Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Palladium catalyzed β-Selective Oxidative Heck Reaction of Electron-Rich Olefin

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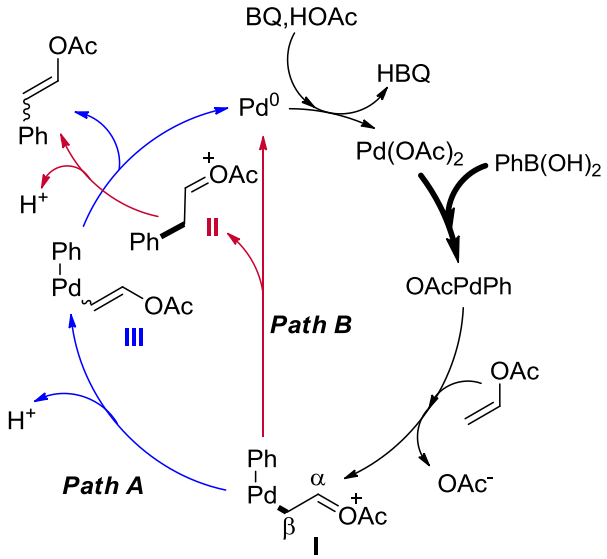
1. General Experimental Methods

The reactions were conducted under air atmosphere. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 100-200 mesh silica gel in petroleum (bp. 60-90 ℃). NMR spectra were recorded on a Bruker Advance III spectrometers at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR). Tetramethylsilane was used as an internal standard). All ^{1}H NMR spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants (*J*) are reported in Hertz (Hz). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument, accurate masses were reported for the molecular ion ($[M+H]^+$).

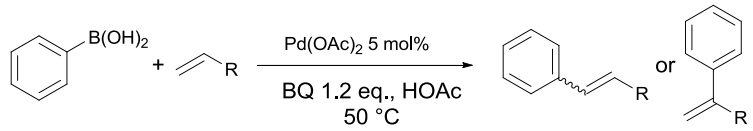
2. Proposed Mechanism for the Palladium Catalyzed arylation of vinyl acetate

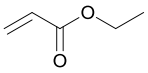
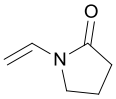
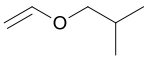


3. General procedure for the Pd-catalyzed β-arylation of VA

5.6 mg (0.025 mmol, 5 mol%) Pd $(OAc)_2$, 64.8 mg (0.6 mmol, 1.2 eq.) BQ , 0.5 mmol (1.0 eq.) $ArB(OH)_2$ were added in a glass tube. 10.0 mmol (20 eq.) of vinyl acetate and 1 mL of DMSO, 1mL HOAc were added in the tube consequently. Then the reaction tube was heated up to 60 ^{o}C and kept stirring 24 h. Then the reaction was quenched by saturated $NaHCO_3$ solution and extracted by ether (10 mL) 3 times. The organic parts were combined together and the pure product was obtained by flash column chromatography (petroleum and acetic ether).

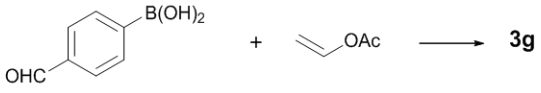
SI-1. Arylation of different olefin

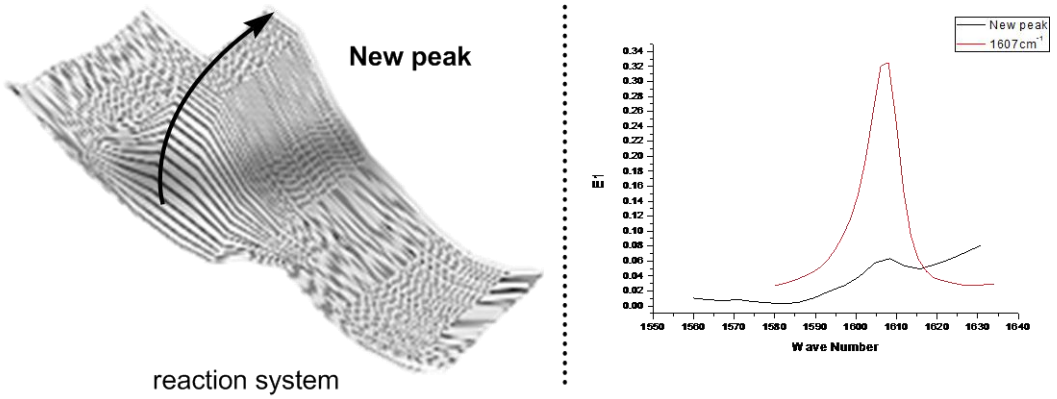


Entry	alkene (20 eq.)	β-arylation	α-arylation
1			none
2			none
3		none	
4		24%	
5		none	

4. General procedure for *in-situ* IR experiment

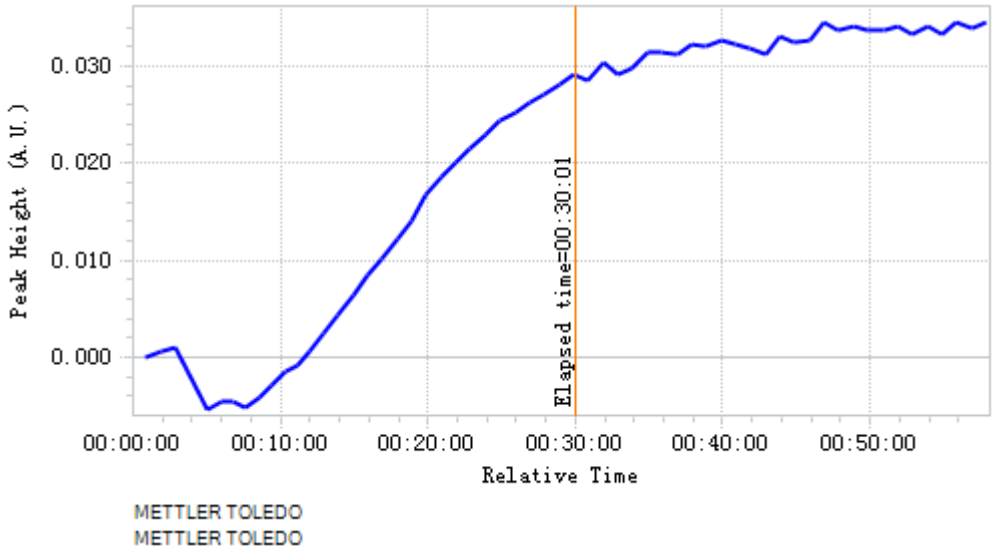
Firstly BQ with (4-formylphenyl)boronic acid was added in a three neck tube. Then the three neck tube was put onto *in-situ* IR, and sealed with septa. After that HOAc (1 mL), DMSO (1 mL) and vinyl acetate (10 mmol) were injected in the tube via syringe. At last $Pd(OAc)_2$ was added in and the reaction was heated up to 60 ℃. The yield was determined by GC with biphenyl as internal standard.



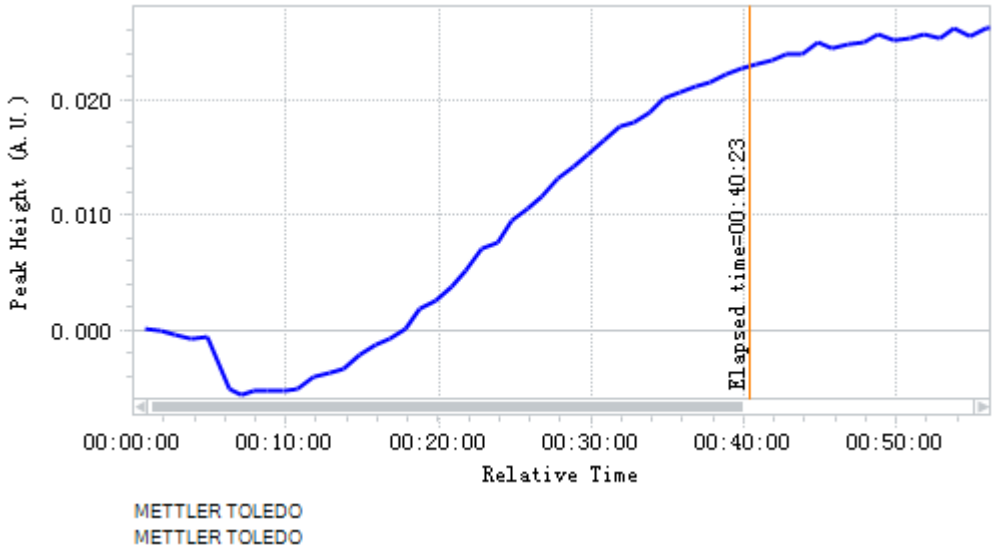


When the reaction system was monitored by in-situ IR a new peak could be found at 1607 cm^{-1} after the reaction started. And the product **3g** has an infrared absorption peak at 1607 cm^{-1}, so the peak at 1607 cm^{-1} was chose to monitor the kinetic of this reaction.

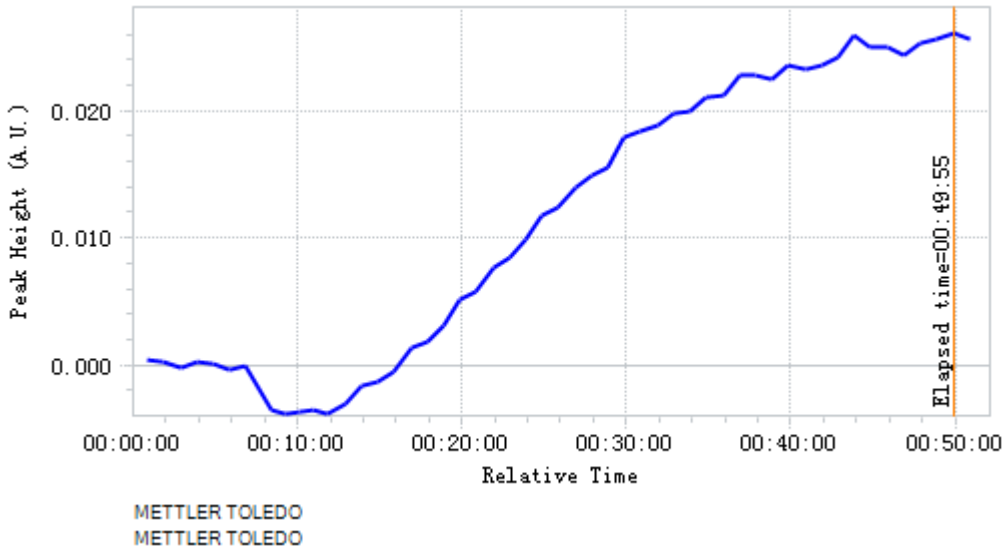
The trends of the reaction while using 10 mol% of catalyst (The reaction was carried out in 0.5 mol scale with 0.5 mmol BQ as oxidant)



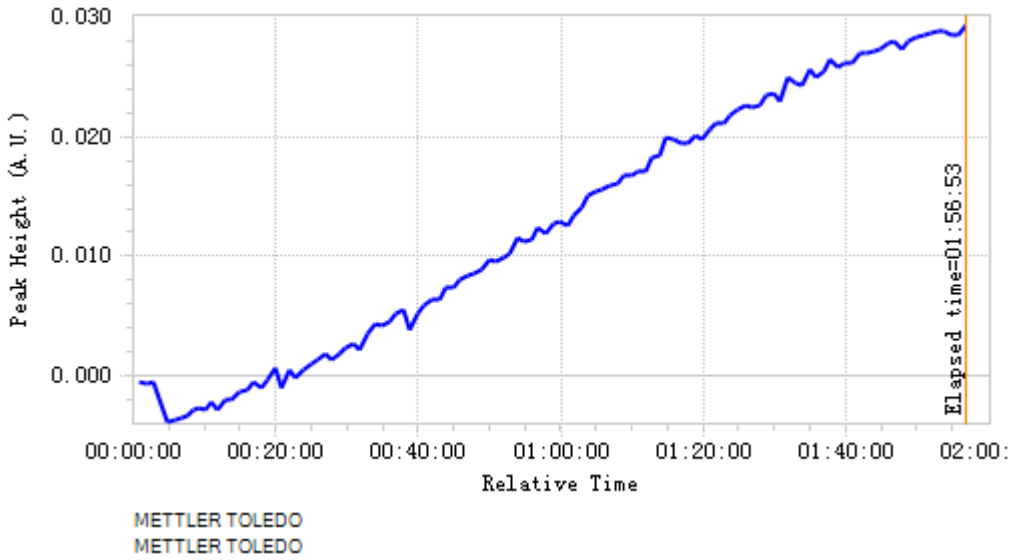
The trends of the reaction while using 7.5 mol% catalyst (The reaction was carried out in 0.5 mol scale with 0.5 mmol BQ as oxidant)



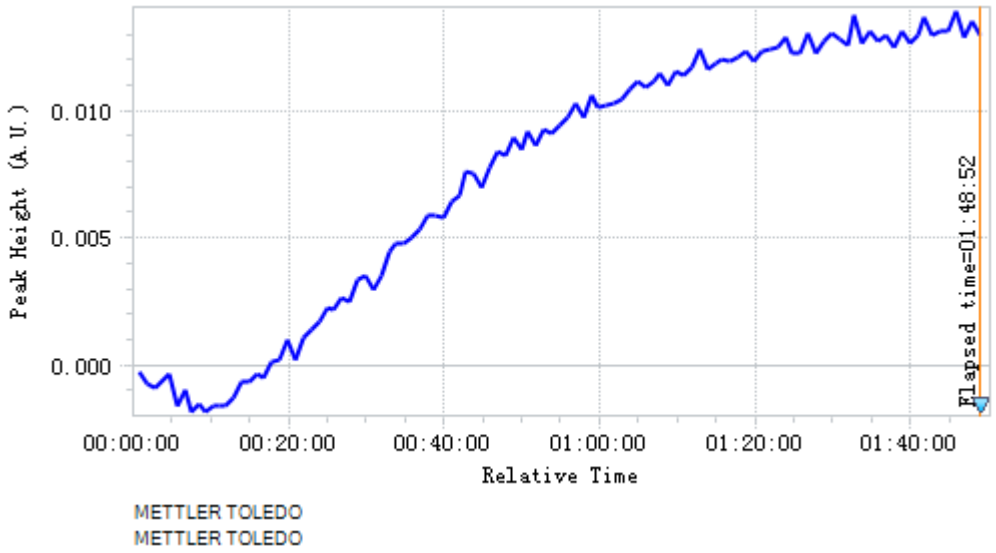
The trends of the reaction while using 5 mol% of catalyst (The reaction was carried out in 0.5 mol scale with 0.5 mmol BQ as oxidant)



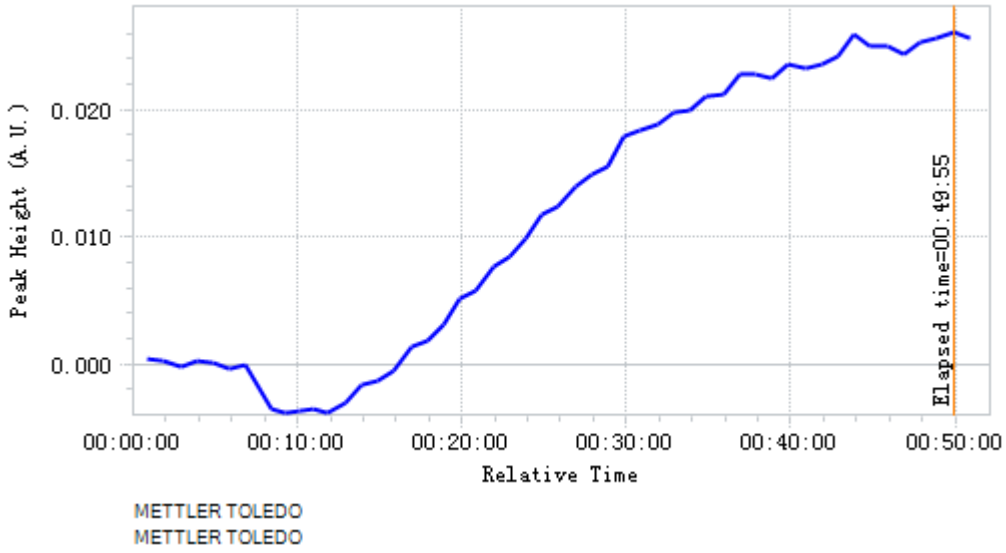
The trends of the reaction while using 2.5 mol% of catalyst (The reaction was carried out in 0.5 mol scale with 0.5 mmol BQ as oxidant)



