

## Supporting Information

# Solvent Controlled Radical Cyclization of Propargylamines for Multi-Iodinated Quinoline Formation

Yu Zhang<sup>a</sup>, Xue-Ke Liu<sup>a</sup>, Zheng-Guang Wu<sup>a\*</sup>, Yi Wang<sup>a\*</sup> and Yi Pan<sup>abc</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210023, China.

<sup>b</sup> State of Key Laboratory of Coordination, Nanjing University, Nanjing, 210093, China.

<sup>c</sup> Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing, 210093, China.

Tel: +862586863153 Fax: +862583309123 E-mail: yiwang@nju.edu.cn

\* Corresponding author

### 1. General information

Commercially available reagents were used as received without purification. Column chromatography was carried out on silica gel (300–400 mesh). Analytical thin-layer chromatography was performed on glass plates of Silica Gel GF–254 with detection by UV. Infrared spectroscopy was measured by Agilent Cary 630 FTIR Spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a 400M Bruker spectrometer. The chemical shift references were as follows: <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.26 ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) 77.0 ppm. HRMS spectra were carried out on TOF MS EI<sup>+</sup> and ESI. Melting point determination was taken on a Melt–Temp apparatus (X-4) and was uncorrected.

**2. Synthesis of propargylamines 1** following reported procedures (*J. Am. Chem. Soc.*, **2002**, *124*, 5638; *J. Org. Chem.* **2006**, *71*, 2064–2070; *Org. Lett.* **2006**, *8*, 2405–2408; *Tetrahedron*, **2014**, *70*, 3134–3140.) The mixture of aldehyde (0.2 mmol), phenylacetylene (0.3 mmol), aniline (0.24 mmol) and copper (I) chloride (10 mol %) was heated at 60°C for two hours. The mixture in water was extracted with diethyl ether. The organic layer was washed with water and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed in *vacuo*. After flash column chromatography on silica gel with EtOAc/hexane as eluent, the product was isolated as a yellow oil.

### 3. General procedure

Propargylamine **1** (0.1 mmol) and *N*-iodosuccinimide (0.12 mmol) were stirred in 1,4-dioxane (2 ml) at room temperature for 6 h to give a red-brown solution. The solution was evaporated to dryness and the crude product was purified by column chromatography to afford pure product **2**.

Propargylamine **1** (0.1 mmol) and *N*-iodosuccinimide (0.3 mmol) were stirred in methanol (2 ml) at 60 °C for 6 h to give a brown solution. The solution was evaporated to dryness and the crude product purified by column chromatography with EtOAc/hexane as eluent to obtain the final product **3**.

### 4. Characterization data

**3-iodo-2,4-diphenylquinoline (2a):** White solid, mp 121–122 °C. Yield: 27.3 mg (67%). IR ν<sub>max</sub>

$\text{cm}^{-1}$  (KBr disc): 2951, 2834, 1550, 1391, 1322, 1243, 1100, 1048, 961, 834.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.17 (m, 1H), 7.78 – 7.69 (m, 1H), 7.69 – 7.62 (m, 2H), 7.60 – 7.37 (m, 8H), 7.35 – 7.27 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)  $\delta$  161.9, 154.7, 146.9, 143.8, 142.2, 130.1, 129.4, 129.3, 129.1, 128.7, 128.6, 128.5, 128.0, 127.4, 127.3, 126.9, 98.5. HRMS (ESI): Calcd. for  $\text{C}_{21}\text{H}_{15}\text{IN} (\text{M}+\text{H})^+$  408.0249, found 408.0247.

**3-iodo-5,7-dimethyl-2,4-diphenylquinoline (2b):** White solid. mp 157-158 °C. Yield: 27.8 mg (64%). IR  $\nu_{\text{max}}$   $\text{cm}^{-1}$  (KBr disc): 2967, 1534, 1492, 1384, 1261, 1045, 943, 825, 811, 766.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (s, 1H), 7.61 (m, 2H), 7.57 – 7.33 (m, 6H), 7.25 (m, 2H), 7.13 (s, 1H), 2.46 (s, 3H), 1.85 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)  $\delta$  161.2, 153.9, 148.5, 146.6, 144.1, 139.9, 134.8, 133.0, 129.5, 129.3, 128.5, 128.3, 128.2, 127.9, 127.8, 124.5, 100.6, 24.5, 21.4. HRMS (ESI): Calcd. for  $\text{C}_{23}\text{H}_{19}\text{IN} (\text{M}+\text{H})^+$  436.0562, found 436.0557.

**6-(tert-butyl)-3-iodo-2,4-diphenylquinoline (2c):** White solid. Yield: 37.5 mg (81%). IR  $\nu_{\text{max}}$   $\text{cm}^{-1}$  (KBr disc): 3058, 2950, 1535, 1440, 1087, 1027, 922, 749, 697, 609.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (m, 1H), 7.83 (m, 1H), 7.71 – 7.41 (m, 8H), 7.31 (m, 3H), 1.26 (s, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)  $\delta$  161.3, 154.5, 150.3, 145.5, 143.9, 142.3, 129.3, 129.1, 129.1, 128.9, 128.6, 128.5, 128.4, 128.0, 127.1, 121.8, 98.4, 35.0, 31.0. HRMS (ESI): Calcd. for  $\text{C}_{25}\text{H}_{23}\text{IN} (\text{M}+\text{H})^+$  464.0875, found 464.0873.

**3-iodo-6-methoxy-2,4-diphenylquinoline (2d):** White solid. Melting point: 137-138 °C. Yield: 32.8 mg (75%). IR  $\nu_{\text{max}}$   $\text{cm}^{-1}$  (KBr disc): 2836, 2758, 1562, 1498, 1346, 1276, 1252, 1134, 1028, 954.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.06 (d,  $J = 9.2$  Hz, 1H), 7.65 – 7.41 (m, 8H), 7.38 (m, 1H), 7.33 – 7.27 (m, 2H), 6.63 (m, 1H), 3.69 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 158.3, 153.2, 143.8, 143.1, 142.4, 130.9, 129.4, 129.1, 128.8, 128.5, 128.5, 128.4, 128.0, 122.5, 104.9, 99.1, 55.4. HRMS (ESI): Calcd. for  $\text{C}_{22}\text{H}_{17}\text{INO} (\text{M}+\text{H})^+$  438.0355, found 438.0350.

**6-(tert-butyl)-2-(4-fluorophenyl)-3-iodo-4-phenylquinoline (2e):** White solid. Melting point: 252-253 °C. Yield: 34.6 mg (72%). IR  $\nu_{\text{max}}$   $\text{cm}^{-1}$  (KBr disc): 3067, 2957, 2868, 1539, 1507, 1217, 1157, 1084, 1013, 978.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.08 (m, 1H), 7.83 (m, 1H), 7.67 – 7.49 (m, 5H), 7.35 – 7.27 (m, 3H), 7.21 – 7.13 (m, 2H), 1.26 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.7, 150.4, 145.3, 142.2, 131.3 (d,  $J = 8.3$  Hz), 129.2, 129.1, 128.8, 128.6, 128.5, 127.1, 121.9, 115.1, 114.9 (d,  $J = 21.7$  Hz), 98.3, 35.0, 31.0.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  -113.1. HRMS (ESI): Calcd. for  $\text{C}_{25}\text{H}_{22}\text{FIN}(\text{M}+\text{H})^+$  482.0781, found 482.0781.

**6-(tert-butyl)-3-iodo-4-phenyl-2-(p-tolyl)quinolone (2f):** White solid. Melting point: 244-245 °C. Yield: 36.3 mg (76%). IR  $\nu_{\text{max}}$   $\text{cm}^{-1}$  (KBr disc): 3054, 2950, 1559, 1362, 1256, 1084, 1019, 980, 918, 745.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.09 (m, 1H), 7.82 (m, 1H), 7.61 – 7.49 (m, 5H), 7.35 – 7.26 (m, 5H), 2.43 (s, 3H), 1.25 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.3, 154.5, 150.1, 145.5, 142.4, 141.0, 138.4, 129.2, 129.1, 129.0, 128.8, 128.6, 128.6, 128.4, 127.0, 121.8, 98.6, 35.0, 31.01, 21.4. HRMS (ESI): Calcd. for  $\text{C}_{26}\text{H}_{25}\text{IN} (\text{M}+\text{H})^+$  478.1032, found 478.1026.

**6-(tert-butyl)-3-iodo-2-phenyl-4-(p-tolyl)quinolone (2g):** White solid. Melting point: 227-229 °C. Yield: 37.2 mg (78%). IR  $\nu_{\text{max}}$   $\text{cm}^{-1}$  (KBr disc): 2954, 2866, 1560, 1491, 1334, 1256, 1202, 1088, 921, 766.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.09 (m, 1H), 7.82 (m, 1H), 7.62 (m, 2H), 7.53 – 7.33 (m, 6H), 7.19 (m, 2H), 2.49 (s, 3H), 1.27 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.3, 154.7, 150.2, 145.5, 144.0, 139.3, 138.2, 129.3, 129.2, 129.0, 129.0, 128.9, 128.4, 127.9, 127.3, 122.0, 98.8, 35.0, 31.1, 21.6. HRMS (ESI): Calcd. for  $\text{C}_{26}\text{H}_{25}\text{IN}[\text{M}+\text{H}]^+$  478.1032, found: 478.1028.

**6-chloro-3-iodo-2,4-diphenylquinoline (2h):** White solid. mp: 183-184 °C. Yield: 30.9mg (70%). IR  $\nu_{\text{max}}$   $\text{cm}^{-1}$  (KBr disc): 2976, 2818, 1556, 1423, 1384, 1204, 945, 844, 775, 684.  $^1\text{H}$  NMR

(CDCl<sub>3</sub>, 400 MHz) δ 8.13–8.06 (m, 1H), 7.69–7.45 (m, 9H), 7.38 (m, 1H), 7.30–7.26 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.2, 154.0, 145.4, 143.4, 141.5, 133.2, 131.1, 129.2, 129.0, 128.9, 128.8, 128.0, 127.9, 125.6, 99.8. HRMS (ESI): Calcd. for C<sub>21</sub>H<sub>14</sub>ClIN (M+H)<sup>+</sup> 441.9859, found 441.9851.

**3-iodo-2,4-diphenyl-6-(trifluoromethyl)quinolone (2i):** White solid. Melting point: 245–246 °C. Yield: 33.8mg (71%). IR ν<sub>max</sub> cm<sup>-1</sup> (KBr disc): 3066, 1625, 1560, 1441, 1336, 1383, 1314, 1293, 977, 900. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.27 (m, 1H), 7.90 (m, 1H), 7.71 (s, 1H), 7.68 – 7.45 (m, 8H), 7.30 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.2, 154.8, 147.9, 143.2, 141.2, 130.7, 129.2, 129.1, 129.0, 128.9, 128.6, 128.1, 126.3, 125.8 (q, J = 2.9 Hz) 125.1, 124.8 (q, J = 4.5 Hz), 122.4, 100.1. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 100 MHz) δ -62.4. HRMS (ESI): Calcd. for C<sub>22</sub>H<sub>14</sub>F<sub>3</sub>I<sub>2</sub>N (M+H)<sup>+</sup> 476.0123, found 476.0118.

**3,6-diido-2,4-diphenylquinoline (3a):** White solid, yield: 40.5mg (76%), mp: 223–225 °C. IR ν<sub>max</sub> cm<sup>-1</sup> (KBr disc): 3056, 2344, 1528, 1441, 1328, 1025, 971, 883, 827, 743. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.97 (m, 1H), 7.87 (m, 1H), 7.76 (s, 1H), 7.67 – 7.43 (m, 9H), 7.32 – 7.27 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz) δ 162.5, 153.7, 145.9, 143.4, 141.4, 139.0, 135.5, 131.1, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.0, 99.6, 93.3. HRMS (ESI): calcd for C<sub>21</sub>H<sub>14</sub>I<sub>2</sub>N (M+H)<sup>+</sup> 533.9216, found 533.9211

**7-fluoro-3,6-diido-2,4-diphenylquinoline (3b):** Yellow solid, yield: 34.7 mg (63%), mp: 201–202 °C. IR ν<sub>max</sub> cm<sup>-1</sup> (KBr disc): 3062, 1556, 1463, 1338, 1180, 1085, 885, 747, 693, 557. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.85 (d, J = 6.7 Hz, 1H), 7.78 (d, J = 8.7 Hz, 1H), 7.65 – 7.55 (m, 5H), 7.52 – 7.46 (m, 3H), 7.29 – 7.25 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz) δ 163.6, 162.7, 160.2, 153.7, 153.7, 147.7 (d, J = 11.8 Hz), 143.2, 141.3, 138.2, 138.2, 129.2, 129.0, 128.9, 128.1, 125.8, 113.18 (d, J = 23.7 Hz), 98.4, 84.0 (d, J = 28.6 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 100 MHz) δ -90.6. HRMS (ESI): calcd for C<sub>21</sub>H<sub>13</sub>FI<sub>2</sub>N (M+H)<sup>+</sup> 551.9121, found 551.9192.

**3,6-diido-5,7-dimethyl-2,4-diphenylquinoline (3c):** White solid, yield 41.5mg (74%), mp 201–202 °C. IR ν<sub>max</sub> cm<sup>-1</sup> (KBr disc): 3056, 2344, 1491, 1437, 1157, 1028, 988, 971, 848, 704. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.94 (s, 1H), 7.77 – 7.56 (m, 2H), 7.56 – 7.36 (m, 6H), 7.25 – 7.22 (m, 2H), 2.66 (s, 3H), 2.14 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz) δ 162.0, 153.1, 147.3, 146.7, 143.8, 143.6, 138.5, 129.6, 129.2, 128.7, 128.6, 128.5, 128.0, 127.6, 125.0, 113.4, 100.9, 31.9, 31.1. HRMS (ESI): calcd for C<sub>23</sub>H<sub>18</sub>I<sub>2</sub>N (M+H)<sup>+</sup> 561.9529, found 561.9563.

