

An Efficient and Chemoselective Deprotection of Aryl *tert*-Butyldimethylsilyl (TBDMS) Ethers by NaCN

Xue-jun Qiao, Xiao Hou, Wu-hong Fang, Xue-fei Bao and Guo-liang Chen*

Key Laboratory of Structure-Based Drug Design & Discovery, Ministry of Education, Shenyang Pharmaceutical University, 110016 Shenyang, China

General experimental procedure for preparation of *tert*-butyldimethylsilyl ethers

A 100 mL three-neck flask was equipped with a thermometer, condenser. Chloro(1,1-dimethylethyl)dimethylsilane (1.5 eq) and imidazole (2.5 eq) were added into a mixture of phenol (1 eq) in 20 mL of *N,N*-dimethylformamide (DMF). Then, the mixture was continually stirred at 50 °C and the reaction progress was monitored by TLC. The reaction mixture was concentrated *in vacuo* to obtain crude product, which was purified by silica column chromatography. Other *tert*-butyldimethylsilyl ethers were prepared in similar methods.

General experimental procedure for deprotection of *tert*-butyldimethylsilyl ethers

A 100 mL three-neck flask was equipped with a thermometer, condenser. NaCN (0.1 eq) were added into a mixture of the phenol protected with chloro(1,1-dimethylethyl)dimethylsilane (1 eq) in ethanol (15 mL) and water (1 mL). Then, the mixture was continually stirred at appropriate temperature (Table 3) until the completion of the reaction (monitored by TLC). Then, the reaction mixture was concentrated *in vacuo*; the residue was dissolved in water and extracted with dichloromethane three times. The organic layer was washed with saturated sodium chloride solution and dried over anhydrous sodium sulfate. After the desiccant was filtered off, the filtrate was evaporated to gain crude product, which was purified by column chromatography on silica gel (81.9 ca. 95.2% yield).

The spectra of related *tert*-butyldimethylsilyl ethers

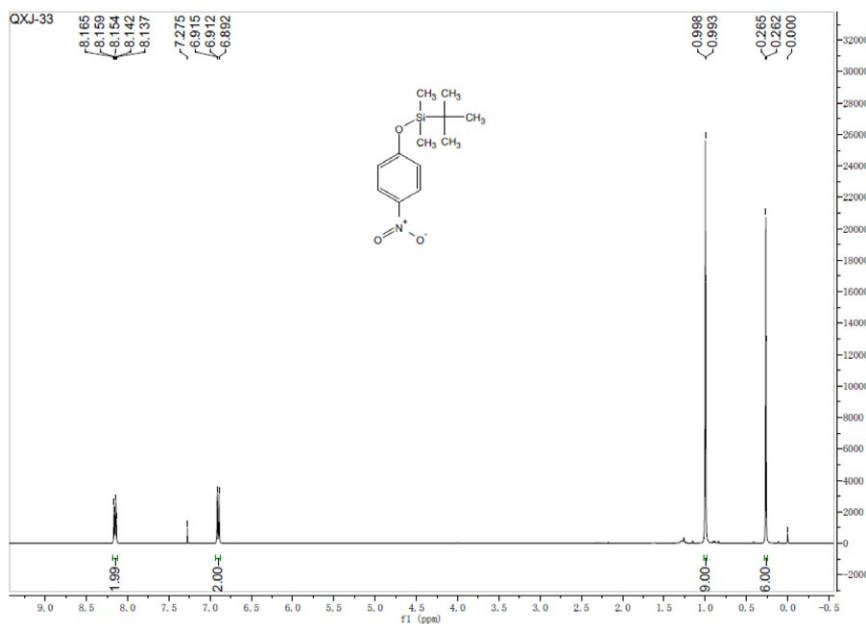


Figure S1. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 1.

*e-mail: guoliang222@gmail.com

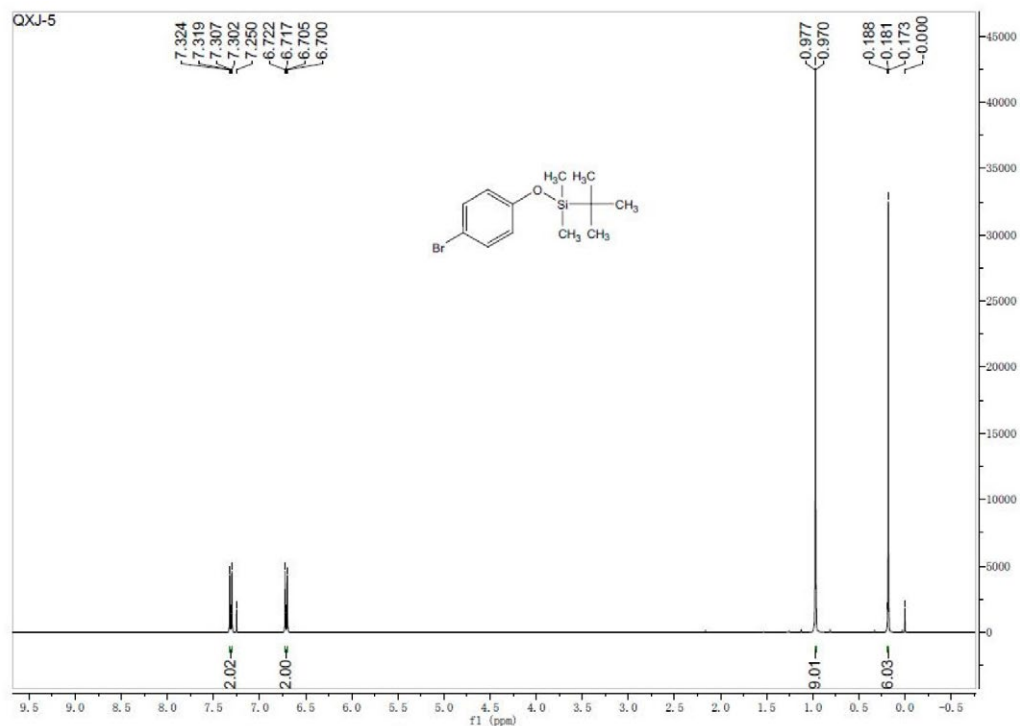


Figure S2. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 2.

