Supporting Information

Electrochemical Oxidative C-H/S-H Cross-Coupling between Enamines and Thiophenols with H_2 Evolution

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Contents

1. General information

All glassware was oven dried at 110 °C for hours and cooled down under vacuum. The instrument for electrolysis was dual display potentiostat (DJS-292B) (made in China). Cyclic voltammograms were obtained on a CHI 605E potentiostat. All undivided cells were purchased from Jiehengda® limited liability company (https://www.whjiehengda.com). All the electrode clamps were purchased from Gaoss Uinon® (https://gaossunion.cn.made-in-china.com). The anode electrode is carbon cloth electrodes (1.5 × 1.5 cm^2) and cathode electrode is Fe plate electrodes (1.5 × 1.5 cm^2). Enamines were synthesized according to literature procedures.[1] Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 silica gel or neutral alumina in petroleum (bp. 60-90 °C). ^1H and ^{13}C NMR data were recorded with Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (0 ppm for ^1H, 77.00 ppm for ^{13}C) or DMSO-d6 (2.50 ppm for ^1H, 39.6 ppm for ^{13}C), respectively. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker X-band A200 spectrometer.

2. Set-up diagram of electrochemical reaction

As experimental set-up, a carbon cloth electrode (1.5 × 1.5 × 0.036 cm^3), a Fe plate electrode (1.5 × 1.5 × 0.1 cm^3), two electrode clamps (pt-3), rubber plugs, an undivided three-necked bottle, a dual display potentiostat (DJS-292B) and a heating magnetic whisk were used.

a. a carbon cloth, a Fe plate, two electrode clamps (pt-3), and rubber plugs

b. Assembly of electrode

c. Assembly of electrochemical cell

d. Current controlled electrolysis

3. Experimental procedure

General procedure for the electro-oxidative enamines and thiophenols cross-coupling: In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, enamines (0.2 mmol), thiophenols (0.4 mmol), $^{n}Bu_4NBF_4$ (32.9 mg, 0.1 mmol) and CH_3CN (10 mL) were combined and added. The flask was equipped with The flask was equipped with carbon cloth electrodes (1.5 × 1.5 × 0.036 cm^3) as anode and Fe plate electrodes (1.5 × 1.5 × 0.1 cm^3) as cathode. The flask was flushed with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 3 mA under room temperature for 5 h. When the reaction was finished, the solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent.

Procedure for gram scale synthesis: In an oven-dried undivided three-necked flask (100 mL) equipped with a stir bar, (Z)-ethyl 3-(allylamino)-3-phenylacrylate **1a** (695.0 mg, 3.0 mmol), 4-chlorobenzenethiol **2a** (868.0 mg, 6.0 mmol), $^{n}Bu_4NBF_4$ (247.0 mg, 0.75 mmol) and CH_3CN (75 mL) were combined and added to a flask. The flask was equipped with carbon cloth electrodes (1.5 × 1.5 × 0.036 cm^3) as anode and Fe plate electrodes (1.5 × 1.5 × 0.1 cm^3) as cathode. The flask was flushed with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 3 mA under room temperature for 48 h. When the reaction was finished, the solvent was removed with a rotary evaporator. The pure product was obtained by flash column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent.

General procedure for cyclic voltammetry (CV): Cyclic voltammetry was performed in a three electrode cell connected to a schlenk line under nitrogen at room temperature. The working electrode was a glassy carbon electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. 10 mL of CH_3CN containing 0.01 M $^{n}Bu_4NBF_4$ were poured into the electrochemical cell in all experiments. The scan rate is 0.05 V/s, ranging from 0 V to

2.0 V. The peak potentials vs. Ag/AgCl for used. An obvious oxidation peak of **1a** was observed at 1.35 V. The oxidation peak of **2a** could also be observed at 1.44 V. At the same time, the CV of **1a** and **2a** was also tested, with the oxidation peaks at 1.38 V.

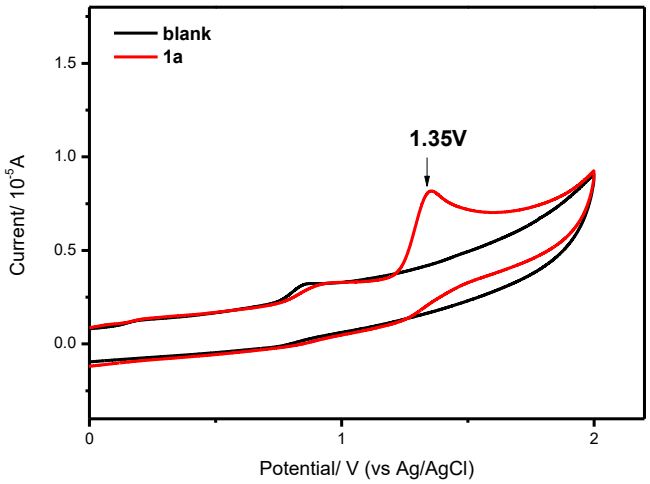


Figure S1. Cyclic voltammetry of **1a** (5×10^{-4} M) in CH_3CN with $^nBu_4NBF_4$ (0.01 M) under nitrogen at a scan rate of v=50 mV/s.

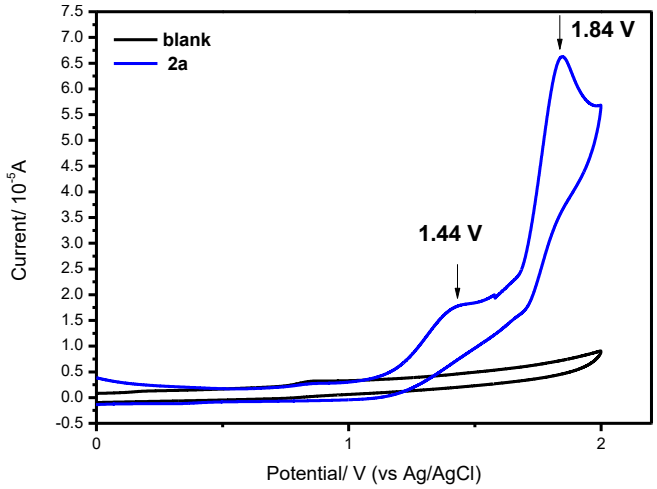


Figure S2. Cyclic voltammetry of **2a** (10^{-3} M) in CH_3CN with $^nBu_4NBF_4$ (0.01 M) under nitrogen at a scan rate of v=50 mV/s.

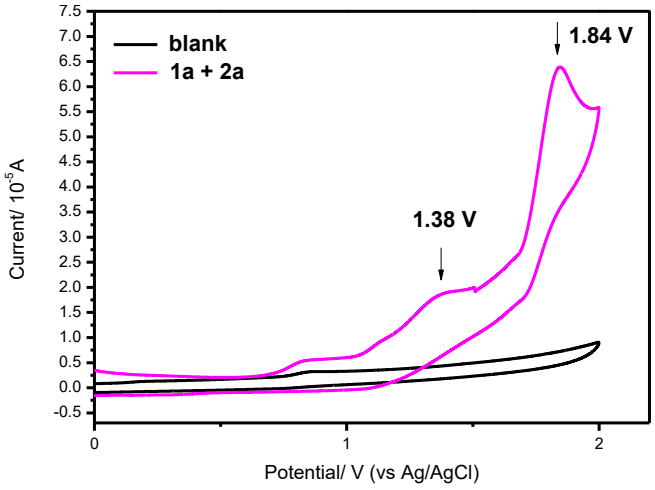


Figure S3. Cyclic voltammetry of **1a** (5×10^{-4} M) and **2a** (10^{-3} M) in CH_3CN with $^{n}Bu_4NBF_4$ (0.01 M) under nitrogen at a scan rate of v=50 mV/s.

EPR experiments:

a) Under constant current conditions, a dried three-necked flask equipped with a stir bar was loaded with **1a** (0.20 mmol), $^{n}Bu_4NBF_4$ (0.1 mmol) and DMPO (30 μL) in 10.0 mL CH_3CN was stirred under an N_2 atmosphere at 25 ºC. After 8 minutes, the solution sample was taken out into a small tube and analyzed by EPR. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.810565 GHz. Typical spectrometer parameters are shown as follows, scan range: 100 G; center field set: 350.0655 G; time constant: 163.84 ms; scan time: 30 s modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 1.00×104; microwave power: 21.59 mW.PR. In this spectra, three type of radical have been trapped by DMPO. 1. DMPO-H: A_N = 14.1 G, A_H = 14.0 G, A_H = 14.0 G; 2. DMPO-C: A_N = 14.5 G, A_H = 21.3 G (this type of radicals also has been detected by HRMS (ESI) ($C_{20}H_{27}N_2O_3$:343.2016, found: 343.2011). 3. Uncertain free radical trapped by DMPO: A_N = 14.5 G, A_H = 21.3 G.

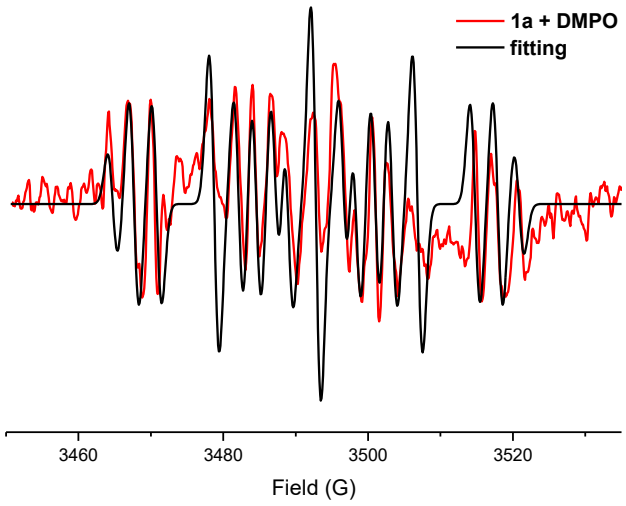


Figure S4. EPR measurements of a solution in CH_3CN of $^nBu_4NBF_4$, and **1a** in the presence of DMPO under constant current conditions for 8 min.

b) Under constant current conditions, a dried three-necked flask equipped with a stir bar was loaded with **1a** (0.20 mmol), **2a** (0.4 mmol), $^nBu_4NBF_4$ (0.1 mmol) and DMPO (30 μL) in 10.0 mL CH_3CN was stirred under an N_2 atmosphere at 25 ºC. After 5 minutes, the solution sample was taken out into a small tube and analyzed by EPR. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.821452 GHz. Typical spectrometer parameters are shown as follows, scan range: 100 G; center field set: 3504.54 G; time constant: 163.84 ms; scan time: 30 s modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 1.00×104; microwave power: 21.59 mW.PR. What's more, the S-centred radicals trapped by DMPO have been detected by HRMS (ESI) ($C_{12}H_{15}ClNOS$: 255.0559, found: 255.0557).

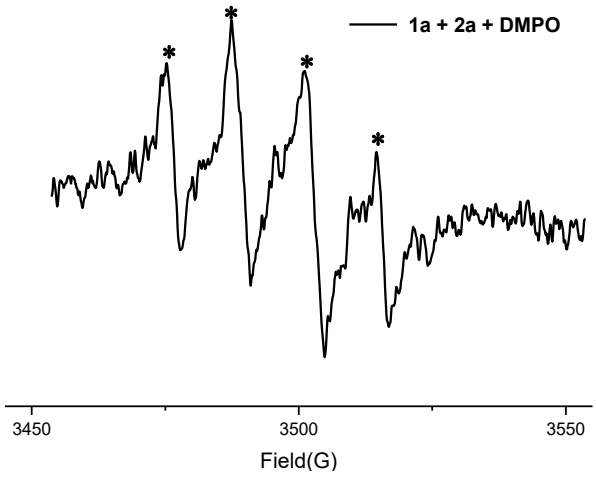
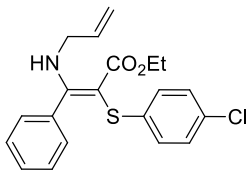
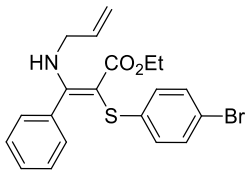


Figure S5. EPR measurements of a solution in CH_3CN of $^nBu_4NBF_4$, **1a** and **2a** in the presence of DMPO under constant current conditions for 5 min.

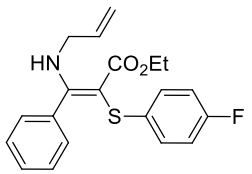
4. Detail descriptions for products



(E)-ethyl 3-(allylamino)-2-((4-chlorophenyl)thio)-3-phenylacrylate (3aa): white solid was obtained with 89% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (t, *J* = 6.1 Hz, 1H), 7.39 – 7.28 (m, 3H), 7.17 – 7.11 (m, 2H), 7.08 – 7.03 (m, 2H), 6.98 – 6.91 (m, 2H), 5.80 – 5.70 (m, 1H), 5.25 – 5.04 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.58 – 3.54 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.38, 171.07, 140.33, 134.53, 134.17, 129.52, 128.92, 128.30, 128.18, 126.58, 126.02, 116.52, 82.92, 60.18, 47.79, 14.38. HRMS (ESI) calculated for $C_{20}H_{20}ClNNaO_2S$ $[M+Na]^+$: 396.0795; found: 396.0803.

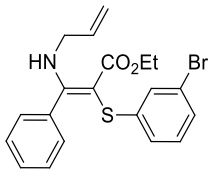


(E)-ethyl 3-(allylamino)-2-((4-bromophenyl)thio)-3-phenylacrylate (3ab): white solid was obtained with 80% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ10.15 (d, *J* = 5.7 Hz, 1H), 7.45 – 7.21 (m, 5H), 7.10 – 7.00 (m, 2H), 6.95 – 6.79 (m, 2H), 5.79 – 5.70 (m, 1H), 5.26 – 5.05 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.66 – 3.48 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.38, 171.02, 141.03, 134.49, 134.14, 131.15, 128.91, 128.17, 126.54, 126.30, 117.26, 116.51, 82.70, 60.17, 47.78, 14.37. HRMS (ESI) calculated for $C_{20}H_{20}BrNNaO_2S$ $[M+Na]^+$: 440.0290; found: 440.0293.

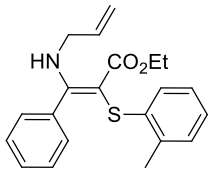


(E)-ethyl 3-(allylamino)-2-((4-fluorophenyl)thio)-3-phenylacrylate (3ac): white solid was obtained with 76% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (t, *J* = 6.3 Hz, 1H), 7.31 –

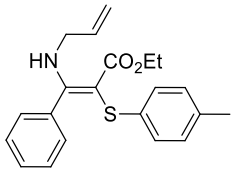
7.21 (m, 3H), 7.03 – 6.95 (m, 2H), 6.92 – 6.86 (m, 2H), 6.84 – 6.77 (m, 2H), 5.72 – 5.62 (m, 1H), 5.18 – 5.00 (m, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.49 – 3.46 (m, 2H), 1.10 (t, J = 7.1 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -119.42. ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.20, 171.17, 160.47 ($J_{C\text{-}F}$ = 242.7 Hz), 136.53 ($J_{C\text{-}F}$ = 3.0 Hz), 134.66, 134.24, 128.85, 128.13, 126.86, 126.77 ($J_{C\text{-}F}$ = 2.7 Hz), 116.46, 115.24 ($J_{C\text{-}F}$ = 21.7 Hz), 84.08, 60.13, 47.77, 14.37. HRMS (ESI) calculated for $C_{20}H_{20}FNNaO_2S$ $[M+Na]^+$: 380.1091; found: 380.1095.



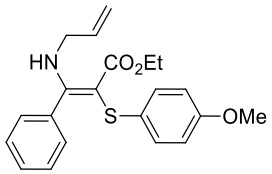
(E)-ethyl 3-(allylamino)-2-((3-bromophenyl)thio)-3-phenylacrylate (3ad): white solid was obtained with 80% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (t, J = 6.2 Hz, 1H), 7.41 – 7.27 (m, 3H), 7.17 – 7.11 (m, 2H), 7.09 – 6.98 (m, 3H), 6.93 – 6.90 (m, 1H), 5.76 – 5.72 (m, 1H), 5.25 – 5.12 (m, 2H), 4.20 (q, J = 7.1 Hz, 2H), 3.59 – 3.52 (m, 2H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.47, 170.96, 144.27, 134.46, 134.14, 129.56, 128.97, 128.20, 127.27, 126.93, 126.60, 123.36, 122.49, 116.55, 82.47, 60.17, 47.81, 14.38. HRMS (ESI) calculated for $C_{20}H_{20}BrNNaO_2S$ $[M+Na]^+$: 440.0290; found: 440.0296.



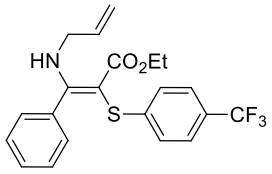
(E)-ethyl 3-(allylamino)-3-phenyl-2-(o-tolylthio)acrylate (3ae): white solid was obtained with 86% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.14 (t, J = 6.2 Hz, 1H), 7.48 – 7.27 (m, 3H), 7.15 – 7.10 (m, 1H), 7.08 – 7.02 (m, 2H), 7.00 – 6.88 (m, 3H), 5.82 – 8.72 (m, 1H), 5.11 (dq, J = 13.8, 1.8 Hz, 2H), 4.06 (q, J = 7.0 Hz, 2H), 3.55 – 3.52 (m, 2H), 1.91 (s, 3H), 1.03 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.20, 170.44, 140.40, 135.30, 134.43, 132.91, 129.51, 128.88, 128.11, 126.64, 126.22, 123.71, 115.91, 81.36, 59.49, 47.28, 19.15, 14.40. HRMS (ESI) calculated for $C_{21}H_{23}NNaO_2S$ $[M+Na]^+$: 376.1342; found: 376.1350.



(E)-ethyl 3-(allylamino)-3-phenyl-2-(p-tolylthio)acrylate (3af): white solid was obtained with 87% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ10.03 (t, *J* = 6.3 Hz, 1H), 7.28 – 7.18 (m, 3H), 7.05 – 6.96 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.86 – 6.81 (m, 2H), 5.72 – 5.62 (m, 1H), 5.18 – 5.02 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.49 – 3.46 (m, 2H), 2.19 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.35, 171.08, 137.95, 134.79, 134.36, 133.56, 129.00, 128.71, 128.06, 126.79, 125.13, 116.34, 83.94, 60.06, 47.74, 20.84, 14.37. HRMS (ESI) calculated for $C_{21}H_{23}NNaO_2S$ $[M+Na]^+$: 376.1342; found: 376.1345.

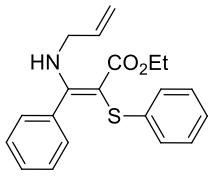


(E)-ethyl 3-(allylamino)-2-((4-methoxyphenyl)thio)-3-phenylacrylate (3ag): white solid was obtained with 80% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (t, *J* = 6.2 Hz, 1H), 7.35 – 7.22 (m, 3H), 7.05 – 6.98 (m, 2H), 6.92 – 6.86 (m, 2H), 6.73 – 6.63 (m, 2H), 5.70 – 5.62 (m, 1H), 5.14 – 5.01 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.68 (s, 3H), 3.49 – 3.45 (m, 2H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.39, 170.90, 157.18, 134.86, 134.38, 132.23, 128.72, 128.07, 127.47, 126.98, 116.35, 113.97, 85.15, 60.08, 55.25, 47.74, 14.42. HRMS (ESI) calculated for $C_{21}H_{23}NNaO_3S$ $[M+Na]^+$: 392.1291; found: 392.1297.

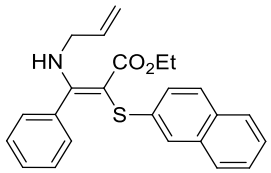


(E)-ethyl 3-(allylamino)-3-phenyl-2-((4-(trifluoromethyl)phenyl)thio)acrylate (3ah): white solid was obtained with 53% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.20 (t, *J* = 6.2 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.35 (t, *J* = 5.6 Hz, 3H), 7.13 (d, *J* = 8.3 Hz, 4H), 5.83 – 5.69 (m, 1H), 5.18 – 5.04 (m, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.59 – 3.55 (m, 2H), 1.02 (t, *J* = 7.0 Hz, 3H). ^{19}F

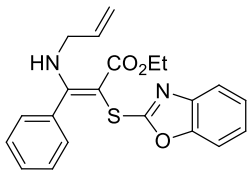
NMR (377 MHz, DMSO) δ -60.38. ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.58, 170.95, 147.11, 134.45, 134.13, 129.05, 128.27, 126.53 (q, J = 2.6 Hz), 126.08, 125.08 (q, J = 3.8 Hz), 124.31, 116.62, 99.90, 82.00, 60.24, 47.84, 14.34. HRMS (ESI) calculated for $C_{21}H_{20}F_3NNaO_2S$ $[M+Na]^+$: 430.1059; found: 430.1063.



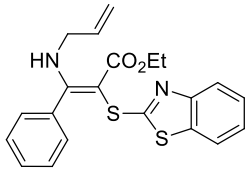
(E)-ethyl 3-(allylamino)-3-phenyl-2-(phenylthio)acrylate (3ai): white solid was obtained with 69% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ10.13 (t, J = 6.2 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.19 (t, J = 7.7 Hz, 2H), 7.13 – 7.07 (m, 2H), 7.04 – 6.97 (m, 1H), 6.96 – 6.89 (m, 2H), 5.79 – 5.74 (m, 1H), 5.14 – 5.04 (m, 2H), 4.05 (q, J = 7.0 Hz, 2H), 3.58 – 3.49 (m, 2H), 1.02 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.31, 170.32, 141.39, 135.29, 134.48, 128.96, 128.62, 128.21, 126.68, 124.09, 124.01, 115.95, 81.56, 59.50, 47.26, 14.41. HRMS (ESI) calculated for $C_{20}H_{21}NNaO_2S$ $[M+Na]^+$: 362.1185; found: 362.1190.



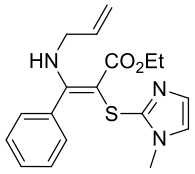
(E)-ethyl 3-(allylamino)-2-(naphthalen-2-ylthio)-3-phenylacrylate (3aj): white solid was obtained with 52% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (t, J = 6.2 Hz, 1H), 7.82 – 7.61 (m, 3H), 7.49 – 7.15 (m, 6H), 7.22 – 7.01 (m, 3H), 5.84 – 5.70 (m, 1H), 5.31 – 5.12 (m, 2H), 4.19 (q, J = 7.1 Hz, 2H), 3.59 (td, J = 5.3, 2.6 Hz, 2H), 1.13 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.47, 171.36, 139.46, 134.67, 134.32, 133.77, 131.03, 128.86, 128.13, 127.67, 127.63, 126.75, 126.67, 126.09, 124.50, 124.20, 121.83, 116.48, 83.07, 60.16, 47.83, 14.41. HRMS (ESI) calculated for $C_{24}H_{23}NNaO_2S$ $[M+Na]^+$: 412.1342; found: 412.1345.



(E)-ethyl 3-(allylamino)-2-(benzo[d]oxazol-2-ylthio)-3-phenylacrylate (3ak): white solid was obtained with 83% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (t, *J* = 6.2 Hz, 1H), 7.66 – 7.50 (m, 1H), 7.42 – 7.29 (m, 4H), 7.28 – 7.15 (m, 4H), 5.77 – (m, 1H), 5.29 – 5.05 (m, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.62 – 3.58 (m, 2H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.13, 170.18, 166.98, 151.79, 142.35, 134.21, 133.89, 129.20, 128.44, 126.83, 123.86, 123.17, 118.40, 116.81, 109.68, 78.99, 60.32, 47.92, 14.34. HRMS (ESI) calculated for $C_{21}H_{20}N_2NaO_3S$ $[M+Na]^+$: 403.1087; found: 403.1090.

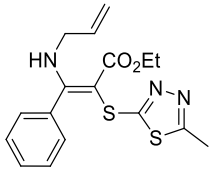


(E)-ethyl 3-(allylamino)-2-(benzo[d]thiazol-2-ylthio)-3-phenylacrylate (3al): white solid was obtained with 39% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.30 (t, *J* = 6.3 Hz, 1H), 7.75 – 7.58 (m, 2H), 7.33 – 7.21 (m, 4H), 7.20 – 7.14 (m, 1H), 7.12 (dd, *J* = 8.0, 1.6 Hz, 2H), 5.75 – 5.65 (m, 1H), 5.27 – 5.07 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.64 – 3.45 (m, 2H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.98, 172.20, 170.38, 155.02, 135.14, 133.89, 133.75, 129.36, 128.46, 126.58, 125.72, 123.27, 121.35, 120.71, 116.72, 83.25, 60.48, 47.88, 14.35. HRMS (ESI) calculated for $C_{21}H_{20}N_2NaO_2S_2$ $[M+Na]^+$: 419.0858; found: 419.0857.

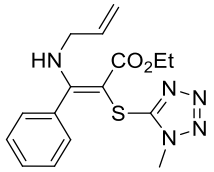


(E)-ethyl 3-(allylamino)-2-((1-methyl-1H-imidazol-2-yl)thio)-3-phenylacrylate (3am): white solid was obtained with 87% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6 δ 9.87 (t, *J* = 6.2 Hz, 1H), 7.41 – 7.38 (m, 3H), 7.33 – 7.23 (m, 2H), 7.03 (d, *J* = 1.2 Hz, 1H), 6.83 (d, *J* = 1.2 Hz, 1H), 5.86 – 5.66 (m, 1H), 5.11 – 5.02 (m, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 3.53 – 3.49 (m, 2H), 3.32 (s, 3H),

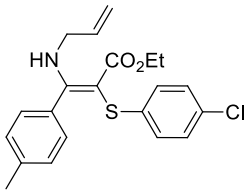
1.07 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.93, 169.88, 143.51, 135.28, 134.58, 128.93, 128.30, 128.13, 127.59, 121.94, 116.00, 83.16, 59.55, 47.18, 32.66, 14.38. HRMS (ESI) calculated for $C_{18}H_{21}N_3NaO_2S$ $[M+Na]^+$: 366.1247; found: 366.1249.



