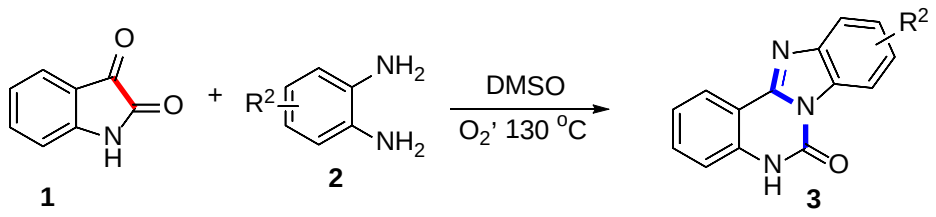
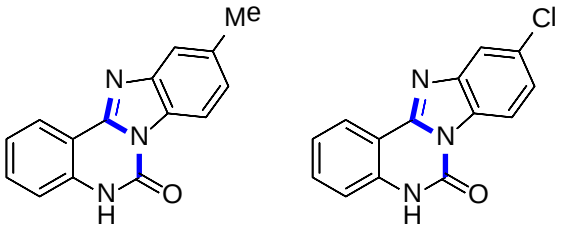
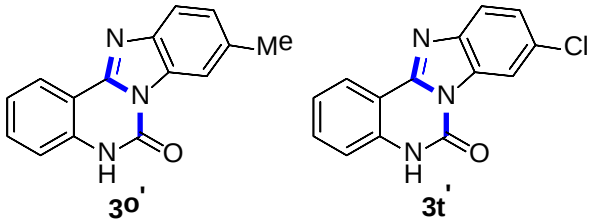


We suppose that the structure might be:

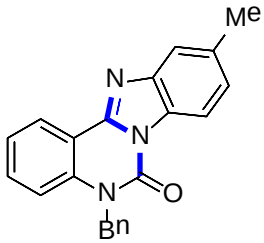


3o, 67% **3t**, 71%

Another possibility:



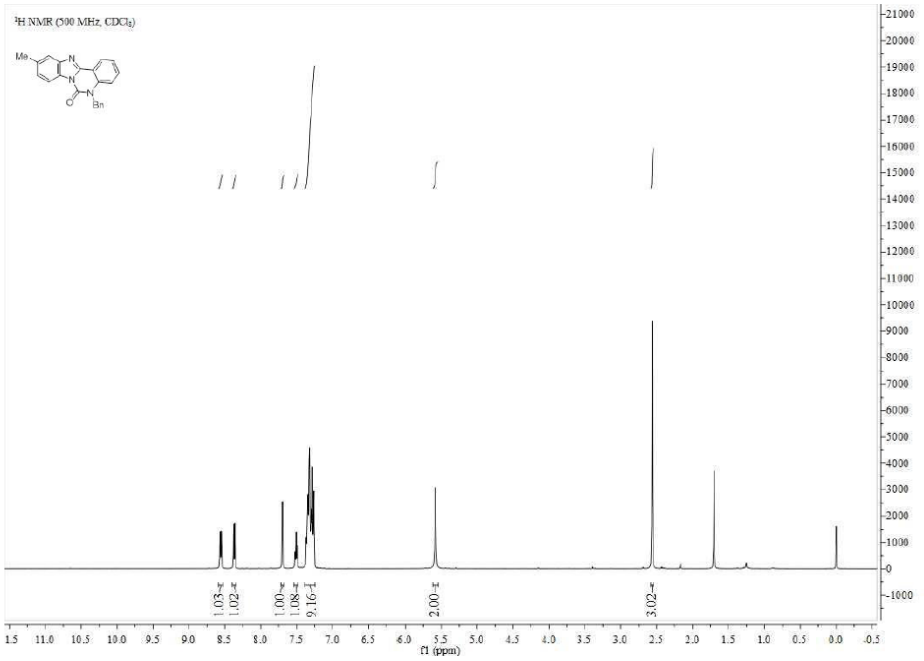
For substrates with one substituent at the benzene ring of *o*-phenylene diamine (as described above), two possible isomers (**3o** vs **3o'**; **3t** vs **3t'**) might be produced. Luckily, the selectivity of reaction in our work is very good and only one isomer is obtained. Then one key issue came to our thoughts about how to determine the accurate structure of these compounds. We tried to determine the structures of compounds of **3o** and **3t** based on x-ray analysis. However, it did not work. Then we tried to do functionalization of **3o** by adding a benzyl group at the N atom according to a reference (*Angew. Chem. Int. Ed.* **2017**, *56*, 587-590). In the reference, the compound structure is shown as below:

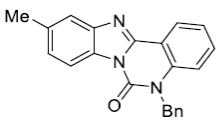


According the NMR analysis, there is no difference between the NMR spectra of the product with a benzyl group at **3o** and the one from the supporting information of the above-mentioned reference (attached below). Therefore, we can draw a conclusion that we have obtained the isomer **3o** with high regioselectivity.

The ^{1}H NMR for the compound (**3aj**) in reference:

Compound 3aj





5-Benzyl-10-methylbenzo[4,5]imidazo[1,2-*c*]quinazolin-6(5*H*)-one (3aj). Yield = 79%; Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (dd, J = 7.8, 1.6 Hz, 1H), 8.37 (d, J = 8.3 Hz, 1H), 7.70 (s, 1H), 7.54–7.48 (m, 1H), 7.39–7.25 (m, 8H), 5.58 (s, 2H), 2.56 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 145.0, 144.4, 137.5, 135.8, 135.7, 132.3, 129.4, 129.2, 127.9, 126.6, 126.0, 125.8, 124.0, 119.5, 115.5, 115.1, 113.8, 47.2, 22.0; IR (neat, cm^{-1}): 2917, 1689, 1584, 1387, 1247, 1194, 748; ESI HRMS m/z $(M+H)^+$ calcd 340.1444, obsd 340.1445.

The ^{1}H NMR for the compound (with a benzyl group at the N atom of **3o**) that we measured: