Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Palladium-Catalyzed Aerobic Oxidative Double Allylic C-H Oxygenation of Alkenes: A Novel and Straightforward Route to *α,β*-Unsaturated Esters

Wanfei Yang,[a] Huoji Chen,[a] Jianxiao Li,[a] Chunsheng Li,[a] Wanqing Wu[a] and Huanfeng Jiang*[a,b]

[a.] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, P. R. China

Fax: (+86)20-8711-2906; E-mail: jianghf@scut.edu.cn

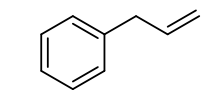
[b.] State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

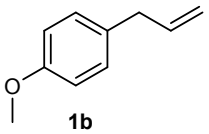
List of Contents

A. General Methods

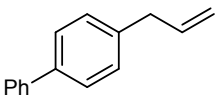
^{1}H NMR spectra were recorded in $CDCl_3$ at 400 MHz, ^{19}F NMR spectra were recorded in $CDCl_3$ at 376 MHz and ^{13}C NMR spectra were recorded in $CDCl_3$ at 100 MHz, respectively, and the chemical shifts (d) were referenced to TMS. GC−MS data were obtained using electron ionization. HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucker Vector 22 spectrometer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm.

alkenes

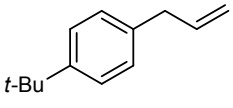

1a



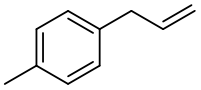
1b

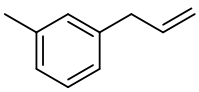


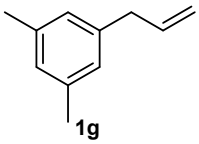
1c

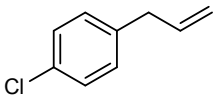


1d

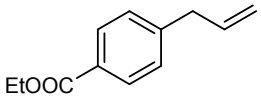

1e


1f

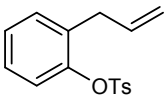

1g



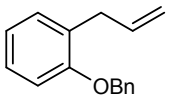
1h



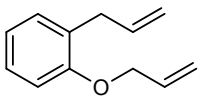
1i



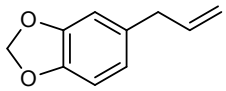
1j



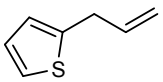
1k



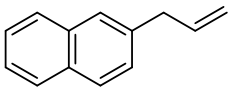
1l

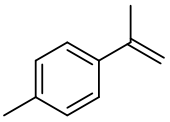


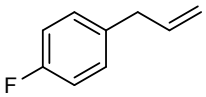
1m



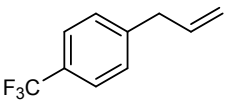
1n


1o

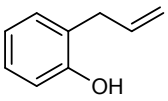

1p



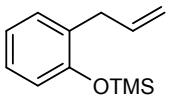
1q



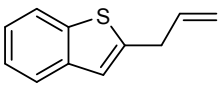
1r



1s

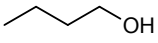


1t

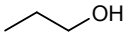


1u

alcohols and phenol

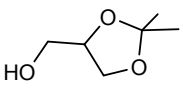


2a



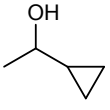
2b

2c

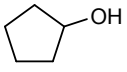


2d

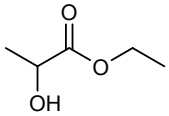
2e



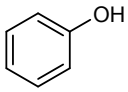
2f



2g



2h



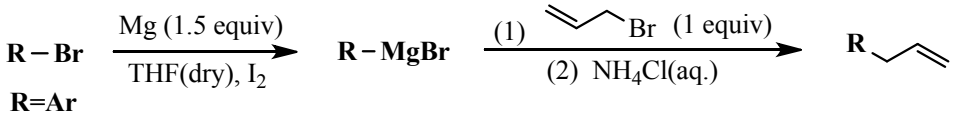
2i

Substrates

Alkenes substrates **1a, 1b, 1p, 1s, 1t** alcohols and phenol were commercial available reagents. Alkenes **1c**, **1d-h**, **1m-o**, **1q**, **1r**, **1u** were synthesized through Grignard reaction. Other alkene substrates were synthesized according to the following procedures **3** and **4**.

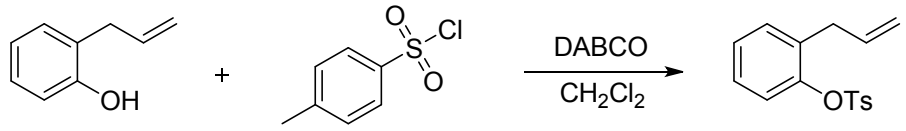
B. General Procedures

Grignard Reaction for the Synthesis of Alkenes 1



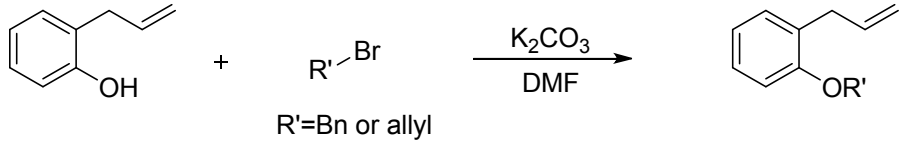
Aryl bromide (5 mmol) was reacted with magnesium (1.5 equiv.) in 5 mL THF using I_2 as initiator at room temperature. After the reaction was finished, the combined organics was added to the THF solution of allyl bromide with magnetic stirring. After 1 h, NH_4Cl (aq.) was added to the reaction mixture, washing with water and then concentrated for further purification.

Typical Reaction Procedure for the Synthesis of Alkene 1j



p-Toluenesulfonyl chloride (1.9g, 10 mmol) and 2-allylphenol (10 mmol) were dissolved in 15 mL dichloromethane. DABCO (1.35g, 12 mmol) in 5 mL dichloromethane was added, resulting in rapid warming and precipitate formation. After completion, 3 mL of 1M NaOH was added and the reaction was diluted into 100 mL ethyl acetate. The organic layer was extracted with 5% aqueous $NaHCO_3$ (3 × 50 mL), 0.1M HCl (3 × 50 mL), water (25 mL), and brine (25 mL). The solvent was dried over $MgSO_4$ and removed in vacuum.

Typical Reaction Procedure for the Synthesis of Alkenes 1k and 1l



Benzyl bromide or allyl bromide (10 mmol) and 2-allylphenol (10 mmol) were dissolved in 15 mL *N*,*N*-dimethylformamide (DMF). K_2CO_3 (1.37g, 10 mmol) in 5 mL DMF was added, stirred at 50 ^oC overnight. After cooling, the reaction was washed with water (150 mL) and the aqueous phase was separated and extracted with diethyl ether (3 × 10 mL). The combined organic phases were washed with NaOH (2 M, 50 mL) and dried over $MgSO_4$. The mixture was filtered and the solvent was removed in vacuum.

Palladium-Catalyzed Regioselective Double Oxygenation of Allylic C-H Bonds

(1) General procedure for the reaction condition screening (Table 1). In 25 mL Schlenk tube, allylbenzene **1a** (0.5 mmol), *n*-butanol **2a** (0.5 mL) , catalyst (0.05 mmol) and H_2O (1.5 equiv, 14 mg)

were combined in 1.5 mL of solvent. The reaction tubes with different Pd^{II}-catalysts or solvents were placed into a dioxygen atmosphere (1 atm) and stirred for 24 h. After the reactions were finished, the reaction mixture was added diphenyl ether (0.5 mL of a known concentration solution in ethyl acetate). The oxidative double oxygenation product was evaluated by GC relative to an internal standard. The results were summarized in Table 1.

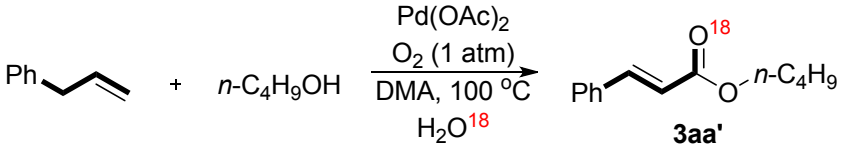
(2) Typical procedure for Pd-catalyzed double allylic oxygenation of various alkenes to form *α,β*-unsaturated esters (Table 2): $Pd(OAc)_2$ (11.0 mg) was added to a 25 mL Schlenk tube equipped with a magnetic stirred bar, and a balloon filled with O_2 (1 atm) was connected to the Schlenk tube through the side arm, and purged three times. An alkene **1** (0.5 mmol), *n*-butanol **2a** (0.5 mL), DMA (1.5 mL) and H_2O (1.5 equiv, 14 mg) were then injected into the tube by syringe. The reaction was then heated to 100 ^oC and stirred for 24 h. Upon completion, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with H_2O and brine, dried over $MgSO_4$, filtered, and concentrated. Purification of the residue on a preparative TLC afforded the desired product.

(3) Typical procedure for Pd-catalyzed double allylic oxygenation of allylbenzene with various alcohols or phenol to form *α,β*-unsaturated esters (Table 3): $Pd(OAc)_2$ (11.0 mg) was added to a 25 mL schlenk tube equipped with a magnetic stirred bar, and a balloon filled with O_2 (1 atm) was connected to the Schlenk tube through the side arm, and purged three times. Allylbenzene **1a** (0.5 mmol), alcohol **2** (3 mmol), DMA (1.5 mL) and H_2O (1.5 equiv., 14mg) were then injected into the tube by syringe. The reaction was then heated to 100 ^oC and stirred for 24 h. Upon completion, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with H_2O and brine, dried over $MgSO_4$, filtered, and concentrated. Purification of the residue on a preparative TLC afforded the desired product.

(4) Typical procedure for Pd-catalyzed intramolecular double allylic oxygenation of 2-allylphenol to form 2*H*-chromen-2-one: In a glass tube, 2-allylphenol **1s** (0.5 mmol) and $Pd(OAc)_2$ (0.05 mmol) were combined in 1.5 mL of solvent. The reaction tubes were placed into a dioxygen atmosphere (1 atm) and stirred for 12 h. After the reactions were completed, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with H_2O and brine, dried over $MgSO_4$, filtered, and concentrated. Purification of the residue on a preparative TLC afforded the desired products (**3s**).

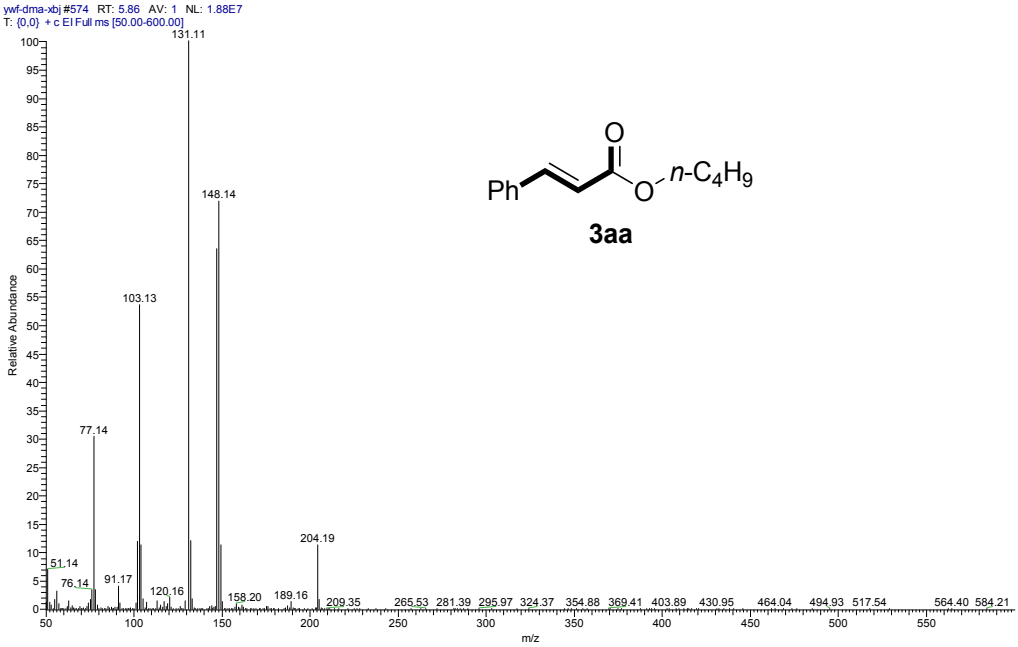
(5) Typical procedure for applications of the novel synthetic sequence to benzofuran-2-carboxylate: $Pd(OAc)_2$ (11.0 mg, 0.015 mmol) was added to a 25 mL Schlenk tube equipped with a magnetic stirred bar, and a balloon filled with O_2 (1 atm) was connected to the Schlenk tube through the side arm, and purged three times. Alkene **1t** (0.5 mmol), alcohol **2** (0.5 mL), DMA (1.5 mL) and H_2O (1.5 equiv, 14 mg) were then injected into the tube by syringe. The reaction was then heated to 100 ^oC and stirred for 24 h. Upon completion, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with H_2O and brine, dried over $MgSO_4$, filtered, and concentrated. Purification of the residue on a preparative TLC afforded the desired product.

Control Studies: Support Experiments for the Proposed Mechanism of the Pd-Catalyzed Double Oxygenation Reaction to *α,β*-Unsaturated Esters

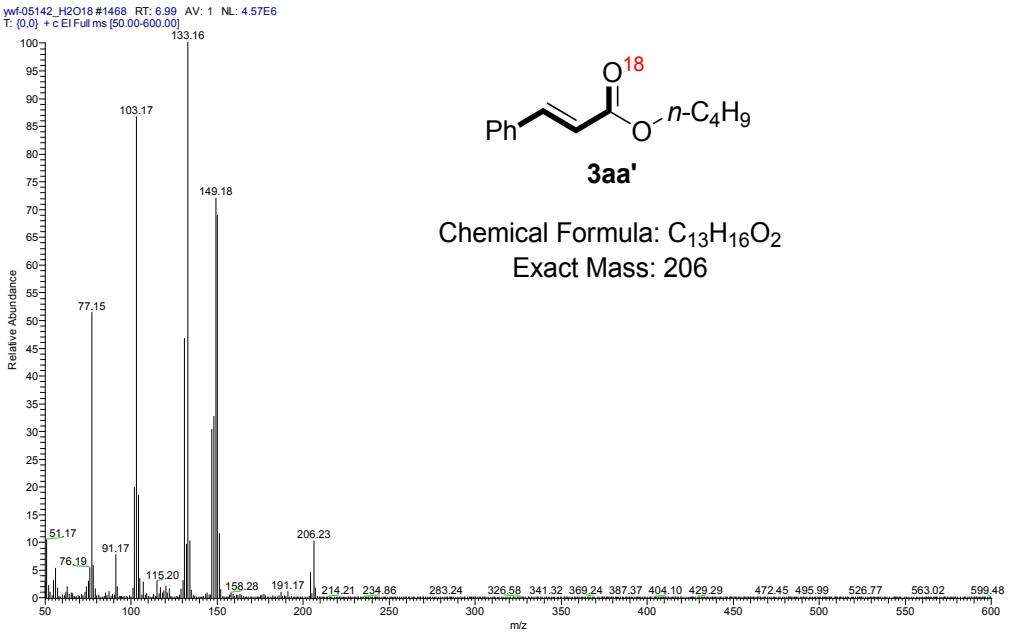


3aa'

(1)

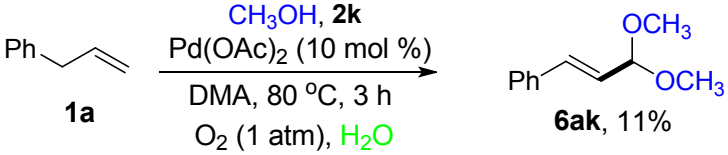


3aa



3aa'

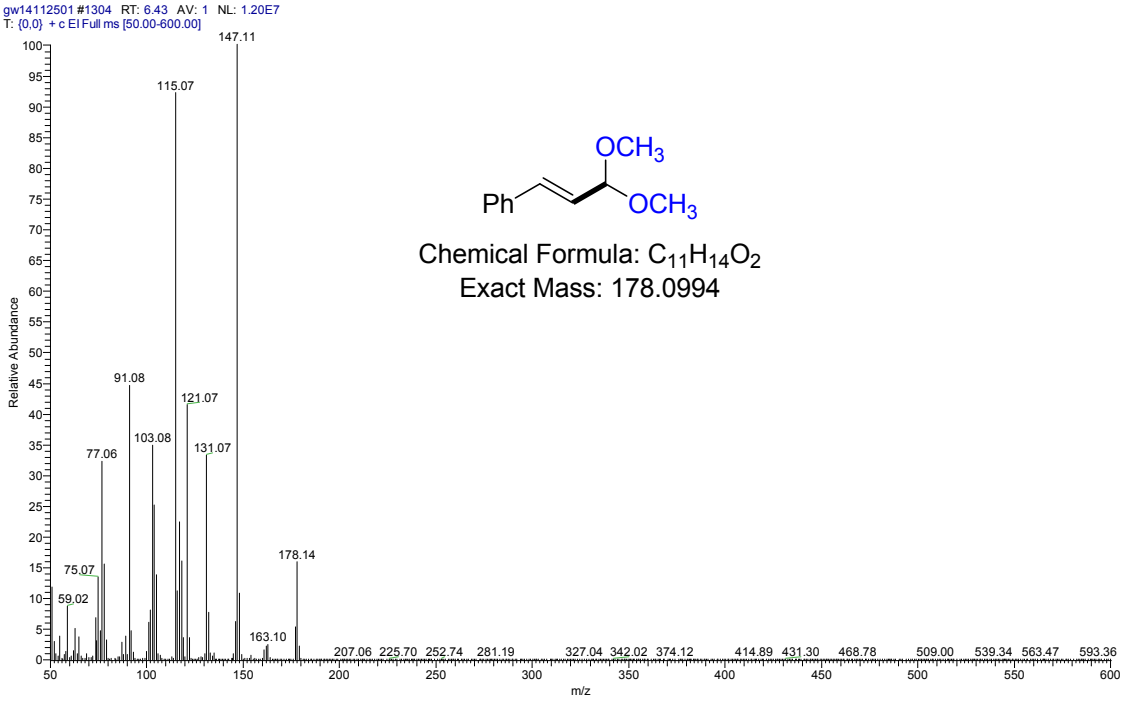
Chemical Formula: $C_{13}H_{16}O_2$
Exact Mass: 206



1a

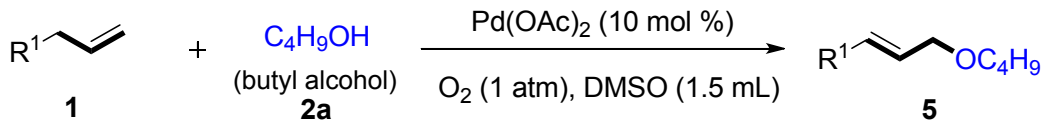
6ak, 11%

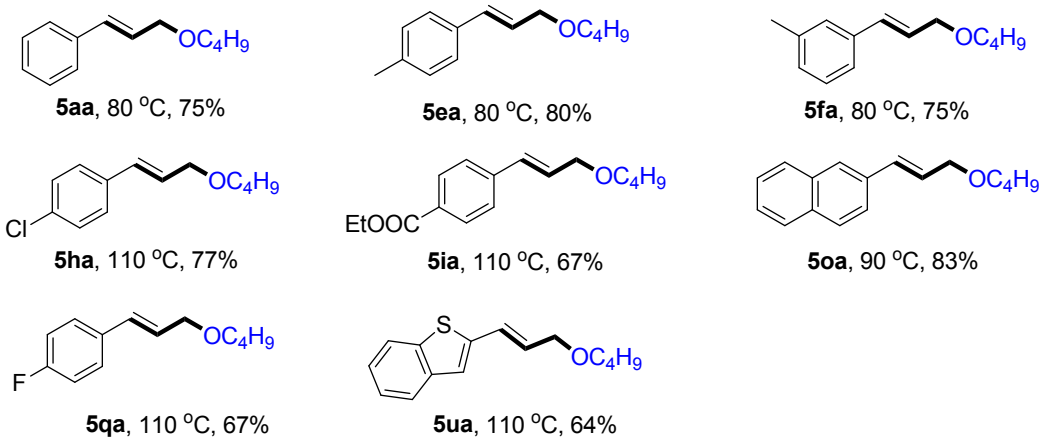
(4)



Oxidation-Controlled Synthesis of *β*-Unsaturated Ethers

Table 4. Oxidation-controlled synthesis of *β*-unsaturated ether in anhydrous DMSO.[a]



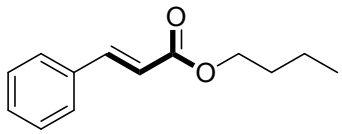


[a] Conditions: 1 (0.5 mmol), 2**a** (0.5 mL), O_2 balloon, DMSO (1.5 mL), 24 h, yield determined by GC using diphenyl ether as the internal standard.

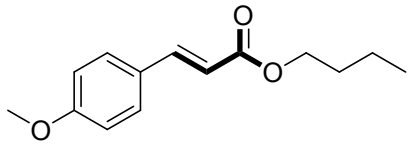
General procedure for the reaction to *β*-unsaturated ethers: $Pd(OAc)_2$ (11.0 mg) was added to a 25 mL Schlenk tube equipped with a magnetic stirred bar, and a balloon filled with O_2 (1 atm) was connected to the Schlenk tube through the side arm, and purged three times. Alkene **1** (0.5 mmol), *n*-butanol **2a** (0.5 mL) and anhydrous DMSO (1.5 mL) were then injected into the tube by syringe. The

reaction was then heated and stirred for 24 h. Upon completion, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with H_2O and brine, dried over $MgSO_4$, filtered, and concentrated. Purification of the residue on a preparative TLC afforded the desired product.

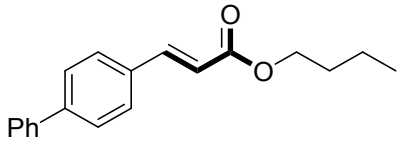
C. Characterization Data for All Prepared Compounds:



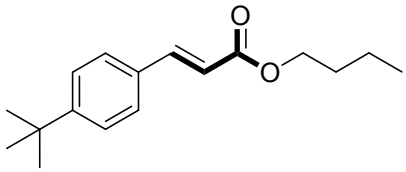
Butyl cinnamate (3aa[1]) Light yellow liquid (0.086 g, 84%)**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 16.0 Hz, 1H), 7.53 (dd, J = 6.1, 2.5 Hz, 2H), 7.42 - 7.35 (m, 3H), 6.44 (d, J = 16.1 Hz, 1H), 4.21 (t, J = 6.5 Hz, 2H), 1.73 - 1.65 (m, 2H), 1.49 - 1.39 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 144.6, 134.5, 130.2, 128.9, 128.1, 118.3, 64.4, 30.8, 19.2, 13.8; IR (KBr, cm^{-1}) ν 2958, 2925, 1716, 1639, 1270, 1172; MS (EI): m/z (%) 204 (M^+), 148, 131.



(*E*)-Butyl 3-(4-methoxyphenyl)acrylate (3ba) Yellow liquid (0.102 g, 87%)**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 16.0 Hz, 1H), 7.48 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 6.31 (d, J = 16.0 Hz, 1H), 4.20 (t, J = 6.7 Hz, 2H), 3.83 (s, 3H), 1.72 - 1.64 (m, 2H), 1.44 (dq, J = 14.6, 7.3 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 161.3, 144.2, 129.7, 127.2, 115.8, 114.3, 64.3, 55.4, 30.8, 19.2, 13.8; IR (KBr, cm^{-1}) ν 2958, 2929, 1710, 1605, 1253, 1168; HRMS (ESI) calcd for $C_{14}H_{18}O_3$ $[M+H]^+$: 235.1329 found: 235.1332.

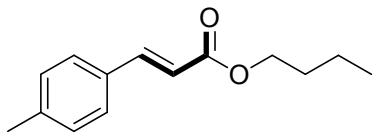


(*E*)-Butyl 3-([1,1'-biphenyl]-4-yl)acrylate (3ca[2]) Yellow liquid (0.123 g, 88%)**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 16.2 Hz, 1H), 7.64 (s, 7H), 7.49 (t, J = 7.5 Hz, 3H), 7.40 (t, J = 7.3 Hz, 1H), δ 6.51 (d, J = 16.5 Hz, 1H), 4.26 (t, J = 6.5 Hz, 2H), 1.78 - 1.70 (m, 2H), 1.48 (dt, J = 14.5, 7.3 Hz, 2H), 1.01 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 144.1, 143.0, 140.2, 133.5, 128.9, 128.6, 127.9, 127.5, 127.1, 118.2, 64.5, 30.8, 19.2, 13.8; IR (KBr, cm^{-1}) ν 2958, 2928, 1711, 1634, 1266, 1171; MS (EI): m/z (%) 280 (M^+), 224, 207.

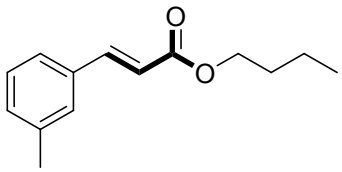


(*E*)-Butyl 3-(4-(*tert*-butyl)phenyl)acrylate (3da[3]) Yellow liquid (0.113 g, 87%)**;** ^{1}H NMR (400 MHz, CDCl3) δ 7.70 (d, J = 15.9 Hz, 1H), 7.50 (d, J = 7.7 Hz, 2H), 7.43 (d, J = 7.7 Hz, 2H), 6.44 (d, J = 15.9 Hz, 1H), 4.23 (t, J = 6.5 Hz, 2H), 1.71 (dd, J = 13.4, 6.6 Hz, 1H), 1.48 (dt, J = 15.1, 7.0 Hz, 2H), 1.35 (s, 2H), 0.99 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 167.3, 153.7, 144.5, 131.7, 127.9,

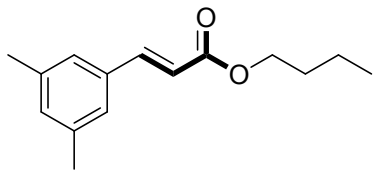
125.9, 117.4, 64.4, 34.9, 31.2, 30.8, 19.2, 13.8; IR (KBr, cm^{-1}) *v* 2961, 2870, 1715, 1636, 1268, 1171; MS (EI): m/z (%) 260 (M^+), 245, 204.



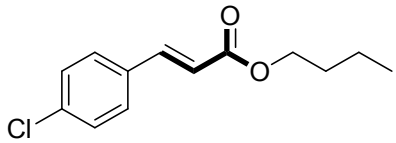
(*E*)-Butyl 3-(*p*-tolyl)acrylate (3ea) Light yellow liquid (0.089 g, 82%)**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 6.42 (d, *J* = 15.8 Hz, 1H), 4.23 (t, *J* = 6.6 Hz, 2H), 2.40 (s, 3H), 1.76 - 1.68 (m, 2H), 1.47 (dq, *J* = 14.6, 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 144.6, 129.6, 129.3, 128.9, 128.1, 117.2, 64.4, 30.8, 21. 5, 19.2, 13.8; IR (KBr, cm^{-1}) *v* 2987, 1744, 1376, 1243, 1409, 916, 738; HRMS (ESI) calcd for $C_{14}H_{18}NaO_2[M+Na]^+$: 241.1199, found: 241.1195.



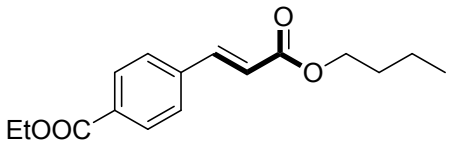
(*E*)-Butyl 3-(*m*-tolyl)acrylate (3fa) Light yellow liquid (0.086 g, 79%)**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 16.0 Hz, 1H), 7.27 (m, 1H), 7.19 (d, *J* = 4.1 Hz, 2H), 7.12 (d, *J* = 6.7 Hz, 1H), 6.36 (d, *J* = 16.2 Hz, 1H), 4.14 (t, *J* = 6.6 Hz, 2H), 2.30 (s, 3H), 1.66 - 1.58 (m, 2H), 1.36 (dt, *J* = 14.5, 7.4 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 144.7, 138.5, 134.5, 131.0, 128.8, 128.7, 125.2, 118.1, 64.4, 30.8, 21.3, 19.2, 13.7; IR (KBr, cm^{-1}) *v* 2986, 1742, 1375, 1243, 1049, 915, 736; HRMS (ESI) calcd for $C_{14}H_{18}NaO_2[M+Na]^+$: 241.1199, found: 241.1199.



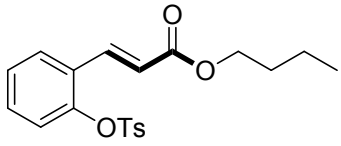
(*E*)-Butyl 3-(3,5-dimethylphenyl)acrylate (3ga) Yellow liquid (0.097 g, 82%)**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 16.0 Hz, 1H), 7.14 (s, 2H), 7.01 (s, 1H), 6.41 (d, *J* = 16.1 Hz, 1H), 4.20 (t, *J* = 6.6 Hz, 2H), 2.32(s, 6H), 1.72 - 1.64 (m, 2H), 1.49 - 1.38 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 144.9, 138.4, 134.4, 132.0, 125.9, 117.9, 64.3, 30.8, 21.2, 19.2, 13.8; IR (KBr, cm^{-1}) *v* 2960, 2927, 1715, 1637, 1254, 1165; HRMS (ESI) calcd for $C_{14}H_{18}$ Na O_2 $[M+Na]^+$: 235.1329 found: 235.1332.



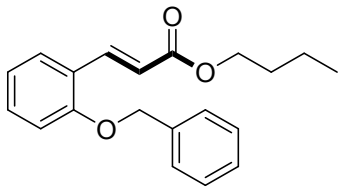
(*E*)-Butyl 3-(4-chlorophenyl)acrylate (3ha) Yellow liquid (0.068 g, 57%); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.62 (d, *J* = 16.0 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.72 - 1.65 (m, 2H), 1.44 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.8, 143.1, 136.1, 133.0, 129.2, 129.2, 118.9, 64.6, 30.7, 19.2, 13.7; IR (KBr, cm^{-1}) *v* 2925, 1714, 1639, 1494, 1312, 1266, 1173; HRMS (ESI) calcd for $C_{13}H_{15}ClNaO_2[M+Na]^+$: 361.0653, found: 361.0652.



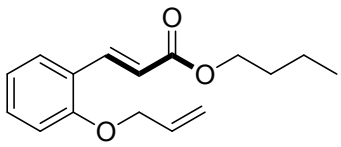
(*E*)-Ethyl 4-(3-butoxy-3-oxoprop-1-en-1-yl)benzoate (**3ia**[4]) Yellow liquid (0.097 g, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.1 Hz, 2H), 7.71 (d, J = 16.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 6.54 (d, J = 16.0 Hz, 1H), 4.41 (dd, J = 14.2, 7.1 Hz, 2H), 4.25 (t, J = 6.6 Hz, 2H), 1.76 - 1.67 (m, 2H), 1.52 - 1.40 (m, 5H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 166.0, 143.2, 138.6, 131.7, 130.1, 127.8, 120.6, 64.7, 61.2, 30.74 (s, 1H), 19.2, 14.3, 13.7; IR (KBr, cm^{-1}) ν 2987, 1746, 1375, 1243, 1172; MS (EI): m/z (%) 276 (M^+), 131, 103.



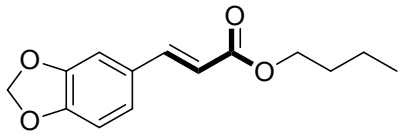
(*E*)-Butyl 3-(2-(tosyloxy)phenyl)acrylate (**3ja**) Yellow liquid (0.097 g, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.7 Hz, 2H), 7.50 (dd, J = 11.8, 3.9 Hz, 2H), 7.43 - 7.33 (m, 3H), 7.27 (d, J = 8.3 Hz, 2H), 6.14 (d, J = 16.1 Hz, 1H), 4.19 (t, J = 6.6 Hz, 2H), 2.42 (s, 3H), 1.75 - 1.66 (m, 2H), 1.51 - 1.41 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 147.8, 145.7, 137.1, 131.9, 131.1, 130.1, 129.9, 128.6, 127.5, 127.4, 124.0, 120.4, 64.5, 30.8, 21.6, 19.2, 13.7; IR (KBr, cm^{-1}) ν 2963, 1740, 1600, 1376, 1244, 1175; HRMS (ESI) calcd for $C_{20}H_{22}NaO_5S$ $[M+Na]^+$: 397.1080, found: 397.1082.



