Electronic Supplementary Material (ESI) for Green Chemistry.

Metal-free, visible-light-induced decarboxylative alkylation of Baylis-Hillman acetates with *N*-(acyloxy)phthalimides

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1. Experimental section

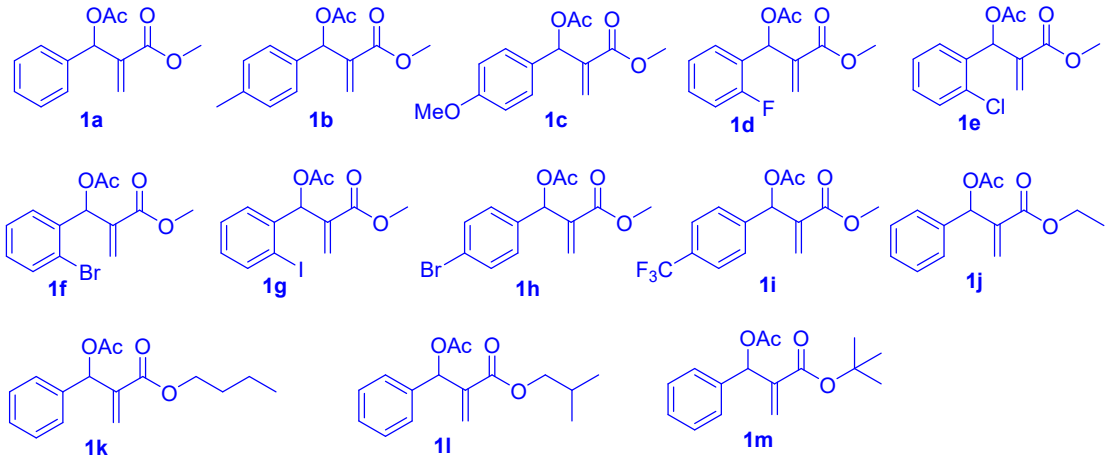
All chemicals were purchased from the Wencai New Material Technology and Merck in high purity and were used directly without any purification. Solvents were freshly distilled prior to use. All reactions were carried out under argon atmosphere unless noted. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance III 500 or Avance HD 600 MHz spectrometer in $CDCl_3$ solution. High resolution mass (HRMS) spectra were measured with a VG Auto Spec-3000 spectrometer. Melting points (m.p.) were determined with a digital electro thermal apparatus without further correction. TLC analyses were performed on commercial glass plates bearing a 0.25mm layer of Merck silica gel 60 F254. Silica gel (200-300mesh) was used for column chromatography.

2. Experimental procedures

A. General procedure for preparation of Baylis-Hillman acetates (1a-m)[1]

The Morita-Baylis-Hillman (MBH) adducts was synthesized by literature[2]. To a stirred solution of MBH products (1.0 equiv.) in dichloromethane was added acetic anhydride (1.5 equiv.) and *N,N*-dimethylaminopyridine (0.2 equiv.) at room temperature. After stirring at the same temperature for 1 hour, the reaction mixture was treated with water and extracted with dichlorormethane. The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure and purified by silica gel column chromatography.

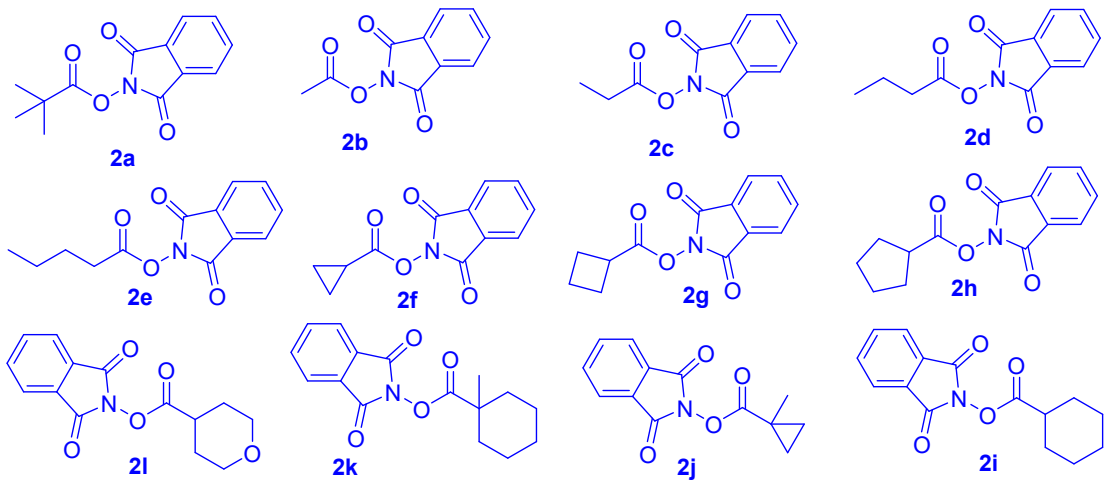
Baylis-Hillman acetates (1a-m) were synthesized using the above method:

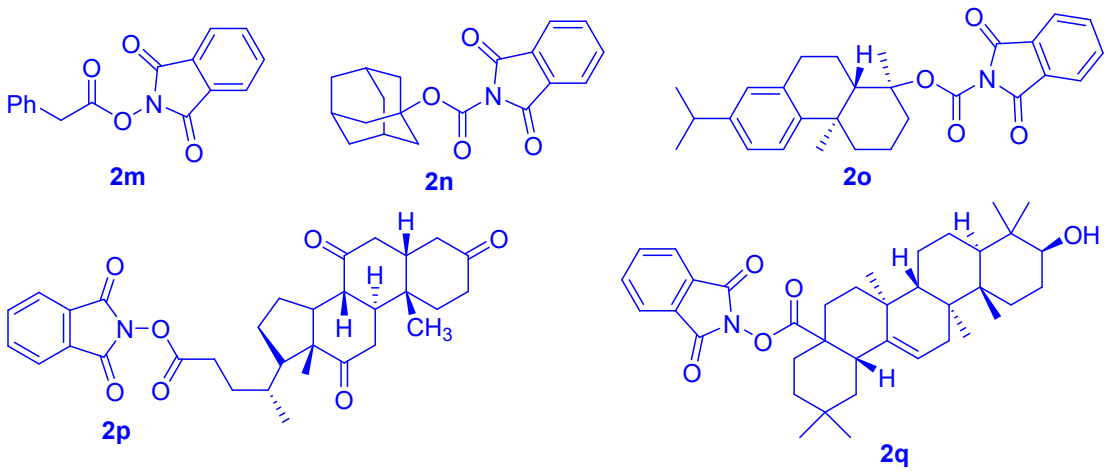


B. General procedure for preparation of NHPI Esters (2a-q)[3]

To an oven-dried round-bottom flask with a magnetic stir bar was added acid (1.0 equiv.), N-hydroxyphthalimide (1.1 equiv.), DCC (1.2 equiv.) and DMAP (0.1 equiv.). Dry dichloromethane (10 mL) was added and the mixture was allowed to stir at room temperature until the acid was consumed (followed by TLC). Typical reaction times were between 0.5 h and 12 h. The white precipitates were filtered off and the solvent was removed under reduced pressure. The desired products were obtained in the corresponding yields after purification by flash chromatography on silica gel eluting with hexane/ethyl acetate or hexane/dichloromethane.

NHPI Esters (2a-q) were synthesized using the above method:



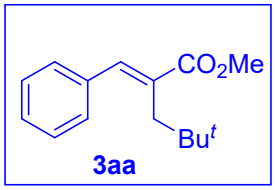


2m 2n 2o 2p 2q

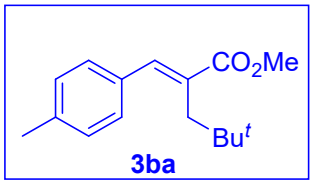
C. General Procedure for Synthesis of trisubstituted alkyl acrylate derivatives

An 25 mL oven-dried Schlenk tube was equipped with a stirring bar, Baylis-Hillman acetates **1** (0.2 mmol), *N*-(acyloxy)phthalimides **2** (0.3 mmol, 1.5 equiv.), and Rose bengal (0.01 mmol, 5 mol%). The mixture was degassed by using standard Schlenk techniques with an oil pump. Then DIPEA (0.4 mmol, 2.0 equiv.) and DCE/H_2O (v:v = 5:1, 2 mL) were in jected into the reaction tube. The solution was placed in a distance of 3 cm from 15 W blue LED at room temperature for 12 h. Upon completion, quench the reaction with saturated NaCl (10 mL), and the mixture was extracted with dichloromethane (3×15 mL). The combined organic layer was washed three times with H_2O (3×10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was purified by SiO_2 column chromatography to afford the desired products.

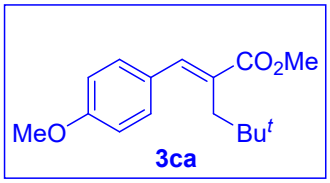
3. ^{1}H and ^{13}C NMR data of trisubstituted alkyl acrylates (3aa-3ma, 3ab-3aq)



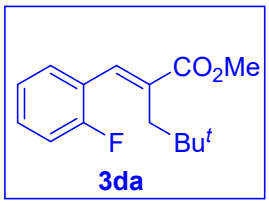
methyl (*E*)-2-benzylidene-4,4-dimethylpentanoate (3aa): Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.35 (d, J = 4.7 Hz, 4H), 7.29 (s, 1H), 3.80 (s, 3H), 2.65 (s, 2H), 0.75 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 139.9, 136.6, 132.7, 128.9, 128.3, 127.8, 51.9, 38.3, 33.3, 29.6. HRMS (ESI) [M+H$^+$] Calcd For $C_{15}H_{21}O_2$: 233.1536, Found: 233.1540.



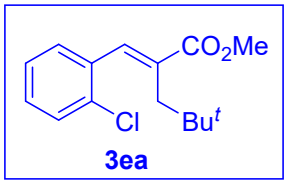
methyl (*E*)-4,4-dimethyl-2-(4-methylbenzylidene)pentanoate (3ba): White solid, Mp: 56-58 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 3.79 (s, 3H), 2.67 (s, 2H), 2.35 (s, 3H), 0.77 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 139.9, 137.8, 133.6, 131.8, 129.1, 129.1, 51.8, 38.3, 33.4, 29.6, 21.3. HRMS (ESI) [M+H$^+$] Calcd For $C_{16}H_{23}O_2$: 247.1693, Found: 247.1696.



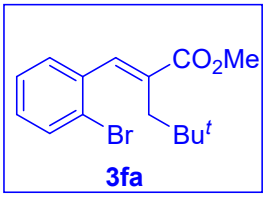
methyl (*E*)-2-(4-methoxybenzylidene)-4,4-dimethylpentanoate (3ca): Colourless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.36 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 2.68 (s, 2H), 0.79 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 159.3, 139.7, 130.8, 129.6, 128.9, 113.8, 55.2, 51.9, 38.2, 33.5, 29.6. HRMS (ESI) [M+H$^+$] Calcd For $C_{16}H_{23}O_3$: 263.1642, Found: 263.1646.



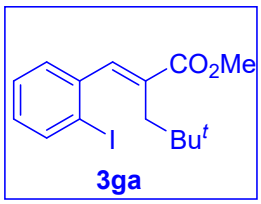
methyl (*E*)-2-(2-fluorobenzylidene)-4,4-dimethylpentanoate (3da): Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.29 (t, J = 7.2 Hz, 2H), 7.12 (t, J = 7.5 Hz, 1H), 7.06 (t, J = 9.3 Hz, 1H), 3.80 (s, 3H), 2.54 (s, 2H), 0.72 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 160.9, 158.9, 134.9, 133.2, 130.1(d, J_{CF} = 2.5 Hz), 129.7(d, J_{CF} = 7.6 Hz), 123.9(d, J_{CF} = 3.8 Hz), 115.7(d, J_{CF} = 21.4 Hz), 52.0, 38.8, 33.1, 29.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.8. HRMS (ESI) [M+H$^+$] Calcd For $C_{15}H_{20}FO_2$: 251.1442, Found: 251.1447.



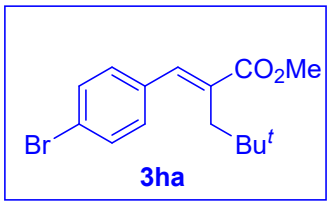
methyl (*E*)-2-(2-chlorobenzylidene)-4,4-dimethylpentanoate (3ea): Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.41-7.37 (m, 1H), 7.29-7.27 (m, 1H), 7.25-7.22 (m, 2H), 3.81 (s, 3H), 2.52 (s, 2H), 0.71 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 137.4, 135.3, 134.0, 133.8, 130.0, 129.5, 129.0, 126.5, 52.0, 38.4, 33.1, 29.3. HRMS (ESI) [M+H$^+$] Calcd For $C_{15}H_{20}ClO_2$: 267.1146, Found: 267.1149.



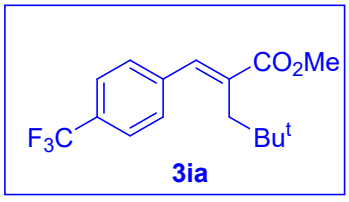
methyl (*E*)-2-(2-bromobenzylidene)-4,4-dimethylpentanoate (3fa): Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.32-7.26 (m, 2H), 7.15 (t, J = 8.5 Hz, 1H), 3.81 (s, 3H), 2.51 (s, 2H), 0.71 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 139.3, 137.1, 133.6, 132.7, 130.2, 129.2, 127.1, 124.0, 52.1, 38.3, 33.1, 29.4. HRMS (ESI) [M+H$^+$] Calcd For $C_{15}H_{20}BrO_2$: 311.0641, Found: 311.0647.



methyl (*E*)-2-(2-iodobenzylidene)-4,4-dimethylpentanoate (3ga): Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 7.9 Hz, 1H), 7.51 (s, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.24 (d, J = 6.8 Hz, 1H), 6.97 (t, J = 7.6 Hz, 1H), 3.82 (s, 3H), 2.50 (s, 2H), 0.71 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 143.1, 140.6, 139.2, 133.2, 129.7, 129.2, 128.0, 99.9, 52.2, 38.4, 33.4, 29.6. HRMS (ESI) [M+H$^+$] Calcd For $C_{15}H_{20}IO_2$: 359.0502, Found: 359.0506.

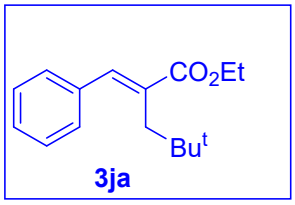


methyl (*E*)-2-(4-bromobenzylidene)-4,4-dimethylpentanoate (3ha): White solid, Mp: 70-72 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 3.80 (s, 3H), 2.61 (s, 2H), 0.74 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.0, 138.5, 135.5, 133.4, 131.6, 130.6, 121.9, 52.1, 38.3, 33.5, 29.6. HRMS (ESI) [M+H$^+$] Calcd For $C_{15}H_{20}BrO_2$: 311.0641, Found: 311.0644.

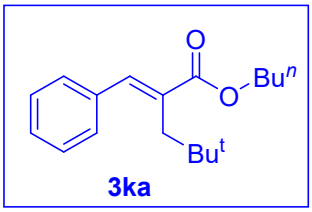


methyl (*E*)-4,4-dimethyl-2-(4-(trifluoromethyl)benzylidene)pentanoate (3ia): White solid, Mp:

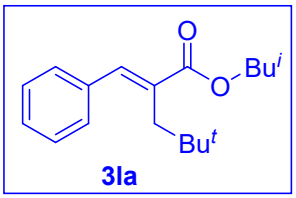
50-52 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.62 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 3.81 (s, 3H), 2.60 (s, 2H), 0.73 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9, 140.5（d, J_{CF} = 1.3 Hz）, 138.2, 134.8, 129.3, 125.5(q, J_{CF} = 3.8 Hz), 52.2, 38.6, 33.6, 29.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.6. HRMS (ESI) [M+H$^+$] Calcd For $C_{16}H_{20}F_3O_2$: 301.1410, Found: 301.1413.



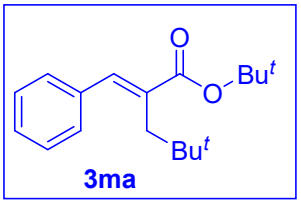
ethyl (*E*)-2-benzylidene-4,4-dimethylpentanoate(3ja): Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.35 (d, J = 4.4 Hz, 4H), 7.30-7.27 (m, 1H), 4.27 (s, 2H), 2.66 (s, 2H), 1.36 (s, 3H), 0.76 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 139.6, 136.7, 133.0, 128.9, 128.3, 127.7, 60.8, 38.2, 33.4, 29.6, 14.3. HRMS (ESI) [M+H$^+$] Calcd For $C_{16}H_{23}O_2$: 247.1693, Found: 247.1697.



butyl (*E*)-2-benzylidene-4,4-dimethylpentanoate(3ka): Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.35 (d, J = 4.5 Hz, 4H), 7.29-7.27 (m, 1H), 4.20 (t, J = 6.7 Hz, 2H), 2.66 (s, 2H), 1.73-1.68 (m, 2H), 1.48-1.43 (m, 2H), 0.98 (d, J = 7.4 Hz, 3H), 0.76 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 139.6, 136.9, 133.1, 129.1, 128.4, 127.8, 64.8, 38.3, 33.5, 30.9, 29.7, 19.4, 13.9. HRMS (ESI) [M+H$^+$] Calcd For $C_{18}H_{27}O_2$: 275.2006, Found: 275.2009.

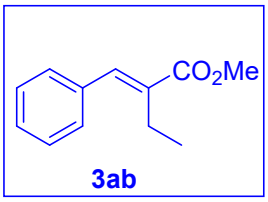


isobutyl (*E*)-2-benzylidene-4,4-dimethylpentanoate (3la): Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.38-7.34 (m, 4H), 7.28 (d, J = 4.7 Hz, 1H), 3.99 (s, 2H), 2.67 (s, 2H), 2.04 (dt, J = 13.4, 6.7 Hz, 1H), 1.02 (s, 6H), 0.76 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 139.6, 136.9, 133.2, 129.1, 128.5, 127.8, 71.2, 38.3, 33.5, 29.7, 28.0, 19.4. HRMS (ESI) [M+H$^+$] Calcd For $C_{18}H_{27}O_2$: 275.2006, Found: 275.2011.

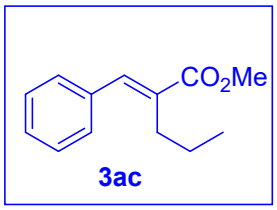


tert-butyl (*E*)-2-benzylidene-4,4-dimethylpentanoate (3ma): Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.34 (d, J = 4.4 Hz, 4H), 7.28-7.26 (m, 1H), 2.61 (s, 2H), 1.54 (s, 9H), 0.76 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 138.8, 137.1, 134.5, 129.0, 128.4,

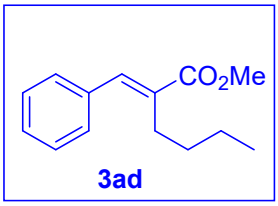
127.6, 80.6, 38.2, 33.5, 29.8, 28.2. HRMS (ESI) [M+H$^+$] Calcd For $C_{18}H_{27}O_2$: 275.2006, Found: 275.2009.



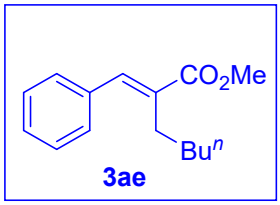
methyl (*E*)-2-benzylidenebutnoate (3ab): Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.41-7.36 (m, 4H), 7.33 (d, *J* = 8.7 Hz, 1H), 3.82 (s, 3H), 2.55 (q, *J* = 7.4 Hz, 2H), 1.18 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 138.7, 136.0, 134.9, 129.3, 128.6, 128.5, 52.0, 21.0, 14.0. HRMS (ESI) [M+H$^+$] Calcd For $C_{12}H_{15}O_2$: 191.1067, Found: 191.1071.



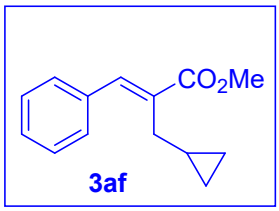
methyl (*E*)-2-benzylidenepentanoate (3ac): Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.36 (td, *J* = 14.0, 7.0 Hz, 5H), 3.82 (s, 3H), 2.54-2.47 (m, 2H), 1.61-1.54 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 139.0, 136.0, 133.7, 129.3, 128.6, 128.4, 52.0, 29.7, 22.7, 14.3. HRMS (ESI) [M+H$^+$] Calcd For $C_{13}H_{17}O_2$: 205.1223, Found: 205.1227.



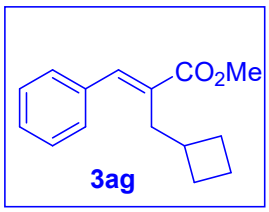
methyl (*E*)-2-benzylidenehexanoate (3ad): Colourless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.41-7.34 (m, 4H), 7.32 (s, 1H), 3.81 (s, 3H), 2.54-2.49 (m, 2H), 1.53 (s, 2H), 1.38 (d, *J* = 7.5 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1, 138.9, 135.9, 133.7, 129.3, 128.6, 128.4, 52.1, 31.6, 27.4, 23.0, 14.0. HRMS (ESI) [M+H$^+$] Calcd For $C_{14}H_{19}O_2$: 219.1380, Found: 219.1385.



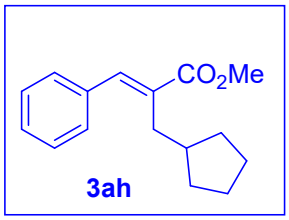
methyl (*E*)-2-benzylideneheptanoate (3ae): Colourless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.41-7.35 (m, 4H), 7.32 (t, *J* = 7.1 Hz, 1H), 3.81 (s, 3H), 2.53-2.48 (m, 2H), 1.54 (s, 2H), 1.33 (d, *J* = 3.6 Hz, 4H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1, 138.8, 135.8, 133.7, 129.2, 128.5, 128.3, 52.0, 31.9, 29.0, 27.5, 22.4, 14.1. HRMS (ESI) [M+H$^+$] Calcd For $C_{15}H_{21}O_2$: 233.1536, Found: 233.1539.



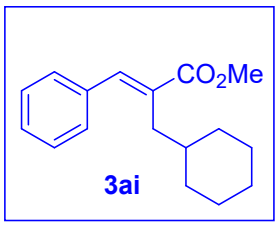
methyl (*E*)-2-(cyclopropylmethyl)-3-phenylacrylate (3af): Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.39 (d, *J* = 6.9 Hz, 5H), 3.83 (s, 3H), 2.51 (d, *J* = 6.5 Hz, 2H), 0.95 – 0.87 (m, 1H), 0.45 – 0.40 (m, 2H), 0.15 (q, *J* = 4.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 139.0, 135.8, 133.0, 129.2, 128.4, 128.3, 51.9, 31.1, 10.5, 4.5. HRMS (ESI) [M+H$^+$] Calcd For $C_{14}H_{17}O_2$: 217.1223, Found: 217.1227.



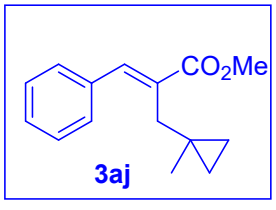
methyl (*E*)-2-(cyclobutylmethyl)-3-phenylacrylate (3ag)[4]: Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.38 (d, *J* = 8.5 Hz, 4H), 7.32 (d, *J* = 6.7 Hz, 1H), 3.81 (s, 3H), 2.68 (d, *J* = 7.2 Hz, 2H), 2.53-2.48 (m, 1H), 1.98 (d, *J* = 8.1 Hz, 2H), 1.74 (dt, *J* = 18.9, 8.9 Hz, 2H), 1.64 (q, *J* = 8.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3, 139.2, 136.1, 132.6, 129.3, 128.5, 128.3, 52.0, 36.1, 33.6, 28.5, 18.5. HRMS (ESI) [M+H$^+$] Calcd For $C_{15}H_{19}O_2$: 231.1380, Found: 231.1385.



methyl (*E*)-2-(cyclopentylmethyl)-3-phenylacrylate (3ah)[4]: Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.38 (d, *J* = 4.4 Hz, 4H), 7.33-7.29 (m, 1H), 3.82 (s, 3H), 2.62 (d, *J* = 7.3 Hz, 2H), 2.03 (s, 1H), 1.68 (s, 2H), 1.54 (s, 2H), 1.47 (s, 2H), 1.11 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3, 138.9, 136.1, 133.6, 129.2, 128.4, 128.1, 51.9, 40.1, 32.4, 24.7.

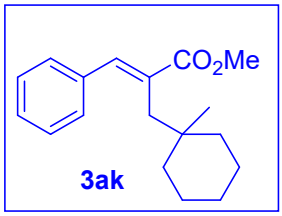


methyl (*E*)-2-(cyclohexylmethyl)-3-phenylacrylate (3ai)[4]: Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.37 (d, *J* = 5.8 Hz, 4H), 7.31 (s, 1H), 3.81 (s, 3H), 2.49 (d, *J* = 7.1 Hz, 2H), 1.65 (t, *J* = 11.3 Hz, 6H), 1.20-1.11 (m, 3H), 0.88 (t, *J* = 11.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 139.4, 136.1, 132.8, 129.3, 128.4, 128.1, 51.9, 37.8, 34.4, 33.2, 26.4, 26.3.