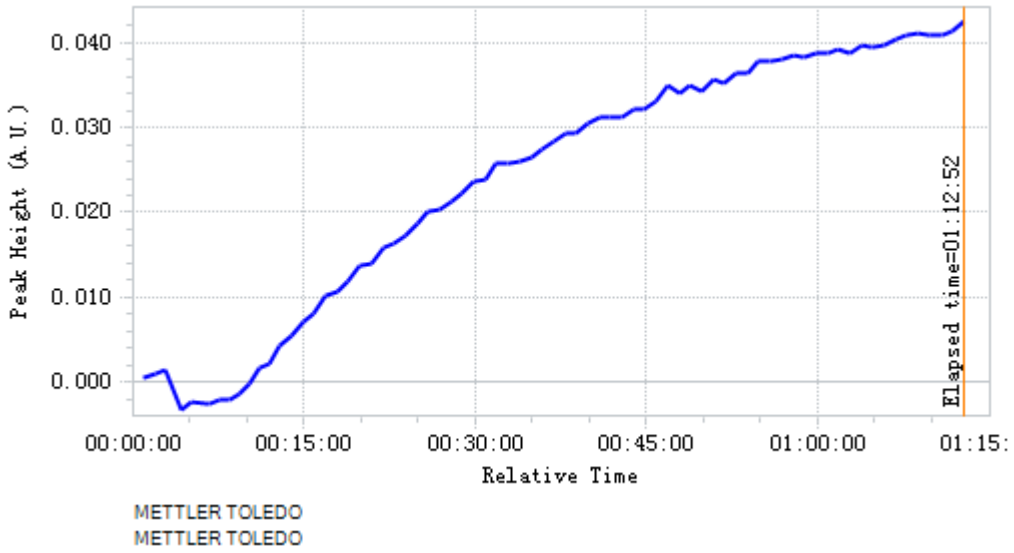
The trends of the reaction while the reaction was carried in 0.25 mmol scale (The reaction was carried out with 0.5 mol% of catalyst and 0.5 mmol BQ as oxidant)



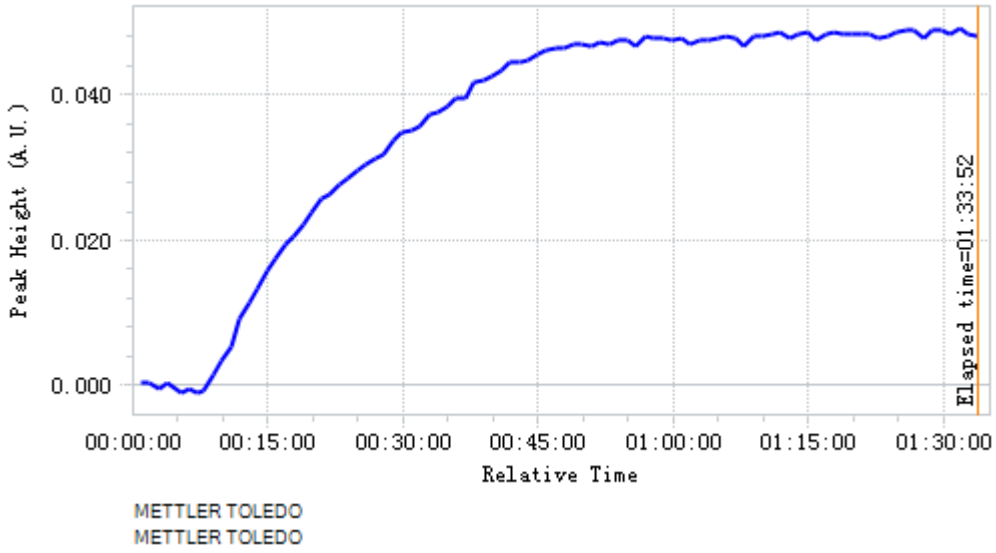
The trends of the reaction while the reaction was carried in 0.5 mmol scale (The reaction was carried out with 0.5 mol% of catalyst and 0.5 mmol BQ as oxidant)



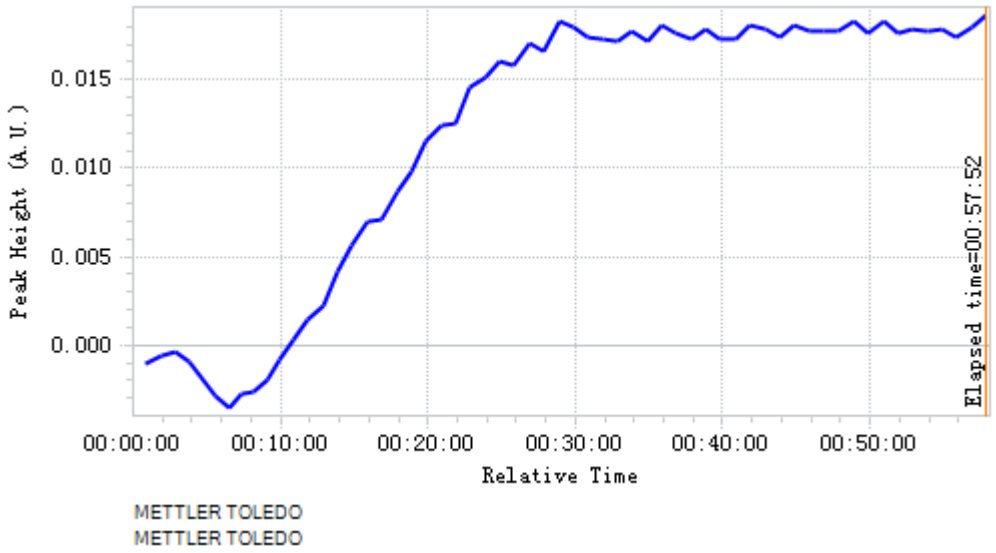
The trends of the reaction while the reaction was carried in 0.75 mmol scale (The reaction was carried out with 0.5 mol% of catalyst and 0.5 mmol BQ as oxidant)



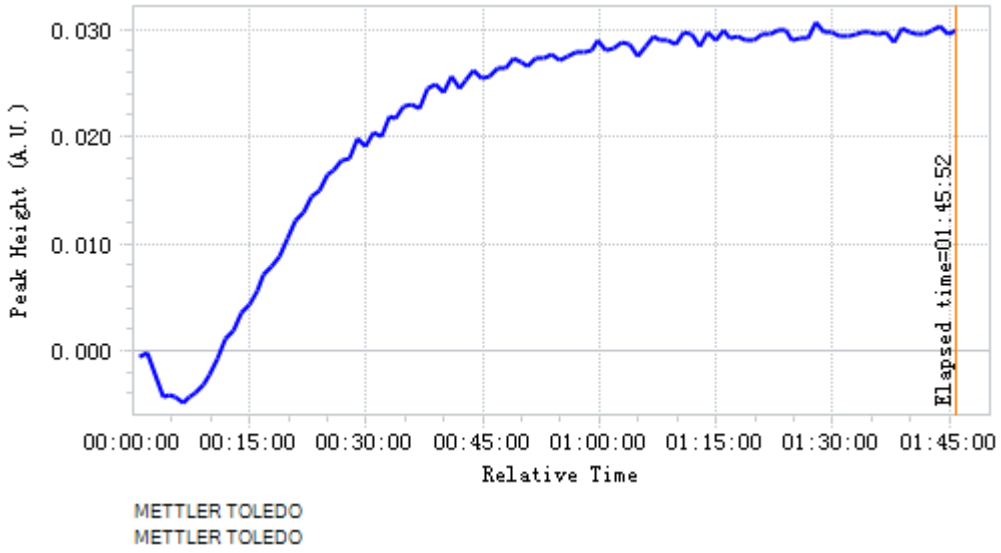
The trends of the reaction while the reaction was carried in 1.5 mmol scale (The reaction was carried out with 0.5 mol% of catalyst and 0.5 mmol BQ as oxidant)



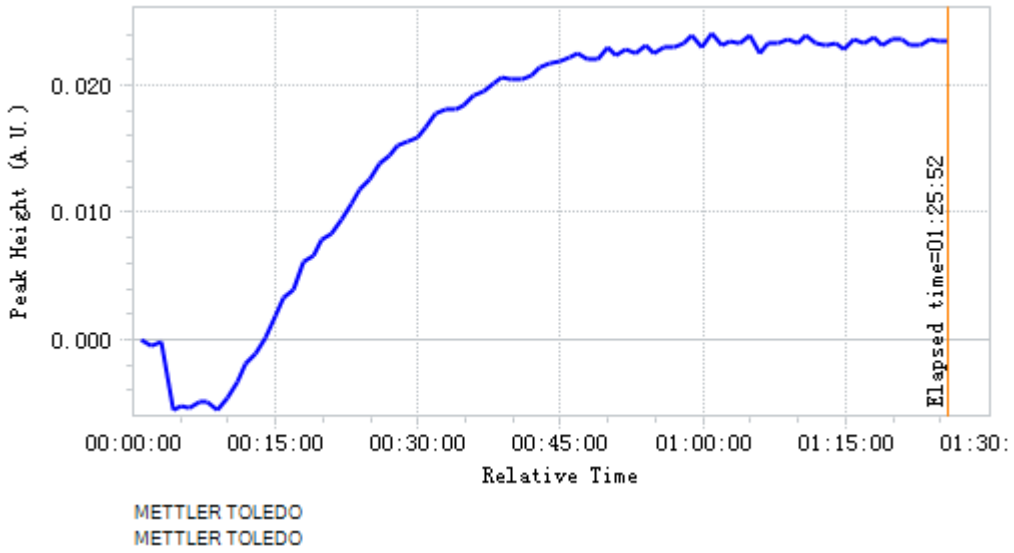
The trends of the reaction while using 0.25 mmol of BQ as oxidant (The reaction was carried out in 0.5 mmol scale with 0.5 mol% of catalyst)



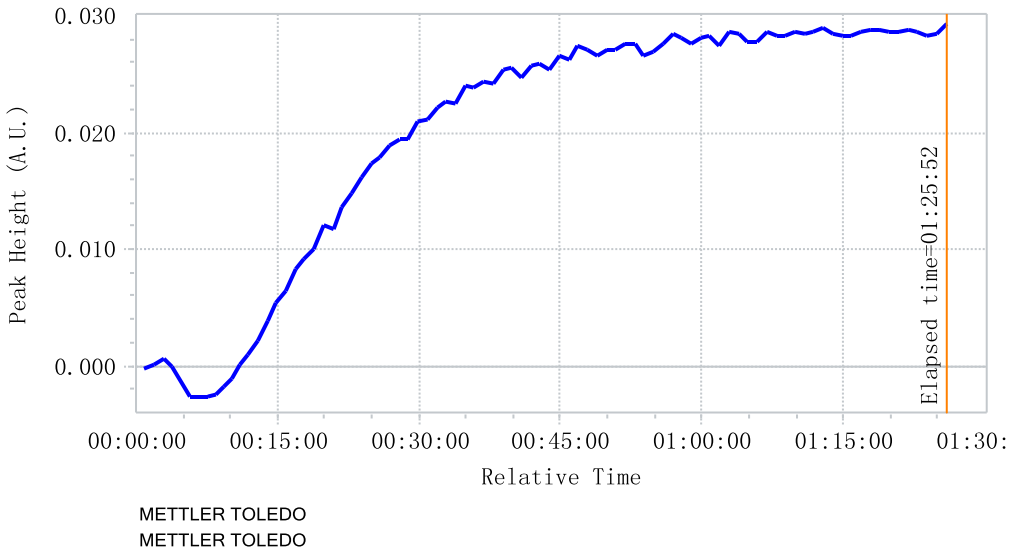
The trends of the reaction while using 0.5 mmol of BQ as oxidant (The reaction was carried out in 0.5 mmol scale with 0.5 mol% of catalyst)



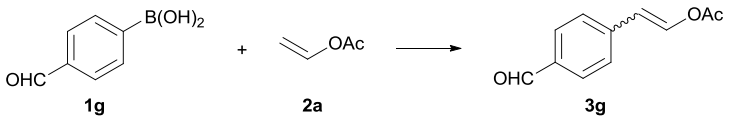
The trends of the reaction while using 0.75 mmol of BQ as oxidant (The reaction was carried out in 0.5 mmol scale with 0.5 mol% of catalyst)

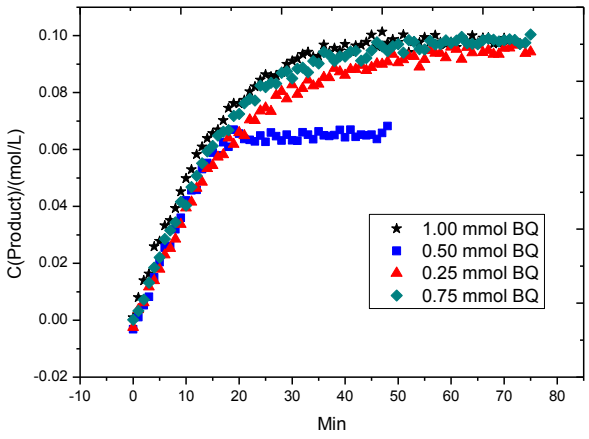


The trends of the reaction while using 1.0 mmol of BQ as oxidant (The reaction was carried out in 0.5 mmol scale with 0.5 mol% of catalyst)

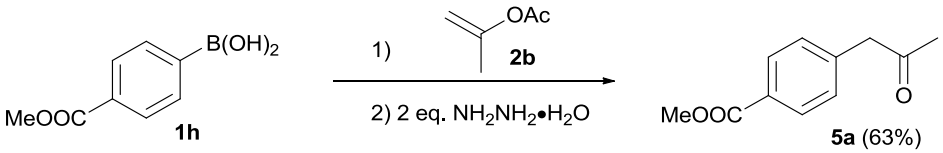


Kinetic profiles of different oxidant concentration





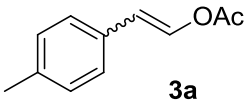
The reaction conditions for 5a synthesis



1): **1h** 0.5 mmol, 2b 10 mmol, $Pd(OAc)_2$ 5 mol%, BQ 0.6 mmol, HOAc 1mL, DMSO 1mL, 60 ℃, 12h.

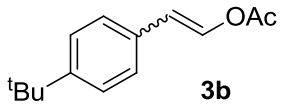
2): After added 5 mL acetic ether, HOAc and DMSO were removed by washing with saturated solution of sodium hydrogen carbonate. The organic phase was collected and acetic ether was removed under vacuum. Then 1 mmol of hydrazine hydrate was added in the reaction mixture and kept them under nitrogen atmosphere. After stirring for another 2 hours 5a could be obtained. The total yield was 63%.

5. Detail descriptions of products



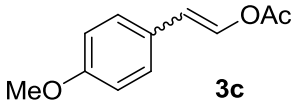
3a

4-Methylstyryl acetate (3a)[3](E/Z=1/0.4)**:** Purification by column chromatography (Petroleum ether/EtOAc = 100/1) afforded **3a** (61%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 12.8 Hz, 1H), 7.50 (d, 8.4 Hz, 0.8H), 7.29-7.14 (m, 4.8H), 6.39 (d, *J* = 12.8 Hz, 1H), 5.71 (d, *J* = 7.2 Hz, 0.4H), 2.38 (s, 1.2H), 2.36 (s, 3H), 2.29 (s, 1.2H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.07, 168.56, 137.27, 137.16, 133.27, 131.18, 131.14, 129. 42, 129.13, 129.04, 126.13, 115.19, 111.81, 21.28, 21.20, 20.97, 20.80.



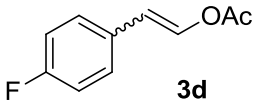
3b

4-(*tert*-Butyl)styryl acetate (3b) [3] (E/Z=1/0.3)**:** Purification by column chromatography (Petroleum ether/EtOAc = 100/1) afforded **3b** (63%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 12.8 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 0.6H), 7.43-7.30 (m, 4.6H), 6.42 (d, *J* = 12.8 Hz, 1H), 5.73 (d, *J* = 7.2 Hz, 0.3H), 2.30 (s, 0.9H), 2.22 (s, 3H), 1.37(s, 2.7H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.06, 167.54, 150.56, 150.39, 135.77, 133.44, 131.24, 131.21, 128.89, 125.99, 125.66, 125.37, 115.06, 111.71, 34.59, 31.29, 20.79.



3c

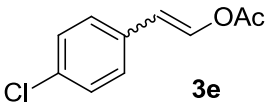
4-Methoxystyryl acetate (3c) (E/Z=1/0.5)**:** Purification by column chromatography (Petroleum ether/EtOAc = 100/1) afforded **3c** (24%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 12.8 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.30-7.27 (m, 2H), 7.24 (d, *J* = 7.2 Hz, 0.5H), 6.91 (d, *J* = 9.2 Hz, 1H), 6.89-6.86 (m, 2H), 6.37 (d, *J* = 12.8 Hz, 1H), 5.67(d, *J* = 7.6 Hz, 0.5H), 3.85 (s, 1.5H), 3.83(s, 3H), 2.29(s, 1.5H), 2.21(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.13, 167.55, 159.07, 158.72, 134.85, 132.44, 130.43, 127.39, 126.54, 114.89, 114.18, 113.83, 111.42, 55.30, 55.27, 20.96, 20.80.



3d

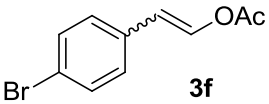
4-Fluorostyryl acetate (3d) [3] (E/Z=1/0.5)**:** Purification by column chromatography (Petroleum ether/EtOAc = 100/1) afforded **3d** (49%) as a colorless oil. ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.79 (d, *J* = 12.8 Hz, 1H), 7.60-7.56 (m, 1H), 7.33-7.28 (m, 2.5H), 7.08-7.00 (m, 3H), 6.38 (d, *J* = 12.8 Hz, 1H), 5.70-5.68(d, J = 7.2 Hz, 0.5H), 2.29 (s, 1.5H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.00, 167.35, 163.39, 163.00, 160. 94, 160.54, 136.00, 135.97, 133.54, 133.52, 130.80, 130.72, 130.19, 130.15, 127.76, 127.68, 115.78, 115.57, 115.44, 115.23, 114.26, 110.70, 20.71.