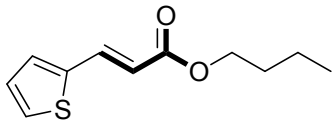
(*E*)-Butyl 3-(2-(benzyloxy)phenyl)acrylate (**3ka**) Yellow liquid (0.097 g, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 16.2 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.45 - 7.35 (m, 4H), 7.30 (dd, J = 15.9, 7.8 Hz, 2H), 6.96 (t, J = 8.5 Hz, 2H), 6.53 (d, J = 16.2 Hz, 1H), 5.15 (s, 2H), 4.19 (t, J = 6.6 Hz, 2H), 1.72 - 1.63 (m, 2H), 1.48 - 1.38 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 157.4, 139.8, 136.7, 131.3, 128.7, 128.6, 128.0, 127.2, 124.0, 121.1, 118.9, 112.8, 70.4, 64.2, 30.8, 19.2, 13.8; IR (KBr, cm^{-1}) ν 2990, 1764, 1378, 1243, 1055, 744; HRMS (ESI) calcd for $C_{20}H_{22}NaO_3[M+Na]^+$: 333.1461, found: 333.1459.



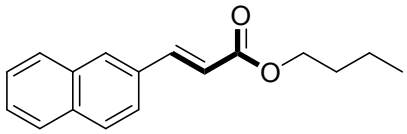
(*E*)-Butyl 3-(2-(allyloxy)phenyl)acrylate (**3la**) Yellow liquid (0.097 g, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 16.2 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.23 - 7.18 (m, 1H), 6.91 - 6.82 (m, 2H), 6.45 (d, J = 16.2 Hz, 1H), 6.05 - 5.93 (m, 1H), 5.40 - 5.33 (m, 1H), 5.24 (d, J = 10.7 Hz, 1H), 4.55 (d, J = 4.4 Hz, 2H), 4.14 (t, J = 6.6 Hz, 2H), 1.62 (dt, J = 13.9, 6.8 Hz, 2H), 1.37 (dq, J = 13.8, 6.9 Hz, 2H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 157.3, 139.9, 132.9, 131.3, 128.7, 120.9, 120.1, 118.8, 117.7, 112.5, 69.2, 64.3, 30.8, 19.2, 13.8; IR (KBr, cm^{-1}) ν 2957, 2926, 1765, 1515, 1243, 746; HRMS (ESI) calcd for $C_{16}H_{20}NaO_3[M+Na]^+$: 283.1305, found: 283.1304.



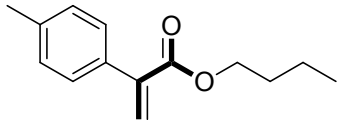
(*E*)-Butyl 3-(benzo[d][1,3]dioxol-5-yl)acrylate (**3ma**) Yellow liquid (0.097 g, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 15.9 Hz, 1H), 7.04 - 6.98 (m, 2H), 6.80 (d, J = 8.0 Hz, 1H), 6.26 (d, J = 15.9 Hz, 1H), 4.19 (t, J = 6.7 Hz, 2H), 1.72 - 1.64 (m, 2H), 1.42 (dt, J = 14.6, 7.4 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 149.5, 148.3, 144.2, 128.9, 124.3, 116.3, 108.5, 106.5, 101.5, 64.3, 30.8, 19.2, 13.7; IR (KBr, cm^{-1}) v 2960, 1708, 1495, 1447, 1251, 1171, 1037, 742; HRMS (ESI) calcd. for $C_{14}H_{16}NaO_4[M+Na]^+$: 271.0941, found: 271.0942.



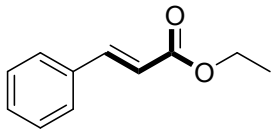
(*E*)-Butyl 3-(thiophen-2-yl)acrylate (**3na**[5]) Yellow liquid (0.097 g, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 15.7 Hz, 1H), 7.36 (d, J = 5.0 Hz, 1H), 7.27 - 7.24 (m, 1H), 7.07 - 7.02 (m, 1H), 6.24 (d, J = 15.7 Hz, 1H), 4.19 (t, J = 6.7 Hz, 2H), 1.72 - 1.64 (m, 2H), 1.43 (dq, J = 14.4, 7.3 Hz, 2H), 0.96 (t, J = 9.4, 5.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 139.6, 137.0, 130.8, 128.3, 128.1, 117.1, 64.4, 30.8, 19.2, 13.7; IR (KBr, cm^{-1}) v 2957, 1710, 1624, 1512, 1462, 1267, 1166; MS (EI): m/z (%) 210 (M^+), 154, 137.



(*E*)-Butyl 3-(naphthalen-2-yl)acrylate (**3oa**[6]) Yellow liquid (0.095 g, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.82 (dd, J = 16.9, 7.6 Hz, 4H), 7.64 (d, J = 8.5 Hz, 1H), 7.48 (dd, J = 8.7, 4.4 Hz, 2H), 6.54 (d, J = 16.0 Hz, 1H), 4.23 (t, J = 6.7 Hz, 2H), 1.74 - 1.66 (m, 2H), 1.50 - 1.40 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 144.6, 134.2, 133.3, 132.0, 129.9, 128.7, 128.6, 127.8, 127.2, 126.7, 123.5, 118.5, 64.5, 30.8, 19.3, 13.8; IR (KBr, cm^{-1}) v 2960, 2932, 1711, 1634, 1262, 1172, 981, 742; MS (EI): m/z (%) 254 (M^+), 207, 198.

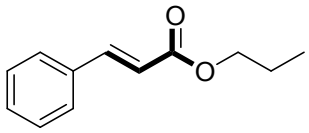


Butyl 2-(*p*-tolyl)acrylate (**3pa**) Yellow liquid (0.051 g, 47%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 5.46 (s, 1H), 5.19 (s, 1H), 4.32 (t, J = 6.5 Hz, 2H), 2.17 (s, 3H), 1.79 - 1.72 (m, 2H), 1.47 (dt, J = 14.5, 7.4 Hz, 2H), 0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 145.6, 142.6, 129.5, 129.4, 125.4, 114.5, 64.8, 30.8, 21.7, 19.3, 13.8; IR (KBr, cm^{-1}) v 2924, 1720, 1512, 1377, 1273, 1107; HRMS (ESI) calcd for $C_{14}H_{19}O_2$ $[M+H]^+$: 235.1380 found: 235.1375.

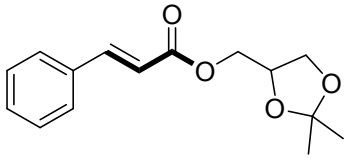


(*E*)-Cinnamic acid ethyl ester (**3ab**[7]) Light yellow liquid (0.080 g, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 16.0 Hz, 1H), 7.55 - 7.49 (m, 2H), 7.39 - 7.35 (m, 3H), 6.44 (d, J = 16.0 Hz, 1H),

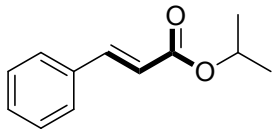
4.26 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 144.6, 134.5, 130.2, 128.9, 128.1, 118.3, 60.5, 14.3; IR (KBr, cm^{-1}) ν 2925, 1714, 1638, 1511, 1458, 1312, 1267, 1172; MS (EI): m/z (%) 176 (M^+), 131, 103.



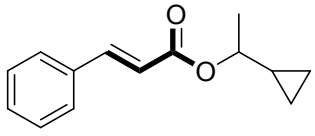
Propyl cinnamate (**3ac**[8]) Yellow liquid (0.090 g, 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 16.0 Hz, 1H), 7.45 (dd, J = 5.8, 2.2 Hz, 2H), 7.32 - 7.29 (m, 3H), 6.37 (d, J = 16.0 Hz, 1H), 4.10 (t, J = 6.7 Hz, 2H), 1.73 - 1.59 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 144. 6, 134.5, 130.2, 128.9, 128.1, 118.3, 66.2, 22.1, 10.5; IR (KBr, cm^{-1}) ν 2924, 1711, 1512, 1465, 1264, 1172; MS (EI): m/z (%) 190 (M^+), 131, 103.



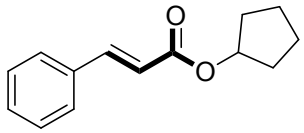
(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl cinnamate (**3ad**) Yellow liquid (0.081 g, 62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 16.0 Hz, 1H), 7.52 (s, 3H), 7.39 (s, 4H), 6.48 (d, J = 16.0 Hz, 1H), 4.40 (dd, J = 11.1, 5.9 Hz, 1H), 4.31 (dd, J = 11.5, 4.6 Hz, 2H), 4.22 (dd, J = 11.5, 6.0 Hz, 1H), 4.12 (dt, J = 17.9, 9.2 Hz, 2H), 3.83 - 3.78 (m, 1H), 1.46 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 145.5, 134.3, 130.4, 128.9, 128.1, 117.5, 109.9, 73.8, 66.4, 64.9, 26.7, 25.4; IR (KBr, cm^{-1}) ν 2986, 1741, 1375, 1244, 1048, 916, 735; HRMS (ESI) calcd for $C_{15}H_{18}NaO_4$ $[M+Na]^+$: 285.1097 found: 285.1101.



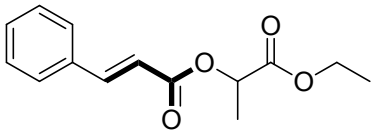
Isopropyl cinnamate (**3ae**[7]) Yellow liquid (0.086 g, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 16.0 Hz, 0H), 7.55 - 7.49 (m, 0H), 7.39 - 7.35 (m, 1H), 6.42 (d, J = 16.0 Hz, 0H), 5.13 (dq, J = 12.3, 6.1 Hz, 0H), 1.31 (d, J = 6.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 144.3, 134.6, 130.1, 128.9, 128.0, 118.8, 67.8, 22.0; IR (KBr, cm^{-1}) ν 2962, 2927, 1712, 1639, 1264, 1173; MS (EI): m/z (%) 190 (M^+), 131, 103.



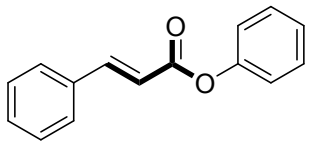
1-Cyclopropylethyl cinnamate (**3af**) Yellow liquid (0.100 g, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 16.0 Hz, 1H), 7.56 - 7.49 (m, 2H), 7.38 (dd, J = 8.9, 5.5 Hz, 3H), 6.45 (d, J = 16.0 Hz, 1H), 4.51 - 4.43 (m, 1H), 1.37 (d, J = 6.3 Hz, 3H), 1.12 - 1.01 (m, 1H), 0.60 - 0.48 (m, 2H), 0.47 - 0.40 (m, 1H), 0.30 (dd, J = 9.4, 4.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 144.4, 134.6, 130.1, 128.9, 128.0, 118.8, 75.4, 19.9, 16.5, 3.7, 2.6; IR (KBr, cm^{-1}) ν 2984, 1743, 1710, 1374, 1243, 1176, 1051; HRMS (ESI) calcd for $C_{14}H_{16}NaO_2$ $[M+Na]^+$: 239.1043 found: 239.1047; MS (EI): m/z (%) 216 (M^+), 131, 103.



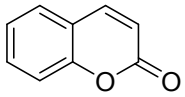
Cyclopentyl cinnamate (**3ag**[9]) Yellow liquid (0.102 g, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 15.9 Hz, 1H), 7.55 - 7.48 (m, 2H), 7.37 (d, J = 2.2 Hz, 3H), 6.41 (d, J = 16.0 Hz, 1H), 5.29 (br, 1H), 1.98 - 1.87 (m, 2H), 1.78 (br, 4H), 1.63 (d, J = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 144.3, 134.6, 130.1, 128.9, 128.0, 118.8, 77.2, 32.8, 23.8; IR (KBr, cm^{-1}) ν 2960, 2926, 1710, 1638, 1316, 1273, 1165; MS (EI): m/z (%) 216 (M^+), 149, 131.



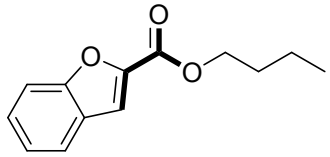
1-Ethoxy-1-oxopropan-2-yl cinnamate (**3ah**[10]) Yellow liquid (0.062 g, 50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 16.0 Hz, 1H), 7.56 (d, J = 2.8 Hz, 2H), 7.42 (s, 3H), 6.53 (d, J = 16.0 Hz, 1H), 5.24 (q, J = 7.0 Hz, 1H), 4.26 (dd, J = 14.1, 7.0 Hz, 2H), 1.59 (d, J = 7.0 Hz, 3H), 1.32 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 166.2, 145.9, 134.3, 130.5, 128.9, 128.2, 117.3, 68.8, 61.4, 17.1, 14.1; IR (KBr, cm^{-1}) ν 2986, 2929, 1741, 1375, 1244, 1048; MS (EI): m/z (%) 248 (M^+), 131, 103.



Phenyl cinnamate (**3ai**[7]) Yellow Oil (0.043 g, 39%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 16.0 Hz, 1H), 7.64 - 7.61 (m, 2H), 7.45 (dd, J = 10.1, 5.3 Hz, 5H), 7.29 (m, 1H), 7.21 (d, J = 8.0 Hz, 2H), 6.67 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 150.8, 146.6, 134.2, 130.7, 129.5, 129.0, 128.3, 125.8, 121.7, 117.4; IR (KBr, cm^{-1}) ν 2923, 1730, 1636, 1310, 1197, 1139; MS (EI): m/z (%) 224 (M^+), 131, 103.

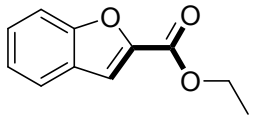


***2H*-Chromen-2-one** (**3s**[11]) Yellow Oil (0.047 g, 65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 9.5 Hz, 1H), 7.56 - 7.47 (m, 2H), 7.34 - 7.26 (m, 2H), 6.42 (d, J = 9.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 154.1, 143.5, 131.8, 127.9, 124.4, 118.9, 116.9, 116.7; IR (KBr, cm^{-1}) ν 1734, 1608, 1517, 1454, 1375, 1244, 1101; MS (EI): m/z (%) 146 (M^+), 118, 90.

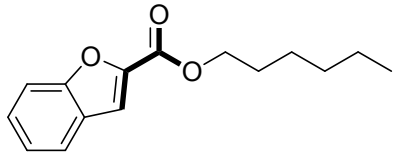


Butyl benzofuran-2-carboxylate (**4ta**) Yellow liquid (0.092 g, 76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.9 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.52 (s, 1H), 7.44 (t, J = 7.8 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 4.39 (t, J = 6.7 Hz, 2H), 1.83 - 1.74 (m, 2H), 1.54 - 1.43 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 155.7, 145.8, 127.5, 127.0, 123.8, 122.8, 113.7, 112.4, 65.3, 30.7,

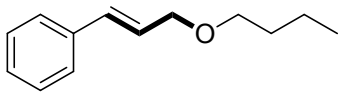
19.2, 13.7; IR (KBr, cm^{-1}) ν 2925, 1728, 1463, 1296, 1178, 749; HRMS (ESI) calcd for $C_{13}H_{15}NaO_3$ $[M+Na]^+$: 219.1016 found: 219.1016; MS (EI): m/z (%) 218 (M^+), 162, 145.



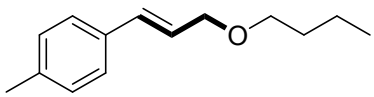
Ethyl benzofuran-2-carboxylate (**4tb**[12]) Yellow liquid (0.077 g, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.8 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.55 (s, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 4.47 (q, J = 6.9 Hz, 2H), 1.45 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 155.7, 145.7, 127.6, 127.0, 123.8, 122.8, 113.8, 112.4, 61.6, 14.4; IR (KBr, cm^{-1}) ν 2923, 1728, 1464, 1296, 1179, 751; MS (EI): m/z (%) 190 (M^+), 162, 145.



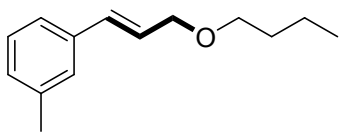
Hexyl benzofuran-2-carboxylate (**4tj**) Yellow liquid (0.092 g, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.9 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.55 (s, 1H), 7.50 - 7.45 (m, 1H), 7.33 (t, J = 7.5 Hz, 1H), 4.41 (t, J = 6.8 Hz, 2H), 1.86 - 1.78 (m, 2H), 1.47 (dd, J = 15.2, 6.4 Hz, 2H), 1.40 - 1.36 (m, 4H), 0.94 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 155.7, 145.8, 127.5, 127.0, 123.8, 122.8, 113.7, 112.4, 65.7, 31.4, 28.7, 25.6, 22.5, 14.0; IR (KBr, cm^{-1}) ν 2925, 1733, 1512, 1295, 1178, 753; HRMS (ESI) calcd for $C_{15}H_{18}NaO_3$ $[M+Na]^+$: 269.1148 found: 269.1154.



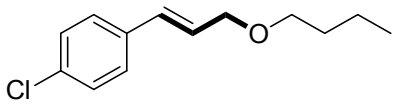
Butyl cinnamyl ether (**5aa**[13]). Light yellow liquid (0.071 g, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.7 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.23 (dd, J = 12.0, 4.2 Hz, 1H), 6.60 (d, J = 15.9 Hz, 1H), 6.30 (dt, J = 15.9, 5.9 Hz, 1H), 4.13 (d, J = 6.0 Hz, 2H), 3.48 (t, J = 6.6 Hz, 2H), 1.65 – 1.56 (m, 2H), 1.40 (dd, J = 14.6, 7.3 Hz, 2H), 0.93 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.1, 128.5, 127.6, 126.5, 71.8, 70.9, 70.3, 31.9, 19.4, 14.0; IR (KBr, cm^{-1}) ν 2926, 1739, 1703, 1514, 1459, 1110; MS (EI): m/z (%) 190 (M^+), 129, 115.



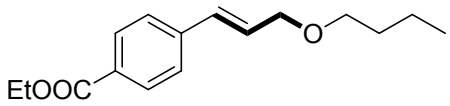
(*E*)-1-(3-butoxyprop-1-en-1-yl)-4-methylbenzene (**5ea**[14]) Light yellow liquid (0.081 g, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 - 7.24 (m, 2H), 7.11 (d, J = 7.6 Hz, 2H), 6.56 (d, J = 15.9 Hz, 1H), 6.31 - 6.19 (m, 1H), 4.11 (d, J = 6.0 Hz, 2H), 3.47 (t, J = 6.6 Hz, 2H), 2.33 (s, 2H), 1.59 (t, J = 10.6 Hz, 2H), 1.40 (dq, J = 14.6, 7.5 Hz, 2H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 134.1, 132.1, 129.2, 126.4, 125.4, 71.5, 70.2, 31.9, 21.2, 19.4, 13.9; IR (KBr, cm^{-1}) ν 2925, 1740, 1647, 1514, 1460, 1268, 1106; MS (EI): m/z (%) 204 (M^+), 143, 129.



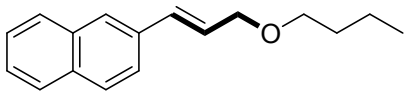
(*E*)-1-(3-Butoxyprop-1-en-1-yl)-3-methylbenzene (**5fa**) Yellow liquid (0.076 g, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 5.3 Hz, 1H), 7.05 (d, *J* = 4.0 Hz,3H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.28 (dt, *J* = 15.8, 6.0 Hz, 1H), 4.12 (d, *J* = 6.0 Hz, 1H), 3.48 (t, *J* = 6.6 Hz, 2H), 2.34 (s, 3H), 1.64 - 1.56 (m, 2H), 1.40 (dq, *J* = 14.3, 7.3 Hz, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 136.8, 132.2, 128.4, 127.2, 126.3, 123.6, 71.4, 70.2, 31.9, 21.4, 19.4, 13.9; IR (KBr, cm^{-1}) *v* 2925, 1740, 1702, 1514, 1461, 1370, 1106; HRMS (ESI) calcd for $C_{14}H_{20}NaO$ $[M+Na]^+$: 227.1406 found: 227.1407.



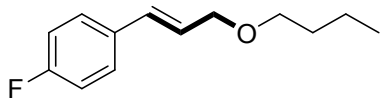
(*E*)-1-(3-Butoxyprop-1-en-1-yl)-4-Chlorobenzene (**5ha**) Yellow liquid (0.086 g, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.29 (dd, *J* = 15.0, 8.4 Hz, 4H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.27 (dt, *J* = 15.9, 5.9 Hz, 1H), 4.11 (d, *J* = 5.8 Hz, 2H), 3.48 (t, *J* = 6.6 Hz, 2H), 1.64 - 1.56 (m, 2H), 1.45 - 1.35 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 135.4, 133.2, 130.7, 128.7, 127.7, 127.2, 71.2, 70.4, 31.9, 19.4, 13.9; IR (KBr, cm^{-1}) *v* 2925, 1740, 1704, 1514, 1463, 1375, 1095; HRMS (ESI) calcd for $C_{13}H_{17}$ NaClO $[M+Na]^+$: 247.0866 found: 247.0867.



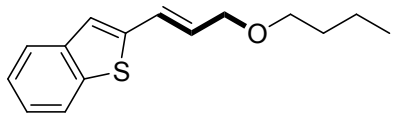
(*E*)-Ethyl 4-(3-butoxyprop-1-en-1-yl)benzoate (**5ia**) Yellow liquid (0.088 g, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.98 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.41 (dt, *J* = 16.1, 5.8 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.15 (d, *J* = 5.7 Hz, 2H), 3.50 (t, *J* = 6.6 Hz, 2H), 1.66 - 1.60 (m, 2H), 1.44 - 1.37 (m, 5H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.4, 141.3, 130.8, 129.9, 129.3, 126.3, 71.1, 70.5, 60.9, 31.9, 19.4, 14.3, 13.9; IR (KBr, cm^{-1}) *v* 2925, 1722, 1569, 1458, 1273, 1105; HRMS (ESI) calcd for $C_{16}H_{22}NaO_3$ $[M+Na]^+$: 285.1461 found: 285.1457.



(*E*)-2-(3-Butoxyprop-1-en-1-yl)naphthalene (**5oa**) Yellow liquid (0.100 g, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.78 (t, *J* = 6.9 Hz, 3H), 7.73 (s, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.48 - 7.40 (m, 2H), 6.76 (d, *J* = 15.9 Hz, 1H), 6.43 (dt, *J* = 12.2, 5.9 Hz, 1H), 4.18 (d, *J* = 5.9 Hz, 2H), 3.51 (t, *J* = 6.6 Hz, 2H), 1.62 (dt, *J* = 14.0, 6.9 Hz, 2H), 1.41 (dt, *J* = 14.5, 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 134.3, 133.6, 133.0, 132.1, 128.2, 128.0, 127.7, 126.9, 126.4, 126.2, 125.9, 123.7, 71.5, 70.4, 31.9, 19.4, 14.0; IR (KBr, cm^{-1}) *v* 2926, 1695, 1513, 1370, 1271, 1117; HRMS (ESI) calcd for $C_{17}H_{20}NaO$ $[M+Na]^+$: 263. 1406 found: 263.1404.



(*E*)-1-(3-Butoxyprop-1-en-1-yl)-4-fluorobenzene (**5qa**) Yellow liquid (0.070 g, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.34 (dd, *J* = 8.0, 5.7 Hz, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.21 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.11 (d, *J* = 5.9 Hz, 2H), 3.48 (t, *J* = 6.6 Hz, 2H), 1.59 (dd, *J* = 14.5, 6.9 Hz, 2H), 1.45 - 1.35 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 162.3 (d, *J* = 246.7 Hz), 133.0 (d, *J* = 3.3 Hz), 130.9, 128.0 (d, *J* = 8.0 Hz), 126.3, 115.4 (d, *J* = 21.6 Hz), 71.3, 70.3, 31.9, 19.4, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) *δ* -114.54 - -114.65 (m, 1F); IR (KBr, cm^{-1}) *v* 2923, 1742, 1697, 1560, 1460, 1106; HRMS (ESI) calcd for $C_{13}H_{17}FNaO$ $[M+Na]^+$: 231.1156 found: 231.1154.



(*E*)-2-(3-Butoxyprop-1-en-1-yl)benzo[b]thiophene (**5ua**) Yellow liquid (0.079 g, 64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.8 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.44 - 7.32 (m, 3H), 6.88 (d, J = 15.9 Hz, 1H), 6.37 (dt, J = 15.9, 5.9 Hz, 1H), 4.18 (d, J = 5.9 Hz, 2H), 3.52 (t, J = 6.6 Hz, 2H), 1.67 - 1.58 (m, 2H), 1.42 (dq, J = 14.4, 7.3 Hz, 2H), 0.95 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 137.7, 133.6, 128.2, 124.4, 124.2, 122.9, 122.2, 122.0, 71.5, 70.4, 31.9, 19.4, 14.0; IR (KBr, cm^{-1}) v 2925, 1700, 1647, 1516, 1460, 1267, 1109; HRMS (ESI) calcd for $C_{15}H_{18}NaOS$ $[M+Na]^+$: 269.0971 found: 269.0968.

D. References

[1] T. Mino, Y. Shirae, Y. Sasai, M. Sakamoto and T. Fujita, *J. Org. Chem.*, 2006, **71**, 6834.

[2] X. Zhang, A. Liu and W. Chen, *Org. Lett*., 2008, **10**, 3849.

[3] X. Zhou, J. Luo, J. Liu, S. Peng and G.-J. Deng, *Org. Lett.*, 2011, **13**, 1432.

[4] M. Oberholzer, R. Gerber and C. M. Frecha, *Adv. Synth. Catal.*, 2012, **354**, 627.

[5] S.-H. Huang, J.-R. Chen and F.-Y. Tsai, *Molecules*, 2010, **15**, 315.

[6] B. Karimi and D. Enders, *Org. Lett.*, 2006, **8**, 1237.

[7] S. De Sarkar, S. Grimme and A. Studer, *J. Am. Chem. Soc.*, 2010. **132**, 1190.

[8] S. Morrissey, I. Beadham and N. Gathergood, *Green Chem.*, 2009, **11**, 466.

[9] Z.-H. Shi, N.-G. Li, Q.-P. Shi, H. Tang and Y.-P. Tang, *Drug Develop. Res*., 2012, **73**, 317.

[10] N. N. Rao and H. J. Roth, *Arch. Pharm. Chem. Life Sci.*, 2006, **322**, 523.

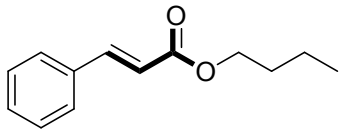
[11] J. Ferguson, F. Zeng and H. Alper, *Org. Lett.*, 2012, **14**, 5602.

[12] S. Ushijima, K. Moriyama and H. Togo, *Tetrahedron*, 2012, **68**, 4701.

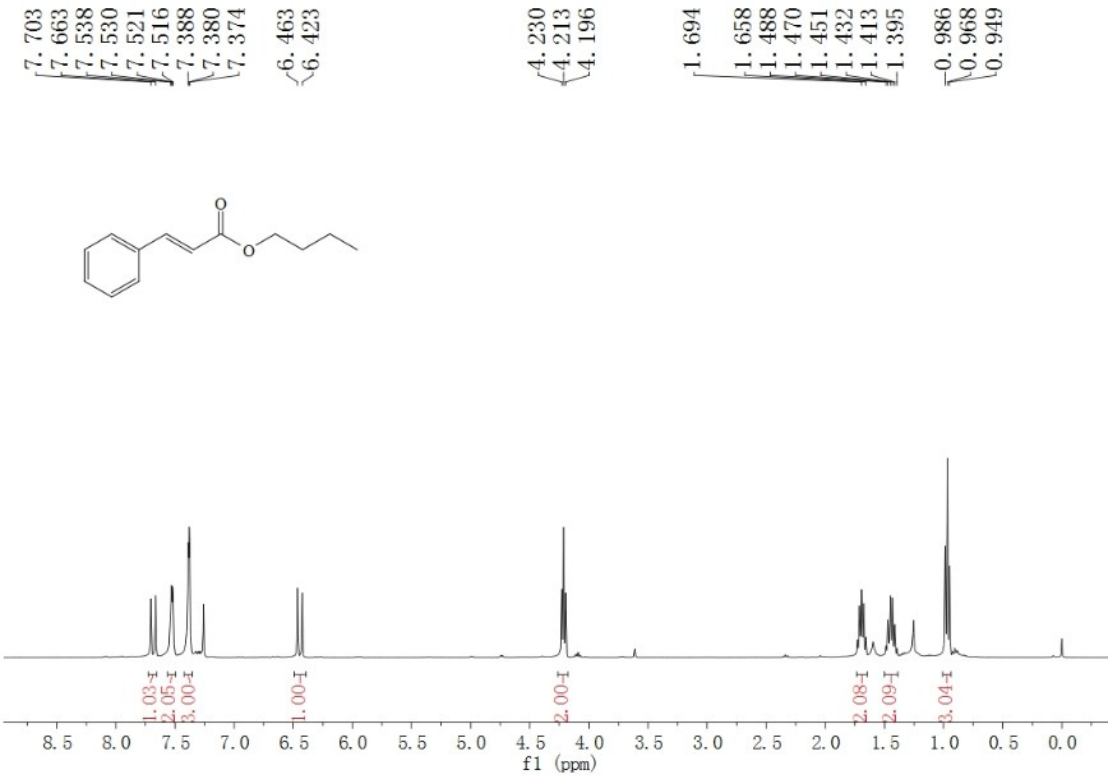
[13] Y. Kasashima, A. Uzawa, K. Hashimoto, T. Nishida, K. Murakami, T. M. Sakamoto and T. Fujita, *J. Oleo Sci.*, 2010, **59**, 549.

[14] N. Nishina and Y. Yamamoto, *Tetrahedron*, 2009, **65**, 1799.

