Electronic Supplementary Material (ESI) for Green Chemistry.

Iron-catalysed 1,2-acyl migration of tertiary α-azido ketones and 2-azido-1,3-dicarbonyl compounds

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Supplementary Information

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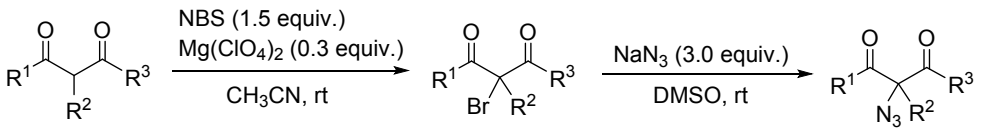
General methods

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III-400 MHz spectrometer or a Varian Mercury plus-300 MHz spectrometer with $CDCl_3$, d_6-acetone, or d_6-DMSO as the solvent. In $CDCl_3$, the chemical shifts in ^{1}H NMR spectra were determined with $Si(CH_3)_4$ as the internal standard (δ = 0.00 ppm); the chemical shifts in ^{13}C NMR spectra were determined based on the chemical shift of $CDCl_3$ (δ = 77.00 ppm). In d_6-DMSO, the chemical shifts in ^{1}H NMR and ^{13}C NMR spectra were determined based on those of DMSO (δ = 2.50 ppm and 40.00 ppm, respectively). In d_6-acetone, the chemical shifts in ^{1}H NMR and ^{13}C NMR spectra were determined based on those of acetone (δ = 2.05 ppm and 206.00 ppm, respectively). The EI-MS spectra were measured on an HP 5988A spectrometer by direct inlet at 70 eV. The high resolution mass spectra (HRMS) were measured on a Bruker micrOTOF QII by ESI. The Fourier transformation infrared spectra (FT-IR) were measured on a NEXUS 670 spectrometer. Melting points were measured on an XT-4 melting point apparatus and were uncorrected. Flash column chromatography was carried out on silica gel (200-300 mesh). $FeBr_2$ was purchased from ALDRICH. $FeCl_2$ was purchased from ACROS Organics. Anhydrous CH_3CN was purchased from ACROS Organics. 1,2-Bis(diphenylphosphanyl)benzene was purchased from Energy Chemicals. Other commercial reagents were purchased from Energy Chemicals and used as received. The unspecified substrates were prepared as the author has reported.[1]

General experimental procedures

General procedure for the preparation of compounds 5c, 5r, 5s, 5t, 5v and 5w



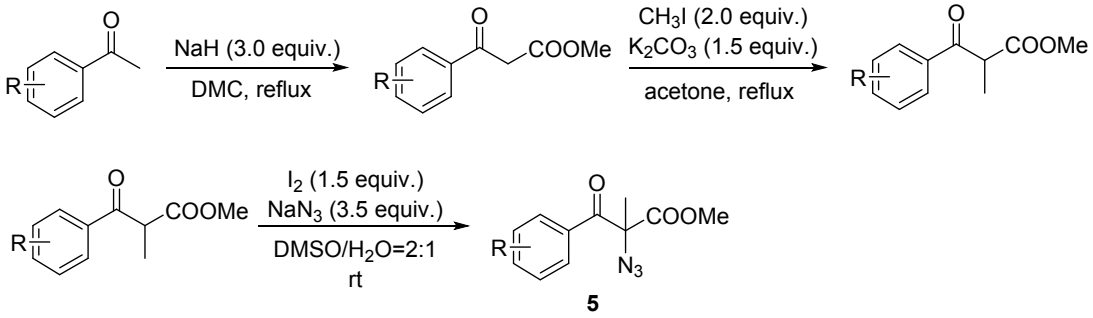
S-Scheme 1

To a 50 mL round-bottom flask equipped with a magnetic stirring bar was charged with a solution of 1,3-dicarbonyl compounds (5.0 mmol), $Mg(ClO_4)_2$ (1.5 mmol, 0.335 g) and *N*-bromobutanimide (7.5 mmol, 1.340 g) in 25 mL CH_3CN, which was

stirred at room temperature for 6 h. After that, the reaction mixture was poured into water (20 mL), and was extracted with ethyl acetate (3×30 mL). The combined organic phases were washed with brine (2×50 mL), dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure on a rotary evaporator.

The crude product was dissolved in CH_3CN (15 mL) along with NaN_3 (15 mmol, 0.975 g), and the solution was stirred overnight at room temperature. After that, the reaction mixture was poured into water (50 mL), and was extracted with ethyl acetate (3×30 mL). The combined organic phases were washed with brine (6×50 mL), dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure on a rotary evaporator. The residual was treated with silica gel column chromatography (with petroleum ether (PE) and ethyl acetate (EA)) to yield product .

General procedure for the preparation of compounds 5f-5p[1]



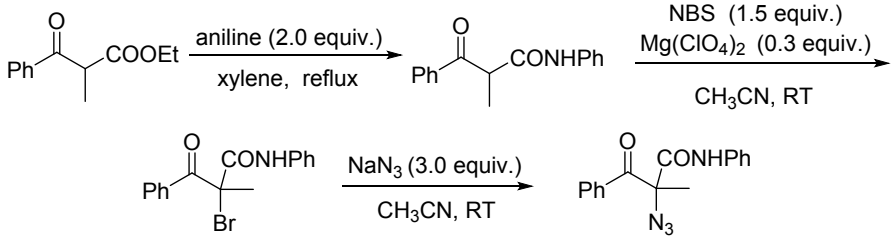
S-Scheme 2

To a 100 mL two-neck flask charged with a suspension of 60% NaH (30 mmol, 1.200 g) in 30 mL dimethyl carbonate (DMC) was added dropwise acetophenone (10 mmol) in 10 mL dimethyl carbonate. The resulting solution was refluxed at 100 ^oC for 4 h. After cooling to room temperature, the mixture was added into 100 mL cold water, the pH value of which was then adjusted to pH < 4 with HCl of 1 mol/L. The aqueous phase was extracted with EtOAc (3×30 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure on a rotary evaporator.

5 mmol (estimated) of crude product was dissolved in 35 mL of DMSO, and an aqueous solution of NaN_3 (1 mol/L, 18 mL) was added the DMSO solution, followed by the addition of 7.5 mmol of I_2 (1.920 g). The solution was then stirred at room

temperature for 4 h. The reaction was quenched by saturated aqueous $Na_2S_2O_3$ solution (10 mL). The aqueous phase was extracted with EtOAc (3×50 mL). The combined organic phases were washed with brine (6×100 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residual was purified by flash chromatography on silica (eluent: PE:EA = 10:1) to yield the pure product.

Preparation of compound 5u[1]



S-Scheme 3

A 50 mL round bottom flask was charged with a solution of 10 mmol ethyl 2-methyl-3-oxo-3-phenylpropanoate and 20 mmol of aniline (2 mL) in 25 mL xylene under argon atmosphere. The resulting mixture was refluxed for 24 h, and the solvent was removed by distillation. After cooling to room temperature, 20 mL of n-hexane was added and the mixture was stirred for 5 min. The mixture was then filtered and the filter cake was repeatedly rinsed with n-hexane for several times. The resulting solid was dried in vacuo to give the amide product.

A 50 mL flask was charged with a solution of the amide product (5 mmol), $Mg(ClO_4)_2$ (1.5 mmol, 0.335 g) and *N*-bromobutanimide (NBS) (7.5 mmol, 1.340 g) in 25 mL CH_3CN at room temperature for 24 h. After that, the reaction mixture was poured into water (20 mL), and was extracted with ethyl acetate (3×30 mL). The combined organic phases were washed with brine (2×50 mL), dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure on a rotary evaporator.

The crude product was dissolved in CH_3CN (15 mL) along with NaN_3 (15 mmol, 0.975 g), and the solution was stirred overnight at room temperature. After that, the reaction mixture was poured into water (50 mL), and was extracted with ethyl acetate (3×30 mL). The combined organic phases were washed with brine (2×50 mL), dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure on a rotary evaporator. The residual was treated with silica gel column chromatography (PE and

EA) to yield **5u.**

Preparation of Cat-1,[2] Cat-2[3] and Cat-3[4]

Preparation of $Fe(dpbz)Br_2$ (Cat-1): An oven-dried 100 mL two-necked flask equipped with a magnetic stirring bar and a reflux condenser was charged with a solution of anhydrous $FeBr_2$ (4.0 mmol, 0.863 g) and 1,2-bis (diphenylphosphino) benzene (4.4 mmol, 1.926 g) in ethanol (40 mL). The solution was refluxed under stirring for 18 h, at this time pale brown colored precipitate was formed. The reaction mixture was cooled to room temperature. The brown solid was filtered and the solid was washed with hot ethanol (3×20 mL). The resulting yellow solid **Cat-1** (1.560 g, 59%) was dried under high vacuum for 12 h. Elem. Anal. calcd. for $C_{30}H_{24}Br_2FeP_2$: C, 54.42, H 3.65%; found: C, 55.57; H, 3.72%.

Preparation of $Fe(dpbz)Cl_2$ (Cat-2): $FeCl_2{\cdot}4H_2O$ (2.00 mmol, 0.398 g) was dissolved in THF in a Schlenk tube equipped with a magnetic stirring bar. After stirring for 15 min, the solvent was removed *in vacuo*. This was repeated twice. 1,2-Bis(diphenylphosphino)benzene (2.00 mmol, 0.893 g) was then added to the resulting $FeCl_2(THF)_{1.5}$, followed by anhydrous acetone (25 mL), and the mixture was stirred at room temperature for 24 h. The suspension was filtered through a Büchner funnel and the solid was washed with cold Et_2O to yield **Cat-2** as a light green powder (0.821 g, 70%). Elem. Anal. calcd. for $C_{30}H_{24}Cl_2FeP_2$: C, 62.86, H 4.22%; found: C, 61.56; H, 4.17%.

Preparation of $[Fe(dpbz)Cl]_2$ (Cat-3): $FeCl_2{\cdot}4H_2O$ (2.00 mmol, 0.398 g) was dissolved in THF in a Schlenk tube equipped with a magnetic stirring bar. After stirring for 15 min, the solvent was removed *in vacuo*. This was repeated twice. 1,2-Bis(diphenylphosphino)benzene (3.9 mmol, 0.739 g) was then added to the resulting $FeCl_2(THF)_{1.5}$, followed by anhydrous acetone (30 mL), and the mixture was stirred for 24 h. The suspension was filtered through a Büchner funnel and the solid was washed with cold Et_2O to yield **Cat-3** (1.390 g, 78%). Elem. Anal. calcd. for $C_{60}H_{48}Cl_2FeP_4$: C, 70.56, H 4.74%; found: C, 69.76; H, 4.86%.

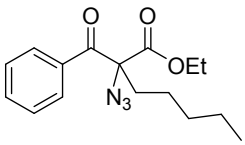
General procedure for Cat-1-catalyzed reactions (Method A)

Compound **1**, **3** or **5** (0.5 mmol) and **Cat-1** (0.025 mmol, 16.6 mg) were dissolved in anhydrous CH_3CN (2.5 mL) contained in a 25 mL Schlenk reaction vessel equipped with a magnetic stirring bar. After the reaction tube is placed in an ice bath, the air in it is quickly exchanged with nitrogen gas for more than five times using a double-row gas exchange tube. The mixture was then stirred at 65 ^oC or 80 ^oC (oil bath temperature) under N_2 for 12-24 h. After reaction completed, the mixture was cooled to room temperature, and was filtered through silica gel, which was eluted then with EtOAc (3×30 mL). The combined filtrates were then concentrated under reduced pressure on a rotary evaporator. The residual was treated with silica gel column chromatography (eluent: PE and EA) to yield the pure product.

General procedure for $FeBr_2$/Et_3N-catalyzed reactions (Method B)

The substrate (0.5 mmol), Et_3N (0.1 mmol, 14 uL) and $FeBr_2$ (0.1 mmol, 21.6 mg) were dissolved in anhydrous CH_3CN (5 mL) contained in a 25 mL Schlenk reaction vessel equipped with a magnetic stirring bar. After the reaction tube is placed in an ice bath, the air in it is quickly exchanged with nitrogen gas for more than five times using a double-row gas exchange tube. The mixture was stirred at 50 ^oC, 65 ^oC or 80 ^oC (oil bath temperature) under N_2 for 12-24 h. After reaction completed, the mixture was cooled to room temperature, and was filtered through silica gel, which was eluted then with EtOAc (3×30 mL). The combined filtrates were then concentrated under reduced pressure on a rotary evaporator. The residual was treated with silica gel column chromatography (eluent: PE and EA) to yield the pure product(s).

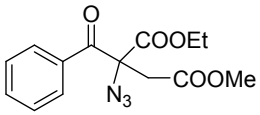
Characterization data for compounds 5 and 7



Ethyl 2-azido-2-benzoylheptanoate (5c)

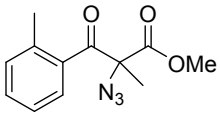
Yellow liquid (1.20 g, 79%); R_f = 0.63 (PE : EA = 10:1); ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.98–7.96 (m, 2 H), 7.54–7.50 (m, 1 H), 7.42–7.38 (m, 2 H), 4.15 (q, *J* = 7.2 Hz, 2 H), 2.38–2.34 (m, 2 H), 1.60–1.56 (m, 1 H), 1.34–1.24 (m, 5 H), 1.04 (t, *J* = 7.2 Hz, 3 H), 0.86 (t, *J* = 6.8 Hz, 3 H) ; ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 189.2,

168.1, 133.8, 133.2, 129.3, 128.3, 67.2, 63.0, 38.4, 31.6, 24.4, 22.2, 13.8, 13.6; FT-IR (KBr, cm^{-1}): 2101.0; ESI-HRMS: m/z calcd for $C_{16}H_{21}N_3O_3$+Na^+: 326.1475, found 326.1480.



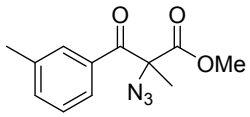
1-Ethyl 4-methyl 2-azido-2-benzoylsuccinate (5e)

Colorless oil (0.63 g, 41%); R_f = 0.35 (PE : EA = 10:1); ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.06–8.03 (m, 2 H), 7.58–7.52 (m, 1 H), 7.45–7.39 (m, 2 H), 4.24 (q, *J* = 7.2 Hz, 2 H), 3.73 (s, 3 H), 3.57 (q, *J* = 16.5 Hz, 2 H), 1.42 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 188.8, 169.4, 166.9, 133.5, 129.8, 128.3, 63.7, 60.5, 52.2, 44.4, 13.6; FT-IR (KBr, cm^{-1}): 2116.7; ESI-HRMS: m/z calcd for $C_{14}H_{15}N_3O_5$+Na^+: 328.0904, found 328.0912.



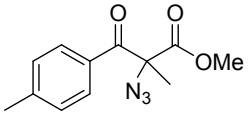
Methyl 2-azido-2-methyl-3-oxo-3-(o-tolyl)propanoate (5h)

Colorless liquid (0.98 g, 79%); R_f = 0.57 (PE : EA = 10:1); ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.57–7.54 (m, 1 H), 7.41–7.35 (m, 1 H), 7.29–7.19 (m, 1 H), 3.78 (s, 3 H), 2.42 (s, 3 H), 1.75 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 196.0, 169.7, 138.5, 134.7, 131.8, 131.5, 127.3, 125.3, 72.2, 53.3, 20.8, 20.5; FT-IR (KBr, cm^{-1}): 2118.4; ESI-HRMS: m/z calcd for $C_{12}H_{13}N_3O_3$+Na^+: 270.0849, found 270.0852.



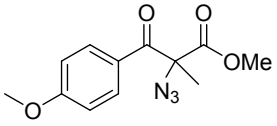
Methyl 2-azido-2-methyl-3-oxo-3-(*m*-tolyl)propanoate (5g)

Colorless liquid (0.78 g, 67%); R_f = 0.54 (PE : EA = 10:1); ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.79–7.74 (m, 2 H), 7.41–7.31 (m, 2 H), 3.75 (m, 3 H), 2.40 (s, 3 H), 1.81 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 191.0, 170.3, 138.6, 134.6, 133.3, 129.8, 128.4, 126.4, 71.0, 53.4, 21.3, 20.3; FT-IR (KBr, cm^{-1}): 2120.0; ESI-HRMS: m/z calcd for $C_{12}H_{13}N_3O_3$+Na^+: 270.0849, found 270.0855.



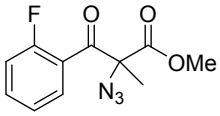
Methyl 2-azido-2-methyl-3-oxo-3-(p-tolyl)propanoate (5f)

Yellow liquid (0.55 g, 46%); R_f = 0.52 (PE : EA = 10:1); ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.90–7.86 (m, 2 H), 7.27–7.24 (m, 2 H), 3.75 (s, 3 H), 2.41 (m, 3 H), 1.82 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 190.4, 170.4, 144.9, 130.7, 129.5, 129.4, 71.0, 53.4, 21.3, 20.3; FT-IR (KBr, cm^{-1}): 2116.7; ESI-HRMS: m/z calcd for $C_{12}H_{13}N_3O_3$+Na^+: 270.0849, found 270.0851.



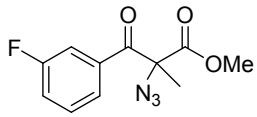
Methyl 2-azido-3-(4-methoxyphenyl)-2-methyl-3-oxopropanoate (5i)

Colorless oil (0.92 g, 70%); R_f = 0.45 (PE : EA = 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.00–7.97 (m, 2 H), 6.94–6.91 (m, 2 H), 3.87 (s, 3 H) 3.75 (s, 3 H), 1.81 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 189.2, 170.4, 163.9, 131.8, 126.0, 113.9, 71.1, 55.4, 53.3, 20.3; FT-IR (KBr, cm^{-1}): 2111.8; ESI-HRMS: m/z calcd for $C_{12}H_{13}N_3O_4$+Na^+: 286.0798, found 286.0800.



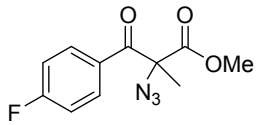
Methyl 2-azido-3-(2-fluorophenyl)-2-methyl-3-oxopropanoate (5j)

Colorless oil (0.85 g, 69%); R_f = 0.44 (PE : EA = 10:1); ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.70–7.65 (m, 1.0 H), 7.48–7.43 (m, 1.0 H), 7.21–7.14 (m, 1.0 H), 7.07–7.00 (m, 1.0 H), 3.72 (s, 2.7 H), 3.59 (s, 0.3 H), 1.69 (s, 2.7 H), 1.40 (m, 0.3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 191.0 (d, J = 4 Hz), 169.0, 161.8, 158.5, 134.9, 134.8, 134.0, 131.1, 131.1, 130.8, 124.6, 124.5, 122.8, 116.4, 116.3, 116.1, 116.0, 72.2, 53.2, 53.2, 22.7, 22.7, 19.9; FT-IR (KBr, cm^{-1}): 2110.7; ESI-HRMS: m/z calcd for $C_{11}H_{10}N_3O_3F$+Na^+: 274.0598, found 274.0600.



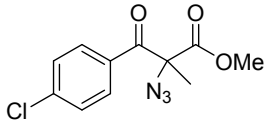
Methyl 2-azido-3-(3-fluorophenyl)-2-methyl-3-oxopropanoate (5k)

Colorless oil (0.75 g, 60%); R_f = 0.44 (PE : EA = 10:1); ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.78–7.75 (m, 1 H), 7.71–7.68 (m, 1 H), 7.48–7.41 (m, 1 H), 7.33–7.26 (m, 1 H), 3.77 (s, 3 H), 1.84 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 189.6, 170.1, 162.5 (d, *J* = 249 Hz), 135.2 (d, *J* = 7 Hz), 130.0 (d, *J* = 8 Hz), 125.1 (d, *J* = 3 Hz), 120.8 (d, *J* = 21 Hz), 116.3 (d, *J* = 23 Hz), 70.9, 53.6, 20.0; FT-IR (KBr, cm^{-1}): 2109.3; ESI-HRMS: m/z calcd for $C_{11}H_{10}N_3O_3F$+Na$^+$: 274.0598, found 274.0601.



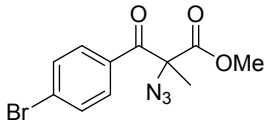
Methyl 2-azido-3-(4-fluorophenyl)-2-methyl-3-oxopropanoate (5l)

Colorless oil (0.58 g, 47%); R_f = 0.44 (PE : EA = 10:1); ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.04–8.00 (m, 2 H), 7.15–7.09 (m, 2 H), 3.74 (m, 3 H), 1.81 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 189.1, 170.3, 165.9 (d, *J* = 278 Hz), 133.2 (d, *J* = 10 Hz), 129.6, 116.3 (d, *J* = 22 Hz), 70.9, 53.6, 20.1; FT-IR (KBr, cm^{-1}): 2110.8; ESI-HRMS: m/z calcd for $C_{11}H_{10}N_3O_3F$+Na$^+$: 274.0598, found 274.0600.



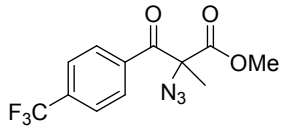
Methyl 2-azido-2-methyl-3-oxo-3-(4-chlorophenyl)-phenyl)propanoate (5m)

Colorless oil (1.00 g, 75%); R_f = 0.58 (PE : EA = 10:1); ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.93–7.89 (m, 2 H), 7.42–7.39 (m, 2 H), 3.73 (m, 3 H), 1.80 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 189.5, 170.1, 140.3 131.5, 130.8, 128.9, 70.8, 53.5, 20.0; FT-IR (KBr, cm^{-1}): 2126.1; ESI-HRMS: m/z calcd for $C_{11}H_{10}N_3O_3Cl$+Na$^+$: 290.0303, found 290.0310.



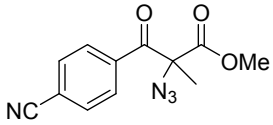
Methyl 2-azido-3-(4-bromophenyl)-2-methyl-3-oxopropanoate (5n)

Colorless oil (0.91 g, 58%); R_f = 0.55 (PE : EA = 10:1); ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.83–7.80 (m, 2 H), 7.57–7.54 (m, 2 H), 3.72 (m, 3 H), 1.79 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 189.6, 170.0, 131.9, 130.8, 129.0, 70.7, 53.5, 19.9; FT-IR (KBr, cm^{-1}): 2128.7; ESI-HRMS: m/z calcd for $C_{11}H_{10}N_3O_3Br+Na^+$: 333.9798, found 333.9800.



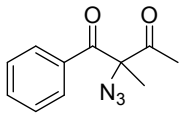
Methyl 2-azido-2-methyl-3-oxo-3-(4-(trifluoromethyl)phenyl)propanoate (5o)

Colorless oil (1.13 g, 75%); R_f = 0.50 (PE : EA = 10:1); ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.09–8.06 (m, 2 H), 7.72–7.69 (m, 2 H), 3.76 (s, 3 H), 1.84 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 189.9, 170.0, 136.2, 134.7 (q, *J* = 32 Hz), 129.8, 125.7, 125.6, 125.6, 125.1, 121.5, 70.8, 53.7, 19.9; FT-IR (KBr, cm^{-1}): 2131.7; ESI-HRMS: m/z calcd for $C_{12}H_{10}N_3O_3F_3+Na^+$: 324.0566, found 324.0565.



Methyl 2-azido-3-(4-cyanophenyl)-2-methyl-3-oxopropanoate (5p)

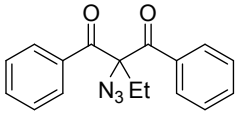
White solid (0.40 g, 75%); m.p. = 85–86 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): δ 8.19 – 8.01 (d, *J* = 8.5 Hz, 2H), 7.86 – 7.66 (d, *J* = 8.6 Hz, 2H), 3.87 – 3.69 (s, 3H), 2.10 – 1.54 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz , δ ppm): 189.59, 169.84, 136.60, 132.31, 129.75, 117.59, 116.79, 70.79, 53.67, 19.75; FT-IR (KBr, cm^{-1}): 2118.2; ESI-HRMS: m/z calcd for $C_{12}H_{10}N_4O_3+H^+$:281.0671, found 281.0675.



2-Azido-2-methyl-1-phenylbutane-1,3-dione (5r)

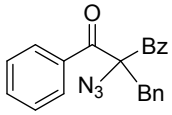
Colorless oil (0.89 g, 82%); R_f = 0.81 (PE : EA = 10:1); ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.94–7.90 (m, 2 H), 7.61–7.56 (m, 1 H), 7.48–7.42 (m, 2 H), 2.24 (s, 3 H), 1.80 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 202.9, 192.8, 133.8, 133.5, 129.5, 128.6, 77.1, 25.5, 19.2; FT-IR (KBr, cm^{-1}): 2119.7; ,ESI-HRMS: m/z calcd for

$C_{11}H_{11}N_3O_2$+Na^+: 240.0743, found 240.0742.



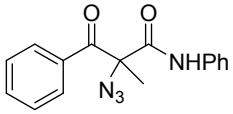
2-Azido-2-ethyl-1,3-diphenylpropane-1,3-dione (5s)

White solid (1.16 g, 79%); m.p. = 55–56 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.84–7.81 (m, 4 H), 7.38–7.33 (m, 2 H), 7.26–7.21 (m, 4 H), 2.60 (q, *J* = 7.2 Hz, 2 H), 0.90 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 191.1, 133.8, 133.5, 129.6, 128.6, 77.4, 32.6, 9.1; FT-IR (KBr, cm^{-1}): 2106.7; ESI-HRMS: m/z calcd for $C_{17}H_{15}N_3O_2$+Na^+: 316.1056, found 316.1060.



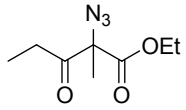
2-Azido-2-benzyl-1,3-diphenylpropane-1,3-dione (5t)

White solid (1.26 g, 71%);m.p. = 99–100 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.81–7.79 (m, 4 H), 7.45–7.42 (m, 2 H), 7.32–7.28 (m, 4 H), 7.21–7.17 (m, 3 H), 7.07–7.05 (m, 2 H), 4.03 (s, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 191.5, 134.2, 134.1, 133.4, 130.9, 128.4, 128.0, 127.5, 75.6, 45.1; ESI-HRMS: m/z calcd for $C_{22}H_{17}N_3O_2$+Na^+: 378.1218, found 378.1220.



2-Azido-2-methyl-3-oxo-*N*,3-diphenylpropanamide (5u)

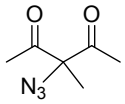
White solid (1.13 g, 77%); m.p. = 112–113 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.45 (br, s, 1 H), 8.02–8.00 (m, 2 H), 7.56–7.51 (m, 3 H), 7.43–7.30 (m, 4 H), 7.18–7.13 (m, 1 H), 1.94 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 191.9, 166.6, 136.5, 133.7, 133.6, 129.1, 128.6, 125.2, 120.0, 71.1, 20.6; FT-IR (KBr, cm^{-1}): 2120.8; ESI-HRMS: m/z calcd for $C_{16}H_{14}N_4O_2$+Na^+: 317.1009, found 317.1011.



Ethyl-2-azido-2-methyl-3-oxopentanoate (5v)

Colorless oil (0.24 g, 24%); R_f = 0.67 (PE : EA = 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 4.27 (q, *J* = 1.2 Hz, 2 H), 2.92–2.67 (m, 2 H), 1.30 (t, *J* = 7.2 Hz, 3 H), 1.41

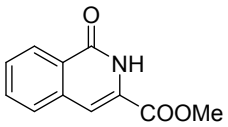
(q, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 203.2, 168.6, 72.8, 62.7, 31.0, 19.3, 13.9, 7.7; FT-IR (KBr, cm^{-1}): 2112.0; ESI-HRMS: m/z calcd for $C_8H_{13}N_3O_3$+Na^+: 222.0849, found 222.0850.



2-Azido-3-methylpentane-2,4-dione (5w)

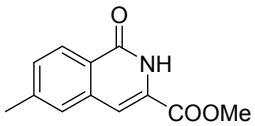
Colorless oil (0.34 g, 44%); R_f = 0.77 (PE : EA = 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 2.24 (s, 6 H), 1.61 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 202.2, 78.7, 25.8, 18.3; FT-IR (KBr, cm^{-1}): 2095.1; ESI-HRMS: m/z calcd for $C_6H_9N_3O_2$+Na^+: 178.0587, found 178.0589.

Characterization data for product



Methyl 1-oxo-1,2-dihydroisoquinoline-3-carboxylate (2a)

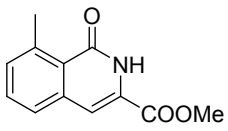
White solid (**Method A:** 92 mg, 91%; **Method B**: 92 mg, 91%); m.p. = 158–160 °C; **Method A**: ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 9.99 (br, s, 1 H), 8.42 (dd, J = 8.1 Hz, J = 0.6 Hz, 1 H), 7.67–7.52 (m, 3 H), 7.32 (s, 1 H), 3.94 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 162.1, 162.0, 135.7, 132.8, 129.1, 128.0, 128.0, 127.7, 127.6, 111.2, 53.0; **Method B**: ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 10.00 (br, s, 1 H), 8.46 (d, J = 7.5 Hz, 1 H), 7.72–7.59 (m, 3 H), 7.37 (s, 1 H), 4.00 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 162.1, 162.0, 135.7, 132.8, 129.1, 128.0, 128.0, 127.7, 127.7, 111.2, 53.0; EI-MS: m/z (rel.int., %): 203 (M^+, 100.00), 145 (40.38), 143 (54.03), 115 (25.03), 89 (26.78).



Methyl 6-methyl-1-oxo-1,2-dihydroisoquinoline-3-carboxylate (2b)

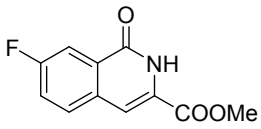
White solid (97 mg, 89%); m.p. = 123–124 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 9.66 (s, 1.0 H), 8.26 (d, J = 0.9 Hz, 1 H), 7.59–7.53 (m, 2 H), 7.36 (s, 1 H), 3.99 (s, 3

H), 2.52 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 162.3, 161.8, 139.9, 134.3, 133.4, 128.0, 127.5, 126.8, 111.4, 53.0, 21.6; EI-MS: m/z (rel.int., %): 217 (M^+, 100.00), 159 (29.66), 157 (58.07), 129 (26.47), 77 (11.17).



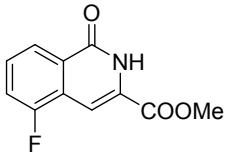
Methyl 8-methyl-1-oxo-1,2-dihydroisoquinoline-3-carboxylate (2c)

White solid (101 mg, 93%); m.p. = 125–126 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 9.26 (s, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.45 (d, *J* = 7.6 Hz, 1 H), 7.33 (d, *J* = 7.6 Hz, 1 H), 7.25 (s, 1 H), 3.97 (s, 3 H), 2.94 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 162.8, 162.0, 142.2, 137.5, 132.3, 132.0, 127.4, 126.4, 126.4, 111.7, 52.9, 23.4; EI-MS: m/z (rel.int., %): 217 (M^+, 65.84), 185 (19.69), 157 (100.00), 129 (22.38), 77 (9.74).



Methyl 7-fluoro-1-oxo-1,2-dihydroisoquinoline-3-carboxylate (2d)

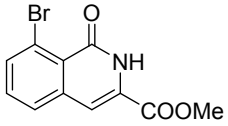
White solid (103 mg, 93%); m.p. = 105–106 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 9.34 (s, 1 H), 8.11 (dd, *J* = 9.2 Hz, 2.8 Hz, 1 H), 7.70 (dd, *J* = 8.4 Hz, 4.8 Hz, 1 H), 7.47 (dt, *J* = 2.8 Hz, 8.4 Hz, 1 H), 7.38 (s, 1 H), 4.01 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 163.0 (d, *J* = 250 Hz), 162.1, 160.9, 132.5 (d, *J* = 2 Hz), 130.5 (d, *J* = 8 Hz), 130.3 (d, *J* = 8 Hz), 127.2 (d, *J* = 3 Hz), 121.8 (d, *J* = 24 Hz), 113.5 (d, *J* = 23 Hz), 110.6, 53.3; EI-MS: m/z (rel.int., %): 221 (M^+, 100.00), 163 (28.29), 161 (84.67), 133 (17.13), 107 (22.20).



Methyl 5-fluoro-1-oxo-1,2-dihydroisoquinoline-3-carboxylate (2e)

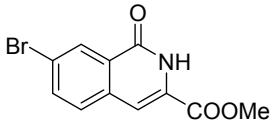
White solid (99 mg, 90%); m.p. = 85–85 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 9.43 (s, 1 H), 8.25 (d, *J* = 8.0 Hz, 1 H), 7.62–7.56 (m, 2 H), 7.46–7.42 (m, 1 H), 4.02 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 162.0, 160.7, 158.7 (d, *J* = 253 Hz),

129.8 (d, J = 8 Hz), 129.7 (d, J = 3 Hz), 128.1, 125.4 (d, J = 17 Hz), 123.6 (d, J = 4 Hz), 118.2 (d, J = 20 Hz), 103.7 (d, J = 5 Hz), 53.4; EI-MS: m/z (rel.int., %): 221 (M^+, 100.00), 163 (38.47), 161 (74.50), 133 (37.24), 107 (44.30).



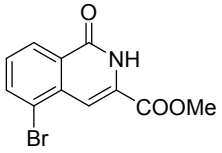
Methyl 8-bromo-1-oxo-1,2-dihydroisoquinoline-3-carboxylate (2f)

Gray solid (127 mg, 90%); m.p. = 199–200 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 9.35 (s, 1 H), 7.79 (d, J = 7.6 Hz, 1 H), 7.56 (d, J = 7.6 Hz, 1 H), 7.44–7.41 (m, 1 H), , 7.23 (s, 1 H), 3.97 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 161.6, 160.1, 139.0, 136.1, 132.8, 128.3, 128.0, 125.5, 123.3, 110.7, 53.2; EI-MS: m/z (rel.int., %): 283 (M^++2, 99.10), 281 (M^+, 100.00), 223 (54.32), 221 (50.15), 169 (27.10), 167 (25.11).



Methyl 7-bromo-1-oxo-1,2-dihydroisoquinoline-3-carboxylate (2g)

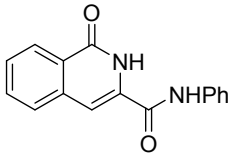
White solid (122 mg, 87%); m.p. =194–195 °C; ^{1}H NMR (d_6-DMSO, 400 MHz, δ ppm): 11.42 (s, 1 H), 8.31 (s, 1 H), 7.98–7.96 (m, 1 H), 7.89–7.87 (m, 1 H), 7.45 (s, 1 H), 3.88 (s, 3 H); ^{13}C NMR (d_6-DMSO, 75 MHz, δ ppm): 162.0, 160.6, 136.2, 135.1, 131.1, 129.9, 129.8, 129.6, 122.7. 109.9, 53.3; ESI-HRMS: m/z calcd for $C_{11}H_8BrNO_3$+Na^+: 303.9580, found 303.9577.



Methyl 5-bromo-1-oxo-1,2-dihydroisoquinoline-3-carboxylate (2h)

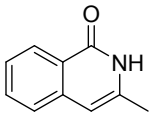
White solid (129 mg, 91%); m.p. = 218–219 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 9.65 (s, 1 H), 8.40 (d, J = 8.0 Hz, 1 H), 7.93 (dd, J = 8.0 Hz, 1.2 Hz, 1 H), 7.70 (d, J = 0.4 Hz, 1 H), 7.43 (t, J = 8.0 Hz, 1 H), 4.01 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 162.0, 161.1, 136.9, 135.5, 129.9, 129.7, 128.7, 127.4, 122.8, 109.6, 53.3; EI-MS: m/z (rel.int., %): 283 (M^++2, 100.00), 281 (M^+, 99.39), 223 (71.85), 221 (49.14),

169 (20.75), 167 (20.56).



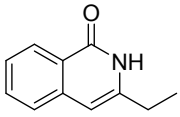
1-Oxo-*N*-phenyl-1,2-dihydroisoquinoline-3-carboxamide (2i)

White solid (112 mg, 85%); m.p. = 250–251 °C; ^{1}H NMR (d_6-DMSO, 400 MHz, δ ppm): 10.94 (s, 1 H), 10.52 (s, 1 H), 8.26 (d, *J* = 8.0 Hz, 1 H), 7.83–7.75 (m, 4 H), 7.64–7.60 (m, 1 H), 7.46 (s, 1 H), 7.40–7.36 (m, 2 H), 7.14 (t, *J* = 7.6 Hz, 1 H); ^{13}C NMR (d_6-DMSO, 100 MHz, δ ppm): 161.8, 160.5, 138.8, 136.4, 133.5, 133.4, 129.2, 128.8, 128.3, 127.5, 127.4, 124.7, 120.8, 107.1; ESI-HRMS: m/z calcd for $C_{16}H_{12}N_2O_2$+Na^+: 287.0791, found 287.0789.



3-Methylisoquinolin-1(2*H*)-one (2j)

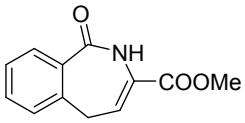
White solid (**Method A**: 43 mg, 54%; **Method B**: 71 mg, 89%); m.p. = 235–236 °C; **Method A**: ^{1}H NMR (d_6-DMSO, 400 MHz, δ ppm): 11.27 (s, 1 H), 8.12 (d, *J* = 8.0 Hz, 1 H), 7.61 (td, *J* = 7.6 Hz, 0.8 Hz, 1 H), 7.50 (d, *J* = 8.0 Hz, 1 H), 7.38 (t, *J* = 8.0 Hz, 1 H), 6.29 (s, 1 H), 2.19 (s, 3 H); ^{13}C NMR (d_6-DMSO, 100 MHz, δ ppm): 163.0, 139.1, 138.8, 132.8, 127.1, 126.0, 125.8, 124.7, 103.3, 19.2; **Method B**: ^{1}H NMR (d_6-DMSO, 400 MHz, δ ppm): 11.32 (s, 1 H), 8.13 (d, *J* = 8.0 Hz, 1 H), 7.60 (td, *J* = 7.6 Hz, 0.8 Hz, 1 H), 7.48 (d, *J* = 8.0 Hz, 1 H), 7.37 (t, *J* = 8.0 Hz, 1 H), 6.27 (s, 1 H), 2.19 (s, 3 H); ^{13}C NMR (d_6-DMSO, 100 MHz, δ ppm): 163.0, 139.1, 138.9, 132.8, 127.1, 126.0, 125.9, 124.7, 103.4, 19.3; EI-MS: m/z (rel.int., %): 159 (M^+, 100.00), 158 (14.66), 131 (16.79), 130 (55.66).



2-Ethylisoquinolin-1(2*H*)-one (2k)

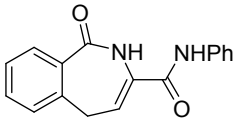
White solid (**Method A**: 27 mg, 31%; **Method B**: 51 mg, 59%); m.p. = 127–129 °C; **Method A**: ^{1}H NMR (d_6-DMSO, 400 MHz, δ ppm): 11.07 (s, 1 H), 7.96 (d, *J* = 8.0 Hz, 1 H), 7.45 (td, *J* = 7.6 Hz, 0.8 Hz, 1 H), 7.36 (d, *J* = 8.0 Hz, 1 H), 7.22 (td, *J* = 8.0

Hz, 0.8 Hz, 1 H), 6.14 (s, 1 H), 2.32 (q, *J* = 7.6 Hz, 1 H), 1.02 (t, *J* = 7.6 Hz, 1 H); ^{13}C NMR (d_6-DMSO, 100 MHz, δ ppm): 163.2, 144.7, 138.9, 132.9, 127.1, 126.3, 126.0, 124.9, 101.8, 26.1, 13.3; **Method B**: ^{1}H NMR (d_6-DMSO, 400 MHz, δ ppm): 11.12 (s, 1 H), 7.99 (d, *J* = 8.0 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 1 H), 7.36 (d, *J* = 8.0 Hz, 1 H), 7.23 (t, *J* = 8.0 Hz, 1 H), 6.14 (s, 1 H), 2.33 (q, *J* = 7.6 Hz, 1 H), 1.03 (t, *J* = 7.6 Hz, 1 H); ^{13}C NMR (d_6-DMSO, 100 MHz, δ ppm): 163.2, 144.6, 138.9, 132.8, 127.1, 126.3, 126.0, 124.9, 101.8, 26.1; EI-MS: m/z (rel.int., %): 173 (M^+, 100.00), 172 (74.73), 158(35.17), 89 (13.11).



Methyl 1-oxo-2,5-dihydro-1*H*-benzo[c]azepine-3-carboxylate (4a)

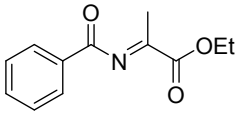
Yellow solid (**Method A**: 49 mg, 45%; **Method B**: 47 mg, 43%); m.p. = 164–165 °C; **Method A**: ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.02 (s, 1 H), 7.93 (dd, *J* = 7.5 Hz, 0.9 Hz, 1 H), 7.46 (td, *J* = 6.0 Hz, 0.9 Hz, 1 H), 7.35 (td, *J* = 6.0 Hz, 0.4 Hz, 1 H), 7.15 (d, *J* = 7.5 Hz, 1 H), 6.73 (td, *J* = 7.5 Hz, 1.2 Hz, 1 H), 3.80 (s, 3 H), 3.44 (d, *J* = 7.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 168.5, 163.3, 140.0, 132.7, 132.2, 131.2, 128.6, 127.2, 124.0, 52.6, 31.8; **Method B**: ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.05 (s, 1 H), 7.93 (d, *J* = 7.5 Hz, 1 H), 7.47(t, *J* = 7.5 Hz, 1 H), 7.35 (t, *J* = 7.5 Hz, 1 H), 7.15 (d, *J* = 7.5 Hz, 1 H), 6.74 (t, *J* = 7.5 Hz, 1 H), 3.81 (s, 3 H), 3.44 (d, *J* = 7.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 168.5, 163.3, 140.0, 132.7, 132.2, 131.2, 128.6, 127.2, 124.1, 52.7, 31.8; EI-MS: m/z (rel.int., %): 217 (M^+, 64.93), 185 (17.36), 158 (100.00), 131 (34.57), 103 (26.20).



1-Oxo-*N*-phenyl-2,5-dihydro-1*H*-benzo[c]azepine-3-carboxamide (4b)

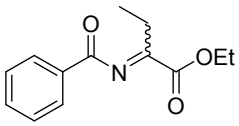
White solid (65 mg, 47%); m.p. = 201–203 °C; ^{1}H NMR (d_6-DMSO, 400 MHz, δ ppm): 10.06 (s, 1 H), 9.37 (s, 1 H), 7.77 (d, *J* = 6.8 Hz, 1 H), 7.68–7.66 (m, 2 H), 7.49 (dd, *J* = 7.6 Hz, 1.2 Hz, 1 H), 7.38–7.28 (m, 4.0 H), 7.07 (t, *J* = 7.2 Hz, 1 H), 6.59 (t, *J* = 7.2 Hz, 1 H), 3.43–3.39 (m, 2 H); ^{13}C NMR (d_6-DMSO, 100 MHz, δ ppm): 168.5,

162.5, 141.9, 139.1, 133.4, 133.4, 132.5, 130.9, 129.0, 127.6, 127.2, 124.2, 121.4, 120.7, 31.3; ESI-HRMS: m/z calcd for $C_{17}H_{15}N_2O_2$+Na^+: 301.0947, found 301.0943.



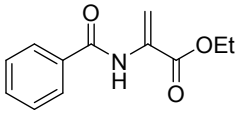
Ethyl 2-(benzoylimino)propanoate (6a)

Colorless oil (45 mg, 41%); R_f = 0.33 (PE : EA = 10:1); ^{1}H NMR (d_6-acetone, 300 MHz, δ ppm): 7.91–7.88 (m, 2 H), 7.67–7.61 (m, 1 H), 7.56–7.49 (m, 2 H), 4.26–4.18 (m, 2 H), 2.34–2.33 (m, 3 H), 1.25–1.19 (m,3 H);^{13}C NMR (d_6-acetone, 75 MHz, δ ppm): 179.0, 162.0, 160.1, 134.2, 133.2, 129.8, 129.6, 63.2, 21.9, 14.3; ESI-HRMS: m/z calcd for $C_{12}H_{13}NO_3$+Na^+: 242.0788, found 242.0789.



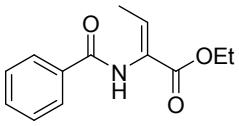
Ethyl 2-(benzoylimino)butanoate (6b)

Colorless oil (57 mg, 49%); R_f = 0.36 (PE : EA = 10:1); ^{1}H NMR (d_6-acetone, 400 MHz, δ ppm): 7.90–7.86 (m, 1.75 H), 7.72–7.69 (m, 0.25 H), 7.65–7.60 (m, 1.00 H), 7.53–7.49 (m, 2.00 H), 4.16 (q, *J* = 7.2 Hz, 2.00 H), 2.81 (q, *J* = 7.2 Hz, 2.00 H), 1.24–1.20 (m,3.00 H), 1.15 (t, *J* = 7.2 Hz, 3.00 H); ^{13}C NMR (d_6-acetone, 75 MHz, δ ppm): 179.2, 163.5, 161.2, 133.9, 133.8, 133.8, 130.3, 129.6, 129.5, 129.1, 63.2, 28.9, 14.1, 10.0; ESI-HRMS: m/z calcd for $C_{13}H_{15}NO_3$+Na^+: 256.0955, found 256.0958.



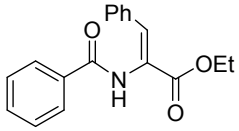
Mthyl 2-benzamidoacrylate (7a)

Colorless oil (81 mg, 75%); R_f = 0.40 (PE : EA = 10:1); ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.59 (br, s, 1 H), 7.86–7.83 (m, 2 H), 7.54–7.45 (m, 3 H), 6.79 (s, 1 H), 6.00 (s, 1 H), 4.33 (q, *J* = 6.9 Hz, 2 H), 1.37 (q, *J* = 7.2 Hz, 3 H) ; ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 165.6, 164.1, 134.1, 131.9, 131.1, 128.6, 108.4, 62.2, 14.0; EI-MS: m/z (rel.int., %): 219 (M^+, 1.04), 217 (64.93), 158 (100.00), 131 (35.29), 103 (26.20).



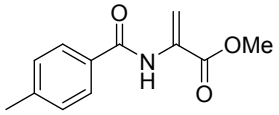
Ethyl (*Z*)-2-benzamidobut-2-enoate (7b)

Yellow liquid (74 mg, 64%); R_f = 0.46 (PE : EA = 3:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.88–7.82 (m, 3 H), 7.54–7.50 (m, 1 H), 7.45–7.42 (m, 2 H), 6.88 (q, *J* = 7.2 Hz, 1 H), 4.22 (q, *J* = 7.2 Hz, 2 H), 1.83 (d, *J* = 7.2 Hz, 3 H), 1.29 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 165.4, 164.6, 133.8, 133.3, 131.8, 128.5, 127.3, 126.2, 61.3, 14.8, 14.1; EI-MS: m/z (rel.int., %): 233 (M^+, 9.00), 187 (22.6), 128 (18.92), 105 (100.00), 77 (35.33).



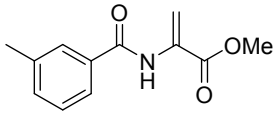
Ethyl (*Z*)-2-benzamido-3-phenylacrylate (7d)

Yellow oil (59 mg, 42%); R_f = 0.40 (PE : EA = 3:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.87–7.85 (m, 3 H), 7.56–7.44 (m, 6 H), 7.35–7.29 (m, 3 H), 4.30 (q, *J* = 7.2 Hz, 2 H), 1.34 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 165.3, 133.9, 133.5, 132.1, 131.2, 129.6, 129.3, 128.7, 128.5, 127.4, 124.3, 61.9, 14.2;ESI-HRMS: m/z calcd for $C_{18}H_{17}NO_3$+Na^+: 318.1101, found 318.1104.



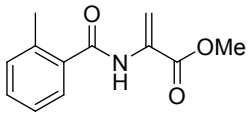
Methyl 2-(3-methylbenzamido)acrylate (7f)

White solid (72 mg, 67%); m.p. = 298–300 °C ; ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.52 (br, s, 1 H), 7.74–7.72 (m, 2 H), 7.27–7.25, (m, 2 H), 6.78 (m, 1 H), 6.00 (s, 1 H), 3.86 (m, 3 H), 2.39 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 165.5, 164.7, 142.5, 131.2, 130.9, 129.3, 126.8, 108.5, 53.0, 21.4; ESI-HRMS: m/z calcd for $C_{12}H_{13}NO_3$+Na^+: 242.0788, found 242.0788.



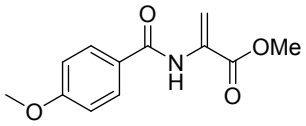
Methyl 2-(3-methylbenzamido)acrylate (7g)

Colorless oil (75 mg, 69%); R_f = 0.41 (PE : EA = 10:1); ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.54 (br, s, 1 H), 7.65–7.62 (m, 2 H), 7.36–7.34 (m, 2 H), 6.80 (s, 1 H), 6.00 (s, 1 H), 3.88 (s, 3 H), 2.41 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 165.8, 164.7, 138.6, 134.1, 132.7, 130.9, 128.5, 127.5, 123.8, 108.7, 53.0, 21.3; ESI-HRMS: m/z calcd for $C_{12}H_{13}NO_3$+Na^+: 242.0788, found 242.0790.



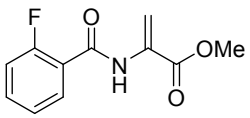
Methyl 2-(2-methylbenzamido)acrylate (7h)

Colorless oil (40 mg, 37%); R_f = 0.44 (PE : EA = 10:1); ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.12 (br, s, 1 H), 7.47–7.44 (m, 1 H), 7.39–7.34 (m, 1 H), 7.27–7.23 (m, 1 H), 6.70 (s, 1 H), 6.00 (s, 1 H), 3.86 (s, 3 H), 2.50 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 168.3, 164.5, 136.4, 135.6, 131.3, 131.0, 130.5, 126.8, 125.9, 108.9, 53, 19.9; ESI-HRMS: m/z calcd for $C_{12}H_{13}NO_3$+Na^+: 242.0788, found 242.0791.



Methyl 2-(4-methoxybenzamido)acrylate (7i)

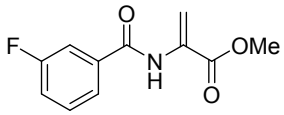
Colorless oil (68 mg, 57%); R_f = 0.41 (PE : EA = 10:1); ; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.46 (br, s, 1 H), 7.81–7.79 (m, 2 H), 6.96–6.94 (m, 2 H), 6.76 (m, 1 H), 5.95 (s, 1 H), 3.88 (m, 3 H), 3.85 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 165.2, 164.8, 162.6, 131.0, 128.8, 126.4, 113.9, 108.3, 55.3, 53.0; ESI-HRMS: m/z calcd for $C_{12}H_{13}NO_4$+Na^+: 258.0737, found 258.0738.



Methyl 2-(2-fluorobenzamido)acrylate (7j)

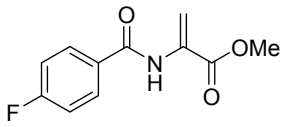
White solid (94 mg, 84%); m.p. = 267–269 °C ; ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.52 (br, d, *J* = 14.7 Hz, 1 H), 8.13–8.08 (m, 1 H), 7.56–7.49, (m, 1 H), 7.32–7.14, (m, 2 H), 6.82 (s, 1 H), 6.01 (m, 1 H), 3.89 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 164.3, 161.9, 161.6, 161.5, 158.6, 133.8 (d, *J* = 13.7 Hz), 131.8, 131.8, 131.1, 124.8 (d, *J* = 5 Hz), 120.8 (d, *J* = 14 Hz), 116.2 (d, *J* = 23 Hz), 109.5, 53.0; ESI-HRMS: m/z

calcd for $C_{11}H_{10}NFO_3$+Na^+: 246.0537, found 246.0536.



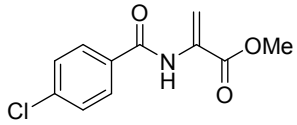
Methyl 2-(3-fluorobenzamido)acrylate (7k)

Colorless oil (80 mg, 72%); R_f = 0.31 (PE : EA = 10:1); ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.53 (br, s, 1 H), 7.60–7.55 (m, 2 H), 7.49–7.42, (m, 1 H), 7.27–7.22 (m, 1 H), 6.78 (s, 1 H), 6.01 (s, 1 H), 3.89 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 164.5, 164.3, 164.3, 161.0, 136.5 (d, *J* = 9 Hz), 130.7, 130.4, 130.3, 122.2, 122.2, 119.0 (d, *J* = 28 Hz), 114.3 (d, *J* = 31 Hz), 109.2, 53.1; ESI-HRMS: m/z calcd for $C_{11}H_{10}NFO_3$+Na^+: 246.0537, found 246.0539.



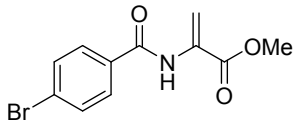
Methyl 2-(4-fluorobenzamido)acrylate (7l)

White solid (72 mg, 65%); m.p. = 282–283 °C ; ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.49 (br, s, 1 H), 7.88–7.83 (m, 2 H), 7.18–7.13, (m, 2 H), 6.77 (s, 1 H), 6.00 (s, 1 H), 3.89 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 165.0 (d, *J* = 253 Hz), 164.6, 164.5, 130.8, 130.3, 129.3, 129.2, 115.7 (d, *J* = 29 Hz), 108.9, 53.1; ESI-HRMS: m/z calcd for $C_{11}H_{10}NFO_3$+Na^+: 246.0537, found 246.0539.



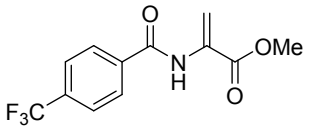
Methyl 2-(4-chlorobenzamido)acrylate (7m)

White solid (85 mg, 71%); m.p. = 103–104 °C ; ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.51 (br, s, 1 H), 7.79–7.76 (m, 2 H), 7.46–7.42, (m, 2 H), 6.78 (s, 1 H), 6.00 (m, 1 H), 3.89 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 164.6, 164.5, 138.2, 132.4, 130.7, 128.9, 128.3, 109.1, 53.1; ESI-HRMS: m/z calcd for $C_{11}H_{10}NClO_3$+Na^+: 262.0241, found 262.0241.



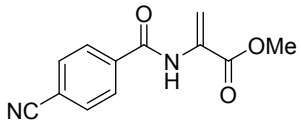
Methyl 2-(4-bromobenzamido)acrylate (7n)

White solid (105 mg, 74%); m.p. = 94–95 °C ; ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.50 (br, s, 1 H), 7.71–7.59 (m, 4 H), 6.77 (s, 1 H), 6.00 (m, 1 H), 3.88 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 164.6, 164.5, 132.9, 131.9, 130.7, 128.4, 126.7, 109.1, 53.1; EI-MS: m/z (rel.int., %): 285 (M^++2, 13.90), 283 (M^+, 15.63), 253 (20.62), 251 (20.06), 185 (91.89), 183 (100.00), 157 (24.43), 155 (24.07).



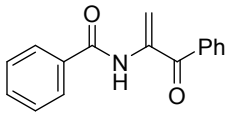
Methyl 2-(4-(trifluoromethyl)benzamido)acrylate (7o)

White solid (106 mg, 78%); m.p. = 147–149 °C ; ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.59 (br, s, 1 H), 7.97–7.94 (m, 2 H), 7.76–7.73, (m, 2 H), 6.81 (s, 1 H), 6.04 (s, 1 H), 3.89 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 164.4 (d, *J* = 16 Hz), 137.3, 135.5 (q, *J* = 32 Hz), 130.7, 127.4, 125.7 (q, *J* = 4 Hz), 125.3, 121.6, 109.5, 53.1; ESI-HRMS: m/z calcd for $C_{12}H_{10}NF_3O_3$+Na^+: 296.0505, found 296.0503.



Methyl 2-(4-cyanobenzamido)acrylate (7p)

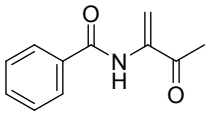
White solid (94mg, 82%); m.p. = 170–171 °C ; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): δ 8.60 – 8.51 (s, 1H), 7.97 – 7.91 (m, 2H), 7.83 – 7.75 (m, 2H), 6.83 – 6.77 (s, 1H), 6.09 – 6.02 (d, *J* = 1.3 Hz, 1H), 3.94 – 3.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 163.76, 137.9, 132.6, 130.6, 127.6, 117.7, 115.3, 109.7, 53.2; ESI-HRMS: m/z calcd for $C_{12}H_{10}N_2O_3$+Na^+: 253.0584, found 253.0585.



***N*-(3-Oxo-3-phenylprop-1-en-2-yl)benzamide (7q)**

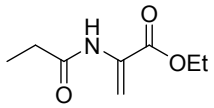
Yellow oil (96 mg, 72%); R_f = 0.37 (PE : EA = 10:1); ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.93 (s, 1 H), 7.92–7.89 (m, 2 H), 7.56–7.72 (m, 2 H), 7.60–7.44 (m, 6 H), 7.27

(s, 1 H), 5.71 (s, 1.0 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 193.0, 166.0, 137.8, 135.6, 134.1, 132.4, 132.0, 129.3, 128.7, 128.2, 127.0, 115.0; EI-MS: m/z (rel.int., %): 251 (M^+, 0.75), 240 (10.98), 105 (100.00), 77 (24.16).



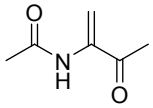
_N_-(3-Oxobut-1-en-2-yl)benzamide (7r)

Yellow solid (57 mg, 60%); m.p. = 107–108 °C ; ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.19 (br, s, 1 H), 7.72–7.45 (m, 5 H), 7.09 (s, 1 H), 5.61 (m, 1 H), 2.21 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 192.9, 169.3, 135.7, 132.3, 129.3, 128.2, 114.8, 24.7; ESI-HRMS: m/z calcd for $C_{11}H_{11}NO_2$+Na^+: 212.0682, found 212.0680.



