Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

The Direct Decarboxylative Allylation of N-arylglycine derivates by Photoredox Catalysis

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1. General Procedures

All reactions were carried out under an atmosphere of Ar with dry solvents in flame-dried glassware unless otherwise noted. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. ^{1}HNMR and ^{13}CNMR spectra were recorded on a Bruker AVANCE III–400 spectrometer at room temperature. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. Abbreviations for signal couplings are: s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; m, multiplet. High resolution mass spectra were obtained on a high–resolution mass spectrometer in the ESI mode. The 36 W fluorescent lights were directly got from the supermarket. All other reagents were purchased from commercial sources and used as received.

2. General procedure for the synthesis of N-arylglycine 1b-1l, 1u, 1v.

To a solution of aniline (5 mmol, 1 equiv.) in ethanol (10 mL) was added sodium carbonate (1.5 equiv.) and ethyl bromoacetate (1.2 equiv.) and the suspension stirred at reflux for 12 h. After cooling to room temperature, the precipitated salts were removed by filtration. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography to obtain ethyl arylglycinate.

To a solution of ethyl arylglycinate (3 mmol) in MeOH-H_2O (30 mL, MeOH : H_2O = 4:1) at 0 °C was slowly added LiOH(3 equiv.). The reaction mixture was allowed to warm to room temperature overnight. Methanol was removed in vacuo and the residual aqueous solution was partitioned with ethyl acetate (20 mL), then the organic phase was extracted with H_2O (5-10 mL, two times). The combined aqueous extracts were acidified to pH 4-5 with 1N HCl. The aqueous phase was extracted with EA three times. The combined organic extract was dried over Na_2SO_4 and concentrated in vacuo and subjected to chromatography on silica gel to afford the products.

Compounds (**1n, 1o**)[1], (**1p, 1q, 1r**)[2], (**2a, 2y**)[3]. These compounds were prepared according to the literatures.

3.1 Typical Procedure for Visible-Light-Catalyzed Decarboxylative Radical Allylation.

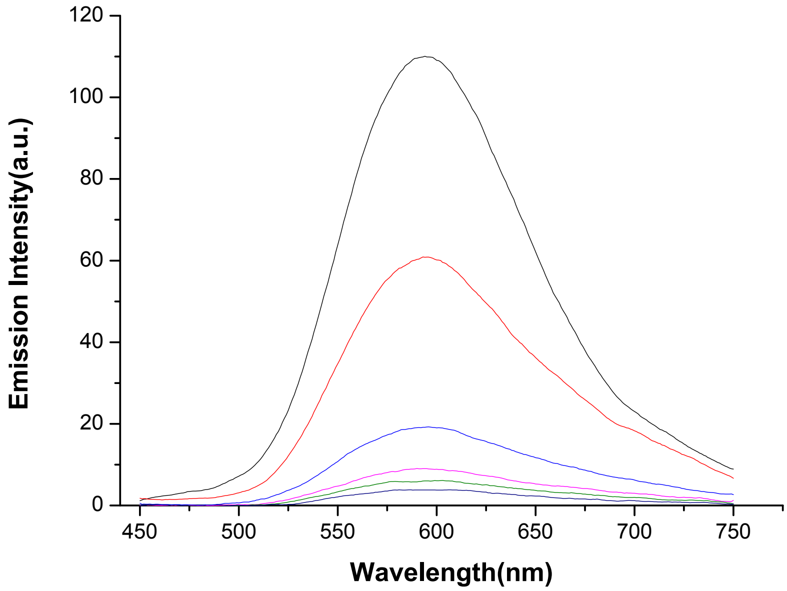
An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1** (0.2 mmol), $Ir(ppy)_2(bpy)PF_6$ (0.01 equiv, 0.001 mmol, 1.6 mg), **2** (1.3equiv, 0.26 mmol), Cs_2CO_3 (1.5 equiv, 0.30 mmol, 97 mg). The flask was evacuated and backfilled with Ar for 3 times. 1 ml $CH_3CN:H_2O$ (1:1) was added with syringe under Ar. The tube was placed at a distance (app.5 cm) from 36 W fluorescent lights, and the resulting solution was stirred at ambient temperature under visible-light irradiation and monitored by TLC. After the reaction was finished, the resulting reaction mixture was extracted with ethyl acetate (5 × 2 mL), dried over anhydrous Na_2SO_4, concentrated in vacuo and subjected to chromatography on silica gel to afford the **3**.

3.2 General procedure for the synthesis of compound 11.

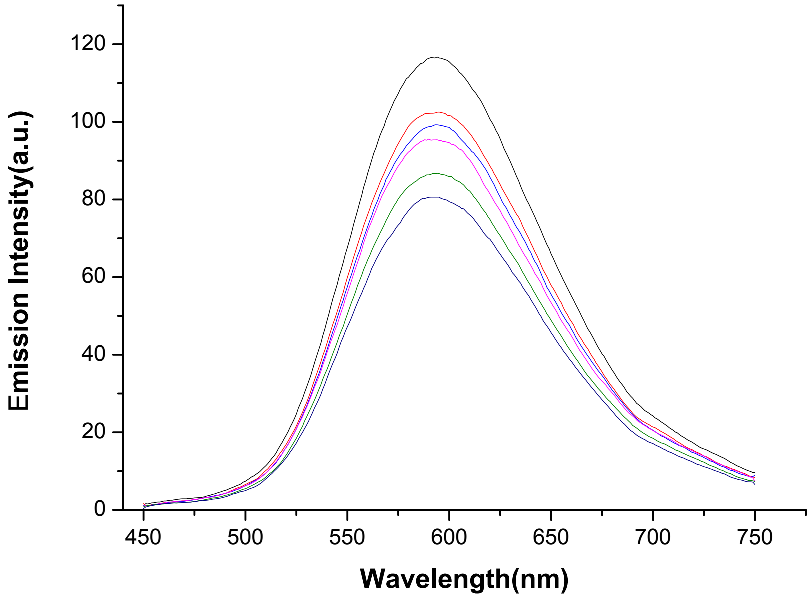
To a solution of ethyl 2-methylene-4-(phenylamino)butanoate **3a** (0.1 mmol) in THF (2 mL) at 0 °C was slowly added NaH (2 equiv.). The reaction mixture was allowed to warm to room temperature overnight. After the reaction was finished, the resulting reaction mixture was extracted with ethyl acetate (5 × 2 mL), dried over anhydrous Na_2SO_4, concentrated in vacuo and subjected to chromatography on silica gel to afford the **11** (50%).

4 Luminescence Quenching

The luminescence quenching experiment was taken using a Cary Eclipse fluorescence spectrophotometer (Varian, USA). The experiments were carried out in 0.5 mmol/L of $Ir(ppy)_2(bpy)PF_6/CH_3CN\text{-}H_2O$(1:1) at 25 °C and the excitation wavelength was 250nm. The concentrations of quenchers (amino acid **1a** and allylsulfone **2a**) in $CH_3CN\text{-}H_2O$ were 0, 0.33 mmol/L, 0.66 mmol/L, 1 mmol/L, 1.3 mmol/L, and 1.7 mmol/L.

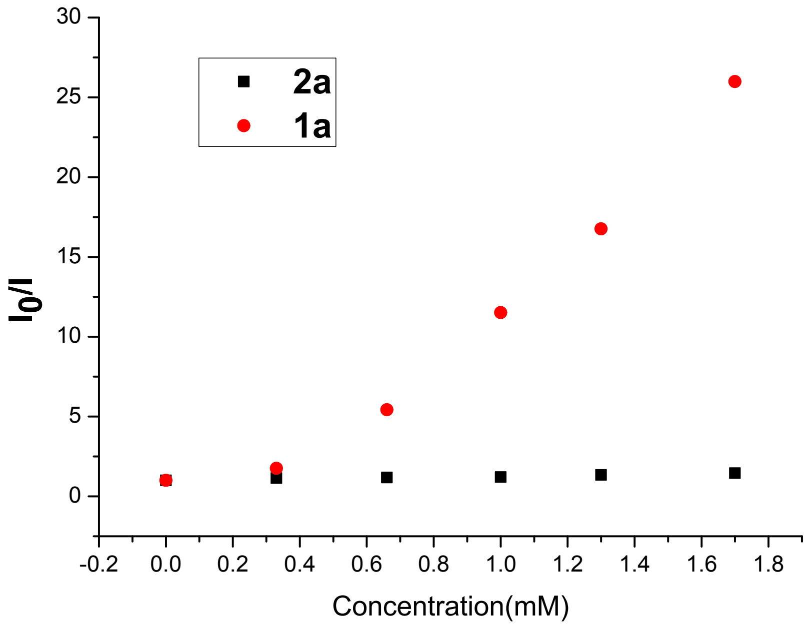


Luminescence quenching of $Ir(ppy)_2(bpy)PF_6$ by amino acid **1a**



Lumine

scence quenching of Ir(ppy)$_2$(bpy)PF$_6$ by allylsulfone **2a**



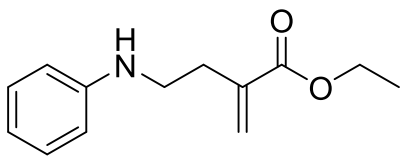
5. References for known substrates

(1) Z. Lu and R. J. Twieg, *Tetrahedron Lett.* 2005, **46**, 2997.

(2) Y. Li, F. Jia and Z. Li, *Chem. Eur. J.* 2013, **19**, 82.

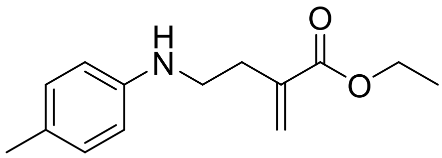
(3) J. Zhang, Y. Li, F. Zhang, C. Hu and Y. Chen, *Angew. Chem. Int. Ed.* 2016, **55**, 1872.

6. Characterizations of Products.



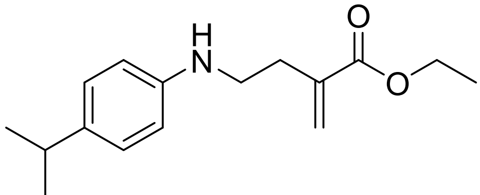
3a

Following general procedure, the reaction afforded **3a** (95% yield) as slight yellow oil. Reaction time: 12h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.19 (m, 2H), 6.75 – 6.64 (m, 2H), 6.29 (s, 1H), 5.66 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.33 (t, J = 6.8 Hz, 1H), 2.66 (t, J = 6.8 Hz, 1H), 1.35 (t, J = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.02, 147.97, 138.30, 129.26, 126.63, 117.35, 112.85, 60.89, 42.89, 31.98, 14.21. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}NO_2$ 220.1332; Found 220.1333.



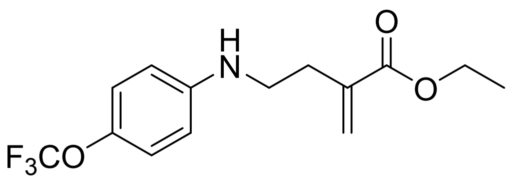
3b

Following general procedure, the reaction afforded **3b** (79% yield) as slight yellow oil. Reaction time: 12h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (d, J = 8.3 Hz, 2H), 6.55 (d, J = 8.3 Hz, 2H), 6.24 (s, 1H), 5.60 (s, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.26 (t, J = 6.8 Hz, 2H), 2.61 (t, J = 6.8 Hz, 2H), 2.23 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl3): δ 166.99, 145.15, 138.21, 129.80, 127.09, 126.69, 113.48, 60.89, 43.50, 31.86, 20.43, 14.23. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}NO_2$ 234.1489; Found 234.1490.



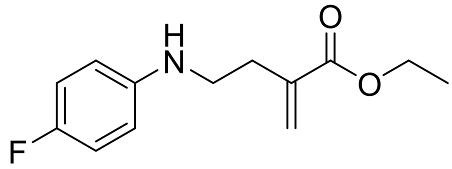
3c

Following general procedure, the reaction afforded **3c** (77% yield) as slight yellow oil. Reaction time: 12h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (d, J = 8.5 Hz, 2H), 6.58 (d, J = 8.5 Hz, 2H), 6.24 (d, J = 1.3 Hz, 1H), 5.61 (d, J = 1.2 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.27 (t, J = 6.8 Hz, 2H), 2.83 – 2.78 (m, 1H), 2.61 (t, J = 6.5 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H), 1.20 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.03, 145.74, 138.30, 138.15, 127.15, 126.64, 113.14, 60.90, 43.32, 33.20, 31.98, 24.29, 14.24. HRMS (ESI) m/z: [M+H] $^+$ Calcd for $C_{16}H_{23}NO_2$ 262.1802; Found 262.1804.



3d

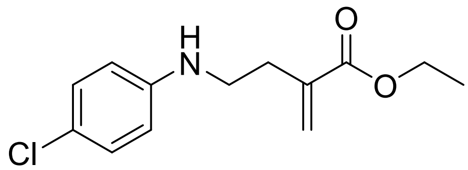
Following general procedure, the reaction afforded **3d** (70% yield) as slight yellow oil. Reaction time: 12h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (d, J = 8.7 Hz, 2H), 6.56 (d, J = 8.9 Hz, 2H), 6.25 (s, 1H), 5.63 (s, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.27 (t, J = 6.8 Hz, 2H), 2.62 (t, J = 6.8 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.01, 146.68, 140.37, 138.08, 126.83, 122.41, 121.99, 119.46, 60.96, 43.18, 31.83, 14.14. HRMS (ESI) m/z: [M+H] $^+$ Calcd for $C_{14}H_{16}F_3NO_3$ 304.1155; Found 304.1154.



3e

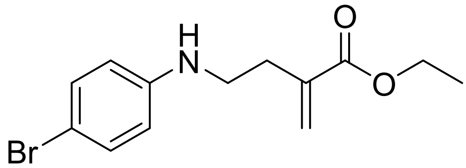
Following general procedure, the reaction afforded **3e** (77% yield) as slight yellow oil. Reaction time: 12h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90-6.86 (m, 2H), 6.56-6.53 (m, 2H), 6.24

(d, J = 1.1 Hz, 1H), 5.61 (s, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.24 (t, J = 6.8 Hz, 2H), 2.61 (t, J = 6.7 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.98, 156.92, 154.59, 144.27, 138.16, 126.71, 115.75, 115.53, 113.67, 113.60, 60.91, 43.54, 31.91, 14.19. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{16}FNO_2$ 238.1238; Found 238.1237.



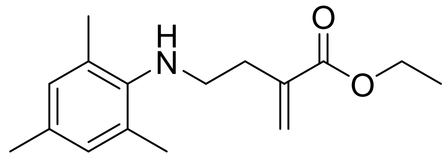
3f

Following general procedure, the reaction afforded **3f** (70% yield) as slight yellow oil. Reaction time: 12h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, J = 8.6 Hz, 2H), 6.52 (d, J = 8.6 Hz, 2H), 6.24 (s, 1H), 5.61 (s, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.25 (t, J = 6.8 Hz, 2H), 2.60 (t, J = 6.8 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.00, 146.52, 138.08, 129.05, 126.86, 121.78, 113.87, 60.96, 43.05, 31.83, 14.21. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{16}ClNO_2$ 254.0942; Found 254.0943.



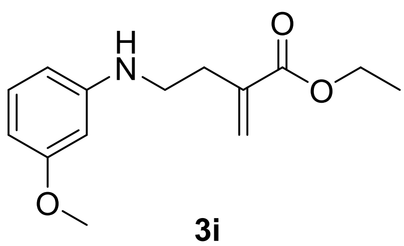
3g

Following general procedure, the reaction afforded **3g** (64% yield) as slight yellow oil. Reaction time: 12h. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.26 – 7.22 (m, 2H), 6.51 – 6.47 (m, 2H), 6.24 (d, J = 1.3 Hz, 1H), 5.61 (d, J = 1.2 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.25 (t, J = 6.8 Hz, 2H), 2.62 – 2.58 (m, 2H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.99, 146.85, 138.04, 131.93, 126.90, 114.42, 108.88, 60.97, 43.00, 31.80, 14.22. HRMS (ESI) m/z: [M+H] $^+$ Calcd for $C_{13}H_{16}BrNO_2$ 298.0437; Found 298.0437.



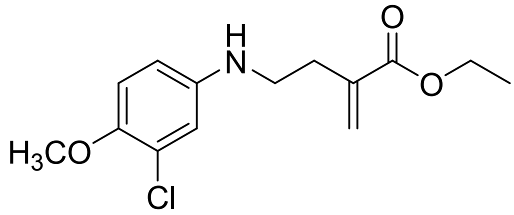
3h

Following general procedure, the reaction afforded **3h** (58% yield) as slight yellow oil. Reaction time: 12h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (s, 2H), 6.23 (d, J = 1.4 Hz, 1H), 5.62 (d, J = 1.3 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.09 (t, J = 7.1 Hz, 2H), 2.61 – 2.57 (m, 2H), 2.23-2.22 (m, 9H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.00, 142.98, 138.55, 131.38, 129.64, 129.46, 126.22, 60.80, 47.40, 33.45, 20.56, 18.38, 14.23.HRMS (ESI) m/z: [M+H] $^+$ Calcd for $C_{16}H_{23}NO_2$ 262.1802; Found 262.1803.



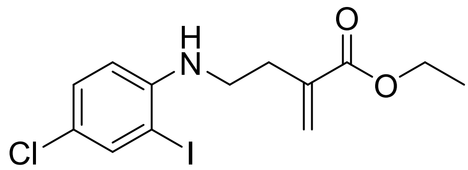
3i

Following general procedure, the reaction afforded **3i** (70% yield) as slight yellow oil. Reaction time: 12h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (t, J = 8.1 Hz, 1H), 6.27 – 6.18 (m, 4H), 5.62 (s, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.76 (s, 3H), 3.27 (t, J = 6.8 Hz, 2H), 2.61 (t, J = 6.8 Hz, 2H), 1.31 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.02, 160.88, 149.35, 138.23, 129.99, 126.71, 106.02, 102.49, 98.80, 60.91, 55.08, 42.90, 31.91, 14.22. HRMS (ESI) m/z: [M+H] $^+$ Calcd for $C_{14}H_{19}NO_3$ 250.1438; Found 250.1438.



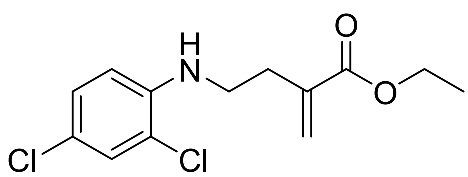
3j

Following general procedure, the reaction afforded **3j** (38% yield) as slight yellow oil. Reaction time: 12h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (d, J = 8.8 Hz, 1H), 6.69 (d, J = 2.8 Hz, 1H), 6.50 (dd, J = 8.8, 2.8 Hz, 1H), 6.25 (d, J = 1.3 Hz, 1H), 5.62 (d, J = 1.2 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.82 (s, 3H), 3.23 (t, J = 6.8 Hz, 2H), 2.62 – 2.59 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.97, 147.39, 142.67, 138.08, 126.82, 123.44, 115.04, 114.32, 112.18, 60.94, 57.05, 43.62, 31.87, 14.22. HRMS (ESI) m/z: [M+H] $^+$ Calcd for $C_{14}H_{18}ClNO_3$ 284.1048; Found 284.1050.