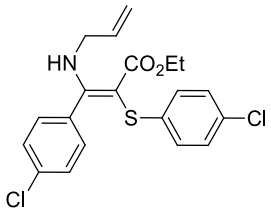
(E)-ethyl 3-(allylamino)-2-((5-methyl-1,3,4-thiadiazol-2-yl)thio)-3-phenylacrylate (3an): white solid was obtained with 92% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ10.22 (t, J = 6.2 Hz, 1H), 7.37 (q, J = 6.5 Hz, 3H), 7.20 – 7.08 (m, 2H), 5.80 – 5.69 (m, 1H), 5.29 – 5.05 (m, 2H), 4.20 (q, J = 7.1 Hz, 2H), 3.70 – 3.52 (m, 2H), 2.66 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.50, 171.41, 169.87, 163.85, 133.72, 133.71, 129.29, 128.38, 126.46, 116.60, 83.63, 60.33, 47.72, 15.65, 14.26. HRMS (ESI) calculated for $C_{17}H_{19}N_3NaO_2S_2$ $[M+Na]^+$: 384.0811; found: 384.0814.



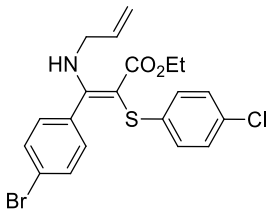
(E)-ethyl 3-(allylamino)-2-((1-methyl-1H-tetrazol-5-yl)thio)-3-phenylacrylate (3ao): white solid was obtained with 90% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (t, J = 6.2 Hz, 1H), 7.36 – 7.26 (m, 3H), 7.16 (dd, J = 8.0, 1.5 Hz, 2H), 5.70 – 5.61 (m, 1H), 5.21 – 5.01 (m, 2H), 4.09 (q, J = 7.1 Hz, 2H), 3.62 (s, 3H), 3.52 – 3.48 (m, 2H), 1.11 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.23, 169.54, 156.30, 134.07, 133.60, 129.16, 128.31, 126.88, 116.80, 78.37, 60.31, 47.81, 33.14, 14.21. HRMS (ESI) calculated for $C_{16}H_{19}N_5NaO_2S$ $[M+Na]^+$: 368.1152; found: 368.1155.



(E)-ethyl 3-(allylamino)-2-((4-chlorophenyl)thio)-3-(p-tolyl)acrylate (3ba): white solid was obtained with 90% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (t, *J* = 6.2 Hz, 1H), 7.07 – 7.02 (m, 4H), 6.94 – 6.79 (m, 4H), 5.77 – 5.58 (m, 1H), 5.21 – 4.98 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.51 – 3.47 (m, 2H), 2.25 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.61, 171.03, 140.43, 138.82, 134.24, 131.62, 129.42, 128.86, 128.26, 126.49, 125.95, 116.41, 82.82, 60.09, 47.76, 21.32, 14.35. HRMS (ESI) calculated for $C_{21}H_{22}ClNNaO_2S$ $[M+Na]^+$: 410.0952; found: 410.0958.

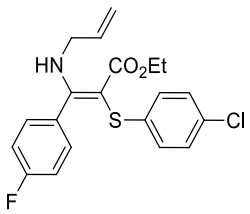


(E)-ethyl 3-(allylamino)-3-(4-chlorophenyl)-2-((4-chlorophenyl)thio)acrylate (3ca): white solid was obtained with 88% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (t, *J* = 6.2 Hz, 1H), 7.27 – 7.18 (m, 2H), 7.15 – 7.00 (m, 2H), 6.92 (d, *J* = 8.3 Hz, 2H), 6.90 – 6.78 (m, 2H), 5.71 – 5.62 (m, 1H), 5.25 – 5.02 (m, 2H), 4.10 (t, *J* = 7.1 Hz, 2H), 3.51 – 3.46 (m, 2H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.95, 170.20, 140.03, 135.00, 134.05, 132.86, 129.74, 128.56, 128.44, 128.13, 125.94, 116.63, 83.32, 60.30, 47.77, 14.36. HRMS (ESI) calculated for $C_{20}H_{19}Cl_2NNaO_2S$ $[M+Na]^+$: 430.0406; found: 430.0408.

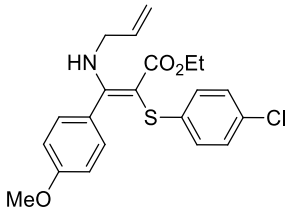


(E)-ethyl 3-(allylamino)-3-(4-bromophenyl)-2-((4-chlorophenyl)thio)acrylate (3da): white solid was obtained with 73% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (t, *J* = 6.3 Hz, 1H),

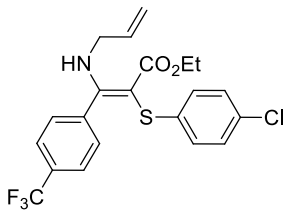
7.47 – 7.27 (m, 2H), 7.16 – 7.00 (m, 2H), 6.97 – 6.80 (m, 4H), 5.74 – 5.65 (m, 1H), 5.17 – 5.04 (m, 2H), 4.11 (q, J = 7.1 Hz, 2H), 3.50 – 3.46 (m, 2H), 1.10 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.93, 170.17, 140.00, 134.04, 133.33, 131.48, 129.74, 128.43, 128.35, 125.93, 123.22, 116.63, 83.25, 60.30, 47.77, 14.36. HRMS (ESI) calculated for $C_{20}H_{19}BrClNNaO_2S$ $[M+Na]^+$: 473.9901; found: 473.9907.



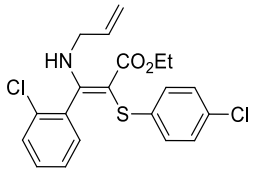
(E)-ethyl 3-(allylamino)-2-((4-chlorophenyl)thio)-3-(4-fluorophenyl)acrylate (3ea): white solid was obtained with 89% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (t, J = 6.1 Hz, 1H), 7.10 – 7.03 (m, 2H), 7.01 – 6.88 (m, 4H), 6.87 – 6.81 (m, 2H), 5.70 – 5.63 (m, 1H), 5.17 – 5.01 (m, 2H), 4.11 (q, J = 7.0 Hz, 2H), 3.51 – 3.47 (m, 2H), 1.09 (t, J = 7.1 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.50. ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.96, 170.43, 162.77 ($J_{C\text{-}F}$ = 249.0 Hz), 140.11, 134.07, 130.41 (($J_{C\text{-}F}$ = 3.6 Hz), 129.64, 128.65 ($J_{C\text{-}F}$ = 8.4 Hz), 128.37, 125.91, 116.53, 115.35 ($J_{C\text{-}F}$ = 21.9 Hz), 83.40, 60.22, 47.73, 14.33. HRMS (ESI) calculated for $C_{20}H_{19}ClFNNaO_2S$ $[M+Na]^+$: 414.0701; found:414.0706.



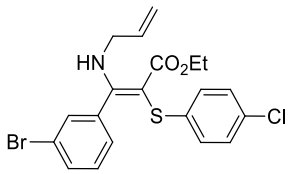
(E)-ethyl 3-(allylamino)-2-((4-chlorophenyl)thio)-3-(4-methoxyphenyl)acrylate (3fa): white solid was obtained with 82% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (t, J = 6.2 Hz, 1H), 7.08 – 7.03 (m, 2H), 6.97 – 6.84 (m, 4H), 6.79 – 6.70 (m, 2H), 5.71 – 5.64 (m, 1H), 5.23 – 4.96 (m, 2H), 4.09 (q, J = 7.0 Hz, 2H), 3.70 (s, 3H), 3.54 – 3.50 (m, 2H), 1.08 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.42, 171.06, 159.85, 140.47, 134.28, 129.41, 128.27, 128.11, 126.75, 125.93, 116.37, 113.49, 83.07, 60.09, 55.09, 47.78, 14.35. HRMS (ESI) calculated for $C_{21}H_{22}ClNNaO_3S$ $[M+Na]^+$: 426.0901; found: 426.0907.



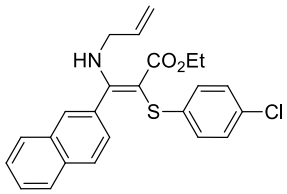
(E)-ethyl 3-(allylamino)-2-((4-chlorophenyl)thio)-3-(4-(trifluoromethyl)phenyl)acrylate (3ga): white solid was obtained with 82% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (t, *J* = 6.3 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.16 – 6.99 (m, 4H), 6.92 – 6.80 (m, 2H), 5.71 – 5.61 (m, 1H), 5.19 – 4.99 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.47 – 3.43 (m, 2H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.75. ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.82, 169.67, 139.78, 137.98, 133.88, 130.96 (q, *J* = 32.9 Hz), 129.83, 128.44, 127.16, 125.93, 125.23 (q, *J* = 3.8 Hz), 123.67 (d, *J* = 272.5 Hz), 116.66, 83.36, 60.34, 47.72, 14.29. HRMS (ESI) calculated for $C_{21}H_{19}ClF_3NNaO_2S$ $[M+Na]^+$: 464.0669; found: 464.0673.



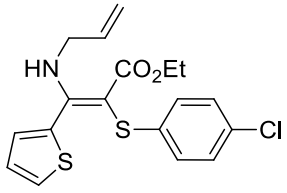
(E)-ethyl 3-(allylamino)-3-(2-chlorophenyl)-2-((4-chlorophenyl)thio)acrylate (3ha): white solid was obtained with 85% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (t, *J* = 6.0 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.33 (td, *J* = 7.7, 1.7 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.17 – 7.11 (m, 2H), 7.03 – 6.95 (m, 3H), 5.84 – 5.77 (m, 1H), 5.24 – 5.14 (m, 2H), 4.25 – 4.18 (m, 2H), 3.73 – 3.62 (m, 1H), 3.58 – 3.44 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.87, 167.72, 139.54, 133.66, 133.55, 131.83, 130.24, 129.73, 129.51, 128.33, 128.23, 126.59, 126.49, 117.08, 83.35, 60.27, 47.71, 14.35. HRMS (ESI) calculated for $C_{20}H_{19}Cl_2NNaO_2S$ $[M+Na]^+$: 430.0406; found: 430.0413.



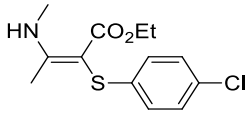
(E)-ethyl 3-(allylamino)-3-(3-bromophenyl)-2-((4-chlorophenyl)thio)acrylate (3ia): white solid was obtained with 77% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (t, *J* = 6.2 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.17 – 7.02 (m, 4H), 6.90 (dt, *J* = 7.7, 1.3 Hz, 1H), 6.87 – 6.82 (m, 2H), 5.72 – 5.62 (m, 1H), 5.17 – 4.97 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.59 – 3.41 (m, 2H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.90, 169.48, 139.95, 136.28, 133.95, 132.00, 129.85, 129.75, 128.41, 126.27, 125.25, 122.19, 116.69, 83.66, 60.29, 47.81, 14.35. HRMS (ESI) calculated for $C_{20}H_{19}BrClNNaO_2S$ $[M+Na]^+$: 473.9901; found: 473.9904.



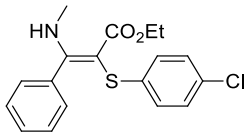
(E)-ethyl 3-(allylamino)-2-((4-chlorophenyl)thio)-3-(naphthalen-2-yl)acrylate (3ja): white solid was obtained with 63% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (t, *J* = 6.2 Hz, 1H), 7.78 – 7.68 (m, 2H), 7.68 – 7.60 (m, 1H), 7.48 – 7.36 (m, 3H), 7.06 (m, 3H), 6.92 – 6.79 (m, 2H), 5.67 (m, 1H), 5.24 – 4.97 (m, 2H), 4.24 – 4.03 (m, 2H), 3.53 – 3.49 (m, 2H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.30, 171.12, 140.35, 134.21, 133.14, 132.49, 131.95, 129.62, 128.31, 128.25, 128.04, 127.78, 126.77, 126.55, 126.20, 125.95, 124.43, 116.55, 83.39, 60.23, 47.91, 14.42. HRMS (ESI) calculated for $C_{24}H_{22}ClNNaO_2S$ $[M+Na]^+$: 446.0952; found: 446.0961.



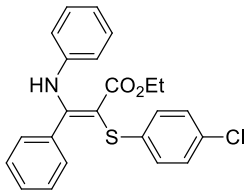
(E)-ethyl 3-(allylamino)-2-((4-chlorophenyl)thio)-3-(thiophen-2-yl)acrylate (3ka): white solid was obtained with 85% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (t, *J* = 6.2 Hz, 1H), 7.28 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.14 – 7.02 (m, 2H), 6.95 – 6.81 (m, 3H), 6.78 (dd, *J* = 3.5, 1.2 Hz, 1H), 5.83 – 5.64 (m, 1H), 5.22 – 4.99 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.77 – 3.49 (m, 2H), 1.07 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.56, 164.59, 140.28, 134.26, 133.84, 129.66, 128.38, 127.44, 126.88, 126.67, 126.08, 116.55, 85.59, 60.32, 47.97, 14.29. HRMS (ESI) calculated for $C_{18}H_{18}ClNNaO_2S_2$ $[M+Na]^+$: 402.0360; found: 402.0363.



(E)-ethyl 2-((4-chlorophenyl)thio)-3-(methylamino)but-2-enoate (3la): white solid was obtained with 79% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.10 (d, J = 5.1 Hz, 1H), 7.28 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 3.98 (q, J = 7.0 Hz, 2H), 2.99 (d, J = 5.0 Hz, 3H), 2.24 (s, 3H), 1.03 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 171.23, 170.11, 140.44, 128.73, 128.60, 125.74, 78.24, 59.07, 30.97, 16.99, 14.55. HRMS (ESI) calculated for $C_{13}H_{16}ClNNaO_2S$ $[M+Na]^+$: 308.0482; found: 308.0484.



(E)-ethyl 2-((4-chlorophenyl)thio)-3-(methylamino)-3-phenylacrylate (3ma): white solid was obtained with 68% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.98 (d, J = 5.3 Hz, 1H), 7.46 – 7.33 (m, 3H), 7.27 – 7.18 (m, 2H), 7.18 – 7.05 (m, 2H), 7.01 – 6.90 (m, 2H), 4.04 (q, J = 7.0 Hz, 2H), 2.61 (d, J = 5.0 Hz, 3H), 1.03 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.10, 169.98, 140.90, 134.84, 128.87, 128.46, 128.27, 126.44, 125.63, 79.86, 59.35, 32.41, 14.49. HRMS (ESI) calculated for $C_{18}H_{18}ClNNaO_2S$ $[M+Na]^+$: 370.0639; found: 370.0641.



(E)-ethyl 2-((4-chlorophenyl)thio)-3-phenyl-3-(phenylamino)acrylate (3na): white solid was obtained with 70% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.70 (s, 1H), 7.31 – 7.20 (m, 5H), 7.17 (dd, J = 7.9, 1.5 Hz, 2H), 7.13 – 7.04 (m, 4H), 6.97 (t, J = 7.4 Hz, 1H), 6.78 (d, J = 7.4 Hz, 2H), 4.11 (q, J = 7.1 Hz, 2H), 1.04 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.99, 166.99, 139.82, 139.09, 134.37, 129.30, 128.83, 128.81, 128.68, 128.55, 128.04, 126.24, 124.74, 123.70, 86.29, 60.24, 14.29. HRMS (ESI) calculated for $C_{23}H_{20}ClNNaO_2S$ $[M+Na]^+$: 432.0795; found: 432.0798.

5. References

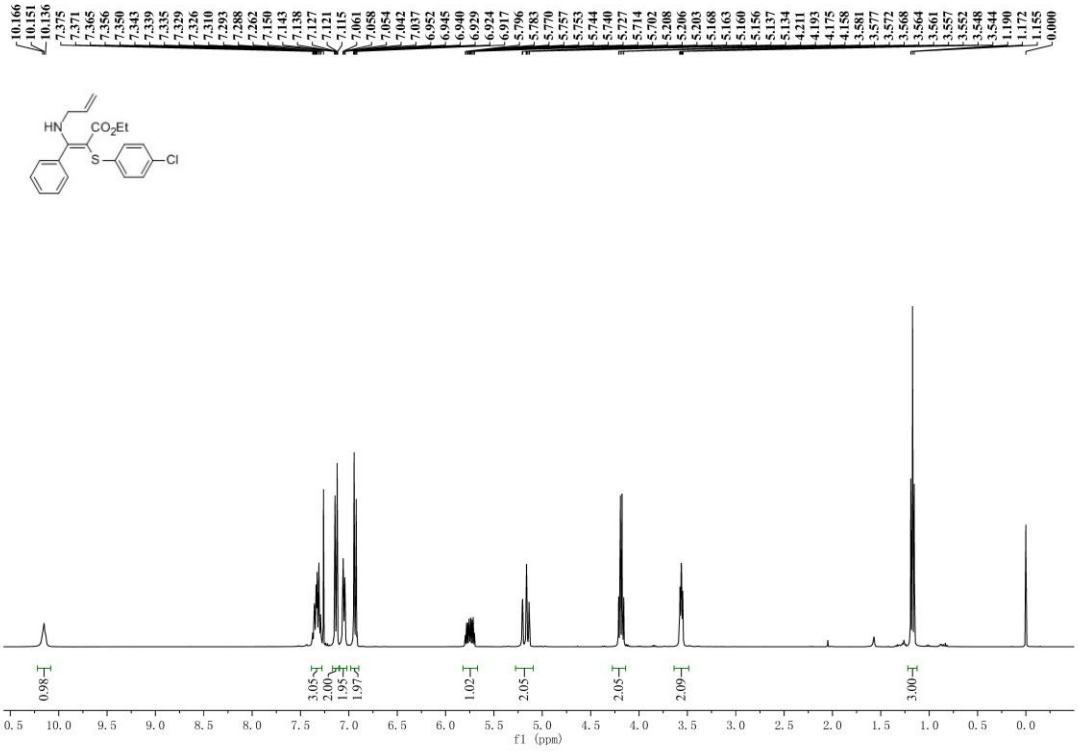
1. Toh, K. K.; Wang, Y.-F.; Ng, E. P. J.; Chiba, S. *J. Am. Chem. Soc.* **2011**, *133*, 13942.