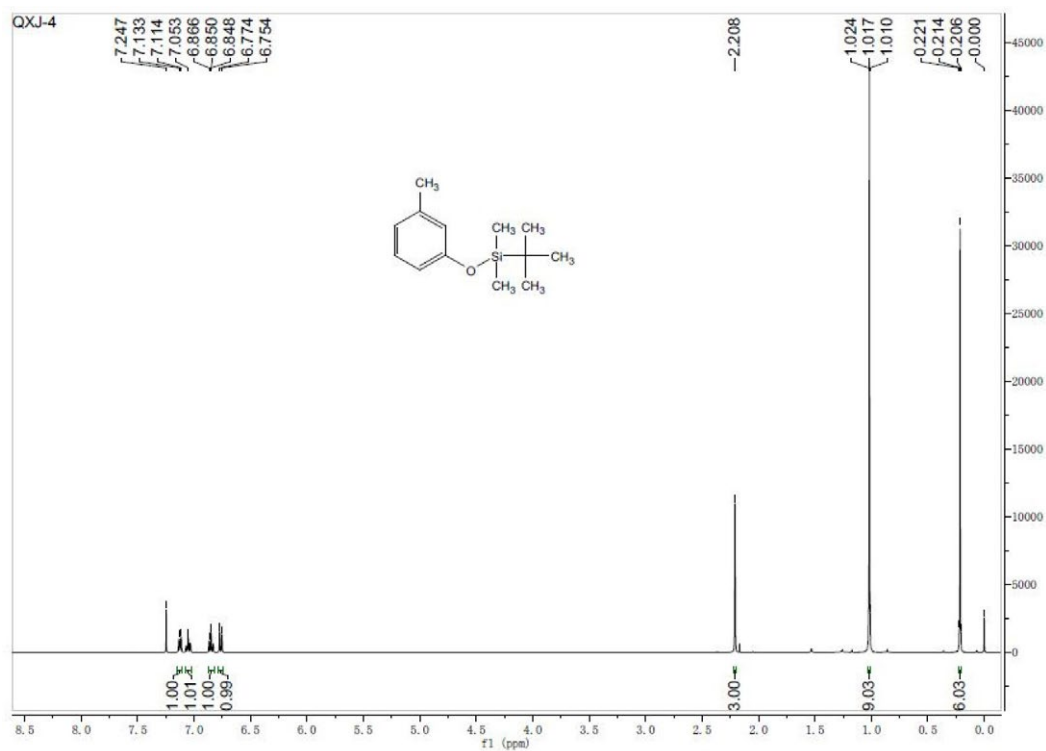


Figure S3. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 3.

