One-pot Cascade Ring Enlargement of Isatin-3-Oximes to 2,4-Dichloroquinazolines Mediated by Bis(trichloromethyl)carbonate and Triarylphosphine Oxide

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**Supplemental Materials**

***Characterization data of 2***

### 2,4-Dichloroquinazoline (2a)

Light yellow solid, 93% yield, mp 119-121 oC (Lit.,[1] mp 118 oC). 1H NMR (400MHz, CDCl3) δ: 8.26 (d, *J* = 8.4 Hz, 1H), 8.01 – 7.97 (m, 2H), 7.76 – 7.70 (m, 1H). *13*C NMR (100 MHz, CDCl3) δ: 163.7, 154.9, 152.1, 135.9, 129.0, 127.8, 125.8, 122.2.

### 2,4-6-methoxyDichloroquinazoline (2b)

Light yellow solid, 94% yield, mp 170-171 °C (Lit.,[2] mp 171 oC). 1H NMR (400 MHz, CDCl3) δ: 7.89 (d, *J* = 9.2 Hz, 1H), 7.60 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.40 (d, *J* = 2.8 Hz, 1H), 3.99 (s, 3H). 13C NMR (100 MHz, CDCl3) δ: 161.5, 159.4, 152.5, 148.4, 129.3, 129.0, 123.3, 102.7, 56.0.

### 2,4-Dichloro-6-methylquinazoline (2c)

White solid, 93% yield, mp 140-141 °C (Lit.,[3] mp 140-141 °C). 1H NMR (400 MHz, CDCl3) δ: 8.00 (s, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.80 (dd, *J* = 8.6, 1.8 Hz, 1H), 2.61 (s, 3H). 13C NMR (100 MHz, CDCl3) δ: 162.9, 154.0, 150.7, 139.8, 138.2, 127.5, 124.5, 122.1, 22.0.

### 2,4-Dichloro-6,7-dimethoxyquinazoline (2d)

White solid, 92% yield, mp 161-162 °C (Lit.,[2] mp 157-159 °C). 1H NMR (400 MHz, CDCl3) δ: 7.33 (s, 1H), 7.25 (s, 1H), 4.07 (s, 3H), 4.05 (s, 3H). 13C NMR (100 MHz, CDCl3) δ: 159.9, 157.6, 153.4, 151.4, 150.4, 117.7, 106.2, 102.7, 56.8, 56.5.

### 2,4-Dichloro-5,7-dimethyquinazoline (2e)

White solid, 92% yield, mp 141-142 oC (Lit.,[4] mp 140-143 oC). 1H NMR (400 MHz, CDCl3) δ: 7.59 (s, 1H), 7.30 (s, 1H), 2.96 (s, 3H), 2.52 (s, 3H). 13C NMR (100 MHz, CDCl3) δ: 162.2, 154.6, 154.0, 146.5, 136.2, 134.2, 125.7, 120.0, 24.8, 21.9.

### 2,4,6-Trichloroquinazoline (2f)

White solid, 88% yield, mp 132-136°C (Lit.,[1] mp 129-131 °C). 1H NMR (400 MHz, CDCl3) δ: 8.22 (d, *J* = 2.0 Hz, 1H), 7.98 – 7.88 (m, 2H). 13C NMR (100 MHz, CDCl3) δ: 162.6, 155.2, 150.6, 136.9, 135.1, 129.5, 124.7, 122.8.

### 2,4,8-Trichloroquinazoline (2g)

Light yellow solid, 87% yield, mp 152-153 °C (Lit.,[5] mp 151-153 °C). 1H NMR (400 MHz, CDCl3) δ: 8.19 (dd, *J* = 8.8, 1.2 Hz, 1H), 8.07 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.65 (dd, *J* = 8.2, 7.8 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ: 164.2, 155.8, 148.9, 135.7, 132.6, 128.8, 124.7, 123.4.

### 2,4-Dichloro-7-fluoroquinazoline (2h)

White solid, 74% yield, mp 143-145 °C (Lit.,[5] mp 142-145 °C). 1H NMR (400 MHz, CDCl3) δ: 8.29 (dd, *J* = 8.6, 5.8 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.49 (t, *J* = 8.6 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ: 161.5 (d, *J*1 = 295 Hz), 158.1, 150.9, 148.7 (d, *J*3 = 14 Hz), 123.8(d, *J*3= 11 Hz), 114.5 , 114.2 (d, *J*3=16 Hz), 106.9 (d, *J*2 = 28 Hz).

### 2,4-Dichloro-6-fluoroquinazoline (2i)

White solid, 85% yield, mp 136-137 °C (Lit.,[1] mp 136-137 °C). 1H NMR (400 MHz, CDCl3) δ: 8.03 (dd, *J* = 9.2, 4.8 Hz, 1H), 7.87 (dd, *J* = 8.0, 2.8 Hz, 1H), 7.75 (td, *J* =8.0, 2.8 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ: 163.0 (d, *J*4 = 6 Hz), 161.1 (d, *J*1 = 252 Hz), 154.5 (d, *J*4 = 3 Hz), 149.2, 130.7 (d, *J*4 = 9 Hz), 126.4 (d, *J*2 = 26 Hz), 123.1 (d, *J*3 = 10 Hz), 109.7 (d, *J*2 = 24 Hz).

### 2,4-Dichloro-6-bromoquinazoline (2j)

White solid, 71% yield, mp 134-135 °C (Lit.,[6] mp 131-136 °C). 1H NMR (400MHz, CDCl3) δ: 8.40 (d, *J* = 2.0Hz, 1H), 8.04 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ: 162.5, 155.2, 150.8, 139.5, 129.5, 128.0, 123.2, 123.1.

### 2,4-Dichloro-6-nitroquinazoline (2k)

White solid, 63% yield, mp 121-123 °C (Lit.,[5] mp 122-124 °C). 1H NMR (400MHz, CDCl3) δ: 9.16 (dd, *J* = 2.4, 0.4 Hz, 1H), 8.73 (dd, *J* = 9.2, 2.4 Hz, 1H), 8.16 (dd, *J* = 9.2, 0.4 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ: 162.3, 155.1, 151.0, 139.3, 129.3, 128.0, 123.0, 122.9.

### 2,4,5,7-Tetrachloroquinazoline (2l)

White solid, 66% yield, mp 100-101 °C. (Lit.,[5] mp 100-101 °C). 1H NMR (400MHz, CDCl3) δ: 7.90 (d, *J* = 2.0 Hz, 1H), 7.73 (d, *J* = 2.0 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ: 162.0, 156.0, 154.5, 141.3, 132.5, 126.8, 118.8.

### 2,4-Dichloro-8-bromoquinazoline (2m)

White solid, 71% yield. mp 146-147 °C. (Lit.,[5] mp 146-147 °C). 1H NMR (400 MHz, CDCl3) δ: 8.27 (m, 2H), 7.60 (dd, J = 8.3, 7.7 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ: 164.6, 156.2, 150.1, 139.6, 129.6, 125.8, 123.7, 123.2.

### 2,4,6-Trichloro-8-methylquinazoline (2n)

White solid, 82% yield. mp 143-144 °C. (Lit.,[1] mp 143-145°C). 1H NMR (400 MHz, CDCl3) δ: 8.04 (d, J = 2.0 Hz, 1H), 7.78 – 7.70 (m, 1H), 2.71 (s, 3H). 13C NMR (100 MHz, CDCl3) δ: 163.1, 154.5, 150.4, 139.4, 136.7, 134.7, 123.1, 122.5, 17.4.

***Characterization data of 3***

### Tris(4-methylphenyl)phosphine oxide (3b)

Colourless solid, 39% yield. mp 141-144 oC. (lit.[7] mp 140 oC). 1H NMR (400 MHz, CDCl3) δ: 7.53 (dd, J = 11.8, 8.0 Hz, 6H), 7.26 – 7.22 (m, 6H), 2.38 (s, 9H).

### Tris(3,4,5-trifluorophenyl)phosphine oxide (3c)

Colourless solid, 36% yield. mp 211-218 oC.( (lit.[7] mp 219-221 oC). 1H NMR (400 MHz, CDCl3) δ: 7.34 – 7.21 (m, 6H).