2. Toh, K. K.; Biswas, A.; Wang, Y.-F.; Tan, Y. Y.; Chiba, S. *J. Am. Chem. Soc.* **2014**, *136*, 6011.

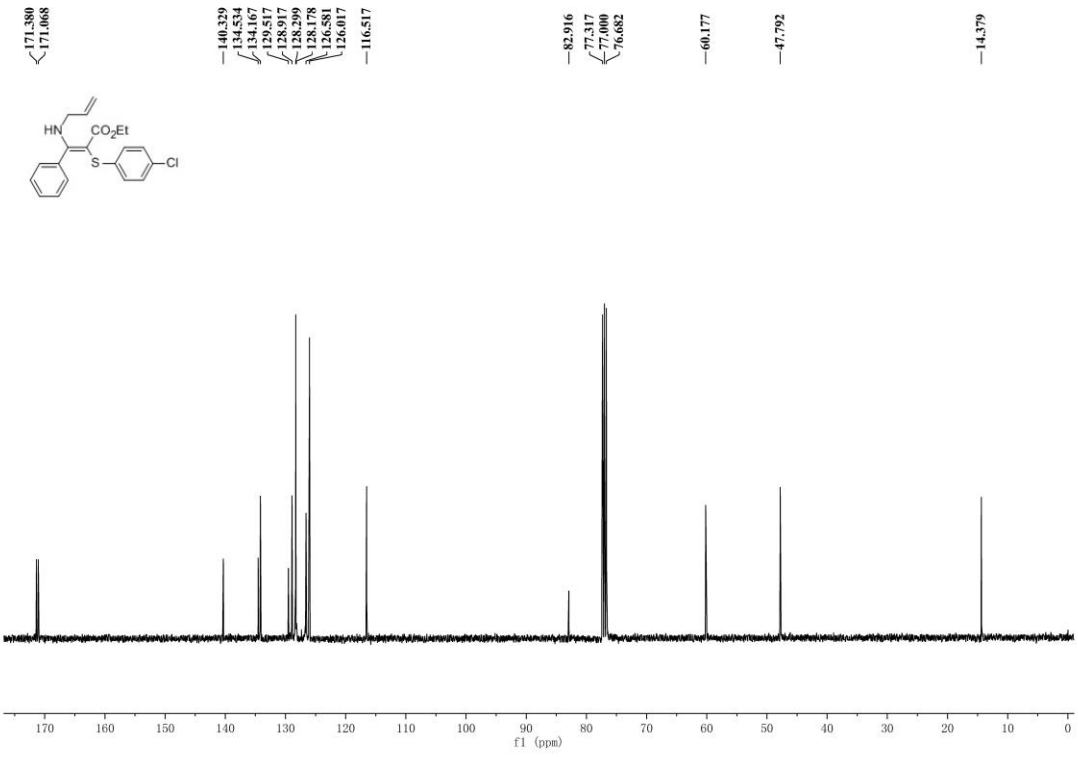
6. Copies of product NMR Spectra

3aa

^{1}H NMR

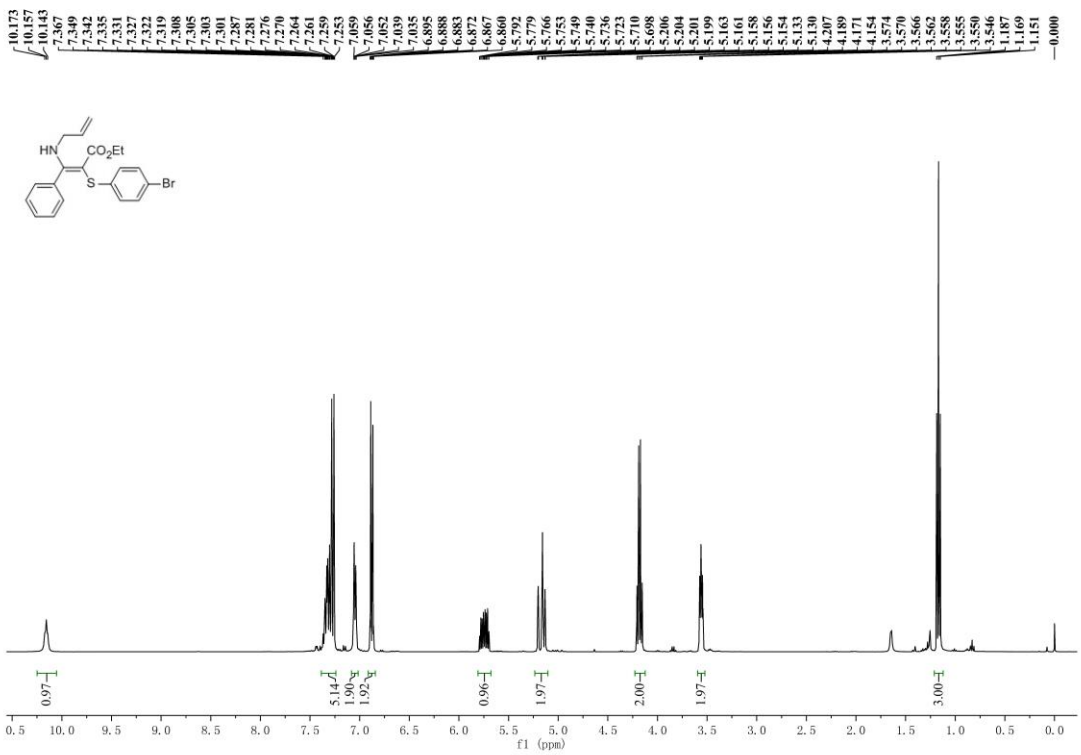


^{13}C NMR

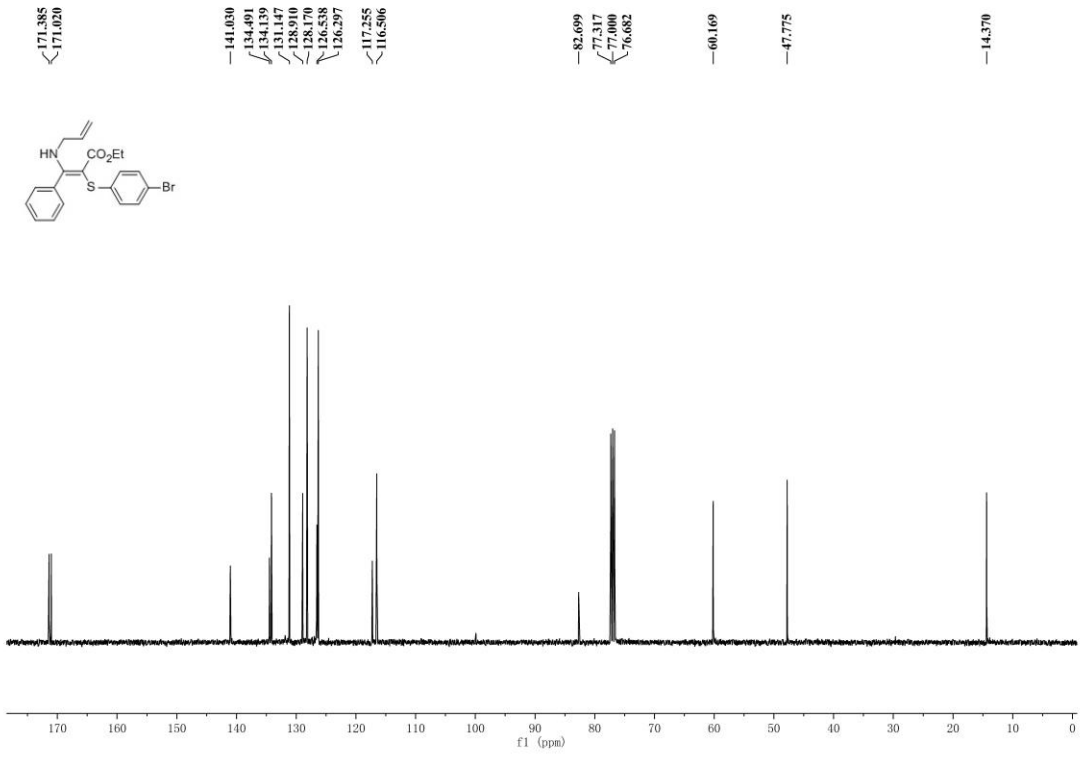


3ab

^{1}H NMR



^{13}C NMR



3ac

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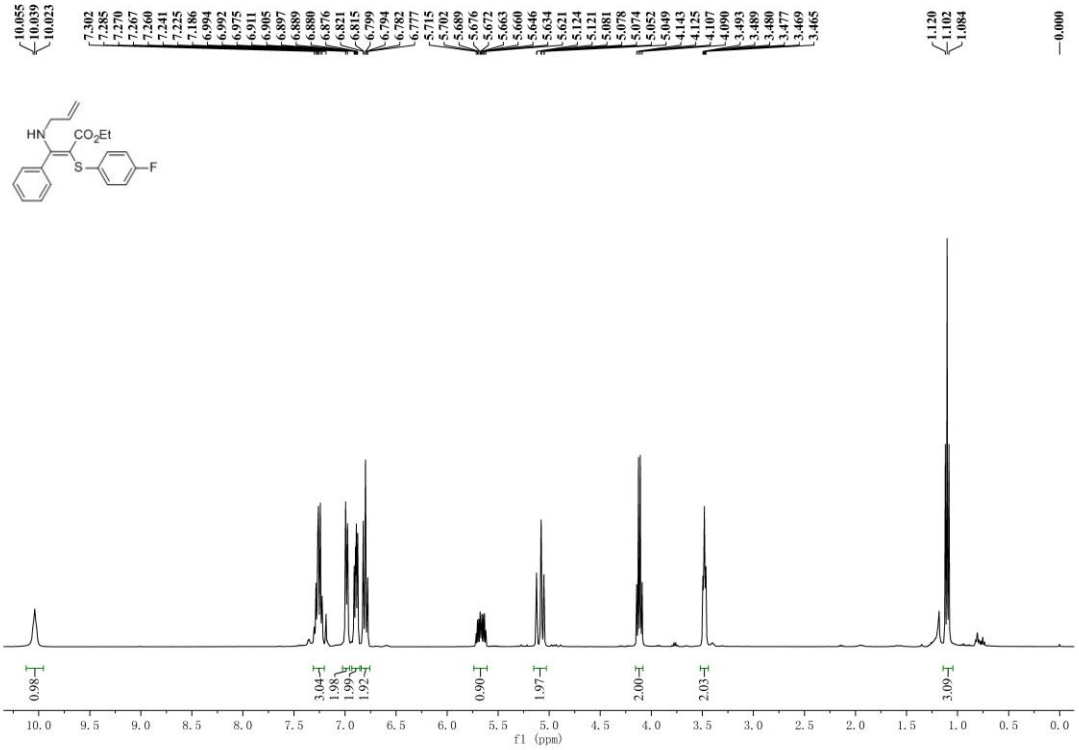
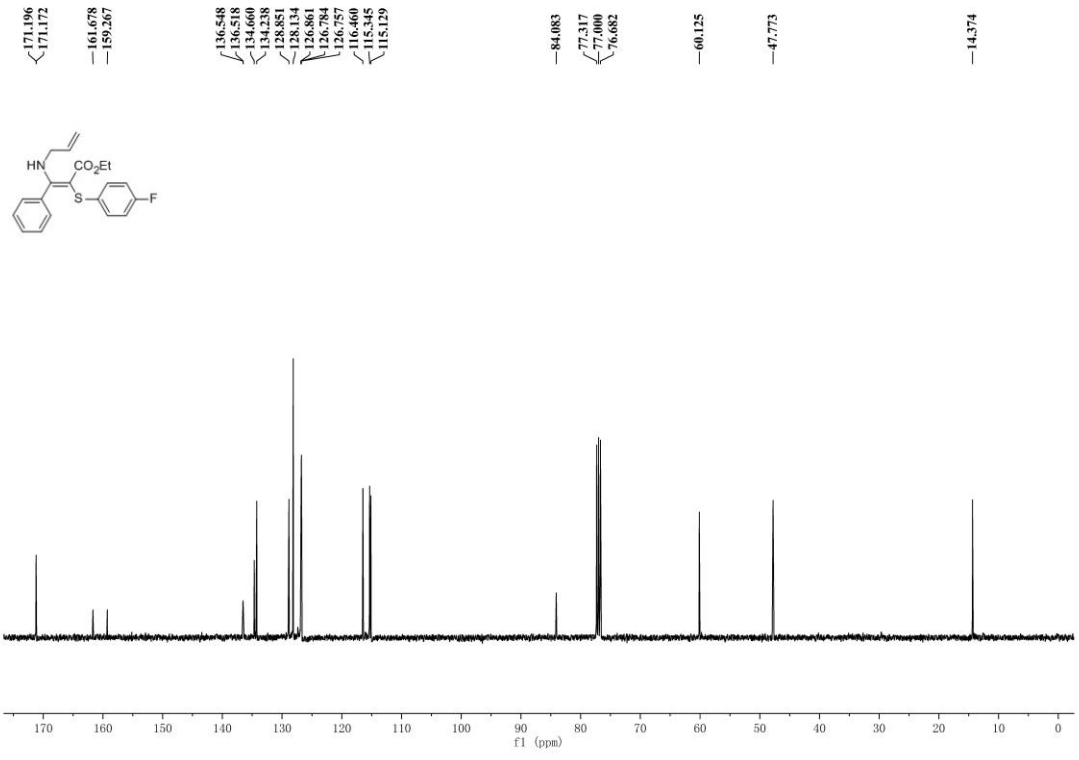
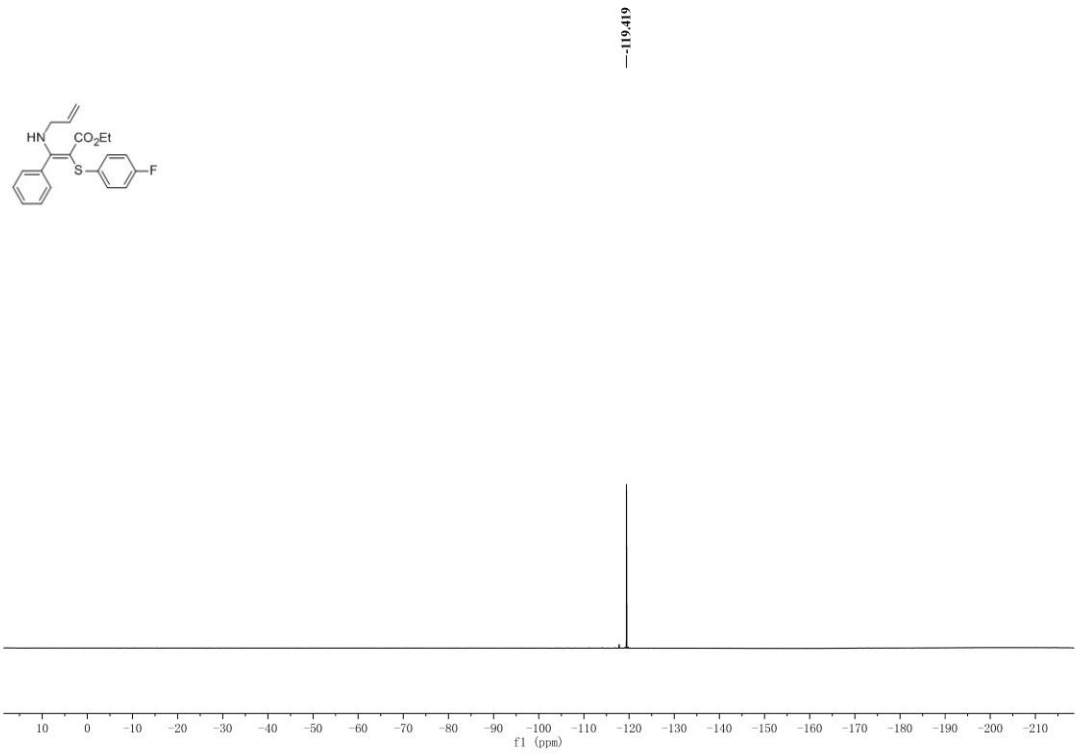


^{13}C NMR



^{19}F NMR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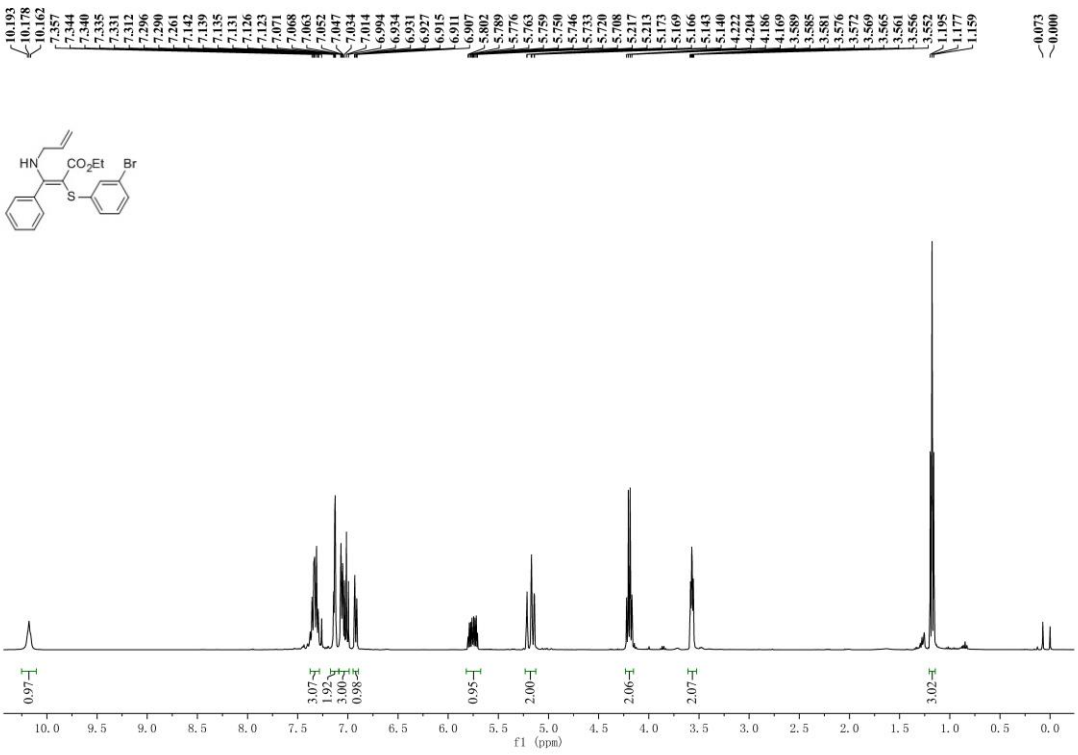
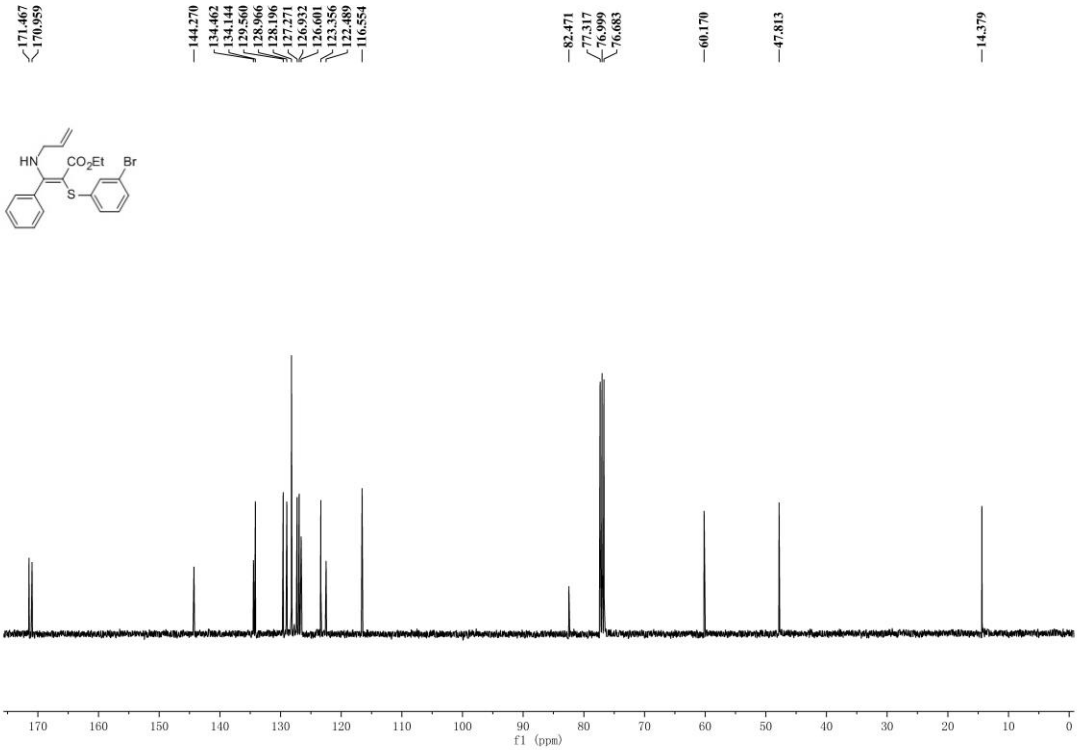
HN
CO2Et
S
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

3ad

^{1}H NMR

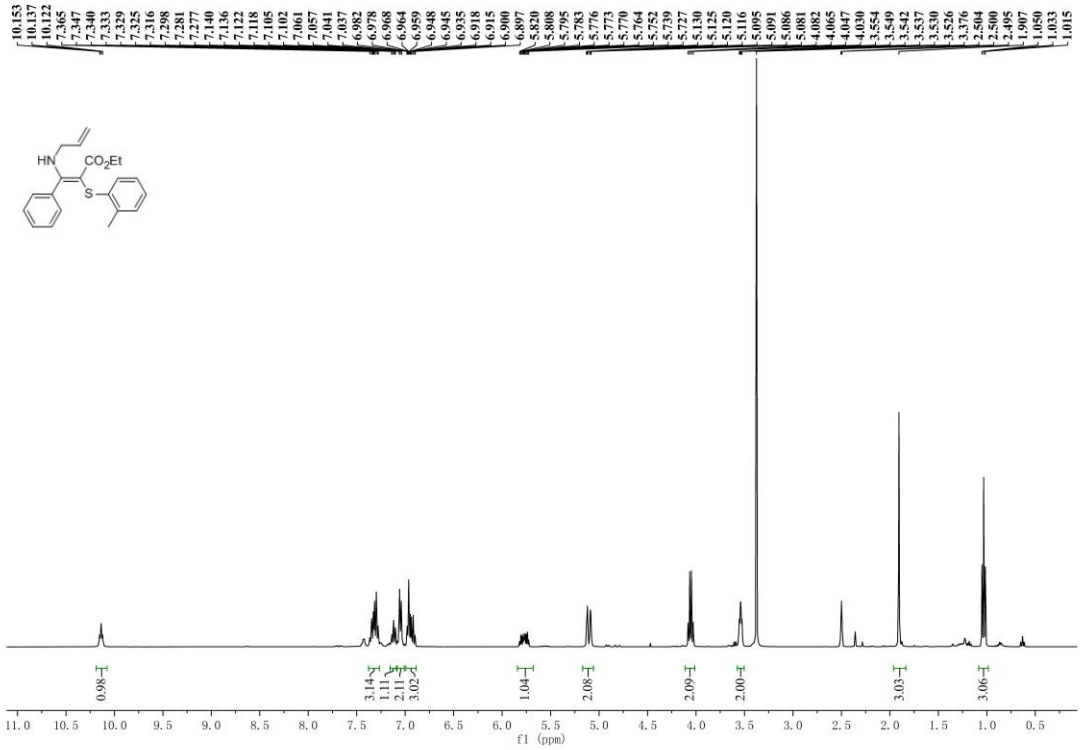


^{13}C NMR



3ae

^{1}H NMR



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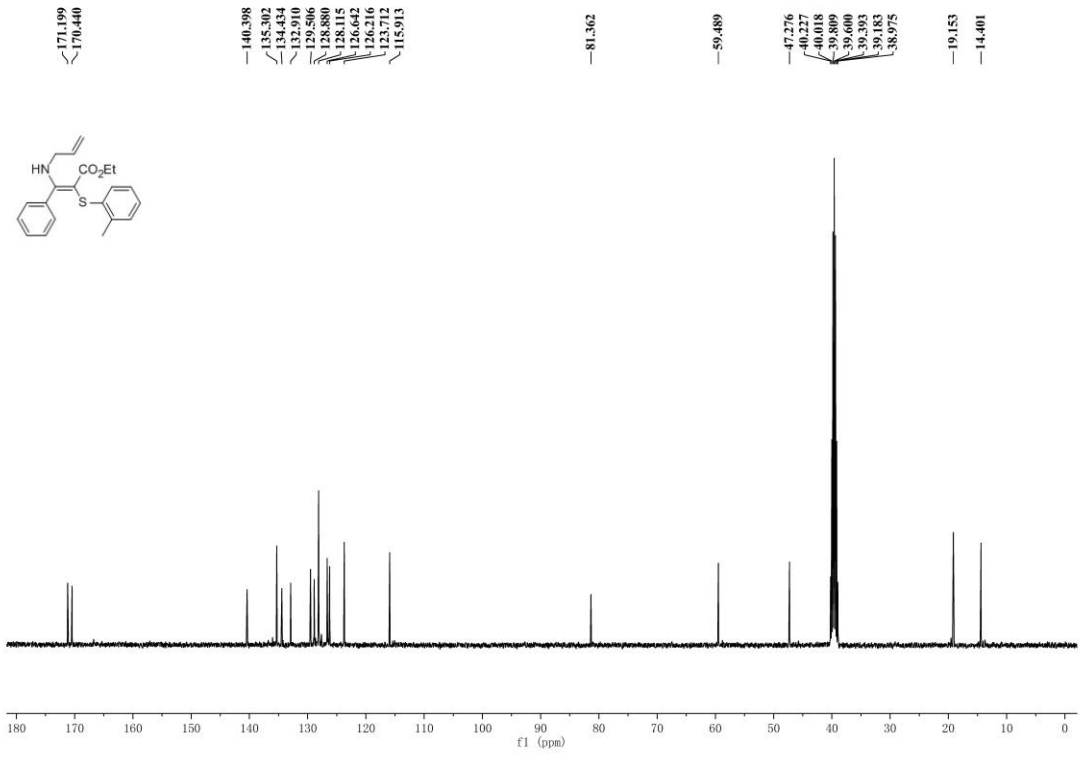

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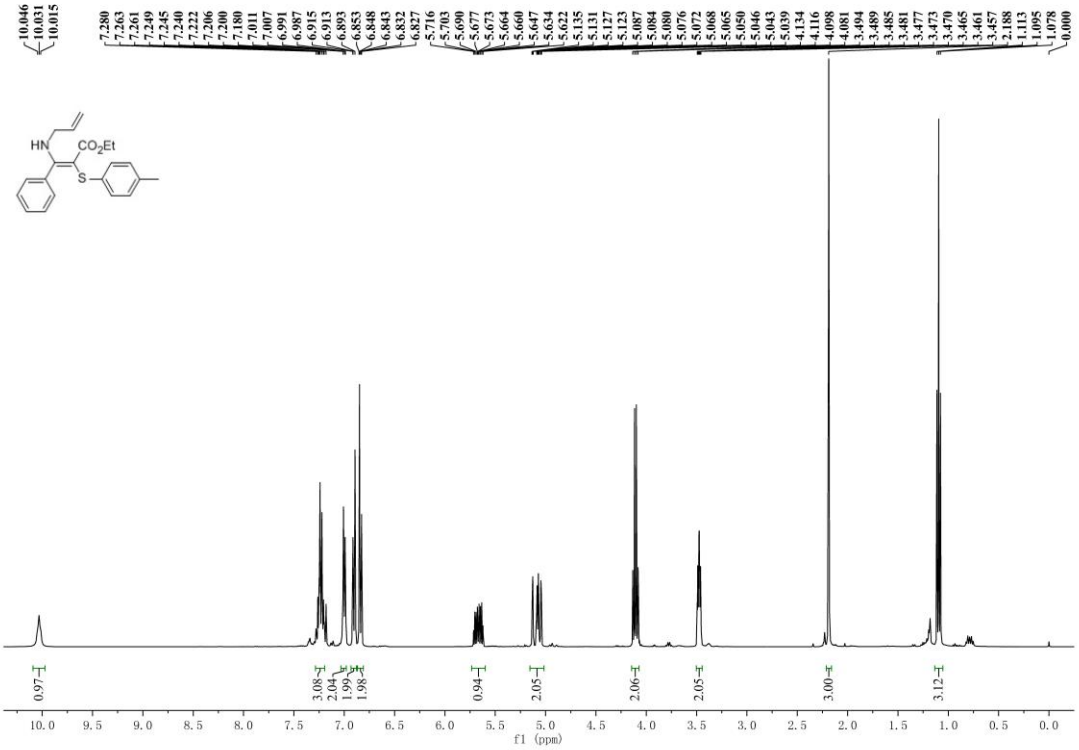
^{1}H NMR



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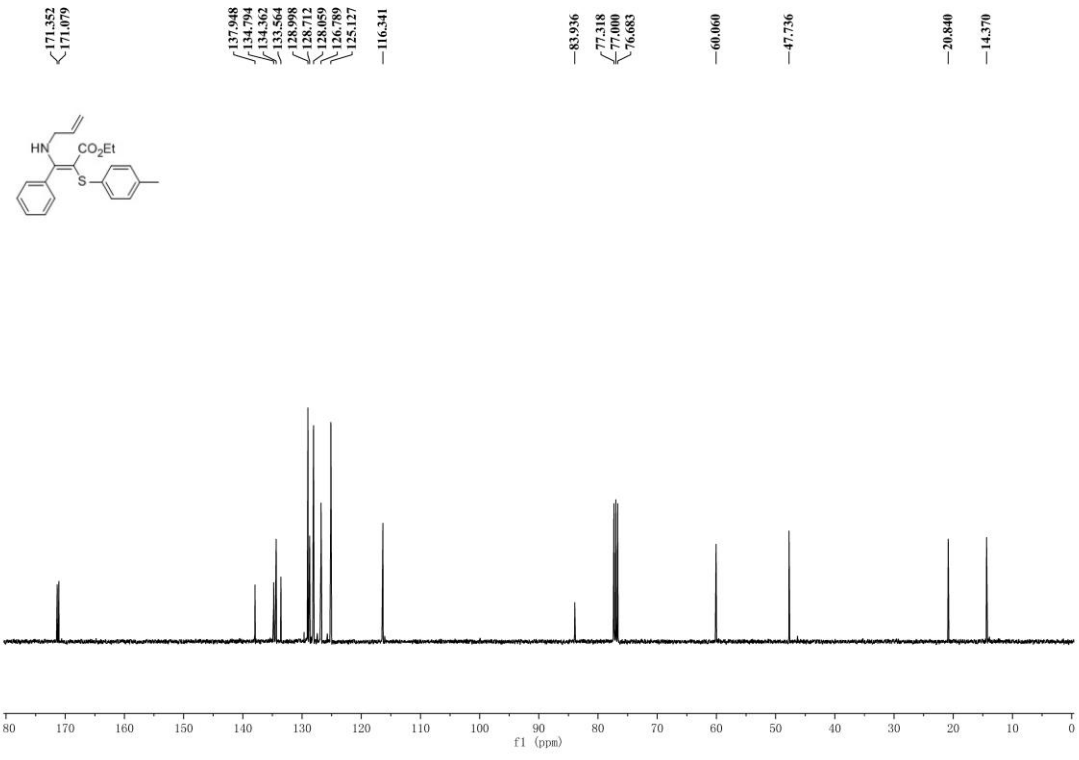

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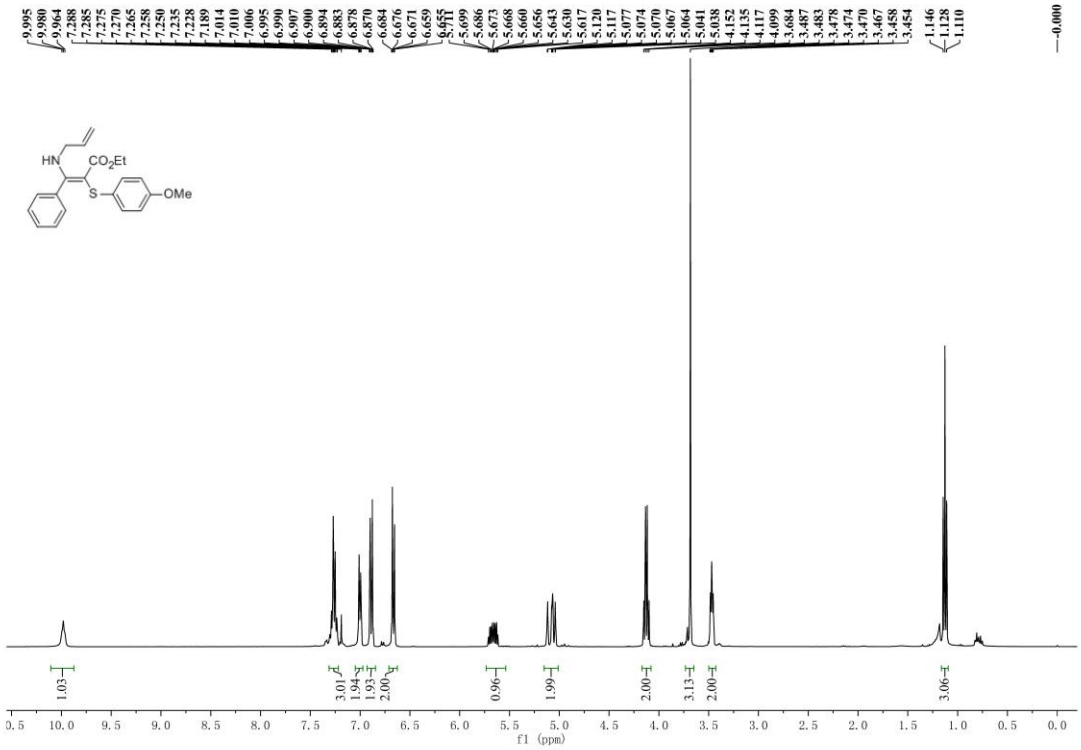
^{1}H NMR