Direct Mass Spectrometry Analysis

Analysis Name: 15042924.d
Sample Name: QX-3

Instrument: LC-MSD-Trip-SL
Operator: sl

Print Date: 4/29/2015 7:36:33 PM
Acq. Date: 4/29/2015 7:34:15 PM

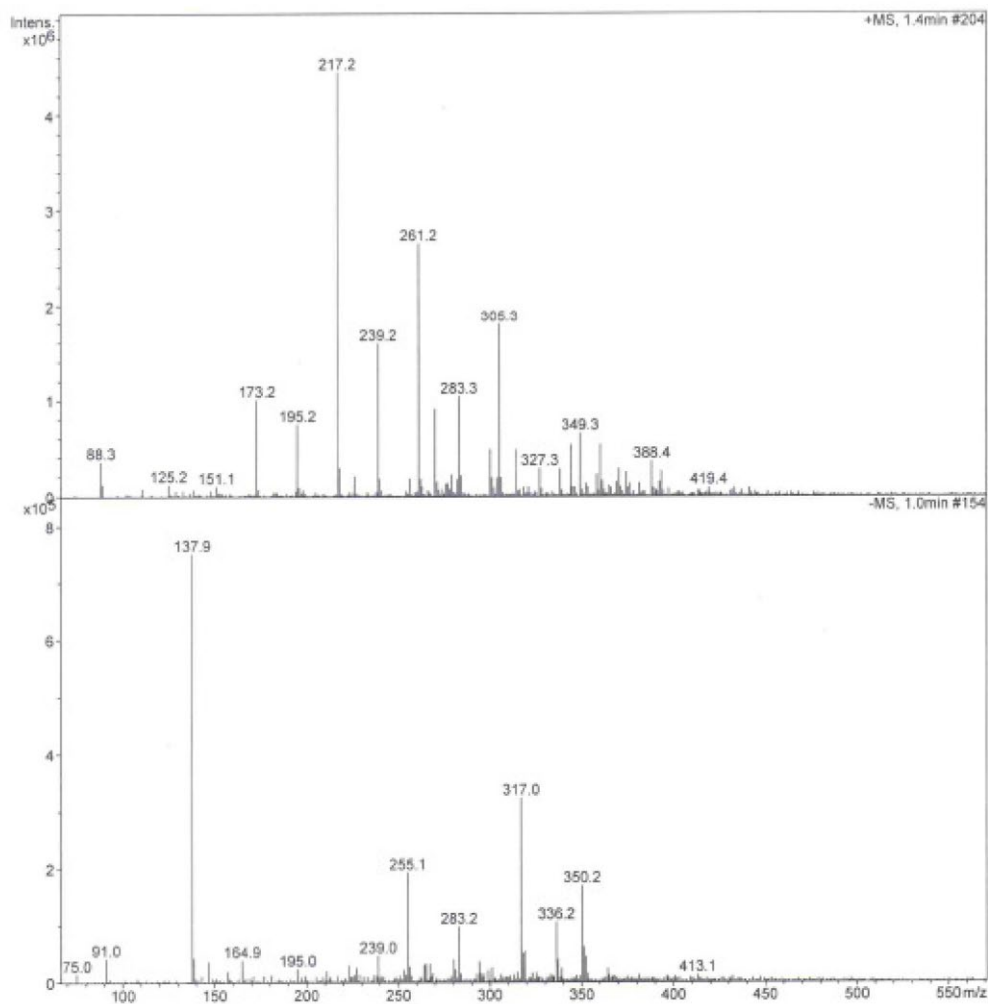


Figure S4. Mass spectrum of compound 3.

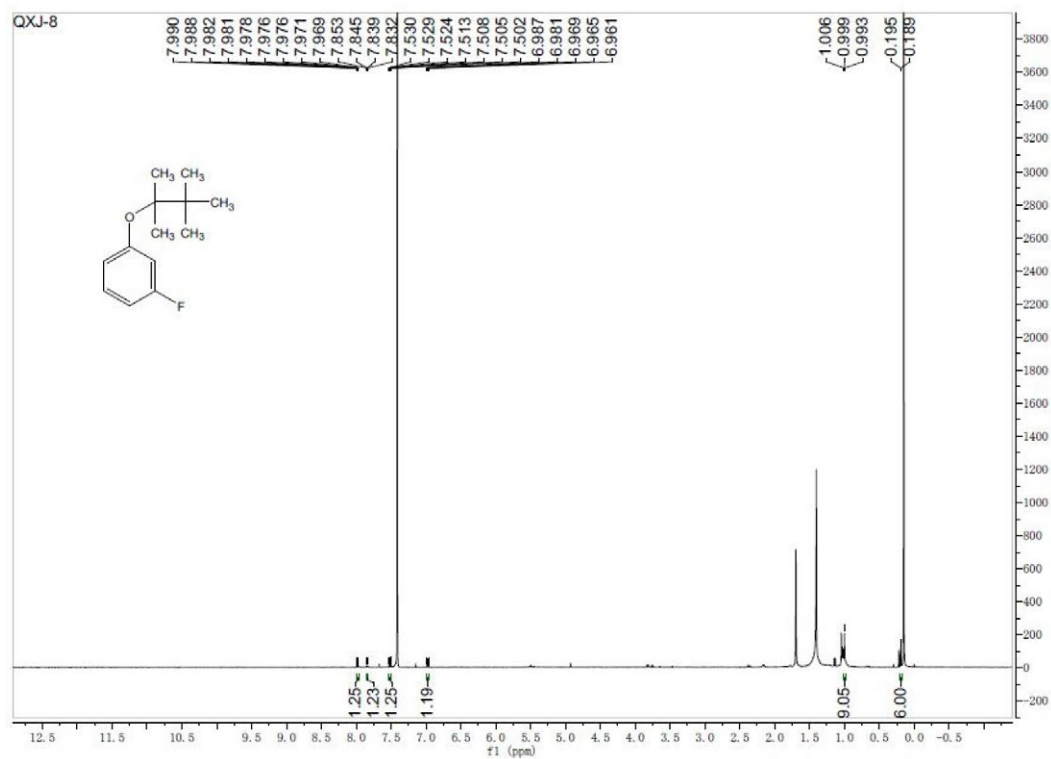


Figure S5. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 4.



Figure S6. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 5.

