Supporting Information

The D-glucosamine-derived pyridyl-triazole@palladium recoverable catalyst for Mizoroki-Heck reactions under solvent-free conditions

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1. General Information

a. Materials

All reagents were commercially available and used without purification, unless otherwise noted. Aryl halides and sulfinic acid salts were purchased from Alfa Aesar. Other chemicals were obtained commercially and used without any prior purification. ^{1}H NMR spectra were recorded on a Bruker AvanceII 400 spectrometer using TMS as the internal standard. All products were isolated by short chromatography on a silica gel (200–300 mesh) column using petroleum ether (60-90 °C), unless otherwise noted. The pivaloylated sugar substrates were prepared according to our previous reports.[1] All compounds were characterized by ^{1}H NMR, ^{13}C NMR and mass spectroscopy, which are consistent with those reported in the literature.[2-5]

b. Methods

Melting points were determined on an X-5 Data microscopic melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400 spectrometer at ambient temperature with $CDCl_3$ or DMSO-d_6 as solvent unless otherwise noted and tetramethylsilane (TMS) as the internal standard. Mass spectra (GC-MS) were acquired on an Agilent 5975 spectrometer. IR spectra were recorded on a Nicolet 380 FT-IR spectrophotometer using KBr discs. Scanning electron microscope (SEM) images were collected on FEI XL40 instrument. Transmission electron microscopy (TEM) images were taken on FEI T20 microscope. The small-angle X-ray diffraction (SAXRD) data were taken on a German Bruker D4 X-ray diffractometer with Niltered Cu Ka radiation (40 kV, 40 mA). Thermogravimetric analyses were performed with a SII Nano Technology EXTAR TG/DTA7220 thermal analyzer at 10 °C/min in nitrogen atmosphere (10 ml/min). 5 mg of each sample in an alumina pan was analyzed in the 40-900 °C temperature range. Analytical thin layer chromatography (TLC) was performed on Merk precoated TLC (silica gel 60 F254) plates.

2. Experimental Section

General procedure for the Mizoroki-Heck reaction in the presence of the catalyst (5)

To a flask, a mixture of D-glucosamine-derived triazole@palladium catalyst **5** (0.05 g of the catalyst, 0.1 mol%), aryl halide (1 mmol), olefin (2 mmol) and Et_3N (3 mmol) were added and heated at 80 ^{o}C under solvent-free conditions. After completion of the reaction, ethylacetate (10 mL) was added to the flask. The catalyst was separated by simple filtration. Water (3×15 mL) was added to the ethylacetate phase and decanted. The organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the resulted crude products was purified by column chromatography (hexane/ethylacetate) giving the pure products in excellent yields.

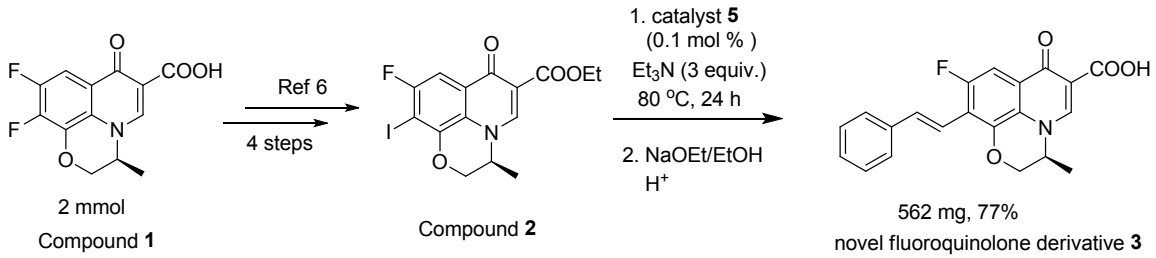
Recycling of the catalyst in Mizoroki-Heck reaction

After completion of the reaction at the first run, the reaction mixture was cooled down to room temperature and ethylacetate (5 mL) was added to the reaction mixture to extract organics. The ethylacetate phase was sucked from the vial by a syringe and the catalyst was dried under vacuum. After complete drying, the catalyst was reused for the similar reaction. This process was repeated for five runs.

General procedure for synthesis of Axitini under solvent-free condition.

To a flask, a mixture of intermediate **11** (1 mmol), 2-vinylpyridine **7e** (2 mmol), Et_3N (3 mmol) and D-glucosaminederived triazole@palladium catalyst **5** (0.1 mol%) were added and heated at 100 ^oC under solvent-free conditions. The reaction progress was monitored by TLC. After completion of the reaction, the mixture was allowed to cool to room temperature, ethylacetate (10 mL) was added to the flask. The catalyst was separated by simple filtration and the aqueous phase was extracted with CH_2Cl_2 for 3 times (3×2 mL). Then the combined organic layers were dried over anhydrous Na_2SO_4, concentrated under vacuum and purified by column chromatography (hexane/ethyl acetate 10:1) to afford the desired product. Residual Pd content in solvent was determined to be not more than 20 ppm by atomic absorption spectroscopy.

General procedure for synthesis of novel fluoroquinolone derivative under solvent-free condition.



Scheme S1

To a flask, a mixture of compound **2** (2 mmol) (which was prepared from commercially available compound **1** by 4 steps[6]), styrene (4 mmol), Et_3N (6 mmol) and D-glucosamine

derived triazole@palladium catalyst **5** (0.2 mol%) were added and heated at 100 ^{o}C under solvent-free conditions. The reaction progress was monitored by TLC. After completion of the reaction, the mixture was allowed to cool to room temperature and the catalyst was separated by simple filtration. Then 10 mL NaOEt/EtOH solution was added and the mixture was stirred for 3 h. Upon completion, 1 M HCl was added until the solution was at neutral pH, and was filtered. The solution was concentrated in vacuo and purified by flash chromatography 7:1 ethyl acetate/MeOH to give the novel fluoroquinolone derivative **3** (562 mg, 77%)

3. Characterization of the Catalysts and Prouducts

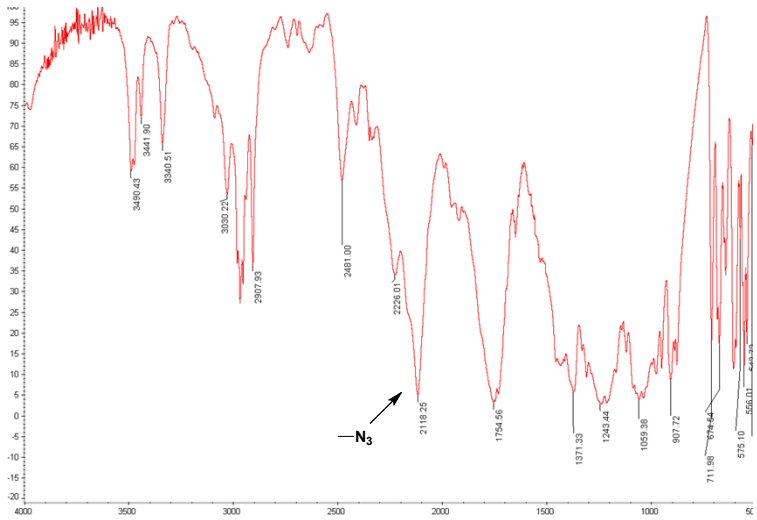


Figure S1. FT-IR spectrum of D-glucosamine-based azide (**3**).

Figure S2. FT-IR spectrum of D-glucosamine-derived triazole(**4**) .

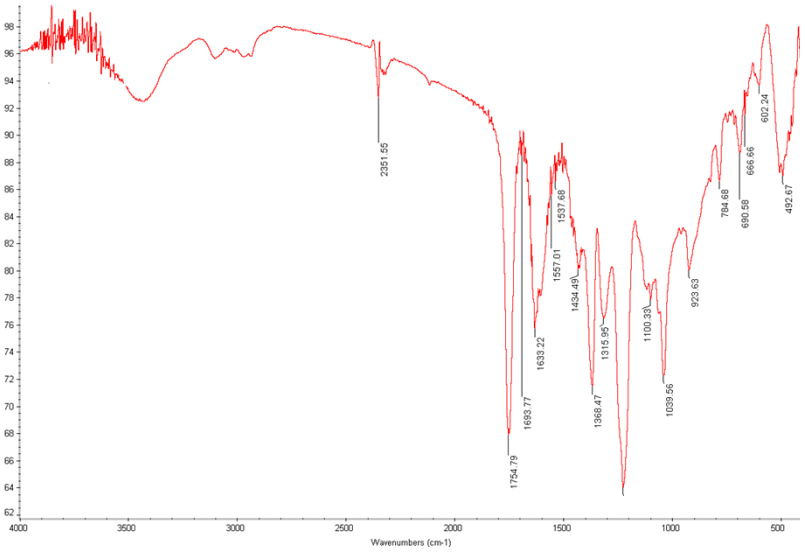


Figure S3. FT-IR spectrum of catalyst(**5**) .

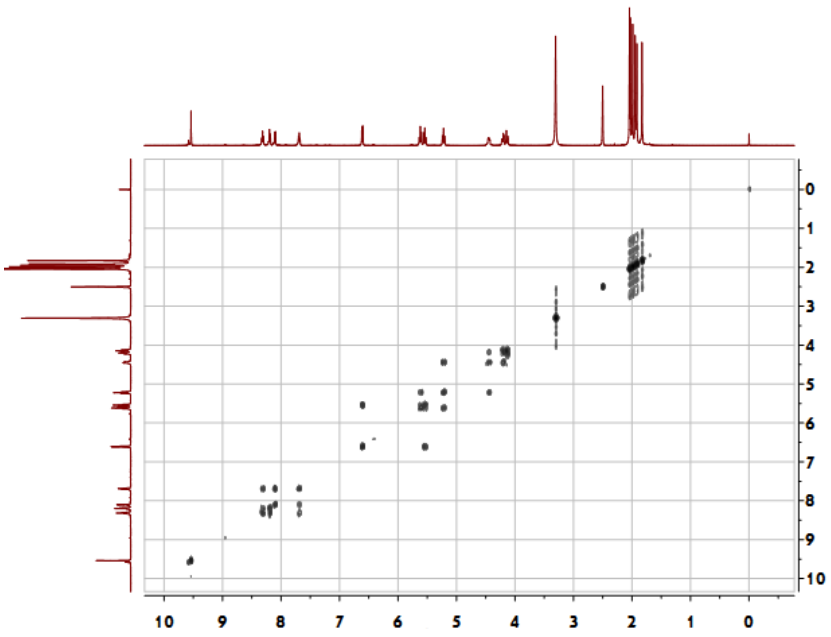
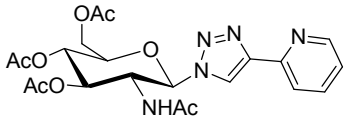


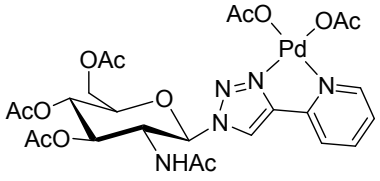
Figure S4. 2D ROESY NMR spectrum of Pd catalyst **5**.

D-glucosamine-derived triazole(**4**):



Obtained as a white solid in 92% yield; M.p. 214-215 °C. ^{1}H NMR (500 MHz, $CDCl_3$)：δ 9.54 (s, 1H),8.32 (t, J = 6.0 Hz, 1H), 8.20 (t, J = 6.0 Hz, 1H), 8.11 (d, J = 4.0 Hz, 1H), 7.69 (t, J = 5.2 Hz, 1H), 6.62 (d, J = 7.2 Hz, 1H, G_1H), 5.63 (t, J = 7.2 Hz, 1H, G_2H), 5.55 (t, J = 7.2 Hz, 1H, G_4H),5.23 (t, J = 7.6 Hz, 1H, G_3H), 4.46-4.44 (m, 1H, G_5H), 4.23-4.13 (m, 2H, G_6H), 2.05-1.84 (m, 19H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.0, 169.8. 150.2,137.7, 122.7, 84.6, 73.8, 72.5, 70.7, 68.1, 20.9, 20.8, 20.7, 20.4. Anal. calcd. for $C_{21}H_{25}N_5O_8$: C, 53.05; H, 5.30; N, 14.73; found: C, 53.12; H, 5.38; N, 14.77.