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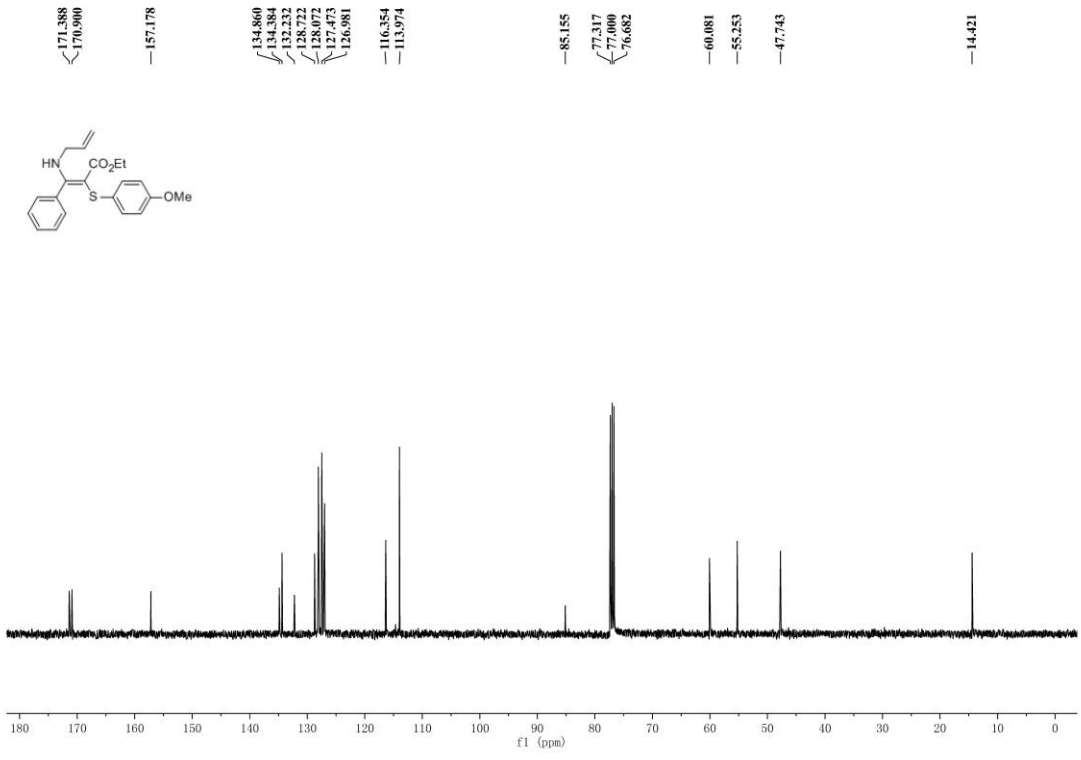

3ah

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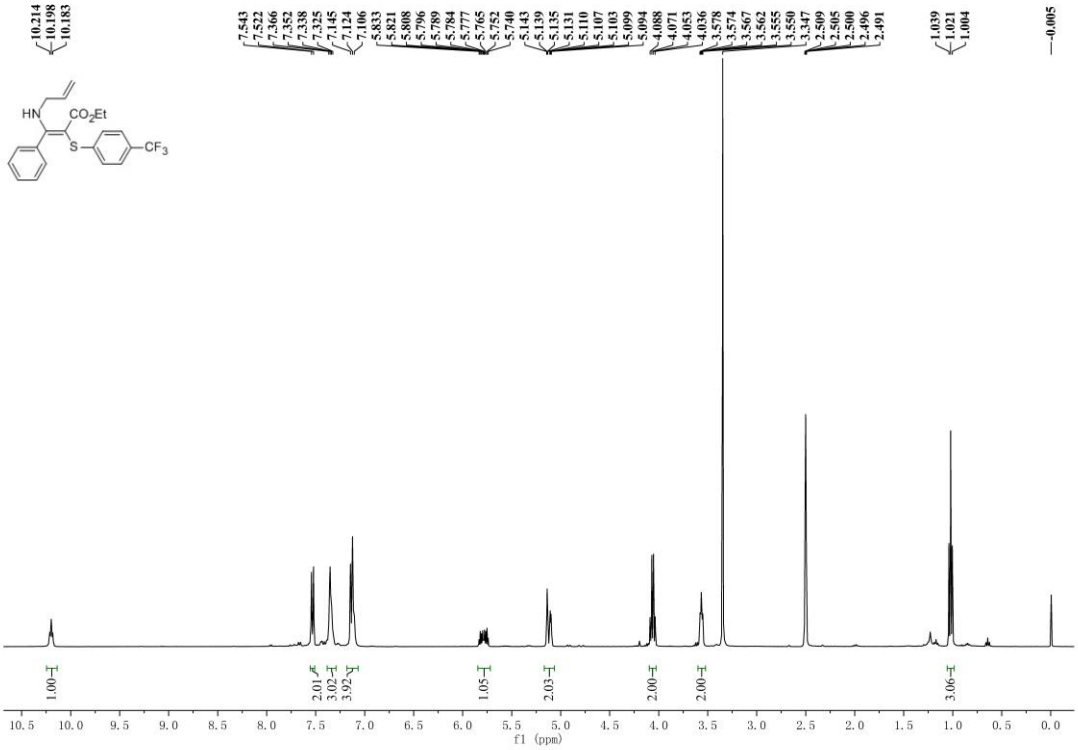

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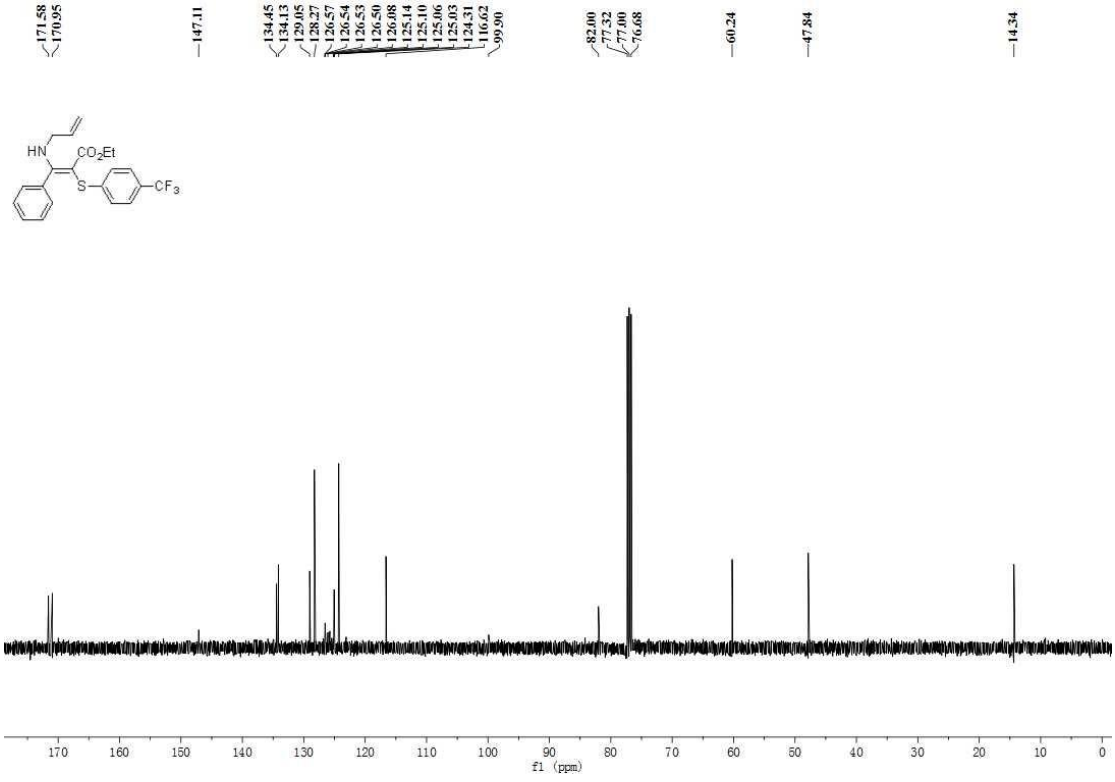
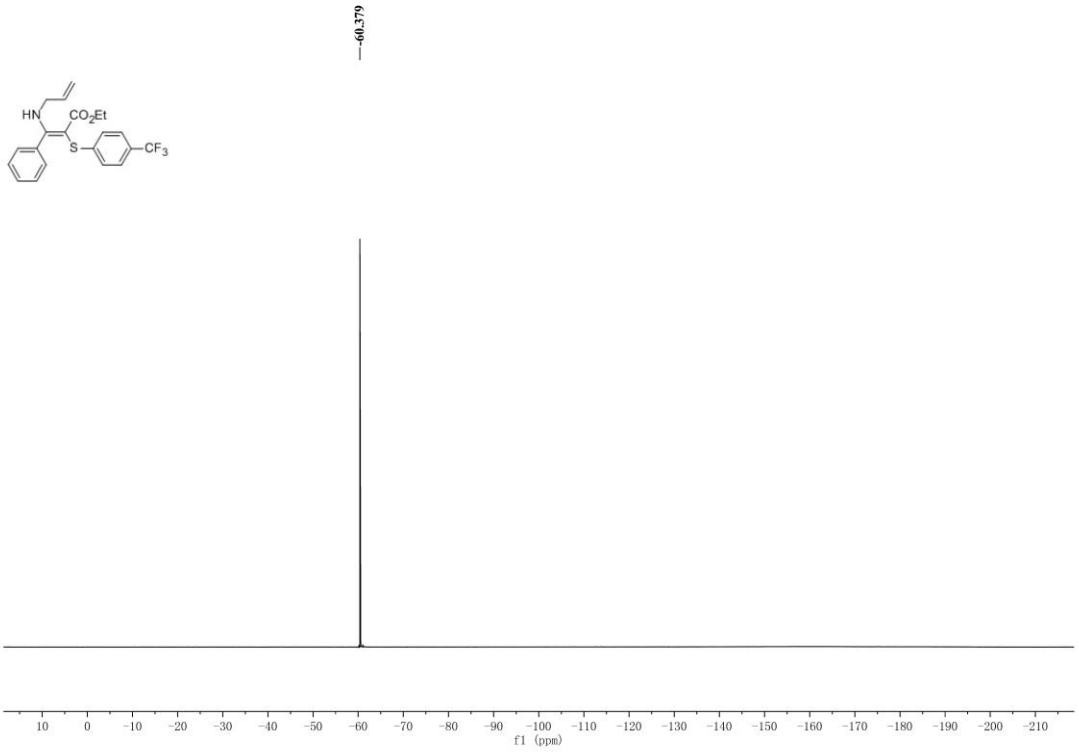
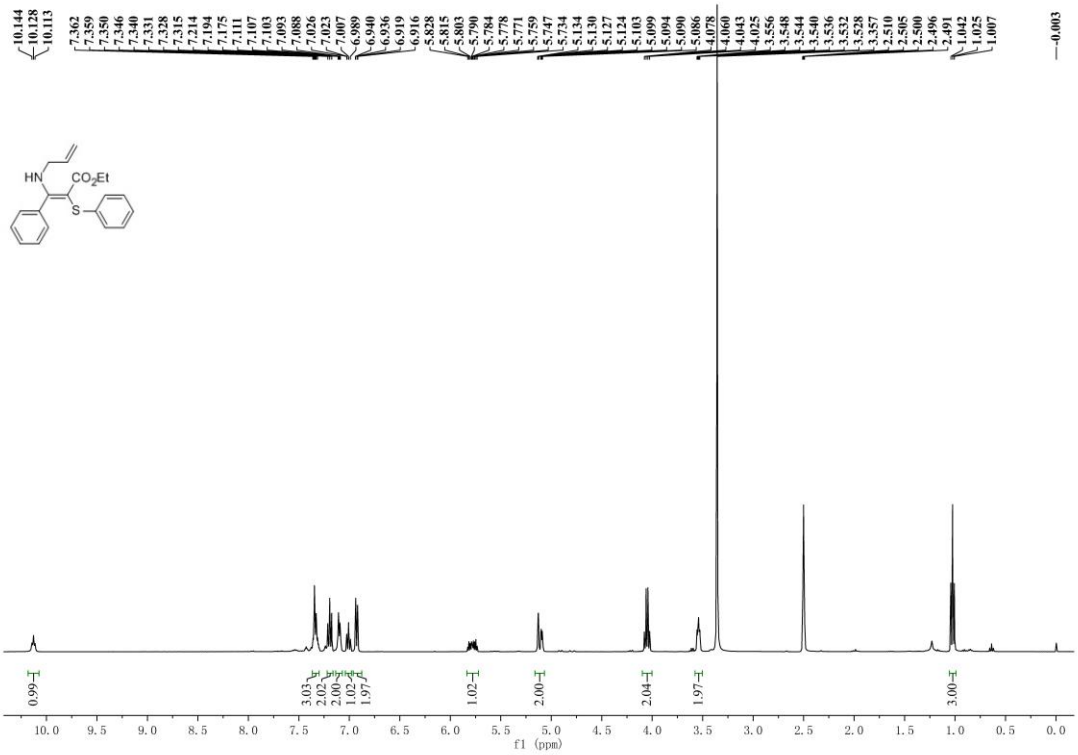


^{19}F NMR


-60.379
HN
CO2Et
S
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

3ai

^{1}H NMR



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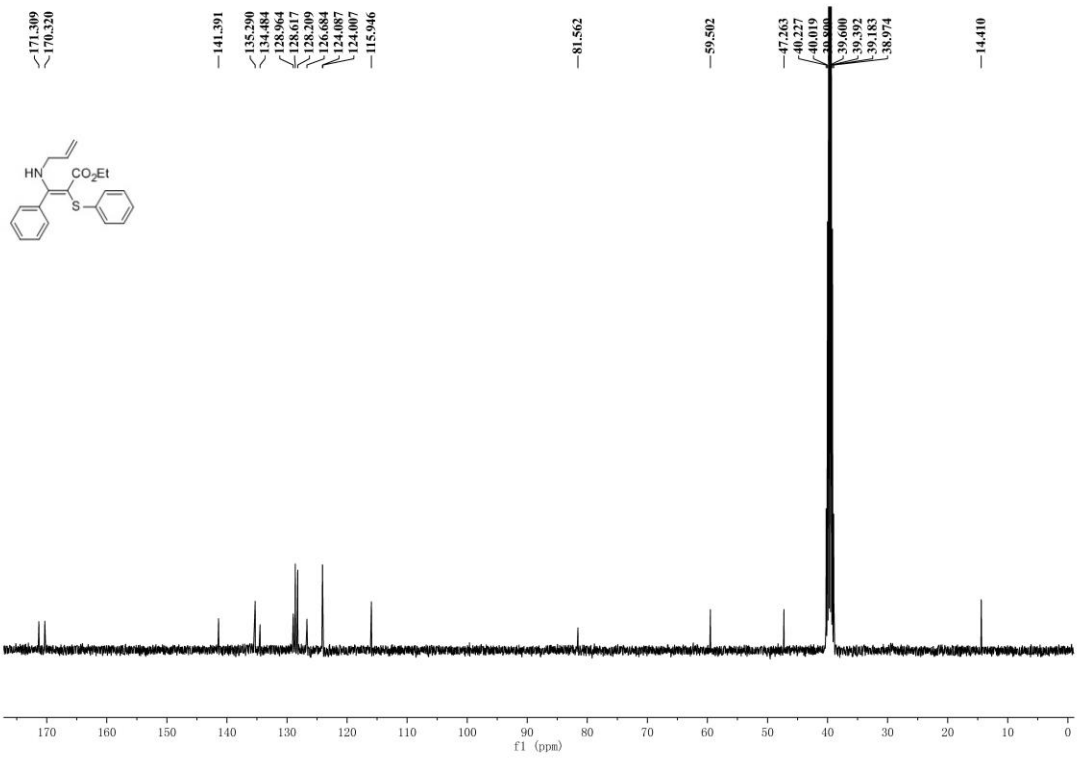

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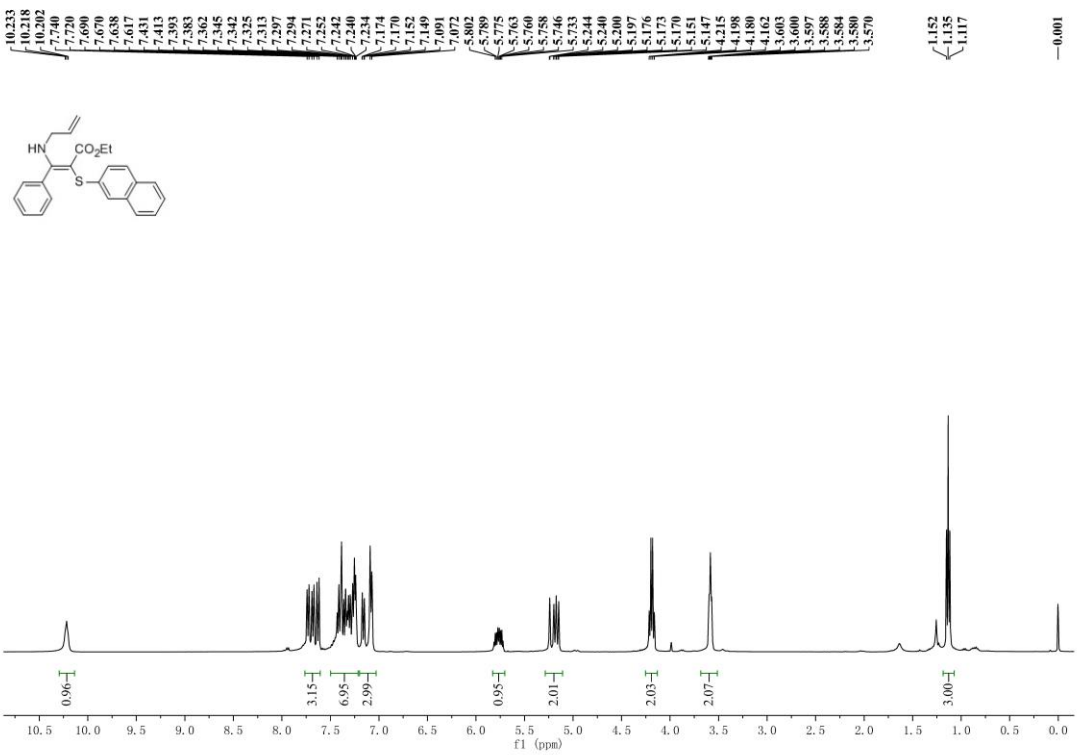

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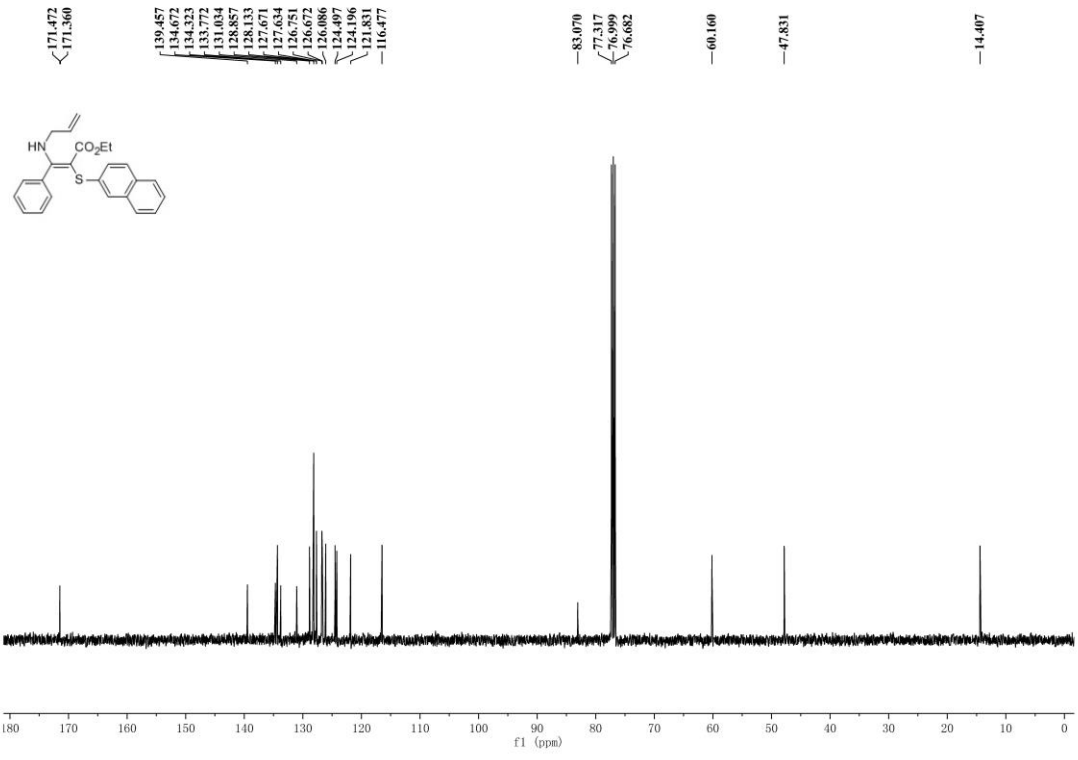

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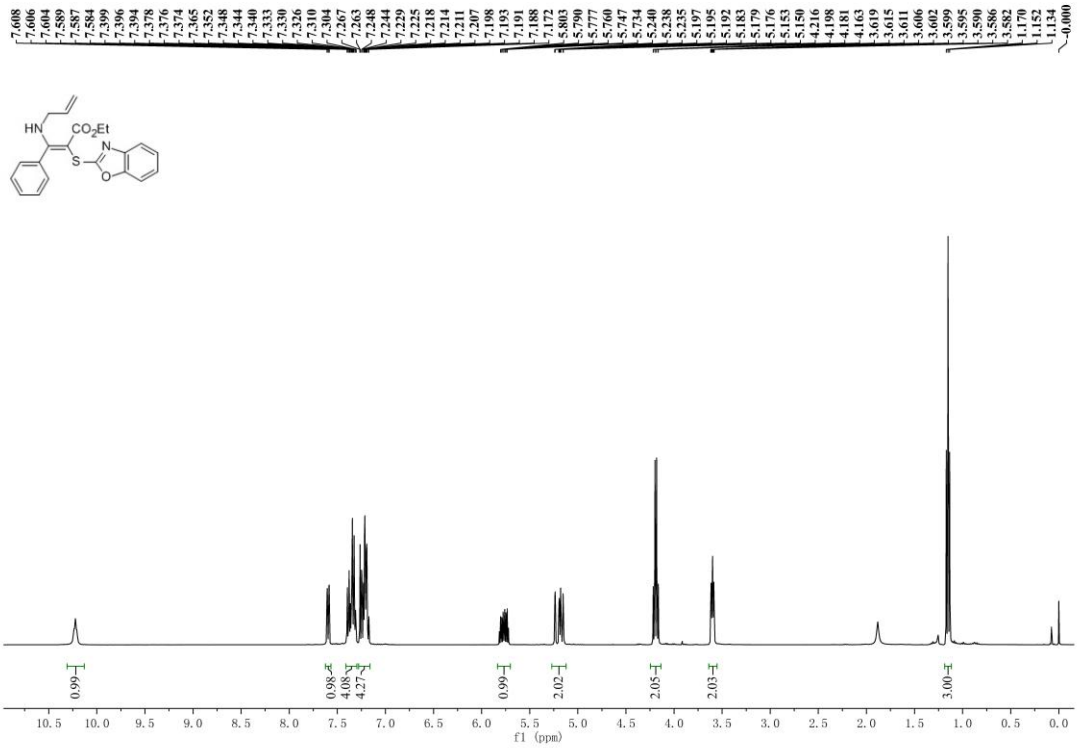

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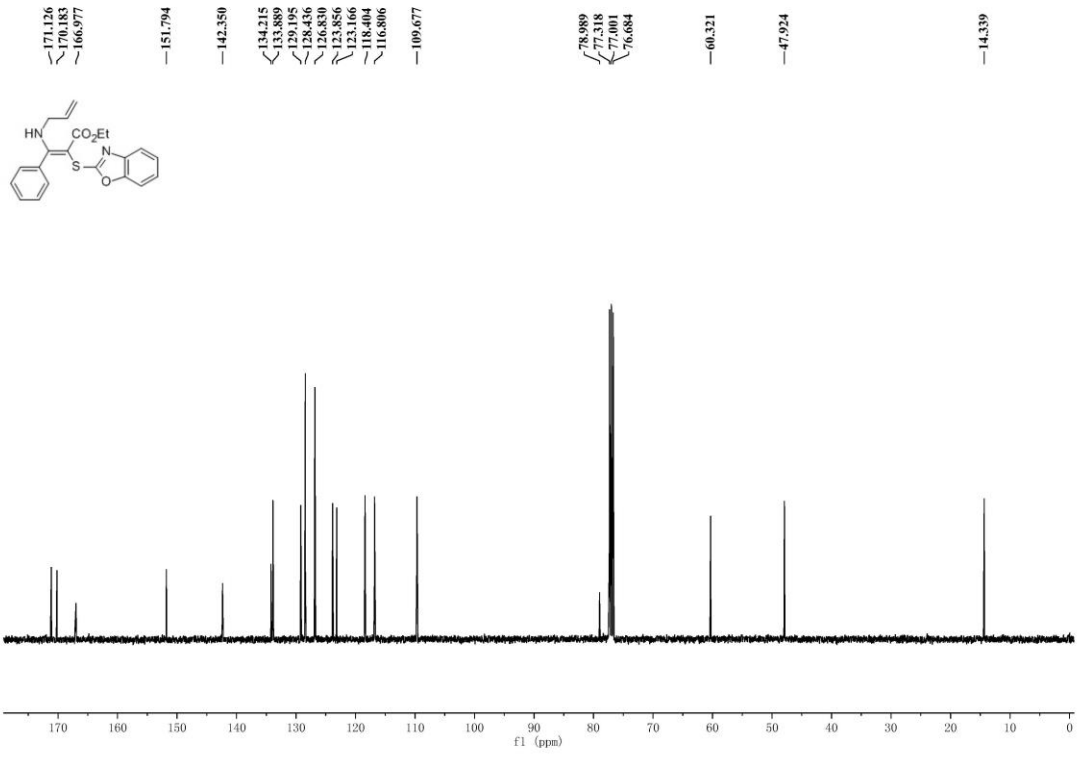

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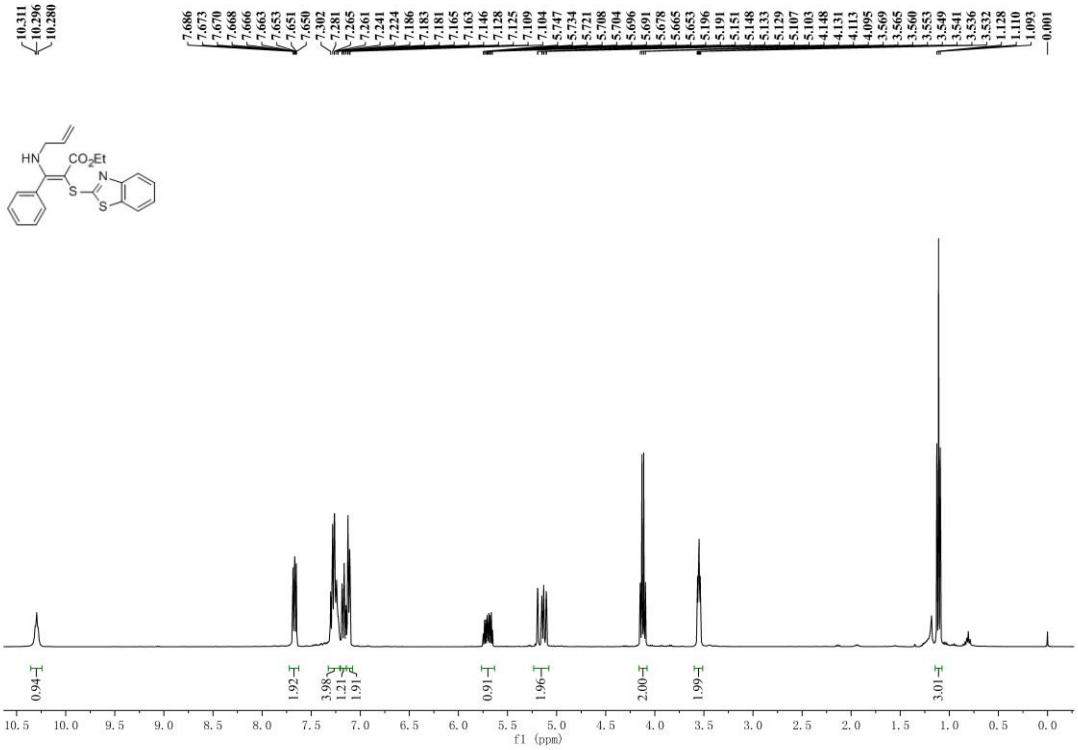
^{1}H NMR



