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Supporting Information available

TFA/TBHP-Promoted Oxidative Cyclisation for the Construction of Tetracyclic Quinazolinones and Rutaecarpine

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1. General

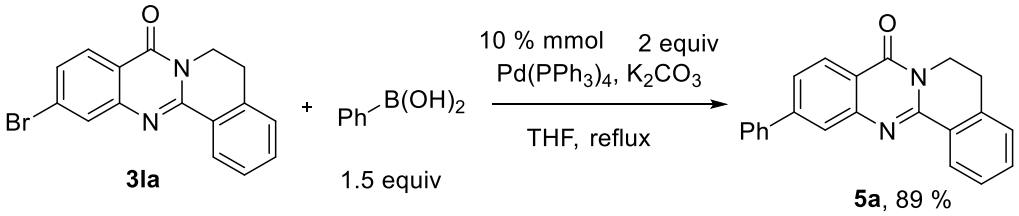
1. All isatins (**1a-1o**), 1,2,3,4-tetrahydroisoquinolines (**2a**-**2e**) and other reagents were obtained from commercial suppliers and used without further purification. Compound **7**[1] is obtained by removing hydrochloric acid from commercially purchased 6,7-dimethoxy-3,4-dihydroisoquinoline, hydrochloride (CAS: 20232-39-7) with sodium hydroxide solution. Compound **8**[2] was prepared from according to the reported methods. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200-300 mesh). ^{1}H NMR spectra were recorded on a Varian Mercury 400 or 600 MHz spectrometer Chemical shifts are reported in ppm, relative to the internal standard of tetramethylsilane (TMS). HRMS were obtained on an Apex-Ultra MS equipped with an electrospray source. Melting points were determined using XT-4 apparatus and not corrected.

2. Experimental procedures

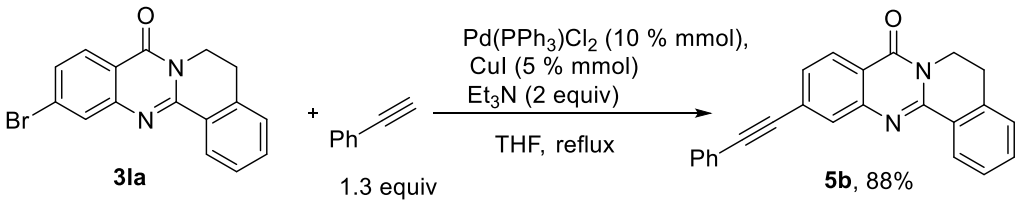
1. General procedure for preparation of 3 (3aa as an example)

General procedure: A sealed tube was charged with isatin **1a** (74 mg, 0.5 mmol) , 1,2,3,4-tetrahydroisoquinoline **2a** (67 mg, 0.5 mmol), TBHP (tert-Butyl hydroperoxide, 70% solution in water, 192 mg, 1.5 mmol) and TFA (17 mg, 0.15 mmol) at room temperature, and then dried solvent Tol(4 mL) was added. The resulting mixture was stirred at 120 °C in a sealed vessel under air, after disappearance of the reactant (monitored by TLC), then added 50mL water to the mixture, extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 30% NaCl solution (V/V), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Petroleum ether / ethyl acetate = 10:1) to yield the desired product **3aa** as a white solid (75% yield).

2.Further Functionalization of product **5la**

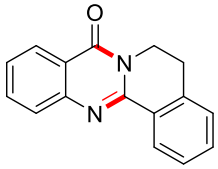


An oven dried Schlenk tube of 10 mL equipped with a magnetic stir bar was charged with **3la** (0.3 mmol), phenylboronic acid (1.5 equiv, 0.45 mmol) $Pd(PPh_3)_4$ (10 mol%) and K_2CO_3 (2 equiv, 0.6 mmol). and THF (3 mL) was added under nitrogen atmosphere, and the mixture was refluxed for 12 h. After cooling down to room temperature, the precipitate was removed by filtration and washed with EtOAc, and the filtrate was washed with brine, dried over Na_2SO_4 and then concentrated under vacuum. The residue was purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20/1) to afford a white solid **5a** in 89 % yield (86 mg).



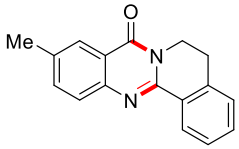
An oven dried Schlenk tube of 10 mL equipped with a magnetic stir bar was charged with **3la** (0.3 mmol), $Pd(PPh_3)_2Cl_2$ (10 mol %) and CuI (5 mol %). After charging nitrogen for three times, phenylacetylene (0.39 mmol, 1.3 eq.), Et_3N (0.6 mmol, 2 equiv.) and THF (3 mL) was added under nitrogen atmosphere, and the mixture was refluxed for 12 h. After cooling down to room temperature, the precipitate was removed by filtration and washed with EtOAc, and the filtrate was washed with brine, dried over anhydrous Na_2SO_4 and then concentrated under vacuum. The residue was purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20/1) to afford a white solid **5b** in 88% yield (92 mg).

3. Spectral data of compound 3aa-3ad，Rutaecarpine



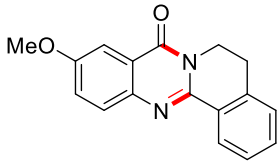
5,6-dihydro-8H-isoquinolino[1,2-b]quinazolin-8-one （3aa）[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.50 (d, *J* = 7.6 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 7.84–7.69 (m, 2H), 7.53–7.39 (m, 3H), 7.28 (d, *J* = 7.2 Hz, 1H), 4.41 (t, *J* = 6.4 Hz, 2H), 3.10 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.6, 149.2, 147.7, 136.9, 134.1, 131.6, 129.4, 127.9, 127.49, 127.47, 127.4, 126.7, 126.4, 120.6, 39.5, 27.3.



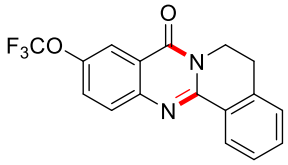
10-methyl-5,6-dihydro-8H-isoquinolino[1,2-b]quinazolin-8-one （3ba）[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.49 (d, *J* = 7.2 Hz, 1H), 8.10 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.0, 1H), 7.50–7.39 (m, 2H), 7.28 (d, *J* = 7.6 Hz, 1H), 4.41 (t, *J* = 6.4 Hz, 2H), 3.10 (t, *J* = 6.4 Hz, 2H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* = 161.6, 148.5, 145.7, 136.8, 136.6, 135.7, 131.4, 129.5, 127.8, 127.5, 127.4, 127.3, 126.2, 120.3, 39.5, 27.4, 21.3.



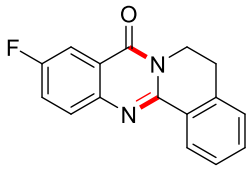
10-methoxy-5,6-dihydro-8H-isoquinolino[1,2-b]quinazolin-8-one （3ca）[3]

^{1}H NMR (600 MHz, $CDCl_3$) *δ* = 8.37 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.59 (s, 1H), 7.45–7.32 (m, 2H), 7.32–7.25 (m, 1H), 7.20 (d, *J* = 6.6 Hz, 1H), 4.36 (t, *J* = 6.6 Hz, 2H), 3.88 (s, 3H), 3.04 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ* = 161.1, 158.0, 147.0, 142.2, 136.4, 131.0, 129.4, 128.9, 127.4, 127.3, 127.2, 124.3, 121.2, 105.9, 55.6, 39.5, 27.2.



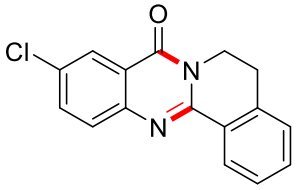
10-(trifluoromethoxy)-5,6-dihydro-8H-isoquinolino[1,2-b]quinazolin-8-one (3da)
white solid. m.p.:194-195 ºC.^{1}H NMR (400 MHz, $CDCl_3$) *δ* = 8.45 (d, *J* = 7.6 Hz, 1H),

8.12 (s, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.58-7.54 (m, 1H), 7.50–7.40 (m, 2H), 7.28(d, J = 7.2 Hz, 1H), 4.40 (t, J = 6.8 Hz, 2H), 3.10 (t, J = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.9, 149.7, 147.0, 146.3, 137.0, 132.0, 129.6, 129.1, 128.0, 127.7, 127.5, 121.7, 121.5, 119.2, 118.1, 39.7, 27.3. HRMS (ESI) calcd for $C_{17}H_{12}F_3N_2O_2$ $(M+H)^+$ 333.0851, found 333.0852.



10-fluoro-5,6-dihydro-8H-isoquinolino[1,2-b]quinazolin-8-one （3ea）[2]

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.44 (*d*, J = 7.8 Hz, 1H), 7.94-7.90 (m, 1H), 7.78-7.74 (m, J = 9.0, 4.8 Hz, 1H), 7.49-7.40 (m, 3H), 7.28 (d, J = 7.8 Hz, 1H), 4.40 (t, J = 6.6 Hz, 2H), 3.10 (t, J = 6.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 161.5, 161.0, 159.9, 148.7, 144.4, 136.9, 131.8, 129.94, 129.88, 129.2, 127.9, 127.6, 127.5, 122.9, 122.8, 121.8, 111.7, 111.5, 39.7, 27.3.



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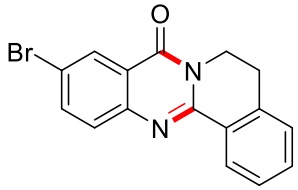
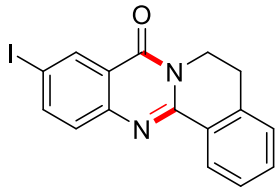
10-chloro-5,6-dihydro-8H-isoquinolino[1,2-b]quinazolin-8-one （3fa）[3]

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.44 (d, J = 7.8 Hz, 1H), 8.24 (s, 1H), 7.71-7.64 (m, 2H), 7.48 (t, J = 7.8 Hz, 1H), 7.43 (t, J = 7.2 Hz, 1H), 7.28 (d, J = 7.2 Hz, 1H), 4.39 (t, J = 6.6 Hz, 2H), 3.10 (t, J = 6.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 160.6, 149.6, 146.2, 137.0, 134.6, 132.1, 131.9, 129.2, 129.1, 128.0, 127.6, 127.5, 126.1, 121.6, 39.7, 27.3.



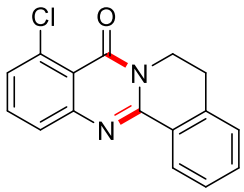
10-bromo-5,6-dihydro-8H-isoquinolino[1,2-b]quinazolin-8-one （3ga）[3]

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.44 (d, J = 7.8 Hz, 1H), 8.41 (s, 1H), 7.83–7.75 (m, 1H), 7.62 (d, J = 9.0 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.8 Hz, 1H), 7.28 (d, J = 7.2 Hz, 1H), 4.39 (t, J = 6.6 Hz, 2H), 3.10 (t, J = 6.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 160.5, 149.7, 146.5, 137.3, 137.0, 131.9, 129.3, 129.2, 128.0, 127.7, 127.5, 122.0, 119.9, 39.7, 27.3.



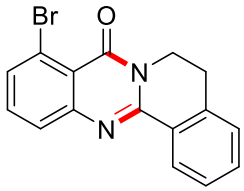
10-iodo-5,6-dihydro-8H-isoquinolino[1,2-b]quinazolin-8-one （3ha）

Brown solid. m.p.:188-189 ºC.^{1}H NMR (600 MHz, CDCl3) δ = 8.61 (s, 1H), 8.43 (d, *J* = 7.2 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 6.6 Hz, 1H), 4.38 (t, *J* = 6.6 Hz, 2H), 3.09 (t, *J* = 6.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ* = 160.2, 149.9, 146.9, 142.9, 137.0, 135.6, 132.0, 129.3, 129.1, 128.0, 127.6, 127.5, 122.2, 90.8, 39.7, 27.3. HRMS (ESI) calcd for $C_{16}H_{12}IN_2O$ $(M+H)^+$ 374.9989, found 374.9996.



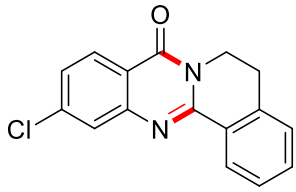
9-chloro-5,6-dihydro-8H-isoquinolino[1,2-*b*]quinazolin-8-one （3ia）[4]

^{1}H NMR (600 MHz, $CDCl_3$) *δ* = 8.41 (d, *J* = 7.2 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.49-7.36 (m, 3H), 7.24 (d, *J* = 6.6 Hz, 1H), 4.33 (d, *J* = 6.0 Hz, 2H), 3.07 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ* = 159.7, 150.0, 149.8, 137.1, 134.0, 133.5, 132.0, 129.1, 128.9, 127.9, 127.54, 127.47, 126.8, 117.8, 39.5, 27.3.



9-bromo-5,6-dihydro-8H-isoquinolino[1,2-*b*]quinazolin-8-one (3ja)

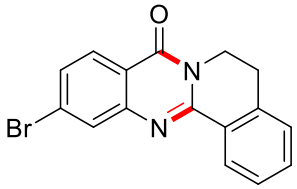
Brown solid. m.p.:223-225 ºC.^{1}H NMR (600 MHz, $CDCl_3$) *δ* = 8.44 (d, *J* = 7.2 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1 H), 7.68 (d, *J* = 7.8 Hz, 1 H), 7.52-7.45 (m, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 6.6 Hz, 1H), 4.36 (t, *J* = 6.6 Hz, 2H), 3.09 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ* = 159.8, 149.9, 149.7, 137.1, 133.8, 132.9, 132.0, 128.9, 127.9, 127.61, 127.57, 127.5, 121.4, 118.7, 39.7, 27.3. HRMS (ESI) m/z calcd for $C_{16}H_{12}BrN_2O$ $(M+H)^+$ 327.0127, found 327.0132.



11-chloro-5,6-dihydro-8H-isoquinolino[1,2-b]quinazolin-8-one (3ka)[4]

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.45 (d, *J* = 7.2 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.75

(s, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 7.2 Hz, 1H), 4.39 (t, *J* = 6.0 Hz, 2H), 3.10 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.0, 150.5, 148.5, 140.4, 137.1, 132.1, 129.0, 128.3, 128.2, 127.7, 127.5, 127.1, 126.9, 119.1, 39.6, 27.3.



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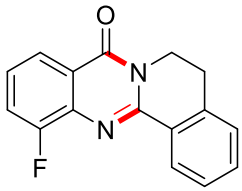
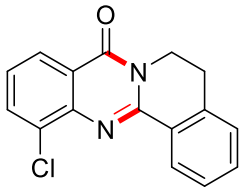
11-bromo-5,6-dihydro-8H-isoquinolino[1,2-*b*]quinazolin-8-one (3la)[4]

^{1}H NMR (600 MHz, $CDCl_3$) *δ* = 8.42 (d, *J* = 7.8 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.92 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 6.6 Hz, 1H), 4.37 (t, *J* = 6.6 Hz, 2H), 3.09 (t, *J* = 6.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 161.1, 150.4, 148.7, 137.0, 132.0, 130.1, 129.7, 129.1, 128.8, 128.3, 128.1, 127.6, 127.5, 119.4, 39.5, 27.2.



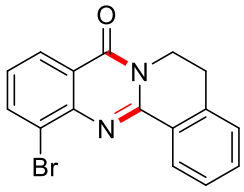
12-fluoro-5,6-dihydro-8H-isoquinolino[1,2-b]quinazolin-8-one (3ma)[3]

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.50 (d, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.51–7.33 (m, 4H), 7.25 (d, *J* = 7.2 Hz, 1H), 4.40 (t, *J* = 6.6 Hz, 2H), 3.10 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.8, 160.7, 158.4, 155.9, 149.8, 137.4, 137.3, 136.9, 132.0, 129.2, 128.3, 127.7, 127.4, 126.33, 126.25, 122.5, 122.30, 122.26, 119.5, 119.3, 39.7, 27.2.



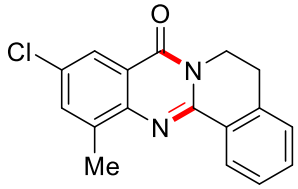
12-chloro-5,6-dihydro-8H-isoquinolino[1,2-b]quinazolin-8-one (3na)[4]

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.56 (d, *J* = 7.2 Hz, 1H), 8.19 (d, *J* = 7.2 Hz, 1H), 7.80 (d, *J* = 7.2 Hz, 1H), 7.51–7.40 (m, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 6.6 Hz, 1H), 4.40 (t, *J* = 6.6 Hz, 2H), 3.10 (t, *J* = 6.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 161.1, 149.8, 144.4, 136.9, 134.4, 132.02, 131.99, 129.2, 128.4, 127.7, 127.4, 126.3, 125.6, 122.1, 39.7, 27.2.



12-bromo-5,6-dihydro-8H-isoquinolino[1,2-*b*]quinazolin-8-one (3oa)

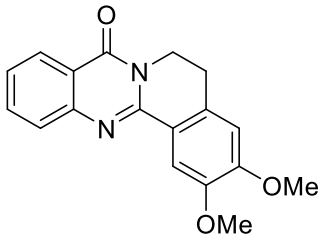
Brown solid. m.p.:233-235 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.58 (d, J = 6.6 Hz, 1H), 8.24 (d, J = 7.2 Hz, 1H), 8.01 (d, J = 7.2 Hz, 1H), 7.45 (t, J = 7.2 Hz, 2H), 7.33–7.22 (m, 2H), 4.40 (t, J = 6.6 Hz, 2H), 3.10 (t, J = 6.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 161.2, 149.9, 145.4, 137.8, 136.9, 132.1, 129.2, 128.5, 127.8, 127.4, 126.8, 126.4, 122.8, 122.1, 39.7, 27.2. HRMS (ESI) m/z calcd for$C_{16}H_{12}BrN_2O$ $(M+H)^+$ 327.0127, found 327.0136.



