 (d, J = 8.0 Hz, 2H), 3.26 (t, J = 7.6 Hz, 4H), 2.41 (s, 3H), 1.66-1.52 (m, 4H), 0.88 (t, J = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 142.0, 137.8, 129.5, 127.8, 94.3, 22.8, 21.6, 10.9. HR-MS(ESI), m/z (%): Calcd for $C_{15}H_{22}ClSNNaO_2$ ($[M+Na]^+$): 338.0952, Found: 338.0944.

Methyl (*E*)-3-(2,5-dioxopyrrolidin-1-yl)acrylate (3da) [5]



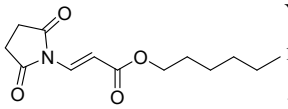
Yield: 67%, V_{PE}: V_{EA} = 3:1, light yellow oily liquid, 61.4 mg.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 14.8 Hz, 1H), 6.91 (d, J = 14.8 Hz, 1H), 3.72 (s, 3H), 2.80 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 167.2, 131.1, 110.1, 51.8, 27.8.

Ethyl (E)-3-(2,5-dioxopyrrolidin-1-yl)acrylate (3db) [5]



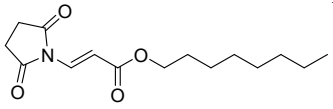
Yield: 69%, V_{PE}: V_{EA} = 3:1, light yellow oily liquid, 68.1 mg.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 14.8 Hz, 1H), 6.92 (d, J = 14.8 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 2.79 (s, 4H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 166.8, 130.9, 110.8, 60.8, 27.8, 14.3.

Hexyl (E)-3-(2,5-dioxopyrrolidin-1-yl)acrylate (3dc)



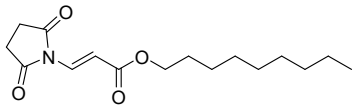
Yield: 60%, V_{PE}: V_{EA} = 3:1, light yellow oily liquid, 76.0 mg.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 14.8 Hz, 1H), 6.98 (d, J = 14.8 Hz, 1H), 4.15 (t, J = 6.7 Hz, 2H), 2.82 (s, 4H), 1.65 (p, J = 6.8 Hz, 2H), 1.37-1.27 (m, 6H), 0.90-0.86 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 167.0, 130.9, 111.0, 65.1, 31.5, 28.7, 27.9, 25.7, 22.7, 14.1.

Octyl (E)-3-(2,5-dioxopyrrolidin-1-yl)acrylate (3dd)



Yield: 52%, V_{PE}: V_{EA} = 3:1, light yellow oily liquid, 73.0 mg.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 14.8 Hz, 1H), 6.97 (d, J = 14.8 Hz, 1H), 4.15 (t, J = 6.7 Hz, 2H), 2.81 (s, 4H), 1.69-1.61 (m, 2H), 1.35-1.23 (m, 10H), 0.92-0.81 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 167.0, 130.9, 111.0, 65.1, 31.9, 29.3 (2C), 28.7, 27.9, 26.0, 22.7, 14.2.

Nonyl (E)-3-(2,5-dioxopyrrolidin-1-yl)acrylate (3de)



Yield: 51%, V_{PE}: V_{EA} = 3:1, light yellow oily liquid, 75.6 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 14.8 Hz, 1H), 6.97 (d, J = 14.8 Hz, 1H), 4.14 (t, J = 6.7 Hz, 2H), 2.81 (s, 4H), 1.64 (dt, J = 8.0, 6.5 Hz, 2H), 1.35-1.24 (m, 12H), 0.89-0.84 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 166.6, 130.6, 110.7, 64.7, 31.6, 29.3, 29.0 (2C), 28.4, 27.6, 25.7, 22.4, 13.9.

4. Reference:

[1] H.-J. Gais, K. Hafner and M. Neuenschwander, *Helv. Chim. Acta*, 1969, **52**, 2641-2657.

[2] (a)L. Liu, K. Sun, L. Su, J. Dong, L. Cheng, X. Zhu, C.-T. Au, Y. Zhou and S.-F. Yin, *Org. Lett.*, 2018, **20**, 4023-4027；(b) J. S. Oakdale, R. K. Sit and V. V. Fokin, *Chem. Eur. J.*, 2014, **20**, 11101-11110.

[3] G. Ieronimo, G. Palmisano, A. Maspero, A. Marzorati, L. Scapinello, N. Masciocchi, G. Cravotto, A. Barge, M. Simonetti, K. L. Ameta, K. M. Nicholas and A. Penoni, *Org. Biomol. Chem.*, 2018, **16**, 6853-6859.

[4] X. Y. Chen, L. Zhang, Y. Tang, S. Yuan, B. Zhu, G. Chen and X. Cheng, *Synlett*, 2020, **31**, 878-882.

[5] (a) L. Mola, J. Font, L. Bosch, J. Caner, A. M. Costa, G. Etxebarría-Jardí, O. Pineda, D. de Vicente and J. Vilarrasa, *J. Org. Chem.*, 2013, **78**, 5832-5842; (b) Y. Liu, D. Li and C.-M. Park, *Angew. Chem. Int. Ed.*, 2011, **50**, 7333-7336; (c) A. Ramazani, M. Kardan and N. Noshiranzadeh, *Synth. Commun.*, 2008, **38**, 383-390.

5. Characterization of the products

Table **S1** Crystal data and structure refinement of product **3aj**

Identification code	1
Empirical formula	C_9 H_{14} Br N O_3
Formula weight	264.12
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 4.5418(3) A alpha = 109.638(4) deg. b = 10.9707(7) A beta = 92.037(4) deg. c = 11.8989(6) A gamma = 101.081(5) deg.
Volume	544.76(6) A^3
Z, Calculated density	2, 1.610 Mg/m^3

Absorption coefficient	3.756 mm^-1
F(000)	268
Crystal size	0.280 x 0.240 x 0.200 mm
Theta range for data collection	3.163 to 27.657 deg.
Limiting indices	-5<=h<=5, -14<=k<=14, -15<=l<=15
Reflections collected / unique	5605 / 2473 [R(int) = 0.0188]
Completeness to theta = 25.242	98.3 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2473 / 0 / 128
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0355, wR2 = 0.0907
R indices (all data)	R1 = 0.0451, wR2 = 0.0953
Extinction coefficient	n/a
Largest diff. peak and hole	0.802 and -0.575 e.A^-3

Table **S2**. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for product **3aj**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	9802(1)	1492(1)	9339(1)	63(1)
C(1)	3267(8)	-3302(3)	5712(3)	70(1)
C(2)	3368(6)	-1886(3)	5856(2)	54(1)
C(3)	4445(7)	-2750(3)	7762(3)	67(1)
C(4)	4567(7)	-1304(3)	7999(2)	56(1)
C(5)	7499(5)	-20(2)	6850(2)	40(1)
C(6)	9518(5)	1010(2)	7650(2)	40(1)
C(7)	11599(5)	1841(2)	7162(2)	42(1)
C(8)	15525(6)	3727(3)	7541(2)	54(1)
C(9)	17572(7)	4723(3)	8592(3)	70(1)
N(1)	5379(5)	-1006(2)	6929(2)	46(1)
O(1)	2377(5)	-3577(2)	6752(2)	73(1)
O(2)	11692(5)	1635(2)	6098(2)	65(1)
O(3)	13430(4)	2875(2)	7997(2)	50(1)

Table **S3**. Bond lengths [A] and angles [deg] for product **3aj**.

Br(1)-C(6)	1.892(2)
C(1)-O(1)	1.424(4)
C(1)-C(2)	1.495(5)
C(2)-N(1)	1.465(3)
C(3)-O(1)	1.417(4)
C(3)-C(4)	1.505(4)
C(4)-N(1)	1.460(3)
C(5)-N(1)	1.334(3)
C(5)-C(6)	1.357(3)
C(6)-C(7)	1.457(3)
C(7)-O(2)	1.213(3)
C(7)-O(3)	1.337(3)
C(8)-O(3)	1.452(3)
C(8)-C(9)	1.493(4)
O(1)-C(1)-C(2)	111.5(3)
N(1)-C(2)-C(1)	110.0(2)
O(1)-C(3)-C(4)	111.9(3)
N(1)-C(4)-C(3)	108.9(2)
N(1)-C(5)-C(6)	134.8(2)
C(5)-C(6)-C(7)	116.90(19)
C(5)-C(6)-Br(1)	125.91(17)
C(7)-C(6)-Br(1)	117.17(16)
O(2)-C(7)-O(3)	122.0(2)
O(2)-C(7)-C(6)	124.0(2)
O(3)-C(7)-C(6)	114.03(19)
O(3)-C(8)-C(9)	107.2(2)
C(5)-N(1)-C(4)	128.4(2)
C(5)-N(1)-C(2)	119.5(2)
C(4)-N(1)-C(2)	112.0(2)
C(3)-O(1)-C(1)	109.7(2)
C(7)-O(3)-C(8)	115.42(19)

Symmetry transformations used to generate equivalent atoms:

Table **S4**. Anisotropic displacement parameters (A^2 x 10^3) for 1.

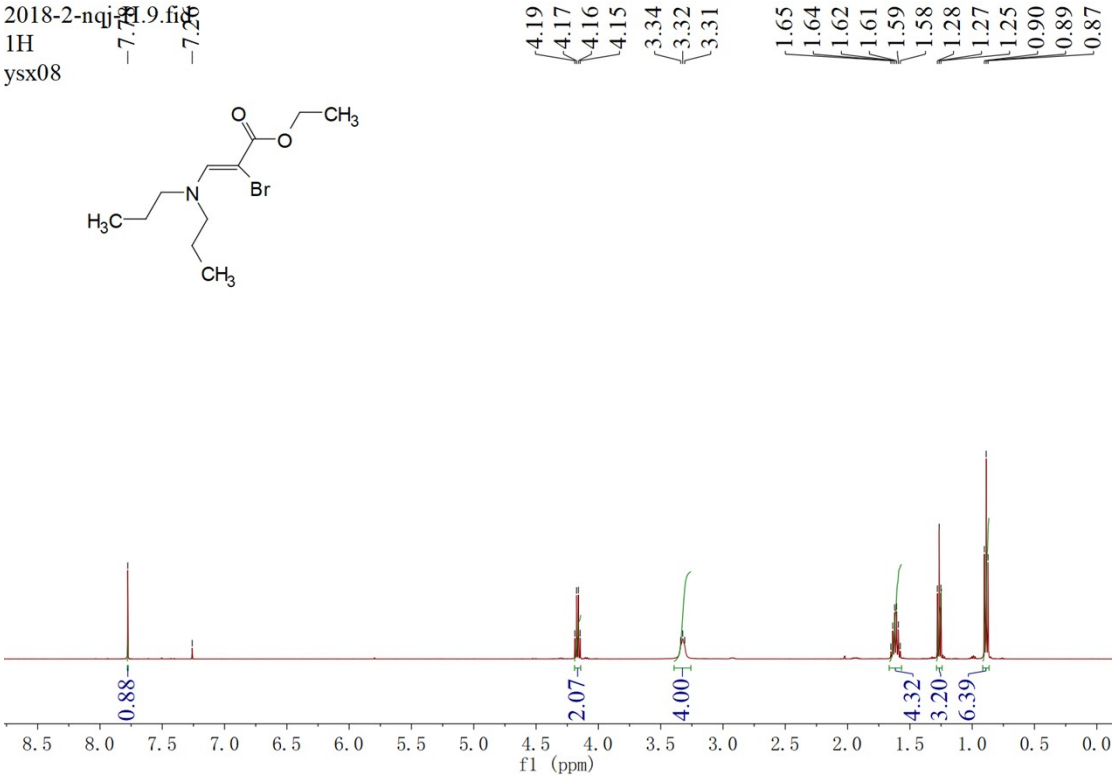
The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

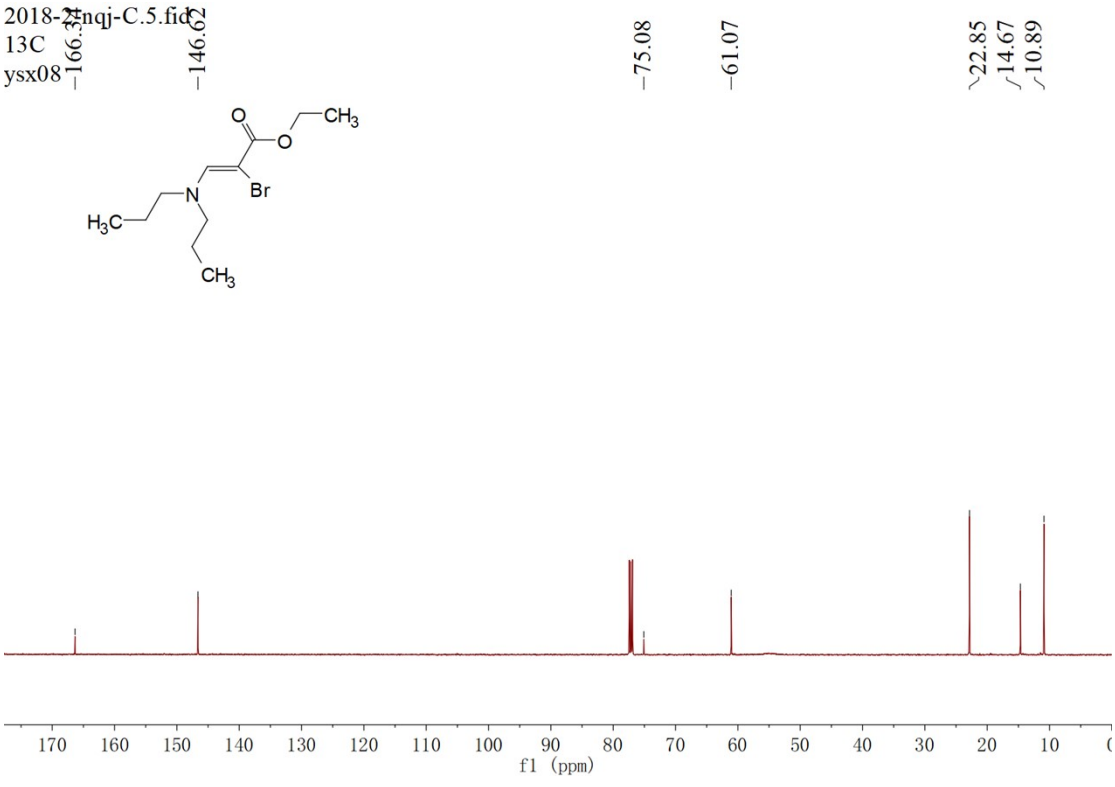
	U11	U22	U33	U23	U13	U12
Br(1)	93(1)	58(1)	30(1)	16(1)	5(1)	-4(1)
C(1)	80(2)	54(2)	59(2)	9(1)	12(1)	-8(1)
C(2)	50(1)	63(2)	44(1)	21(1)	1(1)	-3(1)
C(3)	74(2)	63(2)	73(2)	42(2)	8(2)	2(1)
C(4)	69(2)	55(1)	44(1)	25(1)	12(1)	0(1)
C(5)	48(1)	42(1)	34(1)	19(1)	7(1)	11(1)
C(6)	52(1)	40(1)	31(1)	16(1)	6(1)	8(1)
C(7)	49(1)	42(1)	34(1)	14(1)	3(1)	7(1)
C(8)	61(1)	51(1)	48(1)	22(1)	5(1)	-2(1)
C(9)	77(2)	57(2)	63(2)	19(1)	-4(1)	-9(1)
N(1)	55(1)	45(1)	36(1)	18(1)	5(1)	1(1)
O(1)	85(1)	54(1)	73(2)	29(1)	11(1)	-12(1)
O(2)	74(1)	74(1)	35(1)	21(1)	2(1)	-17(1)
O(3)	62(1)	45(1)	39(1)	16(1)	3(1)	-4(1)

Table **S5**. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 1.

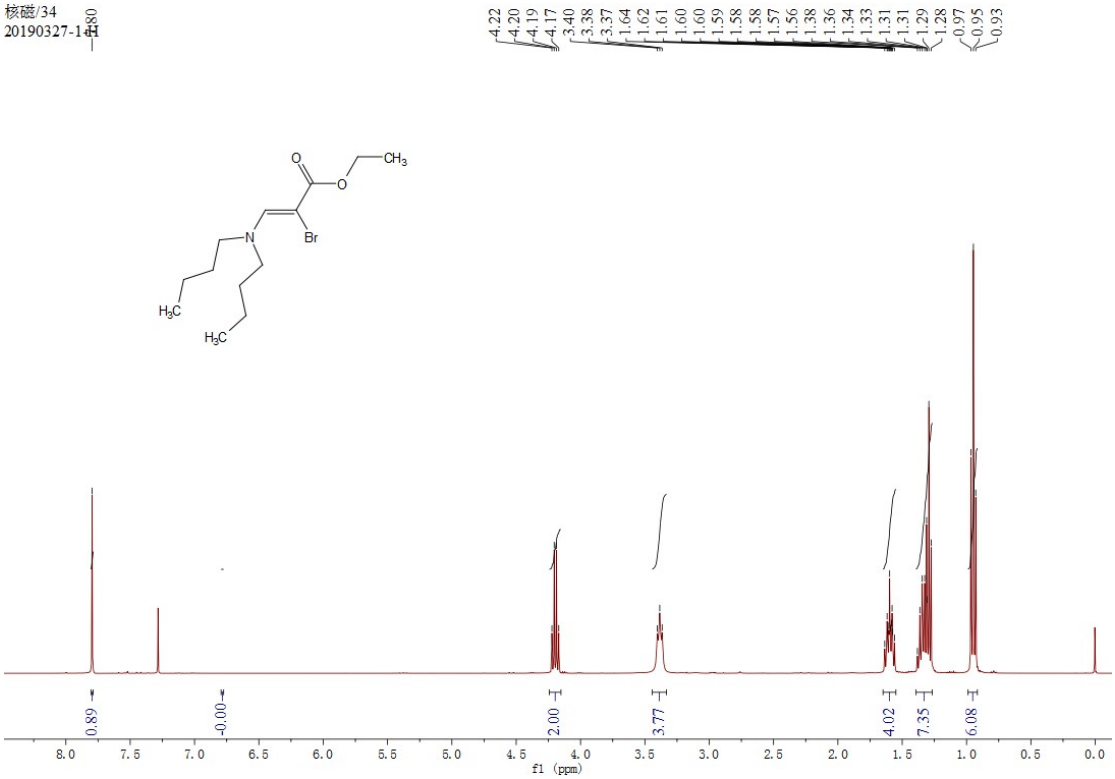
	x	y	z	U(eq)
H(1A)	1854	-3875	5022	84
H(1B)	5246	-3492	5563	84
H(2A)	4087	-1716	5153	65
H(2B)	1354	-1714	5927	65
H(3A)	6439	-2927	7626	81
H(3B)	3855	-2959	8463	81
H(4A)	2617	-1104	8193	67
H(4B)	6053	-765	8675	67
H(5)	7621	-45	6064	48
H(8A)	14436	4169	7138	65
H(8B)	16683	3208	6972	65
H(9A)	16412	5256	9130	105
H(9B)	19049	5280	8318	105
H(9C)	18572	4273	9002	105

6. NMR spectra of products





核磁/34
20190327-1-H



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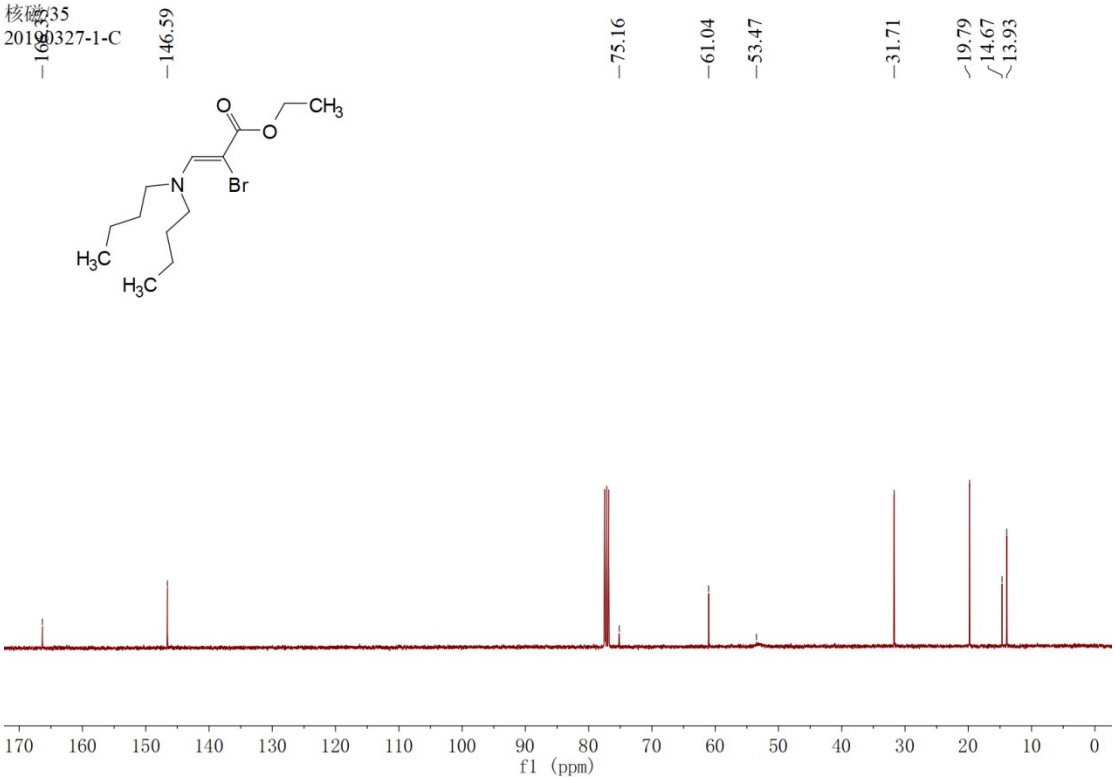
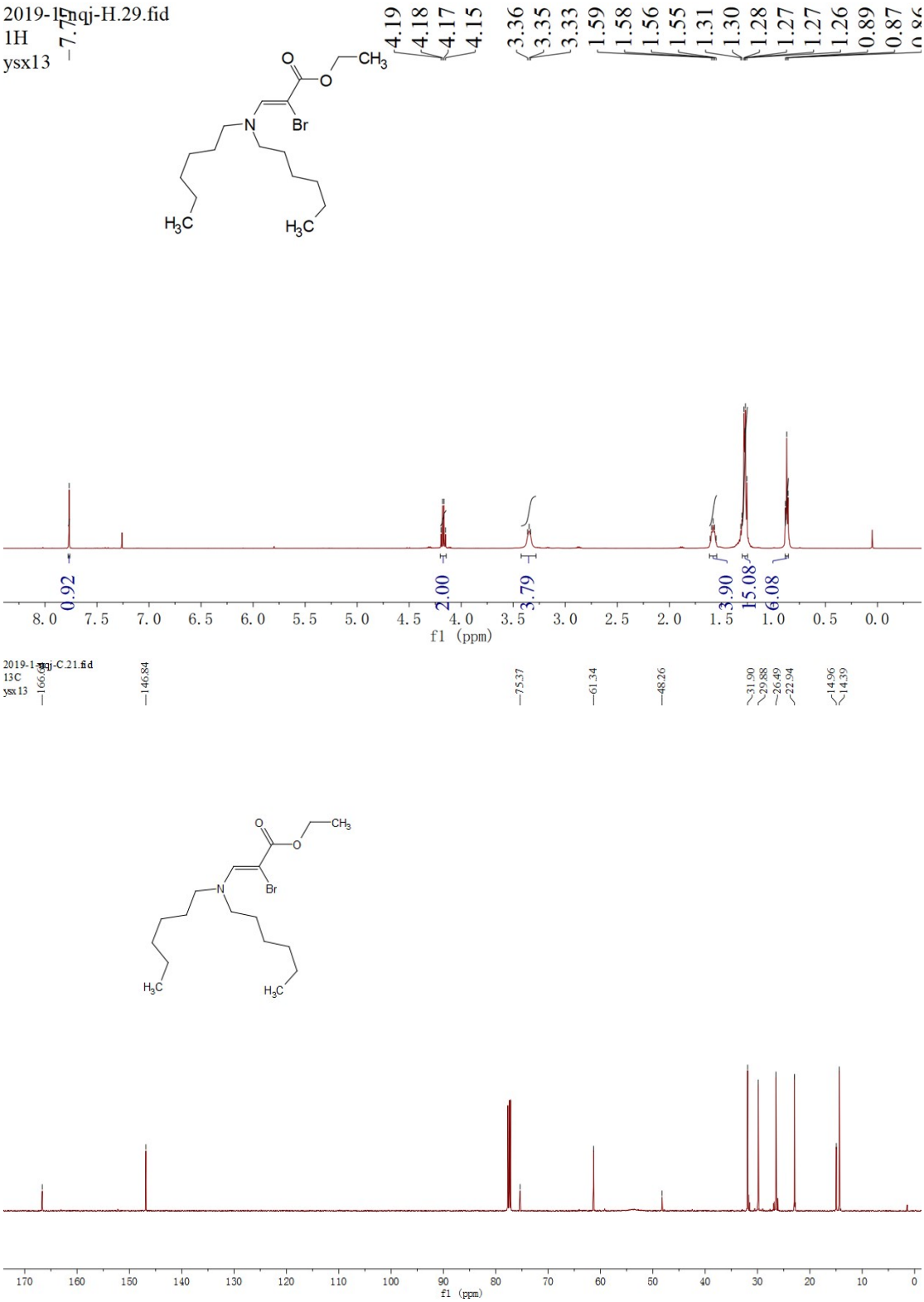
20190327-1-C