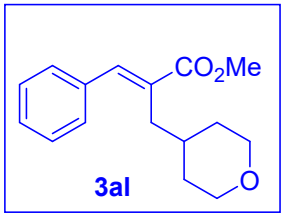


methyl (*E*)-2-((1-methylcyclopropyl)methyl)-3-phenylacrylate (3aj): Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.41 (dd, *J* = 16.9, 7.4 Hz, 4H), 7.32 (t, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 2.73 (s, 2H), 1.01 (s, 3H), 0.33 (s, 2H), 0.20 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.7,

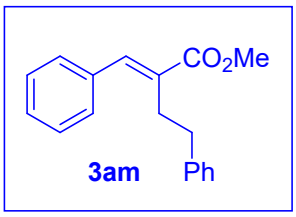
140.3, 136.0, 131.7, 129.6, 128.5, 128.4, 52.0, 33.9, 24.4, 15.2, 12.0. HRMS (ESI) [M+H$^+$] Calcd For $C_{15}H_{19}O_2$: 231.1380, Found: 231.1384.



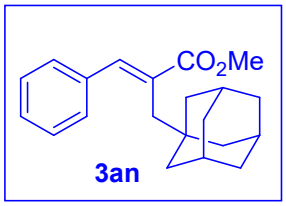
methyl (*E*)-2-((1-methylcyclohexyl)methyl)-3-phenylacrylate (3ak): White solid, Mp: 48-50 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.34 (d, *J* = 6.4 Hz, 4H), 7.28 (d, *J* = 3.6 Hz, 1H), 3.80 (s, 3H), 2.66 (s, 2H), 1.32-1.25 (m, 5H), 1.12 (dd, *J* = 8.1, 4.7 Hz, 5H), 0.70 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 139.8, 136.8, 132.5, 128.9, 128.3, 127.7, 51.9, 37.8, 35.9, 26.2, 24.0, 21.9. HRMS (ESI) [M+H$^+$] Calcd For $C_{18}H_{25}O_2$: 273.1849, Found: 273.18456.



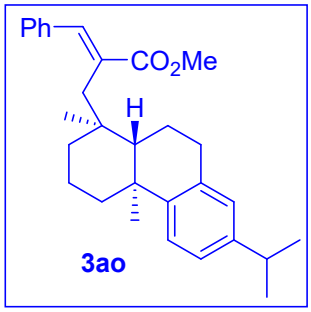
methyl (*E*)-3-phenyl-2-((tetrahydro-2H-pyran-4-yl)methyl)acrylate (3al): Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.34 (dt, *J* = 17.2, 8.2 Hz, 5H), 3.87 (d, *J* = 14.6 Hz, 2H), 3.81 (s, 3H), 3.29 (t, *J* = 11.1 Hz, 2H), 2.55 (d, *J* = 7.2 Hz, 2H), 1.76 (s, 1H), 1.53 (d, *J* = 13.0 Hz, 2H), 1.27-1.19 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 140.4, 135.9, 131.6, 129.2, 128.6, 128.4, 68.0, 52.1, 35.0, 33.9, 33.0. HRMS (ESI) [M+H$^+$] Calcd For $C_{16}H_{21}O_3$: 261.1485, Found: 261.1489.



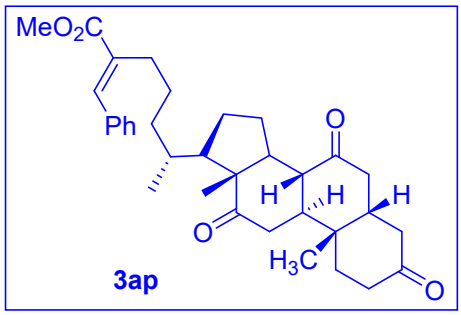
methyl (*E*)-2-benzylidene-4-phenylbutanoate (3am)[5]: Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.30 (dd, *J* = 16.4, 7.8 Hz, 5H), 7.21 (d, *J* = 7.5 Hz, 3H), 3.85 (s, 3H), 2.86 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 141.5, 139.8, 135.6, 132.6, 129.0, 128.5, 128.4, 128.4, 126.0, 52.0, 35.3, 29.6.



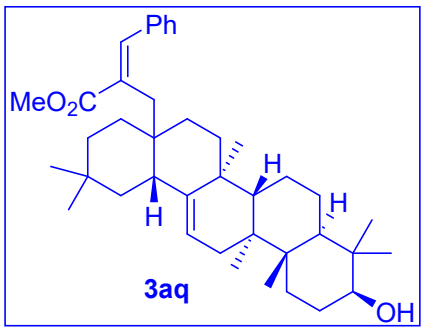
methyl (*E*)-2-(((3r,5r,7r)-adamantan-1-yl)methyl)-3-phenylacrylate (3an): Colourless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.36 (d, *J* = 4.4 Hz, 4H), 7.30-7.27 (m, 1H), 3.80 (s, 3H), 2.52 (s, 2H), 1.83 (s, 3H), 1.60-1.50 (m, 6H), 1.32 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.4, 140.1, 136.6, 131.3, 129.0, 128.4, 127.8, 52.0, 42.3, 39.4, 36.8, 35. 5, 28.7. HRMS (ESI) [M+H$^+$] Calcd For $C_{21}H_{27}O_2$: 311.2006, Found: 311.2011.



methyl (*E*)-2-(((1S,4aS,10aS)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-3-phenylacrylate (3ao): Colourless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.25 (s, 3H), 7.19 (s, 1H), 7.14 (s, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.87 (s, 1H), 6.78 (s, 1H), 3.70 (s, 3H), 2.92 (s, 1H), 2.74 (s, 2H), 2.61 (s, 1H), 2.51 (s, 1H), 2.08 (s, 1H), 1.71 (s, 1H), 1.50 (d, *J* = 47.9 Hz, 2H), 1.22 (d, *J* = 15.9 Hz, 2H), 1.13 (d, *J* = 6.9 Hz, 6H), 1.04 (s, 3H), 0.90 (s, 2H), 0.78 (s, 1H), 0.67 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 147.7, 145.5, 140.2, 136.7, 134.9, 132.4, 129.0, 128.5, 127.9, 126.8, 124.0, 123.8, 52.1, 49.0, 39.6, 38.4, 38.3, 37.8, 37.6, 33.5, 30.1, 25.5, 24.1, 19.3, 19.3, 18.7. HRMS (ESI) [M+H$^+$] Calcd For $C_{30}H_{39}O_2$: 431.2954, Found: 431.2957.



methyl (6R)-2-((*E*)-benzylidene)-6-((5S,8R,9S,10S,13R,17S)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)heptanoate (3ap):White solid, Mp: 164-166°C.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.37-7.31 (m, 3H), 3.82 (s, 3H), 2.95-2.85 (m, 3H), 2.48 (d, *J* = 39.2 Hz, 2H), 2.28 (d, *J* = 49.7 Hz, 6H), 2.15 (s, 2H), 2.01 (d, *J* = 35.8 Hz, 4H), 1.85 (s, 1H), 1.62 (s, 2H), 1.48 (s, 2H), 1.40 (s, 3H), 1.27 (s, 4H), 1.05 (s, 3H), 0.84 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 212.2, 209.3, 209.0, 169.0, 138.8, 135.8, 133.6, 129.2, 128.5, 128.4, 56.9, 52.0, 51.8, 49.0, 46.9, 45.8, 45.6, 45.0, 42.8, 38.7, 36.5, 36.0, 35.7, 35.4, 35.3, 27.8, 26.2, 25.2, 21.9, 18.9, 11.9. HRMS (ESI) [M+H$^+$] Calcd For $C_{34}H_{45}O_5$: 533.3262, Found: 533.3267.



methyl (*E*)-2-(((6aS,6bR,8aR,10S,12aS,12bS,14bR)-10-hydroxy-2,2,6a,9,9,12a,12b-heptamethyl-1,3,4,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-octadecahydropicen-4a(2*H*)-yl)methyl)-3-phenylacrylate(3aq): Colourless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.28 (m, 3H), 4.58 (s, 1H), 3.79 (s, 3H), 3.21 (dd, *J* = 11.3, 4.3 Hz, 1H), 2.66 (d, *J* = 13.5

Hz, 1H), 2.55 (d, *J* = 13.5 Hz, 1H), 1.75-1.70 (m, 3H), 1.64-1.53 (s, 8H), 1.47-1.41 (m, 3H), 1.28-1.26 (m, 3H), 1.07 (s, 3H), 0.99 (s, 3H), 0.94 (s, 3H), 0.92 (s, 3H), 0.88-0.84 (m, 7H), 0.79 (s, 3H), 0.78 (s, 3H), 0.71 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 144.0, 139.5, 136.8, 133.6, 128.8, 128.4, 127.5, 122.5, 79.0, 55.1, 52.0, 47.5, 47.0, 45.8, 41.3, 39.8, 38.8, 38.5, 38.0, 36.9, 34.4, 34.2, 33.1, 32.5, 30.9, 30.7, 28.1, 27.2, 26.5, 26.2, 25.3, 23.6, 23.3, 18.4, 16.9, 15.6, 15.5. HRMS (ESI) [$M+H^+$] Calcd For $C_{40}H_{59}O_3$: 587.4459, Found: 587.4454.

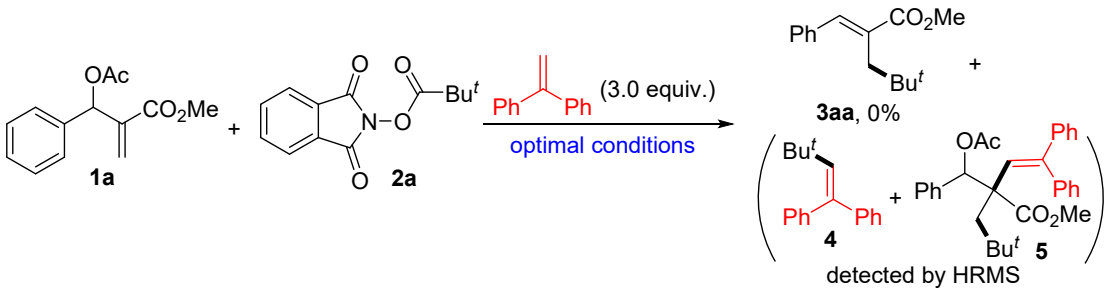
Reference:

1. W.-X. Wang, Q.-Z. Zhang, T.-Q. Zhang, Z.-S. Li, W. Zhang, W. Yu, *Adv. Synth. Catal.* **2015,** *357*, 221.
2. Z. He, B. Wibbeling, A. Studer, *Adv. Synth. Catal.* **2013,** *355*, 3639.
3. G. Pratsch, G. L. Lackner, L. E. Overman, *J. Org. Chem.* **2015,** *80*, 6025.
4. H. Ye, H. Zhao, S. Ren, H. Ye, D. Cheng, X. Li, X. Xu, *Tetrahedron Lett.* **2019,** *60*, 1302.

4. Evidence for a radical pathway

Catalytic reaction interfered with a radical quencher:

An 25 mL oven-dried Schlenk tube was equipped with a stirring bar, Baylis-Hillman acetate **1a** (0.2 mmol), *N*-(acyloxy)phthalimides **2a** (0.3 mmol, 1.5 equiv.), Rose bengal (0.01 mmol, 5 mol%) and 1,1-diphenylethylene (0.6 mmol, 3.0 equiv.). The mixture was degassed by using standard Schlenk techniques with an oil pump. Then DIPEA (0.4 mmol, 2.0 equiv.) and DCE/H_2O (v:v = 5:1, 2 mL) were injected into the reaction tube. The solution was placed in a distance of 3 cm from 15 W blue LED. After being stirred at room temperature for 12 h under air, the solution was used directly for HRMS analysis.



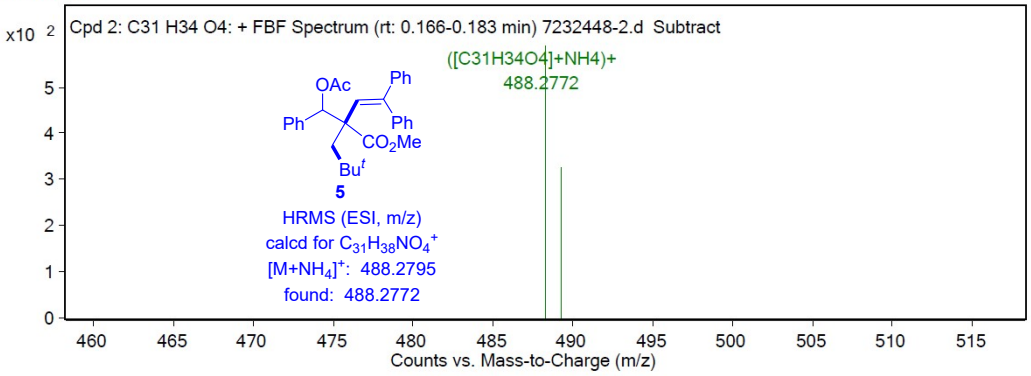
Qualitative Compound Report

Data File	7232448-2.d	**Sample Name**	7232448-2
Sample Type	Sample	**Position**	P1-C9
Instrument Name	Instrument 1	**User Name**	
Acq Method	pos-1min.m	**Acquired Time**	7/30/2022 2:53:39 PM
IRM Calibration Status	Success	**DA Method**	default.m
Comment			
Sample Group		**Info.**	
Stream Name	LC 1	**Acquisition SW Version**	6200 series TOF/6500 series Q-TOF B.08.00 (B8058.0)

Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 2: C31 H34 O4	0.176	470.2433	590	C31 H34 O4	470.2457	-5.17
Cpd 1: C18 H20	0.266	236.1572	50096	C18 H20	236.1565	2.89

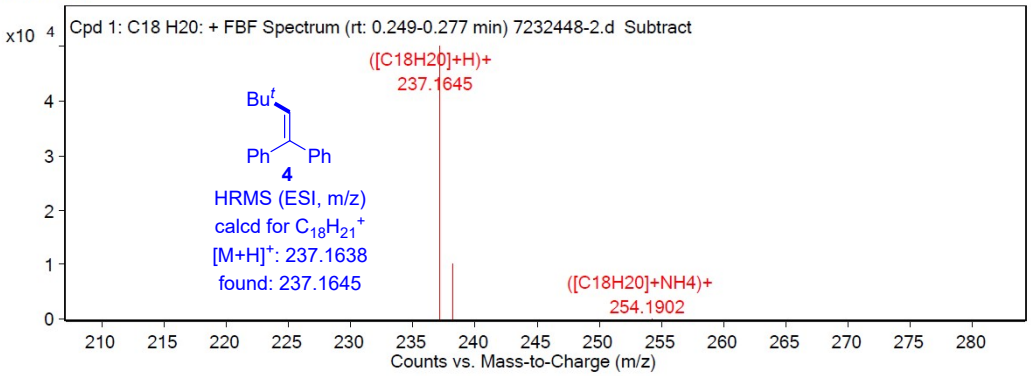
MS Zoomed Spectrum



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
488.2772	1	589.74	C31H34O4	(M+NH4)+
489.2803	1	325.57	C31H34O4	(M+NH4)+

MS Zoomed Spectrum



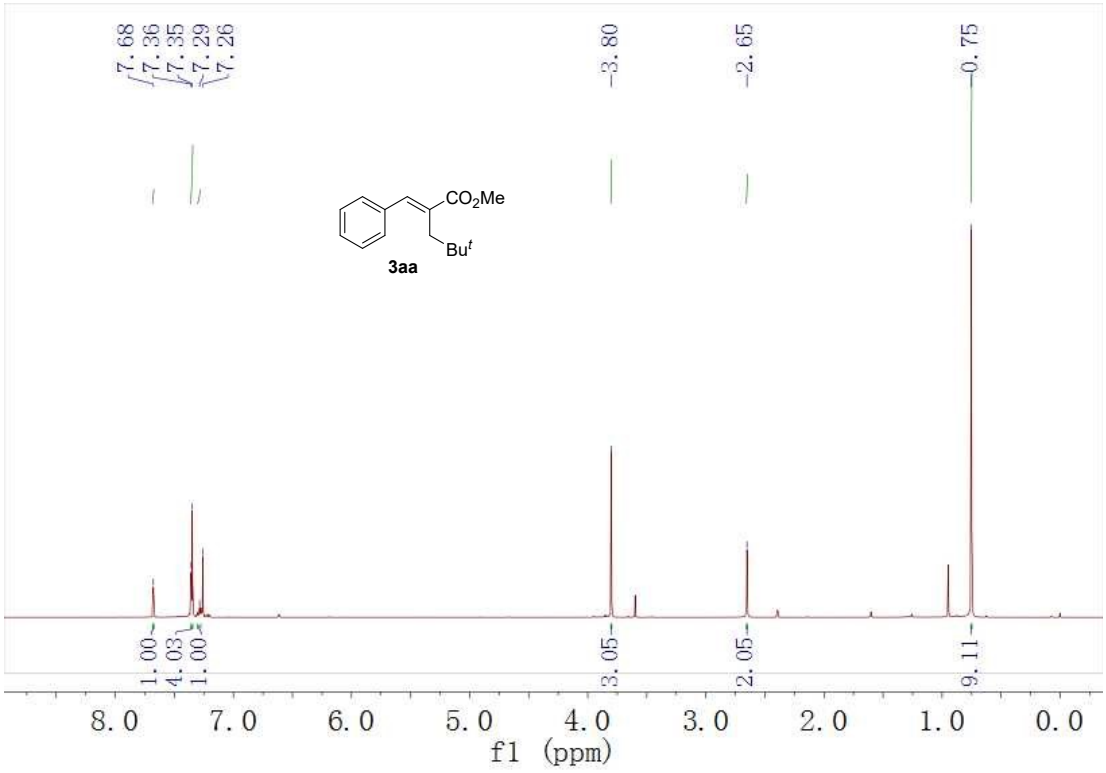
MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
237.1645	1	50096.04	C18H20	(M+H)+
238.1676	1	10046.67	C18H20	(M+H)+
254.1902	1	105.93	C18H20	(M+NH4)+

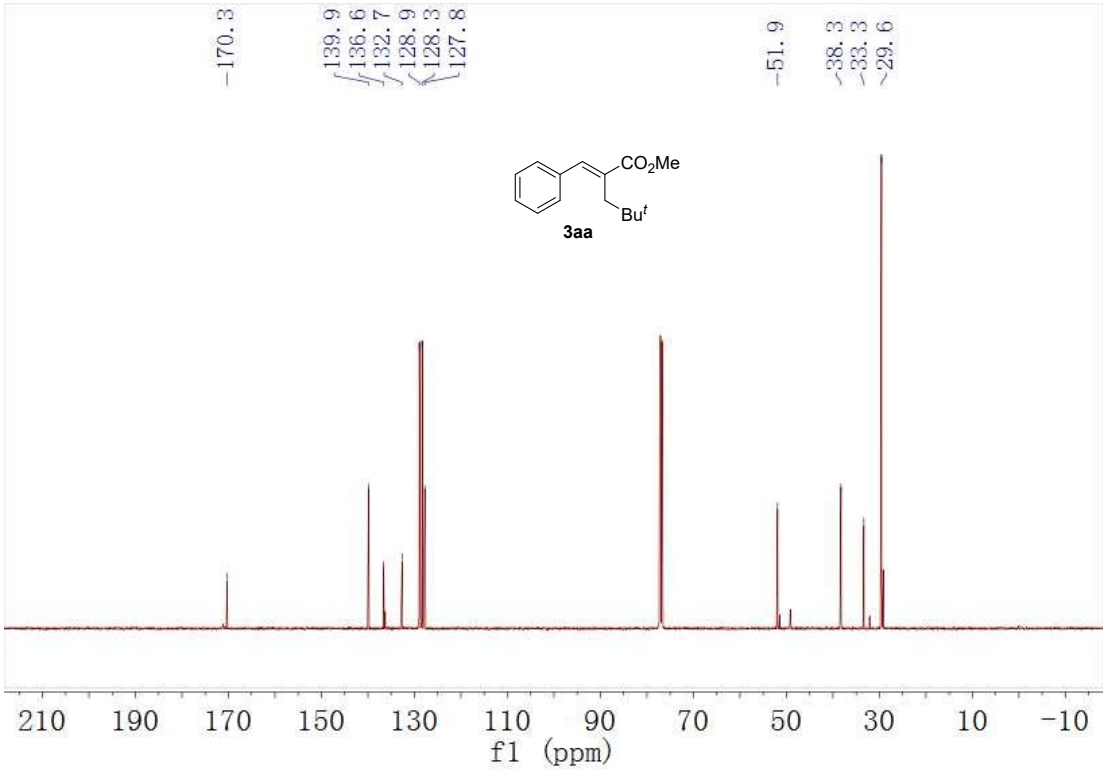
--- End Of Report ---

5. ^{1}H and ^{13}C NMR spectra of trisubstituted alkyl acrylates (3aa-3ma, 3ab-3aq)