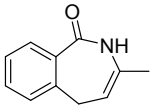
Ethyl 2-propionamidoacrylate (7v)

Colorless oil (47 mg, 55%); R_f = 0.38 (PE : EA = 3:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.77 (br, s, 1 H), 6.60 (s, 1 H), 5.87 (d, *J* = 1.2 Hz, 1 H), 4.29 (q, *J* = 7.2 Hz, 2 H), 2.36 (q, *J* = 7.2 Hz, 2 H), 1.35 (t, *J* = 7.2 Hz, 3 H), 1.20 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 172.4, 164.1, 131.0, 108.0, 62.1, 30.6, 14.0, 9.3; ESI-HRMS: m/z calcd for $C_8H_{13}NO_3$+Na^+: 194.0788, found 194.0790.



_N_-(3-oxobut-1-en-2-yl)acetamide (7w)

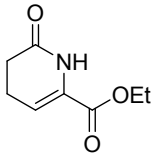
Yellow oil (18 mg, 28%); R_f = 0.10 (PE : EA = 3:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.03 (br, s, 1 H), 6.91 (s, 1 H), 5.78 (s, 1 H), 2.41 (s, 3 H), 2.13 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 194.8, 169.0, 138.3, 110.0, 24.7, 23.7; EI-MS: m/z (rel.int., %): 127 (M^+, 52.23), 99 (4.22), 85(62.69), 43 (100.00).



3-Methyl-2,5-dihydro-1*H*-benzo[c]azepin-1-one (4c)

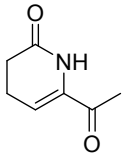
White solid (52 mg, 60%); m.p. = 197–199 °C ; ^{1}H NMR (d_6-DMSO, 300 MHz, δ ppm): 9.43 (s, 1 H), 7.89 (dd, *J* = 1.2 Hz, 7.8 Hz, 1 H), 7.42 (dt, *J* = 1.5 Hz, 7.5 Hz, 1

H), 7.28 (dt, *J* = 0.9 Hz, 7.5 Hz, 1 H), 7.15 (d, *J* = 7.5 Hz, 1 H), 5.24 (t, *J* = 6.9 Hz, 1 H), 3.10 (d, *J* = 6.9 Hz, 2.0 H), 1.75 (s, 3 H); ^{13}C NMR (d_6-DMSO, 75 MHz, δ ppm): 169.0, 143.3, 134.4, 133.8, 132.3, 130.6, 127.0, 126.6, 111.4, 31.4, 20.8; ESI-HRMS: m/z calcd for $C_{11}H_{11}NO+Na^+$: 196.0733, found 196.0737.



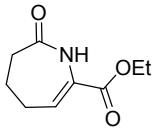
Ethyl 6-oxo-1,4,5,6-tetrahydropyridine-2-carboxylate (9a)

Colorless oil (38 mg, 45%); R_f = 0.16 (PE : EA = 3:1); ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.76 (br, s, 1 H), 6.23 (m, 1 H), 4.25 (q, *J* = 6.6 Hz, 1 H), 2.47 (m, 4 H), 1.29 (d, *J* = 6.6 Hz, 1 H);^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 169.7, 161.6, 128.8, 113.9, 61.8, 29.0, 20.6, 14.0; EI-MS: m/z (rel. int., %): 169 (M^+, 100.00), 140 (44.56), 124 (11.89), 112 (41.50), 96 (55.05).



6-acetyl-3,4-dihydropyridin-2(1*H*)-one (9b)

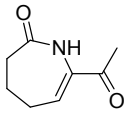
White solid (51 mg, 74%); m.p. = 77–78 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.88 (br, s, 1 H), 6.29 (dt, *J* = 1.2 Hz, *J* = 4.8 Hz, 1 H), 2.64–2.58 (m, 2 H), 2.54–2.50 (m, 2 H), 2.39 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm):190.0, 169.2, 136.0, 116.1, 28.8, 23.7, 21.0; ESI-HRMS: m/z calcd for $C_7H_9NO_2+Na^+$: 162.0526, found 162.0526.



Ethyl 7-oxo-4,5,6,7-tetrahydro-1*H*-azepine-2-carboxylate (9c)

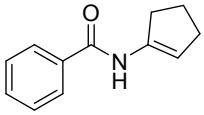
Colorless oil (22 mg, 24%): R_f = 0.49 (PE : EA = 1:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.59 (br, s, 1 H), 6.52 (br, 1 H), 4.27 (q, *J* = 8.1 Hz, 2 H), 2.61–2.59 (m, 2 H), 2.50–2.45 (m, 2 H), 2.02–1.94 (m, 2 H), 1.33 (t, *J* = 8.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 174.2, 163.5, 126.1, 121.8, 62.0, 36.5, 28.5, 21.2, 14.0; ESI-

HRMS: m/z calcd for $C_9H_{13}NO_3$+Na^+: 206.0788, found 206.0787.



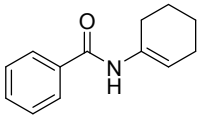
7-Acetyl-1,3,4,5-tetrahydro-2*H*-azepin-2-one (9d)

White solid (50 mg, 65%); m.p. = 56–57 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.92 (br, s, 1 H), 6.41 (t, *J* = 4.8 Hz, 1 H), 2.62–2.56 (m, 4 H), 2.42 (s, 3 H), 2.02–1.96 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 193.2, 173.9, 133.6, 123.8, 36.7, 29.1, 24.1, 20.4; ESI-HRMS: m/z calcd for $C_8H_{11}NO_2$+Na^+: 176.0682, found 176.0682.



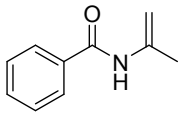
***N*-(Cyclopent-1-en-1-yl)benzamide (11a)**

White solid (83 mg, 89%); m.p. = 187–189 °C ; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.84 (s, 1 H), 7.77–7.73 (m, 2 H), 7.48–7.44 (m, 1 H), 7.40–7.36 (m, 2 H), 6.06 (t, *J* = 2.0 Hz, 1 H), 2.60–2.54 (m, 2 H), 2.47–2.42 (m, 2 H), 1.91–1.84 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 165.7, 136.2, 134.5, 131.2, 128.3, 126.8, 112.1, 33.5, 31.0, 21.2; EI-MS: m/z (rel.int., %): 187 (M^+, 16.05), 128 (11.69), 105 (100.00), 77 (55.09).



***N*-(Cyclohex-1-en-1-yl)benzamide (11b)**

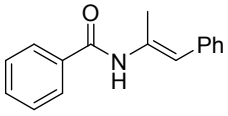
White solid (44 mg, 44%); m.p. = 120–121 °C ; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.76–7.73 (m, 2 H), 7.49–7.44 (m, 1 H), 7.41–7.37 (m, 2 H), 7.18 (br, s, 1 H), 6.21 (s, 1 H), 2.26–2.23 (m, 2 H), 2.17–2.12 (m, 2 H), 1.75–1.69 (m, 2 H), 1.63–1.57 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 165.8, 135.2, 132.7, 131.2, 128.4, 126.8, 114.0, 28.0, 24.0, 22.5, 21.9; EI-MS: m/z (rel.int., %): 201 (M^+, 39.46), 172 (5.72), 105 (100.00), 77 (35.18).



***N*-(Prop-1-en-2-yl)benzamide (11c)**

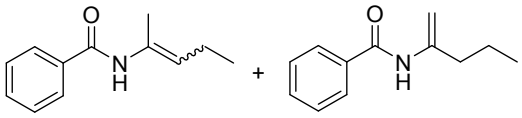
White solid (49 mg, 60%); m.p. = 101–102 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm):

7.76–7.75 (m, 2 H), 7.50–7.47 (m, 1 H), 7.44–7.35 (m, 3 H), 5.56 (s, 1 H), 4.57 (s, 1 H), 2.03 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 166.0, 137.7, 135.0, 131.5, 128.6, 126.8, 99.6, 22.1; EI-MS: m/z (rel.int., %): 161 (M^+, 3.52), 159 (29.77), 105 (100.00), 77 (23.34).



(*E*)-*N*-(1-Phenylprop-1-en-2-yl)benzamide (11d)

Yellow liquid (90 mg, 81%): R_f = 0.44 (PE : EA = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.81–7.79 (m, 2 H), 7.53–7.49 (m, 1 H), 7.46–7.40 (m, 4 H), 7.34–7.31 (m, 2 H), 7.26–7.25 (m, 2 H), 7.20–7.18 (m, 1 H), 7.15 (s, 1 H), 2.21 (m, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 166.0, 136.9, 135.1, 133.0, 131.6, 128.9, 128.7, 128.5, 128.1, 126.9, 126.1, 116.9, 18.1; ESI-HRMS: m/z calcd for $C_{16}H_{15}NO+Na^+$: 260.1046, found 260.1051.



11e-1, 52% **11e-2**, 2%

11e-1 (*Z*:*E* = 1:2)[5], 11e-2

Yellow liquid (50 mg, 54%): ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.81–7.75 (m, 3.40 H), 7.52–7.32 (m, 6.72 H), 5.79 (t, *J* = 7.2 Hz, 1 H), 5.70 (s, 0.06 H), 5.01 (t, *J* = 7.2 Hz, 0.56 H), 4.62 (s, 0.06 H), 2.25 (t, *J* = 8.0 Hz, 0.12 H), 2.13–1.98 (m, 8.48 H), 2.00 (m, 3.33 H), 1.60–1.54 (m, 0.12 H), 1.02–0.97 (m, 5.20 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 165.9, 135.2, 134.8, 131.5, 131.3, 130.4, 130.1, 128.5, 128.4, 127.0, 126.8, 122.2, 120.2, 99.4, 37.8, 21.3, 20.5, 20.2, 16.0, 14.2, 13.7;

References

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2. V. P. Kumar, V. S. Babu, K. Yahata and Y. Kishi, *Org. Lett.*, 2017, **19**, 2766–2768.
3. R. B. Bedford, M. Huwe and M. C. Wilkinson, *Chem. Commun.*, 2009, 600–602.
4. J. E. Barclay and G. J. Leigh, *J. Chem. Soc. Dalton Trans*, 1988, 2866–2870.
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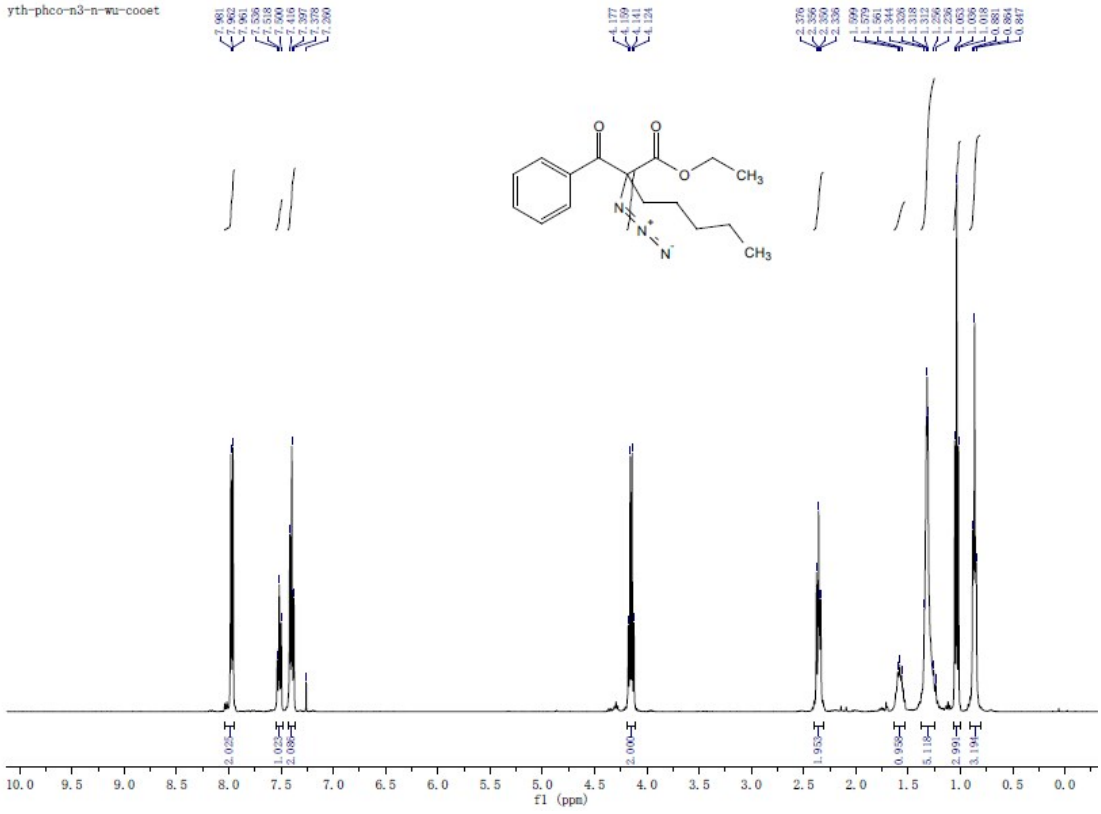
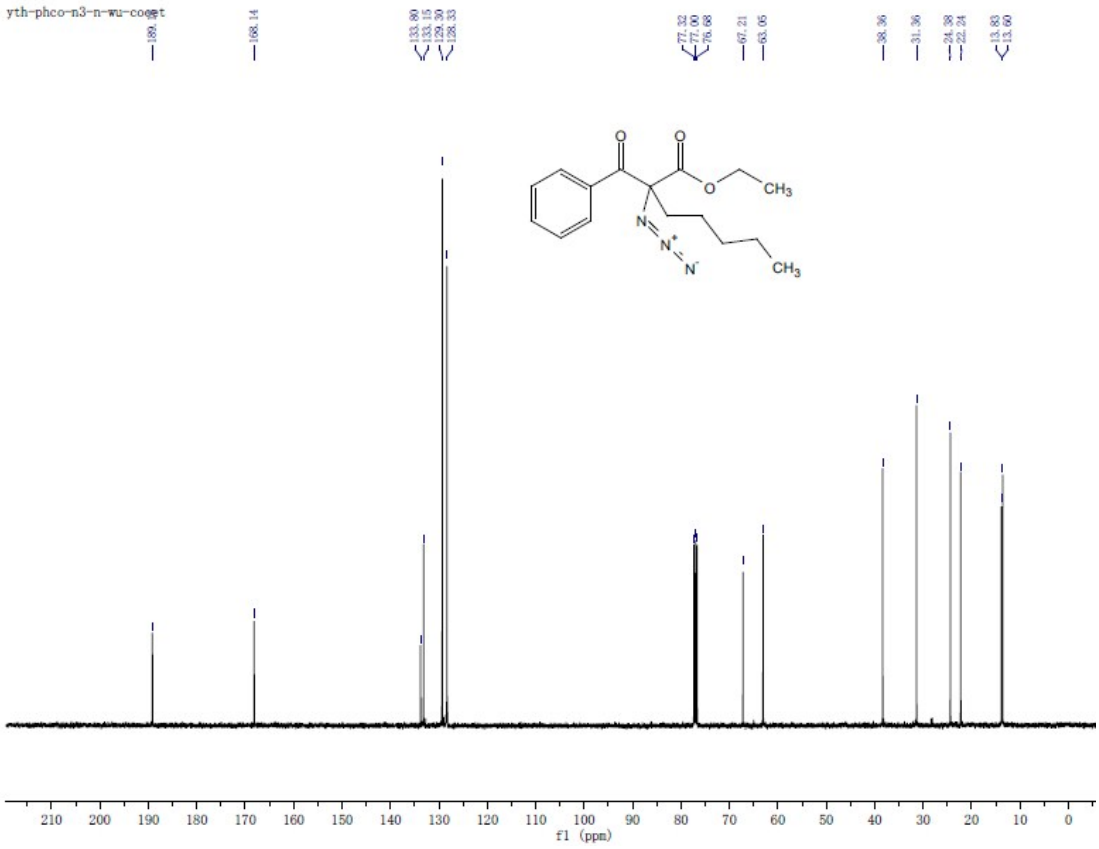
5c

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133.80
133.15
129.30
128.33
77.32
77.00
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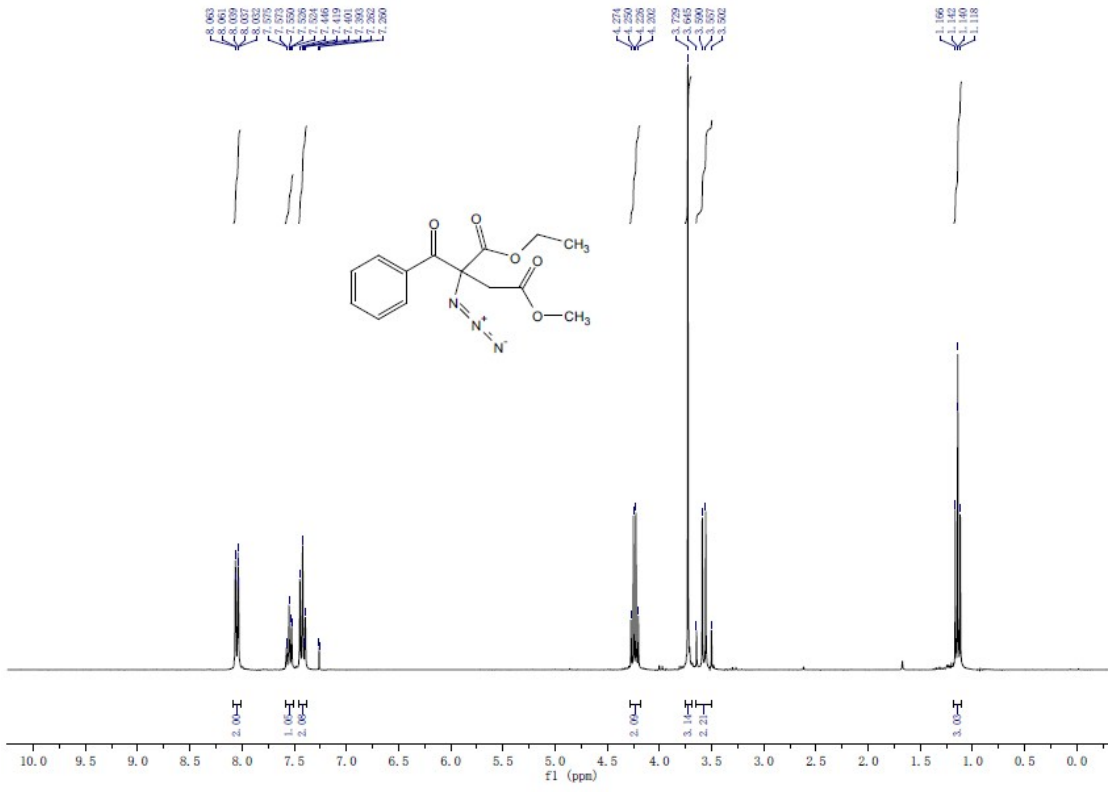
22.24
13.83
13.60
f1 (ppm)

5e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8.037
8.032
7.575
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7.550
7.539
7.524
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7.401
7.393
7.282
7.260
4.274
4.259
4.229
4.202
3.729
3.645
3.599
3.597
3.502
1.166
1.147
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1.06
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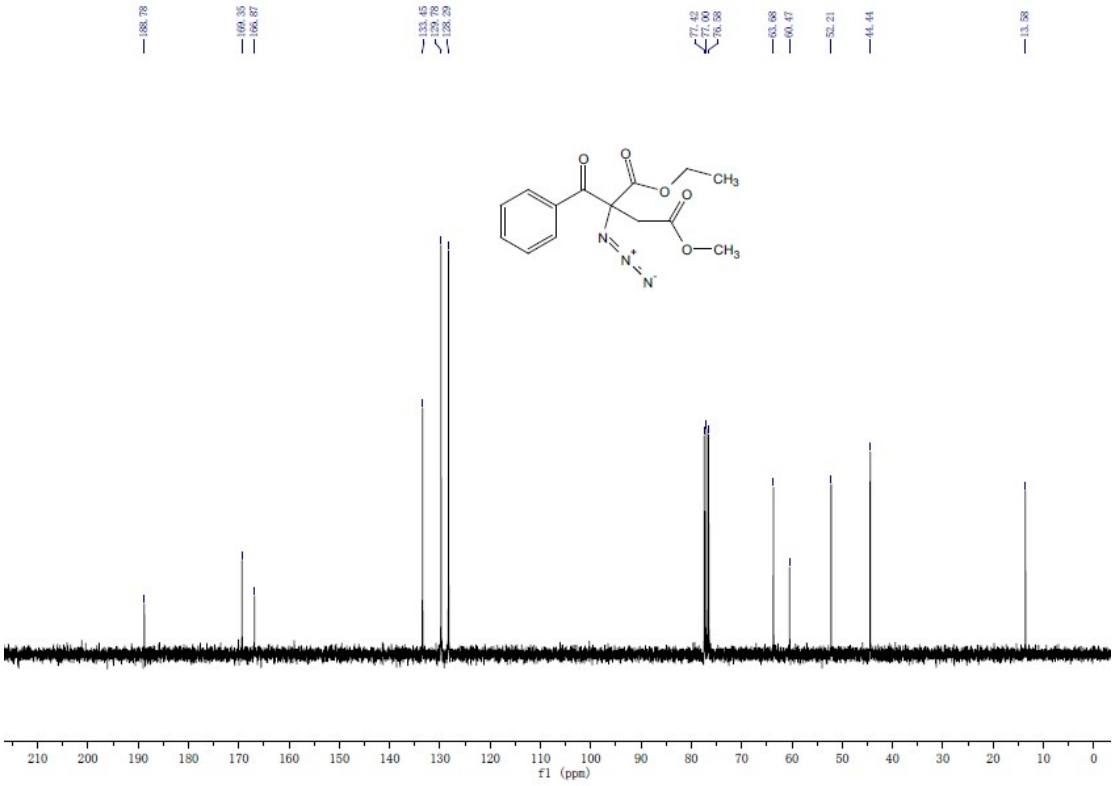
2.00
3.14
2.21
3.06
f1 (ppm)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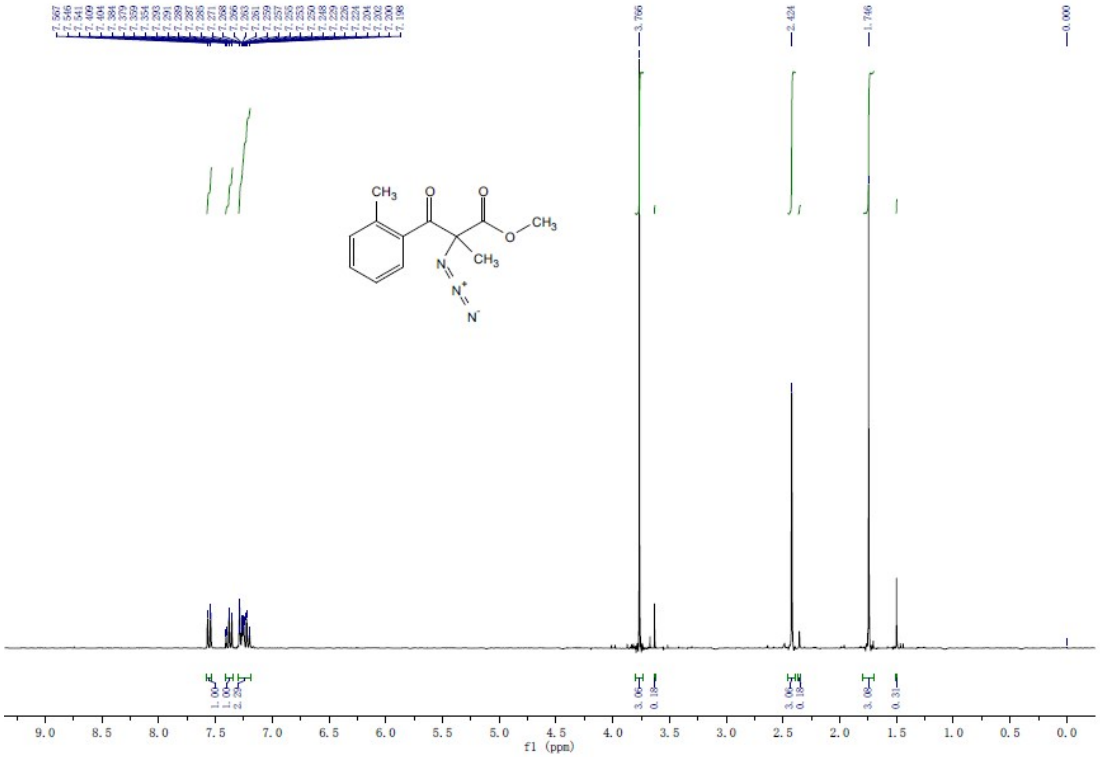
133.45
132.79
128.29
77.42
77.00
76.58
63.68
60.47
52.21
44.44
13.58
O
O
O
CH3
O
O
CH3
N
N+
N-
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5h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7.541
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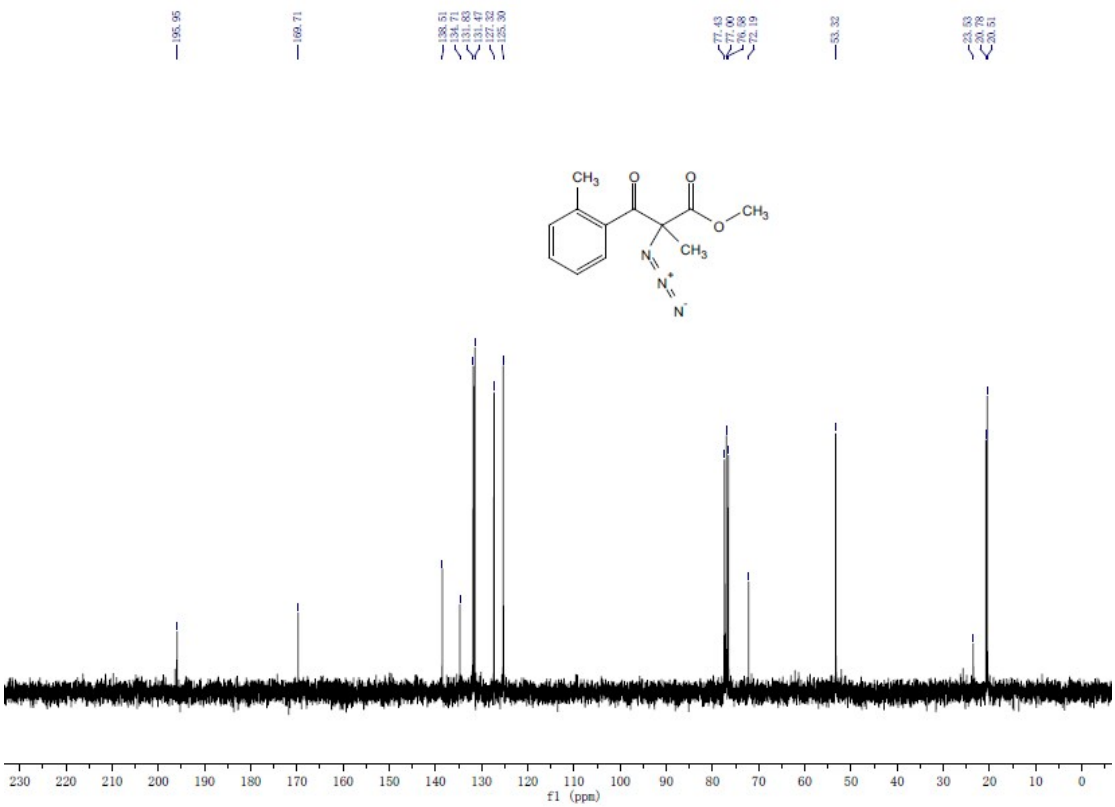
7.379
7.359
7.354
7.293
7.289
7.287
7.285
7.271
7.268
7.266
7.263
7.261
7.259
7.257
7.255
7.253
7.250
7.248
7.229
7.225
7.224
7.204
7.202
7.200
7.198
3.766
2.424
1.746
0.000
CH3
O
O
O
CH3
CH3
N
N+
N-
1.00
1.00
2.25
3.06
0.18
3.06
0.18
3.08
0.31
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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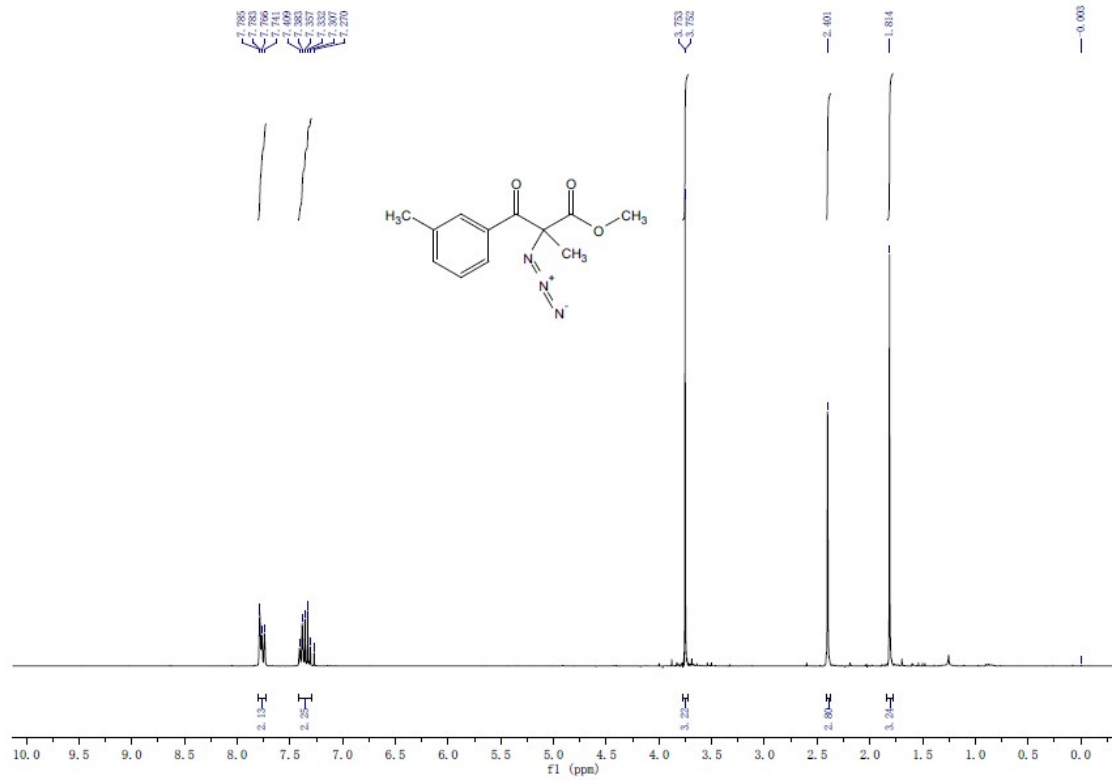
138.51
134.71
131.88
131.47
127.92
125.30
77.43
77.00
76.58
72.19
53.32
23.53
20.78
20.51
CH3
O
O
O
CH3
CH3
N
N+
N-
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5g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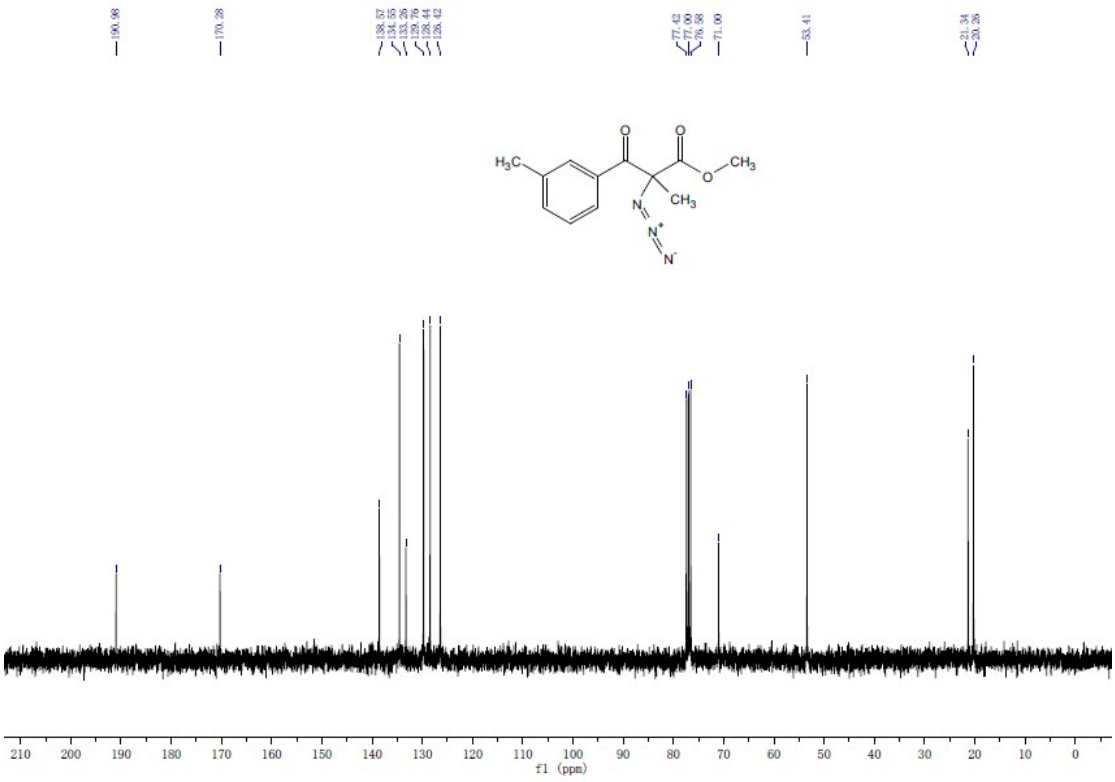
3.752
2.401
1.814
0.000
H3C
O
O
O
CH3
CH3
N
N+
N-
2.13
2.25
3.22
2.80
3.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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126.42
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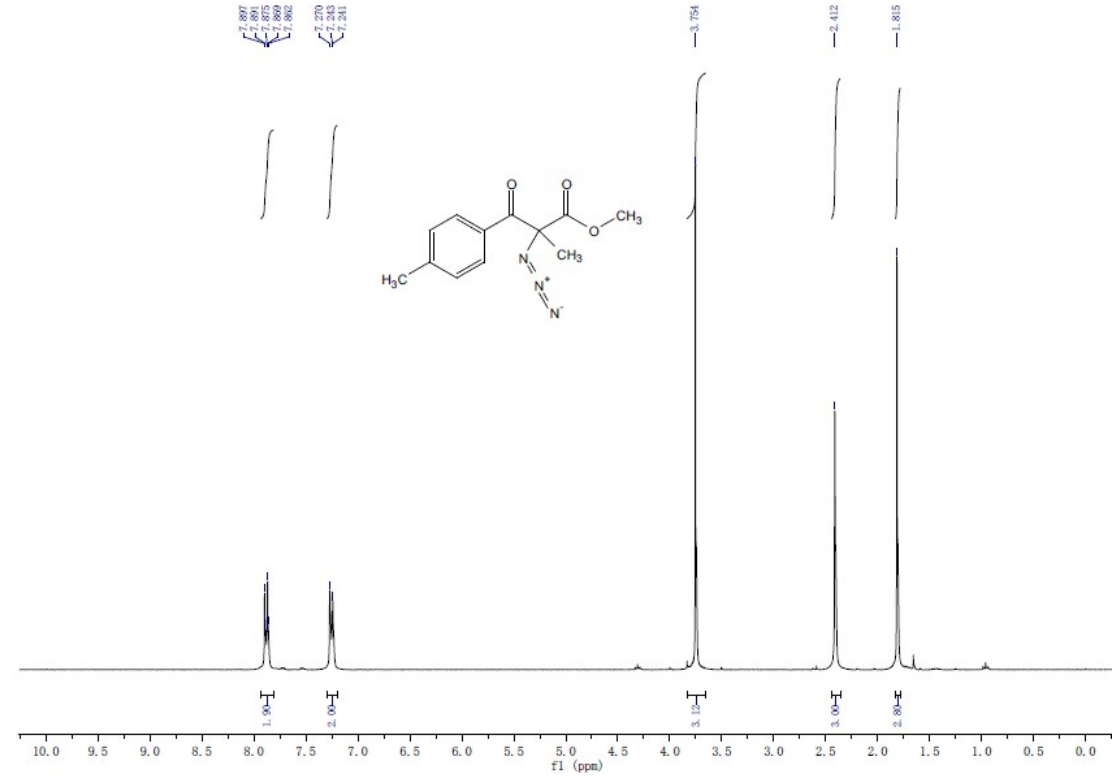
77.00
76.58
71.00
53.41
21.34
20.26
H3C
O
O
O
CH3
CH3
N
N+
N-
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5f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7.270
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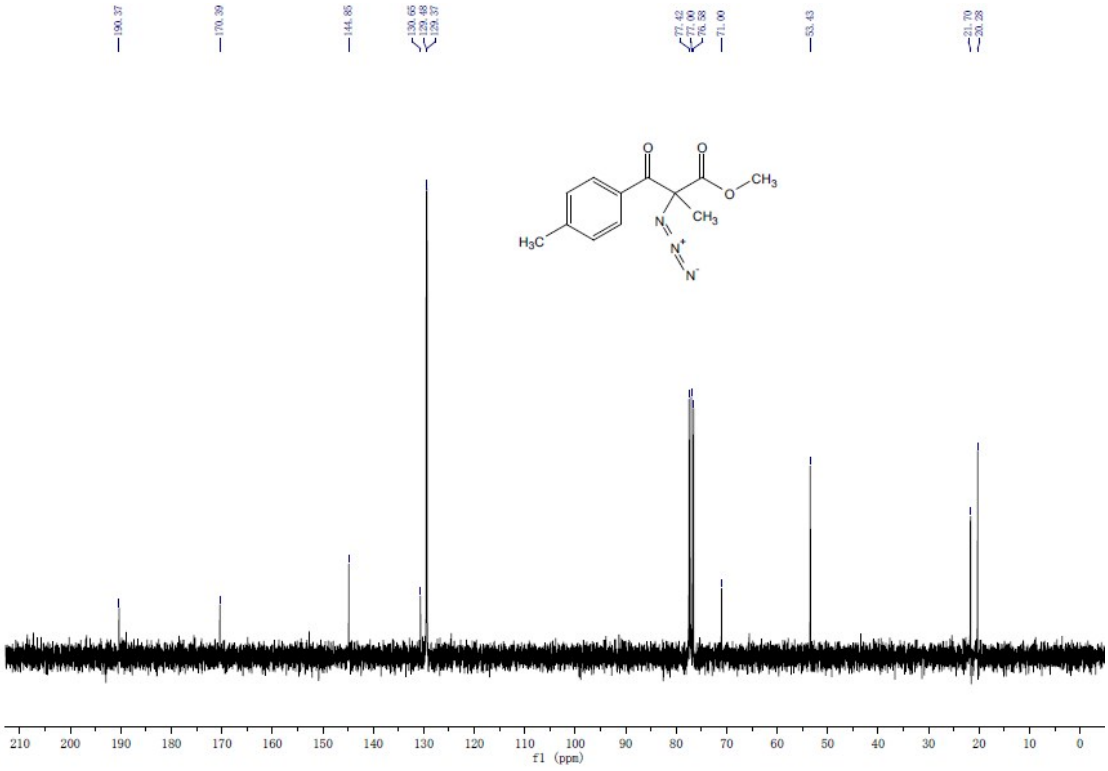
7.241
3.754
2.412
1.815
H3C
O
O
O
CH3
CH3
N
N+
N-
1.90
2.00
3.12
3.00
2.80
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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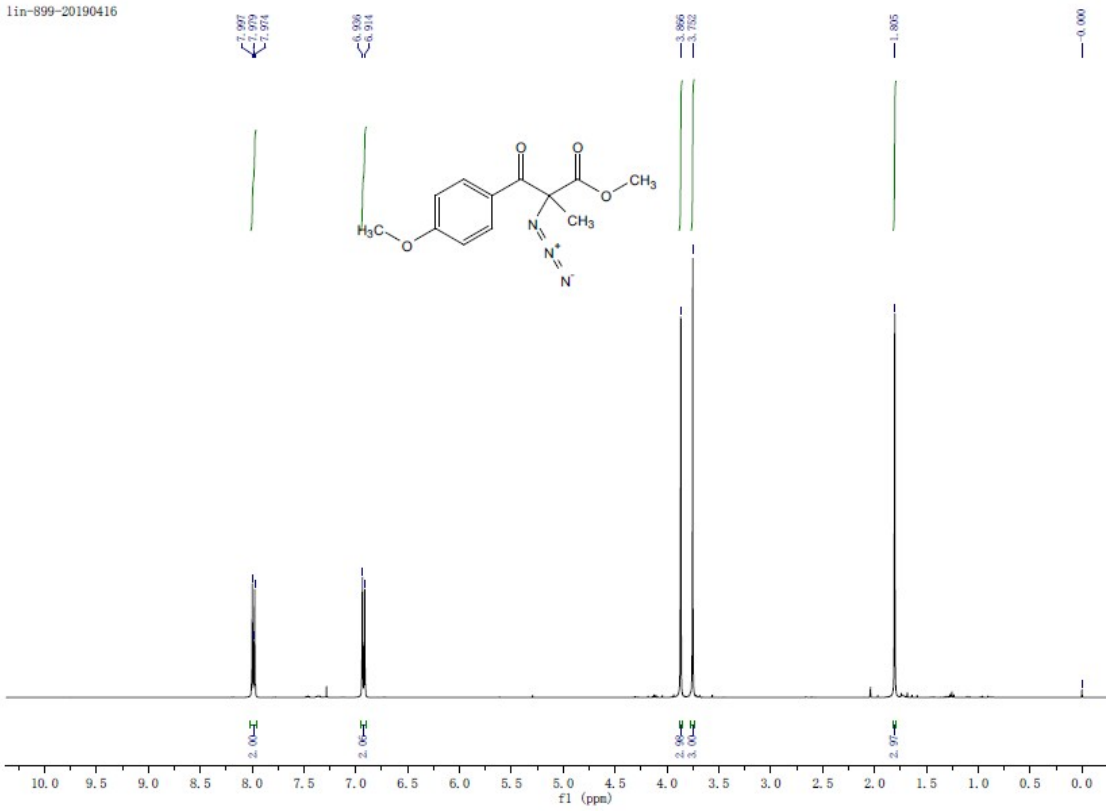
f1 (ppm)

5i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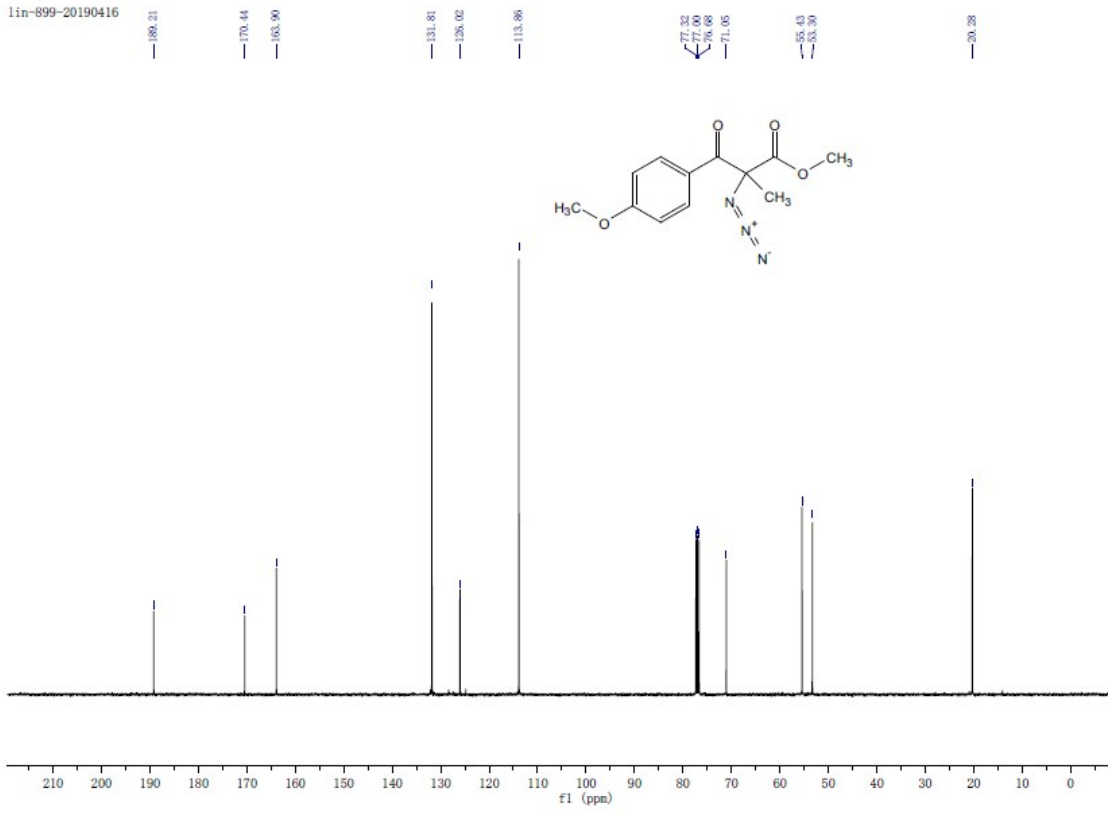
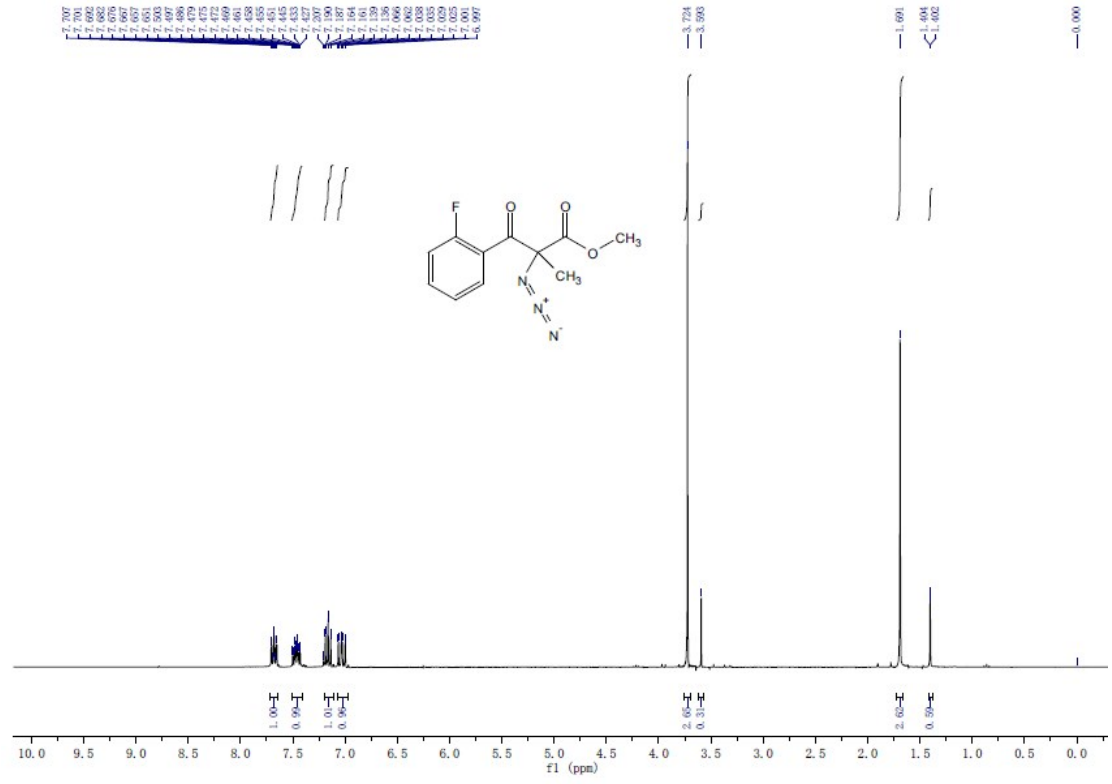
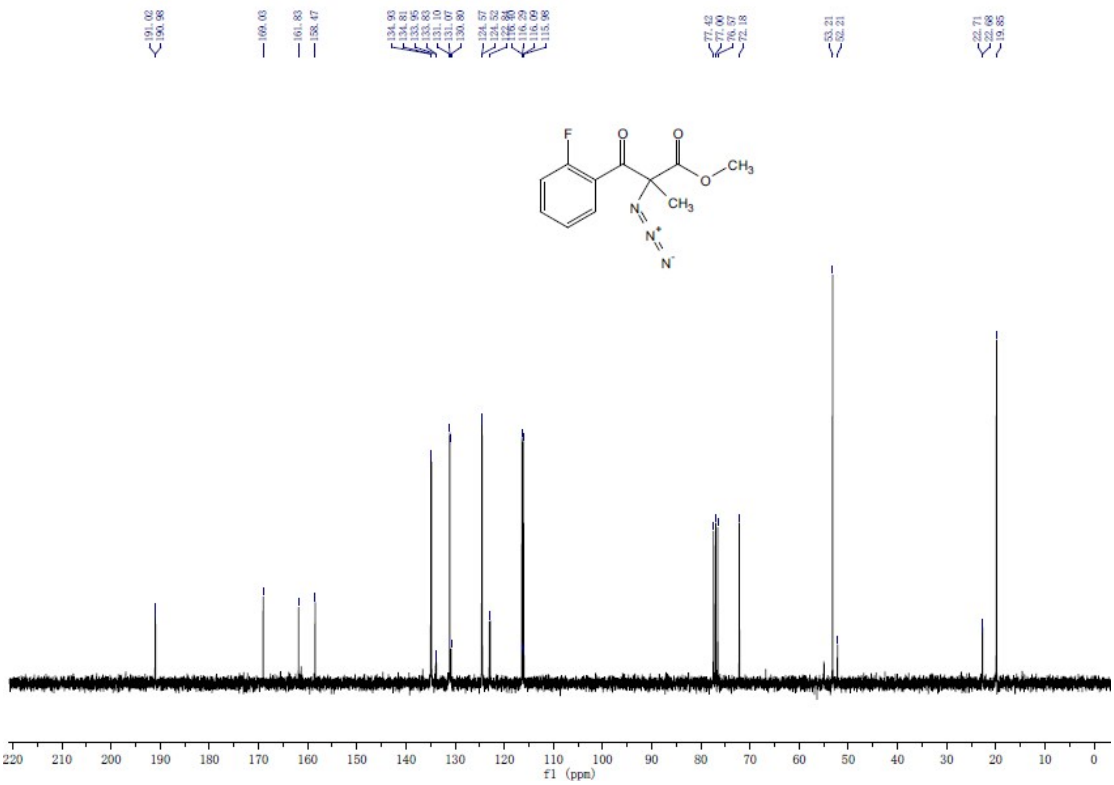
2.06
2.98
3.00
2.97
f1 (ppm)

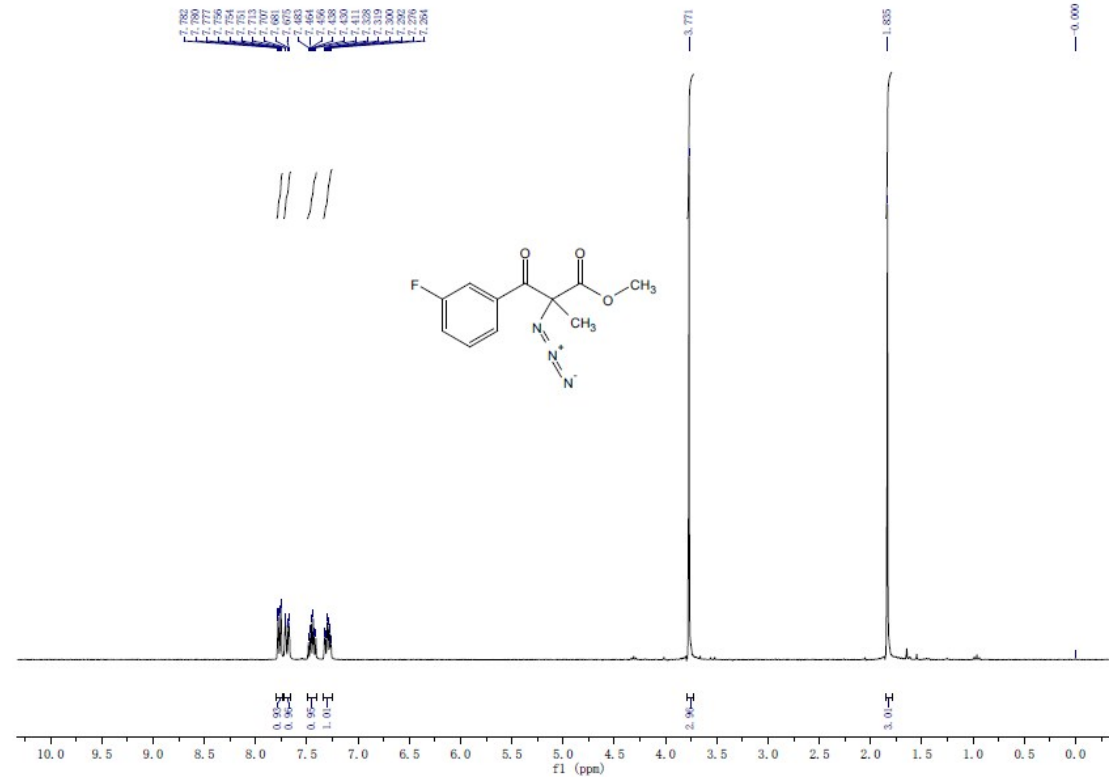

lin-899-20190416
189.21
170.44
163.99
131.81
126.02
113.86
77.32
77.00
76.68
71.05
55.43
55.30
20.28
O
O
O
CH3
CH3
H3C
O
N
N+
N-
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

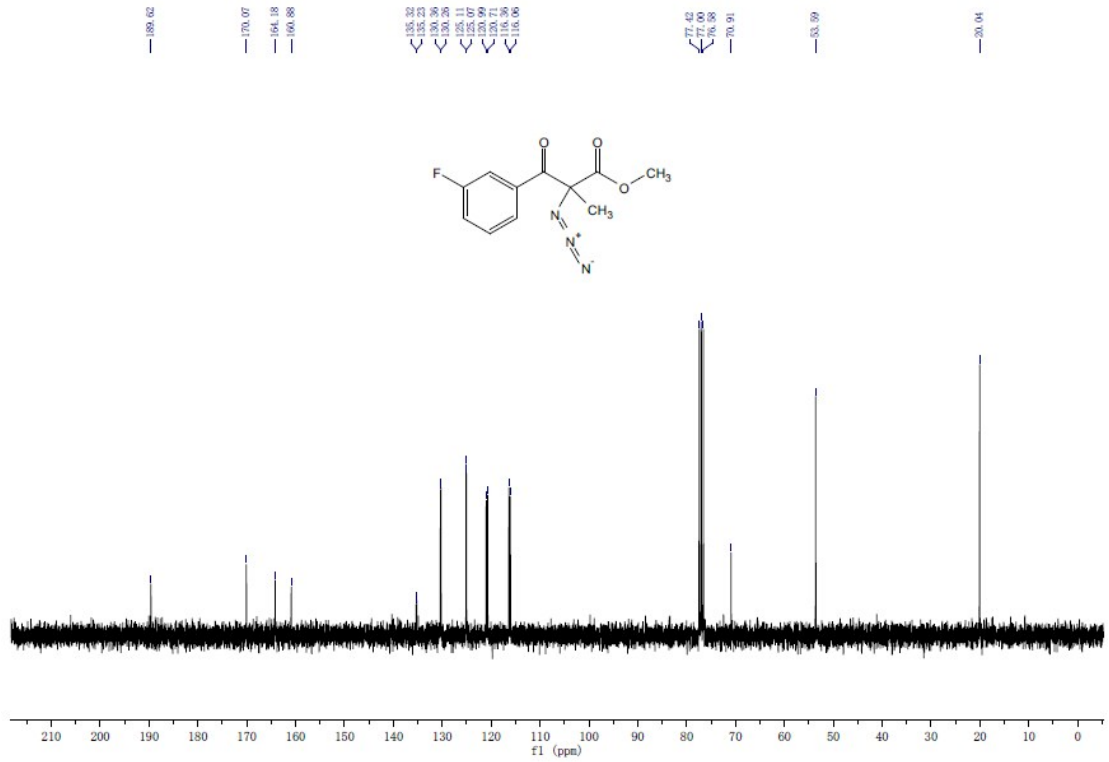
5j


7.707
7.701
7.692
7.682
7.675
7.667
7.661
7.503
7.497
7.486
7.479
7.475
7.472
7.469
7.461
7.458
7.455
7.451
7.445
7.433
7.427
7.207
7.190
7.187
7.164
7.161
7.139
7.136
7.066
7.062
7.038
7.035
7.029
7.025
7.001
6.997
3.724
3.593
1.691
1.404
1.402
0.000
F
O
O
O
CH3
CH3
N
N+
N-
1.00
0.99
1.01
0.96
2.65
0.31
2.62
0.59
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