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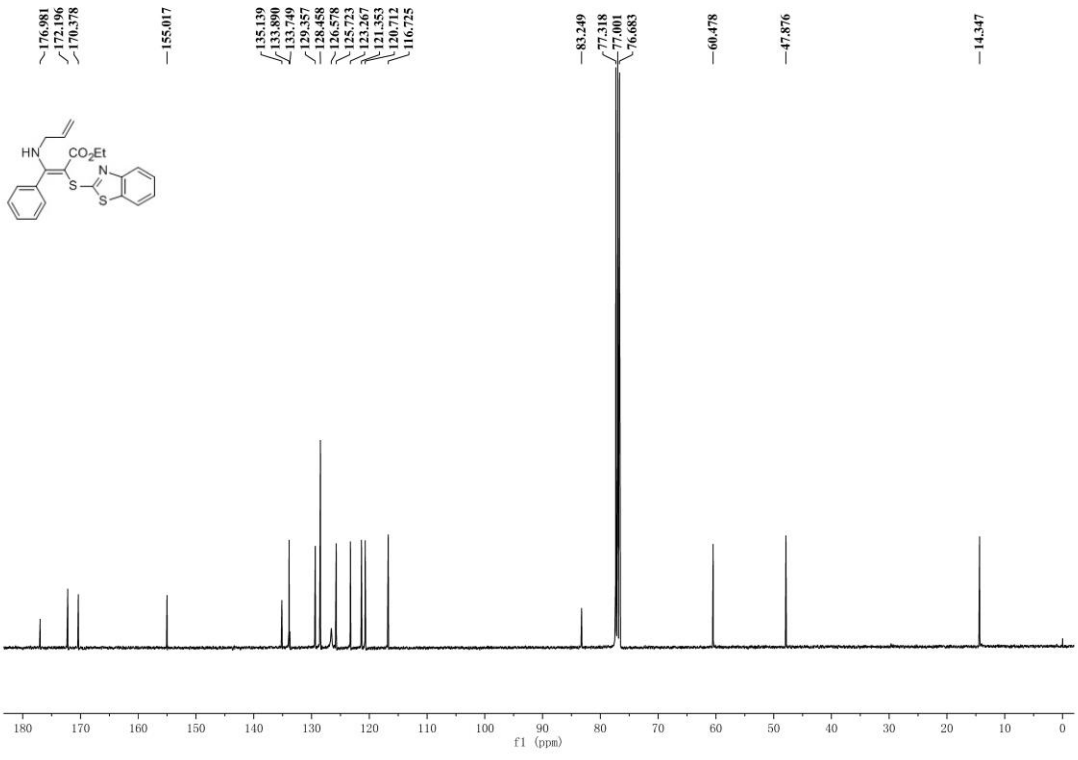

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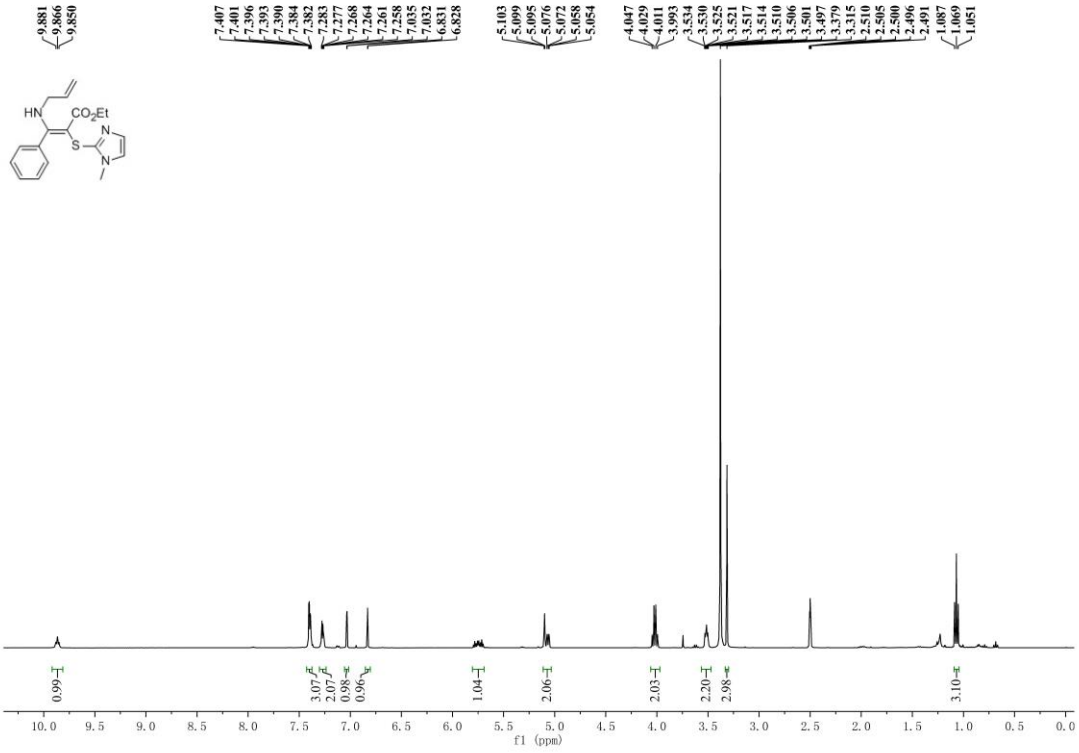

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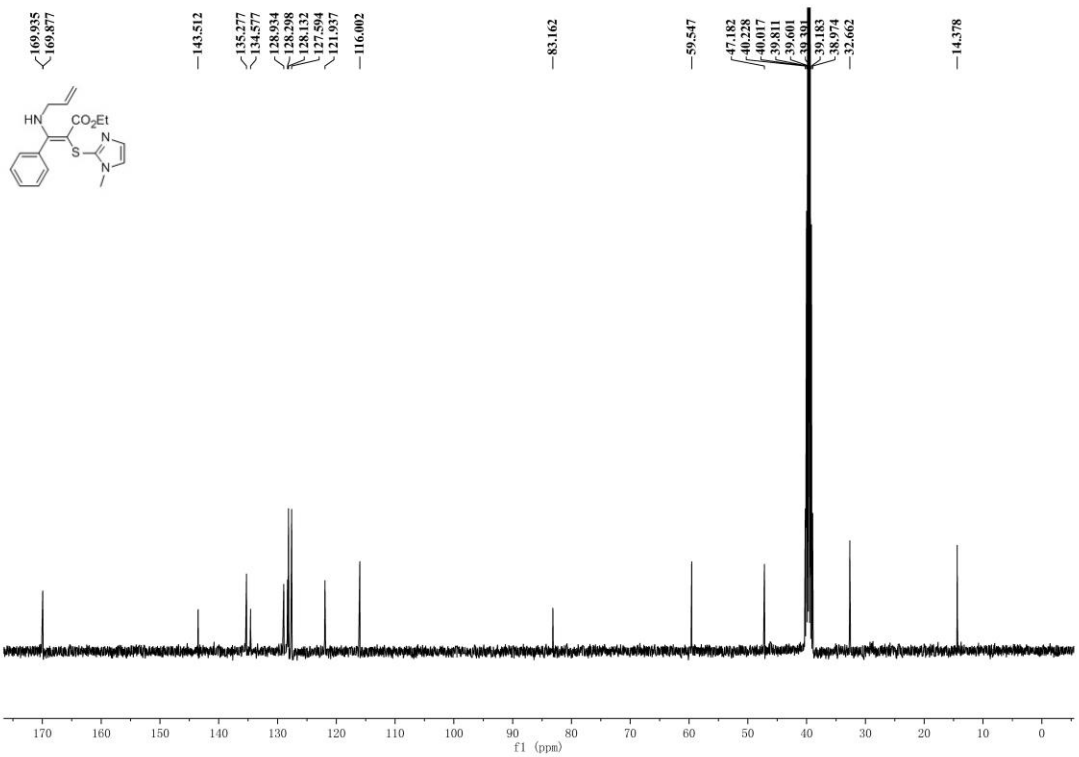

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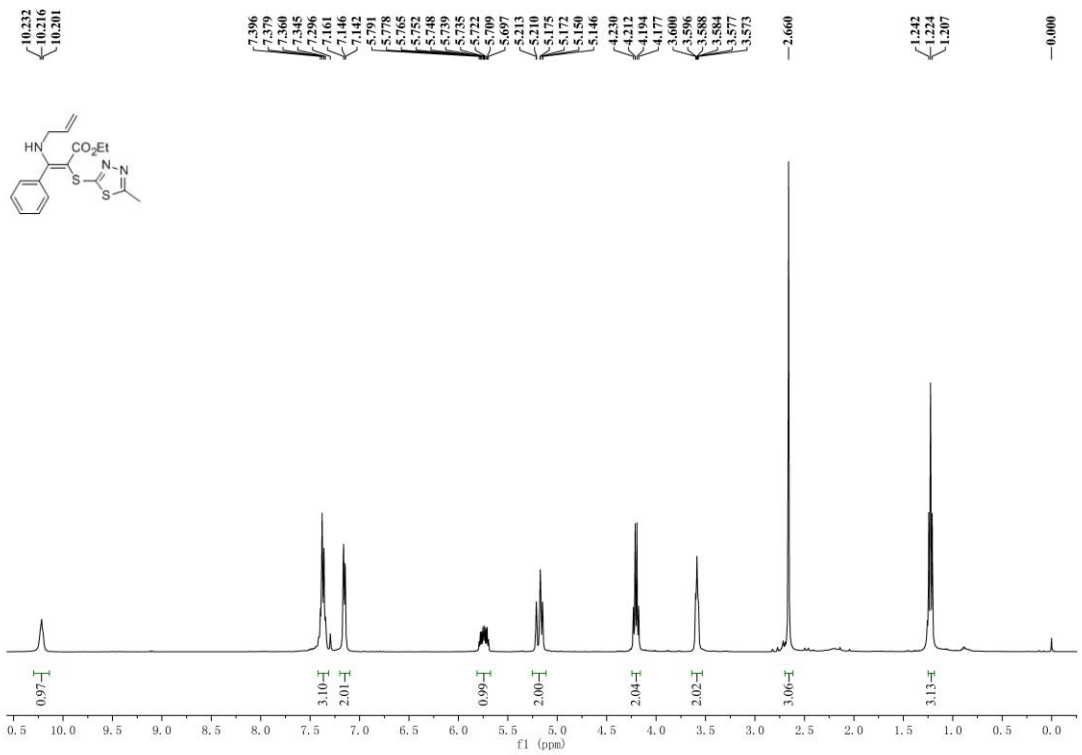

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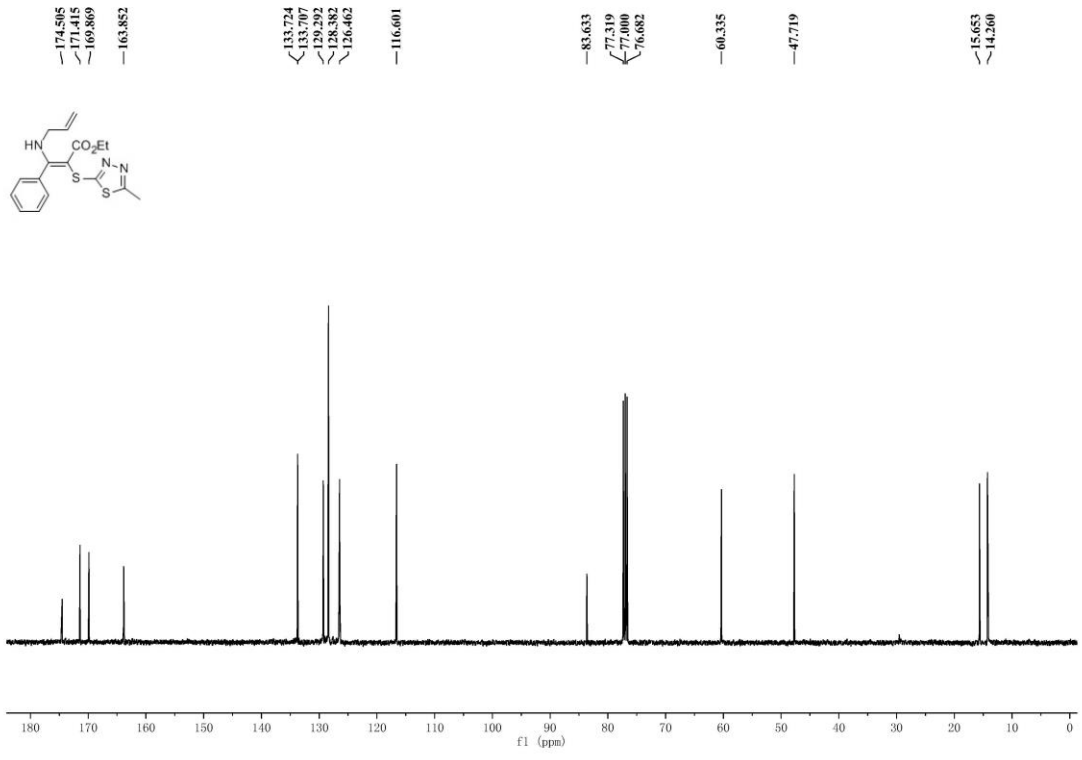

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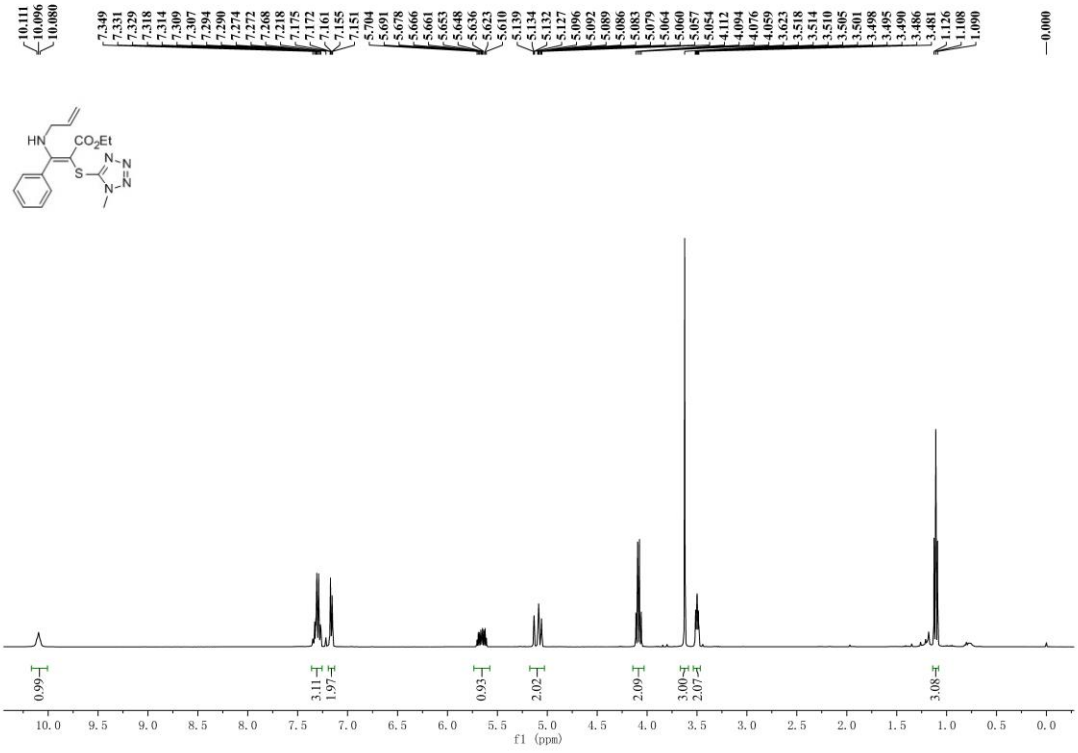
^{1}H NMR



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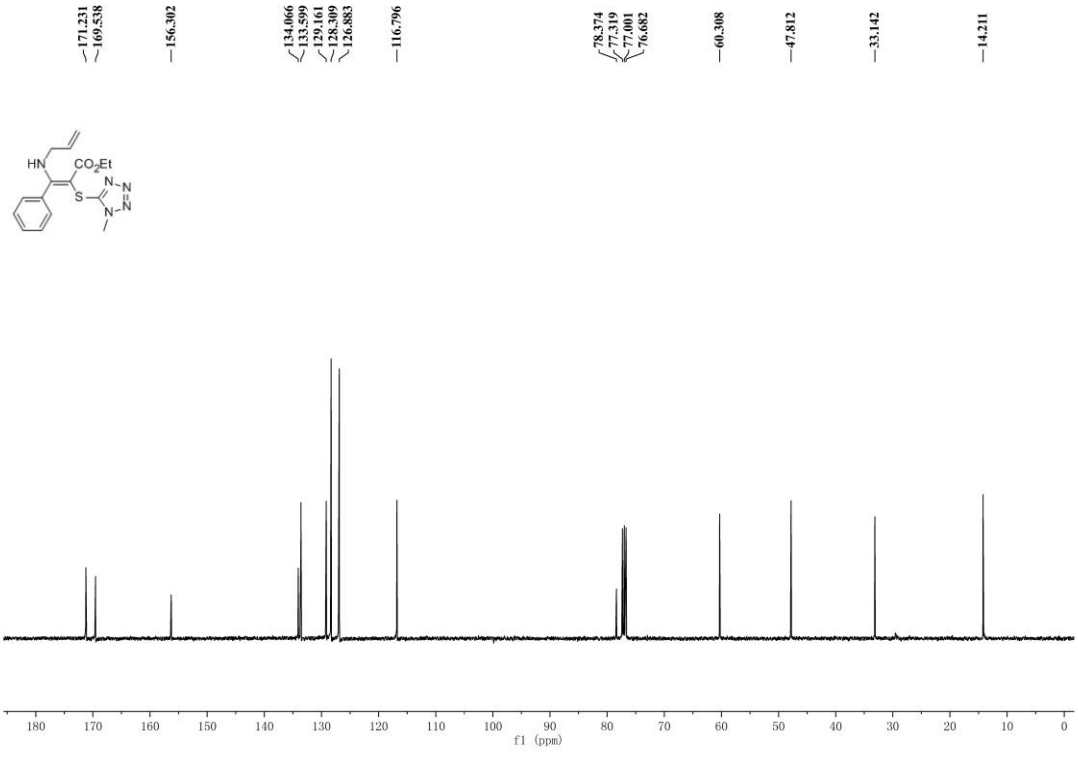

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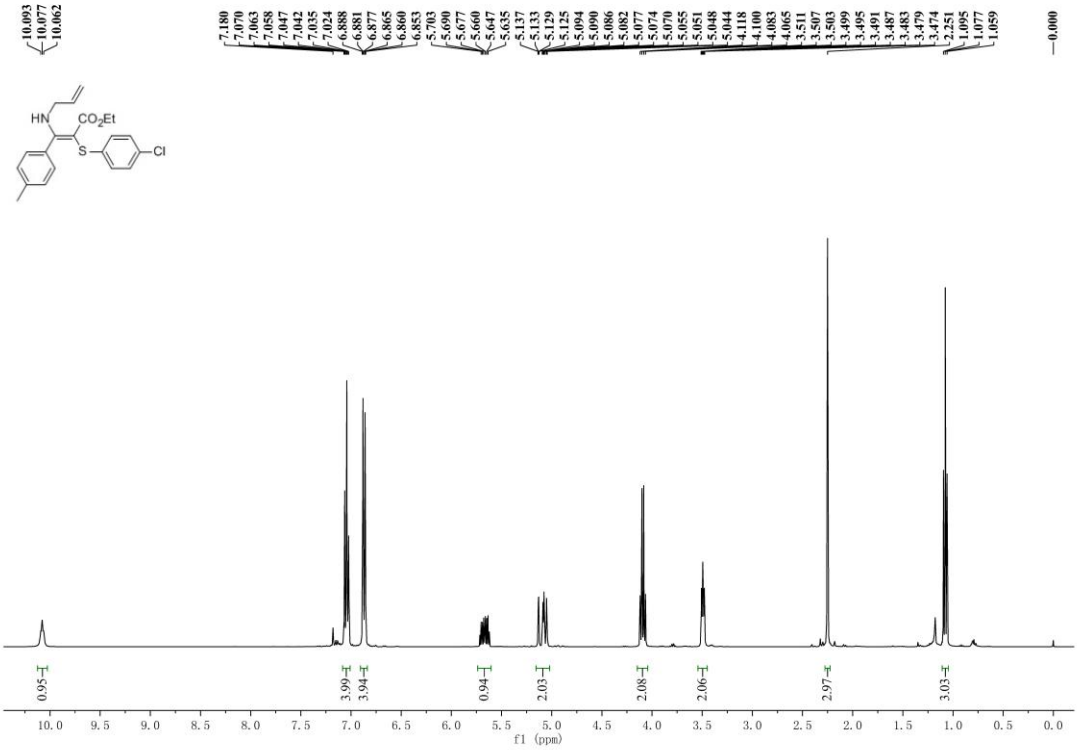

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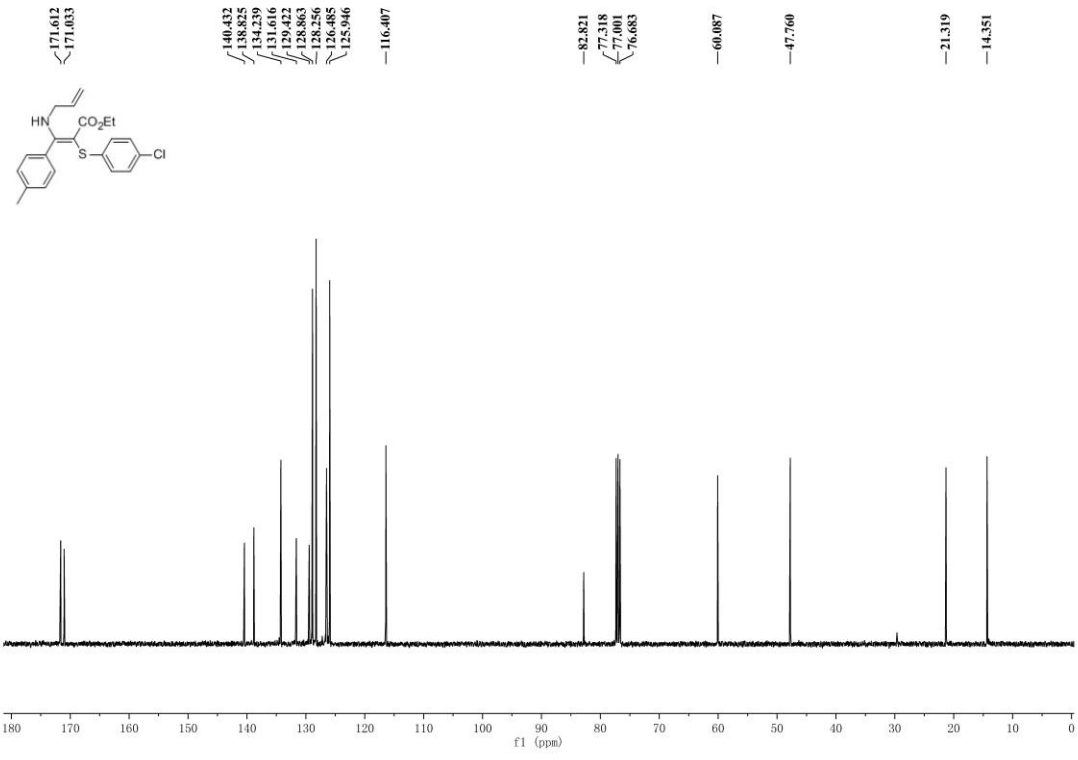

