Supporting Information

Assembly of functionalized π-extended indolizine polycycles through dearomative [3+2] cycloaddition/oxidative decarbonylation

Shaojing Jin, [a,#] Lele Wang,[a,#] Huabin Han,[a] Xiongli Liu,[b] Zhanwei Bu,[a] Qilin Wang[a,*]

[a] Institute of Functional Organic Molecular Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, China

[b] Guizhou Medicine Edible Plant Resources Research and Development Center, Guizhou University, Guiyang 550025, PR China

[#] These authors contribute equally to this work.

E-mail: wangqilin@henu.edu.cn

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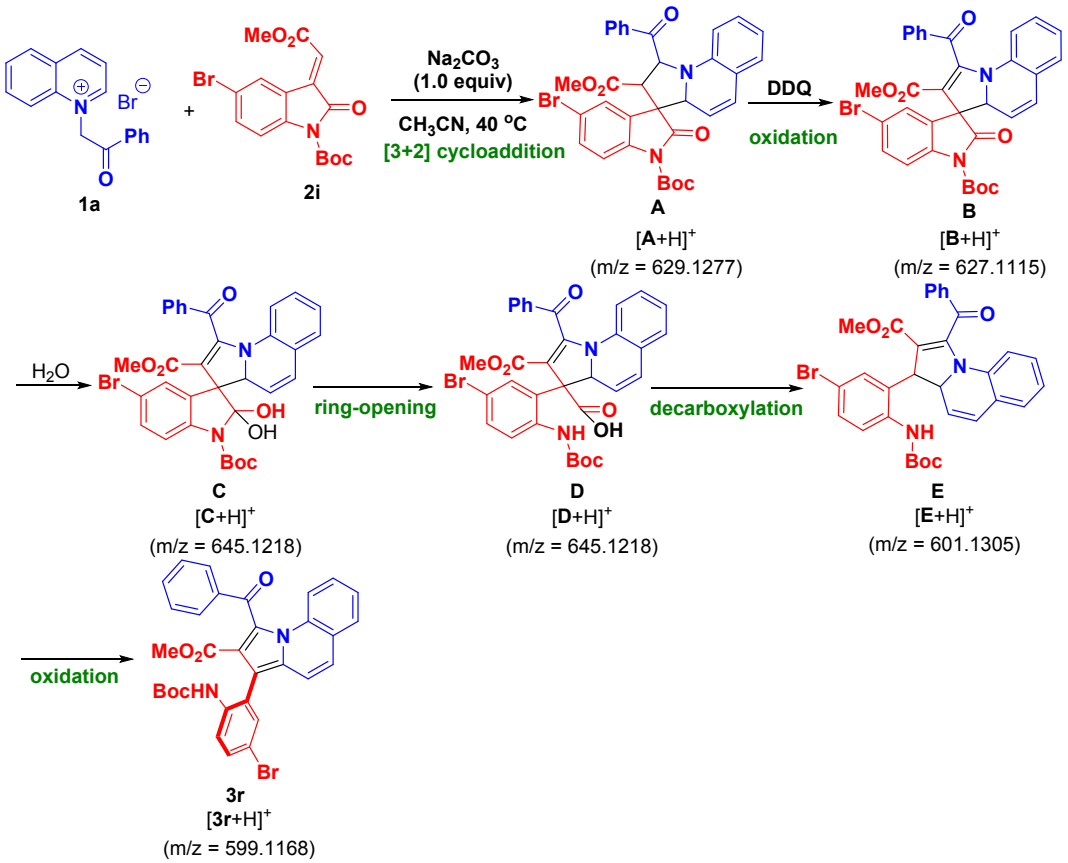
1. General methods

NMR spectra were recorded with tetramethylsilane as the internal standard. ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR spectra were recorded at 100 MHz (Bruker Avance). ^{1}H NMR chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) with the solvent signal as the internal standard ($CDCl_3$ at 7.26 ppm, $(CD_3)_2SO$ at 2.50 ppm). ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.00 ppm, $(CD_3)_2SO$ at 39.52 ppm). Data are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (double of doublet), br (broad) or m (multiplets), coupling constants (Hz) and integration. Flash column chromatography was carried out using silica gel eluting with ethyl acetate and petroleum ether. High resolution mass spectra were obtained with the Q-TOF-Premier mass spectrometer. Reactions were monitored by TLC and visualized with ultraviolet light. IR spectra were recorded on a Thermo Fisher Nicolet Avatar 360 FTIR spectrometer on a KBr beam splitter. All the solvents were used directly without any purification.

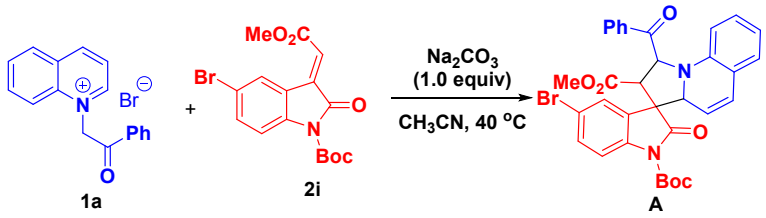
2. Mechanistic studies

On the basis of the experimental outcomes, a plausible mechanism was proposed to rationalize the reaction pathway (Scheme S1, taking the formation of **3r** as an example). Initially, a [3+2] cycloaddition took place between **1a** and **2i** with the assistance of Na_2CO_3 to yield intermediate **A**, which easily underwent dehydrogenation upon addition of one equivalent of DDQ to generate intermediate **B**. Then, the trace amount of water in the reaction system attacked the carbonyl group of intermediate **B**, thus delivering intermediate **C**. **C** was not stable and a ring-opening occurred subsequently to give **D**. Under basic condition, intermediate **D** could be smoothly converted into intermediate **E** through a decarboxylation process. Followed by an oxidation by air or excess DDQ, the desired product **3r** was generated in the end. We considered the decarbonylation step may be caused by the following two factors: 1) the α-carbon of the carboxylic acid was tethered with electron-withdrawing group, which made it more susceptible to undergo decarbonylation under basic conditions; and 2) the decarbonylated intermediate E was easily oxidized into aromatic product and the aromatization process was possibly the other driving force for this cascade.



Scheme S1. Plausible mechanism

To get some evidences, we tried to detect the intermediate of the crude reaction mixture of **1a** and **2i** in the presence of one equivalent of Na_2CO_3 by HRMS analysis (Scheme S2). As shown in Figure S1, after the reaction proceeded for 5 h, **2i** was completely consumed and we could obtain the signal peaks of intermediate **A**.



Scheme S2. Reaction between **1a** and **2i** for 5 h

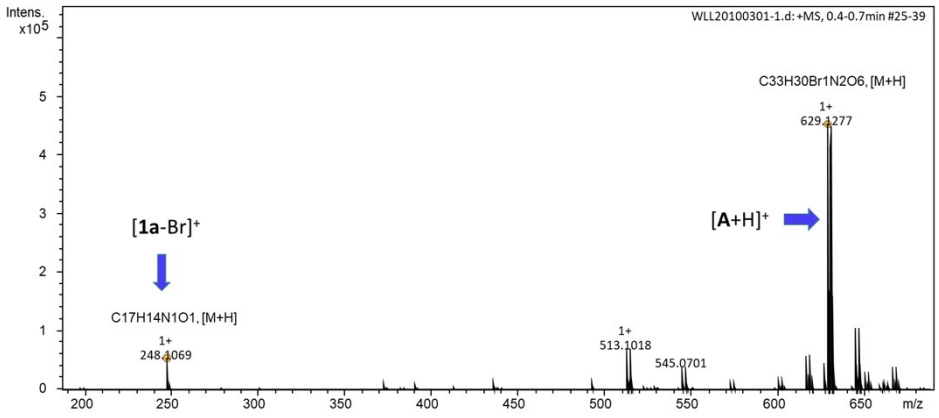
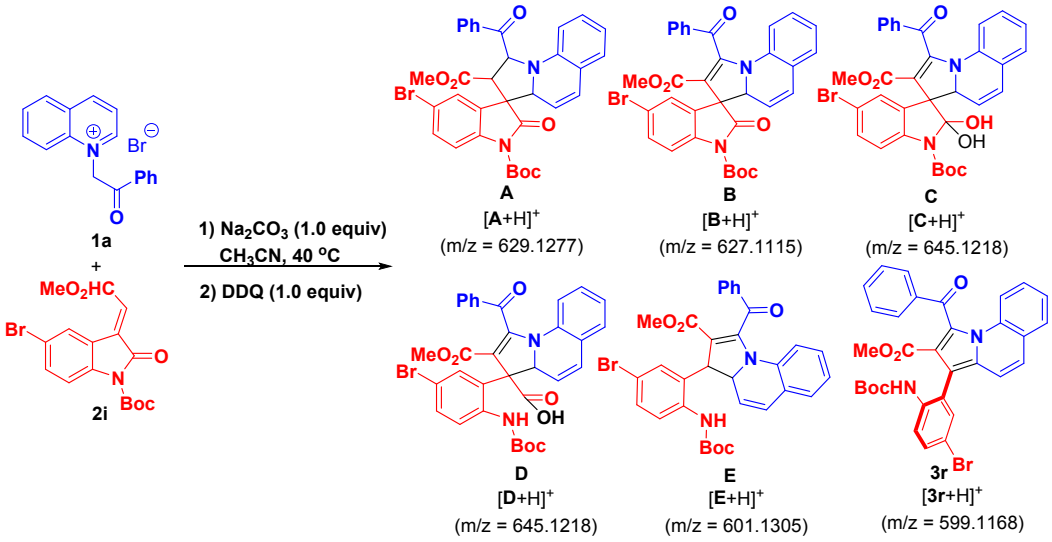


Figure S1. HRMS spectrum of the reaction between **1a** and **2i** for 5 h

After the first [3+2] cycloaddition went completion, we added one equivalent of DDQ to the reaction system (Scheme S3). After the reaction proceeded for 2 h, we could detect the signal peaks of intermediates **B**, **C**, **D** and **E** and the product **3r** (Figure S2).



Scheme S3. Reaction between **1a**, **2i** and DDQ (the second oxidation step)

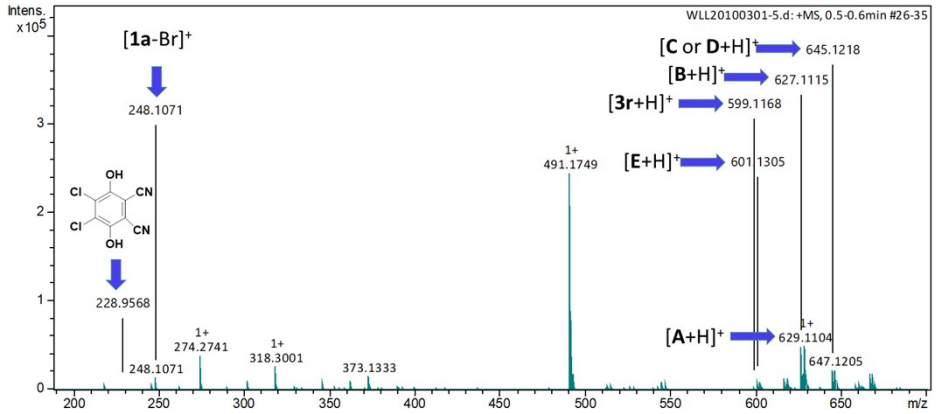
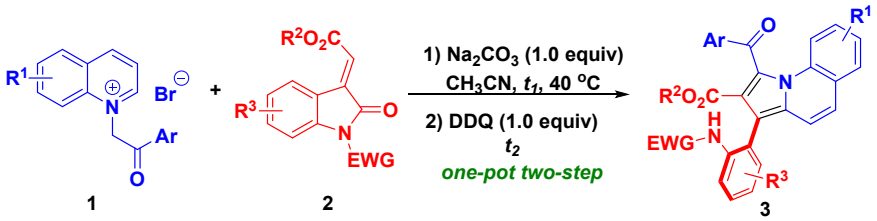
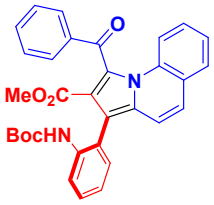


Figure S2. HRMS study on the reaction mixture of **1a**, **2i,** Na_2CO_3 and DDQ (the second oxidation step)

3. Experimental data for the formation of 3

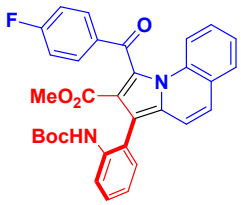


General procedure: *N*-Phenacyl quinolinium salts **1** (0.15 mmol), methyleneindolinones **2** (0.10 mmol), Na_2CO_3 (0.10 mmol) and 1.0 mL of CH_3CN were successively added to a 5.0 mL vial. The resulting mixture was stirred at 40 °C till the full consumption of **2** as monitored by TLC, and then 0.10 mmol of DDQ was added. After the cycloadduct intermediates went complete conversion, the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the corresponding products **3**.



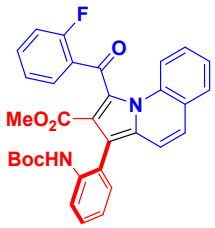
methyl 1-benzoyl-3-(2-((*tert*-butoxycarbonyl)amino)phenyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**3a**)

Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1-20:1), 37.9 mg, 73% yield; t_1 = 5 h, t_2 = 12 h; m. p. 113.4-114.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, $J_1 = J_2$ = 12.0 Hz, 3H), 7.70-7.61 (m, 3H), 7.51 (t, J = 8.0 Hz, 2H), 7.44-7.27 (m, 4H), 7.18-7.08 (m, 3H), 6.55 (s, 1H), 3.35 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 164.2, 153.0, 138.1, 137.5, 134.0, 132.7, 132.7, 131.9, 131.7, 129.5, 129.2, 128.9, 128.8, 128.4, 125.7, 125.4, 123.1, 122.8, 120.5, 120.4, 120.4, 117.6, 117.5, 113.5, 80.2, 51.5, 28.2. IR (KBr) *v* 3425, 2959, 1721, 1248, 1163, 748 cm^{-1}. HRMS (ESI) calcd. for $C_{32}H_{29}N_2O_5$ $[M+H]^+$: 521.2076, found: 521.2071.



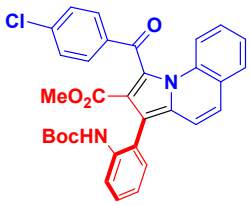
methyl 3-(2-((*tert*-butoxycarbonyl)amino)phenyl)-1-(4-fluorobenzoyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate

Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 25:1-15:1), 38.7 mg, 72% yield; t_1 = 11 h, t_2 = 23 h; m. p. 110.2-110.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (q, J = 8.0 Hz, 3H), 7.67 (t, J = 8.0 Hz, 2H), 7.44-7.28 (m, 4H), 7.22-7.09 (m, 5H), 6.51 (s, 1H), 3.40 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 166.2 (d, J = 340.0 Hz, 1C), 164.1, 153.0, 137.5, 134.6, 134.6, 132.6, 132.2, 132.1, 131.9, 131.6, 129.3, 128.8, 128.4, 128.0, 125.7, 125.5, 123.1, 122.8, 120.4, 117.5, 116.4, 116.1, 113.5, 80.3, 51.6, 28.2. IR (KBr) v 3422, 3297, 2956, 1720, 1234, 1159, 757 cm^{-1}. HRMS (ESI) calcd. for $C_{32}H_{28}FN_2O_5$ [M+H]$^+$: 539.1977, found: 539.1977.



methyl 3-(2-((*tert*-butoxycarbonyl)amino)phenyl)-1-(3-fluorobenzoyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**3c**)

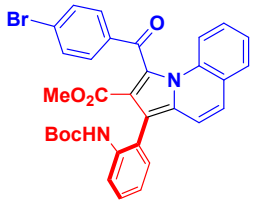
Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 25:1-15:1), 51.3 mg, 95% yield; t_1 = 11 h, t_2 = 12 h; m. p. 119.7-120.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (q, J = 12.0 Hz, 2H), 7.78-7.59 (m, 3H), 7.45-7.28 (m, 5H), 7.22-7.09 (m, 4H), 6.53 (s, 1H), 3.43 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 162.2 (d, J = 405.0 Hz, 1C), 153.0, 137.6, 135.5 (d, J = 11.0 Hz, 1C), 132.7, 131.9, 131.6, 131.5, 129.8, 129.2, 128.8, 128.4, 126.8, 126.7, 125.7, 125.5, 124.6, 124.5, 123.2, 122.7, 120.1, 117.6, 117.4, 117.1, 116.8, 113.5, 80.2, 51.6, 28.2. IR (KBr) v 3420, 2978, 1721, 1454, 1160, 758 cm^{-1}. HRMS (ESI) calcd. for $C_{32}H_{28}FN_2O_5$ [M+H]$^+$: 539.1977, found: 539.1977.



methyl 3-(2-((*tert*-butoxycarbonyl)amino)phenyl)-1-(4-chlorobenzoyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**3d**)

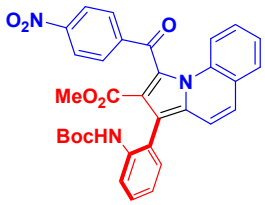
Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 25:1-15:1), 45.0 mg, 81% yield; t_1 = 5 h, t_2 = 12 h; m. p. 145.8-146.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ

8.10 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 12.0 Hz, 2H), 7.65 (dd, J_1 = 8.0 Hz, J_2 = 12.0 Hz, 2H), 7.49 (d, J = 12.0 Hz, 2H), 7.44-7.28 (m, 4H), 7.20-7.09 (m, 3H), 6.51 (s, 1H), 3.40 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 164.1, 153.0, 140.5, 137.5, 136.5, 132.6, 132.0, 131.6, 130.8, 129.3, 129.3, 128.8, 128.5, 127.9, 125.7, 125.6, 123.2, 122.8, 122.7, 120.5, 120.4, 117.5, 113.5, 80.3, 51.6, 28.2, one carbon missing in the aromatic region. IR (KBr) v 3421, 2971, 1718, 1241, 1163, 755 cm^{-1}. HRMS (ESI) calcd. for $C_{32}H_{28}ClN_2O_5$ $[M+H]^+$: 555.1681, found: 555.1683.



methyl 1-(4-bromobenzoyl)-3-(2-((*tert*-butoxycarbonyl)amino)phenyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**3e**)

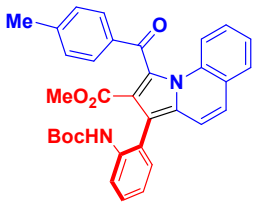
Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1-10:1), 43.7 mg, 73% yield; t_1 = 4 h, t_2 = 12 h; m. p. 166.4-167.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 12.0 Hz, 1H), 7.90 (d, J = 12.0 Hz, 2H), 7.65 (q, J = 12.0 Hz, 4H), 7.44-7.31 (m, 3H), 7.25 (d, J = 8.0 Hz, 1H), 7.20-7.09 (m, 3H), 6.50 (s, 1H), 3.39 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 164.1, 153.0, 137.5, 136.9, 132.5, 132.3, 132.0, 131.6, 130.8, 129.4, 129.3, 128.8, 128.5, 127.8, 125.7, 125.6, 125.6, 123.3, 122.8, 122.7, 120.6, 120.4, 117.5, 113.5, 80.3, 51.7, 28.2. IR (KBr) v 3422, 2973, 1720, 1163, 755 cm^{-1}. HRMS (ESI) calcd. for $C_{32}H_{28}BrN_2O_5$ $[M+H]^+$: 599.1176, found: 599.1177.



methyl 3-(2-((*tert*-butoxycarbonyl)amino)phenyl)-1-(4-nitrobenzoyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**3f**)

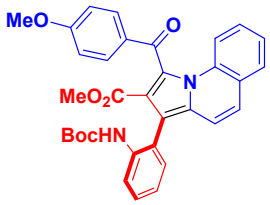
Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1-20:1), 35.5 mg, 63% yield; t_1 = 4.5 h, t_2 = 10 h; m. p. 186.8-187.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 12.0 Hz, 2H), 8.21 (d, J = 12.0 Hz, 2H), 8.09 (d, J = 12.0 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 12.0 Hz, 1H), 7.45-7.36 (m, 3H), 7.28-7.12 (m, 4H), 6.47 (s, 1H), 3.37 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.1, 164.1, 153.0, 150.5, 142.7, 137.4, 132.7,

132.4, 131.6, 130.3, 129.5, 128.9, 128.6, 127.1, 125.8, 125.7, 124.1, 123.9, 122.9, 122.5, 121.6, 120.6, 117.4, 117.4, 113.8, 80.4, 51.8, 28.2. IR (KBr) *v* 3422, 2972, 1715, 1521, 1161, 746 cm^{-1}. HRMS (ESI) calcd. for $C_{32}H_{28}N_3O_7$ $[M+H]^+$: 566.1922, found: 566.1923.



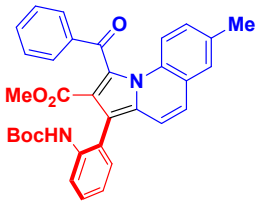
methyl 3-(2-((*tert*-butoxycarbonyl)amino)phenyl)-1-(4-methylbenzoyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**3g**)

Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 25:1-15:1), 16.7 mg, 31% yield; t_1 = 14 h, t_2 = 27 h; m. p. 169.9-170.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.58 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 2H), 7.34-7.17 (m, 6H), 7.02 (q, J = 12.0 Hz, 3H), 6.48 (s, 1H), 3.29 (s, 3H), 2.35 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 164.2, 153.0, 145.1, 137.5, 135.6, 132.6, 131.6, 131.5, 129.7, 129.6, 129.1, 128.7, 128.3, 125.6, 125.3, 122.9, 122.8, 122.7, 120.2, 119.9, 117.5, 117.4, 113.3, 80.2, 51.5, 28.2, 21.8, one carbon missing in the aromatic region. IR (KBr) *v* 3427, 2931, 1718, 1454, 1162, 750 cm^{-1}. HRMS (ESI) calcd. for $C_{32}H_{31}N_2O_5$ $[M+H]^+$: 535.2227, found: 535.2227.



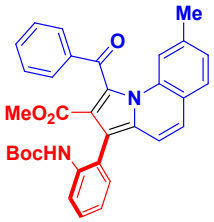
methyl 3-(2-((*tert*-butoxycarbonyl)amino)phenyl)-1-(4-methoxybenzoyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**3h**)

Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1-7:1), 13.3 mg, 24% yield; t_1 = 5 h, t_2 = 18 h; m. p. 145.6-146.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 12.0 Hz, 1H), 7.99 (d, J = 12.0 Hz, 2H), 7.65 (dd, J_1 = J_2 = 12.0 Hz, 2H), 7.44-7.28 (m, 4H), 7.13 (t, J = 12.0 Hz, 3H), 6.97 (d, J = 12.0 Hz, 2H), 6.54 (s, 1H), 3.88 (s, 3H), 3.41 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 164.3, 153.0, 137.5, 132.8, 131.9, 131.7, 131.4, 131.1, 129.1, 128.9, 128.7, 128.4, 125.7, 125.4, 123.0, 123.0, 122.7, 122.7, 120.2, 120.2, 119.6, 117.5, 114.3, 113.3, 80.3, 55.5, 51.6, 28.2. IR (KBr) *v* 3422, 2971, 1717, 1255, 1165, 755 cm^{-1}. HRMS (ESI) calcd. for $C_{33}H_{31}N_2O_6$ $[M+H]^+$: 551.2177, found: 551.2172.



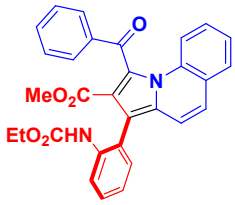
methyl 1-benzoyl-3-(2-((*tert*-butoxycarbonyl)amino)phenyl)-7-methylpyrrolo[1,2-*a*]quinoline-2-carboxylate (**3i**)

Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 25:1-20:1), 39.3 mg, 74% yield; t_1 = 6 h, t_2 = 18 h; m. p. 189.7-190.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 12.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.66-7.38 (m, 6H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.15-7.05 (m, 4H), 6.56 (s, 1H), 3.34 (s, 3H), 2.40 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 164.2, 153.1, 138.2, 137.5, 135.3, 133.9, 131.7, 130.7, 129.6, 129.5, 129.0, 128.9, 128.7, 128.2, 125.7, 123.0, 122.8, 122.7, 120.3, 120.2, 120.2, 117.5, 117.4, 113.3, 80.2, 51.5, 28.3, 20.8. IR (KBr) *v* 3422, 2975, 1719, 1465, 1250, 1161, 765 cm^{-1}. HRMS (ESI) calcd. for $C_{33}H_{31}N_2O_5$ $[M+H]^+$: 535.2227, found: 535.2235.



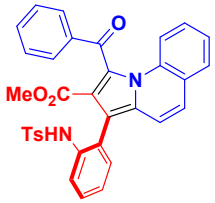
methyl 1-benzoyl-3-(2-((*tert*-butoxycarbonyl)amino)phenyl)-8-methylpyrrolo[1,2-*a*]quinoline-2-carboxylate (**3j**)

Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 25:1-20:1), 40.5 mg, 76% yield; t_1 = 6 h, t_2 = 17 h; m. p. 102.4-103.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 12.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.56-7.50 (m, 4H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.19-7.11 (m, 3H), 7.03 (d, *J* = 12.0 Hz, 1H), 6.57 (s, 1H), 3.36 (s, 3H), 2.29 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 164.3, 153.0, 138.9, 138.2, 137.5, 133.8, 132.7, 132.0, 131.7, 129.4, 128.9, 128.7, 128.2, 126.7, 123.3, 123.0, 123.0, 122.7, 120.6, 120.3, 120.3, 118.0, 116.4, 113.1, 80.2, 51.5, 28.2, 21.9. IR (KBr) *v* 3422, 2971, 1721, 1161, 757 cm^{-1}. HRMS (ESI) calcd. for $C_{33}H_{31}N_2O_5$ $[M+H]^+$: 535.2227, found: 535.2240.



