Supporting Information

Synthesis of Dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-ones *via* Rh(III)-Catalyzed C−H Activation of 2-Aryl Indazoles and Annulation with Iodonium Ylides

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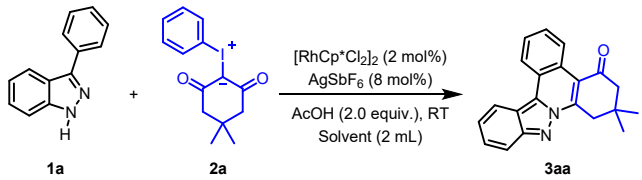
Table of Contents

1. General information

All reactions were carried out under air with no precautions 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 petroleum 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. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Model Avance DMX 400 Spectrometer (^{1}H 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. Indazole[1] and iodonium ylides[2] were prepared according to literatures.

2. Optimization of the reaction conditions (Table S1)[a]

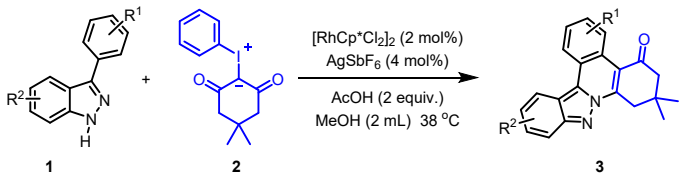


1a 2a 3aa

Entry	Solvent	Time (h)	Yield(%)[b]
1	acetone	30	81
2	EA	24	88
3	DCM	30	62
4	DCE	30	76
5	1,4-dioxane	24	89
6	THF	24	78
7	toluene	24	79
8	**MeOH**	**6**	**99**
9	MeCN	24	N.R.
10	DMSO	30	N.R.
11	DMF	30	Trace
12	HFIP	30	Trace
13	Et_2O	24	34

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.24 mmol, 1.2 equiv.), $[RhCp^*Cl_2]_2$, (2.0 mol %) and AcOH (2.0 equiv.), solvents (2.0 mL), temperature, 18 ˚C. [b] Isolated yield. [c] N.R. = no reaction.

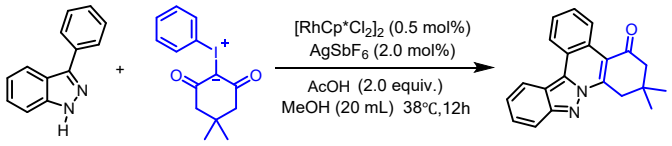
3. General procedure for the synthesis of products 3



1 2 3

An oven-dried 10 mL reaction tube with a magnetic stir bar was charged with indazole **1** (0.2 mmol), iodonium ylides **2** (0.24 mmol, 1.2 equiv.), $[RhCp^*Cl_2]_2$ (2 mol%), $AgSbF_6$ (4 mol%), AcOH (2.0 equiv.) and MeOH (2 mL) under air. The reaction was heated at 38 °C. The reaction was monitored by TLC, and upon completion of the reaction the solvent was evaporated under reduced pressure and the residue was directly purified by a silica gel column chromatography using ethyl acetate/petroleum as the eluent to afford product **3**.

4. Gram-scale synthesis of 3aa



1a (3.5mol) **2a** (1.2 equiv.) **3aa** (1.065g, yield: 97%)

An oven-dried 50 mL reaction tube with a magnetic stir bar was charged with indazole **1a** (3.5 mmol), iodonium ylides **2a** (4.2 mmol, 1.2 equiv.), $[RhCp^*Cl_2]_2$ (0.5 mol%), $AgSbF_6$ (2 mol%), AcOH (2 equiv.) and MeOH (2 mL) under air. The reaction mixture was stirred at 38°C until the **1a** was consumed completely (12 h) detected by TLC. The product was filtered and washed with methanol, and provide the desired product **3aa** (1.0802g, 98%).

The purity of the product is sufficient for NMR, UV and fluorescence characterization. The H-NMR, UV, and fluorescence data of the product were not substantially different from those of the product purified by column chromatography (Please see follow Fig. S1-S3).

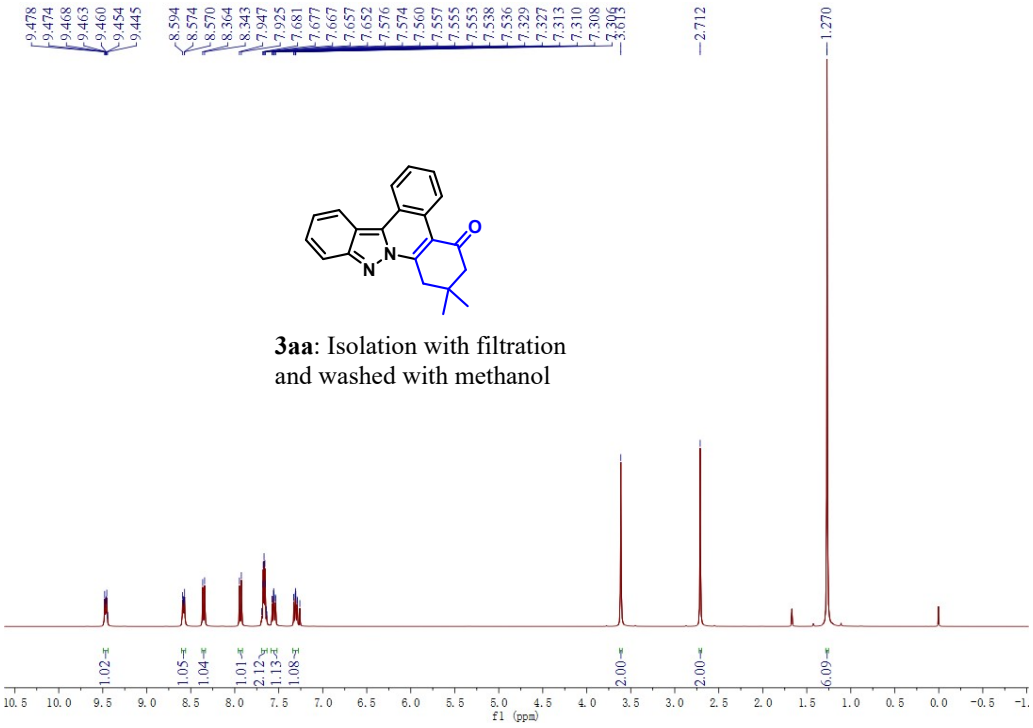


Fig. S1. ^{1}H-NMR of **3aa** isolated with filtration and washed with methanol

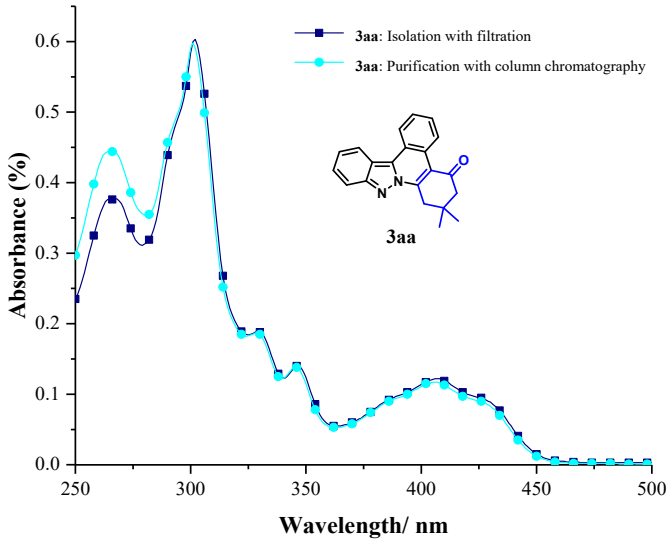


Fig. S2. The comparison of UV absorbance of **3aa** isolated from filtration and column chromatography

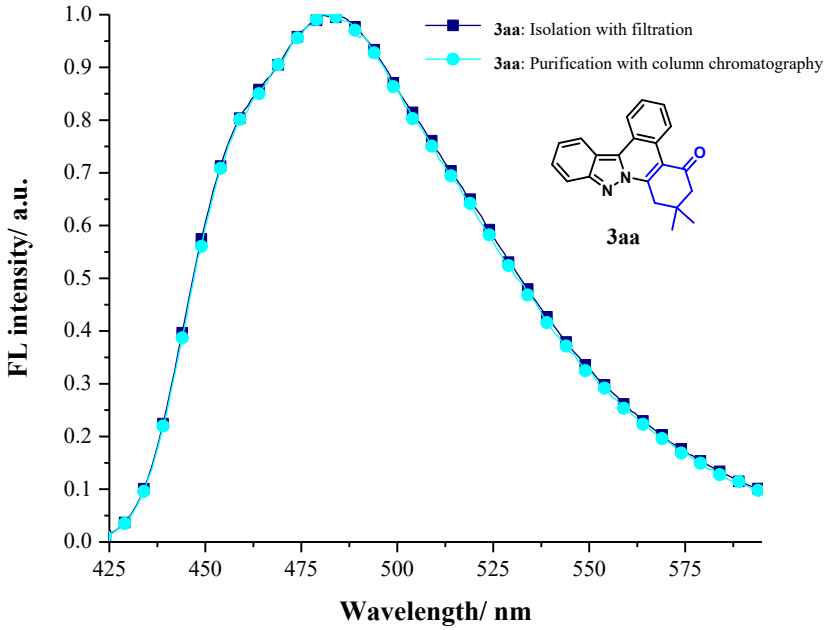


Fig. S3. The comparison of fluorescence of **3aa** isolated from filtration and column chromatography

5. Recycling study of the catalytic system

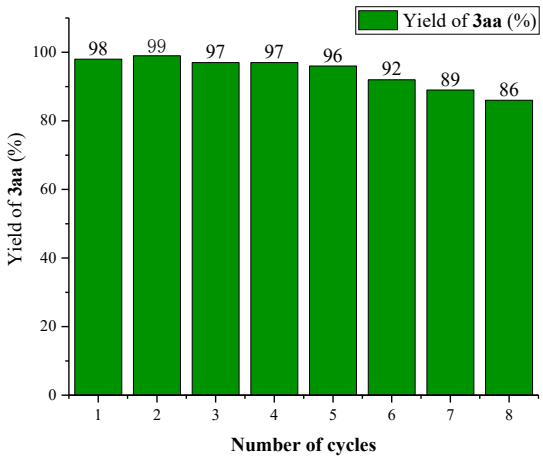
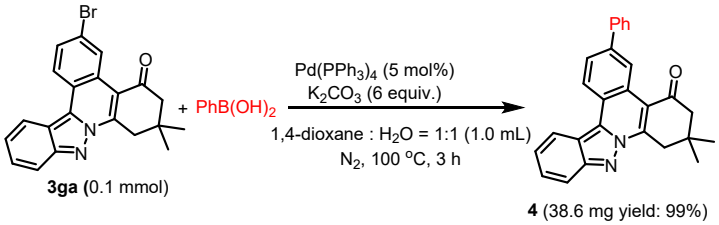


Fig. S4. The recyclability of the rhodium catalyst

An oven-dried 15 mL reaction flask with a magnetic stir bar was charged with indazole **1a** (0.2 mmol), iodonium ylides **2a** (0.24 mmol, 1.2 equiv.), $[RhCp^*Cl_2]_2$ (2 mol%), $AgSbF_6$ (4 mol%), AcOH (2 equiv.) and MeOH (2 mL) under air. The reaction mixture was stirred at 38°C until the **1a** was consumed completely detected by TLC. Afterwards, the product was filtered directly. The filtrate was transferred to the flask, and to which indazole **1a** (0.2 mmol, 1.0 equiv.), iodonium ylides **2a** (0.24 mmol, 1.2 equiv.) was added. The reaction mixture was stirred at 38°C until the **1a**

was consumed completely detected by TLC. The product was filtered directly. The filtrate was transferred to the flask again for the next six times.

6. Derivatization reactions



3ga (0.1 mmol) **4** (38.6 mg yield: 99%)

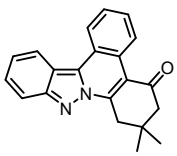
An oven-dried 10 mL schlenk tube with a magnetic stir bar was charged with **3ga** (0.1 mmol), $PhB(OH)_2$ (0.12 mmol, 1.2 equiv.), $Pd(PPh_3)_4$ (5 mol%), K_2CO_3 (0.6 mmol, 6 equiv.), 1,4-dioxane (0.5 mL) and H_2O (0.5 mL) under N_2. The reaction solution was heated at 100 °C for 3 h. Afterwards the reaction was quenched with H_2O (10 mL) and extracted with EtOAc (3×10 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 **4** (38.6 mg, 99%).

3ab (0.2 mmol) **5** (41.2 mg, yield: 50%)

An oven-dried 10 mL reaction tube with a magnetic stir bar was charged with **3ab** (0.2mmol), NIS (0.22 mmol, 1.1 equiv.) and DMSO (2.0 mL) under air. The reaction solution was heated at 80 °C for 3 h. Afterwards the reaction was quenched with H_2O (10 mL) and extracted with EtOAc (3×10 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 **5** (41.2 mg, 50%).

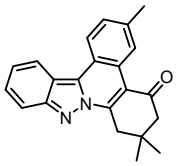
7. Analytical data of the synthesized derivatives

7,7-Dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3aa)



Yellow solid; 62 mg, yield 99%; m.p. 179-180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44-9.38 (m, 1H), 8.50-8.43 (m, 1H), 8.27 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.63-7.58 (m, 2H), 7.53 (dt, J = 7.6, 0.8 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 3.54 (s, 2H), 2.67 (s, 2H), 1.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 150.3, 145.5, 132.2, 128.6, 128.4, 127.9, 126.8, 125.3, 124.9, 122.5, 122.3, 121.7, 117.4, 116.7, 116.5, 53.6, 40.0, 32.4, 28.5; IR (KBr): 3446, 2961, 1672, 1627, 1520, 1486,1466, 1367, 1326,1282, 1233, 752 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{21}H_{18}N_2O$: 315.1492, found: 315.1484.

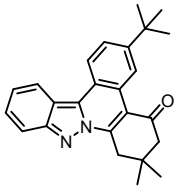
3,7,7-Trimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3ba)



Yellow solid; 65 mg, yield 99%; m.p. 195-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.3 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.8Hz,

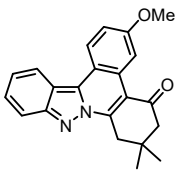
1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 3.50 (s, 2H), 2.63 (s, 2H), 2.53 (s, 3H), 1.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 150.4, 145.4, 138.7, 132.3, 129.4, 128.5, 126.4, 125.4, 122.7, 122.4, 121.9, 121.8, 117.2, 116.4, 116.2, 53.6, 40,0, 32.4, 28.5, 22.3; IR (KBr): 3459, 2957, 1681, 1666, 1626, 1520, 1411,1367, 1281, 1230, 740 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{22}H_{20}N_2O$: 329.1648, found: 329.1648.

3-(*tert*-Butyl)-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3ca)



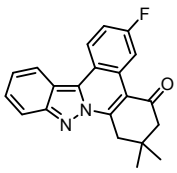
Yellow solid; 73 mg, yield 99%; m.p. 196-198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.56 (d, *J* = 8.8 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 3.62 (s, 2H), 2.72 (s, 2H), 1.49 (s, 9H), 1.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 151.8, 150.5, 145.5, 132.4, 128.6, 126.2, 125.5, 123.0, 122.8, 122.4, 122.0, 121.8, 117.2, 116.7, 116.6, 53.8, 40.1, 35.5, 32.5, 31.4, 28.5;IR (KBr):3456, 2957, 1670, 1627, 1520, 1411, 1366, 1284, 1262, 1233,744 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{25}H_{26}N_2O$: 371.2118, found: 317.2125.

3-Methoxy-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3da)



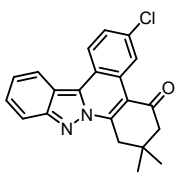
Yellow solid; 68 mg, yield 99%; m.p. 174-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.34 (d, *J* = 8.8 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.51 (t, *J* = 6.8 Hz, 1H), 7.23-7.18 (m, 2H), 3.96 (s, 3H), 3.51 (s, 2H), 2.64 (s, 2H), 1.23 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 159.7, 150.5, 145.9, 132.5, 128.7, 127.1, 123.8, 121.8, 121.6, 119.1, 118.3, 117.0, 115.9, 115.6, 107.4, 55.4, 53.6, 40.0, 32.3, 28.4; IR (KBr): 3449, 2959, 1673, 1627, 1614, 1521, 1414, 1374, 1282, 1230, 739 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{22}H_{20}N_2O_2$: 345.1598, found: 345.1597.

3-Fluoro-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3ea)



Yellow solid; 66 mg, yield 99%; m.p. 197-199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (dd, *J* = 12.0, 2.4 Hz, 1H), 8.32-8.24 (m, 1H), 8.09 (t, *J* = 8.8 Hz, 1H), 7.87 (d,*J* = 8.8 Hz, 1H), 7.52 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.30-7.20 (m, 2H), 3.47 (s, 2H), 2.62 (s, 2H), 1.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 162.1 (d, ^1J = 245.8 Hz), 150.3, 146.4, 131.7, 128.8, 126.9 (d, ^3J = 10.6 Hz), 126.8, 124.3 (d, ^3J = 9.0 Hz), 122.4, 121.4, 117.4, 116.7 (d, ^2J = 24.2 Hz), 116.2, 115.4 (d, ^4J = 4.4 Hz), 112.4 (d,^2J = 25.5 Hz), 53.2, 39.8, 32.2, 28.4; IR (KBr): 3462, 2957, 1670, 1628, 1558, 1426, 1369, 1295, 1282, 1228, 741 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{21}H_{17}FN_2O$: 333.1398, found: 333.1400.

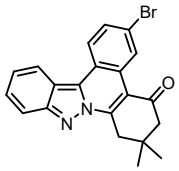
3-Chloro-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3fa)



Yellow solid; 68 mg, yield 97%; m.p. 195-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (d, *J* = 1.6 Hz, 1H), 8.16-7.99 (m, 2H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 1H), 7.28-7.20 (m, 1H), 3.44 (s, 2H), 2.61 (s, 2H), 1.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 150.3, 146.3, 134.5, 131.4, 128.8, 128.2, 126.3, 126.0, 123.4, 122.8, 122.6, 121.4, 117.4, 116.4, 115.1,

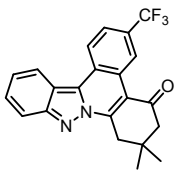
53.2, 39.8, 32.2, 28.4; IR (KBr): 3460, 2956, 1672, 1629, 1540, 1452, 1371, 1295, 1191, 808, 734 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{21}H_{17}ClN_2O$: 349.1102, found: 349.1108.

3-Bromo-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3ga)



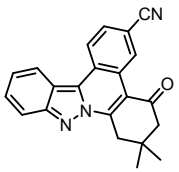
Yellow solid; 70 mg, yield 89%; m.p. 211-213 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.05 (t, *J* = 7.2 Hz, 2H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.56-7.49 (m, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 3.44 (s, 2H), 2.62 (s, 2H), 1.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 150.4, 146.4, 131.4, 131.0, 129.4, 128.8, 126.3, 123.5, 123.1, 122.9, 122.6, 121.4, 117.5, 116.5, 115.1, 53.3, 39.9, 32.3, 28.4; IR (KBr): 3454, 2958, 1676, 1627, 1539, 1519, 1366, 1324, 1281, 1188, 738 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{21}H_{17}BrN_2O$: 393.0597, found: 393.0599.

7,7-Dimethyl-3-(trifluoromethyl)-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3ha)



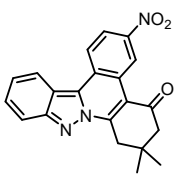
Yellow solid; 65 mg, yield 85%; m.p. 216-218 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 8.48 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 3.52 (s, 2H), 2.69 (s, 2H), 1.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 150.3, 146.7, 131.0, 129.7 (q, ^2J= 32.4 Hz), 129.2, 128.9, 126.5, 124.7, 124.5 (q, ^3J = 4.5 Hz), 124.1 (q, ^1J = 270.9 Hz), 124.0 (q, ^3J= 3.3 Hz), 123.3, 122.9, 121.2, 117.7, 117.0, 115.8, 53.3, 39.9, 32.3, 28.4; IR (KBr): 3456, 2959, 1671, 1626, 1521, 1371, 1322, 1309, 1140, 1078, 748 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{22}H_{17}F_3N_2O$: 383.1366, found: 383.1369.

7,7-Dimethyl-5-oxo-5,6,7,8-tetrahydroindazolo[2,3-f]phenanthridine-3-carbonitrile (3ia)



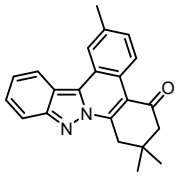
Yellow solid; 67 mg, yield 99%; m.p. up to 250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.70 (d, *J* = 8.4 Hz, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.91 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 3.68 (s, 2H), 2.77 (s, 2H), 1.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 150.6, 147.3, 132.3, 129.9, 129.2, 127.0, 124.9, 123.9, 123.3, 121.3, 118.1, 117.6, 115.5, 111.6, 100.0, 53.4, 40.1, 32.5, 28.5; IR (KBr): 3449, 2959, 2223, 1685, 1630, 1524, 1369, 1300, 1278, 1232, 756 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{22}H_{17}N_3O$: 340.1444, found: 340.1453.

7,7-Dimethyl-3-nitro-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3ja)



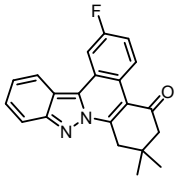
Yellow solid; 71 mg, yield 99%; m.p. up to 250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (d, *J* = 2.4 Hz, 1H), 8.78 (d, *J* = 9.4 Hz, 1H), 8.54 (dd, *J* = 9.2, 2.4 Hz, 1H), 8.45 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.69-7.64 (m, 1H), 7.51-7.46 (m, 1H), 3.72 (s, 2H), 2.80 (s, 2H), 1.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 150.7, 129.3, 128.4, 125.1, 124.2, 123.5, 123.4, 122.3, 121.2, 118.2, 117.8, 116.1, 53.3, 40.1, 32.5, 28.5; IR (KBr): 3450, 2953, 1672, 1626, 1522, 1348, 1333, 1297, 1231, 1190, 756 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{21}H_{17}N_3O_3$: 360.1343, found: 360.1345.

2,7,7-Trimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3ka)



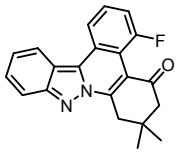
Yellow solid; 59 mg, yield 90%; m.p. 165-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (d, *J* = 8.8 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 8.19 (s, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 3.50 (s, 2H), 2.66 (s, 2H), 2.53 (s, 3H), 1.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 150.2, 144.5, 137.9, 131.9, 130.1, 128.4, 126.6, 124.9, 123.0, 122.1, 122.0, 121.9, 117.3, 116.6, 116.4, 53.5, 39.9, 32.4, 28.5, 21.8; IR (KBr): 3453, 2958, 1672, 1628, 1522, 1496, 1372, 1325, 1297, 1229, 734 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{22}H_{20}N_2O$: 329.1648, found: 329.1641.

2-Fluoro-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3la$_1$)



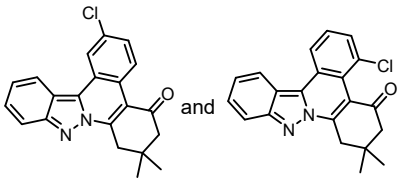
Yellow solid; 60 mg, yield 90%; m.p. 191-193 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.15 (m, 2H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.58-7.49 (m, 2H), 7.29-7.22 (m, 2H), 3.48 (s, 2H), 2.75 (s, 2H), 1.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 158.5 (d, ^1J = 256.7 Hz), 150.1, 143.7, 130.9, 129.2 (d, ^3J = 9.3 Hz), 128.5, 126.9 (d, ^4J = 5.0 Hz), 122.8, 121.3, 118.4 (d, ^4J = 3.4 Hz), 118.3 (d, ^3J = 5.8 Hz), 117.5, 116.7, 114.6 (d, ^2J= 23.1 Hz), 113.08 (d, ^2J = 14.6 Hz), 52.5, 39.5, 33.8, 29.0; IR (KBr): 3437, 2961, 1696, 1626, 1520, 1471, 1365, 1299, 1245, 1203, 749 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{21}H_{17}FN_2O$: 333.1398, found: 333.1389.

4-Fluoro-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3la$_2$)



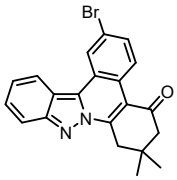
Yellow solid; 6 mg, yield 9%; m.p. 219-222 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (dd, *J* = 9.6, 6.0 Hz, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 8.19 (dd, *J* = 9.2, 2.4 Hz,1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.44-7.34 (m, 2H), 3.62 (s, 2H), 2.73 (s, 2H), 1.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 161.7 (d, ^1J = 265.6 Hz), 150.4, 144.9 (d,^4J = 2.2 Hz), 129.9 (d, ^3J = 8.5 Hz), 128.7,126.4 (d, ^3J = 9.5 Hz), 122.9, 122.0 (d, ^4J = 2.3 Hz), 121.3, 117.6, 117.2, 117.1 (d, ^2J = 22.4 Hz), 117.0, 116.3, 107.8 (d, ^2J = 23.1 Hz), 53.6, 40.0, 32.5, 28.5; IR (KBr): 3455, 2957, 1670, 1620, 1523, 1493, 1366, 1267, 1217, 839, 743 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{21}H_{17}FN_2O$: 333.1398, found: 333.1396.

2-Chloro-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3ma$_1$) and **4-chloro-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3ma$_2$) (78:22)**



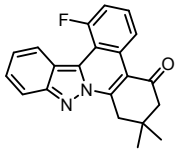
Yellow solid; 69 mg, yield 99%; m.p. 174-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (d, *J* = 8.8 Hz, 0.78H), 8.39 (d, *J* = 8.0 Hz, 0.22H), 8.30 (d, *J* = 1.6 Hz, 0.78H), 8.20 (d, *J* = 8.8 Hz, 0.22H), 8.13 (d, *J* = 8.4 Hz, 0.78H), 7.78 (d, *J* = 8.8, 1H), 7.63 (d, *J* = 8.4 Hz, 0.22H), 7.57-7.49 (m, 2H), 7.29 (d, *J*= 8.0 Hz, 1H), 3.50 (s, 2H), 2.80 (s, 0.44H), 2.67 (s, 1.56H), 1.30 (s, 1.32H), 1.25 (s, 4.68H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 195.9, 150.3, 150.2, 145.6, 144.2, 133.9, 132.2, 131.0, 130.7, 130.2, 128.7, 128.6, 128.5, 128.4, 127.4, 125.7, 123.4, 122.9, 122.8, 122.7, 121.6, 121.2, 121.1, 120.5, 117.7, 117.5, 116.8, 116.6, 115.9, 53.4, 52.3, 39.9, 39.4, 33.7, 32.4, 29.2, 28.5; IR (KBr): 2955, 2867, 1693, 1626, 1519, 1484, 1367, 1285, 1187, 788, 749 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{21}H_{17}ClN_2O$: 349.1102, found: 349.1092.

2-Bromo-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3na)



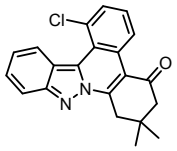
Yellow solid; 73 mg, yield 93%; m.p. 212-214 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (d, *J* = 9.2 Hz, 1H), 8.50 (s, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 3.50 (s, 2H), 2.67 (s, 2H), 1.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 150.2, 145.7, 131.4, 130.5, 128.7, 128.6, 126.0, 124.8, 123.7, 122.9, 122.3, 121.2, 117.5, 116.6, 115.9, 53.4, 39.9, 32.4, 28.5; IR (KBr): 3077, 2954, 1667, 1625, 1518, 1478, 1369, 1322, 1229, 1184, 833, 737 cm^{-1}; HRMS (ESI): *m/z* [M+H]$^+$calcd for $C_{21}H_{17}BrN_2O$: 393.0597, found: 393.0597.

1-Fluoro-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3pa)



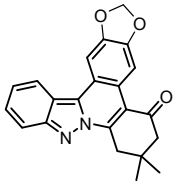
Yellow solid; 66 mg, yield 99%; m.p. 175-177 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, *J* = 8.4 Hz, 1H), 8.45 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.56-7.46 (m, 2H), 7.29 (dd, *J* = 12.4, 8.0 Hz, 1H), 7.20 (t, *J* = 8.0 Hz 1H), 3.56 (s, 2H), 2.68 (s, 2H), 1.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 157.0 (d, ^1J = 249.2 Hz), 150.7, 146.4, 129.3 (d, ^4J = 1.4 Hz), 128.7,128.6, 127.0 (d, ^3J = 4.1 Hz), 124.0 (d, ^2J = 34.7 Hz), 122.4 (d, ^4J = 3.5 Hz), 122.2 (d, ^3J = 6.4 Hz), 117.4, 116.9, 115.9 (d, ^4J = 1.0 Hz), 114..0 (d, ^3J = 16.6 Hz), 113.6 (d, ^2J = 22.0 Hz), 53.6, 40.4, 32.3, 28.5; IR (KBr): 2958, 1672, 1622, 1513, 1476, 1466, 1369, 1325, 1244, 747 cm^{-1}; HRMS (ESI): *m/z* [M+H]$^+$calcd for $C_{21}H_{17}FN_2O$: 333.1398, found: 333.1393.

1-Chloro-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3qa)



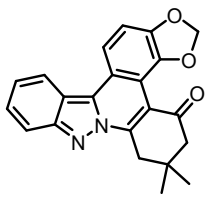
Yellow solid; 47 mg, yield 68%; m.p. 202-204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (d, *J* = 7.6 Hz, 1H), 8.69 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 6.8 Hz, 1H), 7.60-7.51 (m, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 3.66 (s, 2H), 2.72 (s, 2H), 1.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 150.7, 146.2, 131.1, 130.2, 128.6, 128.4, 128.1, 126.3, 125.1, 123.4, 121.3, 117.9, 117.3, 116.2, 53.7, 40.5, 32.3, 28.5; IR (KBr): 3123, 2949, 1680, 1619, 1538, 1466, 1365, 1320, 1198, 1135, 758 cm^{-1}; HRMS (ESI): *m/z* [M+H]$^+$calcd for $C_{21}H_{17}FN_2O$: 349.1102, found: 349.1106.

6,6-Dimethyl-6,7-dihydro-[1,3]dioxolo[4,5-k]indazolo[2,3-f]phenanthridin-4(5*H*)-one (3ta$_1$)



Yellow solid; 64 mg, yield 89%; m.p. 212-214 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.28-7.21 (m, 2H), 6.16 (s, 2H), 3.53 (s, 2H), 2.73 (s, 2H), 1.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 150.2, 147.2, 144.0, 142.7, 132.2, 128.5, 122.1, 121.6, 120.8, 117.3, 117.2, 116.1, 110.6, 109.3, 101.4, 52.6, 39.6, 33.6, 28.9; IR (KBr): 3089, 2947, 1672, 1633, 1526, 1350, 1303, 1286, 1223, 741 cm^{-1}; HRMS (ESI): *m/z* [M+H]$^+$calcd for $C_{22}H_{18}N_2O_3$: 359.1390, found: 359.1393.

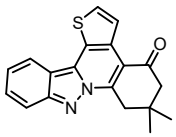
7,7-Dimethyl-7,8-dihydro-[1,3]dioxolo[4,5-j]indazolo[2,3-f]phenanthridin-5(6*H*)-one (3ta$_2$)



Yellow solid; 7 mg, yield 10%; m.p. 239-241 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.28 (d, *J* = 8.8 Hz, 1H), 7.96-7.90 (m, 2H), 7.59-7.54 (m, 1H),

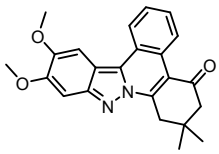
7.29 (t, J = 8.0 Hz, 1H), 6.15 (s, 2H), 3.60 (s, 2H), 2.70 (s, 2H), 1.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.04, 150.6, 149.3, 148.4, 143.7, 132.4, 128.6, 122, 121.6, 121.6, 121.3, 117.1, 116.2, 116.1, 105.3, 102.0, 100.6, 53.7, 40.0, 32.4, 28.5; IR (KBr): 3463, 2955, 1664, 1628, 1495, 1469, 1377, 1300, 1248, 1035, 732 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{22}H_{18}N_2O_3$: 359.1390, found: 359.1383.