### Tris(4-methoxylphenyl)phosphine oxide (3d)

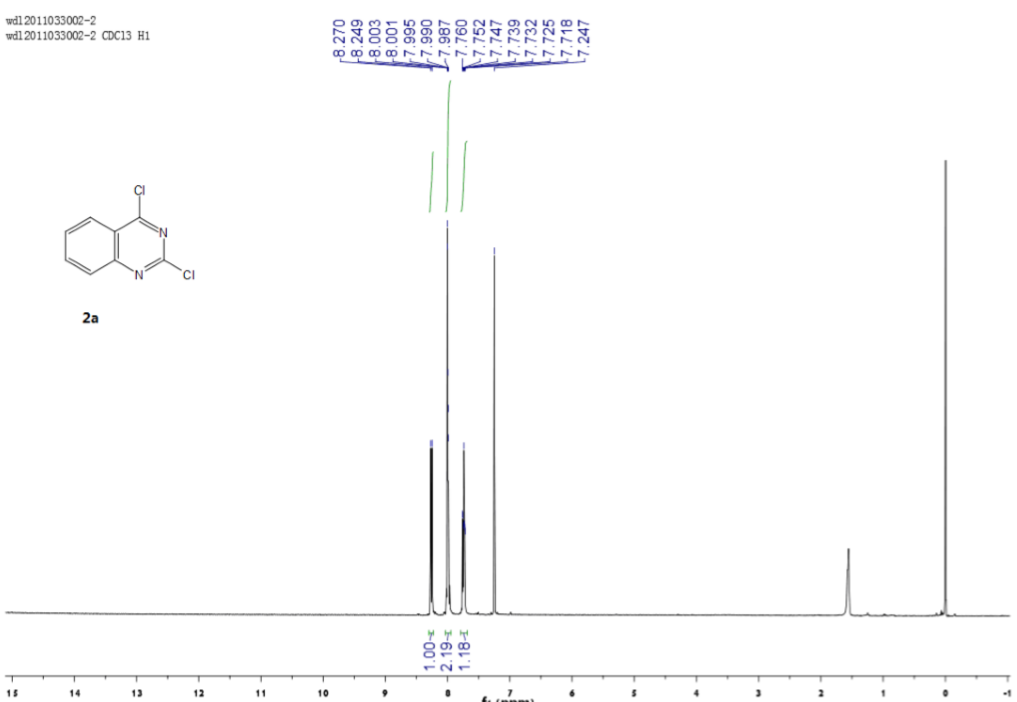
Colourless solid, 39% yield. mp 142-144 oC. (lit.[7] mp 142-143 oC). 1H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.50 (m, 6H), 6.99 – 6.89 (m, 6H), 3.84 – 3.80 (m, 9H).

### Tris([1,1’-biphenyl]-4-yl)phosphine oxide (3e)

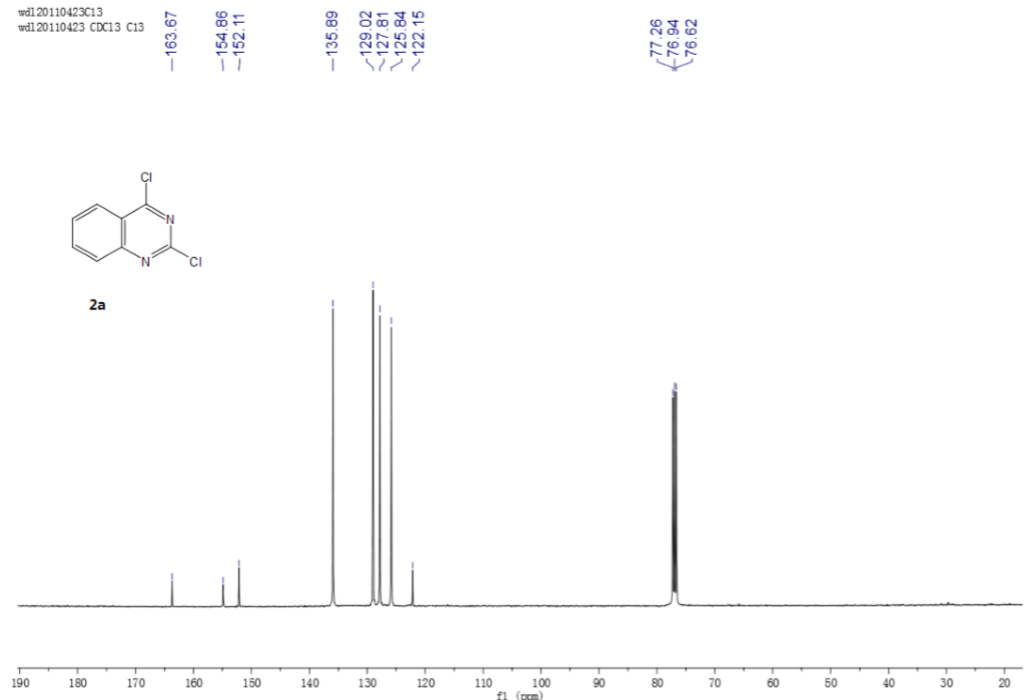
Colourless solid, 33% yield. mp 230-238 oC. (lit.[7] mp 233-234 oC). 1H NMR (400 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 11.5, 8.2 Hz, 6H), 7.76 – 7.68 (m, 6H), 7.63 (d, *J* = 7.4 Hz, 6H), 7.47 (t, *J* = 7.4 Hz, 6H), 7.40 (t, *J* = 7.3 Hz, 3H).