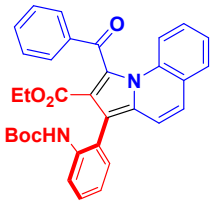
methyl 1-benzoyl-3-(2-((ethoxycarbonyl)amino)phenyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**3k**)

Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1-10:1), 31.0 mg, 63% yield; t_1 = 5 h, t_2 = 11 h; m. p. 145.7-146.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 12.0 Hz, 1H), 8.04 (d, J = 8.0 Hz, 2H), 7.65 (q, J = 12.0 Hz, 3H), 7.52 (t, J = 8.0 Hz, 2H), 7.43 (t, J = 8.0 Hz, 1H), 7.38-7.28 (m, 3H), 7.16 (t, J = 8.0 Hz, 2H), 7.08 (t, J = 16.0 Hz, 1H), 6.80 (s, 1H), 4.12 (q, J = 8.0 Hz, 2H), 3.33 (s, 3H), 1.22 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 164.2, 153.7, 138.0, 137.2, 134.0, 132.6, 131.8, 131.7, 129.4, 129.2, 128.9, 128.9, 128.4, 128.3, 125.6, 125.4, 123.2, 123.0, 120.4, 120.3, 120.3, 117.6, 117.2, 113.3, 61.0, 51.5, 14.4. IR (KBr) v 3286, 2949, 1723, 1217, 753 cm^{-1}. HRMS (ESI) calcd. for $C_{30}H_{25}N_2O_5$ $[M+H]^+$: 493.1758, found: 493.1757.



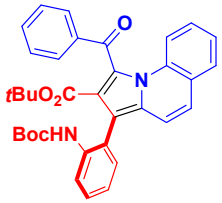
methyl 1-benzoyl-3-(2-((4-methylphenyl)sulfonamido)phenyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**3l**)

Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 15:1-7:1), 35.6 mg, 62% yield; t_1 = 3 h, t_2 = 21 h; m. p. 170.4-170.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (t, J = 8.0 Hz, 3H), 7.74 (t, J = 8.0 Hz, 1H), 7.67 (t, J = 8.0 Hz, 2H), 7.60 (t, J = 8.0 Hz, 3H), 7.47-7.29 (m, 6H), 7.20 (d, J = 8.0 Hz, 1H), 7.01 (d, J = 12.0 Hz, 1H), 6.66 (dd, J_1 = J_2 = 4.0 Hz, 3H), 3.27 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 165.6, 142.5, 138.2, 137.5, 135.5, 134.1, 132.4, 132.3, 129.2, 129.2, 129.2, 128.9, 128.5, 128.3, 127.7, 127.6, 126.3, 125.6, 122.9, 119.9, 117.9, 117.3, 114.0, 51.9, 20.6, four carbons missing in the aromatic region. IR (KBr) v 3427, 2920, 1700, 1633, 750 cm^{-1}. HRMS (ESI) calcd. for $C_{34}H_{27}N_2O_5S$ $[M+H]^+$: 575.1635, found: 575.1647.



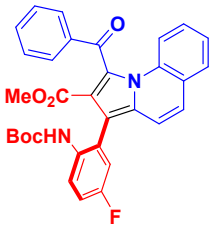
ethyl 1-benzoyl-3-(2-((tert-butoxycarbonyl)amino)phenyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**3m**)

Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 25:1-20:1), 25.0 mg, 47% yield; t_1 = 6 h, t_2 = 16 h; m. p. 70.1-70.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 12.0 Hz, 1H), 8.05 (d, J = 8.0 Hz, 2H), 7.65 (q, J = 8.0 Hz, 3H), 7.51 (t, J = 8.0 Hz, 2H), 7.46-7.28 (m, 4H), 7.13 (q, J = 16.0 Hz, 3H), 6.57 (s, 1H), 3.90-3.80 (m, 2H), 1.42 (s, 9H), 0.80 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 163.6, 153.0, 138.0, 137.7, 134.1, 132.7, 131.7, 131.7, 130.2, 129.6, 129.2, 128.9, 128.7, 128.4, 128.3, 125.7, 125.4, 122.9, 122.6, 120.4, 119.9, 117.6, 117.5, 113.5, 80.2, 60.7, 28.2, 13.2. IR (KBr) v 3421, 2979, 1722, 1456, 1163, 754 cm^{-1}. HRMS (ESI) calcd. for $C_{33}H_{31}N_2O_5$ $[M+H]^+$: 535.2227, found: 535.2219.



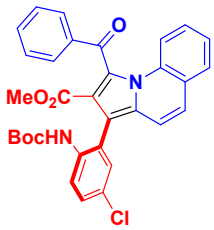
tert-butyl 1-benzoyl-3-(2-((*tert*-butoxycarbonyl)amino)phenyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**3n**)

Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1-20:1), 22.1 mg, 39% yield; t_1 = 7 h, t_2 = 16 h; m. p. 80.2-80.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, J_1 = J_2 = 4.0 Hz, 1H), 8.07 (d, J = 8.0 Hz, 2H), 7.69-7.61 (m, 4H), 7.51 (t, J = 8.0 Hz, 3H), 7.34-7.30 (m, 2H), 7.16-7.06 (m, 3H), 6.61 (s, 1H), 1.44 (s, 9H), 1.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 162.8, 152.8, 138.1, 137.7, 134.0, 132.8, 131.7, 131.6, 130.2, 129.9, 129.1, 128.9, 128.6, 128.3, 127.6, 127.3, 125.7, 125.2, 122.8, 122.7, 122.5, 117.6, 117.5, 113.2, 81.7, 80.2, 28.3, 27.4. IR (KBr) v 3421, 2978, 1724, 1247, 1157, 754 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{35}N_2O_5$ $[M+H]^+$: 563.2540, found: 563.2526.



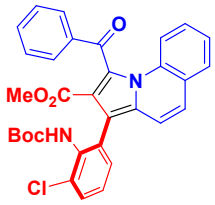
methyl 1-benzoyl-3-(2-((*tert*-butoxycarbonyl)amino)-5-fluorophenyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**3o**)

Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1-20:1), 24.0 mg, 45% yield; t_1 = 6 h, t_2 = 20 h; 184.7-185.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 12.0 Hz, 3H), 7.66 (dd, $J_1 = J_2$ = 12.0 Hz, 3H), 7.52 (t, J = 8.0 Hz, 2H), 7.40-7.31 (m, 2H), 7.22-7.09 (m, 3H), 7.02 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 6.46 (s, 1H), 3.37 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 162.0 (d, J = 207.5 Hz, 1C), 153.3, 138.1, 134.2, 133.8, 133.8, 132.7, 131.8, 129.5, 129.4, 129.1, 128.6, 128.5, 125.7, 125.6, 123.5, 120.1, 118.4, 118.1, 117.7, 117.2, 115.5, 115.2, 112.5, 80.4, 51.6, 28.3. IR (KBr) v 3424, 2954, 1719, 1485, 1234, 1160, 884 cm^{-1}. HRMS (ESI) calcd. for $C_{32}H_{28}FN_2O_5$ $[M+H]^+$: 539.1977, found: 539.1982.



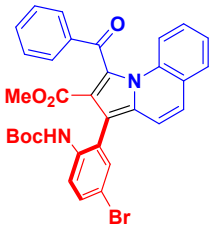
methyl 1-benzoyl-3-(2-((*tert*-butoxycarbonyl)amino)-5-chlorophenyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**3p**)

Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1-20:1), 20.0 mg, 36% yield; t_1 = 4.5 h, t_2 = 10 h; m. p. 199.8-200.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 12.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 2H), 7.66 (dd, $J_1 = J_2$ = 12.0 Hz, 3H), 7.52 (t, J = 8.0 Hz, 2H), 7.39-7.31 (m, 3H), 7.28 (d, J = 4.0 Hz, 1H), 7.20 (d, J = 12.0 Hz, 1H), 7.10 (d, J = 12.0 Hz, 1H), 6.51 (s, 1H), 3.38 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 163.9, 152.8, 137.9, 136.4, 134.1, 132.6, 131.7, 131.3, 129.4, 129.3, 129.0, 128.6, 128.6, 127.5, 125.6, 124.5, 123.5, 121.4, 120.0, 117.6, 117.1, 111.9, 80.6, 51.6, 28.2, two carbons missing in the aromatic region. IR (KBr) v 3420, 2969, 1720, 1500, 1234, 1162, 758 cm^{-1}. HRMS (ESI) calcd. for $C_{32}H_{28}ClN_2O_5$ $[M+H]^+$: 555.1780, found: 555.1769.



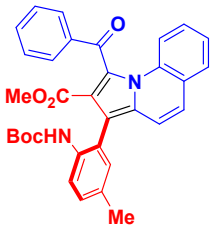
methyl 1-benzoyl-3-(2-((*tert*-butoxycarbonyl)amino)-3-chlorophenyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**3q**)

Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1-10:1), 20.0 mg, 36% yield; t_1 = 23 h, t_2 = 16 h; m. p. 75.0-75.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 2H), 7.54 (t, J = 8.0 Hz, 3H), 7.40 (d, J = 8.0 Hz, 3H), 7.20-7.15 (m, 5H), 7.05 (s, 2H), 3.21 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 170.3, 164.5, 138.2, 134.7, 133.8, 133.5, 133.0, 132.5, 130.2, 129.9, 129.5, 129.3, 129.1, 128.9, 128.2, 128.1, 127.2, 125.6, 125.2, 122.9, 119.9, 117.5, 117.5, 114.7, 80.1, 51.4, 27.9. IR (KBr) v 3410, 2965, 1717, 1254, 1165, 752 cm^{-1}. HRMS (ESI) calcd. for $C_{32}H_{28}ClN_2O_5$ $[M+H]^+$: 555.1681, found: 555.1677.



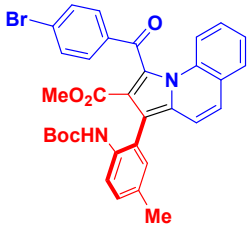
methyl 1-benzoyl-3-(5-bromo-2-((*tert*-butoxycarbonyl)amino)phenyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**3r**)

Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1-20:1), 31.8 mg, 53% yield; t_1 = 4 h, t_2 = 17 h; m. p. 235.4-236.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (t, J = 8.0 Hz, 3H), 7.66 (dd, J_1 = J_2 = 12.0 Hz, 3H), 7.52 (t, J = 12.0 Hz, 3H), 7.42-7.30 (m, 3H), 7.21 (d, J = 16.0 Hz, 1H), 7.10 (d, J = 12.0 Hz, 1H), 6.51 (s, 1H), 3.38 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 163.9, 152.8, 137.9, 136.9, 134.1, 134.1, 132.6, 131.7, 131.6, 129.4, 129.3, 129.0, 128.7, 128.6, 125.6, 125.6, 124.8, 123.5, 121.6, 119.9, 117.6, 117.1, 115.0, 111.8, 80.7, 51.6, 28.2. IR (KBr) v 3419, 2969, 1719, 1501, 1227, 1161, 757 cm^{-1}. HRMS (ESI) calcd. for $C_{32}H_{28}BrN_2O_5$ $[M+H]^+$: 599.1176, found: 599.1176.



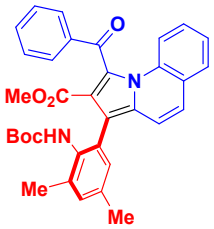
methyl 1-benzoyl-3-(2-((*tert*-butoxycarbonyl)amino)-5-methylphenyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**3s**)

Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1-20:1), 31.6 mg, 59% yield; t_1 = 6 h, t_2 = 18 h; m. p. 196.8-197.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 12.0 Hz, 1H), 7.70-7.61 (m, 3H), 7.51 (t, J = 8.0 Hz, 2H), 7.38-7.13 (m, 5H), 7.09 (s, 1H), 6.48 (s, 1H), 3.34 (s, 3H), 2.35 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 164.3, 153.2, 138.2, 135.0, 133.9, 132.7, 132.3, 132.1, 131.9, 129.5, 129.4, 129.2, 128.9, 128.3, 128.2, 125.7, 125.4, 123.1, 123.0, 120.8, 120.6, 117.7, 117.6, 113.8, 80.0, 51.5, 28.3, 20.8. IR (KBr) v 3424, 2969, 1750, 1456, 1230, 758 cm^{-1}. HRMS (ESI) calcd. for $C_{33}H_{31}N_2O_5$ $[M+H]^+$: 535.2227, found: 535.2235.



methyl 1-(4-bromobenzoyl)-3-(2-((*tert*-butoxycarbonyl)amino)-5-methylphenyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**3t**)

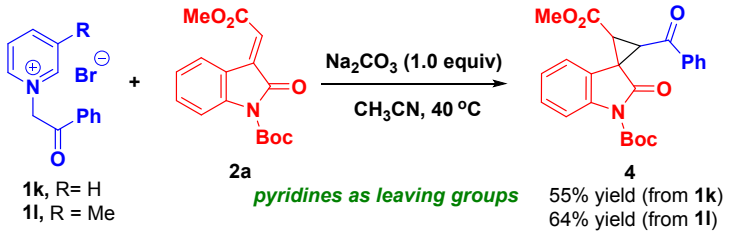
Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 25:1-20:1), 41.0 mg, 67% yield; t_1 = 5 h, t_2 = 12 h; m. p. 86.5-87.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (t, J = 12.0 Hz, 3H), 7.70-7.60 (m, 4H), 7.40-7.31 (m, 2H), 7.23-7.08 (m, 4H), 6.42 (s, 1H), 3.39 (s, 3H), 2.35 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 164.2, 153.2, 137.0, 134.9, 132.6, 132.3, 132.1, 132.0, 130.8, 129.5, 129.3, 129.3, 129.0, 128.4, 127.6, 125.7, 125.6, 123.2, 123.0, 120.8, 120.7, 117.6, 117.5, 113.9, 80.1, 51.7, 28.3, 20.8. IR (KBr) v 3422, 2976, 1721, 1230, 1161, 733 cm^{-1}. HRMS (ESI) calcd. for $C_{33}H_{30}BrN_2O_5$ $[M+H]^+$: 613.1333, found: 613.1321.



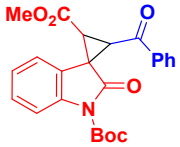
methyl 1-benzoyl-3-(2-((*tert*-butoxycarbonyl)amino)-3,5-dimethylphenyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**3u**)

Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 25:1-15:1), 50.3 mg, 92% yield; t_1 = 11 h, t_2 = 55 h; m. p. 172.6-173.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 2H), 7.69-7.60 (m, 3H), 7.52 (t, J = 12.0 Hz, 2H), 7.35-7.25 (m, 2H), 7.15 (q, J = 12.0 Hz, 3H), 7.01 (s, 1H), 6.49 (s, 1H), 3.26 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 165.0, 153.9, 138.5, 136.4, 135.8, 133.7, 133.2, 132.6, 132.2, 131.4, 130.7, 129.7, 129.4, 129.0, 128.9, 128.0, 127.1, 125.7, 125.2, 122.7, 120.7, 118.0, 117.7, 116.0, 79.1, 51.4, 28.0, 20.9, 18.4. IR (KBr) v 3321, 2971, 1712, 1486, 1223, 1165, 760 cm^{-1}. HRMS (ESI) calcd. for $C_{34}H_{33}N_2O_5$ $[M+H]^+$: 549.2384, found: 549.2380.

4. Experimental data for the formation of 4



General procedure: *N*-Phenacyl pyridinium salts **1k** or **1l** (0.15 mmol), methyleneindolinone **2a** (0.10 mmol), Na_2CO_3 (0.10 mmol) and 1.0 mL of CH_3CN were successively added to a 5.0 mL vial. The resulting mixture was stirred at 40 °C till the full consumption of **2a** as monitored by TLC, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the corresponding products **4**.



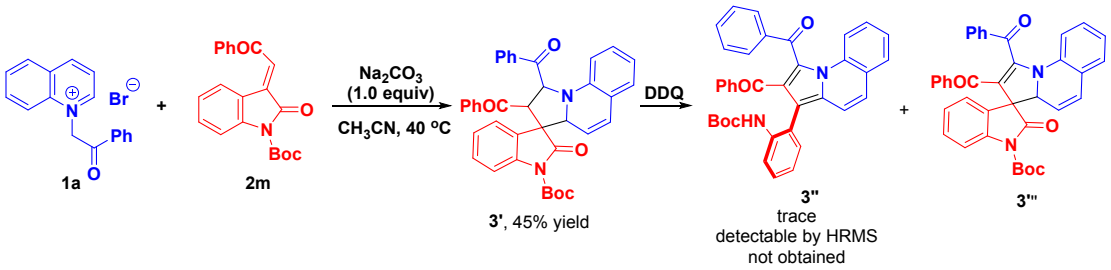
1'-(*tert*-butyl) 3-methyl 2-benzoyl-2'-oxospiro[cyclopropane-1,3'-indoline]-1',3-dicarboxylate (**4**)

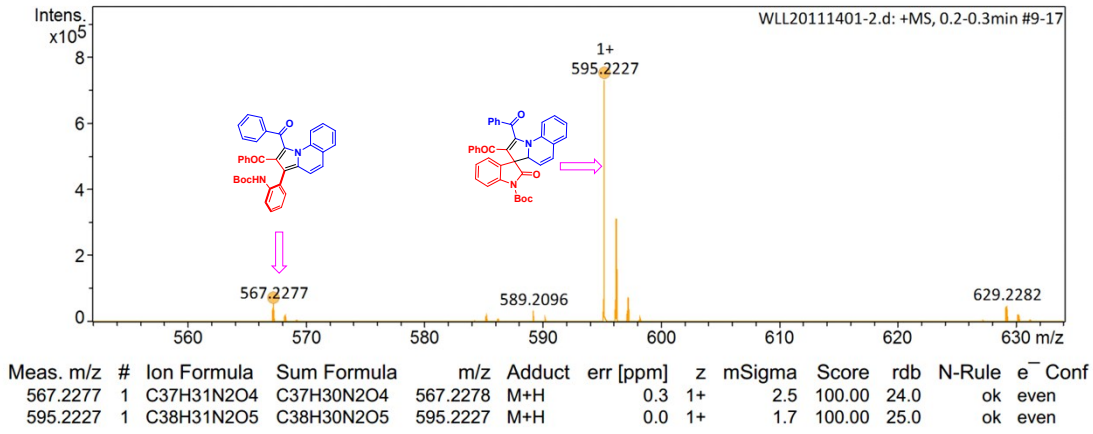
Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1-

10:1); m. p. 115.7-116.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 12.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.18 (q, *J* = 4.0 Hz, 1H), 7.07 (d, *J* = 12.0 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 4.13 (d, *J* = 12.0 Hz, 1H), 3.70 (s, 3H), 3.54 (d, *J* = 12.0 Hz, 1H), 1.57 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 170.4, 166.2, 148.6, 140.0, 136.2, 133.9, 128.7, 128.6, 128.5, 124.4, 122.9, 122.0, 114.9, 84.8, 52.7, 40.3, 39.7, 35.7, 28.0. IR (KBr) *v* 3456, 2985, 1739, 1300, 1217, 1158, 759 cm^{-1}. HRMS (ESI) calcd. for $C_{24}H_{24}NO_6$ $[M+H]^+$: 422.1598, found: 422.1590.

5. Unsuccessful trials

1) Benzoyl substituted 3-alkenyl oxindole 2m as substrate

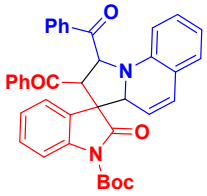




Meas. m/z	#	Ion Formula	Sum Formula	m/z	Adduct	err [ppm]	z	mSigma	Score	rdb	N-Rule	e⁻ Conf
567.2277	1	C37H31N2O4	C37H30N2O4	567.2278	M+H	0.3	1+	2.5	100.00	24.0	ok	even
595.2227	1	C38H31N2O5	C38H30N2O5	595.2227	M+H	0.0	1+	1.7	100.00	25.0	ok	even

Figure S3. HRMS spectrum of the dearomative [3+2]/decarbonylation cascade process

To further examine the substrate scope, we also attempted the benzoyl-substituted 3-alkenyl oxindole **2m**. The first dearomative [3+2] cycloaddition proceeded smoothly to deliver **3'** in 45% yield. However, upon oxidation by DDQ, the reaction system became very complex, and the oxidative decarbonylation product could only be detected by HRMS, but not obtained.

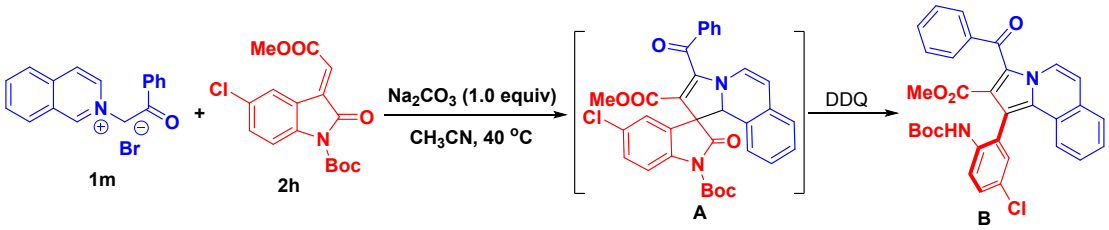


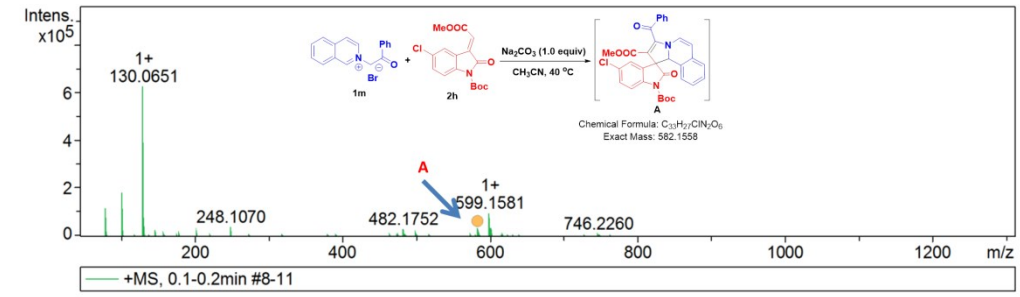
tert-butyl 1',2'-dibenzoyl-2-oxo-1',2'-dihydro-3a'*H*-spiro[indoline-3,3'-pyrrolo[1,2-*a*]quinoline]-1-carboxylate (**3'**)

Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 25:1 to20:1), 27.1 mg, 45% yield; reaction time = 1.5 h; m. p. 97.1-97.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.0 Hz, 2H), 7.59 (t, J = 8.0 Hz, 1H),7.48 (t, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 7.15 (q, J = 8.0 Hz, 5H), 7.09 (d, J = 8.0 Hz, 1H), 7.04-6.97 (m, 2H), 6.79 (d, J = 8.0 Hz, 1H), 6.59 (t, J = 8.0 Hz, 1H), 6.39 (d, J = 4.0 Hz, 1H), 6.22 (d, J = 8.0 Hz, 1H), 6.13 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 5.76 (s, 1H), 4.84 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 4.59 (d, J = 4.0 Hz, 1H), 1.55 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 195.7, 173.5, 148.1, 141.9, 139.1, 136.5, 134.6, 134.0, 133.0, 129.7, 129.1, 128.9, 128.7, 128.3, 128.2, 127.7, 127.5, 126.0, 125.6, 124.5, 120.0, 118.1, 117.7, 114.1, 109.4, 84.4, 71.1, 61.9, 60.7, 59.7, 28.0. IR (KBr) v 3432, 2924, 1669, 1625, 1342, 838 cm^{-1}. HRMS (ESI) calcd. for $C_{38}H_{33}N_2O_5$ $[M+H]^+$: 597.2384, found: 597.2374.

2) Isoquinolinium salt 1m as substrate

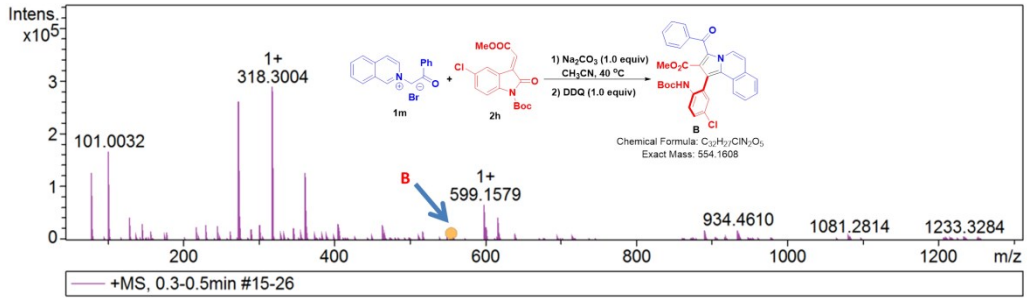
We also explored the reactivity of isoquinolinium salt **1m**. By reacting with 3-alkenyl oxindole **2h** under basic conditions, the first [3+2] cycloaddition could occur smoothly and product **A** through the [3+2] cycloaddition and sequential dehydrogenation process could be detected by HRMS. After oxidation by DDQ, we could also detect the presence of trace of decarbonylated product **B** by HRMS. It should be noted that we failed to separate **A** and **B** from the reaction systems by silica gel column chromatography due to their high instability.