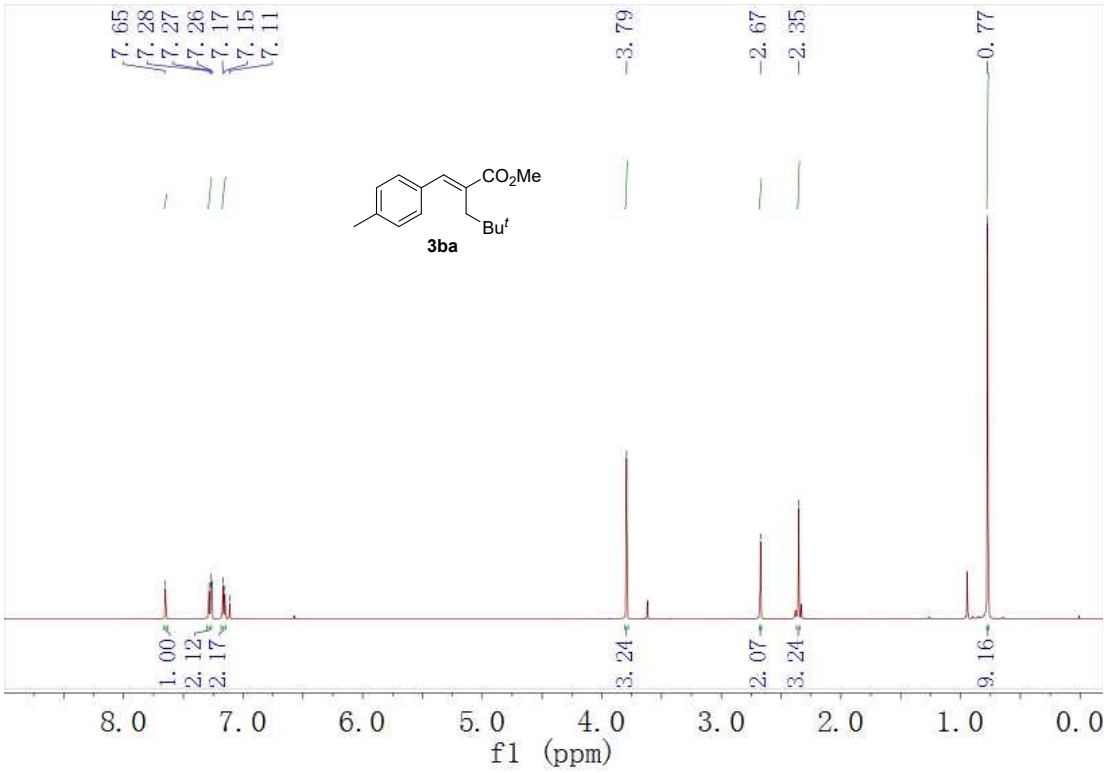
^{1}H NMR of **3aa** in $CDCl_3$



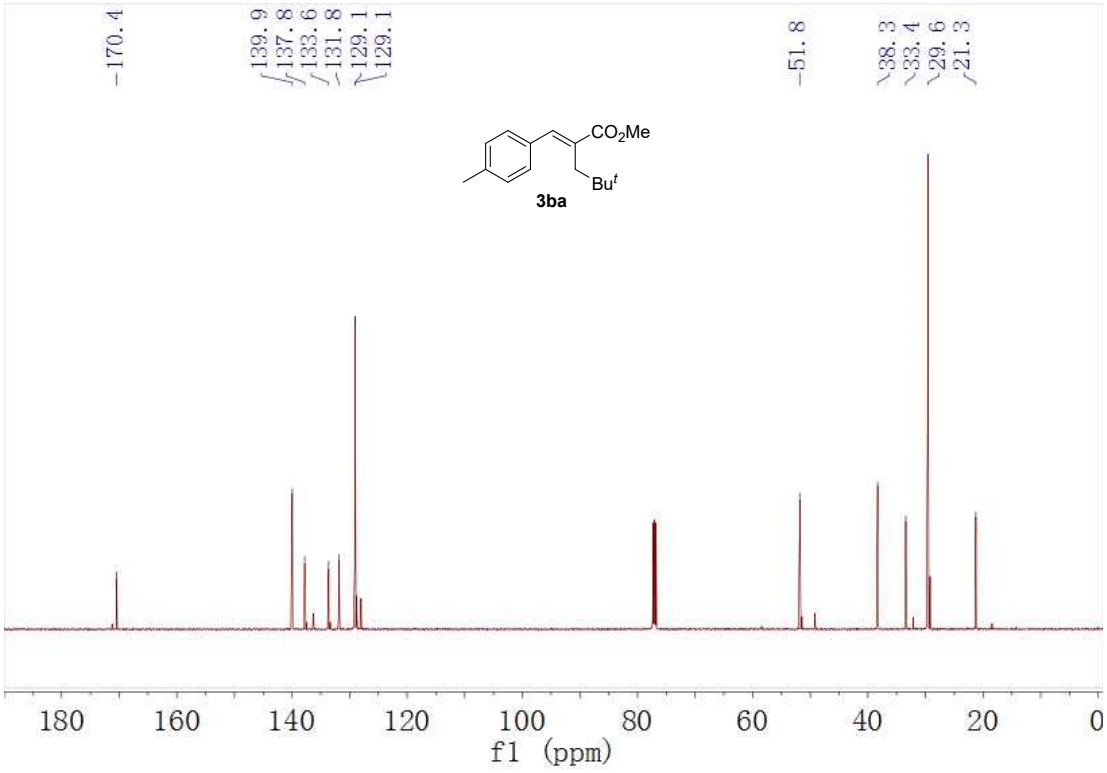
^{13}C NMR of **3aa** in $CDCl_3$



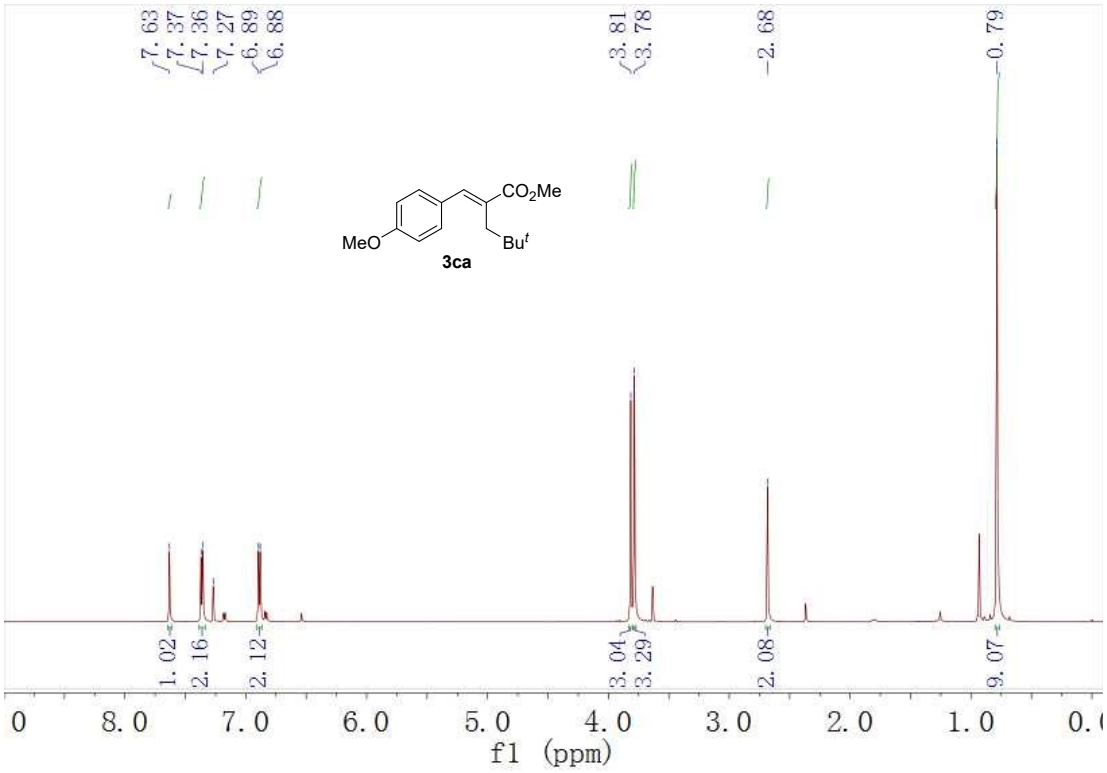
^{1}H NMR of **3ba** in $CDCl_3$



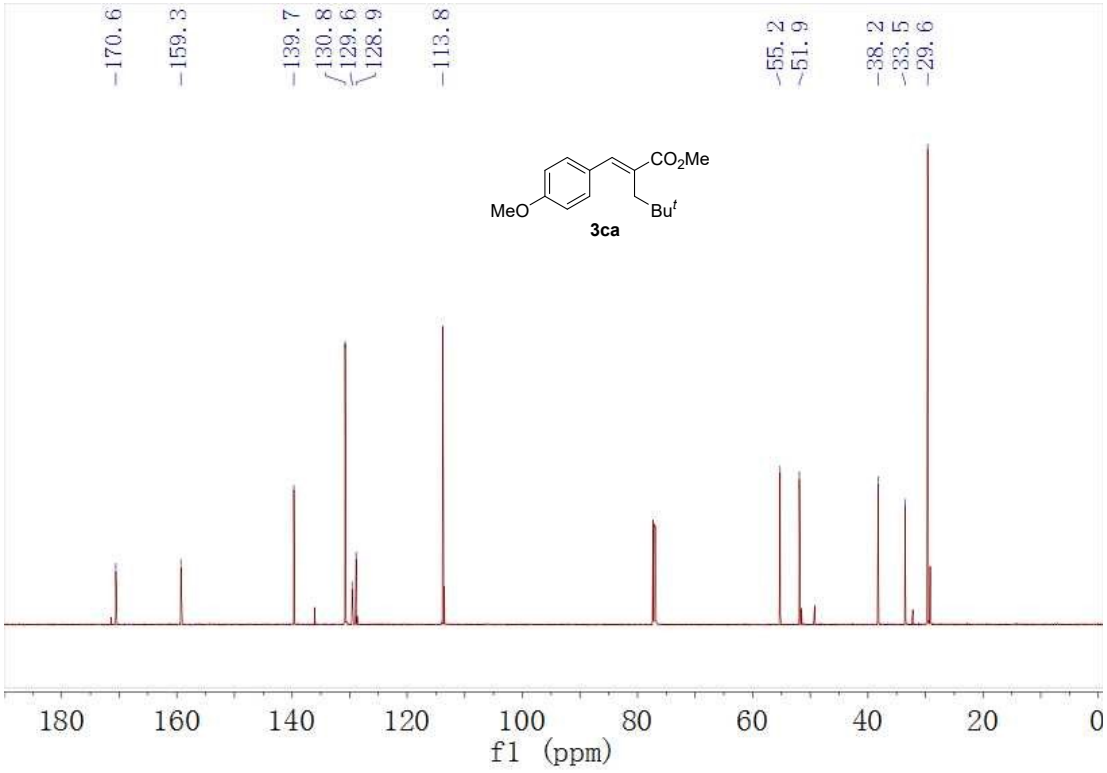
^{13}C NMR of **3ba** in $CDCl_3$



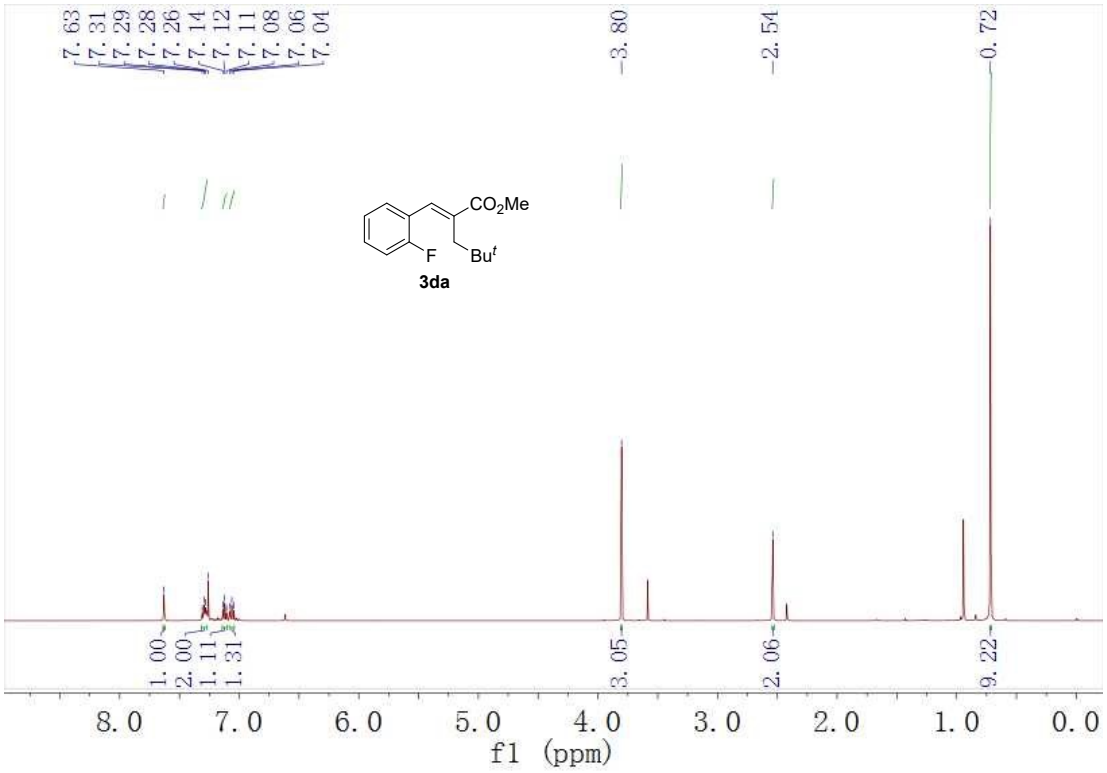
^{1}H NMR of **3ca** in $CDCl_3$



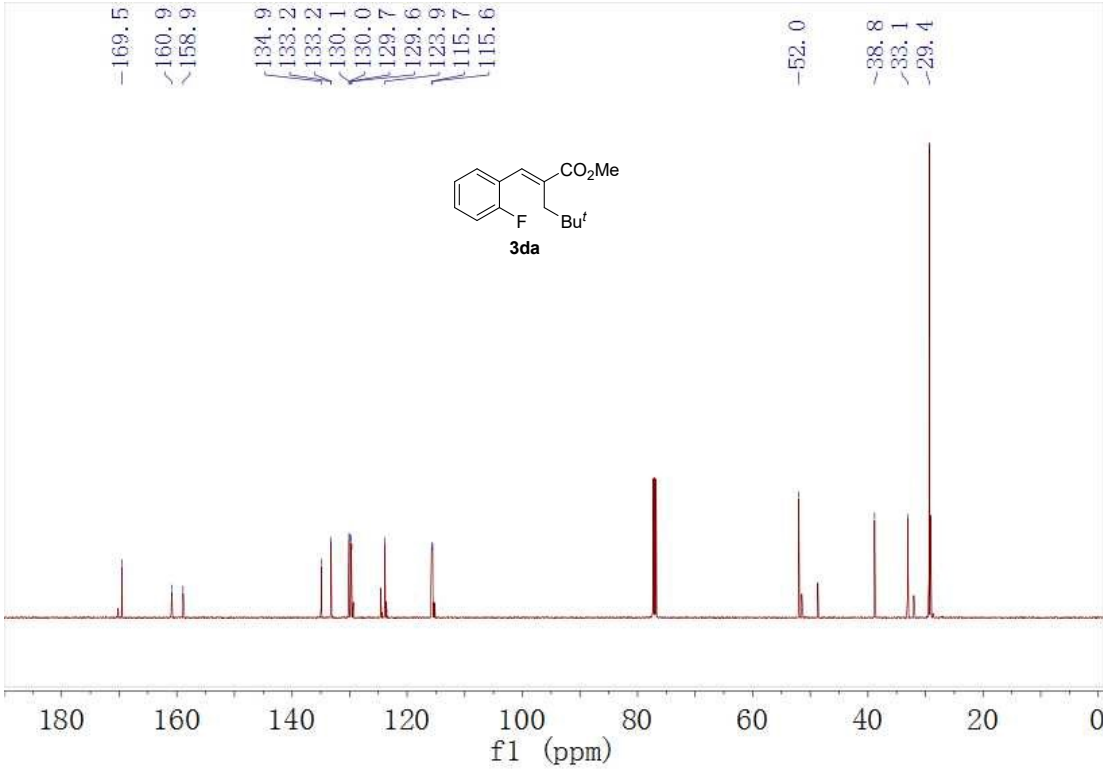
^{13}C NMR of **3ca** in $CDCl_3$



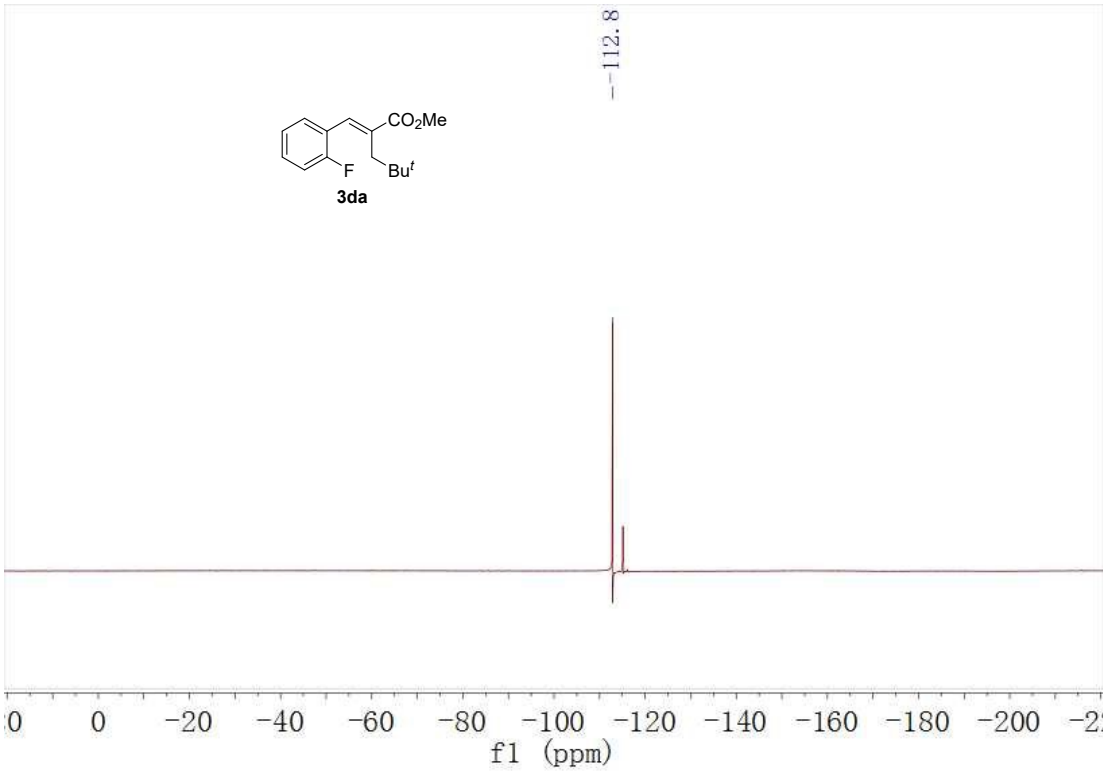
^{1}H NMR of **3da** in $CDCl_3$



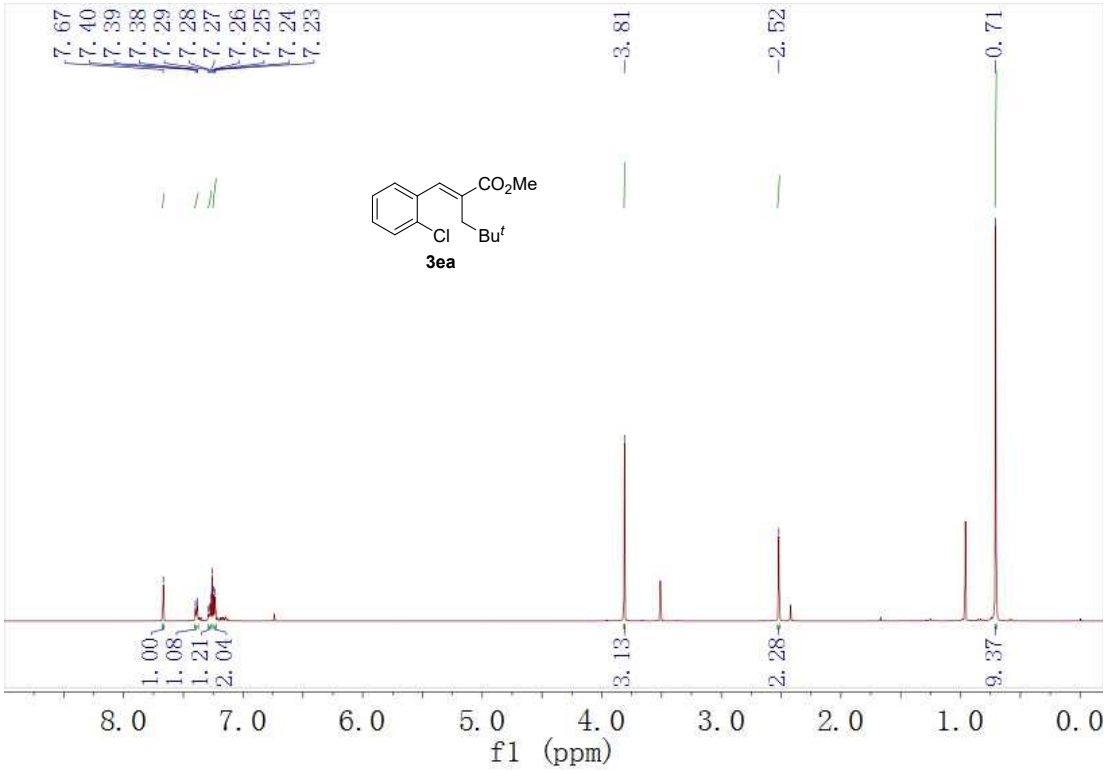
^{13}C NMR of **3da** in $CDCl_3$



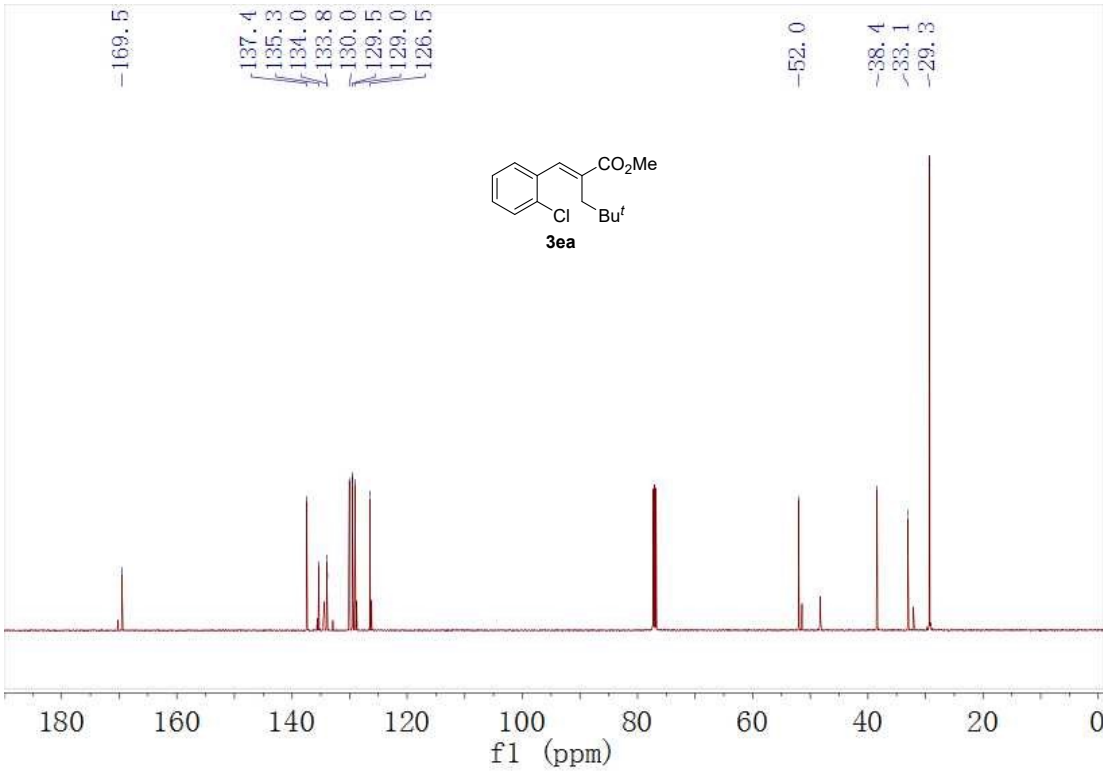
^{19}FNMR of **3da** in $CDCl_3$



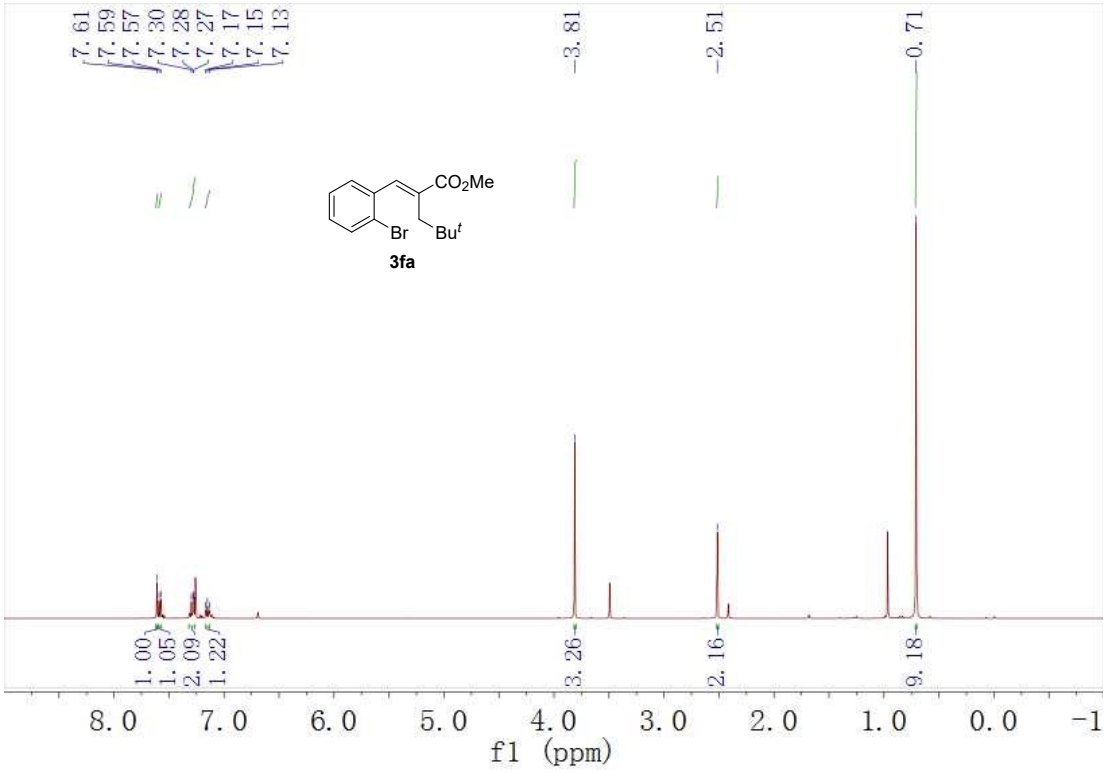