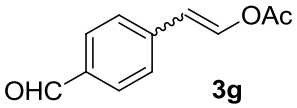
3e

4-Chlorostyryl acetate (3e) [3] (E/Z=1/0.5)**:** Purification by column chromatography (Petroleum ether/EtOAc = 100/1) afforded **3e** (64%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84(d, *J* = 12.8 Hz, 1), 7.54-7.52(m, 1H), 7.34-7.27(m, 5H), 6.36(d, *J* = 12.8 Hz, 1H), 5.67(d, *J* = 7.2 Hz, 0.5H), 2.29(s, 1.5H), 2.21(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.89, 167.24, 136.59, 134.29, 133.02, 132.91, 132.86, 132.52, 130.33, 128.88, 128.57, 127.39, 114.16, 110.61, 20.71.



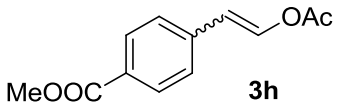
3f

4-Bromostyryl acetate (3f) [3] (E/Z=1/0.5)**:** Purification by column chromatography (Petroleum ether/EtOAc = 100/1) afforded **3f** (64%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86(d, *J* = 12.8 Hz, 1H), 7.48-7.43(m, 4H), 7.34(d, *J* = 7.6 Hz, 0.5H), 7.22-7.20(m, 2H), 6.34(d, *J* = 12.8 Hz, 1H), 5.66(d, *J* = 7.2 Hz, 0.5H), 2.29(s, 1.5H), 2.21(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.87, 167.22, 136.65, 134.42, 133.12, 132.95, 131.82, 131.54, 130.63, 127.71, 121.11, 121.09, 114.20, 110.65, 20.91, 20.73.



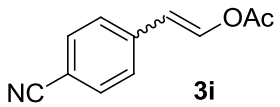
3g

4-Formylstyryl acetate (3g) (E/Z=1/0.3)**:** Purification by column chromatography (Petroleum ether/EtOAc = 50/1) afforded **3g** (76%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96(s, 0.3H), 9.95(s, 1H), 7.98(d, *J* = 12.8 Hz, 1H), 7.86-7.80(m, 1.9H), 7.72(d, *J* = 8 Hz, 0.53H), 7.47-7.41(m, 1.67H), 6.89-6.81(m, 0.38H), 6.41(d, *J* = 12.8 Hz, 0.75H), 5.75(d, *J* = 8H, 0.26H), 2.30(s, 0.91H), 2.21(s, 2.09H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.75, 191.58, 167.74, 167.08, 140.70, 140.21, 138.53, 136.19, 135.21, 134.81, 130.23, 129.86, 129.52, 126.57, 122.41, 118.78, 116.12, 114.22, 110.61, 93.33, 20.87, 20.66.



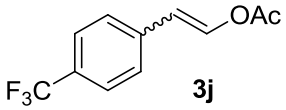
3h

Methyl 4-(2-acetoxyvinyl)benzoate (3h) [3] (E/Z=1/0.4)**:** Purification by column chromatography (Petroleum ether/EtOAc = 50/1) afforded **3h** (77%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.92(m, 3.8H), 7.63(d, *J* = 8.8 Hz, 0.8H), 7.39-7.36(m, 2.4H), 6.39(d, 12.8 Hz, 1H), 5.73(d, 7.6 Hz, 0.4H), 3.91(s, 1.2H), 3.90(s, 3H), 2.29(s, 1.2H), 2.20(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.74, 166.70, 138.95, 138.57, 137.89, 135.53, 130.01, 129.65, 128.92, 128.83, 128.55, 125.98, 114.33, 110.79, 52.06, 52.04, 20.85, 20.66.



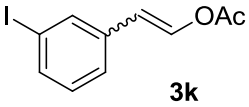
3i

4-Cyanostyryl acetate (3i) [3] (E/Z=1/0.4)**:** Purification by column chromatography (Petroleum ether/EtOAc = 50/1) afforded **3i** (86%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95(d, *J* = 12.8 Hz, 1H), 7.66-7.58(m, 3.6H), 7.44-7.40(m, 2.4H), 6.38(d, *J* = 12.8 Hz, 1H), 5.72(d, *J* = 7.2 Hz, 0.4H), 2.31(s, 1H), 2.22(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.65, 166.91, 139.17, 138.69, 138.63, 136.41, 132.49, 132.16, 129.48, 126.59, 118.91, 118.83, 113.71, 110.59, 110.41, 110.04, 20.86, 20.66.



3j

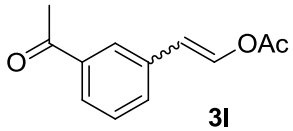
4-(Trifluoromethyl)styryl acetate (3j) [3] (E/Z=1/0.4)**:** Purification by column chromatography (Petroleum ether/EtOAc = 100/1) afforded **3j** (76%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95(d, *J* = 12.8 Hz, 1H), 7.71-7.69(m, 0.8H), 7.63-7.56(m, 2.8H), 7.45-7.41(m, 2.4H), 6.43(d, *J* = 12.8 Hz, 1H), 5.75(d, *J* = 7.6 Hz, 0.4H), 2.31(s, 1.2H), 2.23(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.79, 167.12, 137.94, 137.92, 137.84, 135.56, 129.38, 129.19, 129.06, 126.29, 125.66, 125.62, 125.27, 122.78, 113.95, 110.38, 20.81, 20.64.



3k

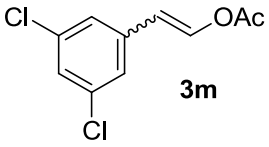
3-Iodostyryl acetate (3k) (E/Z=1/0.5)**:** Purification by column chromatography (Petroleum ether/EtOAc = 100/1) afforded **3k** (45%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.97(m, 0.5H), 7.85(d, *J* = 12.8 Hz, 1H), 7.70-7.69(m, 1H), 7.60-7.54(m, 2H), 7.34-7.29(m, 1.5H), 7.12-7.03(m, 1.5H), 6.30(d, *J* = 12.8 Hz, 1H), 5.62(d, *J* = 7.2 Hz, 0.5H),

2.30(s, 1.5H), 2.22(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.84, 167.20, 137.96, 137.01, 136.43, 136.25, 136.11, 135.02, 134.81, 130.33, 130.05, 128.19, 125.36, 113.78, 110.26, 94.69, 94.37, 20.74.



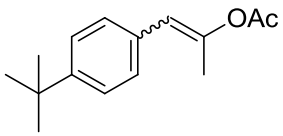
3l

4-Acetylstyryl acetate (3i) (E/Z=1/0.5)**:** Purification by column chromatography (Petroleum ether/EtOAc = 50/1) afforded **3i** (67%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19(s, 0.5H), 7.93-7.89(m, 2H), 7.84-7.77(m, 2H), 7.53-7.35(m, 3H), 6.43(d, *J* = 12.8 Hz, 1H), 5.75(d, 8Hz, 0.5H), 2.62(s, 1.5H), 2.60(s, 3H), 2.30(s, 1.5H), 2.21(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.03, 197.98, 167.90, 167.21, 137.52, 137.21, 137.09, 134.83, 134.74, 134.49, 133.47, 130.47, 128.96, 128.68, 127.28, 127.06, 125.99, 118.77, 116.12, 114.39, 110.85, 93.28, 26.67, 26.61, 20.86, 20.69. HRMS (ESI) calcd for $C_{12}H_{13}O_3$ $[M+H]^+$: 205.0865; found: 205.0859.

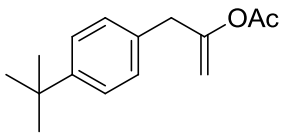


3m

3,5-Dichlorostyryl acetate (3l) (E/Z=1/0.5)**:** Purification by column chromatography (Petroleum ether/EtOAc = 100/1) afforded **3l** (75%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88(d, *J* = 12.8 Hz, 1H), 7.48-7.47(m, 1.0H), 7.38(d, *J* = 7.2 Hz, 0.5H), 7.26-7.21(m, 3.5H), 6.28(d, *J* = 12.8 Hz, 1Hz), 5.60(d, *J* = 7.2Hz, 0.5H), 2.32(s, 1.5H), 2.23(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.67, 166.97, 138.03, 137.34, 136.81, 135.82, 135.24, 134.82, 127.29, 127.18, 127.11, 124.46, 112.95, 109.27, 20.87, 20.68. HRMS (ESI) calcd for $C_{10}H_9Cl_2O_2$ $[M+H]^+$: 230.9980; found: 230.9974.



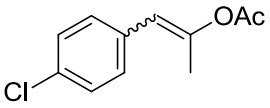
4a^1



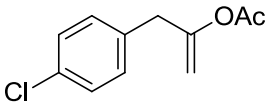
4a^2

1-(4-(*tert*-Butyl)phenyl)prop-1-en-2-yl acetate (4a^1) [1] (E/Z=2/1) **with 3-(4-(*tert*-Butyl)phenyl)prop-1-en-2-yl acetate (4a^2)**($4a^1/4a^2$=1.2/1)**:** Purification by column chromatography (Petroleum ether/EtOAc = 100/1) afforded **3l** (92%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.18(m, 8.8H), 6.26(s, 0.8H), 5.95(s, 0.4H), 4.85-4.73(m, 2H),

3.54(s, 2H), 2.24-2.11(m, 10.2H), 1.35-1.34(m, 19.8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.49, 169.09, 168.64, 155.58, 149.92, 149.86, 149.58, 147.40, 145.70, 133.73, 131.91, 131.57, 128.74, 128.45, 127.87, 125.40, 125.28, 125.24, 118.49, 116.24, 102.87, 39.28, 34.53, 34.44, 31.39, 31.30, 31.27, 21.13, 21.07, 20.69, 17.20. HRMS (ESI) calcd for $C_{15}H_{21}O_2$ $[M+H]^+$: 233.1542; found: 233.1539.

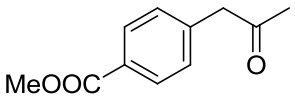


4b^1



4b^2

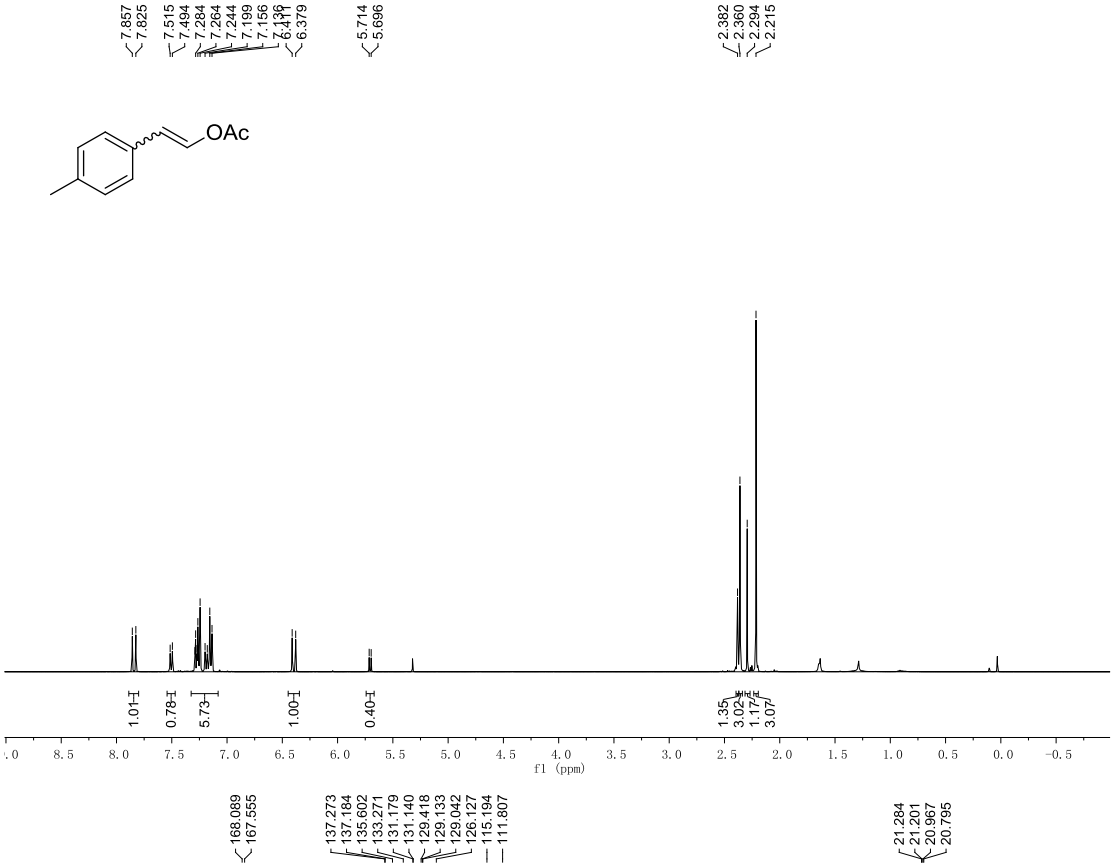
1-(4-chlorophenyl)prop-1-en-2-yl acetate (4b^1) [1] (E/Z=1.5/1) **with 3-(4-chlorophenyl)prop-1-en-2-yl acetate (4b^2)** (4b^1/4b$^{2=}$1/1)**:** Purification by column chromatography (Petroleum ether/EtOAc = 100/1) afforded **3l** (74%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.17(m, 8.0H), 6.22(s, 0.6H), 5.92(s, 0.4H), 4.86-4.71(m, 2H), 3.52(s, 2H), 2.20-2.19(m, 3H), 2.10-2.09(m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.35, 168.95, 168.36, 154.82, 148.36, 146.93, 135.24, 133.33, 132.94, 132.67, 132.61, 132.56, 130.48, 130.02, 129.39, 128.63, 128.62, 128.50, 117.72, 115.42, 103.30, 39.16, 21.07, 20.96, 20.67, 17.14.

