Electronic Supplementary Material (ESI) for RSC Advances.

Palladium-Catalyzed Heck Coupling of Arylhydrazines via C–$NHNH_2$ Bond Activation

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Supporting Information

1. **General procedures**
2. **Typical procedure for the Palladium-Catalyzed Heck Coupling of Arylhydrazines via C–NHNH2 Bond Activation**
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1. General procedures

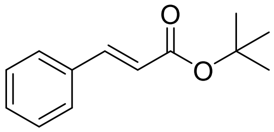
The solvents were distilled from standard drying agents. Unless otherwise stated, commercial reagents purchased from Alfa Aesar, Acros and Aldrich chemical companies were used without further purification. Purification of reaction products was carried out by flash chromatography using Qing Dao Sea Chemical Reagent silica gel (200–300 mesh). ^{1}H NMR spectra were recorded on a Bruker Avance III 400 (400 MHz) spectrometer and referenced internally to the residual proton resonance in $CDCl_3$ (δ = 7.26 ppm), or with tetramethylsilane (TMS, δ = 0.00 ppm) as the internal standard. Chemical shifts were reported as parts per million (ppm) in the δ scale downfield from TMS. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Analytical TLC was performed using EM separations percolated silica gel 0.2 mm layer UV 254 fluorescent sheets.

2. Typical procedure for the palladium-catalyzed Heck coupling of arylhydrazine

A mixture of arylhydrazine **1** (0.36 mmol), acrylate **2** (0.3 mmol), TsCl (0.36 mmol), $Pd(OAc)_2$ (0.015 mmol, 5 mol %), and Et_3N (0.66 mmol, 2.2 equiv) was stirred at 40 ºC in MeOH (2 mL) for 4-12 h. After completion of the reaction (indicated by TLC), the mixture was quenched with saturated NaCl solution, extracted with EtOAc, and dried over Na_2SO_4. The crude product was purified by flash column chromatography to provide the corresponding product **3**.

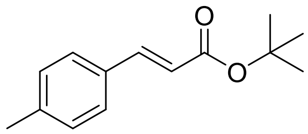
3. Characterization of the products

***tert*-Butyl cinnamate (3a)**[1]



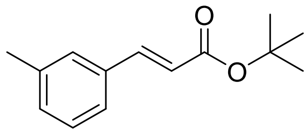
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 16.0 Hz, 1H), 7.51 (dd, J = 6.7, 2.8 Hz, 2H), 7.37 – 7.36 (m, 3H), 6.37 (d, J = 16.0 Hz, 1H), 1.54 (s, 9H).

(*E*)-*tert*-Butyl 3-*p*-tolylacrylate (3b)[1]



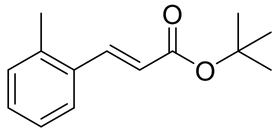
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 16.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 6.32 (d, J = 16.0 Hz, 1H), 2.36 (s, 3H), 1.53 (s, 9H).

(*E*)-*tert*-Butyl 3-*m*-tolylacrylate (3c)[1]



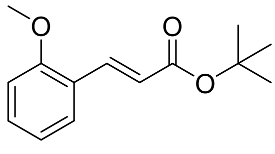
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 16.0 Hz, 1H), 7.31 (d, J = 7.9 Hz, 2H), 7.25 (d, J = 8.6 Hz, 1H), 7.17 (d, J = 7.2 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 2.36 (s, 3H), 1.53 (s, 9H).

(*E*)-*tert*-Butyl 3-*o*-tolylacrylate (3d)[1]



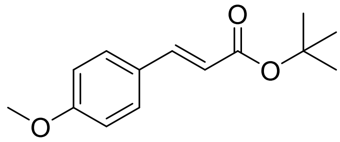
Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 (d, *J* = 15.9 Hz, 1H), 7.55– 7.53 (m, 1H), 7.24 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.18 (dd, *J* = 11.5, 5.9 Hz, 2H), 6.29 (d, *J* = 15.9 Hz, 1H), 2.43 (s, 3H), 1.54 (s, 9H).

(*E*)-*tert*-Butyl 3-(2-methoxyphenyl)acrylate (3e)[2]



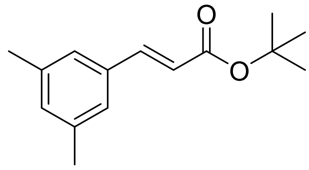
Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 (d, *J* = 16.2 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 6.93 (dd, *J* = 20.0, 7.9 Hz, 2H), 6.44 (d, *J* = 16.1 Hz, 1H), 3.88 (s, 3H), 1.53 (s, 9H).

(*E*)-*tert*-Butyl 3-(4-methoxyphenyl)acrylate (3f)[1]



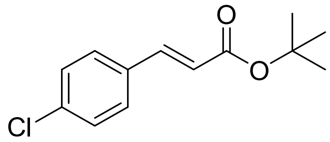
Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.54 (d, *J* = 15.9 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 2H), 6.89 (d, *J* = 7.8 Hz, 2H), 6.24 (d, *J* = 15.9 Hz, 1H), 3.83 (s, 3H), 1.53 (s, 9H).

(*E*)-*tert*-Butyl 3-(3,5-dimethylphenyl)acrylate (3g)[3]



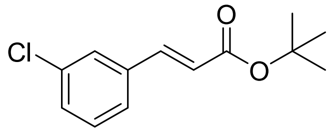
Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) *δ:* 7.53 (d, *J* = 15.9 Hz,, 1H), 7.13 (s, 2H), 7.00 (s, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 2.32 (s, 6H), 1.53 (s, 9H).

(*E*)-*tert*-Butyl 3-(4-chlorophenyl)acrylate (3h)[1]



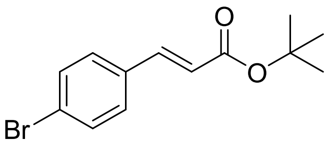
Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.56 (d, *J* = 16.0 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 2.36 (s, 3H), 1.53 (s, 9H).

(*E*)-*tert*-Butyl 3-(3-chlorophenyl)acrylate (3i)[3]



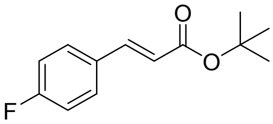
Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.51 (d, *J* = 15.6 Hz, 2H), 7.37 (d, *J* = 7.0 Hz, 1H), 7.35 – 7.28 (m, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 1.53 (s, 9H).

(*E*)-*tert*-Butyl 3-(4-bromophenyl)acrylate (3j)[1]



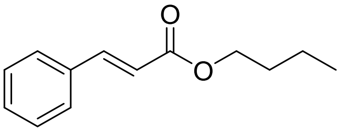
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 1H), 7.49 (s, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 6.35 (d, *J* = 16.0 Hz, 1H), 1.53 (s, 9H).

(*E*)-*tert*-Butyl 3-(4-fluorophenyl)acrylate (3k)[4]



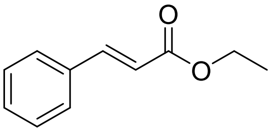
Yellow solid; mp: 47-49 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (m, 3H), 7.06 (m, 2H), 6.29 (d, *J*=16.0 Hz, 1H), 1.53 (s, 9H).