^{1}H NMR of **3ea** in $CDCl_3$



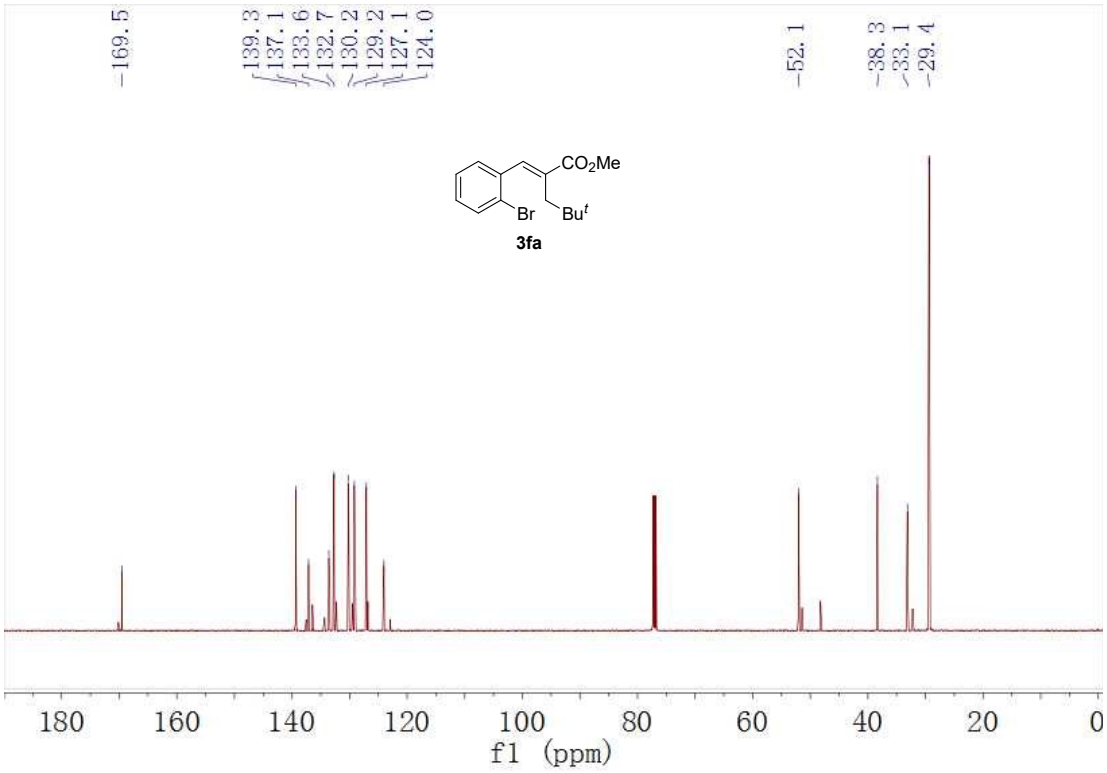
^{13}C NMR of **3ea** in $CDCl_3$



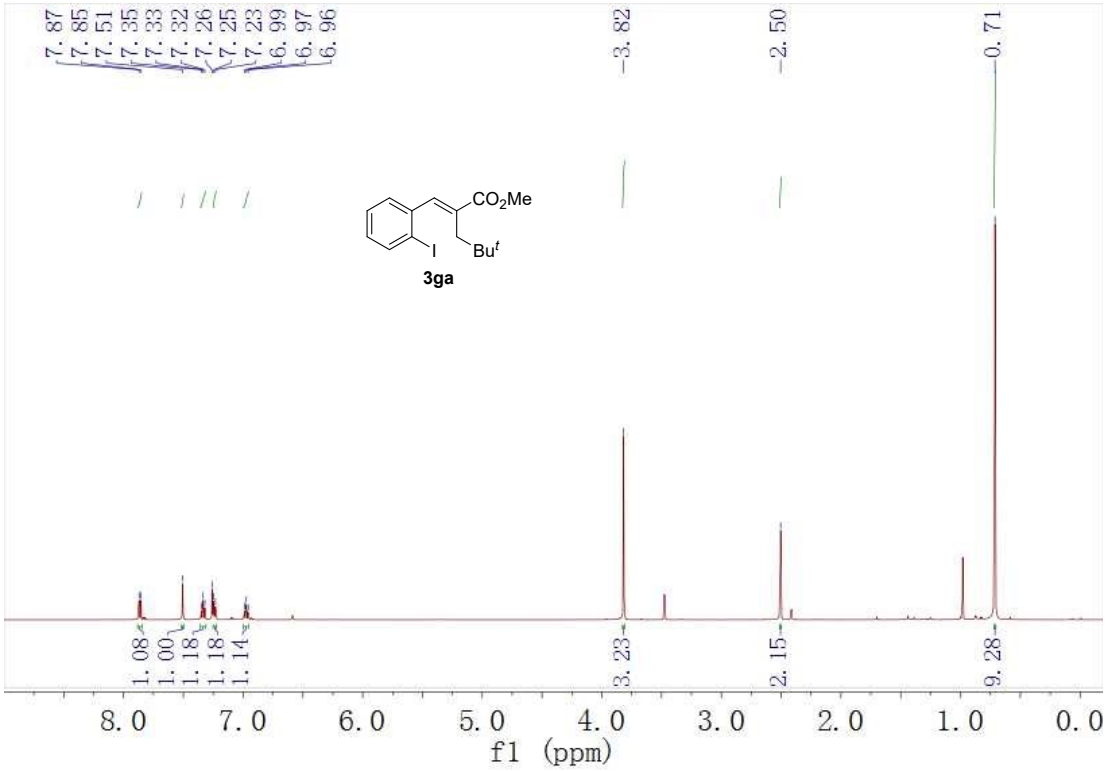
^{1}H NMR of **3fa** in $CDCl_3$



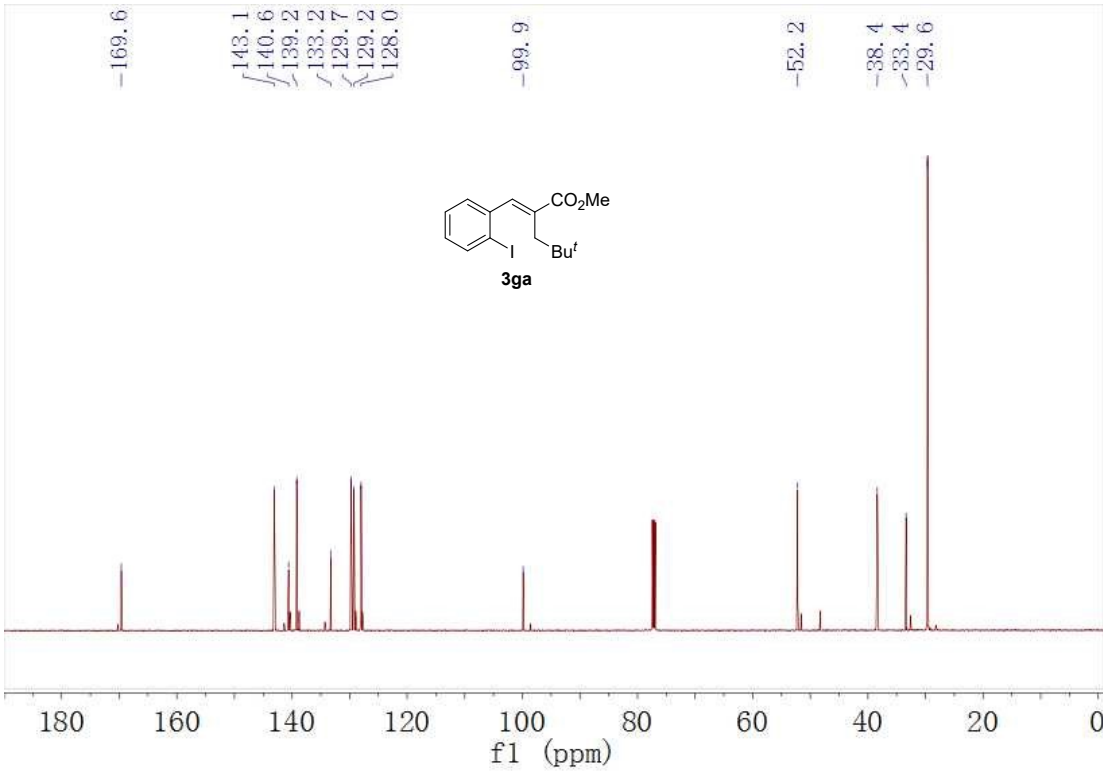
^{13}C NMR of **3fa** in $CDCl_3$



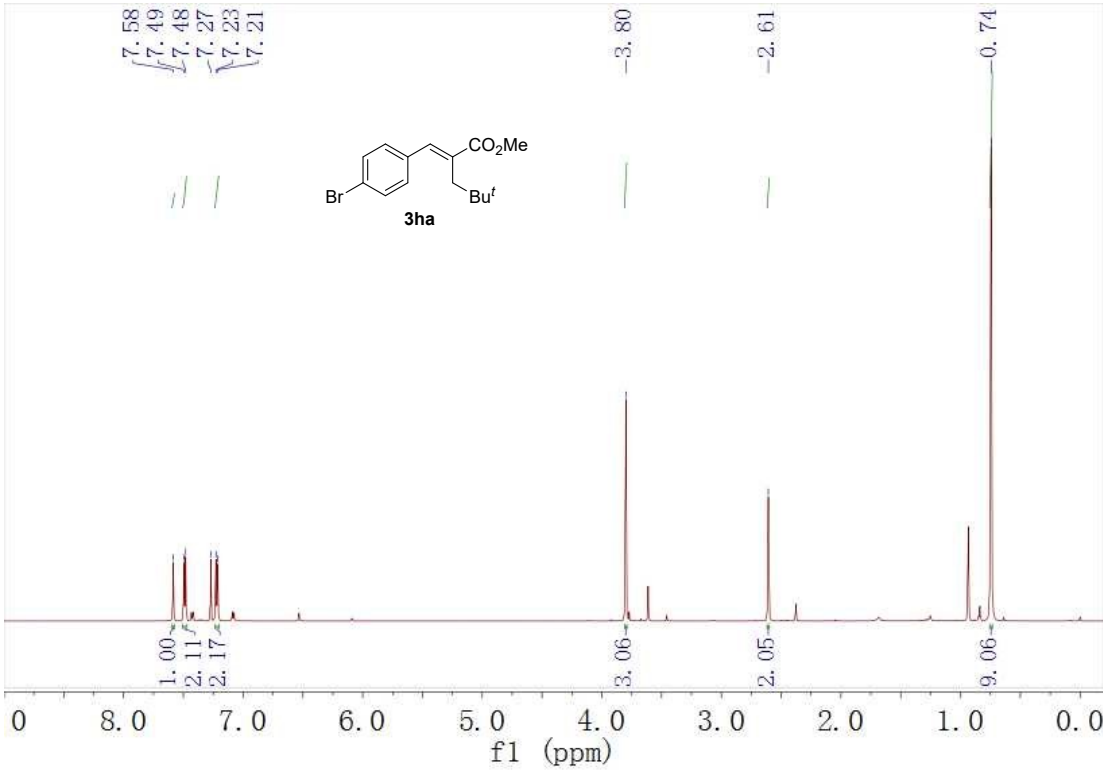
^{1}H NMR of **3ga** in $CDCl_3$



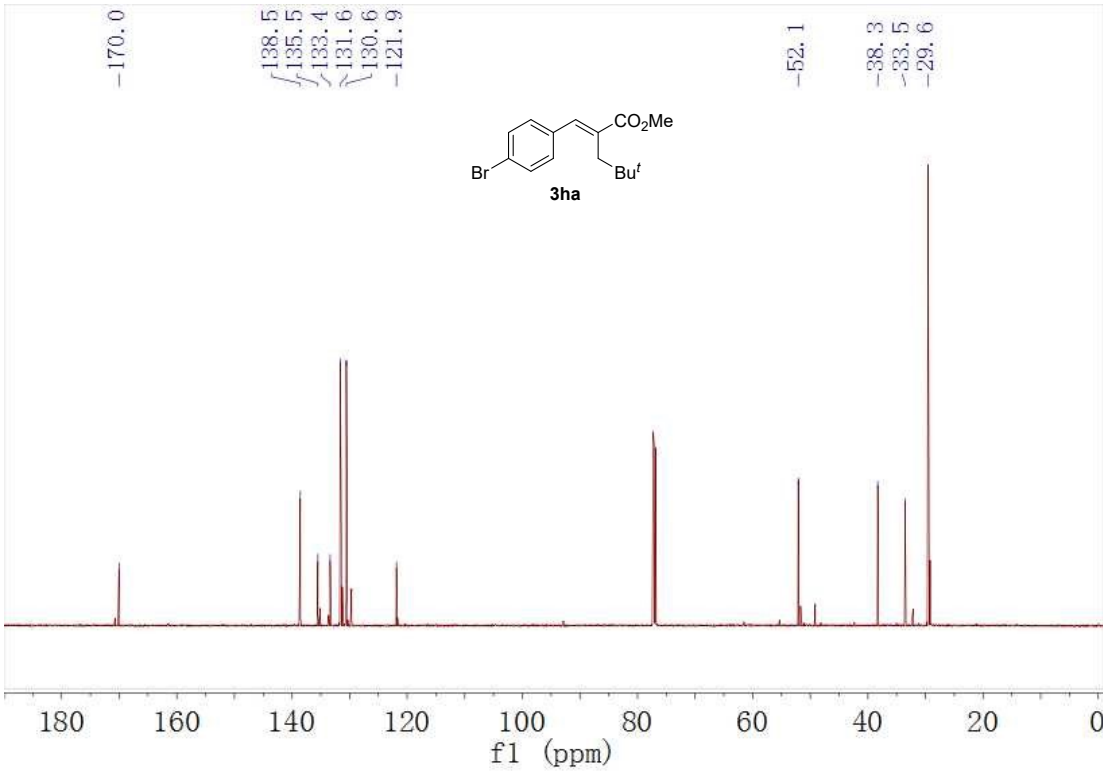
^{13}C NMR of **3ga** in $CDCl_3$



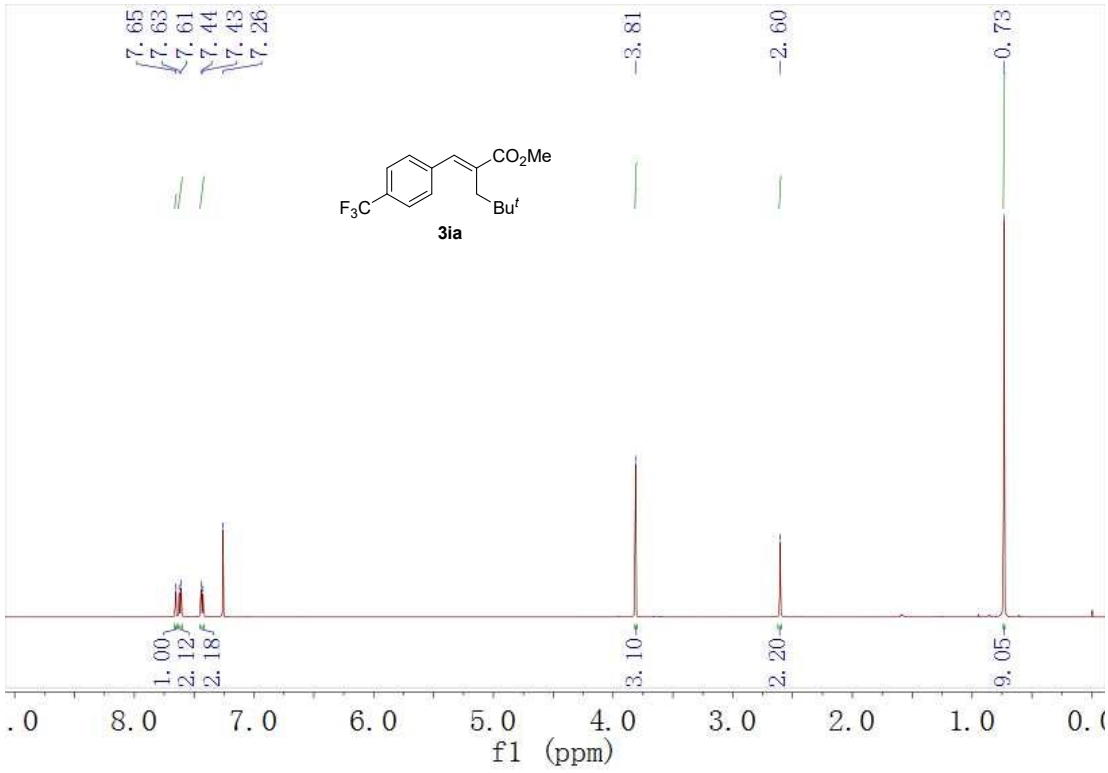
^{1}H NMR of **3ha** in $CDCl_3$



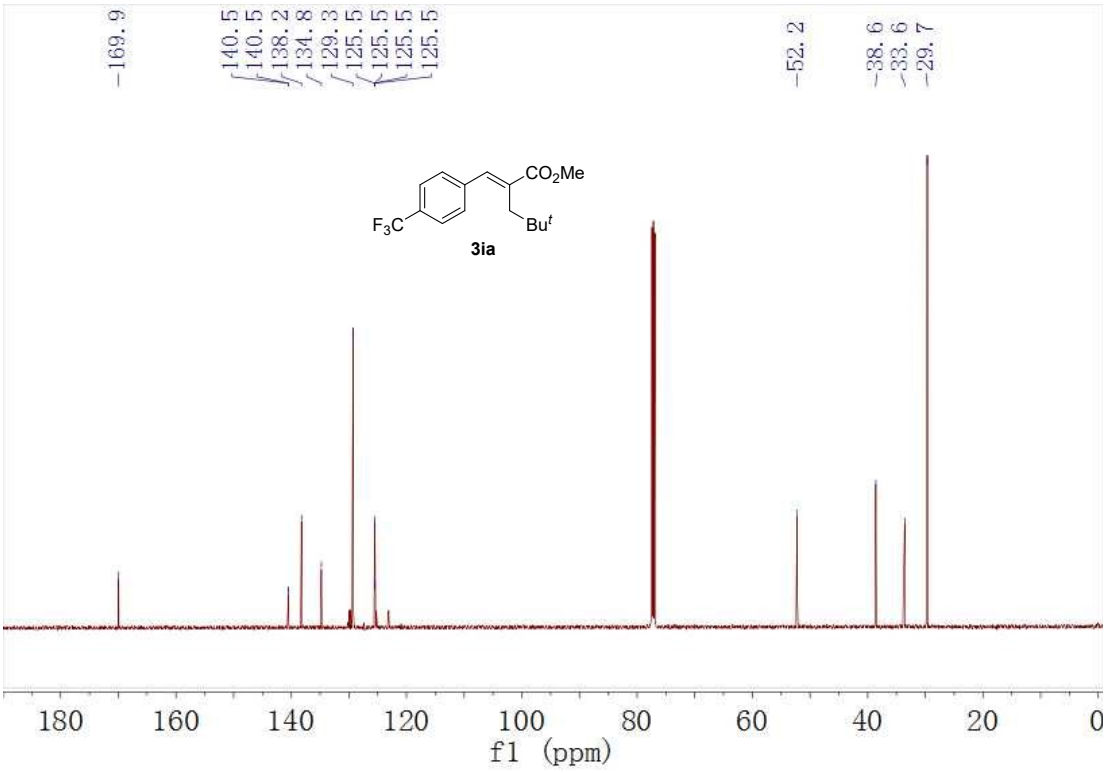
^{13}C NMR of **3ha** in $CDCl_3$



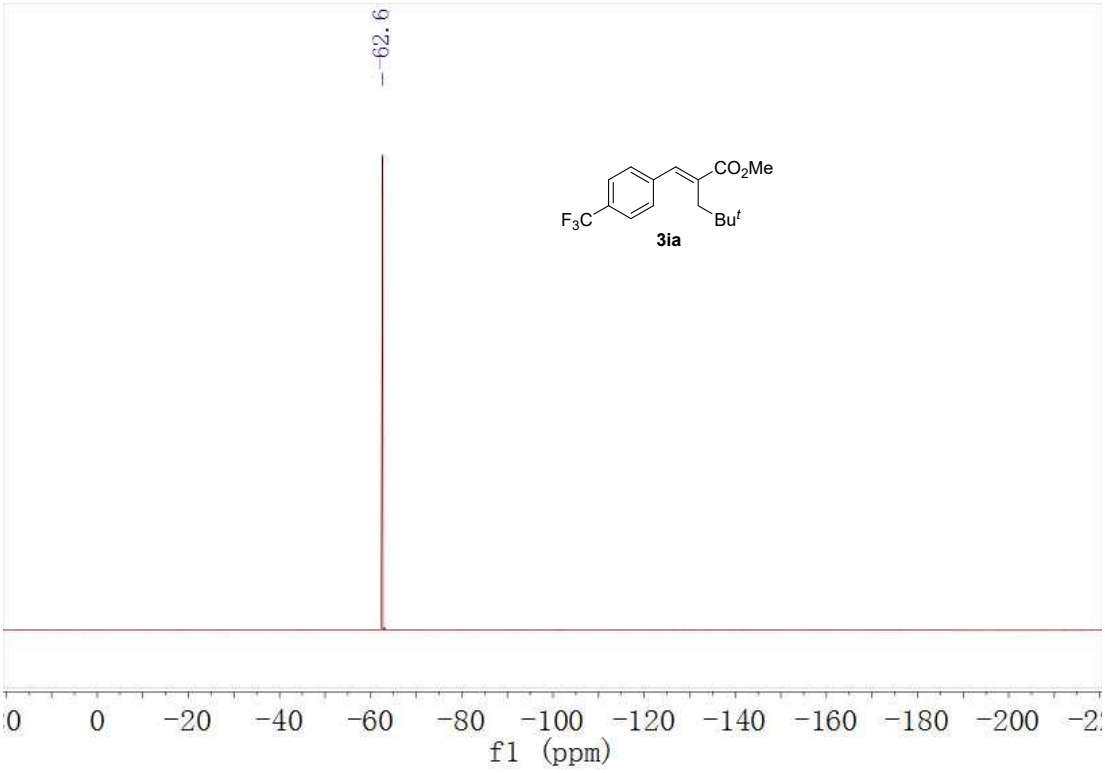
^{1}H NMR of **3ia** in $CDCl_3$



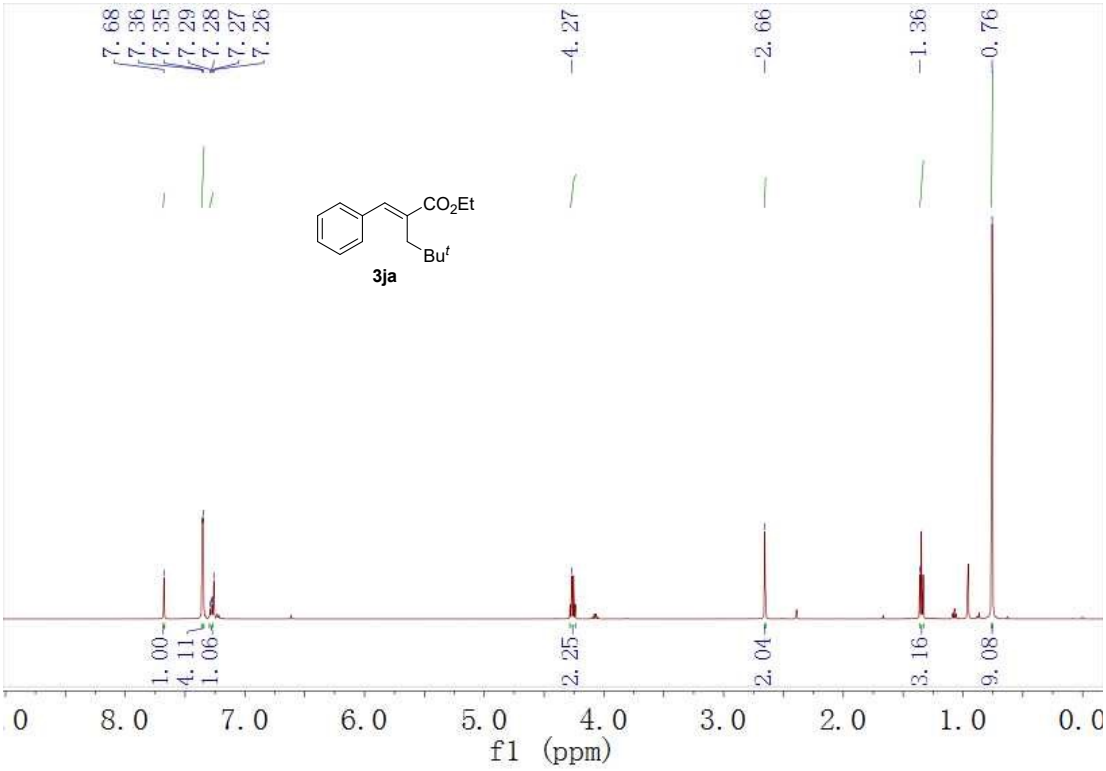
^{13}C NMR of **3ia** in $CDCl_3$



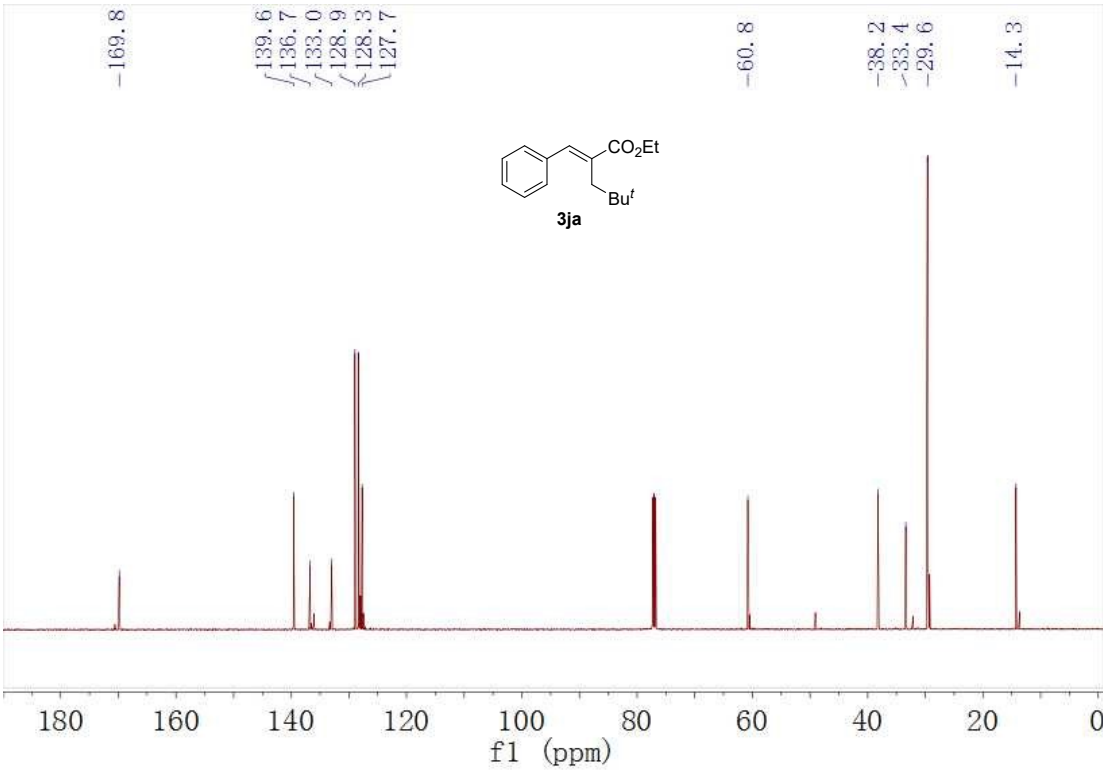
