Electronic Supplementary Material (ESI) for Chemical Communications


# Pd-catalysed direct oxidative carboxylation of alkenes: facile synthesis of vinyl esters

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## Supporting Information

## 1. General Information

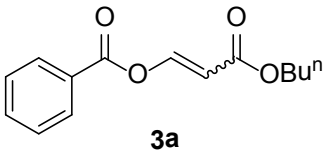
Flash chromatography was performed on silica gel 100-200 m. The solvent system used was a gradient of petroleum ether/ethyl acetate, increasing in polarity to ethyl acetate. Thin layer chromatography (TLC) was performed on glass backed plates pre-coated with silica (GF254), which were developed using standard visualizing agents. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a 600 MHz BRUKER AVANCE spectrometer at 25 $^{o}C$. 1H: Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet, sept = sepetet), integration, coupling constants (*J*) in Hz. $^{13}C$ NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: δ 77.0 ppm). Low resolution mass spectra were recorded on Micromass Autospec, operating in Agilent GC-MS operating in either E.I. or C.I mode. High-resolution mass spectra (HRMS) recorded for accurate mass analysis, were performed on a Q-TOF micro (Waters) spectrometer. Melting points were performed on recrystallized solids and recorded on a national standard melting point apparatus and are uncorrected.

## 2. General Procedures: Synthesis of Vinyl esters and Analogues

**2.1 General Procedure A:** A solution of acid (0.3 mmol), alkene (1.5 mmol), $Pd(OAc)_2$ (10 mol%) and $Ag_2CO_3$ (0.6 mmol) in MeCN (1.5 mL) was refluxed at 80 $^oC$ under 1 atm $O_2$. The reaction was monitored by TLC. After 12-36 h, the reaction mixture was cooled down to room temperature and diluted with ethyl acetate (10 mL). The mixture was filtered and dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure to provide the crude product. The crude product was purified by flash column chromatography on silica gel.

**2.2 General Procedure B:** A solution of acid (0.3 mmol), alkene (1.5 mmol), $Pd(OAc)_2$ (20 mol%) and $Ag_2CO_3$ (0.6 mmol) in MeCN (1.5 mL) was refluxed at 80 $^oC$ under 1 atm $O_2$. The reaction was monitored by TLC. After 12-36 h, the reaction mixture was cooled down to room temperature and diluted with ethyl acetate (10 mL). The mixture was filtered and dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure to provide the crude product. The crude product was purified by flash column chromatography on silica gel.

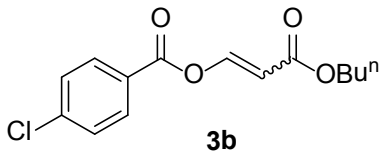
## 3. The synthesis of vinyl esters




**3a**

### 3-Butoxy-3-oxoprop-1-enyl benzoate (3a)

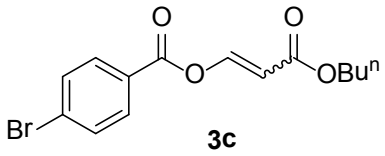
Following general procedure A, a solution of acid **1a** (36.6 mg, 0.3 mmol), n-butyl acrylate (192 mg, 1.5 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%) and $Ag_2CO_3$ (165 mg, 0.6 mmol) in MeCN (1.5 mL) was heated at refluxed for 24 h to give the desired **3a** (68 mg, 91%) as a colourless oil (E:Z = 92:8); **(Major isomer E): $^1$H NMR (400 MHz, $CDCl_3$)**: δ 8.54 (d, *J* = 12.5 Hz, 1H, =CH), 8.13 (d, *J* = 7.5 Hz, 2H, ArH), 7.66 (t, *J* = 7.5 Hz, 1H, ArH), 7.51 (t, *J* = 7.5 Hz, 2H, ArH), 5.91 (d, *J* = 12.5 Hz, 1H, =CH), 4.20 (t, *J* = 7.0 Hz, 2H, $CH_2$), 1.70-1.64 (m, 2H, $CH_2$), 1.45-1.40 (m, 2H, $CH_2$), 0.96 (t, *J* = 7.0 Hz, 3H, $CH_3$); **$^{13}$C NMR (151 MHz, $CDCl_3$)**: δ 166.3, 162.6, 149.8, 134.4, 130.4, 128.8, 127.8, 106.5, 64.5, 30.7, 19.2, 13.7; HRMS (ESI) *m/z* calcd for $C_{14}H_{16}O_4$ 248.1049; found 248.1047.




**3b**

**3-Butoxy-3-oxoprop-1-enyl-4-chlorobenzoate (3b)**

Following general procedure B, a solution of acid **1b** (46.6 mg, 0.3 mmol), n-butyl acrylate (192 mg, 1.5 mmol), $Pd(OAc)_2$ (13.4 mg, 20 mol%) and $Ag_2CO_3$ (165 mg, 0.6 mmol) in MeCN (1.5 mL) was heated at reflux for 24 h under 1 atm $O_2$ to give the desired **3b** (79 mg, 93%) as a light yellow oil (E:Z = 93:7); **(Major isomer E): $^1$H NMR (600 MHz, $CDCl_3$):** δ 8.50 (d, *J* = 12.5 Hz, 1H, =CH), 8.05 (d, *J* = 8.5 Hz, 2H, ArH), 7.48 (d, *J* = 8.5 Hz, 2H, ArH), 5.91 (d, *J* = 12.5 Hz, 1H, =CH), 4.19 (t, *J* = 7.0 Hz, 2H, $CH_2$), 1.70-1.65 (m, 2H, $CH_2$), 1.45-1.39 (m, 2H, $CH_2$), 0.96 (t, *J* = 7.0 Hz, 3H, $CH_3$); **$^{13}$C NMR (151 MHz, $CDCl_3$)**: δ 166.1, 161.8, 149.5, 141.1, 131.7, 129.2, 126.2, 106.8, 64.5, 30.7, 19.2, 13.7; HRMS (ESI) *m/z* calcd for $C_{14}H_{15}{}^{35}ClO_4$ 282.0659; found 282.0662.

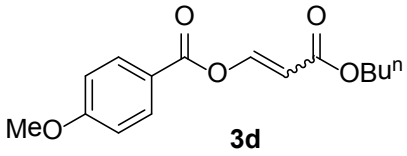



**3c**

**3-Butoxy-3-oxoprop-1-enyl-4-bromobenzoate (3c)**

Following general procedure B, a solution of acid **1c** (60.3 mg, 0.3 mmol), n-butyl acrylate (192 mg, 1.5 mmol), $Pd(OAc)_2$ (13.4 mg, 20 mol%) and $Ag_2CO_3$ (165mg, 0.6 mmol) in MeCN (1.5 mL) was heated at reflux for 24 h to give the desired **3c** (90 mg, 92%) as a white solid (E : Z

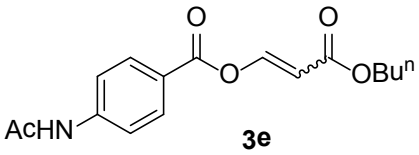
= 91 : 9): Mp 59-61°C; **(Major isomer E): $^{1}$H NMR (600 MHz, $CDCl_3$)**: δ 8.41 (d, *J* = 12.5 Hz, 1H, =CH), 7.89 (d, *J* = 8.5 Hz, 2H, ArH), 7.56 (d, *J* = 8.5 Hz, 2H, ArH), 5.83 (d, *J* = 12.5 Hz, 1H, =CH), 4.11 (t, *J* = 7.0 Hz, 2H, $CH_2$), 1.62-1.56 (m, 2H, $CH_2$), 1.36-1.32 (m, 2H, $CH_2$), 0.88 (t, *J* = 7.0 Hz, 3H, $CH_3$); **$^{13}$C NMR (151 MHz, $CDCl_3$)**: δ 166.1, 161.9, 149.5, 132.2, 131.7, 129.8, 126.7, 106.8, 64.5, 30.7, 19.2, 13.7; HRMS (ESI) *m/z* calcd for $C_{14}H_{15}{}^{79}BrO_4$ 326.0154; found 326.0155.




**3d**

**3-Butoxy-3-oxoprop-1-enyl-4-methoxybenzoate (3d)**

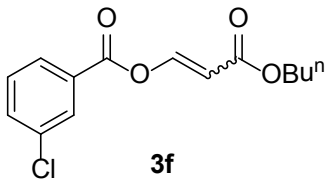
Following general procedure A, a solution of acid **1d** (45.6 mg, 0.3 mmol), n-butyl acrylate (192 mg, 1.5 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%) and $Ag_2CO_3$ (165 mg, 0.6 mmol) in MeCN (1.5 mL) was heated at reflux for 33 h to give the desired **3d** (66 mg, 78%) as a light yellow oil (E:Z = 92:8); **(Major isomer E): $^{1}$H NMR (600 MHz, $CDCl_3$)**: δ 8.53 (d, *J* = 12.5 Hz, 1H, =CH), 8.07（d, *J* = 8.5 Hz, 2H, ArH), 6.97 (d, *J* = 8.5 Hz, 2H, ArH), 5.87(d, *J* = 12.5 Hz, 1H, =CH), 4.19 (t, *J* = 7.0 Hz, 2H, $CH_2$), 3.89 (s, 3H, MeO), 1.68-1.65 (m, 2H, $CH_2$), 1.44-1.40 (m, 2H, $CH_2$), 0.97-0.95(t, *J* = 7.0 Hz, 3H, $CH_3$); **$^{13}$C NMR (151 MHz, $CDCl_3$)**:166.4, 164.6, 162.2, 150.0, 132.6, 119.9, 114.1, 105.9, 64.4, 55.6, 30.7, 19.2, 13.7; HRMS (ESI) *m/z* calcd for $C_{15}H_{18}O_5$ 278.1154; found 278.1152.