6,6-Dimethyl-6,7-dihydroindazolo[2,3-a]thieno[2,3-c]quinolin-4(5*H*)-one (3ua)



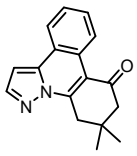
Yellow solid; 63 mg, yield 99%; m.p. 228-230 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 5.2 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.67 (d, J = 5.6 Hz, 1H), 7.57 (t, J = 7.2 Hz, 1H), 7.27 (t, J = 7.2 Hz, 1H), 3.55 (s, 2H), 2.67 (s, 2H), 1.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 150.7, 142.9, 131.7, 130.8, 129.4, 128.4, 128.1, 125.3, 121.3, 120.9, 116.4, 115.9, 114.8, 52.2, 39.3, 32.8, 28.6; IR (KBr): 3475, 2948, 1672, 1634, 1526, 1380, 1350, 1303, 1287, 1224, 741 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{19}H_{16}N_2OS$: 321.1056, found: 321.1054.

12,13-Dimethoxy-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3va)



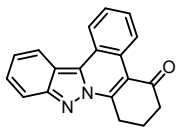
Yellow solid; 74 mg, yield 99%; m.p. 209-230 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (d, J = 7.2 Hz, 1H), 8.18-8.12 (m, 1H), 7.59-7.52 (m, 2H), 7.20 (s, 1H), 7.07 (s, 1H), 3.99 (s, 6H), 3.39 (s, 2H), 2.63 (s, 2H), 1.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 152.9, 148.0, 147.5, 145.7, 131.0, 127.9, 127.4, 126.8, 125.3, 124.4, 122.0, 114.6, 110.6, 98.5, 95.3, 56.1, 56.0, 53.4, 39.8, 32.2, 28.5; IR (KBr): 3385, 2965, 1668, 1639, 1528, 1504, 1461, 1323, 1231, 1202, 810 cm^{-1}; HRMS (ESI): *m/z*$[M+H]^+$calcd for $C_{23}H_{22}N_2O_3$: 375.1703, found: 375.1669.

10,10-Dimethyl-10,11-dihydropyrazolo[1,5-f]phenanthridin-8(9*H*)-one (3wa)



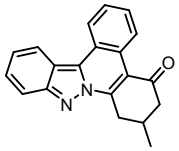
White solid; 11 mg, yield 20%; m.p. 100-101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 2.0 Hz, 1H), 8.07 (dd, J = 7.6, 0.8 Hz, 1H), 7.64-7.59 (m, 1H), 7.58-7.52 (m, 1H), 7.04 (d, J = 2.0 Hz, 1H), 3.45 (s, 2H), 2.66 (s, 2H), 1.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 146.4, 143.6, 140.0, 129.2, 127.4, 126.9, 126.1, 123.4, 123.2, 113.8, 99.28, 53.6, 39.5, 32.3, 28.5; IR (KBr): 2962, 1667, 1600, 1483, 1427, 1409, 1333, 1296, 1269, 757 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{17}H_{16}N_2O$: 265.1335, found: 265.1331.

7,7-Dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3ab)



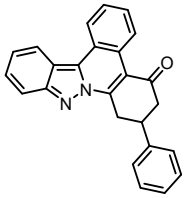
Yellow solid; 56 mg, yield 98%; m.p. 211-213 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (d, J = 8.4 Hz, 1H), 8.38 (d, J = 6.8 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.61-7.49 (m, 3H), 7.25 (t, J = 6.8 Hz, 1H), 3.62 (t, J = 6.4 Hz, 2H), 2.81 (t, J = 6.0 Hz, 2H), 2.39-2.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 150.3, 147.1, 131.8, 128.4, 128.2, 127.8, 126.9, 125.3, 124.7, 122.4, 122.1, 121.7, 117.3, 117.2, 116.6, 39.9, 26.4, 20.8; IR (KBr): 3455, 2964, 2361, 1680, 1628, 1522, 1486, 1372, 1326, 766 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{19}H_{14}N_2O$: 287.1179, found: 287.1175.

7-Methyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3ac)



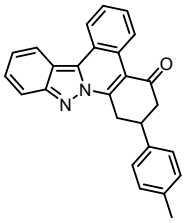
Yellow solid; 59 mg, yield 99%; m.p. 188-190 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (d, *J* = 8.0 Hz, 1H), 8.29 (d, *J* = 7.2 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.56-7.46 (m, 3H), 7.22 (t, *J* = 7.6 Hz, 1H), 3.89 (d, *J* = 18.8 Hz, 1H), 2.90 (dd, *J* = 18.4, 9.6 Hz, 1H), 2.79 (d, *J* = 11.2 Hz, 1H), 2.54-2.40 (m, 2H), 1.27 (d, *J* = 3.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 150.2, 146.4, 131.7, 128.4, 128.2, 127.7, 126.7, 125.1, 124.5, 122.3, 122.1, 121.7, 117.3, 116.7, 116.5, 47.9, 34.2, 28.3, 21.3; IR (KBr): 3450, 2955, 1669, 1627, 1521, 1487, 1375, 1293, 1209, 754 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{20}H_{16}N_2O$: 301.1335, found: 301.1337.

7-Phenyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3ad)



Yellow solid; 72 mg, yield 99%; m.p. 249-251°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (dd, *J* = 8.0, 1.2 Hz,1H), 8.72 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.80-7.72 (m, 2H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.43-7.33 (m, 6H), 4.44 (dd, *J* = 18.0, 4.0 Hz, 1H), 3.78-3.72 (m, 1H), 3.64 (dd, *J* = 18.0, 11.2 Hz, 1H), 3.18-3.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 150.6, 146.4, 142.1, 132.3, 128.9, 128.7 128.6, 128.2, 127.4, 127.2, 126.8, 125.6, 125.2, 122.8, 122.5, 121.8, 117.6, 117.3, 116.9, 46.7, 39.0, 34.2; IR (KBr): 3445, 1668, 1627, 1522, 1384, 1365, 1385, 748 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{25}H_{18}N_2O$: 363.1492, found: 363.1496.

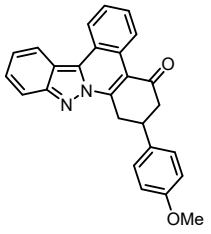
7-(*p*-Tolyl)-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3ae)



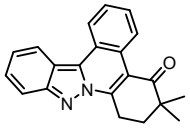
Yellow solid; 74 mg, yield 99%; m.p. 230-232 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (d, *J* = 6.0 Hz, 1H), 8.60 (d, *J* = 5.2 Hz, 1H), 8.37 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.72-7.67 (m, 2H), 7.56 (t, *J* = 6.8 Hz, 1H), 7.35-7.28 (m, 3H), 7.35-7.19 (m, 2H), 4.34 (d, *J* = 18.4 Hz, 1H), 3.72-3.64 (m, 1H), 3.53 (dd, *J* = 18.4, 11.6 Hz, 1H), 3.10 (d, *J* = 8.4 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 150.5, 146.6, 139.3, 136.9, 132.1, 129.5, 128.6, 128.5 128.1, 127.1, 126.7, 125.4, 125.0, 122.6, 122.4, 121.8, 117.5, 117.1, 116.8, 46.8, 38.5, 34.1, 21.1; IR (KBr): 3457, 1664, 1627, 1516, 1485, 1384, 1371, 1291, 764 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{26}H_{20}N_2O$: 377.1648, found: 377.1655.

7-(4-Methoxyphenyl)-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3af)

Yellow solid; 78 mg, yield 99%; m.p. 236-238 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.72 (dd, *J* = 7.6, 1.2 Hz, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.79-7.71 (m, 2H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.38-7.33 (m, 3H), 6.94 (d, *J* = 8.4 Hz, 2H), 4.42 (dd, *J* = 18.0, 4.0 Hz, 1H), 3.83 (s, 3H), 3.75-3.67 (m, 1H), 3.60 (dd, *J* = 18.0, 11.2 Hz, 1H), 3.13 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 158.8, 153.8, 150.7, 146.7, 134.4, 128.7, 128.6, 128.2, 127.8, 127.2, 125.7, 125.2, 122.7, 122.4, 121.8, 117.6, 117.3, 116.9, 114.3, 55.4, 47.0, 38.2, 34.4; IR (KBr): 3450, 2927, 1665, 1629, 1514, 1485, 1372, 1292, 1245, 1188, 763 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{26}H_{20}N_2O_2$: 393.1598, found: 393.1590.

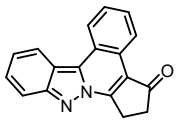


6,6-Dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (3ag)



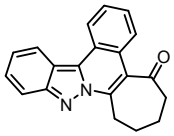
Yellow solid; 60 mg, yield 95%; m.p.140-143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34-9.27 (m, 1H), 8.48-8.44 (m,1H), 8.26 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.63-7.58 (m, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 8.4 Hz, 1H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.21 (t, *J* = 6.4 Hz, 2H), 1.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.5, 150.3, 145.1, 131.8, 128.4, 128.2, 127.8, 127.0, 125.8, 125.1, 122.6, 122.1, 121.7, 117.3, 116.6, 116.1, 42.4, 34.0, 24.5, 23.21; IR (KBr): 3459, 2921, 1627, 1522, 1487, 1370, 1074, 773, 749 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{21}H_{18}N_2O$: 315.1492, found: 315.1489.

6,7-Dihydro-5*H*-cyclopenta[c]indazolo[3,2-a]isoquinolin-5-one (3ah)



Yellow solid; 54 mg, yield 99%; m.p. up to 250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (d, *J* = 7.6, 1.2 Hz,1H), 8.70 (d, *J* = 8.0 Hz, 1H), 8.46 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.781-7.72 (m, 2H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 3.70-3.67 (m, 2H), 3.05-3.02 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 151.4, 142.5, 134.6, 130.5, 128.8, 128.7, 128.6, 124.5, 124.4, 124.0, 123.0, 122.8, 121.6. 117.8, 117.3, 35.9, 39.0, 23.5; IR (KBr): 3450, 1702, 1637, 1531, 1371, 1286, 1238, 1096, 779, 734 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{18}H_{12}N_2O$: 273.1022, found: 273.1028.

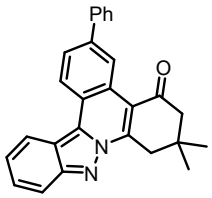
6,7,8,9-Tetrahydro-5*H*-cyclohepta[c]indazolo[3,2-a]isoquinolin-5-one (3ai)



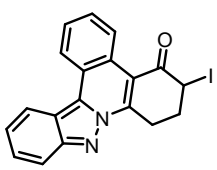
Yellow solid; 20 mg, yield 33%; m.p. 142-144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.0 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 3.86 (t, *J* = 6.4 Hz, 2H), 2.92 (t, *J* = 6.0 Hz, 2H), 2.18-2.07 (m, 2H), 2.03-1.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 149.5, 139.2, 131.2, 128.0, 128.0, 127.8, 125.4, 125.2, 124.9, 124.8, 122.9, 121.9, 121.5, 117.3, 117.0, 42.8, 27.0, 22.9, 22.6; IR (KBr): 3051, 2929, 1673, 1627, 1520, 1370, 1283, 1239, 1152, 751 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{20}H_{16}N_2O$: 301.1335, found: 301.1339.

7,7-Dimethyl-3-phenyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (4)

Yellow solid; 38.6 mg, yield 99%; m.p. 222-224 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (d, *J* = 1.2 Hz, 1H), 8.59 (d, *J* = 8.8 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.96-7.93 (m, 1H), 7.91 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.81-7.78 (m, 2H), 7.59-7.54 (m, 1H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.42-7.38 (m, 1H), 7.33-7.29 (m, 1H), 3.60 (s, 2H), 2.70 (s, 2H), 1.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 150.5, 145.8, 140.7, 140.4, 132.1, 129.0, 128.7, 127.8, 127.5, 126.9, 126.8, 125.7, 124.9, 123.8, 122.9, 122.3, 121.8, 117.4, 116.8, 116.5, 53.6, 40.0, 32.4, 28.5; IR (KBr): 3057, 2958, 2360, 1673, 1626, 1549, 1519, 1409, 1370, 1282, 1230, 751cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{27}H_{22}N_2O$: 391.1805, found: 391.1810.



6-Iodo-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6*H*)-one (5)



Yellow solid; 41.2 mg, yield 50%; m.p.231-233°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47-9.44 (m, 1H), 8.73 (s, 1H), 8.50-8.47 (m,1H), 7.77-7.67 (m,

4H), 3.71 (t, J = 6.4 Hz, 2H), 2.90-2.85 (m, 2H), 2.44-2.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 148.9, 147.0, 136.9, 130.9, 130.6, 128.9, 128.3, 127.3, 125.7, 124.7, 122.5, 119.4, 118.9, 117.9, 86.0, 39.9, 26.5, 20.9; IR (KBr): 3447, 2923, 2360, 1679, 1620, 1509, 1392, 1360, 1267, 1233, 802, 767 cm^{-1}; HRMS (ESI): *m/z* $[M+H]^+$calcd for $C_{19}H_{13}IN_2O$: 413.0145, found:413.0147.

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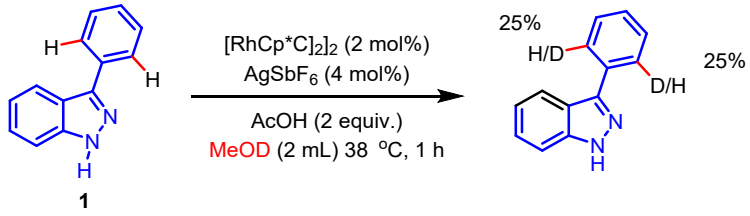
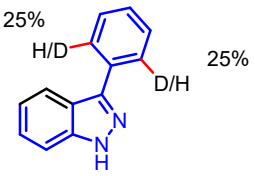
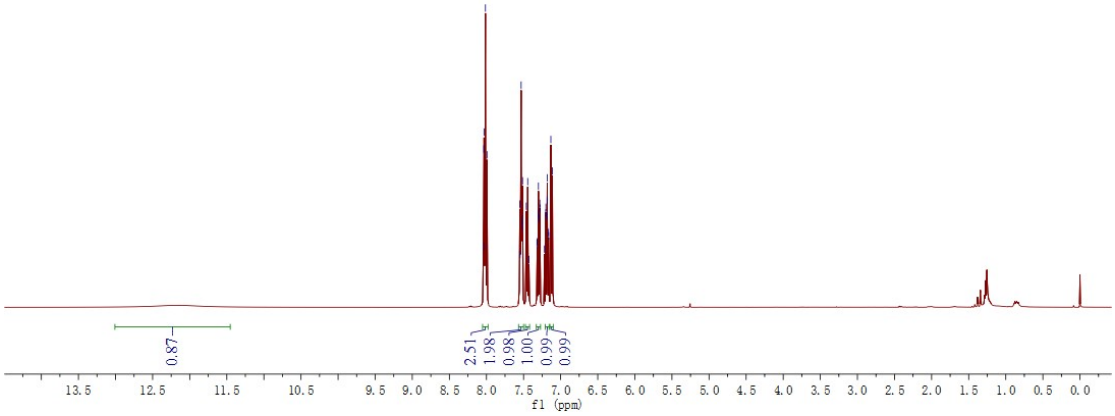
7. Mechanistic study

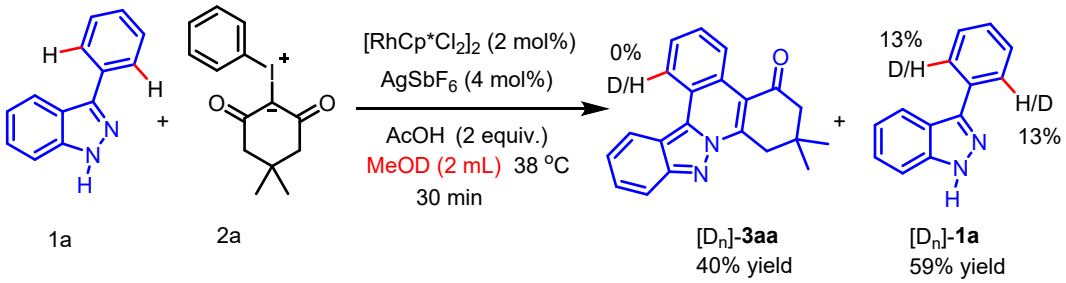
(a) H/D exchange experiments



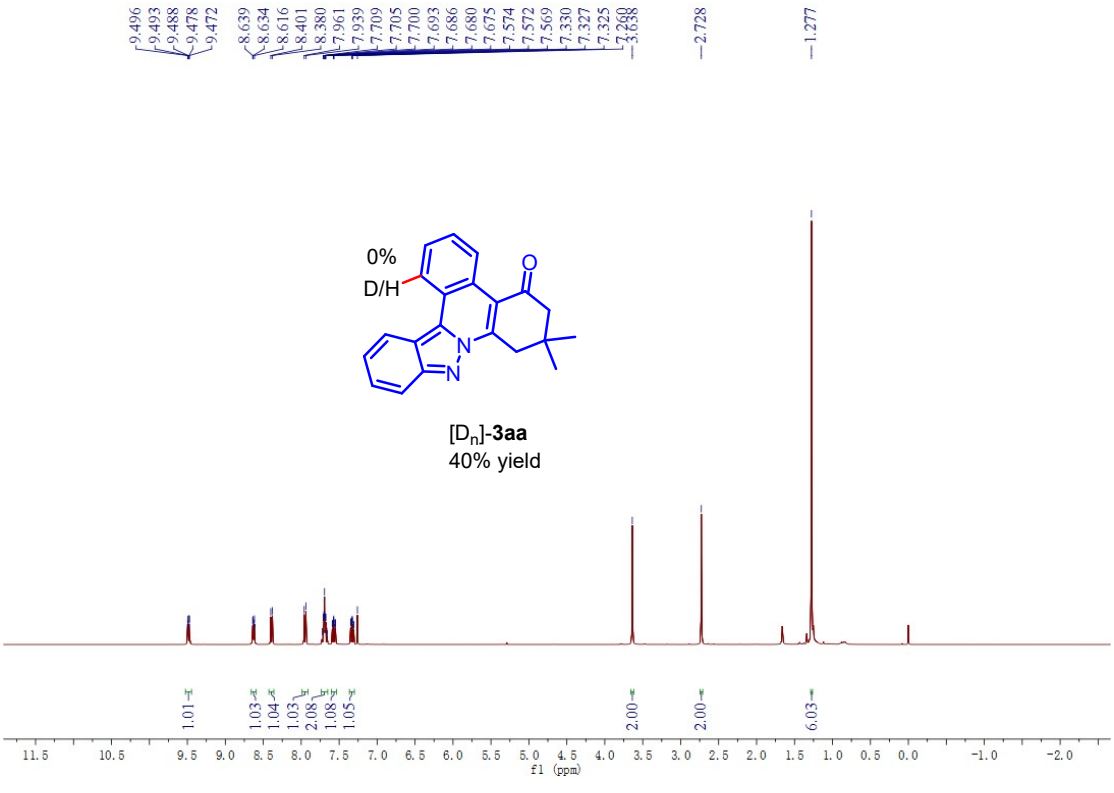
An oven-dried 10 mL reaction tube with a magnetic stir bar was charged with 3-Phenyl-1H-indazole **1** (0.2 mmol, 1.0 equiv.), $[RhCp^*Cl_2]_2$ (2 mol%), $AgSbF_6$ (4 mol%), AcOH (2 equiv.) and MeOD (2 mL) under air. The reaction was heated at 38 °C for 1h. Afterwards the reaction solution was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product. The deuterated ratio was calculation from ^{1}H NMR analysis.

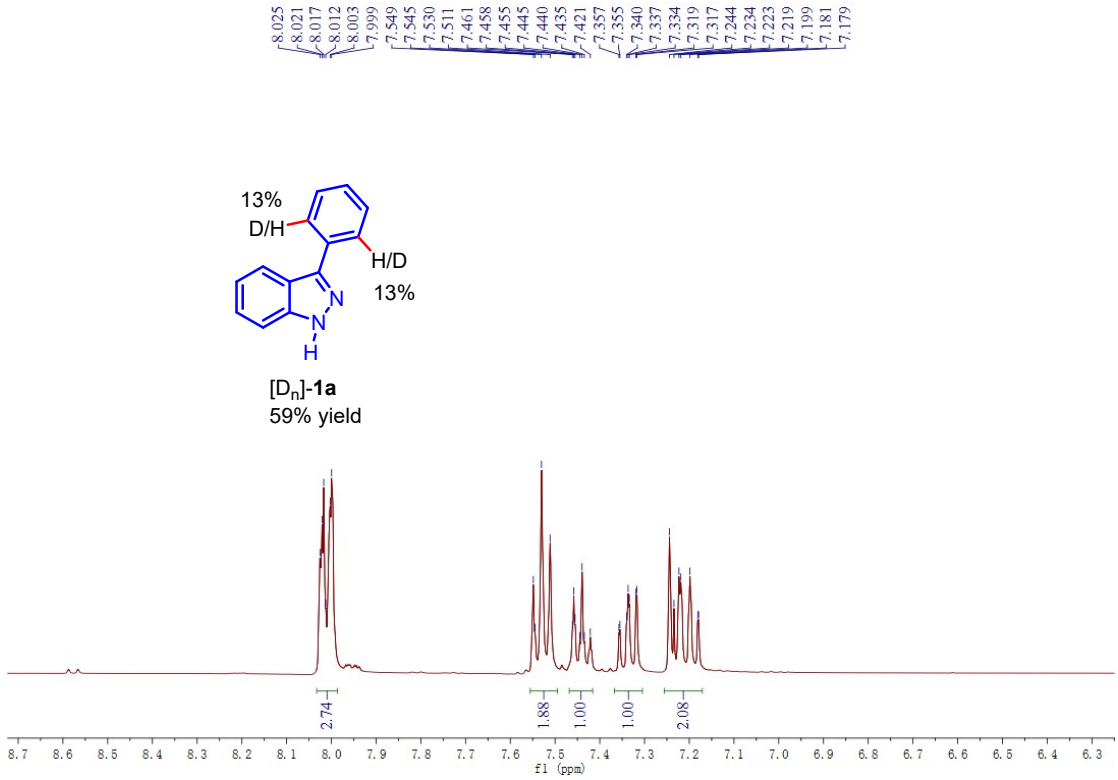




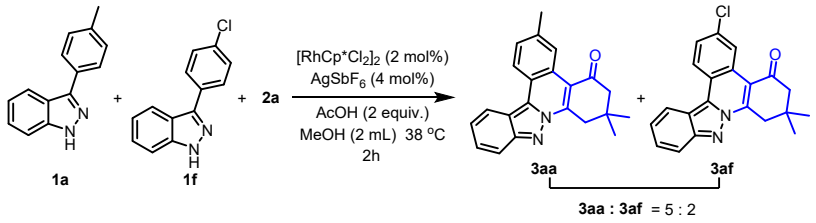


An oven-dried 10 mL reaction tube with a magnetic stir bar was charged with 3-Phenyl-1H-indazole **1** (0.2 mmol, 1.0 equiv.), iodonium ylides **2** (0.24 mmol, 1.2 equiv.), $[RhCp^*Cl_2]_2$ (2 mol%), $AgSbF_6$ (4 mol%), AcOH (2 equiv.) and MeOD (2 mL) under air. The reaction was heated at 38 °C for 30min. Afterwards the reaction solution was concentrated and the residue was purified by column chromatography on silica gel to provide the desired $[D_n]$-**3aa** and $[D_n]$-**1a**. The deuterated ratio was calculation from ^1H NMR analysis.

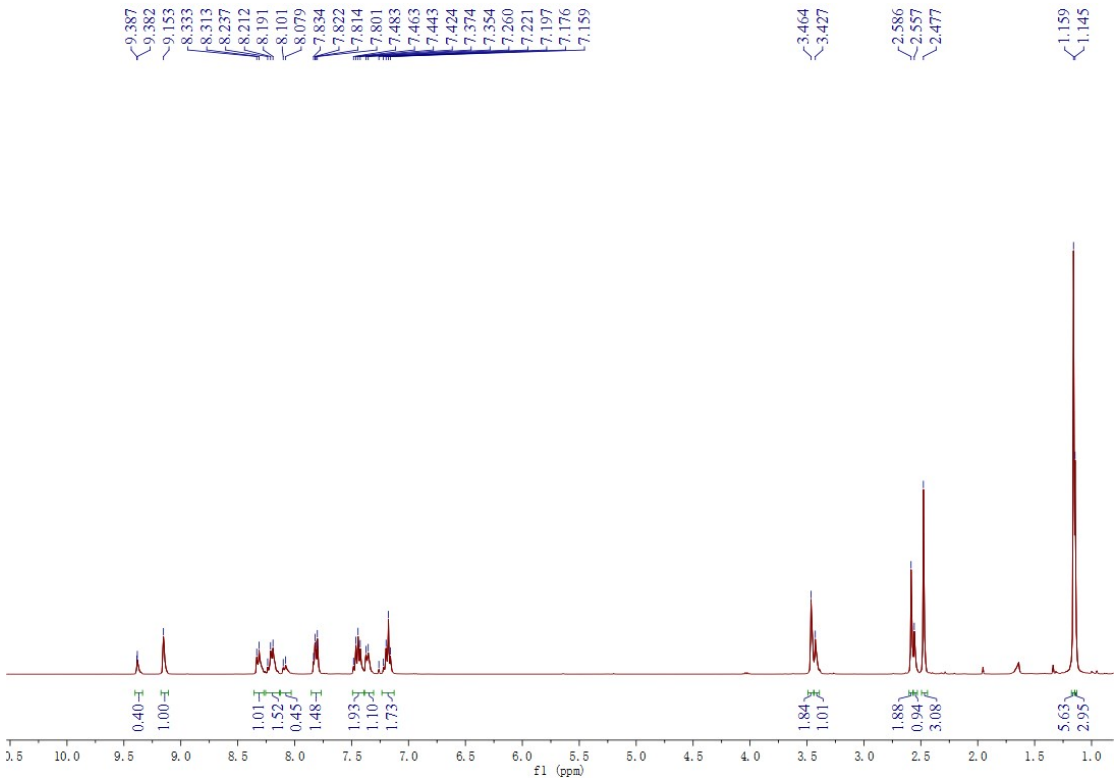




(b) Competition experiment



An oven-dried 10 mL reaction tube with a magnetic stir bar was charged with **1a** (0.2 mmol, 1.0 equiv.), **1f** (0.2 mmol, 1.0 equiv.), iodonium ylide **2a** (0.2 mmol, 1.0 equiv.), $[RhCp^*Cl_2]_2$ (2 mol%), $AgSbF_6$ (4 mol%), AcOH (2 equiv.) and MeOH (2 mL) under air. The reaction is heated for sufficient time at 38°C. Afterwards the reaction solution was concentrated and the residue was purified by column chromatography on silica gel to provide the desired mixture of **3aa** and **3af**. The proportion of **3aa** and **3af** was calculated by NMR analysis (**3aa**: **3af** = 5 : 2).



8. X-ray crystallography date of 3va.

The crystal structure was deposited into the CCDC database (CCDC No. 2189691). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

By slowly volatilizing the $CDCl_3$ solvent, single crystals **3va** suitable for X-ray analysis were obtained. The detailed characteristics and data are shown below.

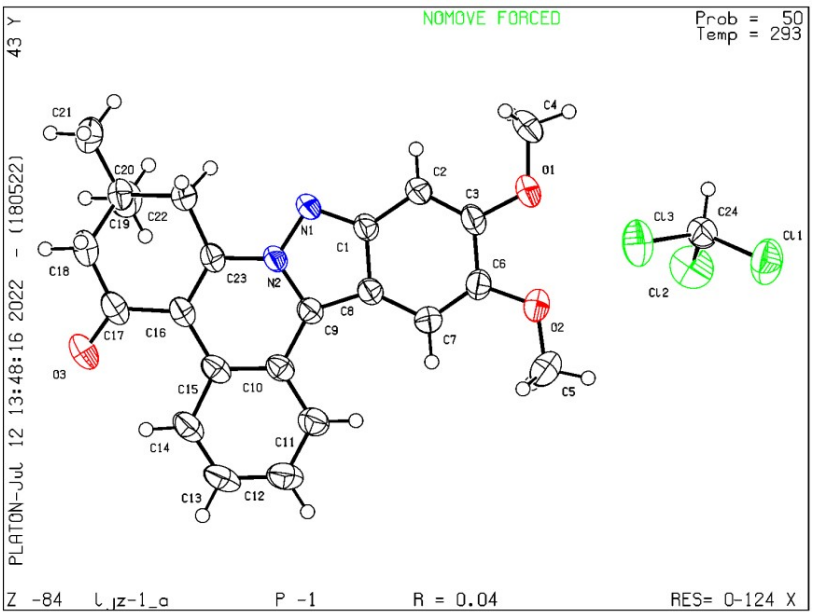


Figure S2. Crystal structure of compound **3va**

Table S2 Crystal data and structure refinement for **3va** (CCDC No. 2189691)

Identification code	**3va**
Empirical formula	C24 H23 Cl3 N2 O3
Formula weight	493.79
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 5.8190(2) Åa= 92.796(4)°.
	b = 9.8242(4) Åb= 92.658(3)°.
	c = 20.3104(10) Åg = 95.189(3)°.
Volume	1153.44(8) $Å^3$
Z	2
Density (calculated)	1.422 Mg/m^3
Absorption coefficient	0.427 mm^{-1}
F(000)	512
Crystal size	0.210 x 0.190 x 0.180 mm^3
Theta range for data collection	3.520 to 25.096°.
Index ranges	-6<=h<=6, -11<=k<=11, -23<=l<=24
Reflections collected	12533
Independent reflections	4077 [R(int) = 0.0229]
Completeness to theta = 25.096°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.31974
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4077 / 0 / 293
Goodness-of-fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0428, wR2 = 0.1082
R indices (all data)	R1 = 0.0544, wR2 = 0.1154
Extinction coefficient	n/a
Largest diff. peak and hole	0.249 and -0.334 $e.Å^{-3}$

9. Photophysical properties

a. The summarized photophysical properties of 3aa-3aj

Table S 3 Photophysical properties of the selected samples[a]

Product	λ_{abs} (nm)	λ_{em}Max (nm)	Stokes shift(nm)	Φ_F (%)
3aa	406	481	75	21.33
3ba	411	489	78	24.62
3ca	410	489	79	24.60
3da	424	508	84	50.44
3ea	412	490	78	28.92
3fa	411	488	77	14.84

3ga	412	486	74	0.88
3ha	403	478	75	16.80
3ia	407	480	73	17.89
3ja	414	555	141	31.19

[a] 5×10^{-6} M in CH_2Cl_2.

b. The UV-Vis and fluorescence spectra of 3ja and it emission picture in different solvents.

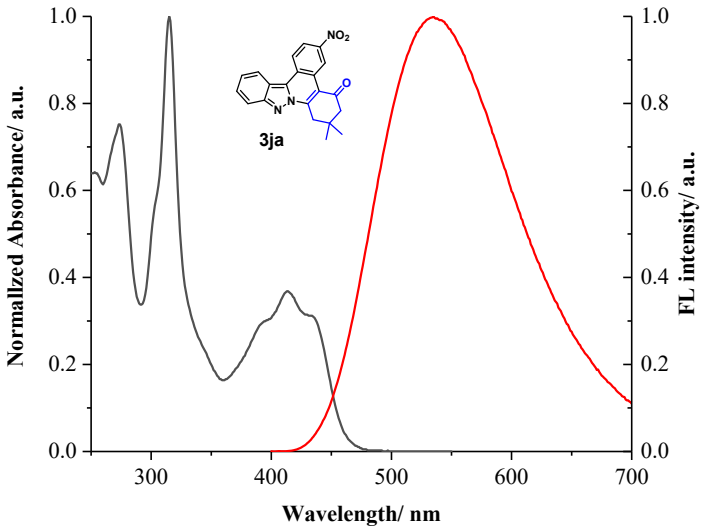


Figure S3 Normalized absorption and emission spectra of **3ja** in DCM solution.