***Copies of 1H NMR and 13C NMR spectra***

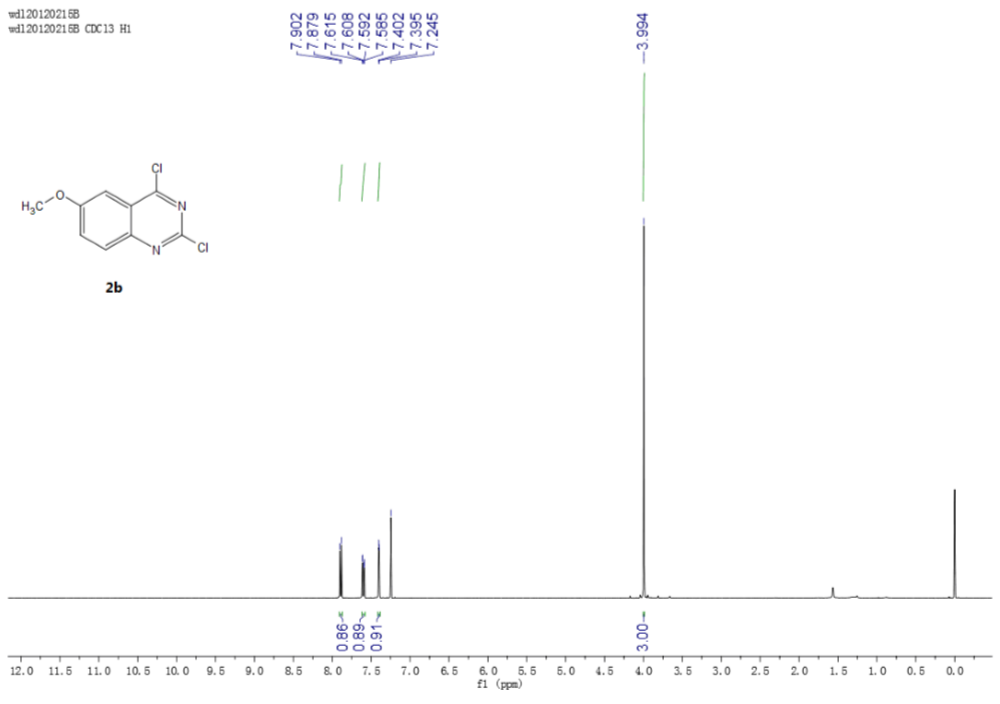
**Figure S 1:** 1H NMR of **2a**



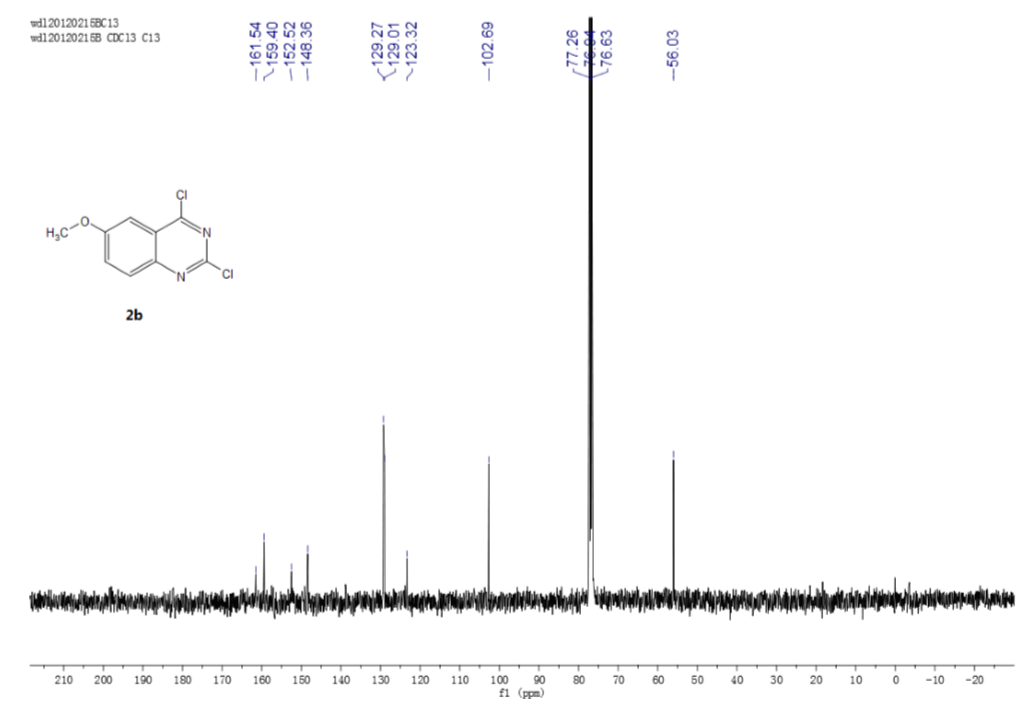
**Figure S 2:** 13C NMR of **2a**



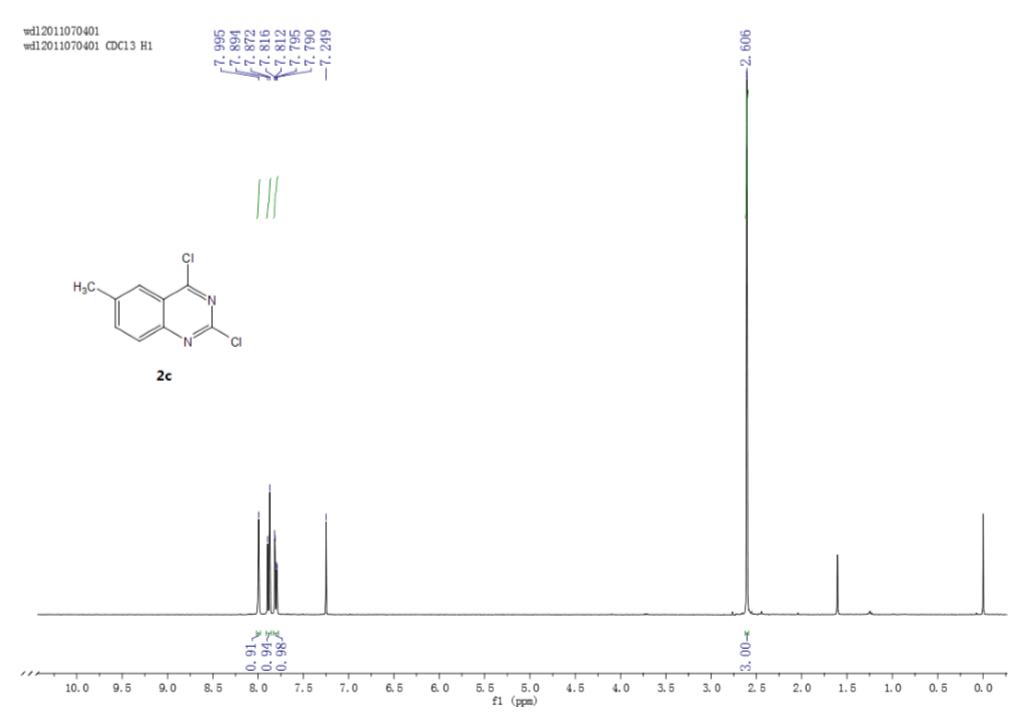
**Figure S 3:** 1H NMR of **2b**



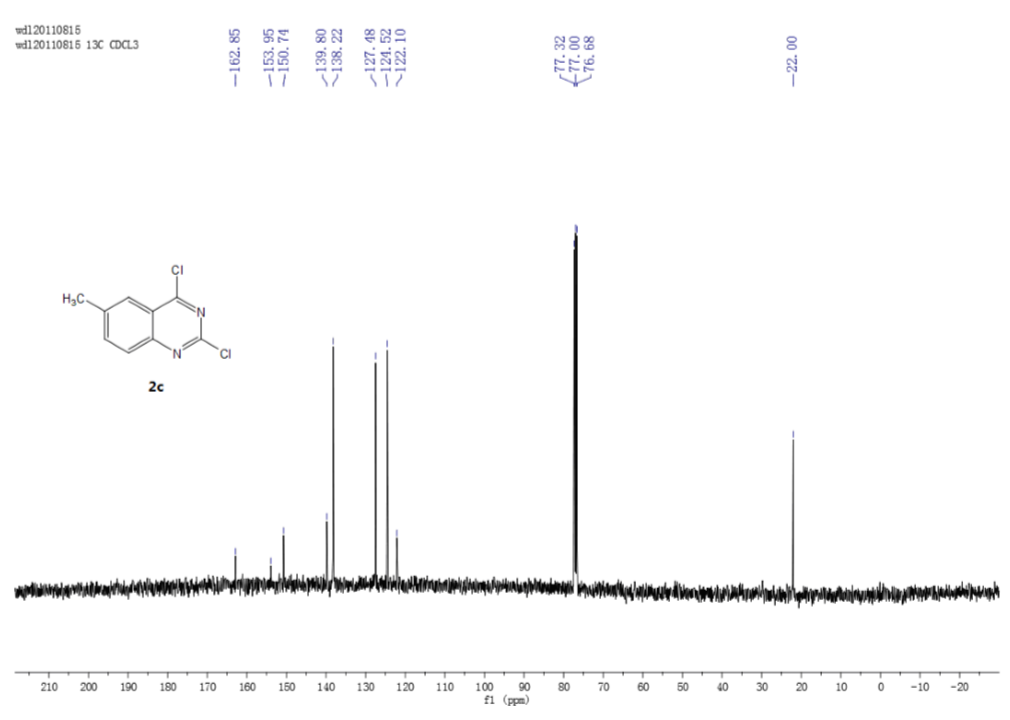
**Figure S 4:** 13C NMR of **2b**



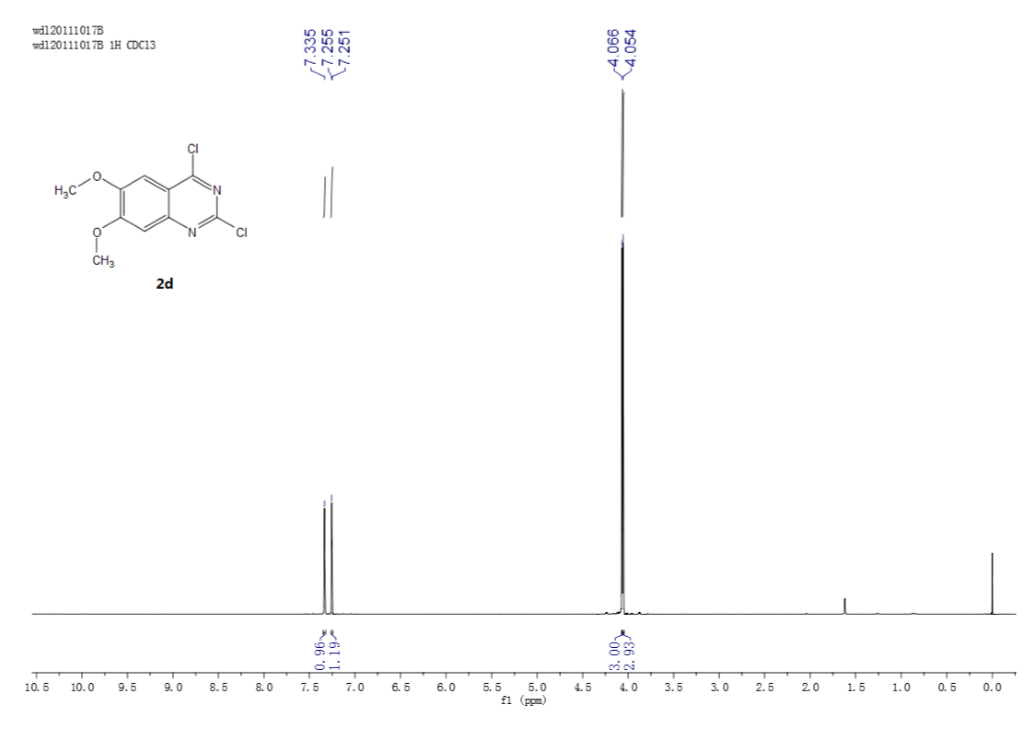