**3e**

**3-Butoxy-3-oxoprop-1-enyl-4-acetamidobenzoate (3e)**

Following general procedure A, a solution of acid **1e** (53.7 mg, 0.3 mmol), n-butyl acrylate (192 mg, 1.5 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%) and $Ag_2CO_3$ (165mg, 0.6 mmol) in MeCN (1.5 mL) was heated at reflux for 24 h under $O_2$ to give the desired **3e** (48 mg, 53%) as a white solid (E:Z = 94:6): Mp 136-137°C; **(Major isomer E): $^1$H NMR (600 MHz, $CDCl_3$):** δ 8.52 (d, *J* = 12.5 Hz, 1H, =CH), 8.07 (d, *J* = 8.5 Hz, 2H, ArH), 7.99 (s, 1H, NH), 7.69 (d, *J* = 8.5 Hz, 2H, ArH), 5.89 (d, *J* = 12.5 Hz, 1H, =CH), 4.19 (t, *J* = 7.0 Hz, 2H, $CH_2$), 2.23 (s, 3H, $CH_3$), 1.70-1.65 (m, 2H, $CH_2$), 1.44-1.40 (m, 2H, $CH_2$), 0.96 (t, *J* = 7.0 Hz, 3H, $CH_3$); **$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 168.8, 166.5, 162.0, 149.9, 143.6, 131.7, 122.7, 119.0, 106.2, 64.5, 30.7, 24.7, 19.2, 13.7; HRMS (ESI) *m/z* calcd for $C_{16}H_{19}NO_5$ 305.1263; found 305.1266.

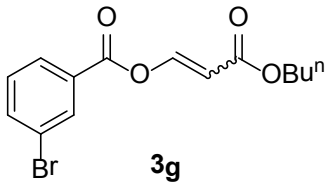



**3f**

**Butoxy-3-oxoprop-1-enyl-3-chlorobenzoate (3f)**

Following general procedure A, a solution of acid **1f** (46.6 mg, 0.3 mmol), n-butyl acrylate (192 mg, 1.5 mmol), $Pd(OAc)_2$ (6.7 mg, 10

mol%) and $Ag_2CO_3$ (165 mg, 0.6 mmol) in MeCN (1.5 mL) was heated at reflux for 24 h to give the desired **3f** (74 mg, 88%) as a colourless oil (E:Z = 91:9); **(Major isomer E): $^1$H NMR (600 MHz, $CDCl_3$)**: δ 8.50 (d, *J* = 12.5 Hz, 1H, =CH), 8.09 (s, 1H, ArH), 8.01 (d, *J* = 8.0 Hz, 1H, ArH), 7.62 (dd, *J* = 8.0, 1.0 Hz, 1H, ArH), 7.45 (t, *J* = 8.0 Hz, 1H, ArH), 5.93 (d, *J* = 12.5 Hz, 1H, =CH), 4.20 (t, *J* = 7.0 Hz, 2H, $CH_2$), 1.71-1.65 (m, 2H, $CH_2$), 1.42-1.40 (m, 2H, $CH_2$), 0.96 (t, *J* = 7.0 Hz, 3H, $CH_3$); **$^{13}$C NMR (151 MHz, $CDCl_3$)**: δ 166.0, 161.5, 149.4, 135.0, 134.4, 130.3, 130.1, 129.5, 128.4, 107.1, 64.6, 30.7, 19.2, 13.7; HRMS (ESI) *m/z* calcd for $C_{14}H_{15}{}^{35}ClO_4$ 282.0659; found 282.0662.

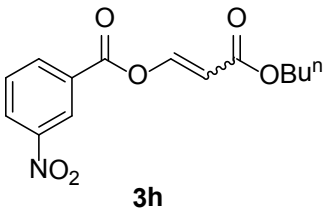



**3g**

**3-Butoxy-3-oxoprop-1-enyl-3-bromobenzoate (3g)**

Following general procedure A, a solution of acid **1g** (60.3 mg, 0.3 mmol), n-butyl acrylate (192 mg, 1.5 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%) and $Ag_2CO_3$ (165 mg, 0.6 mmol) in MeCN (1.5 mL) was heated at refluxed for 24 h to give the desired **3g** (78 mg, 80%) as a colourless oil (E:Z = 92:8); **(Major isomer E): $^1$H NMR (600 MHz, $CDCl_3$):** δ 8.49 (d, *J* = 12.5 Hz, 1H, =CH), 8.24 (s, 1H, ArH), 8.05 (d, *J* = 8.0 Hz, 1H, ArH), 7.77 (d, *J* = 8.0 Hz, 1H, ArH), 7.39 (t, *J* = 7.0 Hz, 1H, ArH), 5.93 (d, *J* = 12.5 Hz, 1H, =CH), 4.20 (t, *J* = 7.0 Hz, 2H, $CH_2$), 1.70-1.65

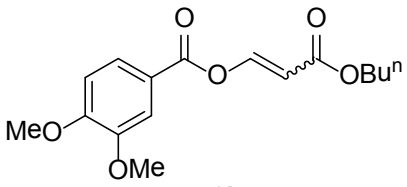
(m, 2H, $CH_2$), 1.46-1.39 (m, 2H, $CH_2$), 0.96 (t, $J$ = 8.0 Hz, 3H, $CH_3$); **$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 166.0, 161.3, 149.4, 137.3, 133.2, 130.3, 129.7, 128.9, 122.8, 107.1, 64.6, 30.7, 19.2, 13.7; HRMS (ESI) *m/z* calcd for $C_{14}H_{15}{}^{79}BrO_4$ (M+H) 326.0154; found 326.0159.




**3h**

**3-Butoxy-3-oxoprop-1-enyl-3-nitrobenzoate (3h)**

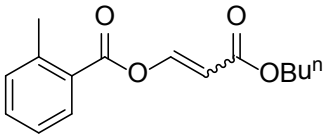
Following general procedure B, a solution of acid **1h** (50.1 mg, 0.3 mmol), n-butyl acrylate (192 mg, 1.5 mmol), $Pd(OAc)_2$ (13.4 mg, 20 mol%) and $Ag_2CO_3$ (165 mg, 0.6 mmol) in MeCN (1.5 mL) was heated at reflux for 24 h to give the desired **3h** (45 mg, 52%) as a colourless oil ( E:Z = 93:7); **(Major isomer E): $^1$H NMR (600 MHz, $CDCl_3$)**: δ 8.87 (s, 1H, =CH), 8.45-8.42 (m, 2H, ArH), 8.38 (d, $J$ = 8.0 Hz, 1H, ArH), 7.67 (t, $J$ = 8.0 Hz, 1H), 5.93 (d, $J$ = 12.5 Hz, 1H, =CH), 4.14 (t, $J$ = 7.0 Hz, 2H, $CH_2$), 1.63-1.60 (m, 2H, $CH_2$), 1.38-1.34 (m, 2H, $CH_2$), 0.89 (t, $J$ = 7.0 Hz, 3H, $CH_3$); **$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 165.8, 160.8, 149.1, 148.5, 135.8, 130.1, 129.7, 128.6, 125.2, 107.8, 64.7, 30.7, 19.2, 13.7; HRMS (ESI) *m/z* calcd for $C_{14}H_{15}NO_6$ (M+H) 293.0899; found 293.0905.




**3i**

**3-Butoxy-3-oxoprop-1-enyl-3,4-dimethoxybenzoate (3i)**

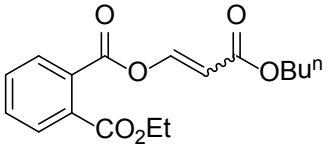
Following general procedure A, a solution of acid **1i** (54.6 mg, 0.3 mmol), n-butyl acrylate (192 mg, 1.5 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%) and $Ag_2CO_3$ (165 mg, 0.6 mmol) in MeCN (1.5 mL) was heated at reflux for 24 h to give the desired **3i** (60 mg, 65%) as a white solid: Mp 82-83$^o$C; **(Major isomer E): $^1$H NMR (600 MHz, $CDCl_3$):** δ 8.53 (d, *J* = 12.5 Hz, 1H, =CH), 7.78 (dd, *J* = 8.5, 2.0 Hz, 1H, ArH), 7.57 (d, *J* = 2.0 Hz, 1H, ArH), 6.94 (d, *J* = 8.5 Hz, 1H, ArH), 5.89 (d, *J* = 12.5 Hz, 1H, =CH), 4.19 (t, *J* = 7.0 Hz, 2H, $CH_2$), 3.97 (s, 3H, OMe), 3.95 (s, 3H, OMe), 1.70-1.65 (m, 2H, $CH_2$), 1.44-1.41 (m, 2H, $CH_2$), 0.96 (t, *J* = 7.0 Hz, 3H, $CH_3$); **$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 166.4, 162.3, 154.3, 150.0, 149.0, 124.9, 120.0, 112.4, 110.5, 106.0, 64.4, 56.1, 30.7, 19.2, 13.7; HRMS (ESI) *m/z* calcd for $C_{16}H_{20}O_6$ 308.1260; found 308.1261.




**3j**

**3-Butoxy-3-oxoprop-1-enyl-2-methylbenzoate (3j)**

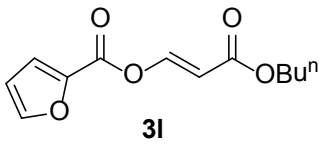
Following general procedure A, a solution of acid **1j** (40.8 mg, 0.3 mmol), n-butyl acrylate (192 mg, 1.5 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%) and $Ag_2CO_3$ (165 mg, 0.6 mmol) in MeCN (1.5 mL) was heated at reflux for 20 h to give the desired **3j** (65 mg, 83%) as a colourless oil (E:Z = 93:7); **(Major isomer E): $^1$H NMR (600 MHz, $CDCl_3$)**: δ 8.53 (d, *J* = 12.5 Hz, 1H, =CH), 8.03 (dd, *J* = 8.0 Hz, 1H, ArH), 7.48 (td, *J* = 7.5, 1.0 Hz, 1H, ArH), 7.32–7.28 (m, 2H, ArH), 5.87 (d, *J* = 12.5 Hz, 1H, =CH), 4.19 (t, *J* = 7.0 Hz, 2H, $CH_2$), 2.64 (s, 3H, $CH_3$) 1.71-1.65 (m, 2H, $CH_2$), 1.46-1.39 (m, 2H, $CH_2$), 0.96 (t, *J* = 7.0 Hz, 3H, $CH_3$); **$^{13}$C NMR (151 MHz, $CDCl_3$)**: δ 166.3, 162.7, 149.8, 142.0, 133.5, 132.1, 131.3, 126.7, 126.0, 106.1, 64.4, 30.7, 21.9, 19.2, 13.7; HRMS (ESI) *m/z* calcd for $C_{15}H_{18}O_4$ 262.1205; found 262.1208.




