Supporting Information

Thiourea Modified Polyacrylnitrile Fibers as Efficient Pd(II) Scavengers

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1. Reagents

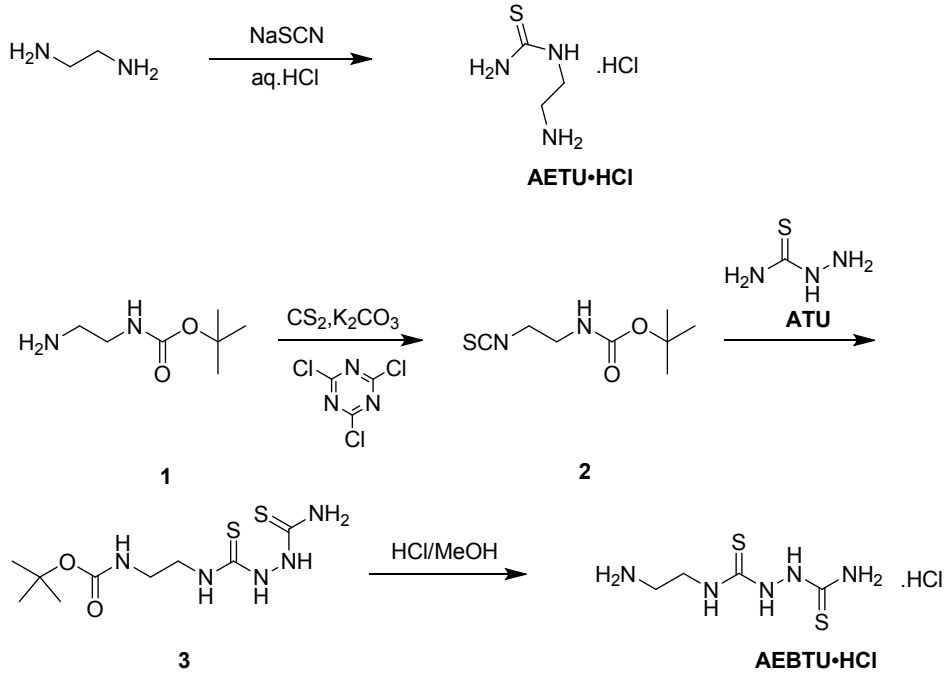
Commercially available PANF with lengths of 2 m and diameter of 20 ± 0.5 μm (from the Fushun Petrochemical Corporation of China) was cut into lengths of 5 cm before use. The water was deionized. Aqueous solutions of Pd(II) were prepared by dissolving $Pd(OAc)_2$ (23.1 mg) in 2 mL of aqueous HNO_3 (4 mol/L). The solutions were then diluted to the desired concentrations, and their pH values were adjusted with aq. NH_4OH (1 mol/L) or aq. HNO_3 (0.5 mol/L) prior to use. Organic solutions of Pd(II) were prepared by dissolving $Pd(OAc)_2$ in various solvents. All reagents and solvents were analytical grade and used as received without further purification.

2. Apparatus and instruments

An Elementar Vario EL instrument was used to perform the elemental analyses (EA) of the original and modified PANFs. A Fourier transform infrared (FTIR) spectrometer (AVATAR 360 Thermo Nicolet) was employed to investigate the infrared spectra of the original and modified PANFs using pressed KBr discs. An X-ray powder diffractometer (D/MAX-2500 X-ray diffract meter) was used to determine the crystallinity of the original and modified samples. The shapes and surface morphologies of the samples were observed with a Hitachi-S-4800 scanning electron microscopy. The pH values were determined with a Model PHS-3C pH meter. ^{1}H NMR and ^{13}C NMR spectra were recorded on an AVANCE III spectrometer (Bruker, 400 MHz) using TMS as an internal standard. The concentrations of Pd(II) and other metal ions were determined using a iCE3300 atomic absorption spectrometer (AAS, Thermo Fisher Scientific), an ICP-9000 (N+M) inductively coupled plasma atomic emission spectrometer (ICP-AES, Thermo Jarrell-Ash) and an Agilent 7700x inductively coupled plasma mass spectrometer (ICP-MS, Agilent). X-ray

photoelectron spectroscopy (XPS) was performed on a PH1600 spectrometer (PERKIN ELMZR).

3. Preparation of thiourea derivatives



Scheme S1 Preparation of the thiourea derivatives

3.1. *N*-(2-aminoethyl)thiourea hydrochloride (**AETU·HCl**)

36% aqueous HCl (30.4 g, 0.30 mol) was added to a cooled suspension of NaSCN (24.3 g, 0.30 mol) in ethylenediamine (18.0 g, 0.30 mol) at 0 °C for 1 h. Then the mixture was heated to 100 °C under stirring for 2 h. After that, the reaction mixture was diluted with methanol (100 mL), cooled to 0 °C and stirred for 0.5 h. Then the formed NaCl was filtered off. The pH of the filtrate was adjusted to 2 with aqueous HCl and the solution was allowed to stand at 0 °C for 6 h. Afterward, the precipitate was filtered, washed with methanol (15 mL) and dried to give **AETU.HCl** (19.6 g, 42% yield) as a white solid; mp = 202-204 °C. ^{1}H NMR (400 MHz, D_2O) δ 3.87 (m, 2H), 3.27 (t, 2H); ^{13}C NMR (400 MHz, D_2O) δ 182.77, 41.61, 39.44.

3.2. 1-(2-aminoethylamino)thiocarbonyl-2-aminothiocarbonyl hydrazine hydrochloride (**AEBTU.HCl**)

Carbon disulfide (6.2 g, 0.081 mol) was added to a cooled mixture of **1** (10.0 g, 0.062 mol) and K_2CO_3 (16.6 g, 0.12 mol) in water (50 mL) at 0 °C for 1 h. Then the mixture was warmed to room temperature and stirred for 2 h. Next the reaction mixture was cooled and added to a solution of 2,4,6-trichloro-1,3,5-triazine (5.7 g, 0.031 mol) in dichloromethane (100 mL). The suspension was stirred at room temperature for 2 h. The pH of the reaction mixture was adjusted to > 11 using aqueous NaOH (6 mol/L). The mixture was then stirred for 1.5 h, and the organic phase was separated. The aqueous phase was extracted with dichloromethane (100 mL). The combined organic phases were concentrated to give a yellow solid which was purified by chromatography (ethyl acetate: petroleum ether = 1: 3) to give compound **2** (10.5 g, 84% yield) as a white solid, mp = 82-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.91 (s, 1H), 3.67 (t, 2H), 3.4 (t, 2H), 1.48 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 155.59, 132.5, 80.17, 45.47, 40.62, 28.34.

A mixture of compound **2** (4.5 g, 0.022 mol) and thiosemicarbazide (2.1 g, 0.023 mol) in ethyl acetate (50 mL) was stirred at reflux for 14 h. The solution was then cooled to room temperature and filtered. The filter cake was dried in vacuum to give compound **3** (6.3 g, 98% yield) as a white solid, mp = 196-198 °C. ^{1}H NMR (400 MHz, DMSO-d6) δ 9.38 (s, 1H), 9.24 (s, 1H), 8.07 (s, 1H), 8.02 (s, 1H), 7.32 (s, 1H), 6.82 (s, 1H), 3.5 (t, 2H), 3.09 (t, 2H), 1.38 (s, 9H); ^{13}C NMR (400 MHz, DMSO-d6) δ 182.90, 181.99, 155.62, 77.48, 43.3, 39.99, 28.24.