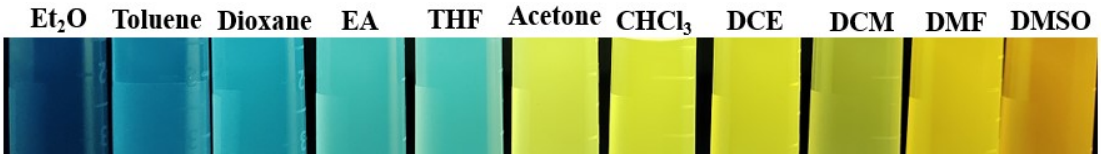


Figure S4 The fluorescence emission image of **3ja** in different solvent, demonstrate a remarkable solvatochromic effect.

c. The photophysical properties of the selected F contain samples

Table S4 Photophysical properties of the selected F contain samples [a],

3aa has been listed as a reference.

Product	λ_{abs} nm	λ_{em}Max nm	Stokes Shiftnm	Φ_F %	CIE coordinate
3aa	406	481	75	21.33	0.16, 0.31
3ea	412	490	78	28.92	0.19, 0.37
3la$_1$	394	472	78	8.28	0.17, 0.31
3la$_2$	404	477	73	15.07	0.17, 0.30

3pa	402	485	83	17.30	0.21, 0.41

a: 5×10^{-6} M in CH_2Cl_2.

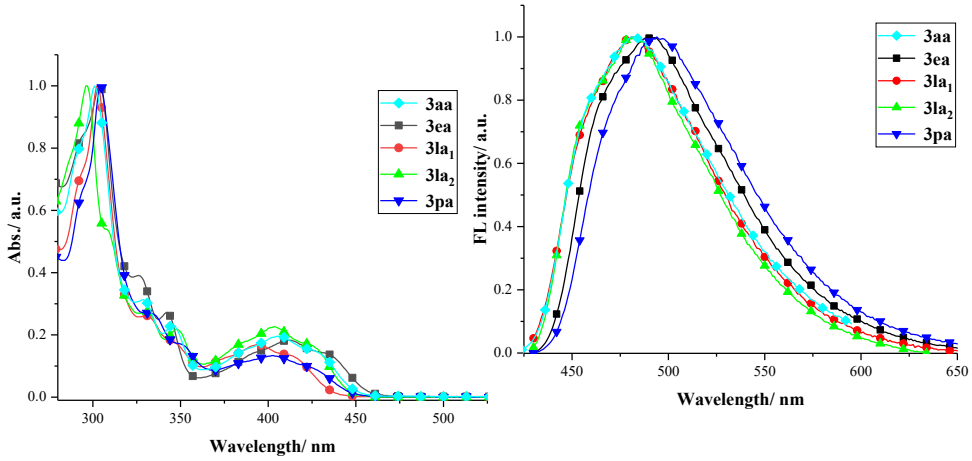


Figure S5 Normalized absorption and emission spectra of **3aa**, **3ea**, **3la**$_1$, **3la**$_2$, and **3pa** in DCM solution.

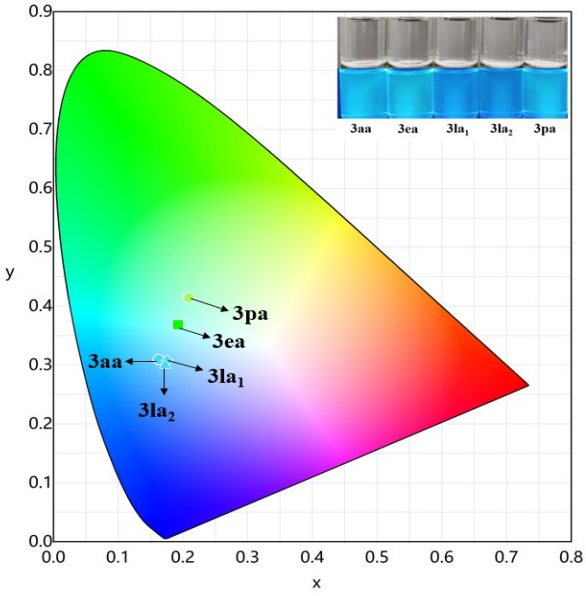


Figure S6 Emission color coordinates of compounds in DCM solutions in the CIE 1931 chromaticity diagram. Inset picture: the DCM solution of selected compounds under daylight and under the irradiation of 365 nm UV-Vis light.

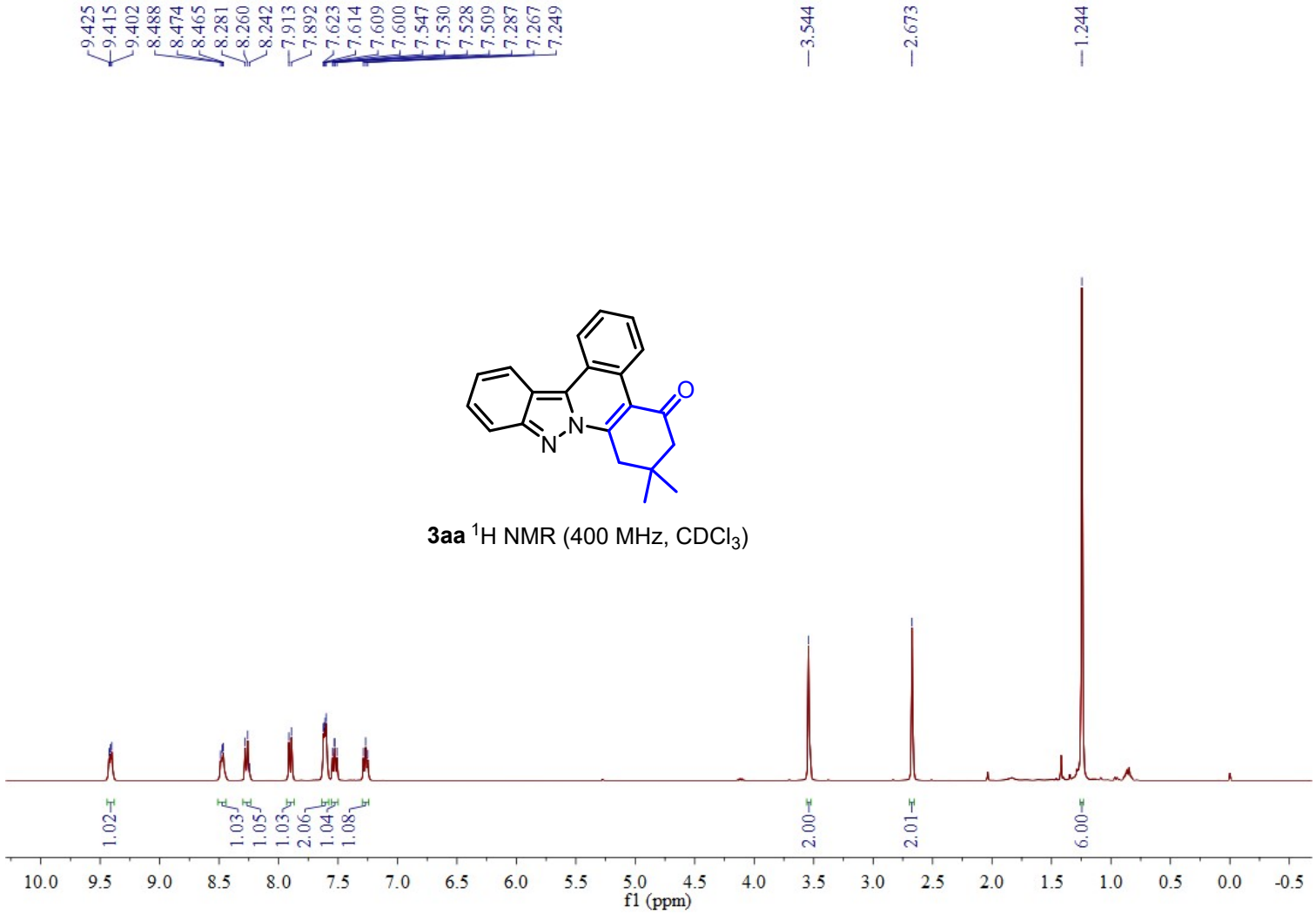
10. References

1. Li, P.; Zhao, J. J.; Wu, C. R.; Larock, R. C.; Shi, F., Synthesis of 3-Substituted Indazoles from Arynes and N-Tosylhydrazones. *Org. Lett.* **2011**, *13*, 3340-3343.

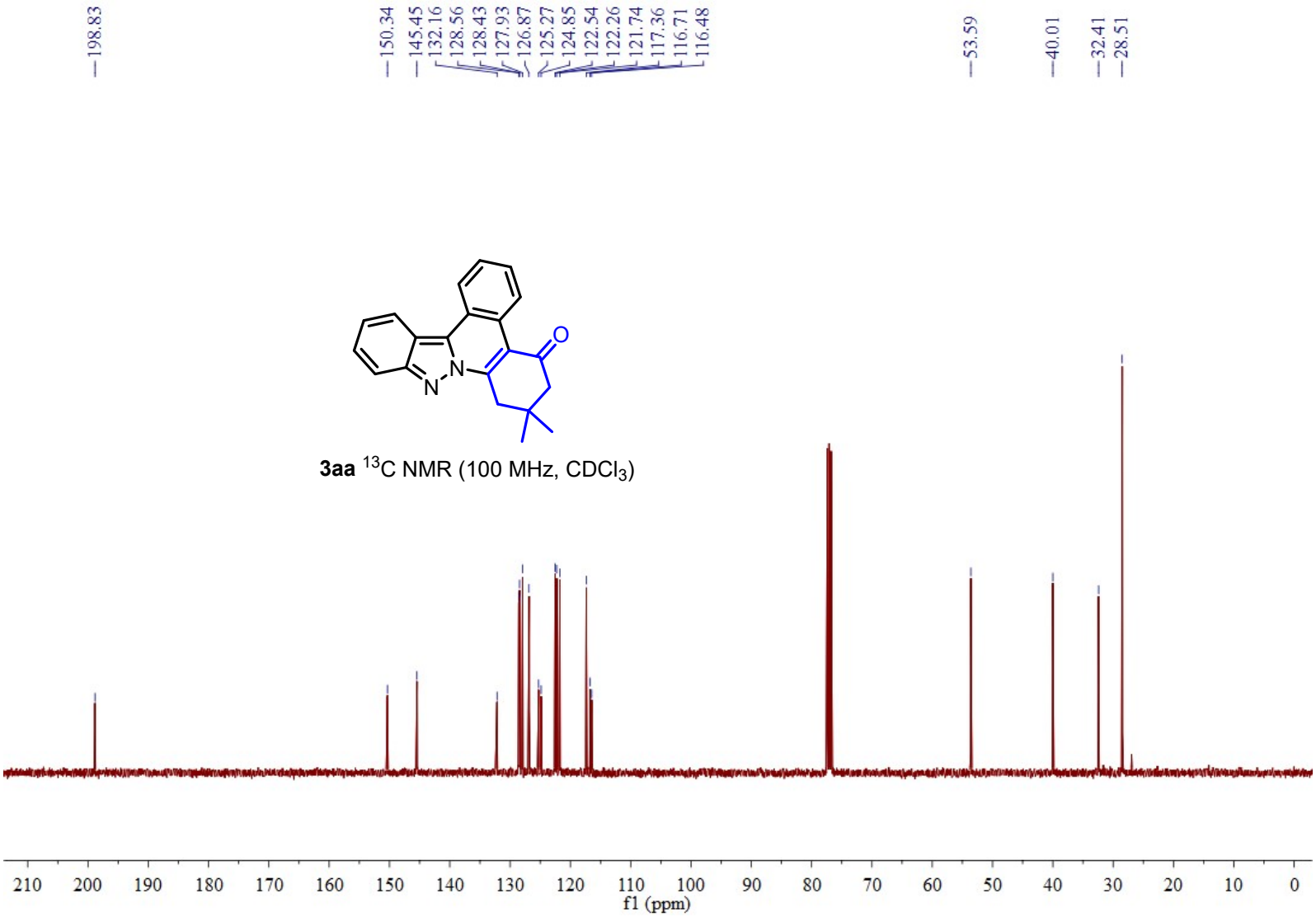
2. Nunewar, S.; Kumar, S.; Pandhare, H.; Nanduri, S.; Kanchupalli, V., Rh(III)-Catalyzed Chemodivergent Annulations between Indoles and Iodonium Carbenes: A Rapid Access to

Tricyclic and Tetracyclic N-Heterocylces. *Org. Lett.* **2021**, *23*, 4233-4238.

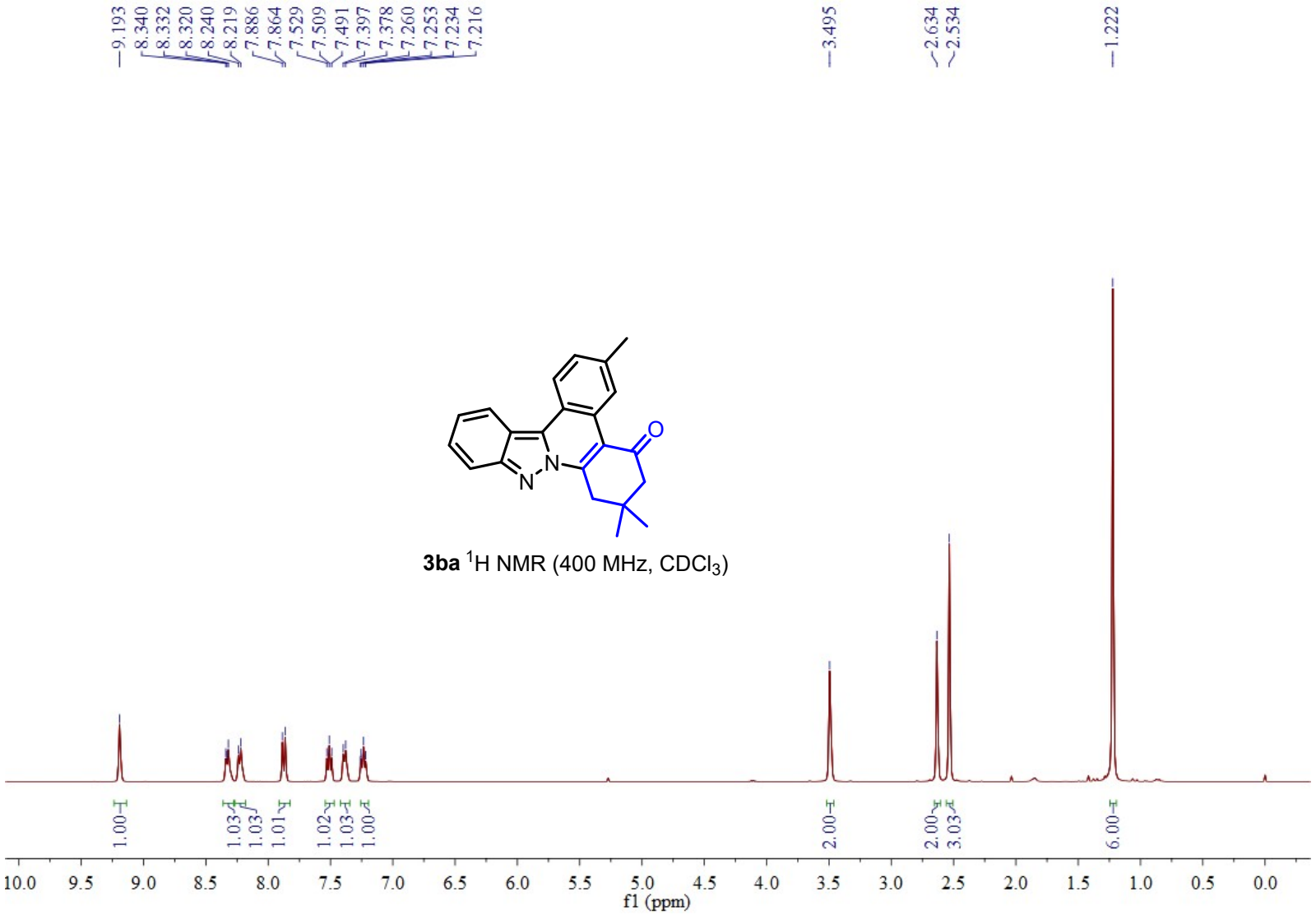
11. Copy of NMR



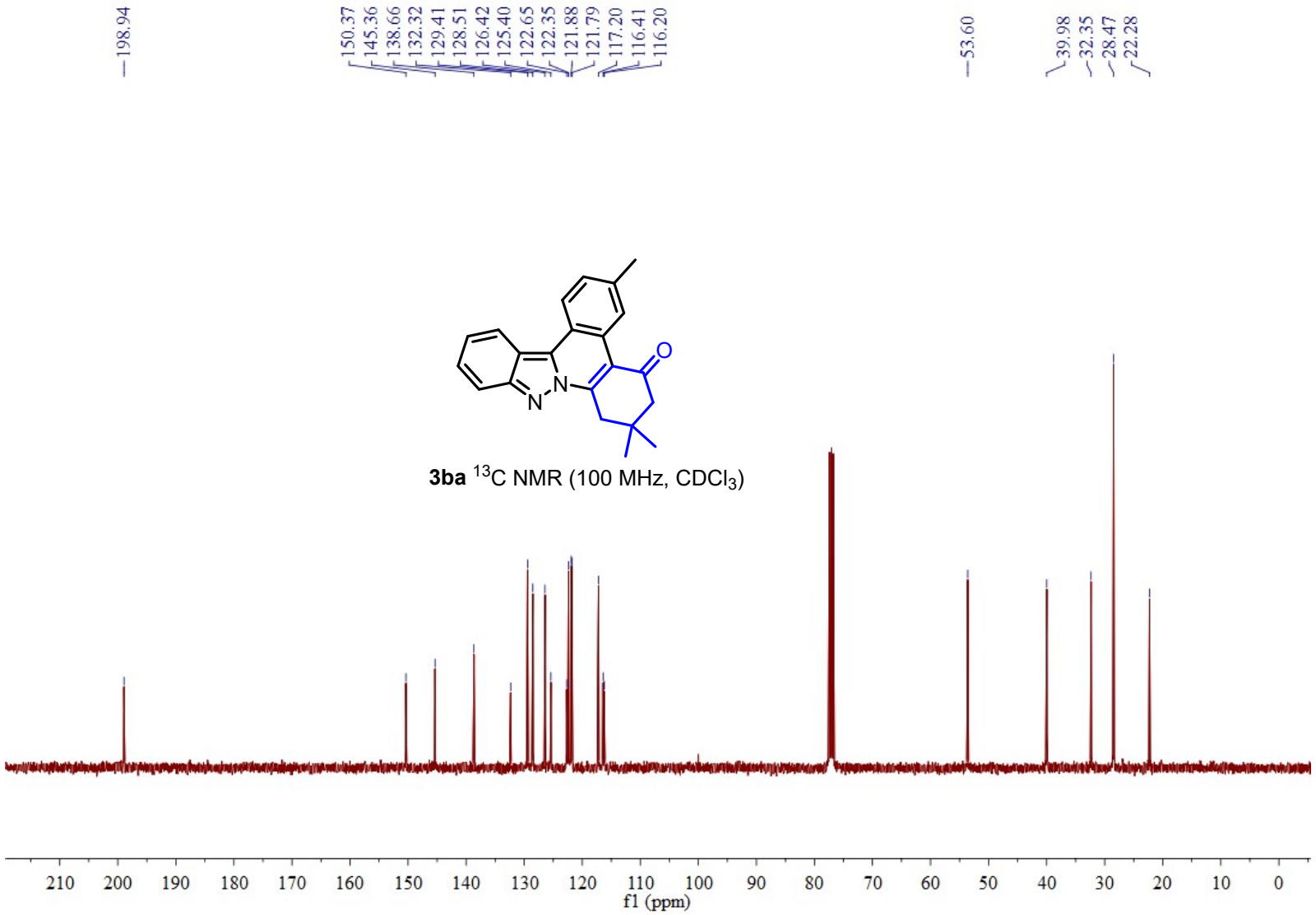
3aa ^{1}H NMR (400 MHz, $CDCl_3$)



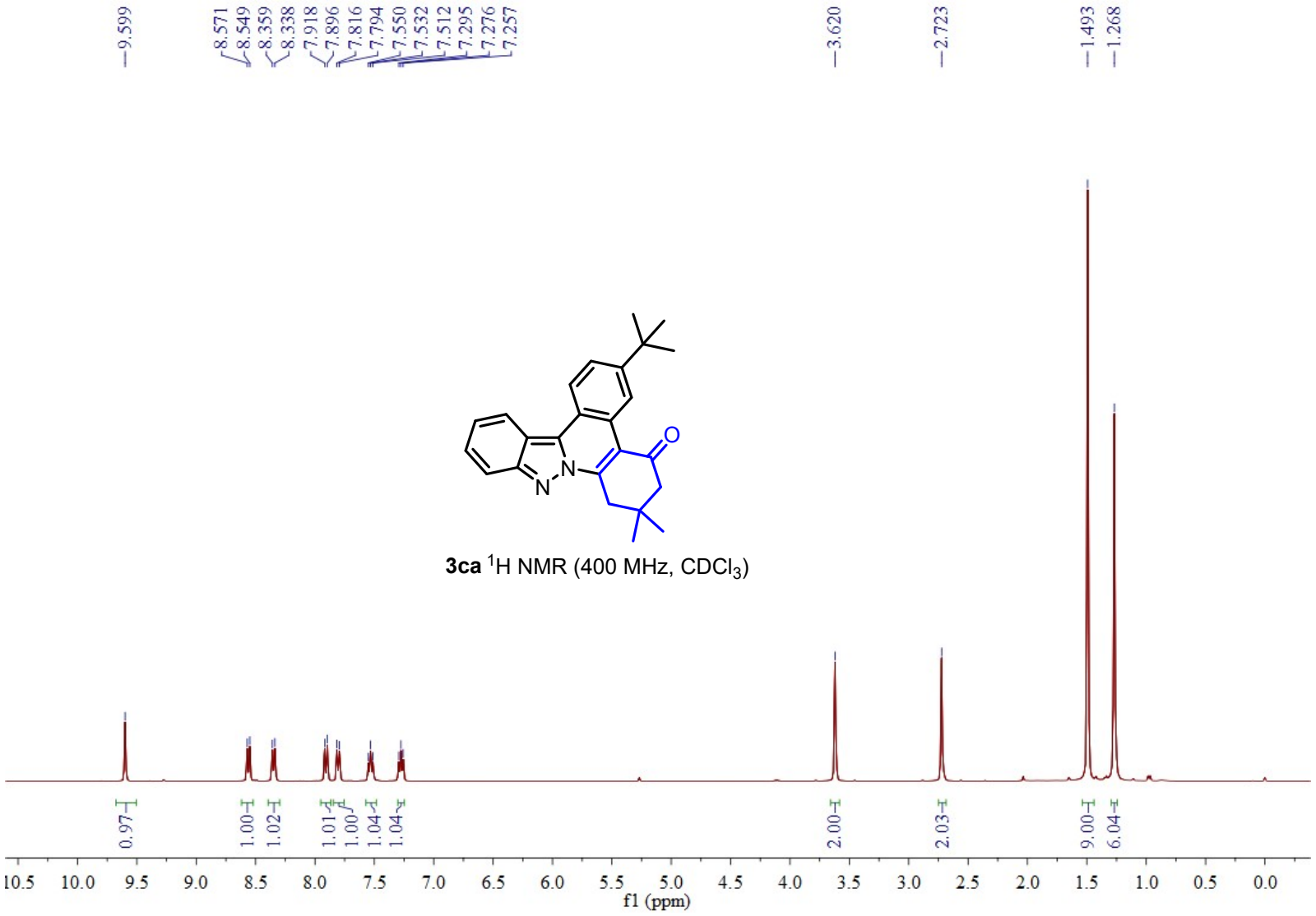
3aa ^{13}C NMR (100 MHz, $CDCl_3$)



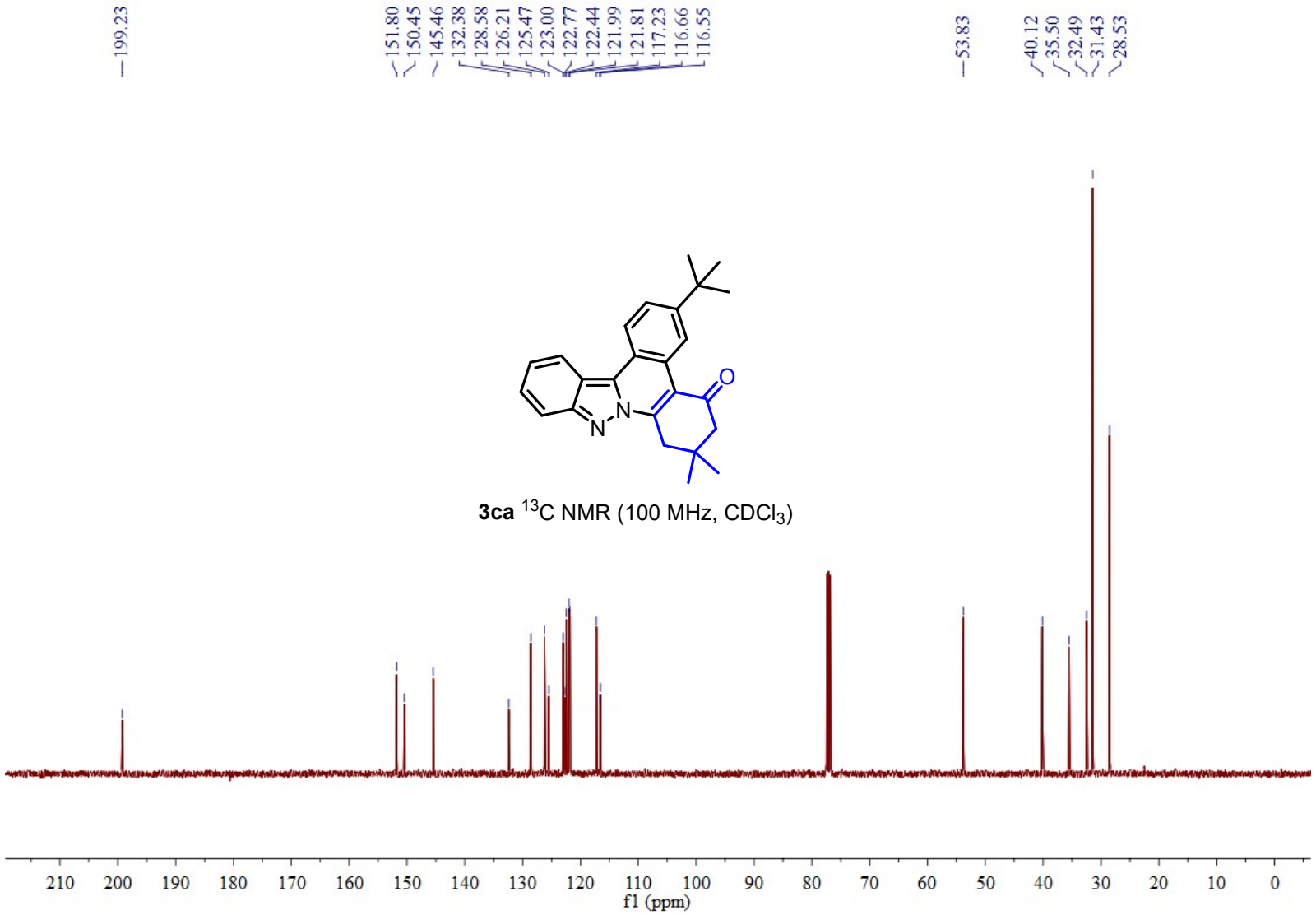
3ba ^{1}H NMR (400 MHz, $CDCl_3$)



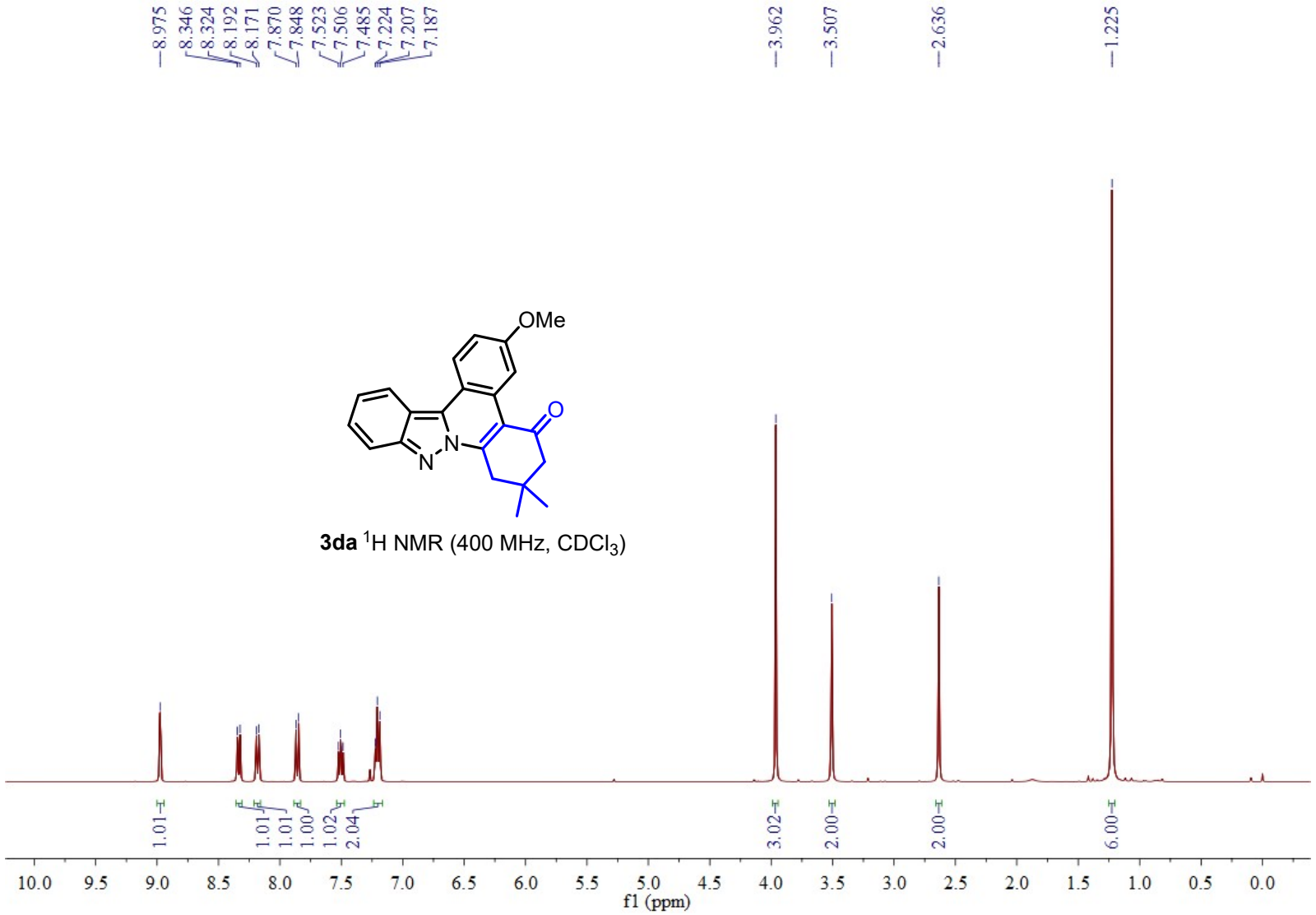
3ba ^{13}C NMR (100 MHz, $CDCl_3$)