Butyl cinnamate (3l)[4]



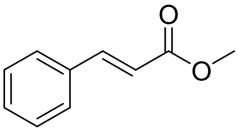
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.53 (m, 2H), 7.38 (m, 3H), 6.42 (dd, *J* = 19.7 Hz, 16.1 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.70 (dt, *J* = 14.6 Hz, 6.8 Hz, 2H), 1.44 (td, *J* = 14.9 Hz, 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

Ethyl cinnamate (3m)[5]



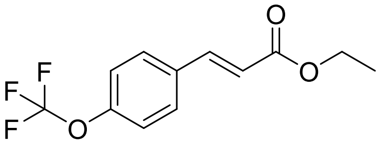
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.53 – 7.51 (m, 2H), 7.39 – 7.37 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).

Methyl cinnamate (3n)[6]



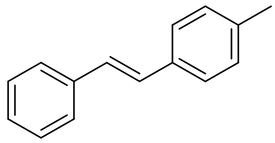
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.53 (m, 2H), 7.39 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H).

(*E*)-Ethyl 3-(4-(trifluoromethoxy)phenyl)acrylate (3o)[7]



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ:* 7.65 (d, *J* = 16.0 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.40 (d, *J* = 16.1 Hz, 1H), 4.27 (q, *J* = 6.7 Hz, 2H), 1.34 (t, *J* = 7.0 Hz, 3H).

(*E*)-1-Methyl-4-styrylbenzene (3s)[8]



White solid; mp: 117-119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ:* 7.50 (d, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.24 (s, 1H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 2.3 Hz, 2H), 2.36 (s, 3H).

References

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[4] J. Masllorens, M. Moreno-Manas, A. Pla-Quintana, A. Roglans, *Org. Lett.*, **2003**, *5*, 1559.

[5] I. Peñafiel, I. M. Pastor, M. Yus, *Eur. J. Org. Chem.* **2012**, 3151.

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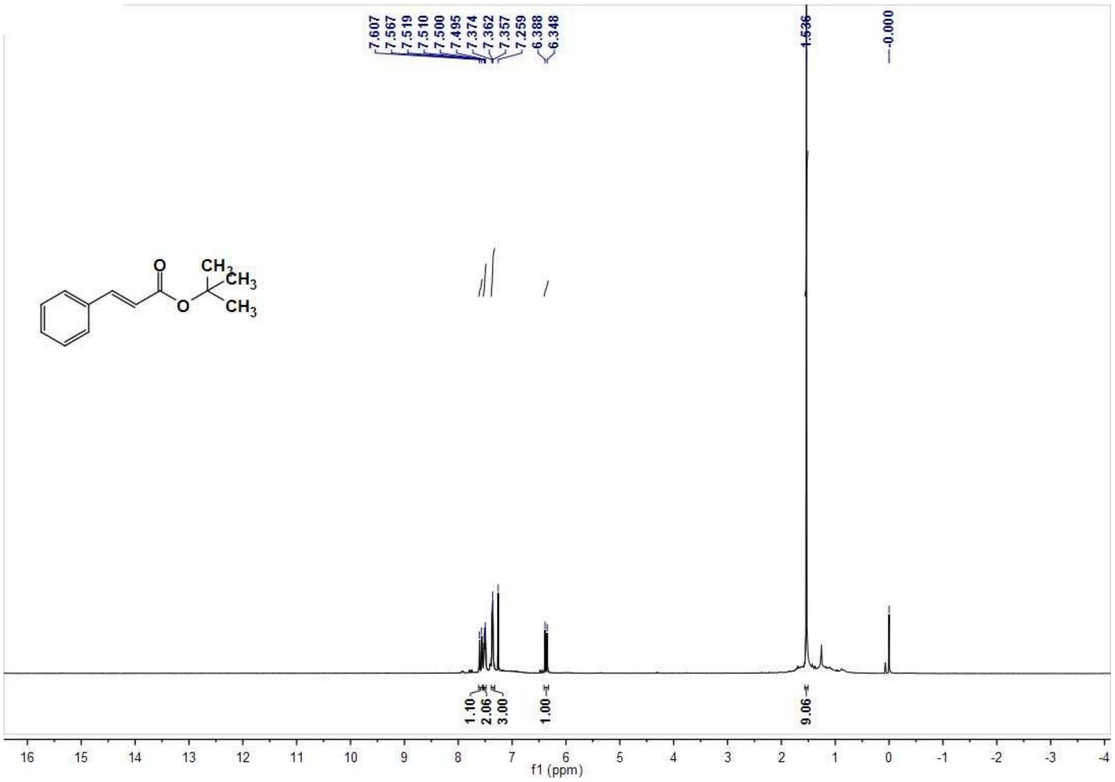
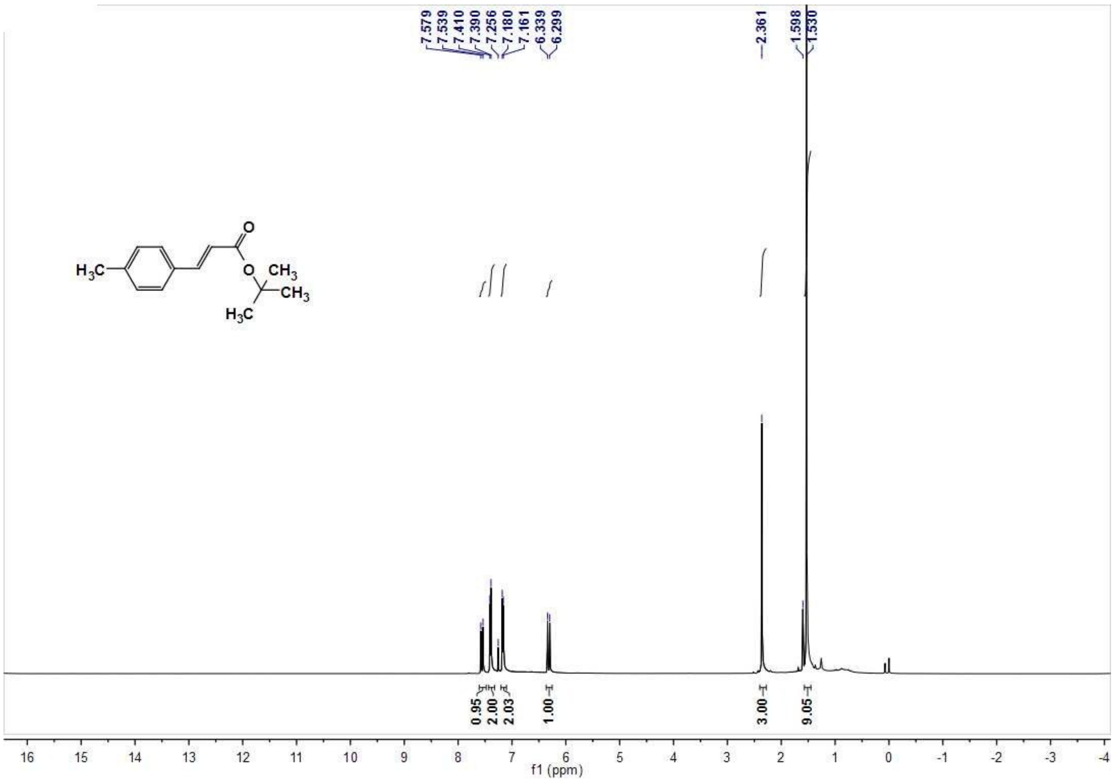
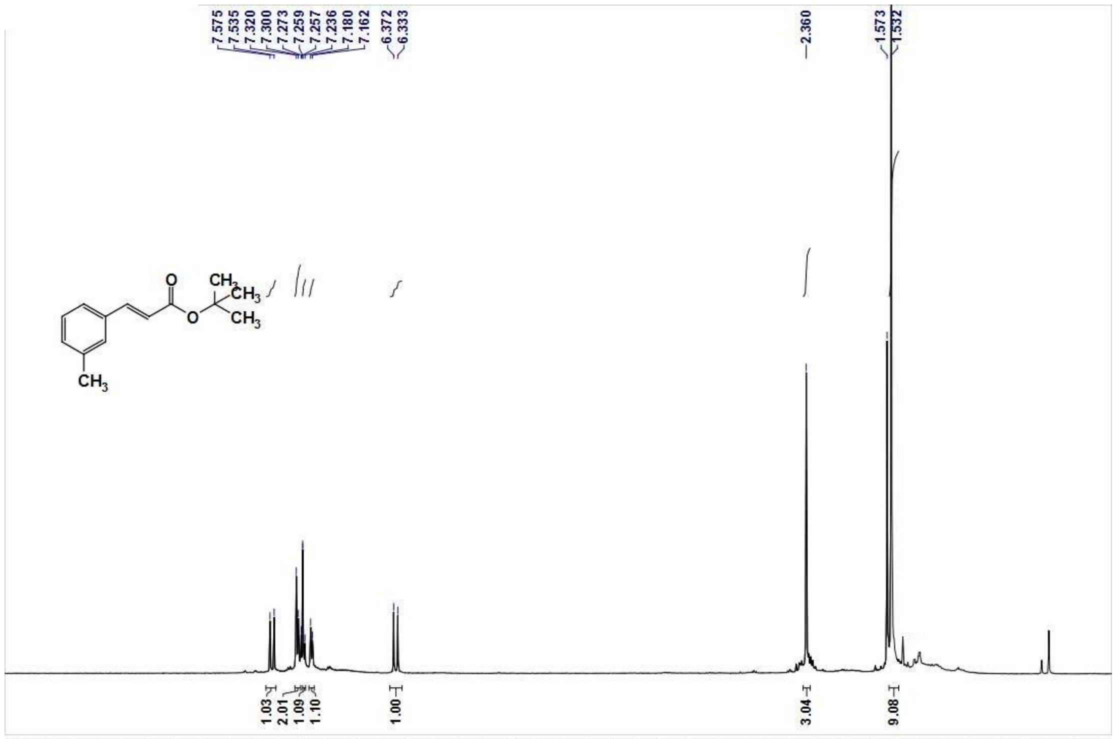
[8] T. Mino, Y. Shirae, Y. Sasai, M. Sakamoto, T. Fujita, *J. Org. Chem.,* **2006**, *71*, 6834.

