

Simple and green synthesis of benzimidazoles and pyrrolo[1,2-*a*]quinoxalines via Mamedov Heterocycle Rearrangement

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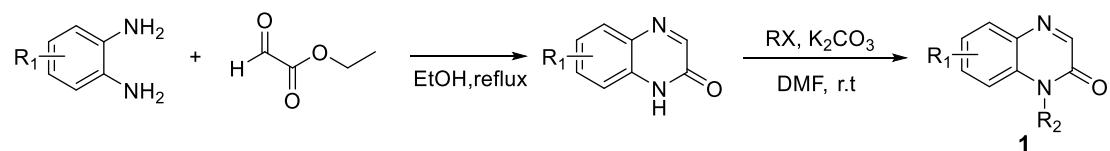
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1. General information

Quinoxalin-2(1*H*)-ones and 2-(1*H*-pyrrol-1-yl)anilines were prepared as literature procedure^{1,2}. Other reagents were commercially available and were used without further purification. All reactions were monitored by thin-layer chromatography (TLC). ¹H NMR and ¹³C NMR spectra were recorded on a Bruker A advance 500 (500 MHz) or 400 (400 MHz) spectrometer using CDCl₃ or DMSO-d₆ as the solvents and tetramethylsilane (TMS) as internal standard. HRMS spectra (ESI) were confirmed on a Q-TOF6510 spectrograph. The melting points were determined on a Tech X-4 instrument.

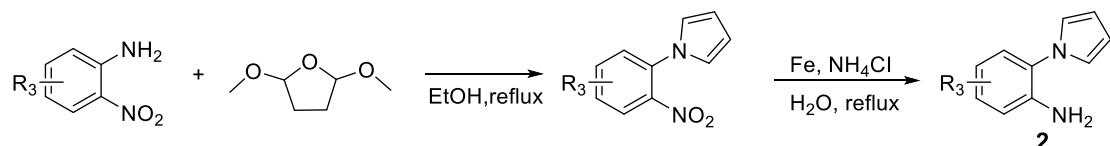
2. Experimental procedures

2.1 General experimental procedures for the synthesis of compound **1**.



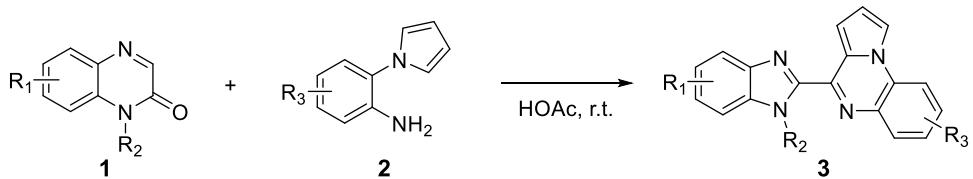
A mixture of *o*-phenylenediamines (10 mmol), ethyl glyoxalate (11 mmol) in ethanol (30 mL) was stirred in reflux for 1 hour, then the reaction mixture was filtered and washed with ethanol and dried to obtain quinoxalin-2(1*H*)-ones. Quinoxalin-2(1*H*)-ones, K₂CO₃ (1.2 equiv.) and corresponding alkyl halide (1.6 equiv.) were added in DMF (3 mL/mmol) and the reaction mixture were stirred at room temperature. After the completion of the reaction, the mixture was extracted with ethyl acetate (3×30 mL) and the organic layers were combined and dried with anhydrous Na₂SO₄. The solvent was evaporated under vacuum and the residue was purified by column chromatography on silica gel to afford compound **1**.

2.2 General experimental procedures for the synthesis of compound **2**.



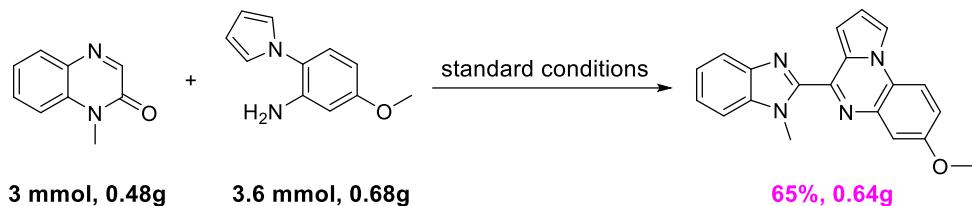
A mixture of substituted *o*-nitroanilines (10 mmol) and 2,5-dimethoxytetrahydrofuran (11 mmol) in HOAc (30 mL) was refluxed with vigorous stirring for 1-3 hours. The reaction mixture was neutralized with aqueous NaHCO₃, and then extracted with ethyl acetate (3×30 mL). The organic layers were combined and dried with anhydrous Na₂SO₄ and were evaporated under vacuum to afford a residue. Then the residue, iron powder (40 mmol) and NH₄Cl (10 mmol) was added in water (30 mL) and refluxed for 3-8 hours. After the completion of the reaction, the mixture was extracted with ethyl acetate (3×30 mL). The organic layers were combined and dried with anhydrous Na₂SO₄, and the solvent was evaporated under vacuum to afford a residue. The residue was purified by column chromatography on silica gel to afford compound **2**.

2.3 General experimental procedures for the synthesis of compound 3



A mixture of compound **1** (0.3 mmol) and compound **2** (0.36 mmol) in HOAc (2 mL) was stirred at room temperature for 3 days. The reaction was monitored by TLC (thin layer chromatography). Once the reaction was completed, the mixture was extracted with CH_2Cl_2 (4×30 mL). The organic layers were combined and dried by anhydrous Na_2SO_4 , and the solvent was evaporated under vacuum to afford a residue. The residue was purified by column chromatography on silica gel to afford compound **3**.

3. Gram scale synthesis of compound 3j



A mixture of 1-methylquinoxalin-2-one (3 mmol, 0.48g) and 5-methoxy-2-(1H-pyrrol-1-yl)aniline (3.6 mmol, 0.68g) in HOAc (20 mL) was stirred at room temperature for 3 days. This method is scalable with no significant decrease in yield (65%, 0.64g) compared to **3j** (68%), which made this transformation possible towards industrialization.

4. X-Ray crystal data for compound 3b

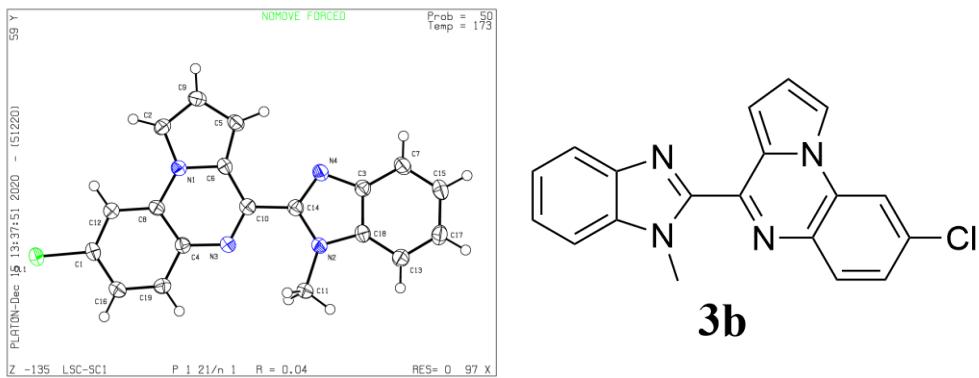
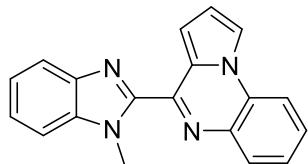


Table 1 Crystal data and structure refinement for LSC-SC1.

Identification code	LSC-SC1
Empirical formula	C ₁₉ H ₁₃ ClN ₄
Formula weight	332.78
Temperature/K	173.00(10)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	7.9110(3)
b/Å	17.8896(7)
c/Å	10.7223(3)
α/°	90
β/°	94.549(3)
γ/°	90
Volume/Å ³	1512.69(9)
Z	4
ρ _{calc} g/cm ³	1.461
μ/mm ⁻¹	2.287
F(000)	688
Crystal size/mm ³	0.05 × 0.03 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.64 to 134.154
Index ranges	-9 ≤ h ≤ 8, -21 ≤ k ≤ 21, -12 ≤ l ≤ 9
Reflections collected	8394
Independent reflections	2662 [R _{int} = 0.0375, R _{sigma} = 0.0418]
Data/restraints/parameters	2662/0/218
Goodness-of-fit on F ²	1.055
Final R indexes [I>=2σ (I)]	R ₁ = 0.0381, wR ₂ = 0.0979
Final R indexes [all data]	R ₁ = 0.0456, wR ₂ = 0.1031

Largest diff. peak/hole / e Å⁻³ 0.22/-0.32

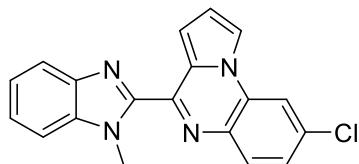
5. Characterization data



4-(1-methyl-benzimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3a)

Yellow solid (0.0564 g, 63%, m.p. 150-152°C)

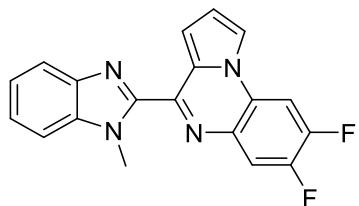
¹H NMR (500 MHz, CDCl₃): δ 8.04-8.02(m, 2H), 7.95-7.91(m, 2H), 7.79 (dd, J = 4.0, 1.0 Hz, 1H), 7.58(td, J = 7.5, 1.5 Hz, 1H), 7.51-7.47(m, 2H), 7.41(td, J = 7.5, 1.0 Hz, 1H), 7.35(td, J = 7.5, 1.0 Hz, 1H), 6.99 (dd, J = 4.25, 2.5 Hz, 1H), 4.29 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 148.3, 144.9, 142.6, 136.8, 135.2, 130.3, 128.5, 127.5, 125.2, 123.9, 122.7, 120.7, 114.8, 114.7, 113.9, 110.9, 109.9, 32.6; HRMS(ESI): m/z [M+H]⁺ Calculated for C₁₉H₁₄N₄: 299.1290, found.299.1290.



8-chloro-4-(1-methyl-benzimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3b)

Yellow solid (0.0498 g, 50%, m.p. 192-194°C)

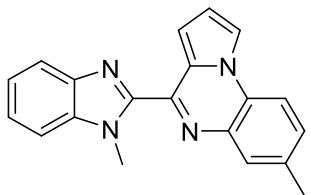
¹H NMR (400 MHz, CDCl₃): δ 7.93-7.90 (m, 3H), 7.87 (d, J = 2.5 Hz, 1H), 7.82 (dd, J = 5.0, 1.5 Hz, 1H), 7.48-7.46 (m, 1H), 7.41-7.33 (m, 3H), 6.98 (dd, J = 5.0, 3.0 Hz, 1H), 4.25 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 147.9, 144.9, 142.6, 136.8, 134.0, 133.7, 131.4, 128.0, 125.7, 125.0, 124.0, 122.8, 120.7, 115.3, 114.9, 114.0, 111.6, 110.0, 32.6; HRMS(ESI): m/z [M+H]⁺ Calculated for C₁₉H₁₃N₄Cl: 333.0901, found 333.0908.



7,8-difluoro-4-(1-methyl-benzimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3c)

Yellow solid (0.0469 g, 47%, m.p. 220-222°C)

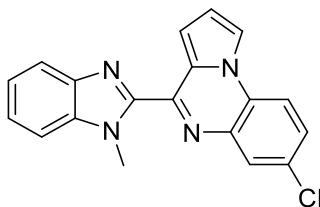
¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, J = 7.6 Hz, 1H), 7.85-7.79 (m, 3H), 7.67(dd, J = 10.4, 7.2 Hz, 1H), 7.49-7.47 (m, 1H), 7.41(td, J = 7.6, 0.8 Hz, 1H), 7.36(td, J = 8.0, 1.2 Hz, 1H), 6.99 (dd, J = 3.6, 2.8 Hz, 1H), 4.25 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 151.5 (d, J = 15 Hz), 149.2 (dd, J = 34, 14 Hz), 147.5, 146.9 (d, J = 14 Hz), 145.1 (d, J = 3 Hz), 142.3, 136.7, 131.7 (dd, J = 9, 3 Hz), 124.6, 124.2, 124.0 (dd, J = 18, 2 Hz), 122.9, 120.7, 117.6 (dd, J = 18, 1 Hz), 115.3 (d, J = 34 Hz), 111.7, 110.0, 102.5 (d, J = 23 Hz), 32.7; HRMS(ESI): m/z [M+H]⁺ Calculated for C₁₉H₁₂N₄F₂: 335.1102, found 335.1110.



7-methyl-4-(1-methyl-benzimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3d)

Yellow solid (0.0457 g, 49%, m.p. 177-179°C)

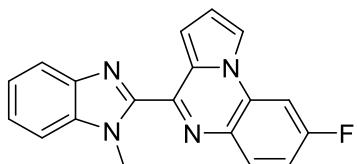
¹H NMR (400 MHz, CDCl₃): δ 7.96-7.92 (m, 2H), 7.81-7.74 (m, 3H), 7.47 (d, J = 7.2 Hz, 1H), 7.36 (qd, J = 7.6, 1.2 Hz, 3H), 6.94 (dd, J = 4.0, 2.8 Hz, 1H), 4.25 (s, 3H), 2.50 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 148.4, 144.8, 142.7, 136.8, 135.1, 135.0, 130.0, 129.7, 125.3, 125.1, 123.8, 122.6, 120.7, 114.5, 113.6, 110.6, 109.9, 32.5, 21.0; HRMS(ESI): m/z [M+H]⁺ Calculated for C₂₀H₁₆N₄: 313.1447, found 313.1449.



7-chloro-4-(1-methyl-benzimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3e)

Yellow solid (0.0464 g, 46%, m.p. 204-206°C)

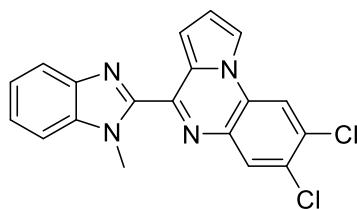
¹H NMR (500 MHz, CDCl₃): δ 8.02 (d, J = 2.0 Hz, 1H), 8.00 (dd, J = 3.0, 1.0 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.88 (dd, J = 4.0, 1.5 Hz, 1H), 7.84 (d, J = 8.5 Hz, 1H), 7.53-7.51 (m, 2H), 7.44 (td, J = 7.5, 1.0 Hz, 1H), 7.38 (td, J = 7.5, 1.0 Hz, 1H), 7.01 (dd, J = 4.0, 2.5 Hz, 1H), 4.30 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): 147.8, 145.9, 142.7, 136.8, 136.0, 130.3, 129.5, 128.4, 126.0, 125.0, 124.1, 122.8, 120.8, 115.1, 115.0, 115.0, 111.7, 110.0, 32.7; HRMS(ESI): m/z [M+H]⁺ Calculated for C₁₉H₁₃N₄Cl: 333.0901, found 333.0907.



8-fluoro-4-(1-methyl-benzimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3f)

Yellow solid (0.0485 g, 51%, m.p. 205-207°C)

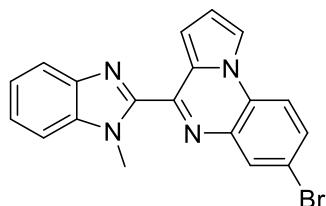
¹H NMR (500 MHz, CDCl₃): δ 7.92 (dd, J = 9.0, 5.5 Hz, 1H), 7.85 (d, J = 7.5 Hz, 1H), 7.81 (dd, J = 3.0, 1.0 Hz, 1H), 7.73 (dd, J = 4.0, 1.0 Hz, 1H), 7.49 (dd, J = 9.0, 3.0 Hz, 1H), 7.41 (d, J = 7.0 Hz, 1H), 7.32 (td, J = 7.5, 1.0 Hz, 1H), 7.28 (td, J = 7.5, 1.0 Hz, 1H), 7.11 (td, J = 8.5, 2.5 Hz, 1H), 6.92 (dd, J = 4.0, 3.0 Hz, 1H), 4.18 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): 162.1 (d, J = 247.5 Hz), 148.1, 144.2 (d, J = 2.5 Hz), 142.7, 136.8, 132.2 (d, J = 10.0 Hz), 131.8 (d, J = 1.2 Hz), 128.3 (d, J = 11.2 Hz), 124.8, 123.9, 122.7, 120.7, 115.2, 114.8, 113.3 (d, J = 22.5 Hz), 111.3, 109.9, 100.7 (d, J = 23.7 Hz), 32.6; HRMS(ESI): m/z [M+H]⁺ Calculated for C₁₉H₁₃N₄F: 317.1196, found 317.1201.



7,8-dichloro-4-(1-methyl-benzimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3g)

Yellow solid (0.0813 g, 74%, m.p. 260-262°C)

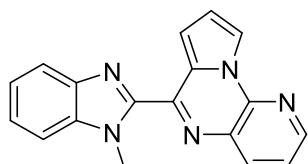
¹H NMR (500 MHz, CDCl₃): δ 8.04 (s, 1H), 7.93 (s, 1H), 7.87-7.86 (m, 2H), 7.82 (dd, J = 4.0, 3.0 Hz, 1H), 7.44(d, J = 8.0 Hz, 1H), 7.35 (td, J = 7.5, 1.0 Hz, 1H), 7.30 (td, J = 8.0, 1.0 Hz, 1H), 6.94 (dd, J = 4.0, 2.5 Hz, 1H), 4.21 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): 145.9, 142.5, 136.8, 134.6, 132.0, 131.0, 128.9, 126.6, 124.9, 124.3, 122.9, 120.8, 115.6, 115.5, 115.3, 112.4, 110.0, 32.7; HRMS(ESI): m/z [M+H]⁺ Calculated for C₁₉H₁₂N₄Cl₂: 367.0511, found 367.0516.



7-bromo-4-(1-methyl-benzimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3h)

Yellow solid (0.0701 g, 62%, m.p. 209-211°C)

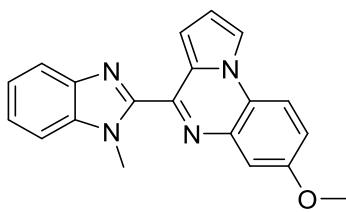
¹H NMR (400 MHz, CDCl₃): δ 8.12 (d, J = 2.4Hz, 1H), 7.93-7.91 (m, 2H), 7.85 (dd, J = 4.0, 3.2 Hz, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.59 (dd, J = 8.8, 2.0 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.39 (td, J = 7.2, 0.8 Hz, 1H), 7.36 (td, J = 8.0, 1.2 Hz, 1H), 6.96 (d, J = 4.0, 2.8 Hz, 1H), 4.24 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 147.7, 145.7, 142.6, 136.8, 136.3, 132.5, 131.1, 126.4, 125.0, 124.1, 122.8, 120.8, 117.7, 115.2, 115.1, 115.0, 111.8, 110.0, 32.7; HRMS(ESI): m/z [M+H]⁺ Calculated for C₁₉H₁₃N₄Br: 377.0396, found 377.0399.



6-(1-methyl-benzimidazol-2-yl)pyrido[3,2-e]pyrrolo[1,2-a]pyrazine (3i)

Yellow solid (0.0655 g, 73%, m.p. 184-186°C)

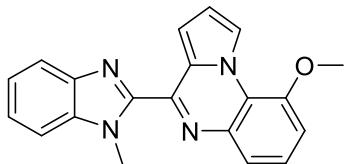
¹H NMR (500 MHz, CDCl₃): δ 8.59 (dd, J = 4.5, 1.5 Hz, 1H), 8.50 (dd, J = 3.0, 1.5 Hz, 1H), 8.29 (dd, J = 8.0, 1.5 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.87 (dd, J = 3.5, 1.0 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.47 (dd, J = 8.0, 5.0 Hz, 1H), 7.41 (td, J = 7.5, 1.0 Hz, 1H), 7.36 (td, J = 8.0, 1.0 Hz, 1H), 7.02 (dd, J = 4.0, 2.5 Hz, 1H), 4.27 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): 147.8, 147.6, 145.7, 142.7, 139.3, 137.4, 136.8, 130.0, 126.8, 124.1, 122.8, 121.6, 120.9, 116.1, 115.3, 112.7, 110.0, 32.6; HRMS(ESI): m/z [M+H]⁺ Calculated for C₁₈H₁₃N₅: 300.1243, found 300.1247.