^{19}F NMR of **3ia** in $CDCl_3$



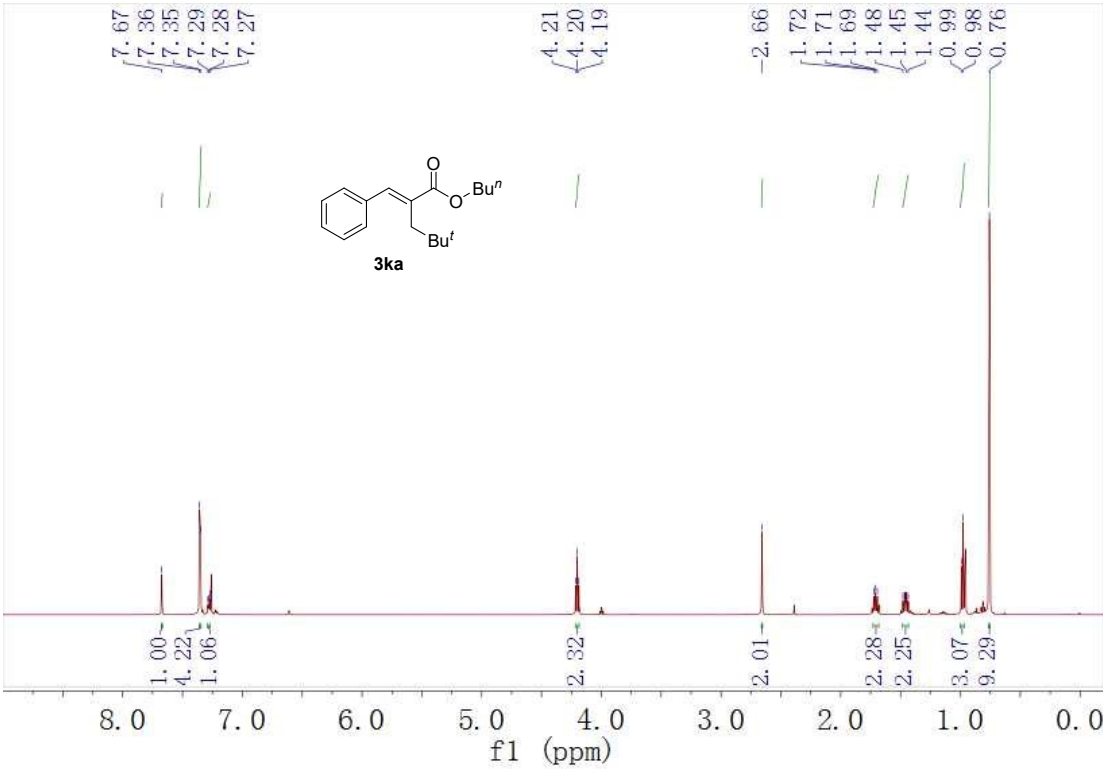
^{1}H NMR of **3ja** in $CDCl_3$



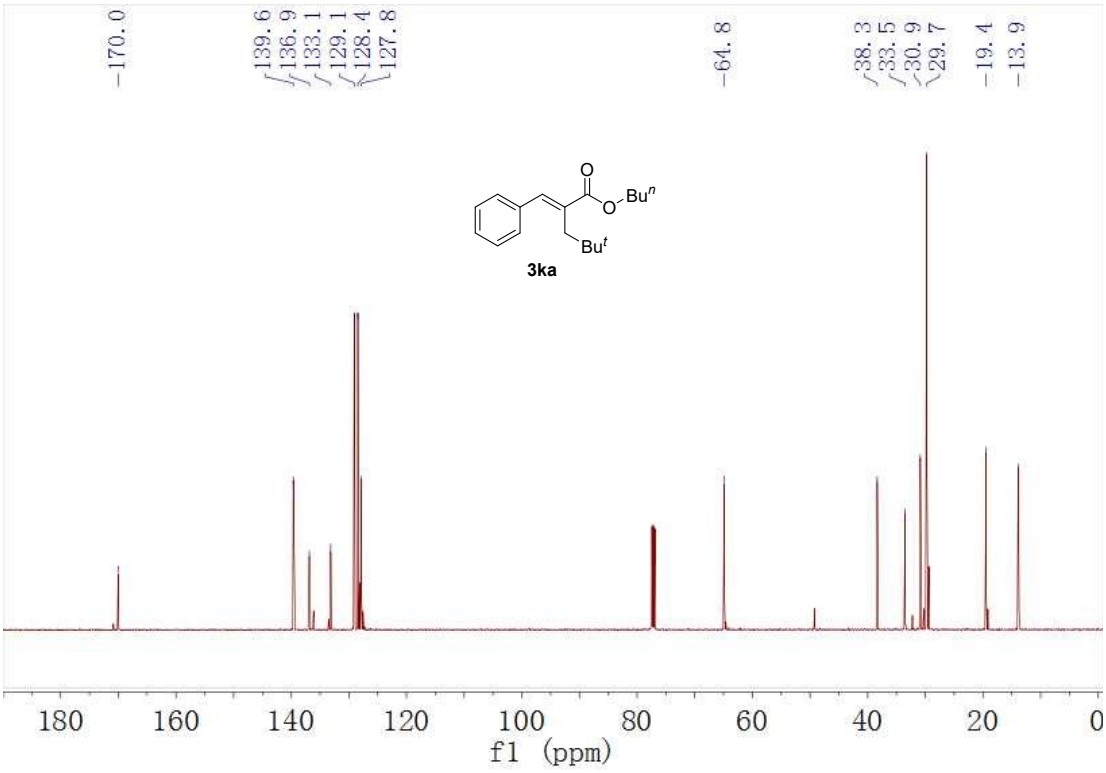
^{13}C NMR of **3ja** in $CDCl_3$



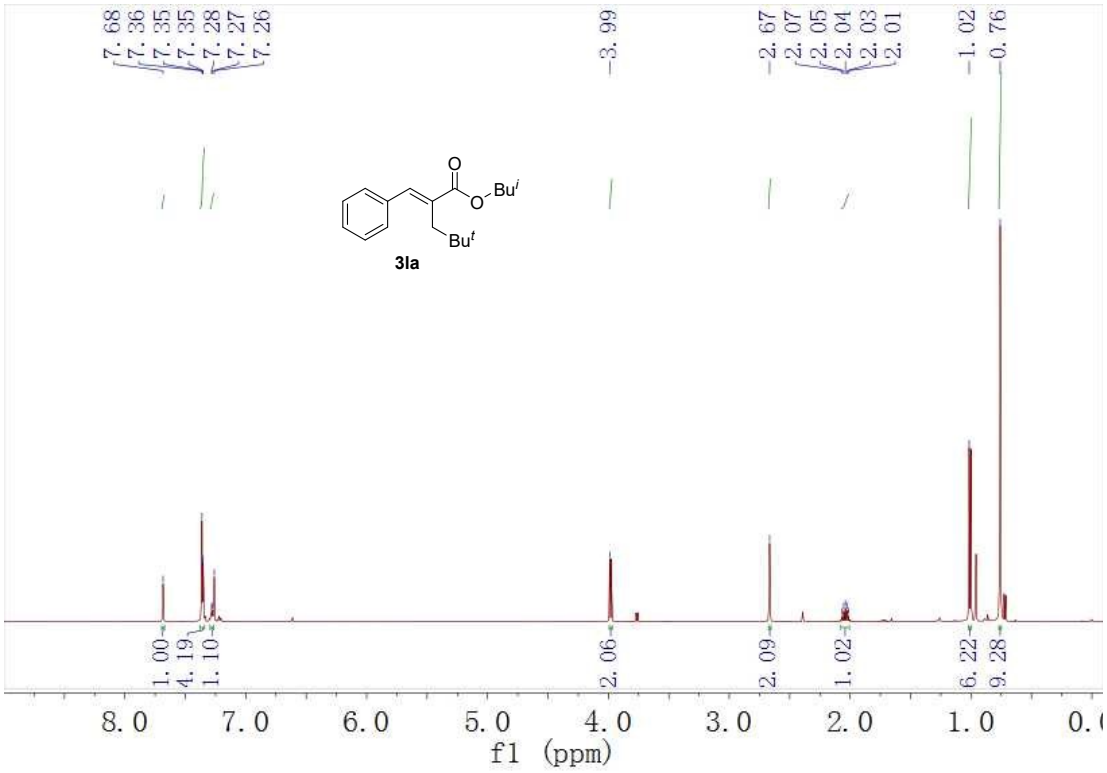
^{1}H NMR of **3ka** in $CDCl_3$



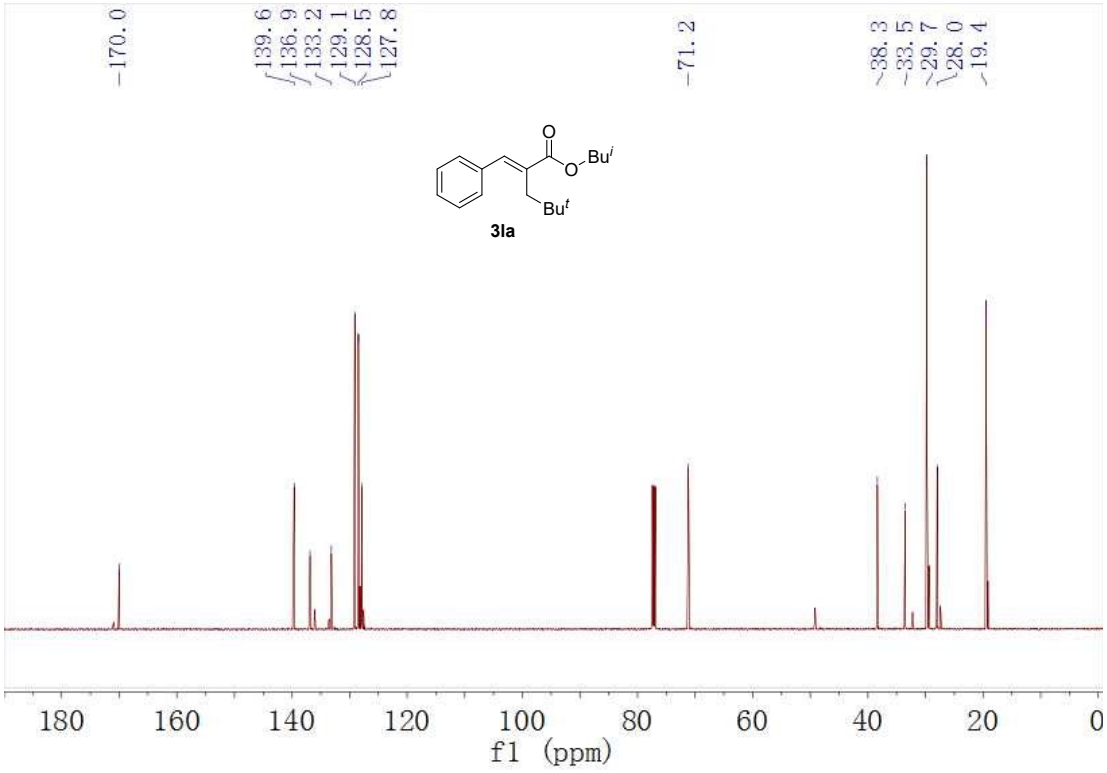
^{13}C NMR of **3ka** in $CDCl_3$



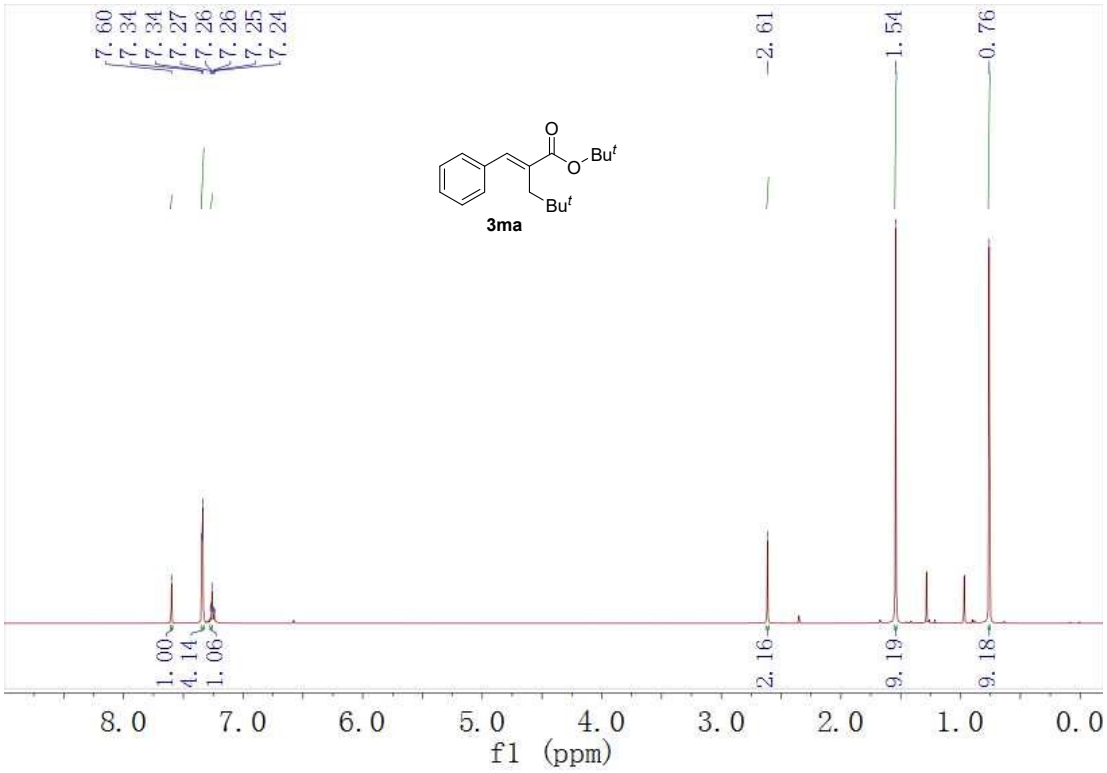
^{1}H NMR of **3la** in $CDCl_3$



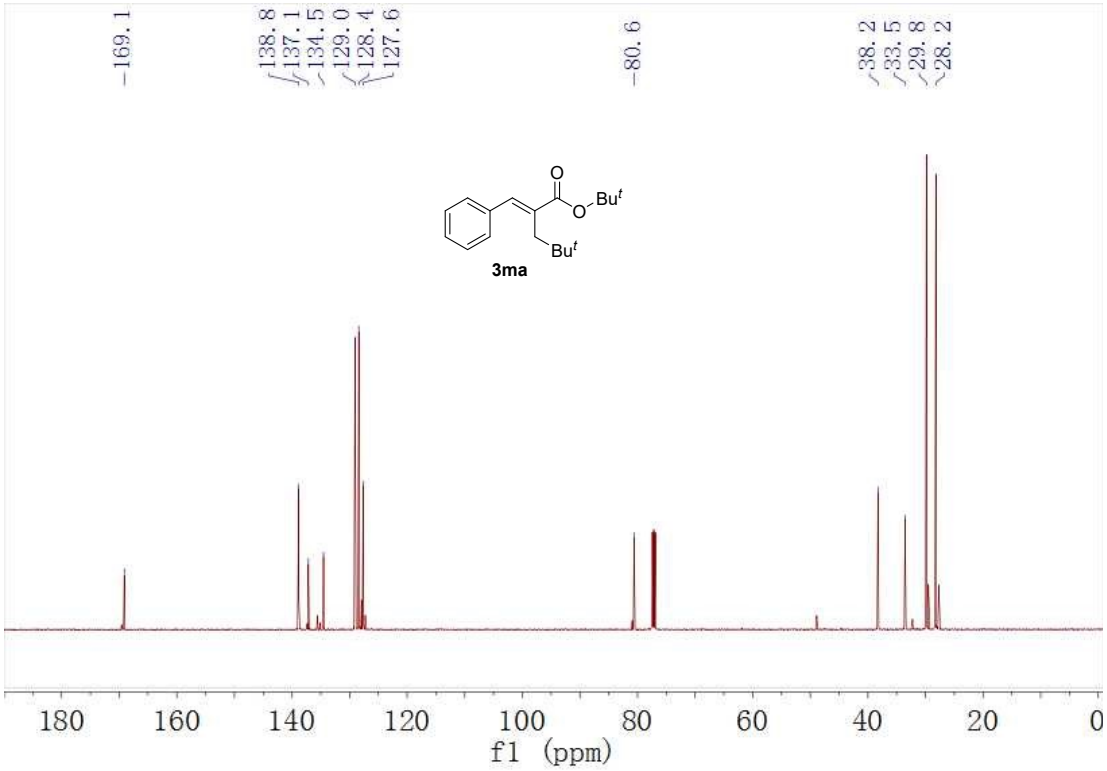
^{13}C NMR of **3la** in $CDCl_3$



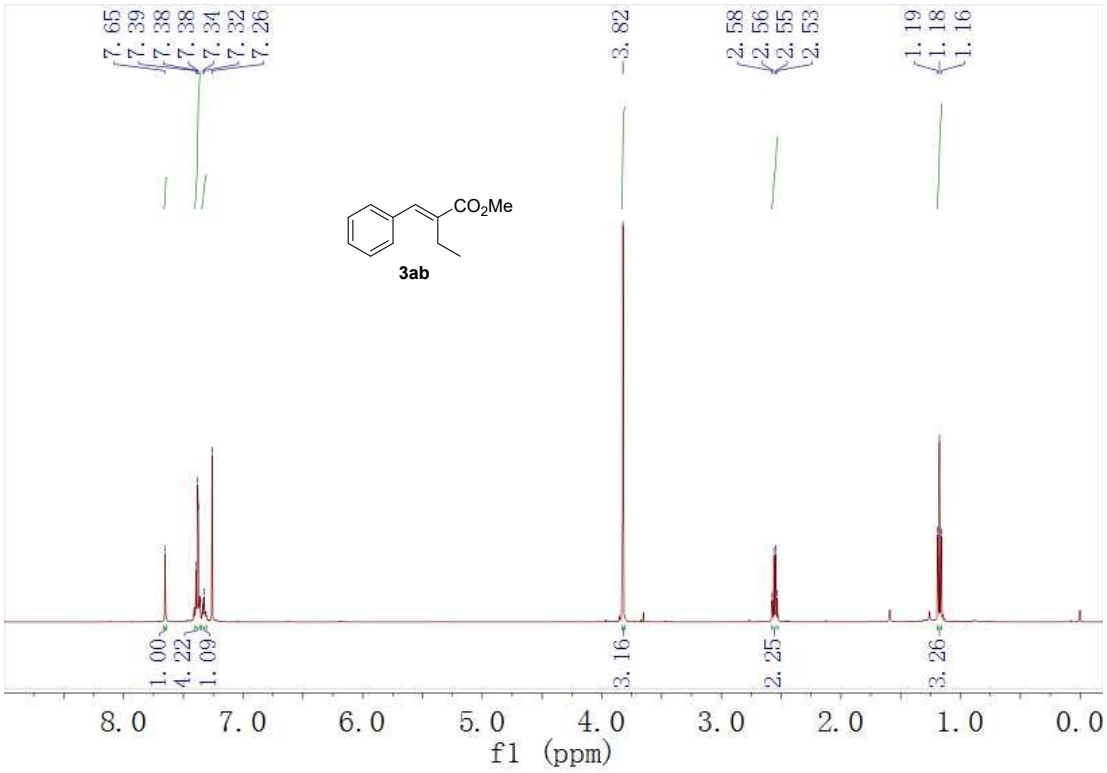
^{1}H NMR of **3ma** in $CDCl_3$



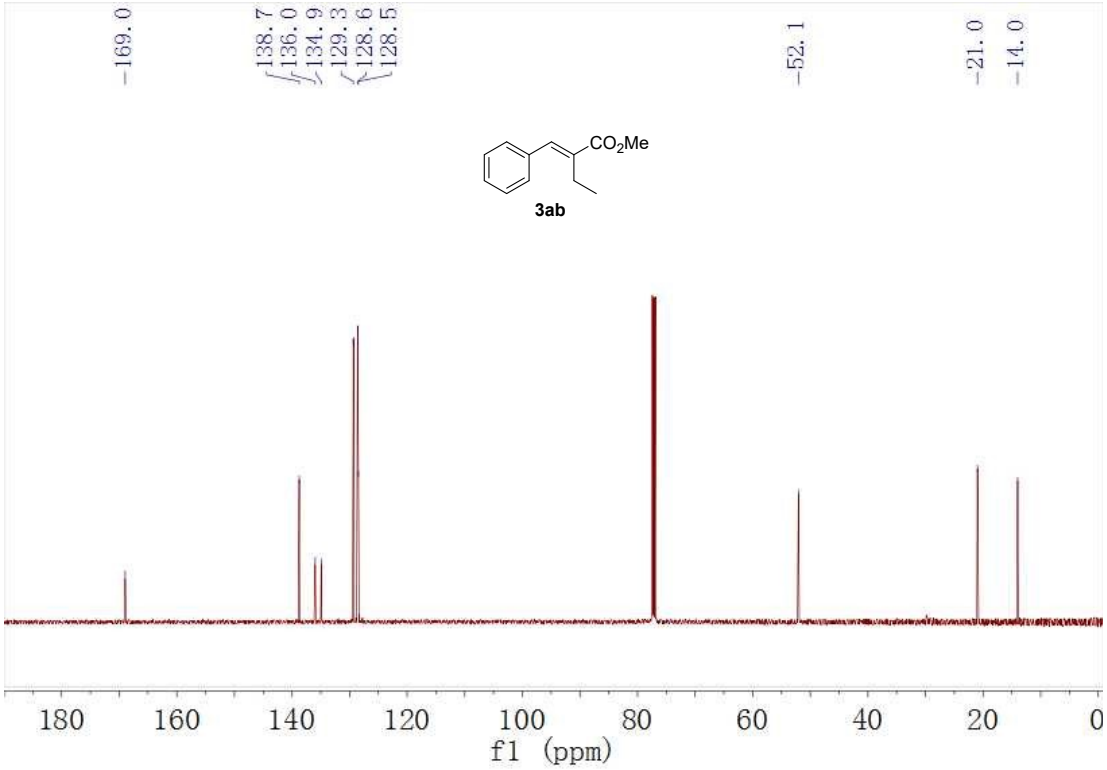
^{13}C NMR of **3ma** in $CDCl_3$



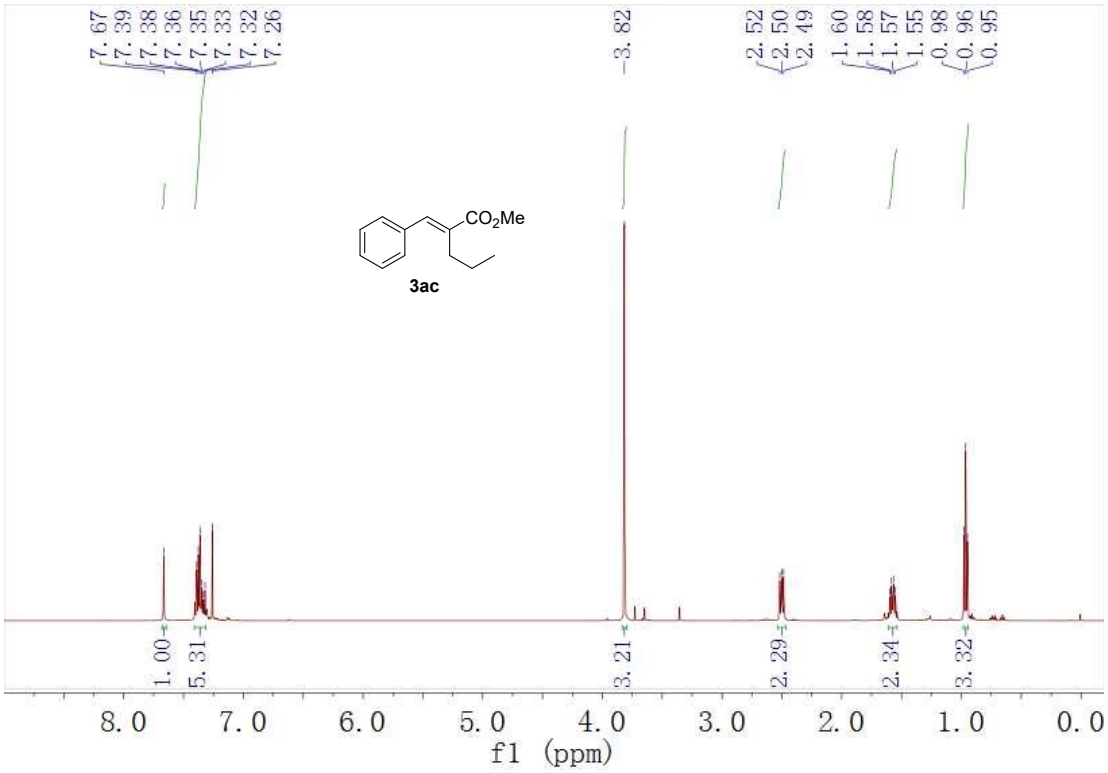
^{1}H NMR of **3ab** in $CDCl_3$