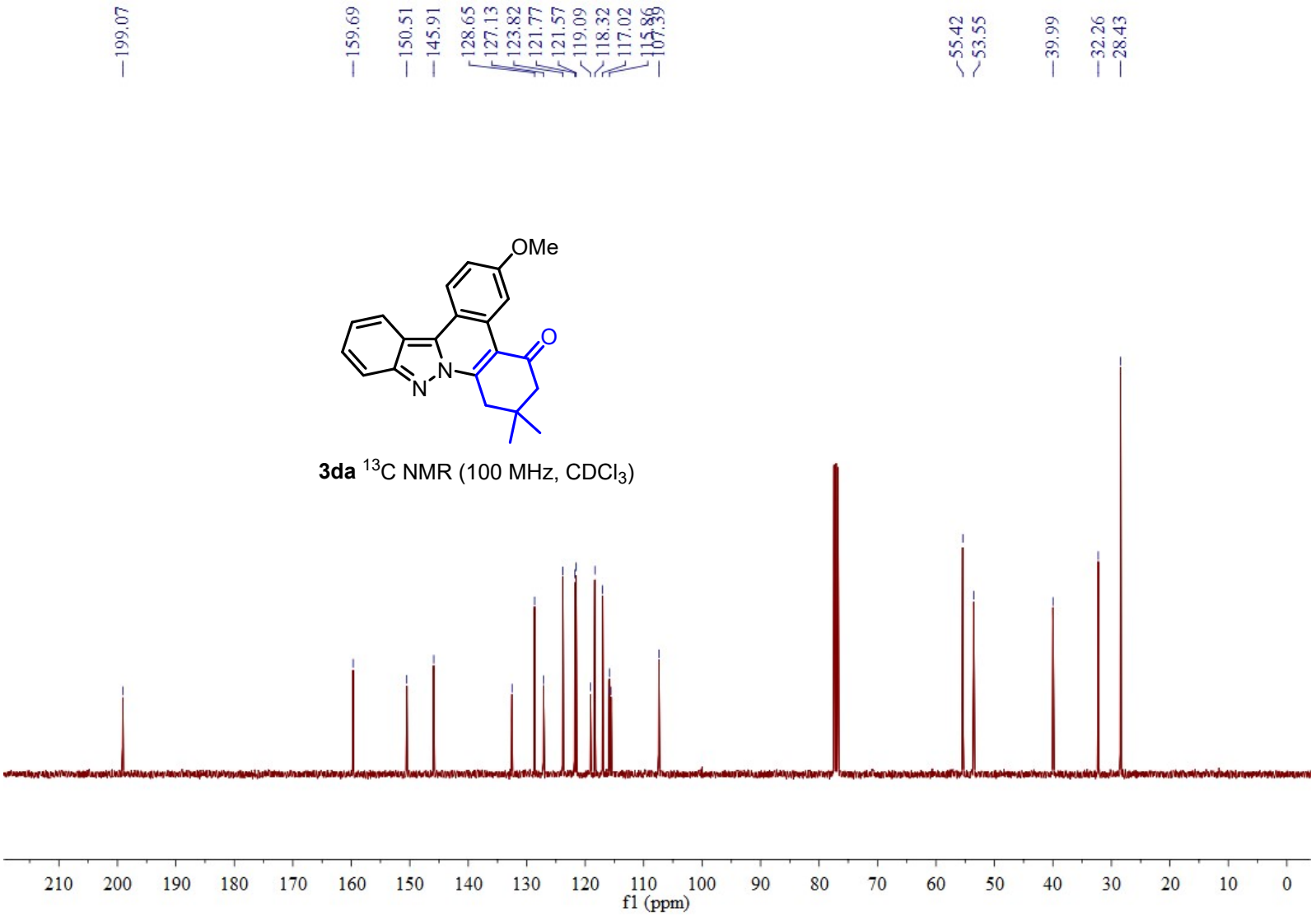
3ca ^{1}H NMR (400 MHz, $CDCl_3$)



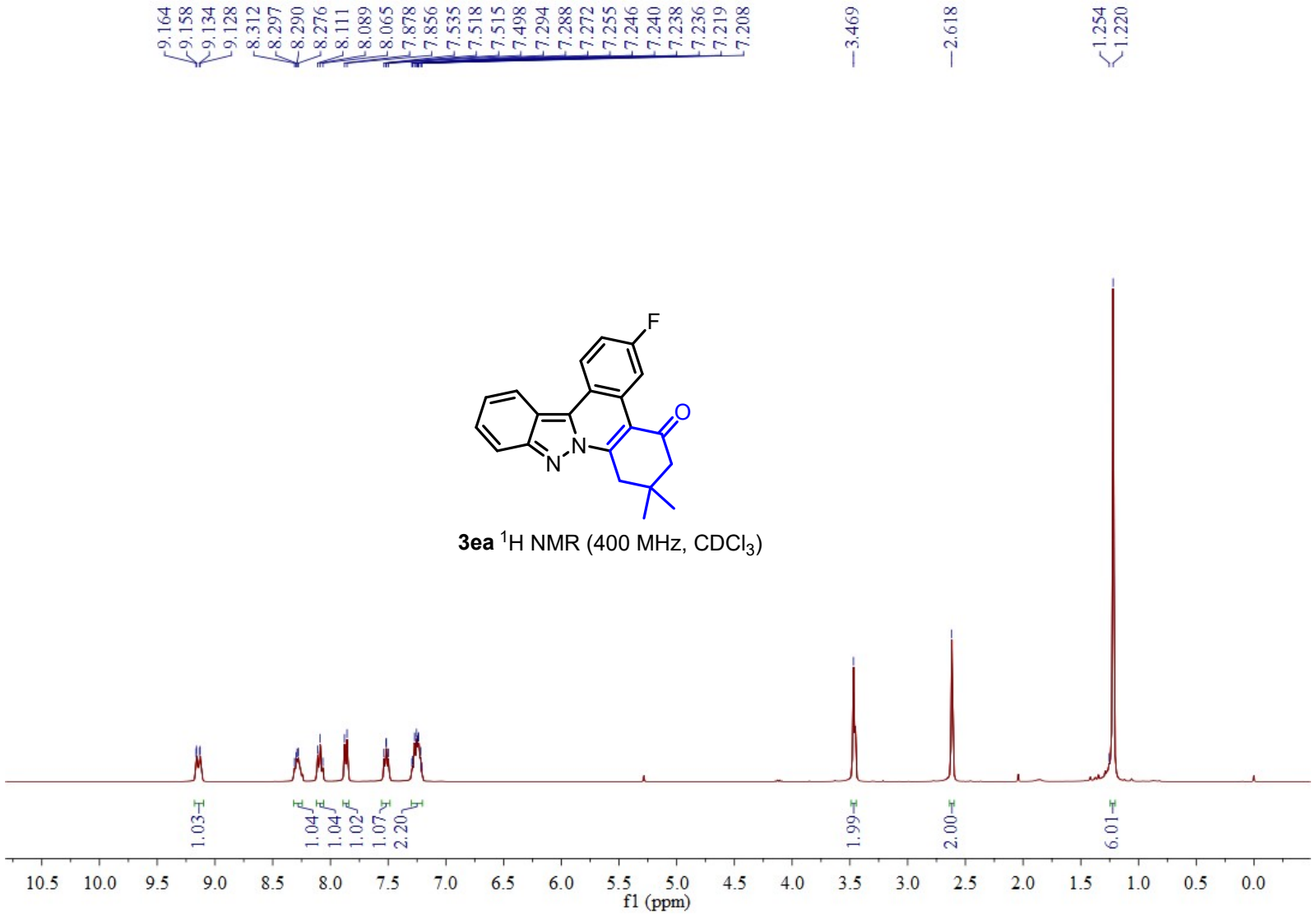
3ca ^{13}C NMR (100 MHz, $CDCl_3$)



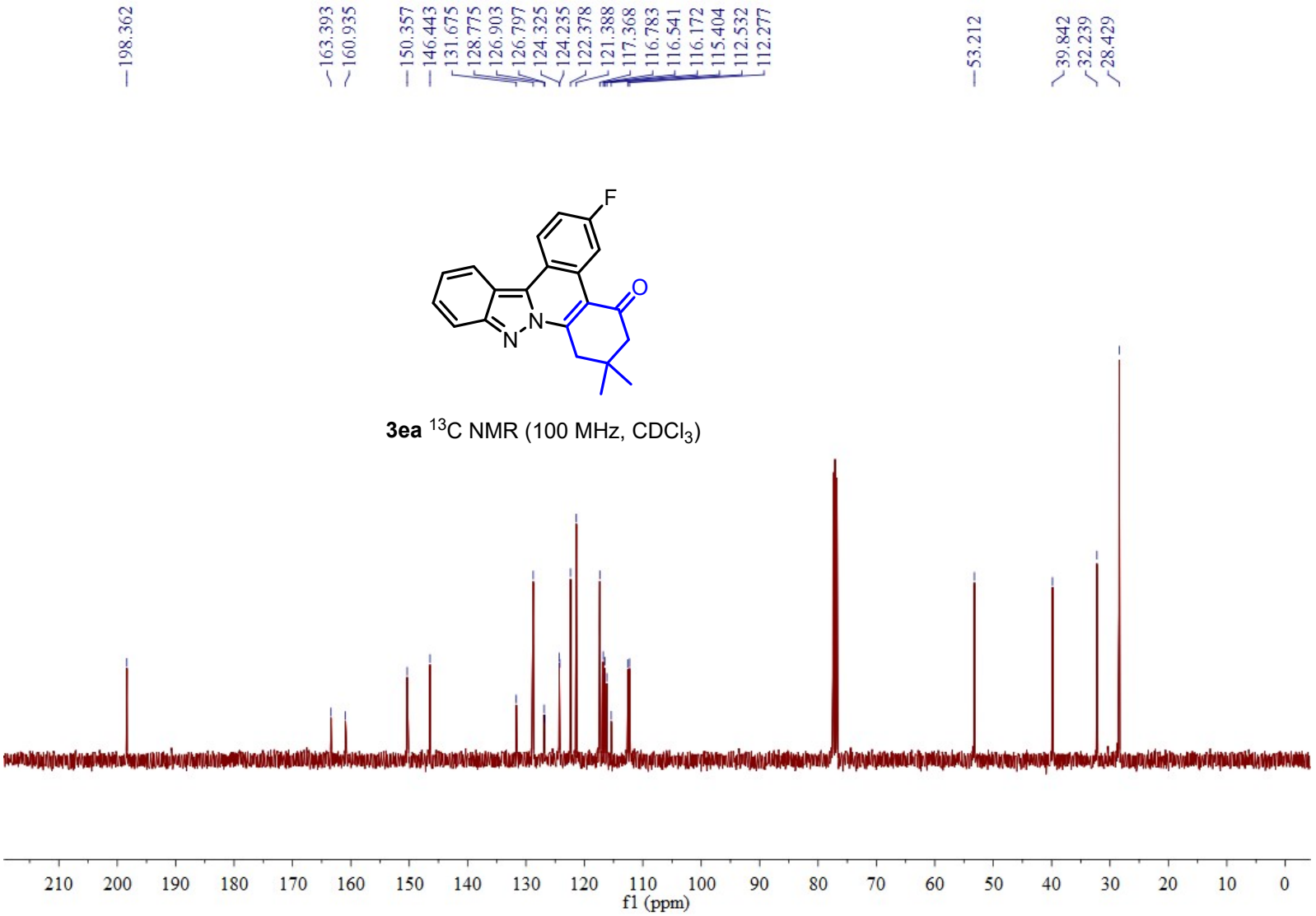
3da ^{1}H NMR (400 MHz, $CDCl_3$)



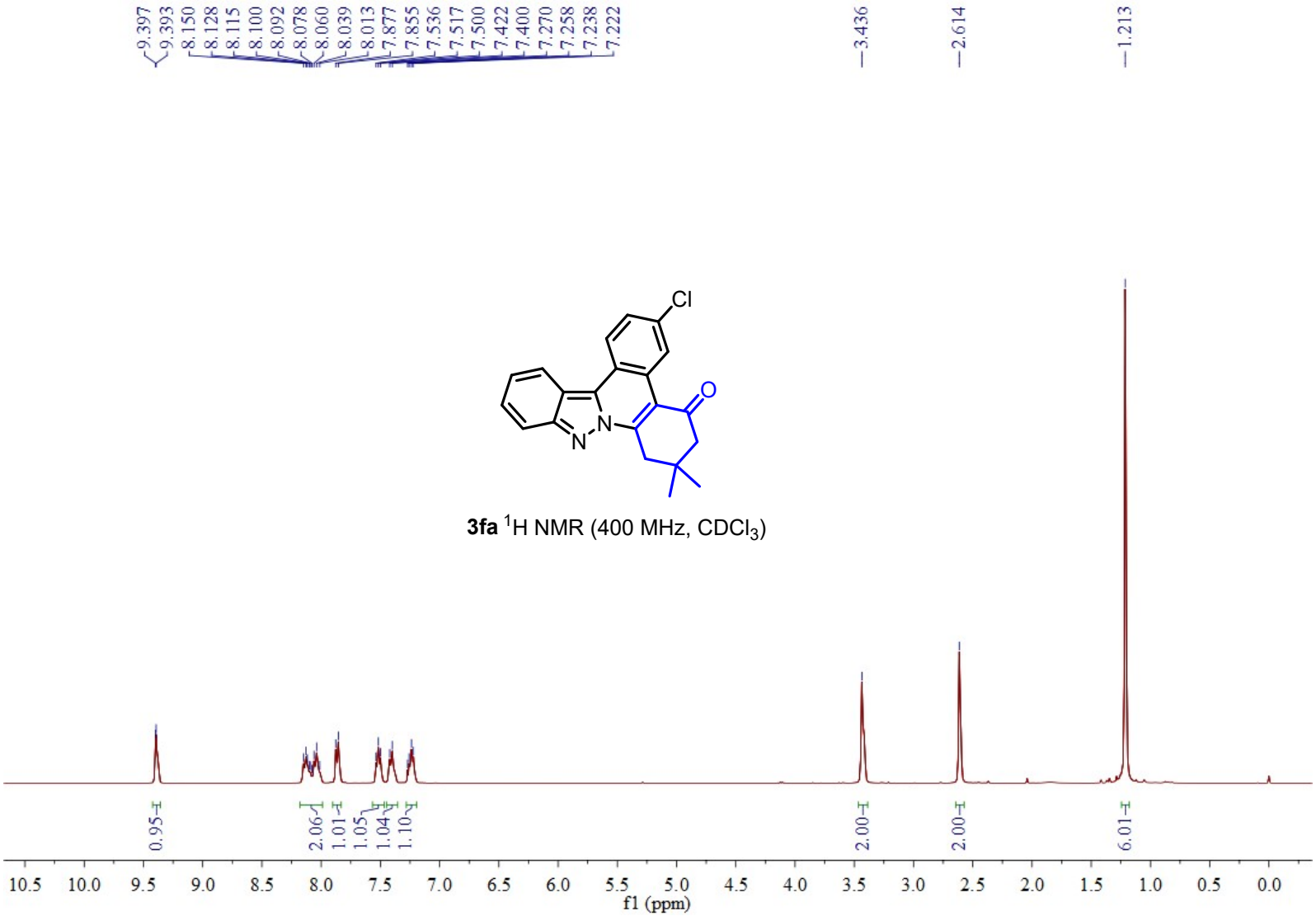
3da ^{13}C NMR (100 MHz, $CDCl_3$)



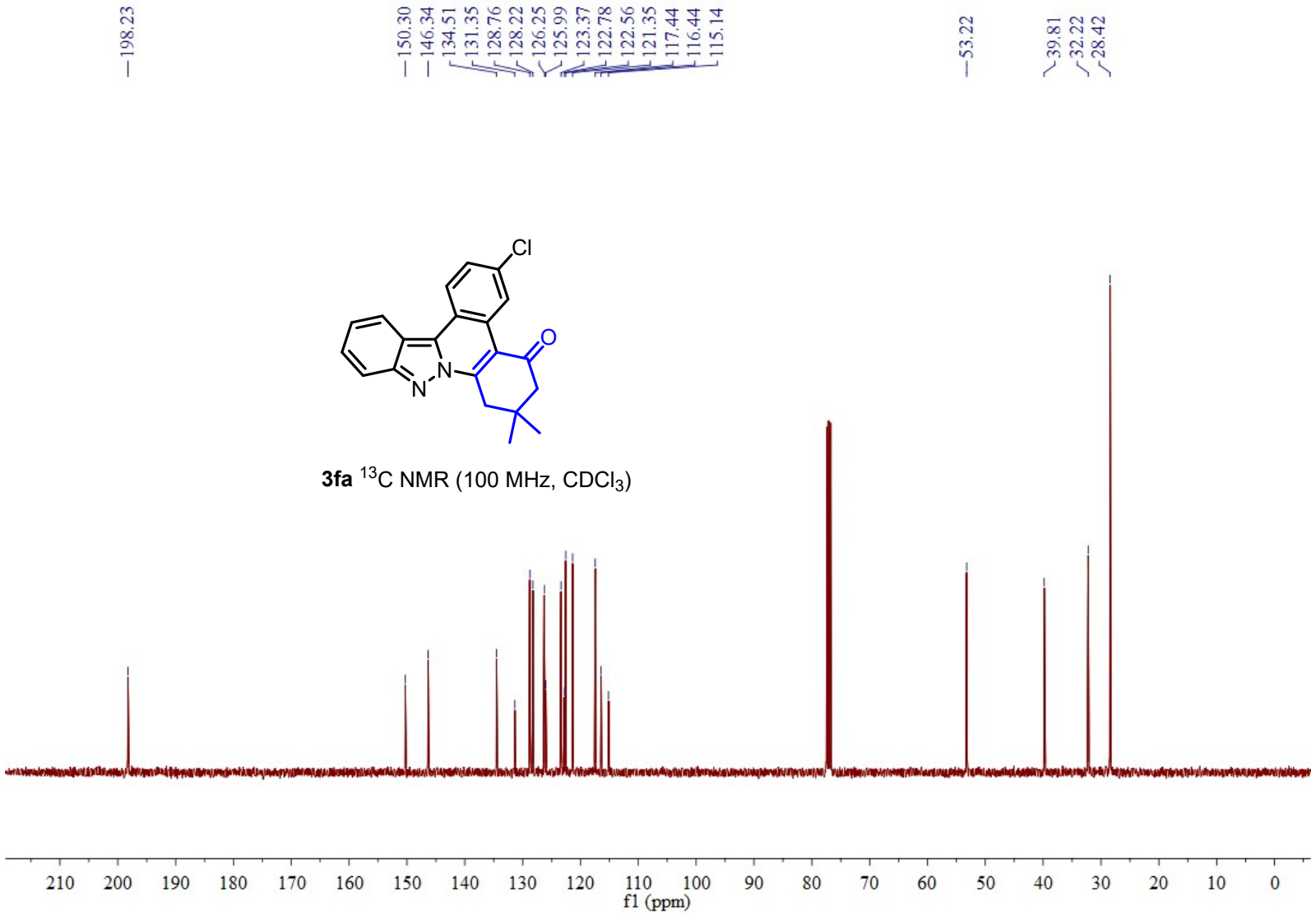
3ea ^{1}H NMR (400 MHz, $CDCl_3$)



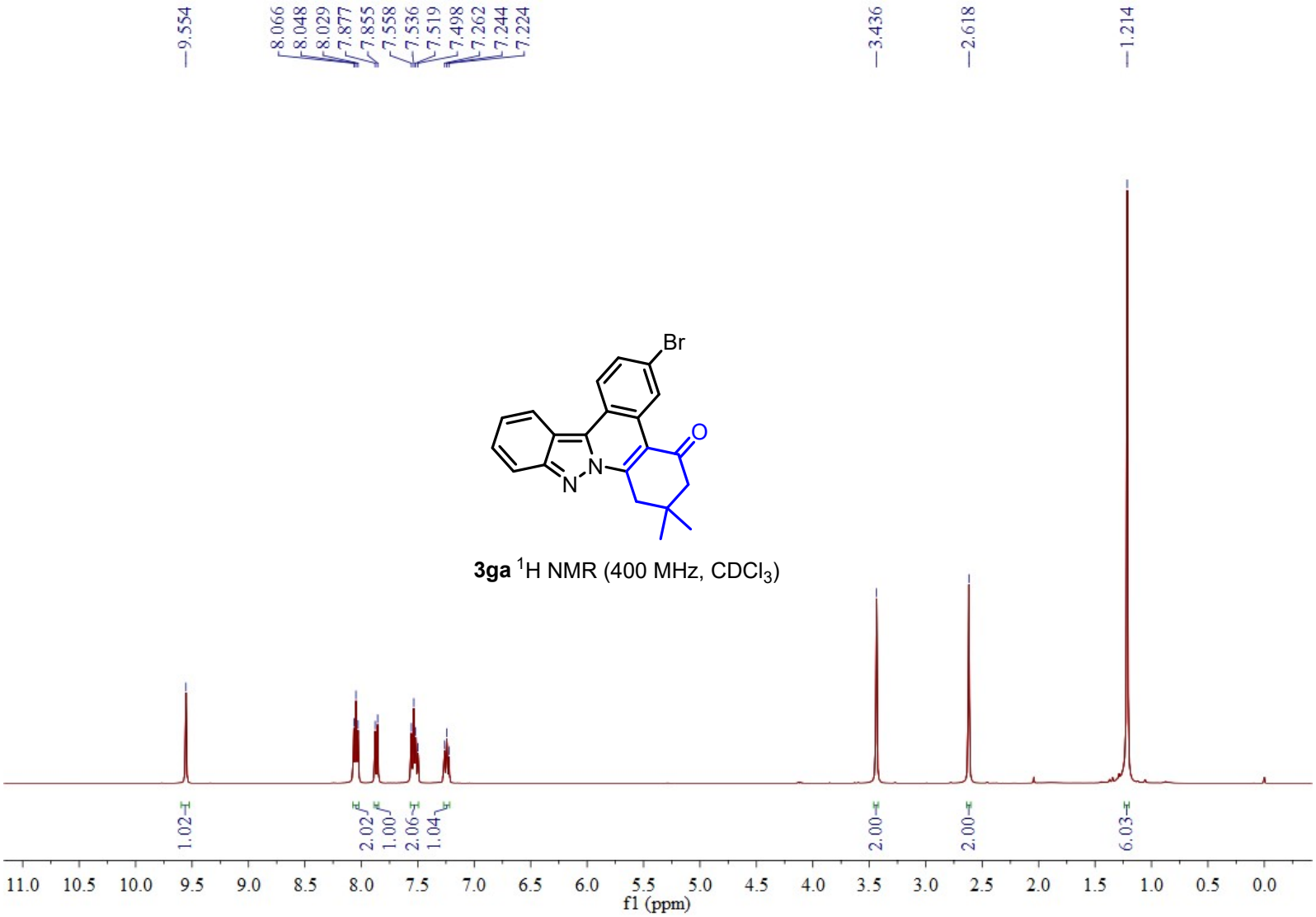
3ea ^{13}C NMR (100 MHz, $CDCl_3$)



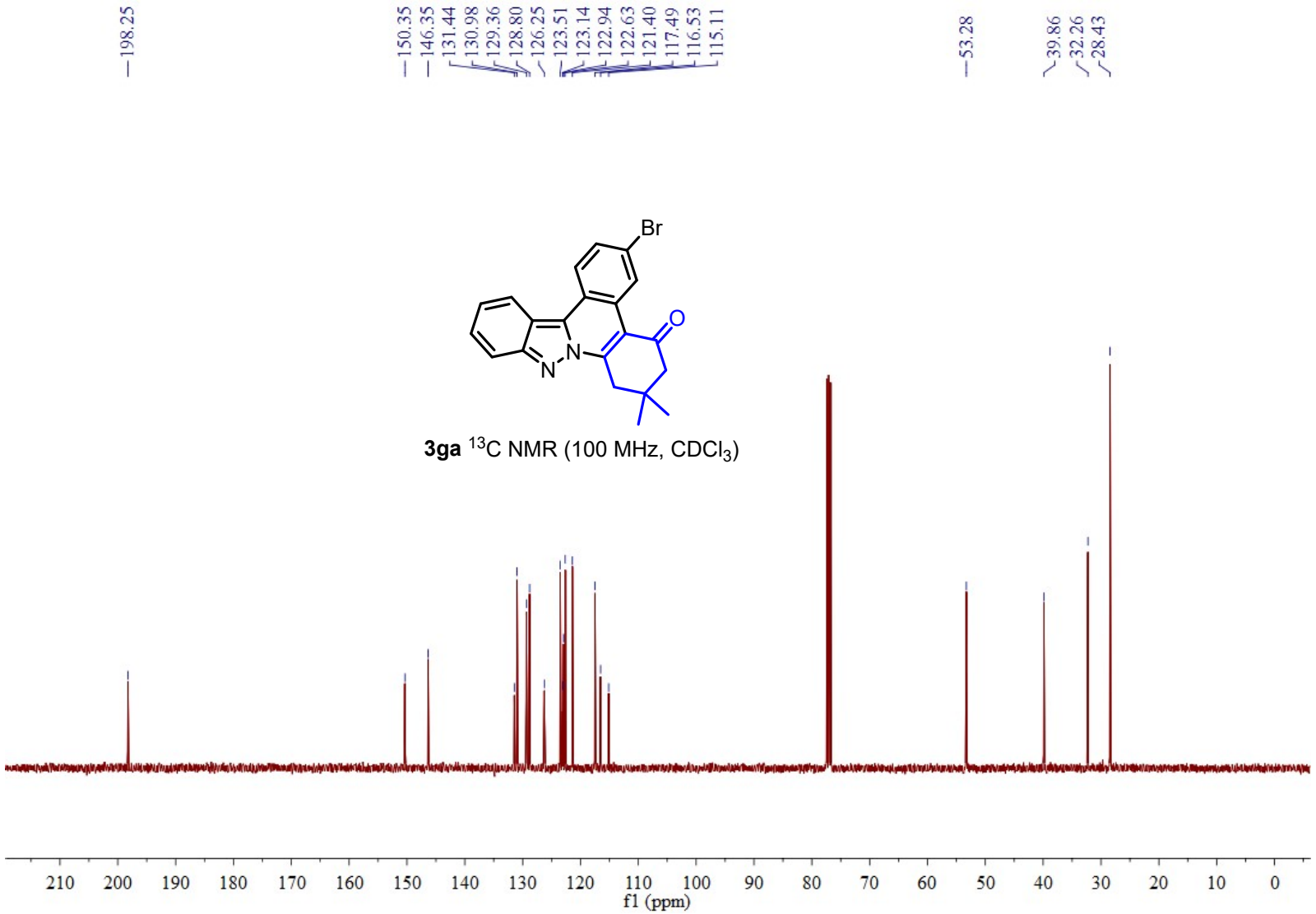
3fa ^{1}H NMR (400 MHz, $CDCl_3$)



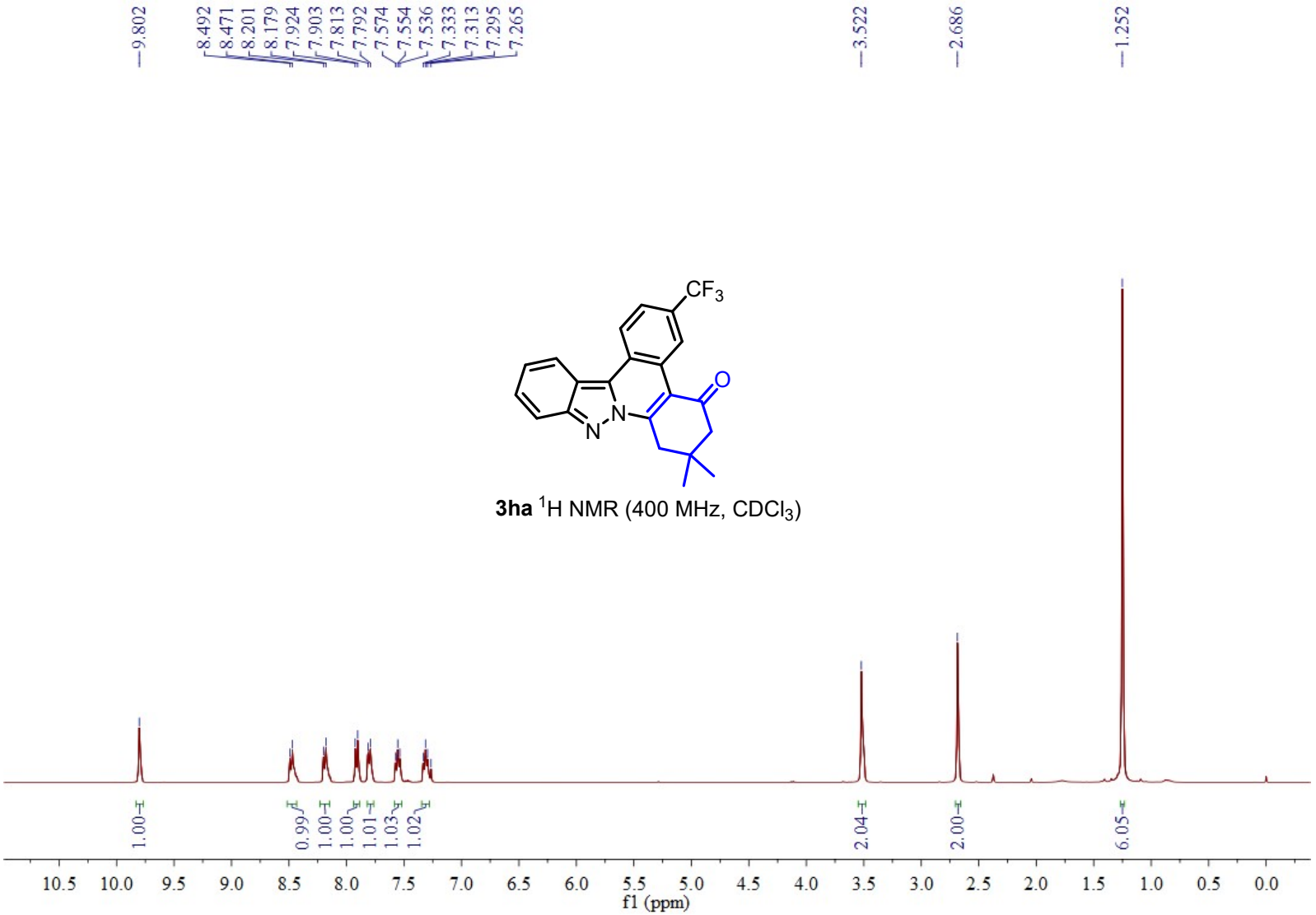
3fa ^{13}C NMR (100 MHz, $CDCl_3$)



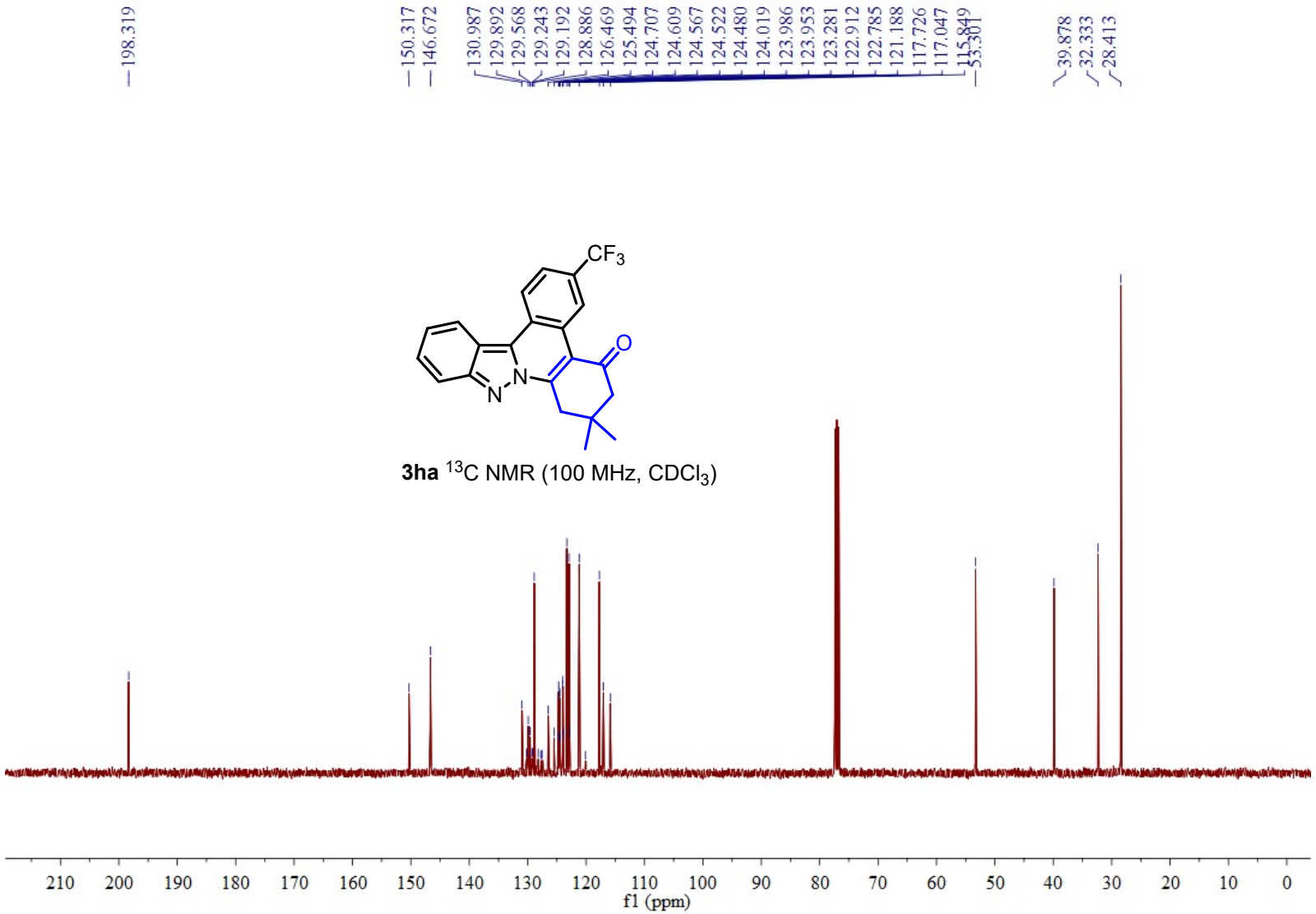
3ga ^{1}H NMR (400 MHz, $CDCl_3$)