7-methoxy-4-(1-methyl-benzimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3j)

Yellow solid (0.0670 g, 68%, m.p. 184-187°C)

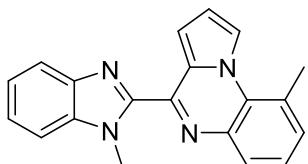
¹H NMR (400 MHz, CDCl₃): δ 7.95-7.91 (m, 2H), 7.78 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 4.0, 1.2 Hz, 1H), 7.48-7.44 (m, 2H), 7.36 (qd, J = 7.2, 1.2 Hz, 2H), 7.15 (dd, J = 8.8, 2.8 Hz, 1H), 6.92 (dd, J = 4.0, 2.8 Hz, 1H), 4.24 (s, 3H), 3.91 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 157.2, 148.3, 145.0, 142.5, 136.7, 136.2, 125.0, 123.9, 122.7, 121.8, 120.7, 117.6, 114.8, 114.4, 114.4, 111.4, 110.5, 109.9, 55.7, 32.6; HRMS(ESI): m/z [M+H]⁺ Calculated for C₂₀H₁₆N₄O: 329.1396, found 329.1396.



9-methoxy-4-(1-methyl-benzimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3k)

Yellow solid (0.0452 g, 46%, m.p. 169-171°C)

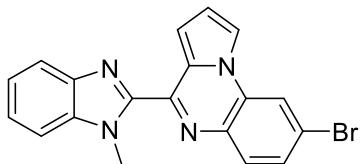
¹H NMR (500 MHz, CDCl₃): δ 8.86 (dd, J = 2.5, 1.5 Hz, 1H), 7.93 (d, J = 6.5 Hz, 1H), 7.77 (dd, J = 4.0, 1.5 Hz, 1H), 7.66 (dd, J = 8.0, 1.5 Hz, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.44-7.31 (m, 3H), 7.10 (dd, J = 8.0, 1.0 Hz, 1H), 6.93 (dd, J = 4.0, 3.0 Hz, 1H), 4.24 (s, 3H), 4.10 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): 149.8, 148.4, 145.1, 142.7, 137.4, 136.7, 125.8, 124.4, 123.8, 122.6, 122.5, 122.2, 120.7, 118.8, 113.8, 110.1, 109.9, 109.8, 56.2, 32.4; HRMS(ESI): m/z [M+H]⁺ Calculated for C₂₀H₁₆N₄O: 329.1396, found 329.1397.



9-methyl-4-(1-methyl-benzimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3l)

Yellow solid (0.0602 g, 64%, m.p. 157-159°C)

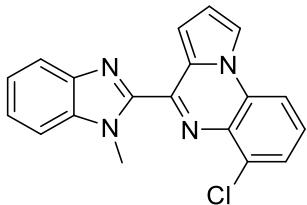
¹H NMR (400 MHz, CDCl₃): δ 7.96-7.93 (m, 2H), 7.88 (dd, J = 4.0, 1.2 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.46 (d, J = 7.2 Hz, 1H), 7.42-7.28 (m, 4H), 6.95 (dd, J = 4.0, 2.8 Hz, 1H), 4.30 (s, 3H), 2.7 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): 148.5, 143.3, 142.7, 138.9, 136.8, 133.8, 128.0, 127.4, 126.2, 125.0, 123.8, 122.6, 120.7, 114.7, 114.6, 111.6, 110.7, 109.8, 32.9, 18.5; HRMS(ESI): m/z [M+H]⁺ Calculated for C₂₀H₁₆N₄: 313.1447, found 313.1447.



8-bromo-4-(1-methyl-benzimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3m)

Yellow solid (0.0652 g, 58%, m.p. 174-176°C)

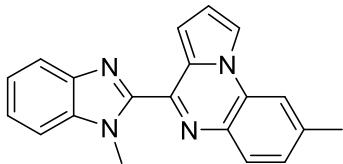
¹H NMR (500 MHz, CDCl₃): δ 8.00 (d, J = 2.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.83-7.80 (m, 2H), 7.52 (dd, J = 8.5, 2.0 Hz, 1H), 7.45 (d, J = 8.5 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.34 (t, J = 7.0 Hz, 1H), 6.97 (t, J = 3.0 Hz, 1H), 4.23 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): 147.9, 145.1, 142.6, 136.8, 134.0, 131.5, 128.4, 128.2, 125.0, 124.0, 122.7, 121.8, 120.7, 117.0, 115.3, 114.9, 111.7, 109.9, 32.7; HRMS(ESI): m/z [M+H]⁺ Calculated for C₁₉H₁₃N₄Br: 377.0396, found 377.0390.



6-chloro-4-(1-methyl-benzoimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3n)

Yellow solid (0.0556 g, 56%, m.p. 200-202°C)

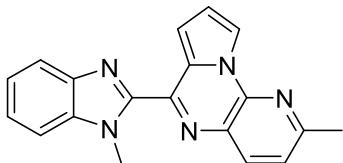
¹H NMR (400 MHz, CDCl₃): δ 8.03 (dd, J = 4.0, 1.2 Hz, 1H), 7.98 (dd, J = 2.8, 1.2 Hz, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.78 (dd, J = 8.4, 0.8 Hz, 1H), 7.54 (dd, J = 8.0, 0.8 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.44-7.32 (m, 3H), 4.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 147.6, 144.8, 142.6, 137.0, 134.9, 132.2, 128.6, 128.1, 125.8, 124.8, 124.2, 122.8, 120.8, 115.4, 115.3, 112.5, 112.0, 110.0, 33.3; HRMS(ESI): m/z [M+H]⁺ Calculated for C₁₉H₁₃N₄Cl: 333.0901, found 333.0897.



8-methyl-4-(1-methyl-benzoimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3o)

Yellow solid (0.0539 g, 58%, m.p. 158-160°C)

¹H NMR (500 MHz, CDCl₃): δ 7.97 (dd, J = 3.0, 1.5 Hz, 1H), 7.93 (d, J = 7.5 Hz, 1H), 7.90 (d, J = 8.5 Hz, 1H), 7.74 (dd, J = 9.0, 1.5 Hz, 1H), 7.70 (s, 1H), 7.47 (d, J = 7.5 Hz, 1H), 7.39 (td, J = 7.5, 1.0 Hz, 1H), 7.34 (td, J = 7.5, 1.5 Hz, 1H), 7.28 (dd, J = 8.0, 1.0 Hz, 1H), 6.96 (dd, 4.0, 2.0 Hz, 1H), 4.25 (s, 3H), 2.57 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): 148.5, 144.0, 142.7, 139.3, 136.8, 133.2, 130.0, 127.2, 126.6, 123.7, 122.6, 120.7, 114.6, 114.3, 113.9, 110.5, 109.9, 32.5, 21.9; HRMS(ESI): m/z [M+H]⁺ Calculated for C₂₀H₁₆N₄: 313.1447, found 313.1445.

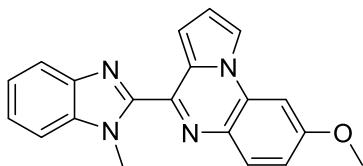


2-methyl-6-(1-methyl-benzoimidazol-2-yl)pyrido[3,2-e]pyrrolo[1,2-a]pyrazine (3p)

Yellow solid (0.0650 g, 69%, m.p. 205-207°C)

¹H NMR (500 MHz, CDCl₃): δ 8.48 (dd, J = 3.0, 1.5 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 7.5 Hz, 1H), 7.81 (dd, J = 4.0, 1.5 Hz, 1H), 7.47 (d, J = 7.5 Hz, 1H), 7.38 (td, J = 7.5, 1.0 Hz, 1H), 7.35 (td, J = 7.5, 1.5 Hz, 1H), 7.28 (d, J = 9.0 Hz, 1H), 6.98 (dd, J = 4.0, 3.0 Hz, 1H), 4.24 (s, 3H), 2.72 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): 157.9, 148.0, 144.6, 142.7, 138.4, 137.4, 136.8, 127.7, 126.8, 123.9, 122.7, 121.5, 120.8, 115.6, 115.0, 112.0, 109.9, 32.5, 24.7; HRMS(ESI): m/z [M+H]⁺

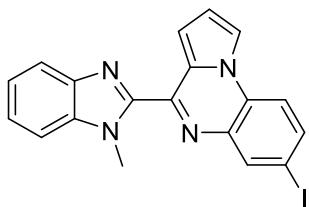
Calculated for C₁₉H₁₅N₅: 314.1399, found 314.1399.



8-methoxy-4-(1-methyl-benzoimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3q)

Yellow solid (0.0664 g, 67%, m.p. 132-134°C)

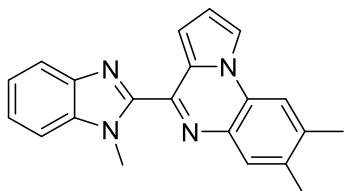
¹H NMR (500 MHz, CDCl₃): δ 7.93-7.91 (m, 2H), 7.78 (dd, J = 3.0, 1.0 Hz, 1H), 7.74 (dd, J = 4.0, 1.5 Hz, 1H), 7.47 (d, J = 7.5 Hz, 1H), 7.38 (td, J = 7.5, 1.0 Hz, 1H), 7.34 (td, J = 7.5, 1.0 Hz, 1H), 7.28 (d, J = 2.5 Hz, 1H), 7.05 (dd, J = 9.0, 3.0 Hz, 1H), 6.96 (dd, J = 4.0, 3.0 Hz, 1H), 4.24 (s, 3H), 3.96 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): 160.0, 148.6, 142.7, 142.4, 136.8, 131.6, 129.6, 128.3, 125.1, 123.6, 122.5, 120.6, 114.8, 114.1, 113.1, 110.3, 109.8, 97.4, 55.8, 32.5; HRMS(ESI): m/z [M+H]⁺ Calculated for C₂₀H₁₆N₄O: 329.1396, found 329.1393.



7-iodo-4-(1-methyl-benzoimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3r)

Yellow solid (0.0653 g, 51%, m.p. 195-197°C)

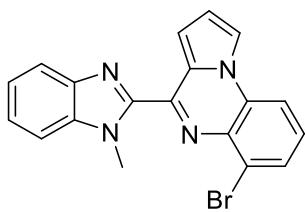
¹H NMR (400 MHz, CDCl₃): δ 8.33 (d, J = 1.6 Hz, 1H), 7.94-7.92 (m, 2H), 7.87 (d, J = 3.2 Hz, 1H), 7.76 (dd, J = 8.4, 1.6 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.42-7.34 (m, 2H), 6.98-6.96 (m, 1H), 4.25 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 147.7, 145.5, 142.6, 138.7, 136.8, 136.7, 136.4, 127.0, 125.0, 124.1, 122.8, 120.8, 115.4, 115.1, 114.9, 111.8, 110.0, 88.1, 32.7; HRMS(ESI): m/z [M+H]⁺ Calculated for C₁₉H₁₃N₄I: 425.0257, found 425.0255.



7,8-dimethyl-4-(1-methyl-benzoimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3s)

Yellow solid (0.0489 g, 50%, m.p. 190-192°C)

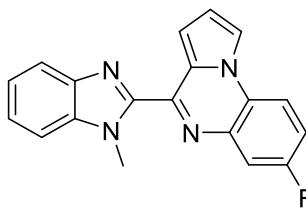
¹H NMR (400 MHz, CDCl₃): δ 7.96 (dd, J = 2.4, 1.2 Hz, 1H), 7.93 (dd, J = 7.2, 1.2 Hz, 1H), 7.78 (s, 1H), 7.72 (dd, J = 4.0, 1.2 Hz, 1H), 7.67 (s, 1H), 7.48 (dd, J = 7.2, 1.2 Hz, 1H), 7.39 (td, J = 7.6, 1.2 Hz, 1H), 7.44 (td, J = 7.2, 1.2 Hz, 1H), 6.94 (dd, J = 4.0, 2.8 Hz, 1H), 4.26 (s, 3H), 2.47 (s, 3H), 2.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 148.6, 143.9, 142.7, 138.3, 136.7, 134.1, 133.4, 130.3, 125.4, 125.2, 123.7, 122.5, 120.6, 114.4, 114.3, 114.1, 110.2, 109.8, 32.5, 20.4, 19.5; HRMS(ESI): m/z [M+H]⁺ Calculated for C₂₁H₁₈N₄: 327.1603, found 329.1605.



6-bromo-4-(1-methyl-benzimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3t)

Yellow solid (0.0650 g, 57%, m.p. 204-206°C)

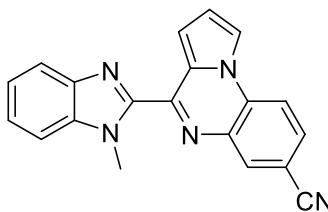
¹H NMR (400 MHz, CDCl₃): δ 8.04 (dd, J = 4.0, 1.2 Hz, 1H), 7.99 (dd, J = 2.8, 1.2 Hz, 1H), 7.93(d, J = 7.6 Hz, 1H), 7.83(d, J = 8.4, 0.8 Hz, 1H), 7.54(dd, J = 8.0, 0.8 Hz, 1H), 7.50(d, J = 8.0 Hz, 1H), 7.42-7.32 (m, 3H), 7.01 (dd, J = 4.0, 2.8 Hz, 1H), 4.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 147.6, 145.1, 142.7, 137.0, 133.3, 129.1, 128.5, 125.9, 124.9, 124.1, 122.7, 120.8, 115.5, 115.3, 113.2, 112.0, 110.2, 33.6; HRMS(ESI): m/z [M+H]⁺ Calculated for C₁₉H₁₃N₄Br: 377.0396, found 377.0402.



7-fluoro-4-(1-methyl-benzimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3u)

Yellow solid (0.0519 g, 55%, m.p. 195-197°C)

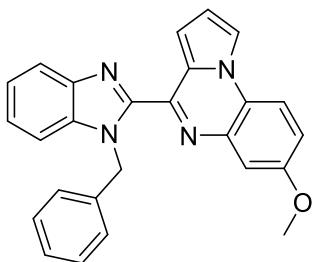
¹H NMR (500 MHz, CDCl₃): δ 7.97 (dd, J = 2.5, 1.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.86-7.82 (m, 2H), 7.68 (dd, J = 9.0, 2.5 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.40 (td, J = 7.5, 1.0 Hz, 1H), 7.36 (td, J = 7.5, 1.5 Hz, 1H), 7.30-7.26 (m, 1H), 6.97 (dd, J = 4.0, 3.0 Hz, 1H), 4.26 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): 159.8(d, J = 242.5 Hz), 147.9, 145.9, 142.6, 136.8, 136.3(d, J = 11.25 Hz), 125.0, 124.1(d, J = 3.75 Hz), 122.8, 120.8, 116.2(d, J = 23.75 Hz), 115.4(d, J = 22.5 Hz), 115.0(d, J = 10 Hz), 114.9, 114.9, 111.5, 110.0, 32.6; HRMS(ESI): m/z [M+H]⁺ Calculated for C₁₉H₁₃N₄F: 317.1196, found 317.1193.



4-(1-methyl-benzod[d]imidazol-2-yl)pyrrolo[1,2-a]quinoxaline-7-carbonitrile (3v)

Yellow solid (0.0649 g, 67%, m.p. 255-257°C)

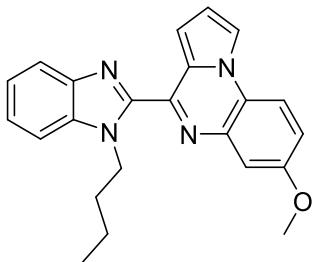
¹H NMR (400 MHz, CDCl₃): δ 8.32 (s, 1H), 8.04 (s, 1H), 7.97-7.94 (m, 3H), 7.79 (d, J = 10.4 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.44 (t, J = 7.2 Hz, 1H), 7.38 (td, J = 7.2 Hz, 1H), 7.07 (s, 1H), 4.30 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 147.2, 146.5, 142.4, 136.8, 135.0, 134.7, 130.9, 130.3, 125.1, 124.5, 123.1, 120.8, 118.3, 116.3, 115.7, 115.1, 113.0, 110.1, 108.7, 32.8; HRMS(ESI): m/z [M+H]⁺ Calculated for C₂₀H₁₃N₅: 324.1143, found 324.1252.



4-(1-benzyl-benzoimidazol-2-yl)-7-methoxypyrido[1,2-a]quinoxaline (3w)

Yellow solid (0.0824 g, 68%, m.p. 147-149°C)

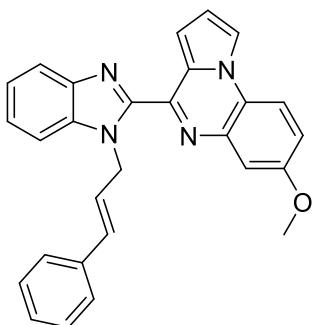
¹H NMR (400 MHz, CDCl₃): δ 8.00 (d, J = 8.0, 1H), 7.94 (d, J = 1.5, 1H), 7.81-7.79 (m, 2H), 7.42-7.15 (m, 10H), 6.96 (dd, J = 4.0, 2.8 Hz, 1H), 6.12 (s, 2H), 3.89 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 157.1, 147.9, 144.7, 142.5, 137.4, 136.2, 136.1, 128.6, 127.4, 126.8, 124.9, 124.2, 123.0, 121.9, 120.7, 117.5, 114.7, 114.5, 114.4, 111.6, 110.7, 110.6, 55.7, 49.1; HRMS(ESI): m/z [M+H]⁺ Calculated for C₂₆H₂₀N₄O: 405.1709, found 405.1709.



4-(1-butyl-benzoimidazol-2-yl)-7-methoxypyrido[1,2-a]quinoxaline (3x)

Yellow solid (0.0860 g, 77%, m.p. 132-134°C)

¹H NMR (400 MHz, CDCl₃): δ 8.00-7.98 (m, 2H), 7.86 (d, J = 8.8 Hz, 1H), 7.76 (dd, J = 4.0, 0.8 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.44-7.36 (m, 2H), 7.22 (dd, J = 8.8, 2.8 Hz, 1H), 6.98 (dd, J = 4.0, 2.8 Hz, 1H), 4.82 (t, J = 7.6 Hz, 2H), 3.97 (s, 3H), 1.98 (q, J = 7.6 Hz, 2H), 1.43 (s, J = 7.6 Hz, 2H), 0.95 (t, J = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): 157.2, 147.8, 145.0, 142.4, 136.1, 135.9, 125.0, 123.9, 122.7, 121.9, 120.7, 117.4, 114.8, 114.5, 114.4, 111.7, 110.6, 110.3, 55.7, 45.3, 32.1, 20.2, 13.7; HRMS(ESI): m/z [M+H]⁺ Calculated for C₂₃H₂₂N₄O: 371.1866, found 371.1871.