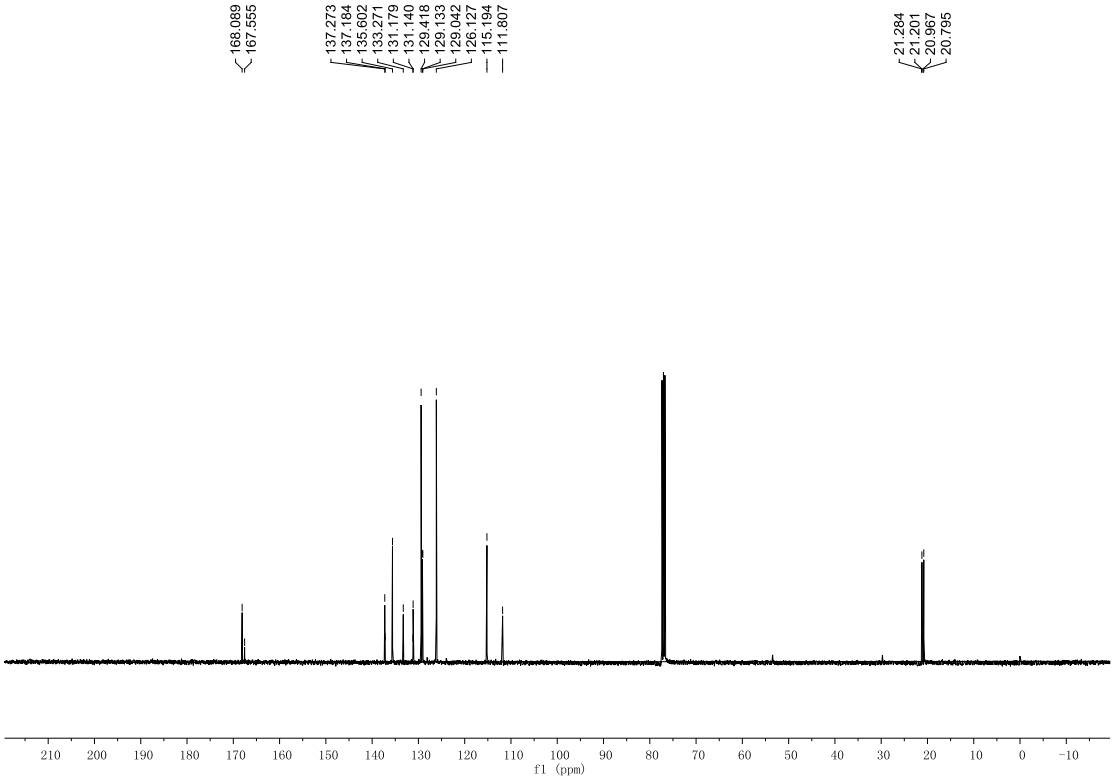


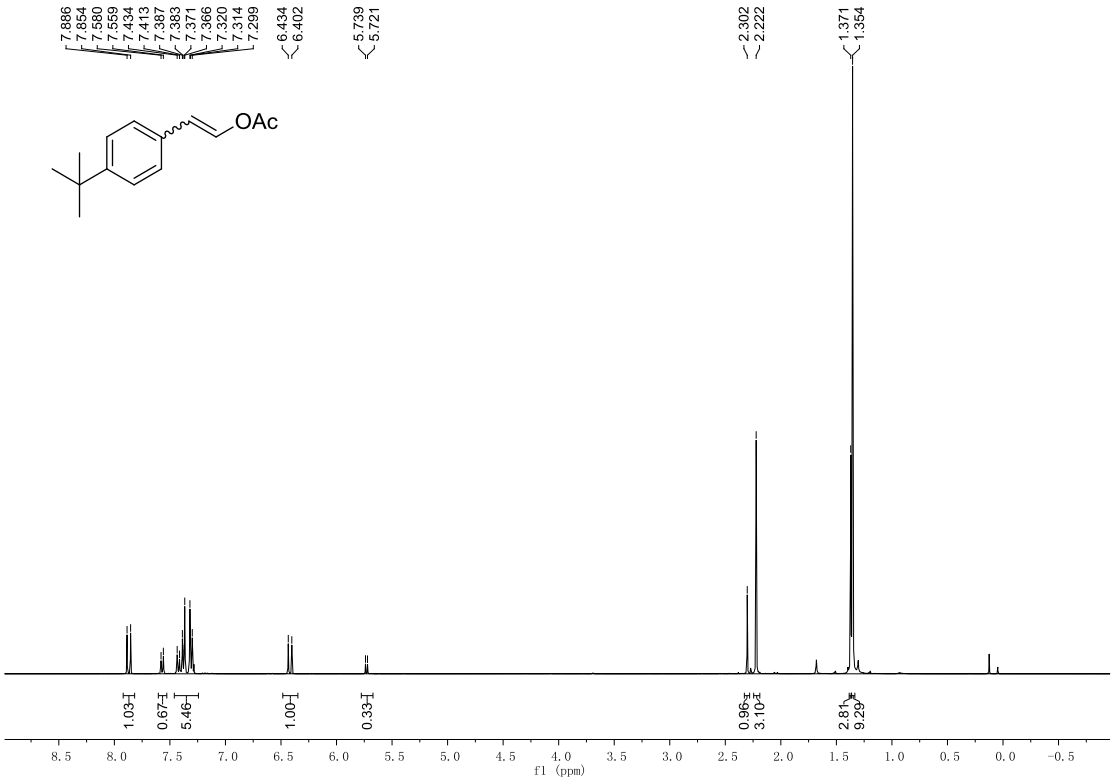
5a

Methyl 4-(2-oxopropyl)benzoate (5a)[2]**:** Purification by column chromatography (Petroleum ether/EtOAc = 100/1) afforded **3l** (63%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00(d, *J* = 8.4 Hz, 2H), 7.27(d, *J* = 8 Hz, 2H), 3.90(s, 3H), 3.76(s, 2H), 2.18(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.24, 166.79, 139.35, 129.93, 129.51, 129.95, 52.08, 50.65, 29.55

