Supporting Information

Installing amino acids and peptides on *N*-heterocycles under visible-light assistance

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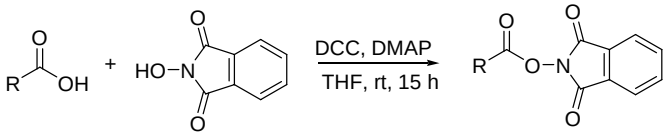
Table of contents

General experimental procedures

Reactions were carried out under N_2 or Ar atmosphere. Proton magnetic resonance spectra (^{1}H NMR) were recorded in the solvent of $CDCl_3$ using tetramethylsilane (TMS) as the internal standard (^{1}H NMR: TMS at 0.00 ppm) and referencing to the residual proton resonance of $CDCl_3$ (7.26 ppm), and carbon magnetic resonance spectra (^{13}C NMR) were recorded in the solvent of $CDCl_3$ referencing to the carbon resonance of $CDCl_3$ (77.2 ppm).

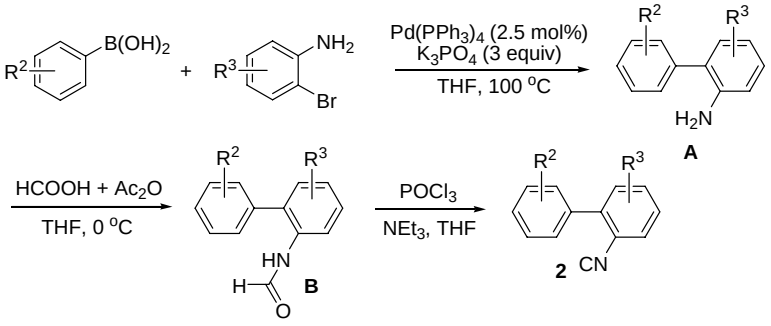
General procedure for synthesis of *N*-protected amino acid and peptide active esters (1)[1]



1

DCC (1.2 mmol) was added to a solution of *N*-protected amino acid or peptide (1 mmol), *N*-hydroxyphthalimide (1.1 mmol) and DMAP (0.1 mmol) in THF (5 mL). Reaction mixture was stirred at room temperature for 15 h, and the resulting mixture was filtered. The filtrate was evaporated by rotary evaporator, and the residue was purified by column chromatography on flash silica gel (CH_2Cl_2 or CH_2Cl_2/EtOAc) to provide *N*-protected amino acid or peptide active ester (**1**).

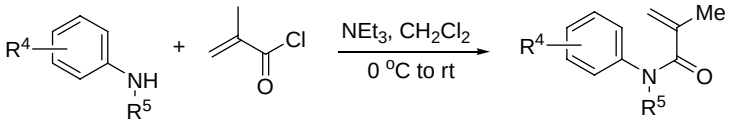
General procedure for synthesis of substituted 2-isocyanobiphenyls (2)[2]



$Pd(PPh_3)_4$ (0.025 mmol, 29 mg), aryl boronic acid (1.5 mmol), substituted 2-bromoaniline (1.0 mmol), K_3PO_4 (3.0 mmol, 636 mg) and THF (5.0 mL) were added to a 25 mL two-neck flask under N_2 atmosphere. The reaction mixture was stirred at 100 ^{o}C for 12 h. After completion of the reaction, the resulting mixture was cooled to room temperature and filtered through a short path of silica gel, eluting with PE : EA (5: 1). The volatile compounds were removed in vacuo, and the residue was

dissolved in 4.0 mL of THF. After being cooled to 0 ^{o}C, acetic formic anhydride (10 mmol, 0.9 mL), which was prepared from the reaction of acetic anhydride with formic acid at 55 ^{o}C for 2 h, was added dropwise to the solution at 0 ^{o}C. After the addition was completed, the mixture was warmed to room temperature and stirred for 1 h. The mixture was treated with saturated aqueous solution of $NaHCO_3$ and extracted with EtOAc three times (3×5 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was dissolved in 3.0 mL of THF, and NEt_3 (6 mmol, 830 μL) was added. The solution was added to an over-dried two-neck flask under N_2 atmosphere. After the reaction mixture was cooled to 0 ^{o}C with ice bath, $POCl_3$ (8.7 mmol, 0.8 mL) was added *via* syring pump for a period of 2 h. The resulting mixture was stirred at 0 ^{o}C for an additional 1 h, and then the reaction was quenched with saturated aqueous solution of $NaHCO_3$. The resulting solution was extracted with EtOAc (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated, and the residue was purified by a silica gel column chromatography to give substituted 2-isocyanobiphenyls (**2**).

General procedure for synthesis of *N*-alkyl-*N*-phenylalkacrylamides (4)



4

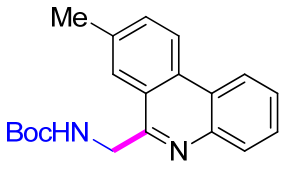
N-Alkyl phenylamine (1.0 mmol) and NEt_3 (1.5 mmol) was dissolved in anhydrous CH_2Cl_2 (10 mL), and the solution was cooled to 0 ^{o}C. Methacryloyl chloride (1.1 mmol) in CH_2Cl_2 (1.0 mL) was dropped to the solution, and the mixture was allowed to warm to room temperature and stirred overnight. The resulting solution was sequentially washed with 1N HCl (two times), saturated $NaHCO_3$ solution (two times) and brine. The organic layer was dried over Na_2SO_4, filtered and evaporated under vacuum. The residue was purified by a silica gel column chromatography to give *N*-alkyl-*N*-phenylalkacrylamides (**4**).

General procedure for synthesis of compounds 3a-af and 5a-e

$[Ru(bpy)_3]Cl_2$ (1.5 μmol, 1.2 mg), **1** (0.45 mmol for synthesis of 3**a-p**; 0.30 mmol for synthesis of the others), **2** (0.15 mmol) or **4** (0.15 mmol), DIPEA (0.6 mmol, 10 μL)

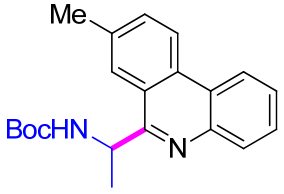
and K_2CO_3 (0.18 mmol, 25 mg) were added to a 25-mL Schlenk tube with DMF (2.0 mL) or mixed solvent of CH_2Cl_2 and DMF (2.0 mL, CH_2Cl_2/DMF (5:1)), and the tube was degassed by argon sparging for over 5 min. The tube was sealed, and then irradiated with a 40 W fluorescent lamp (approximately 2 cm away from the light source). After the complete conversion of the substrates (monitored by TLC), the reaction mixture was diluted with 20 mL of EtOAc, and the solution was filtered by flash chromatography. The filtrate was evaporated by rotary evaporator, and the residue was purified by silica gel column chromatography to give the desired product (**3a-af** and **5a-e**).

Characterization data of compounds 3a-ae and 5a-e



3a

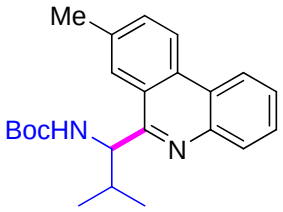
***tert*-Butyl ((8-methylphenanthridin-6-yl)methyl)carbamate (3a).** Eluent: PE/EtOAc (15:1). Yield 30.9 mg (64%). White solid, mp 134-136 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.46 (d, *J* = 8.2 Hz, 2H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.88 (s, 1H), 7.70-7.60 (m, 3H), 6.62 (s, 1H), 4.97 (s, 1H), 2.56 (s, 2H), 1.56 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.2, 154.4, 142.6, 137.8, 132.6, 130.6, 129.6, 128.3, 126.9, 124.2, 124.1, 122.4, 121.9, 79.5, 43.7, 28.6, 21.8. HRMS (ESI^+): Calcd for $C_{20}H_{22}N_2O_2$, $[M+H]^+$ m/z 323.1754. Found 323.1752.



3b

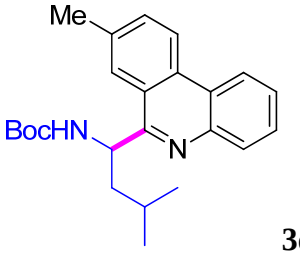
***tert*-Butyl-(1-(8-methylphenanthridin-6-yl)ethyl)carbamate (3b).** Eluent: PE/EtOAc (15:1). Yield 43.0 mg (85%). White solid, mp 162-164 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.48 (t, *J* = 7.8 Hz, 2H), 8.11 (d, *J* = 7.8 Hz, 1H), 8.00 (s, 1H), 7.69-7.58 (m, 3H), 6.75 (d, *J* = 7.3 Hz, 1H), 5.73 (q, *J* = 6.9 Hz, 1H), 2.57 (s, 3H), 1.61 (d, *J* = 6.9 Hz, 3H), 1.52 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.1, 155.6, 142.7, 137.6, 132.4, 131.1, 129.7, 128.3, 126.8, 124.9, 124.0, 123.5, 122.6, 121.9,

79.3, 47.6, 28.6, 23.2, 21.9. HRMS (ESI$^+$): Calcd for $C_{21}H_{24}N_2O_2$, $[M+H]^+$ m/z 337.1911. Found 337.1916.



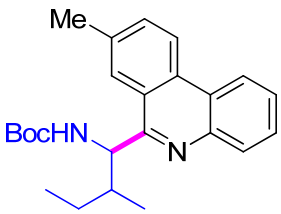
3c

***tert*-Butyl-(2-methyl-1-(8-methylphenanthridin-6-yl)propyl)carbamate (3c).** Eluent: PE/EtOAc (15:1). Yield 44.4 mg (81%). White solid, mp 177-179 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.47 (dd, J_1 = 6.0 Hz, J_2 = 7.3 Hz, 2H), 8.11 (d, J = 8.2 Hz, 1H), 8.06 (s, 1H), 7.68-7.57 (m, 3H), 6.38 (d, J = 8.7 Hz, 1H), 5.63 (dd, J_1 = 8.7 Hz, J_2 = 5.0 Hz, 1H), 2.58 (s, 3H), 2.32-2.25 (m, 1H), 1.48 (s, 9H), 1.08 (d, J = 6.8 Hz, 3H), 0.87 (d, J = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.7, 156.4, 142.7, 137.4, 132.3, 130.9, 129.9, 128.2, 126.7, 125.3, 124.4, 123.9, 122.5, 121.8, 79.1, 55.5, 34.6, 28.6, 22.0, 20.7, 17.2. HRMS (ESI$^+$): Calcd for $C_{23}H_{28}N_2O_2$, $[M+H]^+$ m/z 365.2224. Found 365.2220.



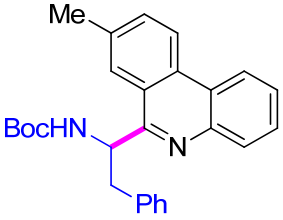
3d

***tert*-Butyl-(3-methyl-1-(8-methylphenanthridin-6-yl)butyl)carbamate (3d).** Eluent: PE/EtOAc (15:1). Yield 48.9 mg (86%). White solid, mp 175-177 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.48 (t, J = 7.8 Hz, 2H), 8.11-8.06 (m, 2H), 7.68-7.57 (m, 3H), 6.34 (d, J = 8.7 Hz, 1H), 5.81 (dd, J_1 = 7.8 Hz, J_2 = 6.0 Hz, 1H), 2.58 (s, 3H), 1.95-1.88 (m, 1H), 1.73-1.70 (m, 1H), 1.48 (s, 9H), 1.20 (d, J = 6.4 Hz, 3H), 0.91 (d, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.6, 156.1. 142.9. 137.5. 132.3. 131.0. 129.8. 128.2. 126.7. 124.9. 124.0. 123.8. 122.5. 121.9. 79.2. 49.7. 47.1. 28.6. 25.4. 23.8. 22.3. 22.0. HRMS (ESI$^+$): Calcd for $C_{24}H_{30}N_2O_2$, $[M+H]^+$ m/z 379.2380. Found 379.2375.



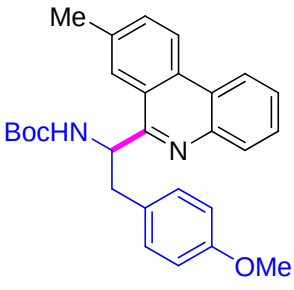
3e

***tert*-Butyl-(2-methyl-1-(8-methylphenanthridin-6-yl)butyl)carbamate (3e).** Eluent: PE/EtOAc (15:1). Yield 50.1 mg (88%). White solid, mp 145-147 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.47 (m, 2H), 8.12-8.04 (m, 2H), 7.68-7.57 (m, 3H), 6.43 and 6.31 (d, J = 8.7 Hz, 1H), 5.79 and 5.65 (dd, J_1 = 8.7 Hz, J_2 = 5.5 Hz, 1H), 2.58 and 2.57 (s, 3H), 2.02 (m, 1H), 1.69 and 1.36 (m, 1H), 1.49 and 1.47 (s, 9H), 1.25-1.17 (m, 1H), 1.12-0.98 (m, 3H), 0.82-0.76 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.0, 159.6, 156.5, 156.3, 142.7, 142.6, 137.7, 137.4, 132.3, 132.2, 131.0, 130.9, 129.9, 128.2, 126.7, 126.6, 125.3, 125.2, 124.6, 124.2, 123.9, 122.5, 122.4, 121.9, 79.1, 55.2, 53.9, 41.4, 41.2, 28.6, 27.8, 23.8, 22.0, 16.9, 13.8, 12.4, 11.8. HRMS (ESI$^+$): Calcd for $C_{24}H_{30}N_2O_2$, $[M+H]^+$ m/z 379.2380. Found 379.2378.



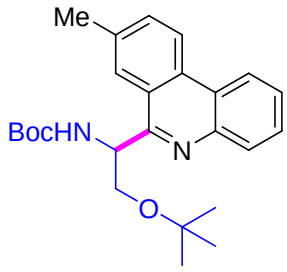
3f

***tert*-Butyl-(1-(8-methylphenanthridin-6-yl)-2-phenylethyl)carbamate (3f).** Eluent: PE/EtOAc (15:1). Yield 48.3 mg (78%). White solid, mp 116-118 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.45 (t, J = 7.3 Hz, 2H), 8.06 (d, J = 7.8 Hz, 1H), 7.80 (s, 1H), 7.65-7.56 (m, 3H), 7.07 (s, 3H), 7.00 (s, 2H), 6.40 (d, J = 7.8 Hz, 1H), 5.93 (q, J = 6.9 Hz, 1H), 3.38 (dd, J_1 = 6.9 Hz, J_2 = 13.3 Hz, 1H), 3.26 (dd, J_1 = 5.5 Hz, J_2 = 13.3 Hz, 1H), 2.46 (s, 3H), 1.46 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.9, 155.5, 142.8, 137.6, 137.3, 132.3, 130.8, 129.9, 129.8, 128.2, 128.0, 126.9, 126.4, 125.2, 124.2, 124.0, 122.3, 121.9, 79.4, 52.5, 43.1, 28.6, 21.8. HRMS (ESI$^+$): Calcd for $C_{27}H_{28}N_2O_2$, $[M+H]^+$ m/z 413.2224. Found 413.2219.



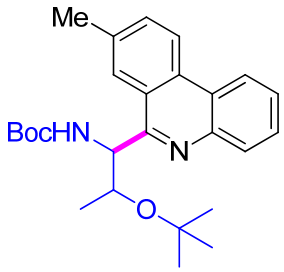
3g

***tert*-Butyl-(2-(4-methoxyphenyl)-1-(8-methylphenanthridin-6-yl)ethyl)carbamate (3g).** Eluent: PE/EtOAc (5:1). Yield 55.2 mg (83%). White solid, mp 138-140 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.49 (dd, J_1 = 5.0 Hz, J_2 = 8.2 Hz, 2H), 8.07 (d, J = 7.3 Hz, 1H), 7.82 (s, 1H), 7.69-7.59 (m, 3H), 6.85 (d, J = 8.2 Hz, 2H), 6.62 (d, J = 8.2 Hz, 2H), 6.40 (d, J = 8.6 Hz, 1H), 5.88 (q, J = 6.4 Hz, 1H), 3.70 (s, 3H), 3.28 (dd, J_1 = 6.9 Hz, J_2 = 13.3 Hz, 1H), 3.21 (dd, J_1 = 6.0 Hz, J_2 = 13.3 Hz, 1H), 2.48 (s, 3H), 1.46 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.0, 158.2, 155.5, 142.8, 137.3, 134.3, 132.3, 130.8, 129.8, 129.7, 128.2, 126.8, 125.2, 124.2, 124.0, 122.3, 121.9, 113.4, 79.3, 55.2, 52.6, 42.1, 28.6, 21.8. HRMS (ESI$^+$): Calcd for $C_{28}H_{30}N_2O_3$, $[M+H]^+$ m/z 443.2329. Found 443.2324.



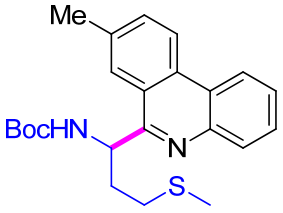
3h

***tert*-Butyl-(2-(tert-butoxy)-1-(8-methylphenanthridin-6-yl)ethyl)carbamate (3h).** Eluent: PE/EtOAc (15:1). Yield 19.6 mg (32%). White solid, mp 195-197 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.51 (d, J = 8.7 Hz, 2H), 8.24 (s, 1H), 8.12 (d, J = 8.7 Hz, 1H), 7.71-7.59 (m, 3H), 6.41 (d, J = 7.3 Hz, 1H), 5.81 (q, J = 6.6 Hz, 1H), 3.84 (dd, J_1 = 5.5 Hz, J_2 = 9.2 Hz, 1H), 3.68 (dd, J_1 = 6.9 Hz, J_2 = 9.2 Hz, 1H), 2.60 (s, 3H), 1.49 (s, 9H), 0.98 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.7, 155.7, 142.9, 137.0, 132.3, 130.7, 129.8, 128.1, 126.8, 126.5, 125.0, 124.1, 122.0, 121.9, 79.3, 73.2, 66.1, 51.8, 28.6, 27.3, 21.8. HRMS (ESI$^+$): Calcd for $C_{25}H_{32}N_2O_3$, $[M+H]^+$ m/z 409.2486. Found 409.2483.



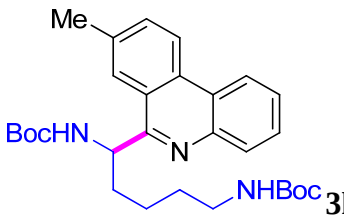
3i

***tert*-Butyl-(2-(tert-butoxy)-1-(8-methylphenanthridin-6-yl)propyl)carbamate (3i).** Eluent: PE/EtOAc (15:1). Yield 56.5 mg (89%). White solid, mp 163-165 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.55-8.47 (m, 2H), 8.28-8.22 (m, 1H), 8.17-8.06 (m, 1H) 7.71-7.58 (m, 3H), 6.54 and 6.36 (d, *J* = 7.3 Hz, 1H), 5.73-5.61 (m, 1H), 4.24-3.83 (m, 1H), 2.60 (s, 1H), 1.49 and 1.46 (s, 9H), 1.35 (brd, *J* = 6.9 Hz, 2H), 1.14 (brd, *J* = 5.5 Hz 1H), 1.05 (brs, 2.7H), 0.62 (brs, 6.3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.8, 157.8, 156.0, 155.9, 142.9, 142.7, 136.8, 132.2, 131.0, 130.3, 130.0, 129.7, 128.1, 128.0, 127.3, 126.8, 126.7, 126.5, 126.0, 125.2, 124.0, 122.2, 121.9, 121.8, 121.7, 79.2, 77.3, 74.2, 73.7, 72.7, 70.4, 55.7, 55.5, 28.6, 28.5, 28.2, 28.0, 22.0, 21.8, 20.5, 19.4. HRMS (ESI$^+$): Calcd for $C_{26}H_{34}N_2O_3$, $[M+H]^+$ m/z 423.2642. Found 423.2639.



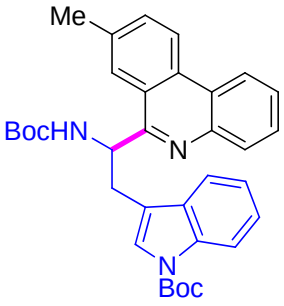
3j

***tert*-Butyl-(1-(8-methylphenanthridin-6-yl)-3-(methylthio)propyl)carbamate (3j).** Eluent: PE/EtOAc (15:1). Yield 55.4 mg (93%). White solid, mp 161-163 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.48 (t, *J* = 7.8 Hz, 2H), 8.11 (s, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.69-7.58 (m, 3H), 6.55 (d, *J* = 7.8 Hz, 1H), 5.92-5.85 (m, 1H), 2.78-2.69 (m, 1H), 2.58 (s, 3H), 2.55-2.46 (m, 1H), 2.38-2.28 (m, 1H), 2.12-2.00 (m, 4H), 1.50 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.9, 156.0, 142.6, 137.7, 132.5, 131.0, 129.8, 128.3, 126.9, 124.9, 124.0, 123.7, 122.6, 121.9, 79.5, 50.4, 36.7, 30.6, 28.6, 21.9, 15.6. HRMS (ESI$^+$): Calcd for $C_{23}H_{28}N_2O_2S$, $[M+H]^+$ m/z 397.1944. Found 397.1939.



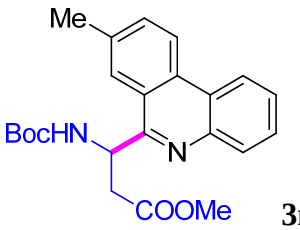
3k

Di-*tert*-butyl-(1-(8-methylphenanthridin-6-yl)pentane-1,5-diyl)dicarbamate (3k). Eluent: PE/EtOAc (5:1). Yield 60.1 mg (81%). White solid, mp 146-148 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.48 (t, *J* = 8.7 Hz, 2H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.99 (s, 1H), 7.68-7.57 (m, 3H), 6.54 (d, *J* = 7.8 Hz, 1H), 5.76-5.66 (m, 1H), 4.70 (s, 1H), 3.16-2.98 (m, 2H), 2.58 (s, 3H), 2.10-1.97 (m, 1H), 1.84-1.72 (m, 1H), 1.68-1.32 (m, 4H), 1.49 (s, 9H) , 1.40 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.5, 156.1, 142.6, 137.6, 132.5, 131.0, 129.8, 128.2, 126.8, 124.8, 124.0, 123.7, 122.6, 121.9, 79.4, 78.9, 50.7, 40.6, 36.9, 29.5, 28.6, 28.5, 22.8, 22.0. HRMS (ESI$^+$): Calcd for $C_{29}H_{39}N_3O_4$, $[M+H]^+$ m/z 494.3013. Found 494.3010.



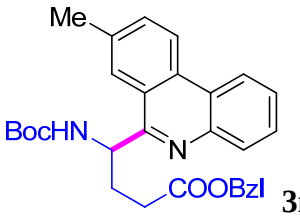
3l

***tert*-Butyl-3-(2-((tert-butoxycarbonyl)amino)-2-(8-methylphenanthridin-6-yl)ethyl)-1H-indole-1-carboxylate (3l).** Eluent: PE/EtOAc (15:1). Yield 50.5 mg (61%). Clear oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.51-8.42 (m, 2H), 8.09-8.01 (m, 2H), 7.74 (s, 1H), 7.69-7.58 (m, 2H), 7.55 (d, *J* = 9.2 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.21 (t, *J* = 8.2 Hz, 1H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.90 (s, 1H), 6.53 (d, *J* = 7.3 Hz, 1H), 6.02 (q, *J* = 7.8 Hz, 1H), 3.40 (d, *J* = 6.9 Hz, 2H), 2.32 (s, 3H), 1.50 (s, 9H), 1.49 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.9, 155.6, 149.5, 142.7, 137.2, 135.4, 132.3, 131.2, 130.7, 129.8, 128.2, 126.9, 125.0, 124.3, 124.2, 124.1, 124.0, 122.5, 122.2, 121.8, 119.1, 116.4, 115.0, 83.0, 79.4, 51.1, 32.4, 28.6, 28.1, 21.6. HRMS (ESI$^+$): Calcd for $C_{34}H_{37}N_3O_4$, $[M+H]^+$ m/z 552.2857. Found 552.2856.



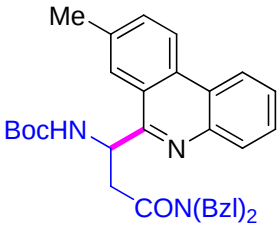
3m

Methyl-3-((*tert*-butoxycarbonyl)amino)-3-(8-methylphenanthridin-6-yl)propanoate (3m). Eluent: PE/EtOAc (5:1). Yield 48.6 mg (82%). White solid, mp 162-164 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.48 (t, *J* = 8.2 Hz, 2H), 8.18 (s, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.68-7.59 (m, 3H), 6.22 (d, *J* = 8.7 Hz, 1H), 6.15-6.07 (m, 1H), 3.66 (s, 3H), 3.11 (dd, J_1 = 5.5 Hz, J_2 = 14.6 Hz, 1H), 2.91 (dd, J_1 = 6.9 Hz, J_2 = 14.6 Hz, 1H), 2.59 (s, 3H), 1.48 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.9, 157.8, 155.3, 142.6, 137.8, 132.6, 131.2, 129.9, 128.3, 127.1, 125.0, 124.2, 123.9, 122.5, 121.9, 79.8, 51.9, 49.0, 40.7, 28.5, 22.0. HRMS (ESI$^+$): Calcd for $C_{23}H_{26}N_2O_4$, $[M+H]^+$ m/z 395.1965. Found 395.1966.



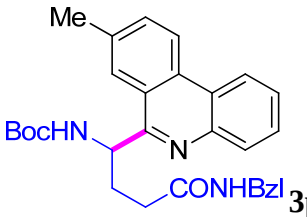
3n

Benzyl-4-((*tert*-butoxycarbonyl)amino)-4-(8-methylphenanthridin-6-yl)butanoate (3n). Eluent: PE/EtOAc (5:1). Yield 55.3 mg (76%). Clear oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.48 (t, *J* = 7.3 Hz, 2H), 8.17 (s, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.68-7.59 (m, 3H), 7.33-7.25 (m, 5H), 6.61 (d, *J* = 7.3 Hz, 1H), 5.88-5.81 (m, 1H), 5.08 (d, *J* = 12.4 Hz, 1H), 5.00 (d, *J* = 12.4 Hz, 1H), 2.69-2.60 (m, 1H), 2.59 (s, 3H), 2.55-2.37 (m, 1H), 2.10-2.01 (m, 1H), 1.49 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.3, 158.8, 156.0, 142.6, 137.8, 136.1, 132.6, 131.0, 129.8, 128.7, 128.6, 128.3, 128.2, 127.0, 125.1, 124.1, 123.8, 122.5, 121.9, 79.5, 66.3, 50.3, 31.7, 30.1, 28.6, 22.0. HRMS (ESI$^+$): Calcd for $C_{30}H_{32}N_2O_4$, $[M+H]^+$ m/z 485.2435. Found 485.2434.



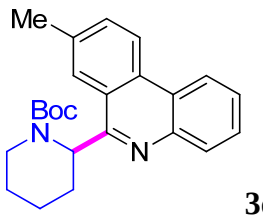
3o

***tert*-Butyl-(3-(dibenzylamino)-1-(8-methylphenanthridin-6-yl)-3-oxopropyl)carbamate (3o).** Eluent: PE/EtOAc (5:1). Yield 56.3 mg (67%). White solid, mp 181-183 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.53 (d, J = 7.9 Hz, 2H), , 8.40 (s, 1H), 8.01 (d, J = 7.6 Hz, 1H), 7.68-7.61 (m, 3H), 7.37-6.98 (m, 10H), 6.39-6.33 (m, 1H), 5.80 (m, 1H), 4.63-4.35 (m, 4H), 3.62-3.55 (m, 1H), 3.16-3.09 (m, 1H), 2.61 (s, 3H), 1.44 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.6, 159.2, 155.2, 142.7, 137.9, 137.2, 136.8, 132.6, 131.2, 129.8, 129.0, 128.5, 128.2, 128.1, 127.6, 127.2, 127.0, 126.7, 125.9, 124.6, 124.5, 122.3, 122.0, 79.7, 50.2, 49.4, 48.1, 37.9, 28.5, 22.0. HRMS (ESI$^+$): Calcd for $C_{36}H_{37}N_3O_3$, $[M+H]^+$ m/z 560.2908. Found 560.2905.



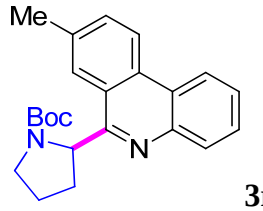
3p

***tert*-Butyl-(4-(benzylamino)-1-(8-methylphenanthridin-6-yl)-4-oxobutyl)carbamate (3p).** Eluent: PE/EtOAc (1:1). Yield 54.5 mg (75%). White solid, mp 176-178 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.51 (dd, J_1 = 4.1 Hz, J_2 = 7.8 Hz, 2H), 8.08 (d, J = 7.8 Hz, 1H), 7.94 (s, 1H), 7.70-7.61 (m, 3H), 7.39-7.23 (m, 5H), 7.11(s, 1H), 6.81 (d, J = 7.3 Hz, 1H), 5.74 (t, J = 7.3 Hz, 1H), 4.56 (dd, J_1 = 5.5 Hz, J_2 = 15.1 Hz, 1H), 4.50 (dd, J_1 = 5.5 Hz, J_2 = 15.1 Hz, 1H), 2.59-2.41 (m, 2H), 2.54 (s, 3H), 2.38-2.27 (m, 1H), 2.02-1.88 (m, 1H), 1.50 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.8, 158.7, 156.8, 142.4, 138.7, 138.0, 132.7, 131.0, 129.7, 128.7, 128.3, 127.9, 127.4, 127.0, 125.0, 124.2, 123.5, 122.5, 122.0, 79.8, 50.6, 43.8, 34.1, 33.2, 28.5, 22.0. HRMS (ESI$^+$): Calcd for $C_{30}H_{33}N_3O_3$, $[M+H]^+$ m/z 484.2595. Found 484.2594.



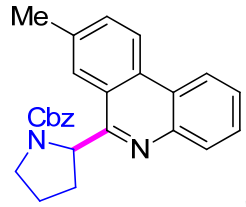
3q

***tert*-Butyl-2-(8-methylphenanthridin-6-yl)piperidine-1-carboxylate (3q).** Eluent: PE/EtOAc (15:1). Yield 51.5 mg (91%). White solid, mp 123-125 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.48 (t, *J* = 8.7 Hz, 2H), 8.09 (d, *J* = 8.2 Hz, 2H), 7.66-7.56 (m, 3H), 6.15 (m, 1H), 4.00 (m, 1H), 3.60 (m, 1H), 2.56 (s, 3H), 2.34 (m, 1H), 2.11-1.82 (m, 2H), 1.78-1.50 (m, 3H), 1.36 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.7, 156.2, 142.8, 137.1, 131.8, 131.0, 130.4, 128.0, 126.6, 125.3, 124.5, 123.8, 122.5, 121.7, 79.4, 52.9, 42.6, 28.6, 28.5, 25.6, 22.0, 19.8. HRMS (ESI$^+$): Calcd for $C_{24}H_{28}N_2O_2$, $[M+H]^+$ m/z 377.2224. Found 377.2224.



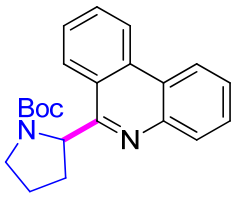
3r

***tert*-Butyl-2-(8-methylphenanthridin-6-yl)pyrrolidine-1-carboxylate (3r).** Eluent: PE/EtOAc (5:1). Yield 49.5 mg (91%). White solid, mp 201-203 °C. The product gives two sets of NMR signals, owing to the presence of rotamers around the tertiary amide.[3] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.56-8.49 (m, 2H), 8.09-8.00 (m, 2H), 7.67-7.59 (m, 3H), 5.90-5.70 (m, 1H), 4.01-3.90 (m, 1H), 3.79-3.58 (m, 1H), 2.61-2.42 (m, 4H), 2.08-1.95 (m, 3H), 1.47 (brs, 3.5H), 0.94 (brs, 5.5H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.9, 160.0, 154.9, 154.8, 143.3, 143.2, 137.0, 131.9, 131.8, 131.2, 130.9, 130.3, 128.2, 127.8, 126.4, 126.3, 124.8, 124.6, 124.3, 124.1, 123.7, 122.6, 121.7, 79.0, 78.8, 59.9, 59.3, 47.2, 47.0, 33.4, 32.2, 28.7, 28.1, 23.8, 23.5, 22.0. HRMS (ESI$^+$): Calcd for $C_{23}H_{26}N_2O_2$, $[M+H]^+$ m/z 363.2067. Found 363.2063.



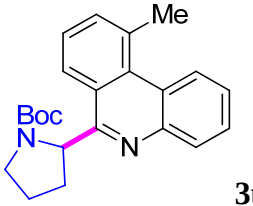
3s

Benzyl-2-(8-methylphenanthridin-6-yl)pyrrolidine-1-carboxylate (3s). Eluent: PE/EtOAc (5:1). Yield 54.8 mg (92%). White solid, mp 111-113 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.52-8.42 (m, 2H), 8.06-7.94 (m, 2H), 7.79-7.54 (m, 4H), 7.42-7.28 (m, 2H), 6.79 and 6.65 (d, *J* = 7.3 Hz, 2H), 5.96 and 5.85 (d, *J* = 7.8 Hz, 1H), 5.22 and 5.12 (d, *J* = 12.8 Hz, 1H), 4.98 and 4.82 (d, *J* = 12.8 Hz, 1H), 4.10-3.99 (m, 1H), 3.84-3.69 (m, 1H), 2.60-2.43 (m, 4H), 2.15-1.91 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.1, 159.7, 156.2, 143.2, 137.1, 136.9, 134.2, 132.0, 131.2, 130.6, 130.5, 128.5, 128.2, 127.9, 127.8, 127.7, 127.1, 126.9, 126.6, 126.5, 124.8, 124.6, 124.2, 124.1, 124.0, 123.9, 123.5, 122.7, 122.6, 121.7, 121.6, 66.6, 66.3, 59.6, 59.5, 47.7, 47.0, 33.4, 32.3, 23.8, 23.2, 22.0. HRMS (ESI$^+$): Calcd for $C_{26}H_{24}N_2O_2$, $[M+H]^+$ m/z 397.1911 Found 397.1909.