**3k**

**3-Butoxy-3-oxoprop-1-enyl ethyl phthalate (3k)**

Following general procedure B, a solution of acid **1k** (58 mg, 0.3 mmol), n-butyl acrylate (192 mg, 1.5 mmol), $Pd(OAc)_2$ (13.4 mg, 20 mol%) and $Ag_2CO_3$ (165 mg, 0.6 mmol) in MeCN (1.5 mL) was heated at reflux for 24 h to give the desired **3k** (65 mg, 68%) as a colourless oil (E:Z = 94:6); **(Major isomer E): $^1$H NMR (600 MHz, $CDCl_3$):** δ 8.48 (d, *J* = 12.5 Hz, 1H, =CH), 7.82 (dd, *J* = 7.5, 1.0 Hz, 1H, ArH), 7.78 (dd, *J* = 7.5, 1.0 Hz, 1H, ArH), 7.61 (td, *J* = 7.5, 1.5 Hz, 2H, ArH), 5.81 (d, *J* = 12.5 Hz, 1H, =CH), 4.37 (q, *J* = 7.0 Hz, 2H, $CH_2$), 4.18 (t, *J* = 7.0 Hz, 2H, $CH_2$), 1.71-1.63 (m, 2H, $CH_2$), 1.42-1.39 (m, 2H, $CH_2$), 1.36 (t, *J* = 7.0 Hz, 3H, $CH_3$), 0.96 (t, *J* = 7.0 Hz, 3H, $CH_3$); **$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 166.8, 166.1, 163.8, 149.6, 132.5, 132.2, 131.3, 129.8, 129.4, 129.3, 106.9, 64.5, 62.0, 30.7, 19.2, 14.1, 13.7; HRMS (ESI) *m/z* calcd for $C_{17}H_{20}O_6$ 320.1260; found 320.1260.

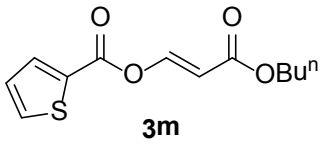



**3l**

**3-Butoxy-3-oxoprop-1-enyl furan-2-carboxylate (3l)**

Following general procedure A, a solution of acid **1l** (33.6 mg, 0.3 mmol), n-butyl acrylate (192 mg, 1.5 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%) and $Ag_2CO_3$ (165 mg, 0.6 mmol) in MeCN (1.5 mL) was heated at reflux for 27 h to give the desired **3l** (30 mg, 42%) as a colourless oil; **$^1$H NMR (600 MHz, $CDCl_3$)**: δ 8.46 (d, *J* = 12.5 Hz, 1H, =CH), 7.69

(s, 1H, ArH), 7.38 (d, $J$ = 3.0 Hz, 1H, ArH), 6.60 (d, $J$ = 3.0 Hz, 1H, ArH), 5.88 (d, $J$ = 12.5 Hz, 1H, =CH), 4.18 (t, $J$ = 7.0 Hz, 2H, $CH_2$), 1.69-1.65 (m, 2H, $CH_2$), 1.43-1.40 (m, 2H, $CH_2$), 0.96 (t, $J$ = 7.0 Hz, 3H, $CH_3$); **$^{13}$C NMR (151 MHz, $CDCl_3$)**: δ 166.1, 154.3, 149.0, 148.2, 142.5, 120.9, 112.5, 106.8, 64.5, 30.7, 19.2, 13.7; HRMS (ESI) *m/z* calcd for $C_{12}H_{14}O_5$ 238.0841; found 238.0846.

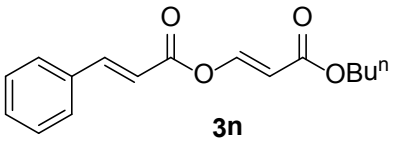



**3m**

**3-Butoxy-3-oxoprop-1-enyl thiophene-2-carboxylate (3m)**

Following general procedure B, a solution of acid **1m** (38.4 mg, 0.3 mmol), n-butyl acrylate (192 mg, 1.5 mmol), $Pd(OAc)_2$ (13.4 mg, 20 mol%) and $Ag_2CO_3$ (165 mg, 0.6 mmol) in MeCN (1.5 mL) was heated at reflux for 25 h to give the desired **3m** (36 mg, 47%) as a white solid (E:Z = 93:7): Mp 53-54 $^{o}$C; **(Major isomer E): $^1$H NMR (600 MHz, $CDCl_3$)**: δ 8.46 (d, $J$ = 12.5 Hz, 1H, =CH), 7.96 (dd, $J$ = 4.0, 1.0 Hz, 1H, ArH), 7.71 (dd, $J$ = 5.0, 1.0 Hz, 1H, ArH), 7.18 (dd, $J$ = 5.0, 4.0 Hz, 1H, ArH), 5.88 (d, $J$ = 12.5 Hz, 1H, =CH), 4.18 (t, $J$ = 7.0 Hz, 2H, $CH_2$), 1.69-1.64 (m, 2H, $CH_2$), 1.44-1.40 (m, 2H, $CH_2$), 0.96 (t, $J$ = 7.0 Hz, 3H, $CH_3$); **$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 166.2, 158.0, 149.4, 135.7, 134.8, 130.9, 128.3, 106.4, 64.5, 30.7, 19.2, 13.7; HRMS (ESI) *m/z* calcd for

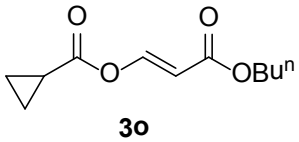
$C_{12}H_{14}O_4S$ 254.0613; found 254.0613.




**3n**

**3-Butoxy-3-oxoprop-1-enyl cinnamate (3n)**

Following general procedure A, a solution of acid **1n** (44.5 mg, 0.3 mmol), n-butyl acrylate (192 mg, 1.5 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%) and $Ag_2CO_3$ (165 mg, 0.6 mmol) in MeCN (1.5 mL) was heated at reflux for 30 h to give the desired **3n** (53 mg, 64%) as a light yellow oil (E:Z = 96:4); **(Major isomer E): $^1$H NMR (600 MHz, $CDCl_3$):** δ 8.44 (d, *J* = 12.5 Hz, 1H, =CH), 7.86 (d, *J* = 16.0 Hz, 1H, =CH), 7.57-7.56 (m, 2H, ArH), 7.44-7.42 (m, 3H, ArH), 6.48 (d, *J* = 16.0 Hz, 1H, =CH), 5.81 (d, *J* = 12.5 Hz, 1H, =CH), 4.18 (t, *J* = 7.0 Hz, 2H, $CH_2$), 1.69-1.64 (m, 2H, $CH_2$), 1.45-1.38 (m, 2H, $CH_2$), 0.95 (t, *J* = 7.4 Hz, 3H, $CH_3$); **$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 166.4, 162.7, 149.8, 148.5, 133.8, 131.3, 129.1, 128.5, 115.4, 106.0, 64.4, 30.7, 19.2, 13.7; HRMS (ESI) *m/z* calcd for $C_{16}H_{18}O_4$ 274.1205; found 274.1207.

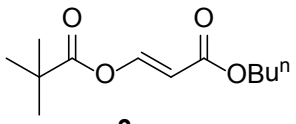



**3o**

**3-Butoxy-3-oxoprop-1-enyl cyclopropanecarboxylate (3o)**

Following general procedure A, a solution of acid **1o** (25.8 mg, 0.3

mmol), n-butyl acrylate (192 mg, 1.5 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%) and $Ag_2CO_3$ (165 mg, 0.6 mmol) in MeCN (1.5 mL) was heated at reflux for 21 h to give the desired **3o** (26 mg, 41%) as a colourless oil; **$^1$H NMR (600 MHz, $CDCl_3$):** δ 8.23 (d, *J* = 12.5 Hz, 1H, =CH), 5.65 (d, *J* = 12.5 Hz, 1H, =CH), 4.08 (t, *J* = 7.0 Hz, 2H, $CH_2$), 1.67-1.64 (m, 1H, CH), 1.60-1.55 (m, 2H, $CH_2$), 1.34-1.31 (m, 2H, $CH_2$), 1.10-1.07(m, 2H, $CH_2$), 0.99-0.95 (m, 2H, $CH_2$), 0.87 (t, *J* = 7.0 Hz, 3H, $CH_3$); **$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 171.1, 166.4, 149.6, 105.5, 64.3, 30.7, 19.1, 13.7, 12.5, 9.8; HRMS (ESI) *m/z* calcd for $C_{11}H_{16}O_4$ 212.1049; found 211.1052.

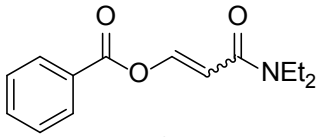



**3p**

**Butyl-3-(pivaloyloxy)acrylate (3p)**

Following general procedure A, a solution of acid **1p** (30.6 mg, 0.3 mmol), n-butyl acrylate (192 mg, 1.5 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%) and $Ag_2CO_3$ (165 mg, 0.6 mmol) in MeCN (1.5 mL) was heated at refluxed for 24 h to give the desired **3p** (29 mg, 42%) as a colourless oil (E:Z = 94:6); **(Major isomer E): $^1$H NMR (600 MHz, $CDCl_3$):** δ 8.23 (d, *J* = 12.5 Hz, 1H, =CH), 5.66 (d, d, *J* = 12.5 Hz, 1H, =CH), 4.09 (t, *J* = 7.0 Hz, 2H, $CH_2$), 1.60-1.55 (m, 2H, $CH_2$), 1.36-1.31 (m, 2H, $CH_2$), 1.20 (s, 9H, $CH_3$), 0.87 (t, *J* = 7.0 Hz, 3H, $CH_3$); **$^{13}$C NMR (151 MHz,**

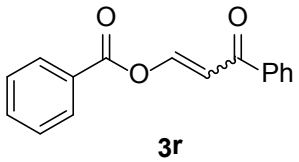
**$CDCl_3$):** δ 174.4, 166.4, 150.0, 105.8, 64.3, 38.9, 30.7, 26.7, 19.1, 13.7; HRMS (ESI) *m/z* calcd for $C_{12}H_{20}O_4$ 228.1362; found 228.1364.




