# Supplementary Information

## Quasi-homogeneous catalytic conversion of $CO_2$ to quinazolinones inside metal-organic framework micro-reactor

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## Experimental section

**Materials：** All the reagents were commercially available and used without further purification: chromic nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$, Aladdin, AR), palladium chloride ($PdCl_2$, Aladdin, 98.5%), triphenylphosphine($PPh_3$, J&K, 99%), 2-iodoaniline (Meryer, 97%), tertbutyl isocyanide ($C_4H_9CN$, MΛCKLIN, 98%), dry acetonitrile (MeCN, 3A Chemicals, 99.5%), 1,8-diazabicyclo[5.4.0]undec-7ene (DBU, Innochem, 99%), Ethanol (EtOH, 3A Chemicals, 99.5%), aqueous hydrofluoric acid (HF , Aladdin, 40%), terephthalic acid ($HO_2CC_6H_4CO_2H$, Aladdin, 99%).

**Characterizations Techniques:** Synchrotron powder X-ray diffraction (Synchrotron PXRD) measurements were measured at PD beamline, Australian SYNCHROTRON (ANSTO) with a wavelength of $\lambda = 0.82505$ Å. To confirm the presence of and coordination of P, samples were characterized by Solid-state NMR (Solid state NMR, Bruker, AVANCE III WB 400). Morphologies of samples were characterized by scanning electron microscope (SEM, ZEISS, MERLIN Compact) and transmission electron microscopy (HRTEM, FEI, Talos F200X G2). Metal loadings in the catalysts were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, SpectroBlue). The samples valence state was tested by X-ray photoelectron spectroscopy (XPS, Kratos Analytical Ltd, Axis Ultra DLD). The Brunauer-Emmett-Teller (BET) surface areas were screened by nitrogen adsorption and desorption at 77 K (Quantachrome NOVA-3000 system). Fourier transform infrared spectra (FT-IR) were carried out using the Bruker Alpha. NMR spectra were recorded on a Brooke, USA, AV400 (1H NMR, 400 MHz; 13C NMR, 400 MHz) spectrometer. Data were reported in the following order: chemical shift in ppm (multiplicity was indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet)).

**Synthesis of MIL-101(Cr):** MIL-101(Cr) was prepared by the hydrothermal method reported by Férey et al.[1] A mixture including $Cr(NO_3)_3 \cdot 9H_2O$, $H_2BDC$, HF, $H_2O$ (molar ratio 1.0:1.0:1.0:267) was kept at 220 ˚C for 8 h in a Teflon autoclave. The solid was separated from the solution by centrifugation and washed with deionized water. For further purification, the solid was then washed respectively with DMF, hot ethanol, water, ammonium fluoride solution (30 ml) at 70 ˚C for 24 h. Finally, the solid was dried at 150 ˚C.

**Synthesis of $Pd(PPh_3)_2Cl_2$:** The compound $Pd(PPh_3)_2Cl_2$ were synthesized by the method described in literature.[2] We need an aqueous solution of HCl ($V_{H_2O}$: $V_{HCl}$=1:1). The mixture of triphenylphosphine (177 mg, 1 mmol) and ethanol (10 mL) were added to two-necked flasks and stirred for about 30 min. Then palladium chloride (78 mg, 0.44 mmol) were respectively added to the above two flasks and stirred at 70 ˚C for 5 h. After cooling to room temperature, a yellow solid was precipitated out. The distilled water was then added to the reaction mixture and continuously stirred for 30 min. The mixture was extracted with ether and the organic solvent was removed by rotary distillation to yield a yellow solid. The yellow solid was dissolved in hot ethanol and then distilled water was added for recrystallization.

**Synthesis of *s*-$Pd(PPh_3)_2Cl_2$@MIL-101(Cr):** ***s*-$Pd(PPh_3)_2Cl_2$@MIL-101(Cr)** were synthesized by "ship in a bottle" method described in literature.[3] 200 mg of MIL-101(Cr) and different amounts of $PPh_3$ (60 mg, 80 mg and 120 mg) were placed in a two-necked evacuated flask. Under an argon atmosphere, 3 mL of ethanol was added and stirred at room temperature for 24 h. After centrifugation, the compounds were evacuated at 100 ˚C. Then, an ethanol solution (6 mL) of $PdCl_2$ (0.44 mmol, 78 mg) was added and refluxed at 70 ˚C for 24 h. After Soxhlet extraction, the catalysts were dried under a vacuum at 150 ˚C.

**General procedure for converting $CO_2$ with 2-haloanilines and isocyanides into quinazolinones (3a) by *s*-$Pd(PPh_3)_2Cl_2$@MIL-101(Cr):**

In a 10 mL Schlenk tube, to a mixture of 2-iodoaniline **1a** (0.6 mmol, 1.0 eq.), *tert*-butyl isocyanide **2a** (0.9 mmol, 1.2 eq.), catalyst (1 mol%), were added in 4mL anhydrous MeCN. The system was used $CO_2$ balloon at 50 ˚C (checked by TLC). After 18 h, cooled to room temperature. The system was evaporated under the reduced pressure directly. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluents to afford pure product **3a**.

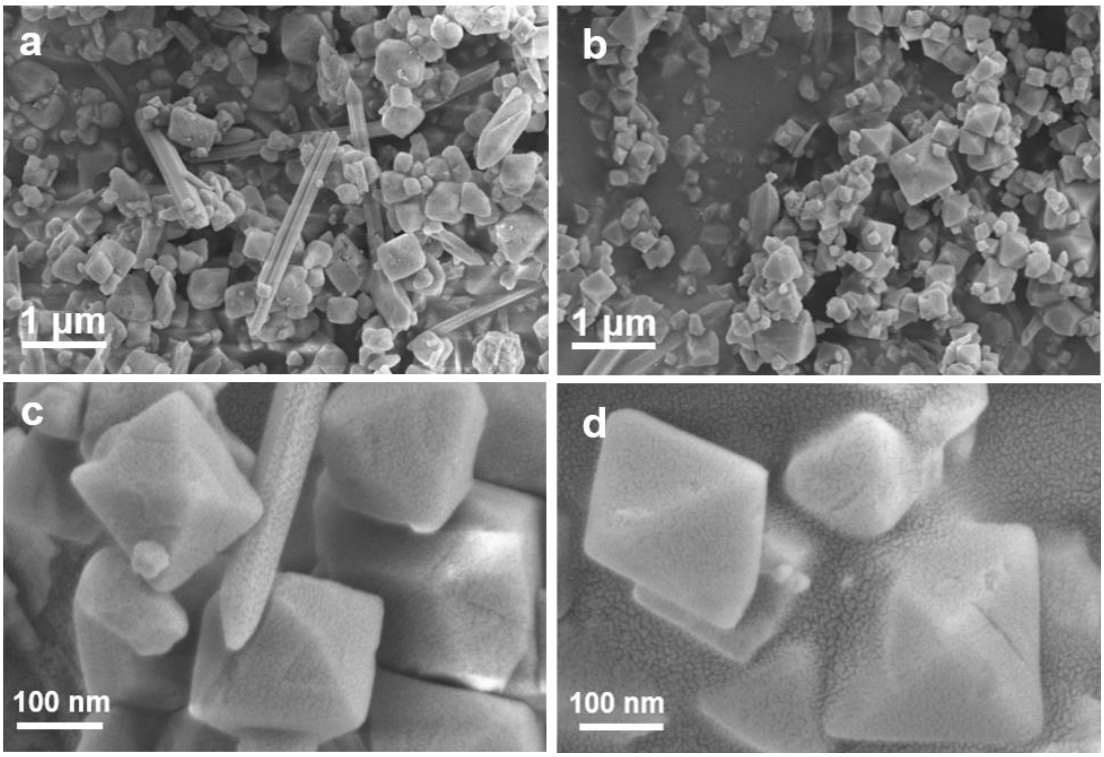



**Figure S1. SEM** a and c Fresh ***s*-Pd(PPh$_3$)$_2$Cl$_2$**@MIL-101, b and d Recycled ***s*-Pd(PPh$_3$)$_2$Cl$_2$**@MIL-101