6. Copies of product ^{1}H NMR and ^{13}C NMR



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7.559
7.434
7.413
7.387
7.383
7.371
7.366
7.320
7.314
7.299
6.434
6.402
5.739
5.721
2.302
2.222
1.371
1.354
OAc
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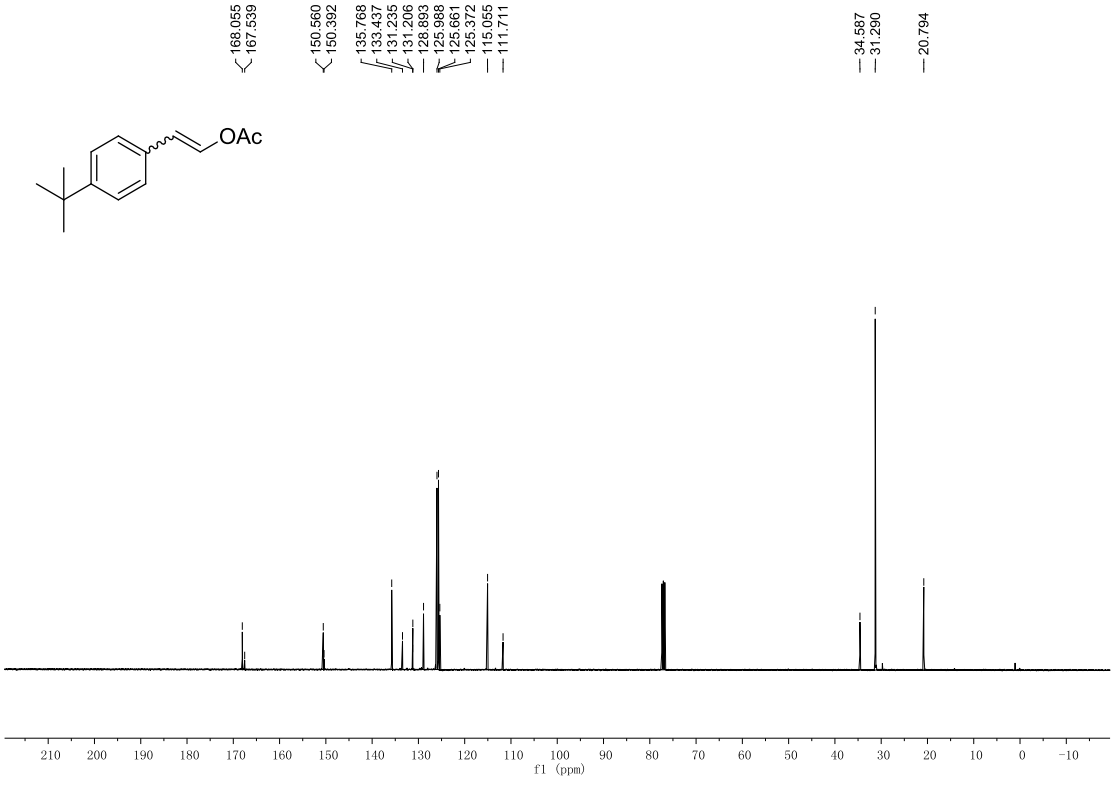
0.67
5.46
1.00
0.33
0.96
3.10
2.81
9.29
f1 (ppm)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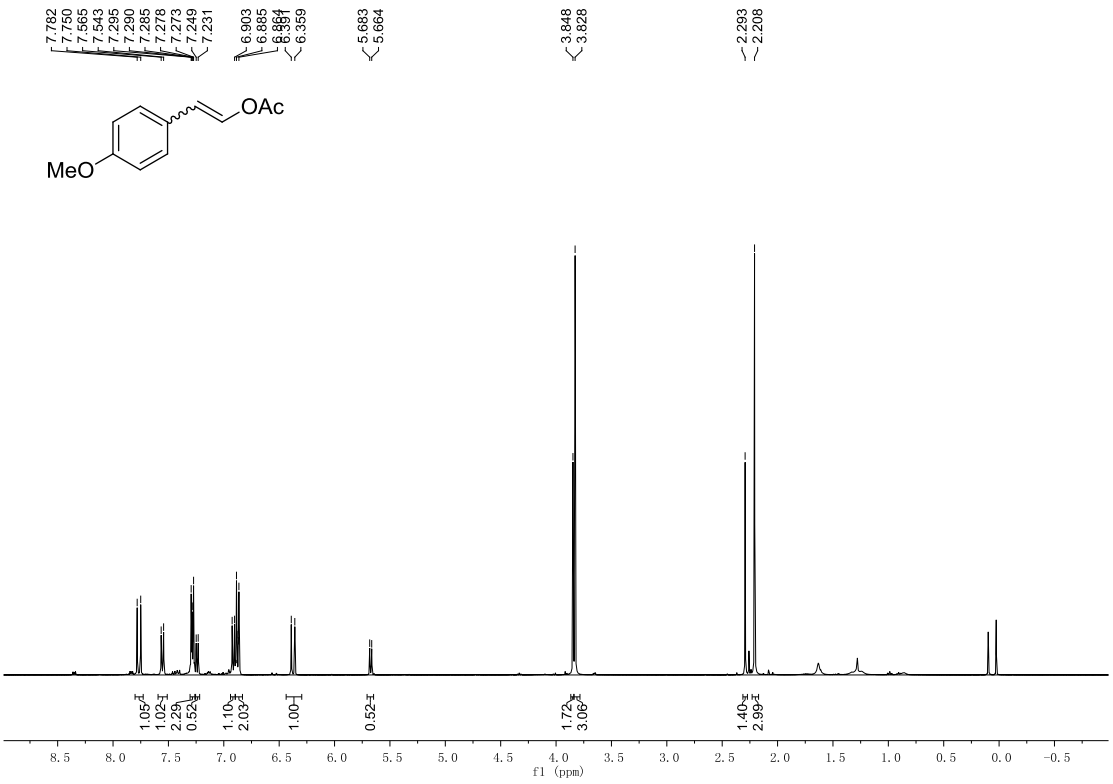
167.539
150.560
150.392
135.768
133.437
131.235
131.206
128.893
125.988
125.661
125.372
115.055
111.711
34.587
31.290
20.794
OAc
f1 (ppm)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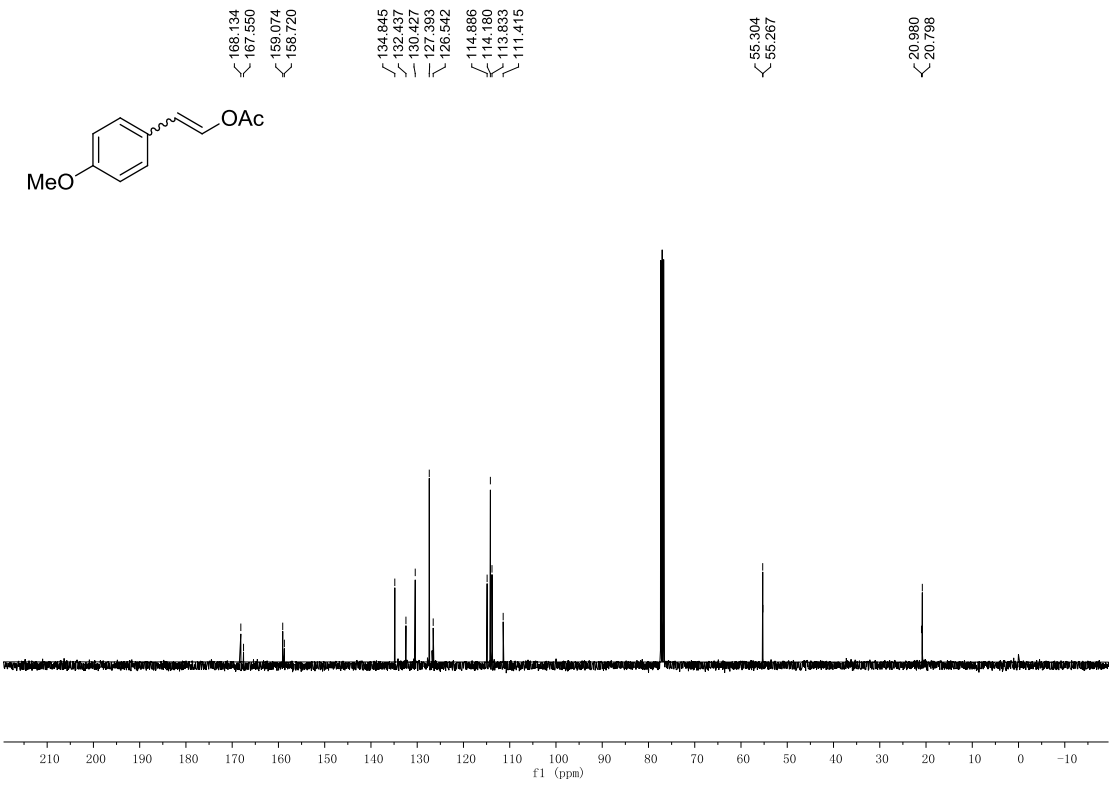
7.750
7.565
7.543
7.295
7.290
7.285
7.278
7.273
7.249
7.231
6.903
6.885
6.864
6.391
6.359
5.683
5.664
3.848
3.828
2.293
2.208
OAc
MeO
1.05
1.02
2.29
0.52
1.10
2.03
1.00
0.52
1.72
3.06
1.40
2.99
f1 (ppm)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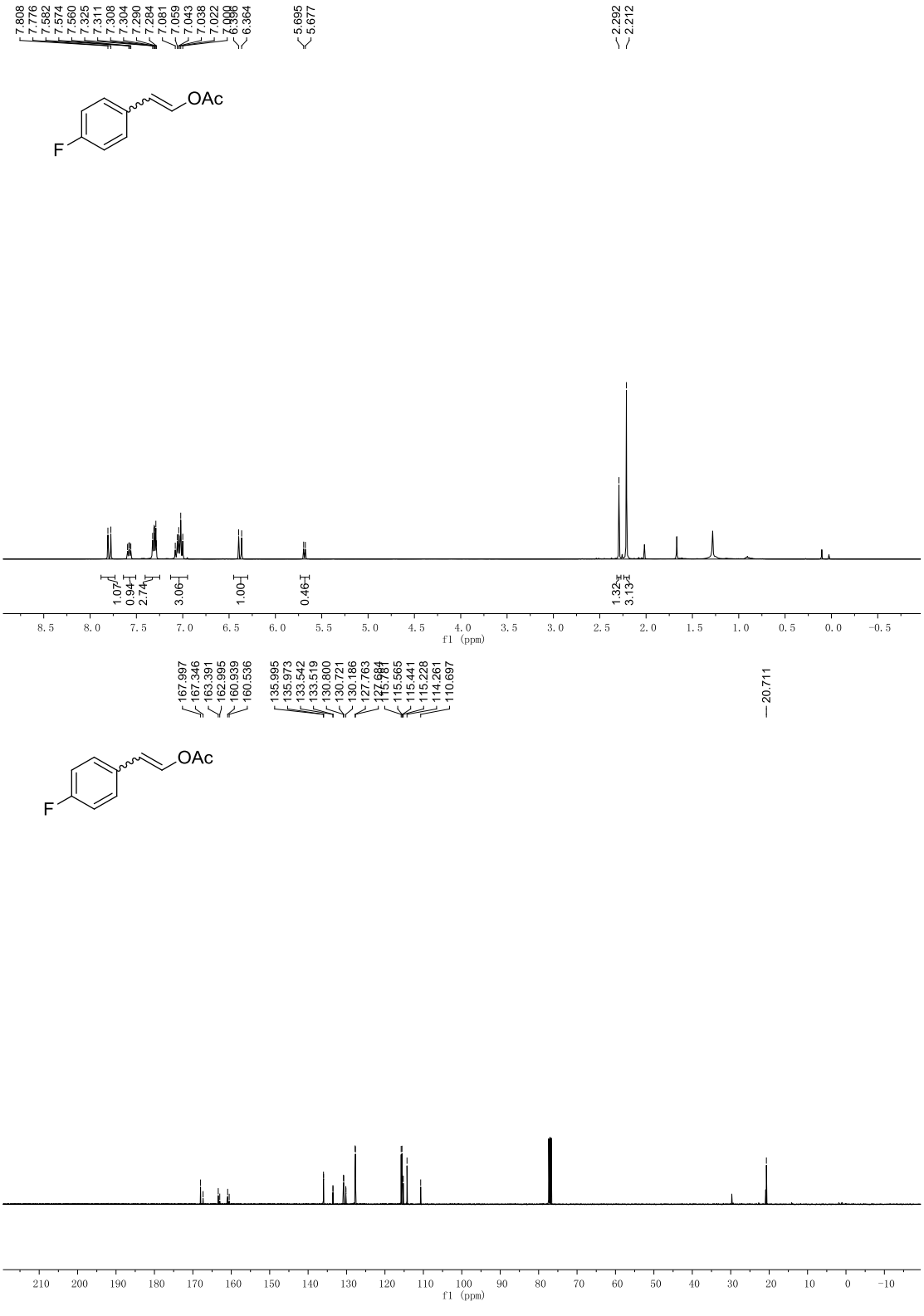
159.074
158.720
134.845
132.437
130.427
127.393
126.542
114.886
114.180
113.833
111.415
55.304
55.267
20.980
20.798
OAc
MeO
f1 (ppm)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7.582
7.574
7.560
7.325
7.311
7.308
7.304
7.290
7.284
7.081
7.059
7.043
7.038
7.022
6.998
6.364
5.695
5.677
2.292
2.212
OAc
F
1.07
0.94
2.74
3.06
1.00
0.46
1.32
3.13
f1 (ppm)
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167.346
163.391
162.995
160.939
160.536
135.995
135.973
133.542
133.519
130.800
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127.763
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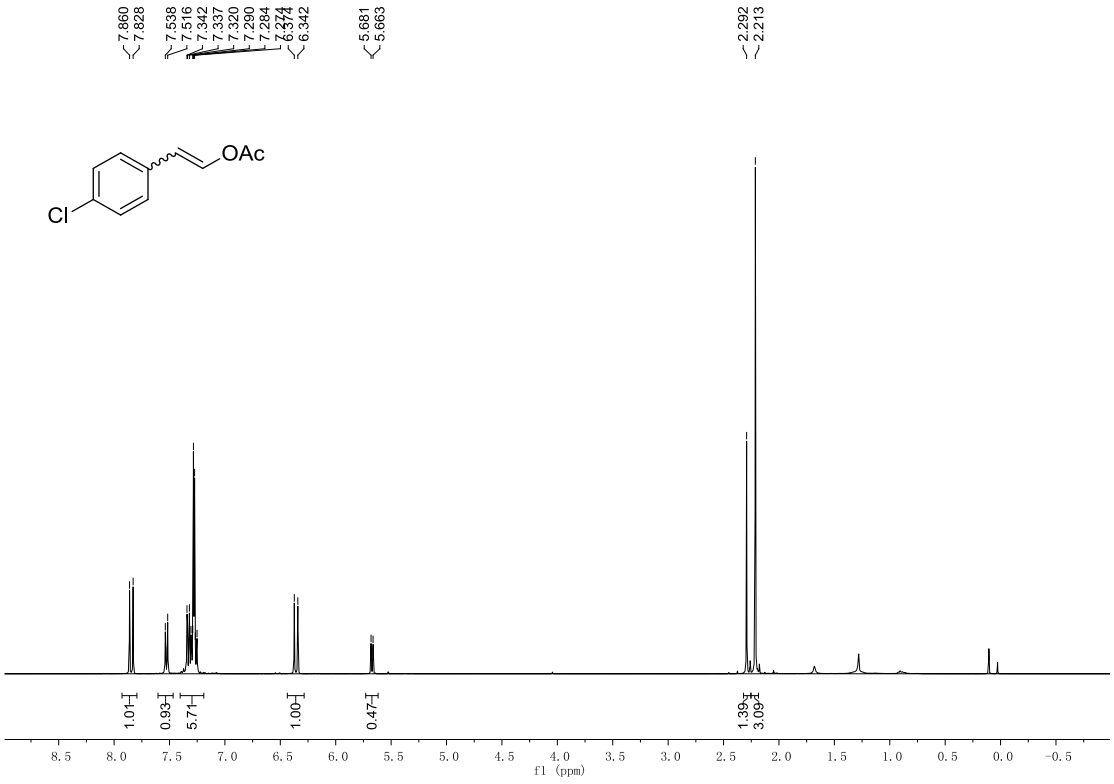
OAc
F
f1 (ppm)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7.516
7.342
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7.290
7.284
7.274
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6.342
5.681
5.663
2.292
2.213
OAc
Cl
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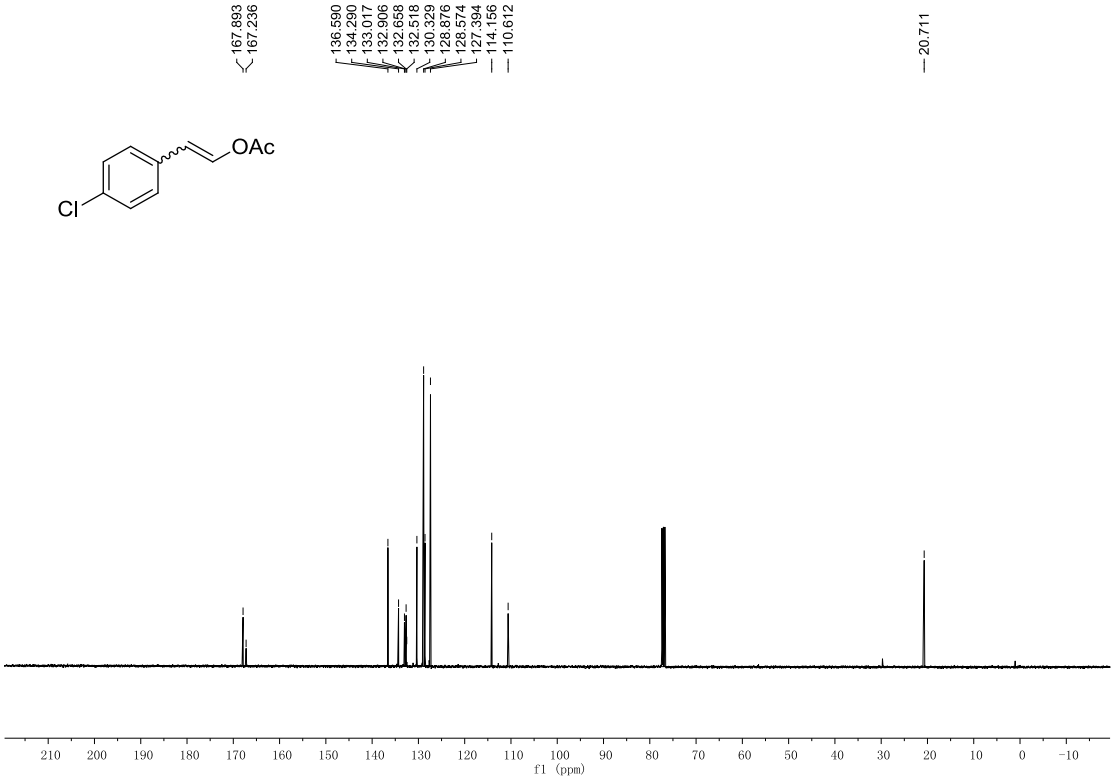
5.71
1.00
0.47
1.39
3.09
f1 (ppm)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134.290
133.017
132.906
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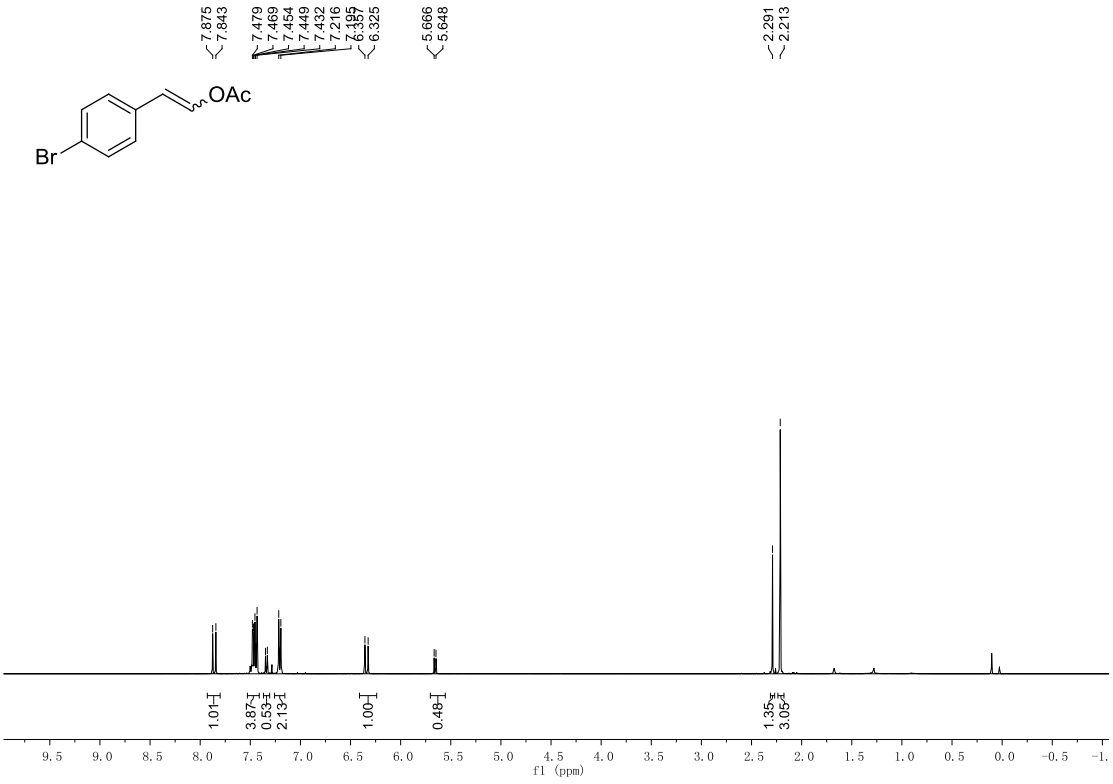
132.518
130.329
128.876
128.574
127.394
114.156
110.612
20.711
OAc
Cl
f1 (ppm)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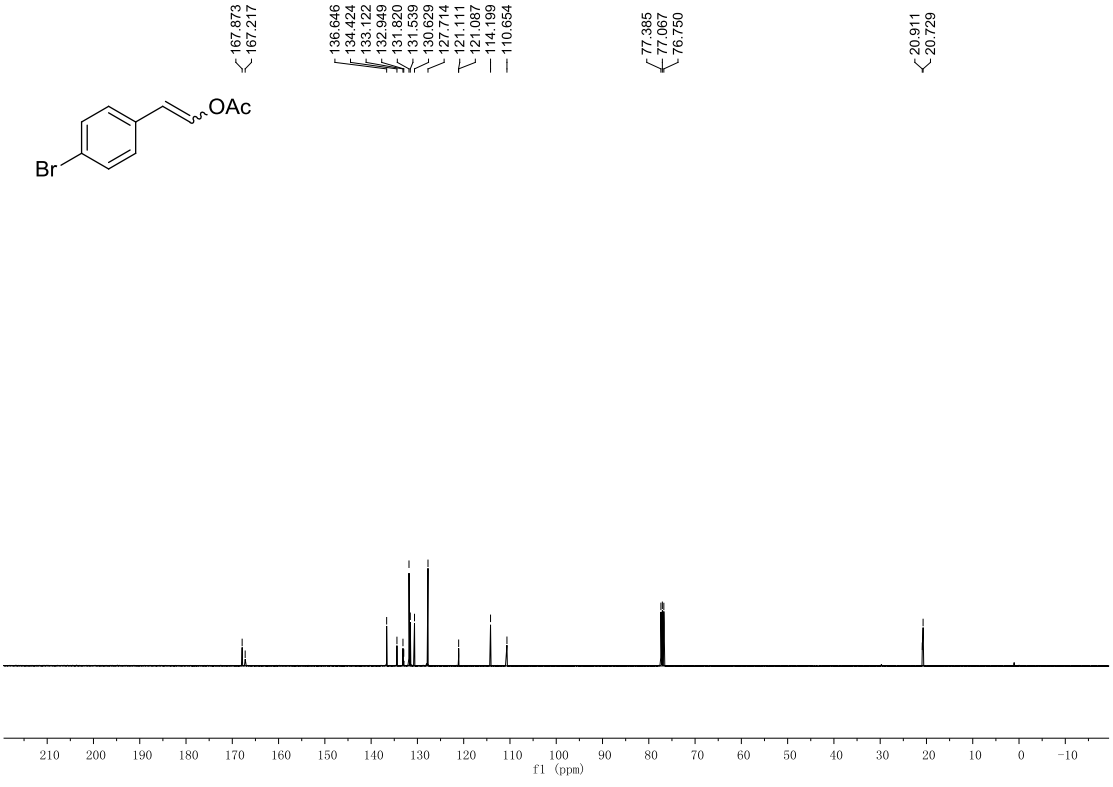
7.843
7.479
7.469
7.454
7.449
7.432
7.216
7.195
6.357
6.325
5.666
5.648
2.291
2.213
OAc
Br
1.01
3.87
0.53
2.13
1.00
0.48
1.35
3.05
f1 (ppm)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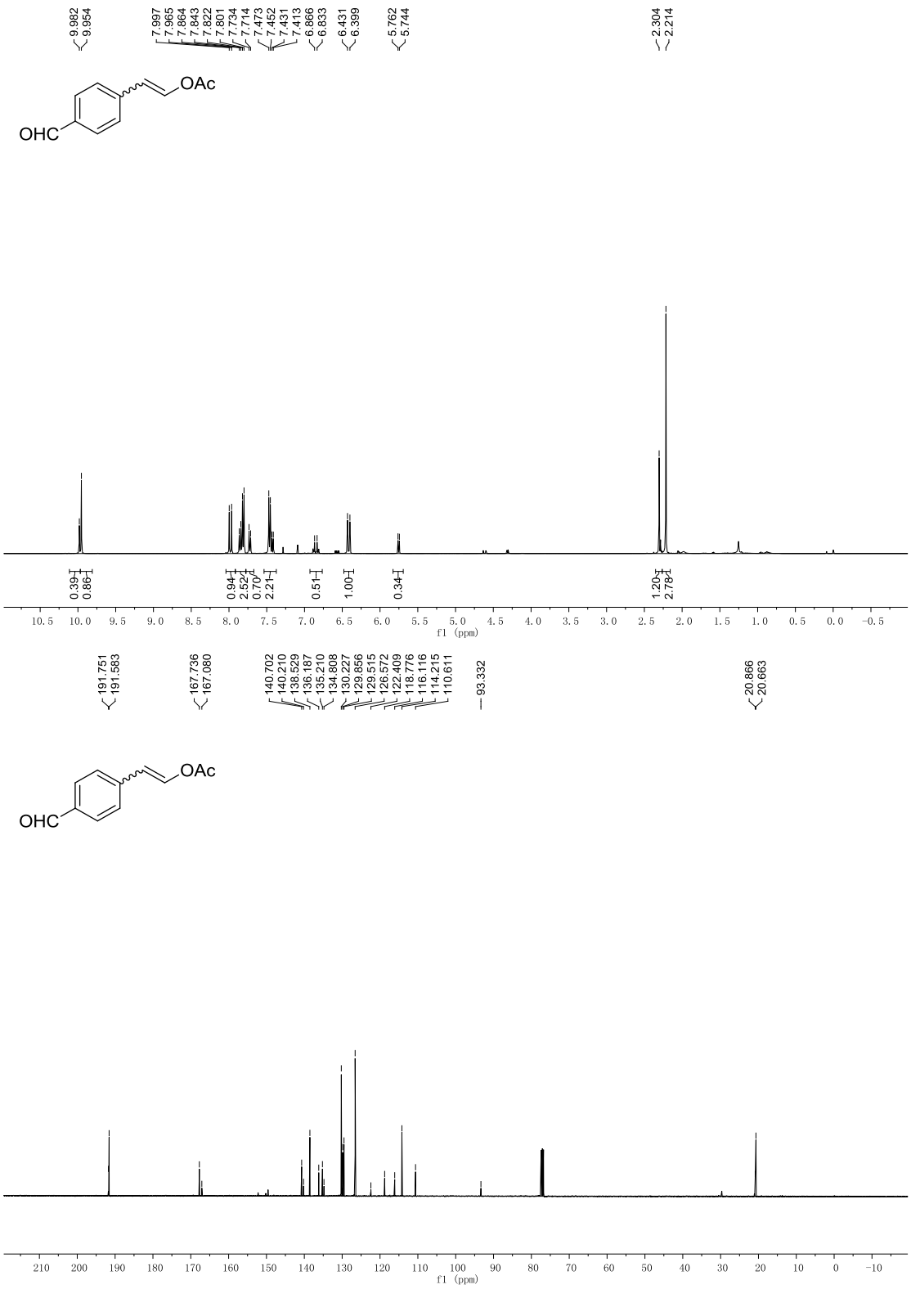
167.217
136.646
134.424
133.122
132.949
131.820
131.539
130.629
127.714
121.111
121.087
114.199
110.654
77.385
77.067
76.750
20.911
20.729
OAc
Br
f1 (ppm)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7.965
7.864
7.843
7.822
7.801
7.734
7.714
7.473
7.452
7.431
7.413
6.866
6.833
6.431
6.399
5.762
5.744
2.304
2.214
OAc
OHC
0.39
0.86
0.94
2.52
0.70
2.21
0.51
1.00
0.34
1.20
2.78
f1 (ppm)
191.751
191.583
167.736
167.080
140.702
140.210
138.529
136.187
135.210
134.808
130.227
129.856
129.515
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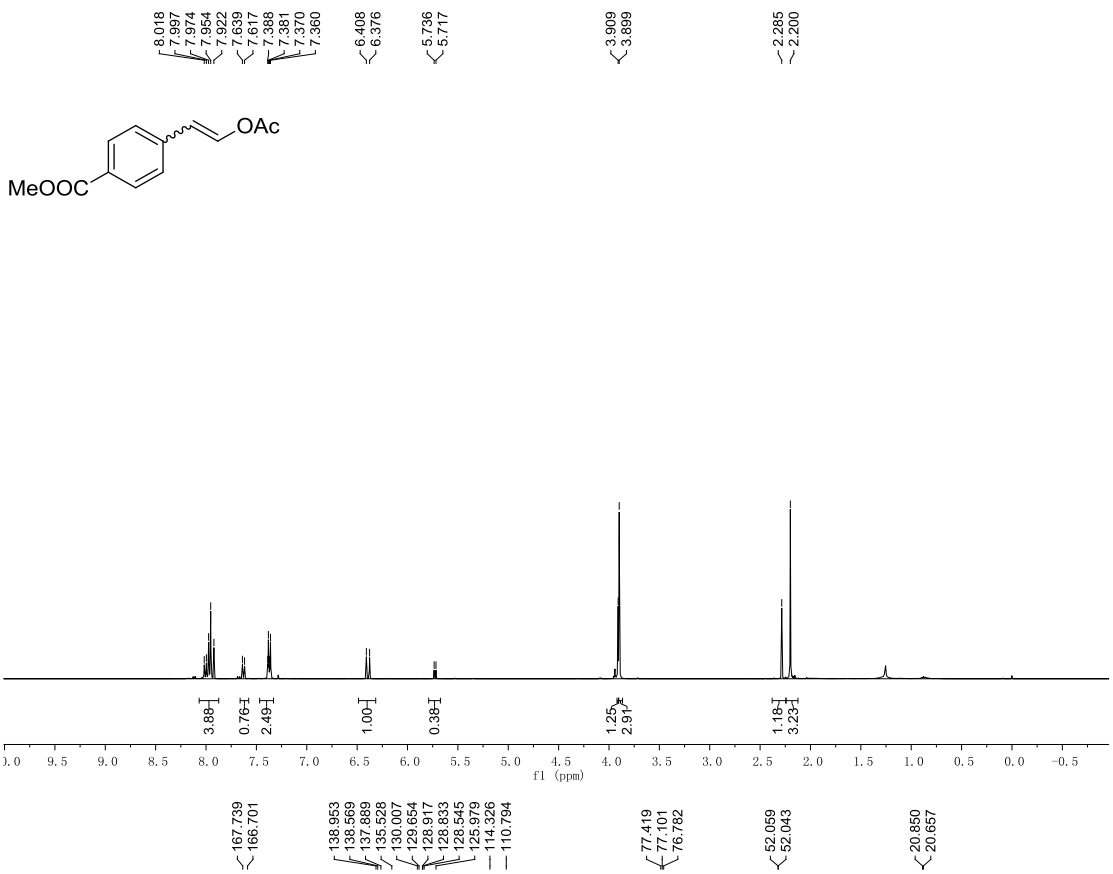
122.409
118.776
116.116
114.215
110.611
93.332
20.866
20.663
OAc
OHC
f1 (ppm)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7.617
7.388
7.381
7.370
7.360
6.408
6.376
5.736
5.717
3.909
3.899
2.285
2.200
OAc
MeOOC
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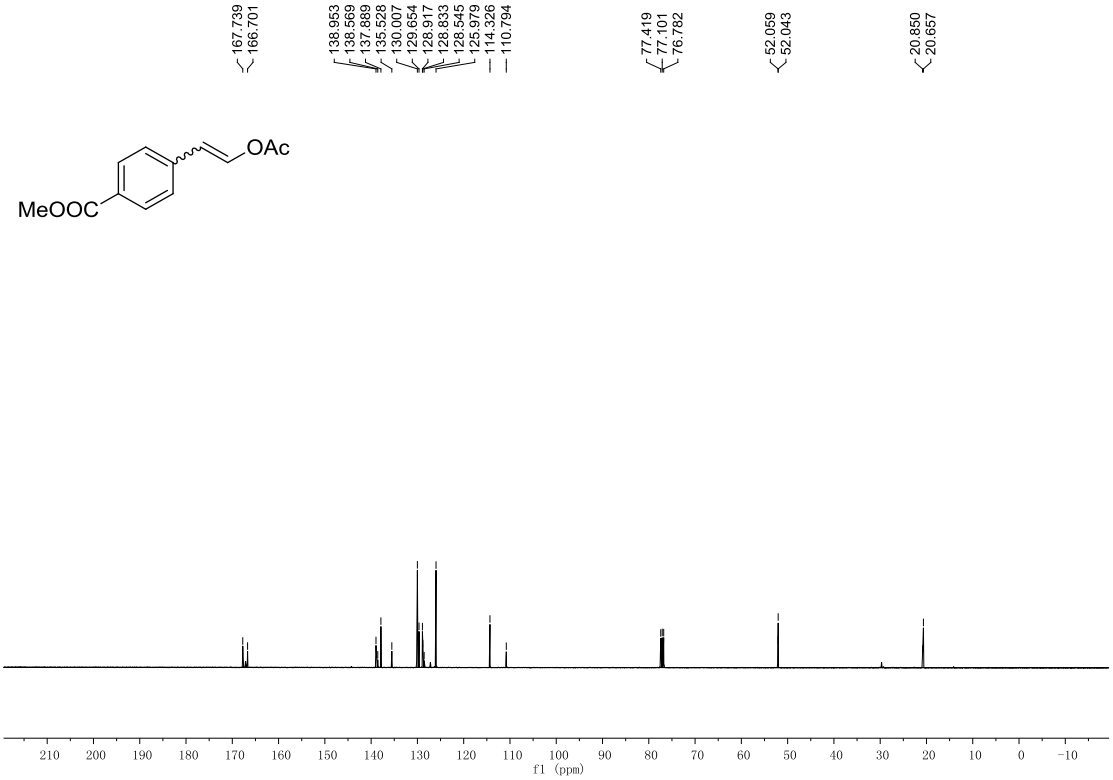
0.76
2.49
1.00
0.38
1.25
2.91
1.18
3.23
f1 (ppm)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125.979
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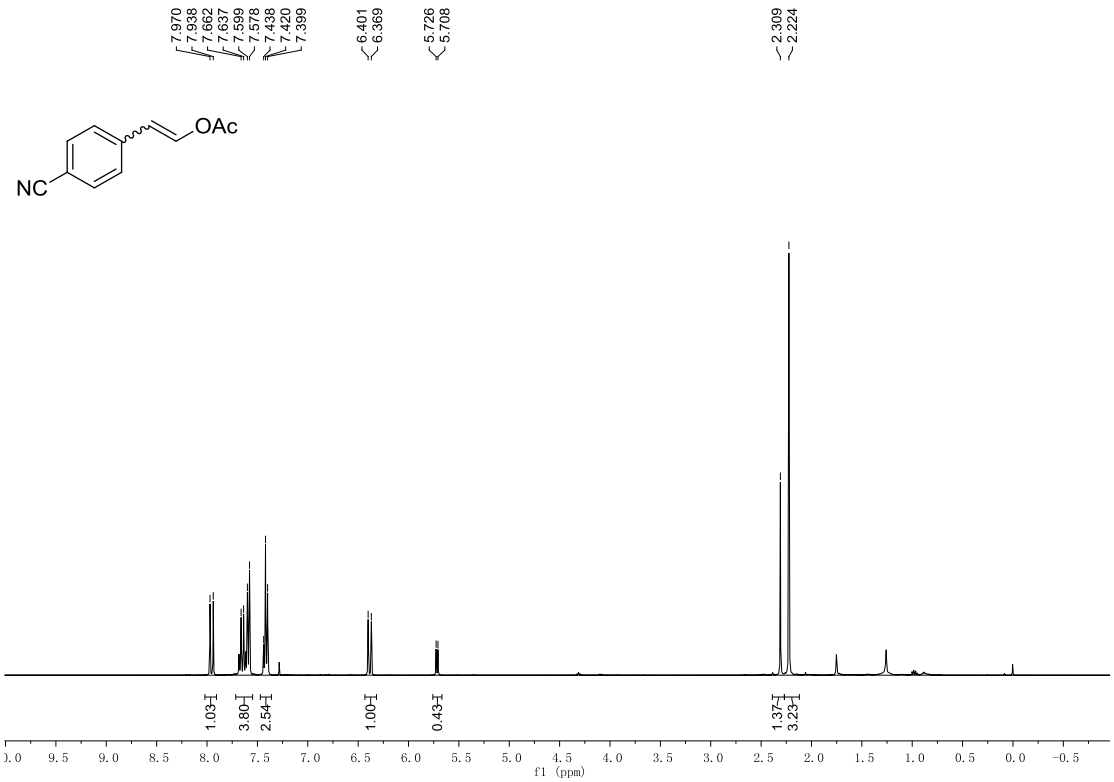
OAc
MeOOC
f1 (ppm)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7.599
7.578
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7.420
7.399
6.401
6.369
5.726
5.708
2.309
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OAc
NC
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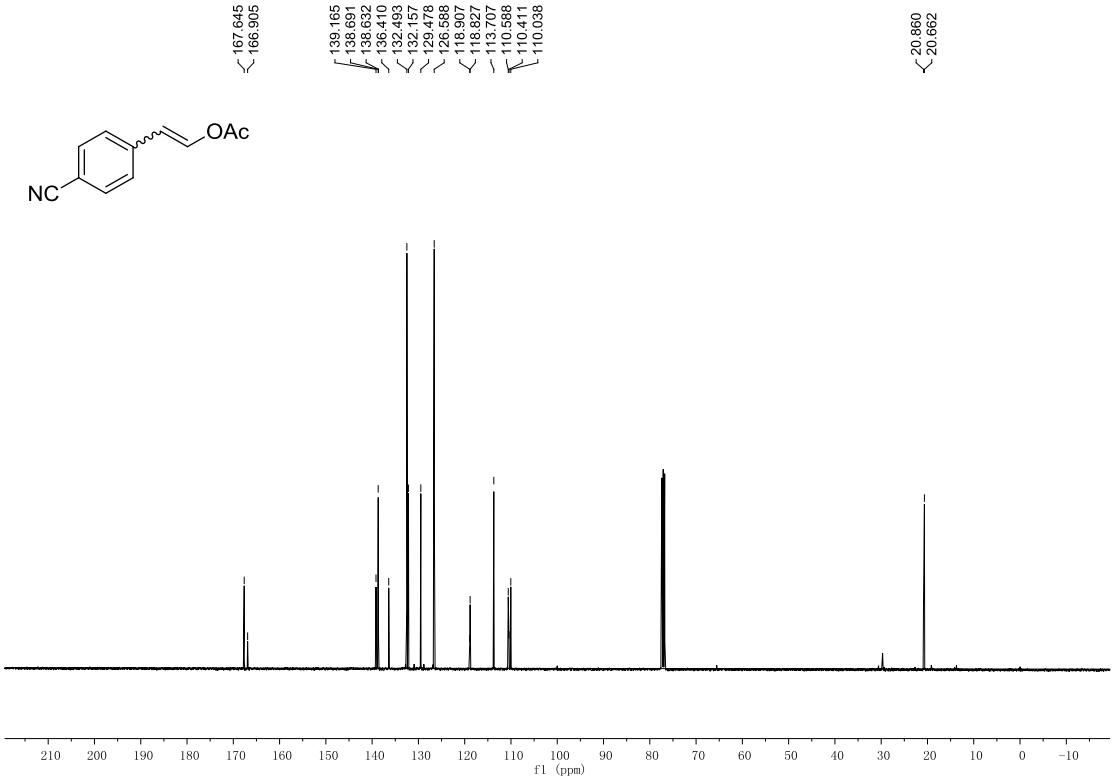
3.80
2.54
1.00
0.43
1.37
3.23
f1 (ppm)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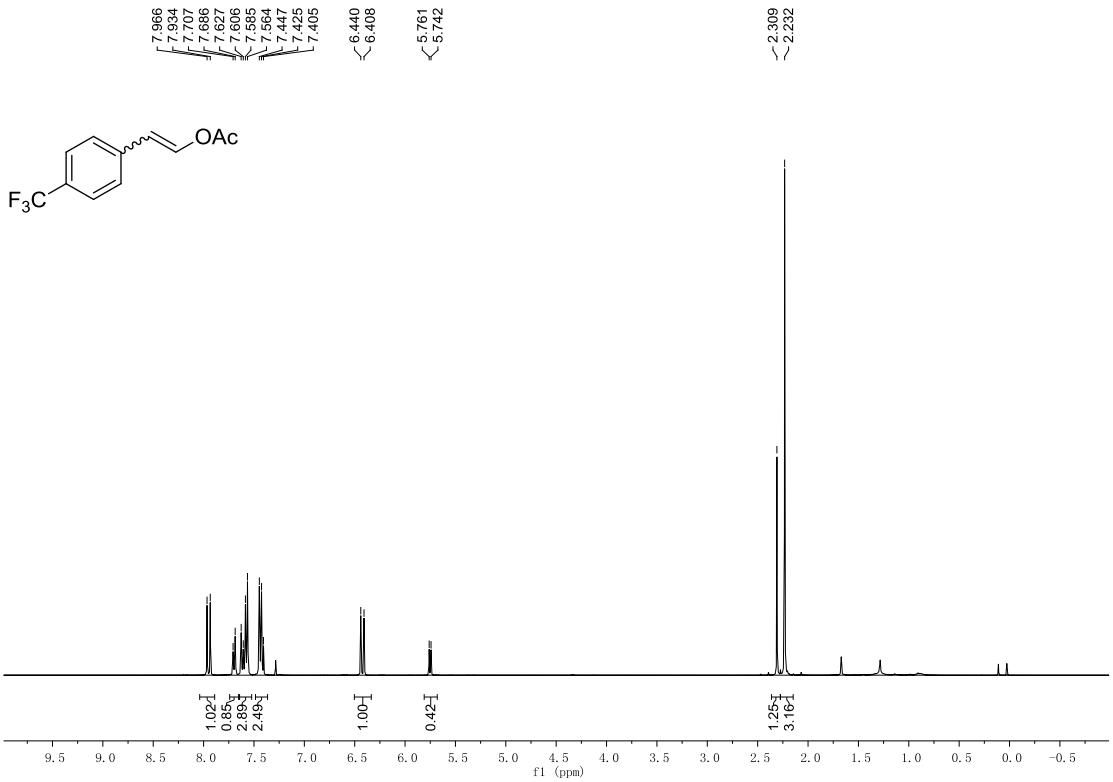
110.038
20.860
20.662
OAc
NC
f1 (ppm)