3t

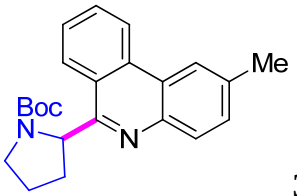
***tert*-Butyl-2-(phenanthridin-6-yl)pyrrolidine-1-carboxylate (3t).** Eluent: PE/EtOAc (5:1). Yield 48.2 mg (92%). White solid, mp 146-148 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.69-8.60 (m, 1H), 8.57-8.48 (m, 1H), 8.29-8.23 (m, 1H), 8.12-8.04 (m, 1H), 7.85-7.76 (m, 1H), 7.72-7.56 (m, 3H), 5.92-5.68 (m, 1H), 4.00-3.87 (m, 1H), 3.76-3.59 (m, 1H), 2.58-2.44 (m, 1H), 2.15-1.86 (m, 3H), 1.47 (brs, 2.9H), 0.93 (brs, 6.1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.3, 160.2, 154.9, 154.8, 143.6, 143.5, 133.4, 133.2, 130.4, 130.2, 130.1, 128.6, 128.3, 127.2, 127.1, 126.5, 126.4, 125.3, 125.0, 124.1, 124.0, 123.9, 123.6, 122.8, 122.7, 121.9, 79.1, 78.8, 60.2, 59.4, 47.2, 47.0, 33.4, 32.3, 28.7, 28.1, 23.8, 23.5. HRMS (ESI$^+$): Calcd for $C_{22}H_{24}N_2O_2$, $[M+H]^+$ m/z 349.1911. Found 349.1915.



3u

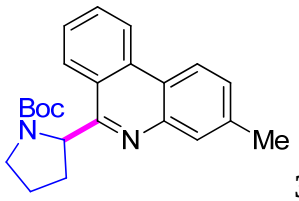
***tert*-Butyl-2-(10-methylphenanthridin-6-yl)pyrrolidine-1-carboxylate (3u).** Eluent:

PE/EtOAc (5:1). Yield 27.2 mg (50%). White solid, mp 131-133 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.81-8.73 (m, 1H), 8.20-8.09 (m, 2H), 7.71-7.53 (m, 4H), 5.92-5.71 (m, 1H), 4.01-3.88 (m, 1H), 3.76-3.59 (m, 1H), 3.14 and 3.10 (s, 3H), 2.60-2.43 (m, 1H), 2.12-1.87 (m, 3H), 1.48 (brs, 3.1H), 0.95 (brs, 5.9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.4, 160.4, 155.0, 154.9, 144.8, 144.7, 135.9, 135.8, 134.4, 134.3, 132.7, 130.8, 127.9, 127.6, 126.6, 126.5, 126.4, 125.7, 125.5, 125.4, 125.3, 125.1, 123.7, 123.4, 79.0, 78.7, 60.3, 59.8, 47.2, 47.0, 33.3, 32.3, 28.7, 28.2, 27.1, 27.0, 23.7, 23.4. HRMS (ESI$^+$): Calcd for $C_{23}H_{26}N_2O_2$, $[M+H]^+$ m/z 363.2067. Found 363.2066.



3v

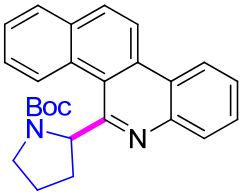
***tert*-Butyl-2-(2-methylphenanthridin-6-yl)pyrrolidine-1-carboxylate (3v).** Eluent: PE/EtOAc (5:1). Yield 50.2 mg (92%). White solid, mp 178-180 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.67-8.59 (m, 1H), 8.33-8.20 (m, 2H), 8.01-7.93 (m, 1H), 7.82-7.74 (m, 1H), 7.67-7.61 (m, 1H), 7.53-7.46 (m, 1H), 5.89-5.66 (m, 1H), 3.98-3.88 (m, 1H), 3.76-3.59 (m, 1H), 2.63-2.43 (m, 4H), 2.14-1.87 (m, 3H), 1.47 (brs, 2.7H), 0.92 (brs, 6.3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.2, 159.2, 154.9, 154.8, 142.0, 141.8, 136.3, 136.1, 133.2, 132.9, 130.3, 130.1, 130.0, 129.8, 127.0, 126.9, 125.2, 125.0, 124.0, 123.8, 123.4, 122.7, 122.6, 121.5, 79.0, 78.8, 60.2, 59.4, 47.2, 47.0, 33.4, 32.2, 28.7, 28.1, 23.8, 23.5, 22.0. HRMS (ESI$^+$): Calcd for $C_{23}H_{26}N_2O_2$, $[M+H]^+$ m/z 363.2067. Found 363.2070.



3w

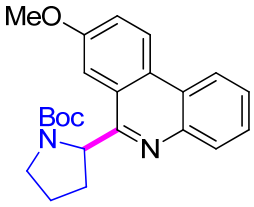
***tert*-Butyl-2-(3-methylphenanthridin-6-yl)pyrrolidine-1-carboxylate (3w).** Eluent: PE/EtOAc (5:1). Yield 51.2 mg (94%). White solid, mp 132-134 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.64-8.53 (m, 1H), 8.43-8.34 (m, 1H), 8.27-8.19 (m, 1H), 7.93-7.57 (m, 3H), 7.46-7.37 (m, 1H), 5.92-5.68 (m, 1H), 4.00-3.87 (m, 1H), 3.77-3.59 (m, 1H), 2.59-2.42 (m, 4H), 2.14-1.87 (m, 3H), 1.48 (brs, 3.1H), 0.94 (brs, 5.9H). ^{13}C NMR

($CDCl_3$, 100 MHz) δ 161.2, 160.3, 154.9, 154.8, 143.8, 143.6, 138.8, 138.4, 134.2, 134.0, 133.4, 133.2, 130.1, 130.0, 129.9, 128.3, 128.1, 126.7, 126.6, 125.3, 125.0, 123.8, 123.6, 122.5, 122.4, 121.7, 121.3, 79.0, 78.8, 60.1, 59.4, 47.2, 47.0, 33.4, 32.3, 28.4, 28.1, 23.8, 23.5, 21.6. HRMS (ESI^+): Calcd for $C_{23}H_{26}N_2O_2$, $[M+H]^+$ m/z 363.2067. Found 363.2067.



3x

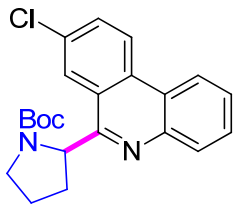
***tert*-Butyl-2-(benzo[i]phenanthridin-5-yl)pyrrolidine-1-carboxylate (3x).** PE/EtOAc (5:1). Yield 52.7 mg (88%). White solid, mp 150-152 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.62-8.51 (m, 3H), 8.15-7.95 (m, 3H), 7.76-7.57 (m, 4H), 6.31-5.99 (m, 1H), 4.13-3.99 (m, 1H), 3.73-3.60 (m, 1H), 2.88-2.54 (m, 2H), 2.39-2.04 (m, 2H), 1.38 (brs, 2.7H), 0.53 (brs, 6.3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.6, 160.8, 154.8, 154.1, 144.3, 143.9, 134.0, 133.5, 133.2, 133.1, 131.8, 131.5, 130.0, 129.6, 129.2, 128.9, 128.8, 128.5, 127.6, 127.5, 127.0, 126.8, 126.5, 126.4, 126.3, 126.2, 123.3, 123.0, 122.6, 122.3, 122.2, 121.8, 120.6, 120.4, 78.8, 78.2, 62.7, 61.8, 47.9, 47.8, 34.1, 33.1, 28.4, 27.6, 23.6, 23.4. HRMS (ESI^+): Calcd for $C_{26}H_{26}N_2O_2$, $[M+H]^+$ m/z 399.2067. Found 399.2071.



3y

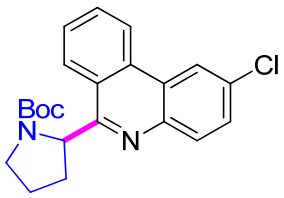
***tert*-Butyl-2-(8-methoxyphenanthridin-6-yl)pyrrolidine-1-carboxylate (3y).** PE/EtOAc (4:1). Yield 54.1 mg (95%). White solid, mp 159-161 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.60-8.51 (m, 1H), 8.47-8.40 (m, 1H), 8.09-8.02 (m, 1H), 7.65-7.52 (m, 3H), 7.48-7.40 (m, 1H), 5.85-5.61 (m, 1H), 4.02-3.87 (m, 4H), 2.58-2.43 (m, 1H), 2.17-1.89 (m, 3H), 1.47 (brs, 3.2H), 0.93 (brs, 5.8H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.3, 159.3, 158.5, 155.0, 154.7, 142.8, 142.7, 130.4, 130.3, 127.8, 127.7, 127.5, 127.3, 126.6, 126.4, 125.3, 125.1, 124.4, 124.3, 124.1, 123.7, 121.4, 120.5, 120.3,

105.8, 79.1, 78.8, 60.6, 59.6, 55.7, 55.6, 47.1, 47.0, 33.1, 31.9, 28.7, 28.1, 23.8, 23.5. HRMS (ESI$^+$): Calcd for $C_{23}H_{26}N_2O_3$, $[M+H]^+$ m/z 379.2016. Found 379.2016.



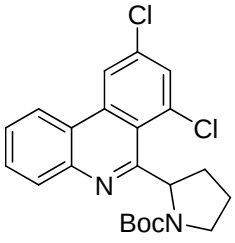
3z

***tert*-Butyl-2-(8-chlorophenanthridin-6-yl)pyrrolidine-1-carboxylate (3z).** Eluent: PE/EtOAc (5:1). Yield 54.1 mg (94%). White solid, mp 188-190 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.62-8.41 (m, 2H), 8.22 (m, 2H), 8.13-8.04 (m, 1H), 7.80-7.55 (m, 3H), 5.82-5.62 (m, 1H), 3.99-3.86 (m, 1H), 3.77-3.60 (m, 1H), 2.61-2.43 (m, 1H), 2.14-1.97 (m, 3H), 1.47 (brs, 3.6H), 0.96 (brs, 5.4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.4, 159.4, 154.8, 154.6, 143.6, 143.4, 133.2, 131.8, 131.5, 130.8, 130.7, 130.5, 129.0, 128.7, 127.0, 126.8, 124.9, 124.7, 124.5, 124.4, 123.4, 123.0, 121.8, 79.2, 78.9, 59.6, 59.3, 47.2, 47.0, 33.4, 32.2, 28.7, 28.1, 23.9, 23.5. HRMS (ESI$^+$): Calcd for $C_{22}H_{23}N_2O_2Cl$, $[M+H]^+$ m/z 383.1521. Found 383.1517.



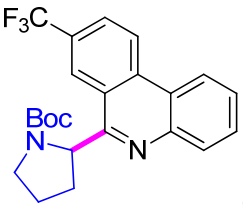
3aa

***tert*-Butyl-2-(2-chlorophenanthridin-6-yl)pyrrolidine-1-carboxylate (3aa).** Eluent: PE/EtOAc (5:1). Yield 53.5 mg (93%). White solid, mp 198-200 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.59-8.45 (m, 2H), 8.29-8.24 (m, 1H), 8.06-7.97 (m, 1H), 7.87-7.78 (m, 1H), 7.74-7.57 (m, 2H), 5.88-5.69 (m, 1H), 3.97-3.87 (m, 1H), 3.76-3.59 (m, 1H), 2.58-2.46 (m, 3H), 1.47 (brs, 3.1H), 0.92 (brs, 5.9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.8, 160.7, 154.9, 124.6, 142.1, 142.0, 132.4, 132.2, 132.1, 131.8, 130.5, 130.4, 129.2, 128.8, 127.9, 127.8, 125.4, 125.1, 124.7, 124.3, 124.1, 122.8, 122.7, 121.6, 79.2, 78.8, 60.0, 59.4, 47.2, 47.0, 33.3, 32.2, 28.7, 28.1, 23.8, 23.5. HRMS (ESI$^+$): Calcd for $C_{22}H_{23}N_2O_2Cl$, $[M+H]^+$ m/z 383.1521. Found 383.1523.



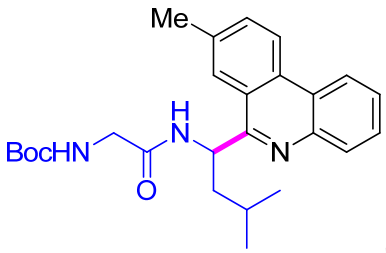
3ab

***tert*-Butyl-2-(7,9-dichlorophenanthridin-6-yl)pyrrolidine-1-carboxylate (3ab).** Eluent: PE/EtOAc (8:1). Yield 39.4 mg (63%). White solid, mp 139-141 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.57 and 8.53 (s, 1H), 8.47-8.32 (m, 1H), 8.09-7.96 (m, 1H), 7.82-7.55 (m, 3H), 6.52-6.32 (m, 1H), 4.02-3.85 (m, 1H), 3.70-3.53 (m, 1H), 2.68-2.46 (m, 1H), 2.32-1.83 (m, 3H), 1.46 (brs, 3.4H), 0.93 (brs, 5.6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.6, 159.0, 155.0, 154.5, 143.1, 143.0, 137.4, 137.0, 135.7, 135.6, 133.0, 132.8, 130.7, 130.4, 130.3, 130.0, 129.7, 127.4, 127.2, 122.3, 122.2, 122.1, 121.7, 121.6, 121.3, 121.2, 78.9, 78.5, 62.4, 62.0, 47.4, 47.3, 34.0, 33.3, 28.7, 28.1, 22.7, 22.5. HRMS (ESI^+): Calcd for $C_{22}H_{22}N_2O_2Cl_2$, $[M+H]^+$ m/z 417.1131. Found 417.1131.



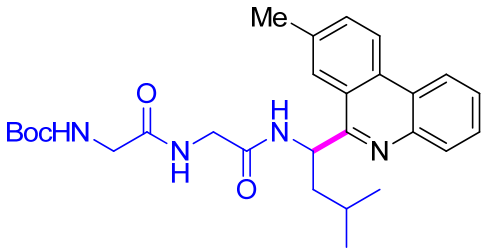
3ac

***tert*-Butyl-2-(8-(trifluoromethyl)phenanthridin-6-yl)pyrrolidine-1-carboxylate (3ac).** PE/EtOAc (5:1). Yield 56.3 mg (90%). White solid, mp 164-166 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.81-8.68 (m, 1H), 8.59-8.47 (m, 2H), 8.17-8.08 (m, 1H), 8.06-7.94 (m, 1H), 7.81-7.59 (m, 2H), 5.91-5.72 (m, 1H), 4.01-3.87 (m, 1H), 3.80-3.63 (m, 1H), 2.64-2.47 (m, 1H), 2.19-1.92 (m, 3H), 1.46 (brs, 3.8H), 0.93 (brs, 5.2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.5, 160.4, 154.8, 154.5, 144.2, 135.6, 135.3, 130.6, 129.9, 129.6, 129.0 (q, J = 33.6 Hz), 127.2, 127.0, 126.1, 124.1 (q, J = 272.2 Hz), 123.9, 123.8, 123.3, 123.0, 122.6, 122.4, 122.3, 79.3, 79.0, 59.6, 59.4, 47.2, 47.1, 33.6, 32.4, 28.6, 28.1, 23.9, 23.6. HRMS (ESI^+): Calcd for $C_{23}H_{23}N_2O_2F_3$, $[M+H]^+$ m/z 417.1784. Found 417.1782.



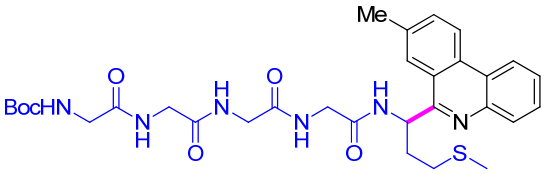
3ad

***tert*-Butyl-(2-((3-methyl-1-(8-methylphenanthridin-6-yl)butyl)amino)-2-oxoethyl) carbamate (3ad).** Eluent: PE/EtOAc (2:1). Yield 47.1 mg (72%). White solid, mp 99-101 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.53 (t, *J* = 8.7 Hz, 2H), 8.10-8.06 (m, 1H), 7.82 (s, 1H), 7.71-7.63 (m, 3H), 6.16-6.08 (m, 1H), 5.24 (s, 1H), 3.95 (s, 2H), 2.62 (s, 3H), 1.90-1.69 (m, 3H), 1.47 (s, 9H), 1.20 (d, *J* = 6.0 Hz, 3H), 0.87 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.8, 159.7, 155.9, 142.6, 137.7, 132.6, 131.1, 129.6, 128.3, 126.9, 124.8, 124.0, 123.7, 122.6, 121.9, 80.0, 48.3, 46.8, 44.5, 28.4, 25.3, 23.7, 22.2, 22.0. HRMS (ESI$^+$): Calcd for $C_{26}H_{33}N_3O_3$, $[M+H]^+$ m/z 436.2595. Found 436.2593.

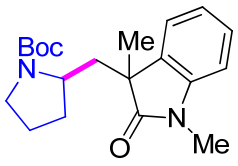


3ae

***tert*-Butyl-(2-((2-((3-methyl-1-(8-methylphenanthridin-6-yl)butyl)amino)-2-oxoet hyl)amino)-2-oxoethyl)carbamate (3ae).** Eluent: DCM/MeOH (20:1). Yield 50.3 mg (68%). White solid, mp 81-83 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.51 (dd, J_1 = 8.7 Hz, J_2 = 11.0 Hz, 2H), 8.09 (d, *J* = 7.8 Hz, 1H), 8.02 (s, 1H), 7.06 (s, 1H), 7.72-7.61 (m, 3H), 6.94 (s, 1H), 6.14-6.06 (m, 1H), 5.26 (s, 1H), 4.13 (d, *J* = 5.0 Hz, 2H), 3.90 (d, *J* = 5.0 Hz, 2H), 2.61 (s, 3H), 1.83-1.72 (m, 3H), 1.44 (s, 9H), 1.19 (d, *J* = 6.0 Hz, 3H), 0.87 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.7, 167.9, 159.5, 156.0, 137.7, 132.7, 132.6, 131.2, 129.5, 128.5, 127.0, 124.7, 124.0, 123.6, 122.7, 121.9, 80.2, 48.6, 46.6, 44.2, 43.0, 28.4, 25.4, 23.7, 22.1, 22.0. HRMS (ESI$^+$): Calcd for $C_{28}H_{36}N_4O_4$, $[M+H]^+$ m/z 493.2809. Found 493.2808.

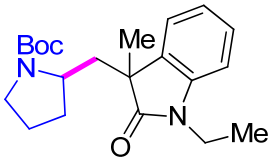


***tert*-Butyl-(5-(8-methylphenanthridin-6-yl)-7,10,13,16-tetraoxo-2-thia-6,9,12,15-tetraazaheptadecan-17-yl)carbamate (3af).** Eluent: DCM/MeOH (10:1). Yield 64.4 mg (69 %). White solid, mp 125-127 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.80-8.72 (m, 2H), 8.49 (d, J = 8.7 Hz, 1H), 8.29 (s, 1H), 8.22-8.15 (m, 2H), 8.12-8.03 (m, 2H), 7.82-7.67 (m, 3H), 7.02 (t, J = 6.0 Hz, 1H), 6.10-5.99 (m, 1H), 3.89-3.73 (m, 6H), 3.60 (d, J = 6.0 Hz, 2H), 2.68-2.54 (m, 5H), 2.39-2.28 (m, 1H), 2.21-2.11 (m, 1H), 2.08 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ 170.3, 169.8, 169.6, 168.9, 159.8, 156.4, 142.8, 138.1, 133.2, 130.9, 129.9, 129.0, 127.6, 125.3, 124.4, 124.1, 123.4, 123.0, 78.6, 49.4, 43.9, 42.6, 34.4, 30.7, 28.7, 22.0, 15.2. HRMS (ESI$^+$): Calcd for $C_{31}H_{40}N_6O_6S$, $[M+H]^+$ 625.2803. Found m/z 625.2794.



5a

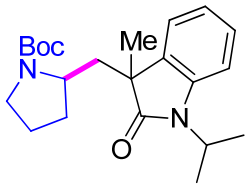
***tert*-Butyl-2-((1,3-dimethyl-2-oxoindolin-3-yl)methyl)pyrrolidine-1-carboxylate (5a).** Eluent: PE/EtOAc (5:1). Yield 33.7 mg (65%). Clear oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 7.2 Hz, 1H), 7.05 (dd, J_1 = 7.6 Hz, J_2 = 7.2 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H), 3.88-3.71 (m, 1H), 3.39-2.98 (m, 5H), 2.61-1.92 (m, 2H), 1.80-1.70 (m, 1H), 1.67-1.53 (m, 2H), 1.45 (s, 9H), 1.40 (s, 3H), 1.22-1.13 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 179.8, 154.5, 143.1, 134.6, 127.9, 122.8, 122.4, 108.1, 79.6, 54.6, 46.7, 45.6, 42.3, 31.1, 28.6, 26.3, 24.8, 23.0. HRMS (ESI$^+$): Calcd for $C_{20}H_{28}N_2O_3$, $[M+H]^+$ m/z 345.2173. Found 345.2169.



5b

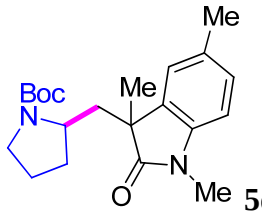
***tert*-Butyl-2-((1-ethyl-3-methyl-2-oxoindolin-3-yl)methyl)pyrrolidine-1-carboxyla**

te (5b). Eluent: PE/EtOAc (5:1). Yield 34.0 mg (63%). Clear oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.23 (dd, J_1 = 7.6 Hz, J_2 = 7.2 Hz, 1H), 7.17 (d, J = 7.2 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.82 (d, J = 7.6 Hz, 1H), 3.84-3.67 (m, 3H), 3.35-2.93 (m, 2H), 2.48-1.86 (m, 2H), 1.77-1.68 (m, 1H), 1.62-1.51 (m, 2H), 1.43 (s, 9H), 1.37 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H), 1.15-1.06 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 179.3, 154.4, 142.0, 134.9, 127.8, 123.0, 122.2, 108.2, 79.6, 54.6, 46.6, 45.6, 42.3, 34.6, 30.9, 28.6, 24.8, 23.0, 12.8. HRMS (ESI$^+$): Calcd for $C_{21}H_{30}N_2O_3$, $[M+H]^+$ m/z 359.2329. Found 359.2324.



5c

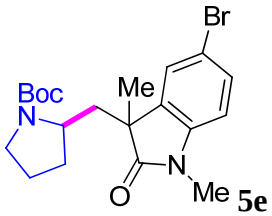
***tert*-Butyl-2-((1-isopropyl-3-methyl-2-oxoindolin-3-yl)methyl)pyrrolidine-1-carboxylate (5c).** Eluent: PE/EtOAc (5:1). Yield 32.5 mg (58%). Clear oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25-7.17 (m, 2H), 7.05-6.98 (m, 2H), 4.71-4.62 (m, 1H), 3.92-3.71 (m, 1H), 3.35-2.91 (m, 2H), 2.54-2.21 (m, 1H), 1.90-1.66 (m, 2H), 1.64-1.51 (m, 2H), 1.47 (d, J = 6.9 Hz, 6H), 1.46 (s, 9H), 1.38 (s, 3H), 1.13-1.05 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 179.3, 154.4, 141.6, 135.1, 127.5, 123.1, 121.8, 109.8, 79.4, 54.6, 46.3, 45.6, 43.5, 42.5, 30.7, 28.6, 24.9, 23.0, 19.6, 19.4. HRMS (ESI$^+$): Calcd for $C_{22}H_{32}N_2O_3$, $[M+H]^+$ m/z 373.2486. Found 373.2485.



5d

***tert*-Butyl-2-((1,3,5-trimethyl-2-oxoindolin-3-yl)methyl)pyrrolidine-1-carboxylate (5d).** Eluent: PE/EtOAc (5:1). Yield 39.9 mg (74%). Clear oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.06 (d, J = 7.2 Hz, 1H), 7.00 (s, 1H), 6.71 (d, J = 7.2 Hz, 1H), 3.88-3.74 (m, 1H), 3.41-3.23 (m, 1H), 3.22-2.99 (m, 4H), 2.50-2.26 (m, 5H), 1.79-1.69 (m, 1H), 1.68-1.55 (m, 2H), 1.45 (s, 9H), 1.38 (s, 3H), 1.26-1.18 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 179.7, 154.3, 140.7, 134.8, 131.9, 128.1, 123.7, 107.8, 79.5, 54.6, 46.8,

45.7, 42.4, 31.2, 28.6, 26.3, 24.8, 23.3, 21.2. HRMS (ESI$^+$): Calcd for $C_{21}H_{30}N_2O_3$, $[M+H]^+$ m/z 359.2329. Found 359.2329.



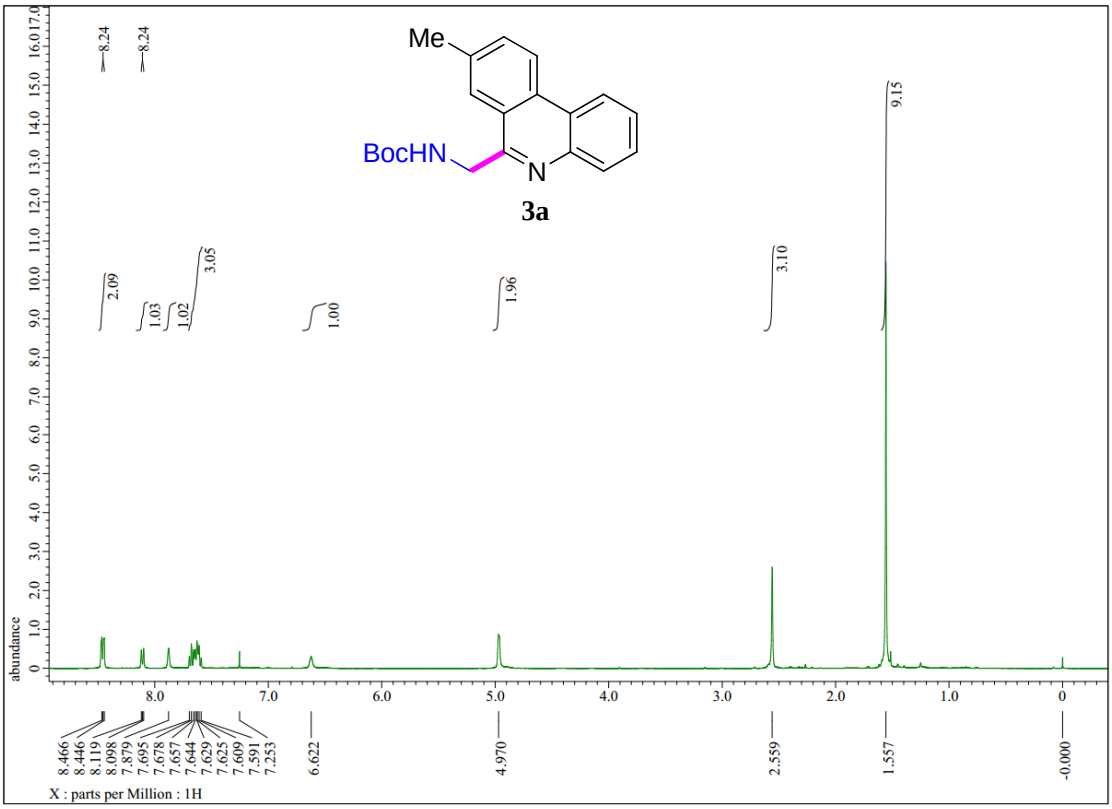
5e

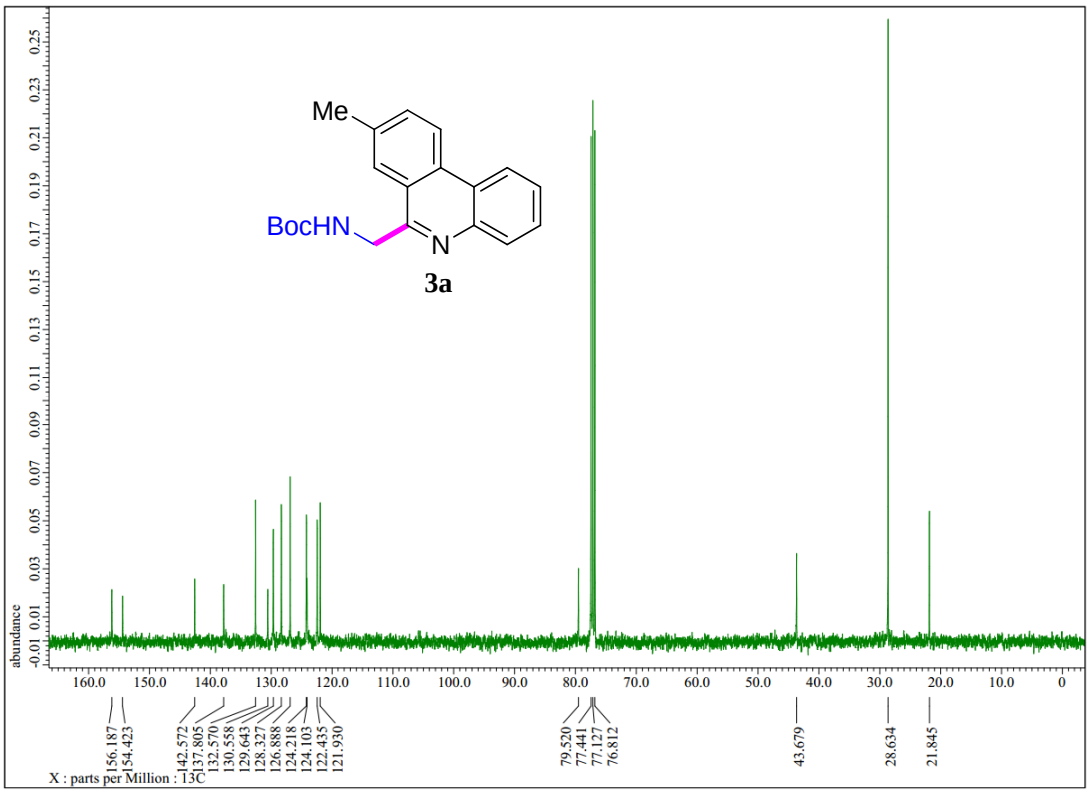
***tert*-Butyl-2-((5-bromo-1,3-dimethyl-2-oxoindolin-3-yl)methyl)pyrrolidine-1-carboxylate (5e).** Eluent: PE/EtOAc (5:1). Yield 39.5 mg (62%). Clear oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39 (d, *J* = 8.2 Hz, 1H), 7.30 (s, 1H), 6.71 (d, *J* = 8.2 Hz, 1H), 3.84-3.73 (m, 1H), 3.42-3.23 (m, 1H), 3.22-2.99 (m, 4H), 2.49-2.23 (m, 2H), 1.79-1.71 (m, 1H), 1.70-1.56 (m, 2H), 1.44 (s, 9H), 1.39 (s, 3H), 1.26-1.18 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 179.3, 154.4, 142.2, 136.7, 130.7, 126.2, 115.1, 109.5, 79.7, 54.4, 47.0, 45.7, 42.3, 31.5, 28.6, 26.4, 24.8, 23.3. HRMS (ESI$^+$): Calcd for $C_{20}H_{27}N_2O_3Br$, $[M+H]^+$ m/z 425.1260. Found 425.1262.