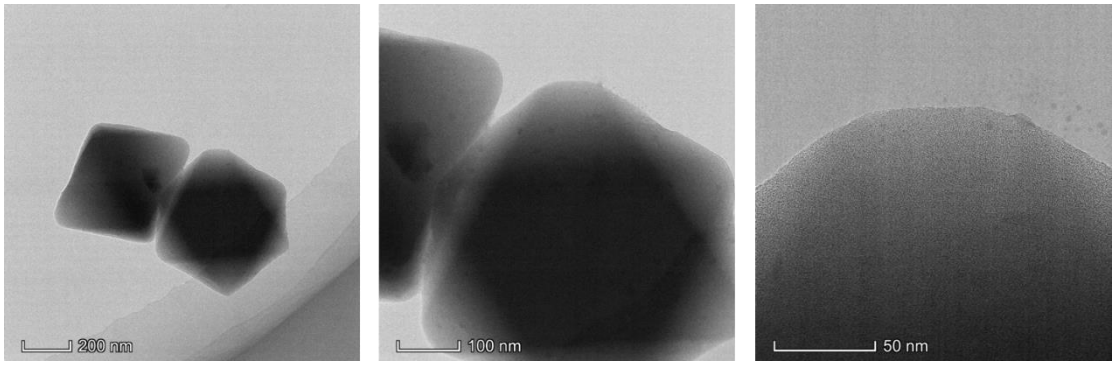



**Figure S2. TEM** image of different sizes of ***s*-Pd(PPh$_3$)$_2$Cl$_2$**@MIL-101 after five times recycling tests.

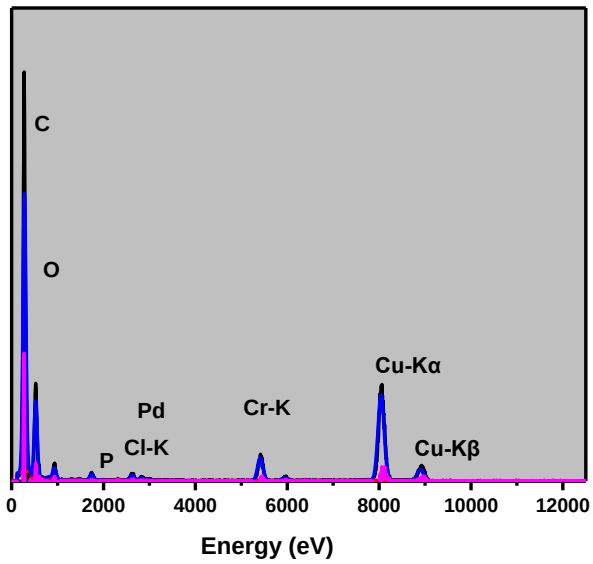



**Figure S3. EDS** image of ***s*-Pd(PPh$_3$)$_2$Cl$_2$**@MIL-101 after five times recycling tests.

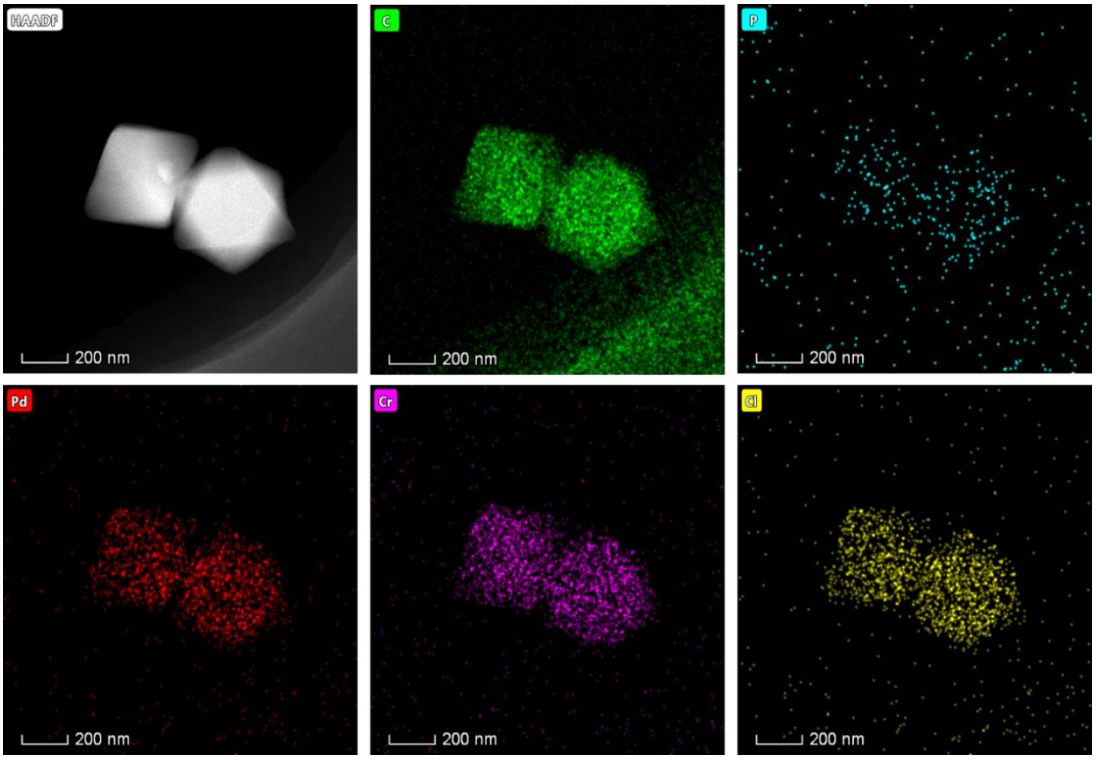



**Figure S4**. **Mapping** image of ***s*-Pd(PPh$_3$)$_2$Cl$_2$**@MIL-101 after five times recycles.

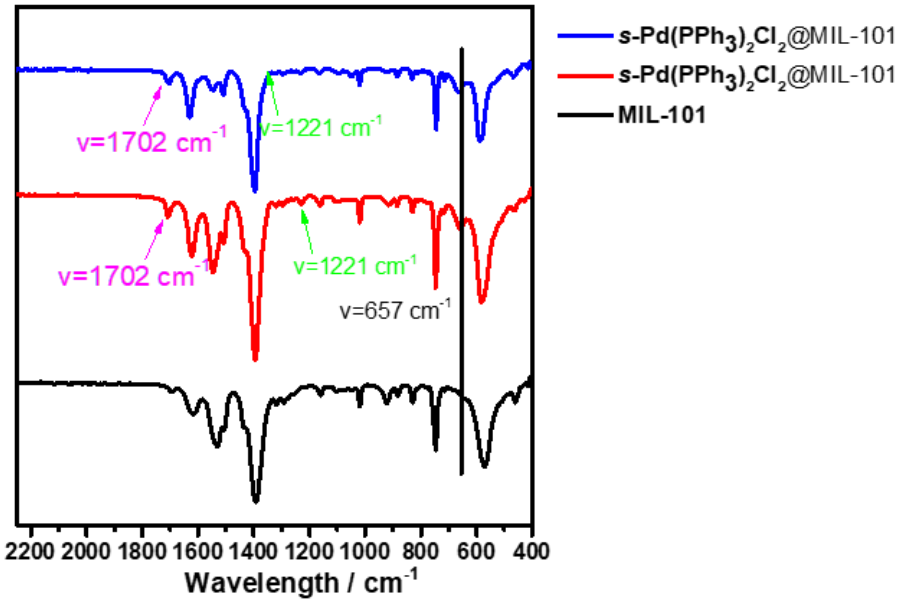



**Figure S5. FT-IR** for MIL-101(Cr), the red line is fresh ***s*-Pd(PPh3)2Cl2**@MIL-101 and the blue line recycled ***s*-Pd(PPh3)2Cl2**@MIL-101.

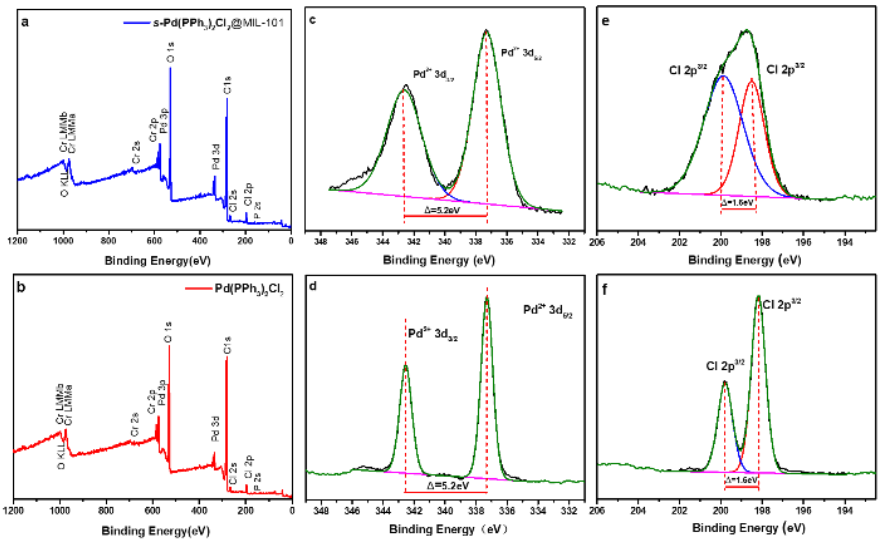



**Figure S6.** a) The XPS full spectrum of ***s*-Pd(PPh3)2Cl2**@MIL-101, b) The XPS full spectrum of pure $Pd(PPh_3)_2Cl_2$, c) after encapsulation of Pd spectrum, d) Pd spectrum, e) after encapsulation of Cl spectrum, f) after encapsulation of Cl spectrum.

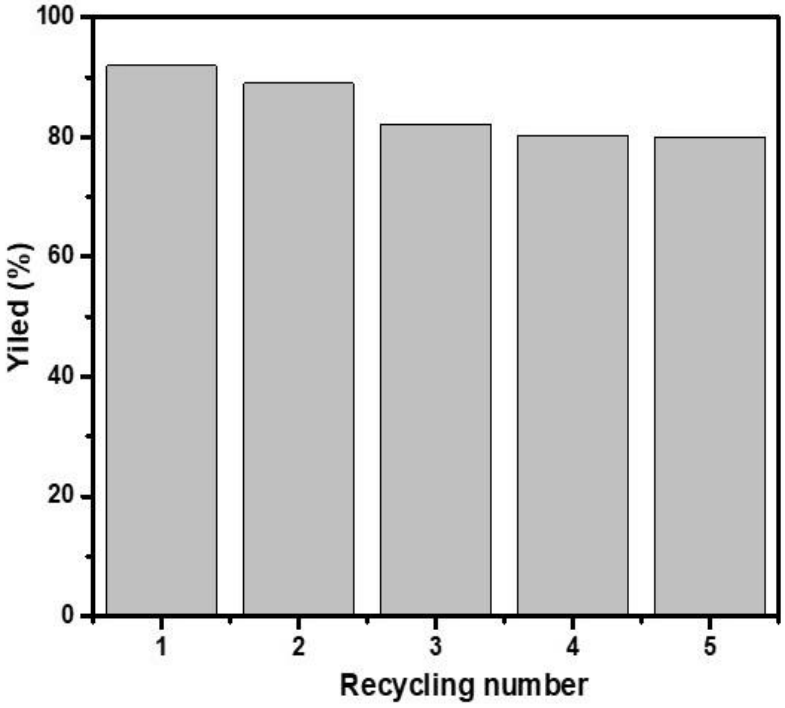



**Figure S7.** Recycling tests of the catalyst **1** for the cycloaddition of epoxides with $CO_2$.

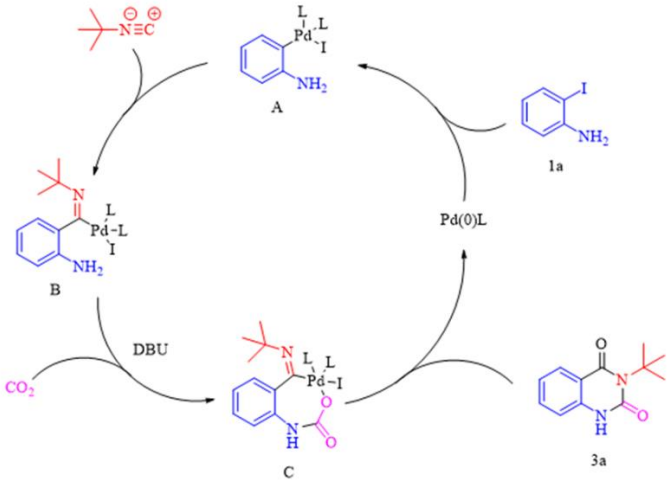



**Figure S8.** Proposed mechanism for the reaction of $CO_2$ with 2-haloanilines and isocyanides.

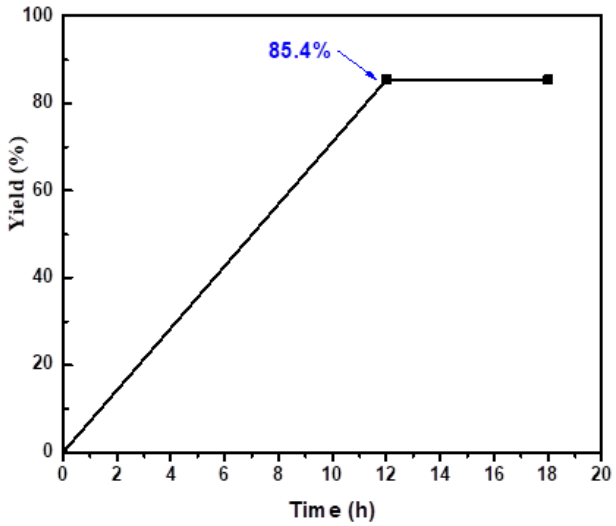
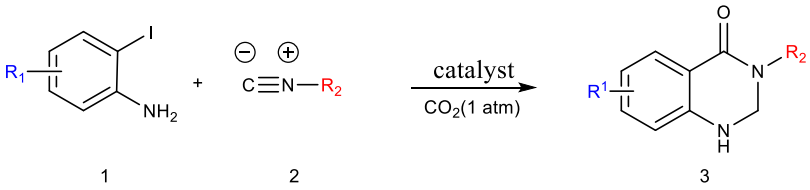



**Figure S9.** Hot filtration test results.

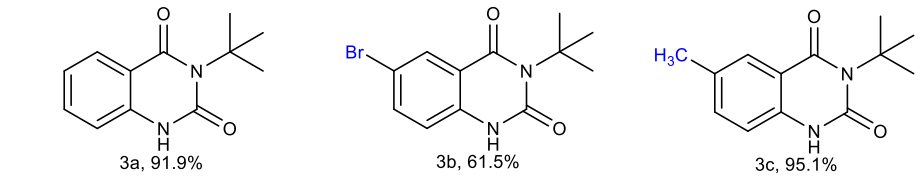
**Table S1.** The content of Pd (wt%) given by ICP measurements.

| Samples | The content of Pd (wt%) | The content of P (wt%) |
|---|---|---|
| Fresh cat 1 | 4.65 | 2.74 |
| Recycled cat 1 | 4.29 | 2.46 |

**Table S2.** Substrate scope




1 2 3



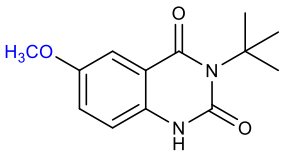

3a, 91.9%



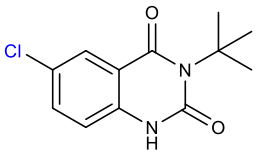

3b, 61.5%



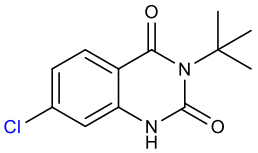

3c, 95.1%



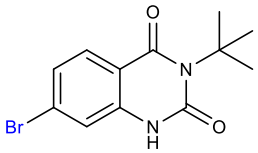

3d, 97.9%



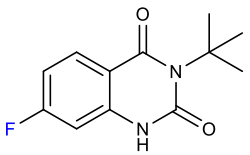

3e,71.9%



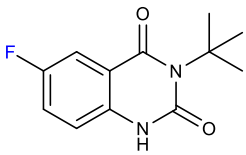

3f, 89.0%



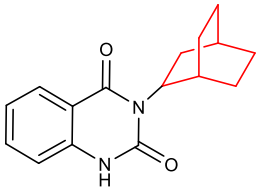

3g, 83.3%



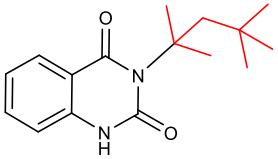

3h, 82.7%



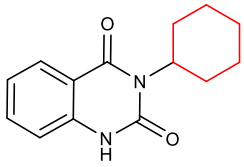

3i, 89.7%




4a, (88.0%)




4b, (59.8%)

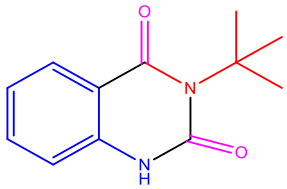



4c, (trace)

Substrate scope of O-iodoaniline and isocyanide. Reaction conditions: **1** (0.60 mmol), **2** (0.90 mmol), catalyst (0.1%), base (0.1 eq.), solvent (4 ml), Schlenk tube, $CO_2$ balloon, 50°C, 18h. All the yield is given by TLC.