7.966
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7.707
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7.627
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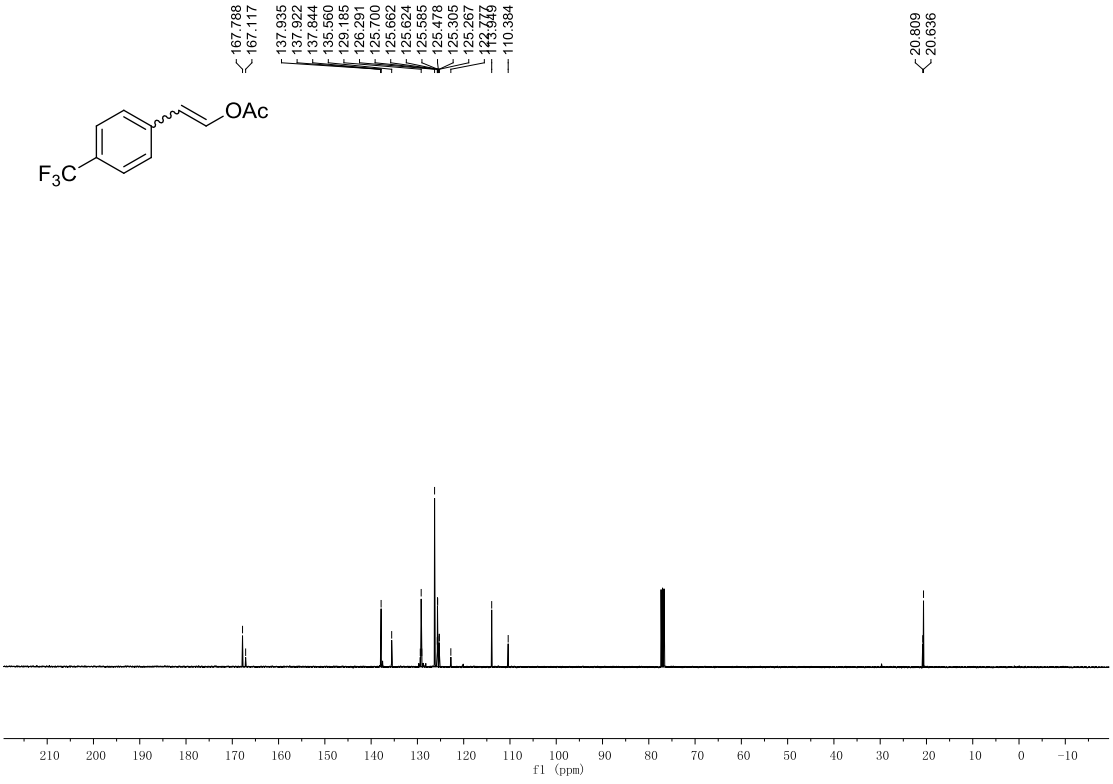
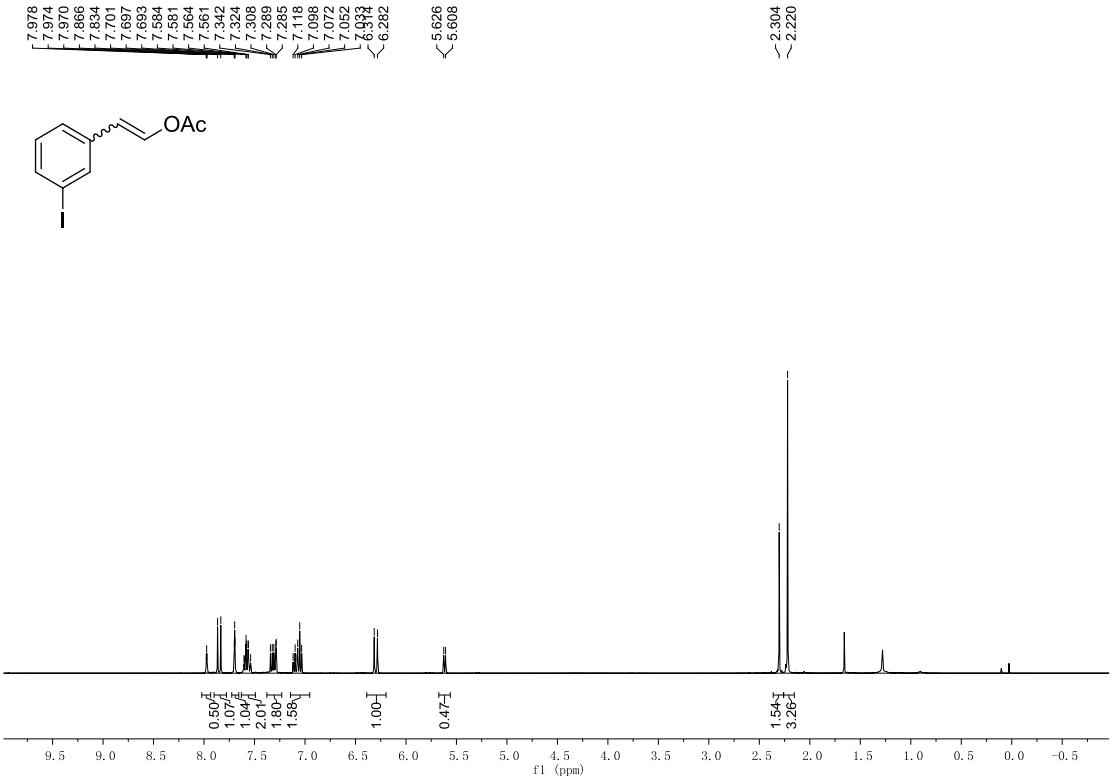
7.585
7.564
7.447
7.425
7.405
6.440
6.408
5.761
5.742
2.309
2.232
OAc
F3C
1.02
0.85
2.89
2.49
1.00
0.42
1.25
3.16
f1 (ppm)