Meas. m/z	#	Ion Formula	Sum Formula	m/z	Adduct	err [ppm]	z	mSigma	Score	rdb	N-Rule	e⁻ Conf
583.1629	1	C33H28ClN2O6	C33H27ClN2O6	583.1630	M+H	0.3	1+	22.4	100.00	21.0	ok	even

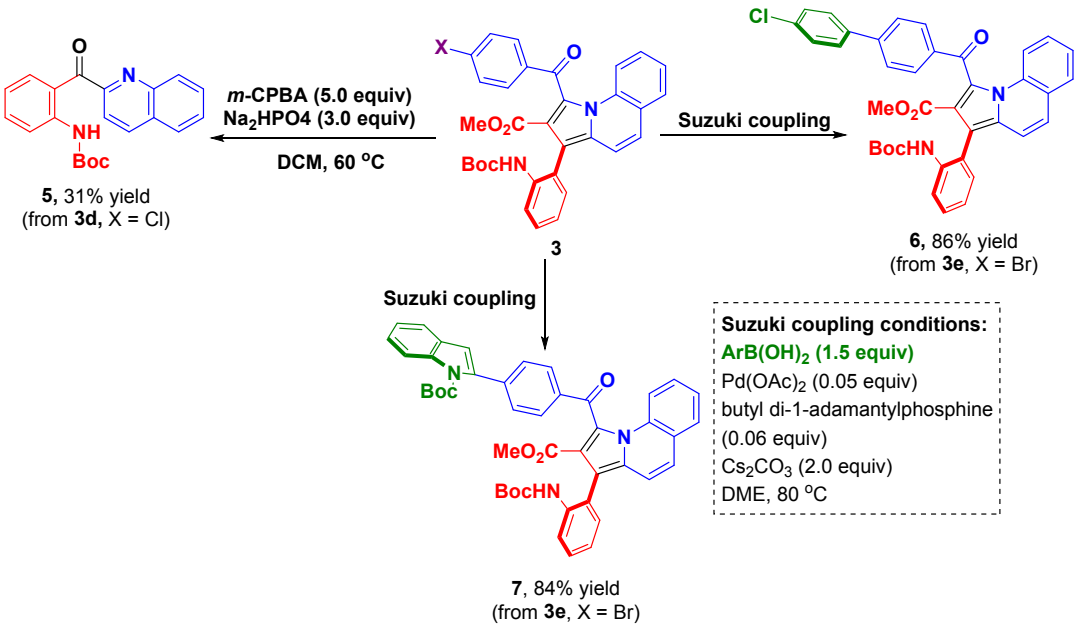
Figure S4. HRMS spectrum of the reaction between **1m** and **2h** for 11 h



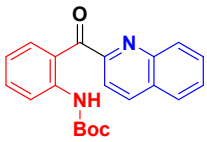
Meas. m/z	#	Ion Formula	Sum Formula	m/z	Adduct	err [ppm]	z	mSigma	Score	rdb	N-Rule	e⁻ Conf
555.1681	1	C32H28ClN2O5	C32H27ClN2O5	555.1681	M+H	0.0	1+	n.a.	100.00	20.0	ok	even

Figure S5. HRMS spectrum of the dearomative [3+2]/decarbonylation cascade process

6. Experimental data for derivations of 3d and 3e



General procedure for the formation of 5: To a solution of **3d** (173.3 mg, 0.31 mmol) in 2.0 mL DCM, *m*-CPBA (269.4 mg, 1.56 mmol) and Na_2HPO4 (132.0 mg, 0.93 mmol) were successively added. The resulting mixture was stirred at 60 °C for 11 h, and then purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 35:1) to afford **5** as a white solid in 31% yield.

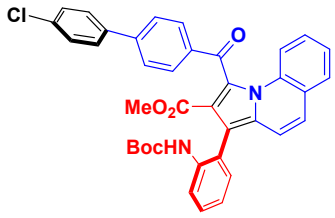


tert-butyl (2-(quinoline-2-carbonyl)phenyl)carbamate (**5**)

White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 35:1), 33.8 mg, 31% yield; reaction time = 11 h; m. p. 118.2-118.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.54 (s, 1H), 8.51 (d, *J* = 12.0 Hz, 1H), 8.35 (d, *J* = 12.0 Hz, 1H), 8.16 (d, *J* = 12.0 Hz, 1H), 7.90 (t, *J* = 12.0 Hz, 3H), 7.79 (t, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 8.0 Hz, 1H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 155.7, 152.9, 146.6, 142.7, 137.1, 135.2, 134.9, 130.3, 130.2, 128.5, 128.3, 127.6, 120.9, 120.6, 119.4, 80.5, 28.2, one carbon missing in the aromatic region. IR (KBr) *v* 3323, 2977, 1735, 1519, 1154, 759 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{21}N_2O_3$ $[M+H]^+$: 349.1547, found: 349.1547.

General procedure for the formation of 6: Under nitrogen atmosphere, compound **3e** (95.9 mg, 0.16 mmol), 4-chlorophenyl boronic acid (37.5 mg, 0.24 mmol, 1.5 equiv), Cs_2CO_3 (104.3 mg,

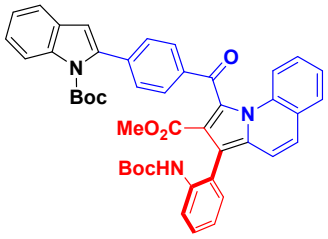
0.32 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.05 equiv) and butyl di-1-adamantylphosphine (0.06 equiv) were successively added to a 15 mL dried tube, followed by addition of 2.0 mL DME. The resulting mixture was stirred at 80 °C for 6 h, and then the reaction mixture was directly subjected to silica gel column chromatography (petroleum ether/ ethyl acetate as eluent) to afford the corresponding product **6** as a yellow solid in 86% yield.



methyl 3-(2-((*tert*-butoxycarbonyl)amino)phenyl)-1-(4'-chloro-[1,1'-biphenyl]-4-carbonyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**6**)

Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1-20:1), 87.0 mg, 86% yield; reaction time = 10 h; m. p. 106.7-107.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 3H), 7.59 (d, *J* = 12.0 Hz, 4H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.34-7.15 (m, 7H), 7.04 (d, *J* = 8.0 Hz, 3H), 6.46 (s, 1H), 3.30 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 164.2, 153.0, 145.2, 138.0, 137.5, 137.1, 134.6, 132.7, 131.8, 131.6, 130.1, 129.2, 129.1, 128.7, 128.5, 128.4, 127.4, 125.7, 125.5, 125.5, 123.0, 122.9, 122.7, 120.4, 120.3, 117.6, 117.5, 113.4, 80.2, 51.5, 28.2. IR (KBr) *v* 3420, 2960, 1723, 1162, 755 cm^{-1}. HRMS (ESI) calcd. for $C_{38}H_{32}ClN_2O_5$ $[M+H]^+$: 631.1994, found: 631.1985.

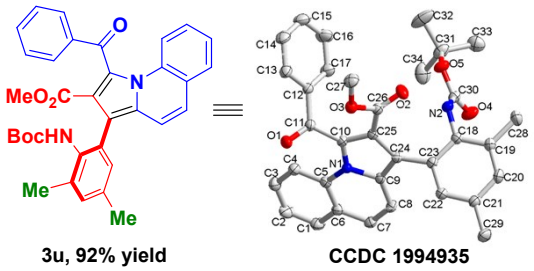
General procedure for the formation of 7: Under nitrogen atmosphere, compound **3e** (95.9 mg, 0.16 mmol), 2-indolylboronic acid (37.5 mg, 0.24 mmol, 1.5 equiv), Cs_2CO_3 (104.3 mg, 0.32 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.05 equiv) and butyl di-1-adamantylphosphine (0.06 equiv) were successively added to a 15 mL dried tube, followed by addition of 2.0 mL DME. The resulting mixture was stirred at 80 °C for 10 h, and then the reaction mixture was directly subjected to silica gel column chromatography (petroleum ether/ ethyl acetate as eluent) to afford the corresponding product **7** as a yellow solid in 84% yield.



methyl 1-(4-(1-(*tert*-butoxycarbonyl)-1*H*-indol-2-yl)benzoyl)-3-(2-((*tert*-butoxycarbonyl)amino)phenyl)pyrrolo[1,2-*a*]quinoline-2-carboxylate (**7**)

Yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1-15:1), 99.0 mg, 84% yield; reaction time = 6 h; m. p. 99.6-100.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 1H), 8.03-7.92 (m, 3H), 7.63-7.39 (m, 6H), 7.34-7.14 (m, 5H), 7.06-6.98 (m, 3H), 6.54 (s, 1H), 6.45 (s, 1H), 3.34 (s, 3H), 1.33 (s, 9H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 164.0, 152.9, 149.8, 146.1, 140.5, 138.9, 137.7, 137.5, 136.7, 132.6, 131.6, 130.1, 129.2, 129.0, 128.9, 128.7, 128.5, 128.3, 127.3, 125.6, 125.4, 124.9, 123.1, 122.8, 122.7, 120.7, 120.3, 119.8, 117.5, 117.4, 115.2, 113.3, 111.4, 83.8, 80.2, 51.5, 28.2, 27.5. IR (KBr) *v* 3421, 2977, 1729, 1323, 1229, 1163, 752 cm^{-1}. HRMS (ESI) calcd. for $C_{45}H_{42}N_3O_7$ $[M+H]^+$: 736.3017, found: 736.3004.

7. Crystal structure of 3u



Bond precision: C-C = 0.0028 A Wavelength =1.54184

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alpha = 90 beta = 105.527(2) gamma = 90

Temperature: 293 K

	Calculated	Reported
Volume	2992.81(13)	2992.81(12)
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Hall group	-P 2yn	-P 2yn
Moiety formula	$C_{34}H_{32}N_2O_5$	$C_{34}H_{32}N_2O_5$
Sum formula	$C_{34}H_{32}N_2O_5$	$C_{34}H_{32}N_2O_5$
Mr	548.62	548.61
Dx,g cm-3	1.218	1.218
Z	4	4

Mu (mm-1)	0.661	0.661
F000	1160.0	1160.0
F000'	1163.53	
h,k,lmax	16,16,20	16,16,20
Nref	5348	5348
Tmin,Tmax	0.847,0.936	0.973,1.000
Tmin'	0.719	

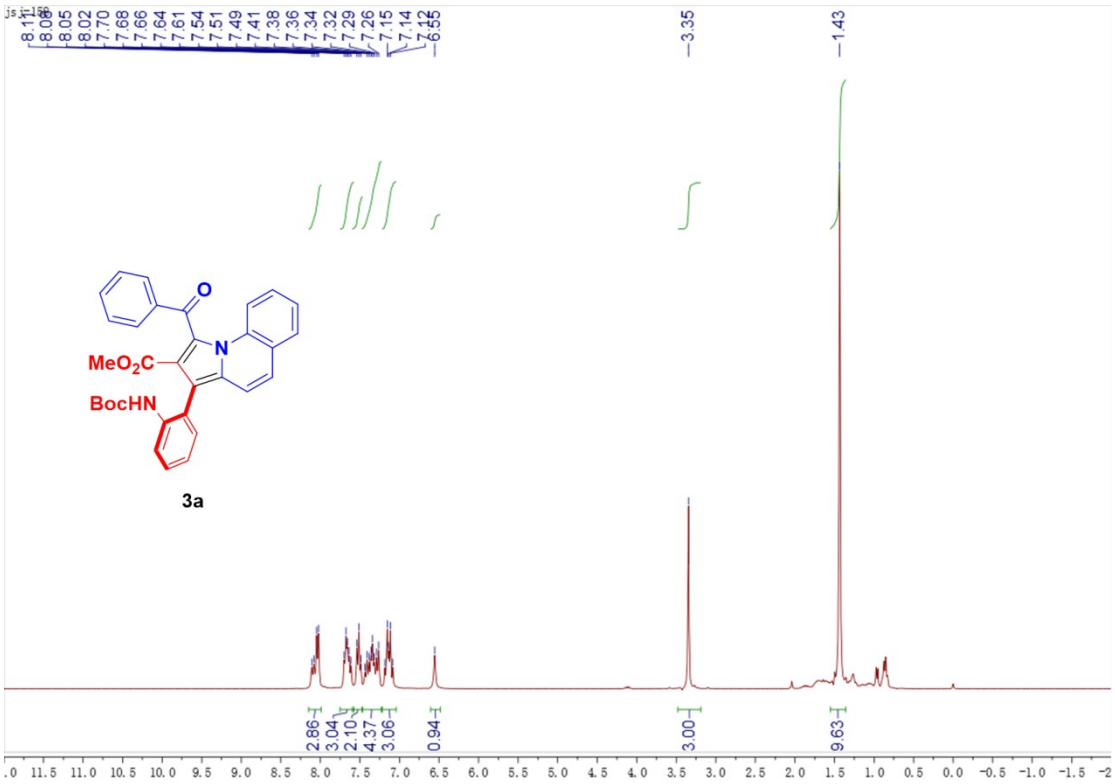
Correction method= # Reported T Limits: Tmin=0.973 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 67.079

R(reflections)= 0.0456(4274) wR2(reflections)= 0.1291(5348)