**Product Characterization**

**3-(*tert*-butyl)quinazoline-2,4(1*H*,3*H*)-dione (3a)**

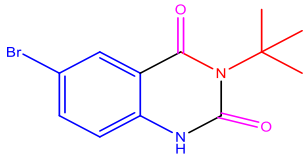


**Yield**: 91.9% (119.6 mg isolated).White solid.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 9.92 (s, 1H), 8.02 (d, 1H), 7.57 –7.52 (m, 1H), 7.18 –7.14 (m, 1H), 6.99 (d, 1H), 1.80 (s, 9H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$164.6, 153.5, 138.5, 134.8, 128.6, 123.3, 117.5, 114.4, 62.5, 30.4 ppm.

**6-bromo-3-(*tert*-butyl)quinazoline-2,4(1*H*,3*H*)-dione (3b)**

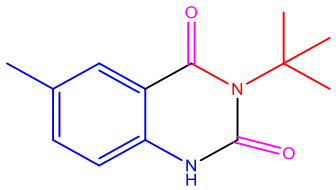


**Yield**: 61.5% (109.2mg isolated).Brown solid.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 10.33 (s, 1H), 8.14 (d, $J$ =4 Hz, 1H), 7.64 (dd, 1H), 6.89 (d, 1H), 1.78 (s, 9H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 162.9, 152.9, 137.2, 136.9, 130.6, 118.4, 115.8, 115.3, 62.5, 29.8 ppm.

**3-(*tert*-butyl)-6-methylquinazoline-2,4(1*H*,3*H*)-dione (3c)**

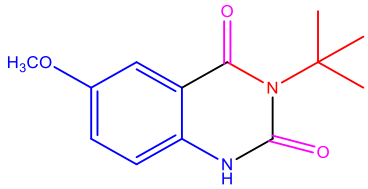


**Yield**: 95.1% (131.8 mg isolated).Gray solid.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$10.35 (d, 1H), 7.80 (s, 1H), 7.35 (dd, 1H), 6.91 (d, $J$ =8 Hz, 1H), 2.36 (s, 3H), 1.79 (s, 9H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 164.4, 153.3, 135.9, 135.3, 132.4, 127.6, 116.7, 113.9, 61.9, 29.9, 20.7 ppm.

**3-(*tert*-butyl)-6-methoxyquinazoline-2,4(1*H*,3*H*)-dione (3d)**

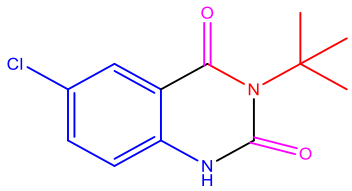


**Yield**: 97.9% (145.0 mg isolated). Brown solid.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 10.53 (s, 1H), 7.45 (s, 1H), 7.15 (dd, 1H), 6.95 (d, 1H), 3.83 (s, 3H), 1.80 (s, 9H) ppm.

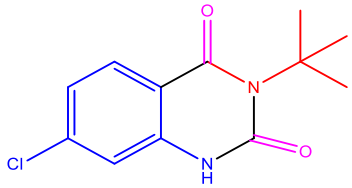
**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 164.3, 155.4, 155.3, 132.3, 123.9, 117.3,115.6, 108.6, 62.1, 55.7, 30.0 ppm.

**3-(*tert*-butyl)-6-chloroquinazoline-2,4(1*H*,3*H*)-dione (3e)**



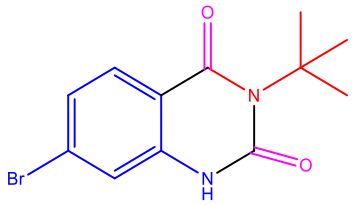

**Yield**:71.9% (108.1 mg isolated).Gray solid.
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$10.07 (s, 1H), 7.98 (d, 1H), 7.49 (dd , 4 Hz, 1H), 6.95 (d, 1H), 1.78 (s, 9H) ppm.
**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 163.1, 152.8, 136.4, 134.4, 128.3, 127.6, 118.0, 115.5, 62.4, 29.8 ppm.

**3-(*tert*-butyl)-7-chloroquinazoline-2,4(1*H*,3*H*)-dione (3f)**



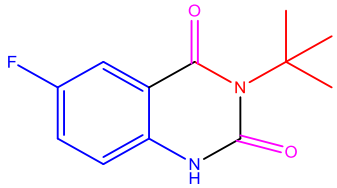

**Yield**: 89% (133.9 mg isolated). Yellow solid.
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 10.6 (m, 1H), 7.94 (d, 1H), 7.12 (dd, 1H), 7.00 (t, $J$ = 4 Hz, 1H), 1.79 (s, 9H) ppm.
**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 163.5, 153.4, 140.5, 139.0, 129.6, 123.4, 115.4, 113.9, 62.5, 30.0 ppm.

**7-bromo-3-(*tert*-butyl)quinazoline-2,4(1*H*,3*H*)-dione (3g)**




**Yield**: 83.3% (148.1 mg isolated). Brown solid.
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 9.89 (m, 1H), 7.86 (d, 1H), 7.30 – 7.26 (m, 1H), 7.17 (d, 1H), 1.80 (s, 9H) ppm.
**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 163.6, 153.1, 138.9, 129.6, 128.9, 126.3, 116.9, 115.8, 62.5, 29.9 ppm.

**3-(*tert*-butyl)-6-fluoroquinazoline-2,4(1*H*,3*H*)-dione (3h)**

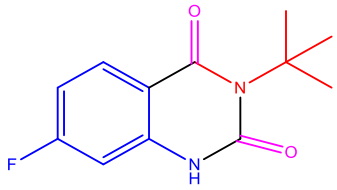



**Yield**: 82.7% (117.0 mg isolated). Brown solid.
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 10.68(s, 1H), 7.69 (d, 1H), 7.01 (td, 1H), 6.99 (dd, 1H), 1.79 (s, 9H) ppm.
**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 163.4, 158.3, 153.5, 134.5, 122.4, 118.0, 115.8, 113.5,

62.4, 29.9 ppm.

**$^{19}$F NMR** (376 MHz, Chloroform-d) δ -118.84 – -118.99 (m).

**3-(*tert*-butyl)-7-fluoroquinazoline-2,4(1*H*,3*H*)-dione (3i)**



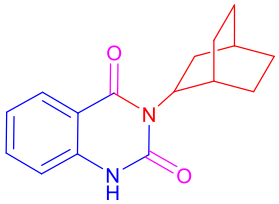

**Yield**: 89.7% (127.0 mg isolated).Brown solid.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) *δ* 10.88 (s, 1H), 8.01 (dd, 1H), 6.86 (td, 1H), 6.69 (dd, 4 Hz, 1H), 1.78 (s, 9H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) *δ* 167.7, 163.4, 153.7, 140.0, 131.0, 113.5, 111.0 , 100.6, 62.4, 30.0 ppm.

**$^{19}$F NMR** (376 MHz, Chloroform-d) δ -102.54 – -102.81 (m).

**3-(adamantan-1-yl)quinazoline-2,4(1H,3H)-dione (4a)**

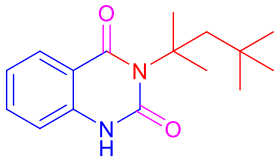



**Yield**:88.0% (156 mg isolated).White solid.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.99 (d, *J* = 8.0, 1.4 Hz, 1H), 7.62 – 7.39 (m, 1H), 7.18 – 7.08 (m, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 2.64 (d, *J* = 3.0 Hz, 6H), 2.18 (s, 3H), 1.76 (dd, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 164.59 , 152.44 , 137.97 , 134.33 , 128.37 , 122.94 , 117.62 , 113.71 , 65.75 , 40.31 , 36.59 , 30.82 ppm.

**3-(2,4,4-trimethylpentan-2-yl)quinazoline2,4(1H,3H)-dione(4b)**




**Yield**: 59.8% (98.7mg isolated).Yellow solid.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 10.76 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 0H), 7.60 – 7.43 (m, 0H), 7.19 – 7.11 (m, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 2.25 (s, 2H), 1.89 (s, 6H), 1.03 (s, 9H). ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 164.75 , 153.94 , 138.31 , 134.48 , 128.35 , 122.92 , 117.01 , 114.10 , 66.60 , 51.34 ,32.11, 31.99, 31.43.ppm.

# References

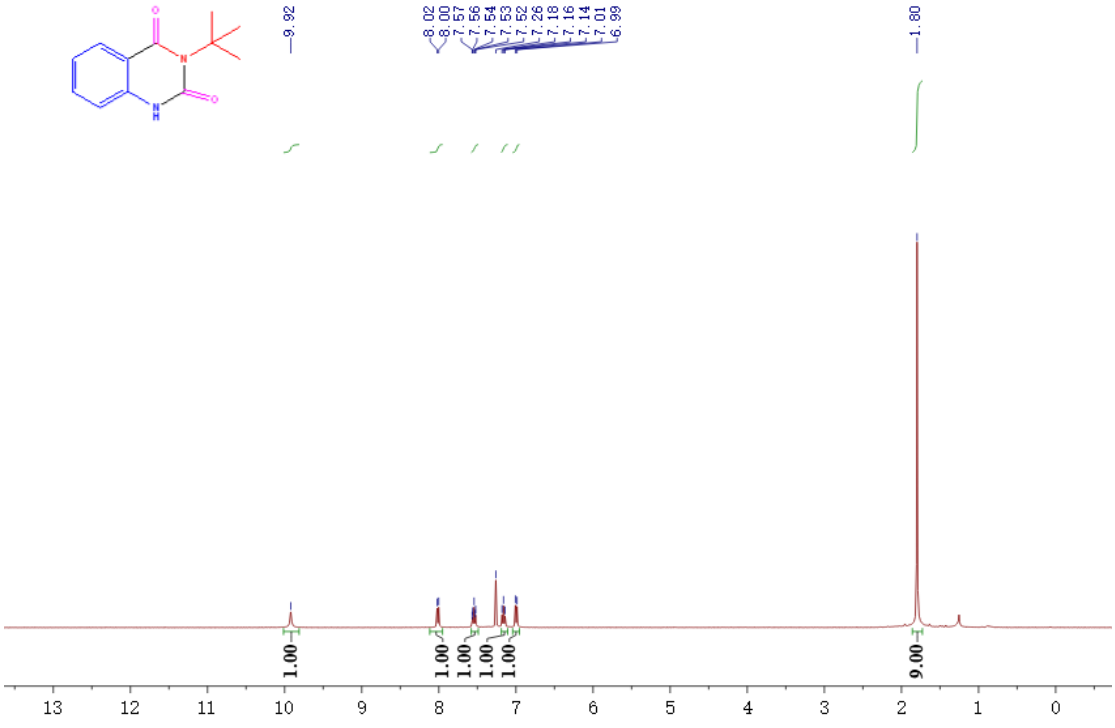

[1] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* **2005**, *309*, 2040-2042.