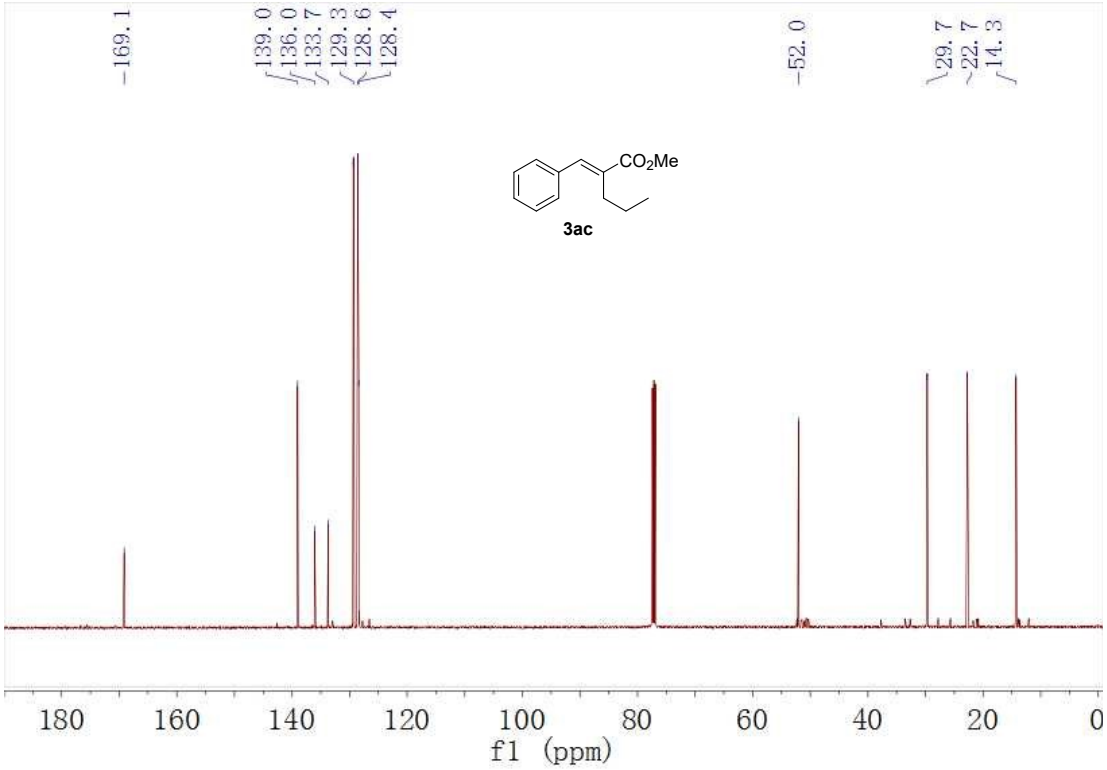
^{13}C NMR of **3ab** in $CDCl_3$



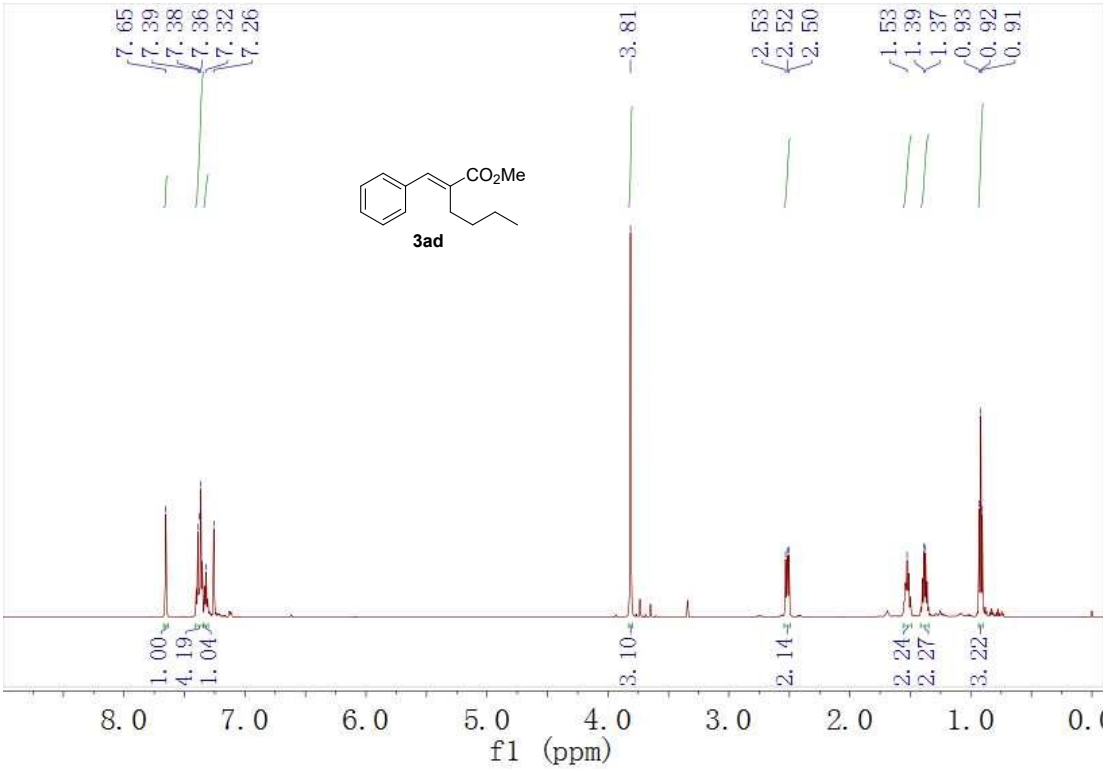
^{1}H NMR of **3ac** in $CDCl_3$



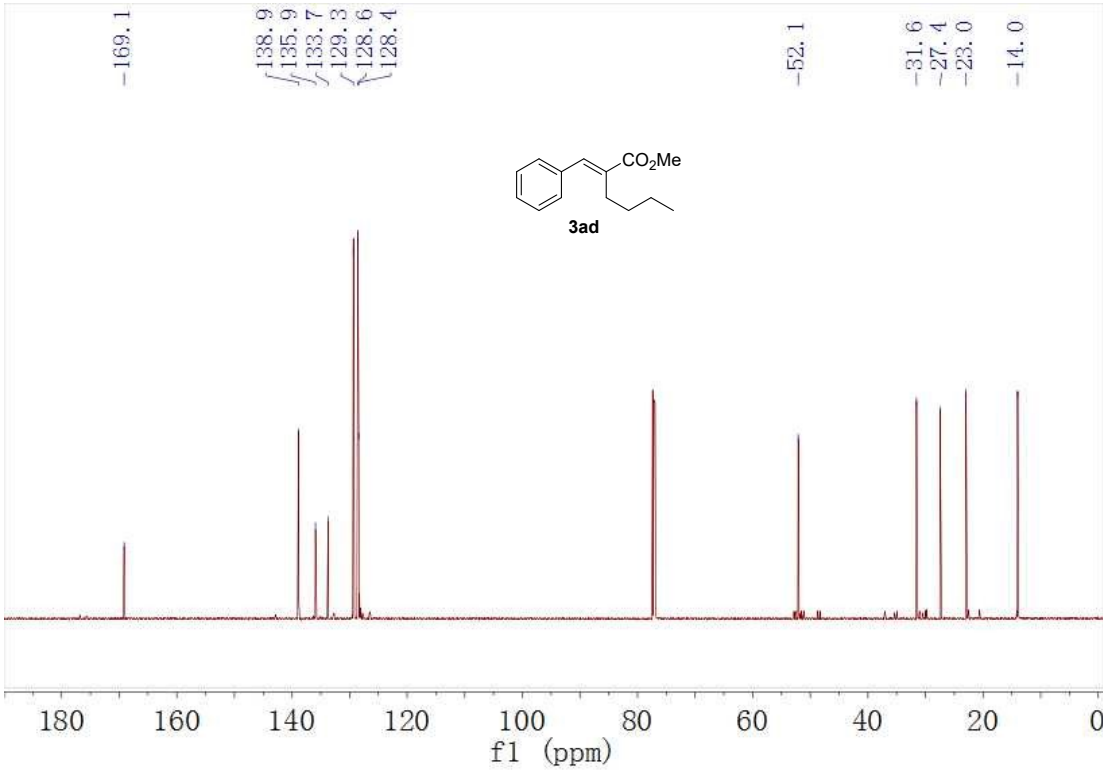
^{13}C NMR of **3ac** in $CDCl_3$



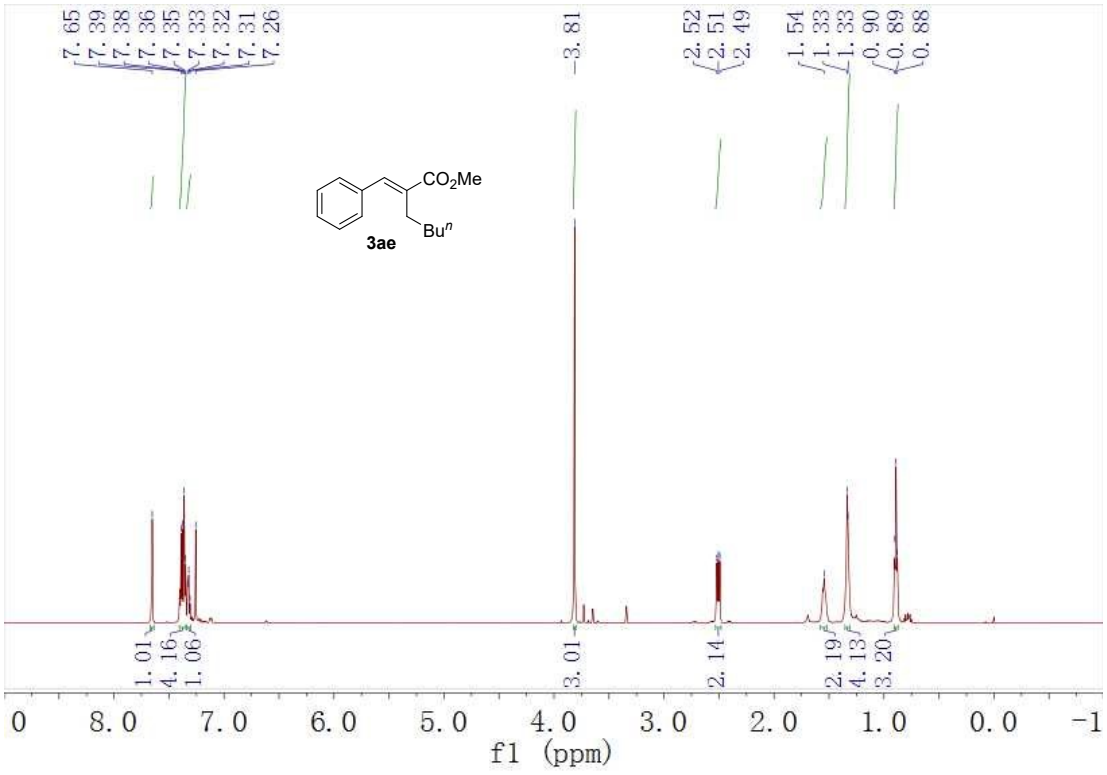
^{1}H NMR of **3ad** in $CDCl_3$



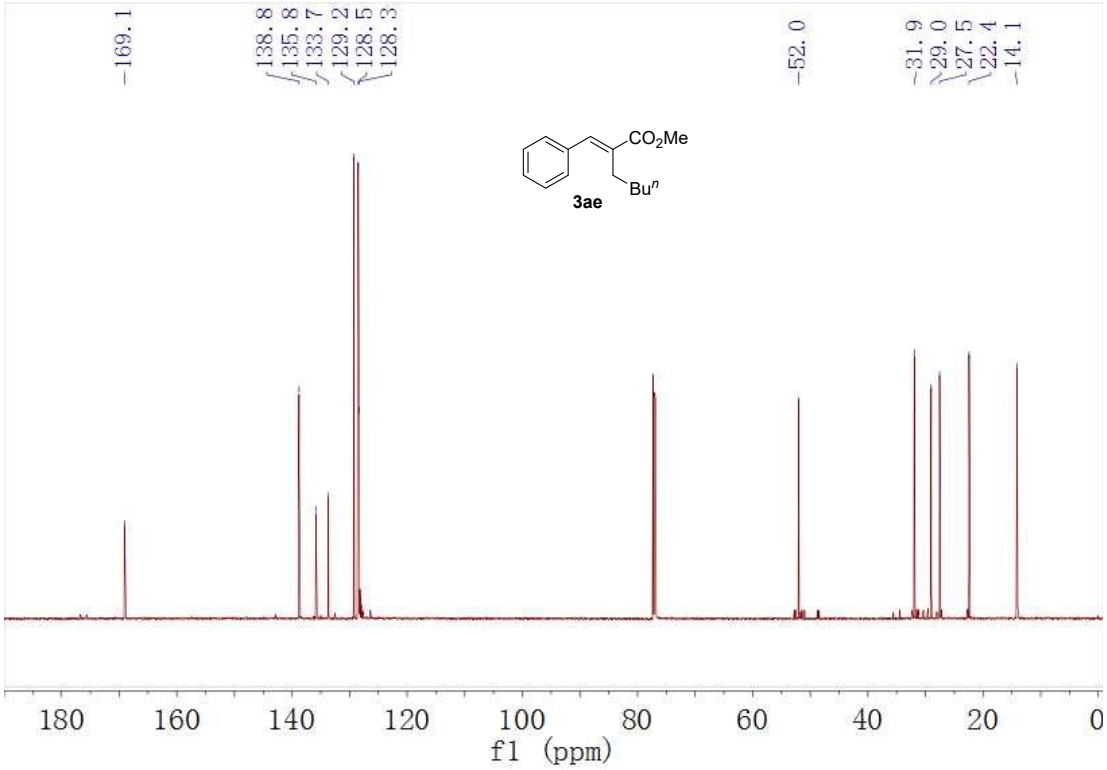
^{13}C NMR of **3ad** in $CDCl_3$



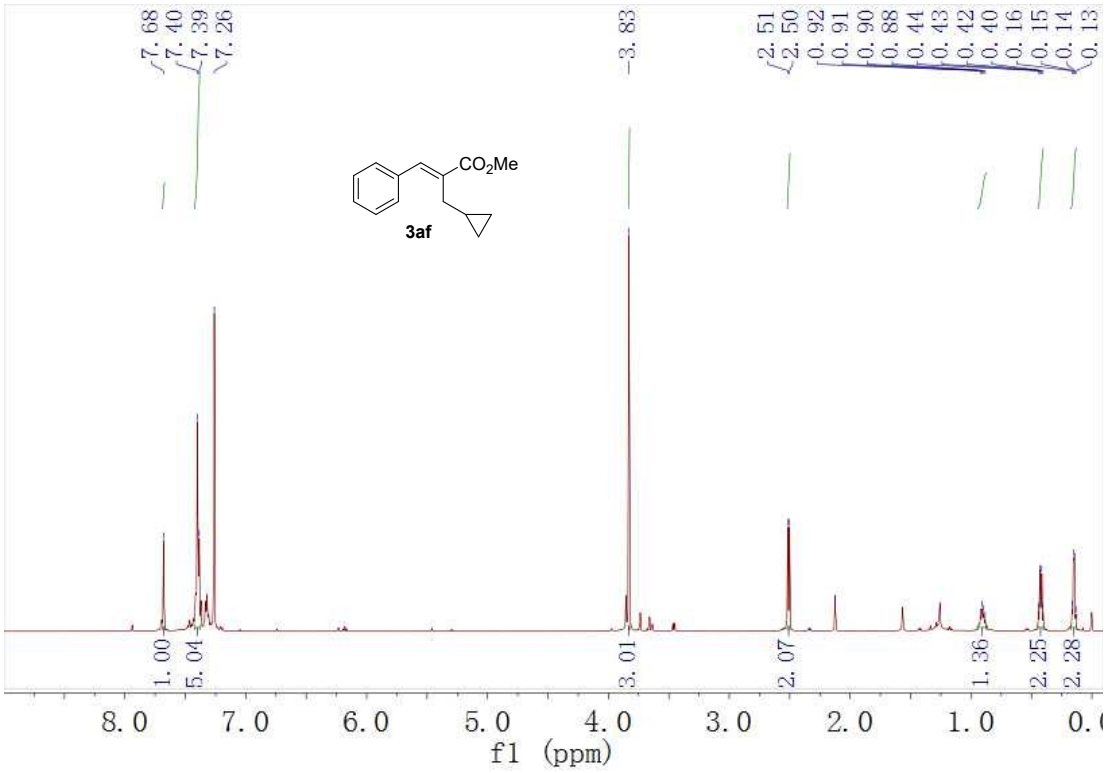
^{1}H NMR of **3ae** in $CDCl_3$



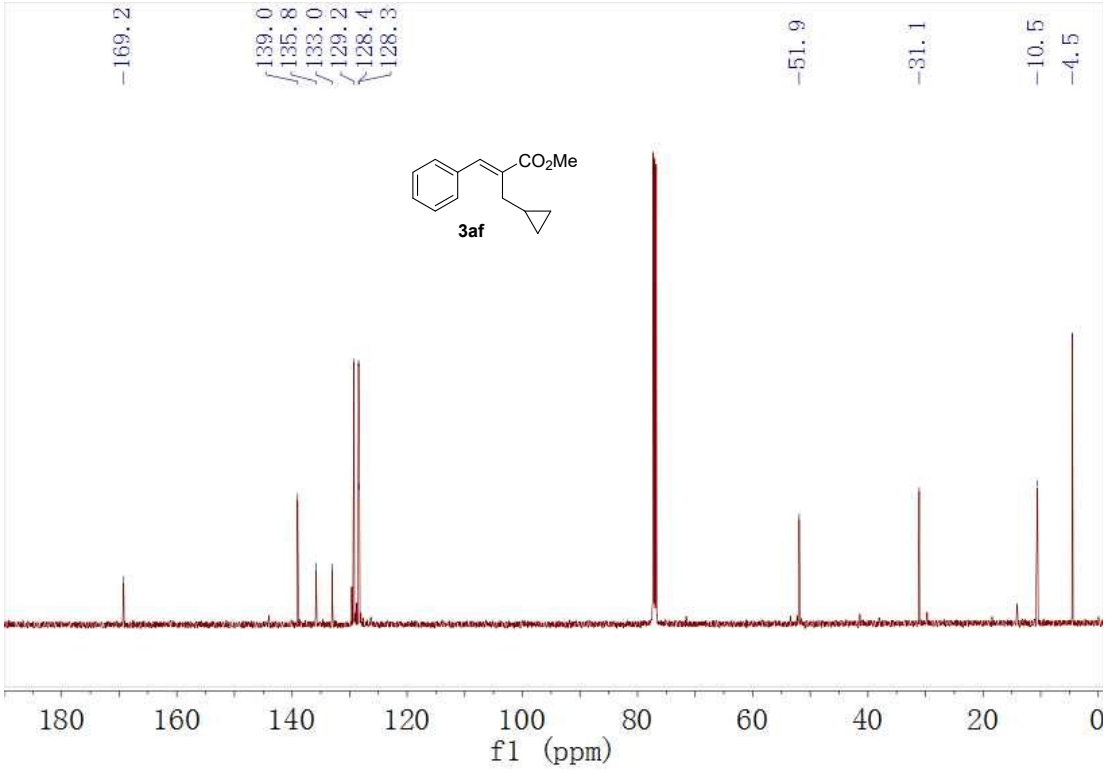
^{13}C NMR of **3ae** in $CDCl_3$



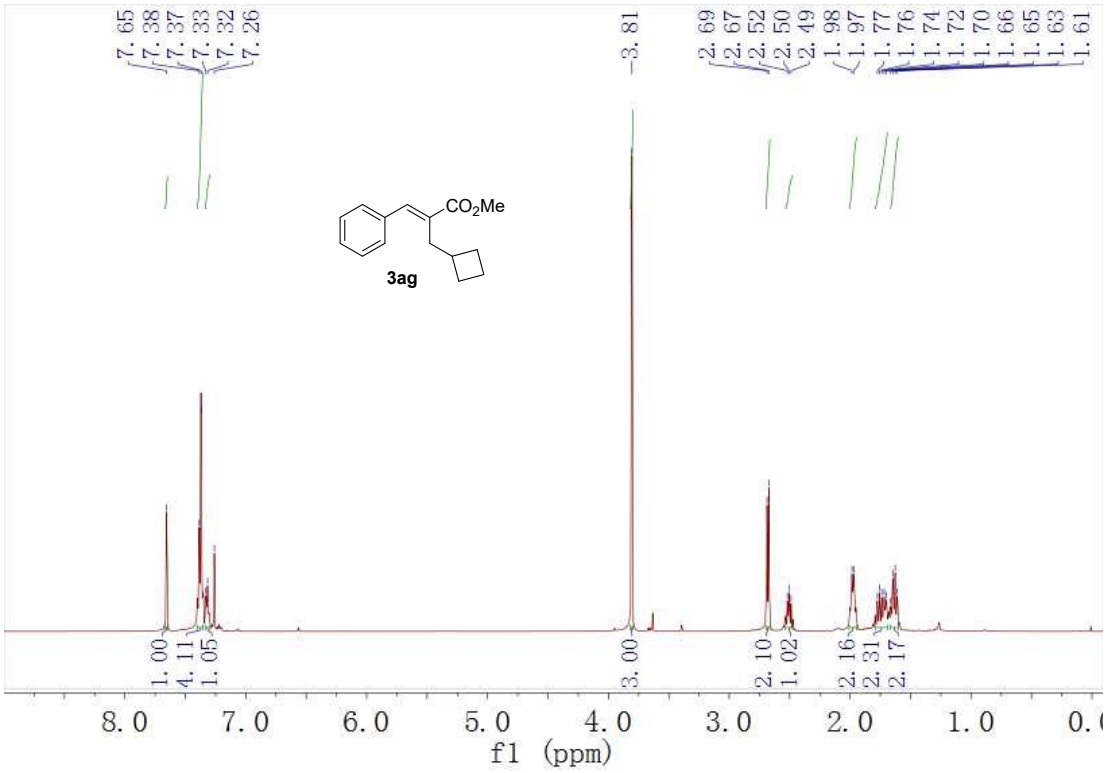
^{1}H NMR of **3af** in $CDCl_3$



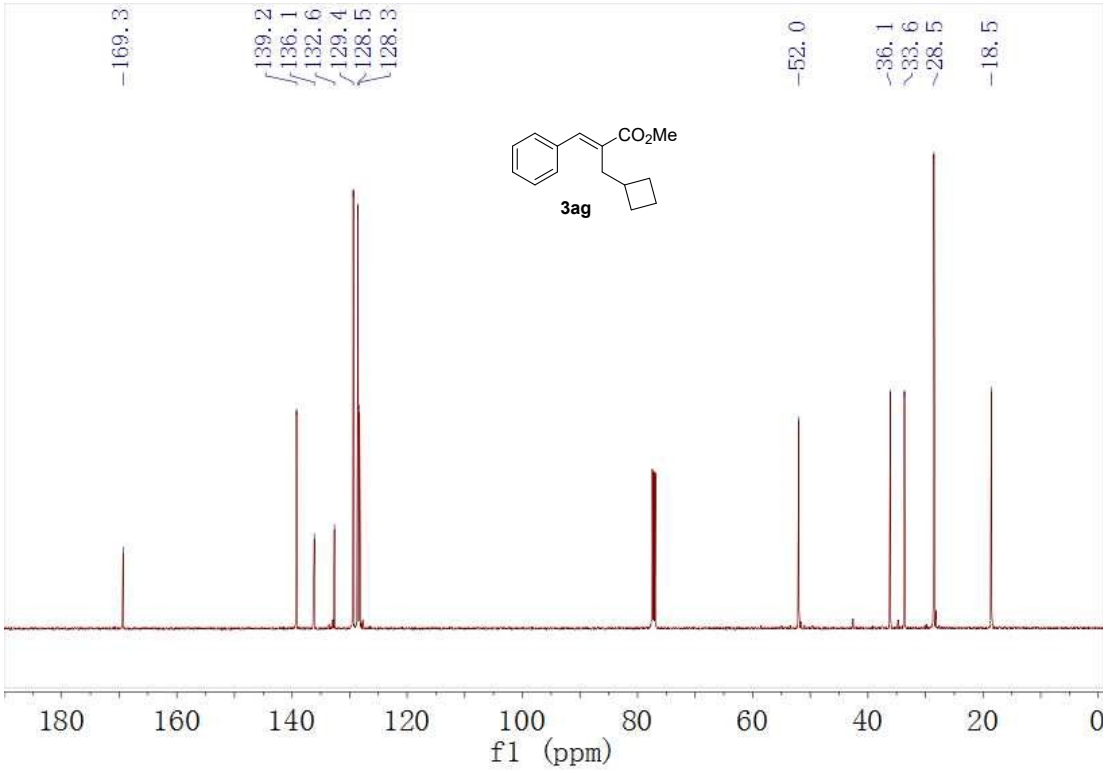
^{13}C NMR of **3af** in $CDCl_3$



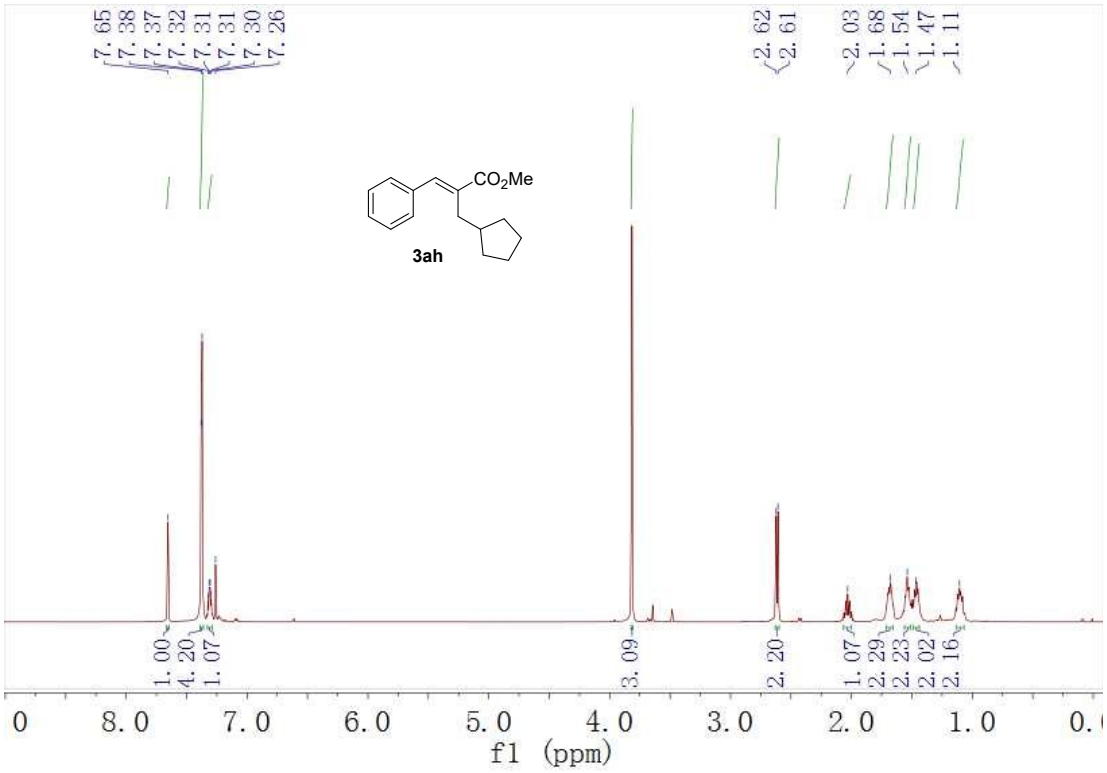
^{1}H NMR of **3ag** in $CDCl_3$