**3q**

**3-(Diethylamino)-3-oxoprop-1-enyl benzoate (3q)**

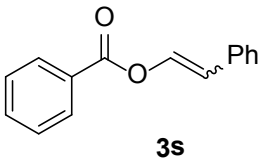
Following general procedure A, a solution of acid **1a** (36.6 mg, 0.3 mmol), N,N-diethylacrylamide (190 mg, 1.5 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%) and $Ag_2CO_3$ (165mg, 0.6 mmol) in MeCN (1.5 mL) was heated at reflux for 24 h to give the desired **3q** (56 mg, 76%) as a light yellow oil; **$^1$H NMR (600 MHz, $CDCl_3$)**: δ 8.52 (d, *J* = 12.0 Hz, 1H, =CH), 8.13 (d, *J* = 7.5 Hz, 2H, ArH), 7.63 (t, *J* = 7.5 Hz, 1H, ArH), 7.49 (t, *J* = 7.5 Hz, 2H, ArH), 6.34 (d, *J* = 12.0 Hz, 1H, =CH), 3.43 (d, *J* = 7.0 Hz, 4H, $CH_2$), 1.21 (d, *J* = 7.0 Hz, 6H, $CH_3$); **$^{13}$C NMR (151 MHz, $CDCl_3$)**: δ 164.7, 162.8, 148.6, 134.0, 130.2, 128.7, 128.2, 106.1, 42.3, 40.7, 29.7, 15.0, 13.2; HRMS (ESI) *m/z* calcd for $C_{14}H_{17}NO_3$ 247.1208; found 247.1209.




**3r**

**3-Oxo-3-phenylprop-1-enyl benzoate (3r)**

Following general procedure A, a solution of acid **1a** (36.6 mg, 0.3 mmol), 1-phenylprop-2-en-1-one (198 mg, 1.5 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%) and $Ag_2CO_3$ (165mg, 0.6 mmol) in MeCN (1.5 mL) was heated at reflux for 24 h to give the desired **3r** (25 mg, 33%) as a light yellow solid: Mp 72-74 °C; **$^1$H NMR (600 MHz, $CDCl_3$):** δ 8.65 (d, *J* = 12.0 Hz, 1H, =CH), 8.16 (d, *J* = 7.5 Hz, 2H, ArH), 7.96 (d, *J* = 7.5 Hz, 2H, ArH), 7.66 (t, *J* = 7.5 Hz, 1H, ArH), 7.59 (t, *J* = 7.5 Hz, 1H, ArH), 7.51 (t, *J* = 7.5 Hz, 4H, ArH), 6.98 (d, *J* = 12.0 Hz, 1H, =CH); **$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 190.4, 162.8, 150.7, 137.9, 134.4, 133.0, 130.4, 128.8, 128.7, 128.4, 127.8, 110.5; HRMS (ESI) *m/z* calcd for $C_{16}H_{12}O_3$ 252.0786; found 252.0786.

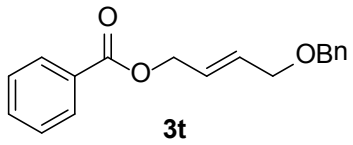



**3s**

**Styryl benzoate (3s)**

Following general procedure D, a solution of acid **1a** (36.6 mg, 0.3 mmol), styrene (156 mg, 1.5 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%), $Li_2CO_3$ (22 mg, 0.3 mmol) and $Ag_2CO_3$ (165 mg, 0.6 mmol) in MeCN (1.5 mL) was refluxed at 80 °C for 24 h to give the desired **3s** (43 mg, 58%) as a colourless oil[1] as a mixture of E and Z isomer (E:Z = 67:33); **(Major isomer E): $^1$H NMR (400 MHz, $CDCl_3$):** δ 8.09 (t, *J* = 7.5 Hz, 3H, ArH), 8.03 (d, *J* = 12.5 Hz, 1H, =CH), 7.63-7.14 (m, 7H, ArH), 6.53

(d, $J$ = 12.5 Hz, 1H, =CH). The analytical data are consistently agreed with those data have been reported previously in the literature.[1]




**3t**

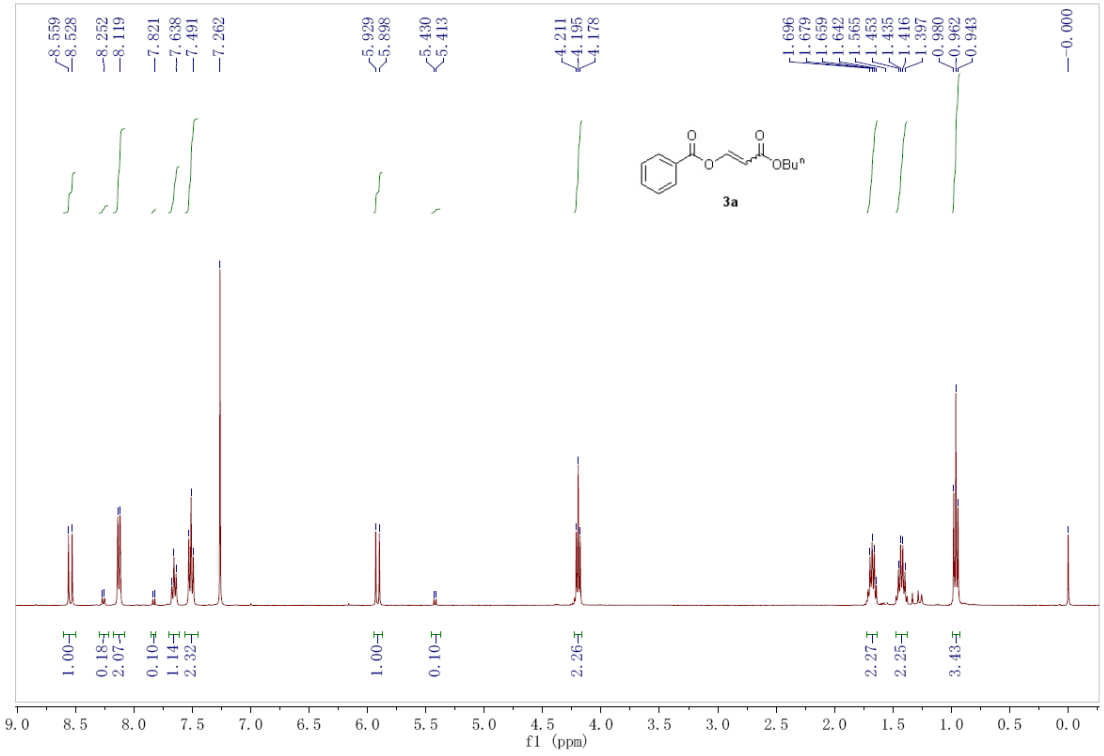
**4-(Benzyloxy)but-2-enyl benzoate (3t)**

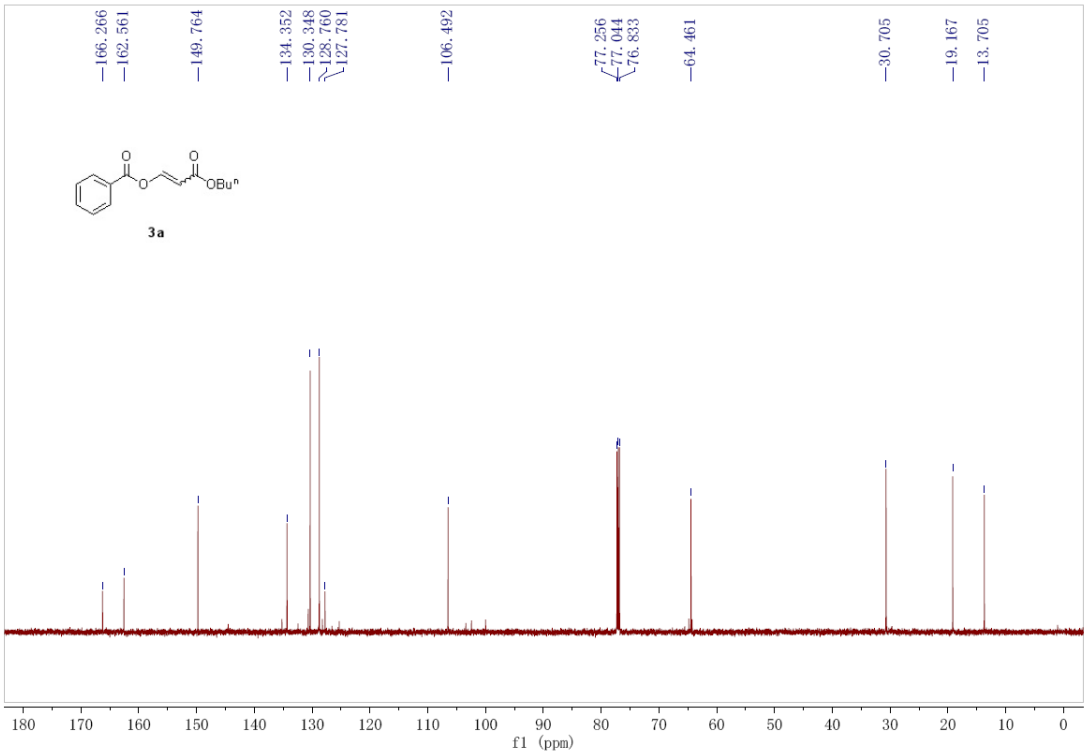
Following general procedure A, a solution of acid **1a** (36.6 mg, 0.3 mmol), ((but-3-enyloxy)methyl)benzene (243 mg, 1.5 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%) and $Ag_2CO_3$ (165 mg, 0.6 mmol) in MeCN (1.5 mL) was heated at reflux for 23 h to give the desired **3t** (55 mg, 65%) as a colourless oil; **$^1$H NMR (600 MHz, $CDCl_3$):** δ 8.06 (d, $J$ = 7.5, 2H, ArH), 7.54 (t, $J$ = 7.5 Hz, 1H, ArH), 7.42 (t, $J$ = 7.5 Hz, 2H, ArH), 7.34-7.33 (m, 4H, ArH), 7.28-7.26 (m, 1H, ArH), 5.98-5.96 (m, 2H, =CH), 4.84-4.83 (m, 2H, $CH_2$), 4.52 (s, 2H, $CH_2$), 4.06-4.05 (m, 2H, $CH_2$); **$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 166.3, 138.2, 133.0, 130.9, 130.2, 129.7, 129.6, 128.44, 128.38, 127.83, 127.79, 127.7, 126.7, 72.5, 69.9, 64.7; HRMS (ESI) *m/z* calcd for $C_{18}H_{18}O_3$ 282.1256; found 282.1255.

