

Supporting Information

Rhodium(III)-Catalyzed Annulation of 3-Arylquinazolinones with Alkynes via Double C–H Activation: An Efficient Route for Quinolino[2,1-*b*]quinazolinones

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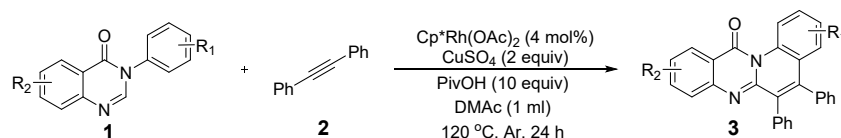
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I. General information

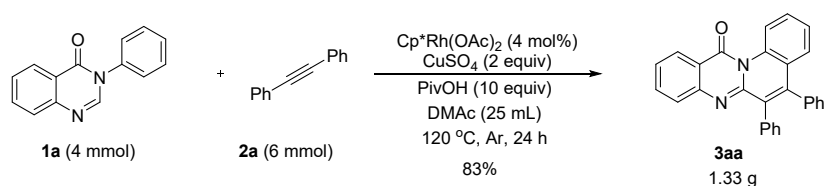
All reactions were carried out under Ar with no precaution in dried glassware unless otherwise noted. All materials were obtained from commercial suppliers and used without further purification. Silica gel-G plates (Merck) were used for TLC analysis with a mixture of hexane and ethyl acetate as the eluent. Column chromatography was performed with silica gel (200-300 mesh). Melting point of the products was measured on Büchi melting point apparatus, MPB-540. Open capillary tubes were used for the measurements and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Model Avance DMX 400 Spectrometer (^1H 400 MHz and ^{13}C 100 MHz, respectively). Chemical shifts (δ) are given in ppm and are referenced to residual solvent peaks. High resolution mass spectrometry (HRMS) spectra were obtained on a Waters Xevo G2-XS Qtof Instrument. X-Ray single-crystal diffraction data were collected on an Agilent Technologies Gemini single-crystal diffractometer. UV-vis spectra were recorded on Agilent spectrophotometer. Fluorescence spectra and absolute quantum yields were collected on a Horiba JobinYvon-Edison Fluoromax-Plus fluorescence spectrometer with a calibrated integrating sphere system. Quinazolinone¹ and alkyne² were prepared according to literatures.

II. General procedure for the synthesis of products 3



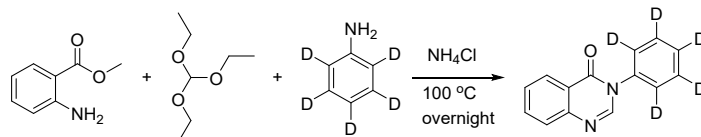
An oven-dried 10 ml schlenk tube with a magnetic stir bar was charged with quinazolinone **1** (0.2 mmol), alkynes **2** (0.3 mmol), $\text{Cp}^*\text{Rh}(\text{OAc})_2$ (4 mol%), CuSO_4 (2 equiv), PivOH (10 equiv) and DMAc (1 ml) under Ar. The tube was sealed with a teflon-coated cap and reaction solution was heated at $120\text{ }^\circ\text{C}$ for 24 h. The reaction was then quenched with saturated NaHCO_3 solution (10 ml) and extracted with EtOAc (3 X 10 ml), washed with brine and dried over anhydrous Na_2SO_4 . The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product **3**.

Gram-scale synthesis of 3aa



An oven-dried 100 ml schlenk flask with a magnetic stir bar was charged with quinazolinone **1** (4 mmol), alkynes **2** (6 mmol), $\text{Cp}^*\text{Rh}(\text{OAc})_2$ (4 mol%), CuSO_4 (2 equiv), PivOH (10 equiv) and DMAc (25 ml) under Ar. The flask was sealed with a rubber stopper and reaction solution was heated at $120\text{ }^\circ\text{C}$ for 24 h. The reaction was then quenched with saturated NaHCO_3 solution (100 ml) and extracted with EtOAc (3 X 50 ml), washed with brine and dried over anhydrous Na_2SO_4 . The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the product **3aa** in 83% yield.

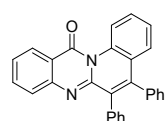
General procedure for the synthesis of products [D₅]-1a



A mixture of methyl 2-aminobenzoate (1.0 mmol), aniline D₅ (1.2 mmol), triethoxymethane (1.5 mmol), and NH₄Cl (0.4 mmol) was heated with stirring at 100 °C for 12h. After cooling, H₂O was added and the product was extracted with EtOAc. Then washed with brine and dried over anhydrous Na₂SO₄. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product in 83% yield.

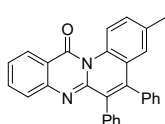
III. Analytical data of the synthesized derivatives

5,6-Diphenyl-12*H*-quinolino[2,1-*b*]quinazolin-12-one (3aa)



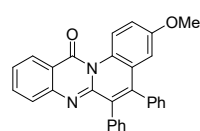
Yellow solid; 79 mg, yield 99%; mp 253-255 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.41 (d, *J* = 8.8 Hz, 1H), 8.43 (d, *J* = 8.0 Hz, 1H), 7.68 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.59-7.52 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.31-7.10 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 147.6, 146.5, 144.7, 136.7, 136.5, 134.8, 134.2, 131.1, 130.0, 128.7, 128.0, 127.6, 127.6, 127.5, 127.3, 127.2, 126.8, 126.1, 126.0, 125.6, 121.4, 119.7; IR (KBr): 2956, 2925, 2854, 1678, 1543, 1465, 1377, 789, 756, 690 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₈H₁₉N₂O: 399.1492, found: 399.1495.

3-Methyl-5,6-diphenyl-12*H*-quinolino[2,1-*b*]quinazolin-12-one (3ba)



Yellow solid; 80mg, yield 97%; mp 253-256 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.35 (d, *J* = 8.8 Hz, 1H), 8.43 (d, *J* = 8.0 Hz, 1H), 7.68 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.45 (ddd, *J* = 8.0, 7.2, 0.8 Hz, 1H), 7.39 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.28-7.25 (m, 3H), 7.21-7.10 (m, 7H), 7.08 (s, 1H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.3, 147.6, 146.5, 144.7, 136.8, 136.6, 135.8, 134.7, 134.1, 132.7, 131.1, 130.0, 129.7, 128.0, 127.5, 127.5, 127.4, 127.3, 127.1, 126.7, 126.0, 125.5, 121.3, 119.7, 21.1; IR (KBr): 2924, 1670, 1595, 1531, 1466, 1339, 1020, 814, 773, 694 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₉H₂₁N₂O: 413.1648, found: 413.1656.

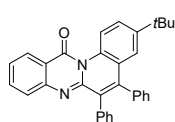
3-Methoxy-5,6-diphenyl-12*H*-quinolino[2,1-*b*]quinazolin-12-one (3ca)



Yellow solid; 79 mg, yield 92%; mp 240-244 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.47 (d, *J* = 9.6 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 7.69 (ddd, *J* = 8.0, 7.2, 0.8 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.27-7.24 (m, 3H), 7.22-7.10 (m, 8H), 6.77 (d, *J* = 3.2 Hz, 1H), 3.72 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.2, 156.9, 147.4, 146.4, 144.4, 136.8, 136.5, 135.3, 134.0, 131.0, 129.9, 128.8, 128.1, 127.6, 127.5, 127.3, 127.2, 127.1, 126.7, 126.0, 123.0, 119.6, 114.9, 111.3, 55.4; IR (KBr): 2957, 2854, 1666, 1537, 1462, 1377, 1026, 818, 768, 694 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₉H₂₁N₂O₂: 429.1598, found: 429.1589.

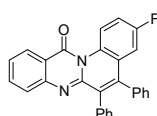
3-(*tert*-Butyl)-5,6-diphenyl-12*H*-quinolino[2,1-*b*]quinazolin-12-one (3da)

Yellow solid; 85 mg, yield 94%; mp 242-245 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.39 (d, *J* =



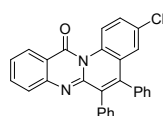
9.2 Hz, 1H), 8.44 (d, $J = 8.0$ Hz, 1H), 7.67 (ddd, $J = 8.0, 7.2, 0.8$ Hz, 1H), 7.62 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.54 (d, $J = 8.4$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 1H), 7.31-7.12 (m, 11H), 1.23 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.3, 148.9, 147.7, 146.5, 145.1, 136.9, 136.6, 134.5, 134.1, 132.6, 131.1, 130.0, 127.9, 127.6, 127.5, 127.3, 127.1, 126.7, 126.2, 125.9, 125.3, 124.1, 121.1, 119.7, 34.6, 31.1; IR (KBr): 2955, 1680, 1537, 1468, 1258, 829, 768, 696 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{27}\text{N}_2\text{O}$: 455.2118, found: 455.2123.

2-Fluoro-5,6-diphenyl-12H-quinolino[2,1-b]quinazolin-12-one (3ea)



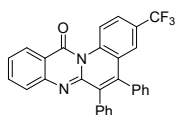
Yellow solid; 75 mg, yield 90%; mp 272-274 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.50 (dd, $J = 9.6, 5.2$ Hz, 1H), 8.42 (d, $J = 8.0$ Hz, 1H), 7.69 (t, $J = 7.2$ Hz, 1H), 7.55 (d, $J = 8.0$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 1H), 7.30-7.10 (m, 11H), 6.97 (dd, $J = 9.6, 2.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.2, 159.7 (d, $^1J = 246.8$ Hz), 147.2, 146.3, 143.8 (d, $^4J = 2.5$ Hz), 136.4, 136.1, 136.0, 134.3, 131.1 (d, $^4J = 2.0$ Hz), 130.9, 129.9, 128.3, 127.9, 127.8 (d, $^3J = 8.0$ Hz), 127.6, 127.3, 127.1, 126.9, 126.3, 123.6 (d, $^3J = 7.8$ Hz), 119.6, 115.8 (d, $^2J = 22.6$ Hz), 113.1 (d, $^2J = 24.3$ Hz); IR (KBr): 3055, 1676, 1610, 1545, 1469, 1279, 816, 764, 692 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{18}\text{FN}_2\text{O}$: 417.1398, found: 417.1389.

3-Chloro-5,6-diphenyl-12H-quinolino[2,1-b]quinazolin-12-one (3fa)



Yellow solid; 60 mg, yield 70%; mp 254-256 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.44 (d, $J = 9.6$ Hz, 1H), 8.42 (dd, $J = 8.0, 0.4$ Hz, 1H), 7.70 (ddd, $J = 8.0, 6.8, 1.2$ Hz, 1H), 7.55 (d, $J = 8.0$ Hz, 1H), 7.51 (dd, $J = 9.6, 2.4$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.30-7.25 (m, 4H), 7.23-7.16 (m, 3H), 7.16-7.09 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.2, 147.2, 146.3, 143.6, 136.3, 136.1, 135.8, 134.4, 133.2, 131.5, 130.9, 129.9, 128.5, 128.3, 127.9, 127.6, 127.3, 127.3, 127.1, 126.9, 126.8, 126.4, 122.9, 119.6; IR (KBr): 2924, 1680, 1537, 1468, 1342, 1207, 953, 820, 766, 692 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{18}\text{ClN}_2\text{O}$: 433.1102, found: 433.1111.

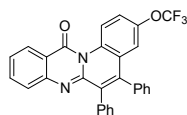
5,6-Diphenyl-3-(trifluoromethyl)-12H-quinolino[2,1-b]quinazolin-12-one (3ga)



Yellow solid; 92 mg, yield 99%; mp 182-186 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.55 (d, $J = 9.2$ Hz, 1H), 8.42 (d, $J = 8.0$ Hz, 1H), 7.78 (d, $J = 8.8$ Hz, 1H), 7.71 (t, $J = 7.6$ Hz, 1H), 7.58-7.53 (m, 2H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.33-7.26 (m, 3H), 7.24-7.18 (m, 3H), 7.17-7.10 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.3, 147.2, 146.3, 143.7, 136.9, 136.3, 136.1, 135.5, 134.6, 130.9, 129.9, 128.4, 128.1, 127.9 (q, $^2J = 33.4$ Hz), 127.7, 127.4, 127.2, 127.0, 126.6, 125.8, 125.0 (q, $^3J = 3.3$ Hz), 124.4 (q, $^3J = 3.9$ Hz), 123.6 (q, $^1J = 272.1$ Hz), 121.9, 119.7; IR (KBr): 2926, 1682, 1545, 1468, 1331, 1182, 1124, 1097, 766, 698 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{18}\text{F}_3\text{N}_2\text{O}$: 467.1366, found: 467.1356.

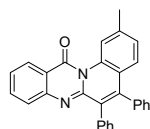
5,6-Diphenyl-3-(trifluoromethoxy)-12H-quinolino[2,1-b]quinazolin-12-one (3ha)

Yellow solid; 48 mg, yield 50%; mp 197-199 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.53 (d, $J = 9.6$ Hz, 1H), 8.41 (dd, $J = 8.0, 0.8$ Hz, 1H), 7.69 (ddd, $J = 8.4, 6.8, 1.6$ Hz, 1H), 7.55 (d, $J = 8.0$ Hz,



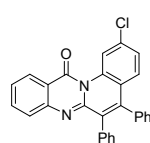
1H), 7.45 (ddd, $J = 8.0, 7.2, 0.8$ Hz, 1H), 7.41 (dd, $J = 9.6, 1.6$ Hz, 1H), 7.32-7.26 (m, 3H), 7.24-7.18 (m, 3H), 7.17-7.09 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.2, 147.2, 146.3, 146.3, 143.6, 136.3, 136.3, 135.7, 134.5, 133.0, 130.9, 129.9, 128.3, 128.0, 127.6, 127.4, 127.4, 127.2, 127.0, 126.5, 123.2, 120.7, 120.4 (q, $^1J = 256.5$ Hz), 119.6, 119.1; IR (KBr): 3063, 1682, 1609, 1542, 1468, 1248, 1169, 1065, 775, 698 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{18}\text{F}_3\text{N}_2\text{O}_2$: 483.1315, found: 483.1317.

2-Methyl-5,6-diphenyl-12H-quinolino[2,1-b]quinazolin-12-one (3ia)



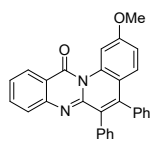
Yellow solid; 68 mg, yield 82%; mp 260-263 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.26 (s, 1H), 8.42 (d, $J = 7.6$ Hz, 1H), 7.68 (ddd, $J = 8.0, 6.8, 1.2$ Hz, 1H), 7.53 (d, $J = 8.0$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 1H), 7.28-7.23 (m, 3H), 7.21-7.09 (m, 9H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.5, 147.8, 146.5, 144.7, 139.2, 136.8, 136.7, 134.8, 134.2, 133.7, 131.1, 130.0, 128.0, 127.5, 127.4, 127.2, 127.1, 127.0, 126.7, 125.9, 123.3, 121.7, 119.7, 22.2; IR (KBr): 3057, 1676, 1606, 1547, 1470, 1290, 816, 766, 694 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{21}\text{N}_2\text{O}$: 413.1648, found: 413.1656.

2-Chloro-5,6-diphenyl-12H-quinolino[2,1-b]quinazolin-12-one (3ja)



Yellow solid; 69 mg, yield 80%; mp 243-246 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.58 (d, $J = 1.2$ Hz, 1H), 8.42 (d, $J = 7.6$ Hz, 1H), 7.69 (t, $J = 7.2$ Hz, 1H), 7.54 (d, $J = 8.4$ Hz, 1H), 7.46 (t, $J = 7.2$ Hz, 1H), 7.30-7.08 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.2, 147.3, 146.3, 143.9, 136.4, 136.1, 135.3, 135.0, 134.9, 134.5, 131.0, 129.9, 128.5, 128.2, 127.8, 127.6, 127.3, 127.2, 126.9, 126.4, 126.3, 124.1, 121.5, 119.6; IR (KBr): 3057, 1676, 1539, 1468, 1344, 872, 770, 694 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{18}\text{ClN}_2\text{O}$: 433.1102, found: 433.1111.

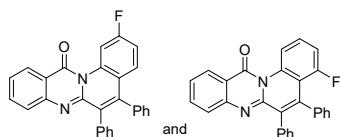
2-Methoxy-5,6-diphenyl-12H-quinolino[2,1-b]quinazolin-12-one (3ka) and 4-methoxy-5,6-diphenyl-12H-quinolino[2,1-b]quinazolin-12-one (3ka') (17:3)



Yellow solid; 80 mg, yield 93%; mp 204-209 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.16 (s, 0.85H), 8.81 (d, $J = 8.4$ Hz, 0.15H), 8.51-8.33 (m, 1H), 7.68 (t, $J = 7.4$ Hz, 1H), 7.55-7.48 (m, 1H), 7.43 (t, $J = 7.2$ Hz, 1H), 7.26-7.00 (m, 10.7H), 6.98 (d, $J = 6.8$ Hz, 0.3H), 6.91 (d, $J = 8.0$ Hz, 0.85H), 6.84 (d, $J = 8.0$ Hz, 0.15H), 3.96 (s, 2.55H), 3.29 (s, 0.45H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.7, 159.8, 148.0, 146.5, 144.7, 136.9, 136.8, 136.3, 134.2, 132.1, 131.3, 131.1, 130.0, 129.0, 128.7, 128.3, 128.0, 127.9, 127.5, 127.4, 127.2, 127.1, 127.1, 126.7, 126.6, 126.4, 125.8, 119.5, 119.3, 114.0, 109.8, 105.9, 56.0, 55.8; IR (KBr): 3055, 1684, 1600, 1543, 1470, 1277, 1069, 760, 696 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{21}\text{N}_2\text{O}_2$: 429.1598, found: 429.1589.

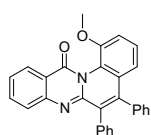
2-Fluoro-5,6-diphenyl-12H-quinolino[2,1-b]quinazolin-12-one (3la) and 4-fluoro-5,6-diphenyl-12H-quinolino[2,1-b]quinazolin-12-one (3la') (6:4)

Yellow solid; 68 mg, yield 80%; mp 235-240 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.35 (d, $J = 12.4$



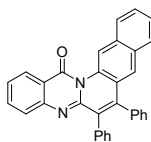
Hz, 0.4H), 9.07 (d, $J = 8.4$ Hz, 0.6H), 8.41 (t, $J = 8.4$ Hz, 1H), 7.75-7.64 (m, 1H), 7.57-7.42 (m, 2.6H), 7.28-7.24 (m, 1.4H), 7.22-6.98 (m, 10H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.3, 163.2, 162.1 (d, $^1J = 251.2$ Hz), 159.1 (d, $^1J = 255.2$ Hz), 147.5, 147.1, 146.4, 146.3, 146.1, 144.1, 140.3 (d, $^4J = 1.0$ Hz) 138.7 (d, $^3J = 4.2$ Hz), 136.7, 136.5, 136.4, 135.9, 135.8, 135.6 (d, $^3J = 2.7$ Hz) 134.5, 134.0, 131.0, 130.9, 129.9, 129.2, 129.1, 129.0, 128.6 (d, $^3J = 4.0$ Hz), 128.2, 127.6 (d, $^2J = 21.2$ Hz), 127.5, 127.4, 127.3, 127.2 (d, $^3J = 3.4$ Hz), 127.1, 126.9 (d, $^2J = 23.5$ Hz), 126.8, 126.4, 126.3, 122.2 (d, $^4J = 2.3$ Hz), 119.7, 119.4, 117.2 (d, $^3J = 3.9$ Hz), 115.0, 114.9, 113.8 (d, $^2J = 22.8$ Hz), 113.7 (d, $^2J = 22.1$ Hz), 109.2, 109.0; IR (KBr): 3057, 1682, 1597, 1547, 1458, 1267, 908, 760, 694 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{18}\text{FN}_2\text{O}$: 417.1398, found: 417.1389.

1-Methoxy-5,6-diphenyl-12H-quinolino[2,1-b]quinazolin-12-one (3ma)



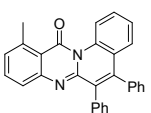
Yellow solid; 61 mg, yield 71%; mp 274-276 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.30 (dd, $J = 7.6, 0.8$ Hz, 1H), 7.66 (ddd, $J = 8.0, 6.8, 1.2$ Hz, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.42 (ddd, $J = 8.0, 7.2, 0.8$ Hz, 1H), 7.35-6.94 (m, 12H), 6.83 (dd, $J = 8.0, 0.8$ Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.7, 151.8, 148.3, 147.0, 144.1, 136.4, 135.8, 134.8, 133.6, 131.1, 129.7, 128.5, 128.0, 127.6, 127.3, 127.3, 126.9, 126.6, 126.4, 125.8, 122.8, 120.1, 119.1, 113.0, 56.4; IR (KBr): 3013, 1699, 1537, 1466, 1263, 1119, 891, 777, 704 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{21}\text{N}_2\text{O}_2$: 429.1598, found: 429.1589.

6,7-Diphenyl-15H-benzo[6,7]quinolino[2,1-b]quinazolin-15-one (3na)



Yellow solid; 60 mg, yield 67%; mp 271-273 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.98 (s, 1H), 8.45 (d, $J = 8.0$ Hz, 1H), 7.99 (d, $J = 8.4$ Hz, 1H), 7.71 (s, 1H), 7.68-7.62 (m, 2H), 7.55-7.48 (m, 2H), 7.46-7.42 (m, 2H), 7.33-7.26 (m, 3H), 7.23-7.16 (m, 7H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.5, 147.7, 146.1, 144.7, 136.9, 136.7, 134.5, 134.2, 132.7, 131.7, 131.1, 130.6, 130.2, 128.6, 128.1, 127.8, 127.7, 127.6, 127.4, 127.4, 127.3, 127.2, 126.7, 126.6, 126.5, 125.1, 120.3, 120.1; IR (KBr): 3053, 1676, 1602, 1547, 1472, 1337, 1200, 887, 770, 696 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{21}\text{N}_2\text{O}$: 449.1648, found: 449.1644.

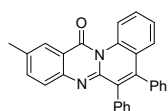
11-Methyl-5,6-diphenyl-12H-quinolino[2,1-b]quinazolin-12-one (3oa)



Yellow solid; 78 mg, yield 94%; mp 239-242 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.10 (d, $J = 8.8$ Hz, 1H), 7.53-7.46 (m, 2H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.27-7.10 (m, 13H), 2.97 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.9, 148.1, 147.3, 144.4, 140.8, 136.6, 136.5, 134.5, 134.4, 133.4, 131.1, 130.1, 128.6, 128.4, 128.0, 127.6, 127.6, 127.3, 126.8, 125.7, 125.6, 125.6, 120.9, 118.5, 23.2; IR (KBr): 3051, 1686, 1545, 1447, 1304, 1022, 748, 689, 581 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{21}\text{N}_2\text{O}$: 413.1648, found: 413.1656.

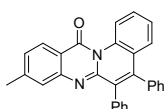
10-Methyl-5,6-diphenyl-12H-quinolino[2,1-b]quinazolin-12-one (3pa)

Yellow solid; 74 mg, yield 89%; mp 236-238 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.41 (d, $J = 8.8$



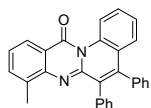
Hz, 1H), 8.21 (s, 1H), 7.56-7.43 (m, 3H), 7.29-7.09 (m, 12H), 2.49 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 147.0, 144.5, 144.1, 136.8, 136.6, 136.3, 135.9, 134.8, 134.8, 131.1, 130.1, 128.5, 128.0, 127.5, 127.4, 127.3, 126.7, 126.4, 125.9, 125.6, 121.4, 119.5, 21.5; IR (KBr): 3051, 1686, 1545, 1445, 1304, 1020, 748, 690, 581 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₉H₂₁N₂O: 413.1648, found: 413.1656.

9-Methyl-5,6-diphenyl-12H-quinolino[2,1-b]quinazolin-12-one (3qa)



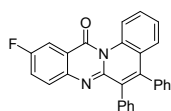
Yellow solid; 73 mg, yield 88%; mp 256-259 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.43 (d, *J* = 8.8 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.59-7.51 (m, 1H), 7.34 (s, 1H), 7.29-7.10 (m, 13H), 2.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.3, 147.8, 146.5, 145.3, 144.5, 136.8, 136.6, 134.9, 134.8, 131.0, 130.0, 128.6, 128.0, 127.9, 127.6, 127.6, 127.3, 127.0, 127.0, 126.7, 125.8, 125.6, 121.4, 117.4, 21.8; IR (KBr): 3059, 1674, 1614, 1543, 1445, 1352, 1032, 758, 698, 582 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₉H₂₁N₂O: 413.1648, found: 413.1656.

8-Methyl-5,6-diphenyl-12H-quinolino[2,1-b]quinazolin-12-one (3ra)



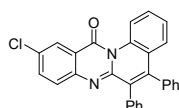
Yellow solid; 58 mg, yield 70%; mp 207-209 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.46 (d, *J* = 8.8 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.58-7.52 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.31-7.24 (m, 5H), 7.21-7.13 (m, 7H), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 146.5, 145.0, 143.9, 136.8, 136.6, 136.0, 135.1, 134.8, 134.6, 131.1, 130.2, 128.6, 128.1, 127.6, 127.0, 126.6, 125.9, 125.8, 125.7, 124.7, 121.4, 119.6, 16.7; IR (KBr): 3065, 1678, 1543, 1443, 1340, 1055, 772, 694, 582 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₉H₂₁N₂O: 413.1648, found: 413.1656.

10-Fluoro-5,6-diphenyl-12H-quinolino[2,1-b]quinazolin-12-one (3sa)

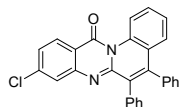


Yellow solid; 73 mg, yield 87%; mp 252-255 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.43 (d, *J* = 8.8 Hz, 1H), 8.06 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.62-7.53 (m, 2H), 7.42 (td, *J* = 8.4, 2.8 Hz, 1H), 7.36-7.31 (m, 2H), 7.28-7.25 (m, 3H), 7.23-7.09 (m, 7H); ¹³C NMR (100 MHz, CDCl₃) δ 162.7 (d, ⁴*J* = 3.7 Hz), 160.5 (d, ¹*J* = 246.3 Hz), 147.1, 144.6, 143.2, 136.5, 136.4, 134.6, 134.5, 131.0, 130.0, 129.9 (d, ³*J* = 6.3 Hz), 128.7, 128.1, 127.4, 127.6 (d, ⁴*J* = 4.1 Hz), 127.3, 126.8, 126.2, 125.7, 123.2 (d, ²*J* = 24.4 Hz), 121.4, 120.6 (d, ³*J* = 8.9 Hz), 111.6 (d, ²*J* = 23.7 Hz); IR (KBr): 3055, 1678, 1545, 1479, 1362, 1248, 760, 698 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₈H₁₈FN₂O: 417.1389, found: 417.1389.

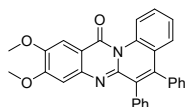
10-Chloro-5,6-diphenyl-12H-quinolino[2,1-b]quinazolin-12-one (3ta)



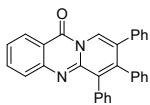
Yellow solid; 73 mg, yield 84%; mp 254-257 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.40 (d, *J* = 8.8 Hz, 1H), 8.36 (d, *J* = 2.4 Hz, 1H), 7.60-7.54 (m, 2H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.32-7.23 (m, 5H), 7.21-7.09 (m, 7H); ¹³C NMR (100 MHz, CDCl₃) δ 162.3, 147.8, 145.1, 144.9, 136.5, 136.4, 134.7, 134.6, 134.6, 131.6, 131.0, 130.0, 129.2, 128.8, 128.1, 127.7, 127.7, 127.3, 126.8, 126.4, 126.2, 125.6, 121.4, 120.5; IR (KBr): 3072, 1678, 1535, 1466, 1281, 1063, 827, 754, 698, 579 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₈H₁₈ClN₂O: 433.1102, found: 433.1111.

9-Chloro-5,6-diphenyl-12H-quinolino[2,1-b]quinazolin-12-one (3ua)

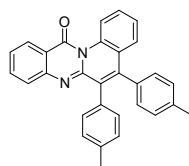
Yellow solid; 65 mg, yield 75%; mp 242-244 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.40 (d, *J* = 8.8 Hz, 1H), 8.32 (d, *J* = 8.8 Hz, 1H), 7.61-7.49 (m, 2H), 7.37-7.30 (m, 3H), 7.27-7.09 (m, 10H); ¹³C NMR (100 MHz, CDCl₃) δ 162.7, 148.7, 147.3, 145.4, 140.5, 136.4, 136.3, 134.6, 131.0, 130.0, 128.9, 128.7, 128.1, 127.8, 127.7, 127.4, 126.9, 126.7, 126.6, 126.2, 125.5, 121.4, 118.0; IR (KBr): 3059, 1680, 1595, 1539, 1454, 1252, 1072, 775, 698 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₈H₁₈ClN₂O: 433.1102, found: 433.1111.

9,10-Dimethoxy-5,6-diphenyl-12H-quinolino[2,1-b]quinazolin-12-one (3va)

Yellow solid; 53 mg, yield 57%; mp 272-274 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.53 (d, *J* = 8.8 Hz, 1H), 7.77 (s, 1H), 7.58 (s, 1H), 7.36-7.26 (m, 4H), 7.25-7.09 (m, 8H), 6.93 (s, 1H), 4.06 (s, 3H), 3.94 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.6, 155.3, 149.0, 146.8, 143.8, 143.1, 136.9, 136.6, 134.8, 134.6, 131.0, 130.1, 128.4, 128.0, 127.5, 127.3, 126.7, 125.8, 125.6, 121.5, 113.2, 107.7, 105.7, 56.4, 56.3; IR (KBr): 3057, 1666, 1499, 1404, 1302, 1238, 1030, 862, 772, 700 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₃₀H₂₃N₂O₃: 459.1703, found: 459.1703.

6,7,8-Triphenyl-11H-pyrido[2,1-b]quinazolin-11-one (3wa)

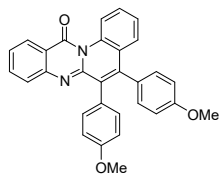
Yellow solid; 46 mg, yield 71%; mp 211-213 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.99 (s, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 7.2 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.25-7.18 (m, 8H), 7.14-7.08 (m, 2H), 7.04-6.97 (m, 3H), 6.85-6.79 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 159.3, 148.6, 146.9, 146.2, 137.0, 136.8, 136.2, 136.1, 134.6, 131.5, 130.4, 129.8, 128.4, 128.2, 128.0, 127.5, 127.4, 127.4, 127.1, 127.1, 127.1, 125.2, 125.0, 115.9; IR (KBr): 3059, 1682, 1530, 1449, 1346, 1306, 1173, 773, 698 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₃₀H₂₁N₂O: 425.1648, found: 425.1641.

5,6-Di-*p*-tolyl-12H-quinolino[2,1-b]quinazolin-12-one (3ab)

Yellow solid; 75 mg, yield 88%; mp 245-249 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.38 (d, *J* = 8.8 Hz, 1H), 8.42 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.67 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.58-7.50 (m, 2H), 7.43 (ddd, *J* = 8.0, 7.2, 0.8 Hz, 1H), 7.32-7.25 (m, 2H), 7.09-7.03 (m, 4H), 7.03-6.98 (m, 4H), 2.32 (s, 3H), 2.30 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 147.8, 146.5, 144.6, 137.1, 136.2, 134.7, 134.6, 134.1, 133.7, 133.6, 131.0, 129.9, 128.8, 128.4, 128.0, 127.6, 127.5, 127.1, 126.0, 125.9, 125.9, 121.3, 119.7, 21.3, 21.3; IR (KBr): 3022, 1678, 1537, 1468, 1342, 1055, 822, 770 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₃₀H₂₃N₂O: 427.1805, found: 427.1803.

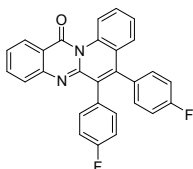
5,6-Bis(4-methoxyphenyl)-12H-quinolino[2,1-b]quinazolin-12-one (3ac)

Yellow solid; 80 mg, yield 87%; mp 205-209 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.37 (d, *J* = 8.8 Hz, 1H), 8.41 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.67 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.58-7.49 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.34 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.8 Hz,



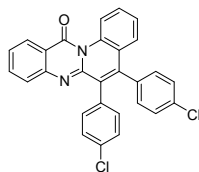
2H), 7.02 (d, $J = 8.4$ Hz, 2H), 6.81 (d, $J = 8.8$ Hz, 2H), 6.75 (d, $J = 8.8$ Hz, 2H), 3.78 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.4, 158.8, 158.2, 147.8, 146.5, 144.4, 134.7, 134.5, 134.2, 132.3, 131.3, 129.1, 128.9, 128.4, 127.6, 127.5, 127.1, 126.0, 125.9, 121.3, 119.7, 113.6, 112.8, 55.2, 55.1; IR (KBr): 2835, 1686, 1607, 1541, 1466, 1286, 1246, 1175, 1030, 830, 758 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{23}\text{N}_2\text{O}_3$: 459.1703, found: 459.1703.

5,6-Bis(4-fluorophenyl)-12H-quinolino[2,1-b]quinazolin-12-one (3ad)



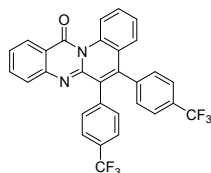
Yellow solid; 61 mg, yield 70%; mp 254-257 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.41 (d, $J = 8.8$ Hz, 1H), 8.42 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.70 (ddd, $J = 8.4, 7.2, 1.2$ Hz, 1H), 7.60-7.52 (m, 2H), 7.46 (ddd, $J = 8.0, 7.2, 0.8$ Hz, 1H), 7.32 (ddd, $J = 8.0, 7.2, 0.8$ Hz, 1H), 7.27 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.12-7.06 (m, 4H), 7.02-6.97 (m, 2H), 6.95-6.89 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.2, 162.1 (d, $^1J = 246.5$ Hz), 161.7 (d, $^1J = 244.6$ Hz), 147.4, 146.3, 143.9, 134.8, 134.4, 134.2, 132.7 (d, $^3J = 8.0$ Hz), 132.4 (d, $^4J = 3.5$ Hz), 132.3 (d, $^4J = 3.6$ Hz), 131.8 (d, $^3J = 8.1$ Hz), 128.9, 127.4, 127.2, 126.3, 126.0, 125.3, 121.5, 119.8, 115.4 (d, $^2J = 21.5$ Hz), 114.5 (d, $^2J = 21.4$ Hz); IR (KBr): 3044, 1680, 1543, 1229, 1155, 1057, 835, 546, 478 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{17}\text{N}_2\text{F}_2\text{O}$: 435.1303, found: 435.1306.

5,6-Bis(4-chlorophenyl)-12H-quinolino[2,1-b]quinazolin-12-one (3ae)



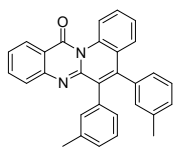
Yellow solid; 83 mg, yield 89%; mp 229-231 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.41 (d, $J = 8.8$ Hz, 1H), 8.42 (d, $J = 8.8$ Hz, 1H), 7.71 (t, $J = 7.6$ Hz, 1H), 7.61-7.51 (m, 2H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.34-7.28 (m, 3H), 7.24-7.14 (m, 3H), 7.11-7.03 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.2, 147.1, 146.2, 143.6, 134.9, 134.8, 134.7, 134.4, 134.0, 133.9, 133.0, 132.4, 131.3, 129.1, 128.7, 127.8, 127.4, 127.4, 127.2, 126.4, 126.1, 125.0, 121.5, 119.8; IR (KBr): 3063, 1680, 1543, 1468, 1344, 1088, 1013, 820, 764, 527 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{17}\text{Cl}_2\text{N}_2\text{O}$: 467.0712, found: 467.0716.

5,6-Bis(4-(trifluoromethyl)phenyl)-12H-quinolino[2,1-b]quinazolin-12-one (3af)



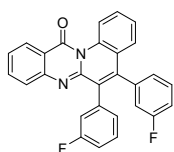
Yellow solid; 105 mg, yield 98%; mp 247-250 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.45 (d, $J = 8.8$ Hz, 1H), 8.41 (dd, $J = 8.0, 0.8$ Hz, 1H), 7.69 (ddd, $J = 8.4, 6.8, 1.6$ Hz, 1H), 7.61-7.56 (m, 3H), 7.52-7.43 (m, 4H), 7.32 (t, $J = 7.6$ Hz, 1H), 7.29-7.25 (m, 4H), 7.17 (dd, $J = 8.0, 1.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.1, 146.8, 146.1, 143.4, 140.0, 139.8, 135.0, 134.5, 133.9, 131.3, 130.4 (q, $^3J = 7.4$ Hz), 130.3 (q, $^2J = 32.4$ Hz), 129.4 (q, $^3J = 6.2$ Hz), 129.3 (q, $^2J = 32.3$ Hz), 127.4, 127.3, 127.2, 126.6, 126.2, 125.3 (q, $^4J = 3.6$ Hz), 124.6, 124.5 (q, $^4J = 3.7$ Hz), 124.2 (q, $^1J = 270.4$ Hz), 123.8 (q, $^1J = 270.7$ Hz), 121.6, 119.8; IR (KBr): 3073, 1680, 1543, 1323, 1173, 1064, 1015, 837, 752, 636 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{17}\text{F}_6\text{N}_2\text{O}$: 535.1240, found: 535.1245.

5,6-Di-*m*-tolyl-12H-quinolino[2,1-b]quinazolin-12-one (3ag)



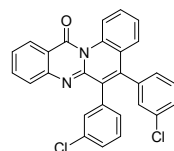
Yellow solid; 52 mg, yield 61%; mp 232-234 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.40 (d, $J = 8.8$ Hz, 1H), 8.43 (d, $J = 7.6$ Hz, 1H), 7.68 (ddd, $J = 8.0, 7.2, 0.8$ Hz, 1H), 7.60-7.51 (m, 2H), 7.44 (t, $J = 7.6$ Hz, 1H), 7.35-7.27 (m, 2H), 7.17-7.07 (m, 2H), 7.03 (d, $J = 7.6$ Hz, 1H), 7.00-6.87 (m, 5H), 2.26 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.4, 147.7, 146.5, 144.8, 137.5, 136.5, 136.5, 136.5, 134.7, 134.7, 134.2, 131.8, 130.7, 128.5, 128.2, 128.2, 127.8, 127.7, 127.5, 127.5, 127.1, 127.1, 127.0, 126.0, 125.9, 125.7, 121.3, 119.7, 21.4, 21.4; IR (KBr): 2914, 1678, 1541, 1468, 1344, 764, 692 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{23}\text{N}_2\text{O}$: 427.1805, found: 427.1803.

5,6-Bis(3-fluorophenyl)-12H-quinolino[2,1-b]quinazolin-12-one (3ah)



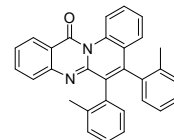
Yellow solid; 50 mg, yield 57%; mp 246-249 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.44 (d, $J = 8.4$ Hz, 1H), 8.44 (dd, $J = 8.0, 0.8$ Hz, 1H), 7.72 (ddd, $J = 8.4, 6.8, 1.2$ Hz, 1H), 7.63-7.54 (m, 2H), 7.49 (ddd, $J = 8.0, 7.2, 0.8$ Hz, 1H), 7.35 (ddd, $J = 8.0, 7.2, 0.8$ Hz, 1H), 7.31-7.26 (m, 2H), 7.22-7.15 (m, 1H), 6.99 (td, $J = 8.4, 2.0$ Hz, 1H), 6.95-6.84 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.4, 162.5 (d, $^1J = 246.3$ Hz), 162.1 (d, $^1J = 243.5$ Hz), 147.0, 146.2, 143.4 (d, $^4J = 1.7$ Hz), 138.4 (d, $^3J = 8.3$ Hz), 138.3 (d, $^3J = 7.8$ Hz), 134.9, 134.4, 133.8 (d, $^4J = 1.7$ Hz), 129.9 (d, $^3J = 8.5$ Hz), 129.2, 128.9 (d, $^3J = 8.4$ Hz), 127.5, 127.4, 127.2, 126.6 (d, $^4J = 2.9$ Hz), 126.4, 126.1, 125.8 (d, $^4J = 3.0$ Hz), 124.8, 121.5, 119.8, 118.1 (d, $^2J = 22.1$ Hz), 117.0 (d, $^2J = 22.2$ Hz), 114.9 (d, $^2J = 21.0$ Hz), 114.1 (d, $^2J = 21.0$ Hz); IR (KBr): 3063, 1678, 1541, 1470, 1217, 1126, 793, 689 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{17}\text{F}_2\text{N}_2\text{O}$: 435.1303, found: 435.1306.

5,6-Bis(3-chlorophenyl)-12H-quinolino[2,1-b]quinazolin-12-one (3ai)



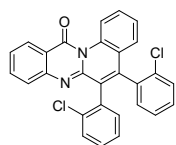
Yellow solid; 48 mg, yield 50%; mp 280-284 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.44 (d, $J = 8.8$ Hz, 1H), 8.45 (d, $J = 7.6$ Hz, 1H), 7.74 (t, $J = 7.2$ Hz, 1H), 7.65-7.55 (m, 2H), 7.50 (t, $J = 7.2$ Hz, 1H), 7.36 (t, $J = 7.6$ Hz, 1H), 7.28-7.23 (m, 3H), 7.22-7.13 (m, 4H), 7.02 (d, $J = 6.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.2, 147.0, 146.2, 143.4, 138.0, 137.8, 134.8, 134.4, 134.3, 133.7, 133.3, 131.0, 129.9, 129.6, 129.2, 129.1, 128.8, 128.2, 127.5, 127.4, 127.3, 127.2, 126.5, 126.2, 124.8, 121.5, 119.8; IR (KBr): 3059, 1678, 1541, 1470, 1346, 1076, 766 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{17}\text{Cl}_2\text{N}_2\text{O}$: 467.0712, found: 467.0716.

5,6-Di-*o*-tolyl-12H-quinolino[2,1-b]quinazolin-12-one (3aj) (2:1 mixture of rotomers)



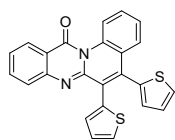
Yellow solid; 48 mg, yield 56%; mp 218-221 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.47 (t, $J = 7.6$ Hz, 1H), 8.46 (d, $J = 7.6$ Hz, 1H), 7.70 (t, $J = 7.2$ Hz, 1H), 7.62-7.44 (m, 3H), 7.36-7.29 (m, 1H), 7.20-6.83 (m, 9H), 2.24 (s, 2H), 2.19 (s, 2H), 2.09 (s, 1H), 1.97 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.5, 146.9, 146.9, 146.7, 144.7, 144.7, 137.2, 137.0, 137.0, 136.2, 135.9, 135.8, 135.8, 135.2, 134.9, 134.8, 134.7, 134.6, 134.3, 131.5, 131.0, 130.1, 129.9, 129.5, 129.2, 128.7, 128.7, 128.1, 128.0, 127.5, 127.3, 127.2, 127.2, 127.0, 126.3, 126.2, 126.1, 125.8, 125.4, 125.2, 125.1, 124.9, 124.6, 121.5, 121.4, 119.8, 119.7, 20.3, 20.3, 20.2, 19.8; IR (KBr): 3014, 1682, 1541, 1466, 1344, 1051, 758 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{23}\text{N}_2\text{O}$: 427.1805, found: 427.1803.

5,6-Bis(2-chlorophenyl)-12H-quinolino[2,1-b]quinazolin-12-one (3ak) (55:45 mixture of rotomers)



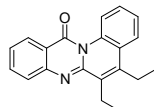
Yellow solid; 34 mg, yield 36%; mp 219-222 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.55 (d, *J* = 8.4 Hz, 0.45H), 9.47 (d, *J* = 8.8 Hz, 0.55H), 8.46 (d, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.64-7.52 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.42-7.31 (m, 2.55H), 7.25-7.04 (m, 7.45H); ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 147.5, 146.5, 146.4, 146.3, 142.8, 142.2, 136.4, 136.4, 135.7, 135.4, 135.1, 134.7, 134.3, 134.3, 134.2, 133.6, 133.4, 133.2, 131.7, 130.0, 129.9, 129.8, 129.4, 129.4, 129.2, 129.2, 128.9, 128.9, 128.7, 127.5, 127.2, 127.2, 127.2, 127.1, 126.9, 126.8, 126.7, 126.5, 126.3, 126.2, 126.2, 124.3, 124.0, 121.6, 121.5, 120.0, 119.9; IR (KBr): 3057, 1684, 1543, 1468, 1342, 1055, 756, 692 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₈H₁₇Cl₂N₂O: 467.0712, found: 467.0716.