A solution of HCl in methanol (1 mol/L, 35 mL) was added dropwise to a mixture of compound **3** (6.2 g, 0.021 mol) in methanol (60 mL) cooled in an ice water bath. The reaction mixture was stirred

at room temperature for 15 h. Then it was filtered, and the filter cake was washed with methanol and dried in vacuum to give **AEBTU.HCl** (4.4 g, 91% yield) as a white solid, mp = 224-226 °C. ^{1}H NMR (400 MHz, DMSO-d6) δ 9.61 (s, 1H), 9.26 (s, 1H), 8.20 (t, 1H), 8.11 (m, 4H), 7.50 (s, 1H), 3.70 (t, 2H), 2.98 (t, 2H); ^{13}C NMR (400 MHz, DMSO-d6) δ 183.20, 182.97, 41.56, 38.42.

4. Typical procedure in hydrogenation experiment for removal of palladium

36% aqueous HCl (1.3 g) and 5% wet Pd/C (0.53 g, 0.13mmol) were added to a solution of compound **4** (5.6g, 0.0063mol) in ethanol (50 mL). The mixture was hydrogenated for about 5 h at 75 ^{o}C and at 50 psi. The mixture was filtered and concentrated. Dichloromethane (25 mL) was then added and the pH was adjusted to 11 with 10% aqueous NaOH solution. Next the mixture was separated by extracting the water phase with dichloromethane (25 mL). The combined organic phases were washed with brine, and concentrated to about 25 mL. To this mixture, 0.27 g of AETU-PANF (4.0 equiv relative to residual Pd) and 0.5 mL of water were added and then the solution was stirred for 4 h. The mixture was filtered and evaporated to afford the crude product which was recrystallized from MeOH and ether to give the purified posaconazole (4.5g, 90%), mp = 165-166 °C ^{1}H NMR (400 MHz, DMSO-d6) δ 8.35 (s, 1H), 8.33 (s, 1H), 7.78 (s, 1H), 7.52 (d, 2H), 7.20 - 7.38 (m, 2H) 7.1 (d, 2H), 6.90 - 7.04 (m, 3H), 6.80 (d, 2H), 4.69 (d, 2H), 4.48 - 4.66 (m, 2H), 4.02 (t, 1H), 3.59 -3.91 (m, 5H), 3.24 - 3.34 (m, 4H), 3.04 - 3.23 (m, 4H), 2.51 - 2.63 (m, 1H), 2.32 - 2.46 (m, 1H), 2.13 (dd, 1H), 1.58 - 1.84 (m, 2H) 1.12 (d, 3H), 0.74 (t, 3H); ^{13}C NMR (400 MHz, DMSO-d6) δ 152.57, 152.37, 150.70, 149.85, 145.57, 145.22, 134.97, 128.45, 126.40, 125.86, 122.86, 117.90, 115.93, 115.15, 111.32, 104.63, 83.45, 70.06, 68.84, 67.29, 62.66, 55.20, 49.75, 48.44, 38.4, 37.5, 21.44, 20.09, 10.75.

5. Typical procedure in Suzuki coupling experiment for removal of palladium

$Pd(dppf)Cl_2$ (365 mg, 0.5 mmol), Cs_2CO_3 (4.9g, 0.015 mol) and compound **7** (4.3g, 0.015mol) were added to a solution of compound **5** (3.9g, 0.0135mol) in dioxane (50 mL). Under a nitrogen atmosphere, the reaction mixture was then heated at reflux for 4 h. The mixture was cooled to room temperature and concentrated and then 50 mL of water and 50 mL of dichloromethane were added. The organic layer was separated and washed with 25 mL of brine. The organic layer was then evaporated to about 25 mL. To this mixture, 1.25 g of AETU-PANF (4.0 equiv relative to residual Pd) and 0.5 mL of water were added and then the mixture was stirred for 4 h. The mixture was filtered and evaporated to afford the crude product which was recrystallized from ethyl acetate and ether to give the purified compound **6** (3.8g, 76%), mp = 201-202 °C. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.94 (s, 1H), 8.24 - 8.21 (m, 2H), 7.78 - 7.73 (m, 2H), 7.54 - 7.52 (m, 1H), 5.28 (s, 1H), 4.77 (t, 1H), 4.48 (s, 3H), 4.16 (t, 1H), 3.91 (t, 1H), 3.73 - 3.69 (m, 1H), 3.60 - 3.57 (m, 1H); ^{13}C NMR (400 MHz, DMSO-d6) δ 164.31, 161.00, 158.46, 154.79, 149.92, 145.48, 140.75, 137.66, 131.88, 131.38, 122.55, 114.45, 105.93, 105.54, 73.93, 62.04, 46.43.

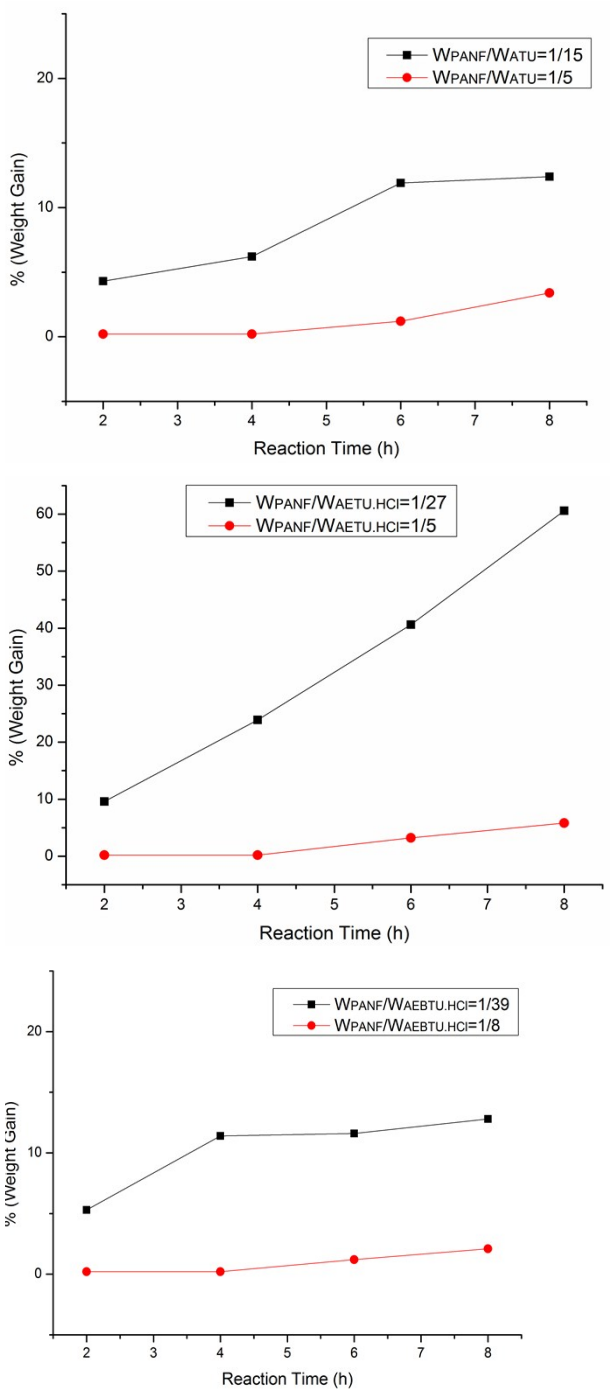
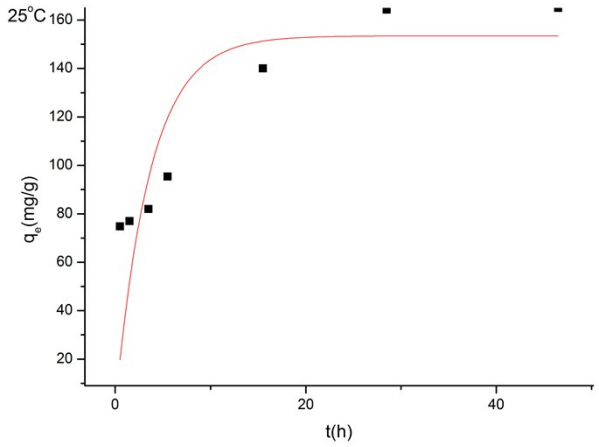
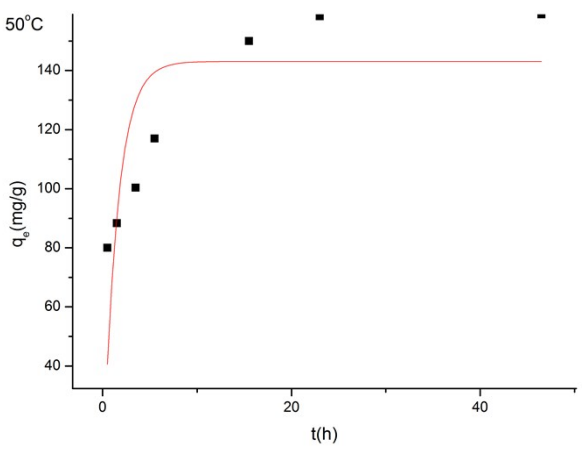