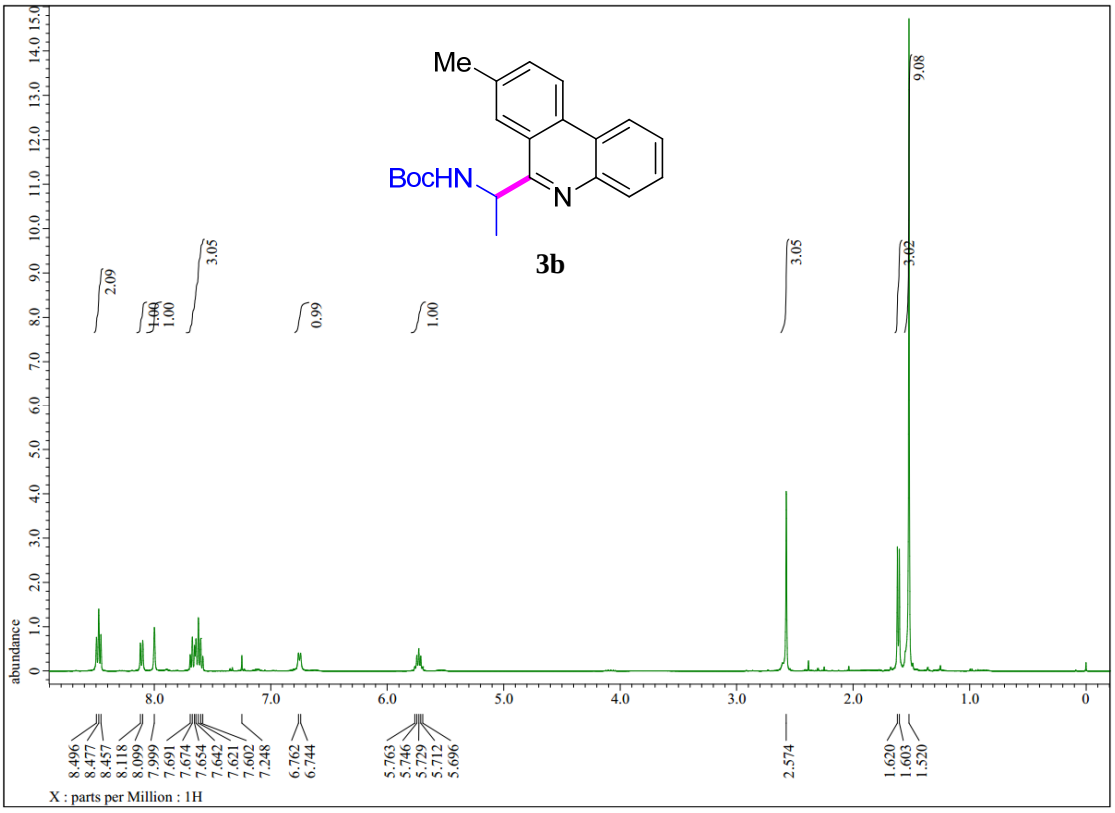
References

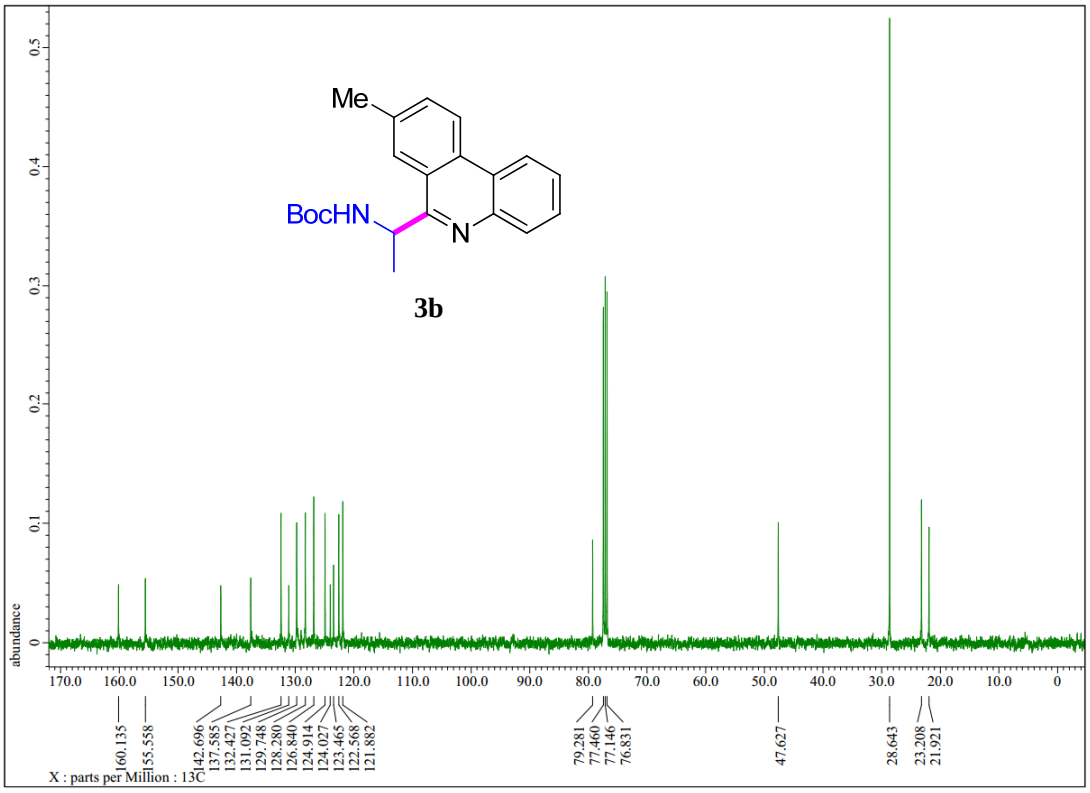
1. Kachkovskyi, G., Faderl, C. & Reiser, O. *Adv. Synth. Catal.* **355**, 2240-2248 (2013).
2. Wang, Q., Dong, X., Xiao, T. & Zhou, L. *Org. Lett.* **15**, 4846-4849 (2013).

The ^{1}H and ^{13}C NMR spectra of compounds **3a-af** and **5a-e**






Me
BocHN
N
3b
abundance
X : parts per Million : 1H


Me
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N
3b
abundance
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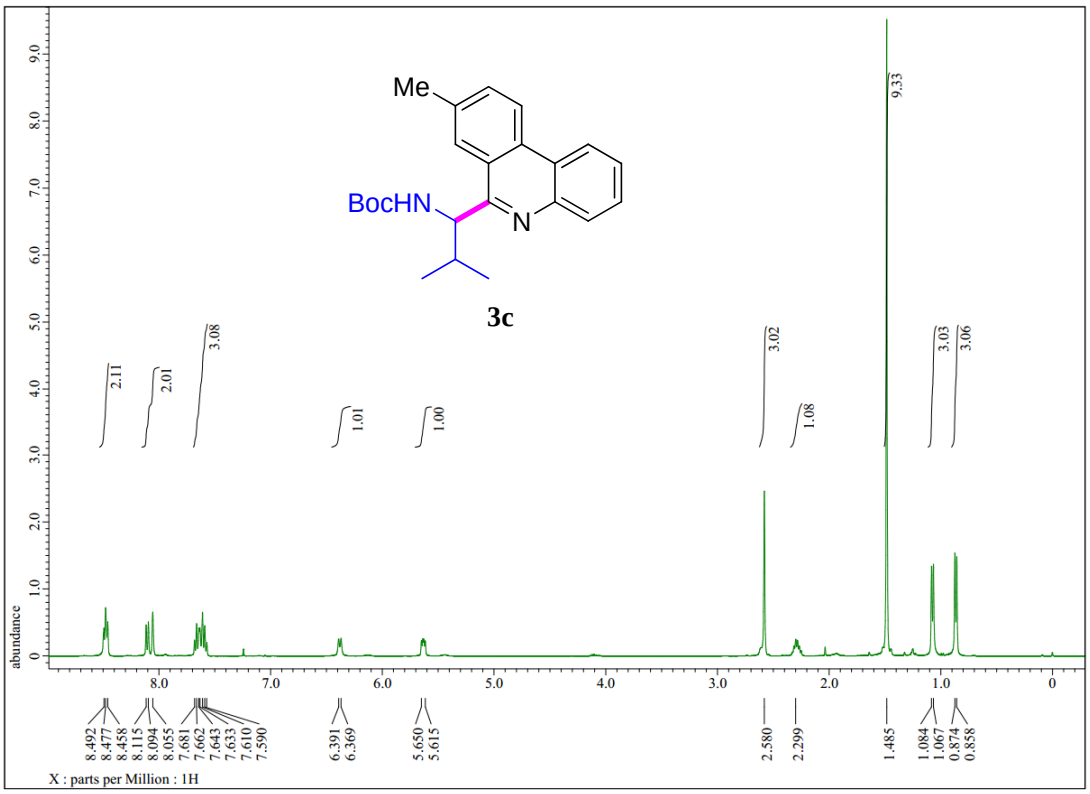
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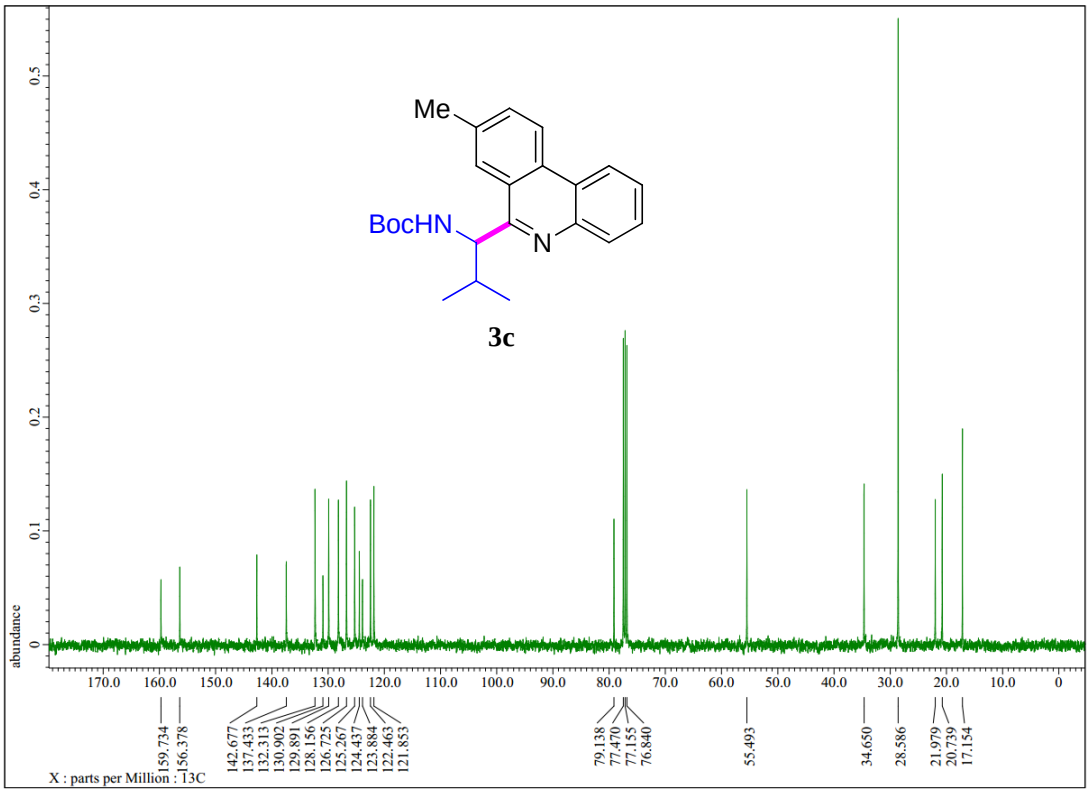
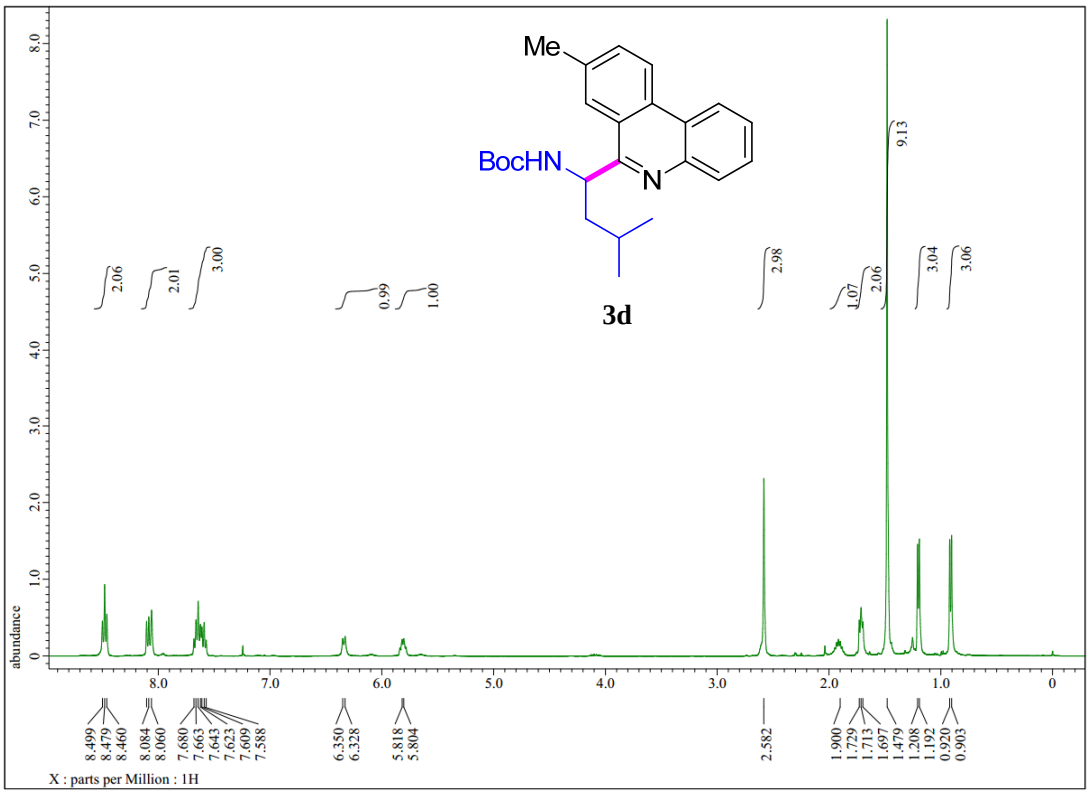
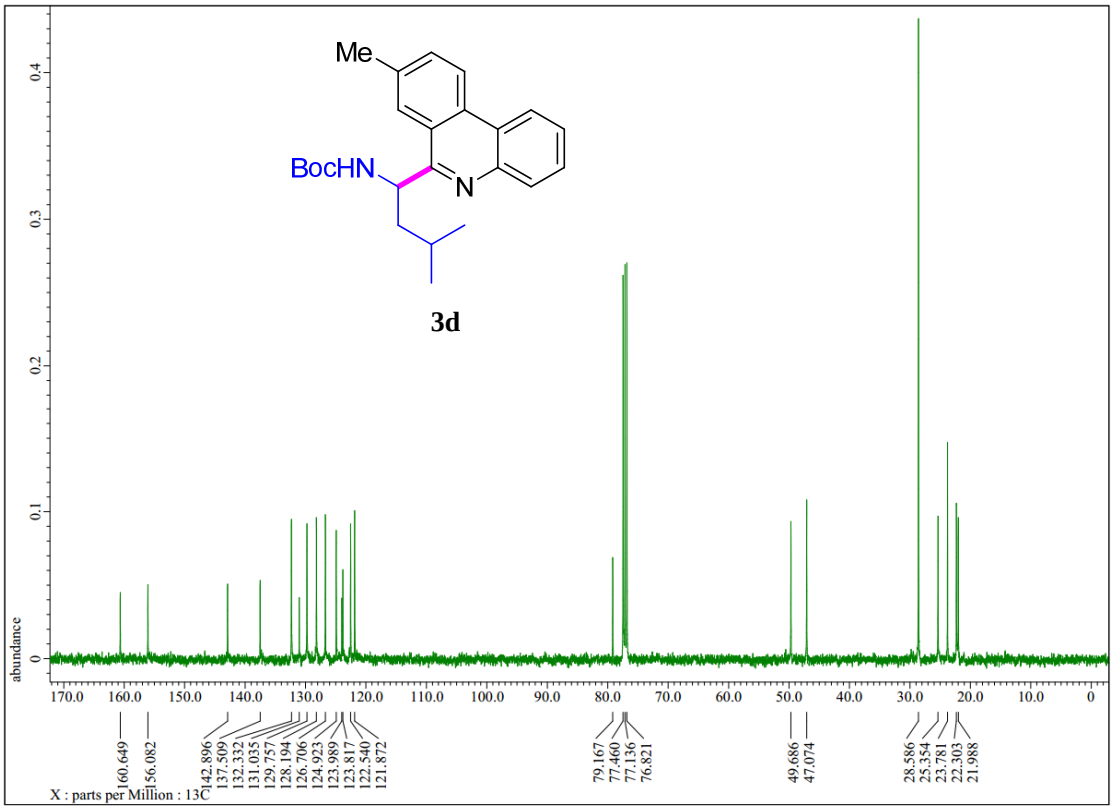
N
3c
abundance
X : parts per Million : 1H