Direct Mass Spectrometry Analysis

Analysis Name: 15042928.d
Sample Name: QXJ-4

Instrument: LC-MSD-Trip-SL
Operator: sl

Print Date: 4/29/2015 7:51:38 PM
Acq. Date: 4/29/2015 7:48:31 PM

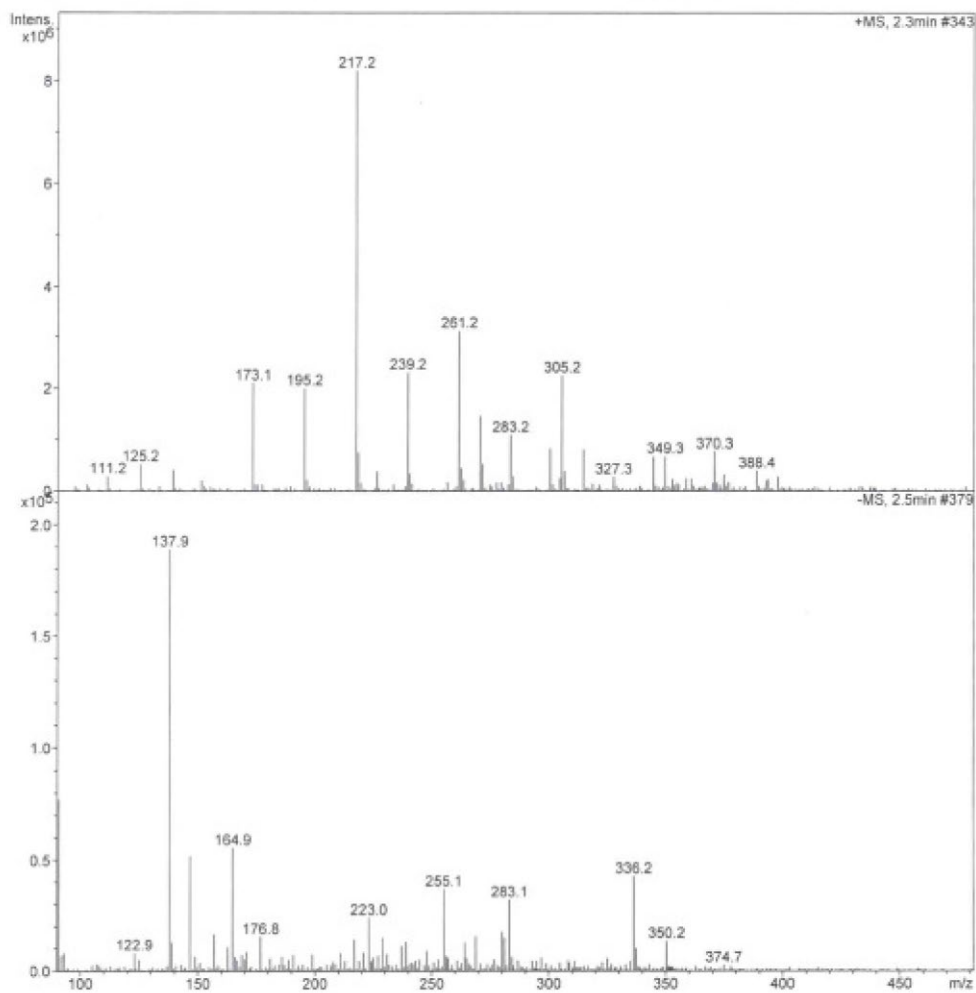


Figure S7. Mass spectrum of compound 5.

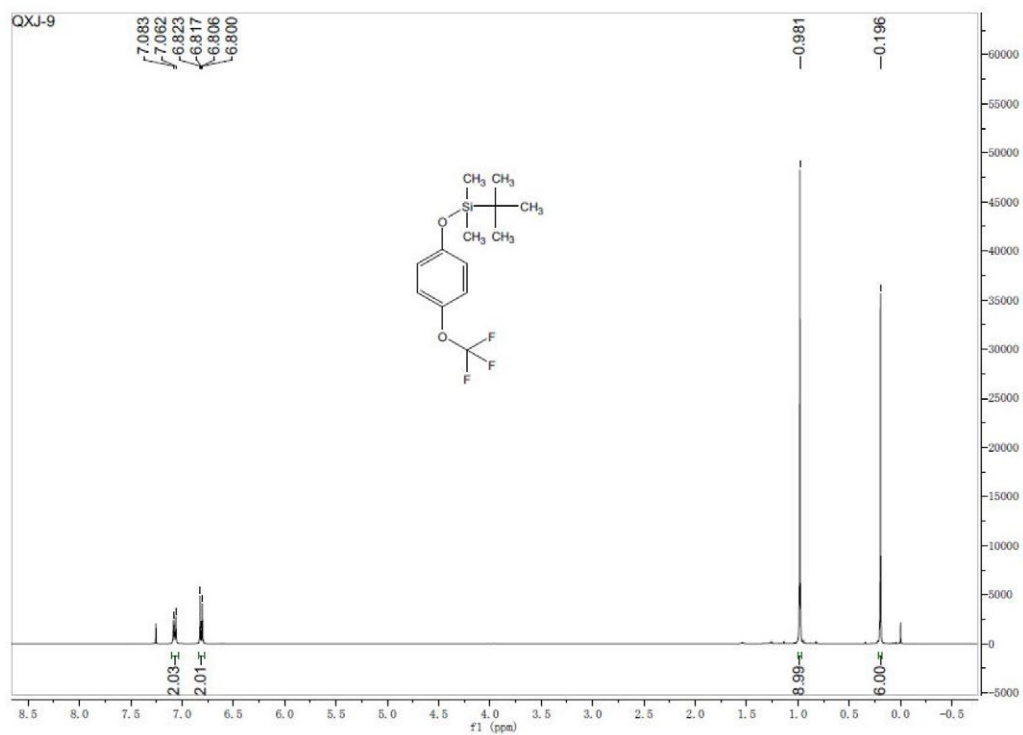


Figure S8. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 6.