**2-([1,1'-biphenyl]-4-yl)-3,6-diido-4-phenylquinoline (3d)** White solid, yield 37.1mg (61%), mp 307–308 °C, IR ν<sub>max</sub> cm<sup>-1</sup> (KBr disc): 3028, 1327, 1243, 1086, 1057, 971, 885, 831, 695, 611. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.97 (m, 1H), 7.88 (m, 1H), 7.79 – 7.53 (m, 10H), 7.47 (m, 2H), 7.37 (m, 1H), 7.29 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz) δ 162.2, 153.7, 146.0, 142.3, 141.7, 141.5, 140.7, 139.0, 135.5, 131.1, 129.8, 129.1, 129.0, 128.9, 128.8, 128.7, 127.6, 127.3, 126.8, 99.4, 93.3. HRMS (ESI): Calcd. for C<sub>27</sub>H<sub>18</sub>I<sub>2</sub>N (M+H)<sup>+</sup> 609.9529, found 609.9581.

**3,6-diido-4-phenyl-2-(4-(trifluoromethyl)phenyl)quinolone (3e):** White solid, yield: 41.5mg (69%), mp 297–298 °C. IR ν<sub>max</sub> cm<sup>-1</sup> (KBr disc): 3069, 1588, 1467, 1318, 1124, 1018, 972, 887, 831, 699. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.99 (dd, J = 8.8, 1.9 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.80 – 7.74 (m, 5H), 7.63 – 7.54 (m, 3H), 7.28 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz) δ 161.1, 154.0, 146.7, 145.9, 141.1, 139.3, 135.6, 131.1, 129.8, 129.1, 129.0, 128.9, 125.1 (q, J = 3.7 Hz), 98.5, 93.9. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 100 MHz) δ -62.6. HRMS (ESI): Calcd. for C<sub>22</sub>H<sub>13</sub>F<sub>3</sub>I<sub>2</sub>N (M+H)<sup>+</sup> 601.9089, found 601.9086.

**2-(4-chlorophenyl)-3,6-diido-4-phenylquinoline (3f):** White solid, yield 37.9 mg (67%), mp

300-301 °C. IR  $\nu_{\text{max}}$  cm<sup>-1</sup> (KBr disc): 3024, 1655, 1489, 1459, 1325, 1090, 1014, 973, 885, 823. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 (m, 1H), 7.84 (m, 1H), 7.76 (m, 1H), 7.58 (m, 5H), 7.47 (m, 2H), 7.33 – 7.25 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  161.3, 153.9, 145.9, 141.7, 141.3, 139.2, 135.5, 135.0, 131.0, 130.8, 129.0, 128.9, 128.8, 128.3, 99.1, 93.6. HRMS (ESI): calcd for C<sub>21</sub>H<sub>13</sub>I<sub>2</sub>N (M+H)<sup>+</sup> 567.8826, found 567.8823.

**2-(4-(tert-butyl)phenyl)-3,6-diodo-4-phenylquinoline (3g)** White solid, yield 44.2 mg (75%), mp 214-216 °C. IR  $\nu_{\text{max}}$  cm<sup>-1</sup> (KBr disc): 2954, 2860, 1523, 1508, 1459, 1323, 1109, 971, 829, 747. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.95 (m, 1H), 7.86 (m, 1H), 7.75 (m, 1H), 7.55 (m, 7H), 7.27 (m, 2H), 1.37 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  162.6, 153.6, 151.8, 145.9, 141.6, 140.5, 138.9, 135.5, 131.1, 129.1, 128.9, 128.8, 128.7, 125.0, 99.7, 93.1, 34.8, 31.4. HRMS (ESI): calcd for C<sub>25</sub>H<sub>21</sub>I<sub>2</sub>N (M+H)<sup>+</sup> 589.9842, found 589.9838.

**4-(3-fluorophenyl)-3,6-diodo-2-phenylquinoline (3h)** White solid, yield 32.5 mg (59%), mp 218-219 °C. IR  $\nu_{\text{max}}$  cm<sup>-1</sup> (KBr disc): 3065, 1578, 1467, 1435, 1329, 1211, 993, 885, 826, 764. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (m, 1H), 7.86 (m, 1H), 7.73 (m, 1H), 7.65–7.43 (m, 7H), 7.24 (m, 1H), 7.08–6.97 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  162.5, 152.2, 152.1, 145.9, 143.2, 139.2, 135.1, 131.2, 130.8 (d, *J* = 8.4 Hz), 129.2, 128.9, 128.4, 128.1, 125.0, 116.5 (d, *J* = 22.3 Hz), 116.0 (d, *J* = 20.9 Hz), 99.3, 93.6. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  -111.4. HRMS (ESI): Calcd for C<sub>21</sub>H<sub>13</sub>FI<sub>2</sub>N (M+H)<sup>+</sup> 551.9121, found 551.9121.

**4-(4-chlorophenyl)-3,6-diodo-2-phenylquinoline (3i)** White solid, yield 39.7 mg (70%), mp 279-280 °C. IR  $\nu_{\text{max}}$  cm<sup>-1</sup> (KBr disc): 3051, 2344, 1587, 1459, 1396, 1329, 1176, 1088, 972, 885. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 (m, 1H), 7.87 (m, 1H), 7.74 (m, 1H), 7.66 – 7.42 (m, 7H), 7.25–7.20 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  152.4, 145.9, 143.2, 139.7, 139.1, 135.1, 135.0, 131.2, 130.6, 129.3, 129.2, 128.9, 128.5, 128.1, 99.5, 93.6. HRMS (ESI): Calcd. for C<sub>21</sub>H<sub>13</sub>ClI<sub>2</sub>N (M+H)<sup>+</sup> 567.8826, found 567.8821.

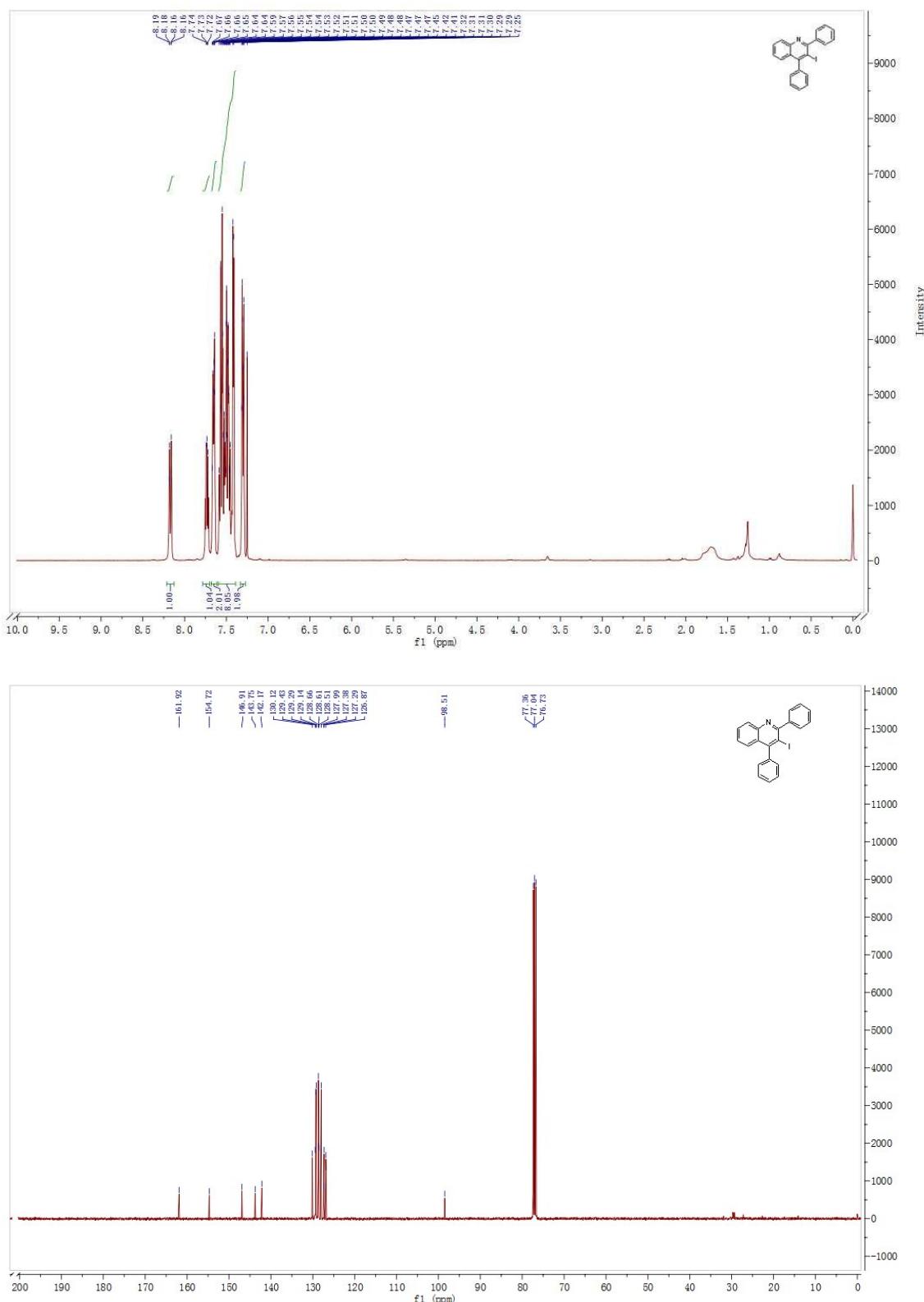
**2,3,4,6-tetraphenylquinoline (4a):** 6-diodo-5,7-diphenylquinoline **3a** (0.267g, 0.5 mmol), sodium carbonate (0.106g, 1 mmol), phenylboronic acid (0.183g, 1.5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.029g, 0.0025mmol) in the molar ratio of 1:2:3:0.05 were stirred in the 1:1 mixture of THF and H<sub>2</sub>O (12 ml) at 70 °C for 12h to give a brown solution. The reaction mixture was allowed to cool to room temperature after which water (10 mL) was added. The mixture was then extracted with dichloromethane (3×10 mL) and the organic extracts dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated in *vacuo*. Purification by flash chromatography furnished the pure cross-coupled product as a white liquid (0.156 g, 72%). IR  $\nu_{\text{max}}$  cm<sup>-1</sup> (KBr disc): 3027, 2343, 1545, 1442, 1351, 1075, 1019, 926, 852, 755. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.33 (m, 1H), 8.00 (m, 1H), 7.77 (m, 1H), 7.59–7.54 (m, 2H), 7.45–7.27 (m, 7H), 7.21 (m, 6H), 7.03–6.99 (m, 3H), 6.91 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  159.0, 147.9, 146.8, 141.2, 140.7, 139.3, 138.4, 136.9, 133.4, 131.4, 130.4, 130.2, 130.0, 129.2, 128.9, 127.9, 127.7, 127.7, 127.6, 127.5, 127.4, 126.9, 126.4, 124.4. HRMS (ESI): Calcd. for C<sub>33</sub>H<sub>24</sub>N (M+H)<sup>+</sup> 434.1909, found 434.1905.

**2, 4-diphenyl-3, 6-bis(phenylethynyl)quinoline (4b):** 6-diodo-5,7-diphenylquinoline **3a** (0.267g, 0.5 mmol), CuI (0.1 mmol), (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> (0.05 mmol) and potassium carbonate (1.5 mmol) was charged in a dry and argon-flushed *Schlenk*-flask. Then phenylacetylene (1.5 mmol) and dry DMF (3.0 mL) were added and the mixture was stirred at 120 °C for 18 h. The reaction mixture was allowed to cool to room temperature after which water (20 mL) was added. The mixture was then extracted with dichloromethane (3×10 mL) and the organic phase was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in *vacuo*. Purification by flash chromatography furnished the pure cross-