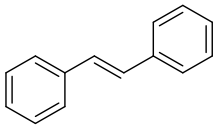
D-glucosamine-derived triazoles@ Pd catalyst **5**



Obtained as a white solid in 90% yield; M.p. 289-291 °C. ^{1}H NMR (500 MHz, $CDCl_3$)：δ 9.54 (s, 1H),8.32 (t, J = 6.0 Hz, 1H), 8.20 (t, J = 6.0 Hz, 1H), 8.11 (d, J = 4.0 Hz, 1H), 7.69 (t, J = 5.2 Hz, 1H), 6.62 (d, J = 7.2 Hz, 1H, G_1H), 5.63 (t, J = 7.2 Hz, 1H, G_2H), 5.55 (t, J = 7.2 Hz, 1H, G_4H),5.23 (t, J = 7.6 Hz, 1H, G_3H), 4.46-4.44 (m, 1H, G_5H), 4.23-4.13 (m, 2H, G_6H), 2.05-1.84 (m, 19H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.0, 169.8. 150.2,137.7, 122.7, 84.6, 73.8,72.5, 70.7, 68.1, 20.9,

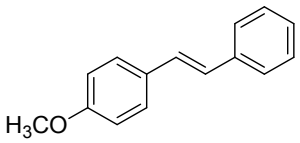
20.8, 20.7, 20.4. Anal. calcd. for $C_{25}H_{31}N_5O_{12}Pd$: C, 42.90; H, 4.46; N, 10.01; found: C, 42.93; H, 4.42; N, 10.05.

(*E*)-1,2-diphenylethene 8a[2]:



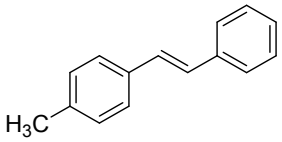
^{1}H NMR (500 MHz, $CDCl_3$)：δ 7.58 (d, *J* = 7.5 Hz, 4H), 7.43 (dd, *J* = 9.8, 5.5 Hz, 4H), 7.36 – 7.29 (m, 2H), 7.18 (d, *J* = 1.3 Hz, 2H).GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{12}$: 180.0, found: 180.

(*E*)-1-methoxyl-4-styrylbenzene 8b[3]:



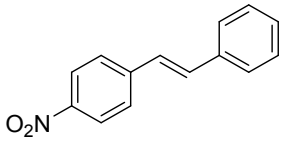
^{1}H NMR (500 MHz, $CDCl_3$)：δ 7.50 – 7.40 (m, 4H), 7.33 (dd, *J* = 10.6, 4.7 Hz, 2H), 7.21 (t, *J* = 3.7 Hz, 1H), 7.05 (d, *J* = 16.3 Hz, 1H), 6.96 (d, *J* = 16.3 Hz, 1H), 6.90 – 6.85 (m, 2H), 3.80 (s, 3H). GC-MS (EI) [M]+: m/z calcd. for $C_{15}H_{14}O$: 210.0, found: 210.

(*E*)-1-methyl-4-styrylbenzene 8c[2]:



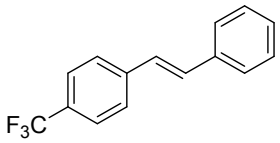
^{1}H NMR (500 MHz, $CDCl_3$)：δ 7.60 – 7.54 (m, 2H), 7.51 – 7.45 (m, 2H), 7.45 – 7.38 (m, 2H), 7.32 (dd, *J* = 8.3, 5.4 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.17 – 7.11 (m, 2H), 2.49 – 2.37 (m, 3H).GC-MS (EI) [M]+: m/z calcd. for $C_{15}H_{14}$: 194.0, found: 194.

(*E*)-1-nitro-4-styrylbenzene 8d[2]:



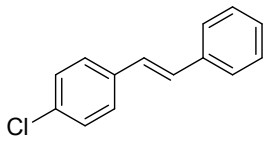
^{1}H NMR (500 MHz, $CDCl_3$)：δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.65 (d, J = 8.7 Hz, 2H), 7.58 (d, *J* = 7.3 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.39 – 7.34 (m, 1H), 7.29 (t, *J* = 4.4 Hz, 1H), 7.17 (d, *J* = 16.3 Hz, 1H). GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{11}NO_2$: 225.0, found: 225.

(*E*)-1-styryl-4-(trifluoromethyl)benzene 8e[3]:



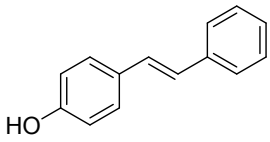
^{1}H NMR (500 MHz, $CDCl_3$)：δ 7.65 (q, *J* = 8.6 Hz, 4H), 7.58 (d, *J* = 7.3 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.37 (dd, *J* = 8.2, 6.5 Hz, 1H), 7.24 (d, *J* = 16.3 Hz, 1H), 7.16 (d, *J* = 16.3 Hz, 1H). GC-MS (EI) [M]+: m/z calcd. for $C_{15}H_{11}F_3$: 248.0, found: 248.

(*E*)-1-chloro-4-styrylbenzene 8f[4]:



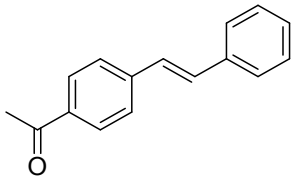
^{1}H NMR (500 MHz, $CDCl_3$)：δ 7.55 (d, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 9.4 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.15 – 7.06 (m, 2H).GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{11}Cl$: 214.0, found: 214.

(*E*)-4-styrylphenol 8g[2]:



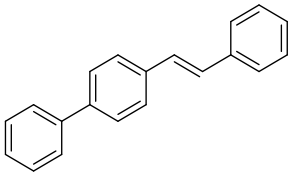
^{1}H NMR (500 MHz, DMSO)：δ 9.55 (d, *J* = 12.0 Hz, 1H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.46 – 7.38 (m, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.26 – 7.18 (m, 1H), 7.18 – 7.09 (m, 1H), 7.02 (d, *J* = 16.4 Hz, 1H), 6.83 – 6.72 (m, 2H). GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{12}O$: 196.0, found: 196.

(*E*)-4-acetyl-4-styrylbenzene 8h[3]:



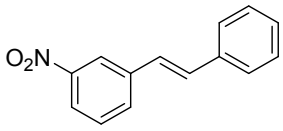
^{1}H NMR (500 MHz, $CDCl_3$)：δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 16.3 Hz, 1H), 7.15 (d, *J* = 16.3 Hz, 1H), 2.62 (s, 3H). GC-MS (EI) [M]+: m/z calcd. for $C_{16}H_{14}O$: 222.0, found: 222.

(*E*)-4-phenyl-4-styrylbenzene 8i[4]:



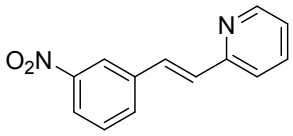
^{1}H NMR (500 MHz, $CDCl_3$)：δ 7.67 – 7.62 (m, 3H), 7.58 – 7.55 (m, 1H), 7.48 (dd, *J* = 10.5, 4.9 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.18 (s, 1H). GC-MS (EI) [M]+: m/z calcd. for $C_{20}H_{16}$: 256.0, found: 256.

(*E*)-1-nitro-3-styrylbenzene 8j[2]:



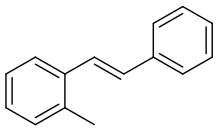
^{1}H NMR (500 MHz, $CDCl_3$)：δ 8.39 (s, 1H), 8.12 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.56 (dd, *J* = 15.7, 7.7 Hz, 3H), 7.47 – 7.39 (m, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.29 (s, 1H), 7.16 (d, *J* = 16.3 Hz, 1H). GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{11}NO_2$: 225.0, found: 225.

(*E*)-1-nitro-3-styrylpyridine 8k:



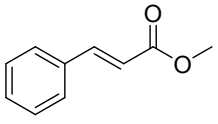
^{1}H NMR (500 MHz, $CDCl_3$)：δ 8.66 (d, *J* = 4.2 Hz, 1H), 8.46 (s, 1H), 8.16 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.74 (dd, *J* = 8.8, 7.1 Hz, 2H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 3.6 Hz, 1H), 7.24 (dd, *J* = 6.7, 4.9 Hz, 1H). GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_{10}N_2O_2$: 226.0, found: 226.

(*E*)-1-methyl-2-styrylbenzene 8l2:



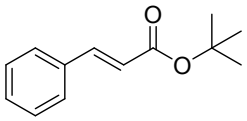
^{1}H NMR (500 MHz, $CDCl_3$)：δ 7.65 (d, *J* = 7.3 Hz, 1H), 7.58 (d, *J* = 7.3 Hz, 2H), 7.44 – 7.37 (m, 3H), 7.34 – 7.30 (m, 1H), 7.29 – 7.26 (m, 1H), 7.24 (t, *J* = 3.7 Hz, 2H), 7.06 (d, *J* = 16.2 Hz, 1H), 2.49 (s, 3H).GC-MS (EI) [M]+: m/z calcd. for $C_{15}H_{14}$: 194.0, found: 194.

Methyl cinnamate 8m[4]:



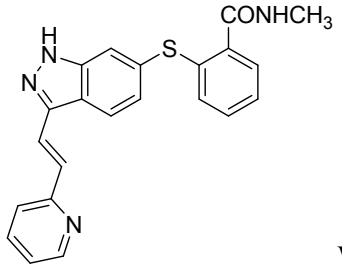
^{1}H NMR (500 MHz, $CDCl_3$)：δ 7.72 (d, *J* = 16.0 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.44 – 7.35 (m, 3H), 6.47 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H).GC-MS (EI) [M]+: m/z calcd. for $C_{10}H_{10}O_2$: 162.0, found: 162.

***tert*-butyl cinnamate 8n[4]:**



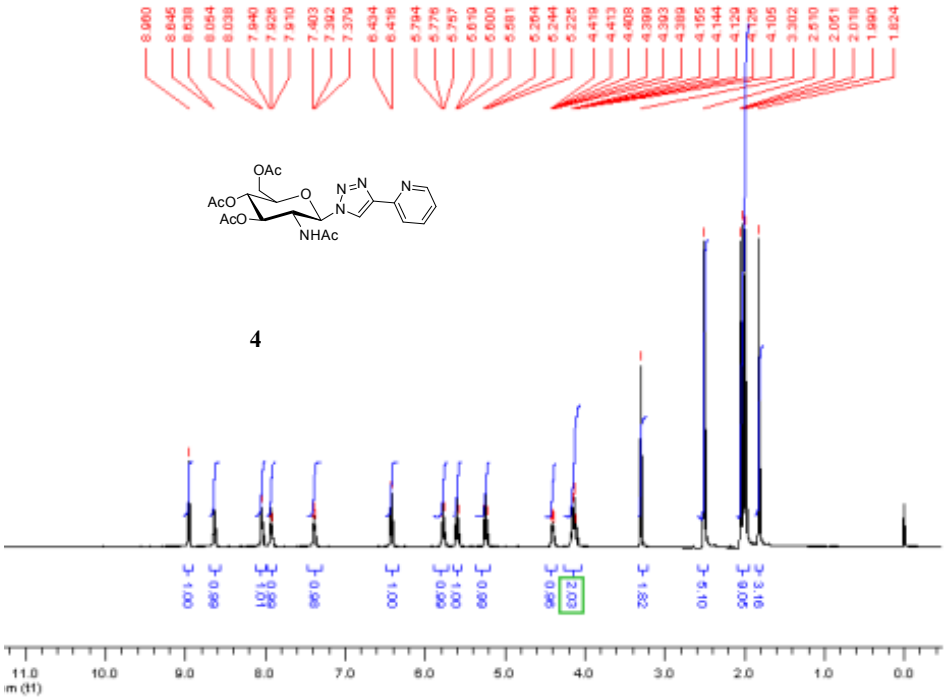
^{1}H NMR (500 MHz, $CDCl_3$)：δ 7.58 (d, *J* = 16.0 Hz, 1H), 7.51 – 7.48 (m, 2H), 7.37 – 7.33 (m, 3H), 6.36 (d, *J* = 16.0 Hz, 1H), 1.53 (s, 9H). GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_{16}O_2$: 204.0, found: 204.