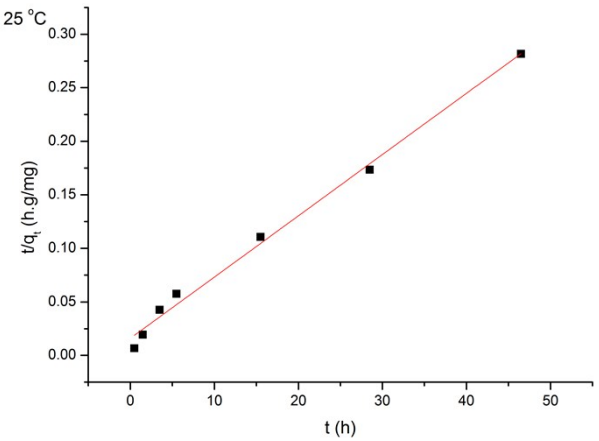
Fig. S1. Optimization of the reaction time for the amination with different feed ratios (weight ratios of PANF and thiourea derivatives).



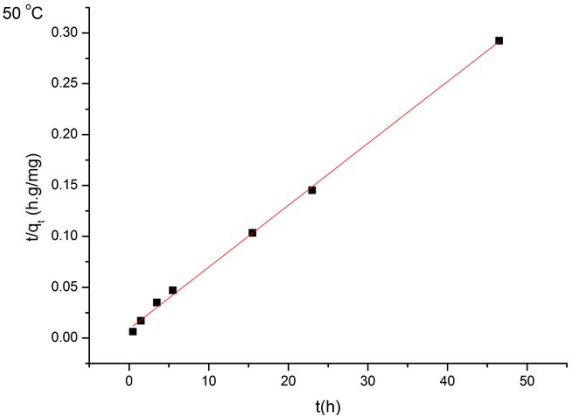
a fitting of pseudo- first-order equation at 25 °C



b fitting of pseudo- first-order equation at 50 °C

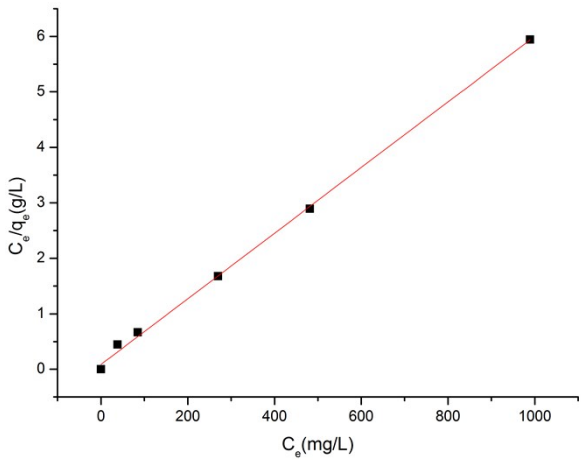


c fitting of pseudo- second-order equation at 25 °C

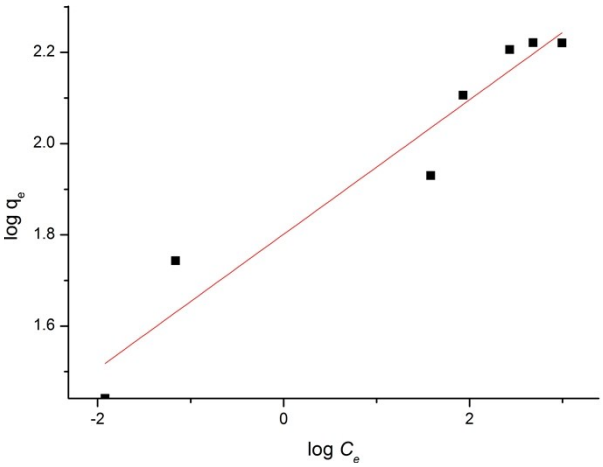


d fitting of pseudo- second-order equation at 50 °C

Fig. S2. The fitting of pseudo first-order and pseudo second-order equations.



a linear fitting of Langmuir isotherm



b linear fitting of Freundlich isotherm

Fig. S3. The linear fitting of Langmuir and Freundlich isotherm.

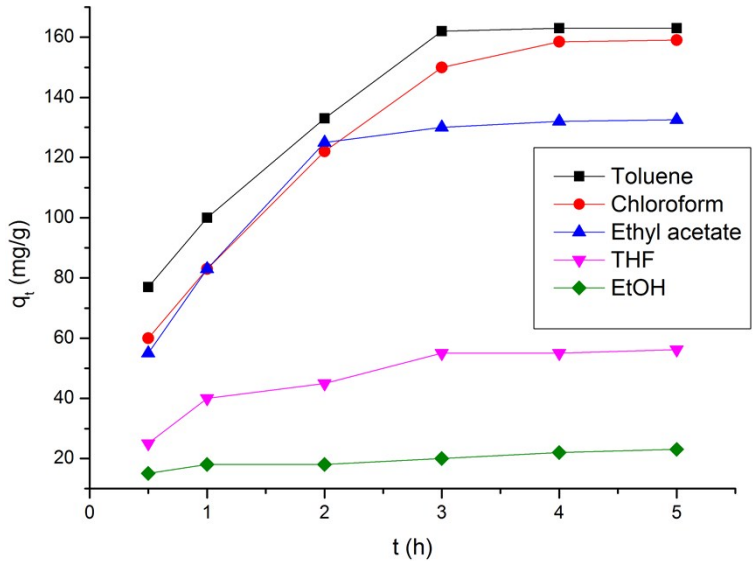


Fig. S4. Adsorption kinetics of the absorption of Pd(II) by AETU-PANF in organic solutions (initial concentration 300 mg/L, adsorbent 1.0 g/L, 25 °C).

Table S5. Scavenging palladium from posaconazole.in dichloromethane with various reagents.