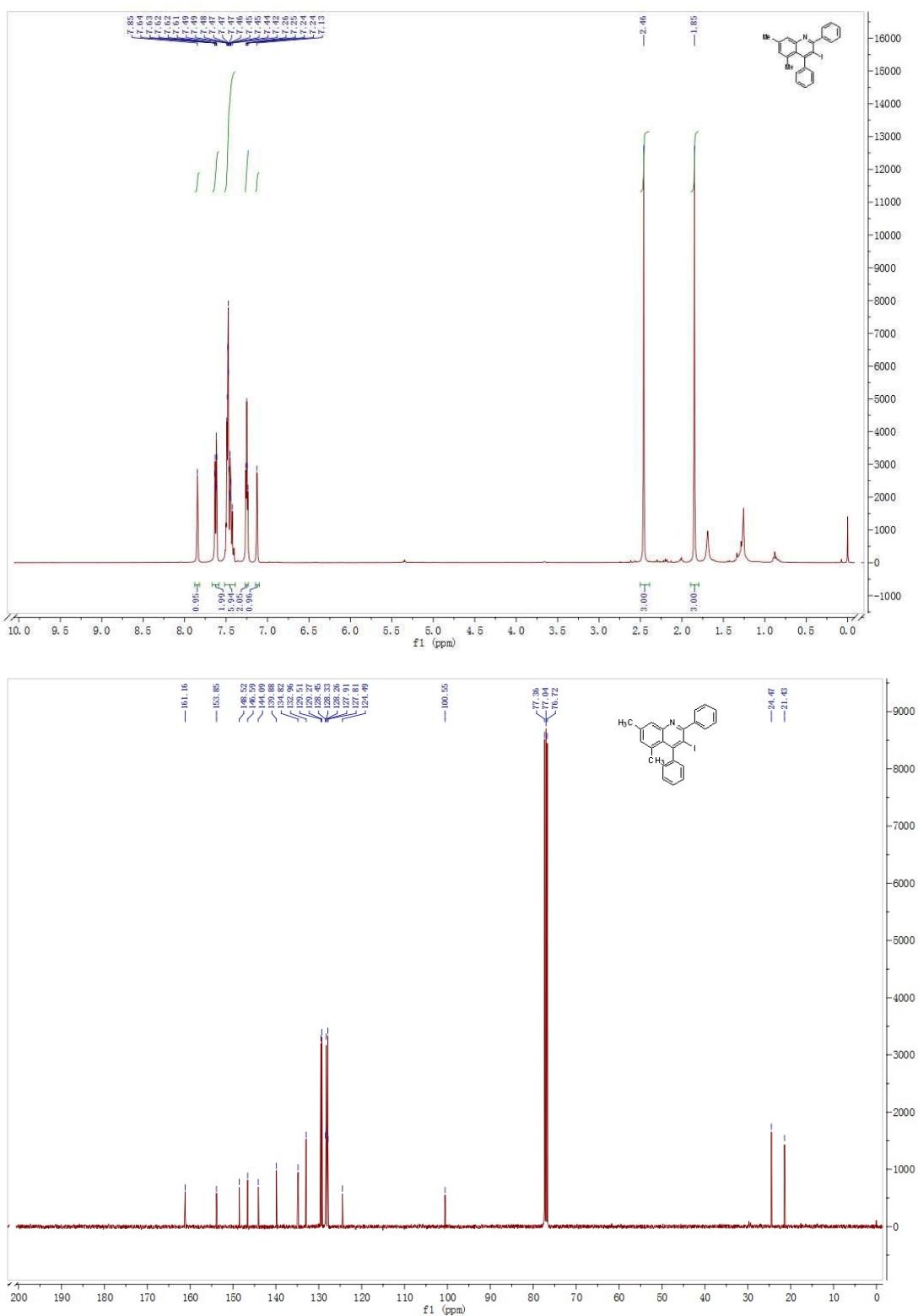
coupling product as a white solid (0.171 g, 71%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17 (d,  $J = 9.1$  Hz, 1H), 8.09 (d,  $J = 7.4$  Hz, 2H), 7.82 (d,  $J = 7.2$  Hz, 2H), 7.57 (ddd,  $J = 24.7, 13.3, 7.3$  Hz, 10H), 7.39 – 7.30 (m, 3H), 7.24 – 7.17 (m, 3H), 6.96 (d,  $J = 7.7$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 151.6, 146.2, 139.9, 136.7, 132.7, 131.7, 131.1, 130.2, 129.6, 129.4, 129.1, 128.7, 128.0, 127.9, 125.6, 122.9, 121.9, 116.2, 98.8, 90.9, 89.3, 87.6. HRMS (ESI): Calcd. for  $\text{C}_{37}\text{H}_{23}\text{NH}$  ( $\text{M}+\text{H})^+$  482.1909, found 482.1906.

#### 4. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra of iodoquinolines 2-4

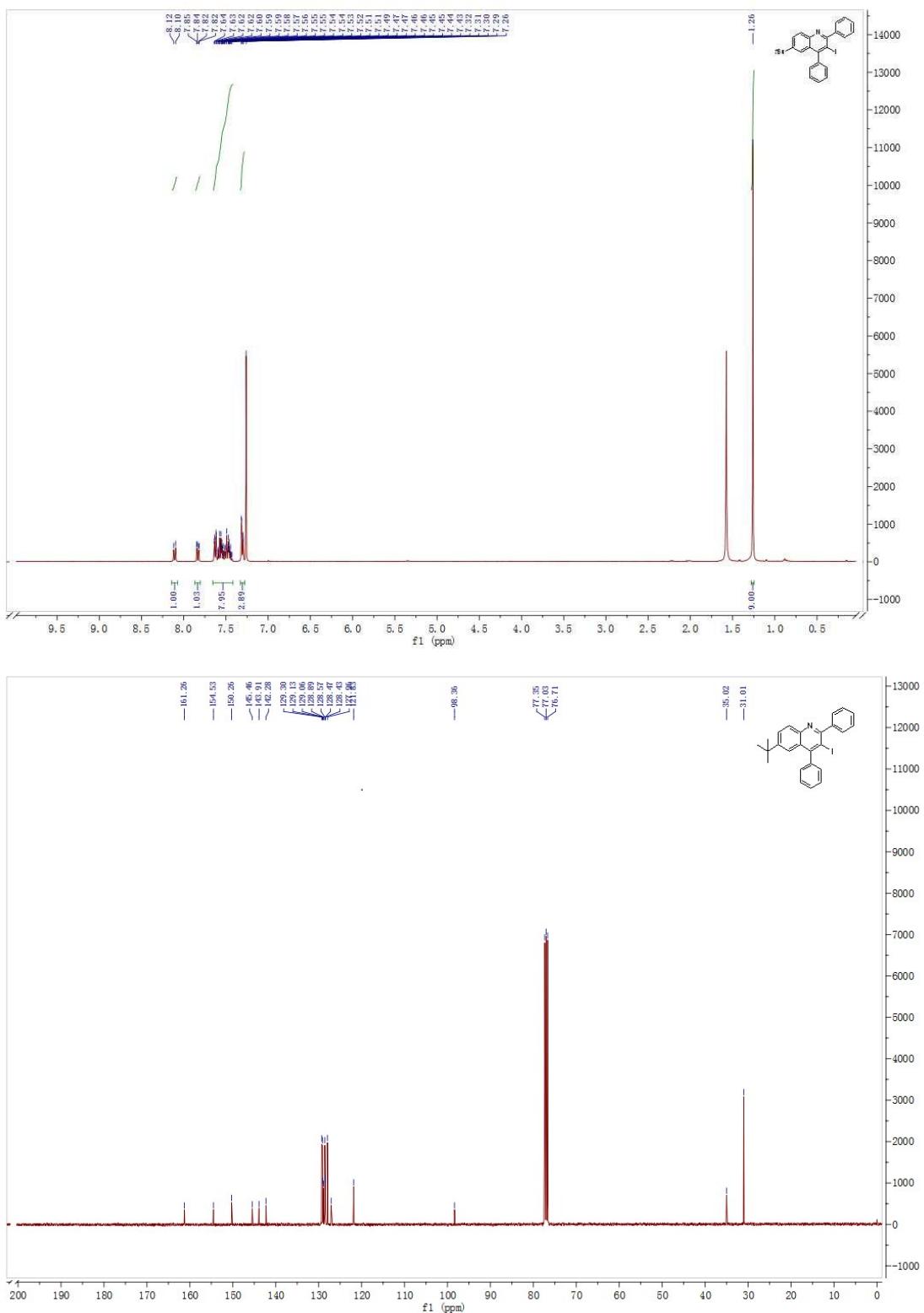
##### 3-iodo-2,4-diphenylquinoline (2a)



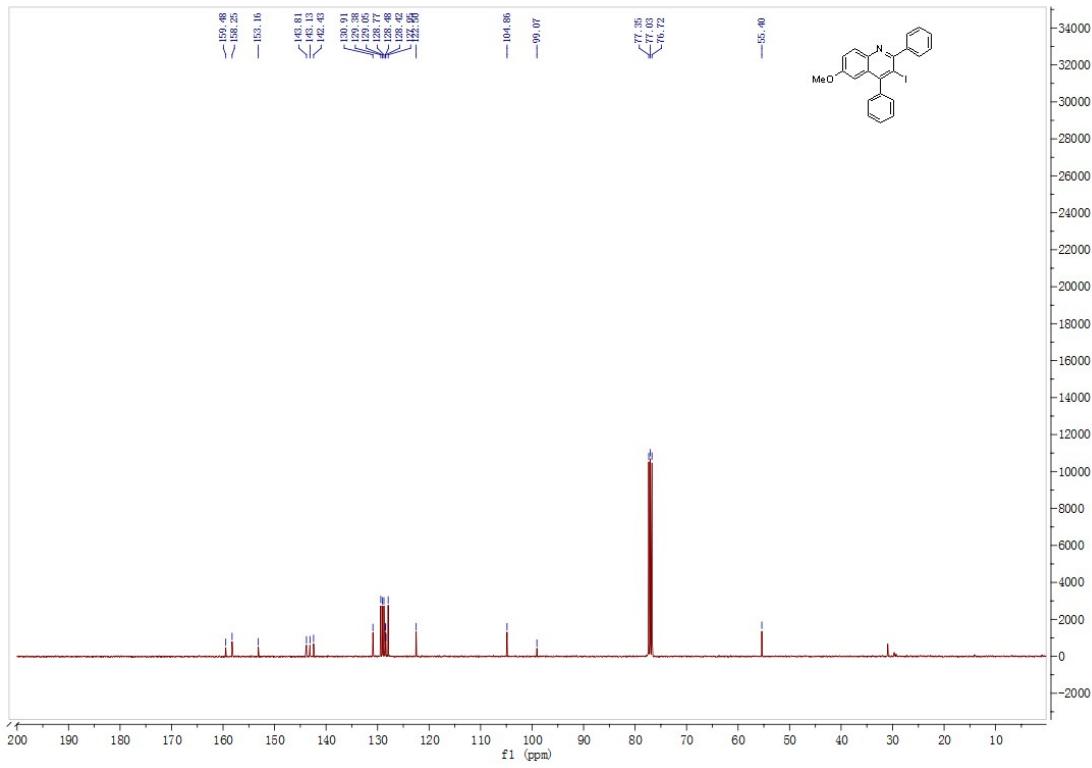
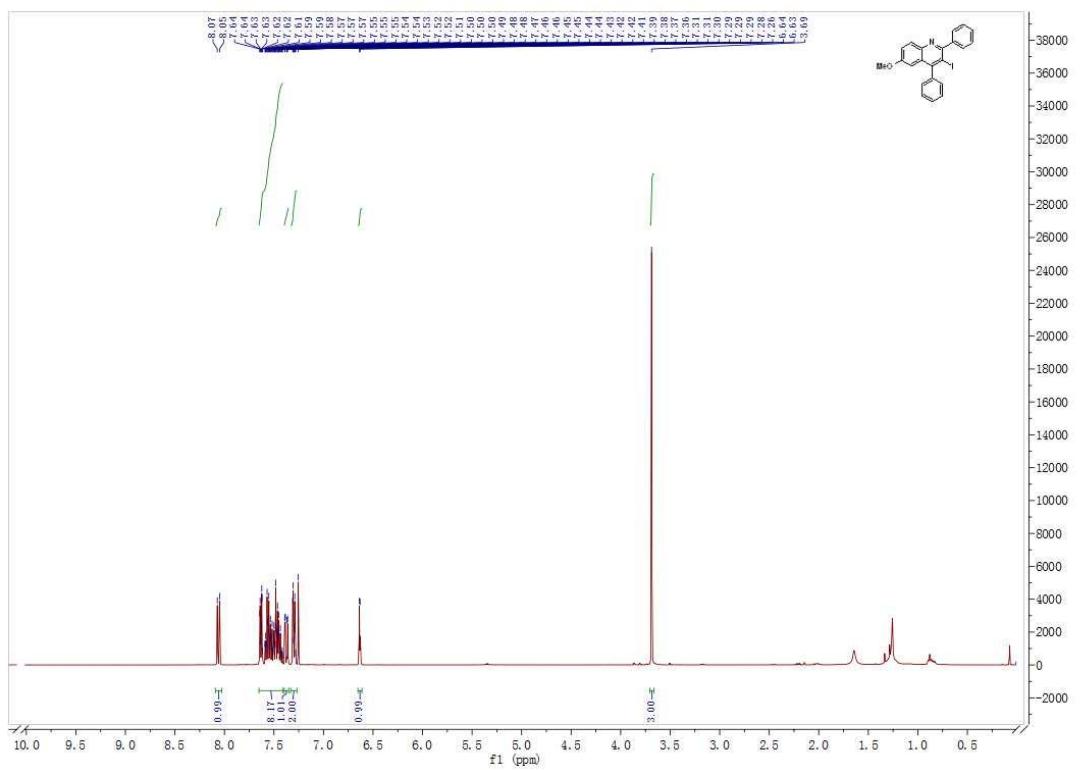
### 3-**iodo**-5,7-dimethyl-2,4-diphenylquinoline (**2b**)