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Br
H3C
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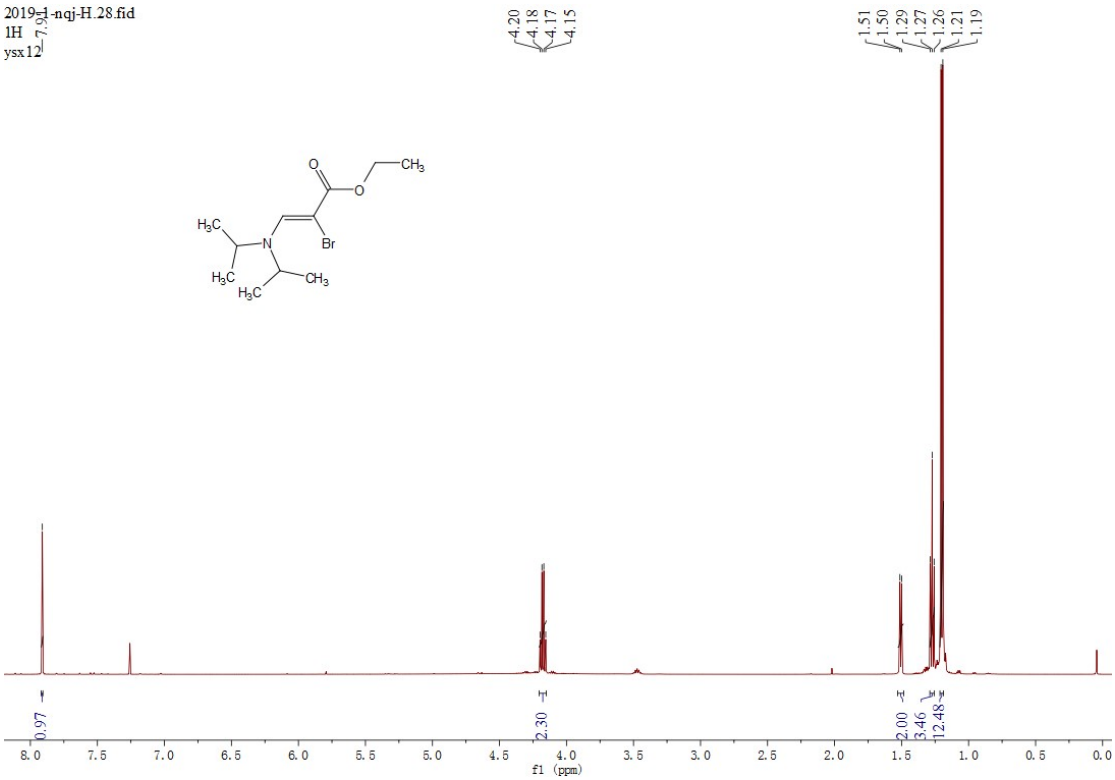
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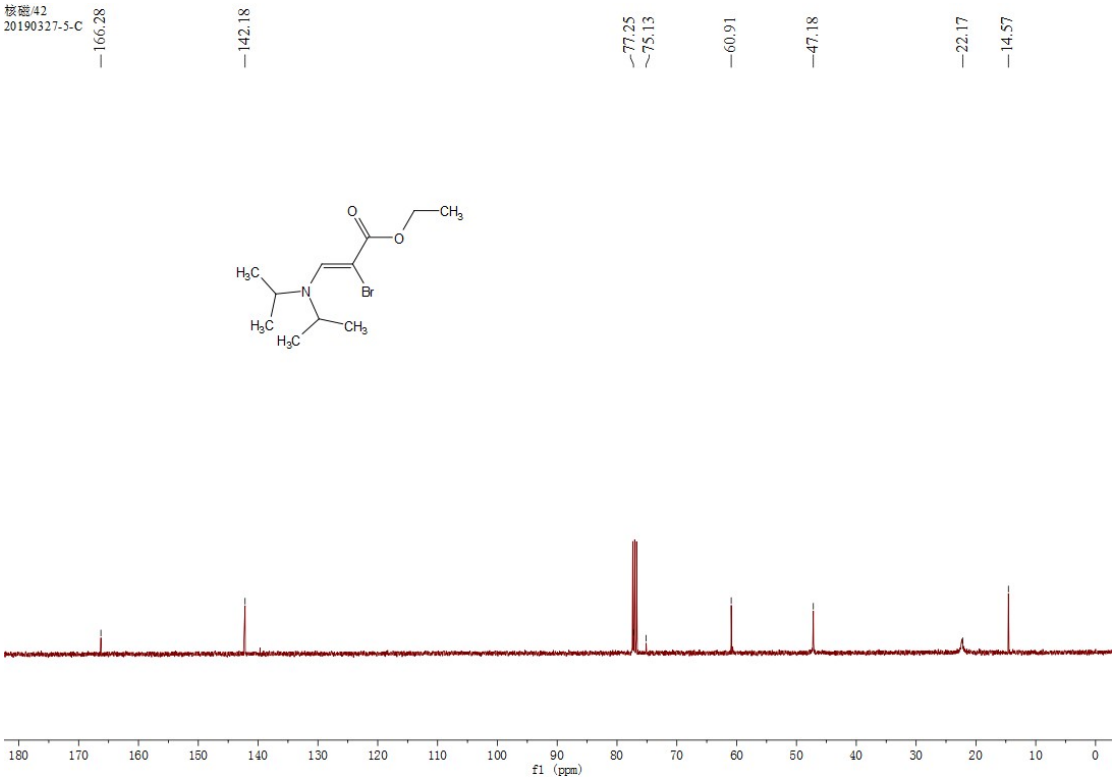
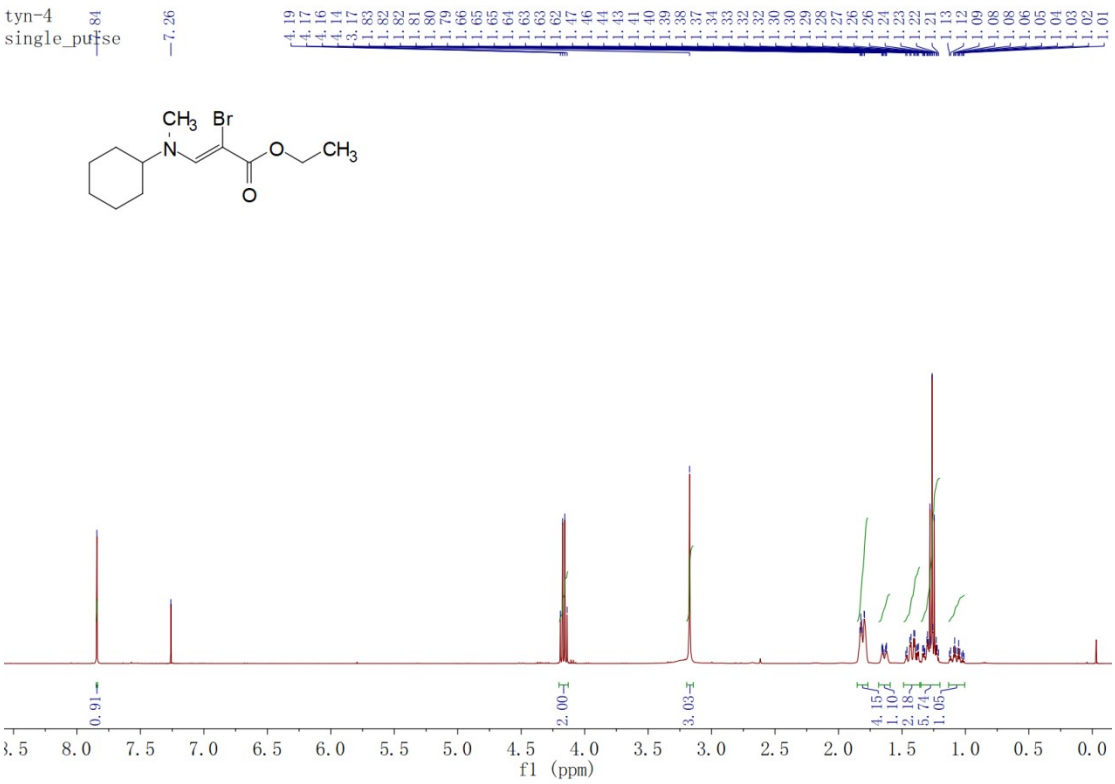
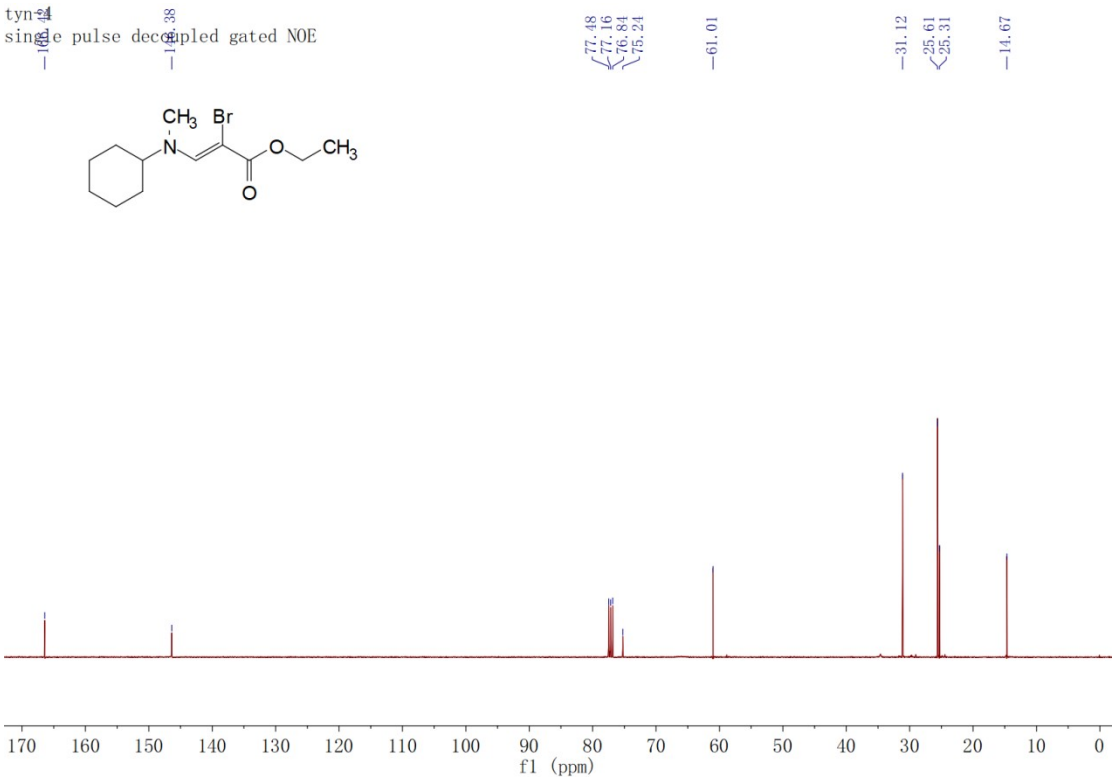
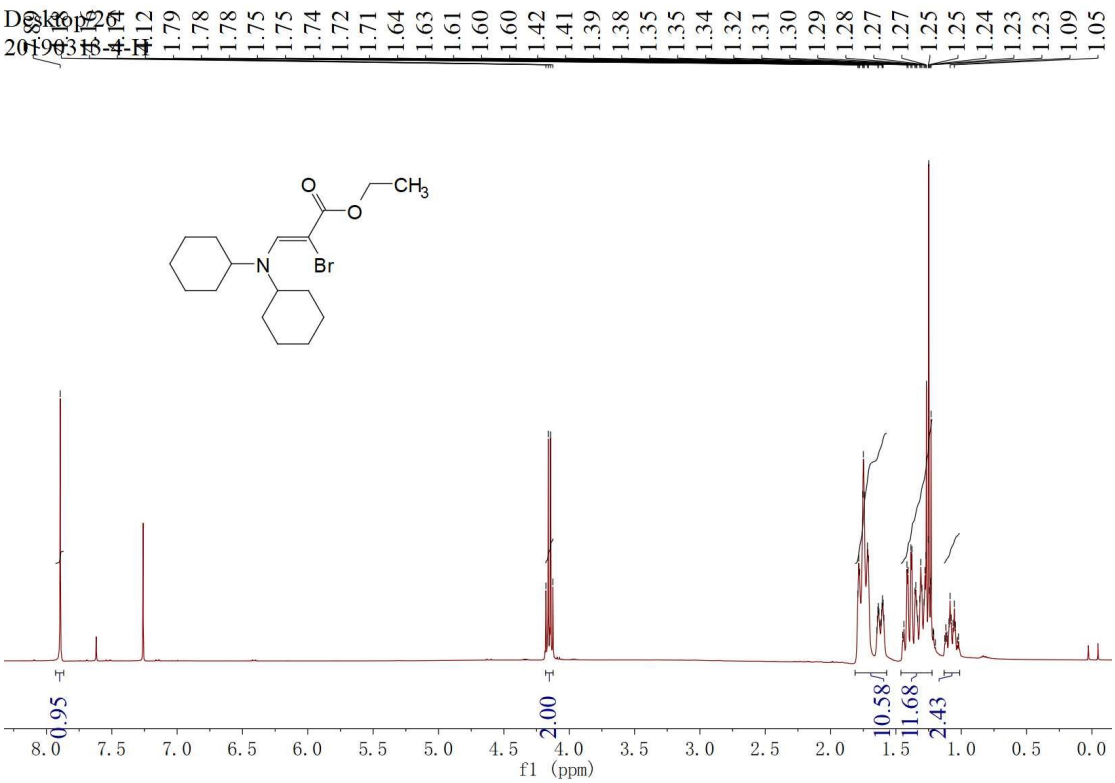
0.0
f1 (ppm)


核磁42
20190327-5-C
166.28
142.18
77.25
75.13
60.91
47.18
22.17
14.57
O
O
CH3
H3C
N
Br
H3C
CH3
H3C
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

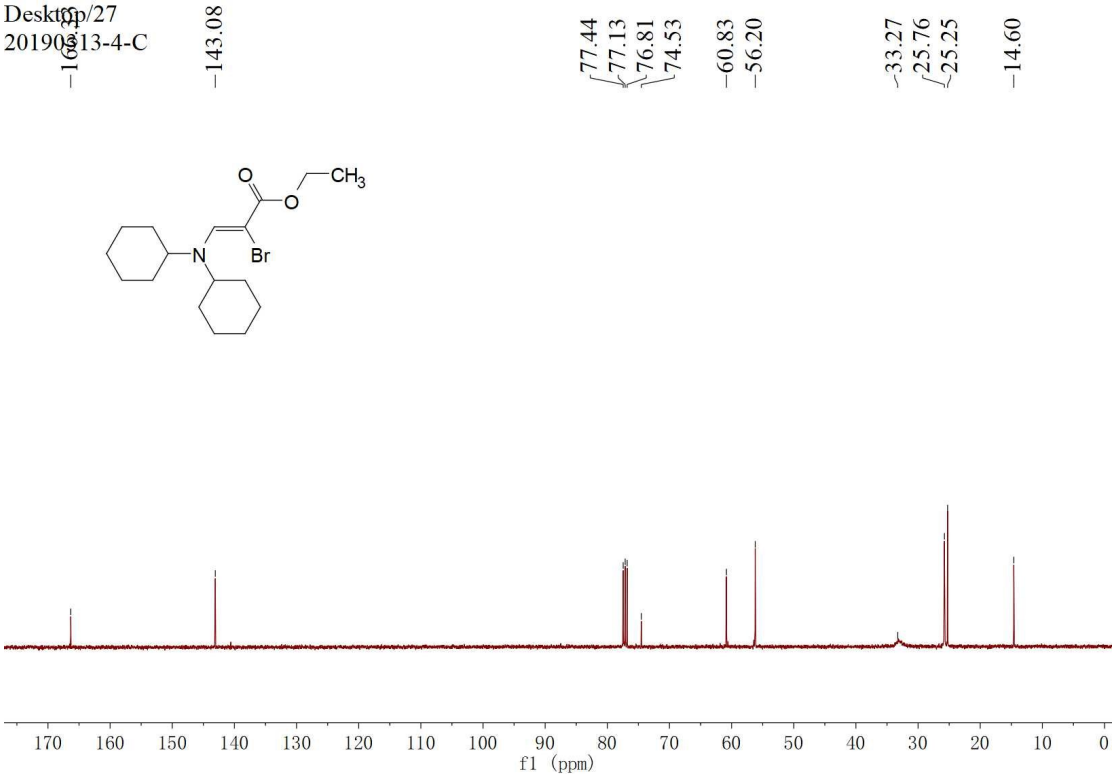

tyn-4
single_pulse
7.84
7.26
4.19 4.17 4.16 4.14 4.17 3.83 1.82 1.82 1.81 1.80 1.79 1.66 1.65 1.65 1.64 1.63 1.63 1.62 1.47 1.46 1.44 1.43 1.41 1.40 1.39 1.38 1.37 1.34 1.33 1.32 1.32 1.30 1.30 1.29 1.28 1.27 1.26 1.26 1.24 1.23 1.22 1.21 1.13 1.12 1.09 1.08 1.08 1.06 1.05 1.04 1.03 1.02 1.01
CH3 Br
N
O
O
CH3
0.91
2.00
3.03
4.15
1.10
2.18
5.74
1.05
f1 (ppm)


tyn-24
single pulse decoupled gated NOE
164.44
138.38
77.48
77.16
76.84
75.24
61.01
31.12
25.61
25.31
14.67
CH3 Br
N
O
O
CH3
f1 (ppm)

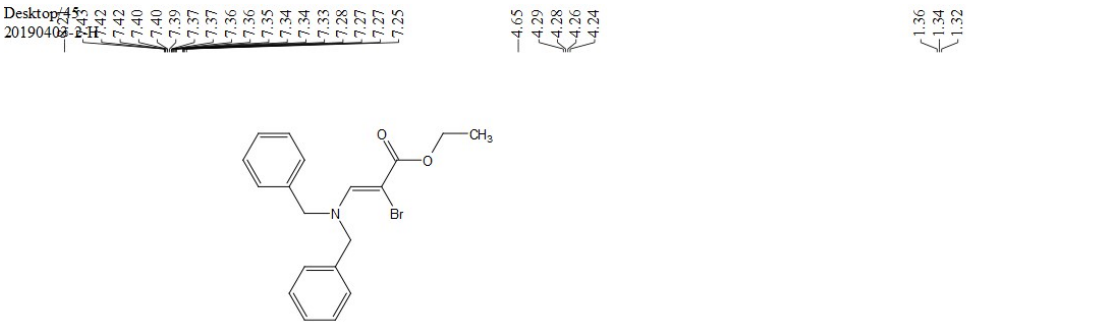
Desktop/26
20190313-4-H

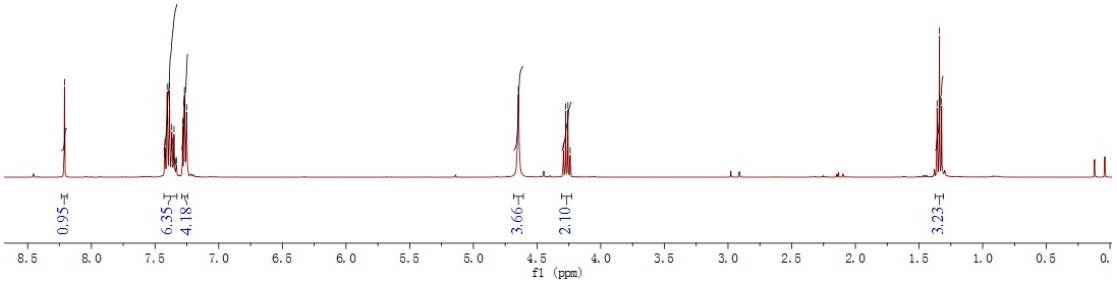


Desktop/27
20190313-4-C

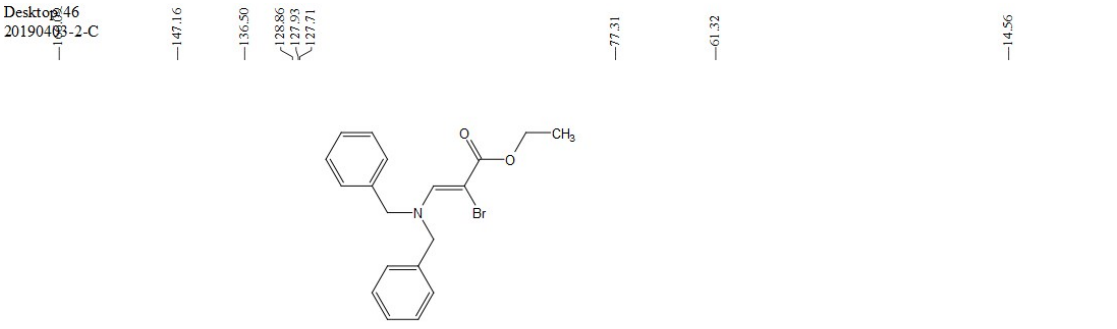


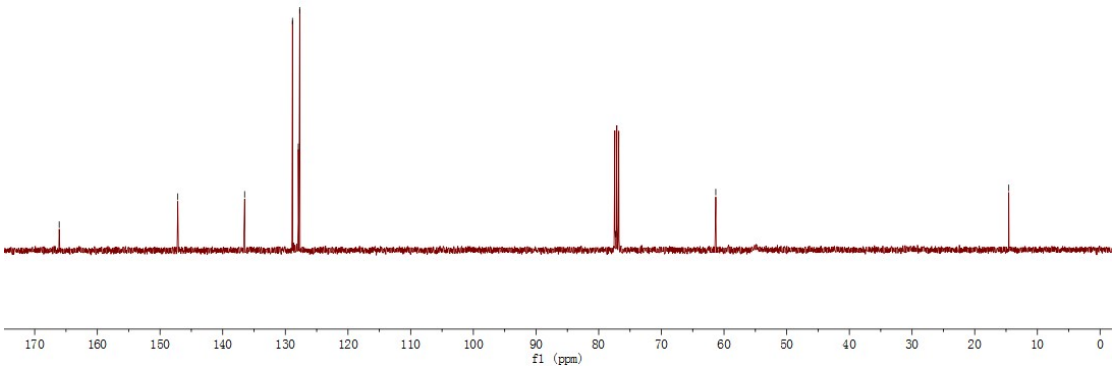
Desktop/45-
20190403-2-H



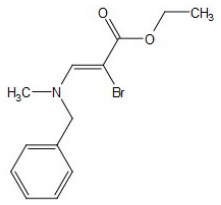


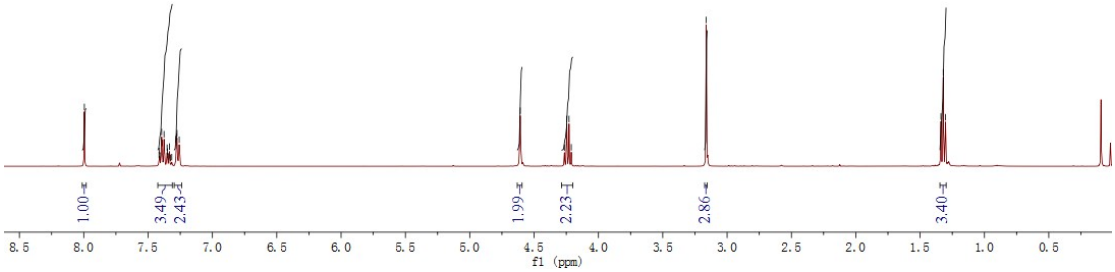
Desktop/46
20190403-2-C



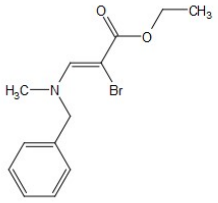


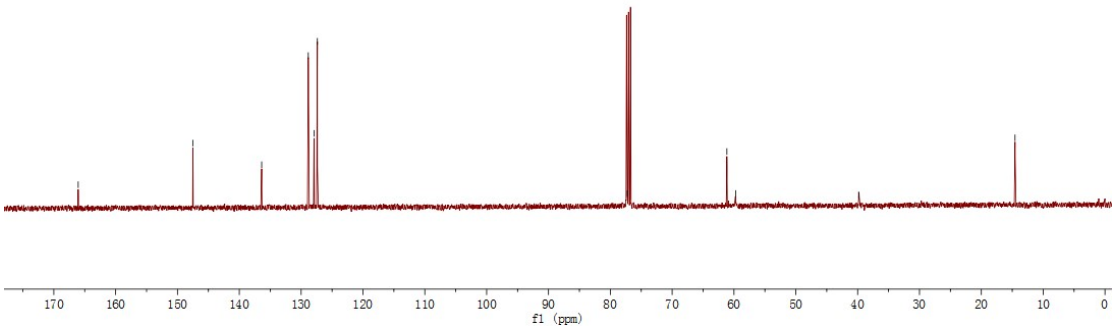
Desktop/47
20190403-1H

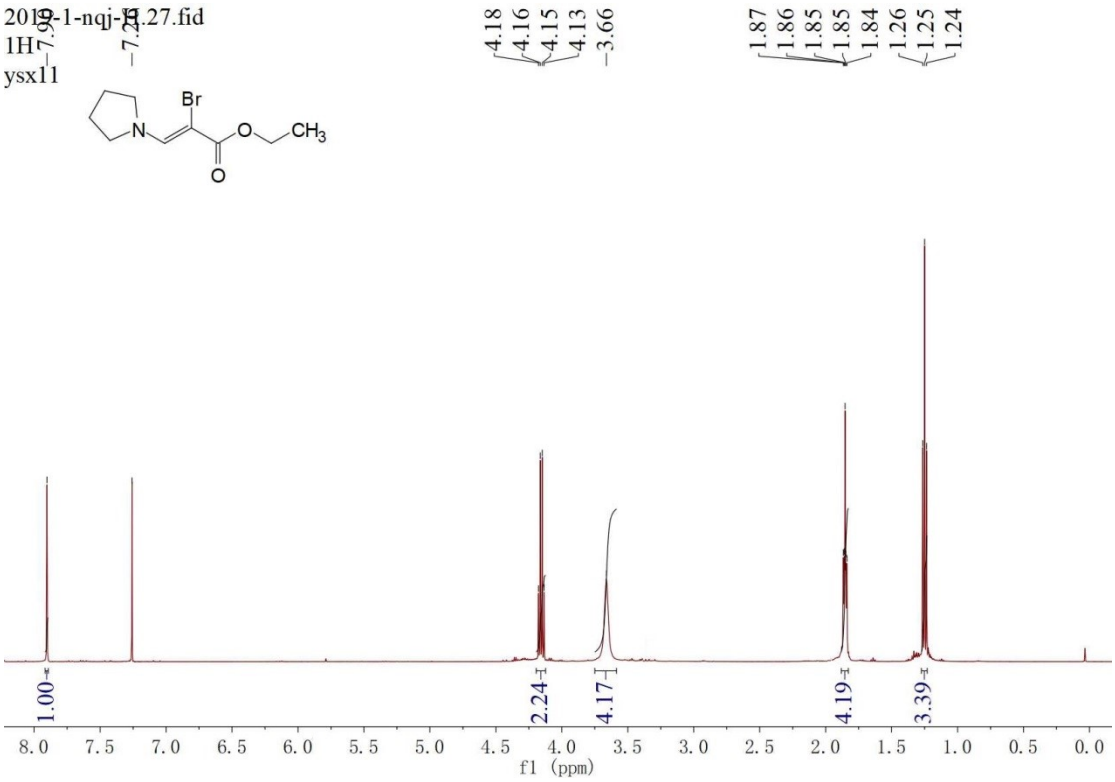


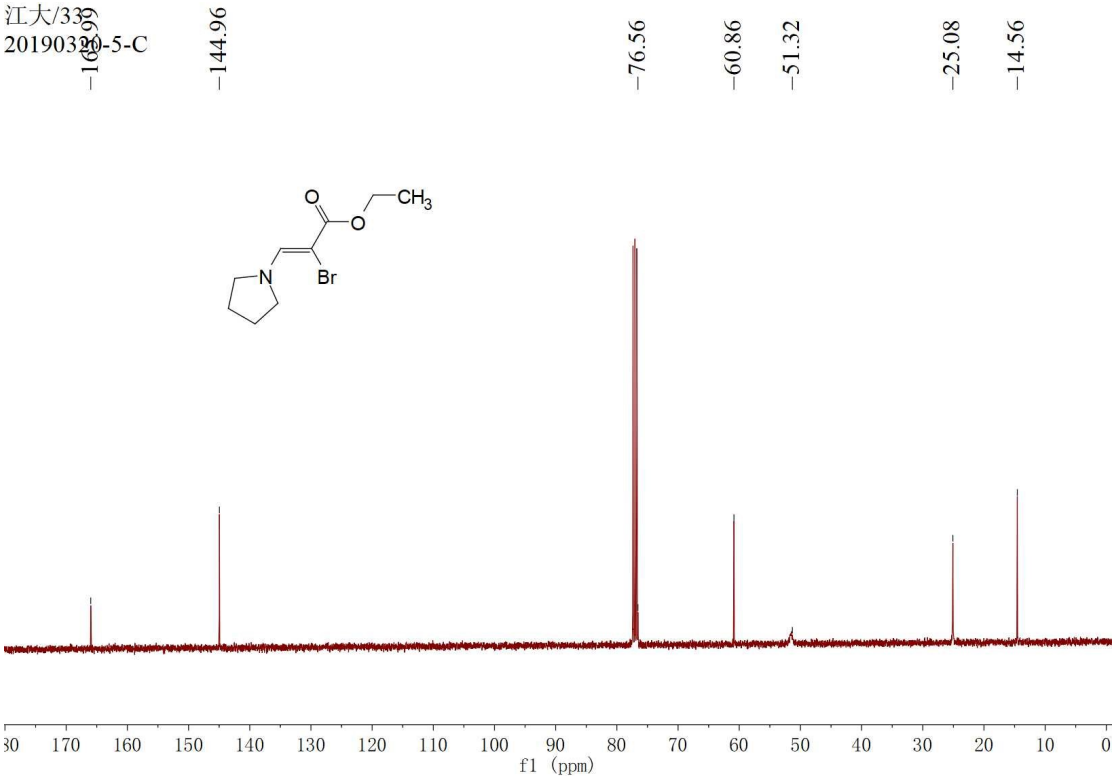


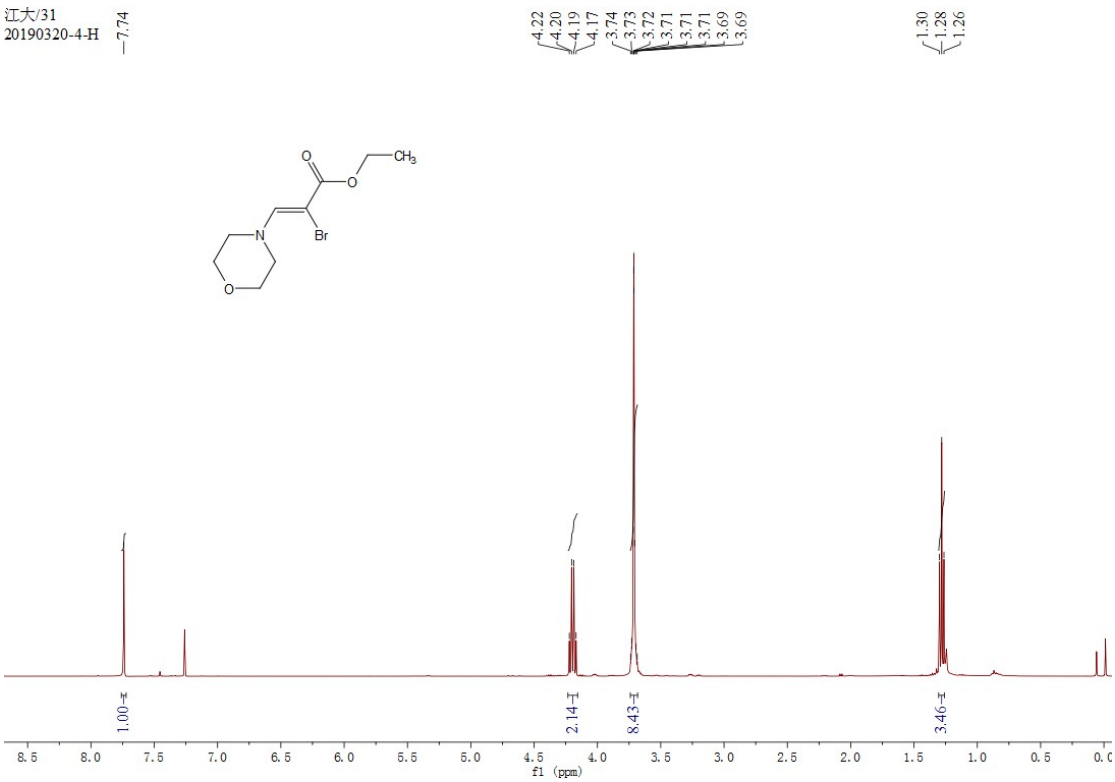
Desktop/48
20190403-13C

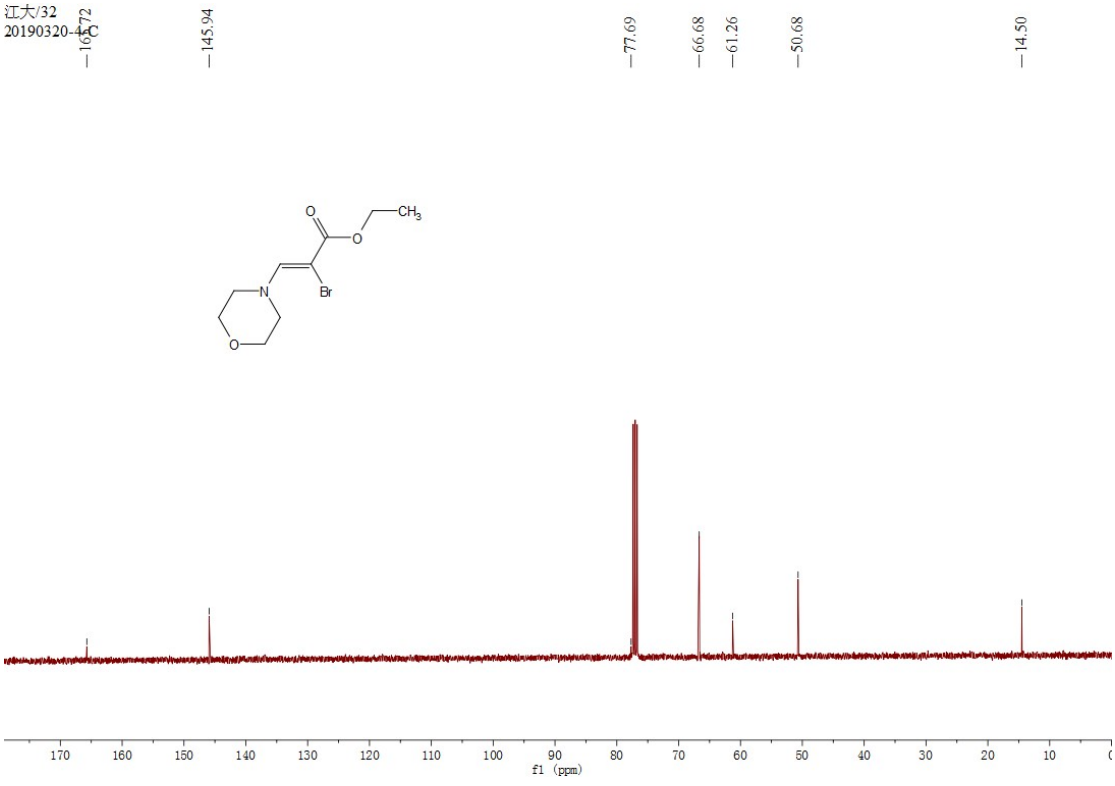




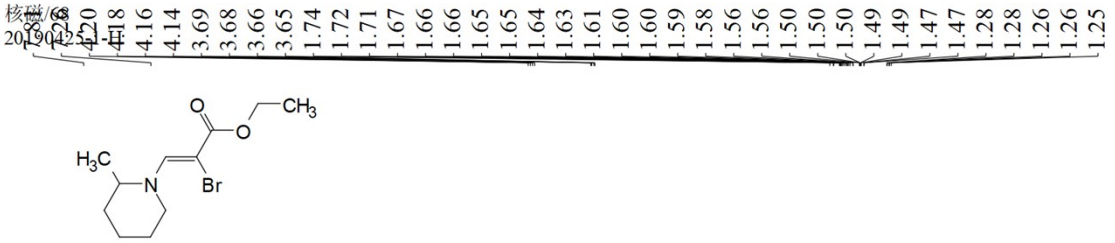

2019-1-nqj-H.27.fid
1H
ysx11
7.99
7.24
4.18
4.16
4.15
4.13
3.66
1.87
1.86
1.85
1.85
1.84
1.26
1.25
1.24
Br
N
O
O
CH3
1.00
2.24
4.17
4.19
3.39
f1 (ppm)