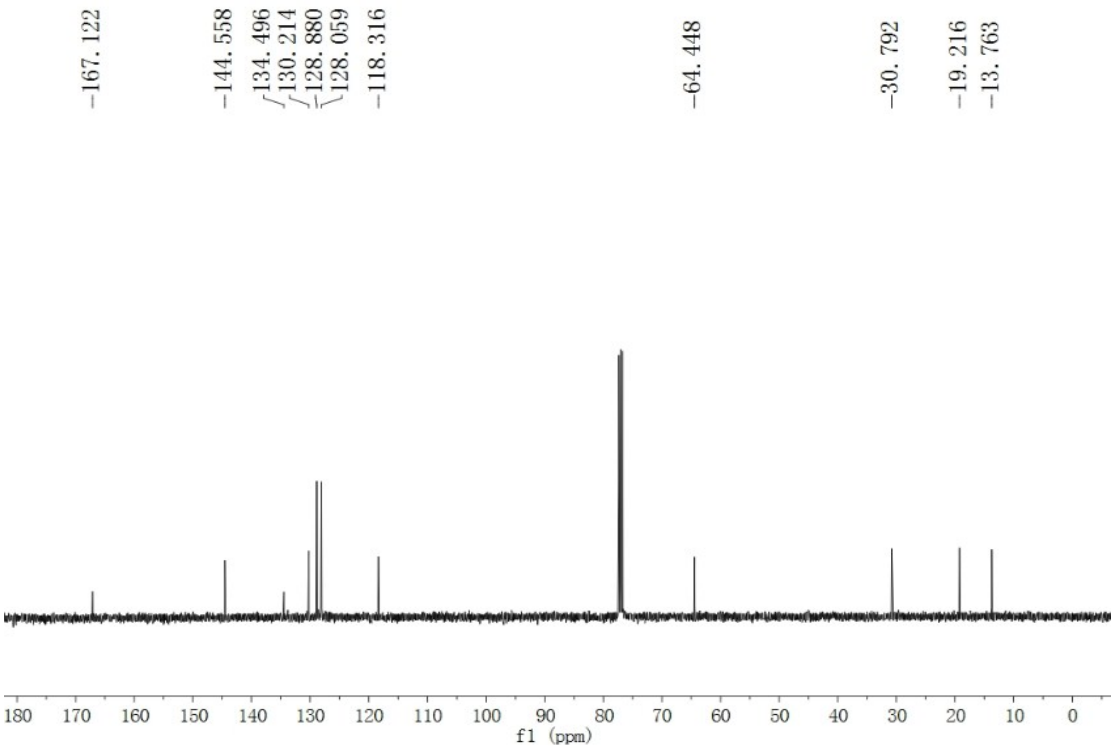
E. NMR Spectra

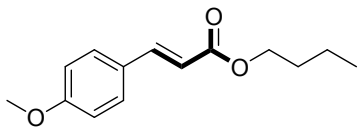


^{1}H NMR Spectrum of **3aa**

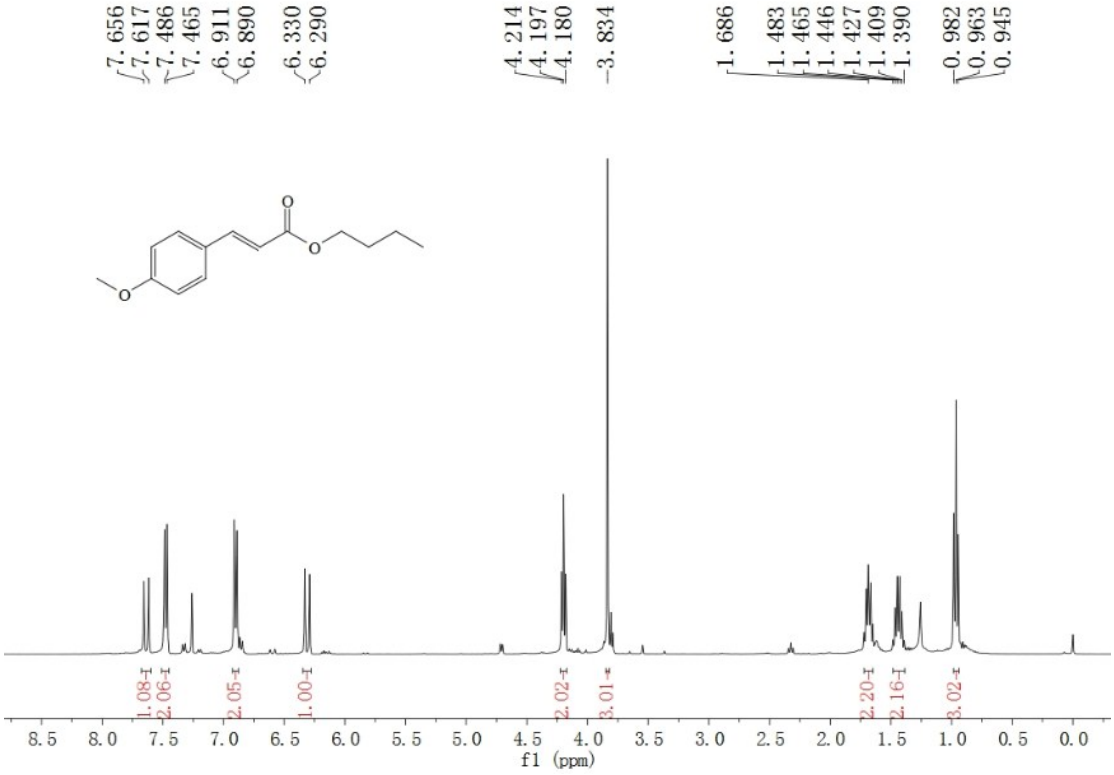


^{13}C NMR Spectrum of **3aa**

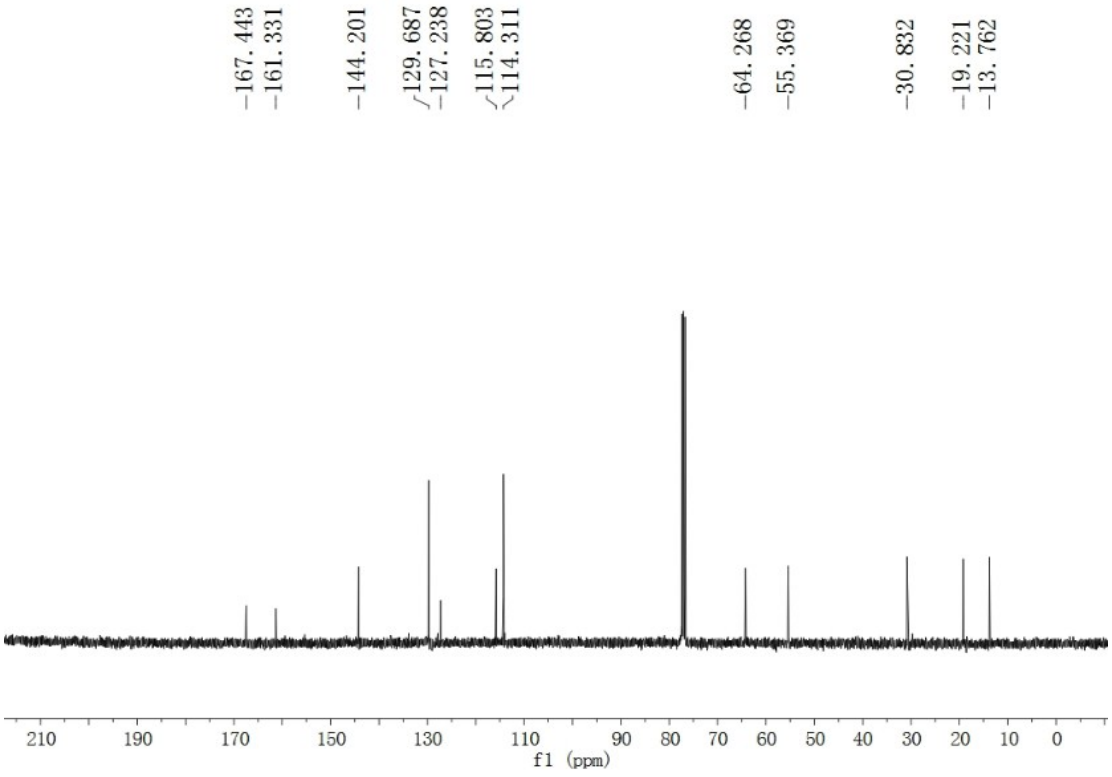


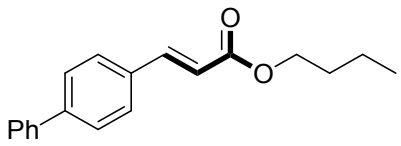


^{1}H NMR Spectrum of **3ba**

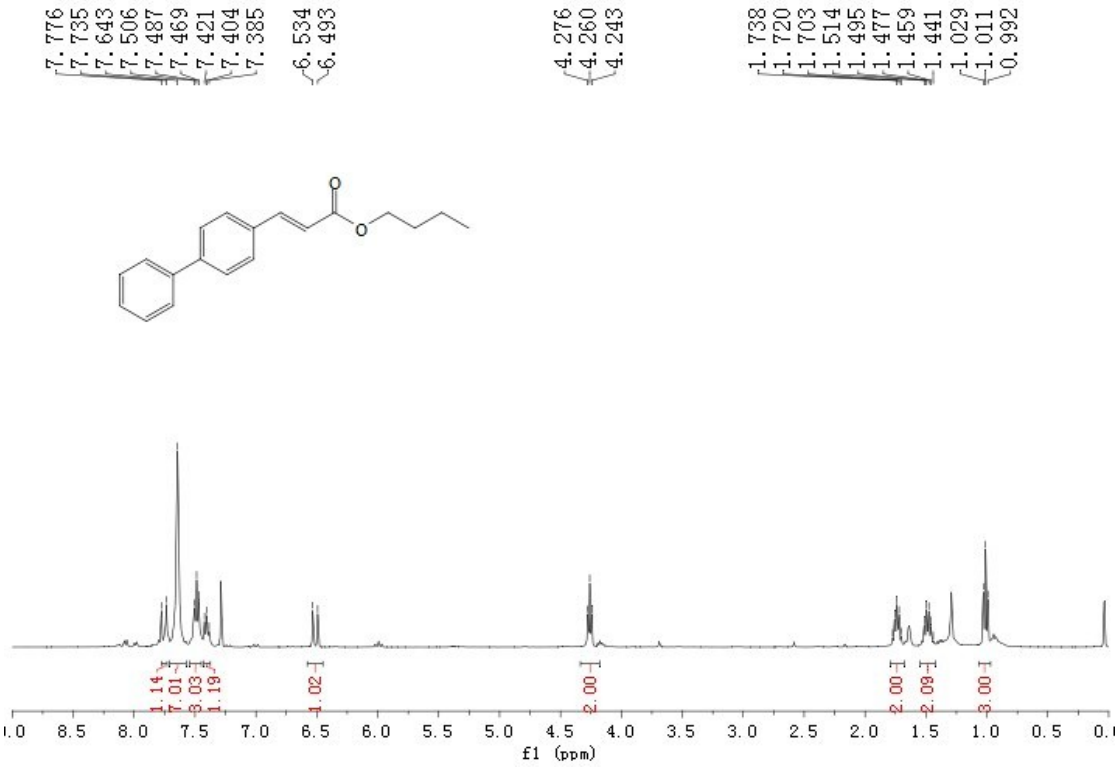


^{13}C NMR Spectrum of **3ba**

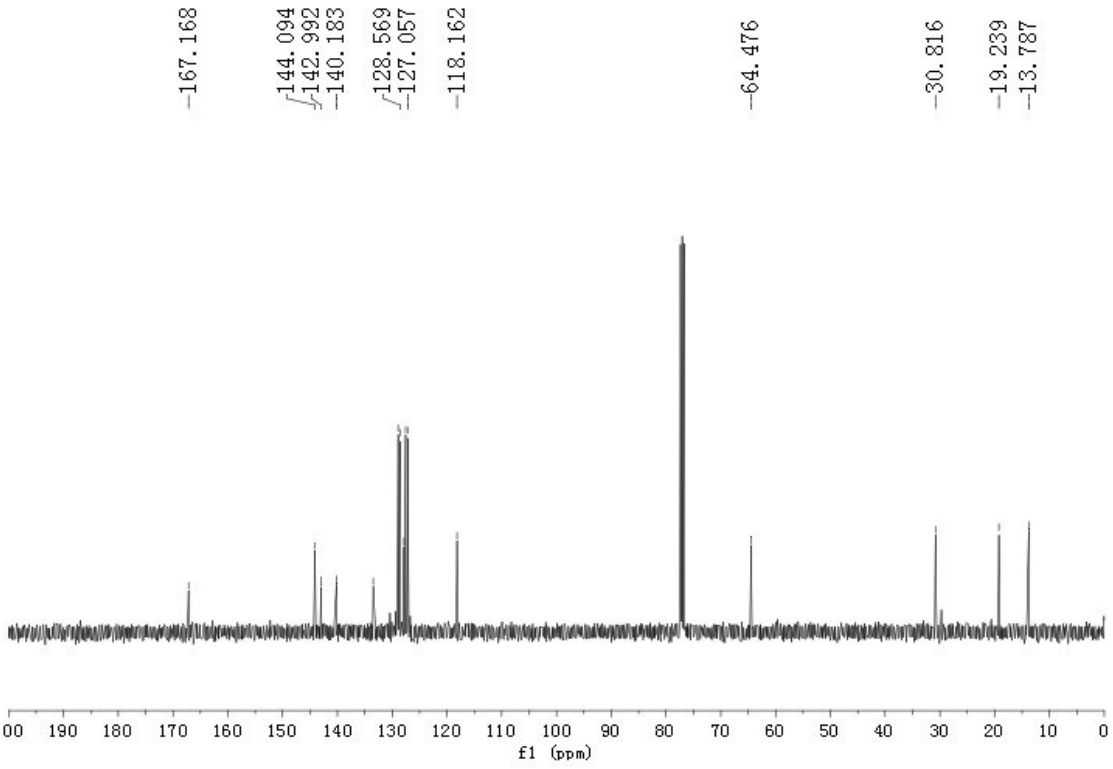


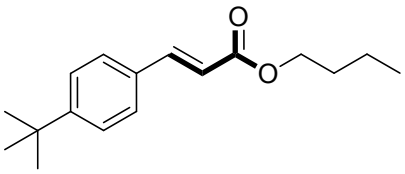


^{1}H NMR pectrum of **3ca**

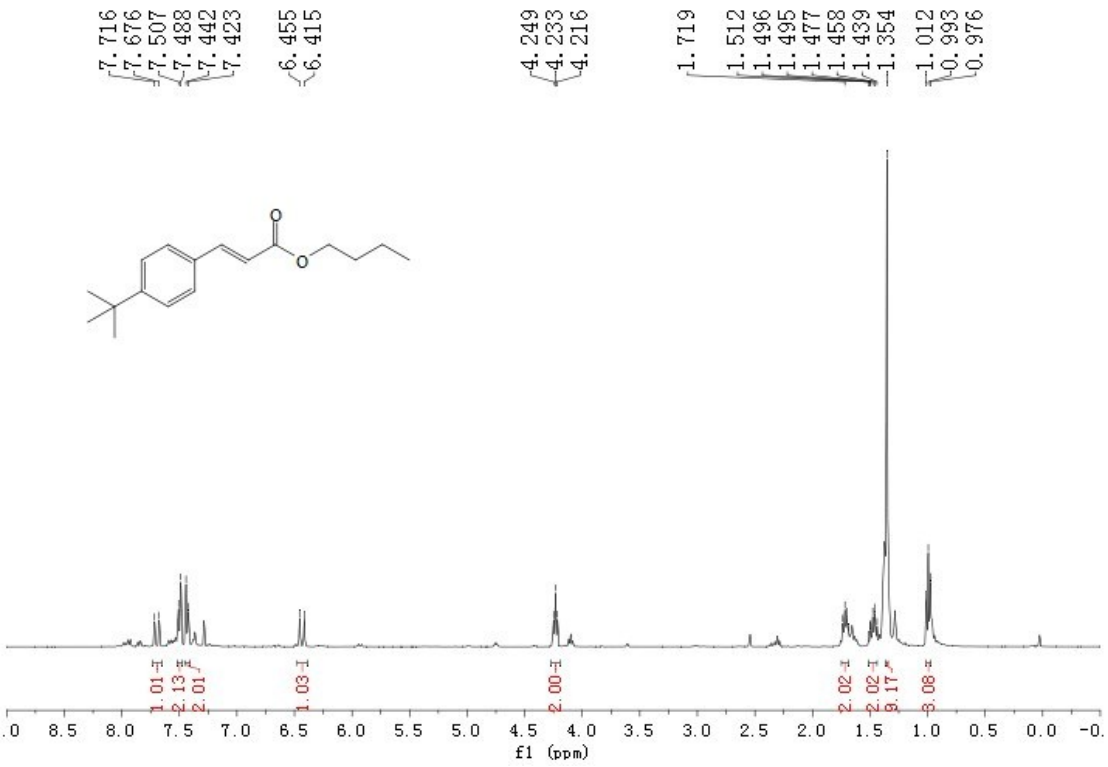


^{13}C NMR Spectrum of **3ca**

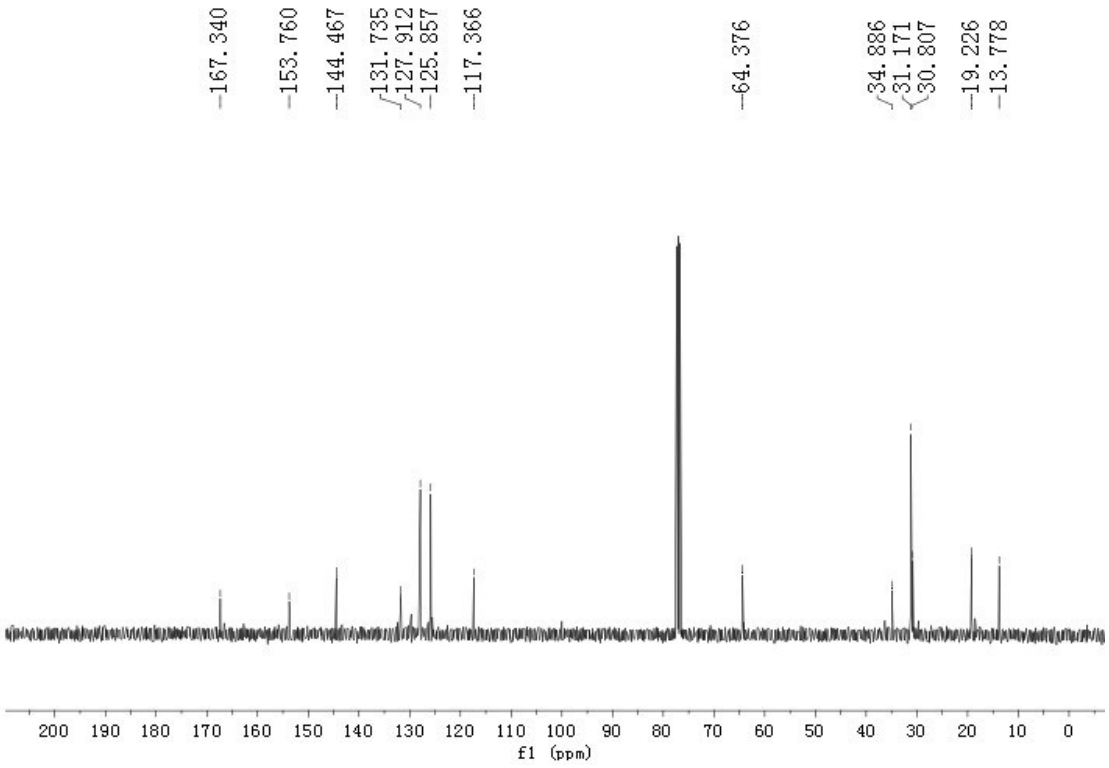


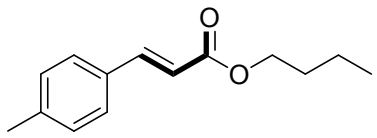


^{1}H NMR Spectrum of **3da**

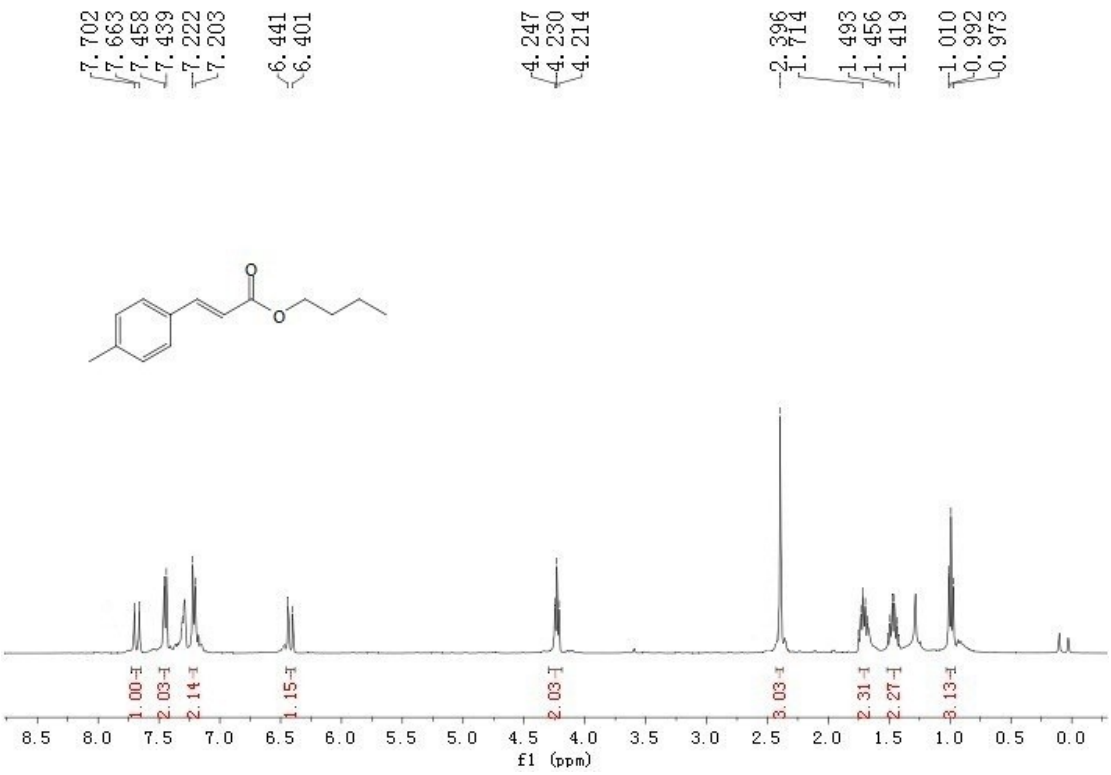


^{13}C NMR Spectrum of **3da**

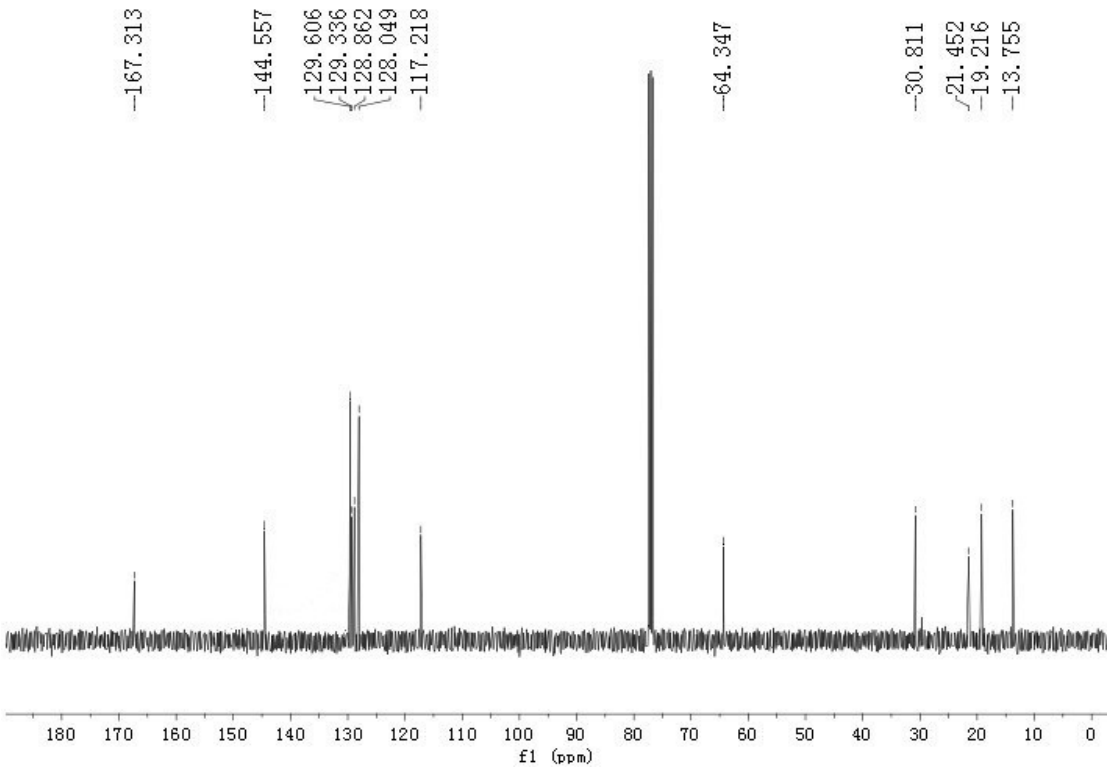


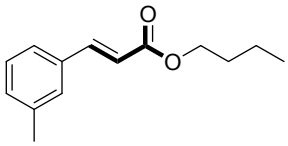


^{1}H NMR Spectrum of **3ea**

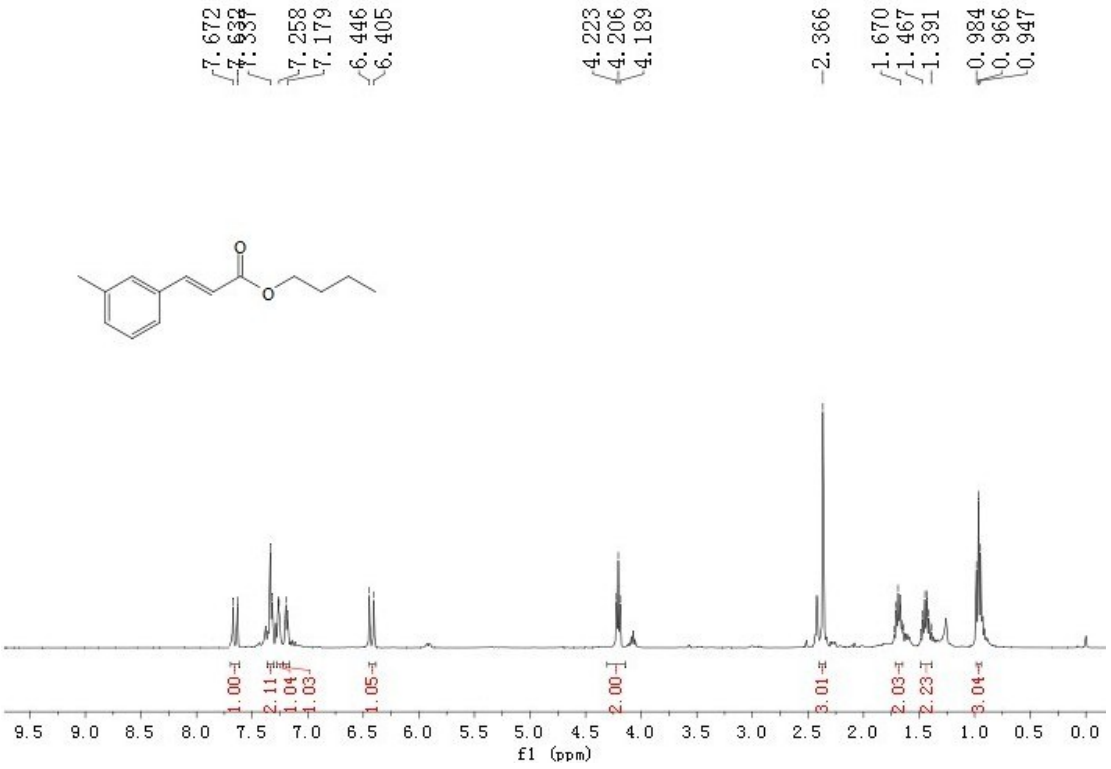


^{13}C NMR Spectrum of **3ea**

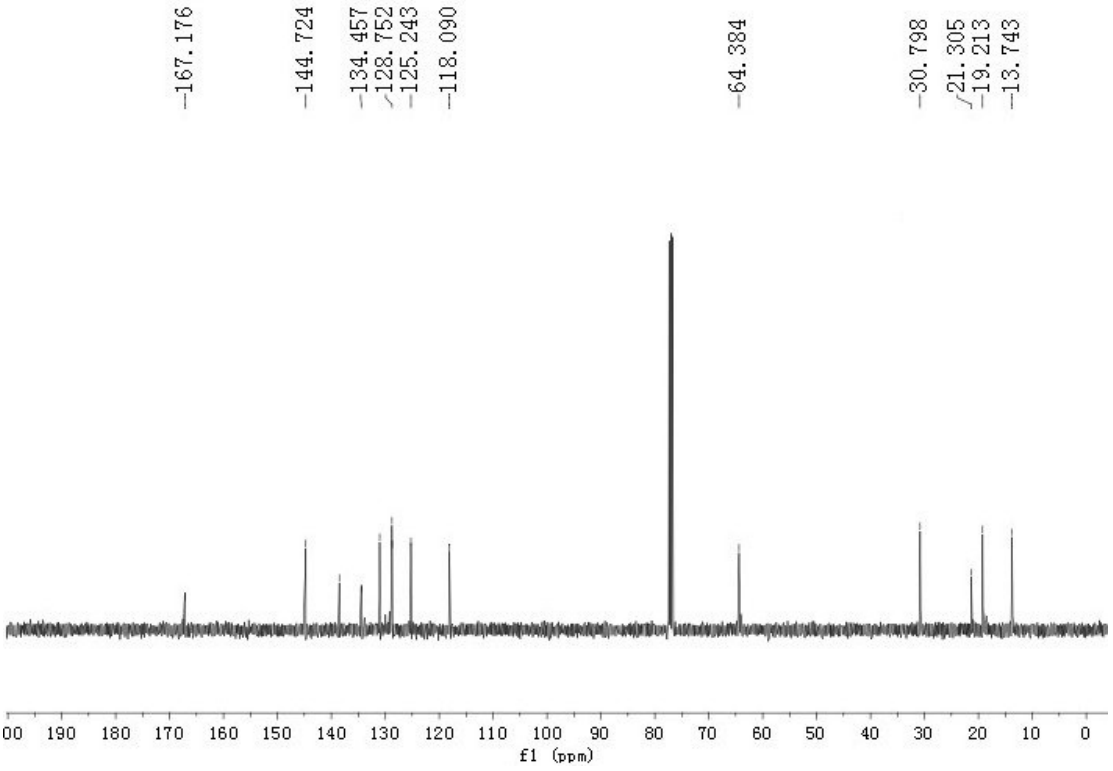


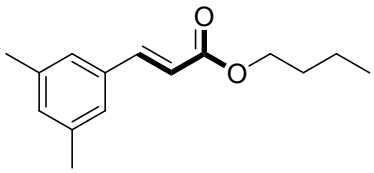


^{1}H NMR Spectrum of **3fa**

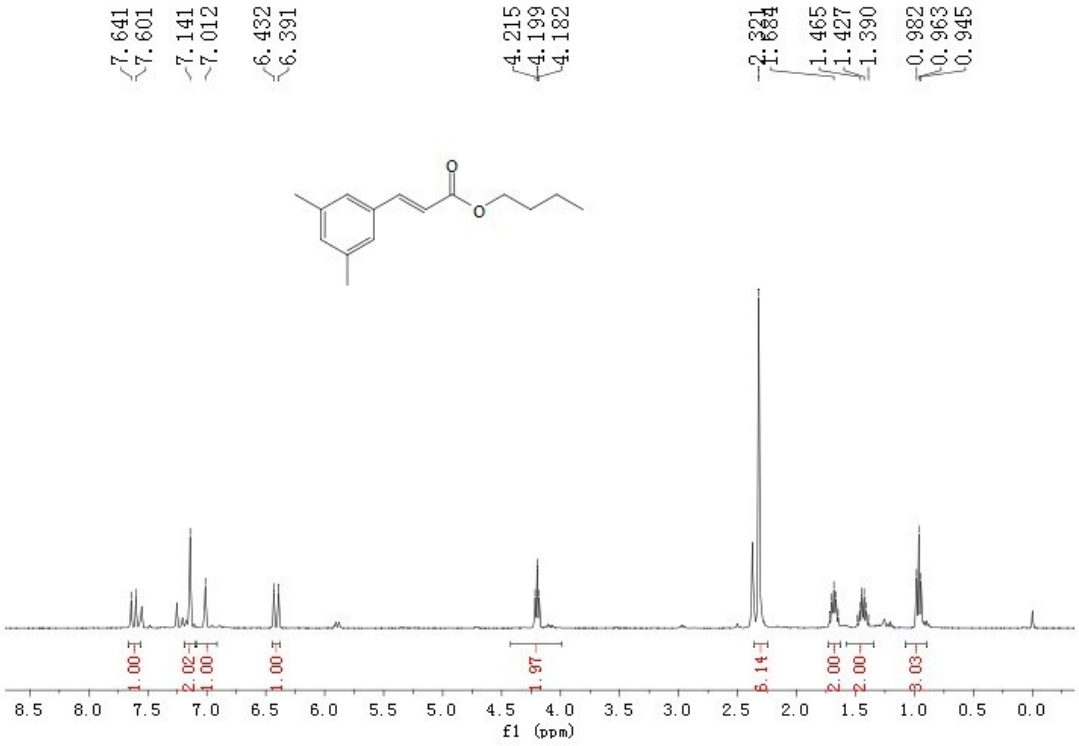


^{13}C NMR Spectrum of **3fa**

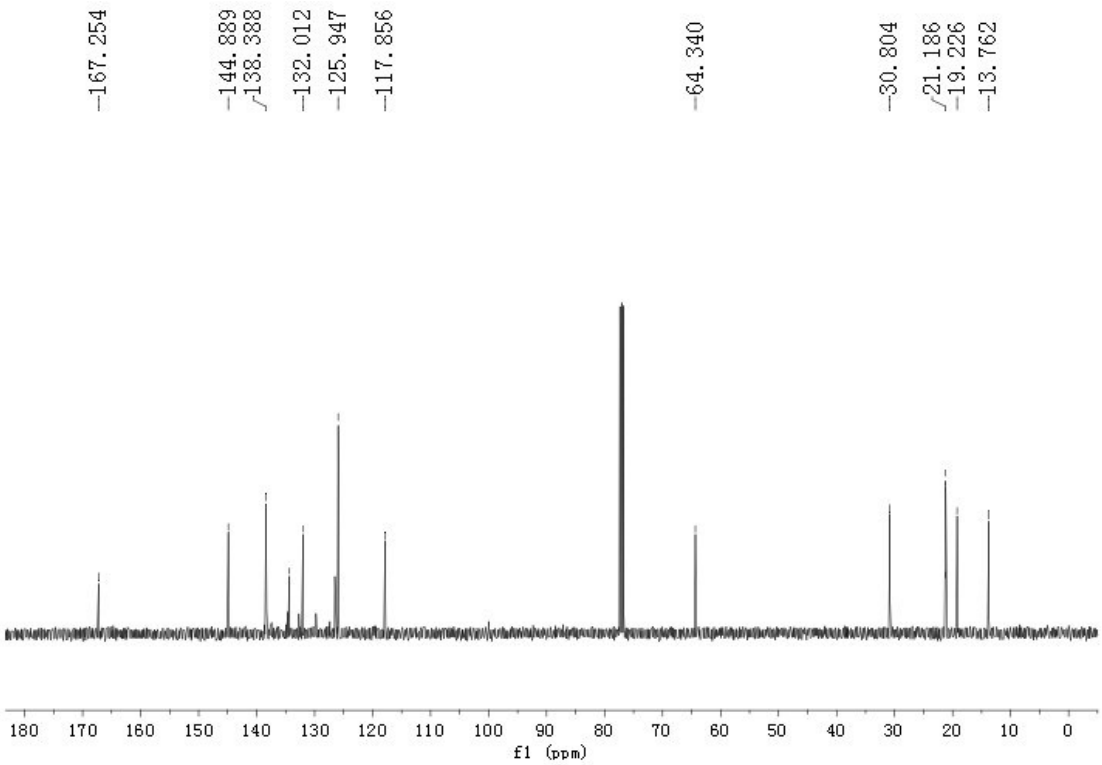


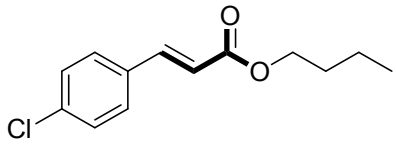