## 3. References

[1] S. Ye, W. K. Leong, *J. Organomet. Chem*., 2006, **691**, 1117.

## 4. 1H and 13C NMR Spectra

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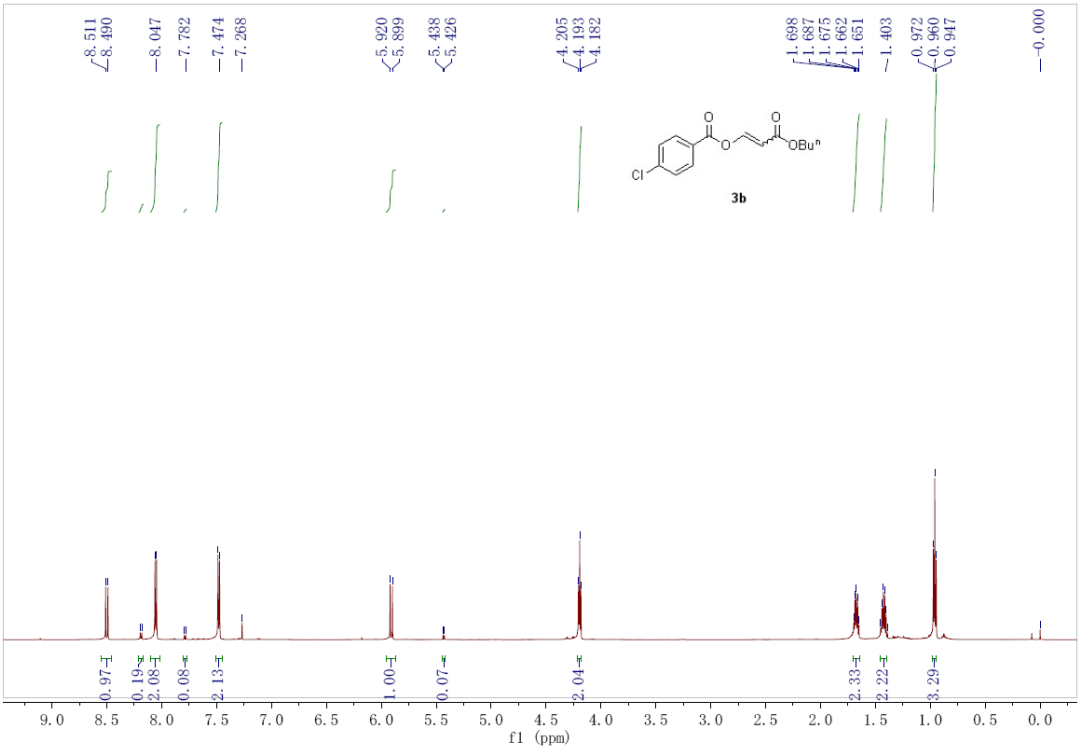
13.705
OBu$^n$
3a
f1 (ppm)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1.698
1.687
1.675
1.662
1.651
1.403
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0.960