10-chloro-12-methyl-5,6-dihydro-8H-isoquinolino[1,2-*b*]quinazolin-8-one

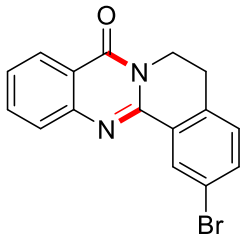
（3pa）

Brown solid. m.p.:195-197 ºC.^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.47 (d, J = 7.2 Hz, 1H), 8.07 (s, 1H), 7.51 (s, 1H), 7.46 (t, J = 6.6 Hz, 1H), 7.42 (t, J = 7.2 Hz, 1H), 7.26 (d, J = 6.6 Hz, 1H), 4.37 (t, J = 6.0 Hz, 2H), 3.08 (t, J = 6.0 Hz, 2H), 2.65 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 161.0, 148.2, 144.8, 138.3, 136.8, 134.7, 131.7, 131.5, 129.5, 128.0, 127.53, 127.47, 123.7, 121.5, 39.6, 27.2, 17.1. HRMS (ESI) calcd for $C_{17}H_{14}ClN_2O$ $(M+H)^+$ 297.0789, found 297.0796.



2,3-dimethoxy-5,6-dihydro-8H-isoquinolino[1,2-b]quinazolin-8-one（3ab）[3]

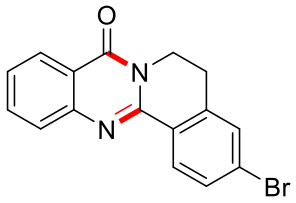
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.27 (d, J = 8.0 Hz, 1H), 7.95 (s, 1H), 7.79–7.67 (m, 2H), 7.41 (t J = 7.2 Hz, 1H), 6.70 (s, 1H), 4.39 (t, J = 6.4 Hz, 2H), 4.03 (s, 3H), 3.95 (s, 3H), 3.02 (t, J = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.7, 152.1, 149.2, 148.4, 147.7, 134.0, 130.8, 127.1, 126.8, 126.0, 121.6, 120.3, 109.8, 109.5, 56.1, 56.0, 39.6, 26.9.



2-bromo-5,6-dihydro-8H-isoquinolino[1,2-b]quinazolin-8-one (3ac)[5]

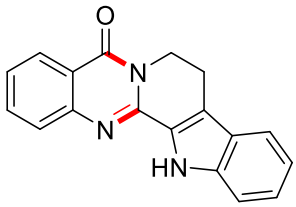
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.64 (s, 1H), 8.30 (d, J = 7.6 Hz, 1H), 7.86–7.73 (m, 2H), 7.59 (d, J = 7.2 Hz, 1H), 7.48 (t, J = 6.4 Hz, 1H), 7.18 (t, J = 8.0 Hz, 1H), 4.40 (t, J = 6.4 Hz, 2H), 3.06 (t, J = 6.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 161.4, 147.9,

147.4, 135.7, 134.4, 134.3, 131.3, 130.6, 129.1, 127.6, 126.84, 126.80, 121.3, 120.7, 39.3, 26.9.



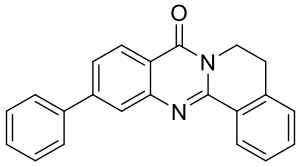
3-bromo-5,6-dihydro-8H-isoquinolino[1,2-b]quinazolin-8-one (3ad)[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.30 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 7.6 Hz, 1H), 7.74–7.64 (m, 2H), 7.49 (d, J = 8.0 Hz, 1H), 7.44–7.35 (m, 2H), 4.33 (t, J = 6.4 Hz, 2H), 3.01 (t, J = 6.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 161.4, 148.5, 147.5, 138.7, 134.3, 130.8, 130.4, 129.6, 128.4, 127.5, 126.8, 126.7, 126.3, 120.7, 39.3, 27.1.



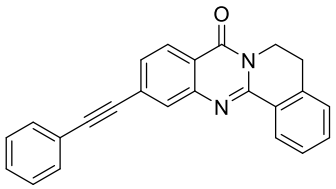
Rutecarpine （4aa）[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.67 (s, 1H), 8.32 (d, J = 8.0 Hz, 1H), 7.73-7.66 (m, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.48–7.36 (m, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 4.59 (t, J = 6.8 Hz, 2H), 3.24 (t, J = 7.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 161.5, 147.2, 145.2, 138.4, 134.4, 127.2, 126.9, 126.3, 126.2, 125.6, 125.5, 121.0, 120.5, 120.0, 118.6, 112.2, 41.1, 19.6.



11-phenyl-5,6-dihydro-8H-isoquinolino[1,2-b]quinazolin-8-one （5a）

white solid. m.p.:200-202 ºC.^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.47 (d, J = 8.8 Hz, 1H), 8.32 (d, J = 8.0 Hz, 1H), 7.94 (s, 1H), 7.72-7.61 (m, 3H), 7.48-7.37 (m, 5H), 7.24 (d, J = 7.6 Hz, 1H), 4.37 (t, J = 6.8 Hz, 2H), 3.06 (t, J = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.4, 149.6, 148.0, 146.8, 139.6, 136.9, 131.6, 129.4, 128.8, 128.2, 127.9, 127.5, 127.4, 127.3, 127.2, 125.5, 125.4, 119.3, 39.4, 27.3. HRMS (ESI) calcd for $C_{22}H_{17}N_2O$ $(M+H)^+$ 325.1321, found 325.1325.



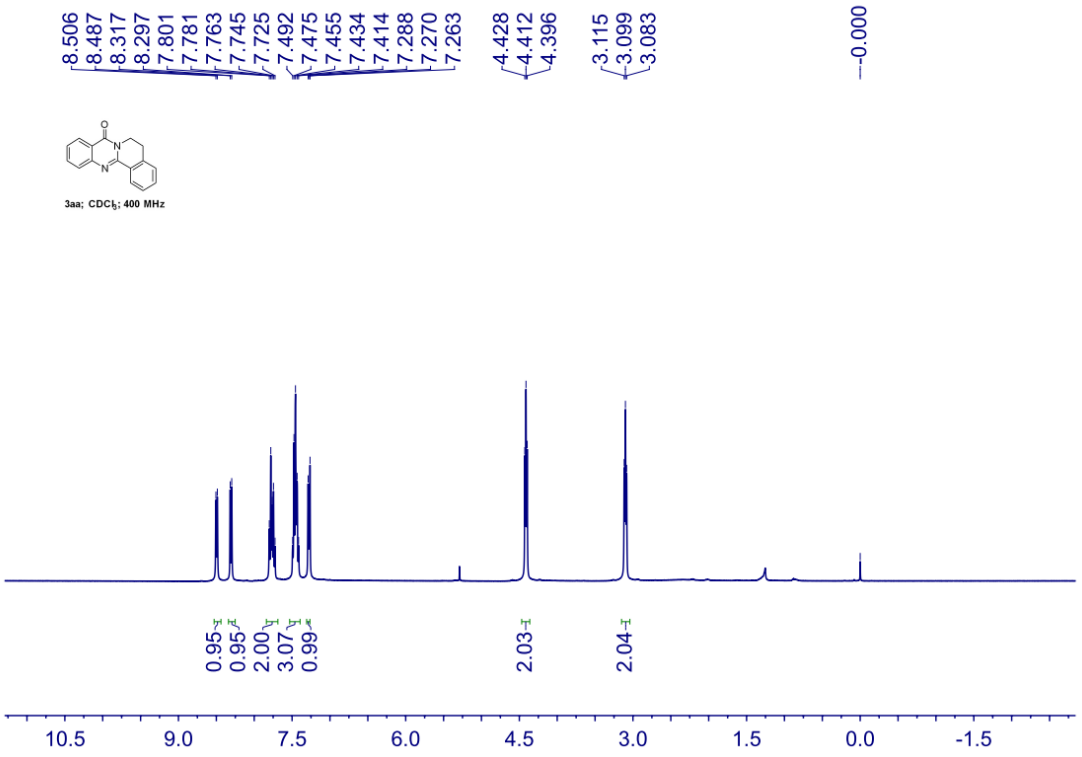
11-(phenylethynyl)-5,6-dihydro-8H-isoquinolino[1,2-b]quinazolin-8-one （5b）

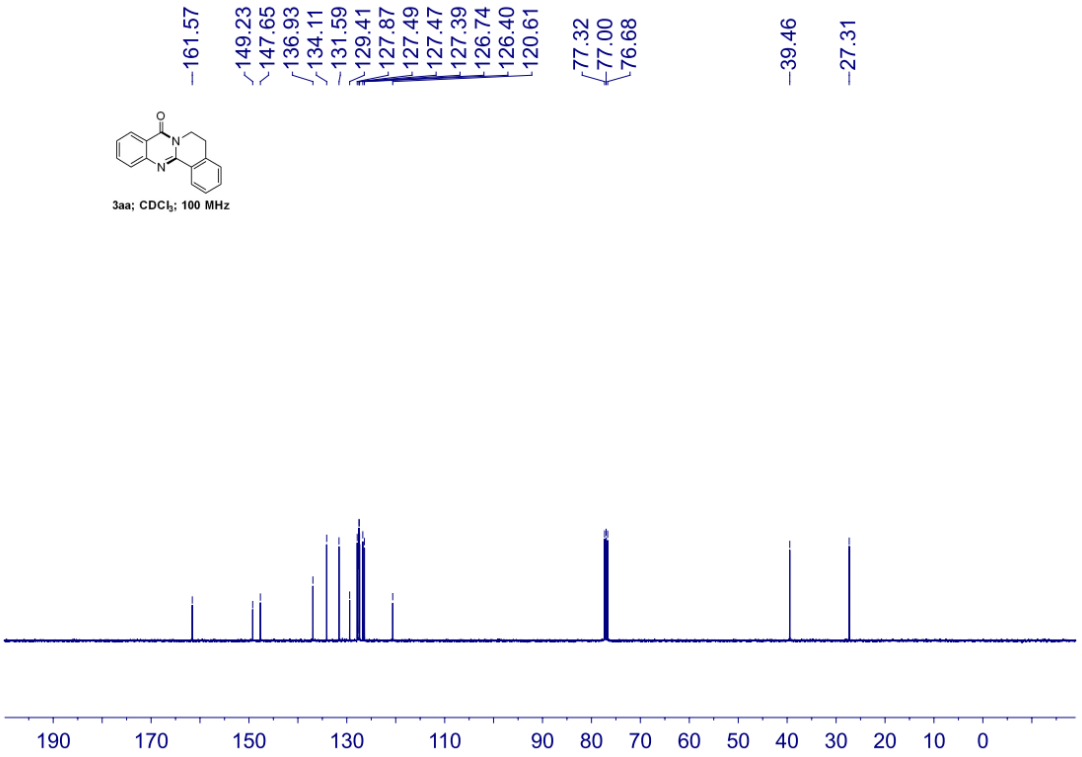
white solid. m.p.:187-188 ºC.^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.46 (d, J = 8.4 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 7.89 (s, 1H), 7.60-7.50 (m, 3H), 7.47-7.39 (m, 2H), 7.38-7.31 (m, 3H), 7.25 (d, J = 8.4 Hz, 1H), 4.37 (t, J = 6.4 Hz, 2H), 3.06 (t, J = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.2, 149.8, 147.6, 136.9, 131.8, 131.7, 130.4, 129.3, 129.1, 128.7, 128.3, 128.0, 127.5, 127.4, 126.8, 122.5, 120.0, 92.4, 88.5, 39.5, 27.3. HRMS (ESI) calcd for $C_{24}H_{17}N_2O$ $(M+H)^+$ 349.1321, found 349.1325.

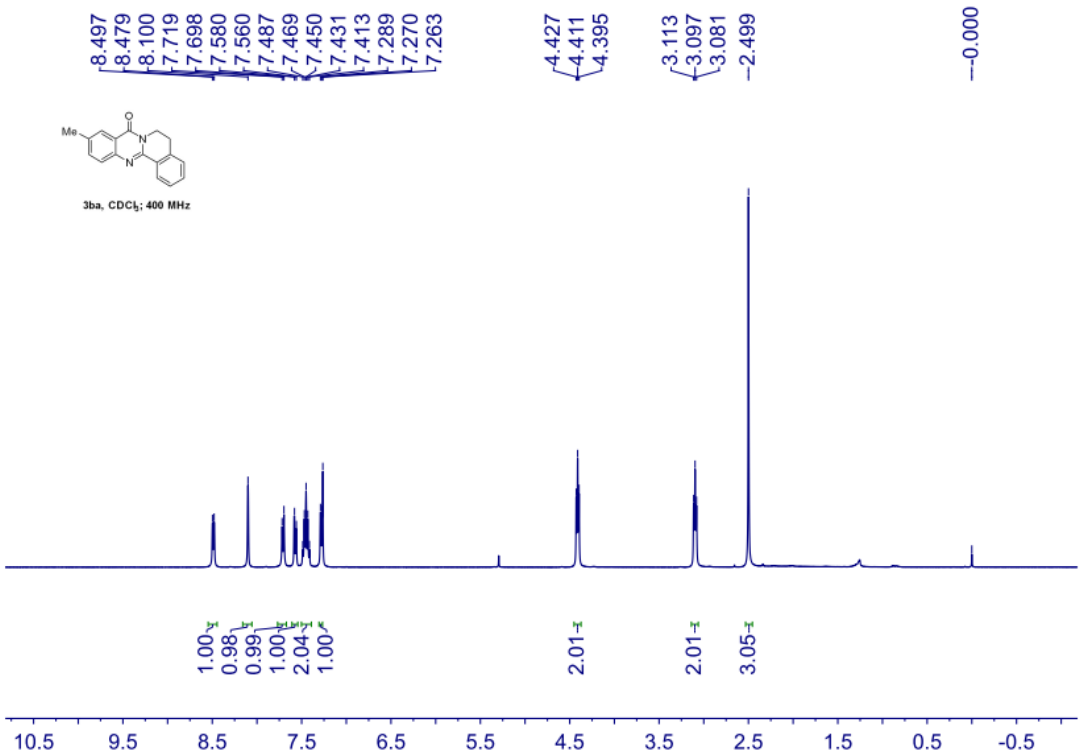
4. Reference:

1. H. L. Cui, L. Jiang, H. Tan and S. Liu, *Adv. Synth. Catal*., 2019, **361**, 4772-4780.
1. L. Xie, C. Lu, D. Jing, X. Ou and K. Zheng, *Eur. J. Org. Chem*., 2019, 3649-3653.
2. F. Xie, Q. H. Chen, R. Xie, H. F. Jiang and M. Zhang, *ACS Catal*., 2018, **8**, 5869-5874.
3. C. Lu, Z. Su, D. Jing, S. Jin, L. Xie, L. Li and K. Zheng, *Org. Lett*., 2019, **21**, 1438-1443.
4. B. A. Granger, K. Kaneda and S. F. Martin, *Org. Lett*., 2011, **13**, 4542-4545.