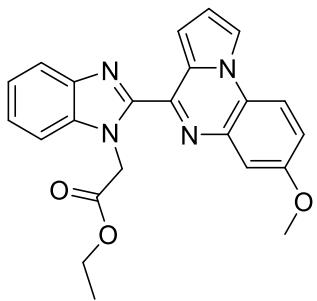


4-(1-cinnamyl-benzoimidazol-2-yl)-7-methoxypyrido[1,2-a]quinoxaline (3y)

Yellow solid (0.1016 g, 78%, m.p. 100-102°C)

¹H NMR (400 MHz, CDCl₃): δ 7.99-7.94 (m, 2H), 7.81 (d, J = 8.8 Hz, 2H), 7.58-7.55 (m, 1H), 7.46 (d, J = 2.4 Hz, 1H), 7.38 (t, J = 4.0 Hz, 1H), 7.30-7.17 (m, 6H), 6.96 (t, J = 3.2 Hz, 1H), 6.62-6.49 (m, 2H), 5.65 (d, J = 5.2 Hz, 1H), 3.92 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 157.2, 147.9, 145.0, 142.7, 136.3, 136.2, 136.1, 132.5, 128.5, 127.8, 126.4, 125.0, 124.1, 122.8, 121.9, 120.8, 117.5, 114.8, 114.5, 114.4, 111.6, 110.6, 55.7, 47.7; HRMS(ESI): m/z [M+H]⁺ Calculated for

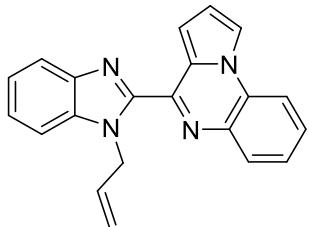
$C_{28}H_{22}N_4O$: 431.1866, found 431.1871.



ethyl 2-(2-(7-methoxypyrrolo[1,2-a]quinoxalin-4-yl)-benzoimidazol-2-yl)acetate (3z)

Yellow solid (0.0322 g, 27%, m.p. 165-167°C)

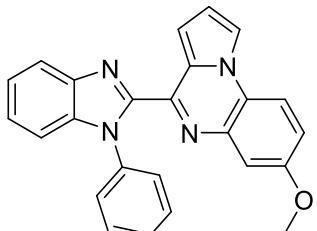
1H NMR (400 MHz, CDCl₃): δ 8.04 (d, J = 4.0 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.95 (s, 1H), 7.81 (d, J = 8.8 Hz, 1H) 7.42-7.37 (m, 4H), 7.18 (dd, J = 9.2, 2.8 Hz, 1H), 6.98-6.96 (m, 1H), 5.56 (s, 2H), 4.18 (q, J = 7.2 Hz, 2H), 3.94 (s, 3H), 1.14 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl₃): 168.4, 157.2, 147.6, 144.4, 142.4, 136.3, 124.5, 124.3, 123.1, 121.9, 121.0, 117.6, 114.7, 114.5, 114.4, 111.4, 111.1, 109.3, 55.7, 47.9, 29.6, 14.1; HRMS(ESI): m/z [M+H]⁺ Calculated for C₂₃H₂₀N₄O₃: 401.1607, found 401.1608.



4-(1-allyl-benzoimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3aa)

Yellow solid (0.0541 g, 56%, m.p. 104-106°C)

1H NMR (400 MHz, CDCl₃): δ 7.99-7.94 (m, 3H), 7.86 (dd, J = 8.0, 0.8 Hz, 1H), 7.82 (dd, J = 4.0, 1.2 Hz, 1H), 7.48-7.41 (m, 2H), 7.39-7.32 (m, 2H), 6.96 (dd, J = 4.0, 2.8 Hz, 1H), 6.15 (m, 1H), 5.47 (d, J = 5.6 Hz, 2H), 5.16-5.11 (m, 2H); ^{13}C NMR (100 MHz, CDCl₃): 147.8, 144.7, 142.7, 136.1, 135.1, 133.5, 130.3, 128.5, 127.5, 125.2, 125.1, 124.0, 122.8, 120.8, 117.2, 114.7, 114.7, 113.8, 111.0, 110.5, 48.0; HRMS(ESI): m/z [M+H]⁺ Calculated for C₂₁H₁₆N₄: 325.1447, found 325.1448.

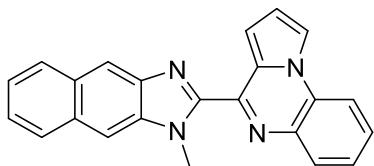


7-methoxy-4-(1-phenyl-benzoimidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3ab)

Yellow solid (0.0606 g 52%, m.p. 203-205°C)

1H NMR (400 MHz, CDCl₃): δ 8.01 (d, J = 8.0 Hz, 1H), 7.88 (dd, J = 2.4, 1.2 Hz, 1H), 7.71 (d, J = 9.2 Hz, 1H), 7.61 (dd, J = 4.0, 0.8 Hz, 1H), 7.43-7.37 (m, 6H), 7.35-7.33 (m, 2H), 7.07 (dd, J = 9.2, 2.8 Hz, 1H), 6.91 (dd, J = 4.4, 2.8 Hz, 1H), 6.88 (d, J = 2.8 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl₃): 156.9, 148.3, 144.1, 142.8, 137.7, 137.0, 136.1, 129.1, 127.9, 127.3, 124.9, 124.4, 123.2, 121.7, 120.8, 117.2, 114.5, 114.3, 111.7, 110.9, 109.6, 55.6; HRMS(ESI): m/z [M+H]⁺

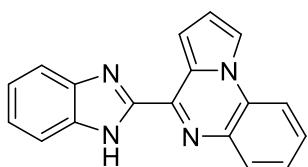
Calculated for C₂₅H₁₈N₄O: 391.1553, found 391.1553.



1-methyl-2-(pyrrolo[1,2-a]quinoxalin-4-yl)-naphtho[2,3-d]imidazole (3ac)

Yellow solid (0.0682 g, 65%, m.p. 190-192°C)

¹H NMR (400 MHz, CDCl₃): δ 8.44 (s, 1H), 8.08-8.05 (m, 3H), 8.01(d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.89 (s, 1H), 7.83 (d, J = 3.6 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.53-7.42 (m, 3H), 7.03 (m, 1H), 4.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 151.9, 144.7, 142.6, 137.3, 135.1, 131.2, 130.6, 130.54, 128.8, 128.6, 127.5, 125.3, 125.3, 124.6, 123.5, 117.8, 114.9, 114.8, 113.9, 111.0, 105.9, 32.7. HRMS(ESI): m/z [M+H]⁺ Calculated for C₂₃H₁₆N₄: 349.1447, found 349.1448.

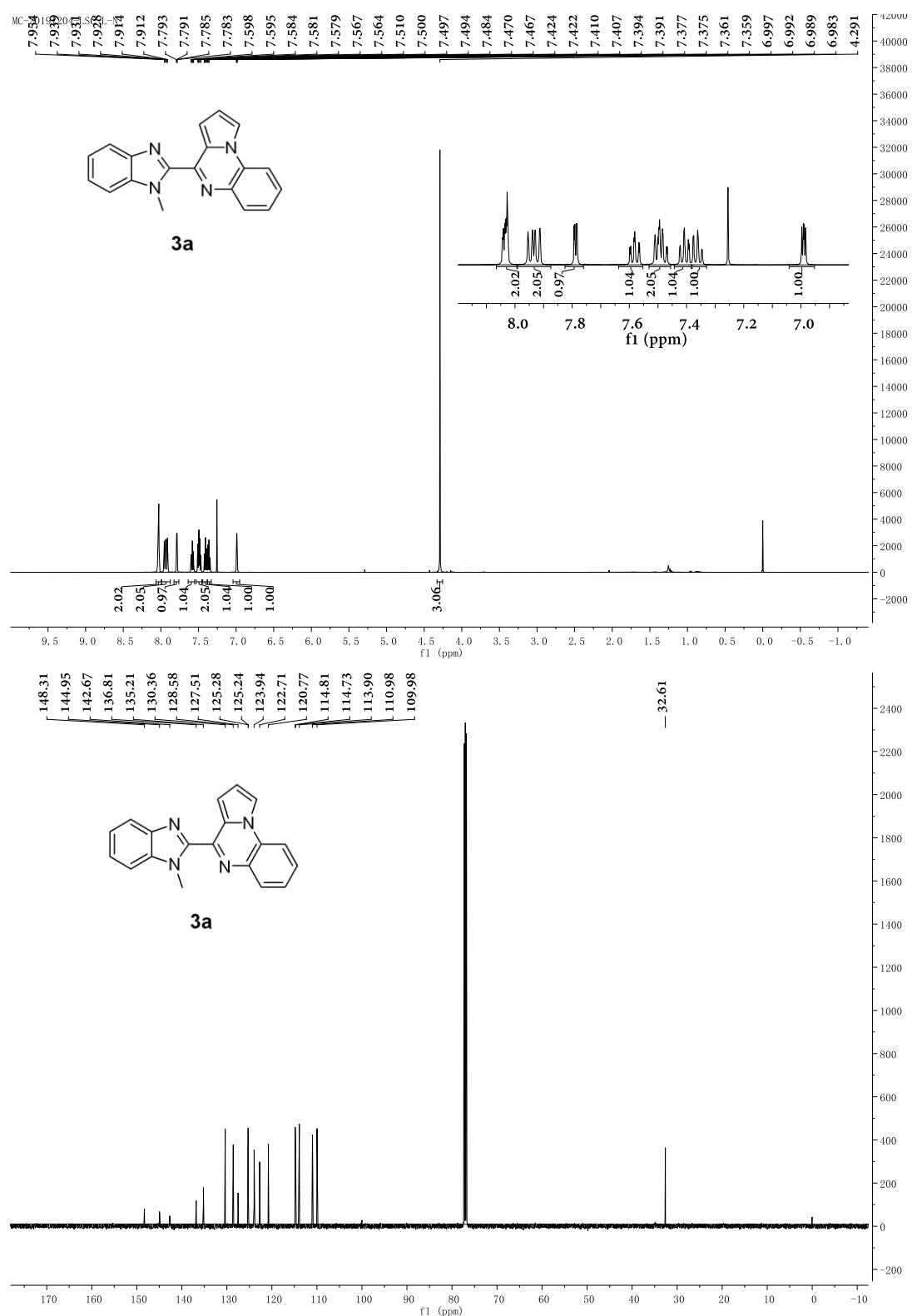


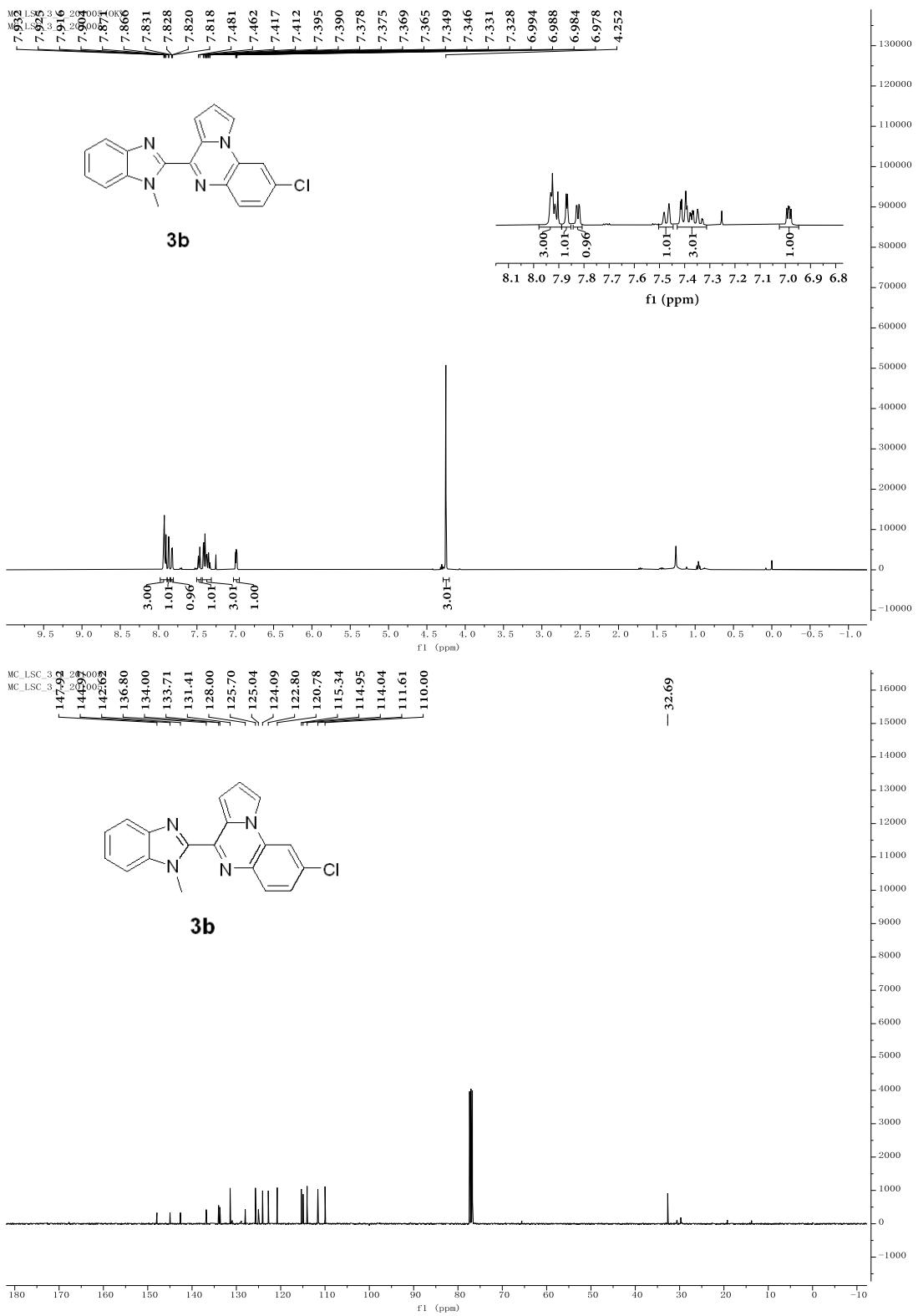
4-(1H-benzo[d]imidazol-2-yl)pyrrolo[1,2-a]quinoxaline (3ad)

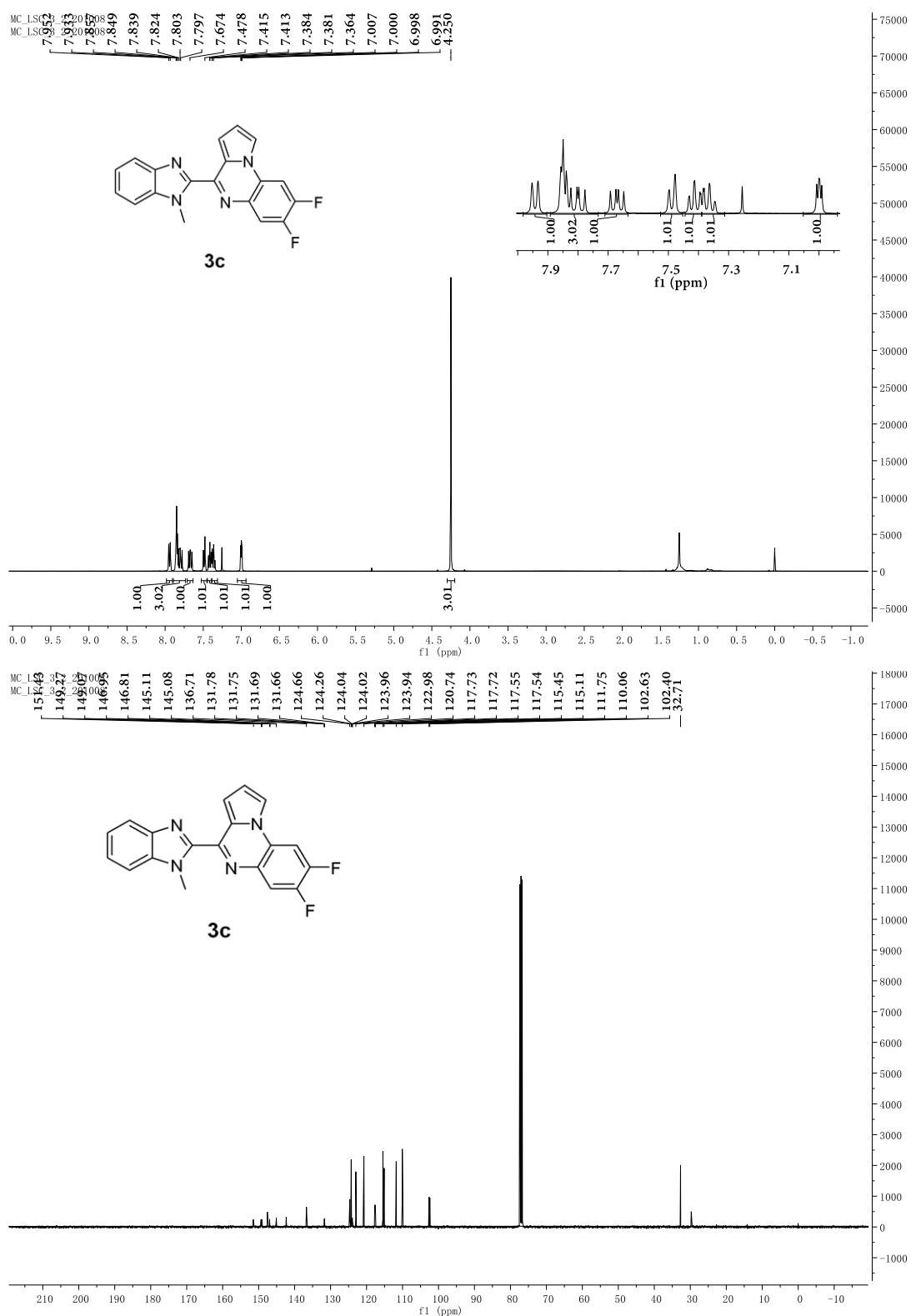
Yellow solid (0.0516 g, 60%, m.p. 120-122°C)

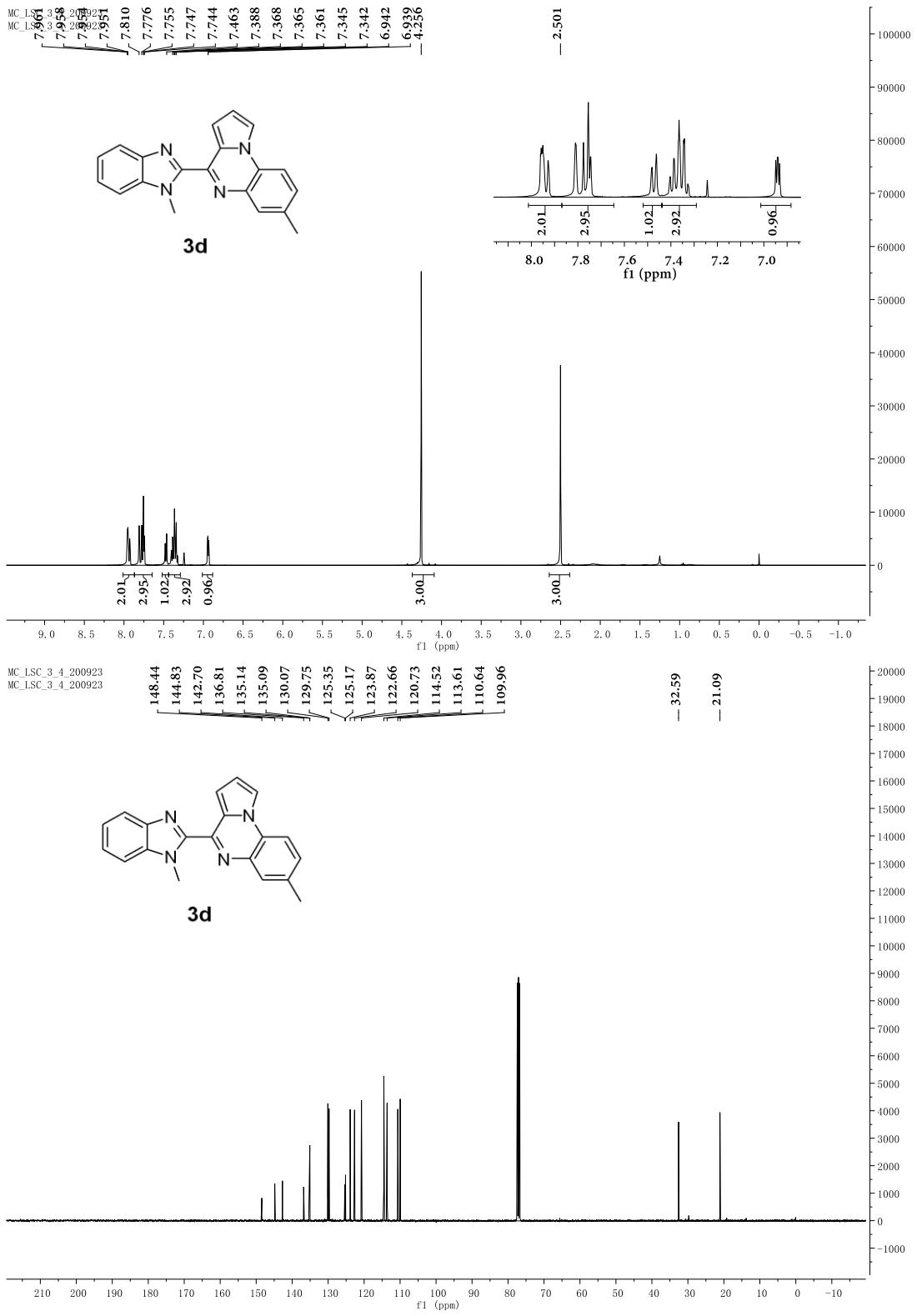
¹H NMR (400 MHz, CDCl₃): δ 11.14 (s, 1H), 8.29 (dd, J = 4.0, 0.8 Hz, 1H), 8.02 (dd, J = 2.8, 1.2 Hz, 1H), 7.98 (dd, J = 7.6 Hz, 2H), 7.88 (dd, J = 8.4, 0.8 Hz, 1H), 7.53 (td, J = 7.6, 1.2 Hz, 1H), 7.43 (td, J = 8.4, 1.2 Hz, 2H), 7.33-7.29 (m, 2H), 7.03 (dd, J = 4.0, 2.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): 149.0, 144.8, 142.6, 134.8, 133.3, 129.5, 128.4, 127.7, 125.4, 124.6, 123.5, 122.7, 120.9, 115.1, 115.0, 113.9, 111.3. HRMS(ESI): m/z [M+H]⁺ Calculated for C₁₈H₁₂N₄: 285.1134, found 285.1135.