4. NMR spectra of the products



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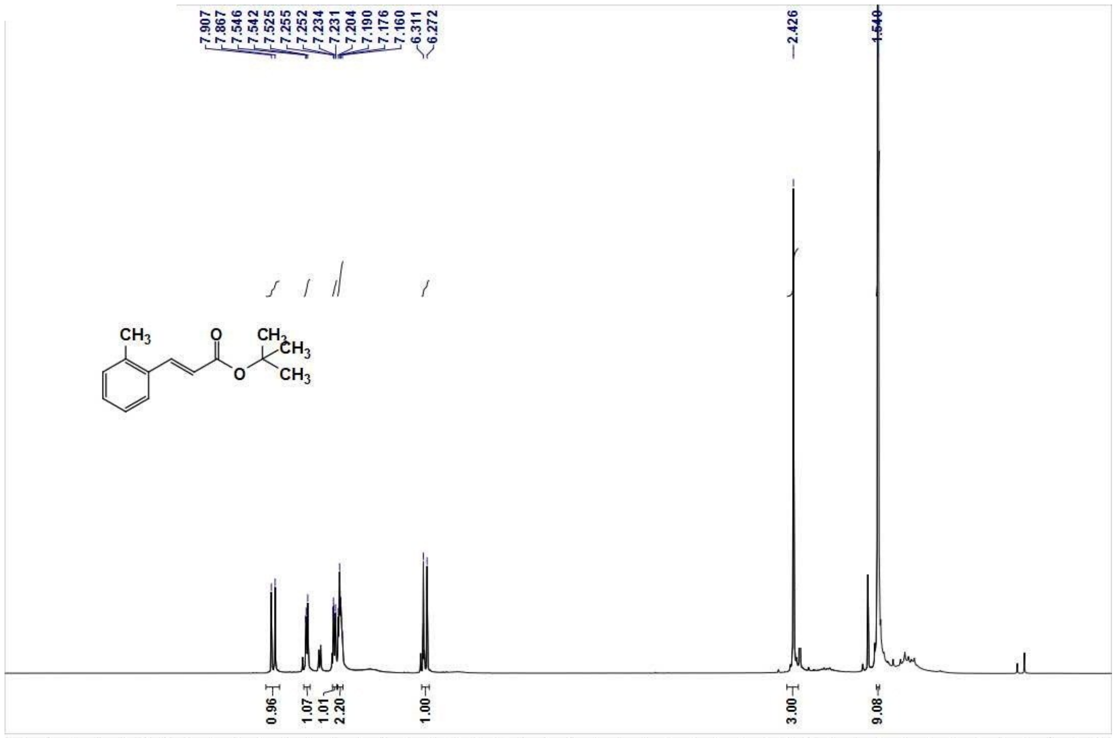
7.535
7.320
7.300
7.273
7.259
7.257
7.236
7.180
7.162
6.372
6.333
2.360
1.573
1.532
O
O
CH3
CH3
CH3
CH3
1.03
2.01
1.09
1.10
1.00
3.04
9.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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7.867
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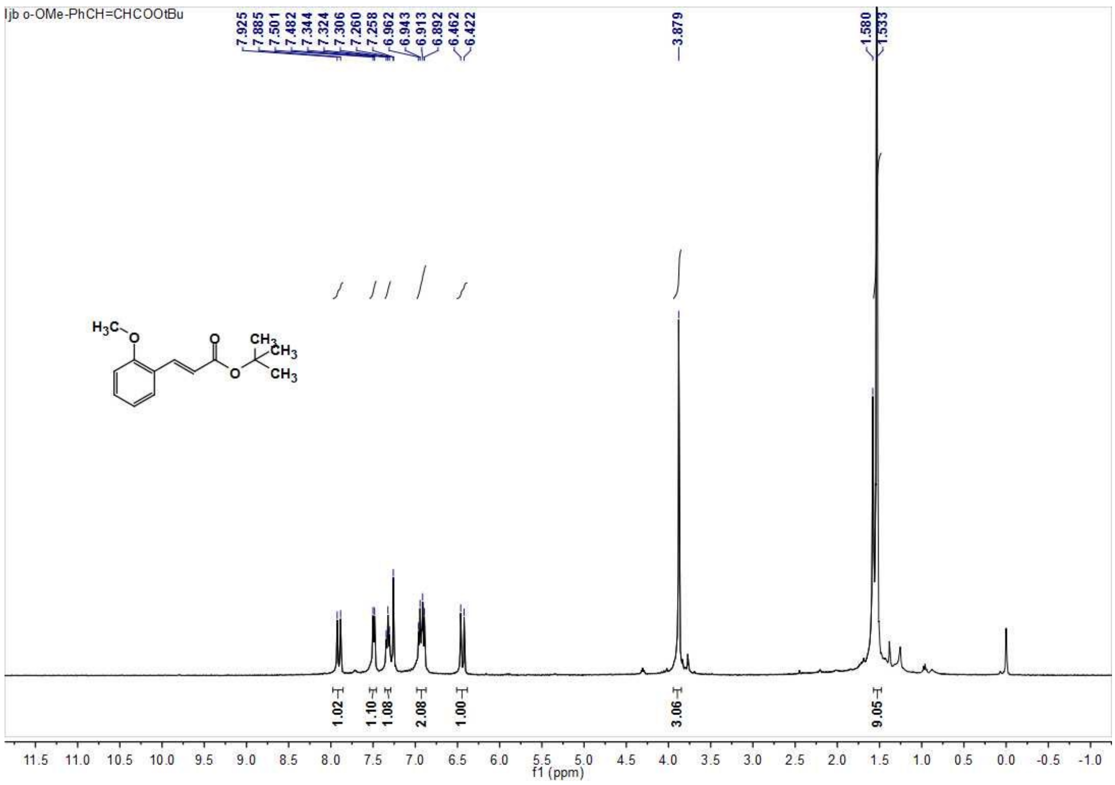
7.542
7.525
7.255
7.252
7.234
7.231
7.204
7.190
7.176
7.160
6.311
6.272
2.426
1.540
CH3
O
O
CH3
CH3
CH3
0.96
1.07
1.01
2.20
1.00
3.00
9.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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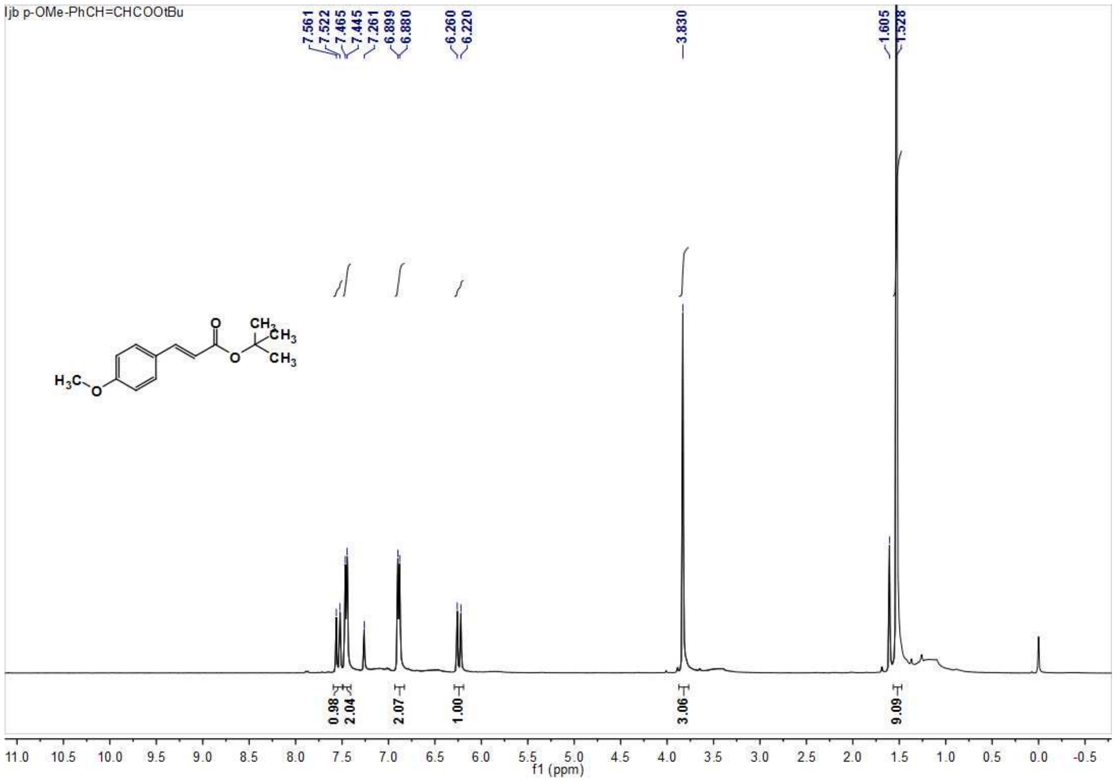
7.482
7.344
7.324
7.306
7.260
7.258
6.962
6.943
6.913
6.892
6.462
6.422
3.879
1.580
1.533
H3C
O
CH3
1.02
1.10
1.08
2.08
1.00
3.06
9.05
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