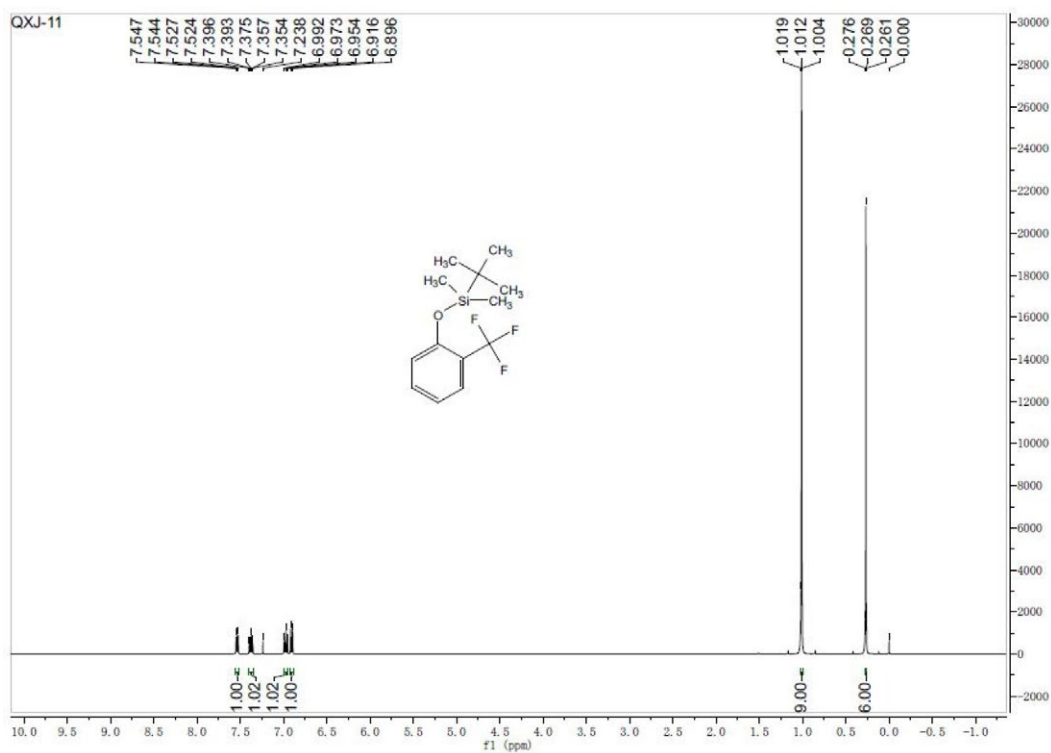


Figure S9. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 7.

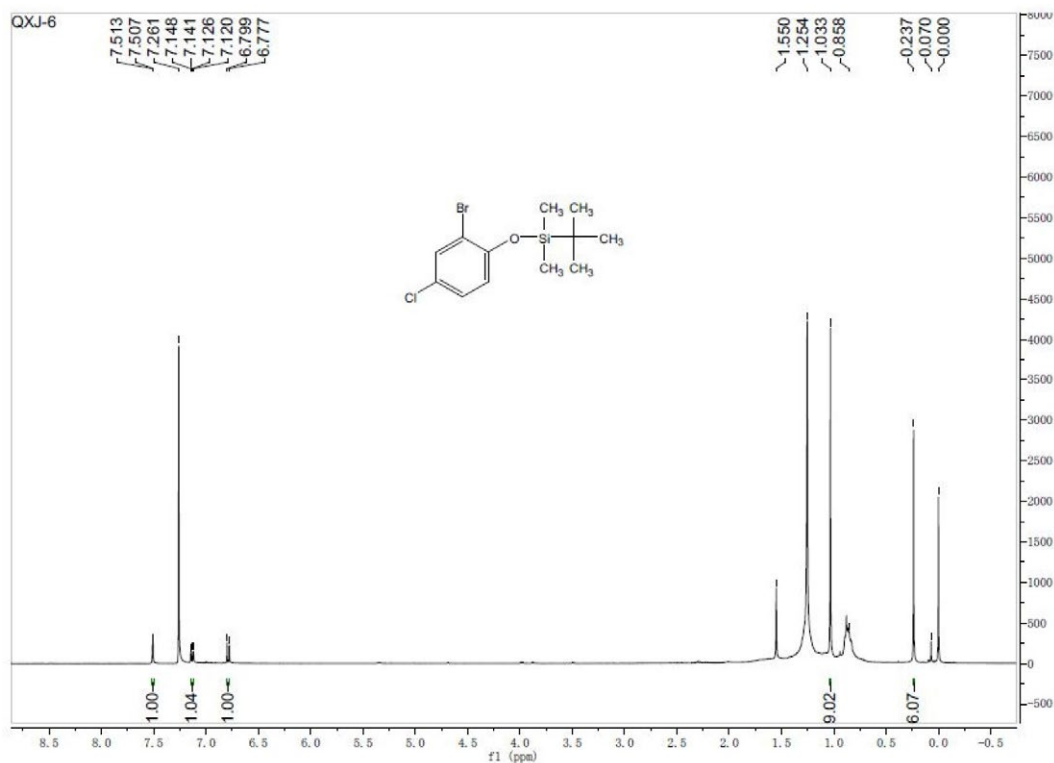


Figure S10. ^1H NMR spectrum (400 MHz, CDCl_3) of compound 8.

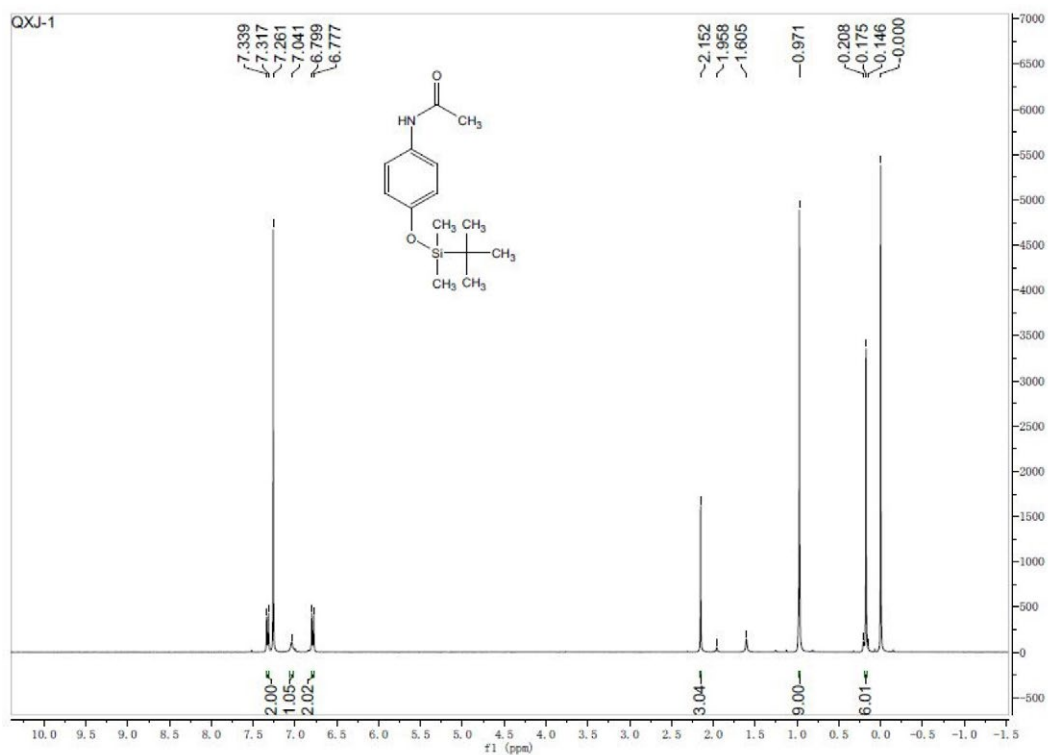


Figure S11. ^1H NMR spectrum (400 MHz, CDCl_3) of compound 9.