167.788
167.117
137.935
137.922
137.844
135.560
129.185
126.291
125.700
125.662
125.624
125.585
125.478
125.305
125.267
110.384
20.809
20.636
OAc
F3C
f1 (ppm)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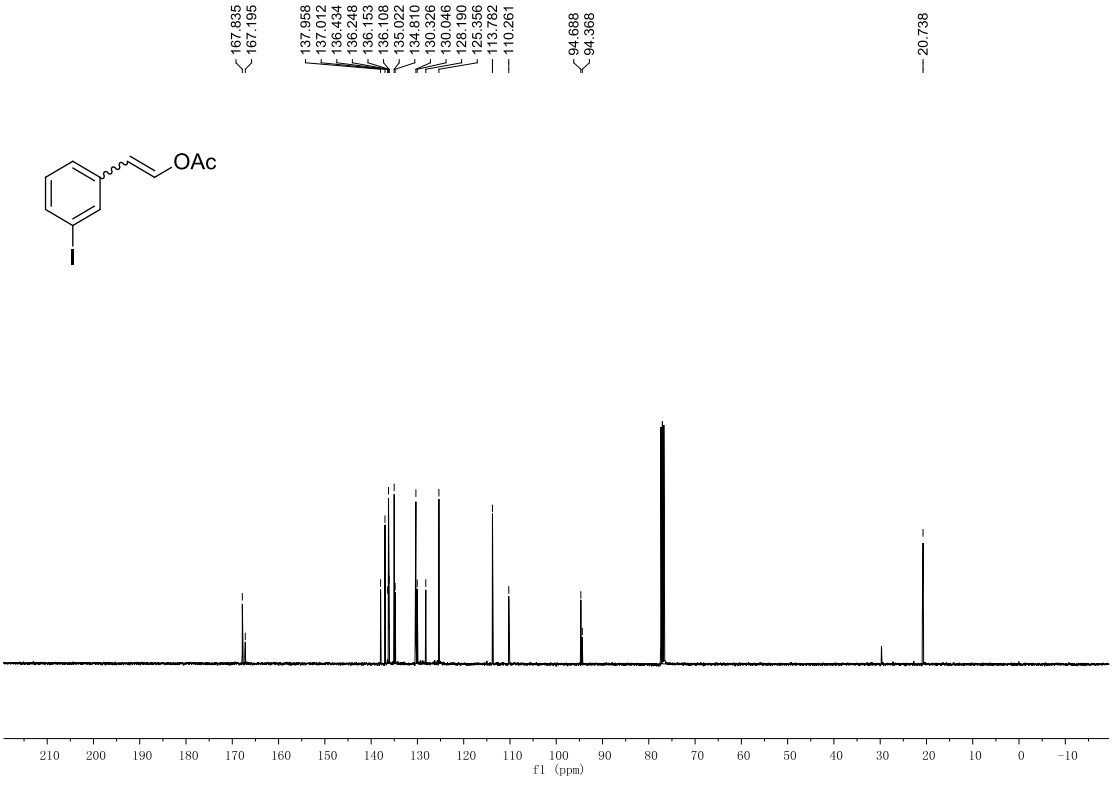
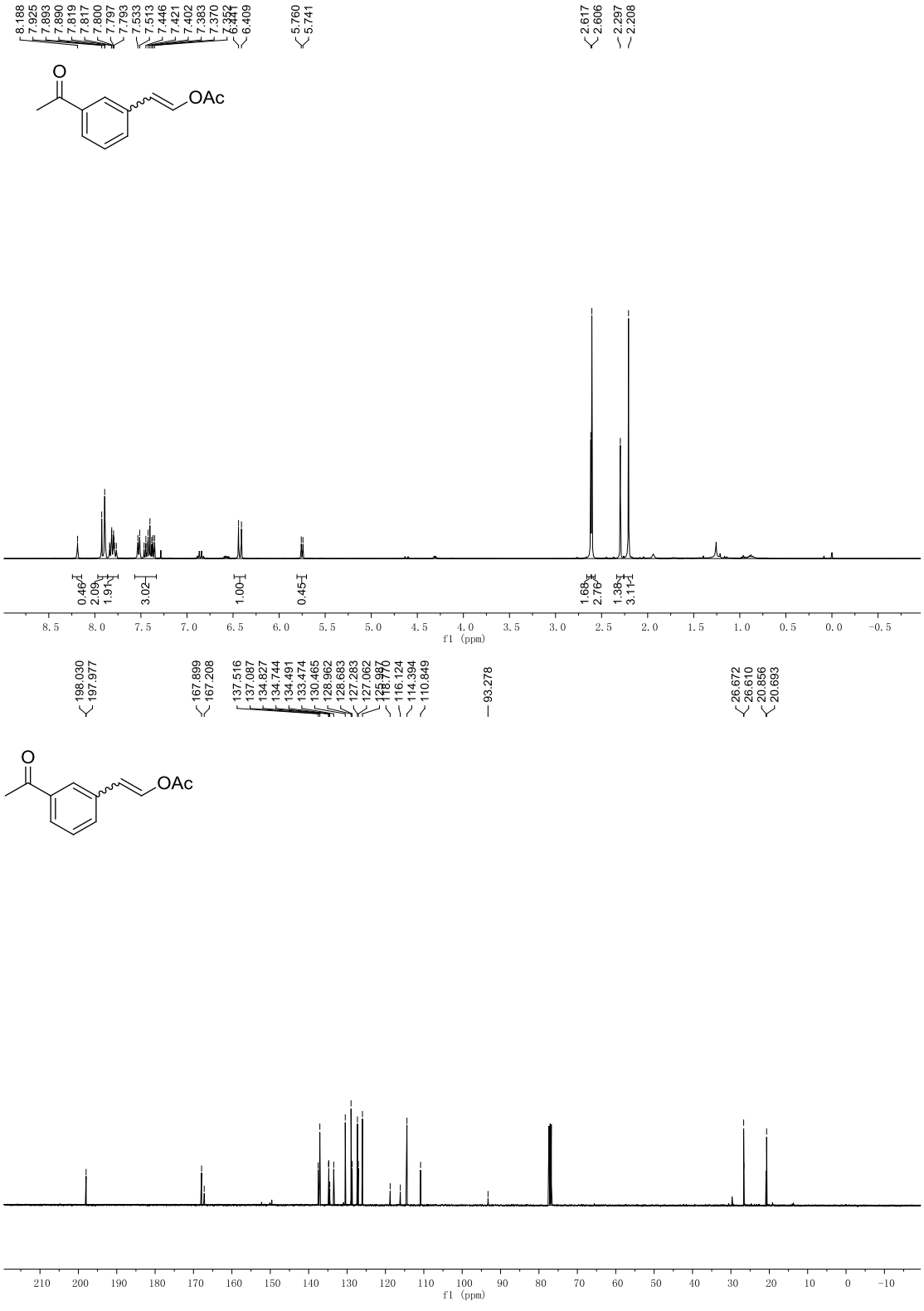
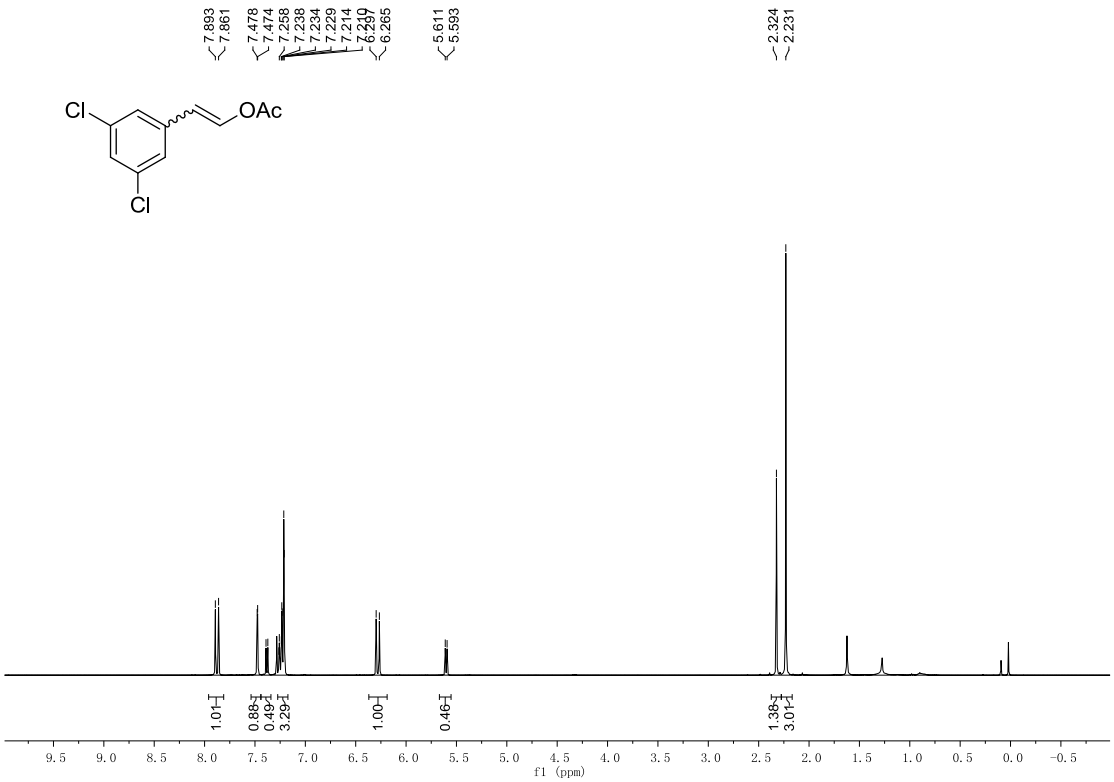
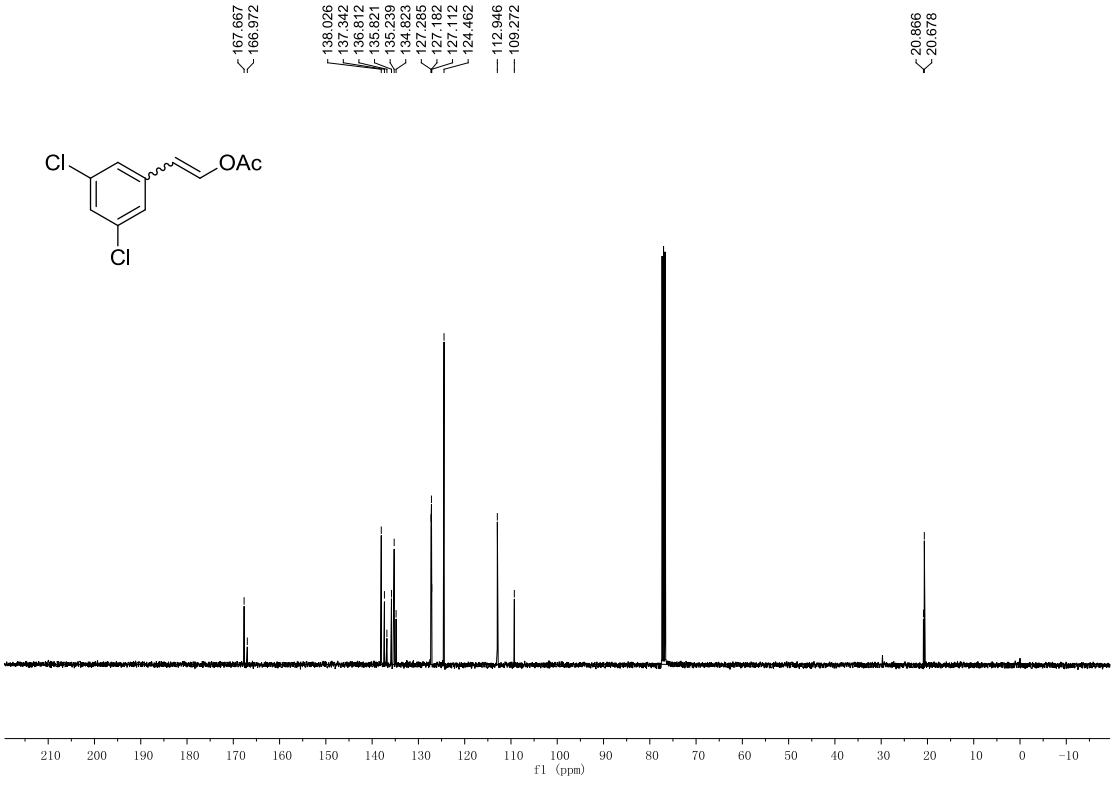
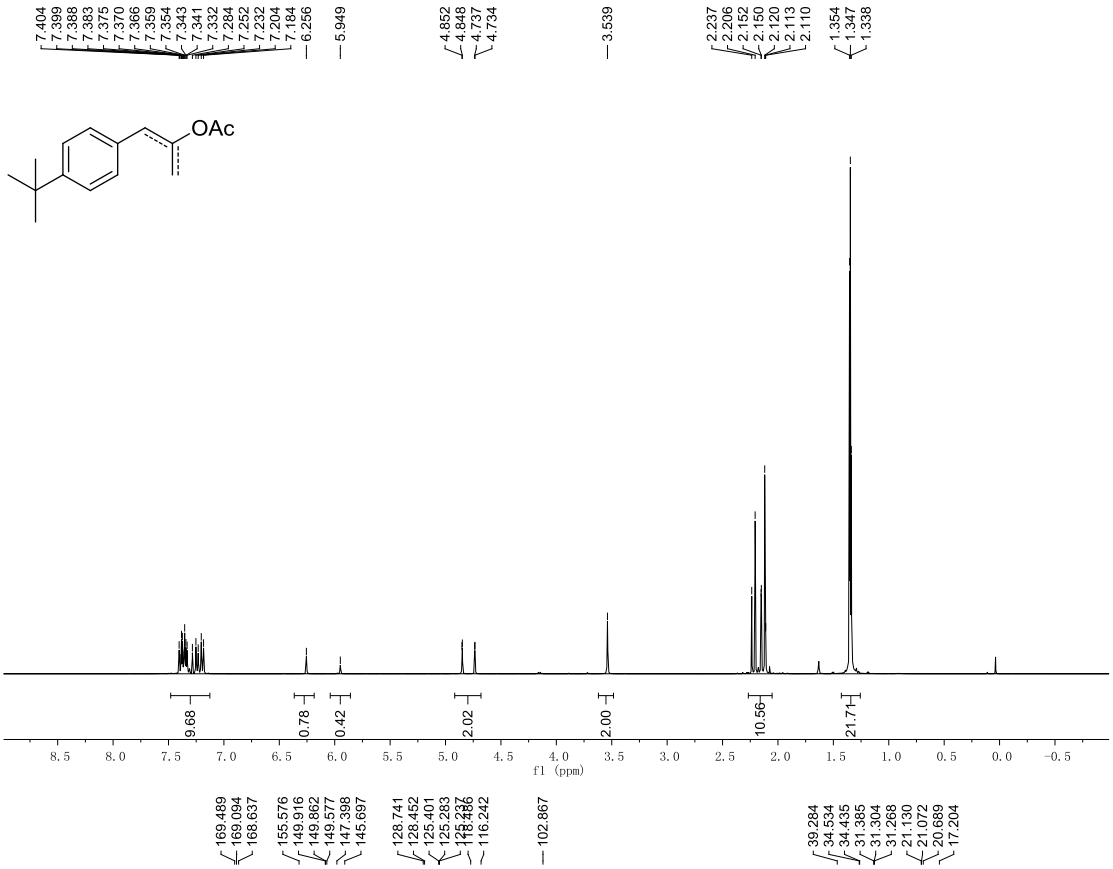
7.974
7.970
7.866
7.834
7.701
7.697
7.693
7.584
7.581
7.564
7.561
7.342
7.324
7.308
7.289
7.285
7.118
7.098
7.072
7.052
7.033
6.314
6.282
5.626
5.608
2.304
2.220
OAc
0.50
1.07
1.04
2.01
1.80
1.58
1.00
0.47
1.54
3.26
f1 (ppm)