ljb p-OMe-PhCH=CHCOOtBu
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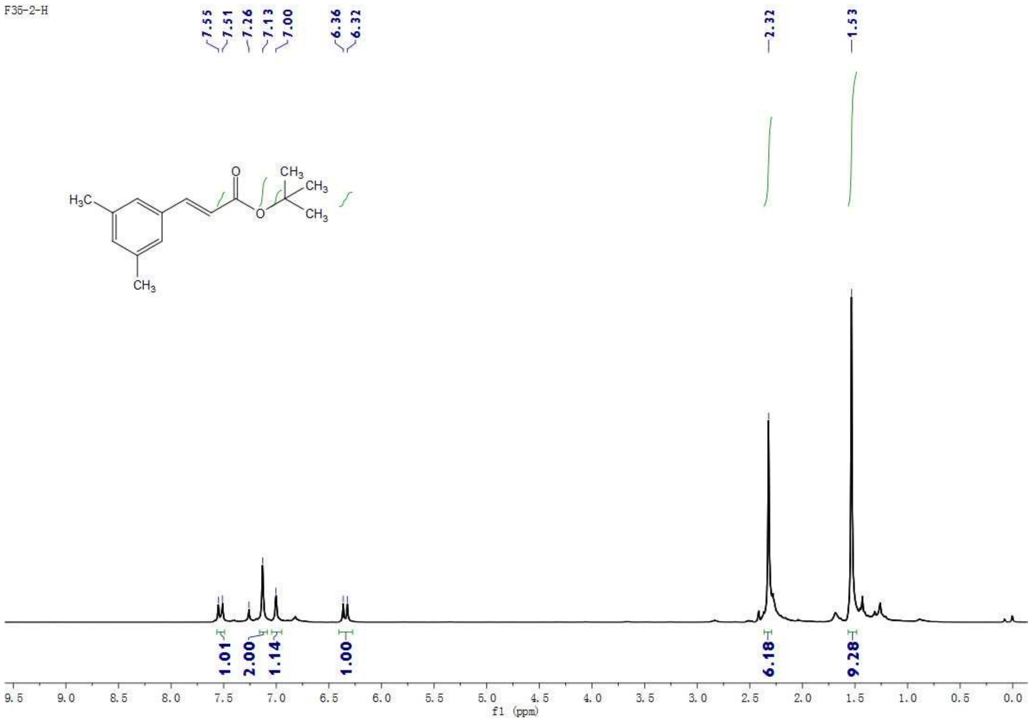
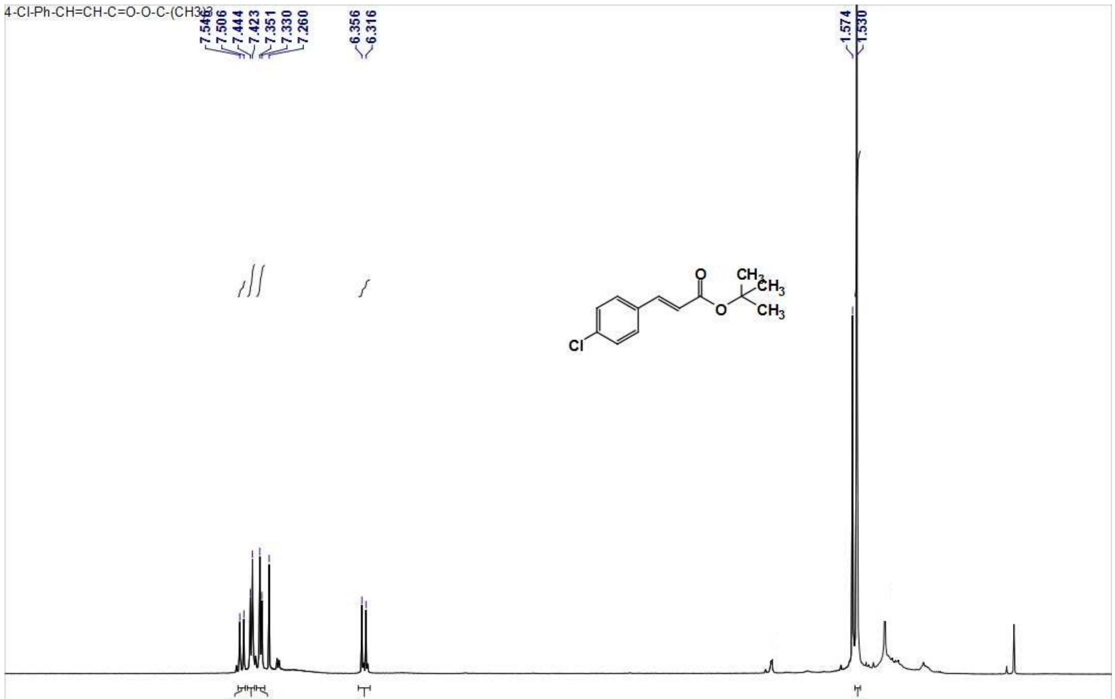
7.445
7.261
6.899
6.880
6.260
6.220
3.830
1.605
1.528
H3C
O
CH3
0.98
2.04
2.07
1.00
3.06
9.09
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


F35-2-H
7.55
7.51
7.26
7.13
7.00
6.36
6.32
2.32
1.53
H$_3$C
CH$_3$
O
O
CH$_3$
CH$_3$
CH$_3$
1.01
2.00
1.14
1.00
6.18
9.28
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


4-Cl-Ph-CH=CH-C=O-O-C-(CH3)3
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7.506
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7.351
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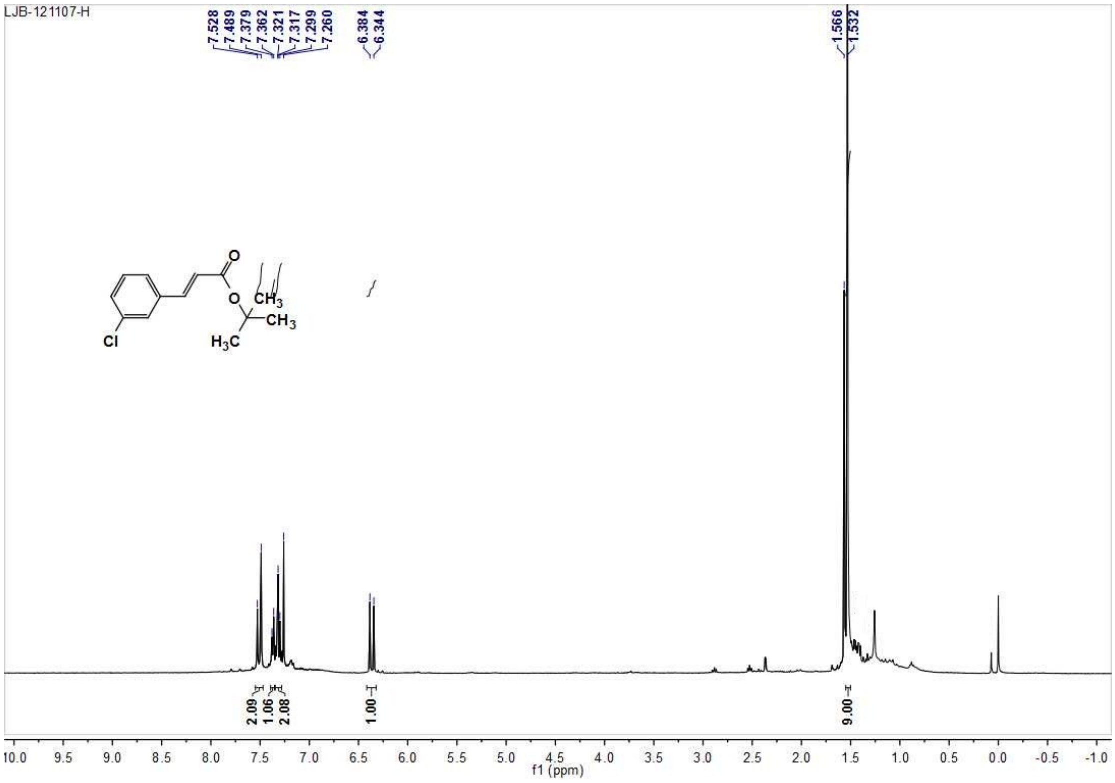
6.356
6.316
1.574
1.530
O
CH$_3$
CH$_3$
CH$_3$
O
Cl
1.00
2.03
1.98
1.06
9.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