Axitinib[5]



White solid, Mp 225-226 °C. ^{1}H NMR (500 MHz, DMSO -*d6*)：δ 13.34 (1H, s), 8.61 (d, *J* = 2.0 Hz, 1H), 8.37 (d, *J* = 3.5 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 16.5 Hz, 1H), 7.82-7.79 (m, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.61-7.57 (m, 2H), 7.32-7.28 (m, 3H), 7.20 (d, *J* = 9.0 Hz, 1H,), 7.07(d, *J* = 7.5 Hz, 1H), 2.78 (d, *J* = 3.5 Hz, 3H). ^{13}C NMR (75MHz, DMSO-*d6*)：δ 168.33, 155.38, 150.01, 142.49, 142.34, 137.61, 137.30, 135.98, 133.07, 130.73, 130.59, 129.76, 128.25, 126.66, 125.95, 124.11, 123.06, 122.93, 122.18, 120.76, 115.09, 26.54.

^{1}H NMR



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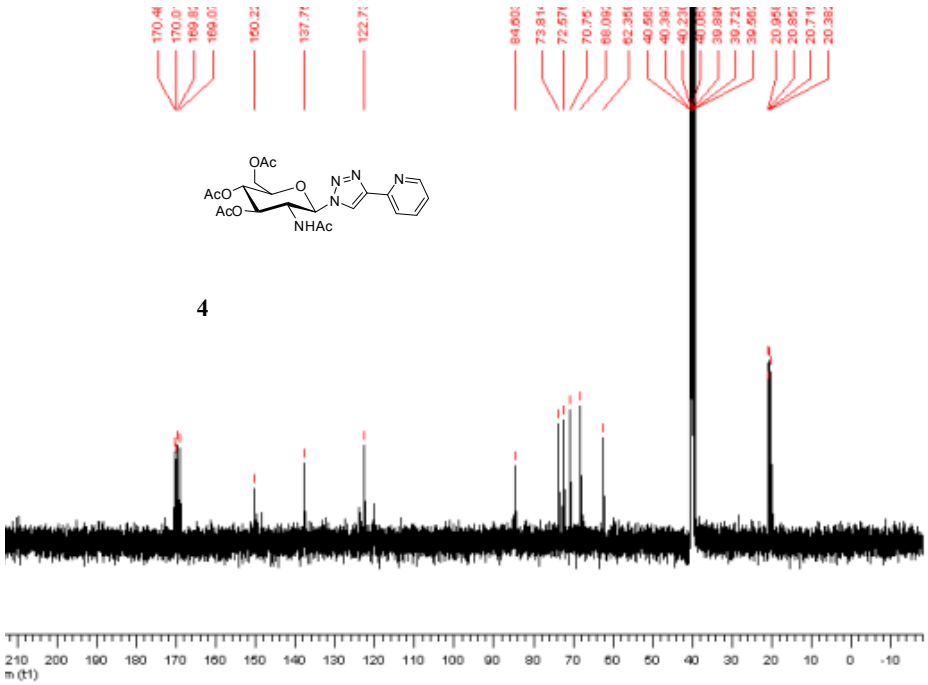
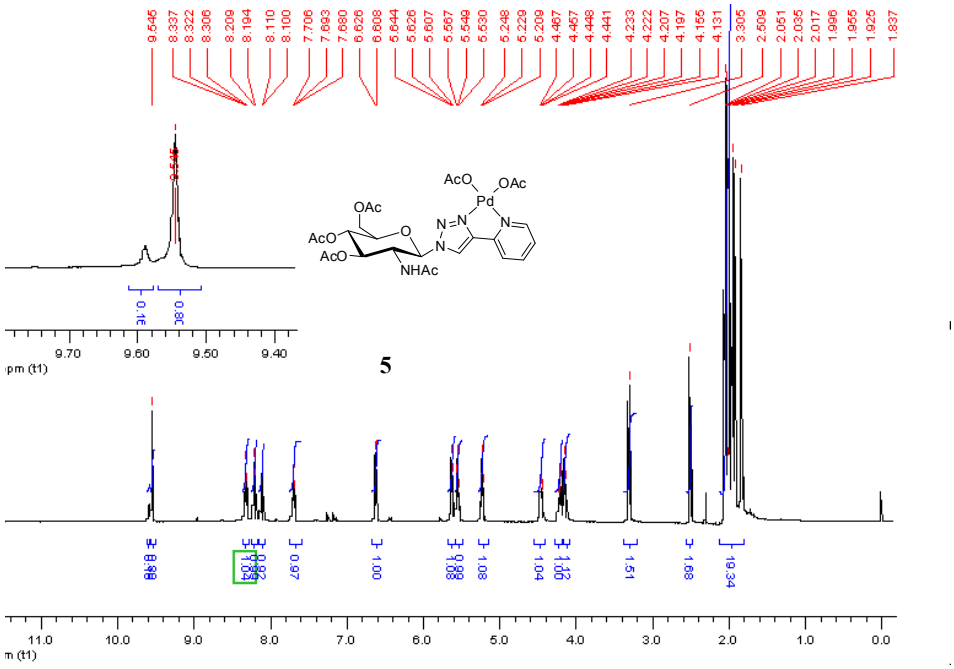
^{13}C NMR