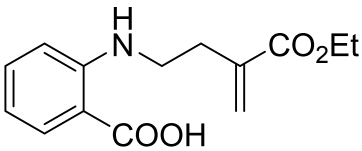
3k

Following general procedure, the reaction afforded **3k** (56% yield) as slight yellow oil. Reaction time: 12h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 2.3 Hz, 1H), 7.17 (dd, J = 8.7, 2.3 Hz, 1H), 6.51 (d, J = 8.7 Hz, 1H), 6.28 (s, 1H), 5.65 (s, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.31 (t, J = 6.8 Hz, 2H), 2.65 (t, J = 6.8 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H). ^{13} C NMR (100 MHz, $CDCl_3$): δ 166.77, 145.78, 137.91, 137.71, 129.23, 127.24, 121.81, 110.84, 84.69, 61.02, 43.37, 31.68, 14.26. HRMS (ESI) m/z: [M+H] $^+$ Calcd for $C_{13}H_{15}ClINO_2$ 379.9909; Found 379.9910.



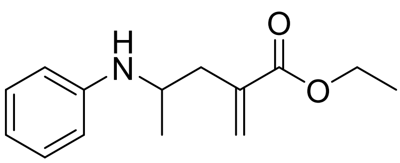
3l

Following general procedure, the reaction afforded **3l** (72% yield) as slight yellow oil. Reaction time: 12h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, J = 2.3 Hz, 1H), 7.09 (dd, J = 8.7, 2.3 Hz, 1H), 6.61 (d, J = 8.7 Hz, 1H), 6.27 (s, 1H), 5.63 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.32 (t, J = 6.8 Hz, 2H), 2.64 (t, J = 6.8 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.85, 142.49, 137.79, 128.69, 127.74, 127.08, 121.01, 119.36, 111.71, 61.01, 42.83, 31.74, 14.21. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}Cl_2NO_2$ 288.0553; Found 288.0551.



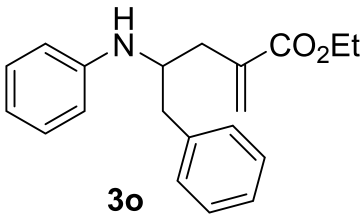
3m

Following general procedure, the reaction afforded **3m** (34% yield) as slight yellow oil. Reaction time: 12h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.0 Hz, 1H), 7.41 (t, J = 7.8 Hz, 1H), 6.78 (d, J = 8.5 Hz, 1H), 6.62 (t, J = 7.5 Hz, 1H), 6.29 (s, 1H), 5.69 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.41 (t, J = 7.0 Hz, 2H), 2.70 (t, J = 7.0 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.84, 166.81, 151.51, 137.73, 135.65, 132.69, 127.18, 114.75, 111.44, 108.74, 60.93, 41.87, 31.99, 14.23. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}NO_4$ 264.1230; Found 264.1230.



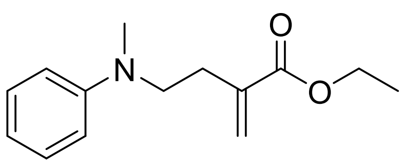
3n

Following general procedure, the reaction afforded **3n** (85% yield) as slight yellow oil. Reaction time: 12h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 – 7.09 (m, 2H), 6.68-6.61 (m, 3H), 6.22 (d, J = 1.4 Hz, 1H), 5.59 (s, 1H), 4.21 (qd, J = 7.1, 1.5 Hz, 2H), 3.74-3.66 (m, 1H), 2.73 (dd, J = 14.0, 6.0 Hz, 1H), 2.31 (dd, J = 13.8, 6.9 Hz, 1H), 1.31 (t, J = 7.1 Hz, 3H), 1.18 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.38, 147.29, 138.12, 129.29, 127.27, 117.01, 113.16, 60.90, 47.93, 39.22, 20.57, 14.23. HRMS (ESI) m/z: [M+H] $^+$ Calcd for $C_{14}H_{19}NO_2$ 234.1489; Found 234.1490.



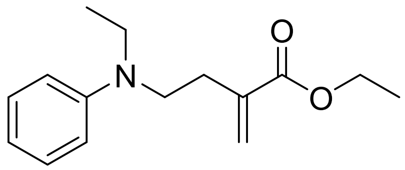
3o

Following general procedure, the reaction afforded **3o** (84% yield) as slight yellow oil. Reaction time: 12h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 – 7.13 (m, 7H), 6.68-6.61 (m, 3H), 6.19 (s, 1H), 5.56 (s, 5H), 4.17 (q, J = 7.1 Hz, 2H), 3.91-3.85 (m, 1H), 2.85 (qd, J = 13.9, 6.0 Hz, 2H), 2.50 (d, J = 6.8 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H). ^{13} C NMR (100 MHz, $CDCl_3$): δ 167.47, 147.22, 138.29, 138.08, 129.50, 129.38, 128.45, 127.23, 126.40, 117.23, 113.27, 60.93, 53.62, 40.38, 36.75, 14.23. HRMS (ESI) m/z: [M+H] $^+$ Calcd for $C_{20}H_{23}NO_2$ 310.1802; Found 310.1804.



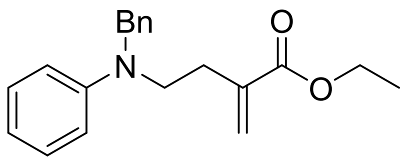
3p

Following general procedure, the reaction afforded **3p** (69% yield) as slight yellow oil. Reaction time: 12h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 – 7.21 (m, 2H), 6.74 (d, J = 8.2 Hz, 2H), 6.68 (t, J = 7.2 Hz, 1H), 6.20 (d, J = 1.2 Hz, 1H), 5.58 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.48 (t, J = 8.0 Hz, 2H), 2.93 (s, 3H), 2.56 (t, J = 8.0 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.00, 147.59, 138.40, 129.33, 126.70, 115.59, 111.80, 60.85, 50.09, 44.99, 30.47, 14.25, 12.47. HRMS (ESI) m/z: [M+H] $^+$ Calcd for $C_{14}H_{19}NO_2$ 234.1489; Found 234.1490.



3q

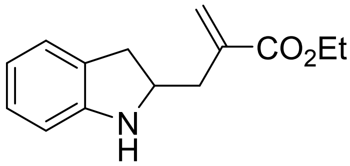
Following general procedure, the reaction afforded **3q** (61% yield) as slight yellow oil. Reaction time: 12h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.20 (m, 2H), 6.75-6.64 (m, 3H), 6.22 (s, 1H), 5.61 (s, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.44-3.34 (m, 4H), 2.59 (t, J = 8.0 Hz, 2H), 1.34 (t, J = 7.2 Hz, 2H), 1.16 (t, J = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 167.00, 147.59, 138.40, 129.33, 126.70, 115.59, 111.80, 60.85, 50.09, 44.99, 30.47, 14.25, 12.47. HRMS (ESI) m/z: [M+H] $^+$ Calcd for $C_{15}H_{21}NO_2$ 248.1645; Found 248.1647.



3r

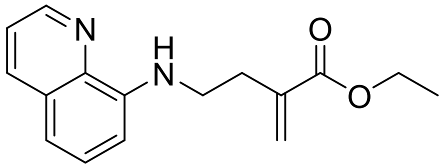
Following general procedure, the reaction afforded **3r** (41% yield) as slight yellow oil. Reaction time: 12h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.17 (m, 7H), 6.76 (d, J = 8.3 Hz, 2H), 6.68 (t, J = 7.2 Hz, 1H), 6.21 (d, J = 1.2 Hz, 1H), 5.59 (s, 1H), 4.55 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.56 (t, J = 8.0 Hz, 2H), 2.66 (t, J = 7.2 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C

NMR (100 MHz, $CDCl_3$): δ 166.87, 148.14, 138.84, 138.18, 129.25, 128.54, 126.83, 126.77, 126.49, 116.23, 112.09, 60.85, 54.35, 50.87, 30.06, 14.20. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}NO_2$ 310.1802; Found 310.1803.



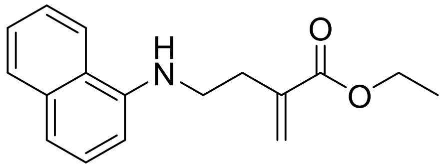
3s

Following general procedure, the reaction afforded **3s** (22% yield) as slight yellow oil. Reaction time: 12h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.07 (d, J = 7.3 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 6.68 (t, J = 7.4 Hz, 1H), 6.59 (d, J = 7.7 Hz, 1H), 6.26 (d, J = 1.4 Hz, 1H), 5.62 (d, J = 1.4 Hz, 1H), 4.22 (q, J = 7.1 Hz, 1H), 4.07 – 4.00 (m, 1H), 3.15 (dd, J = 15.6, 8.7 Hz, 1H), 2.76 – 2.61(m, 2H), 2.50 (dd, J = 13.6, 7.9 Hz, 1H), 1.31 (t, J = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 166.92, 150.37, 137.81, 128.28, 127.34, 127.12, 124.79, 118.61, 109.21, 60.90, 57.75, 39.19, 35.76, 14.23. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}NO_2$ 232.1332; Found 232.1332.



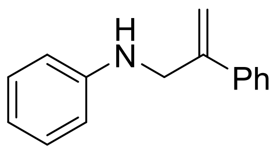
3t

Following general procedure, the reaction afforded **3t** (75% yield) as slight yellow oil. Reaction time: 12h. ^1H NMR (400 MHz, $CDCl_3$): δ 8.69 (dd, J = 4.2, 1.7 Hz, 1H), 8.03 (dd, J = 8.3, 1.6 Hz, 1H), 7.40 – 7.32 (m, 2H), 7.03 (dd, J = 8.2, 0.9 Hz, 1H), 6.74 – 6.72 (m, 1H), 6.27 (d, J = 1.3 Hz, 1H), 5.65 (d, J = 1.2 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.50 (t, J = 7.0 Hz, 2H), 2.78 – 2.75 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.97, 146.66, 144.40, 138.16, 137.99, 136.19, 128.72, 127.89, 126.82, 121.35, 113.83, 104.78, 60.88, 42.40, 31.80, 14.24. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{18}N_2O_2$ 271.1441; Found 271.1443.



3u

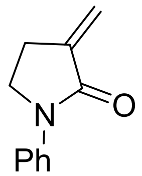
Following general procedure, the reaction afforded **3u** (23% yield) as slight yellow oil. Reaction time: 12h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.79-7.77 (m, 2H), 7.46-7.40 (m, 2H), 7.34 (t, J = 7.9 Hz, 1H), 7.23(t, J = 8.0 Hz,1H), 6.62 (d, J = 7.5 Hz, 1H), 6.28 (s, 1H), 5.70 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.45 (t, J = 6.6 Hz, 2H), 2.79 (t, J = 6.6 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 167.43, 143.15, 138.63, 134.33, 128.62, 126.86, 126.63, 125.71, 124.70, 123.41, 119.94, 117.30, 104.22, 61.07, 43.62, 31.64, 14.22. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{19}NO_2$ 270.1489; Found 270.1488.



3x

Following general procedure, the reaction afforded **3x** (75% yield) as slight yellow oil. Reaction time: 12h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.12 (m, 7H), 6.69 – 6.55 (m, 3H), 5.39 (d, J = 5.4 Hz, 1H), 5.14 (d, J = 5.1 Hz, 1H), 3.22 (q, J = 6.7 Hz, 2H), 2.81 (q, J = 6.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 148.13, 145.82, 140.45, 129.30, 128.53, 127.78, 126.19, 117.44, 114.29, 113.01, 42.27, 35.19. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}N$ 224.1434;

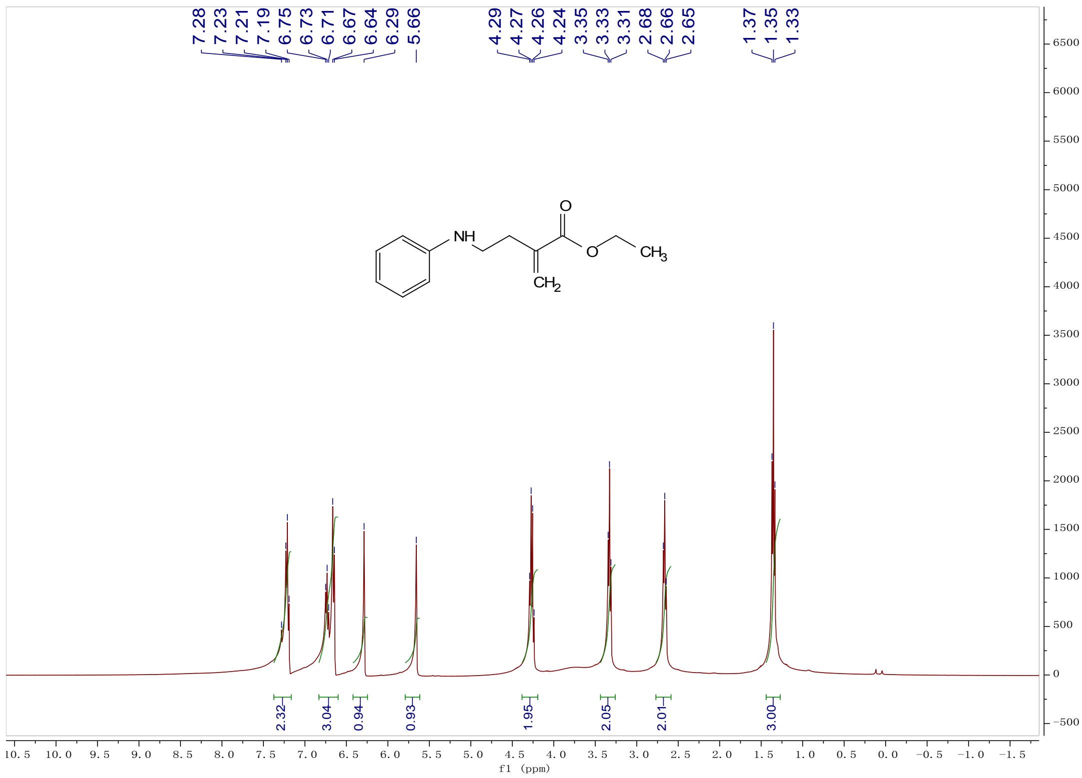
Found 224.1434.



11

3-methylene-1-phenylpyrrolidin-2-one **11** (50% yield), slight yellow oil. Reaction time: 12h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.71 (m, 2H), 7.41 – 7.36 (m, 2H), 7.19 – 7.15 (m, 1H), 6.14 (t, J = 2.8 Hz, 1H), 5.44 (t, J = 2.4 Hz, 1H), 3.87 (t, J = 8.0 Hz, 2H), 2.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.98, 140.15, 139.64, 128.88, 124.77, 119.66, 116.82, 45.16, 23.85. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{12}NO$ 174.0913; Found 174.0913.

7. ^{1}H and ^{13}C NMR spectra of products.



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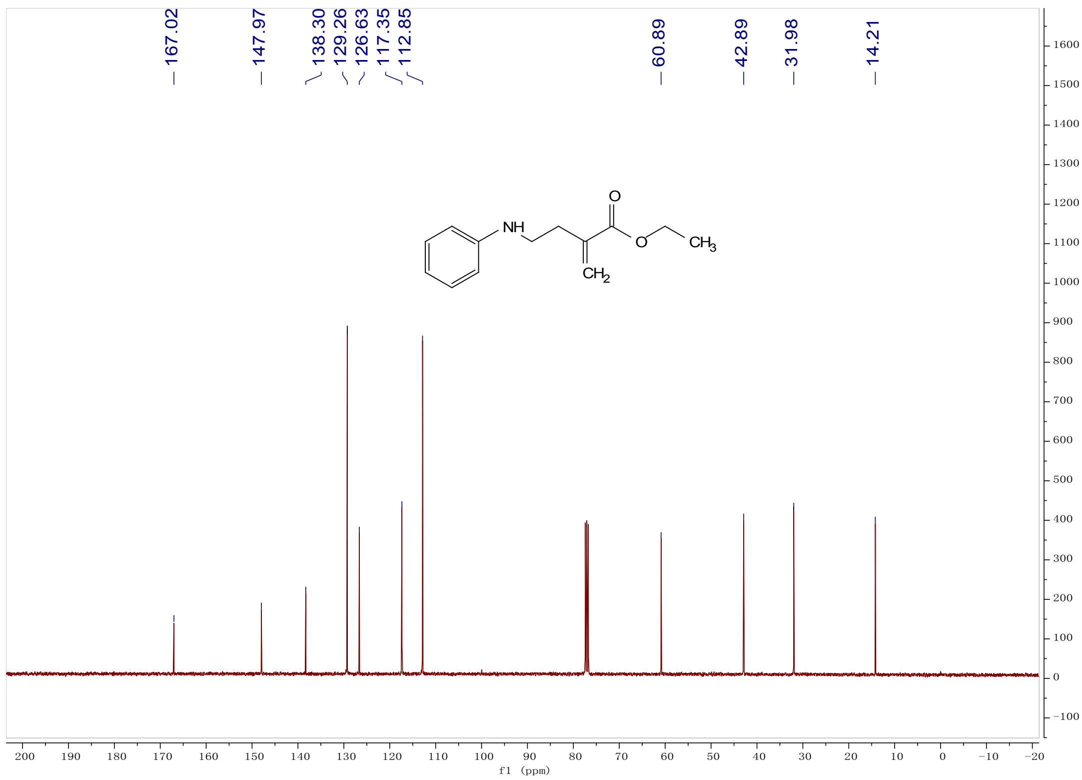