^{1}H NMR Spectrum of **3ga**

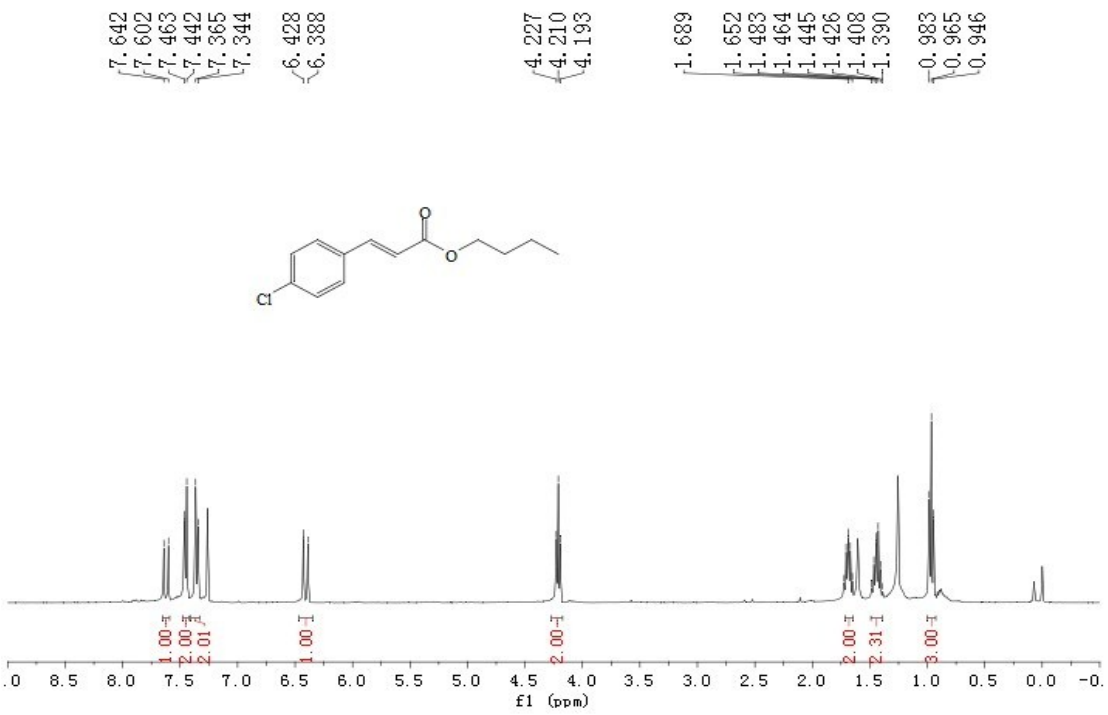


^{13}C NMR Spectrum of **3ga**

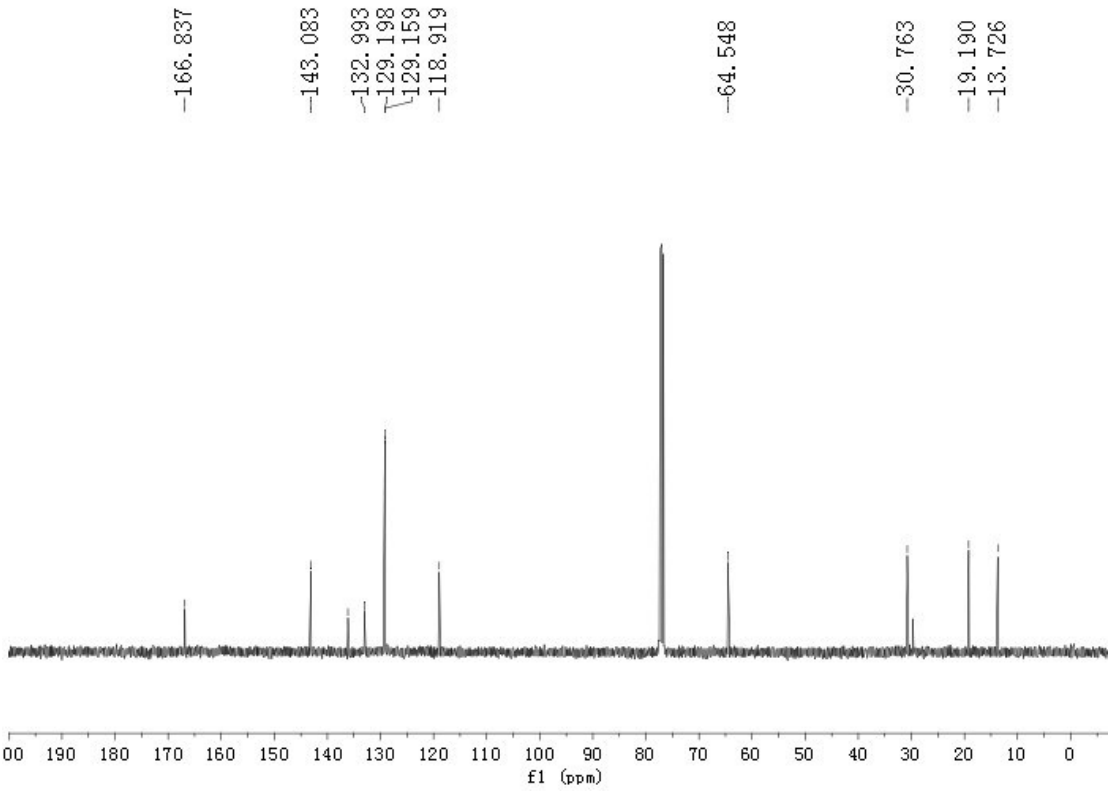


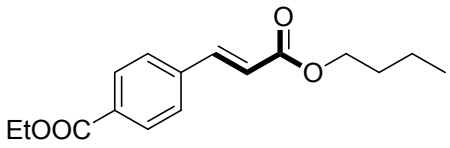


^{1}H NMR Spectrum of **3ha**

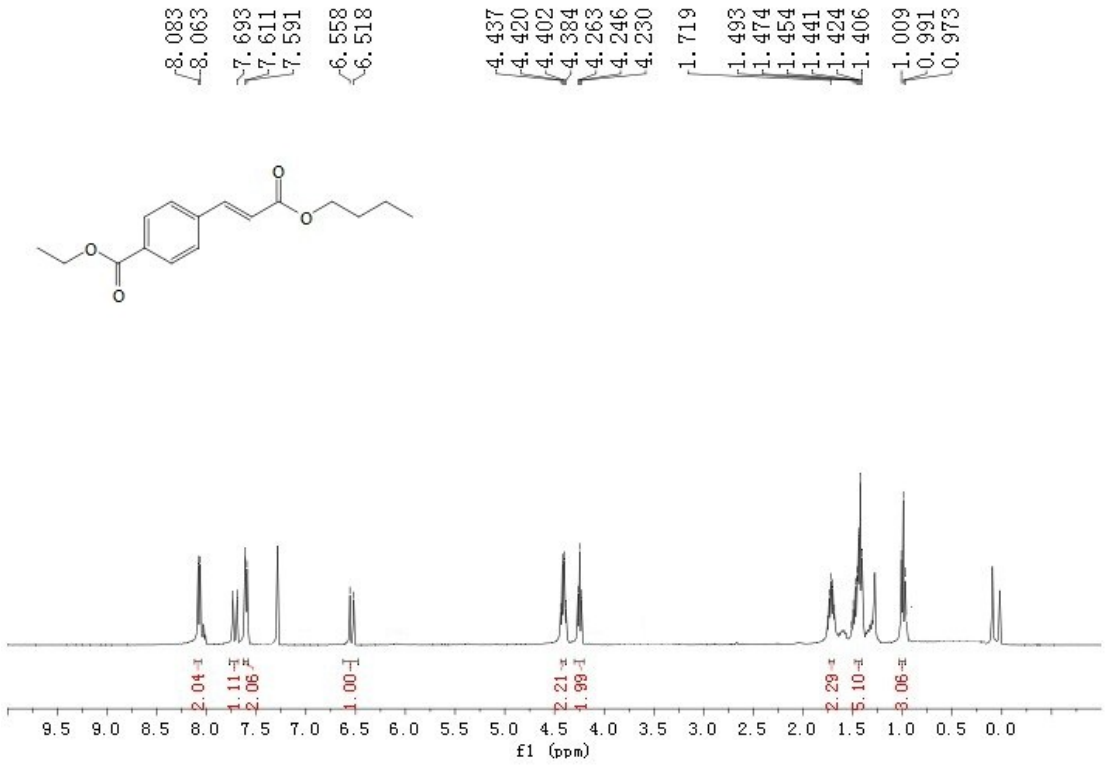


^{13}C NMR Spectrum of 3**ha**

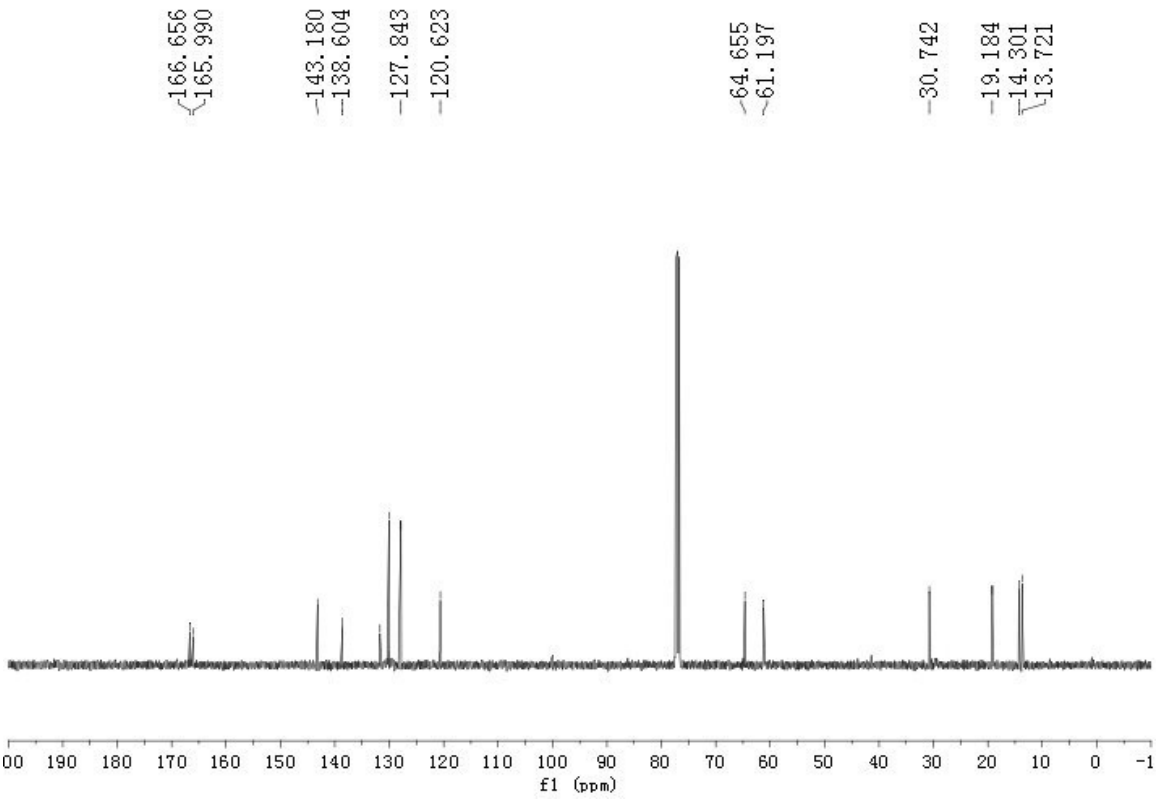


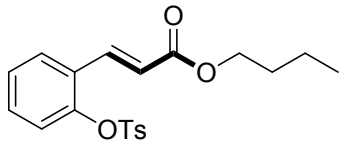


^{1}H NMR Spectrum of **3ia**

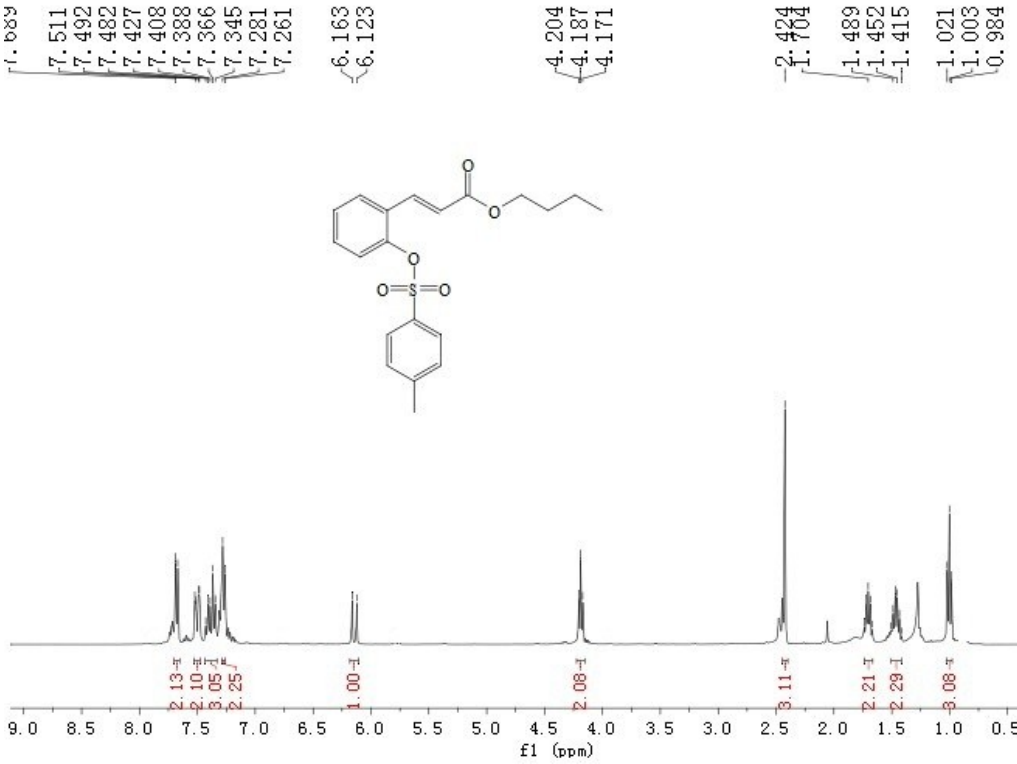


^{13}C NMR Spectrum of **3ia**

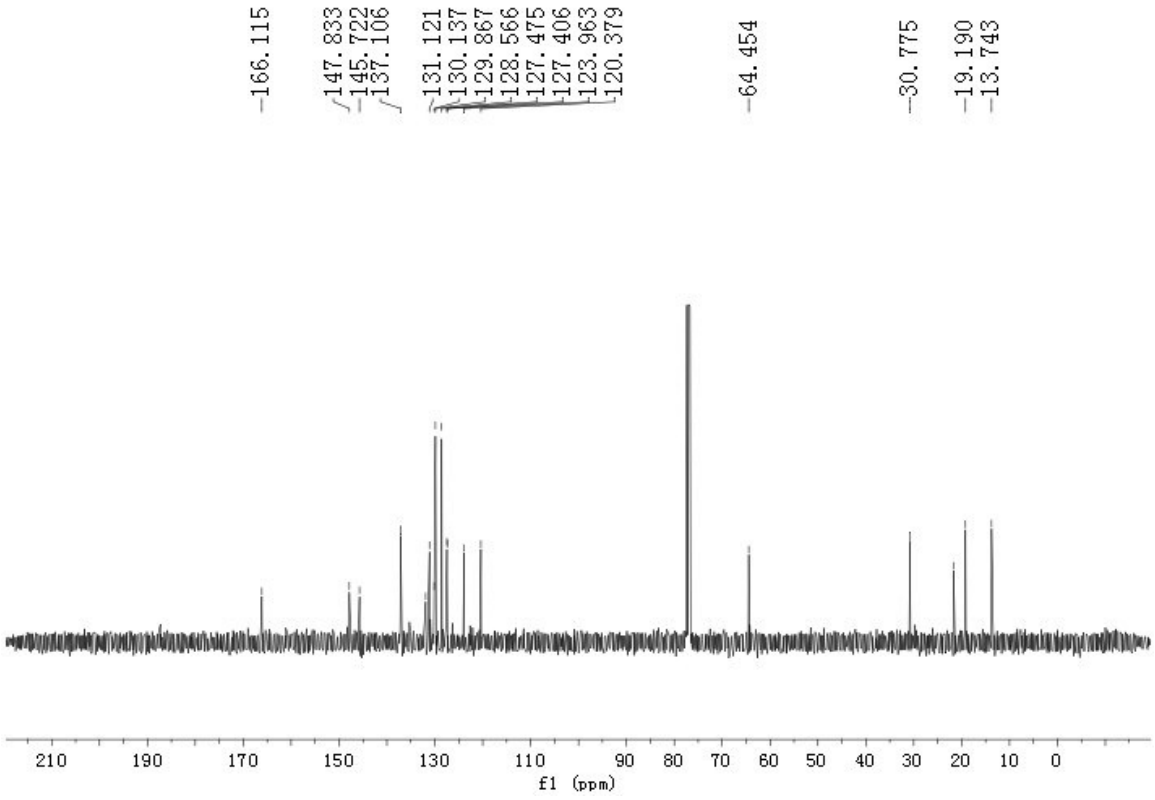


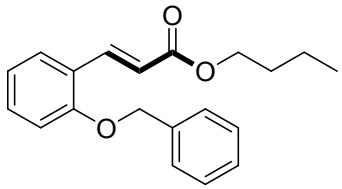


^{1}H NMR Spectrum of **3ja**

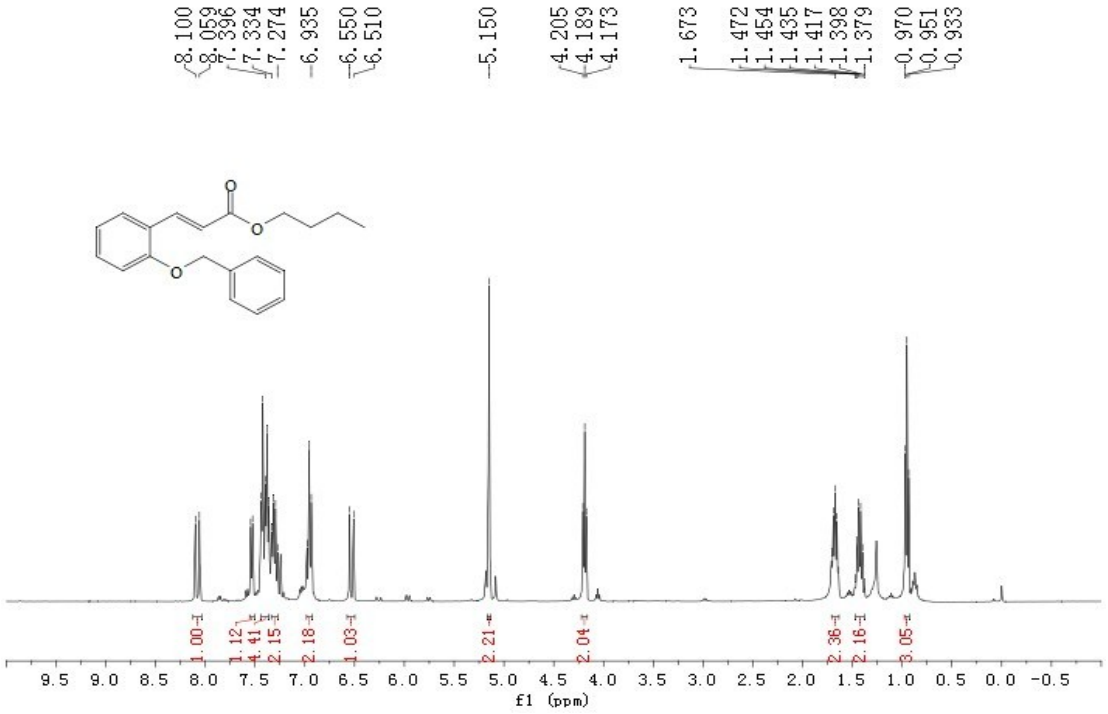


^{13}C NMR Spectrum of **3ja**

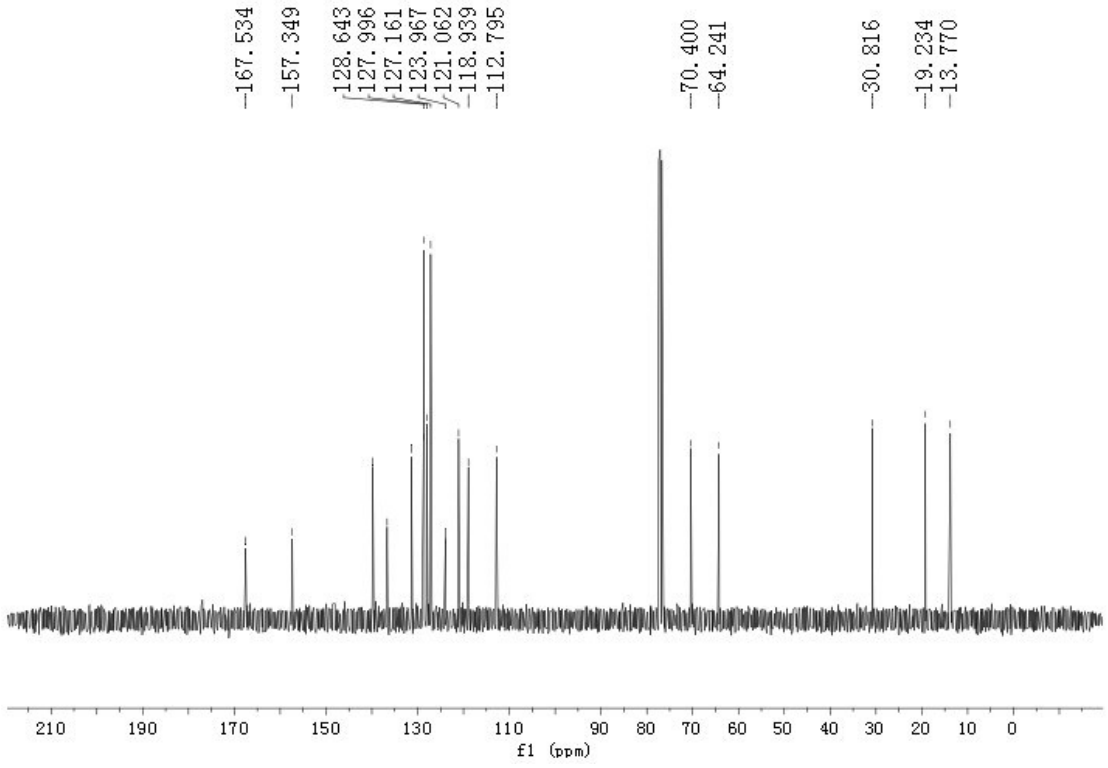


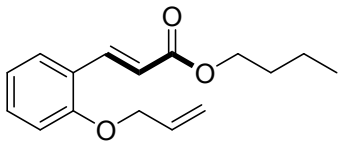


^{1}H NMR Spectrum of **3ka**

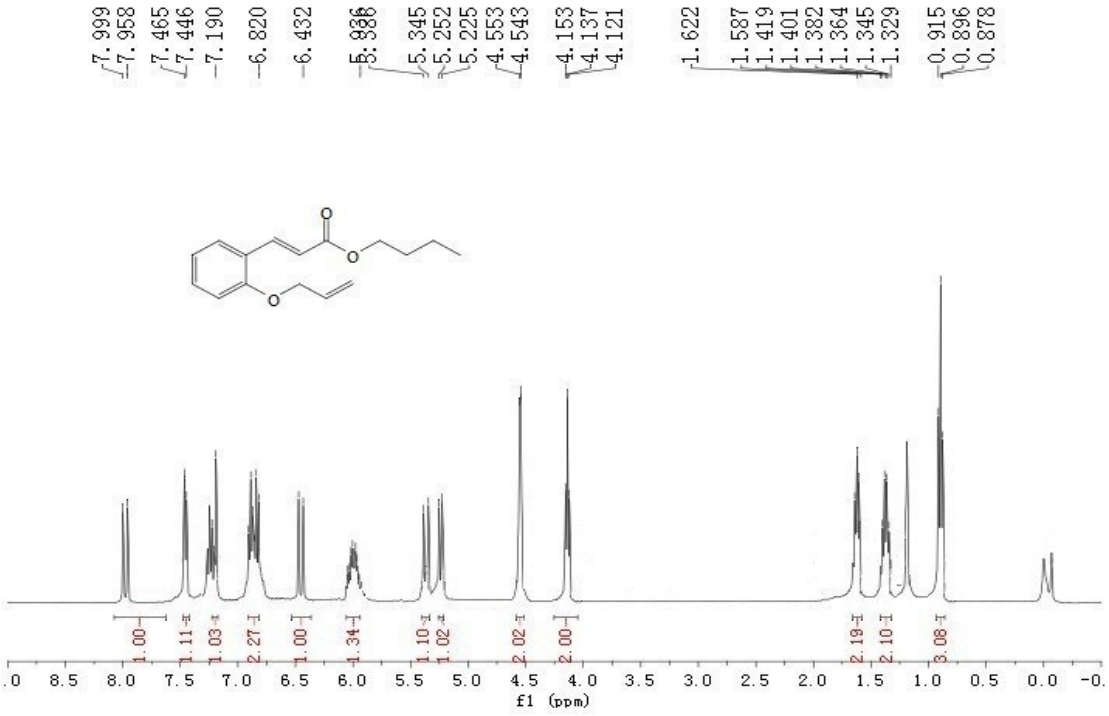


^{13}C NMR Spectrum of **3ka**

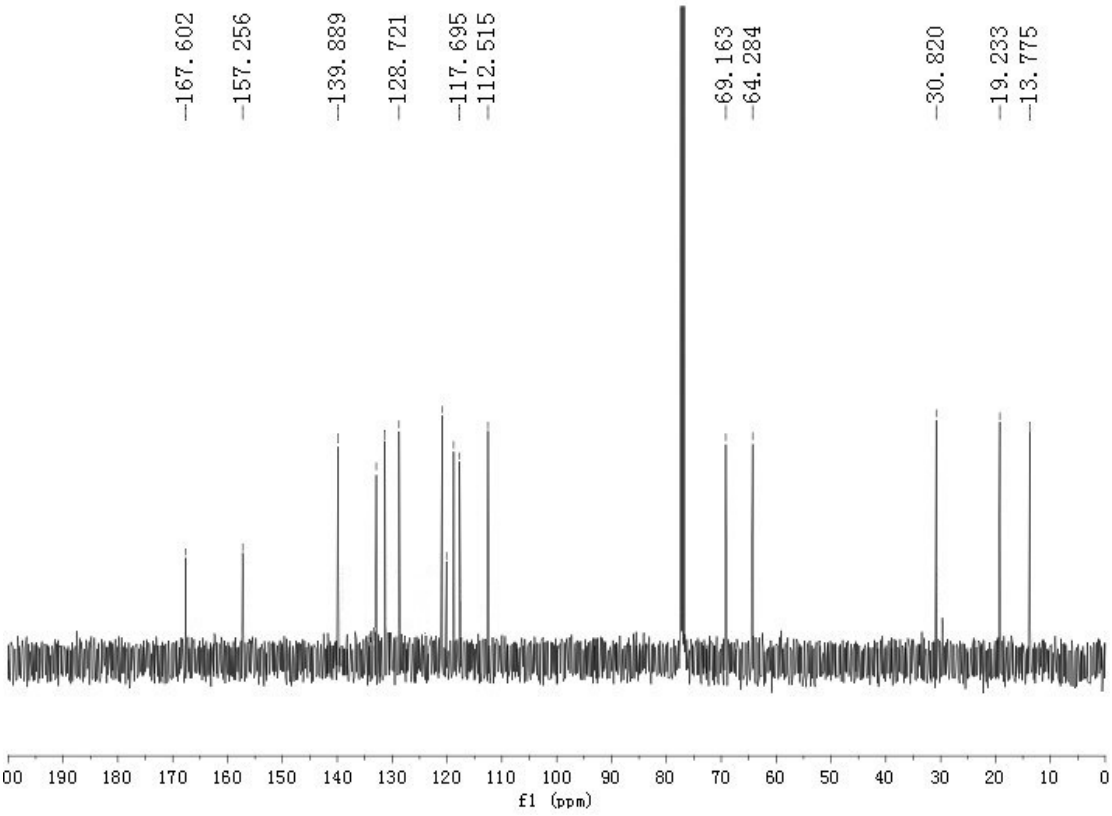


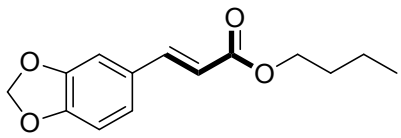


^{1}H NMR Spectrum of **3la**

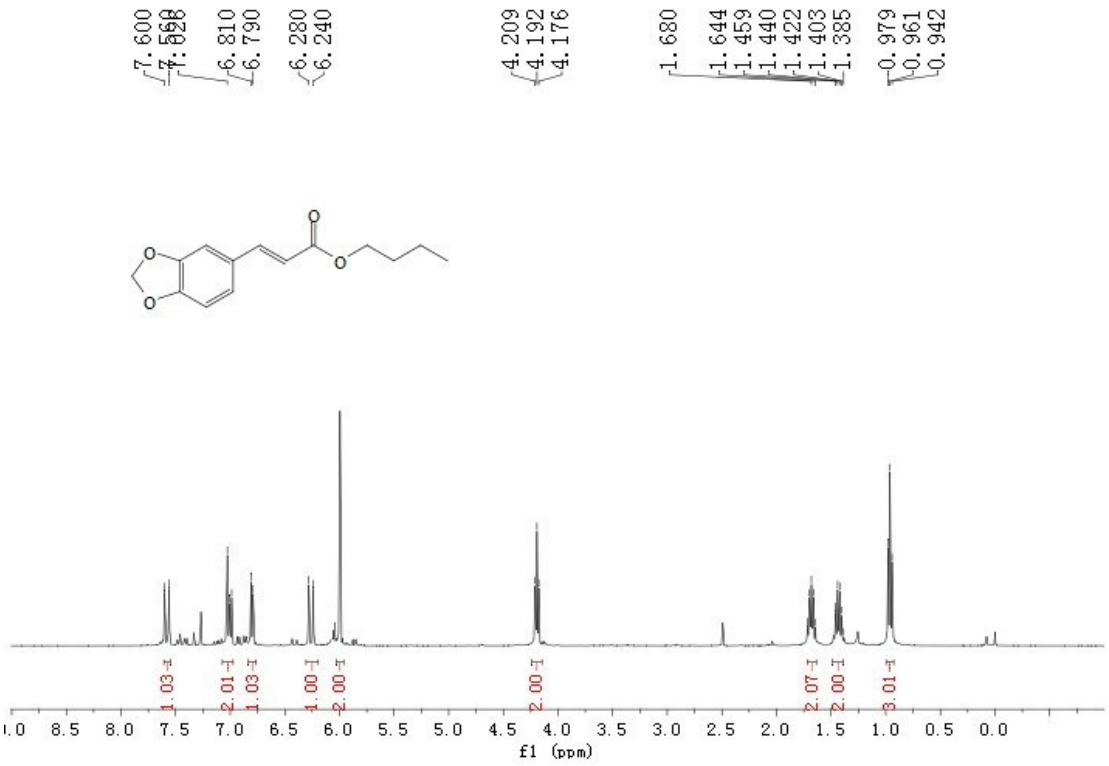


^{13}C NMR Spectrum of **3la**

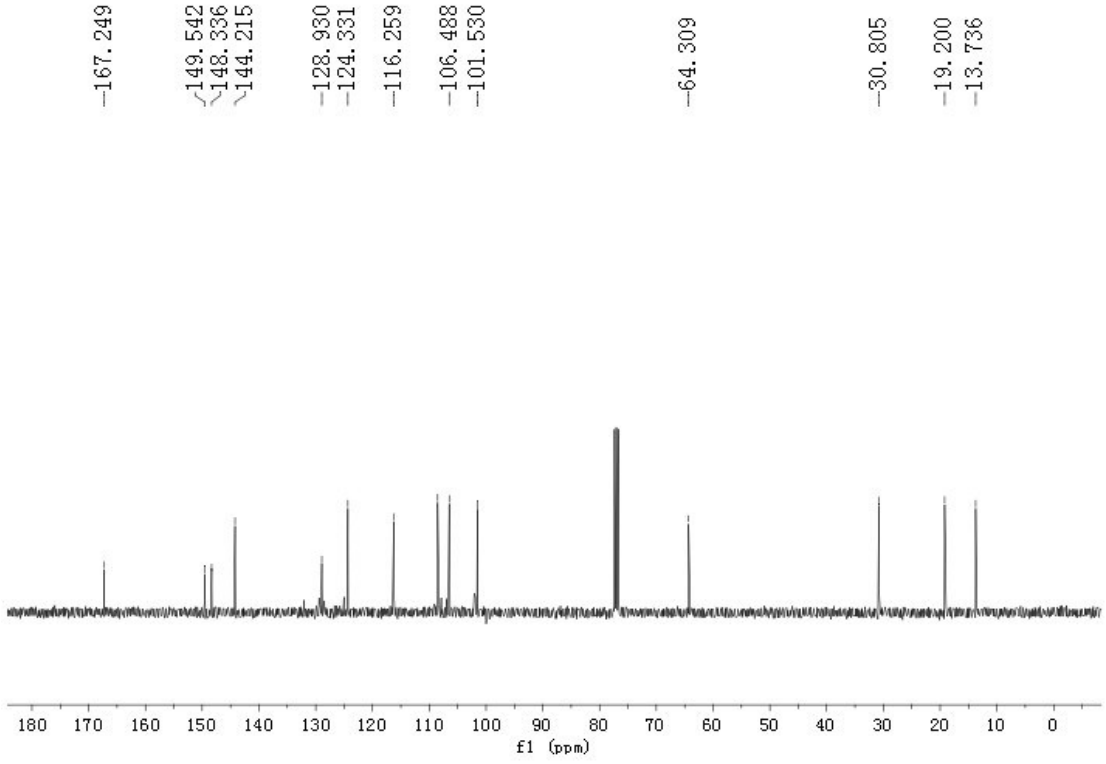


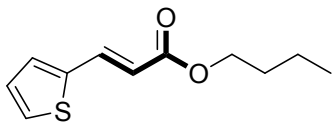


^{1}H NMR Spectrum of **3ma**

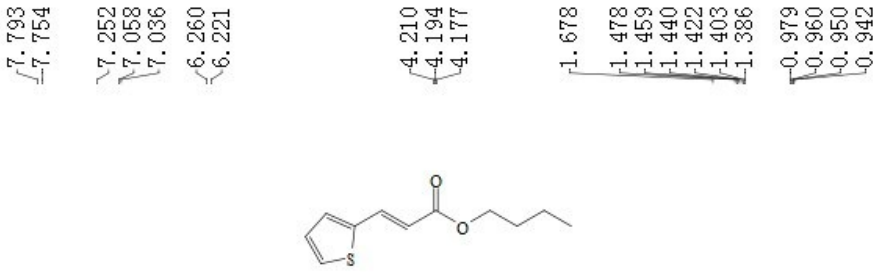