[2] J. Pons, J. Garcı´a-Anto´n, X. Solans, M. Font-Bardia, J. Ros, *Acta. Cryst.* **2008,** *64,* M621-U163.

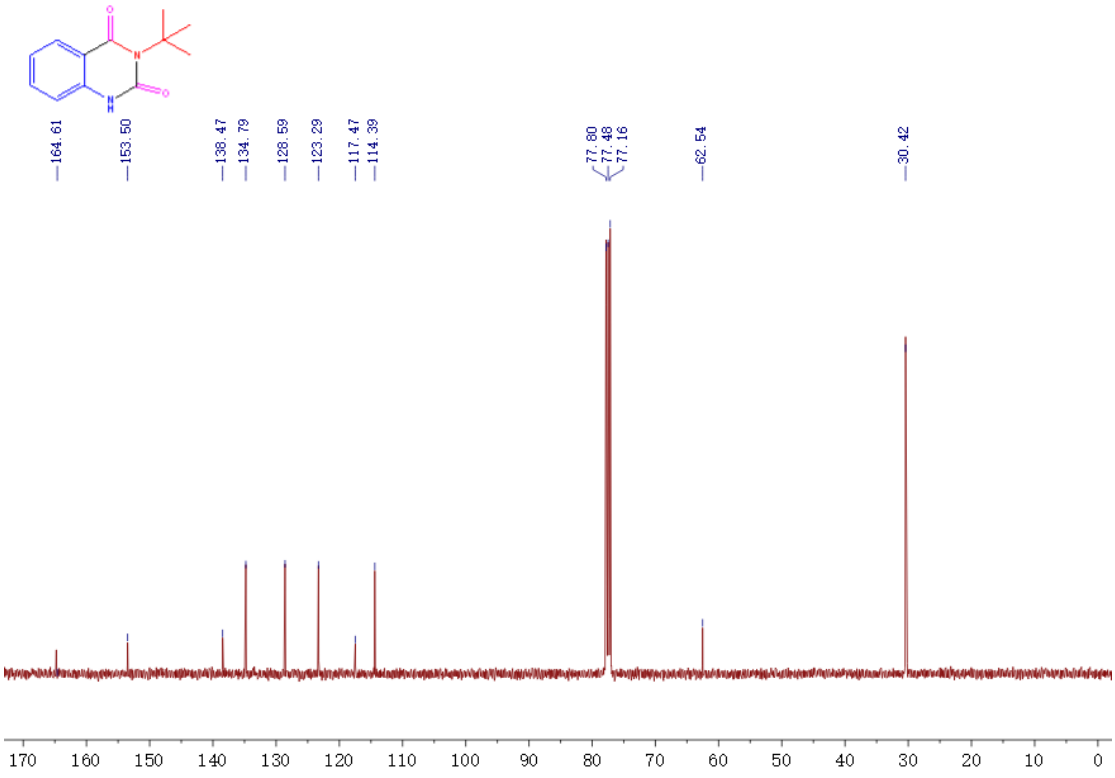
[3] J.-L. Peng, J.-J. Zhao, Z.-W. Hu, D.-D. Liang, J.-B. Huang, Q. Zhu, *Org. Lett.* **2012**, 14, 4966-4969.

# Copies of $^{1}$H NMR and $^{13}$C NMR Spectra

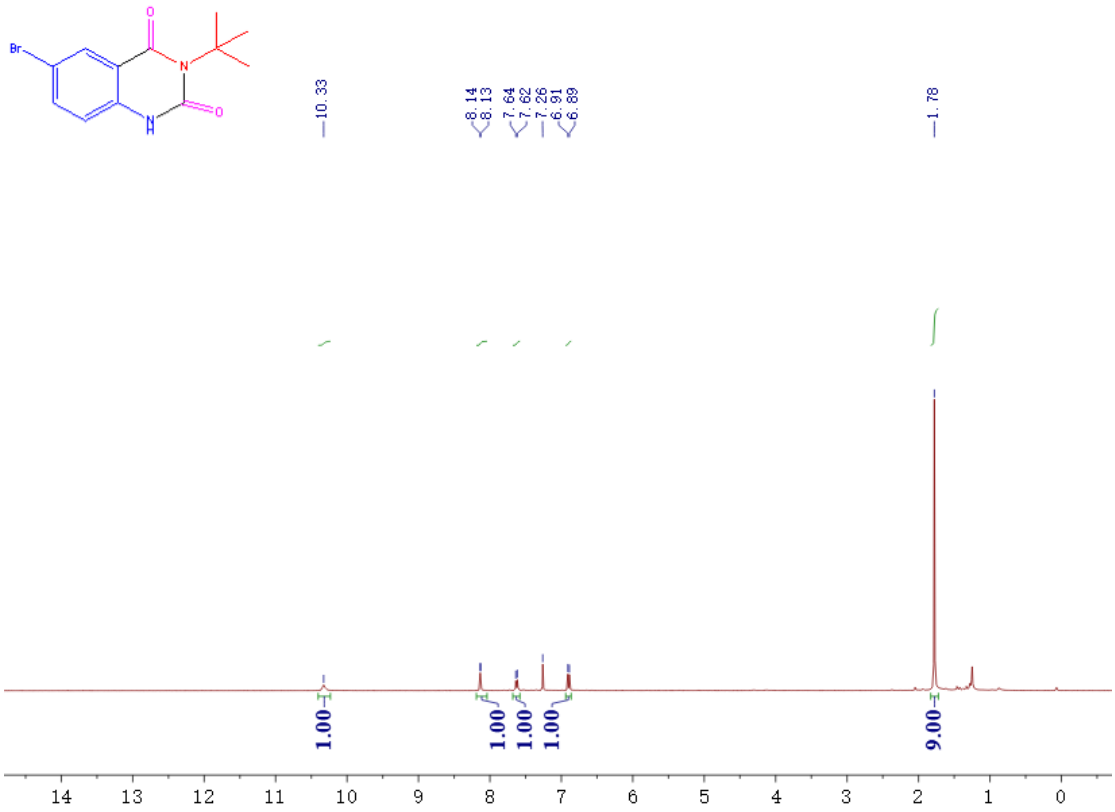
$^{1}$H NMR Spectra of **3a** in $CDCl_3$



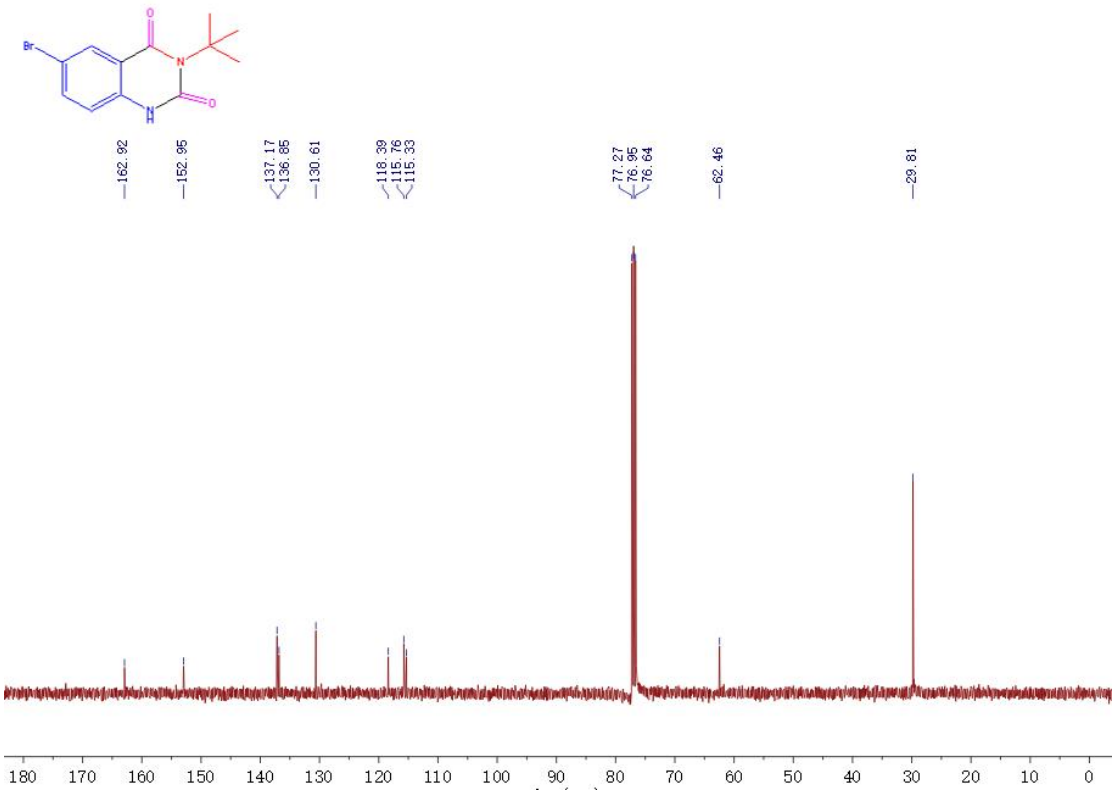

$^{13}$C NMR Spectra of **3a** in $CDCl_3$



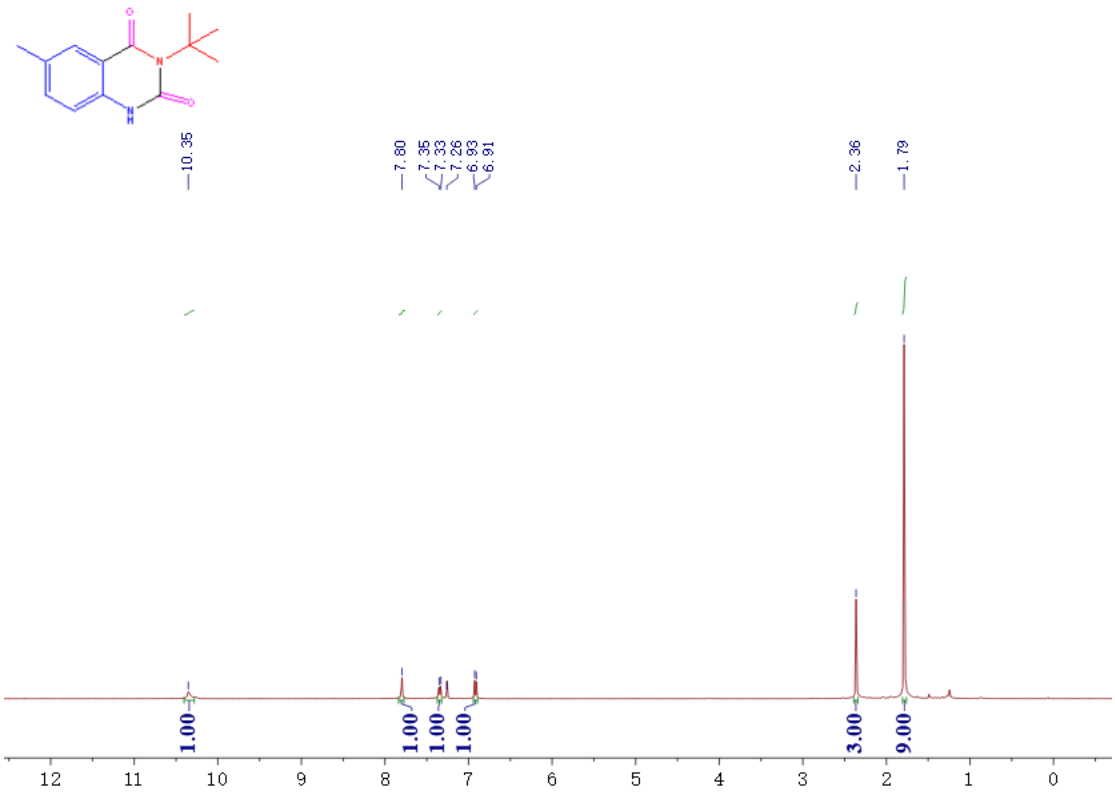
$^{1}$H NMR Spectra of **3b** in $CDCl_3$