LJB-121107-H
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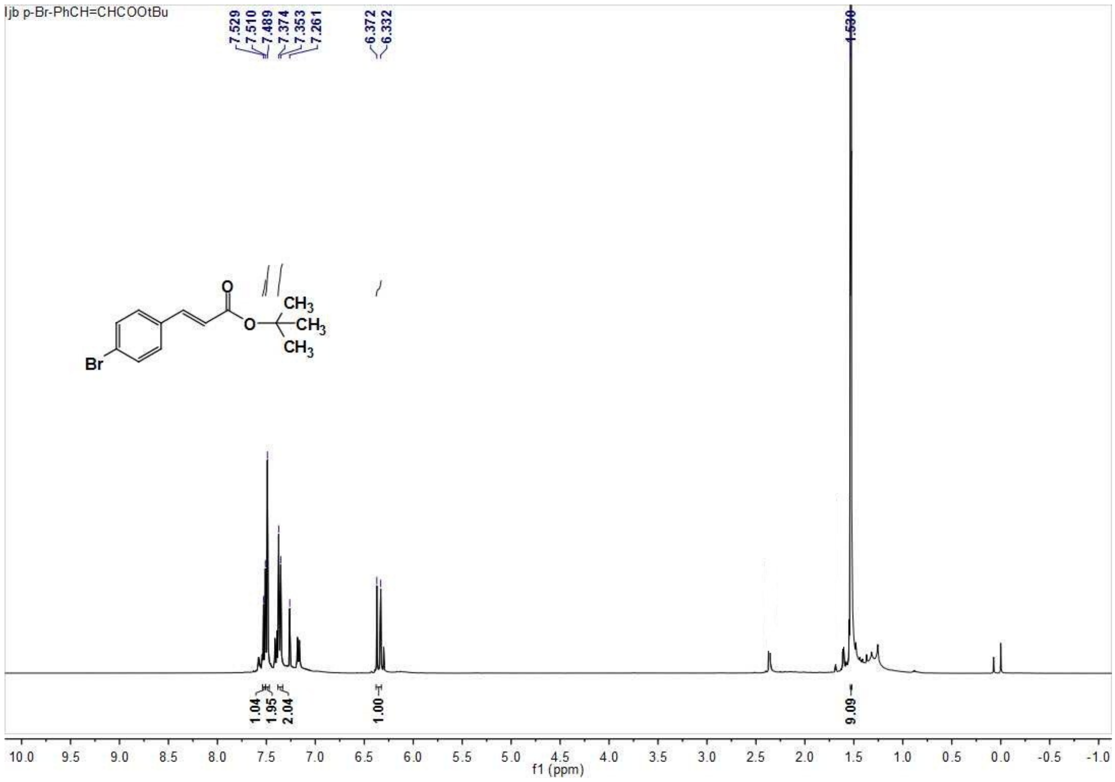
7.489
7.379
7.362
7.321
7.317
7.299
7.260
6.384
6.344
1.566
1.532
O
O
CH3
CH3
H3C
Cl
2.09
1.06
2.08
1.00
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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