**Figure S 5:** 1H NMR of **2c**



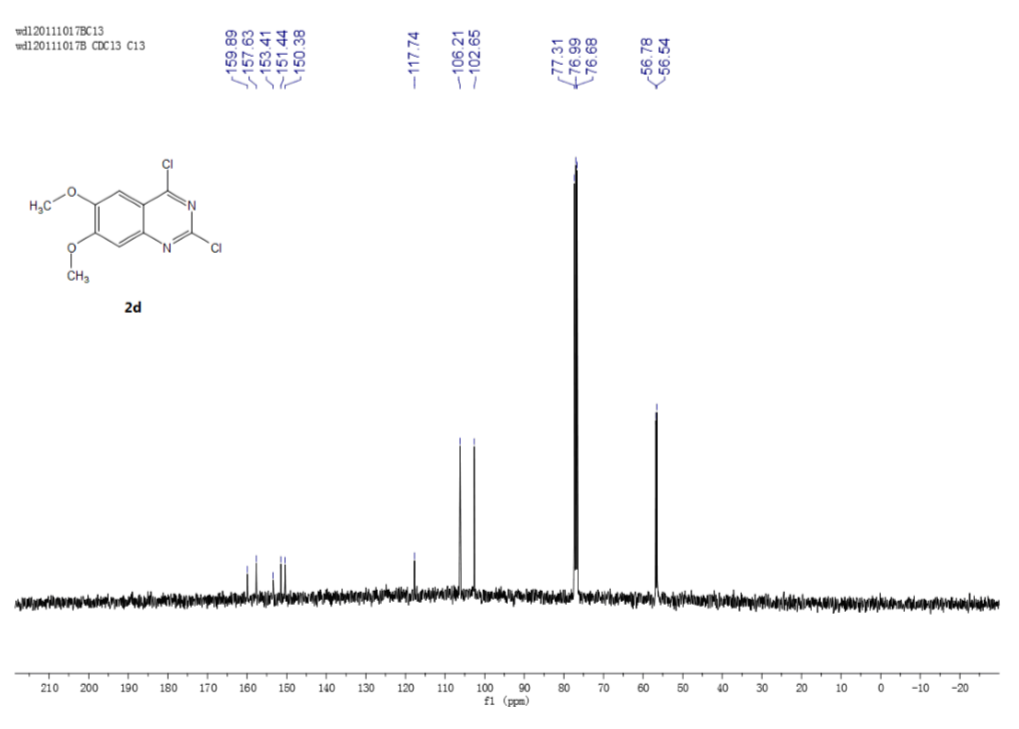
**Figure S 6:** 13C NMR of **2c**



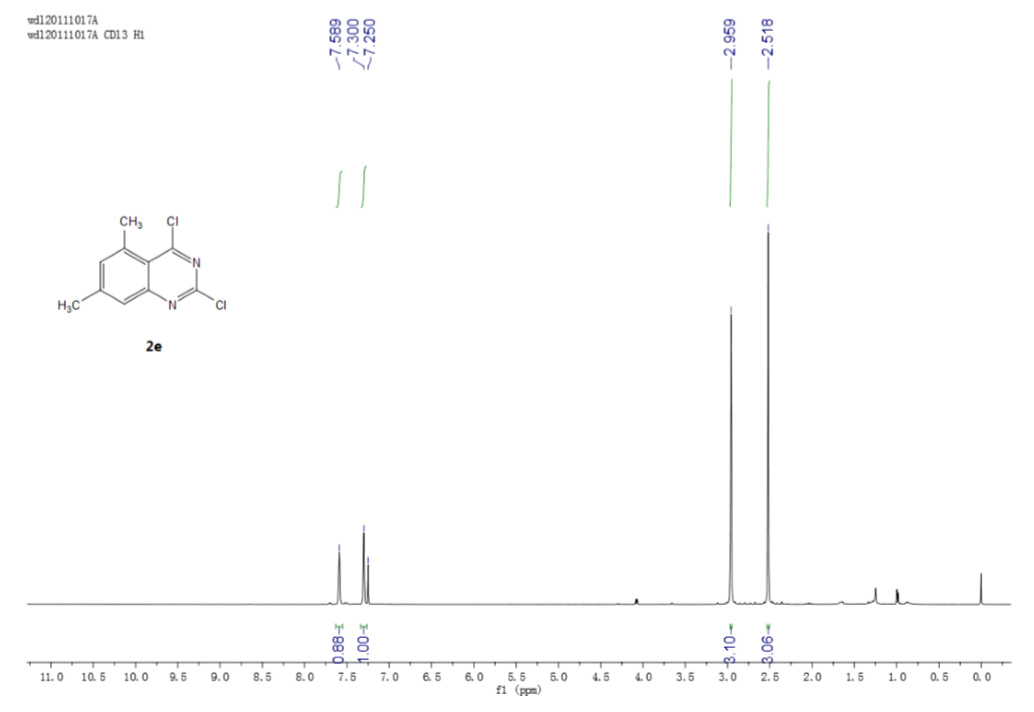
**Figure S 7:** 1H NMR of **2d**



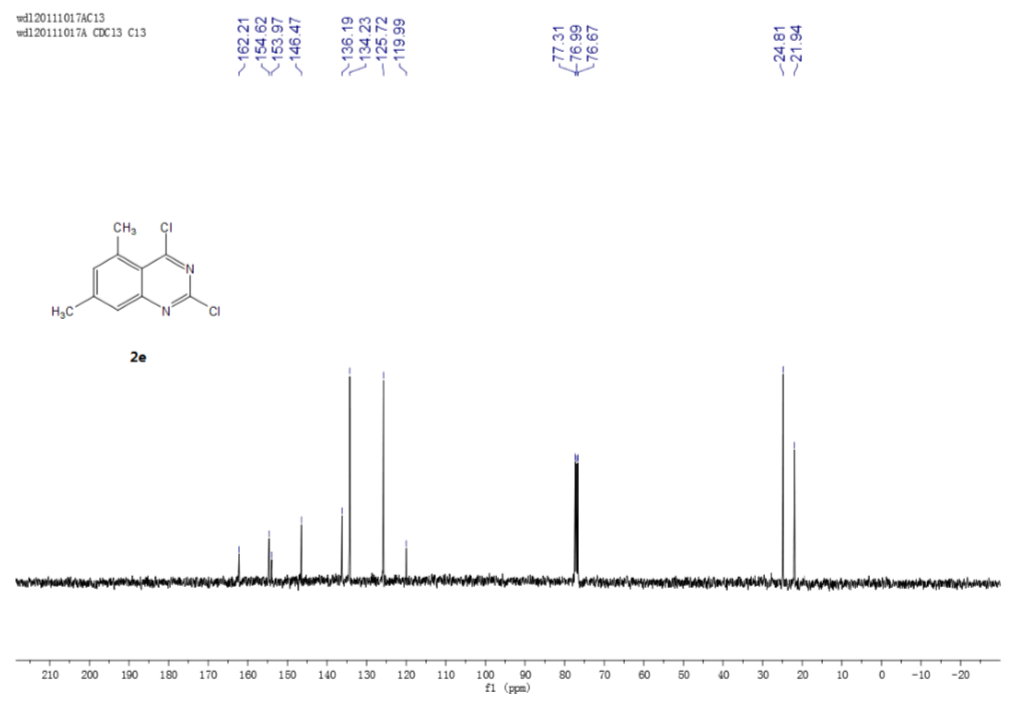
**Figure S 8:** 13C NMR of **2d**



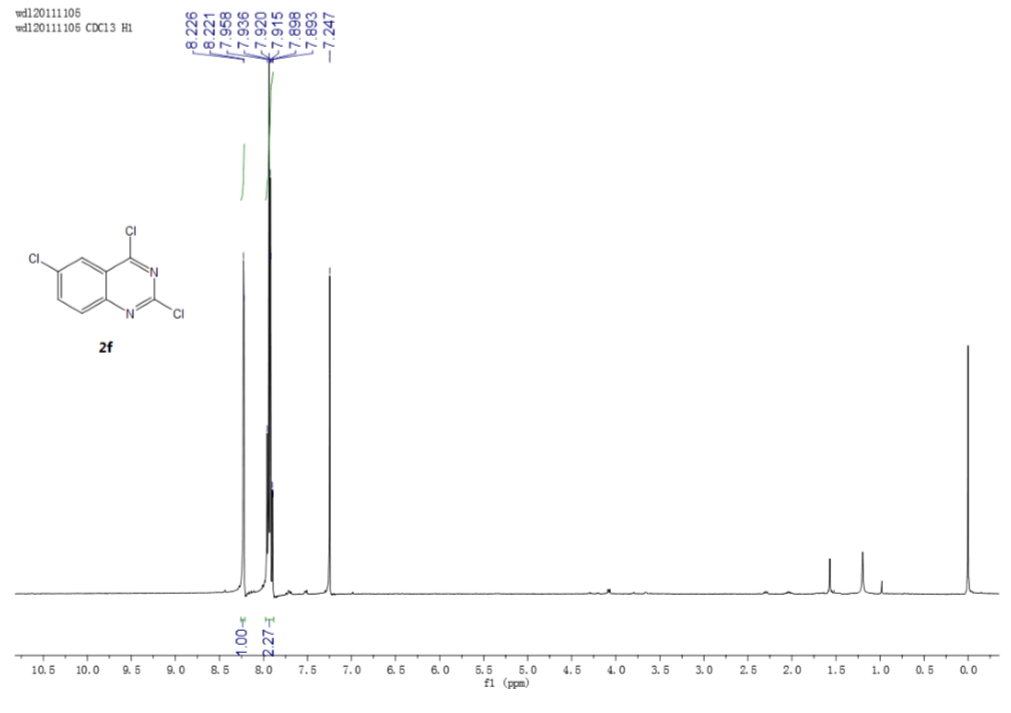