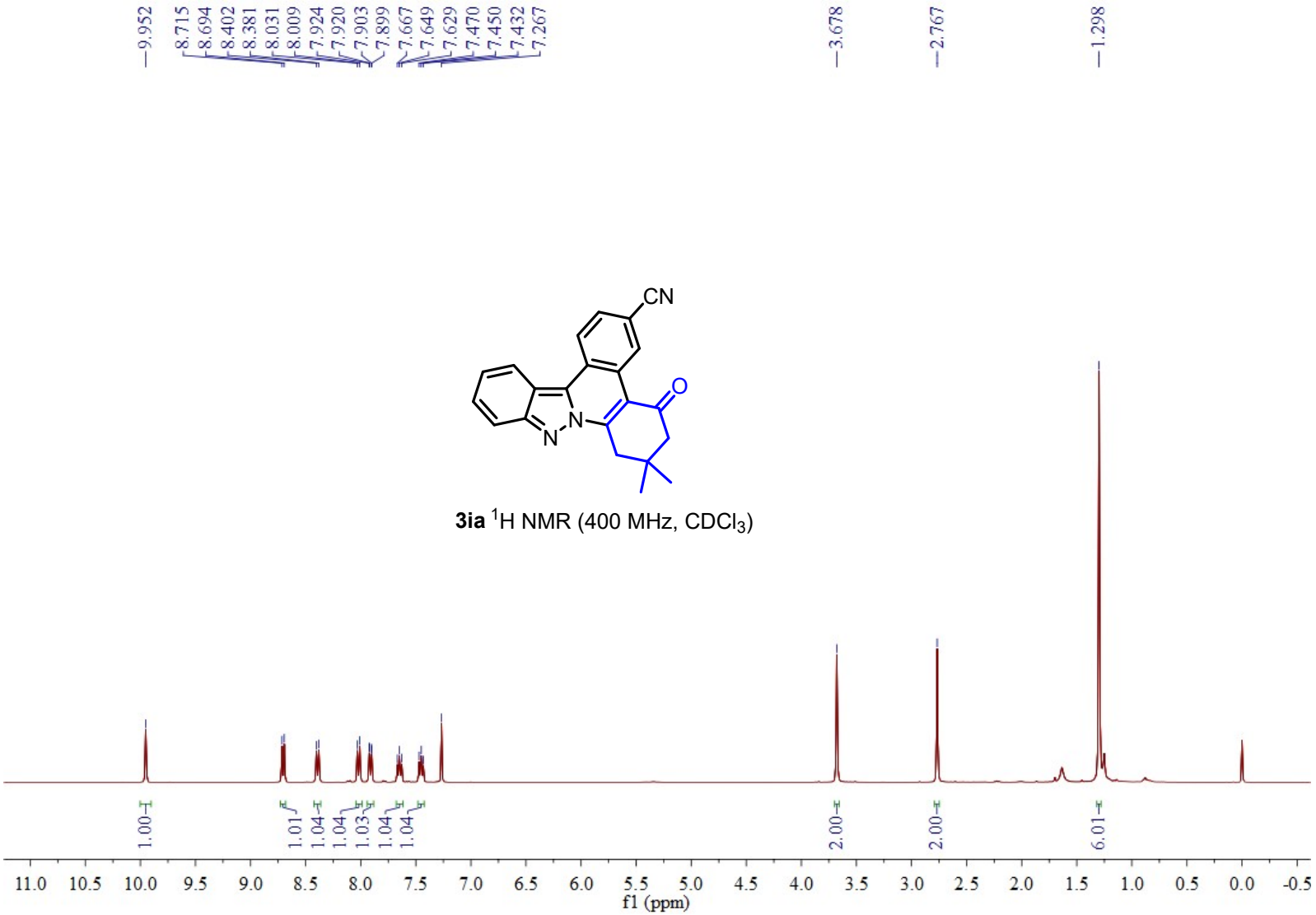
3ga ^{13}C NMR (100 MHz, $CDCl_3$)



3ha ^{1}H NMR (400 MHz, $CDCl_3$)



3ha ^{13}C NMR (100 MHz, $CDCl_3$)



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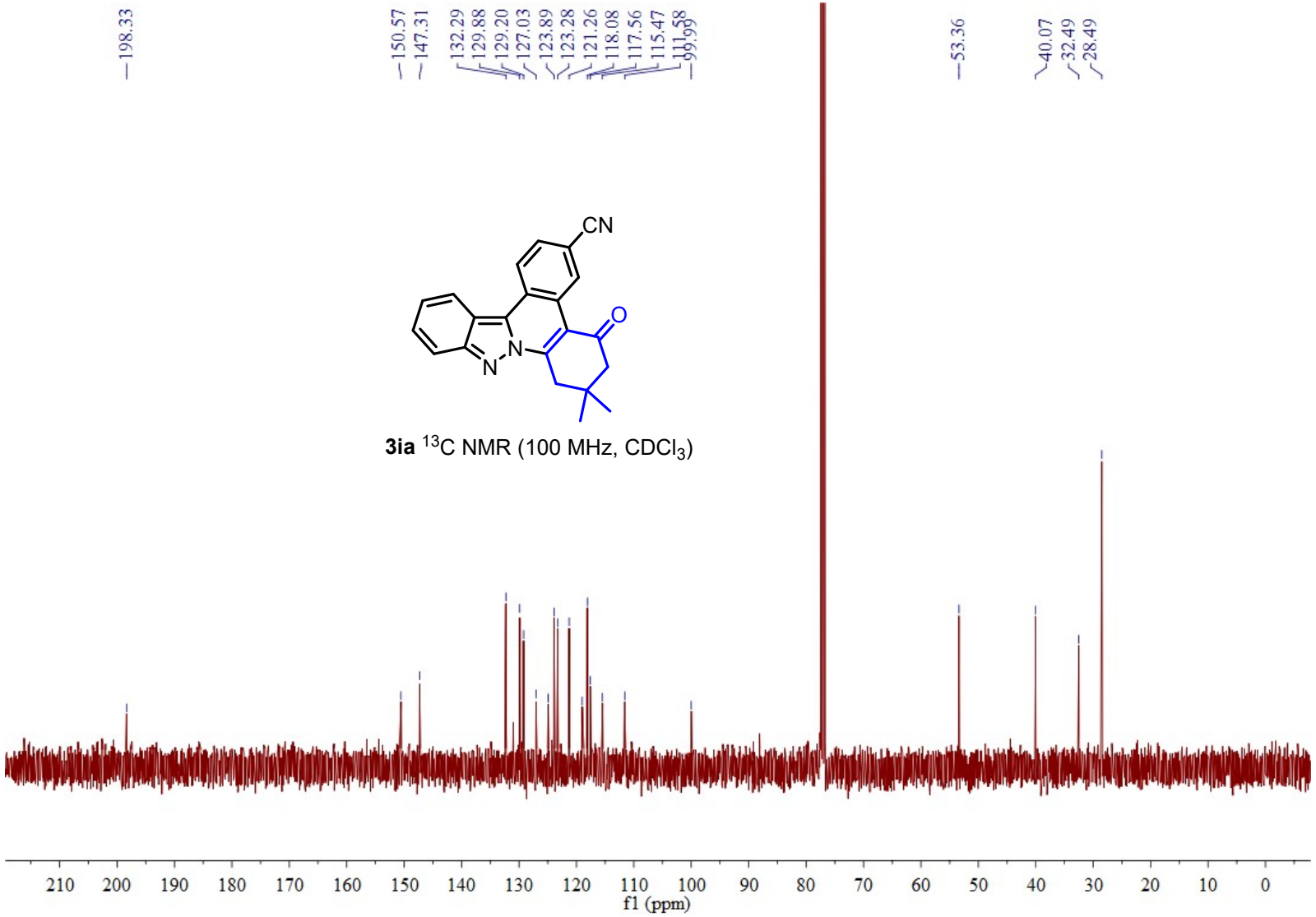
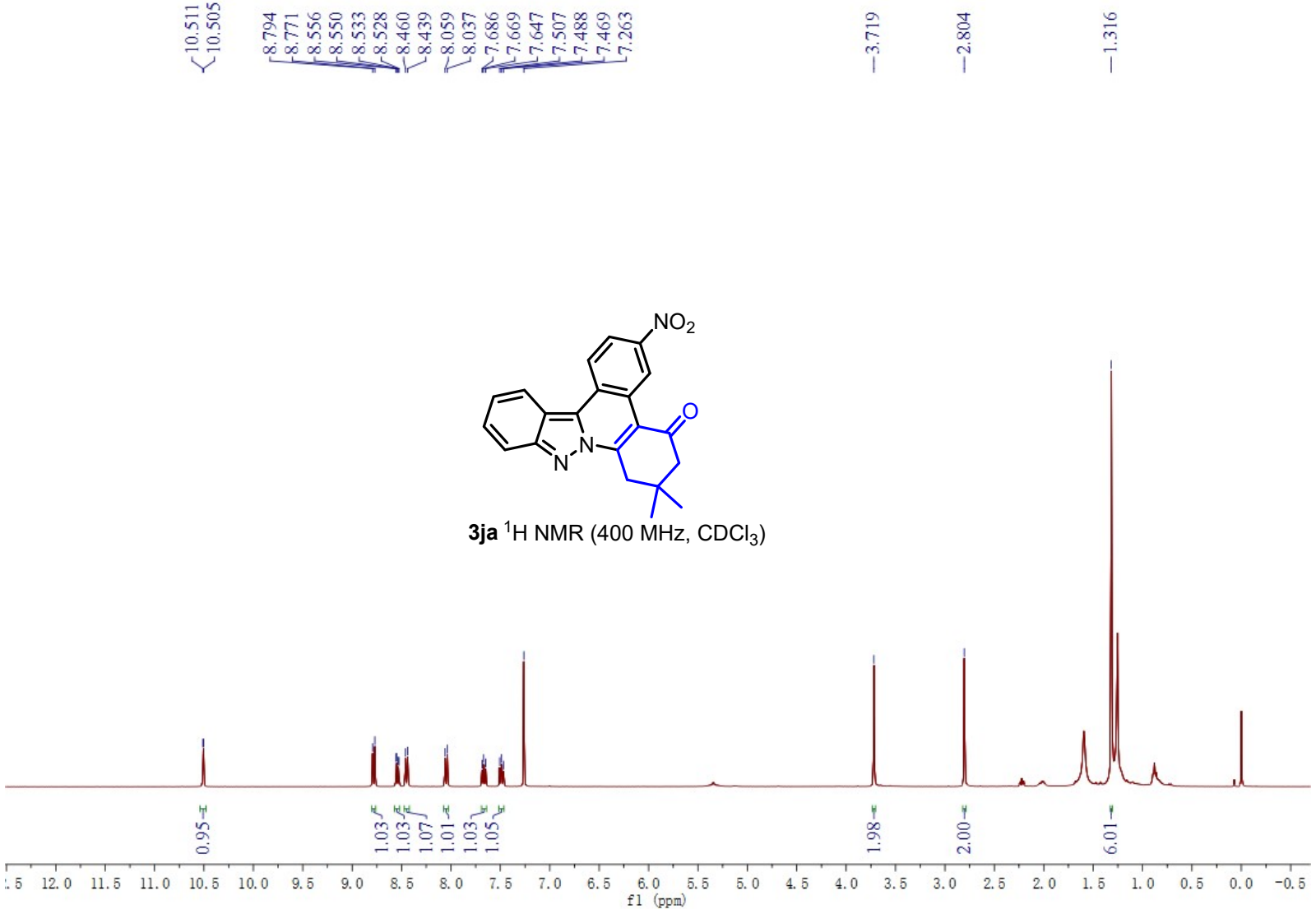


3ia ^{13}C NMR (100 MHz, $CDCl_3$)



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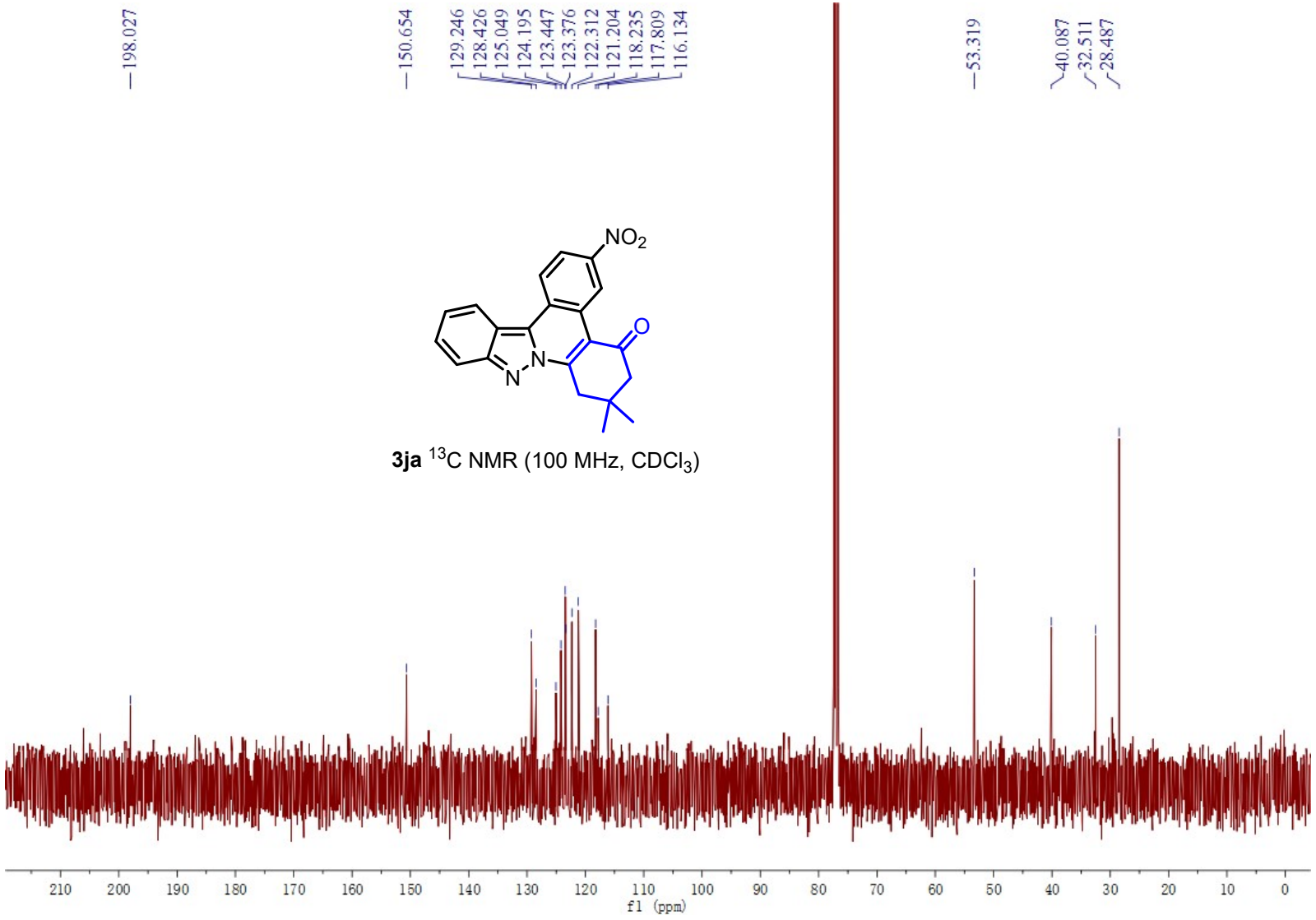

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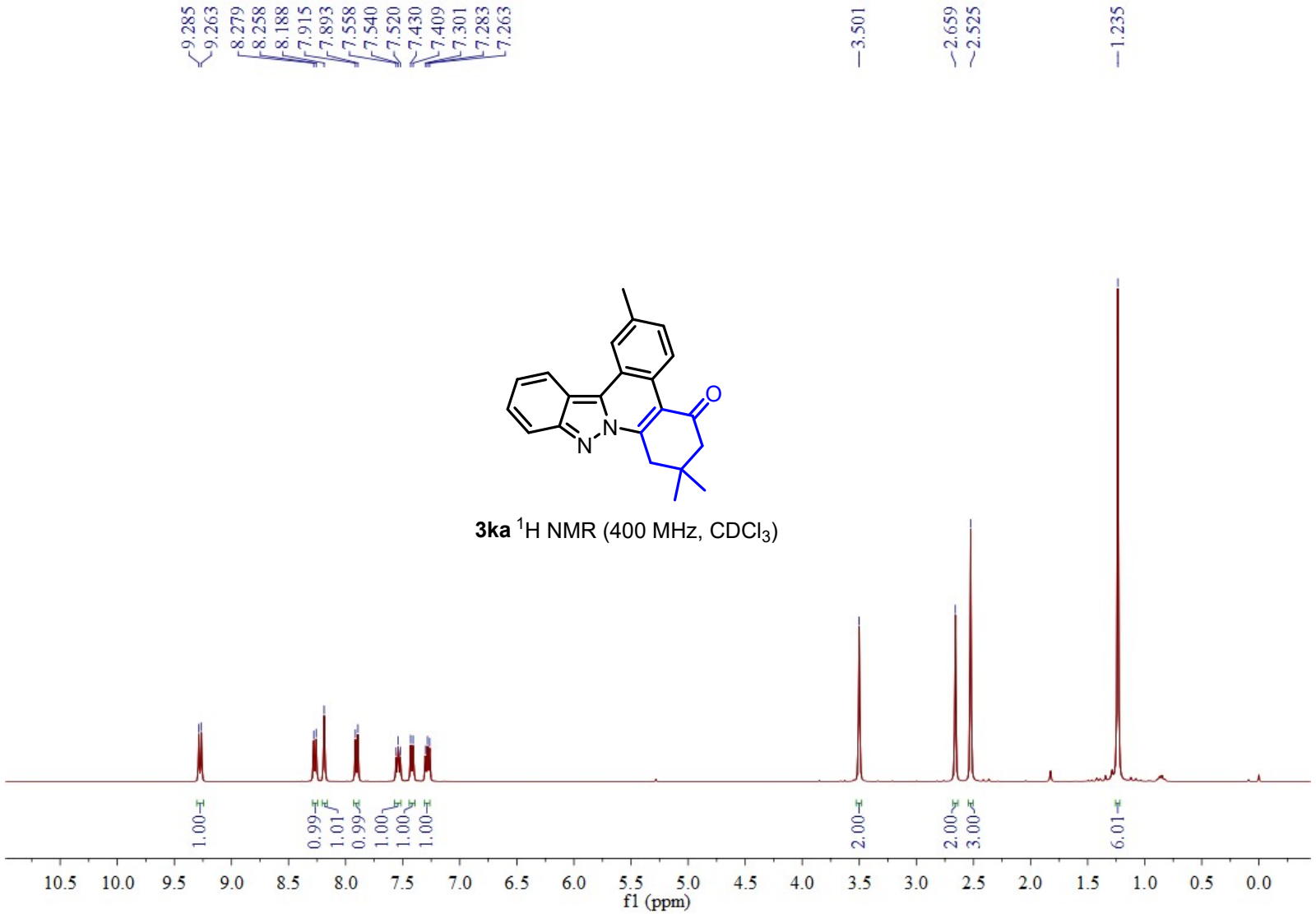

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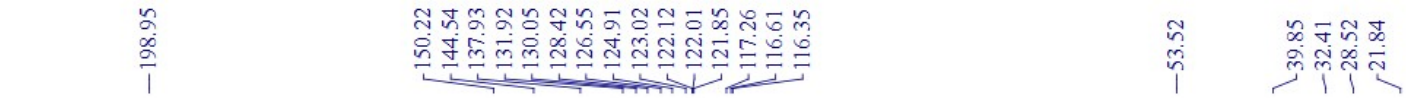

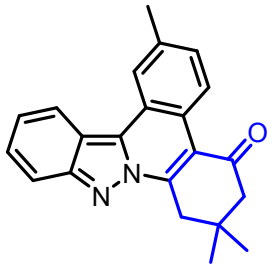

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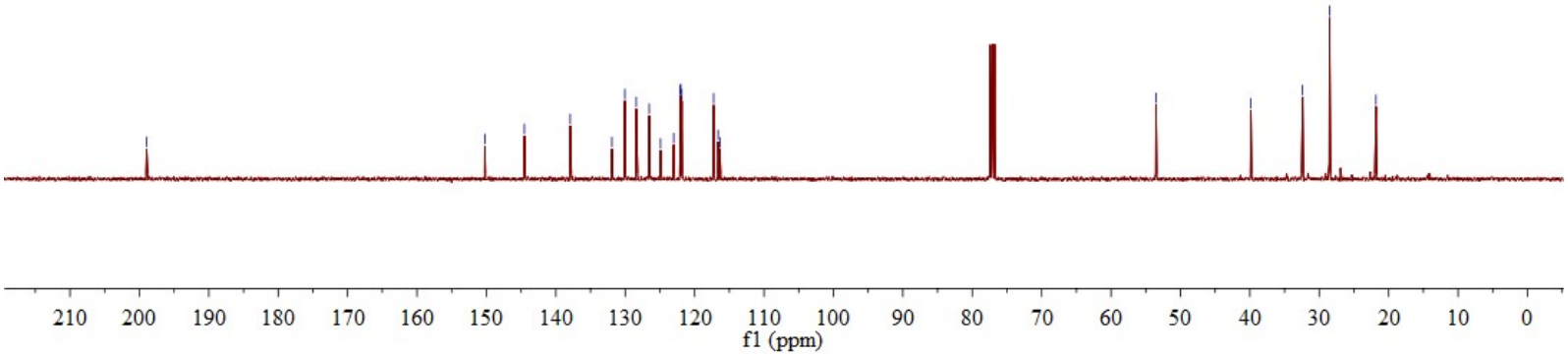

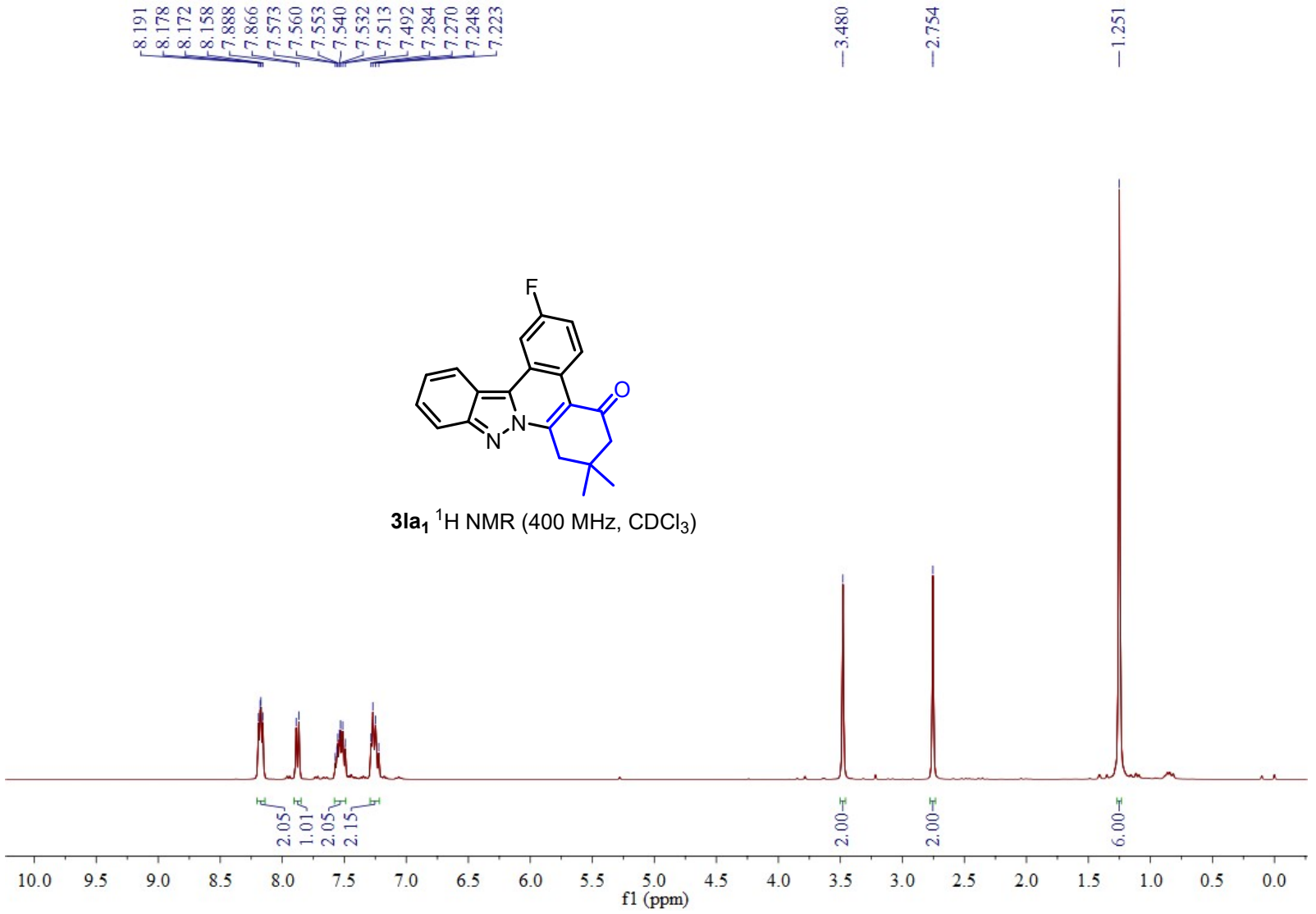

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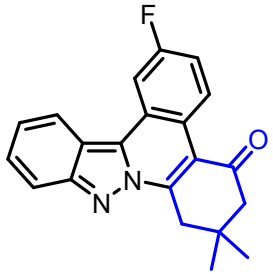

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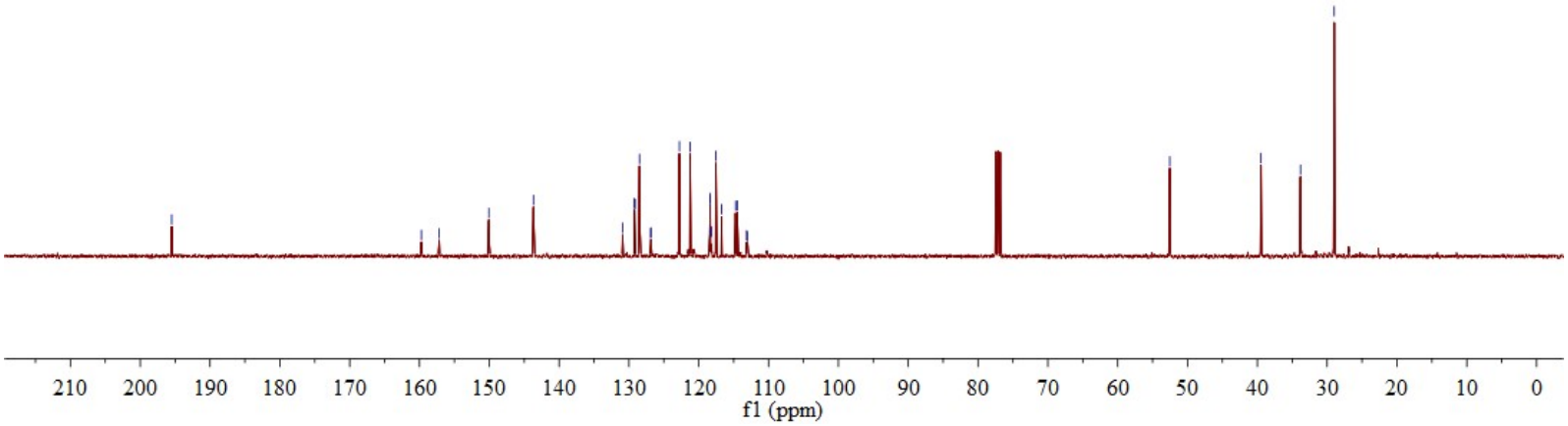