5. Spectral copies of ^{1}H NMR, and ^{13}C NMR



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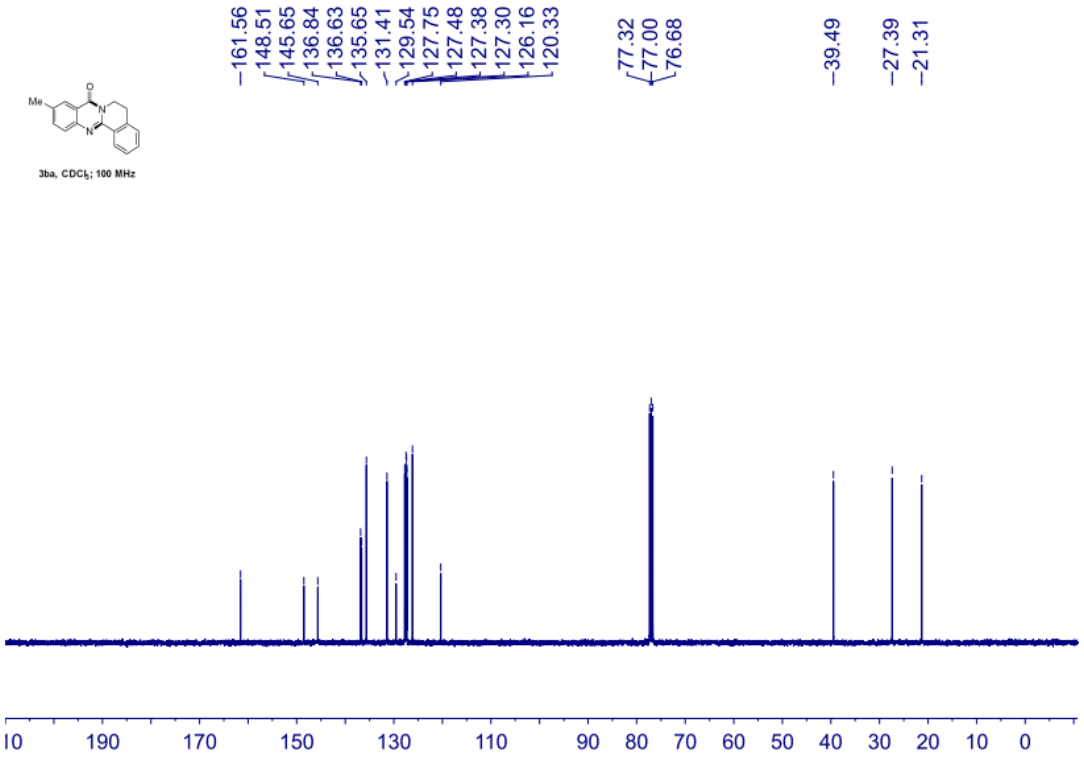
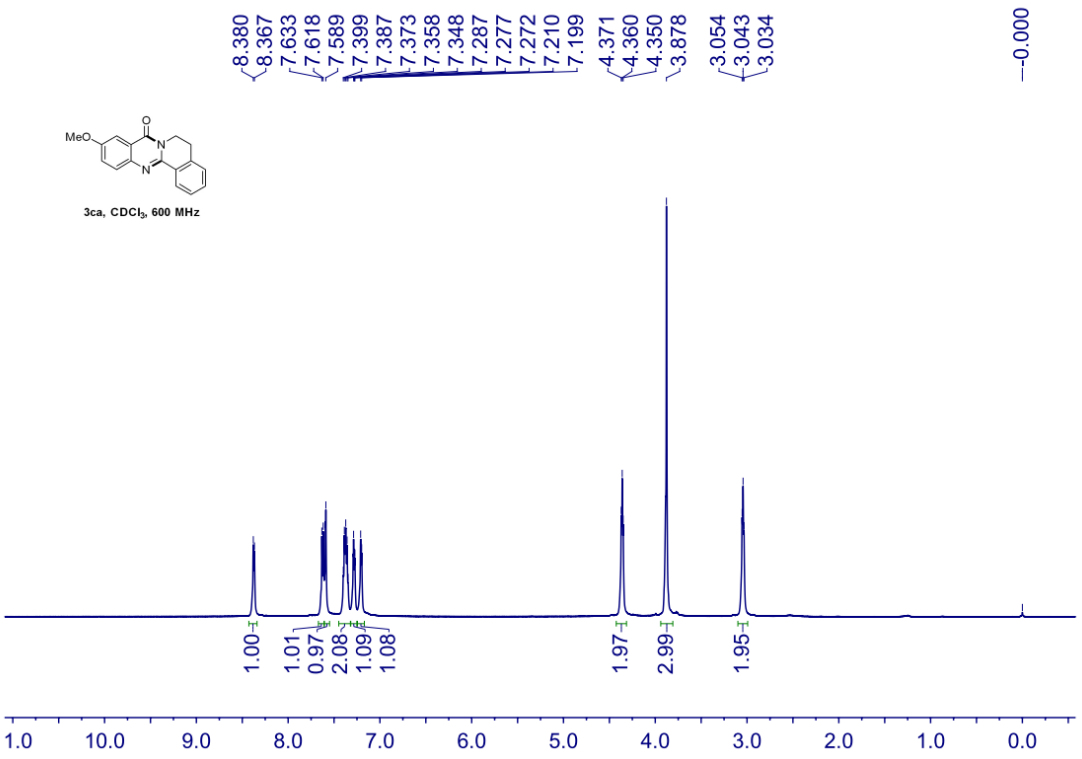
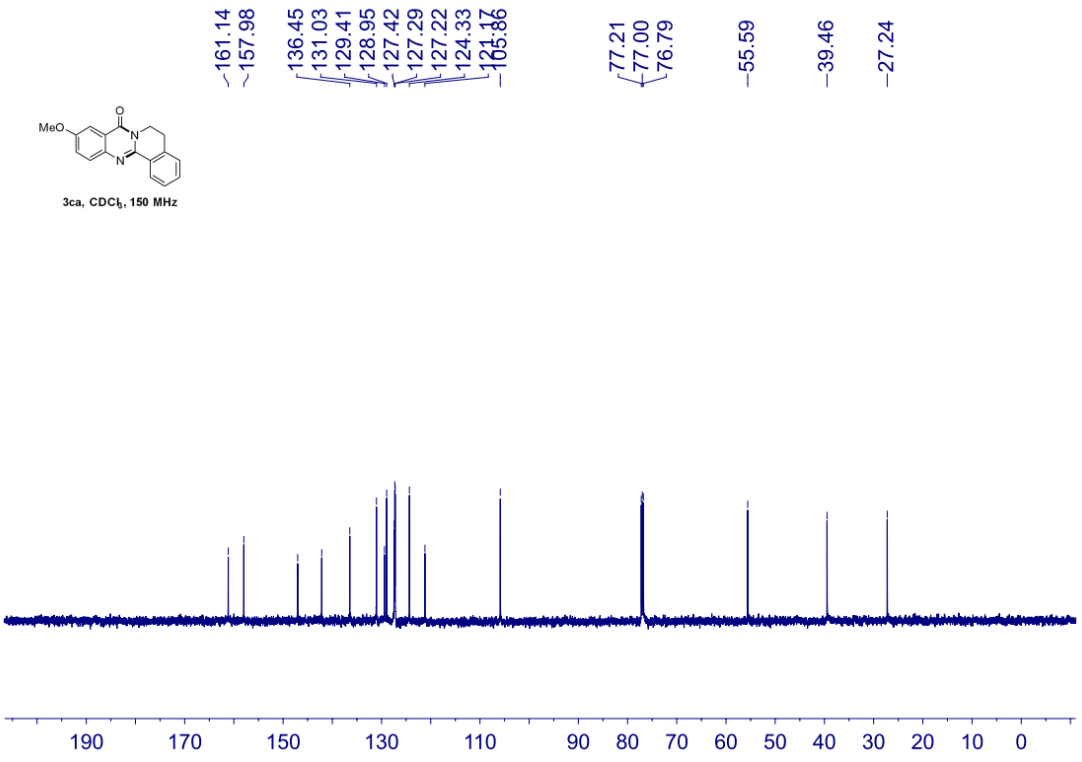
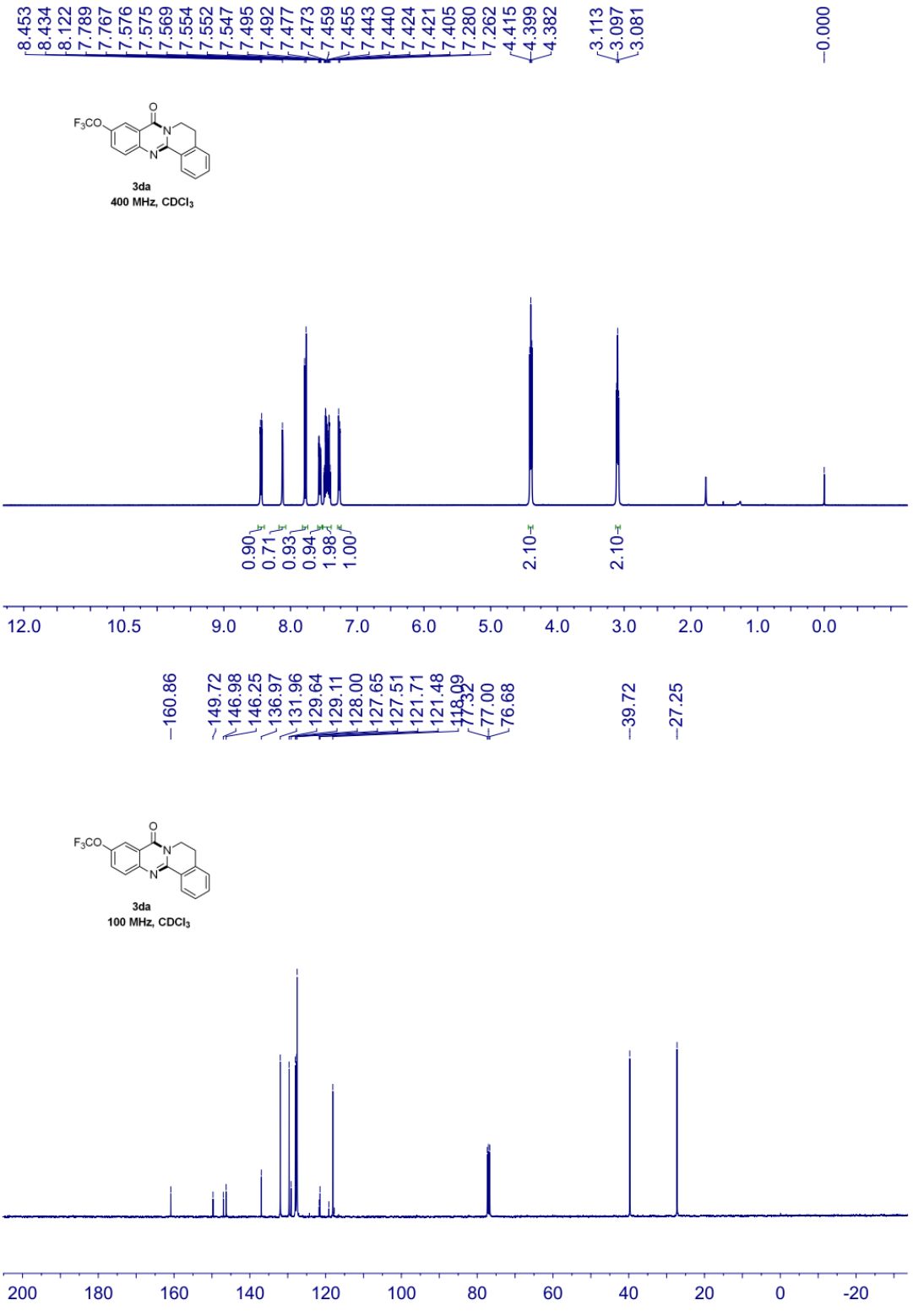
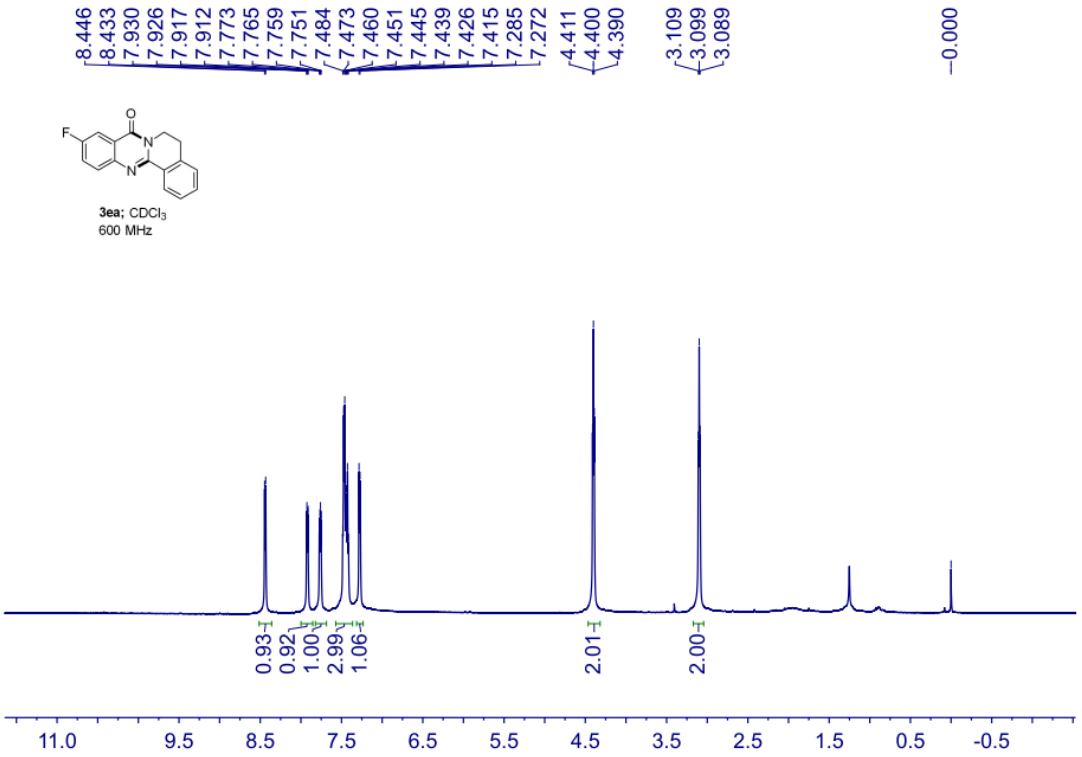
8.479
8.100
7.719
7.698
7.580
7.560
7.487
7.469
7.450
7.431
7.413
7.289
7.270
7.263
4.427
4.411
4.395
3.113
3.097
3.081
2.499
0.000
Me
3ba, CDCl3; 400 MHz
1.00
0.98
0.99
1.00
2.04
1.00
2.01
2.01
3.05
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

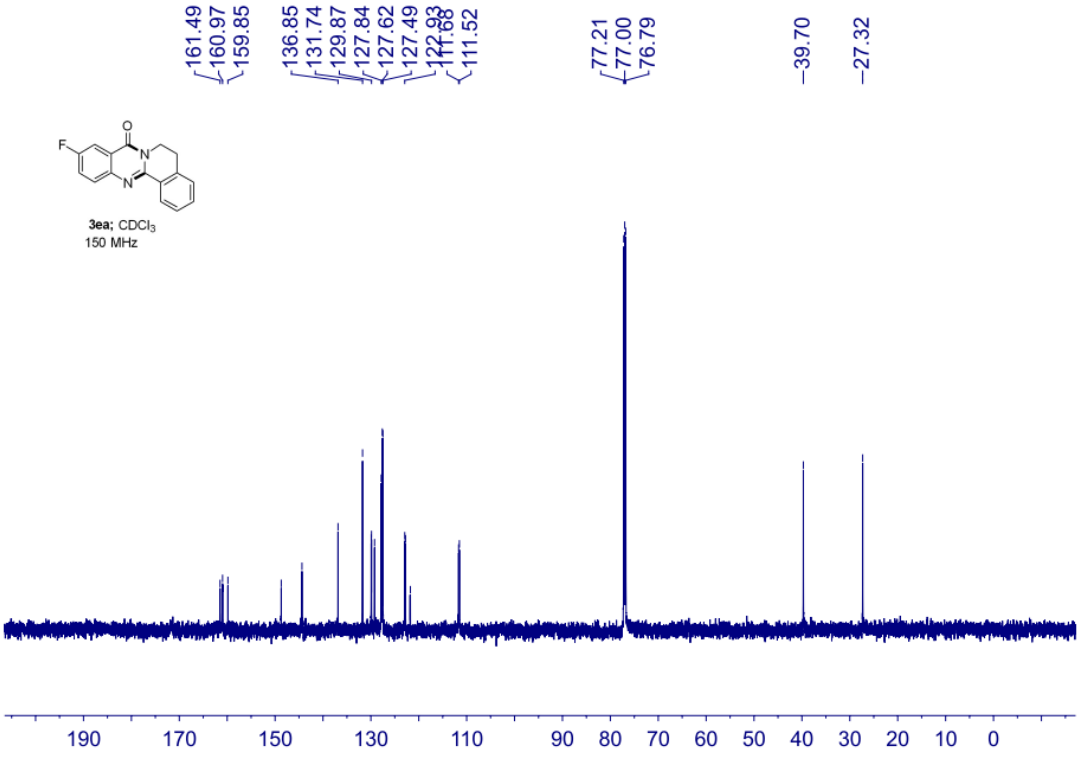

161.56
148.51
145.65
136.84
136.63
135.65
131.41
129.54
127.75
127.48
127.38
127.30
126.16
120.33
77.32
77.00
76.68
39.49
27.39
21.31
Me
3ba, CDCl3; 100 MHz
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

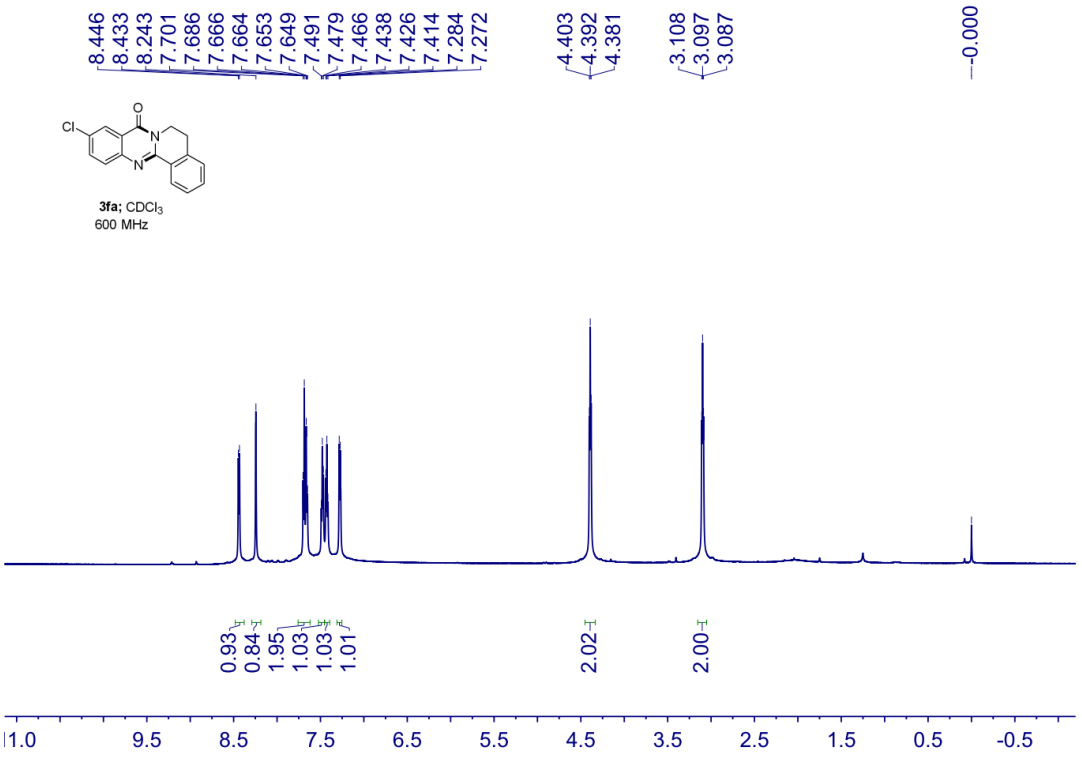

8.380
8.367
7.633
7.618
7.589
7.399
7.387
7.373
7.358
7.348
7.287
7.277
7.272
7.210
7.199
4.371
4.360
4.350
3.878
3.054
3.043
3.034
0.000
MeO
3ca, CDCl3, 600 MHz
1.00
1.01
0.97
2.08
1.09
1.08
1.97
2.99
1.95
1.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