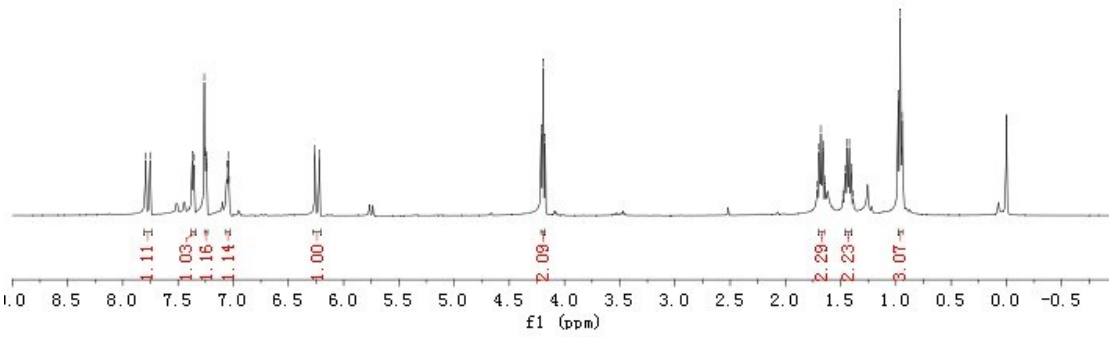
^{13}C NMR Spectrum of **3ma**



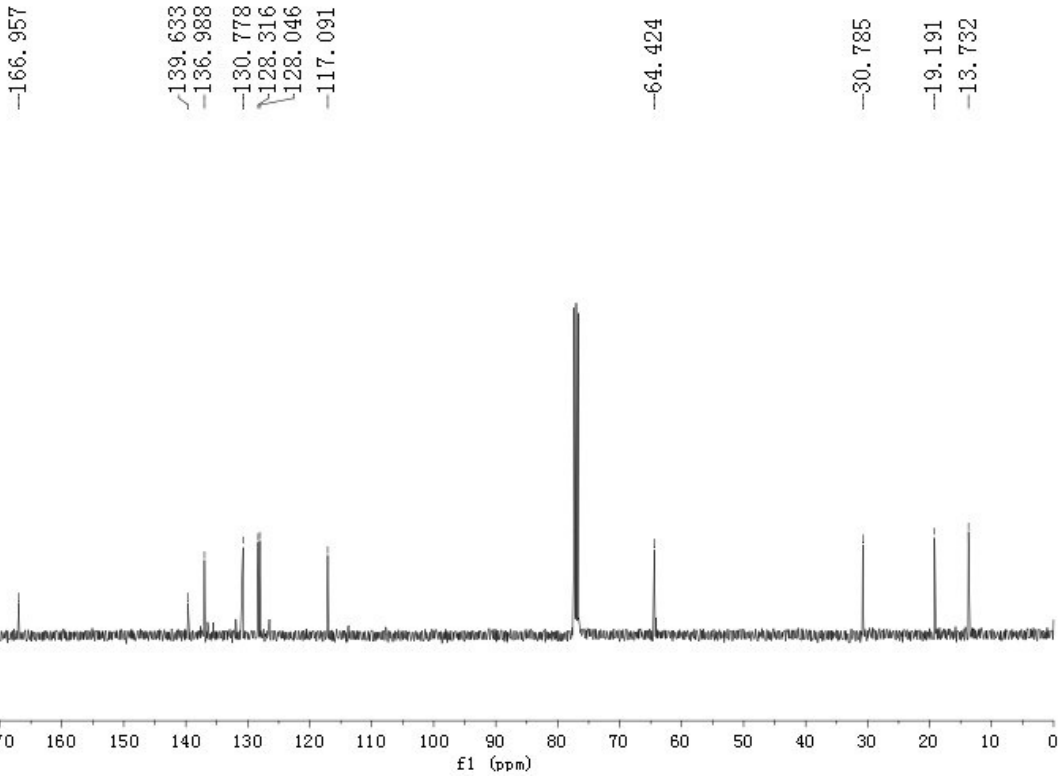


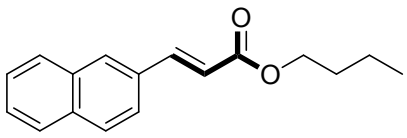
^{1}H NMR Spectrum of **3na**



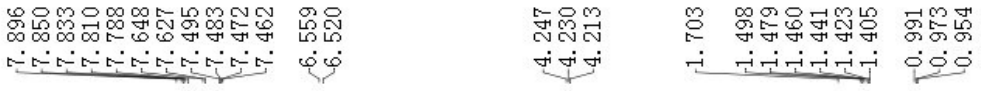


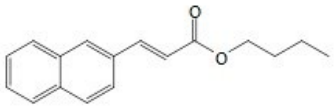
^{13}C NMR Spectrum of **3na**

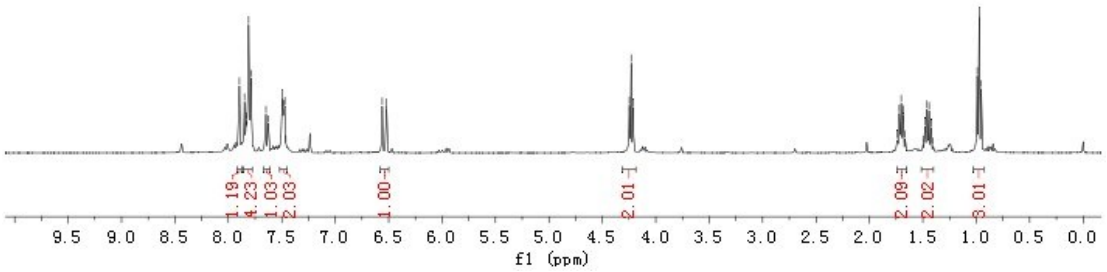




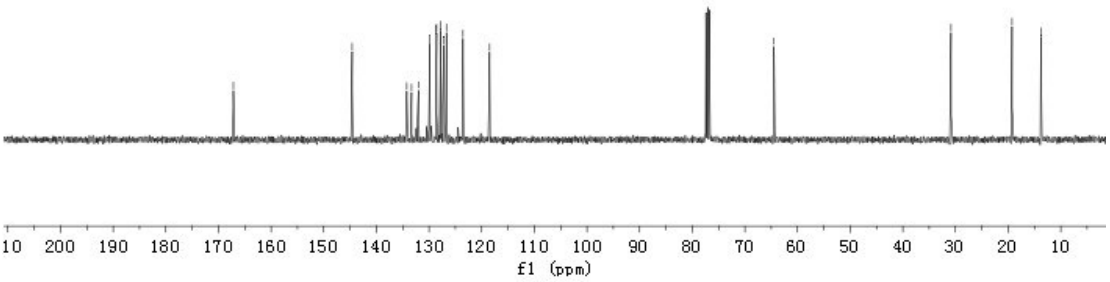
^{1}H NMR Spectrum of **3oa**

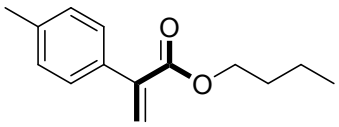




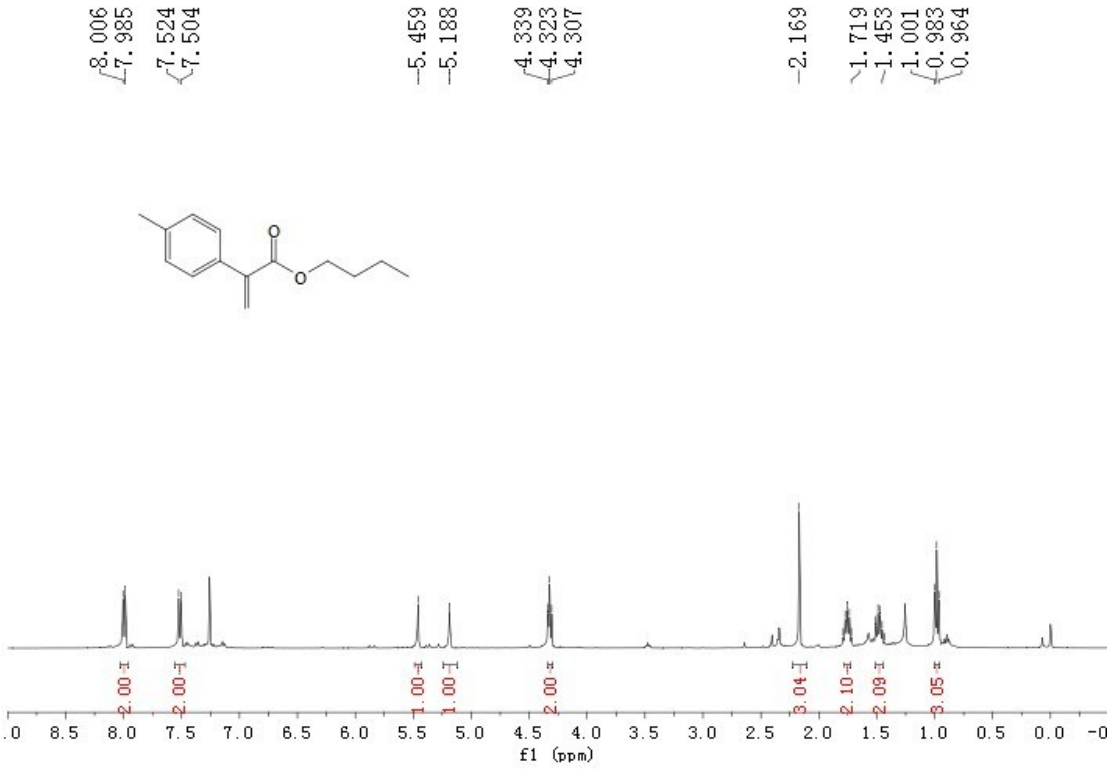


^{13}C NMR Spectrum of **3oa**

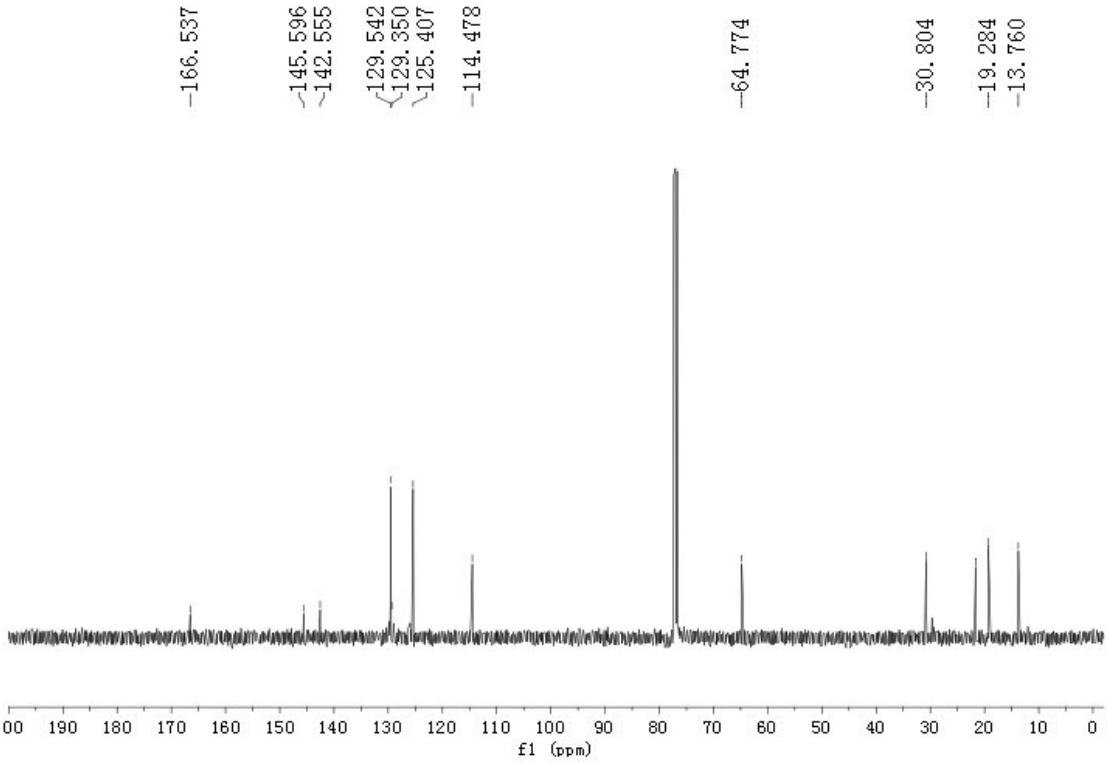


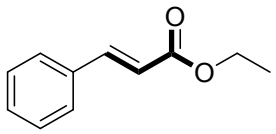


^{1}H NMR Spectrum of **3pa**

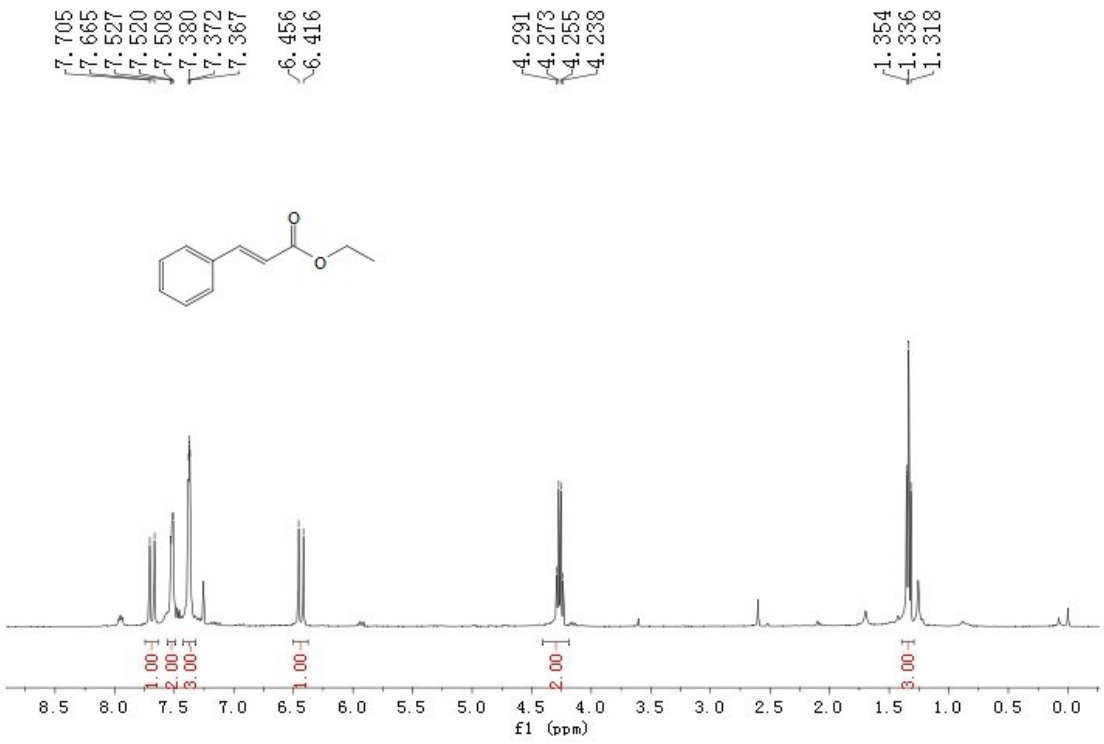


^{13}C NMR Spectrum of **3pa**

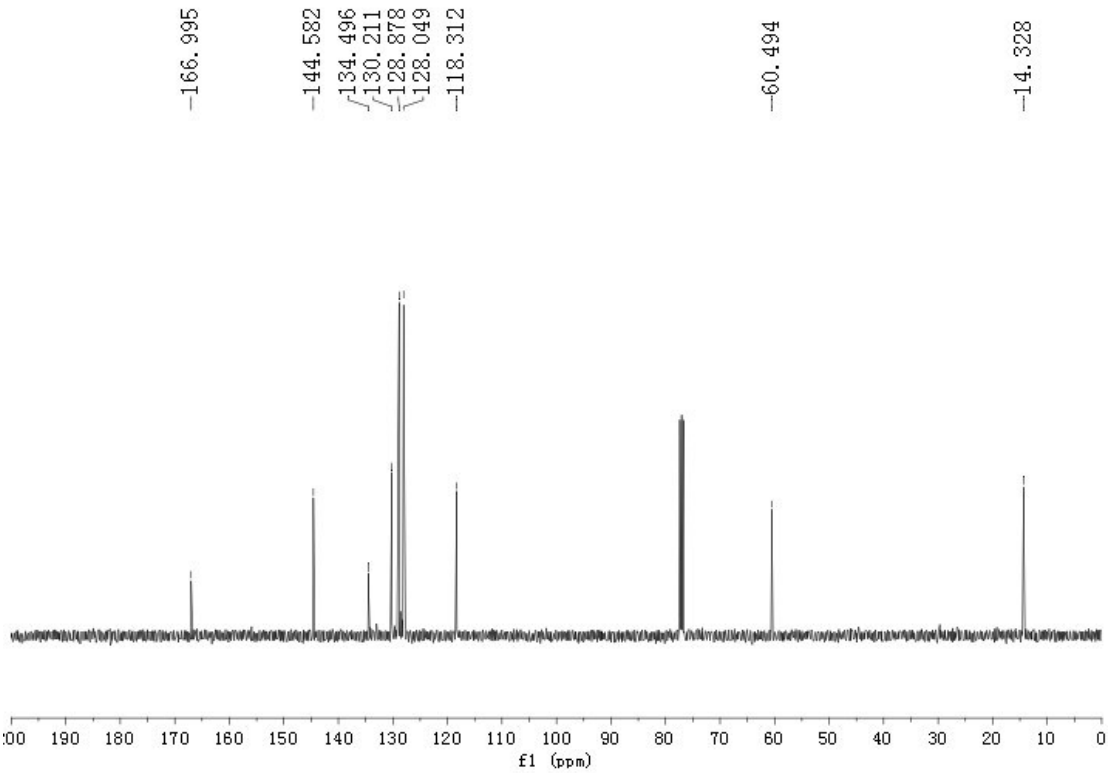


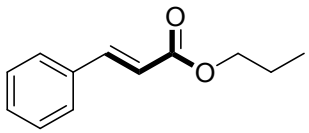


^{1}H NMR Spectrum of **3ab**

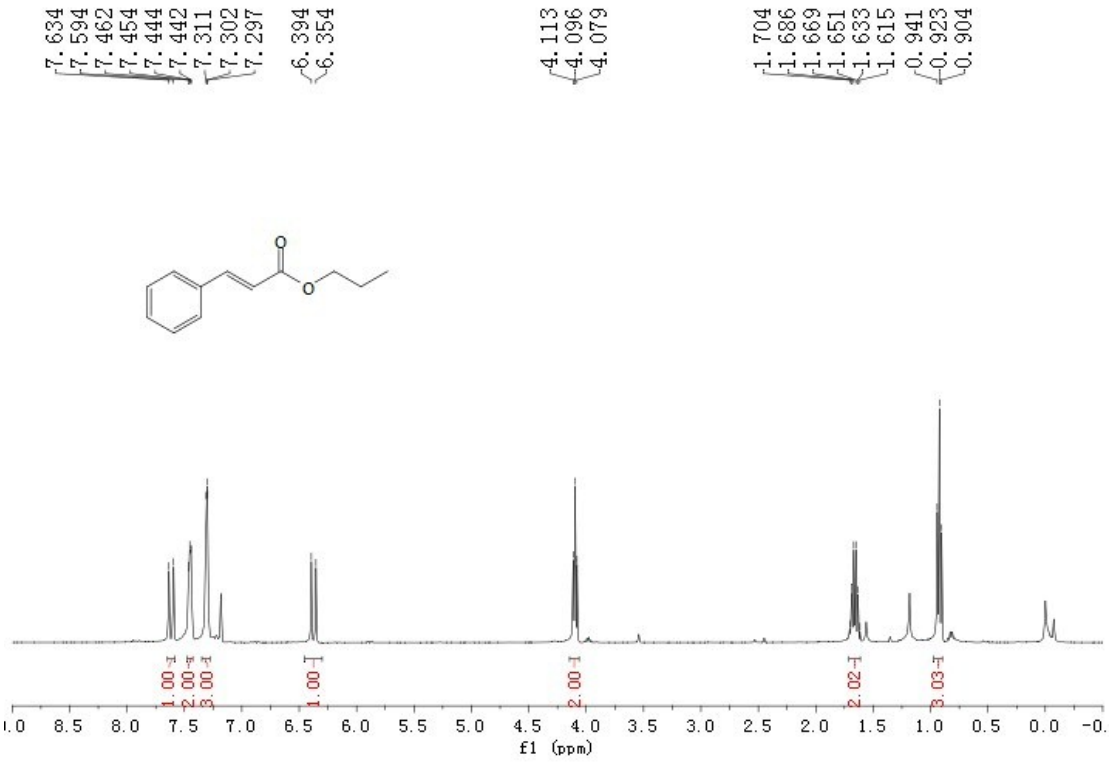


^{13}C NMR Spectrum of **3ab**

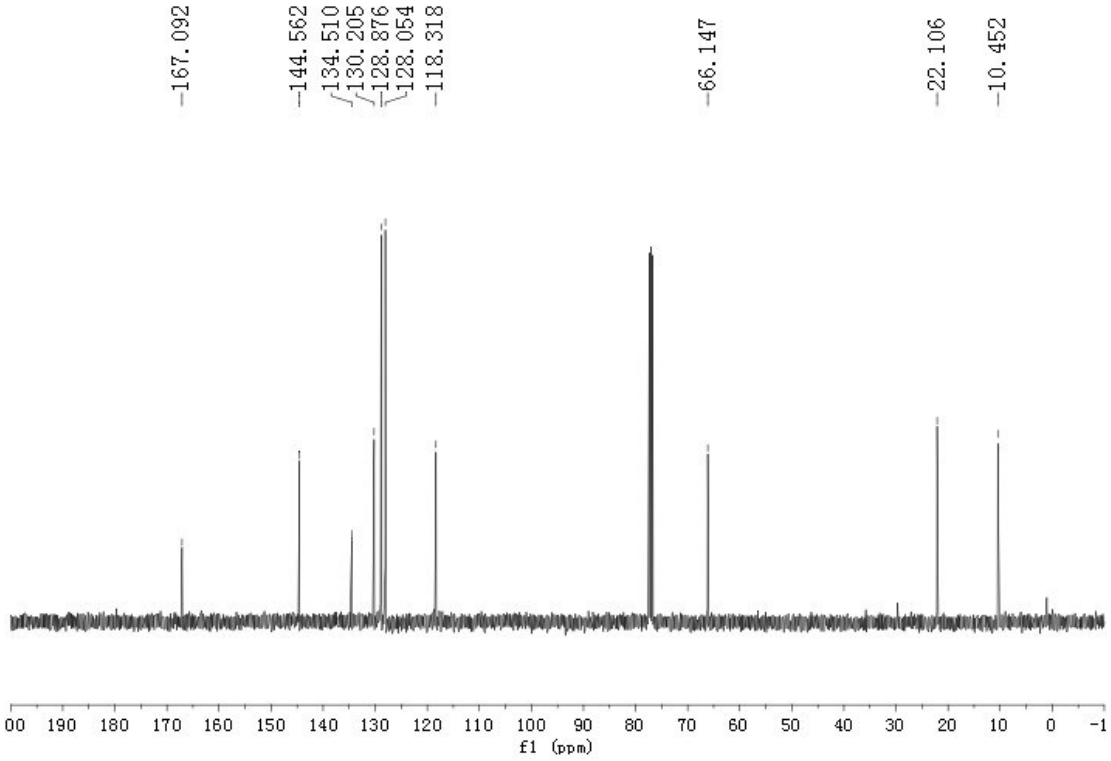


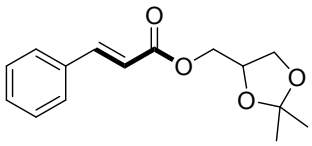


^{1}H NMR Spectrum of **3ac**

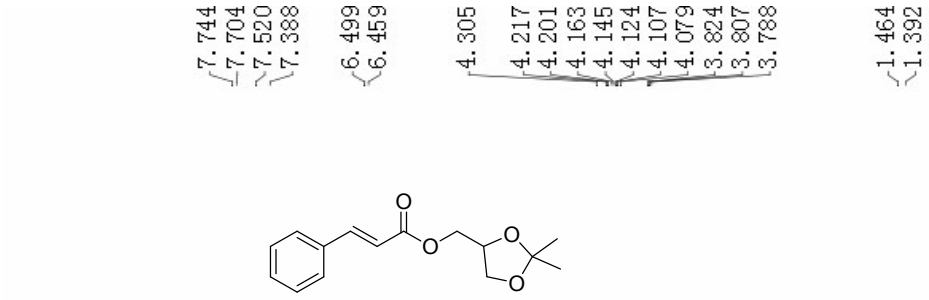


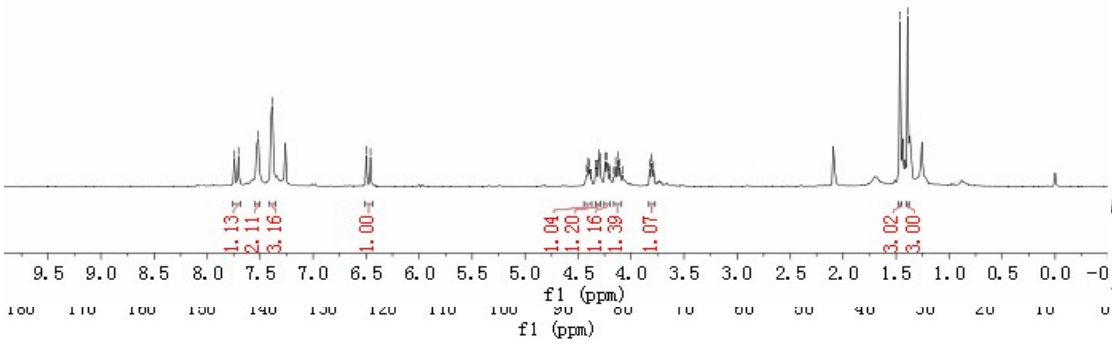
^{13}C NMR Spectrum of **3ac**

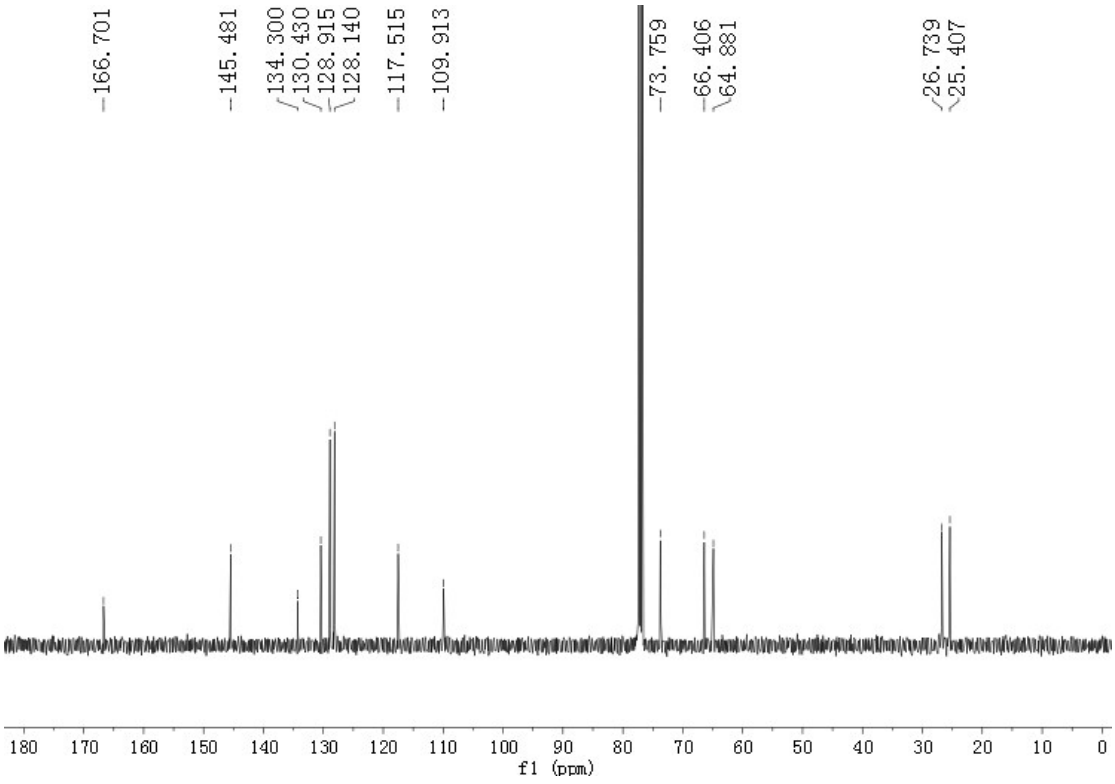


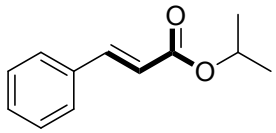