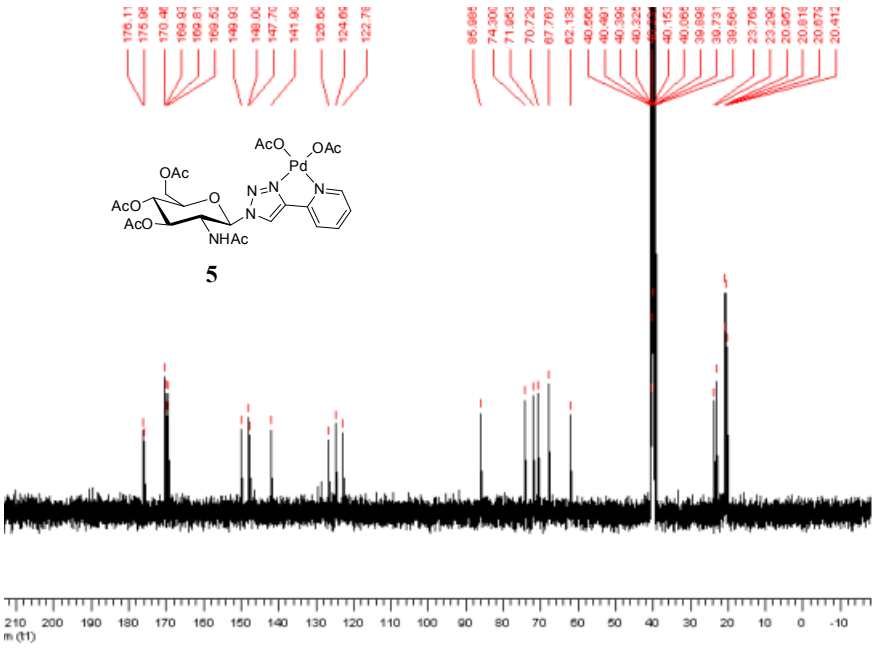


4

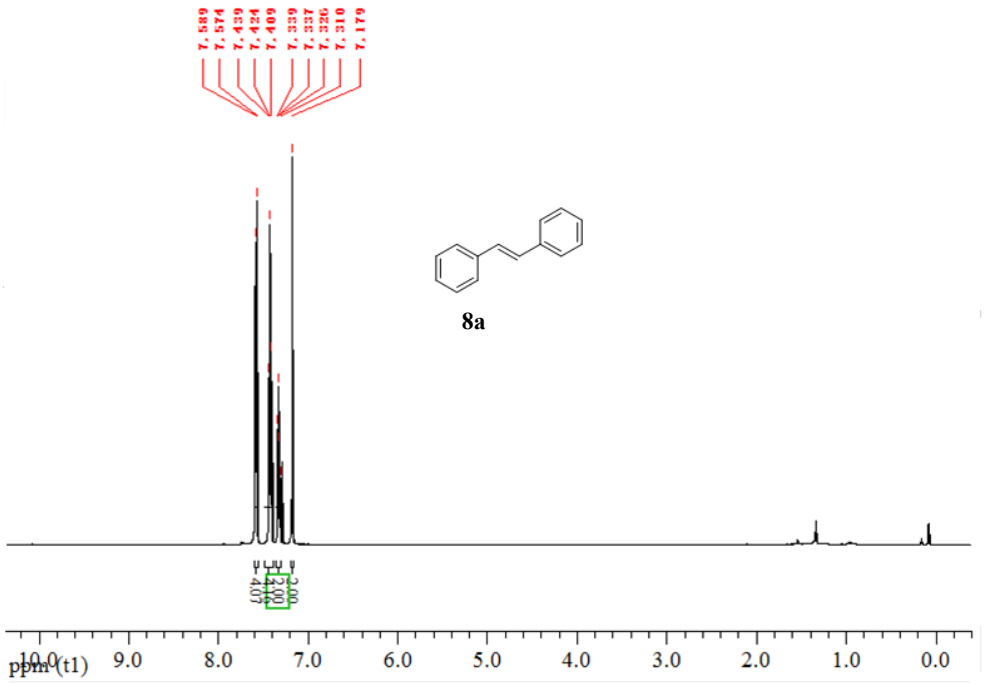
^{1}H NMR



^{13}C NMR

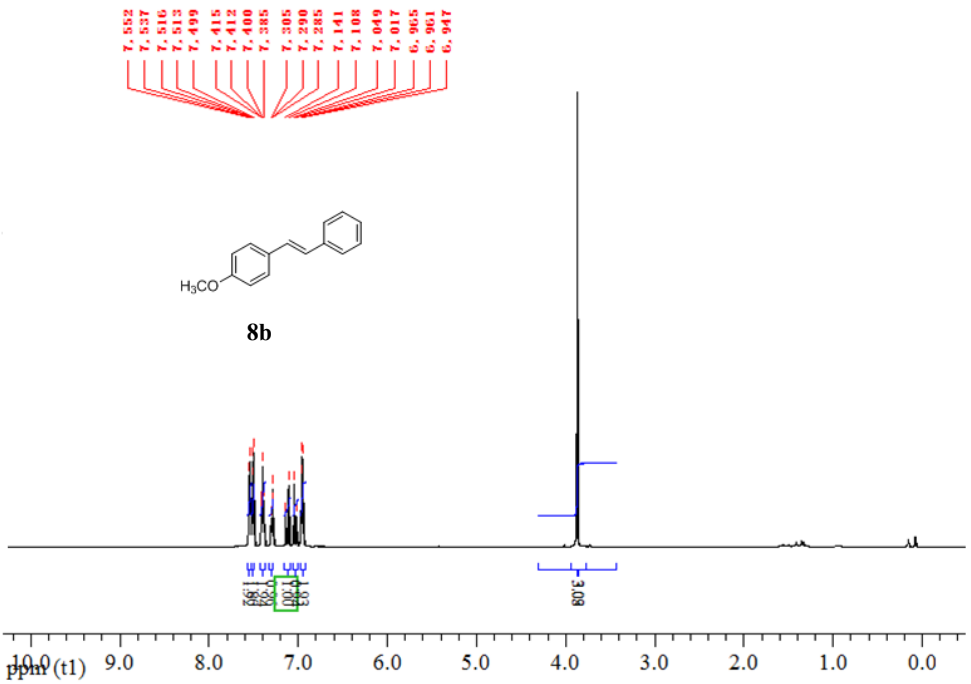


^{1}H NMR

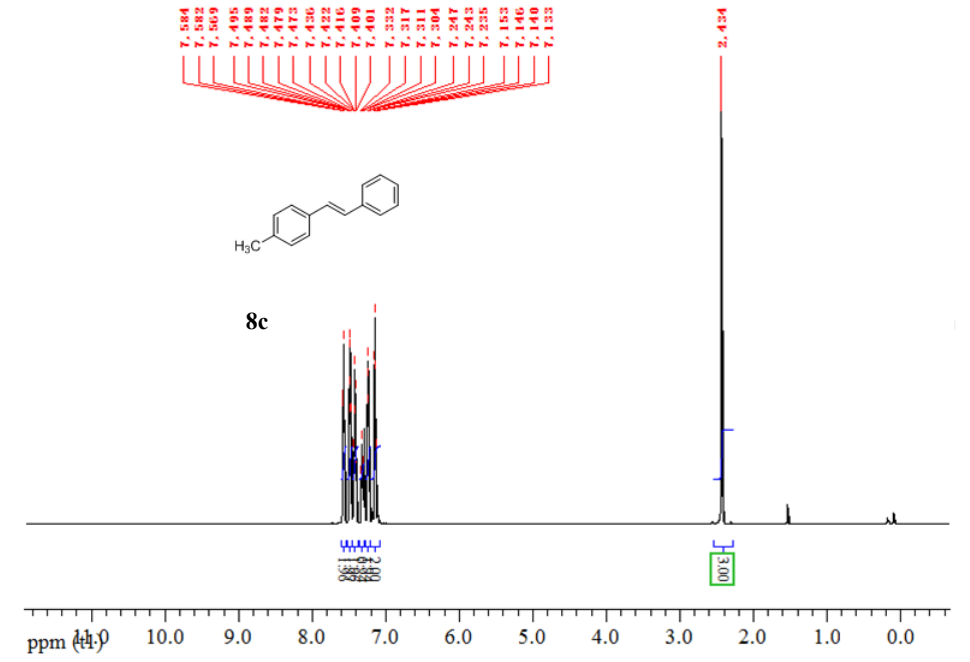


8a

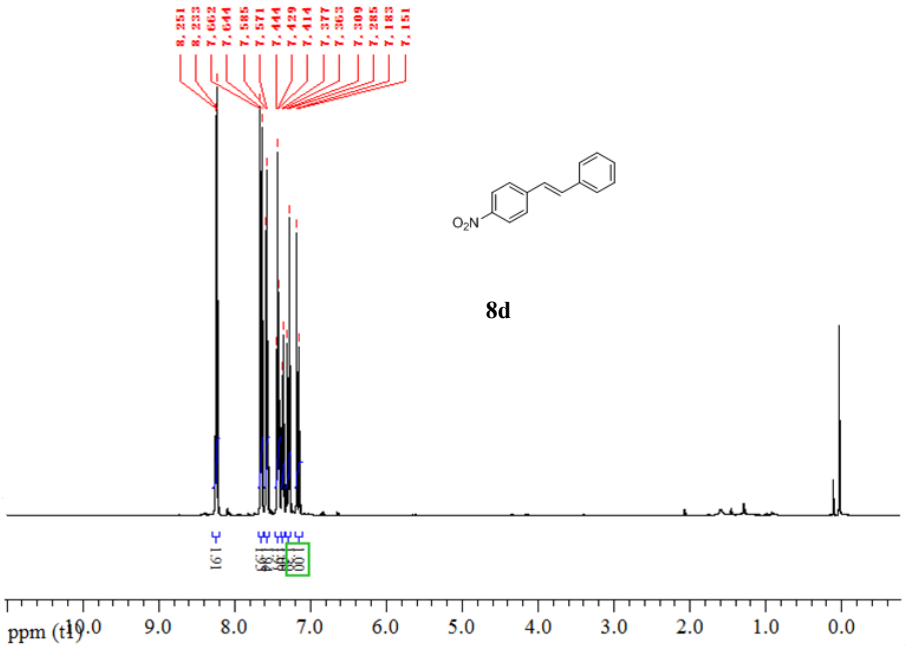
^{1}H NMR


7.552
7.537
7.516
7.513
7.499
7.415
7.412
7.400
7.385
7.305
7.290
7.285
7.141
7.108
7.049
7.017
6.965
6.961
6.947
H3CO
8b
3.09
ppm (t1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

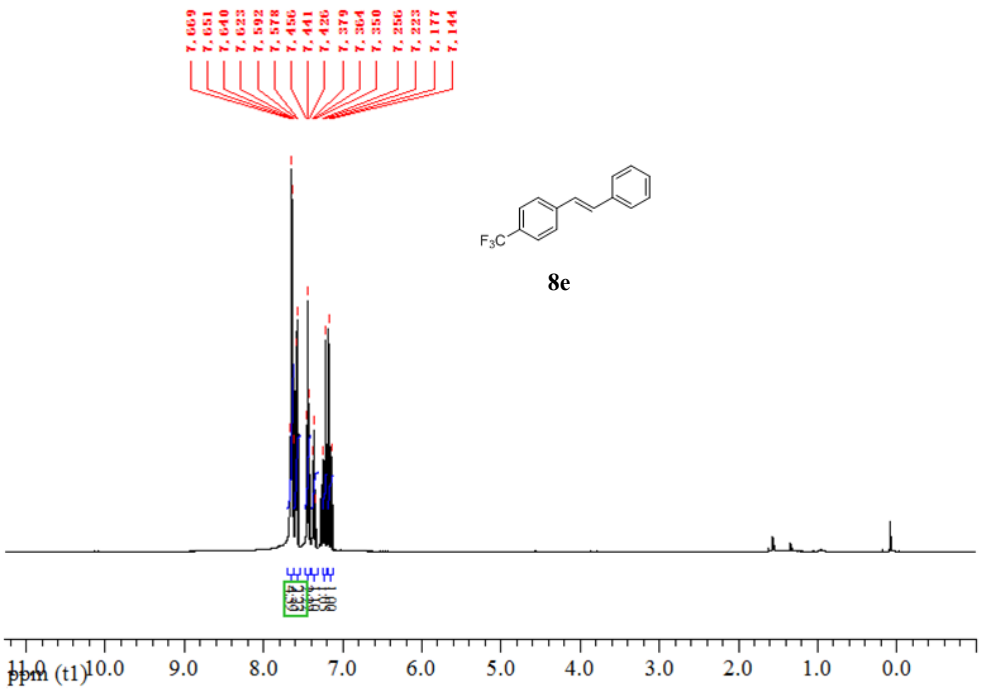
^{1}H NMR


7.584
7.582
7.569
7.495
7.489
7.482
7.479
7.473
7.436
7.422
7.416
7.409
7.401
7.332
7.317
7.311
7.304
7.247
7.243
7.235
7.153
7.146
7.140
7.133
2.434
H3C
8c
3.00
ppm (t1)
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

^{1}H NMR

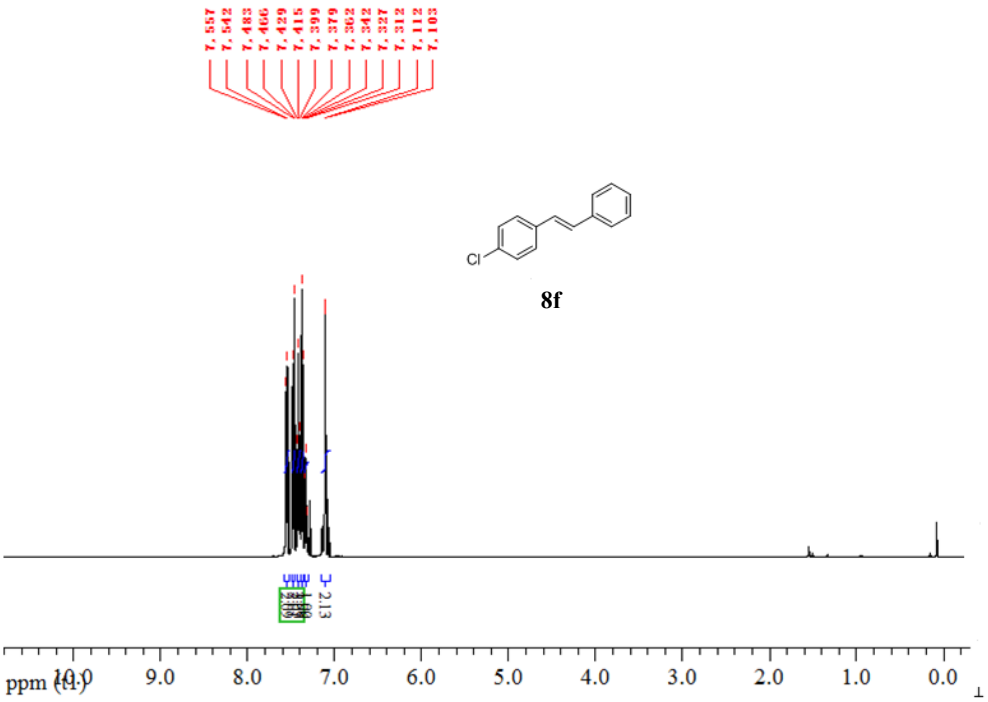

8.251
8.233
7.662
7.644
7.585
7.571
7.444
7.429
7.414
7.377
7.363
7.309
7.285
7.183
7.151
O2N
8d
ppm (t1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

^{1}H NMR


7.669
7.651
7.640
7.623
7.592
7.578
7.456
7.441
7.426
7.379
7.364
7.350
7.256
7.223
7.177
7.144
F3C
ppm (t1)