S = 1.028 Npar= 381

8. ^{1}H NMR and ^{13}C NMR spectra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7.36
7.34
7.32
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7.26
7.15
7.14
7.12
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1.43
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BocHN
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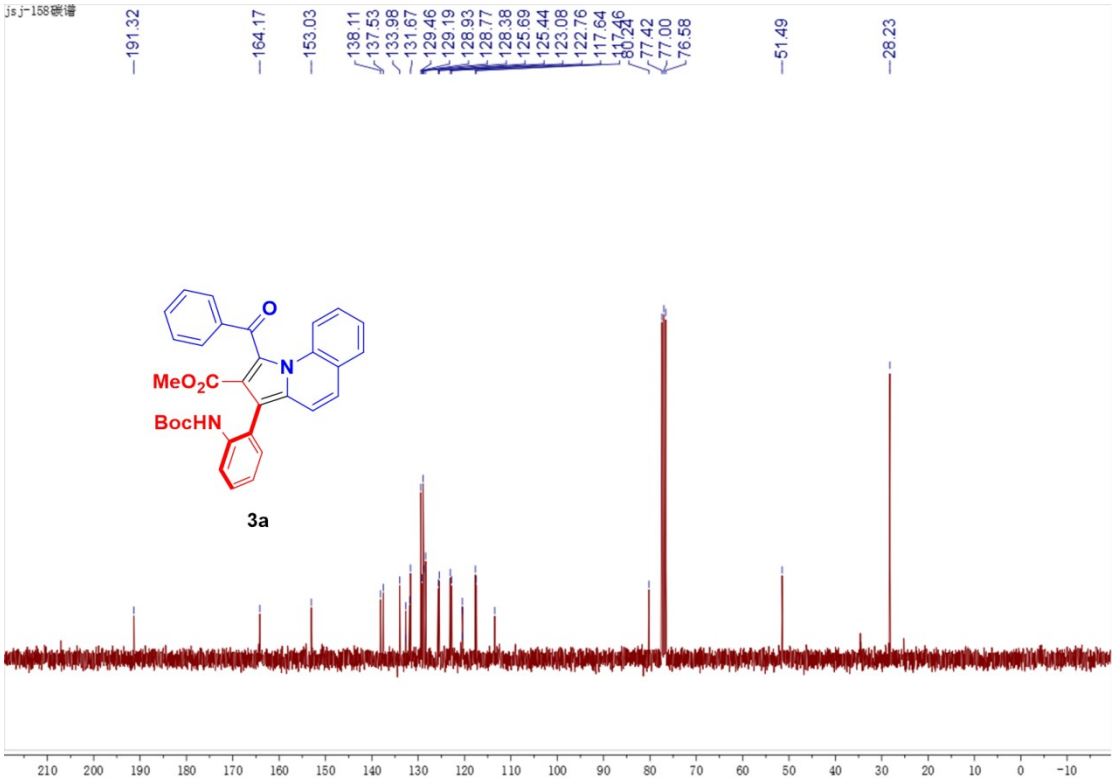
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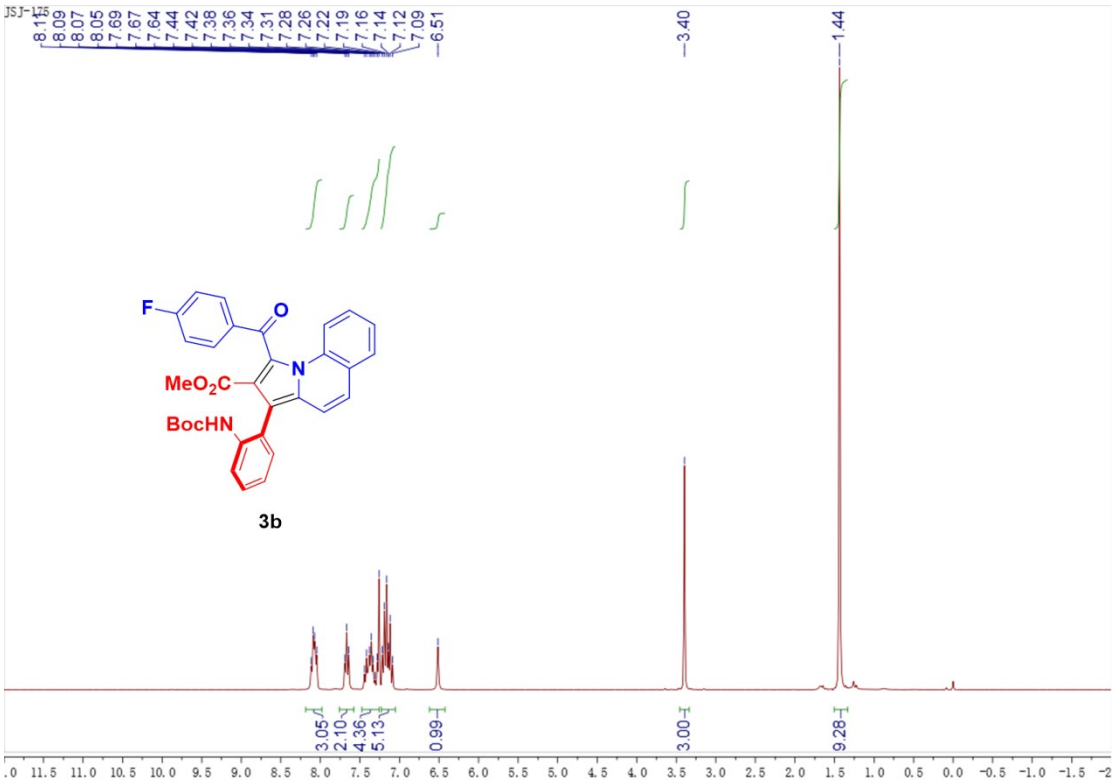
3a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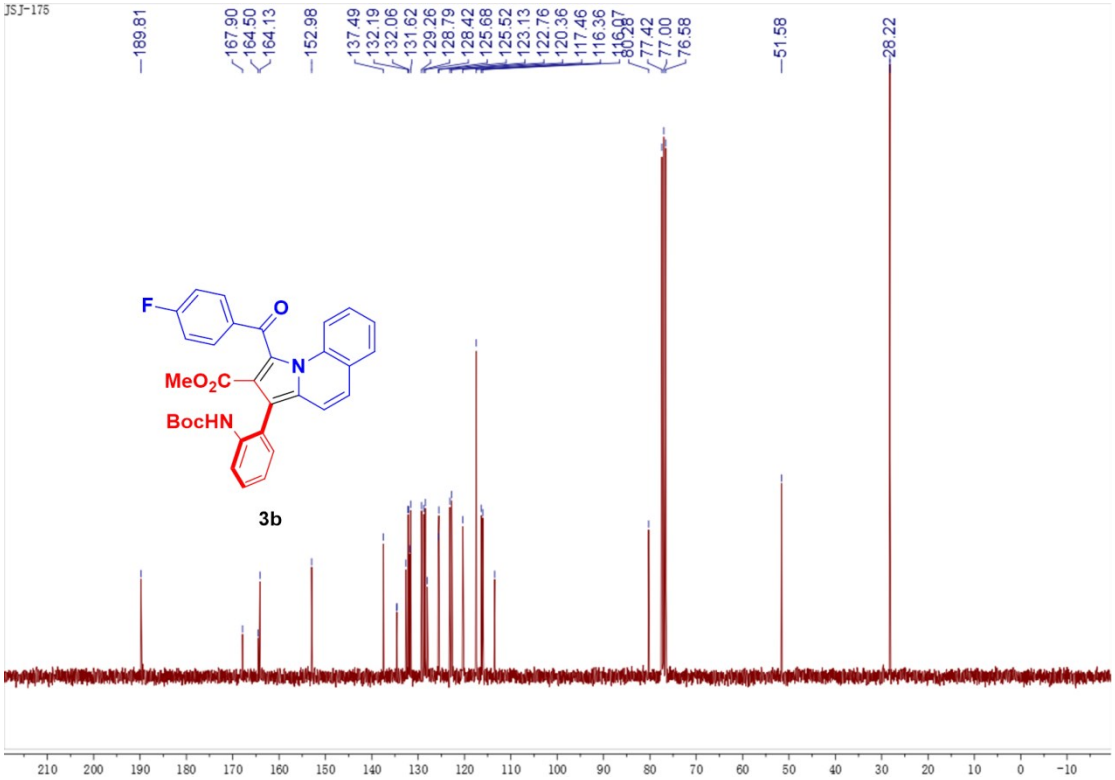
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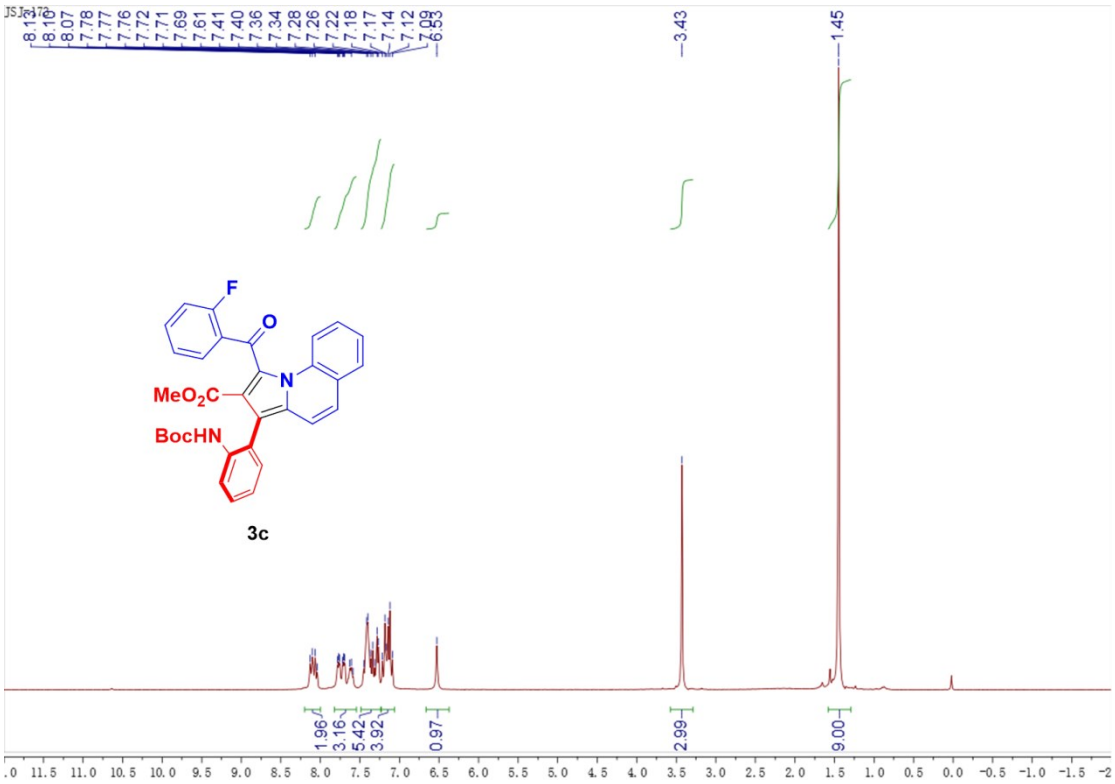
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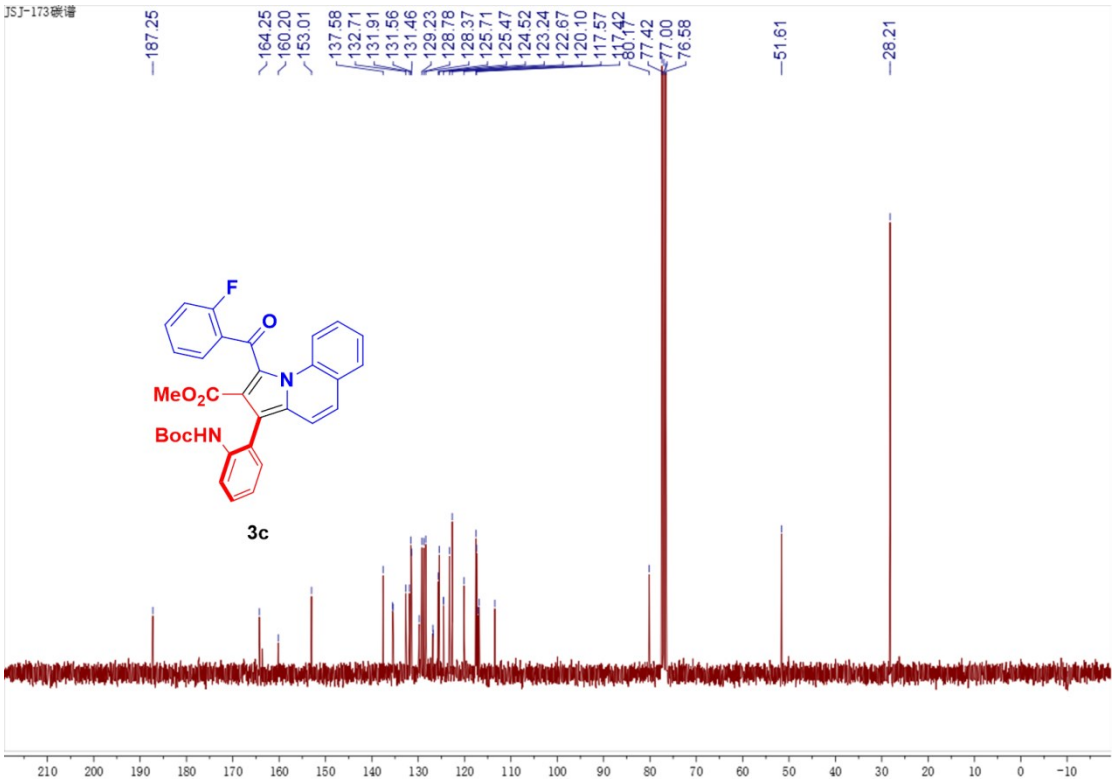
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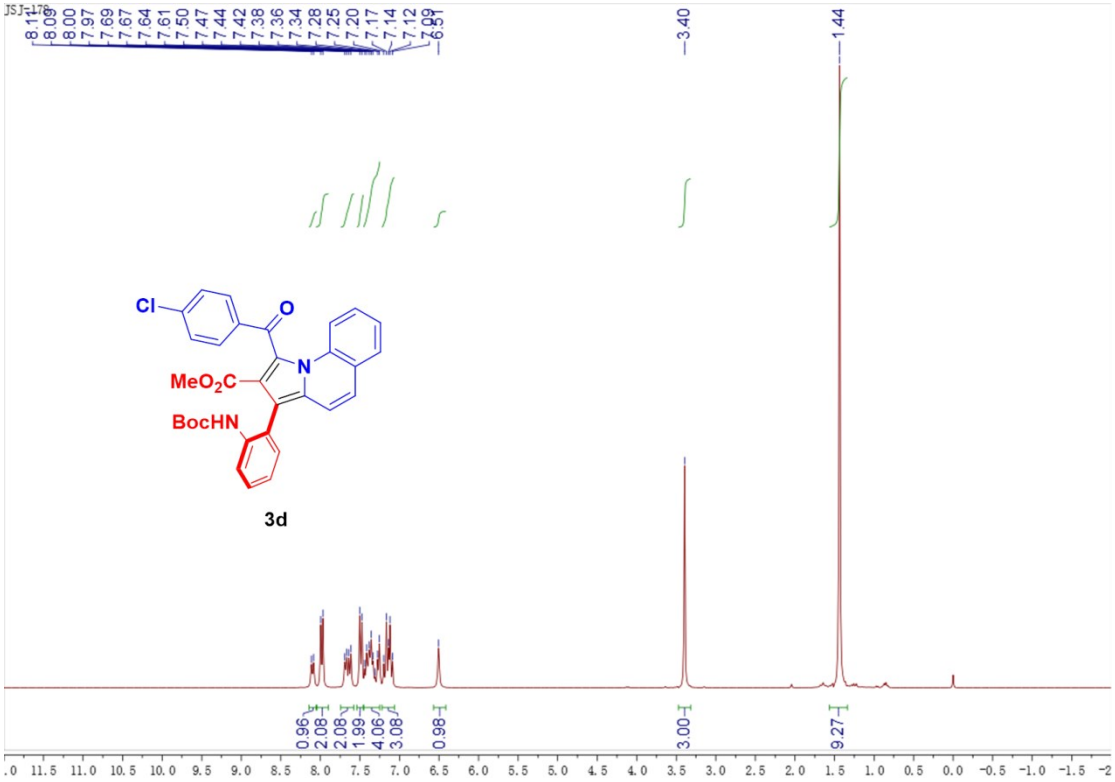
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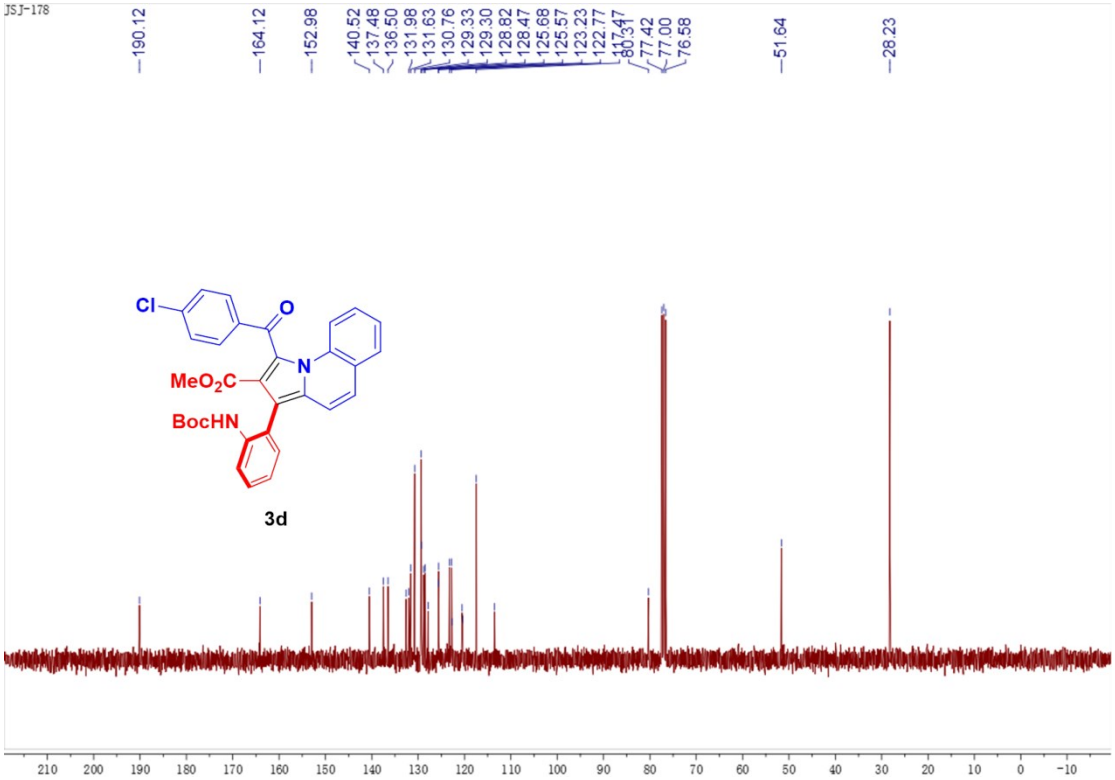
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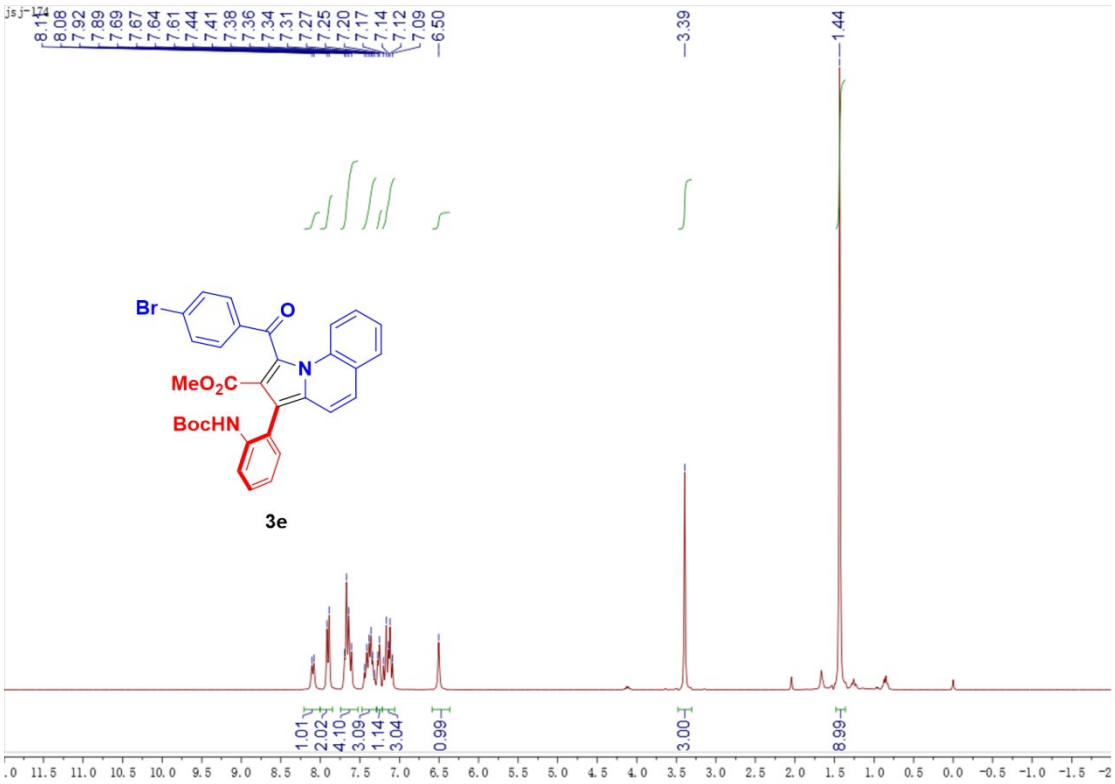
3d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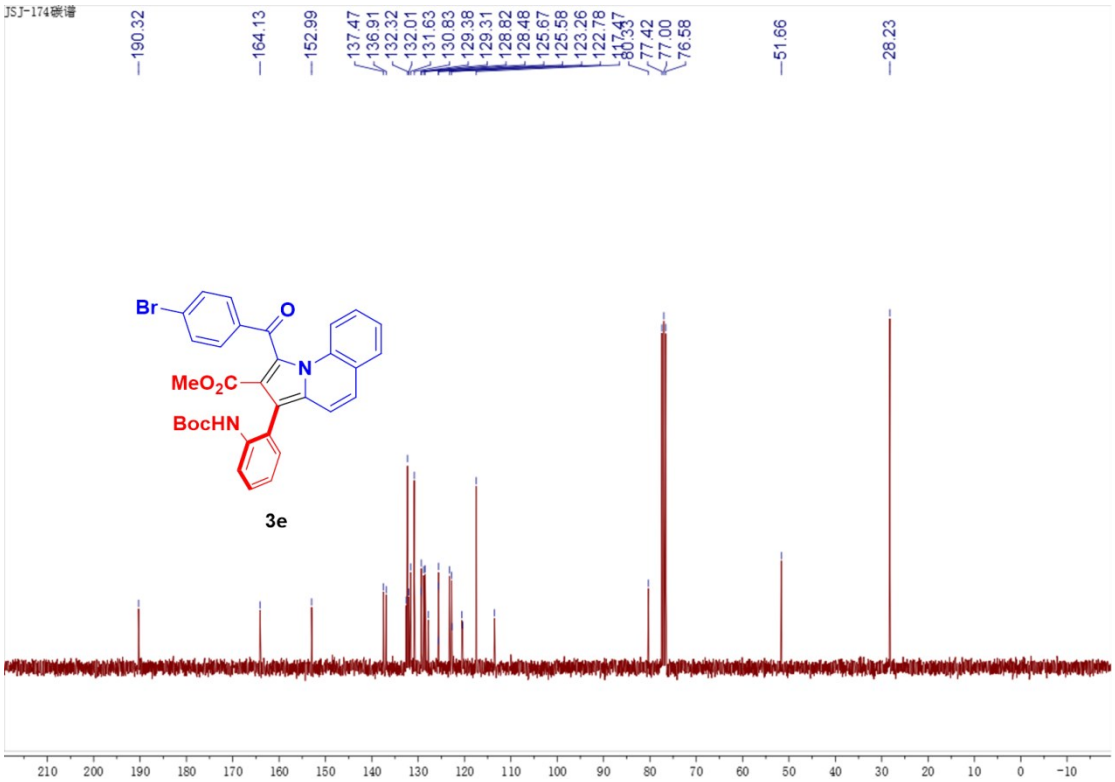
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Br
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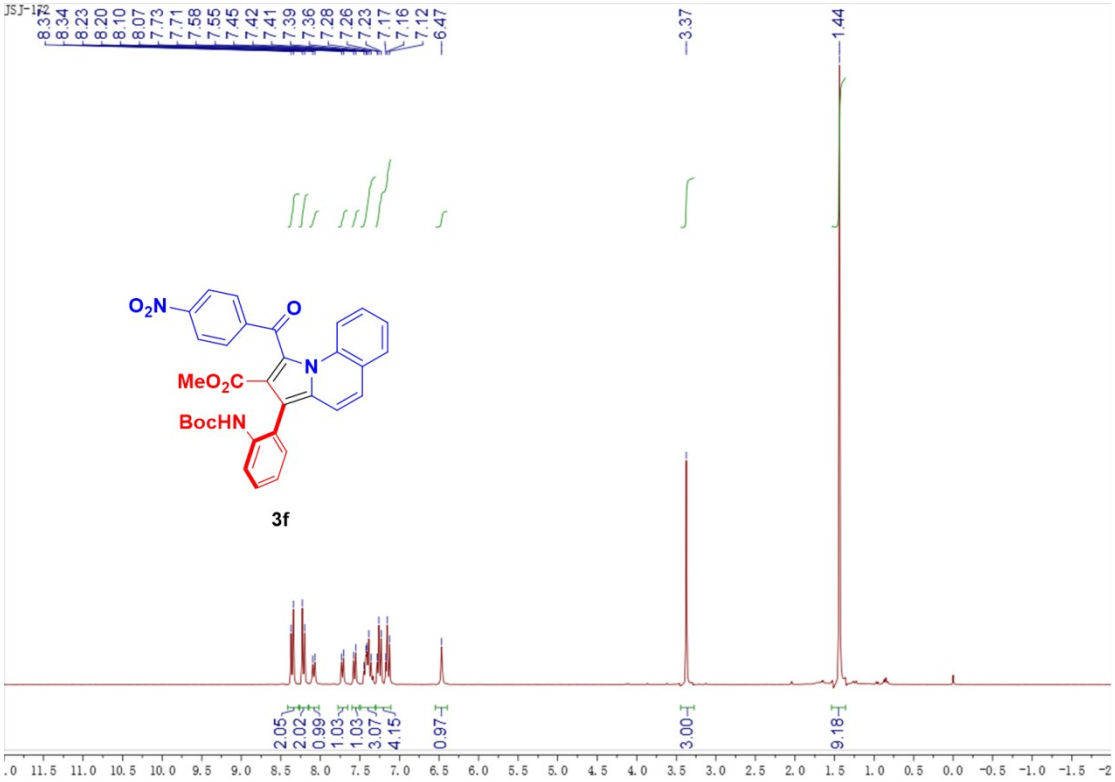
BocHN
3e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MeO2C
BocHN
3f
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2.02
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4.15