5,6-Di(thiophen-2-yl)-12H-quinolino[2,1-b]quinazolin-12-one (3al)



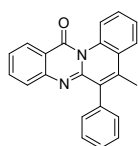
Yellow solid; 47 mg, yield 57%; mp 225-230 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.34 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 7.77-7.66 (m, 2H), 7.62-7.54 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.43-7.33 (m, 3H), 7.09-7.01 (m, 2H), 6.95-6.87 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 163.1, 146.7, 146.1, 139.0, 136.9, 136.5, 134.4, 130.1, 130.0, 129.8, 129.2, 127.7, 127.5, 127.4, 127.3, 127.2, 126.8, 126.5, 126.2, 125.7, 125.4, 121.2, 119.9; IR (KBr): 3069, 1684, 1543, 1468, 1340, 1221, 1045, 770, 692 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₄H₁₅N₂OS₂: 411.0620, found: 411.0627.

5,6-Diethyl-12H-quinolino[2,1-b]quinazolin-12-one (3am)



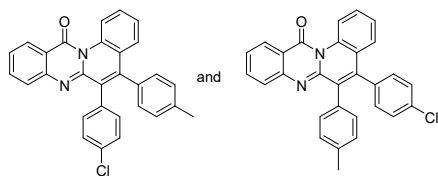
Yellow solid; 35 mg, yield 58%; mp 69-74 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.28 (d, *J* = 8.4 Hz, 1H), 8.40 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.78-7.72 (m, 2H), 7.53-7.42 (m, 3H), 3.12 (q, *J* = 7.2 Hz, 2H), 3.00 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.6, 146.9, 146.8, 142.6, 134.2, 134.2, 134.1, 127.4, 127.2, 127.0, 126.0, 125.5, 124.4, 123.8, 121.5, 119.7, 22.1, 21.6, 14.1, 14.0; IR (KBr): 2963, 1678, 1537, 1468, 1045, 762, 689 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₀H₁₉N₂O: 303.1492, found: 303.1486.

6-Methyl-5-phenyl-12H-quinolino[2,1-b]quinazolin-12-one (3an)



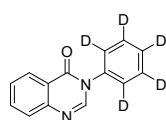
Yellow solid; 34 mg, yield 50%; mp 180-183 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.39 (d, *J* = 8.4 Hz, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.53-7.46 (m, 4H), 7.46-7.40 (m, 2H), 7.30 (d, *J* = 6.8 Hz, 2H), 2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.3, 147.7, 146.5, 139.2, 137.7, 134.7, 134.3, 134.2, 130.4, 128.5, 128.1, 127.4, 127.1, 126.2, 125.8, 125.5, 124.6, 121.4, 119.5, 17.5; IR (KBr): 3063, 1676, 1545, 1474, 1207, 905, 748, 694 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₃H₁₇N₂O: 337.1335, found: 337.1336.

6-(4-Chlorophenyl)-5-(p-tolyl)-12H-quinolino[2,1-b]quinazolin-12-one (3ao) and 5-(4-chlorophenyl)-6-(p-tolyl)-12H-quinolino[2,1-b]quinazolin-12-one (3ao') (1.74:1.26)



Yellow solid; 58 mg, yield 65%; mp 227-229 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.43-9.36 (m, 1H), 8.41 (dd, $J = 8.0, 0.8$ Hz, 1H), 7.71-7.65 (m, 1H), 7.59-7.50 (m, 2H), 7.44 (t, $J = 7.6$ Hz, 1H), 7.33-7.27 (m, 2H), 7.26-7.21 (m, 1H), 7.20-7.17 (m, 1H), 7.11-6.97 (m, 6H), 2.34 (s, 1.74H), 2.32 (s, 1.26H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.3, 163.3, 147.5, 147.4, 146.4, 146.4, 145.0, 143.2, 137.6, 136.6, 135.3, 135.2, 135.1, 134.8, 134.7, 134.3, 134.2, 133.6, 133.4, 133.2, 133.2, 132.6, 132.5, 131.5, 130.8, 129.8, 129.0, 128.8, 128.7, 128.4, 128.2, 127.7, 127.6, 127.5, 127.3, 127.2, 127.2, 127.1, 126.2, 126.1, 126.0, 126.0, 125.6, 125.3, 121.4, 121.3, 119.8, 119.7, 21.3, 21.3; IR (KBr): 3071, 1680, 1537, 1342, 1092, 1013, 834, 822, 762 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{20}\text{ClN}_2\text{O}$: 447.1259, found: 447.1266.

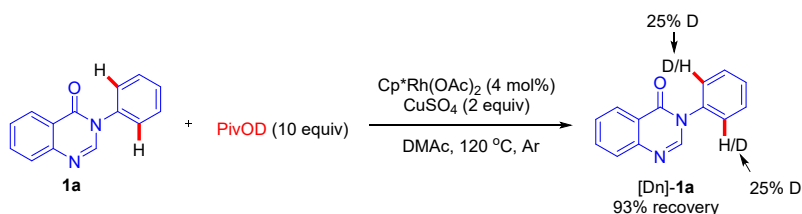
3-(Phenyl- d_5)quinazolin-4(3H)-one [D_5]-1a



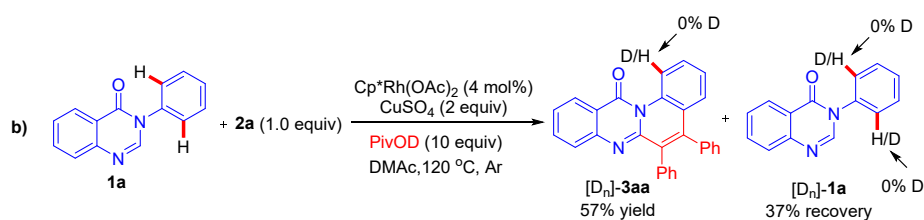
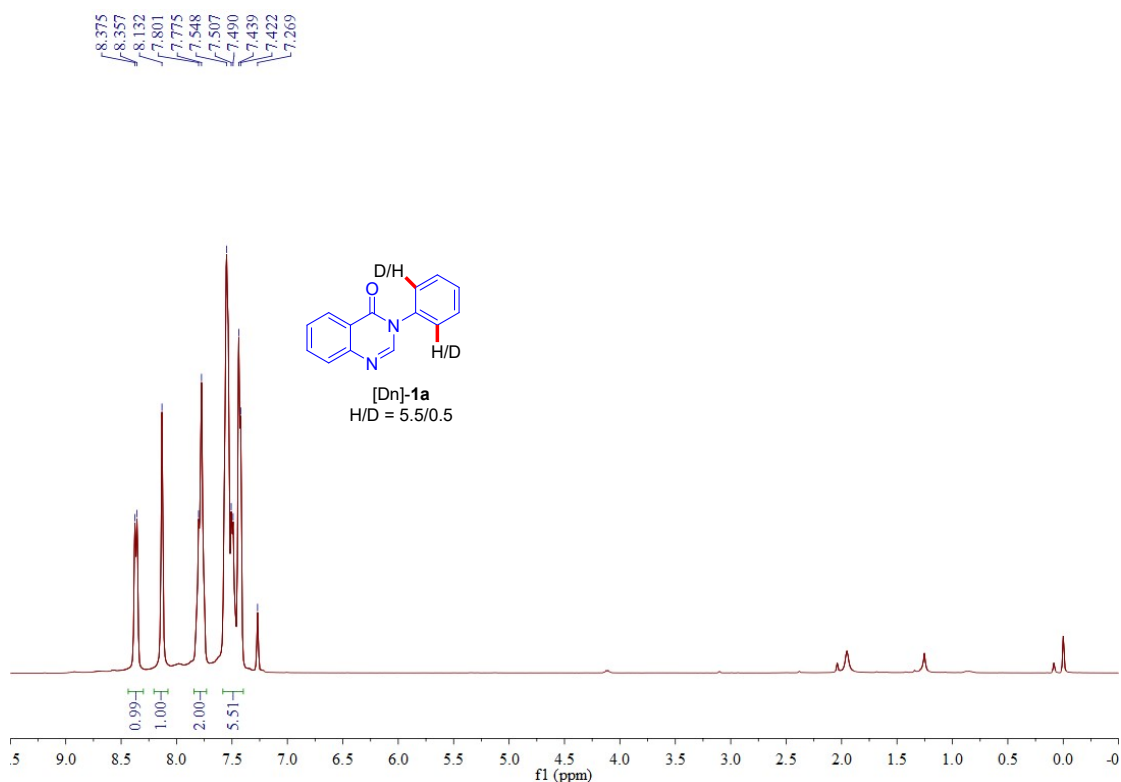
White solid, 189 mg, yield 83%; mp 136-138 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.37 (d, $J = 7.6$ Hz, 1H), 8.13 (s, 1H), 7.84-7.72 (m, 2H), 7.55 (ddd, $J = 7.6, 6.8, 0.8$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 160.8, 147.9, 146.1, 137.4, 134.6, 127.7, 127.6, 127.2, 122.4; IR (KBr): 1671, 1605, 1473, 1386, 1253, 766, 695 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_6\text{D}_5\text{N}_2\text{O}$: 228.1180, found: 228.1181.

IV. Mechanistic study

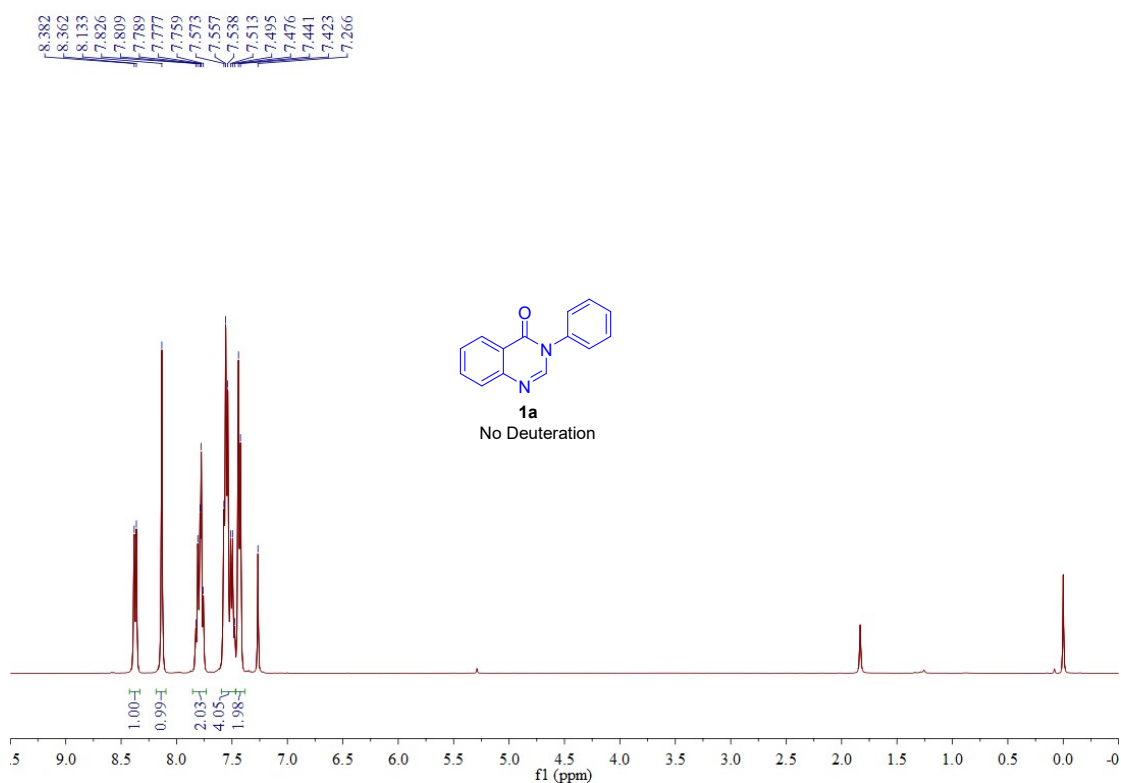
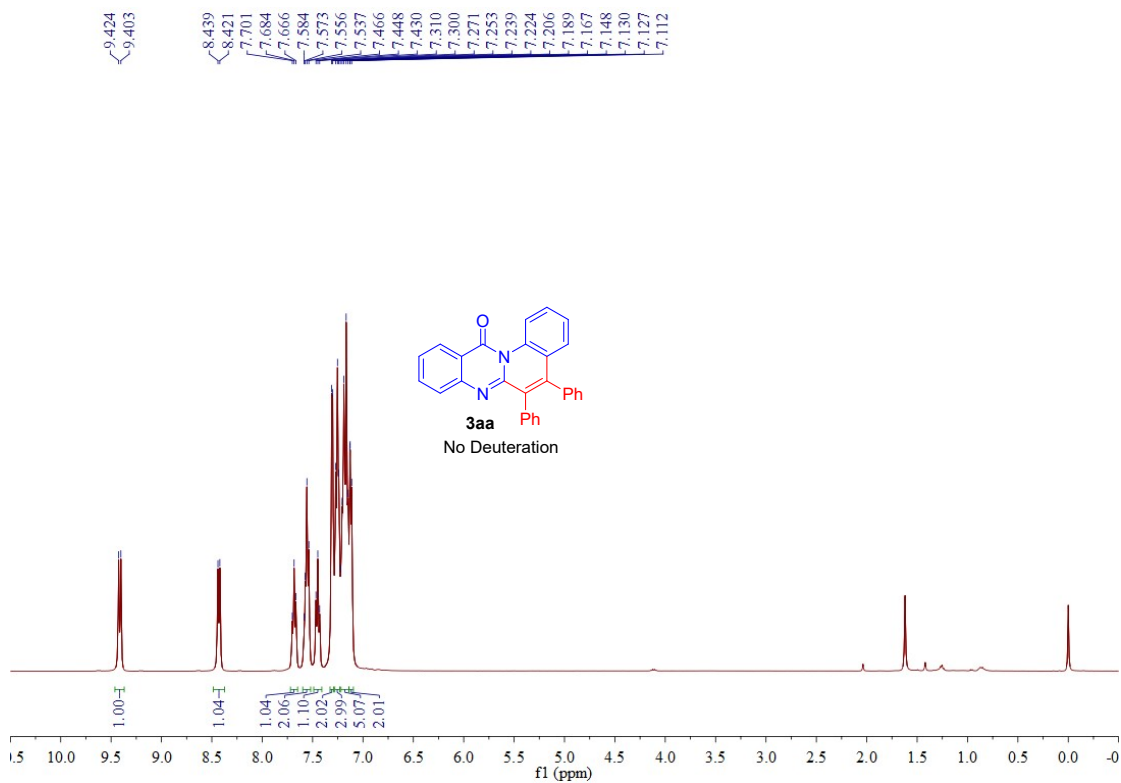
(1) H/D exchange experiment



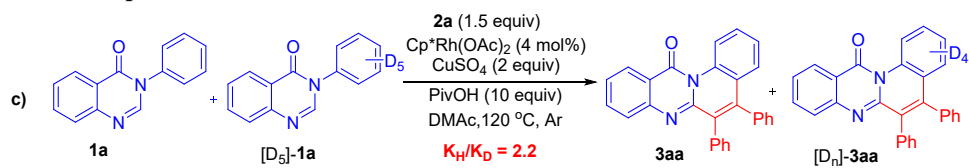
An oven-dried 10 ml schlenk tube with a magnetic stir bar was charged with 3-phenylquinazolin-4(3H)-one **1a** (0.2 mmol), $\text{Cp}^*\text{Rh}(\text{OAc})_2$ (4 mol%), CuSO_4 (2 equiv), PivOD (10 equiv) and DMAc (1 ml) under Ar. The tube was sealed with a teflon-coated cap and reaction solution was heated at 120 °C for 24 h. Afterwards the reaction was quenched with saturated NaHCO_3 solution (10 ml) and extracted with EtOAc (3 X 10 ml), washed with brine and dried over anhydrous Na_2SO_4 . The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product. The deuterated ratio was calculation from ^1H NMR analysis.



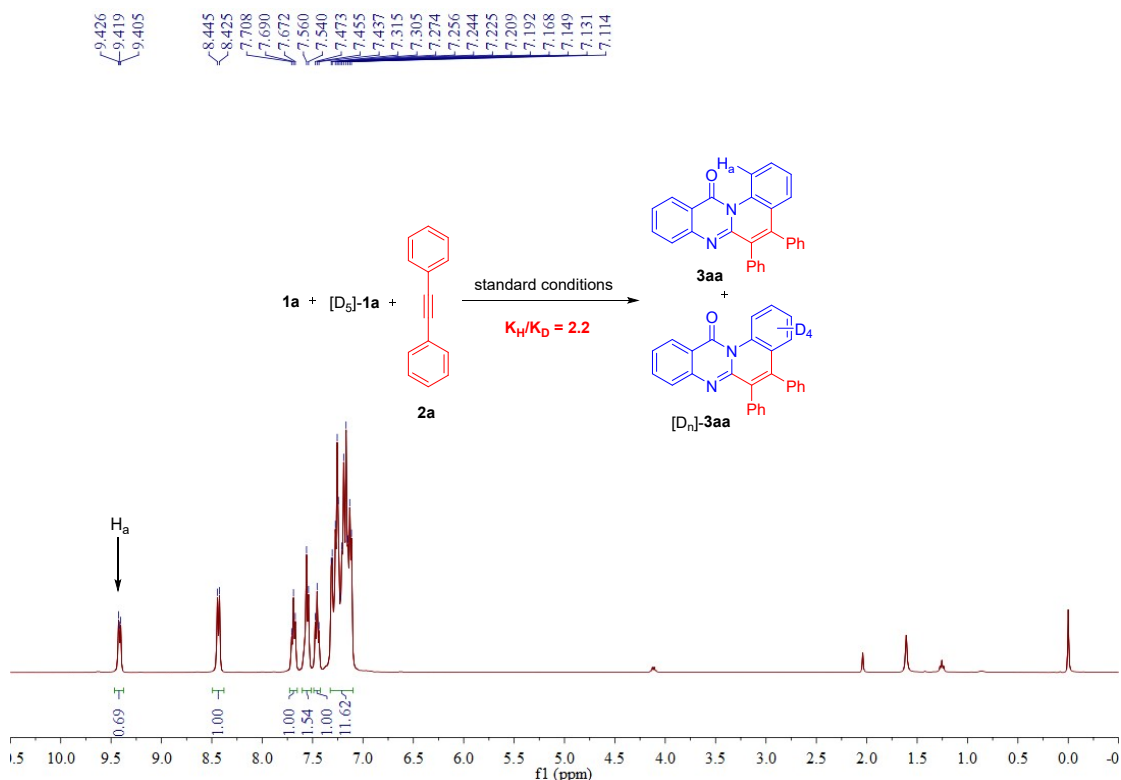
An oven-dried 10 ml schlenk tube with a magnetic stir bar was charged with 3-phenylquinazolin-4(3H)-one **1a** (0.2 mmol), 1,2-diphenylethyne **2a** (0.2 mmol), $\text{Cp}^*\text{Rh}(\text{OAc})_2$ (4 mol%), CuSO_4 (2 equiv), PivOD (10 equiv) and DMAc (1 ml) under Ar. The tube was sealed with a teflon-coated cap and reaction solution was heated at 120 °C for 24 h. Afterwards the reaction was quenched with saturated NaHCO_3 solution (10 ml) and extracted with EtOAc (3 X 10 ml), washed with brine and dried over anhydrous Na_2SO_4 . The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired $[\text{D}_n]\text{-3aa}$ and $[\text{D}_n]\text{-1a}$. ^1H NMR analysis showed that no deuteration was observed.



(2) Kinetic isotope effect



An oven-dried 10 ml schlenk tube with a magnetic stir bar was charged with 3-phenylquinazolin-4(3H)-one **1a** (0.2 mmol), 3-(phenyl-d₅)quinazolin-4(3H)-one [**D**₅]-**1a** (0.2 mmol), 1,2-diphenylethyne **2a** (0.3 mmol), Cp*Rh(OAc)₂ (4 mol%), CuSO₄ (2 equiv), PivOH (10 equiv) and DMAc (1 ml) under Ar. The tube was sealed with a teflon-coated cap and reaction solution was heated at 120 °C for 24 h. Afterwards the reaction was quenched with saturated NaHCO₃ solution (10 ml) and extracted with EtOAc (3 X 10 ml), washed with brine and dried over anhydrous Na₂SO₄. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired [**D**_n]-**3aa** and **3aa**. A KIE value of 2.2 was calculated on the basis of ¹H NMR analysis.



V. X-ray crystallography date of **3ba**.

The crystal structure was deposited into the CCDC database (CCDC No. 2093120). These data can be obtained from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

By slowly volatilizing the DCM solvent, single crystals **3ba** suitable for X-ray analysis were obtained. The detailed characteristics and data are shown below.

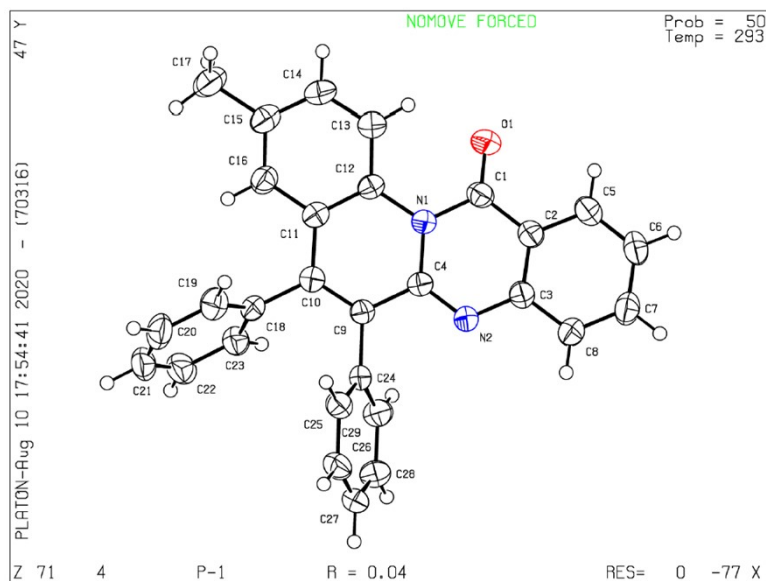


Figure S1.Crystal structure of compound **3ba**

Table S1.Crystal data and structure refinement for **4** (CCDC No. 2093120)

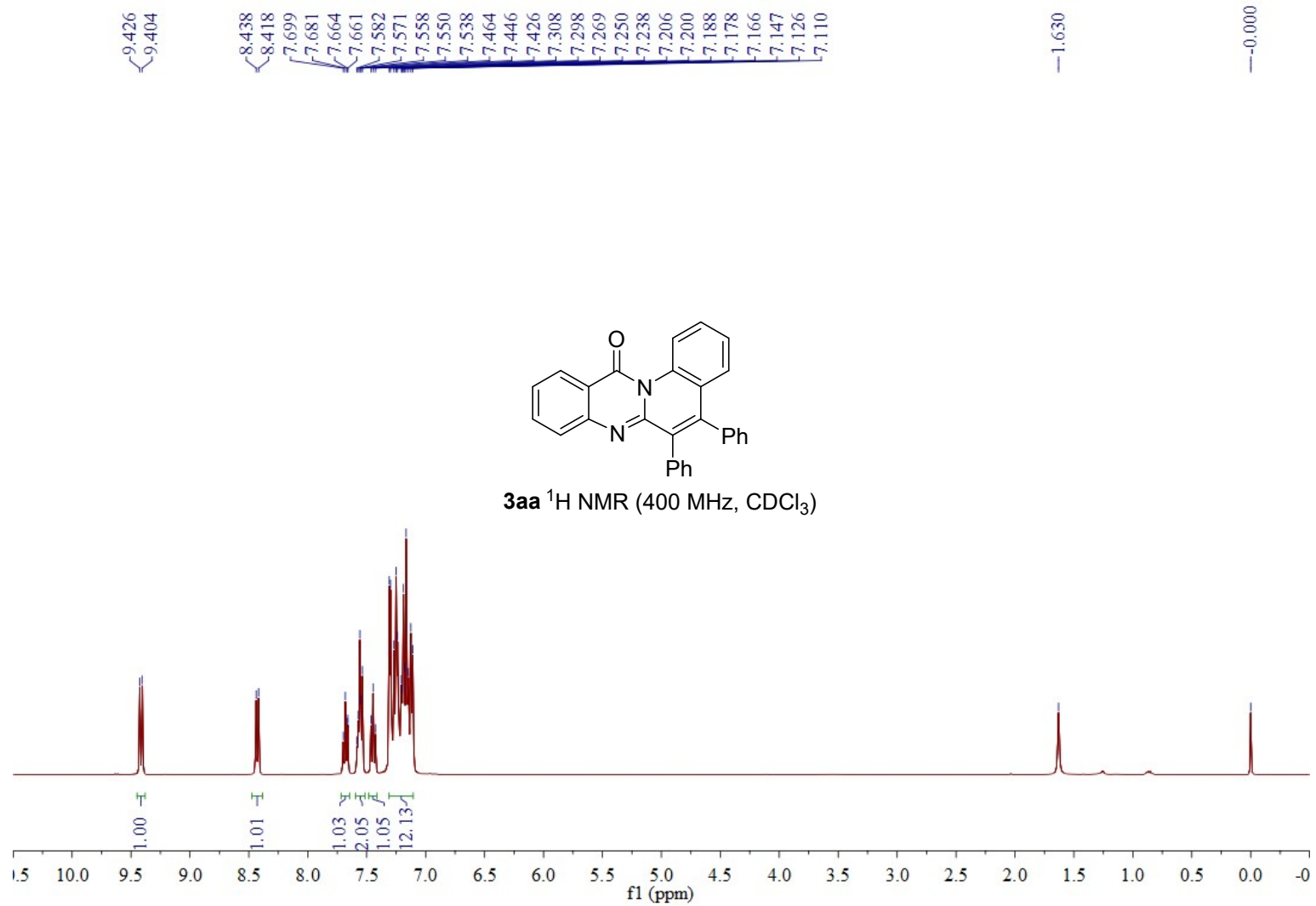
Identification code	4
Empirical formula	C ₂₉ H ₂₀ N ₂ O
Formula weight	412.47
Temperature/K	293(2)
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.4883(6) Å α = 86.863(7) ° b = 10.7030(9) Å β = 70.062(7) ° c = 10.9775(10) Å γ = 80.112(6) °
Volume/Å ³	1032.41(14)
Z	2
Calculated density	1.327 Mg/m ³
Absorption coefficient	0.081 mm ⁻¹
F(000)	432
Crystal size/mm ³	0.23 × 0.21 × 0.19
Radiation	MoKα (λ = 0.71073)
Theta range for data collection /°	3.37 to 25
Limiting indices	-11 ≤ h ≤ 9, -12 ≤ k ≤ 12, -13 ≤ l ≤ 13
Reflections collected/unique	11276/3590 [R _{int} = 0.0214]
Completeness to theta = 25.00	99.0 %
Absorption correction	MULTI SCAN
Max. and min. transmission	1.00000 and 0.81806
Refinement method	Full-matrix least-squares on F ²

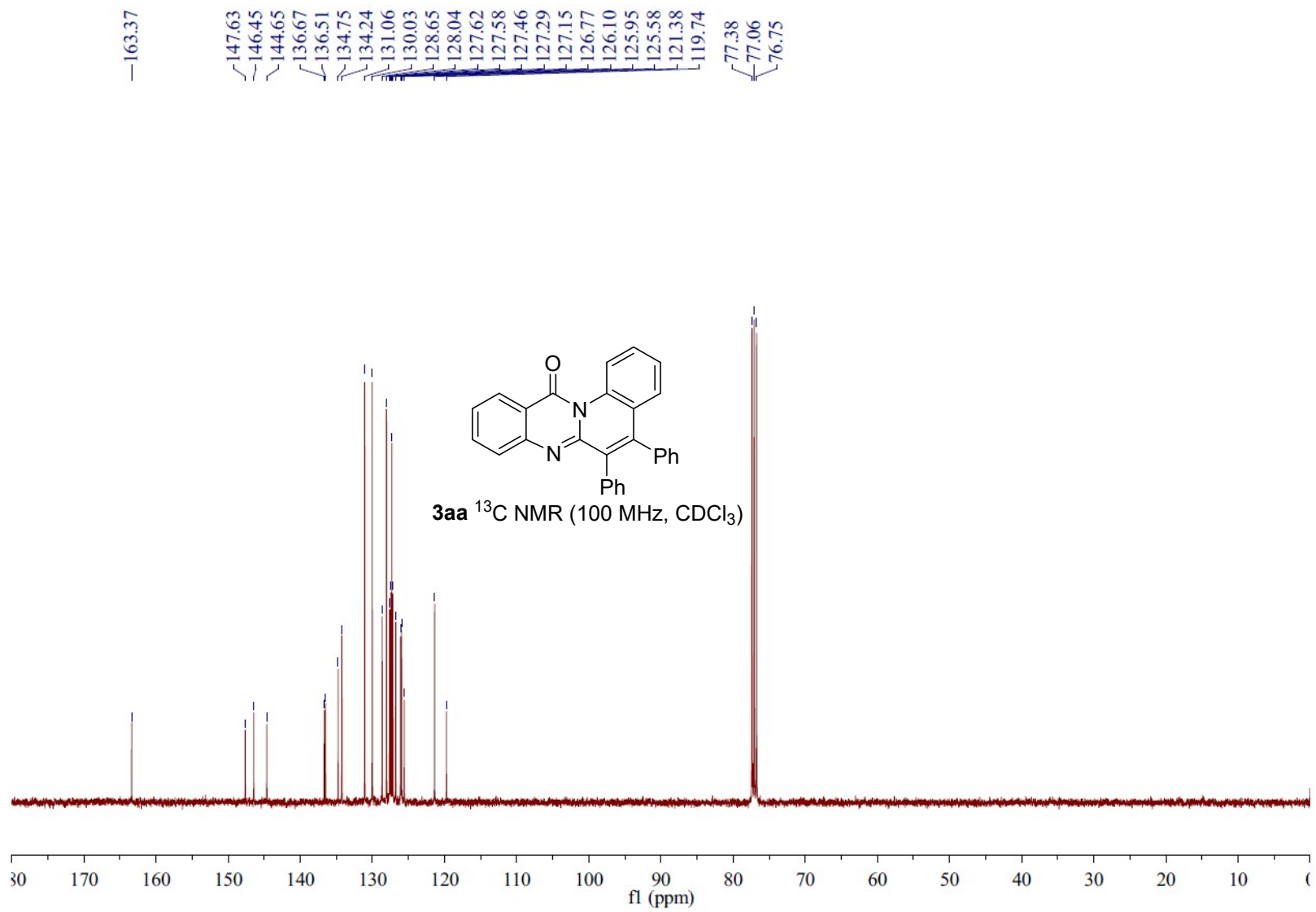
Data/restraints/parameters	3590/0/290
Goodness-of-fit on F ²	1.020
Final R indexes [I>>=2σ (I)]	R ₁ = 0.0446, wR ₂ = 0.1126
Final R indexes [all data]	R ₁ = 0.0541, wR ₂ = 0.1191
Largest diff. peak/hole / e Å ⁻³	0.148/-0.244

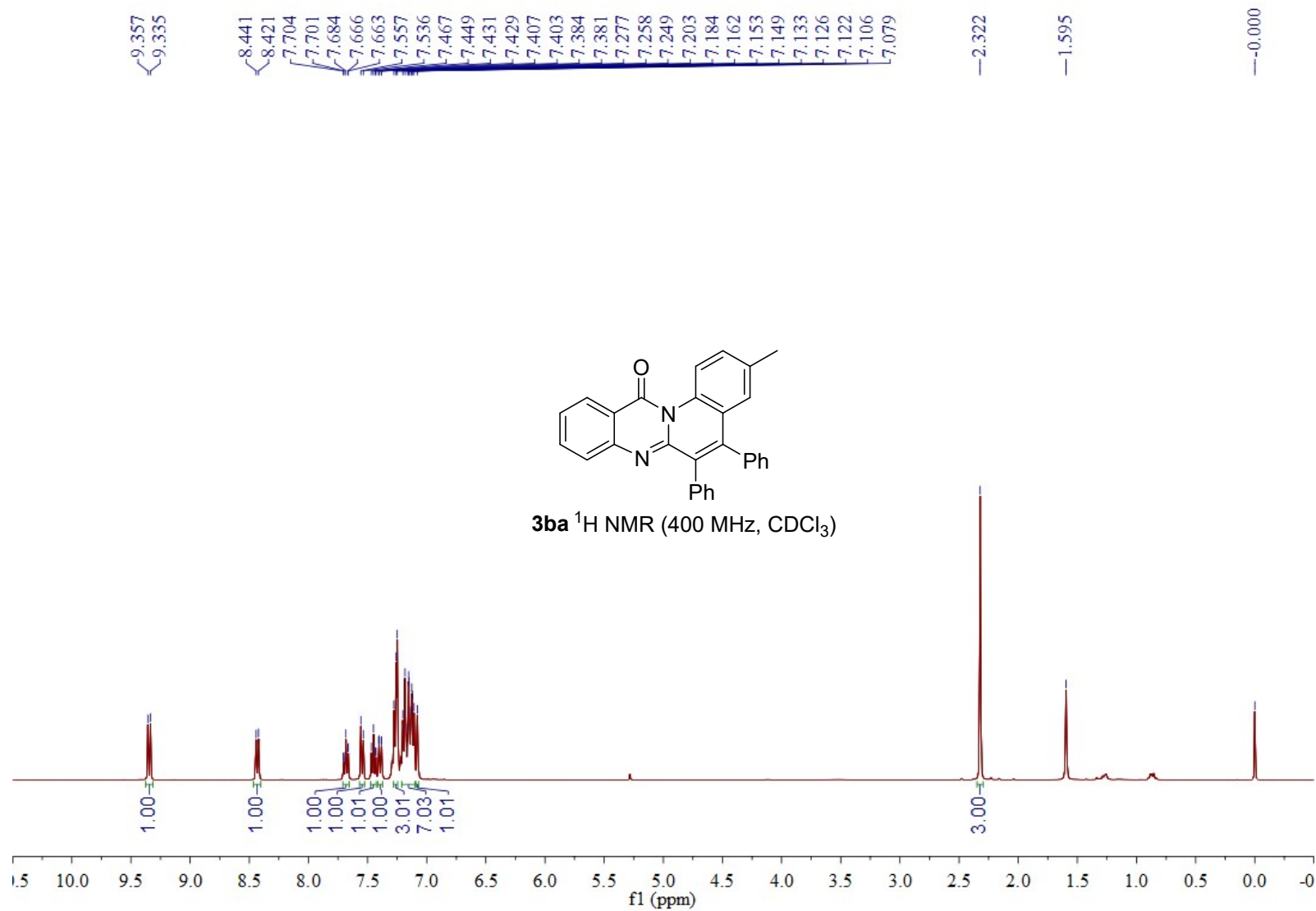
VI. References

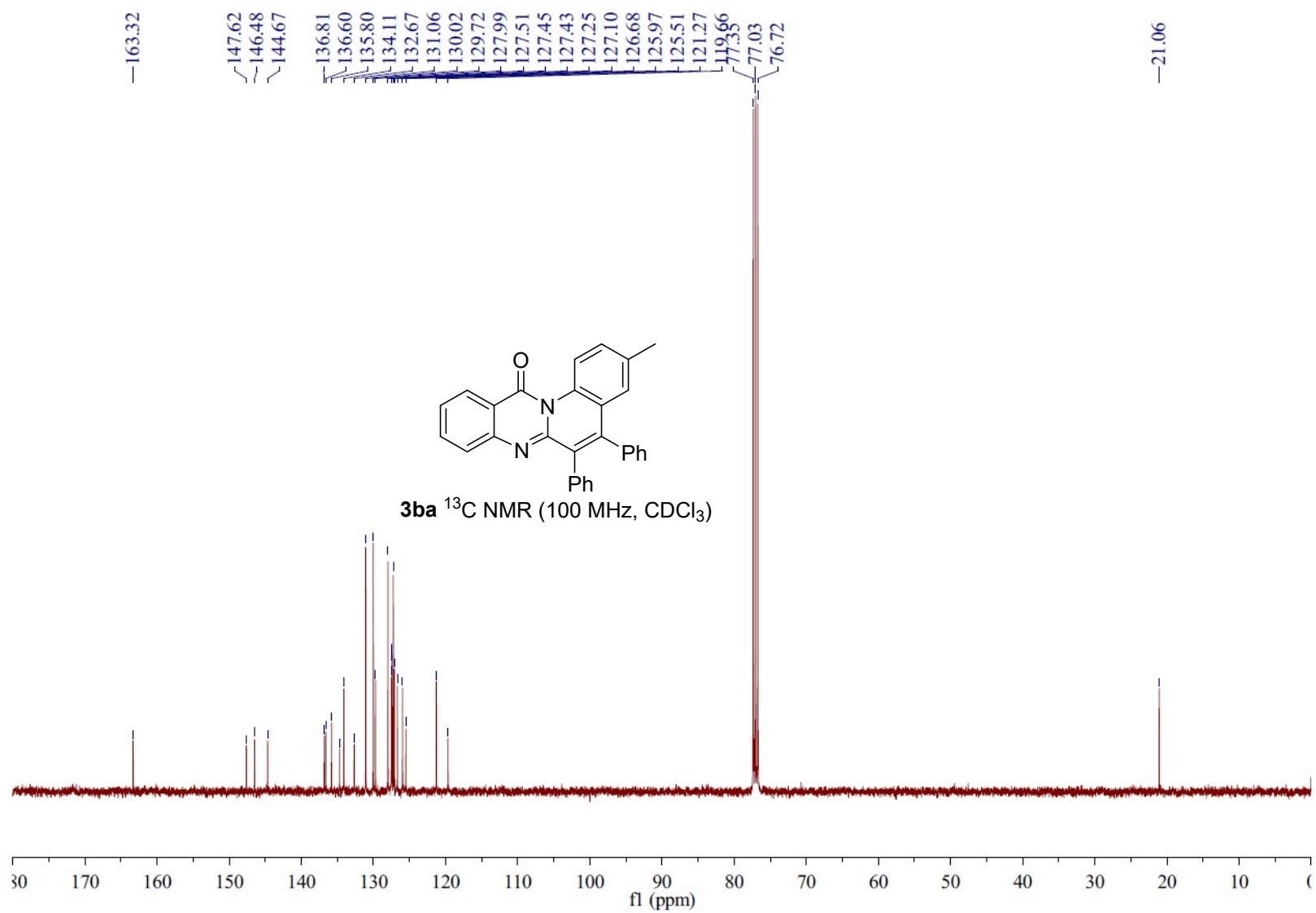
1. G. L. Huang, B. Liu, M. Y. Teng and Y. G. Chen, Ammonium chloride-catalyzed one-pot synthesis of 4(3H)-quinazolinones under solvent-free conditions, *Synthetic Commun*, 2014, **44**, 1786-1794.
2. M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth and P. A. Grieco, One-pot synthesis of symmetrical and unsymmetrical bisarylethynes by a modification of the Sonogashira coupling reaction, *Org. Lett.*, 2002, **4**, 3199-3202.

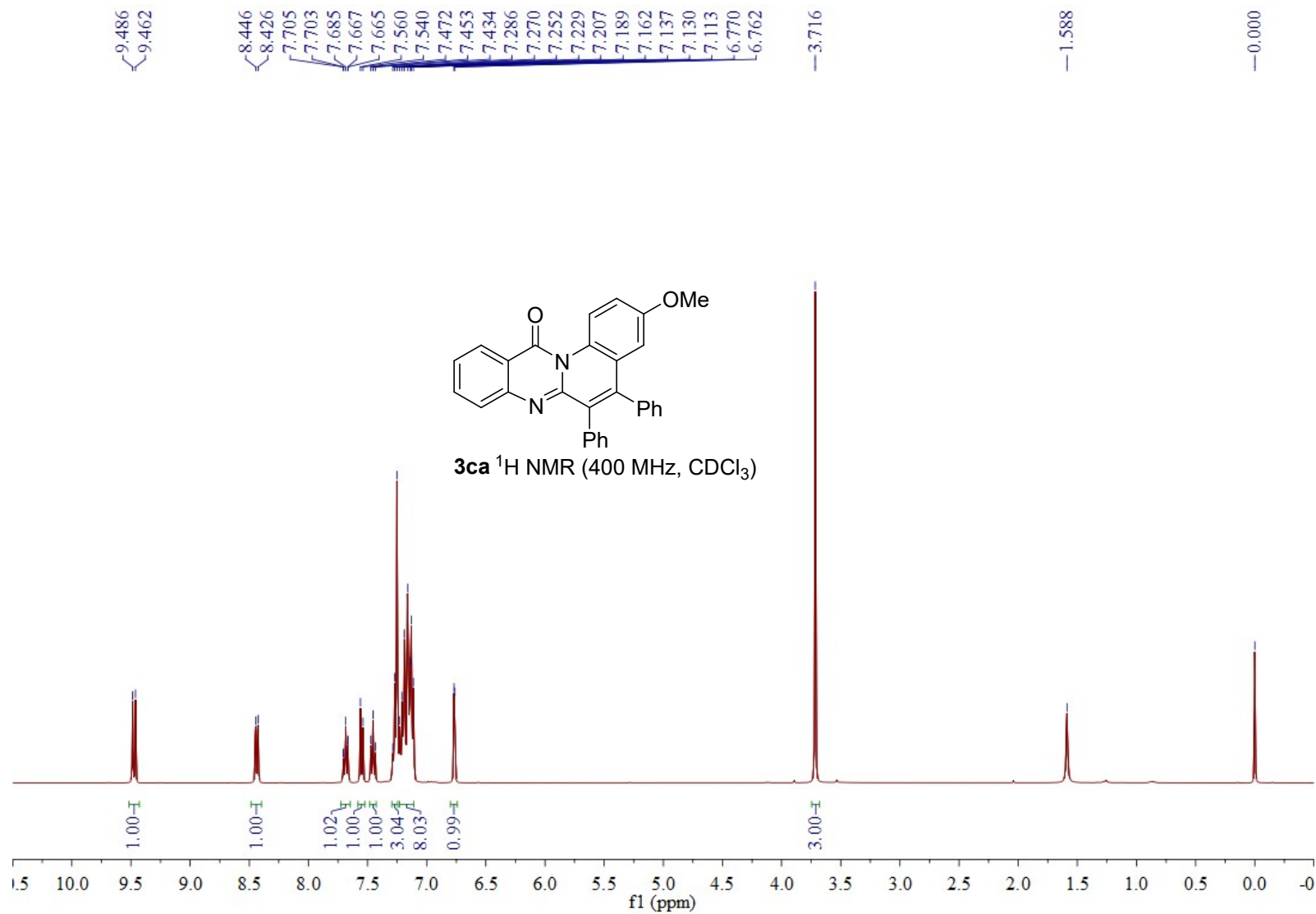
VII. Copy of NMR

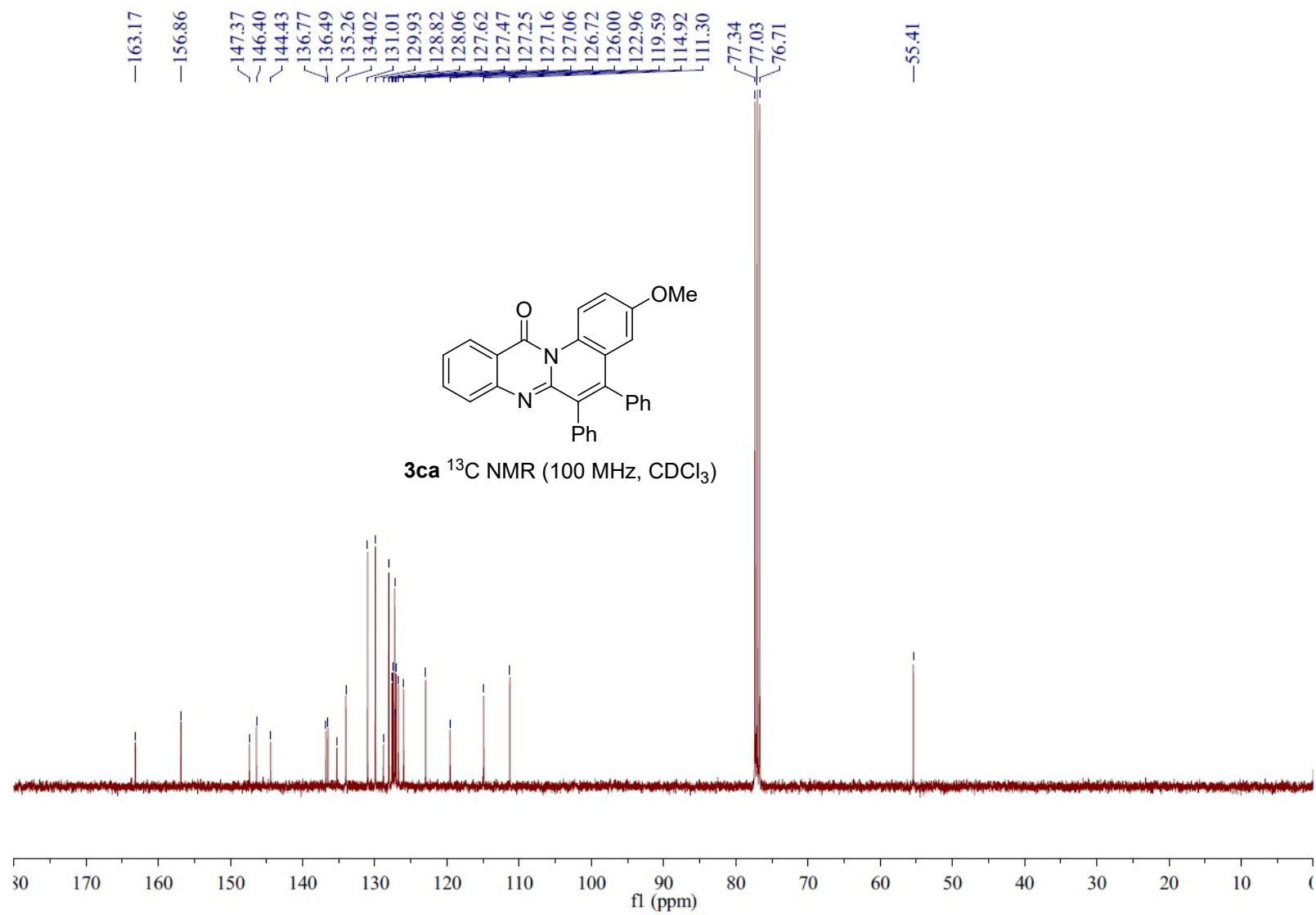


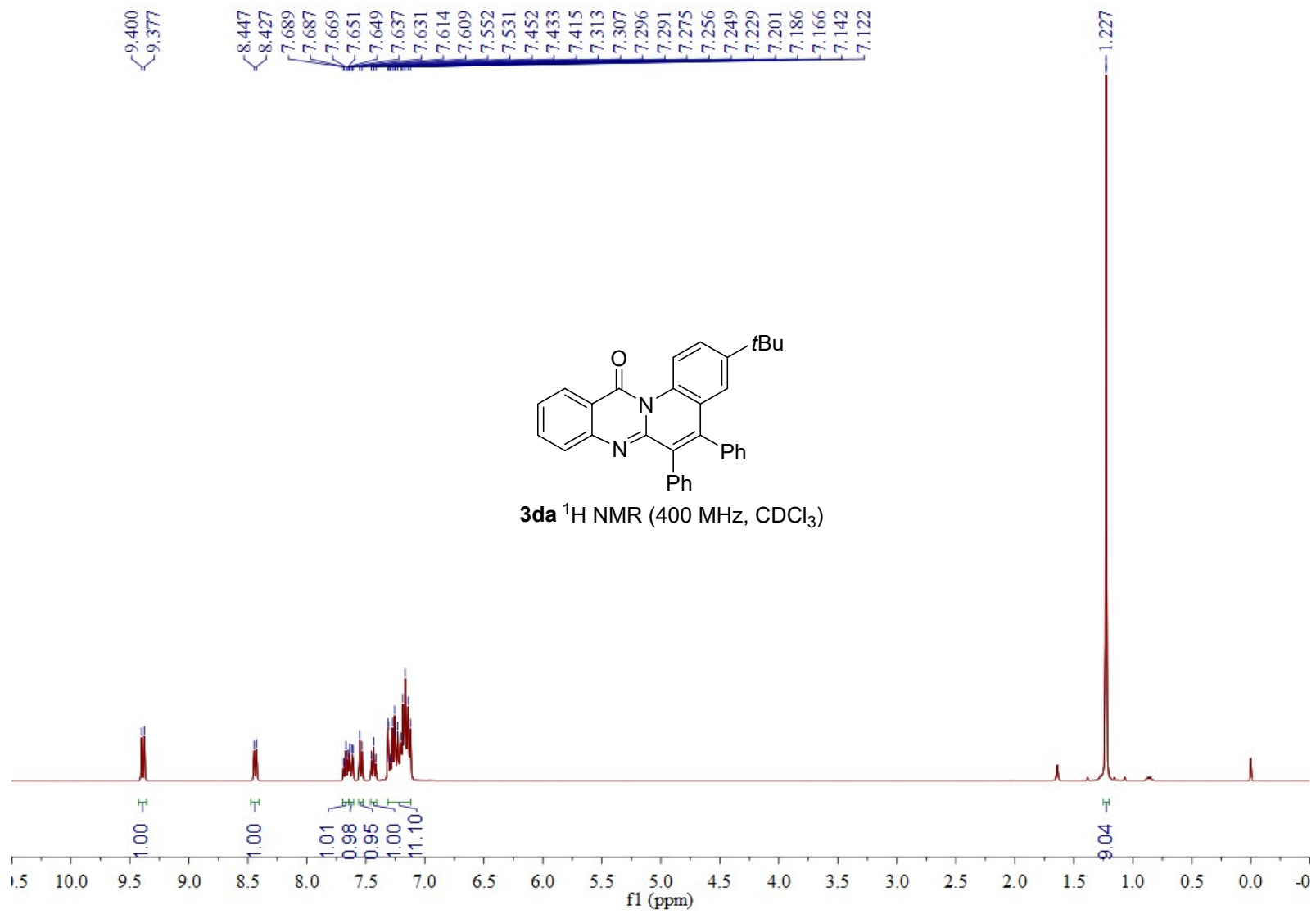


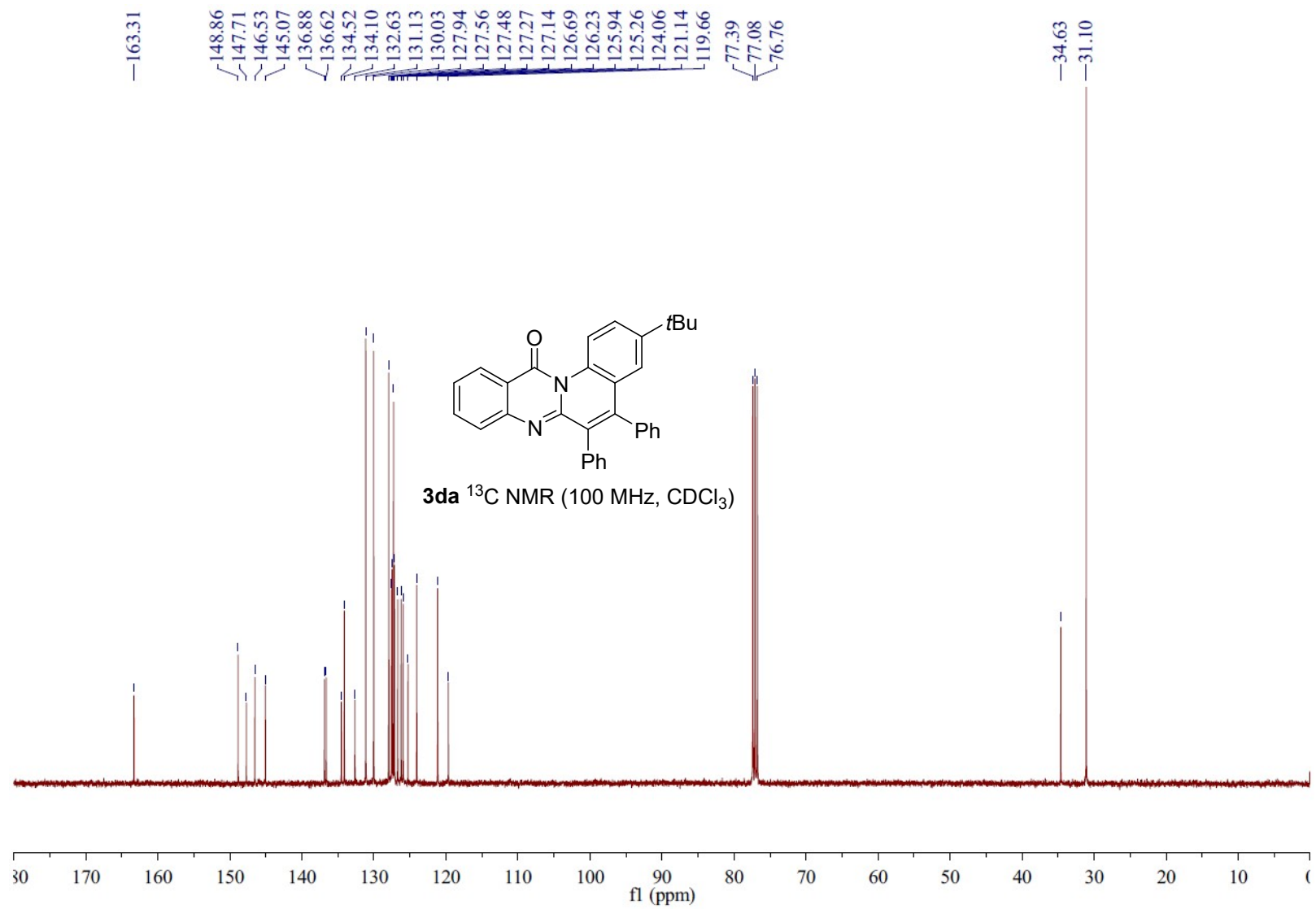


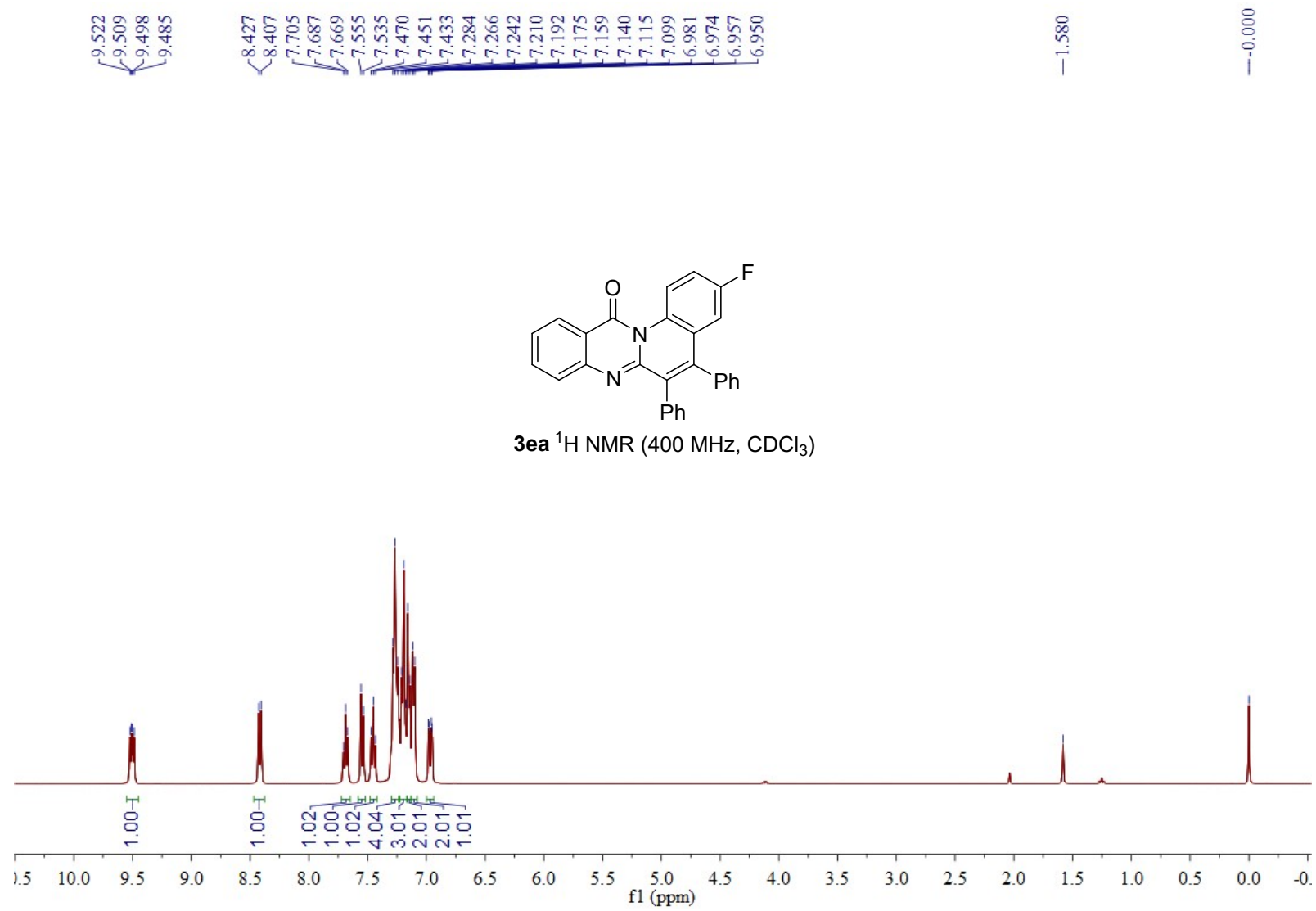


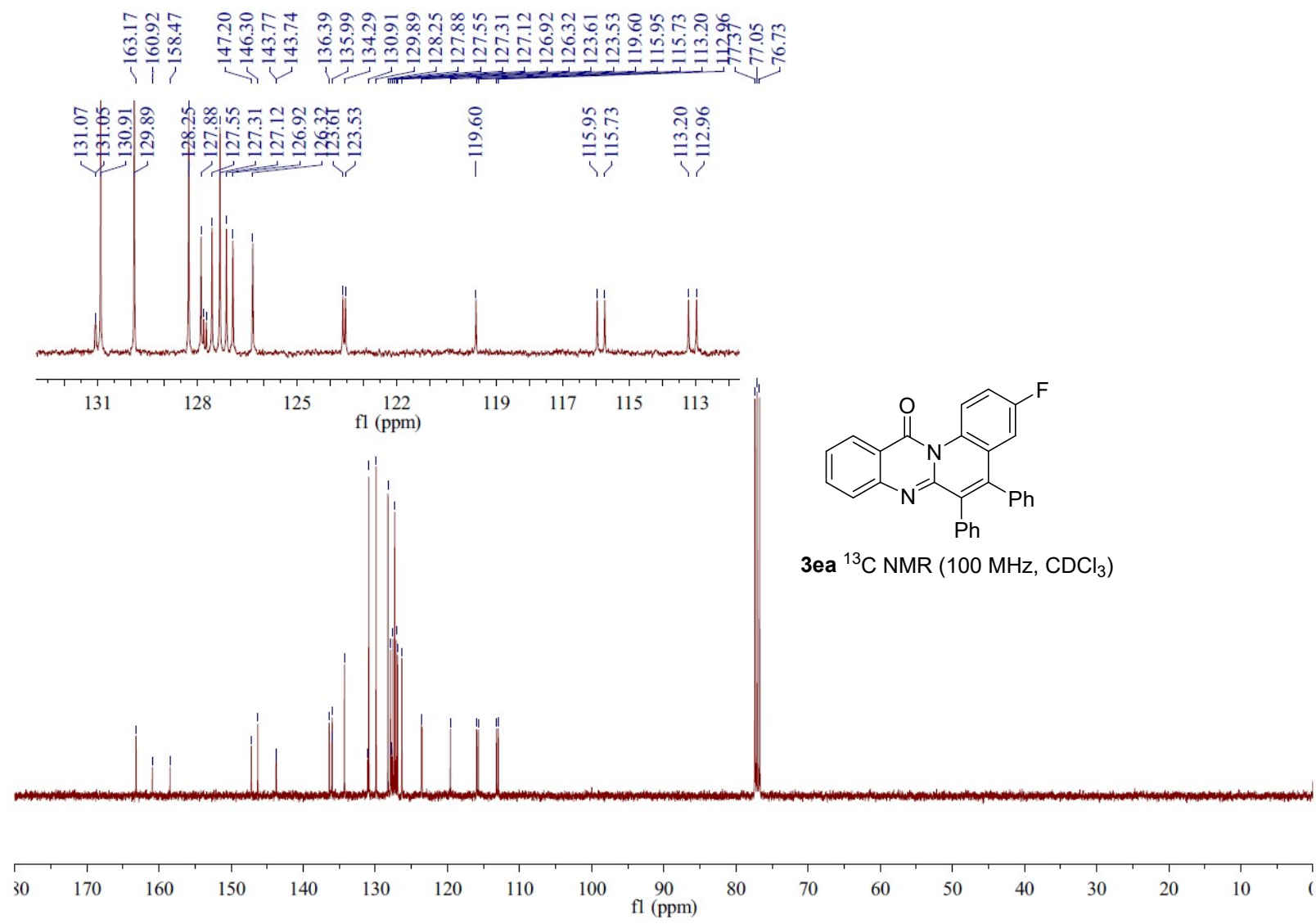


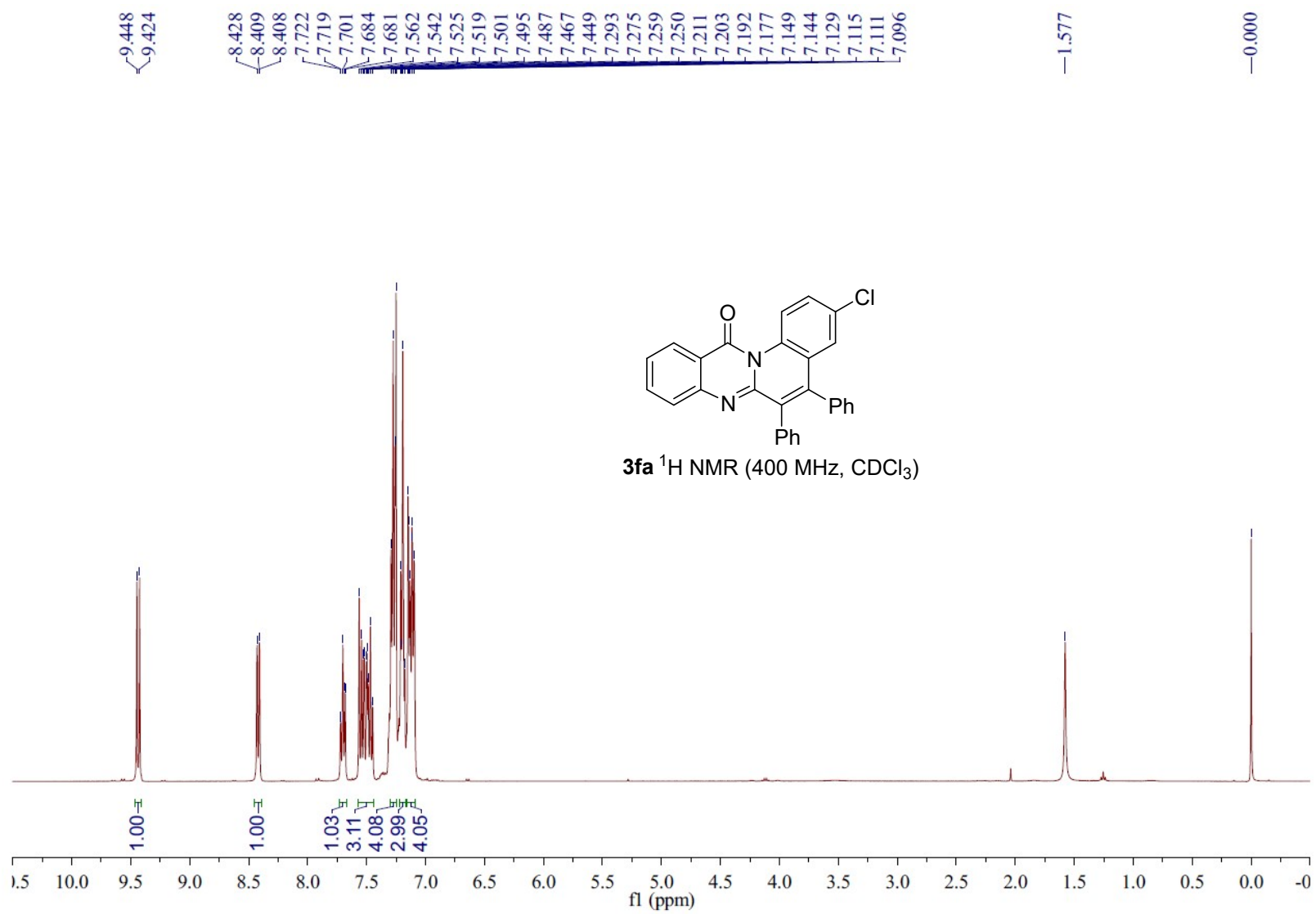


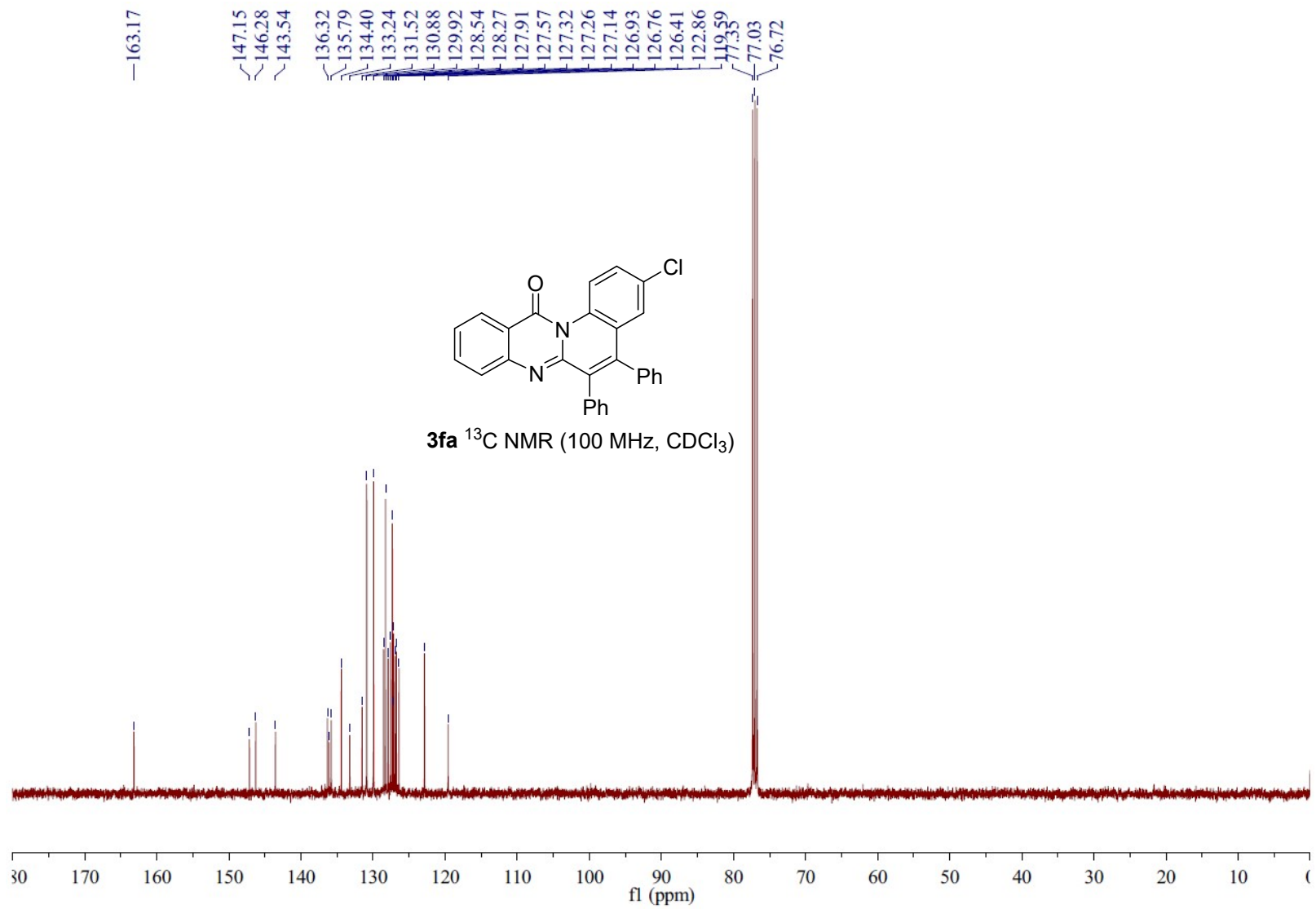


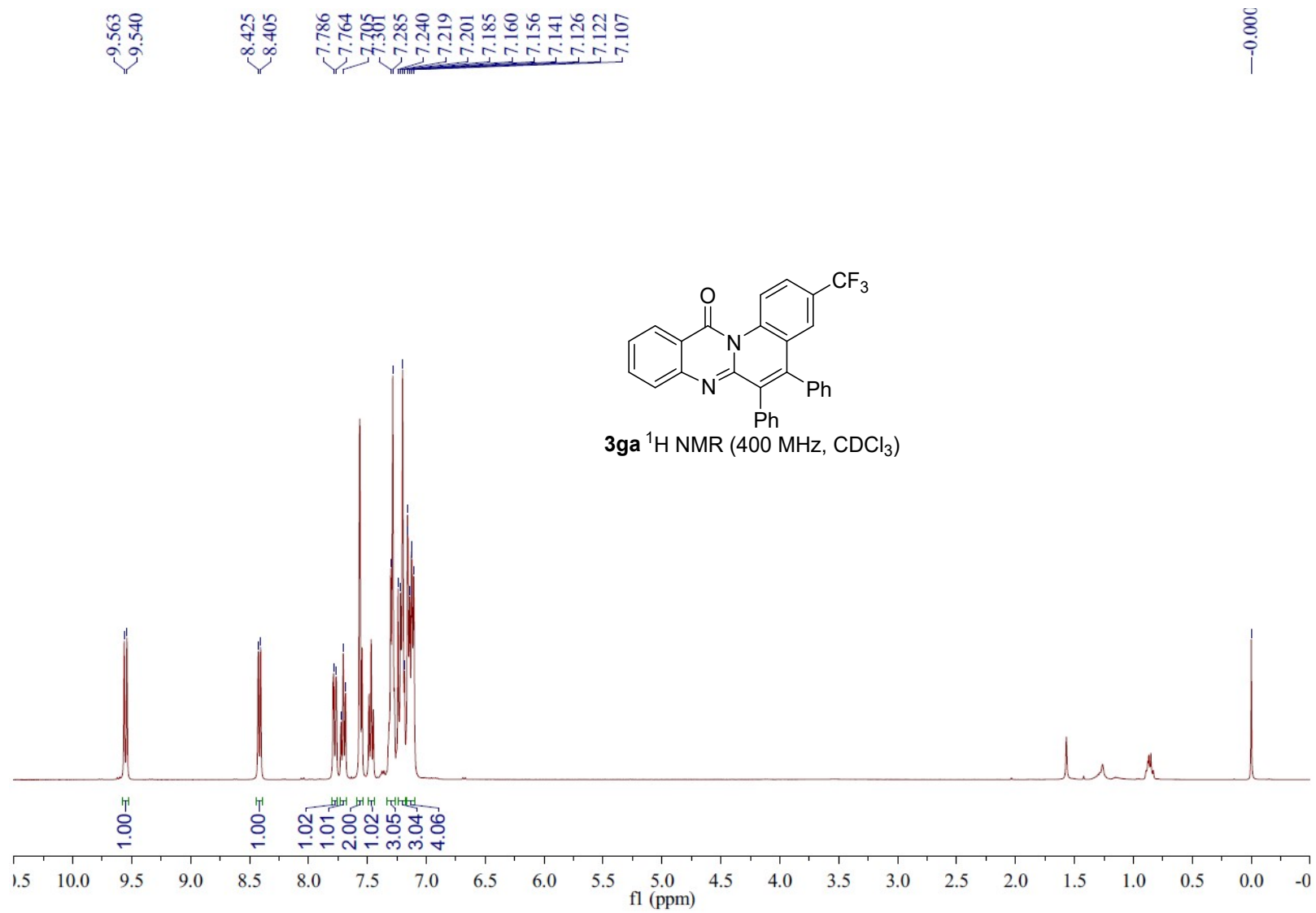


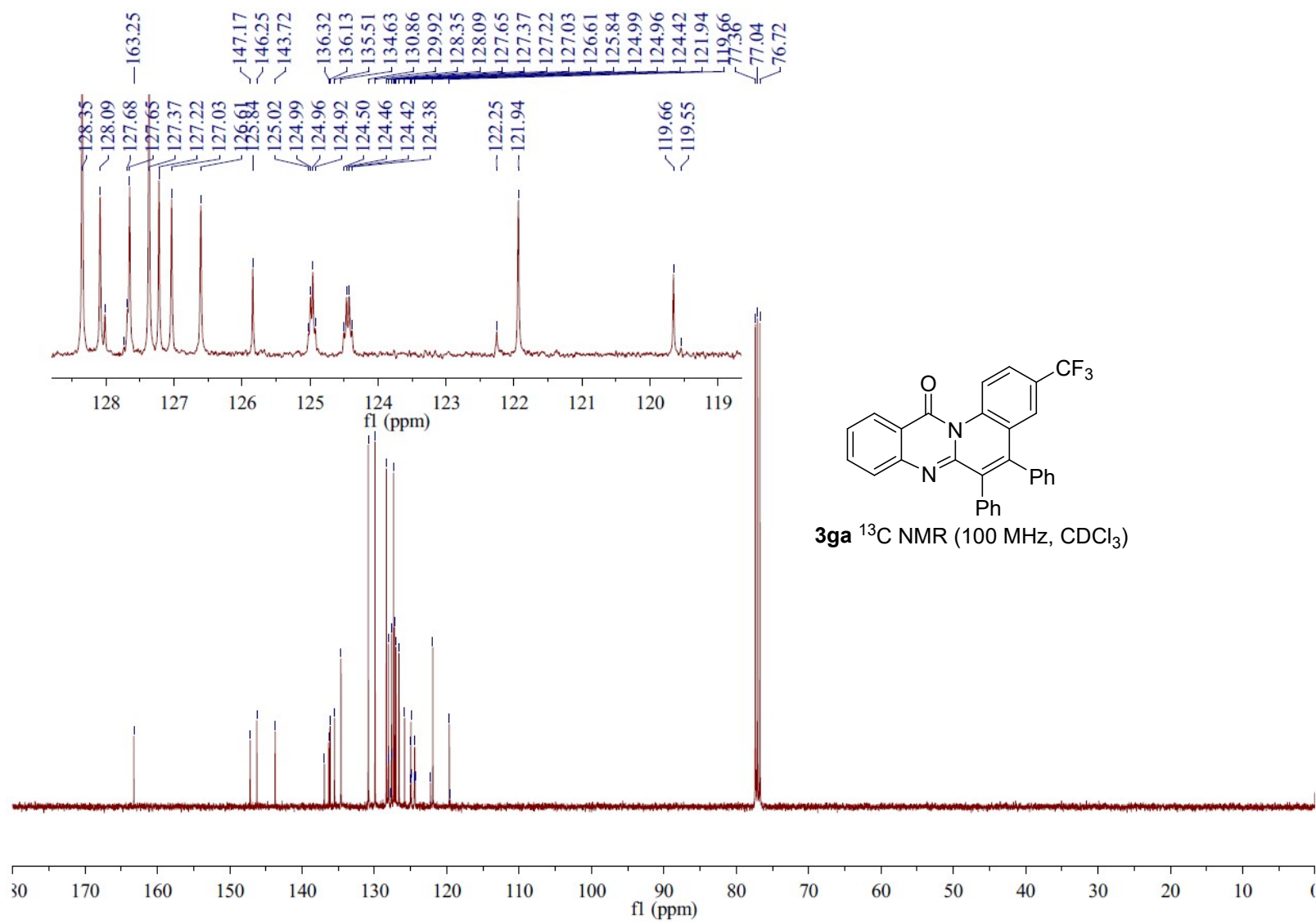


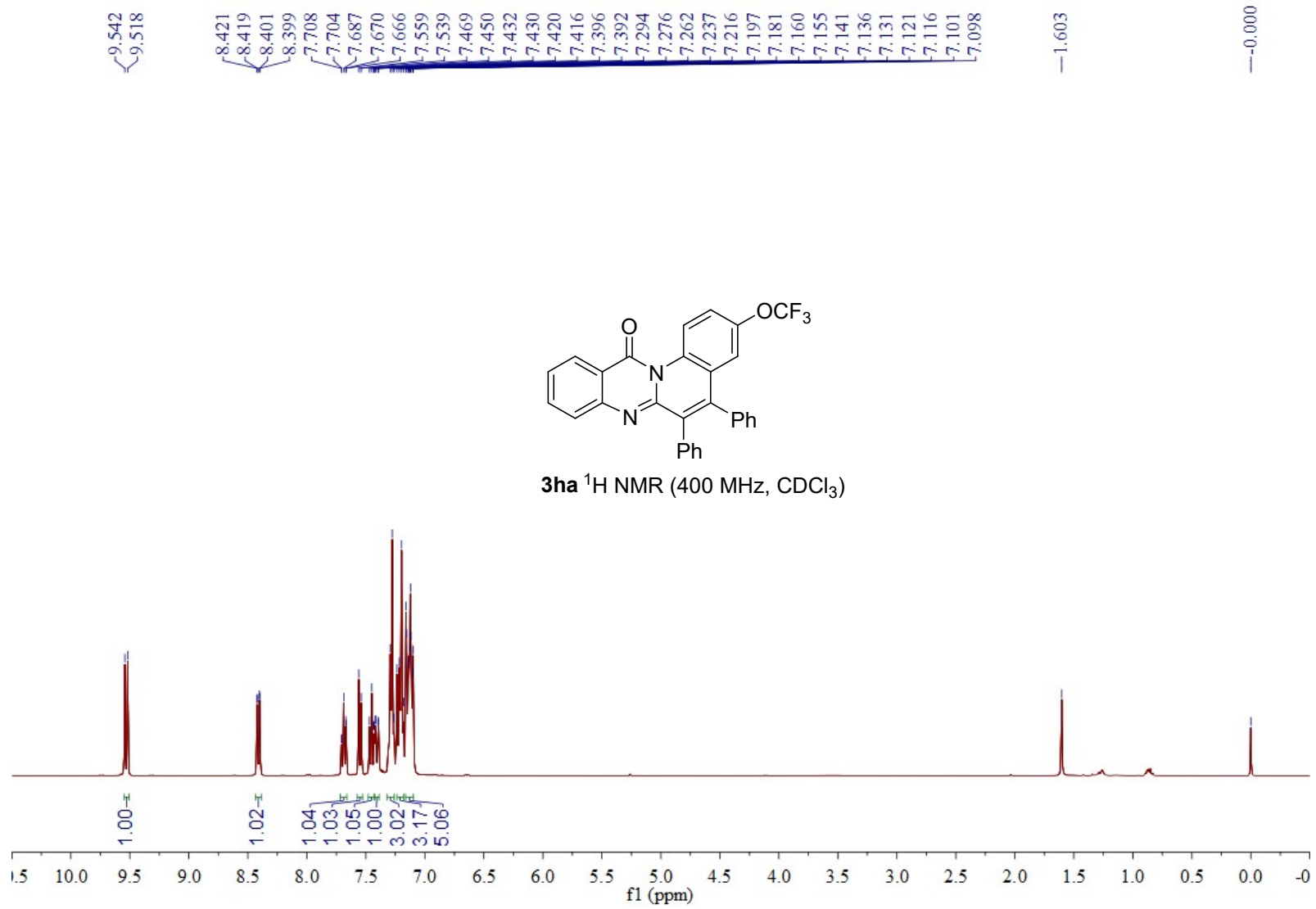


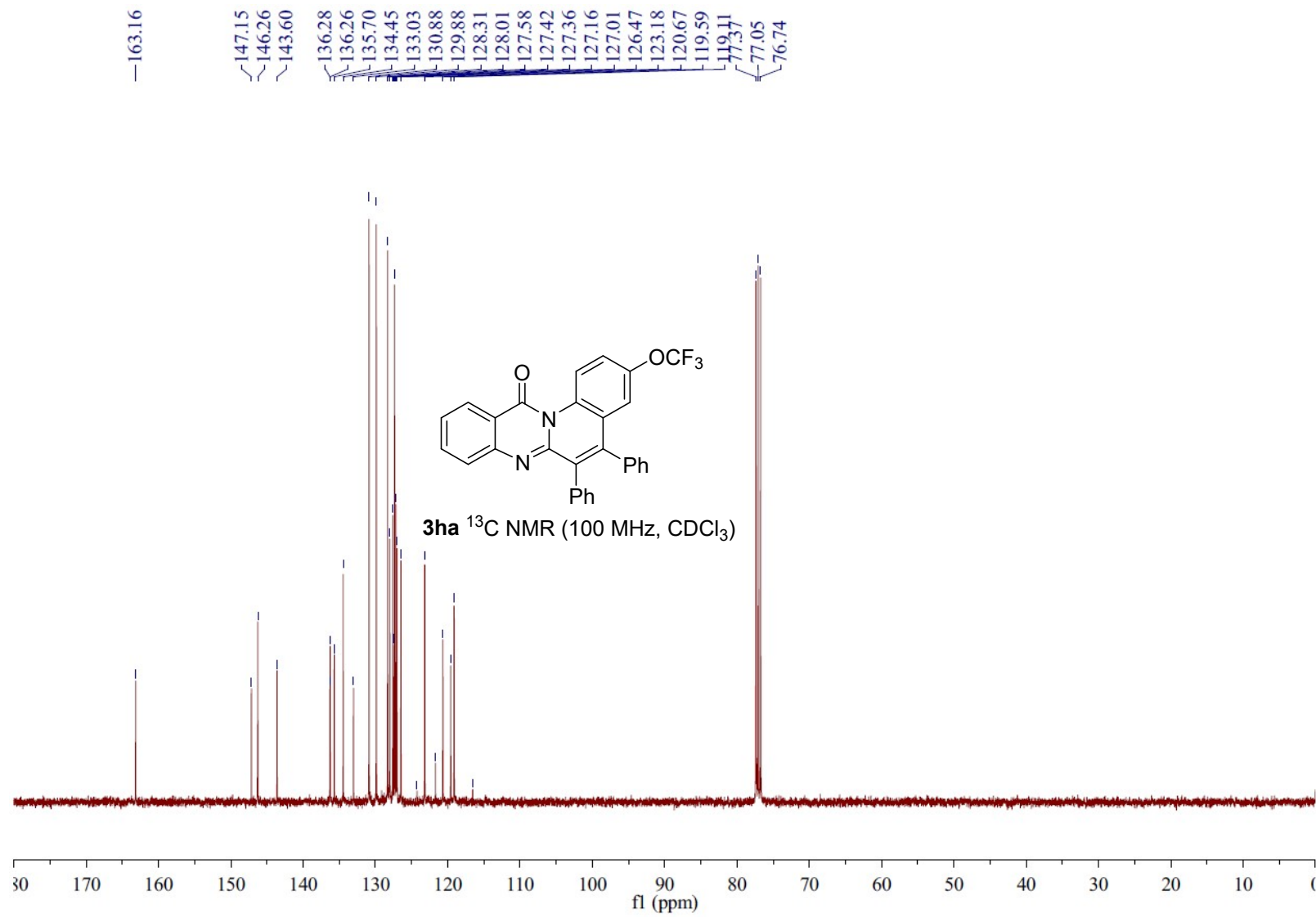


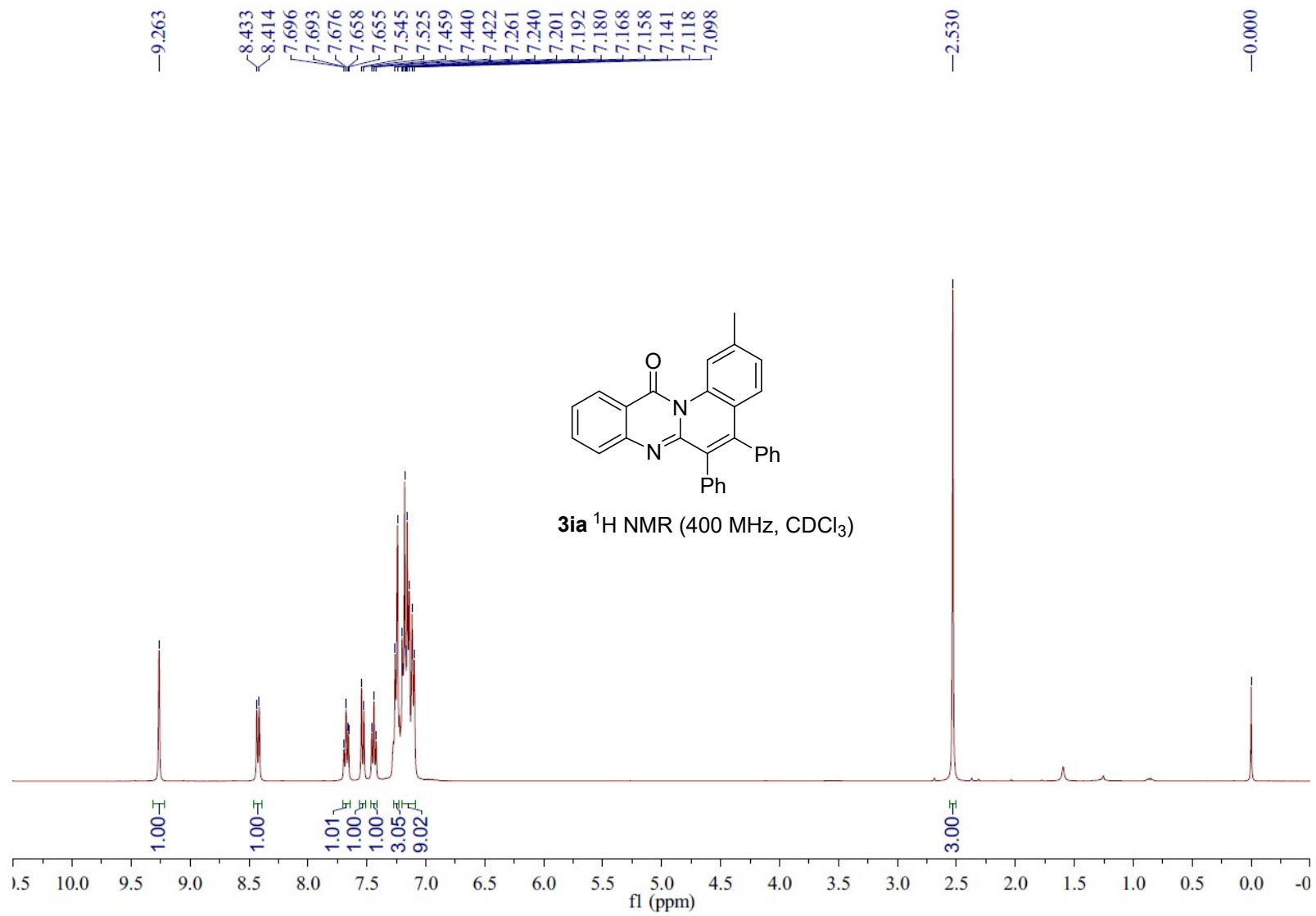


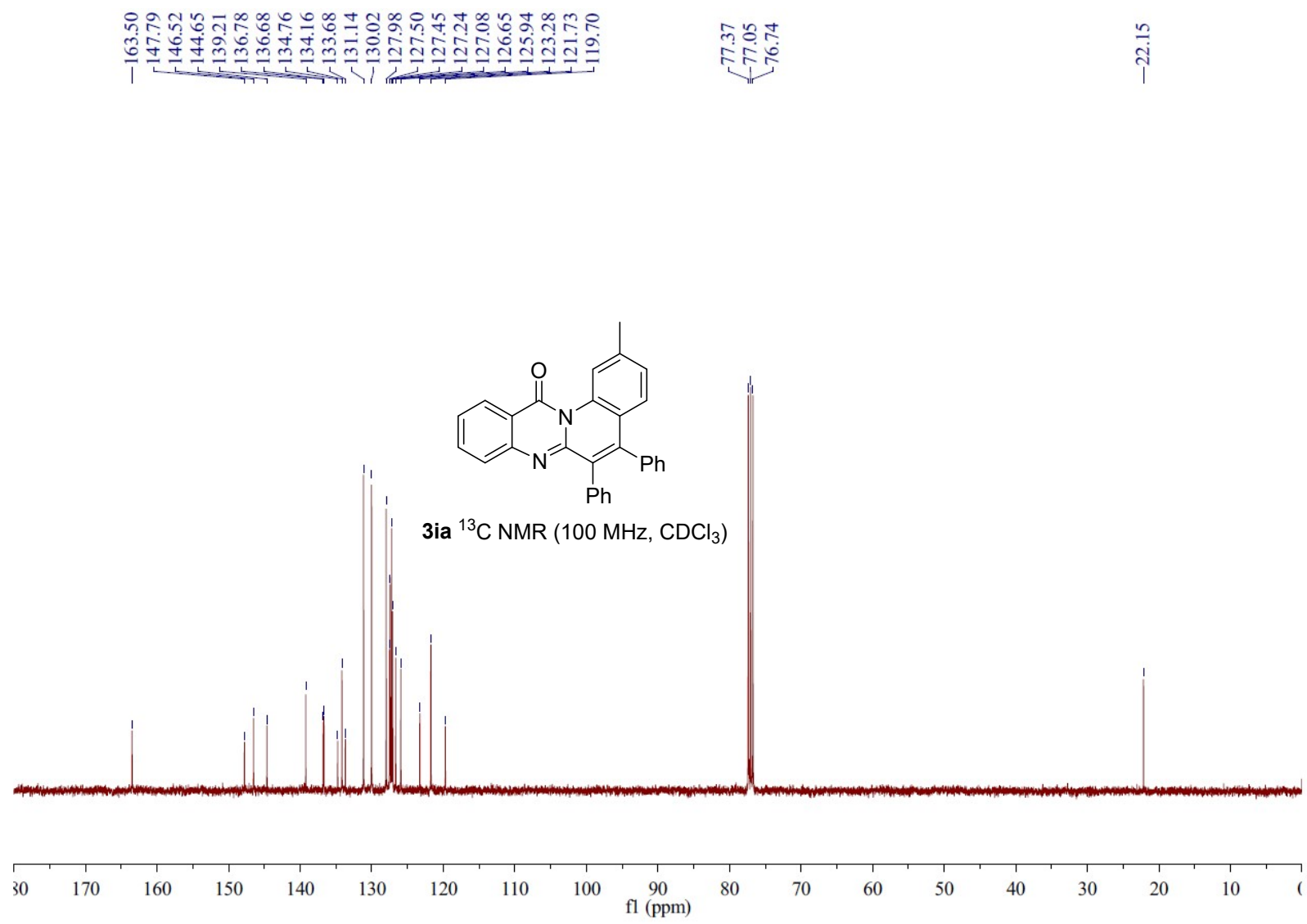


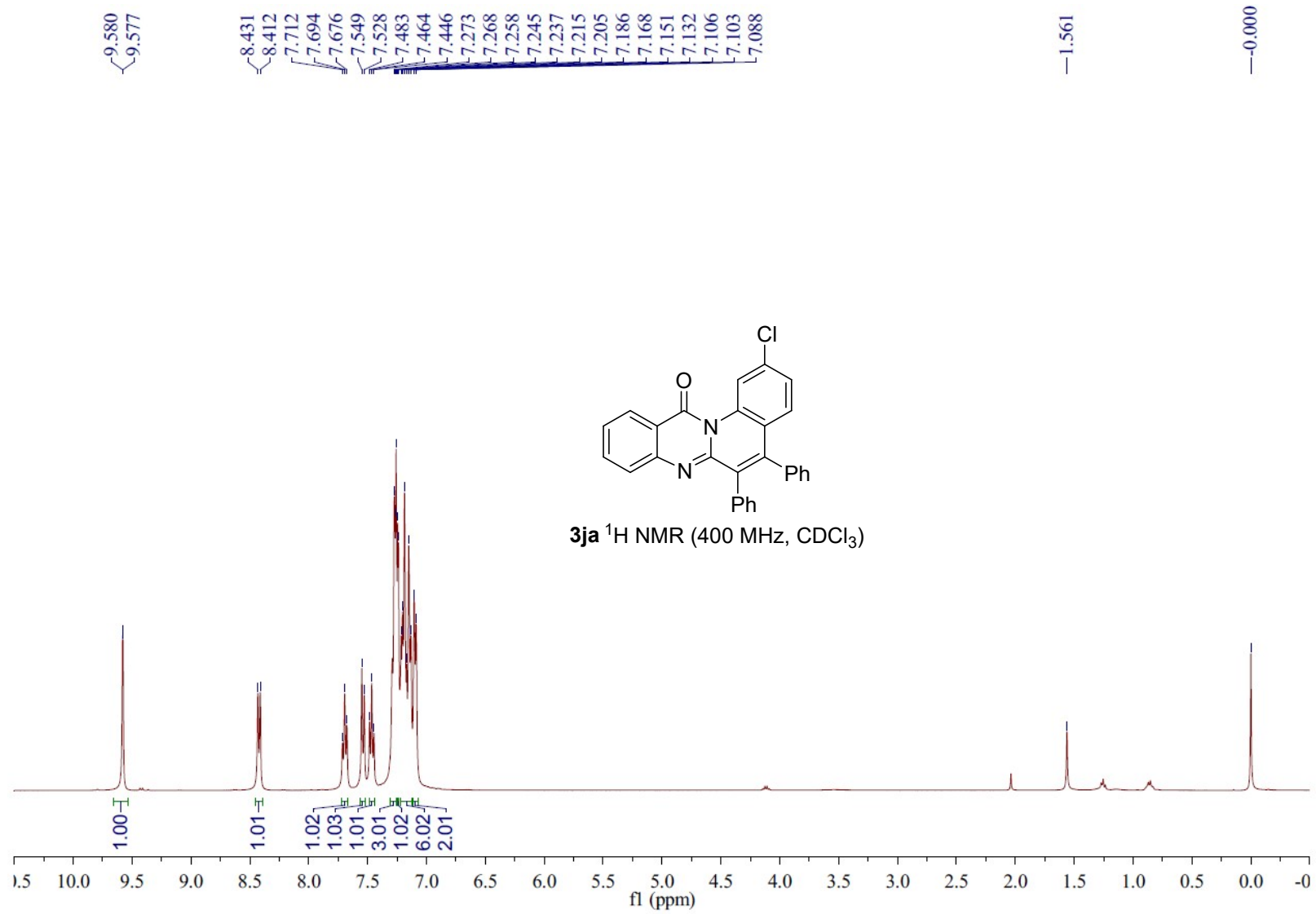


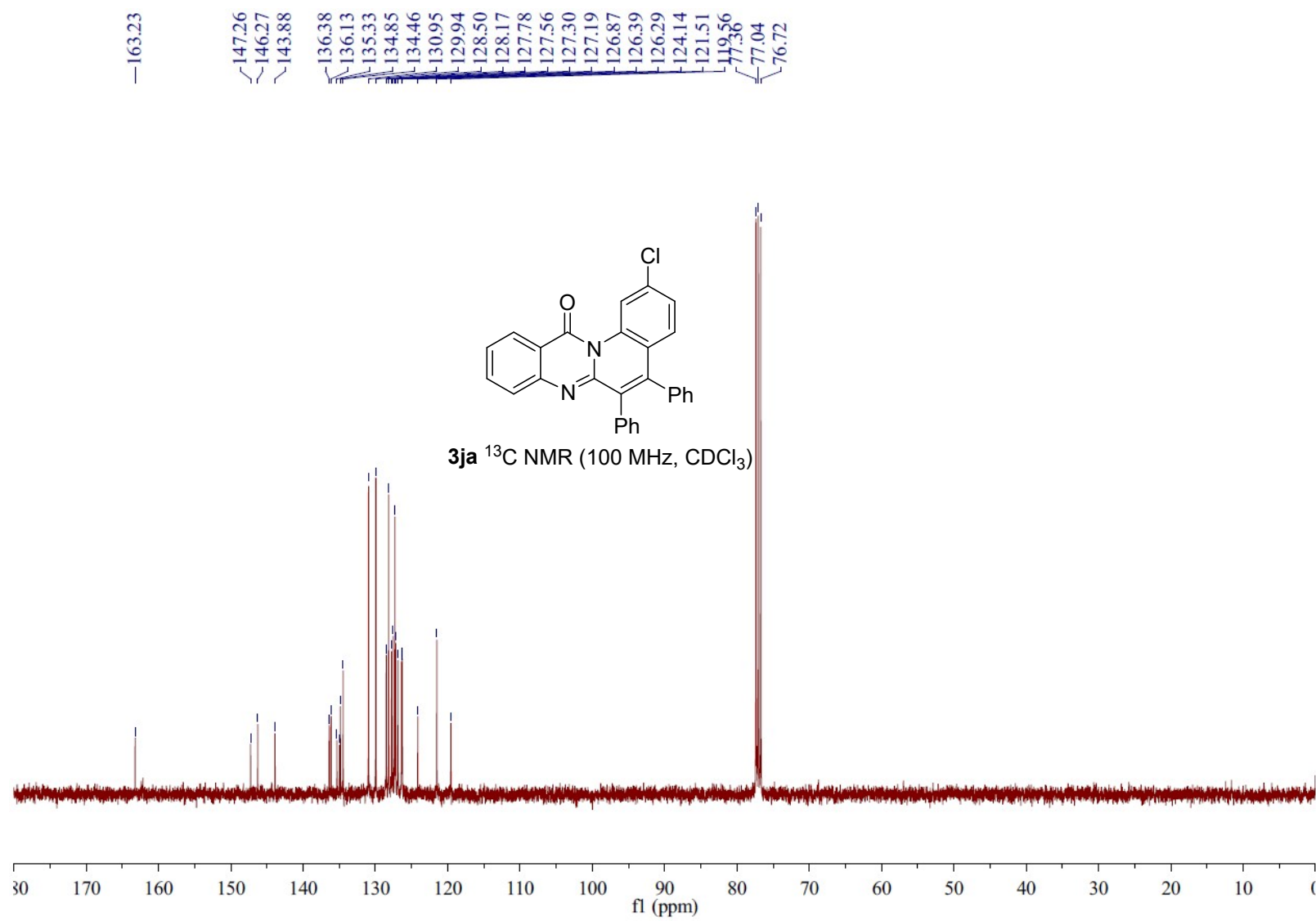


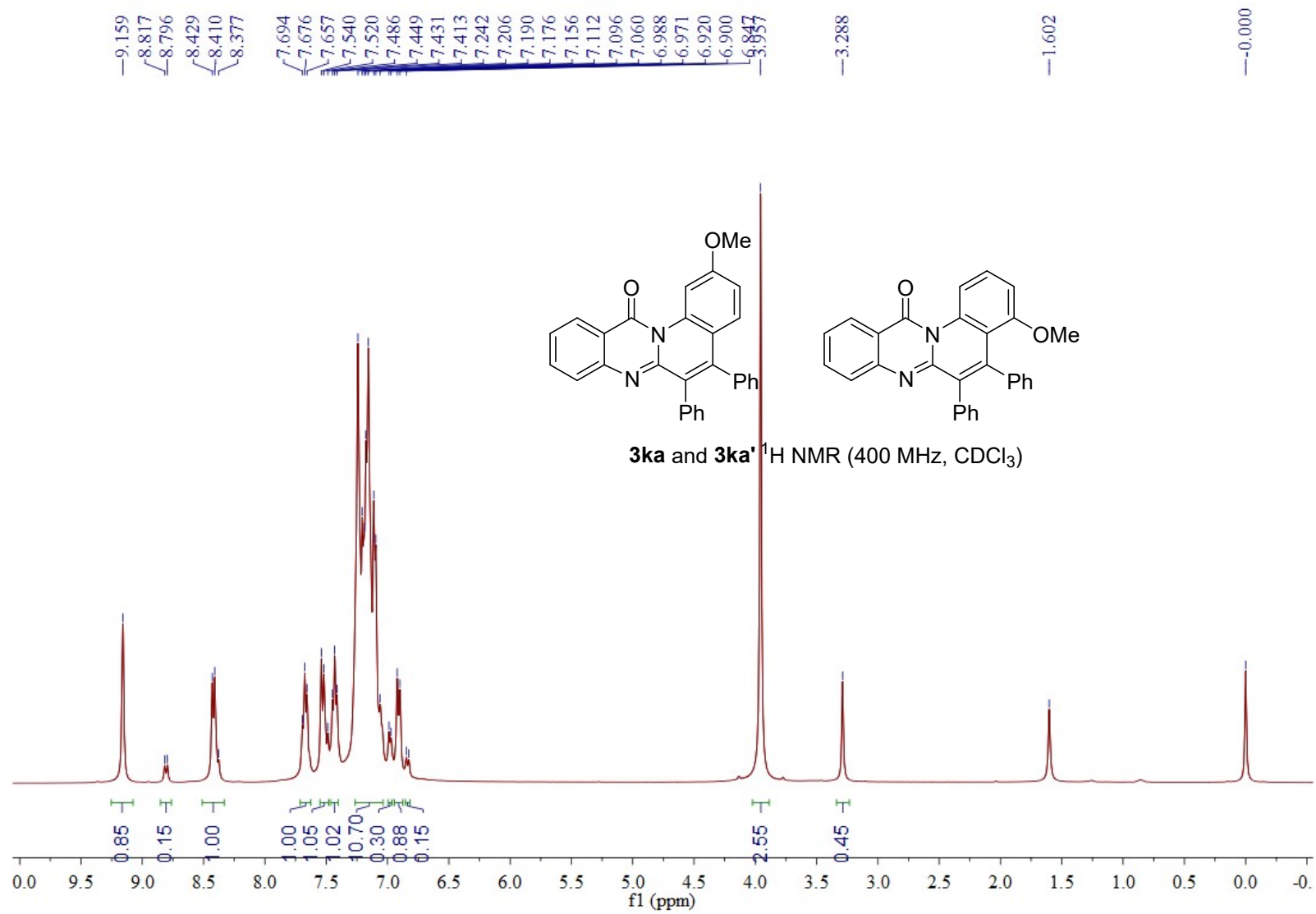




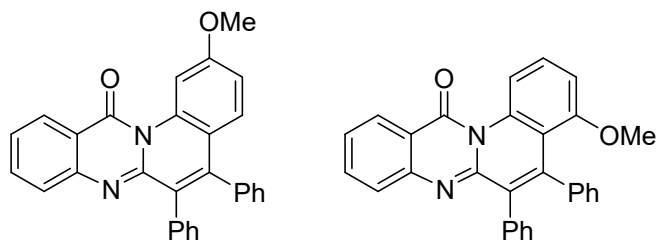




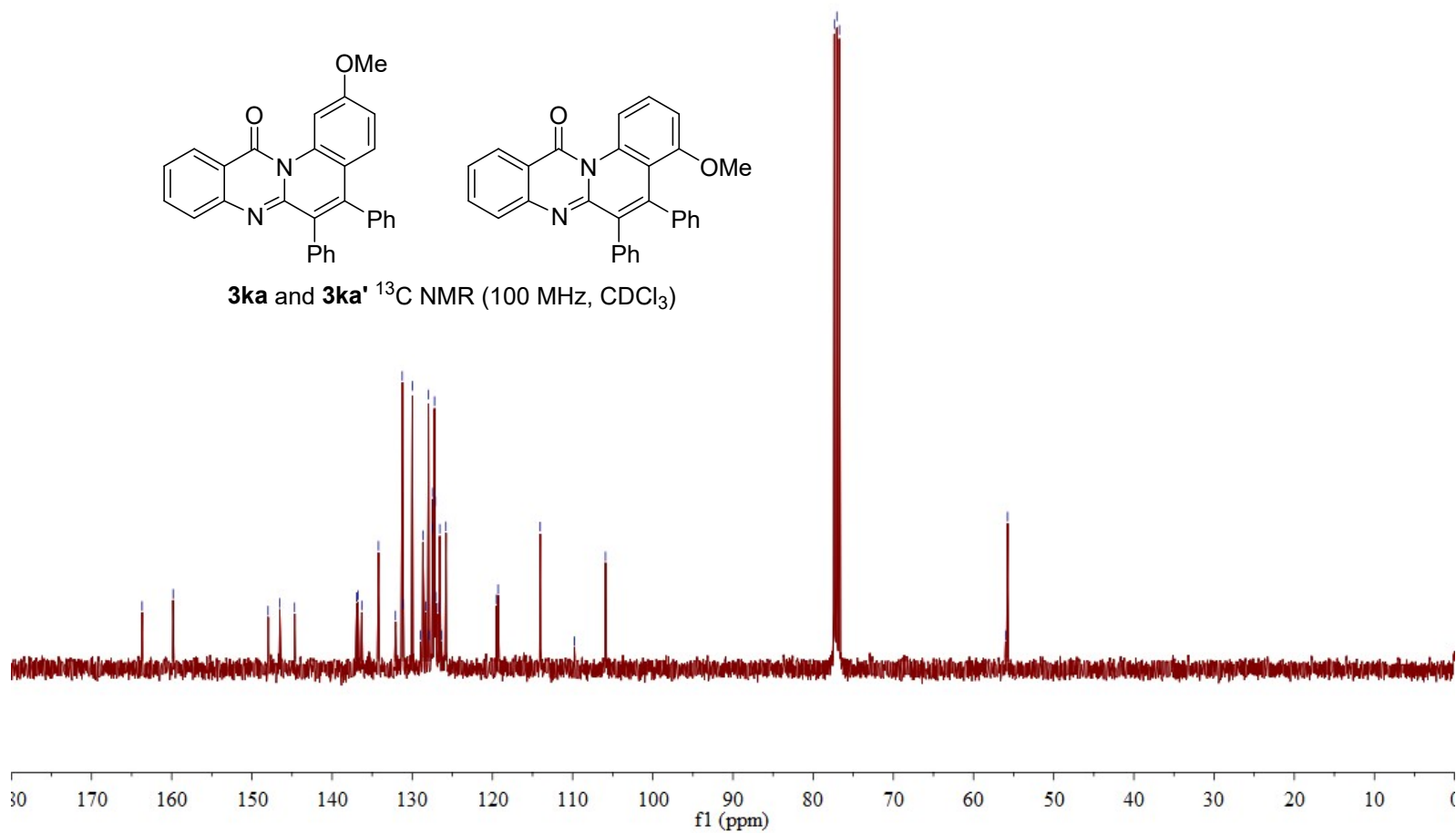


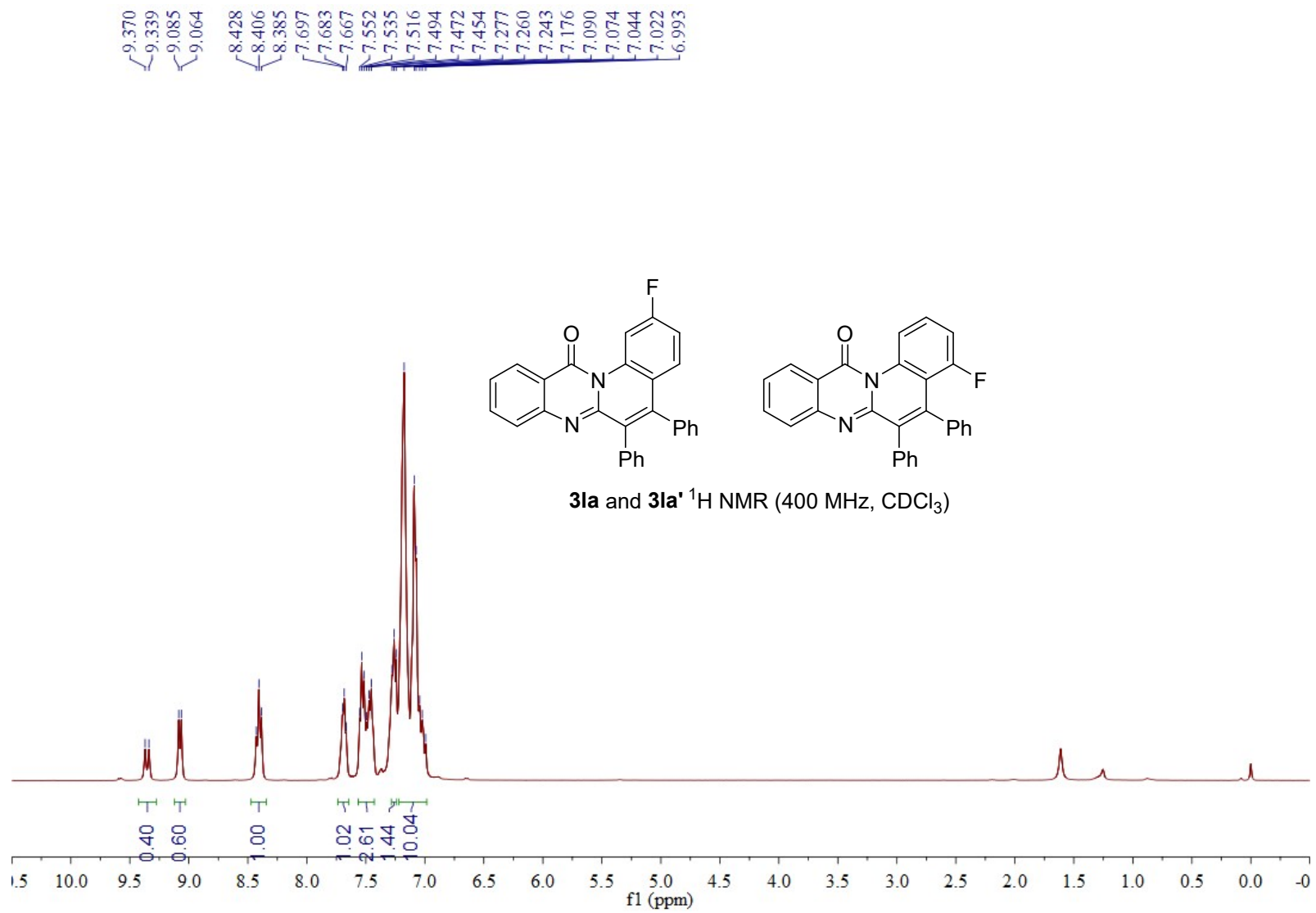


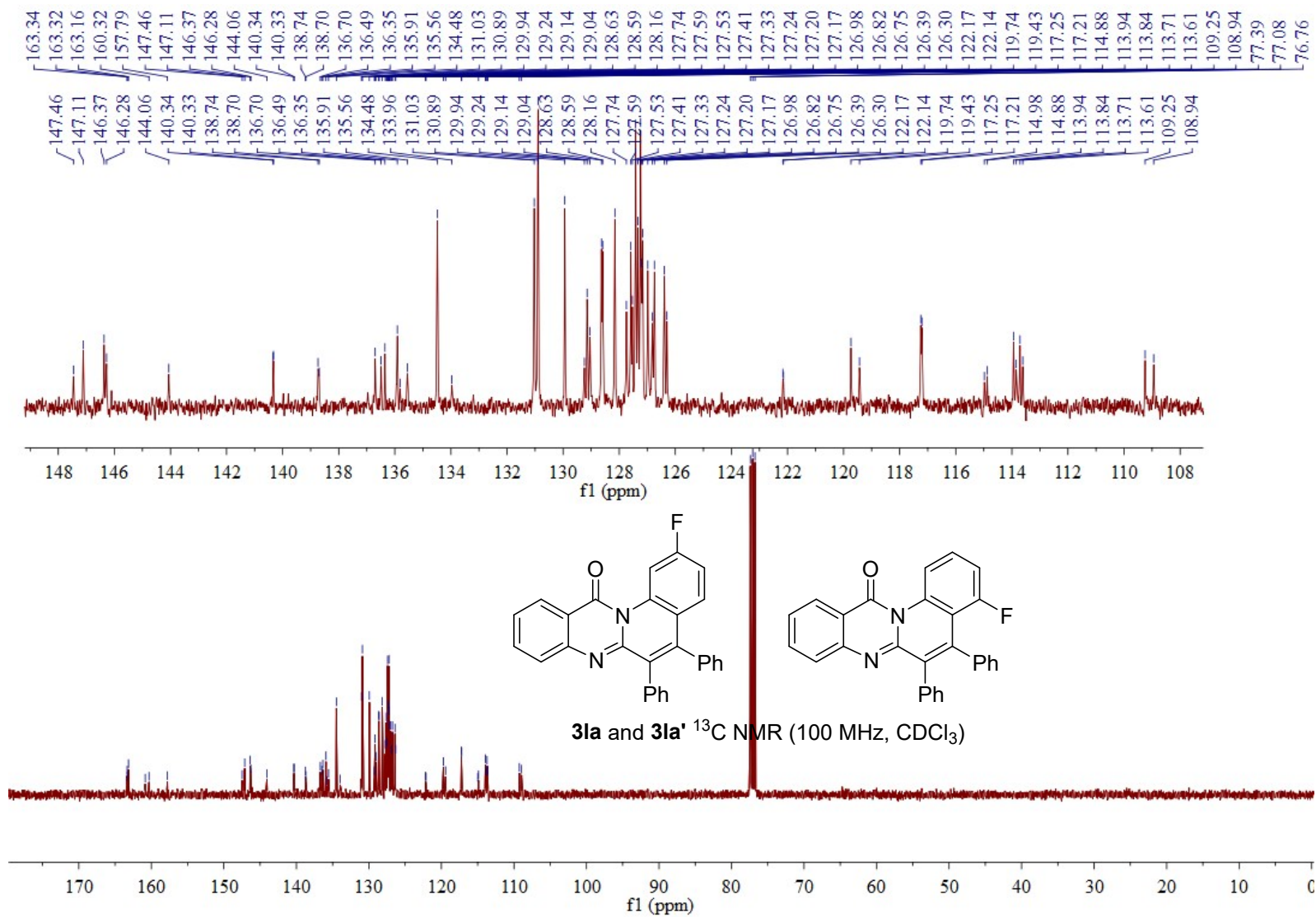
163.69
159.82
147.98
146.52
144.68
131.25
129.99
127.97
127.42
127.23
119.49
119.29
114.04
109.78
105.91
77.36
77.04
76.73
56.00
55.75



3ka and 3ka' ¹³C NMR (100 MHz, CDCl₃)



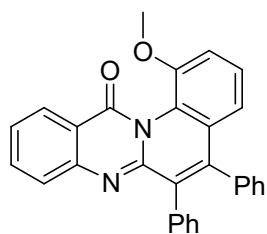




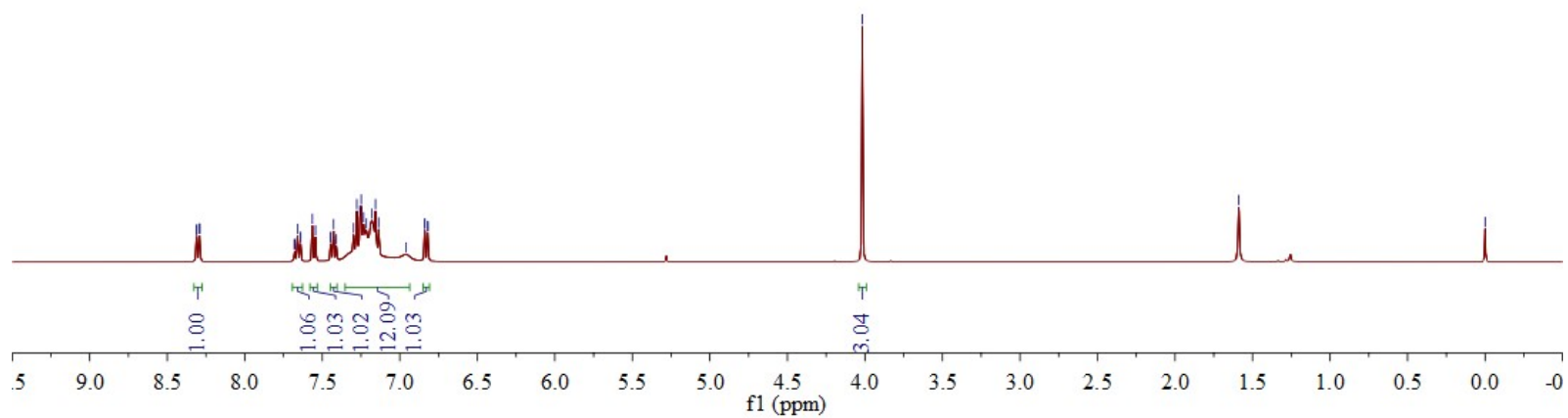
8.311
8.309
8.292
8.290
7.660
7.642
7.639
7.564
7.544
7.447
7.445
7.427
7.409
7.298
7.278
7.257
7.249
7.233
7.216
7.181
7.157
7.137
6.840
6.838
6.820
6.819

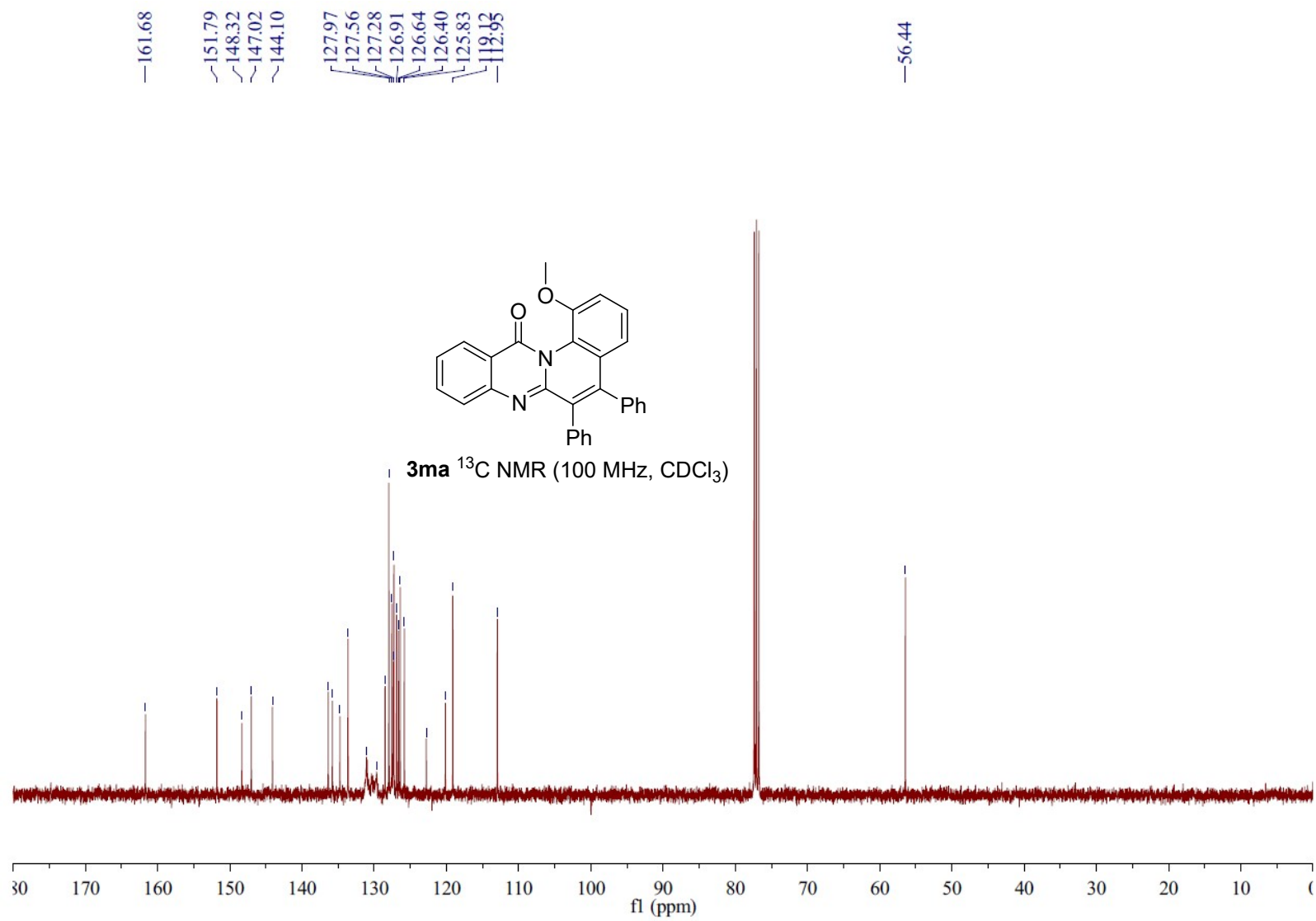
—1.589

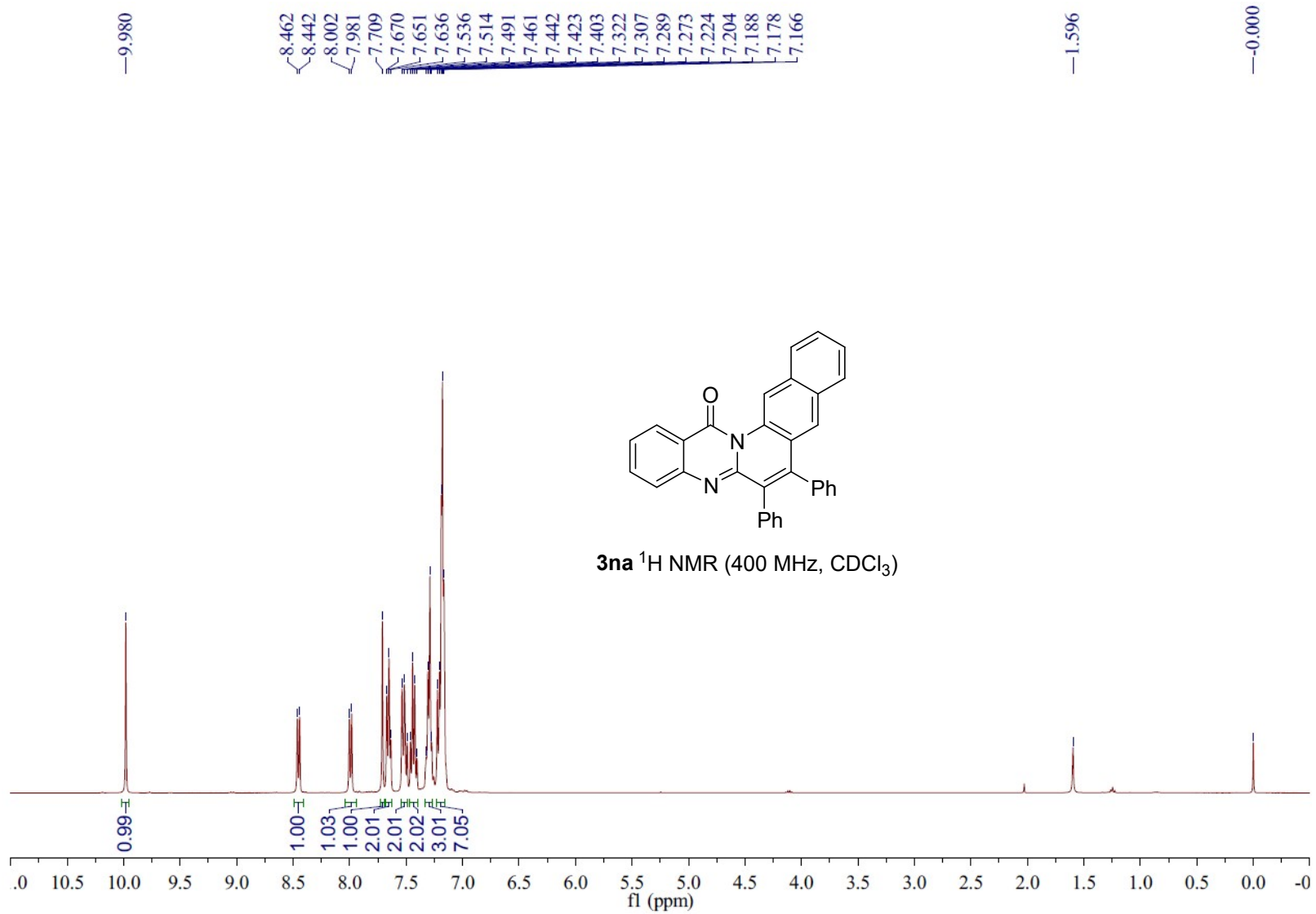
—0.000

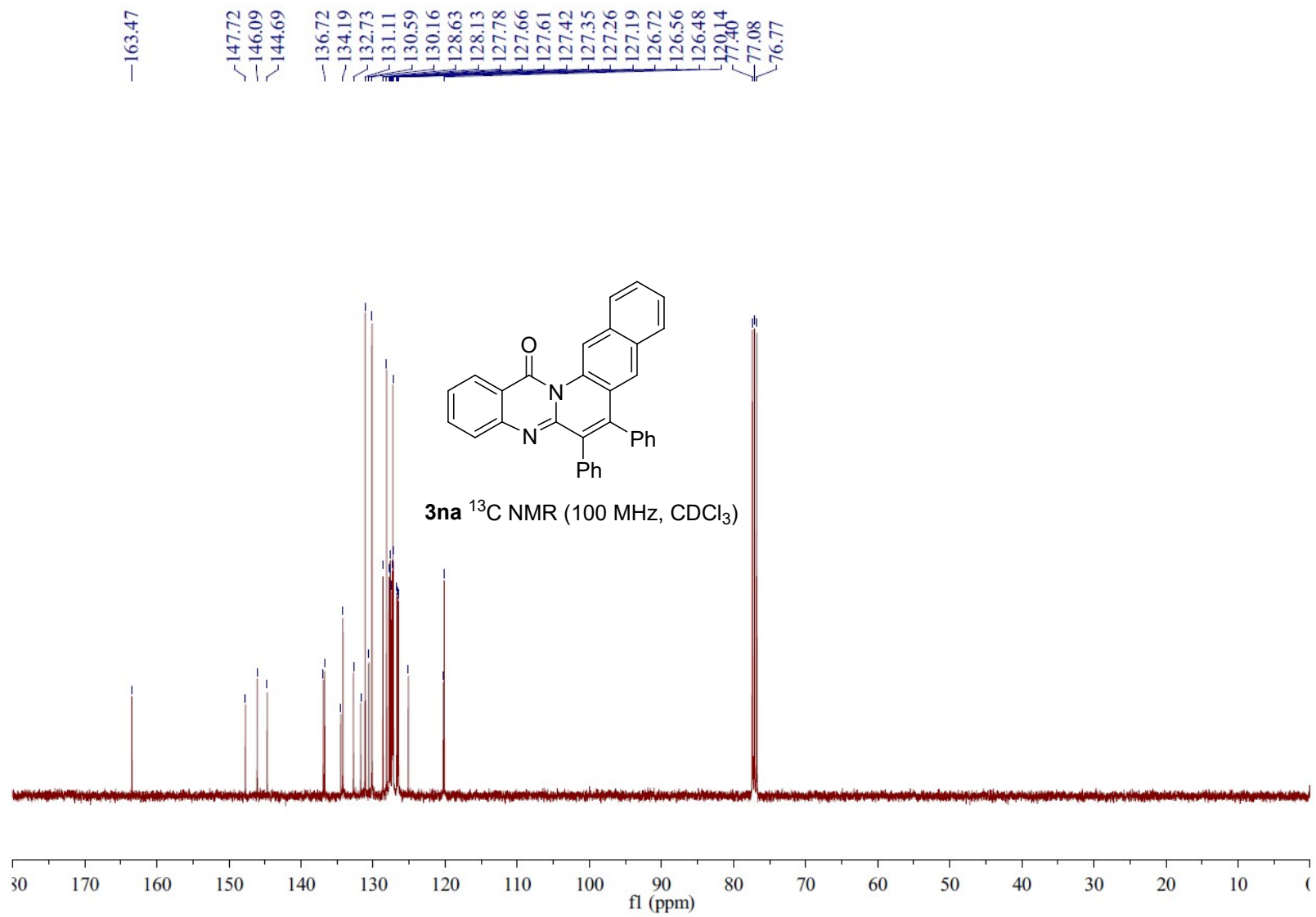


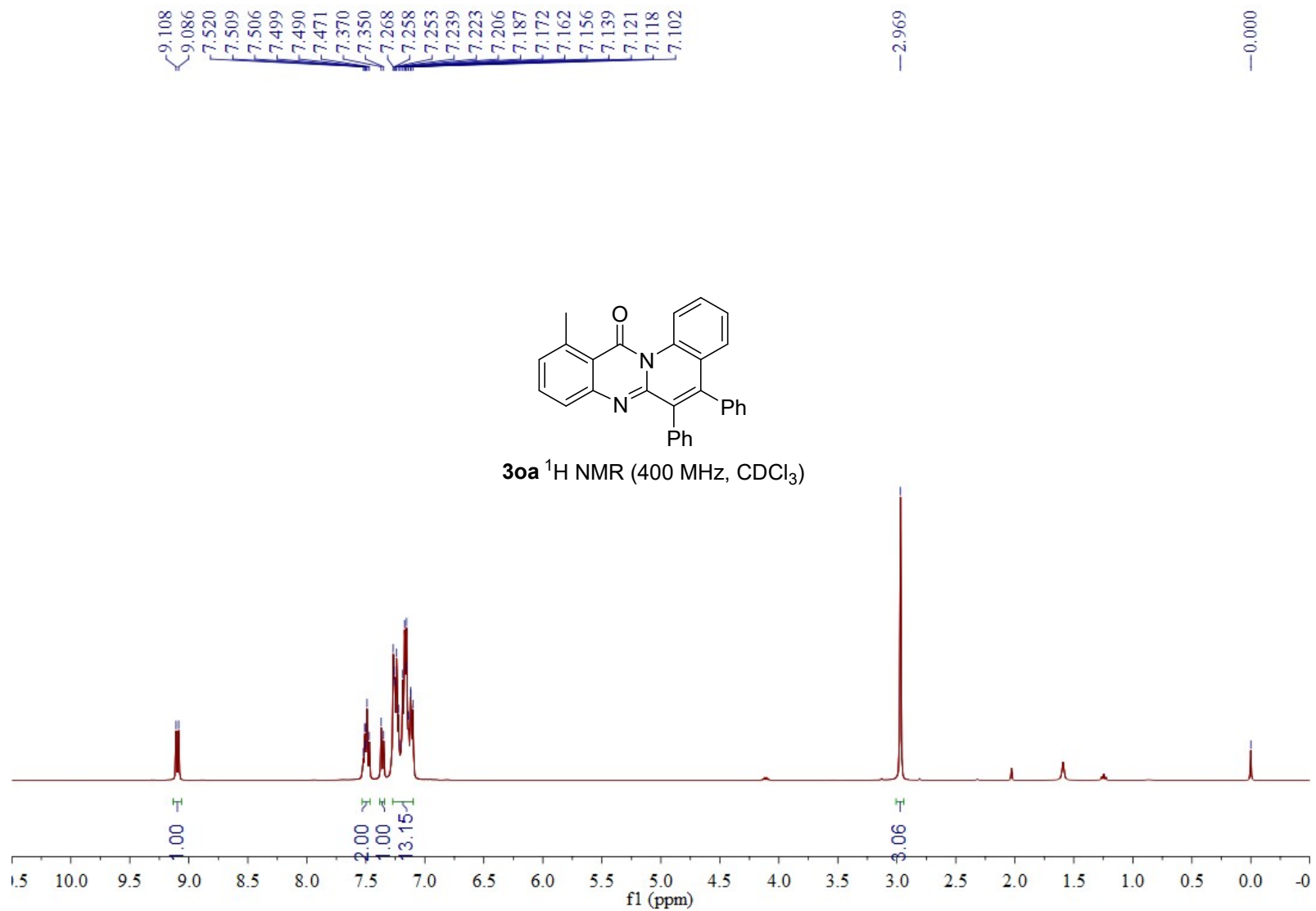
3ma ¹H NMR (400 MHz, CDCl₃)

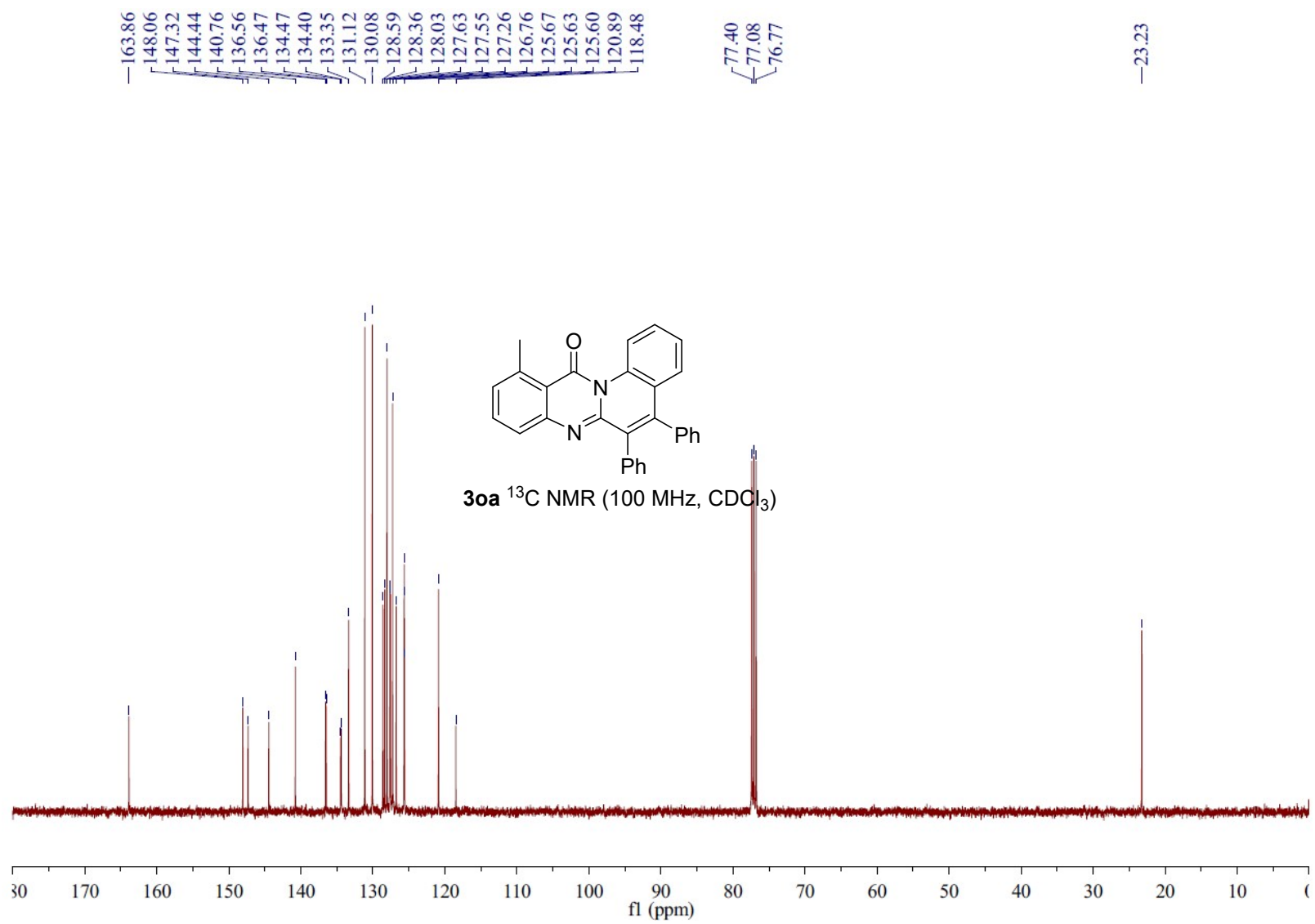


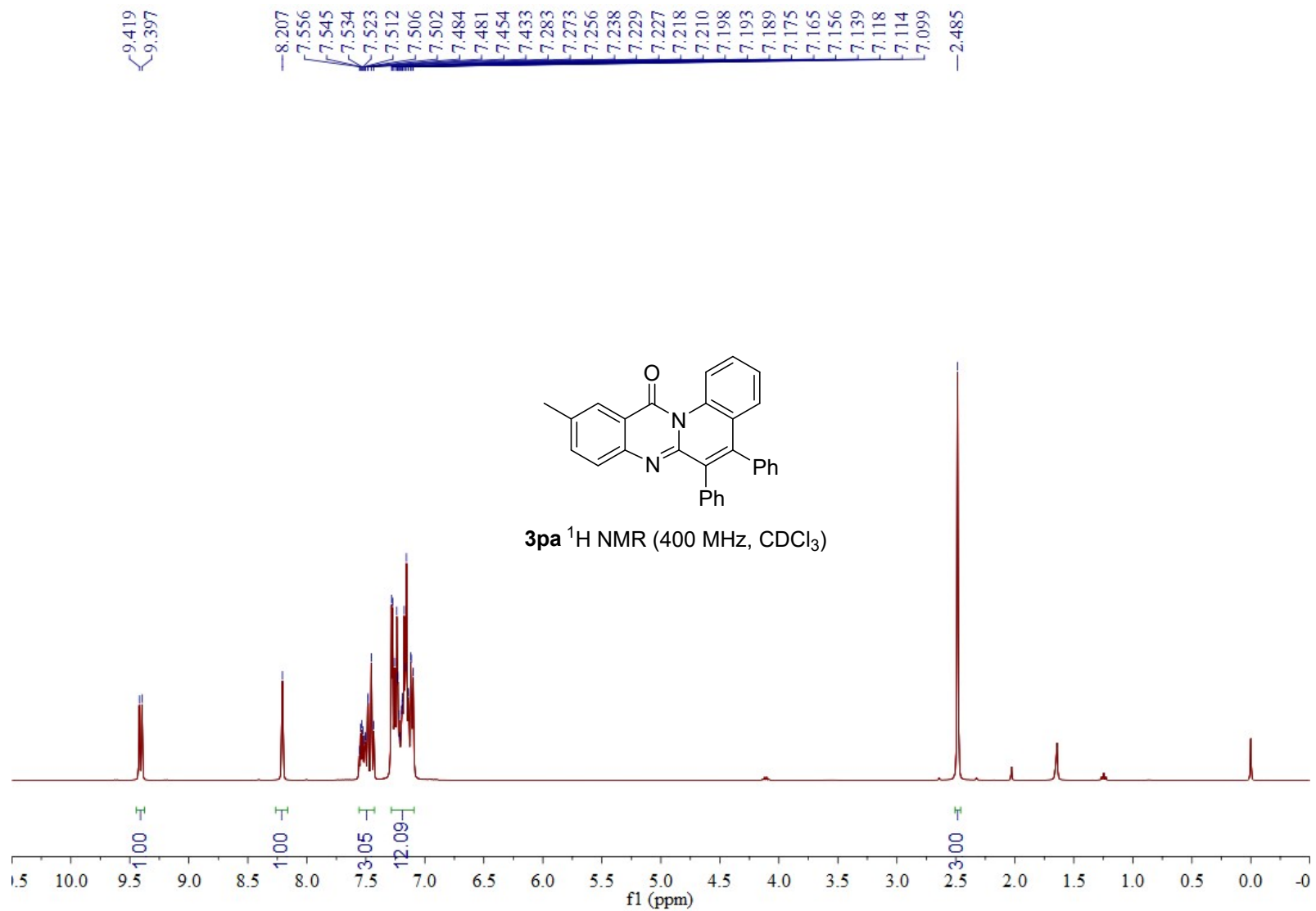


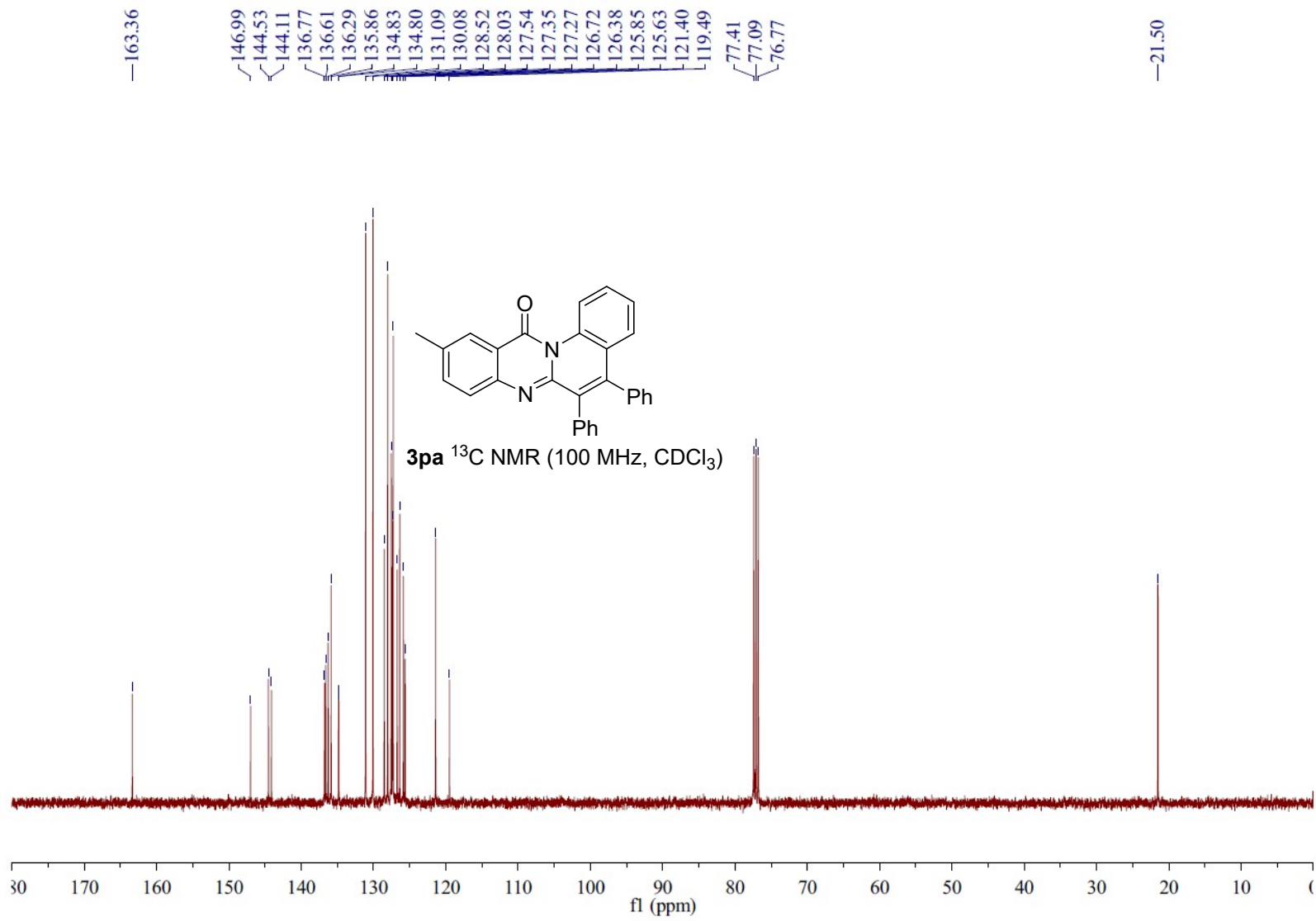


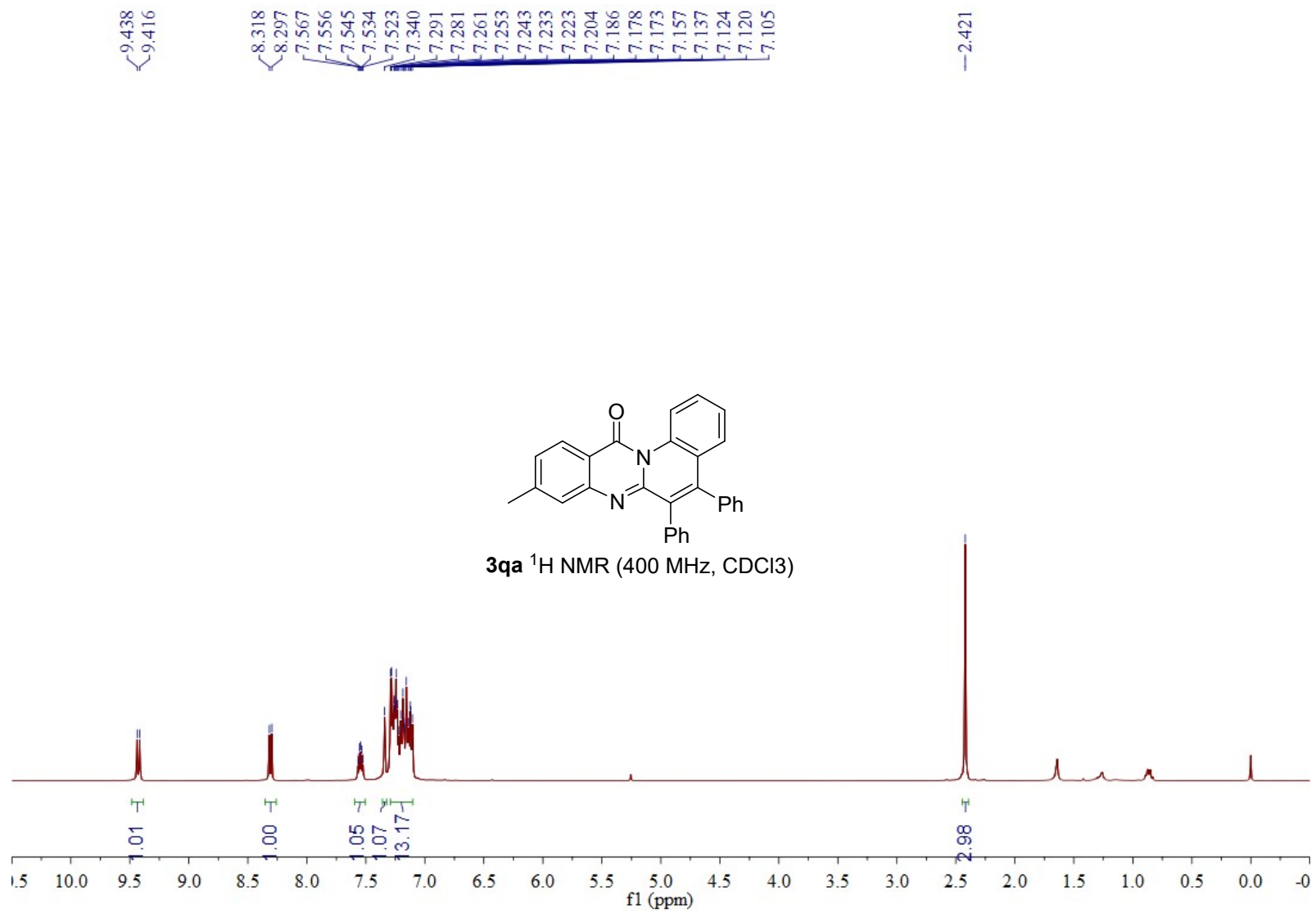


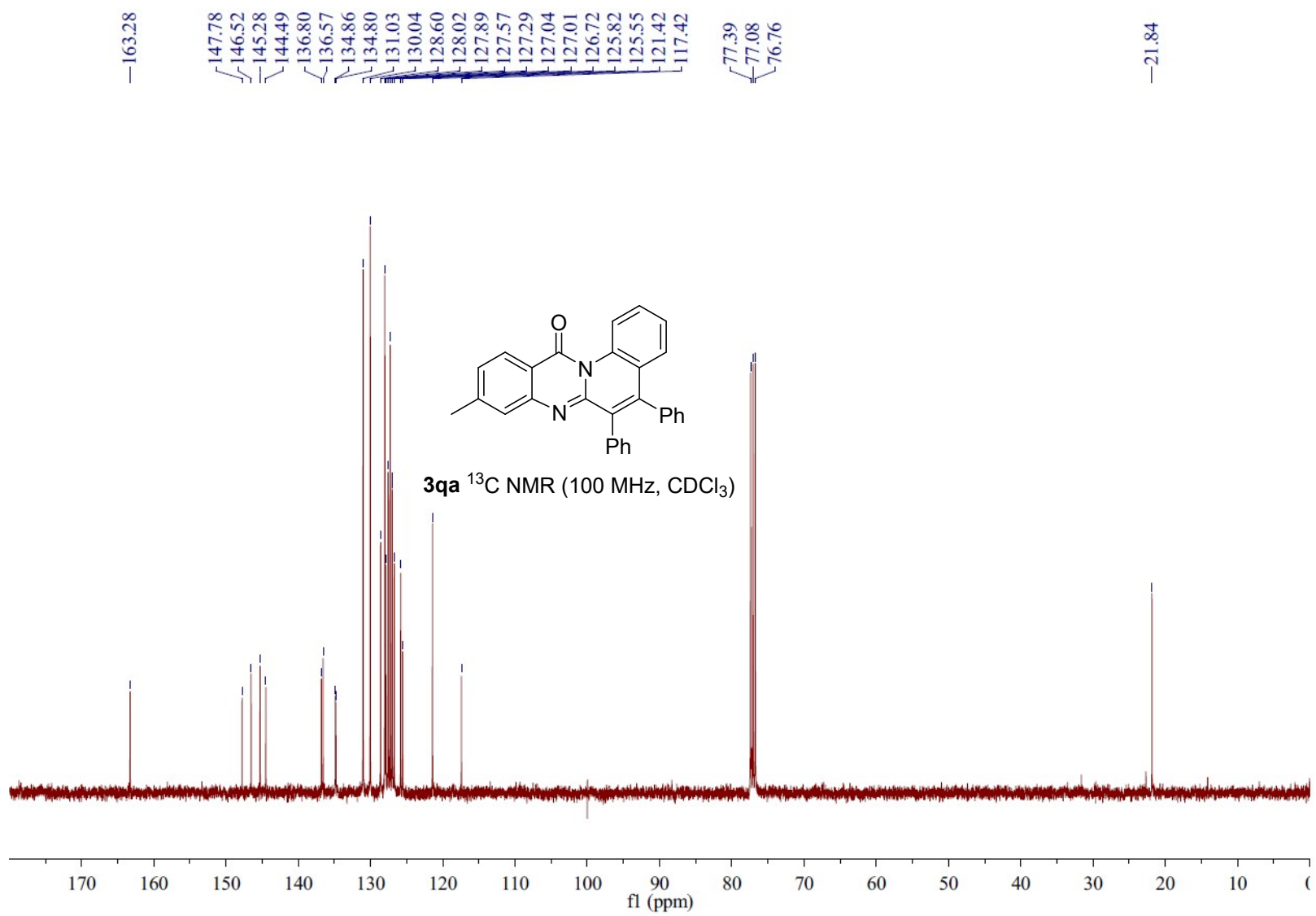


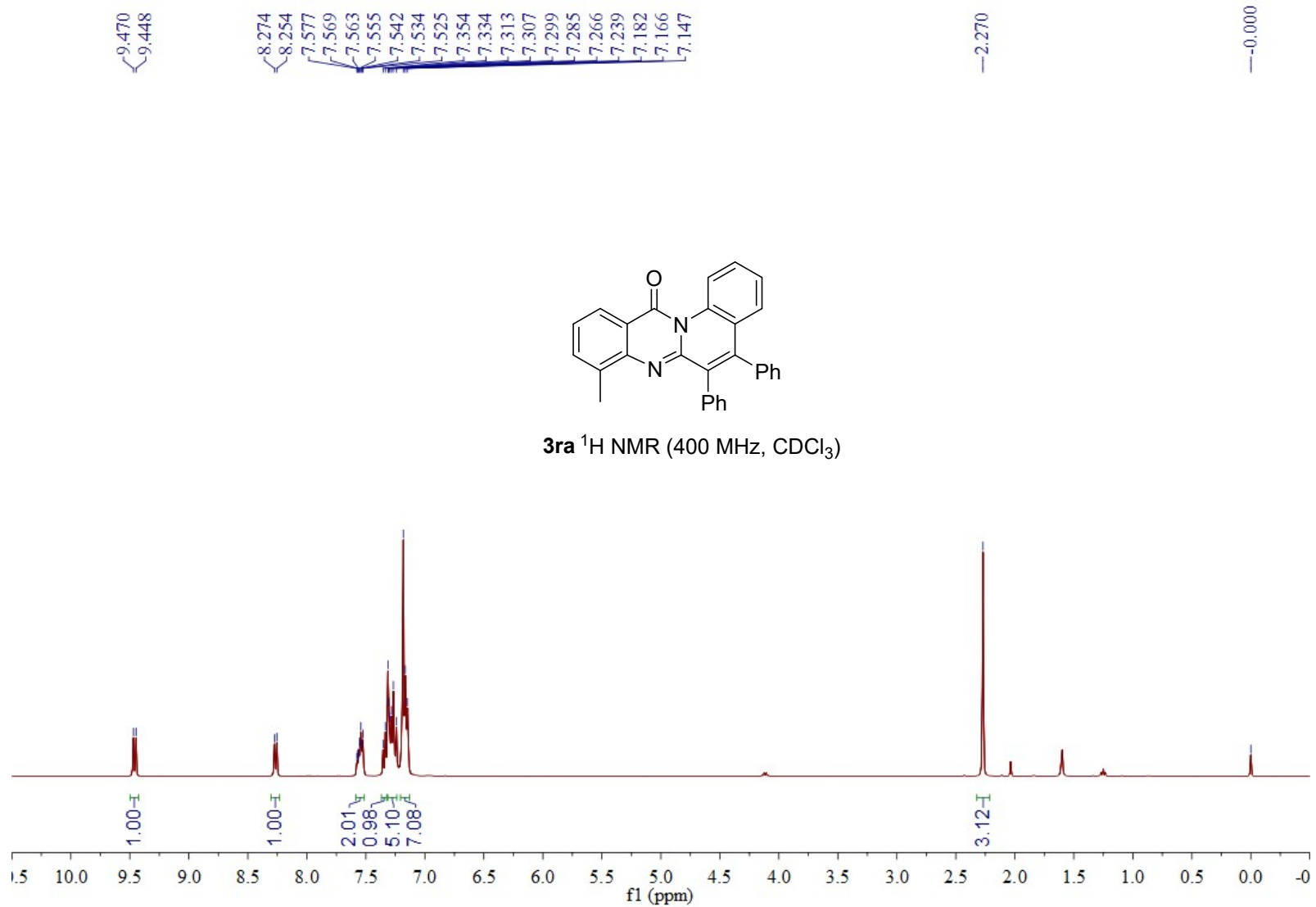


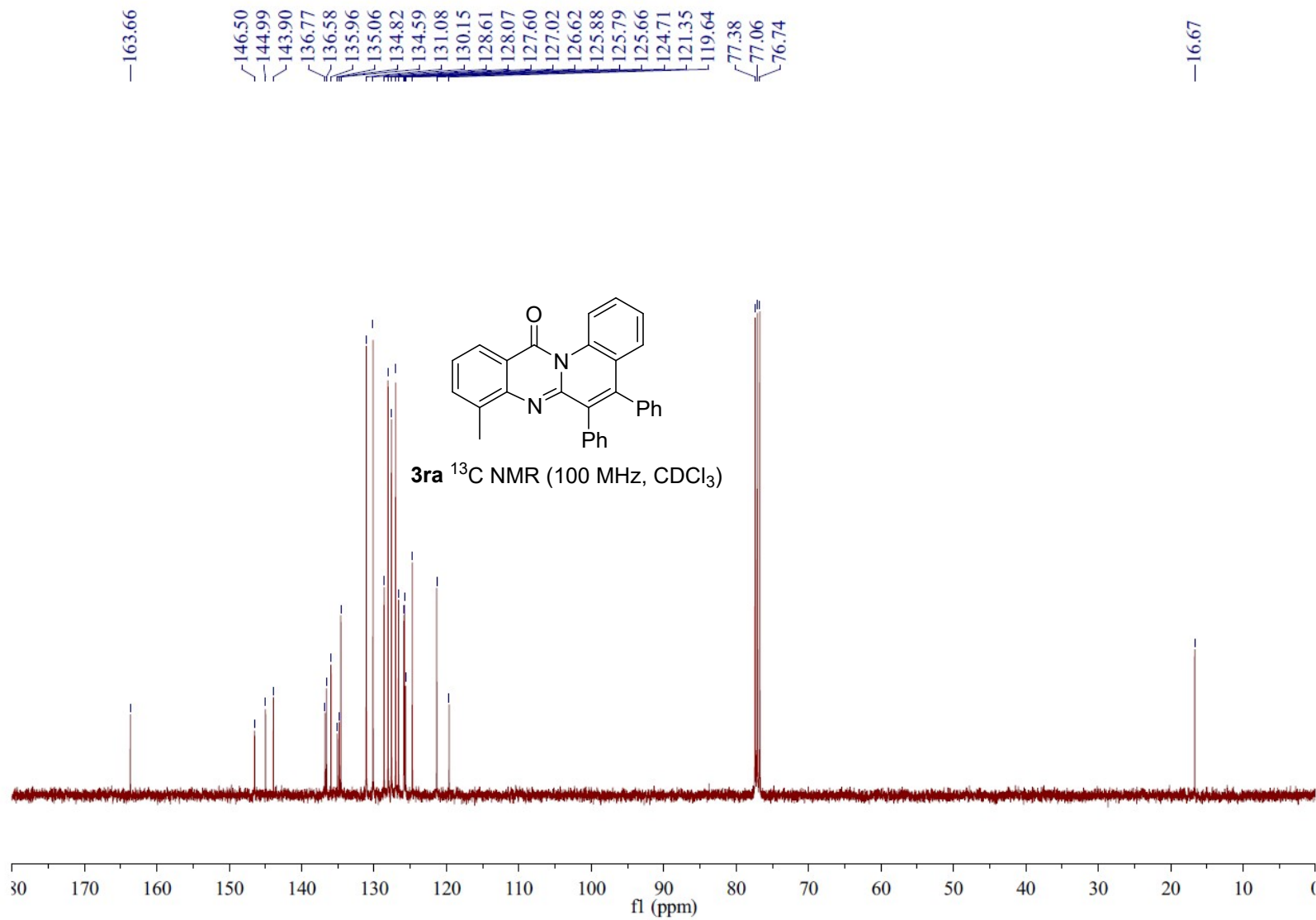


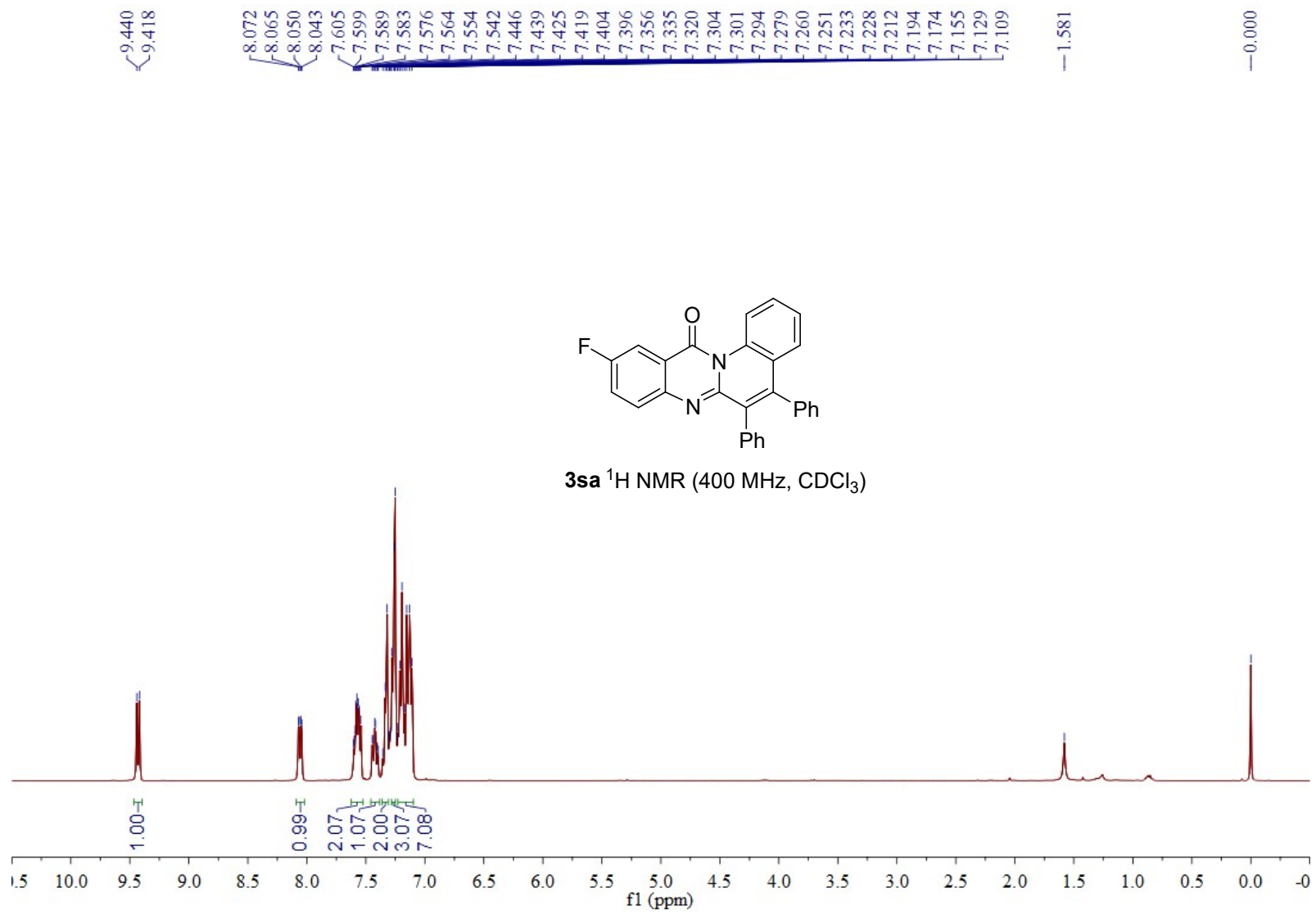


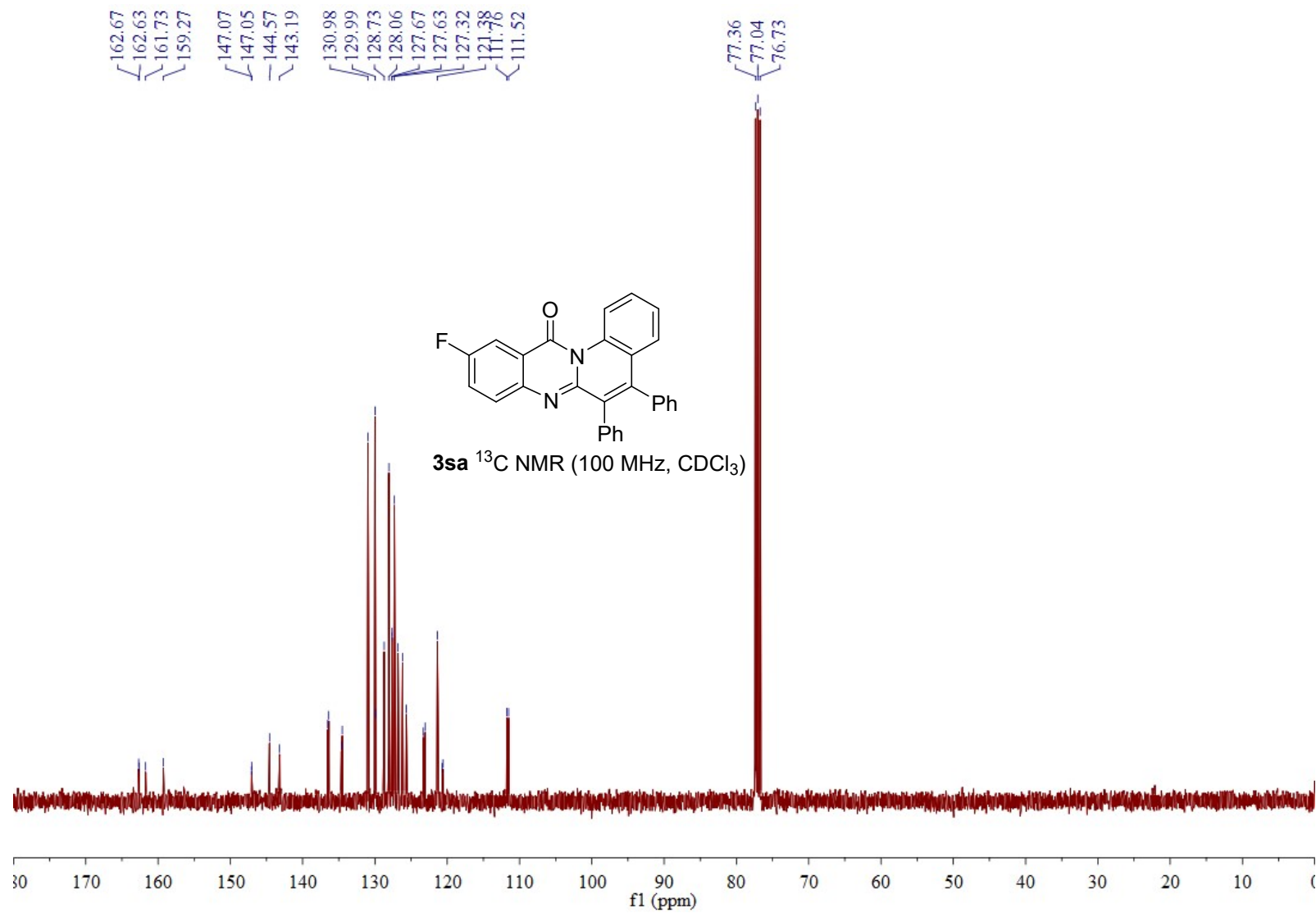


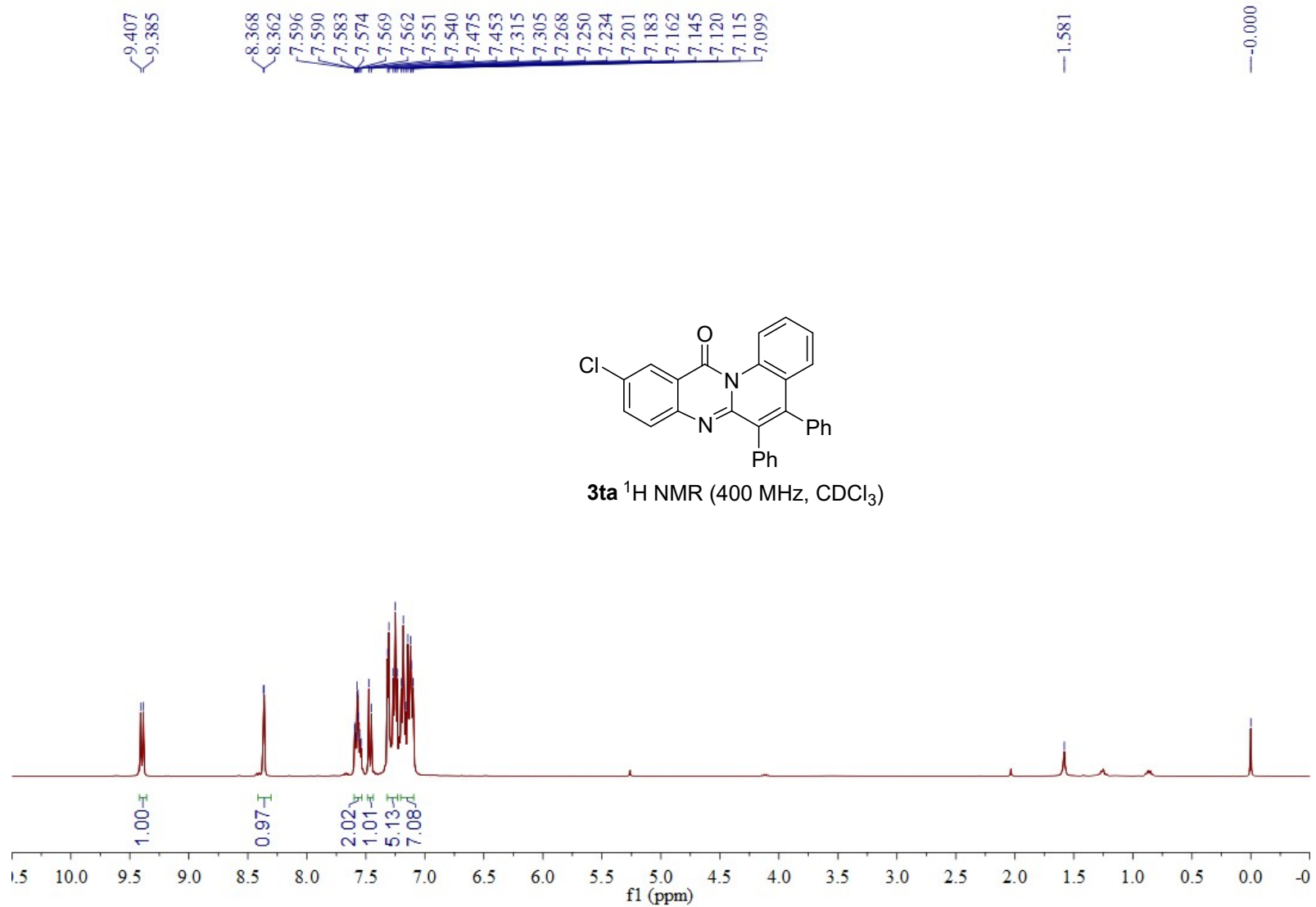


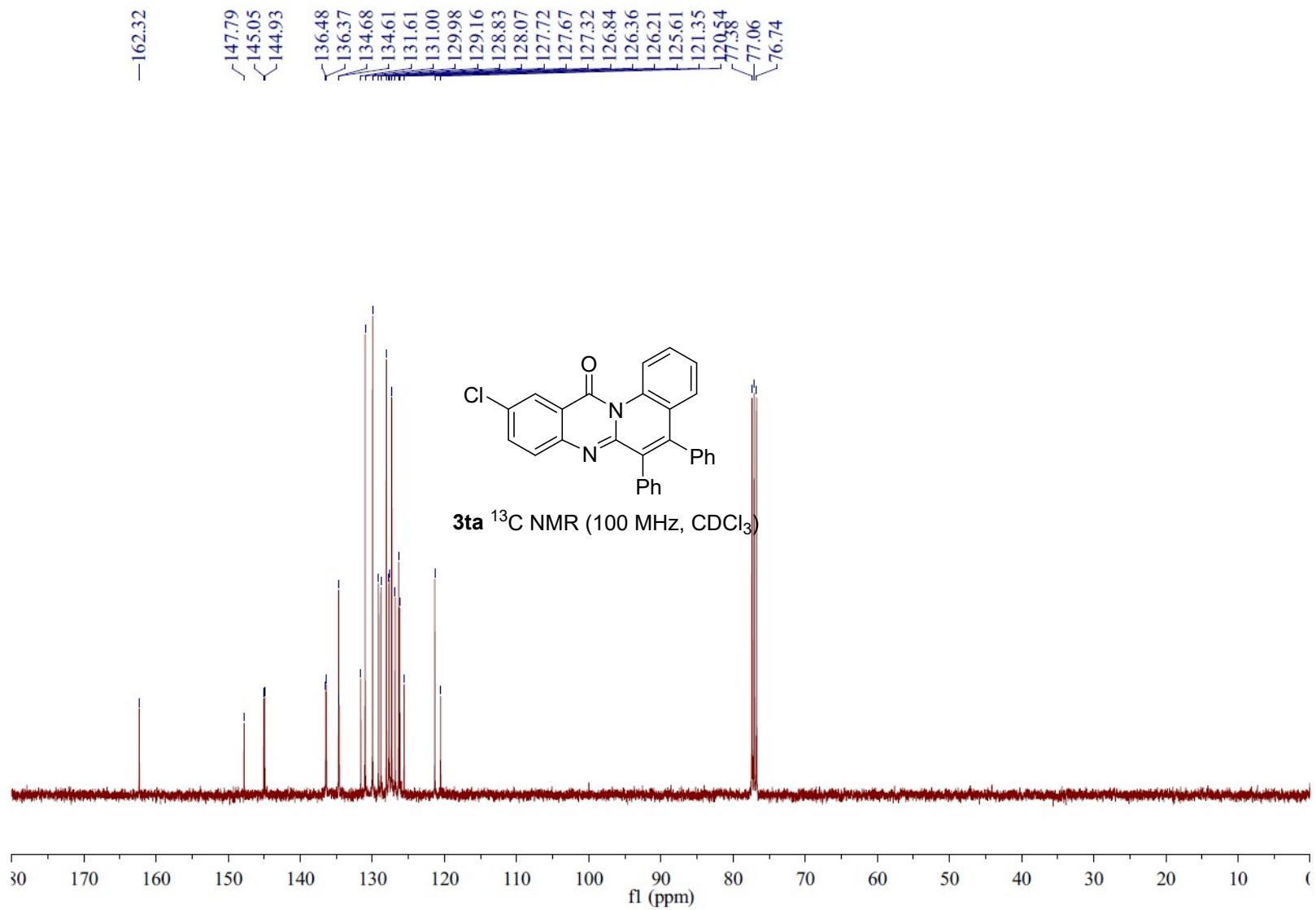






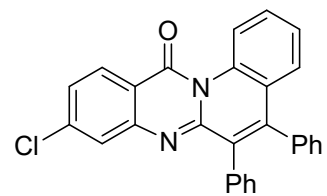




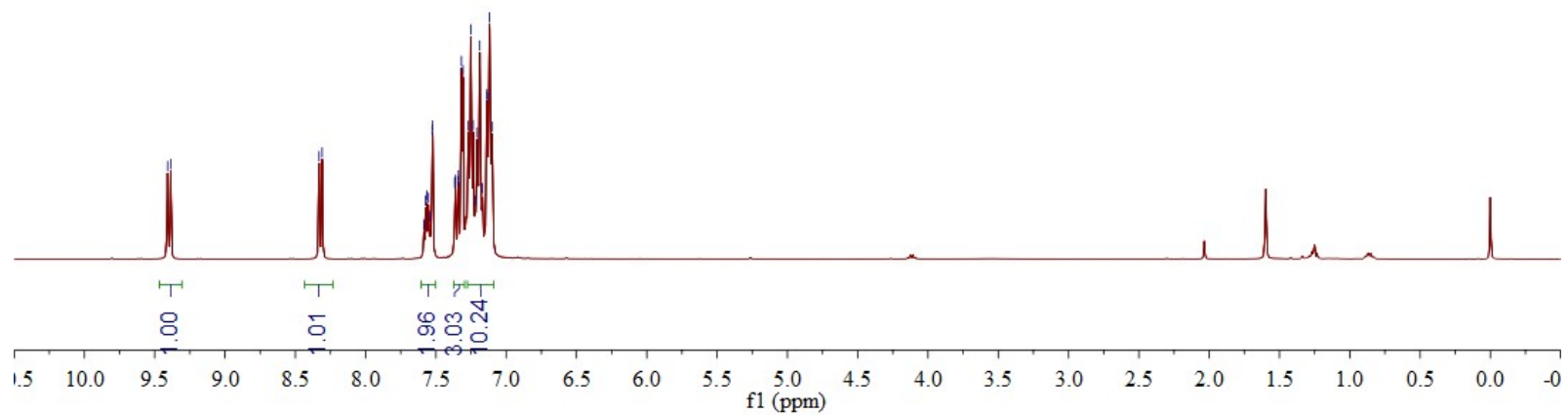


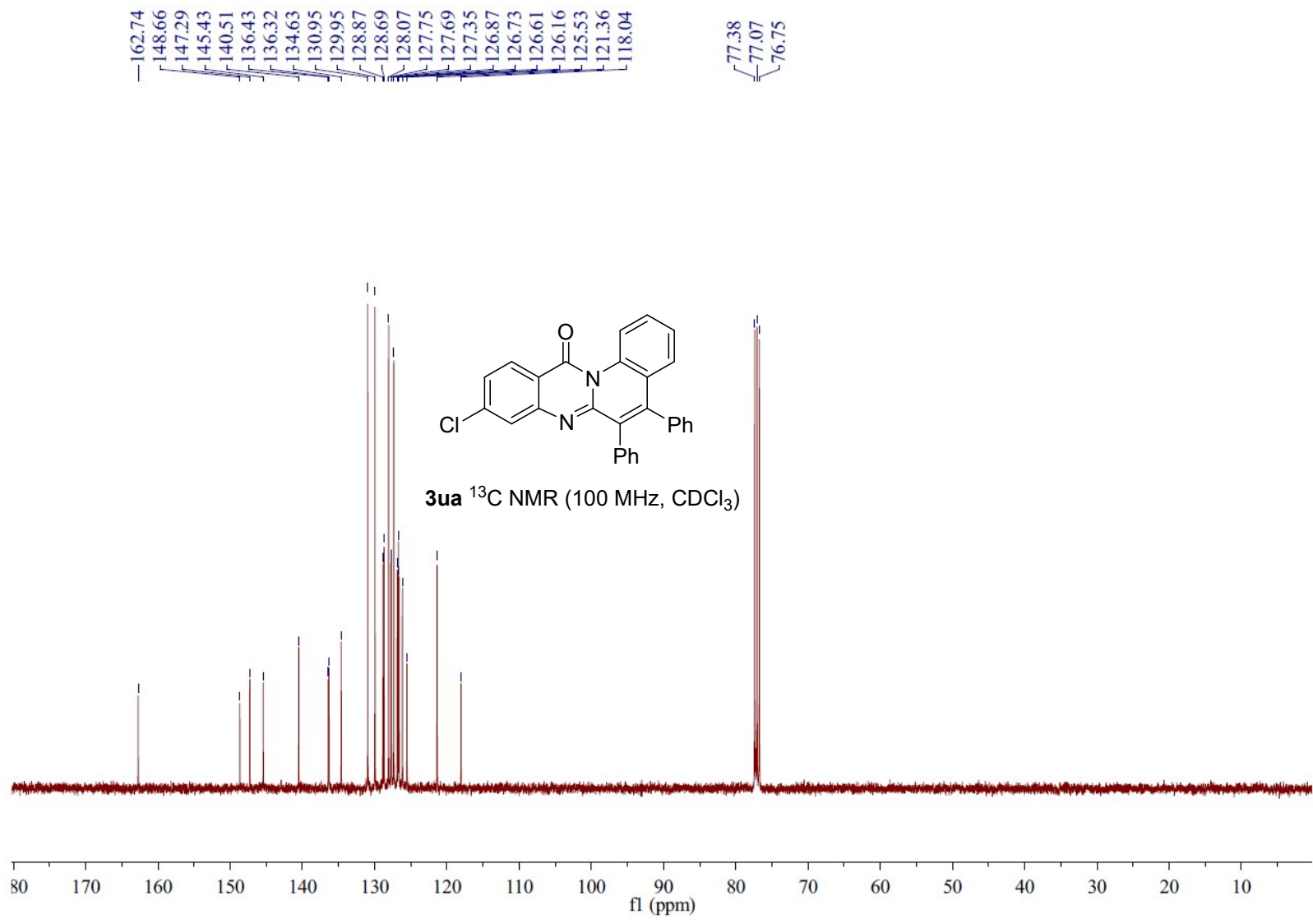
9.408
9.386

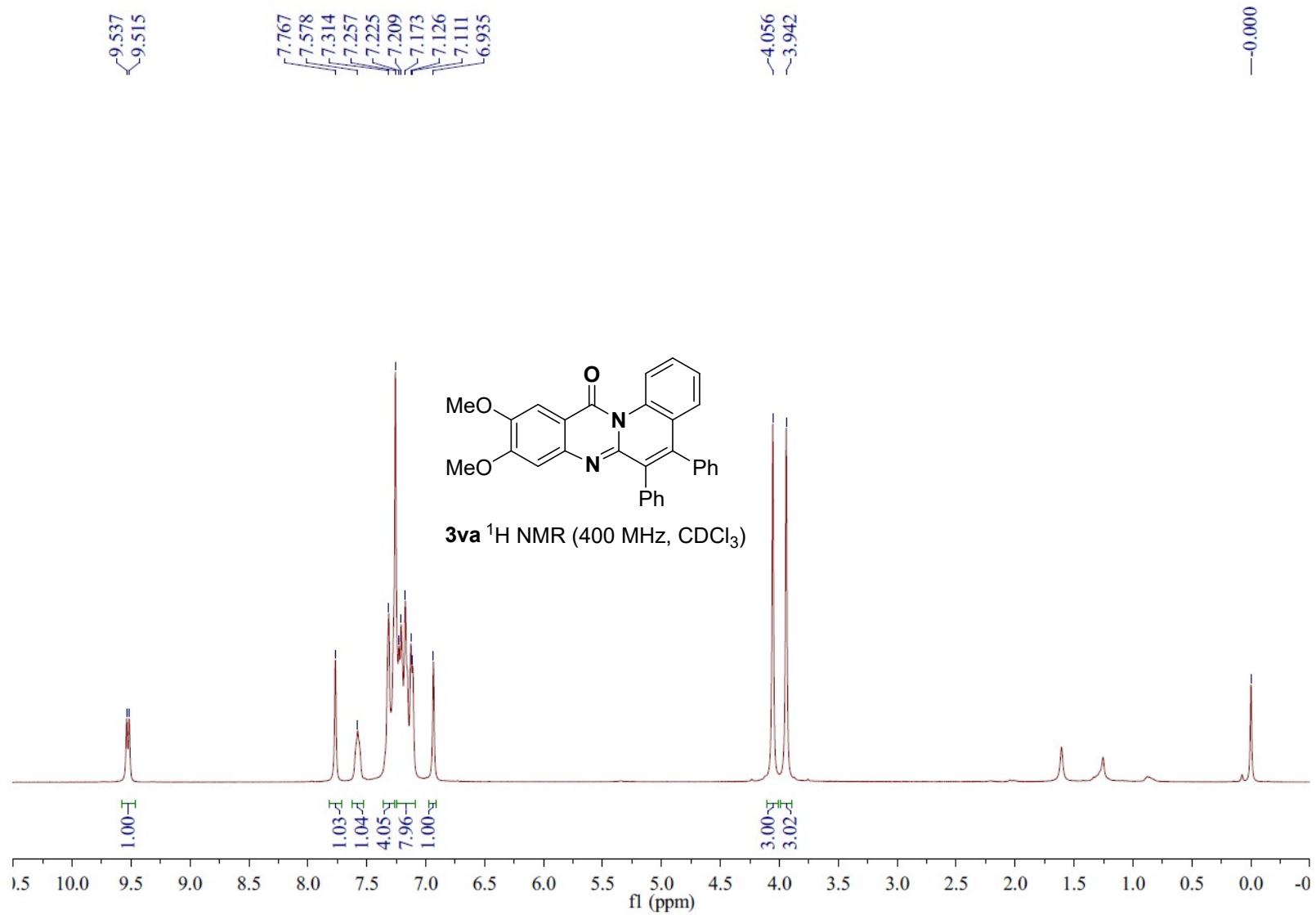
8.331
8.309
7.585
7.574
7.563
7.552
7.541
7.526
7.523
7.365
7.364
7.361
7.344
7.339
7.318
7.307
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7.251
7.236
7.222
7.206
7.188
7.169
7.137
7.134
7.119
7.102

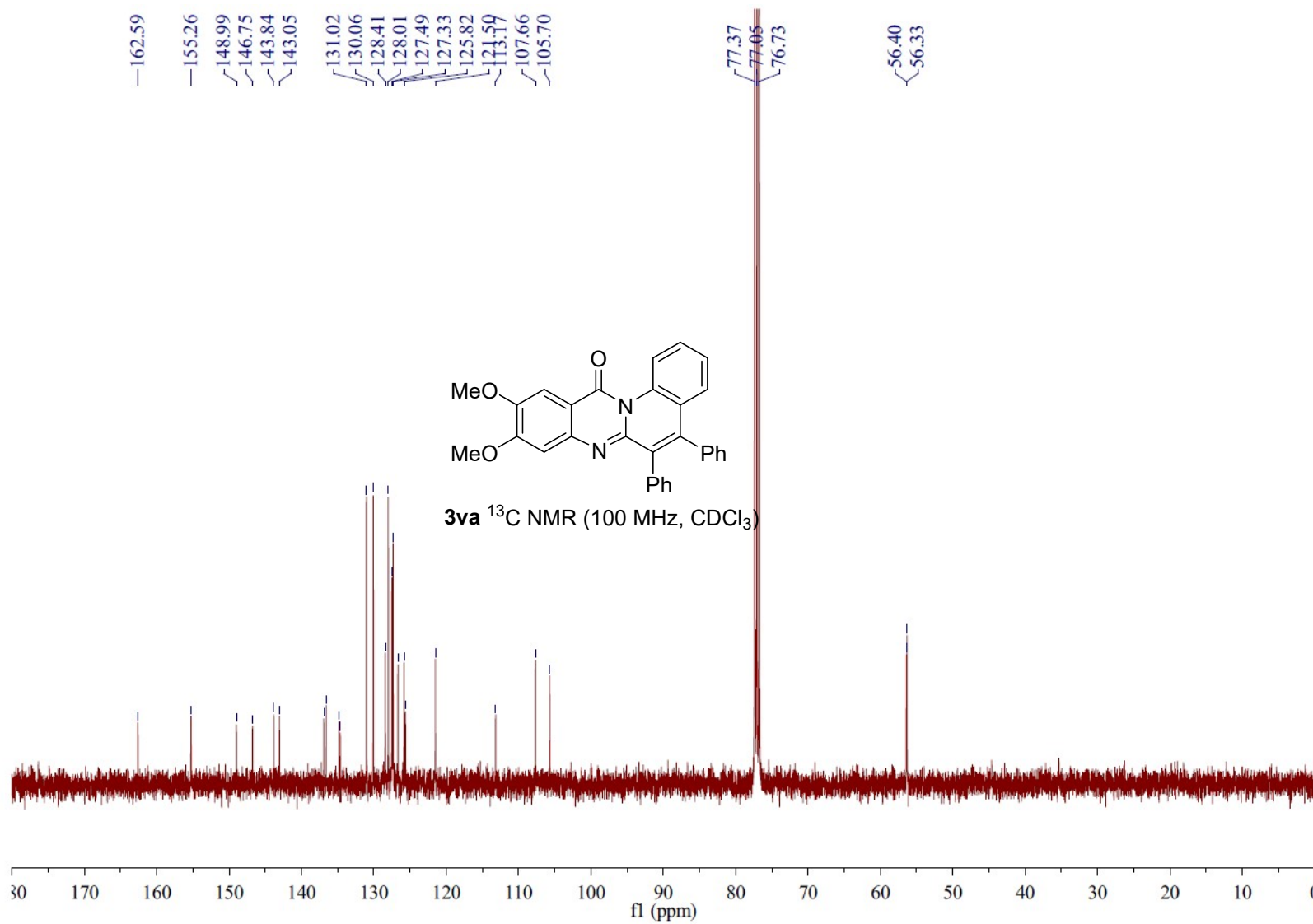


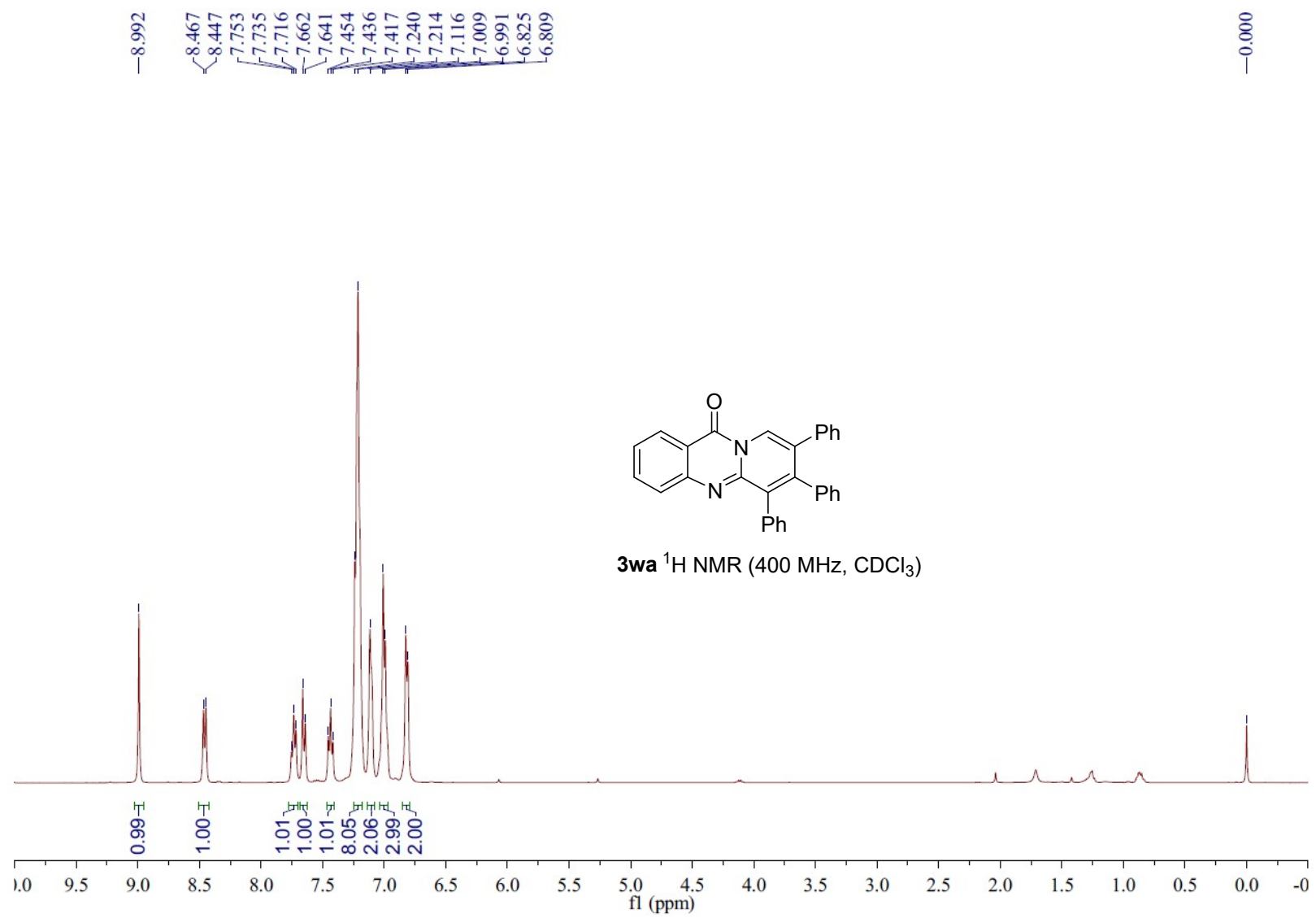
3ua ^1H NMR (400 MHz, CDCl_3)

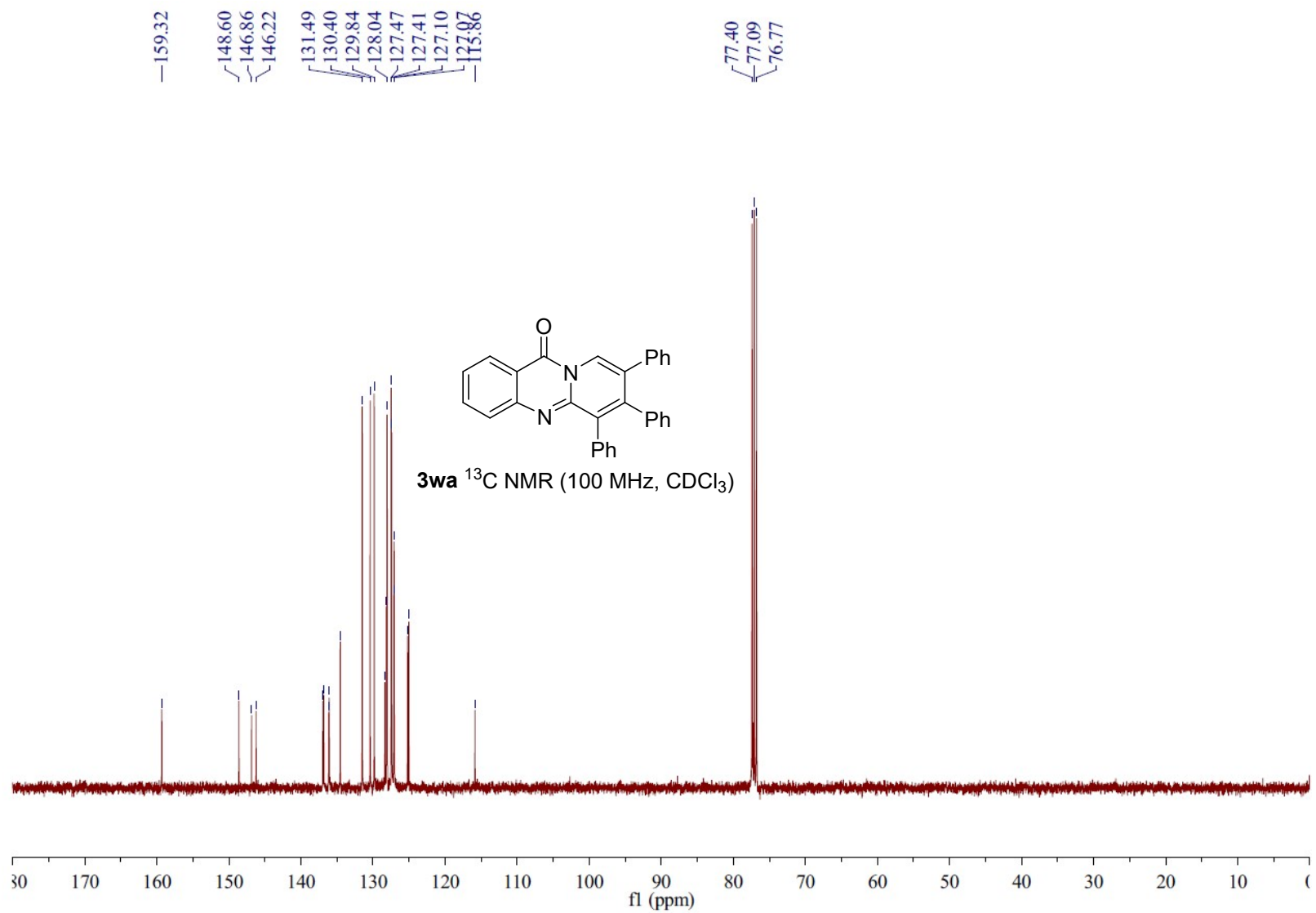


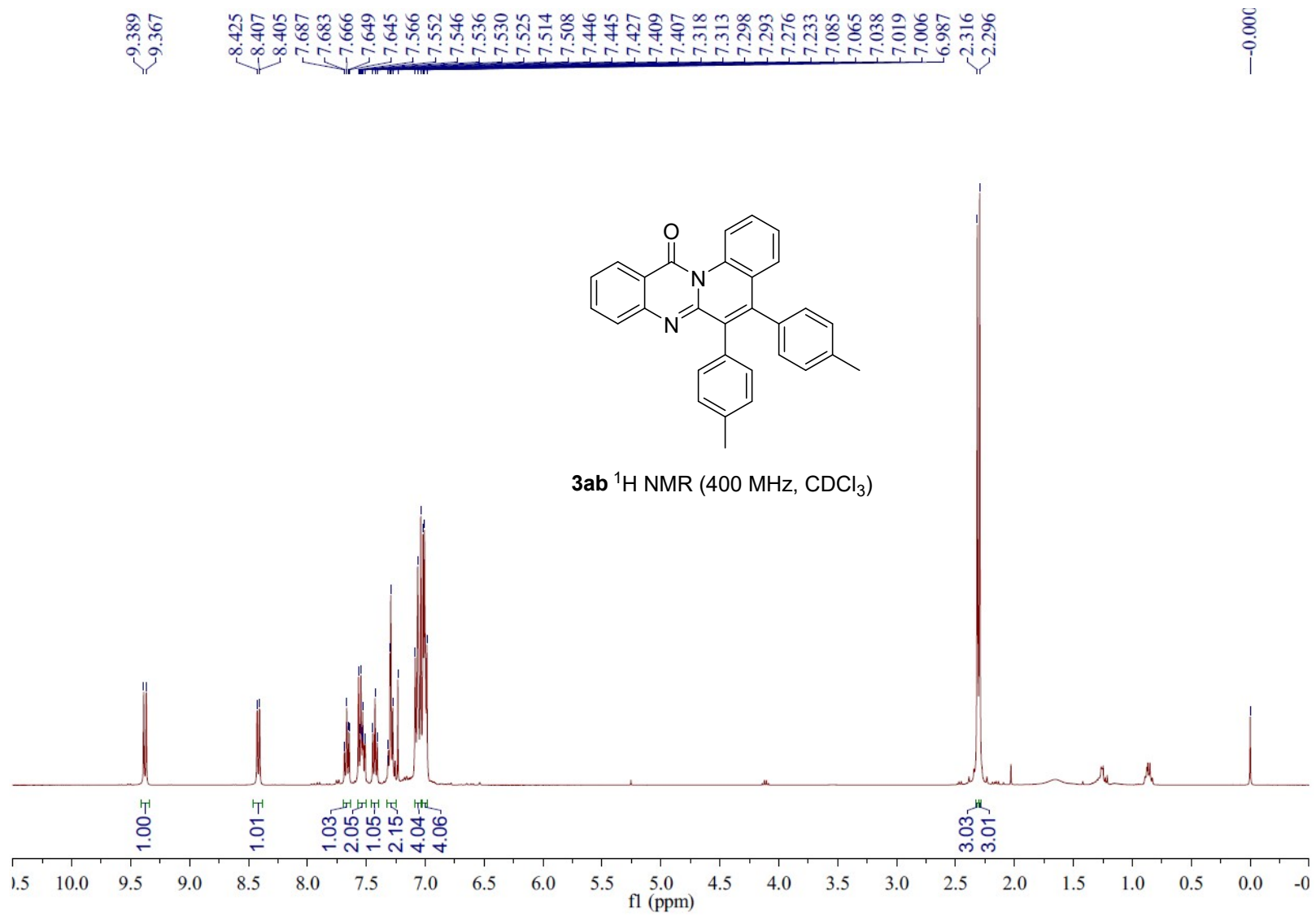


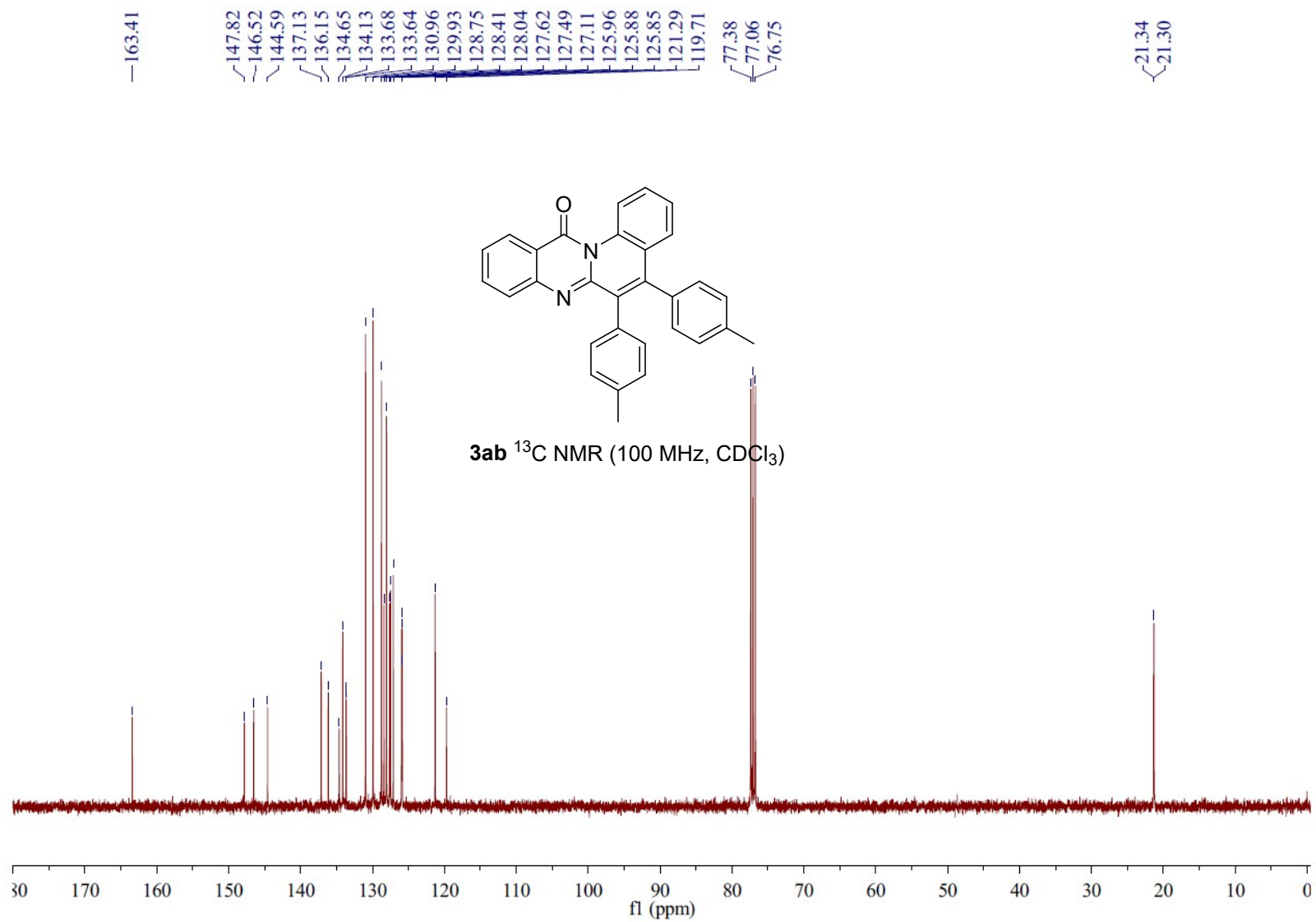


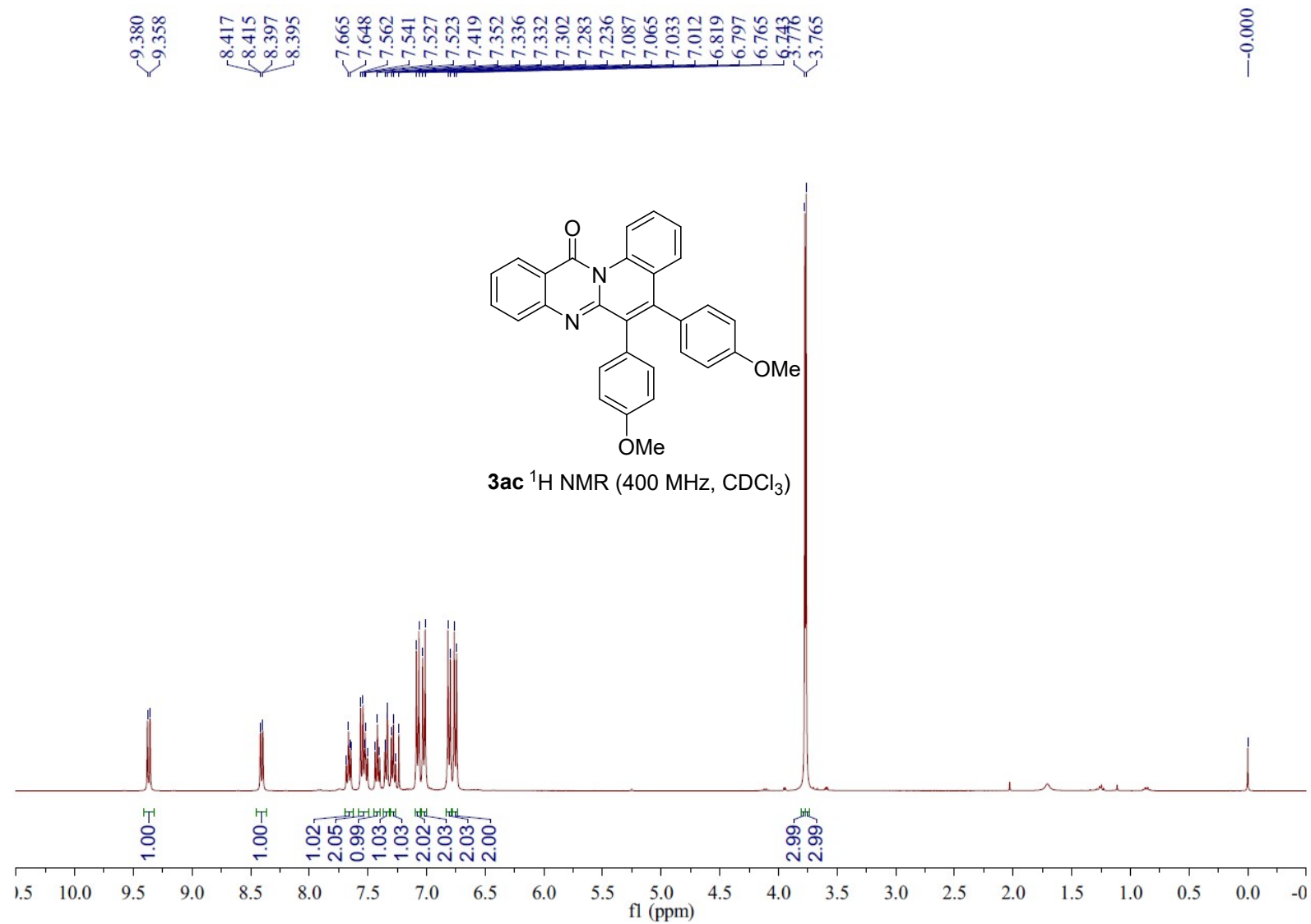


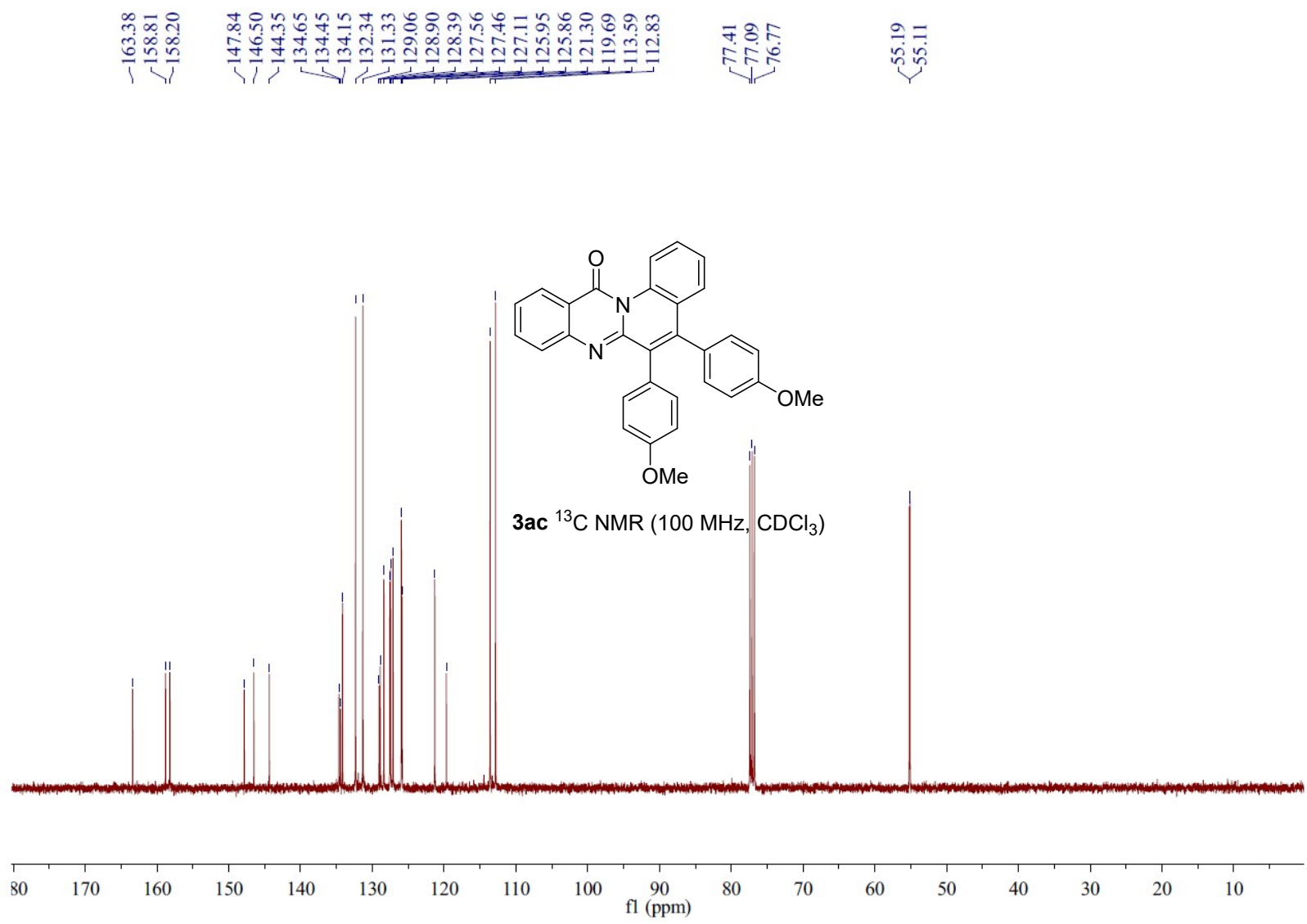


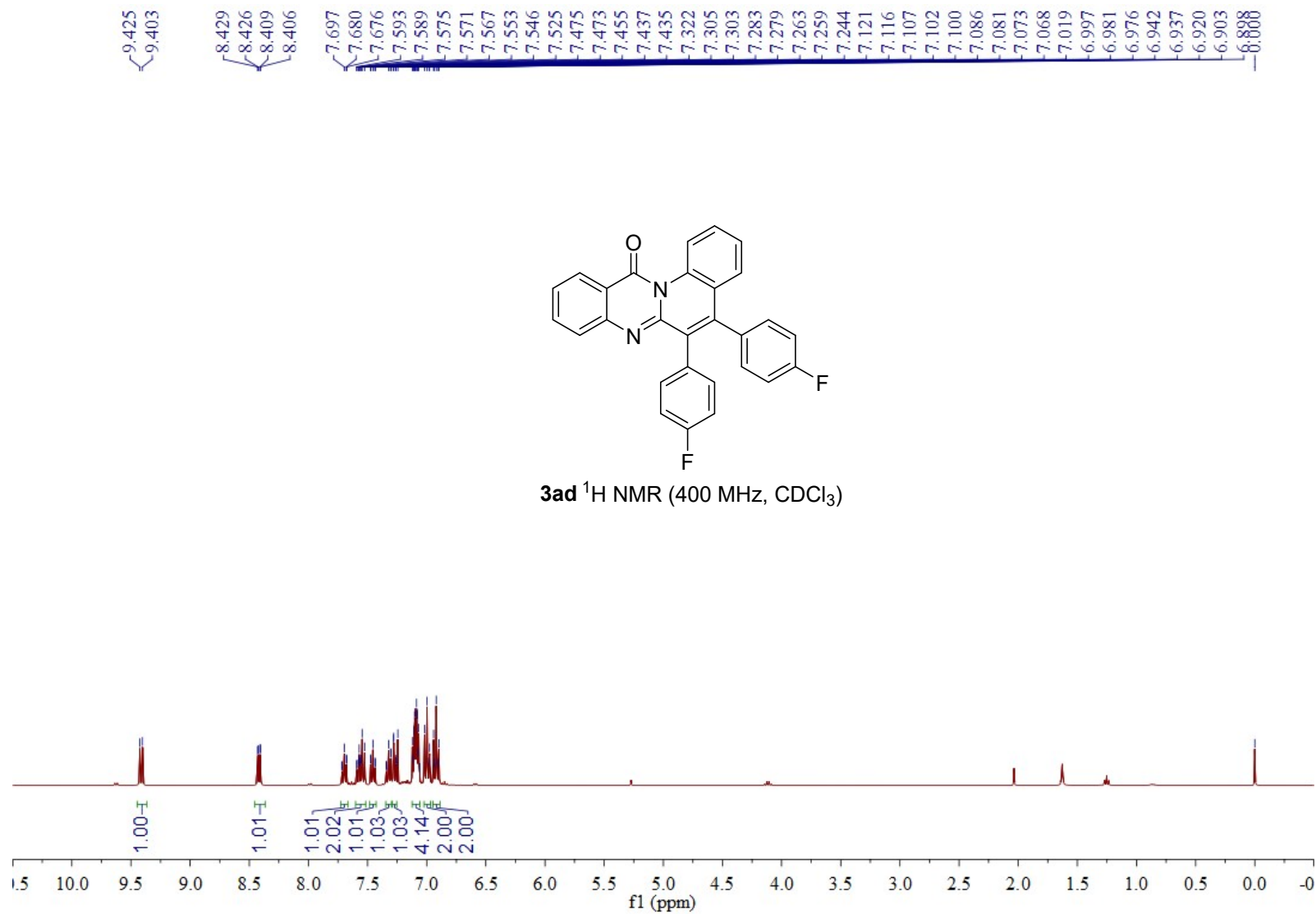


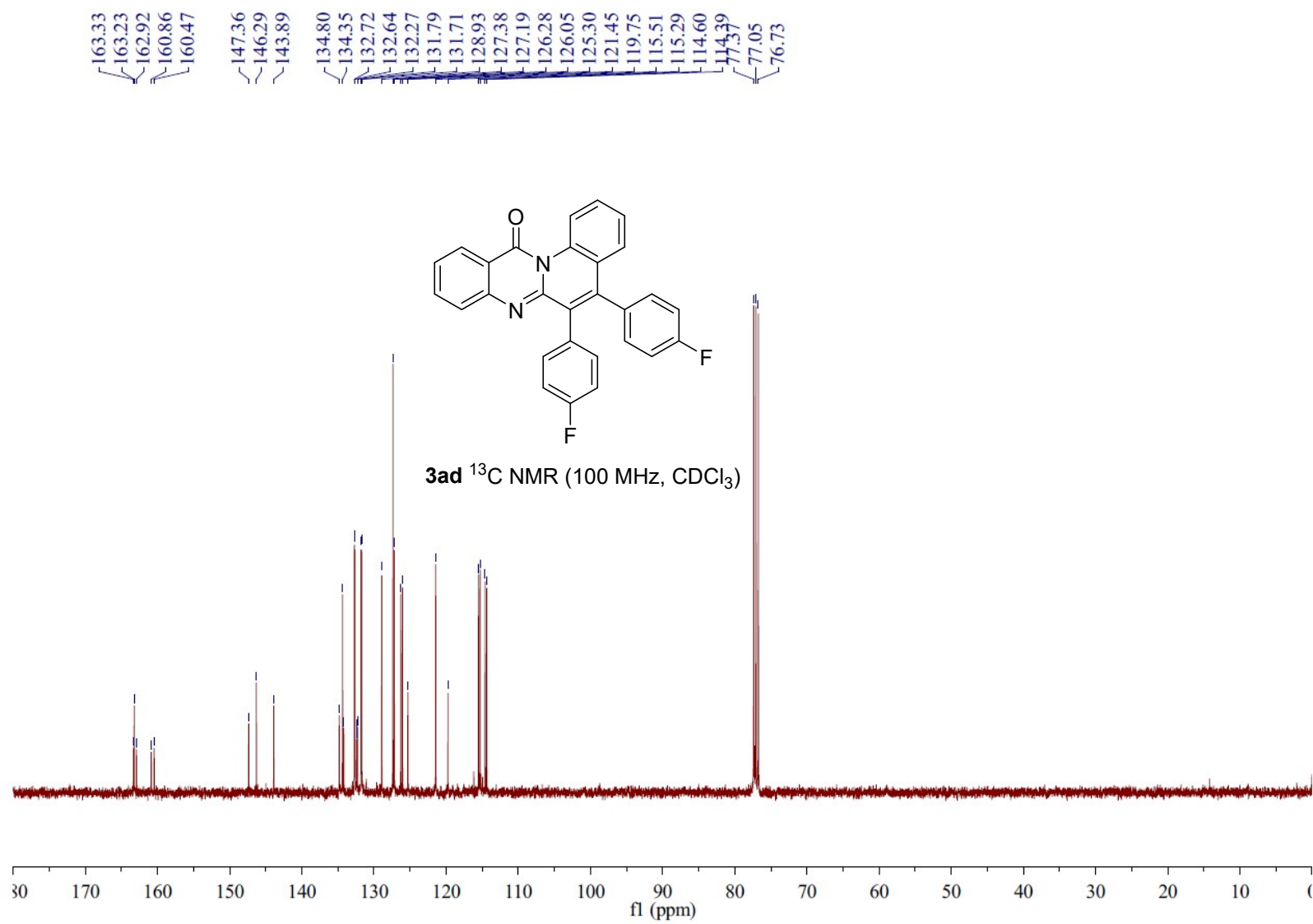


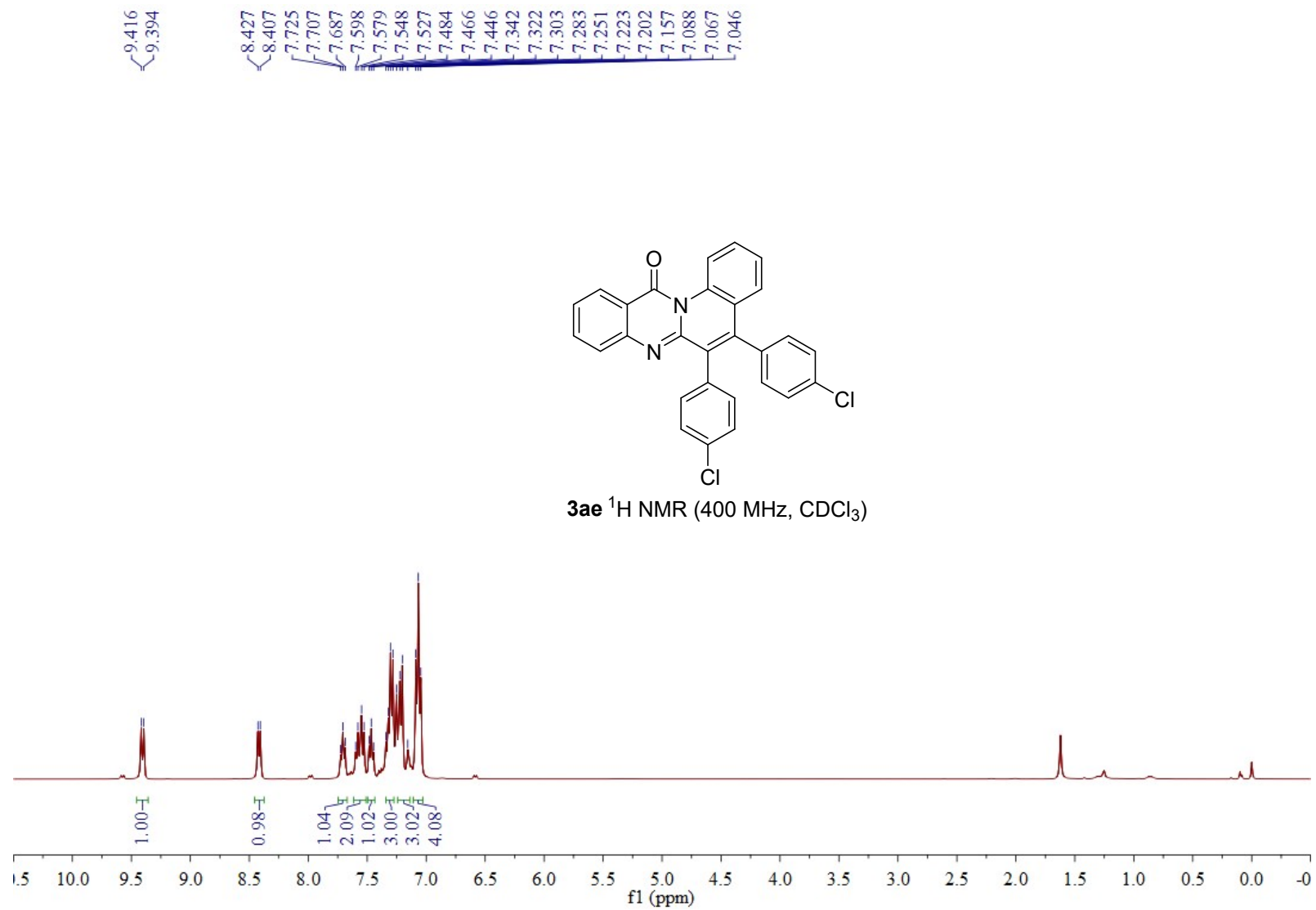


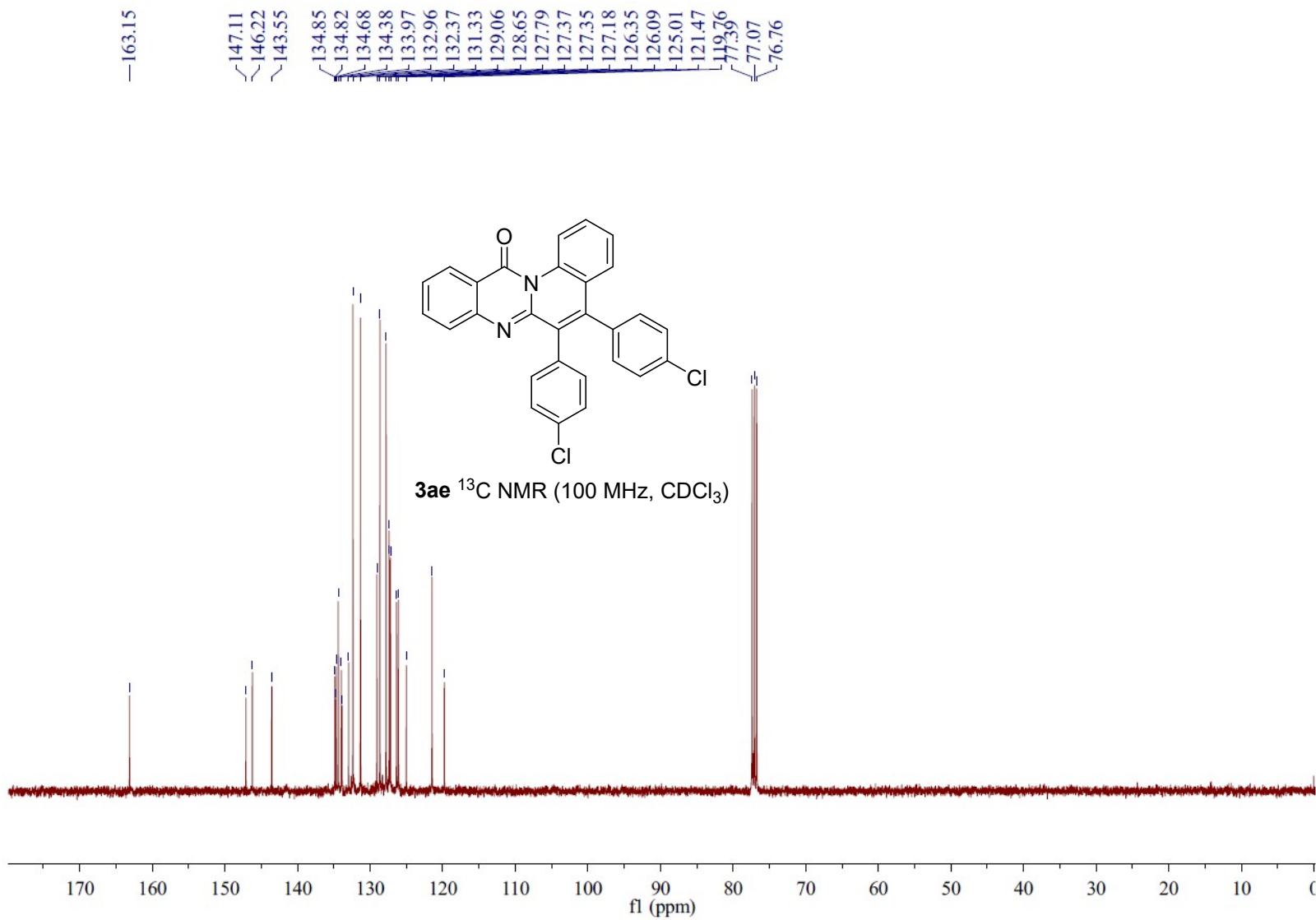


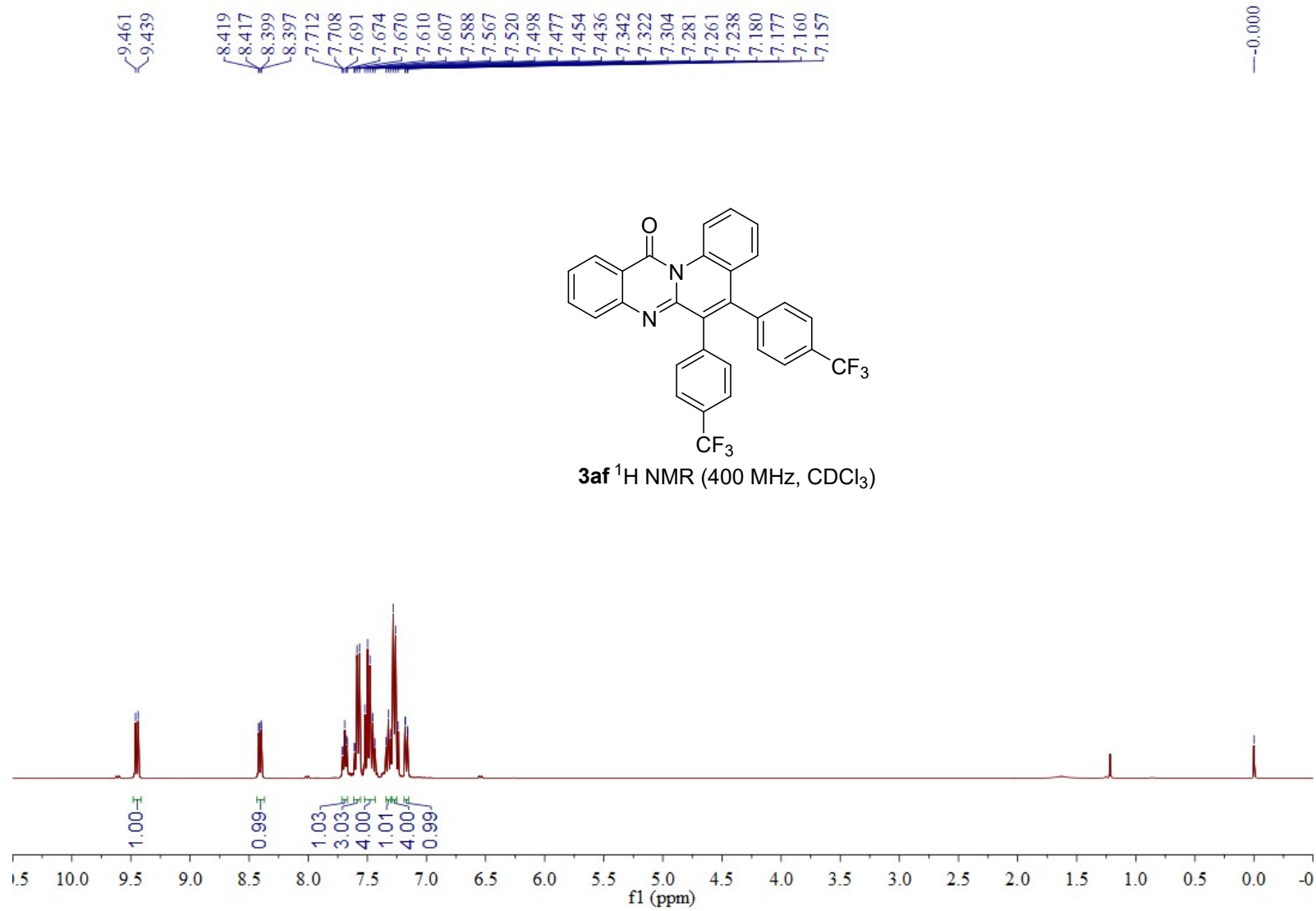


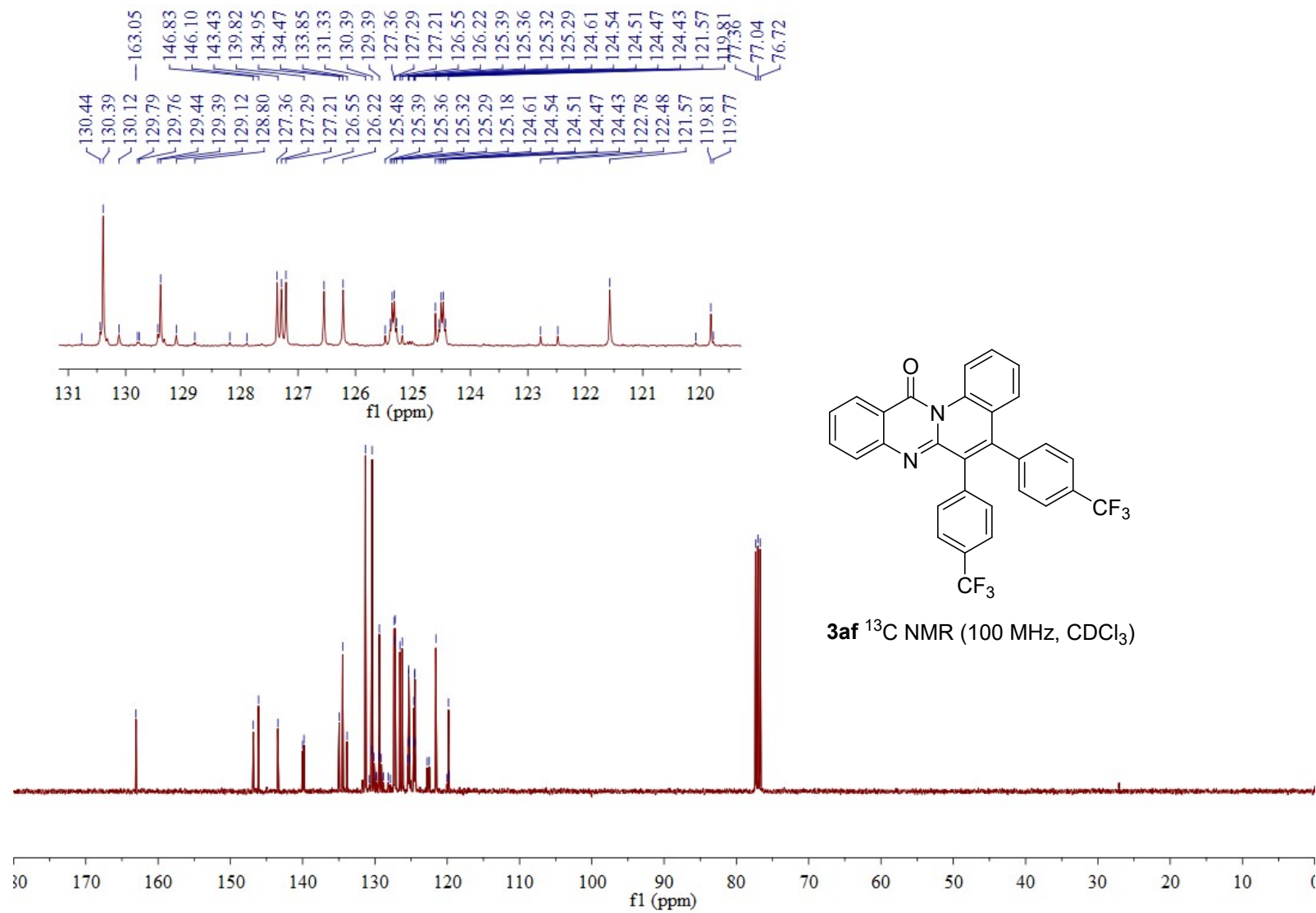


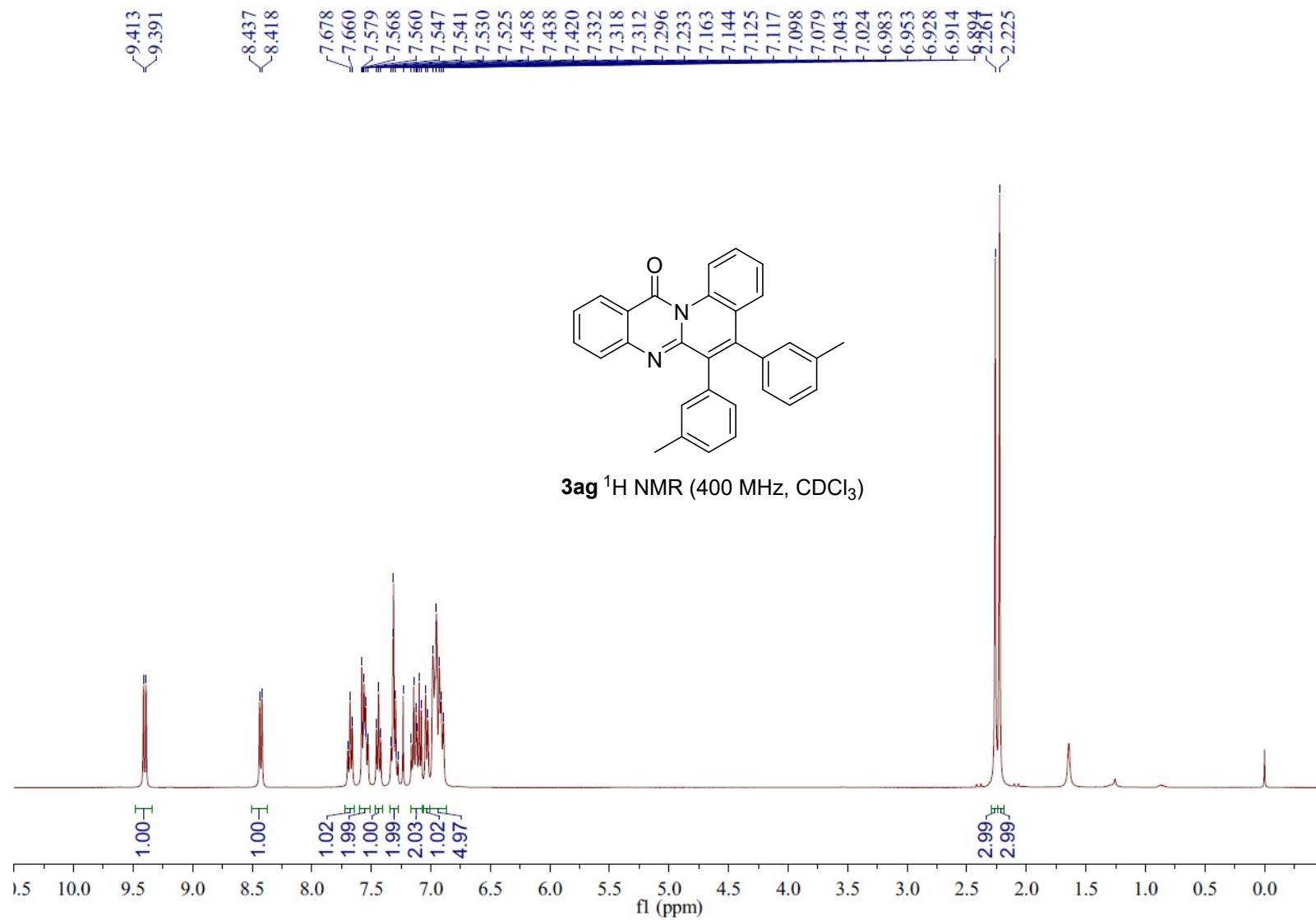


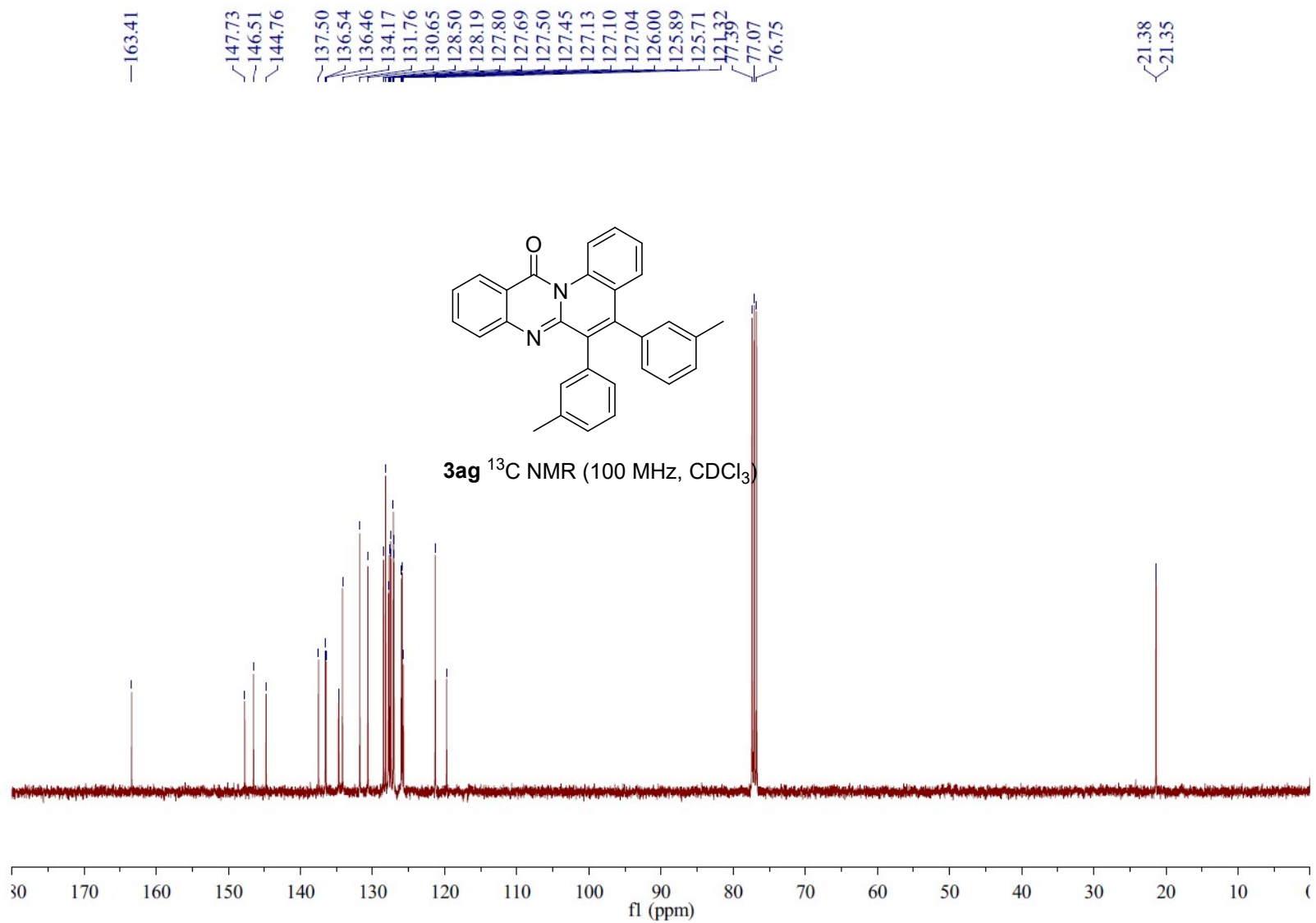


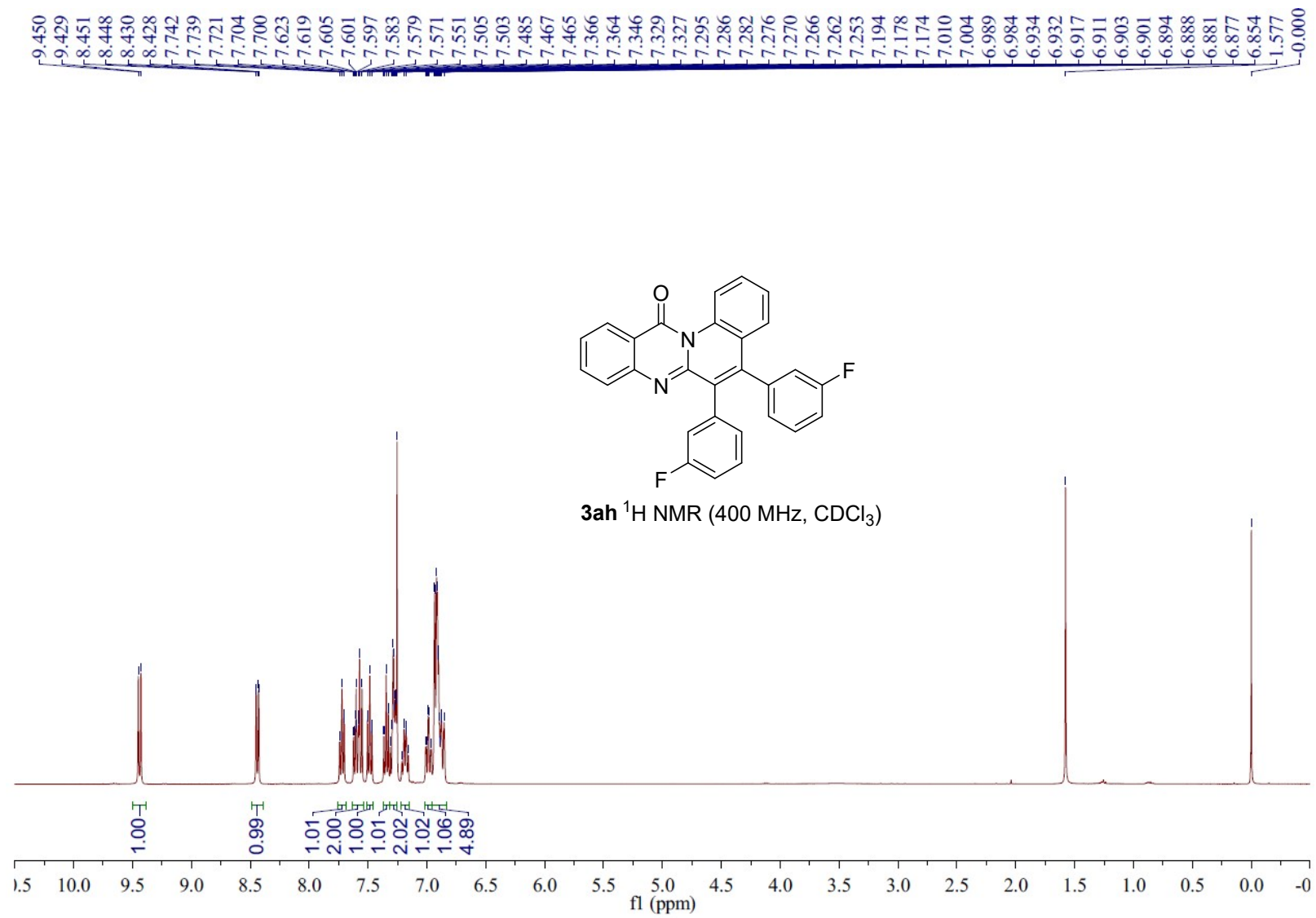


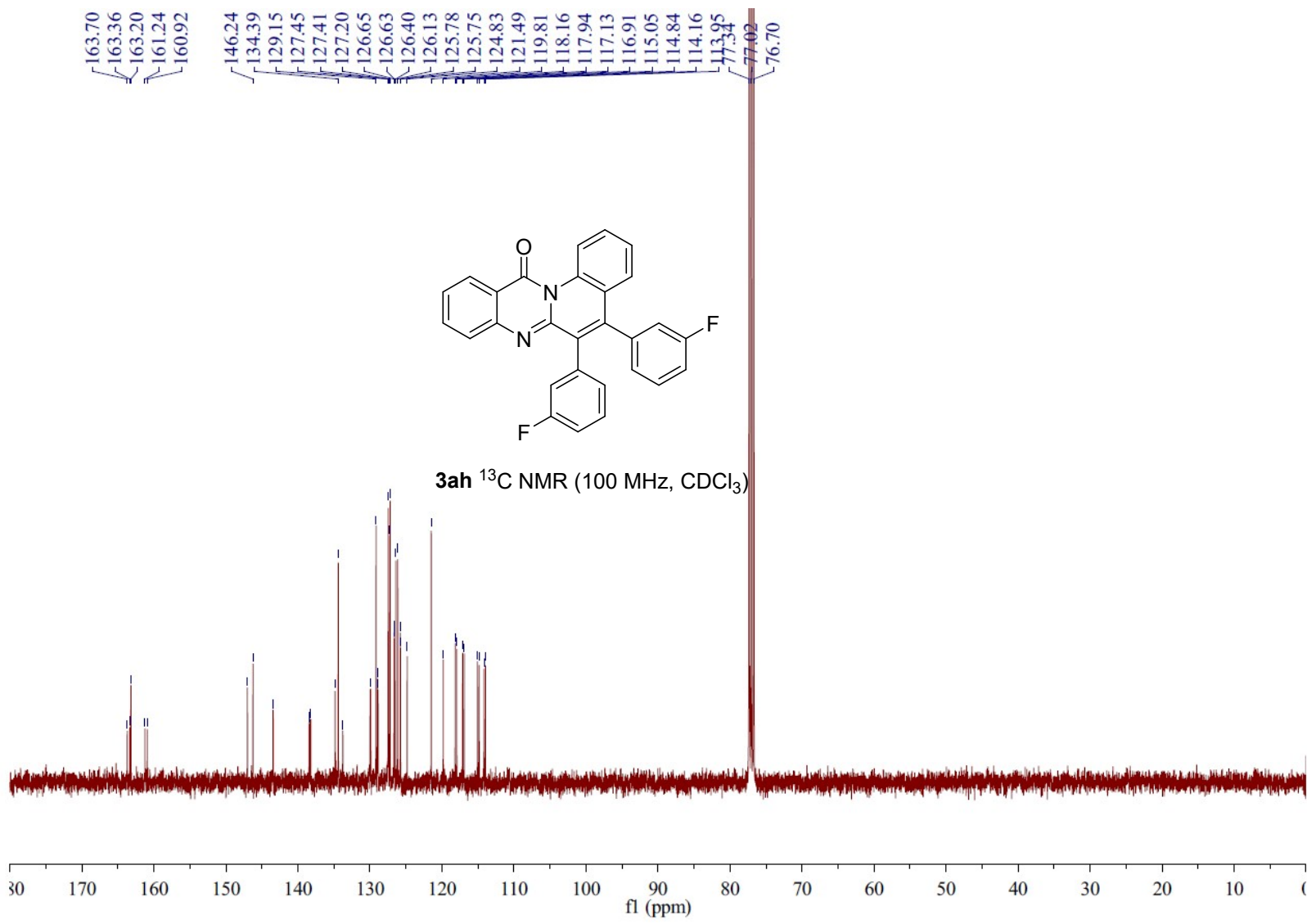


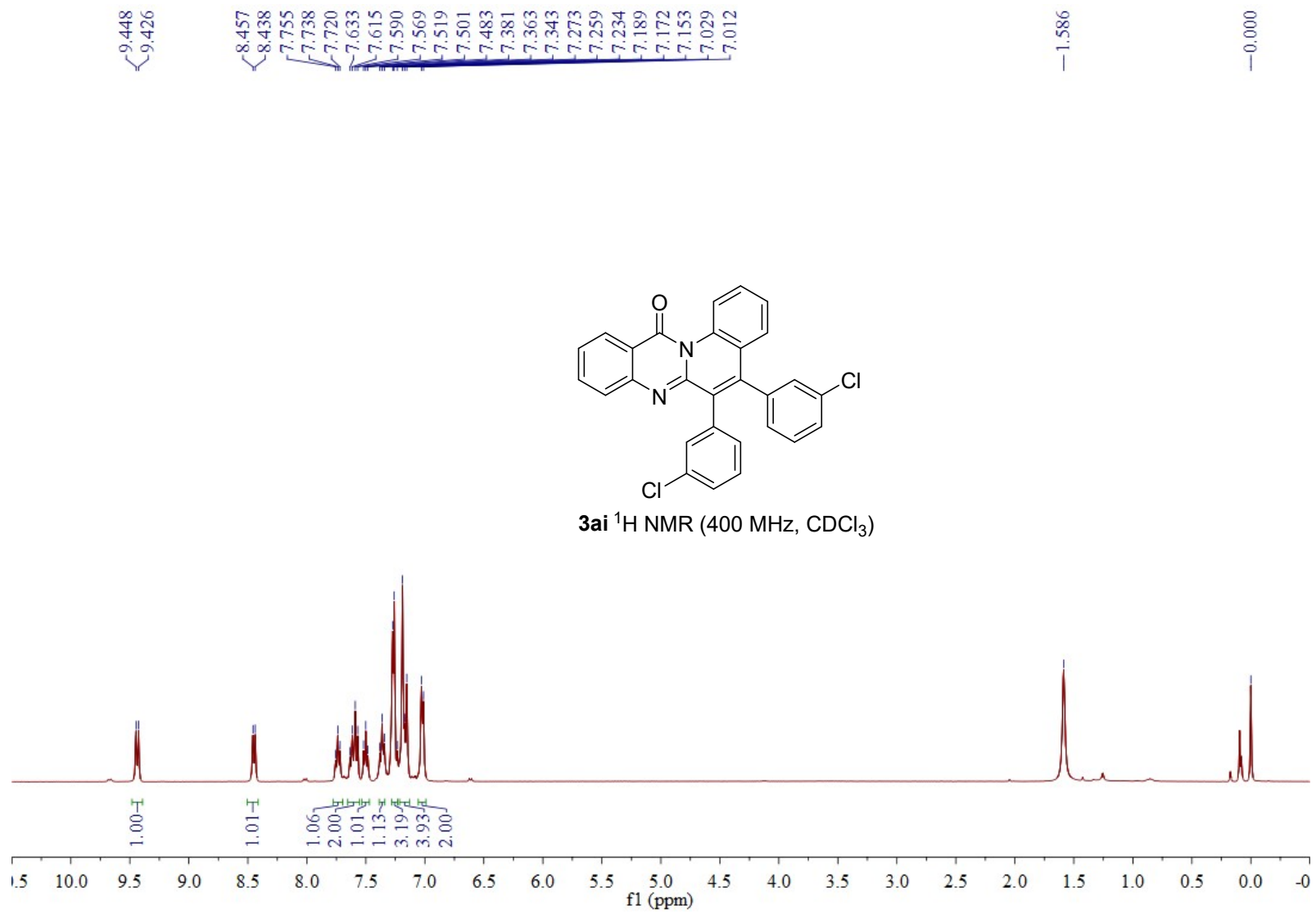


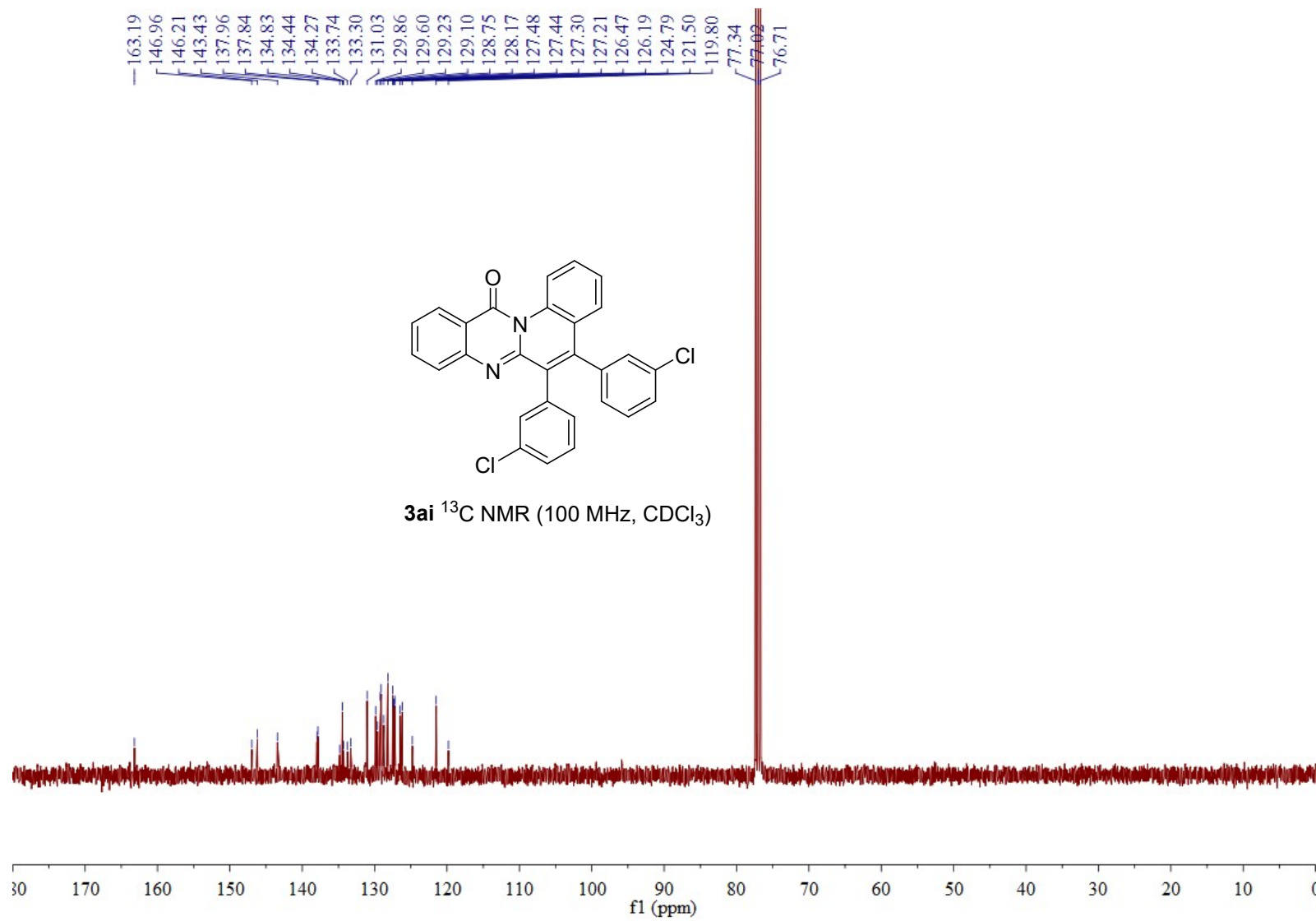


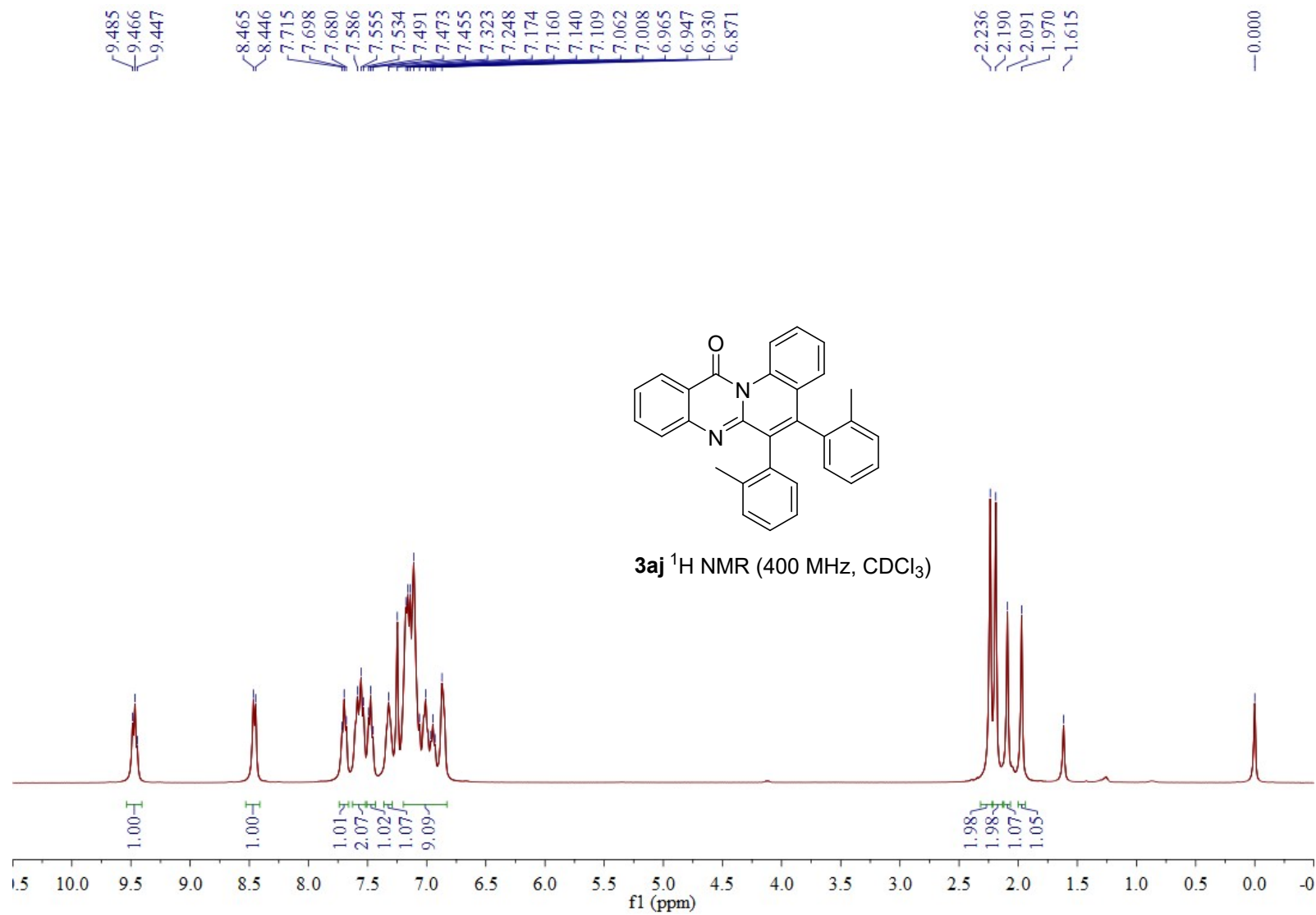


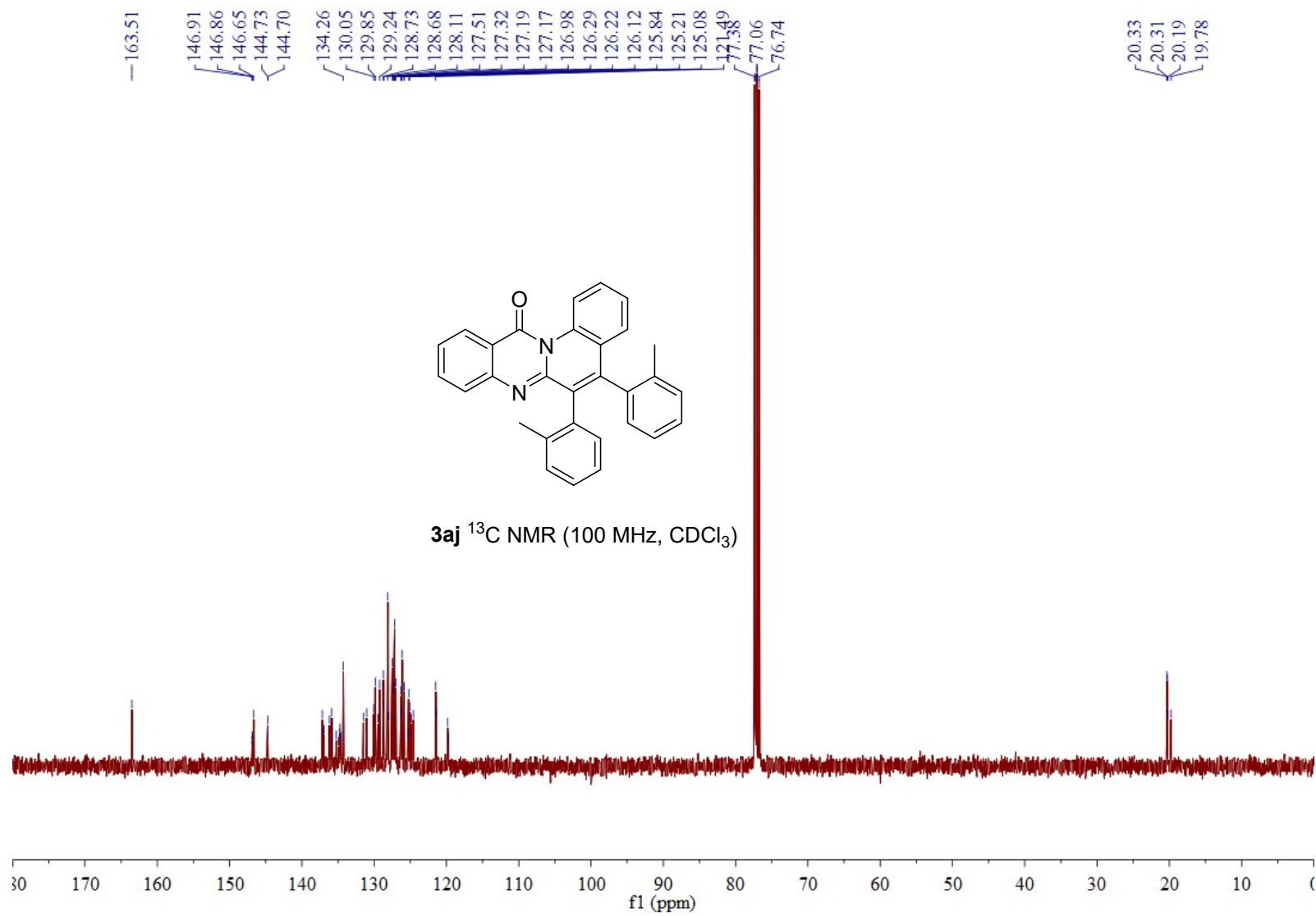


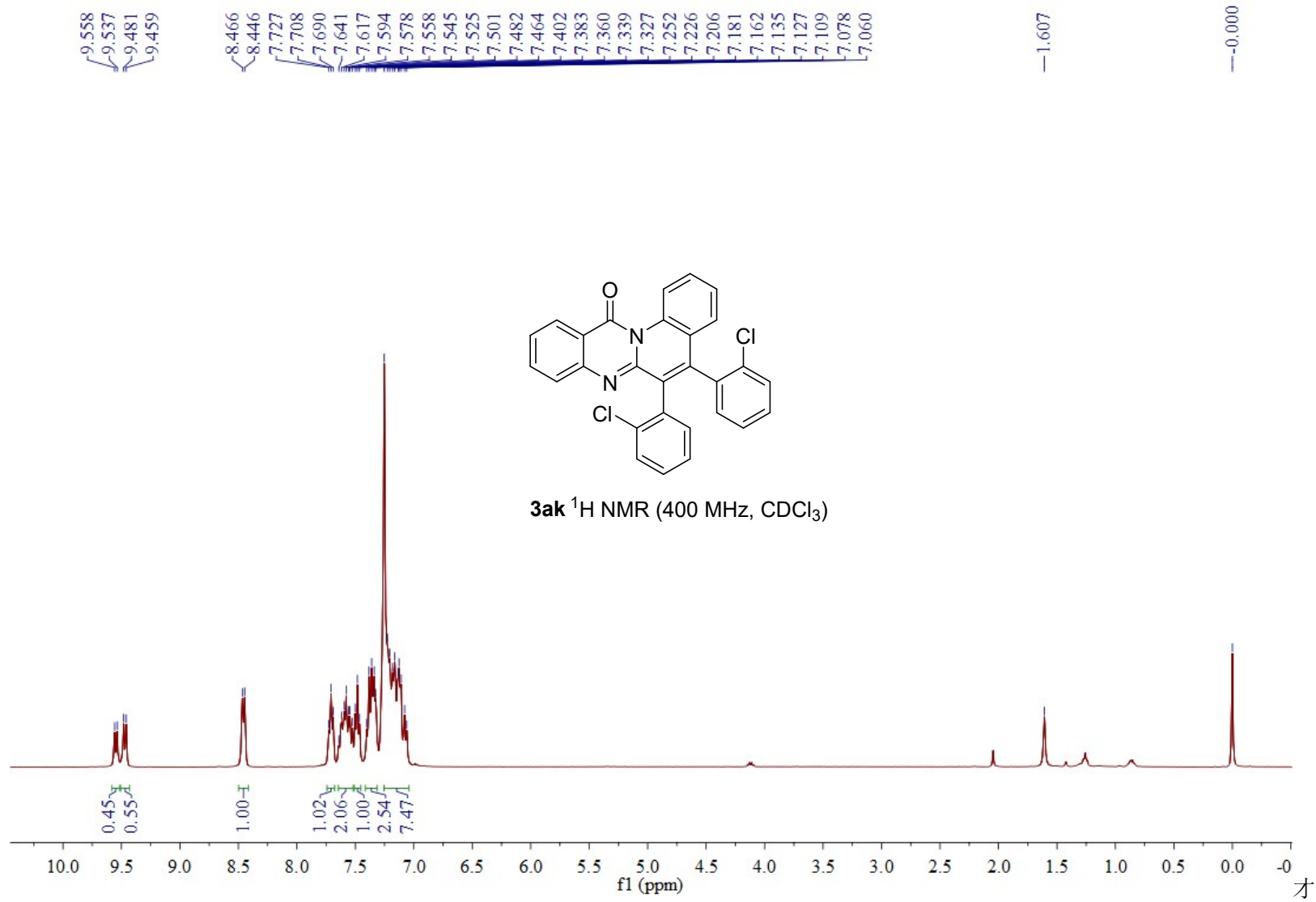


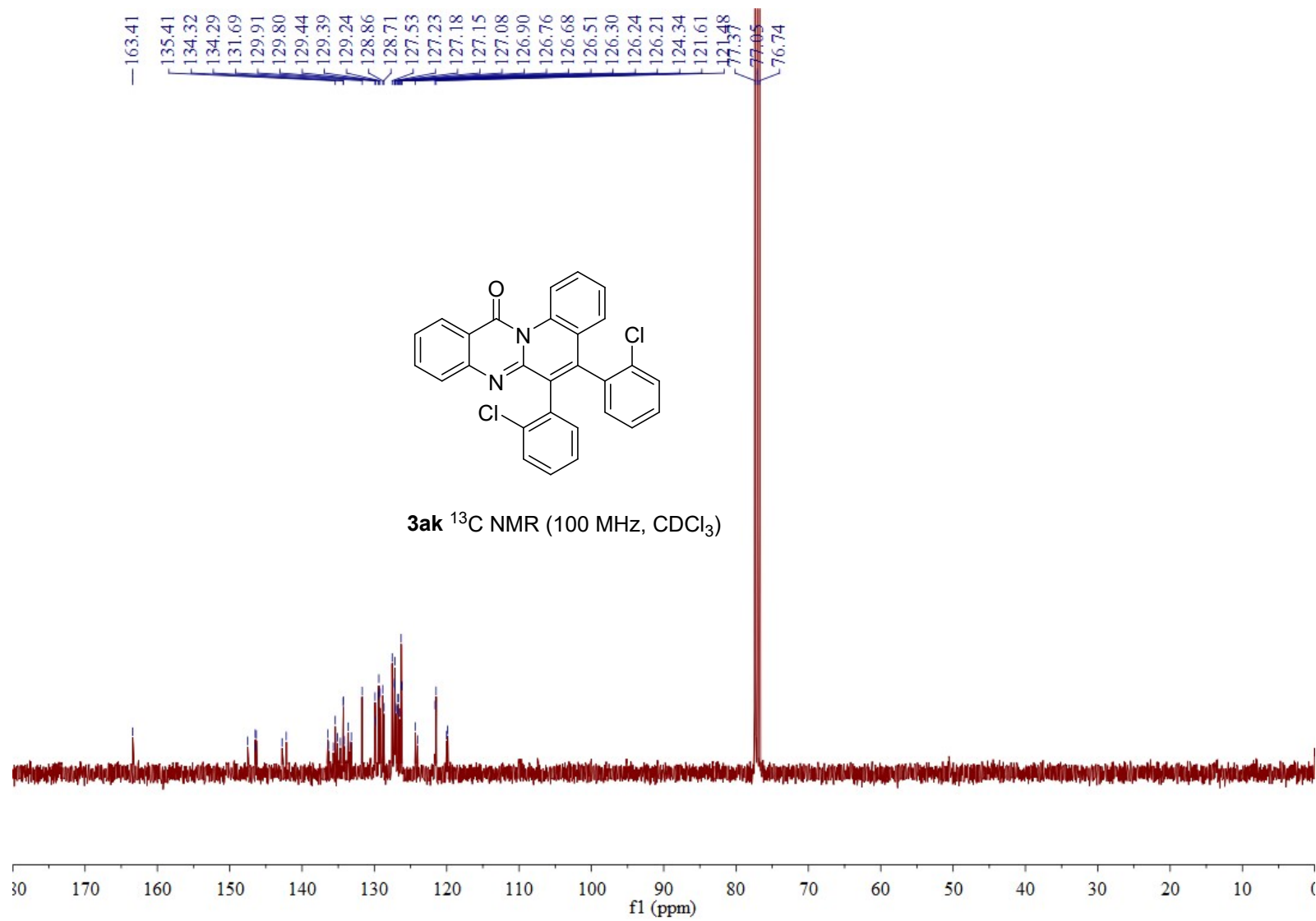




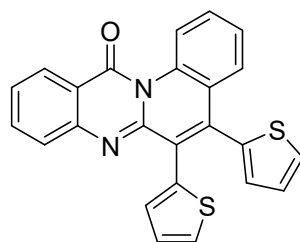




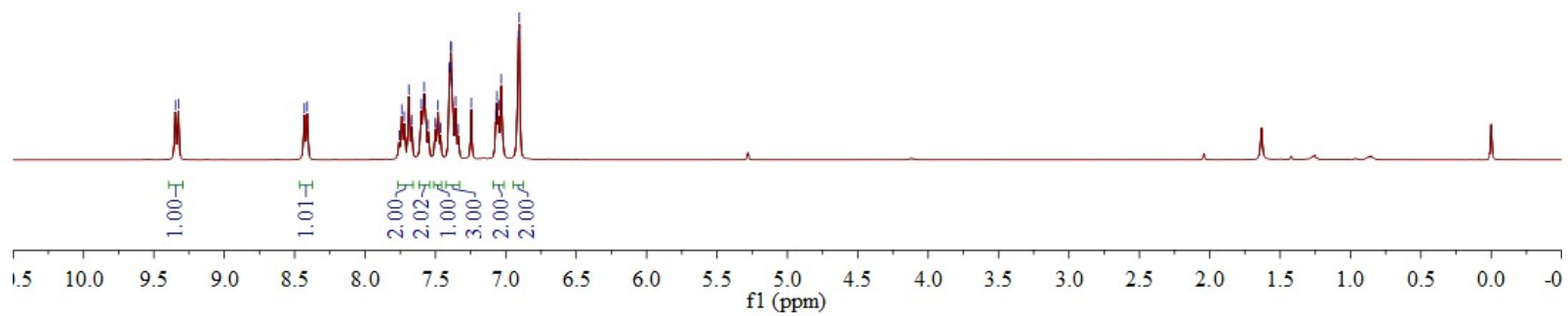


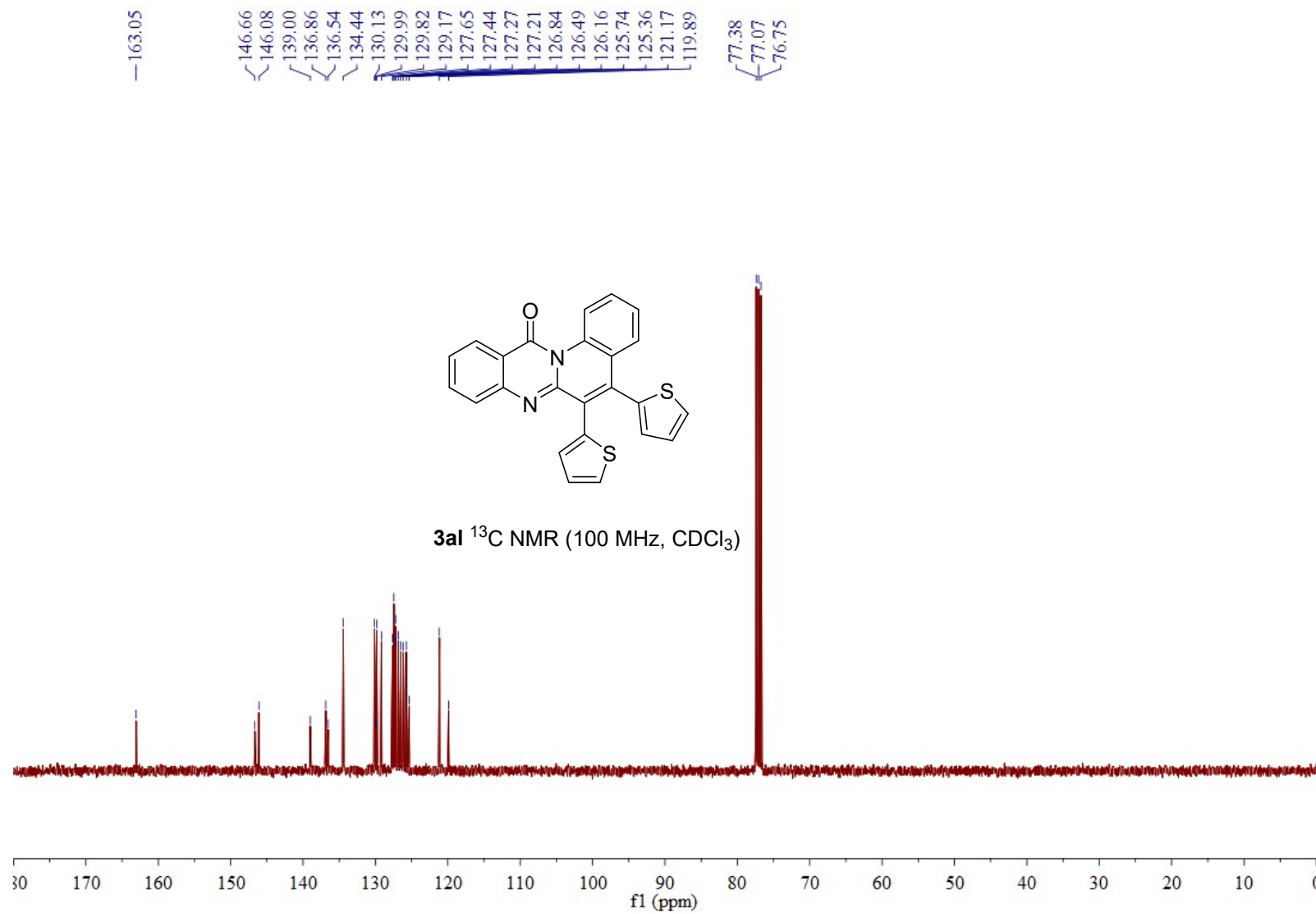


9.347
9.326
8.431
8.411
7.757
7.739
7.722
7.689
7.669
7.600
7.580
7.573
7.551
7.501
7.482
7.464
7.399
7.397
7.390
7.388
7.382
7.357
7.338
7.246
7.072
7.063
7.051
7.033
6.910
6.904



3a1 ^1H NMR (400 MHz, CDCl_3)

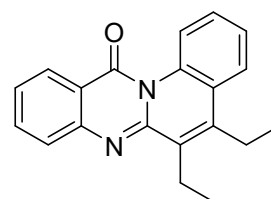




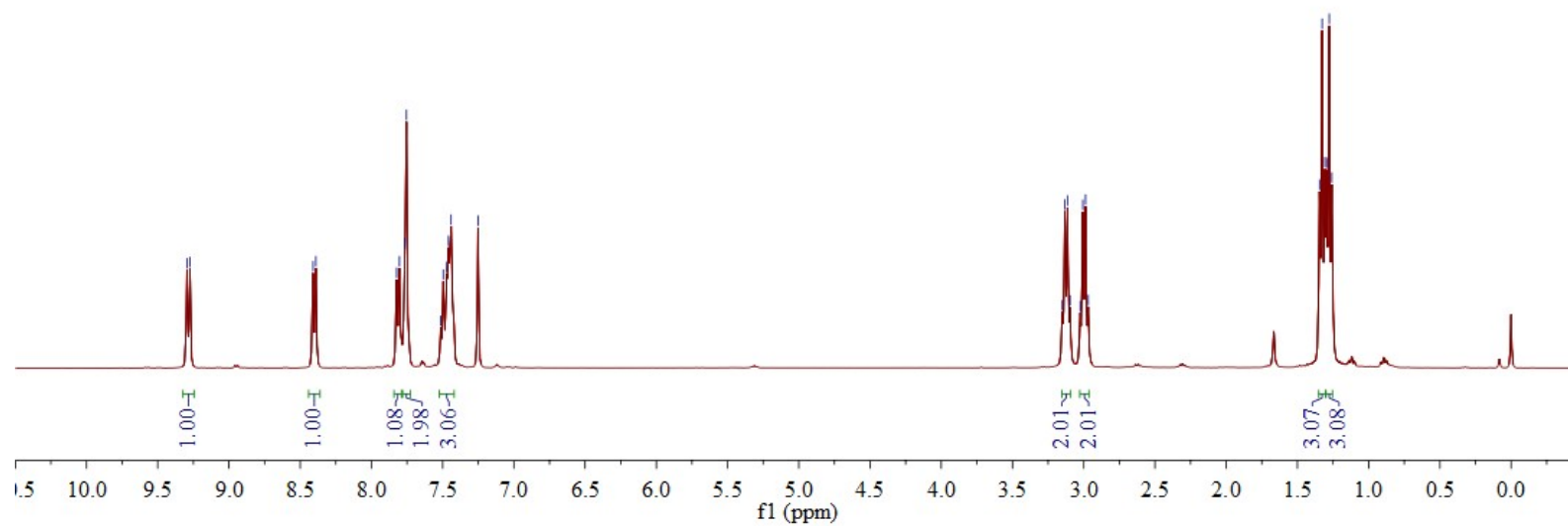
9.295
9.274
8.410
8.390
7.823
7.803
7.767
7.754
7.514
7.496
7.471
7.459
7.441
7.252

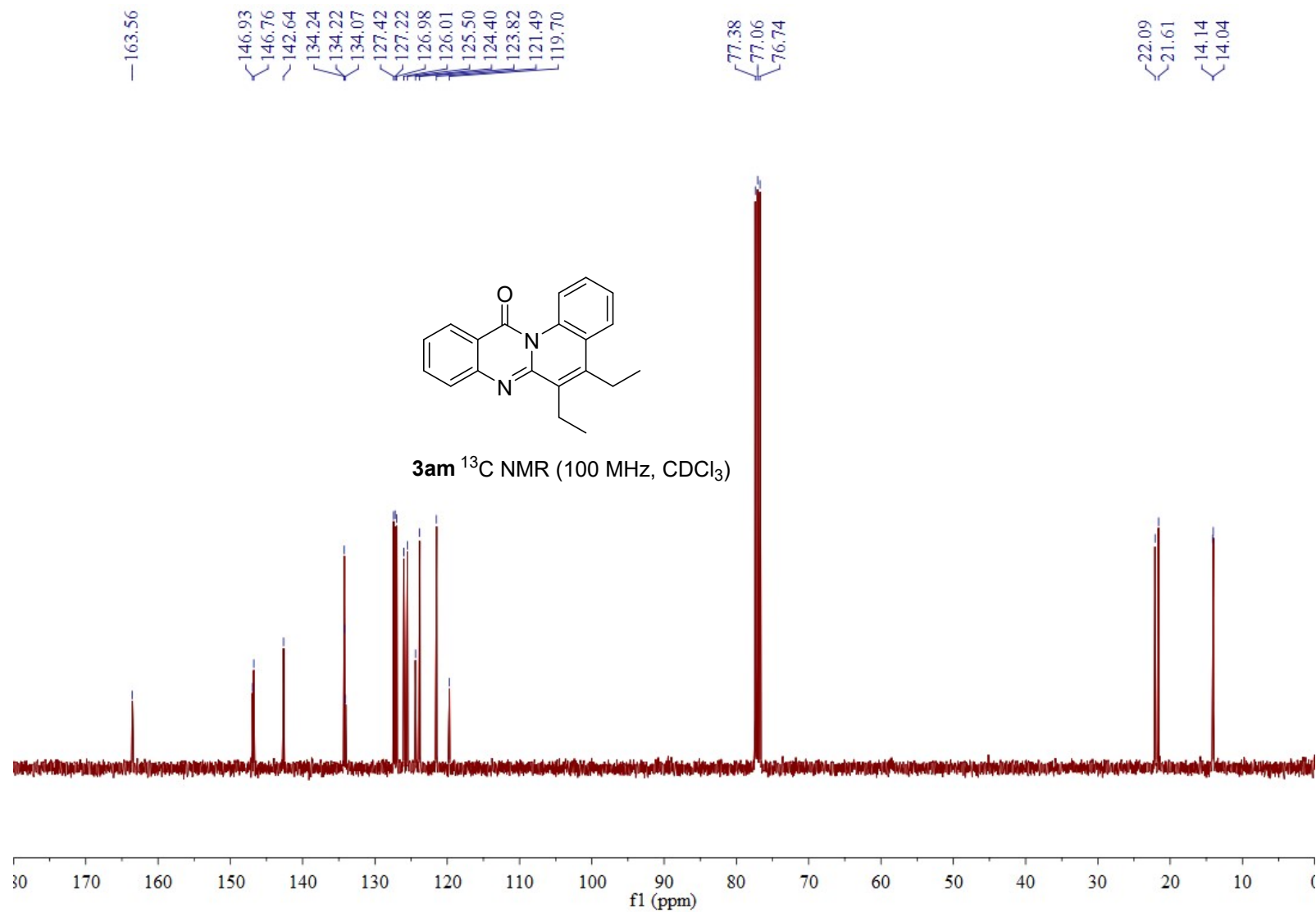
3.151
3.133
3.115
3.096
3.025
3.006
2.987
2.968

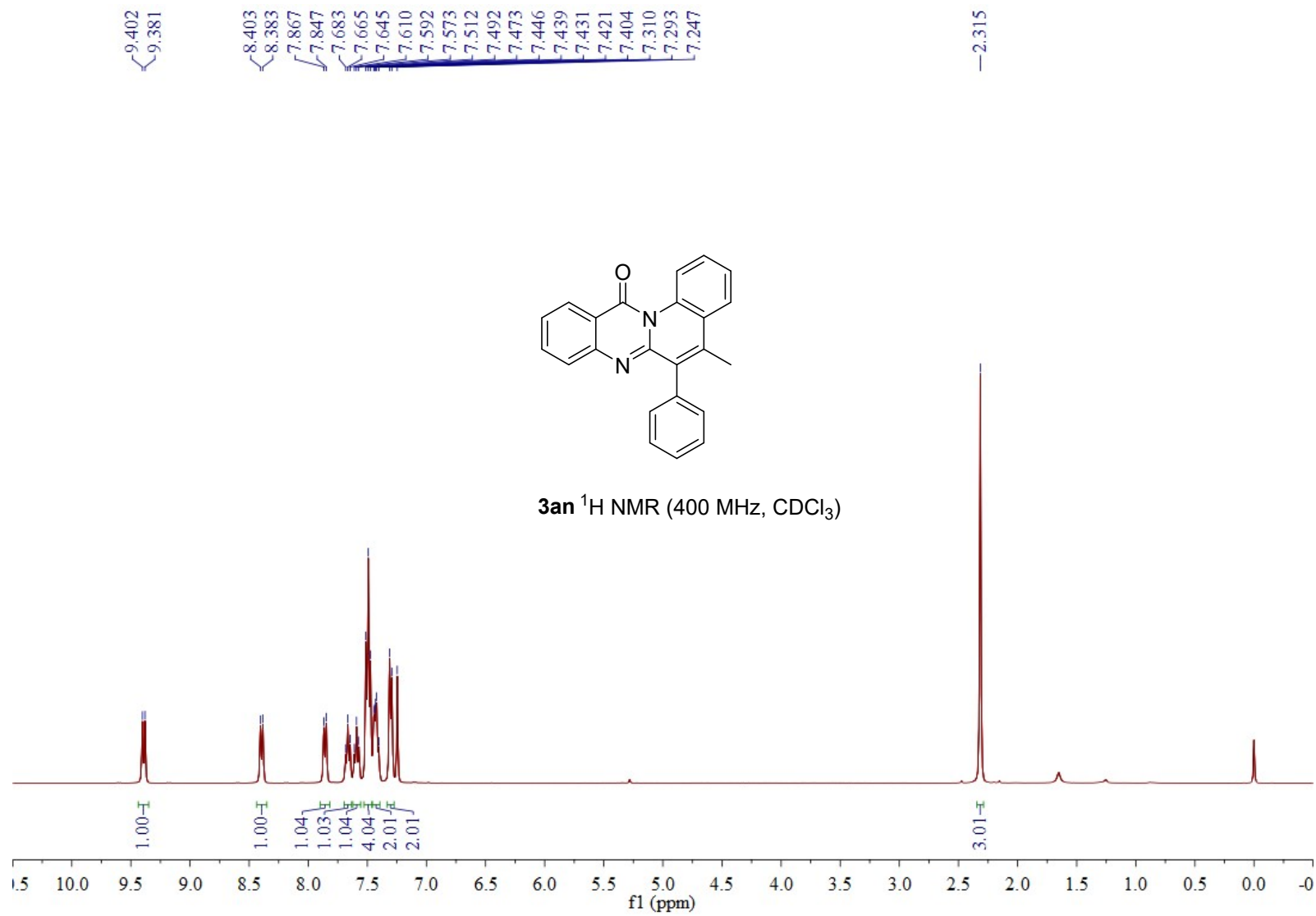
1.345
1.326
1.307
1.295
1.277
1.258

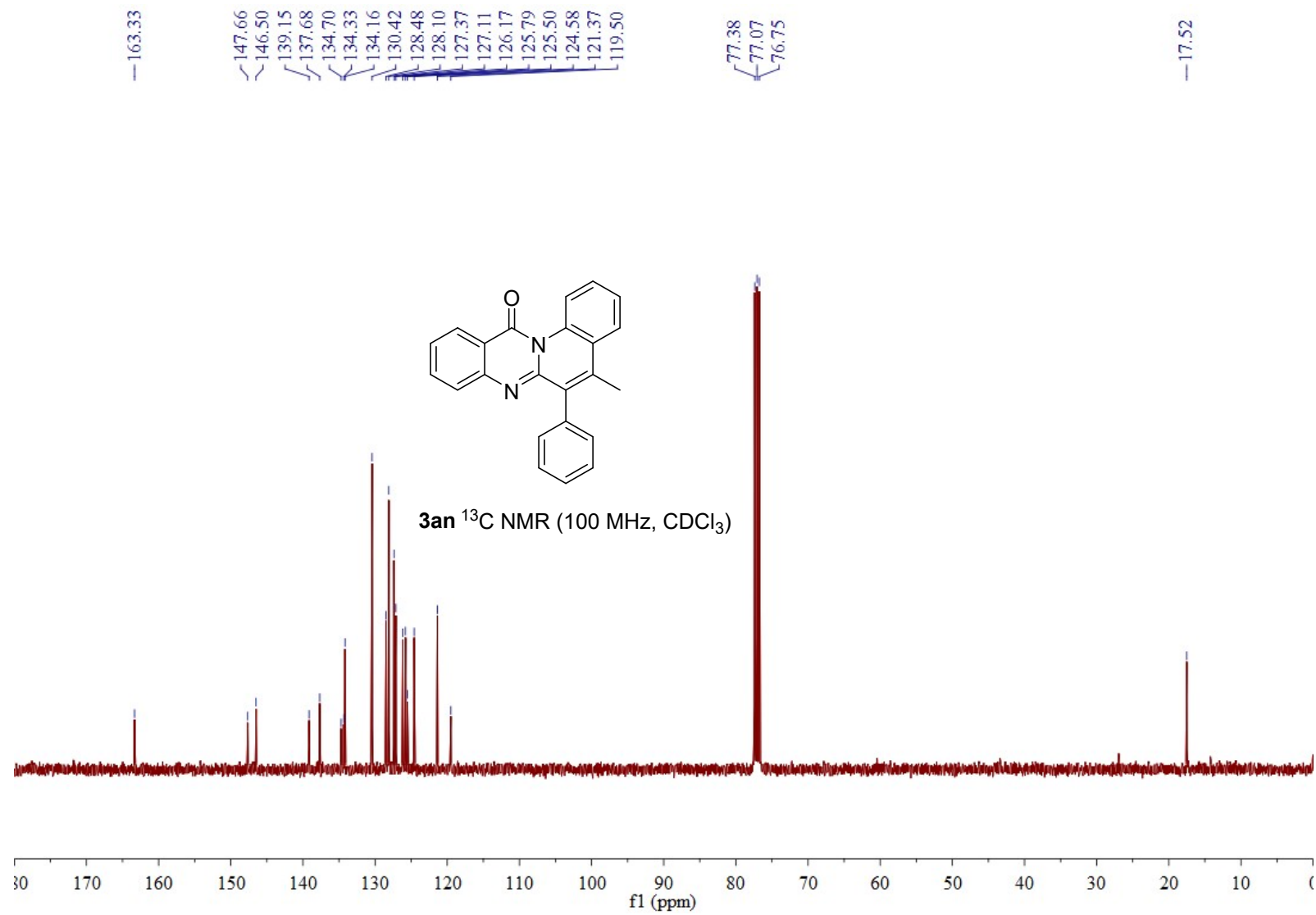


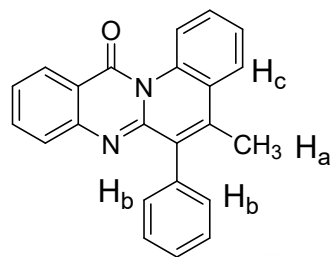
3am ^1H NMR (400 MHz, CDCl_3)



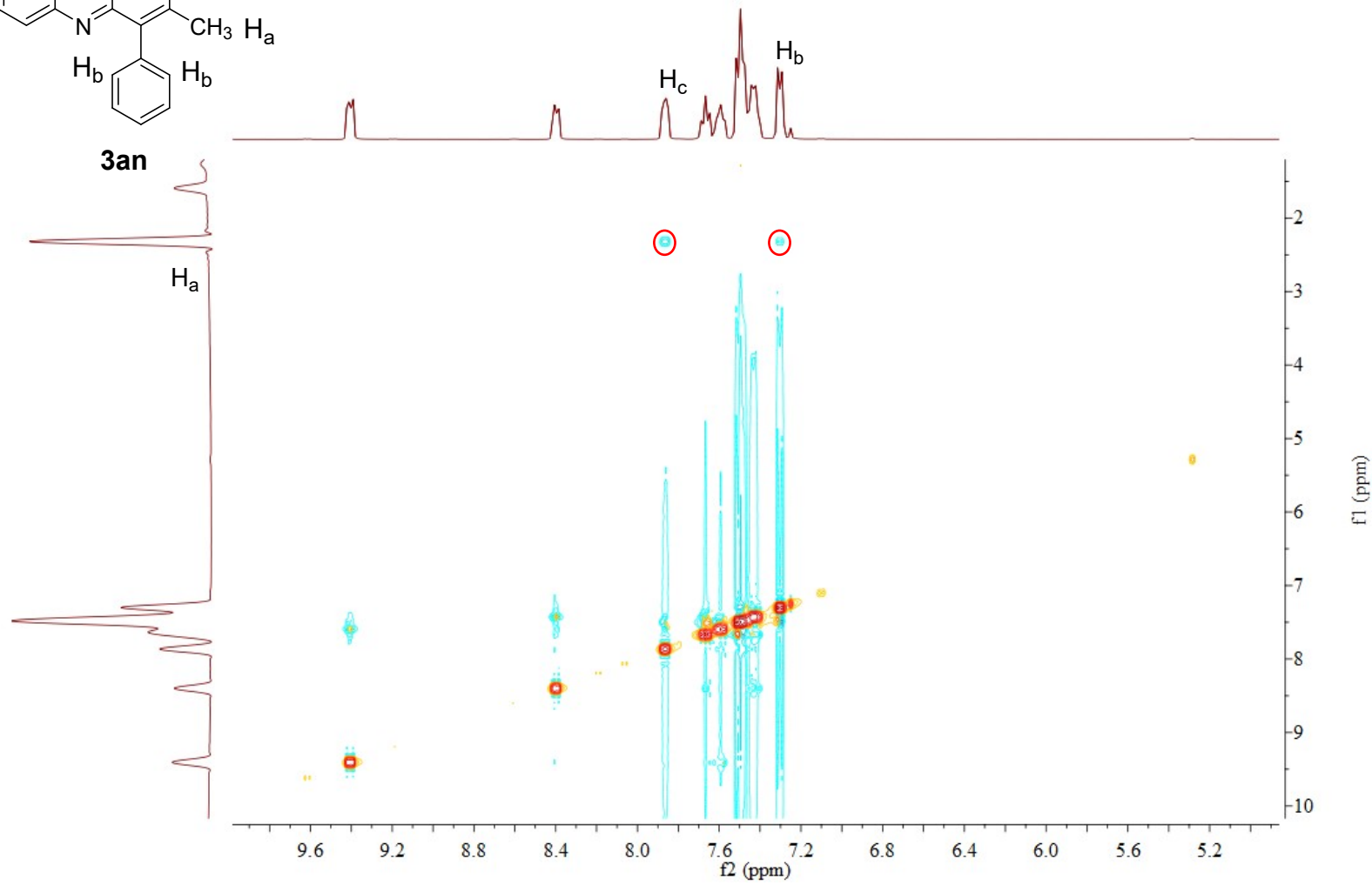


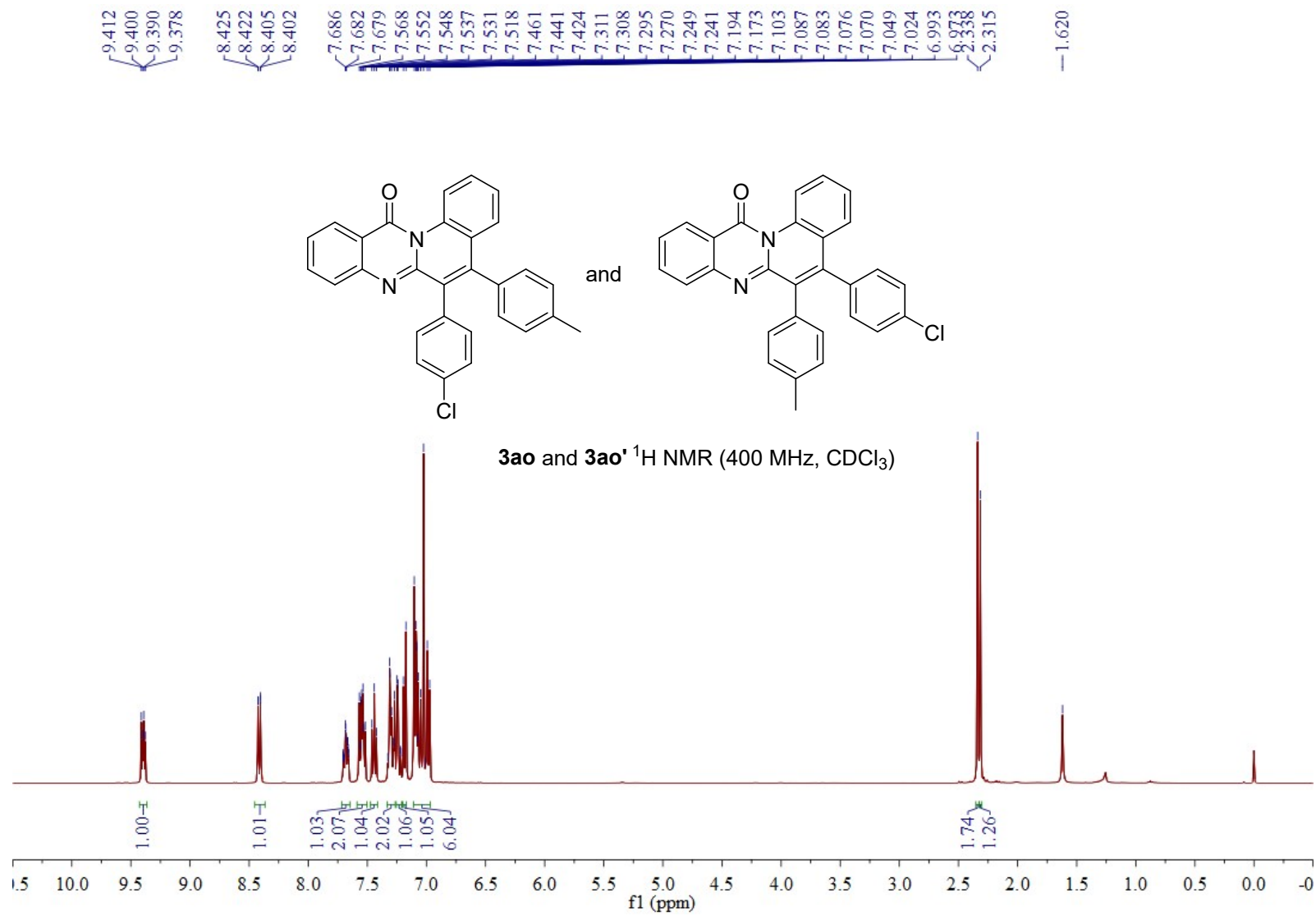


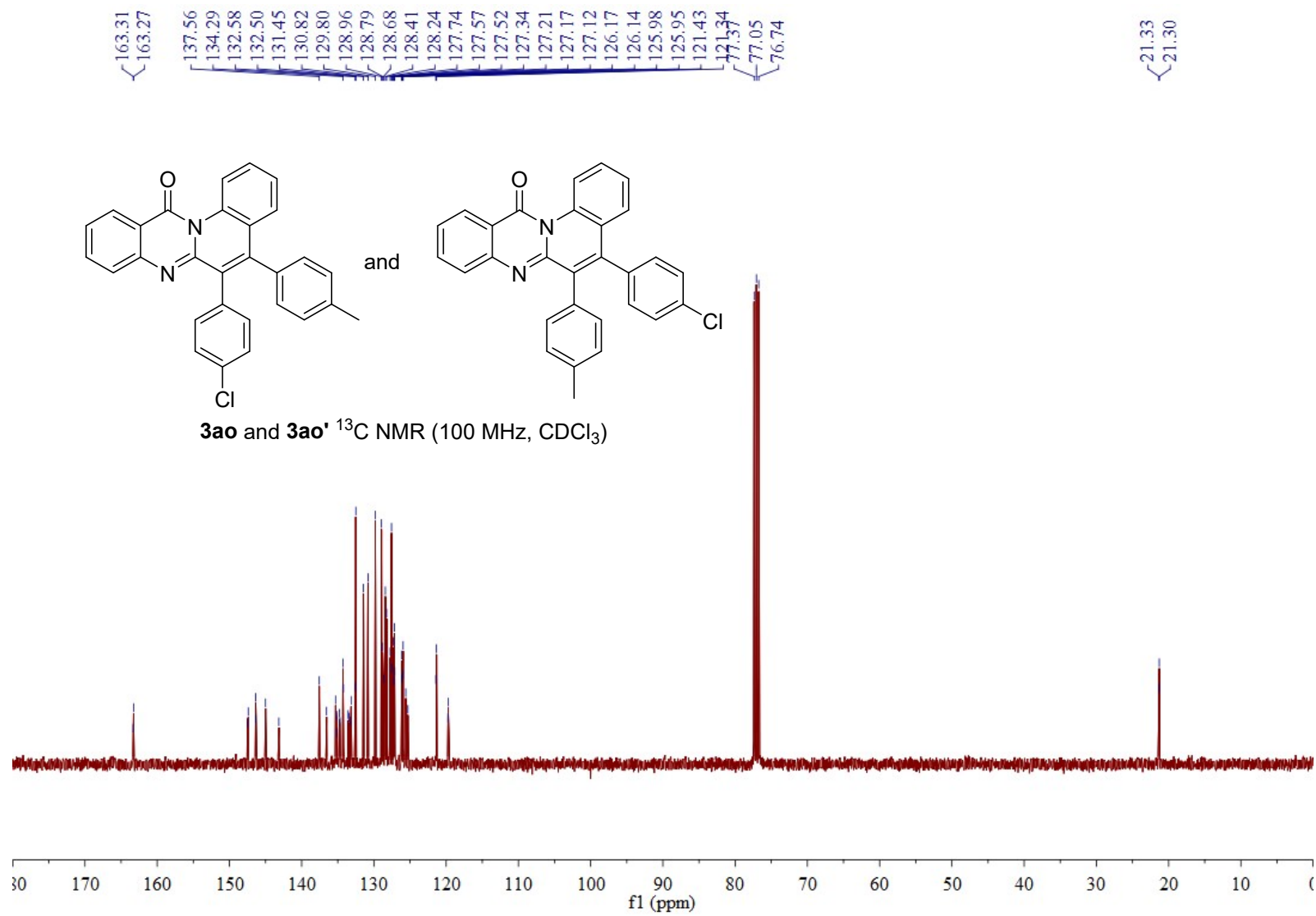


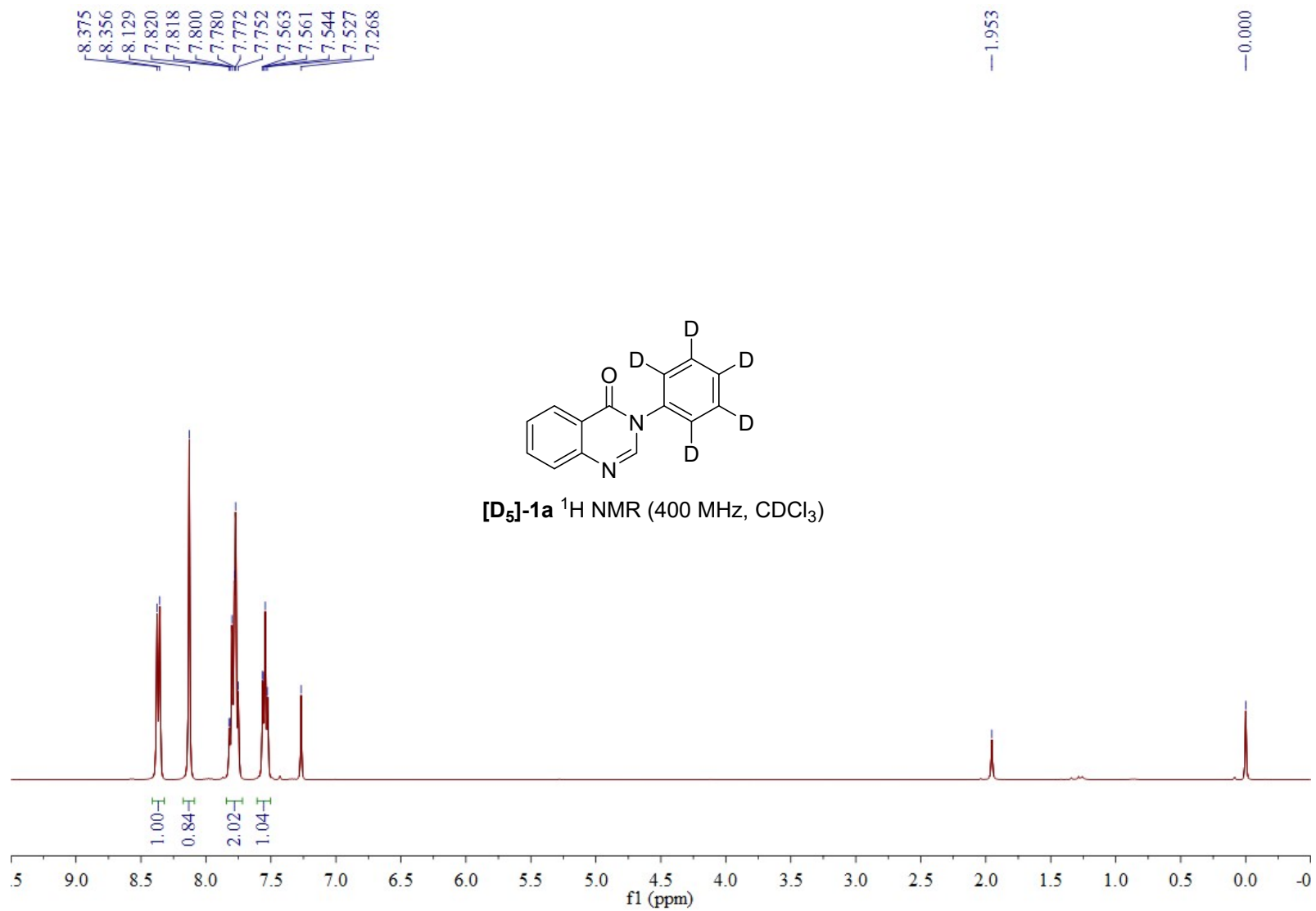


3an

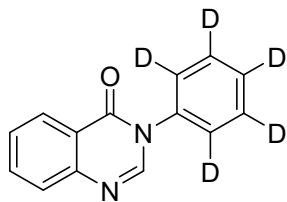




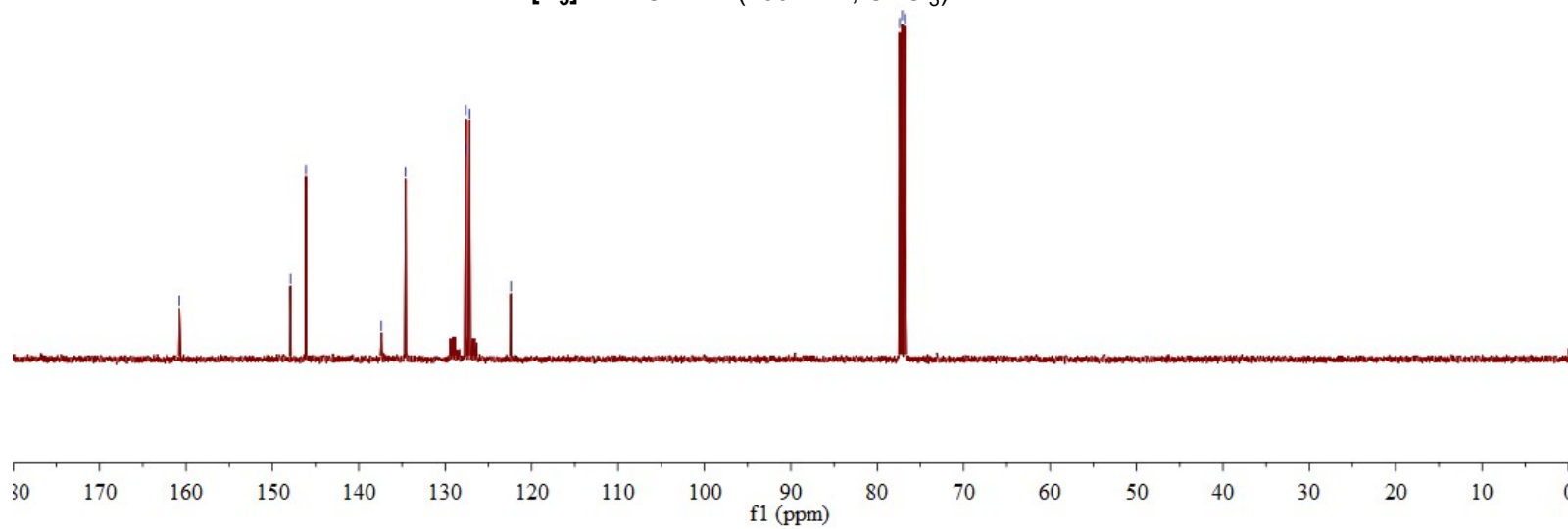




—160.75
~147.91
~146.12
—137.39
—134.58
~127.65
~127.61
~127.19
~122.41
77.41
77.09
76.78



[D₅]-1a ¹³C NMR (100 MHz, CDCl₃)



VIII. UV-Vis and emission spectrum