^{1}H NMR Spectrum of **3ad**

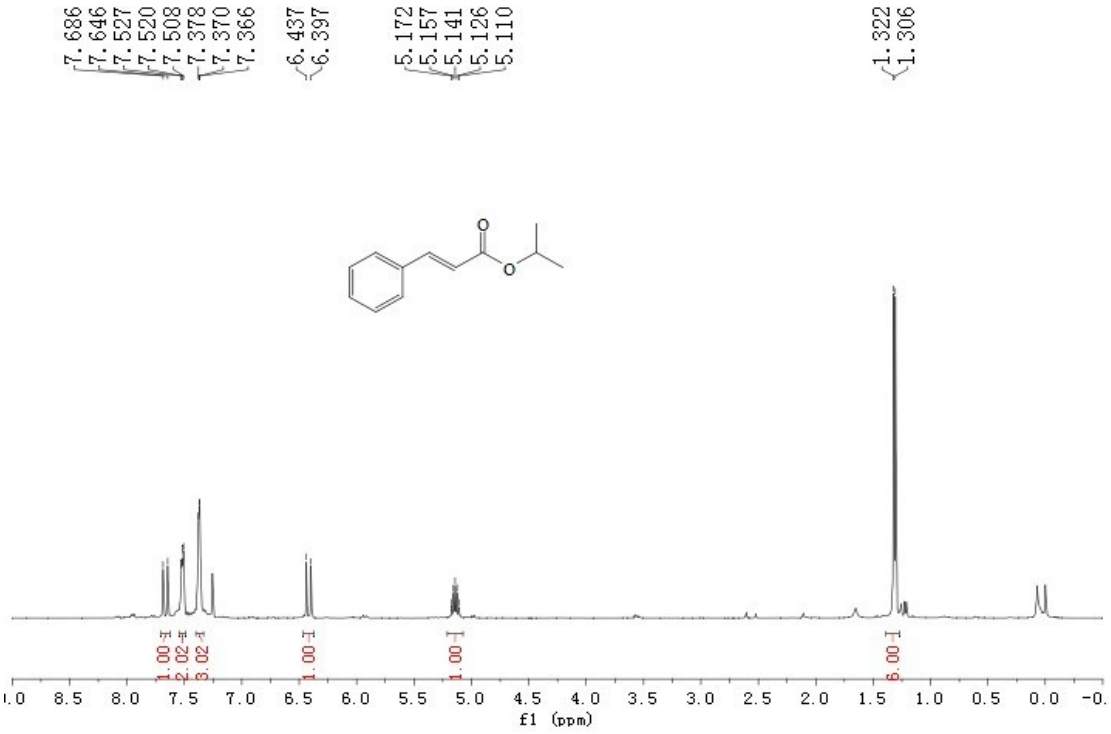




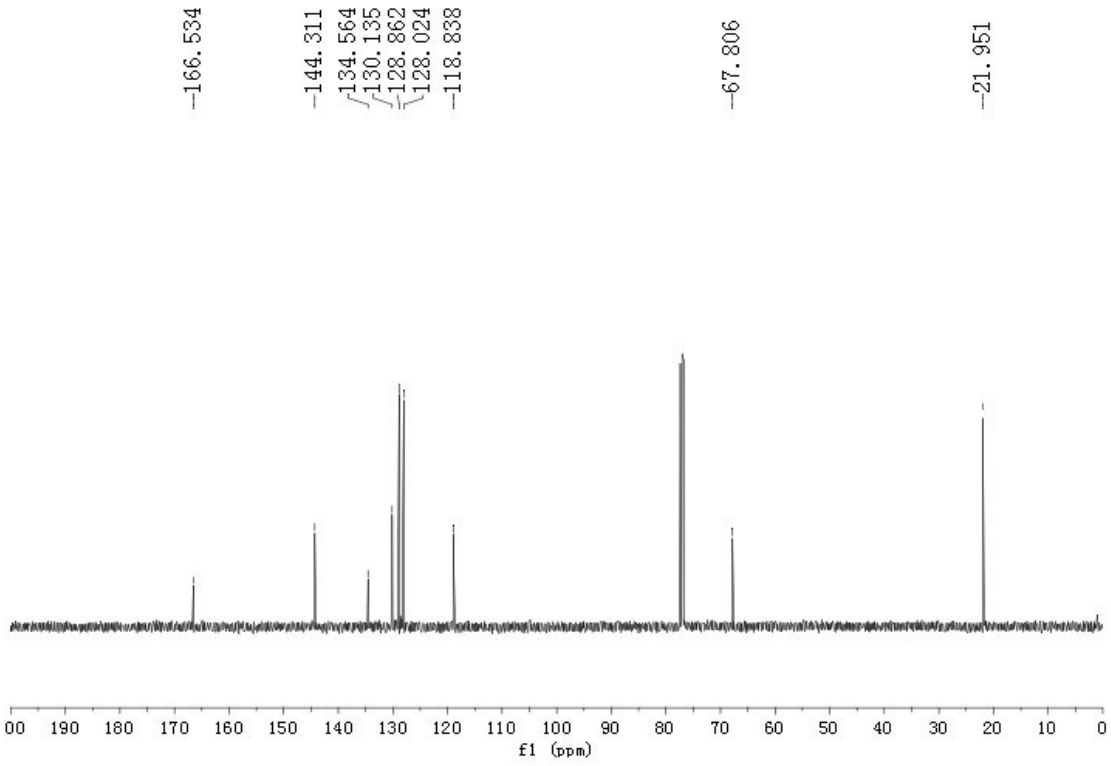


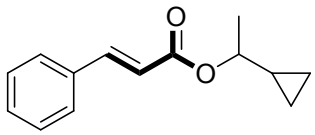


^{1}H NMR Spectrum of **3ae**

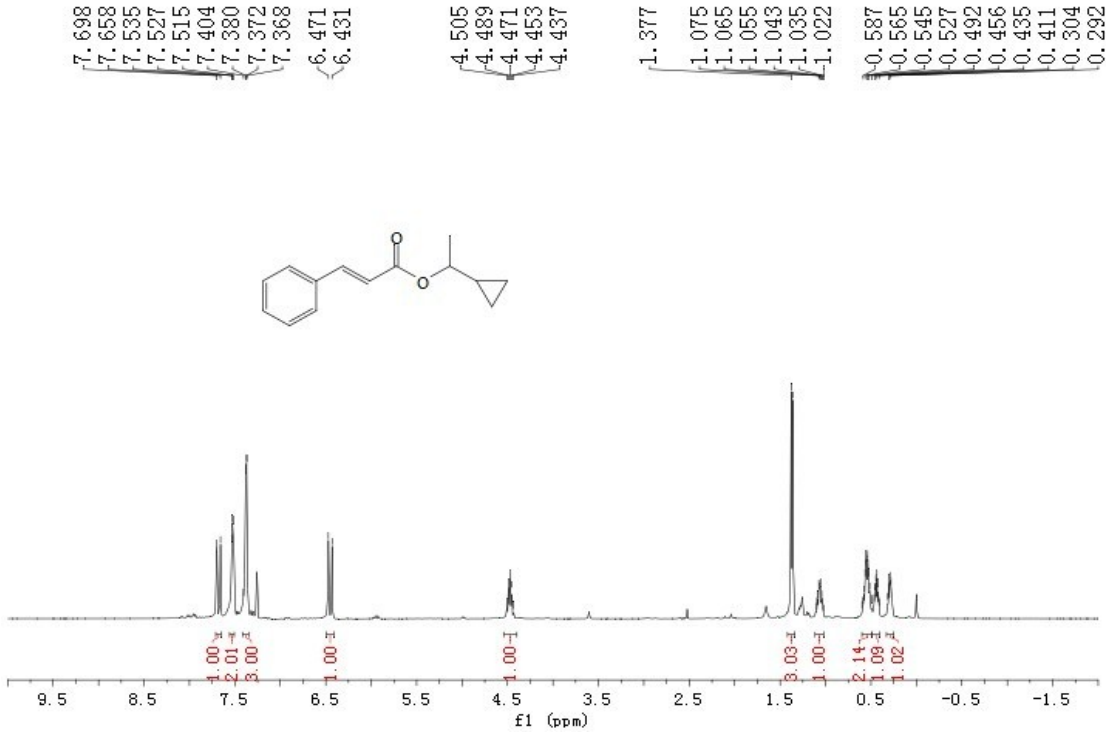


^{13}C NMR Spectrum of **3ae**

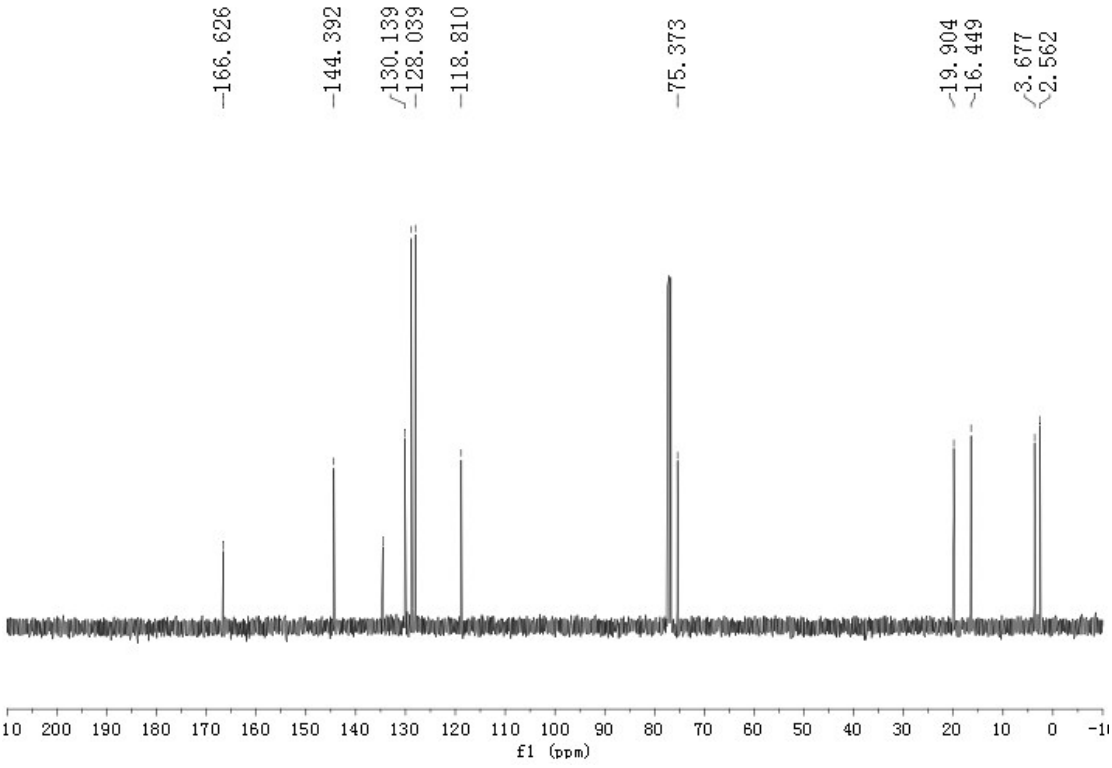


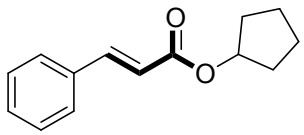


^{1}H NMR Spectrum of **3af**

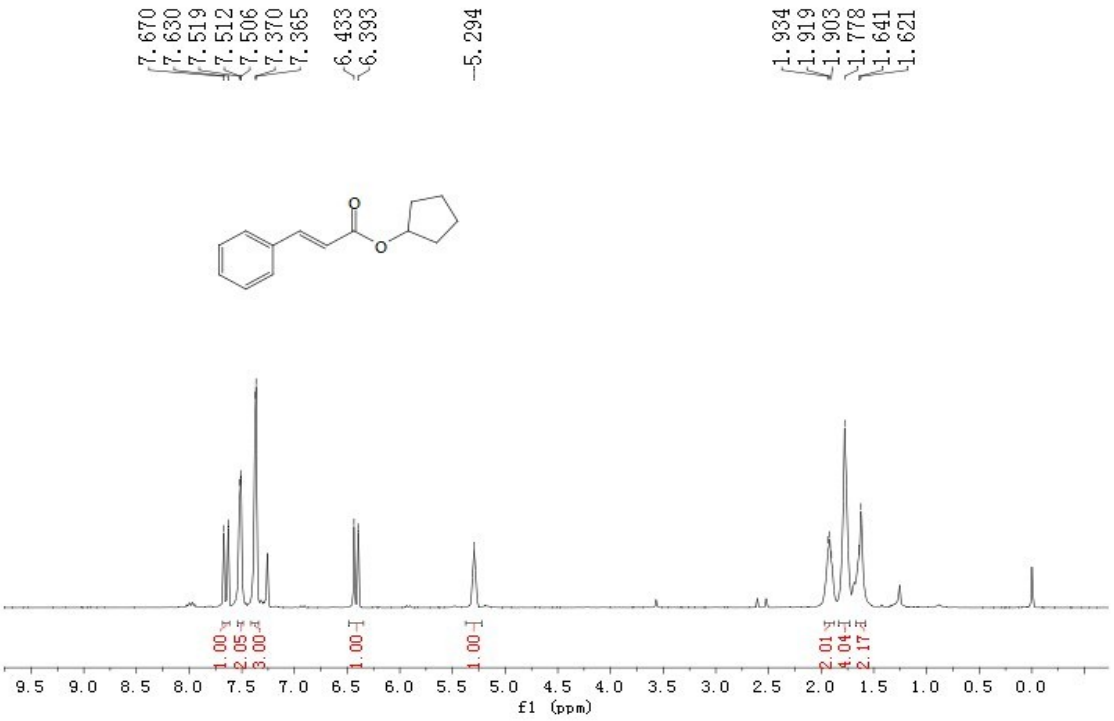


^{13}C NMR Spectrum of **3af**

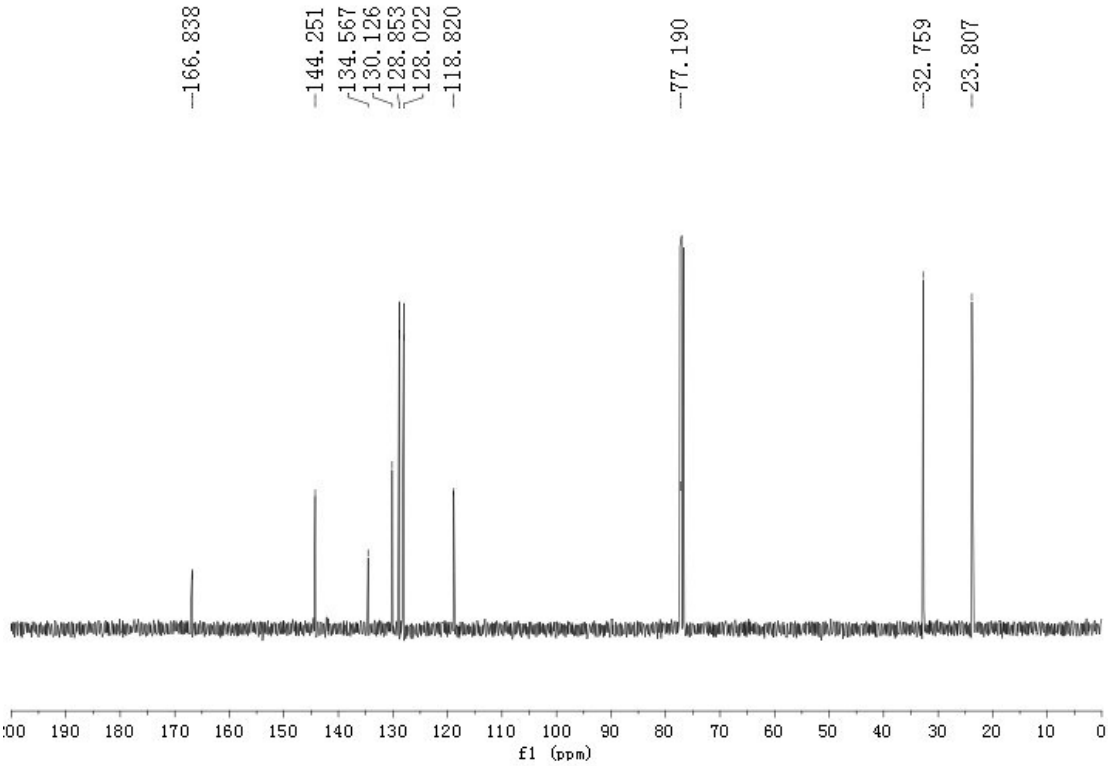


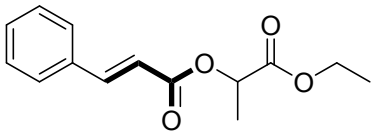


^{1}H NMR Spectrum of **3ag**

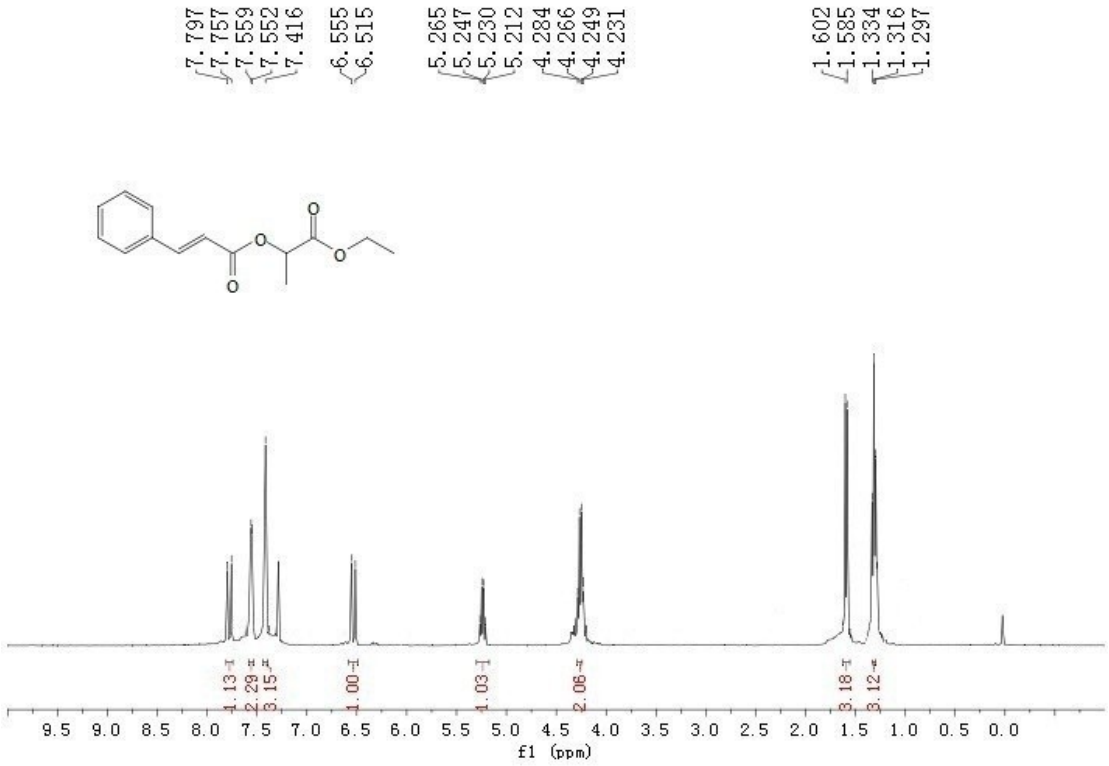


^{13}C NMR Spectrum of **3ag**

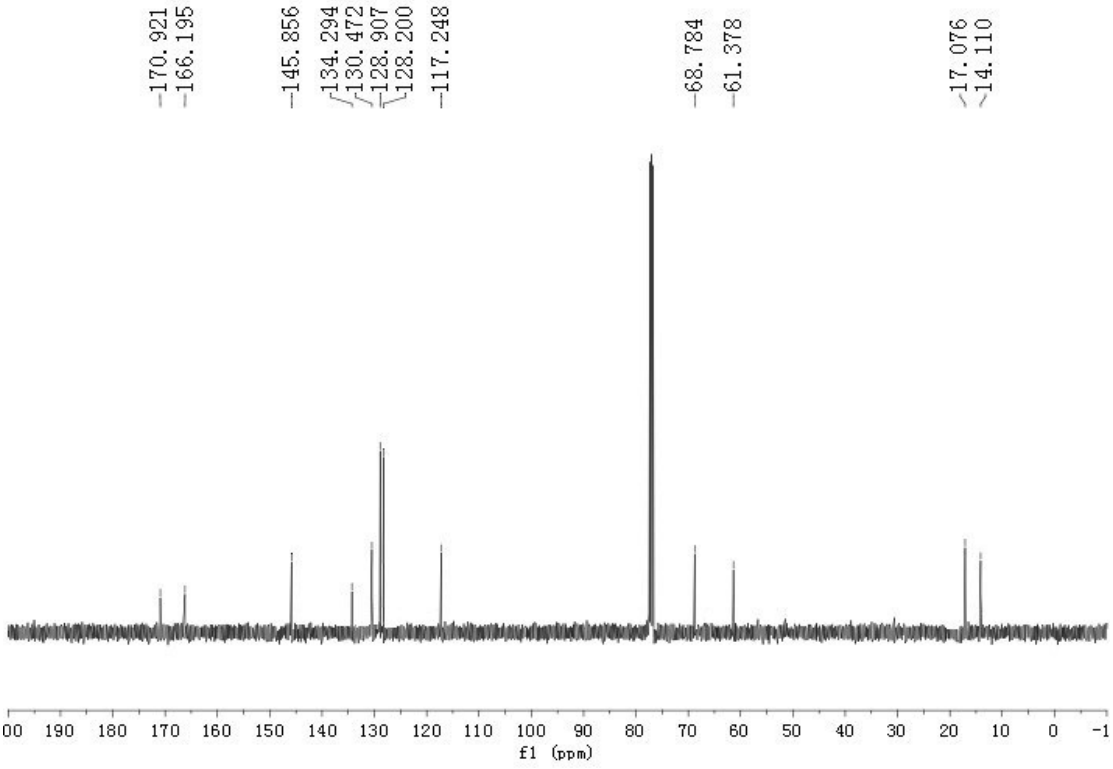


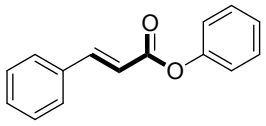


^{1}H NMR Spectrum of **3ah**

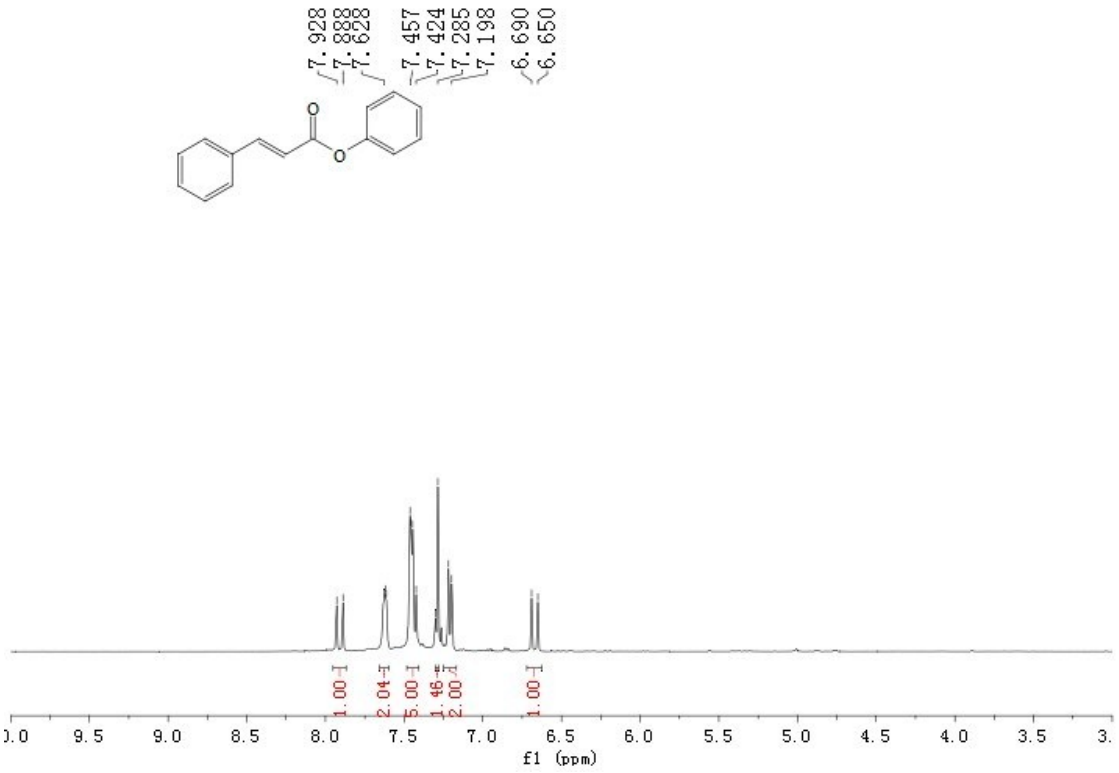


^{13}C NMR Spectrum of **3ah**

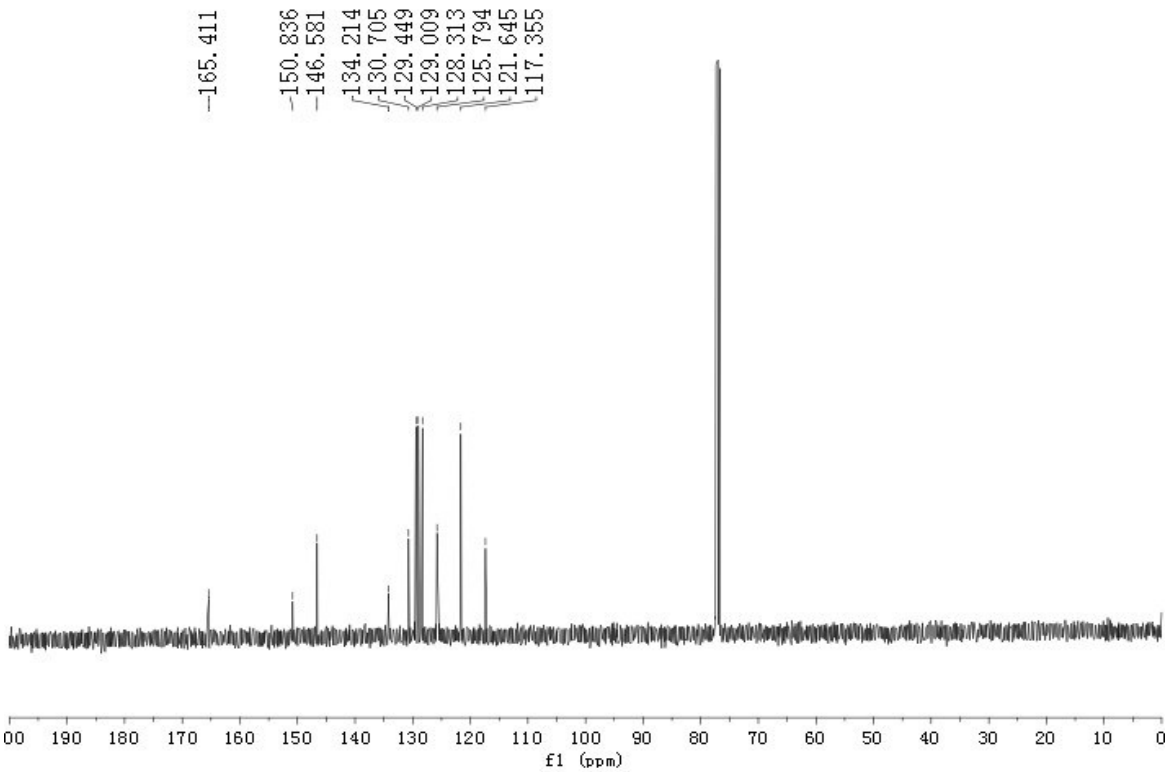


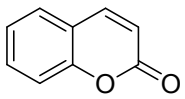


^{1}H NMR Spectrum of **3ai**

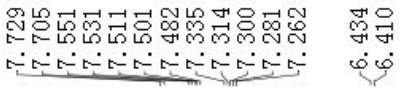


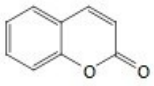
^{13}C NMR Spectrum of **3ai**

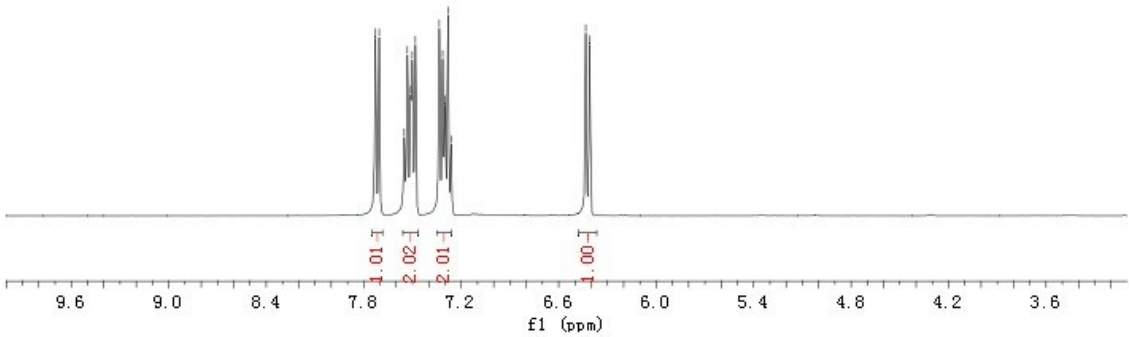




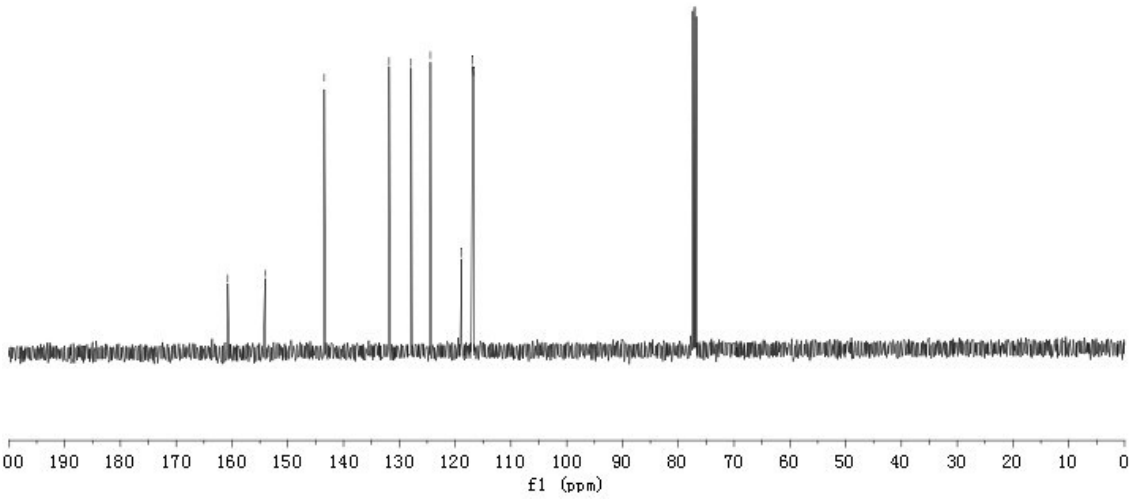
^{1}H NMR Spectrum of **3s**

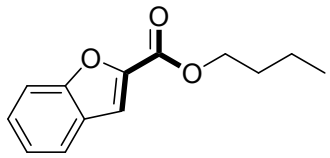