Me
BocHN
N
3c
abundance
X : parts per Million : 13C


Me
BocHN
N
3d
abundance
X : parts per Million : 1H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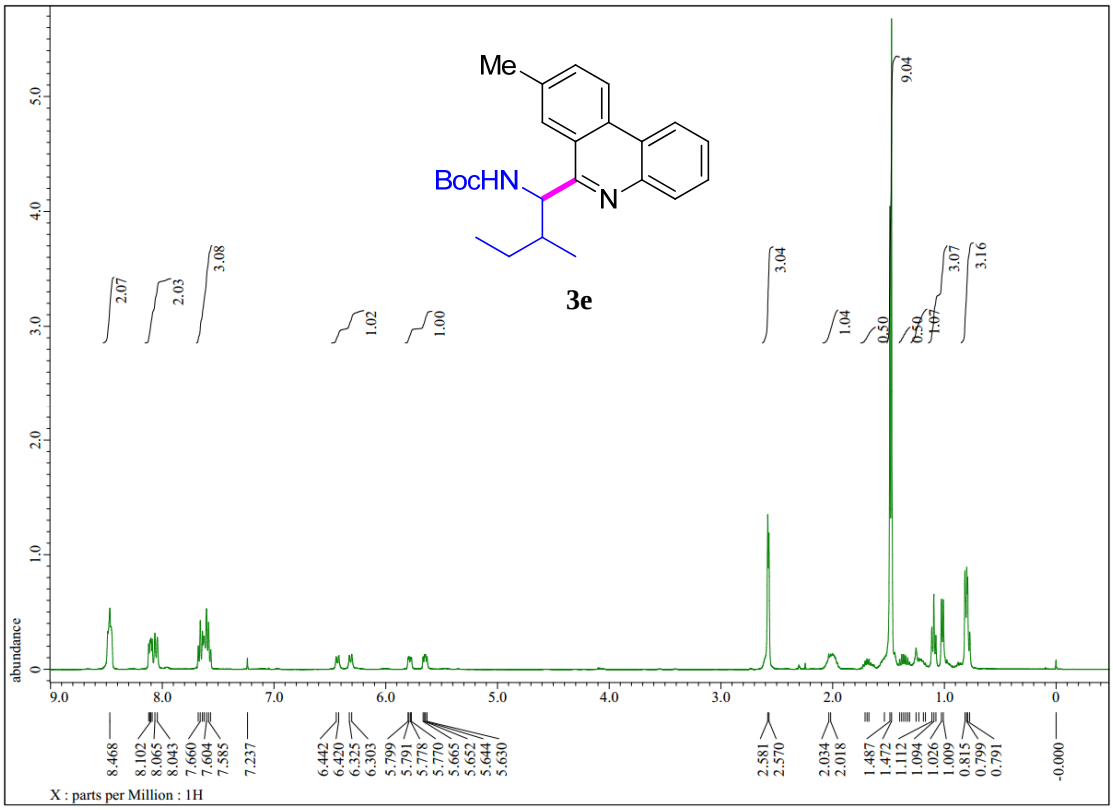
3d
abundance
X : parts per Million : 13C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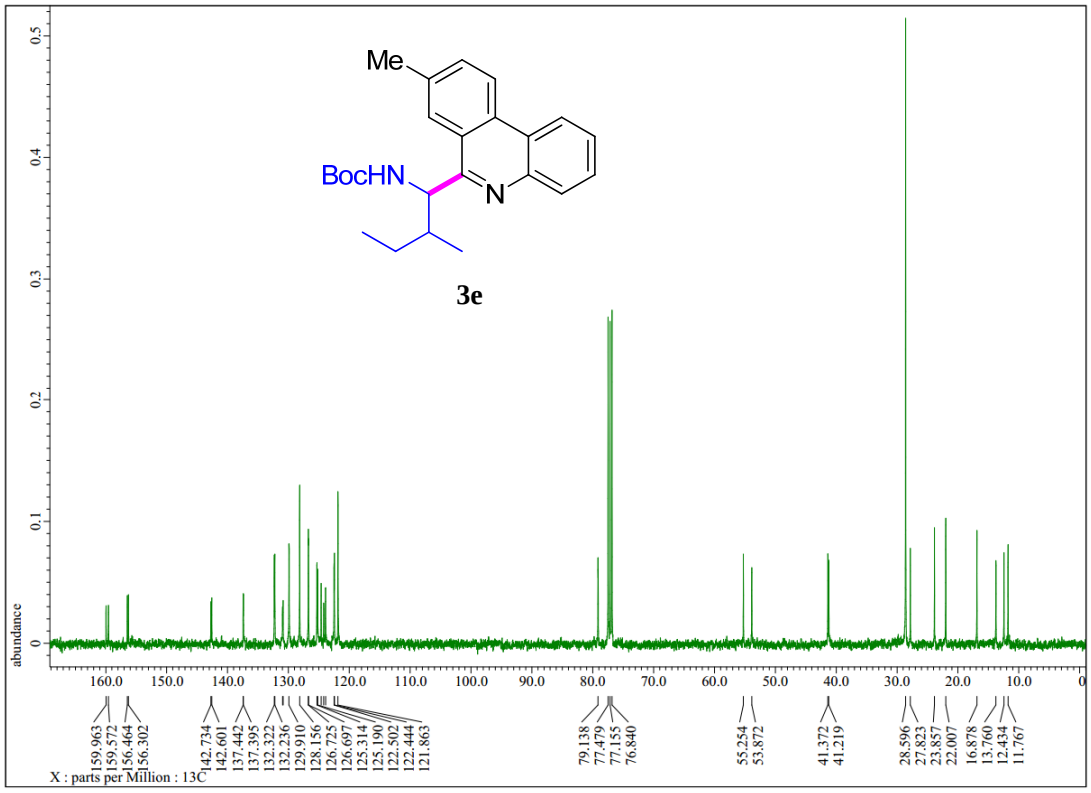
N
3e
abundance
X : parts per Million : 1H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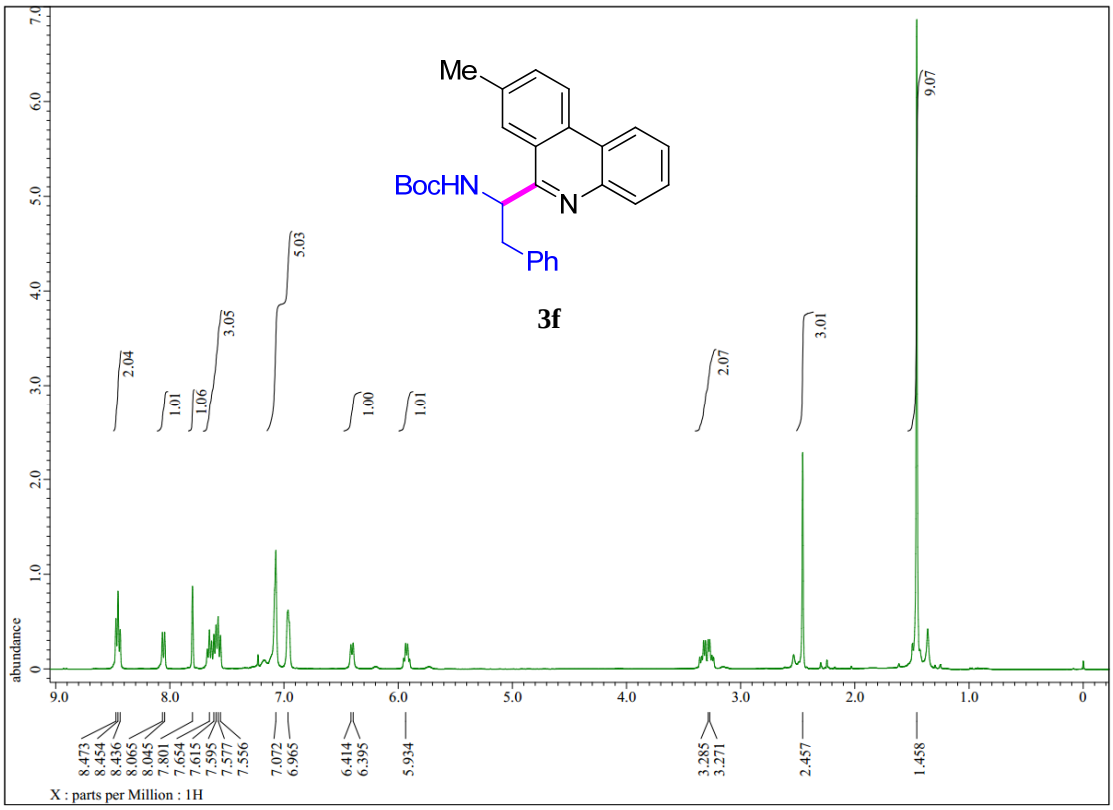
BocHN
N
3e
abundance
X : parts per Million : 13C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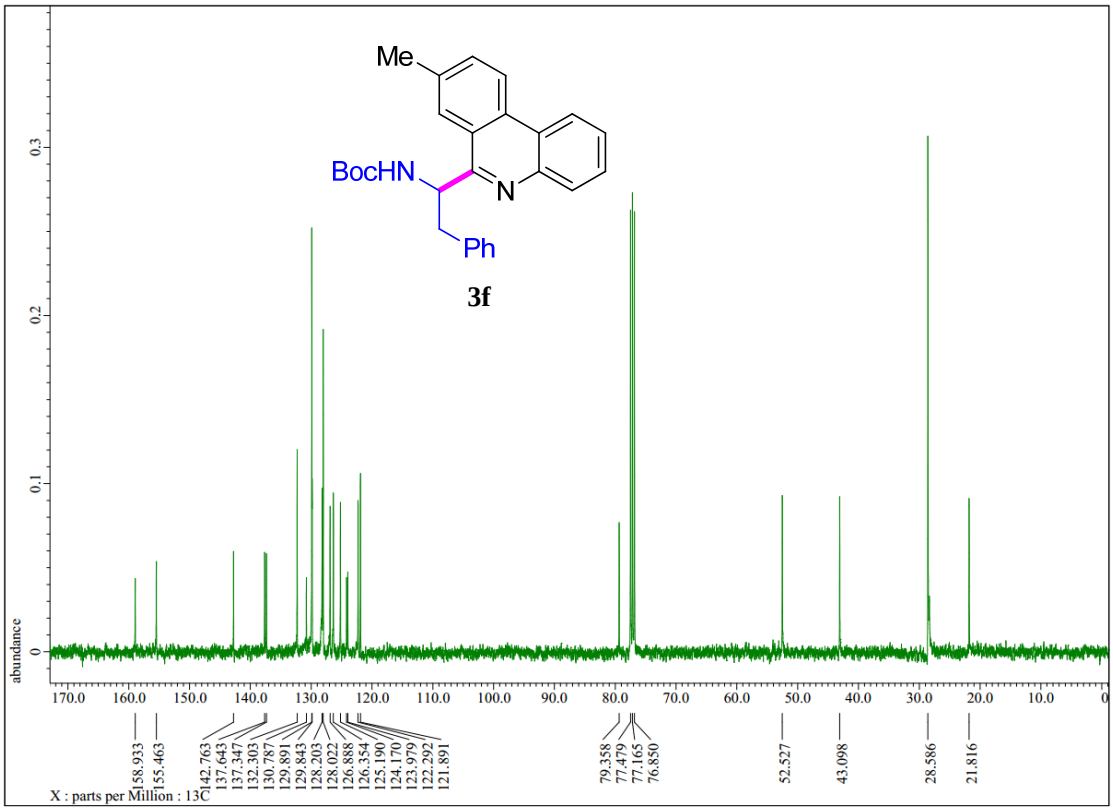
N
Ph
3f
abundance
X : parts per Million : 1H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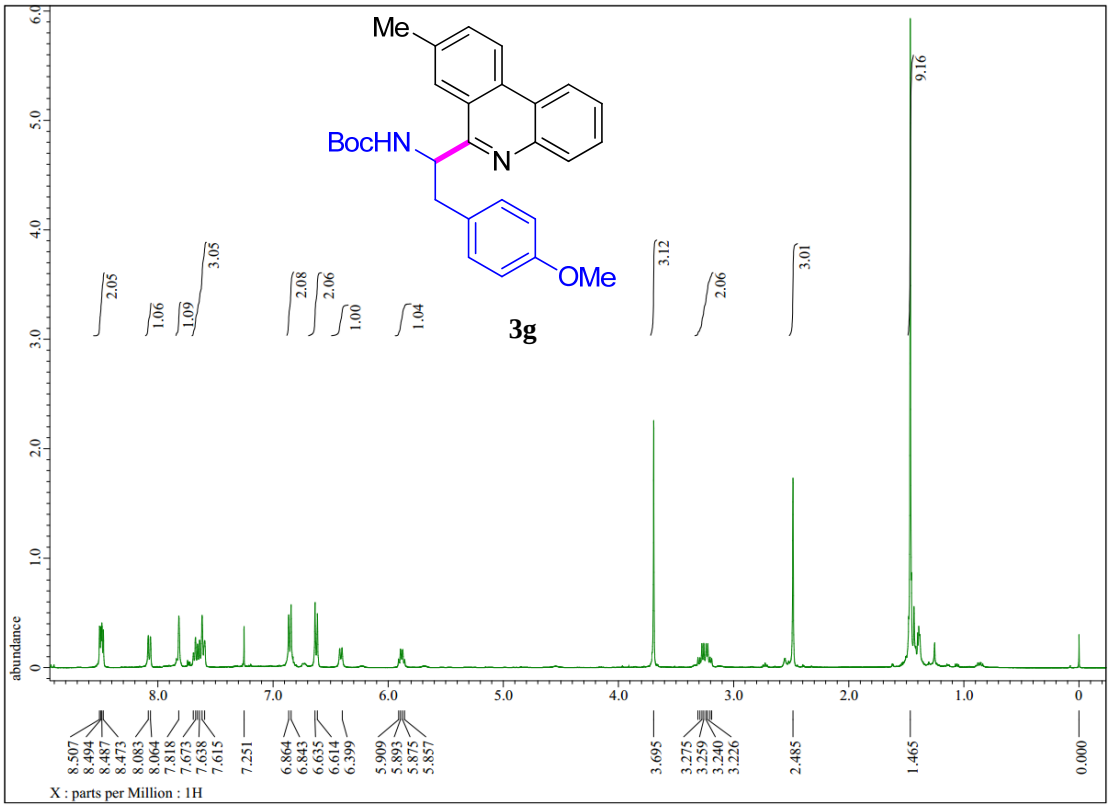
Ph
3f
abundance
X : parts per Million : 13C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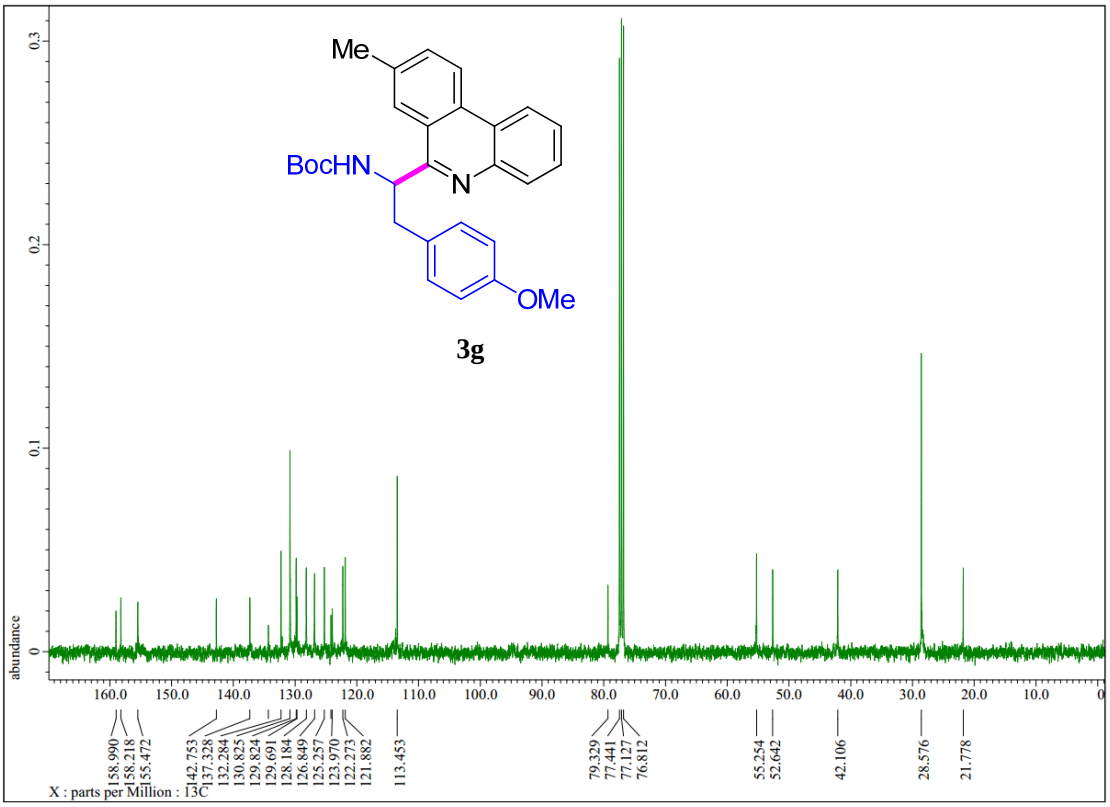
N
OMe
3g
abundance
X : parts per Million : 1H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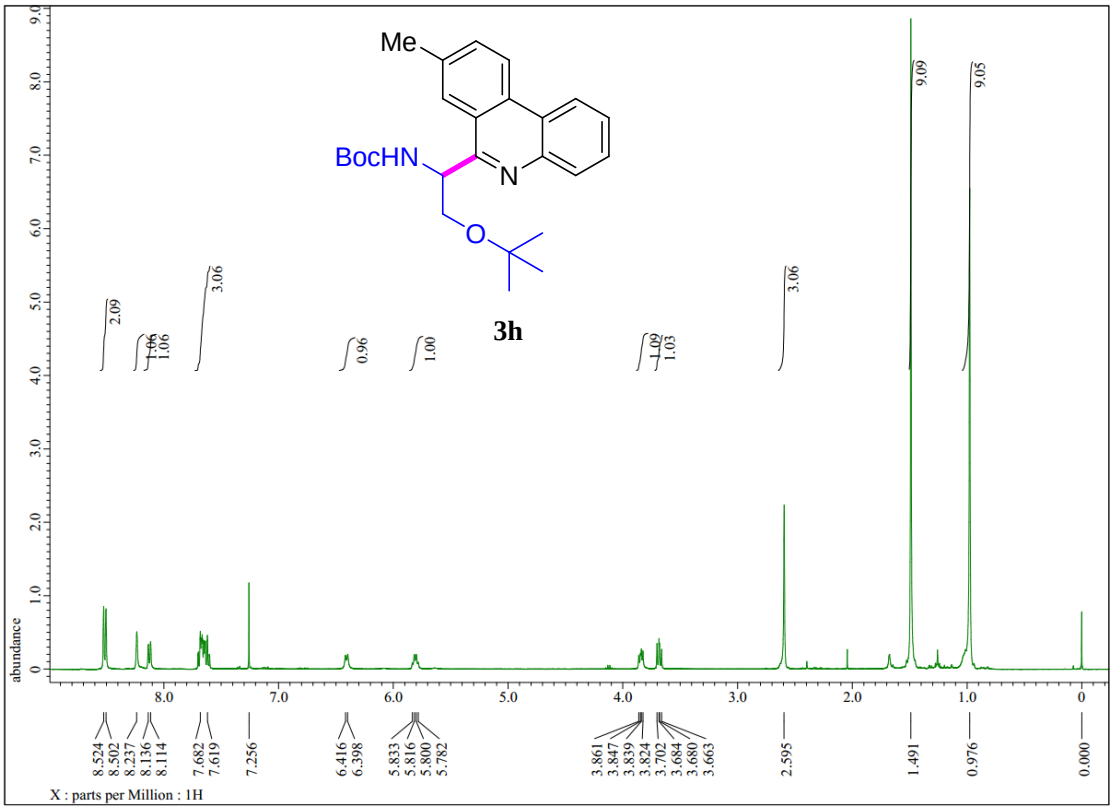
N
OMe
3g
abundance
X : parts per Million : 13C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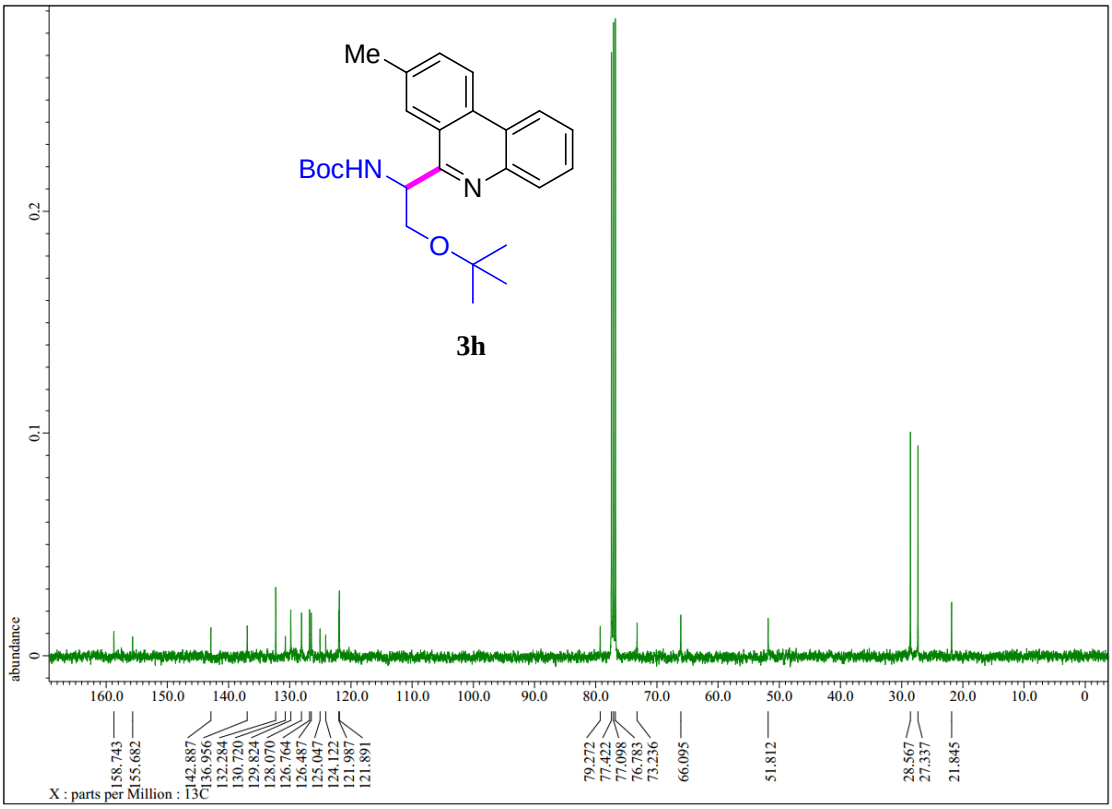
N
O
3h
abundance
X : parts per Million : 1H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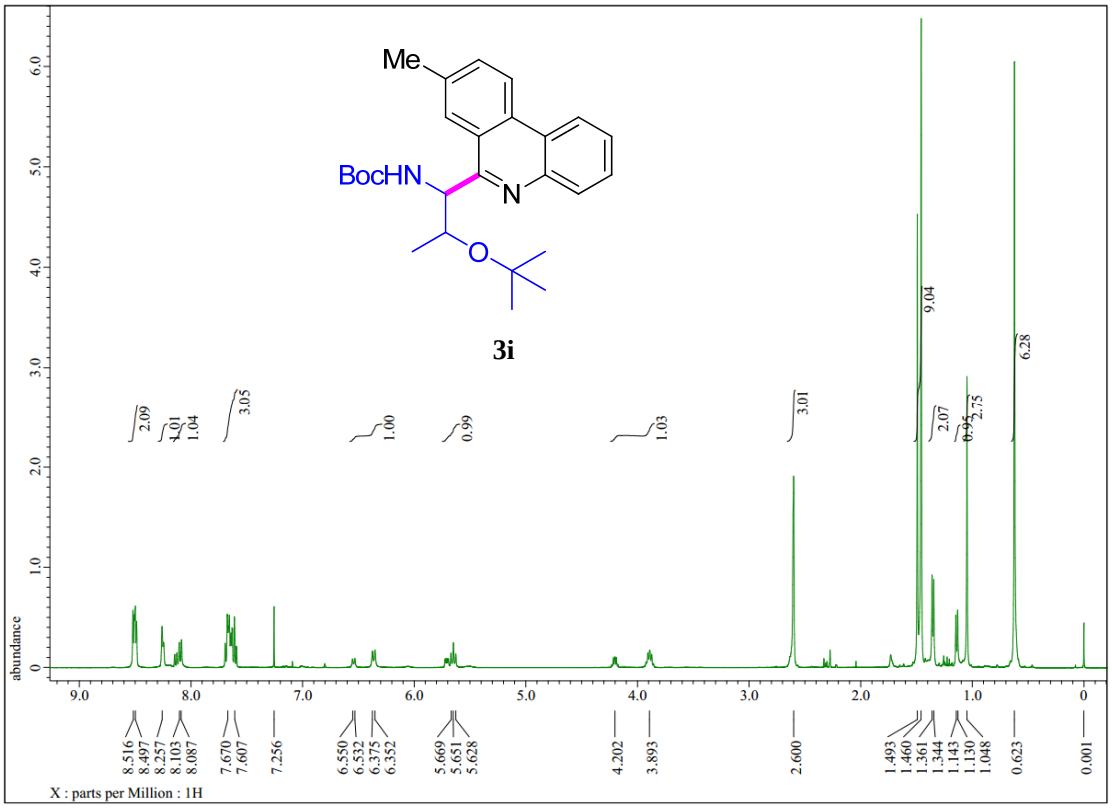
BocHN
N
O
3h
abundance
X : parts per Million : 13C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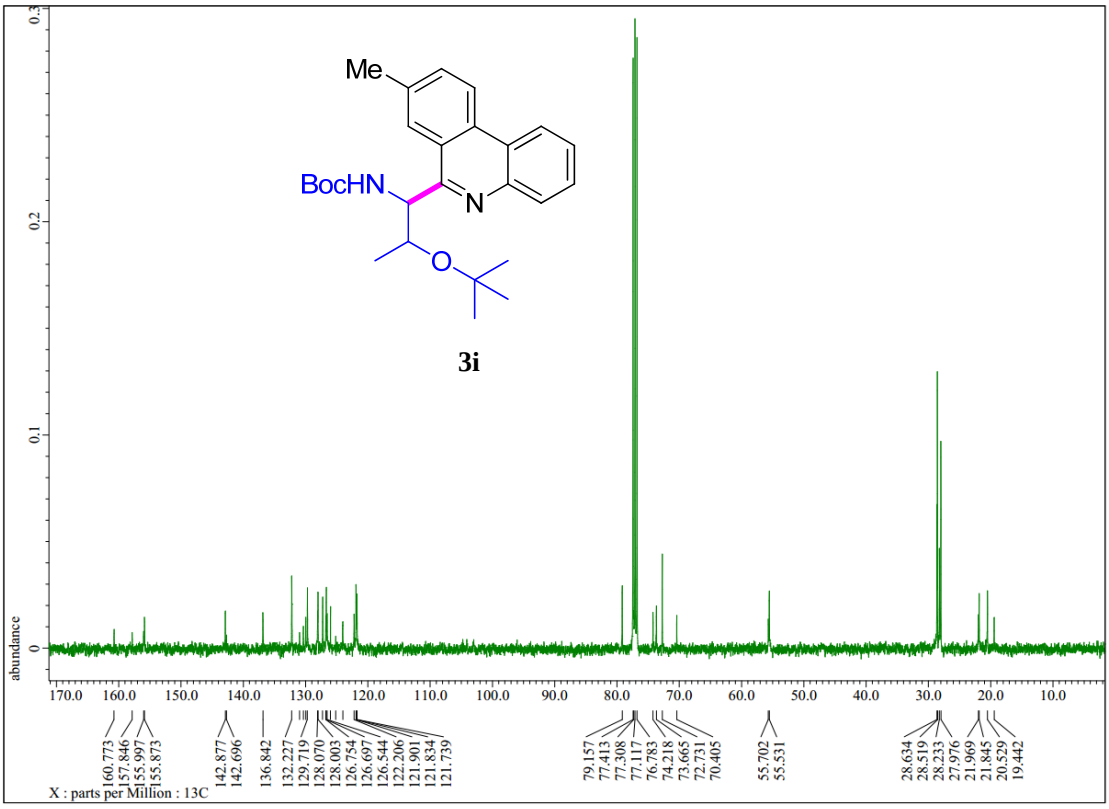
BocHN
N
O
3i
abundance
X : parts per Million : 1H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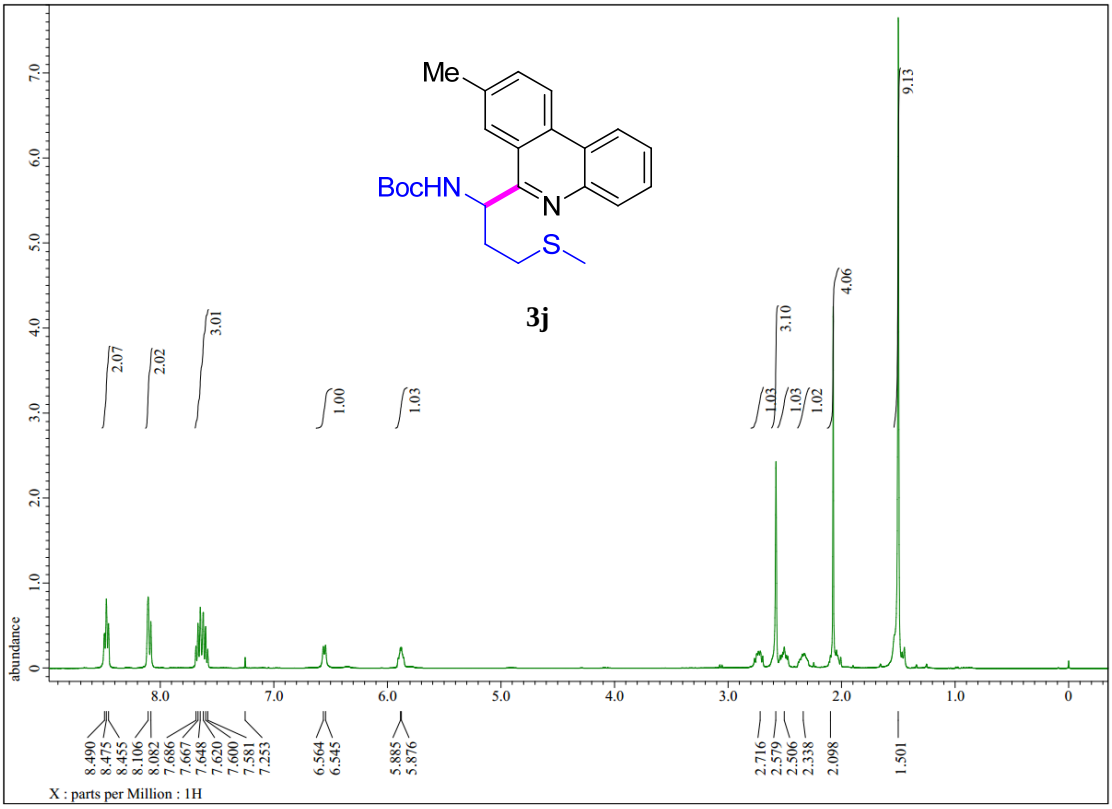