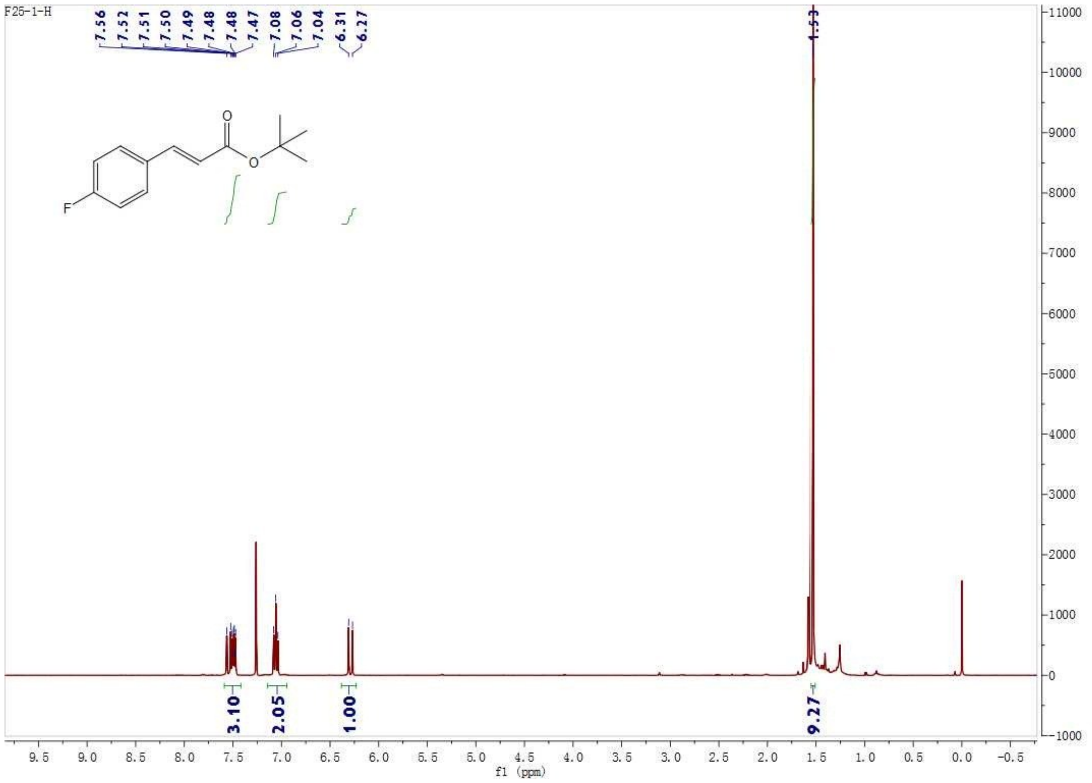
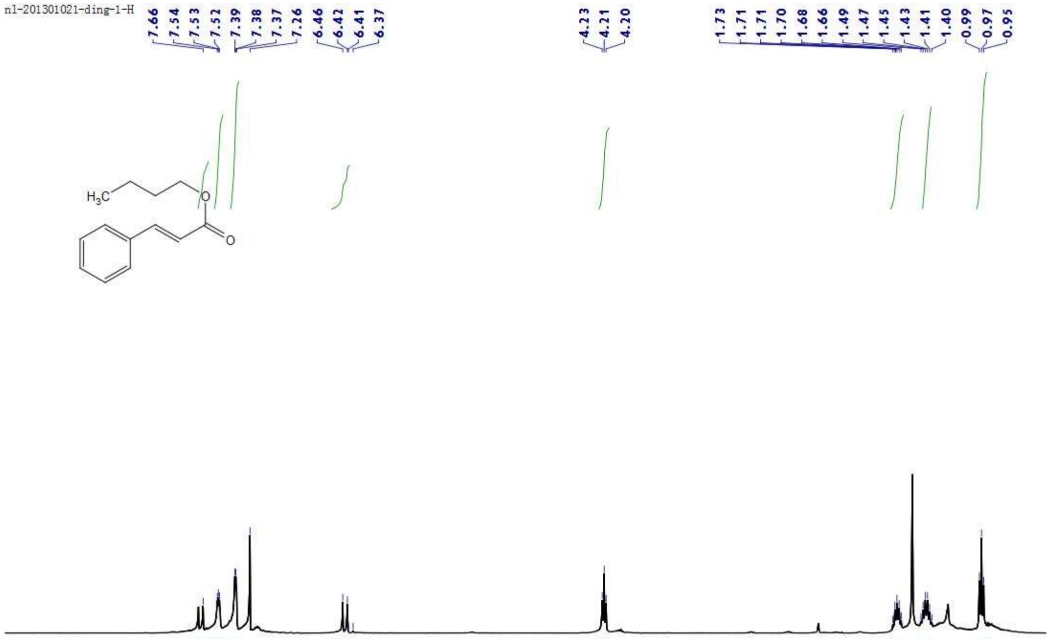
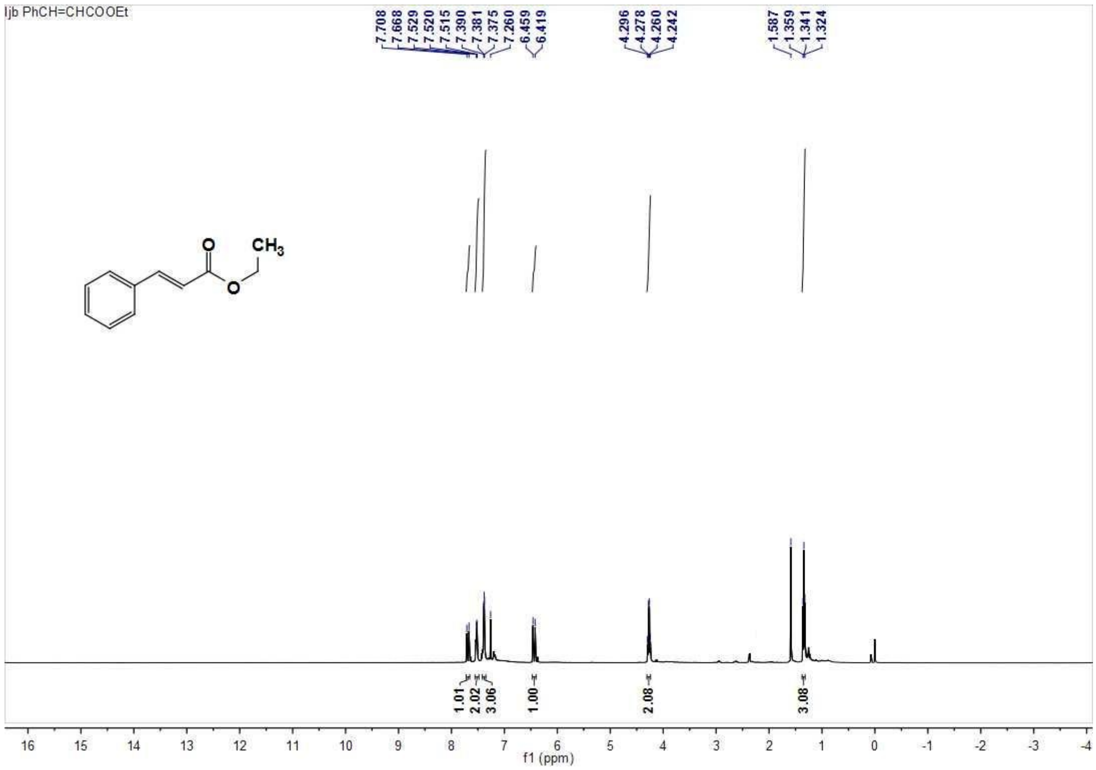
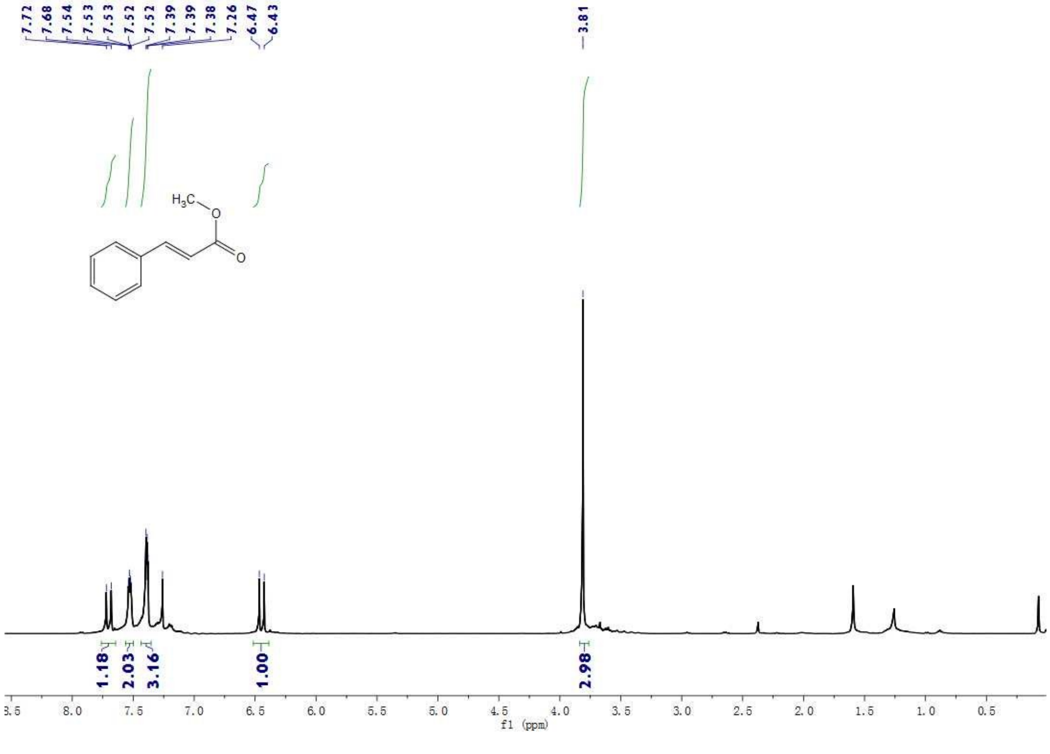
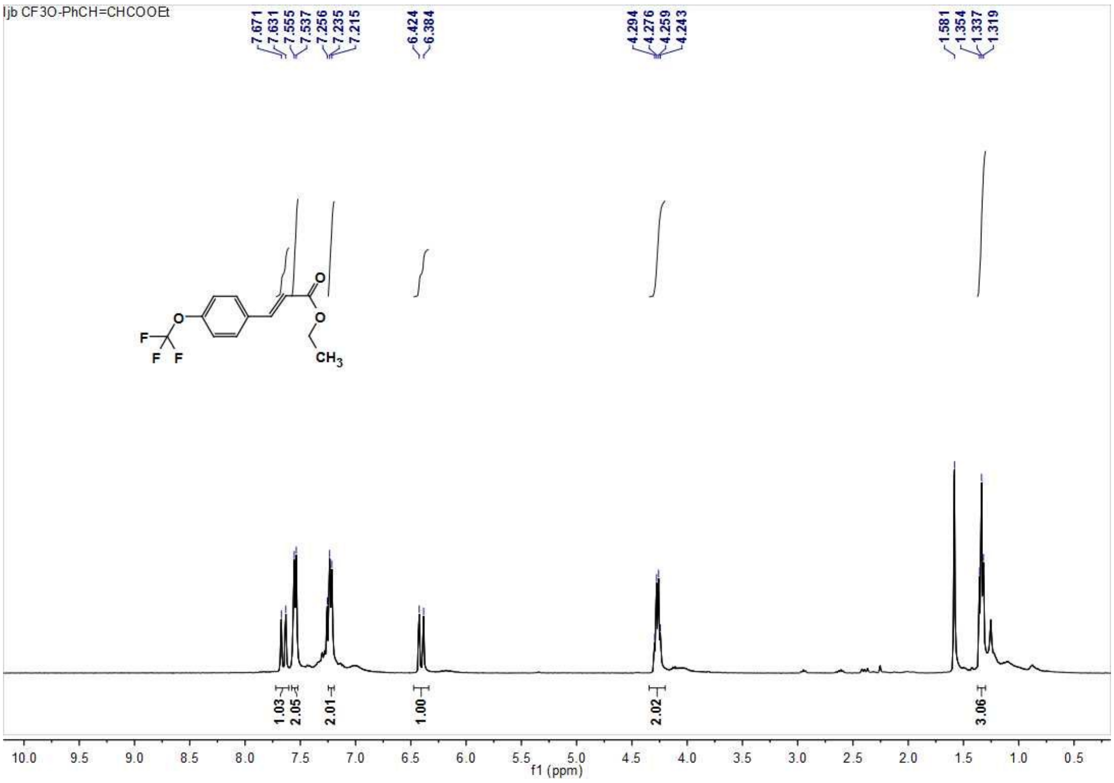
O
O
CH3
CH3
CH3
Br
1.04
1.95
2.04
1.00
9.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