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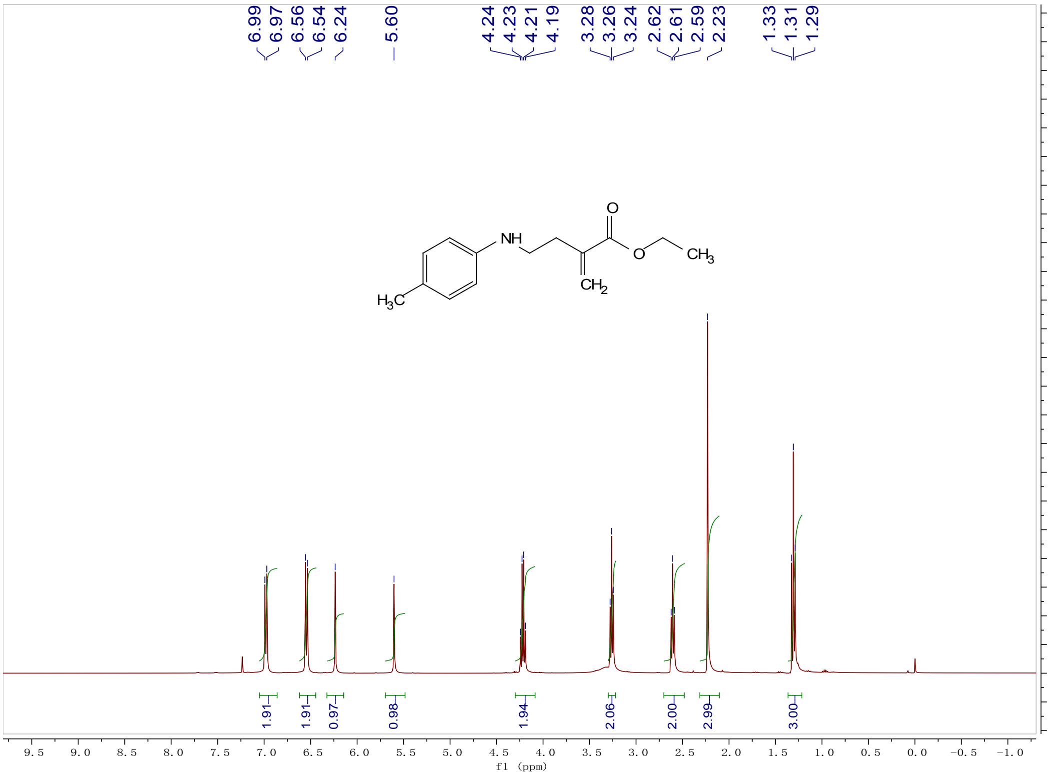
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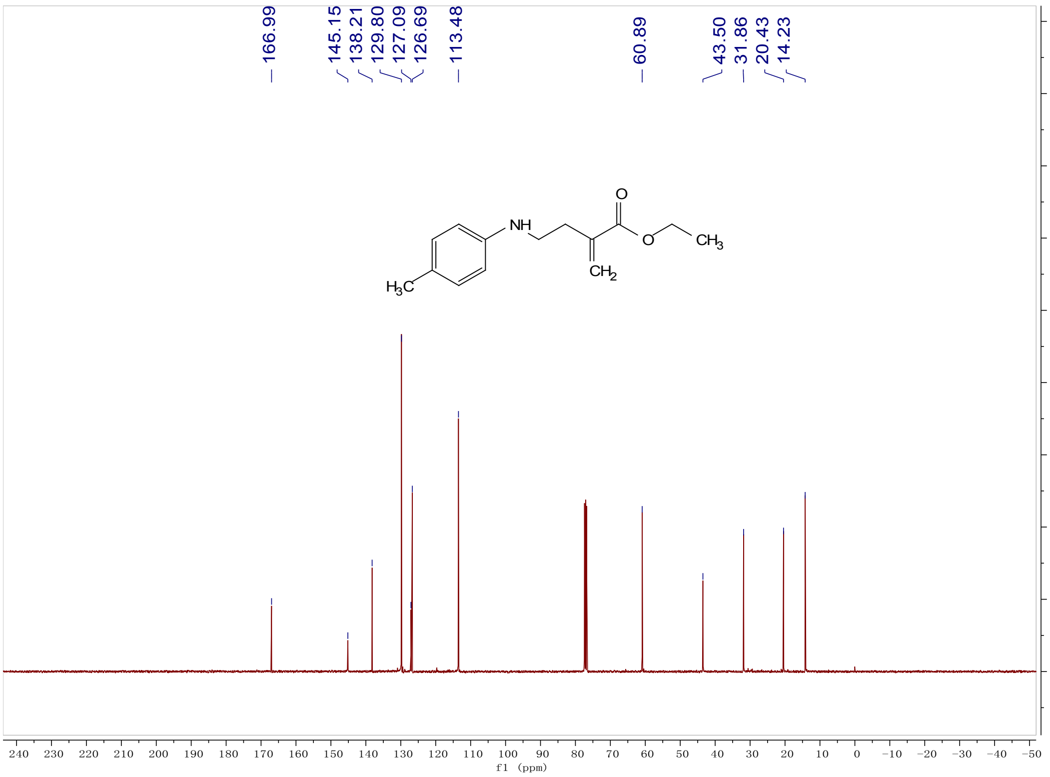
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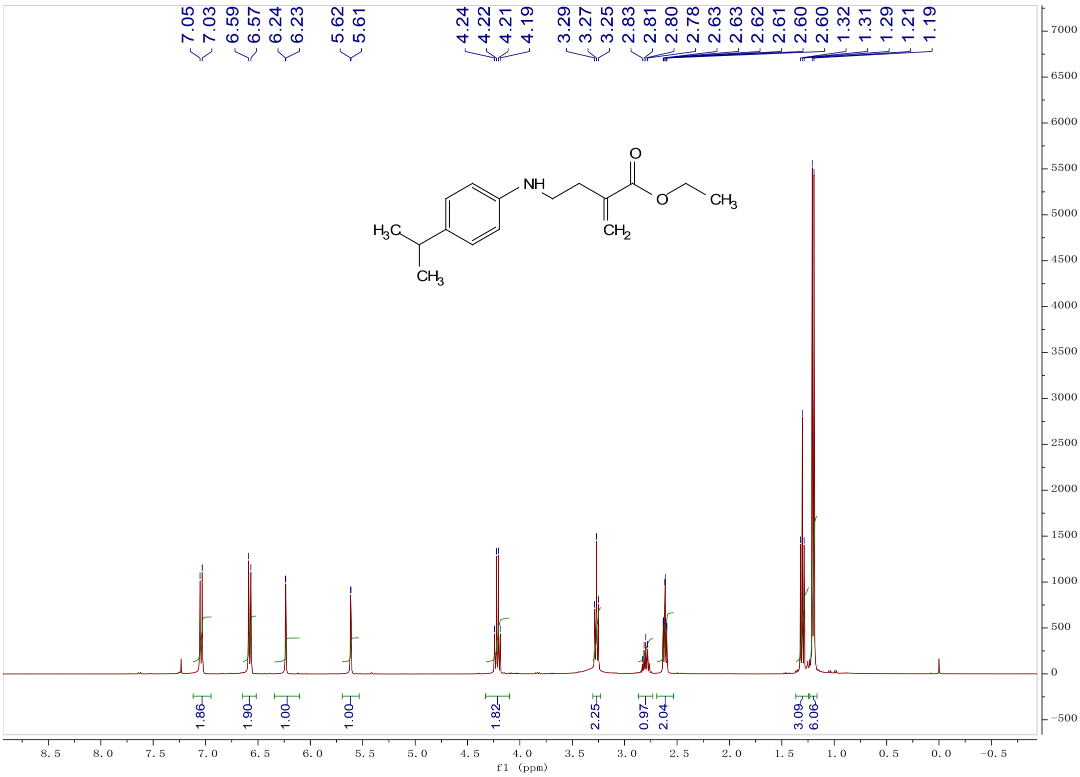
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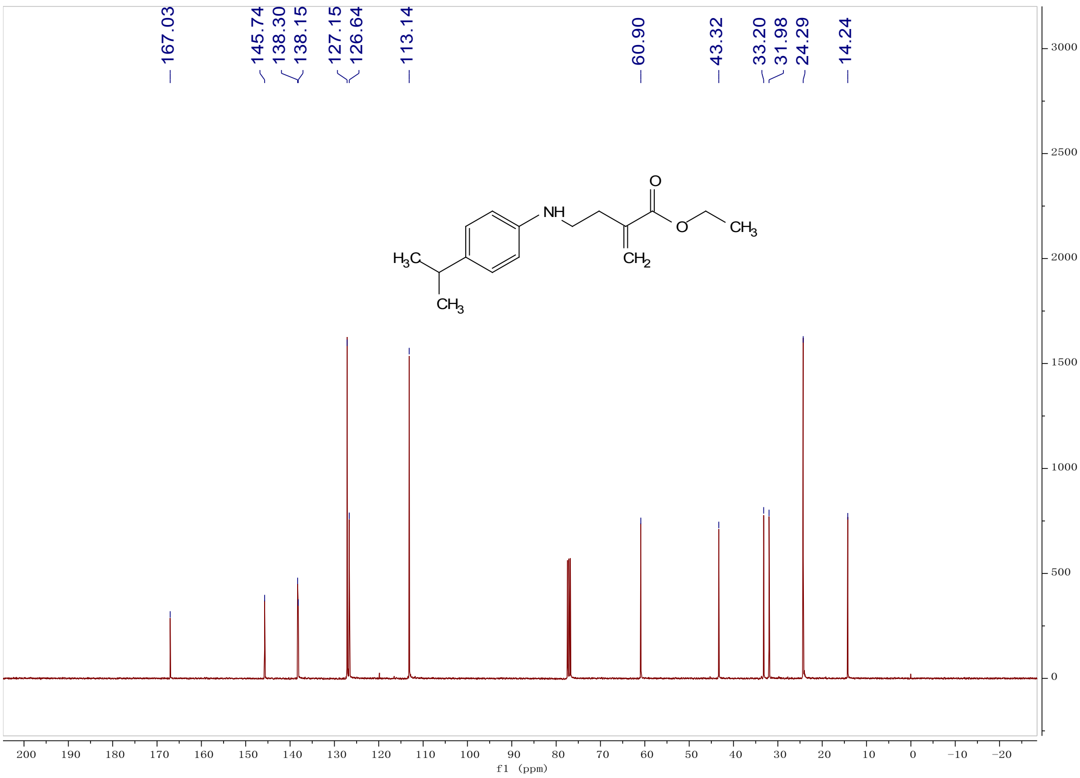
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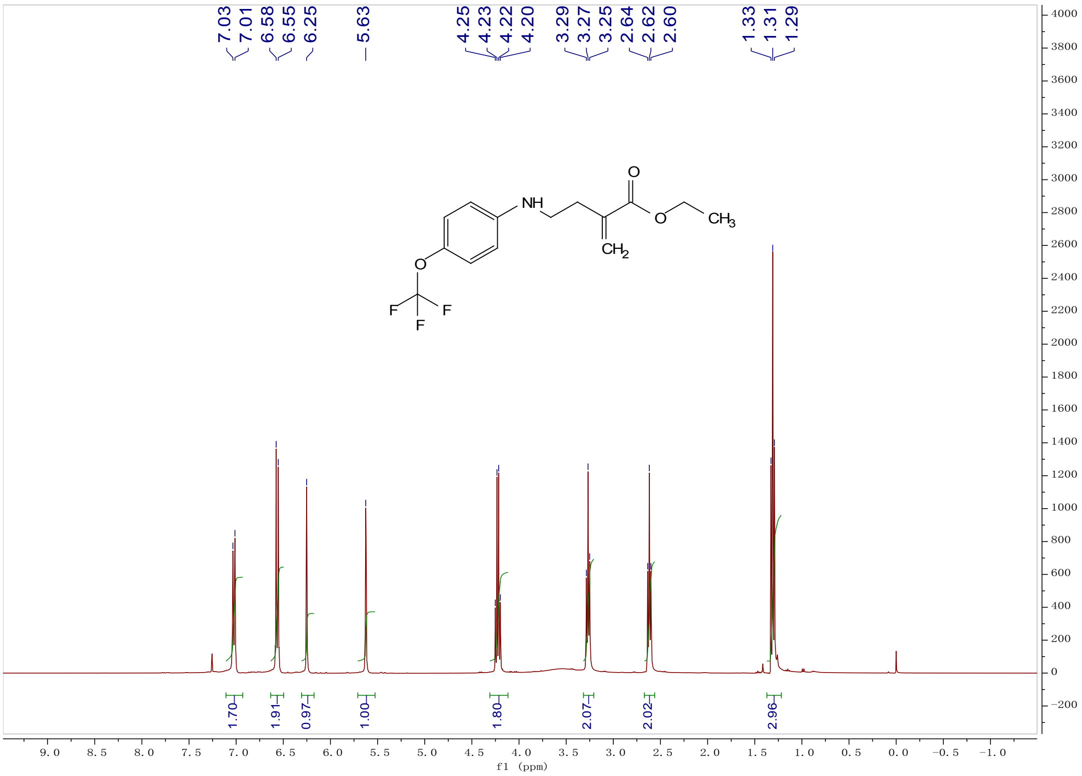

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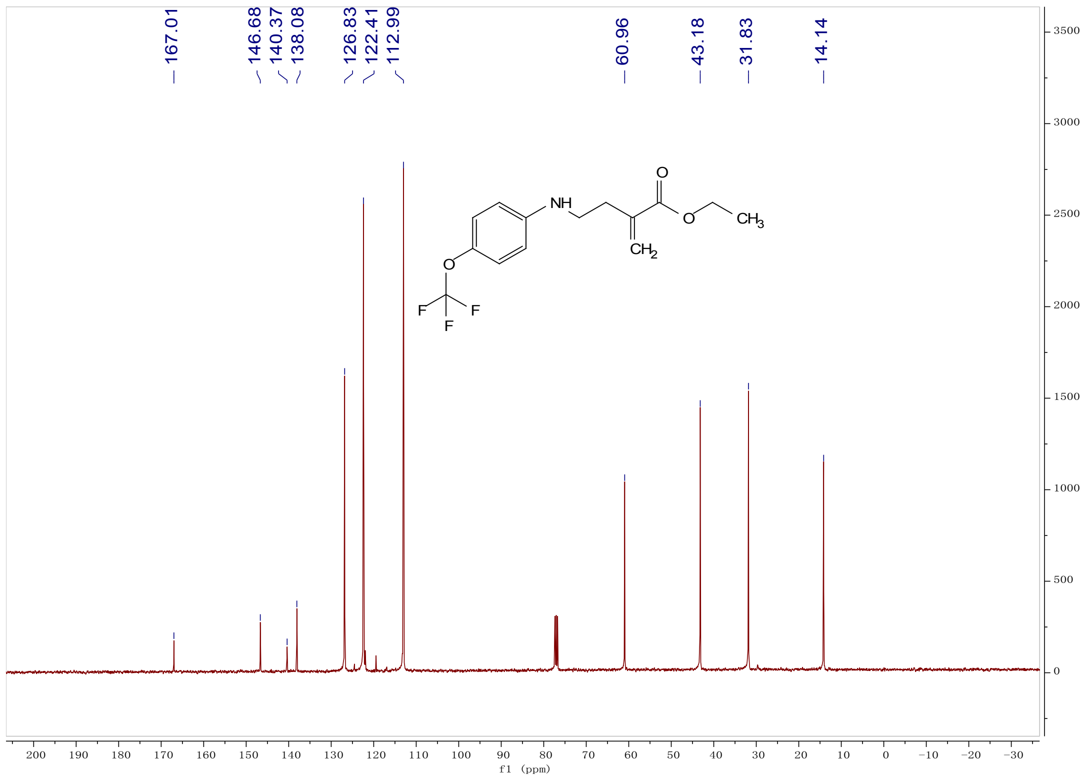
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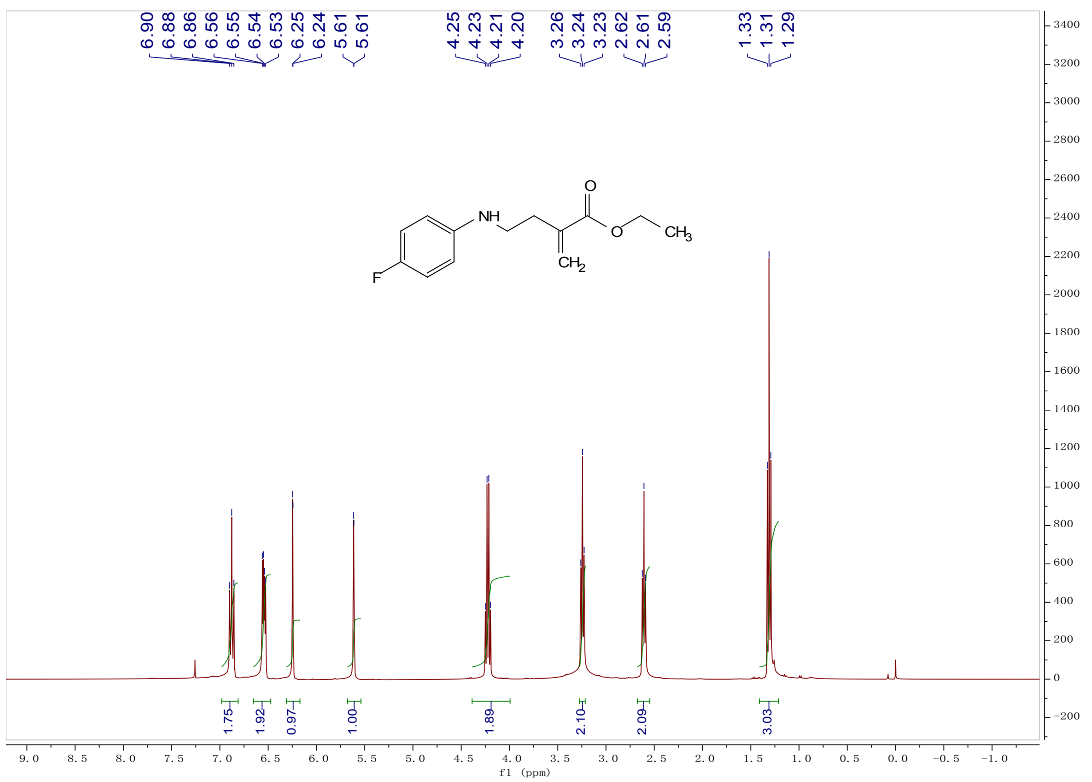
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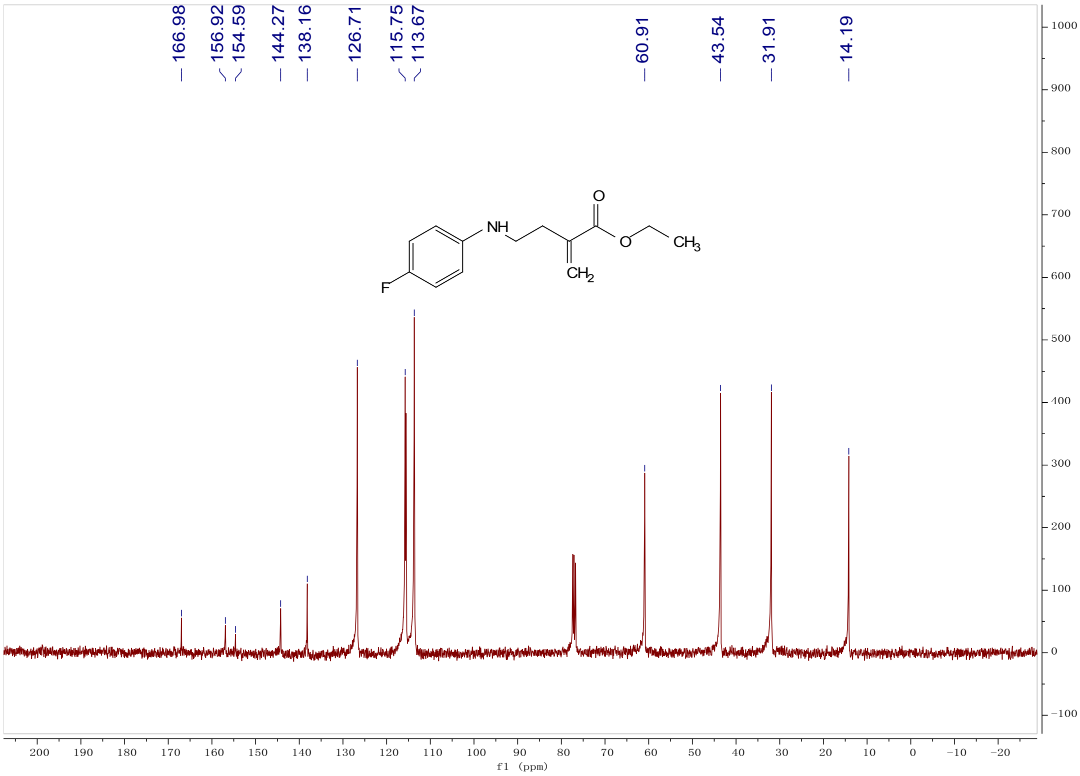
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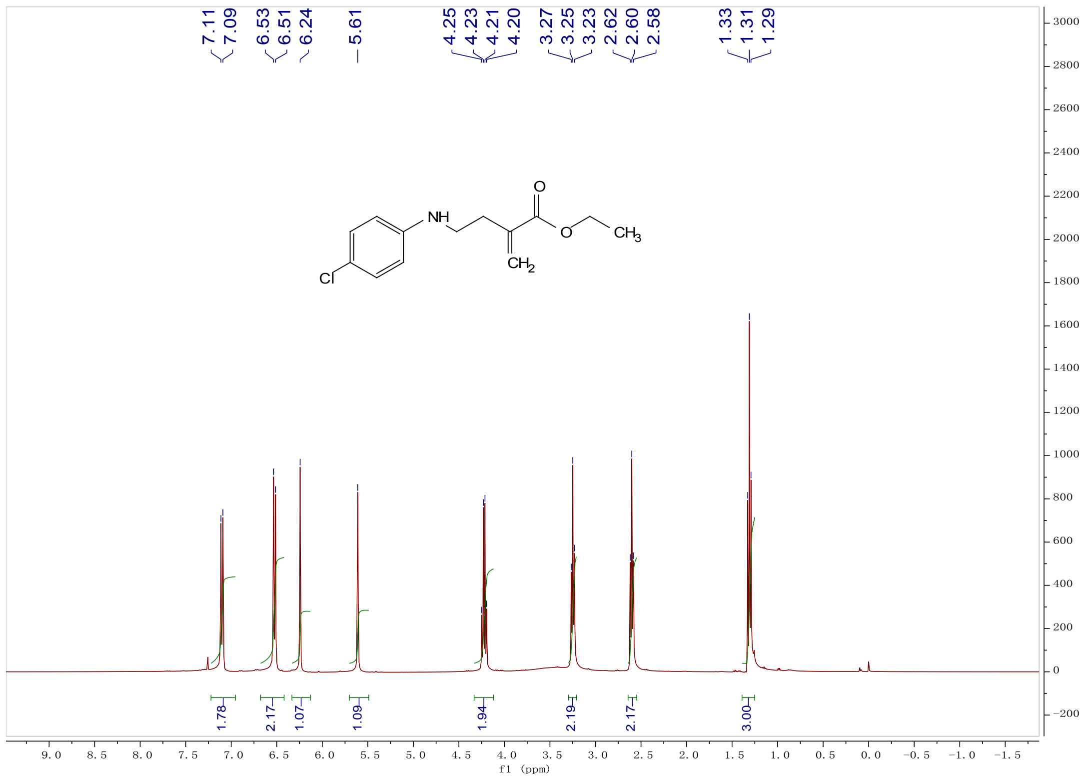

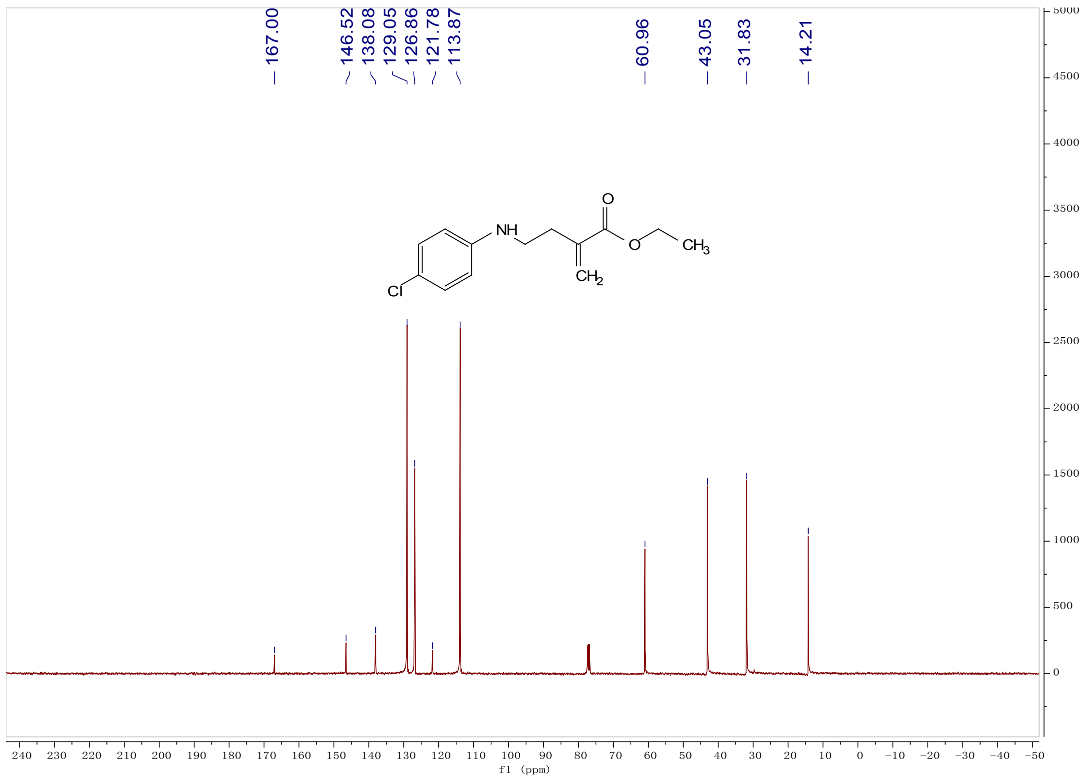

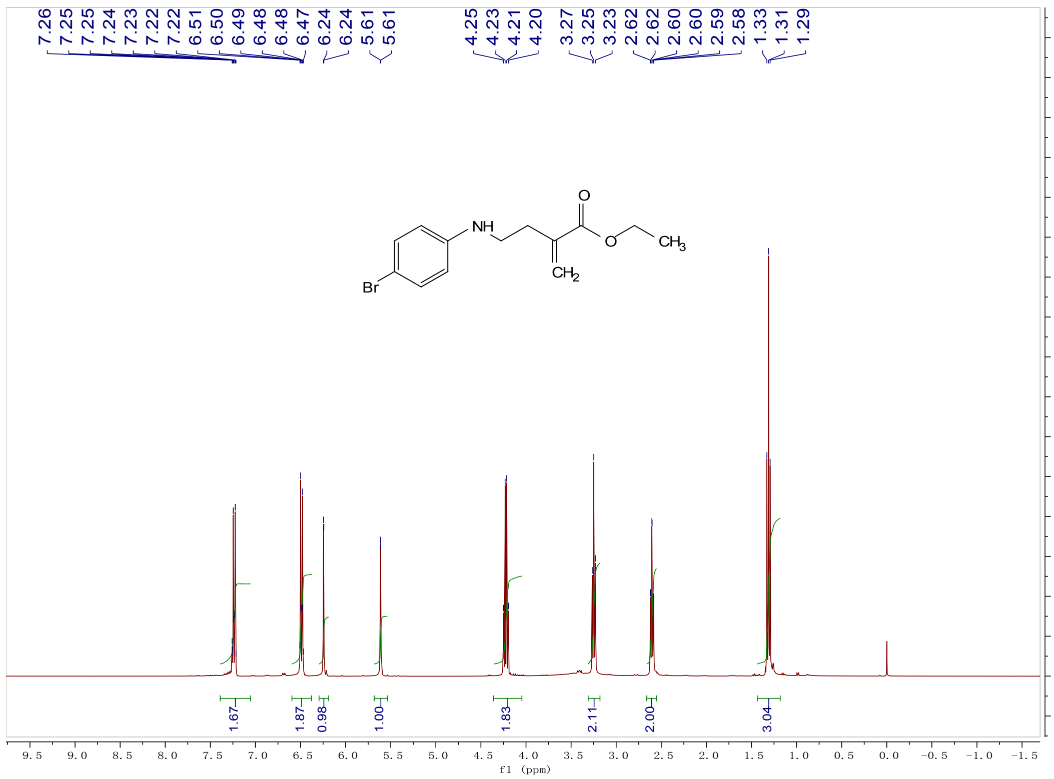
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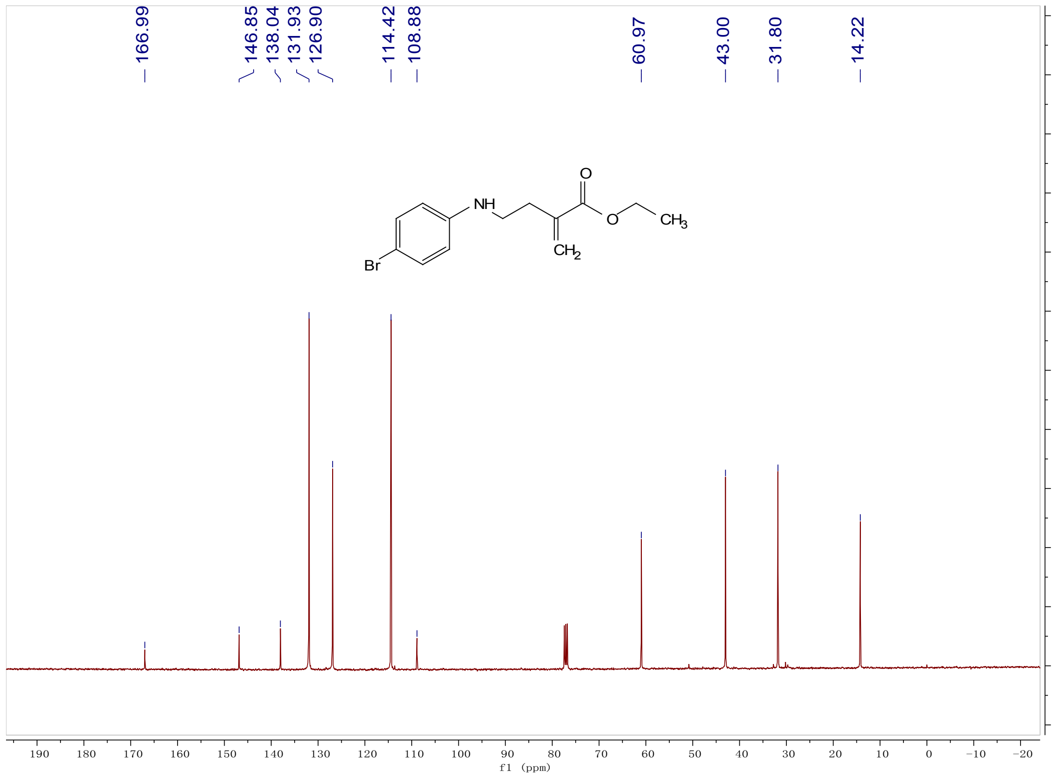
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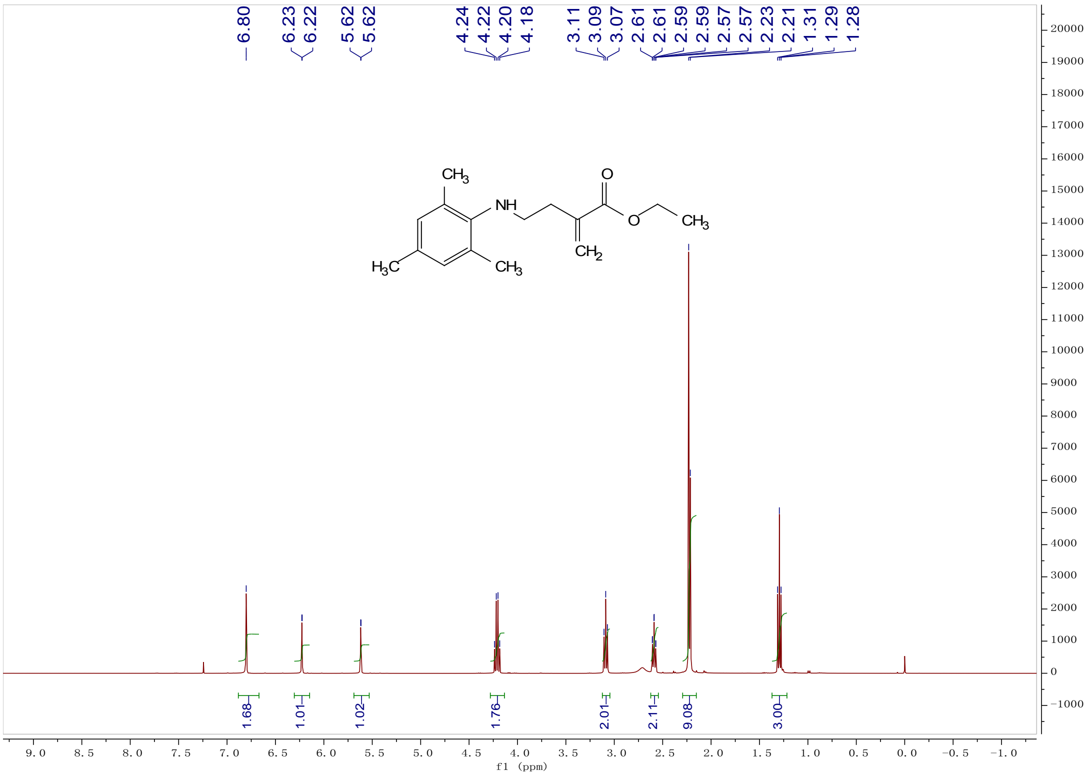
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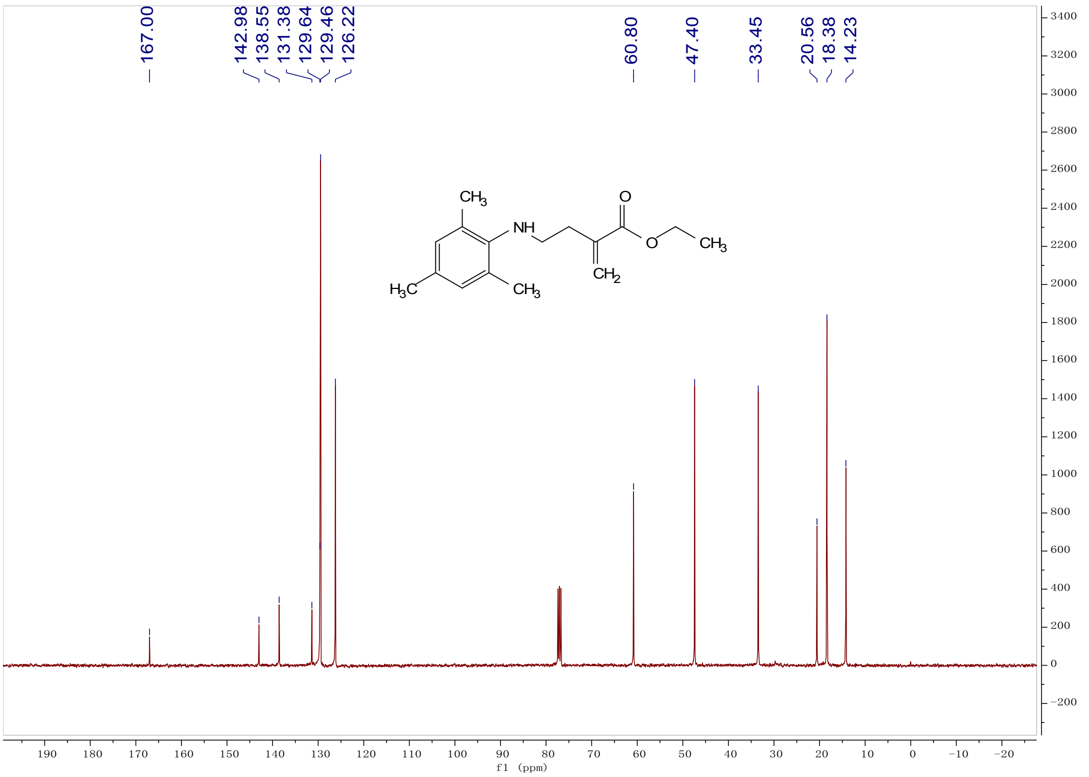
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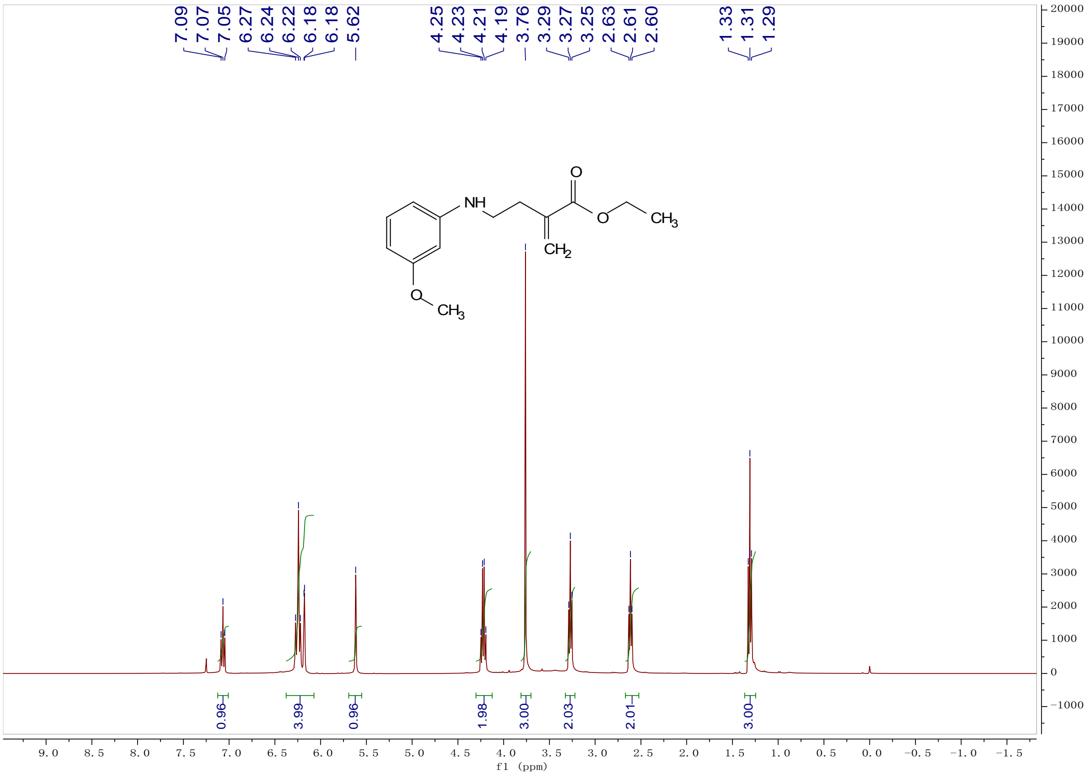
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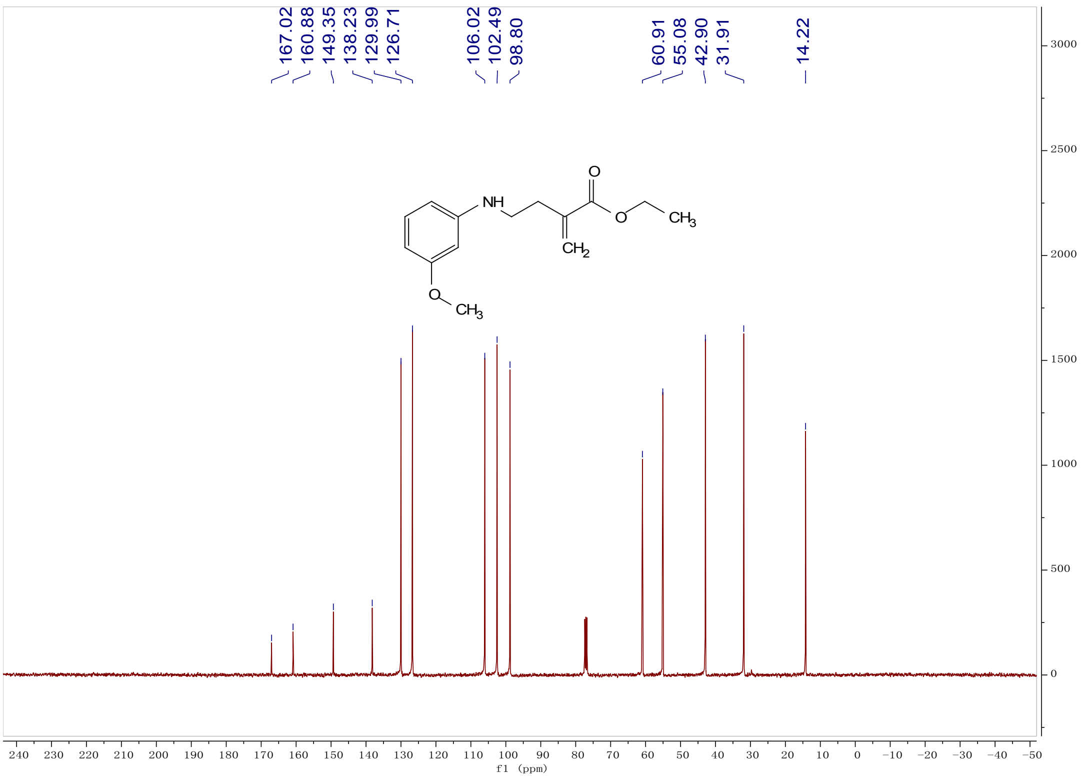
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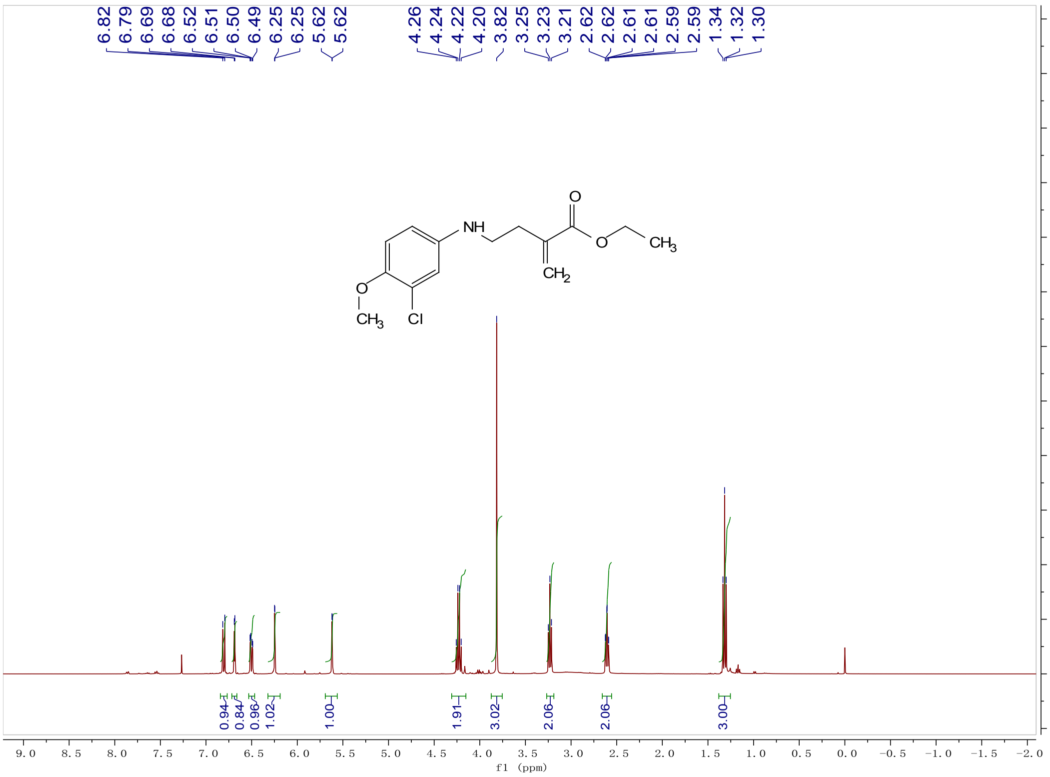
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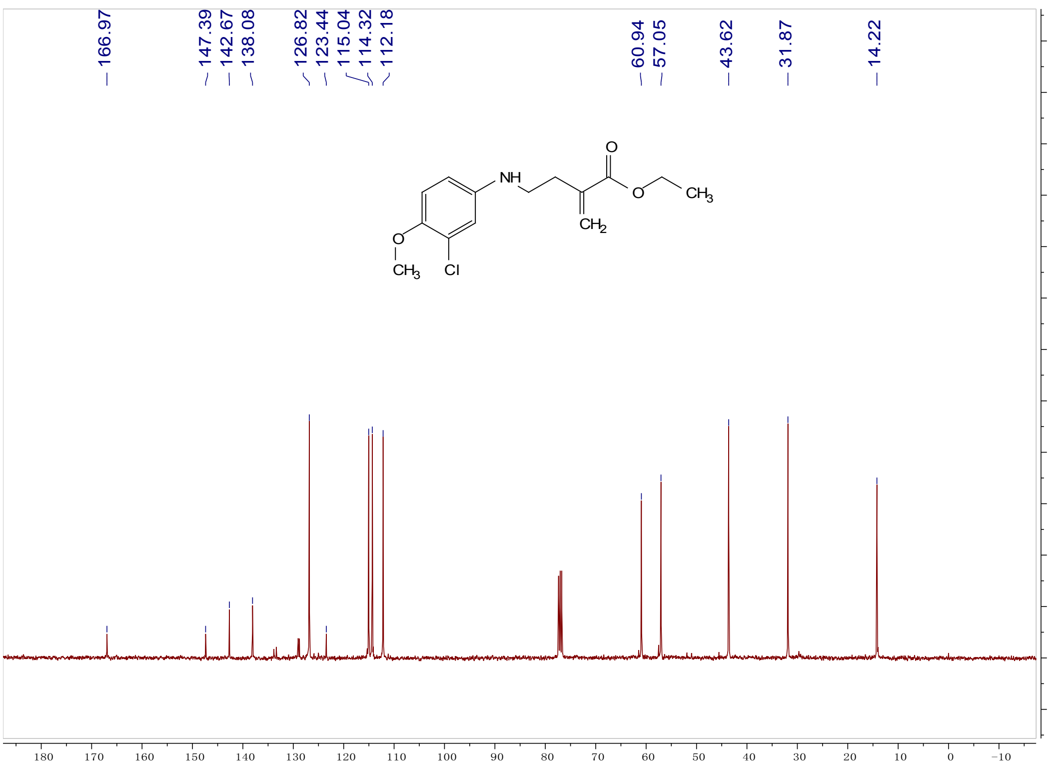
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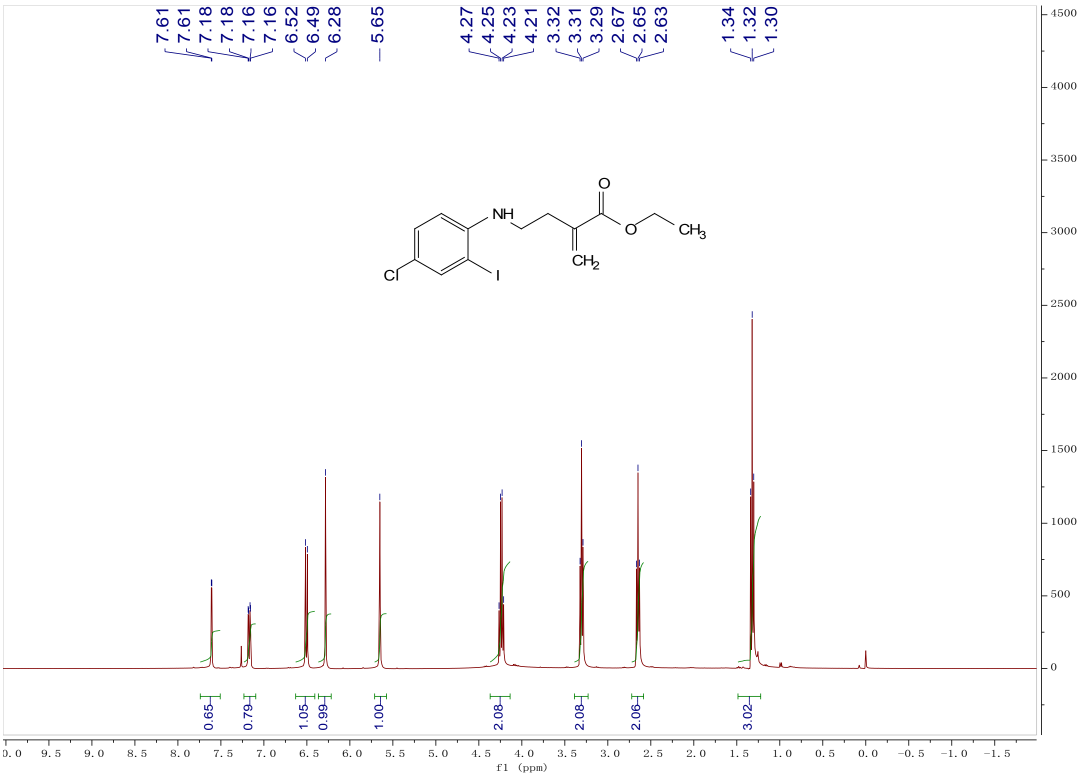
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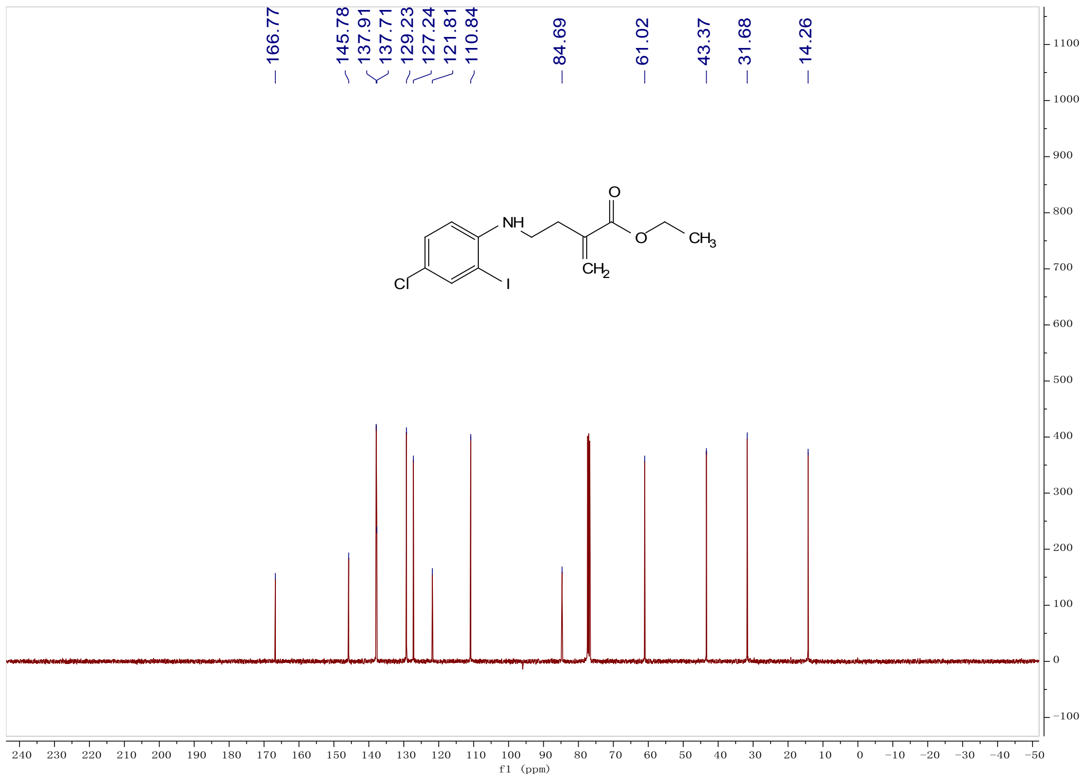
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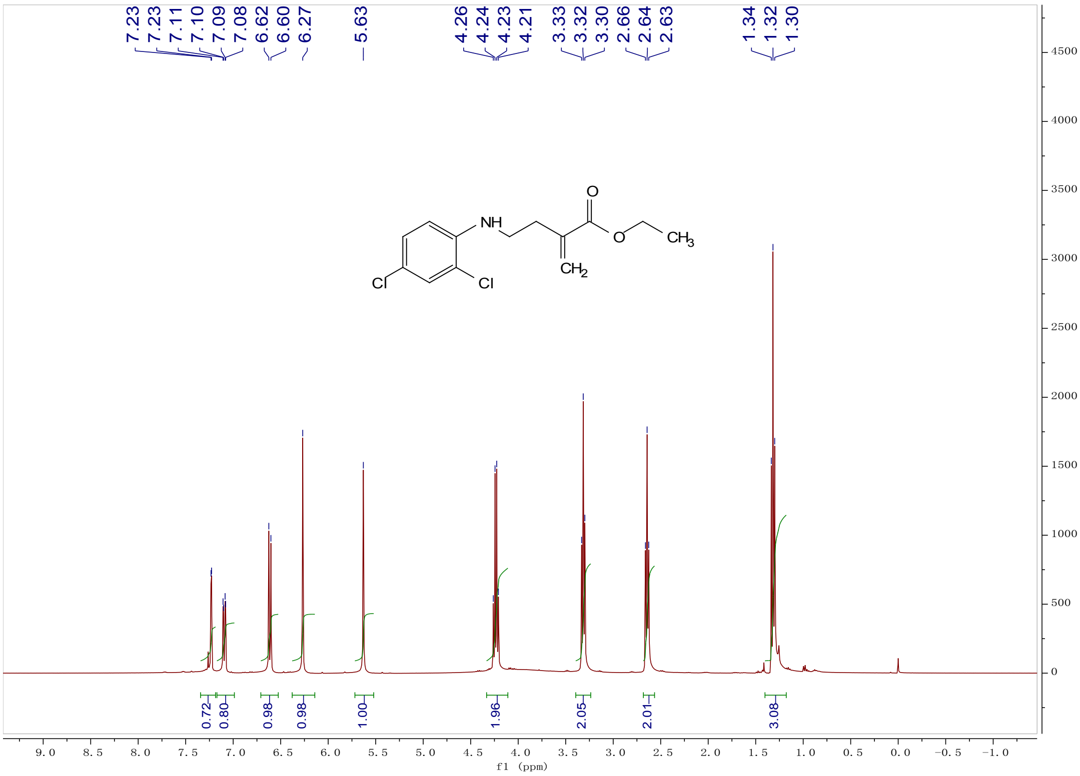
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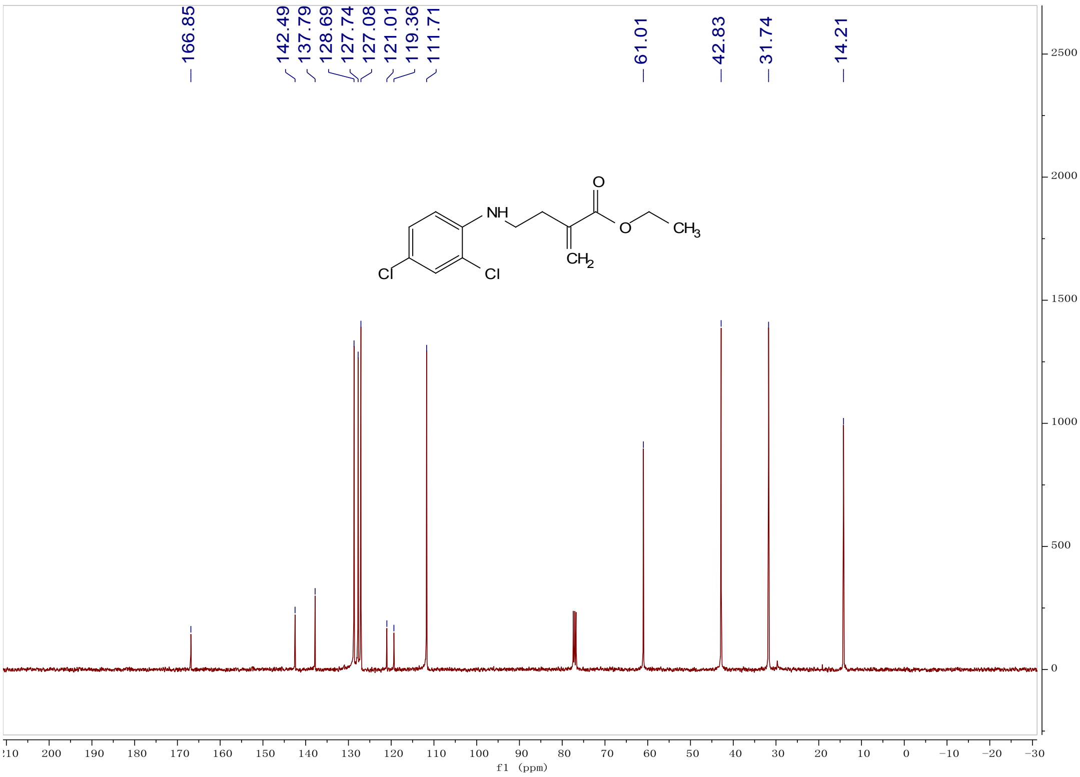
0.98
1.00
1.96
2.05
2.01
3.08