O
3i
abundance
X : parts per Million : 13C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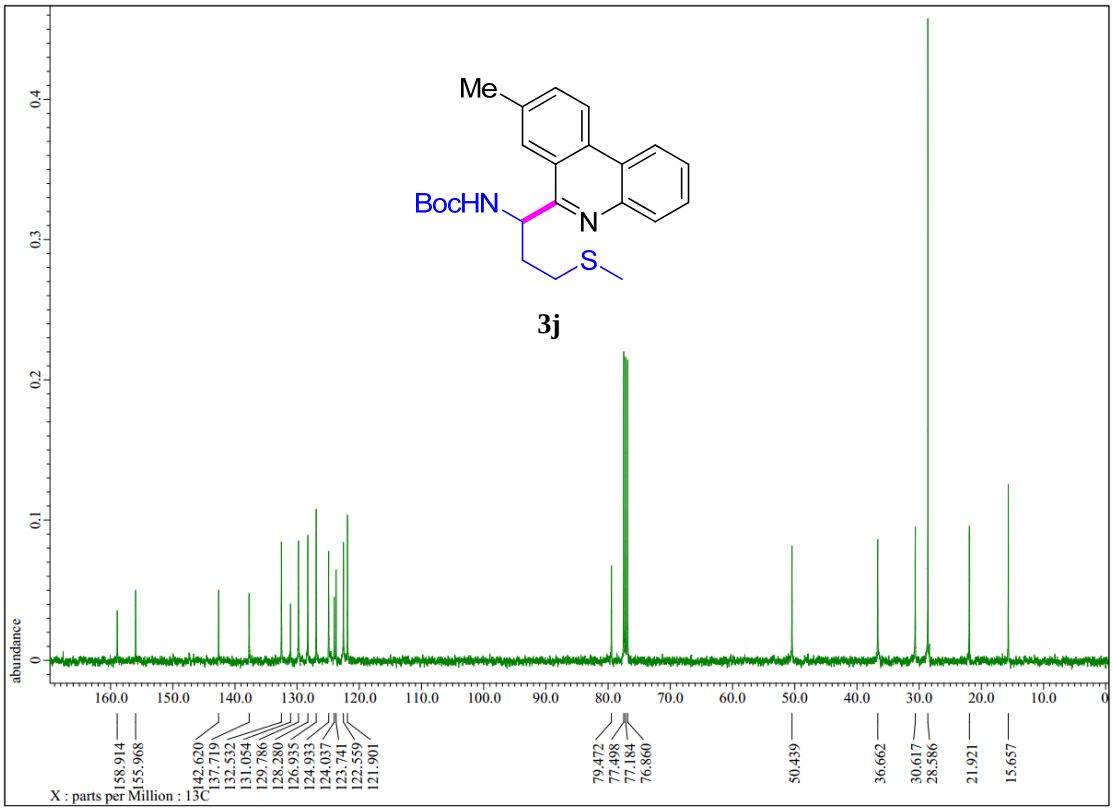
BocHN
N
S
3j
abundance
X : parts per Million : 1H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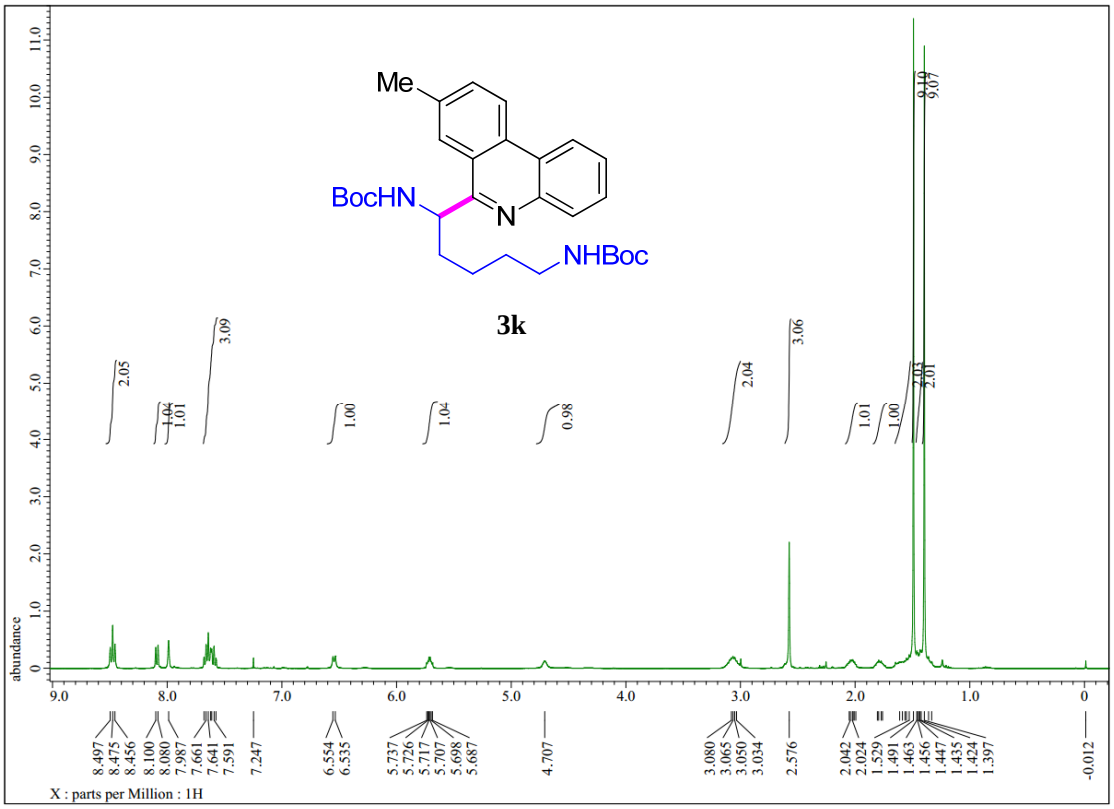
BocHN
N
S
3j
abundance
X : parts per Million : 13C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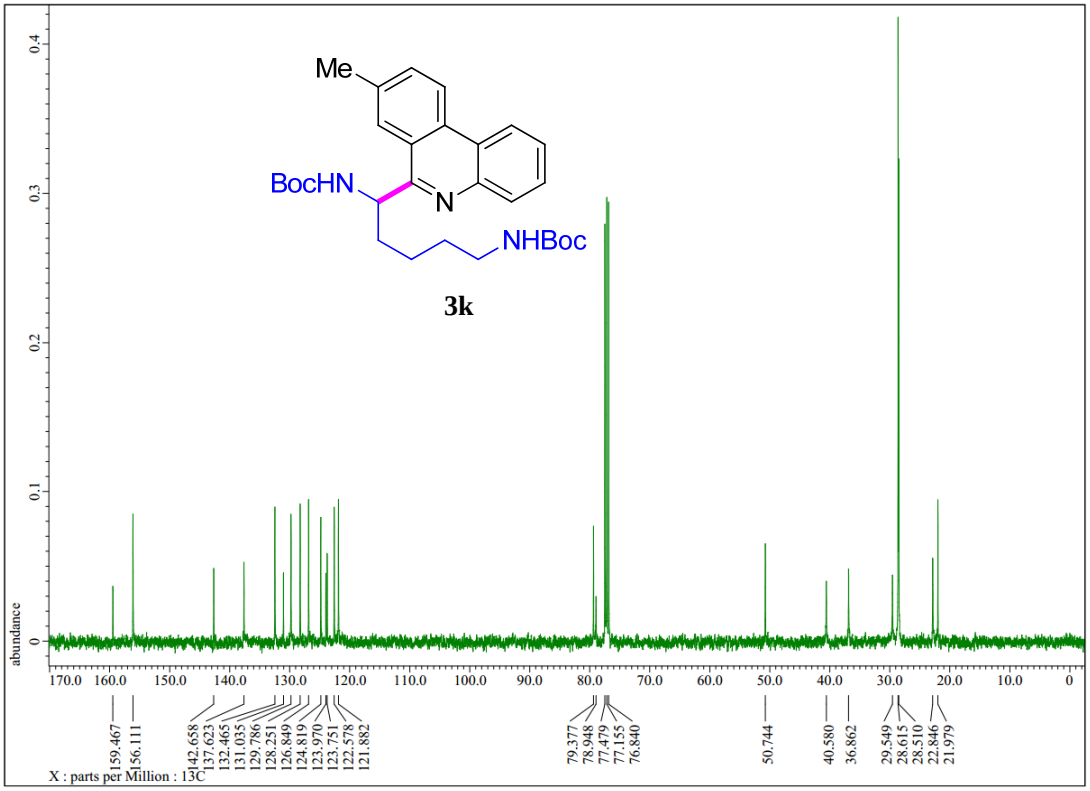
BocHN
N
NHBoc
3k
abundance
X : parts per Million : 1H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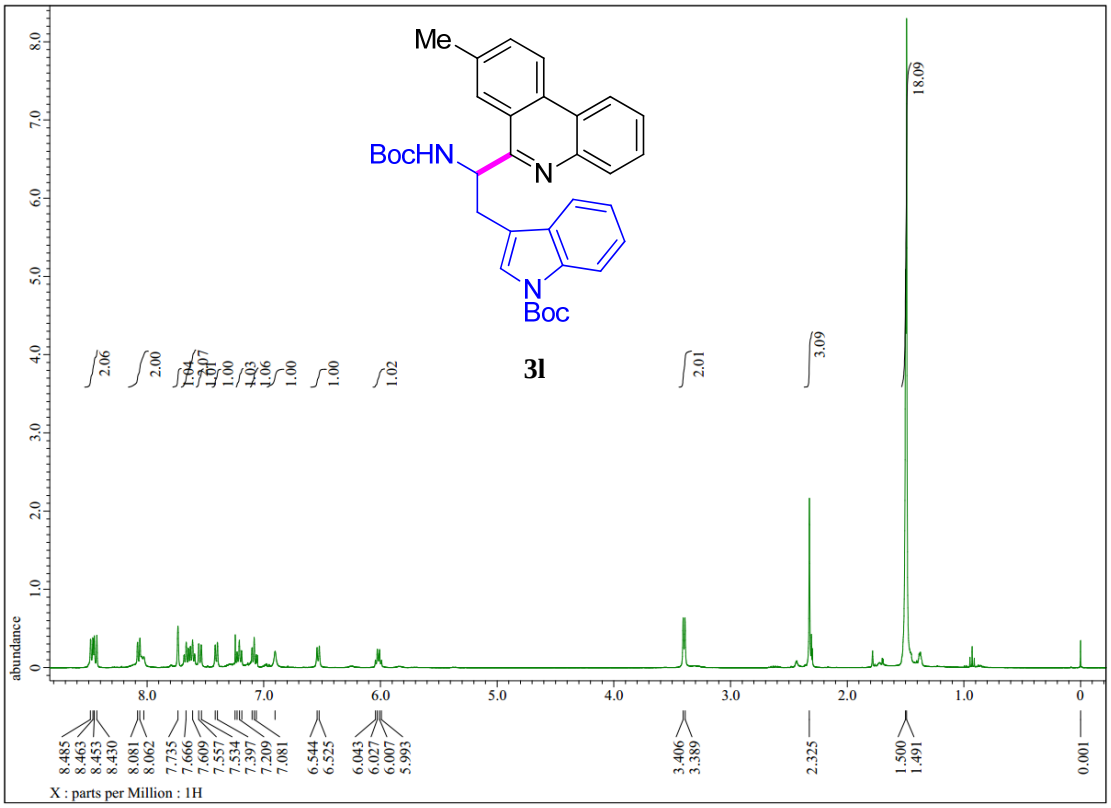
BocHN
N
NHBoc
3k
abundance
X : parts per Million : 13C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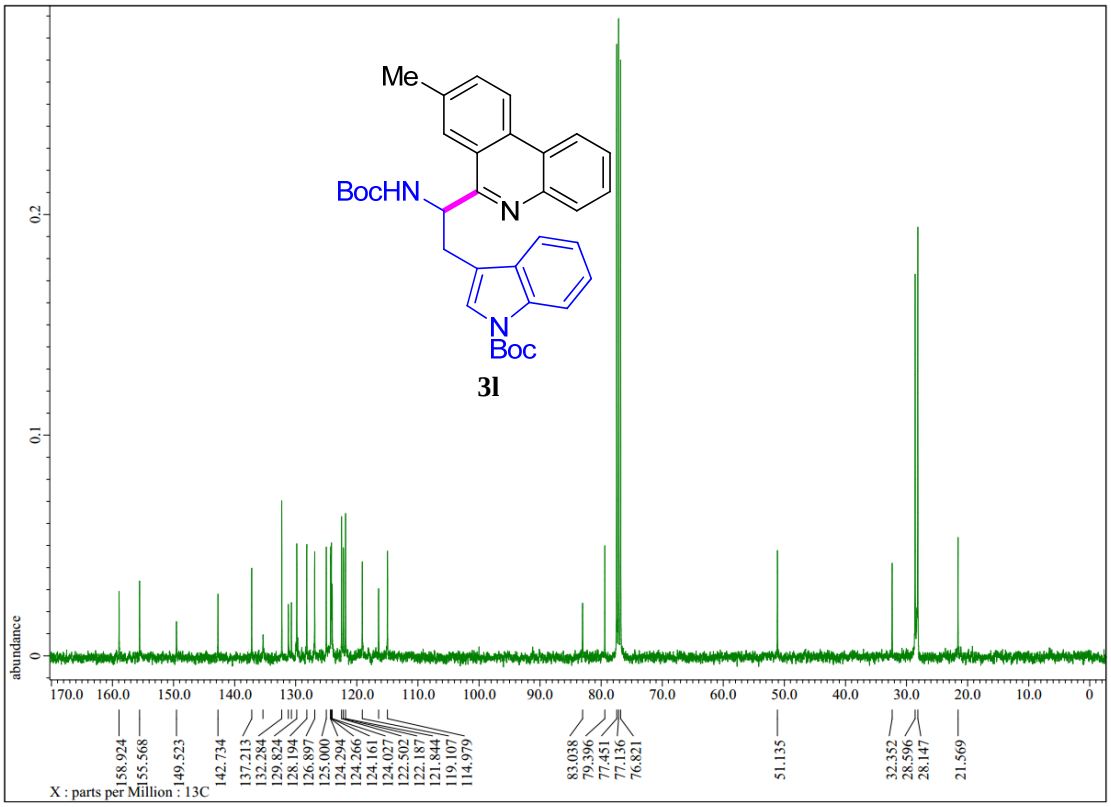
Boc
3l
abundance
X : parts per Million : 1H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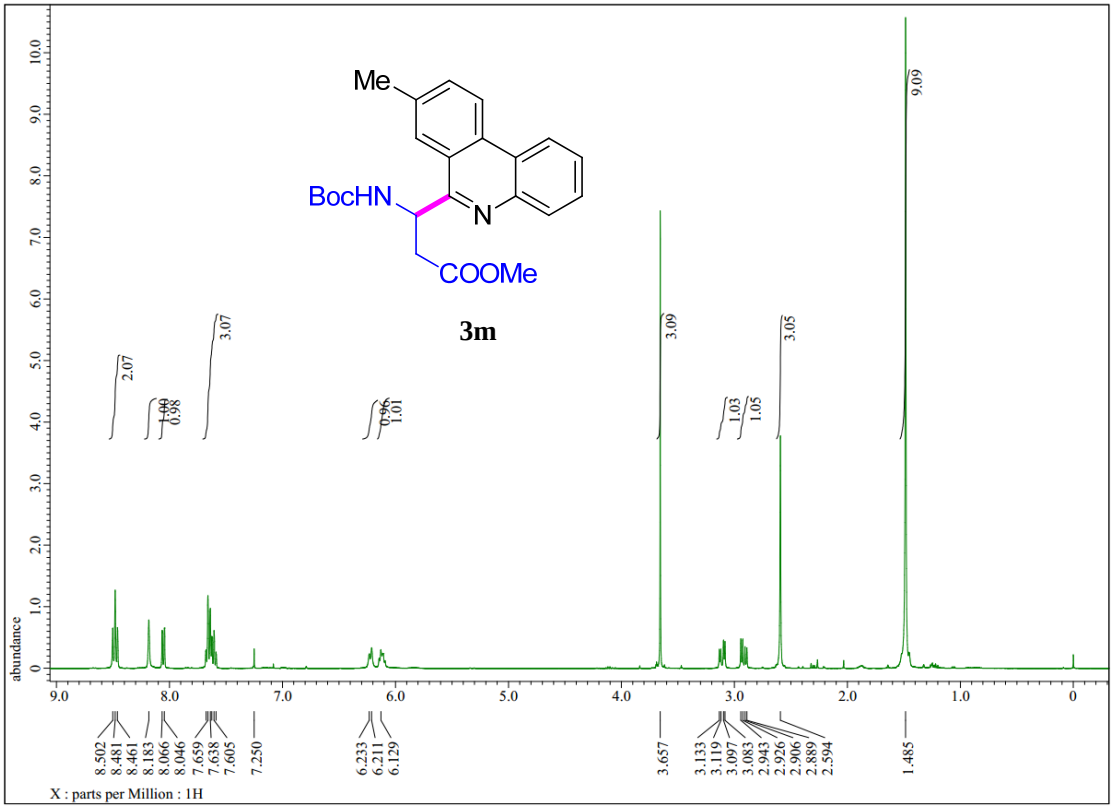
N
Boc
3l
abundance
X : parts per Million : 13C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BocHN
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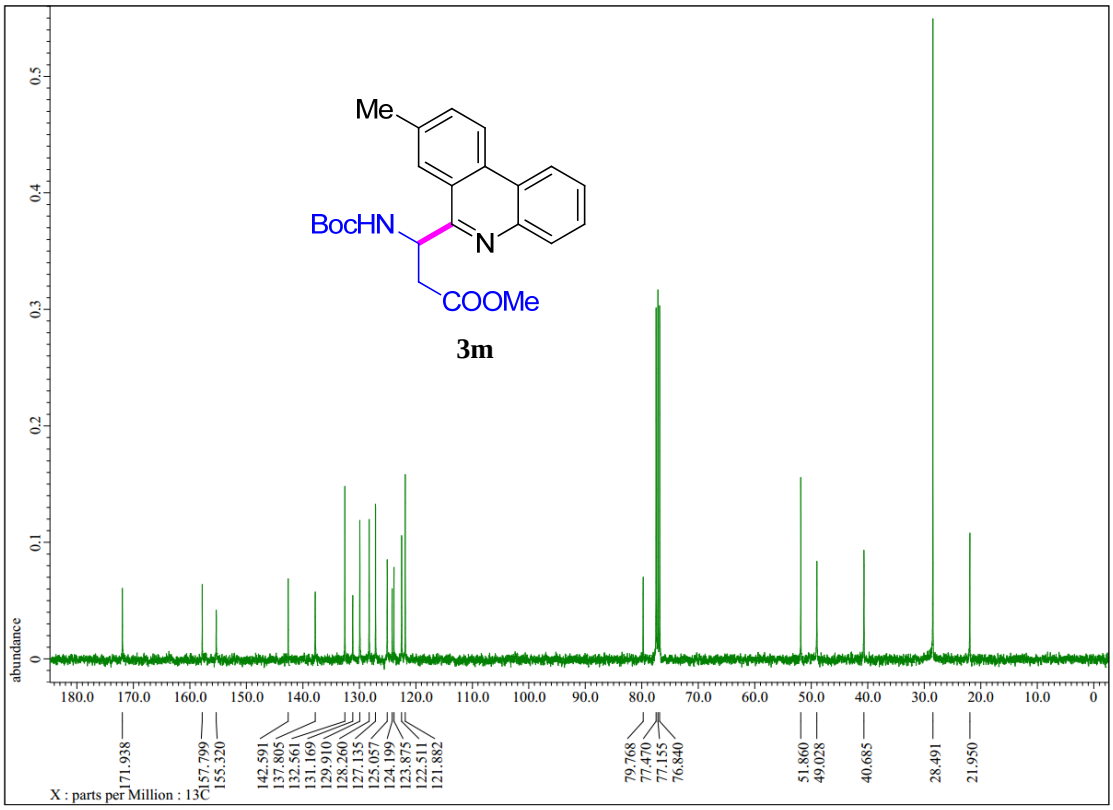
COOMe
3m
abundance
X : parts per Million : 1H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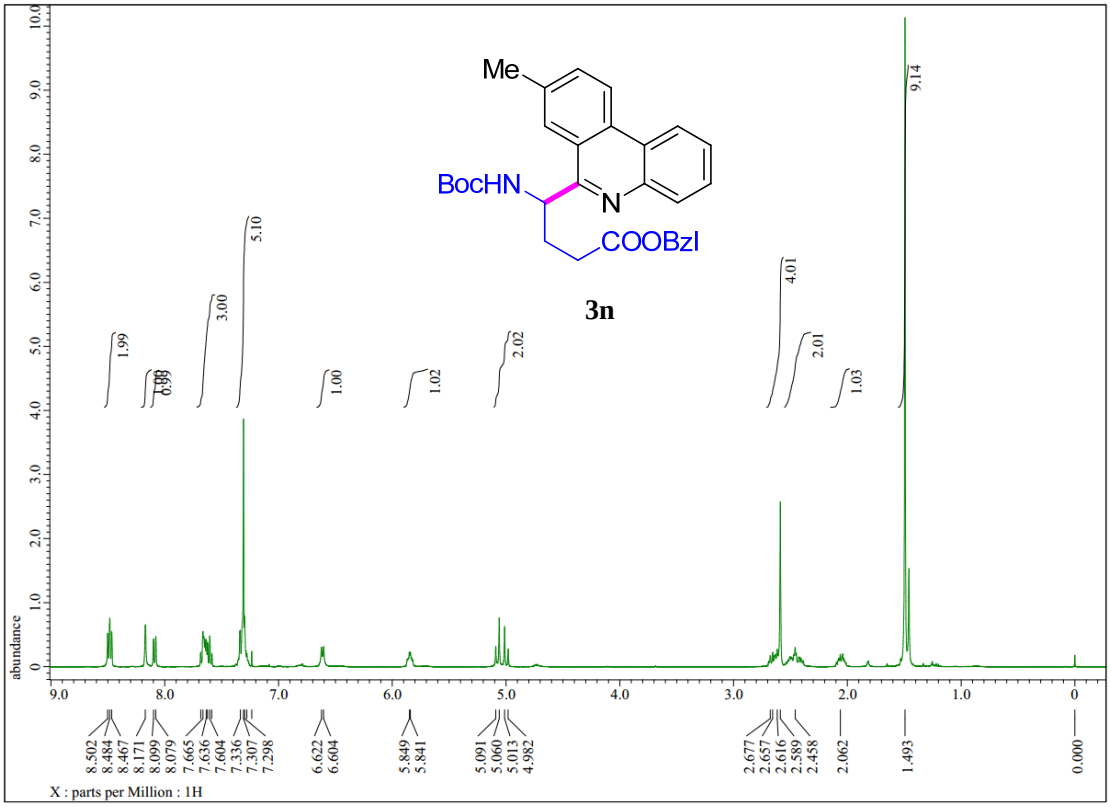
abundance
X : parts per Million : 13C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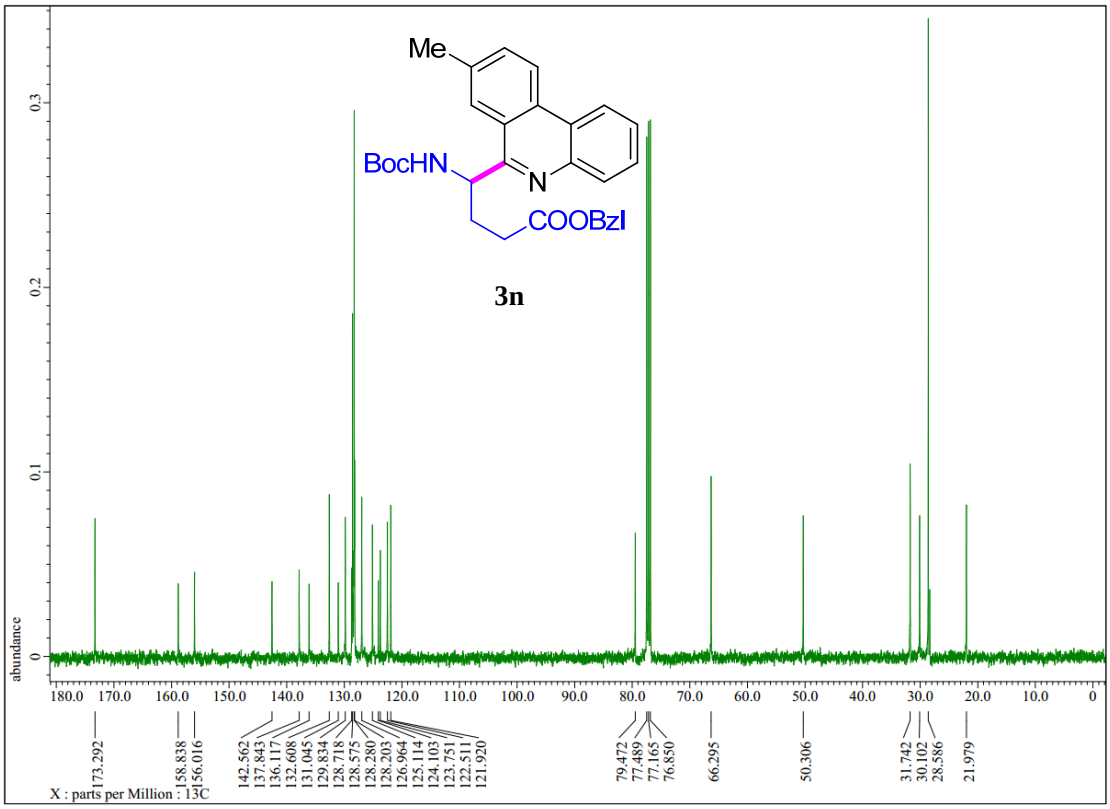
abundance
X : parts per Million : 1H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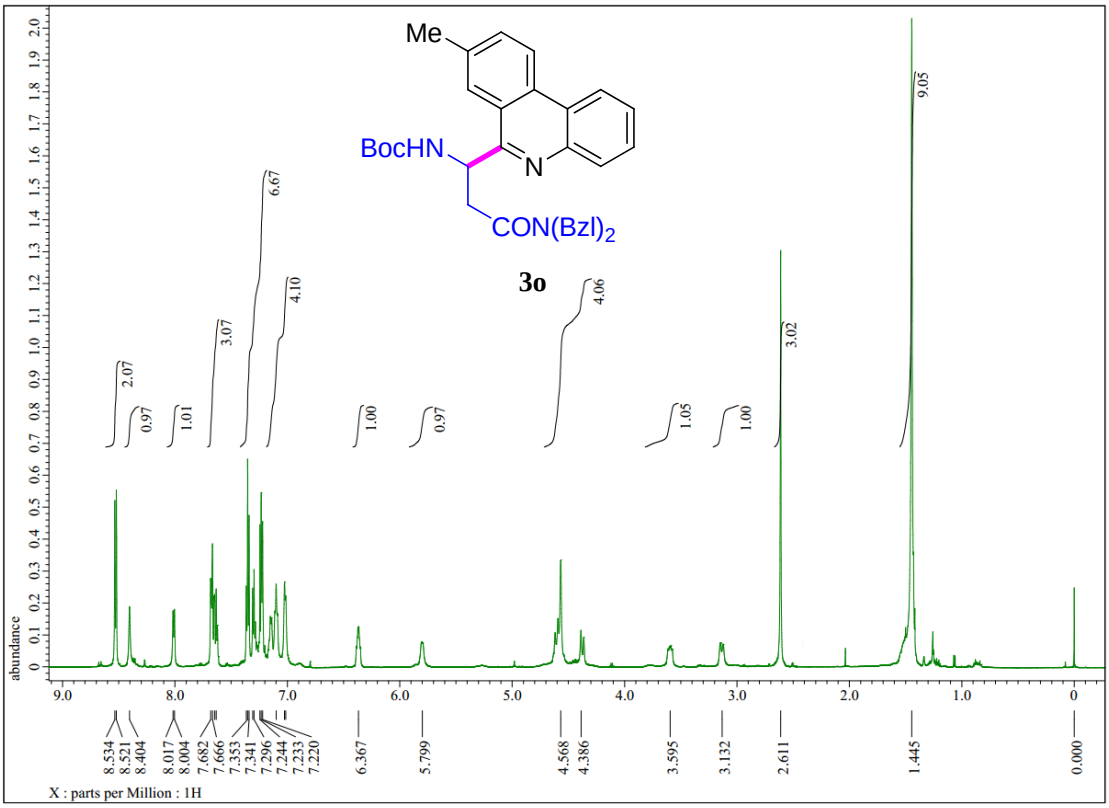
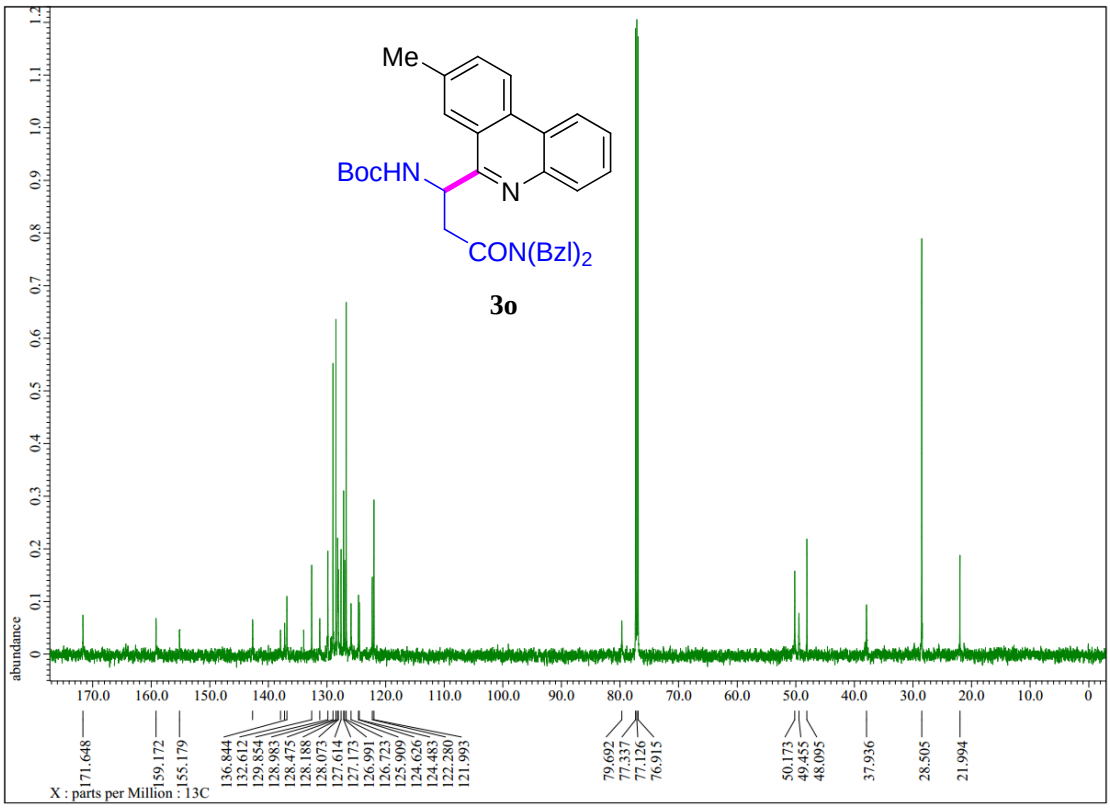
3n
abundance
X : parts per Million : 13C