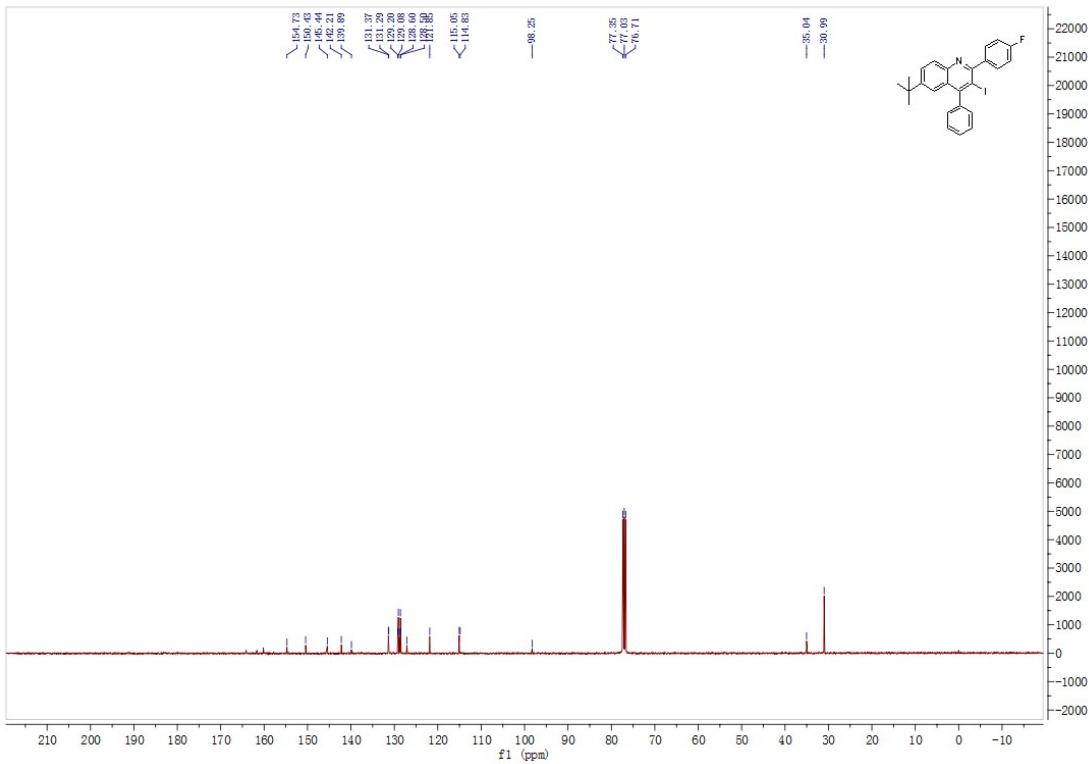
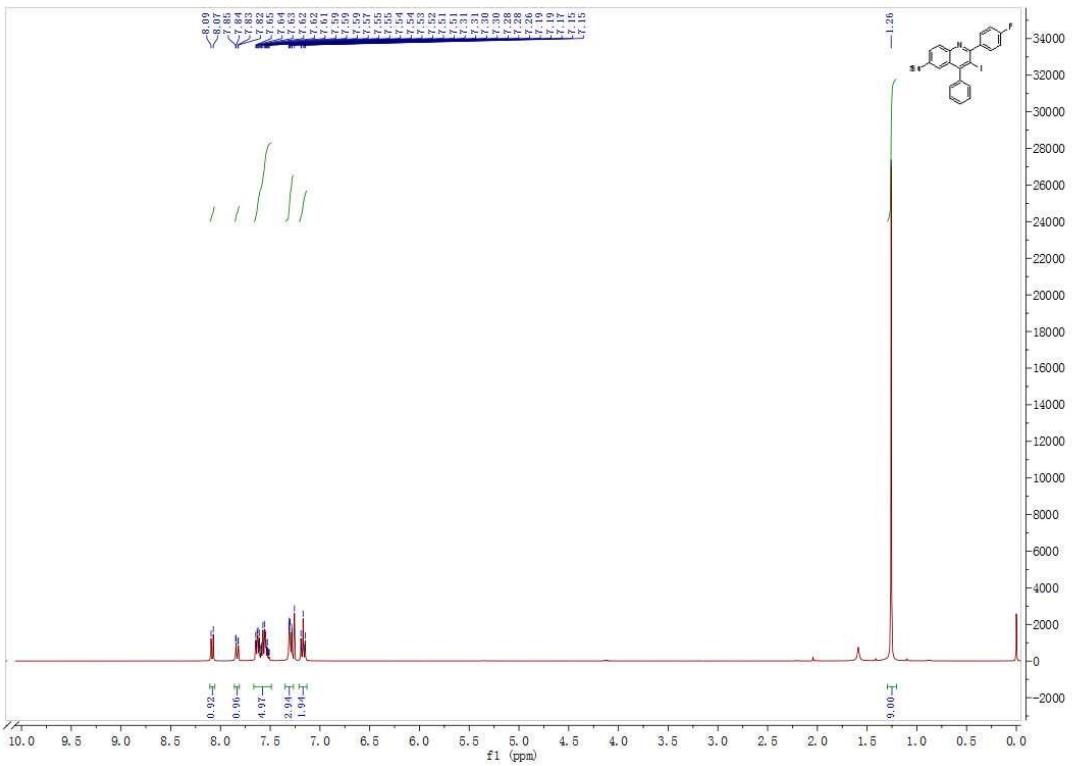
**6-(tert-butyl)-3-iodo-2,4-diphenylquinoline (2c)**



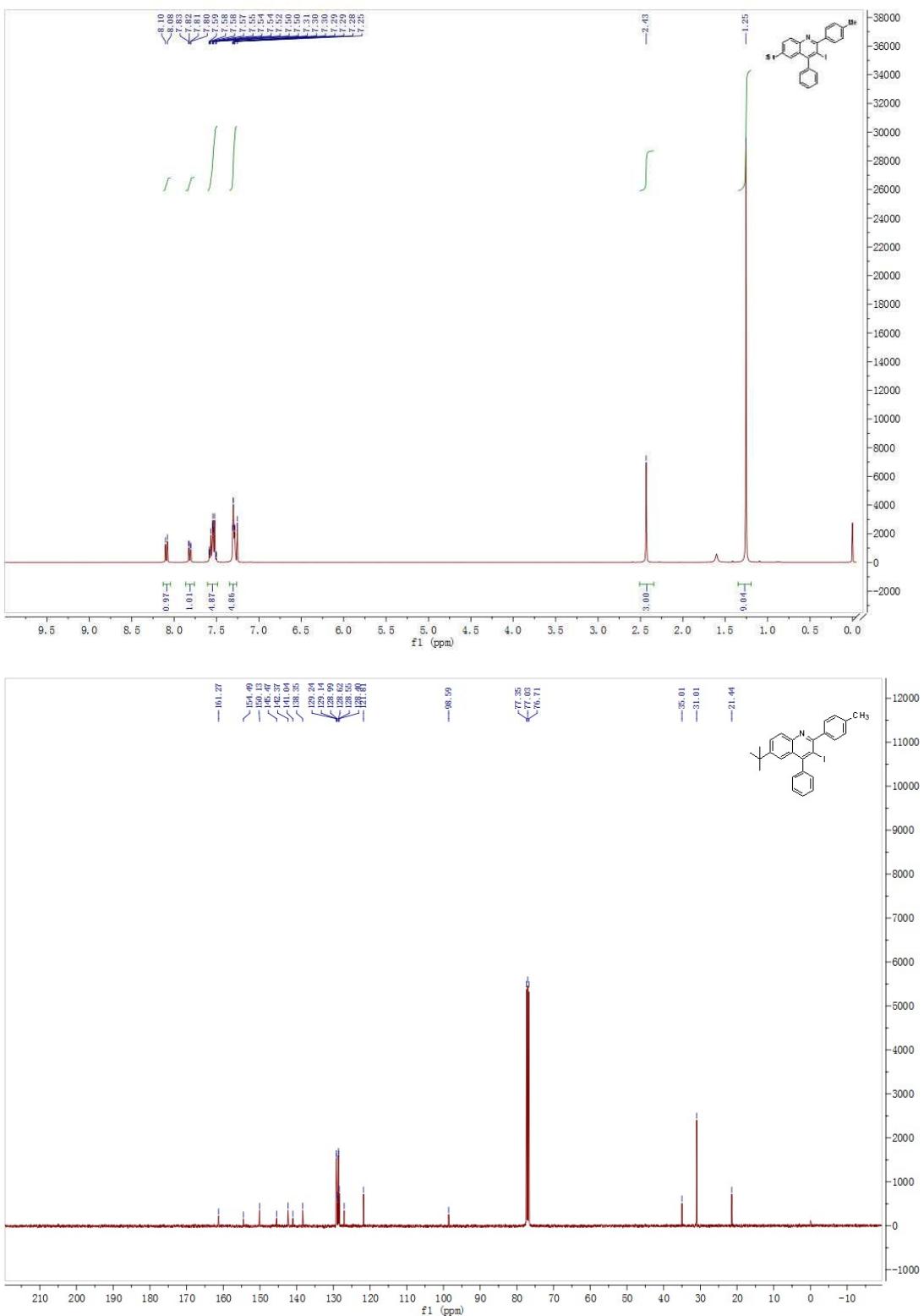
### **3-iodo-6-methoxy-2,4-diphenylquinoline (2d)**



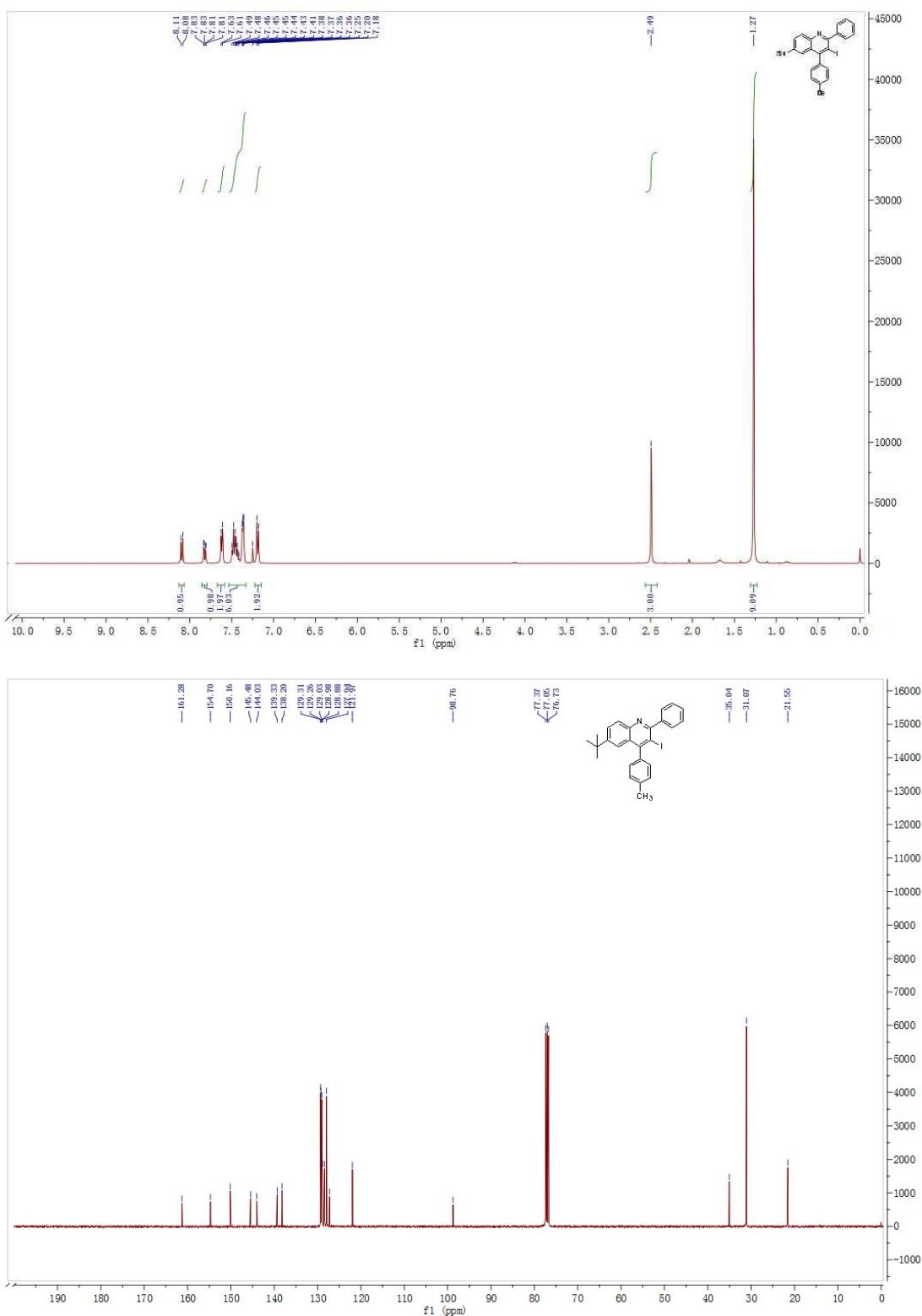
### 6-(tert-butyl)-2-(4-fluorophenyl)-3-iodo-4-phenylquinoline (2e)