**Figure S 9:** 1H NMR of **2e**



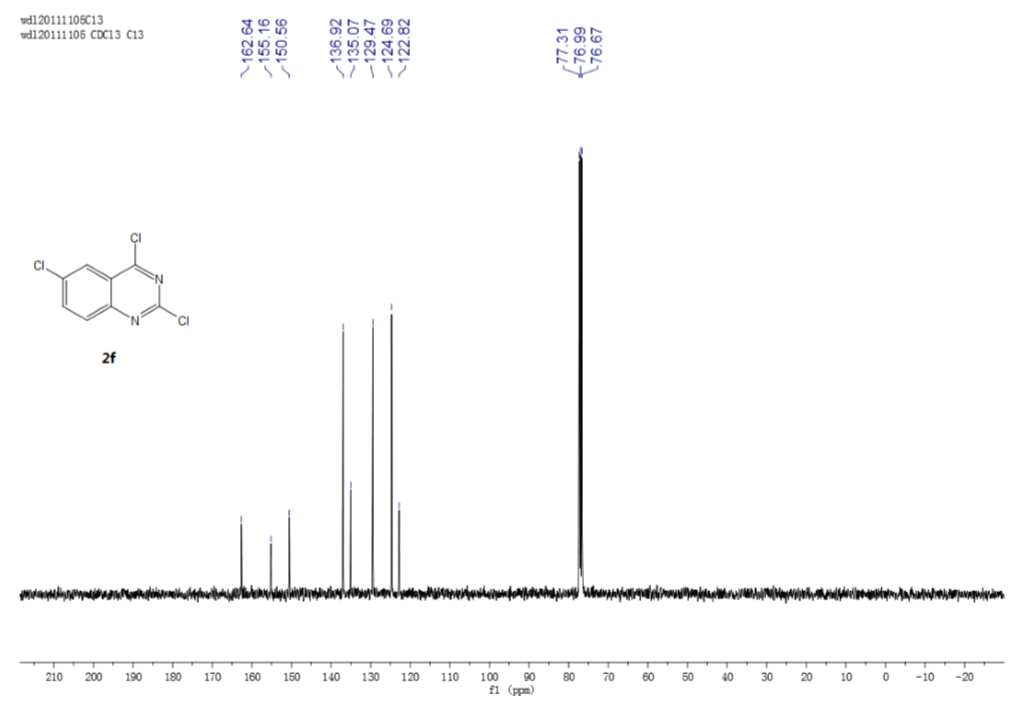
**Figure S 10:** 13C NMR of **2e**



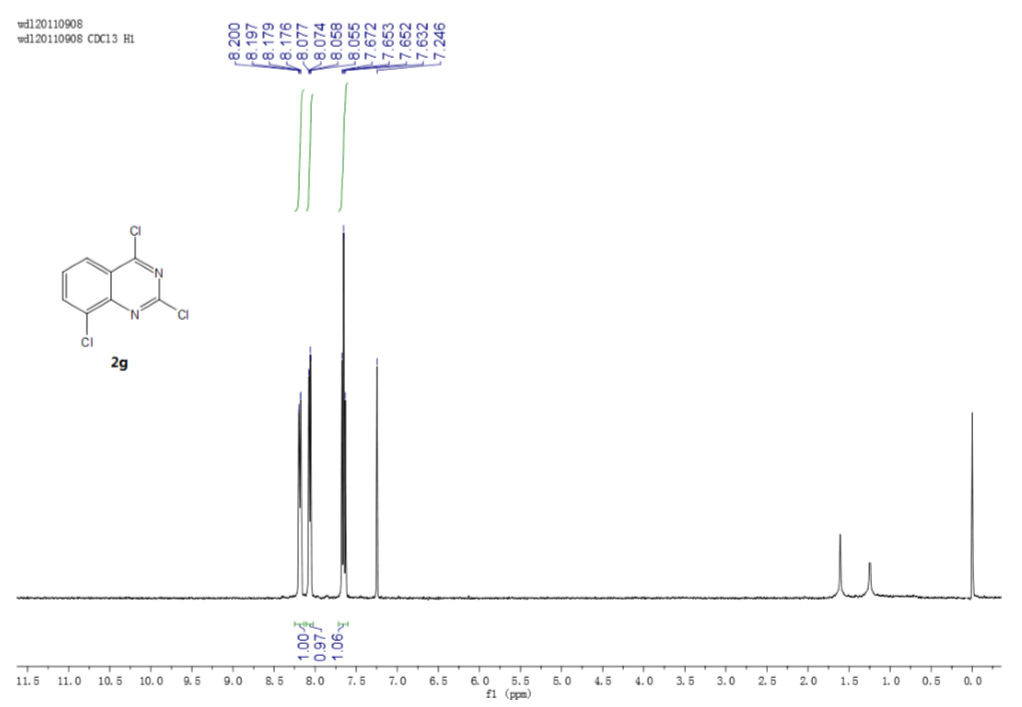
**Figure S 11:** 1H NMR of **2f**



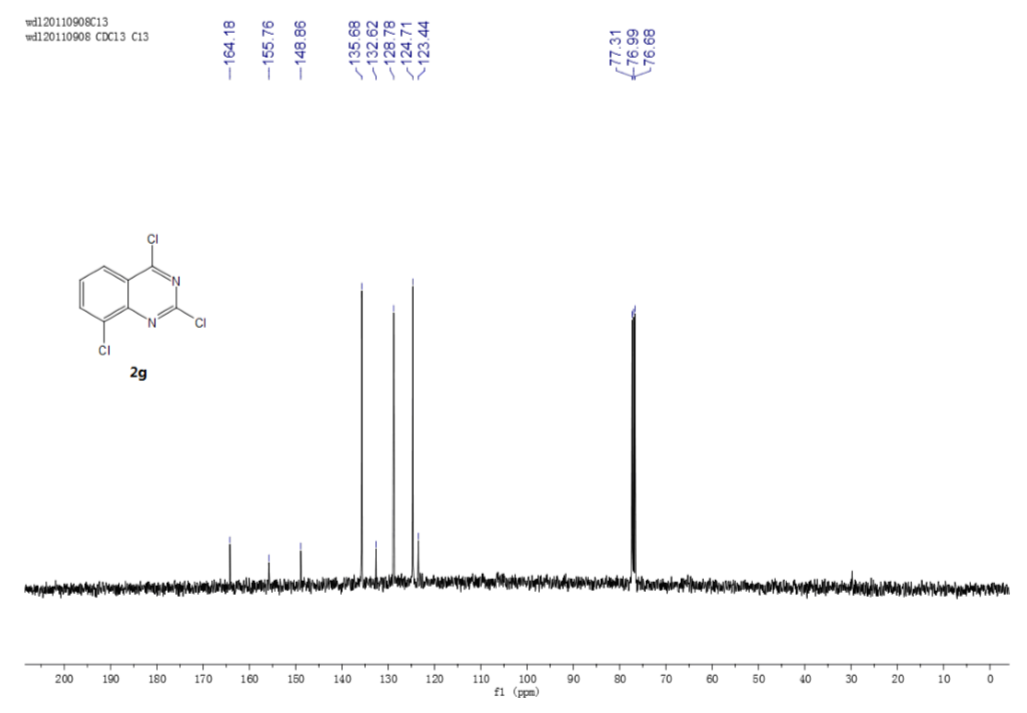
**Figure S 12:** 13C NMR of **2f**



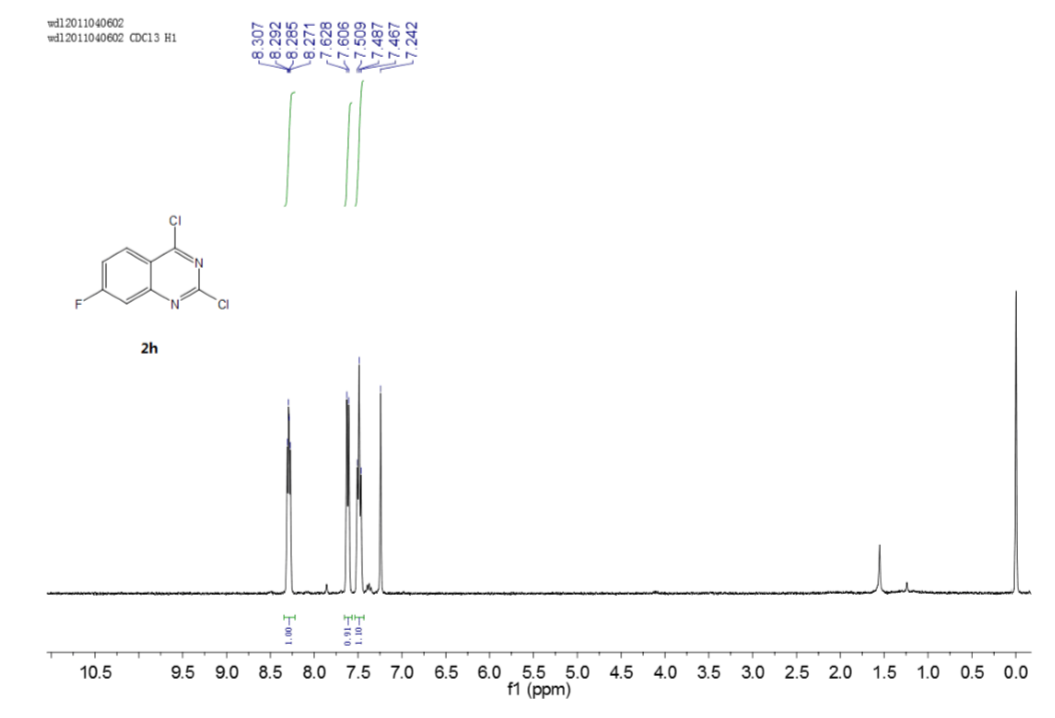
**Figure S 13:** 1H NMR of **2g**



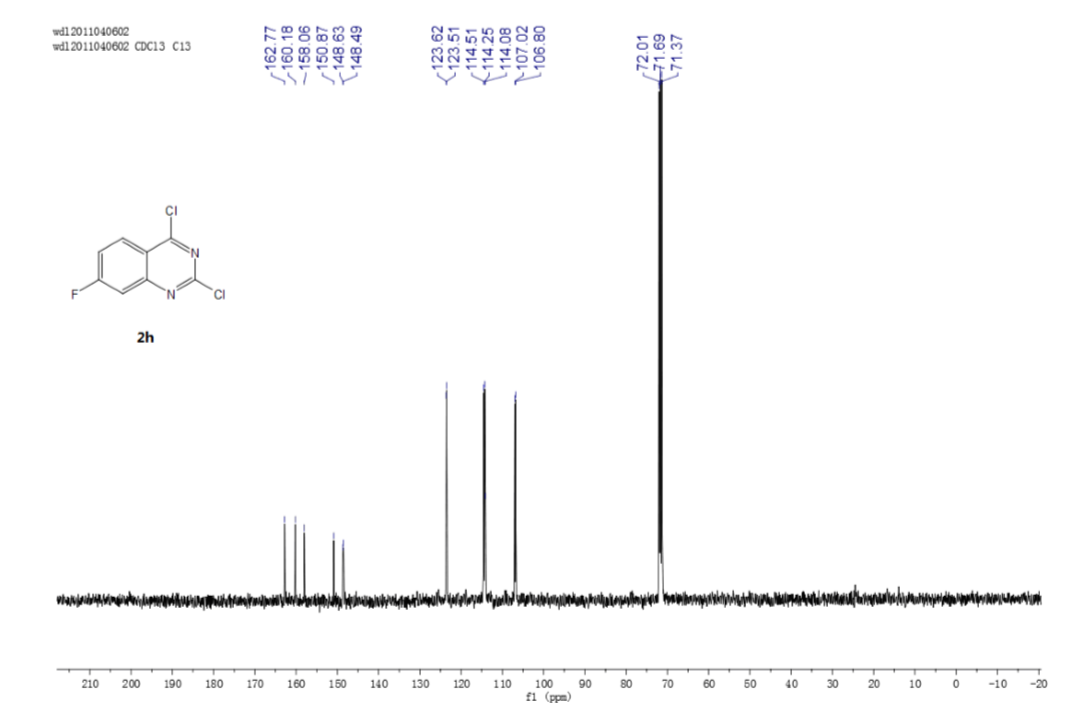