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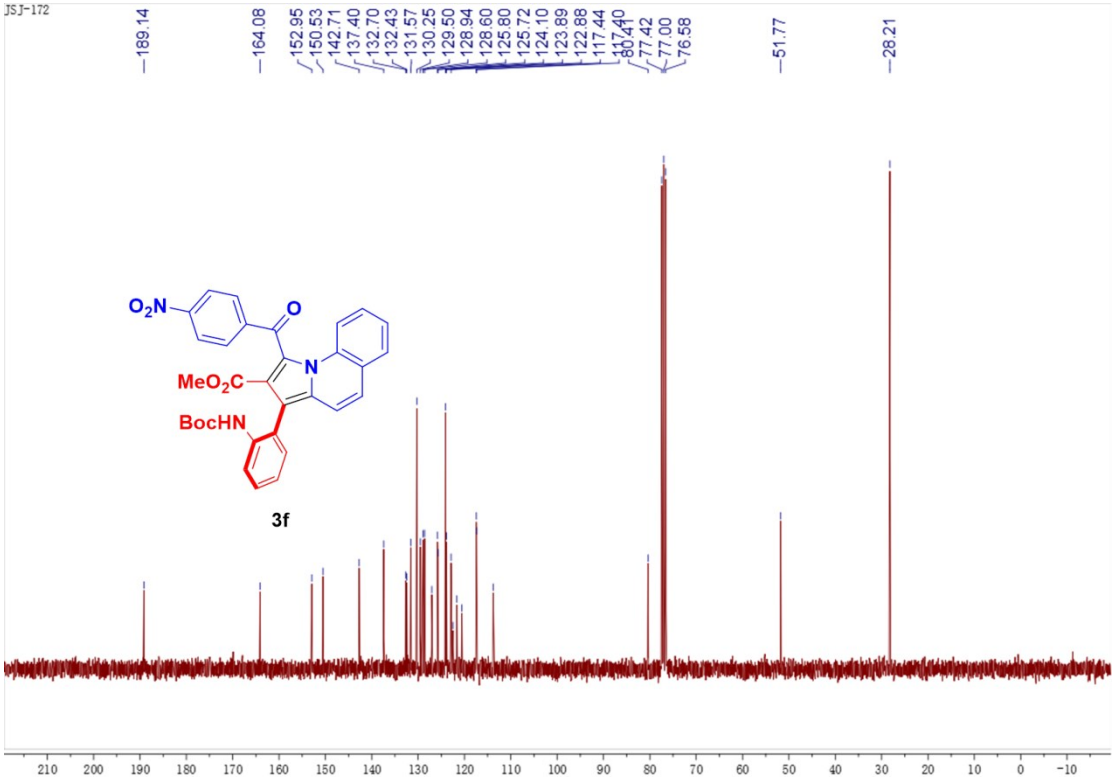
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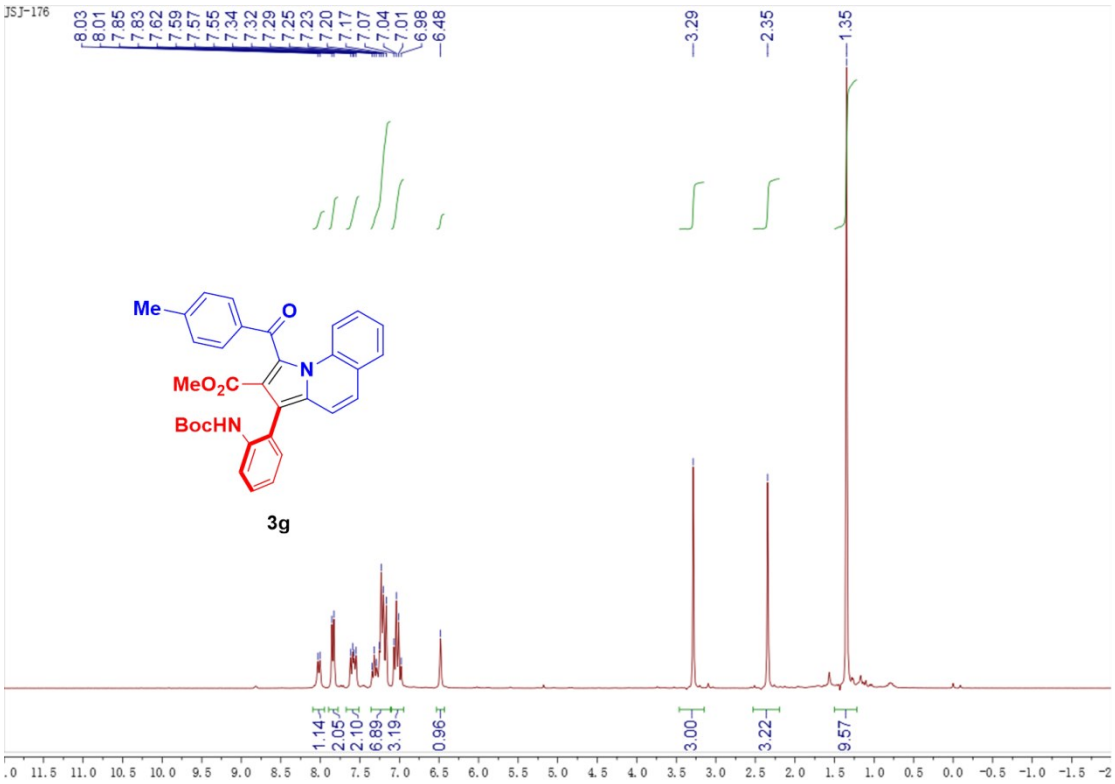
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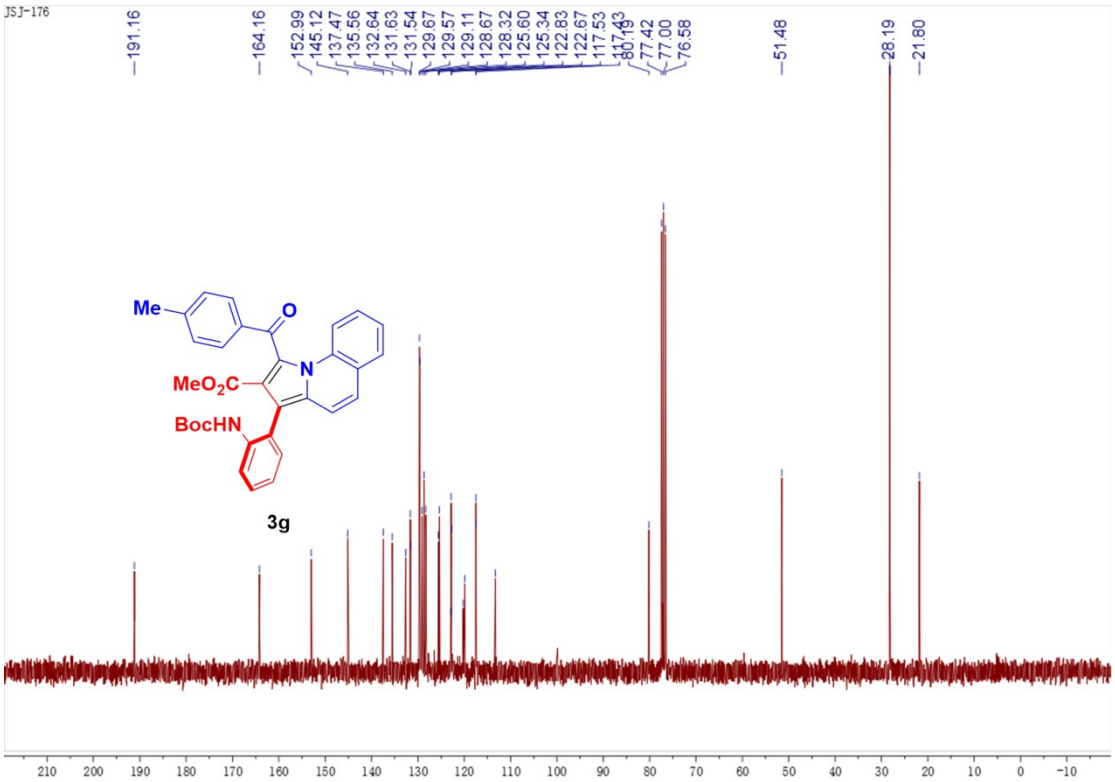
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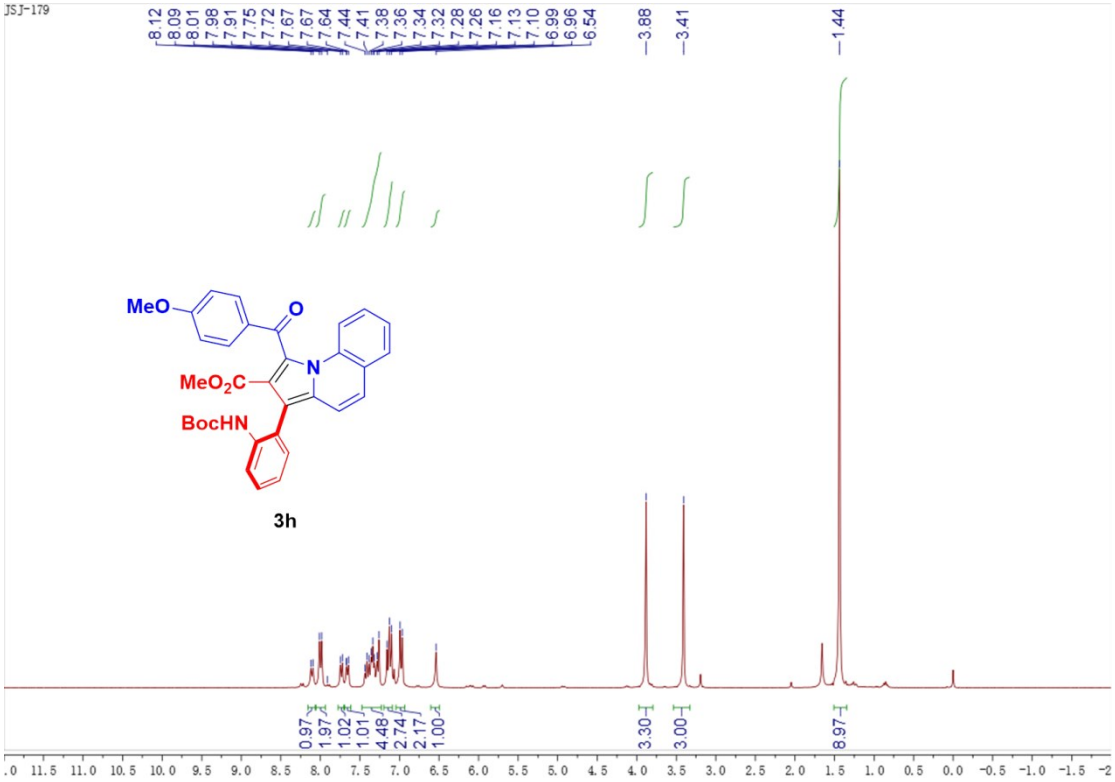
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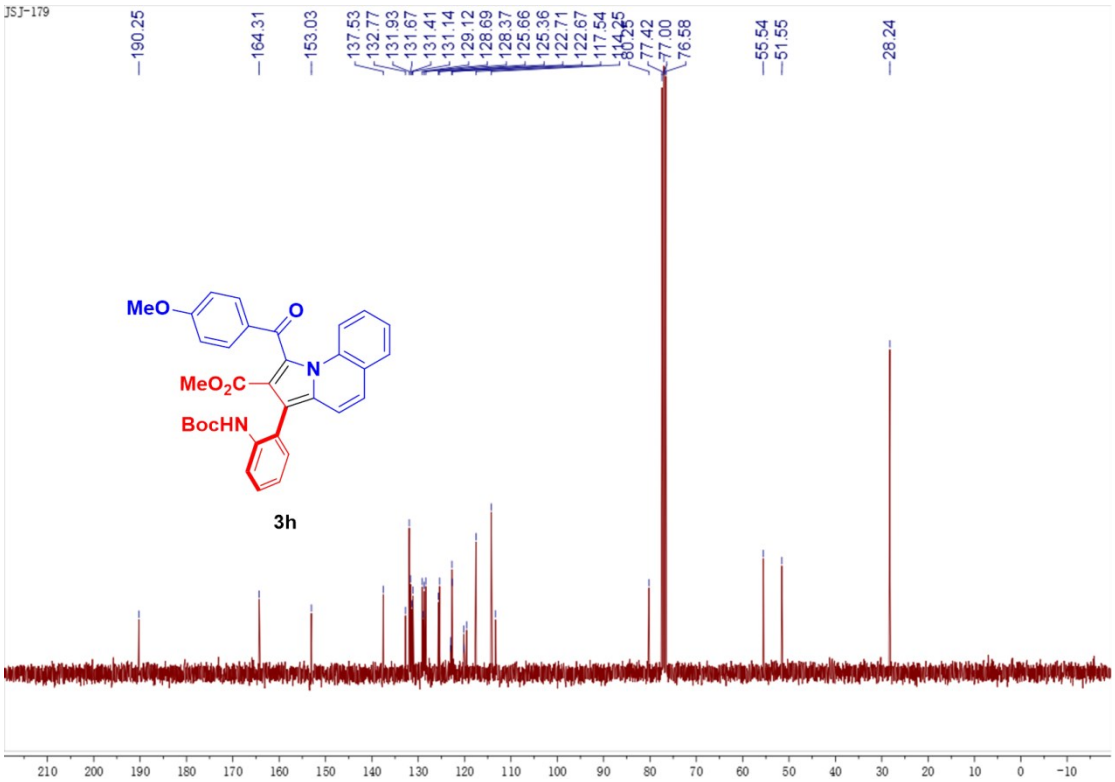
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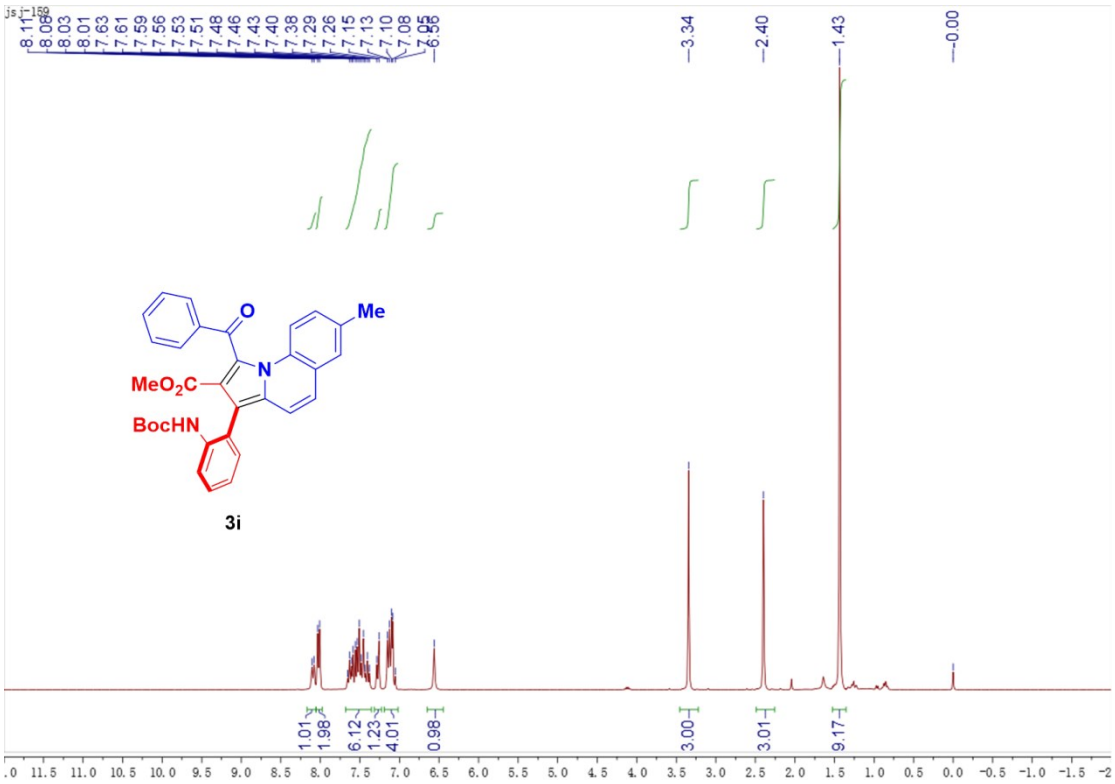
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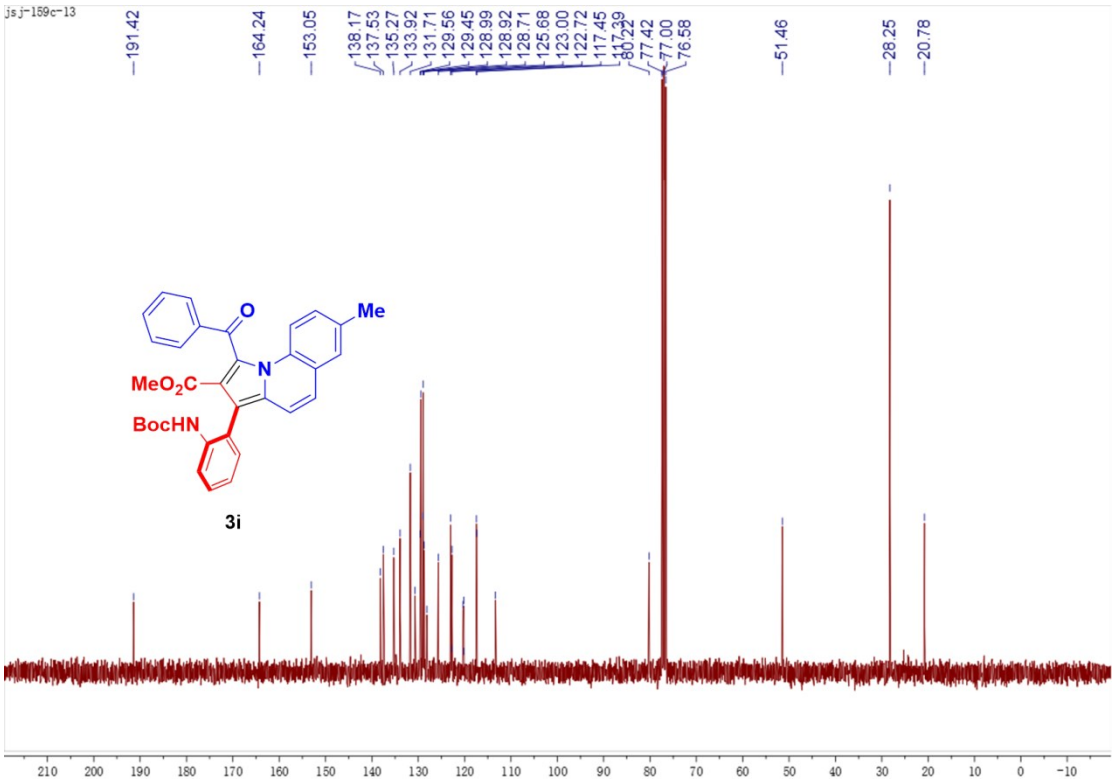
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BocHN
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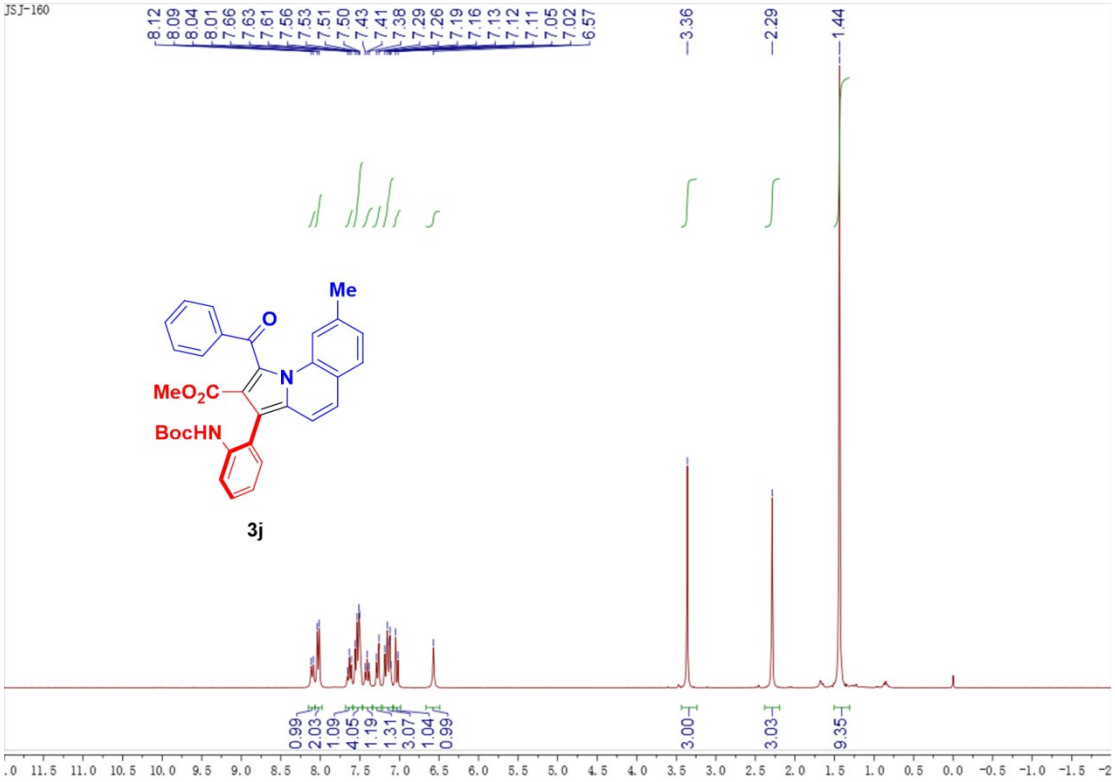
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BocHN
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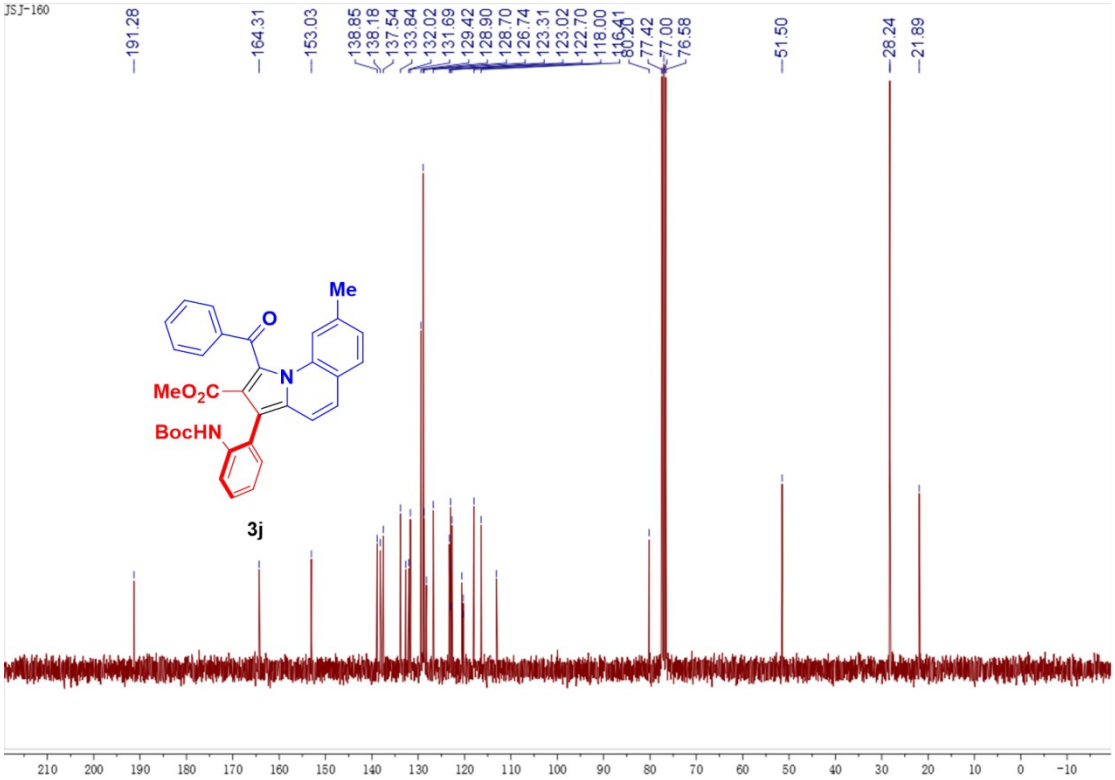
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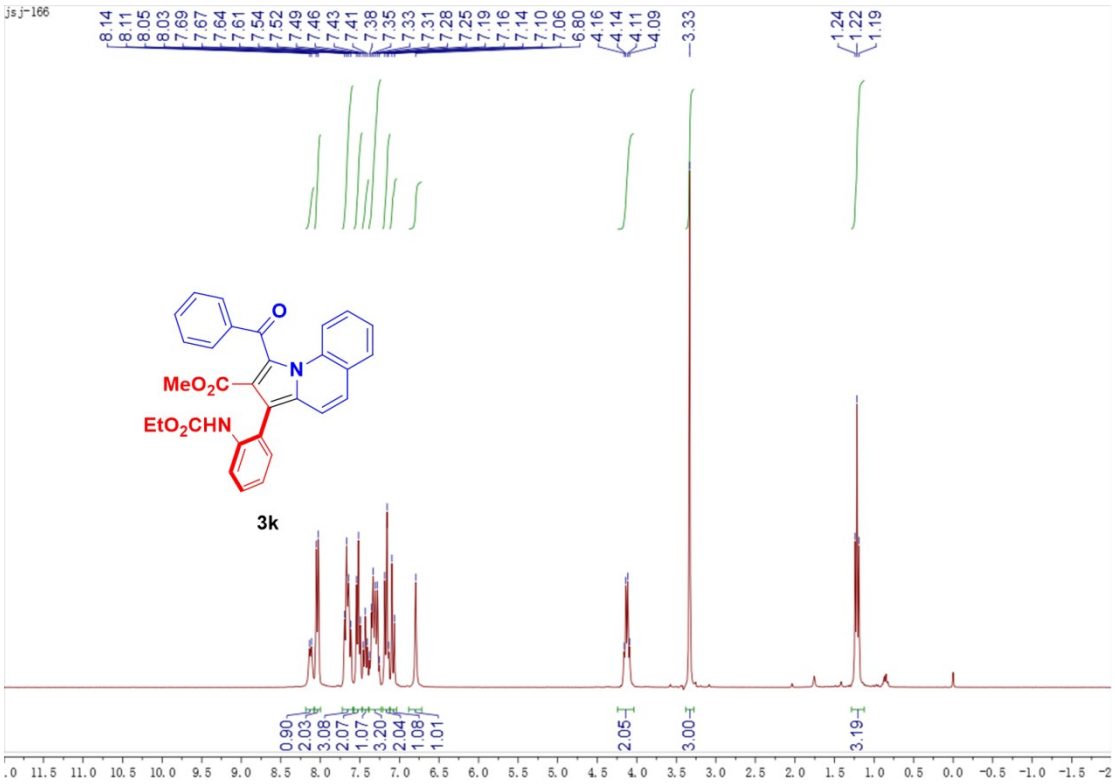
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1.19
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EtO2CHN
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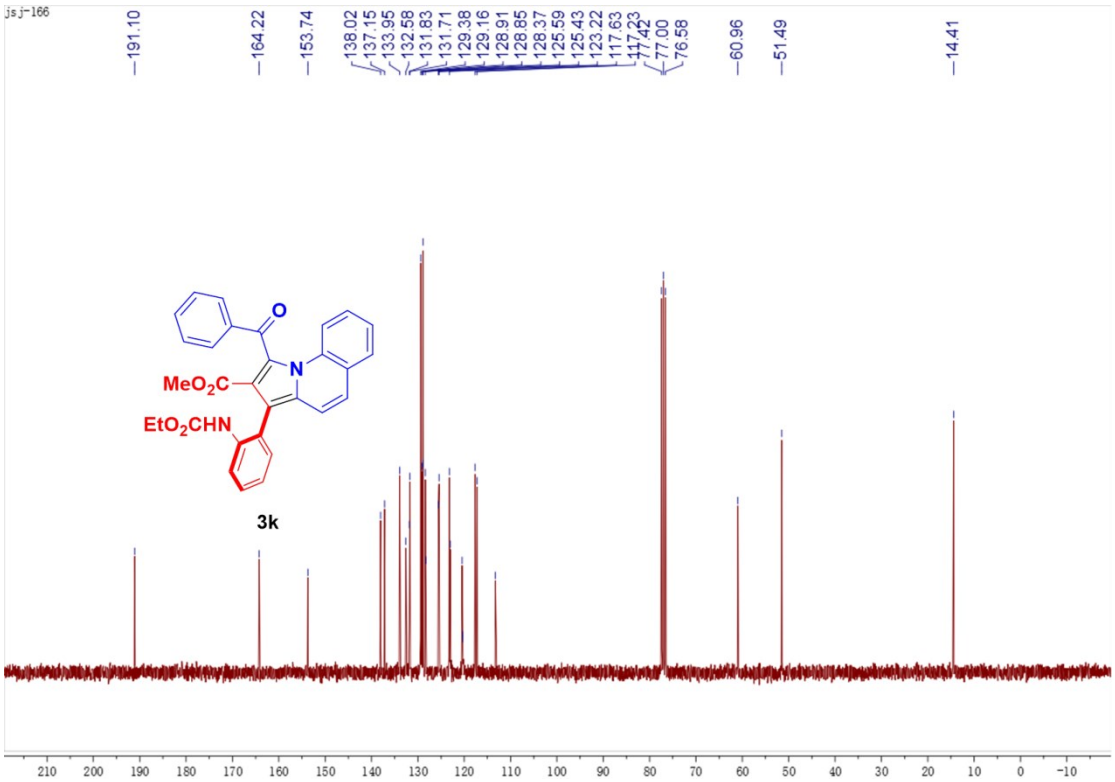
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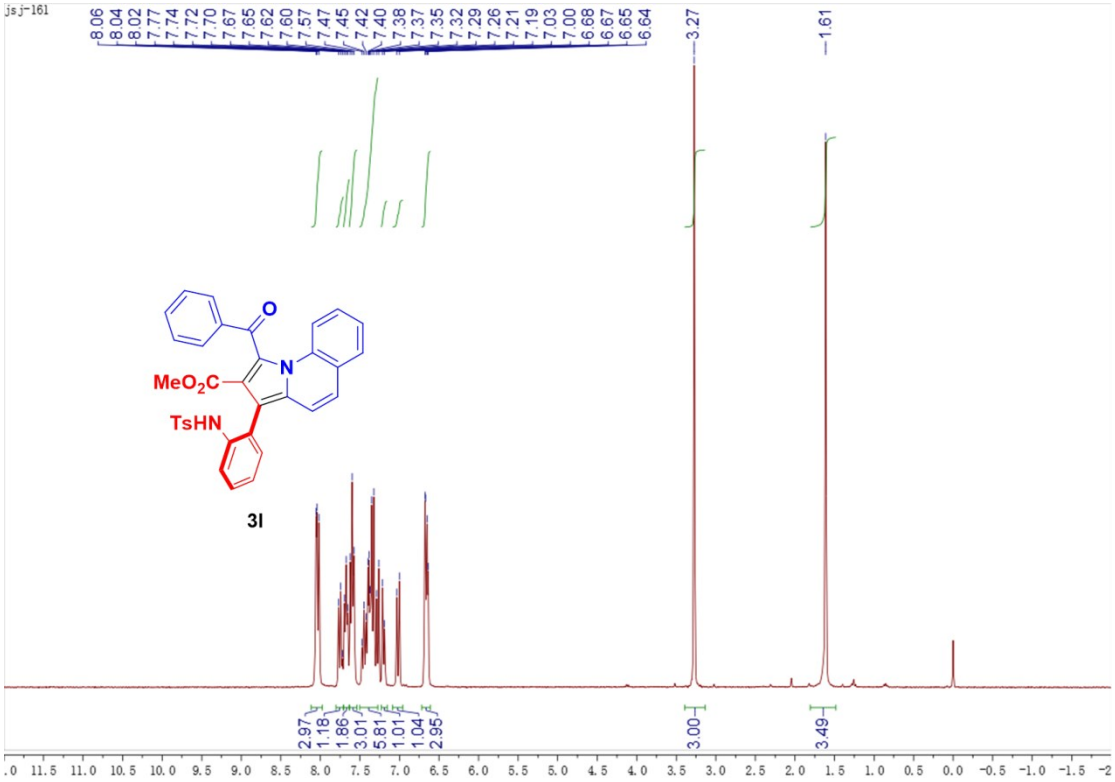
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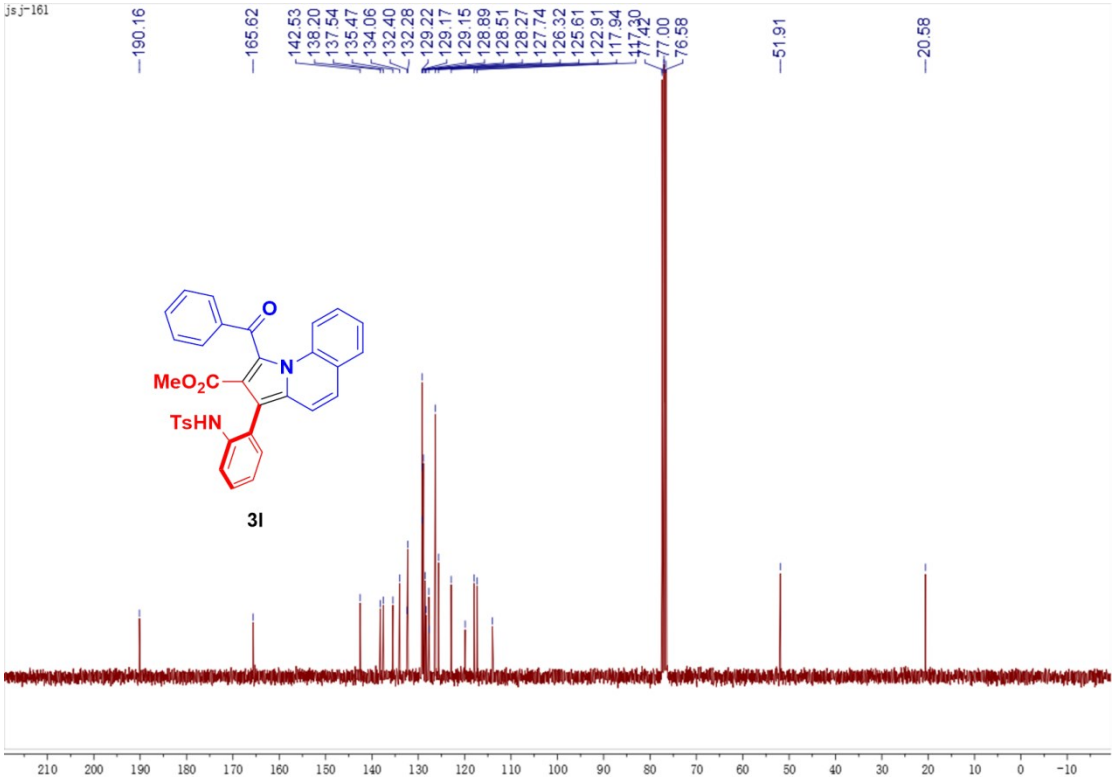
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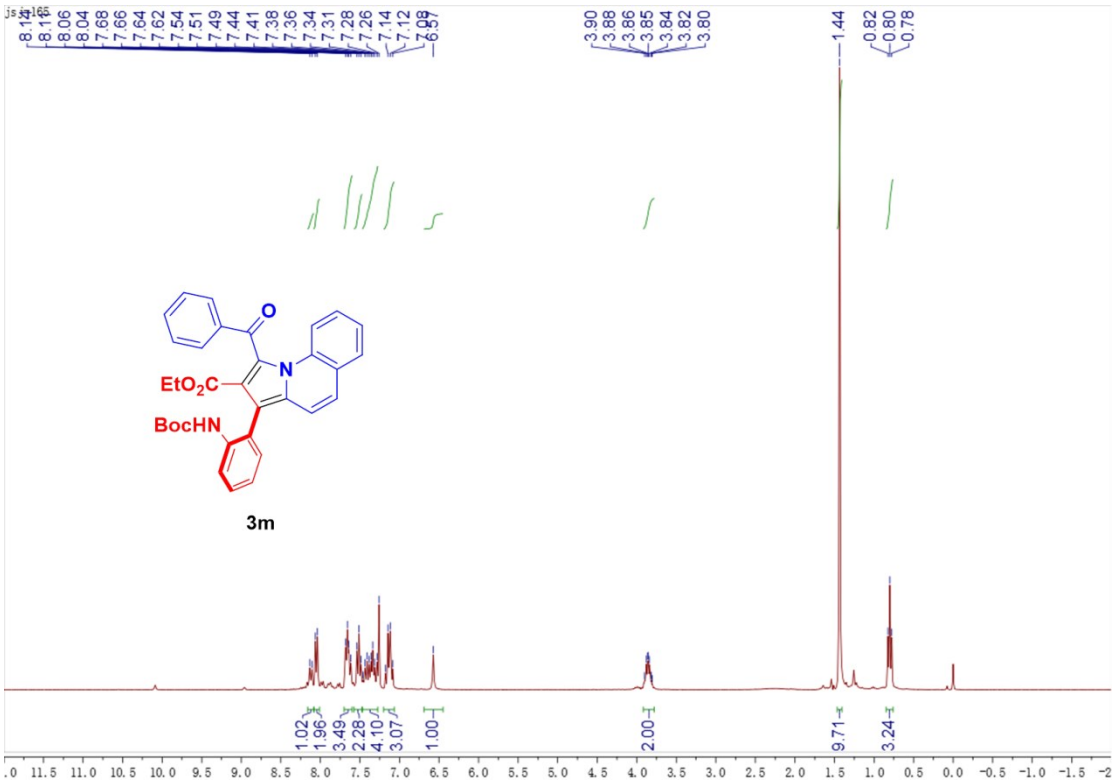
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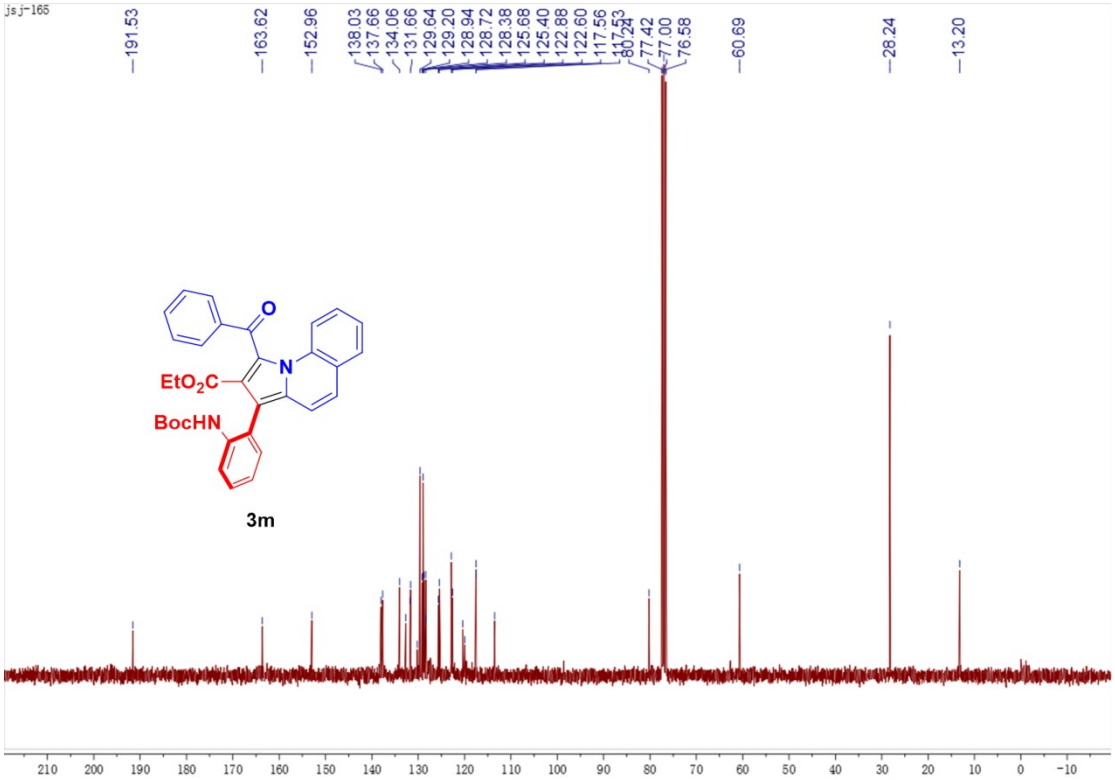
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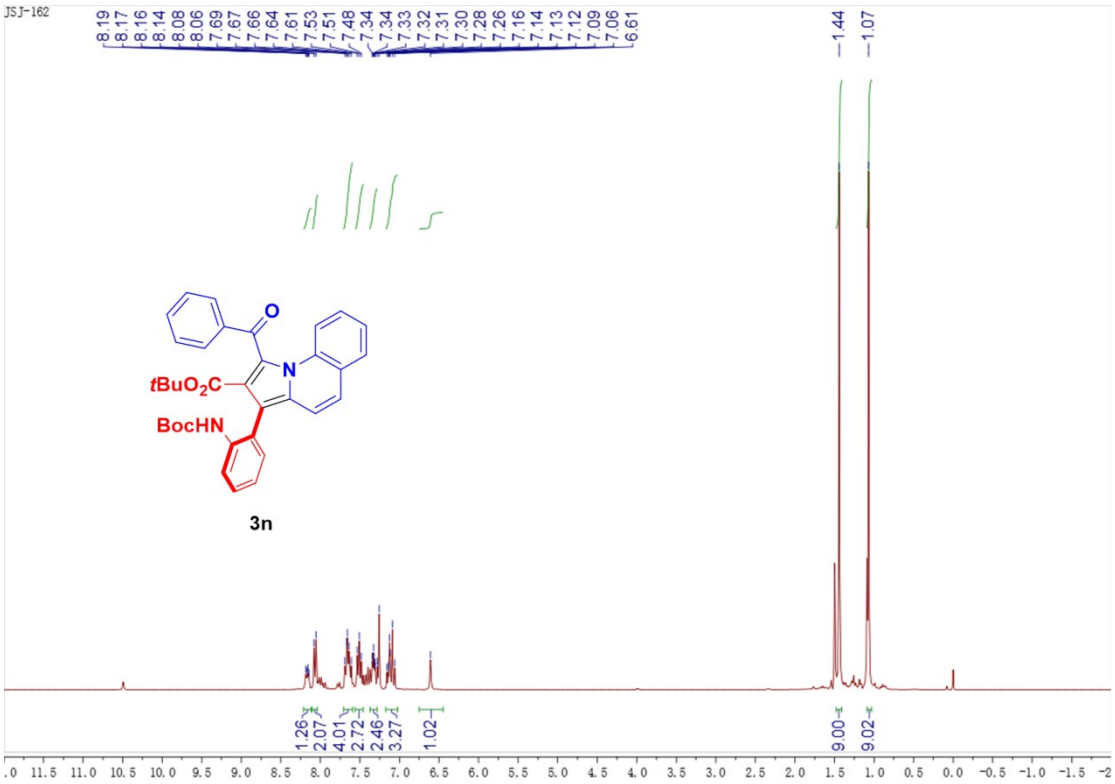
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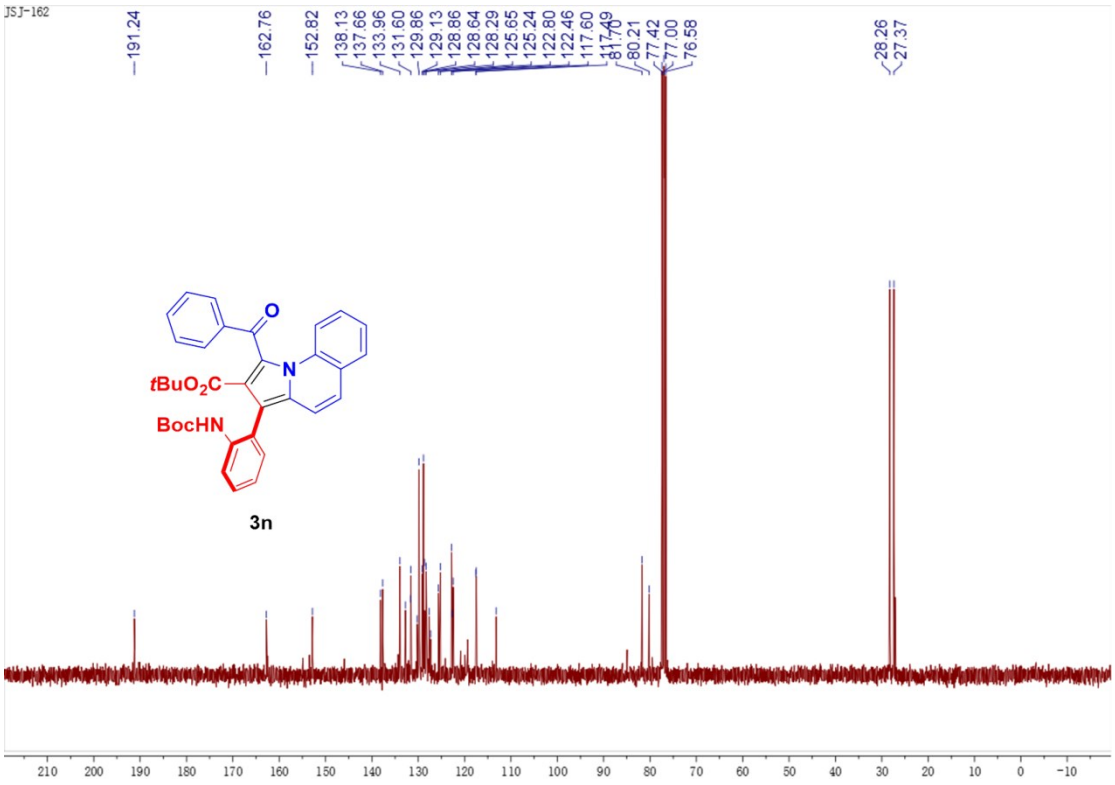
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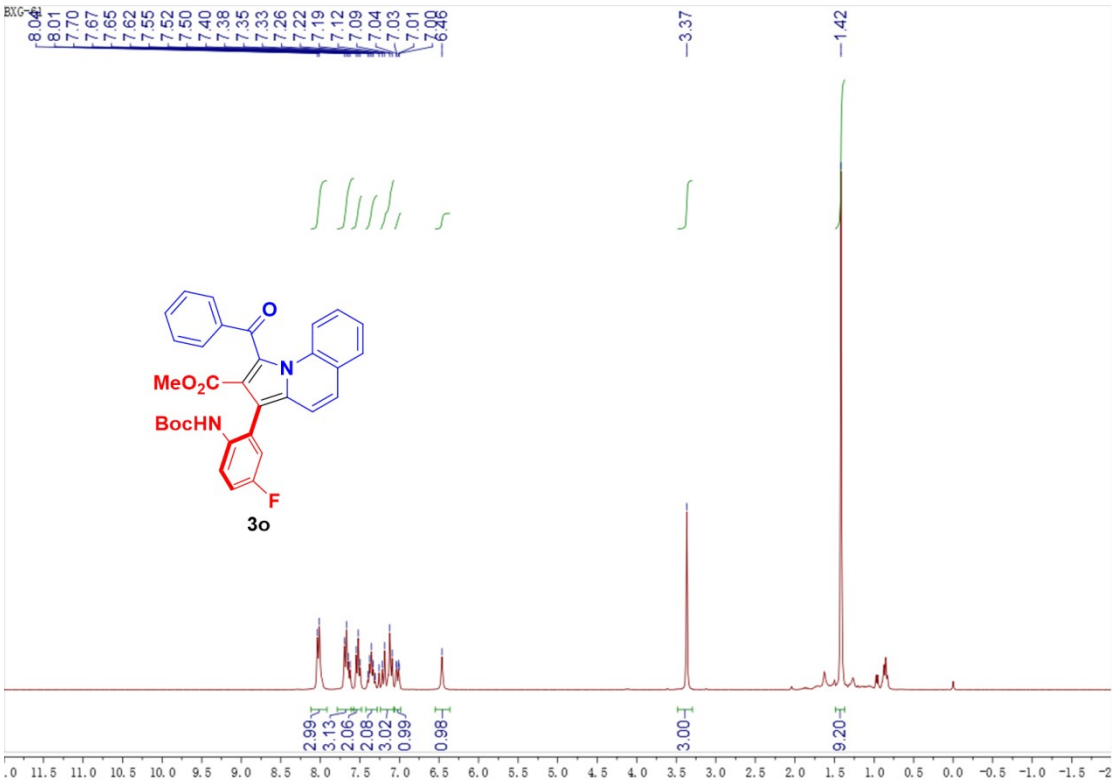
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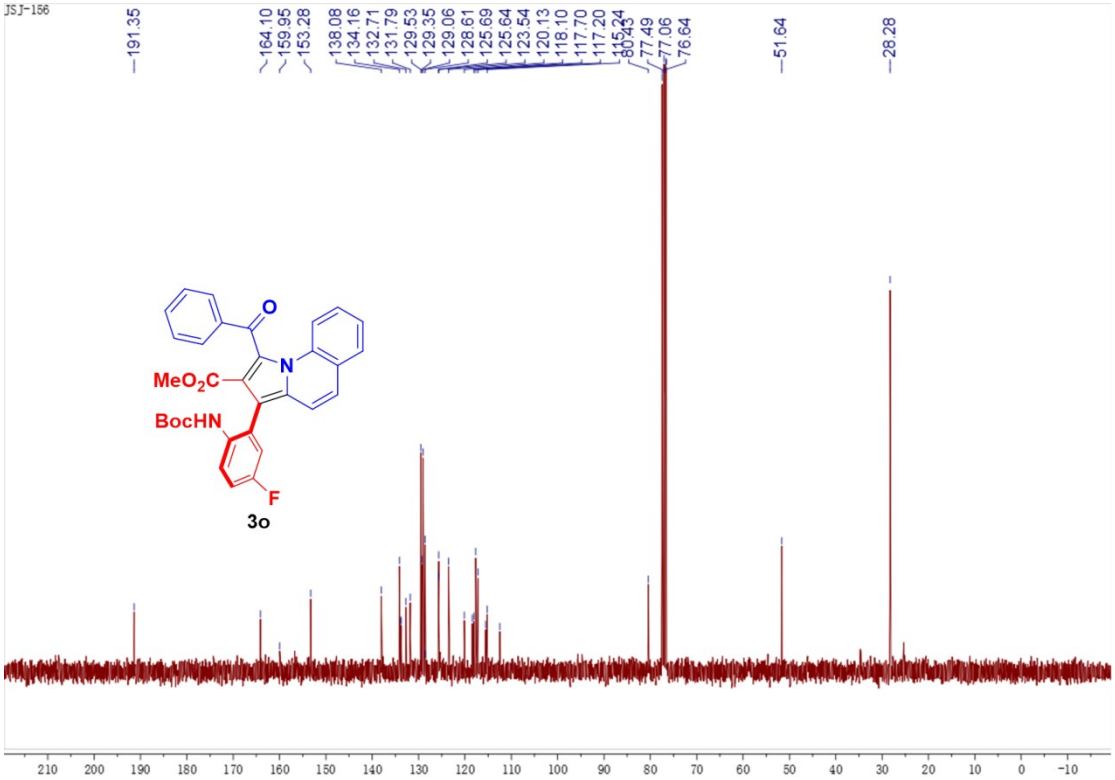
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BocHN
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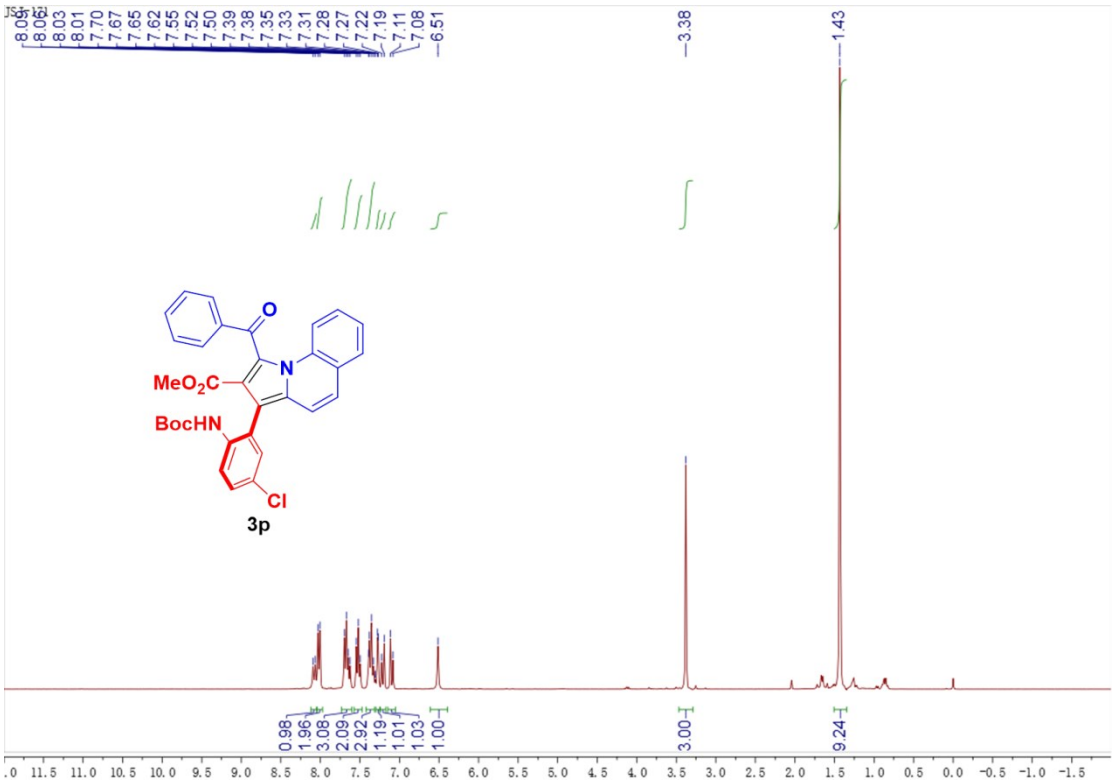
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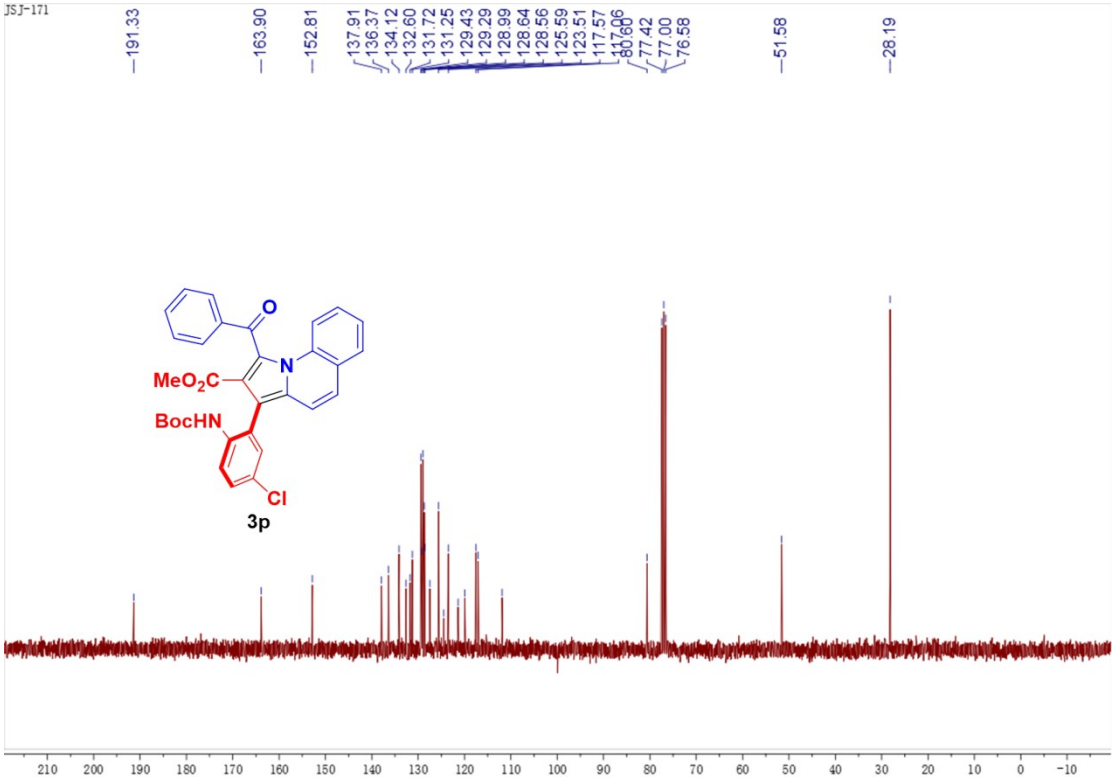
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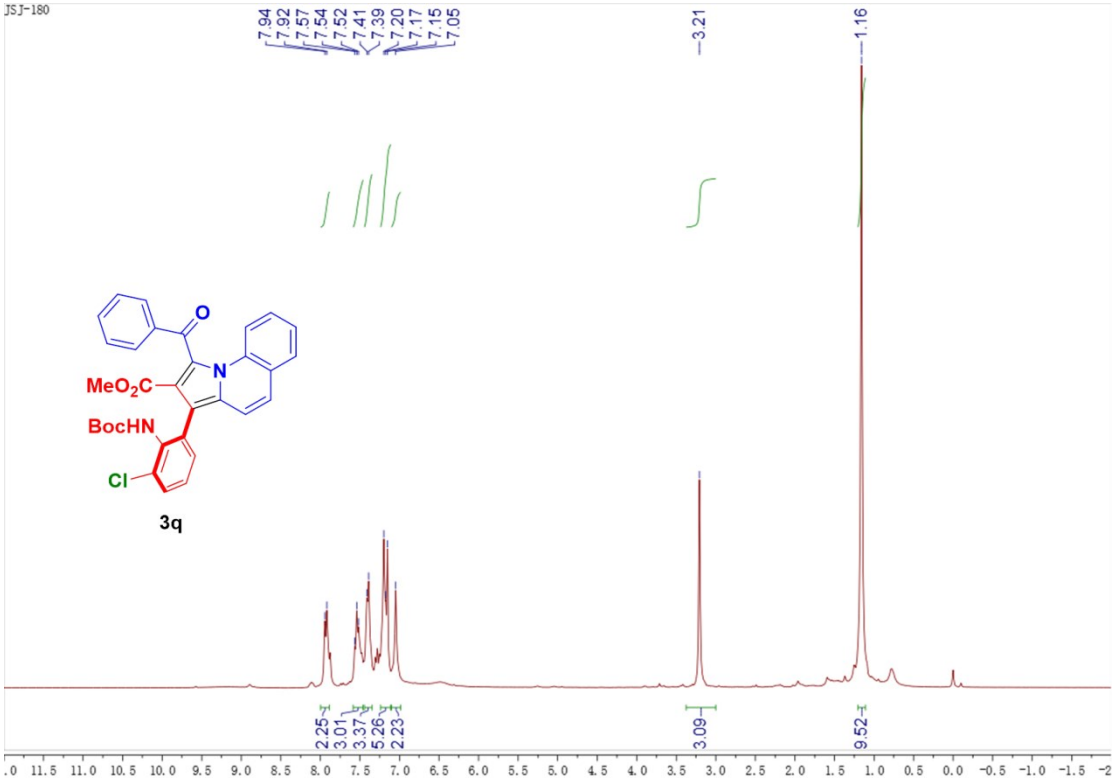
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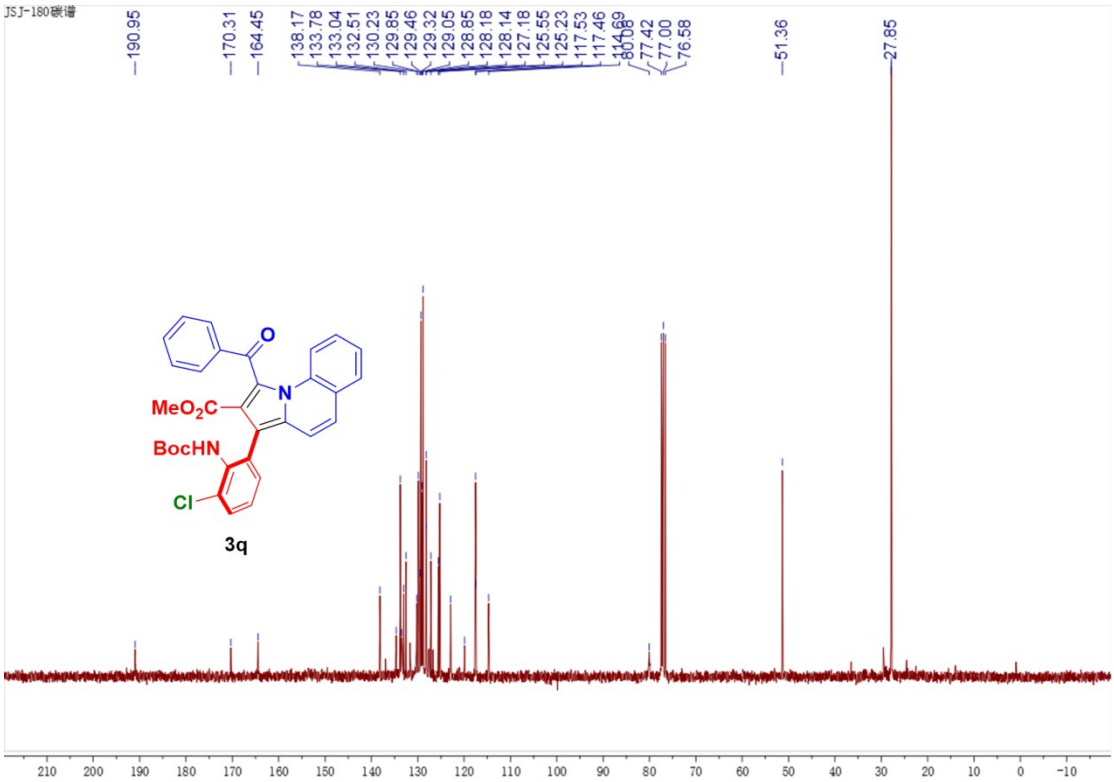
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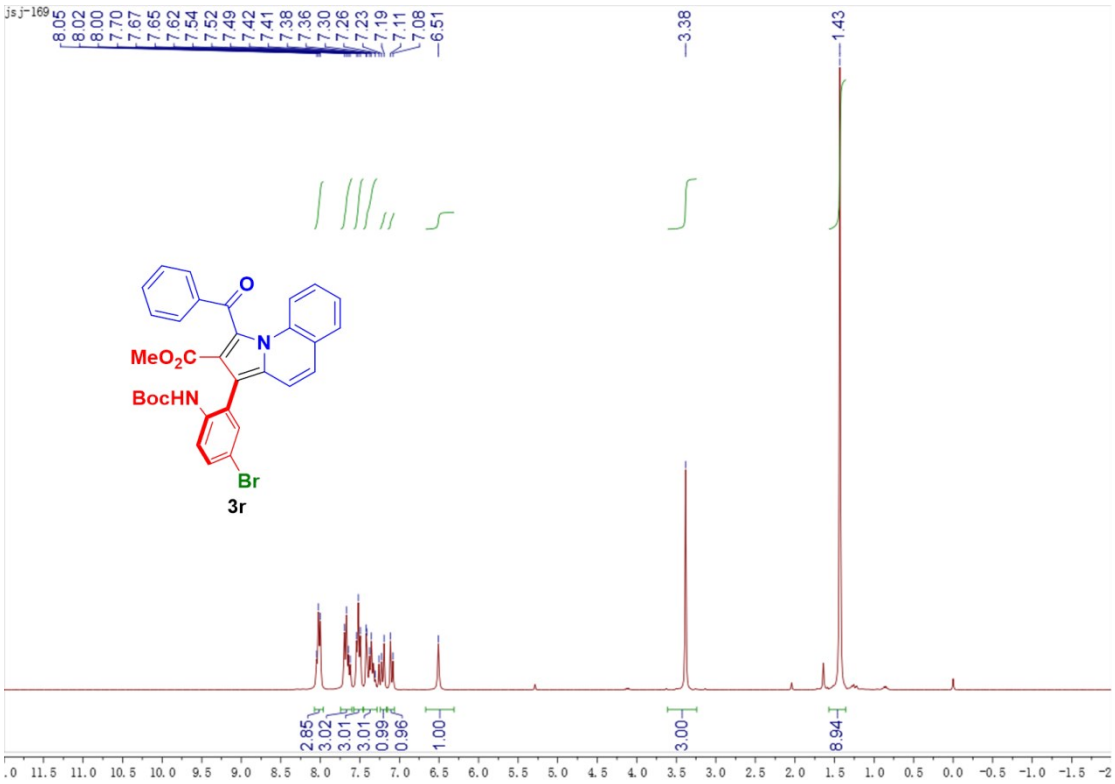
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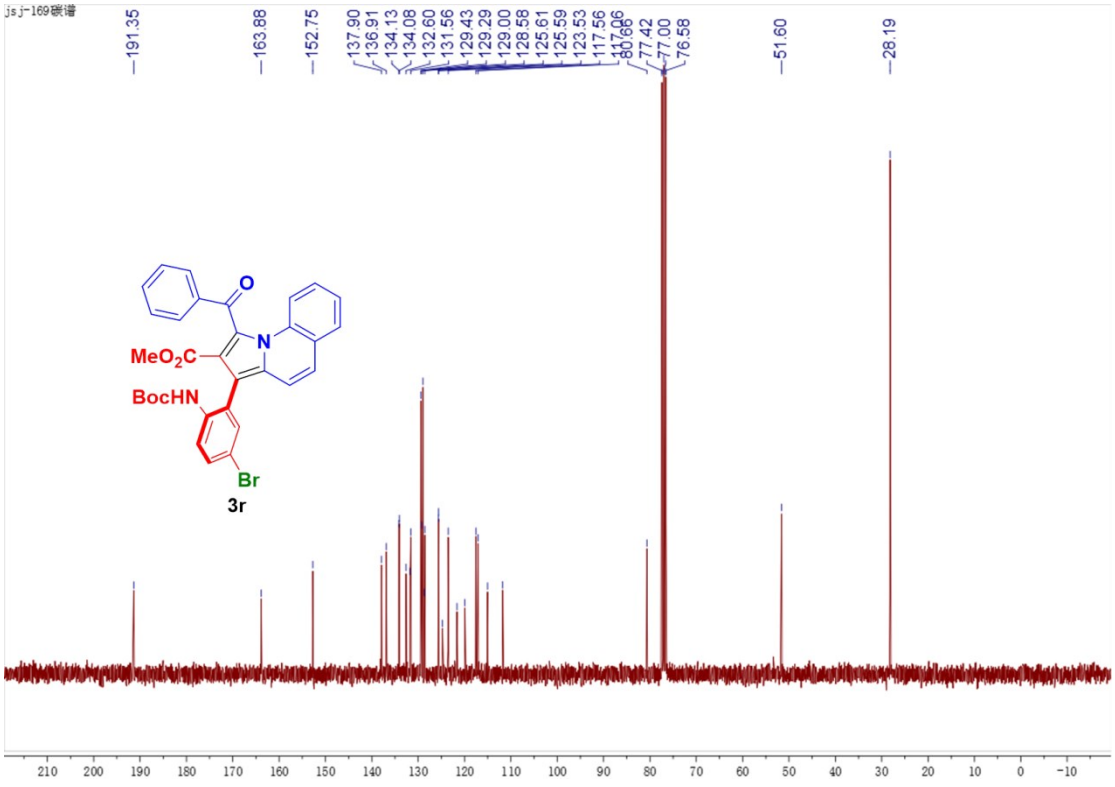
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Br
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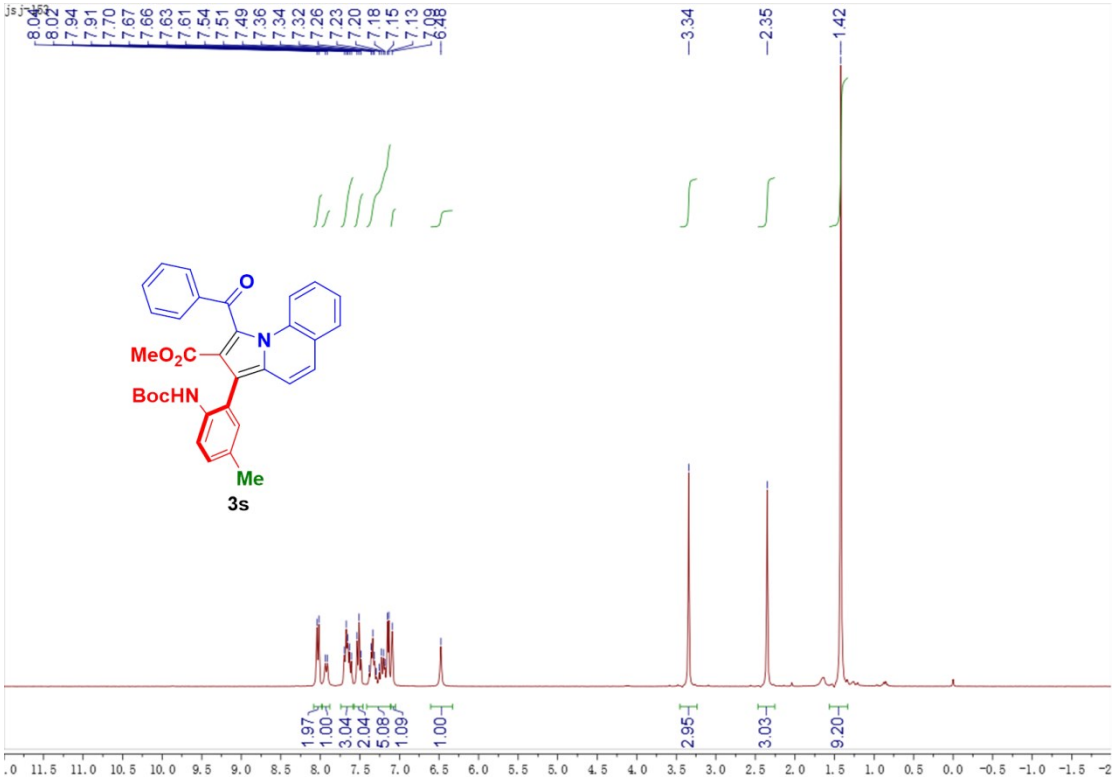
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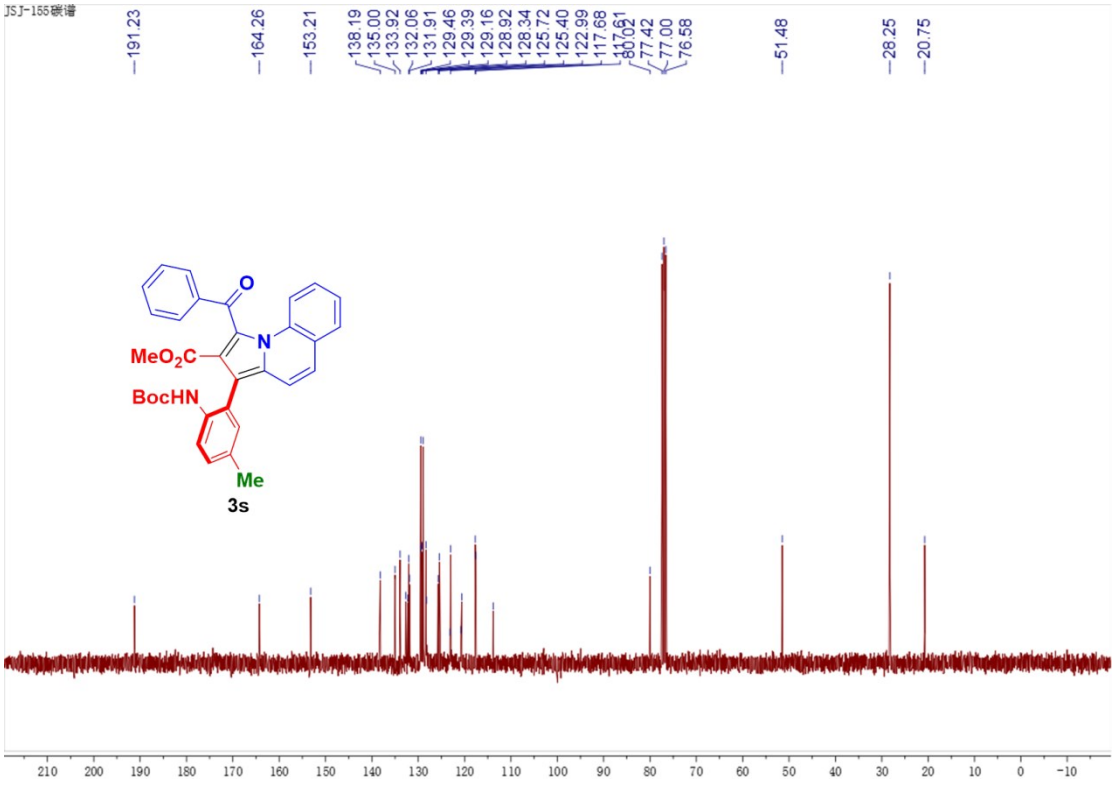
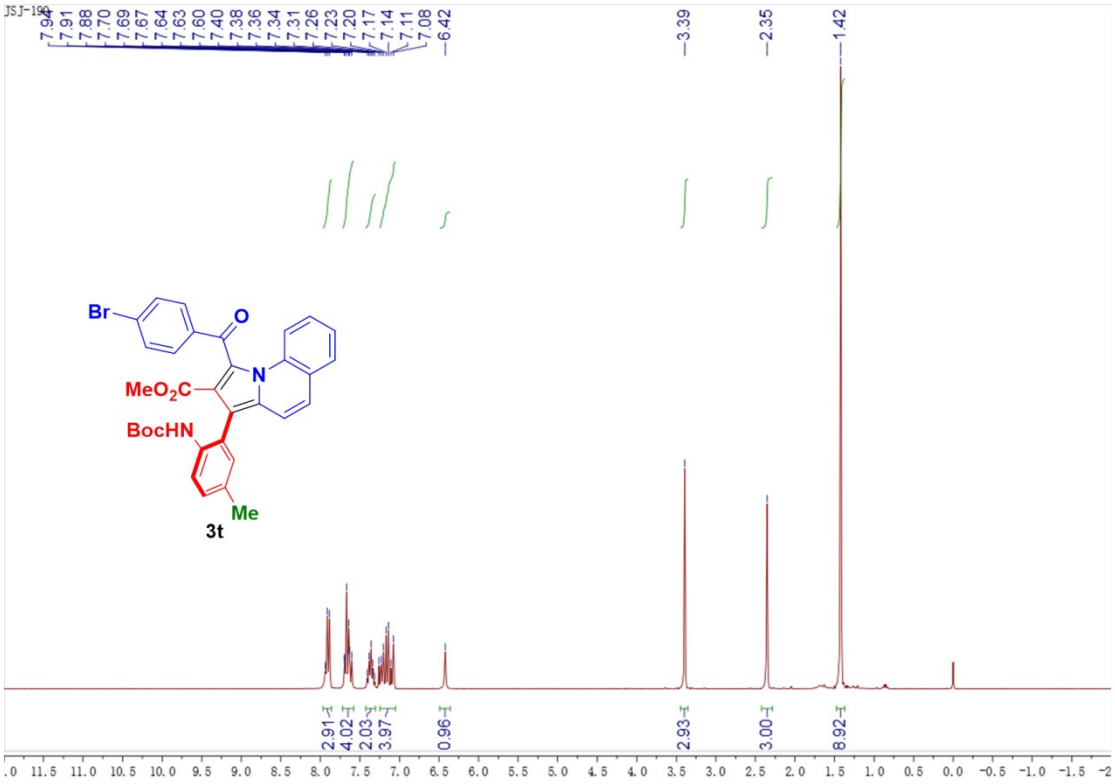
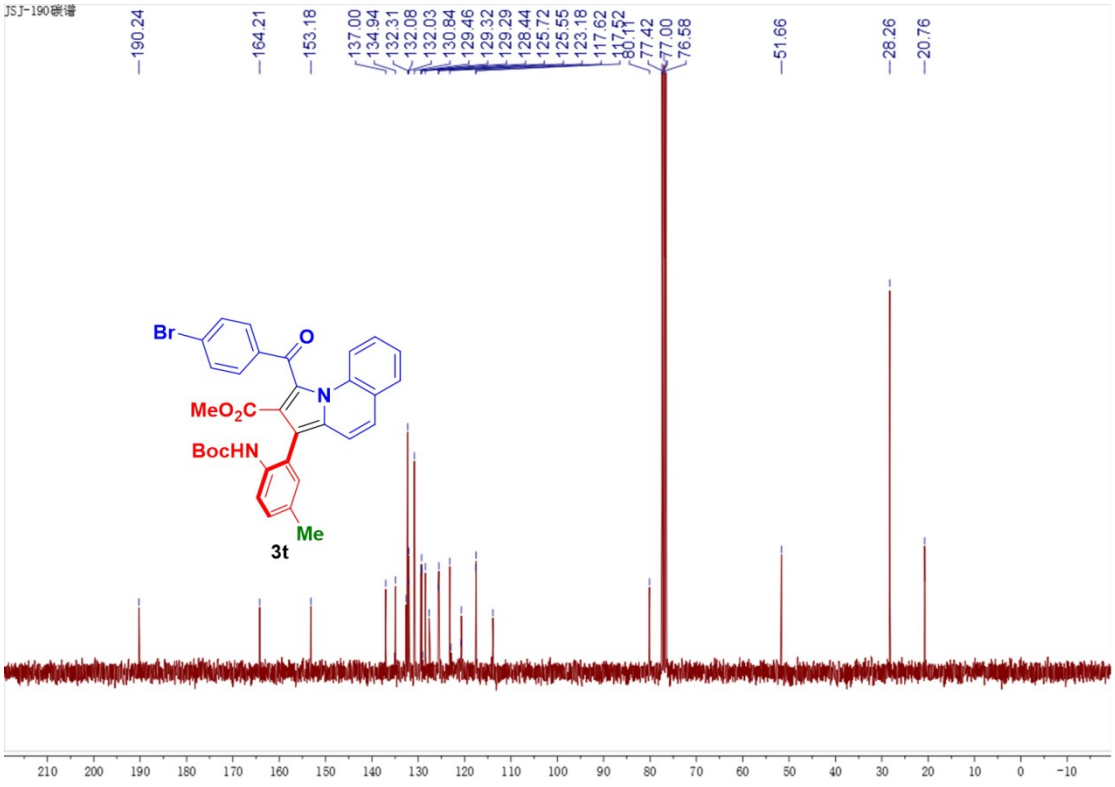
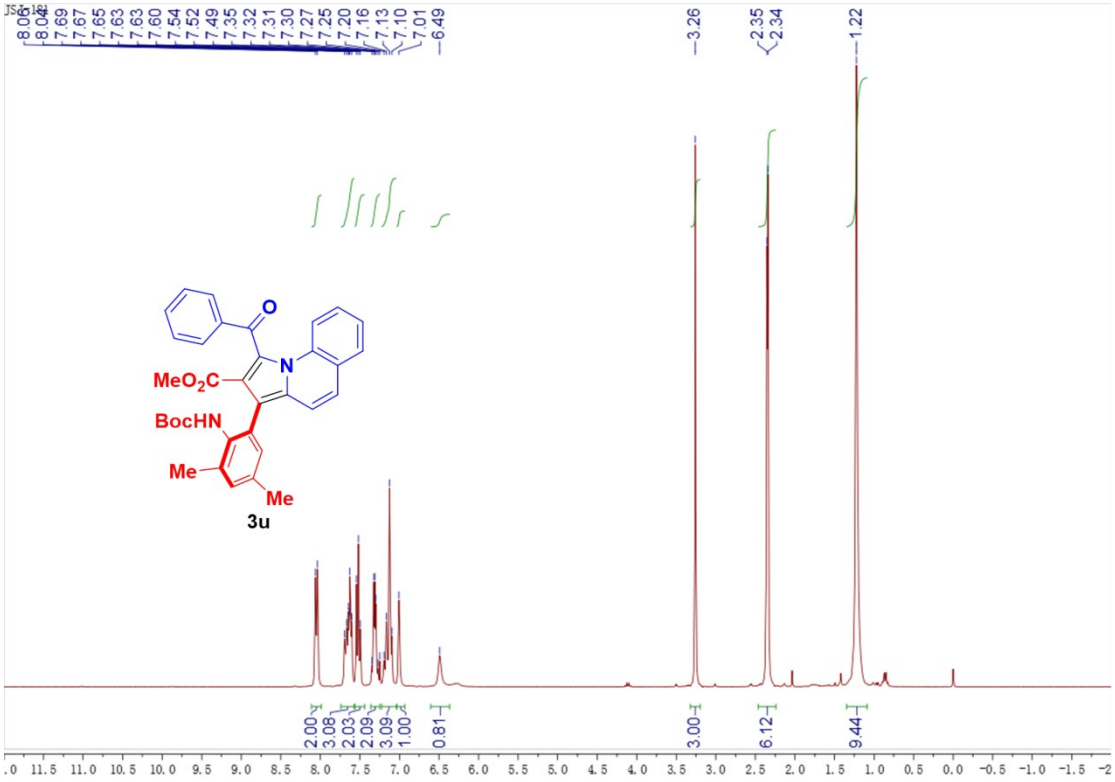
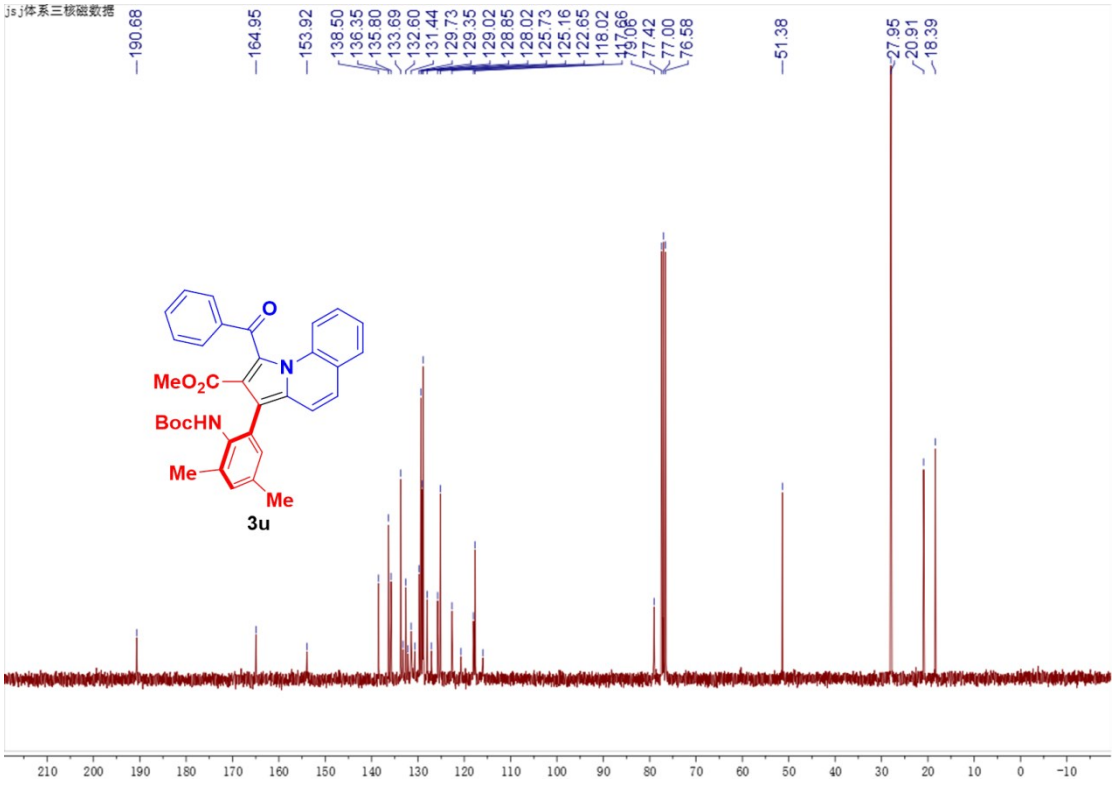
1.09
1.00
2.95
3.03
9.20