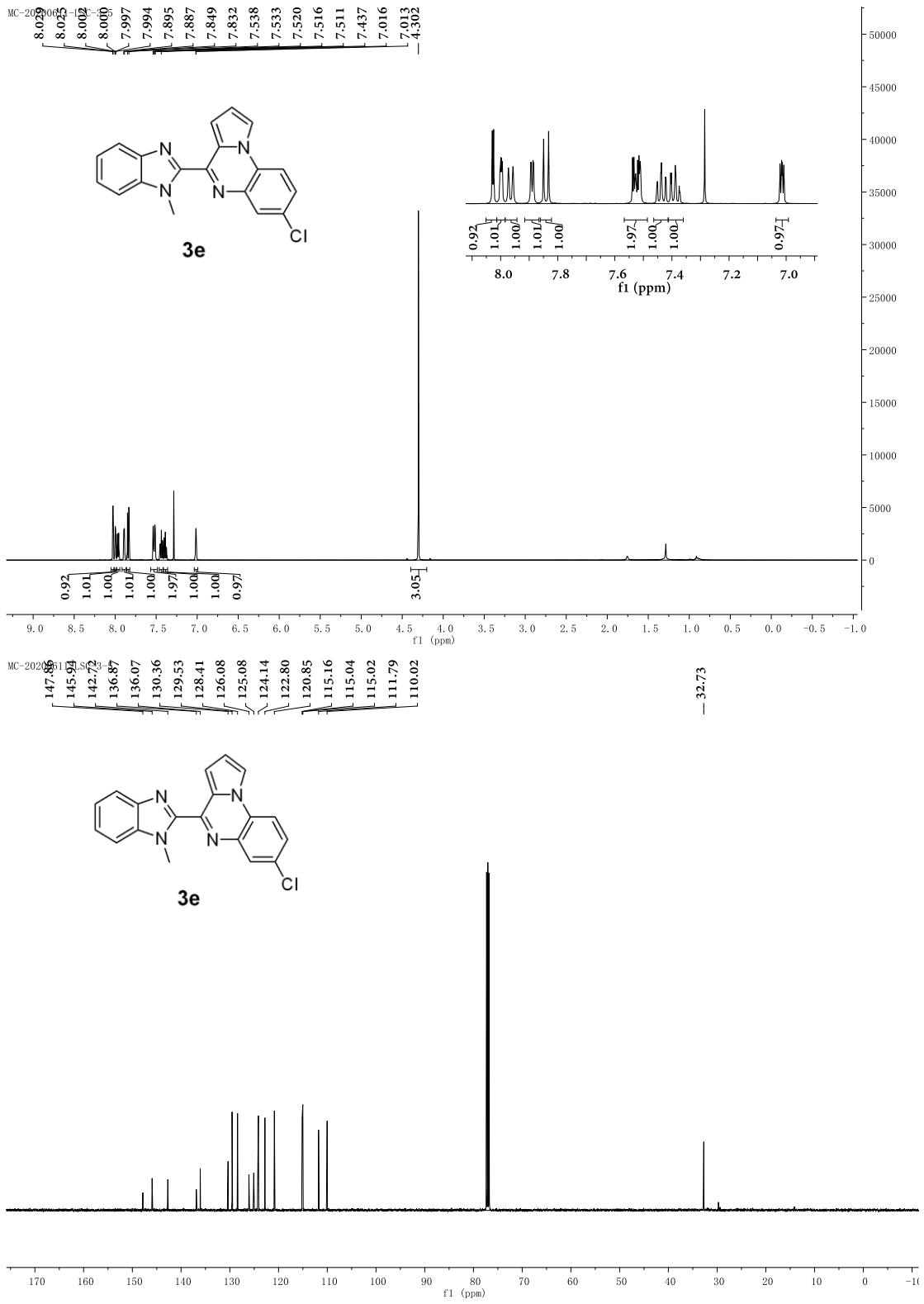
6. Copies of ^1H NMR and ^{13}C NMR spectra