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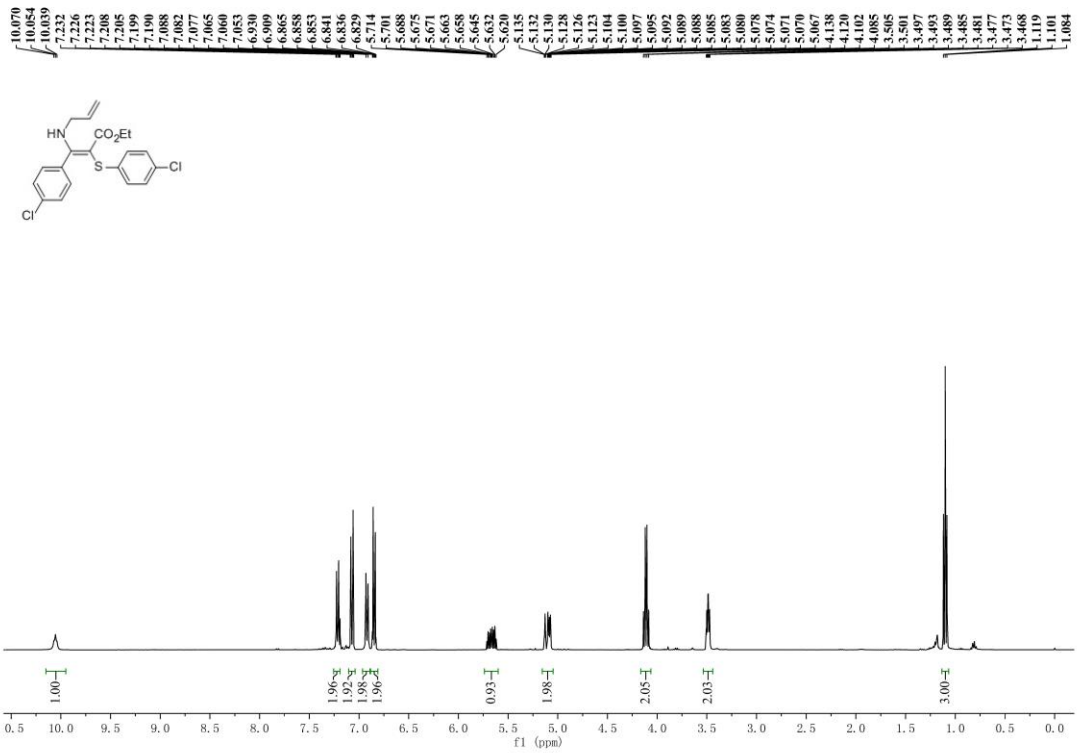
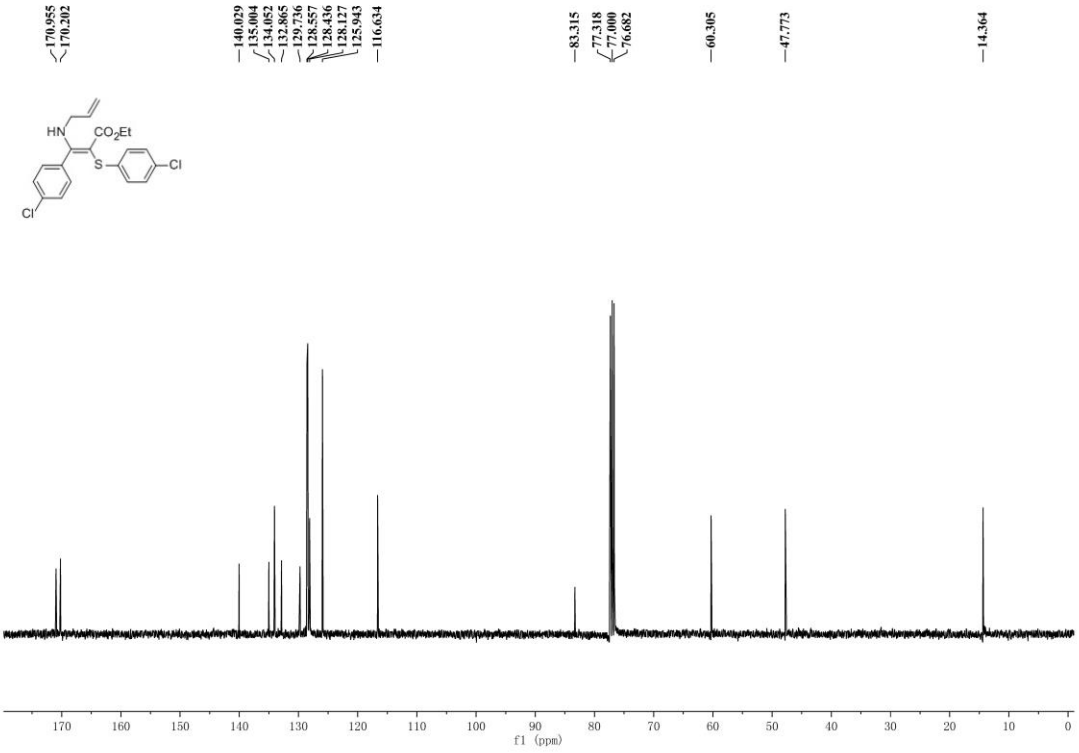


^{13}C NMR



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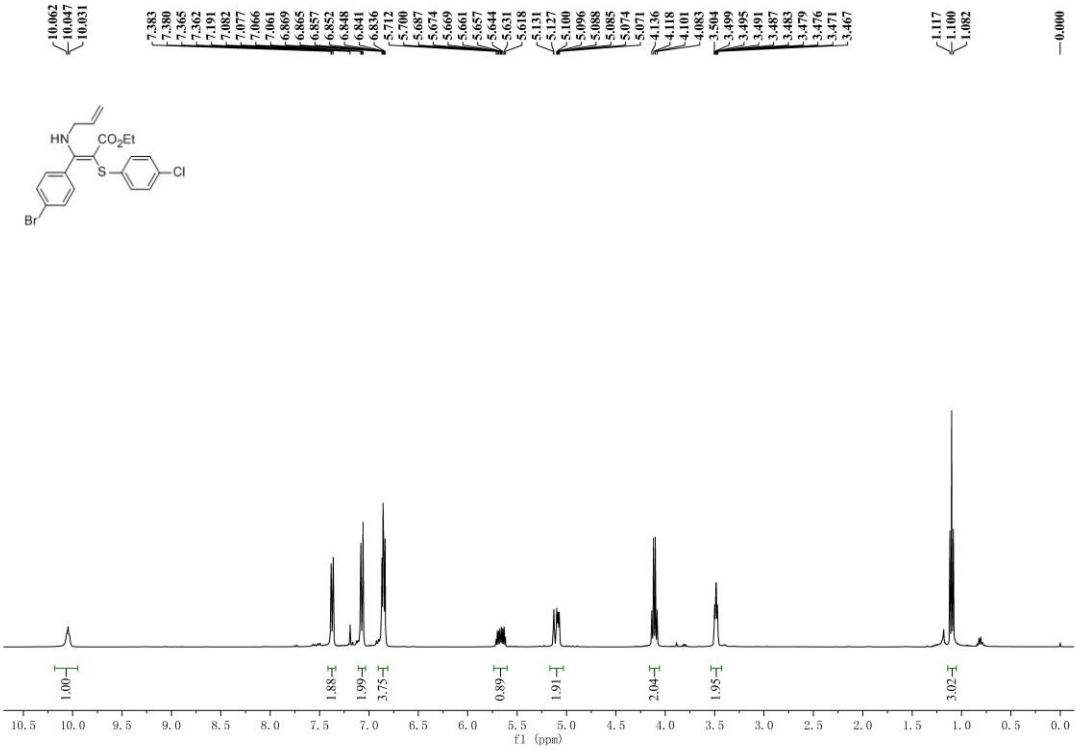
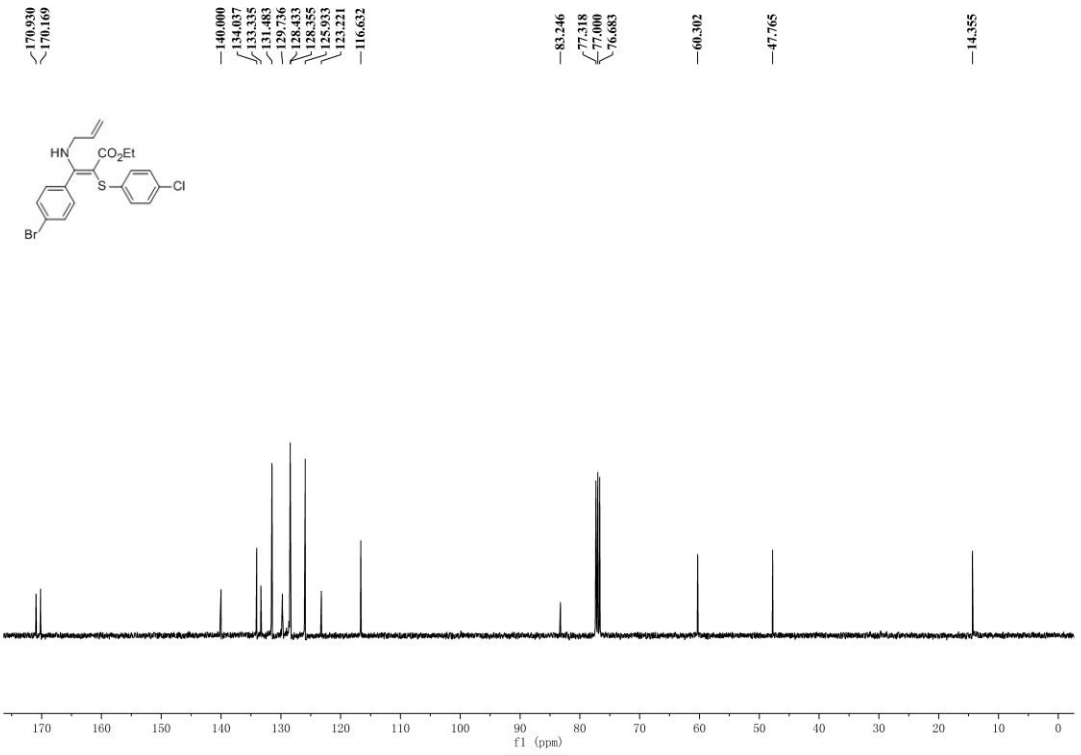
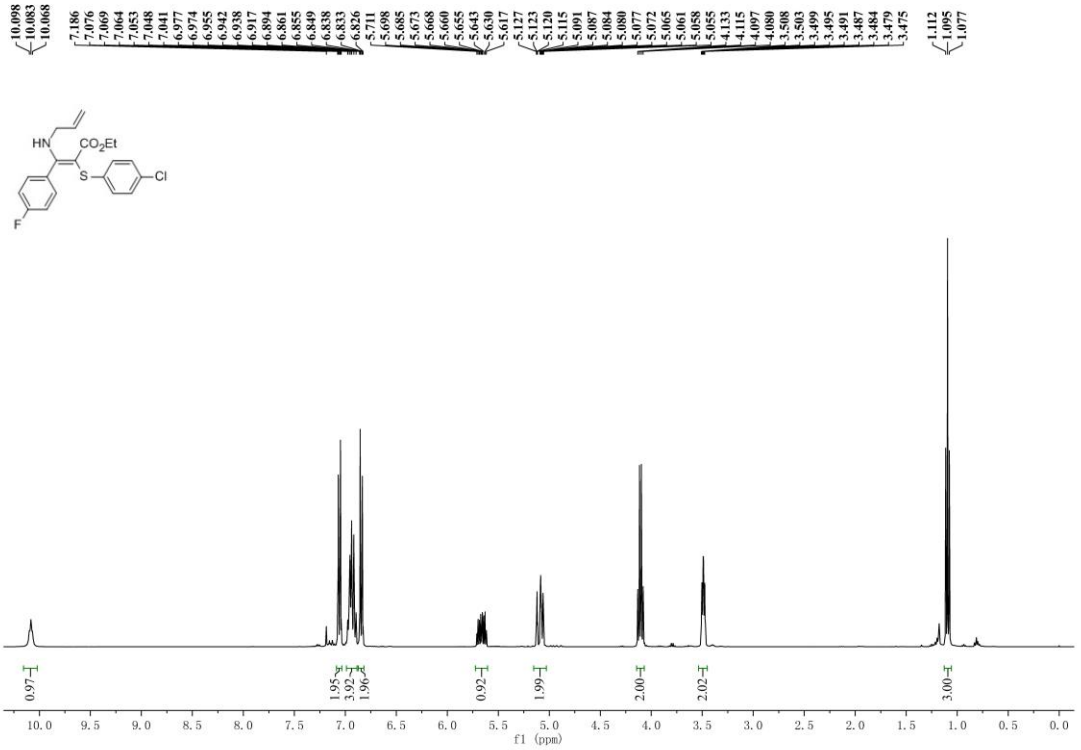


^{13}C NMR

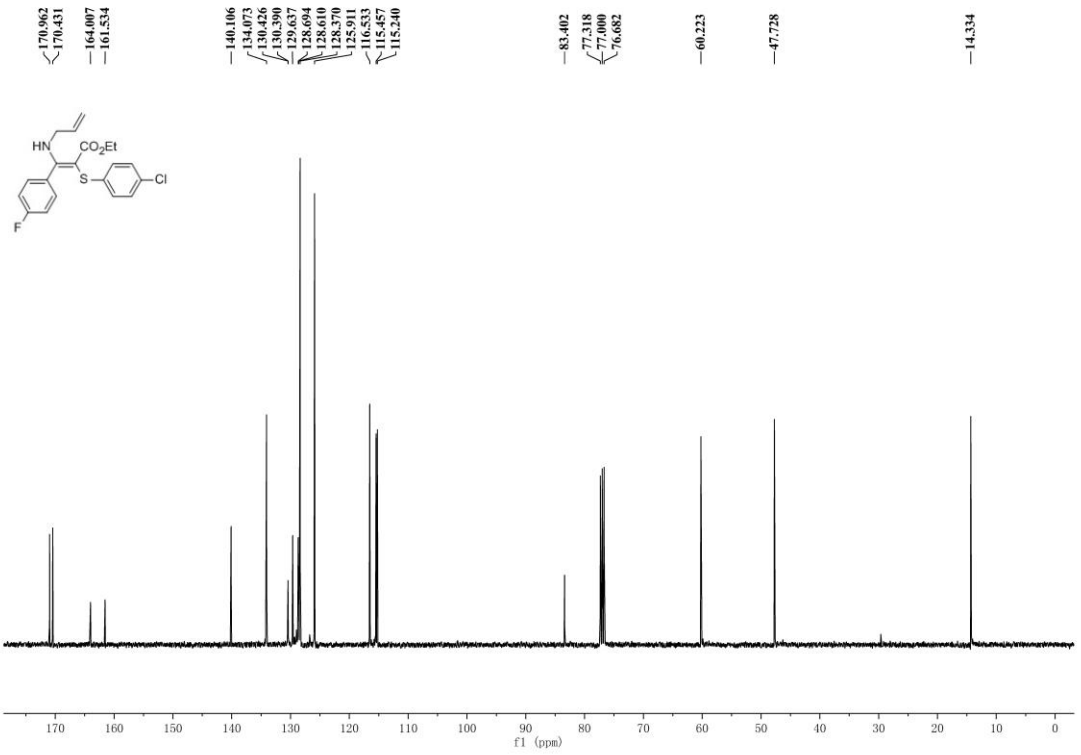


3ea

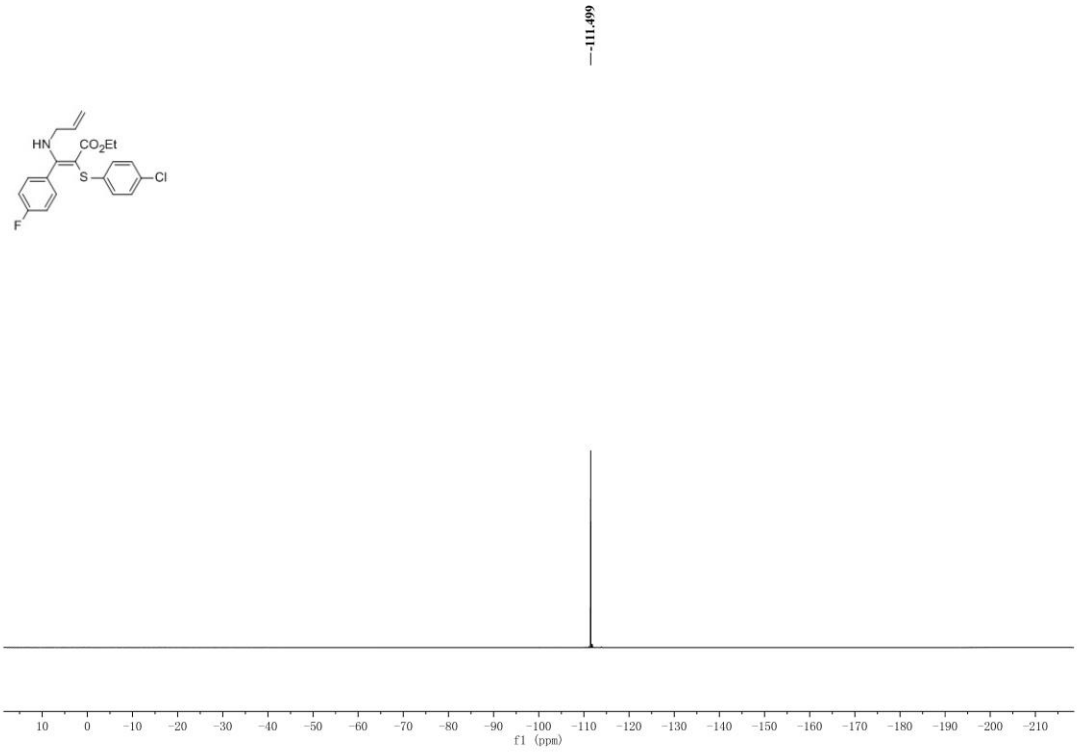
^{1}H NMR



^{13}C NMR



^{19}F NMR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CO2Et
S
Cl
F
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-100
-110
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-150
-160
-170
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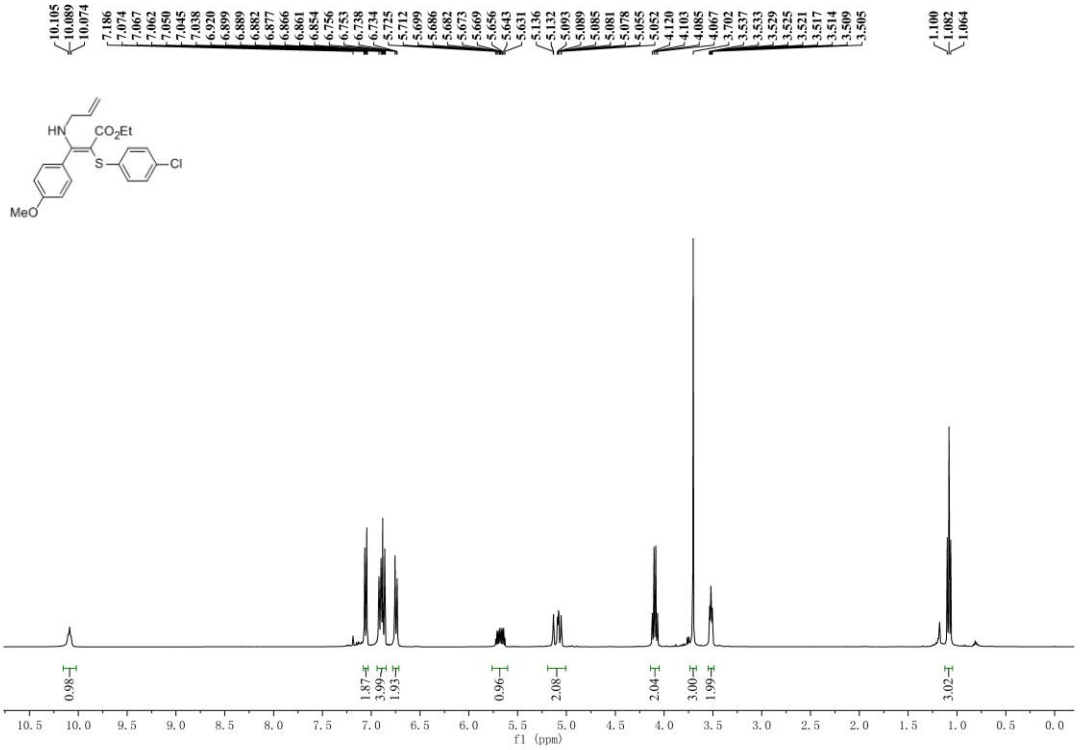
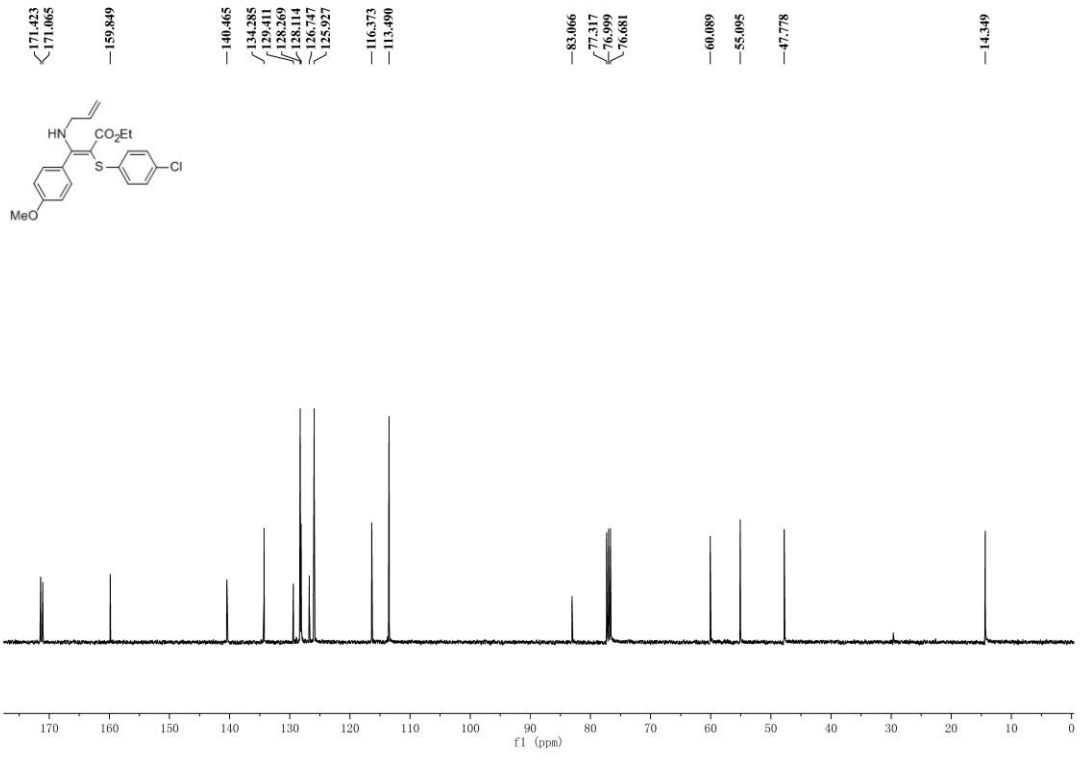
-190
-200
-210
f1 (ppm)