Me
BocHN
N
CON(Bzl)2
3o
abundance
X : parts per Million : 1H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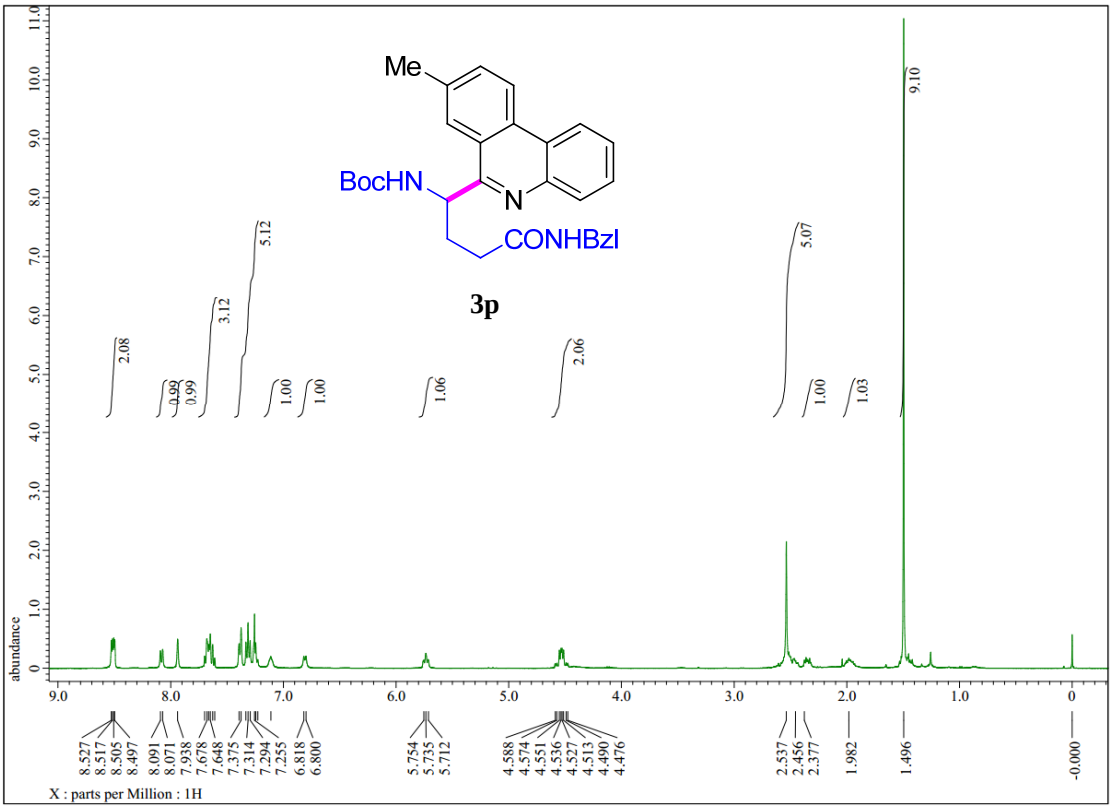
BocHN
N
CON(Bzl)2
3o
abundance
X : parts per Million : 13C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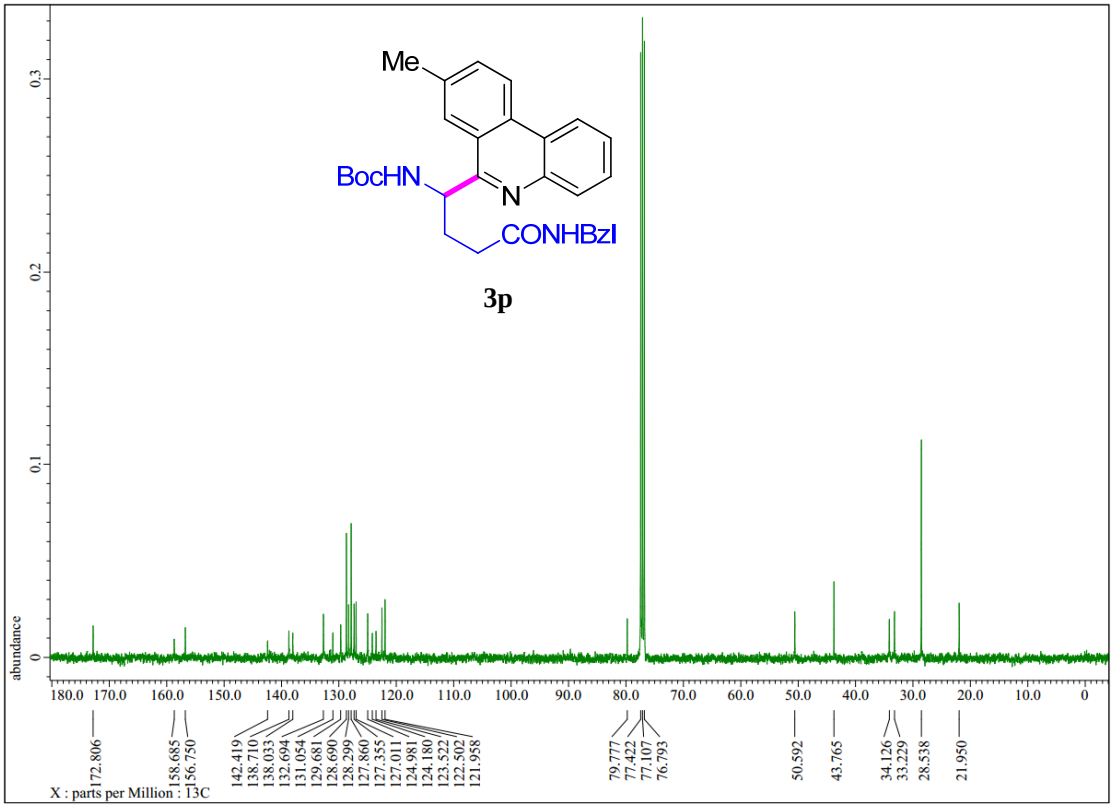
BocHN
N
CONHBzl
3p
abundance
X : parts per Million : 1H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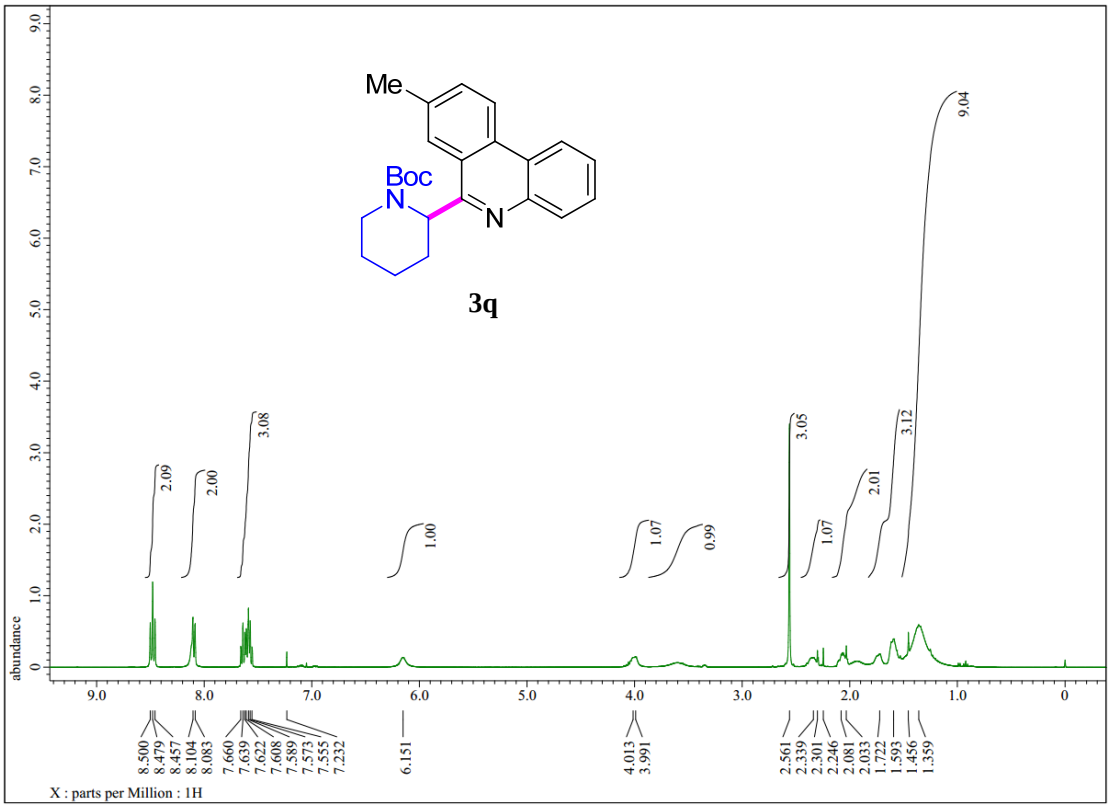
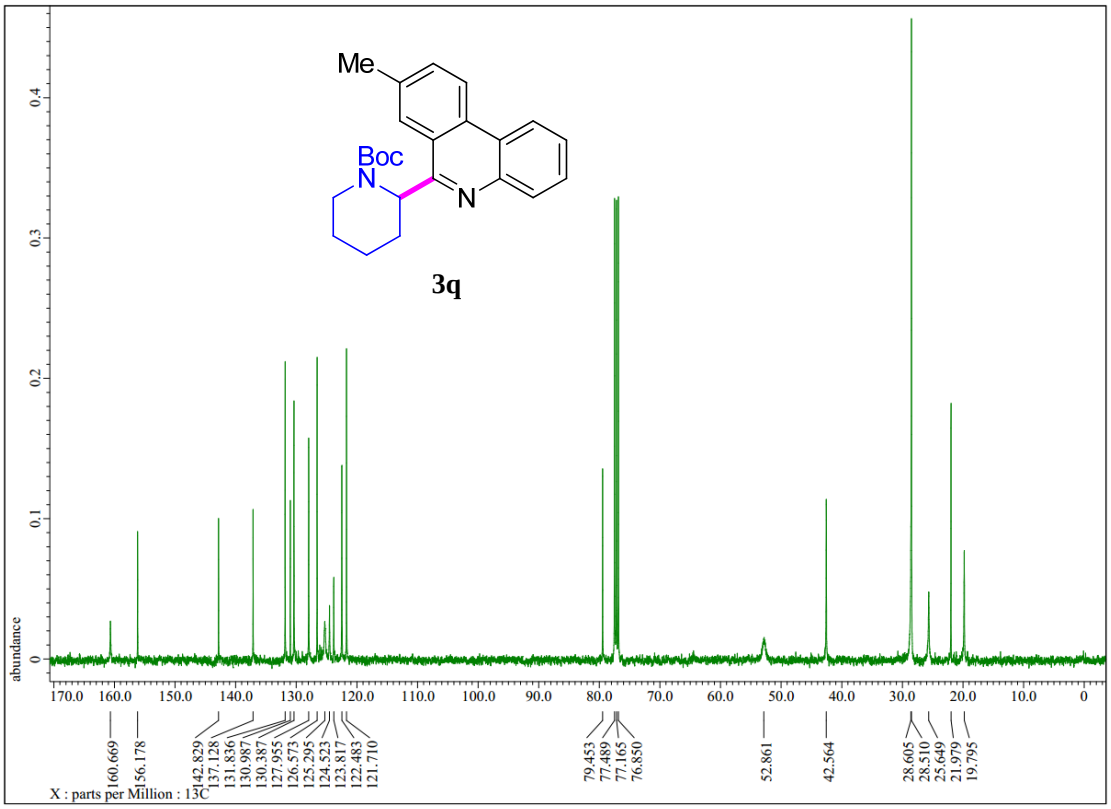
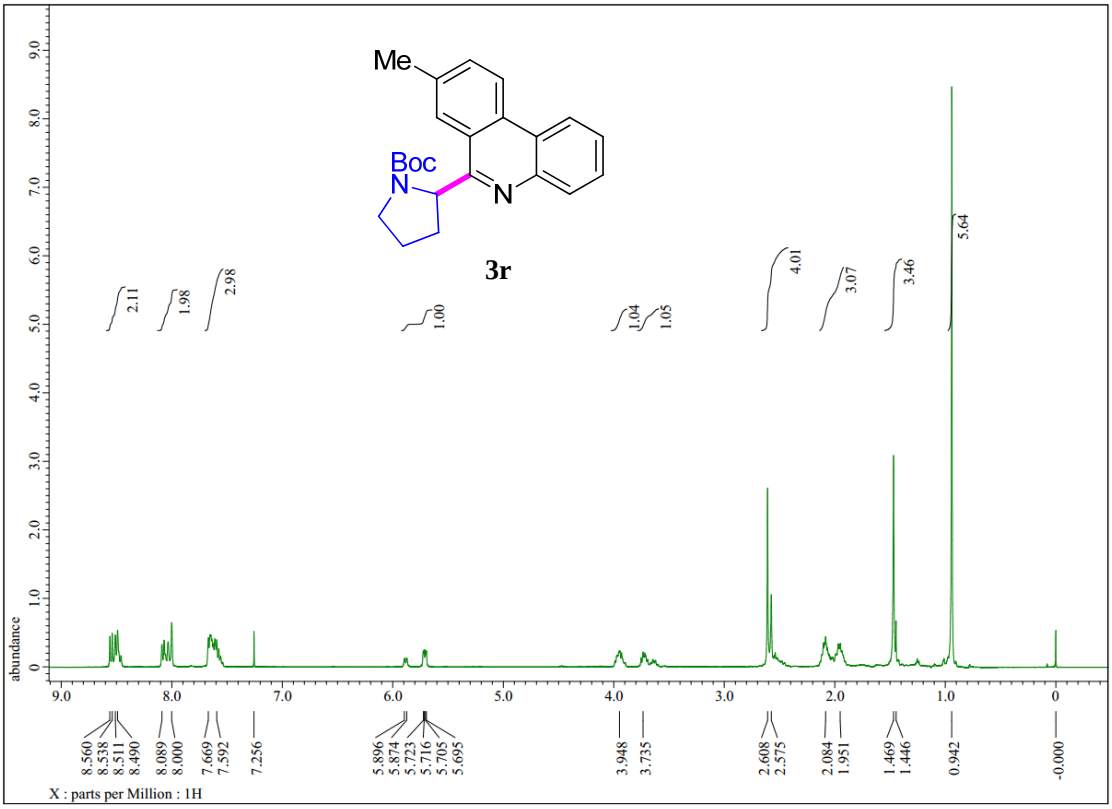
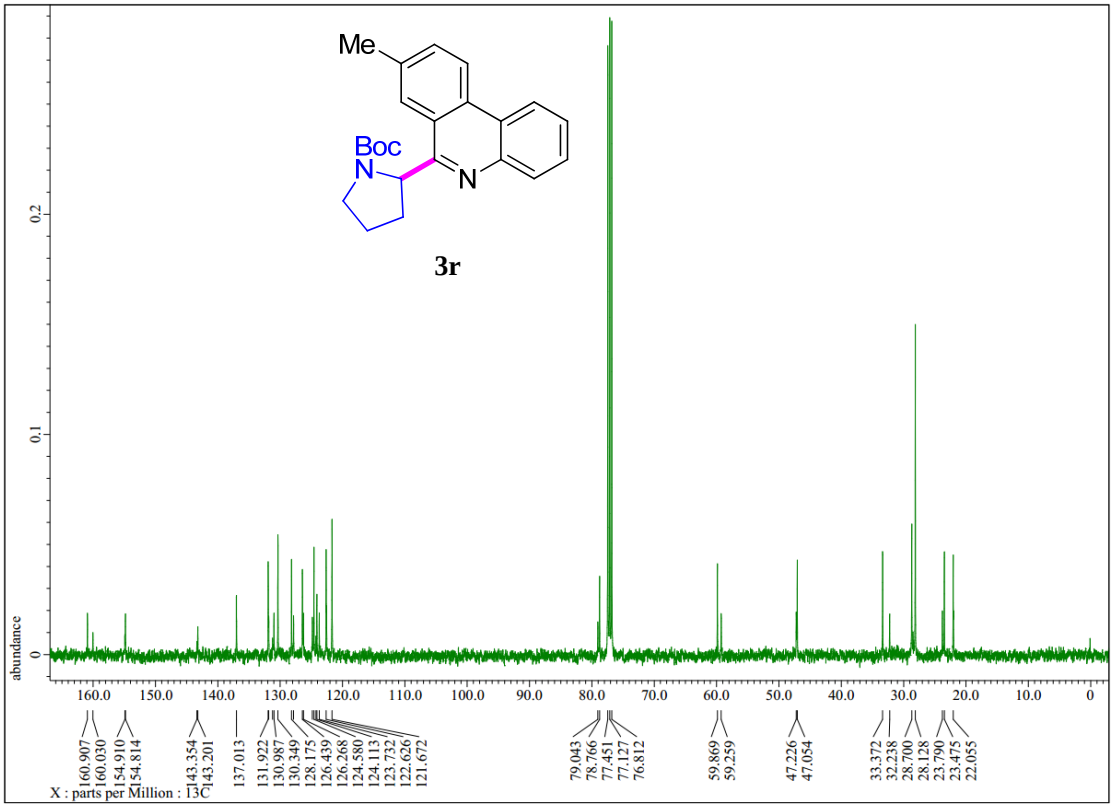
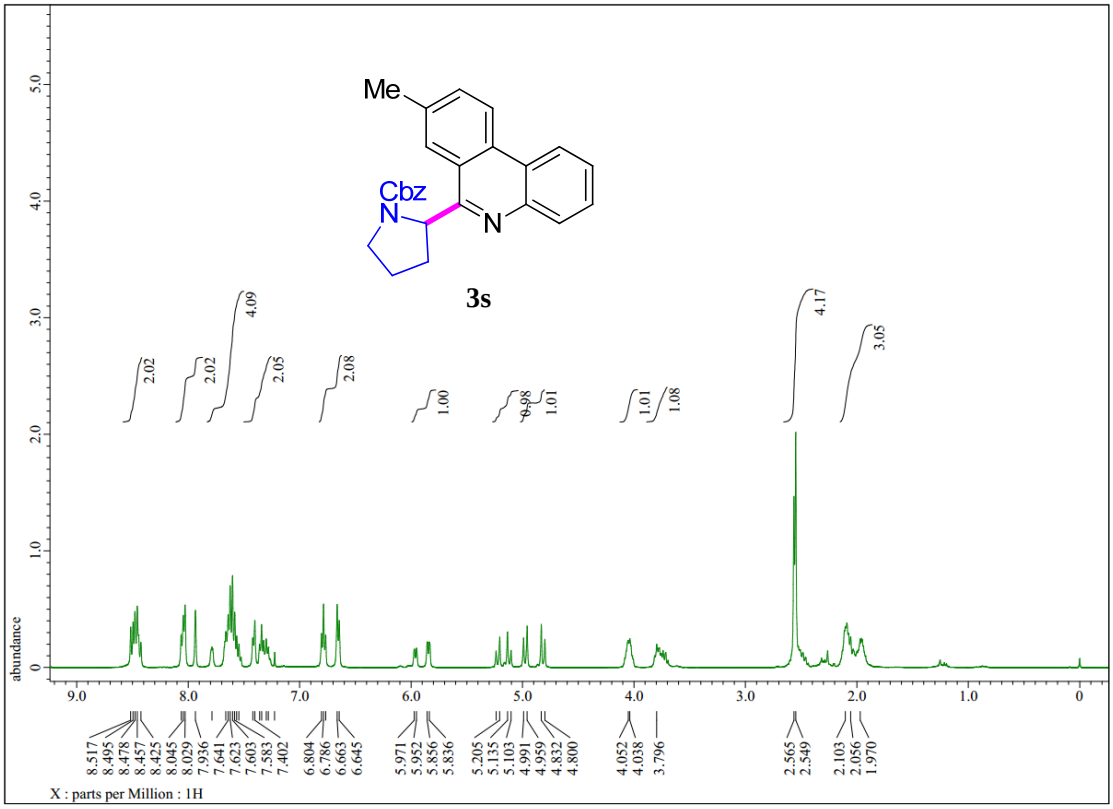
BocHN
N
CONHBzl
3p
abundance
X : parts per Million : 13C

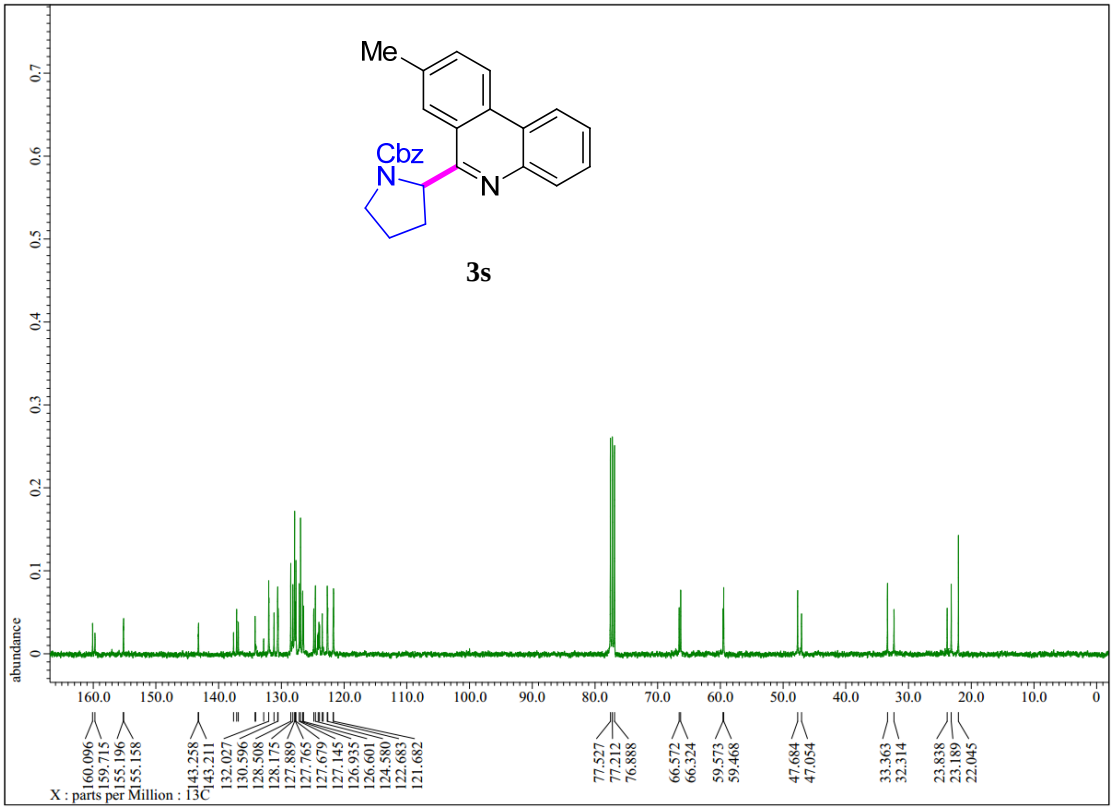

Me
Boc
N
N
3q
abundance
X : parts per Million : 1H

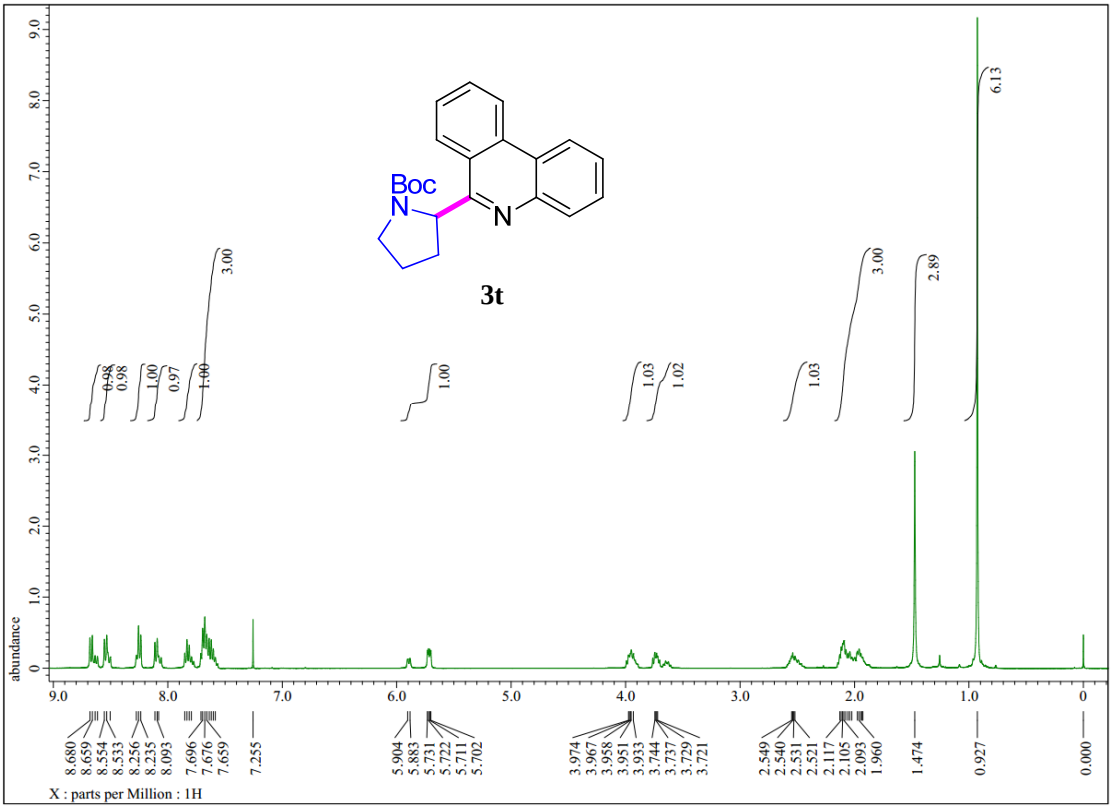

Me
Boc
N
N
3q
abundance
X : parts per Million : 13C

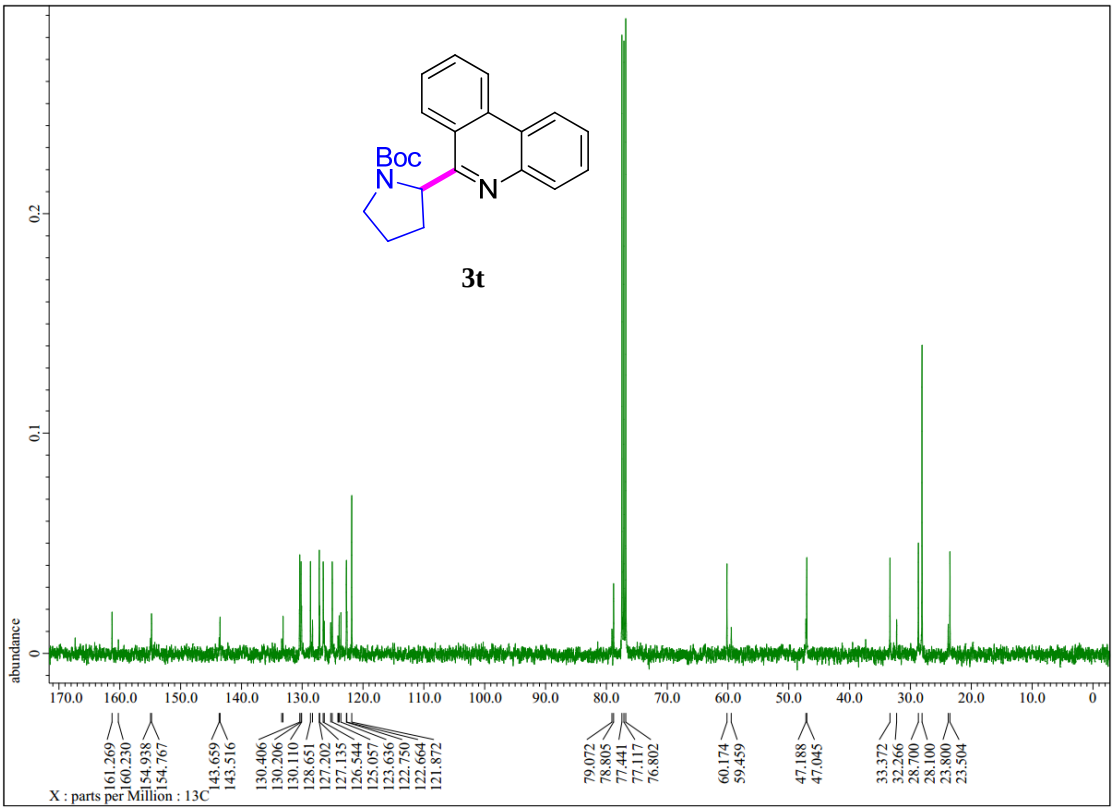

Me
Boc
N
N
3r
2.11
1.98
2.98
1.00
1.04
1.05
4.01
3.07
3.46
5.64
abundance
X : parts per Million : 1H