f1 (ppm)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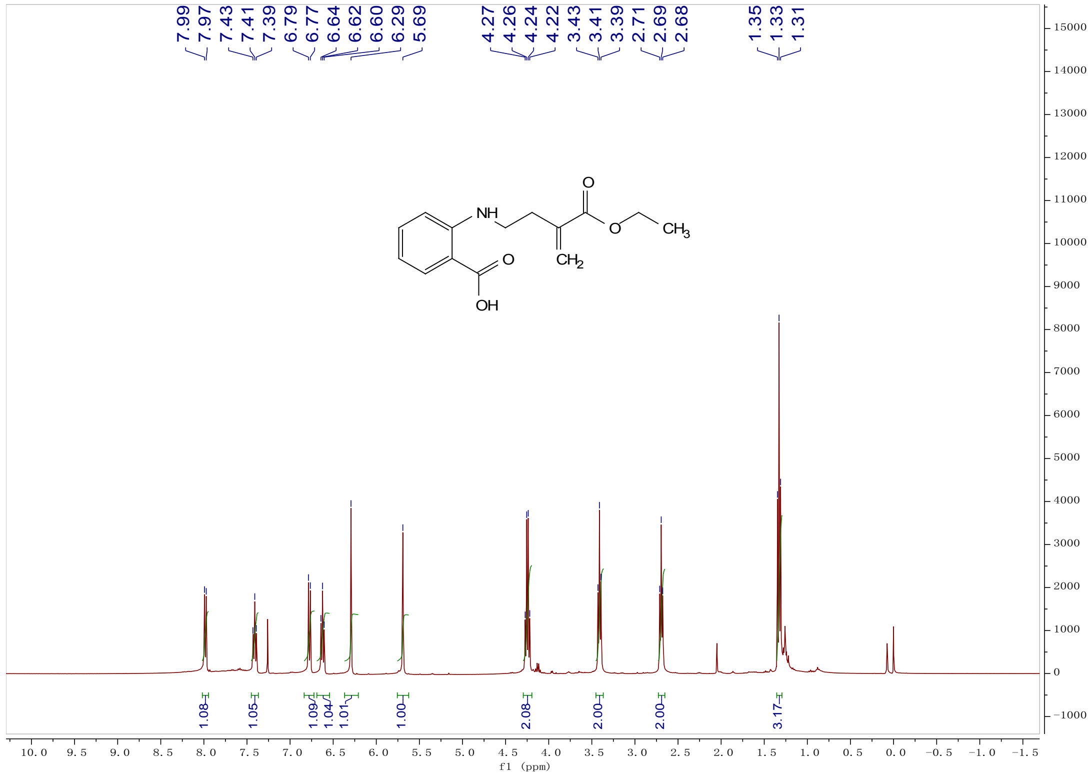
O
CH3
CH2
Cl
Cl
f1 (ppm)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NH
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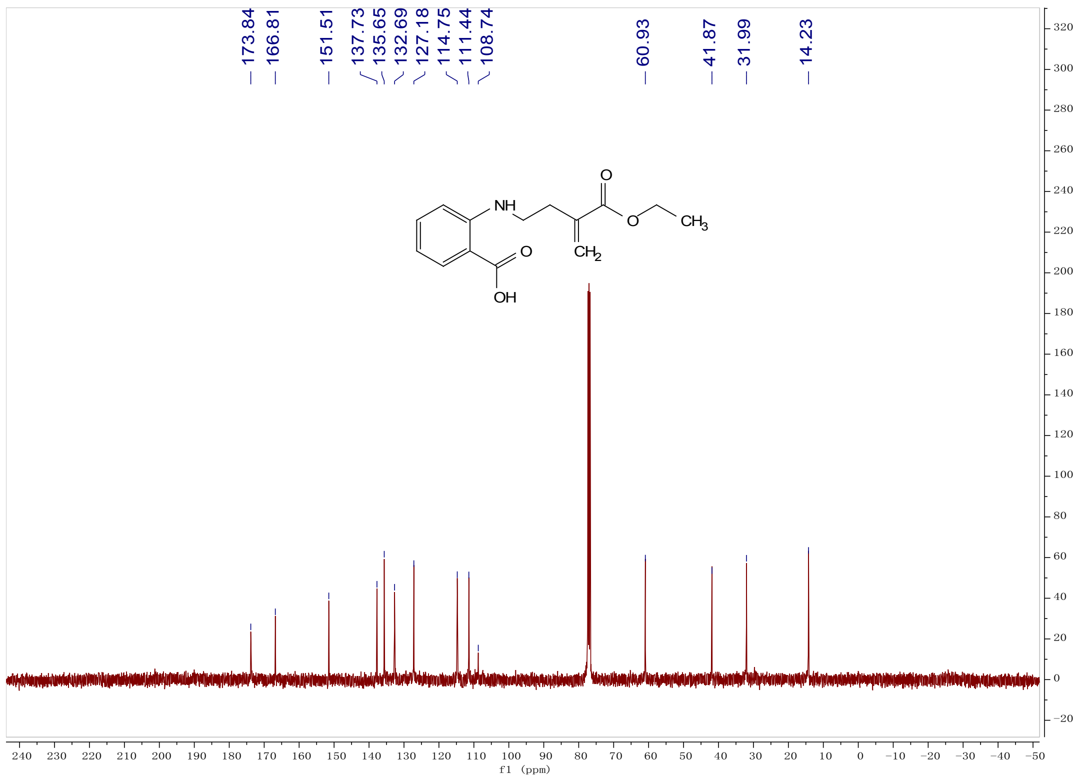
O
CH3
CH2
O
OH
1.08 1.05 1.09 1.04 1.01 1.00 2.08 2.00 2.00 3.17
f1 (ppm)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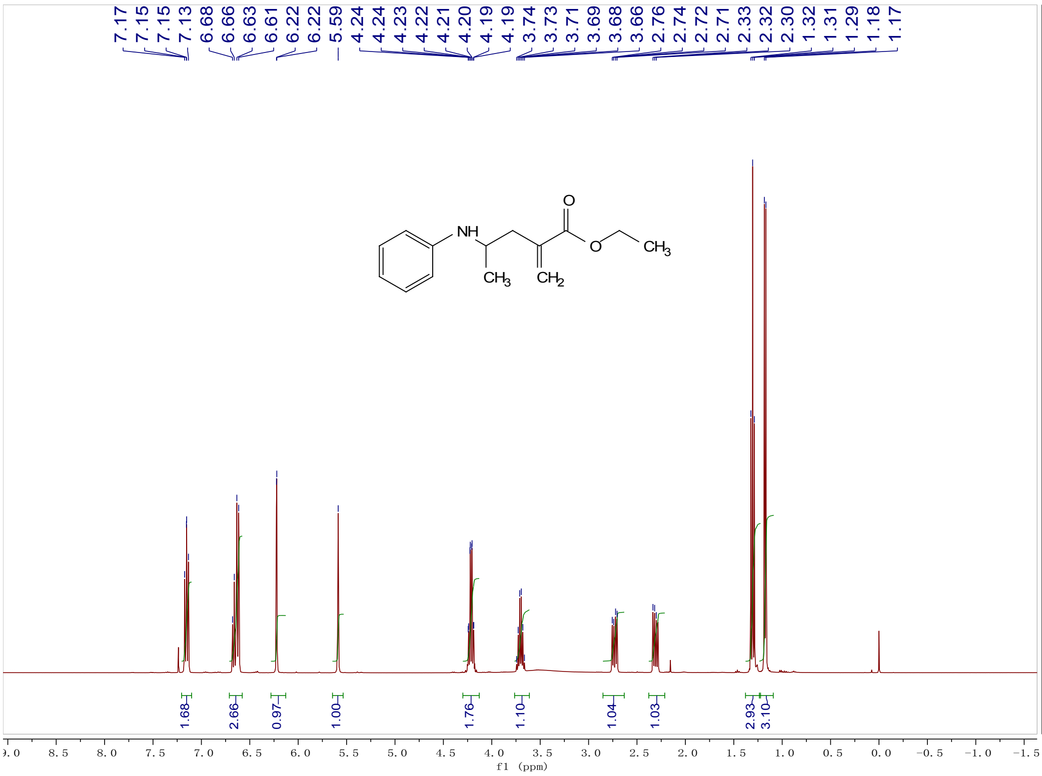
NH
O
O
CH3
CH2
O
OH
f1 (ppm)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6.63
6.61
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6.22
5.59
4.24
4.23
4.22
4.21
4.20
4.19
4.19
3.74
3.73
3.71
3.69
3.68
3.66
2.76
2.74
2.72
2.71
2.33
2.32
2.30
1.32
1.31
1.29
1.18
1.17
NH
O
O
CH3
CH3
CH2
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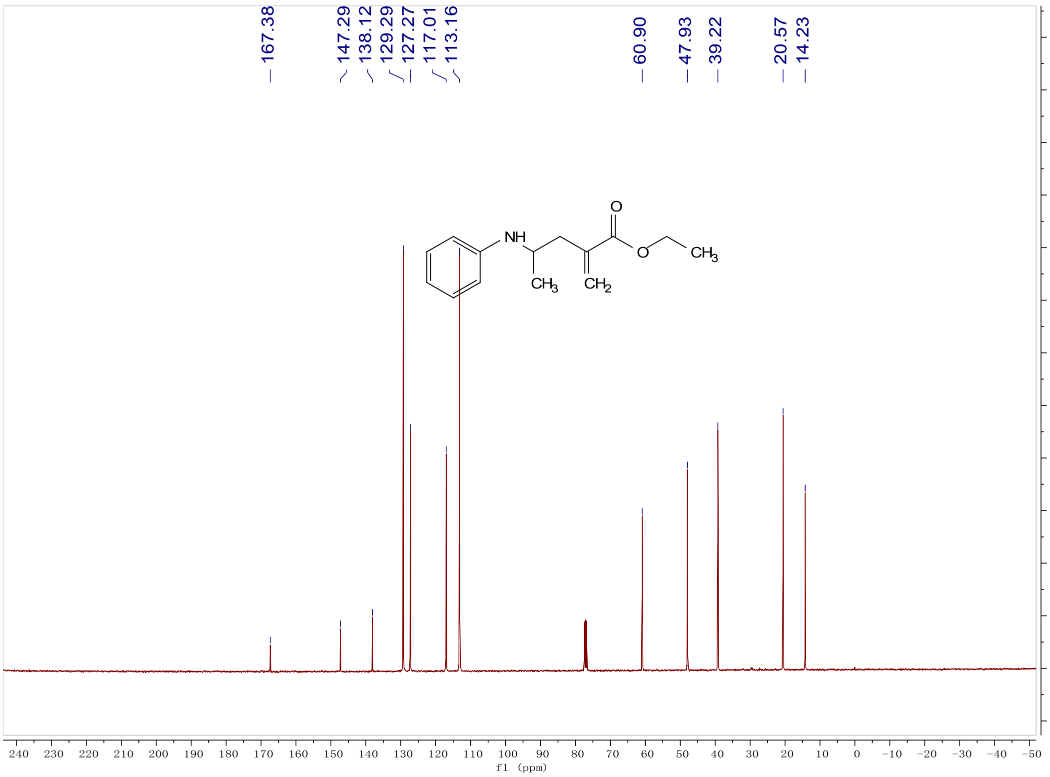
1.00
1.76
1.10
1.04
1.03
2.93
3.10
f1 (ppm)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127.27
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39.22
20.57
14.23
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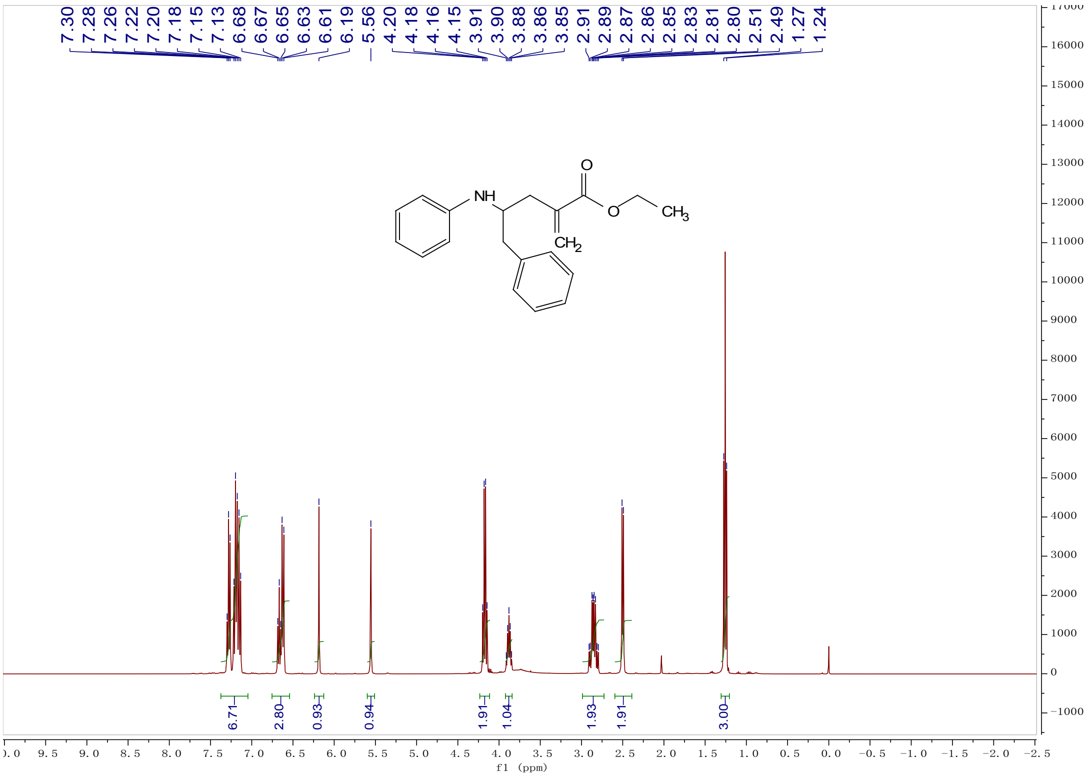
CH3
CH2
f1 (ppm)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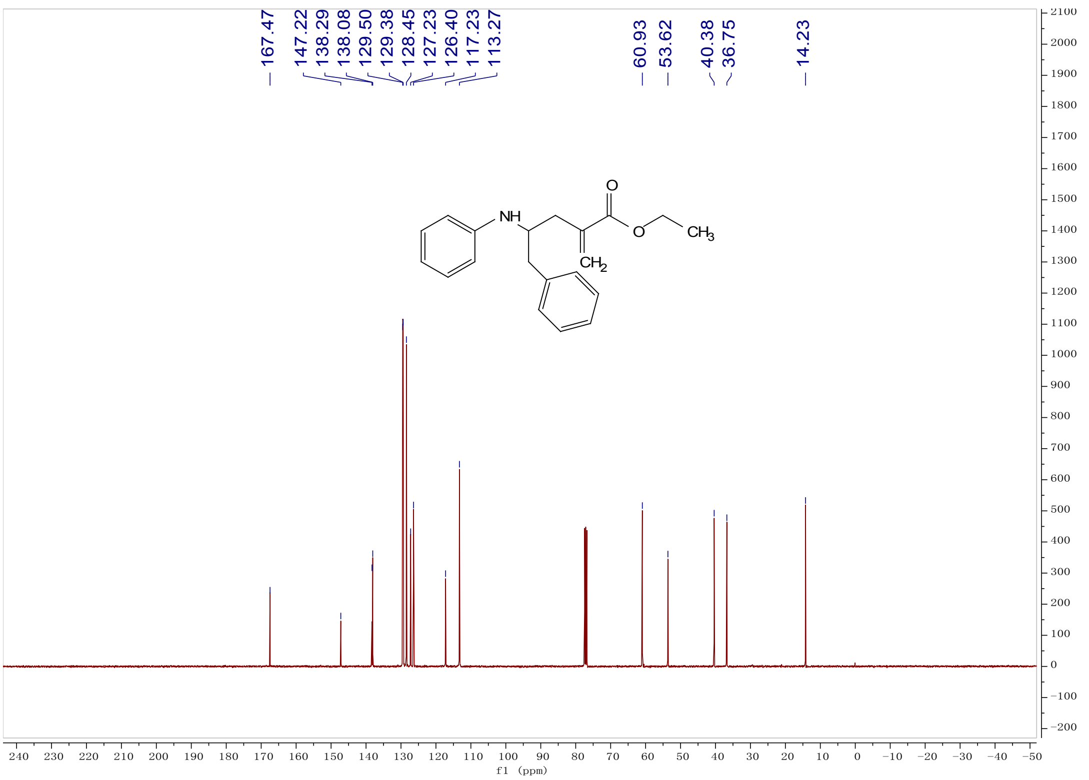