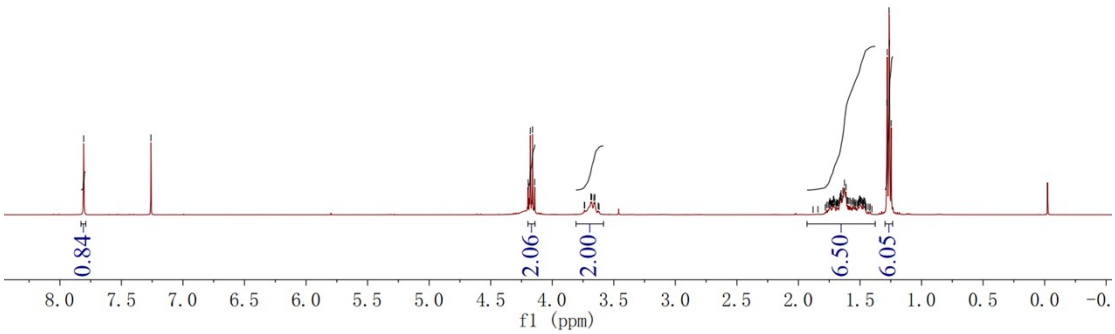

江大/33
20190320-5-C
169.99
144.96
76.56
60.86
51.32
25.08
14.56
O
O
CH3
N
Br
f1 (ppm)


江大/31
20190320-4-H
7.74
4.22
4.20
4.19
4.17
3.74
3.73
3.72
3.71
3.71
3.71
3.69
3.69
1.30
1.28
1.26
O
O
CH3
N
Br
O
1.00
2.14
8.43
3.46
f1 (ppm)

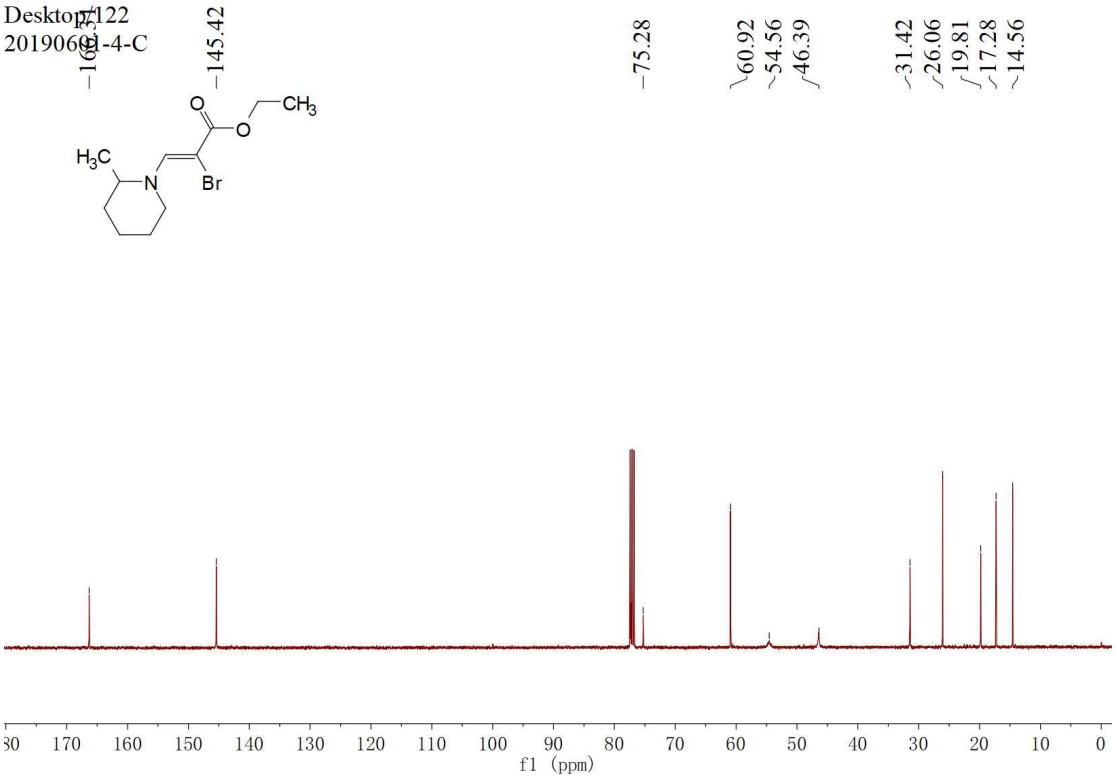

江大/32
20190320-4-C
165.72
145.94
77.69
66.68
61.26
50.68
14.50
O
O
CH3
N
Br
O
f1 (ppm)

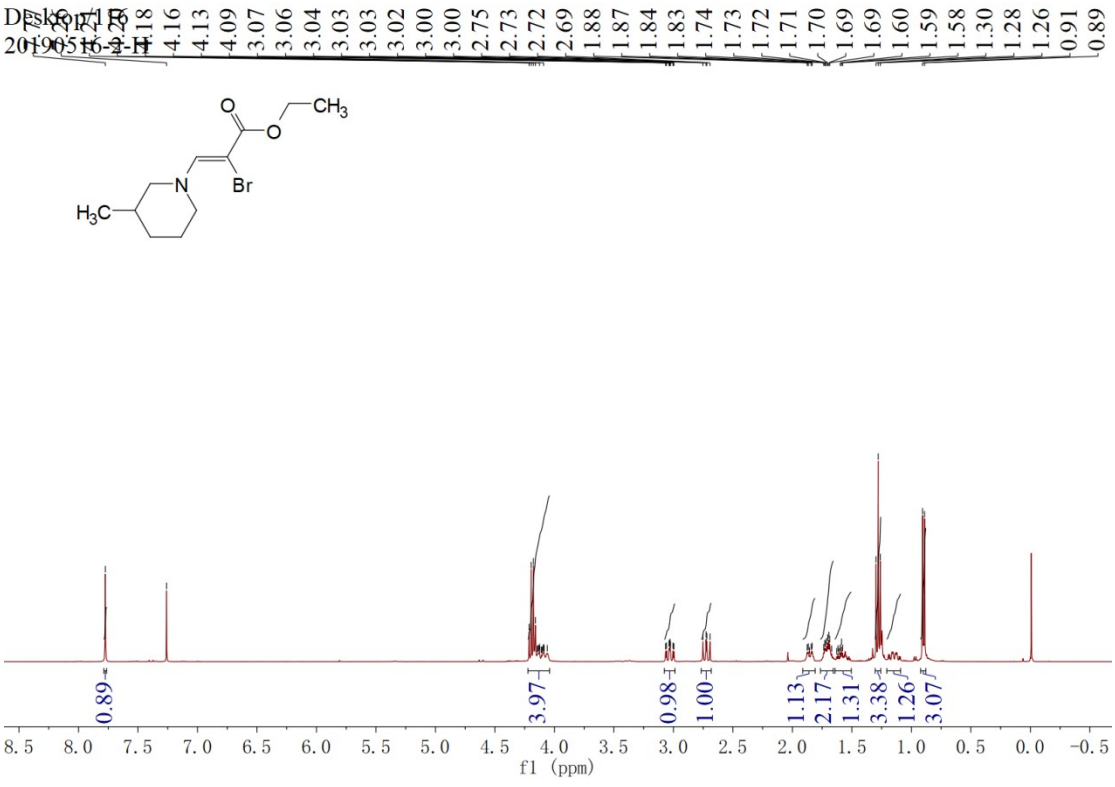
核磁/68
20190425-4-H

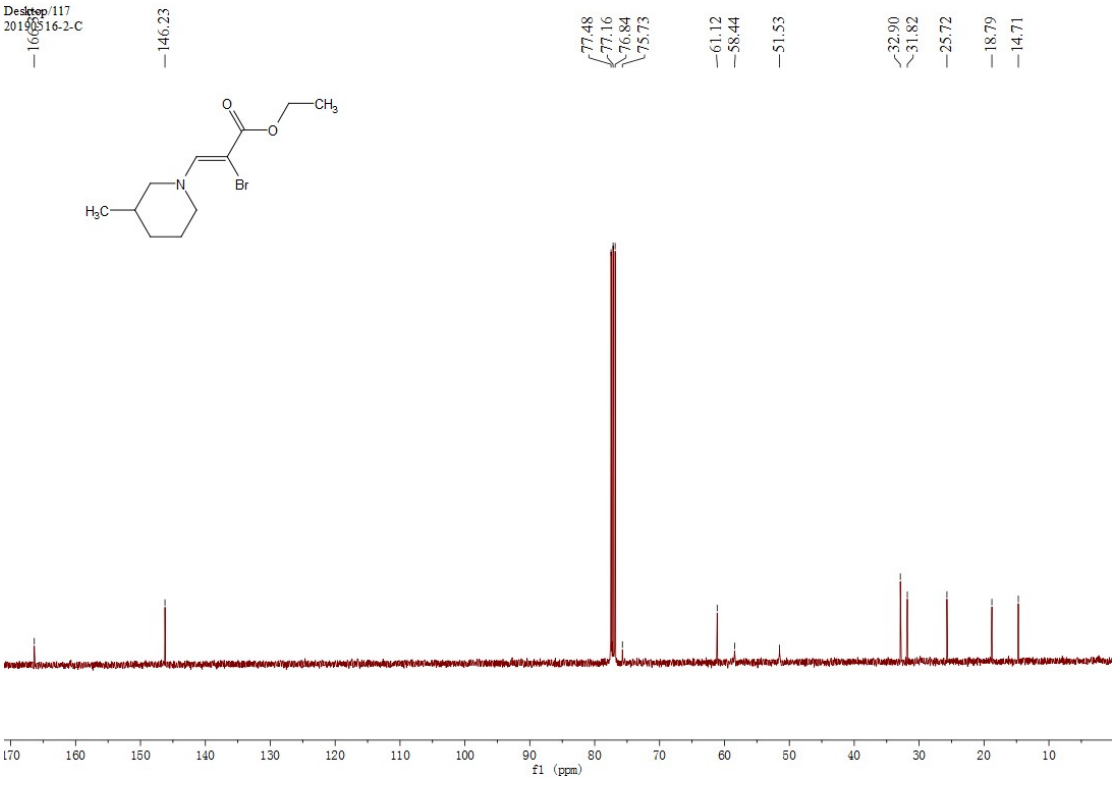




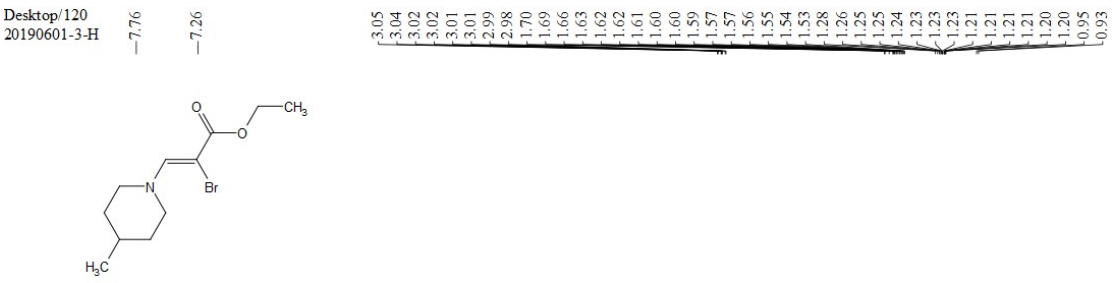
Desktop/122
20190609-4-C

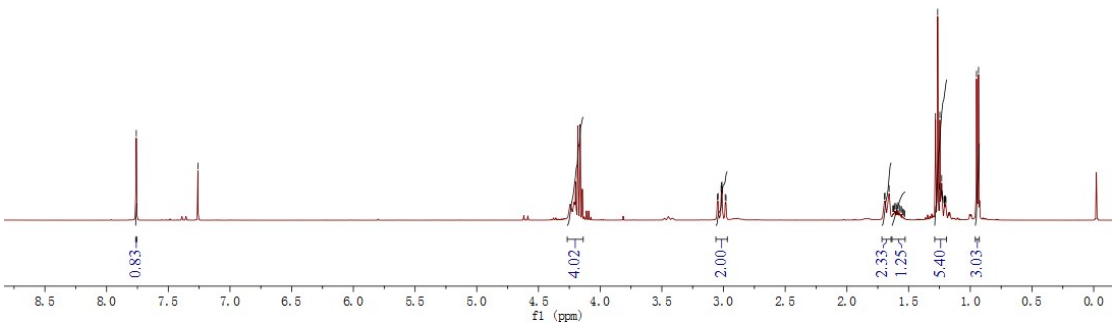



7.26
8.18
4.16
4.13
4.09
3.07
3.06
3.04
3.03
3.03
3.02
3.00
3.00
2.75
2.73
2.72
2.69
1.88
1.87
1.84
1.83
1.74
1.73
1.72
1.71
1.70
1.69
1.69
1.60
1.59
1.58
1.30
1.28
1.26
0.91
0.89
O
O
CH3
N
Br
H3C
0.89
3.97
0.98
1.00
1.13
2.17
1.31
3.38
1.26
3.07
f1 (ppm)

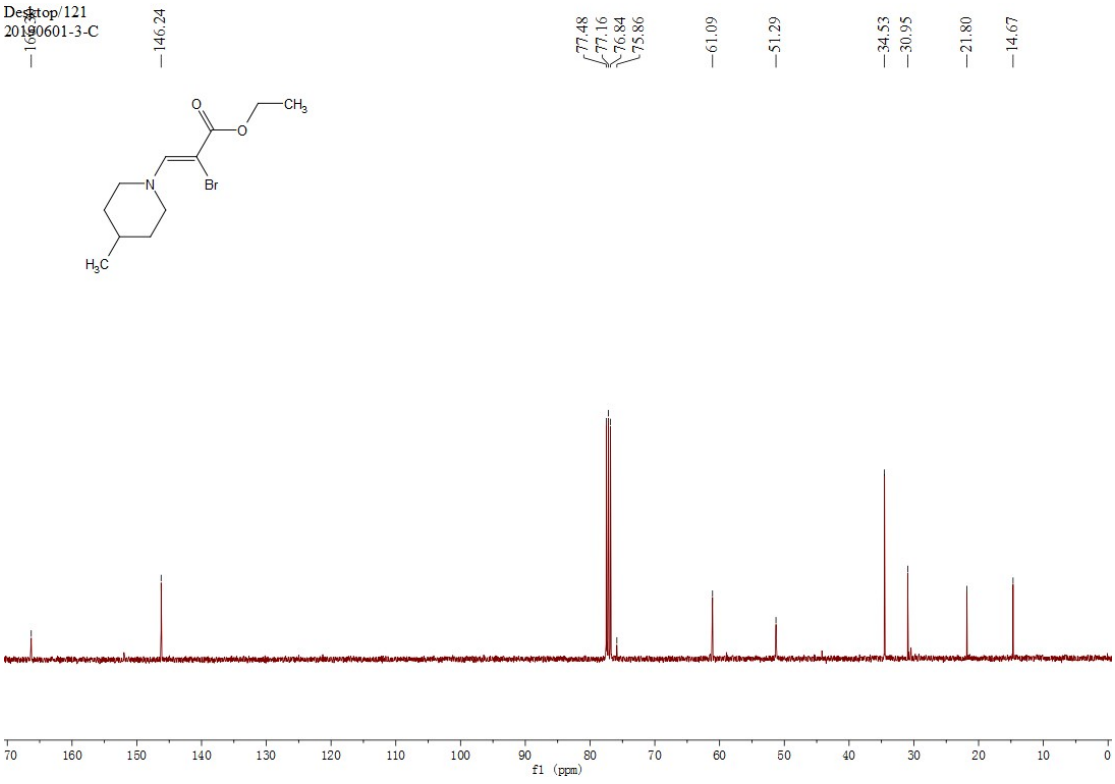

166.25
146.23
77.48
77.16
76.84
75.73
61.12
58.44
51.53
32.90
31.82
25.72
18.79
14.71
O
O
CH3
N
Br
H3C
f1 (ppm)