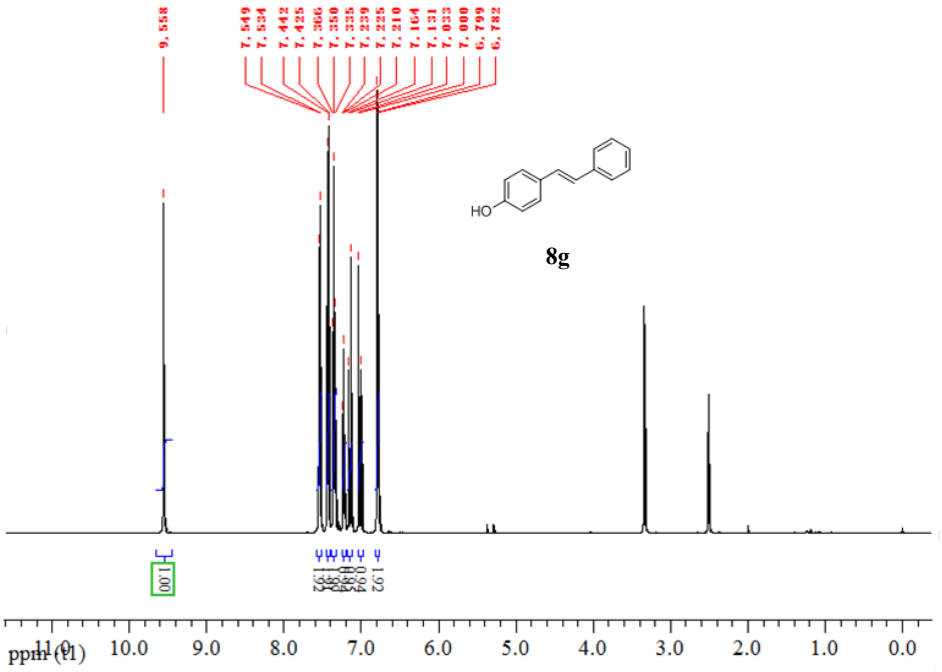
8e

^{1}H NMR

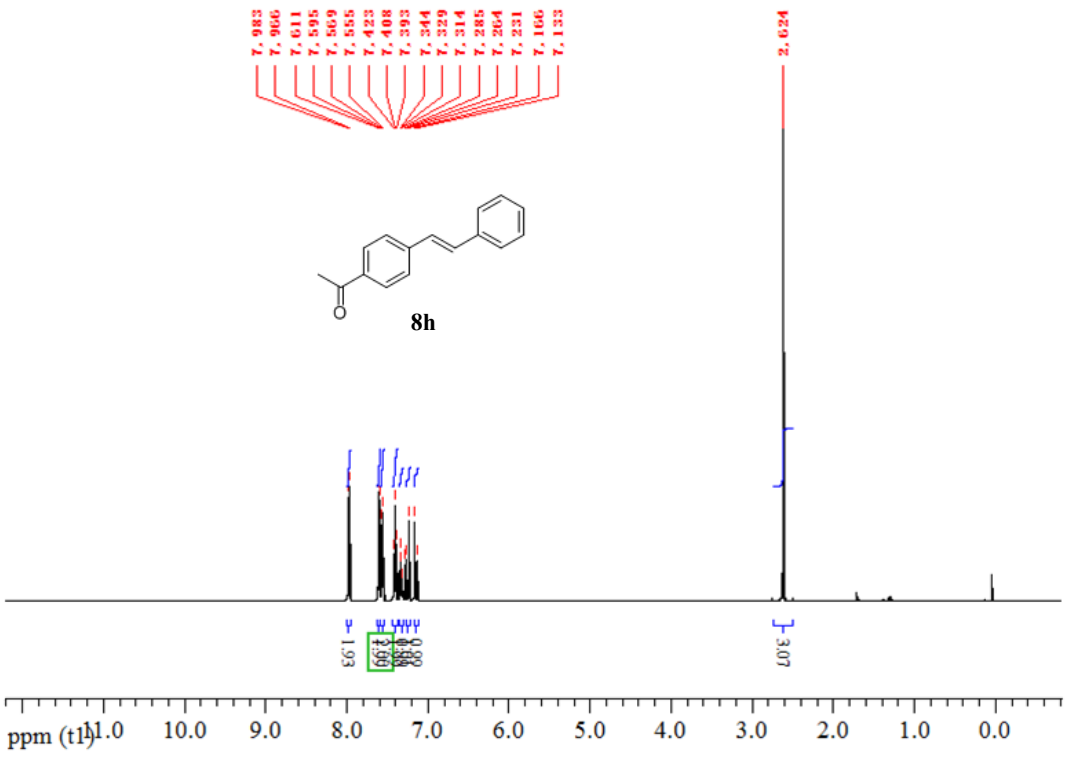

7.557
7.542
7.483
7.466
7.429
7.415
7.399
7.379
7.362
7.342
7.327
7.312
7.112
7.103
Cl
ppm (t1)

8f

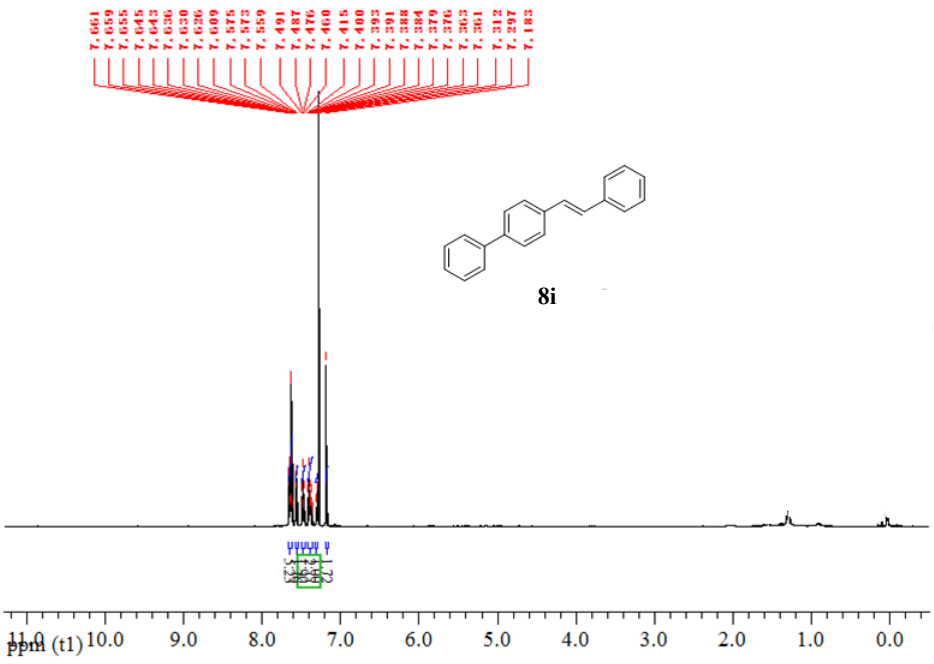
^{1}H NMR


9.558
7.549
7.534
7.442
7.425
7.366
7.350
7.335
7.239
7.225
7.210
7.164
7.131
7.033
7.000
6.799
6.782
HO
8g
1.00
1.92
ppm (f1)
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

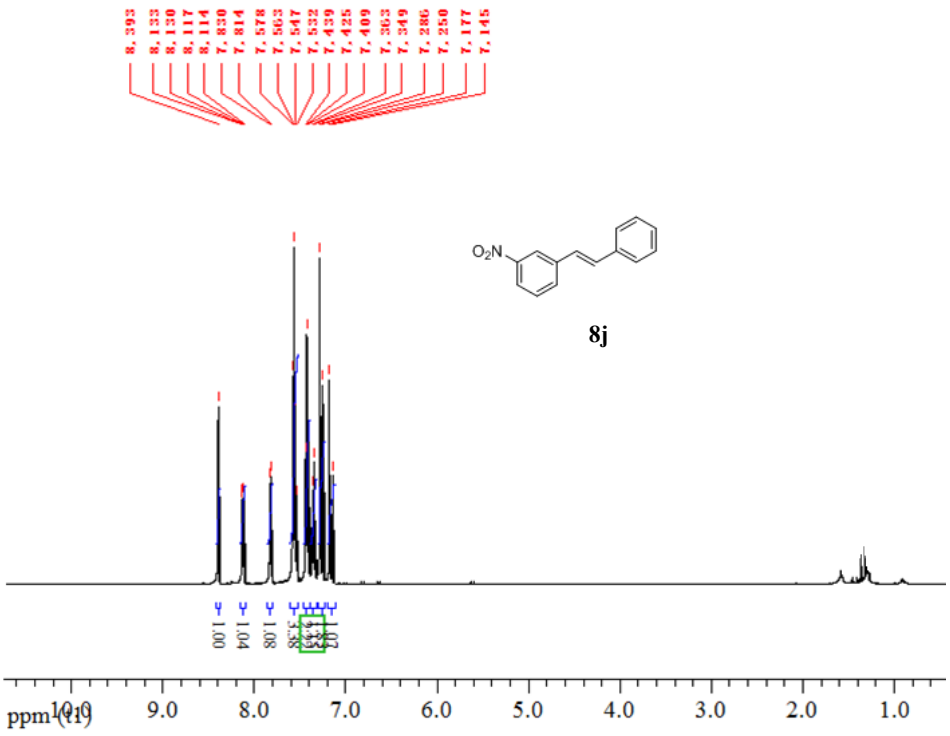
^{1}H NMR


7.983
7.966
7.611
7.595
7.569
7.555
7.423
7.408
7.393
7.344
7.329
7.314
7.285
7.264
7.231
7.166
7.133
2.624
8h
1.93
3.07
ppm (t1)
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

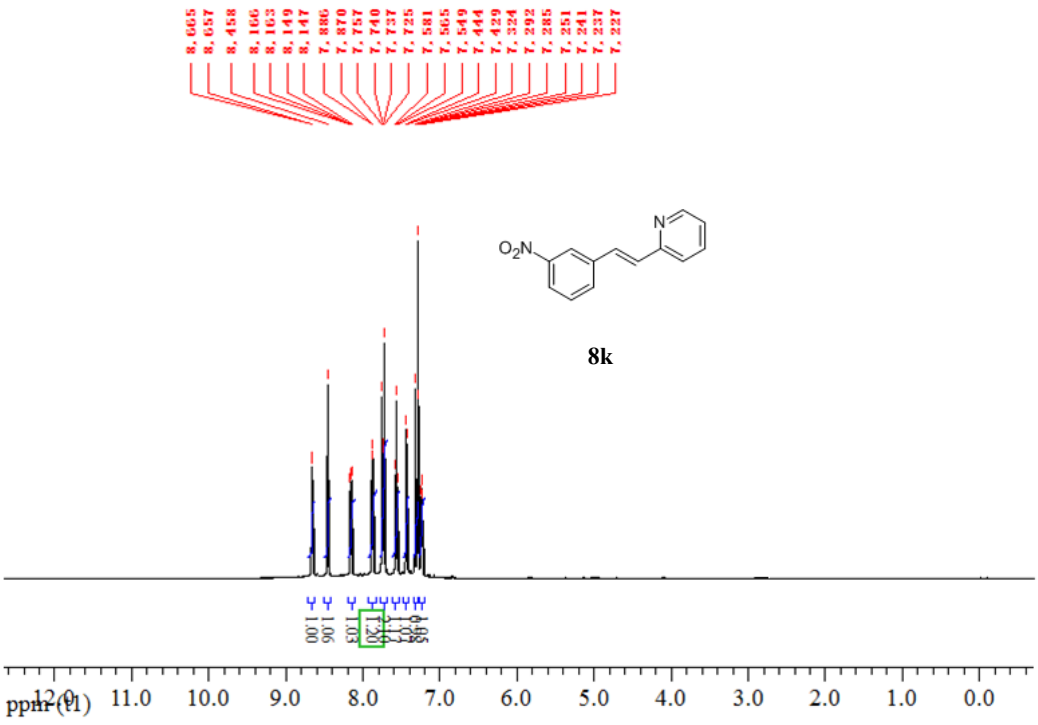
^{1}H NMR


7.661
7.659
7.655
7.645
7.643
7.636
7.630
7.626
7.609
7.575
7.573
7.559
7.491
7.487
7.476
7.460
7.415
7.400
7.393
7.391
7.388
7.384
7.379
7.376
7.363
7.361
7.312
7.297
7.183
8i
ppm (t1)
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