Entry	**Reagent[a]**	**Weight (wt % or equiv)**	**Residual Pd[d] (ppm)**
1	L-tartaric acid	10%[b]	15.7
2	Citric acid	10%[b]	56
3	TMT trisodium salt	20%[b]	51
4	activated charcoal	20%[b]	23
5	SiliaMetS®Thiol	4eq[c]	11.3
6	SiliaMetS®DMT	4eq[c]	5.6
7	AETU-PANF	4eq[c]	0.8
8	AETU-PANF	8eq[c]	0.4

a Methods are reported in references [6], [7],[8] and [23]. The initial Pd concentration was 310 ppm.

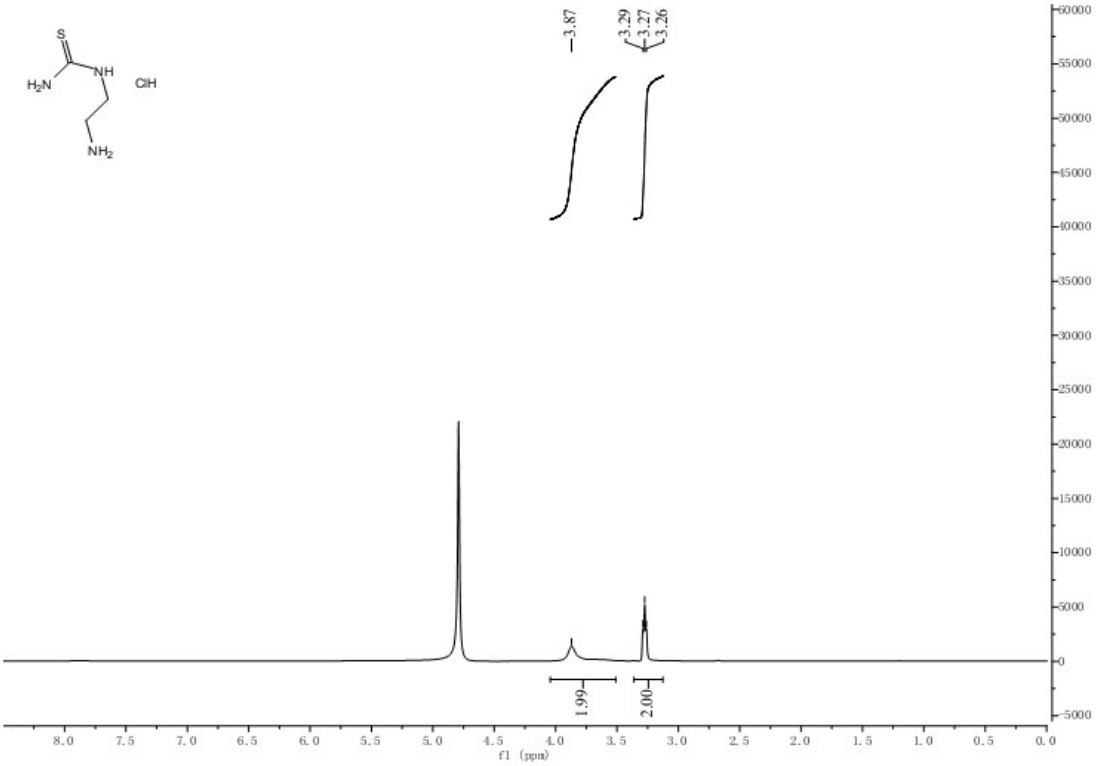
b The amount of reagents was calculated based on the weight of crude posaconazole.

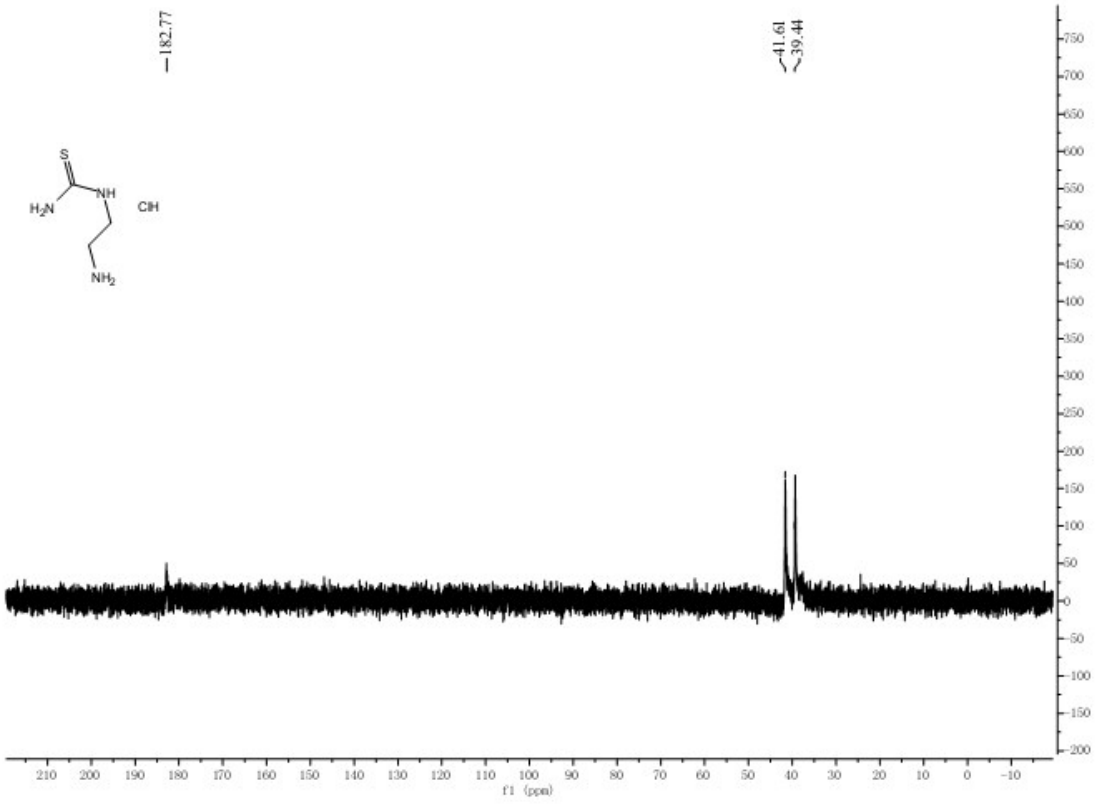
c The amount was calculated based on the molar equivalent of palladium in the solution.

d The palladium content was relative to the isolated solid product.