Desktop/120
20190601-3-H

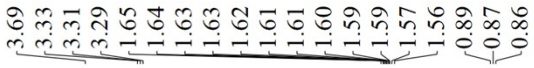


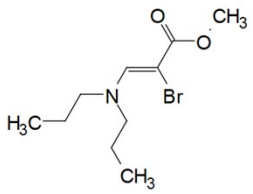


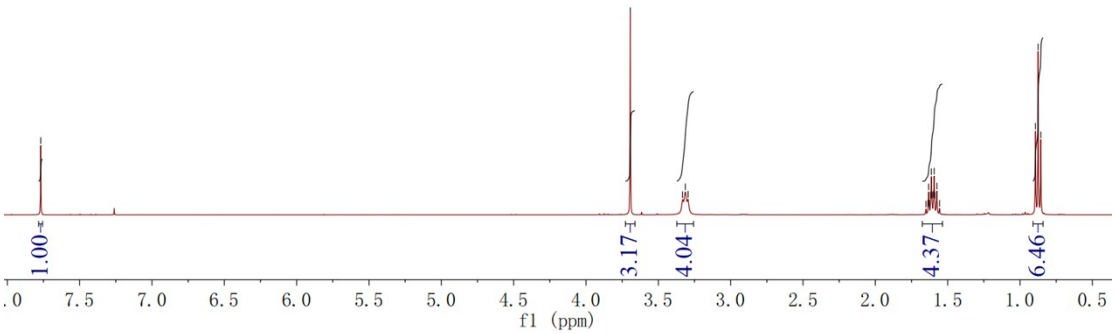
Desktop/121
20190601-3-C



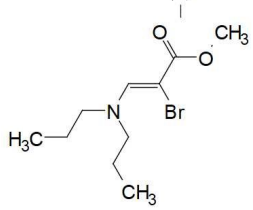
Desktop/22
20190313-2-H

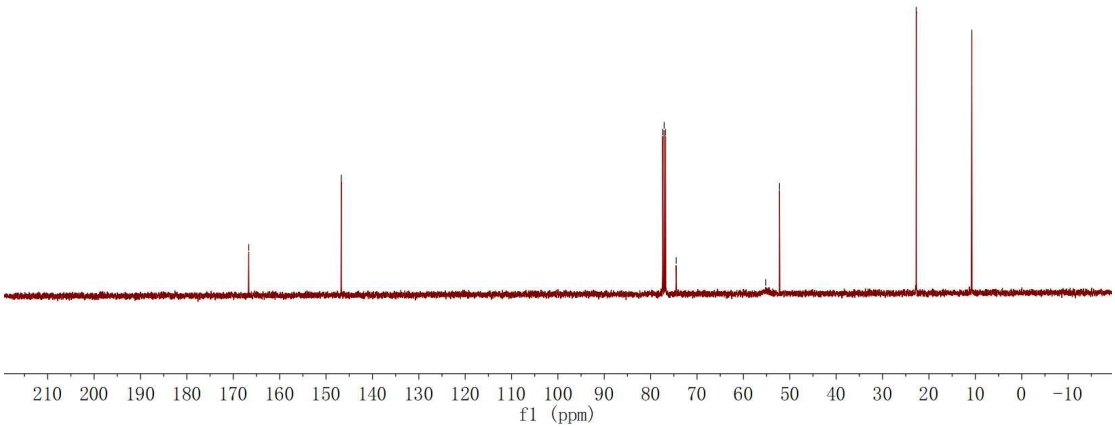


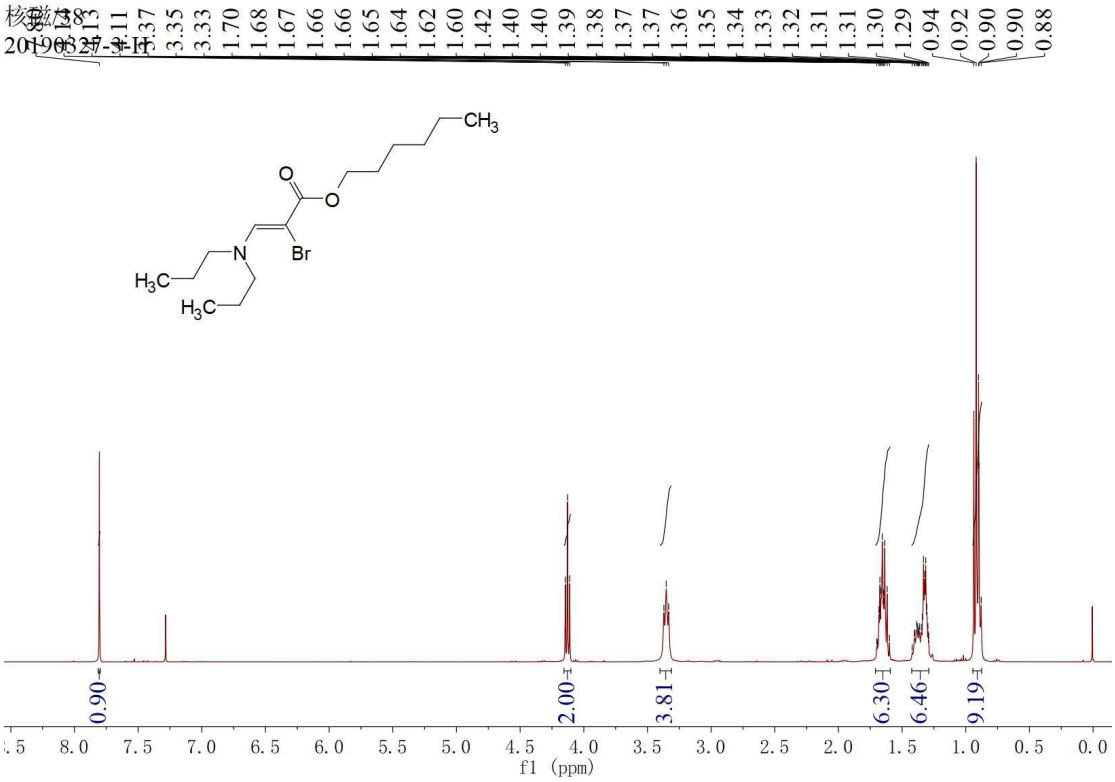


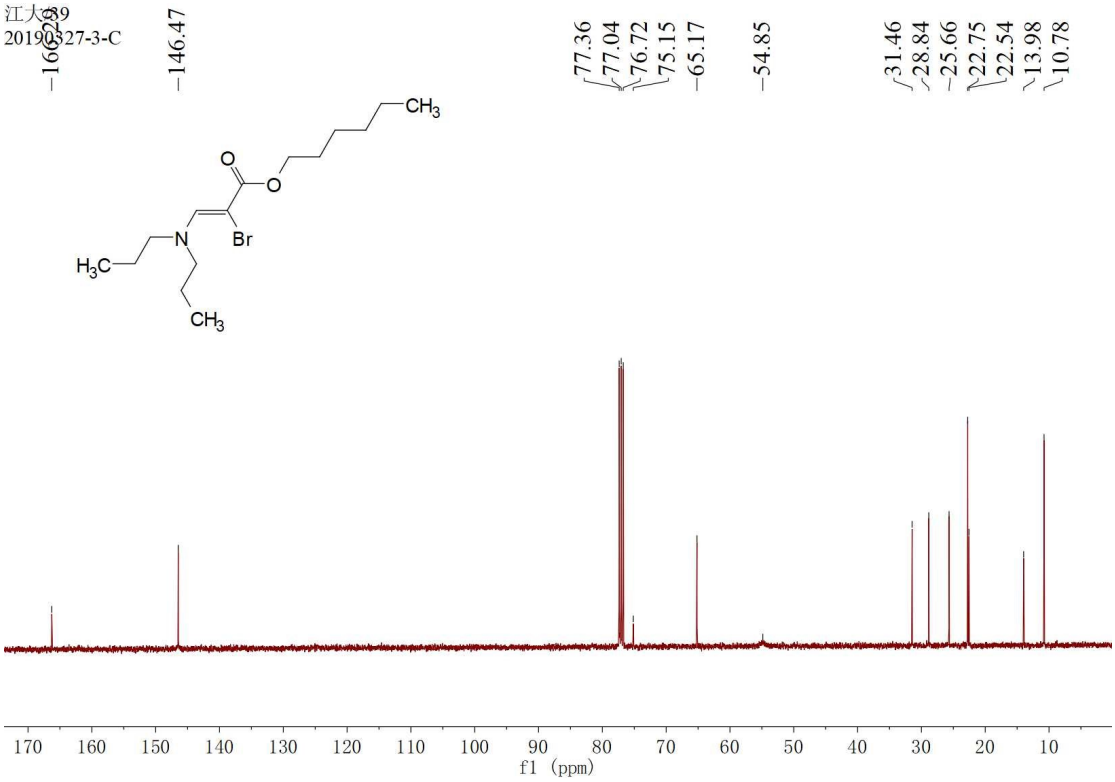


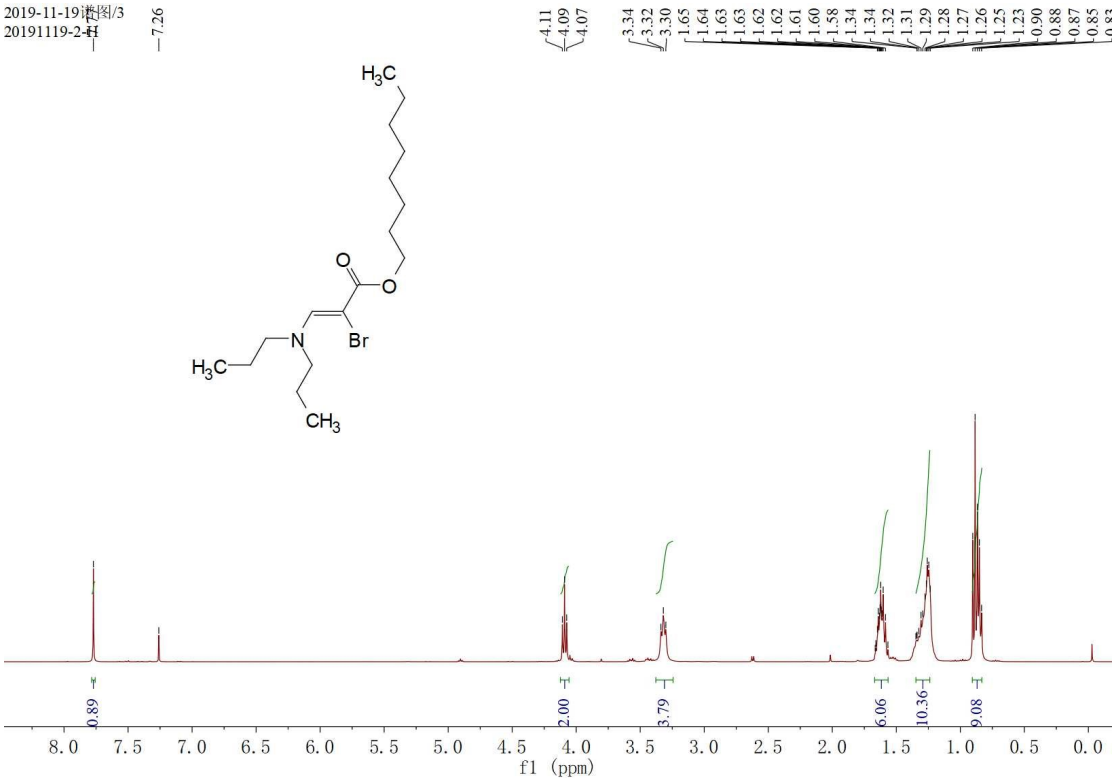
Desktop/23
20190313-2-C

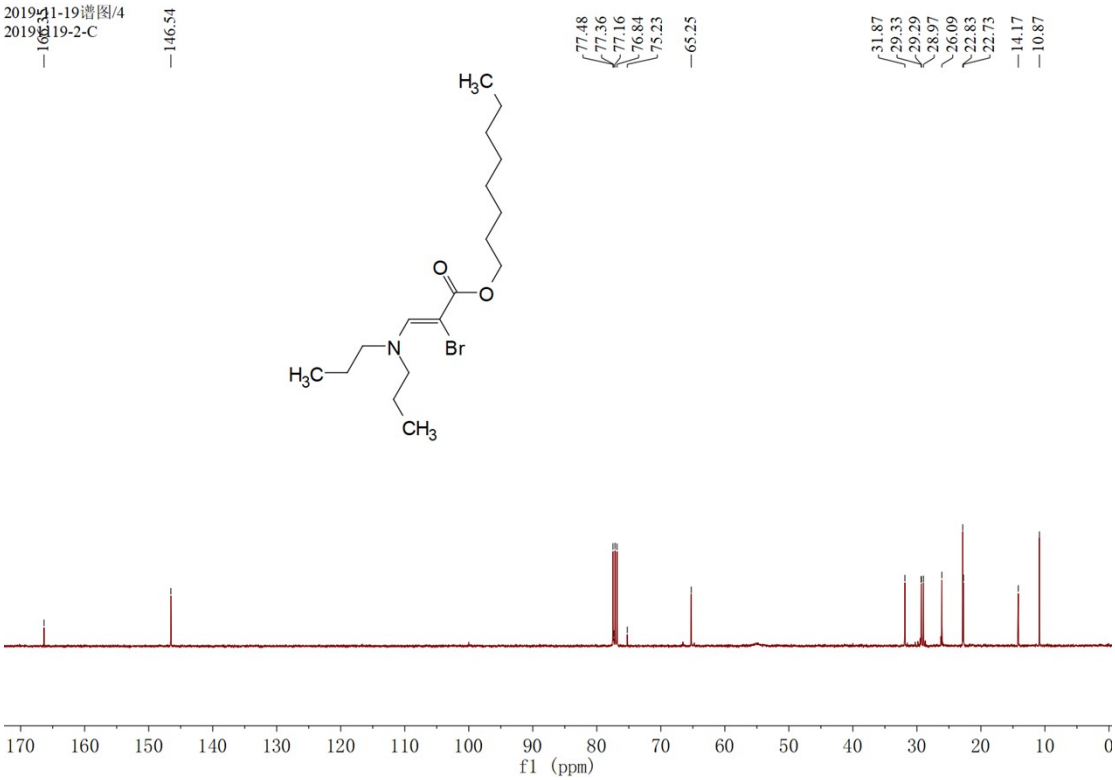


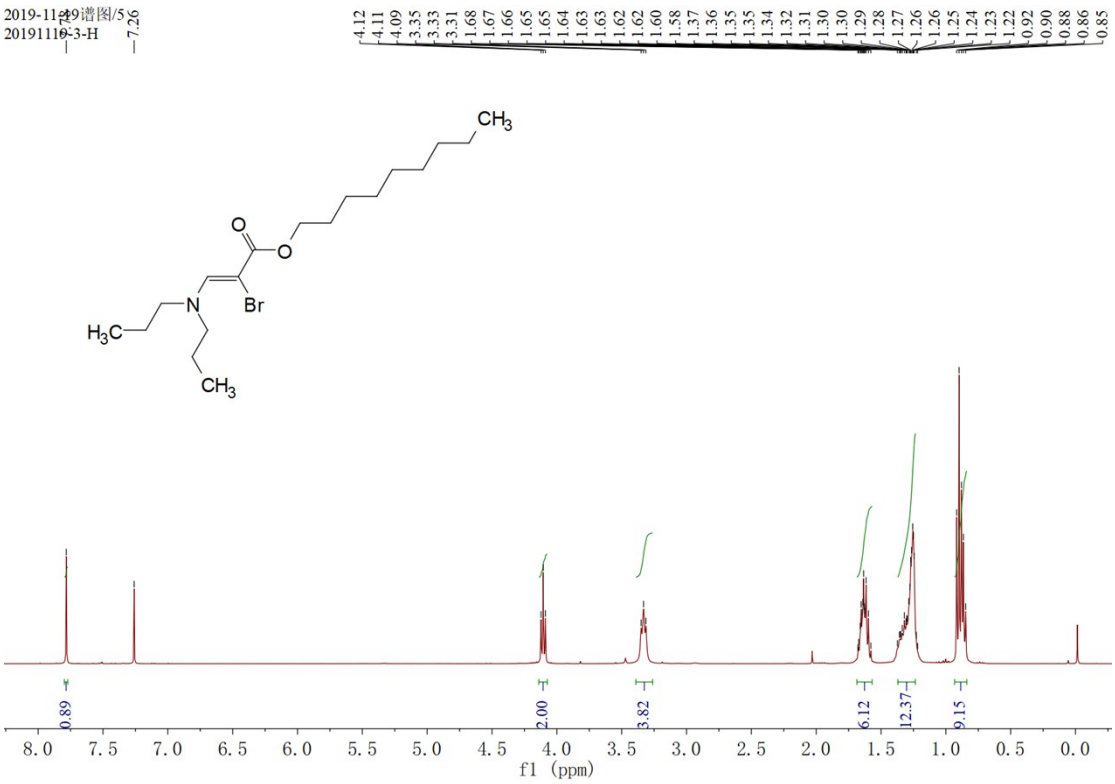


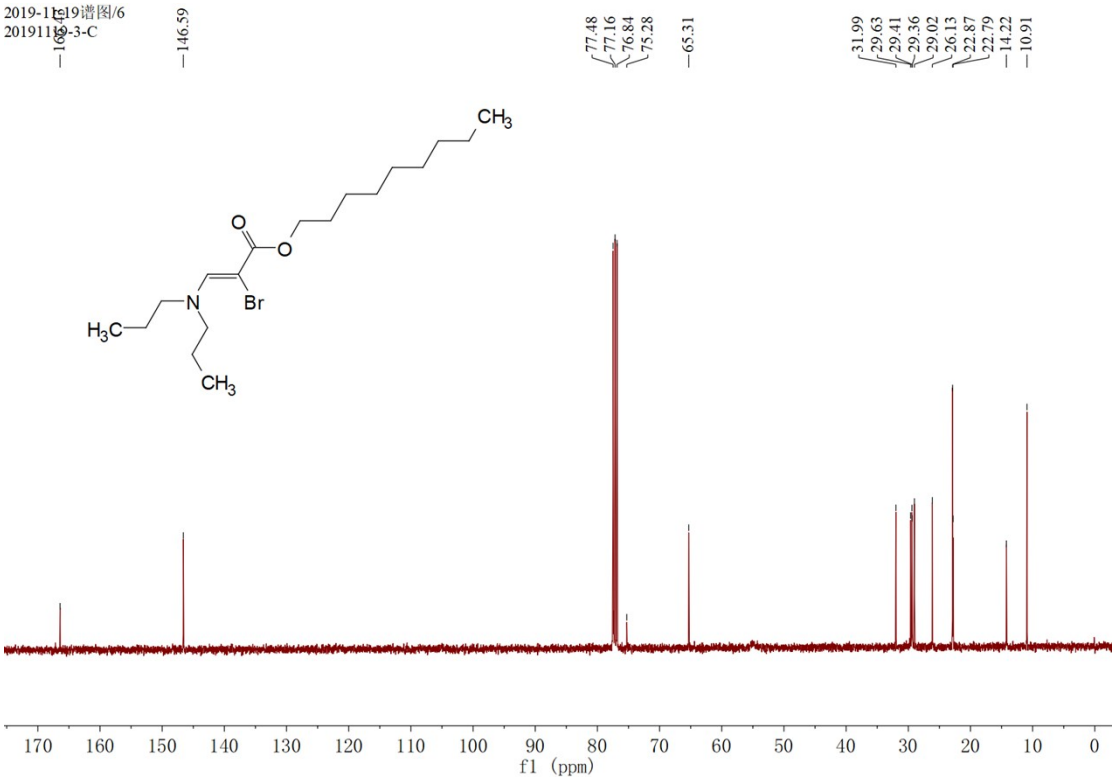

8.13
8.11
7.37
3.35
3.33
1.70
1.68
1.67
1.66
1.66
1.65
1.64
1.62
1.60
1.42
1.40
1.40
1.39
1.38
1.37
1.37
1.36
1.35
1.34
1.33
1.32
1.31
1.31
1.30
1.29
0.94
0.92
0.90
0.90
0.88
CH3
O
O
N
Br
H3C
H3C
0.90
2.00
3.81
6.30
6.46
9.19
f1 (ppm)

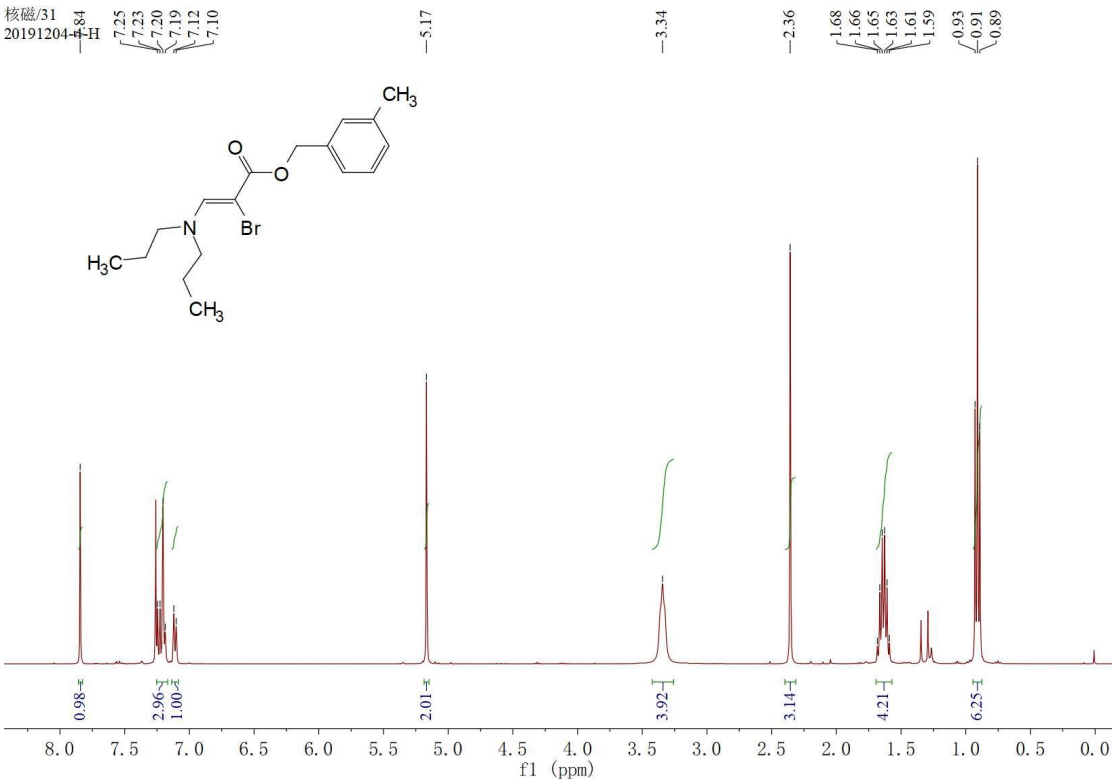

江大239
20190327-3-C
166.23
146.47
77.36
77.04
76.72
75.15
65.17
54.85
31.46
28.84
25.66
22.75
22.54
13.98
10.78
CH3
O
O
N
Br
H3C
CH3
f1 (ppm)

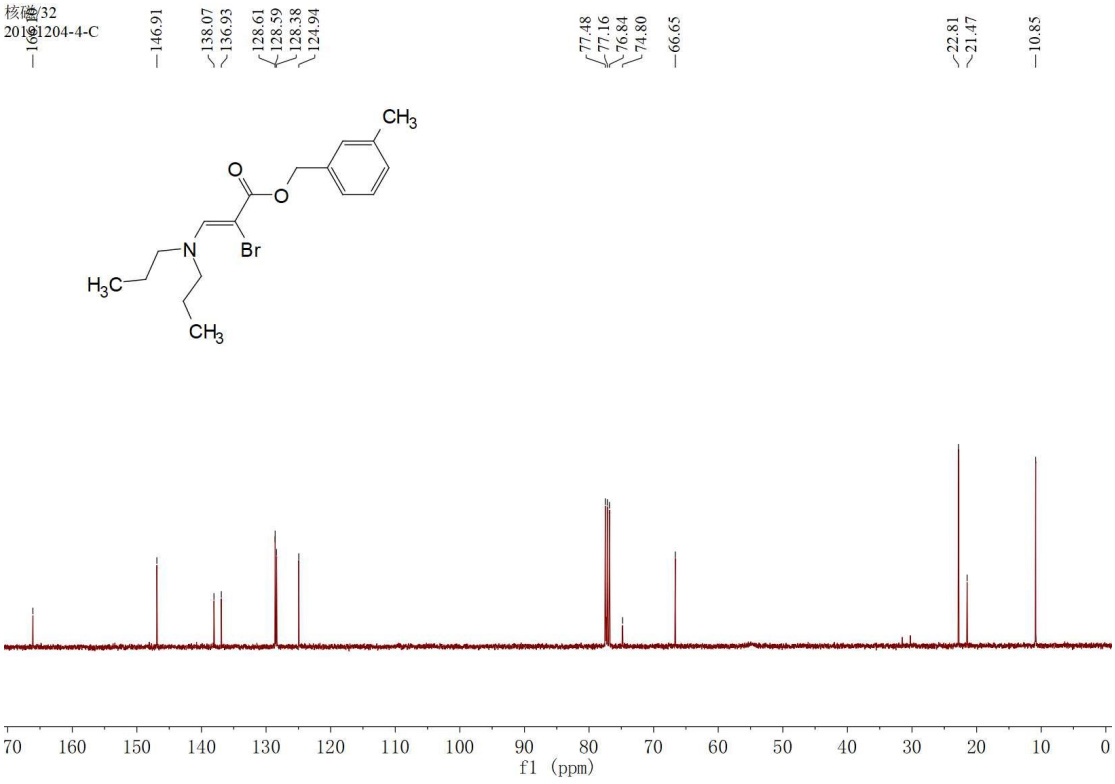

2019-11-19谱图/3
20191119-2-H
7.26
4.11
4.09
4.07
3.34
3.32
3.30
1.65
1.64
1.63
1.63
1.62
1.62
1.61
1.60
1.58
1.34
1.34
1.32
1.31
1.29
1.28
1.27
1.26
1.25
1.23
0.90
0.88
0.87
0.85
H3C
O
O
N
Br
H3C
CH3
0.89
2.00
3.79
6.06
10.36
9.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

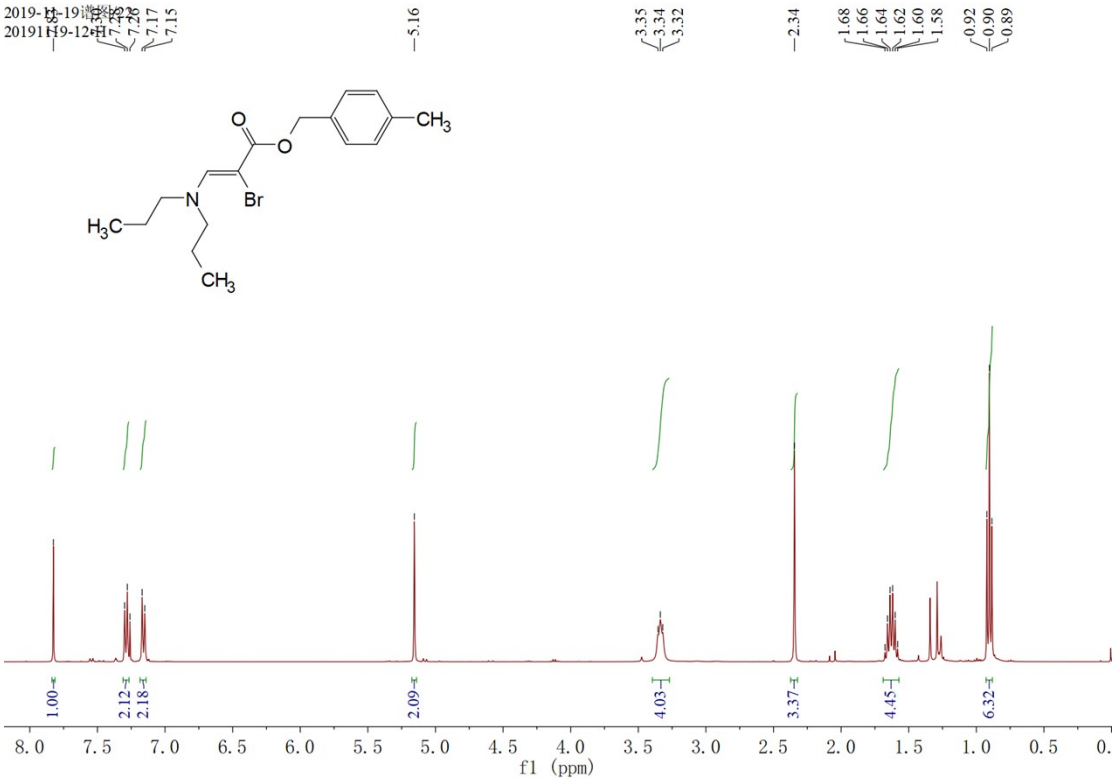

2019-11-19谱图/4
2019-11-19-2-C
165.11
146.54
77.48
77.36
77.16
76.84
75.23
65.25
31.87
29.33
29.29
28.97
26.09
22.83
22.73
14.17
10.87
H3C
O
O
N
Br
H3C
CH3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

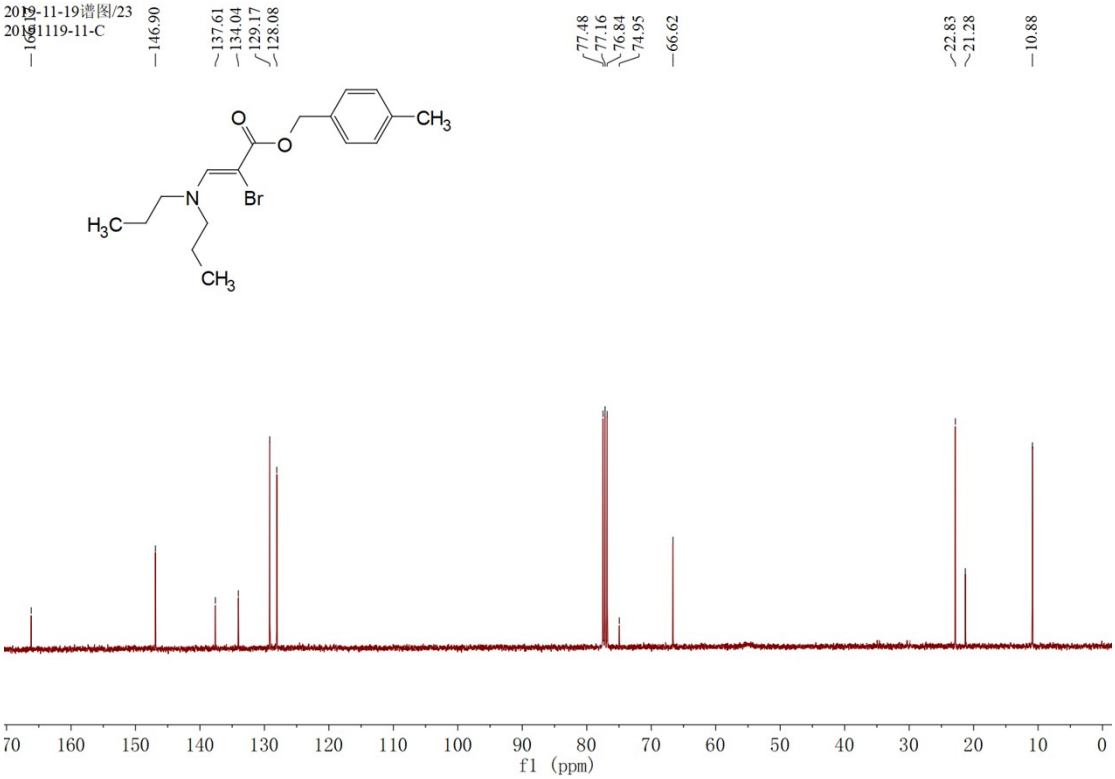

2019-11-19谱图/5
20191119-3-H
7.26
4.12
4.11
4.09
3.35
3.33
3.31
1.68
1.67
1.66
1.65
1.65
1.64
1.63
1.63
1.62
1.62
1.60
1.58
1.37
1.36
1.35
1.35
1.34
1.32
1.31
1.30
1.30
1.29
1.28
1.27
1.26
1.26
1.25
1.24
1.23
1.22
0.92
0.90
0.88
0.86
0.85
CH3
O
O
Br
N
H3C
CH3
0.89
2.00
3.82
6.12
12.37
9.15
8.0
7.5
7.0
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)

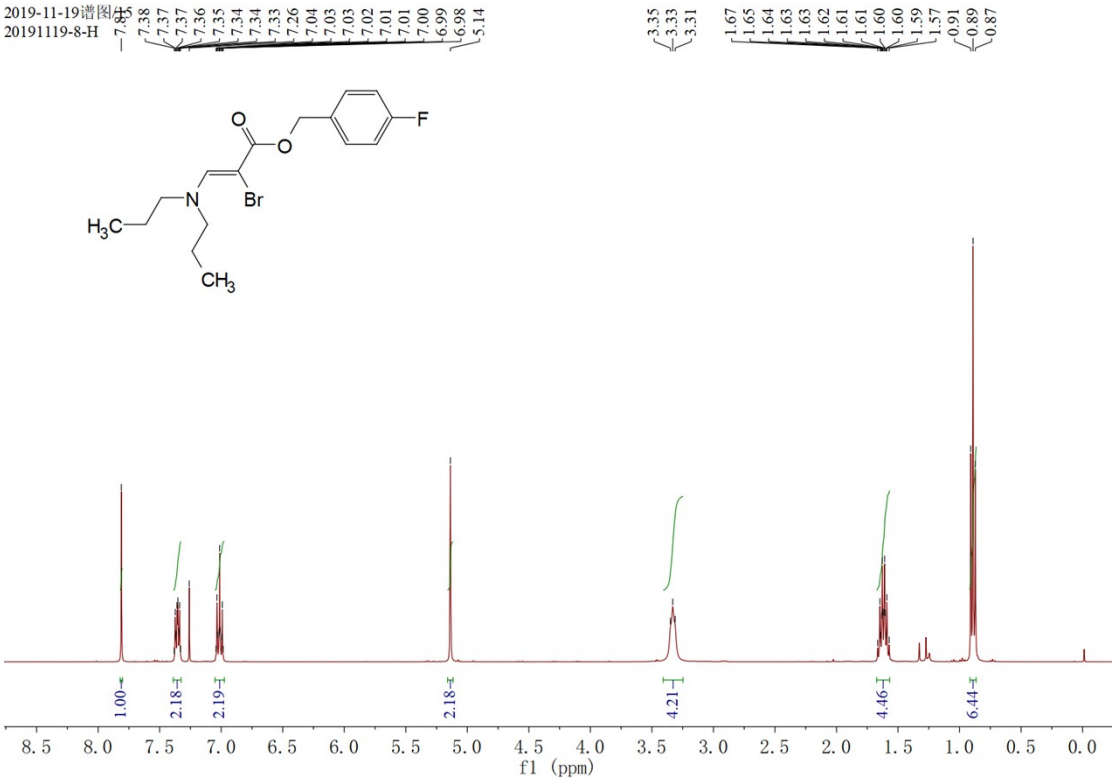

2019-11-19谱图/6
20191119-3-C
165.41
146.59
77.48
77.16
76.84
75.28
65.31
31.99
29.63
29.41
29.36
29.02
26.13
22.87
22.79
14.22
10.91
CH3
O
O
Br
N
H3C
CH3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

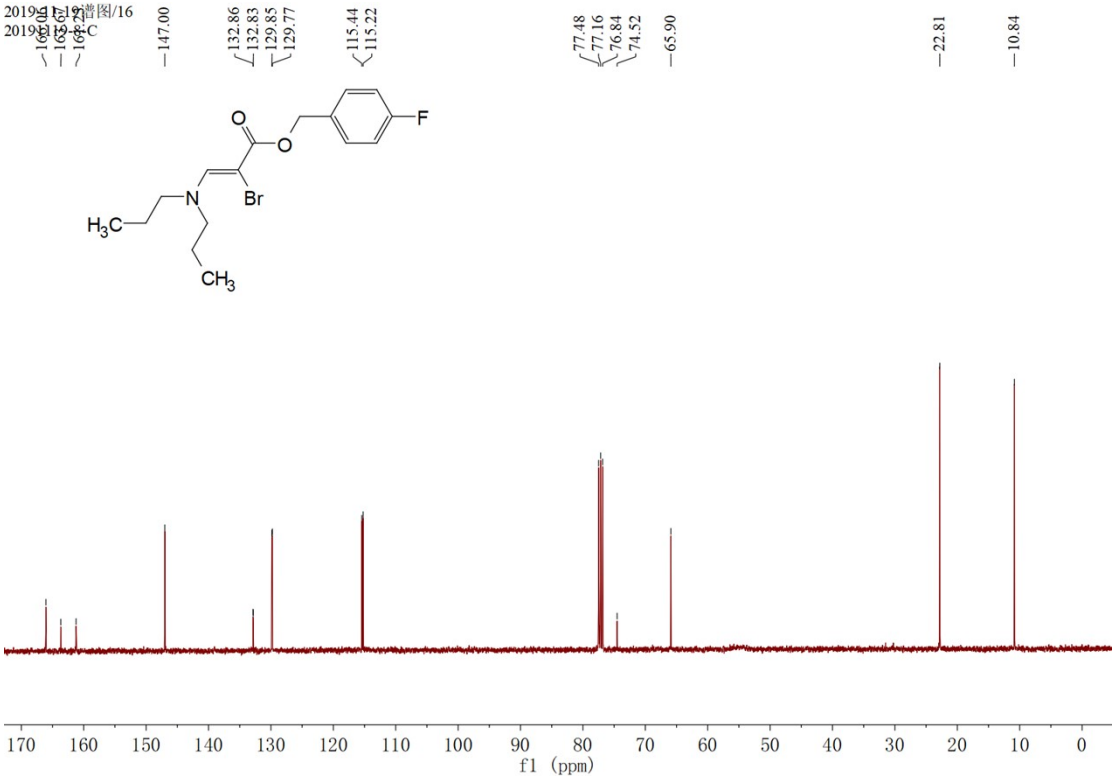

核磁/31
20191204-4-H
8.84
7.25
7.23
7.20
7.19
7.12
7.10
5.17
3.34
2.36
1.68
1.66
1.65
1.63
1.61
1.59
0.93
0.91
0.89
CH3
O
O
N
Br
H3C
CH3
0.98
2.96
1.00
2.01
3.92
3.14
4.21
6.25
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

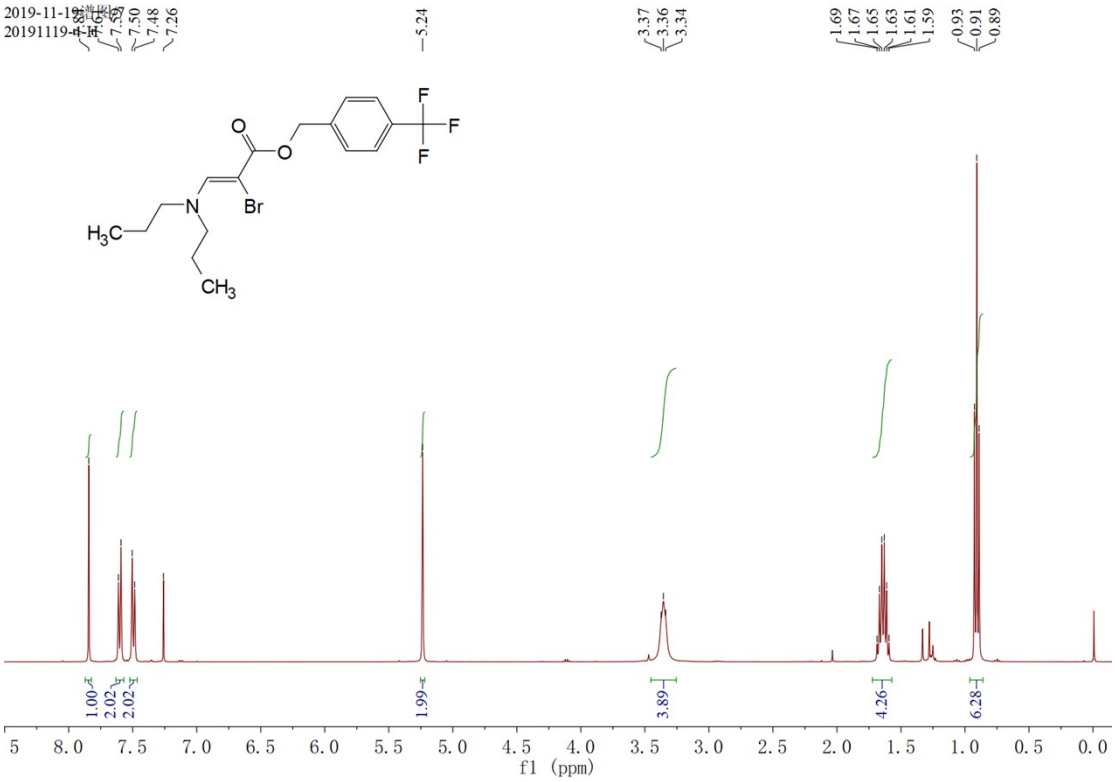

核磁/32
20191204-4-C
166.91
146.91
138.07
136.93
128.61
128.59
128.38
124.94
77.48
77.16
76.84
74.80
66.65
22.81
21.47
10.85
CH3
O
O
N
Br
H3C
CH3
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

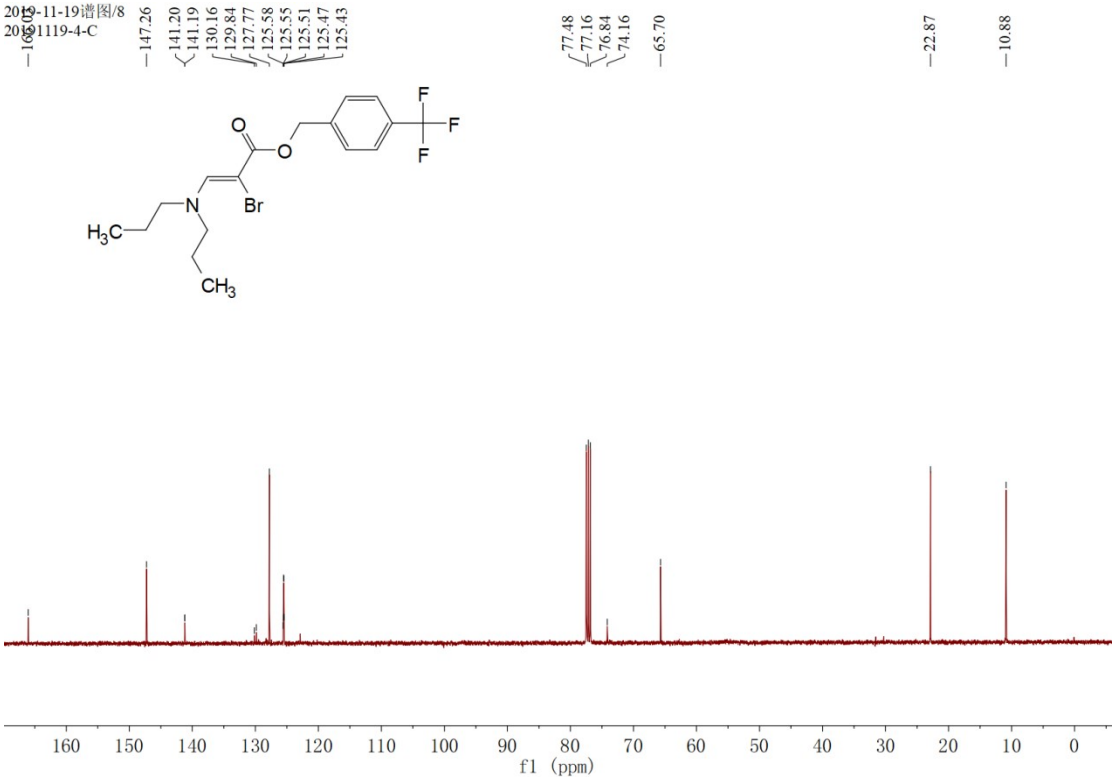

7.26
7.17
7.15
5.16
3.35
3.34
3.32
2.34
1.68
1.66
1.64
1.62
1.60
1.58
0.92
0.90
0.89
O
O
CH3
Br
N
H3C
CH3
1.00
2.12
2.18
2.09
4.03
3.37
4.45
6.32
f1 (ppm)