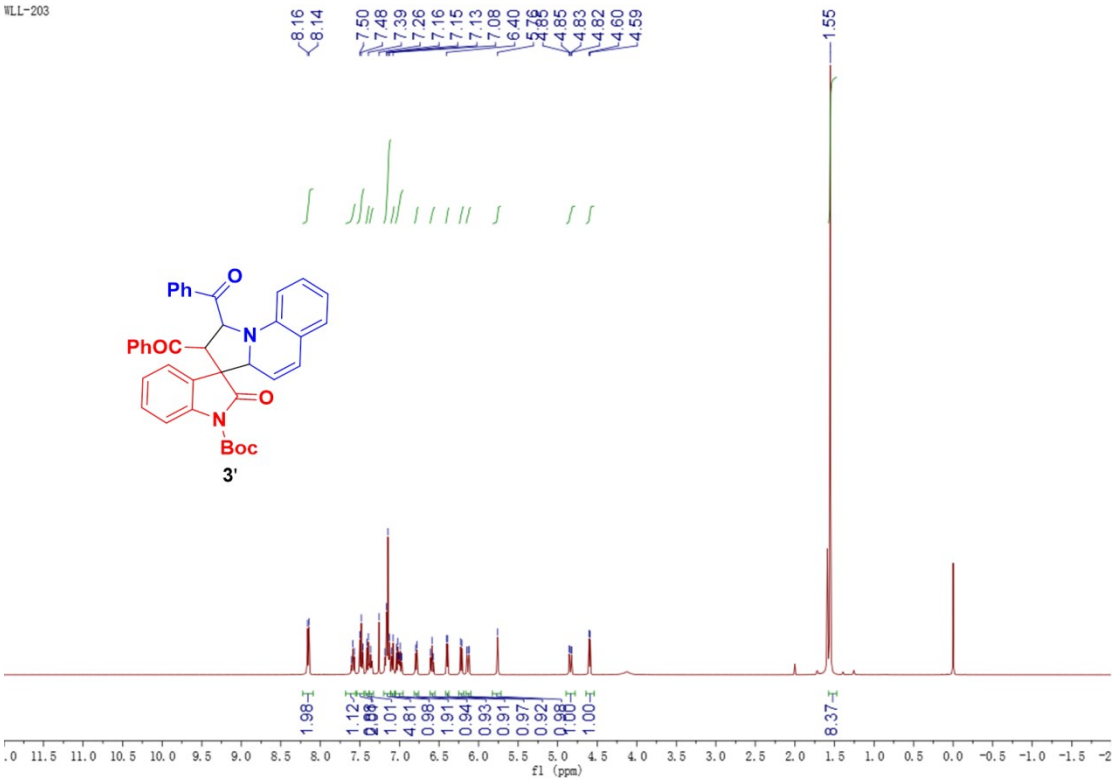

JSJ-155碳谱
191.23
164.26
153.21
138.19
135.00
133.92
132.06
131.91
129.46
129.39
129.16
128.92
128.34
125.72
125.40
122.99
117.68
80.02
77.42
77.00
76.58
51.48
28.25
20.75
O
N
MeO2C
BocHN
Me
3s

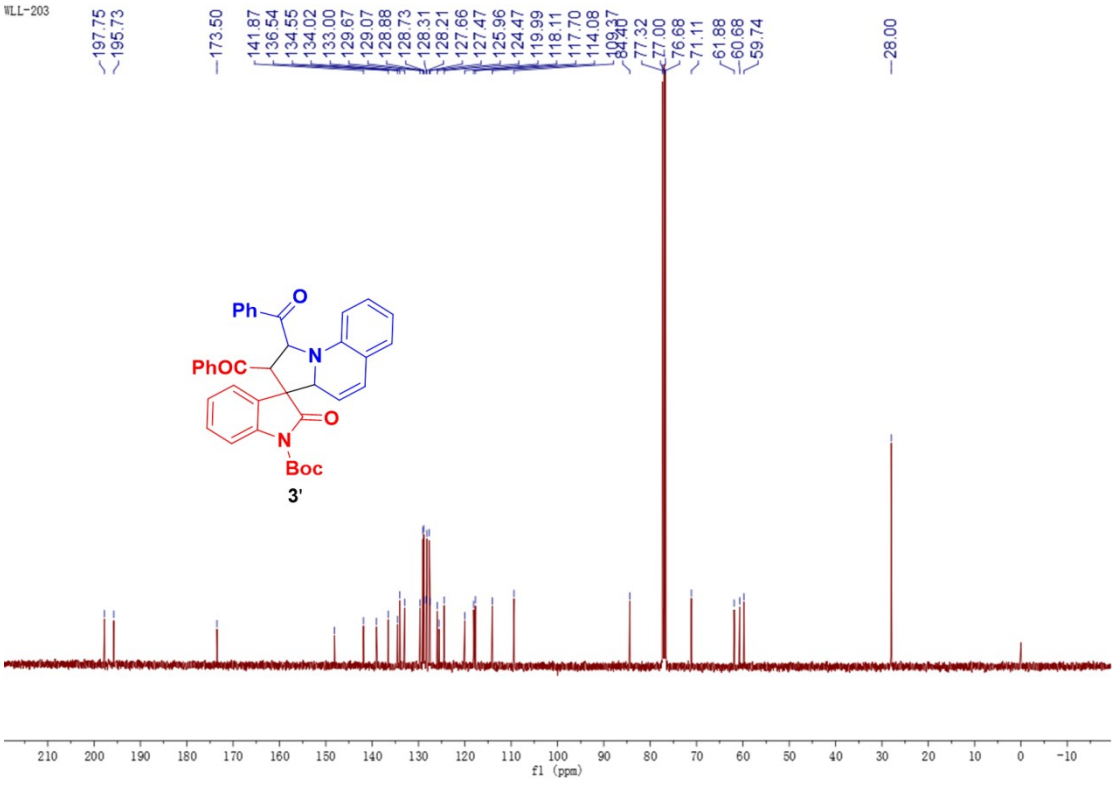

JSJ-190
7.94
7.91
7.88
7.70
7.69
7.67
7.64
7.63
7.60
7.40
7.38
7.36
7.34
7.31
7.26
7.23
7.20
7.17
7.14
7.11
7.08
6.42
3.39
2.35
1.42
Br
O
N
MeO2C
BocHN
Me
3t
2.91
4.02
2.03
3.97
0.96
2.93
3.00
8.92