3fa

^{1}H NMR

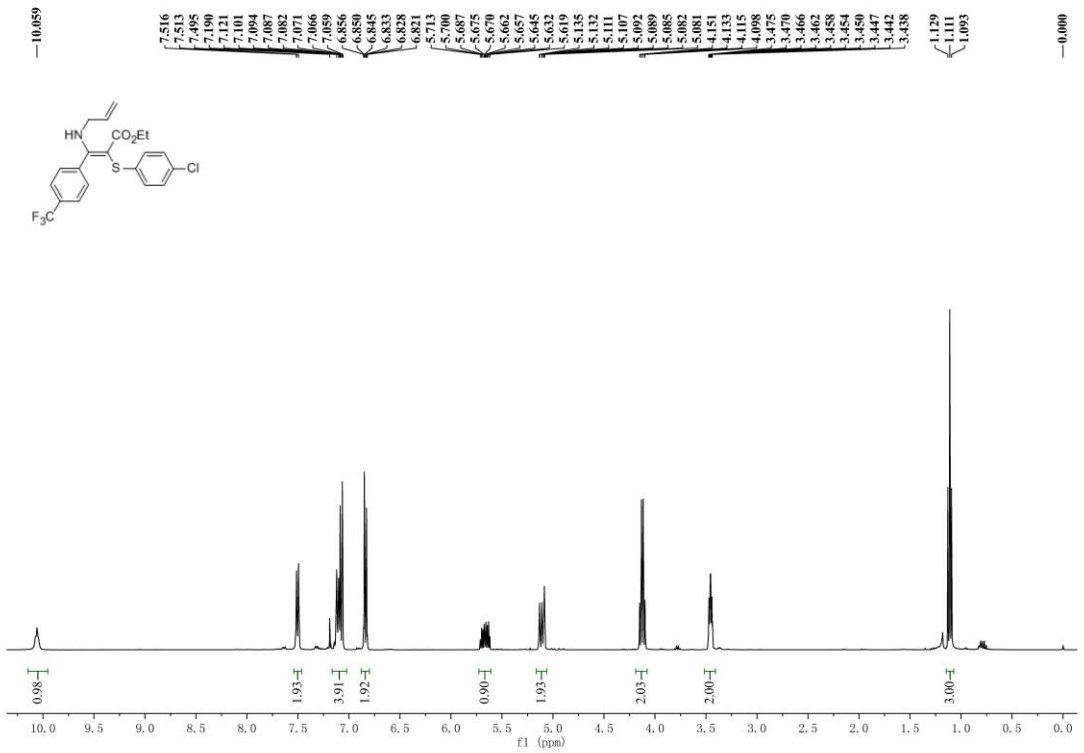


^{13}C NMR

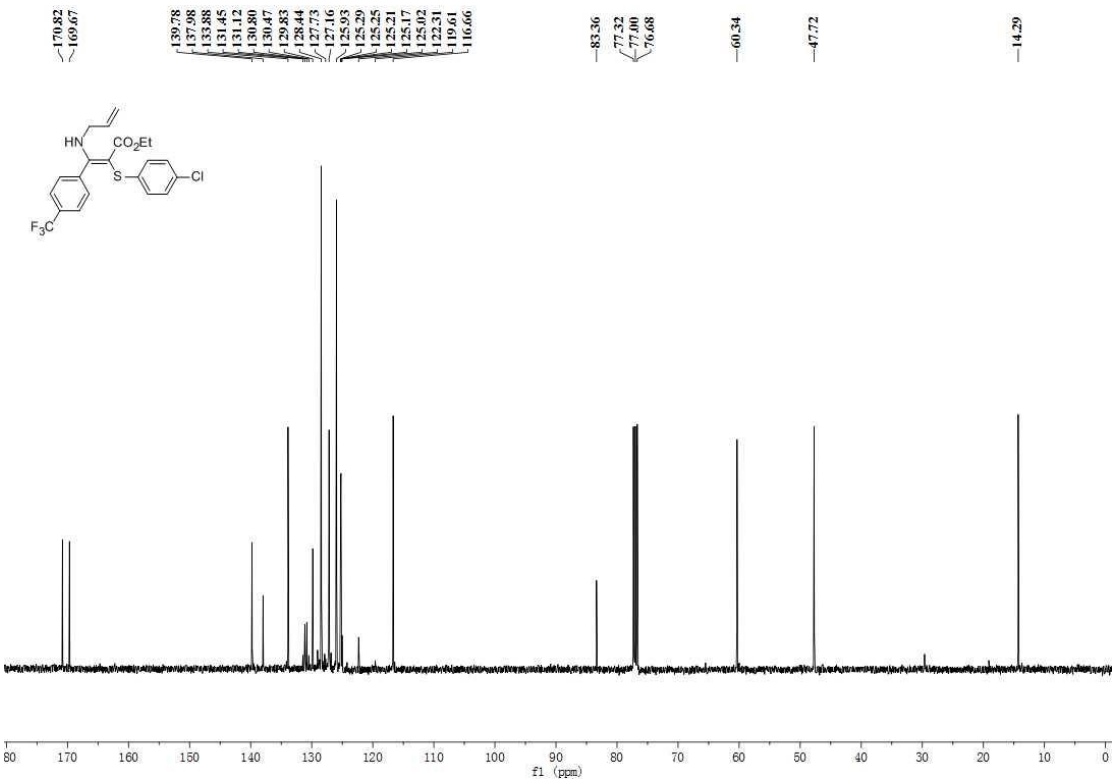


3ga

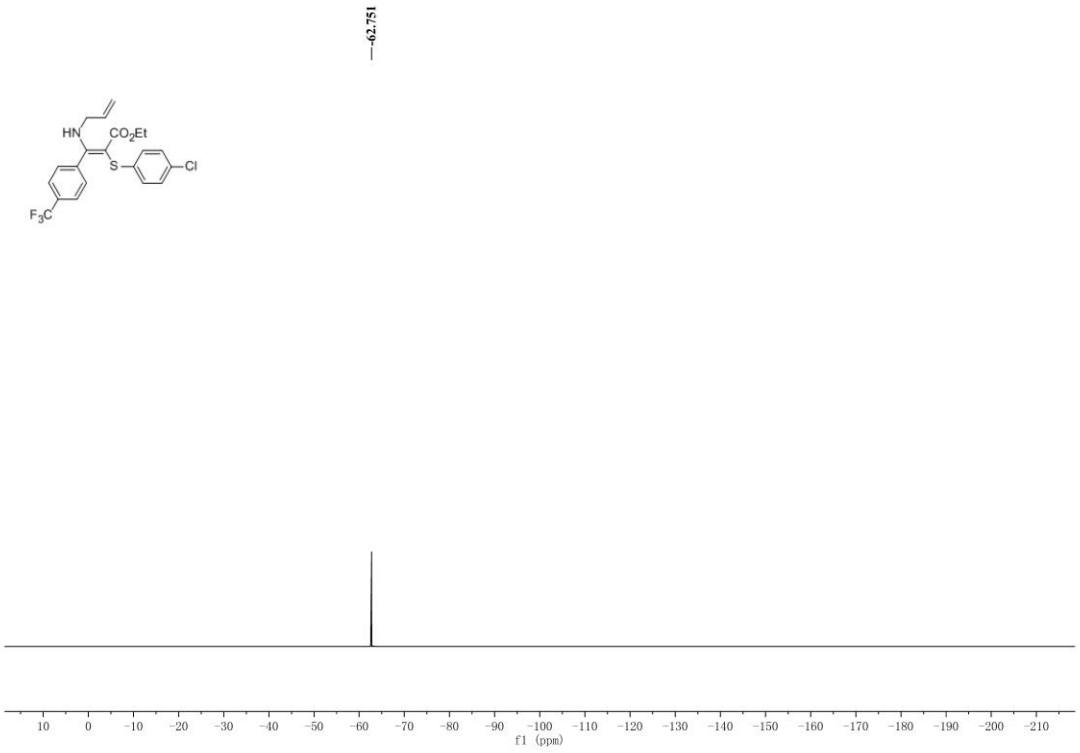
^{1}H NMR



^{13}C NMR

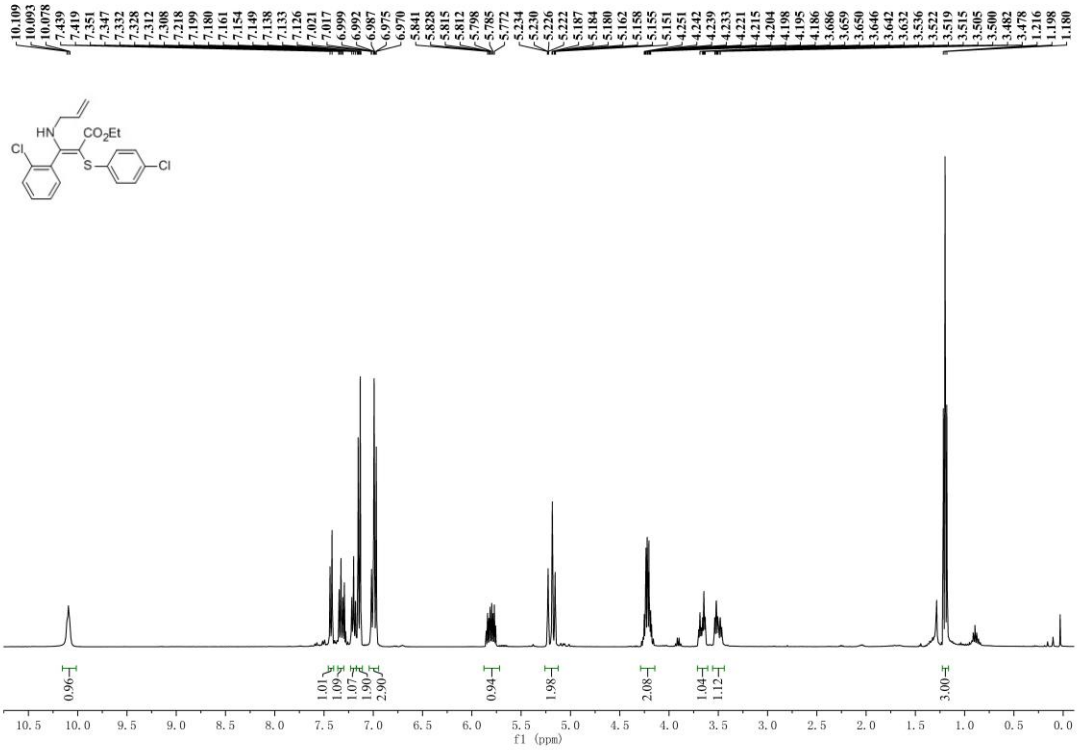


^{19}F NMR

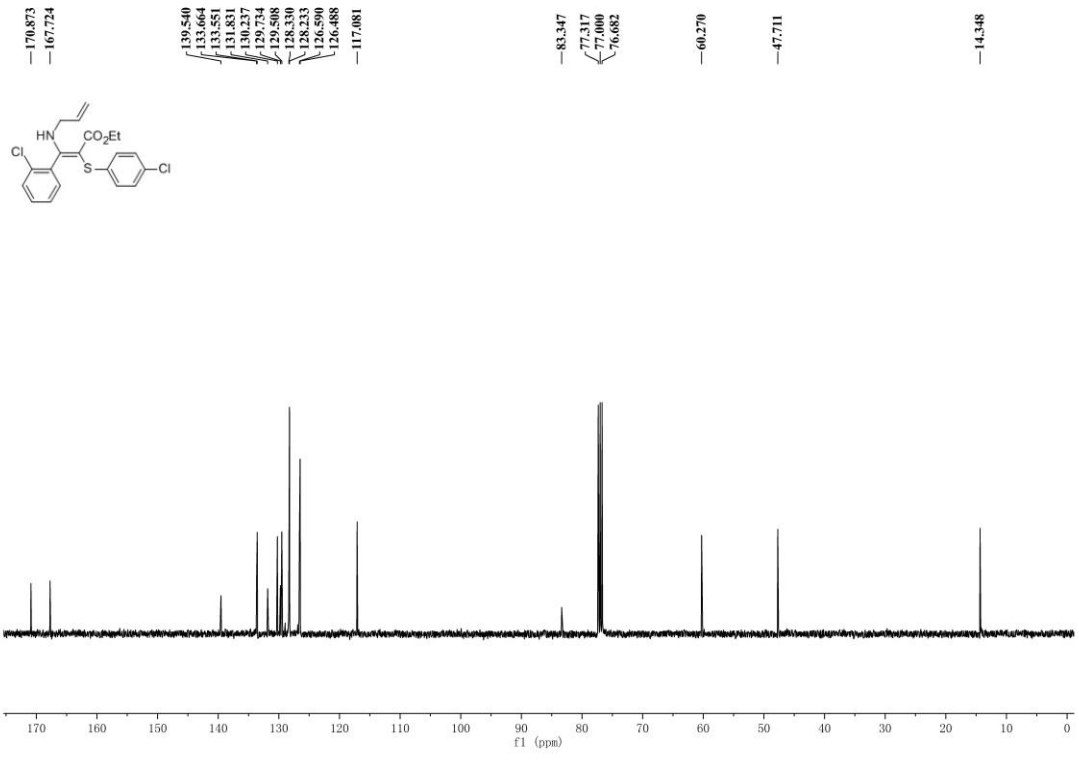

−62.751
HN
CO2Et
S
Cl
F3C
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

3ha

^{1}H NMR

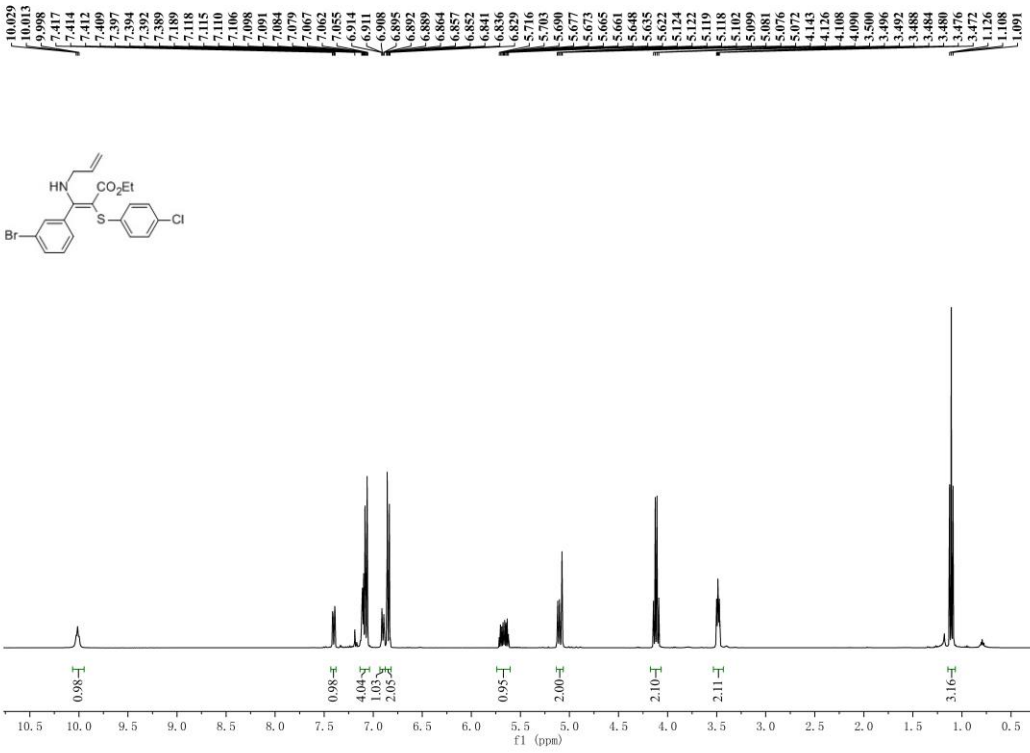


^{13}C NMR

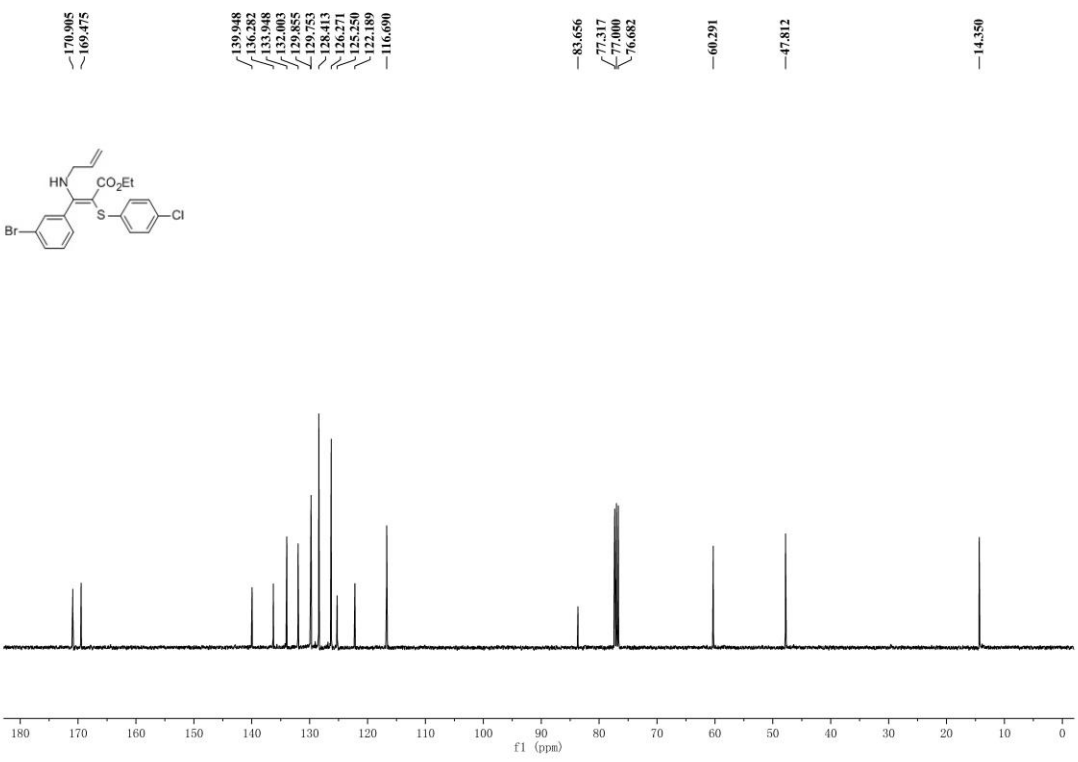


3ia

^{1}H NMR

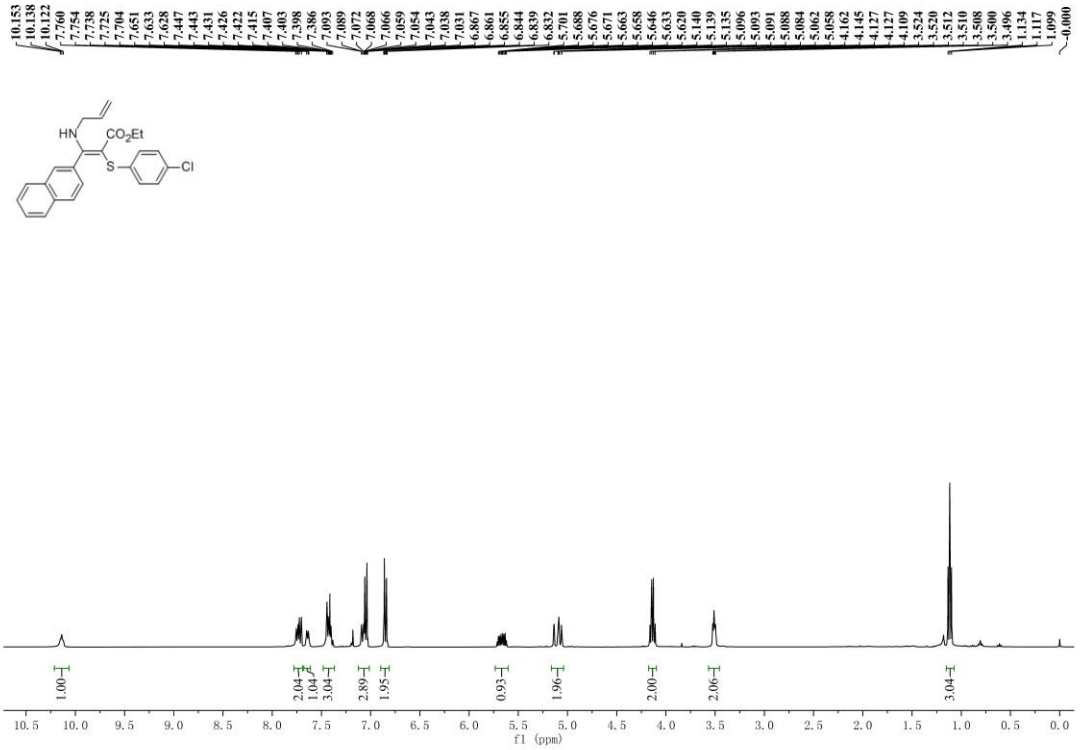


^{13}C NMR

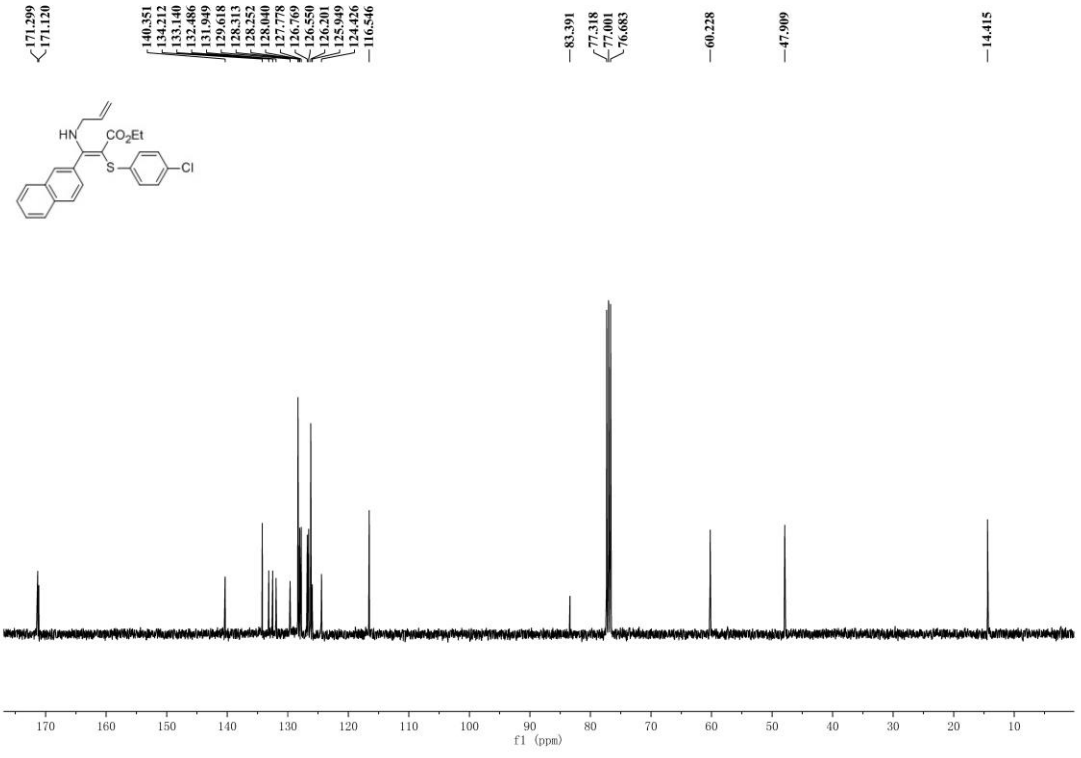


3ja

^{1}H NMR

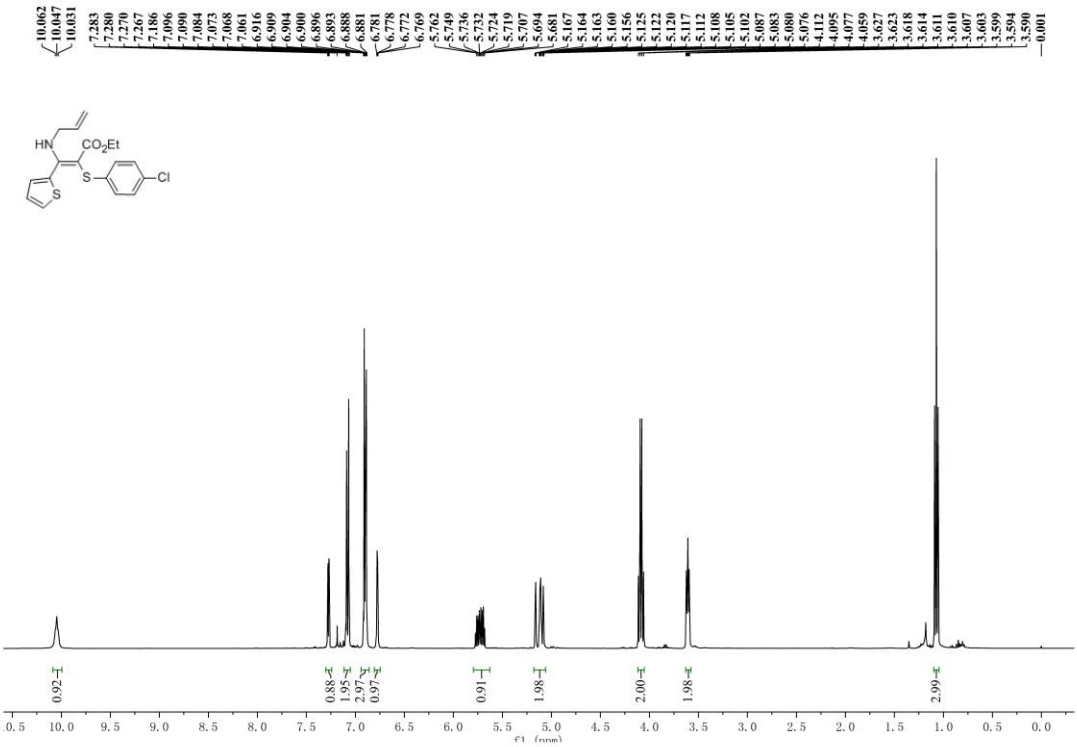


^{13}C NMR

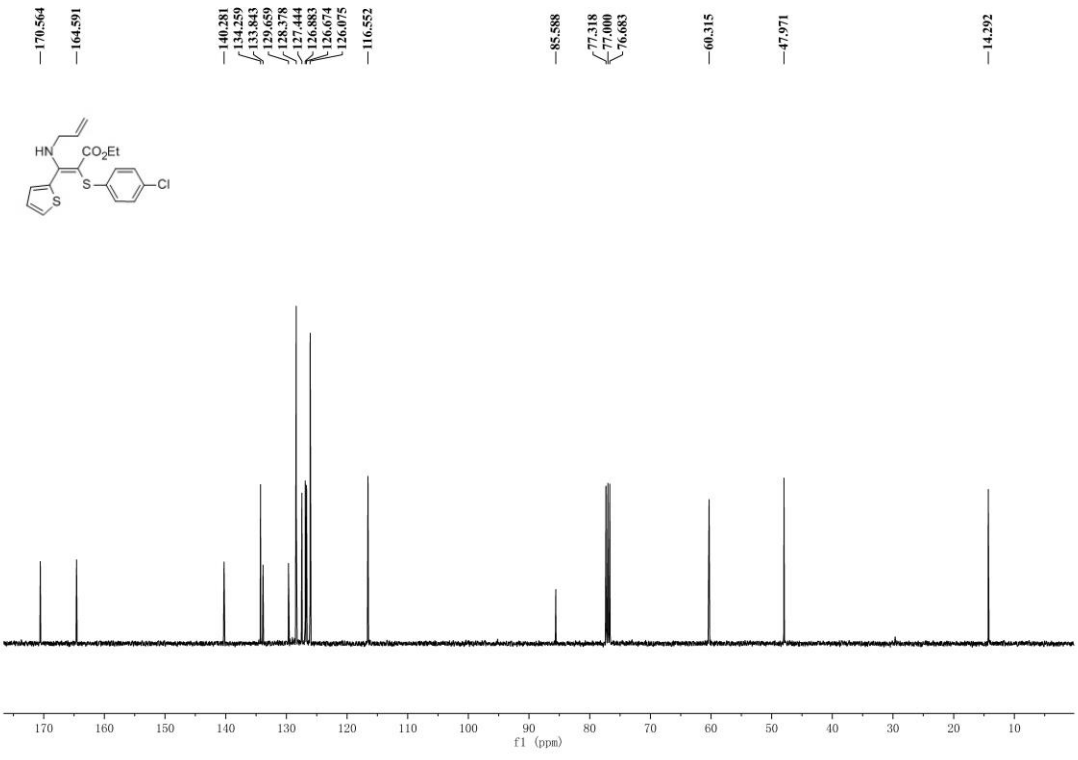


3ka

^{1}H NMR

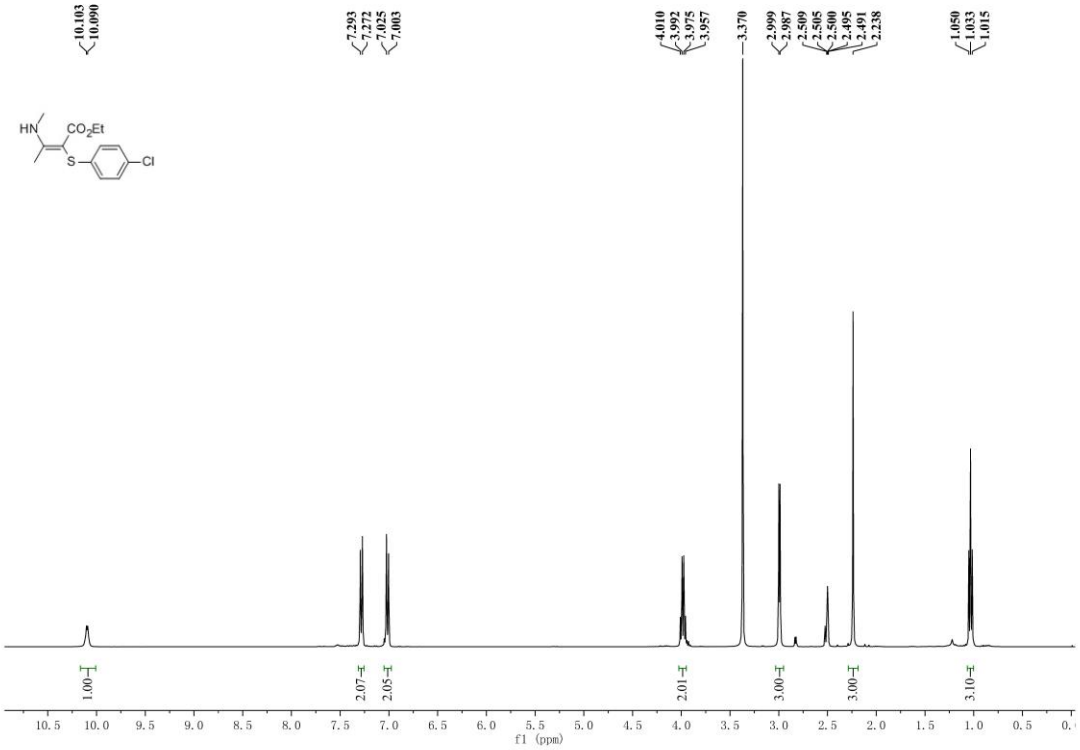


^{13}C NMR

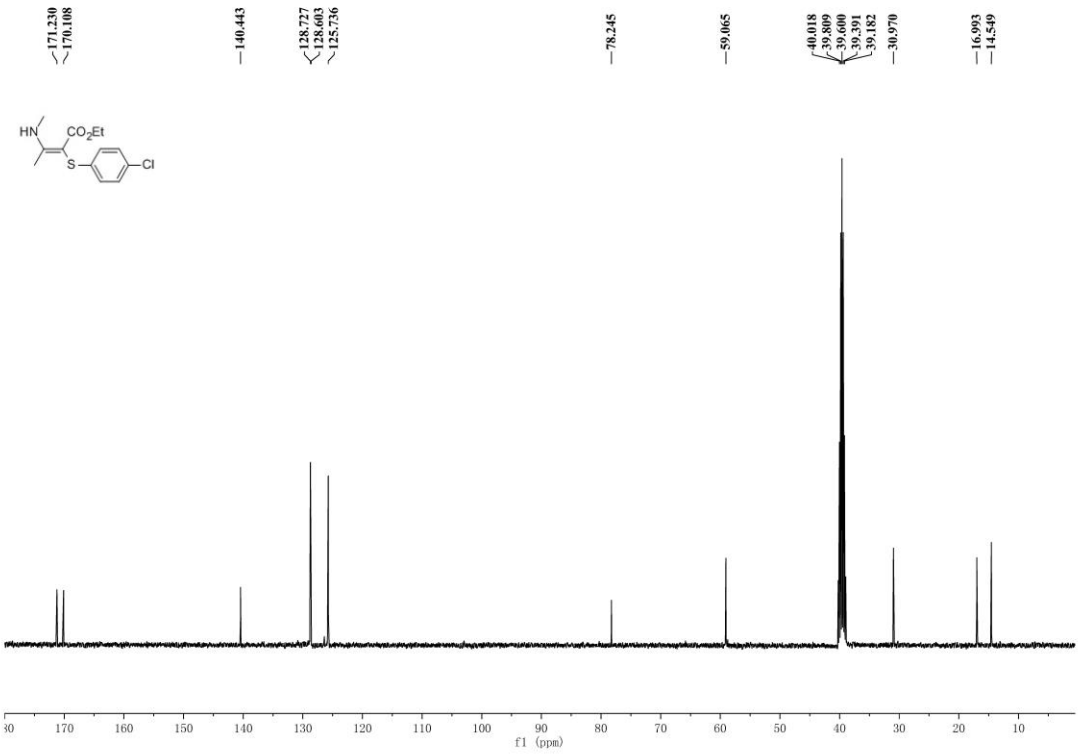


3la

^{1}H NMR

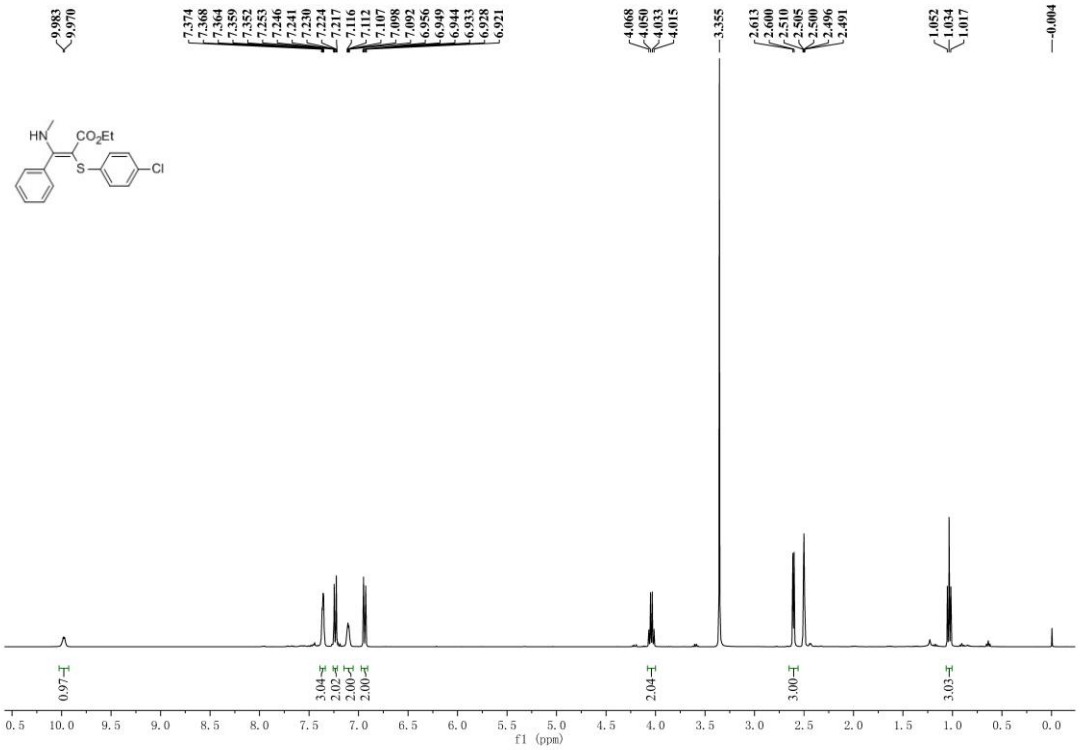


^{13}C NMR

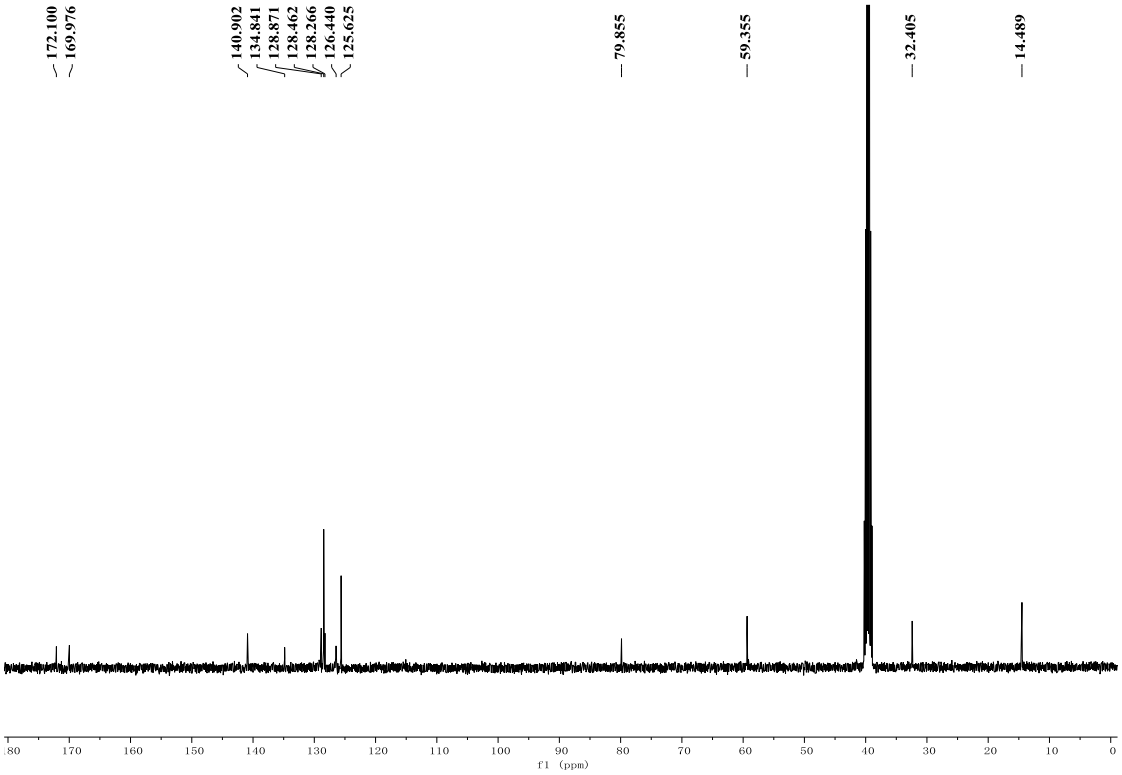


3ma

^{1}H NMR

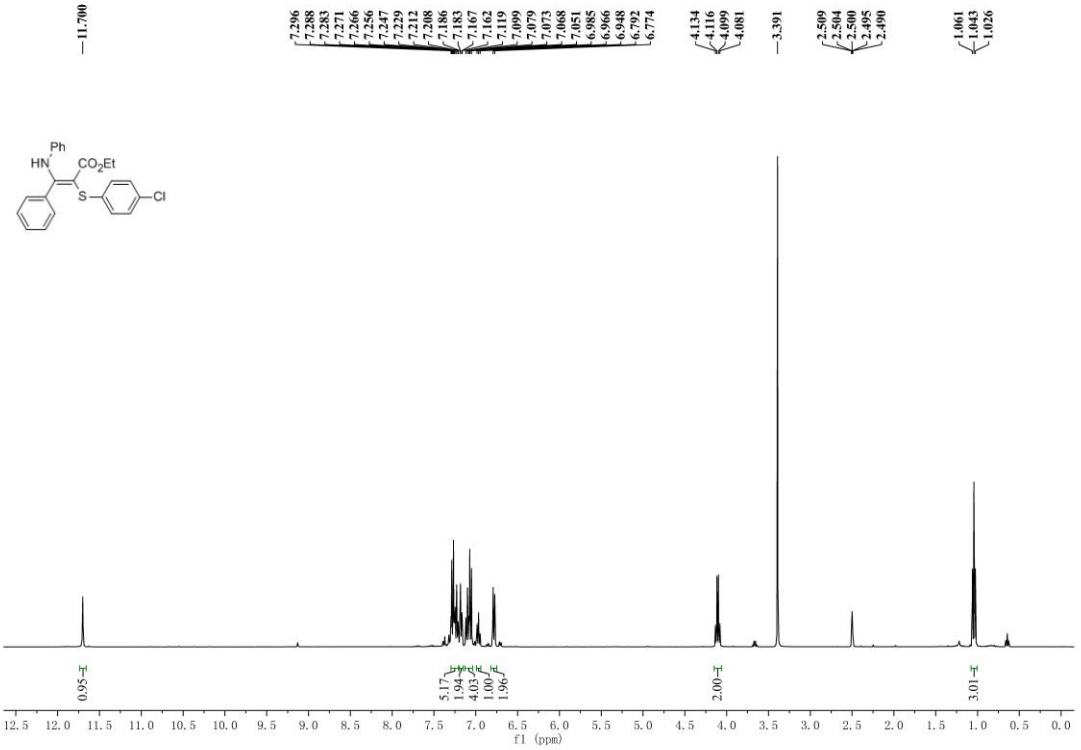


^{13}C NMR

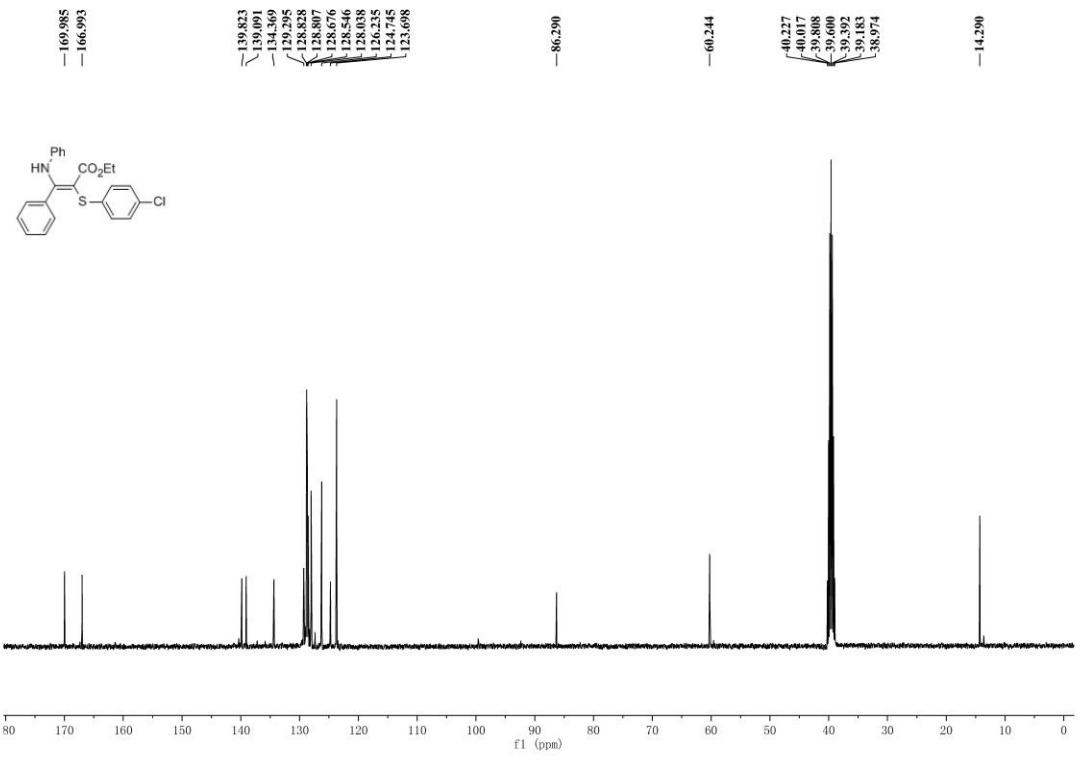


3na

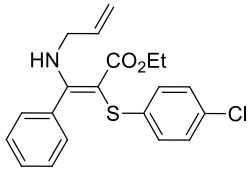
^{1}H NMR



^{13}C NMR



7. Crystallography Data



Crystallography Data of **3aa**：CCDC 1868011 contain the supplementary crystallographic data for **3aa**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.CCDC

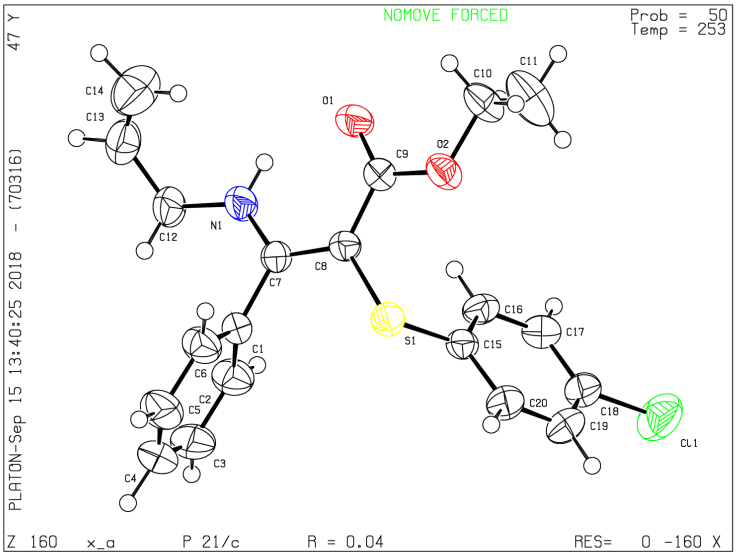


Table 1 Crystal data and structure refinement for 3aa

	3aa
CCDC number[a]	1868011
Empirical formula	$C_{20}H_{20}ClNO_2S$
Formula weight	373.88
Temperature/K	253(2)
Crystal system	monoclinic
Space group	P21/c
a/Å	11.5425(5)
b/Å	20.2515(9)
c/Å	8.2218(4)
α/°	90

β/°	92.176(2)
γ/°	90
Volume/Å3	1920.48(15)
Z	4
ρcalcg/cm3	1.293
μ/mm-1	0.320
F(000)	784.0
Crystal size/mm3	0.16 × 0.08 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.532 to 57.434
Index ranges	-14 ≤ h ≤ 15, -24 ≤ k ≤ 27, -11 ≤ l ≤ 11
Reflections collected	22022
Independent reflections	4969 [Rint = 0.0218, Rsigma = 0.0184]
Data/restraints/parameters	4969/0/295
Goodness-of-fit on F2	1.030
Final R indexes [I>=2σ (I)]	R1 = 0.0408, wR2 = 0.1063
Final R indexes [all data]	R1 = 0.0543, wR2 = 0.1159
Largest diff. peak/hole	0.287/-0.228

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3aa. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ}tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	8881.2(12)	3914.3(7)	6381.0(17)	36.3(3)
C2	8449.4(17)	3373.5(9)	7183(2)	53.6(4)
C3	9184(2)	2856.2(10)	7643(3)	67.1(5)
C4	10337(2)	2882.2(10)	7293(3)	68.1(6)

C5	10770.1(17)	3412.9(11)	6493(3)	66.5(5)
C6	10043.1(14)	3931.1(9)	6022(2)	51.3(4)
C7	8126.0(11)	4492.7(7)	5944.9(16)	34.2(3)
C8	7715.1(12)	4596.9(7)	4355.6(16)	35.2(3)
C9	7066.0(12)	5190.0(7)	3922.6(17)	38.1(3)
C10	6087.6(17)	5804.6(10)	1814(3)	57.3(5)
C11	4834(2)	5665.6(15)	1989(3)	90.5(8)
C12	8281.0(18)	4867(1)	8852(2)	53.2(4)
C13	8707.0(16)	5501.8(11)	9530(2)	58.3(5)
C14	8916(3)	6037.3(15)	8755(4)	87.5(8)
C15	6712.1(13)	3624.5(7)	2343.8(16)	36.6(3)
C16	5659.5(14)	3781.2(8)	3013.3(18)	40.7(3)
C17	4651.4(15)	3452.7(8)	2518(2)	45.2(3)
C18	4701.2(15)	2964.7(8)	1355(2)	48.3(4)
C19	5735.5(17)	2796.9(9)	677(2)	56.0(4)
C20	6736.0(16)	3128.3(9)	1172(2)	49.3(4)
N1	7901.1(13)	4910.3(7)	7148.2(16)	50.0(3)
O1	6784.0(12)	5611.6(6)	4894.4(15)	56.9(3)
O2	6782.3(10)	5238.3(6)	2334.5(13)	46.6(3)
S1	8047.3(3)	4020.7(2)	2839.8(4)	40.58(11)
Cl1	3427.2(5)	2562.2(3)	716.3(8)	78.12(18)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3aa. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	37.2(7)	34.9(7)	36.2(7)	-0.4(5)	-4.6(5)	1.9(5)

C2	54(1)	43.9(9)	63.0(11)	8.3(8)	4.9(8)	-1.5(7)
C3	90.8(16)	37.2(10)	72.3(13)	11.2(9)	-7.3(11)	-0.7(9)
C4	73.9(13)	45.5(10)	83.0(14)	-4.5(9)	-22.0(11)	21.3(9)
C5	43.9(10)	61.9(12)	93.1(15)	-4.1(11)	-6.5(9)	15.2(8)
C6	39.8(8)	47.9(10)	66.3(11)	4.7(8)	0.2(7)	3.4(7)
C7	31.6(6)	34.3(7)	36.8(7)	-0.6(5)	0.1(5)	-0.4(5)
C8	37.8(7)	33.2(7)	34.7(7)	-1.7(5)	0.7(5)	3.7(5)
C9	38.8(7)	37.2(7)	38.2(7)	1.7(6)	-1.0(5)	1.7(6)