2019-11-19谱图/23
20191119-11-C
166.12
146.90
137.61
134.04
129.17
128.08
77.48
77.16
76.84
74.95
66.62
22.83
21.28
10.88
O
O
CH3
Br
N
H3C
CH3
f1 (ppm)

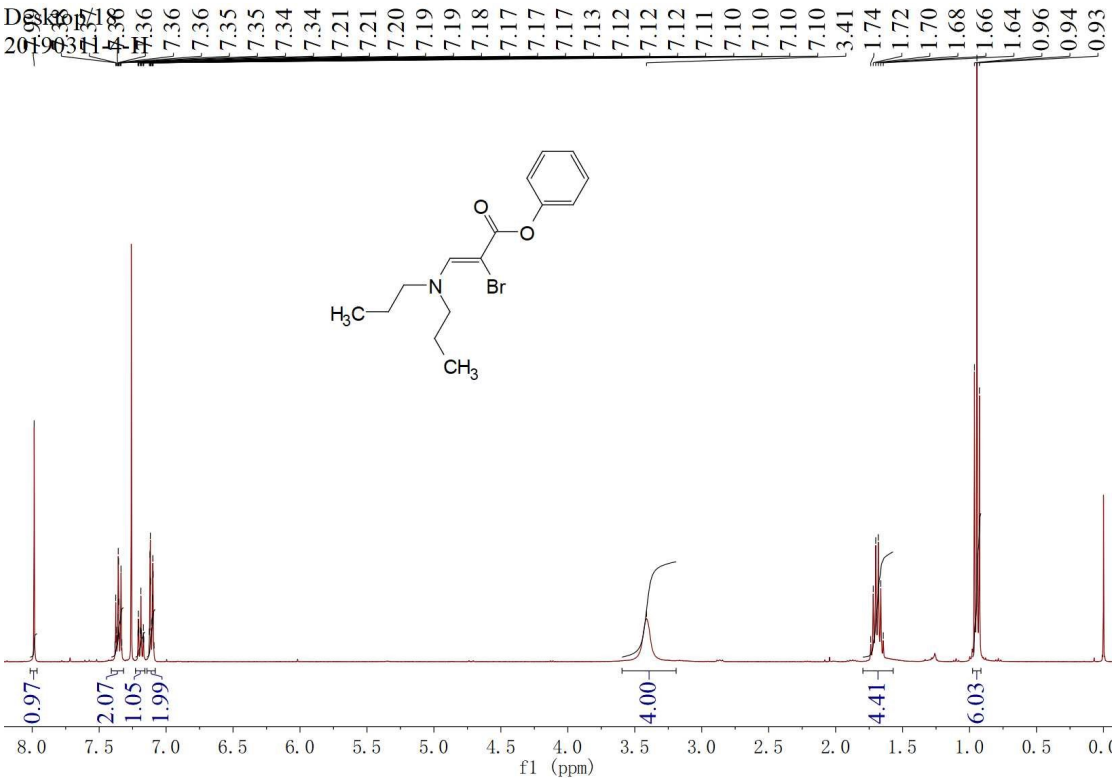

2019-11-19谱图/15
20191119-8-H
7.85
7.38
7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.26
7.04
7.03
7.03
7.02
7.01
7.01
7.00
6.99
6.98
5.14
3.35
3.33
3.31
1.67
1.65
1.64
1.63
1.63
1.62
1.61
1.61
1.60
1.60
1.59
1.57
0.91
0.89
0.87
O
O
F
Br
N
H3C
CH3
1.00
2.18
2.19
2.18
4.21
4.46
6.44
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


2019-11-19谱图/16
2019-11-19-C
163.12
163.12
163.12
163.12
147.00
132.86
132.83
129.85
129.77
115.44
115.22
77.48
77.16
76.84
74.52
65.90
22.81
10.84
O
O
F
Br
N
H3C
CH3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

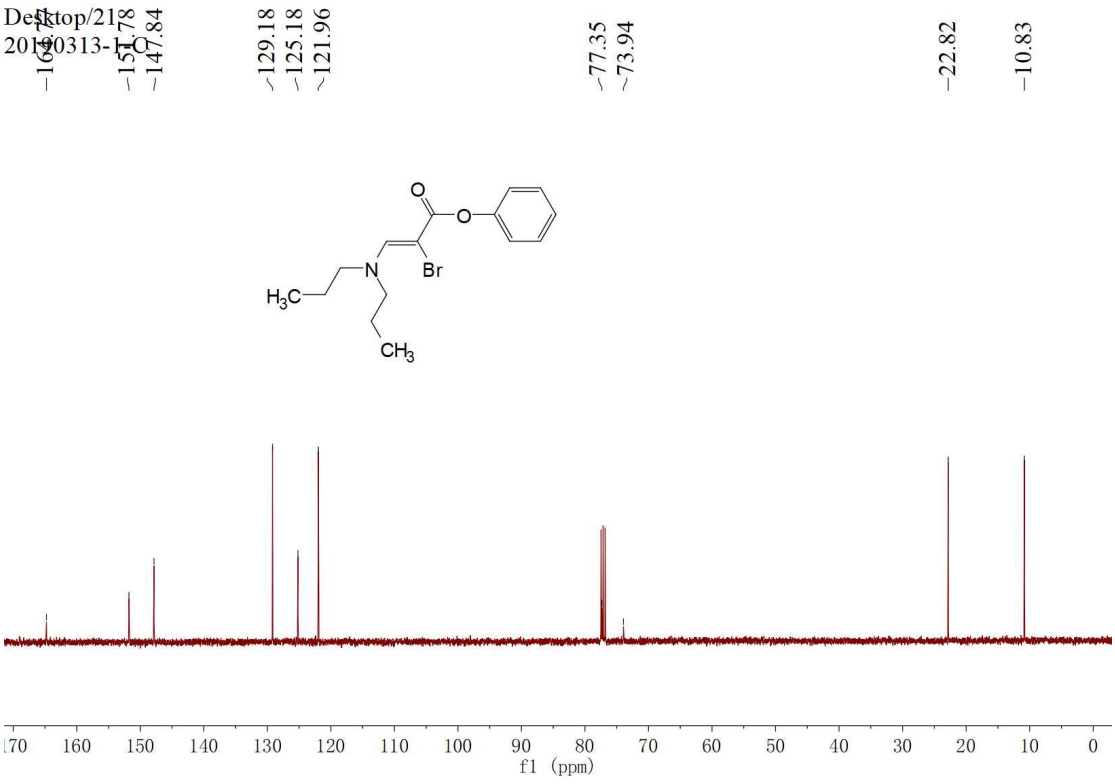

2019-11-19谱图/8
20191119-4-H
7.52
7.50
7.48
7.26
5.24
3.37
3.36
3.34
1.69
1.67
1.65
1.63
1.61
1.59
0.93
0.91
0.89
F
F
F
O
O
Br
N
H3C
CH3
1.00
2.02
2.02
1.99
3.89
4.26
6.28
f1 (ppm)

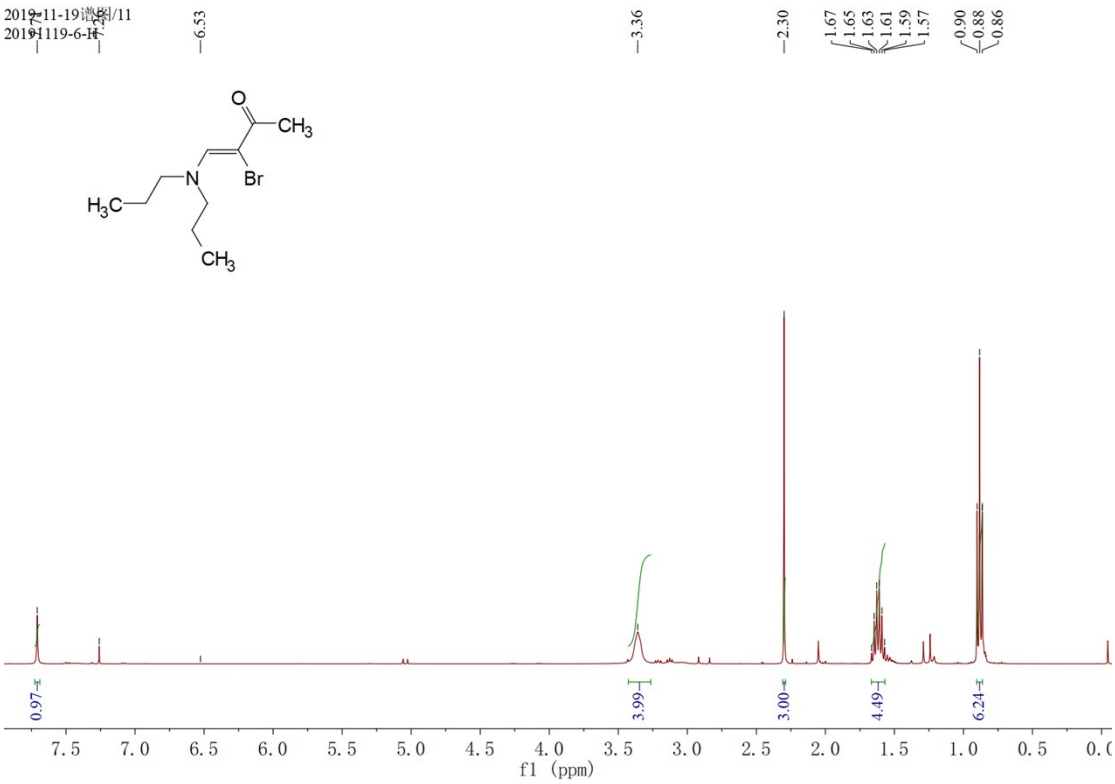

2019-11-19谱图/8
20191119-4-C
147.26
141.20
141.19
130.16
129.84
127.77
125.58
125.55
125.51
125.47
125.43
77.48
77.16
76.84
74.16
65.70
22.87
10.88
F
F
F
O
O
Br
N
H3C
CH3
f1 (ppm)

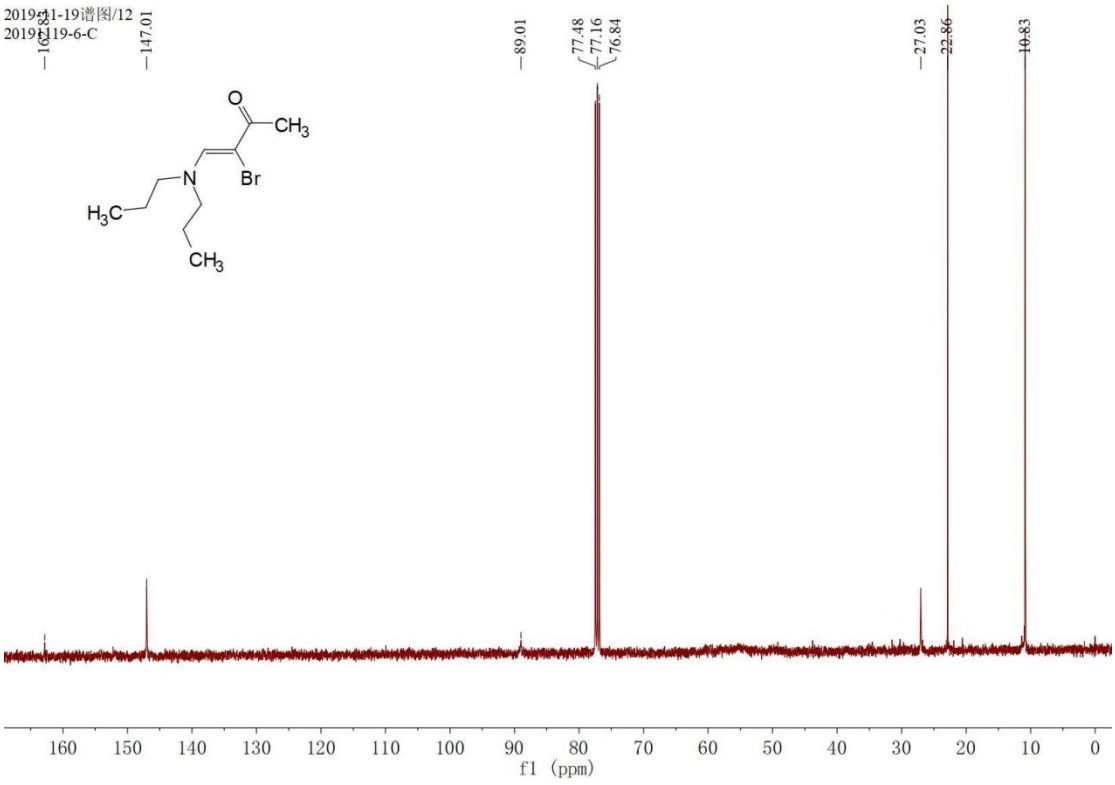
Desktop/18
20190314-1-H

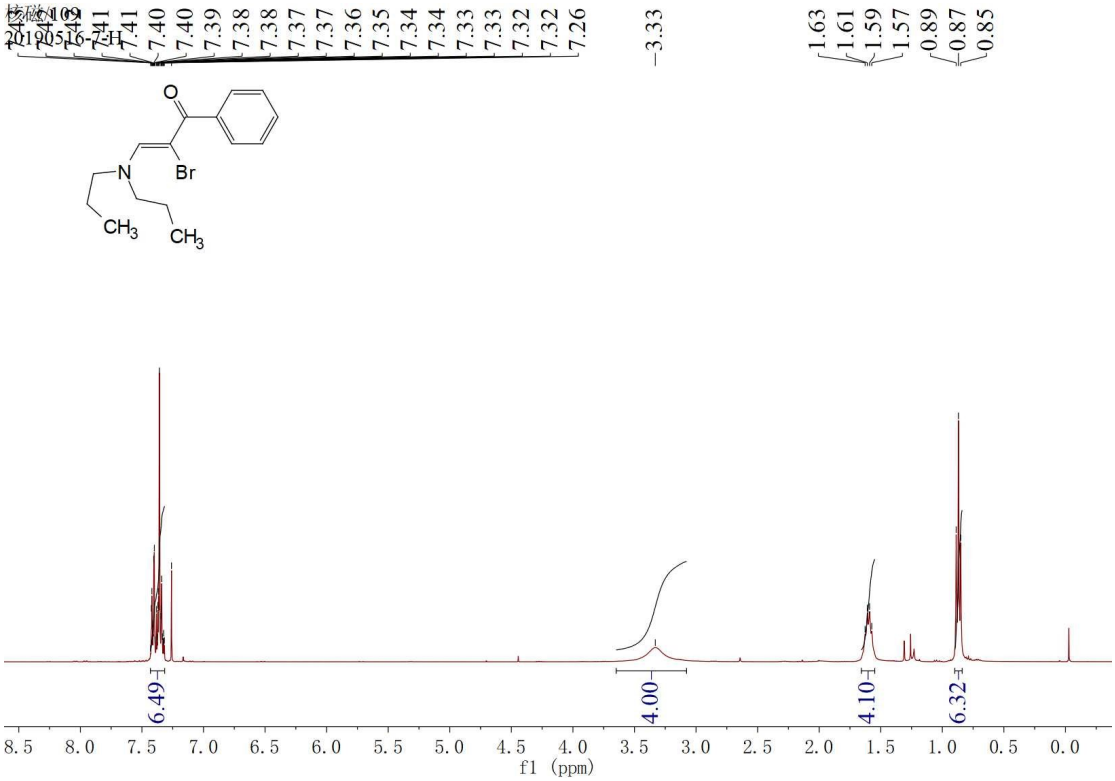


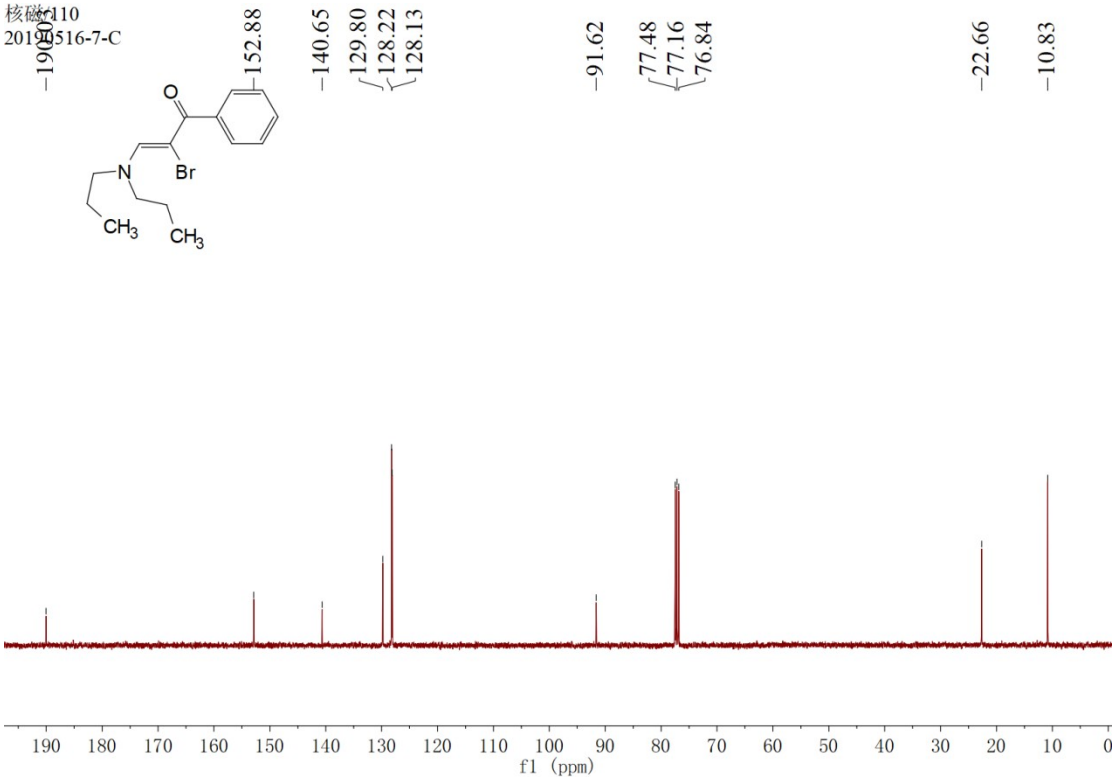
Desktop/21
20190313-1-C

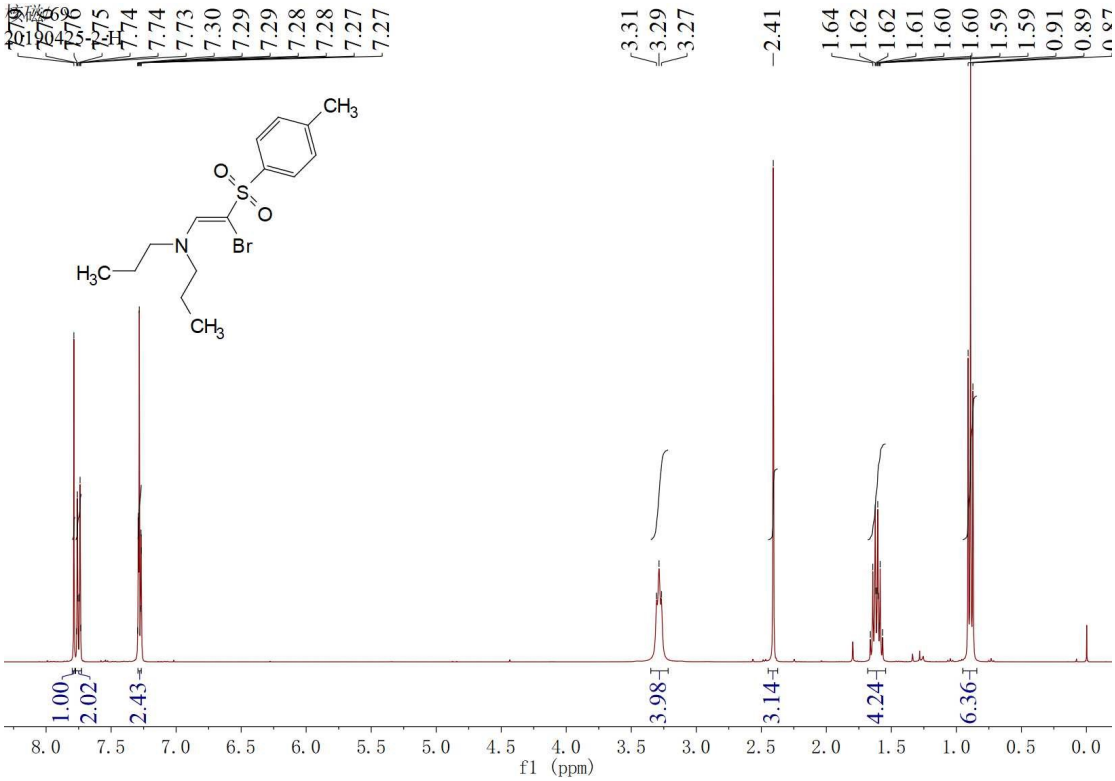


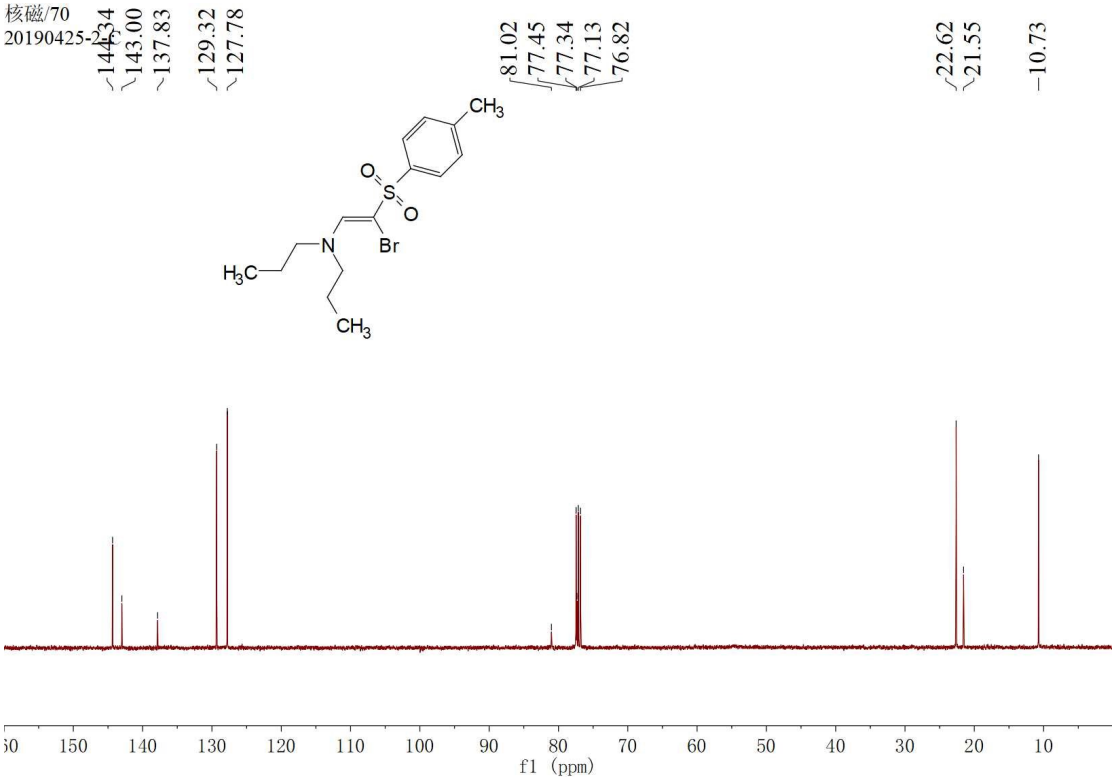

2019-11-19谱图/11
2019-1119-6-H
7.74
7.48
6.53
3.36
2.30
1.67
1.65
1.63
1.61
1.59
1.57
0.90
0.88
0.86
O
CH3
Br
N
H3C
CH3
0.97
3.99
3.00
4.49
6.24
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

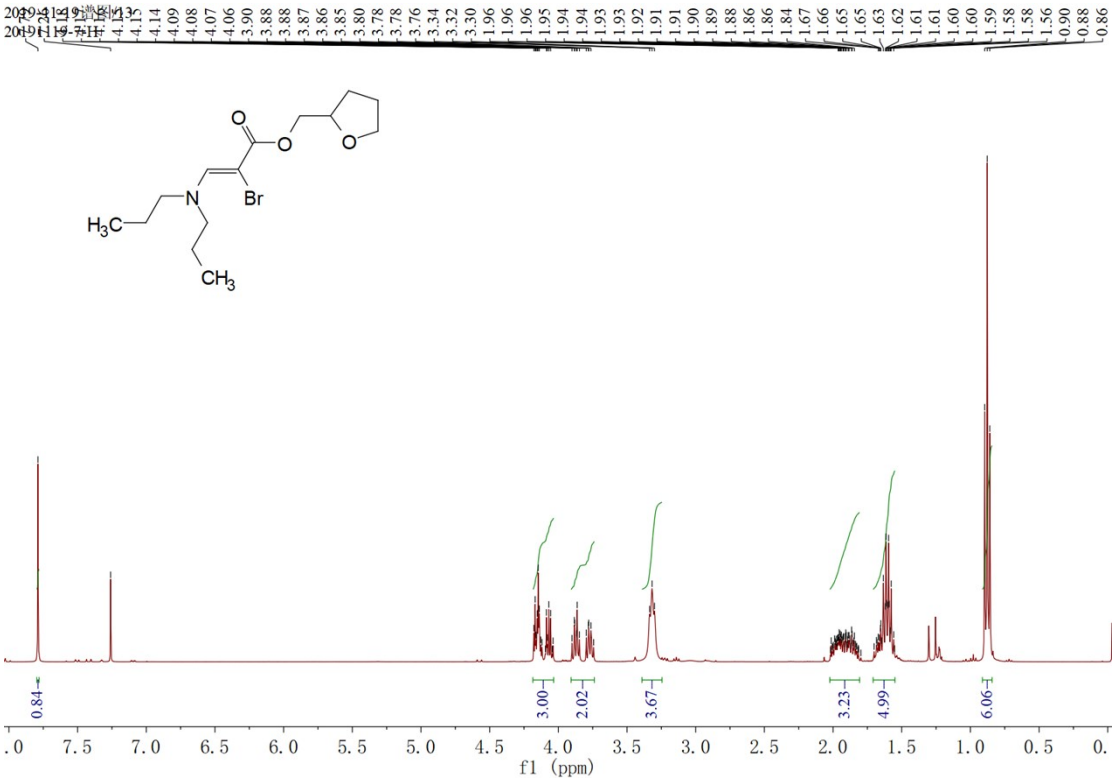

2019-11-19谱图/12
2019-1119-6-C
147.01
89.01
77.48
77.16
76.84
27.03
22.86
10.83
O
CH3
Br
N
H3C
CH3
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

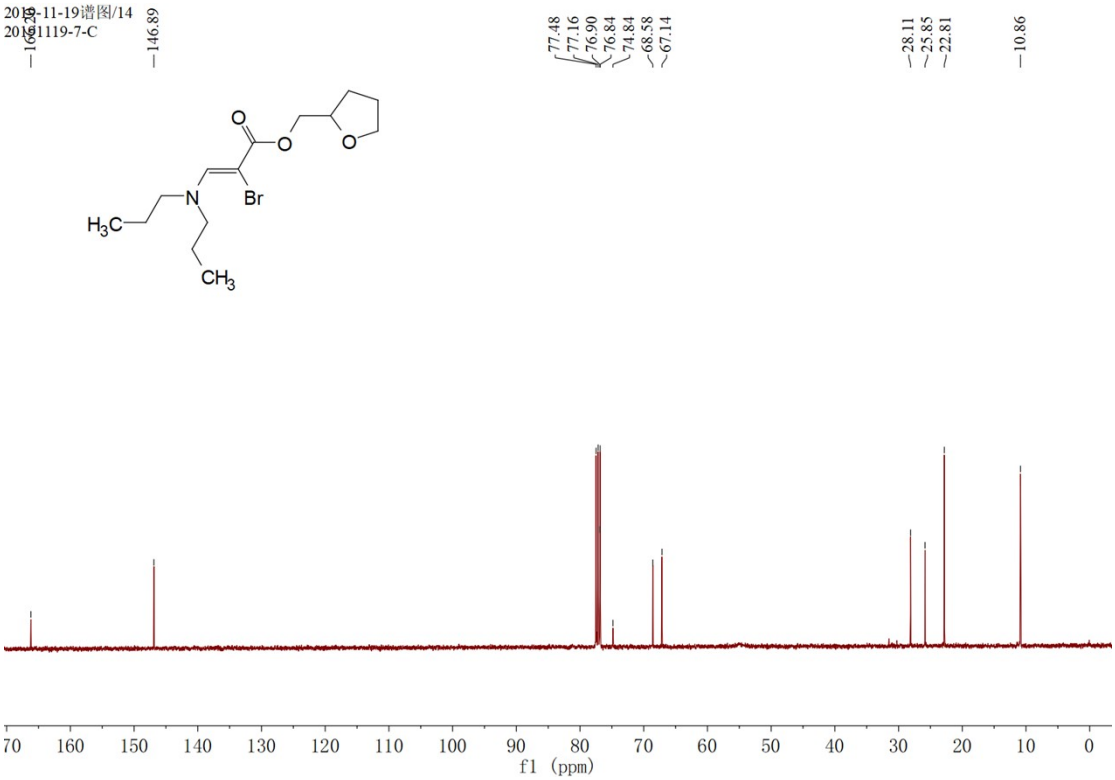

核磁109
20190516-7-H
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.26
3.33
1.63
1.61
1.59
1.57
0.89
0.87
0.85
O
N
Br
CH3
CH3
6.49
4.00
4.10
6.32
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


核磁110
20190516-7-C
190.07
152.88
140.65
129.80
128.22
128.13
91.62
77.48
77.16
76.84
22.66
10.83
O
N
Br
CH3
CH3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