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0.000
Cl
OBu$^n$
3b
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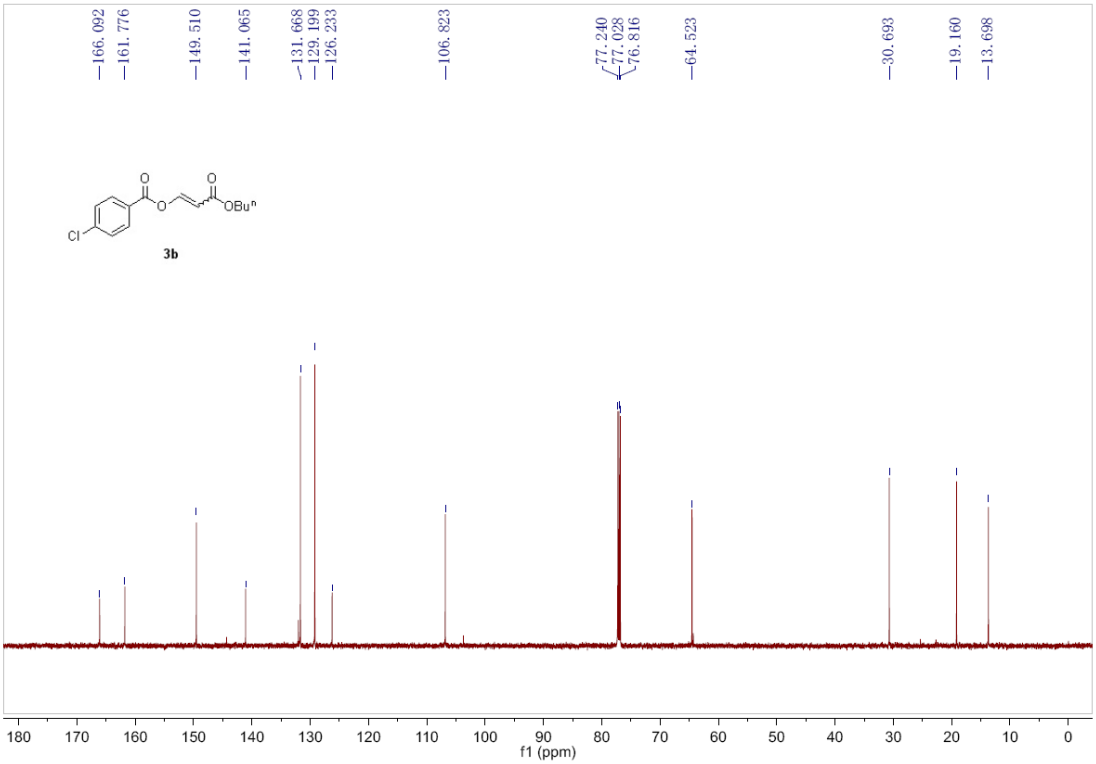
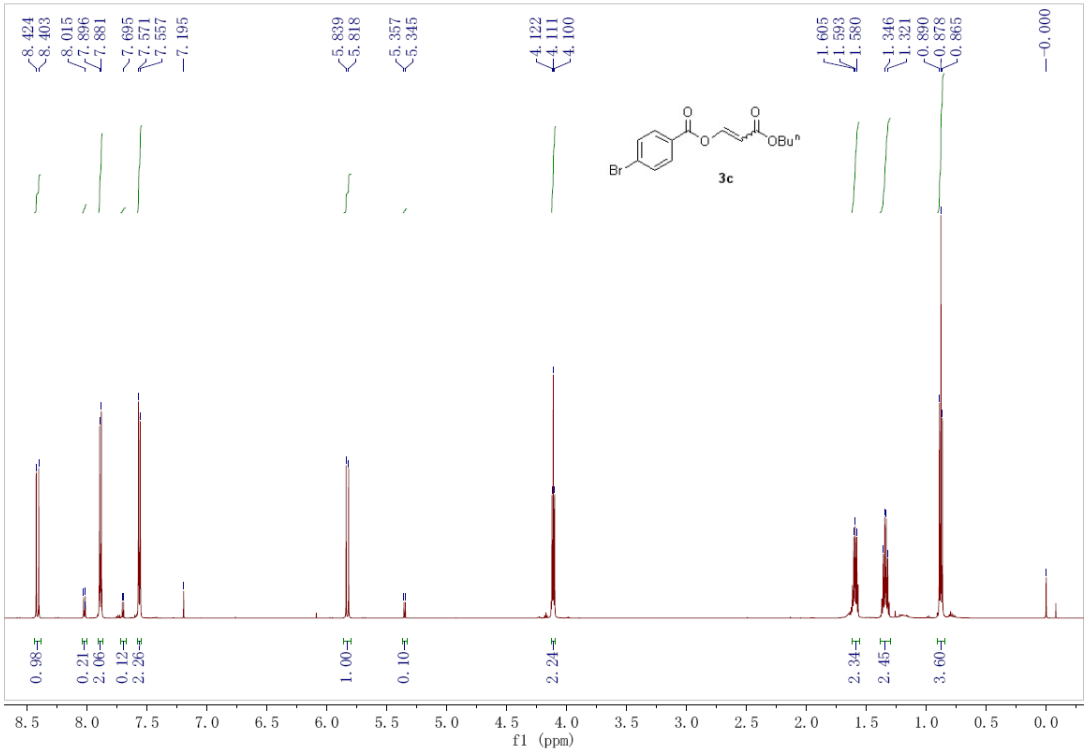
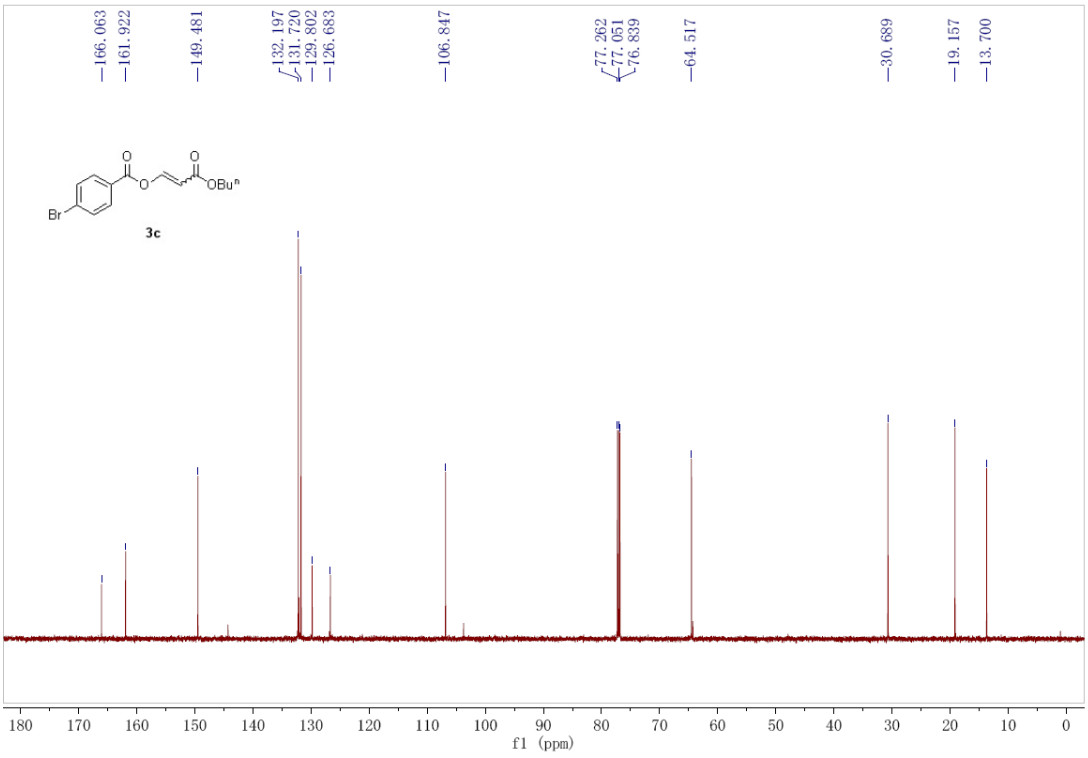
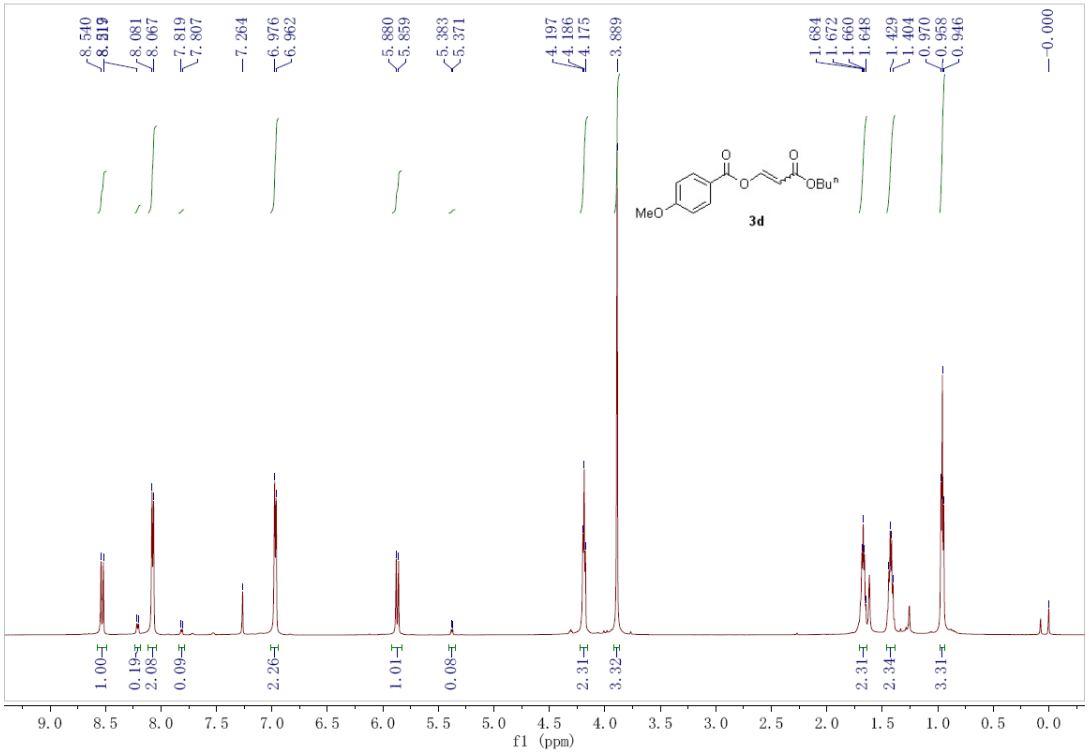
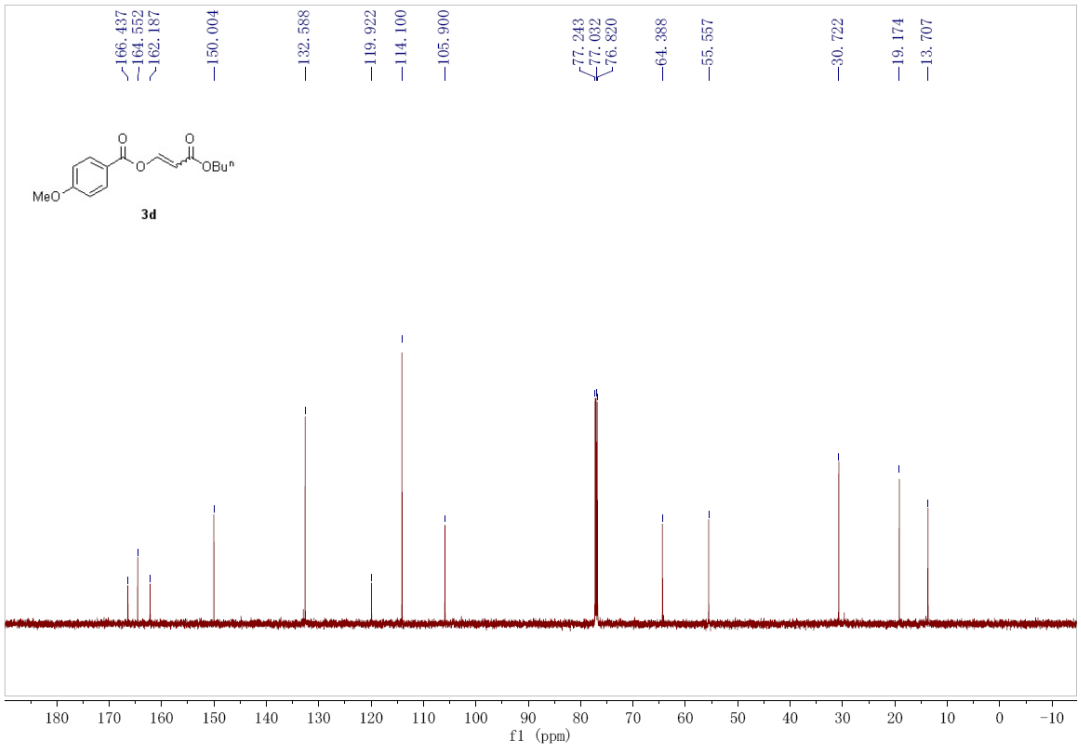
1.00
0.07
2.04
2.33
2.22
3.29
f1 (ppm)