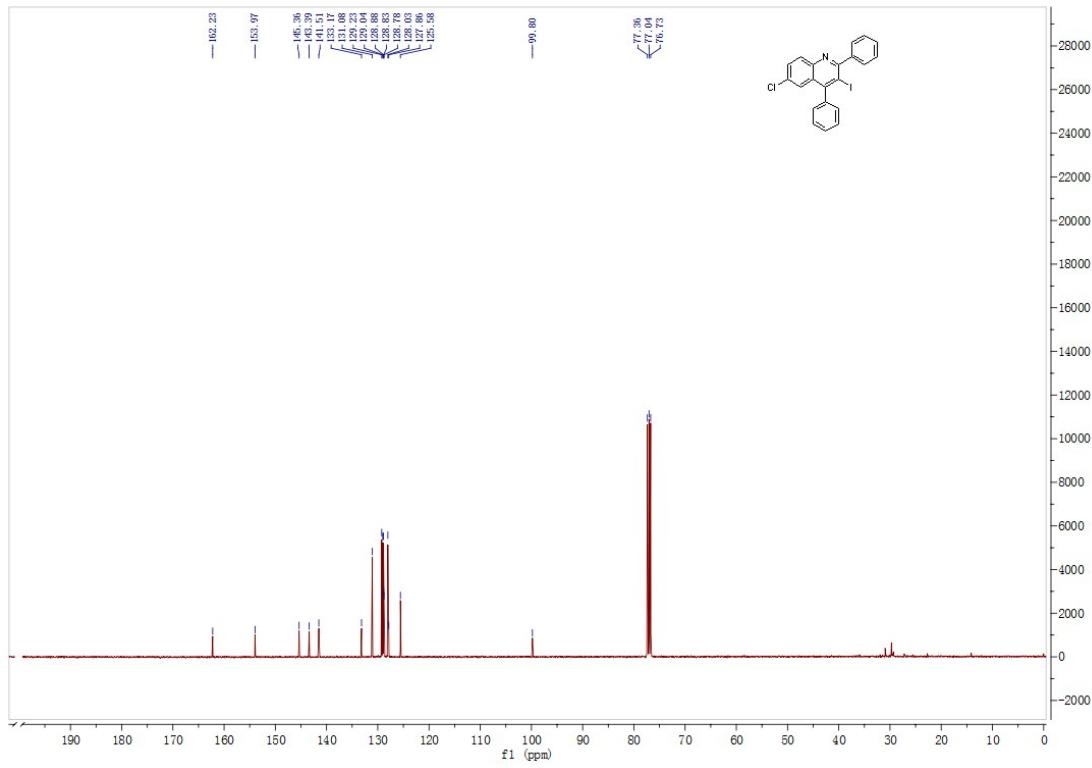
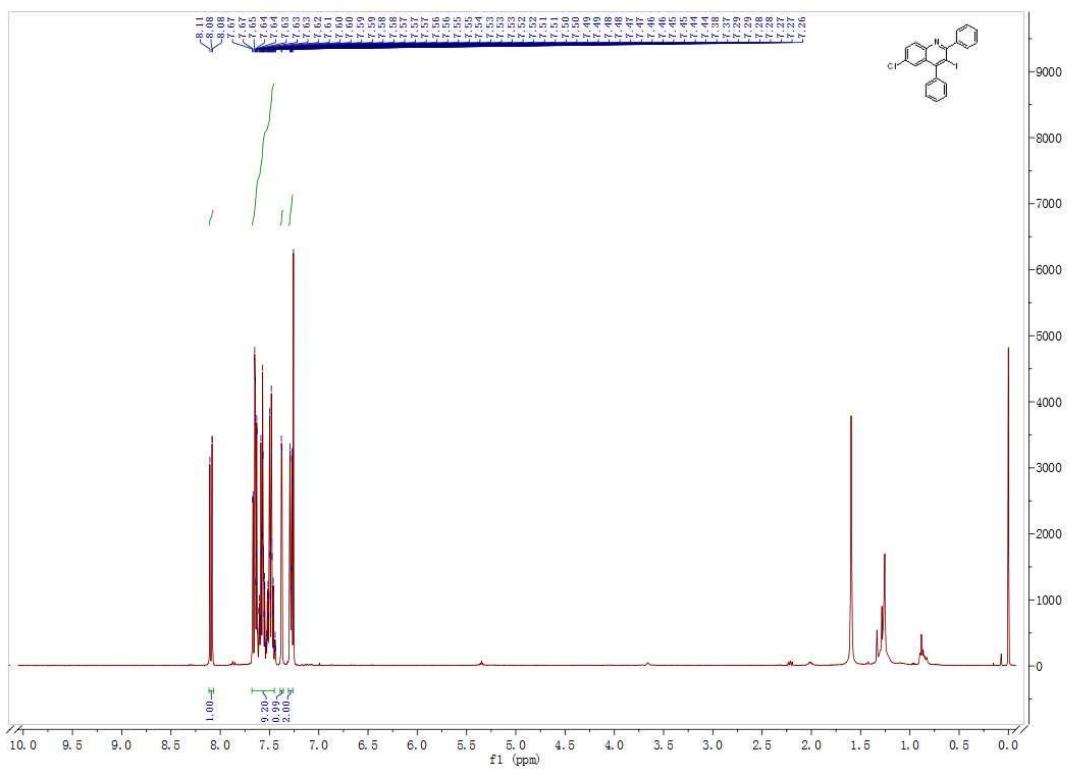
**6-(tert-butyl)-3-iodo-4-phenyl-2-(p-tolyl)quinolone (2f)**



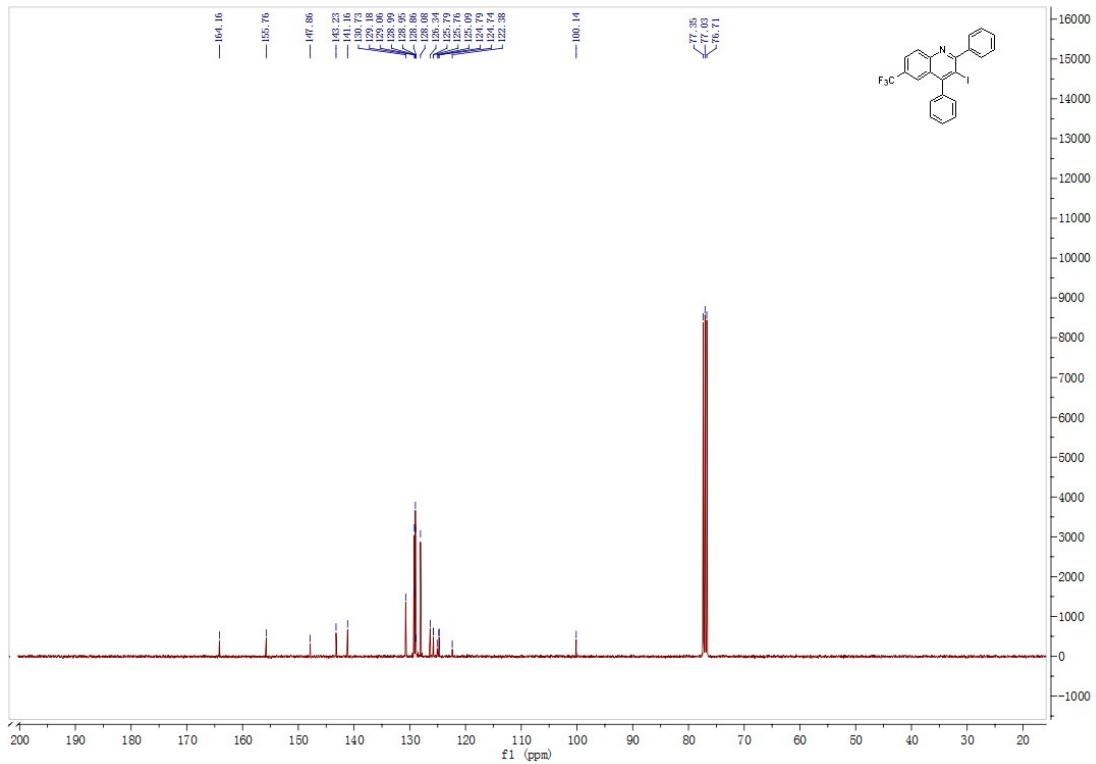
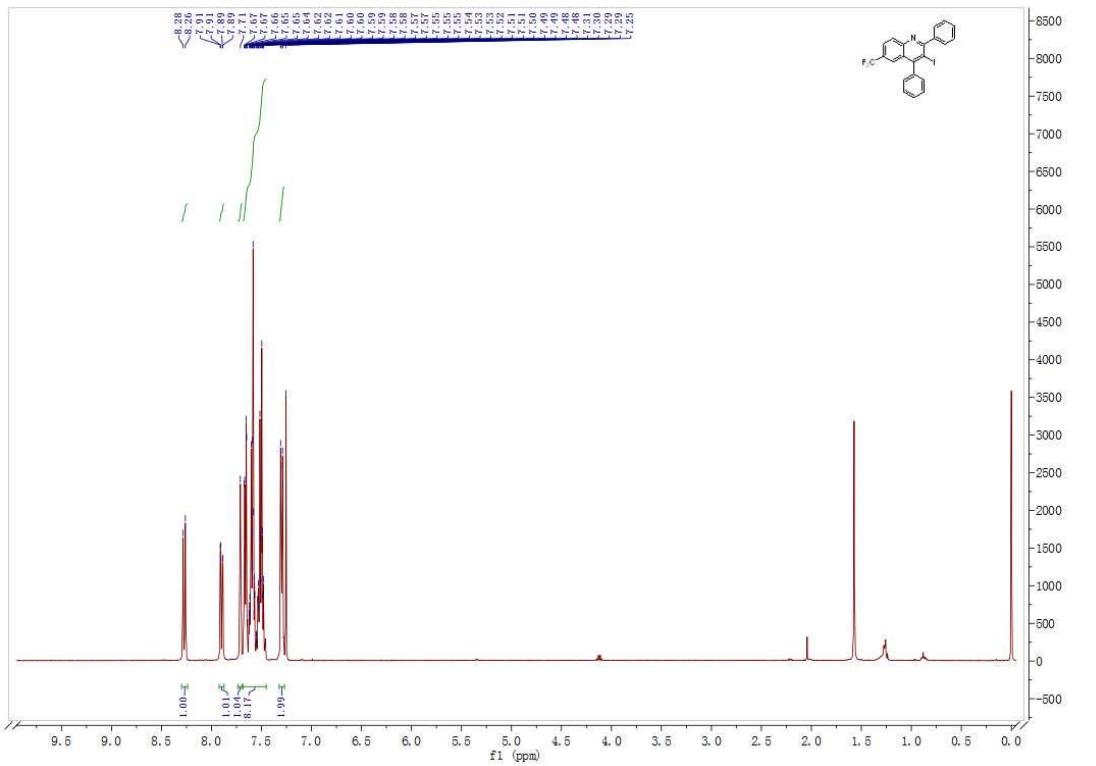
**6-(tert-butyl)-3-iodo-2-phenyl-4-(p-tolyl)quinolone (2g)**



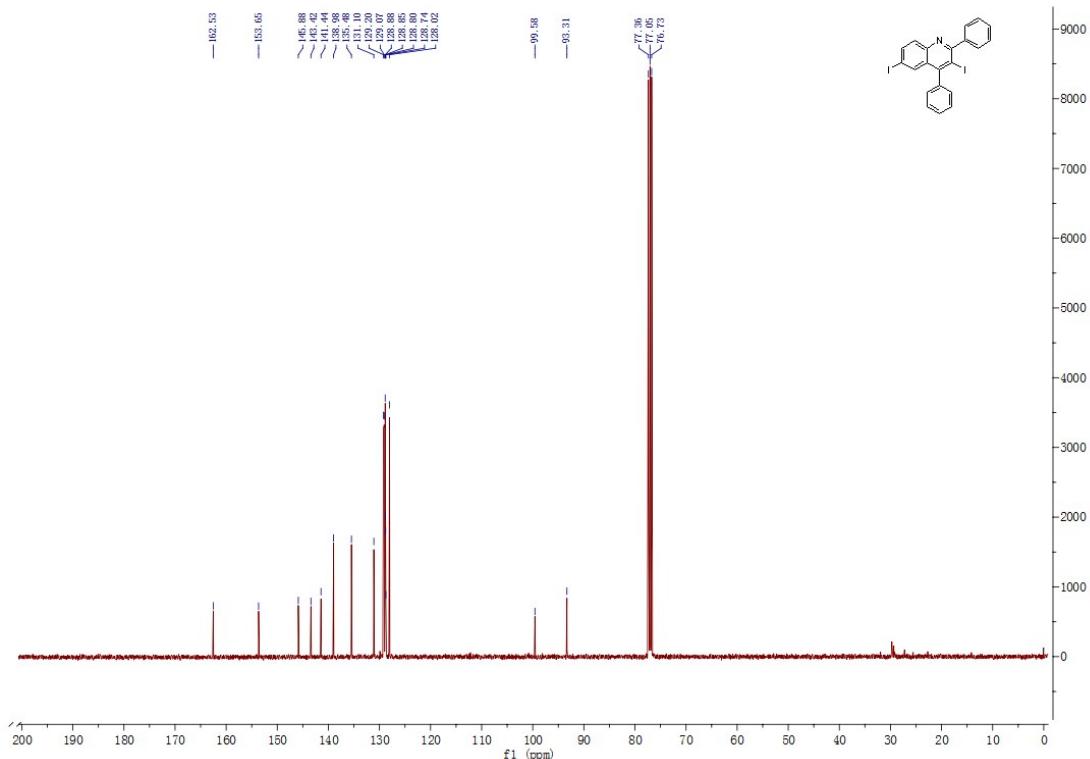
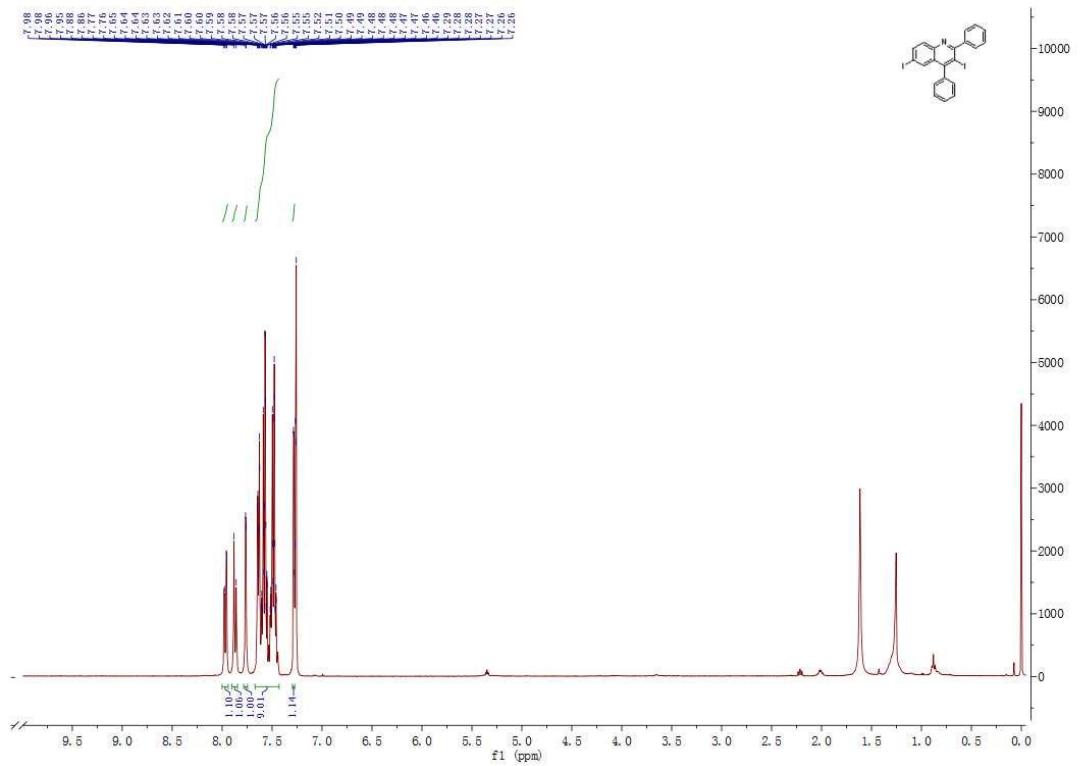
### **6-chloro-3-iodo-2,4-diphenylquinoline (2h)**