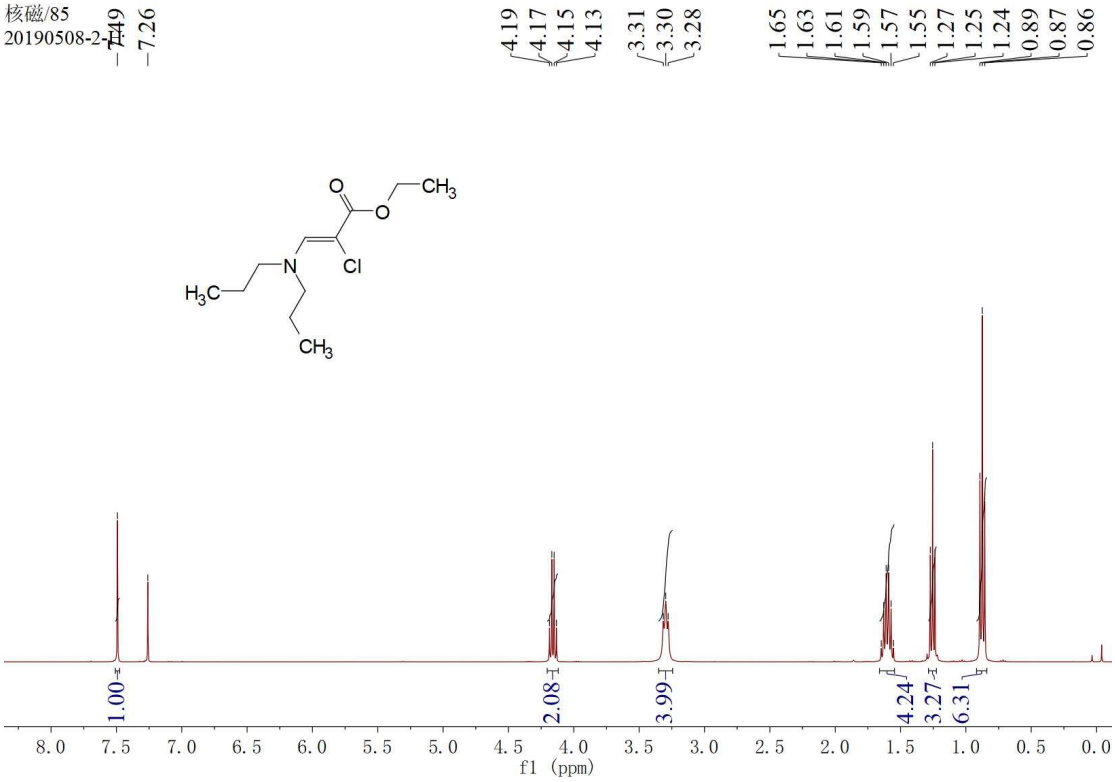

核磁/69
20190425-2-H
7.76
7.75
7.74
7.74
7.73
7.30
7.29
7.29
7.28
7.28
7.27
7.27
3.31
3.29
3.27
2.41
1.64
1.62
1.62
1.61
1.60
1.60
1.59
1.59
0.91
0.89
1.00
2.02
2.43
3.98
3.14
4.24
6.36
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
CH3
O
S
O
N
Br
H3C
CH3


核磁/70
20190425-2-C
144.34
143.00
137.83
129.32
127.78
81.02
77.45
77.34
77.13
76.82
22.62
21.55
10.73
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
CH3
O
S
O
N
Br
H3C
CH3

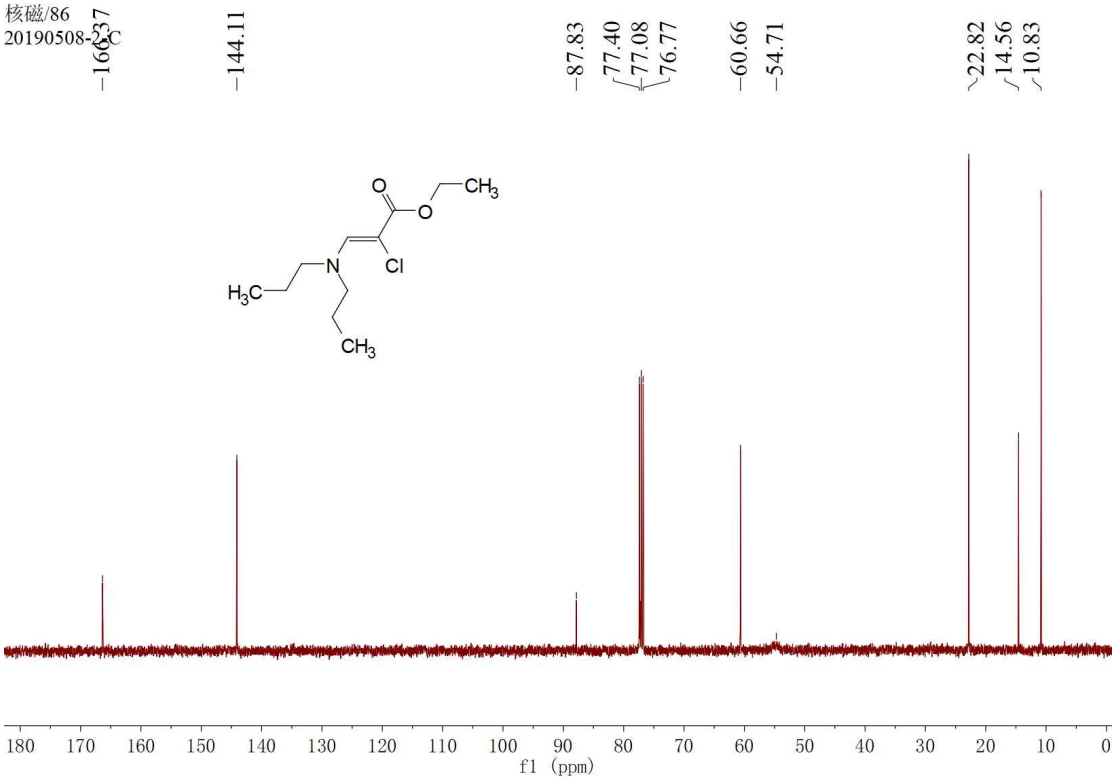

4.15
4.14
4.09
4.08
4.07
4.06
3.90
3.88
3.88
3.87
3.86
3.85
3.80
3.78
3.78
3.76
3.34
3.32
3.30
1.96
1.96
1.95
1.94
1.94
1.93
1.93
1.92
1.91
1.91
1.90
1.89
1.88
1.86
1.86
1.84
1.67
1.66
1.65
1.65
1.63
1.62
1.61
1.61
1.60
1.60
1.59
1.58
1.58
1.56
0.90
0.88
0.86
O
O
O
Br
N
H3C
CH3
0.84
3.00
2.02
3.67
3.23
4.99
6.06
f1 (ppm)


146.89
77.48
77.16
76.90
76.84
74.84
68.58
67.14
28.11
25.85
22.81
10.86
O
O
O
Br
N
H3C
CH3
f1 (ppm)

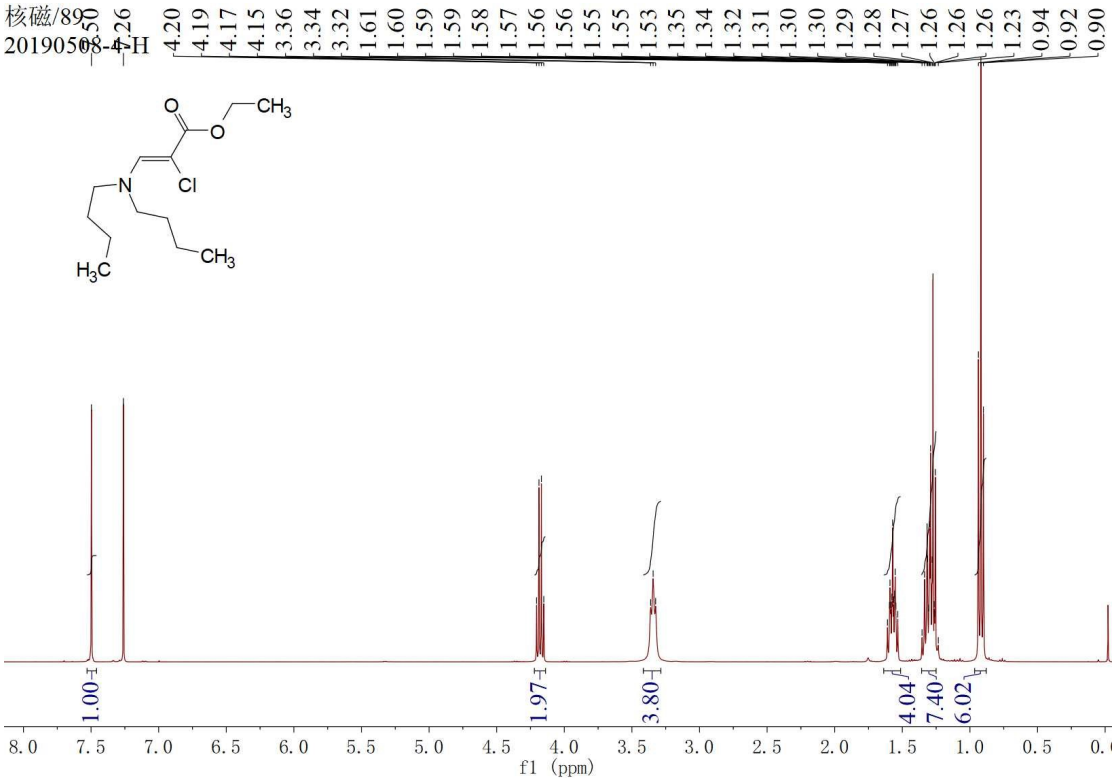
核磁/85
20190508-2-1



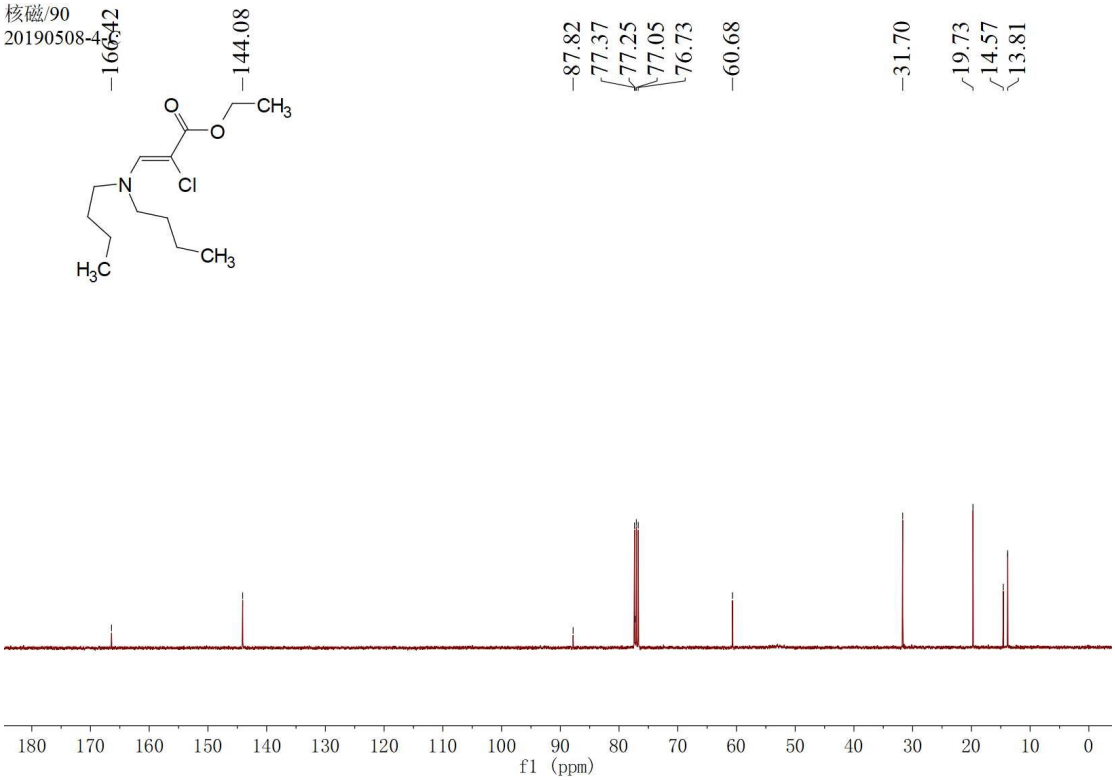
核磁/86
20190508-2-C



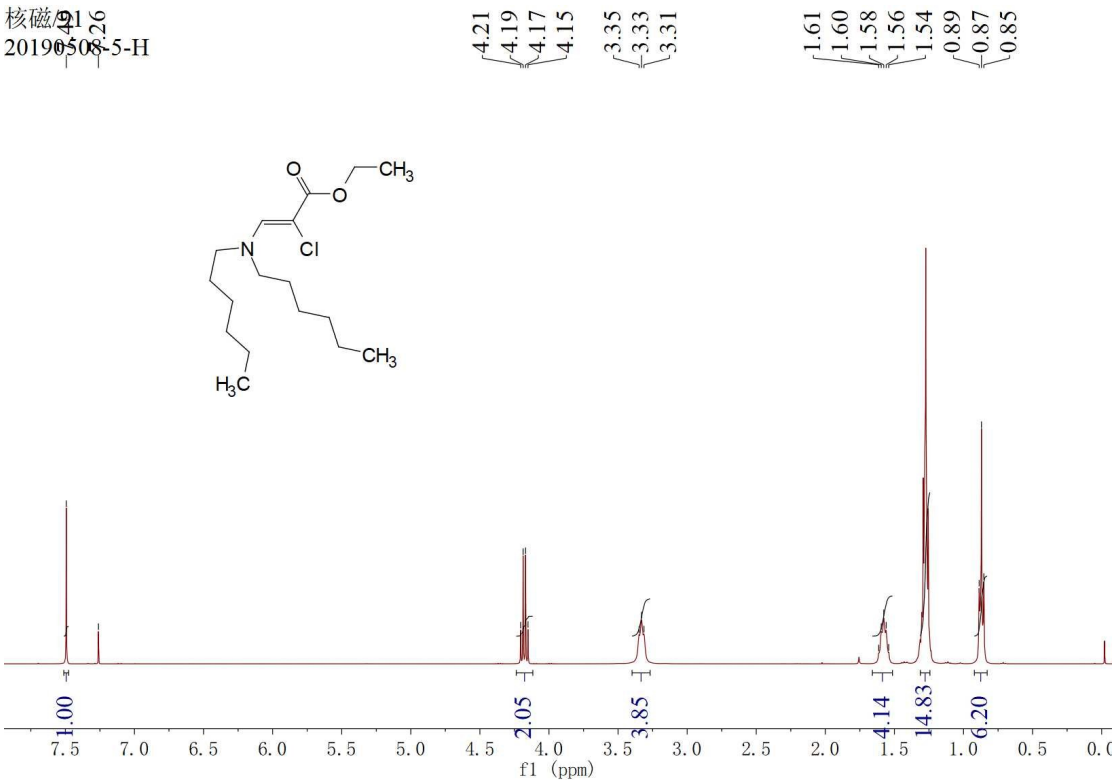
核磁/89
20190508-4-H



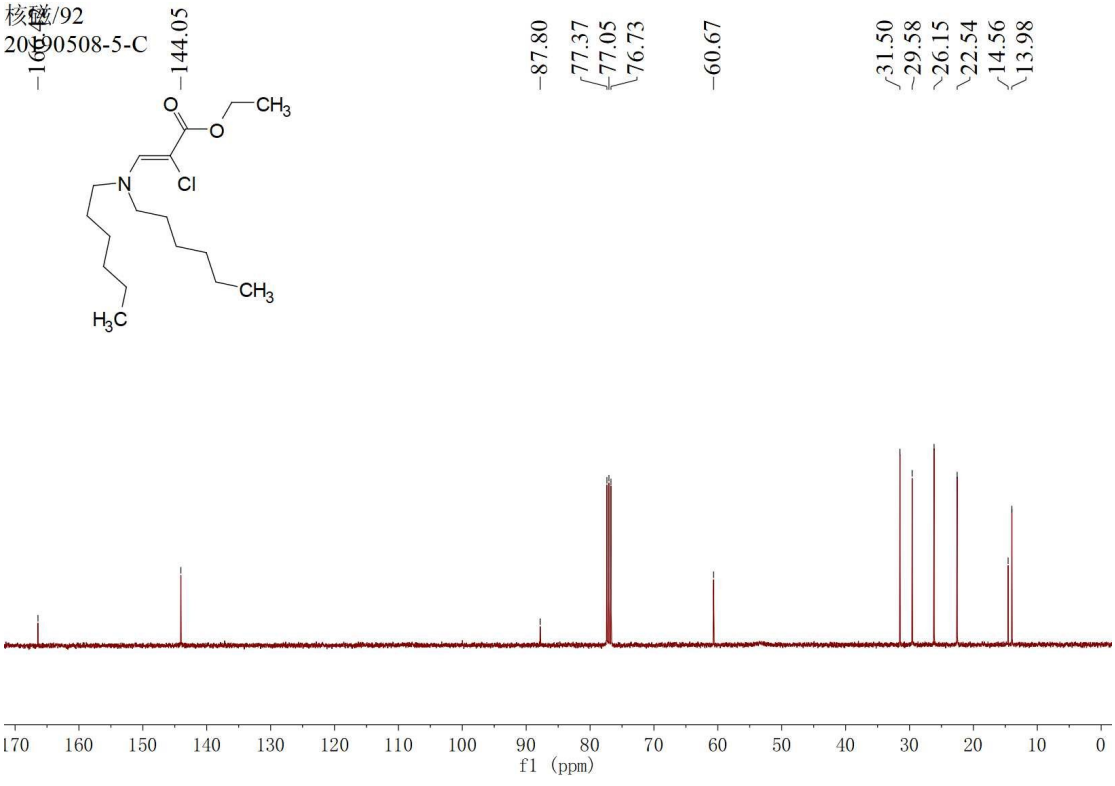
核磁/90
20190508-4-C

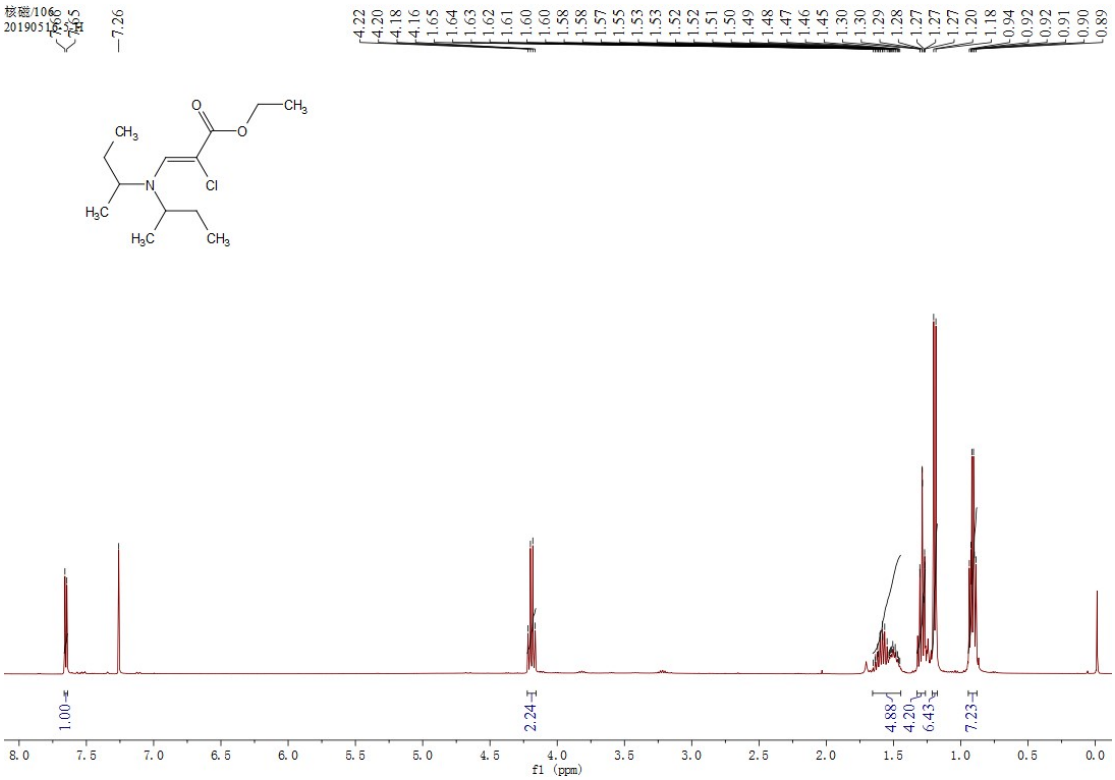


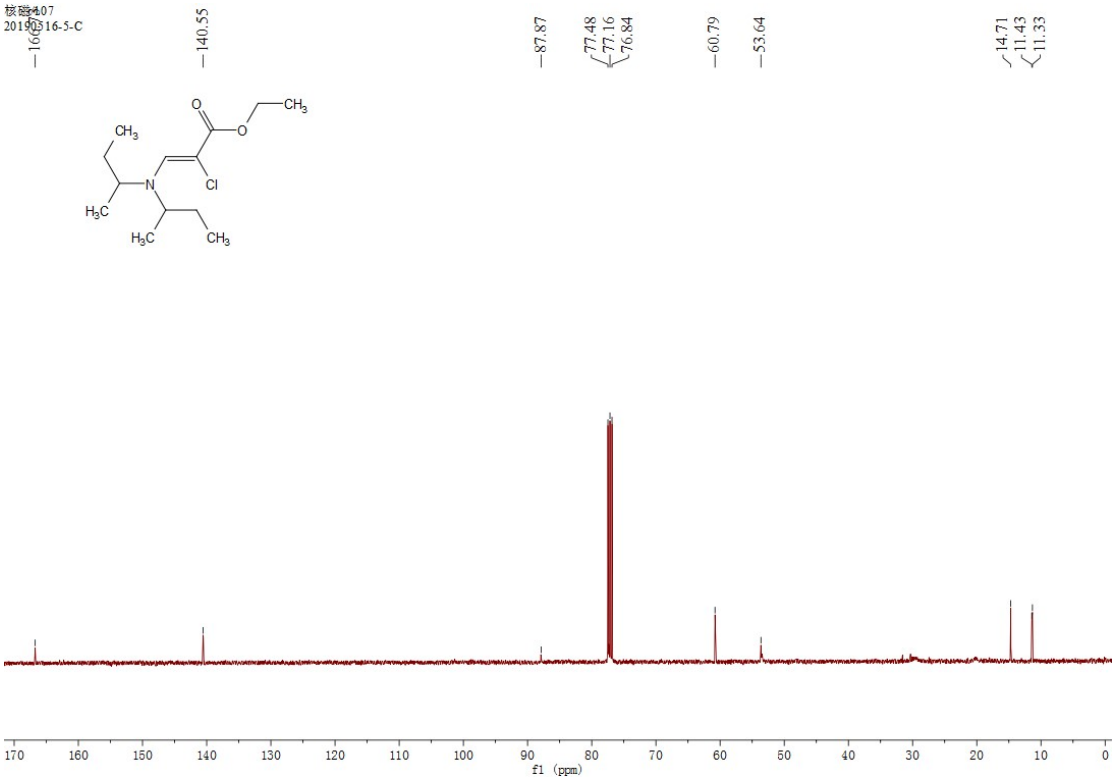
核磁/91
20190508-5-H



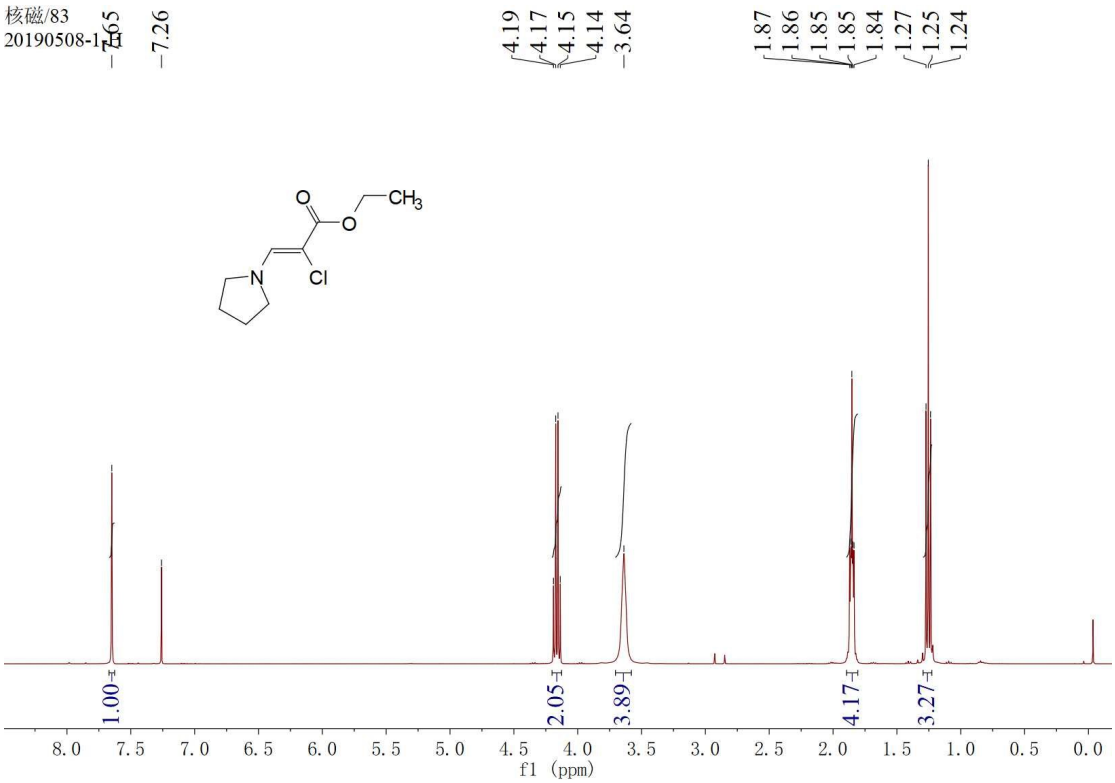
核磁/92
20190508-5-C



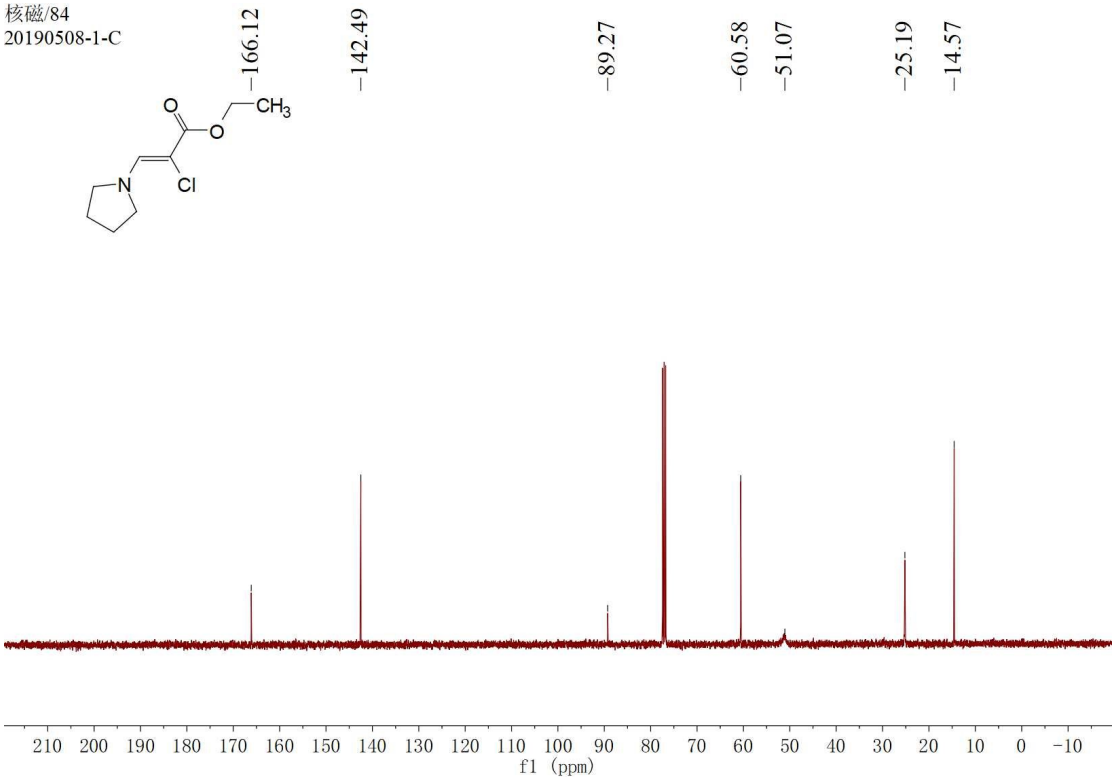

核磁/106
20190516-5-H
7.26
4.22
4.20
4.18
4.16
1.65
1.64
1.63
1.62
1.61
1.60
1.60
1.58
1.58
1.57
1.55
1.53
1.53
1.52
1.52
1.51
1.50
1.49
1.48
1.47
1.46
1.45
1.30
1.29
1.28
1.27
1.27
1.27
1.20
1.18
0.94
0.92
0.92
0.91
0.90
0.89
1.00
2.24
4.88
4.20
6.43
7.23
f1 (ppm)

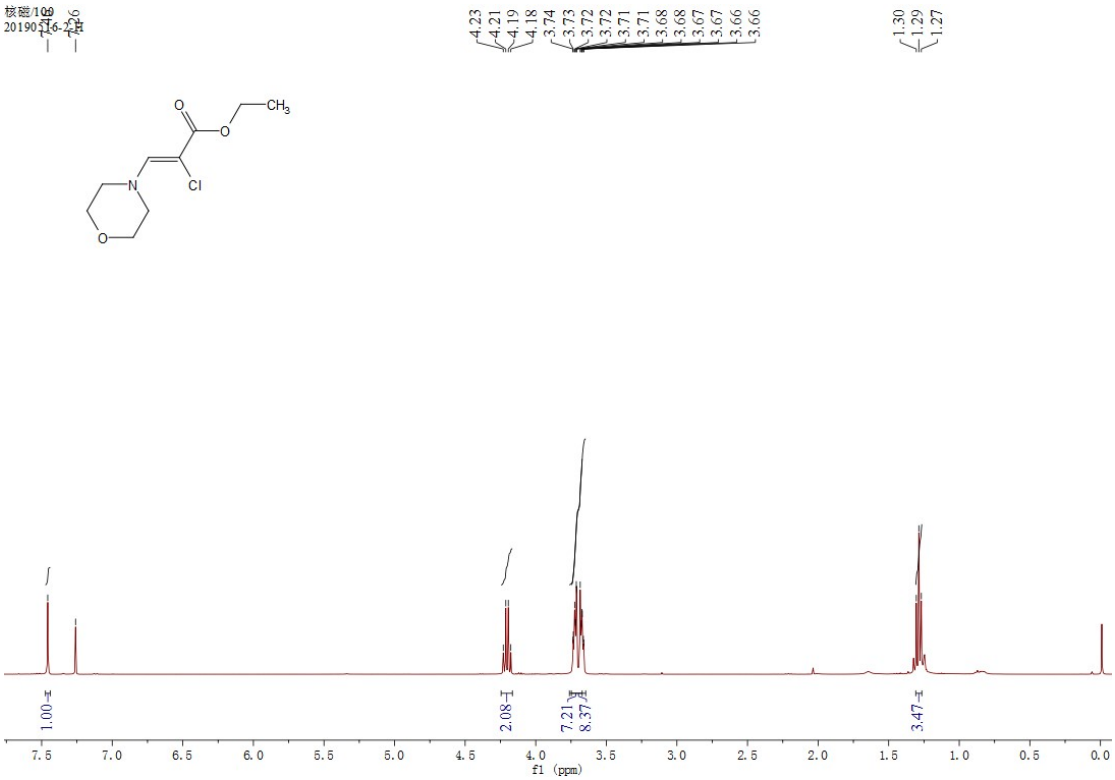

核磁/107
20190516-5-C
166.05
140.55
87.87
77.48
77.16
76.84
60.79
53.64
14.71
11.43
11.33
f1 (ppm)