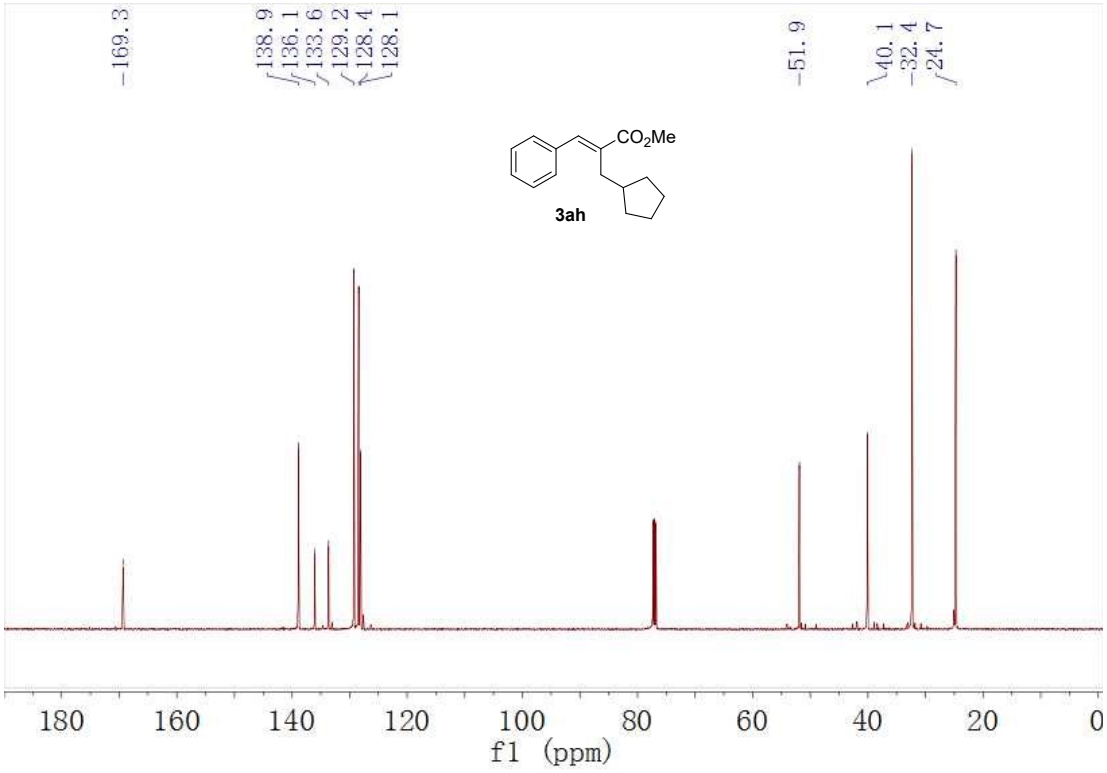
^{13}C NMR of **3ag** in $CDCl_3$



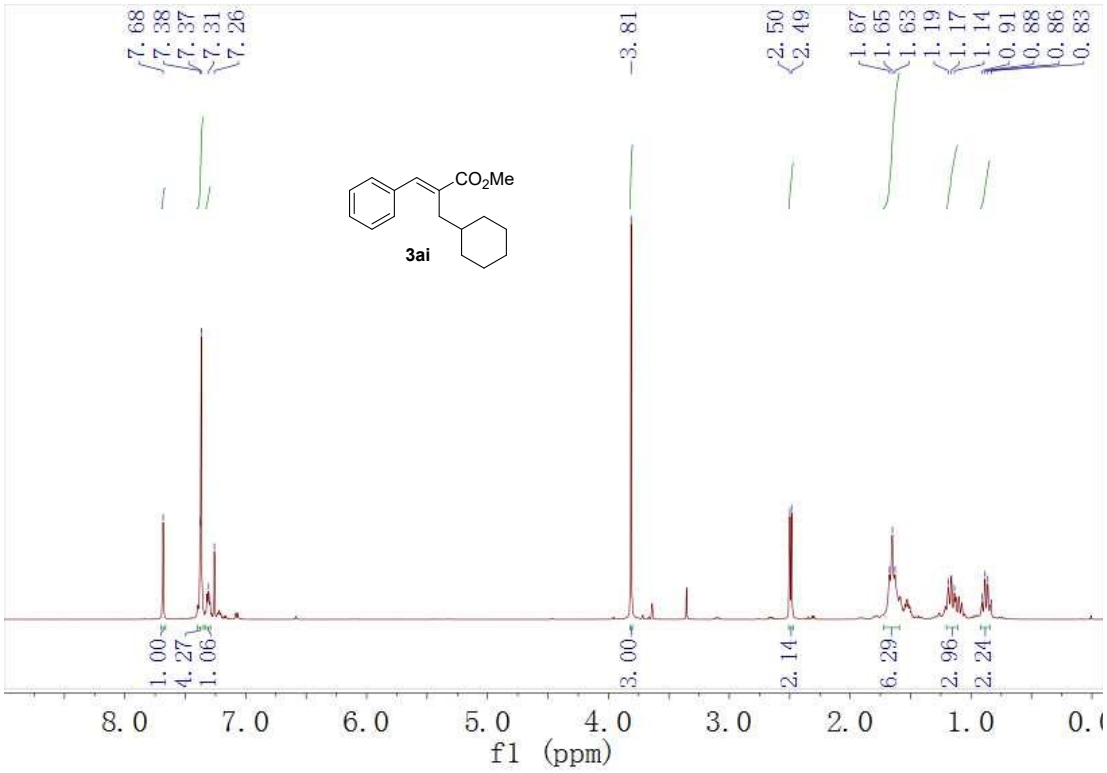
^{1}H NMR of **3ah** in $CDCl_3$



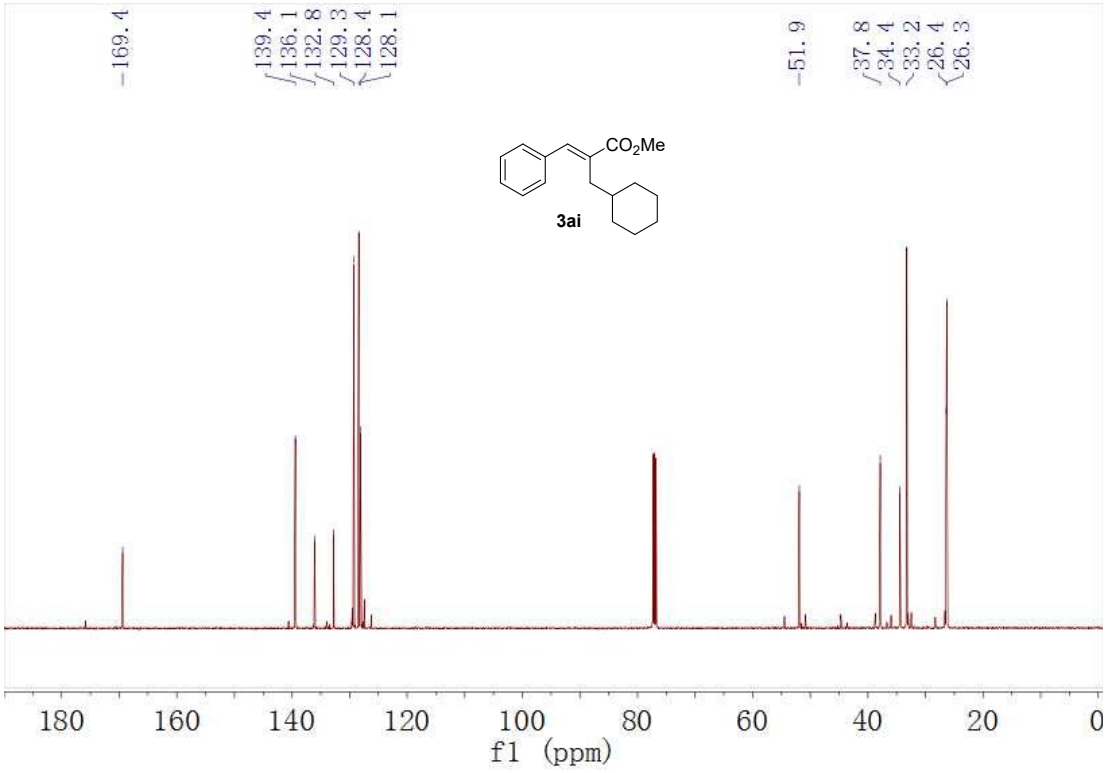
^{13}C NMR of **3ah** in $CDCl_3$



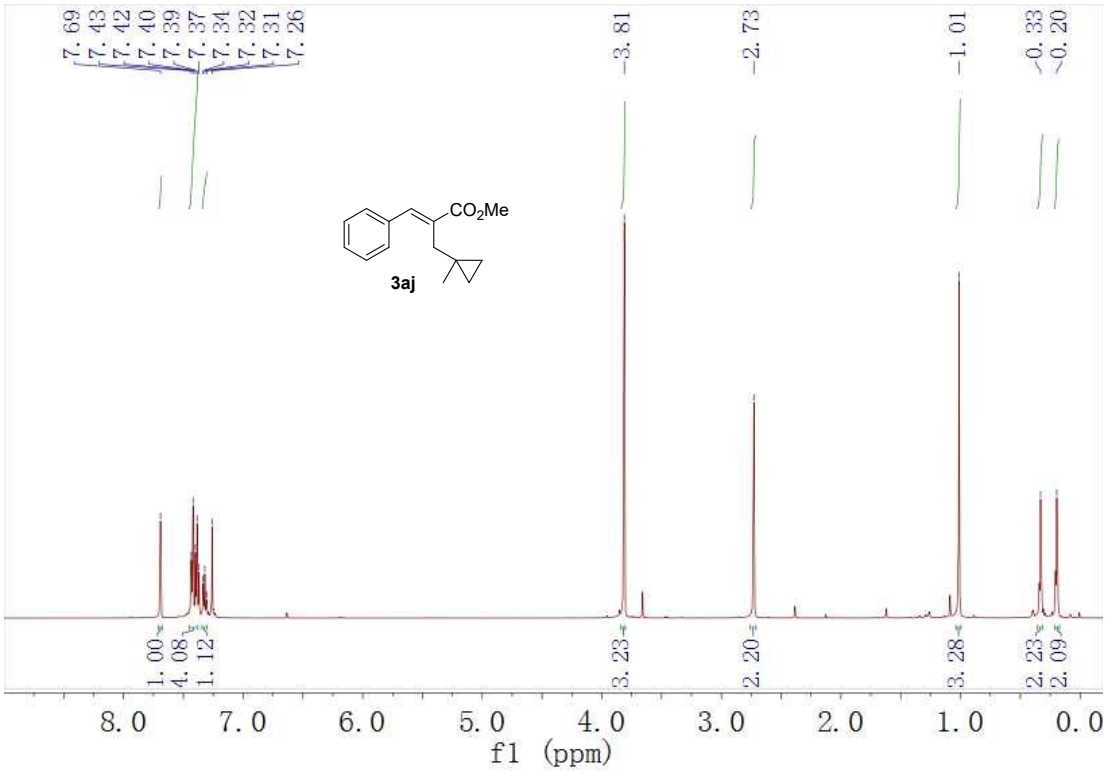
^{1}H NMR of **3ai** in $CDCl_3$



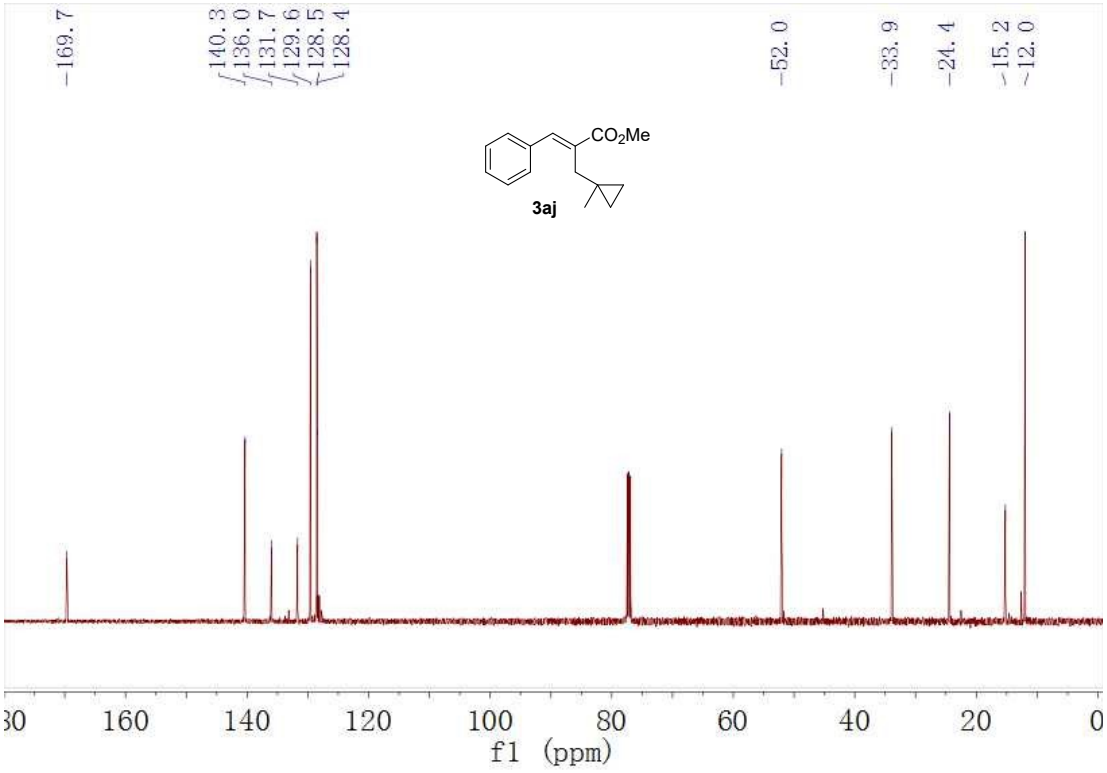
^{13}C NMR of **3ai** in $CDCl_3$



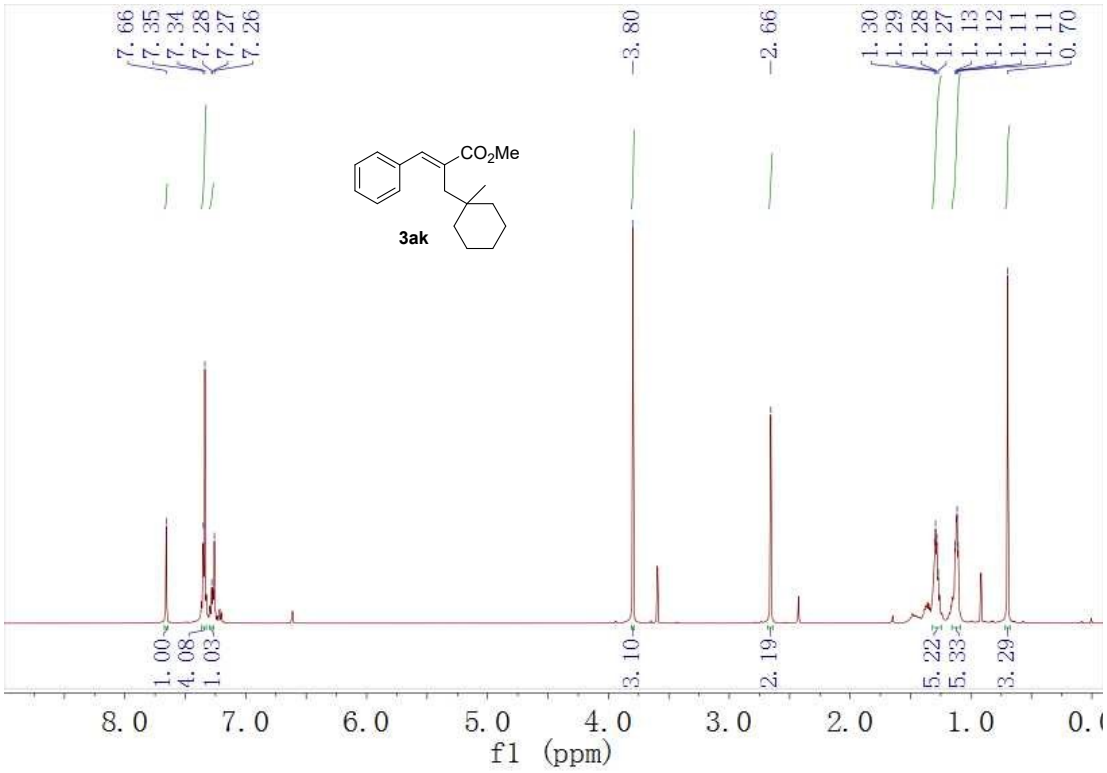
^{1}H NMR of **3aj** in $CDCl_3$



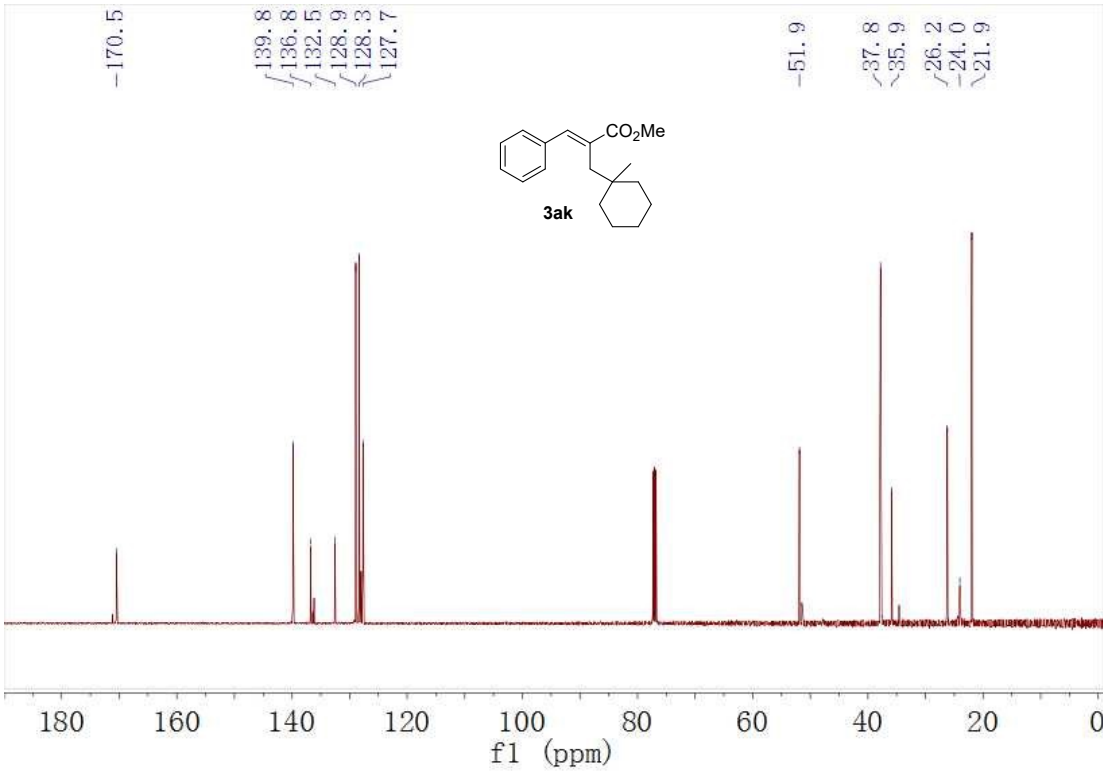
^{13}C NMR of **3aj** in $CDCl_3$



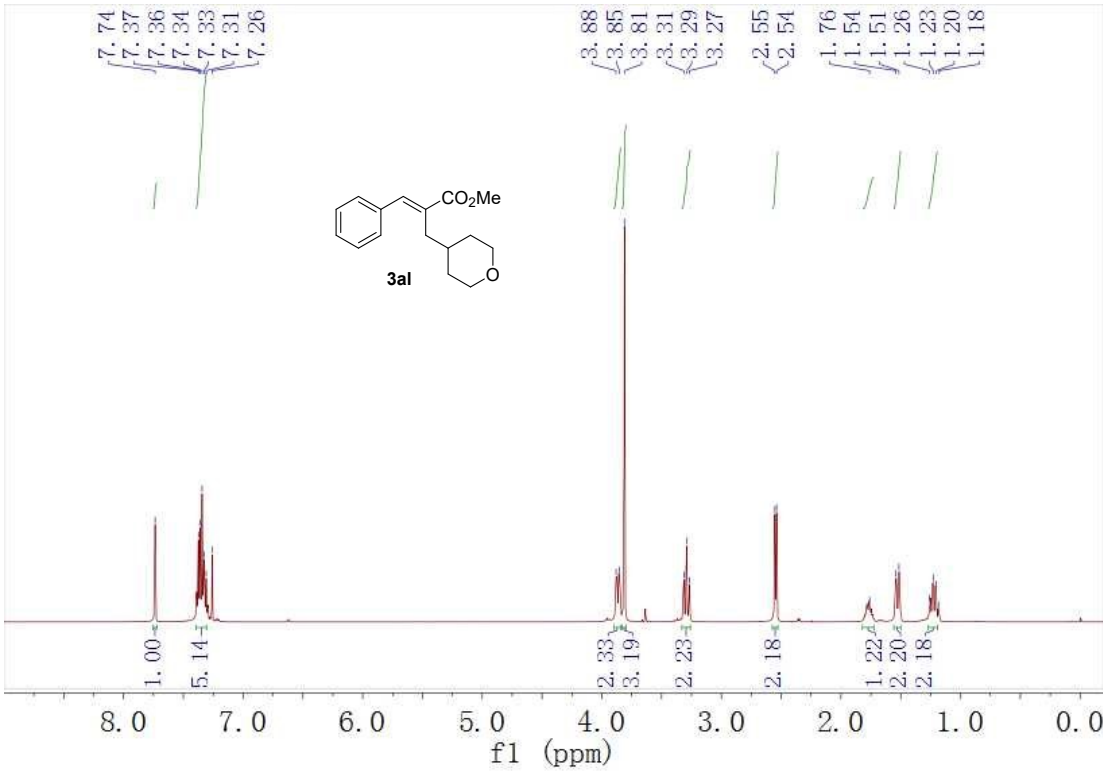
^{1}H NMR of **3ak** in $CDCl_3$



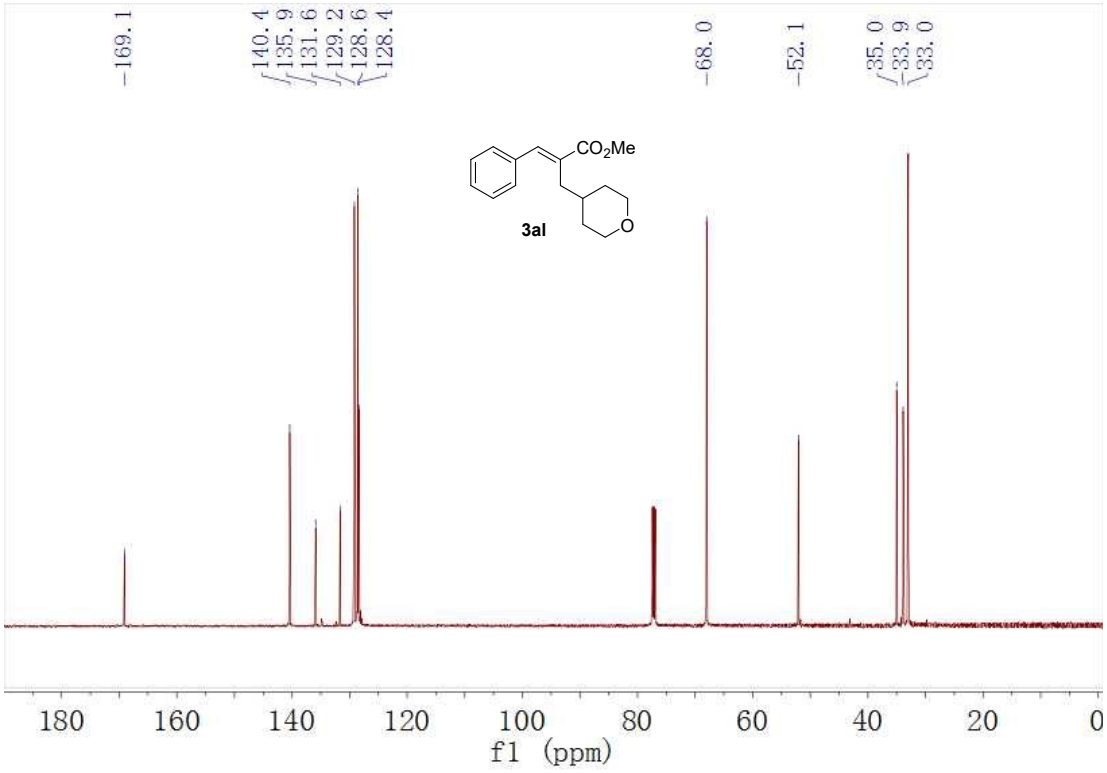
^{13}C NMR of **3ak** in $CDCl_3$



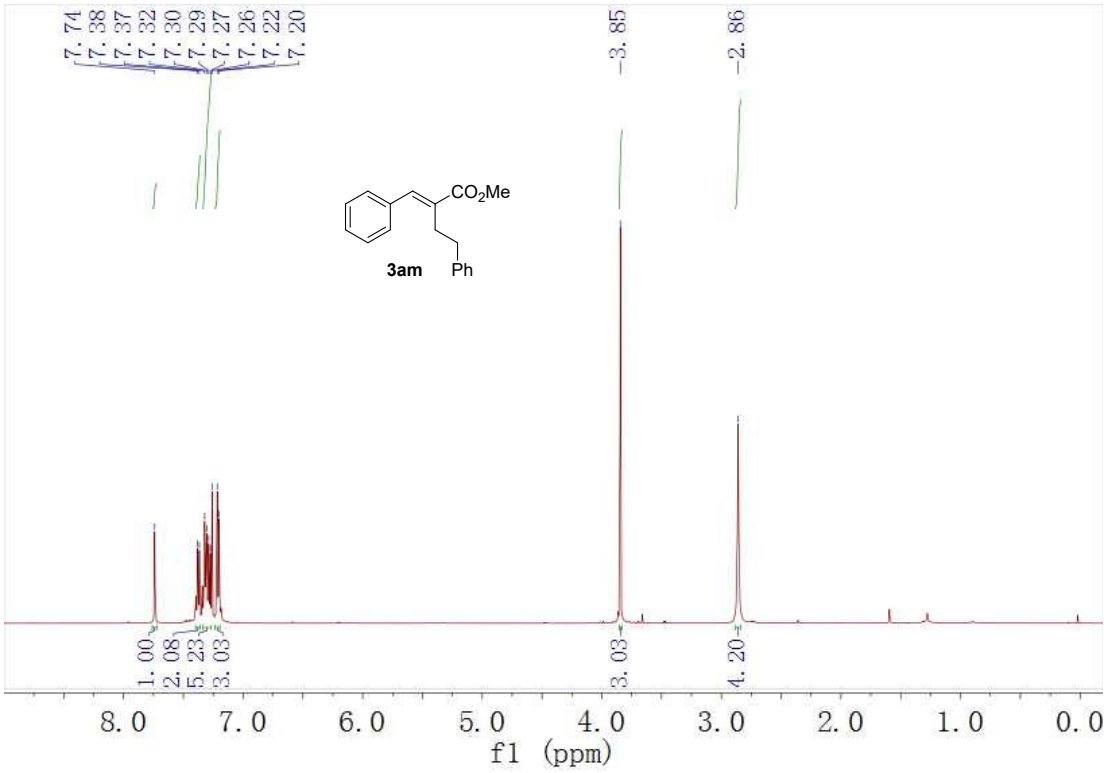