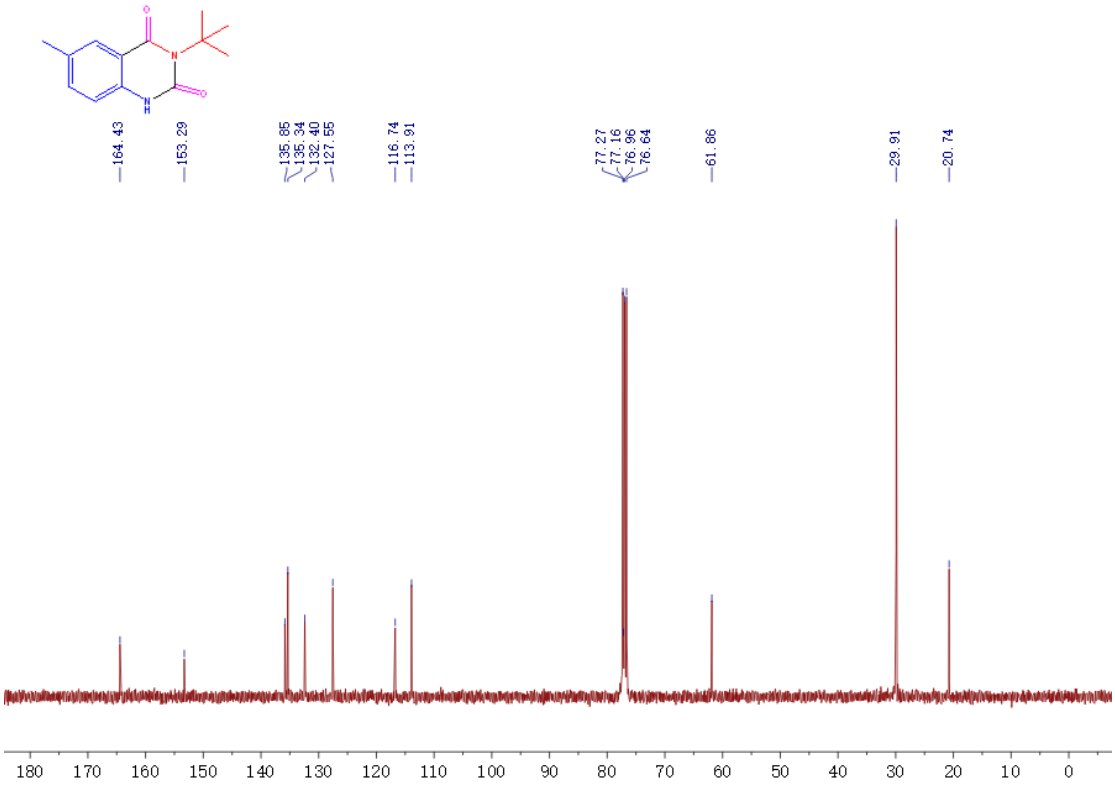

$^{13}$C NMR Spectra of **3b** in $CDCl_3$



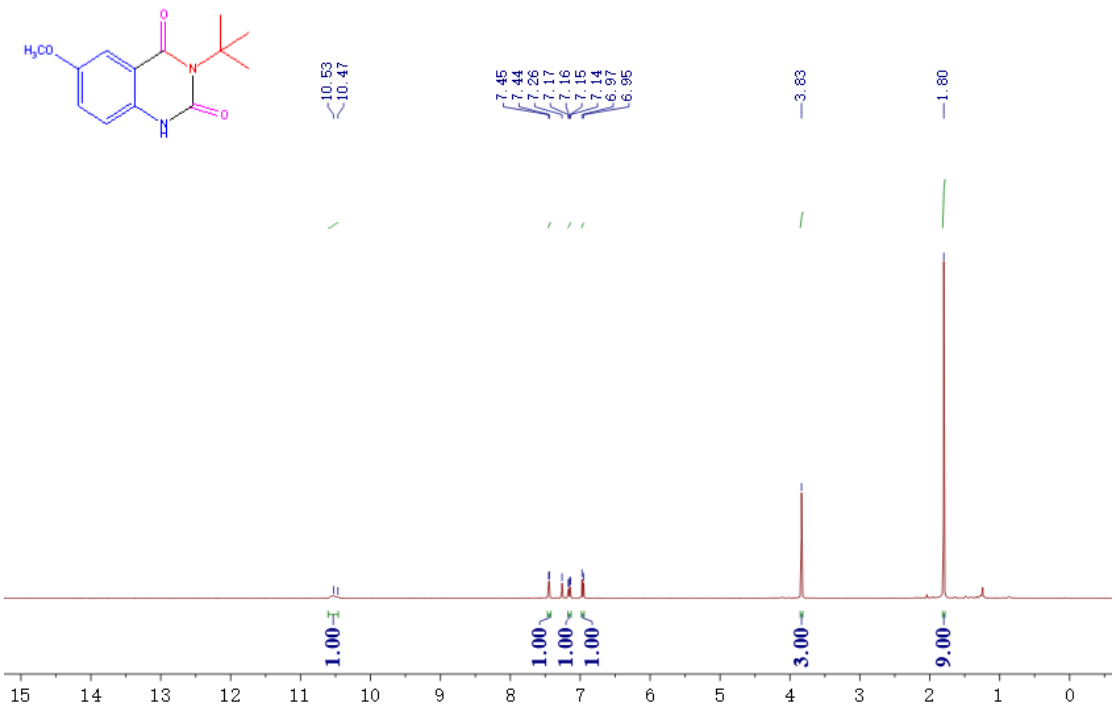

$^{1}$H NMR Spectra of **3c** in $CDCl_3$



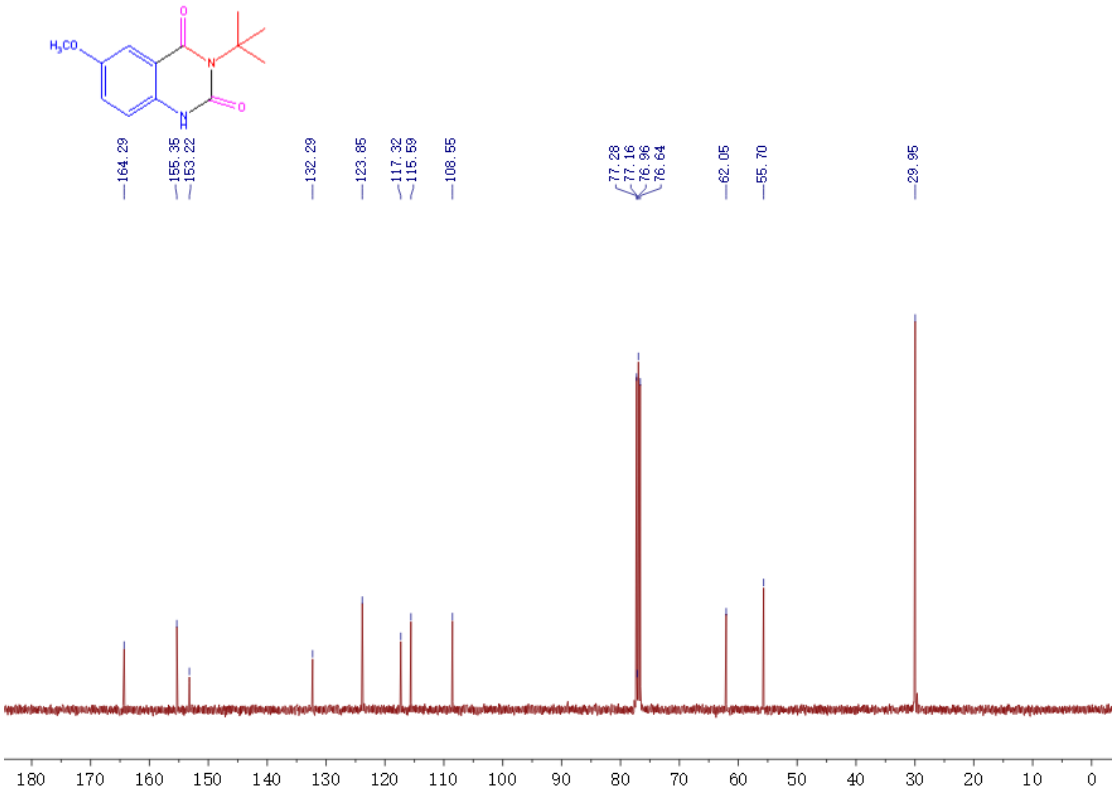

$^{13}C$ NMR Spectra of **3c** in $CDCl_3$



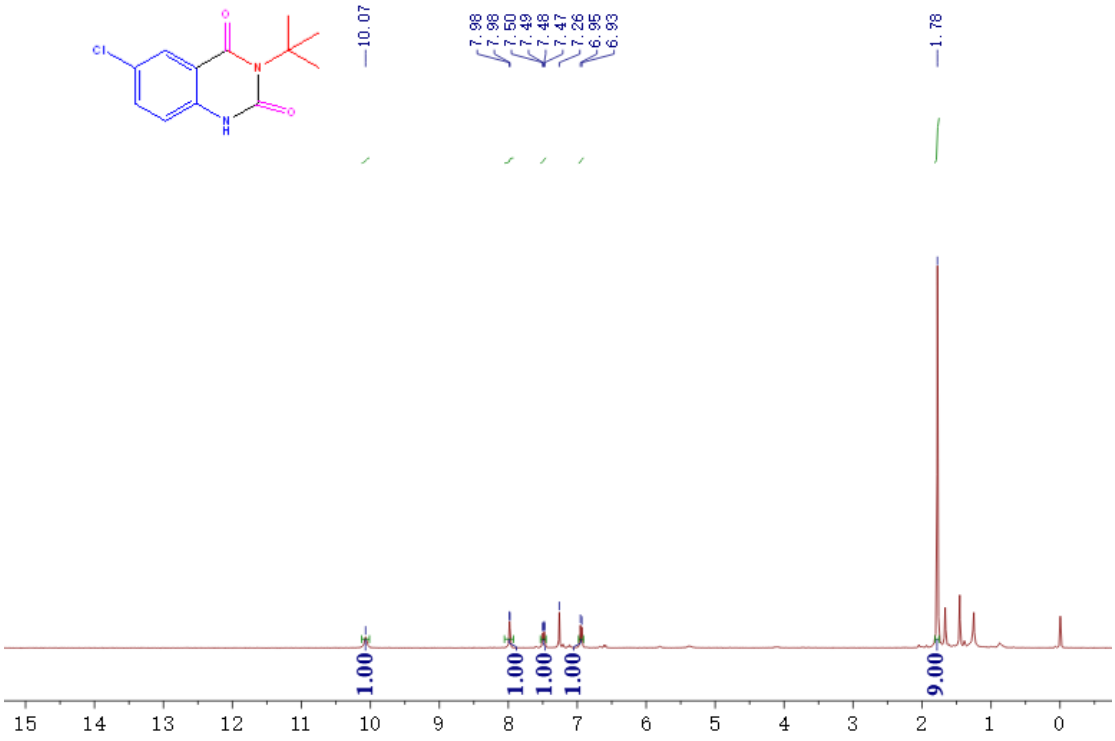
$^{1}$H NMR Spectra of **3d** in $CDCl_3$