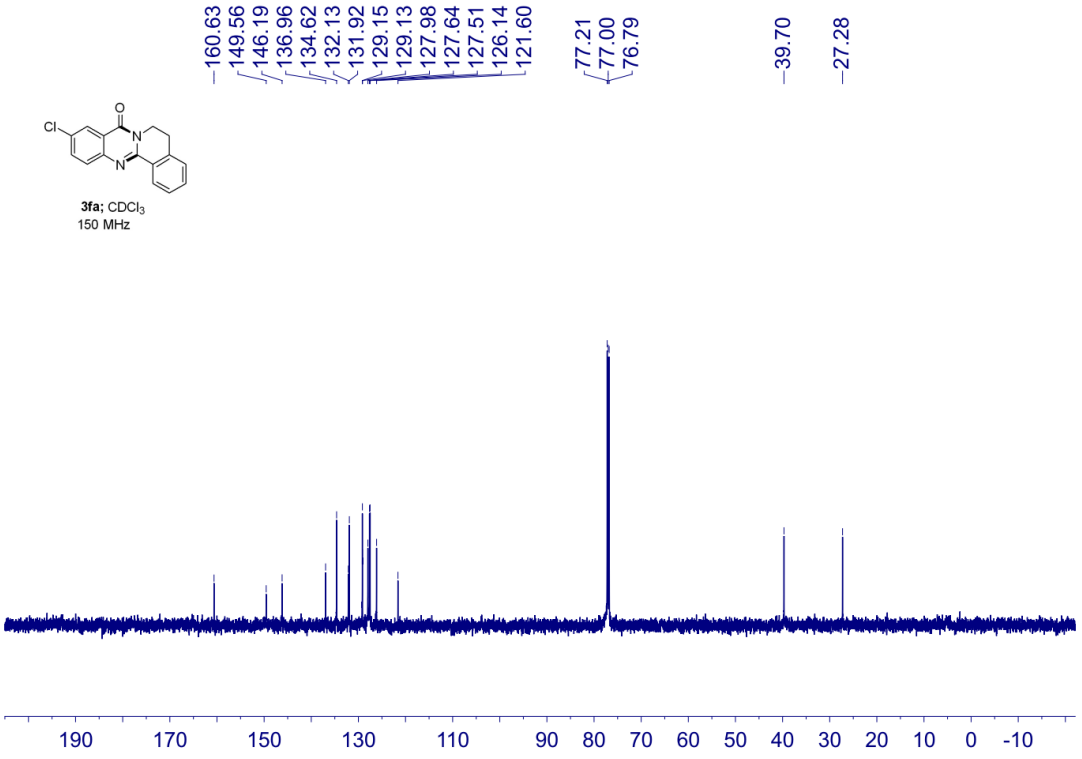

161.14
157.98
136.45
131.03
129.41
128.95
127.42
127.29
127.22
124.33
121.17
105.86
77.21
77.00
76.79
55.59
39.46
27.24
MeO
3ca, CDCl3, 150 MHz
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


8.453
8.434
8.122
7.789
7.767
7.576
7.575
7.569
7.554
7.552
7.547
7.495
7.492
7.477
7.473
7.459
7.455
7.443
7.440
7.424
7.421
7.405
7.280
7.262
4.415
4.399
4.382
3.113
3.097
3.081
0.000
F3CO
3da
400 MHz, CDCl3
0.90
0.71
0.93
0.94
1.98
1.00
2.10
2.10
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
160.86
149.72
146.98
146.25
136.97
131.96
129.64
129.11
128.00
127.65
127.51
121.71
121.48
118.09
77.32
77.00
76.68
39.72
27.25
F3CO
3da
100 MHz, CDCl3
200
180
160
140
120
100
80
60
40
20
0
-20


8.446
8.433
7.930
7.926
7.917
7.912
7.773
7.765
7.759
7.751
7.484
7.473
7.460
7.451
7.445
7.439
7.426
7.415
7.285
7.272
4.411
4.400
4.390
3.109
3.099
3.089
0.000
3ea; CDCl3
600 MHz
0.93
0.92
1.00
2.99
1.06
2.01
2.00
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


161.49
160.97
159.85
136.85
131.74
129.87
127.84
127.62
127.49
111.52
77.21
77.00
76.79
39.70
27.32
3ea; CDCl3
150 MHz
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


8.446
8.433
8.243
7.701
7.686
7.666
7.664
7.653
7.649
7.491
7.479
7.466
7.438
7.426
7.414
7.284
7.272
4.403
4.392
4.381
3.108
3.097
3.087
0.000
Cl
O
N
N
3fa; CDCl3
600 MHz
0.93
0.84
1.95
1.03
1.03
1.01
2.02
2.00
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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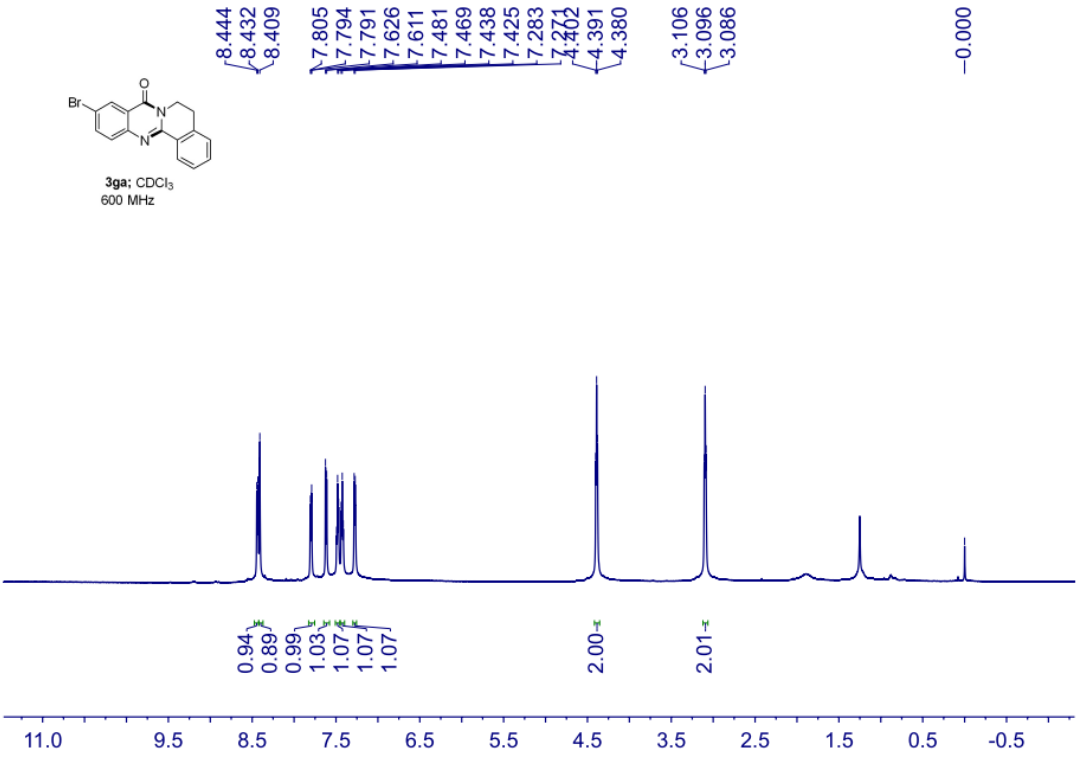
149.56
146.19
136.96
134.62
132.13
131.92
129.15
129.13
127.98
127.64
127.51
126.14
121.60
77.21
77.00
76.79
39.70
27.28
Cl
O
N
N
3fa; CDCl3
150 MHz
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10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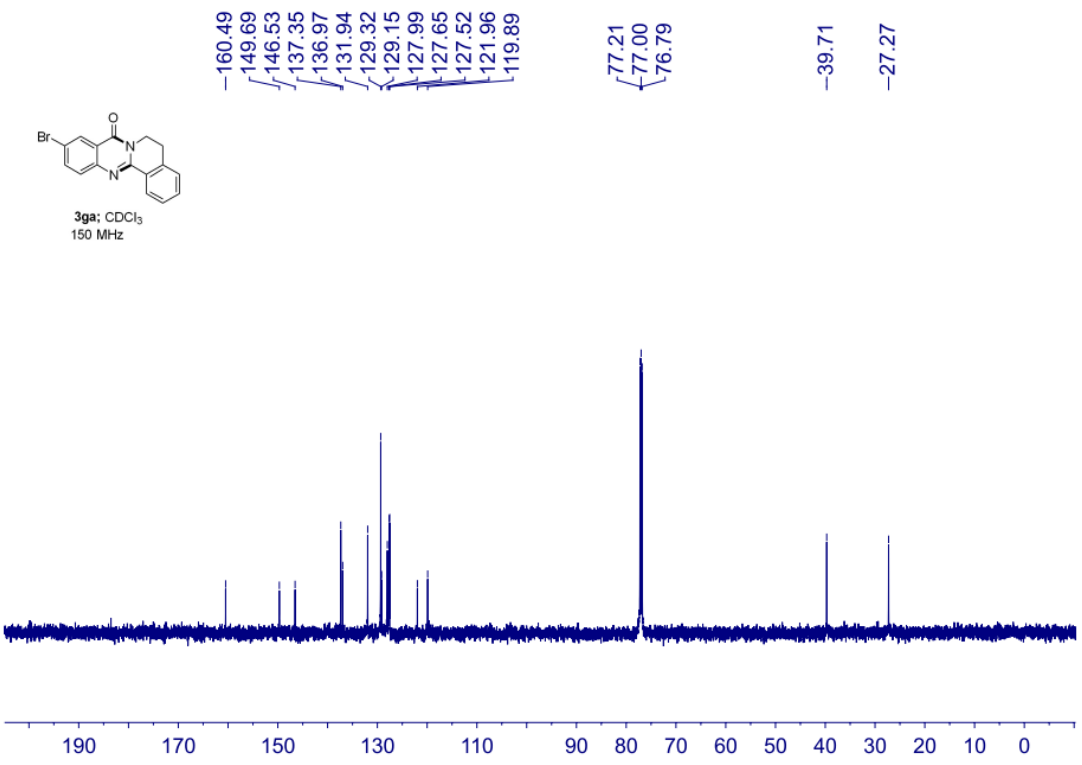
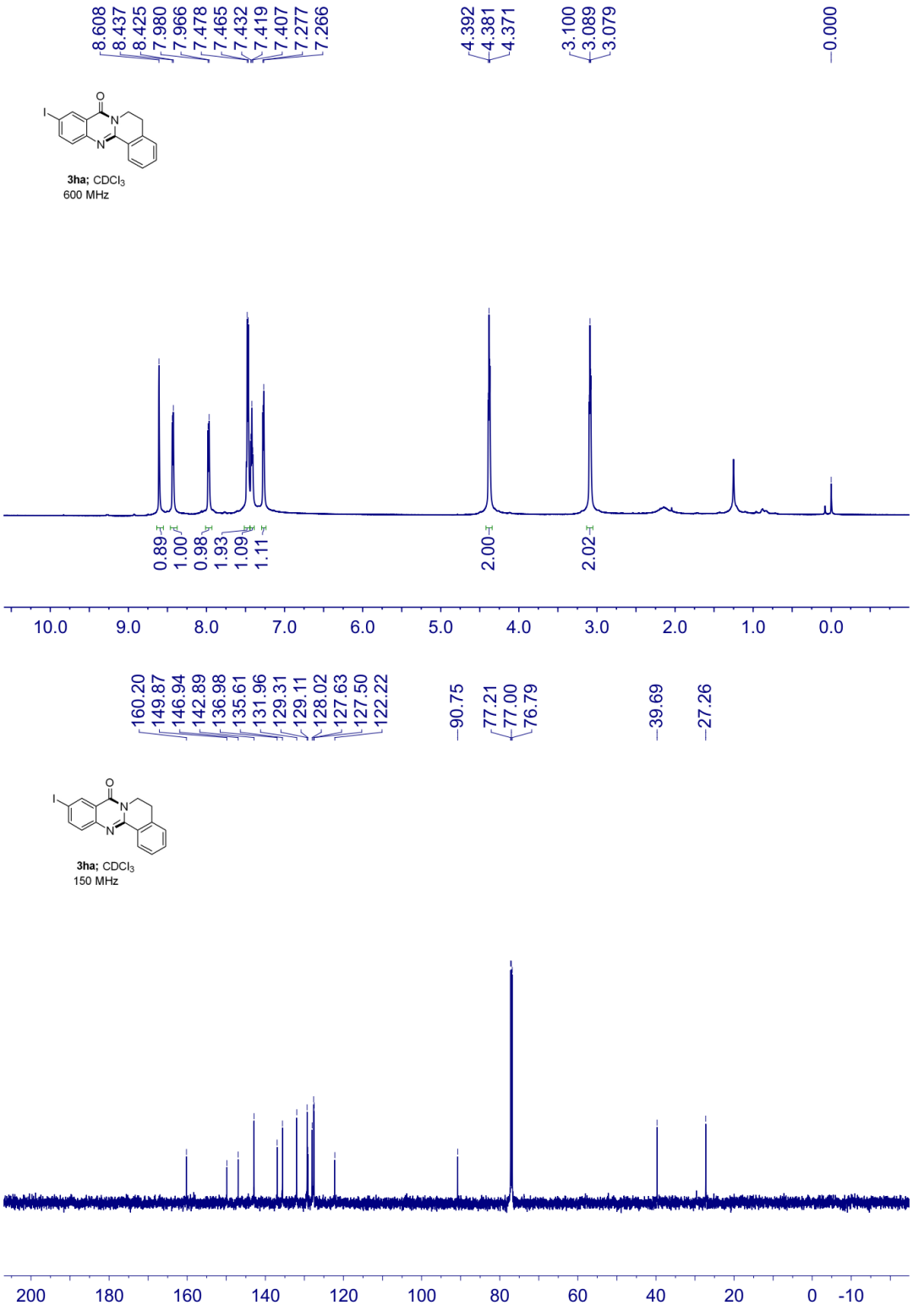
8.432
8.409
7.805
7.794
7.791
7.626
7.611
7.481
7.469
7.438
7.425
7.283
7.271
4.402
4.391
4.380
3.106
3.096
3.086
0.000
Br
O
N
N
3ga; CDCl3
600 MHz
0.94
0.89
0.99
1.03
1.07
1.07
1.07
2.00
2.01
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


160.49
149.69
146.53
137.35
136.97
131.94
129.32
129.15
127.99
127.65
127.52
121.96
119.89
77.21
77.00
76.79
39.71
27.27
Br
O
N
N
3ga; CDCl3
150 MHz
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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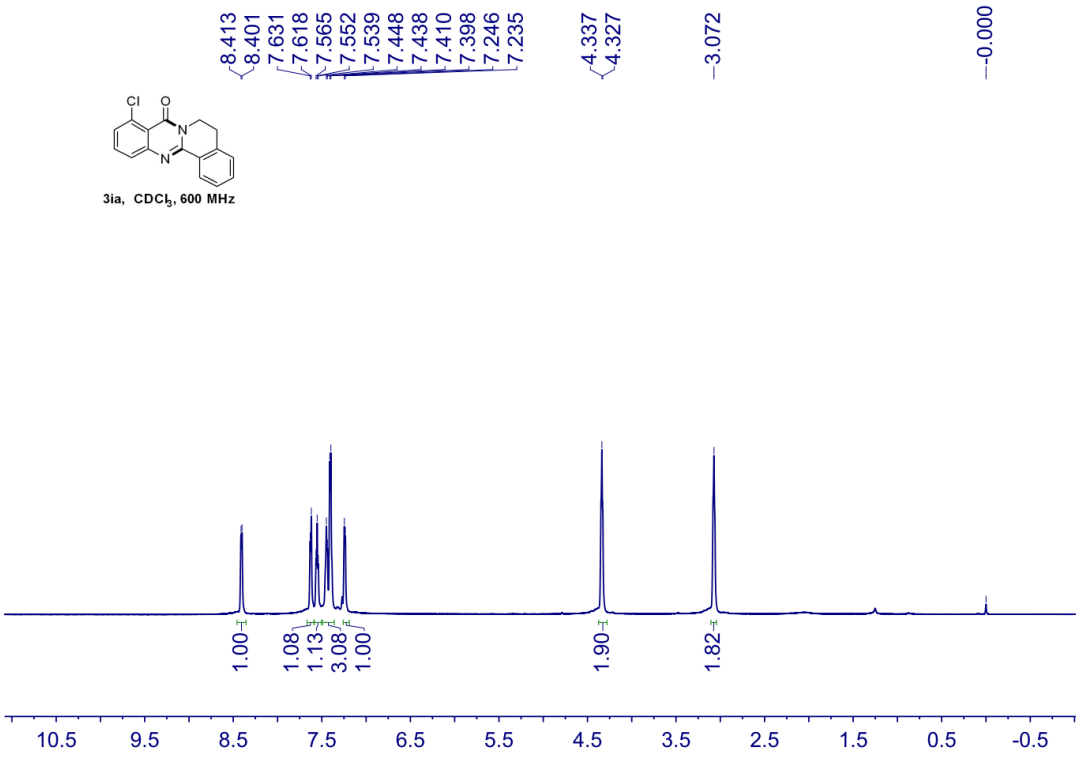
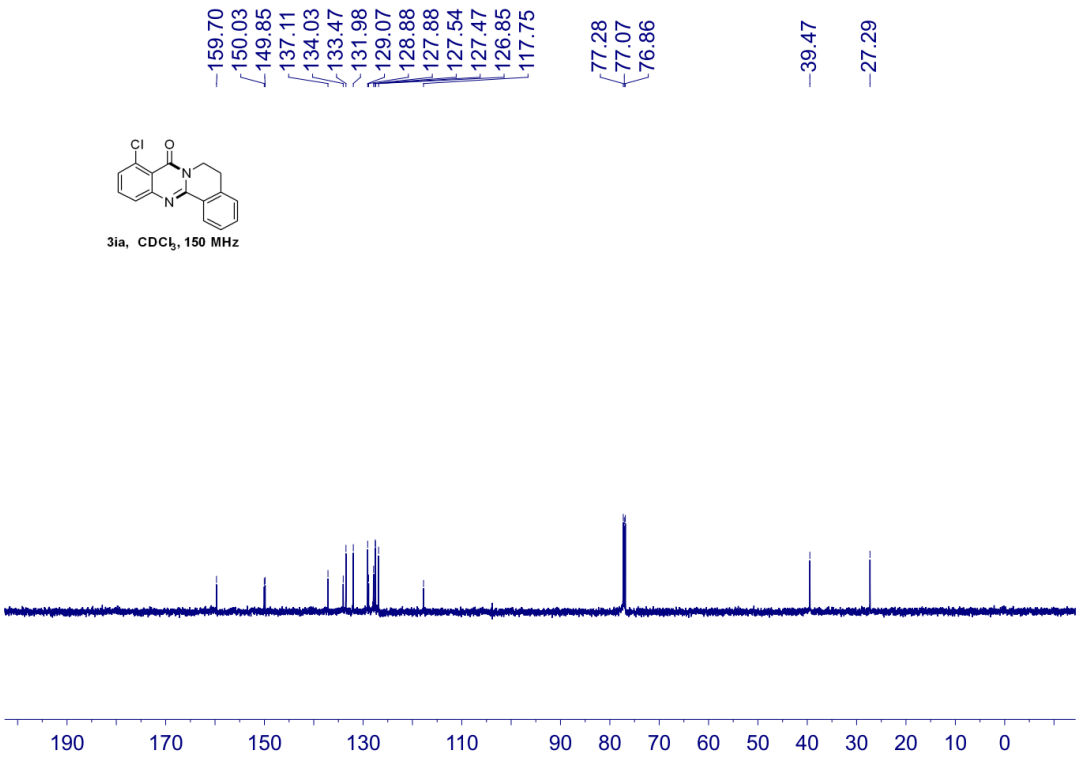
7.432
7.419
7.407
7.277
7.266
4.392
4.381
4.371
3.100
3.089
3.079
0.000
3ha; CDCl3
600 MHz
0.89
1.00
0.98
1.93
1.09
1.11
2.00
2.02
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
160.20
149.87
146.94
142.89
136.98
135.61
131.96
129.31
129.11
128.02
127.63
127.50
122.22
90.75
77.21
77.00
76.79
39.69
27.26
3ha; CDCl3
150 MHz
200
180
160
140
120
100
80
60
40
20
0
-10



3ia, $CDCl_3$, 600 MHz



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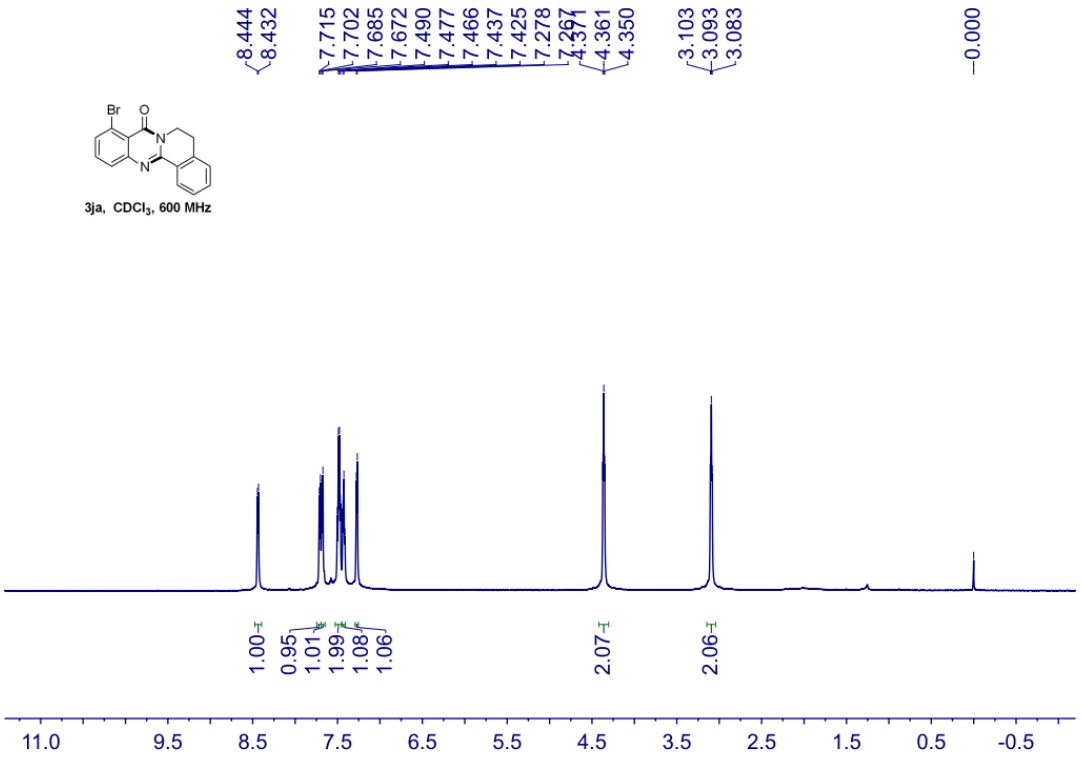
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7.437
7.425
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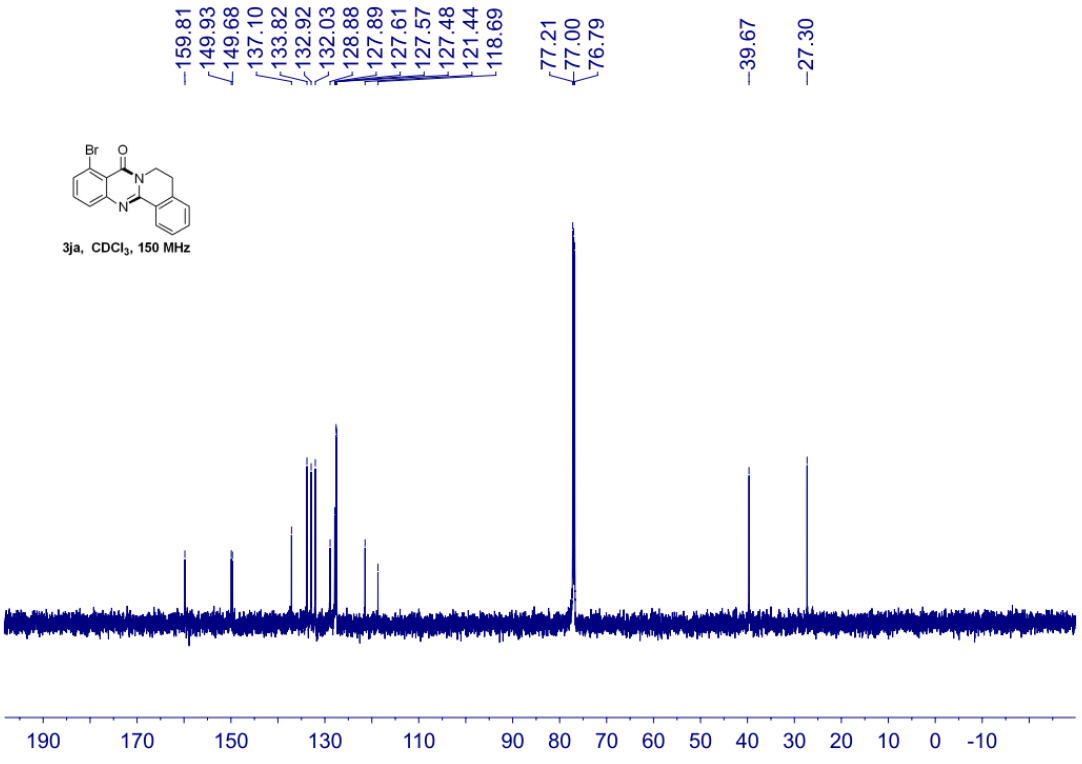
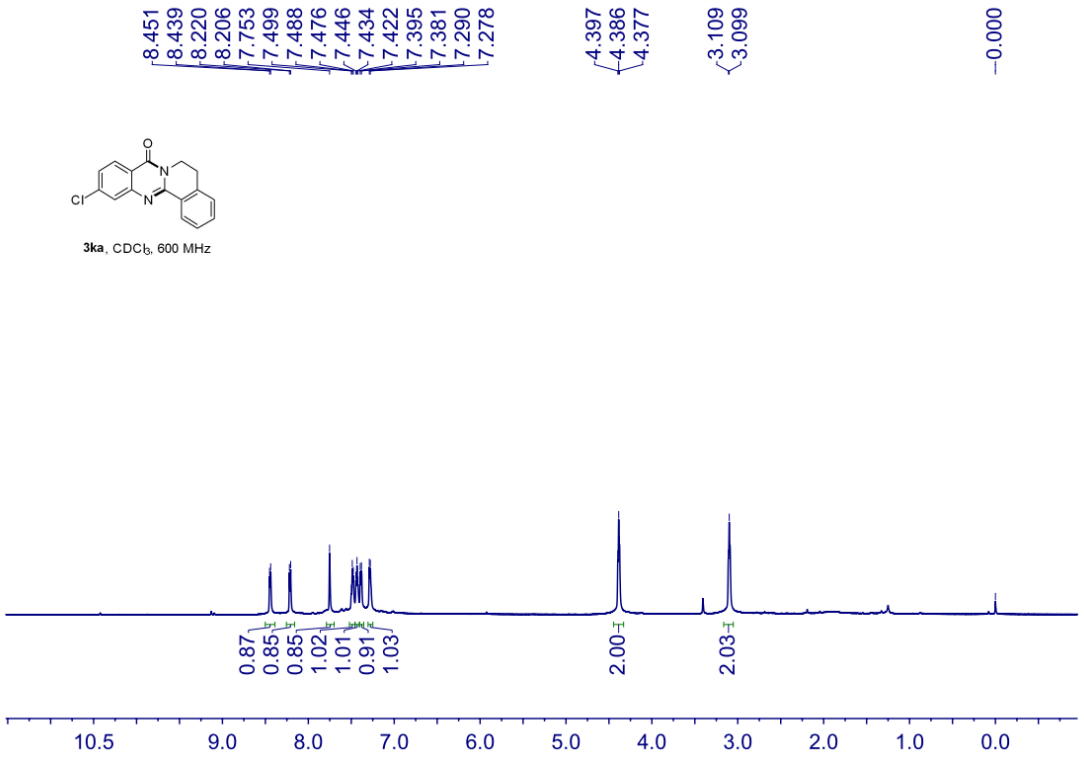
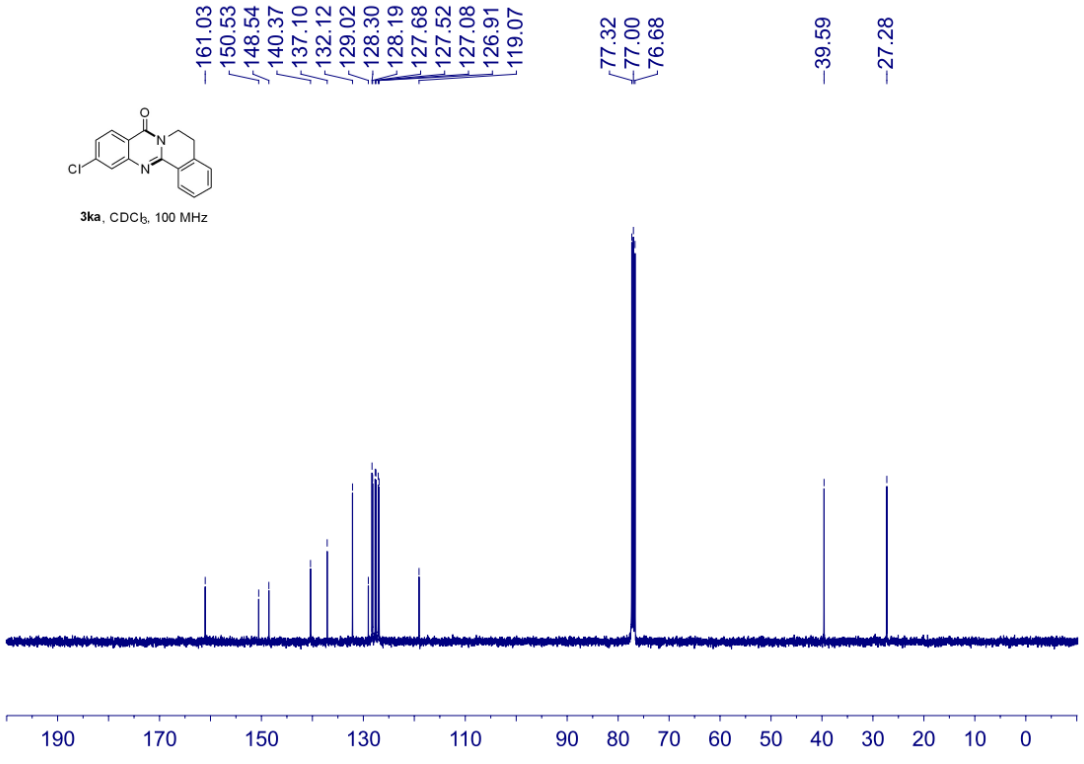
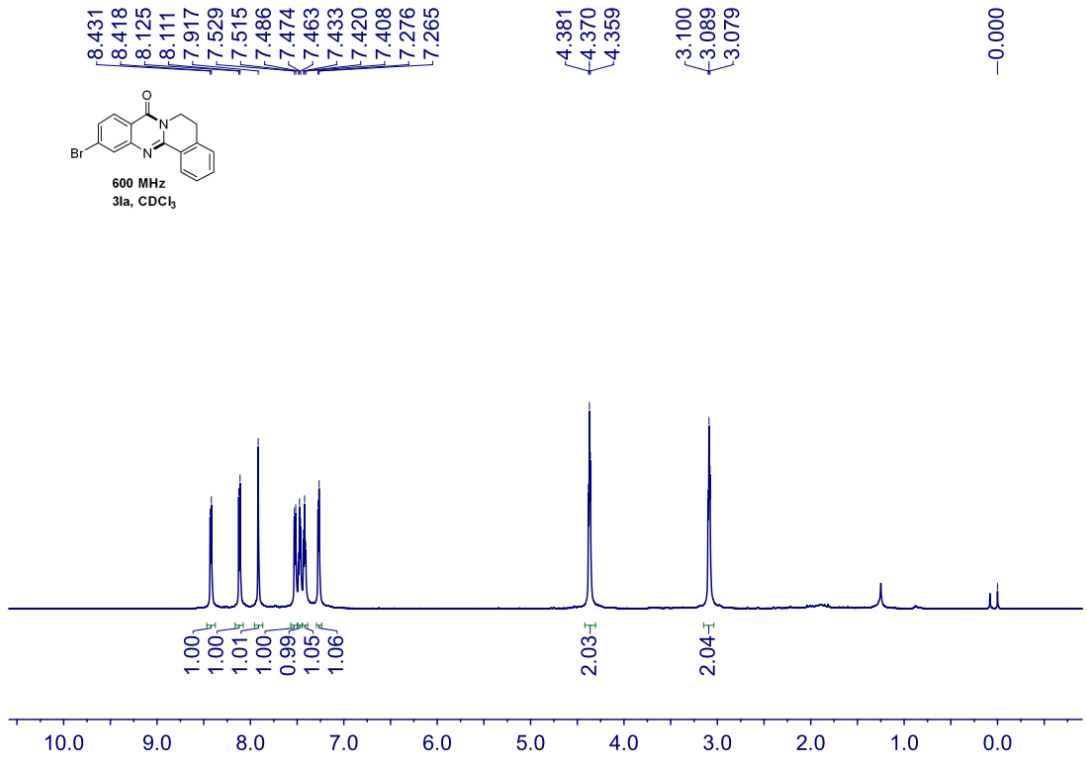
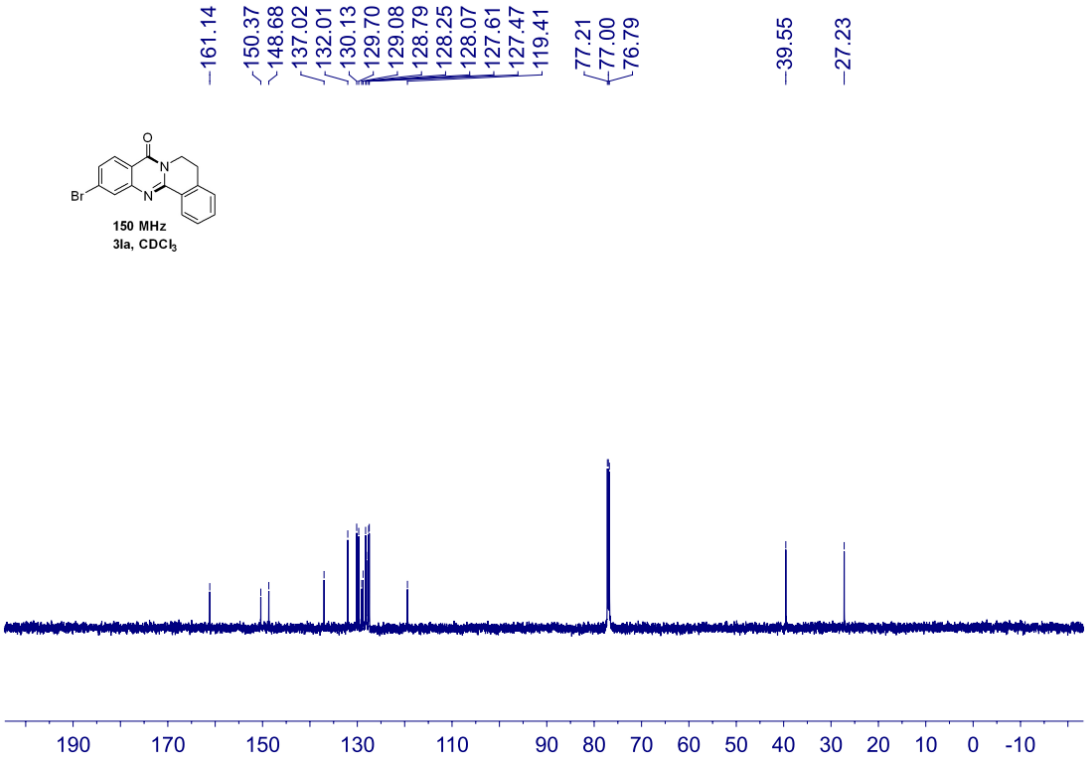
4.350
3.103
3.093
3.083
0.000
Br
O
N
N
3ja, CDCl3, 600 MHz
1.00
0.95
1.01
1.99
1.08
1.06
2.07
2.06
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

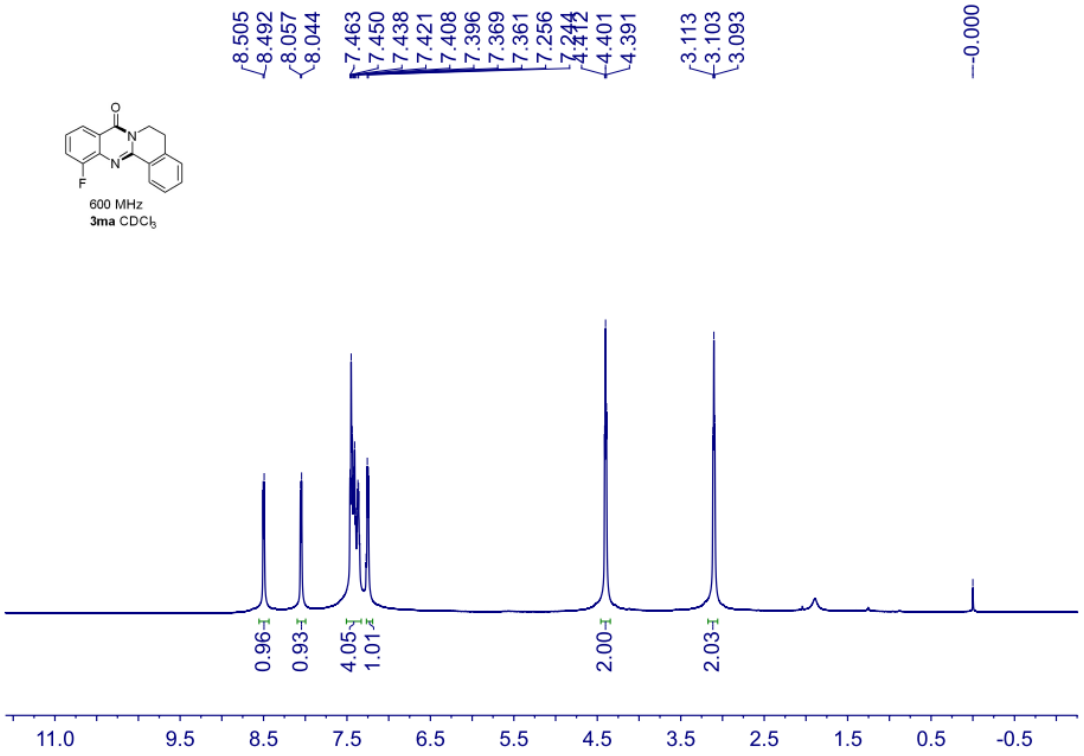

159.81
149.93
149.68
137.10
133.82
132.92
132.03
128.88
127.89
127.61
127.57
127.48
121.44
118.69
77.21
77.00
76.79
39.67
27.30
Br
O
N
N
3ja, CDCl3, 150 MHz
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10

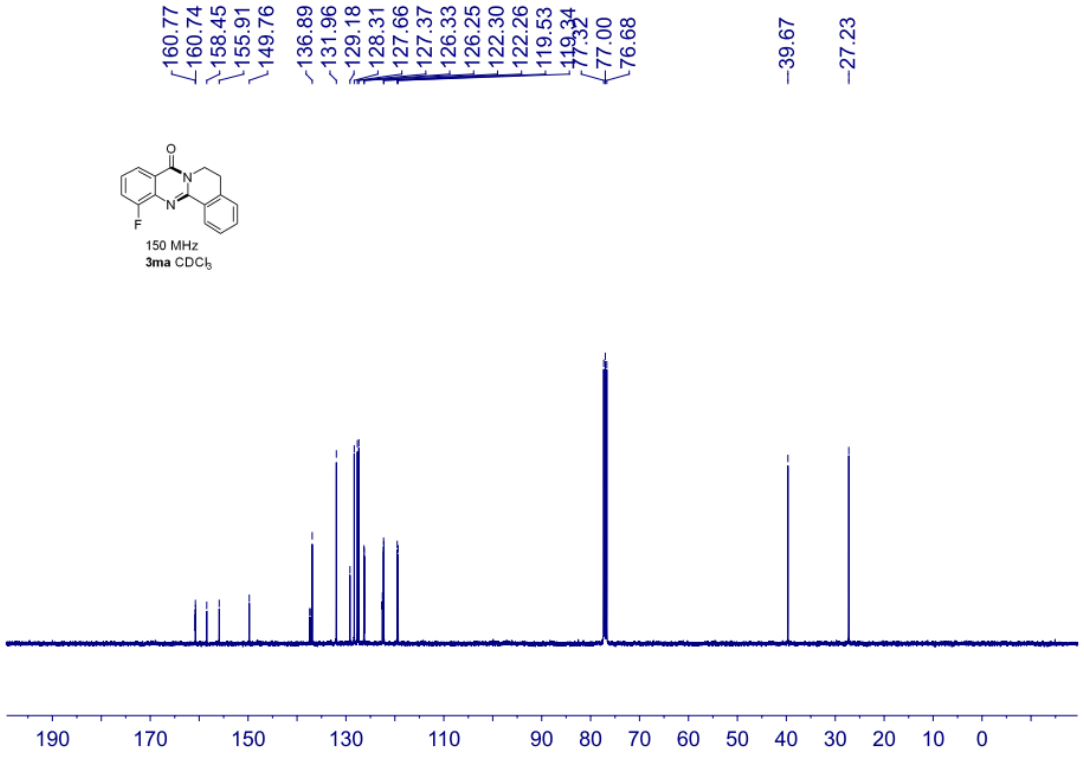

8.451
8.439
8.220
8.206
7.753
7.499
7.488
7.476
7.446
7.434
7.422
7.395
7.381
7.290
7.278
4.397
4.386
4.377
3.109
3.099
0.000
Cl
O
N
N
3ka, CDCl3, 600 MHz
0.87
0.85
0.85
1.02
1.01
0.91
1.03
2.00
2.03
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

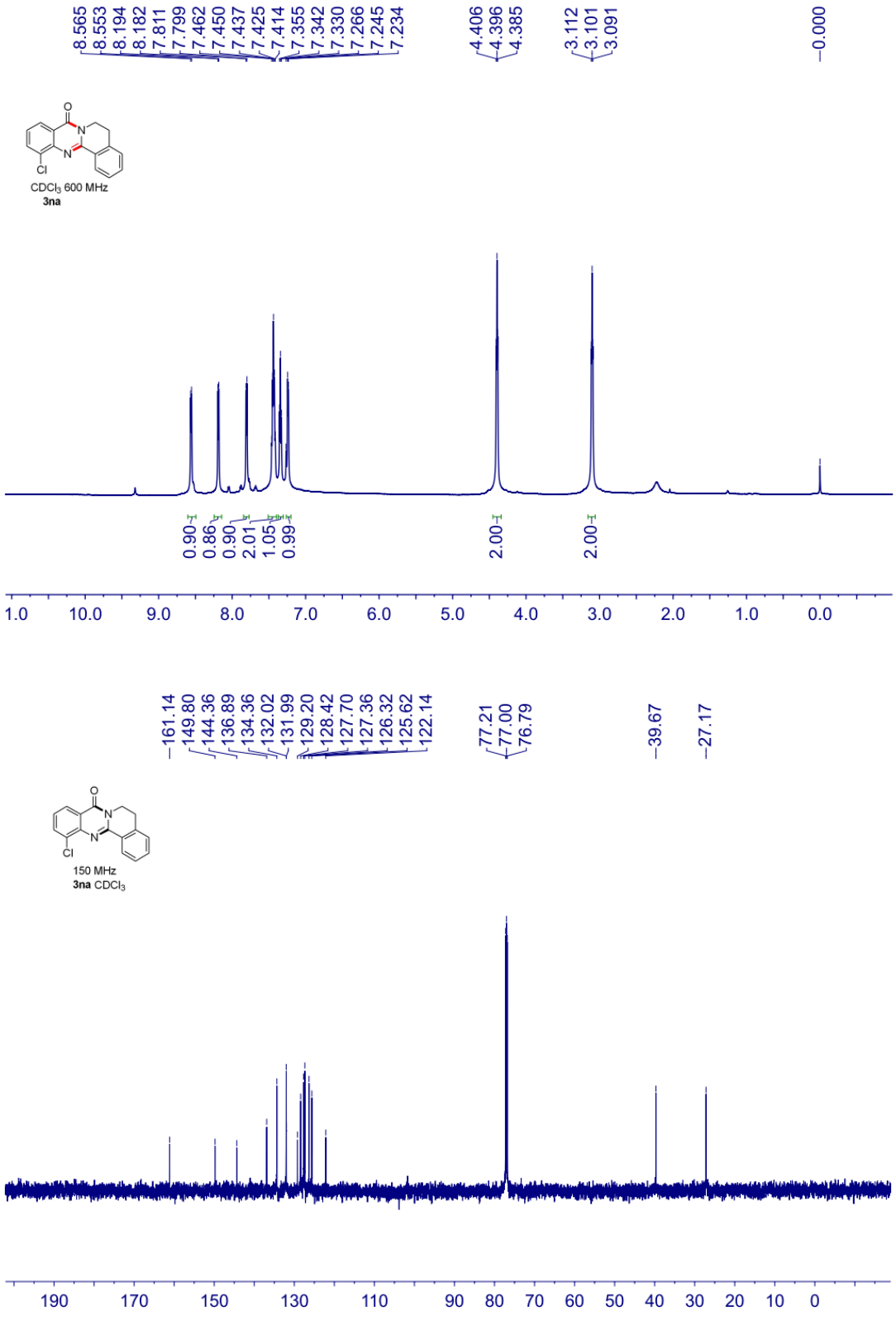

161.03
150.53
148.54
140.37
137.10
132.12
129.02
128.30
128.19
127.68
127.52
127.08
126.91
119.07
77.32
77.00
76.68
39.59
27.28
Cl
O
N
N
3ka, CDCl3, 100 MHz
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

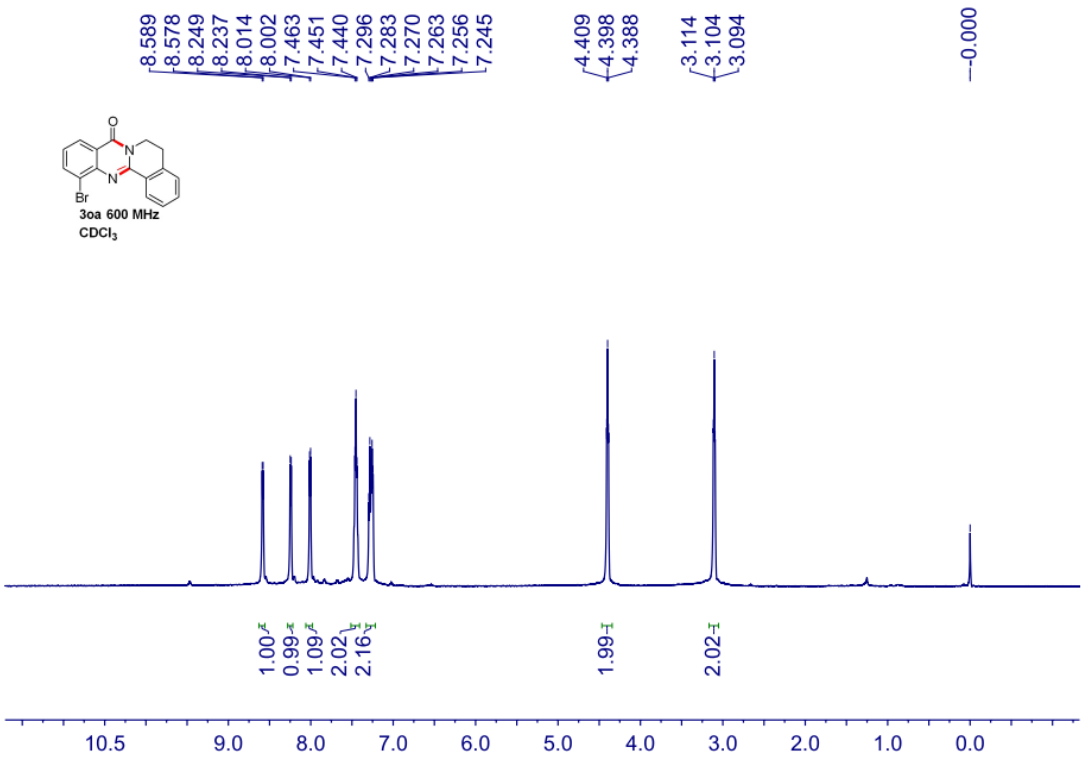

8.431
8.418
8.125
8.111
7.917
7.529
7.515
7.486
7.474
7.463
7.433
7.420
7.408
7.276
7.265
4.381
4.370
4.359
3.100
3.089
3.079
0.000
600 MHz
3la, CDCl3
1.00
1.00
1.01
1.00
0.99
1.05
1.06
2.03
2.04
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

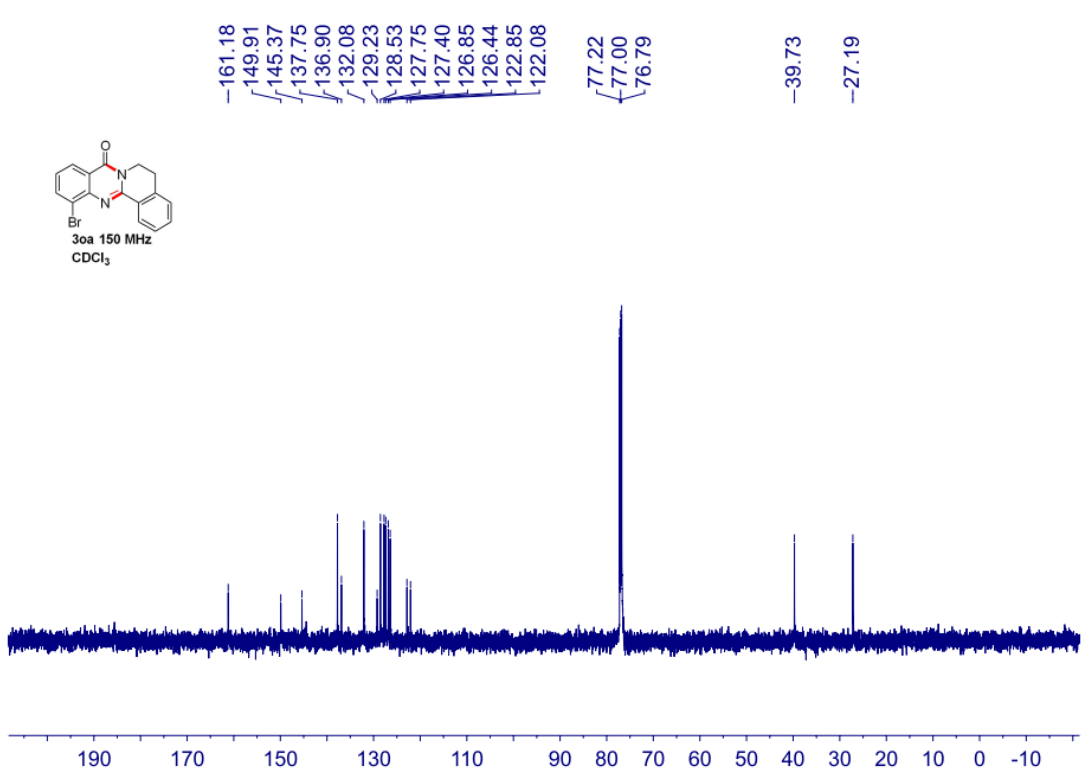

161.14
150.37
148.68
137.02
132.01
130.13
129.70
129.08
128.79
128.25
128.07
127.61
127.47
119.41
77.21
77.00
76.79
39.55
27.23
150 MHz
3la, CDCl3
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10

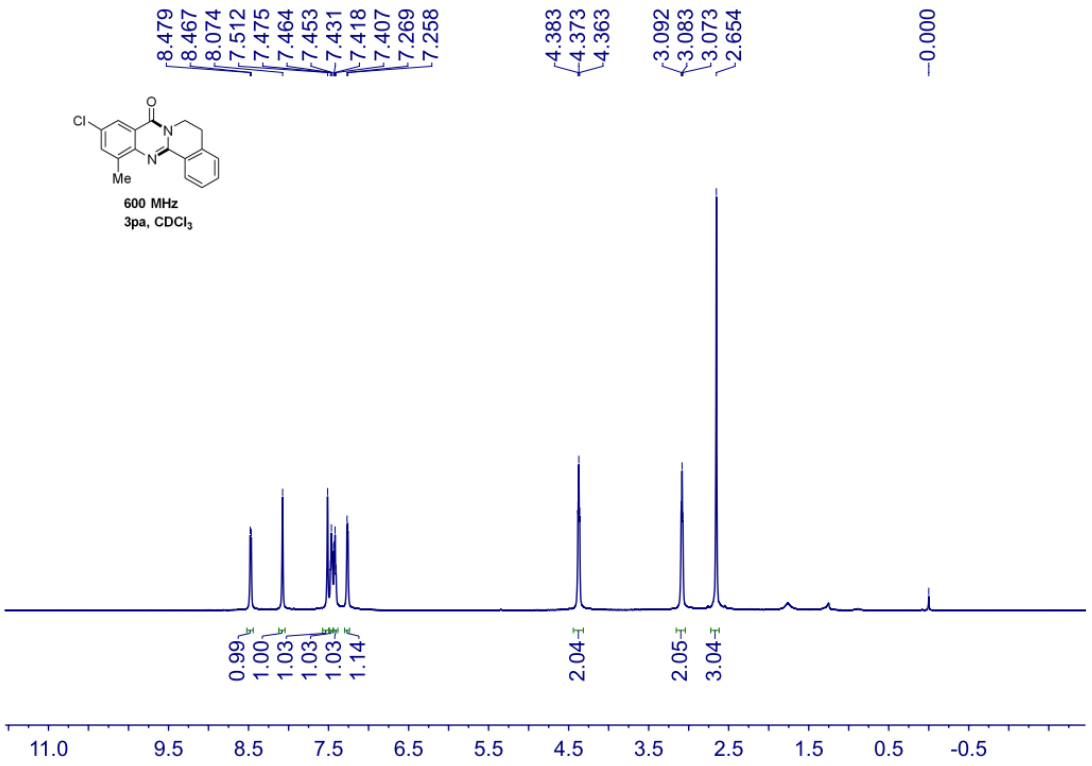

8.505
8.492
8.057
8.044
7.463
7.450
7.438
7.421
7.408
7.396
7.369
7.361
7.256
4.401
4.391
3.113
3.103
3.093
-0.000
600 MHz
3ma CDCl3
0.96
0.93
4.05
1.01
2.00
2.03
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

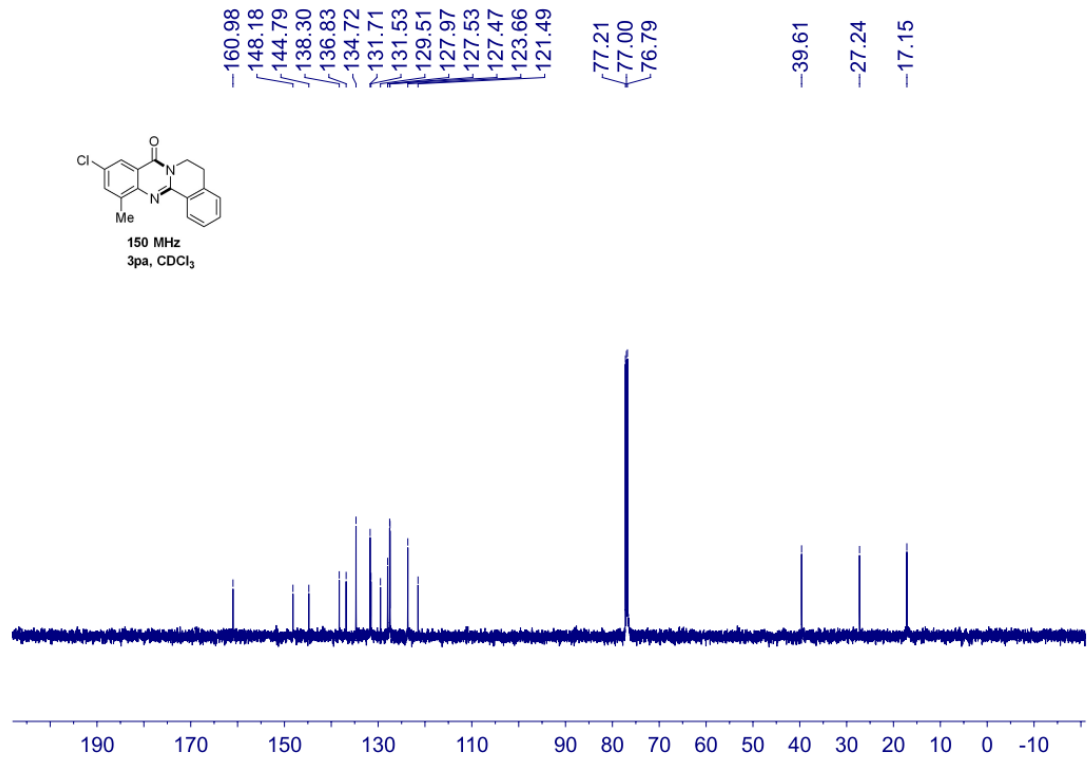

160.77
160.74
158.45
155.91
149.76
136.89
131.96
129.18
128.31
127.66
127.37
126.33
126.25
122.30
122.26
119.53
77.00
76.68
39.67
27.23
150 MHz
3ma CDCl3
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

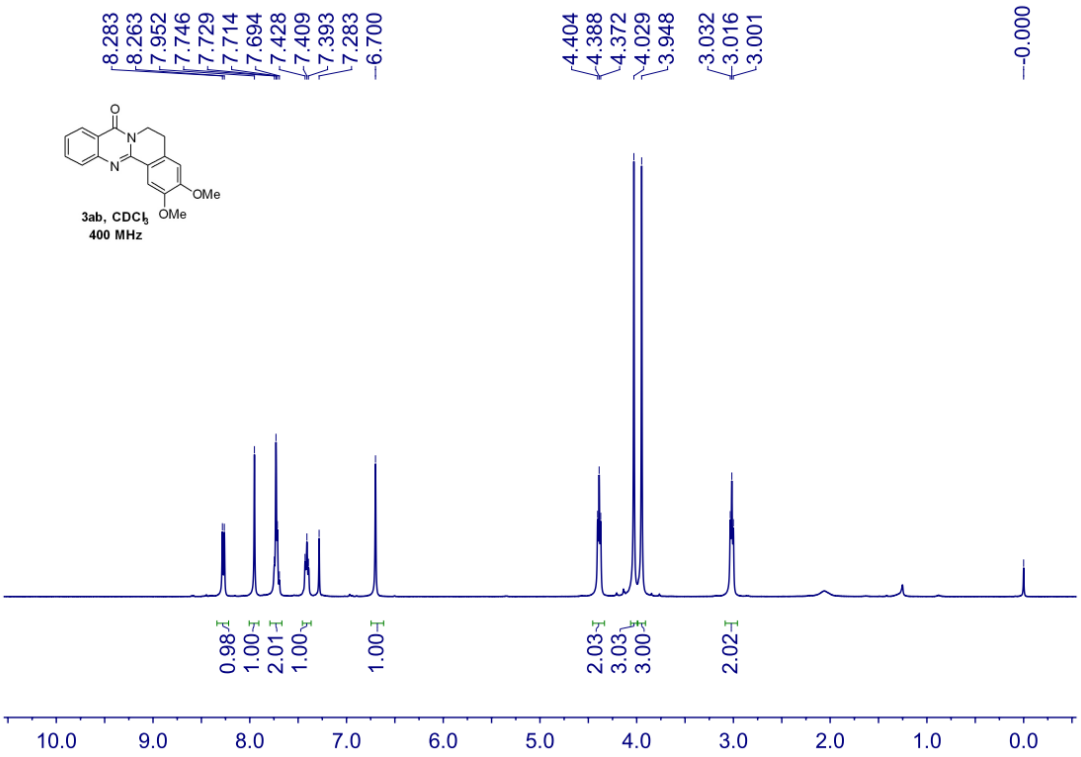

8.565
8.553
8.194
8.182
7.811
7.799
7.462
7.450
7.437
7.425
7.414
7.355
7.342
7.330
7.266
7.245
7.234
4.406
4.396
4.385
3.112
3.101
3.091
0.000
CDCl3 600 MHz
3na
0.90
0.86
0.90
2.01
1.05
0.99
2.00
2.00
1.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
161.14
149.80
144.36
136.89
134.36
132.02
131.99
129.20
128.42
127.70
127.36
126.32
125.62
122.14
77.21
77.00
76.79
39.67
27.17
150 MHz
3na CDCl3
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

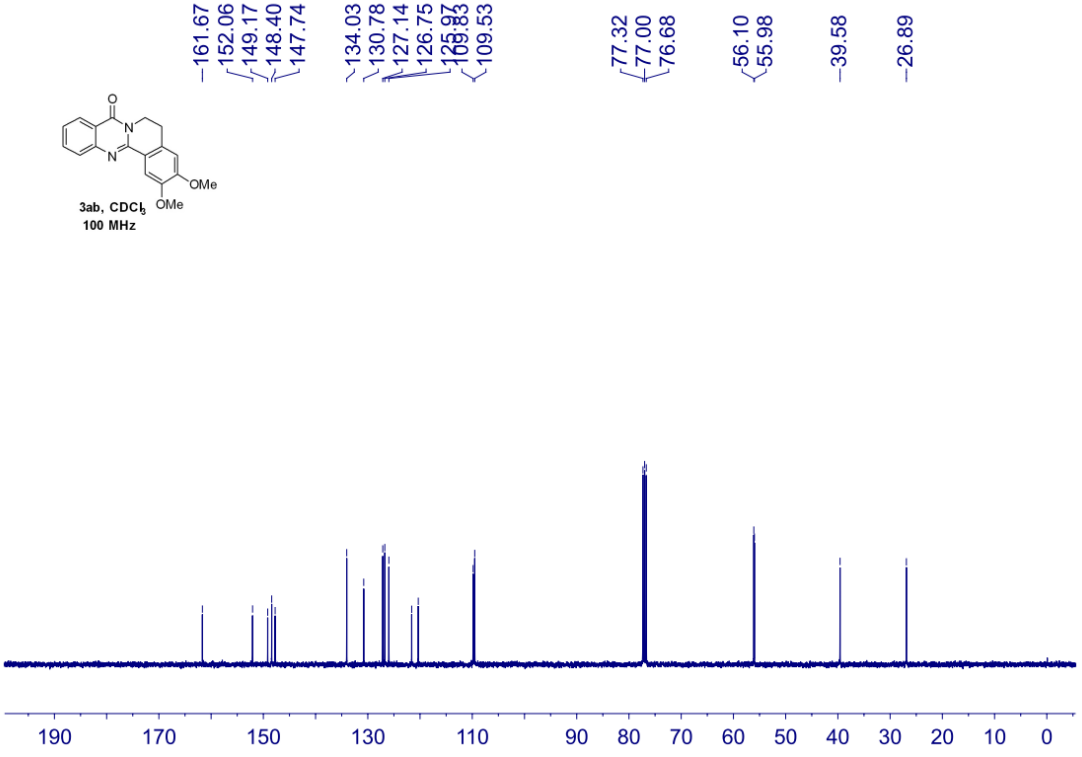

8.589
8.578
8.249
8.237
8.014
8.002
7.463
7.451
7.440
7.296
7.283
7.270
7.263
7.256
7.245
4.409
4.398
4.388
3.114
3.104
3.094
0.000
3oa 600 MHz
CDCl3
1.00
0.99
1.09
2.02
2.16
1.99
2.02
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

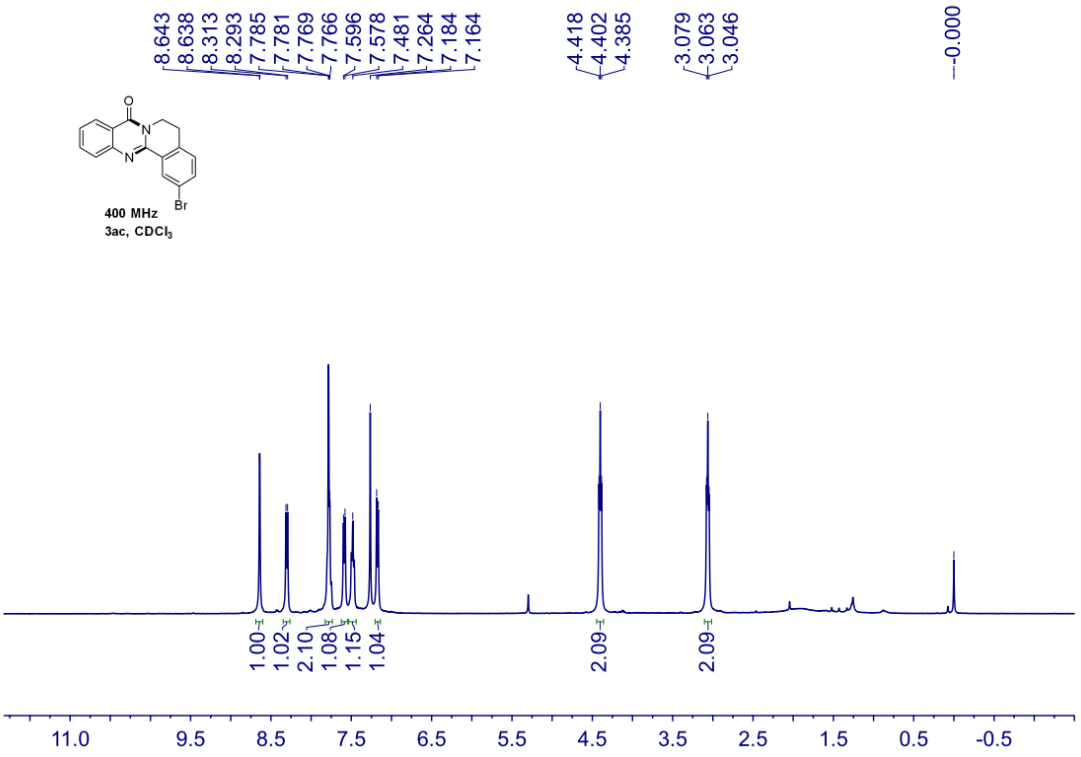

161.18
149.91
145.37
137.75
136.90
132.08
129.23
128.53
127.75
127.40
126.85
126.44
122.85
122.08
77.22
77.00
76.79
39.73
27.19
3oa 150 MHz
CDCl3
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10

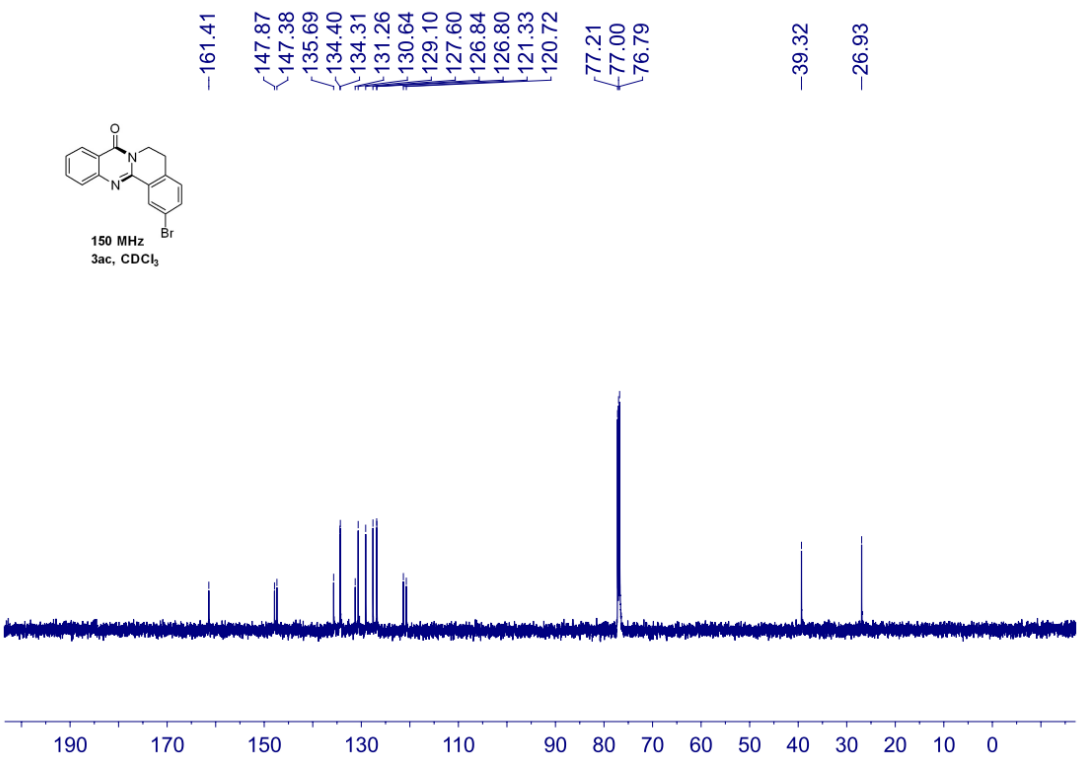

8.479
8.467
8.074
7.512
7.475
7.464
7.453
7.431
7.418
7.407
7.269
7.258
4.383
4.373
4.363
3.092
3.083
3.073
2.654
0.000
Cl
O
N
N
Me
600 MHz
3pa, CDCl3
0.99
1.00
1.03
1.03
1.03
1.14
2.04
2.05
3.04
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

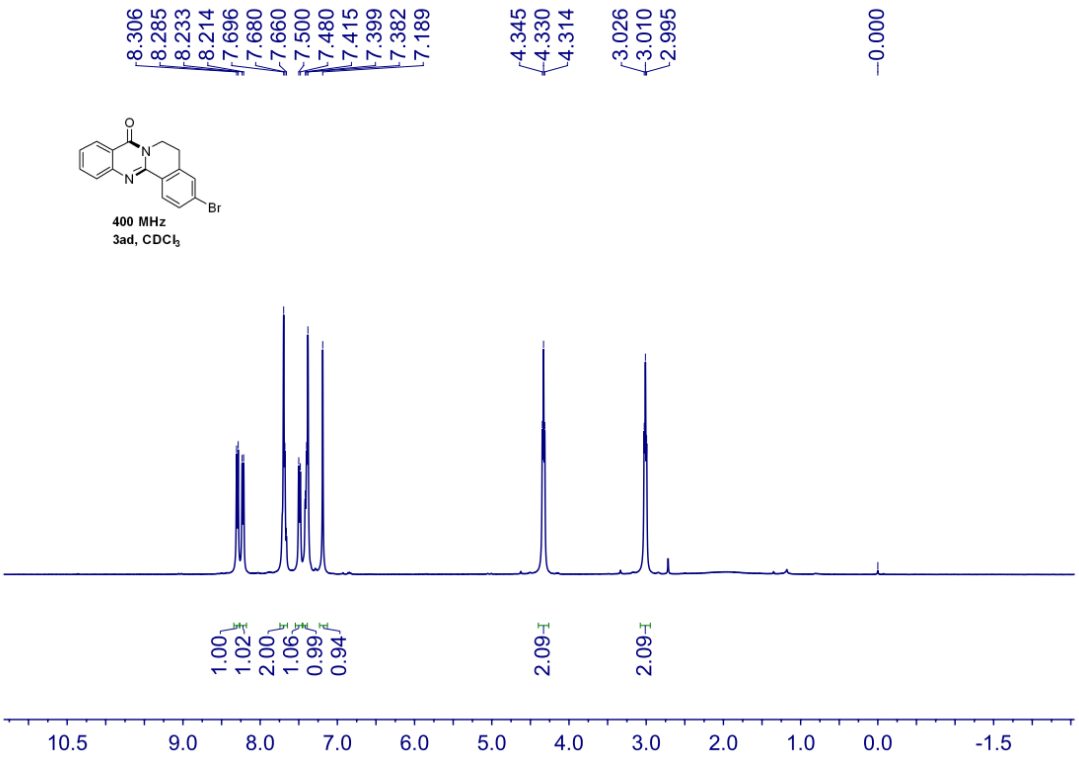

160.98
148.18
144.79
138.30
136.83
134.72
131.71
131.53
129.51
127.97
127.53
127.47
123.66
121.49
77.21
77.00
76.79
39.61
27.24
17.15
Cl
O
N
N
Me
150 MHz
3pa, CDCl3
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10

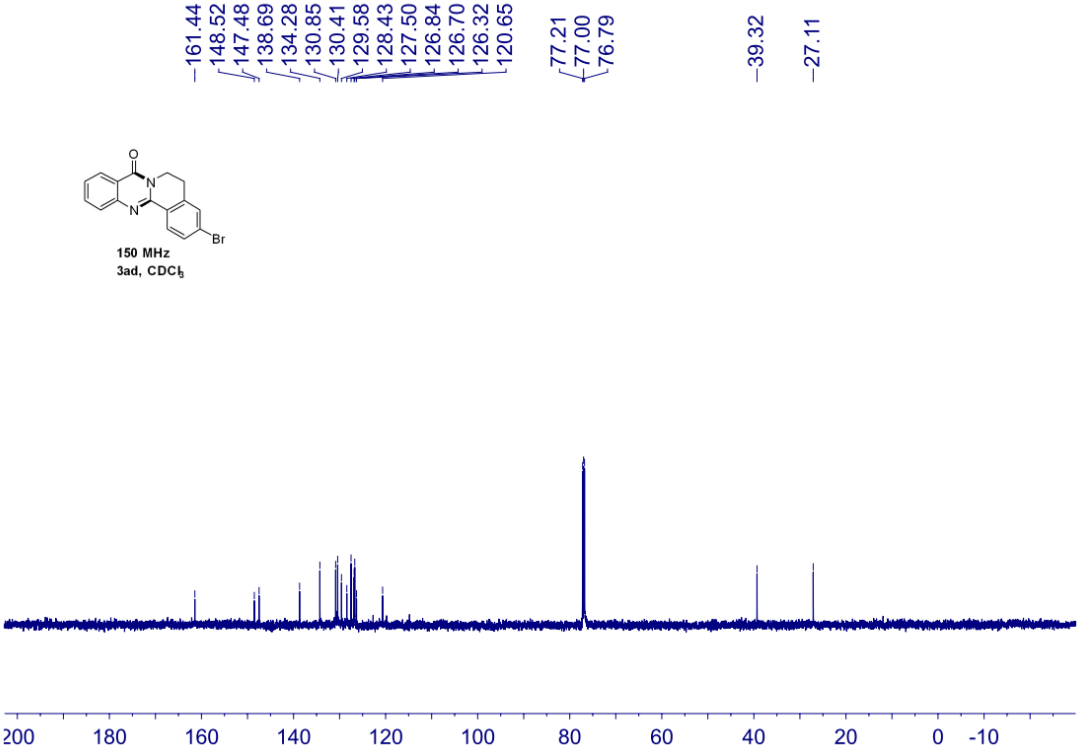

8.283
8.263
7.952
7.746
7.729
7.714
7.694
7.428
7.409
7.393
7.283
6.700
4.404
4.388
4.372
4.029
3.948
3.032
3.016
3.001
0.000
OMe
OMe
3ab, CDCl3
400 MHz
0.98
1.00
2.01
1.00
1.00
2.03
3.03
3.00
2.02
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

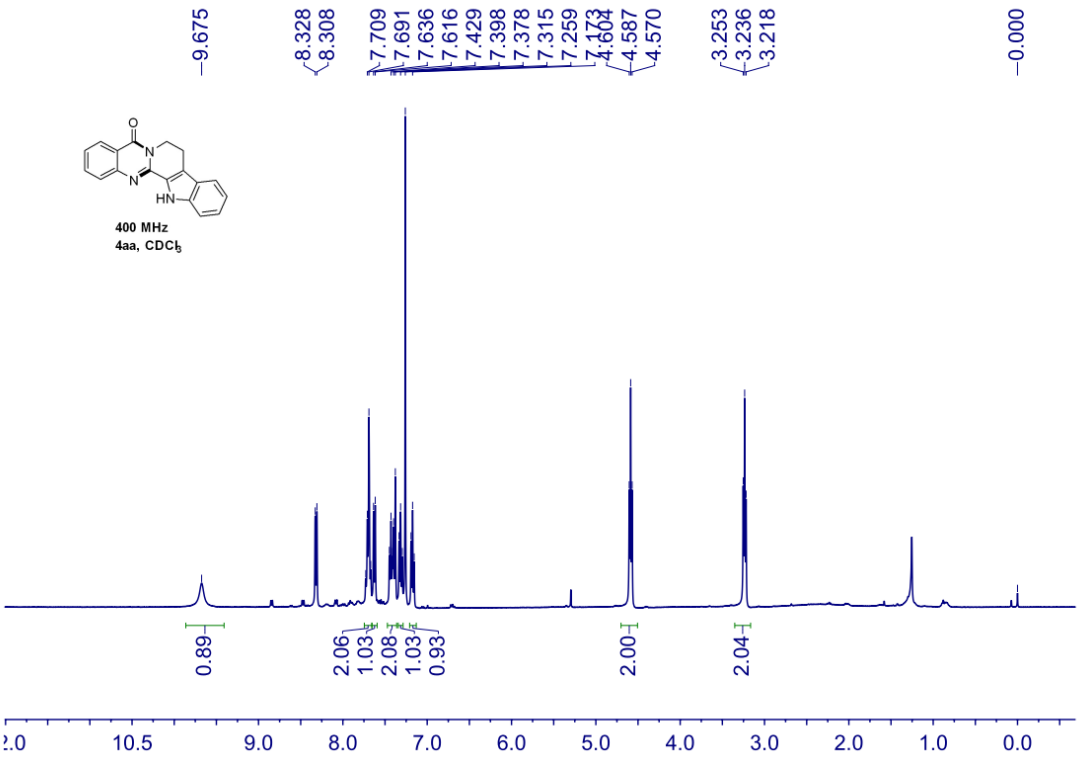

161.67
152.06
149.17
148.40
147.74
134.03
130.78
127.14
126.75
109.53
77.32
77.00
76.68
56.10
55.98
39.58
26.89
OMe
OMe
3ab, CDCl3
100 MHz
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

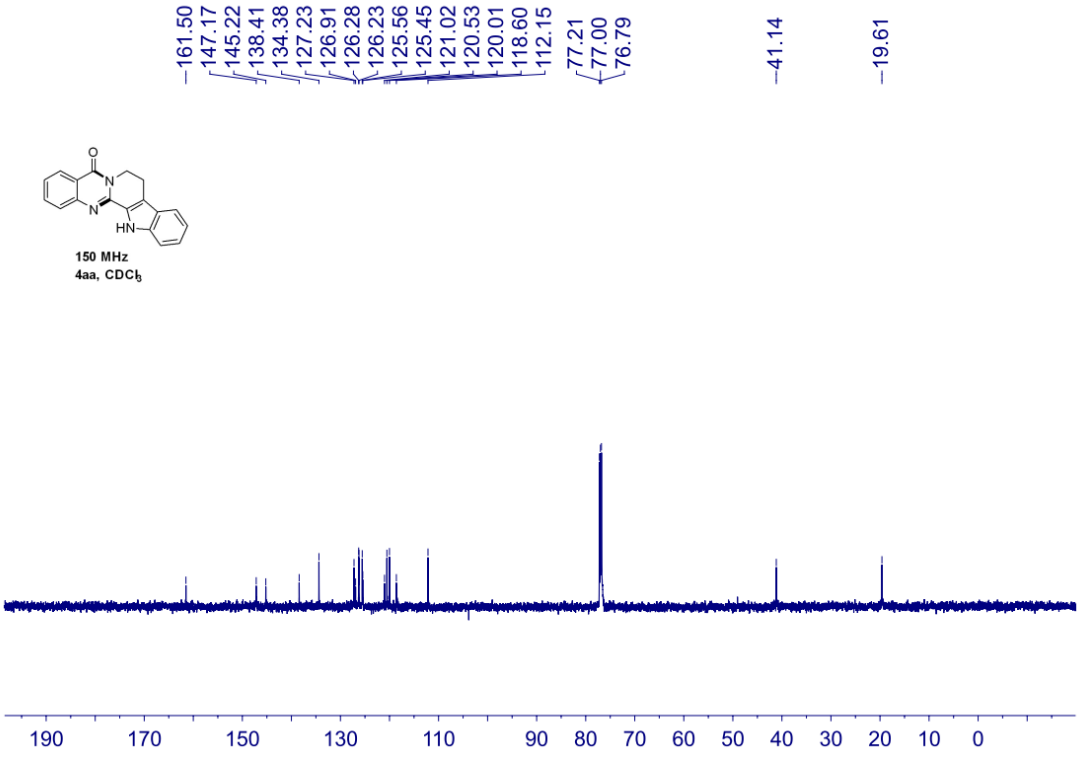

8.643
8.638
8.313
8.293
7.785
7.781
7.769
7.766
7.596
7.578
7.481
7.264
7.184
7.164
4.418
4.402
4.385
3.079
3.063
3.046
0.000
400 MHz
3ac, CDCl3
1.00
1.02
2.10
1.08
1.15
1.04
2.09
2.09
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

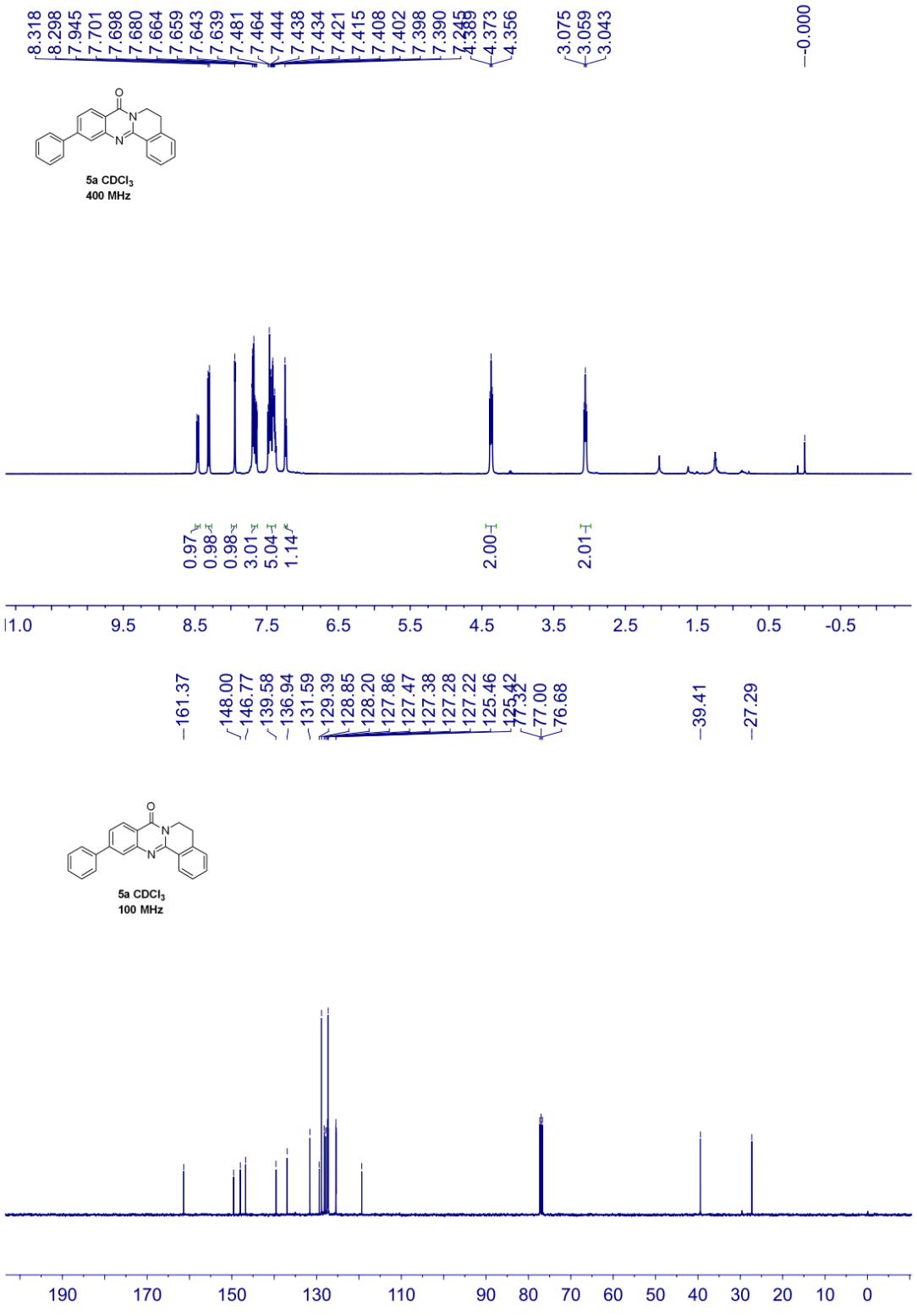

161.41
147.87
147.38
135.69
134.40
134.31
131.26
130.64
129.10
127.60
126.84
126.80
121.33
120.72
77.21
77.00
76.79
39.32
26.93
150 MHz
3ac, CDCl3
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

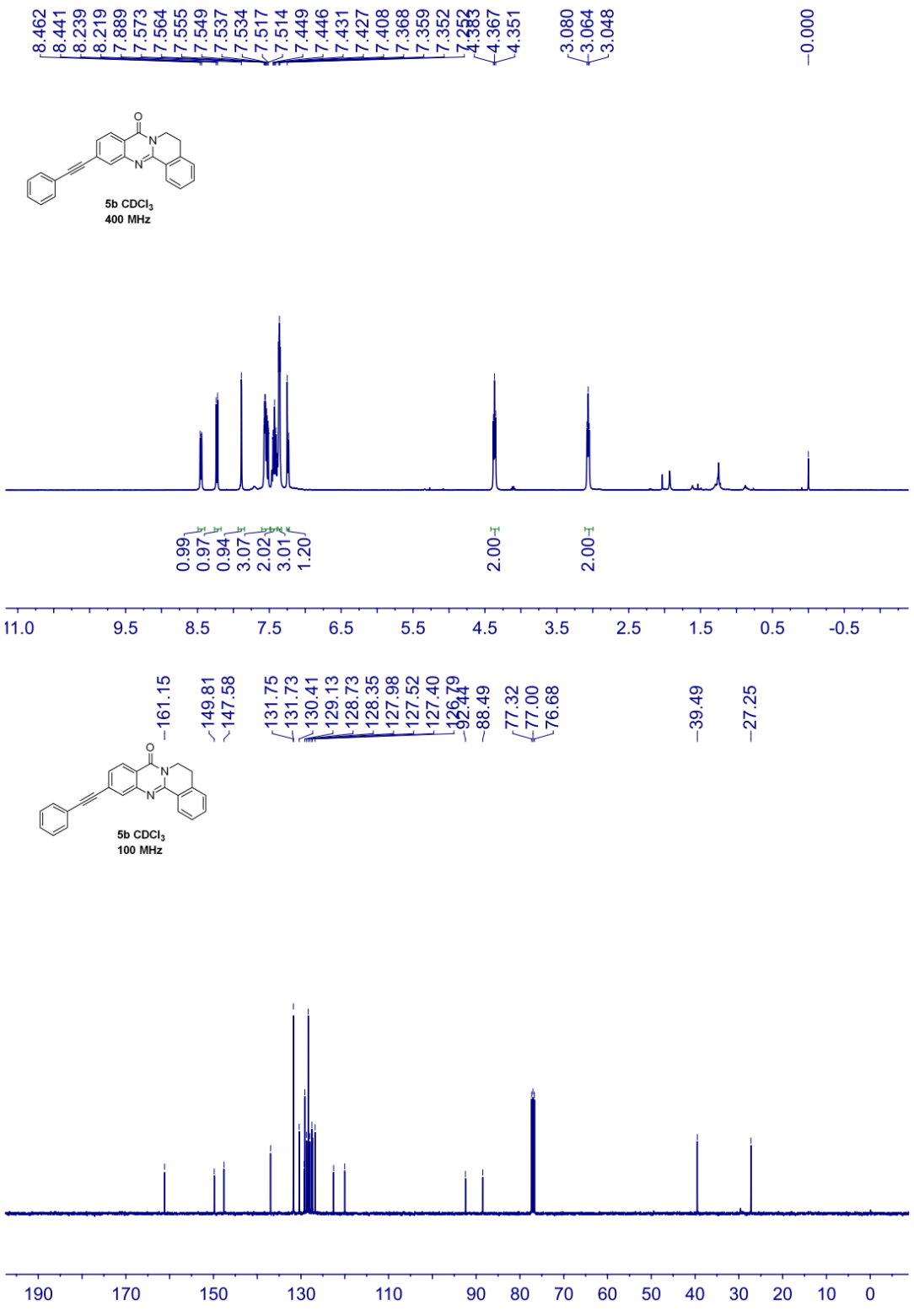

8.306
8.285
8.233
8.214
7.696
7.680
7.660
7.500
7.480
7.415
7.399
7.382
7.189
4.345
4.330
4.314
3.026
3.010
2.995
0.000
400 MHz
3ad, CDCl3
1.00
1.02
2.00
1.06
0.99
0.94
2.09
2.09
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.5


161.44
148.52
147.48
138.69
134.28
130.85
130.41
129.58
128.43
127.50
126.84
126.70
126.32
120.65
77.21
77.00
76.79
39.32
27.11
150 MHz
3ad, CDCl3
200
180
160
140
120
100
80
60
40
20
0
-10


9.675
8.328
8.308
7.709
7.691
7.636
7.616
7.429
7.398
7.378
7.315
7.259
4.604
4.587
4.570
3.253
3.236
3.218
0.000
400 MHz
4aa, CDCl3
0.89
2.06
1.03
2.08
1.03
0.93
2.00
2.04
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


161.50
147.17
145.22
138.41
134.38
127.23
126.91
126.28
126.23
125.56
125.45
121.02
120.53
120.01
118.60
112.15
77.21
77.00
76.79
41.14
19.61
150 MHz
4aa, CDCl3
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


8.318
8.298
7.945
7.701
7.698
7.680
7.664
7.659
7.643
7.639
7.481
7.464
7.444
7.438
7.434
7.421
7.415
7.408
7.402
7.398
7.390
4.373
4.356
3.075
3.059
3.043
-0.000
5a CDCl3
400 MHz
0.97
0.98
0.98
3.01
5.04
1.14
2.00
2.01
161.37
148.00
146.77
139.58
136.94
131.59
129.39
128.85
128.20
127.86
127.47
127.38
127.28
127.22
125.46
125.42
77.32
77.00
76.68
39.41
27.29
5a CDCl3
100 MHz


8.462
8.441
8.239
8.219
7.889
7.573
7.564
7.555
7.549
7.537
7.534
7.517
7.514
7.449
7.446
7.431
7.427
7.408
7.368
7.359
7.352
4.383
4.367
4.351
3.080
3.064
3.048
0.000
5b CDCl3
400 MHz
0.99
0.97
0.94
3.07
2.02
3.01
1.20
2.00
2.00
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
161.15
149.81
147.58
131.75
131.73
130.41
129.13
128.73
128.35
127.98
127.52
127.40
92.44
88.49
77.32
77.00
76.68
39.49
27.25
5b CDCl3
100 MHz
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0