^{1}H NMR of **3al** in $CDCl_3$



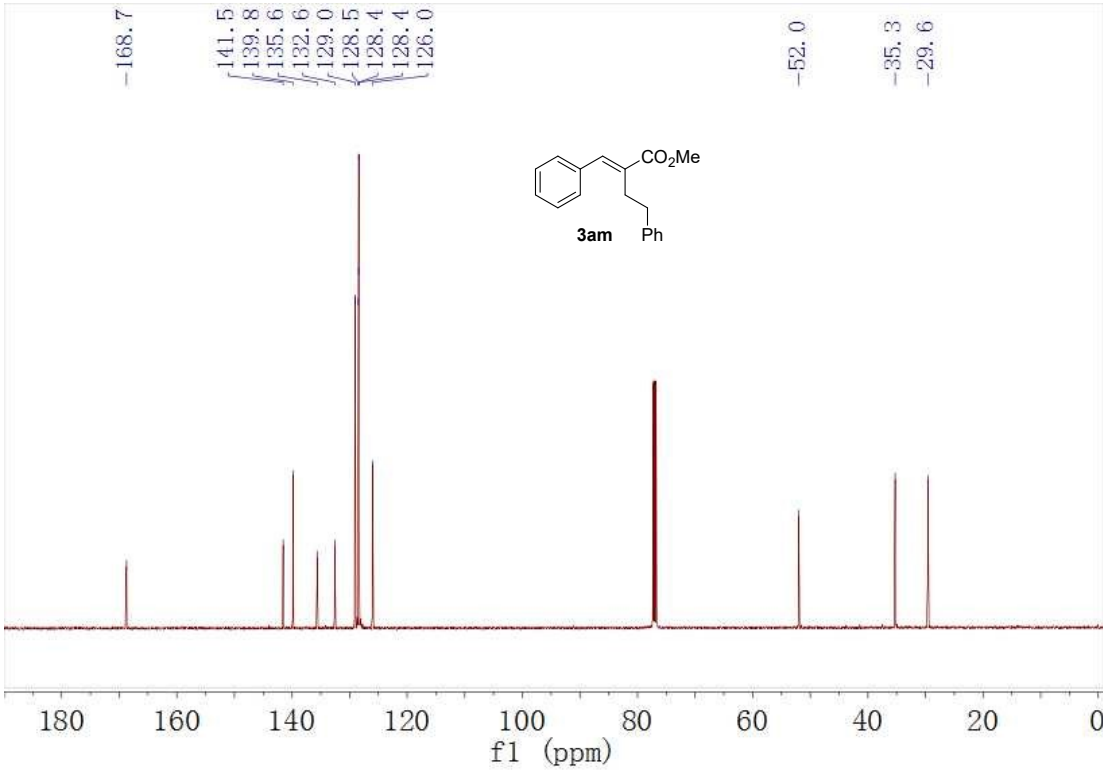
^{13}C NMR of **3al** in $CDCl_3$



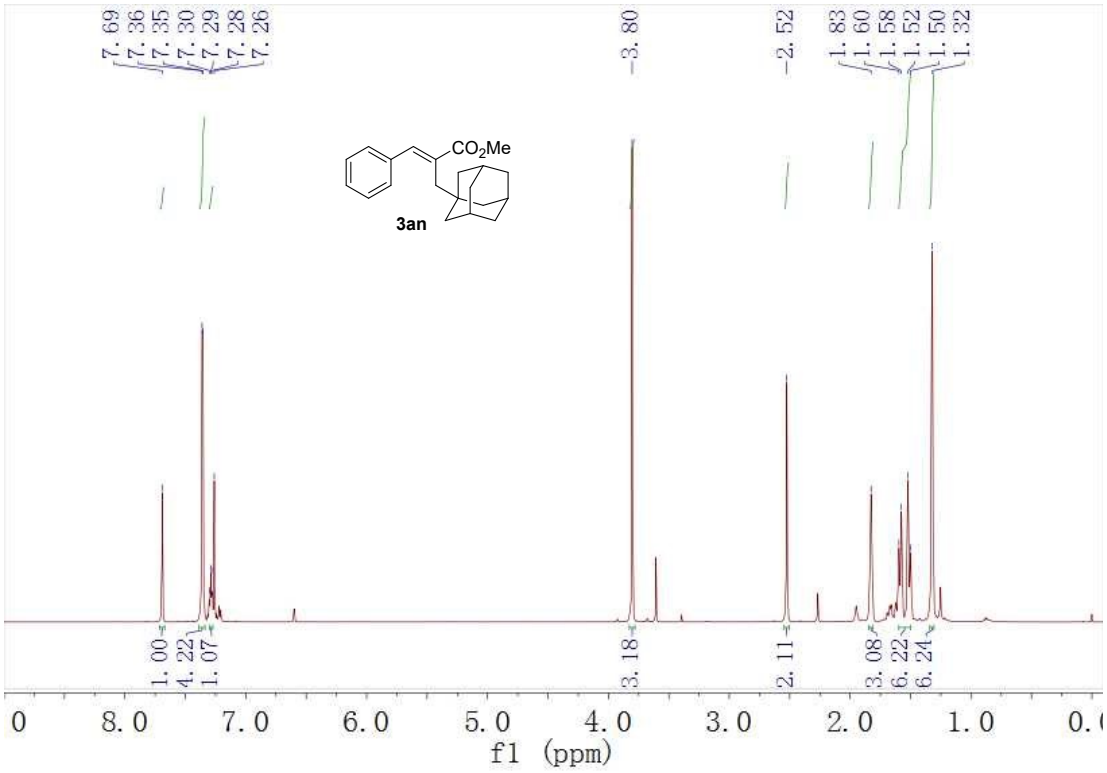
^{1}H NMR of **3am** in $CDCl_3$



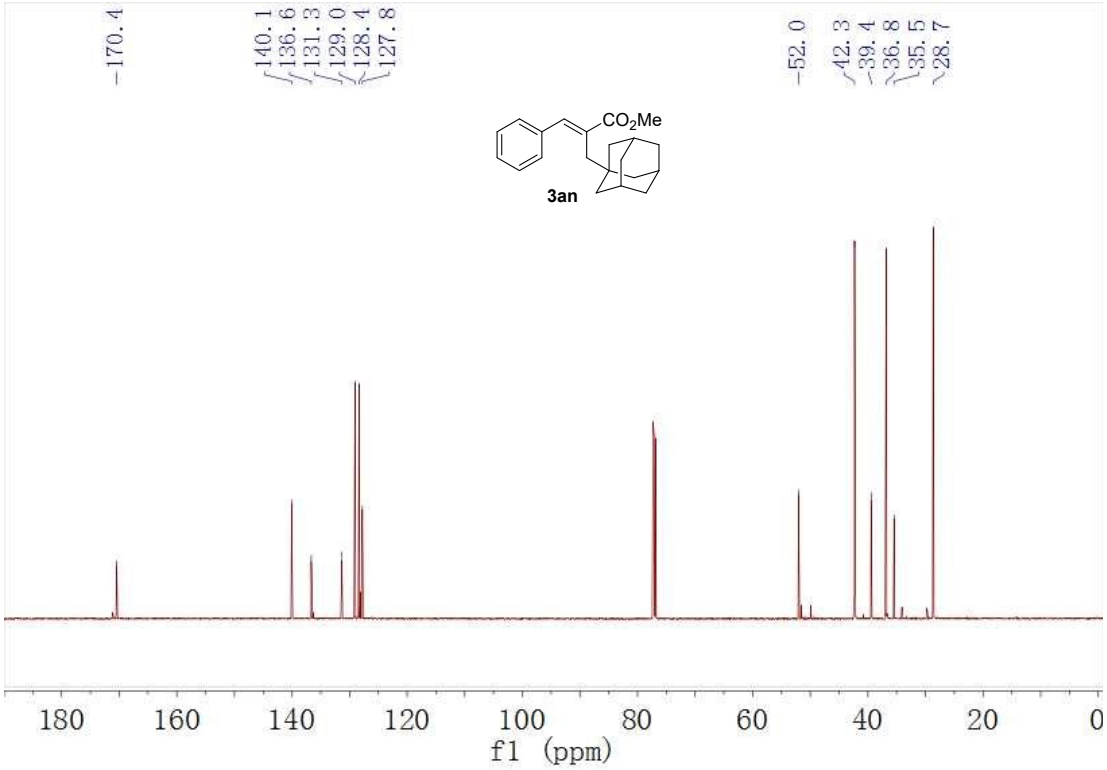
^{13}C NMR of **3am** in $CDCl_3$



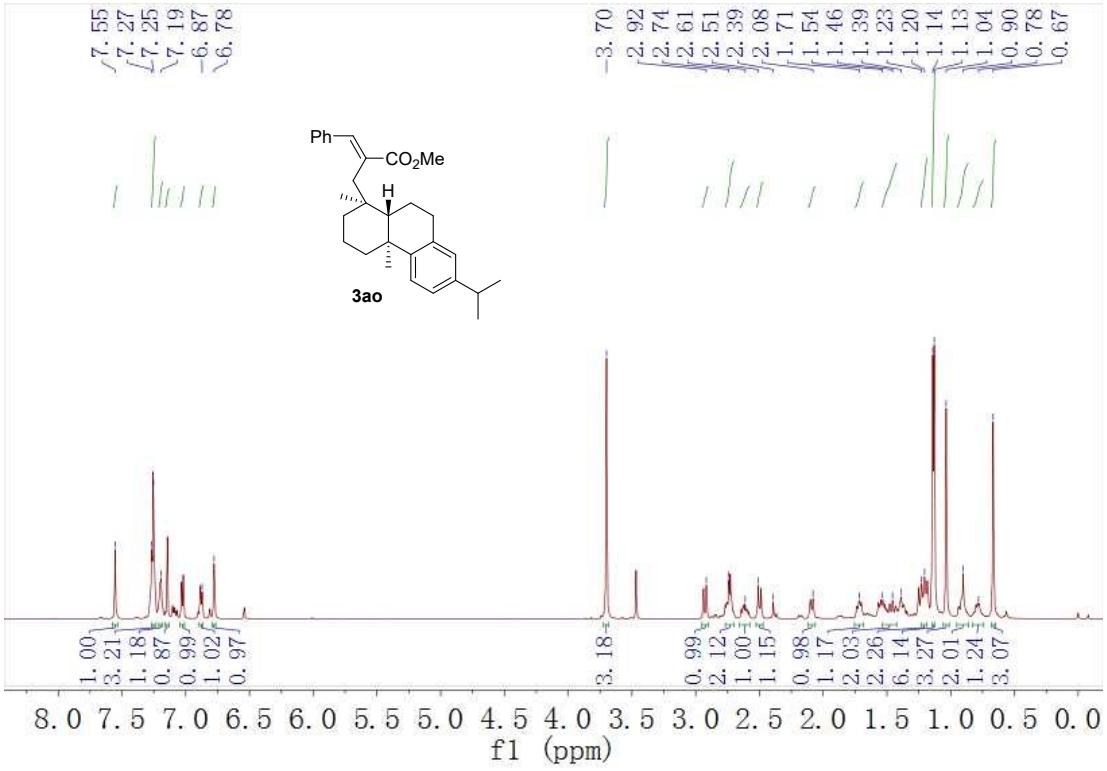
^{1}H NMR of **3an** in $CDCl_3$



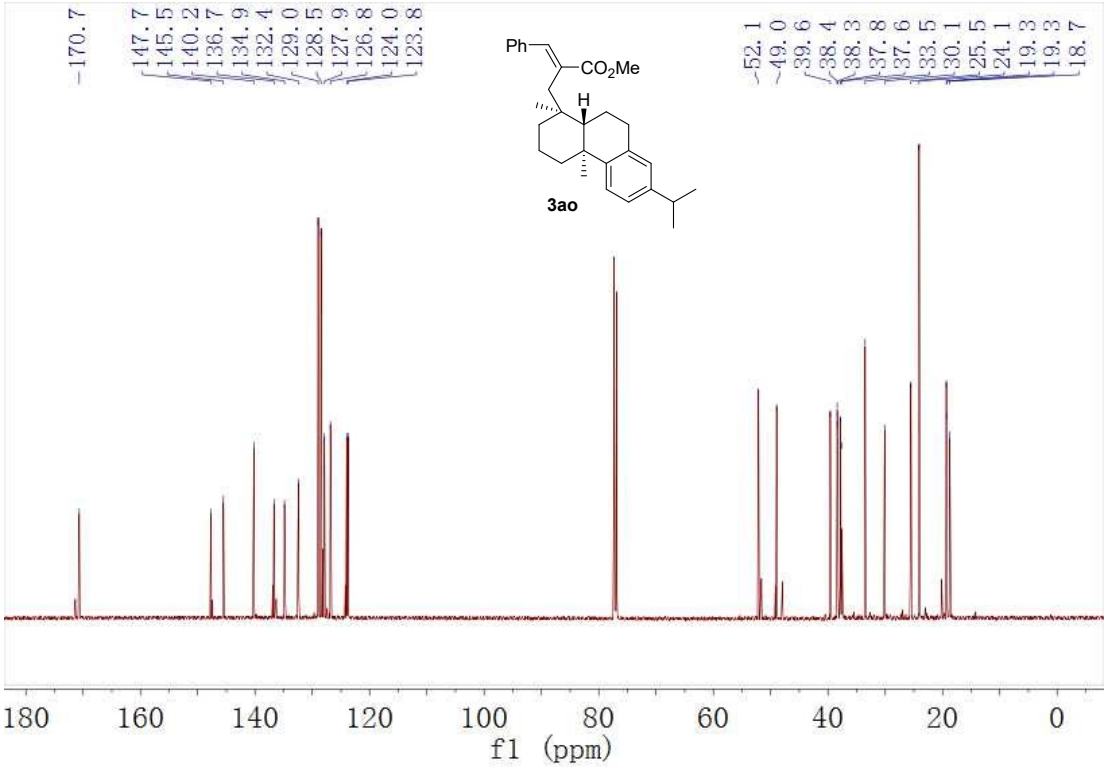
^{13}C NMR of **3an** in $CDCl_3$



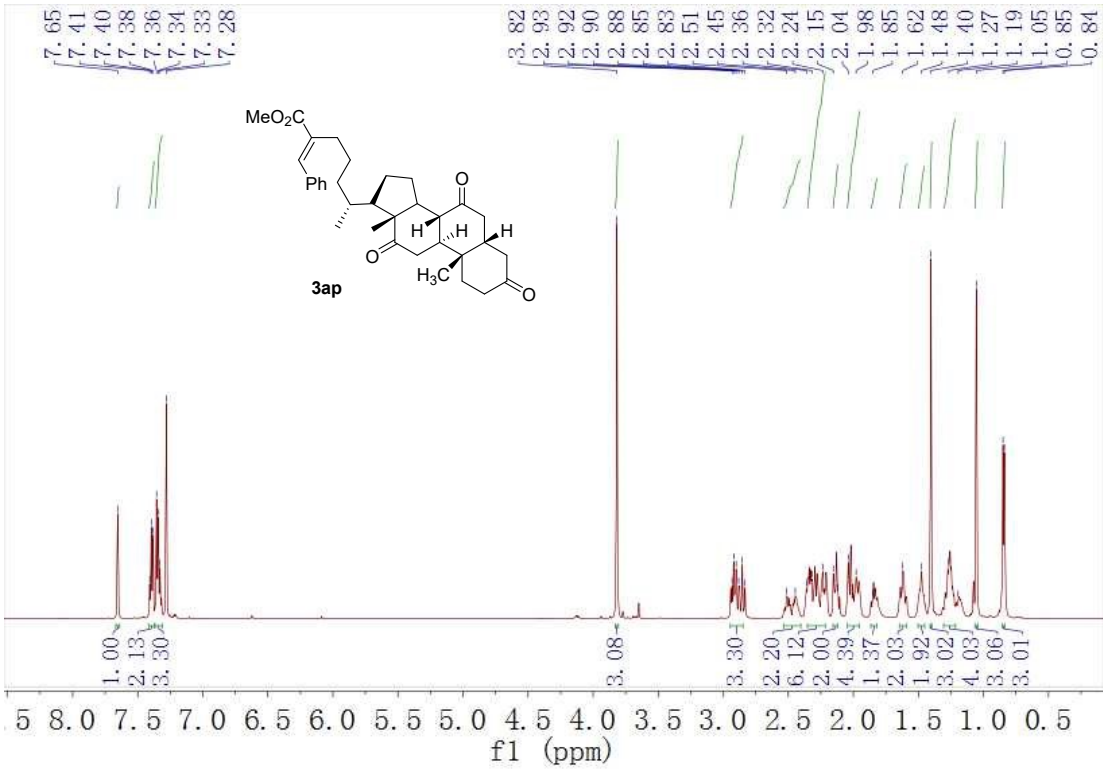
^{1}H NMR of **3ao** in $CDCl_3$



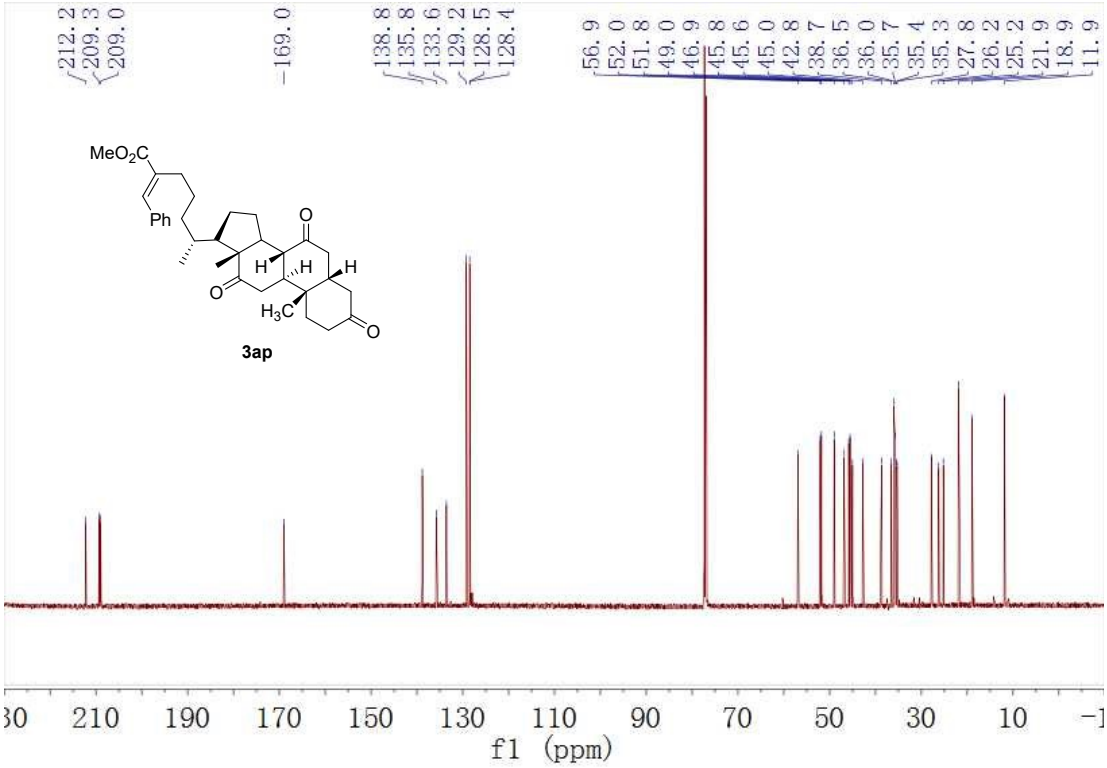
^{13}C NMR of **3ao** in $CDCl_3$



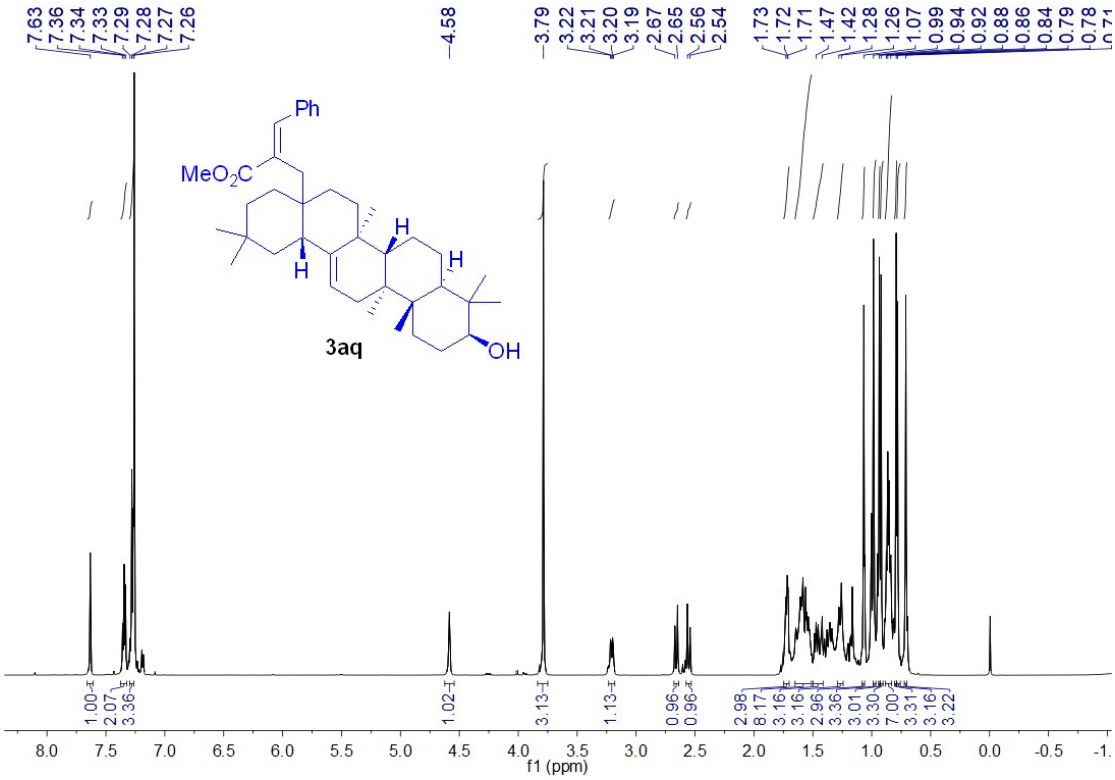
^{1}H NMR of **3ap** in $CDCl_3$



^{13}C NMR of **3ap** in $CDCl_3$



^{1}H NMR of **3aq** in $CDCl_3$



^{13}C NMR of **3aq** in $CDCl_3$