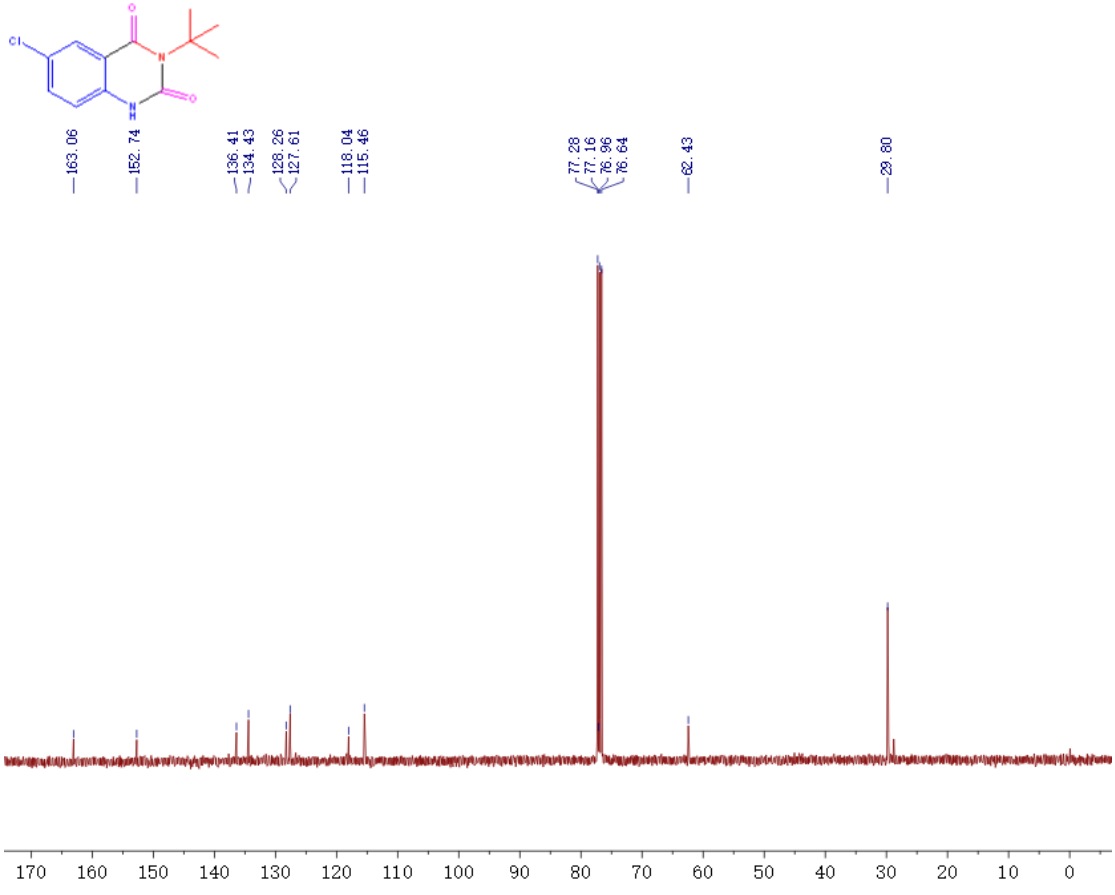

$^{13}$C NMR Spectra of **3d** in $CDCl_3$



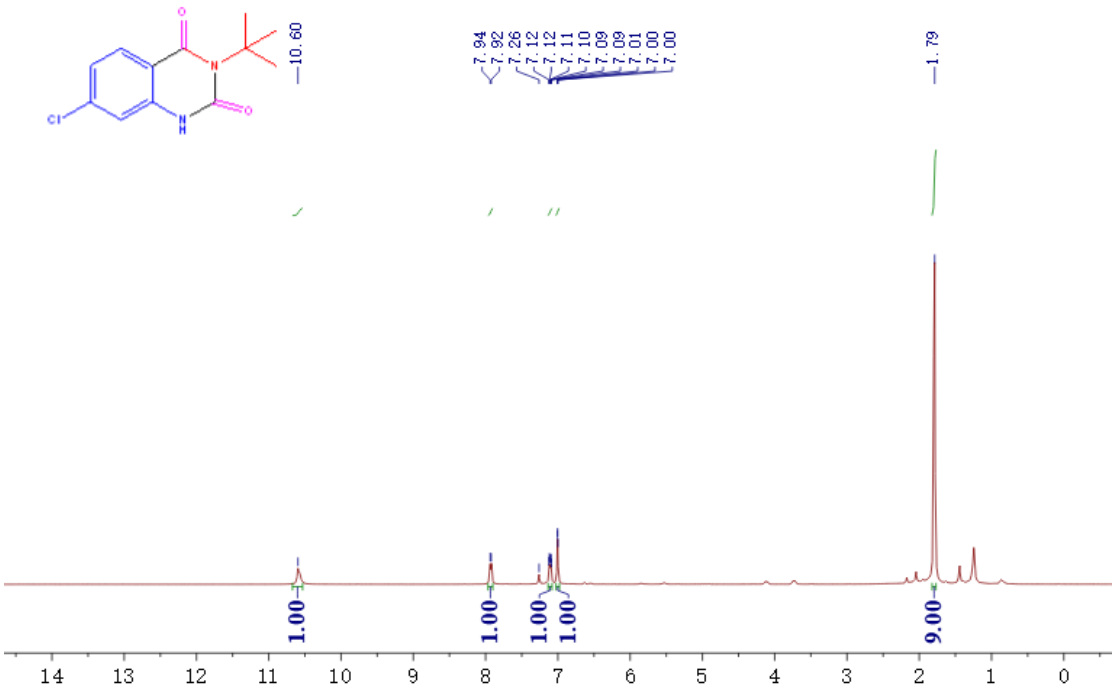
$^{1}$H NMR Spectra of **3e** in $CDCl_3$



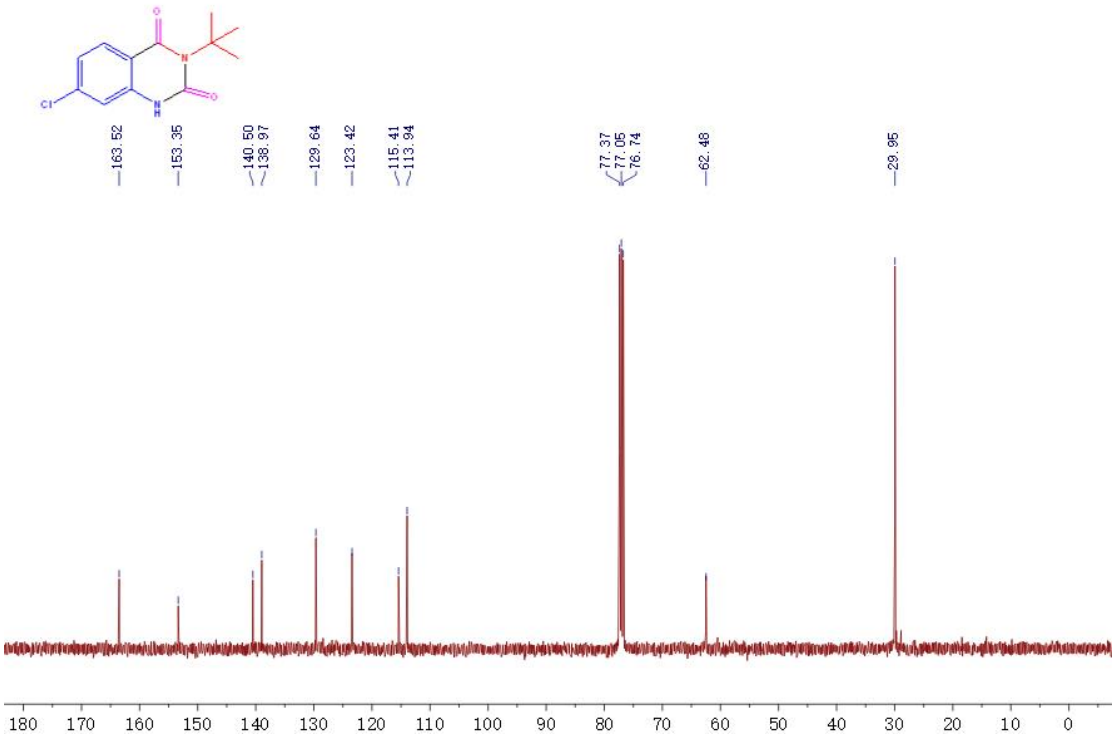

$^{13}$C NMR Spectra of **3e** in $CDCl_3$



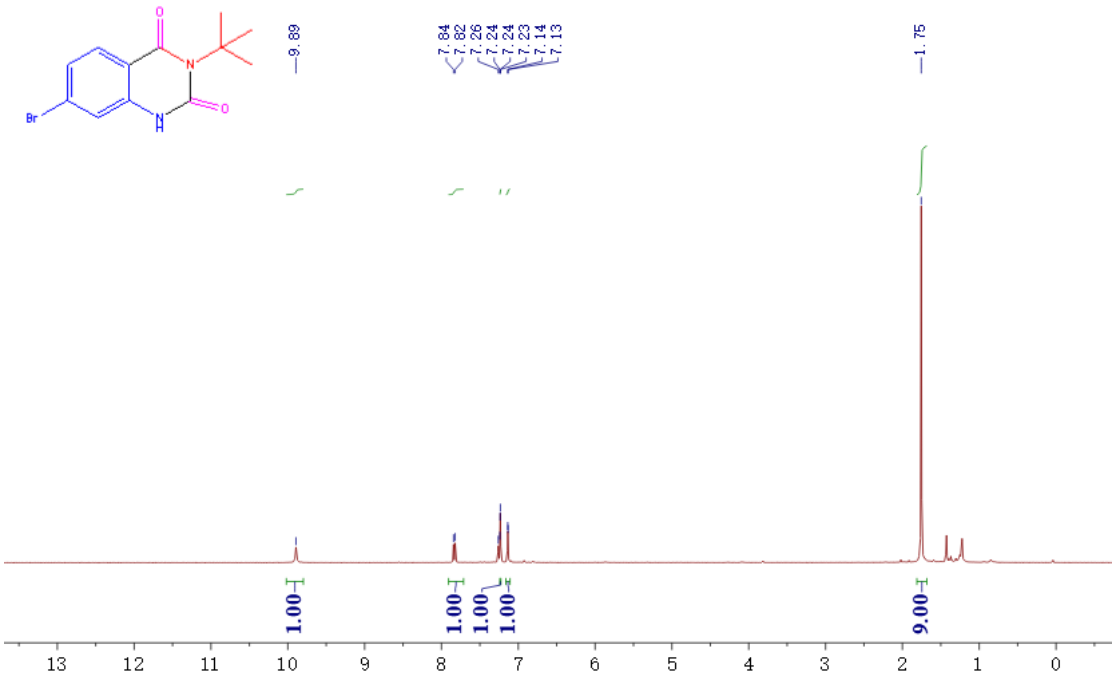
$^{1}$H NMR Spectra of **3f** in $CDCl_3$