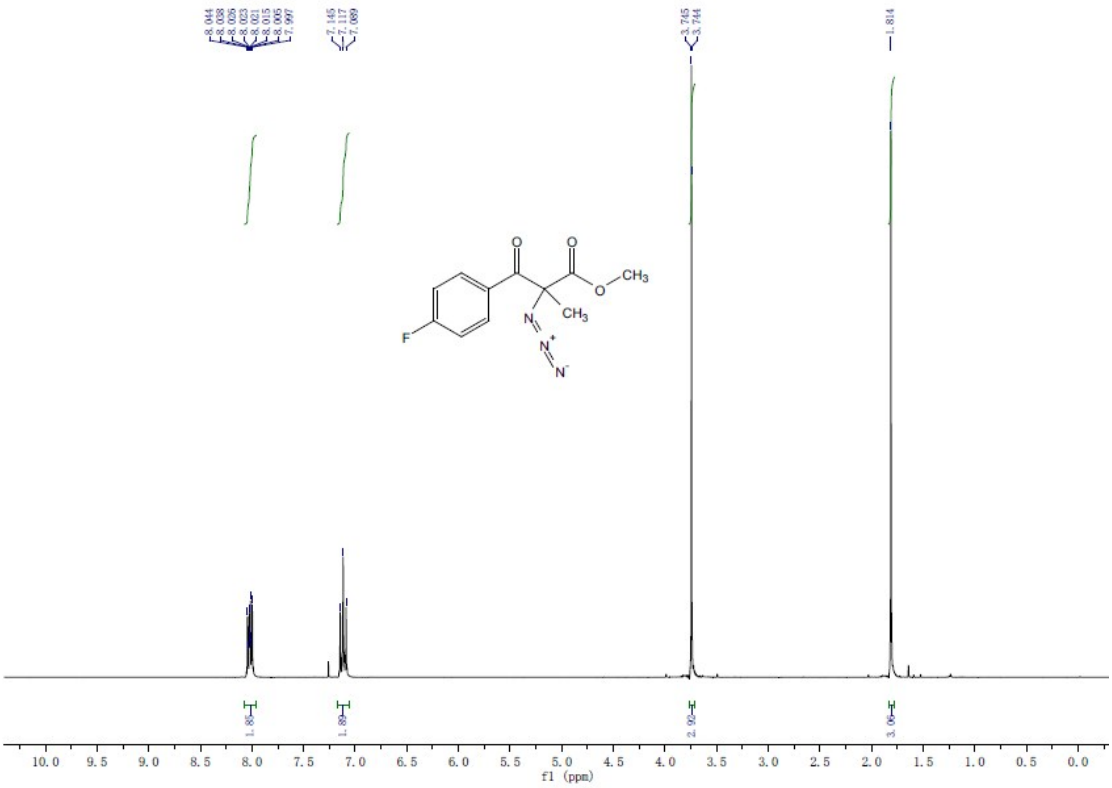

191.02
190.98
169.05
161.83
158.47
134.93
134.81
133.95
133.83
131.10
131.05
130.80
124.57
124.52
116.29
116.09
115.98
77.42
77.00
76.57
72.18
53.21
52.21
22.71
22.68
19.85
F
O
O
O
CH3
CH3
N
N+
N-
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

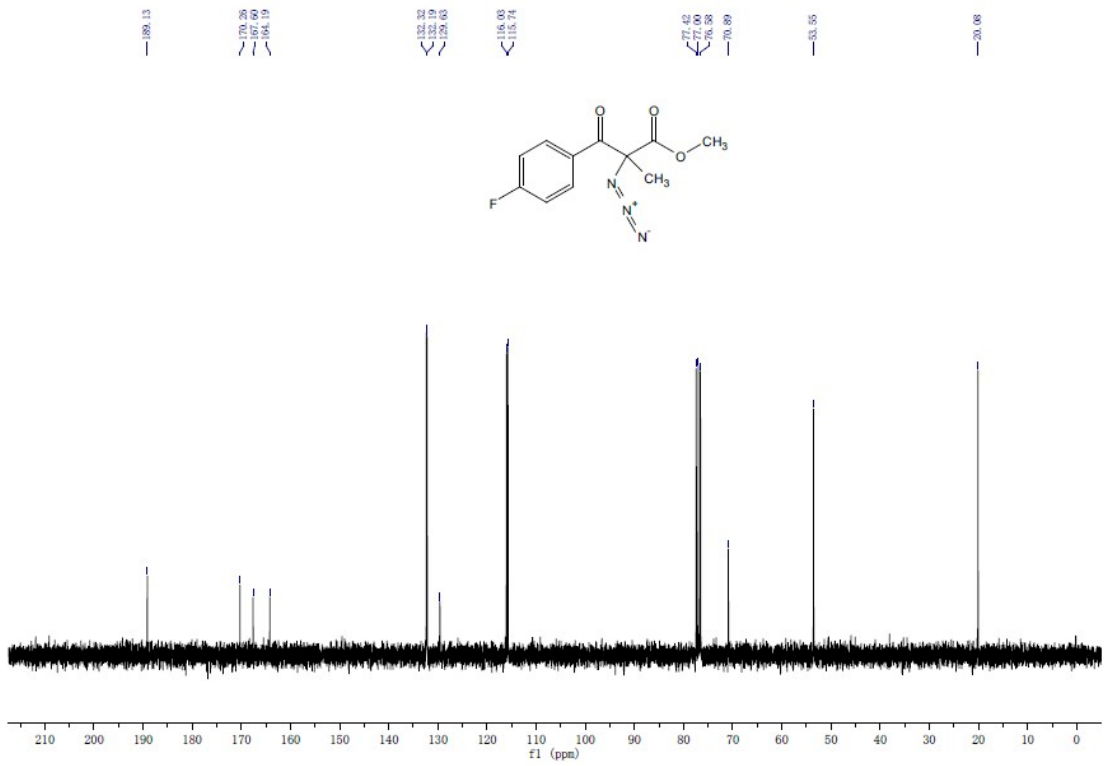
5k


7.782
7.779
7.777
7.759
7.754
7.751
7.733
7.707
7.681
7.675
7.483
7.464
7.456
7.438
7.430
7.411
7.338
7.319
7.300
7.292
7.276
7.264
3.771
1.835
0.000
F
O
O
O
CH3
CH3
N
N+
N-
0.95
0.96
0.95
1.01
2.96
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

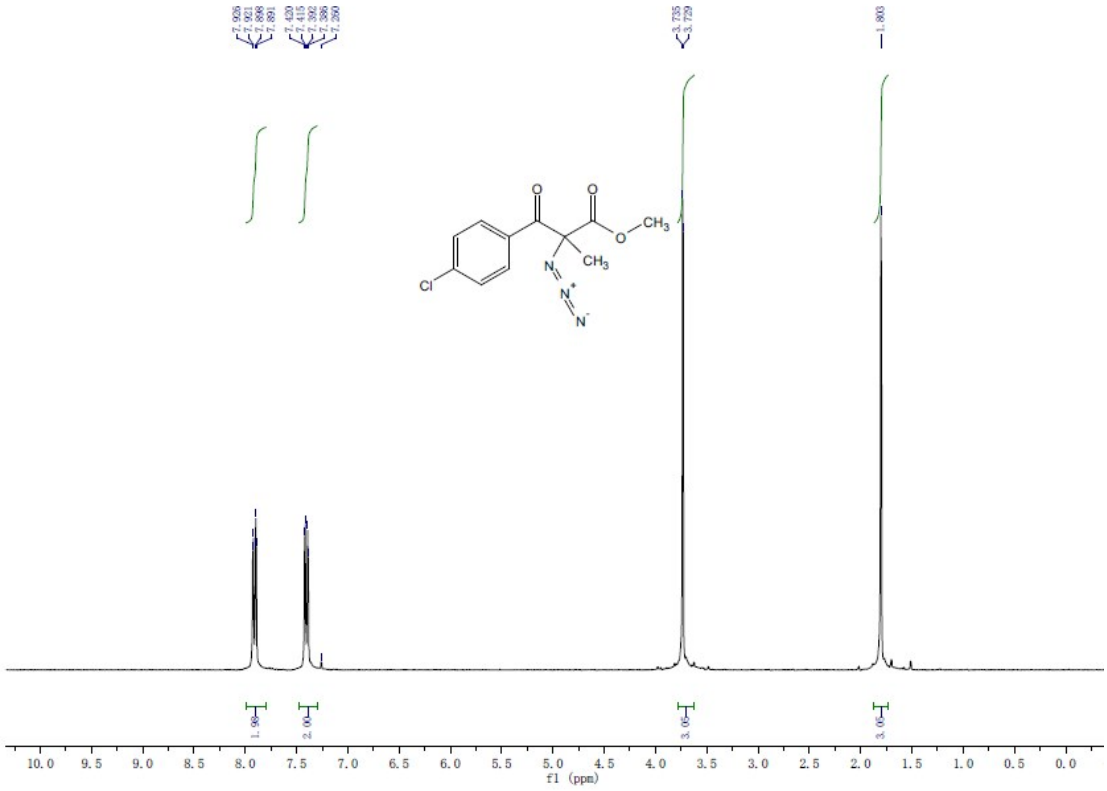

189.62
170.07
164.18
160.88
135.32
135.23
130.36
130.26
125.11
125.07
120.99
120.71
116.36
116.06
77.42
77.00
76.58
70.91
53.59
20.04
F
O
O
O
CH3
CH3
N
N+
N-
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

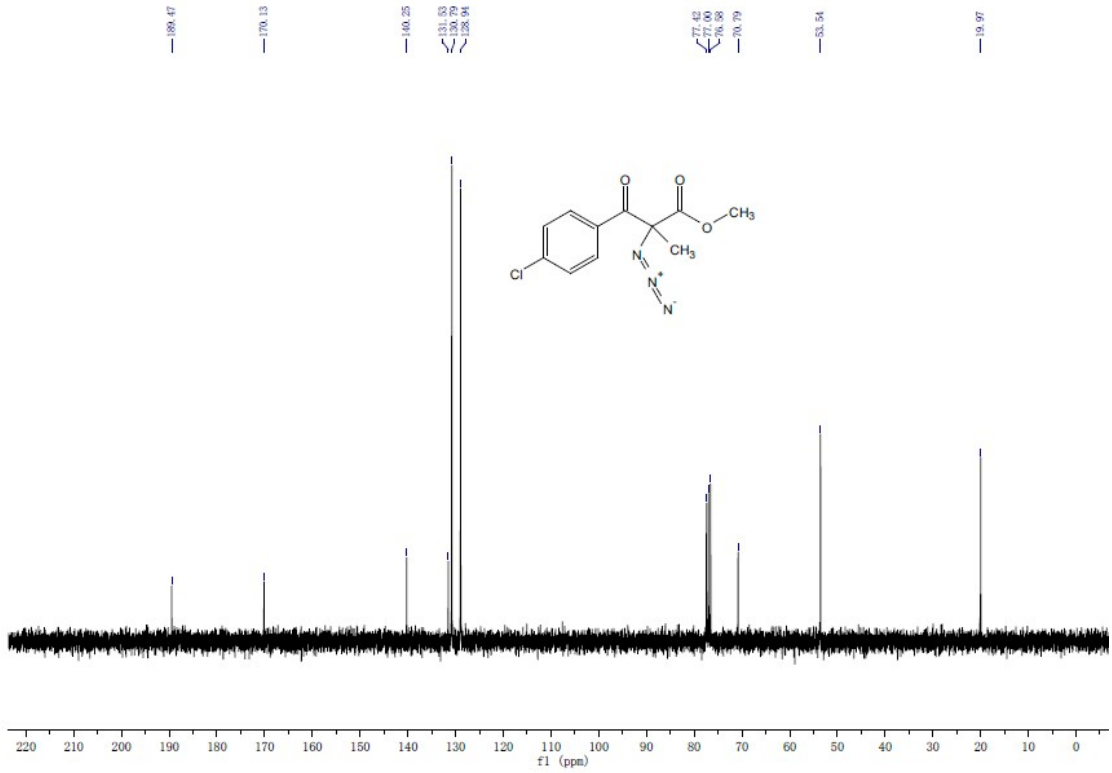
5l


8.044
8.038
8.035
8.023
8.021
8.015
8.005
7.997
7.145
7.117
7.089
3.745
3.744
1.814
F
O
O
O
CH3
CH3
N
N+
N-
1.85
1.89
2.92
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

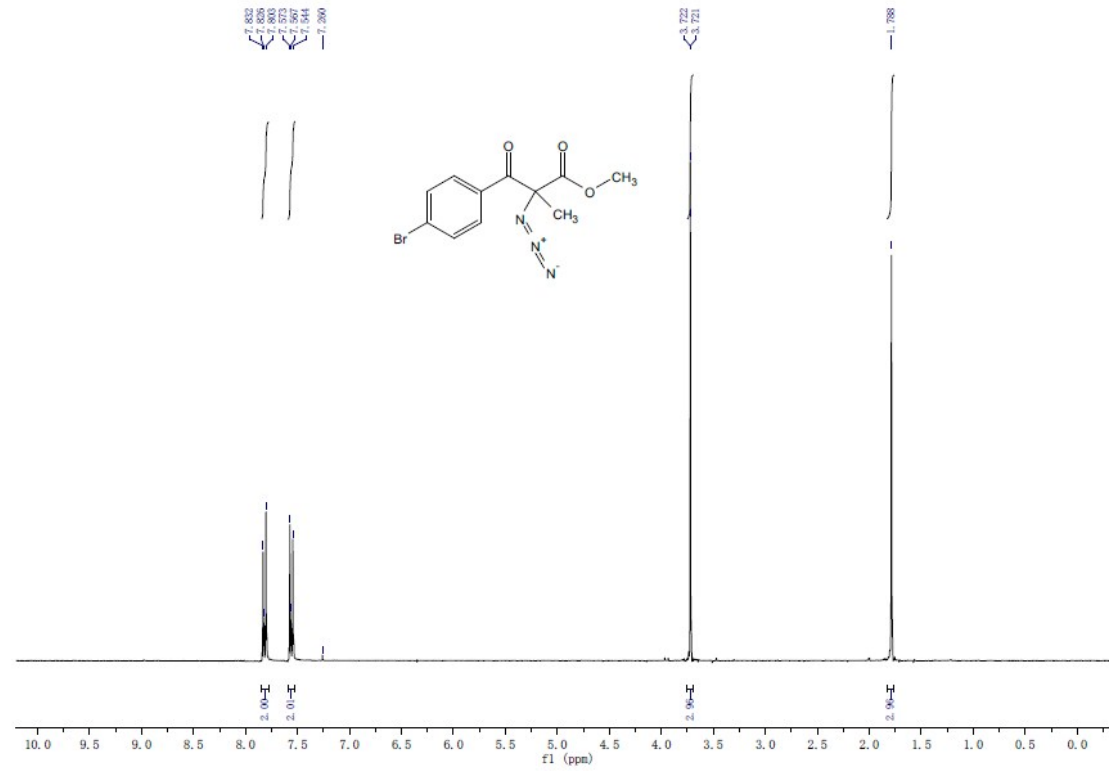

189.13
170.26
167.60
164.19
132.32
132.19
129.63
116.03
115.74
77.42
77.00
76.58
70.89
53.55
20.08
O
O
O
CH3
CH3
N
N+
N-
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

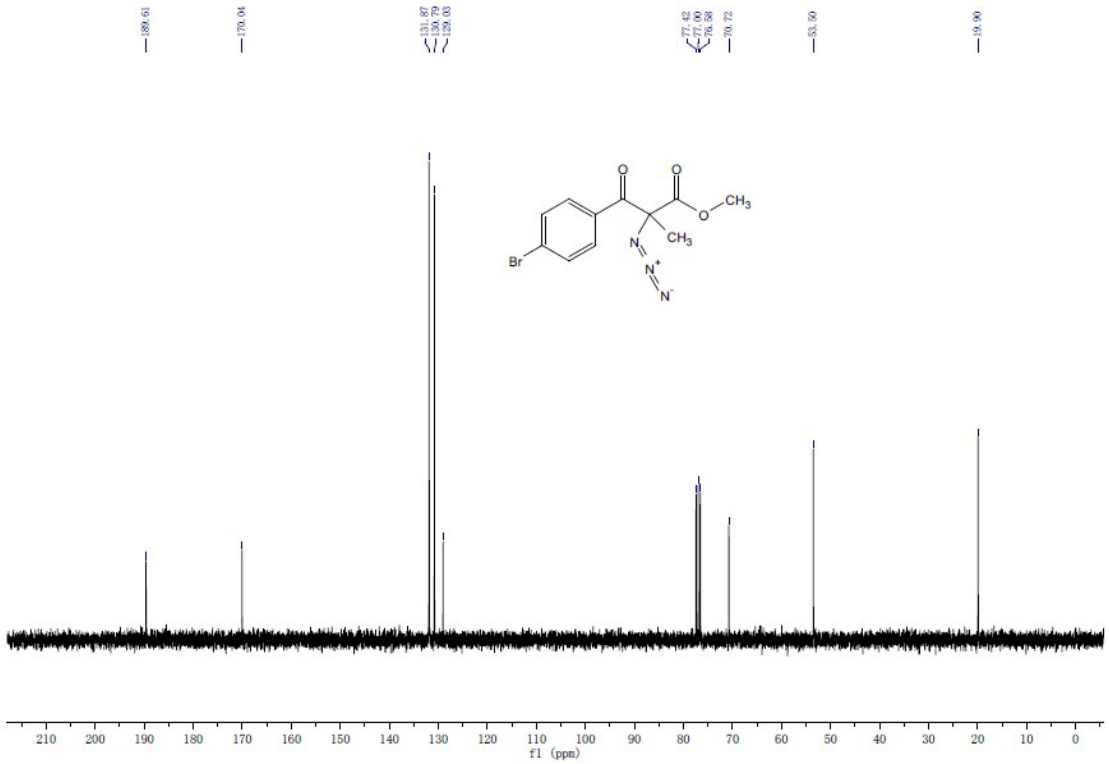
5m


7.926
7.921
7.906
7.901
7.420
7.415
7.392
7.386
7.260
3.735
3.729
1.803
O
O
O
CH3
CH3
N
N+
N-
Cl
1.98
2.00
3.05
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

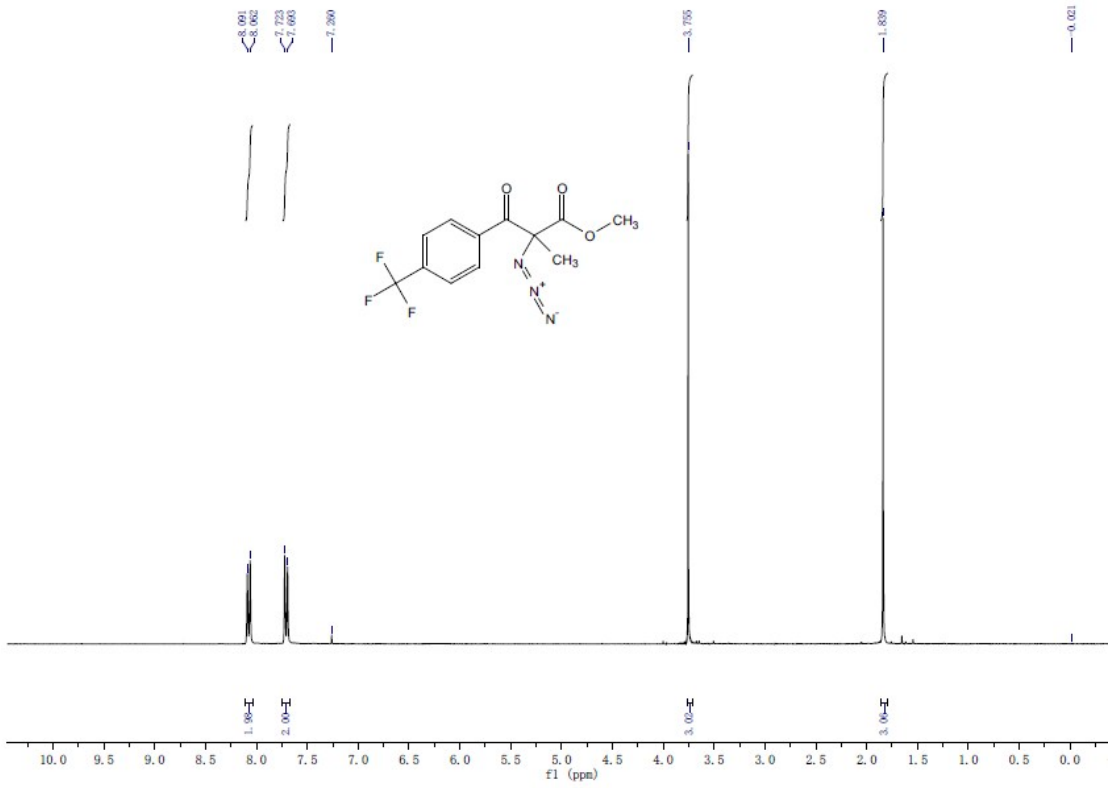

189.47
170.13
140.25
131.53
130.79
128.94
77.42
77.00
76.58
70.79
53.54
19.97
O
O
O
CH3
CH3
Cl
N
N+
N-
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

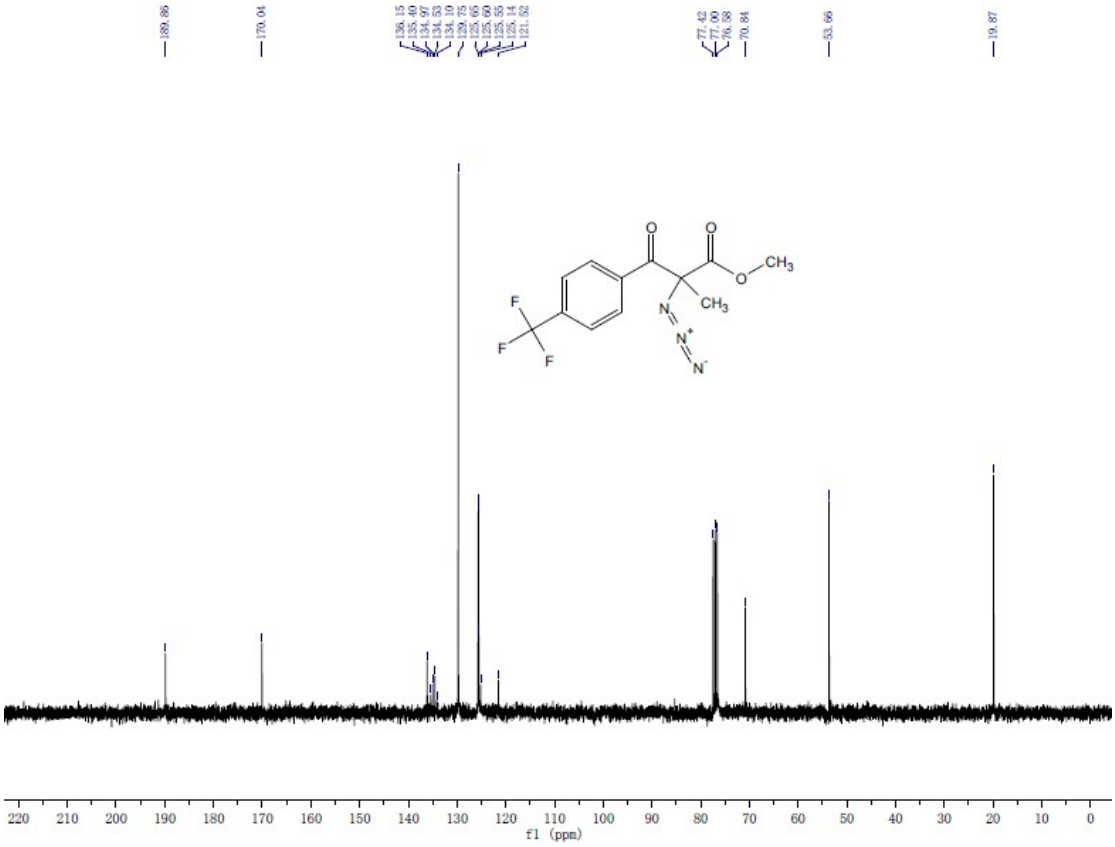
5n


7.832
7.826
7.803
7.573
7.567
7.544
7.260
3.722
3.721
1.788
O
O
O
CH3
CH3
Br
N
N+
N-
2.00
2.01
2.96
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

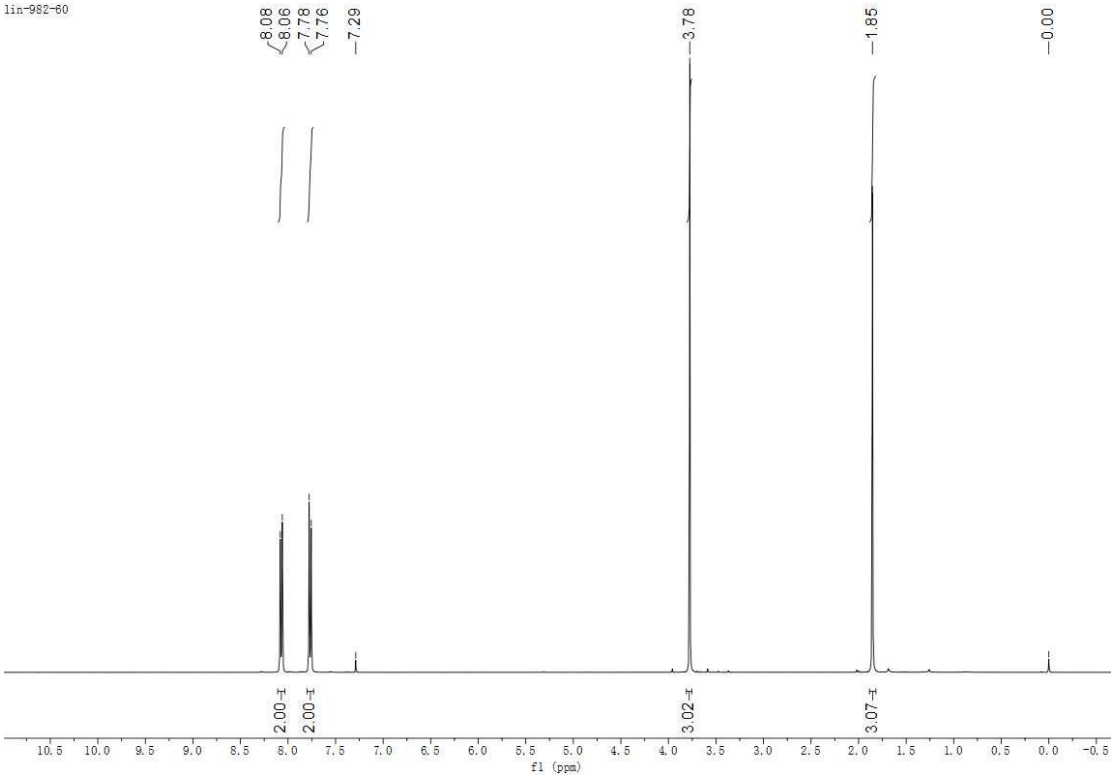

189.61
170.04
131.87
130.79
129.05
77.42
77.04
76.88
70.72
53.50
19.90
O
O
O
CH3
CH3
N
N+
N-
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

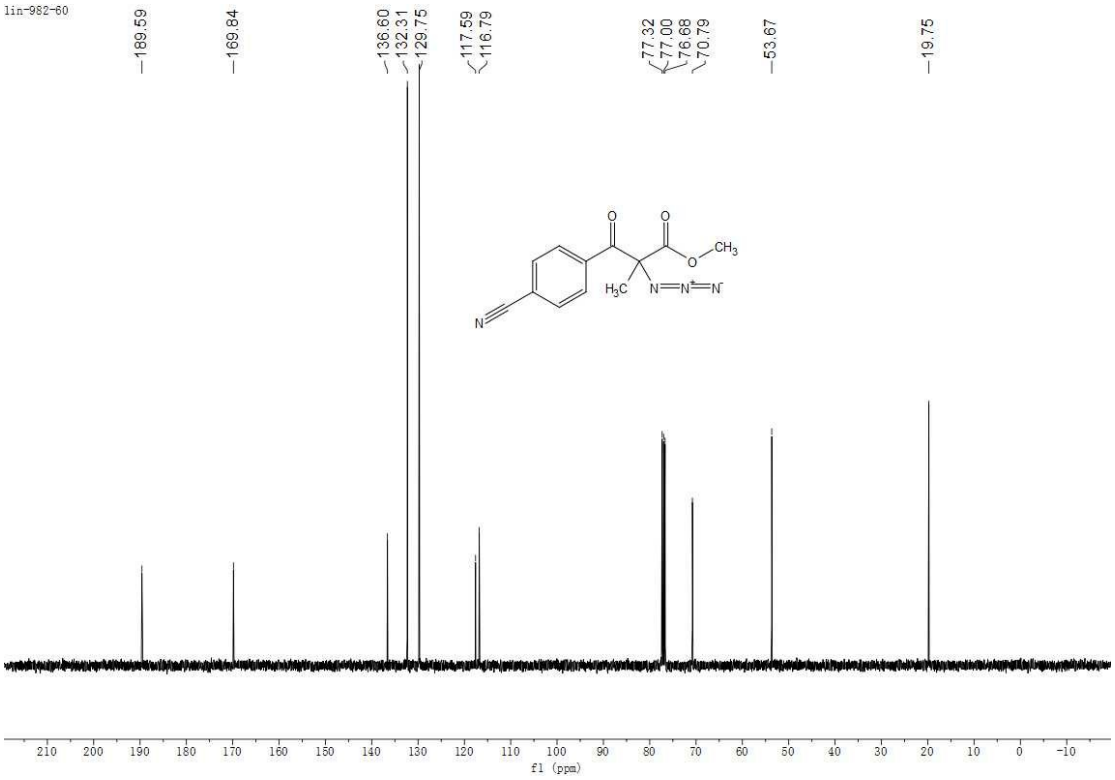
5o


8.091
8.062
7.723
7.693
7.260
3.755
1.839
0.021
O
O
O
CH3
CH3
F
F
F
N
N+
N-
1.98
2.00
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

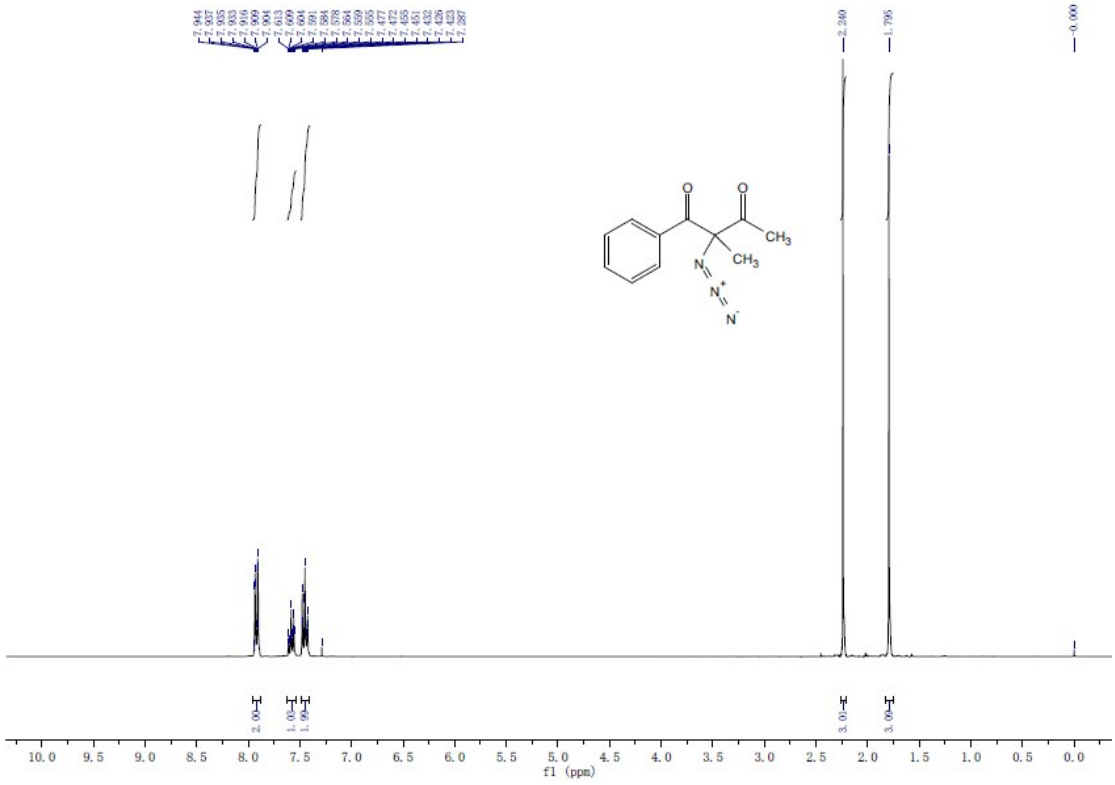

189.86
170.04
136.15
135.49
134.97
134.53
134.10
126.75
125.65
125.60
125.55
125.14
121.02
77.42
77.00
76.58
70.84
53.66
19.87
O
O
O
CH3
CH3
N
N+
N-
F
F
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

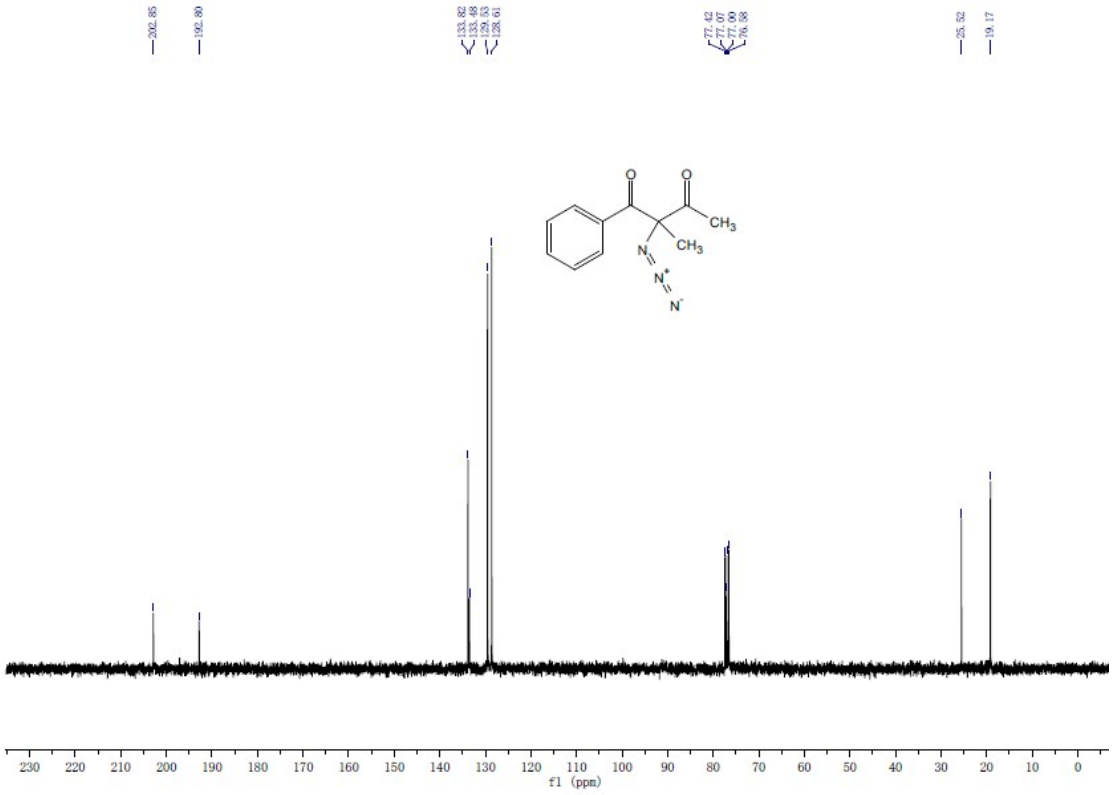
5p


lin-982-60
8.08
8.06
7.78
7.76
7.29
3.78
1.85
0.00
2.00
2.00
3.02
3.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

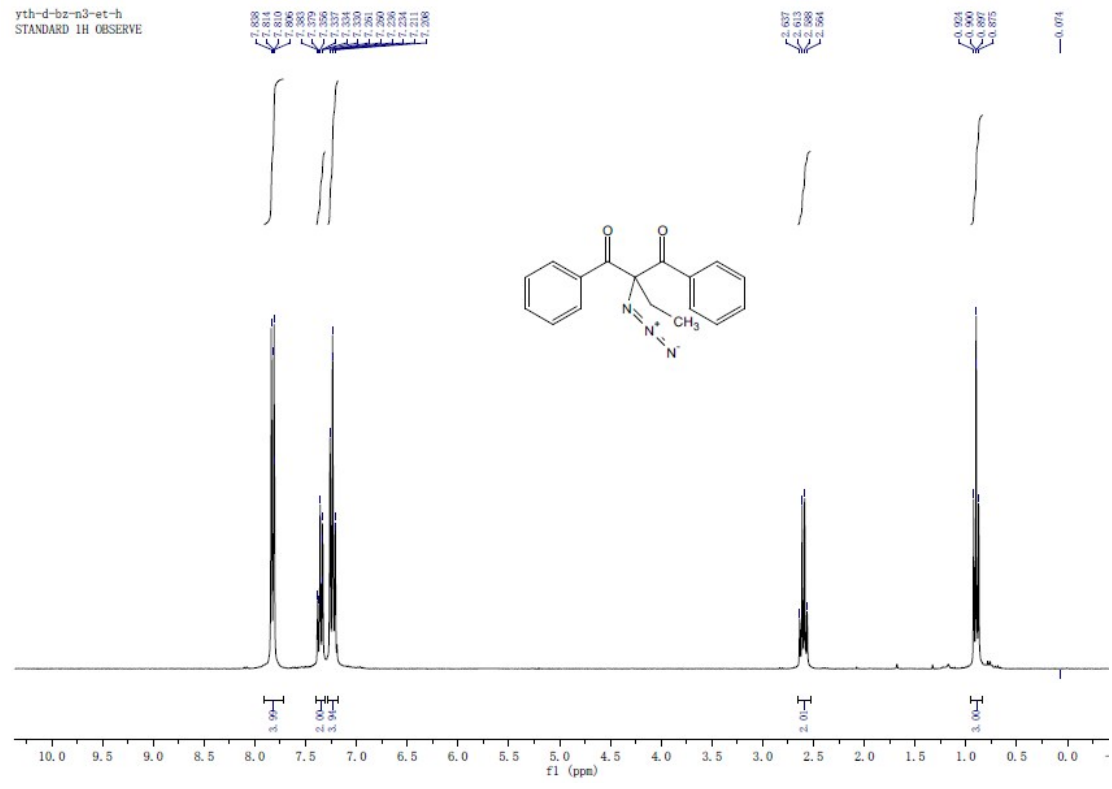

lin-982-60
189.59
169.84
136.60
132.31
129.75
117.59
116.79
77.32
77.00
76.68
70.79
53.67
19.75
f1 (ppm)

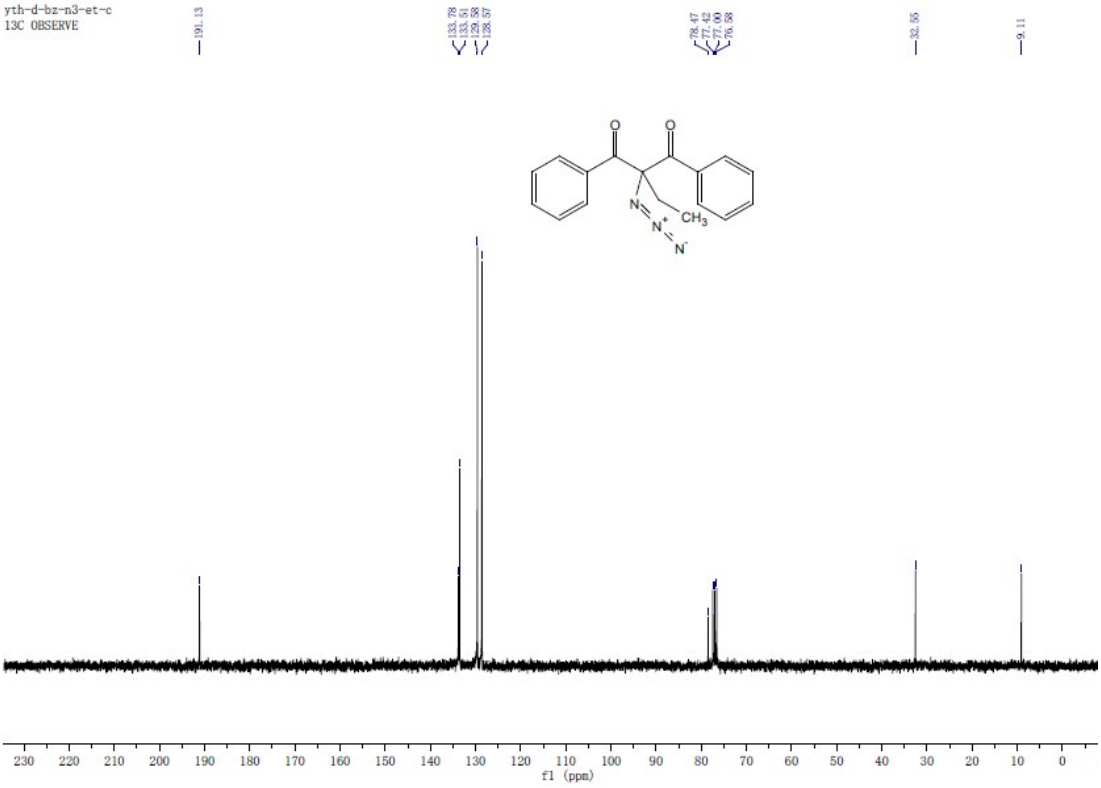
5r


2.240
1.795
0.000
f1 (ppm)

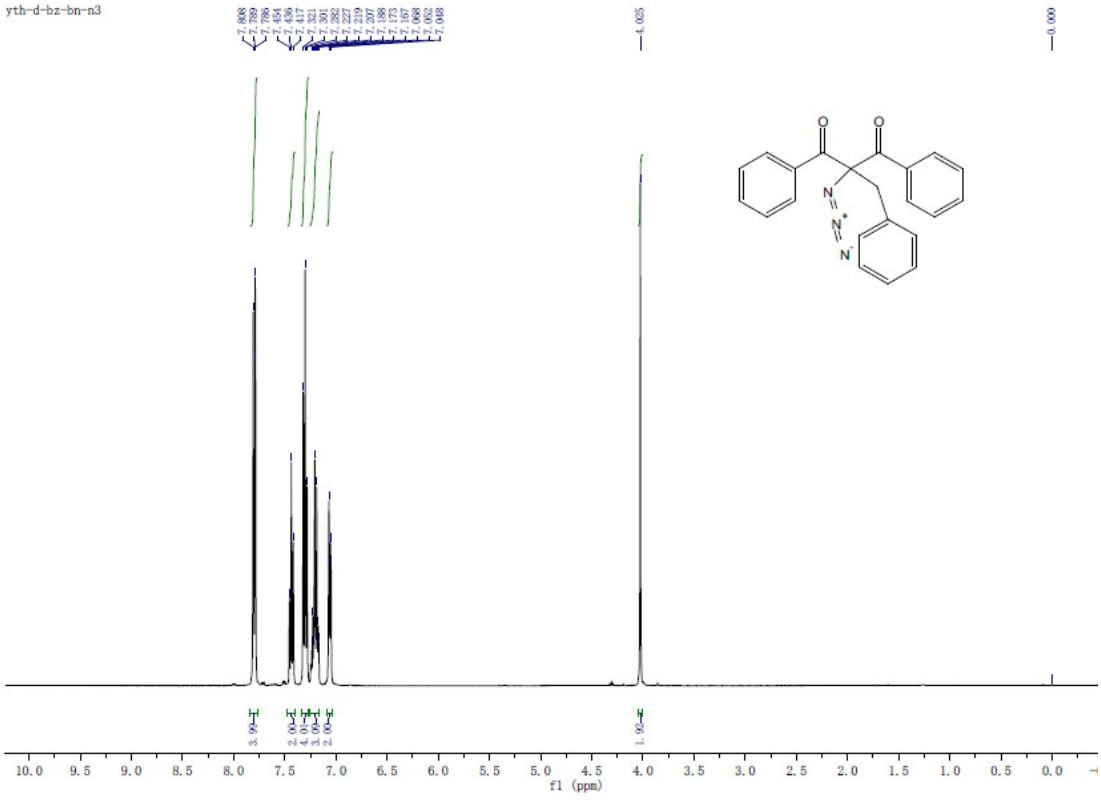

202.85
192.89
133.82
133.48
129.53
128.61
77.42
77.07
77.00
76.58
25.52
19.17
O
O
CH3
CH3
N
N+
N-
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

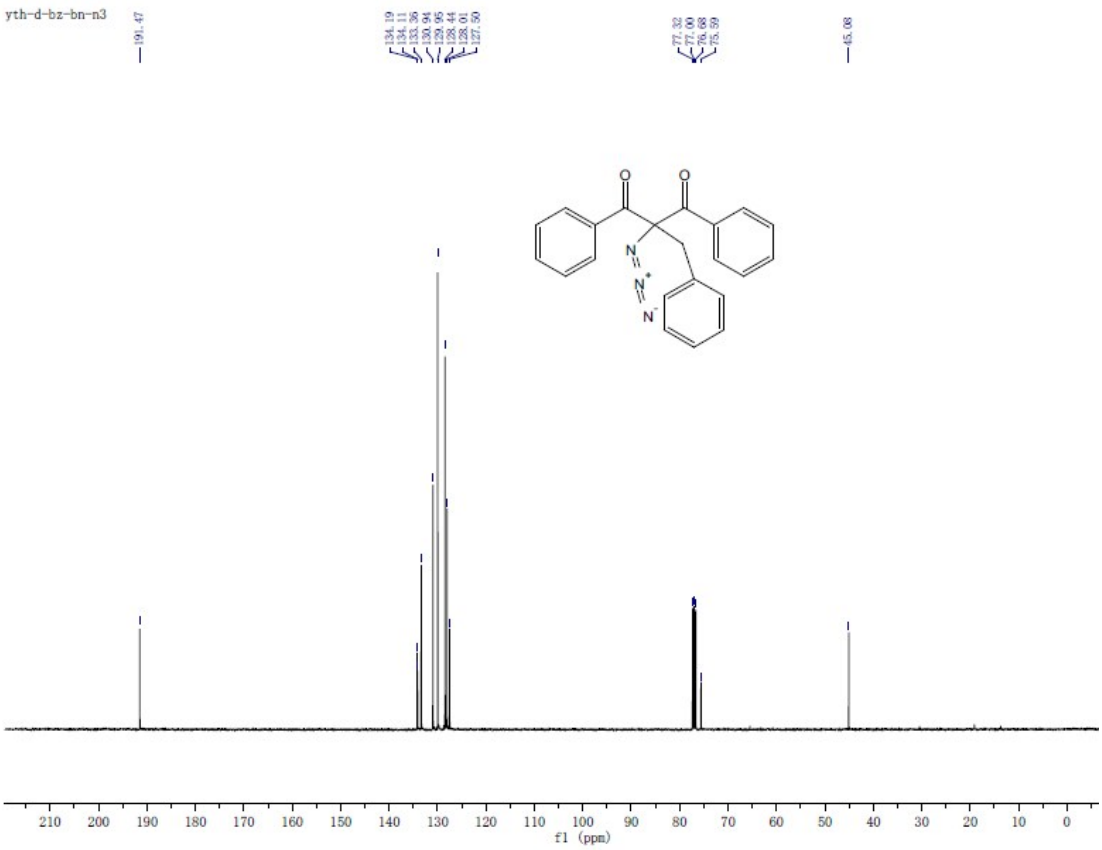
5s


yth-d-bz-n3-et-h
STANDARD 1H OBSERVE
7.838
7.814
7.810
7.806
7.383
7.379
7.356
7.337
7.334
7.330
7.291
7.289
7.236
7.234
7.211
7.208
2.637
2.613
2.588
2.564
0.924
0.900
0.897
0.875
0.074
O
O
CH3
N
N+
N-
3.00
2.00
3.94
2.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

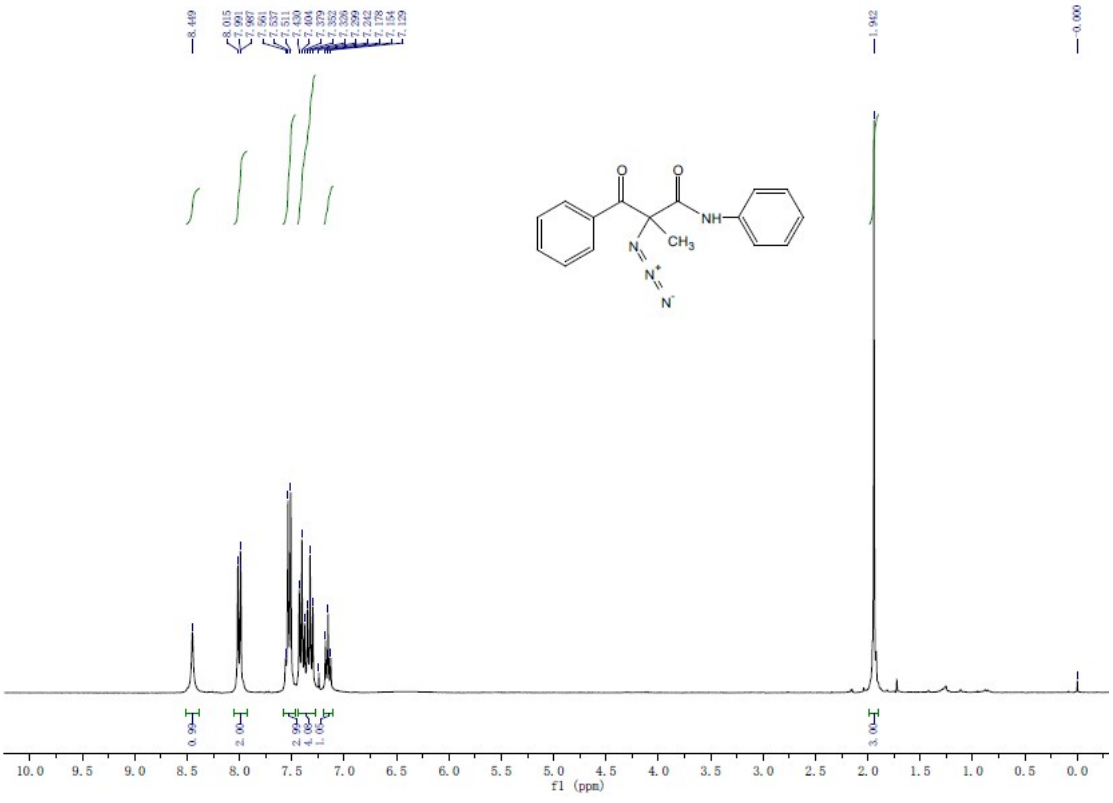

yth-d-bz-n3-et-c
13C OBSERVE
191.13
133.78
133.53
129.58
128.57
78.47
77.42
77.00
76.58
32.55
9.11
f1 (ppm)

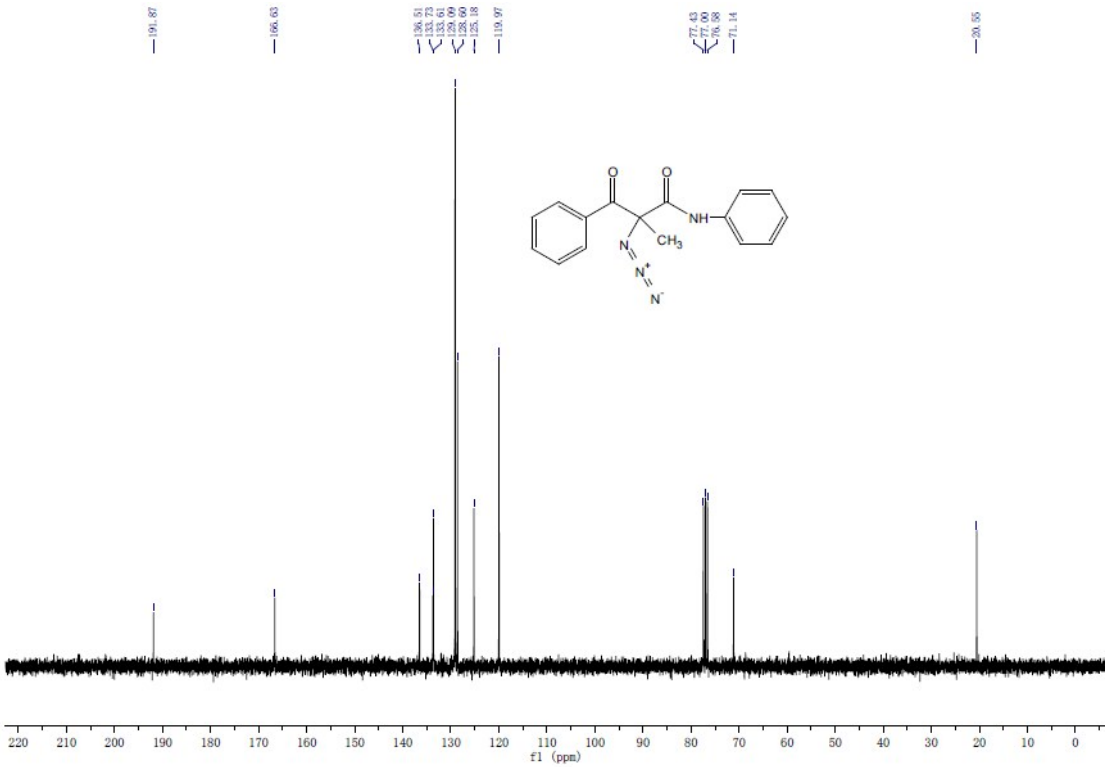
5t


yth-d-bz-bn-n3
7.808
7.789
7.788
7.454
7.436
7.417
7.321
7.301
7.282
7.227
7.219
7.207
7.198
7.173
7.167
7.068
7.052
7.048
4.035
0.000
3.99
2.04
4.01
3.09
2.04
1.92
f1 (ppm)

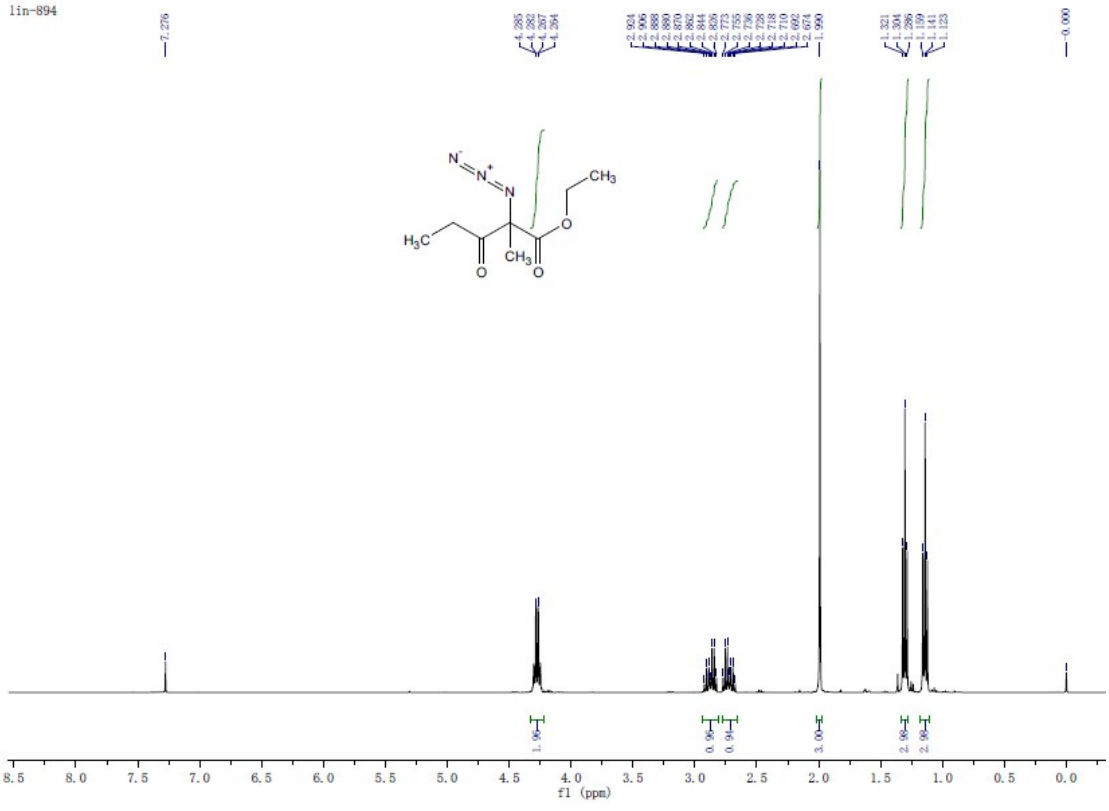

yth-d-bz-bn-n3
191.47
134.19
134.11
133.36
130.94
129.95
128.44
128.01
127.50
77.32
77.00
76.68
75.59
65.08
O
O
N
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

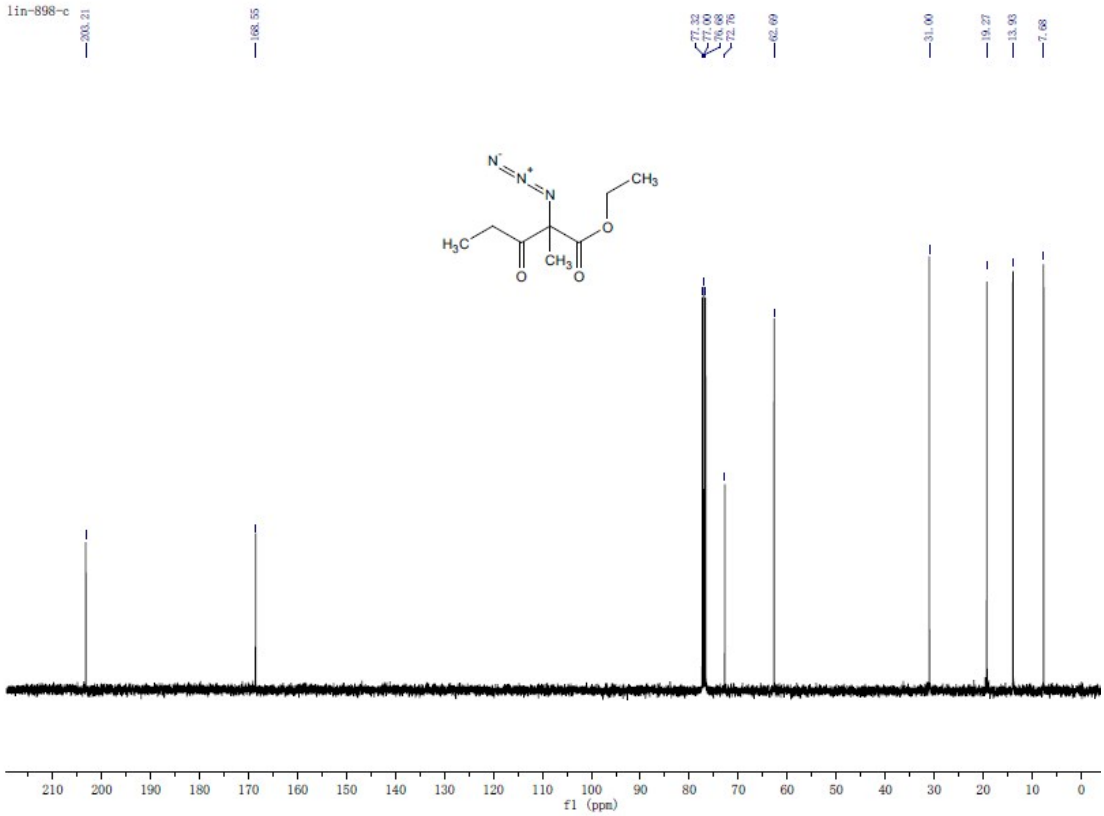
5u


8.449
8.015
7.997
7.981
7.965
7.961
7.537
7.511
7.430
7.394
7.379
7.353
7.326
7.299
7.242
7.178
7.134
7.129
1.942
0.000
O
O
NH
CH3
N
N
N
0.99
2.00
2.99
4.04
1.05
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