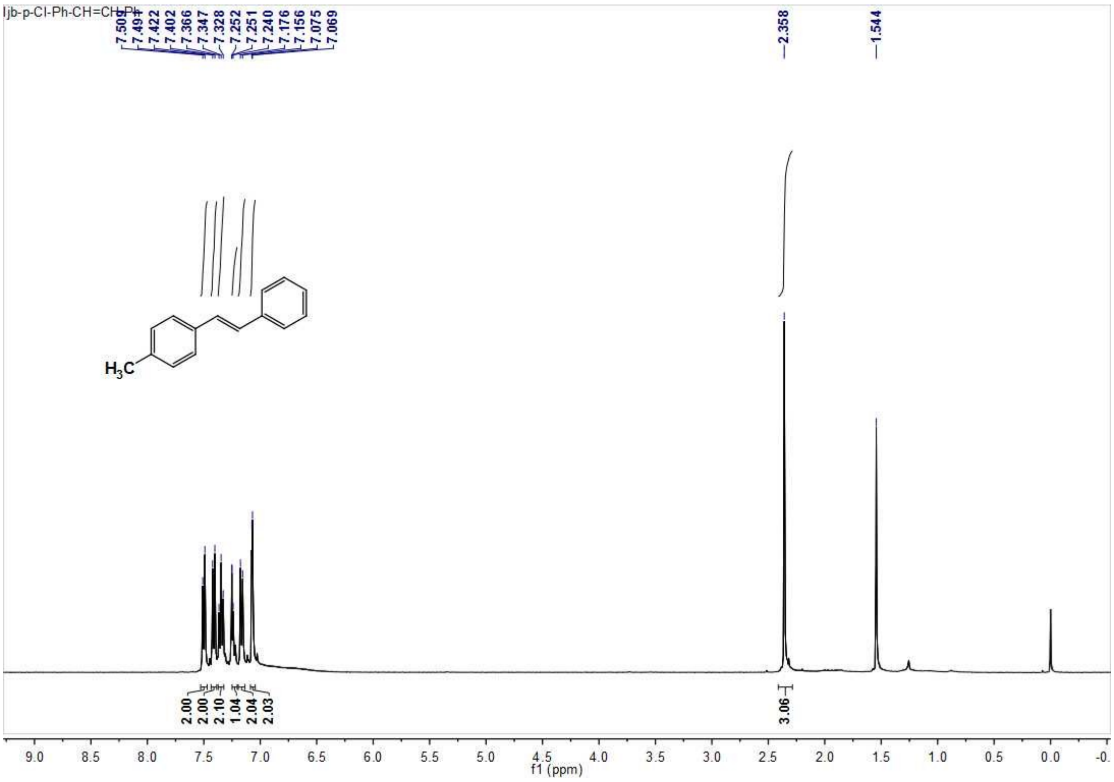

F25-1-H
7.56
7.52
7.51
7.50
7.49
7.48
7.48
7.47
7.08
7.06
7.04
6.31
6.27
1.53
O
O
F
3.10
2.05
1.00
9.27
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


n1-201301021-ding-1-H
7.66
7.54
7.53
7.52
7.39
7.38
7.37
7.26
6.46
6.42
6.41
6.37
4.23
4.21
4.20
1.73
1.71
1.71
1.70
1.68
1.66
1.49
1.47
1.45
1.43
1.41
1.40
0.99
0.97
0.95
H3C
O
O
1.10
2.17
2.94
1.00
1.87
2.17
2.36
3.16
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


ljb PhCH=CHCOOEt
7.708
7.668
7.529
7.520
7.515
7.390
7.381
7.375
7.260
6.459
6.419
4.296
4.278
4.260
4.242
1.587
1.359
1.341
1.324
CH3
O
O
1.01
2.02
3.06
1.00
2.08
3.08
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


7.72
7.68
7.54
7.53
7.53
7.52
7.52
7.39
7.39
7.38
7.26
6.47
6.43
3.81
H3C
O
O
1.18
2.03
3.16
1.00
2.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


ljb CF3O-PhCH=CHCOOEt
7.671
7.631
7.555
7.537
7.256
7.235
7.215
6.424
6.384
4.294
4.276
4.259
4.243
1.581
1.354
1.337
1.319
F
F
F
O
O
O
CH3
1.03
2.05
2.01
1.00
2.02
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


ljb-p-Cl-Ph-CH=CH-Ph
7.509
7.491
7.422
7.402
7.366
7.347
7.328
7.252
7.251
7.240
7.176
7.156
7.075
7.069
2.358
1.544
H3C
2.00
2.00
2.10
1.04
2.04
2.03
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)