NH
O
O
CH3
CH2
6.71 2.80 0.93 0.94 1.91 1.04 1.93 1.91 3.00
f1 (ppm)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NH
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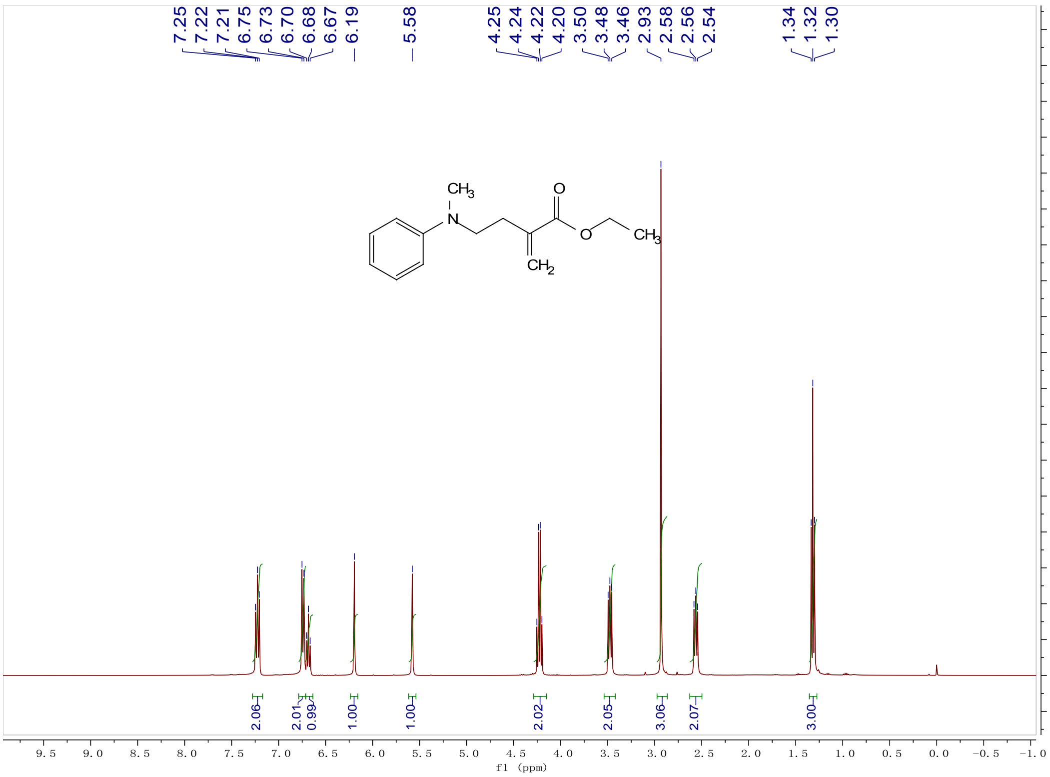
CH3
CH2
f1 (ppm)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7.21
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6.67
6.19
5.58
4.25
4.24
4.22
4.20
3.50
3.48
3.46
2.93
2.58
2.56
2.54
1.34
1.32
1.30
CH3
N
O
O
CH3
CH2
2.06
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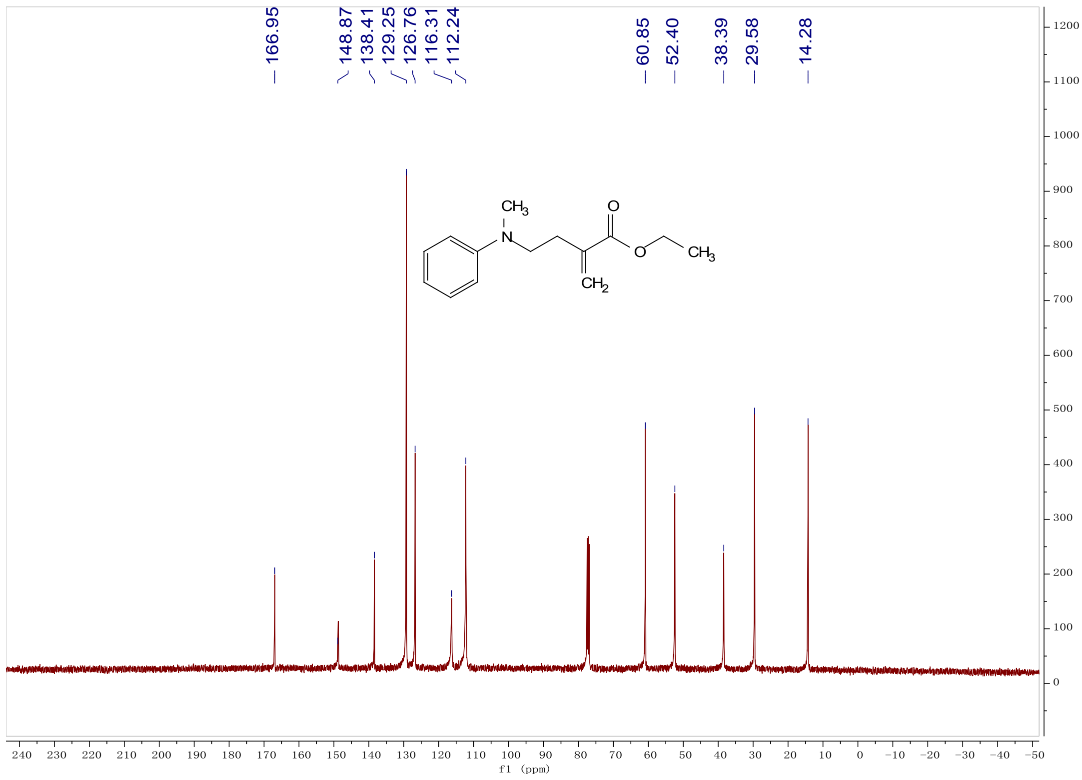
0.99
1.00
1.00
2.02
2.05
3.06
2.07
3.00
f1 (ppm)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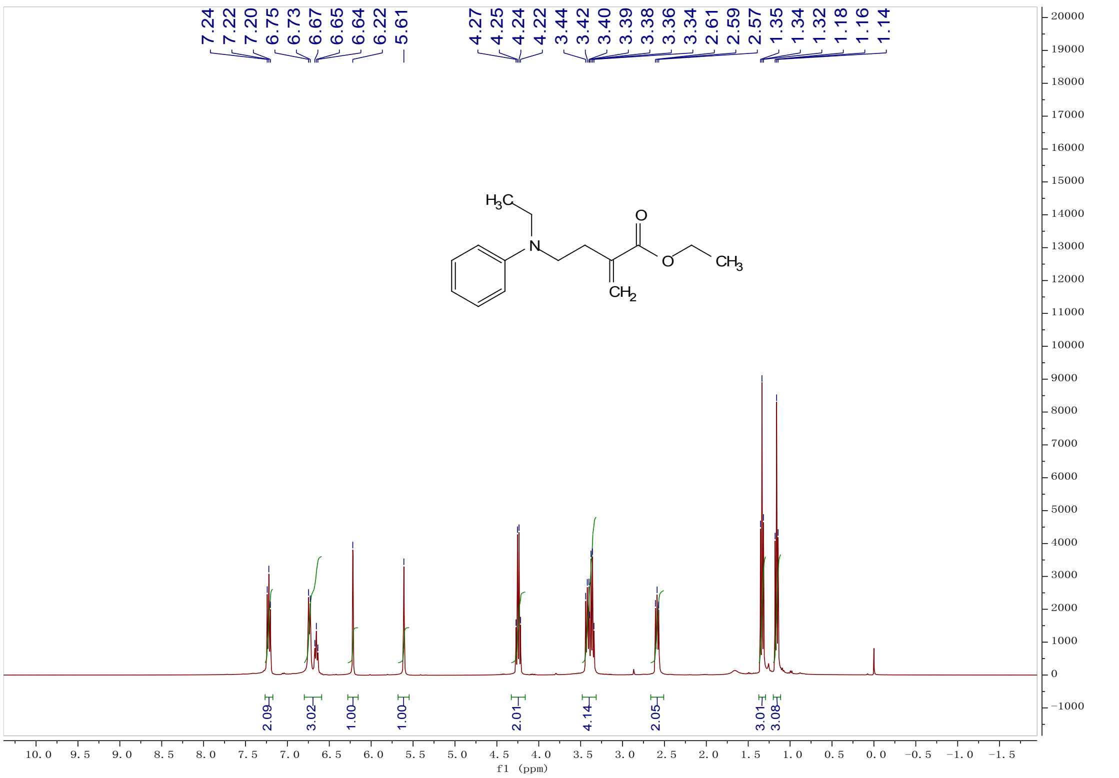
O
CH3
CH2
f1 (ppm)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H_3C
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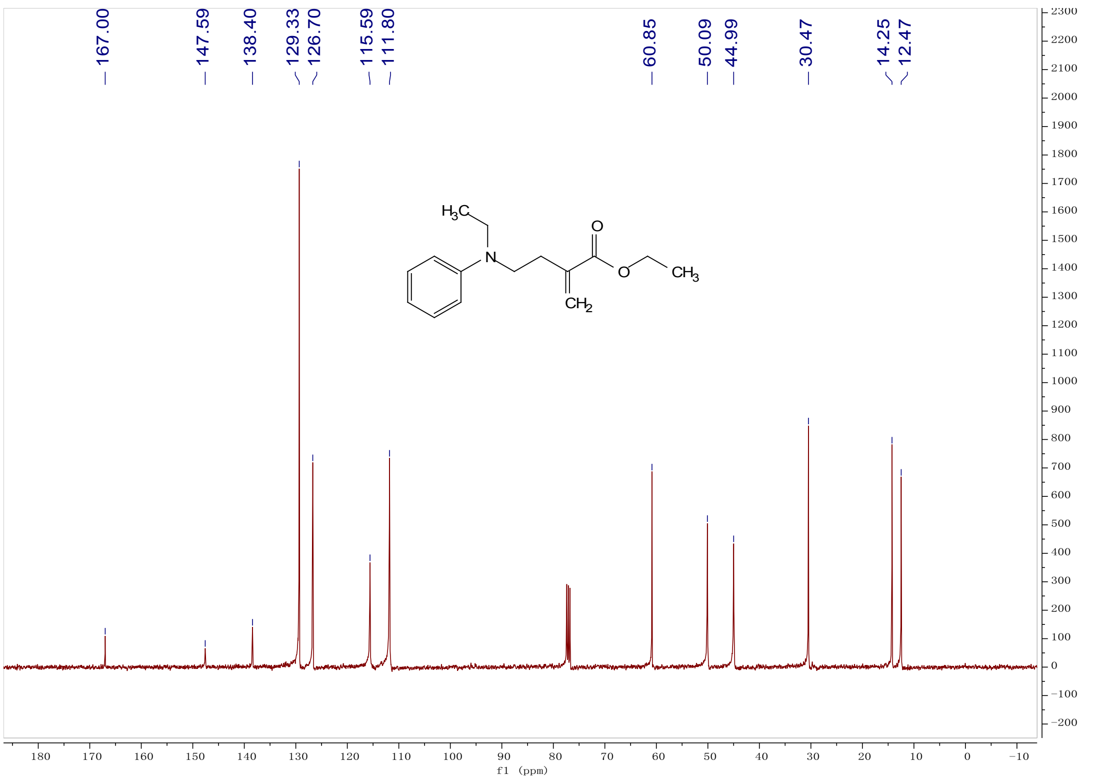
O
O
CH_3
CH_2
2.09 3.02 1.00 1.00 2.01 4.14 2.05 3.01 3.08
f1 (ppm)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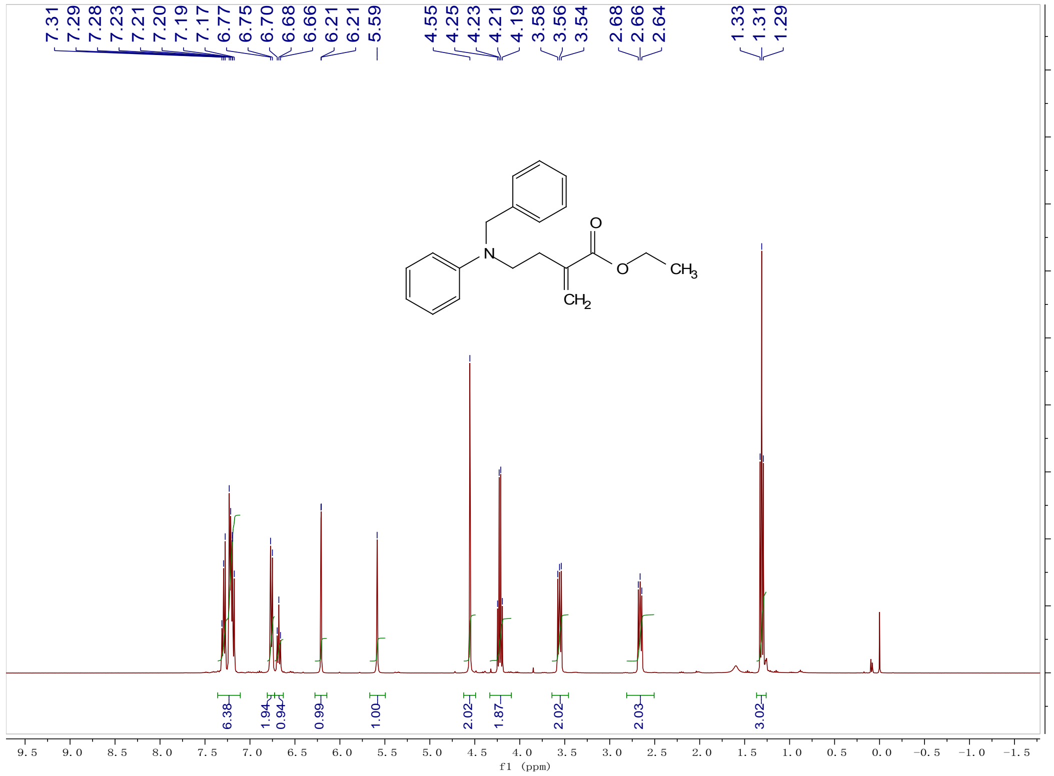
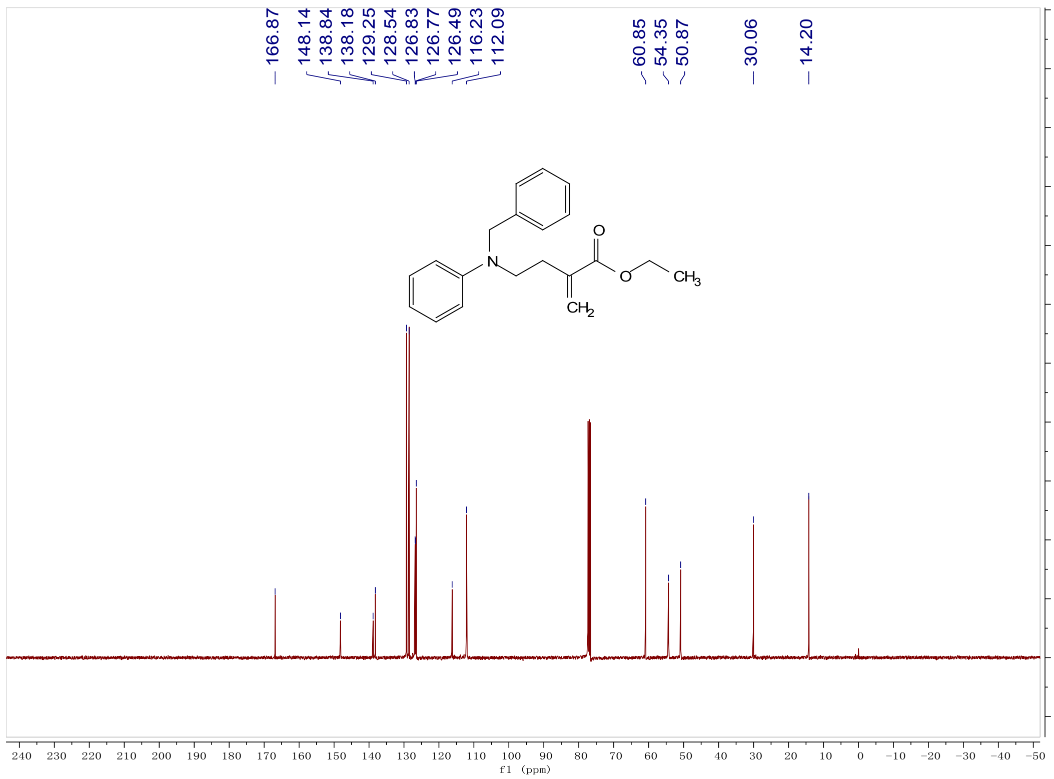
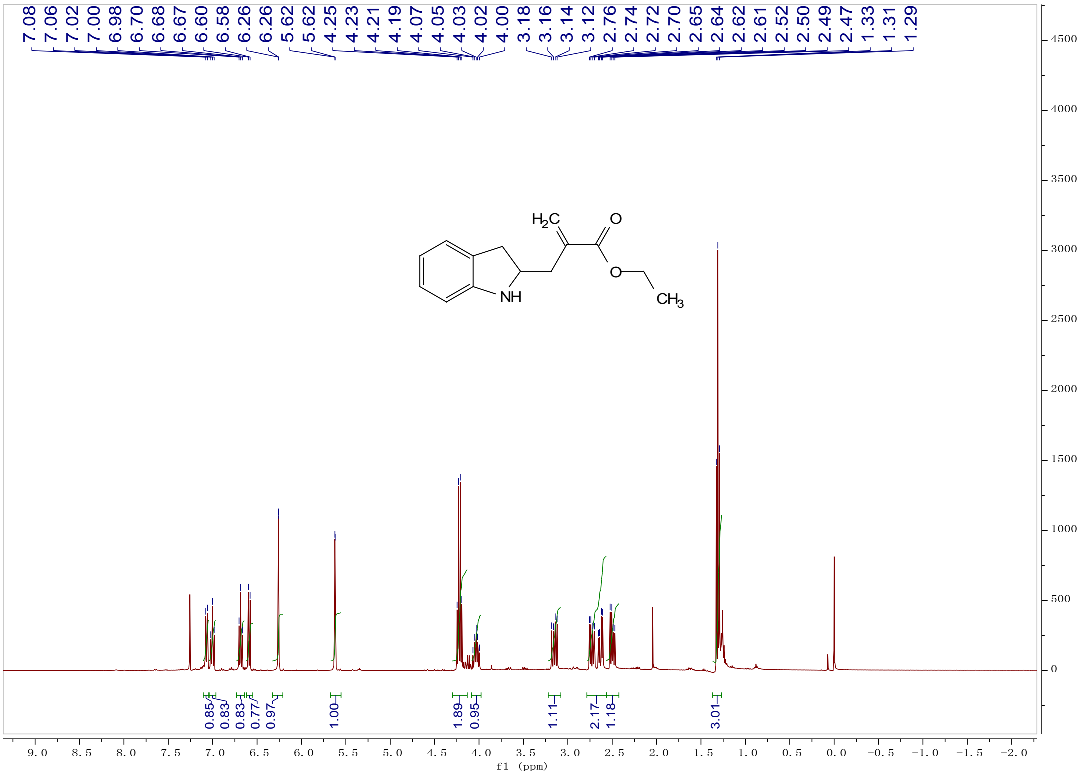
O
CH_3
CH_2
f1 (ppm)