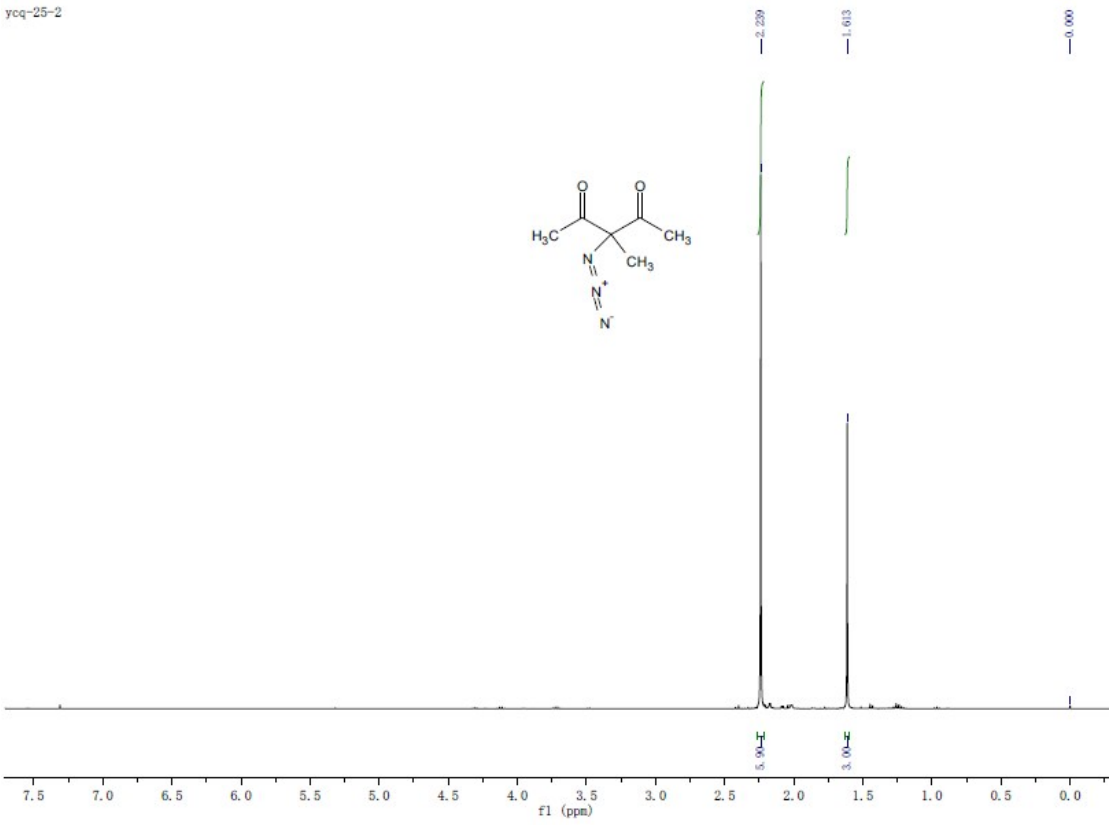

191.87
166.63
136.51
133.73
133.61
129.09
128.60
125.18
119.97
77.43
77.00
76.88
71.14
20.55
O
O
NH
CH3
N
N+
N-
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

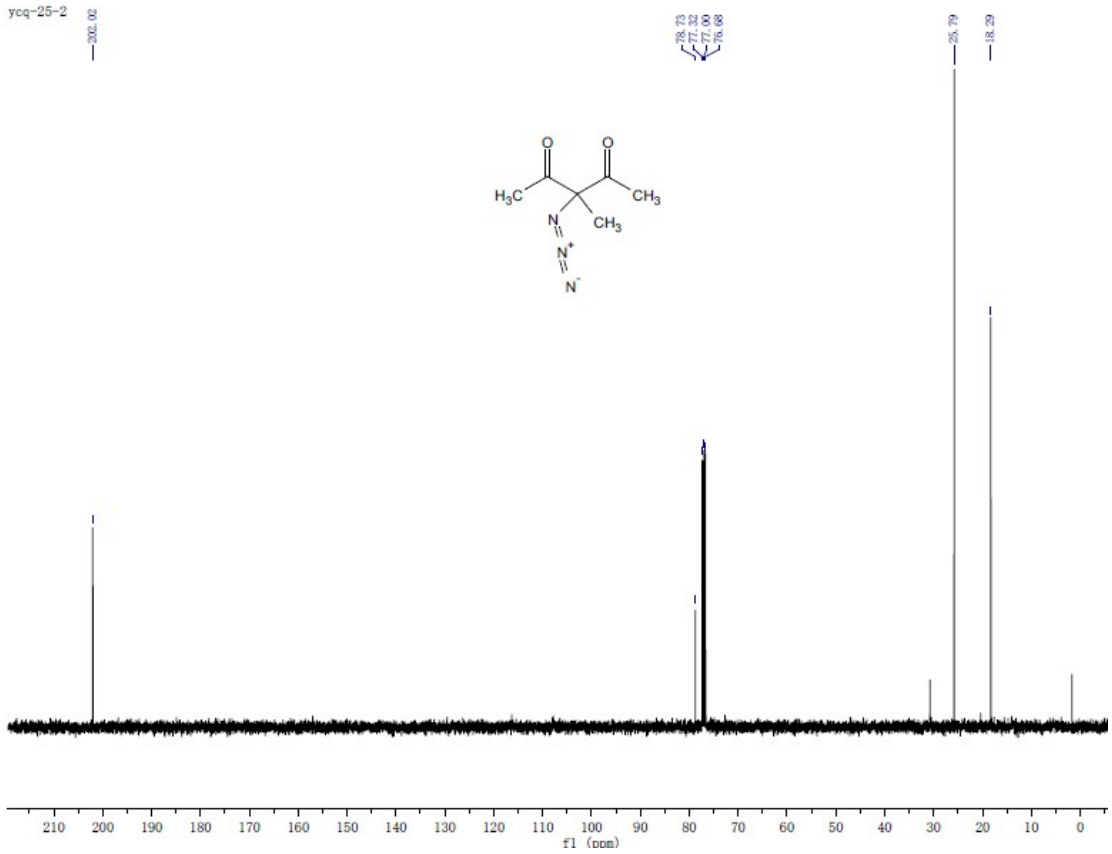
5v


lin-894
7.276
4.285
4.282
4.267
4.264
2.924
2.906
2.888
2.870
2.862
2.844
2.825
2.773
2.755
2.736
2.728
2.718
2.710
2.692
2.674
1.990
1.321
1.304
1.286
1.159
1.141
1.123
0.000
N-
N+
N
CH3
H3C
CH3
O
O
O
1.96
0.96
0.94
3.00
2.96
2.96
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)

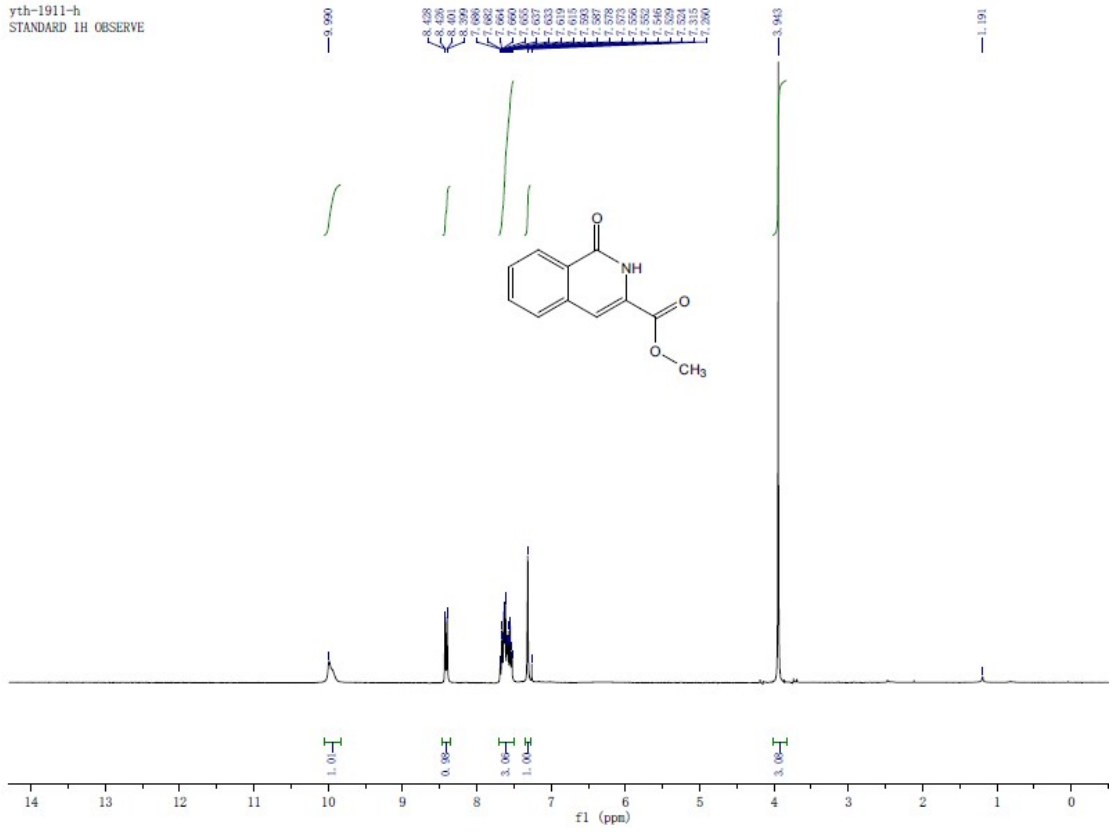

lin-898-c
203.21
168.55
77.32
77.00
76.68
72.76
62.69
31.00
19.27
13.93
7.68
f1 (ppm)

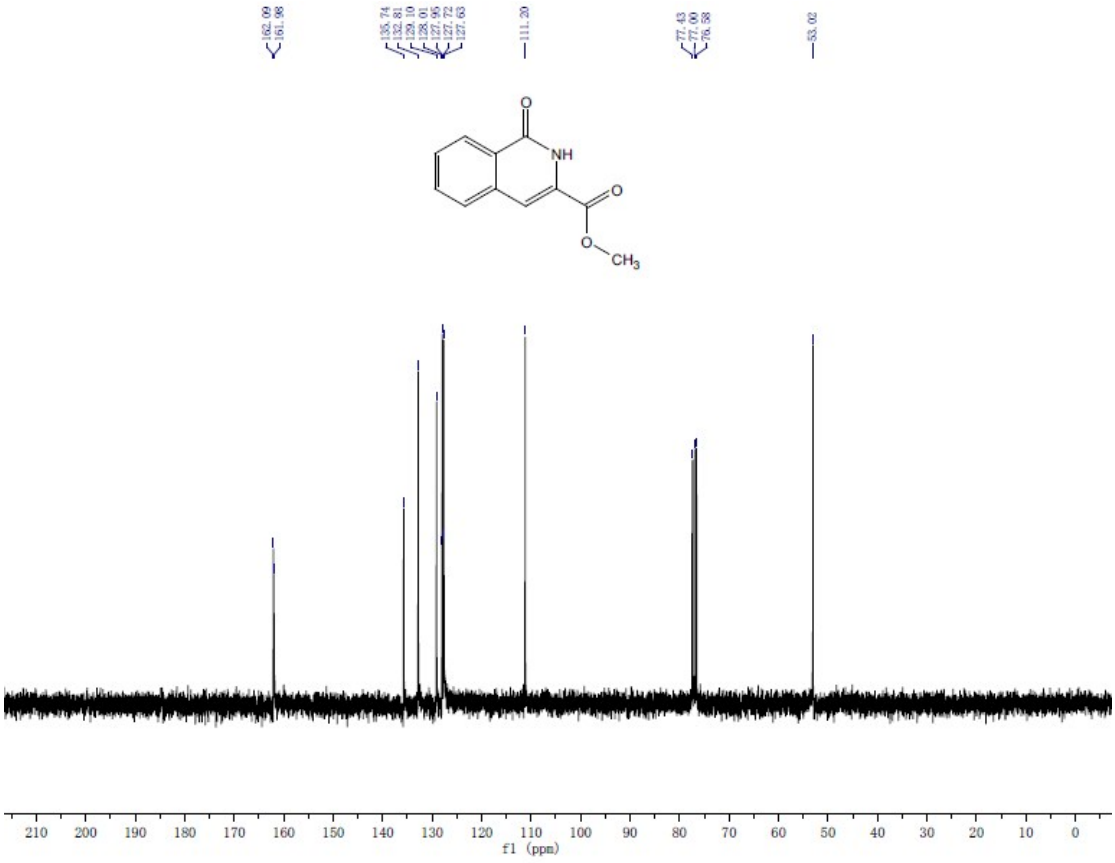
5w


ycq-25-2
2.239
1.613
0.000
5.90
3.00
f1 (ppm)

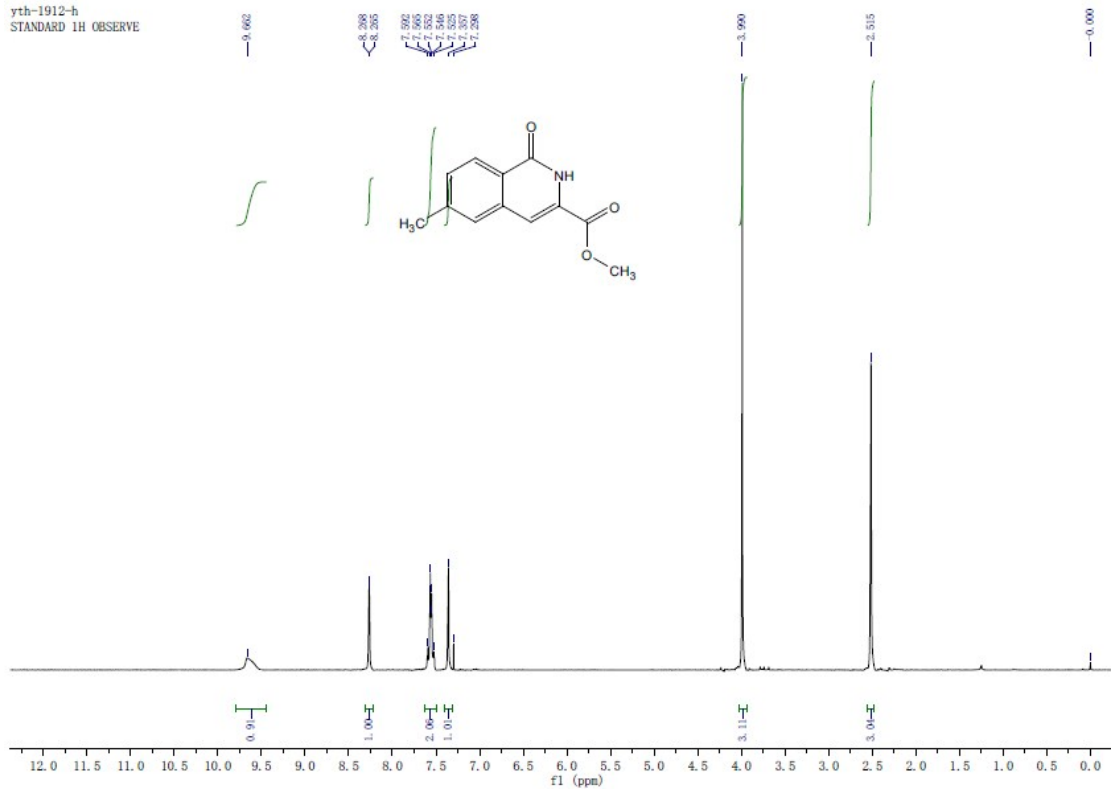

ycq-25-2
202.02
78.73
77.32
77.00
76.68
25.79
18.29
O
O
H3C
CH3
N
CH3
N+
N-
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

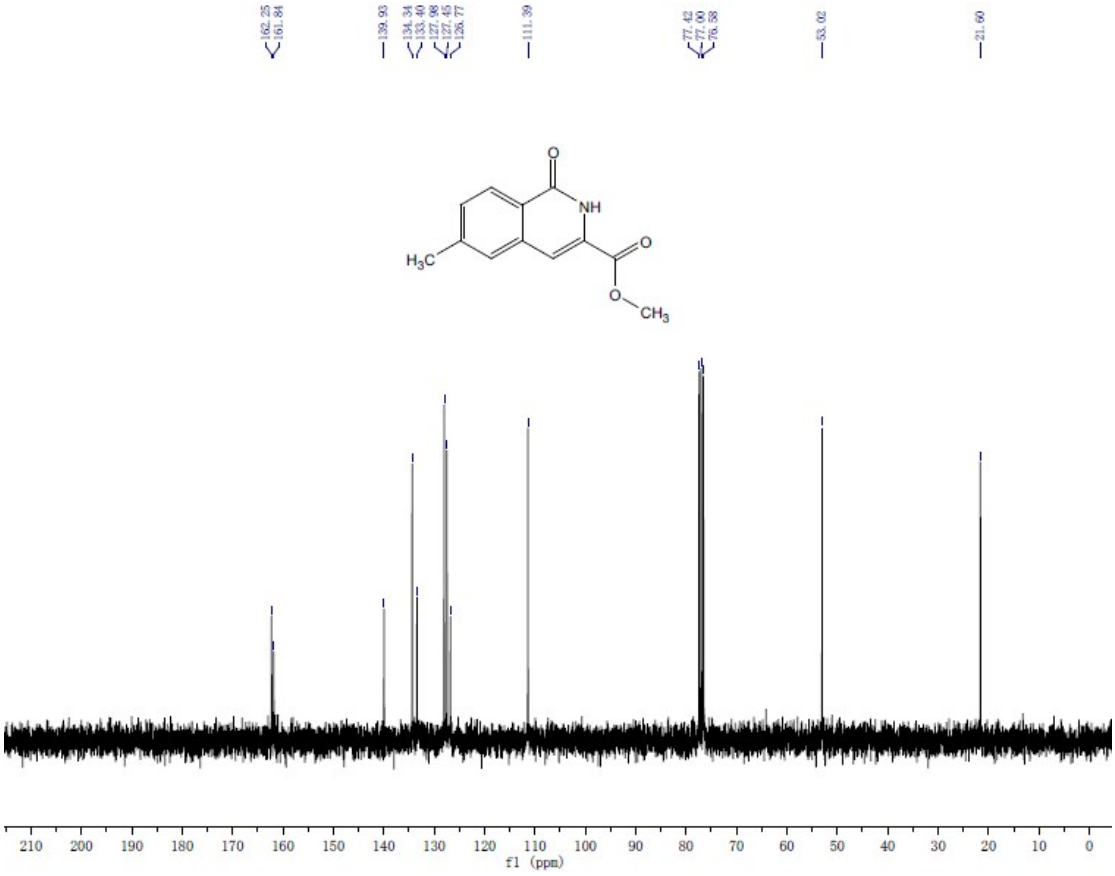
2a


yth-1911-h
STANDARD 1H OBSERVE
9.990
8.428
8.426
8.401
8.399
7.664
7.660
7.655
7.637
7.633
7.619
7.615
7.593
7.587
7.578
7.573
7.556
7.552
7.546
7.529
7.524
7.315
7.290
3.943
1.191
O
NH
O
O
CH3
1.01
0.89
3.06
1.00
3.08
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

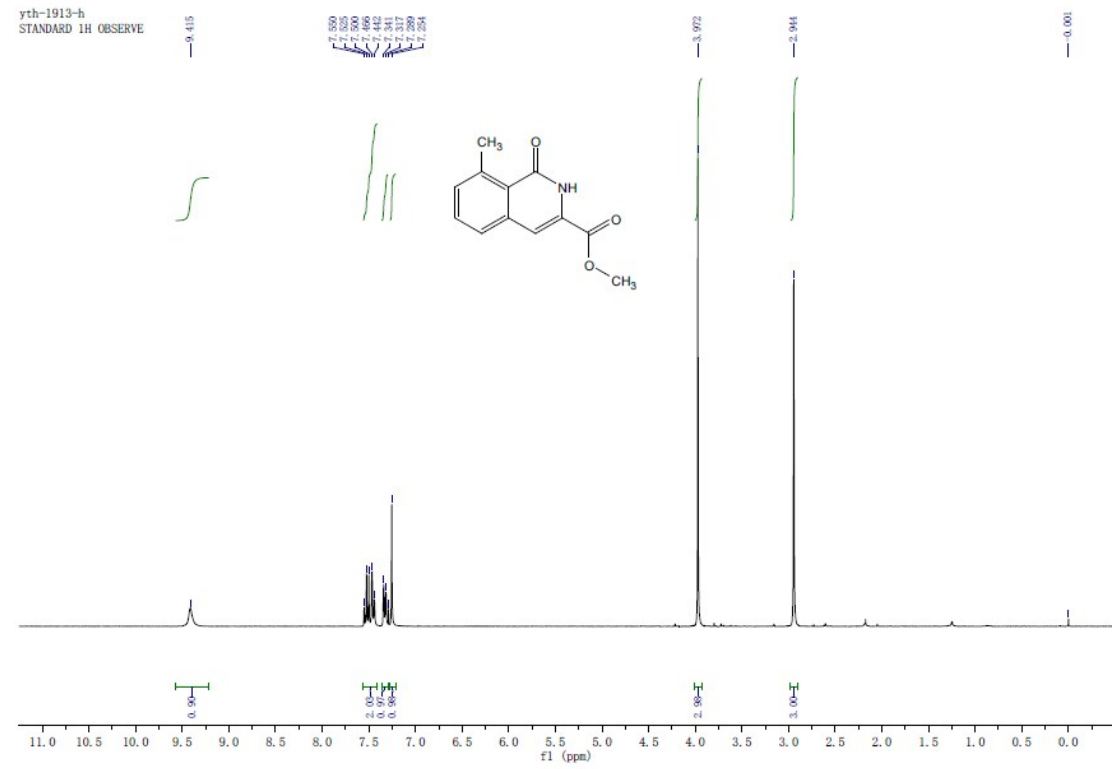

162.09
161.98
135.74
132.81
129.10
128.01
127.95
127.72
127.63
111.20
77.43
77.00
76.58
53.02
O
NH
O
O
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

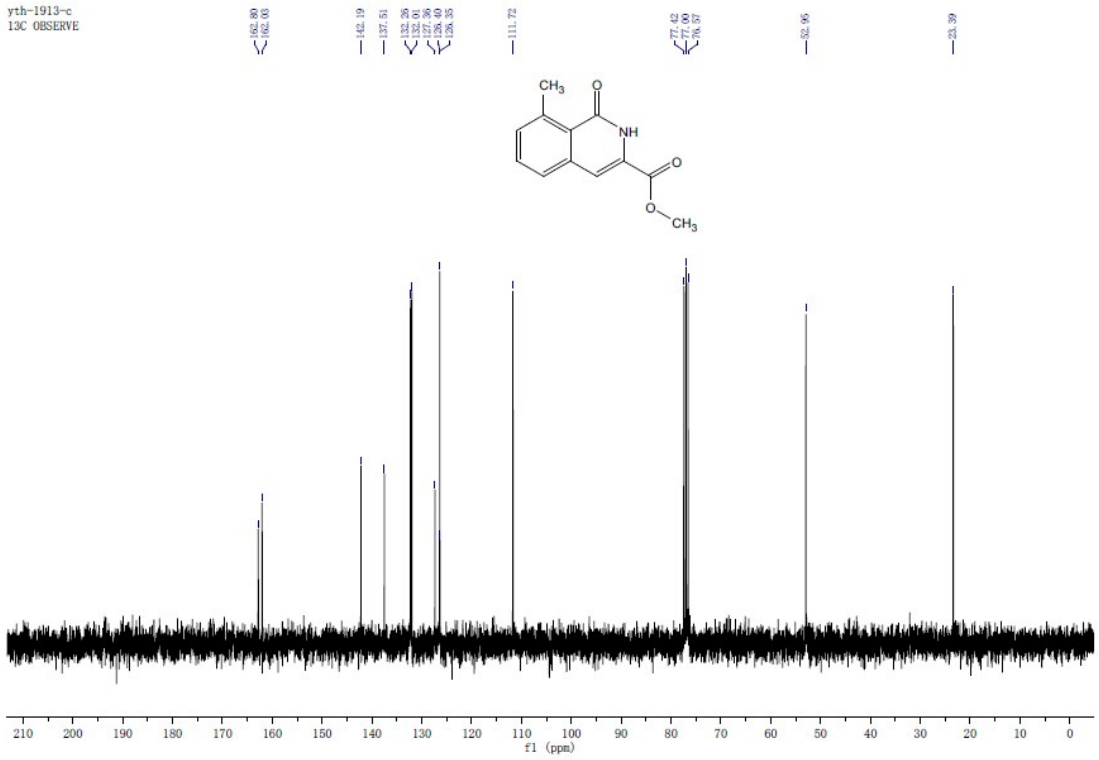
2b


yth-1912-h
STANDARD 1H OBSERVE
9.662
8.288
8.265
7.592
7.565
7.552
7.546
7.525
7.503
7.298
3.999
2.515
0.000
O
NH
H3C
O
O
CH3
0.91
1.00
2.06
1.01
3.11
3.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

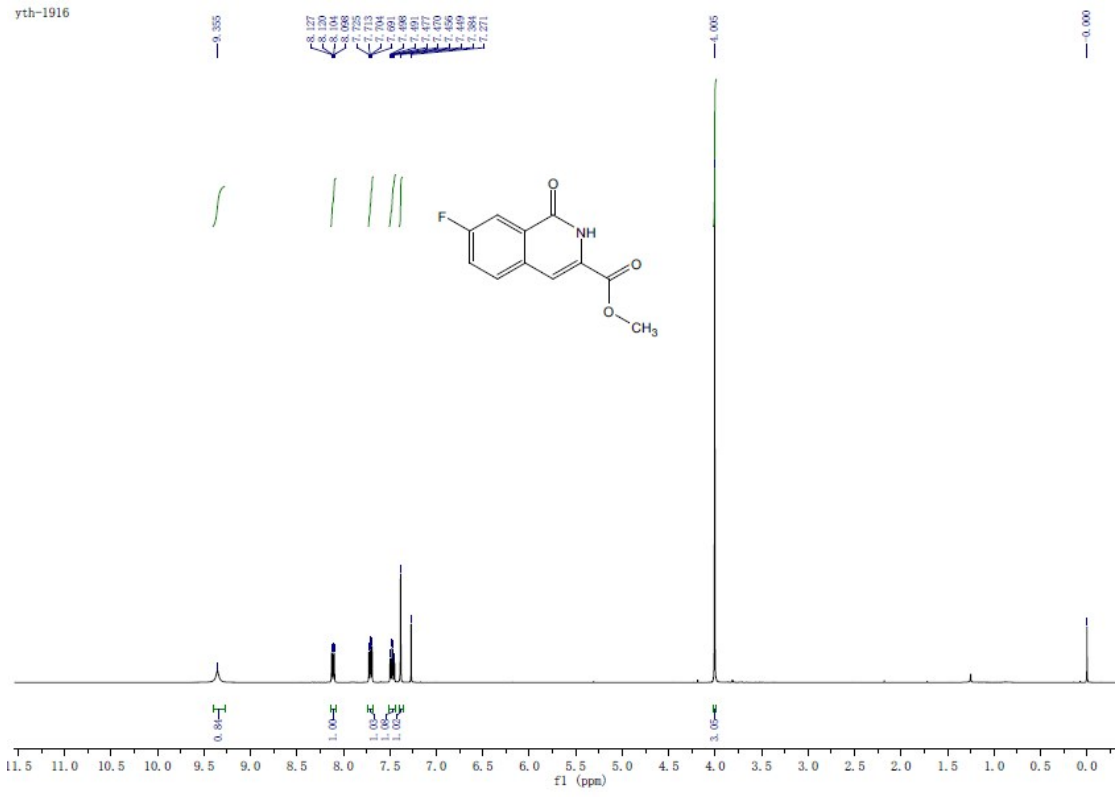

162.25
161.84
139.93
134.34
133.40
127.98
127.45
126.77
111.39
77.42
77.00
76.58
53.02
21.60
O
NH
O
H3C
O
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

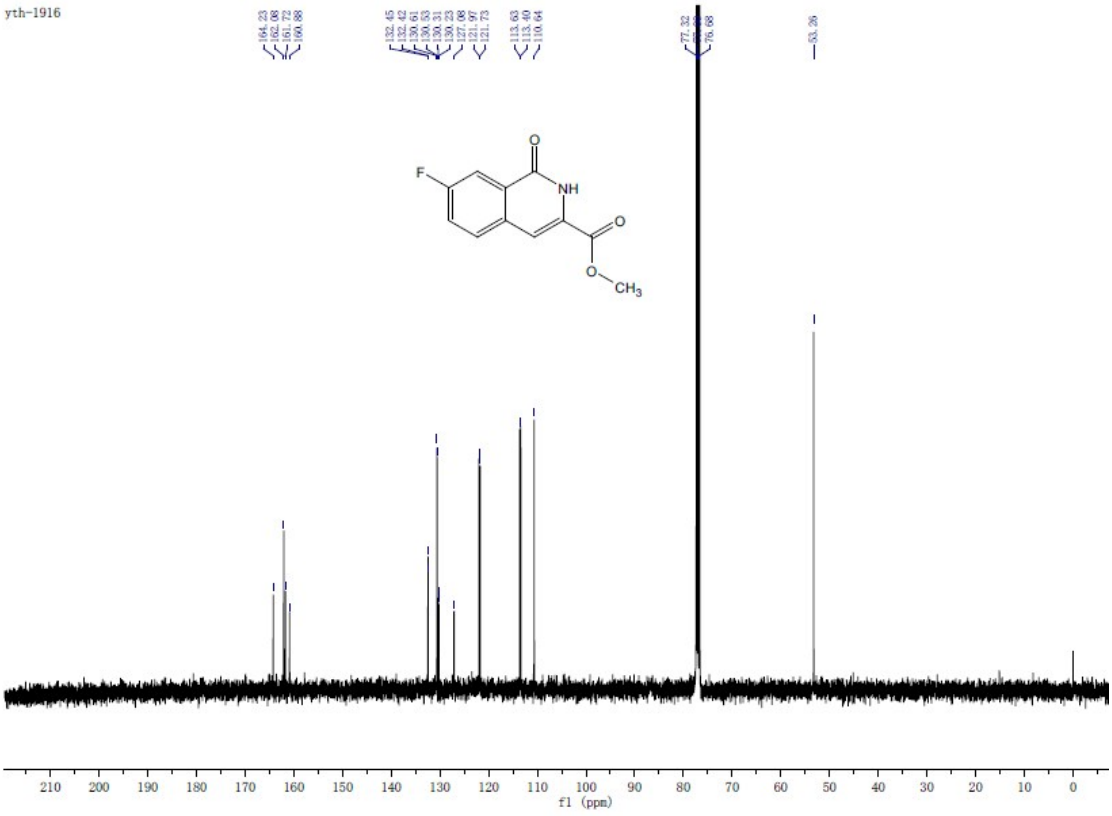
2c


yth-1913-h
STANDARD 1H OBSERVE
9.415
7.550
7.525
7.500
7.466
7.442
7.341
7.317
7.289
7.264
3.972
2.944
0.001
CH3
O
NH
O
O
CH3
0.90
2.00
0.97
0.88
2.88
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

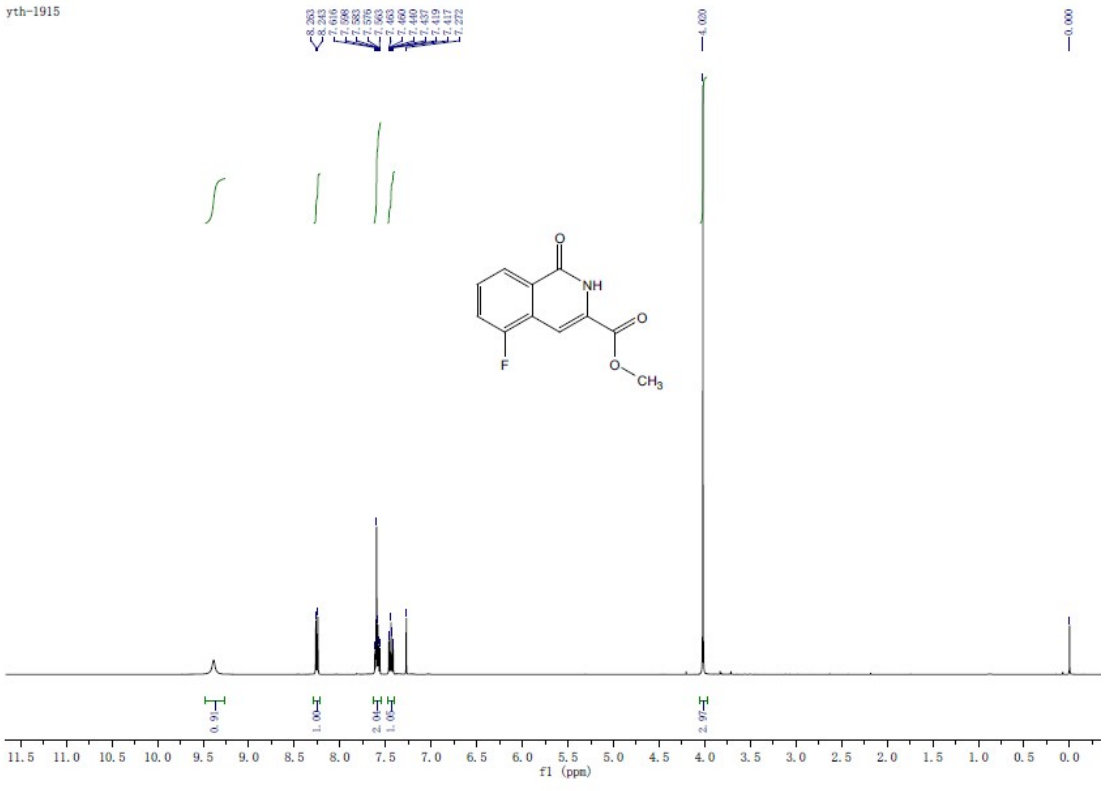

yth-1913-c
13C OBSERVE
162.89
162.03
142.19
137.51
132.26
132.01
127.36
126.69
126.35
111.72
77.42
77.00
76.57
52.95
23.39
CH3
O
NH
O
O
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

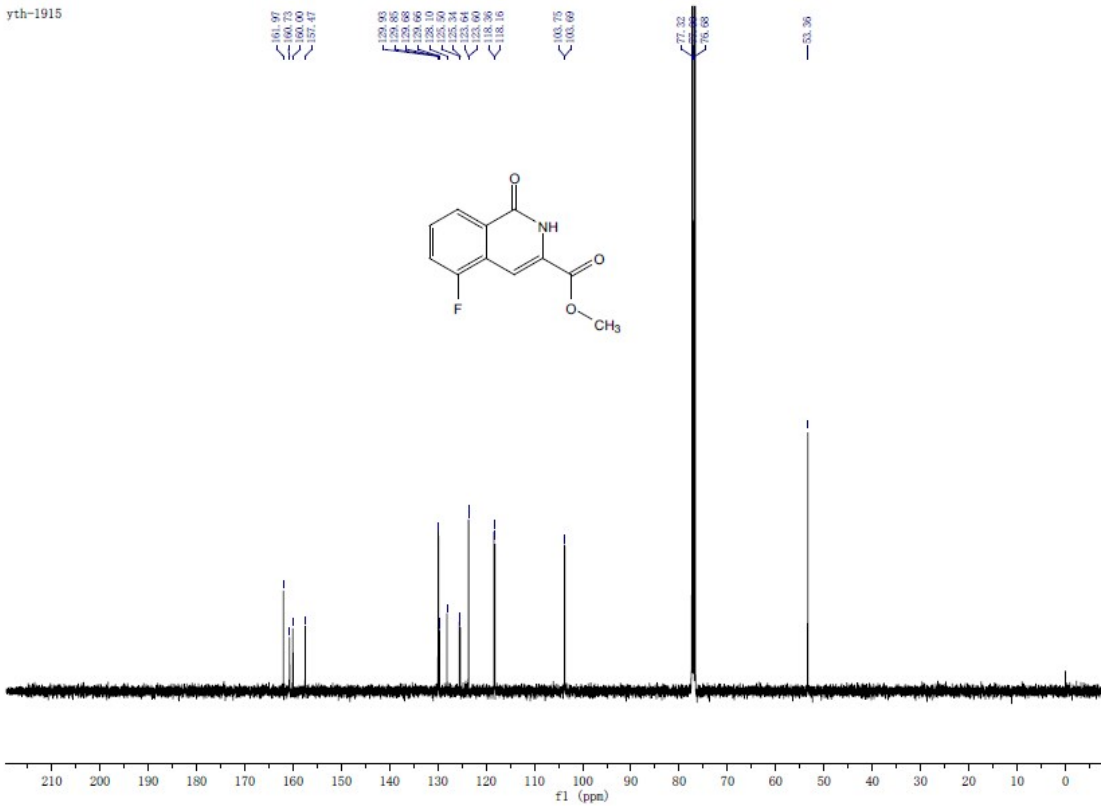
2d


yth-1916
9.355
8.127
8.120
8.104
8.098
7.725
7.713
7.704
7.691
7.498
7.491
7.477
7.470
7.456
7.449
7.384
7.271
4.005
0.000
F
O
NH
O
O
CH3
0.84
1.00
1.03
1.05
1.02
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

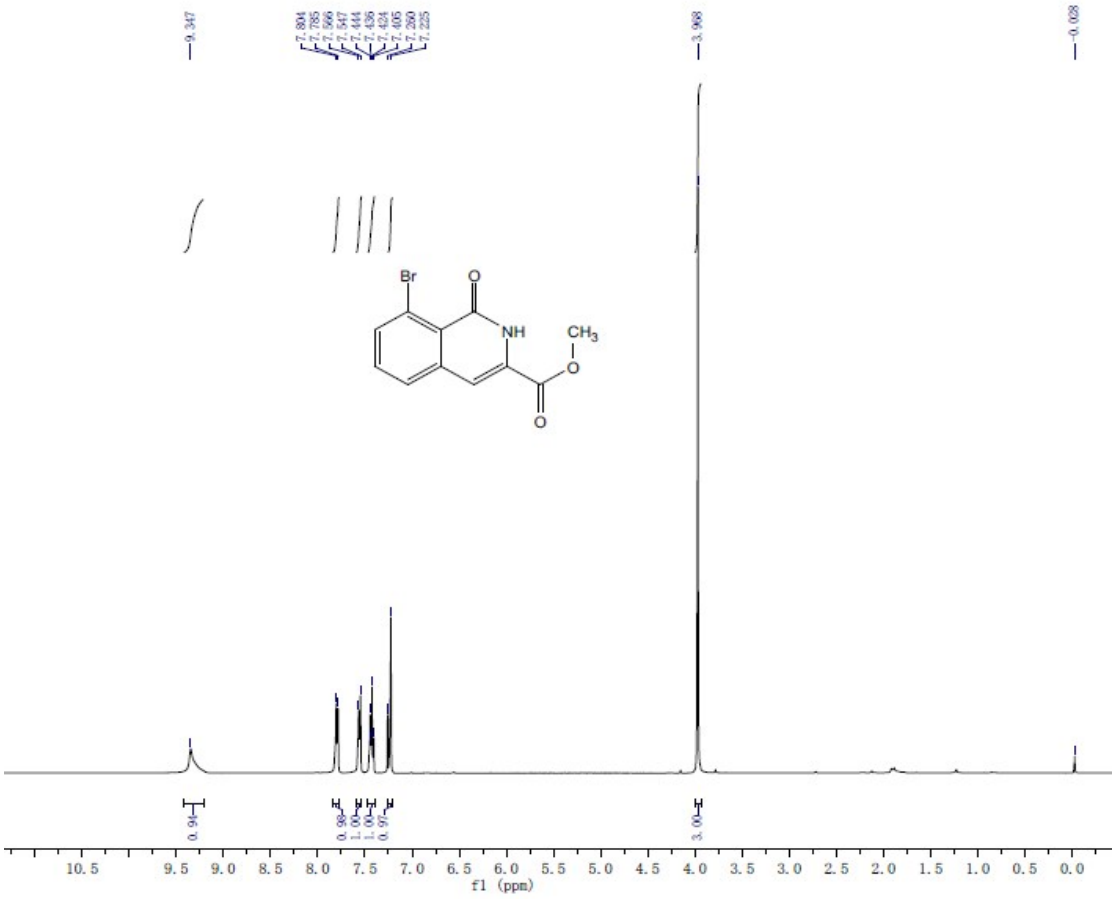

yth-1916
164.23
162.08
161.72
160.88
132.45
132.42
130.61
130.53
130.31
130.23
127.89
121.97
121.73
113.63
113.40
110.64
77.32
76.68
53.26
F
NH
O
O
O
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

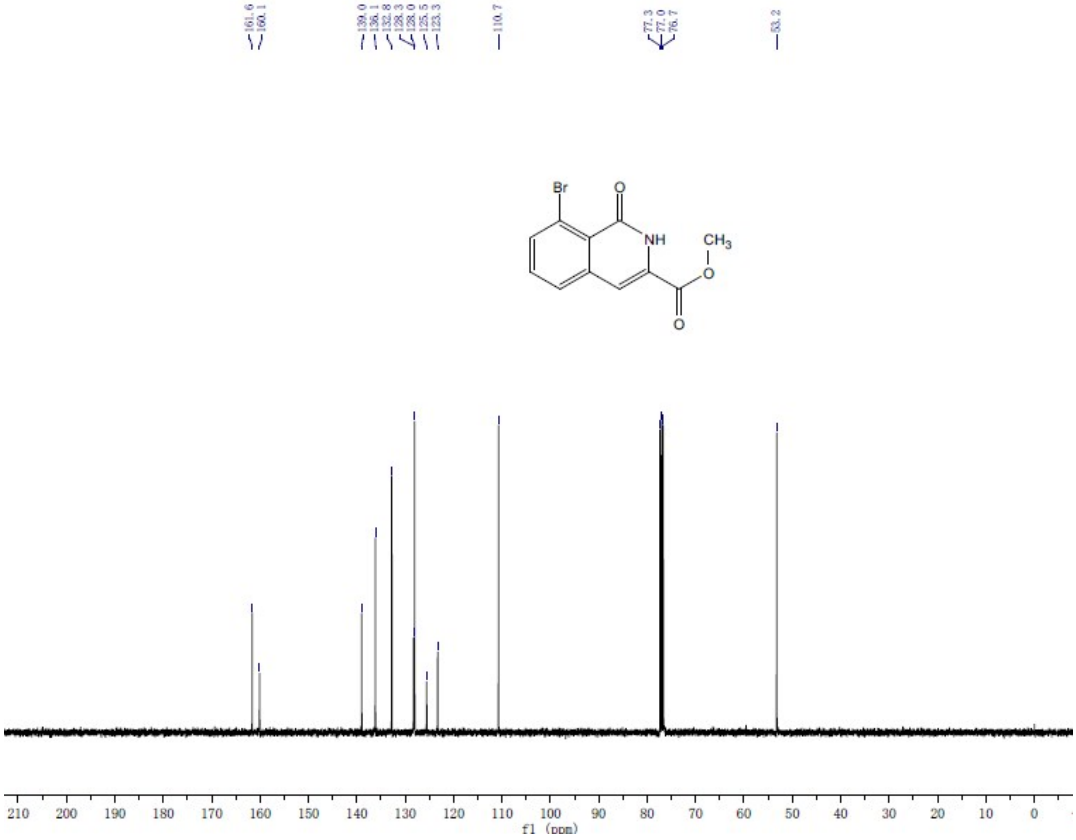
2e


yth-1915
8.263
8.243
7.616
7.598
7.583
7.575
7.563
7.460
7.440
7.437
7.419
7.417
7.272
4.009
3.000
F
NH
O
O
O
CH3
0.91
1.00
2.04
1.05
2.97
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

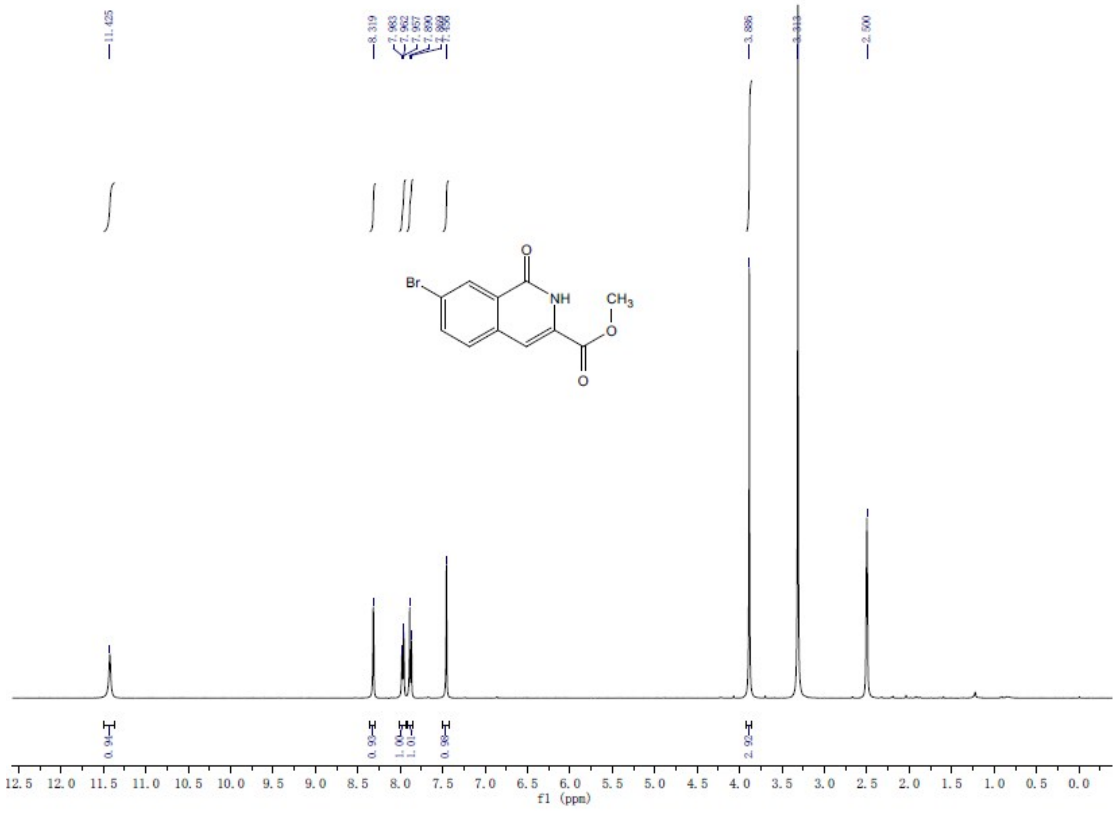

yth-1915
161.97
160.73
160.69
157.47
129.93
129.85
129.68
129.65
128.10
125.50
125.34
125.14
123.60
118.36
118.16
103.75
103.69
77.32
76.68
53.36
O
NH
O
F
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

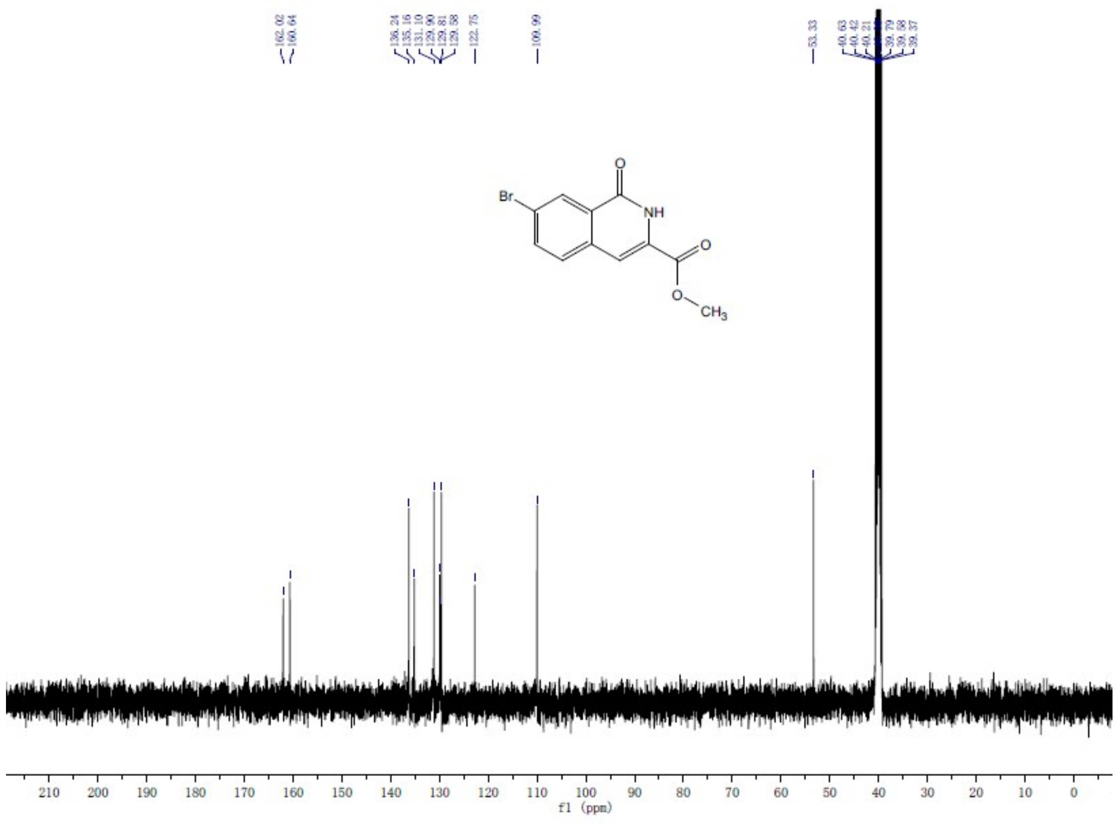
2f


9.347
7.804
7.785
7.566
7.547
7.444
7.436
7.424
7.405
7.269
7.225
3.968
-0.028
Br
O
NH
CH3
O
O
0.94
0.99
1.00
1.00
0.97
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

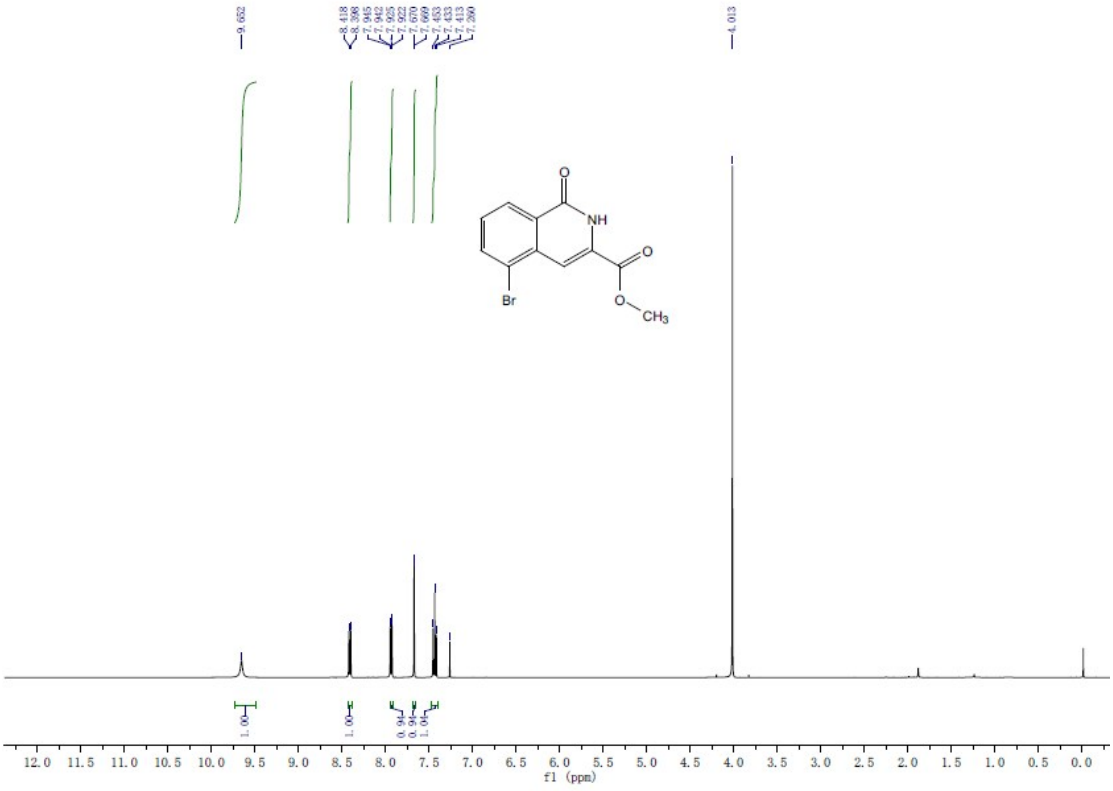

161.6
160.1
139.0
136.1
132.8
128.3
128.0
125.5
123.3
110.7
77.3
77.0
76.7
53.2
Br
O
NH
CH3
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

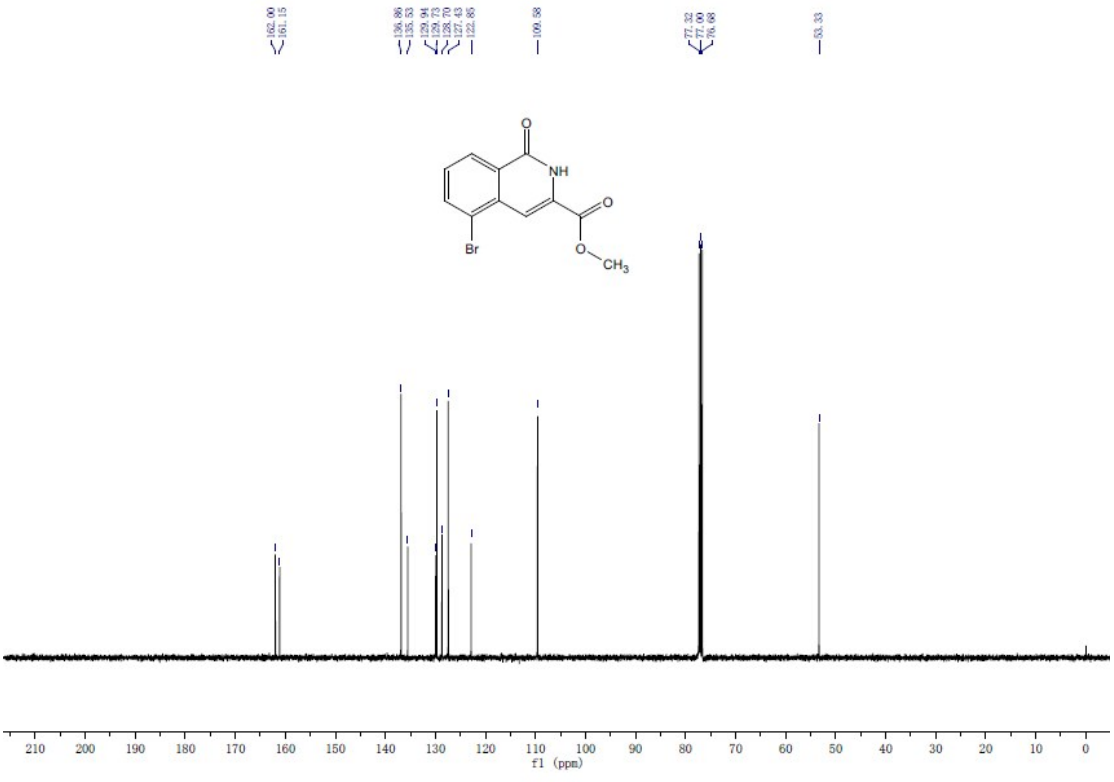
2g



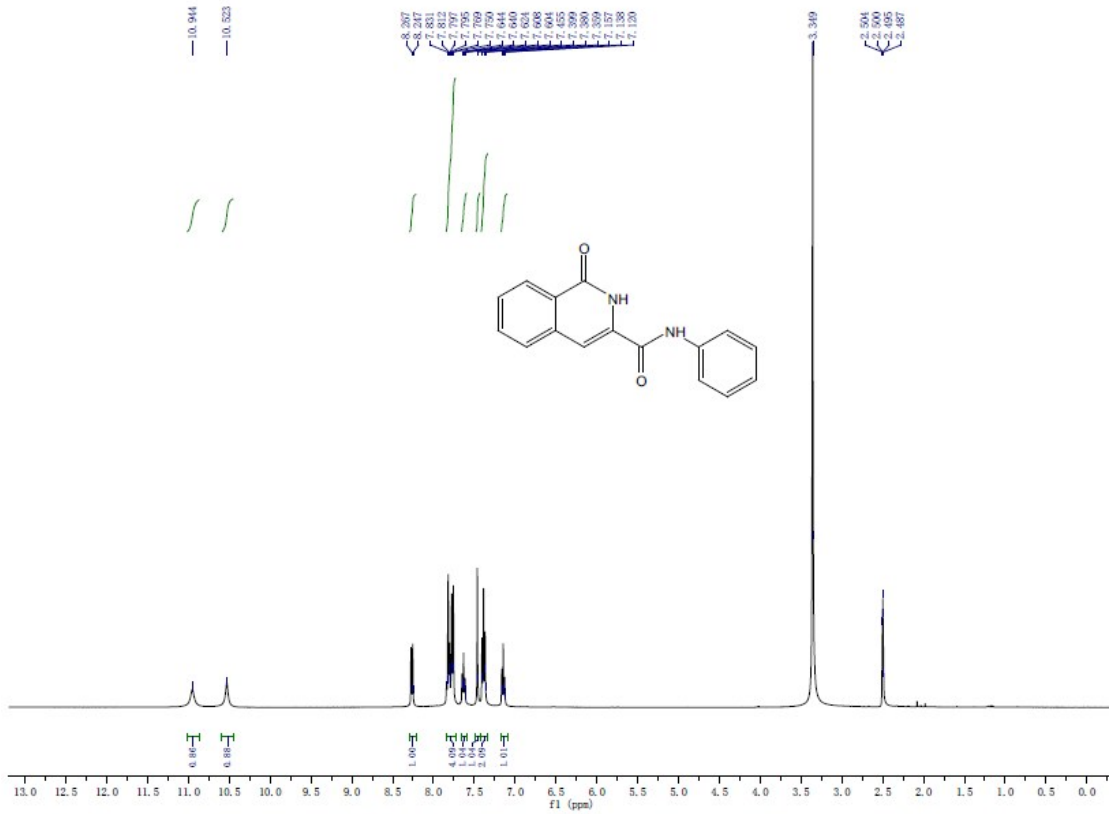


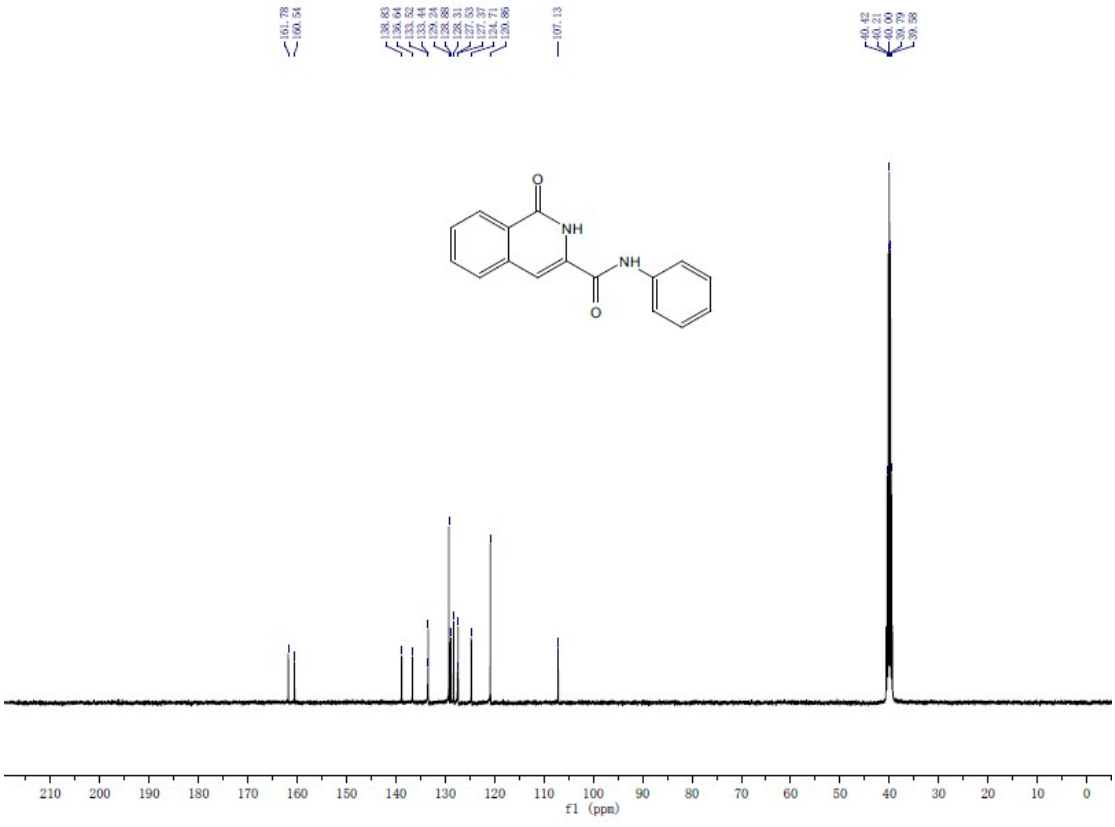
2h


9.652
8.418
8.398
7.945
7.942
7.935
7.922
7.670
7.669
7.653
7.433
7.413
7.390
4.013
O
NH
O
Br
O
CH3
1.00
1.03
0.94
0.95
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