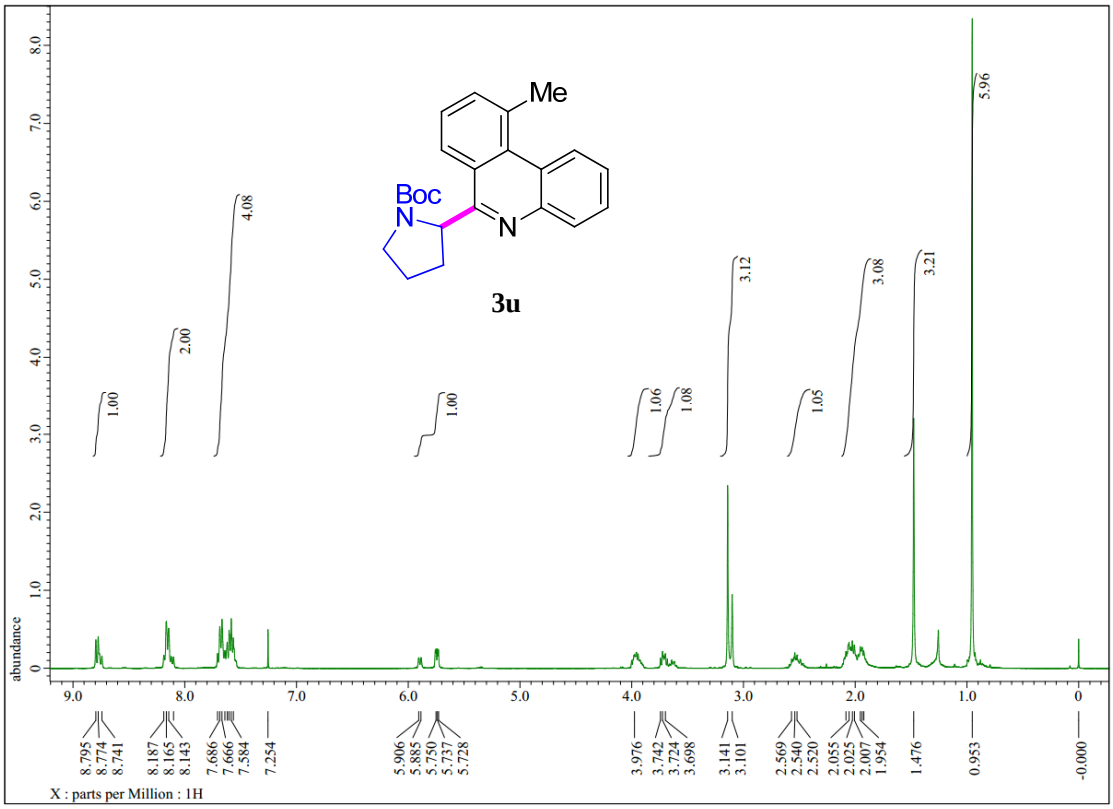

Me
Boc
N
N
3r
abundance
X : parts per Million : 13C

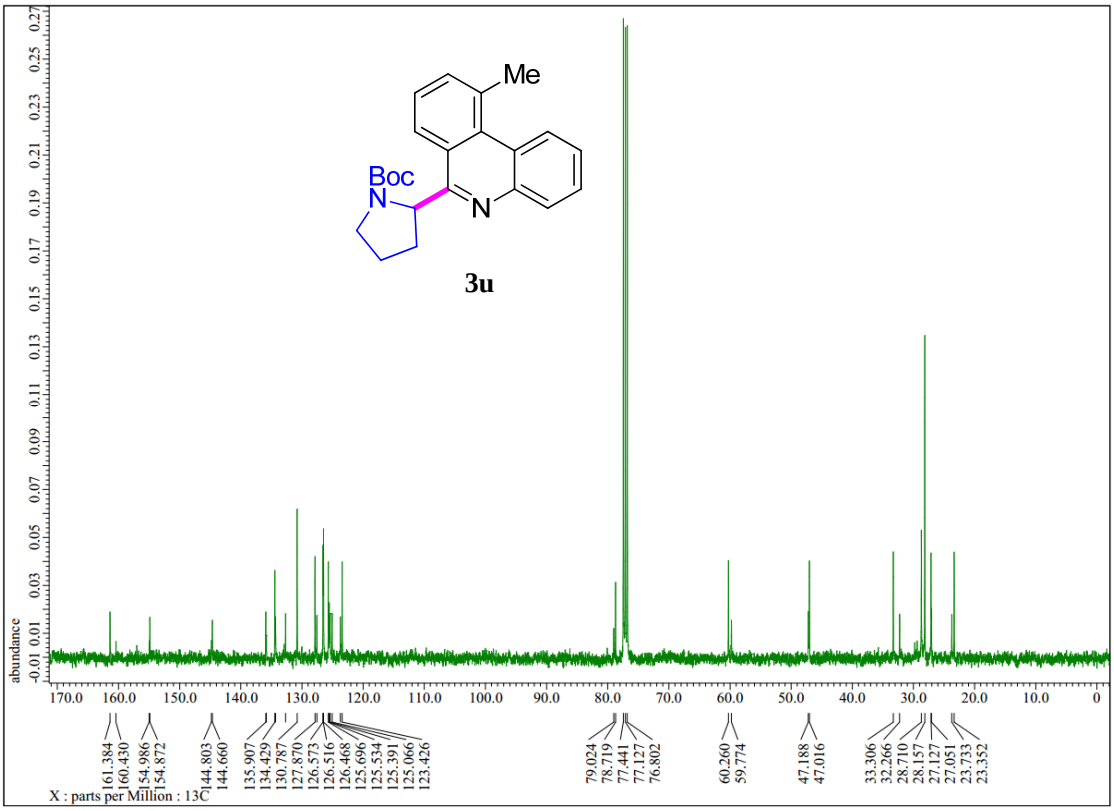

Me
Cbz
N
N
3s
abundance
X : parts per Million : 1H


Me
Cbz
N
N
3s
abundance
X : parts per Million : 13C


Boc
N
N
3t
abundance
X : parts per Million : 1H


Boc
N
N
3t
abundance
X : parts per Million : 13C


Me
Boc
N
N
3u
abundance
X : parts per Million : 1H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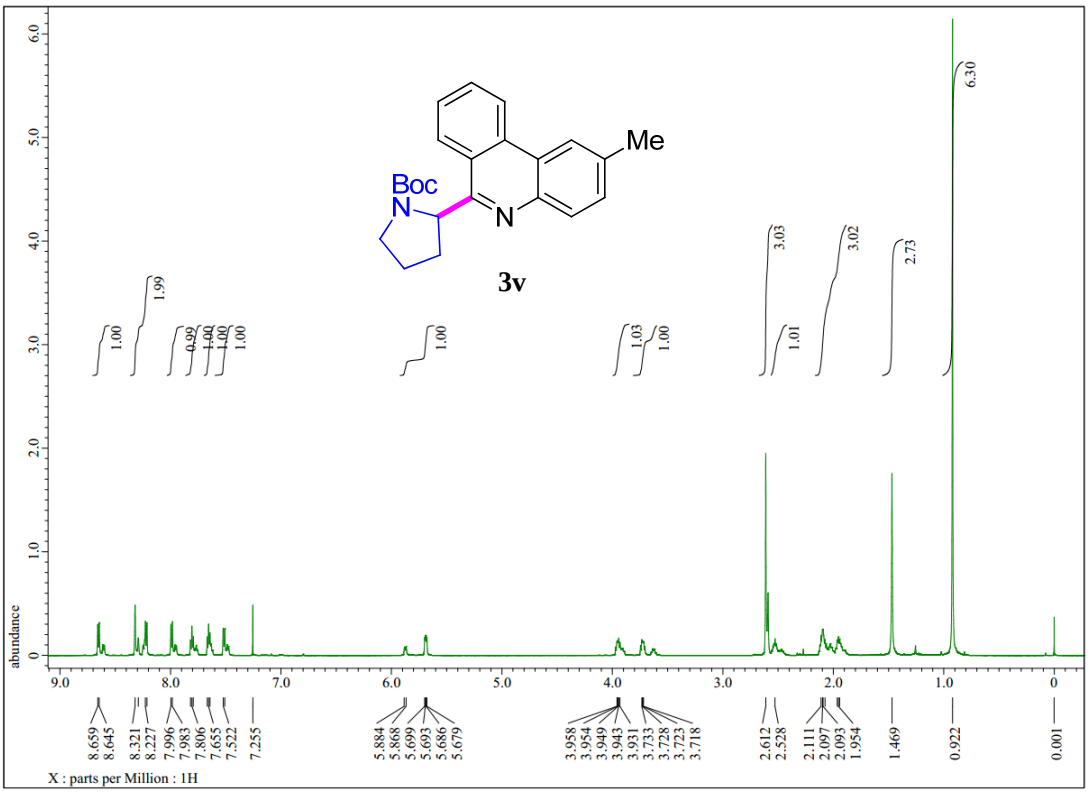
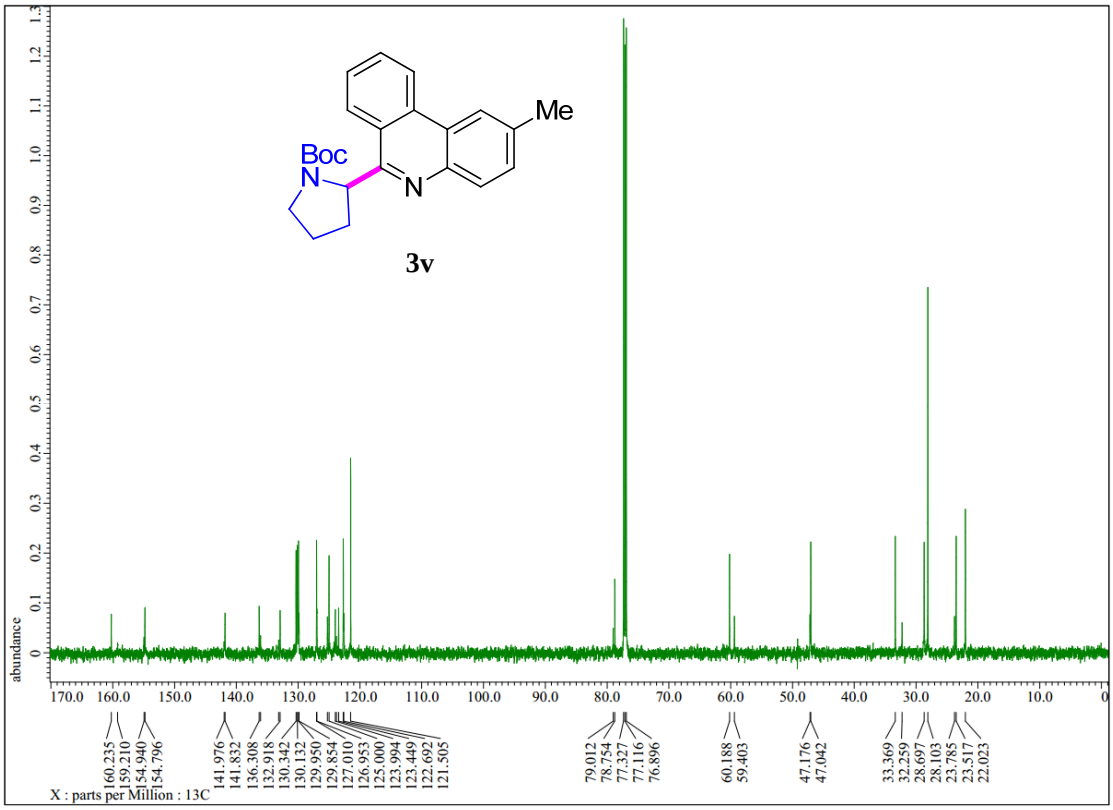
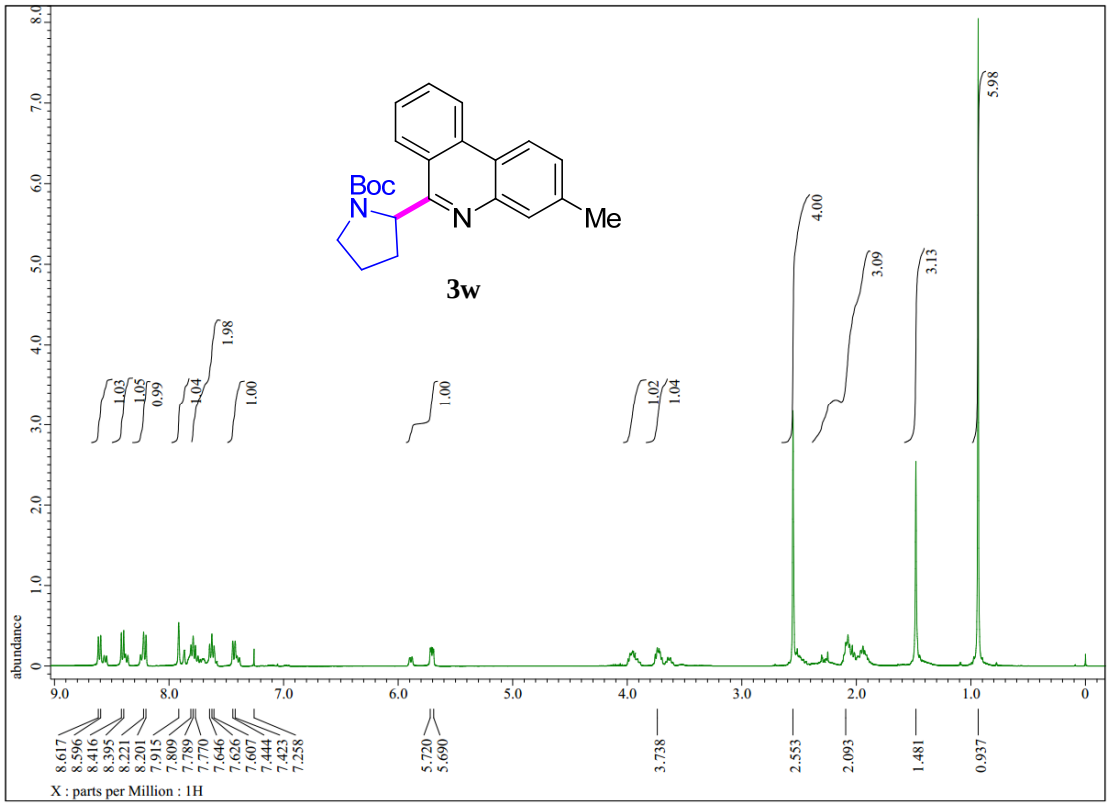
Boc
N
N
3u
abundance
X : parts per Million : 13C


Me
Boc
N
N
3v
abundance
X : parts per Million : 1H


Me
Boc
N
N
3v
abundance
X : parts per Million : 13C


Boc
N
N
Me
3w
abundance
X : parts per Million : 1H
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8.596
8.416
8.395
8.221
8.201
7.915
7.809
7.789
7.770
7.646
7.626
7.607
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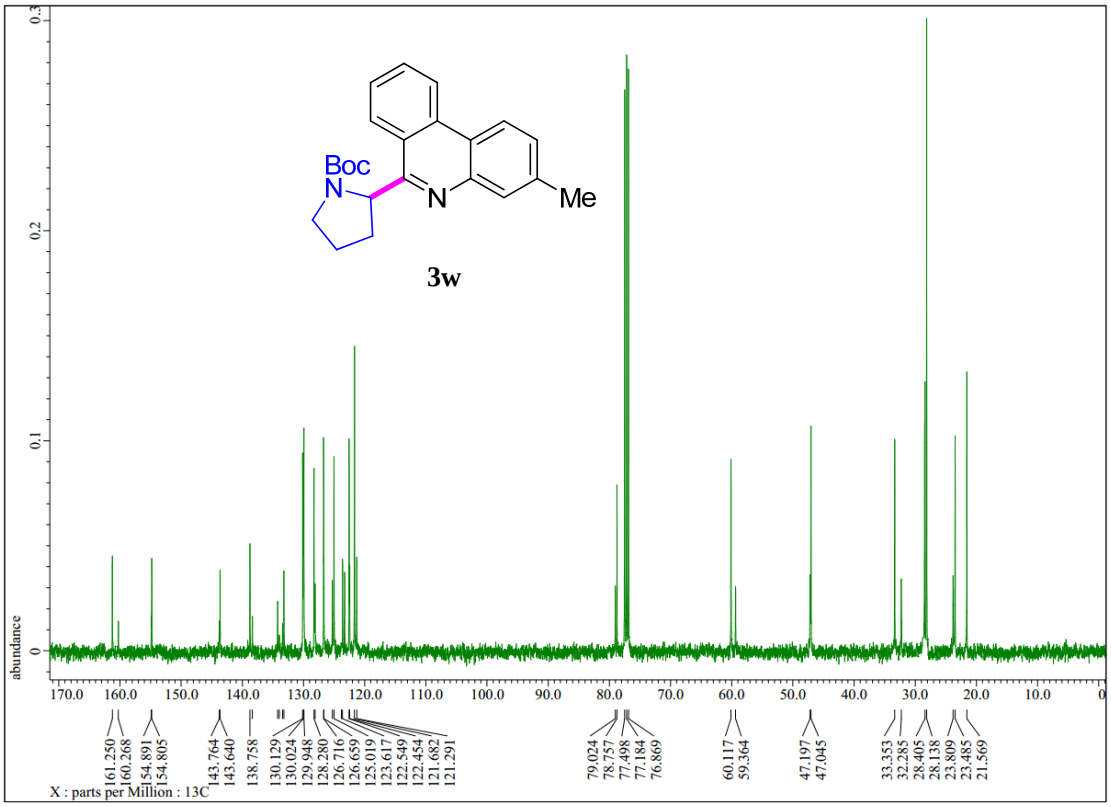
7.423
7.258
5.720
5.690
3.738
2.553
2.093
1.481
0.937


Boc
N
N
Me
3w
abundance
X : parts per Million : 13C
161.250
160.268
154.891
154.805
143.764
143.640
138.758
130.129
130.024
129.948
128.280
126.716
126.659
125.019
123.617
122.549
122.454
121.682
121.291
79.024
78.757
77.498
77.184
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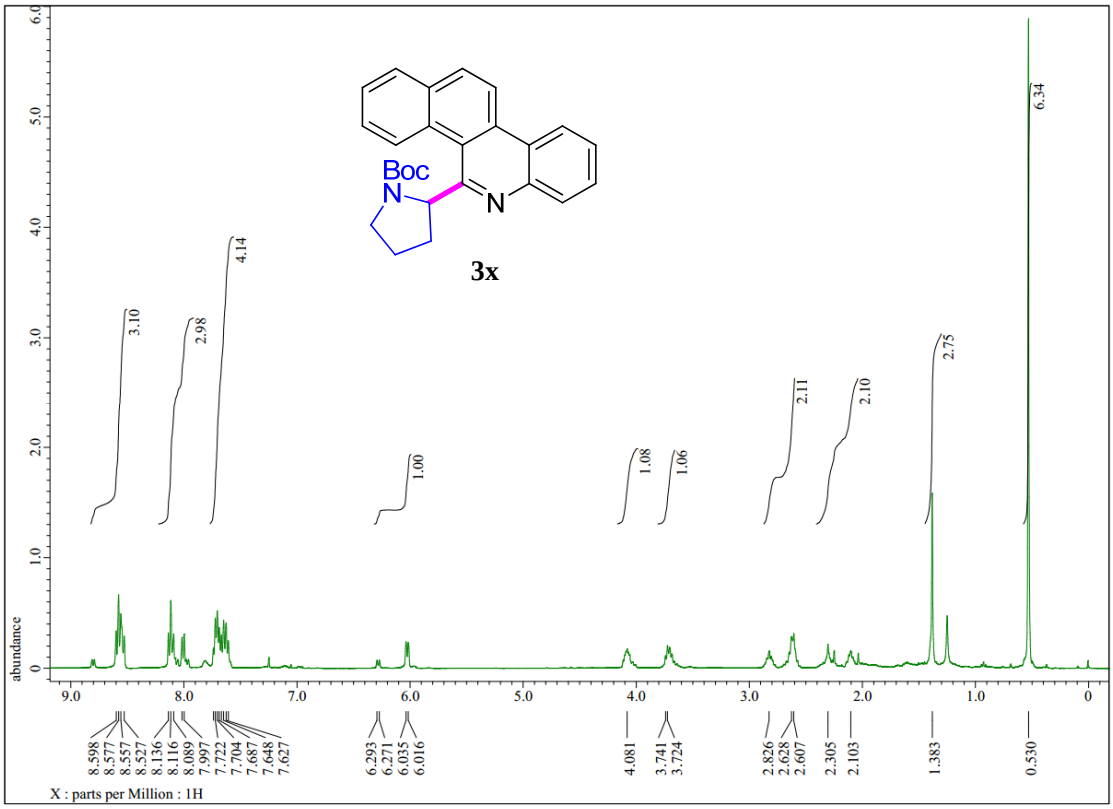
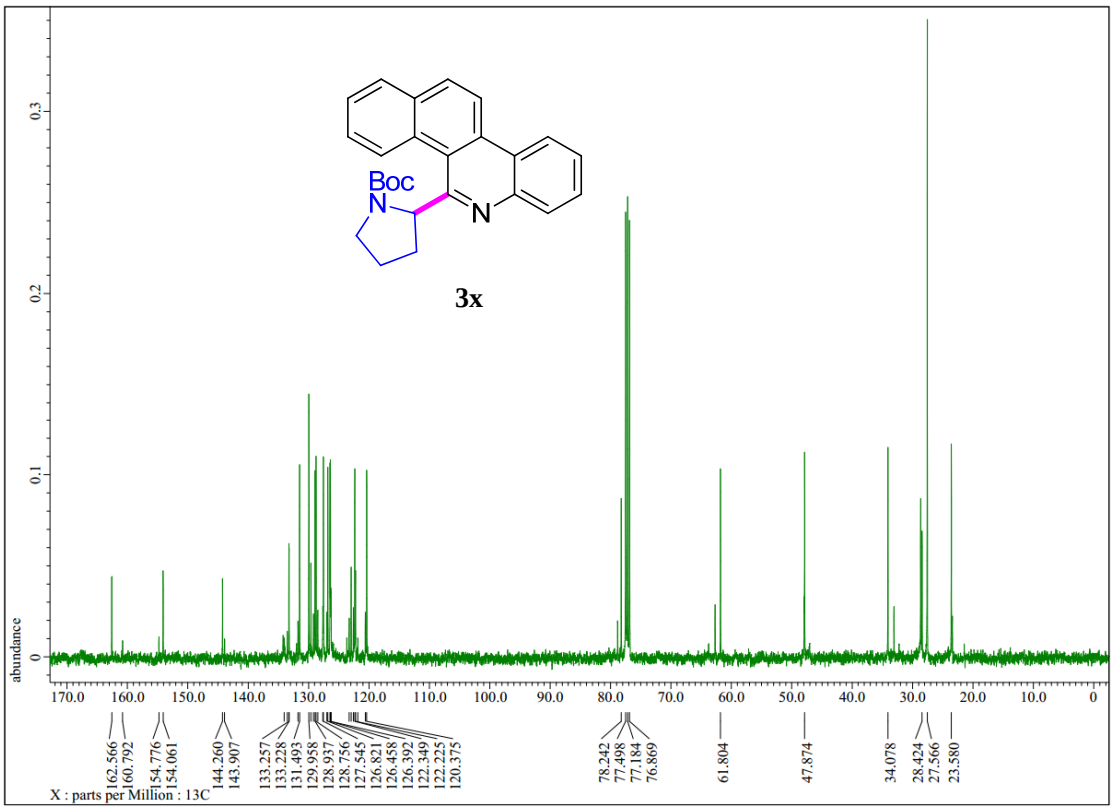
23.485
21.569


Boc
N
N
3x
abundance
X : parts per Million : 1H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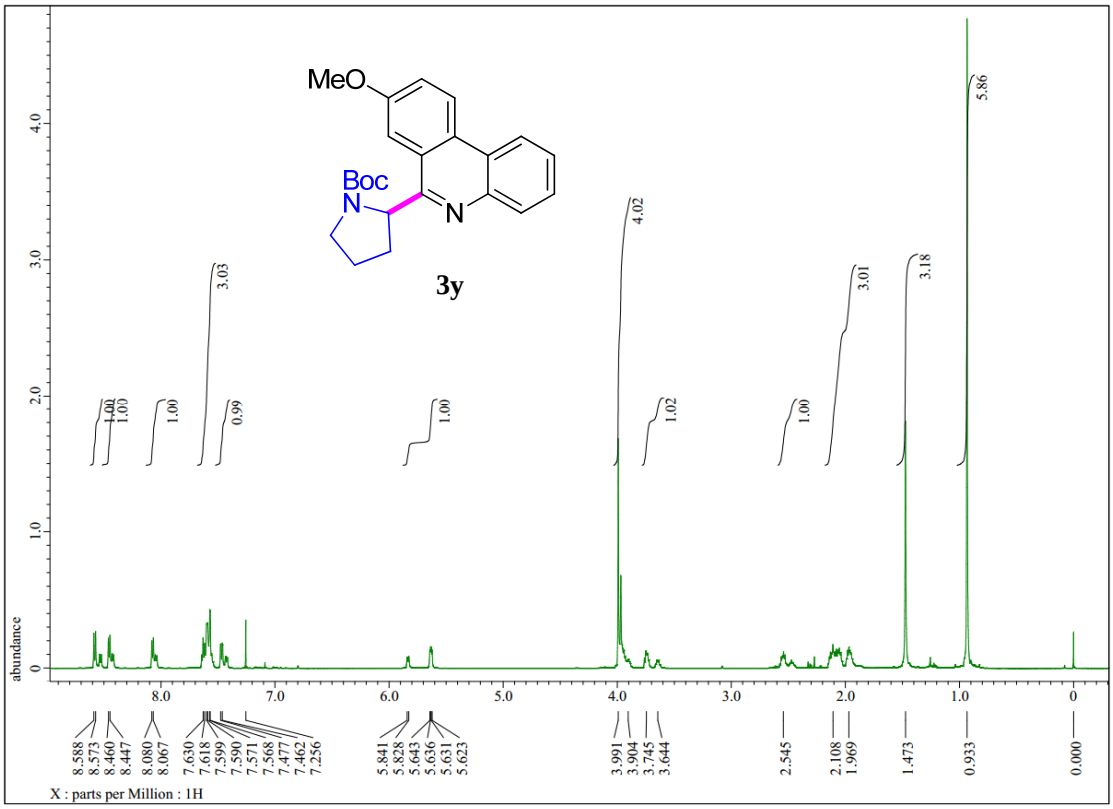
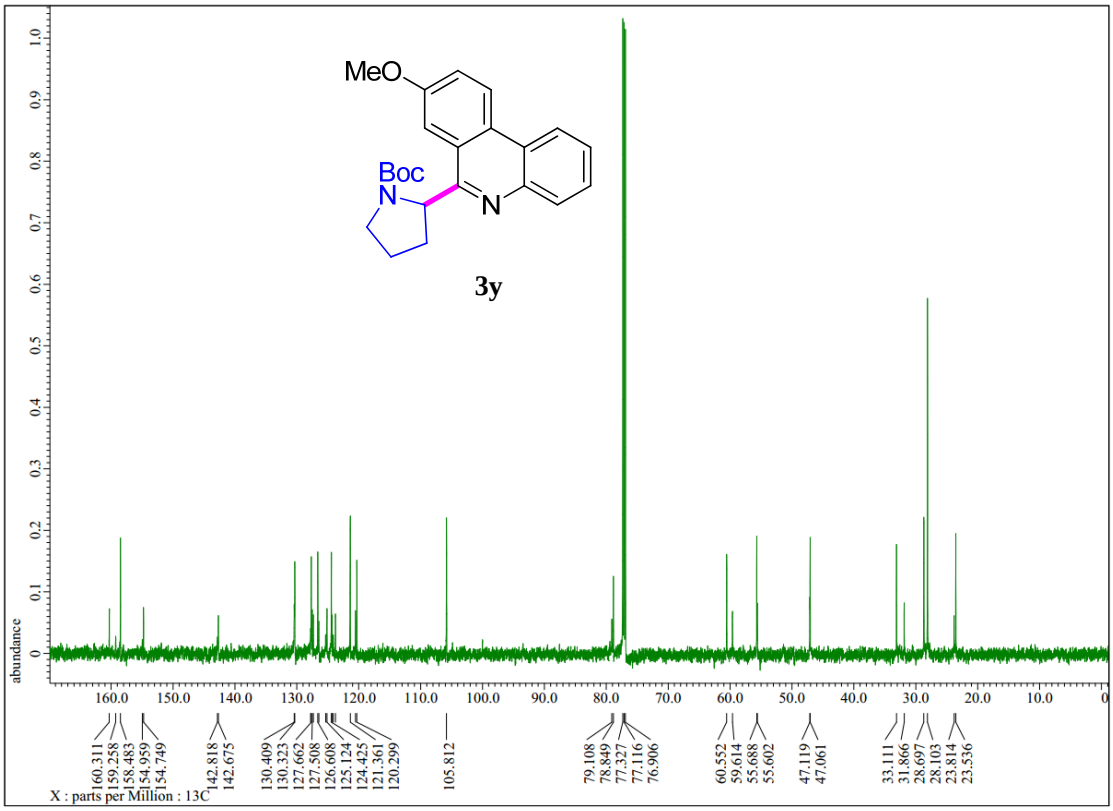
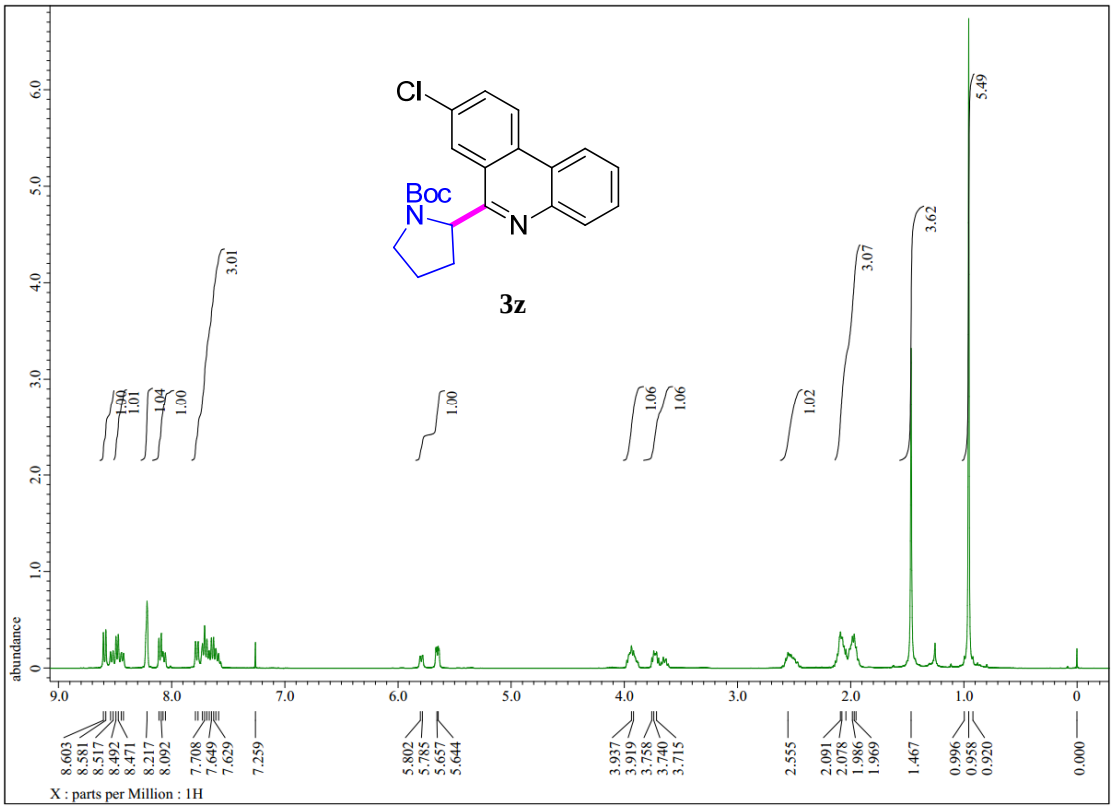
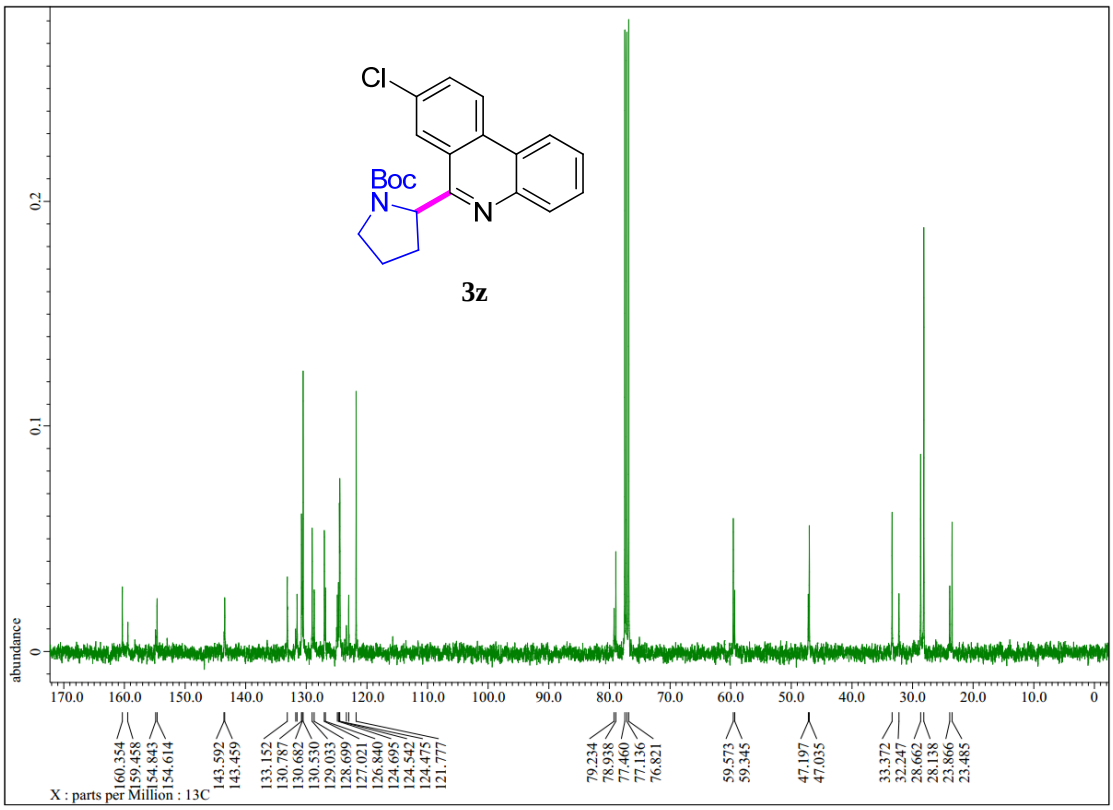
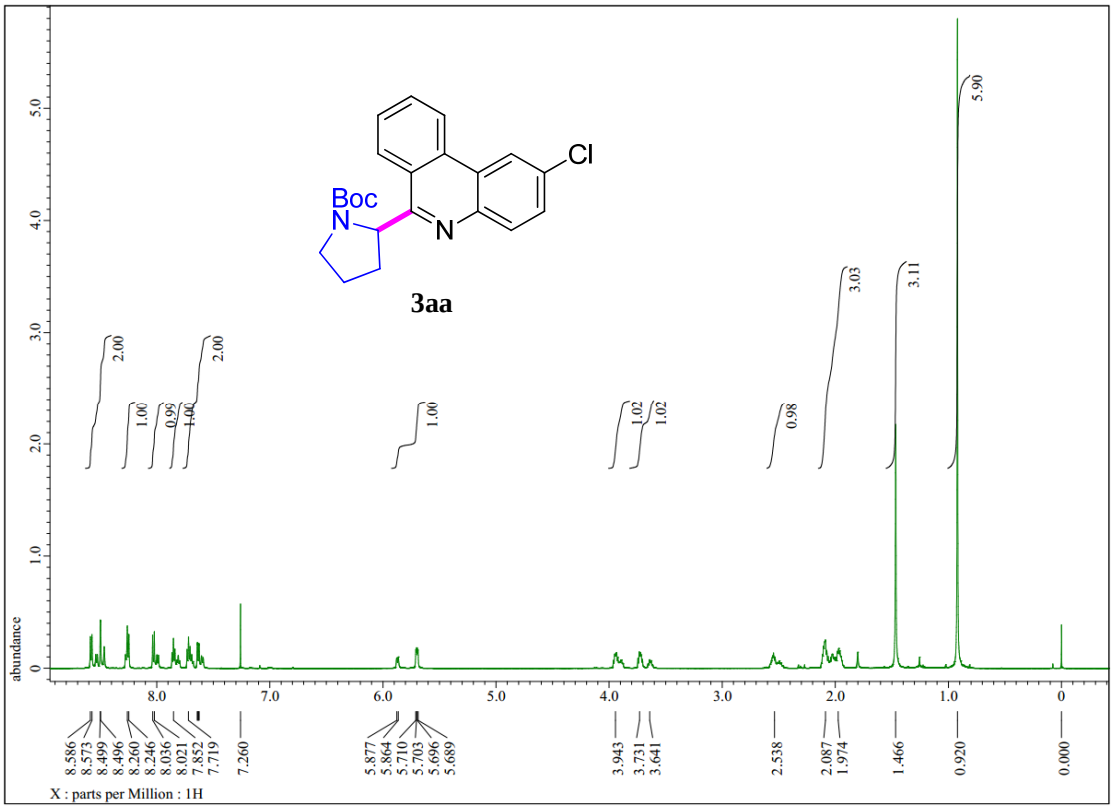
N
3x
abundance
X : parts per Million : 13C