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6.67
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6.58
6.26
6.26
5.62
5.62
4.25
4.23
4.21
4.19
4.07
4.05
4.03
4.02
4.00
3.18
3.16
3.14
3.12
2.76
2.74
2.72
2.70
2.65
2.64
2.62
2.61
2.52
2.50
2.49
2.47
1.33
1.31
1.29
H2C
O
O
NH
CH3
0.85
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0.83
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0.97
1.00
1.89
0.95
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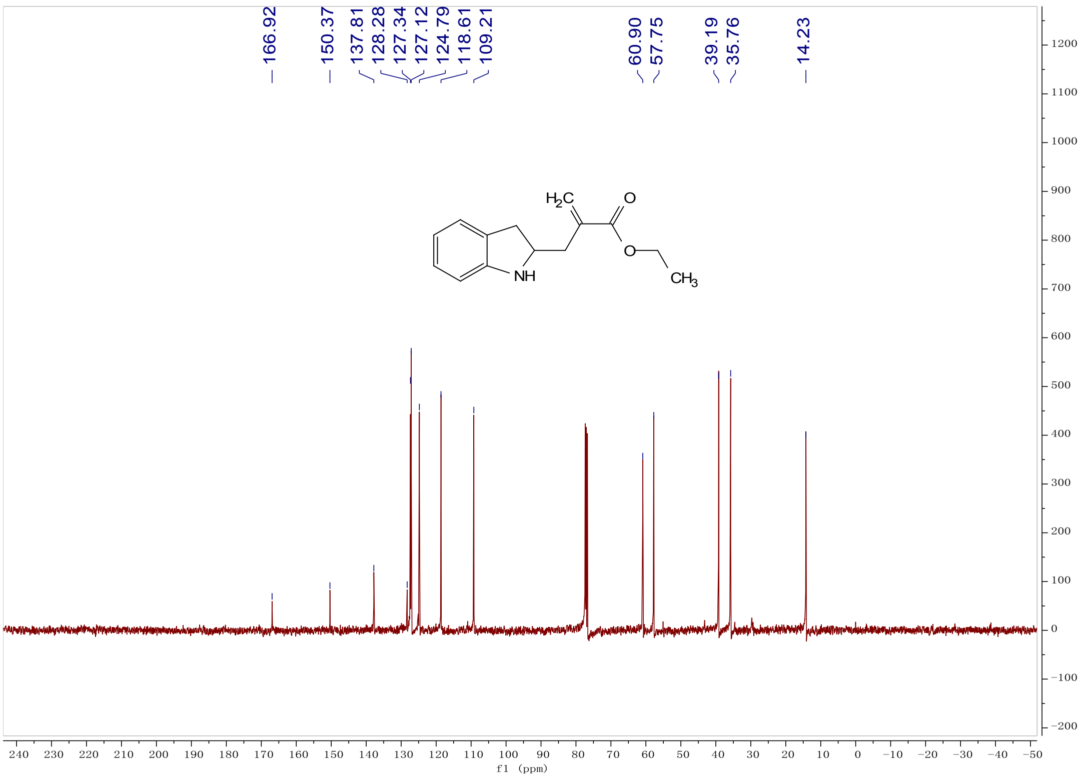
2.17
1.18
3.01
f1 (ppm)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127.12
124.79
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109.21
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57.75
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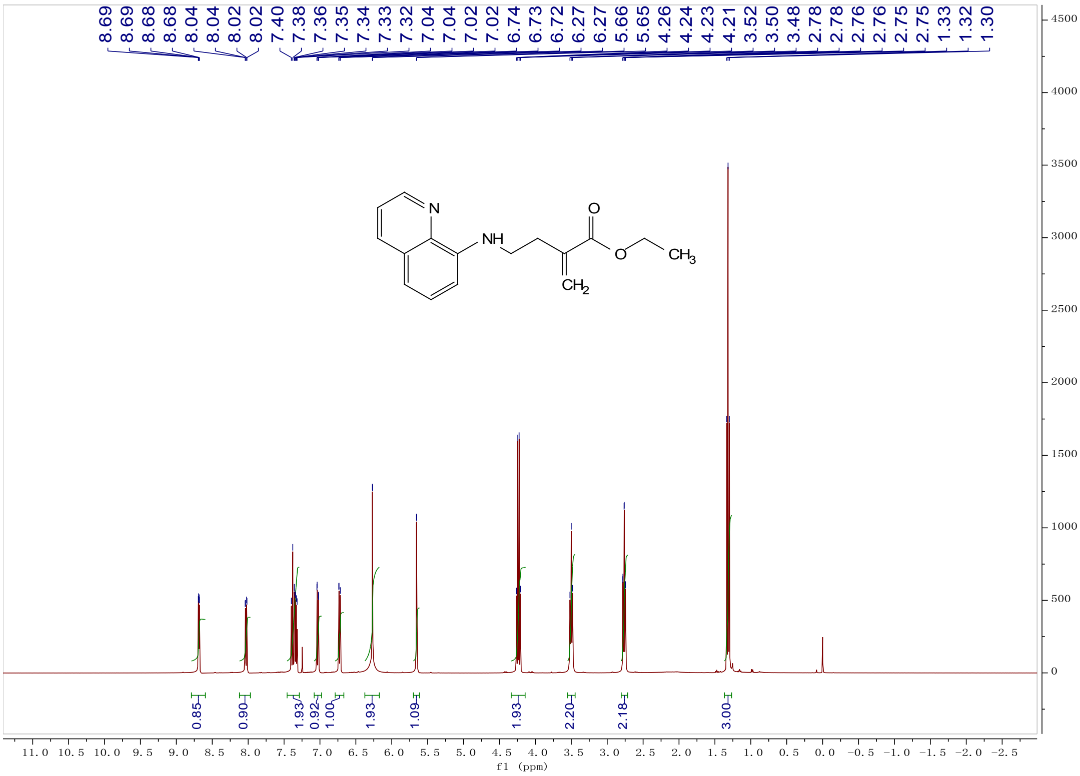
35.76
14.23
H2C
O
O
NH
CH3
f1 (ppm)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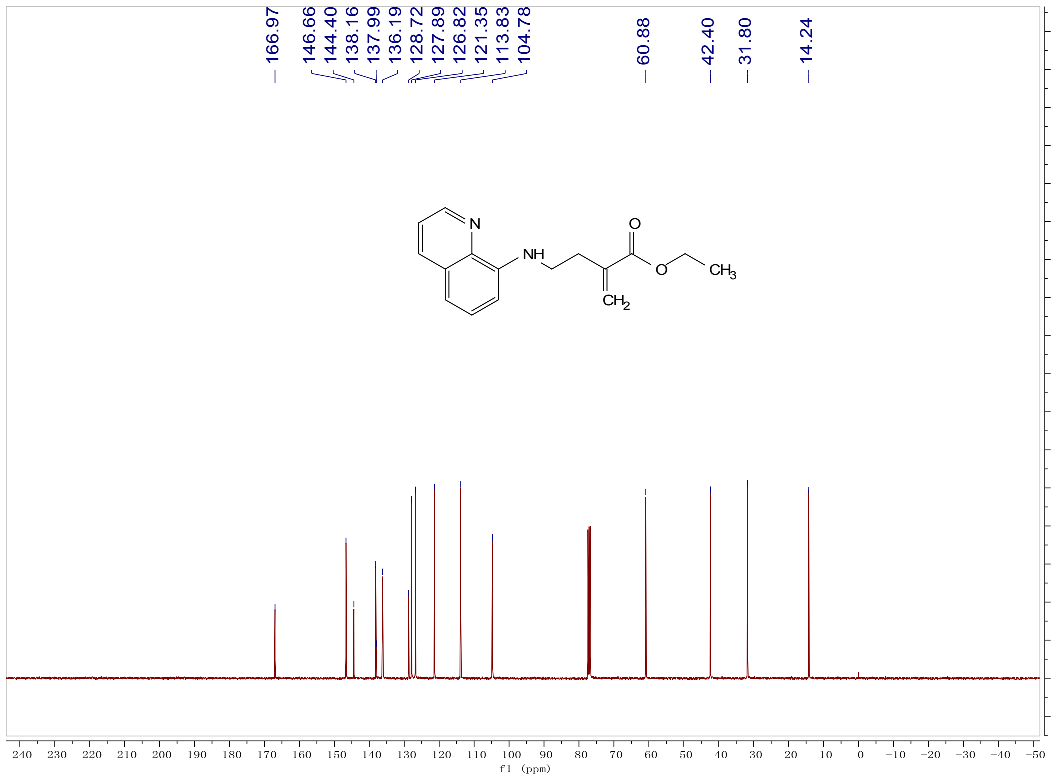
8.68
8.04
8.04
8.02
8.02
7.40
7.38
7.36
7.35
7.34
7.33
7.32
7.04
7.04
7.02
7.02
6.74
6.73
6.72
6.27
6.27
5.66
5.65
4.26
4.24
4.23
4.21
3.52
3.50
3.48
2.78
2.78
2.76
2.76
2.75
2.75
1.33
1.32
1.30
N
NH
O
O
CH_3
CH_2
0.85
0.90
1.93
0.92
1.00
1.93
1.09
1.93
2.20
2.18
3.00
f1 (ppm)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60.88
42.40
31.80
14.24
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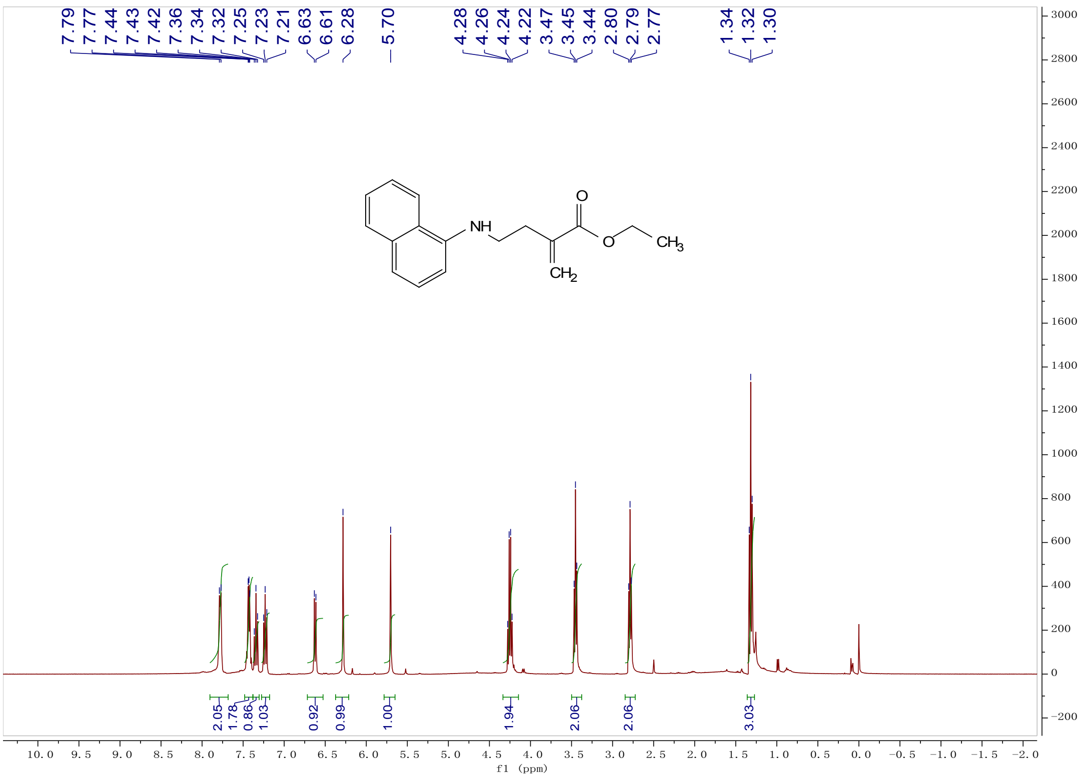
NH
O
O
CH3
CH2
f1 (ppm)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7.21
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6.28
5.70
4.28
4.26
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4.22
3.47
3.45
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2.79
2.77
1.34
1.32
1.30
NH
O
O
CH3
CH2
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0.92
0.99
1.00
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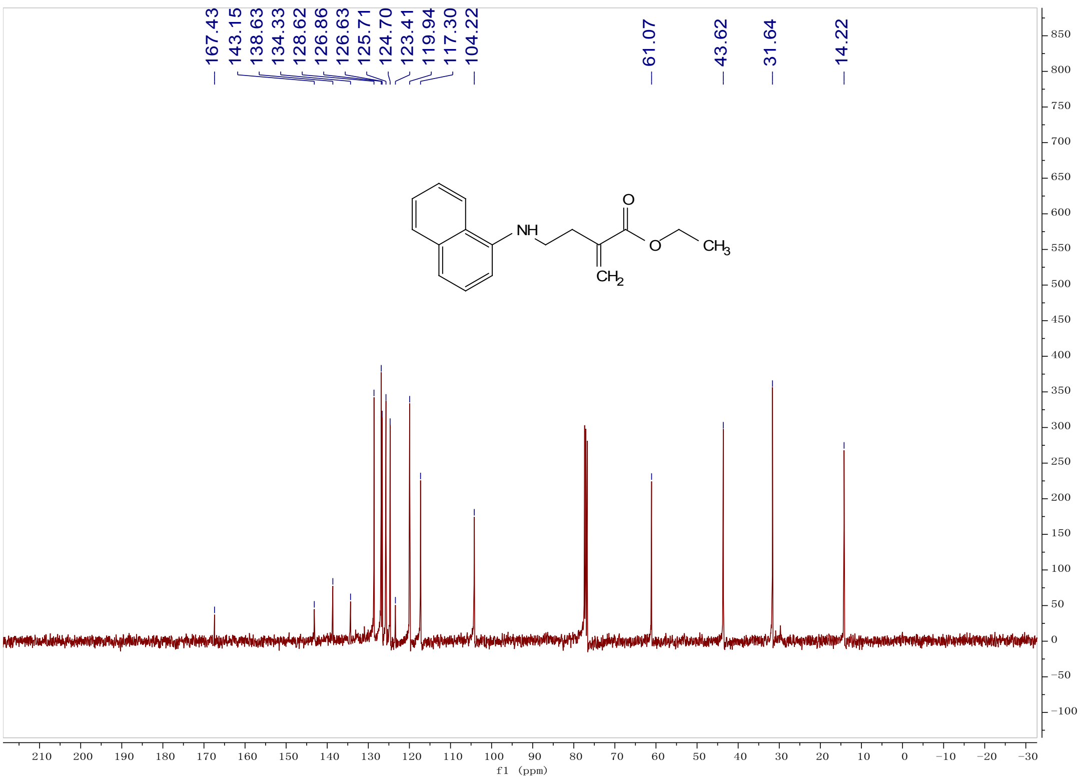
2.06
3.03
f1 (ppm)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124.70
123.41
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117.30
104.22
61.07
43.62
31.64
14.22
NH
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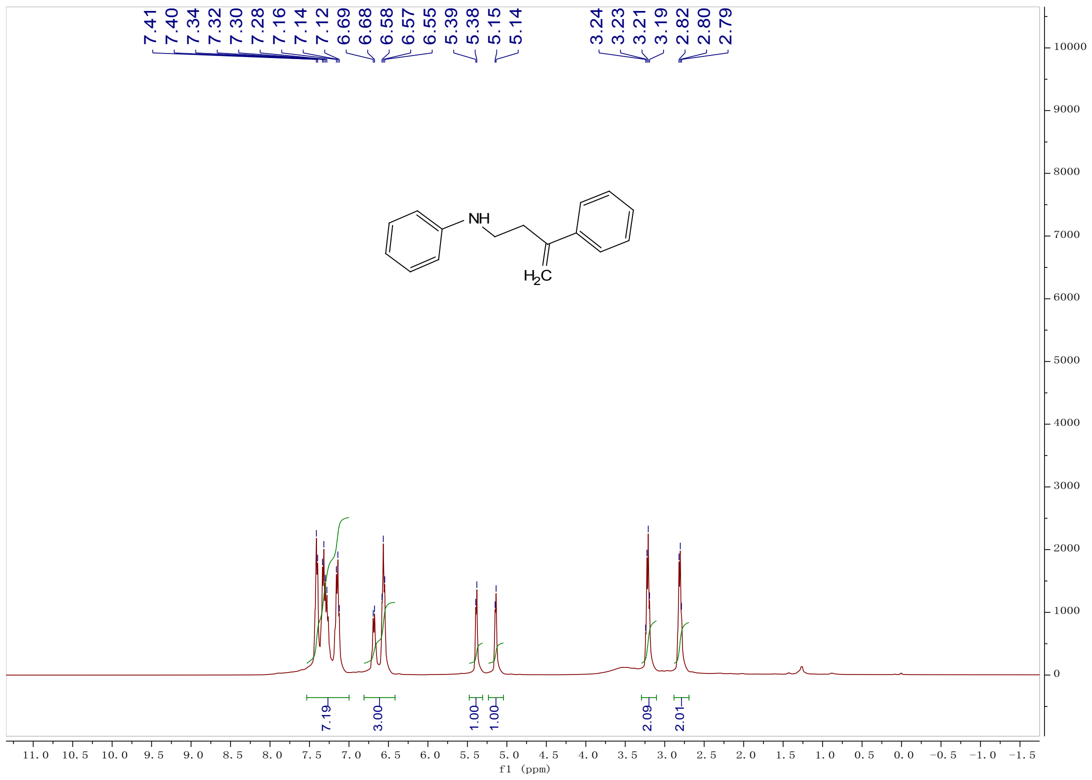
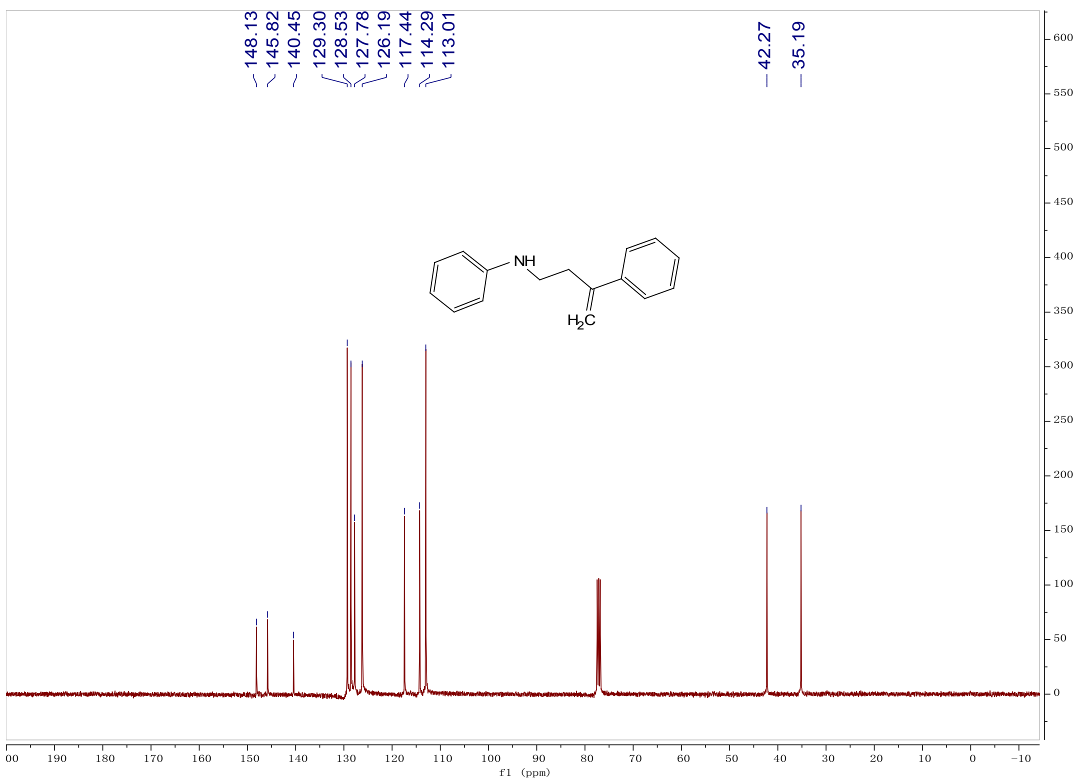
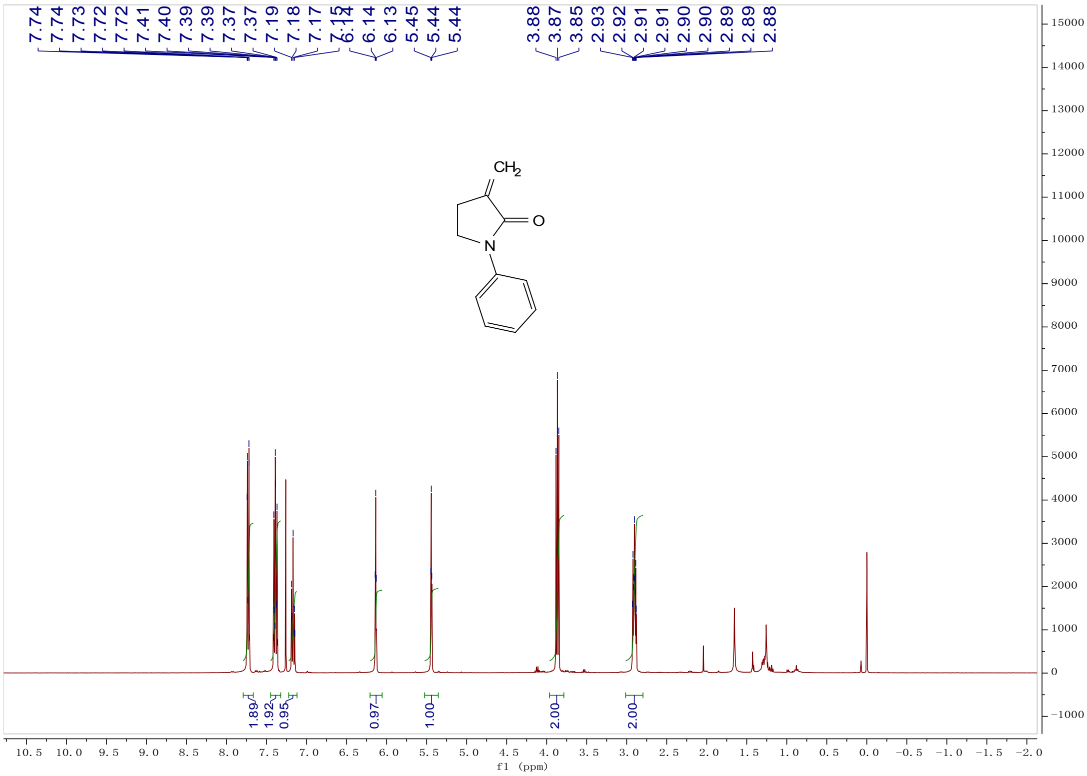
O
CH3
CH2
f1 (ppm)