**Figure S 14:** 13C NMR of **2g**



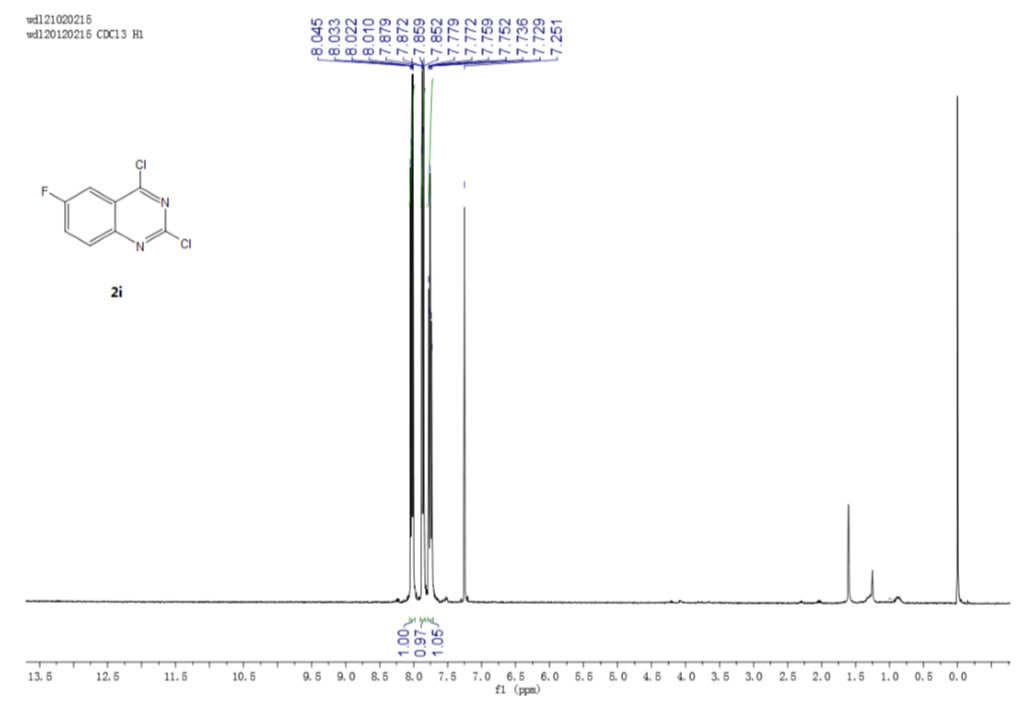
**Figure S 15:** 1H NMR of **2h**



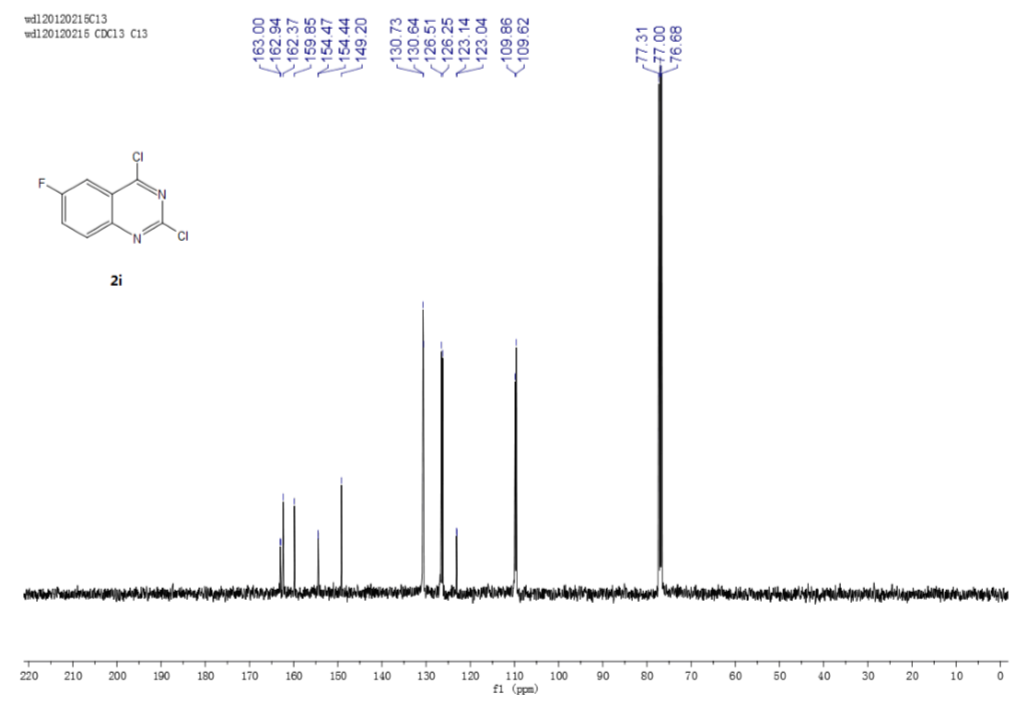
**Figure S 16:** 13C NMR of **2h**



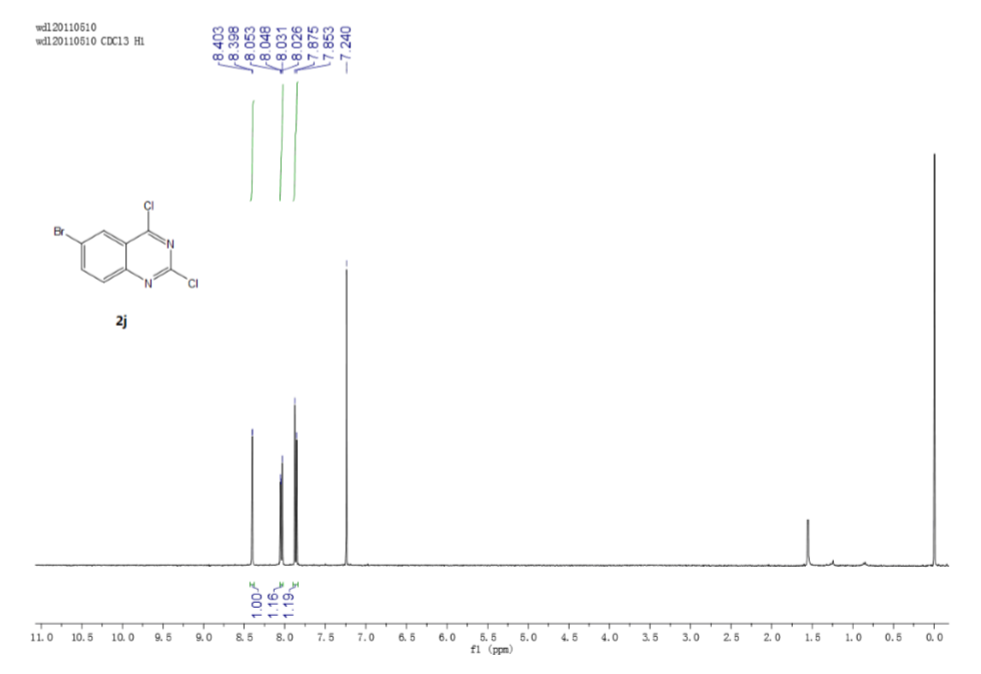
**Figure S 17:** 1H NMR of **2i**



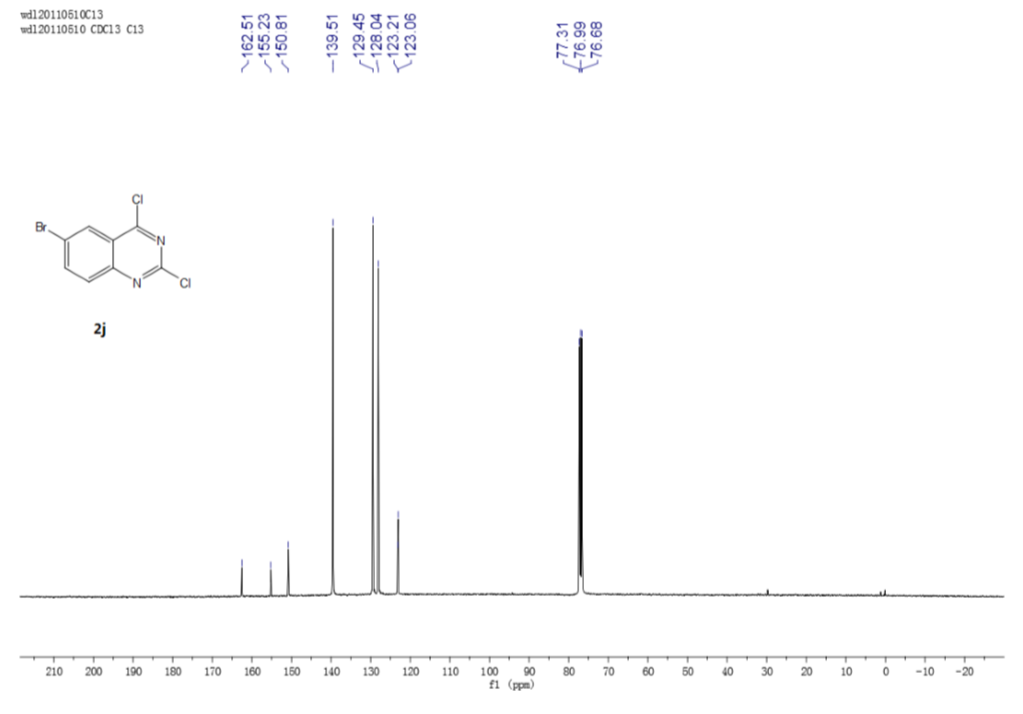