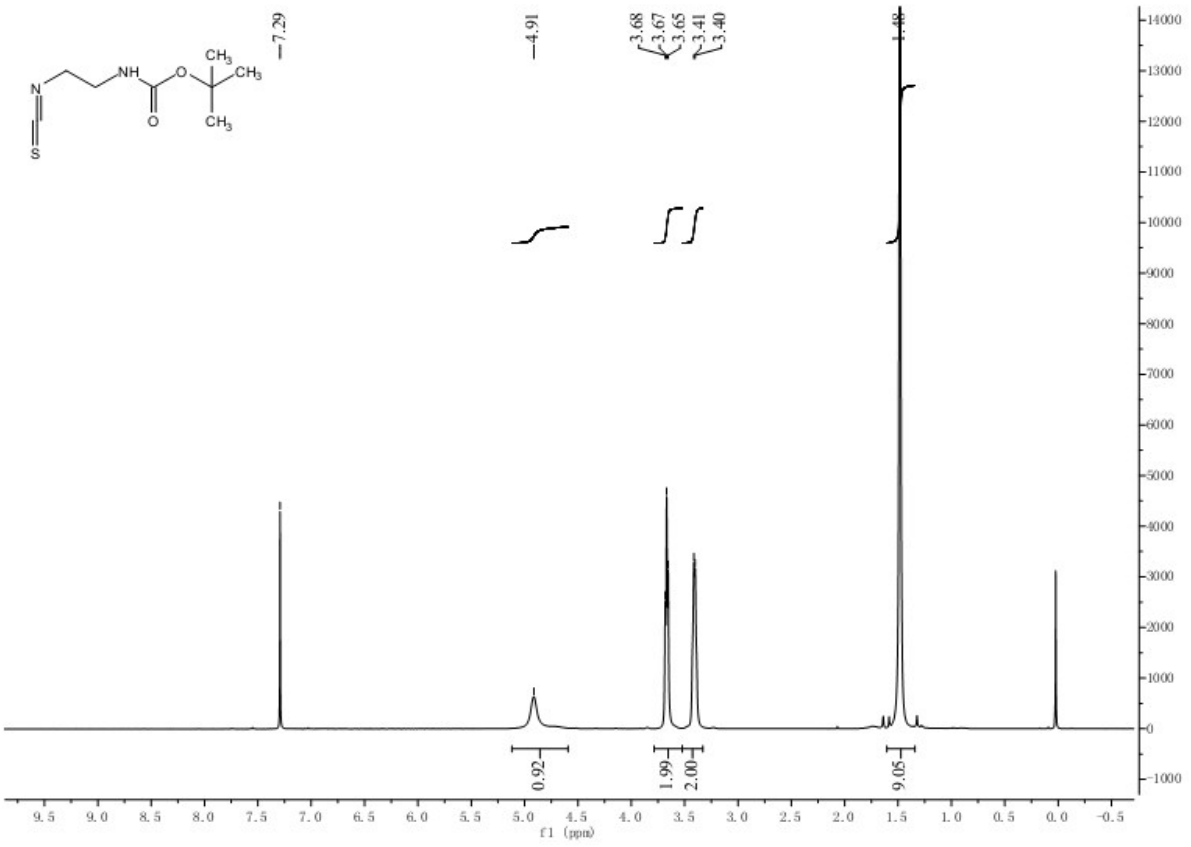
[1]HNMR and [13]CNMR spectra

Compound **AETU.HCl**





Compound **2**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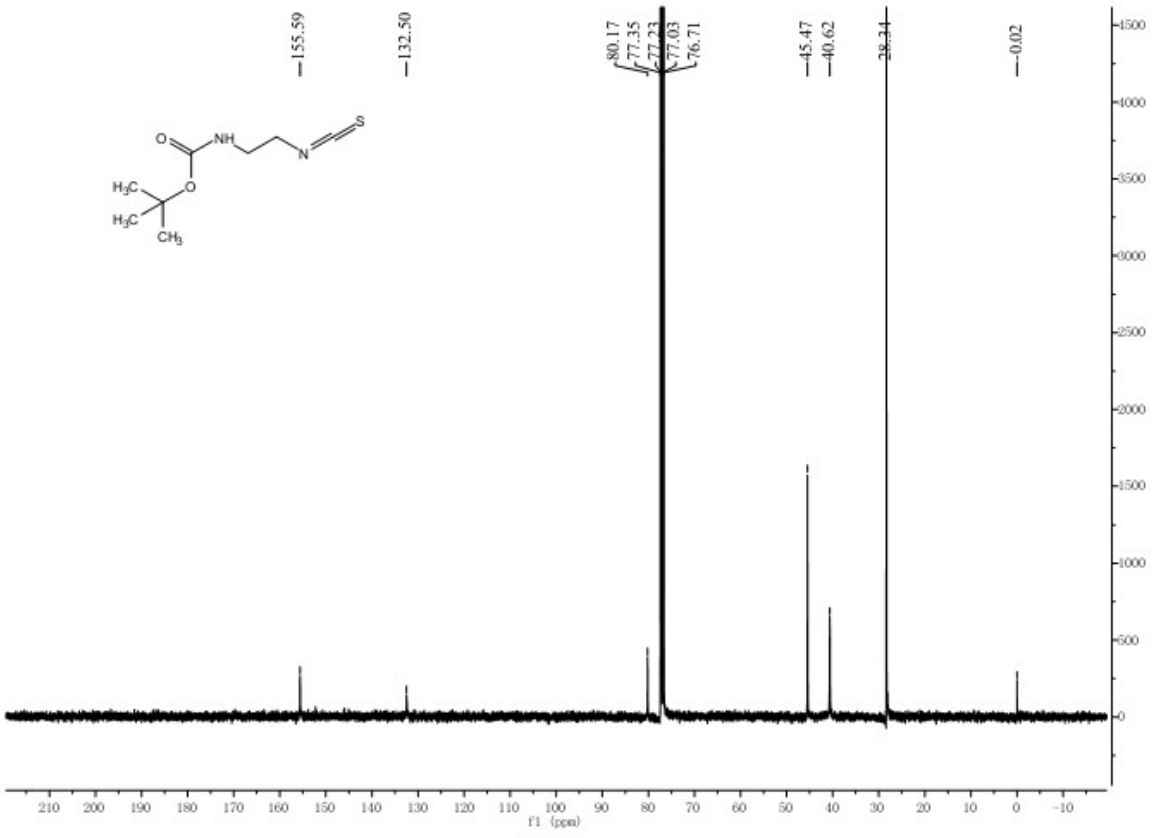
3.68
3.67
3.65
3.41
3.40
1.48
0.92
1.99
2.00
9.05
f1 (ppm)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77.03
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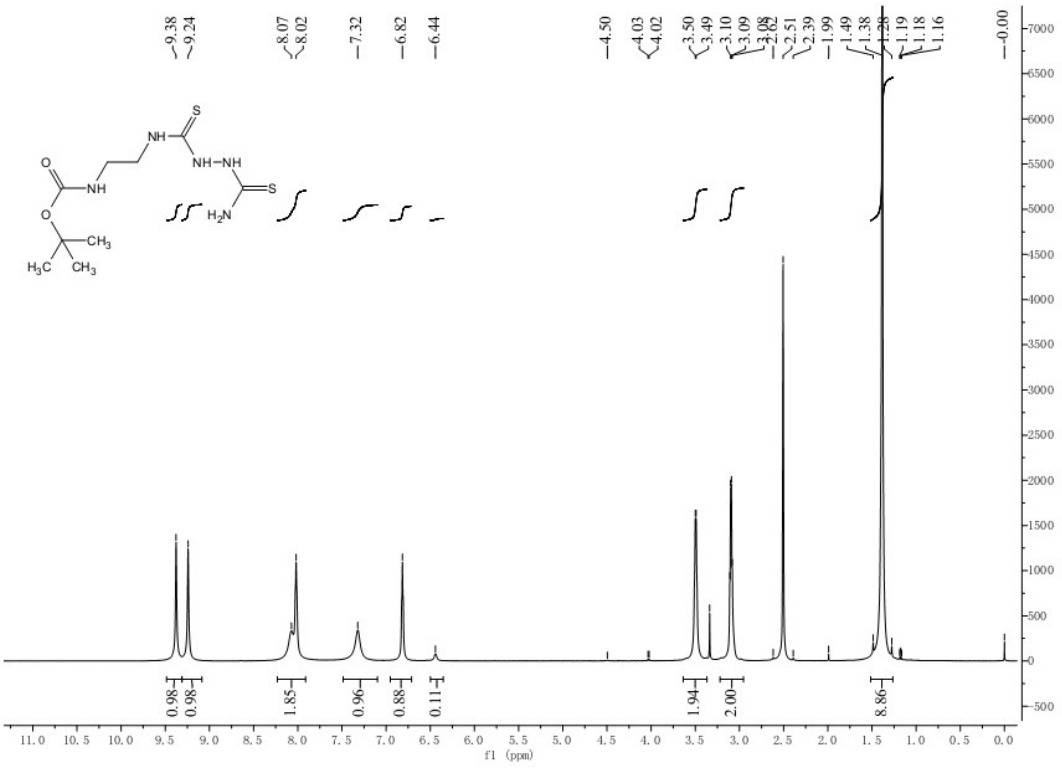
28.34
0.02
f1 (ppm)