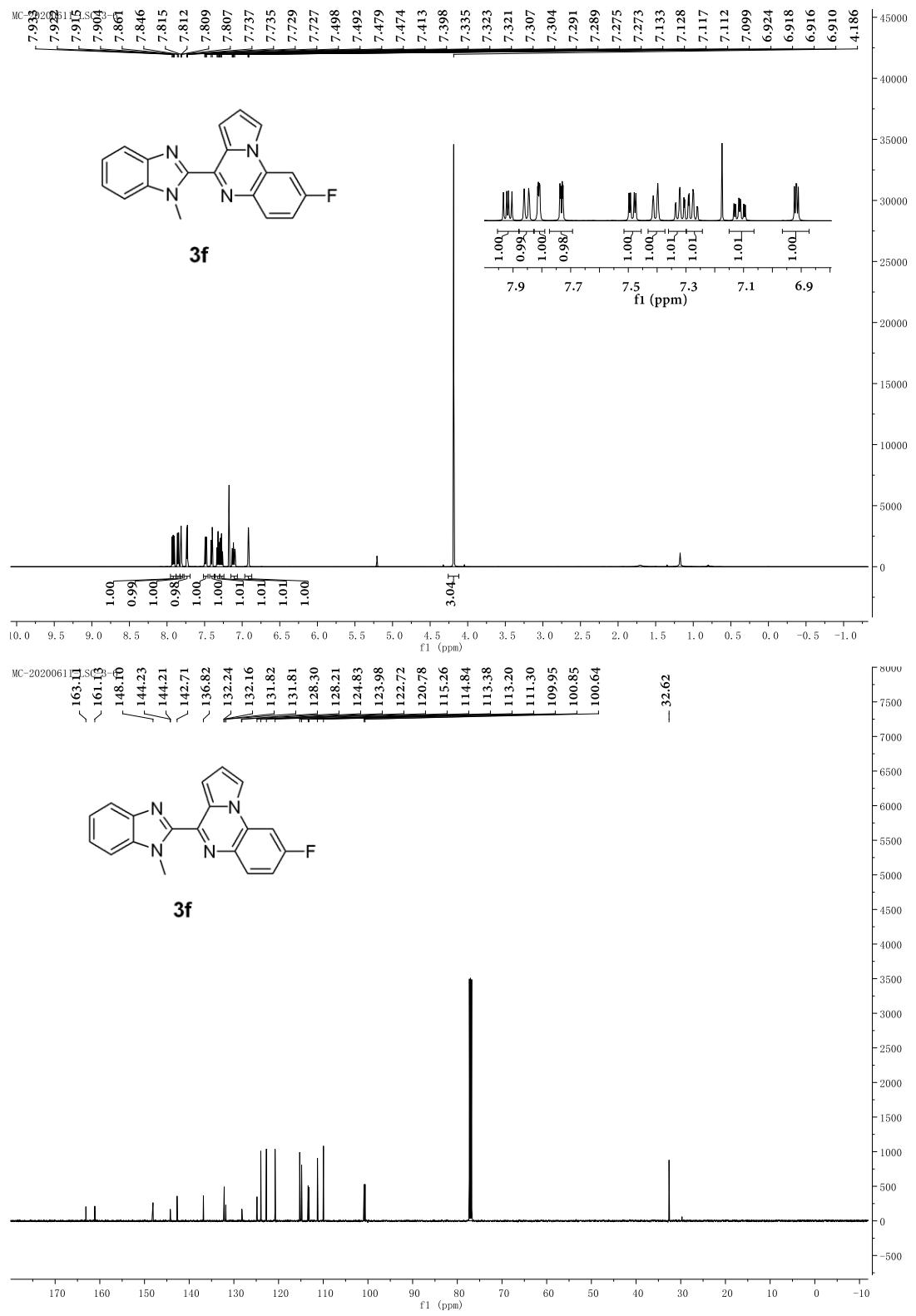


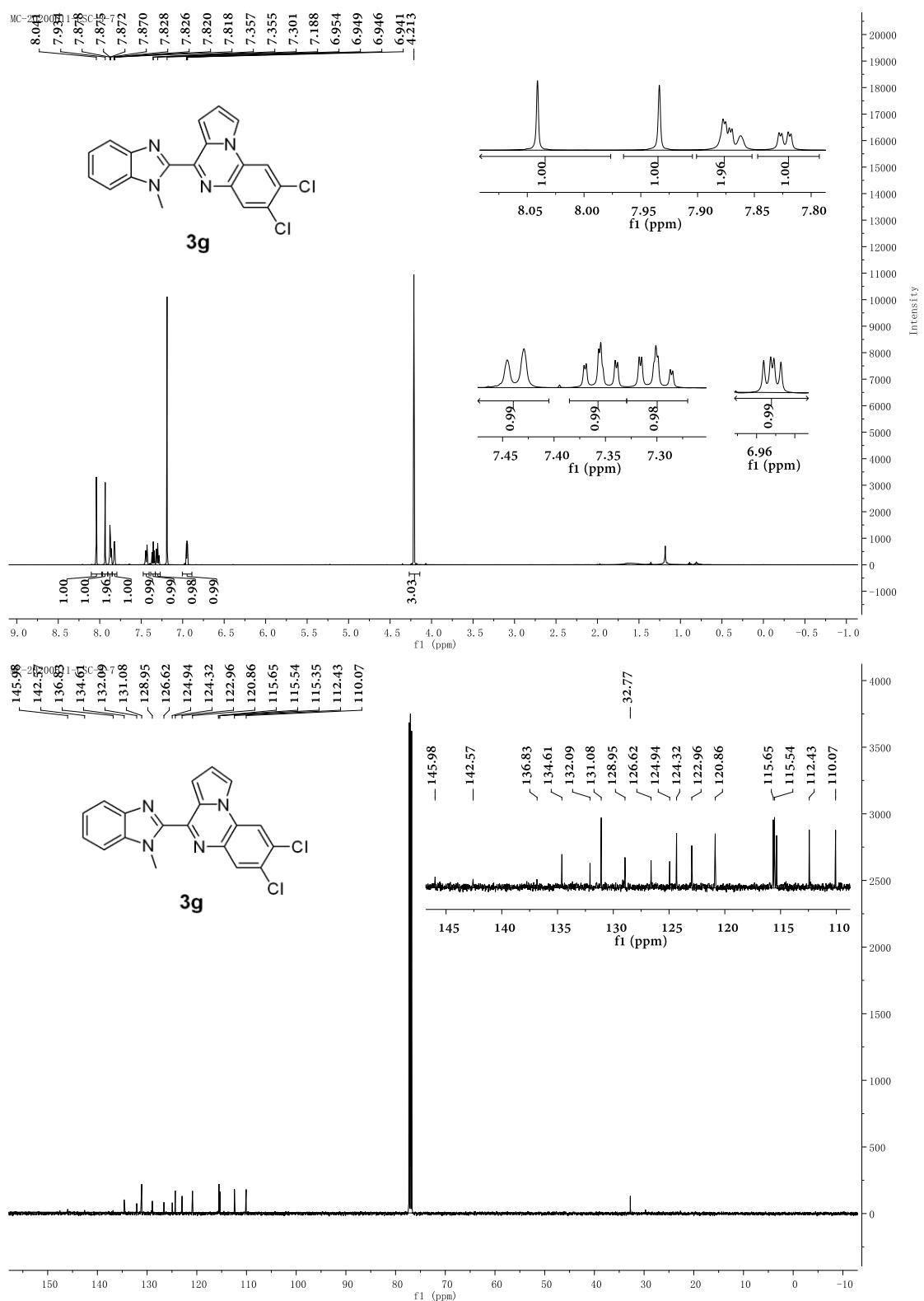


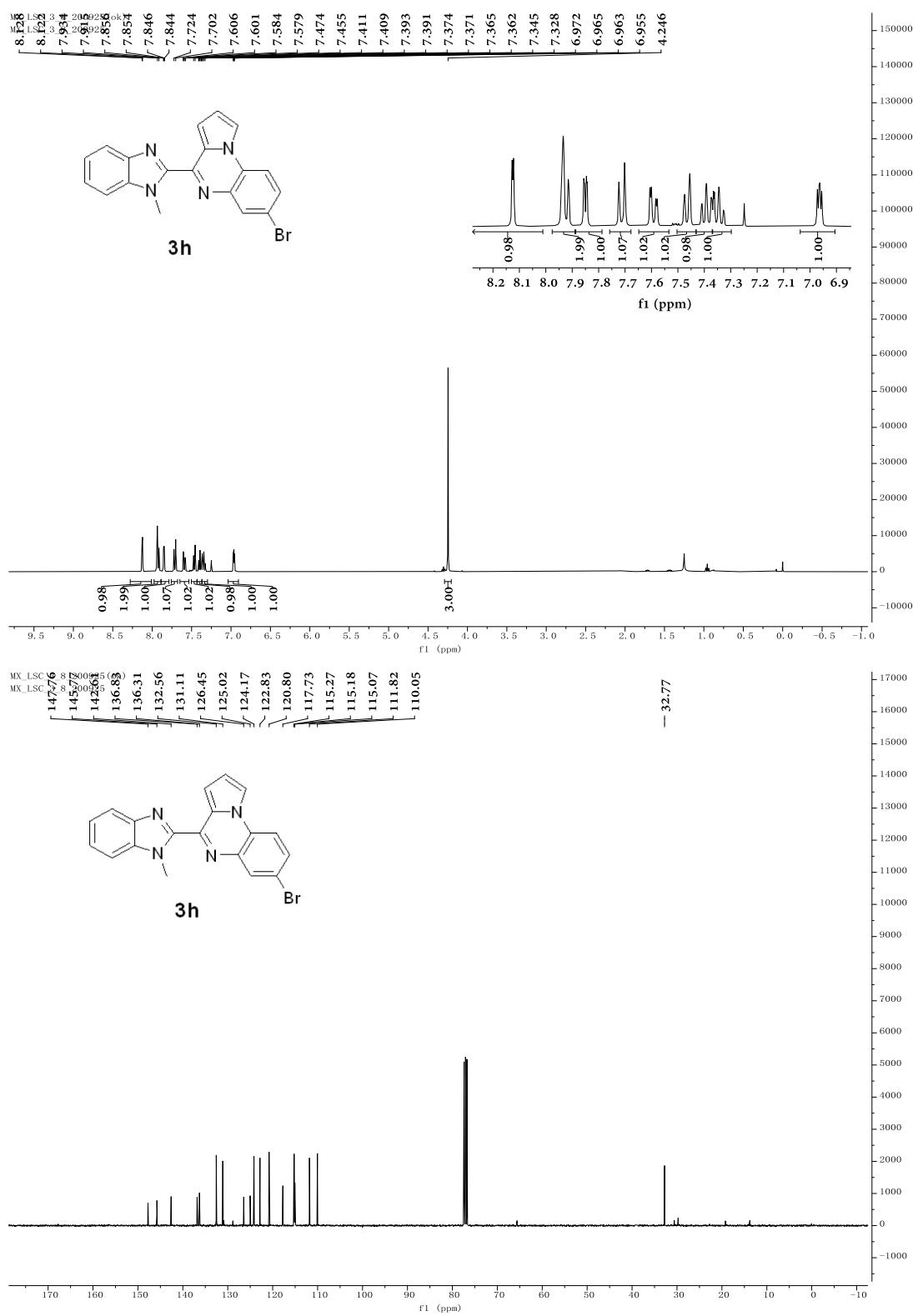


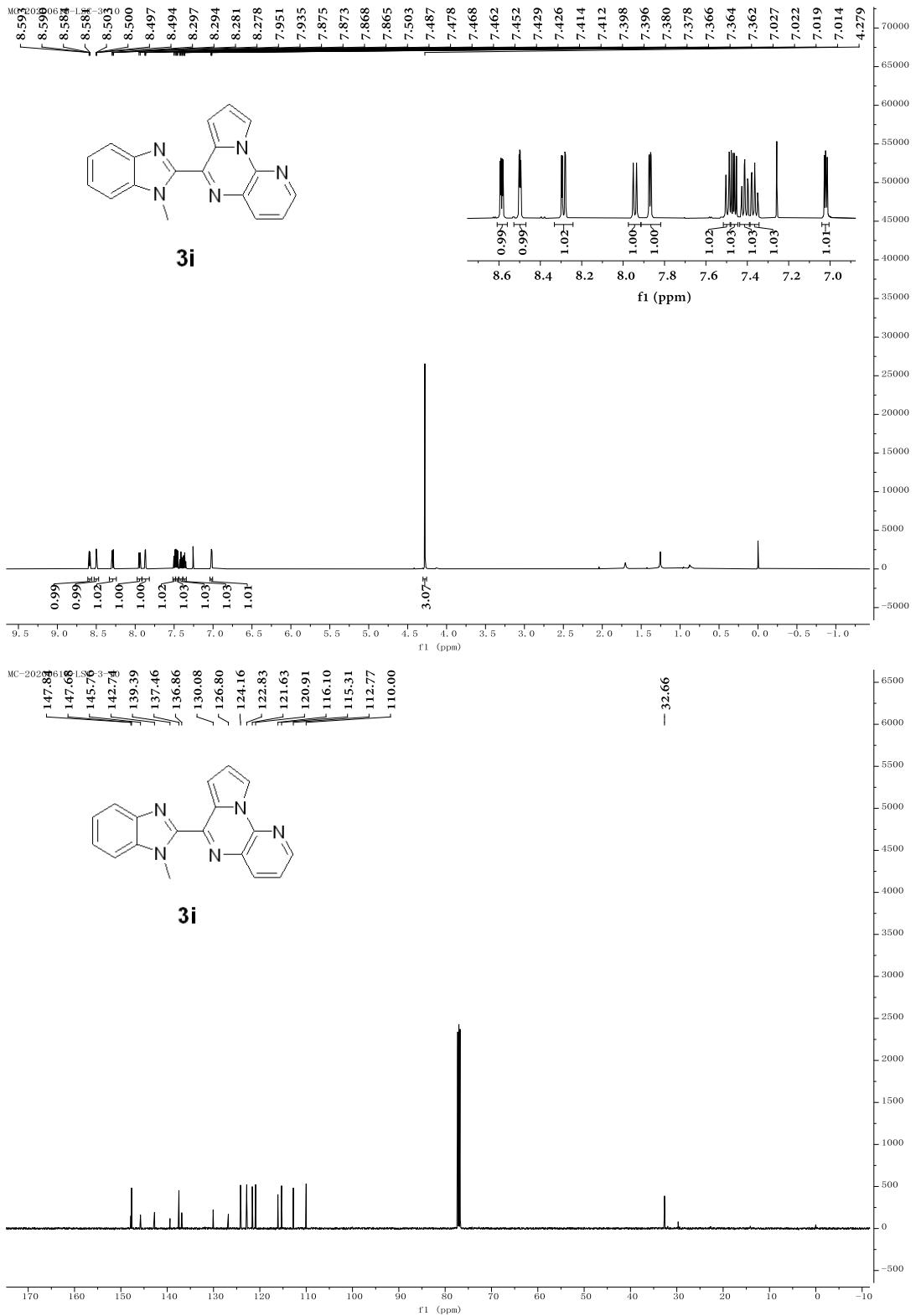


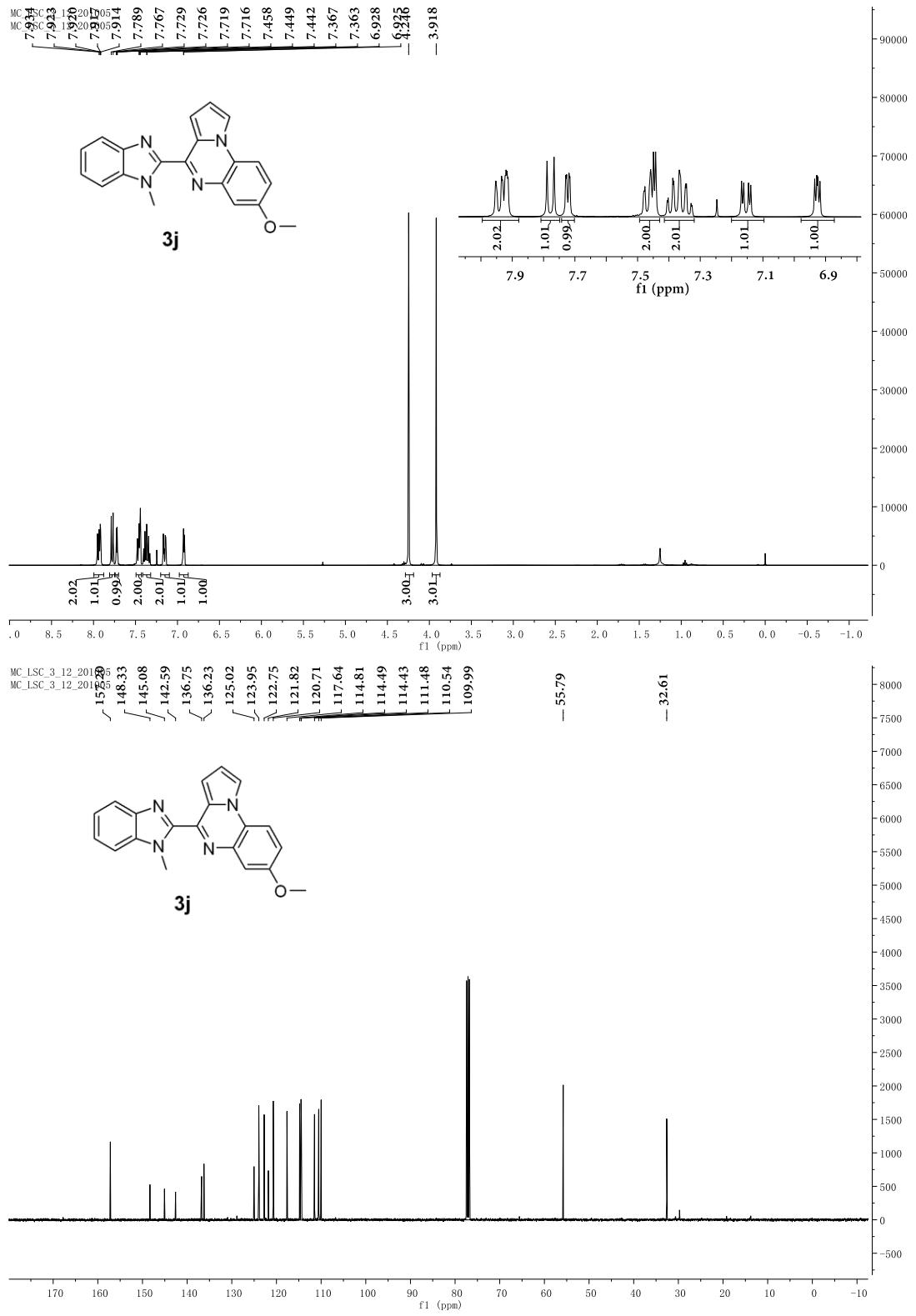


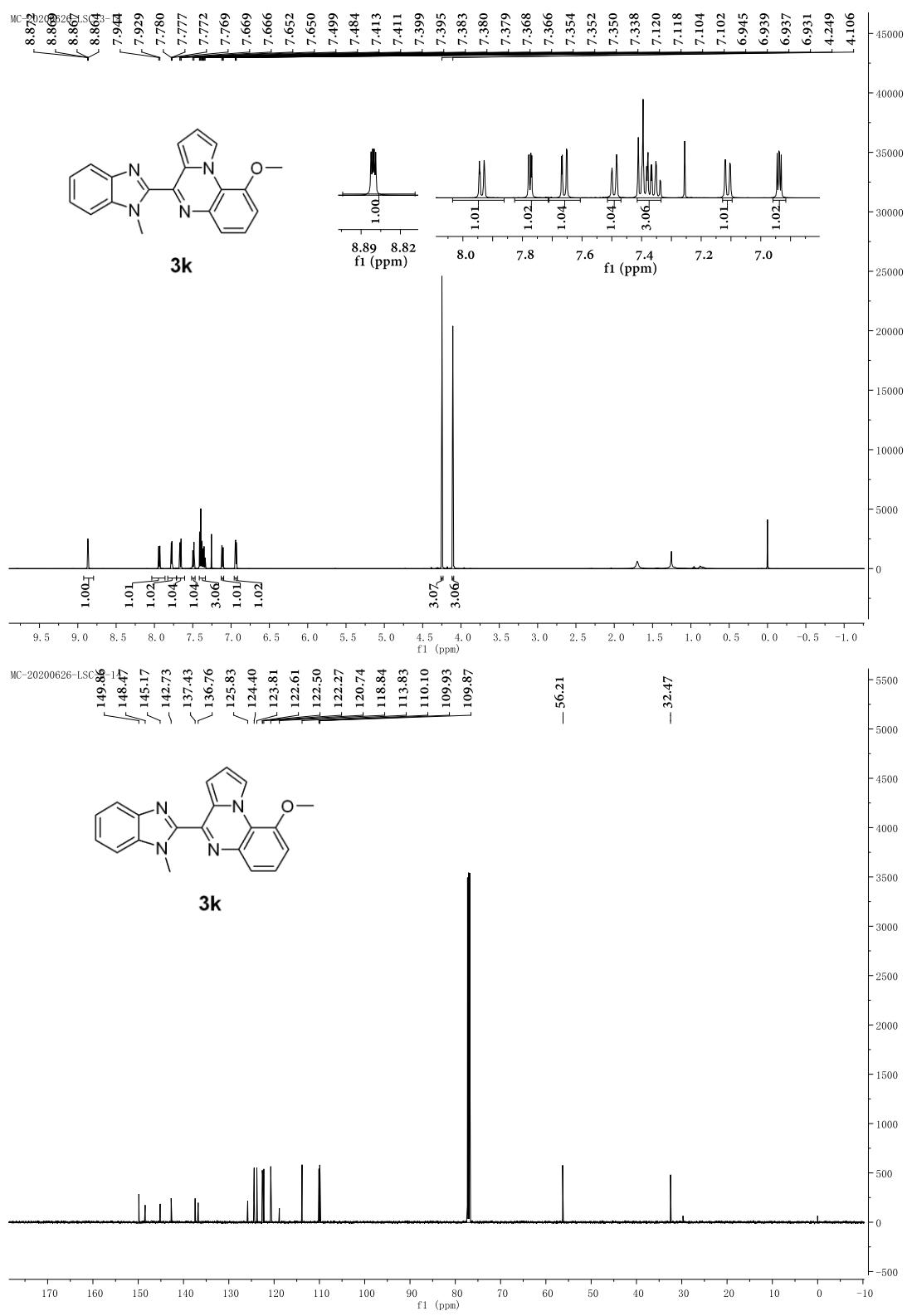


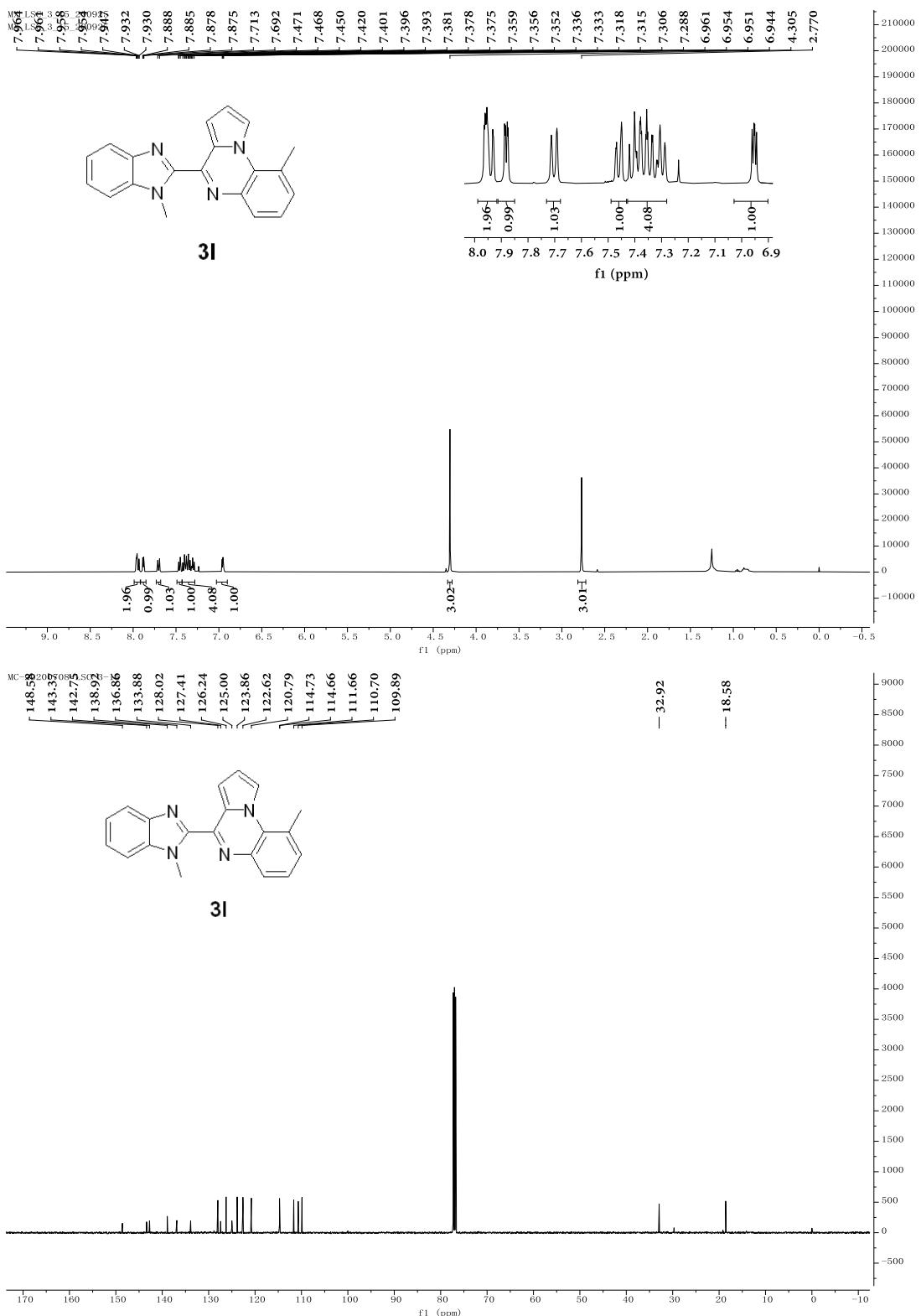


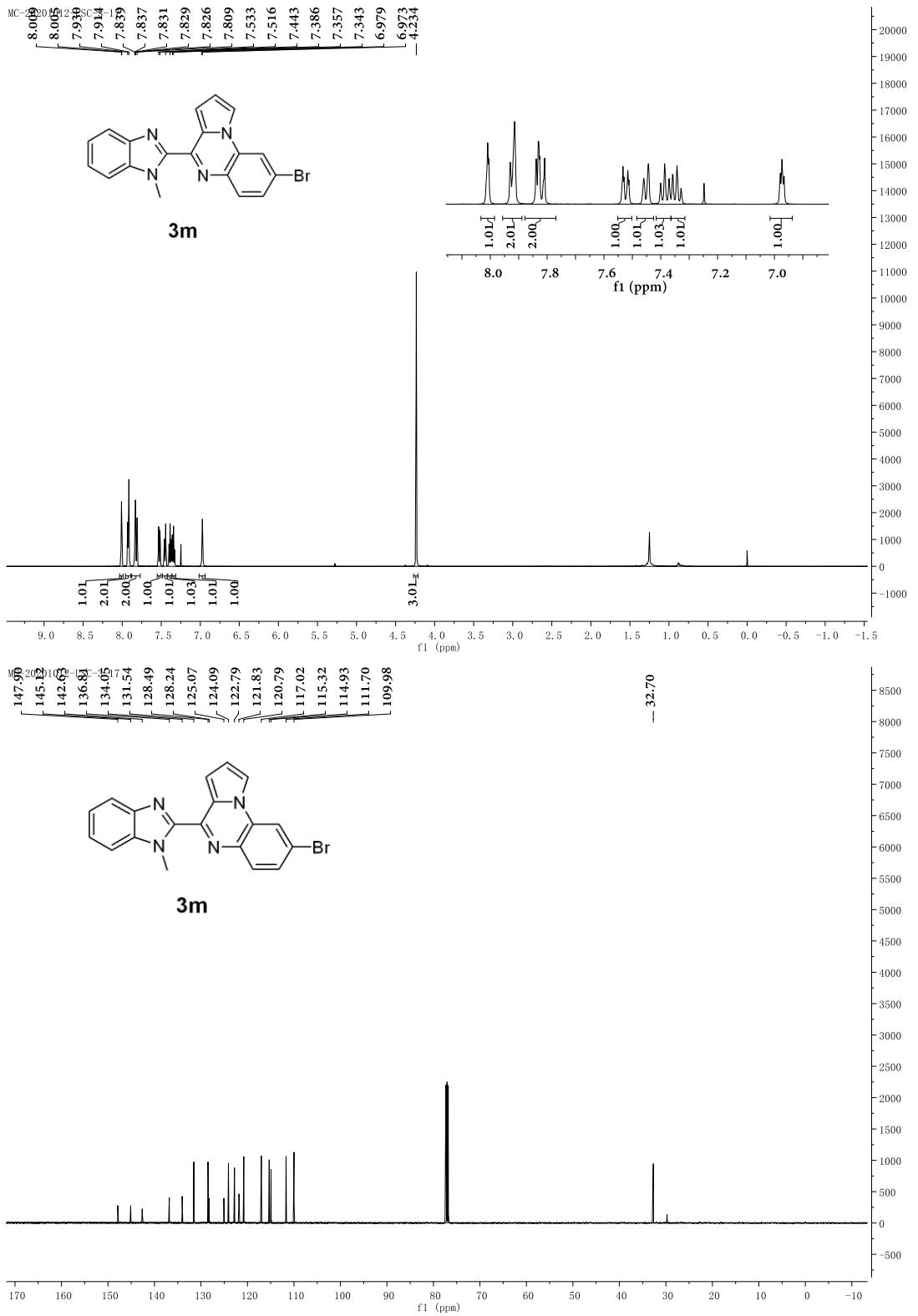


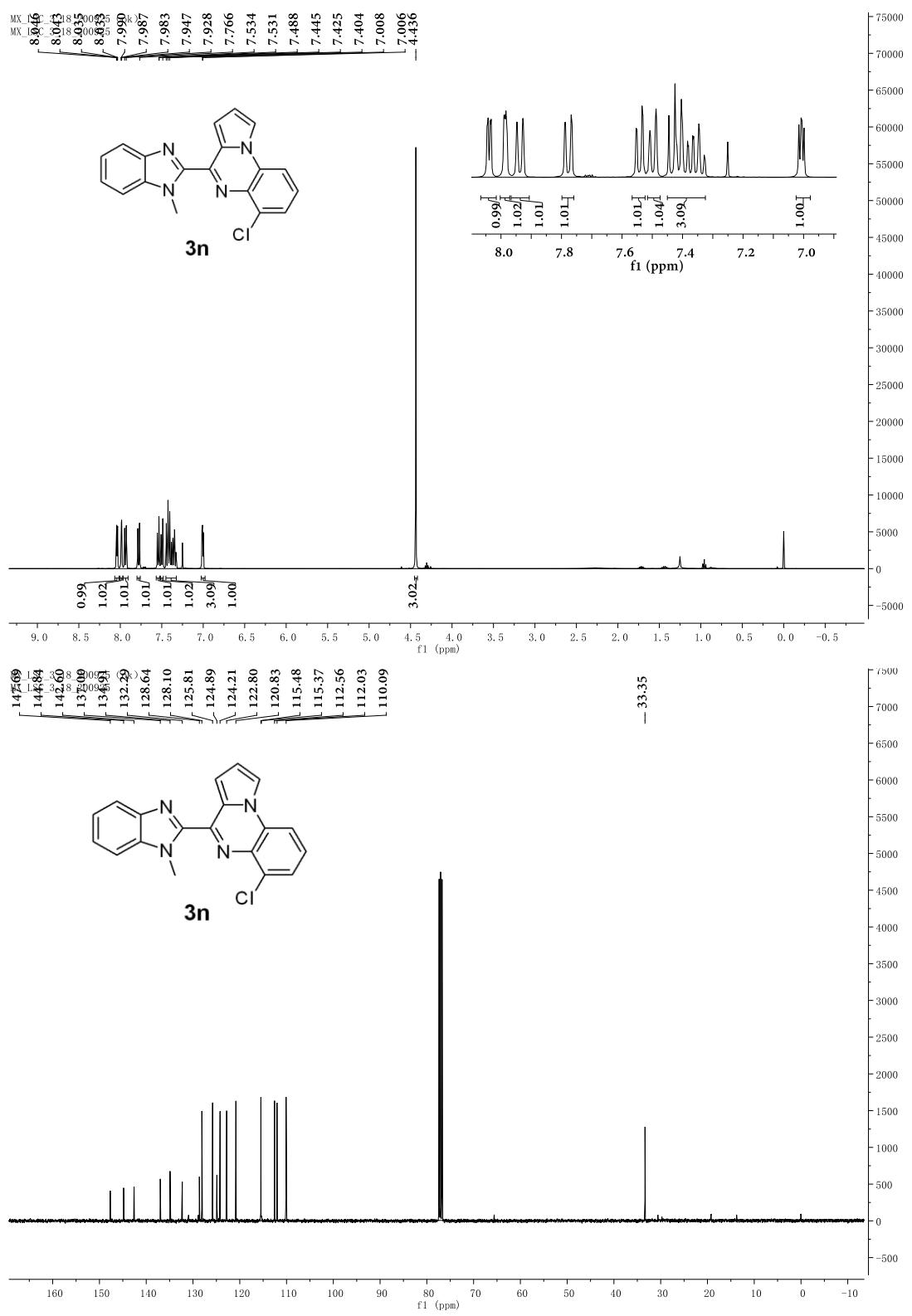


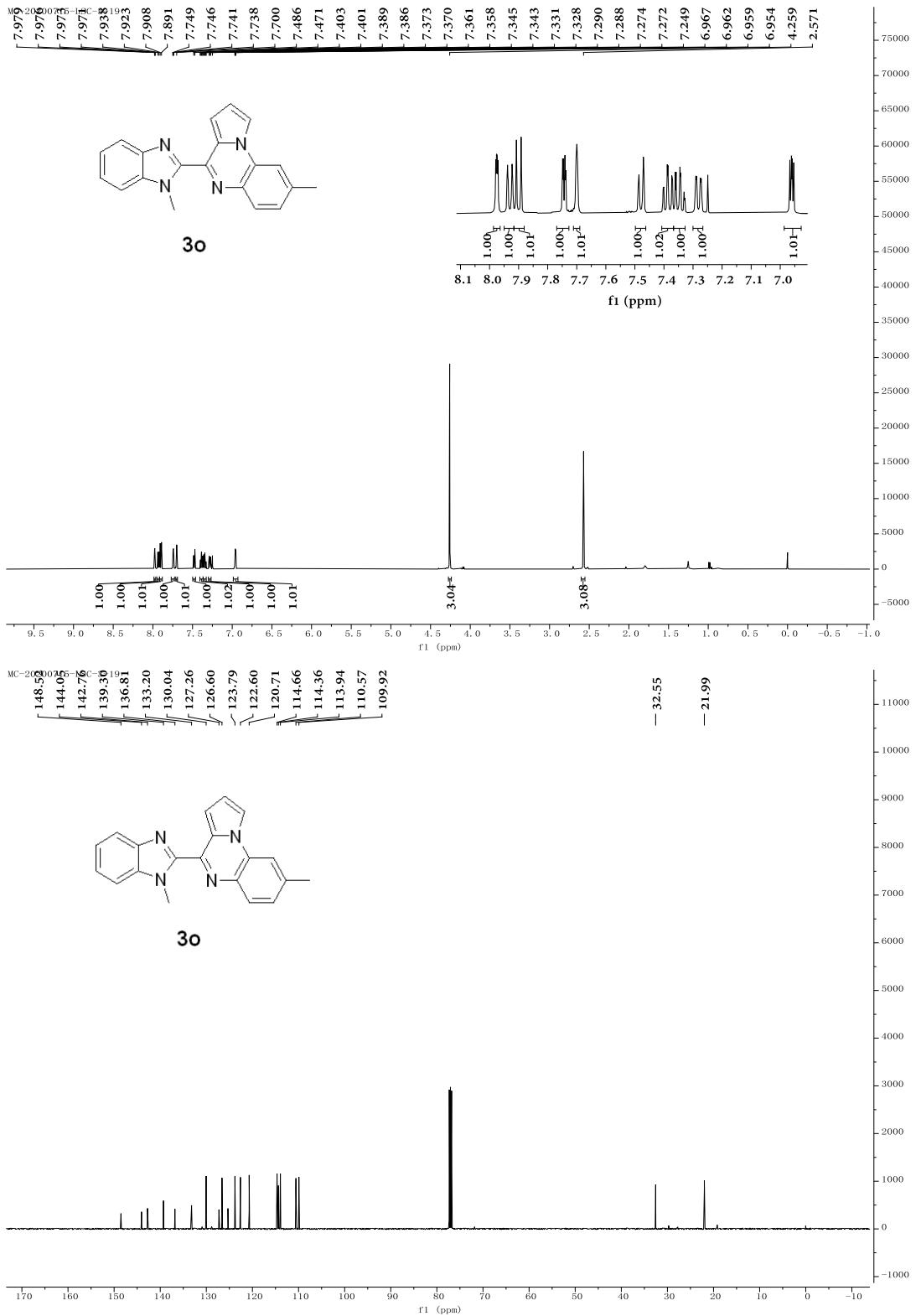


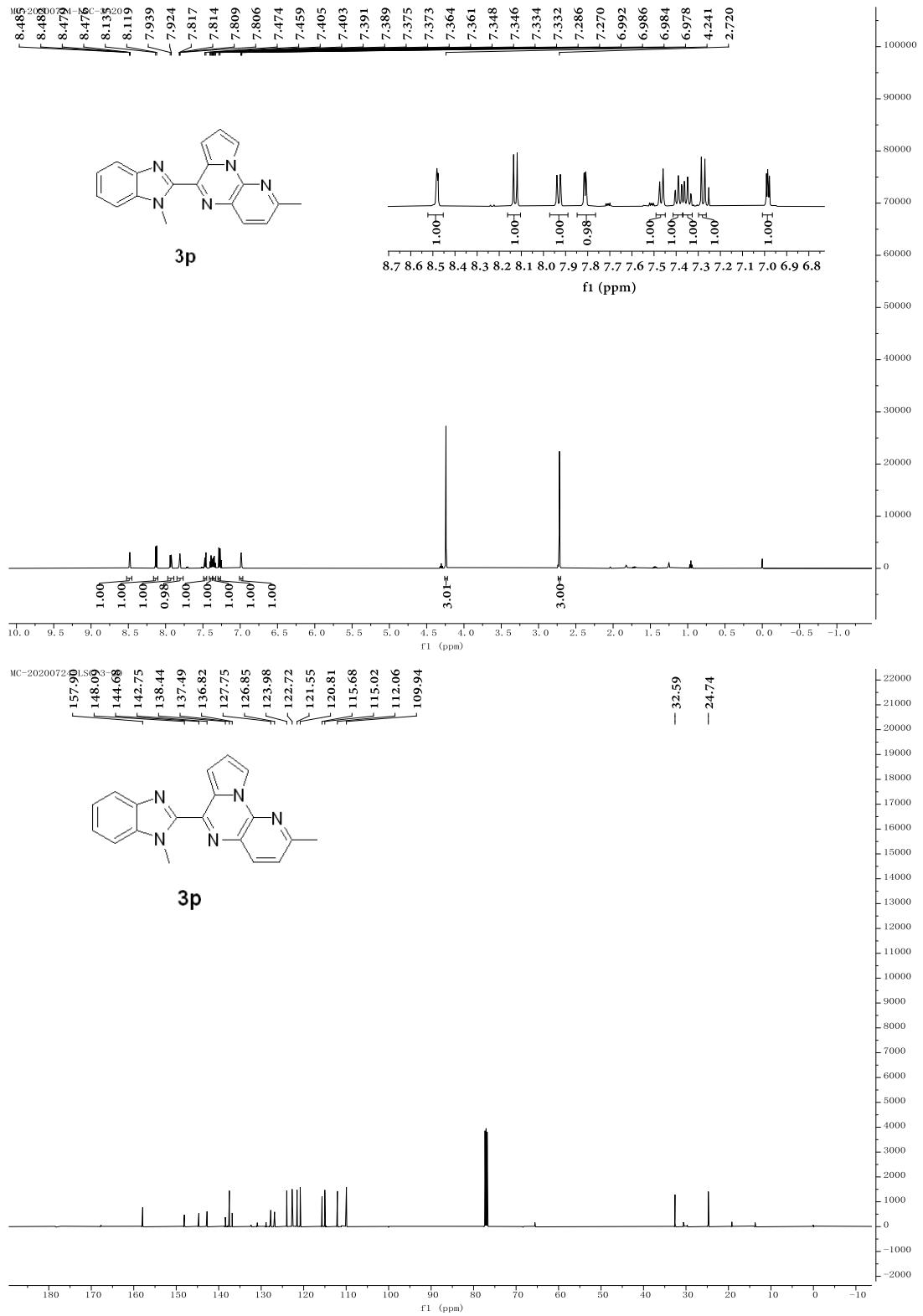


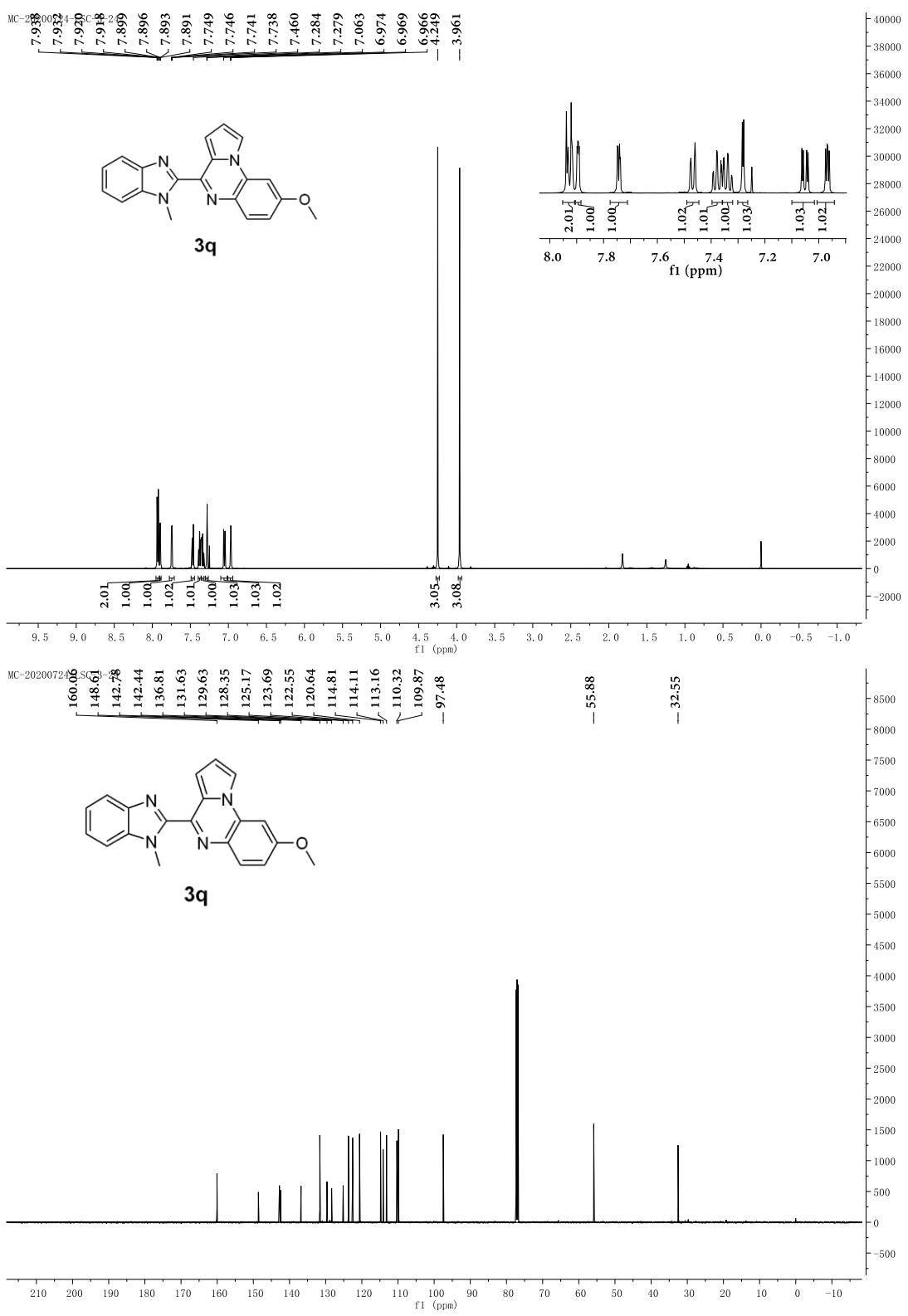


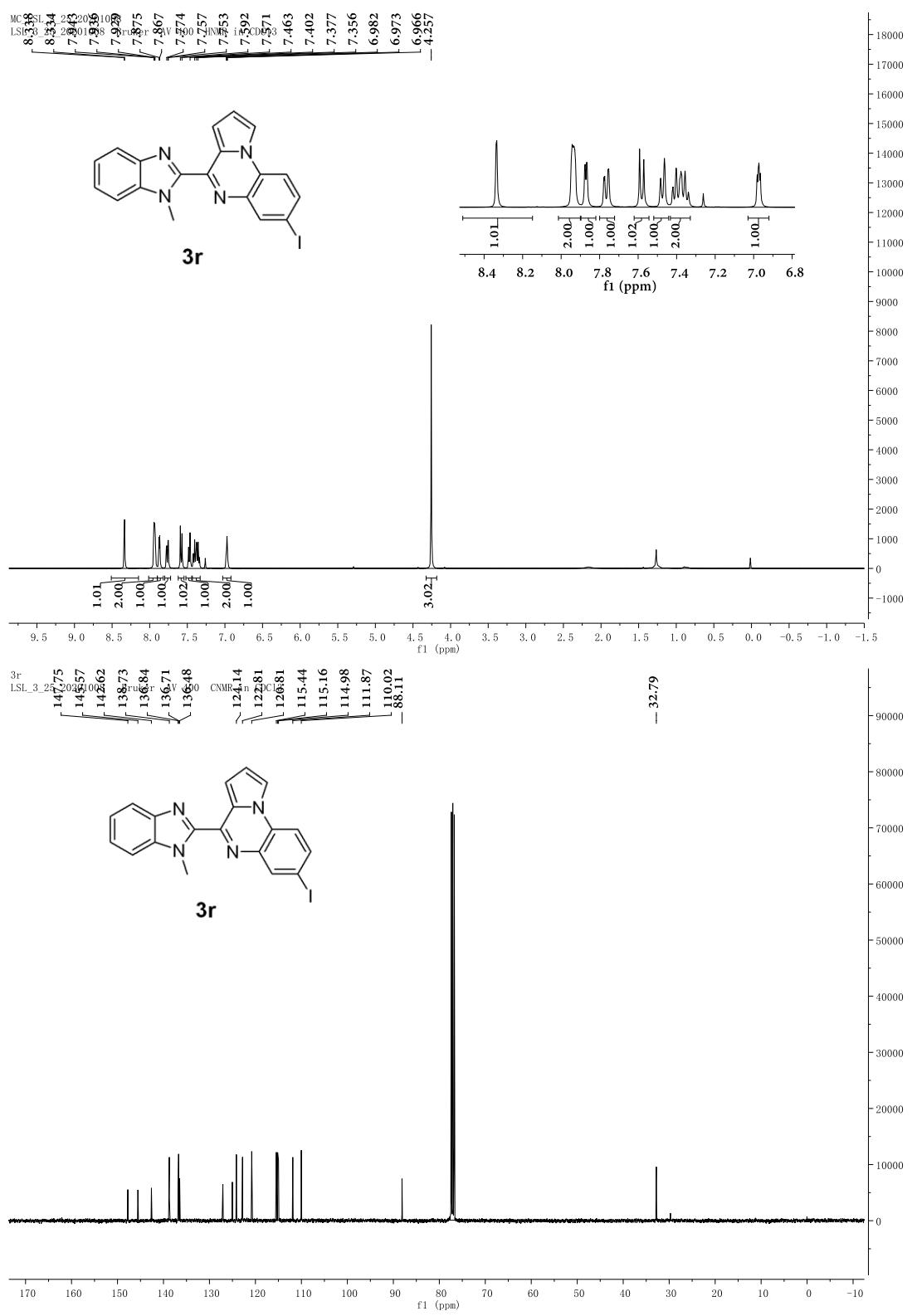


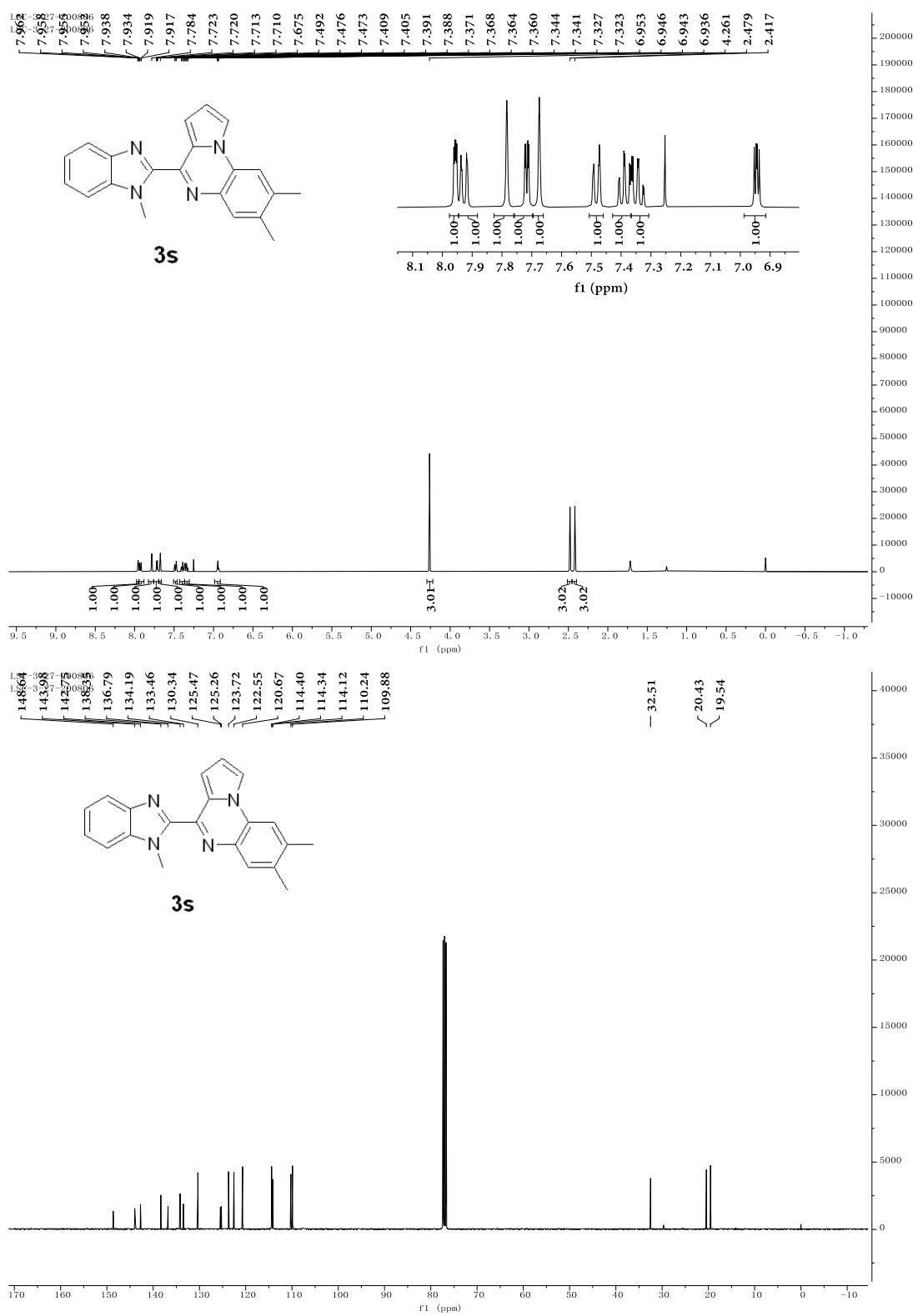


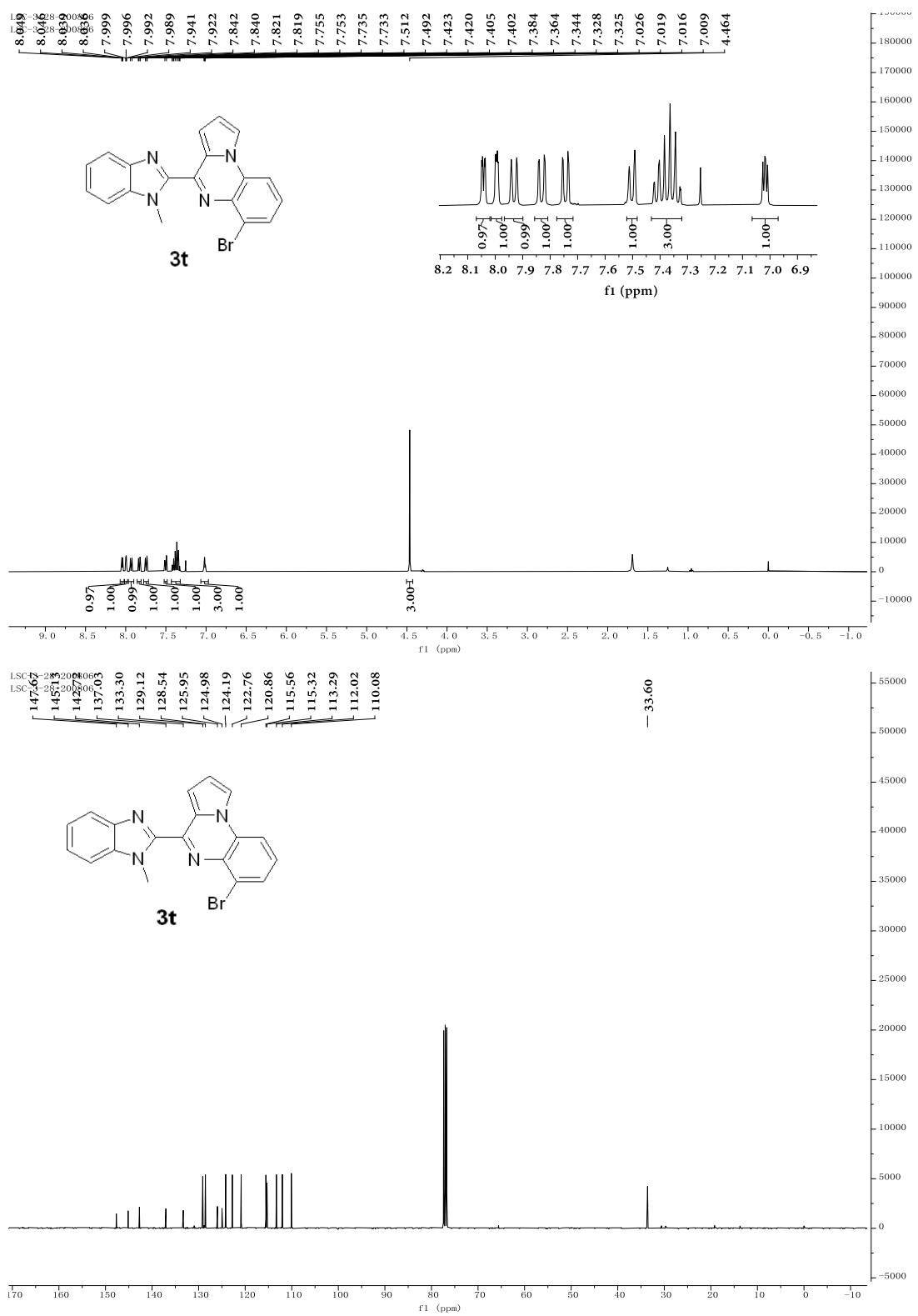


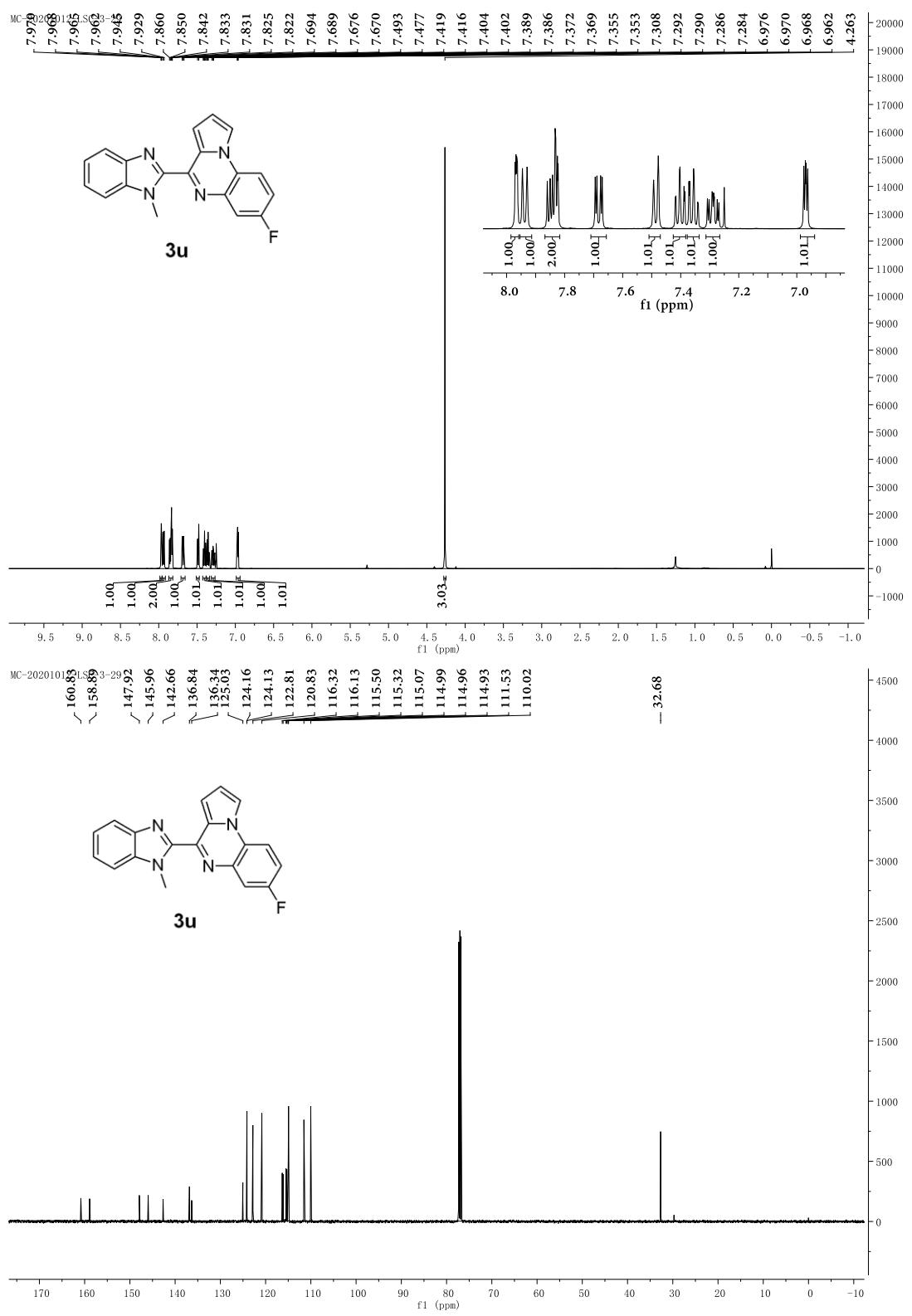


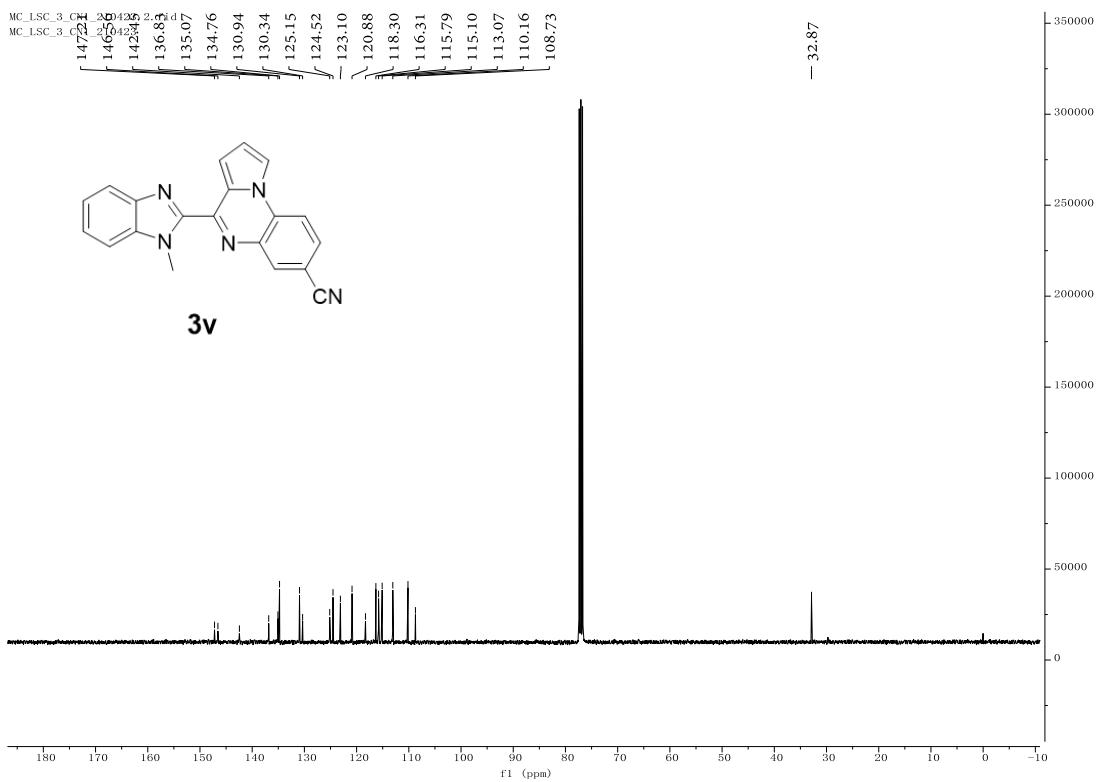
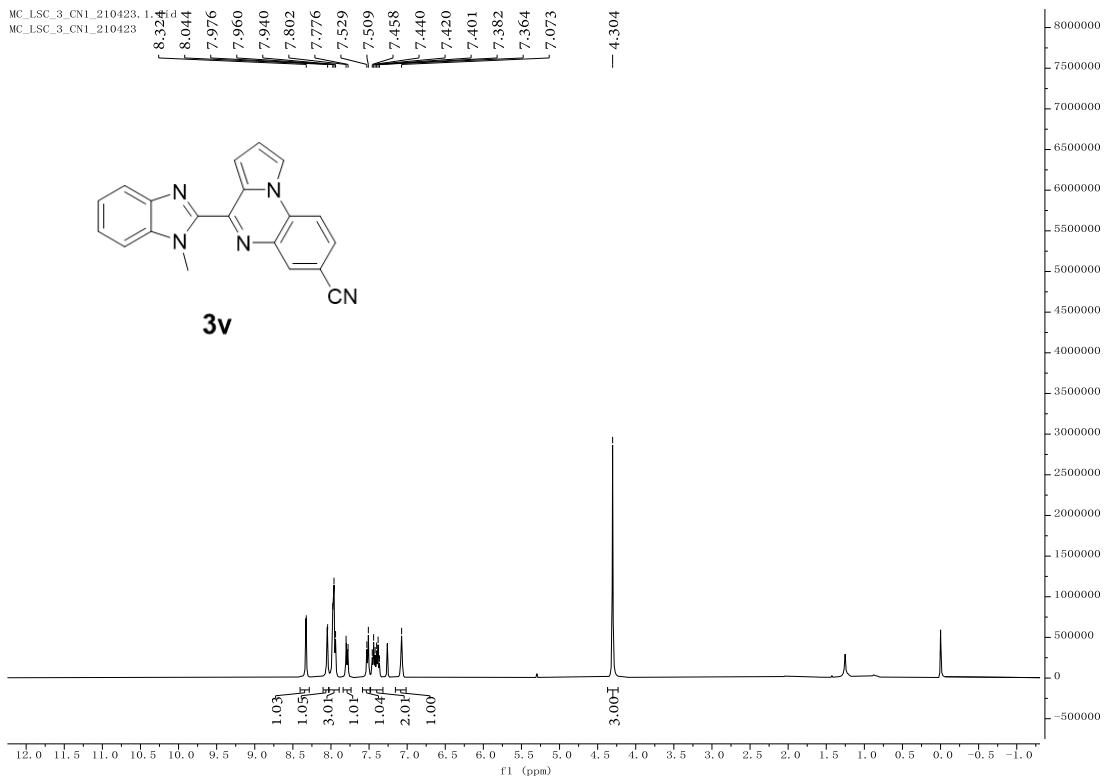