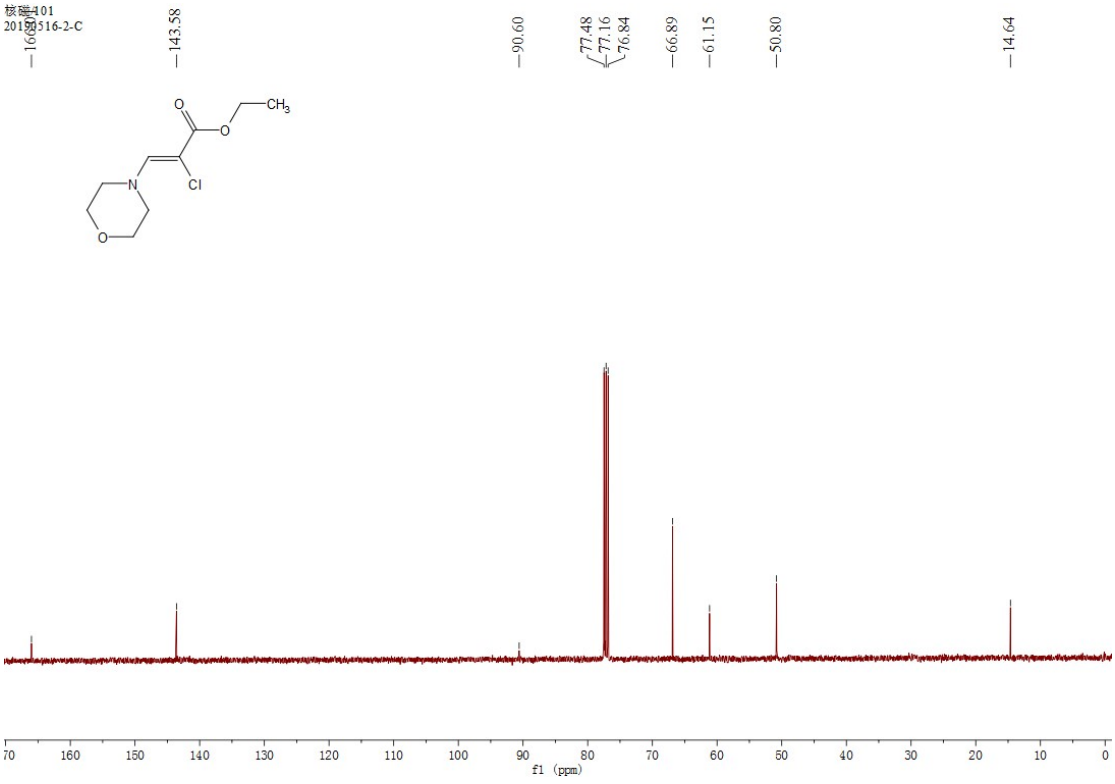
核磁/83
20190508-1-H

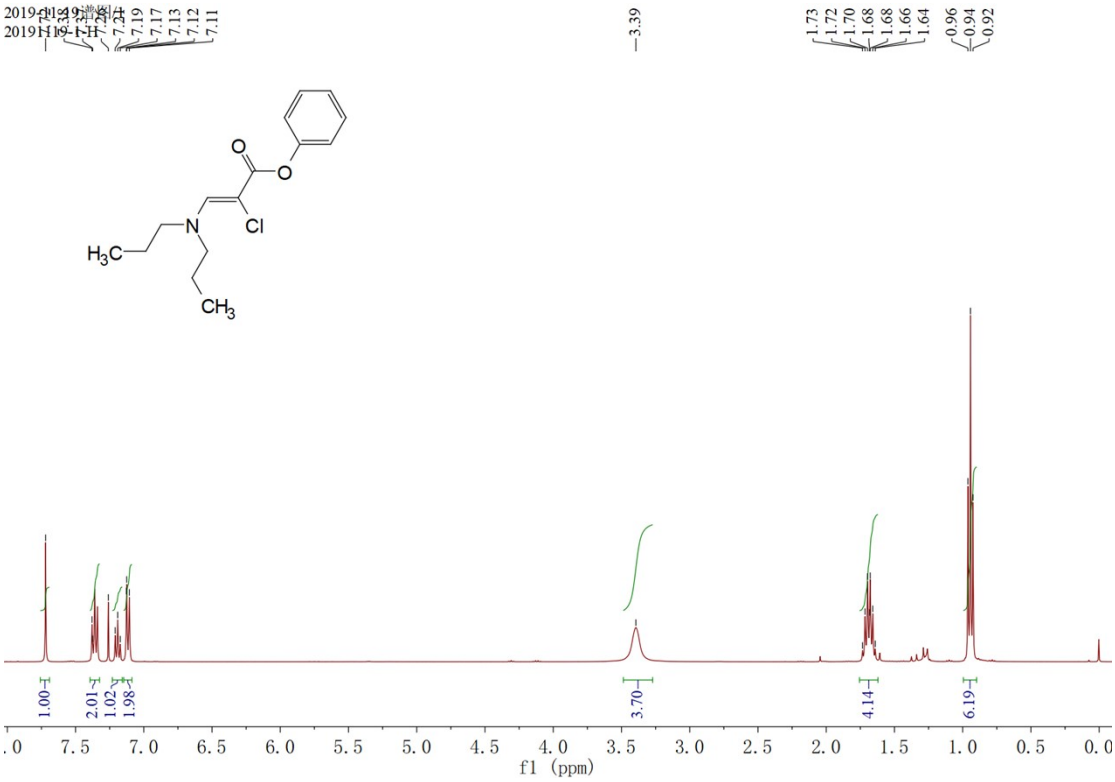


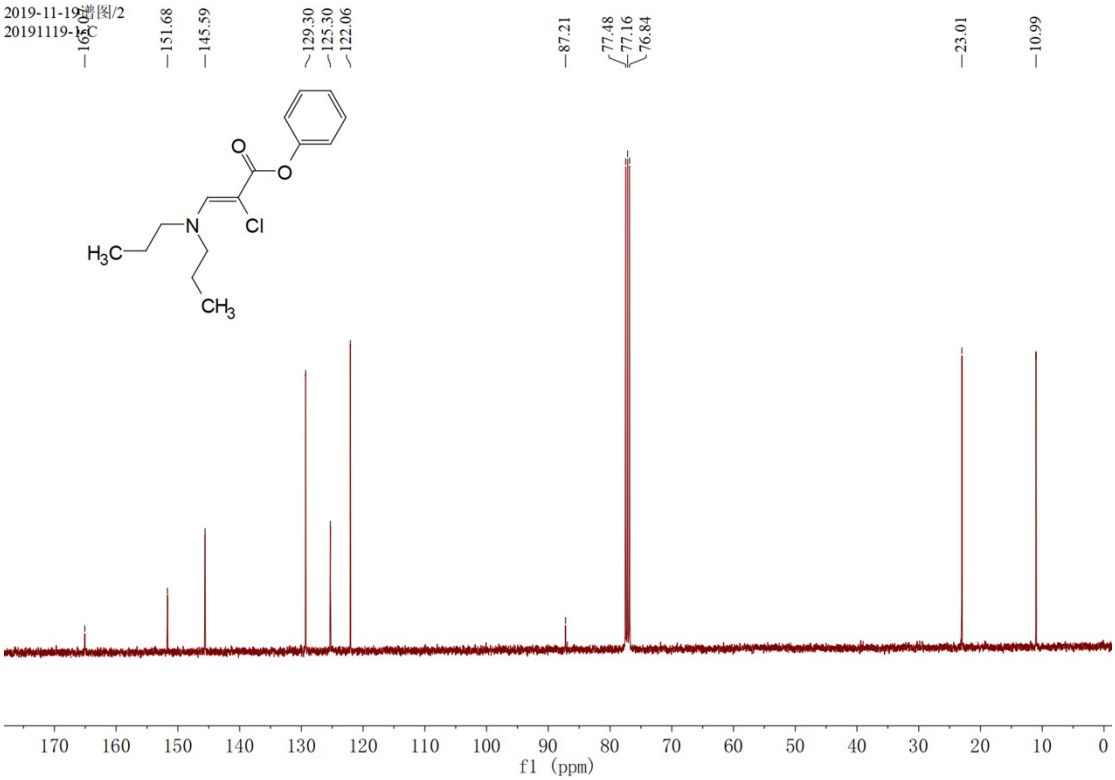
核磁/84
20190508-1-C

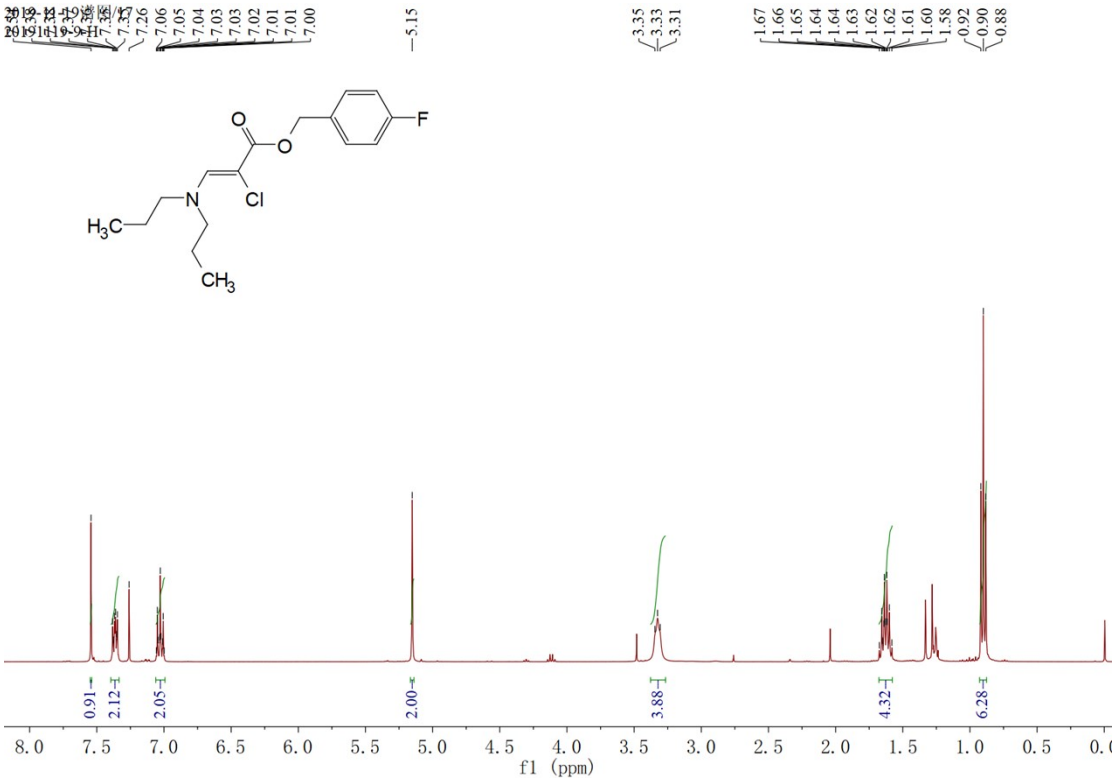


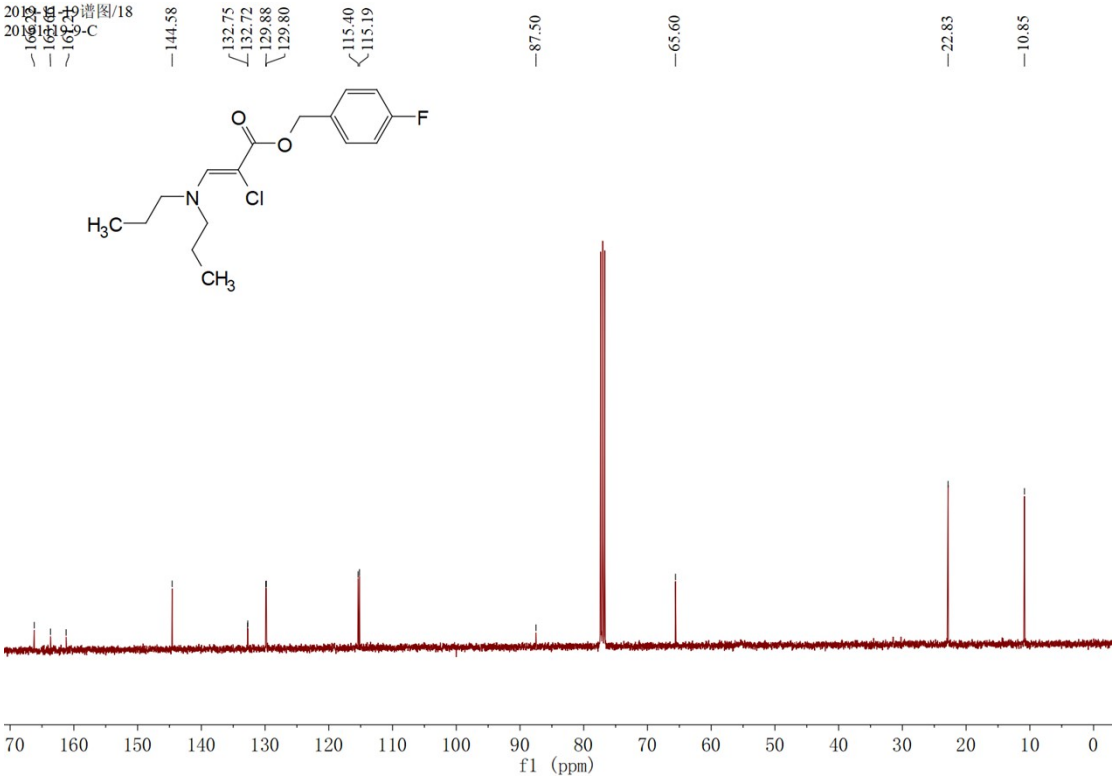

核磁109
20190516-2-H
4.23
4.21
4.19
4.18
3.74
3.73
3.72
3.72
3.72
3.71
3.71
3.68
3.68
3.67
3.67
3.66
3.66
1.30
1.29
1.27
O
O
CH3
Cl
N
O
1.00
2.08
7.21
8.37
3.47
f1 (ppm)

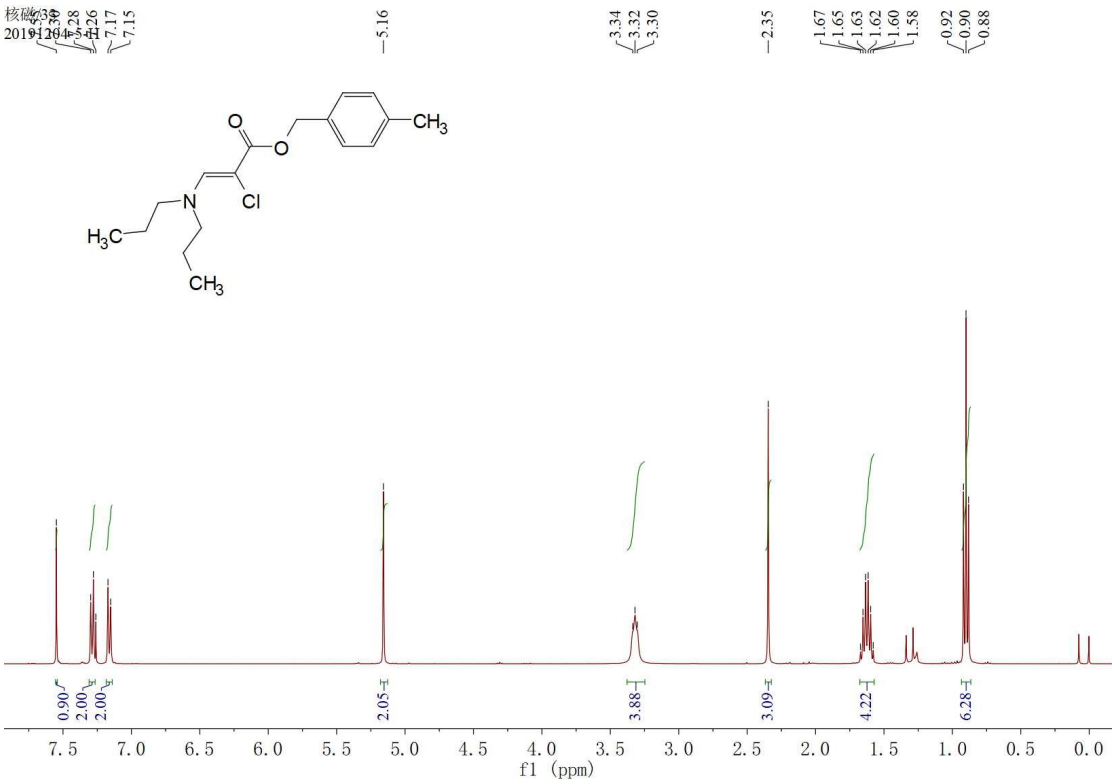

核磁101
20190516-2-C
166.76
143.58
90.60
77.48
77.16
76.84
66.89
61.15
50.80
14.64
O
O
CH3
Cl
N
O
f1 (ppm)

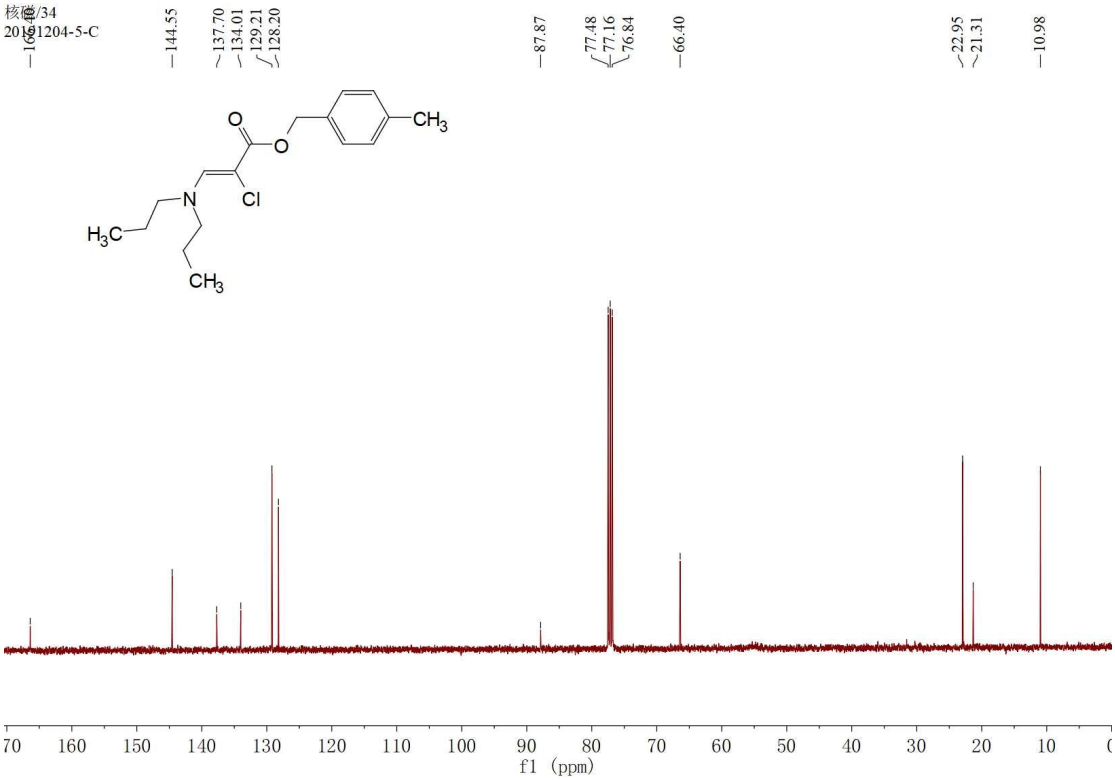

7.33
7.21
7.19
7.17
7.13
7.12
7.11
3.39
1.73
1.72
1.70
1.68
1.68
1.66
1.64
0.96
0.94
0.92
O
O
Cl
N
H3C
CH3
1.00
2.01
1.02
1.98
3.70
4.14
6.19
f1 (ppm)

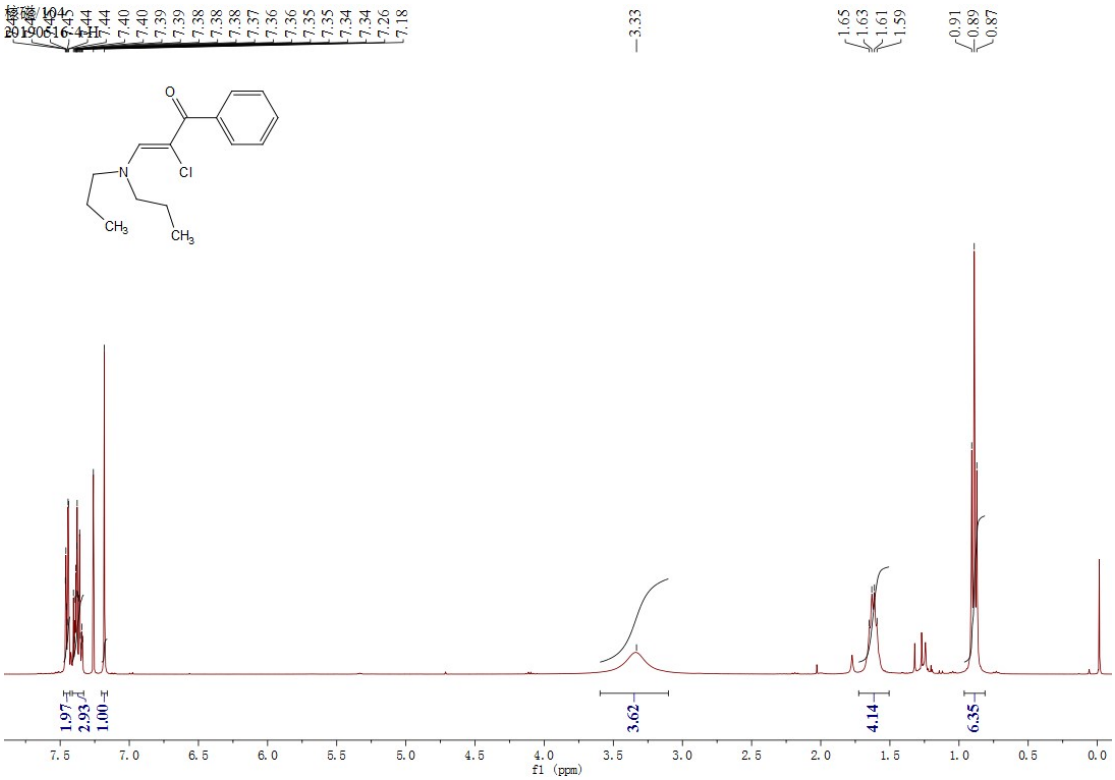

165.01
151.68
145.59
129.30
125.30
122.06
87.21
77.48
77.16
76.84
23.01
10.99
O
O
Cl
N
H3C
CH3
f1 (ppm)

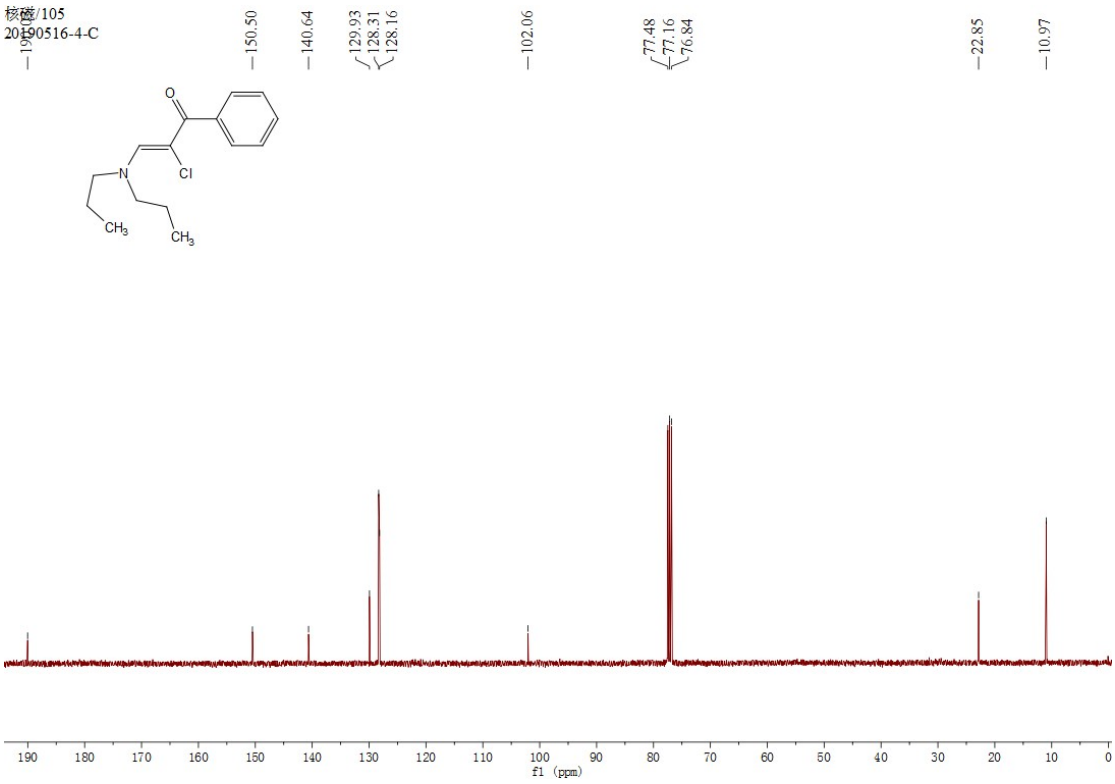

7.26
7.06
7.05
7.04
7.03
7.03
7.02
7.01
7.01
7.00
5.15
3.35
3.33
3.31
1.67
1.66
1.65
1.64
1.64
1.63
1.62
1.62
1.61
1.60
1.58
0.92
0.90
0.88
O
O
F
Cl
N
H3C
CH3
0.91
2.12
2.05
2.00
3.88
4.32
6.28
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


144.58
132.75
132.72
129.88
129.80
115.40
115.19
87.50
65.60
22.83
10.85
O
O
F
Cl
N
H3C
CH3
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

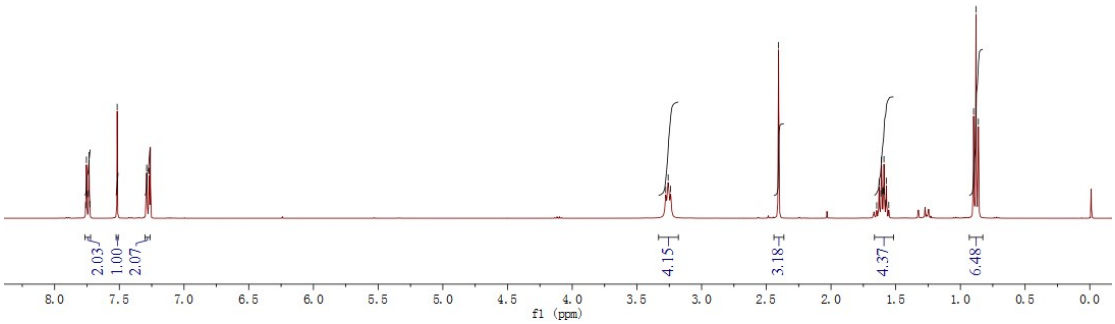

核磁-33
20191204-5-H
7.33
7.28
7.26
7.17
7.15
5.16
3.34
3.32
3.30
2.35
1.67
1.65
1.63
1.62
1.60
1.58
0.92
0.90
0.88
O
O
CH3
N
Cl
H3C
CH3
0.90
2.00
2.00
2.05
3.88
3.09
4.22
6.28
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


核磁-34
20191204-5-C
144.55
137.70
134.01
129.21
128.20
87.87
77.48
77.16
76.84
66.40
22.95
21.31
10.98
O
O
CH3
N
Cl
H3C
CH3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

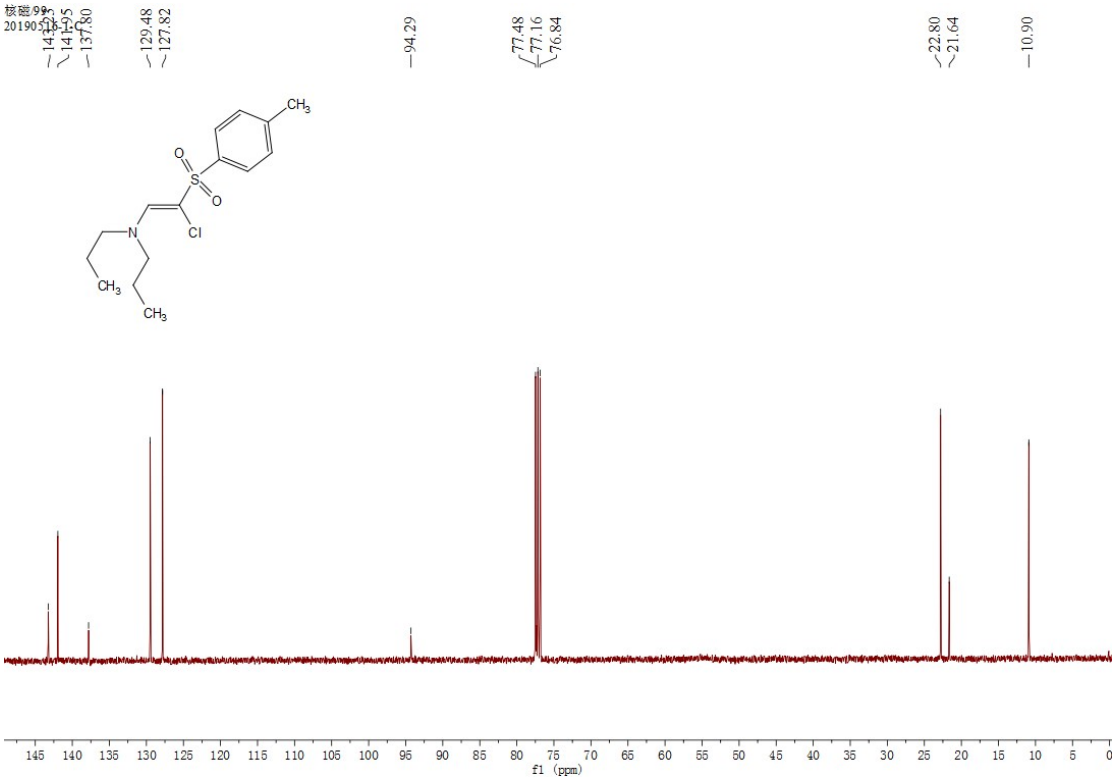

核磁/104
20190516-4-H
7.44
7.40
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.26
7.18
3.33
1.65
1.63
1.61
1.59
0.91
0.89
0.87
O
N
Cl
CH3
CH3
1.97
2.93
1.00
3.62
4.14
6.35
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