167.835
167.195
137.958
137.012
136.434
136.248
136.153
136.108
135.022
134.810
130.326
130.046
128.190
125.356
113.782
110.261
94.688
94.368
20.738
OAc
f1 (ppm)


8.188
7.925
7.893
7.890
7.819
7.817
7.800
7.797
7.793
7.533
7.513
7.446
7.421
7.402
7.383
7.370
6.409
5.760
5.741
2.617
2.606
2.297
2.208
O
OAc
0.46
2.09
1.91
3.02
1.00
0.45
1.68
2.76
1.38
3.11
f1 (ppm)
198.030
197.977
167.899
167.208
137.516
137.087
134.827
134.744
134.491
133.474
130.465
128.962
128.683
127.283
127.062
125.987
118.770
116.124
114.394
110.849
93.278
26.672
26.610
20.856
20.693
O
OAc
f1 (ppm)


7.893
7.861
7.478
7.474
7.258
7.238
7.234
7.229
7.214
6.297
6.265
5.611
5.593
2.324
2.231
Cl
OAc
Cl
1.01
0.88
0.49
3.29
1.00
0.46
1.38
3.01
f1 (ppm)


167.667
166.972
138.026
137.342
136.812
135.821
135.239
134.823
127.285
127.182
127.112
124.462
112.946
109.272
20.866
20.678
Cl
OAc
Cl
f1 (ppm)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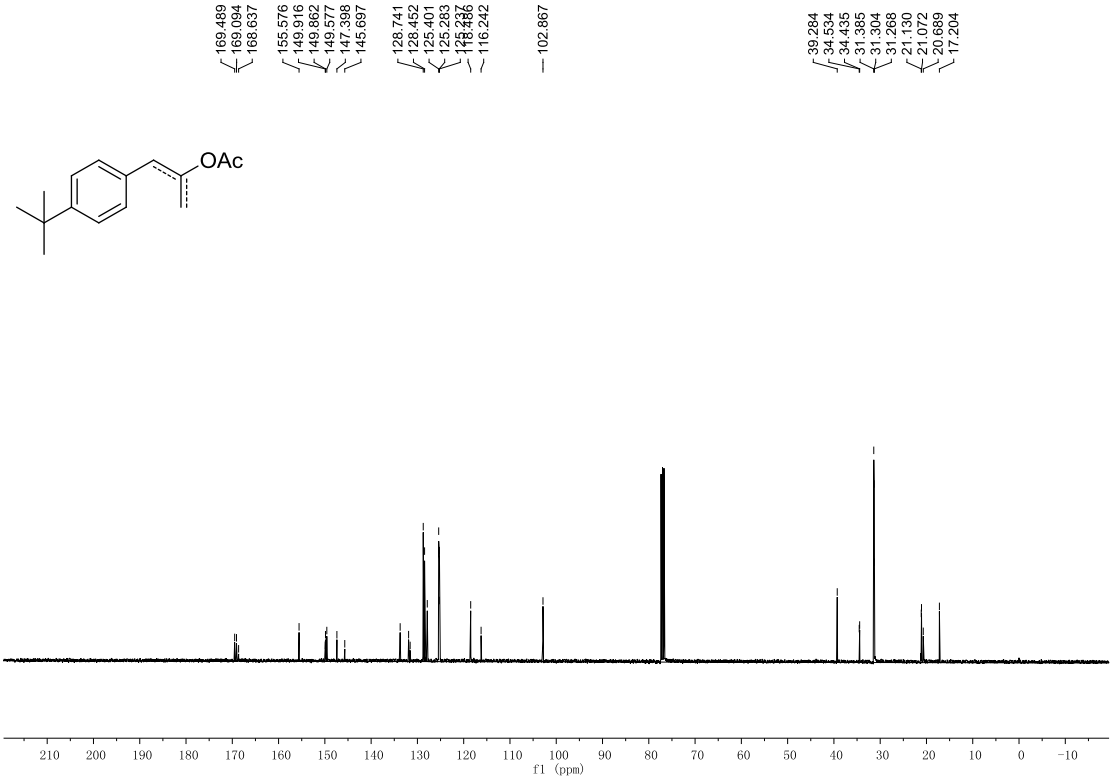
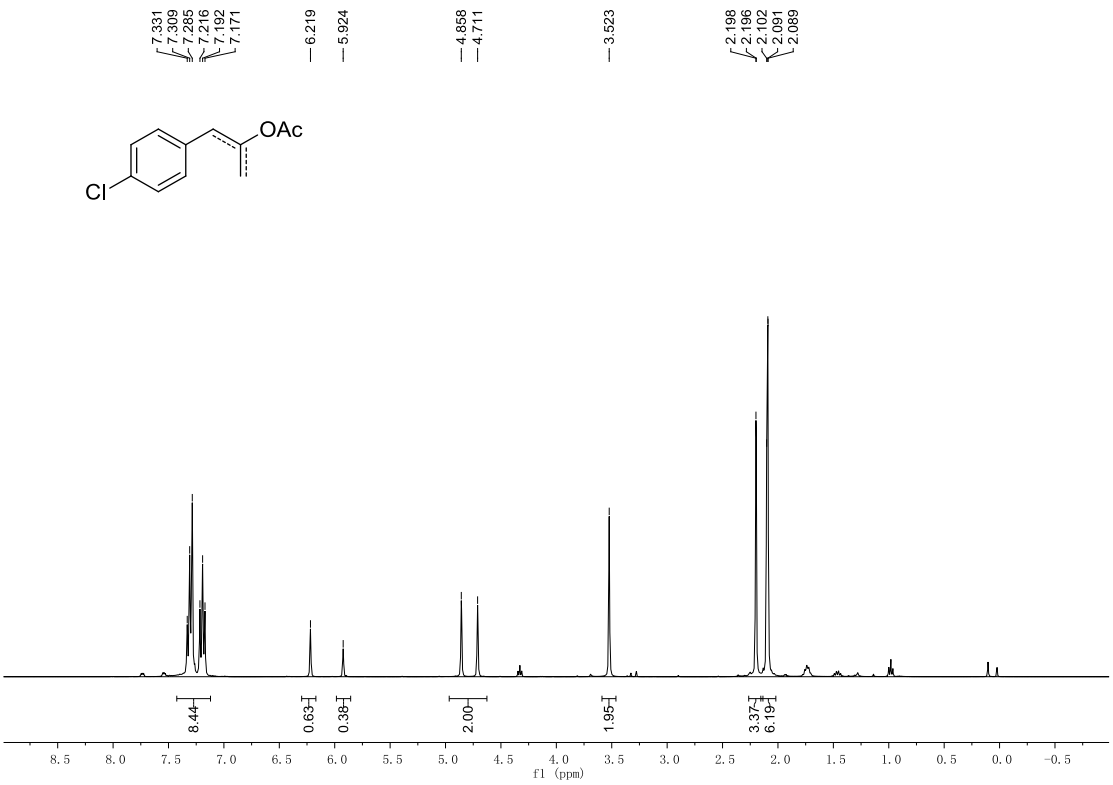
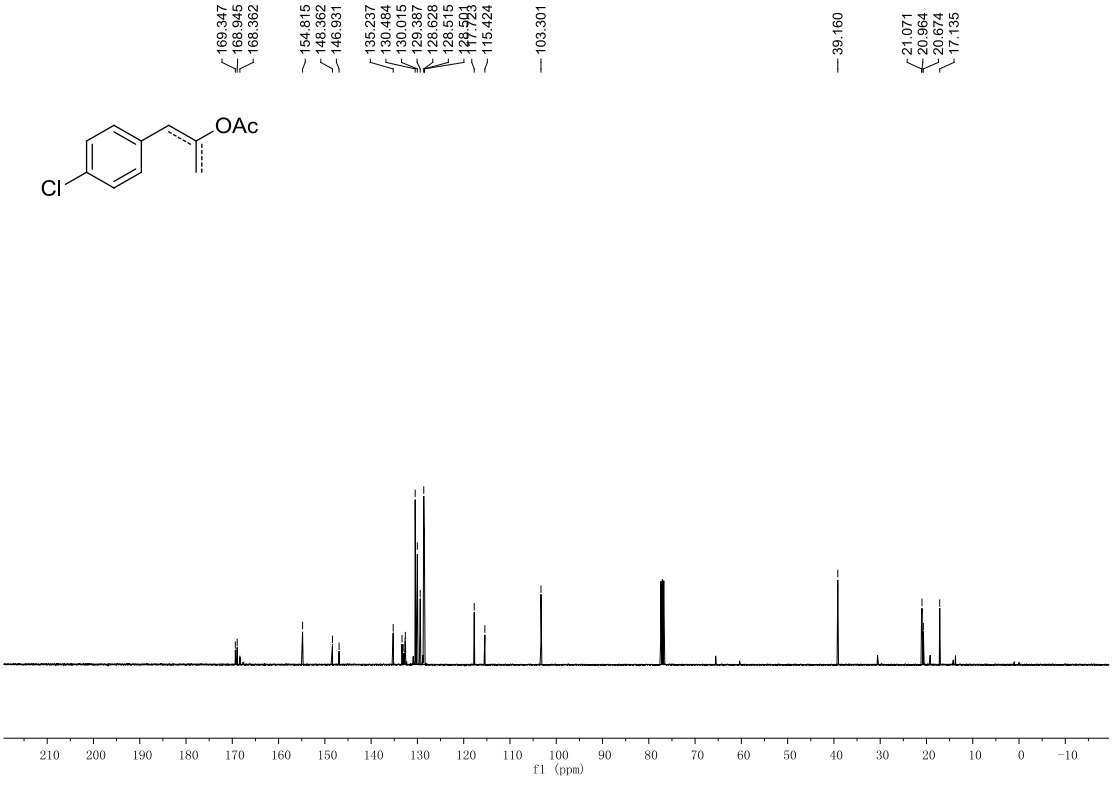
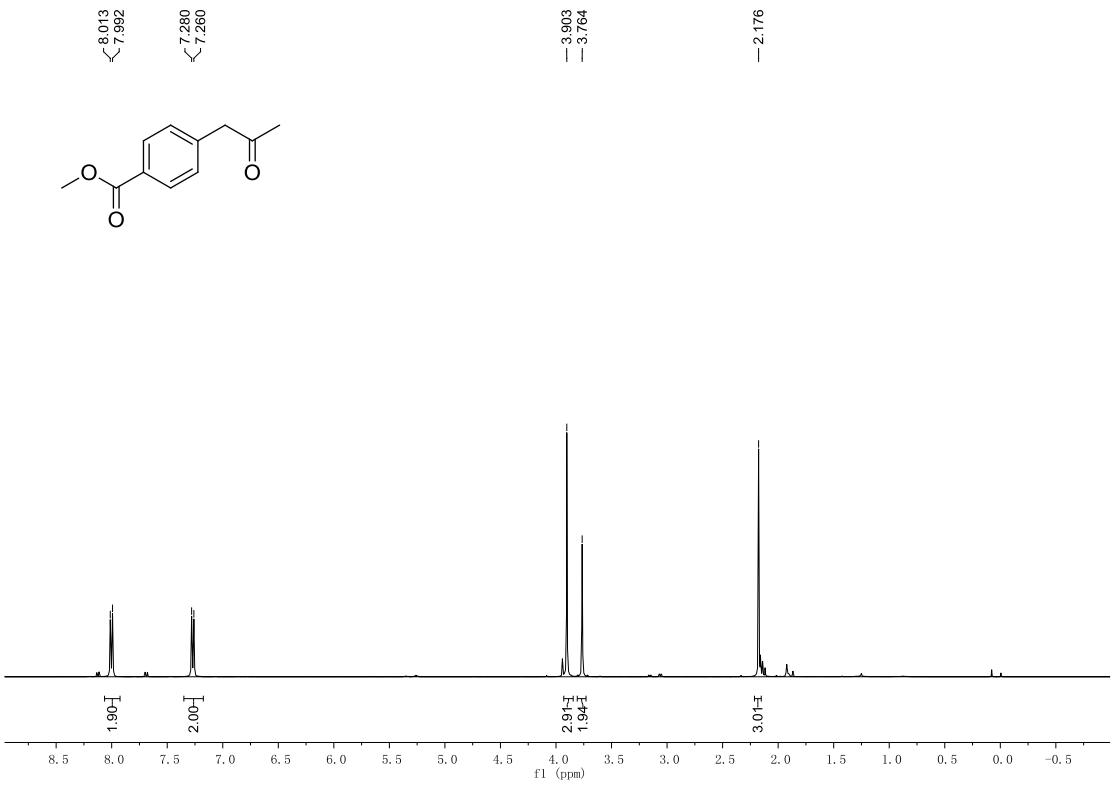
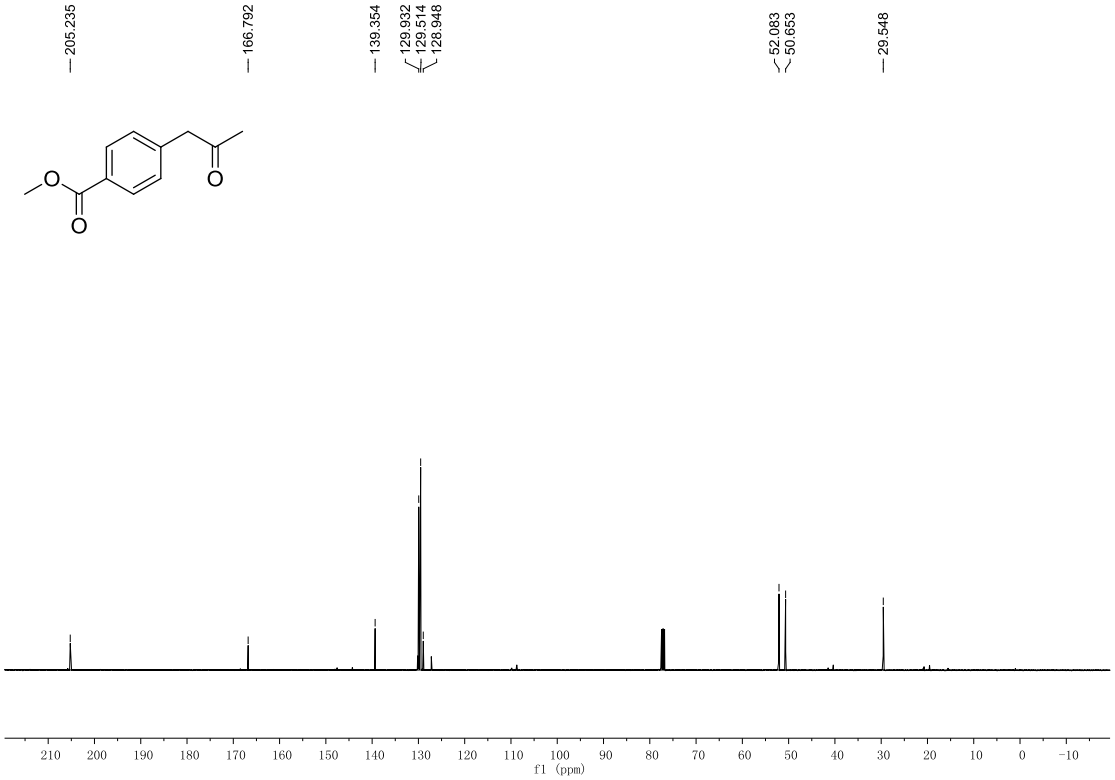
7.388
7.383
7.375
7.370
7.366
7.359
7.354
7.343
7.341
7.332
7.284
7.252
7.232
7.204
7.184
6.256
5.949
4.852
4.848
4.737
4.734
3.539
2.237
2.206
2.152
2.150
2.120
2.113
2.110
1.354
1.347
1.338
OAc
9.68
0.78
0.42
2.02
2.00
10.56
21.71
f1 (ppm)


169.489
169.094
168.637
155.576
149.916
149.862
149.577
147.398
145.697
128.741
128.452
125.401
125.283
125.237
118.486
116.242
102.867
39.284
34.534
34.435
31.385
31.304
31.268
21.130
21.072
20.689
17.204
OAc
f1 (ppm)


7.331
7.309
7.285
7.216
7.192
7.171
6.219
5.924
4.858
4.711
3.523
2.198
2.196
2.102
2.091
2.089
OAc
Cl
8.44
0.63
0.38
2.00
1.95
3.37
6.19
f1 (ppm)


169.347
168.945
168.362
154.815
148.362
146.931
135.237
130.484
130.015
129.387
128.628
128.515
115.424
103.301
39.160
21.071
20.964
20.674
17.135
OAc
Cl
f1 (ppm)


8.013
7.992
7.280
7.260
3.903
3.764
2.176
O
O
O
1.90
2.00
2.91
1.94
3.01
f1 (ppm)


205.235
166.792
139.354
129.932
129.514
128.948
52.083
50.653
29.548
O
O
O
f1 (ppm)

[1] Floris, B., Tassoni, E., *Organometallics* **1994**, *13*, 4746

[2] Durandetti, M., Nédélec, J.-Y., Périchon, J., *J Org Chem* **1996**, *61*, 1748

[3] Poladura, B., Martínez-Castañeda, Á., Rodríguez-Solla, H., Llavona, R., Concellón, C., del Amo, V., *Org Lett* **2013**, *15*, 2810