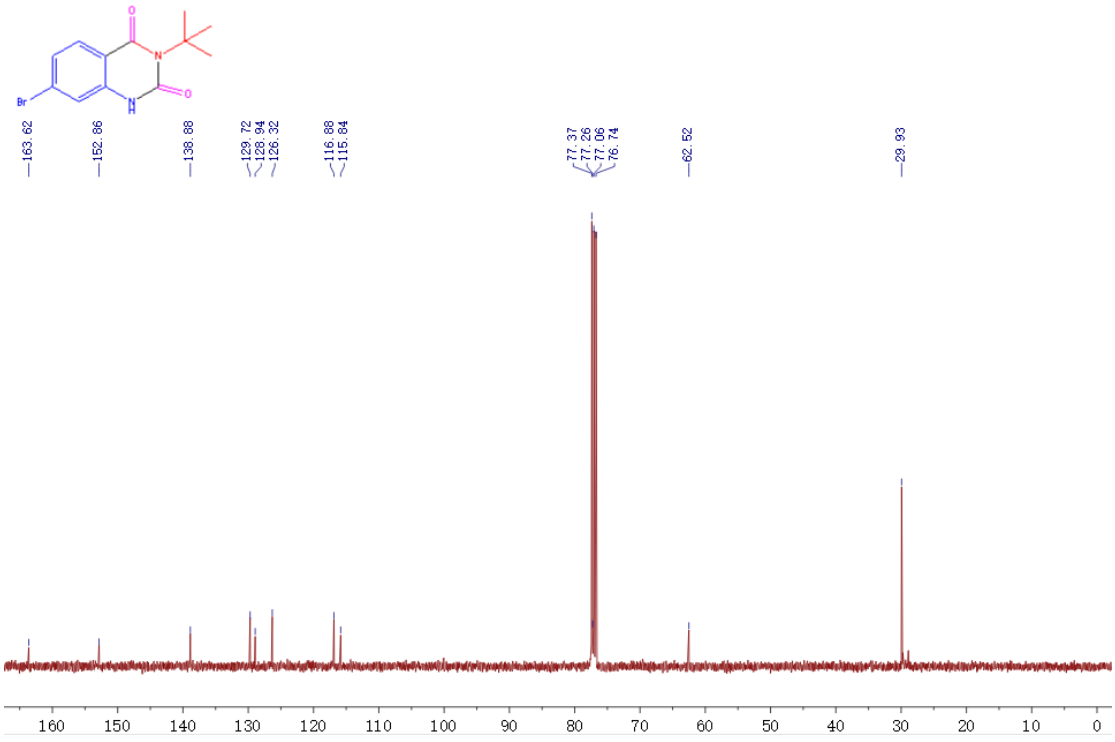

$^{13}$C NMR Spectra of **3f** in $CDCl_3$



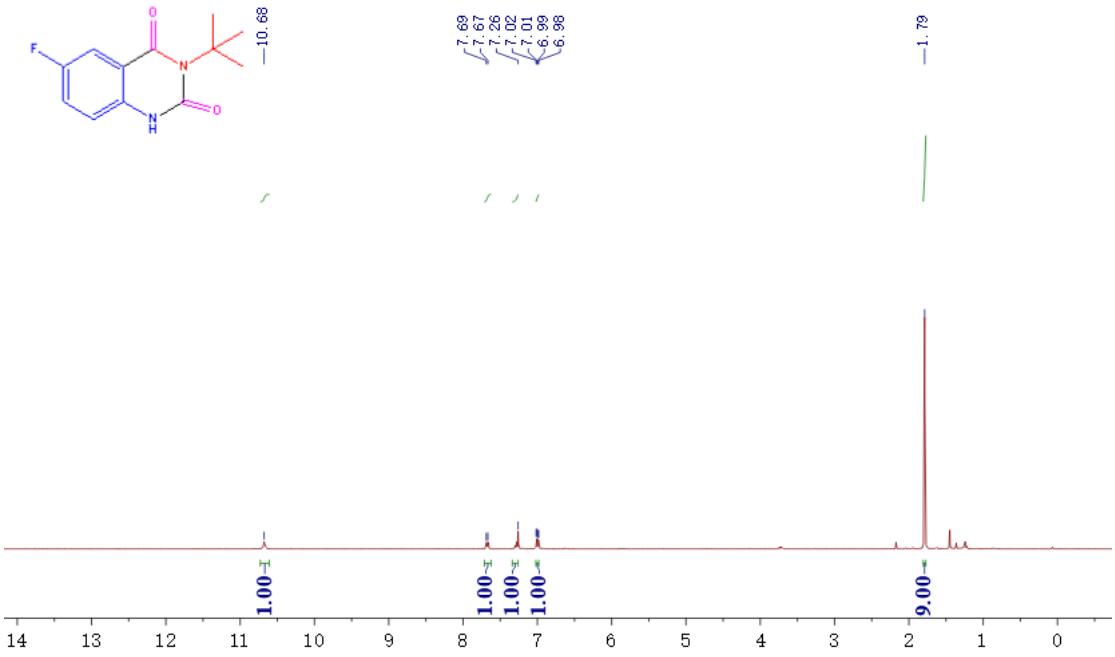
$^{1}$H NMR Spectra of **3g** in $CDCl_3$



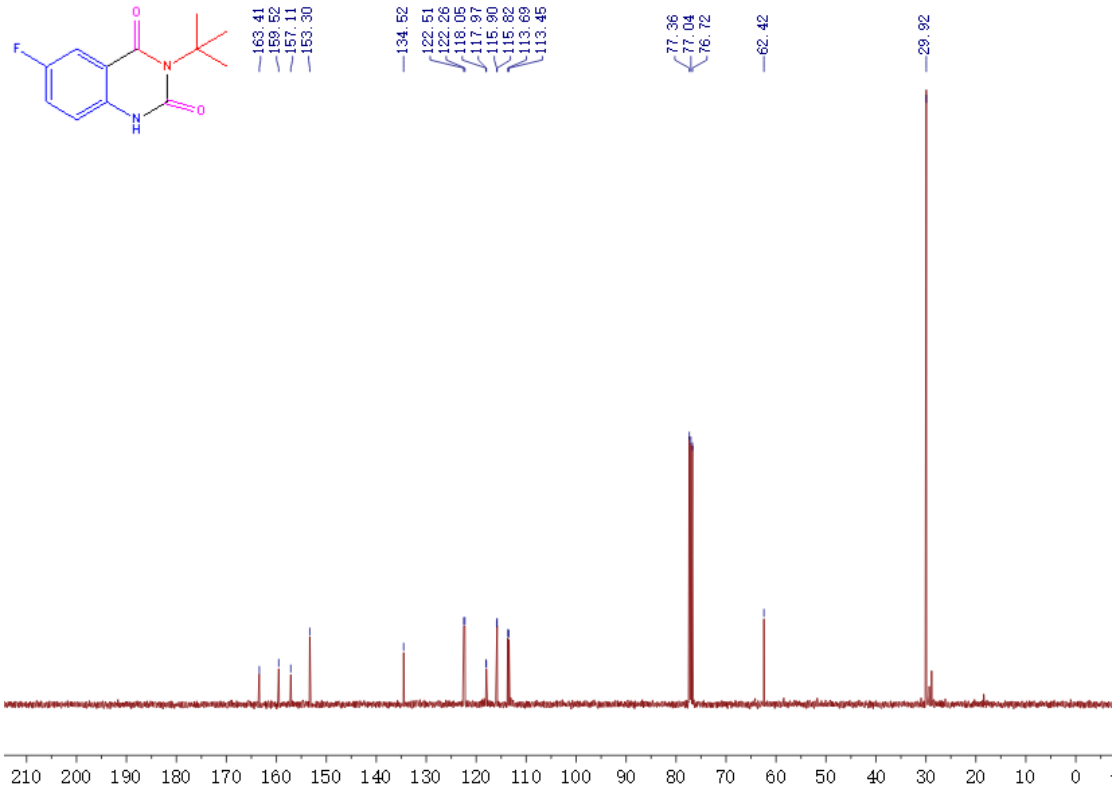

$^{1}$C NMR Spectra of **3g** in $CDCl_3$



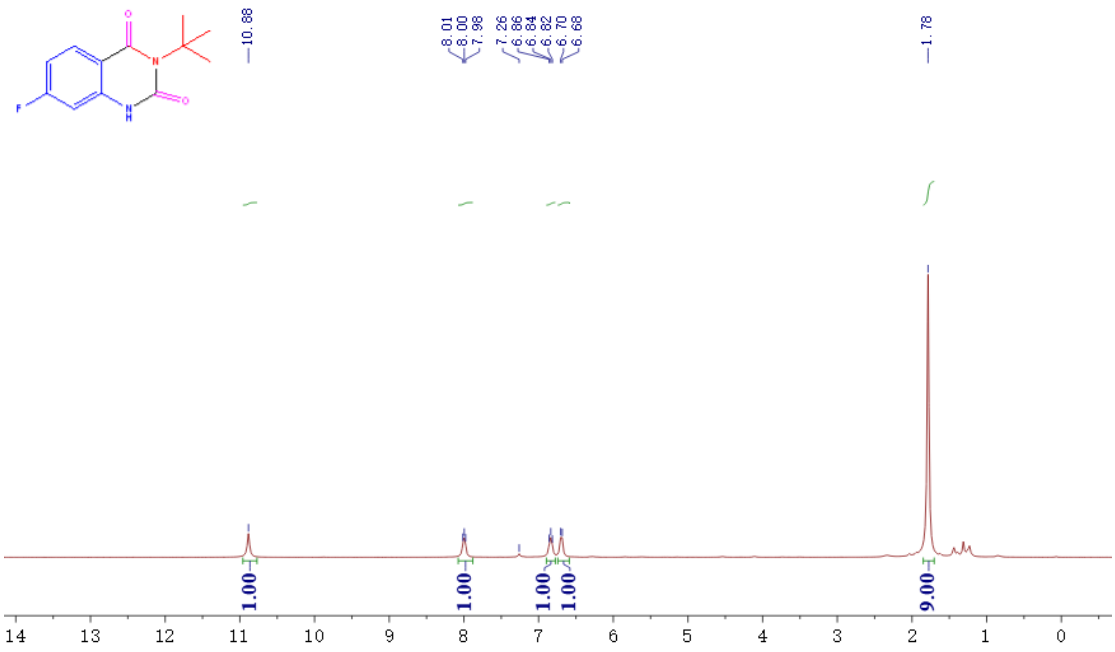
$^{1}$H NMR Spectra of **3h** in $CDCl_3$