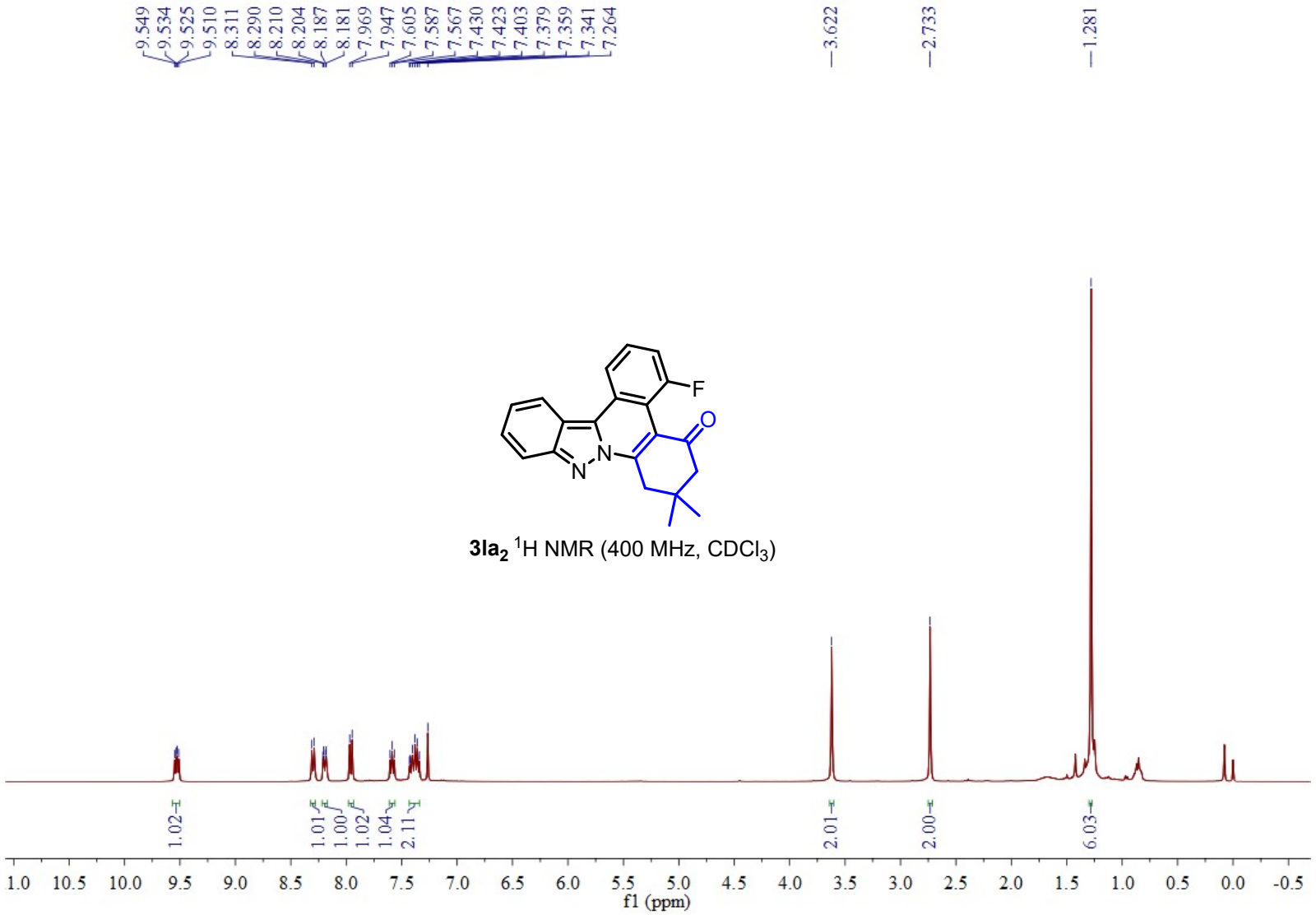

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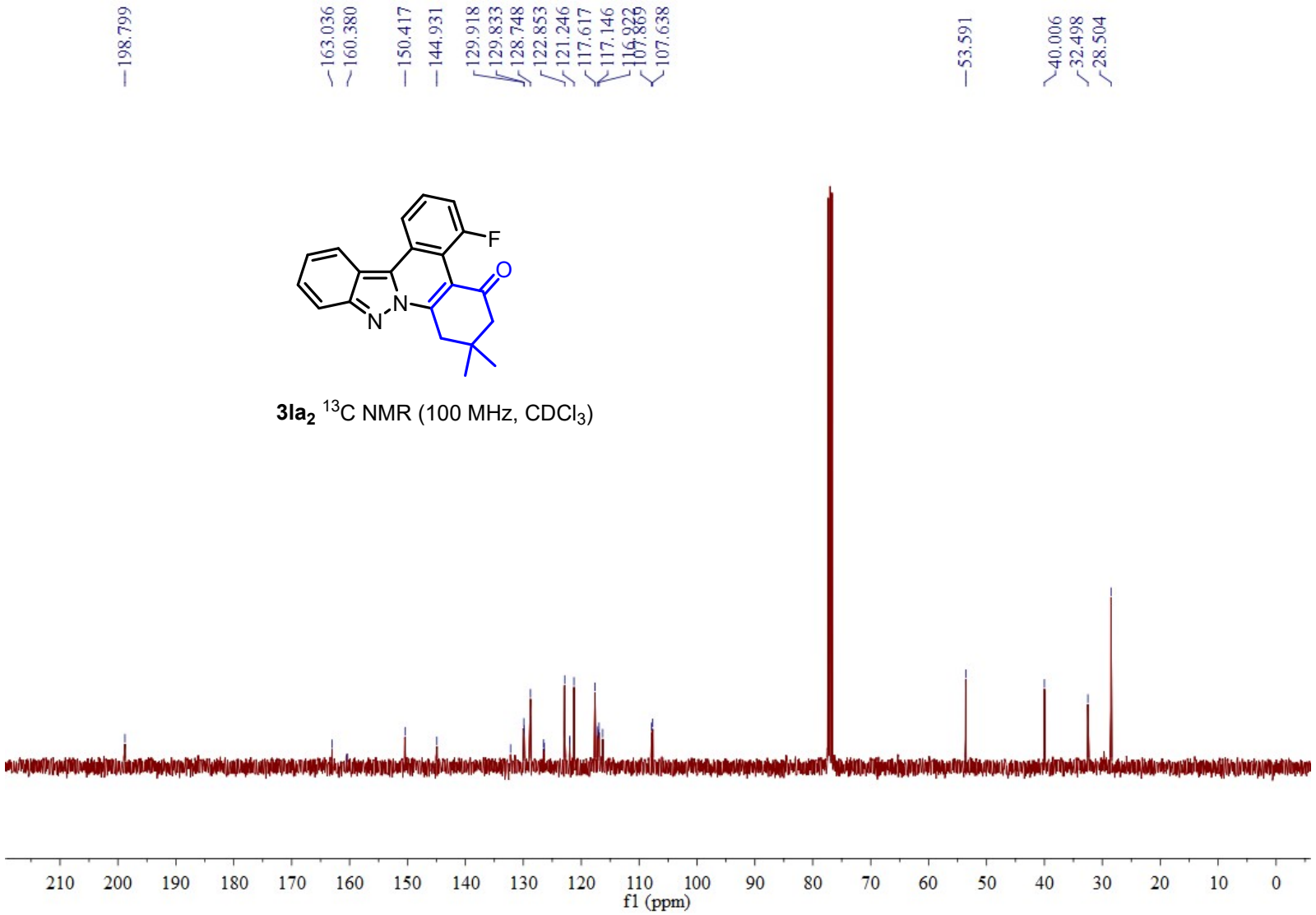

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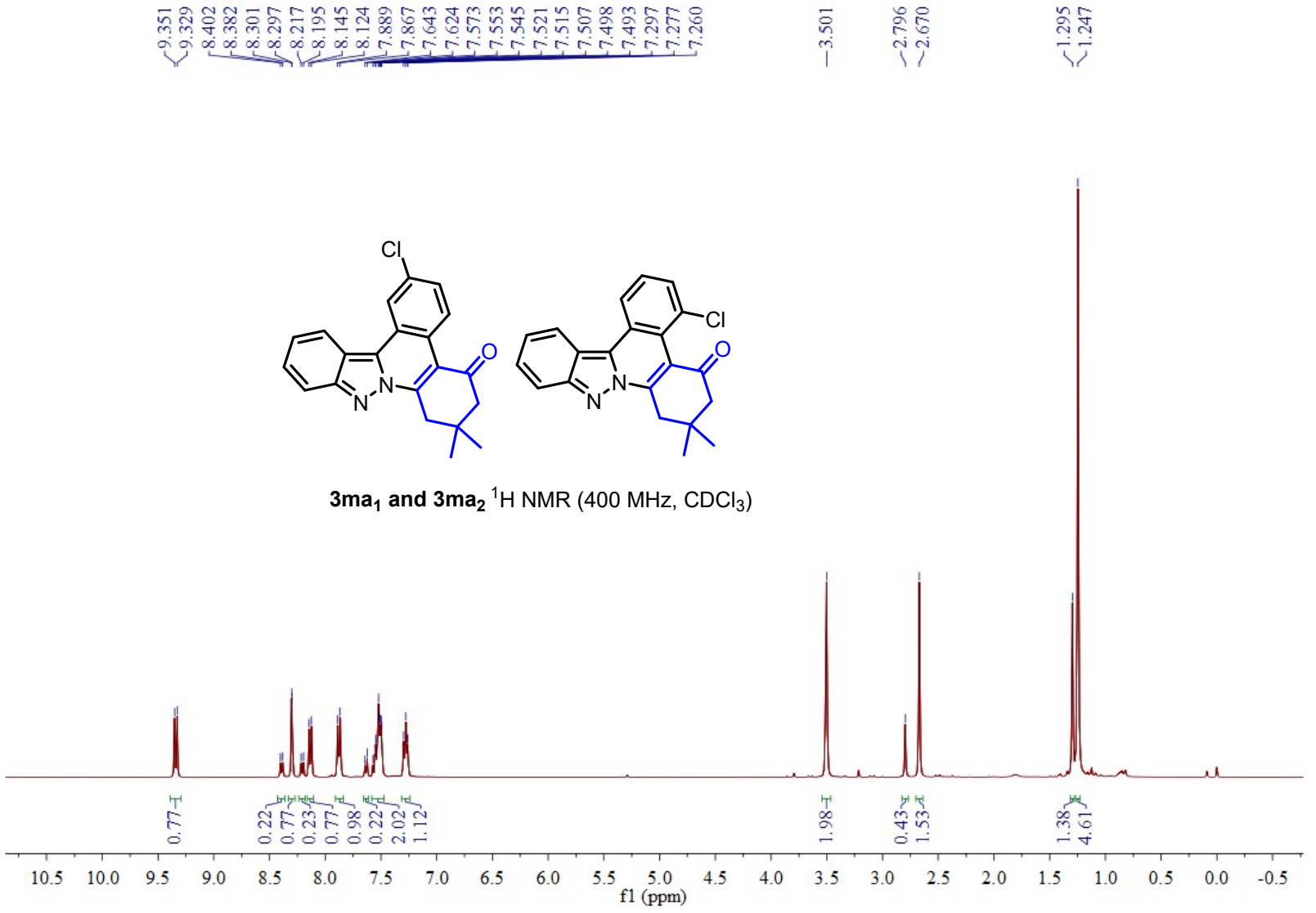

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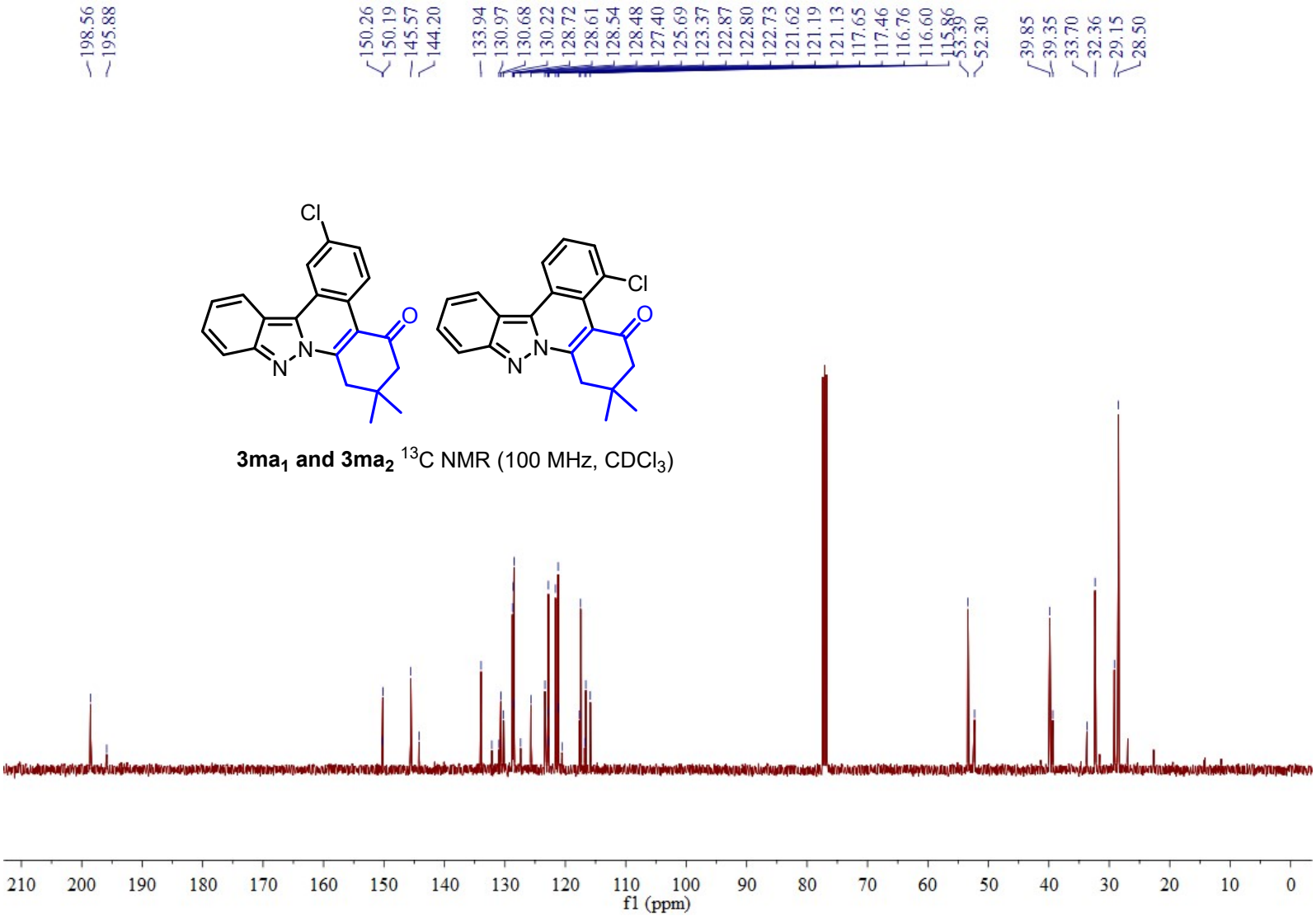

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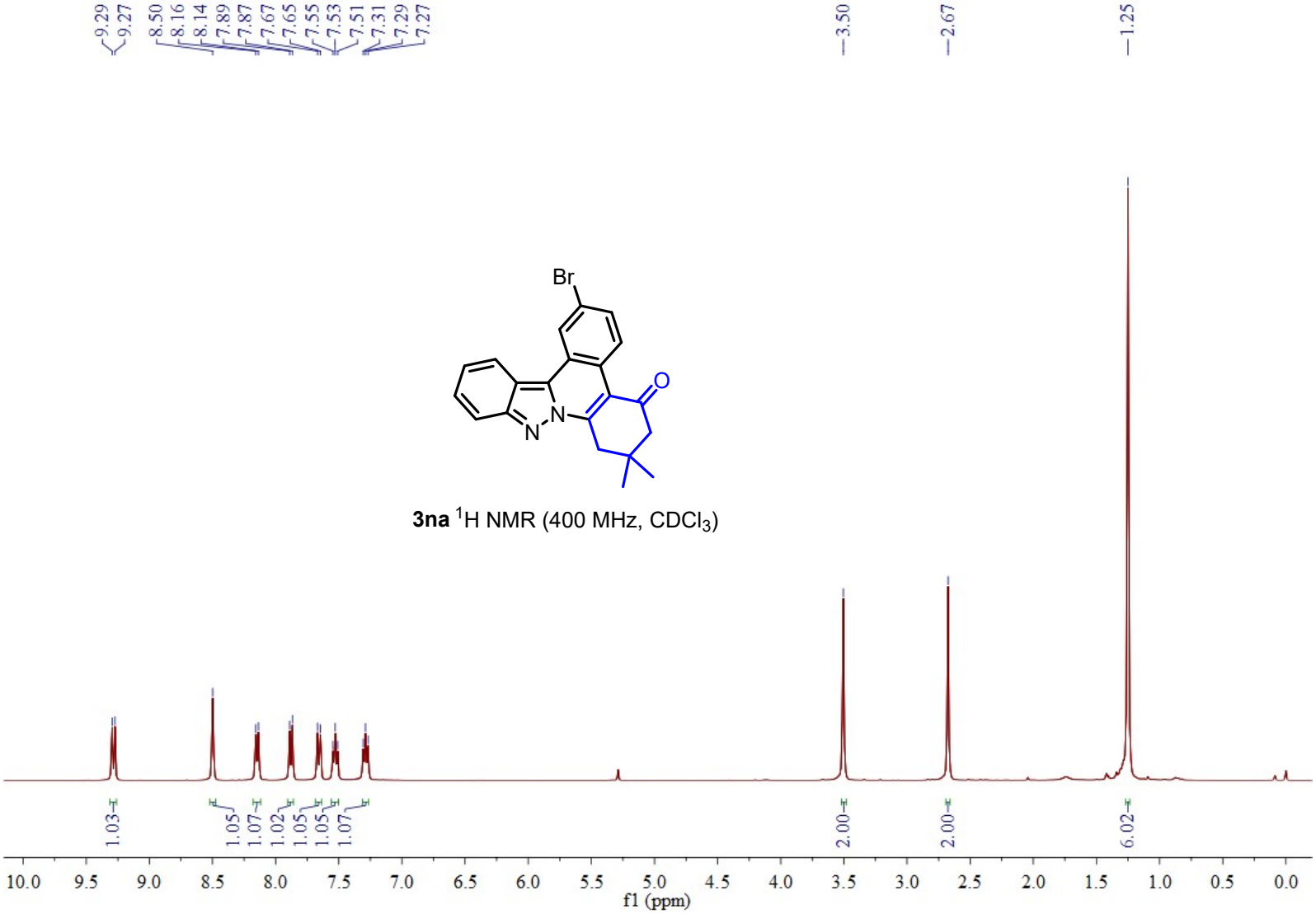

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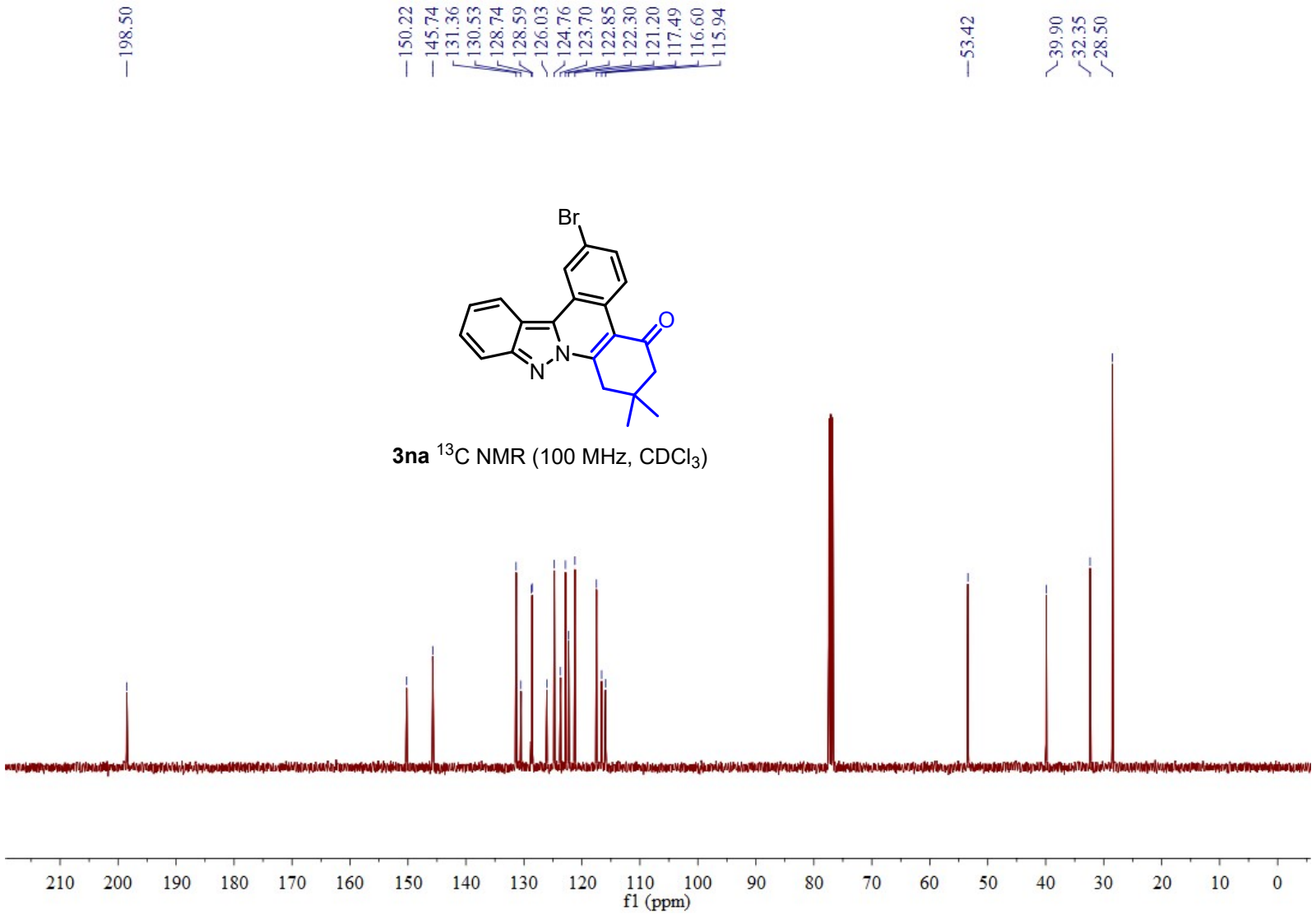

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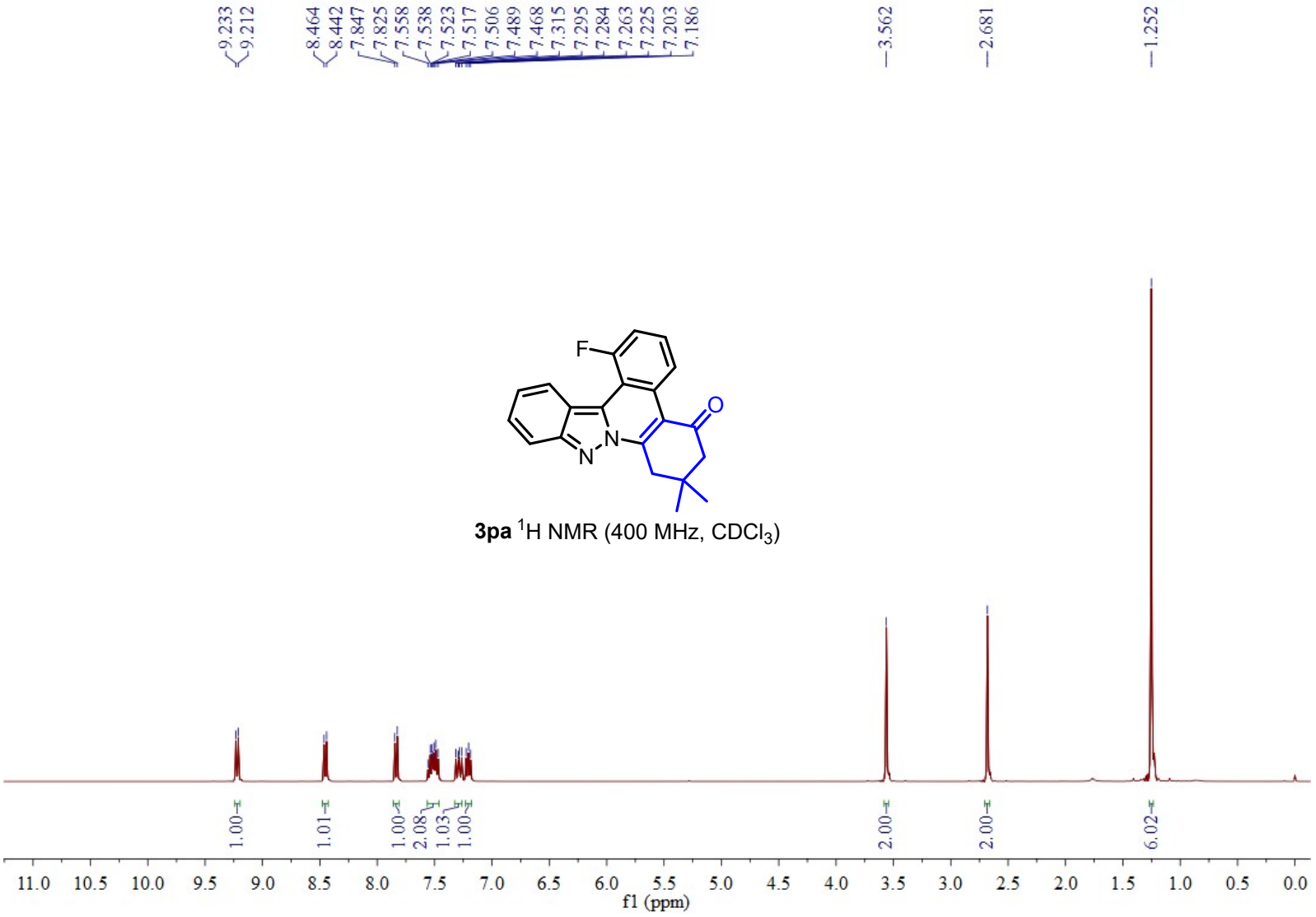

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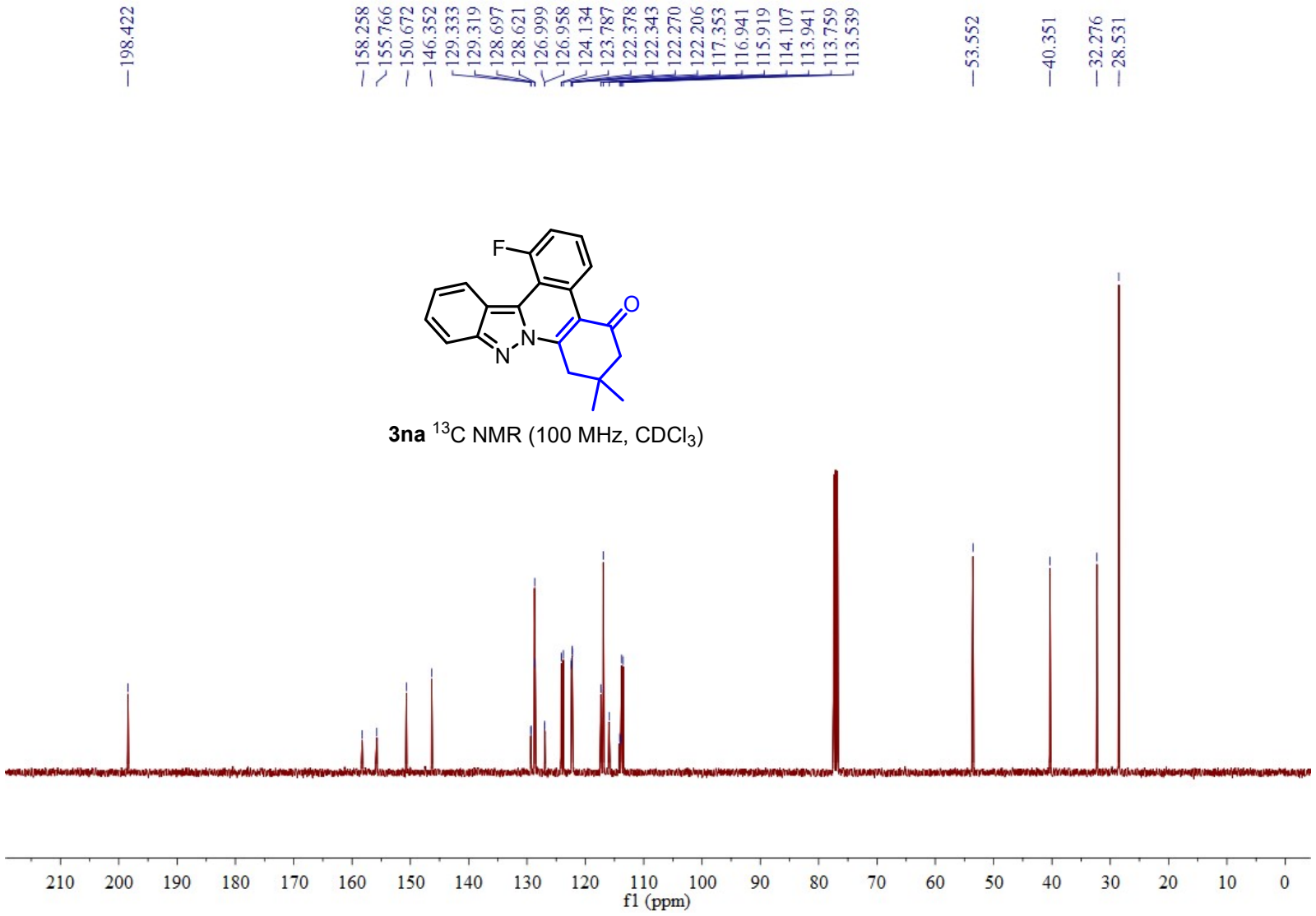

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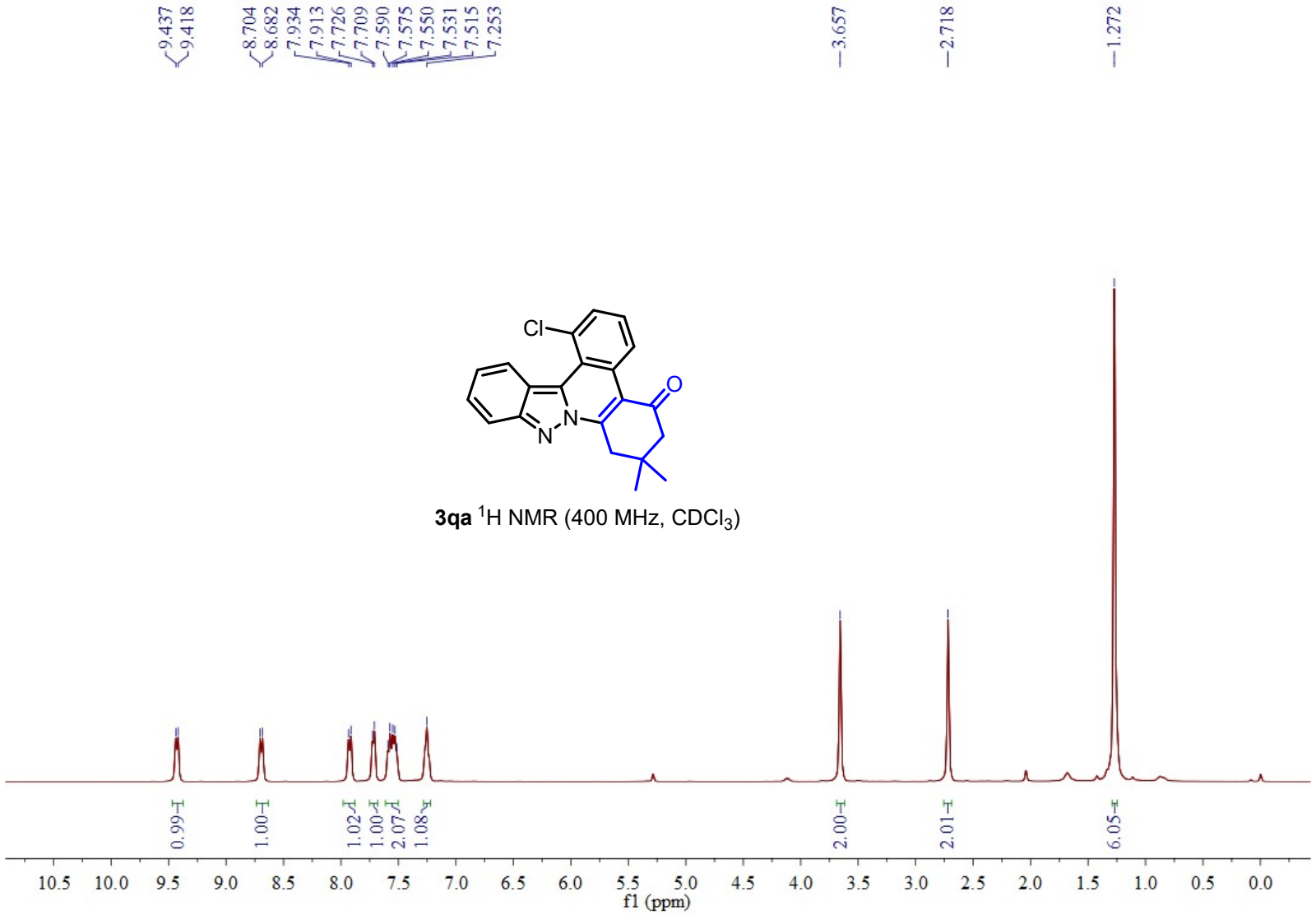
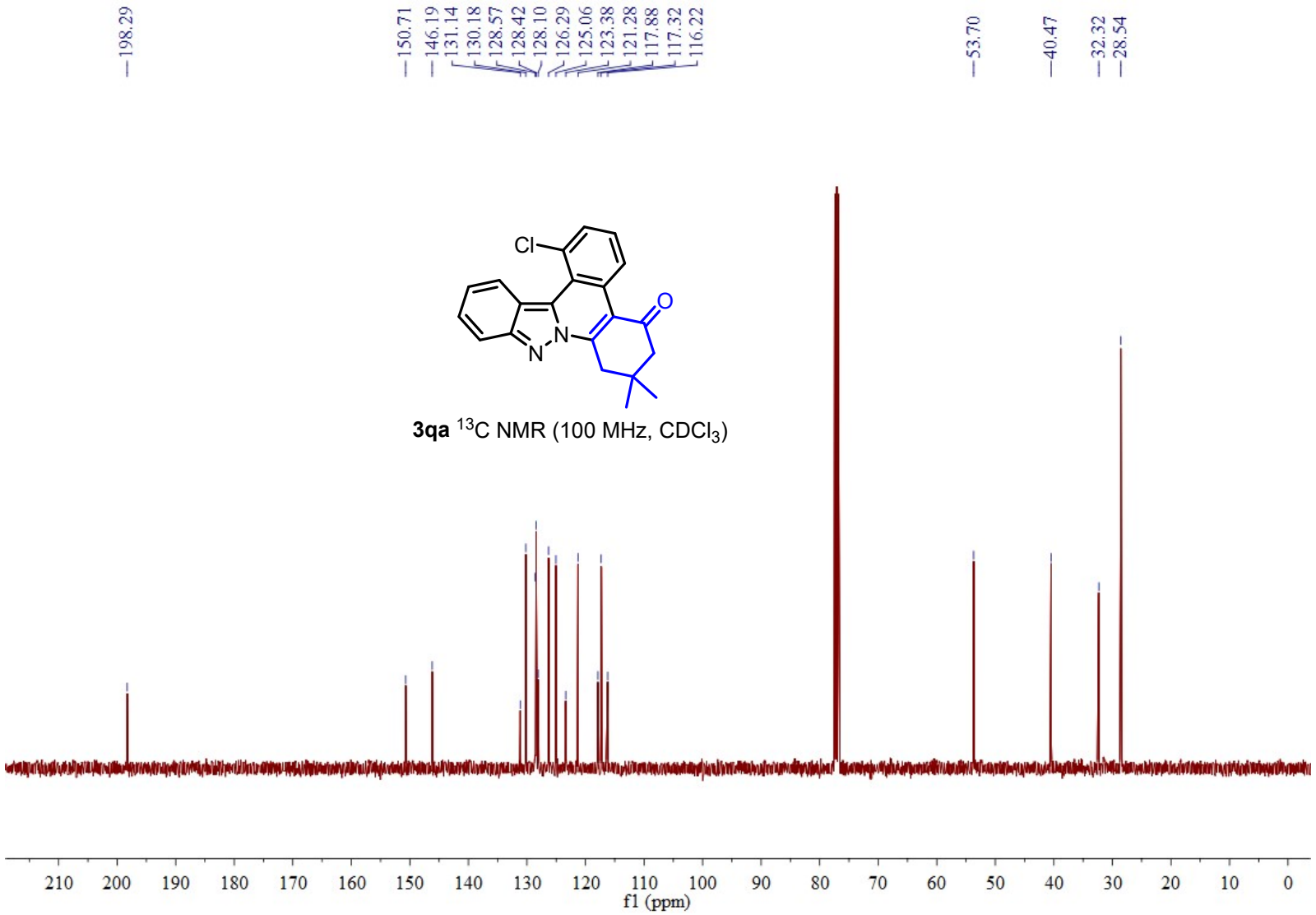