Compound **3**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4.02
3.50
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2.82
2.51
2.39
1.99
1.49
1.38
1.28
1.19
1.18
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0.11
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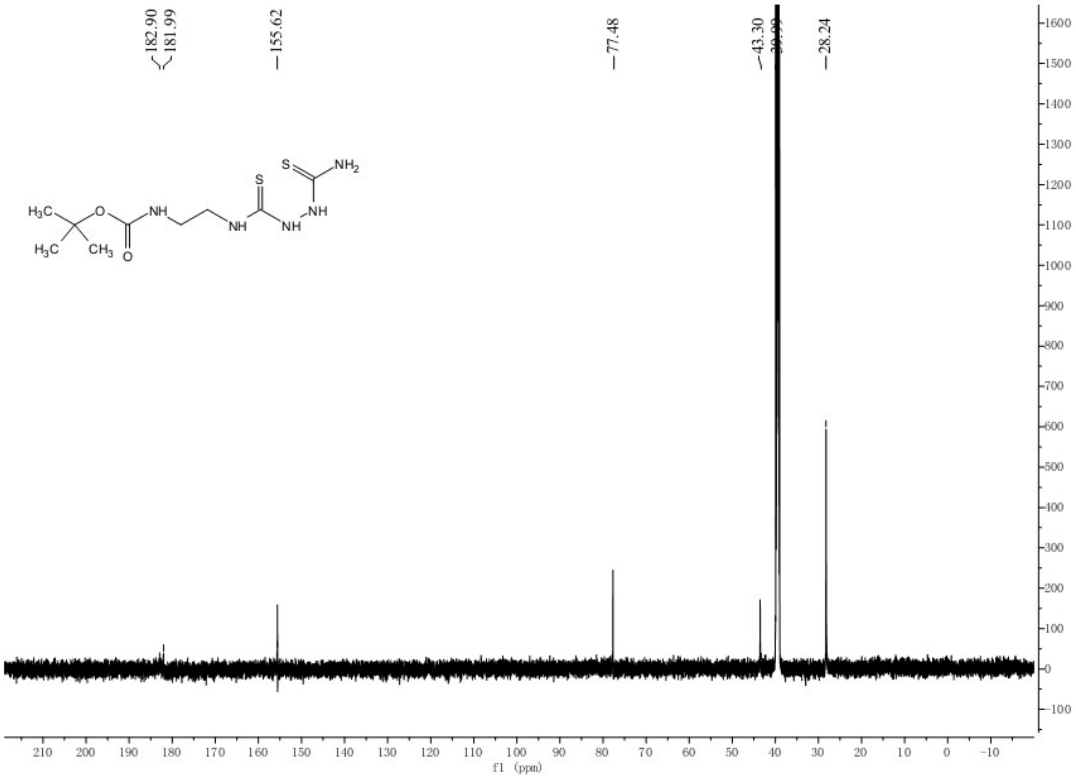
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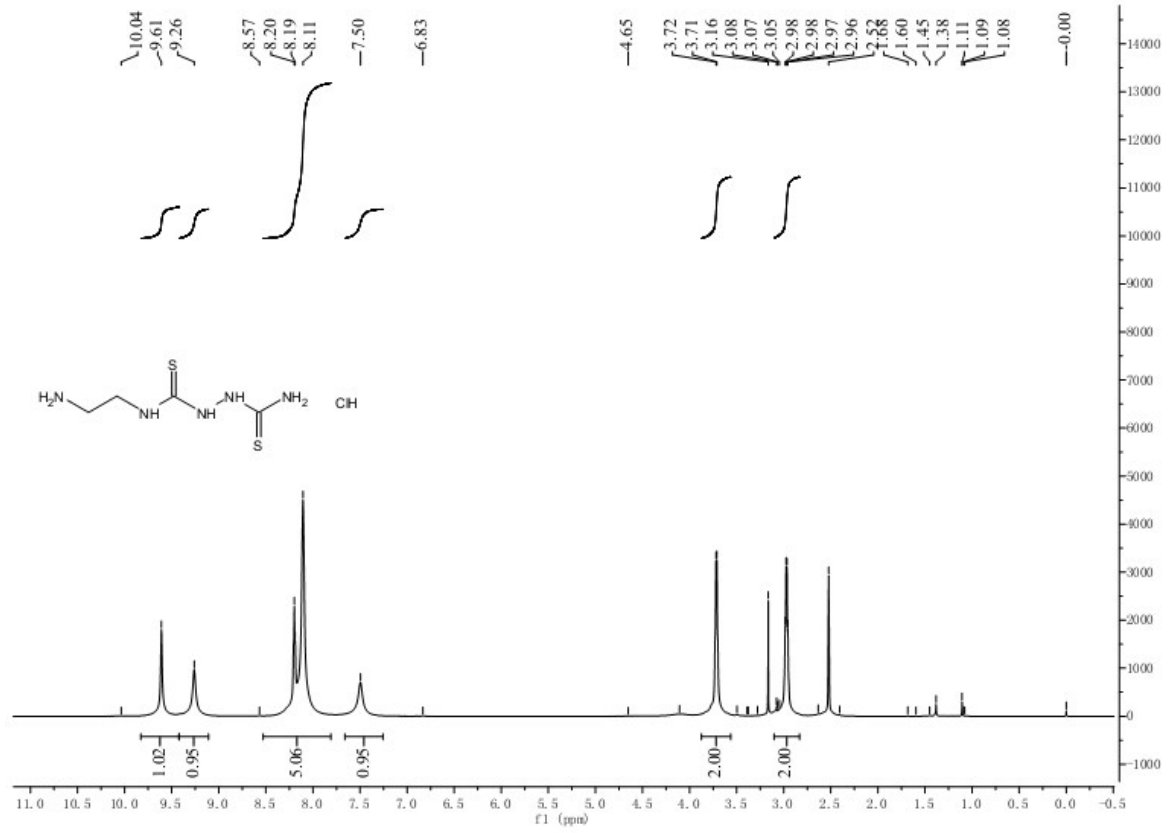
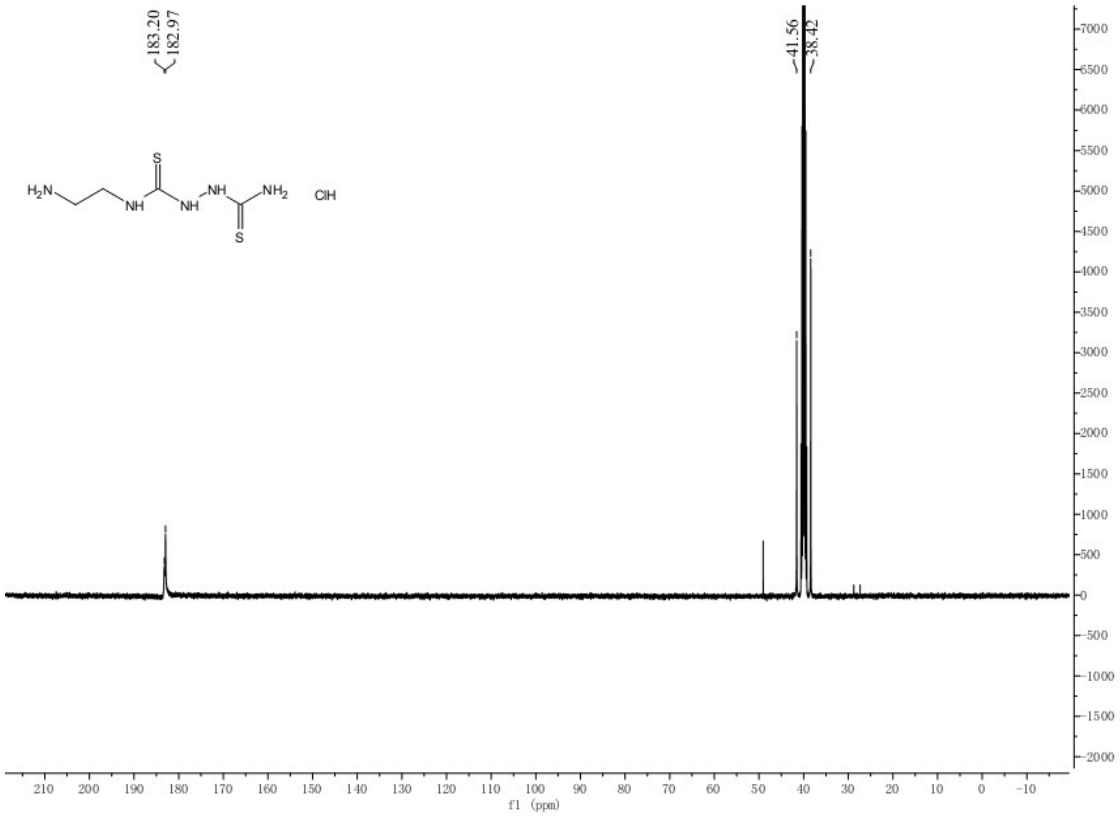
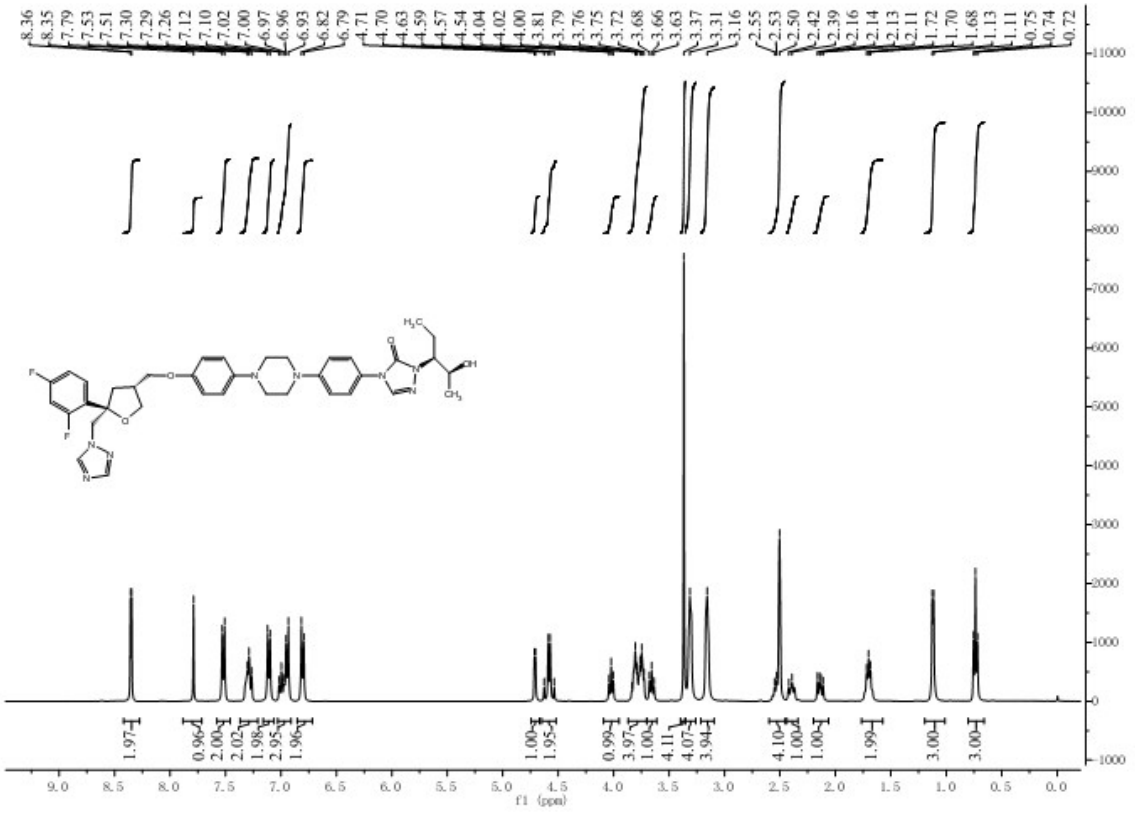
f1 (ppm)