Direct Mass Spectrometry Analysis

Analysis Name: 15042918.d
Sample Name: QXJ-1

Instrument: LC-MSD-Trip-SL
Operator: sl

Print Date: 4/29/2015 7:07:57 PM
Acq. Date: 4/29/2015 7:02:50 PM

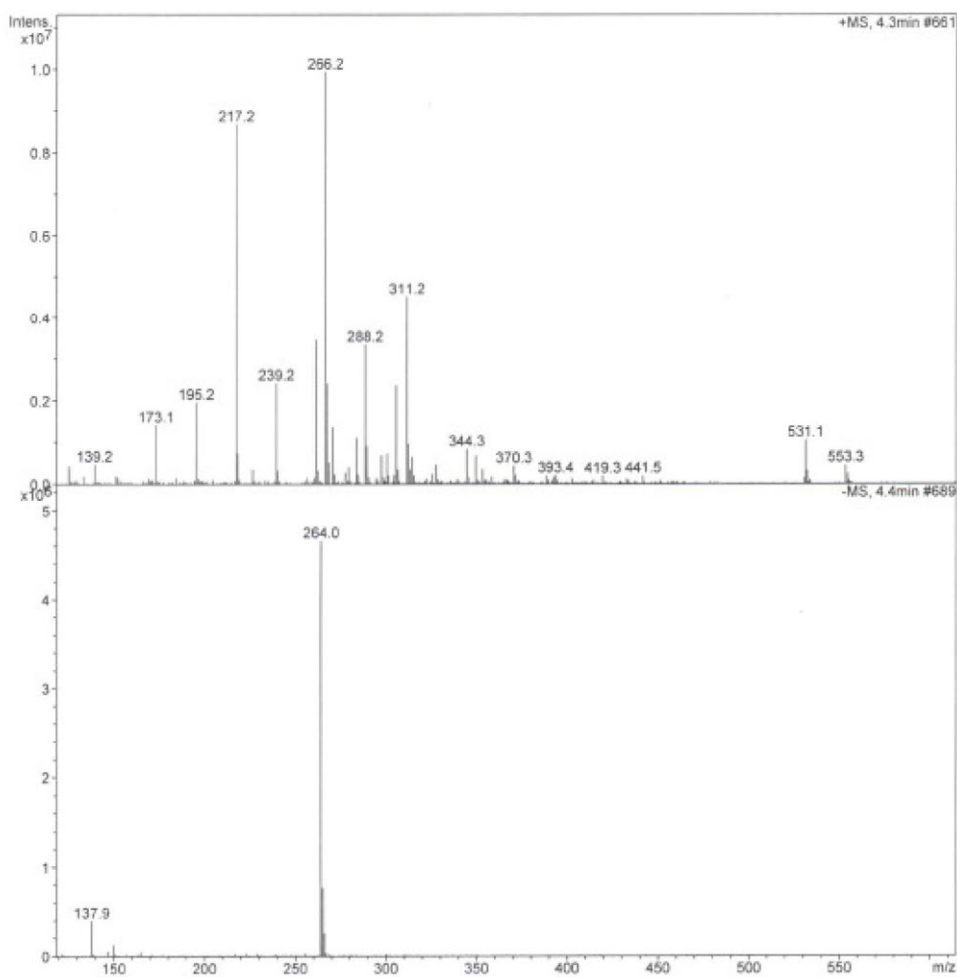


Figure S12. Mass spectrum of compound 9.