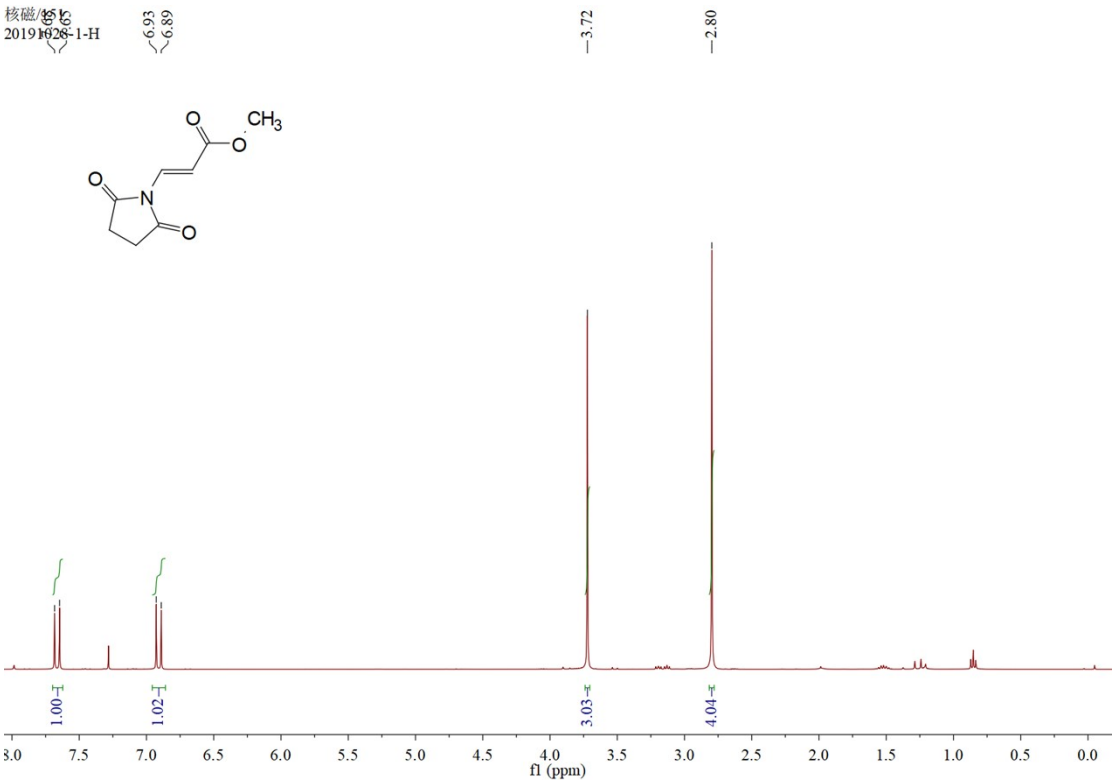

核磁/105
20190516-4-C
150.50
140.64
129.93
128.31
128.16
102.06
77.48
77.16
76.84
22.85
10.97
O
N
Cl
CH3
CH3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

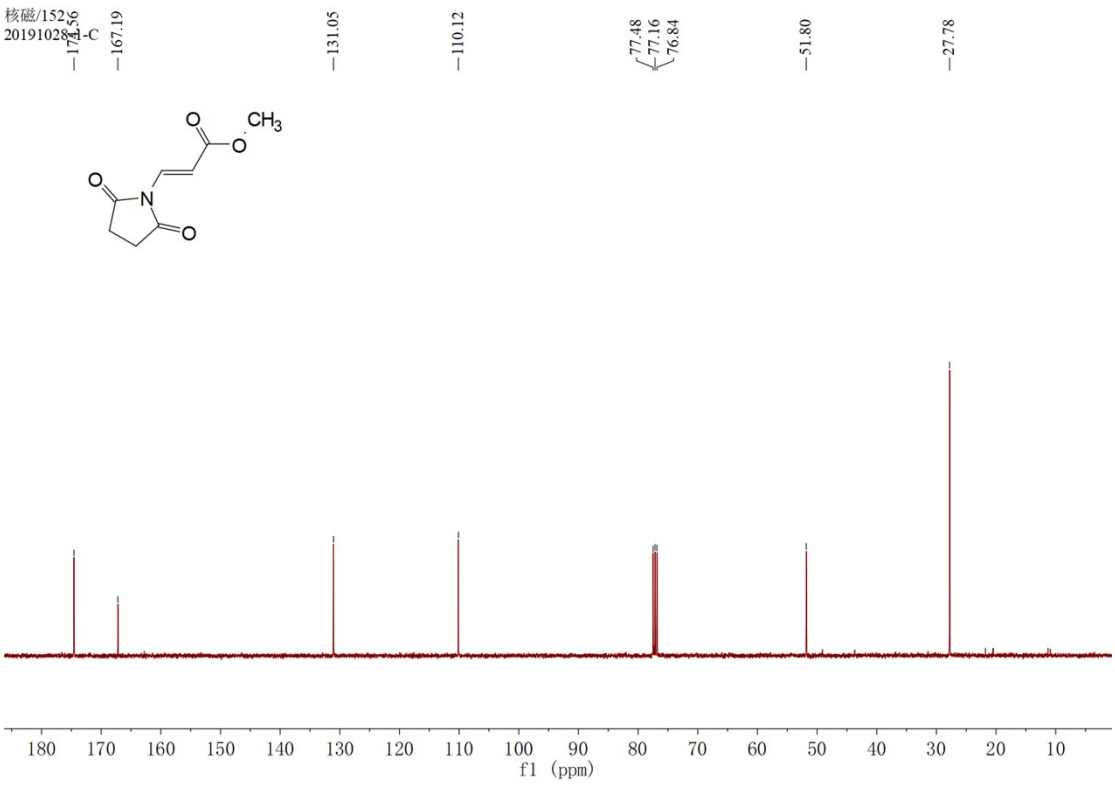
核磁-98
20190516-1-H

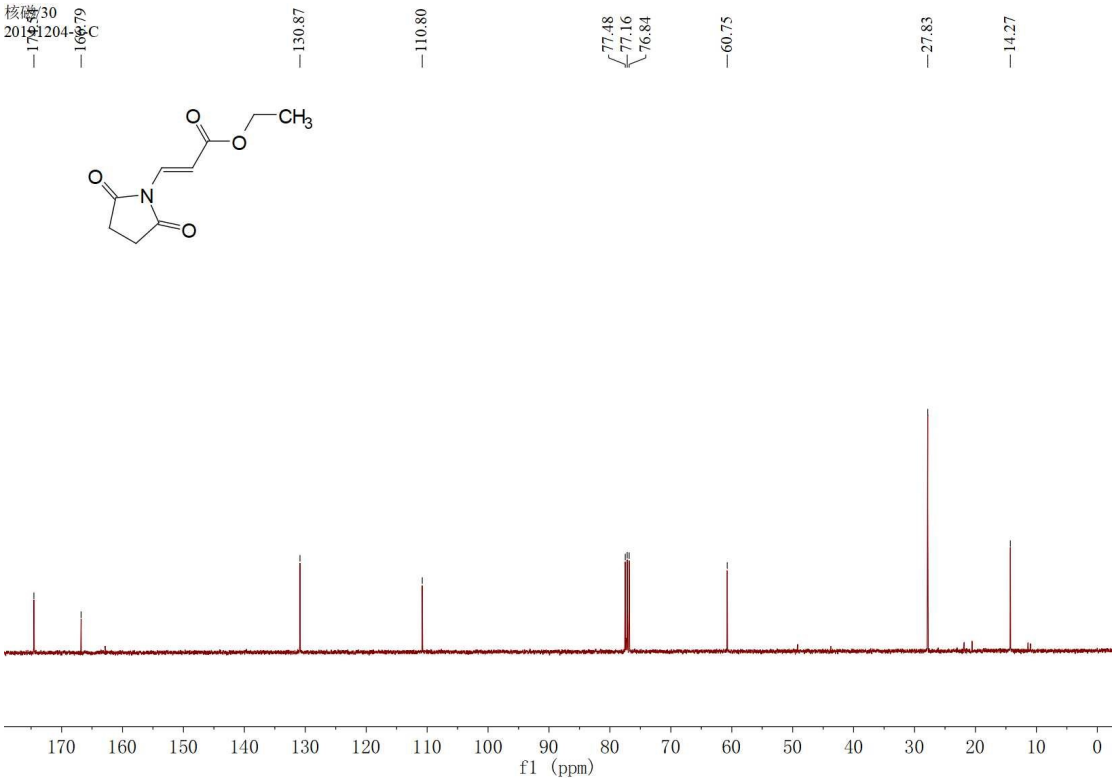


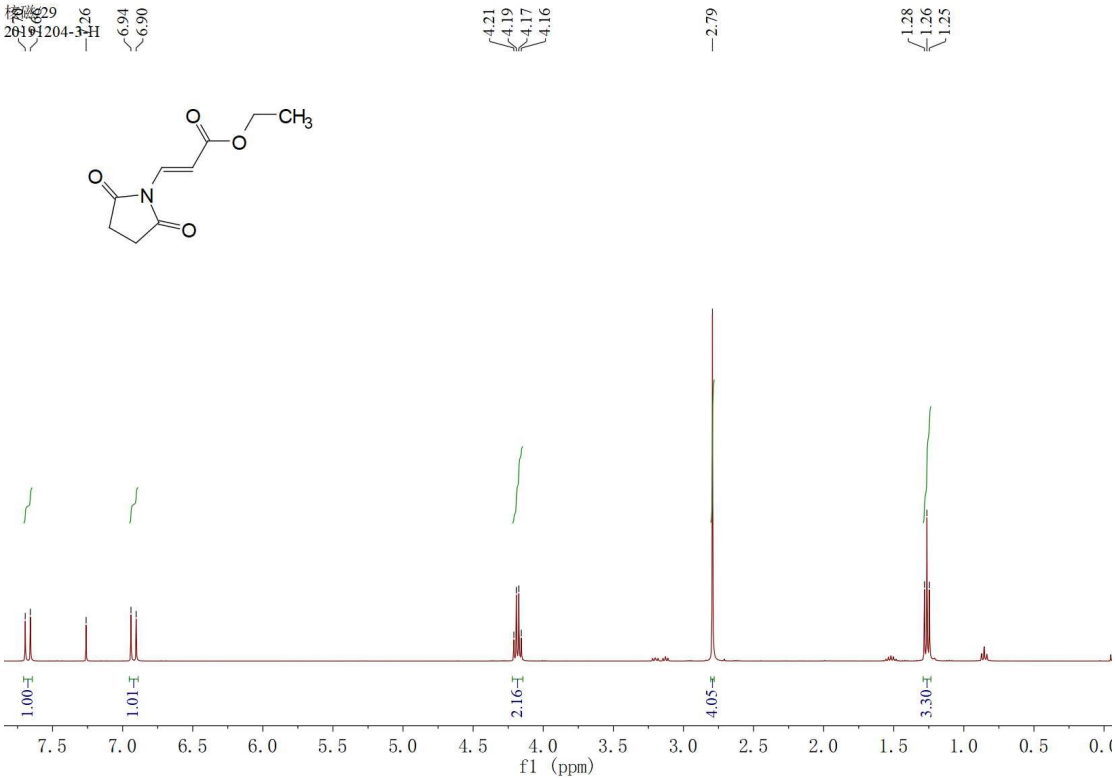
核磁-99
20190516-1-C

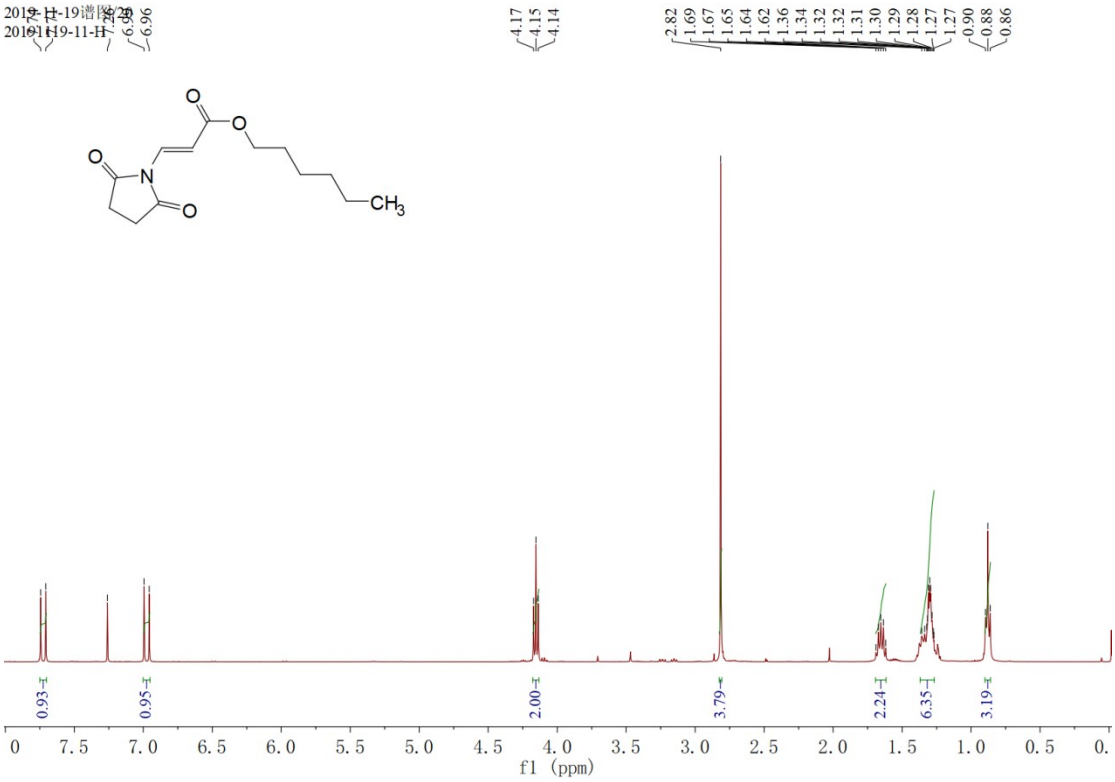


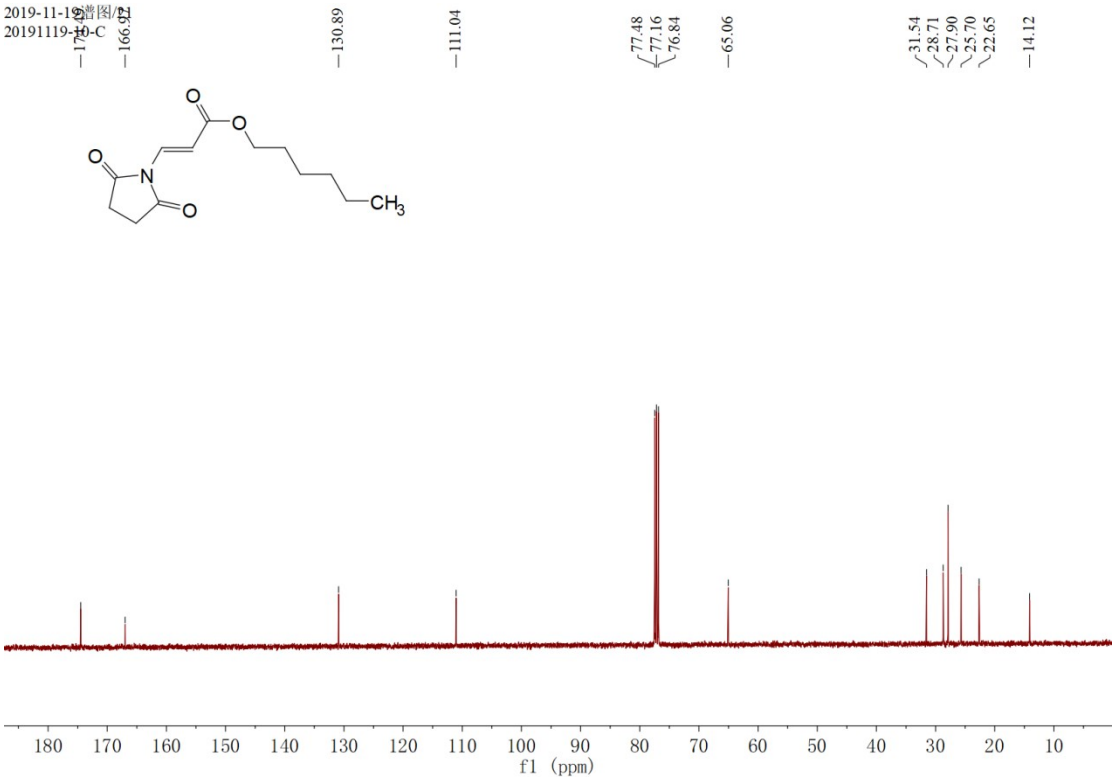

6.93
6.89
3.72
2.80
1.00
1.02
3.03
4.04
f1 (ppm)

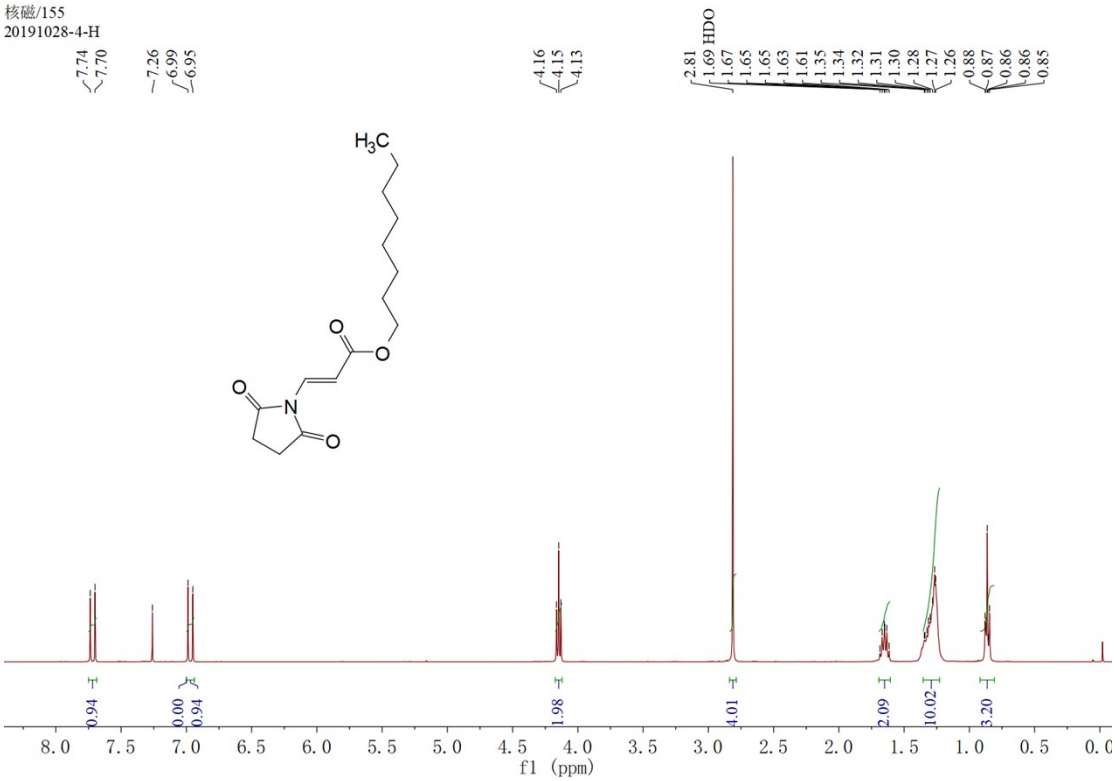

174.56
167.19
131.05
110.12
77.48
77.16
76.84
51.80
27.78
f1 (ppm)

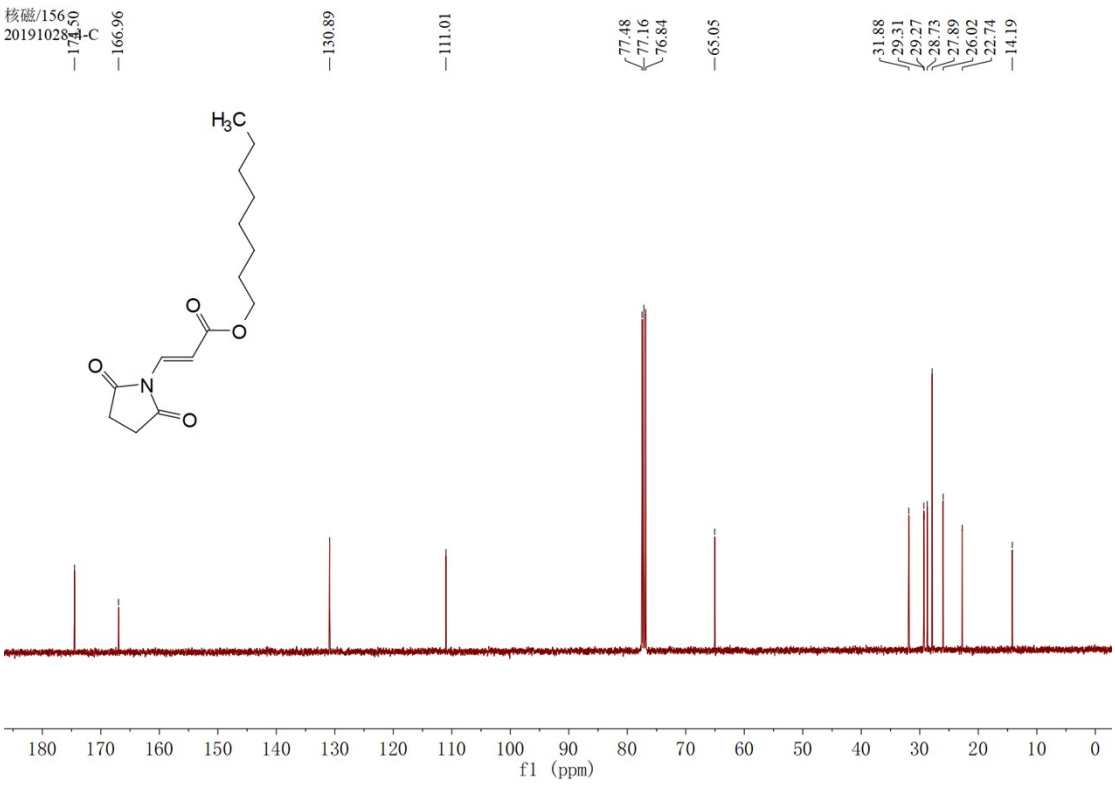

核磁30
20191204-3C
172.47
166.79
130.87
110.80
77.48
77.16
76.84
60.75
27.83
14.27
O
O
CH3
O
N
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

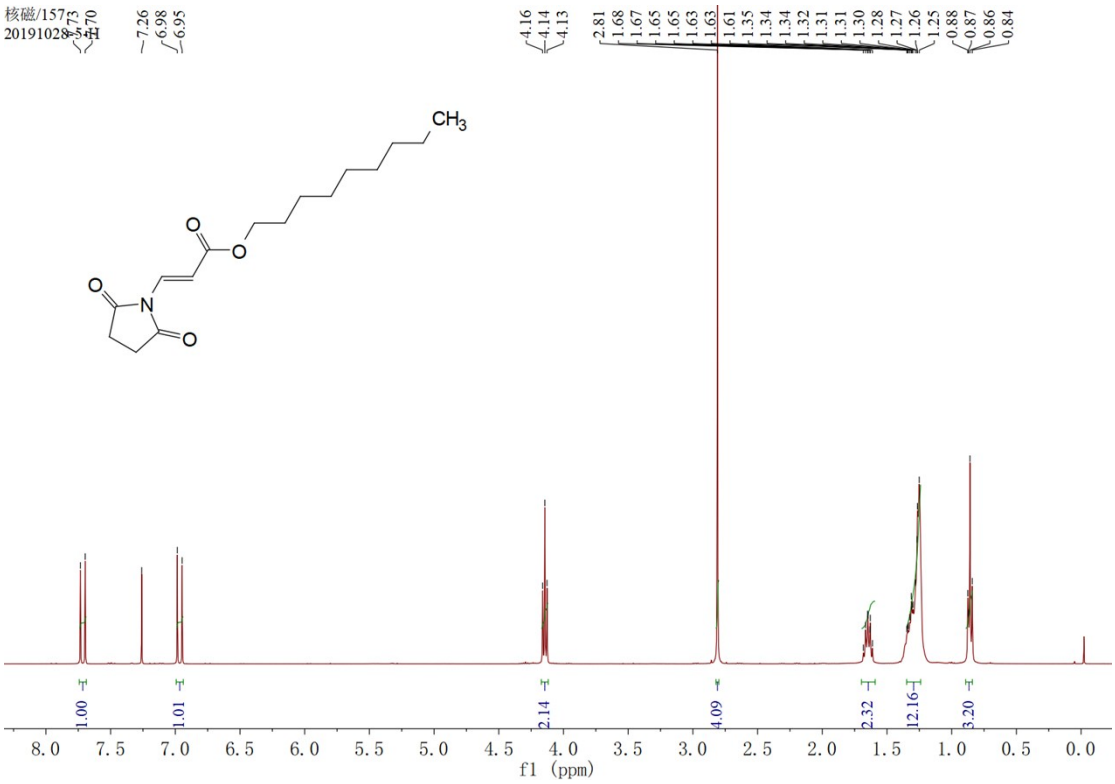

核磁29
20191204-3-H
7.26
6.94
6.90
4.21
4.19
4.17
4.16
2.79
1.28
1.26
1.25
O
O
CH3
O
N
O
1.00
1.01
2.16
4.05
3.30
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

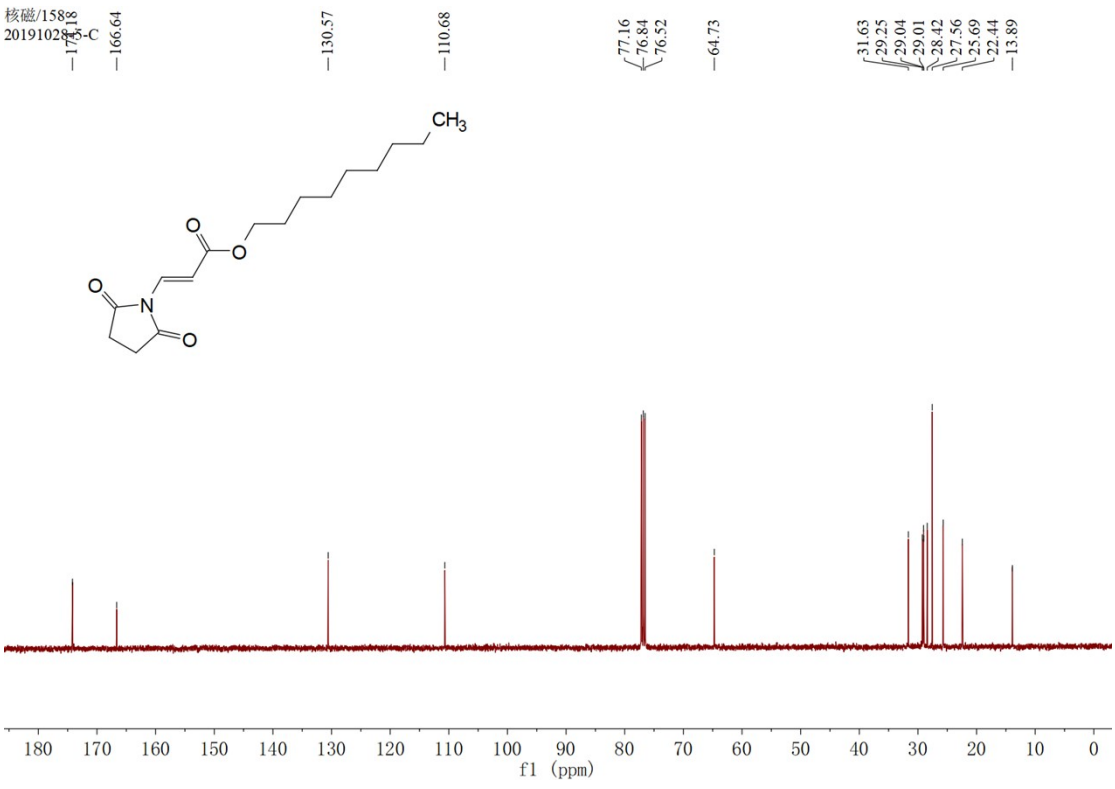

2019-11-19谱图/20
20191119-11-H
7.41
7.26
6.98
6.96
4.17
4.15
4.14
2.82
1.69
1.67
1.65
1.64
1.62
1.36
1.34
1.32
1.32
1.31
1.30
1.29
1.28
1.27
1.27
0.90
0.88
0.86
O
O
O
N
O
CH3
0.93
0.95
2.00
3.79
2.24
6.35
3.19
0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


2019-11-19谱图/21
20191119-10-C
170.20
166.92
130.89
111.04
77.48
77.16
76.84
65.06
31.54
28.71
27.90
25.70
22.65
14.12
O
O
O
N
O
CH3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


核磁/155
20191028-4-H
7.74
7.70
7.26
6.99
6.95
4.16
4.15
4.13
2.81
1.69 HDO
1.67
1.65
1.65
1.63
1.61
1.35
1.34
1.32
1.31
1.30
1.28
1.27
1.26
0.88
0.87
0.86
0.86
0.85
H3C
O
O
O
N
O
0.94
0.00
0.94
1.98
4.01
2.09
10.02
3.20
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)


核磁/156
20191028-4-C
174.50
166.96
130.89
111.01
77.48
77.16
76.84
65.05
31.88
29.31
29.27
28.73
27.89
26.02
22.74
14.19
H3C
O
O
O
N
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


核磁/157
20191028-5-H
7.73
7.70
7.26
6.98
6.95
4.16
4.14
4.13
2.81
1.68
1.67
1.65
1.65
1.63
1.63
1.61
1.35
1.34
1.34
1.32
1.31
1.31
1.30
1.28
1.27
1.26
1.25
0.88
0.87
0.86
0.84
CH3
O
O
O
N
O
1.00
1.01
2.14
4.09
2.32
12.16
3.20
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)


核磁/158
20191028-5-C
170.18
166.64
130.57
110.68
77.16
76.84
76.52
64.73
31.63
29.25
29.04
29.01
28.42
27.56
25.69
22.44
13.89
CH3
O
O
O
N
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)