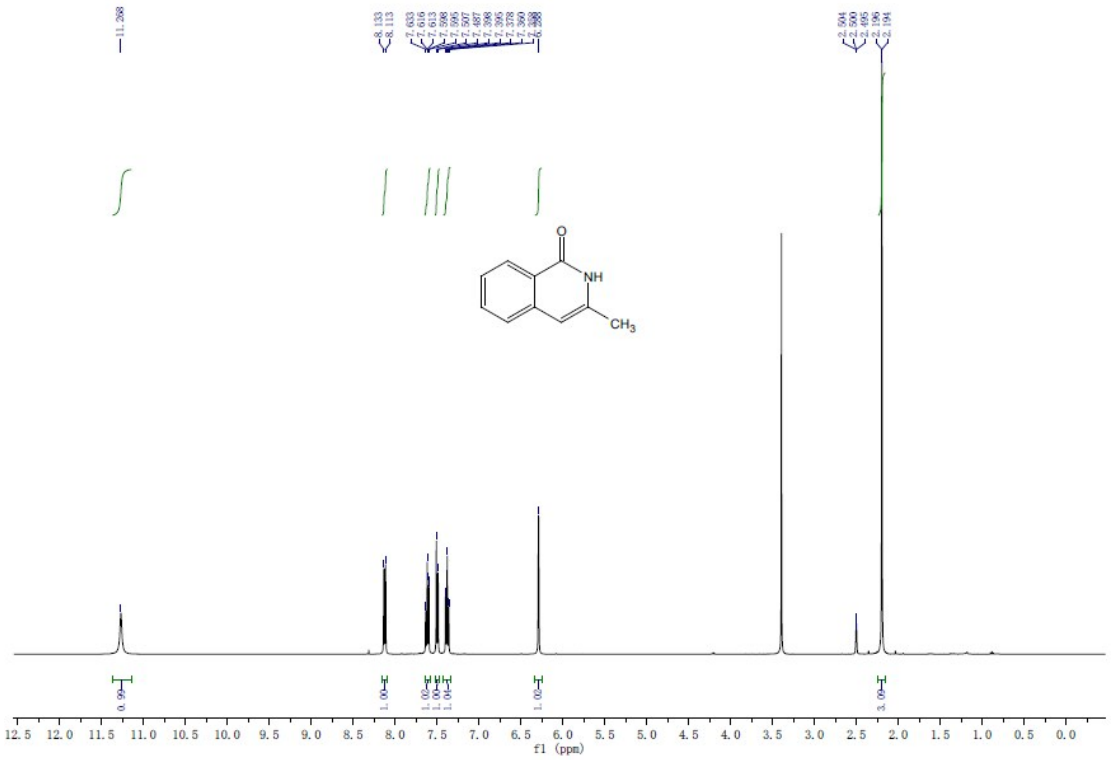

162.00
161.15
136.86
135.53
129.94
128.73
128.70
127.43
122.85
109.58
77.32
77.00
76.68
53.33
O
NH
O
Br
O
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

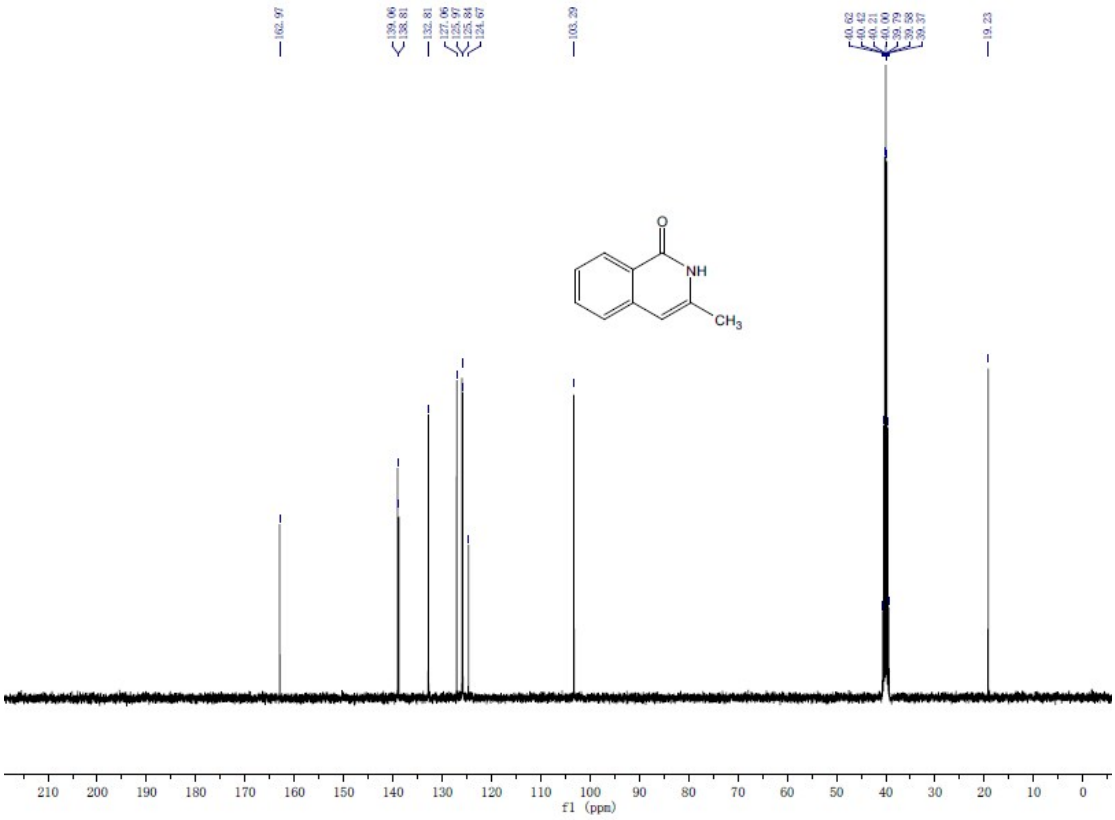
2i


10.944
10.523
8.267
8.247
7.831
7.812
7.797
7.795
7.769
7.759
7.644
7.640
7.624
7.608
7.604
7.455
7.389
7.380
7.339
7.157
7.138
7.129
3.349
2.504
2.500
2.495
2.487
O
NH
NH
O
f1 (ppm)

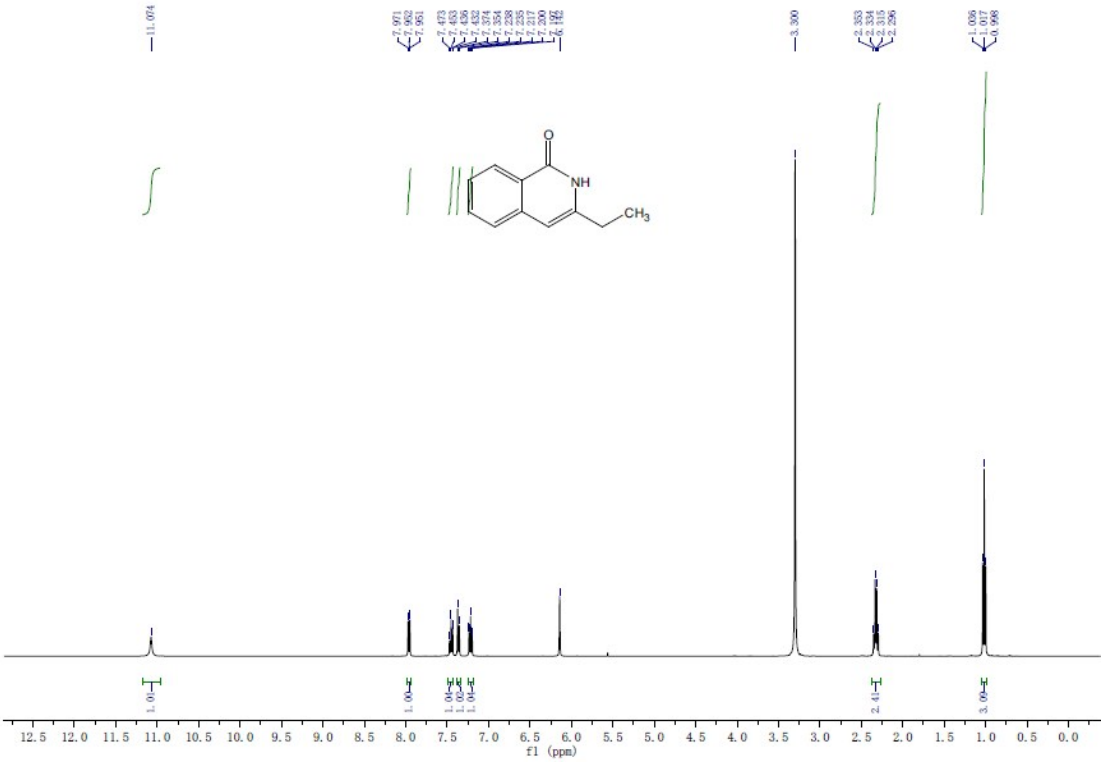

161.78
160.54
138.83
136.64
133.52
133.44
129.24
128.88
128.31
127.53
127.37
124.71
120.86
107.13
40.42
40.21
40.00
39.79
39.58
O
NH
NH
O
f1 (ppm)

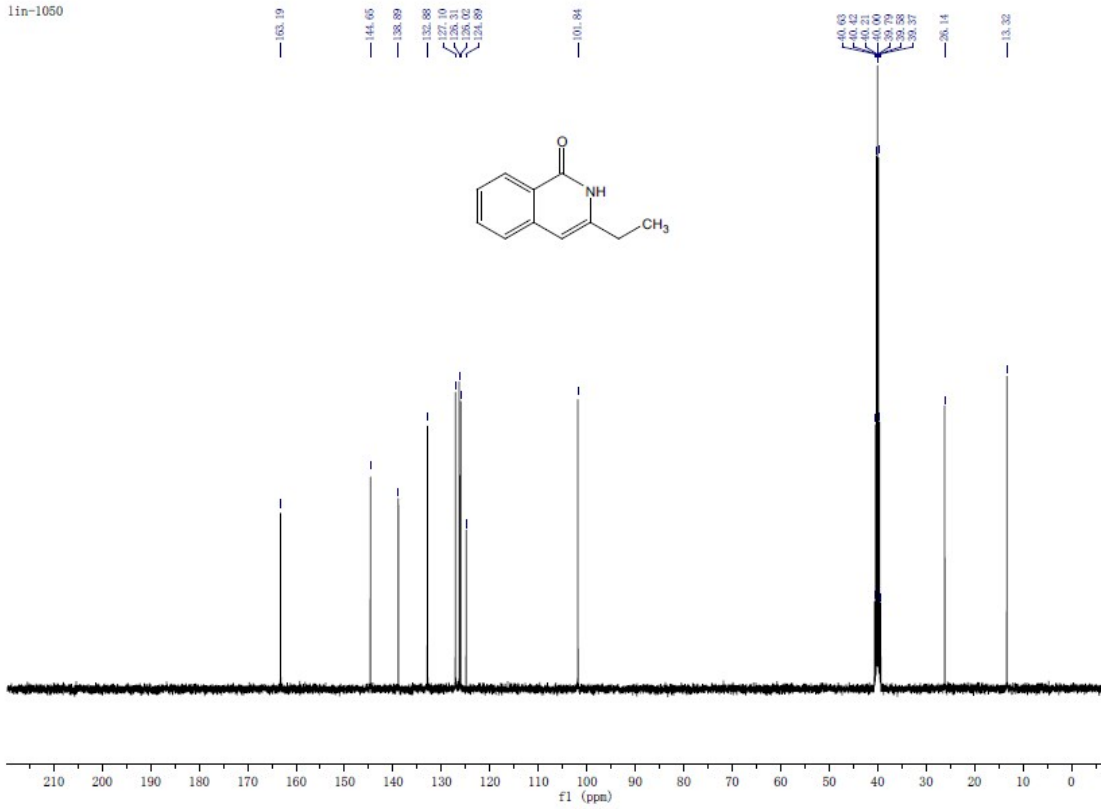
2j


11.268
8.133
8.113
7.633
7.615
7.613
7.598
7.595
7.397
7.397
7.398
7.395
7.378
7.360
7.358
6.588
2.504
2.500
2.495
2.196
2.194
O
NH
CH3
0.99
1.00
1.02
1.04
1.04
1.02
3.09
f1 (ppm)

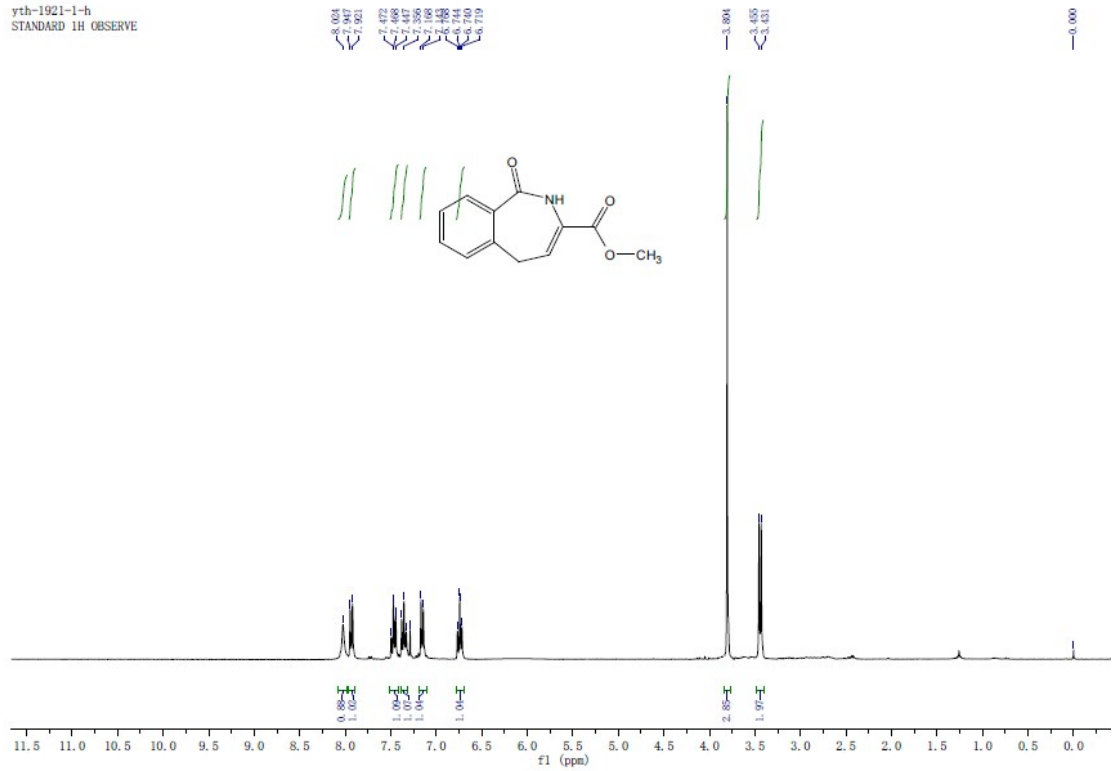

162.97
139.06
138.81
132.81
127.06
125.97
125.84
124.67
103.39
40.62
40.42
40.21
40.00
39.79
39.58
39.37
19.23
O
NH
CH3
f1 (ppm)

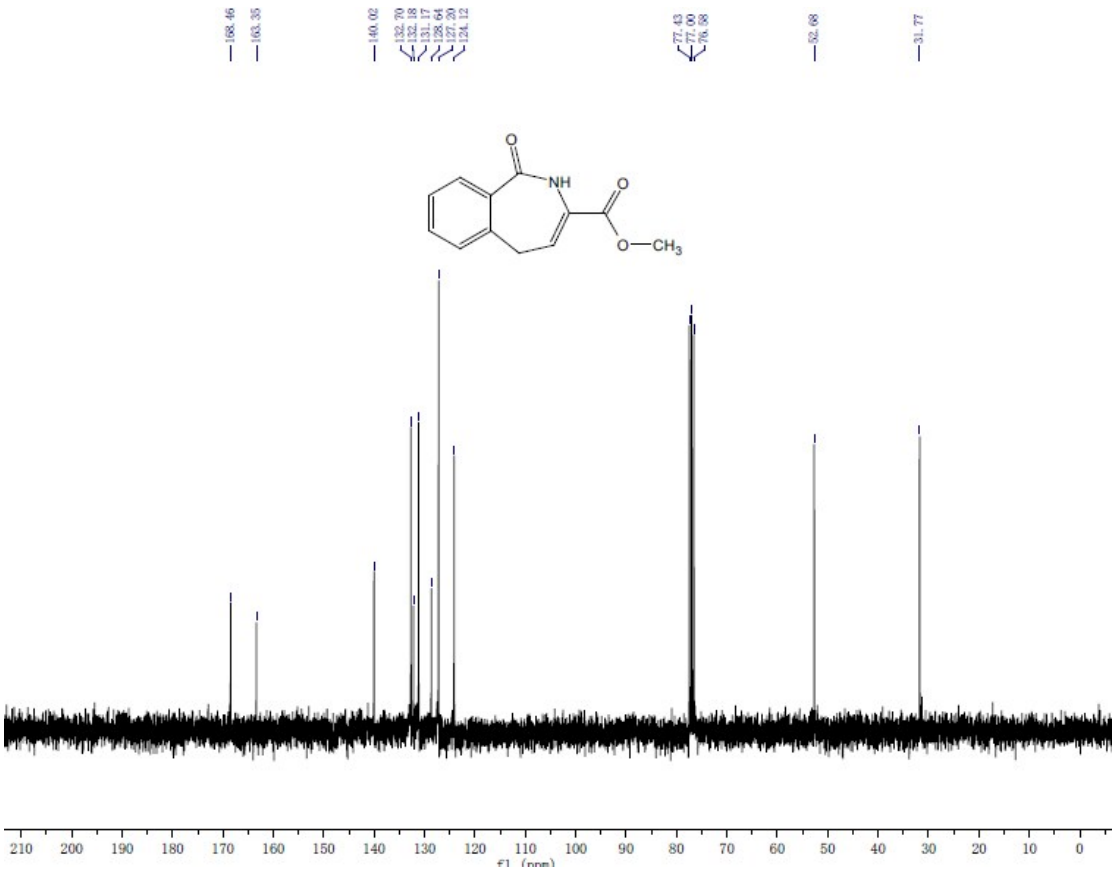
2k


11.074
7.971
7.962
7.951
7.473
7.465
7.436
7.432
7.374
7.354
7.238
7.217
7.200
6.182
3.300
2.353
2.334
2.315
2.296
1.006
1.017
0.998
O
NH
CH3
1.00
1.00
1.00
1.02
1.04
2.41
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

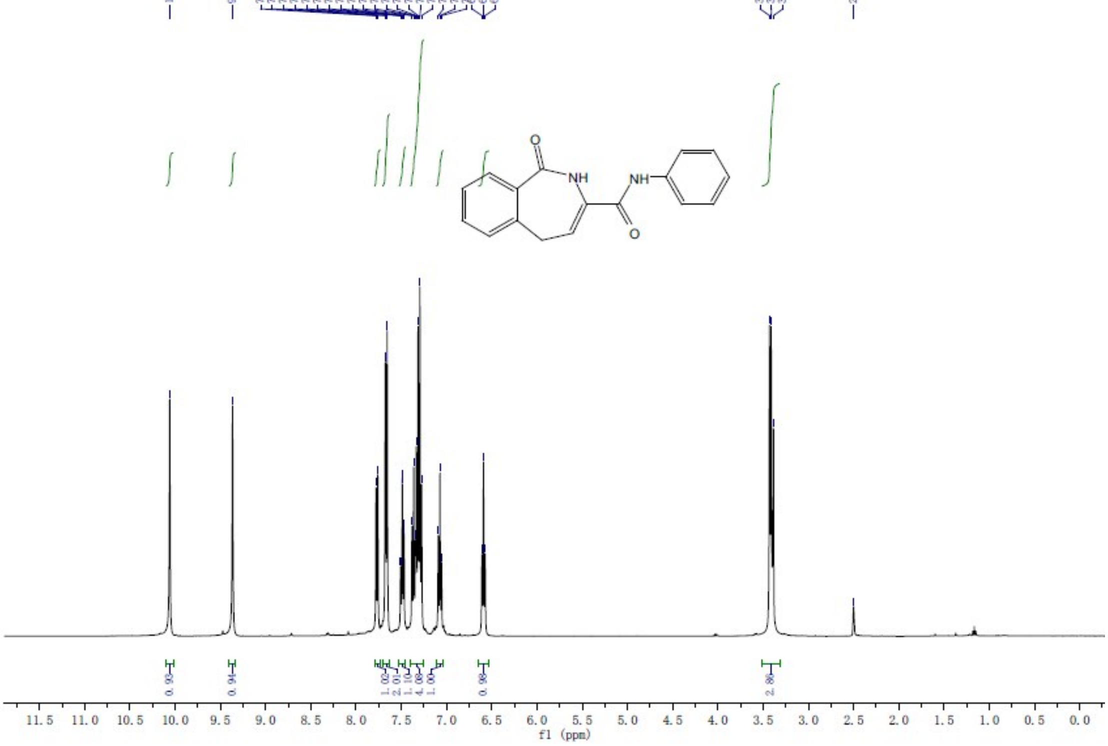

lin-1050
163.19
144.65
138.89
132.88
127.10
126.31
126.02
124.89
101.84
40.63
40.42
40.21
40.00
39.79
39.58
39.37
26.14
13.32
O
NH
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

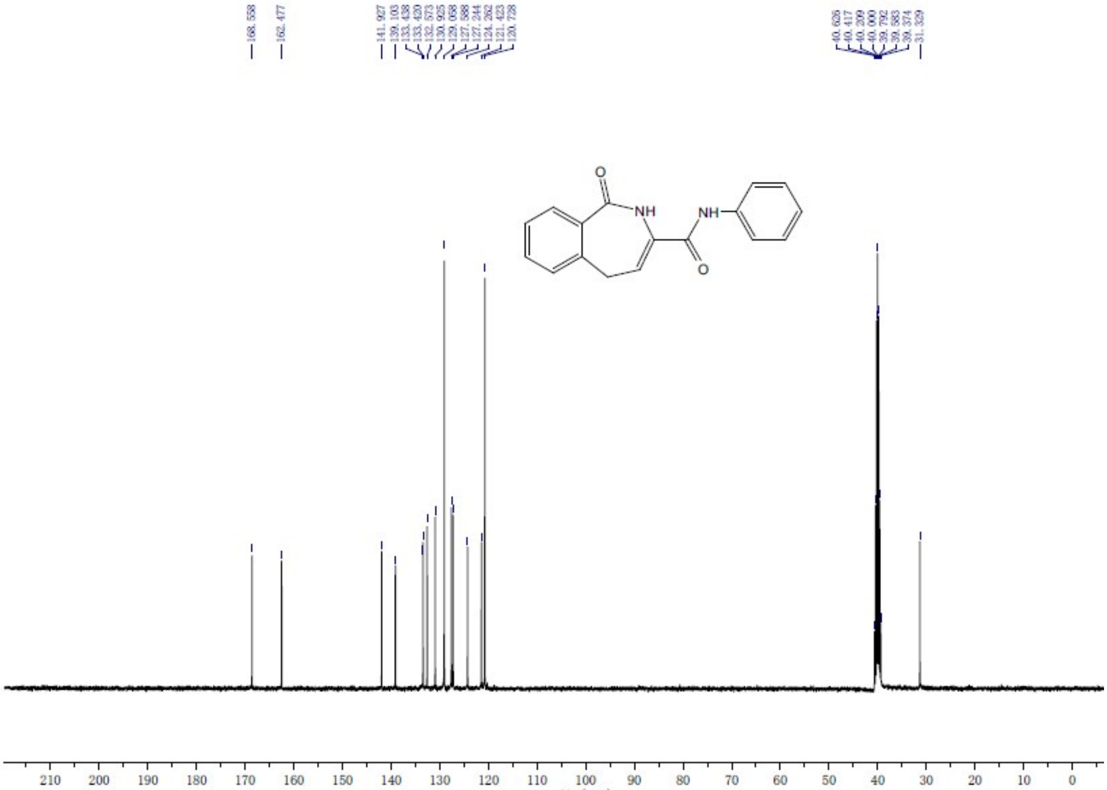
4a



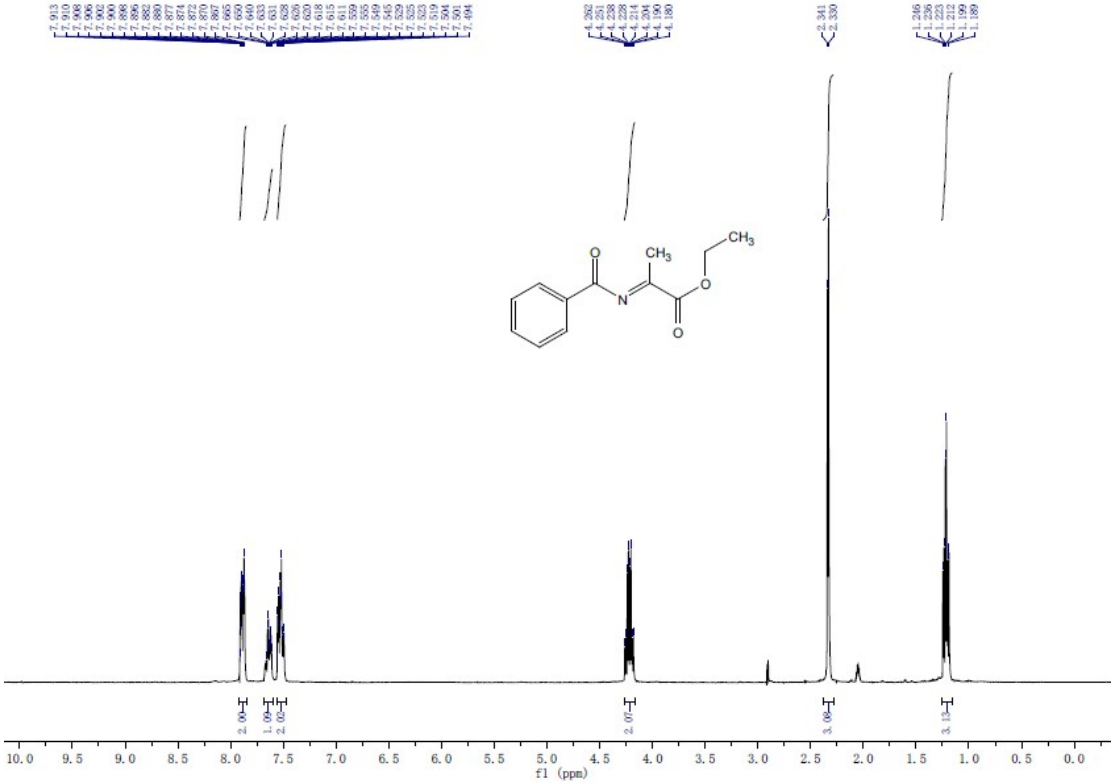


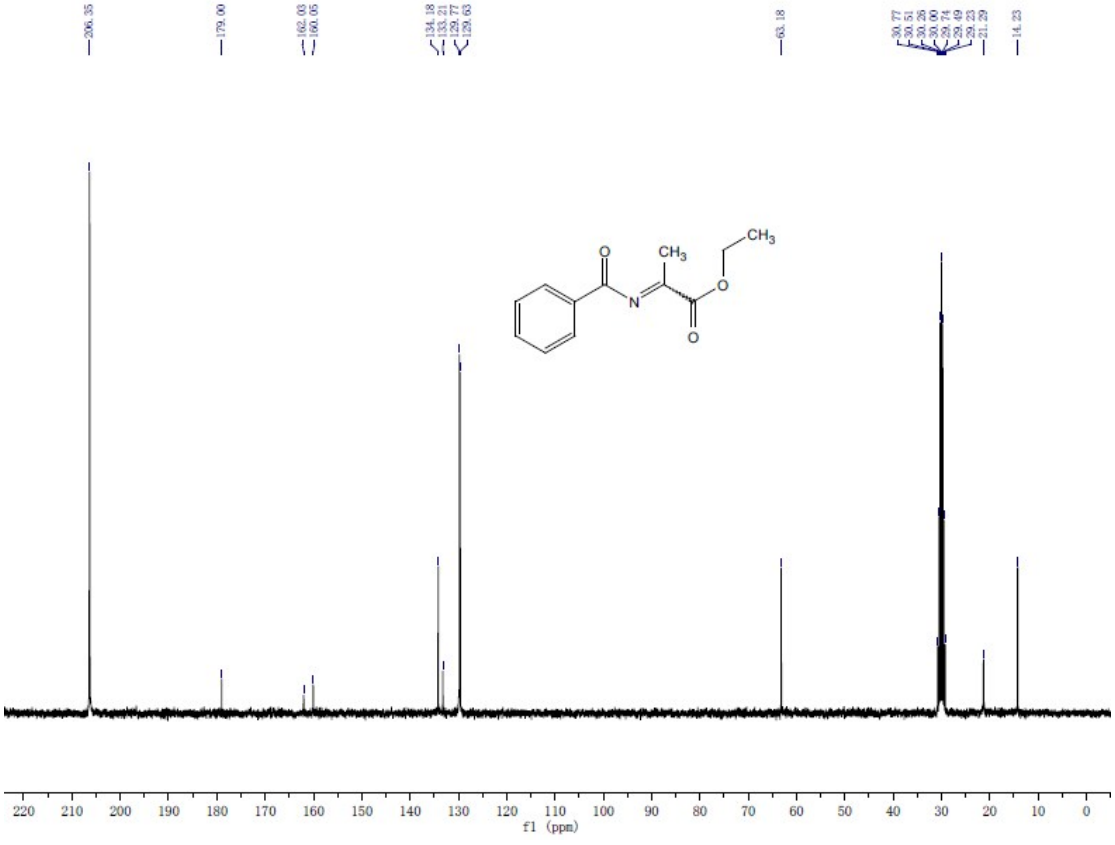
4b


10.060
9.366
7.778
7.761
7.676
7.657
7.506
7.490
7.487
7.472
7.469
7.381
7.363
7.343
7.334
7.315
7.295
7.276
7.091
7.073
6.609
6.591
6.573
3.430
3.412
3.385
2.500
NH
NH
O
O
0.93
0.94
1.02
2.01
1.10
4.08
1.00
0.98
2.86
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

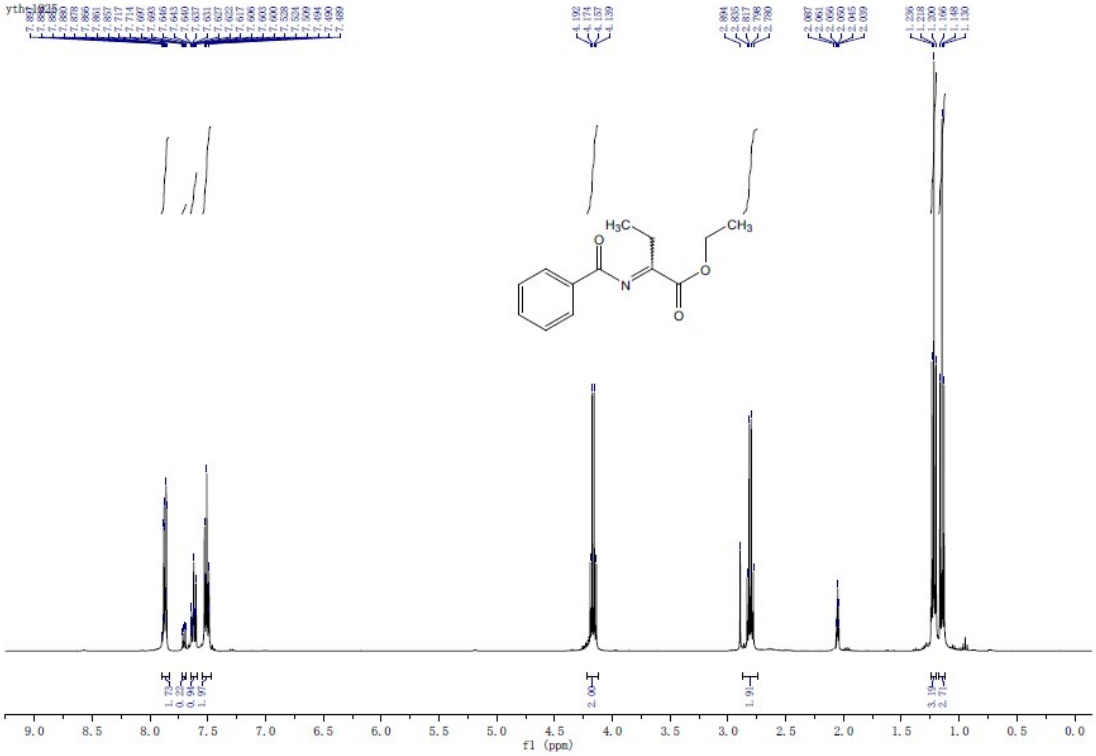

168.558
162.477
141.927
139.103
133.438
132.420
130.673
129.925
129.058
127.588
127.244
124.262
121.423
120.728
40.626
40.417
40.209
40.000
39.792
39.583
39.374
31.329
NH
NH
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

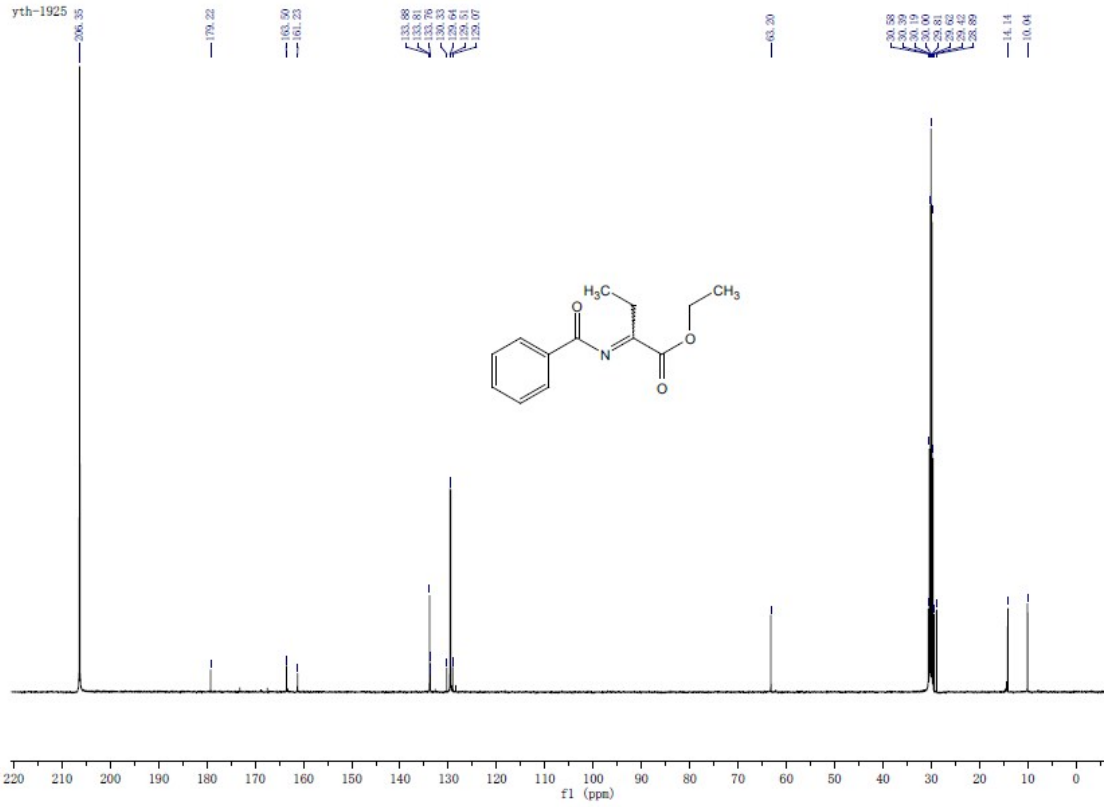
6a


7.913
7.910
7.906
7.906
7.905
7.900
7.888
7.886
7.882
7.880
7.877
7.874
7.872
7.870
7.867
7.865
7.640
7.633
7.631
7.628
7.626
7.620
7.618
7.615
7.611
7.599
7.595
7.549
7.545
7.529
7.525
7.523
7.519
7.504
7.501
7.494
4.262
4.251
4.238
4.228
4.214
4.204
4.190
4.180
2.541
2.330
1.246
1.236
1.233
1.222
1.199
1.189
2.00
1.00
2.02
2.07
3.00
3.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
CH3
N
O
CH3
O
O

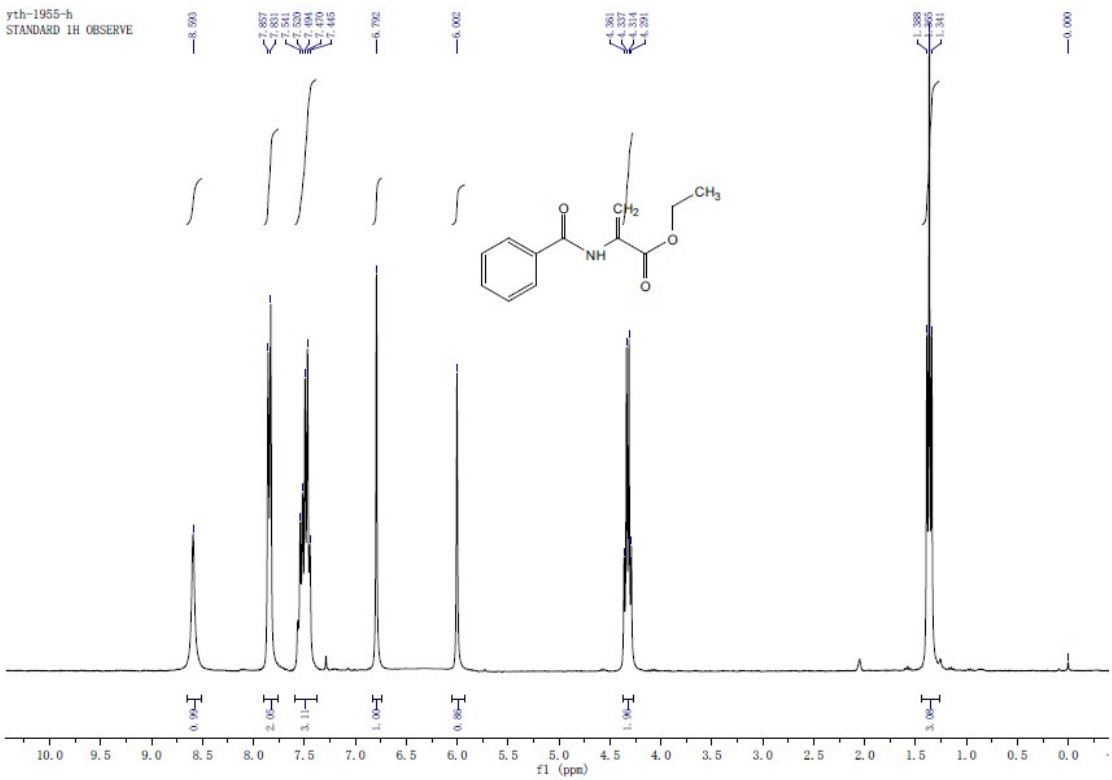

206.35
179.00
162.03
160.05
134.18
133.21
129.77
129.63
63.18
30.77
30.51
30.26
30.00
29.74
29.49
29.23
21.29
14.23
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
CH3
N
O
CH3
O
O

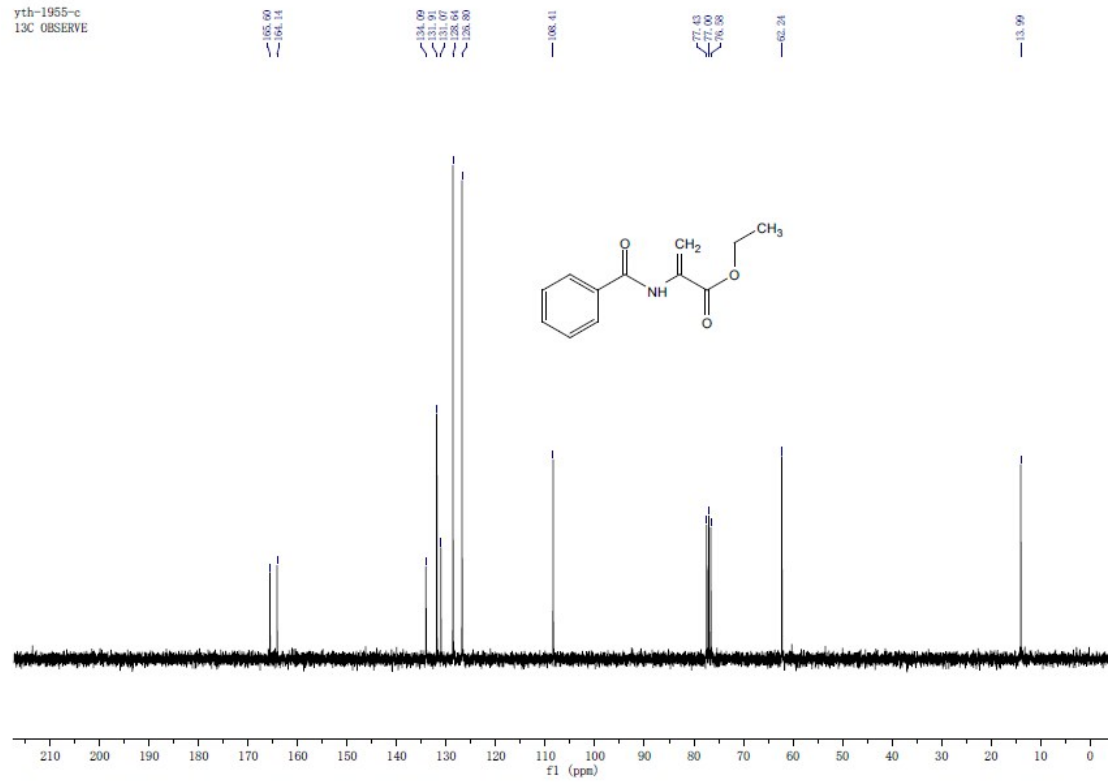
6b


yth-1925
H3C
CH3
O
N
O
O
f1 (ppm)

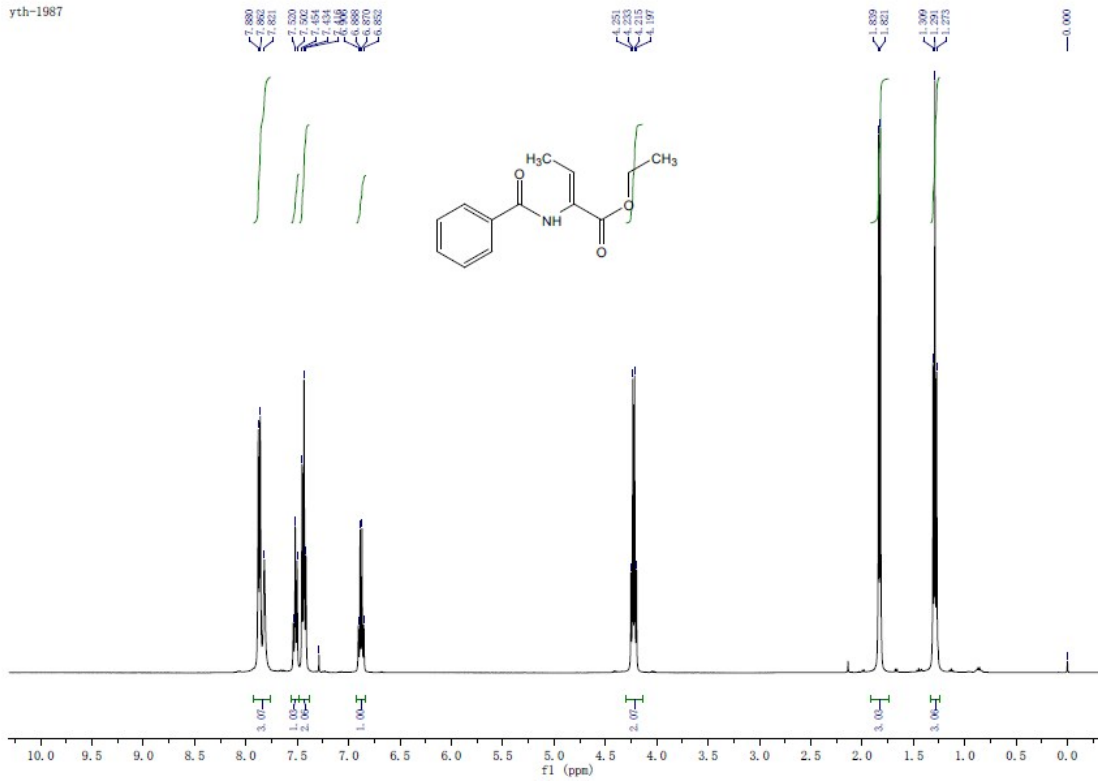

yth-1925
206.35
179.22
163.50
161.23
133.88
133.81
133.76
130.33
129.64
129.51
129.07
63.20
30.58
30.39
30.19
30.00
29.81
29.62
29.42
28.89
14.14
10.04
H3C
CH3
O
N
O
O
f1 (ppm)

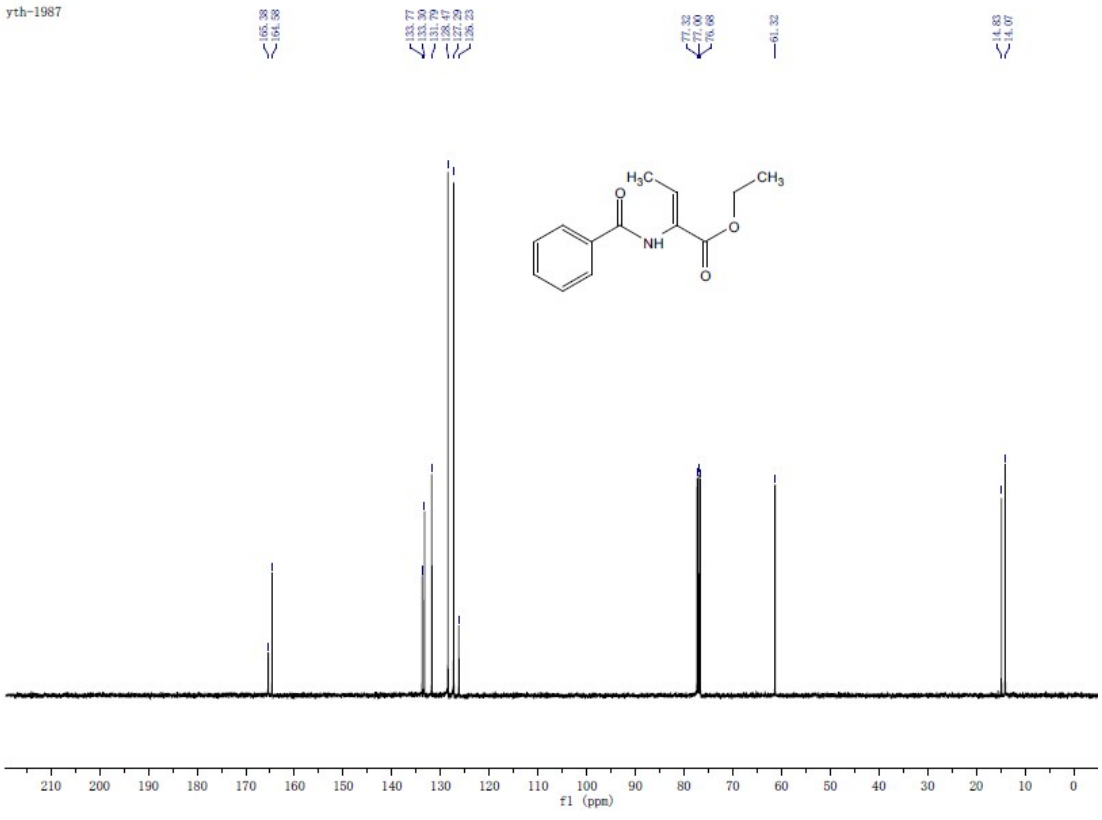
7a


yth-1955-h
STANDARD 1H OBSERVE
f1 (ppm)

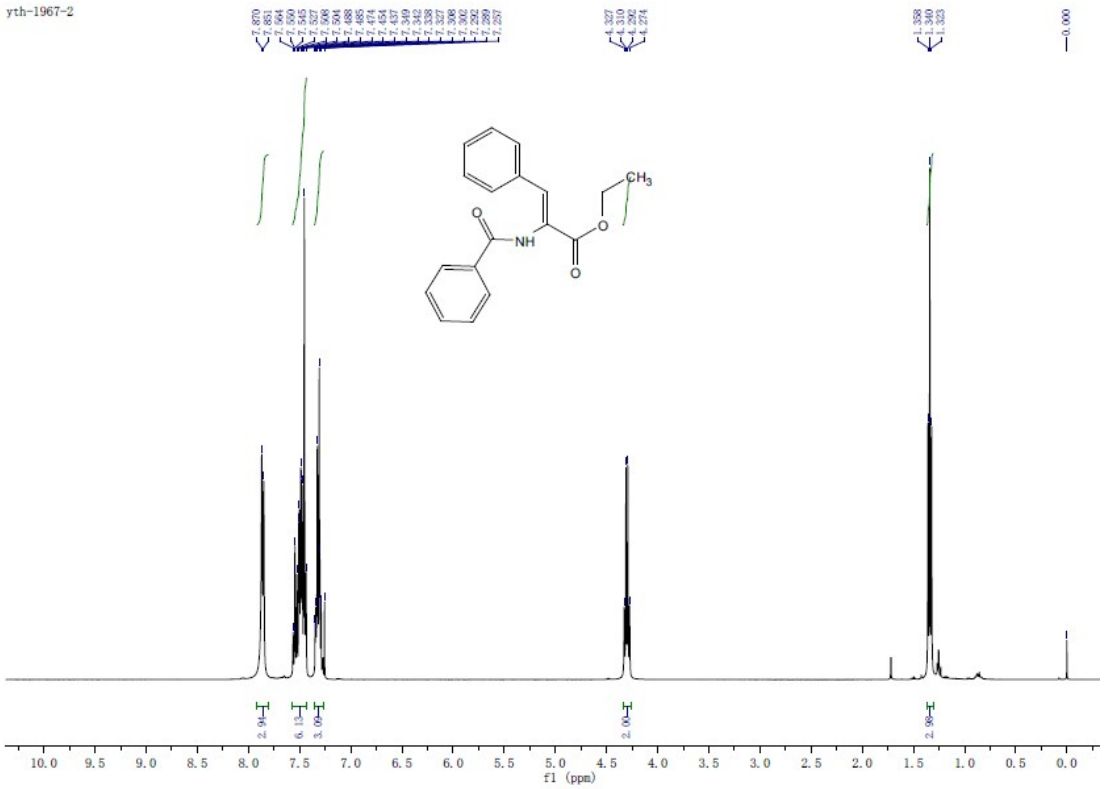

yth-1955-c
13C OBSERVE
f1 (ppm)