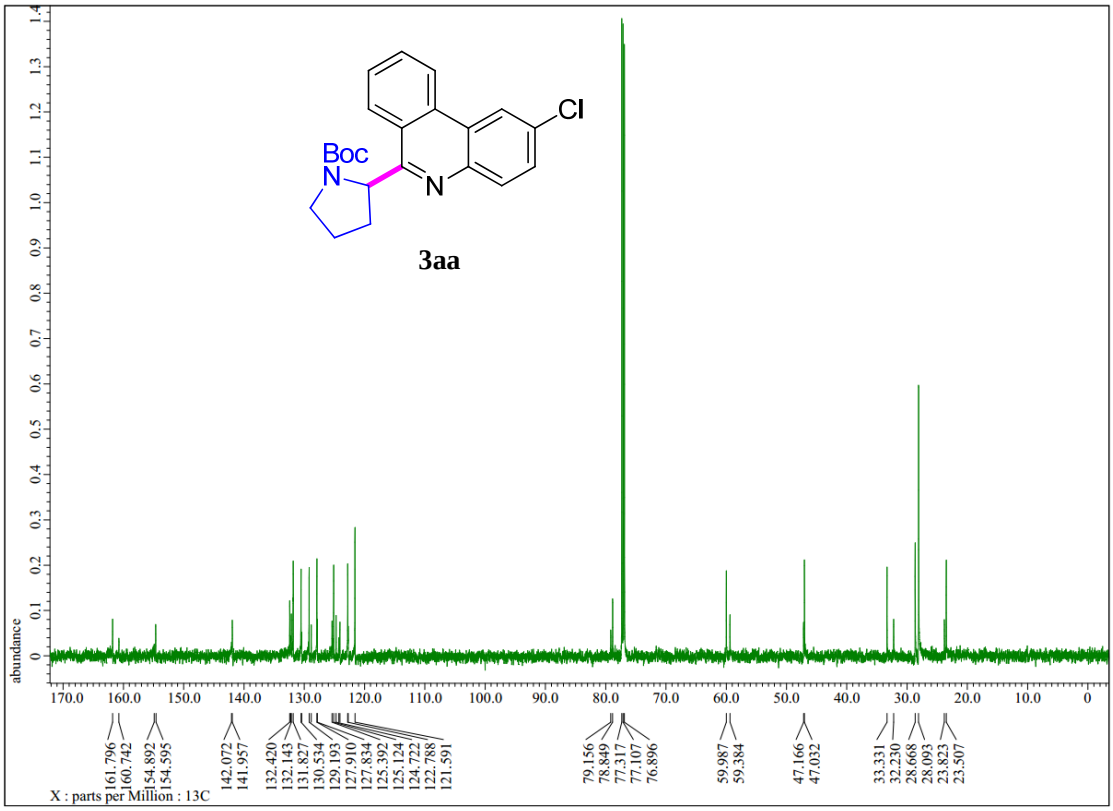

MeO
Boc
N
N
3y
abundance
X : parts per Million : 1H

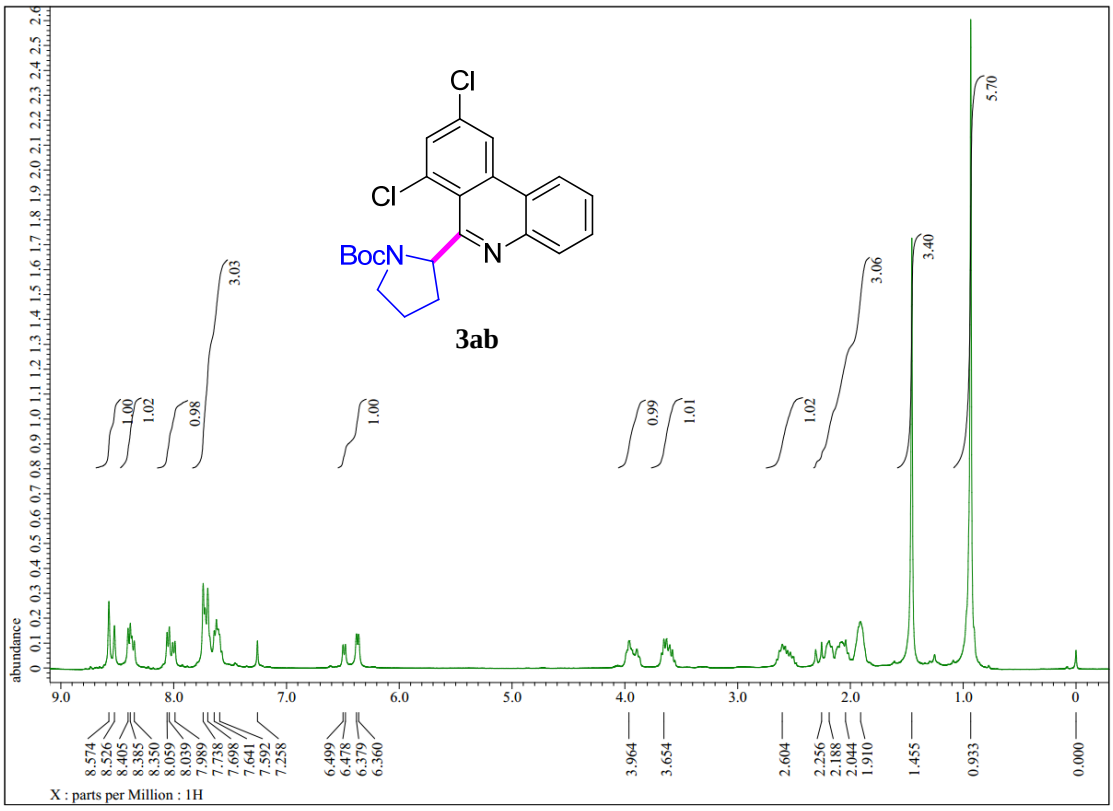

MeO
Boc
N
N
3y
abundance
X : parts per Million : 13C

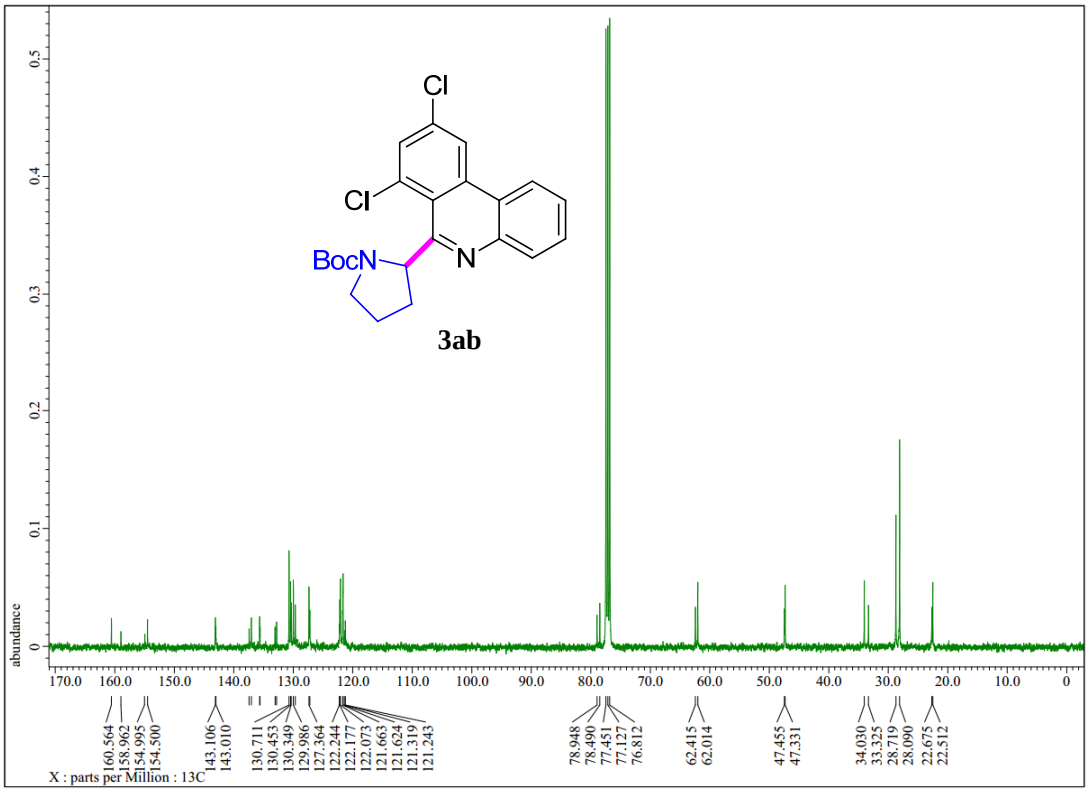

Cl
Boc
N
N
3z
abundance
X : parts per Million : 1H

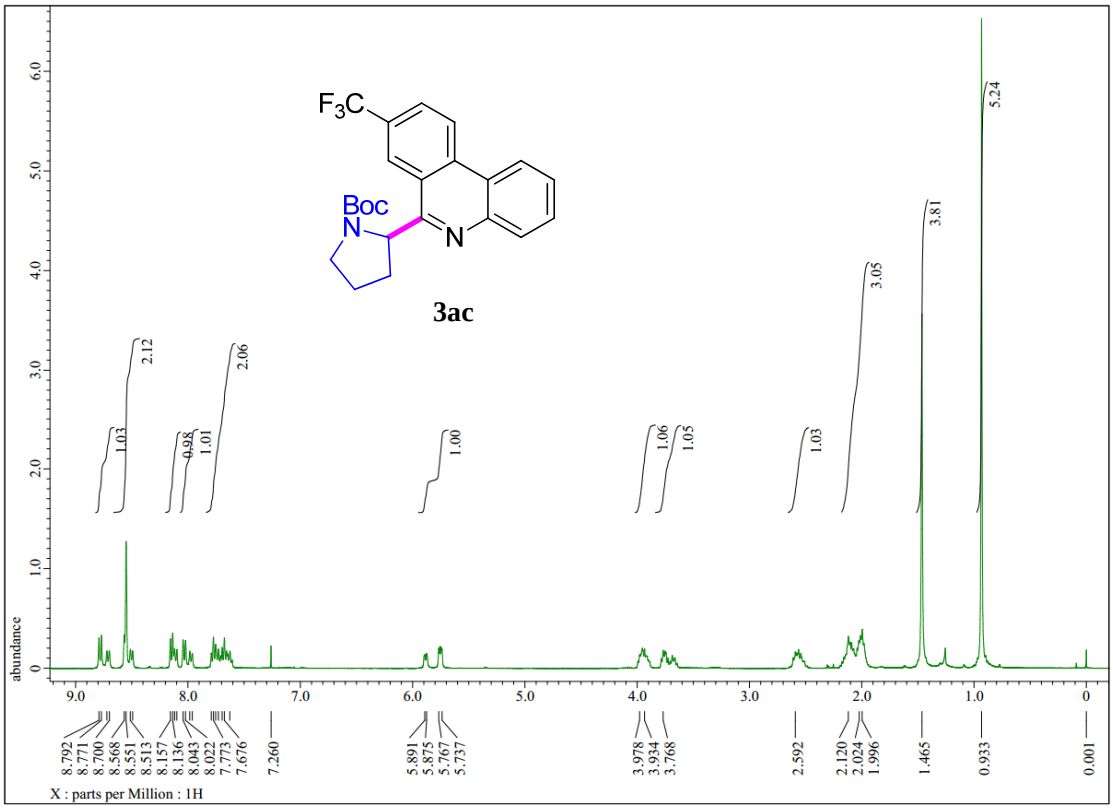

Cl
Boc
N
N
3z
abundance
X : parts per Million : 13C

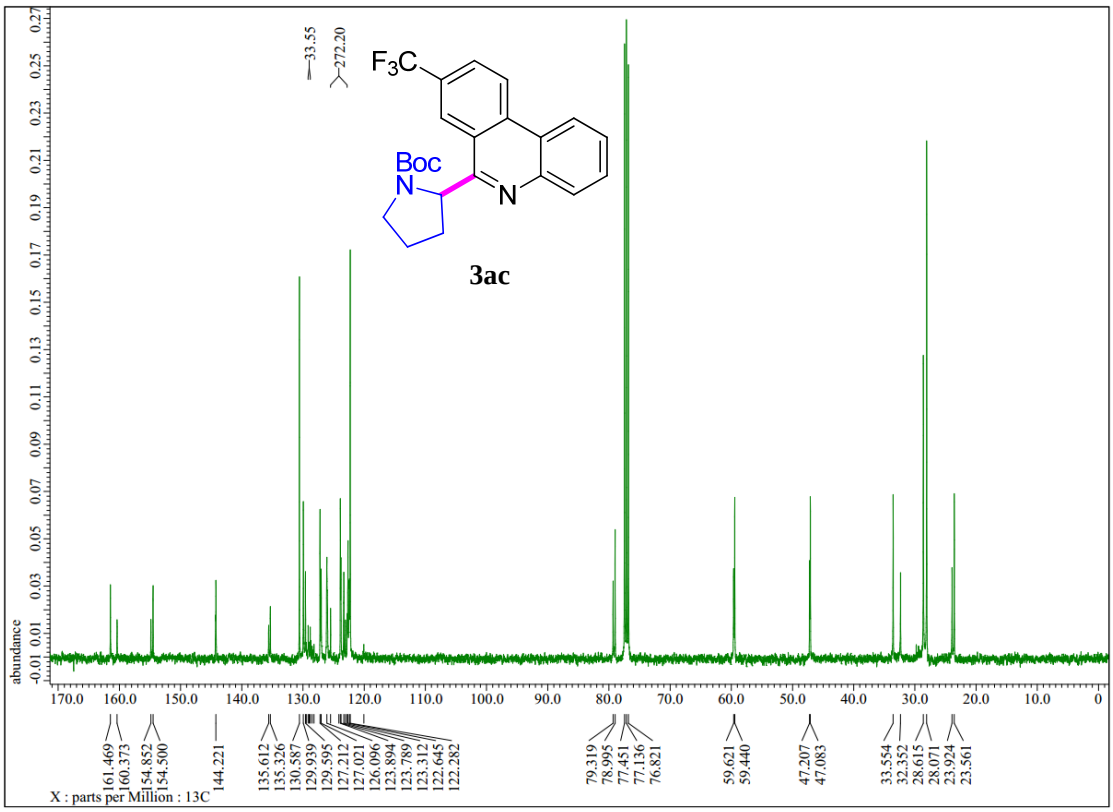

Cl
Boc
N
N
3aa
abundance
X : parts per Million : 1H

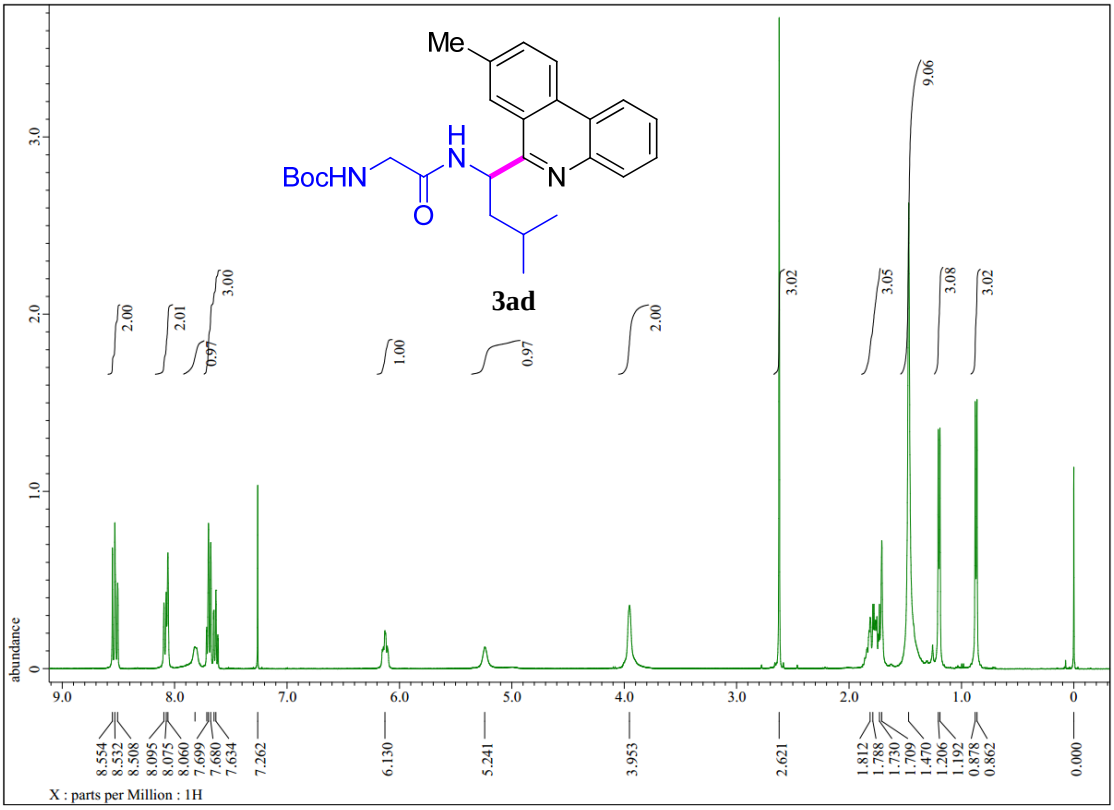

Cl
Boc
N
N
3aa
abundance
X : parts per Million : 13C

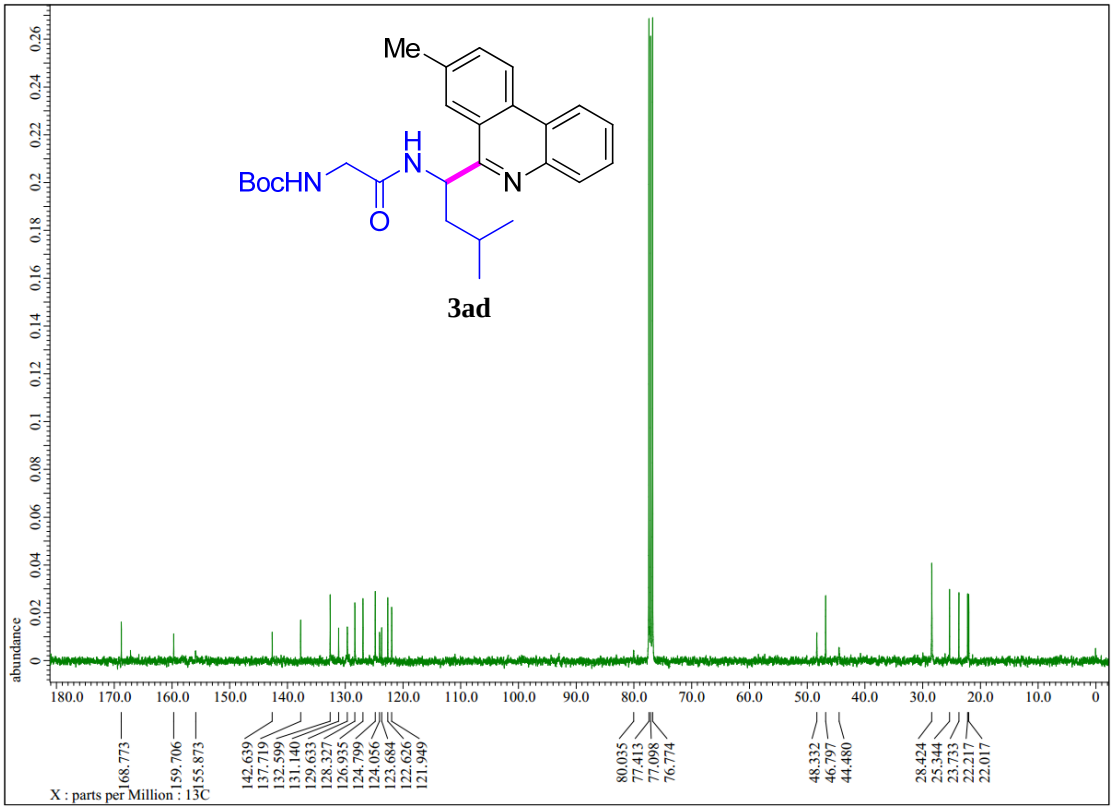

Cl
Cl
BocN
N
3ab
abundance
X : parts per Million : 1H

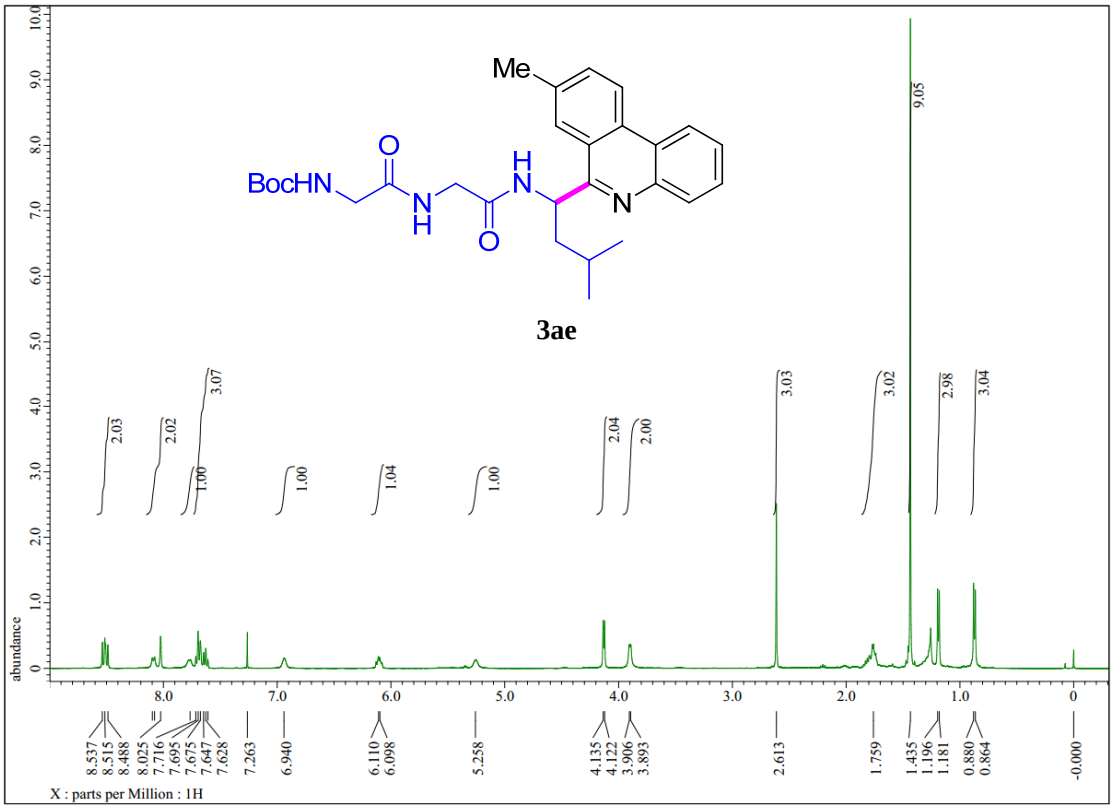

Cl
Cl
BocN
N
3ab
abundance
X : parts per Million : 13C

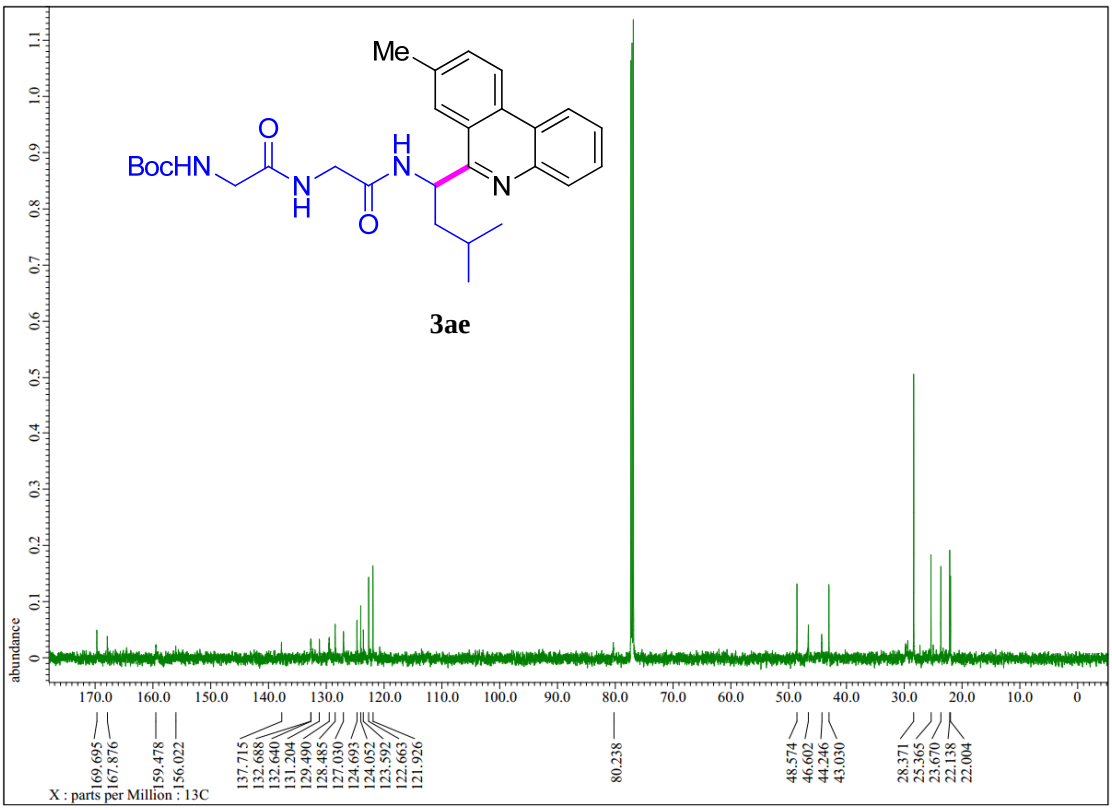

F3C
Boc
N
N
3ac
abundance
X : parts per Million : 1H

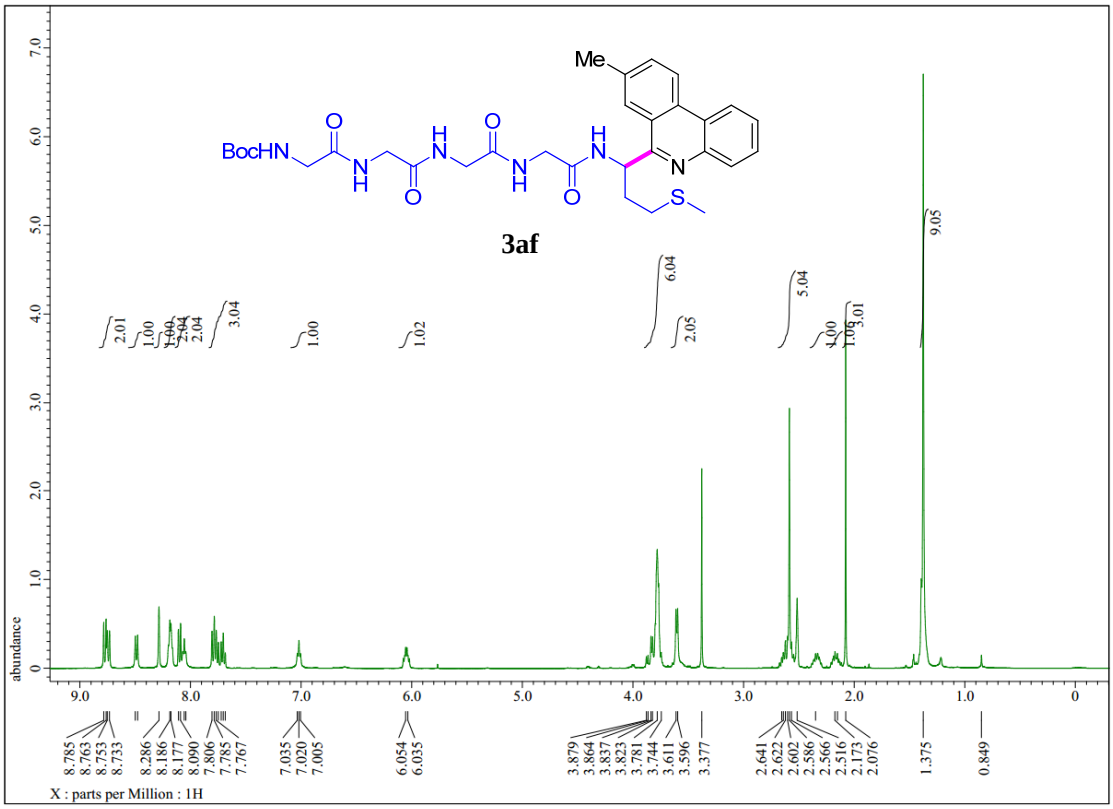

F3C
Boc
N
N
3ac
abundance
X : parts per Million : 13C

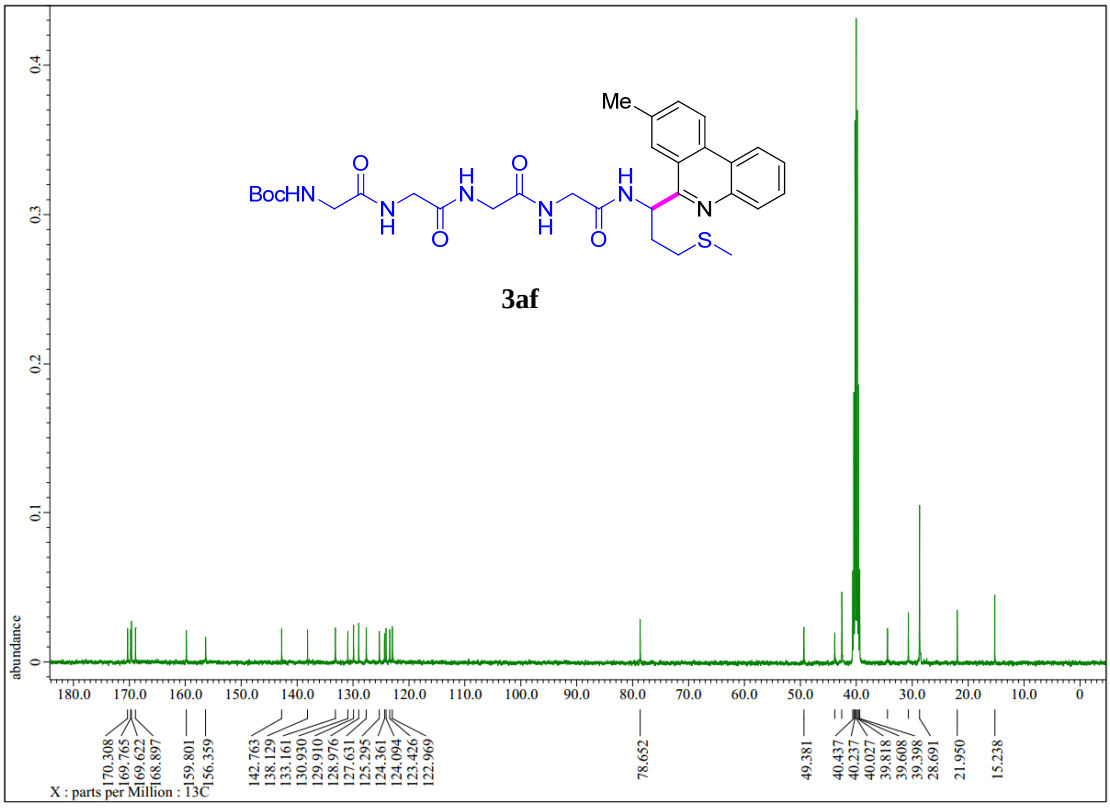

Me
H
N
BocHN
O
N
3ad
abundance
X : parts per Million : 1H

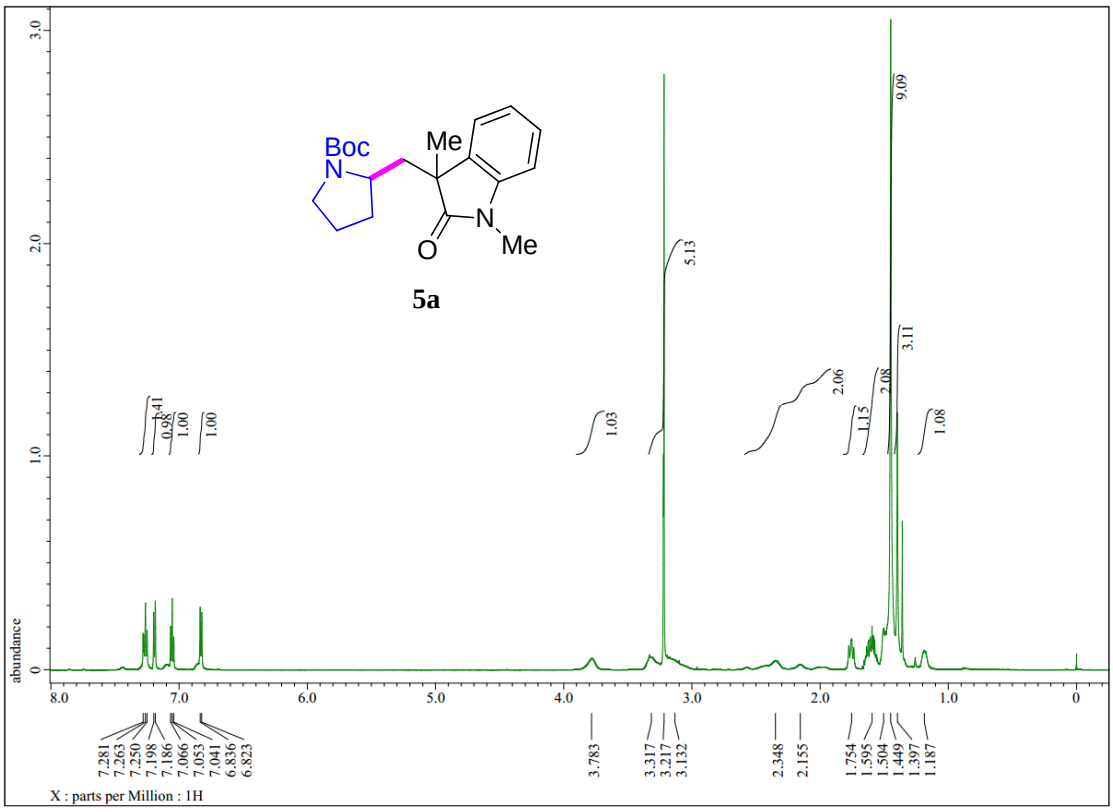

Me
H
N
BocHN
O
N
3ad
abundance
X : parts per Million : 13C

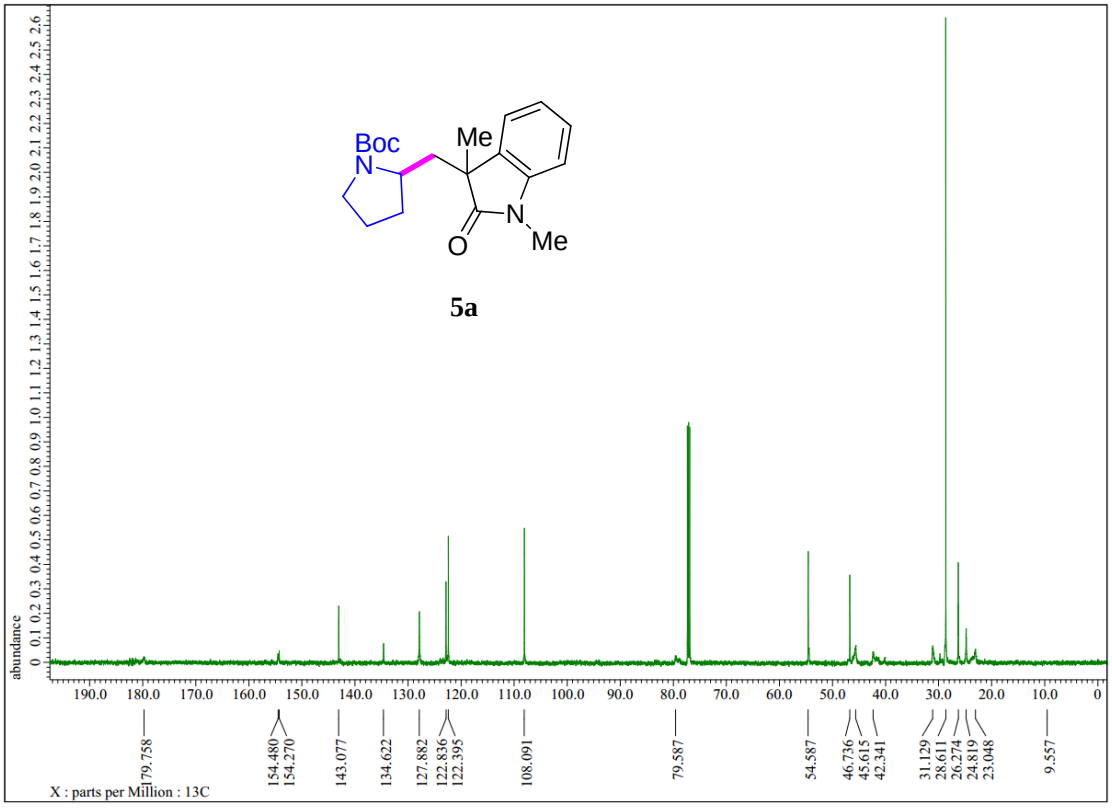

Me
BocHN
O
N
H
H
N
O
N
3ae
abundance
X : parts per Million : 1H

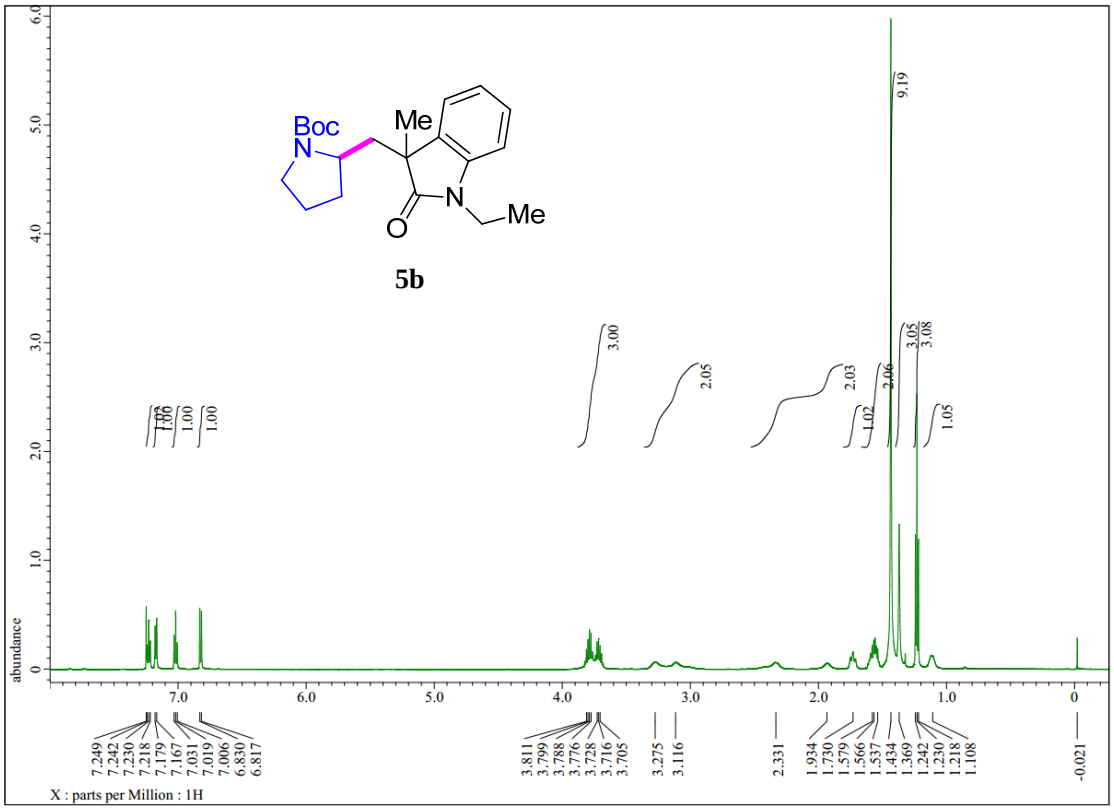

Me
BocHN
O
N
H
H
N
O
N
3ae
abundance
X : parts per Million : 13C

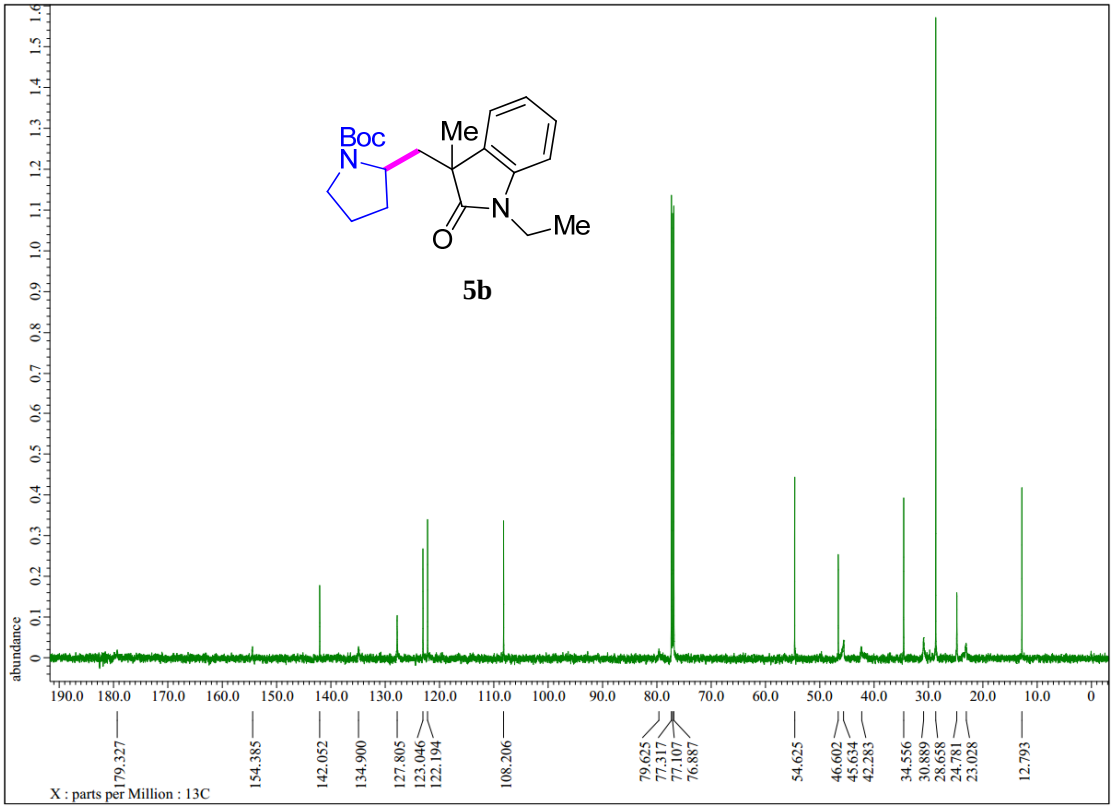

Me
BocHN
O
H
N
N
O
S
3af
abundance
X : parts per Million : 1H

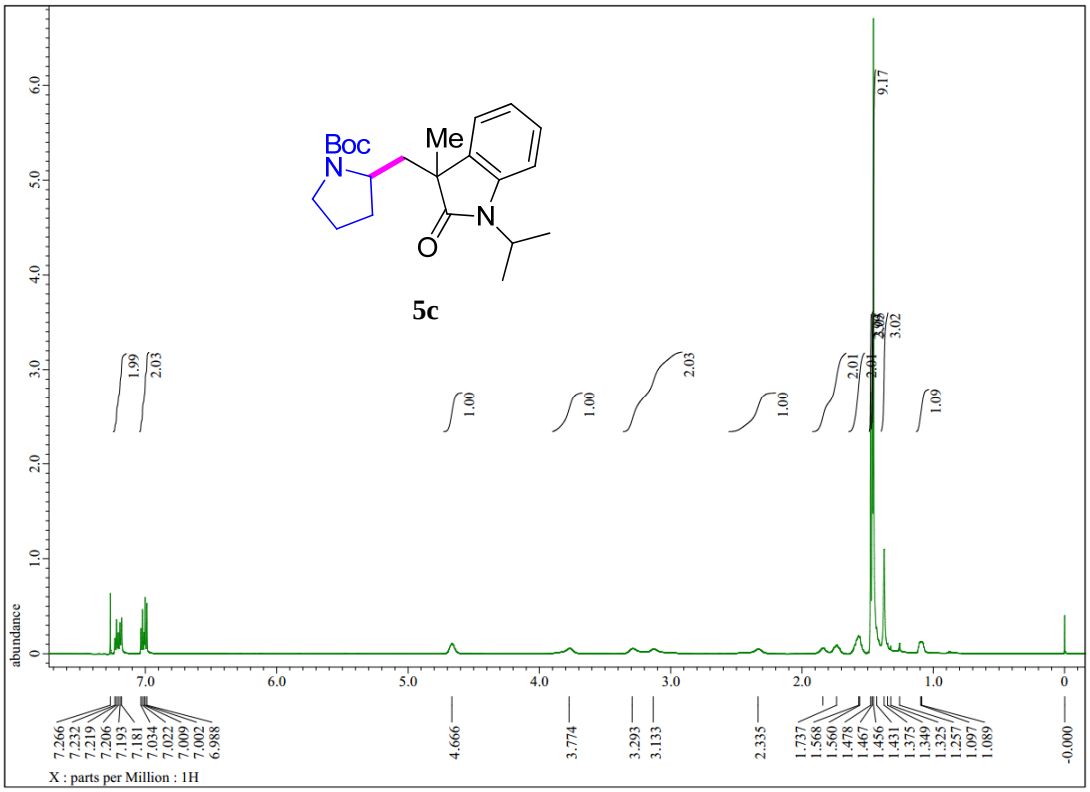

Me
BocHN
O
H
N
N
O
S
3af
abundance
X : parts per Million : 13C

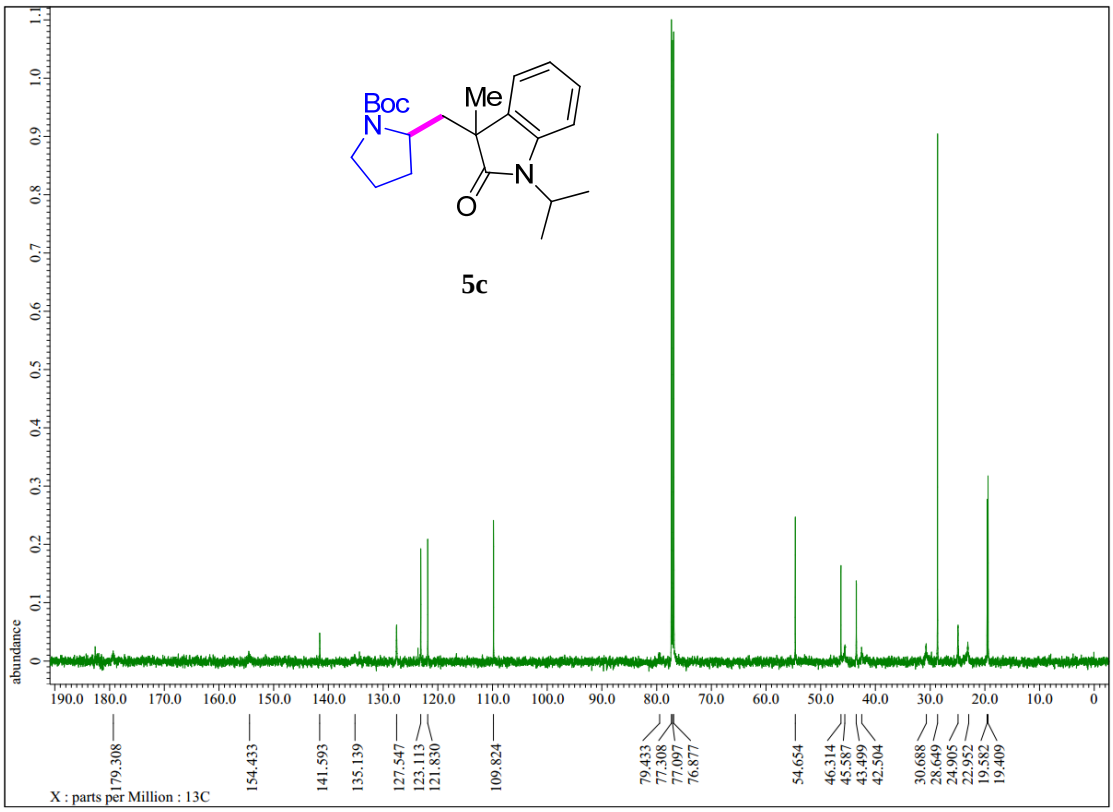

Boc
N
Me
N
Me
O
5a
abundance
X : parts per Million : 1H

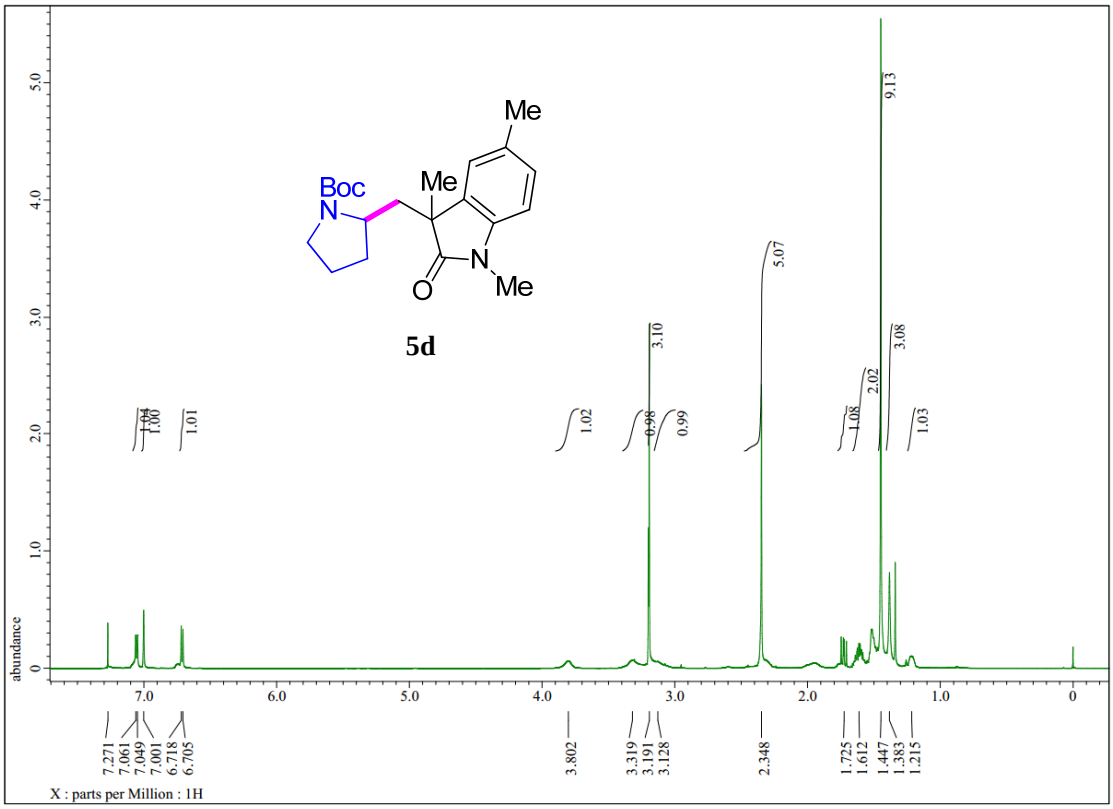

Boc
N
Me
N
Me
O
5a
abundance
X : parts per Million : 13C

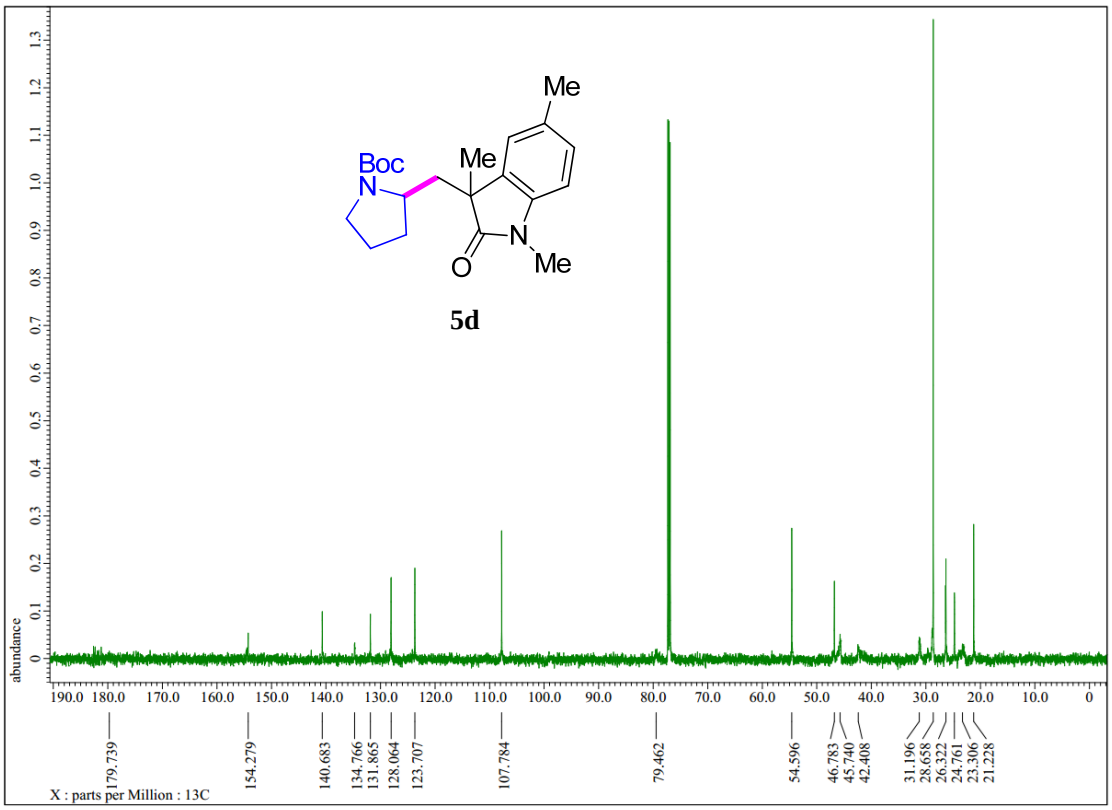

Boc
N
Me
N
Me
O
5b
abundance
X : parts per Million : 1H

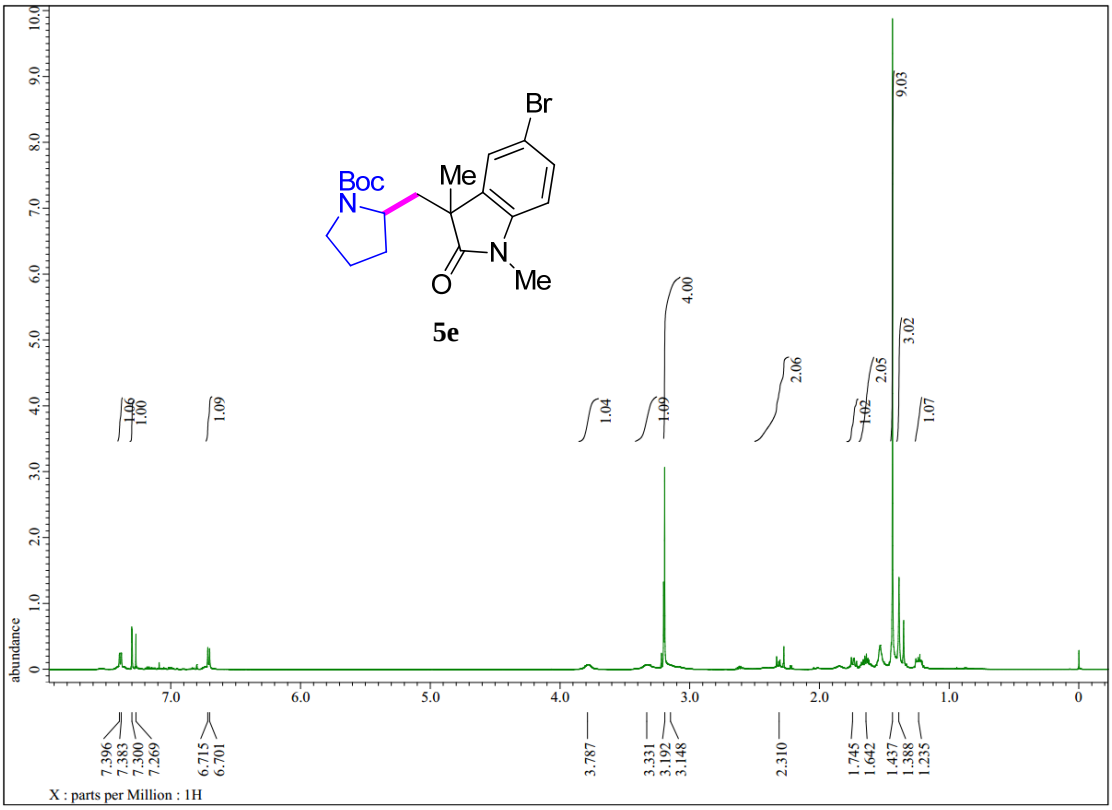

Boc
N
Me
N
Me
O
5b
abundance
X : parts per Million : 13C

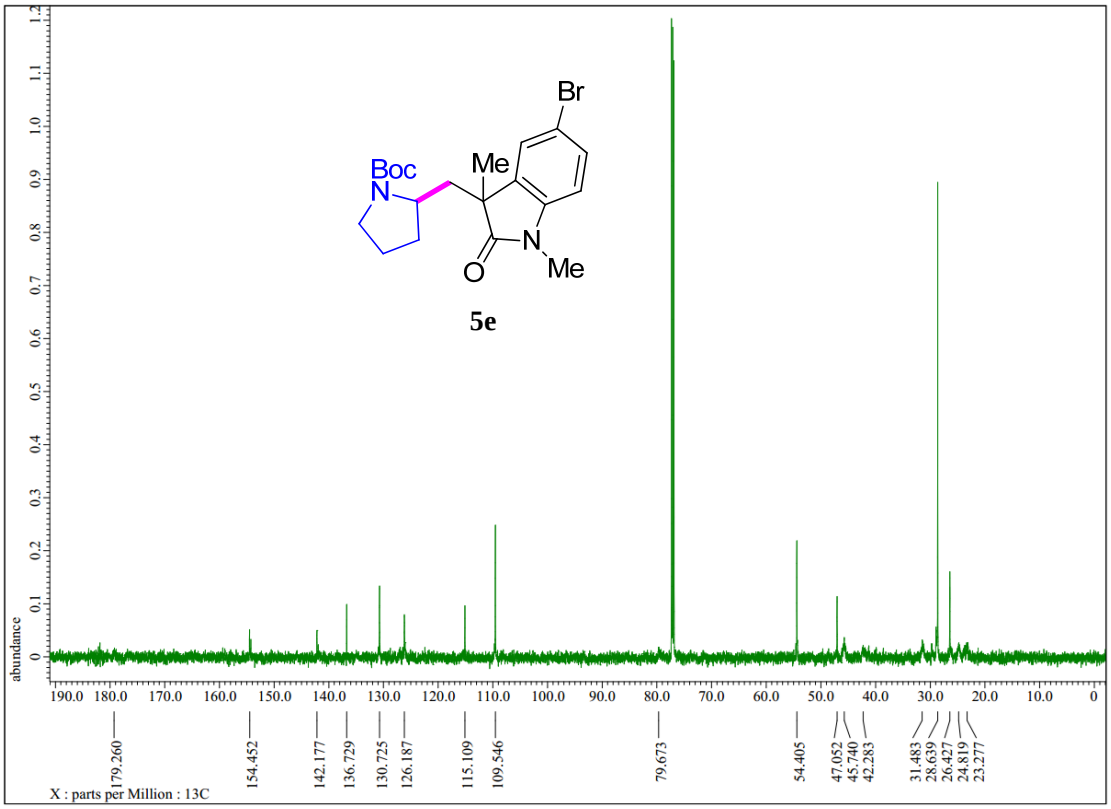

Boc
N
Me
N
O
5c
abundance
X : parts per Million : 1H


Boc
N
Me
N
O
5c
abundance
X : parts per Million : 13C


Me
Boc
N
Me
N
O
Me
5d
abundance
X : parts per Million : 1H


Me
Boc
N
Me
N
O
Me
5d
abundance
X : parts per Million : 13C


Br
Boc
N
Me
N
Me
O
5e
9.03
4.00
3.02
2.06
2.05
1.09
1.04
1.07
abundance
7.396
7.383
7.300
7.269
6.715
6.701
3.787
3.331
3.192
3.148
2.310
1.745
1.642
1.437
1.388
1.235
X : parts per Million : 1H


Br
Boc
N
Me
N
Me
O
5e
abundance
179.260
154.452
142.177
136.729
130.725
126.187
115.109
109.546
79.673
54.405
47.052
45.740
42.283
31.483
28.639
26.427
24.819
23.277
X : parts per Million : 13C