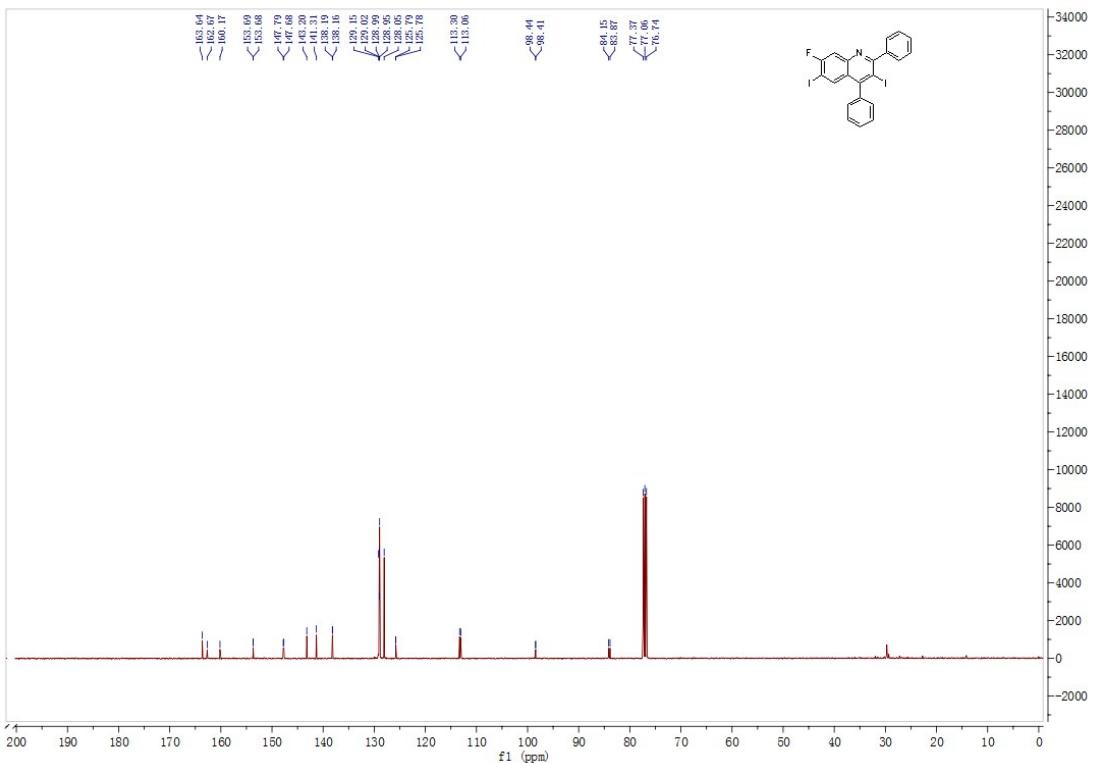
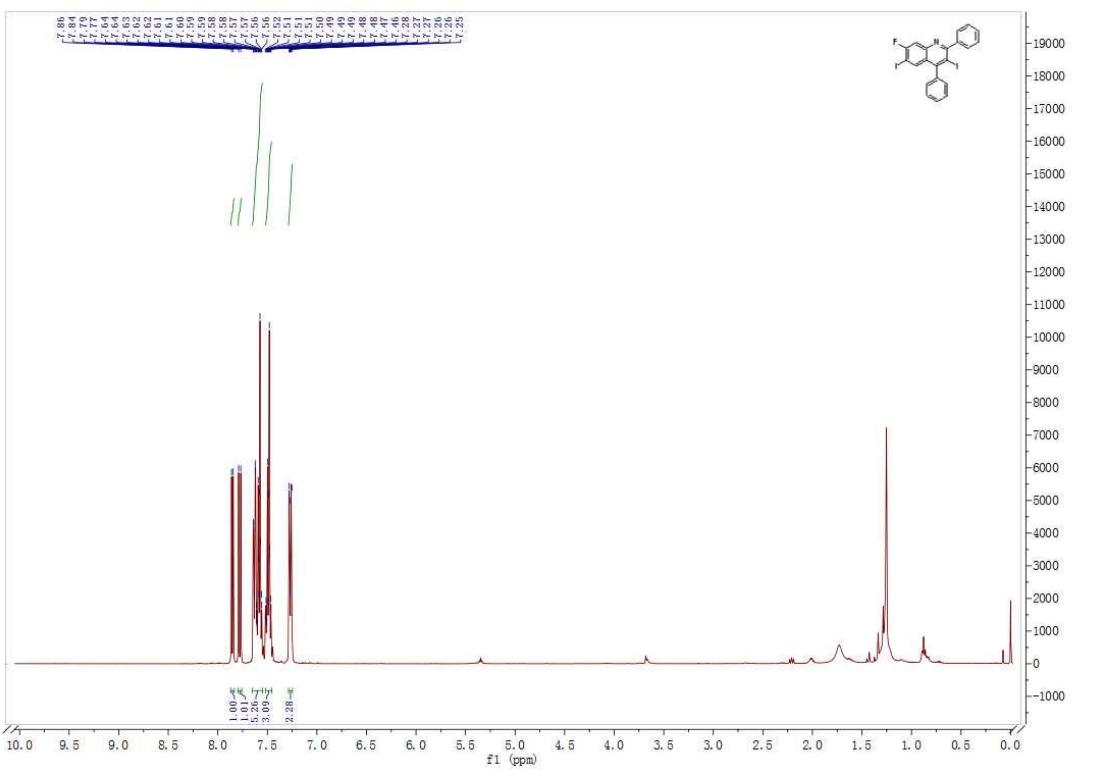
### **3-iodo-2,4-diphenyl-6-(trifluoromethyl)quinolone (2i)**



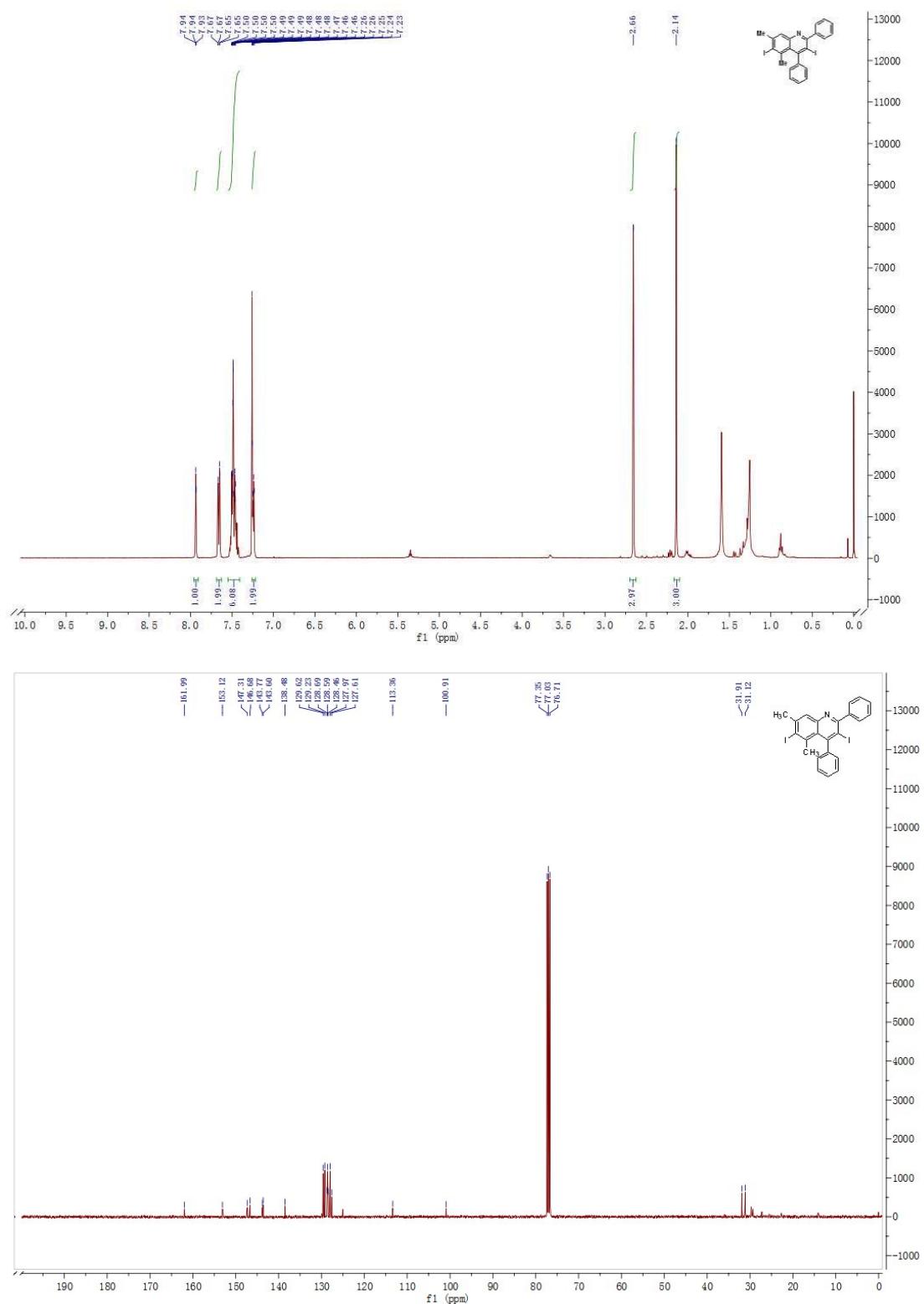
### **3,6-diido-2,4-diphenylquinoline (3a)**



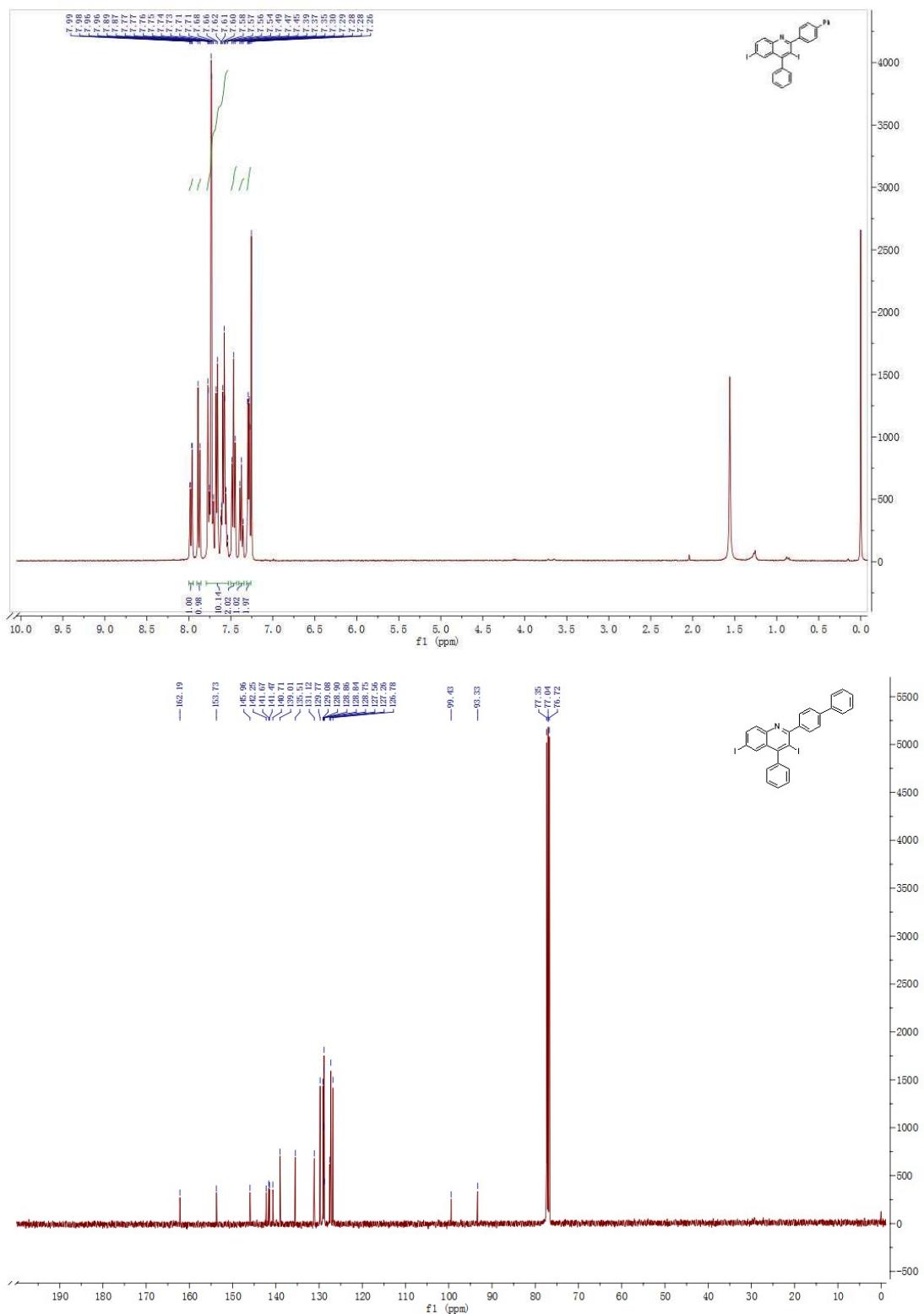
**7-fluoro-3,6-diiodo-2,4-diphenylquinoline (3b)**