**Figure S 18:** 13C NMR of **2i**



**Figure S 19:** 1H NMR of **2j**



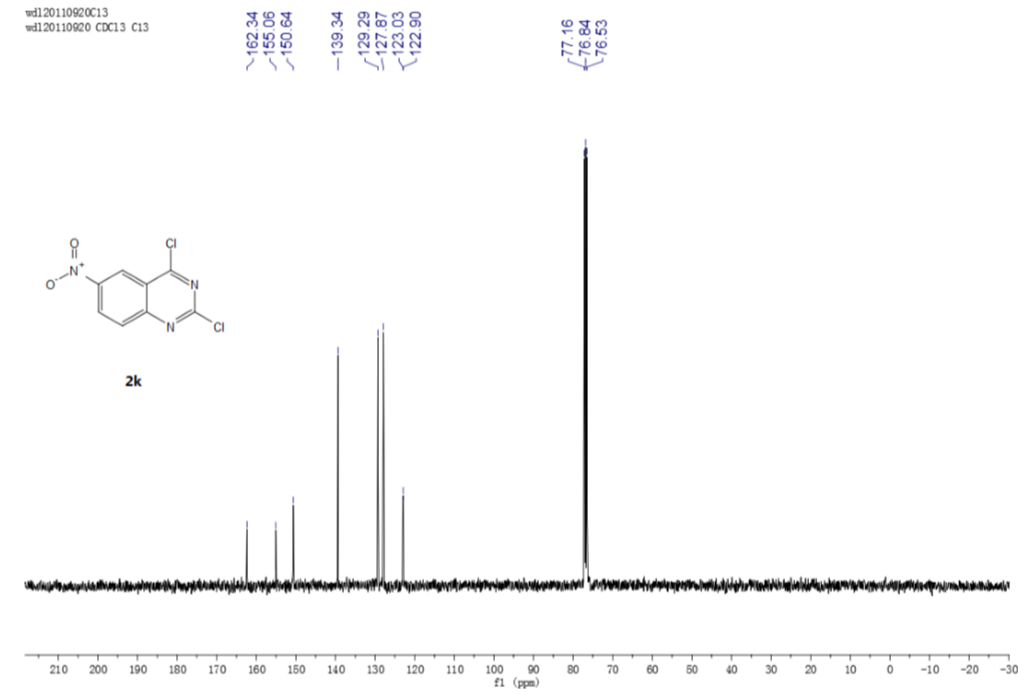
**Figure S 20:** 13C NMR of **2j**



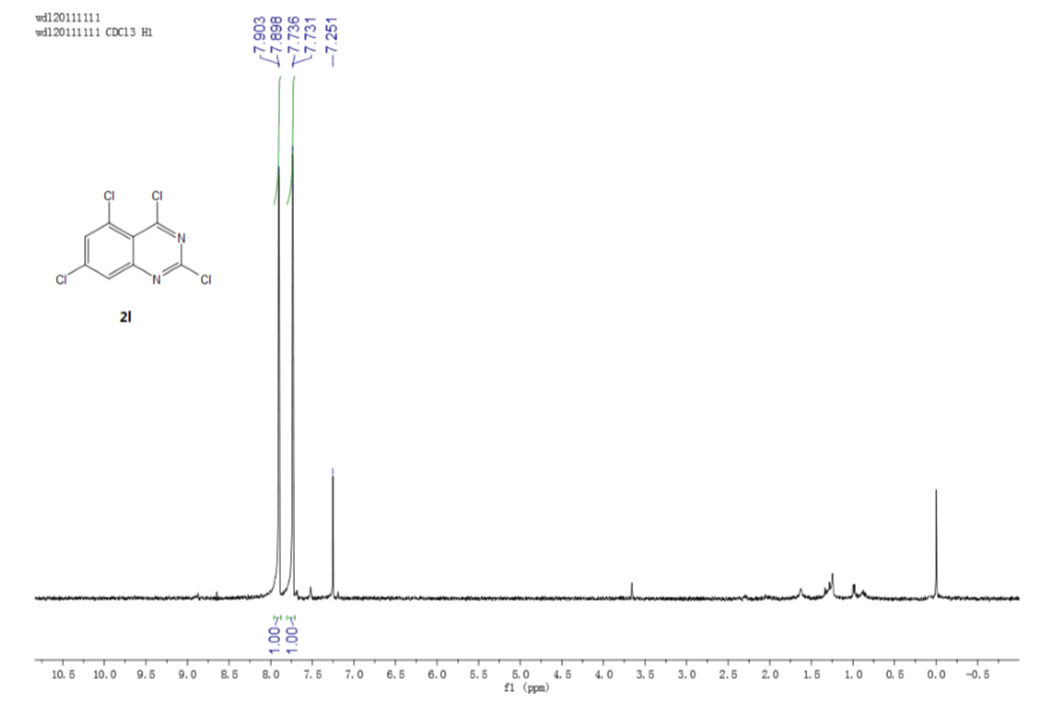
**Figure S 21:** 1H NMR of **2k**



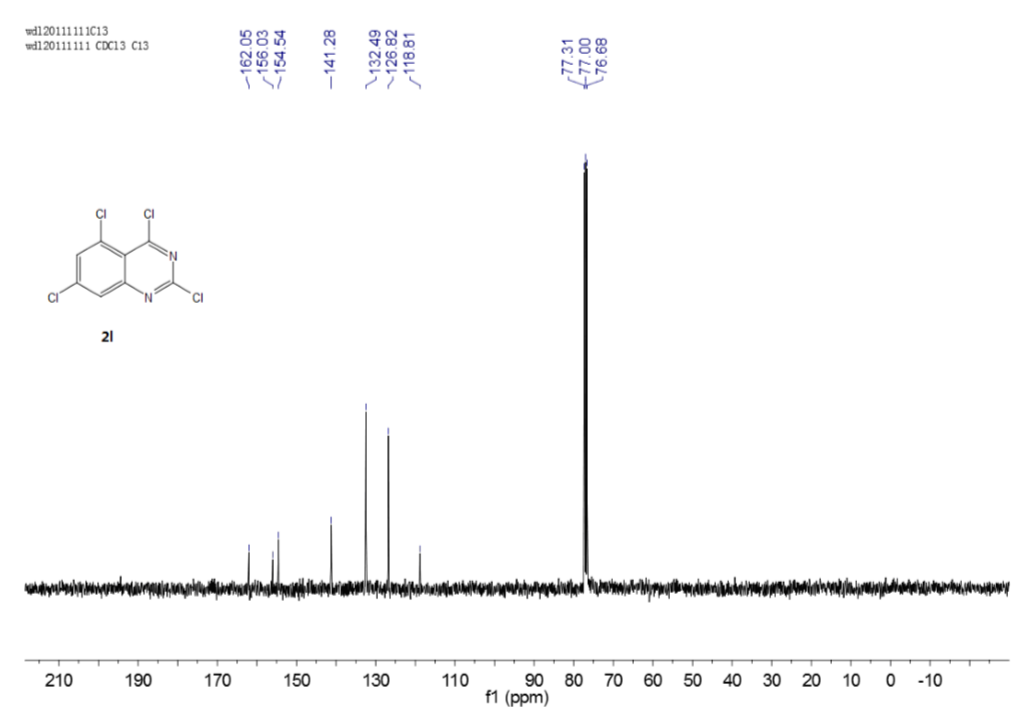
**Figure S 22:** 13C NMR of **2k**



**Figure S 23:** 1H NMR of **2l**



**Figure S 24:** 13C NMR of **2l**



**Figure S 25:** 1H NMR of **2m**



**Figure S 26:** 13C NMR of **2m**



**Figure S 27:** 1H NMR of **2n**



**Figure S 28:** 13C NMR of **2n**



**Figure S 29:** 1H NMR of **3b**



**Figure S 30:** 1H NMR of **3c**



**Figure S 31:** 1H NMR of **3d**



**Figure S 32:** 1H NMR of **3d**



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