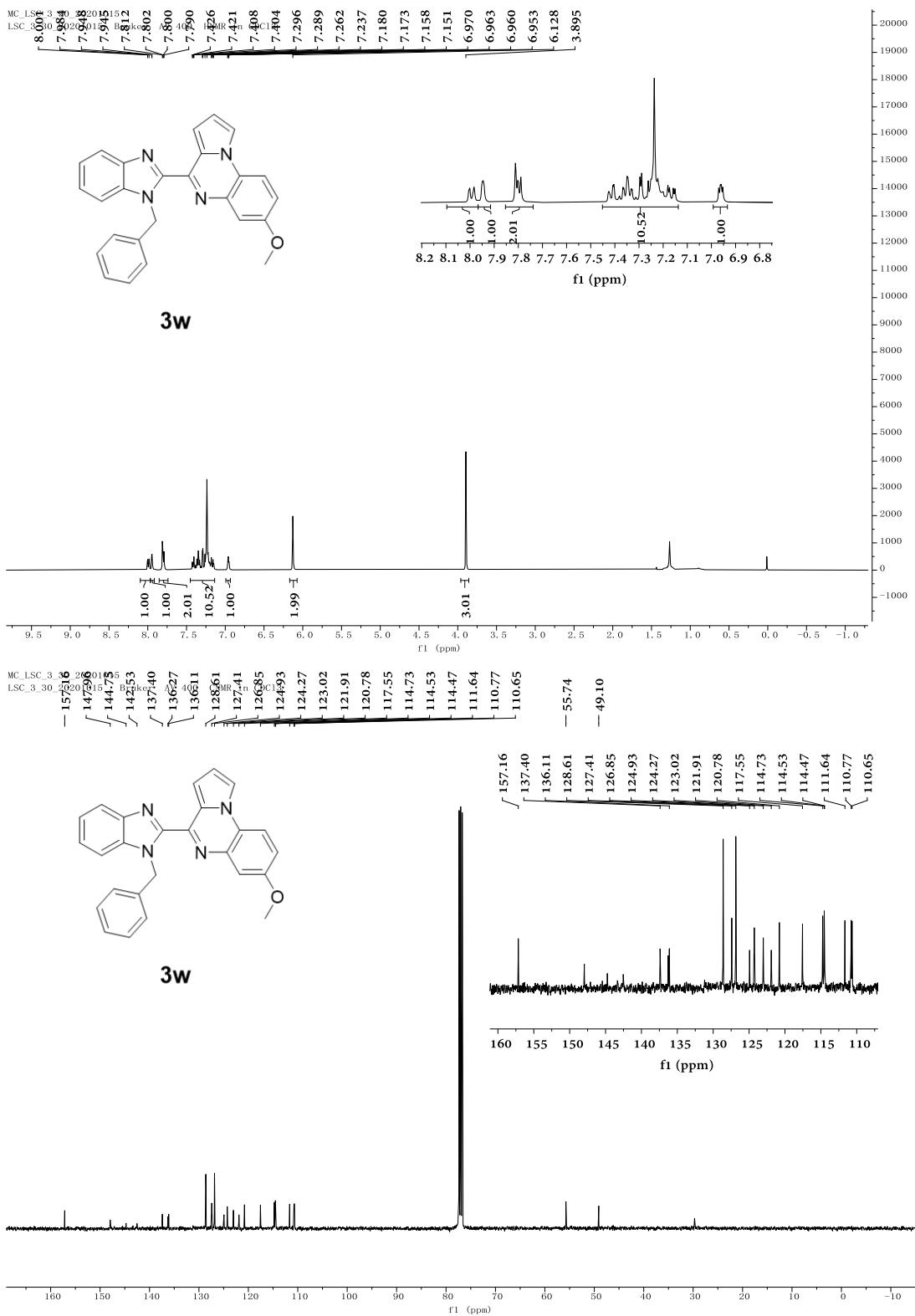


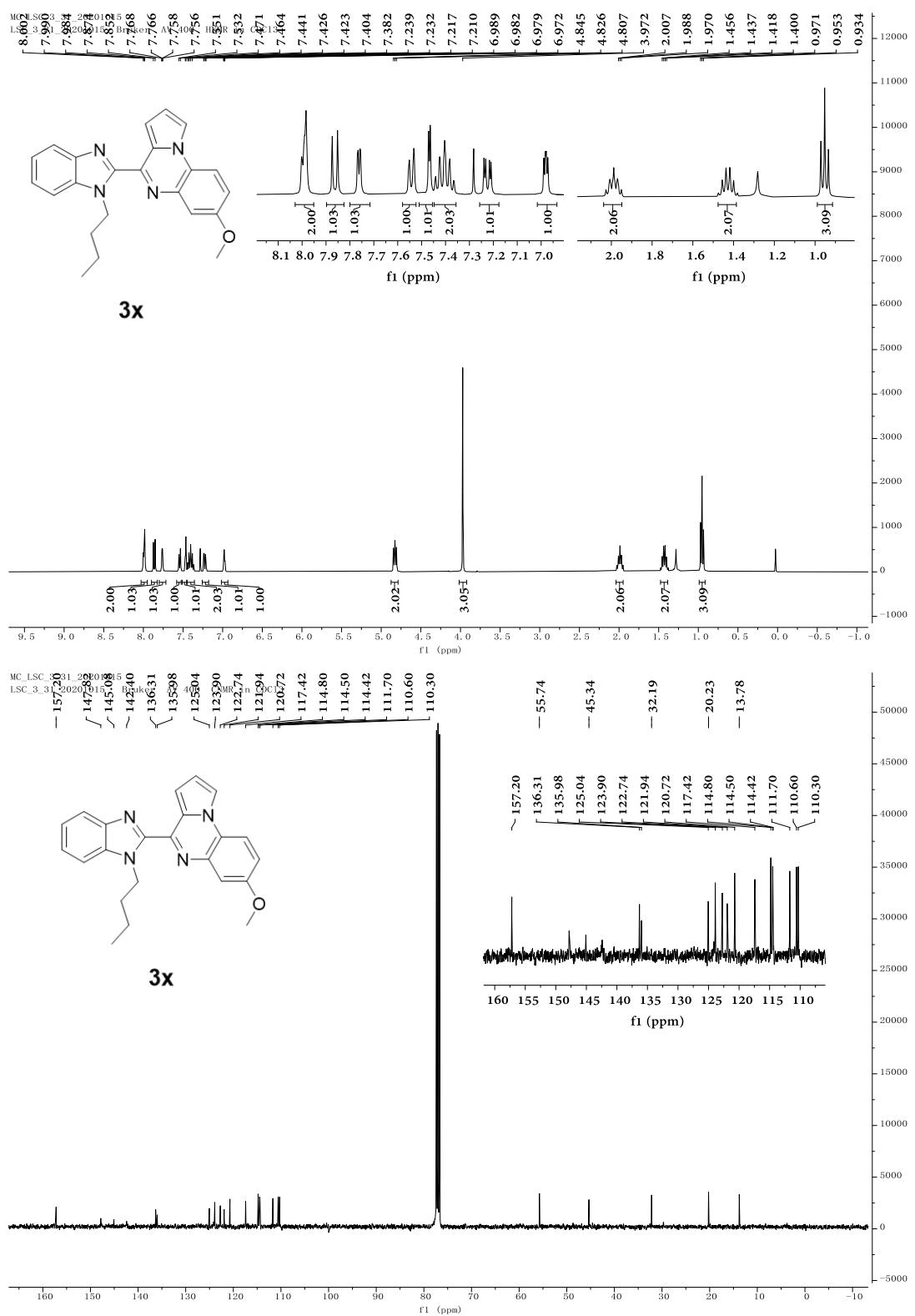


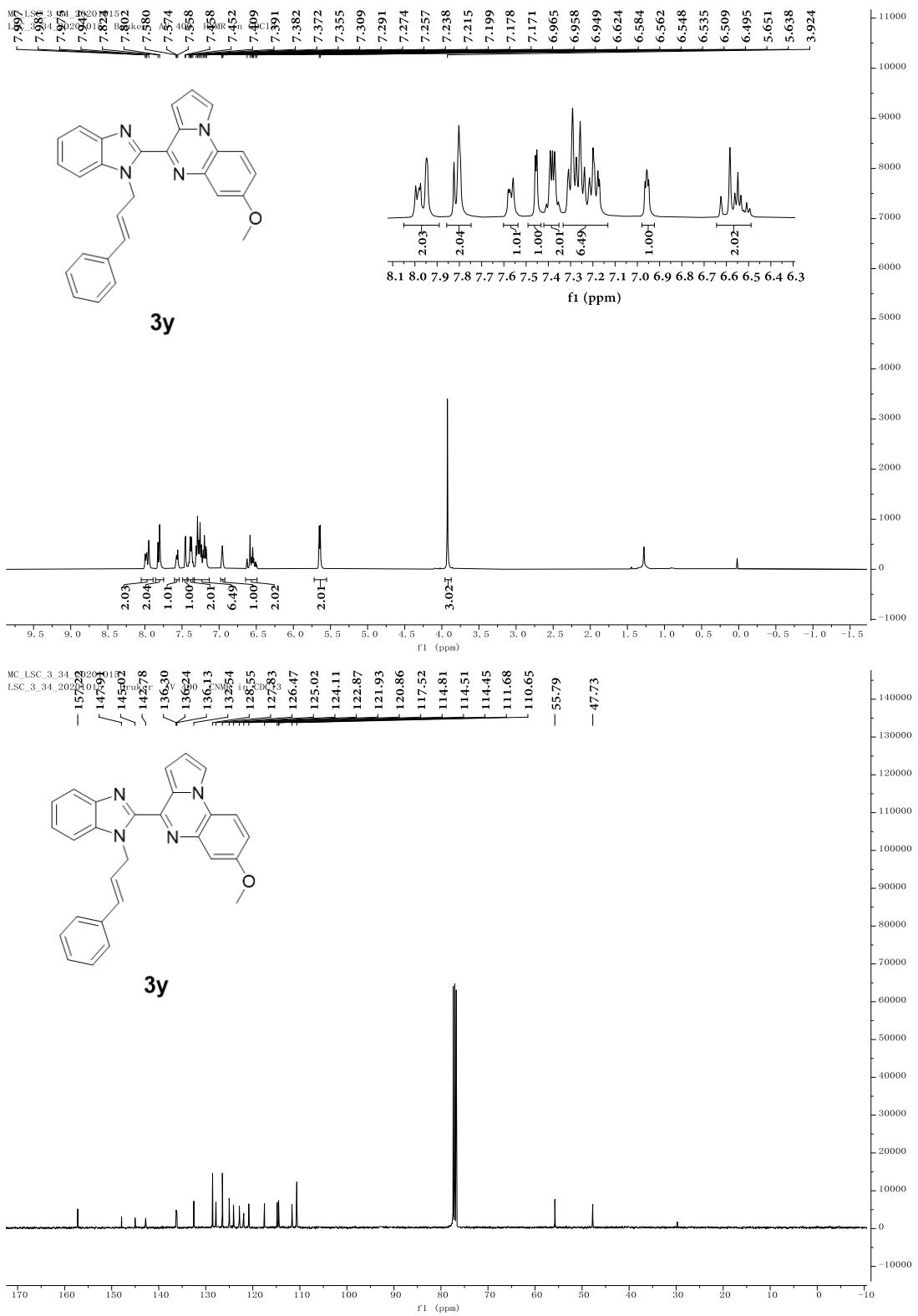


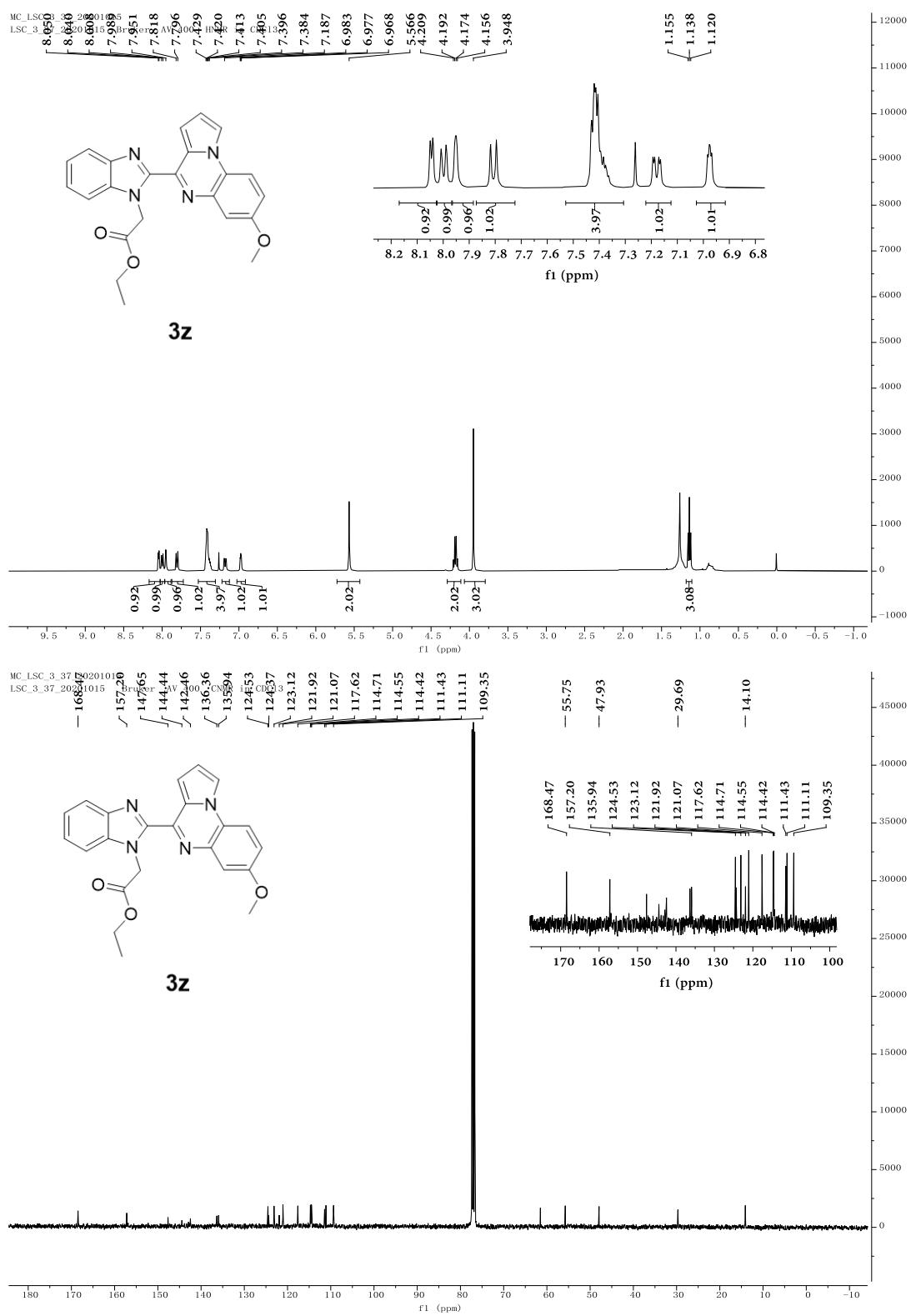


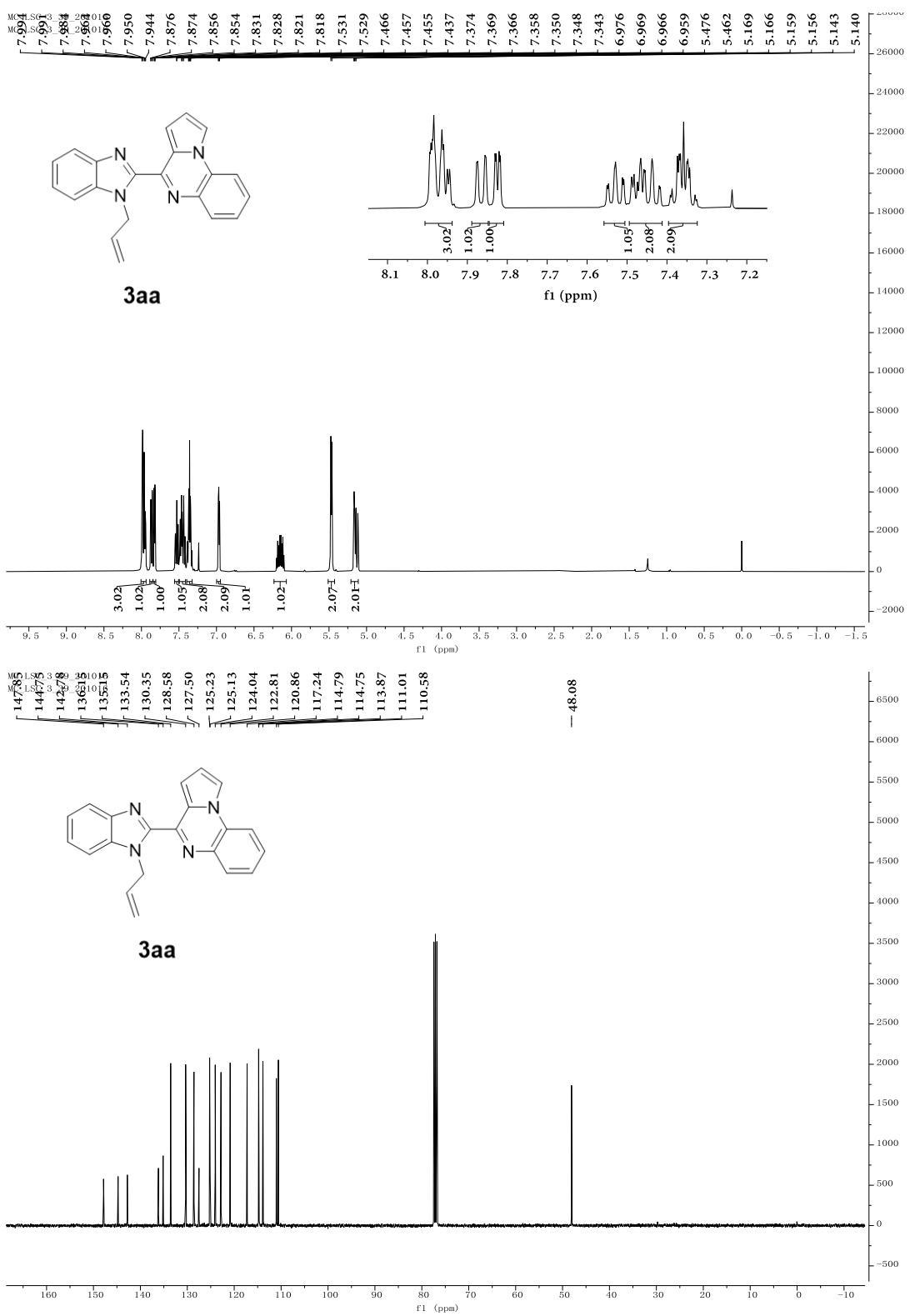


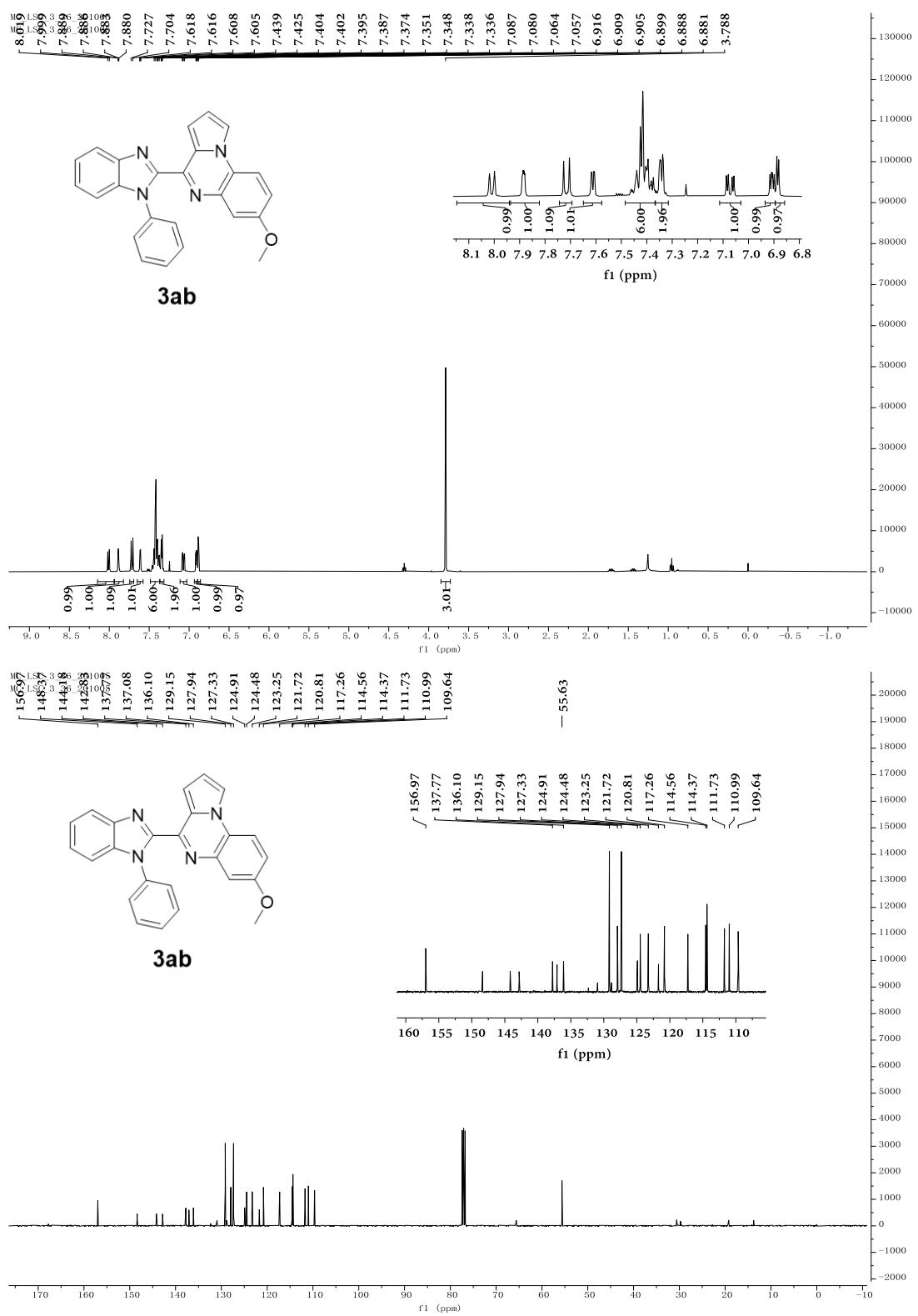


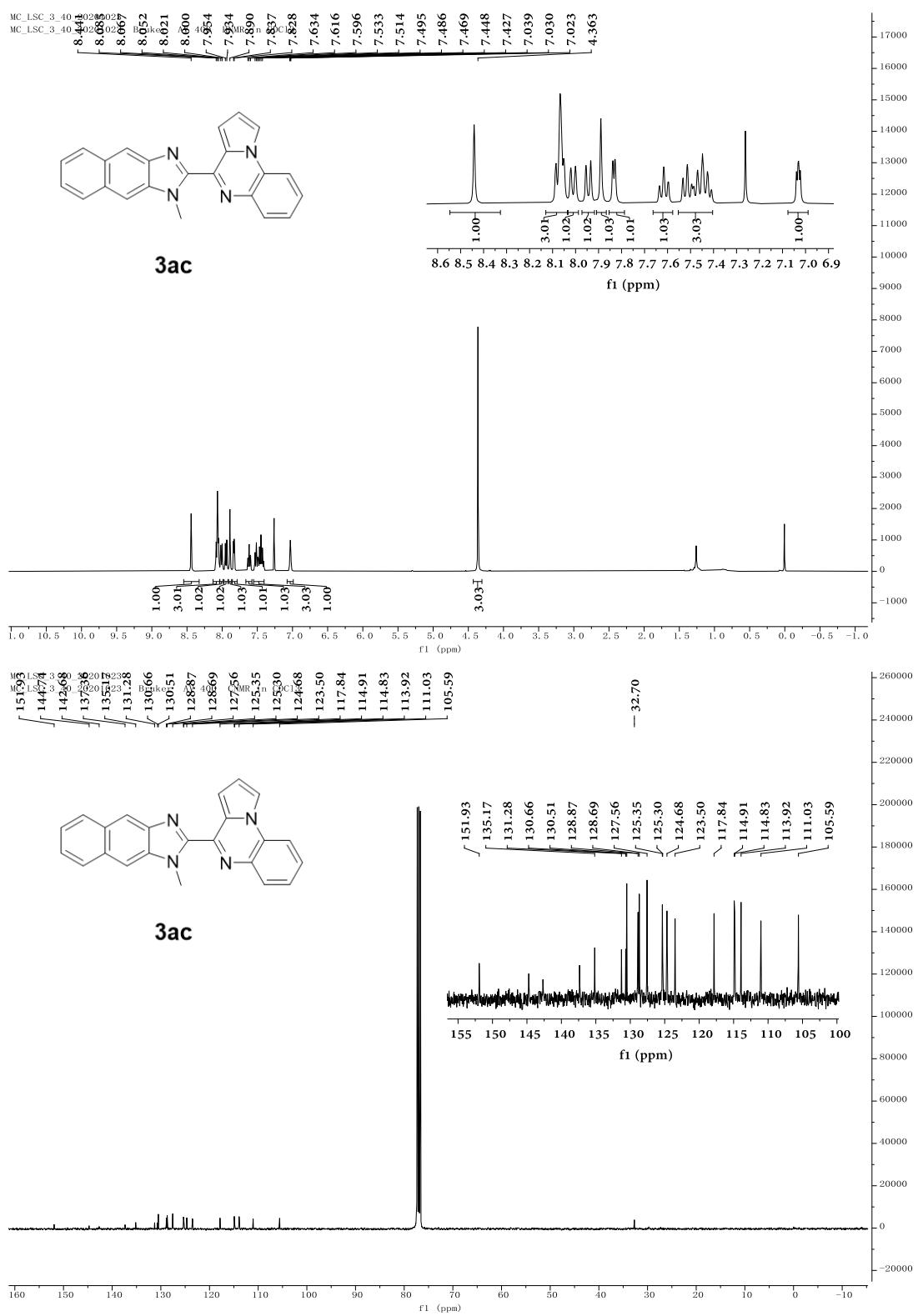


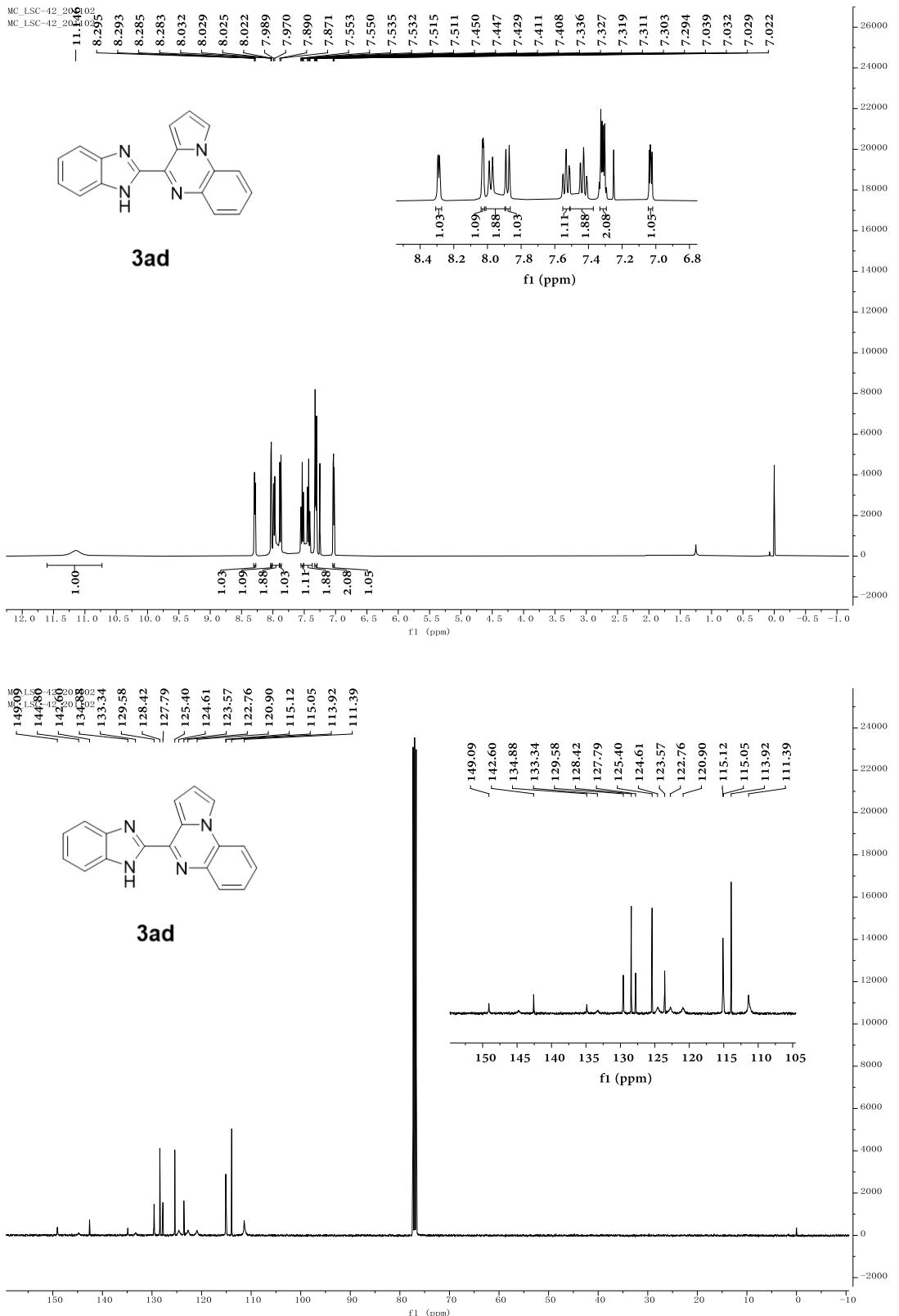












7. References

- [1] A. Carrér, J.-D. Brion, S. Messaoudi, M. Alami, *Org. Lett.* 2013, **15**, 5606-5609.
- [2] Z. Zhang, C. Xie, X. Tan, G. Song, L. Wen, H. Gao, C. Ma, *Org. Chem. Front.* 2015, **2**, 942-946.