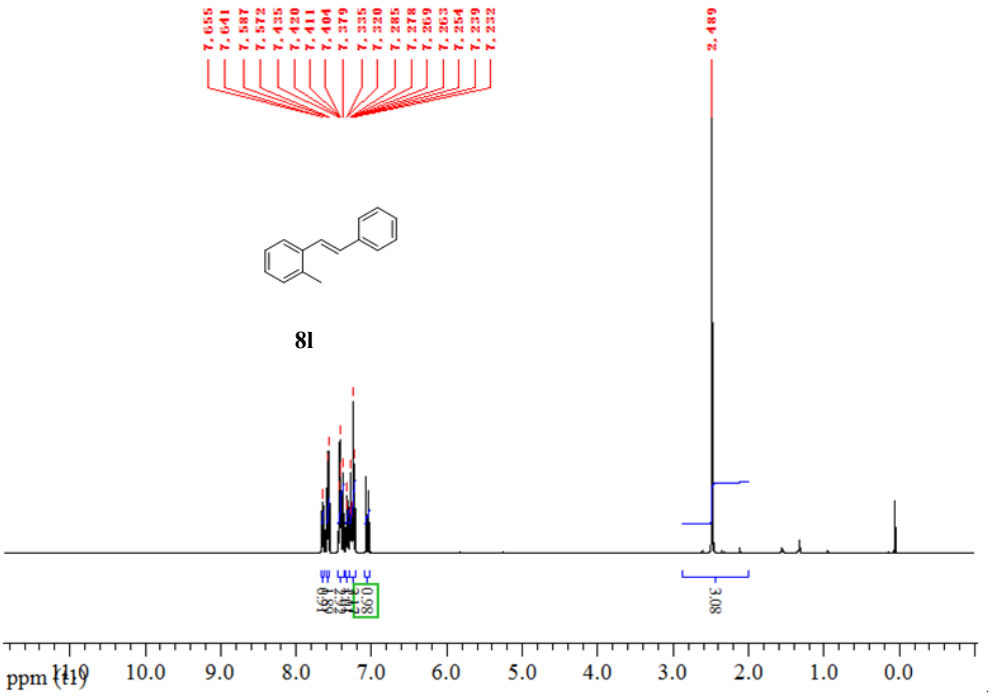
^{1}H NMR


8.393
8.133
8.130
8.117
8.114
7.830
7.814
7.578
7.563
7.547
7.532
7.439
7.425
7.409
7.363
7.349
7.286
7.250
7.177
7.145
O2N
8j
1.00
1.04
1.08
3.38
ppm (t1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

^{1}H NMR

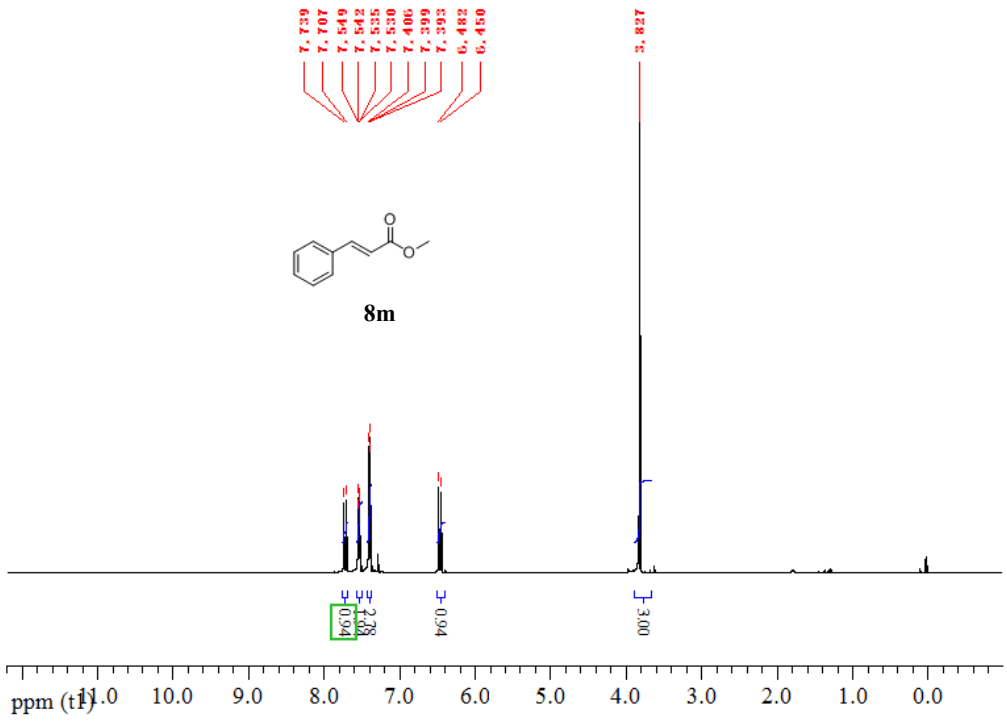

8.665
8.657
8.458
8.166
8.163
8.149
8.147
7.886
7.870
7.757
7.740
7.737
7.725
7.581
7.565
7.549
7.444
7.429
7.324
7.292
7.285
7.251
7.241
7.237
7.227
O2N
N
8k
1.00
0.96
1.03
2.20
1.12
0.98
0.85
0.84
ppm (f1)
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

^{1}H NMR

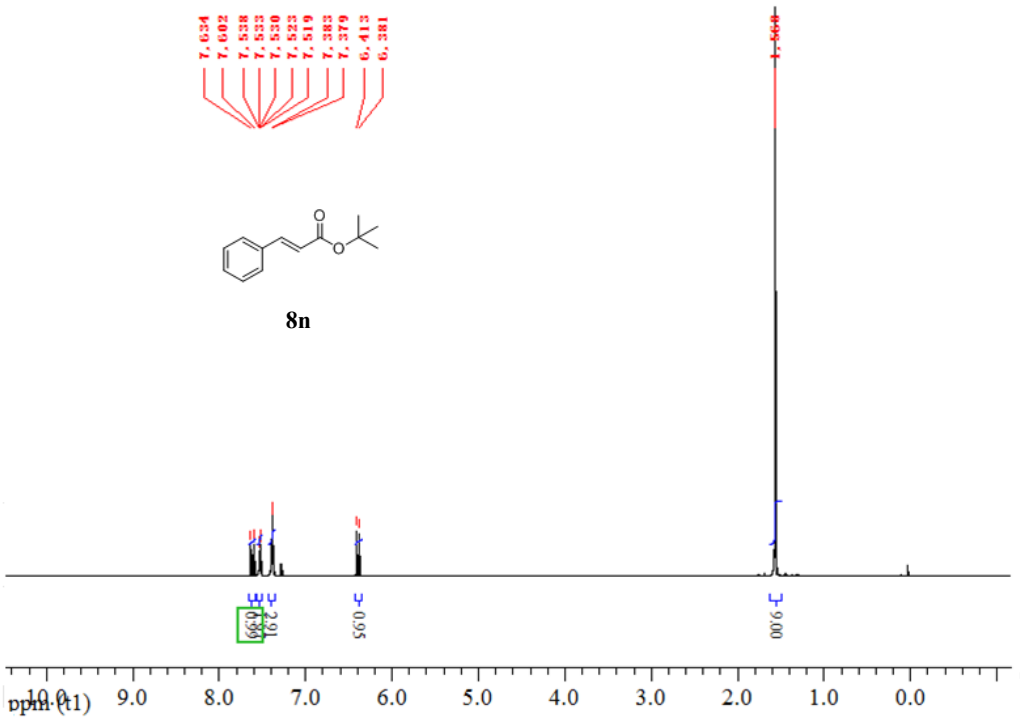

7.655
7.641
7.587
7.572
7.435
7.420
7.411
7.404
7.379
7.335
7.320
7.285
7.278
7.269
7.263
7.254
7.239
7.232
2.489
0.98
3.08
ppm (t1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

8l

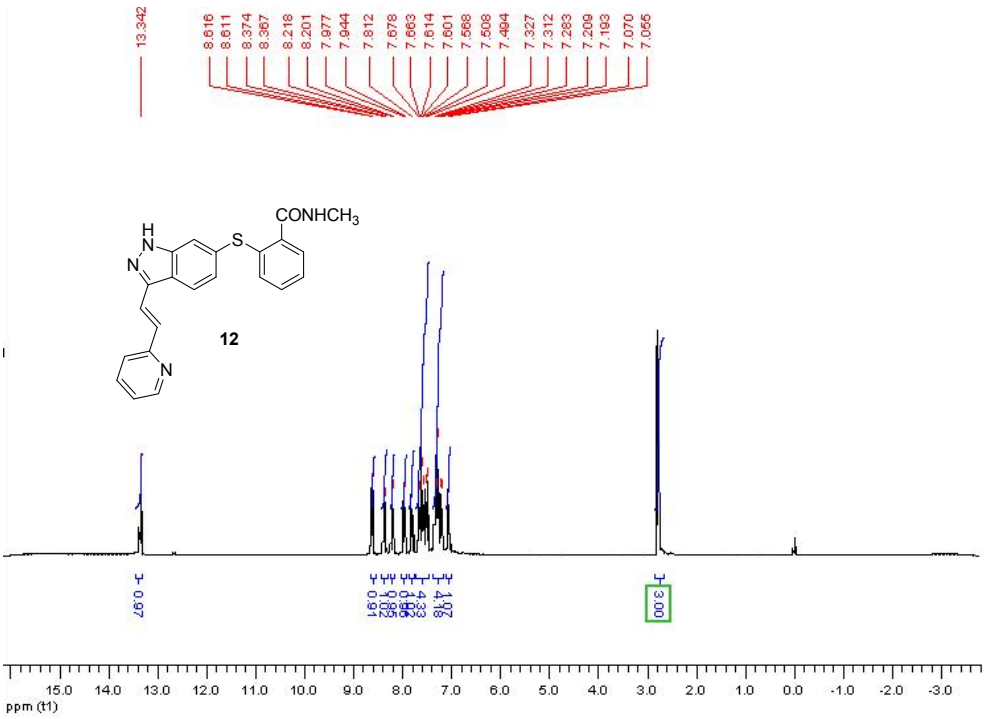
^{1}H NMR


7.739
7.707
7.549
7.542
7.535
7.530
7.406
7.399
7.393
6.482
6.450
3.827
8m
0.94
2.38
2.38
0.94
3.00
ppm (t1)
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

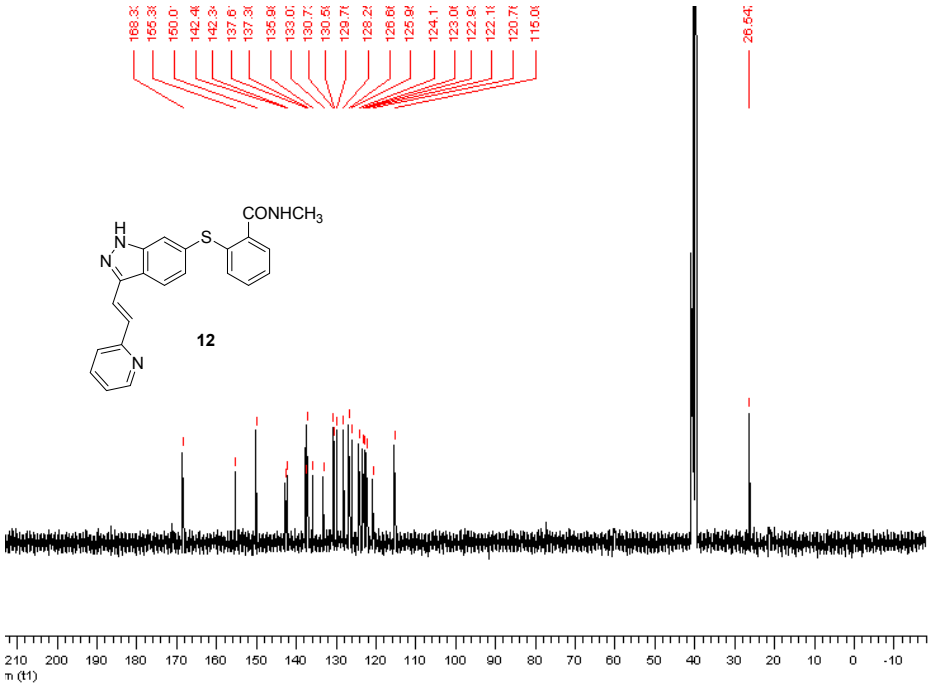
^{1}H NMR


7.634
7.602
7.538
7.533
7.530
7.523
7.519
7.383
7.379
6.413
6.381
1.568
O
O
8n
3.221
1.000
1.095
7.900
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