3qa ^{1}H NMR (400 MHz, $CDCl_3$)



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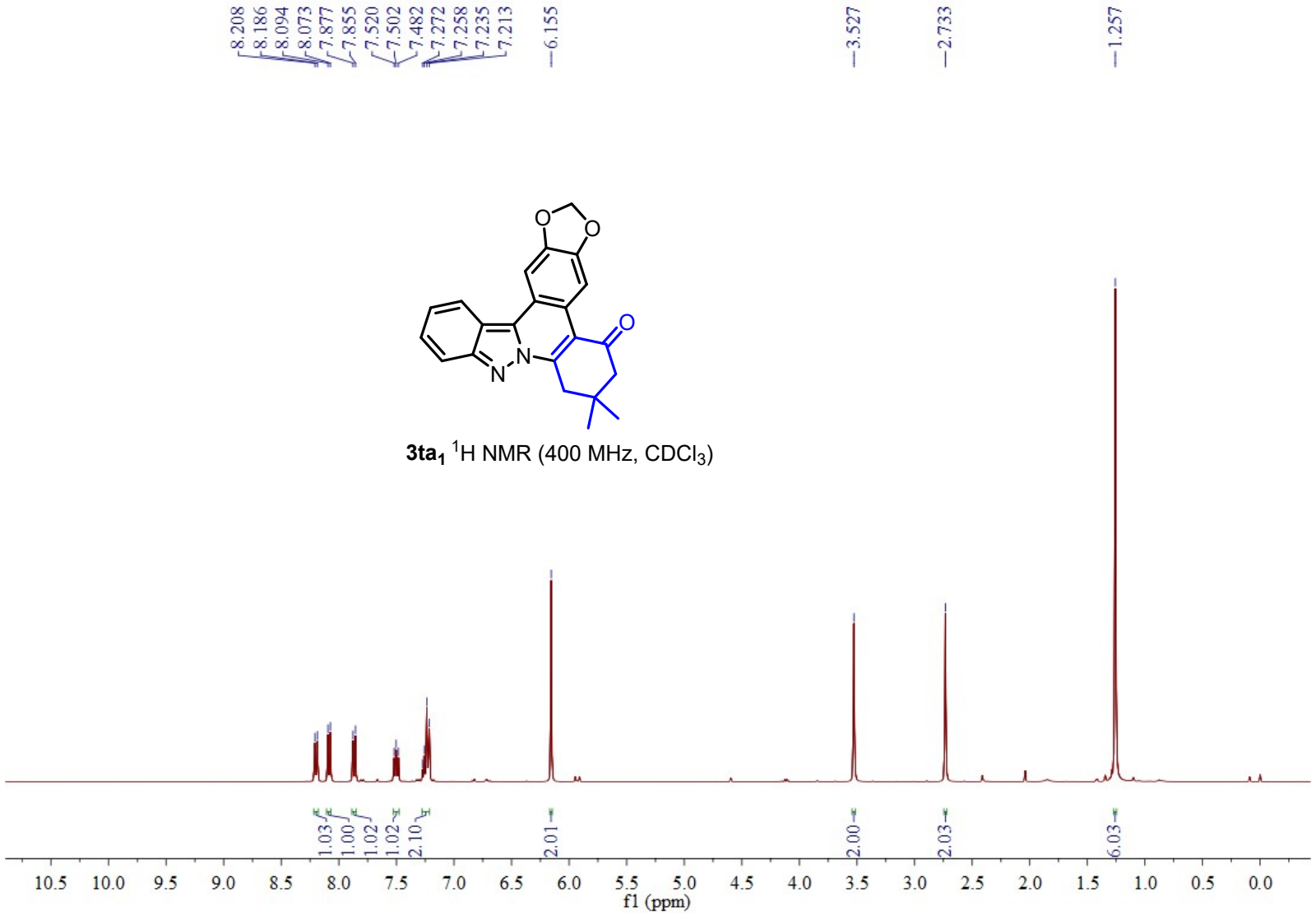

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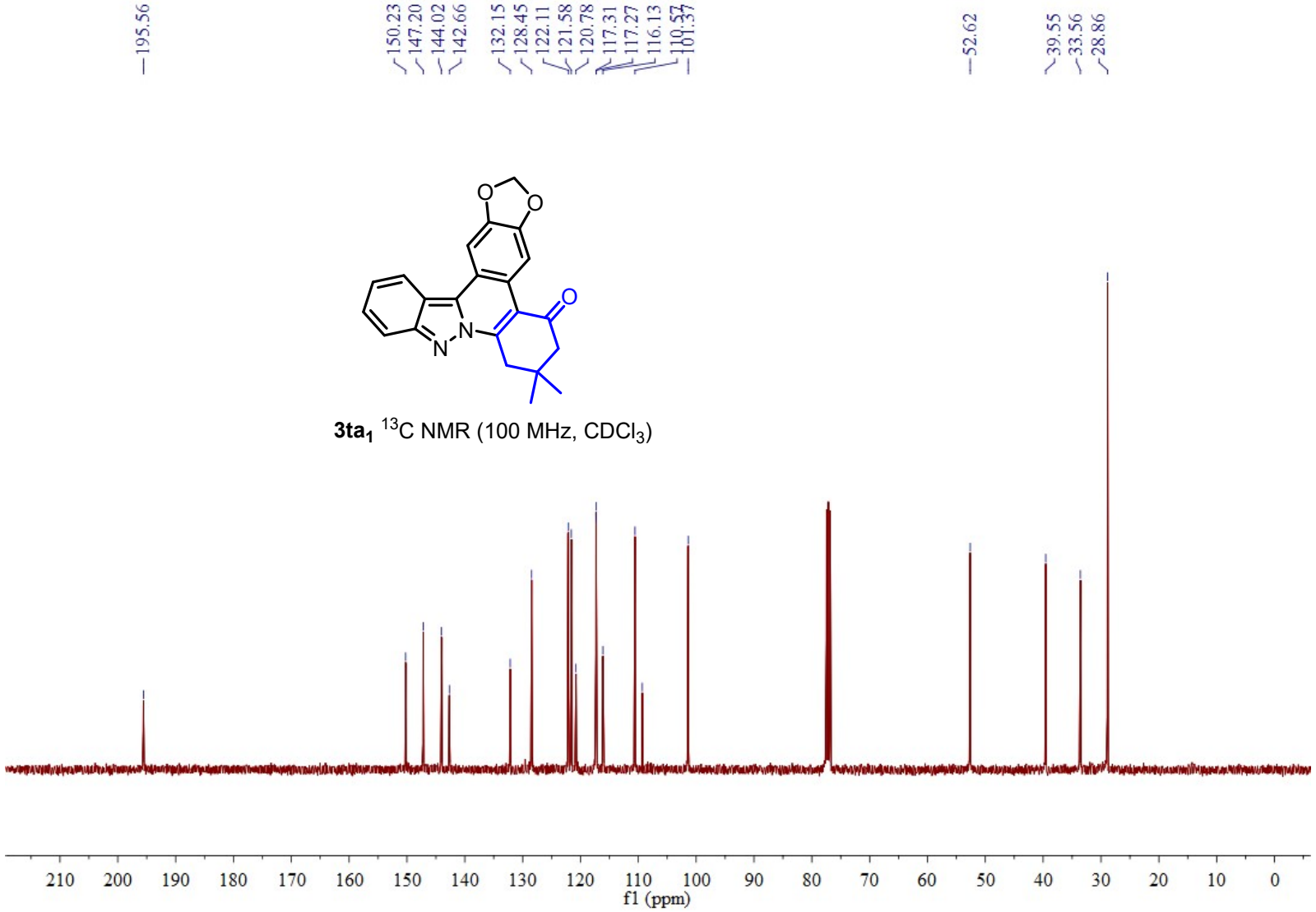

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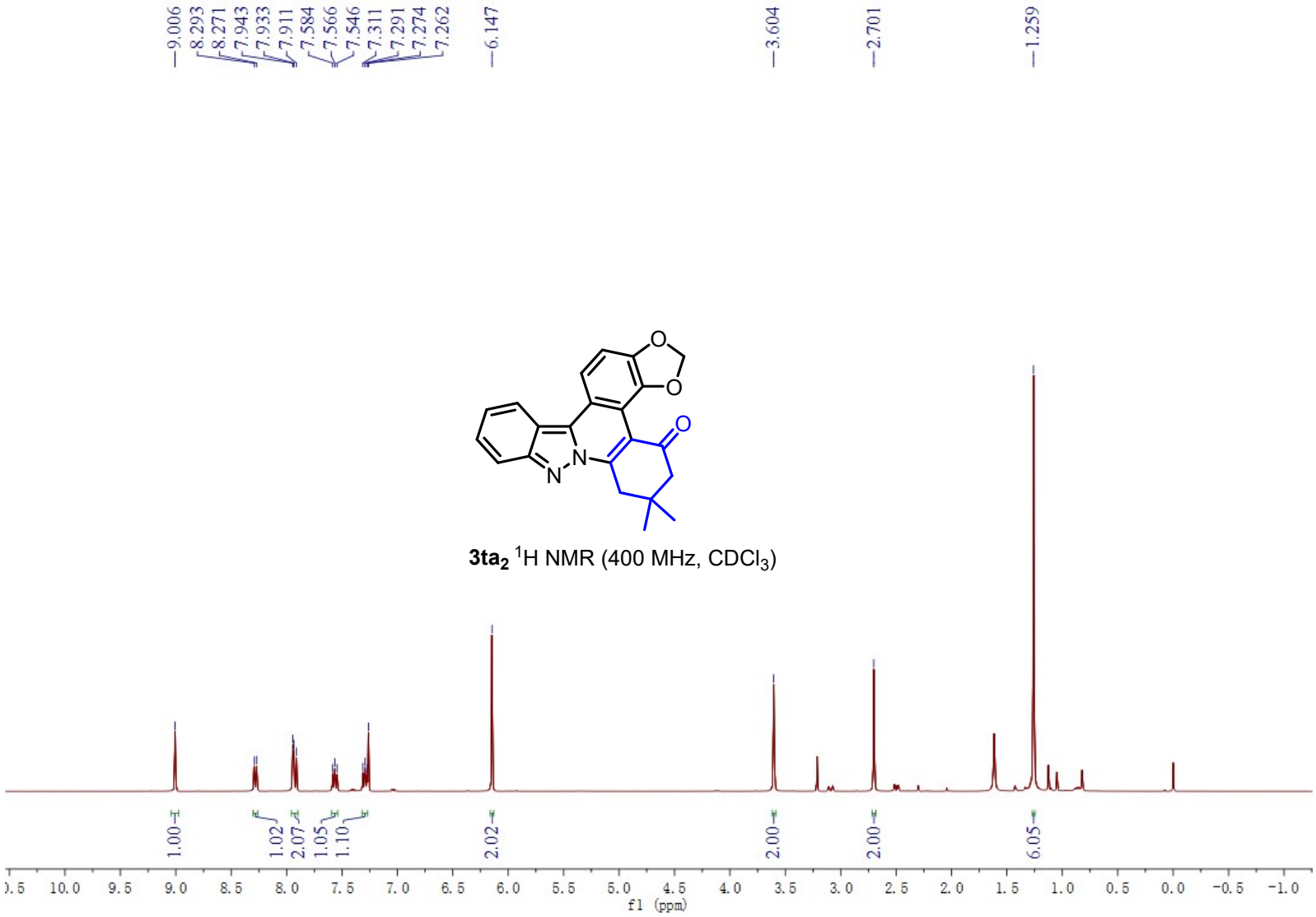

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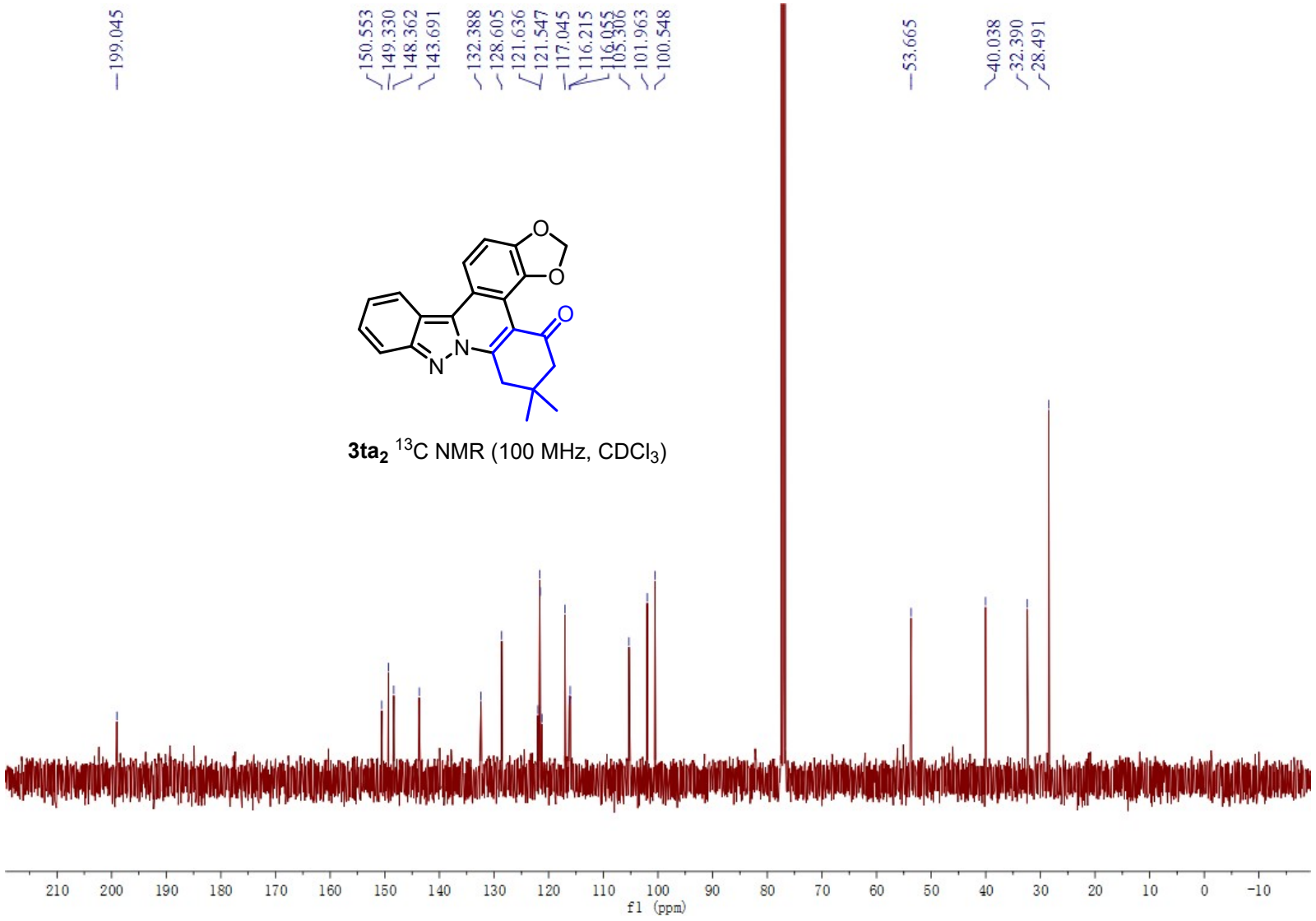

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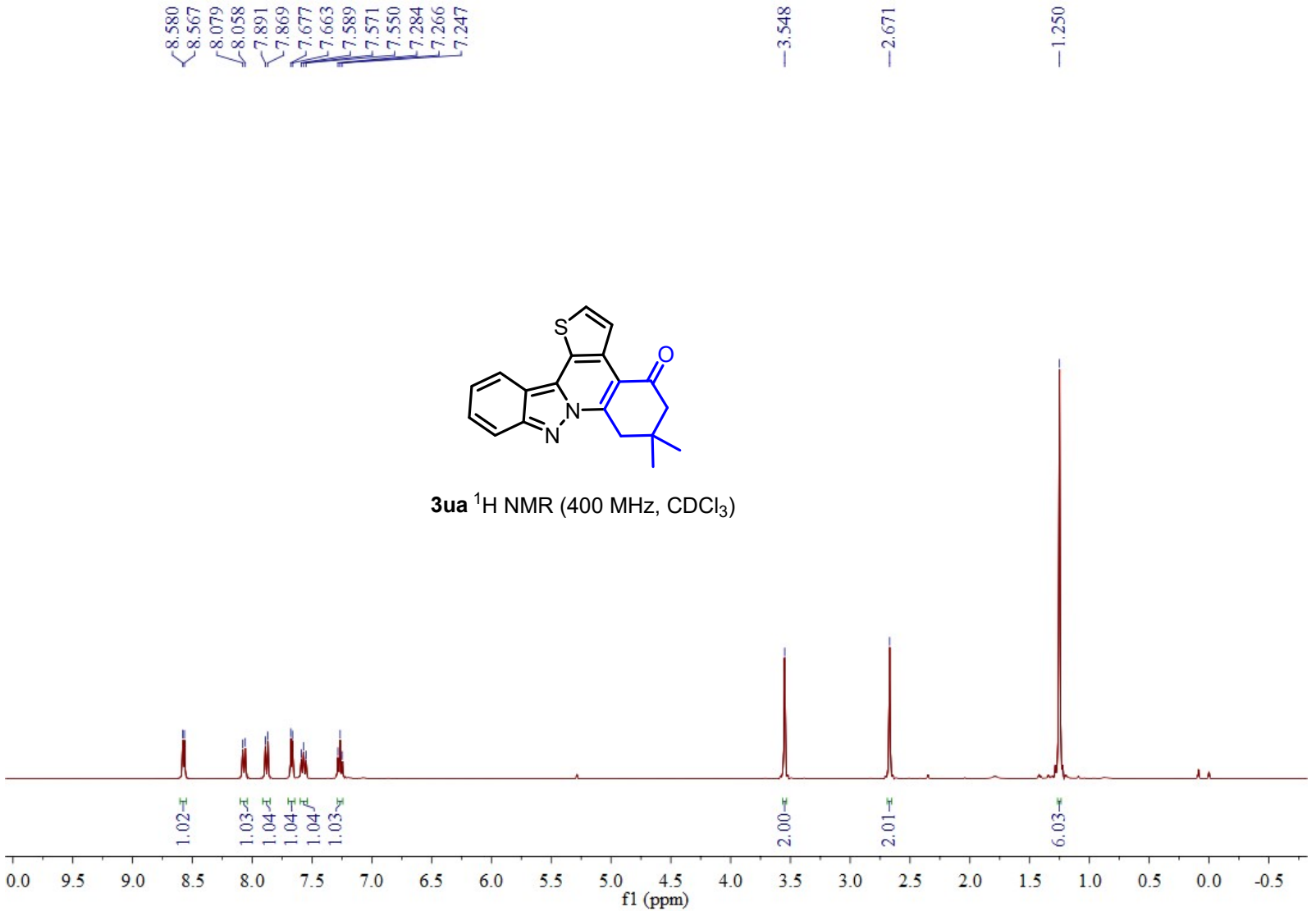
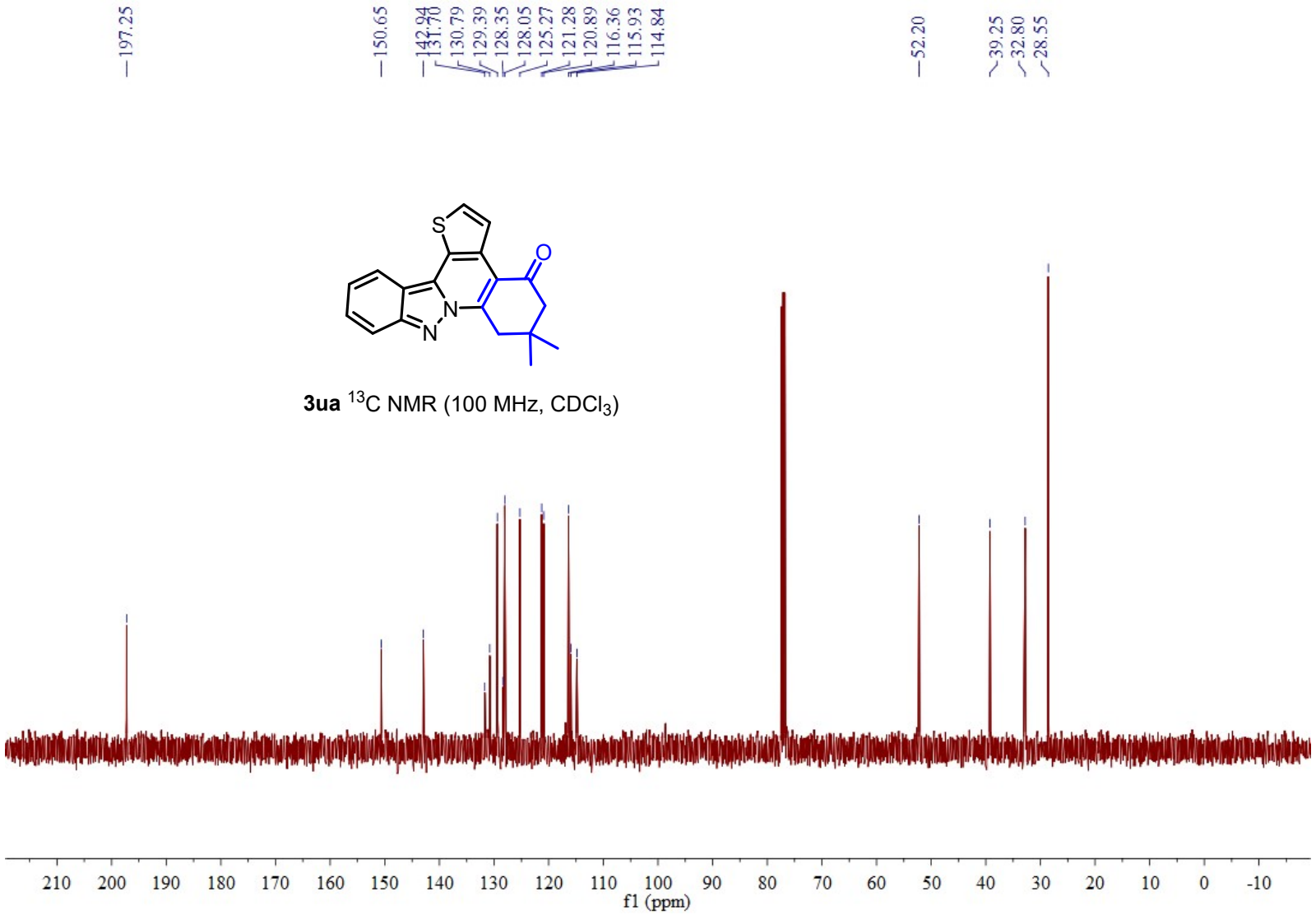


3ua ^{1}H NMR (400 MHz, $CDCl_3$)



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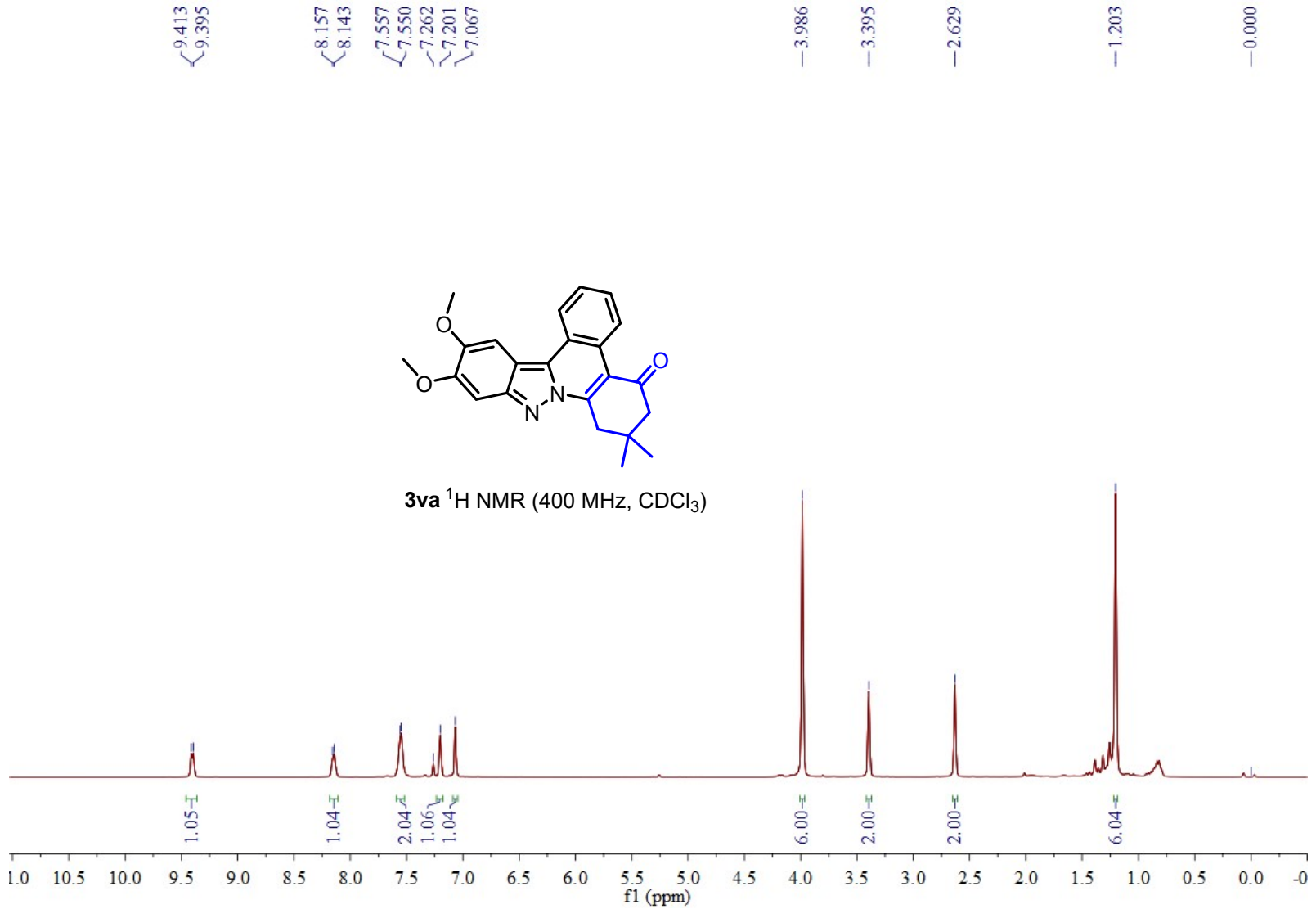

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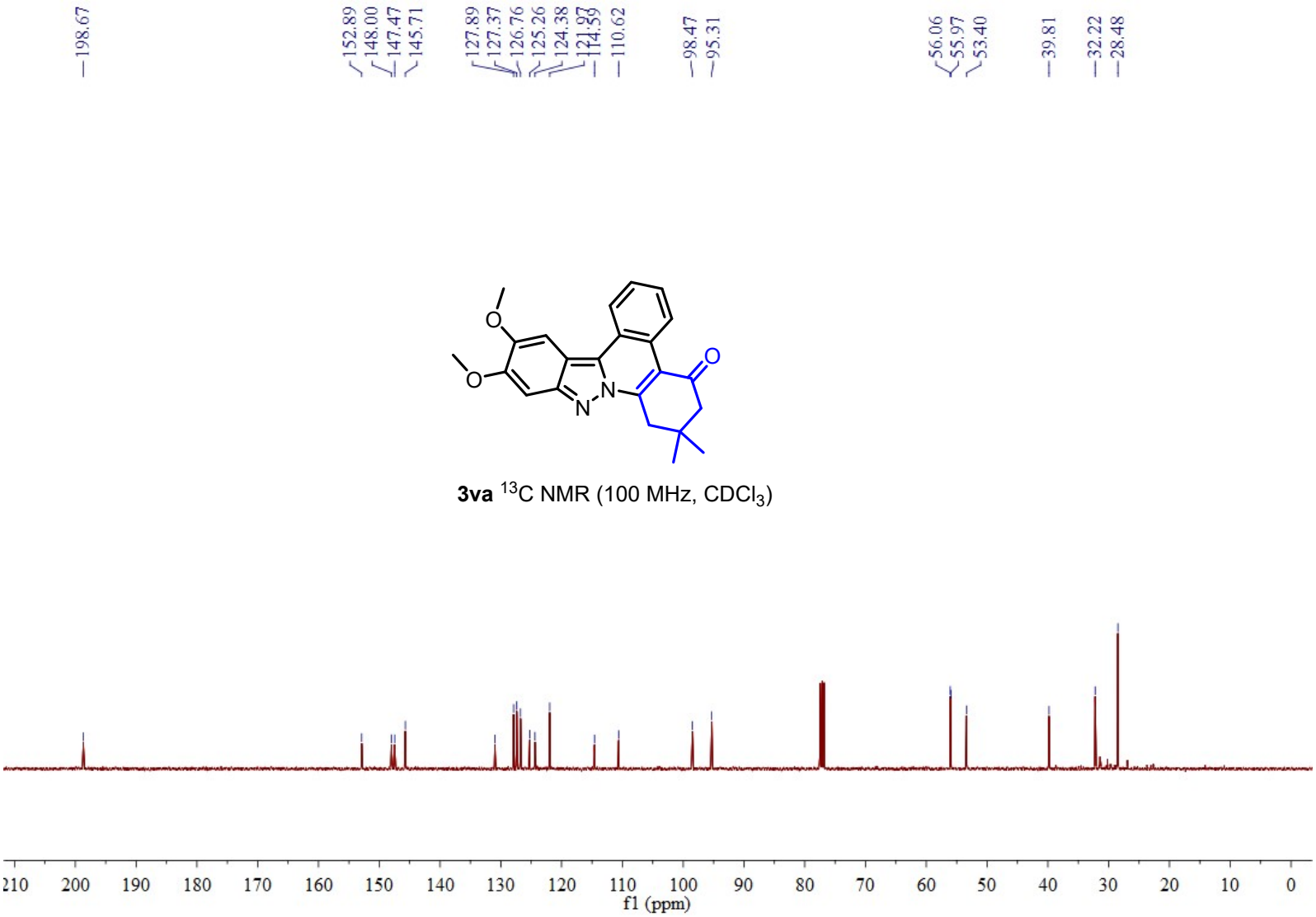