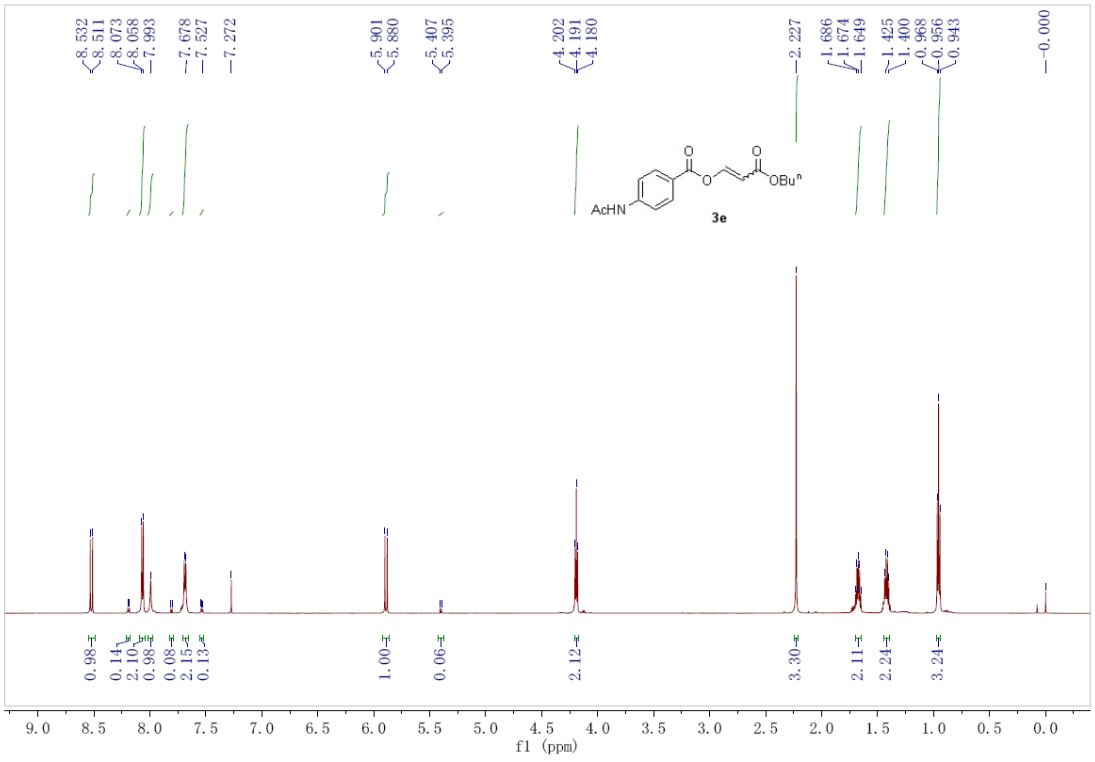


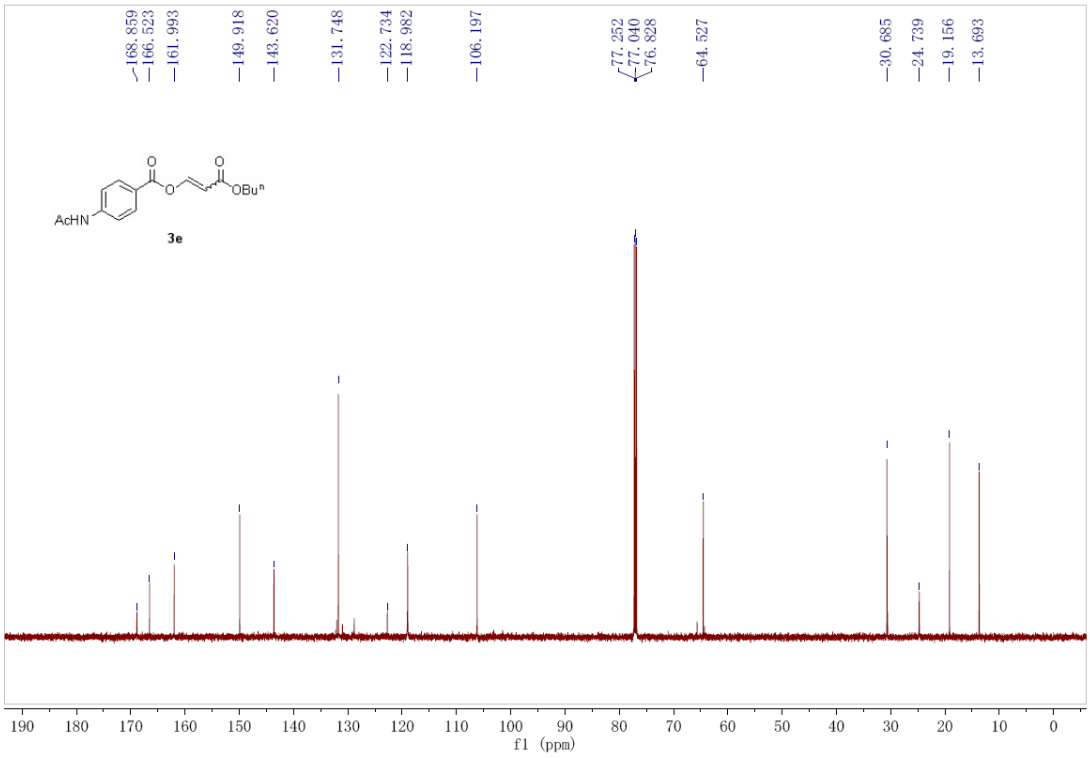



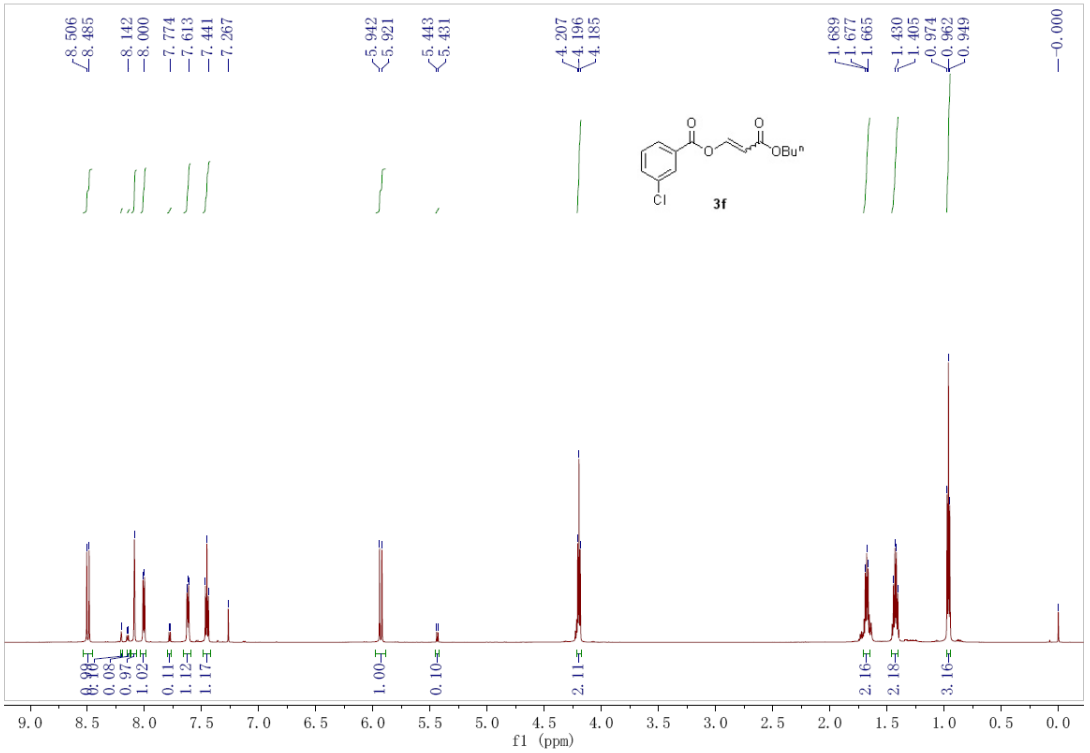


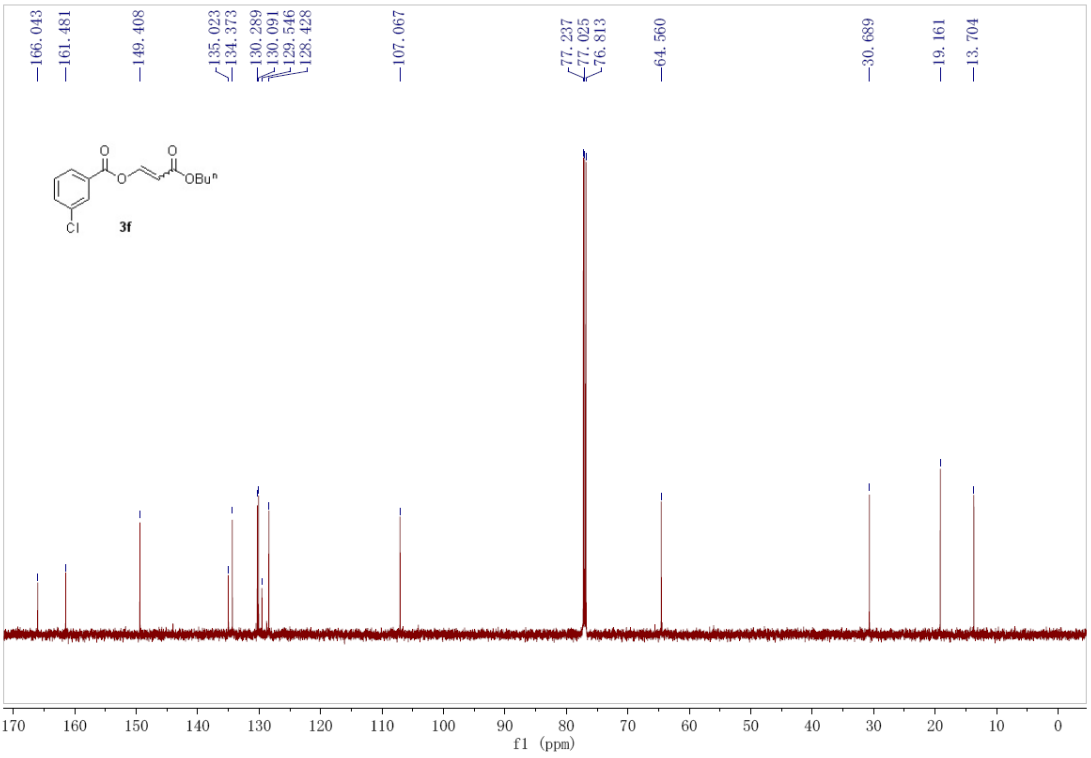



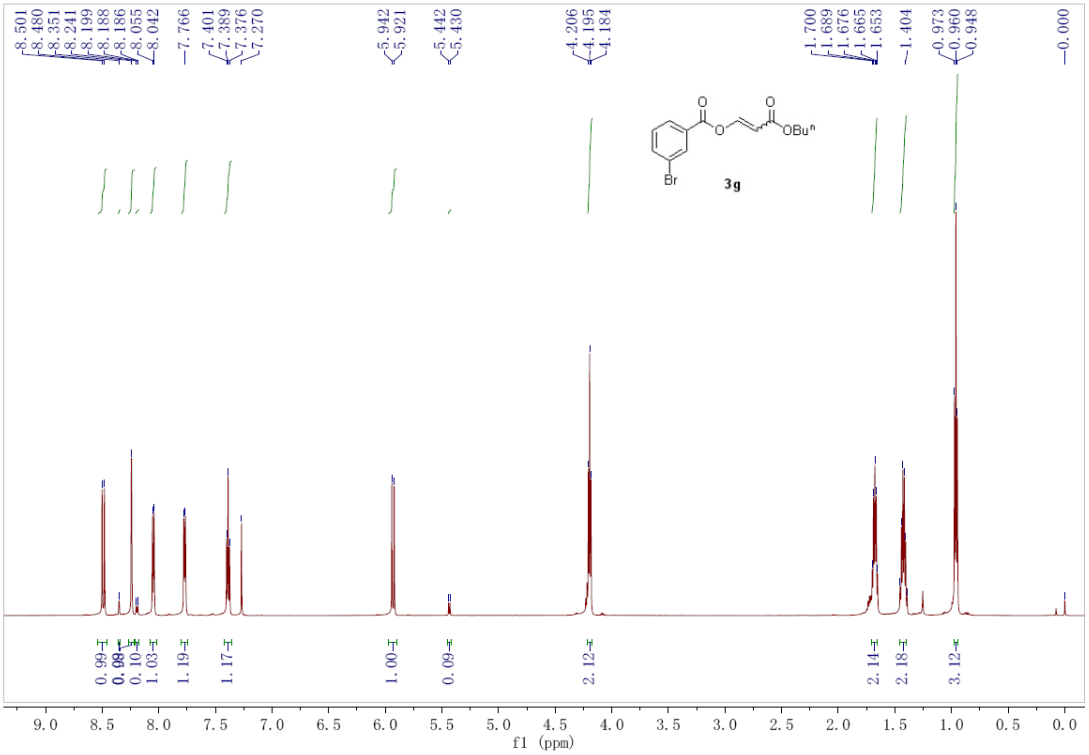


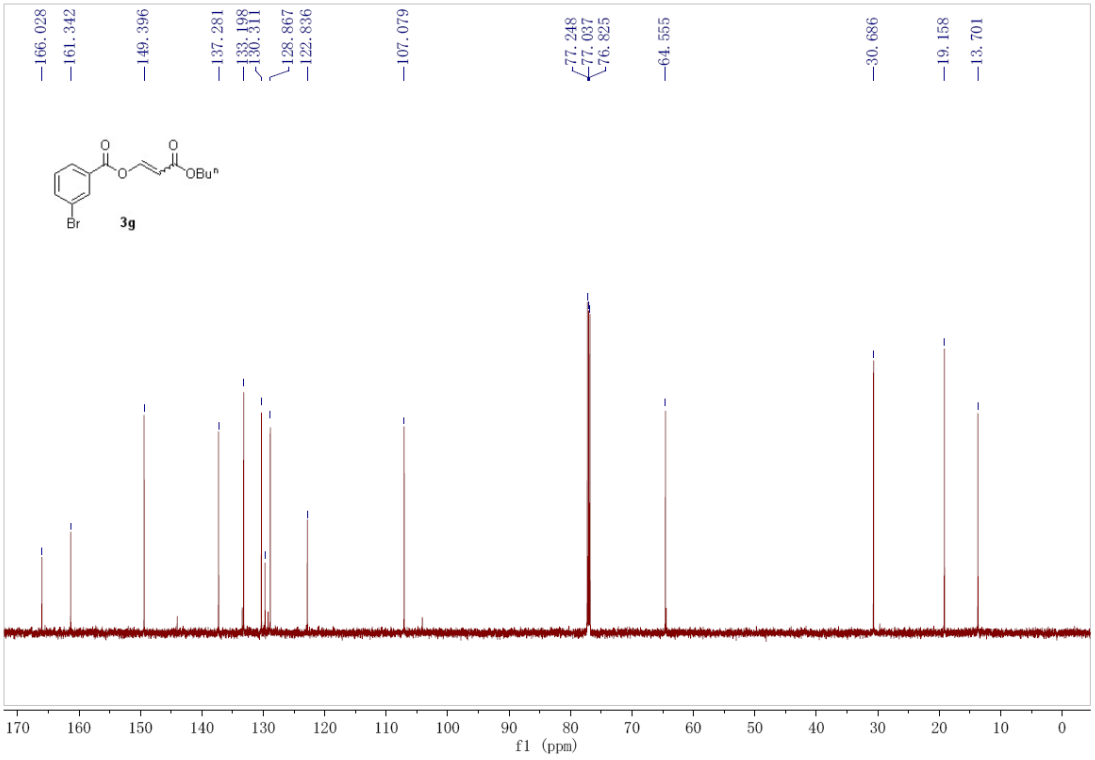



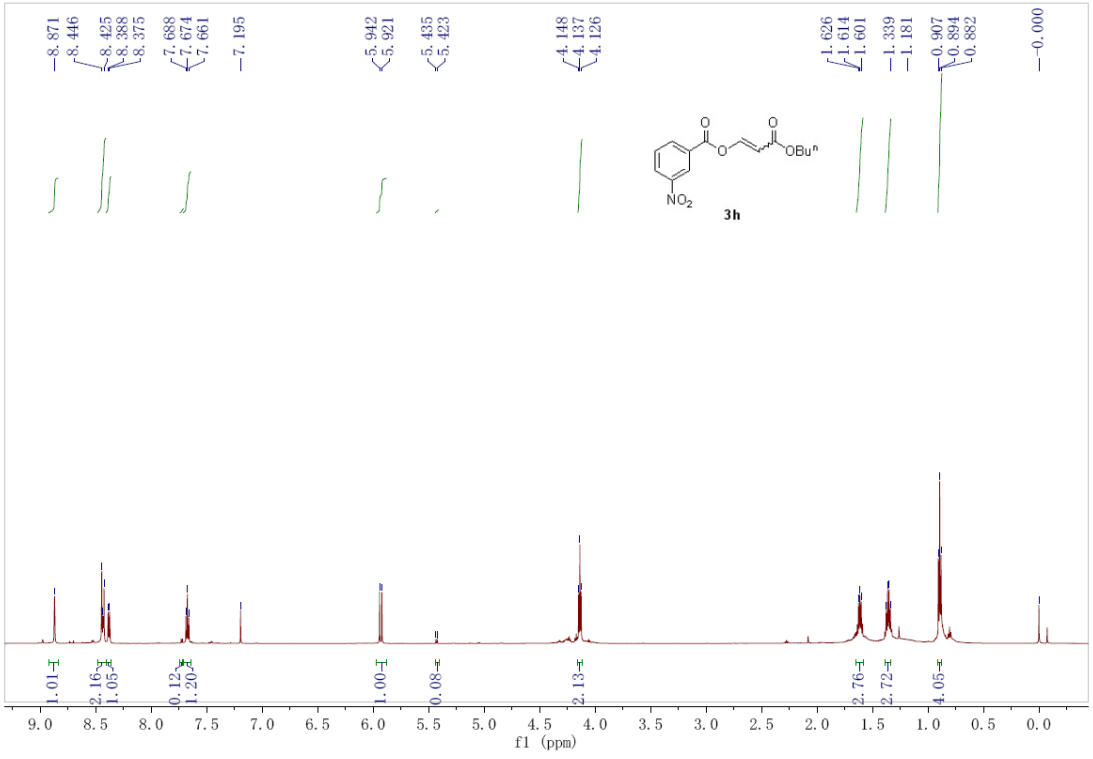


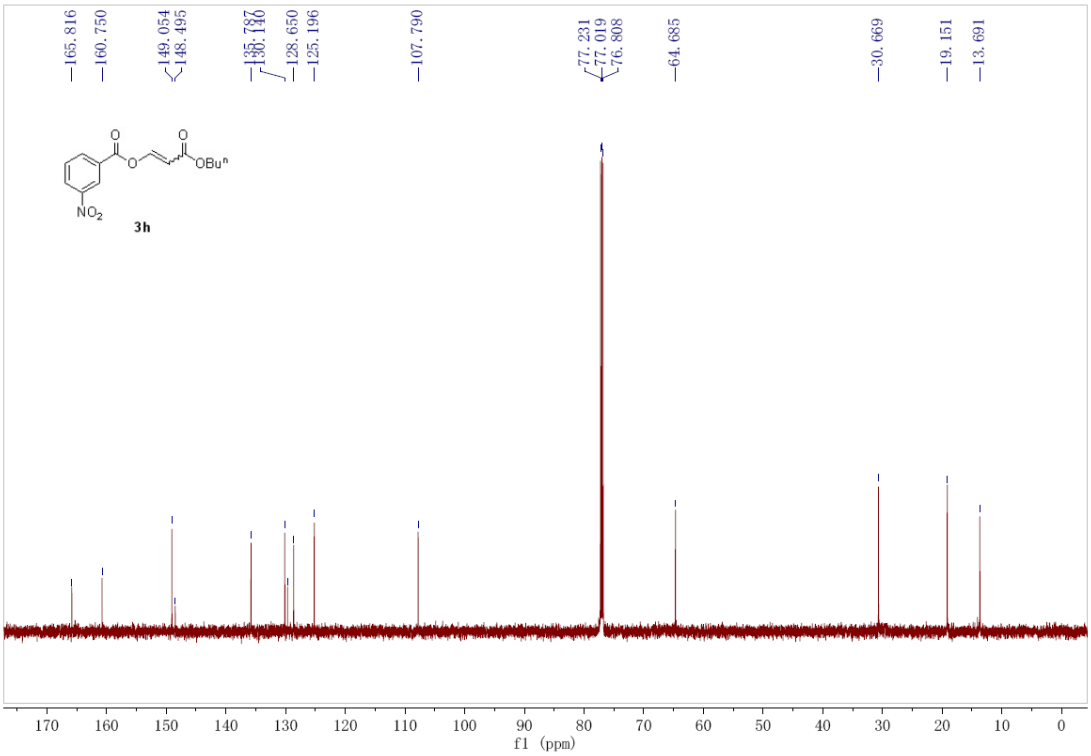