C10	60.9(11)	57.0(11)	53.6(10)	18.0(8)	-3.3(8)	15.8(9)
C11	58.7(13)	117(2)	95.7(18)	28.2(16)	-4.1(12)	24.9(13)
C12	62.2(11)	61.5(11)	35.1(8)	-5.8(7)	-8.3(7)	8.6(9)
C13	51.3(9)	75.5(13)	47.6(9)	-13.7(9)	-3.1(7)	1.5(9)
C14	102(2)	78.8(17)	81.9(18)	-9.4(14)	0.9(14)	-21.0(14)
C15	46.5(8)	33.1(7)	30.2(6)	-0.2(5)	0.1(5)	6.1(6)
C16	51.1(8)	33.6(7)	37.9(7)	-5.0(6)	7.0(6)	2.1(6)
C17	48.5(8)	37.7(8)	49.8(8)	1.3(6)	6.5(7)	1.2(6)
C18	54.4(9)	38.0(8)	52.1(9)	0.1(7)	-4.3(7)	-4.3(7)
C19	67.4(11)	47.3(10)	53(1)	-18.9(8)	-3.3(8)	3.2(8)
C20	52.8(9)	48.7(9)	46.3(8)	-13.8(7)	3.1(7)	11.0(7)
N1	61.6(9)	50.8(8)	36.6(7)	-7.3(6)	-9.6(6)	18.9(7)
O1	74.5(8)	46.4(7)	49.1(6)	-7.8(5)	-8.6(6)	23.4(6)
O2	52.3(6)	49.4(6)	38.0(5)	7.7(4)	-0.8(4)	12.3(5)
S1	40.6(2)	44.9(2)	36.37(19)	-6.00(14)	2.89(13)	7.47(15)
Cl1	69.0(3)	69.8(3)	95.0(4)	-18.2(3)	-4.6(3)	-22.1(3)

Table 4 Bond Lengths for 3aa.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.381(2)	C15	C20	1.393(2)
C1	C6	1.384(2)	C16	C17	1.388(2)
C1	C7	1.4956(19)	C17	C18	1.378(2)
C2	C3	1.391(3)	C18	C19	1.379(3)
C3	C4	1.373(3)	C19	C20	1.383(3)
C4	C5	1.365(3)	N1	C7	1.3346(19)
C5	C6	1.389(2)	N1	C12	1.455(2)
C7	C8	1.3892(19)	O1	C9	1.2219(18)
C8	C9	1.4528(19)	O2	C9	1.3376(17)
C10	C11	1.486(3)	O2	C10	1.455(2)
C12	C13	1.478(3)	S1	C8	1.7601(14)
C13	C14	1.285(4)	S1	C15	1.7712(15)
C15	C16	1.389(2)	Cl1	C18	1.7447(17)

Table 5 Bond Angles for 3aa.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C6	119.42(15)	O2	C10	C11	110.48(18)
C2	C1	C7	121.18(14)	N1	C12	C13	113.23(16)
C6	C1	C7	119.36(14)	C14	C13	C12	127.8(2)
C1	C2	C3	119.97(18)	C16	C15	C20	118.64(15)
C4	C3	C2	119.99(19)	C16	C15	S1	124.86(11)
C5	C4	C3	120.47(17)	C20	C15	S1	116.48(12)
C4	C5	C6	120.02(19)	C17	C16	C15	120.67(14)
C1	C6	C5	120.12(18)	C18	C17	C16	119.40(15)
C8	C7	C1	121.30(12)	C17	C18	C19	121.12(16)

N1	C7	C1	116.53(12)	C17	C18	Cl1	119.15(14)
N1	C7	C8	122.14(13)	C19	C18	Cl1	119.73(13)
C7	C8	C9	120.70(12)	C18	C19	C20	119.18(15)
C7	C8	S1	119.31(10)	C19	C20	C15	120.98(16)
C9	C8	S1	119.92(10)	C7	N1	C12	128.01(14)
O1	C9	C8	124.42(13)	C9	O2	C10	117.19(13)
O1	C9	O2	121.72(13)	C8	S1	C15	104.61(7)
O2	C9	C8	113.86(12)				

Table 6 Torsion Angles for 3aa.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
C1	C2	C3	C4	-0.3(3)	C10	O2	C9	O1	-2.0(2)
C1	C7	C8	C9	-174.67(13)	C12	N1	C7	C1	-1.4(3)
C1	C7	C8	S1	2.32(19)	C12	N1	C7	C8	-179.36(17)
C2	C1	C6	C5	-1.2(3)	C15	C16	C17	C18	0.3(2)
C2	C1	C7	C8	-104.59(18)	C15	S1	C8	C7	109.90(12)
C2	C1	C7	N1	77.43(19)	C15	S1	C8	C9	-73.09(13)
C2	C3	C4	C5	-0.1(3)	C16	C15	C20	C19	0.1(2)
C3	C4	C5	C6	-0.2(3)	C16	C17	C18	C19	0.1(3)
C4	C5	C6	C1	0.8(3)	C16	C17	C18	Cl1	-179.06(12)
C6	C1	C2	C3	0.9(3)	C17	C18	C19	C20	-0.4(3)
C6	C1	C7	C8	77.59(19)	C18	C19	C20	C15	0.3(3)
C6	C1	C7	N1	-100.39(18)	C20	C15	C16	C17	-0.4(2)
C7	C1	C2	C3	-176.92(16)	N1	C7	C8	C9	3.2(2)
C7	C1	C6	C5	176.71(17)	N1	C7	C8	S1	-179.81(12)
C7	C8	C9	O1	-4.0(2)	N1	C12	C13	C14	-10.0(3)

C7	C8	C9	O2	176.57(13)	S1	C8	C9	O1	178.99(13)
C7	N1	C12	C13	135.52(19)	S1	C8	C9	O2	-0.40(18)
C8	S1	C15	C16	2.27(14)	S1	C15	C16	C17	178.44(12)
C8	S1	C15	C20	-178.90(12)	S1	C15	C20	C19	-178.83(14)
C9	O2	C10	C11	-85.5(2)	Cl1	C18	C19	C20	178.77(14)
C10	O2	C9	C8	177.40(14)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3aa.

Atom	*x*	*y*	*z*	U(eq)
H1	7655(19)	3368(10)	7420(20)	60(6)
H2	8900(20)	2498(13)	8130(30)	82(7)
H3	10860(20)	2514(12)	7660(30)	81(7)
H4	11550(30)	3439(14)	6220(40)	105(9)
H5	10320(20)	4305(12)	5470(30)	74(7)
H6	5614(16)	4116(9)	3760(20)	49(5)
H7	3925(17)	3573(9)	2990(20)	54(5)
H8	5798(18)	2465(10)	-100(30)	62(6)
H9	7461(19)	3042(10)	740(20)	63(6)
H10	7482(18)	5248(11)	6860(20)	61(6)
H11	8877(19)	4537(11)	8970(30)	68(6)
H11A	4385.89	6033.4	1582.04	136
H11B	4684.08	5597.46	3117.02	136
H11C	4623.77	5276.19	1381.1	136
H12	7590(20)	4741(11)	9500(30)	71(6)
H13	6240(20)	5856(12)	660(30)	78(7)

H14	6400(20)	6192(13)	2350(30)	84(8)
H15	8820(20)	5506(12)	10790(30)	87(7)
H16	9220(30)	6405(17)	9370(40)	117(10)
H17	8810(20)	6041(13)	7600(40)	95(9)