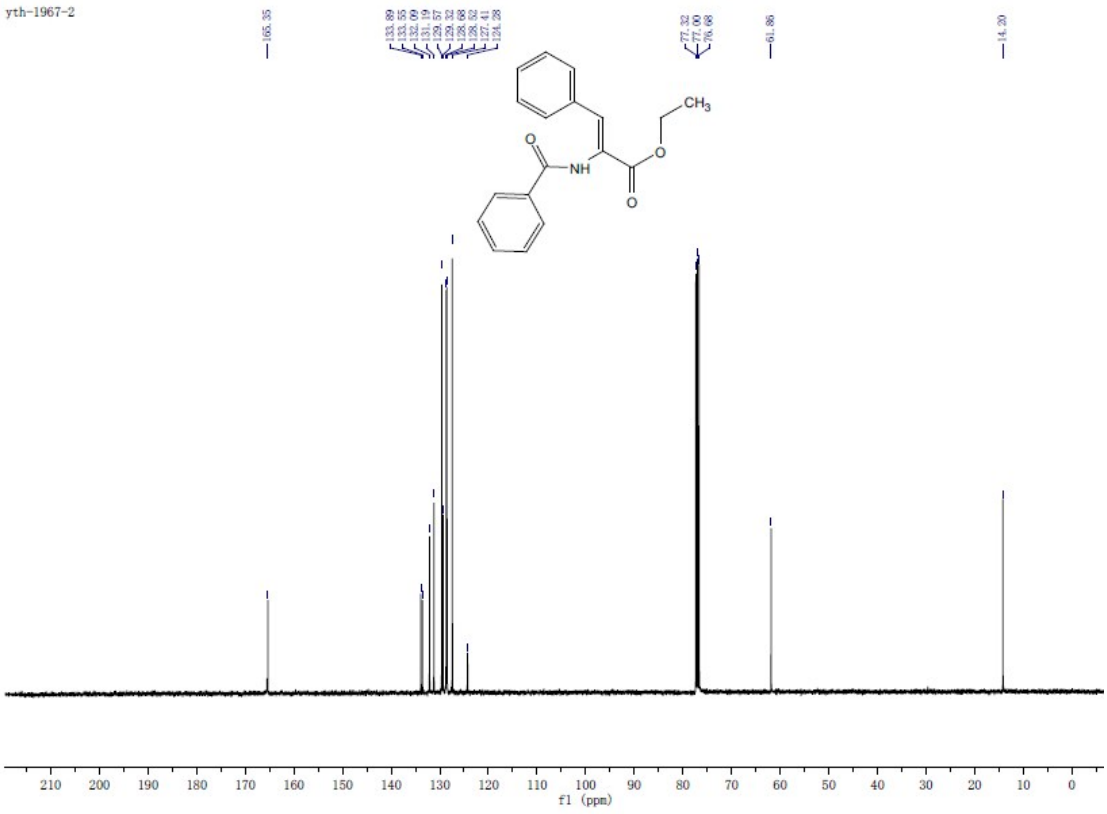
7b



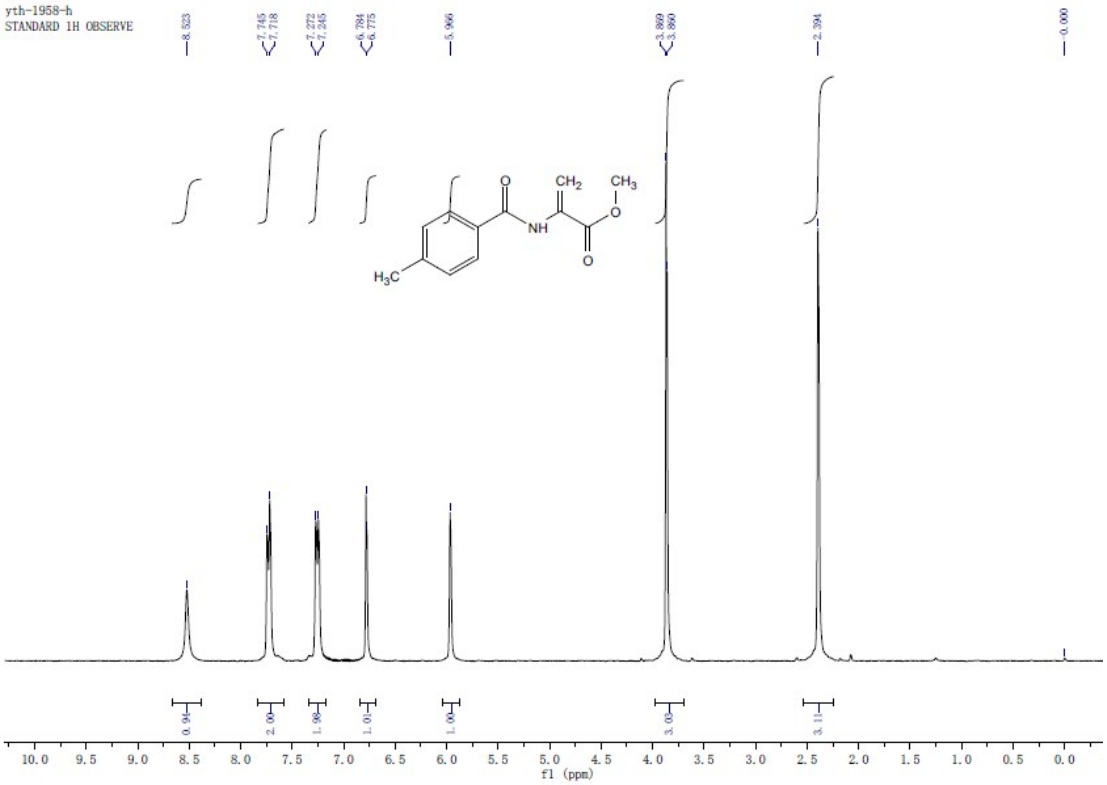


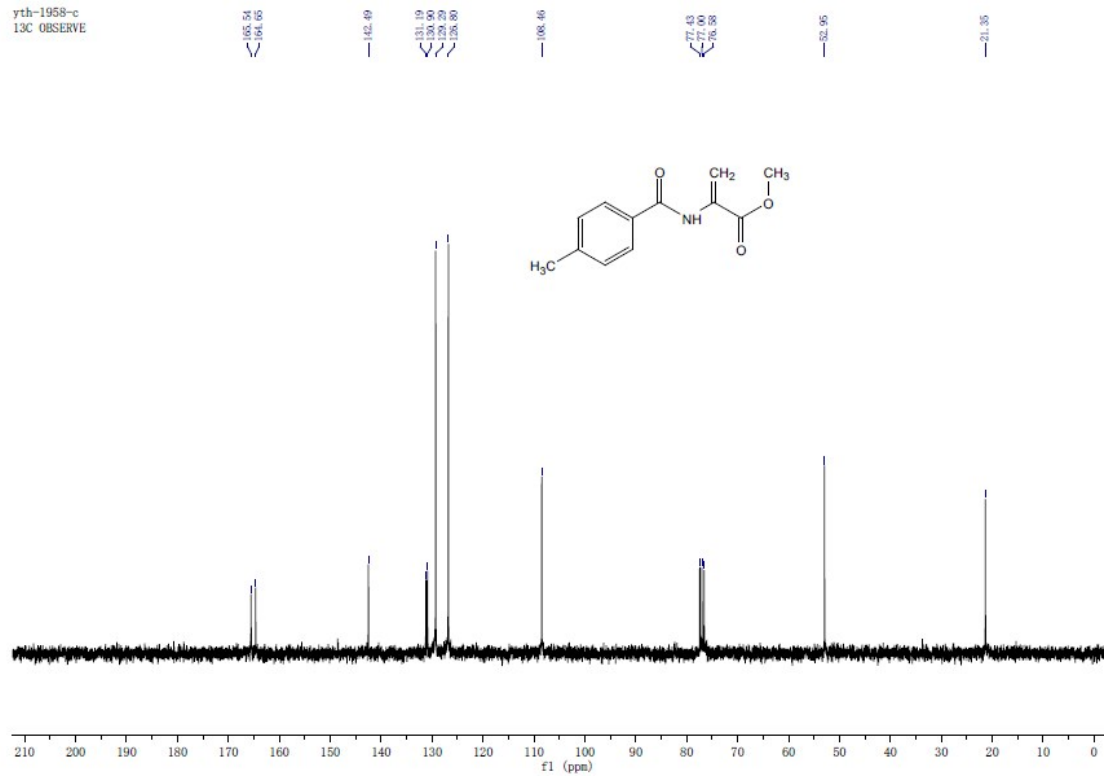
7d


yth-1967-2
7.870
7.861
7.564
7.550
7.545
7.537
7.506
7.504
7.488
7.485
7.474
7.454
7.437
7.349
7.342
7.338
7.337
7.336
7.300
7.292
7.289
7.257
4.327
4.319
4.292
4.274
1.338
1.340
1.323
0.000
2.94
6.13
3.09
2.00
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

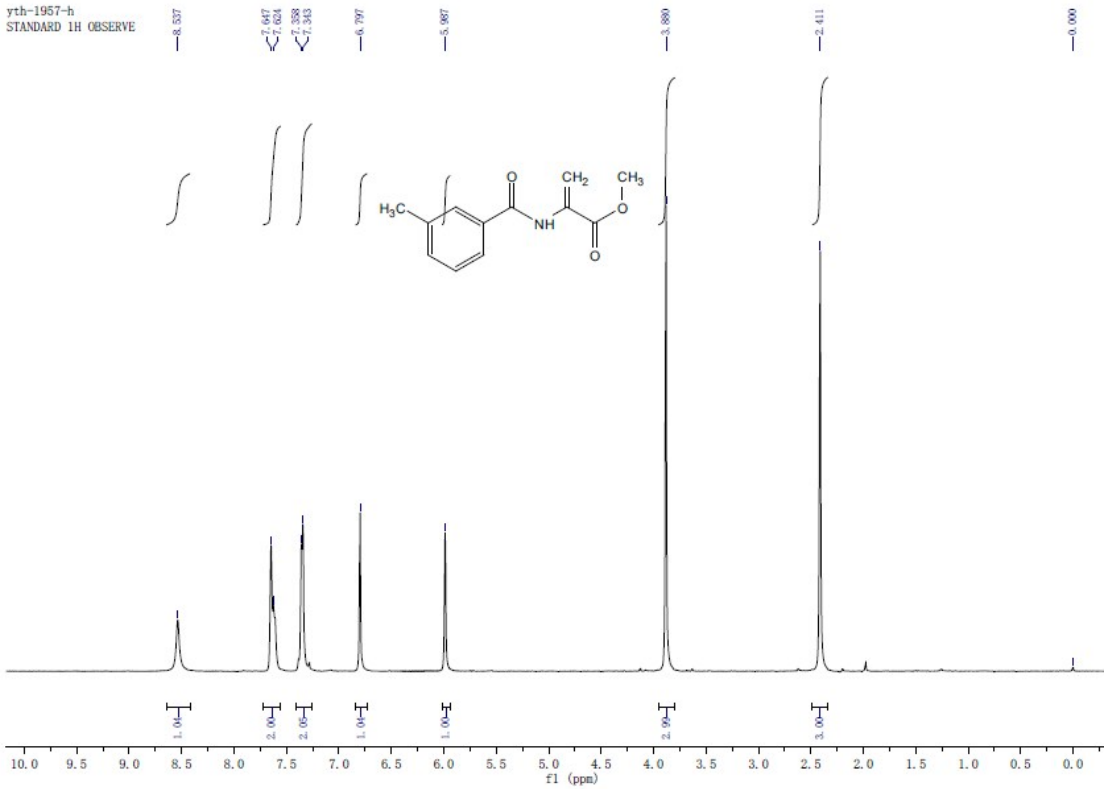

yth-1967-2
165.35
133.89
133.55
132.09
131.19
129.57
129.32
128.68
128.52
127.41
124.28
77.32
77.00
76.68
61.86
14.20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

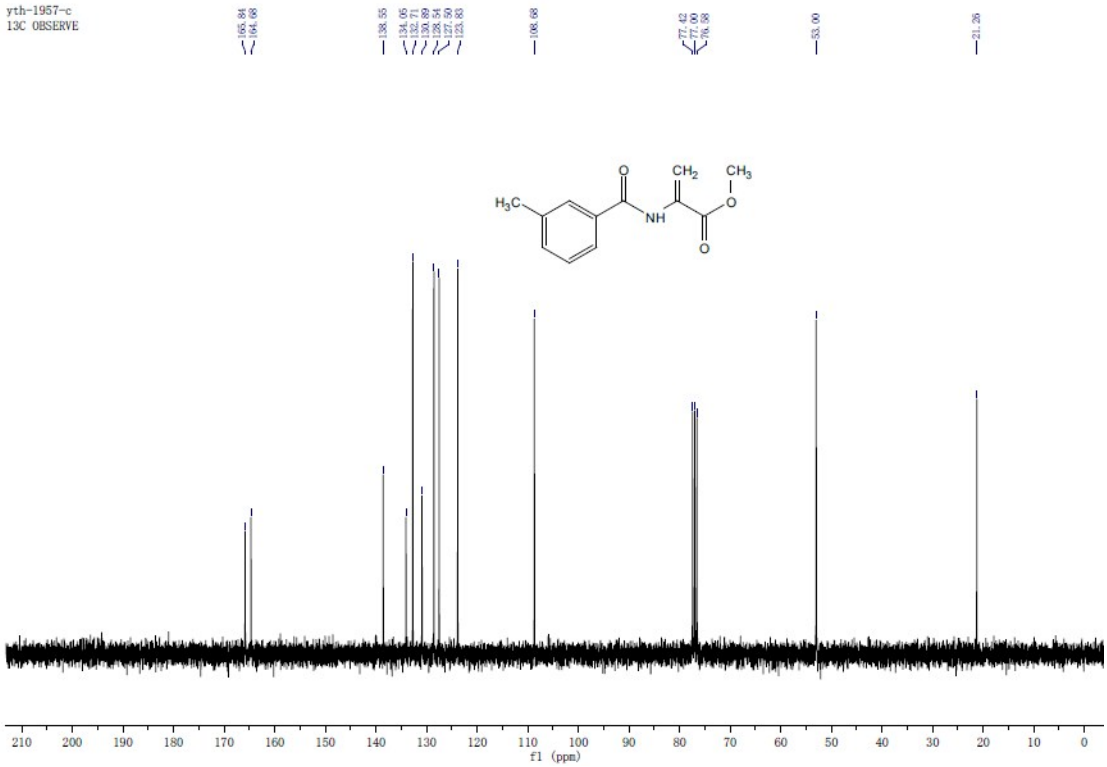
7f


yth-1958-h
STANDARD 1H OBSERVE
8.523
7.745
7.718
7.272
7.245
6.784
6.775
5.966
3.869
3.860
2.394
0.000
0.94
2.00
1.96
1.01
1.00
3.03
3.11
f1 (ppm)

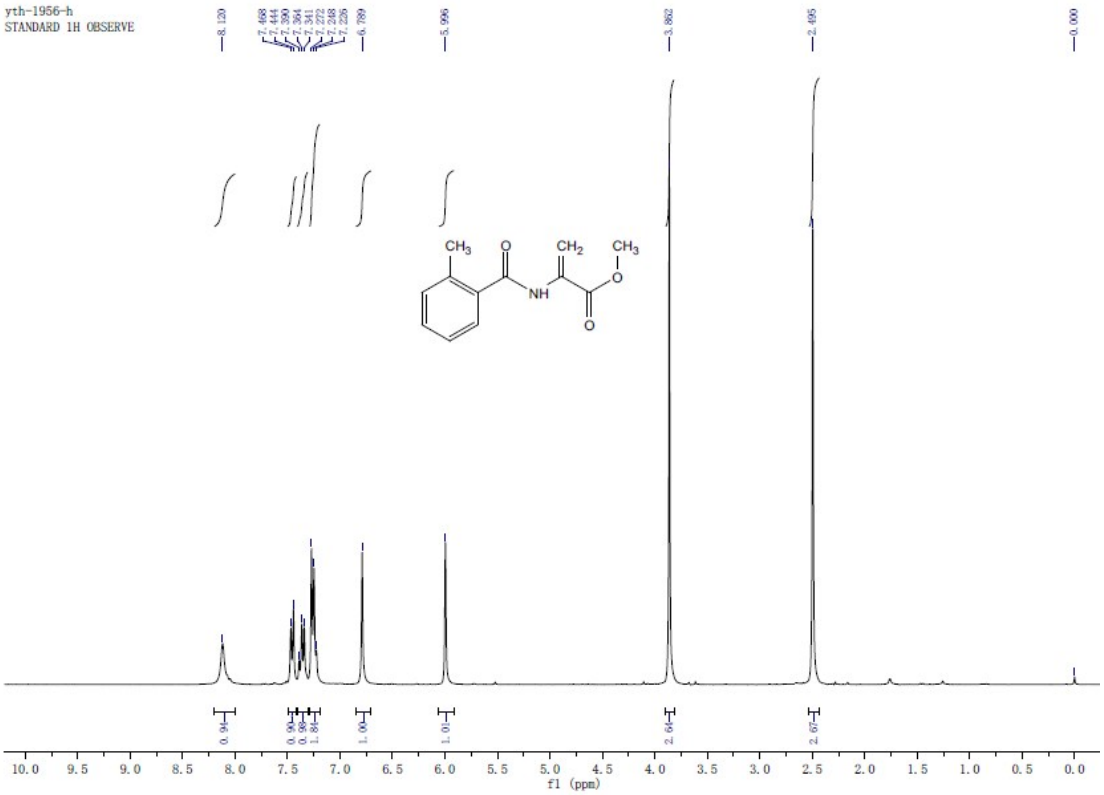

yth-1958-c
13C OBSERVE
165.54
164.66
142.49
131.19
130.90
129.79
128.88
108.46
77.43
77.00
76.58
52.95
21.35
f1 (ppm)

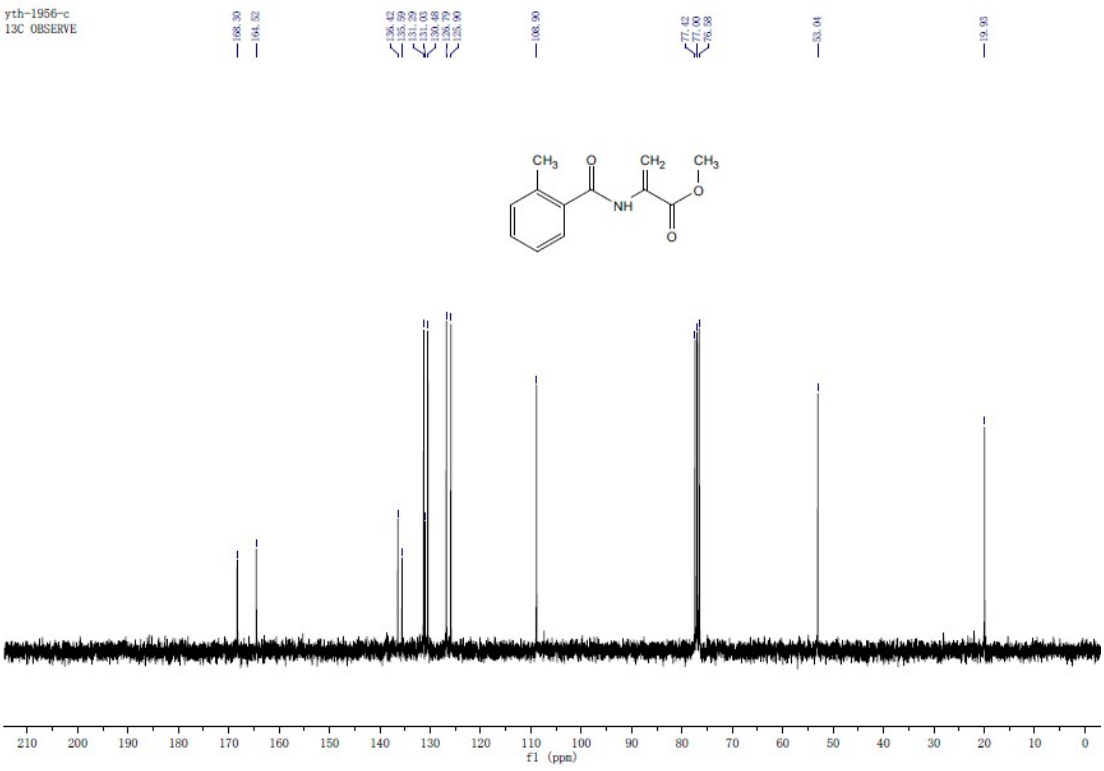
7g


yth-1957-h
STANDARD 1H OBSERVE
8.537
7.647
7.624
7.358
7.343
6.797
5.887
3.880
2.411
0.000
1.00
2.00
2.06
1.04
1.00
2.90
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
CH2
CH3
H3C
NH
O
O

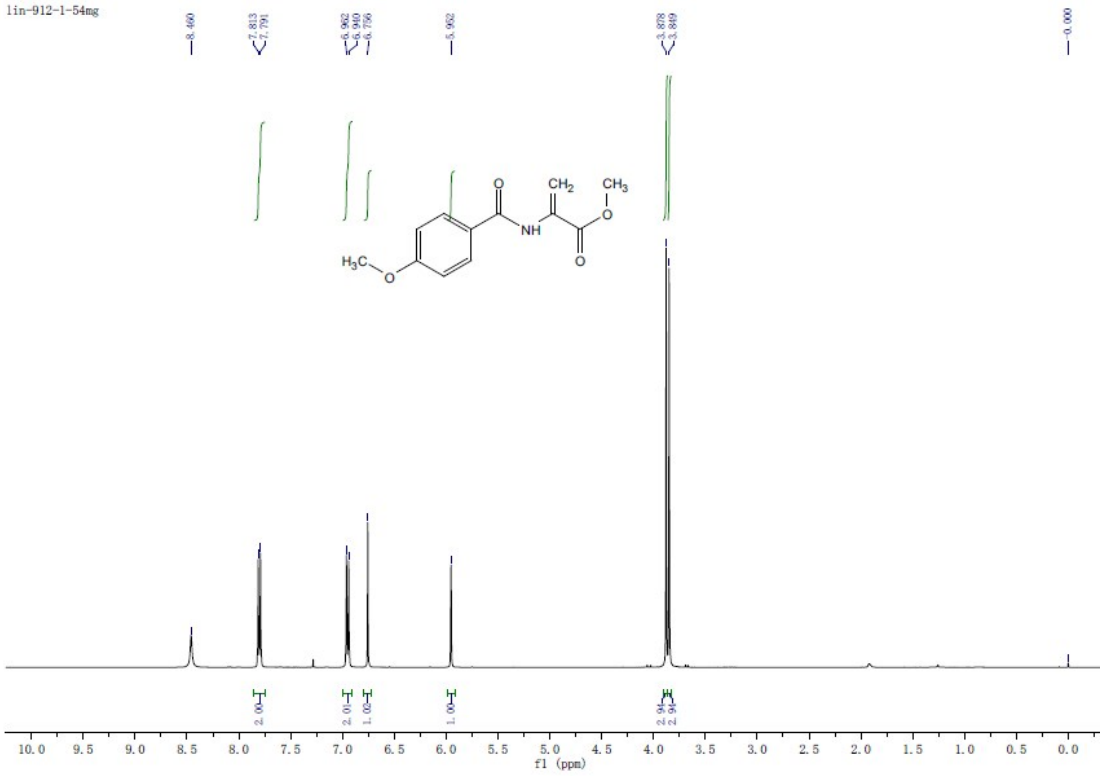

yth-1957-c
13C OBSERVE
165.84
164.68
138.55
134.05
132.71
130.89
128.54
127.50
125.83
108.68
77.42
77.00
76.58
53.00
21.26
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
CH2
CH3
H3C
NH
O
O

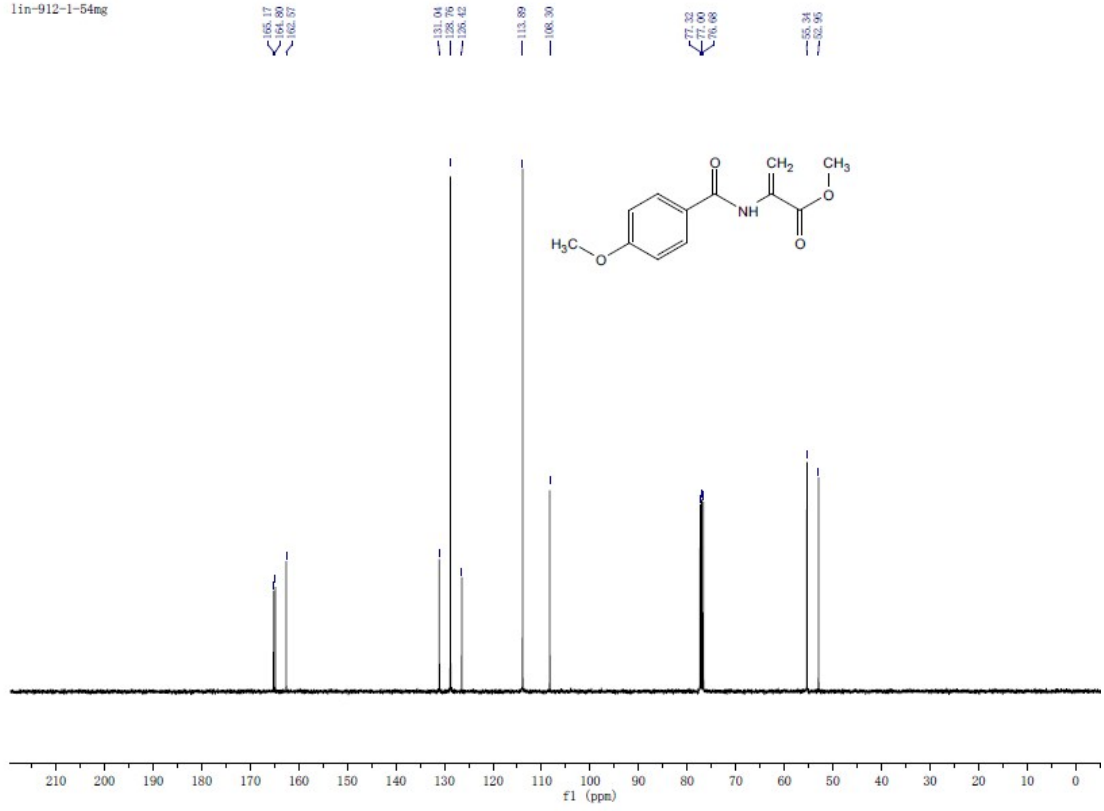
7h


yth-1956-h
STANDARD 1H OBSERVE
8.120
7.468
7.444
7.399
7.394
7.341
7.272
7.248
7.226
6.789
5.996
3.862
2.495
0.000
CH3
O
CH2
CH3
NH
O
O
0.94
0.90
0.96
1.84
1.00
1.01
2.64
2.67
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

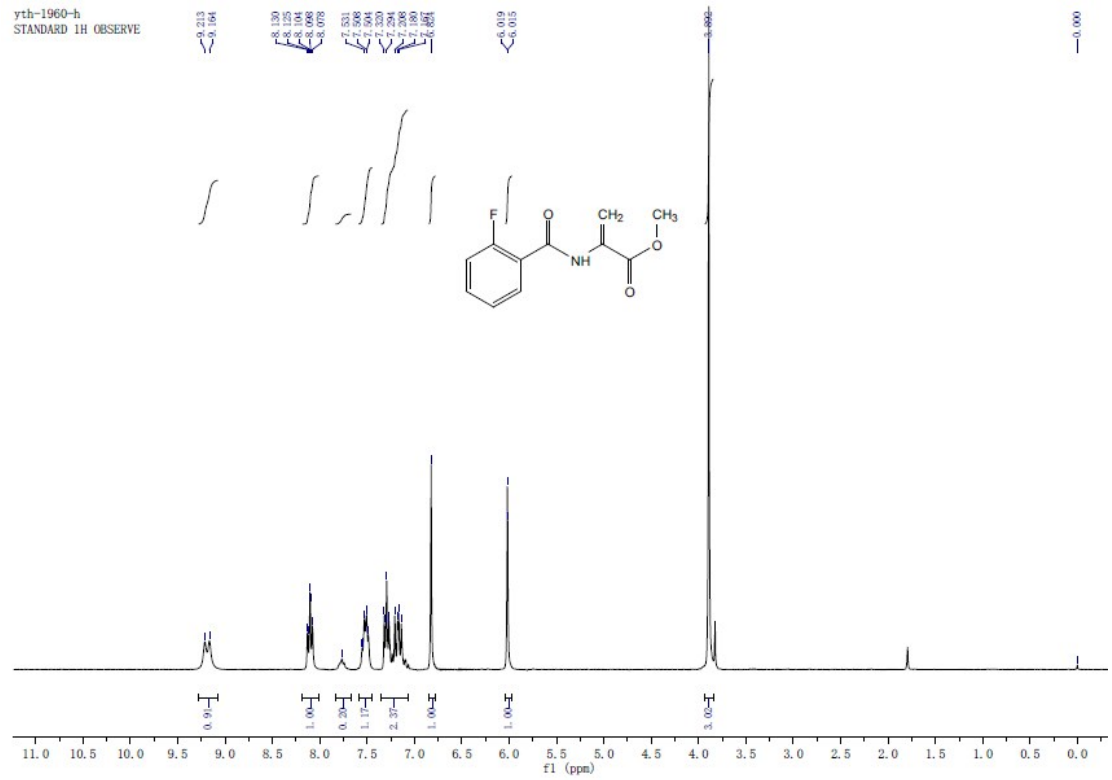

yth-1956-c
13C OBSERVE
168.30
164.52
136.42
135.59
131.29
131.05
130.48
126.79
125.90
108.90
77.42
77.00
76.58
53.04
19.93
CH3
O
CH2
CH3
NH
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

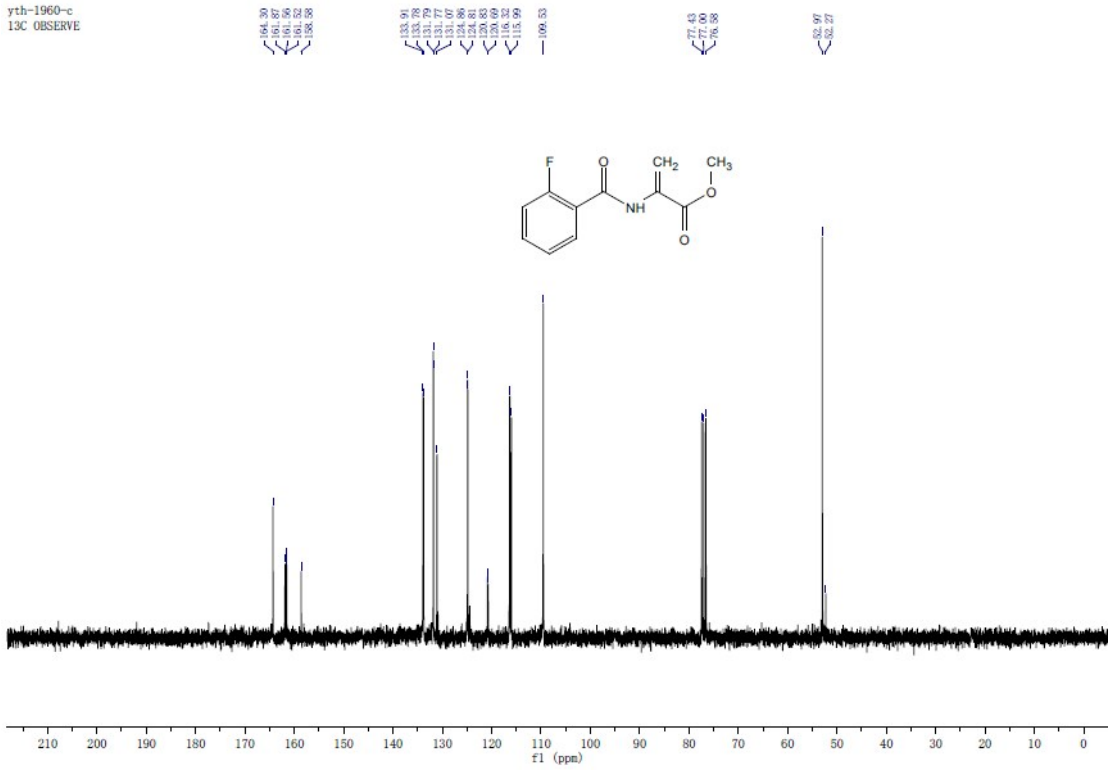
7i


lin-912-1-54mg
8.460
7.813
7.791
6.962
6.940
6.799
5.962
3.878
3.849
0.000
2.00
2.01
1.02
1.00
2.94
2.92
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
CH2
CH3
NH
O
O
H3C
O

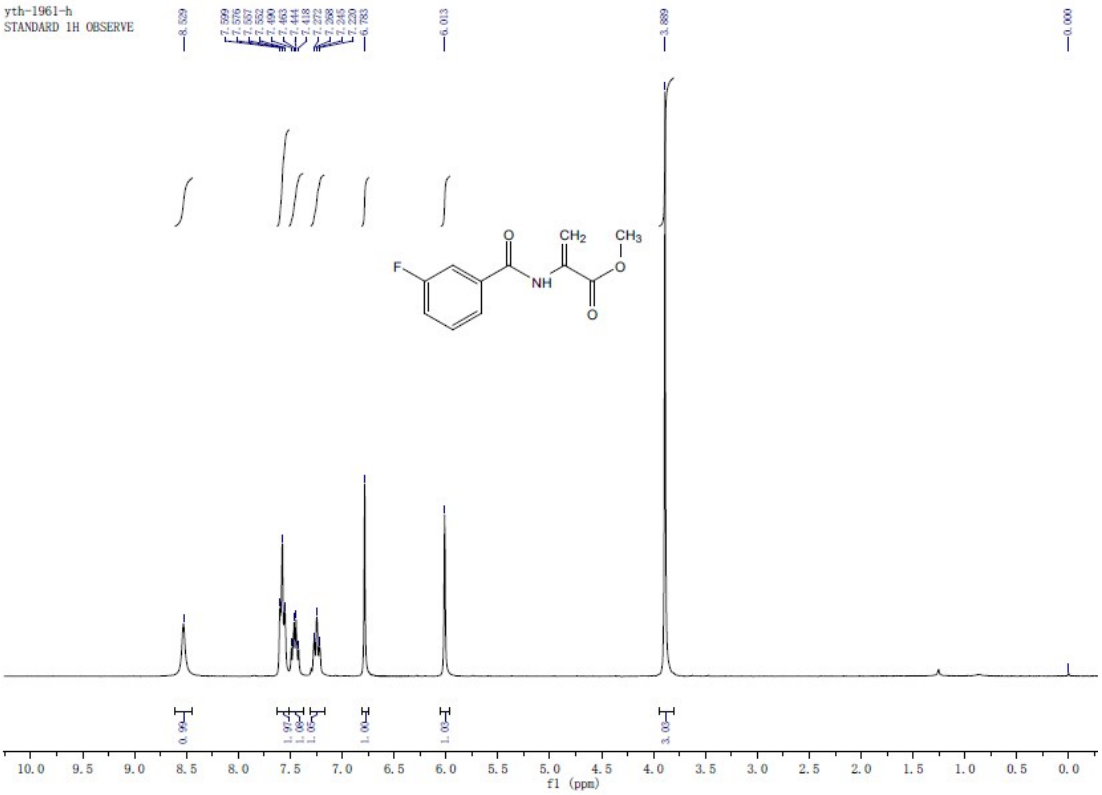

lin-912-1-54mg
165.17
164.80
162.57
131.04
128.76
126.42
113.89
108.30
77.32
77.00
76.68
55.34
52.95
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
CH2
CH3
NH
O
O
H3C
O

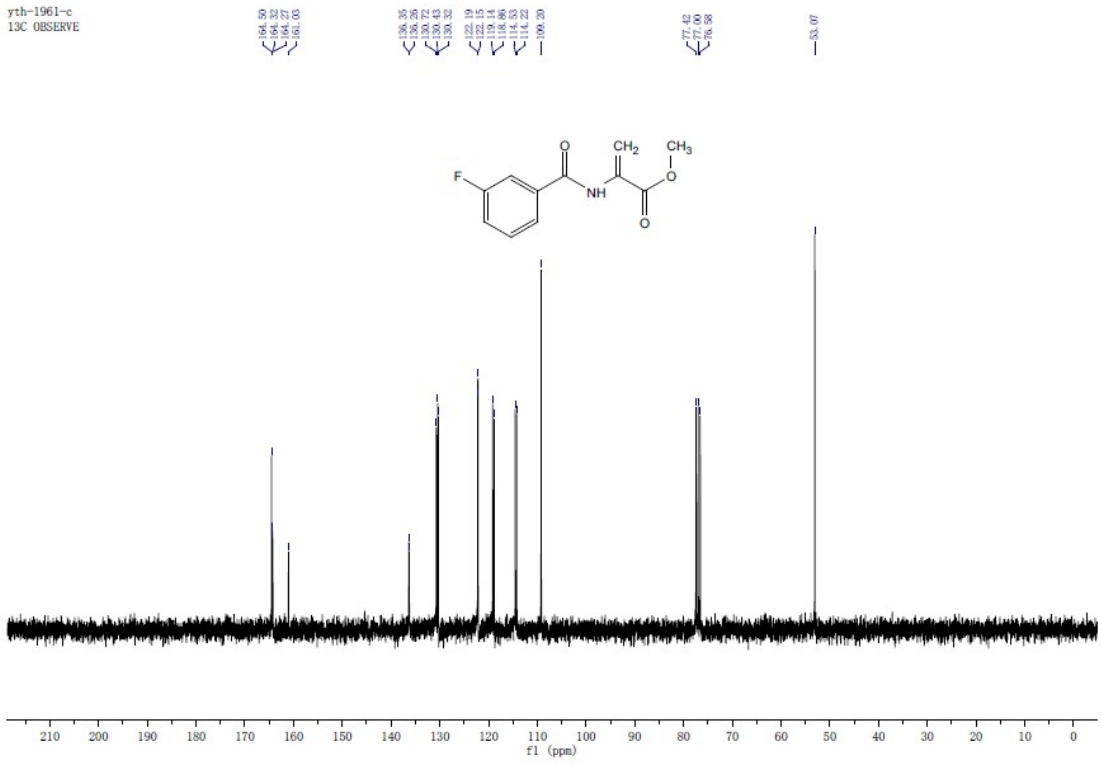
7j


yth-1960-h
STANDARD 1H OBSERVE
F
O
CH2
CH3
NH
O
O
f1 (ppm)

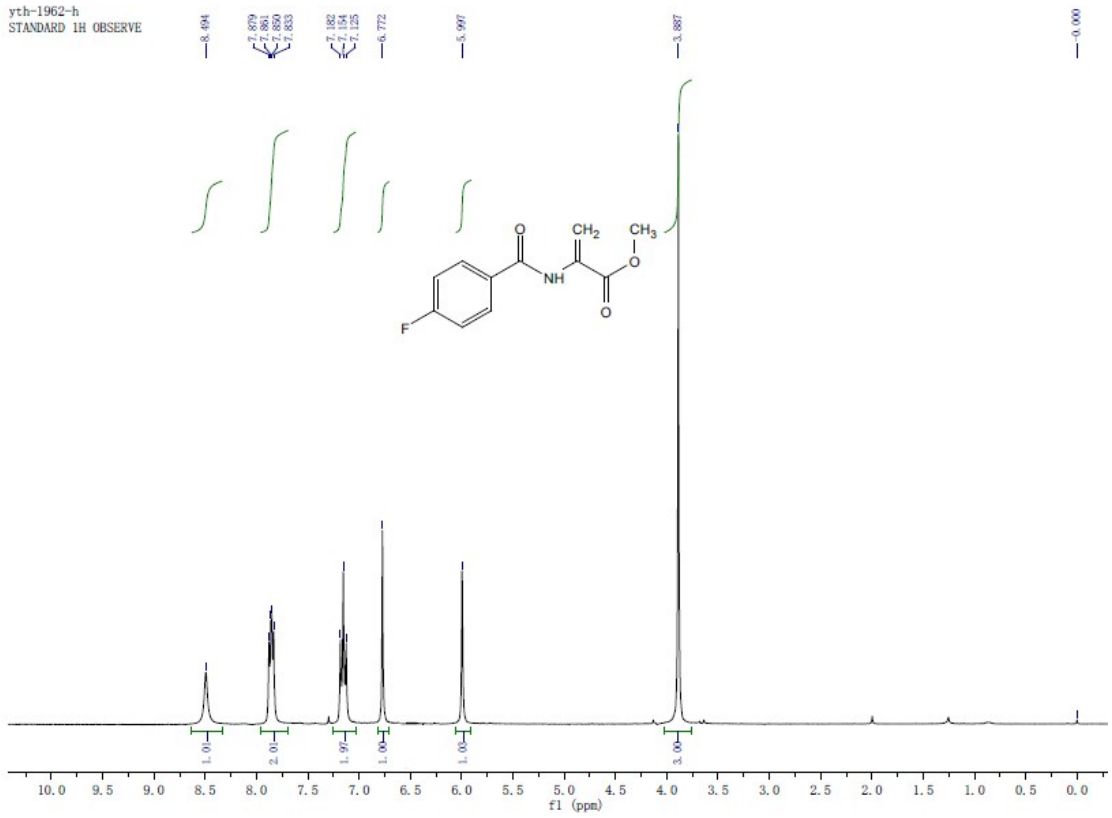

yth-1960-c
13C OBSERVE
F
O
CH2
CH3
NH
O
O
f1 (ppm)

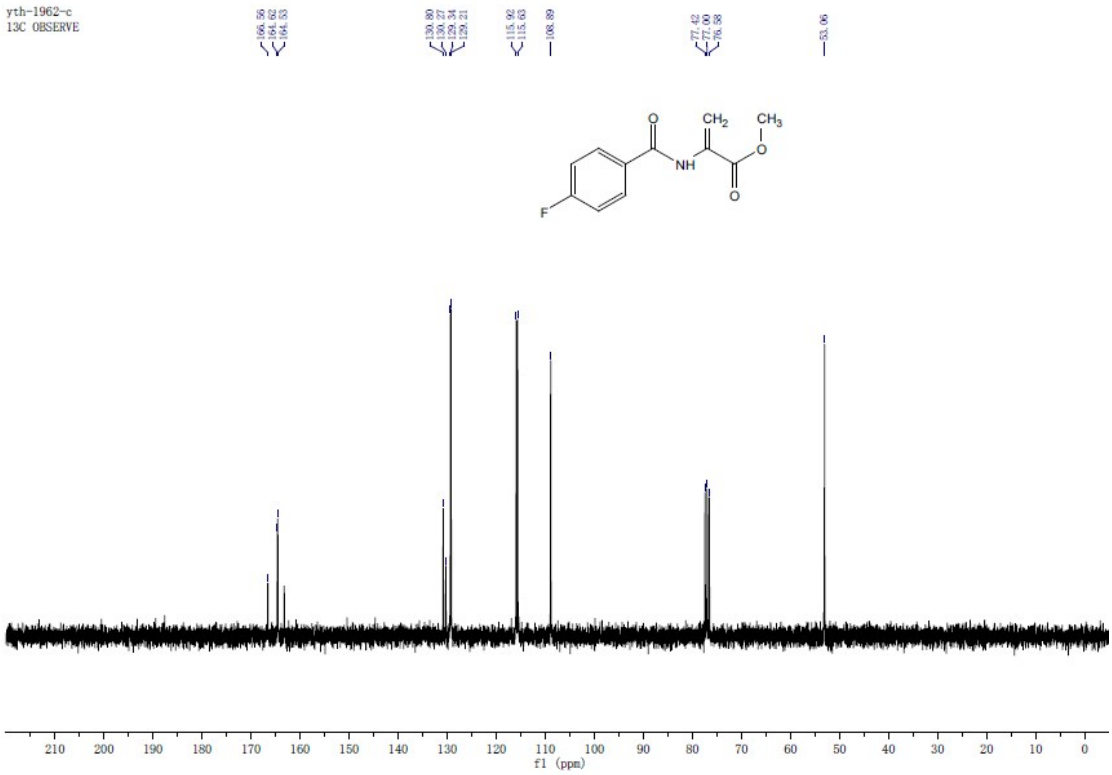
7k


yth-1961-h
STANDARD 1H OBSERVE
f1 (ppm)

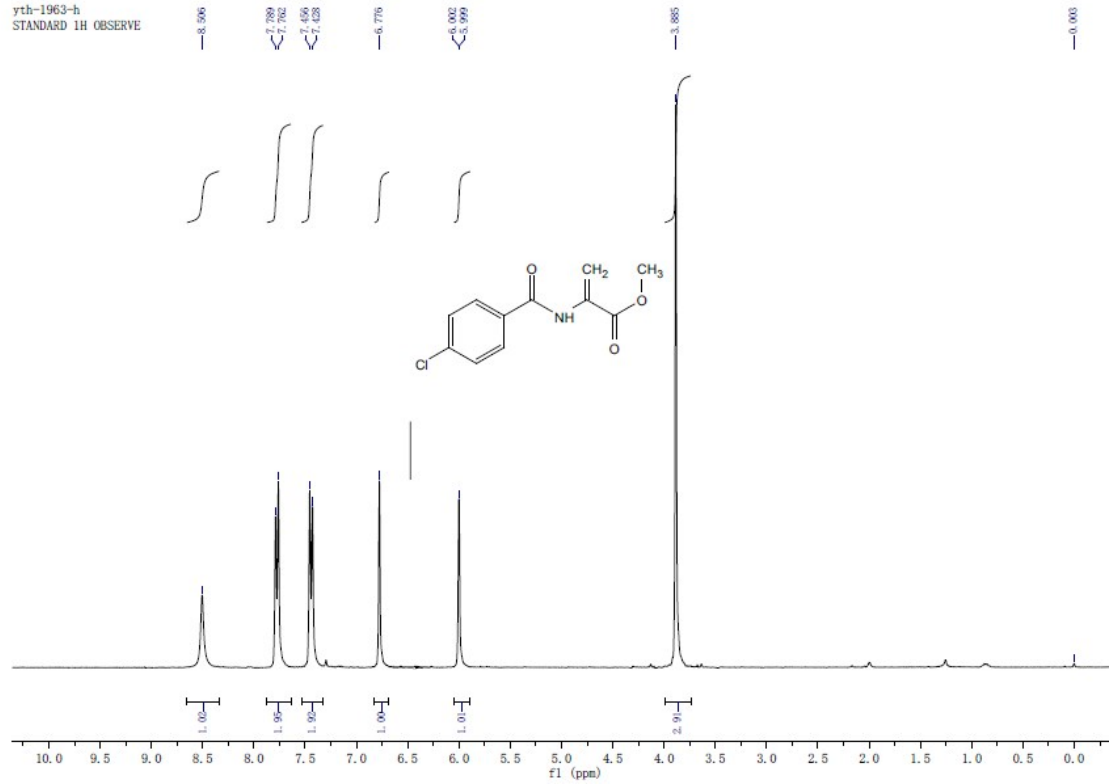

yth-1961-c
13C OBSERVE
f1 (ppm)

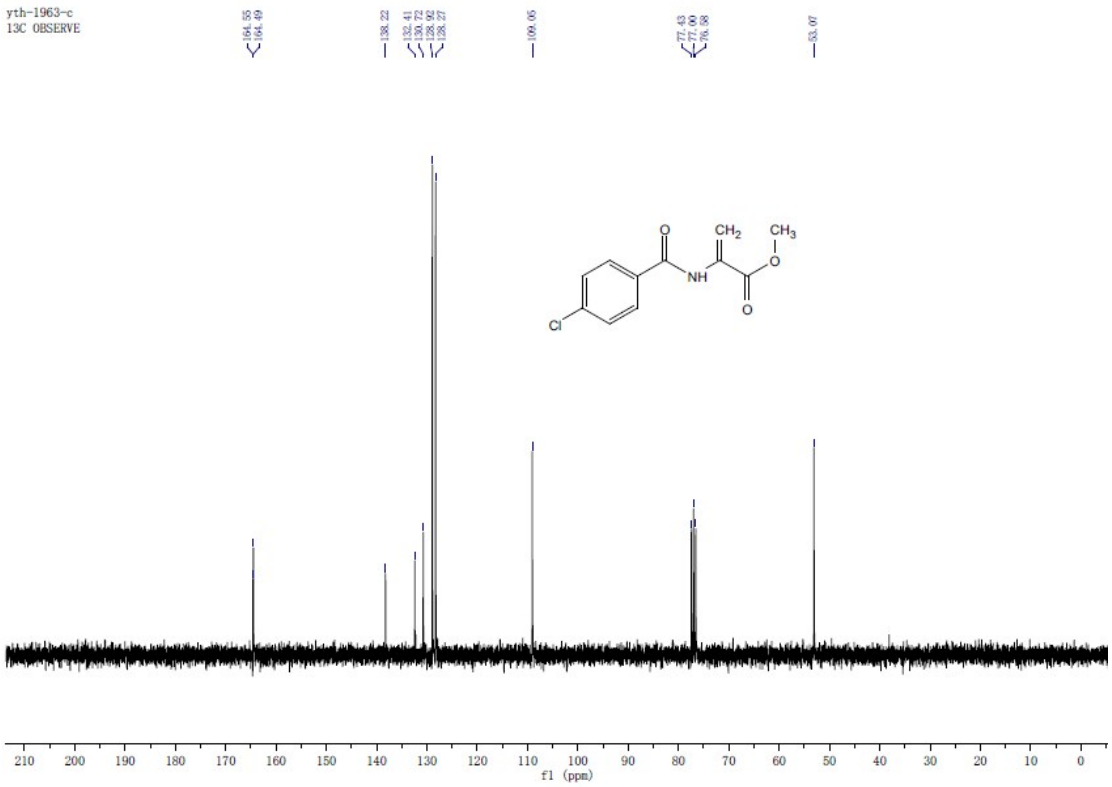
7l


yth-1962-h
STANDARD 1H OBSERVE
8.494
7.879
7.861
7.850
7.833
7.182
7.154
7.125
6.772
5.997
3.887
0.000
O
CH2
CH3
NH
O
O
F
1.01
2.01
1.97
1.00
1.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

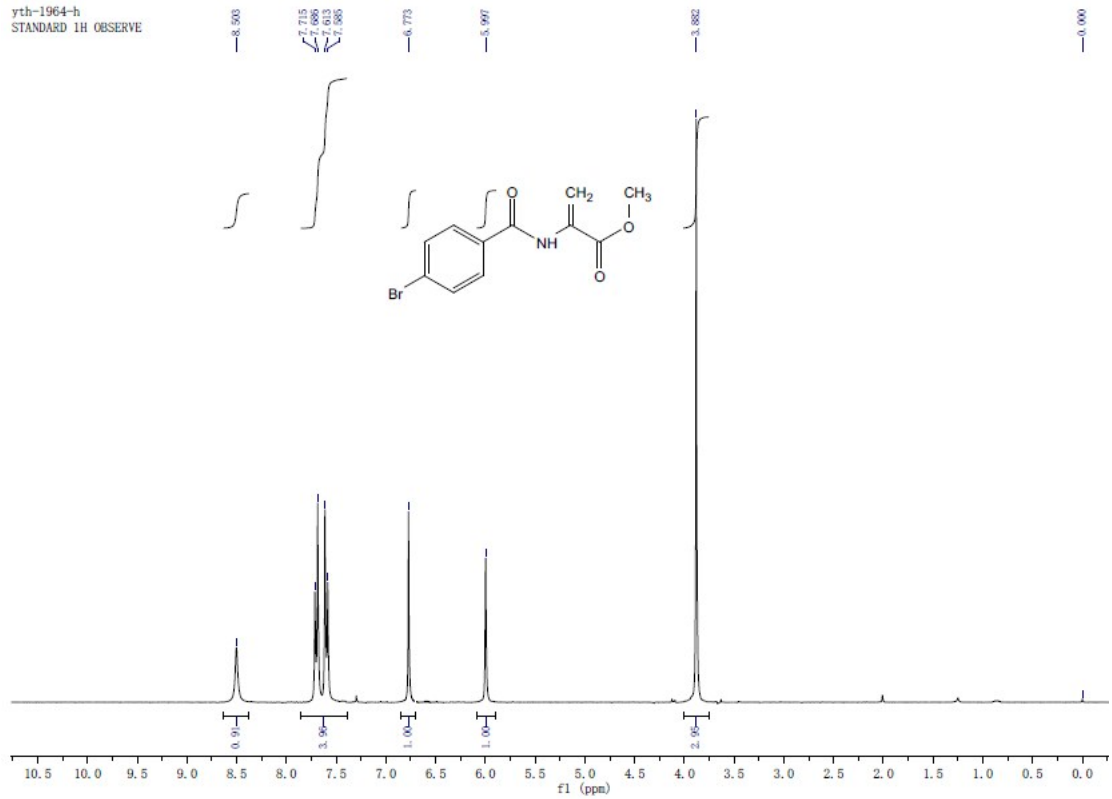

yth-1962-c
13C OBSERVE
166.56
164.62
164.53
130.89
130.27
129.34
129.21
115.92
115.63
108.89
77.42
77.00
76.58
53.06
O
CH2
CH3
NH
O
O
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

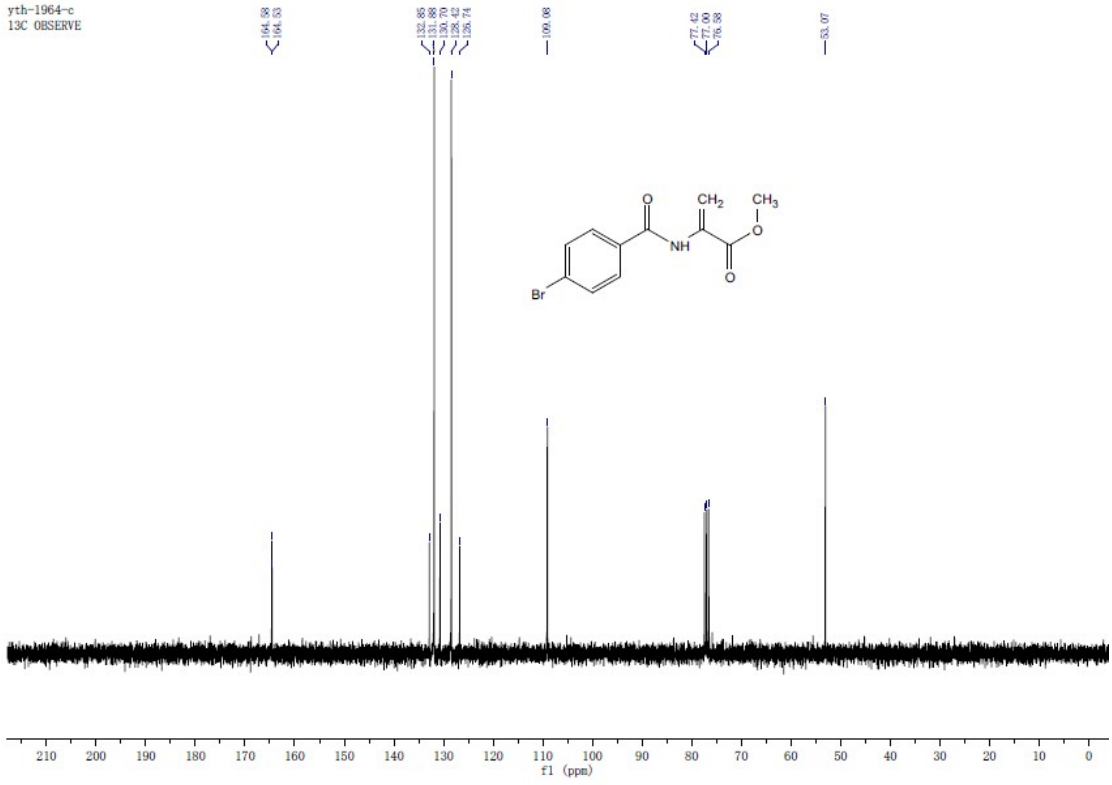
7m


yth-1963-h
STANDARD 1H OBSERVE
8.506
7.789
7.762
7.456
7.428
6.776
6.002
5.999
3.885
0.003
O
CH2
CH3
NH
O
O
Cl
1.00
1.96
1.92
1.00
1.01
2.91
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

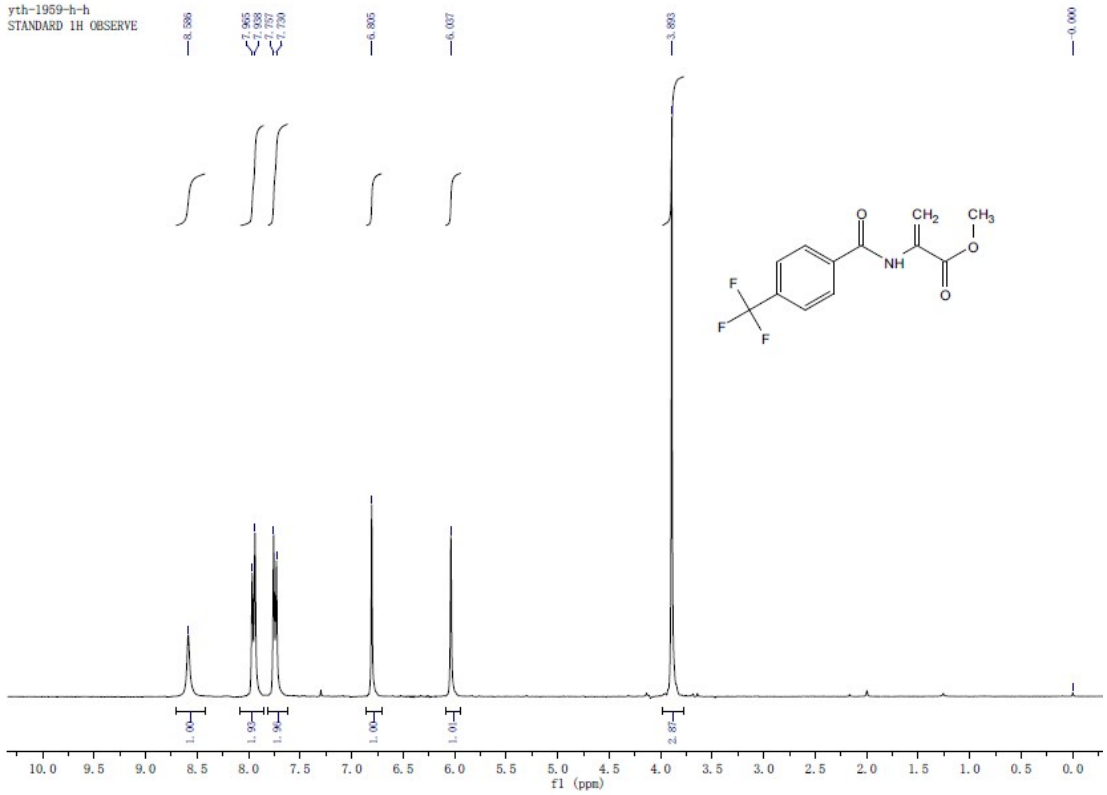

yth-1963-c
13C OBSERVE
164.55
164.49
138.22
135.41
131.72
128.92
128.27
109.05
77.43
77.00
76.58
53.07
O
CH2
CH3
NH
O
O
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

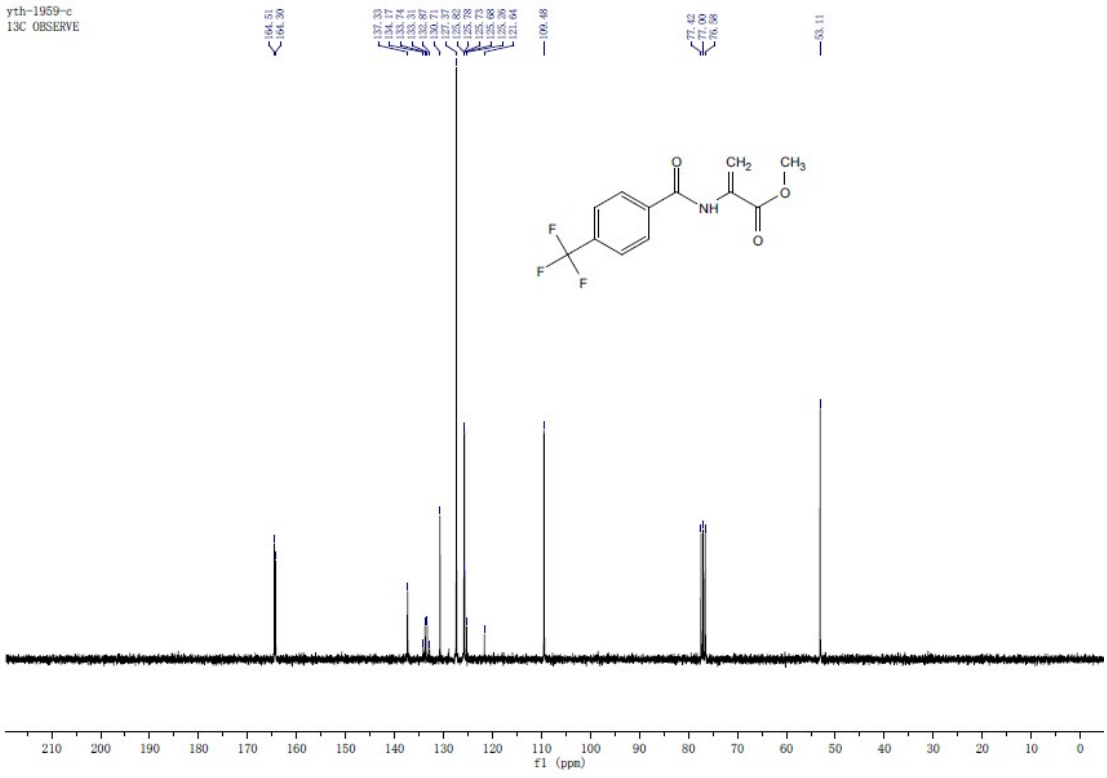
7n


yth-1964-h
STANDARD 1H OBSERVE
8.503
7.715
7.696
7.613
7.595
6.773
5.997
3.882
0.000
O
CH2
CH3
NH
O
O
Br
0.91
3.96
1.00
1.00
2.96
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