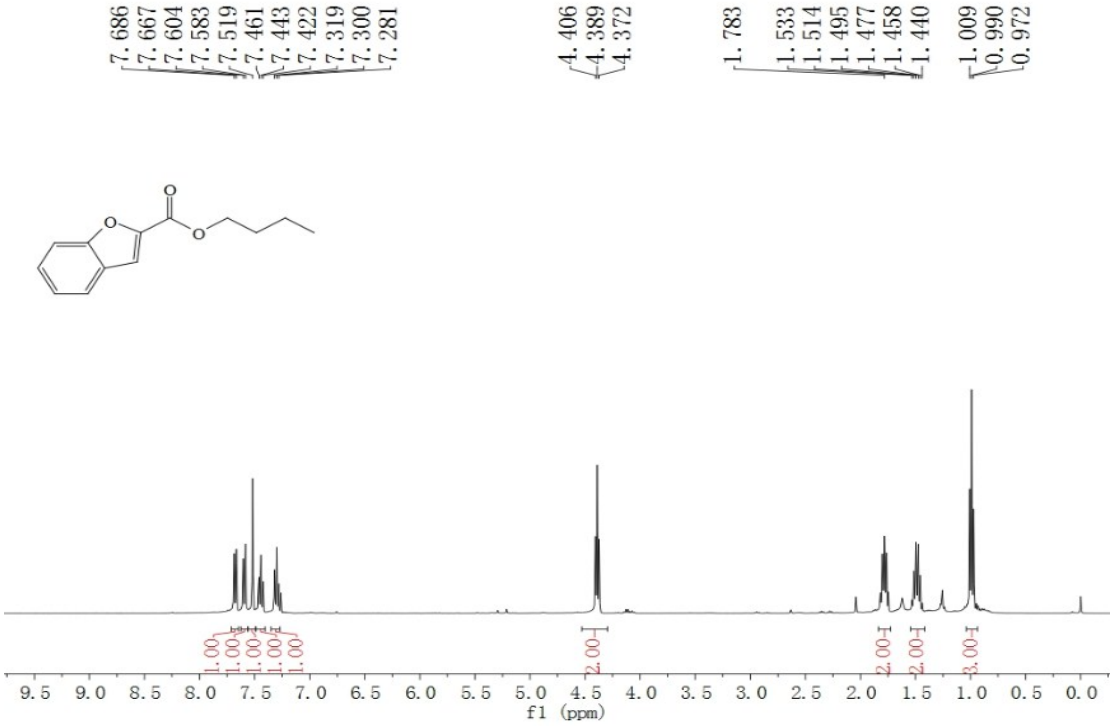


^{13}C NMR Spectrum of **3s**

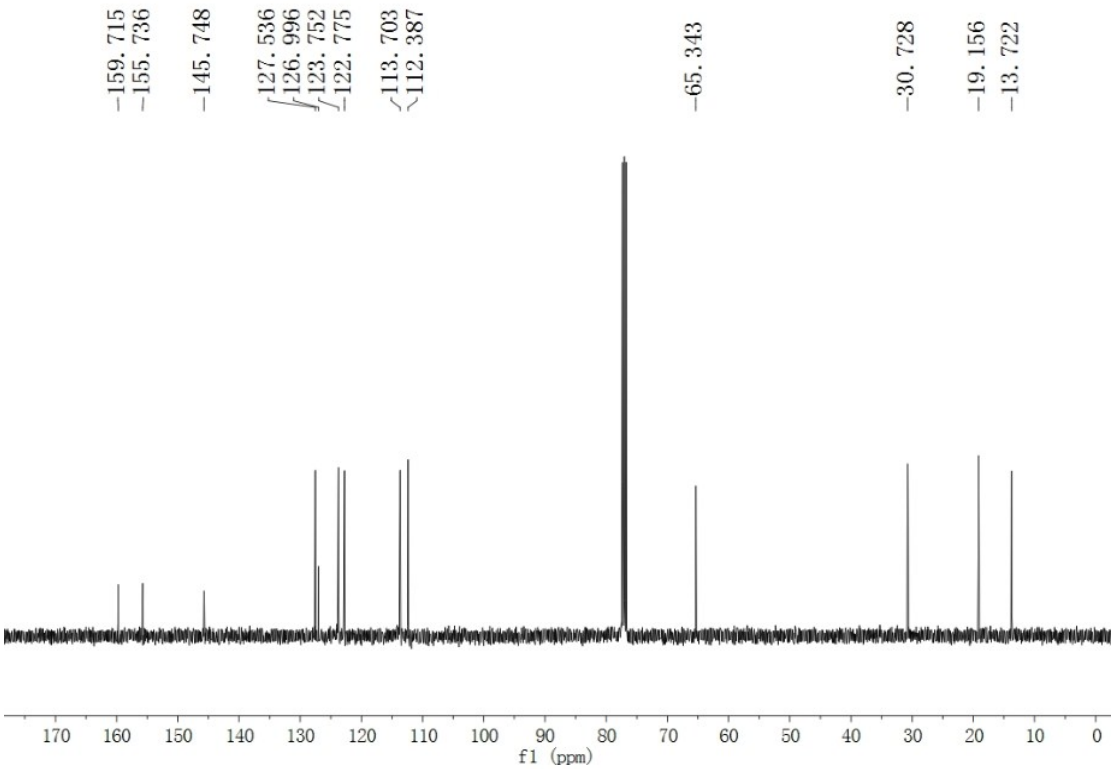


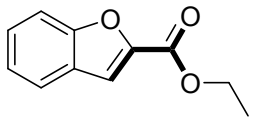


^{1}H NMR Spectrum of **4ta**

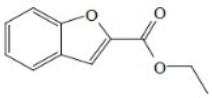


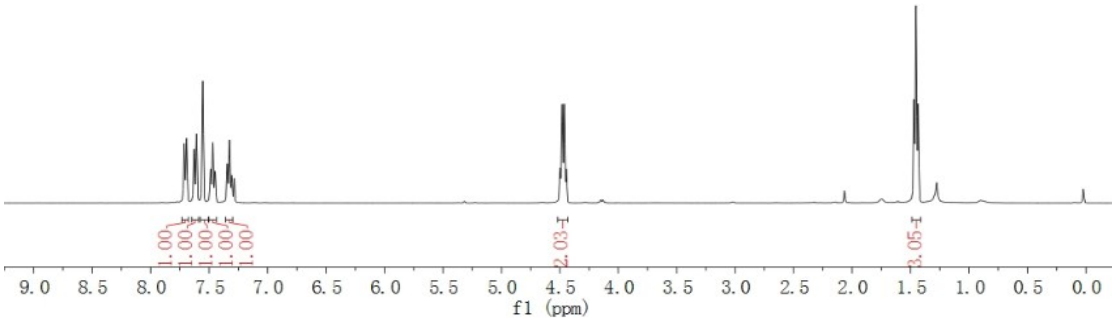
^{13}C NMR Spectrum of **4ta**



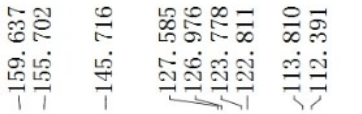


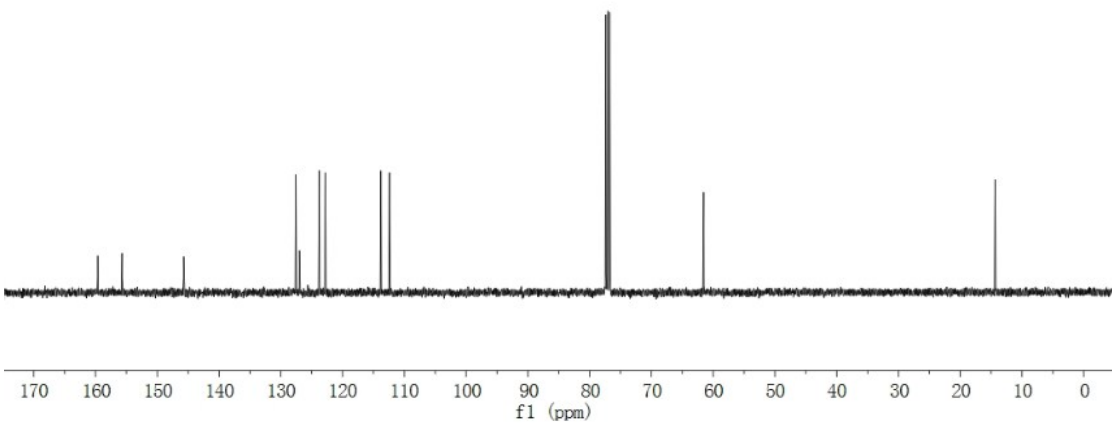
^{1}H NMR Spectrum of **4tb**

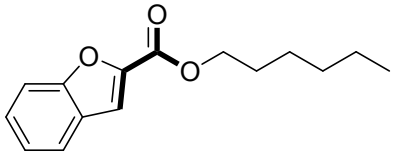




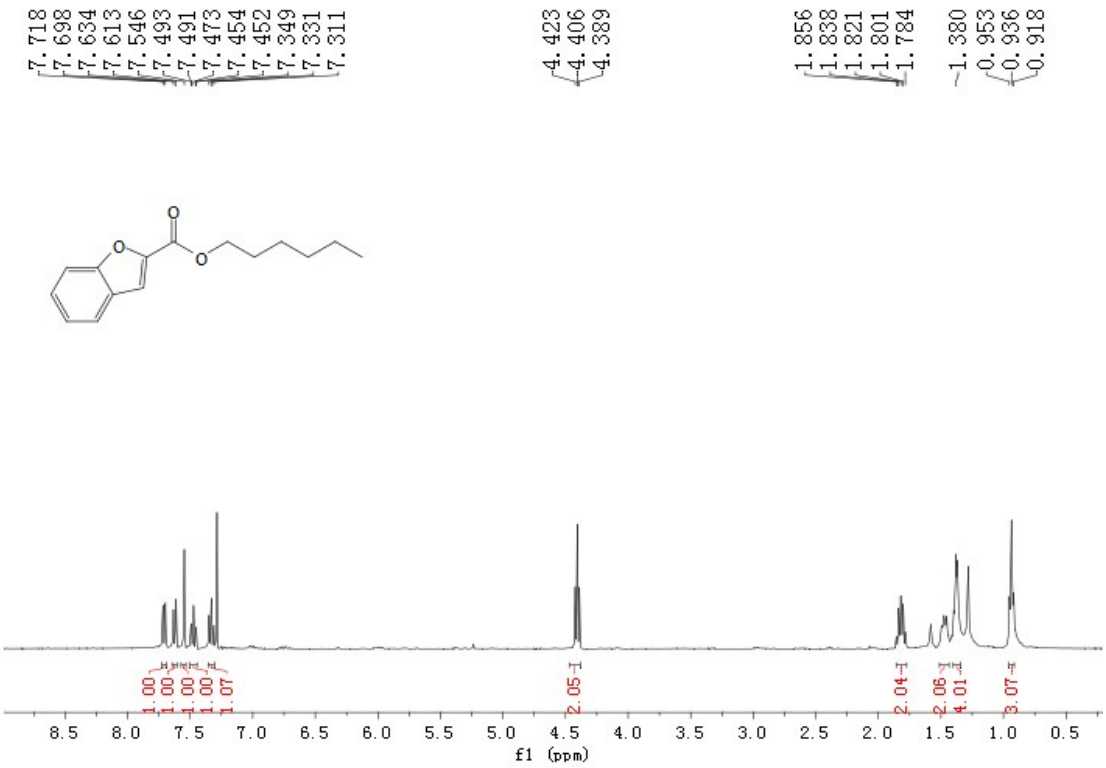
^{13}C NMR Spectrum of **4tb**



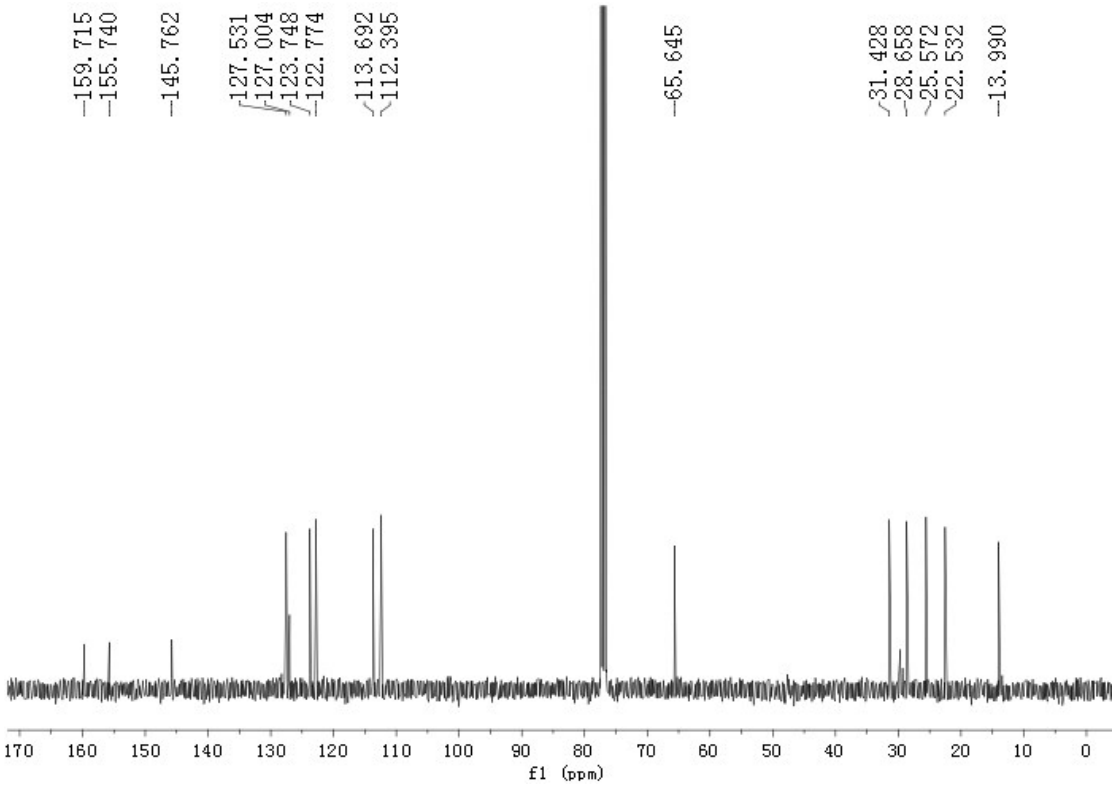


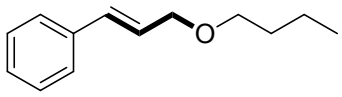


^{1}H NMR Spectrum of **4tj**

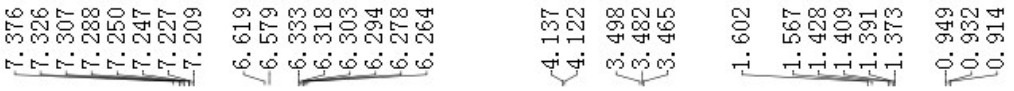


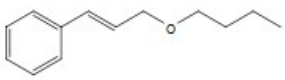
^{13}C NMR Spectrum of **4tj**

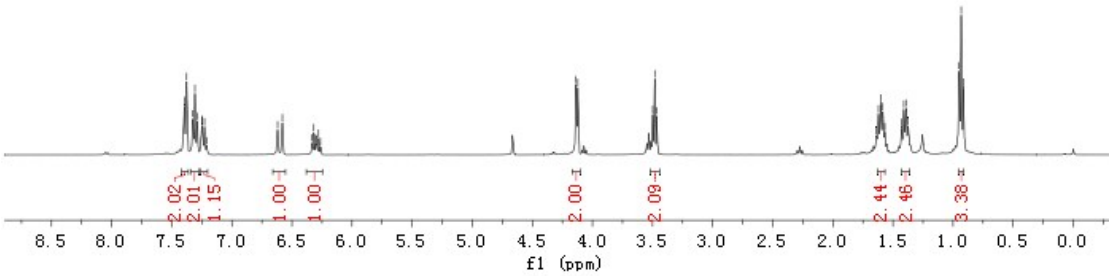




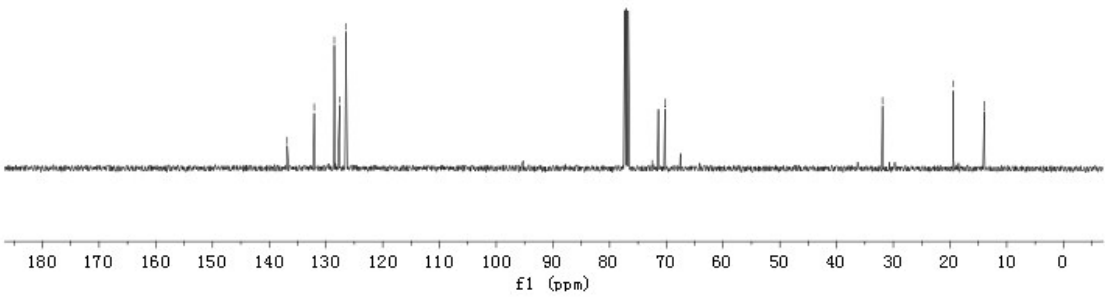
^{1}H NMR Spectrum of **5aa**

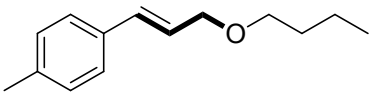




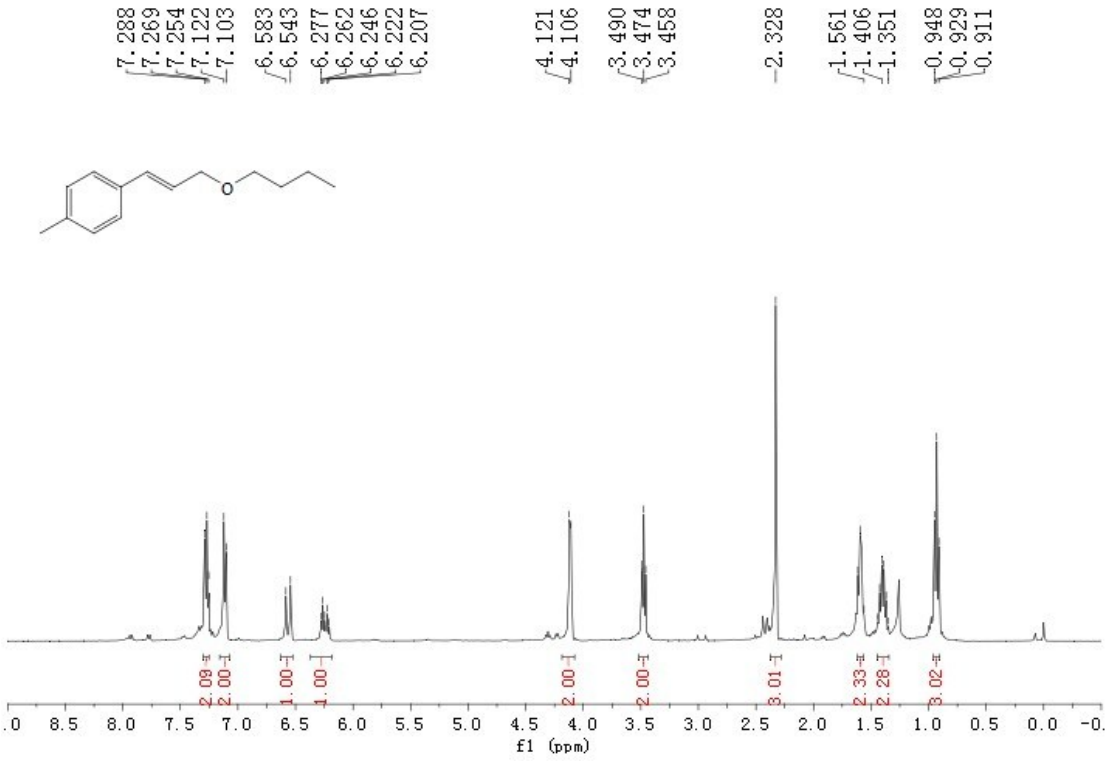


^{13}C NMR Spectrum of **5aa**

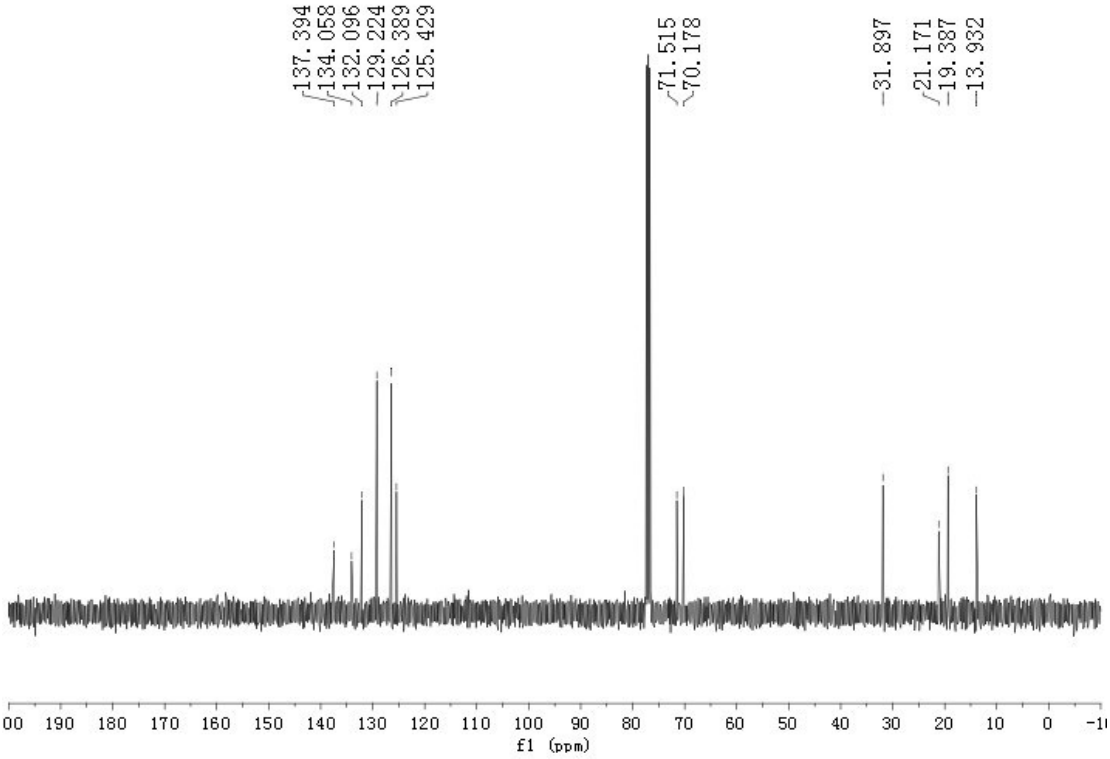


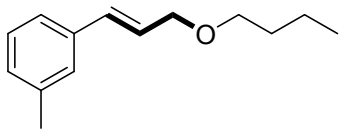


^{1}H NMR Spectrum of **5ea**

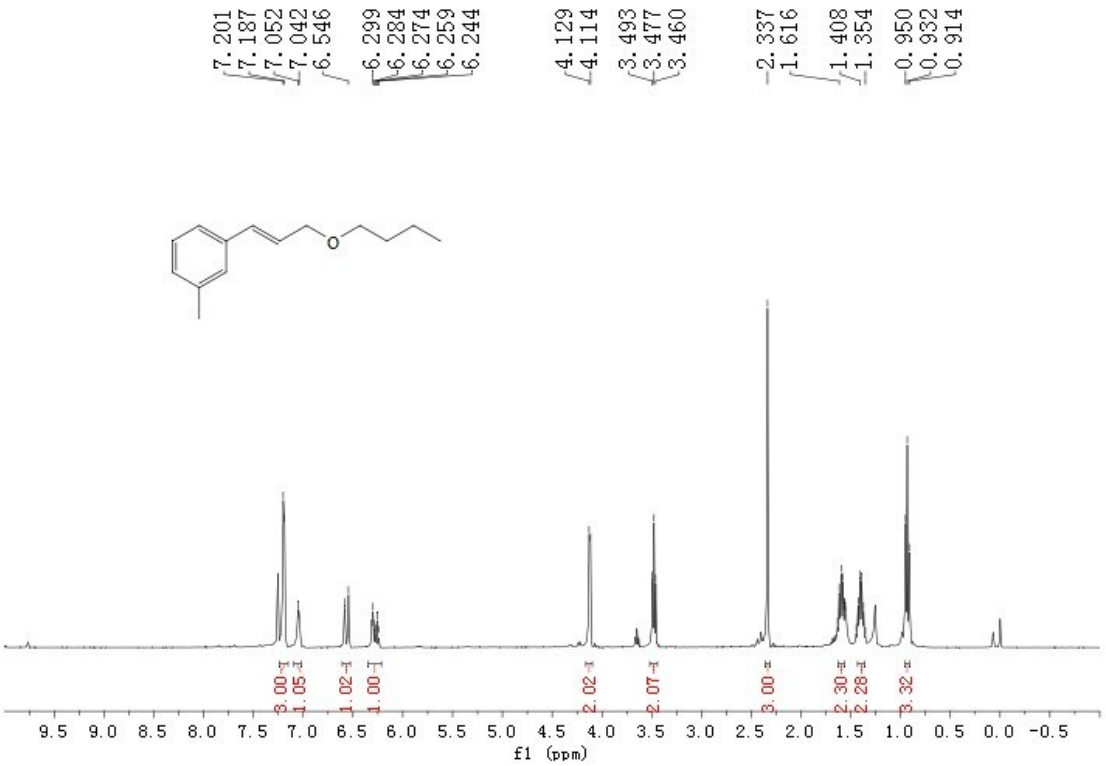


^{13}C NMR Spectrum of **5ea**

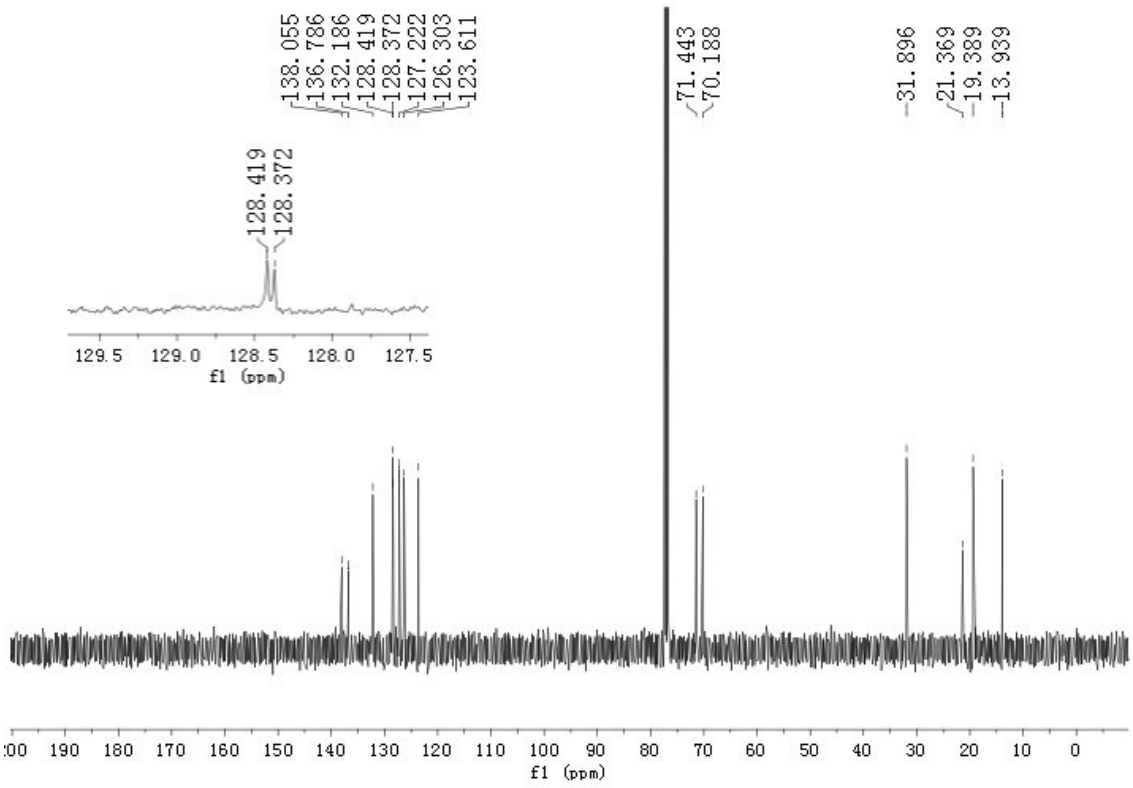