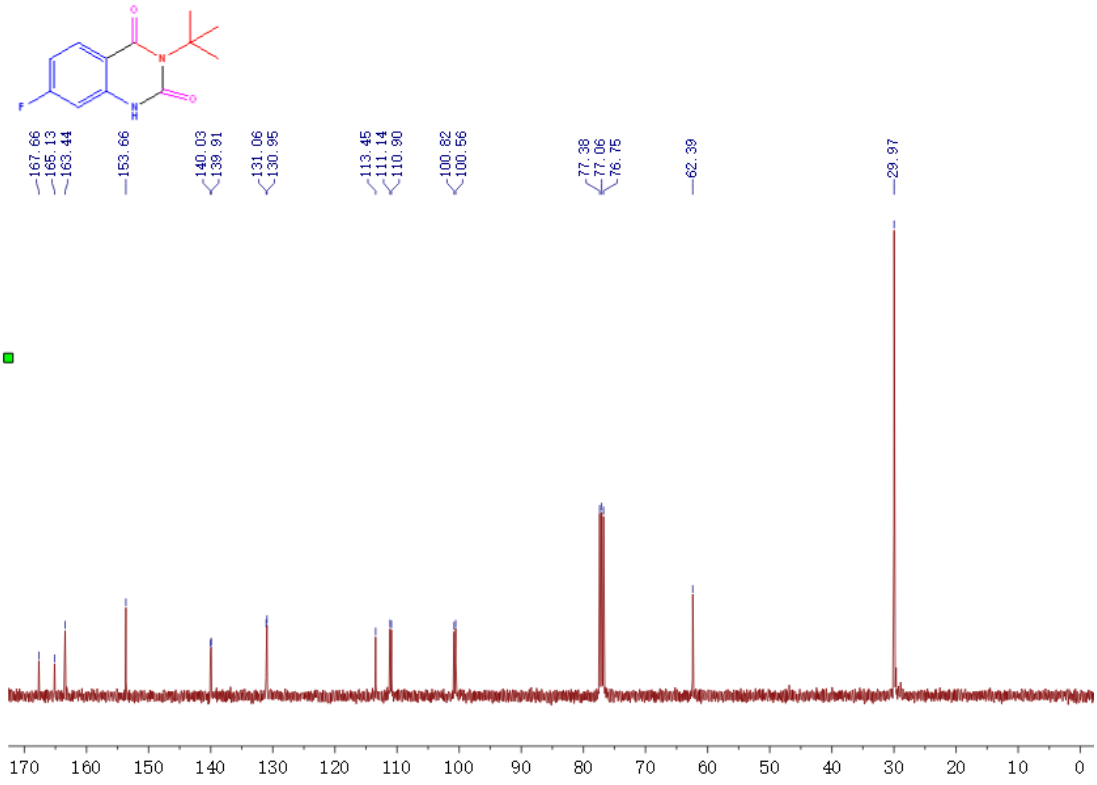

$^{13}$C NMR Spectra of **3h** in $CDCl_3$



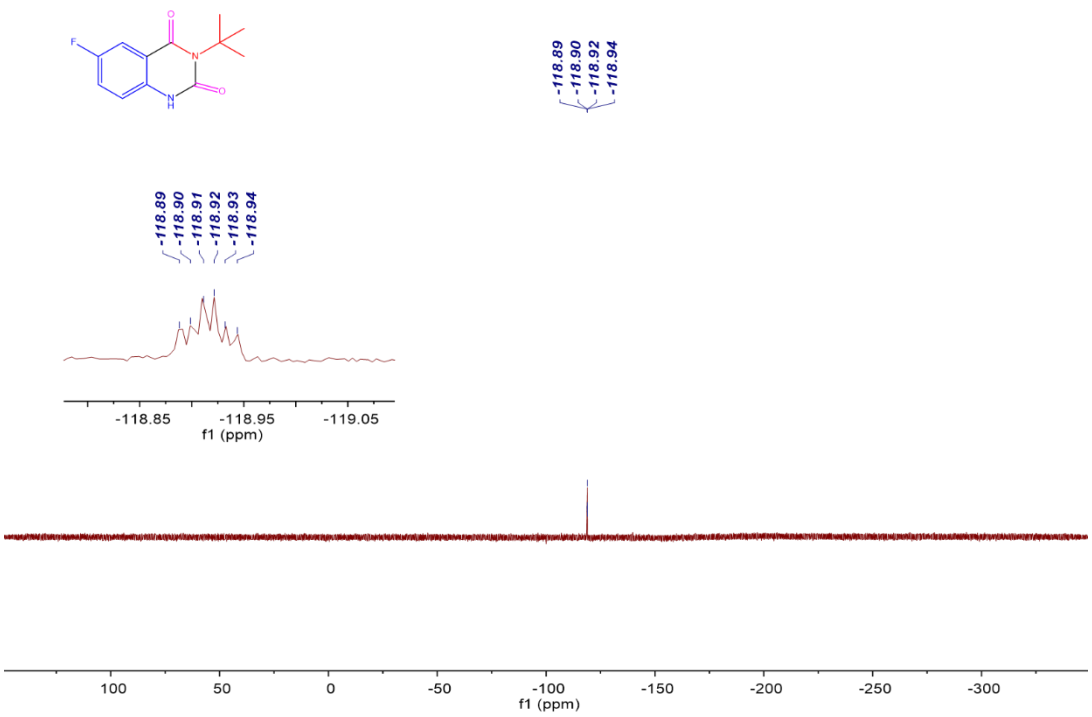
$^{1}$H NMR Spectra of **3i** in $CDCl_3$



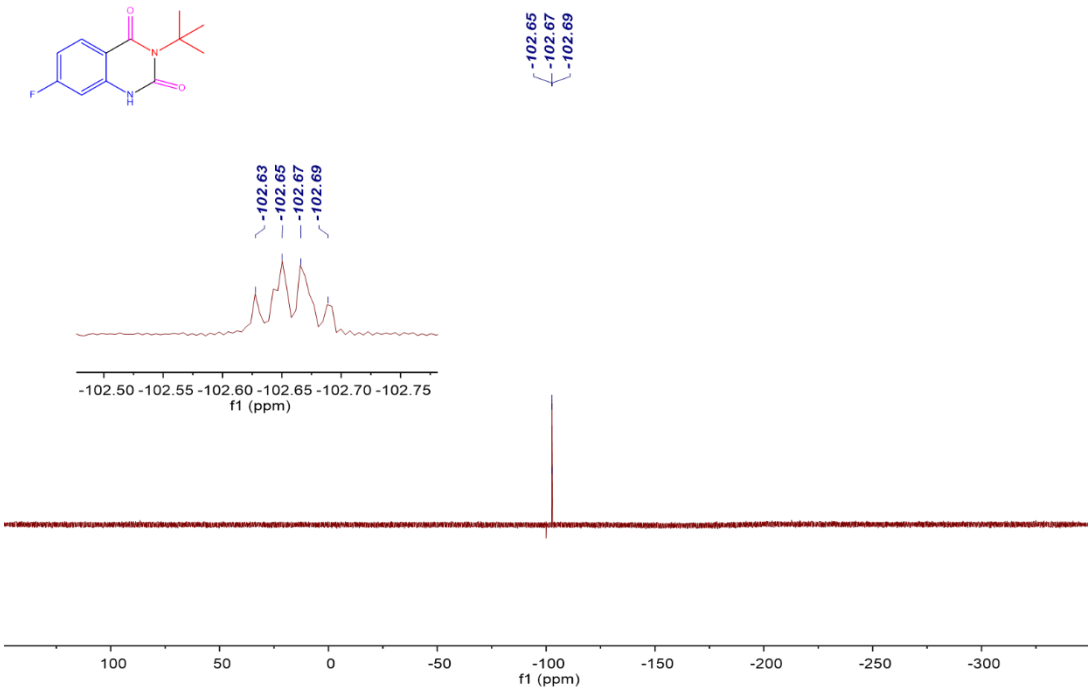

$^{13}$C NMR Spectra of **3i** in $CDCl_3$



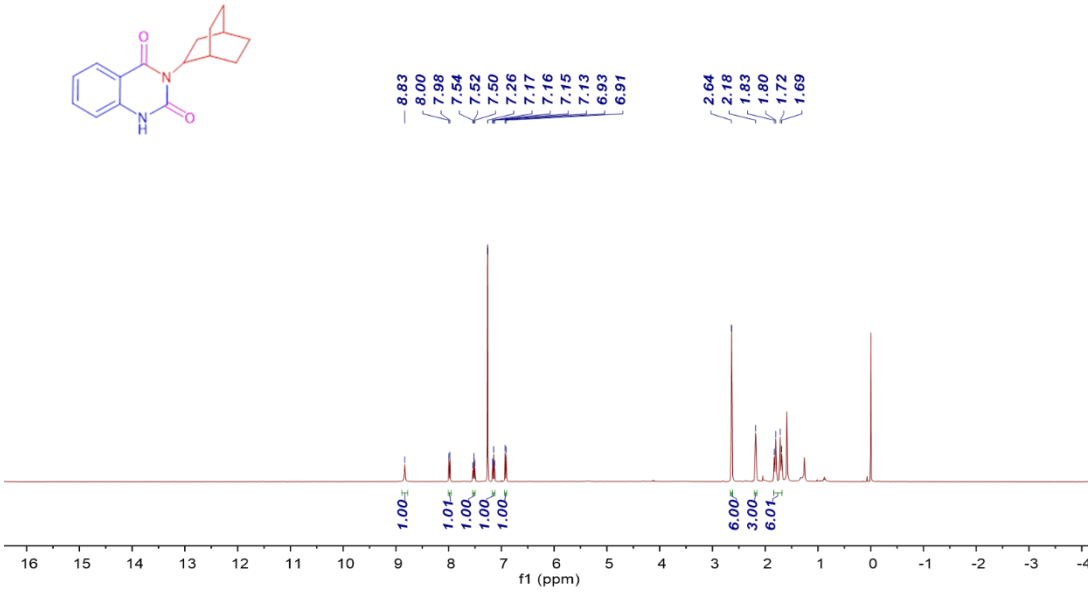
$^{19}$F NMR Spectra of **3h** in $CDCl_3$



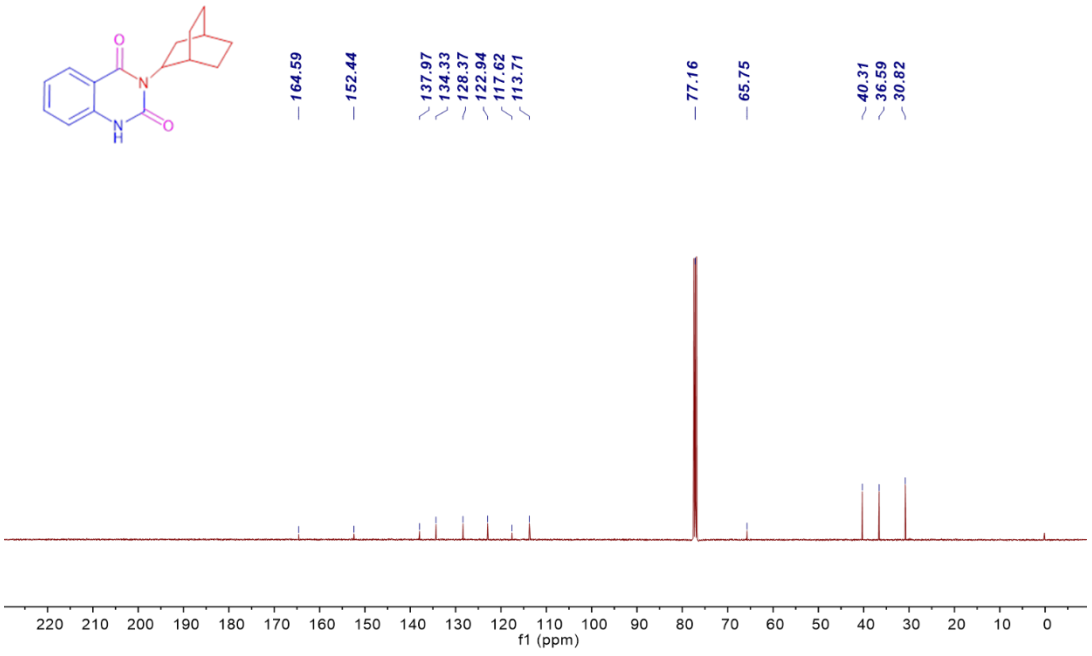

$^{19}$F NMR Spectra of **3i** in $CDCl_3$



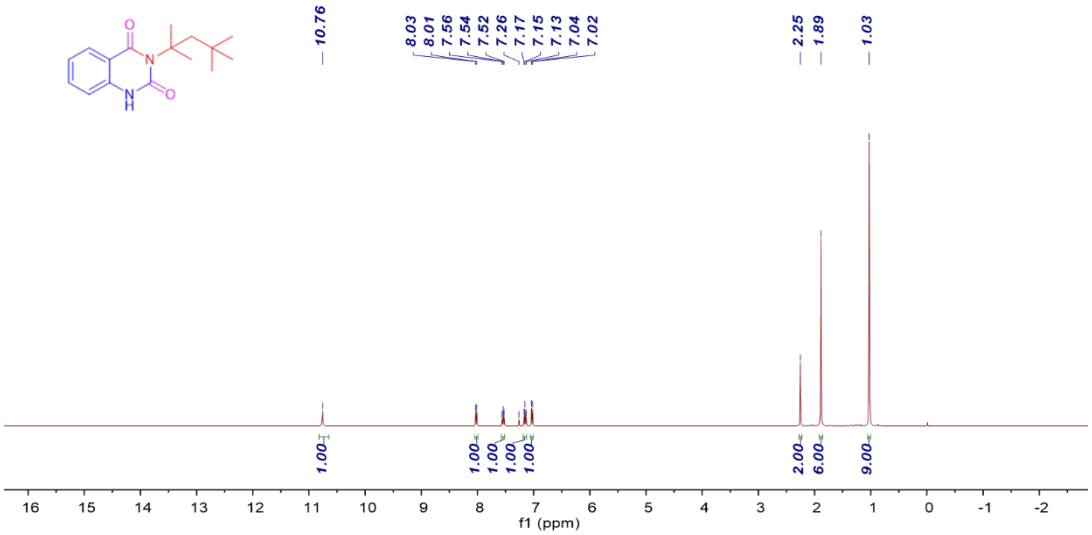
$^{1}$H NMR Spectra of **4a** in $CDCl_3$




$^{13}$C NMR Spectra of **4a** in $CDCl_3$



$^{1}$H NMR Spectra of **4b** in $CDCl_3$




$^{13}$C NMR Spectra of **4b** in $CDCl_3$