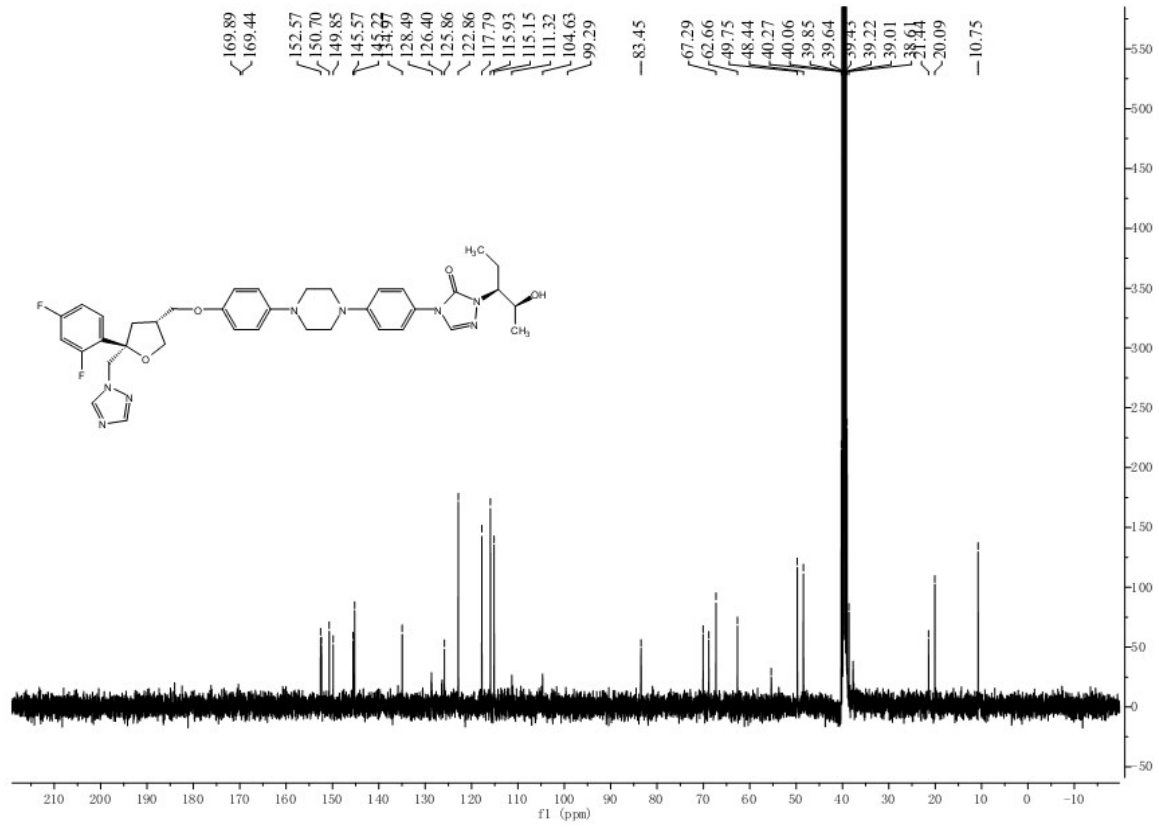
Compound **AEBITU.HCl**



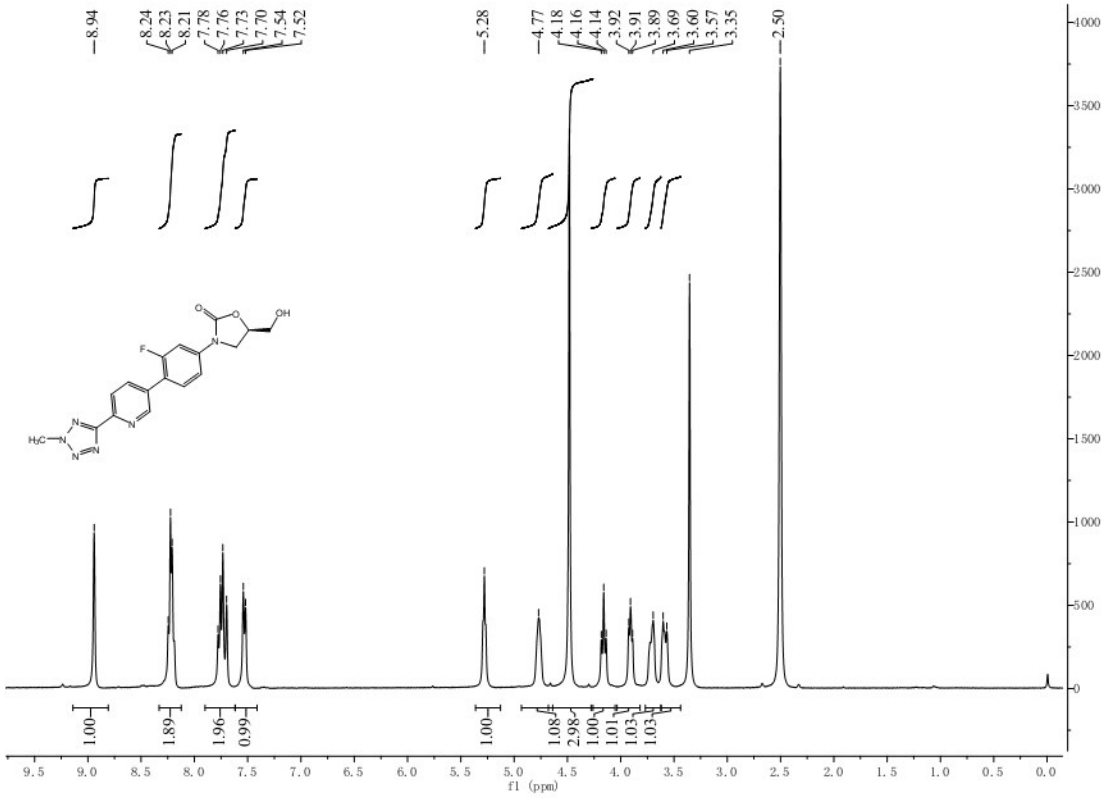


Posaconazole





Compound **6**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4.14
3.92
3.91
3.89
3.69
3.60
3.57
3.35
2.50
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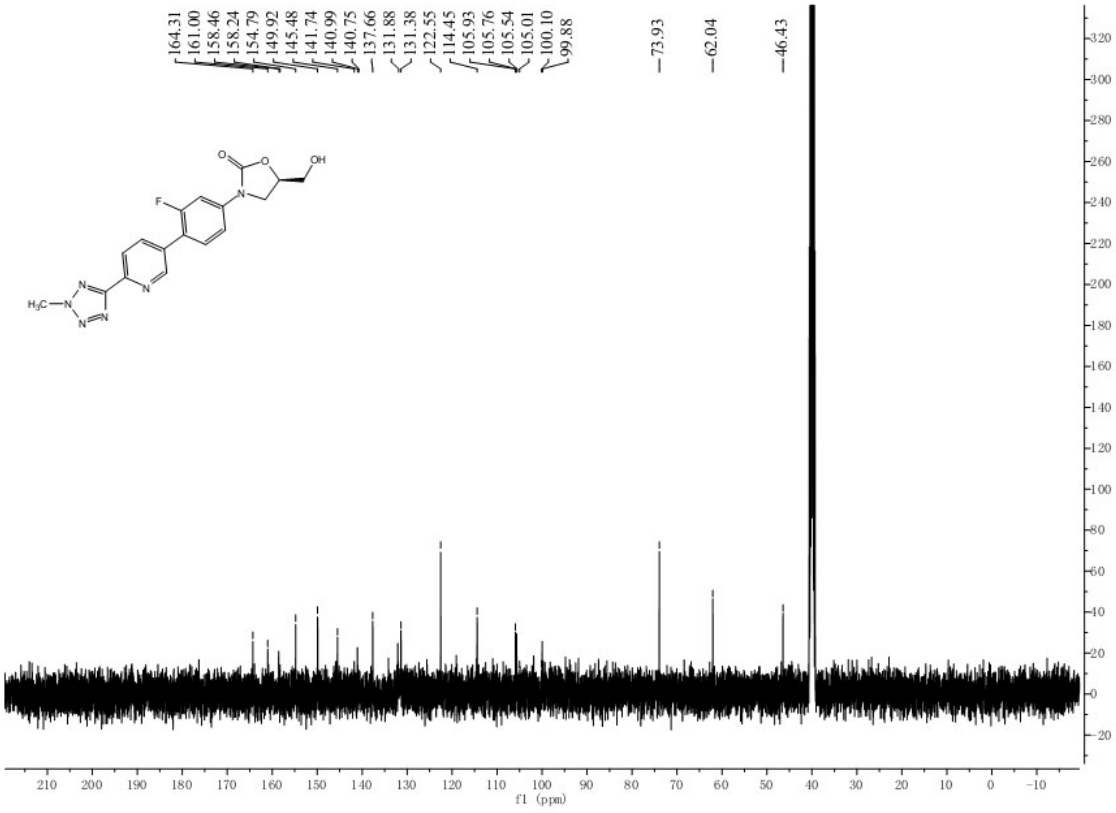
1.03
f1 (ppm)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122.55
114.45
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105.54
105.01
100.10
99.88
73.93
62.04
46.43
f1 (ppm)