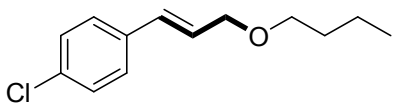


^{1}H NMR Spectrum of **5fa**

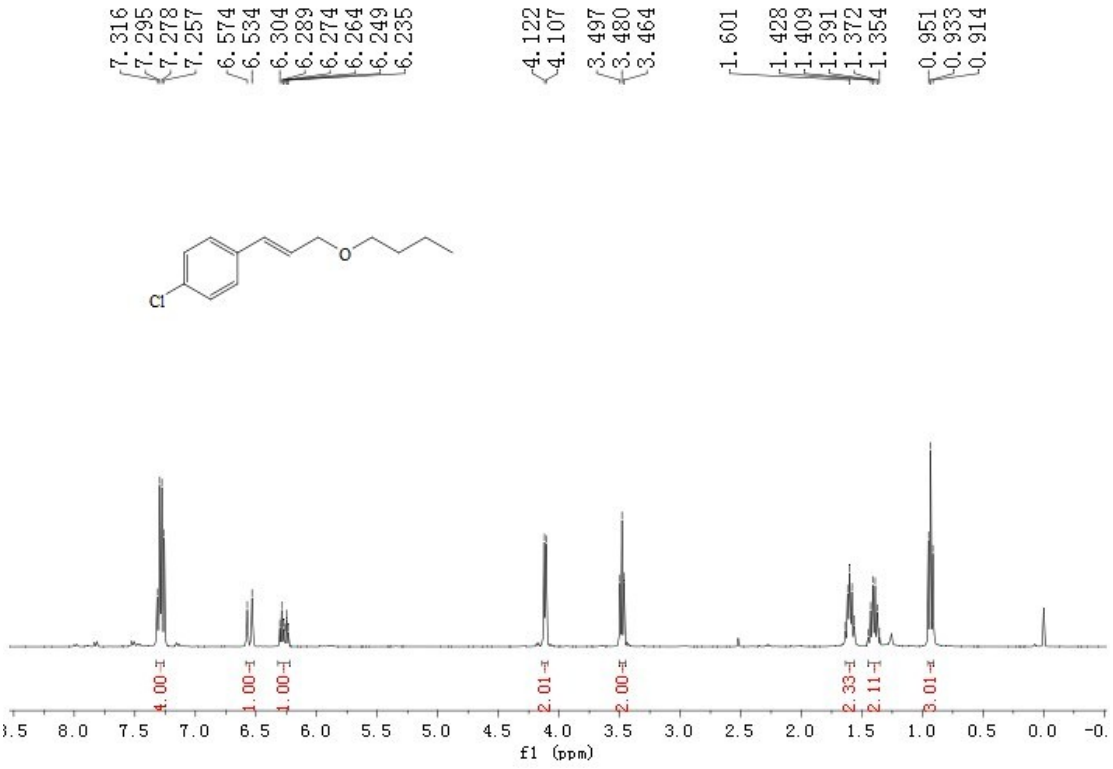


^{13}C NMR Spectrum of **5fa**

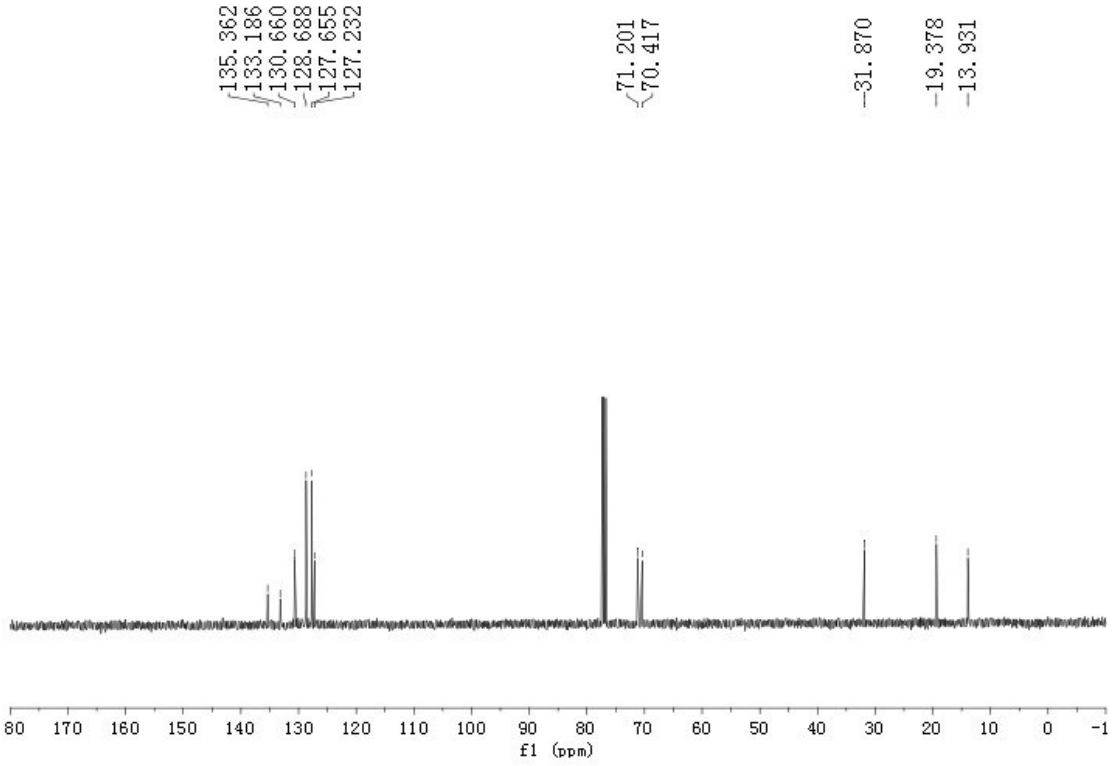


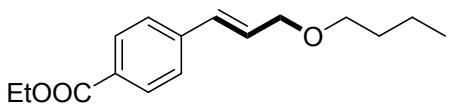


^{1}H NMR Spectrum of **5ha**

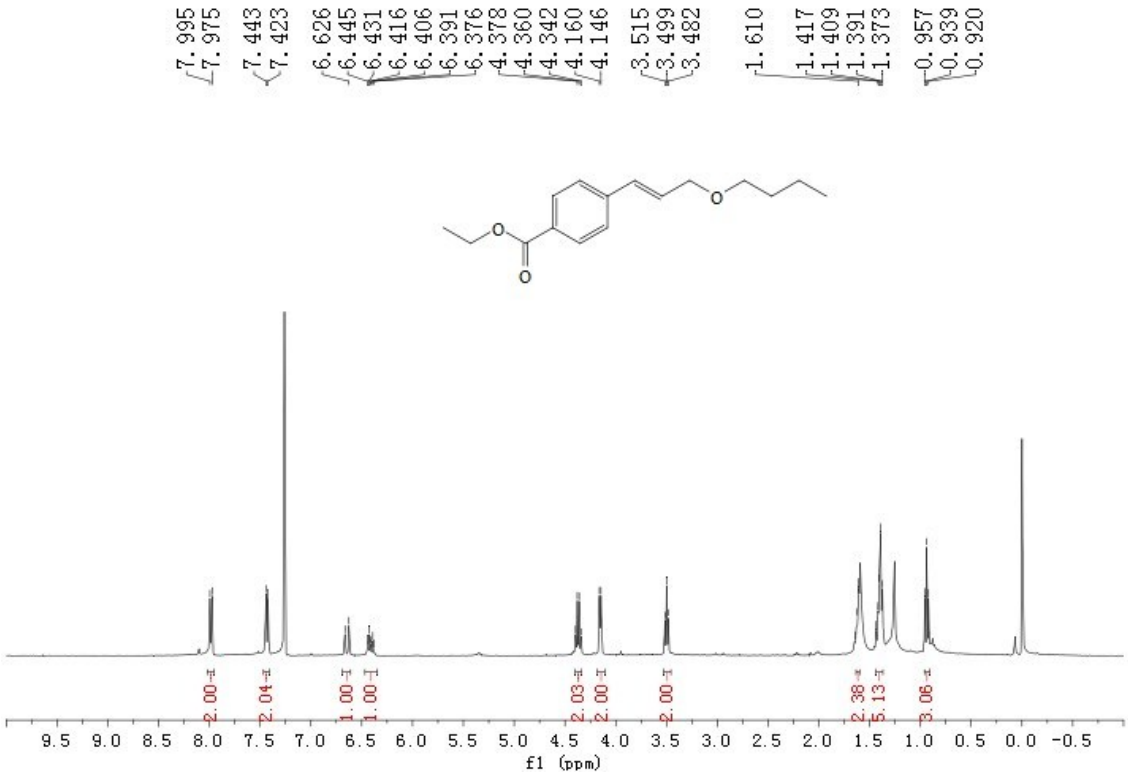


^{13}C NMR Spectrum of **5ha**

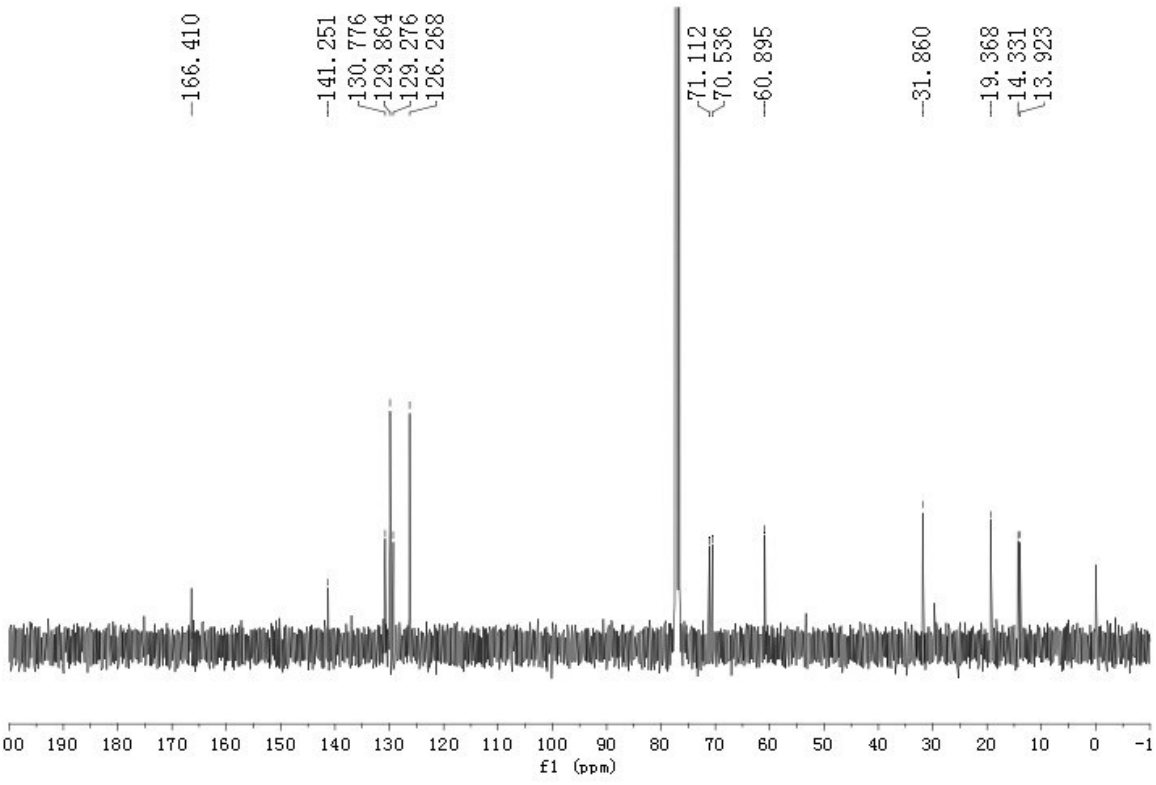


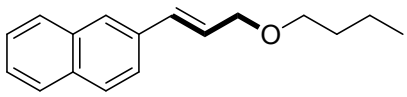


^{1}H NMR Spectrum of **5ia**

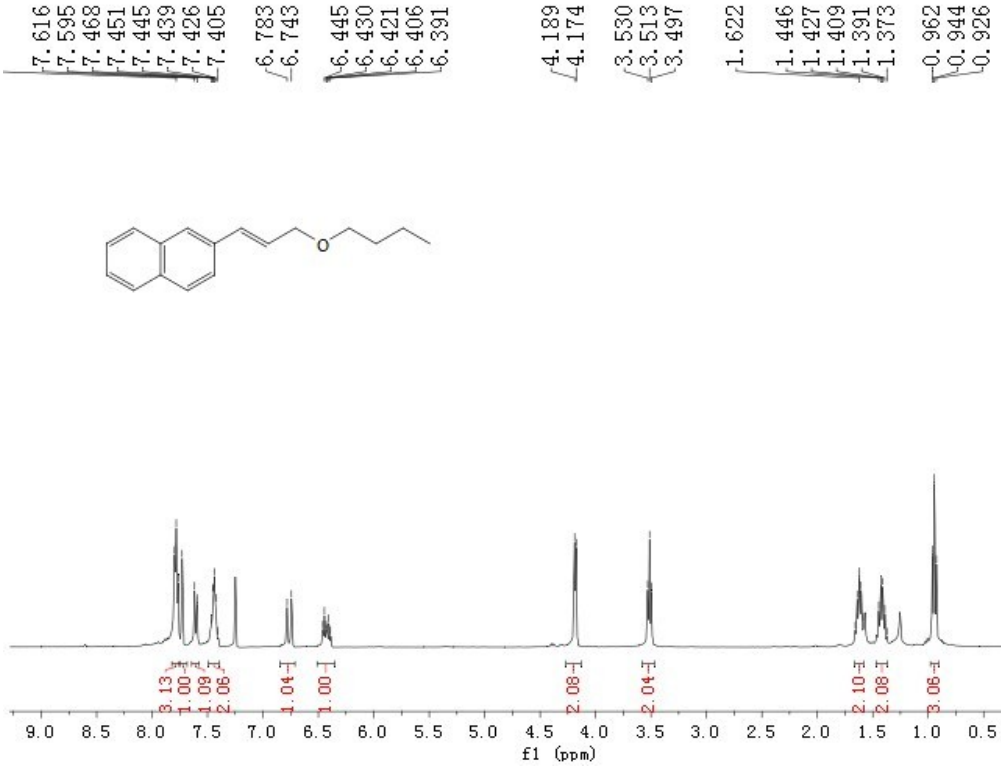


^{13}C NMR Spectrum of **5ia**

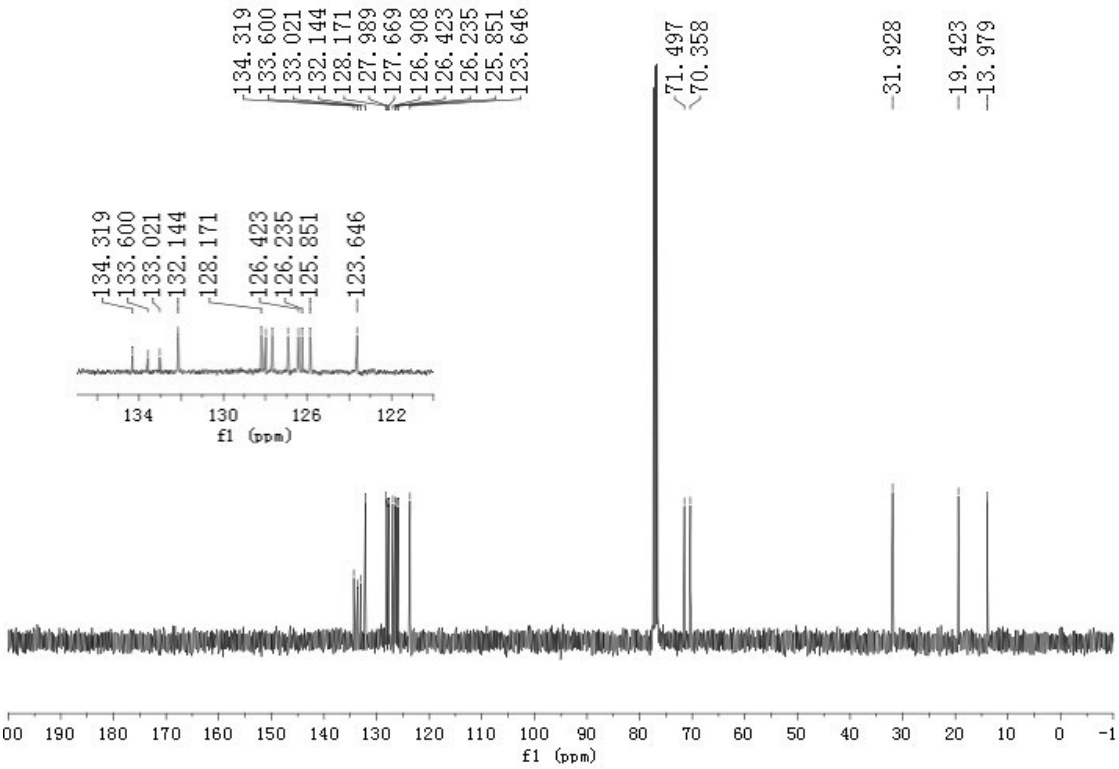


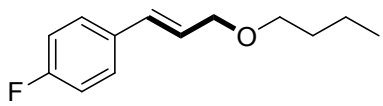


^{1}H NMR Spectrum of **5oa**

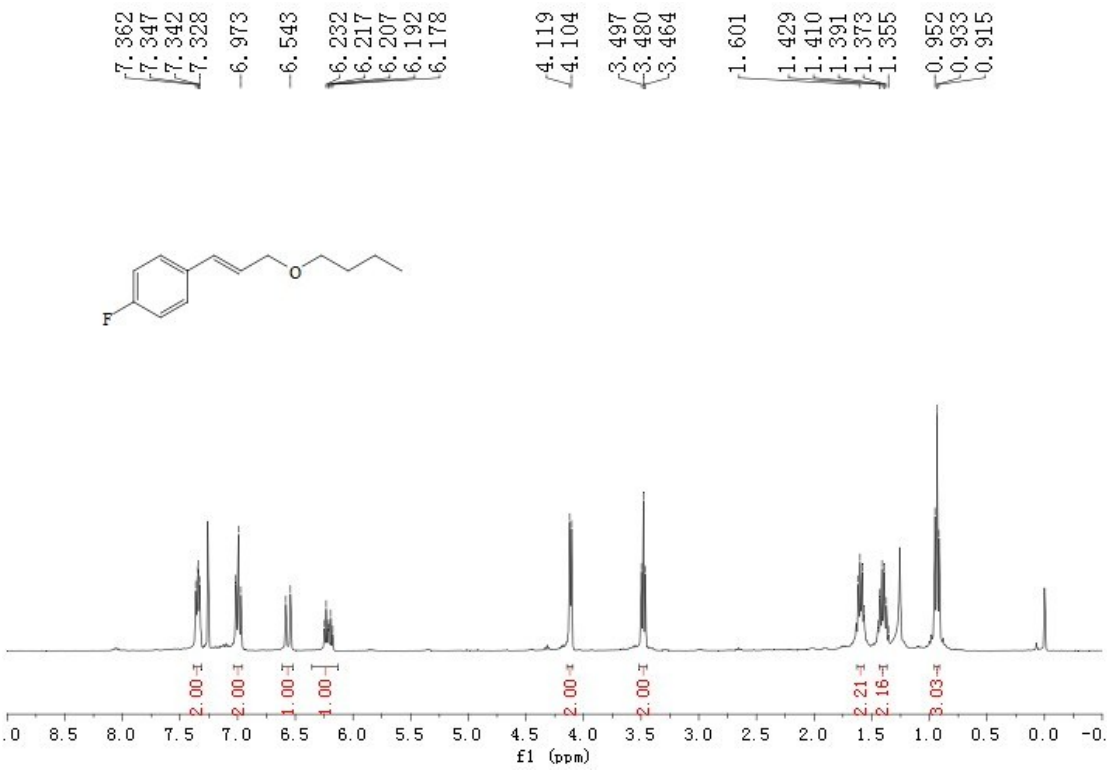


^{13}C NMR Spectrum of **5oa**

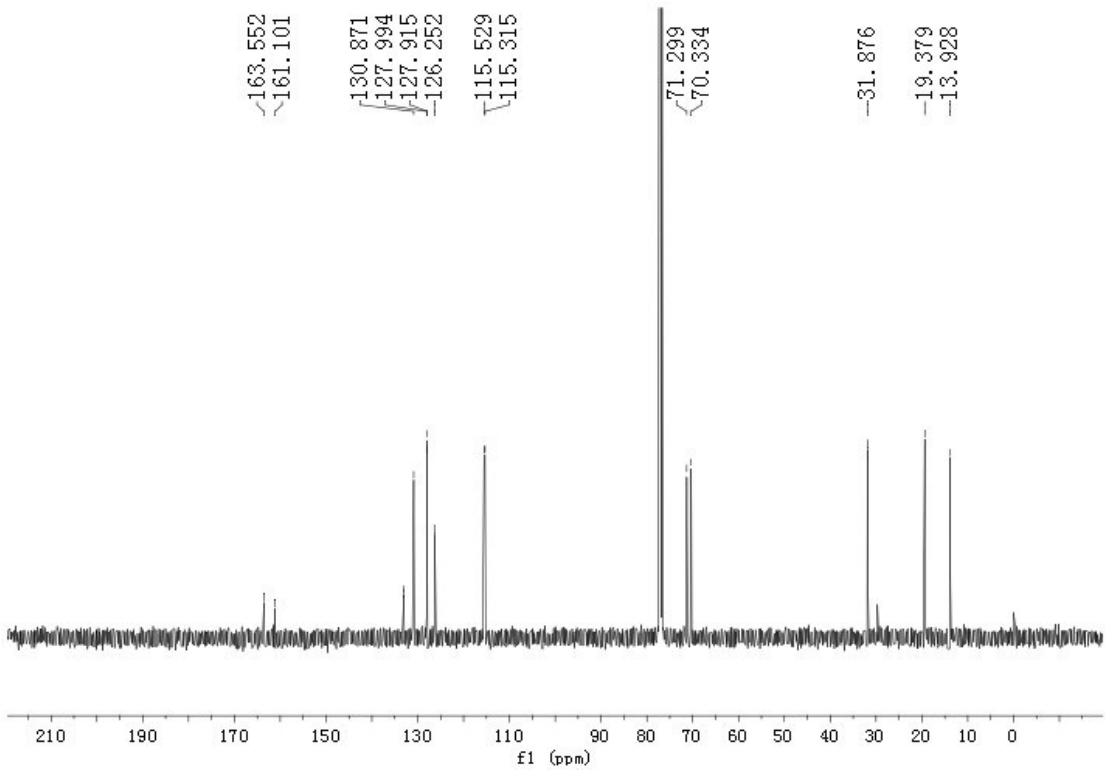




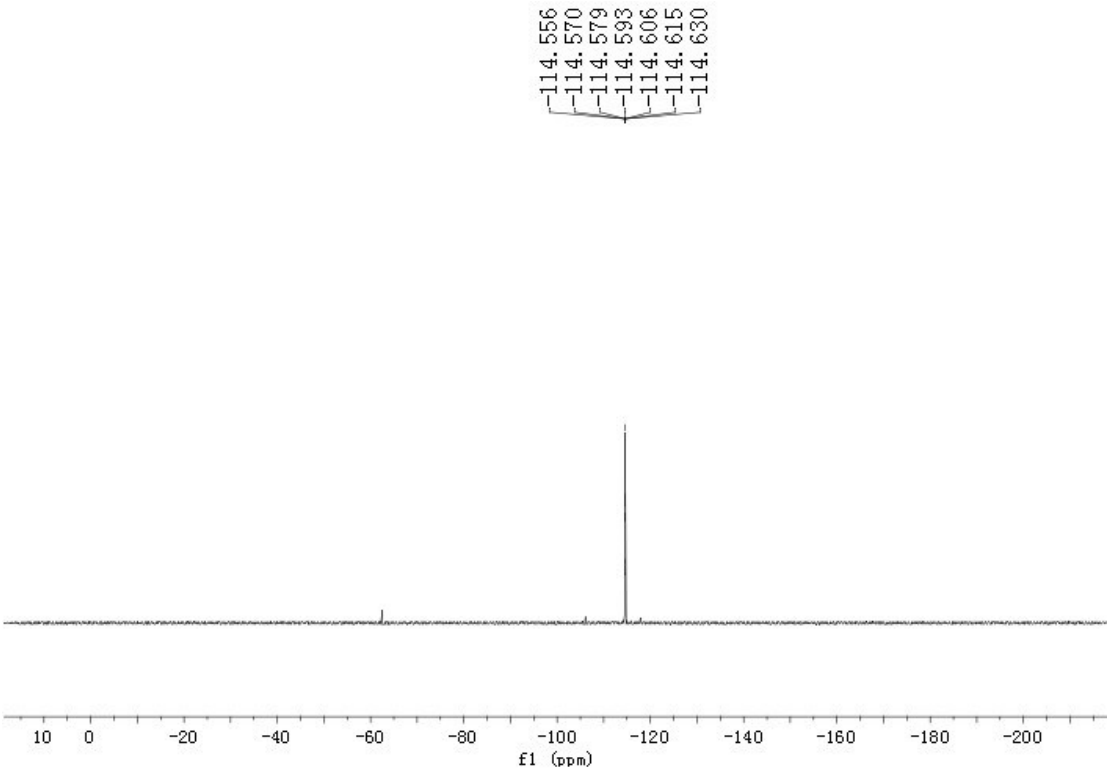
^{1}H NMR Spectrum of **5qa**



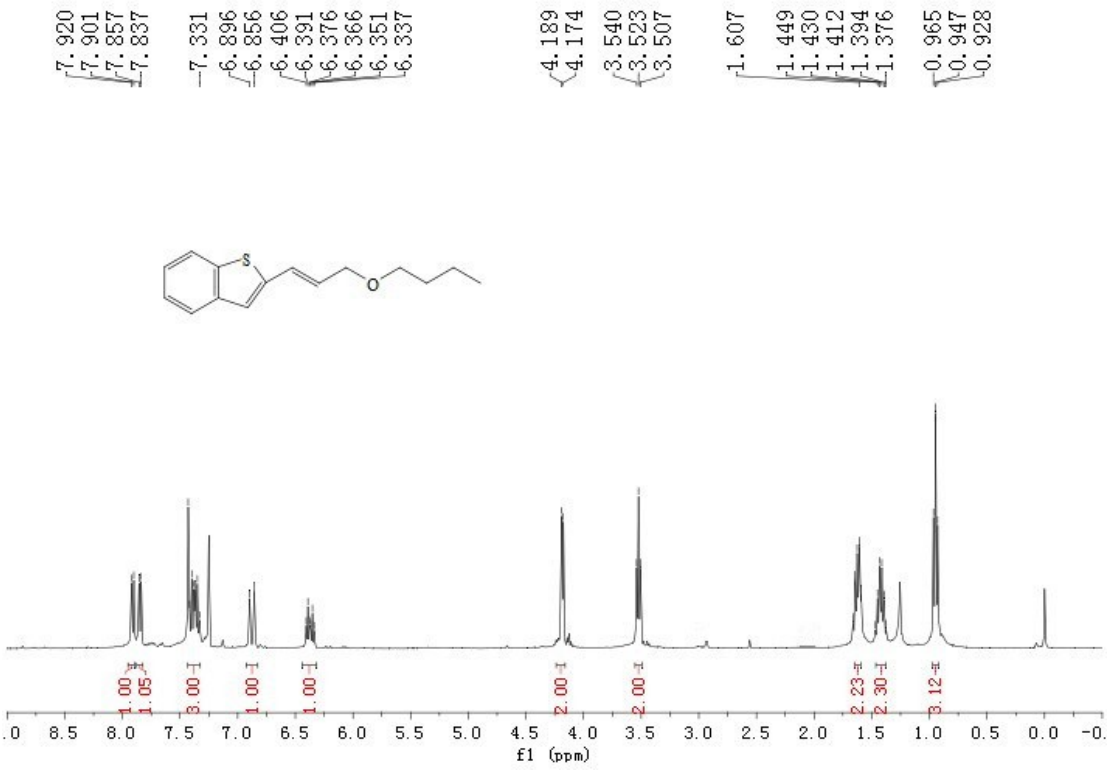
^{13}C NMR Spectrum of **5qa**



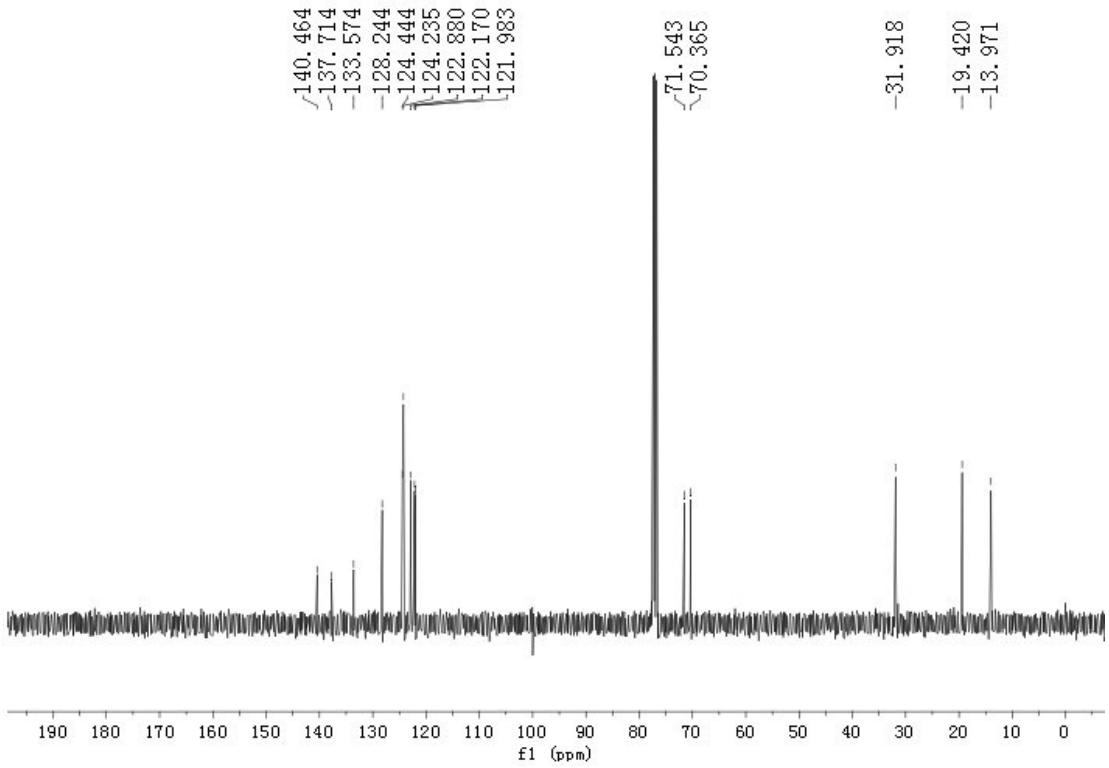
^{19}F NMR Spectrum of **5qa**



^{1}H NMR Spectrum of **5ua**



^{13}C NMR Spectrum of **5ua**


140.464
137.714
133.574
128.244
124.444
124.235
122.880
122.170
121.983
71.543
70.365
31.918
19.420
13.971
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)