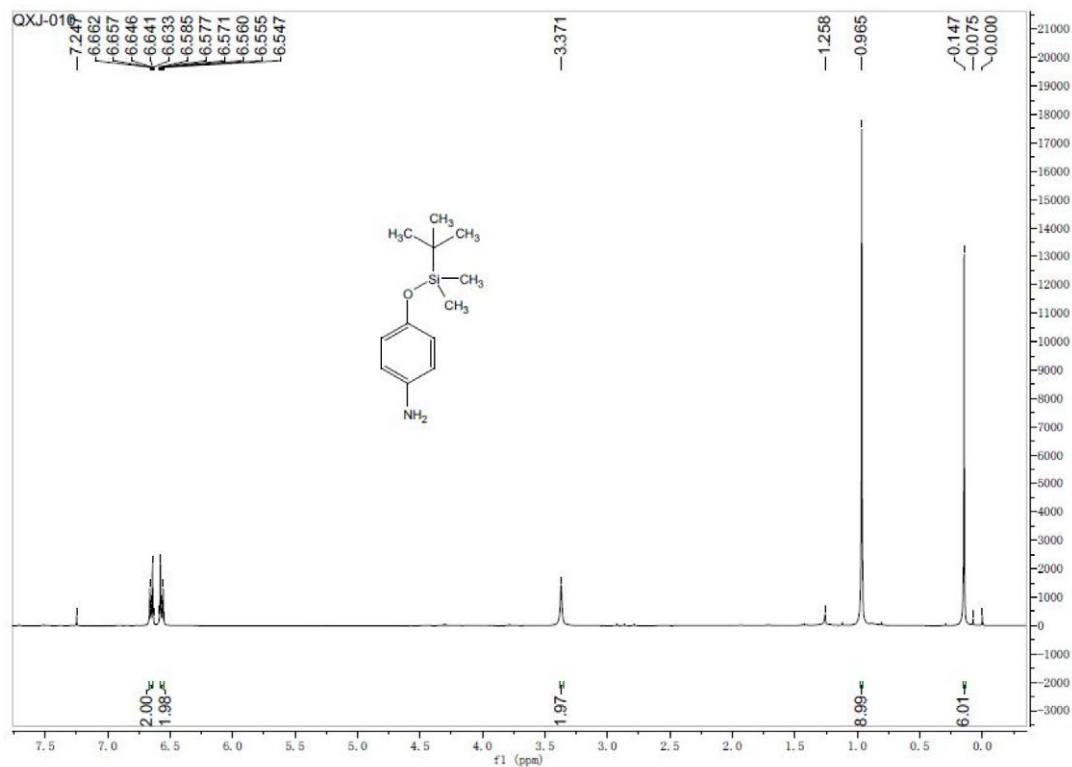


Figure S13. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 10.

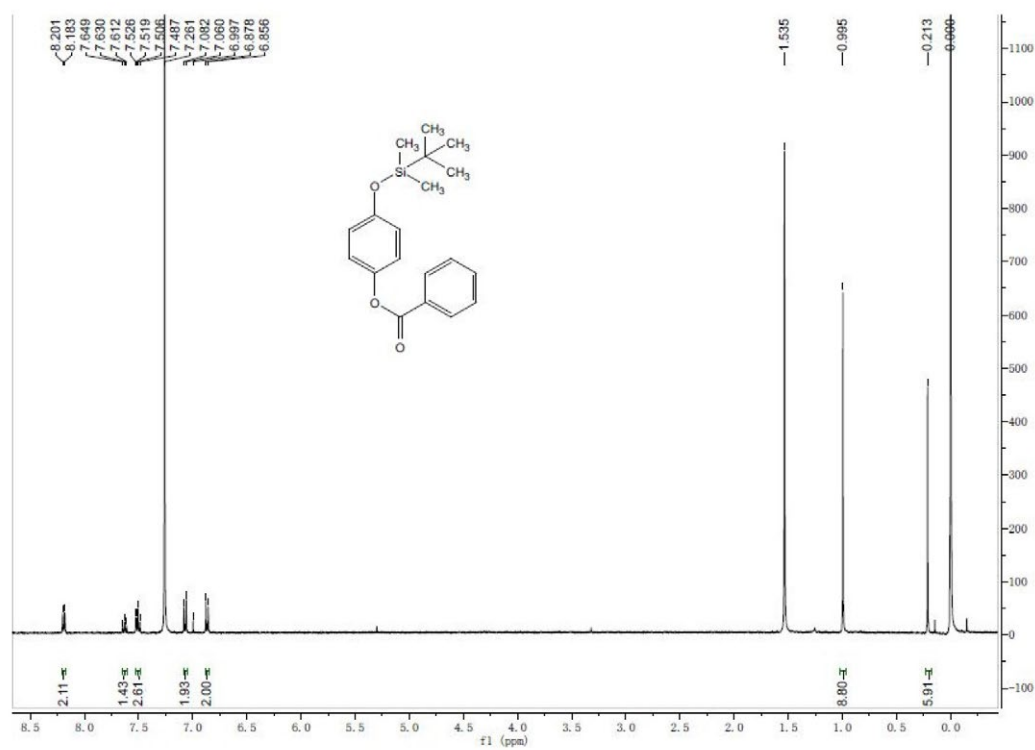


Figure S14. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 11.