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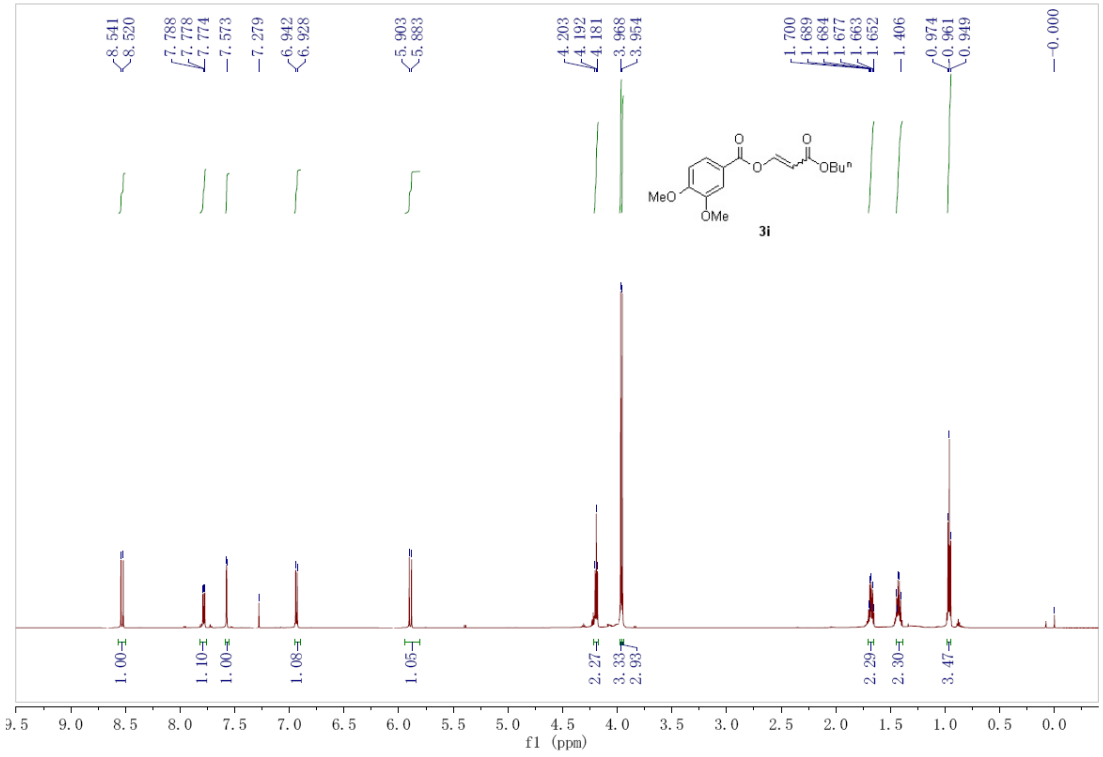
OBu$^n$
$NO_2$
3h
f1 (ppm)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4.181
3.968
3.954
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1.689
1.684
1.677
1.663
1.652
1.406
0.974
0.961
0.949
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OBu$^n$
MeO
OMe
3i
1.00
1.10
1.00
1.08
1.05
2.27
3.33
2.93
2.29
2.30
3.47
f1 (ppm)