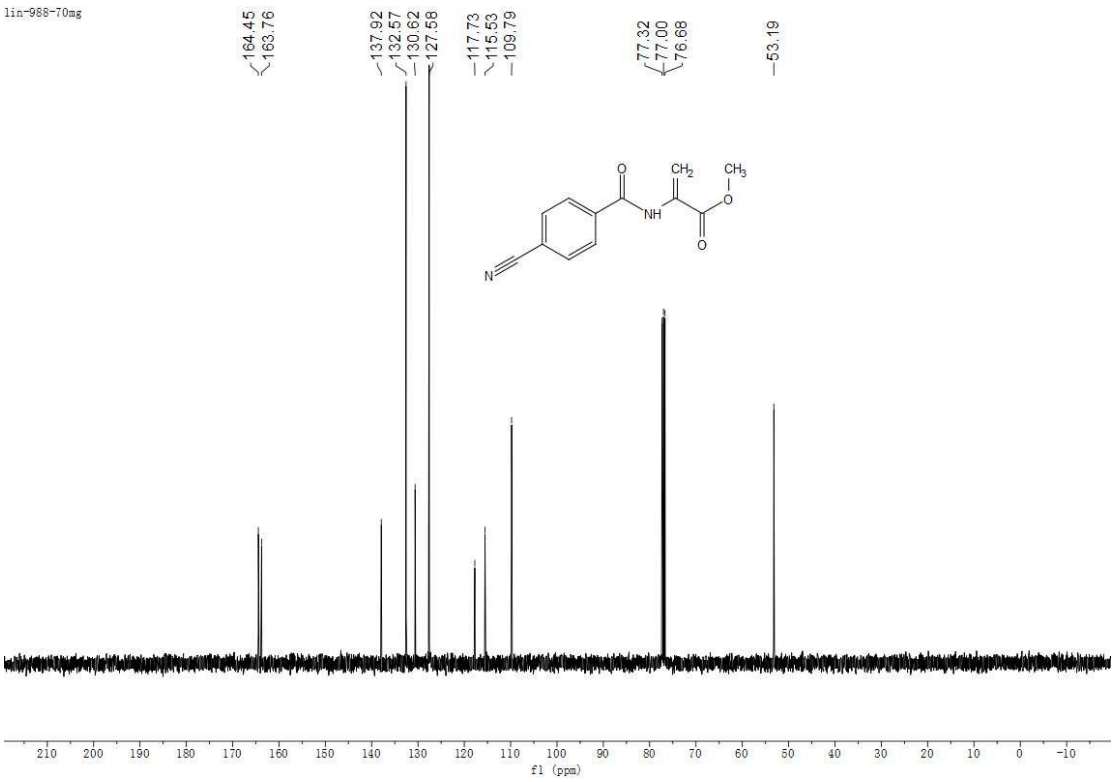

yth-1964-c
13C OBSERVE
164.68
164.53
132.85
131.98
130.70
128.42
126.74
109.08
77.42
77.00
76.58
53.07
O
CH2
CH3
NH
O
O
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

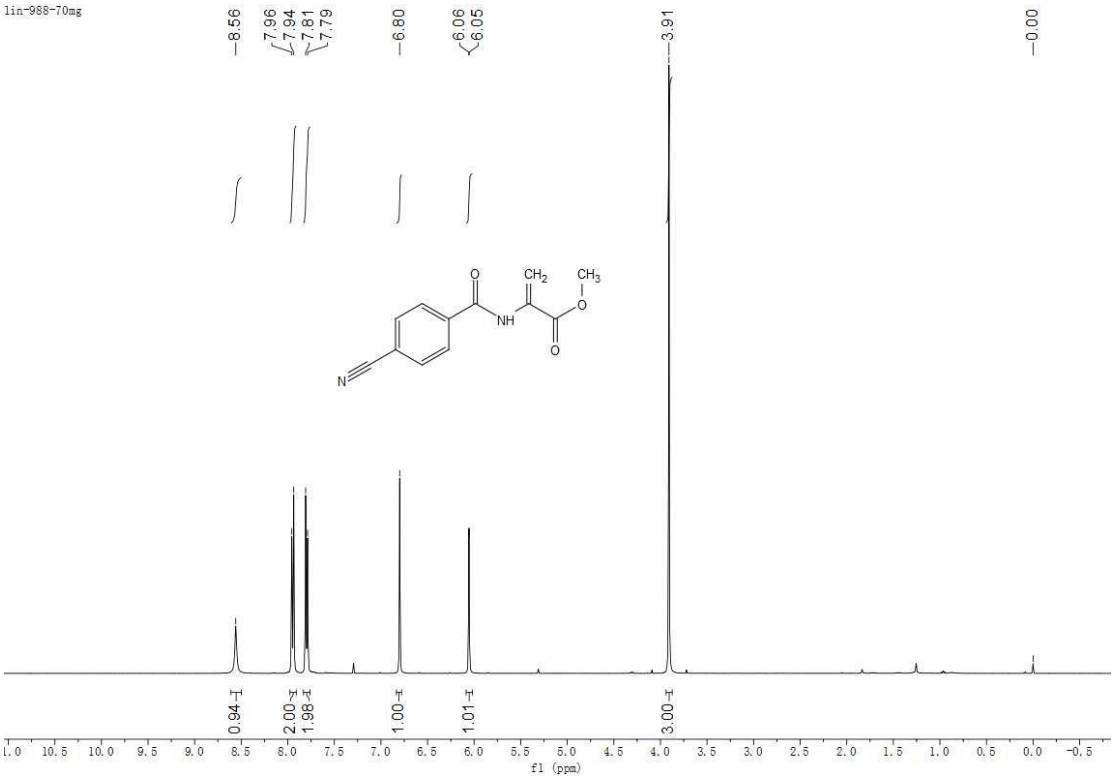
7o


yth-1959-h-h
STANDARD 1H OBSERVE
8.886
7.965
7.939
7.757
7.730
6.805
6.037
3.893
0.000
1.00
1.90
1.96
1.00
1.01
2.87
f1 (ppm)

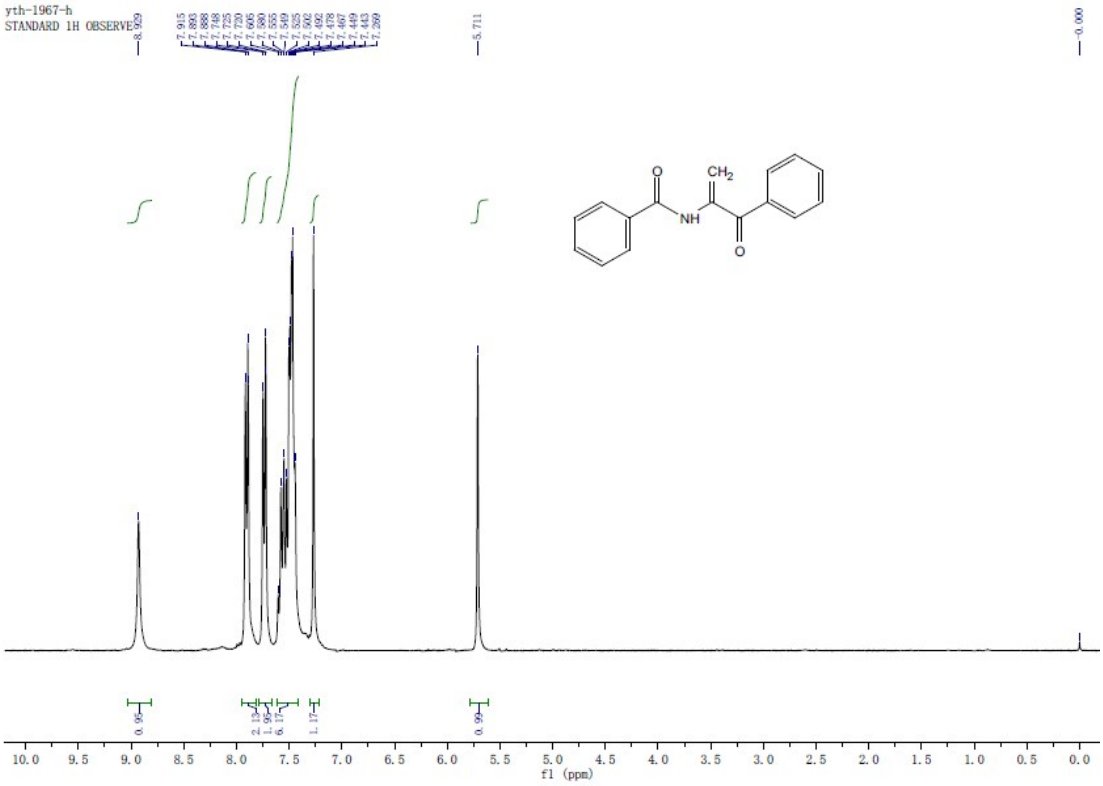

yth-1959-c
13C OBSERVE
164.51
164.30
137.33
134.17
133.74
133.31
132.87
130.71
127.37
125.82
125.78
125.73
125.68
125.26
121.64
109.48
77.42
77.00
76.58
53.11
f1 (ppm)

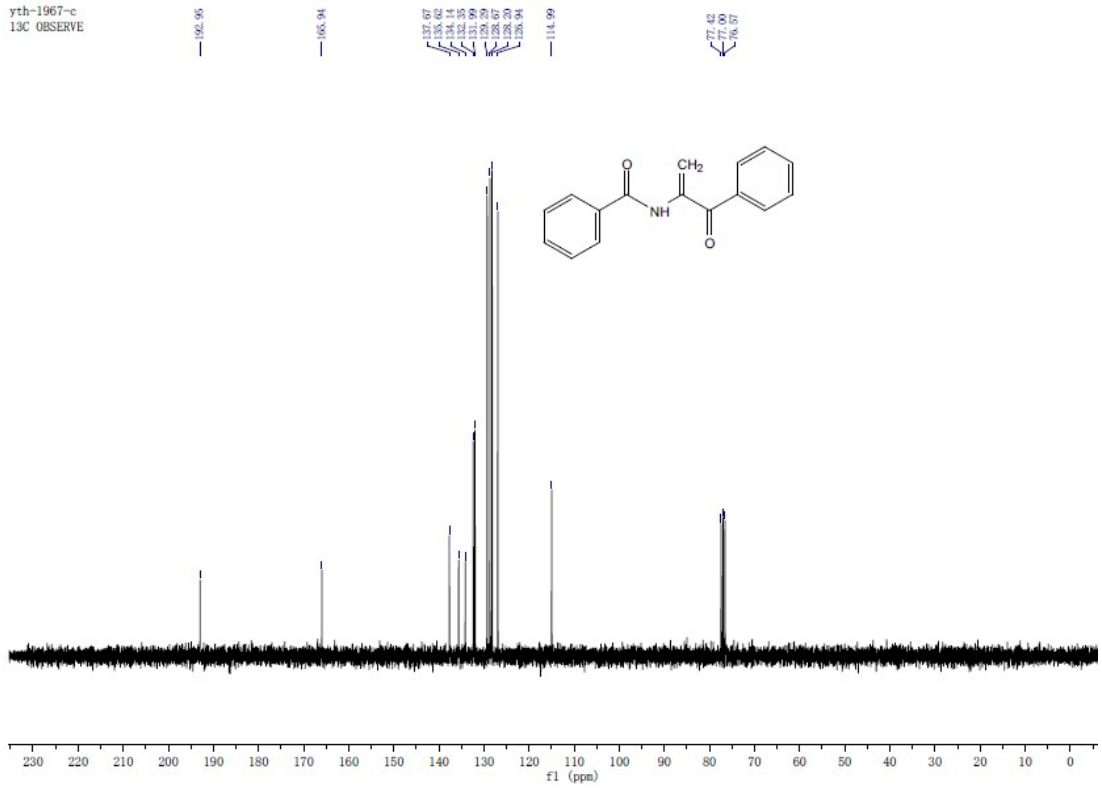
7p


lin-988-70mg
164.45
163.76
137.92
132.57
130.62
127.58
117.73
115.53
109.79
77.32
77.00
76.68
53.19
O
CH2
CH3
NH
O
O
N
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)

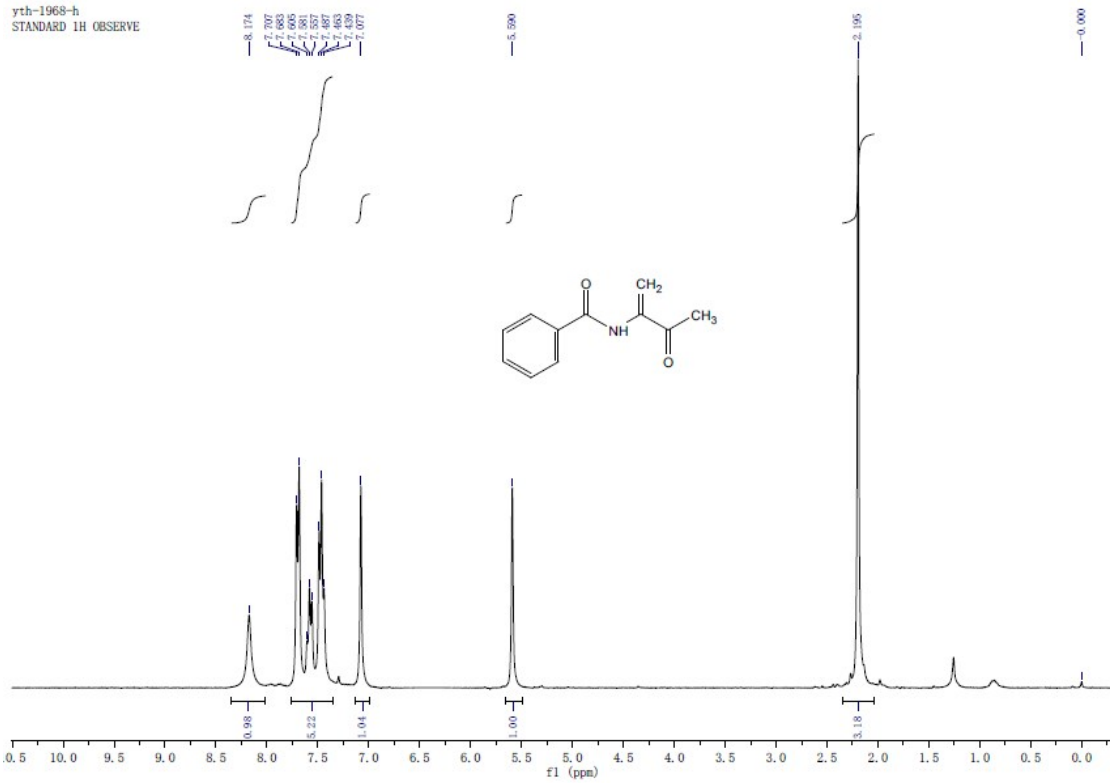

lin-988-70mg
8.56
7.96
7.94
7.81
7.79
6.80
6.06
6.05
3.91
0.00
O
CH2
CH3
NH
O
O
N
0.94
2.00
1.98
1.00
1.01
3.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

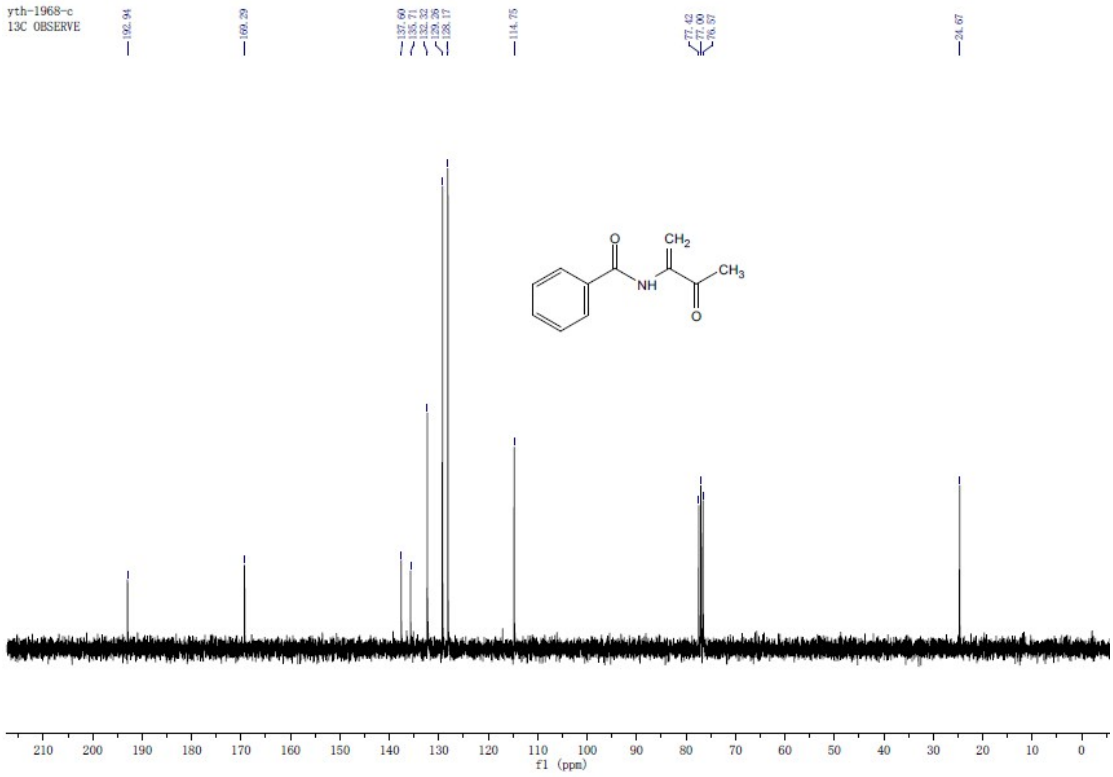
7q


yth-1967-h
STANDARD 1H OBSERVE
8.959
7.915
7.893
7.888
7.748
7.735
7.729
7.606
7.580
7.555
7.549
7.535
7.502
7.478
7.467
7.449
7.443
7.269
5.711
0.000
O
CH2
NH
O
0.95
2.19
1.95
6.17
1.17
0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

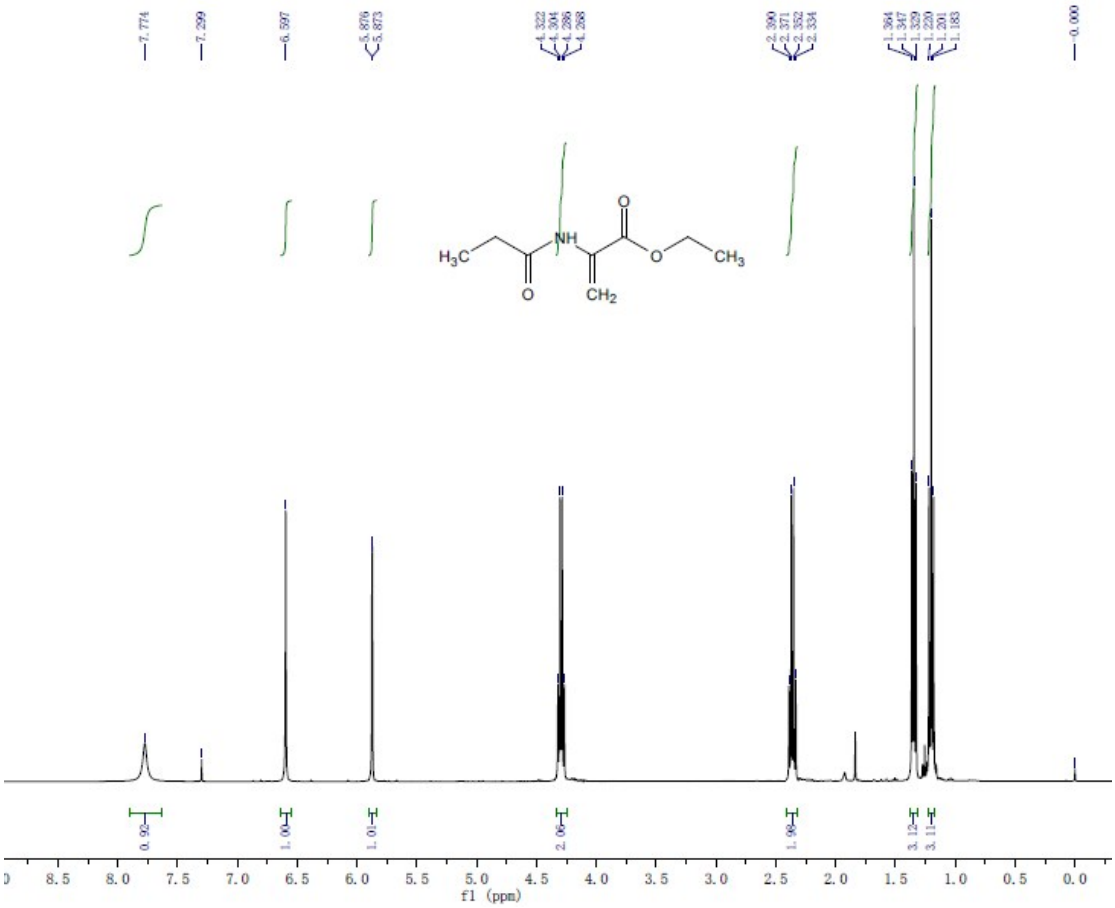

yth-1967-c
13C OBSERVE
192.95
165.94
137.67
135.62
134.14
132.35
131.99
129.29
128.67
128.30
126.94
114.99
77.42
77.00
76.57
O
CH2
NH
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

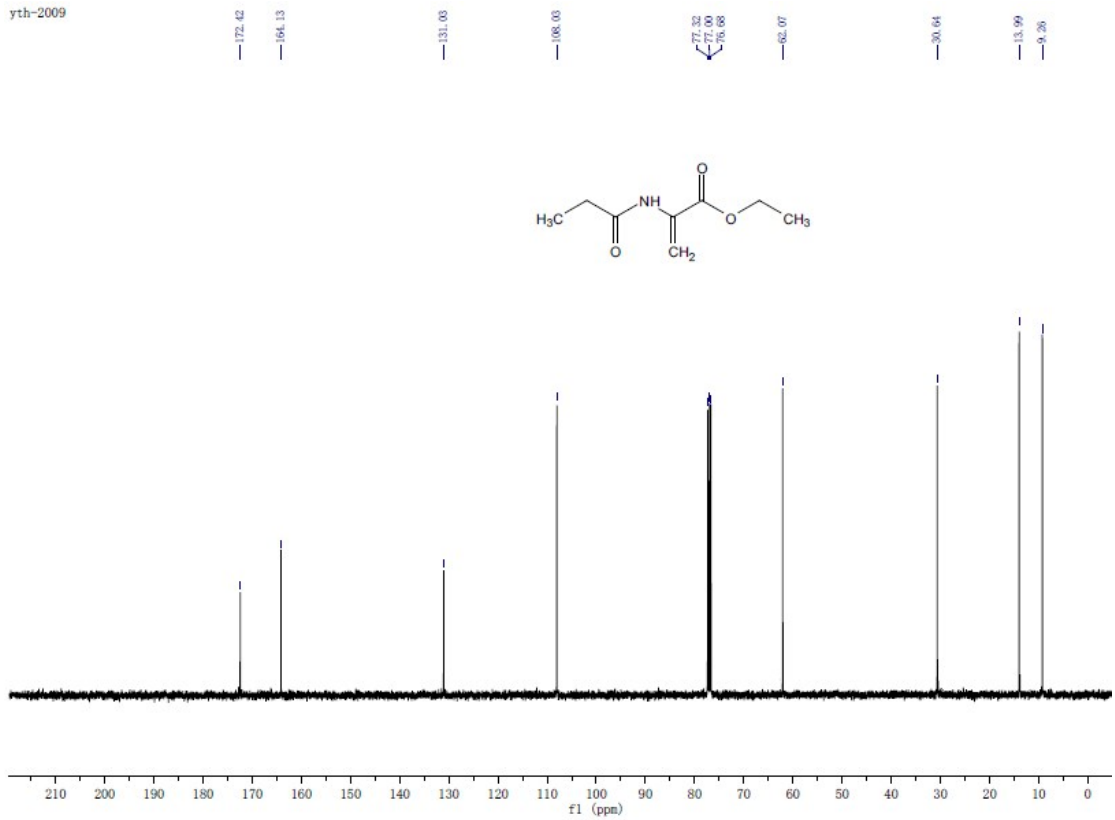
7r


yth-1968-h
STANDARD 1H OBSERVE
8.174
7.707
7.685
7.605
7.581
7.557
7.487
7.463
7.439
7.077
5.599
2.195
0.000
0.98
5.22
1.04
1.00
3.18
f1 (ppm)

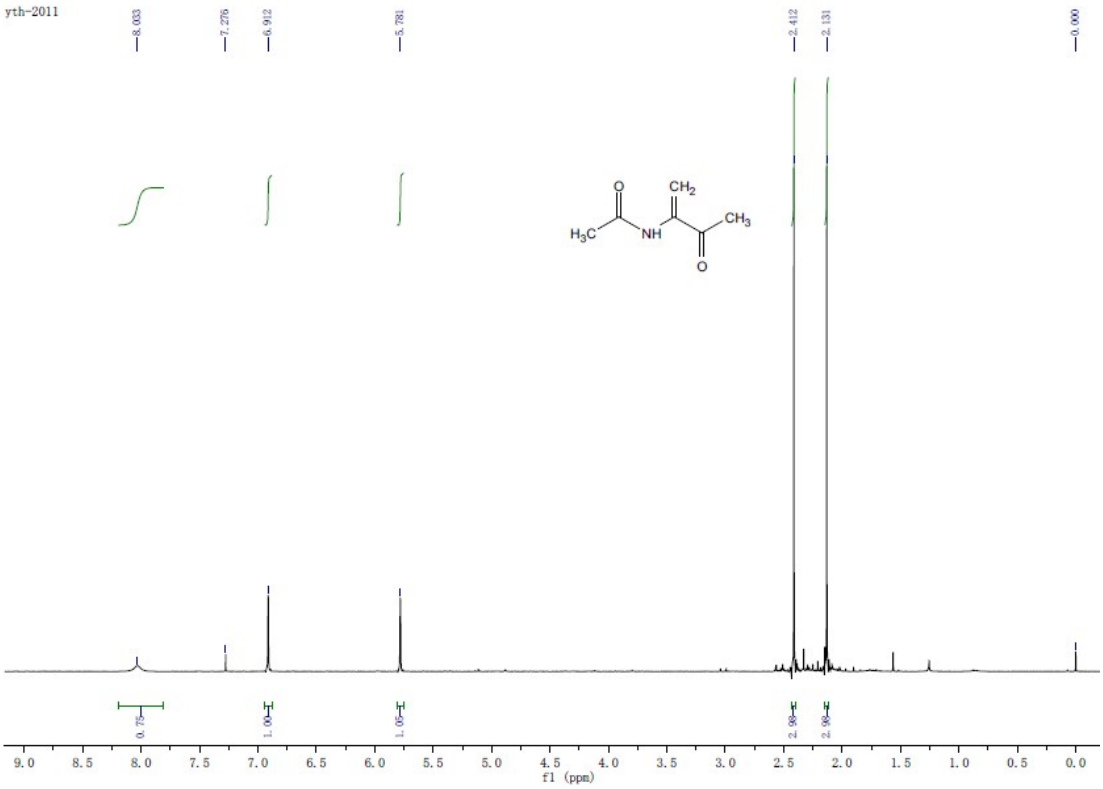

yth-1968-c
13C OBSERVE
192.94
169.29
137.60
135.71
132.32
129.36
128.17
114.75
77.42
77.00
76.57
24.67
f1 (ppm)

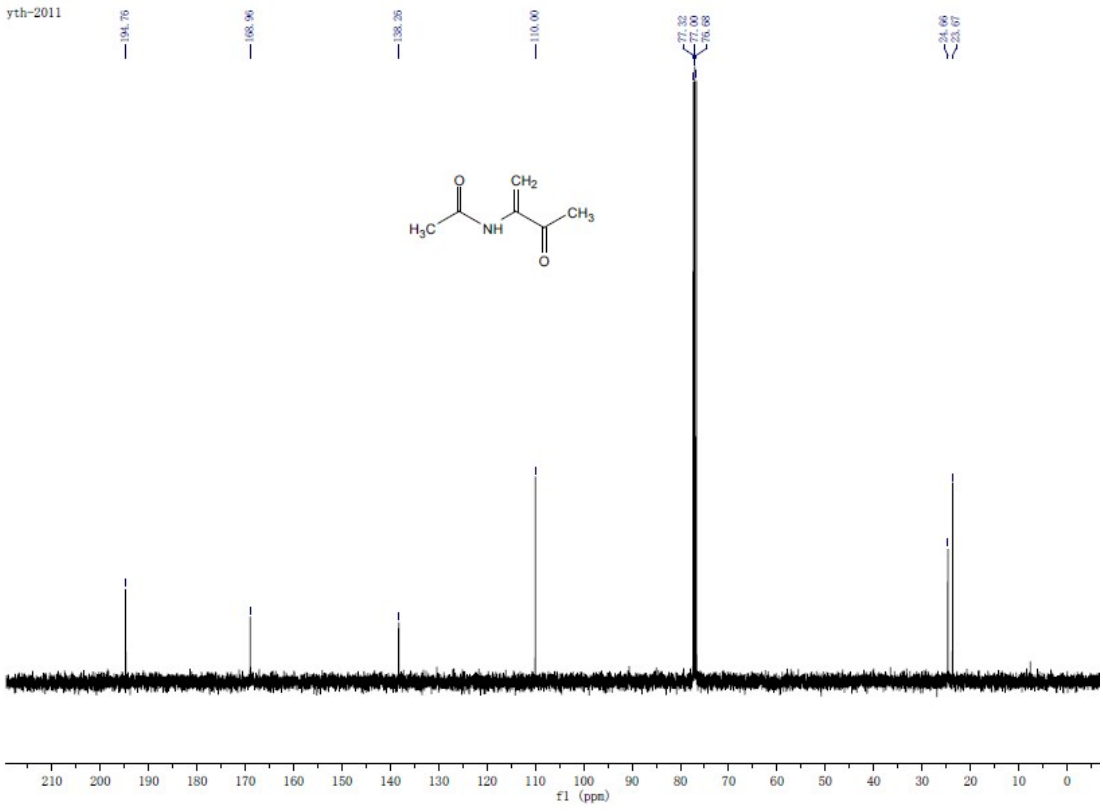
7v


7.774
7.299
6.597
5.876
5.873
4.322
4.304
4.286
4.268
2.390
2.371
2.352
2.334
1.364
1.347
1.329
1.220
1.201
1.183
0.000
NH
O
O
O
H_3C
CH_3
CH_2
0.92
1.00
1.01
2.06
1.99
3.12
3.11
f1 (ppm)

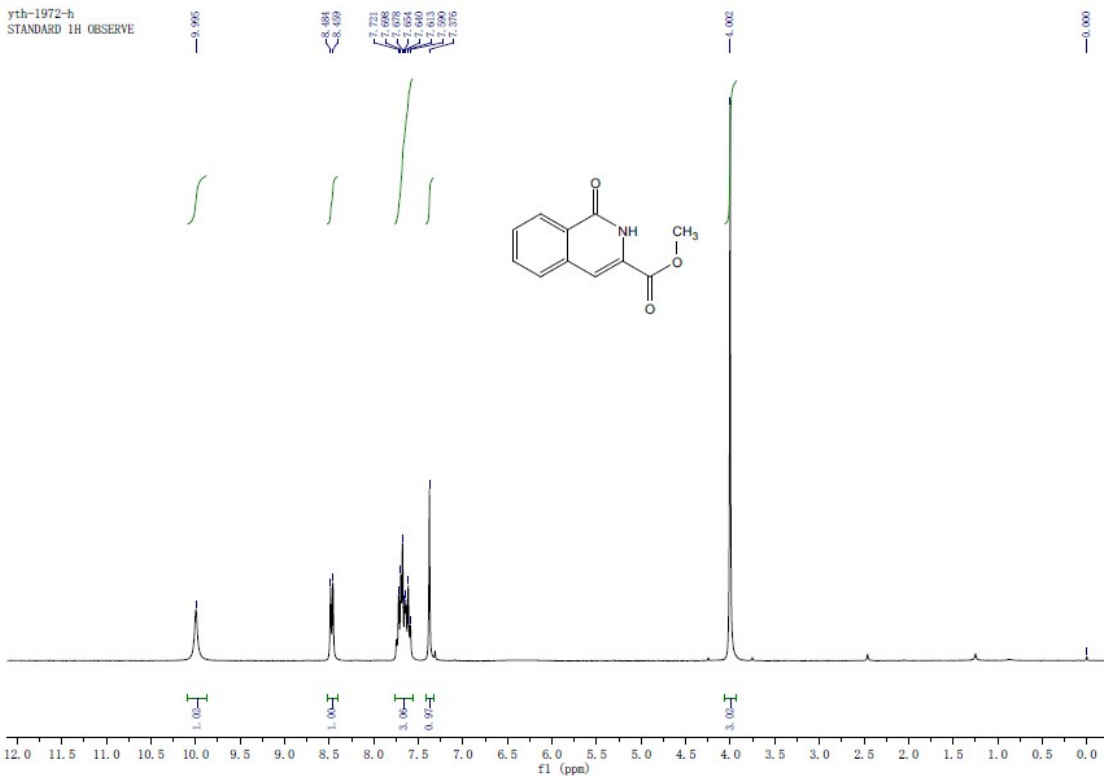

yth-2009
172.42
164.13
131.03
108.03
77.32
77.00
76.68
62.07
30.64
13.99
9.26
NH
O
O
O
H_3C
CH_3
CH_2
f1 (ppm)

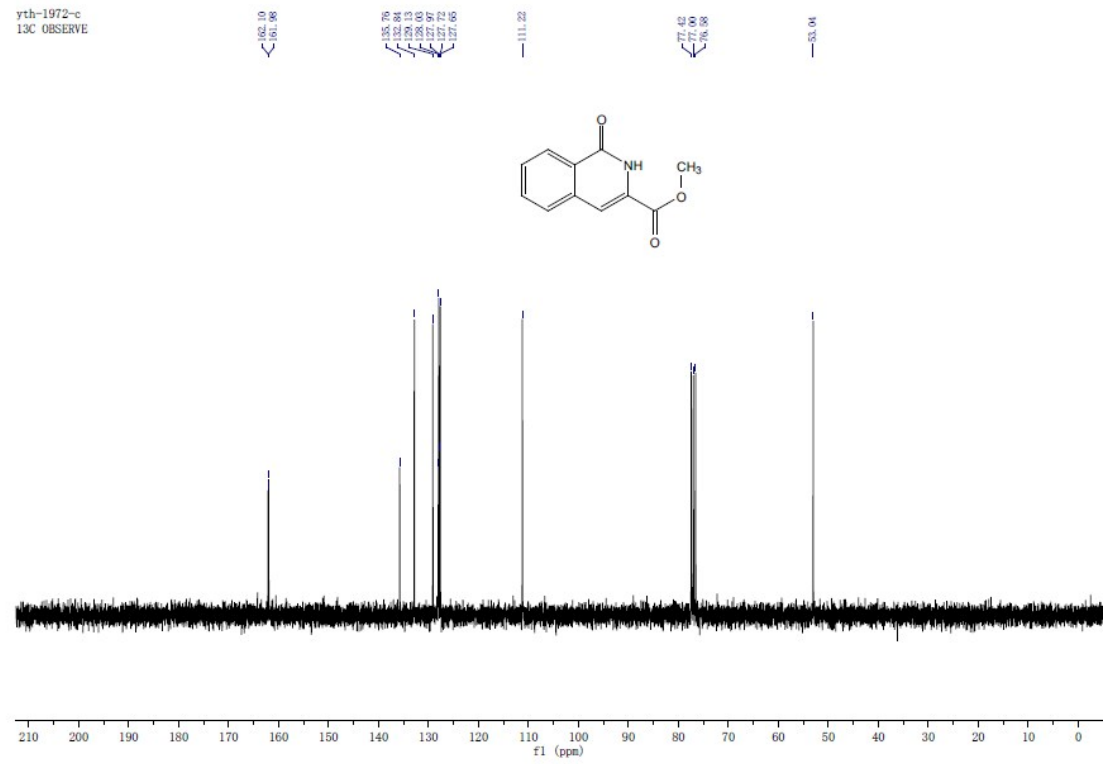
7w


yth-2011
8.033
7.276
6.912
5.781
2.412
2.131
0.000
0.75
1.00
1.05
2.98
2.98
f1 (ppm)

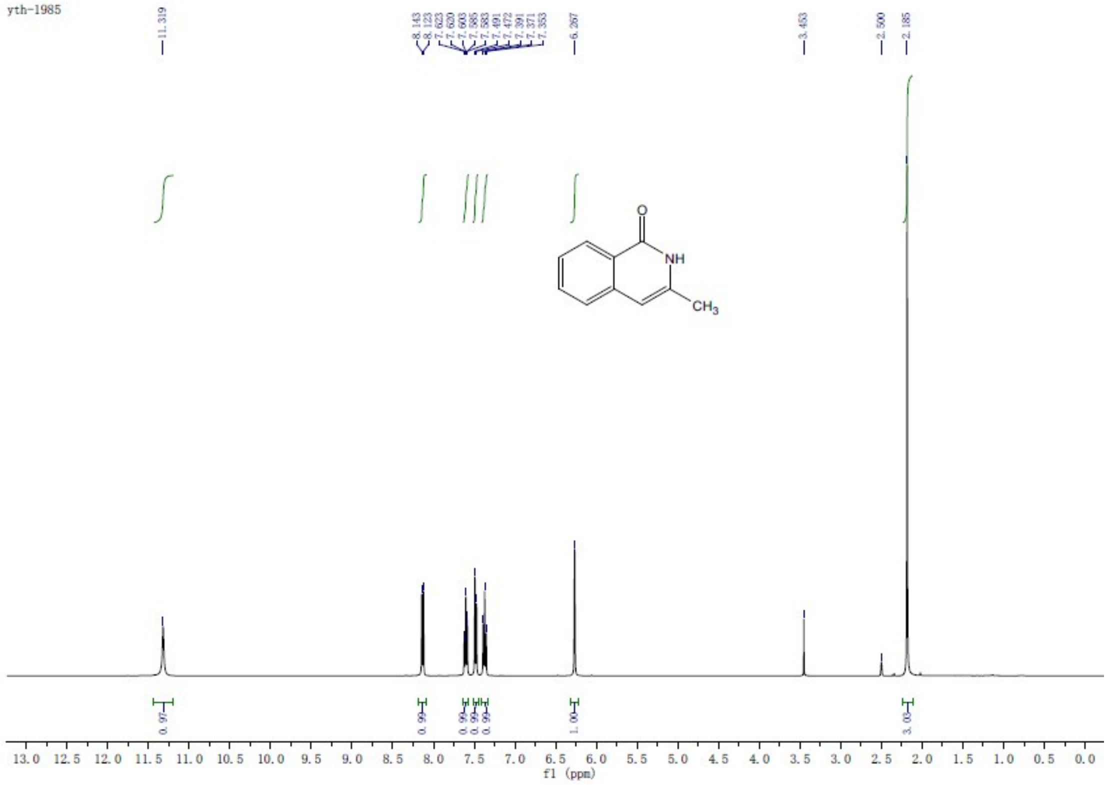

yth-2011
194.76
168.96
138.26
110.00
77.32
77.00
76.68
24.66
23.67
f1 (ppm)

2a (Method B)

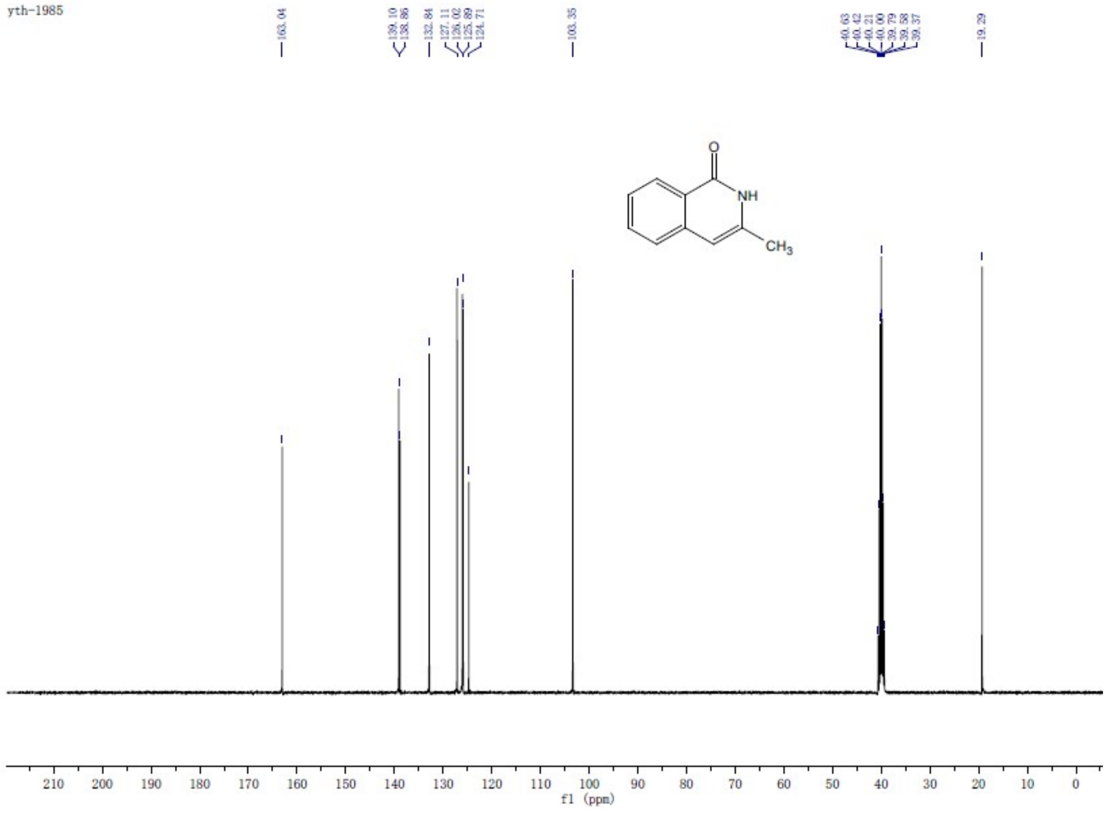

yth-1972-h
STANDARD 1H OBSERVE
9.995
8.484
8.459
7.721
7.698
7.678
7.654
7.640
7.613
7.390
7.376
4.002
0.000
NH
CH3
O
1.00
1.00
3.06
0.97
3.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


yth-1972-c
13C OBSERVE
162.19
161.98
135.76
132.84
129.13
128.03
127.97
127.72
127.65
111.22
77.42
77.00
76.58
53.04
NH
CH3
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2j (Method B)

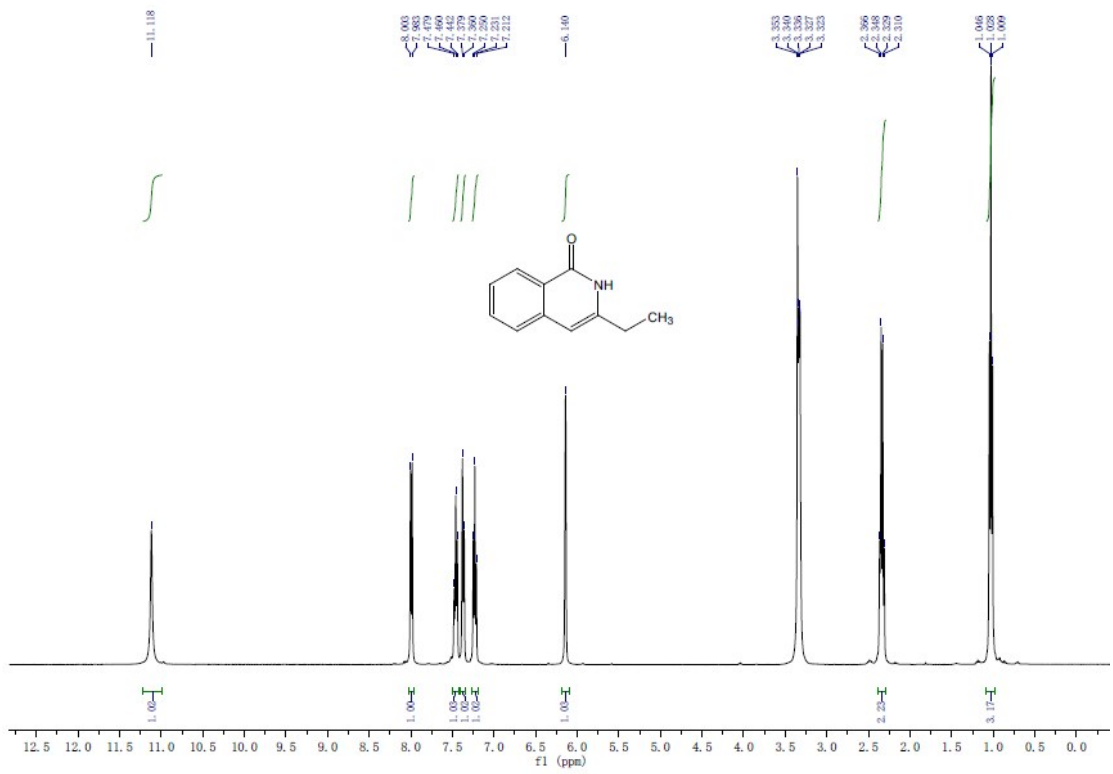


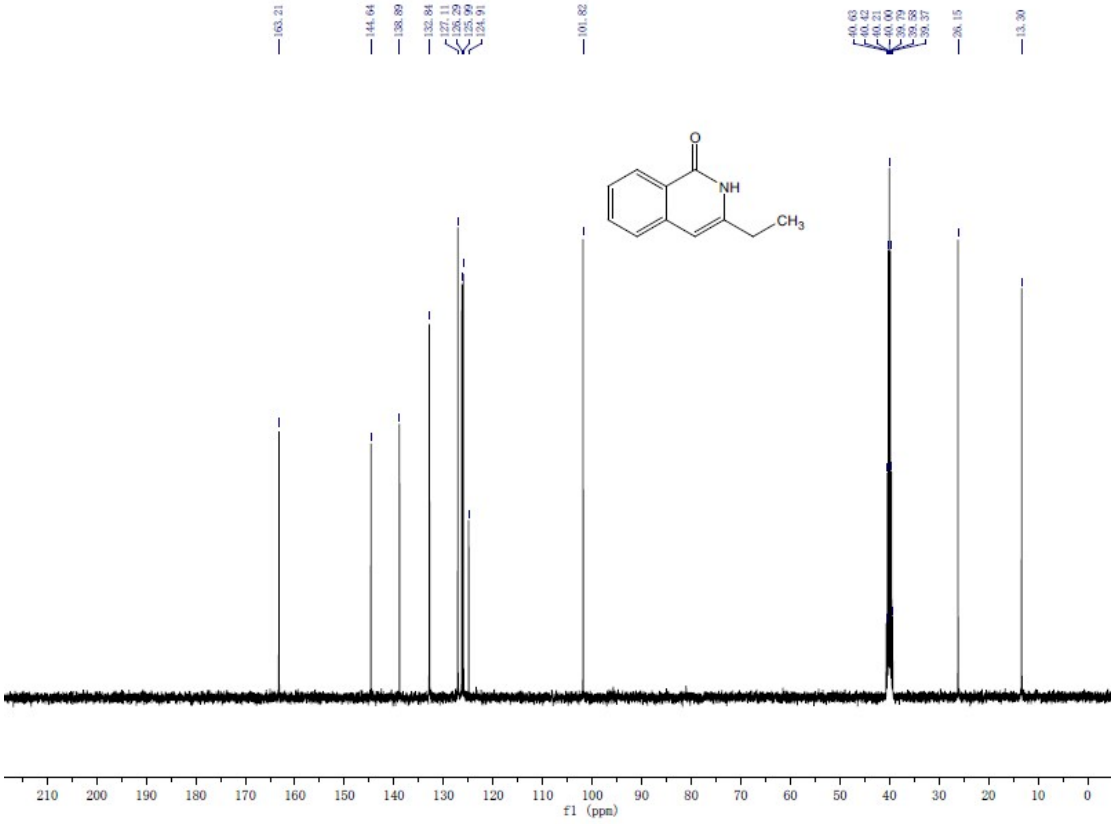
yth-1985
11.319
8.143
8.123
7.623
7.620
7.603
7.585
7.583
7.491
7.472
7.391
7.371
7.353
6.267
3.453
2.500
2.185
NH
O
CH3
0.97
0.99
0.99
0.99
0.99
1.00
3.03
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



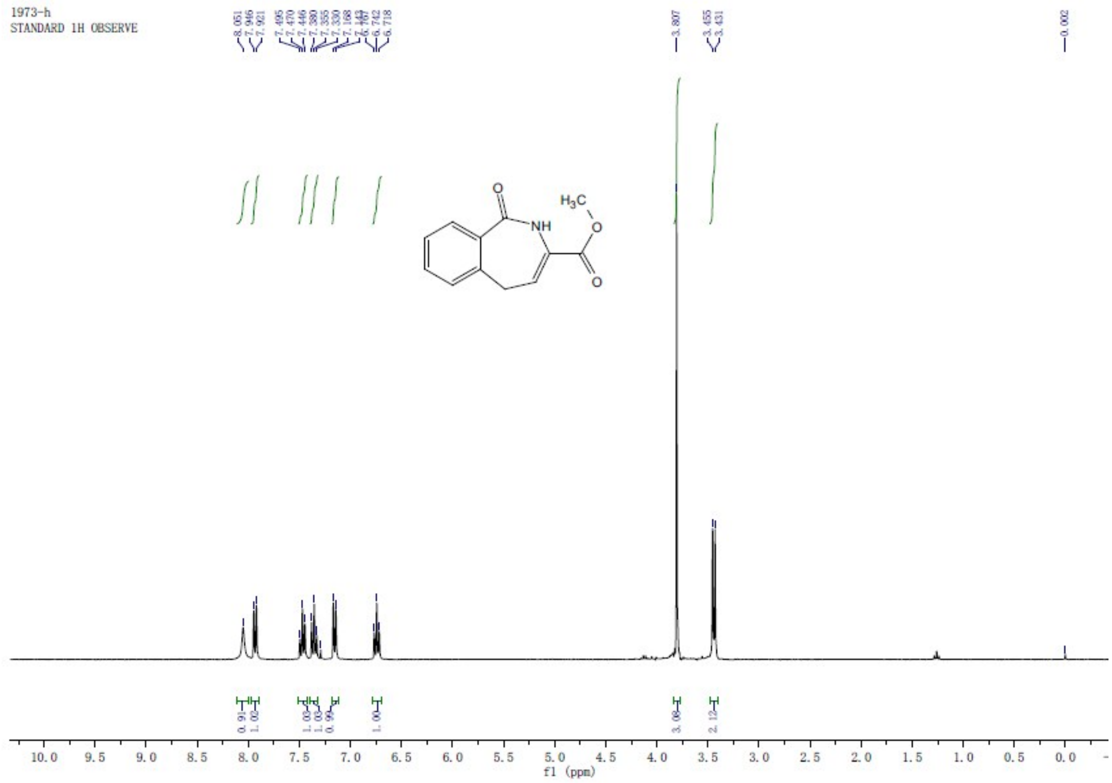
yth-1985
163.04
139.10
138.86
132.84
127.11
126.02
125.89
124.71
103.35
40.63
40.42
40.21
40.00
39.79
39.58
39.37
19.29
NH
O
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

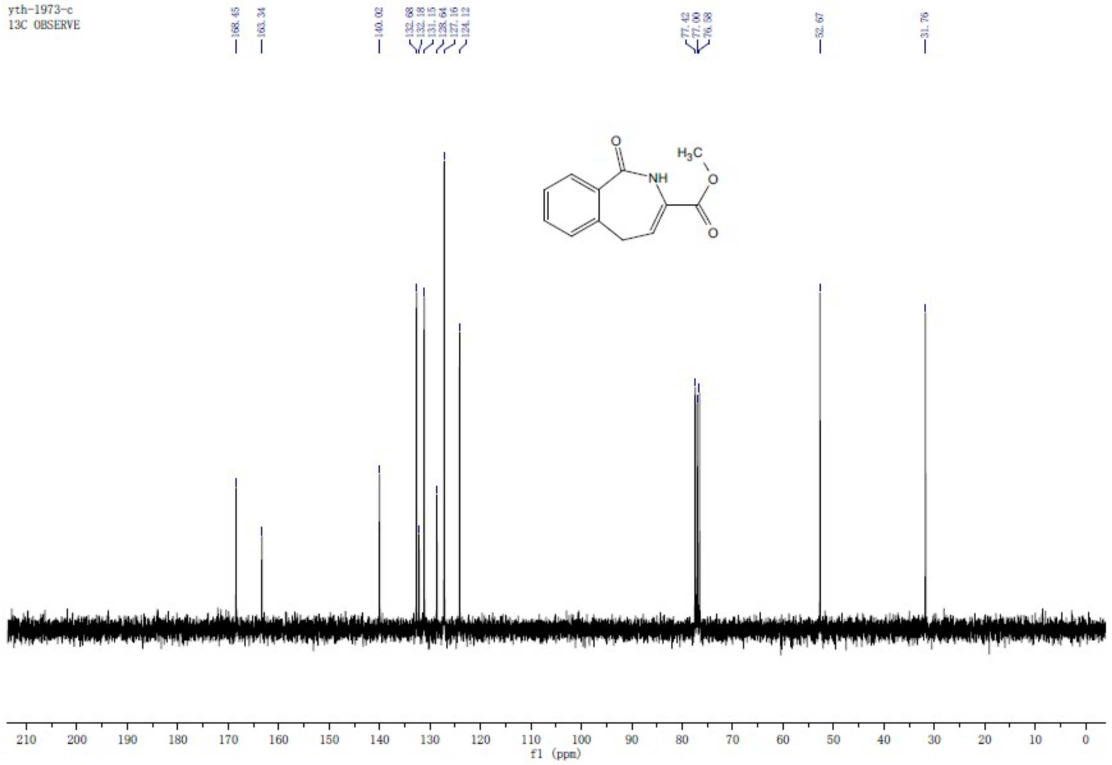
2k (Method B)


11.118
8.000
7.983
7.479
7.460
7.442
7.379
7.369
7.250
7.231
7.212
6.149
3.353
3.340
3.336
3.327
3.323
2.366
2.348
2.329
2.310
1.046
1.028
1.009
O
NH
CH3
1.00
1.00
1.02
1.02
1.00
2.25
3.17
f1 (ppm)

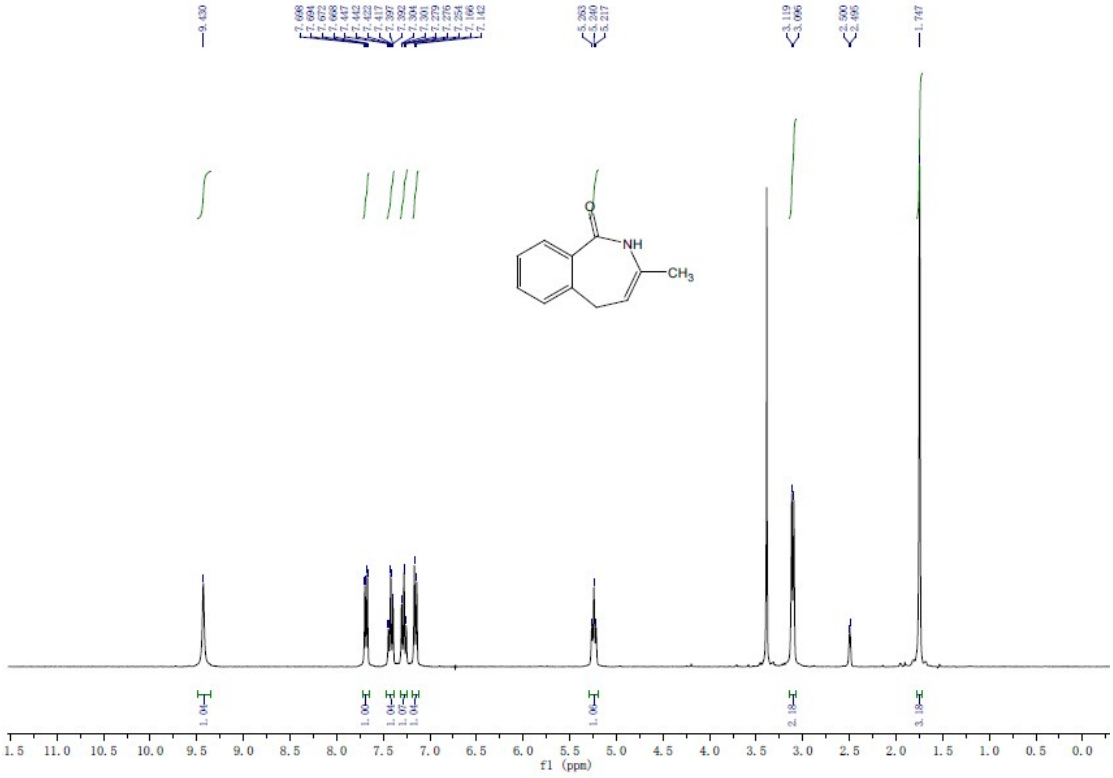

163.21
144.64
138.89
132.84
127.11
126.29
125.99
124.91
101.82
60.63
60.42
60.21
60.00
59.79
59.58
59.37
26.15
13.30
O
NH
CH3
f1 (ppm)