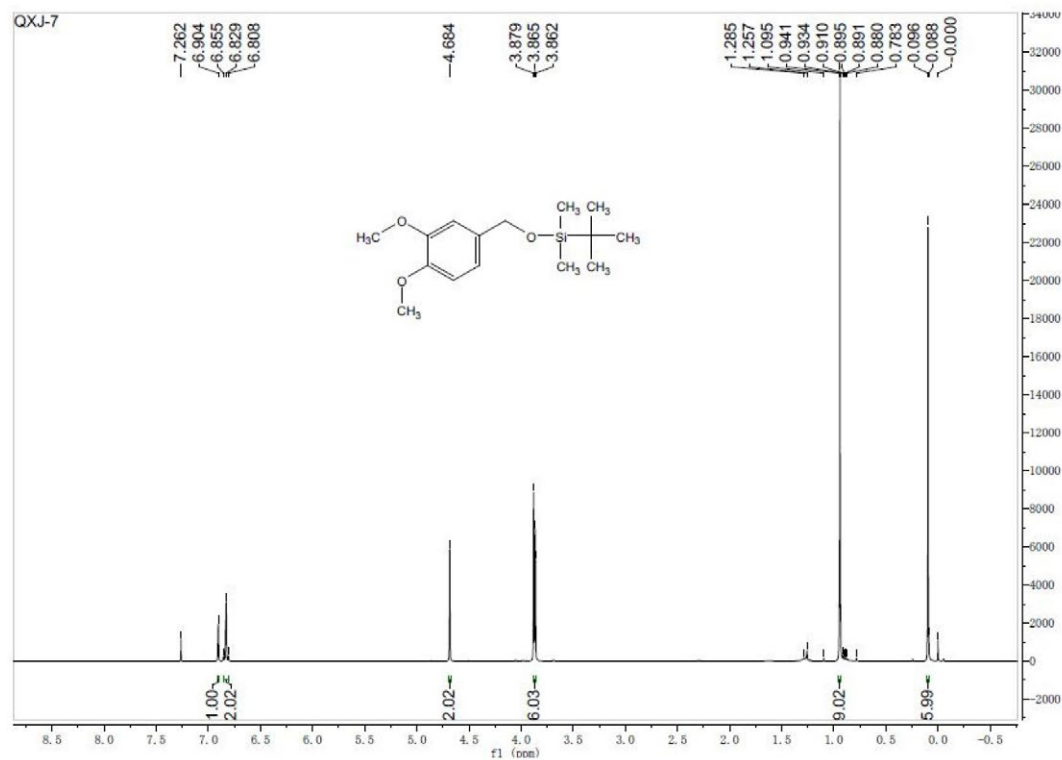


Figure S15. ^1H NMR spectrum (400 MHz, CDCl_3) of compound **12**.

```

nt of window 80: MS Spectrum
-----
ection Date : 5/4/2015 10:04:50 AM      Seq. Line : 41
mple Name   : ZYI-7                    Location  : Vial 41
p. Operator  : MING                     Inj      : 3
                                         Inj Volume: 6 ul
Method      : C:\HPCHEM\1\METHODS\ESIP.M
st changed  : 5/4/2015 10:02:45 AM by MING
              (modified after loading)
Analysis Method: C:\HPCHEM\1\METHODS\ESIP.M
st changed  : 5/4/2015 10:09:23 AM by MING
              (modified after loading)

```

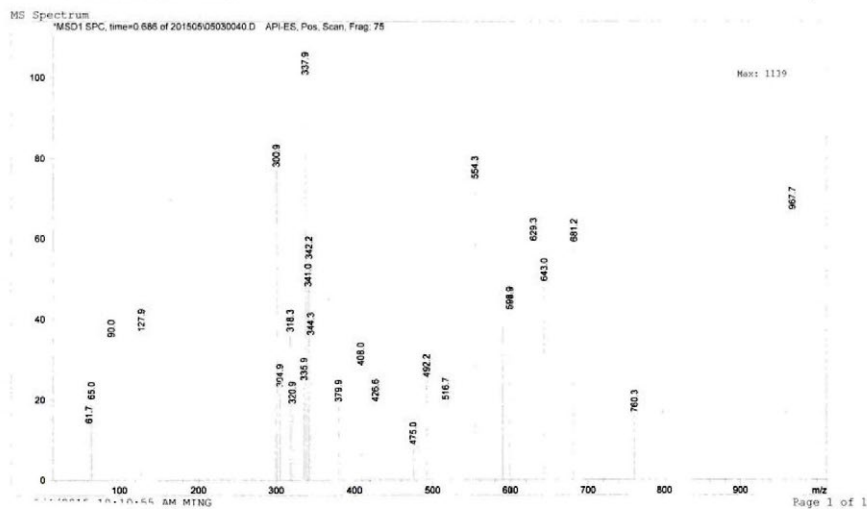


Figure S16. Mass spectrum of compound **12**.

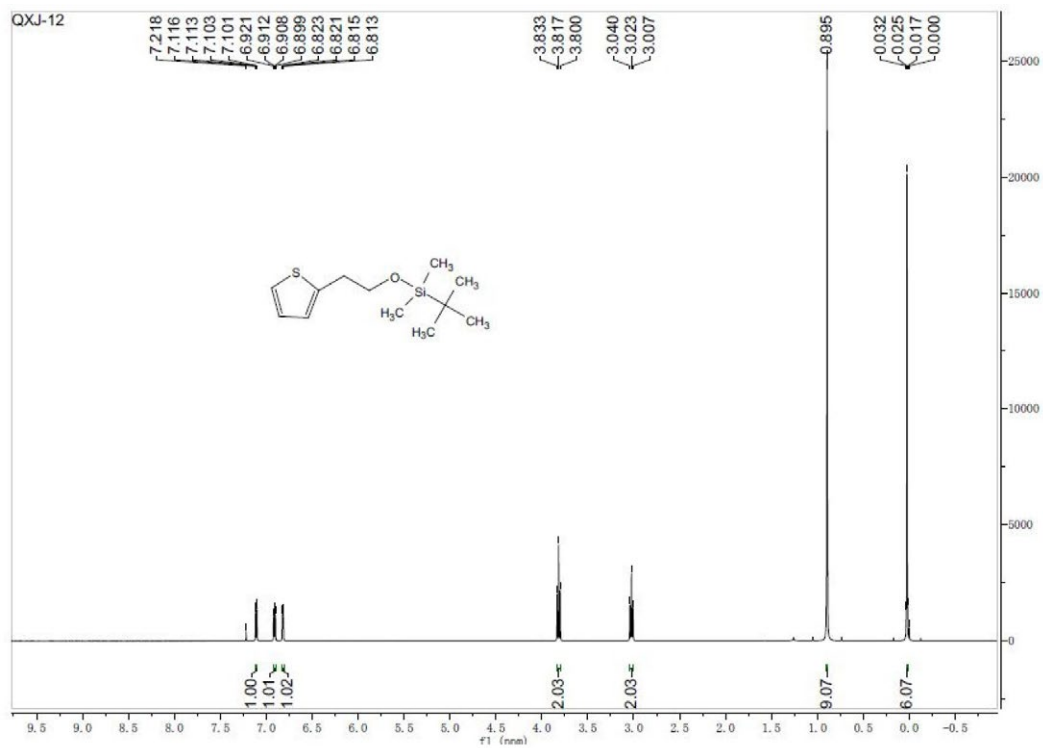


Figure S17. ^1H NMR spectrum (400 MHz, CDCl_3) of compound **13**.