^{1}H NMR


13.342
8.616
8.611
8.374
8.367
8.218
8.201
7.977
7.944
7.812
7.678
7.663
7.614
7.601
7.568
7.508
7.494
7.327
7.312
7.283
7.209
7.193
7.070
7.055
CONHCH3
H
N
N
S
N
12
0.997
1.197
1.433
1.000
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
ppm (t1)

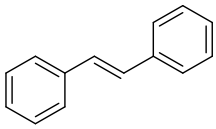
^{13}C NMR

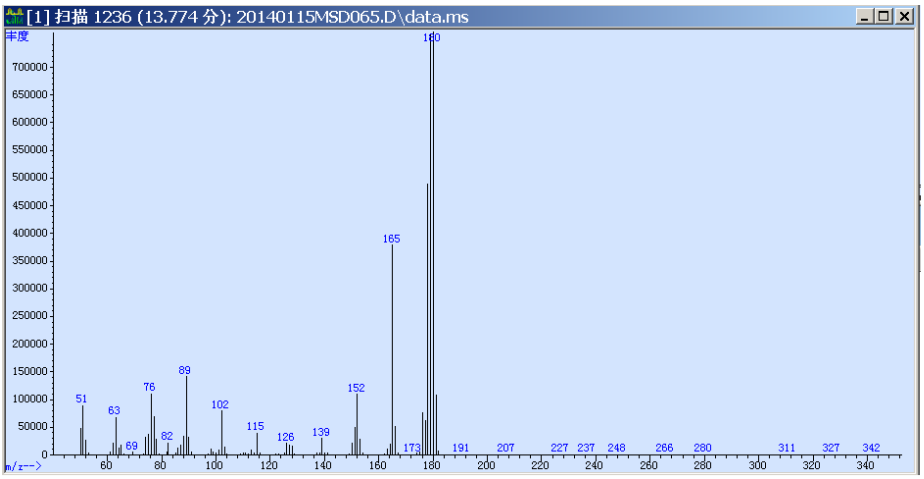


The selected GC-MS chromatogram of products:

(*E*)-1,2-diphenylethene 8a:

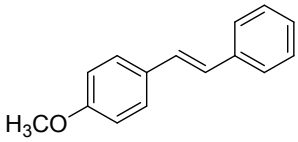
GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{12}$: 180.0, found: 180.

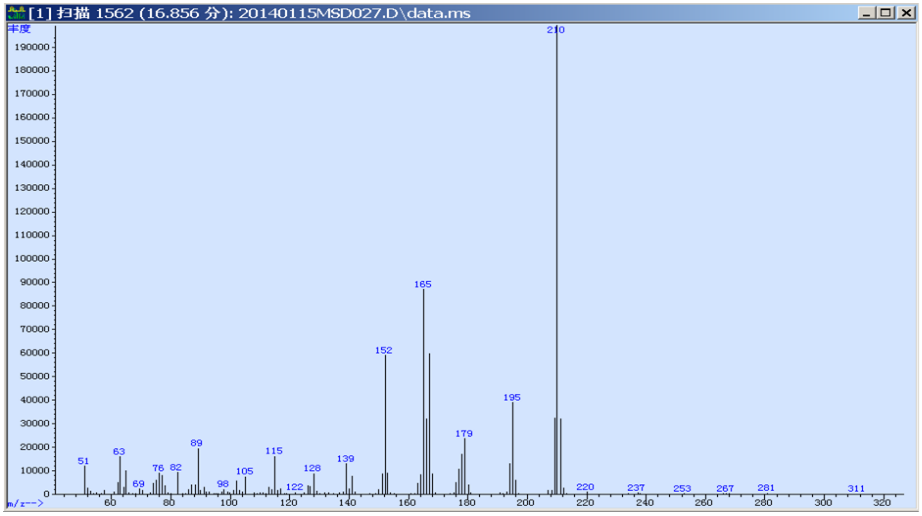




(*E*)-1-methoxyl-4-styrylbenzene 8b:

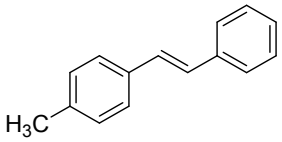
GC-MS (EI) [M]+: m/z calcd. for $C_{15}H_{14}O$: 210.0, found: 210.

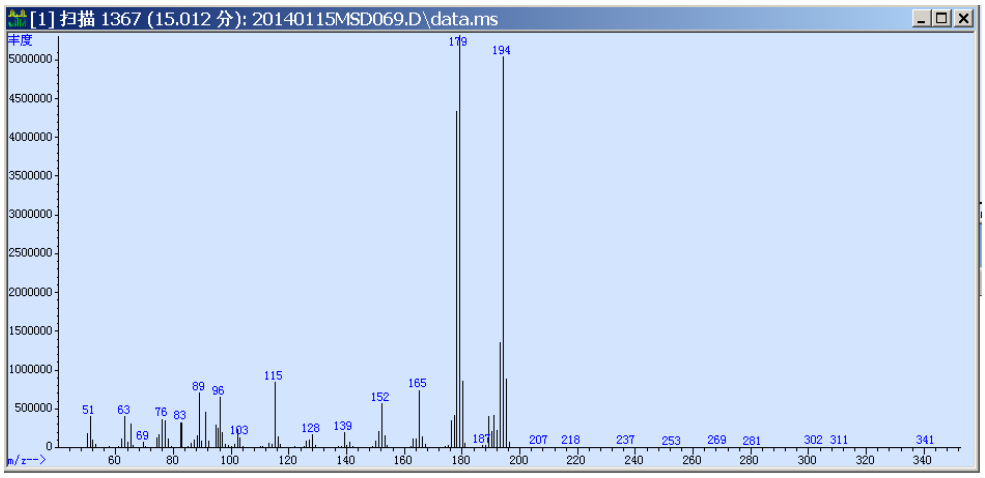




(*E*)-1-methyl-4-styrylbenzene 8c:

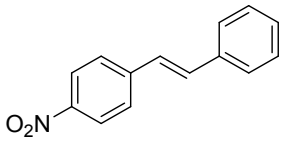
GC-MS (EI) [M]+: m/z calcd. for $C_{15}H_{14}$: 194.0, found: 194.

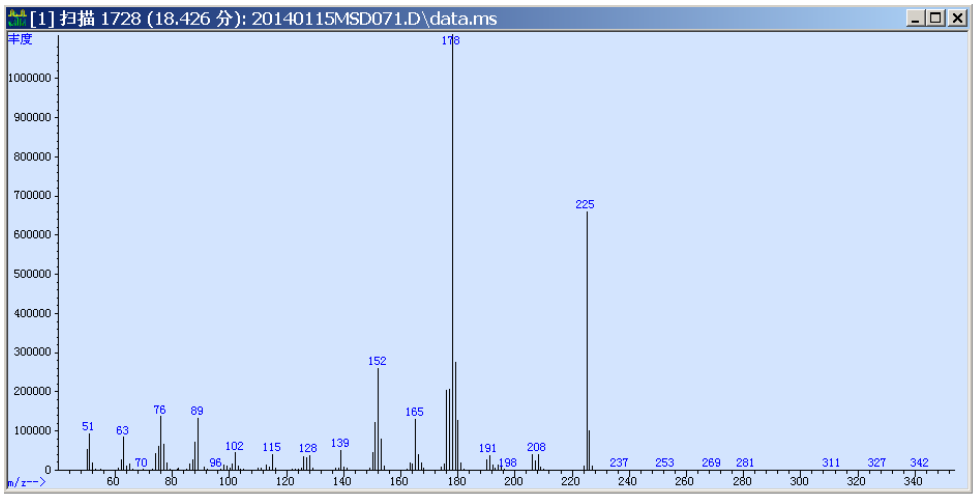




(*E*)-1-nitro-4-styrylbenzene 8d:

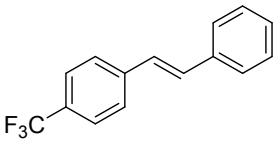
GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{11}NO_2$: 225.0, found: 225.

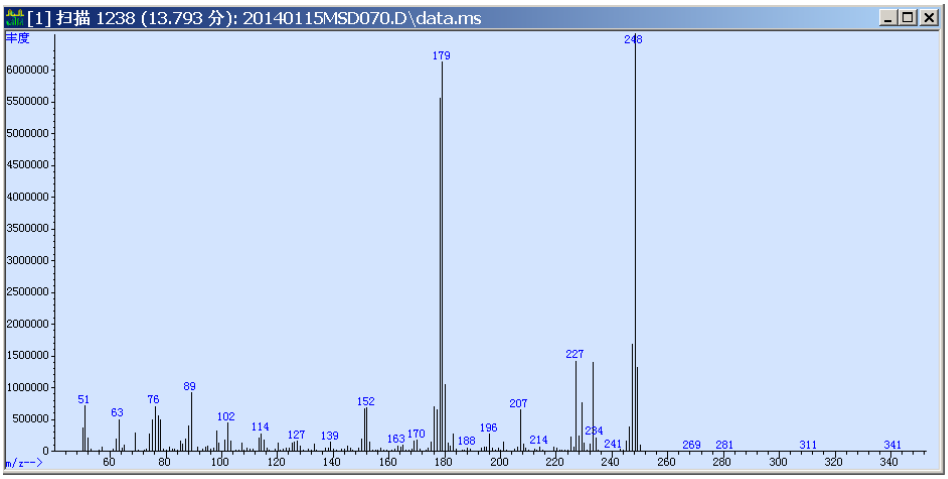




(*E*)-1-styryl-4-(trifluoromethyl)benzene 8e:

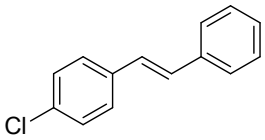
GC-MS (EI) [M]+: m/z calcd. for $C_{15}H_{11}F_3$: 248.0, found: 248.

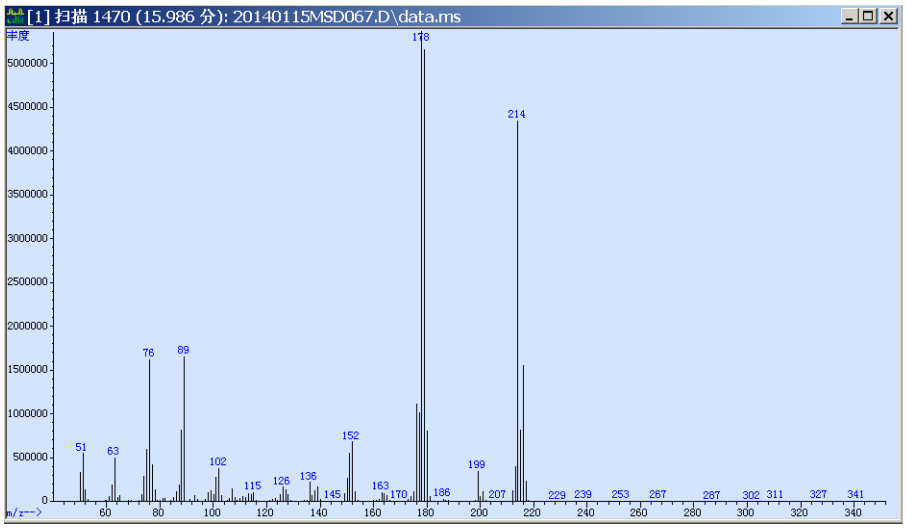




(*E*)-1-chloro-4-styrylbenzene 8f:

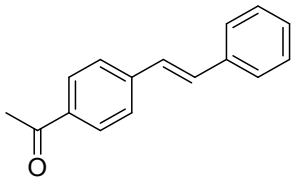
GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{11}Cl$: 214.0, found: 214.