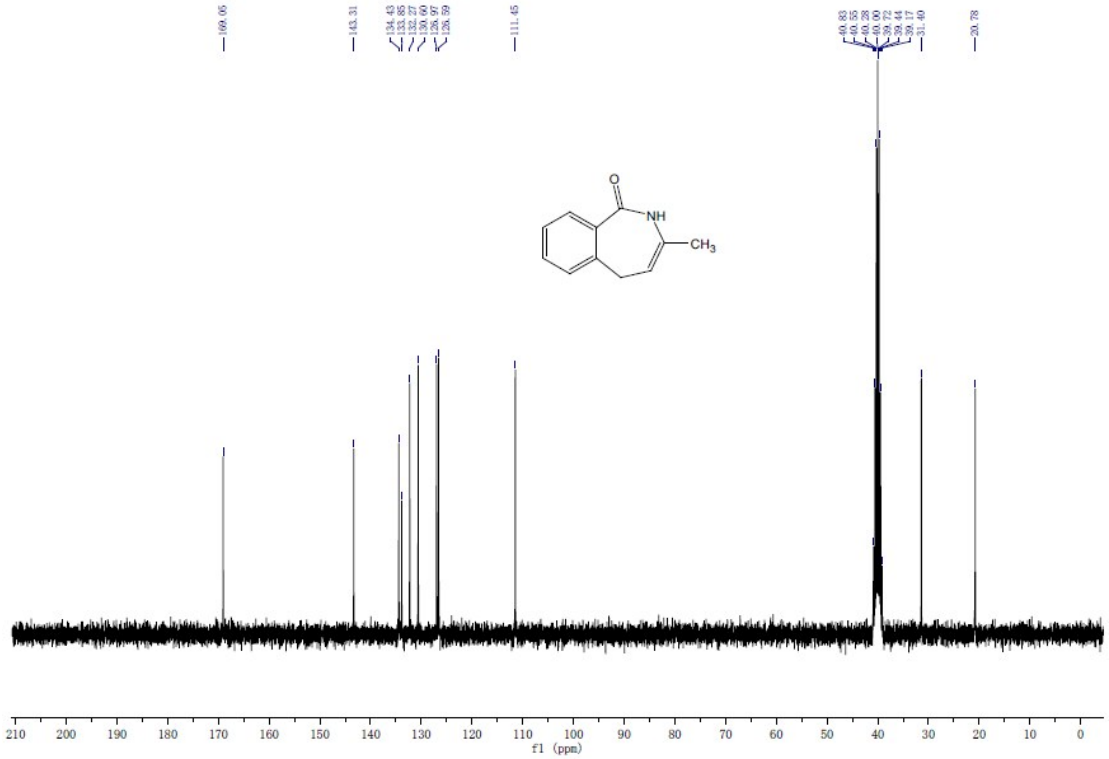
4a (Method B)


1973-h
STANDARD 1H OBSERVE
8.051
7.946
7.921
7.495
7.470
7.446
7.380
7.355
7.330
7.193
7.168
6.767
6.742
6.718
3.807
3.455
3.431
-0.002
H3C
O
NH
O
O
0.91
1.02
1.03
1.03
1.03
0.99
1.00
3.08
2.12
f1 (ppm)

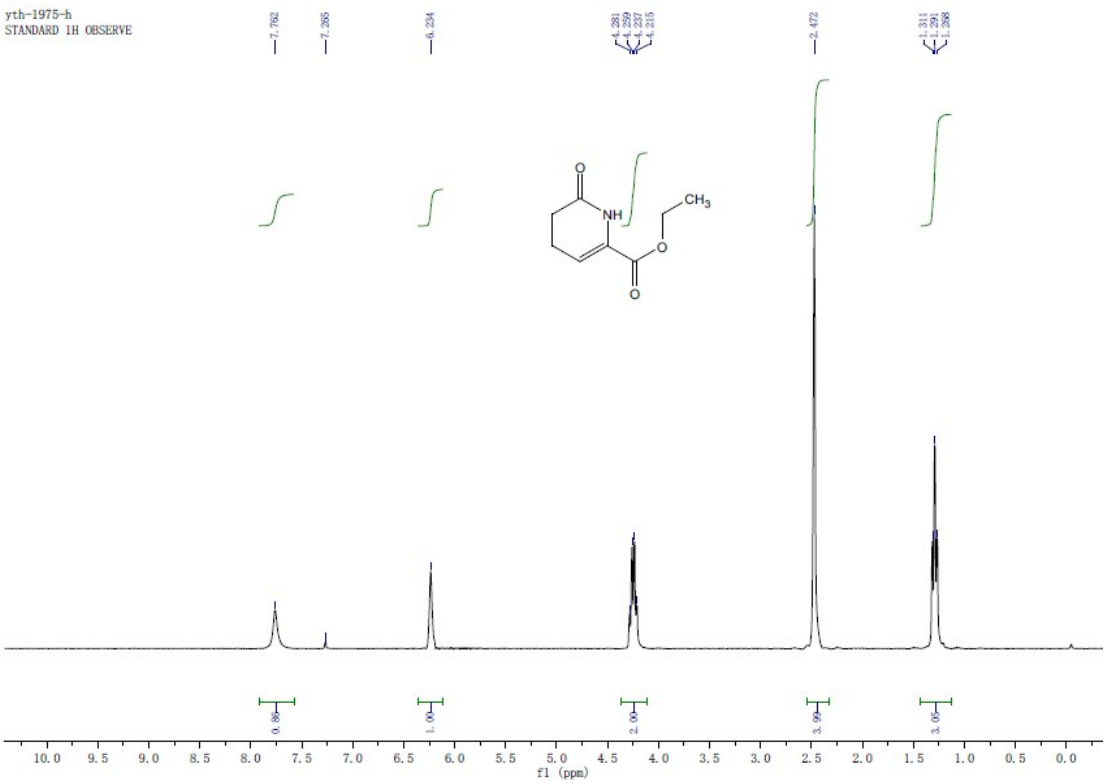

yth-1973-c
13C OBSERVE
168.45
163.34
140.02
132.68
132.18
131.15
128.64
127.16
124.12
77.42
77.00
76.58
52.67
31.76
H3C
O
NH
O
O
f1 (ppm)

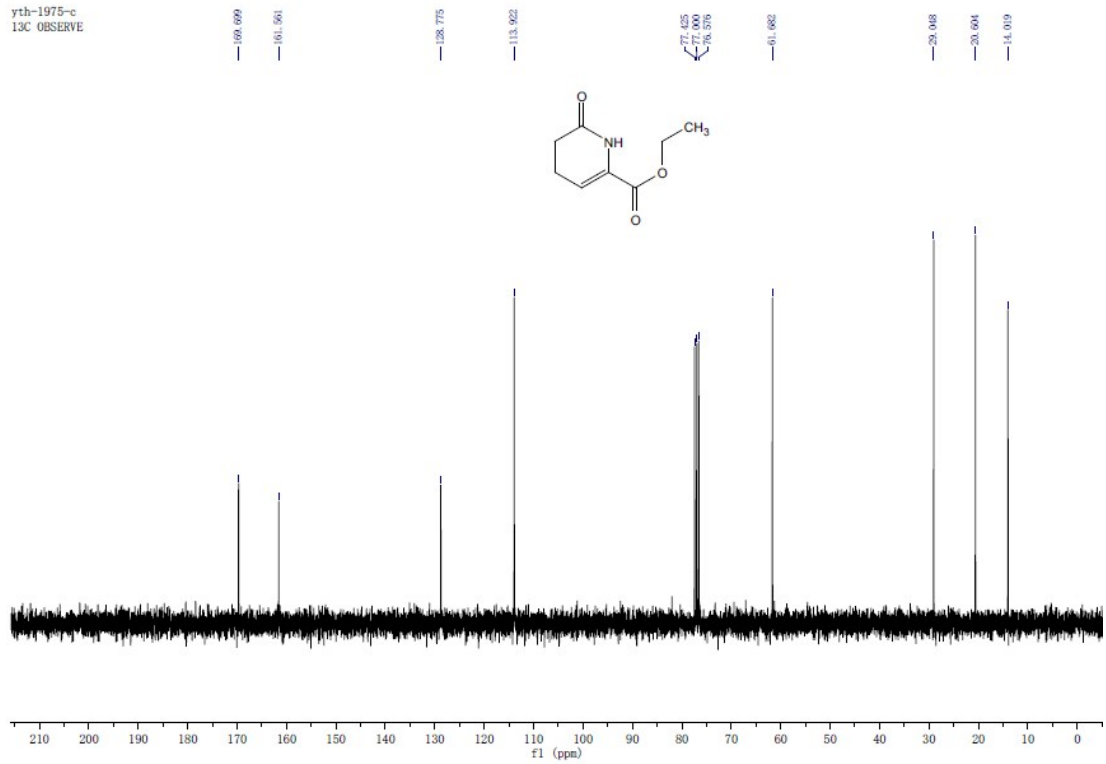
4c (Method B)


9.430
7.698
7.694
7.673
7.668
7.447
7.442
7.422
7.417
7.397
7.392
7.304
7.301
7.279
7.276
7.254
7.166
7.142
5.263
5.240
5.217
3.119
3.066
2.500
2.495
1.747
O
NH
CH3
1.00
1.00
1.04
1.07
1.04
1.00
2.18
3.18
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

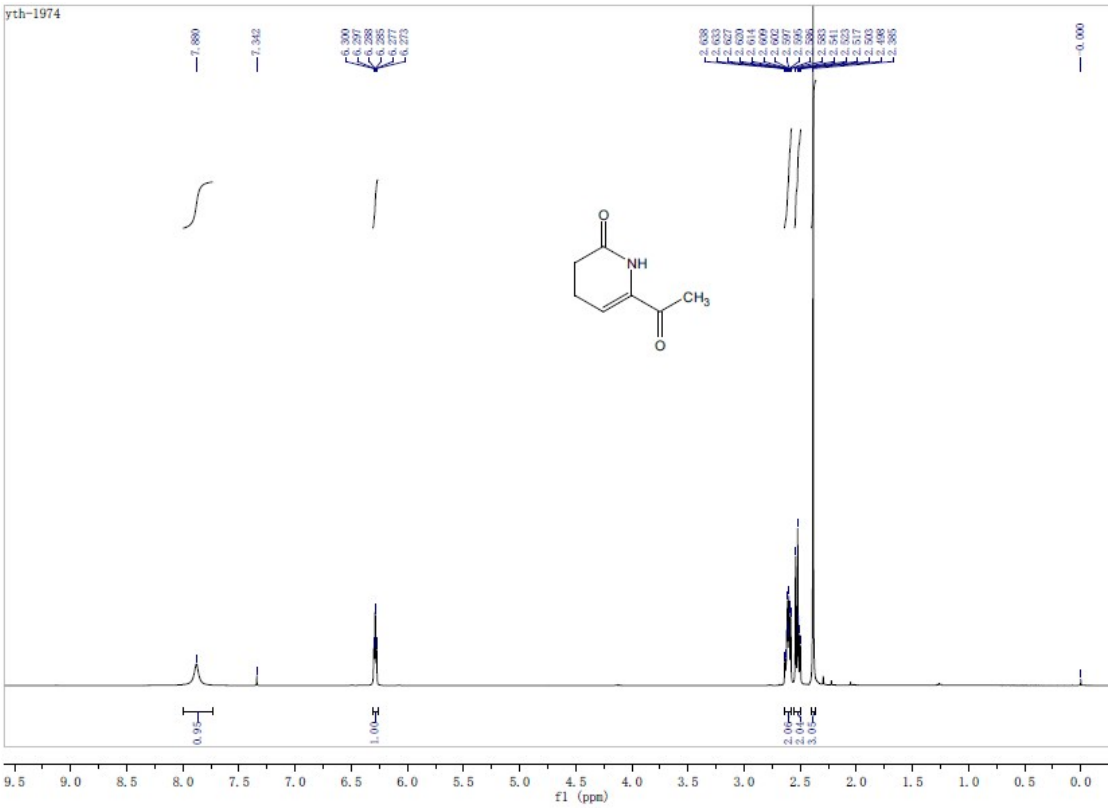

169.05
143.31
134.43
133.85
132.27
130.60
126.97
126.59
111.45
40.83
40.55
40.28
40.00
39.72
39.44
39.17
31.40
20.78
O
NH
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

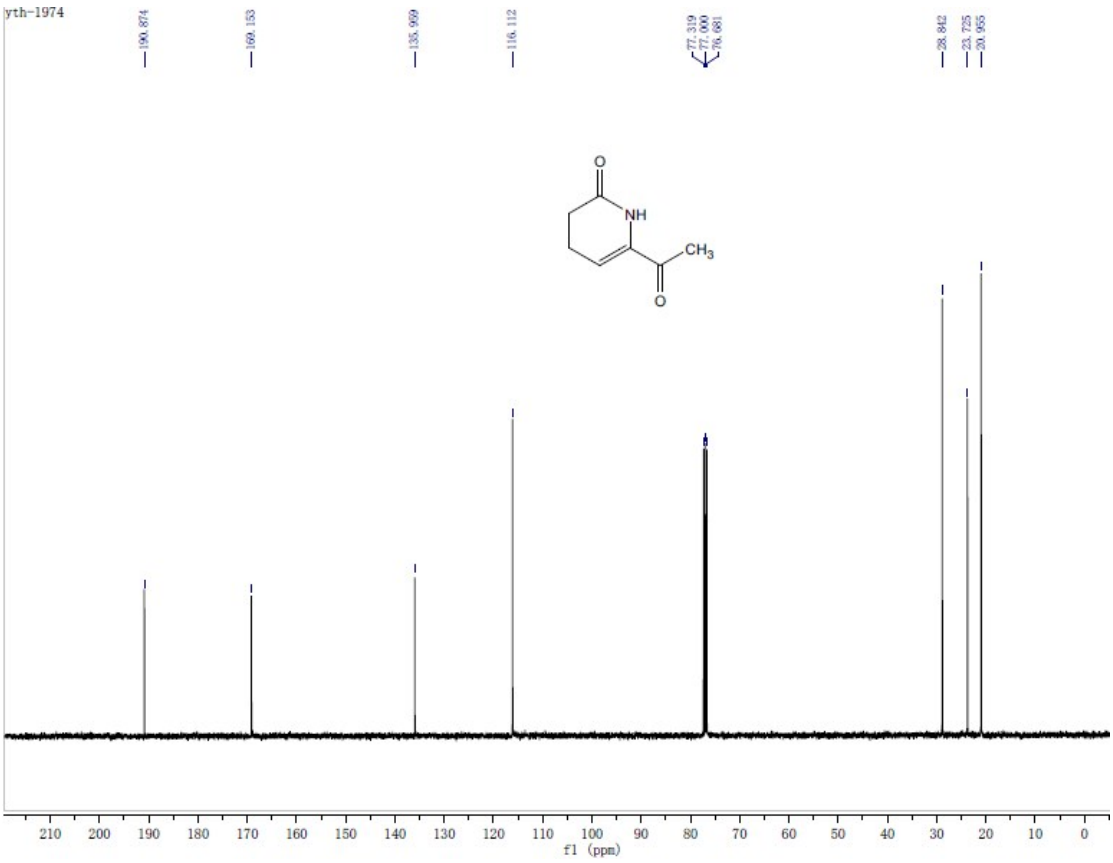
9a


yth-1975-h
STANDARD 1H OBSERVE
7.762
7.265
6.234
4.281
4.259
4.237
4.215
2.472
1.311
1.291
1.268
0.86
1.00
2.00
3.99
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
NH
O
O
CH3

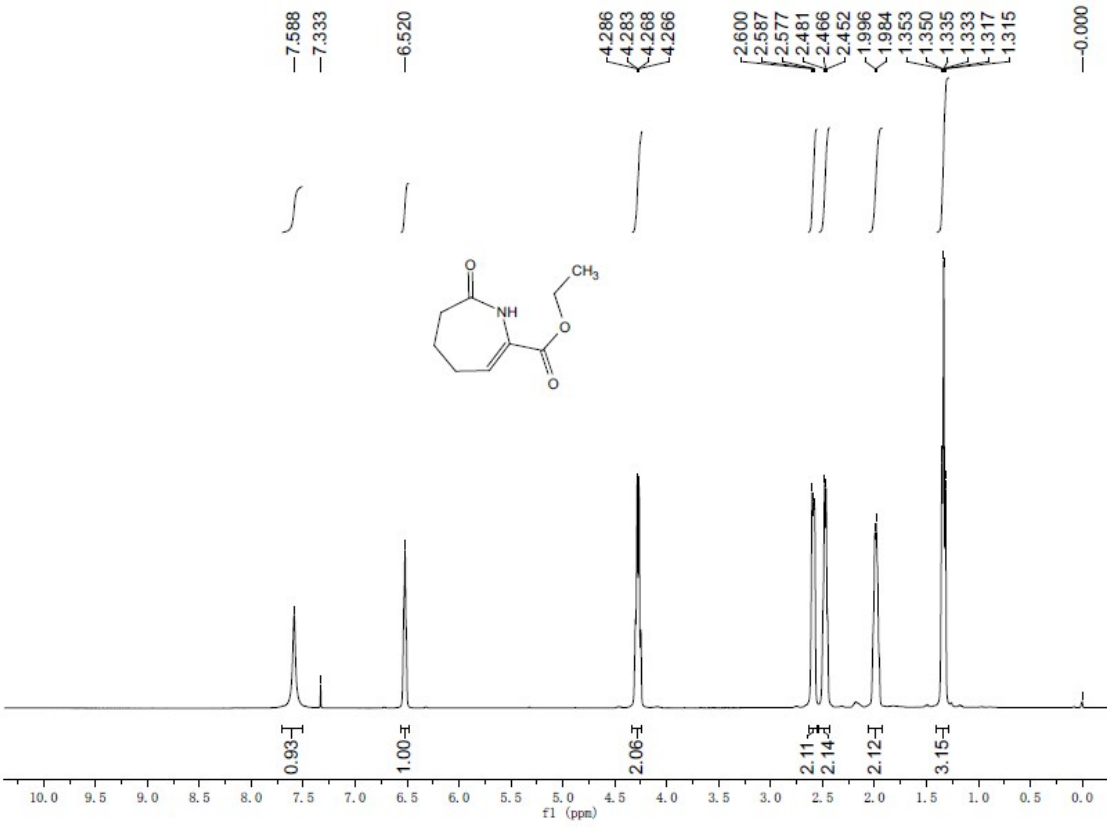

yth-1975-c
13C OBSERVE
169.699
161.561
128.775
113.922
77.425
77.000
76.575
61.682
29.048
20.604
14.019
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
NH
O
O
CH3

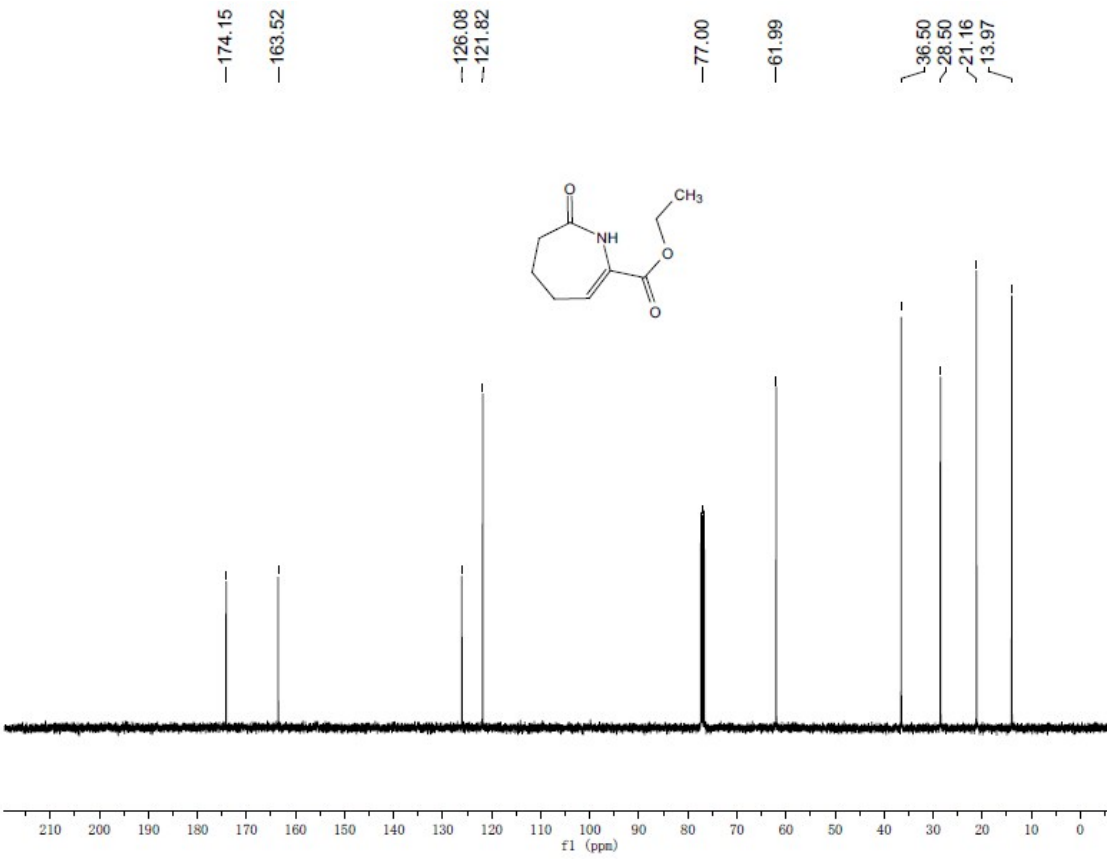
9b


yth-1974
7.889
7.342
6.300
6.297
6.288
6.285
6.277
6.273
2.638
2.633
2.627
2.623
2.614
2.609
2.602
2.597
2.595
2.588
2.583
2.541
2.523
2.517
2.503
2.498
2.385
0.000
NH
CH3
O
0.95
1.00
2.06
2.04
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

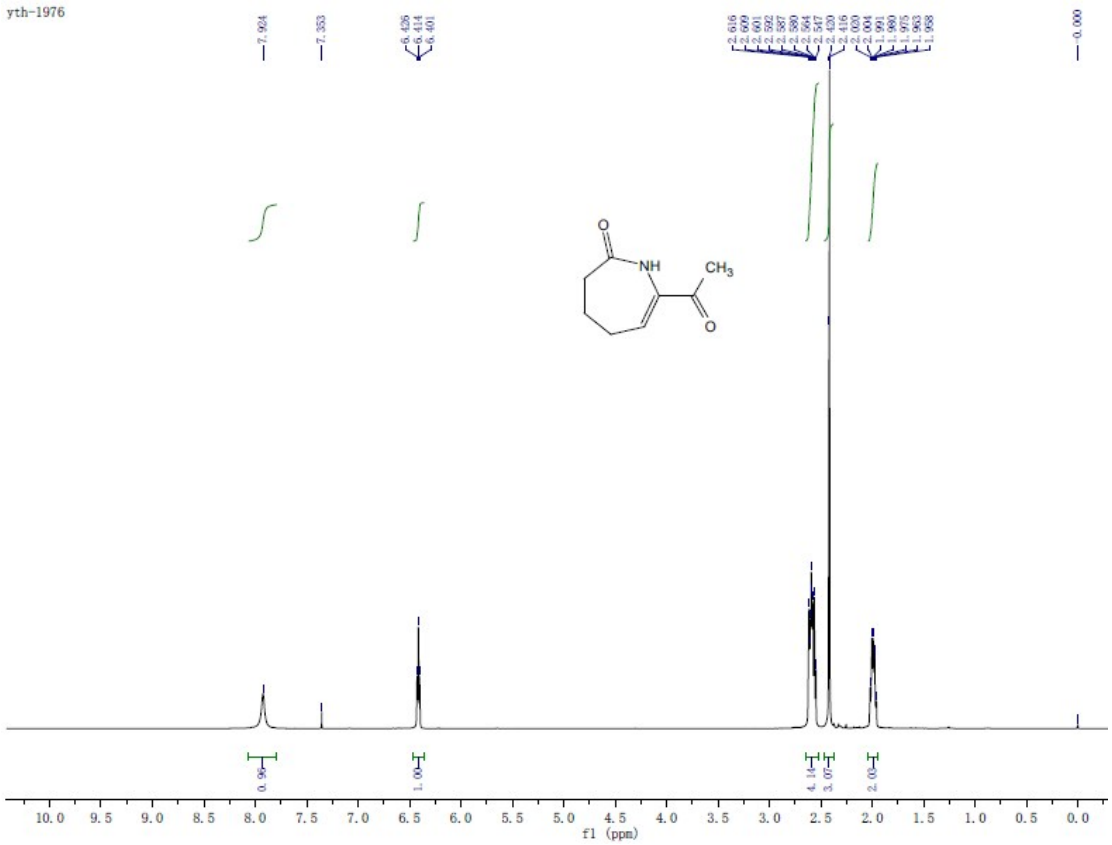

yth-1974
190.874
169.153
135.969
116.112
77.319
77.000
76.681
28.842
23.725
20.955
NH
CH3
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

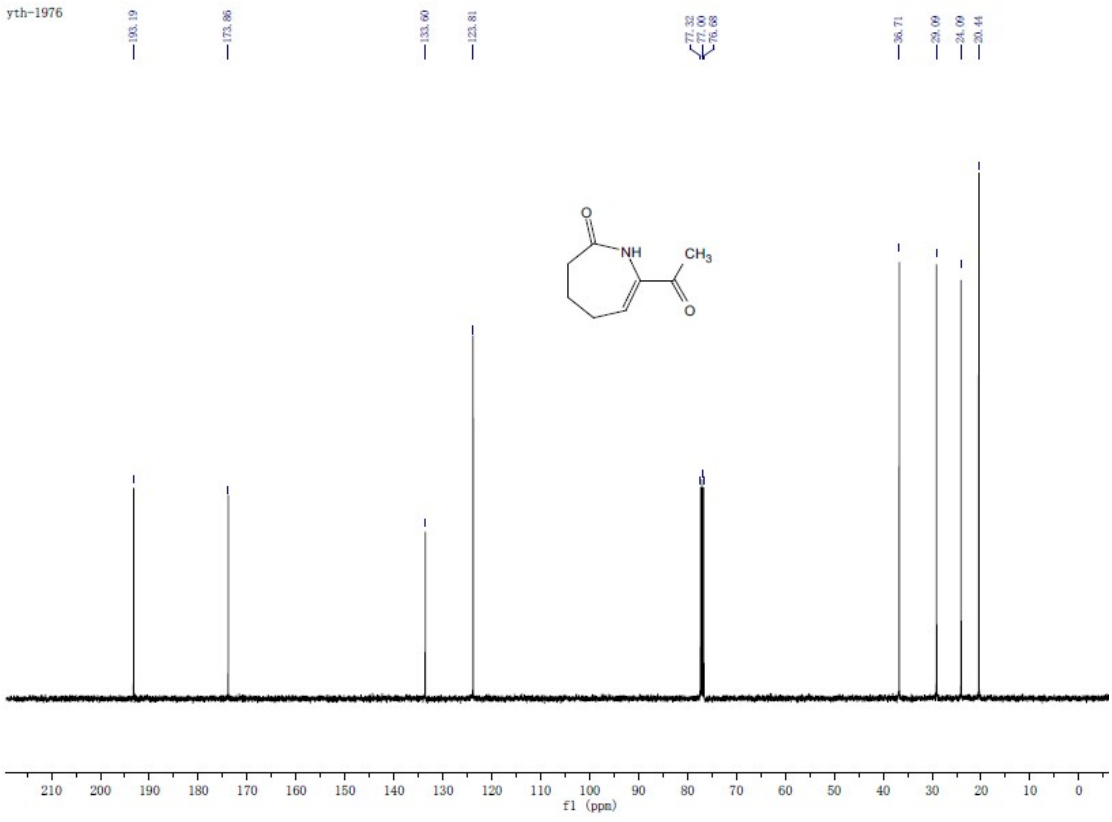
9c


7.588
7.333
6.520
4.286
4.283
4.268
4.266
2.600
2.587
2.577
2.481
2.466
2.452
1.996
1.984
1.353
1.350
1.335
1.333
1.317
1.315
0.000
0.93
1.00
2.06
2.11
2.14
2.12
3.15
f1 (ppm)

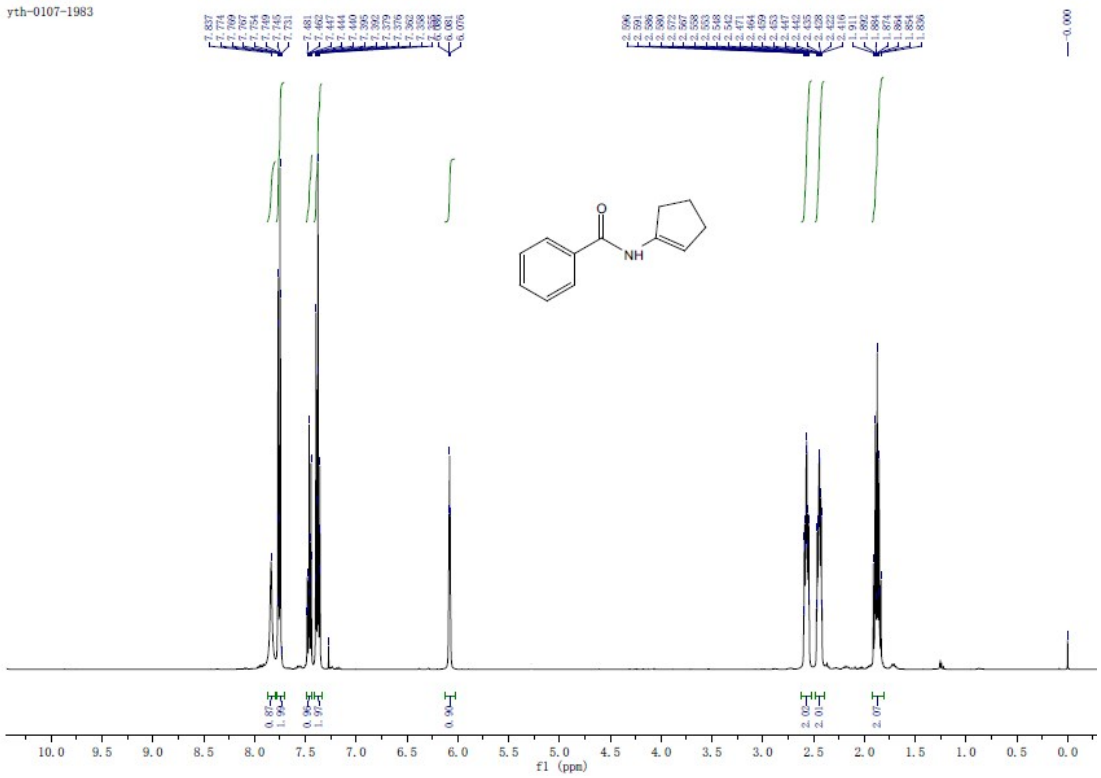

174.15
163.52
126.08
121.82
77.00
61.99
36.50
28.50
21.16
13.97
f1 (ppm)

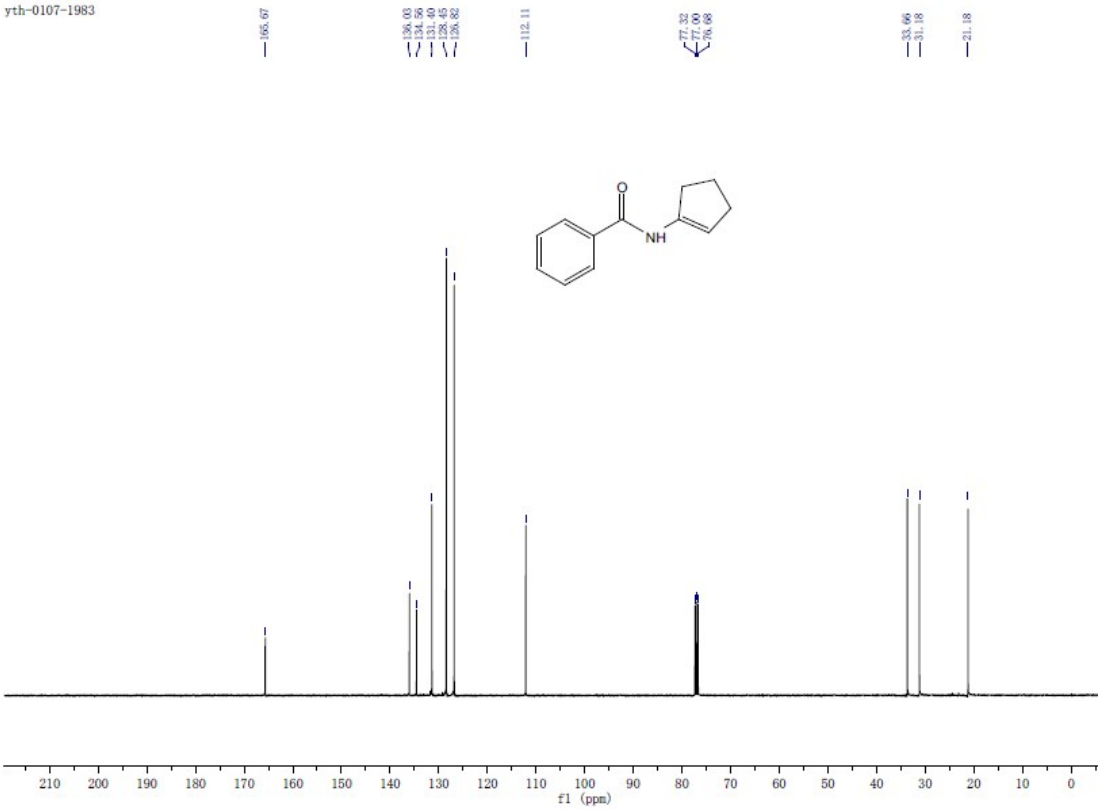
9d


yth-1976
7.924
7.353
6.426
6.414
6.401
2.616
2.609
2.601
2.592
2.587
2.580
2.564
2.547
2.420
2.416
2.020
2.004
1.993
1.980
1.975
1.963
1.958
0.000
NH
CH3
O
O
0.96
1.00
4.14
3.07
2.00
f1 (ppm)

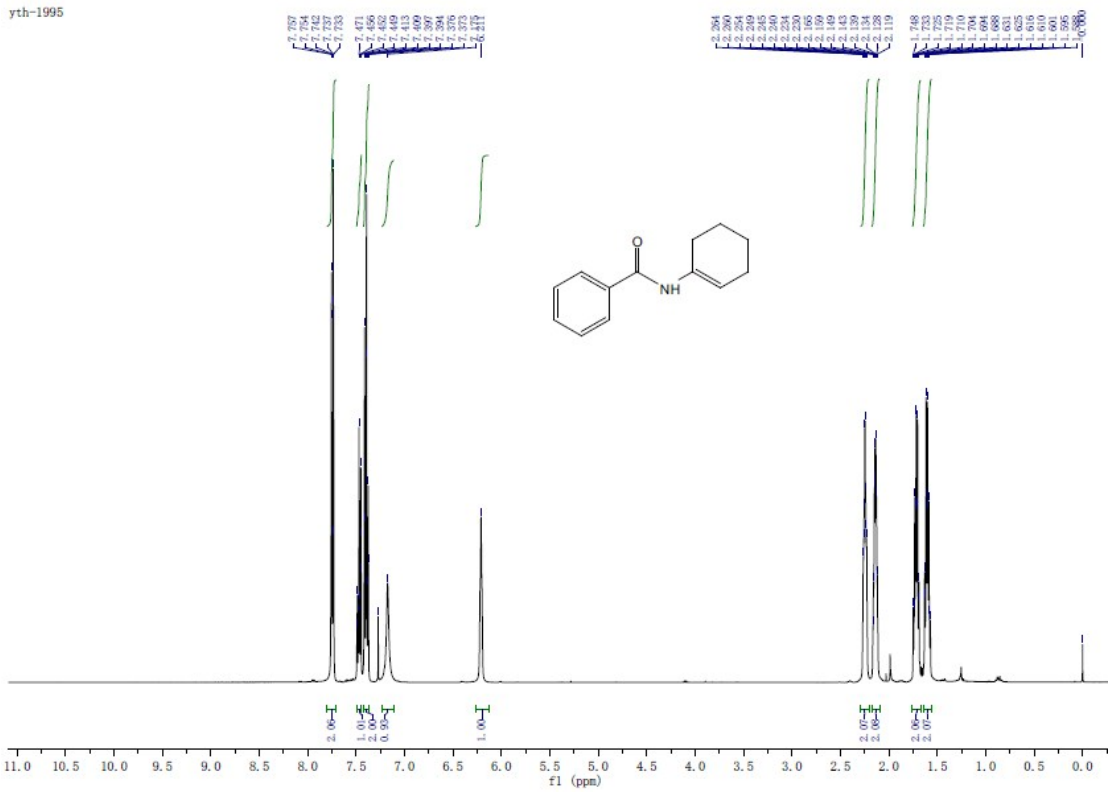

yth-1976
193.19
173.86
133.60
123.81
77.32
77.00
76.68
36.71
29.09
24.09
20.44
NH
CH3
O
O
f1 (ppm)

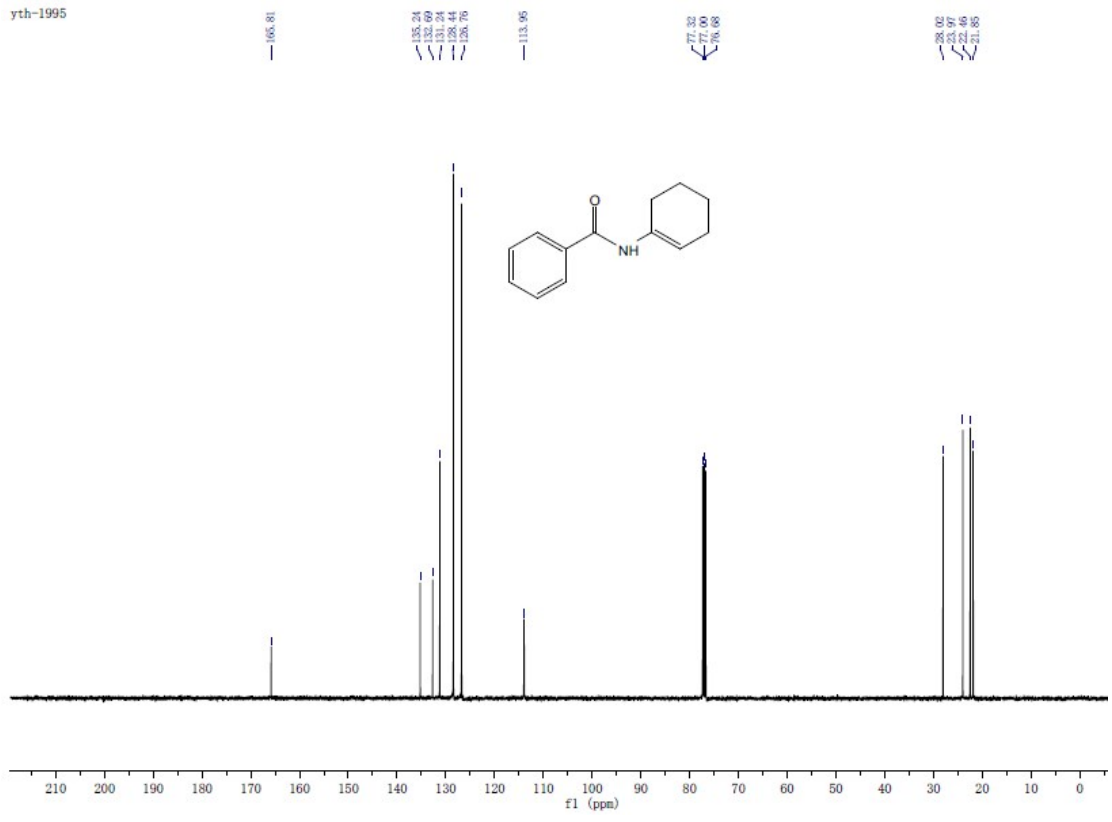
11a



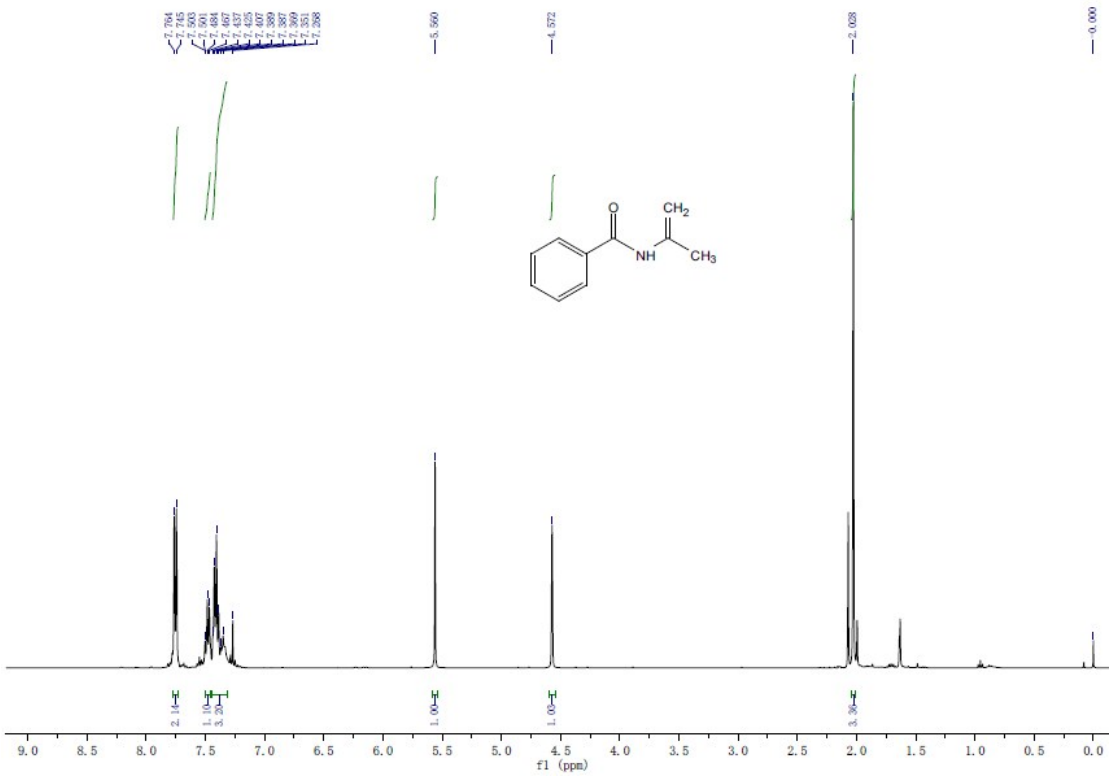


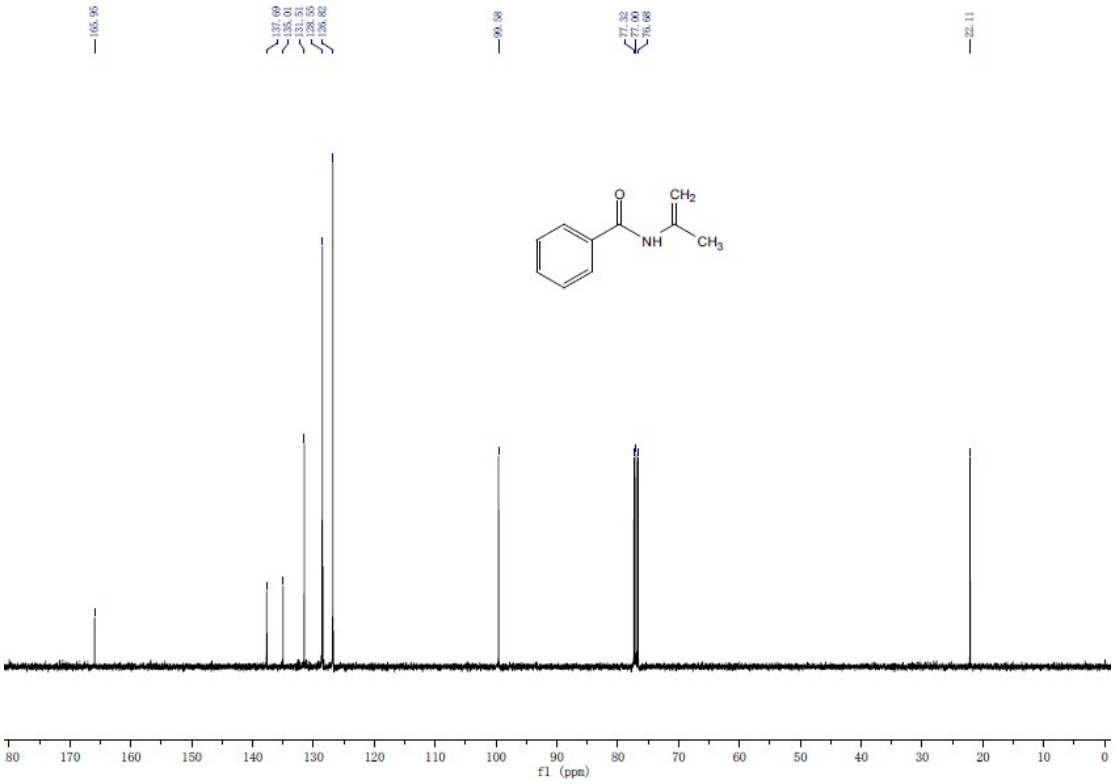
11b



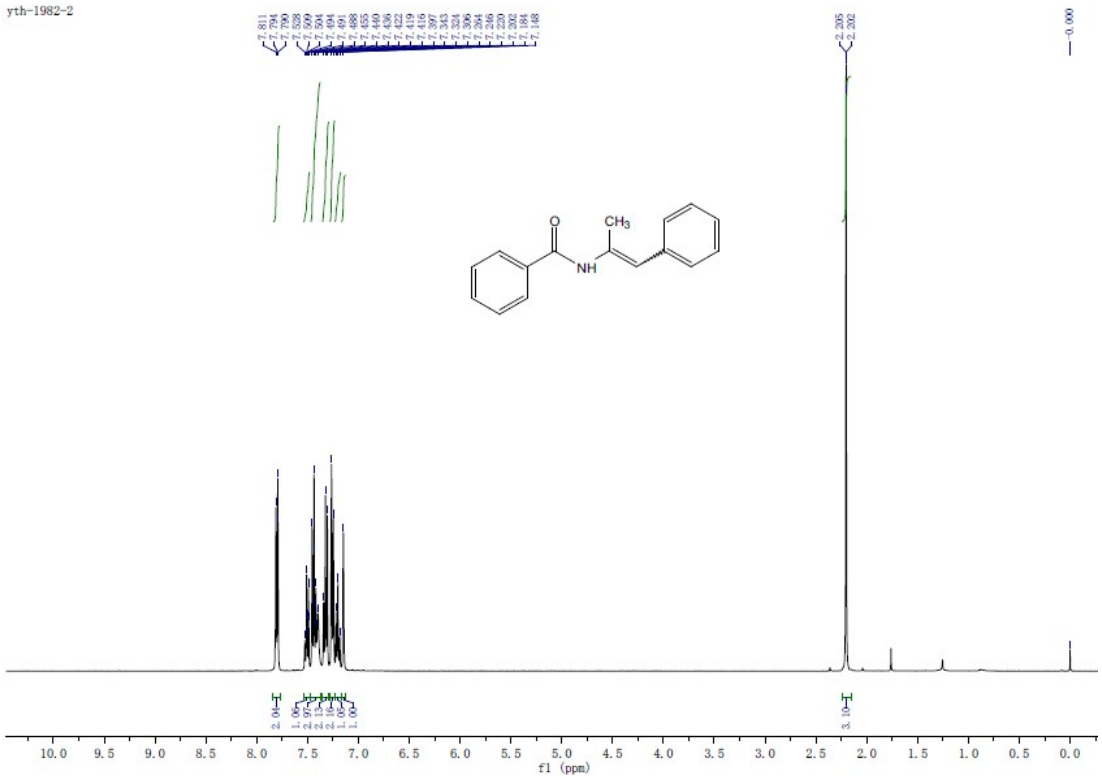


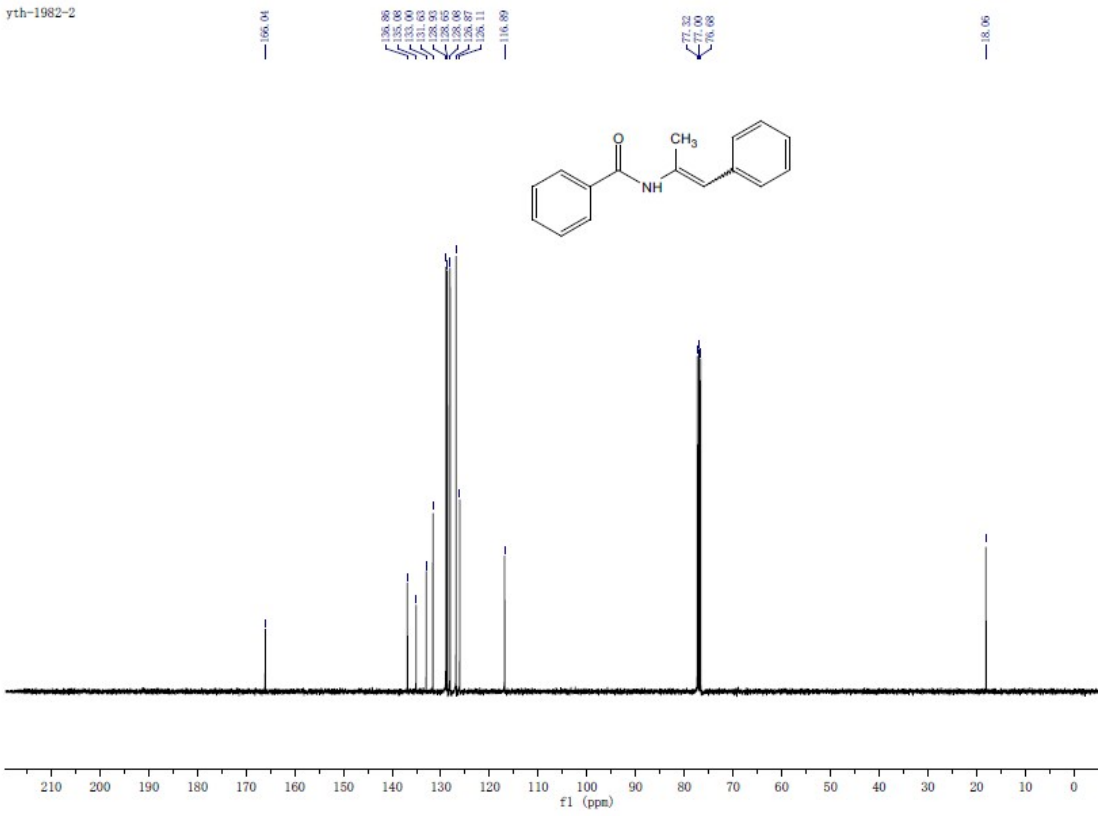
11c


7.704
7.705
7.503
7.501
7.484
7.467
7.457
7.435
7.407
7.389
7.387
7.369
7.351
7.298
5.560
4.572
2.028
0.000
O
CH2
NH
CH3
2.14
1.10
3.20
1.00
1.05
3.36
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)

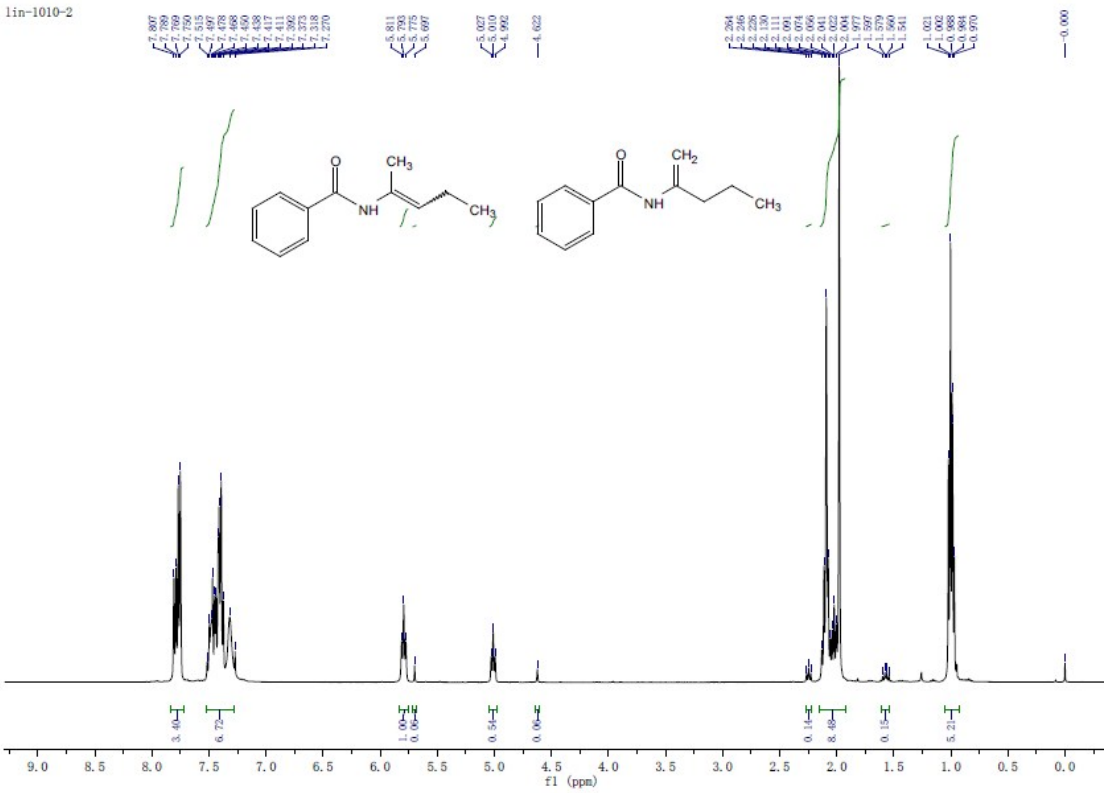

165.95
137.69
135.01
131.51
128.55
126.82
99.88
77.32
77.00
76.68
22.11
O
CH2
NH
CH3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

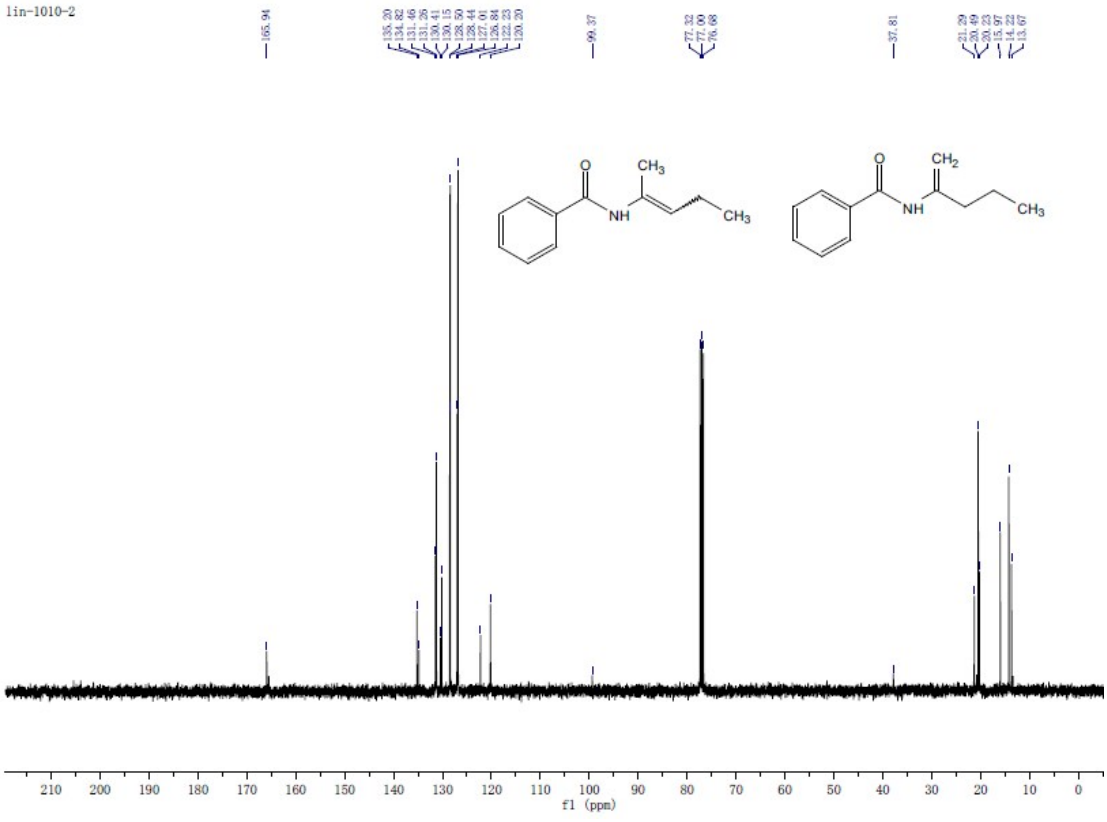
11d





11e


1in-1010-2
7.807
7.789
7.769
7.750
7.515
7.497
7.478
7.460
7.440
7.438
7.417
7.411
7.392
7.373
7.318
7.270
5.811
5.793
5.775
5.697
5.027
5.010
4.992
4.622
2.264
2.246
2.235
2.219
2.111
2.091
2.074
2.056
2.041
2.022
2.004
1.977
1.597
1.579
1.564
1.541
1.021
1.002
0.988
0.984
0.970
-0.000
O
CH3
NH
CH3
O
CH2
NH
CH3
3.40
6.72
1.00
0.86
0.54
0.00
0.14
8.48
0.18
5.21
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)


1in-1010-2
165.94
135.20
134.82
131.46
131.26
130.41
130.15
128.50
128.44
127.01
126.84
122.23
120.20
99.37
77.32
77.00
76.68
37.81
31.29
30.49
20.23
15.97
14.22
13.67
O
CH3
NH
CH3
O
CH2
NH
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)