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CH2
O
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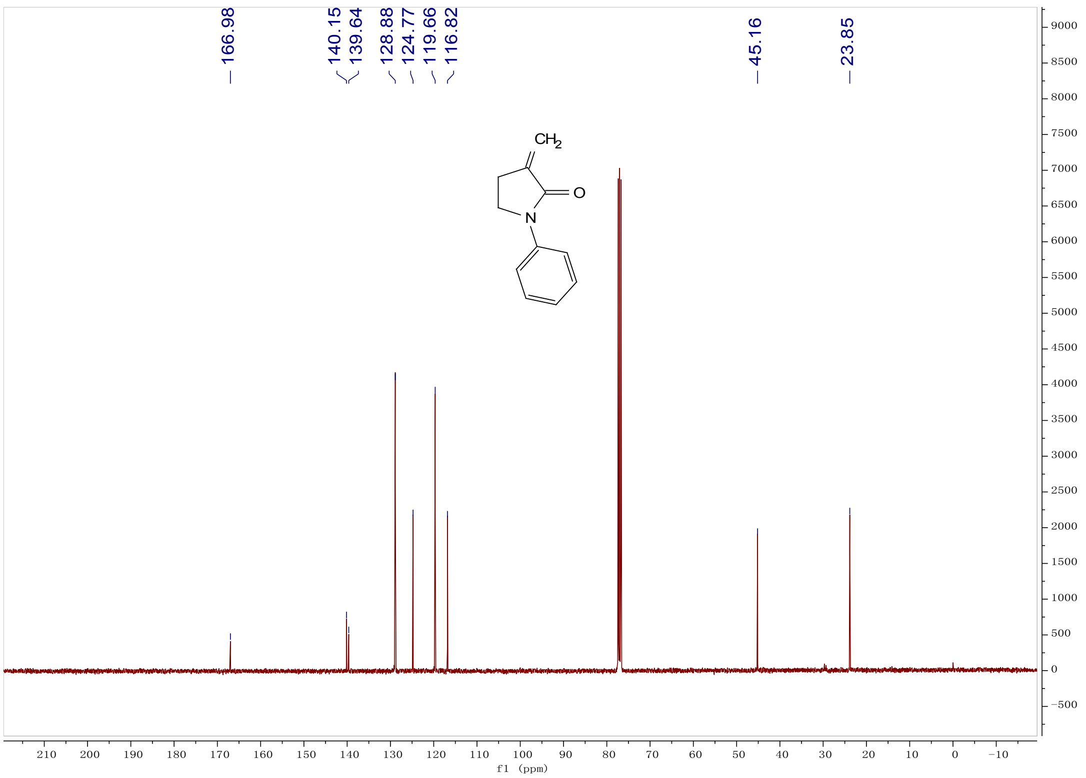
1.89 1.92 0.95 0.97 1.00 2.00 2.00
f1 (ppm)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N
f1 (ppm)