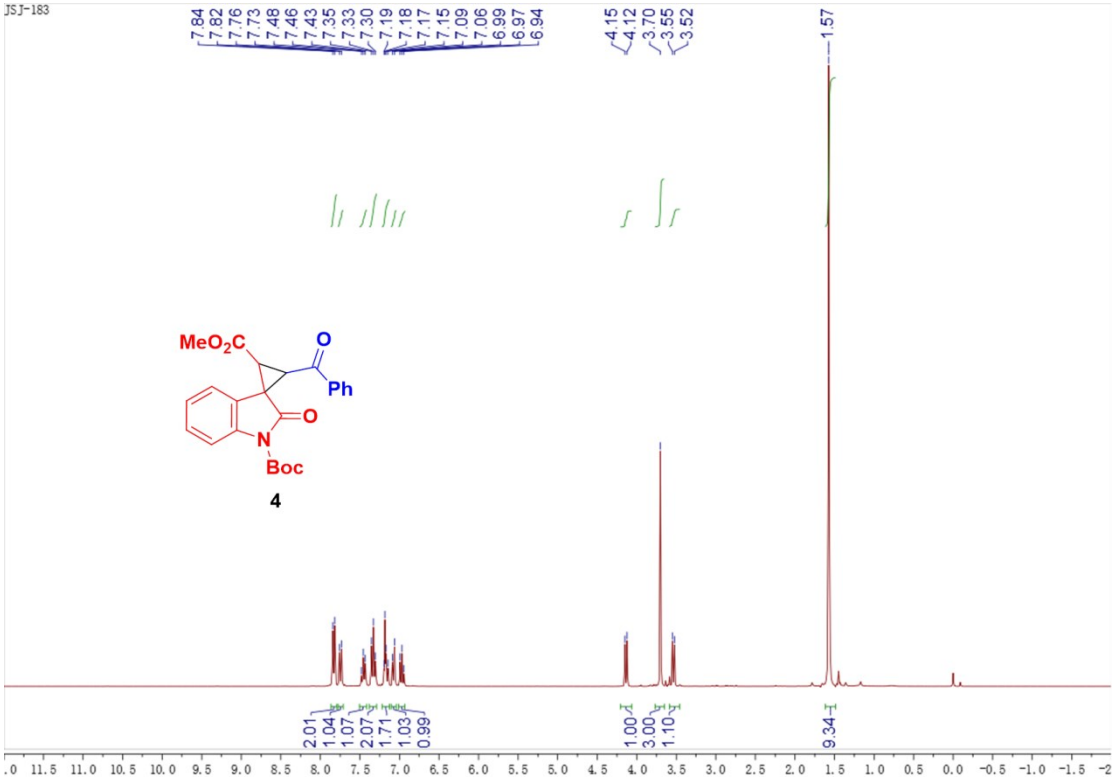

JSJ-190碳谱
190.24
164.21
153.18
137.00
134.94
132.31
132.08
132.03
130.84
129.46
129.32
129.29
128.44
125.72
125.55
123.18
117.62
117.52
80.11
77.42
77.00
76.58
51.66
28.26
20.76
Br
O
N
MeO2C
BocHN
Me
3t

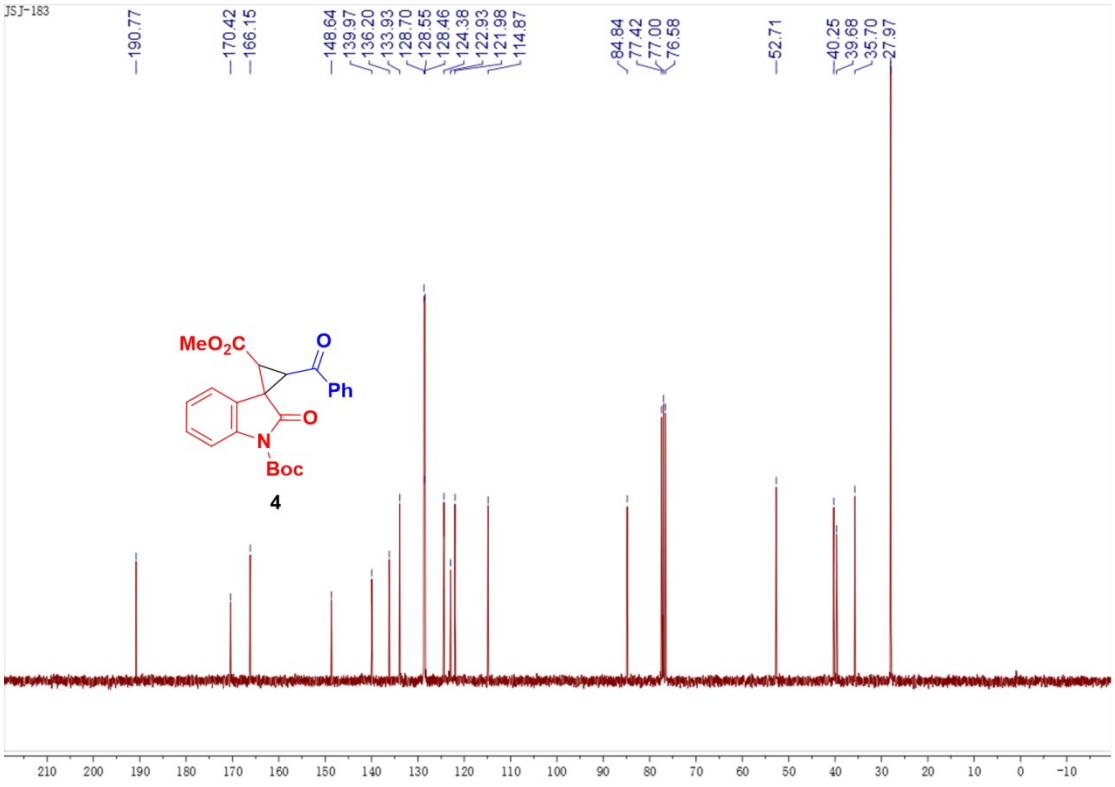

8.06
8.04
7.69
7.67
7.65
7.63
7.63
7.60
7.54
7.52
7.49
7.35
7.32
7.31
7.30
7.27
7.25
7.20
7.16
7.13
7.10
7.01
6.49
3.26
2.35
2.34
1.22
O
N
MeO2C
BocHN
Me
Me
3u
2.00
3.08
2.03
2.09
3.09
1.00
0.81
3.00
6.12
9.44

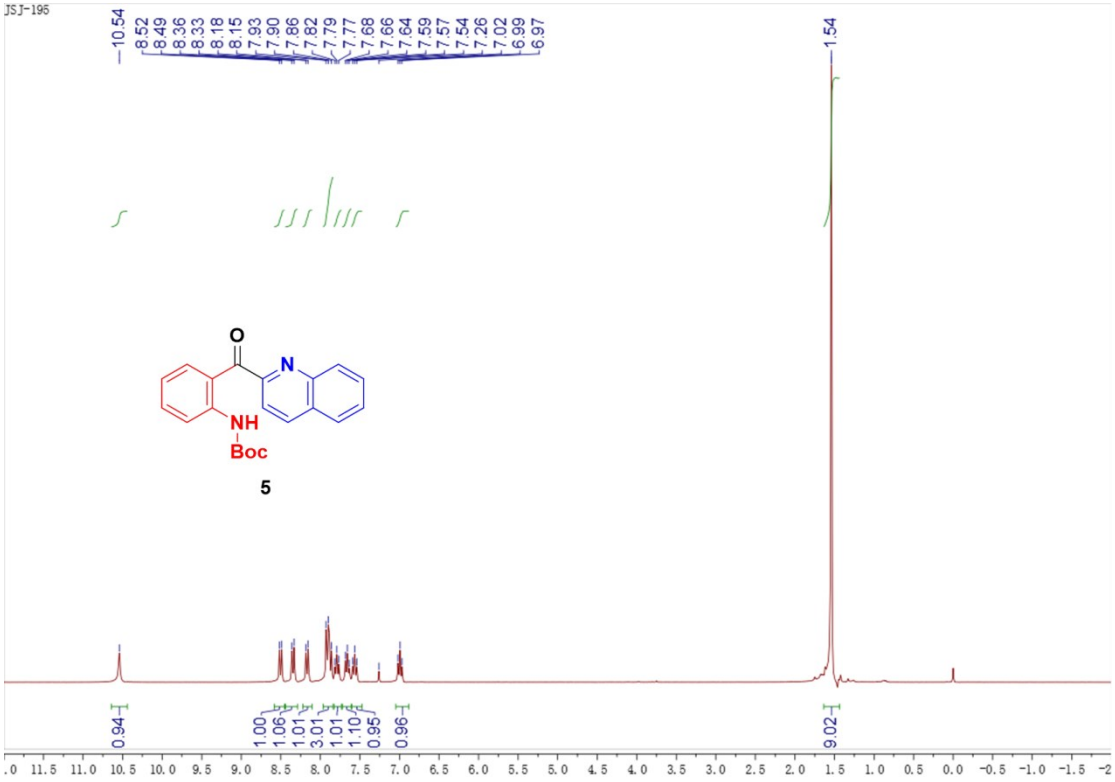

jsj体系三核磁数据
190.68
164.95
153.92
138.50
136.35
135.80
133.69
132.60
131.44
129.73
129.35
129.02
128.85
128.02
125.73
125.16
122.65
118.02
77.42
77.00
76.58
51.38
27.95
20.91
18.39
O
N
MeO2C
BocHN
Me
Me
3u

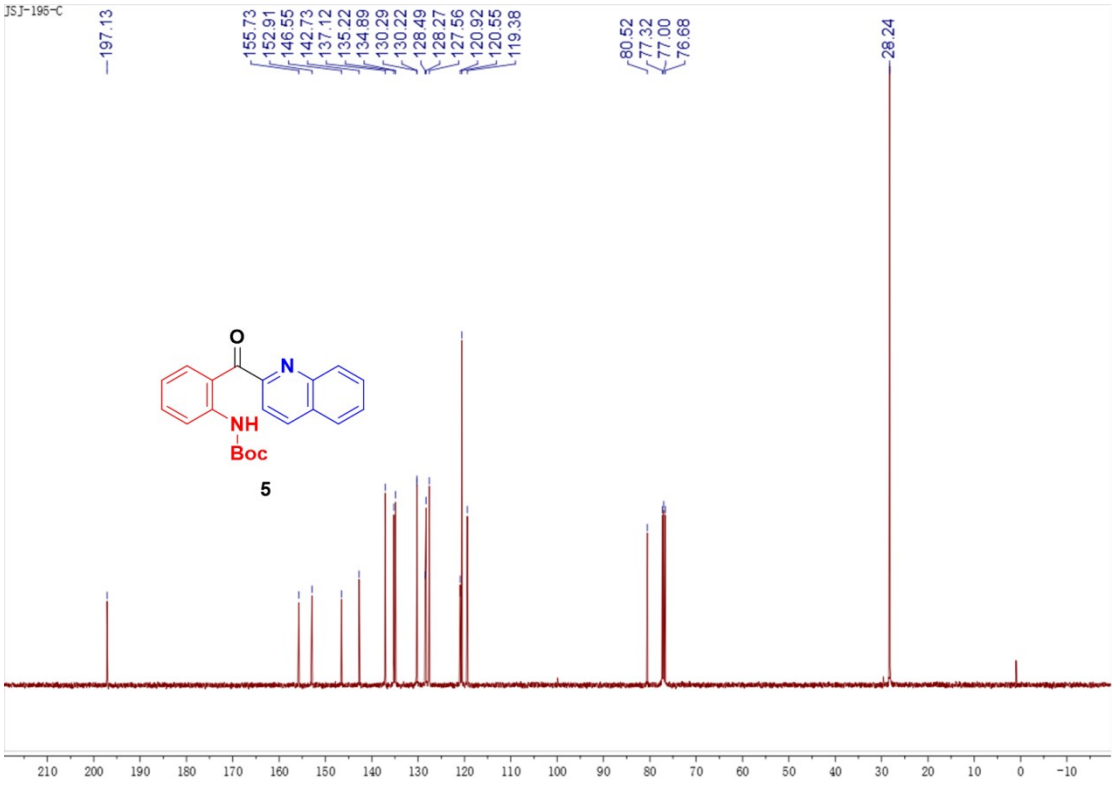

WLL-203
Ph
O
PhOC
N
O
N
Boc
3'
f1 (ppm)

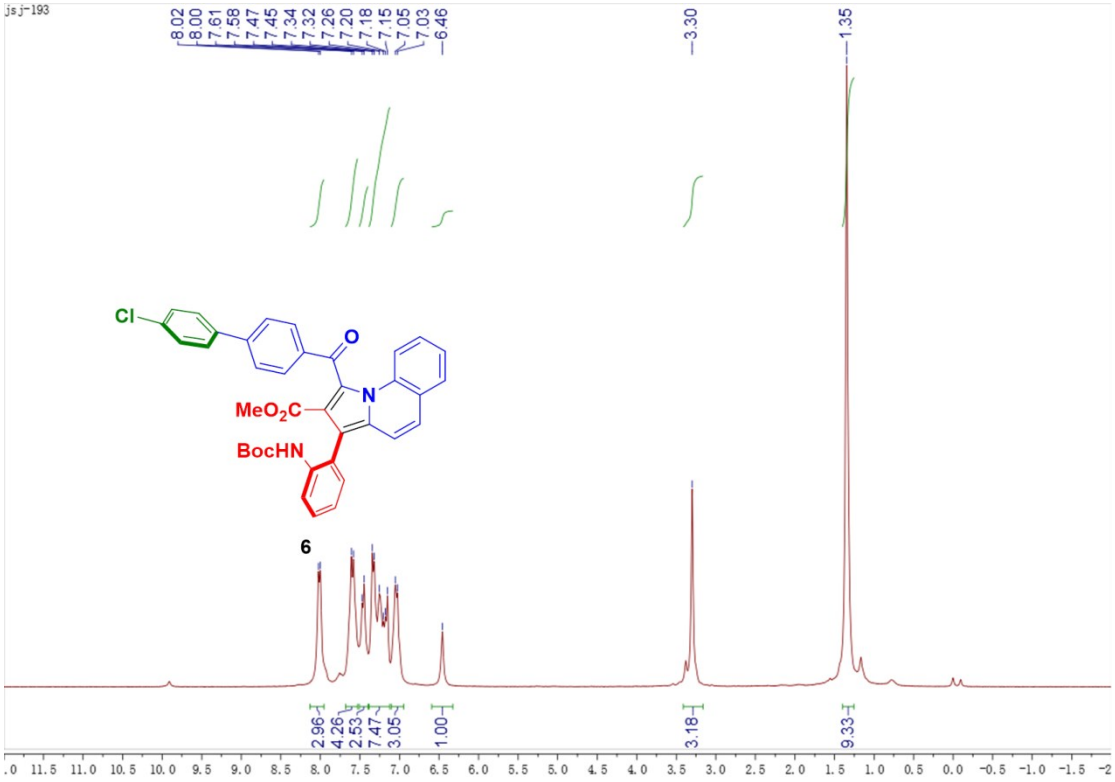

WLL-203
Ph
O
PhOC
N
O
N
Boc
3'
f1 (ppm)

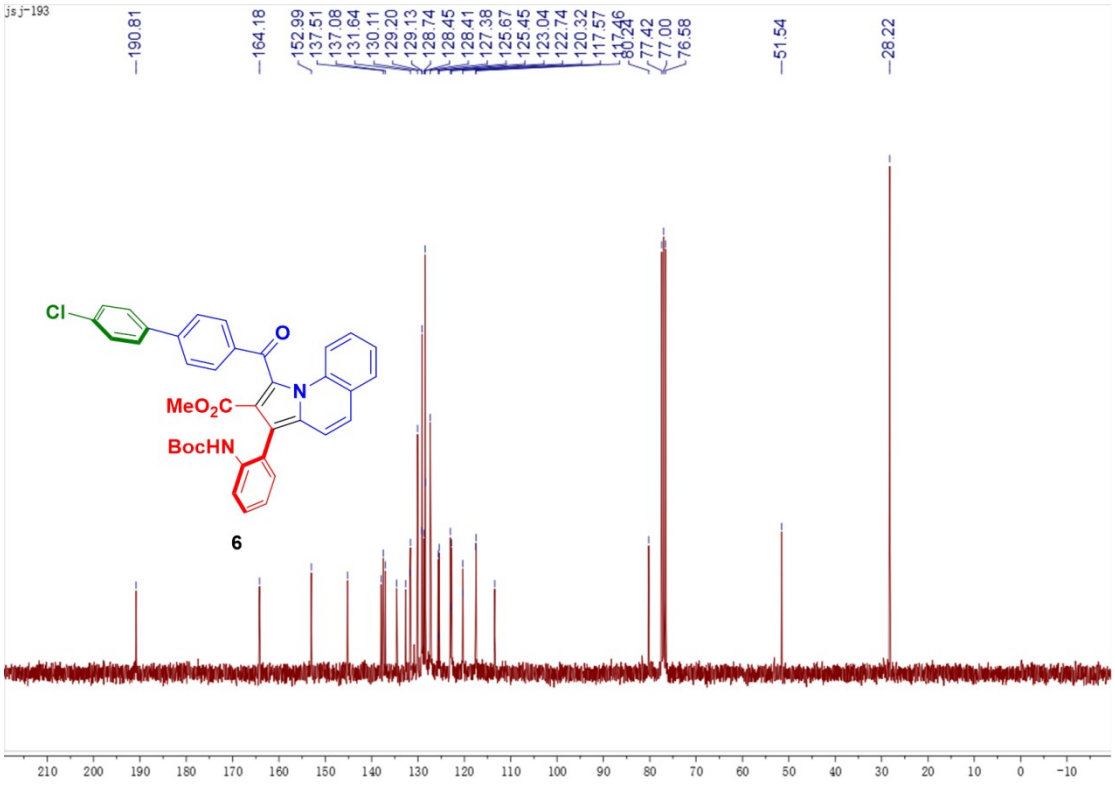

JSJ-183
7.84
7.82
7.76
7.73
7.48
7.46
7.43
7.35
7.33
7.30
7.19
7.18
7.17
7.15
7.09
7.06
6.99
6.97
6.94
4.15
4.12
3.70
3.55
3.52
1.57
MeO2C
O
Ph
O
N
Boc
4
2.01
1.04
1.07
2.07
1.71
1.03
0.99
1.00
3.00
1.10
9.34

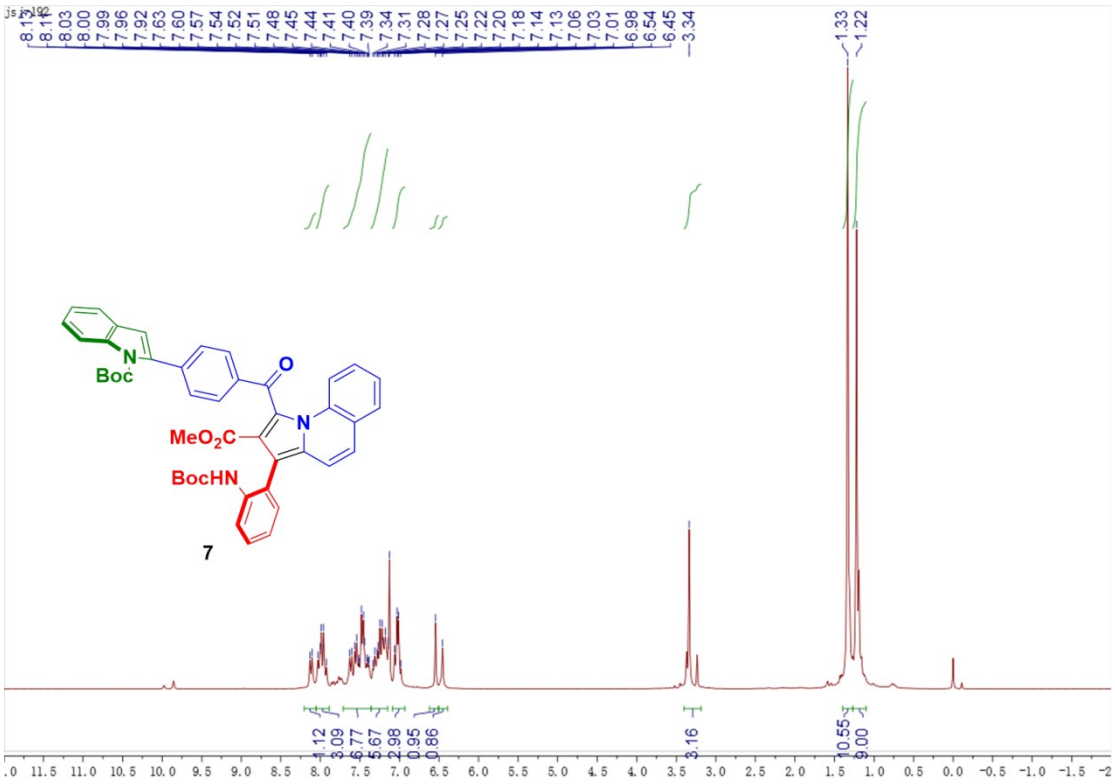

JSJ-183
190.77
170.42
166.15
148.64
139.97
136.20
133.93
128.70
128.55
128.46
124.38
122.93
121.98
114.87
84.84
77.42
77.00
76.58
52.71
40.25
39.68
35.70
27.97
MeO2C
O
Ph
O
N
Boc
4

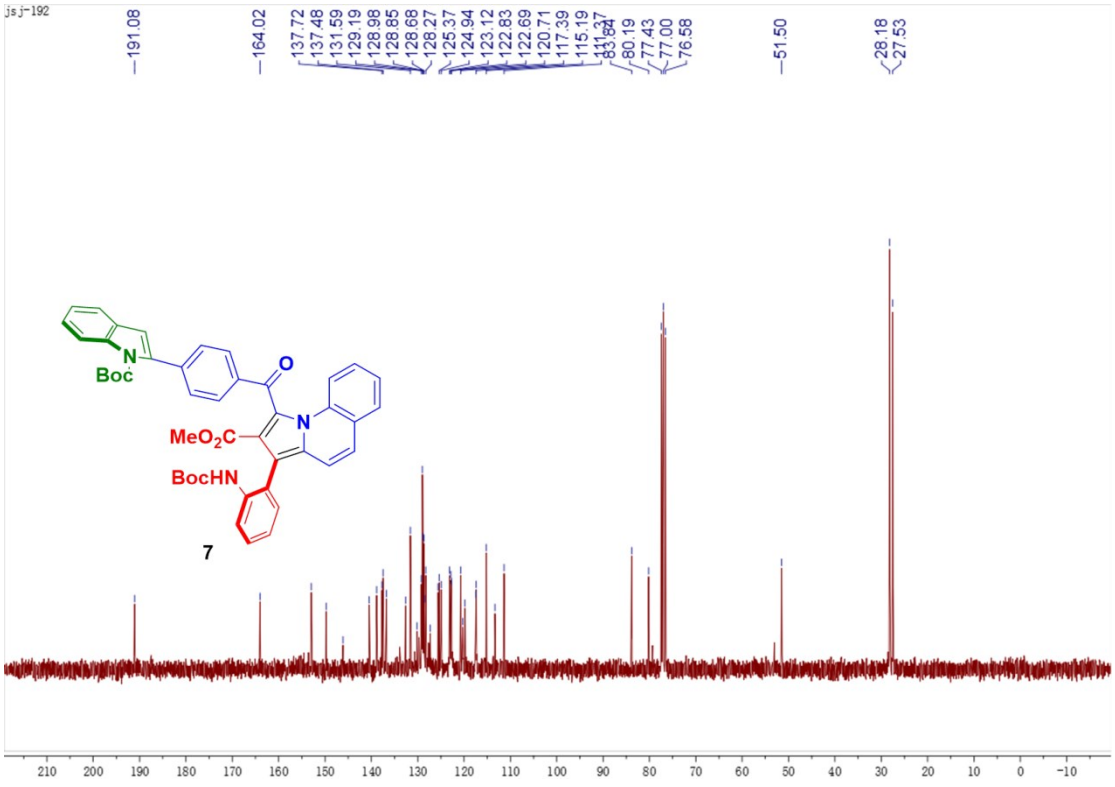

JSJ-196
10.54
8.52
8.49
8.36
8.33
8.18
8.15
7.93
7.90
7.86
7.82
7.79
7.77
7.68
7.66
7.64
7.59
7.57
7.54
7.26
7.02
6.99
6.97
1.54
O
N
NH
Boc
5
0.94
1.00
1.06
1.01
3.01
1.01
1.10
0.95
0.96
9.02


JSJ-196-C
197.13
155.73
152.91
146.55
142.73
137.12
135.22
134.89
130.29
130.22
128.49
128.27
127.56
120.92
120.55
119.38
80.52
77.32
77.00
76.68
28.24
O
N
NH
Boc
5


jsj-193
8.02
8.00
7.61
7.58
7.47
7.45
7.34
7.32
7.26
7.20
7.18
7.15
7.05
7.03
6.46
3.30
1.35
Cl
O
N
MeO2C
BocHN
6
2.96
4.26
2.53
7.47
3.05
1.00
3.18
9.33


jsj-193
190.81
164.18
152.99
137.51
137.08
131.64
130.11
129.20
129.13
128.74
128.45
128.41
127.38
125.67
125.45
123.04
122.74
120.32
117.57
77.42
77.00
76.58
51.54
28.22
Cl
O
N
MeO2C
BocHN
6


Boc
MeO2C
BocHN
O
N
7


Boc
MeO2C
BocHN
O
N
7