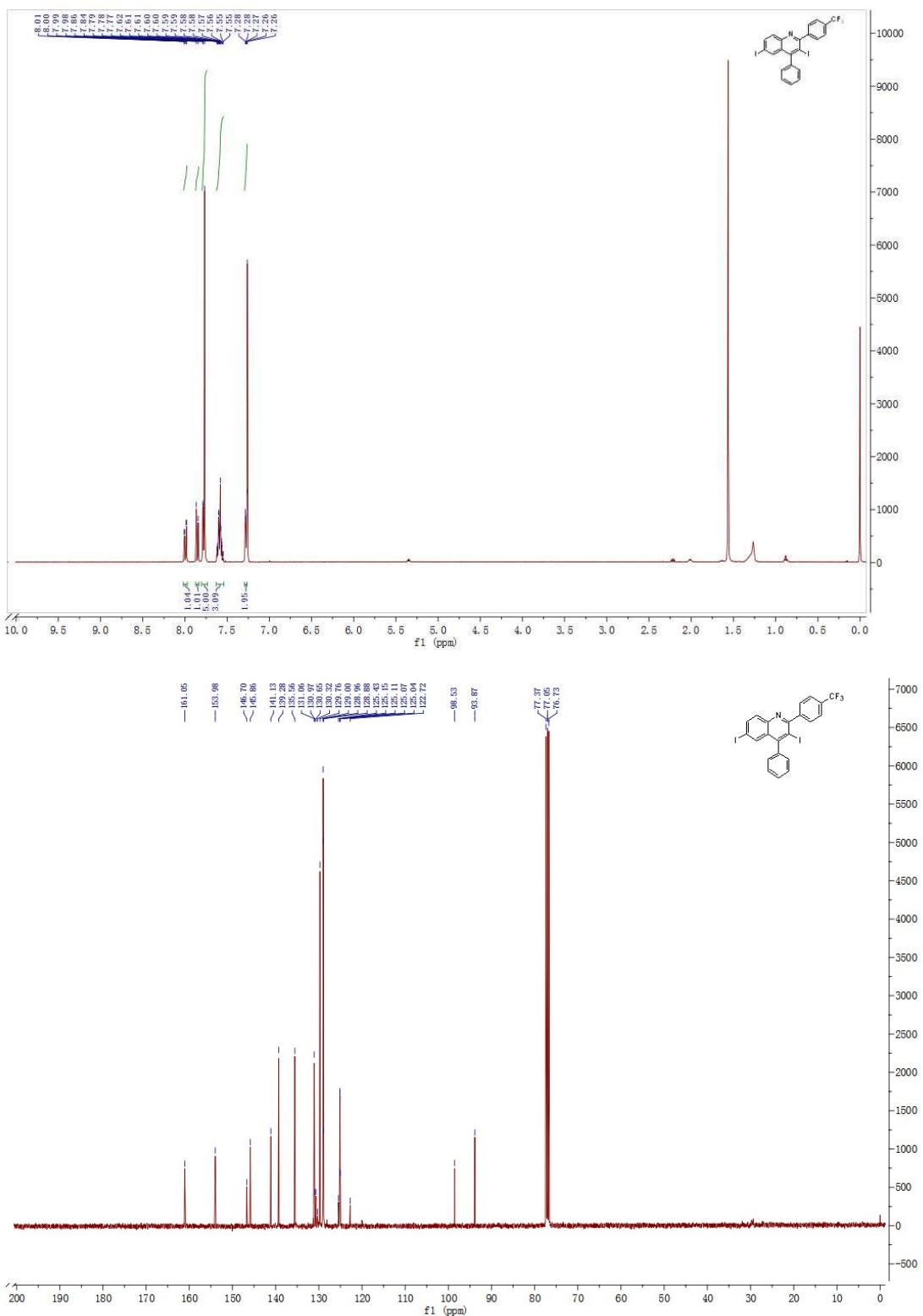
### 3,6-diiodo-5,7-dimethyl-2,4-diphenylquinoline (3c)



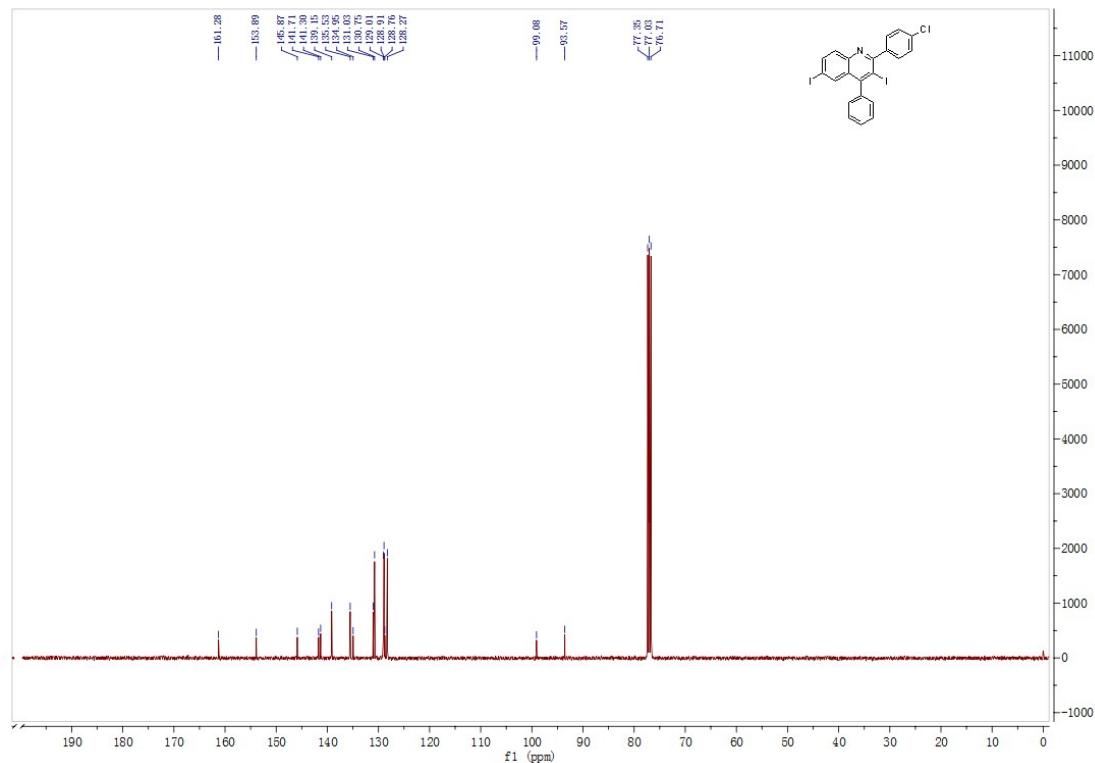
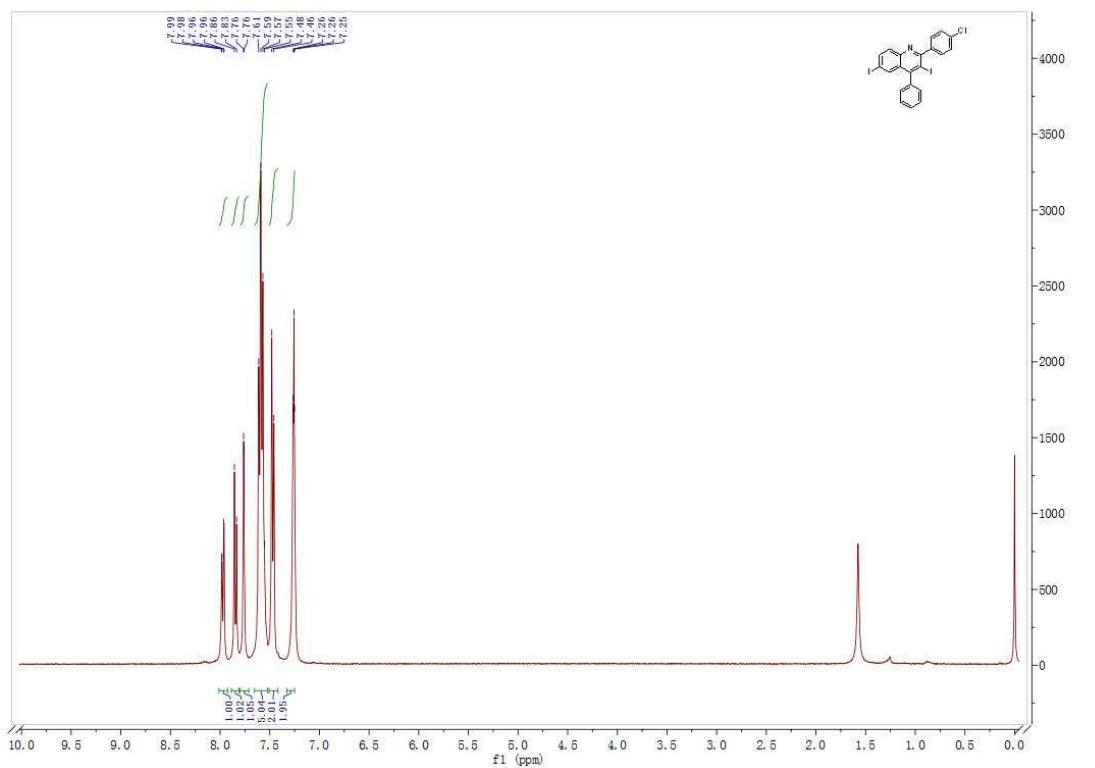
**2-([1,1'-biphenyl]-4-yl)-3,6-diido-4-phenylquinoline (3d)**



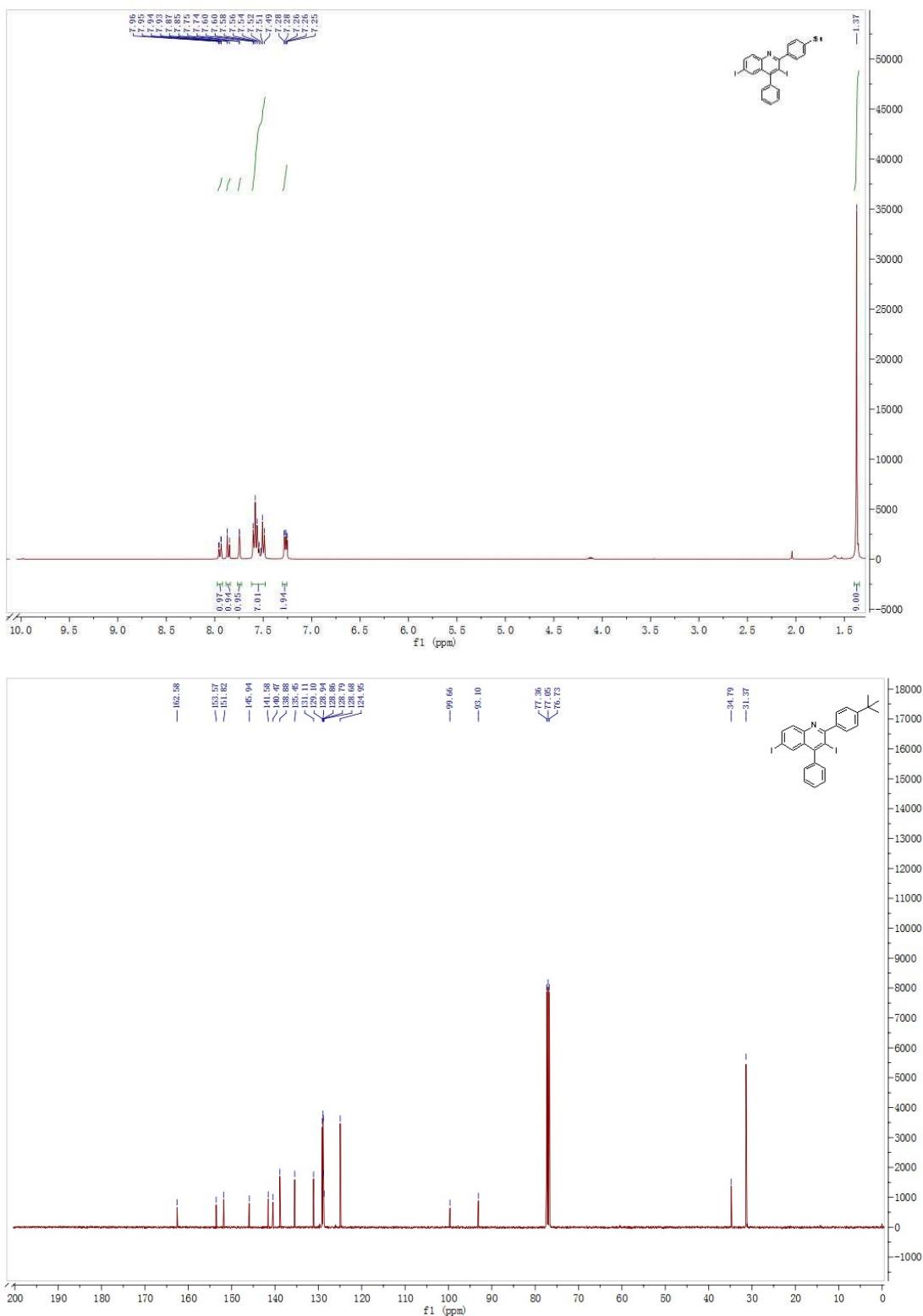
### 3,6-diiodo-4-phenyl-2-(4-(trifluoromethyl)phenyl)quinolone (3e)



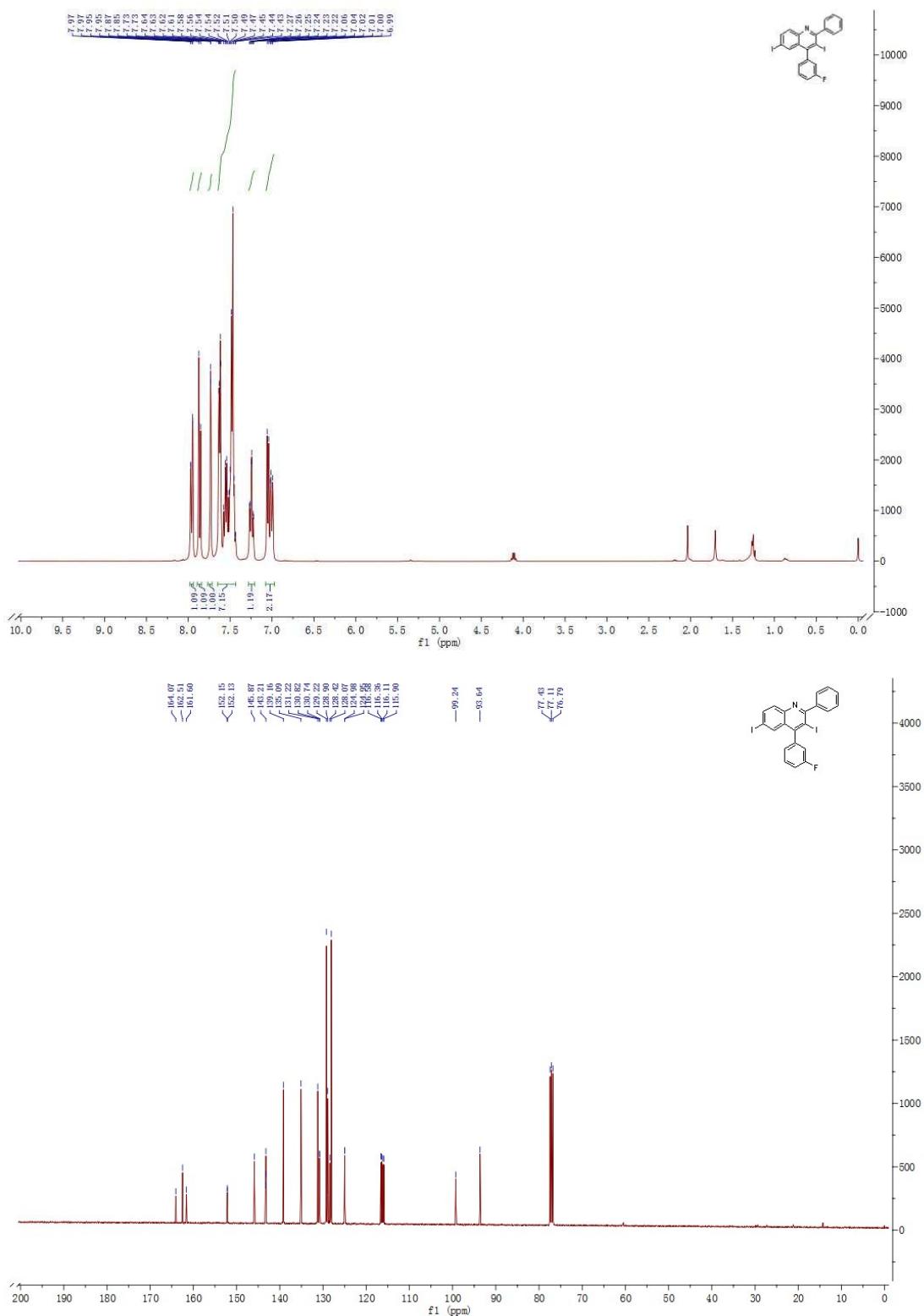
**2-(4-chlorophenyl)-3,6-diiodo-4-phenylquinoline (3f)**



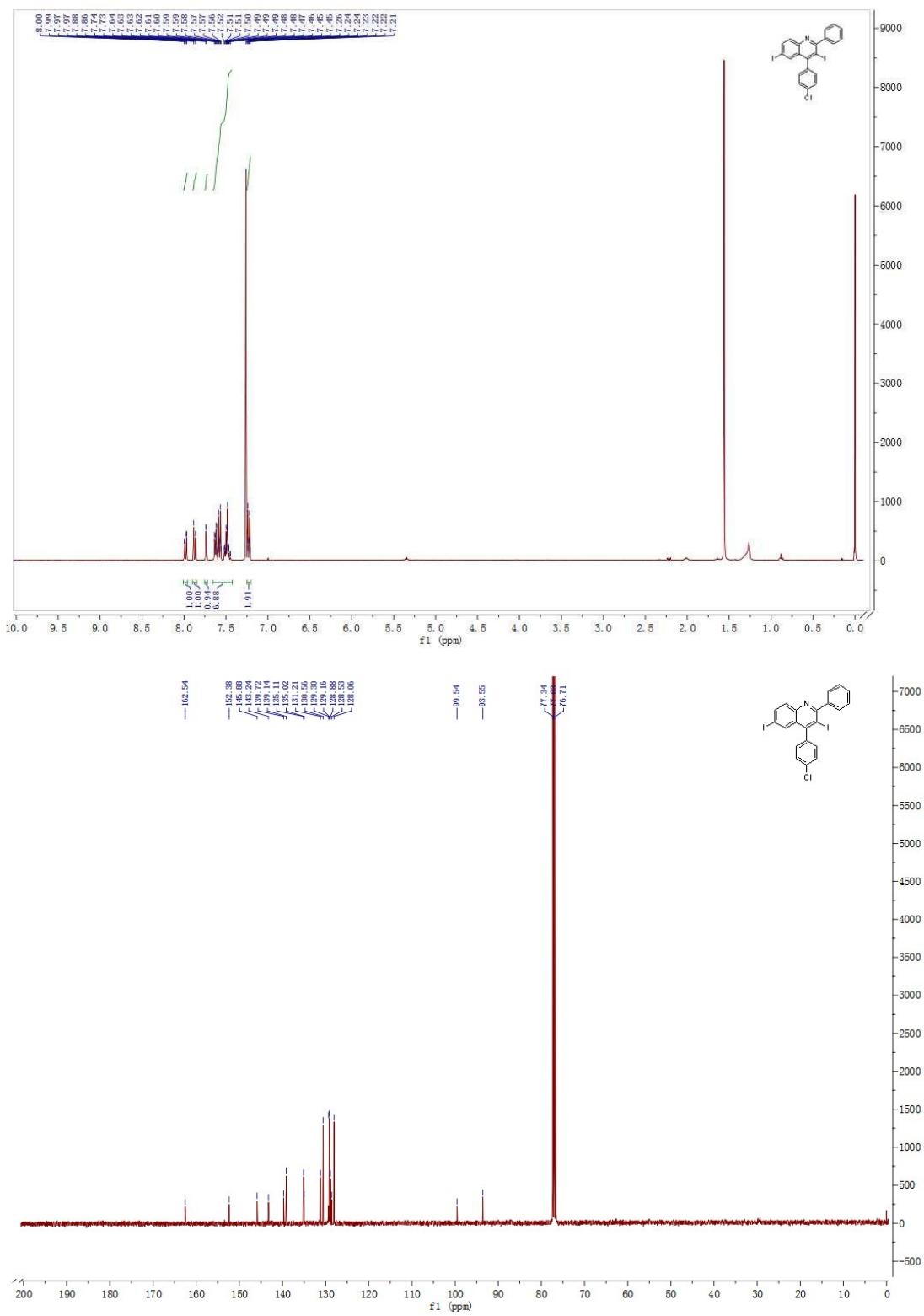
**2-(4-(tert-butyl)phenyl)-3,6-diiodo-4-phenylquinoline (3g)**



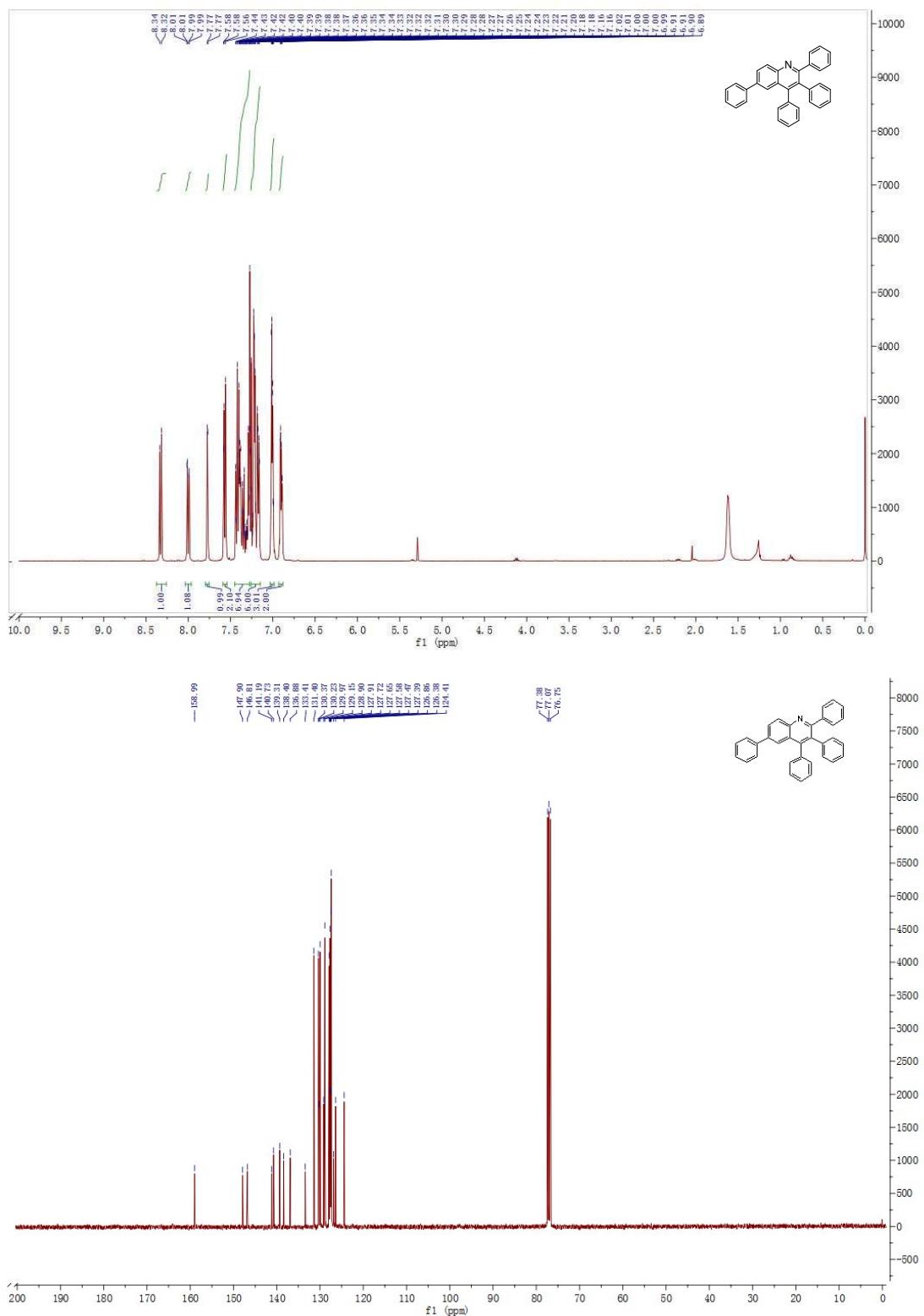
#### 4-(3-fluorophenyl)-3,6-diido-2-phenylquinoline (3h)



#### 4-(4-chlorophenyl)-3,6-diiodo-2-phenylquinoline (3i)



**2,3,4,6-tetraphenylquinoline (4a)**



**2, 4-diphenyl-3, 6-bis(phenylethynyl)quinoline (4b)**