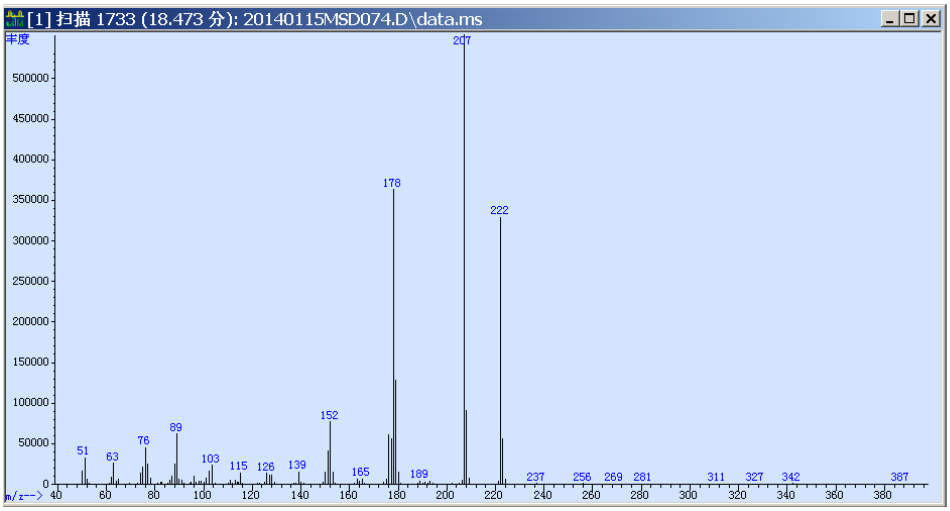




(*E*)-4-acetyl-4-styrylbenzene 8h:

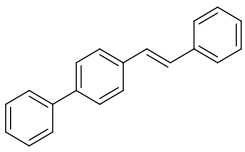
GC-MS (EI) [M]+: m/z calcd. for $C_{16}H_{14}O$: 222.0, found: 222.

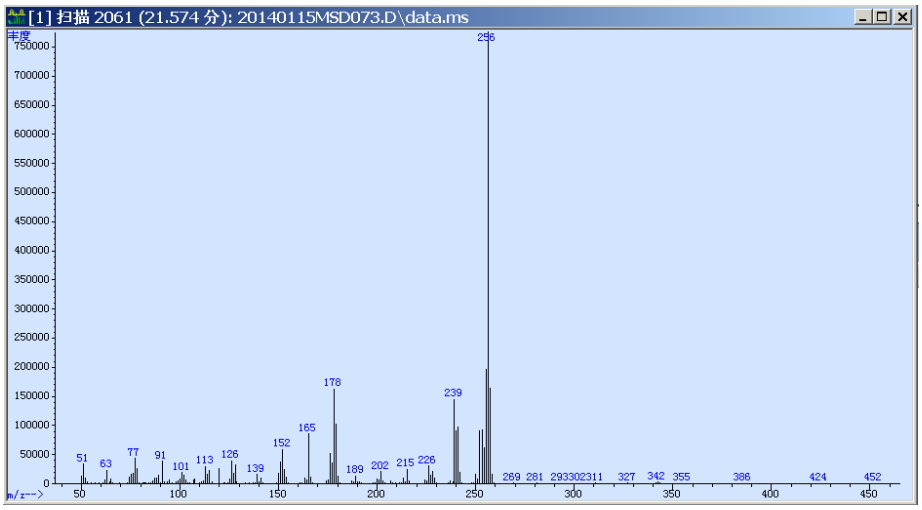




(*E*)-4-phenyl-4-styrylbenzene 8i:

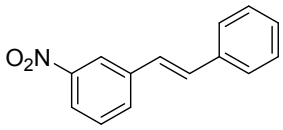
GC-MS (EI) [M]+: m/z calcd. for $C_{20}H_{16}$: 256.0, found: 256.

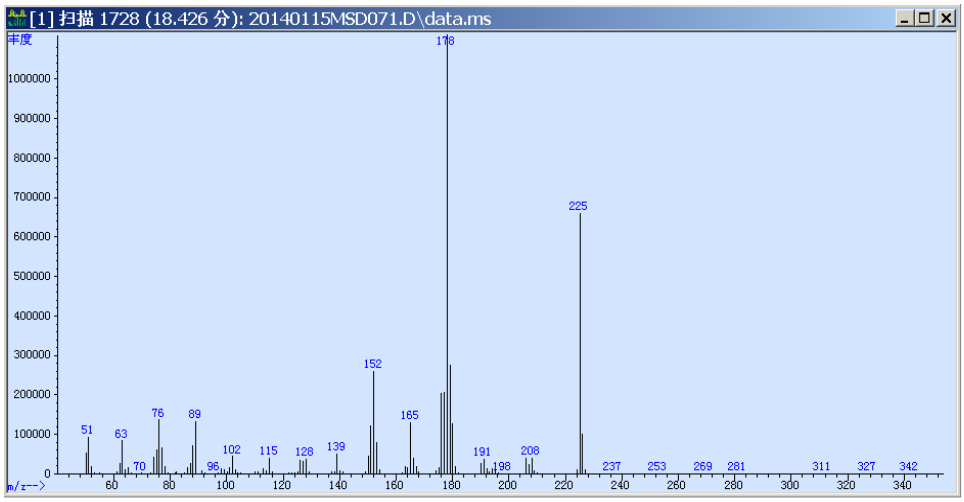




(*E*)-1-nitro-3-styrylbenzene 8j:

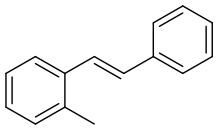
GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{11}NO_2$: 225.0, found: 225.

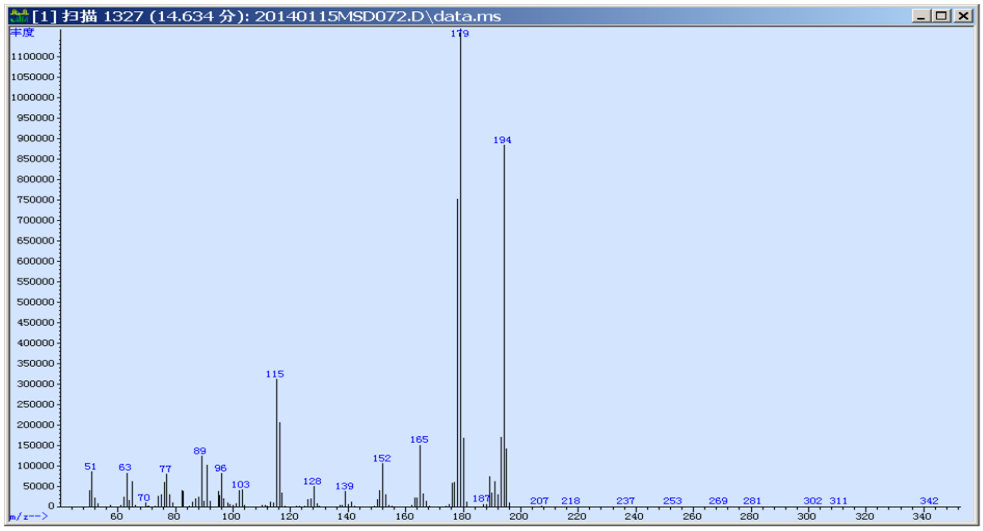




(*E*)-1-methyl-2-styrylbenzene 8l:

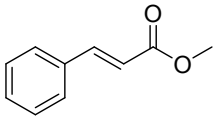
GC-MS (EI) [M]+: m/z calcd. for $C_{15}H_{14}$: 194.0, found: 194.

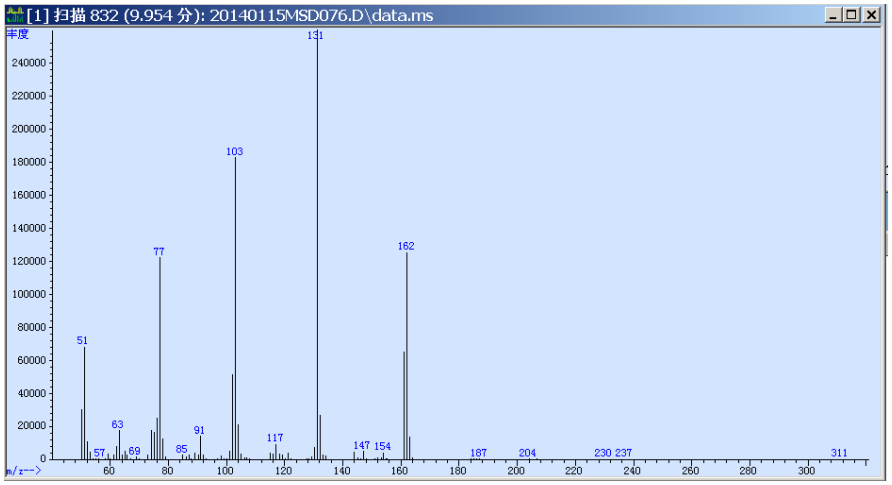




Methyl cinnamate 8m:

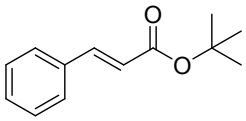
GC-MS (EI) [M]+: m/z calcd. for $C_{10}H_{10}O_2$: 162.0, found: 162.

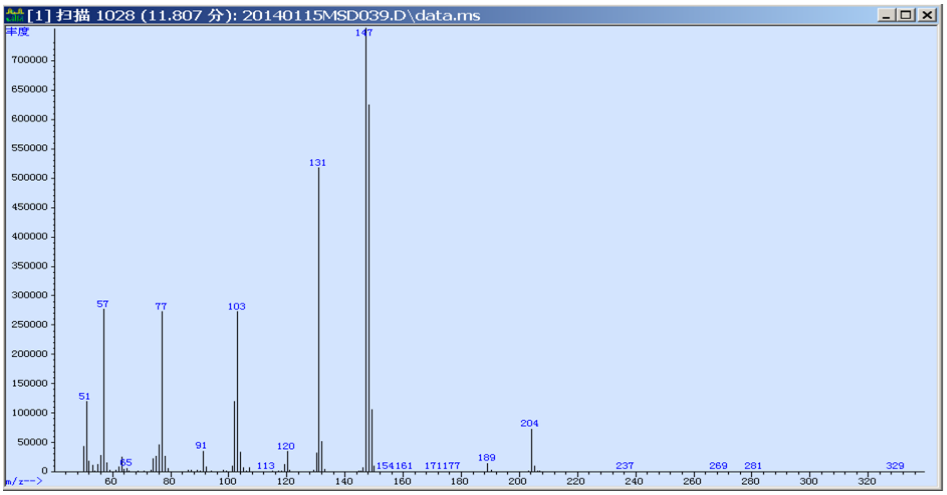




***tert*-butyl cinnamate 8n:**

GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_{16}O_2$: 204.0, found: 204.





4. References

1. G. B. Zhou, P. F. Zhang and Y. J. Pan, *Tetrahedron* **2005**, *61*, 5671.

2. M. Amini, M. Bagherzadeh, Z. Moradi-Shoeili and D. M. Boghaei, *RSC Adv.*, **2012**, *2*, 12091.

3. H.Yang, X. Han, G. Li, and Y. Wang, *Green Chem.*, 2009, **11**, 1184.

4. R.H. Wang, B. Twamley and J. M. Shreeve, *J. Org. Chem.*, 2006, **71**, 426.

5. E. J. Flahive, B. L. Ewanicki, N. W. Sach, S. A. O'Neill-Slawecki, N. S. Stankovic, S.

Yu, S. M. Guinness, J. Dunn, *Org. Process Res. Dev.* 2008, **12**, 637.

6. Q. P. Wang, E. Lucien, A. Hashimoto, G. C. G. Pais, D. M. Nelson, Y. S. Song, J. A. Thanassi, C. W. Marlor, C. L. Thoma, J. J. Cheng, S. D. Podos, Y. S. Ou, M. Deshp-nde, M. J. Pucci, D. D. Buechter, B. J. Bradbury, J. A. Wiles*, J. Med. Chem*. 2007, **50**,199.