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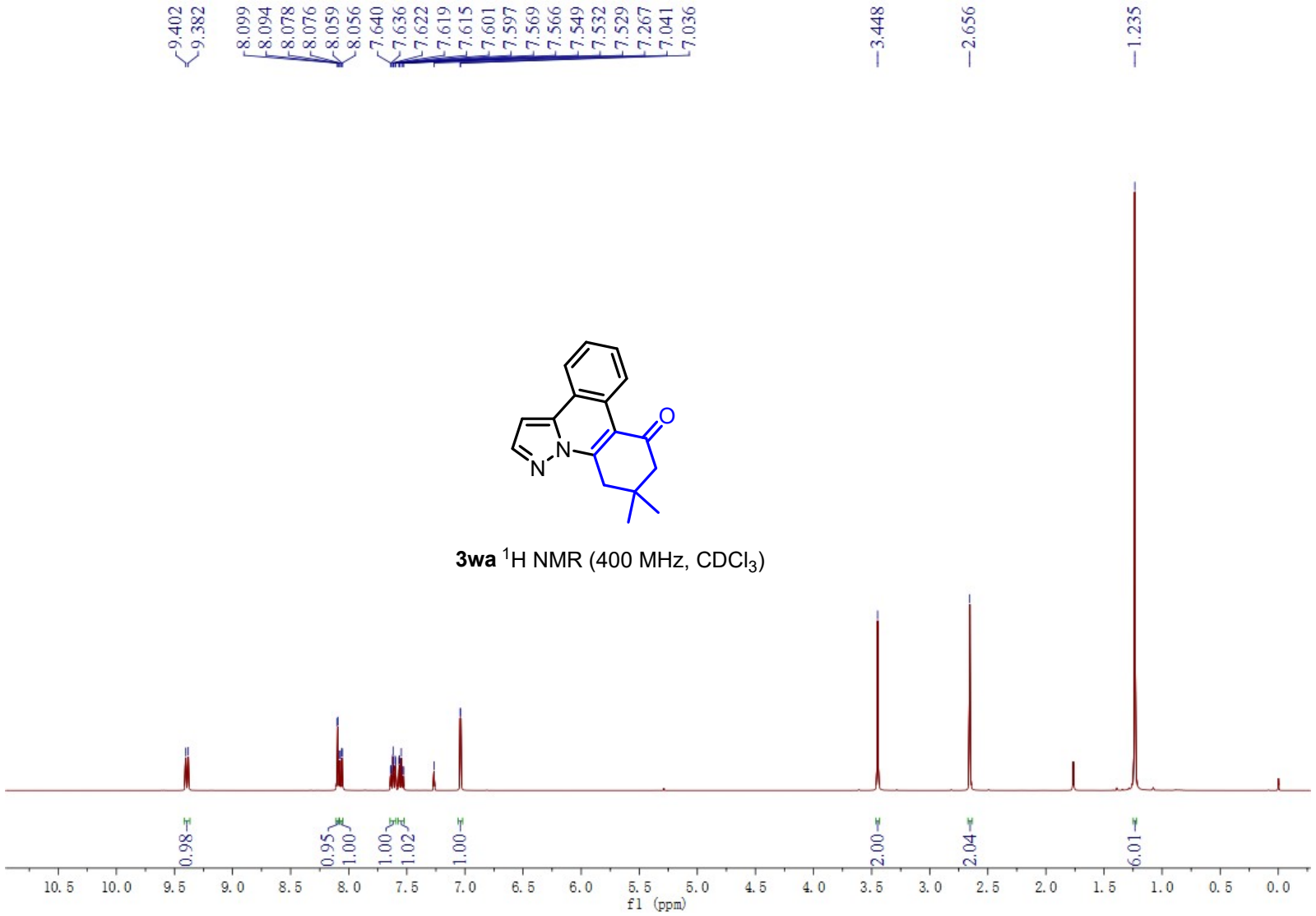

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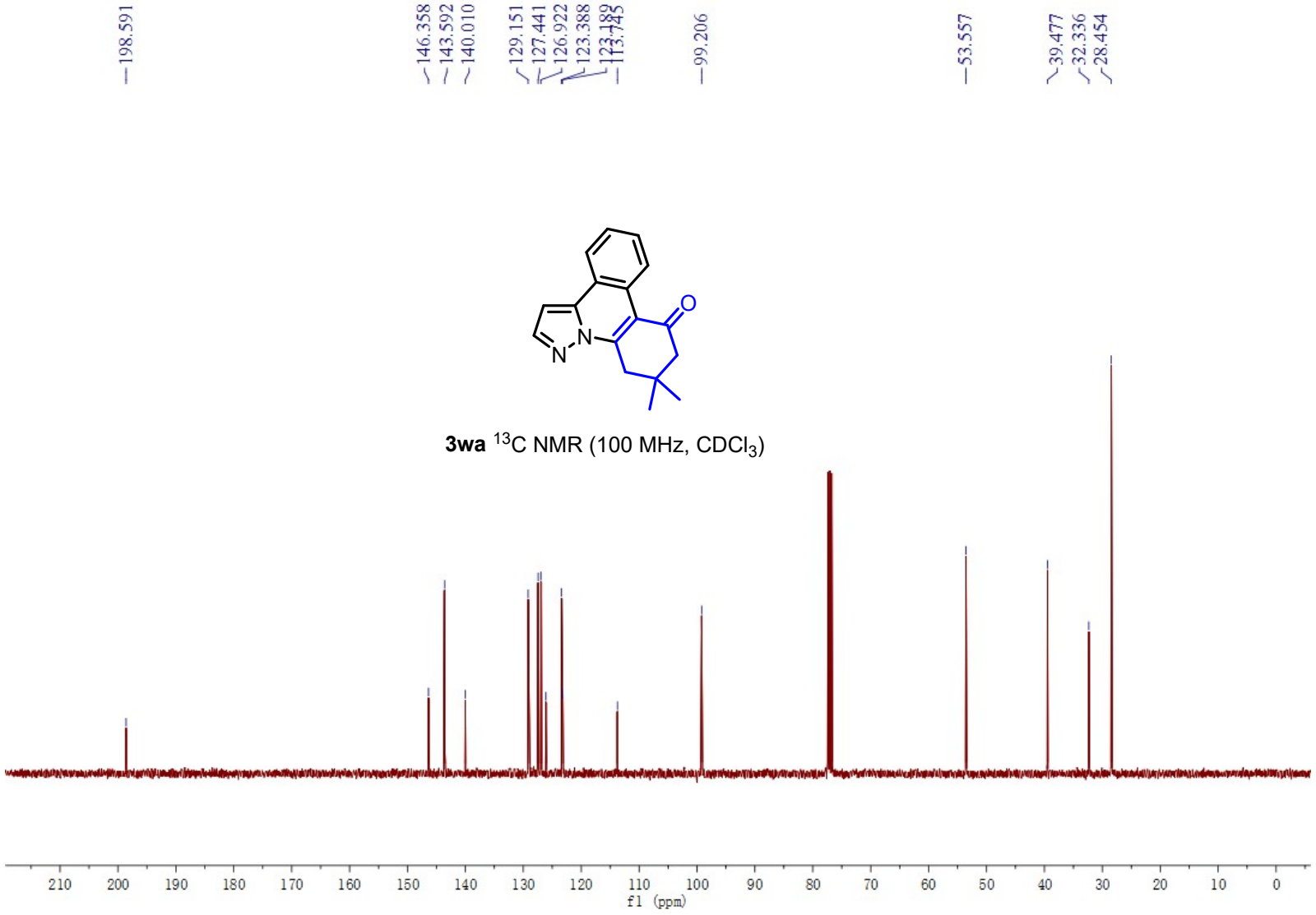
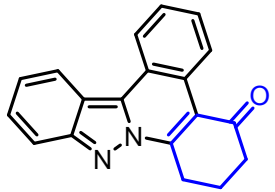
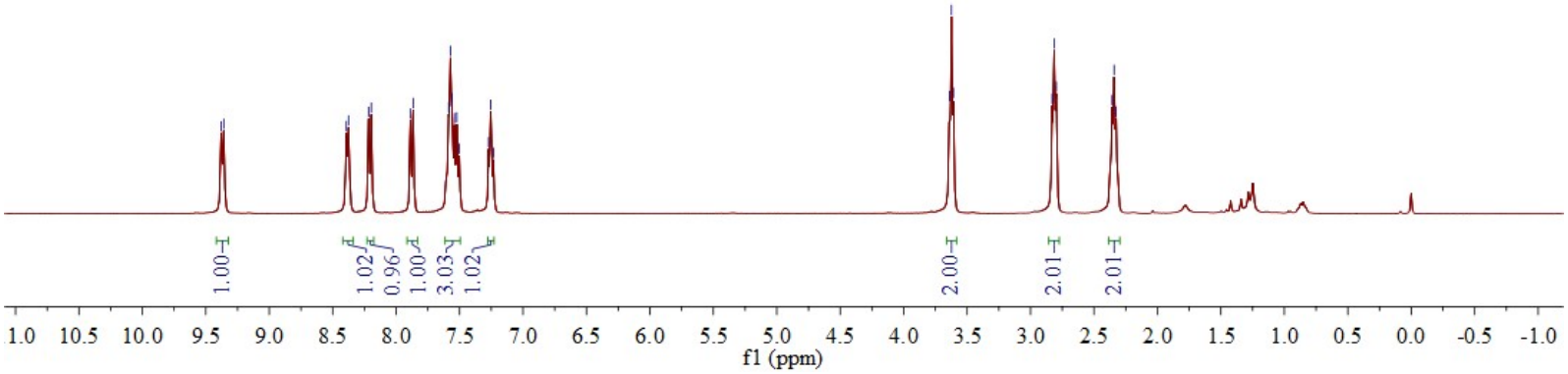
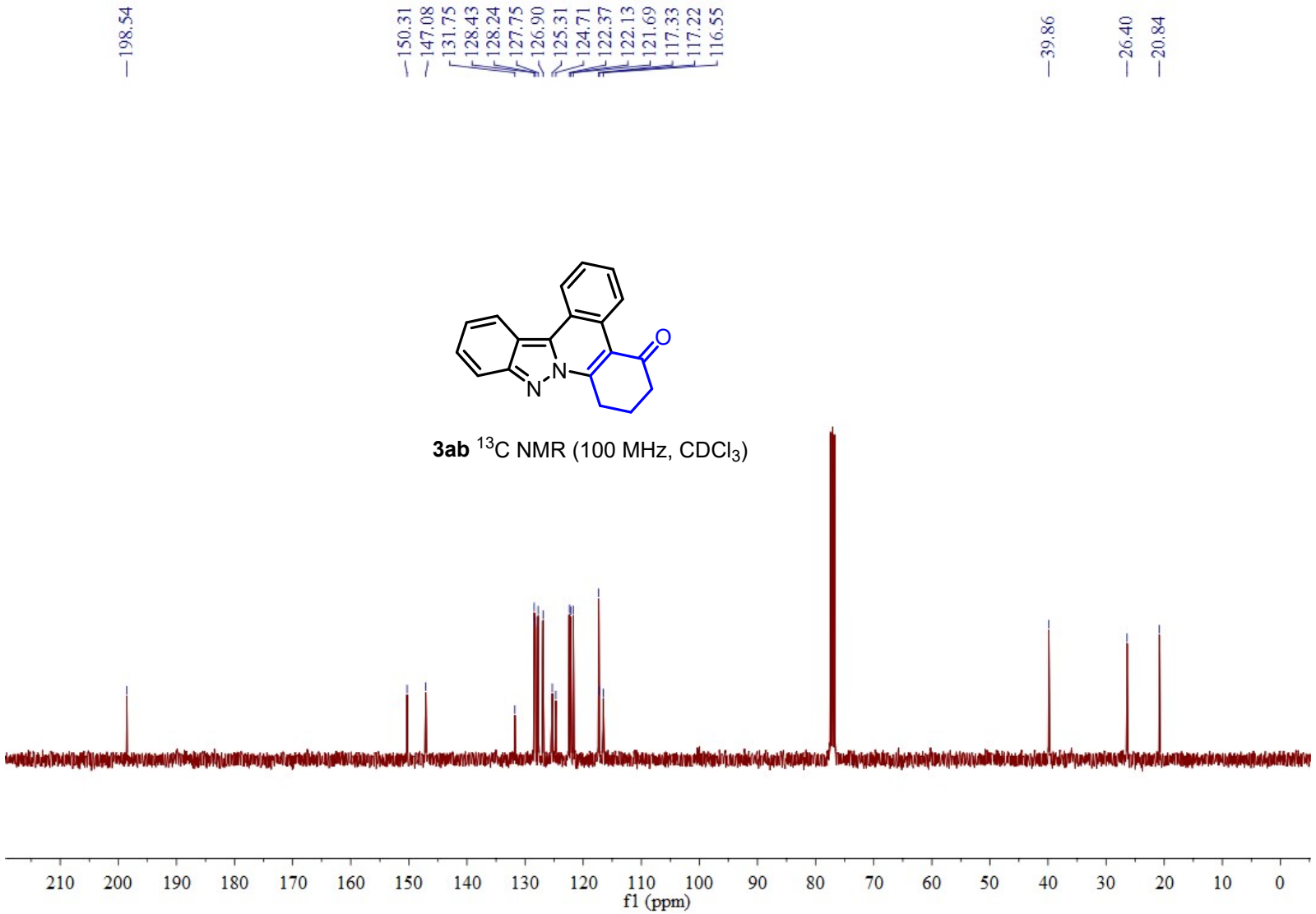


3wa ^{13}C NMR (100 MHz, $CDCl_3$)

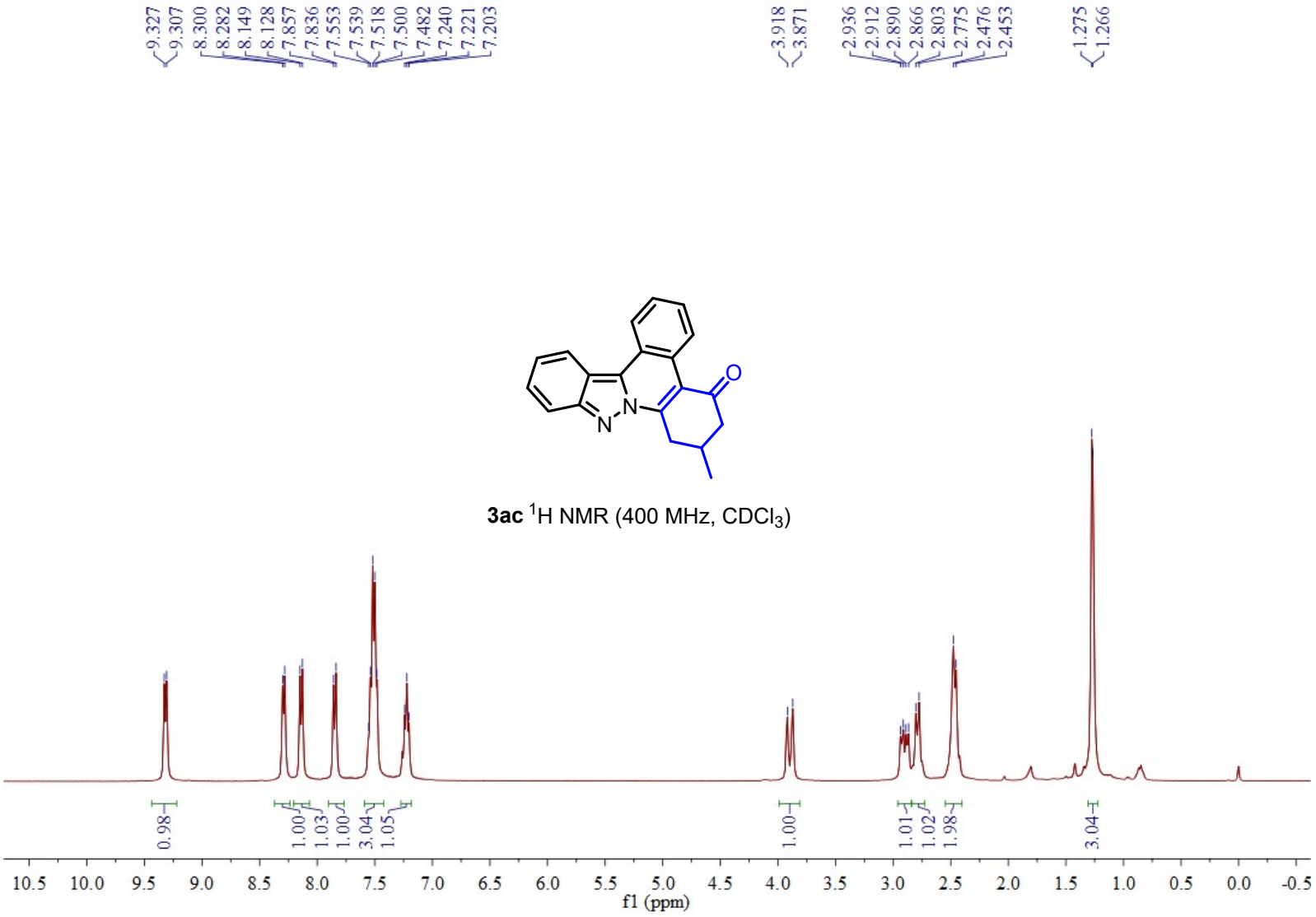


3ab ^{1}H NMR (400 MHz, $CDCl_3$)

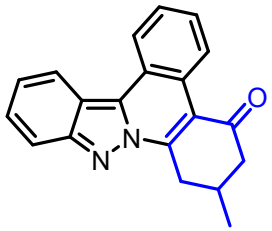




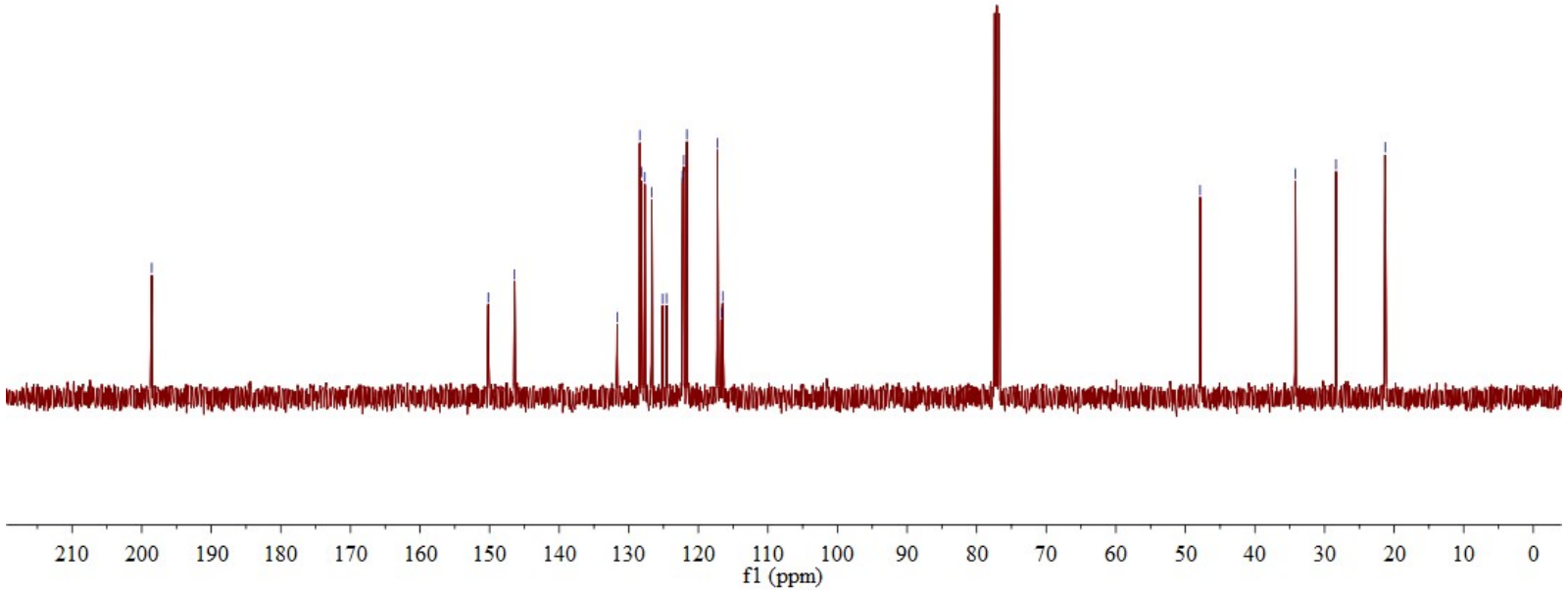
3ab ^{13}C NMR (100 MHz, $CDCl_3$)

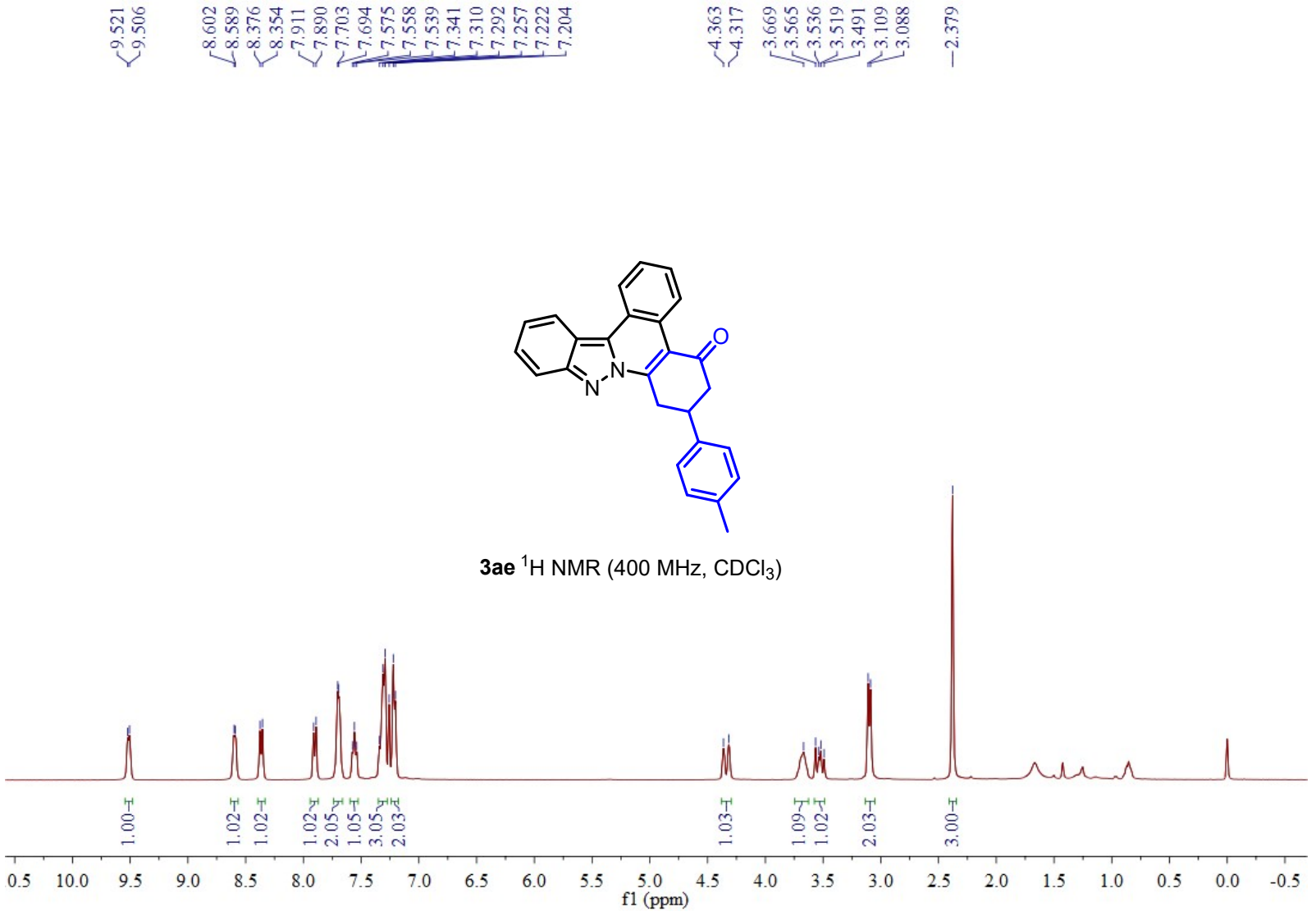


3ac ^{1}H NMR (400 MHz, $CDCl_3$)

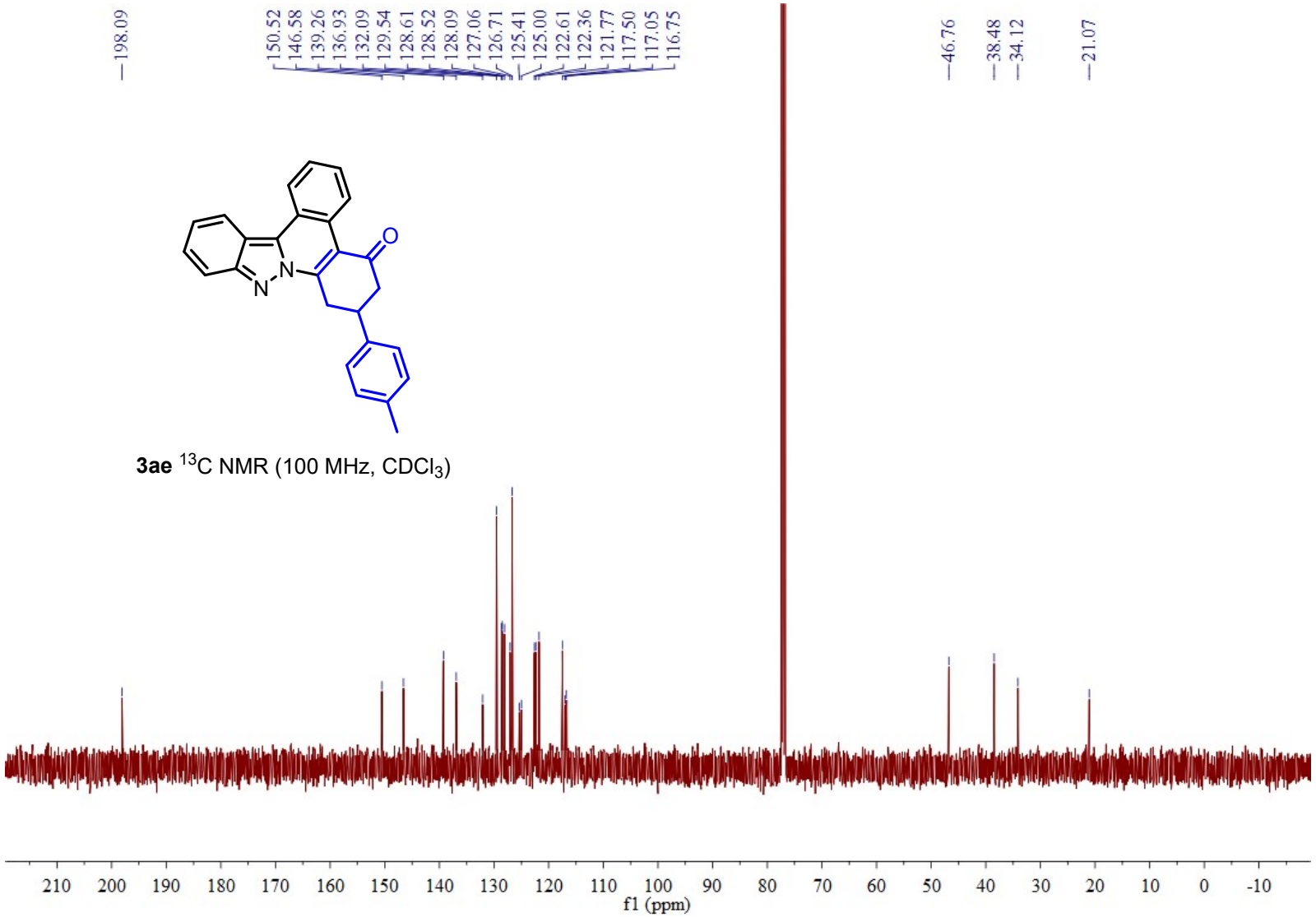


3ac ^{13}C NMR (100 MHz, $CDCl_3$)

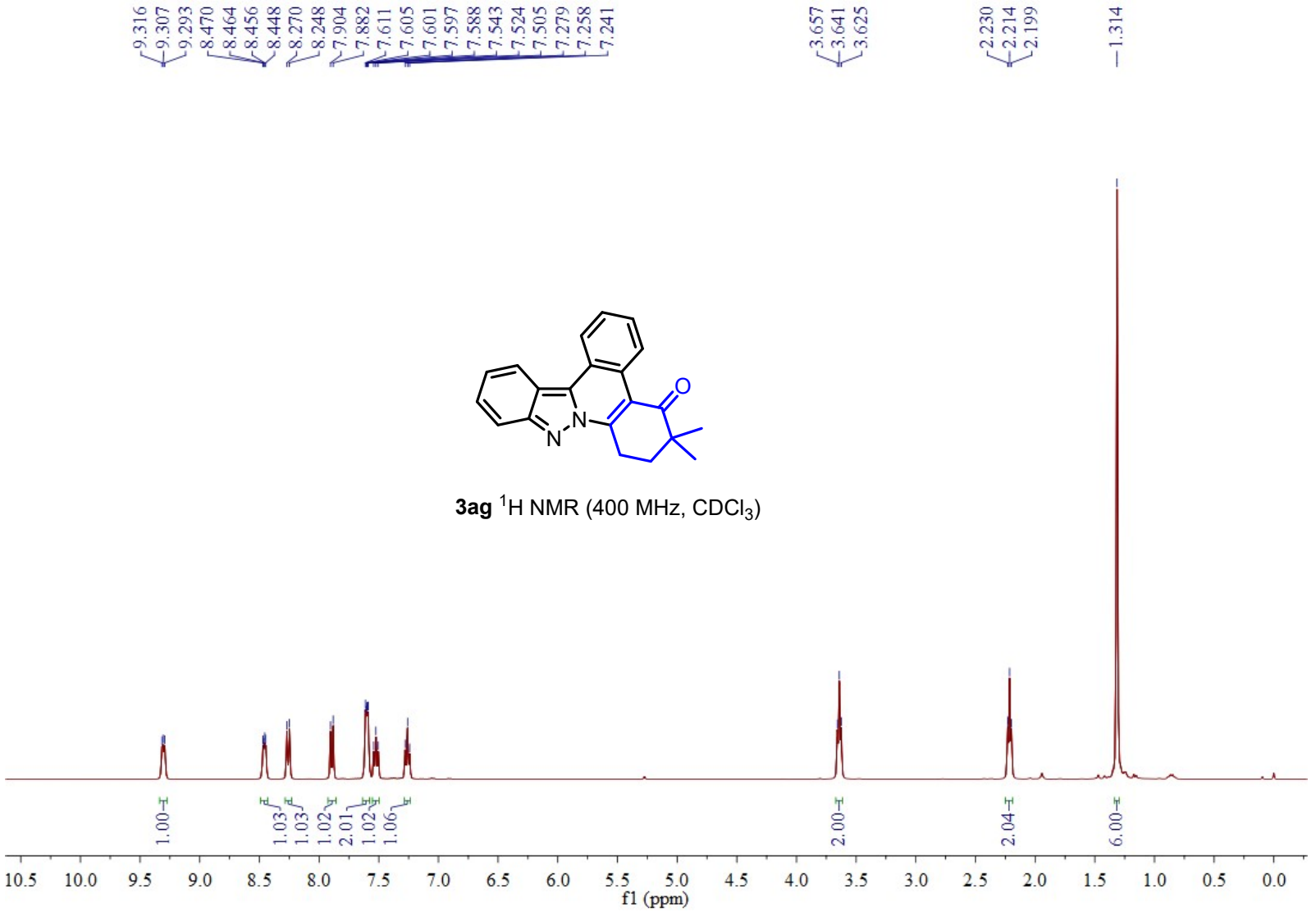




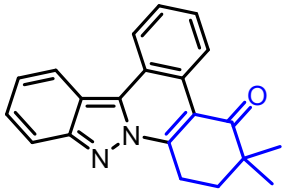
3ae ^{1}H NMR (400 MHz, $CDCl_3$)



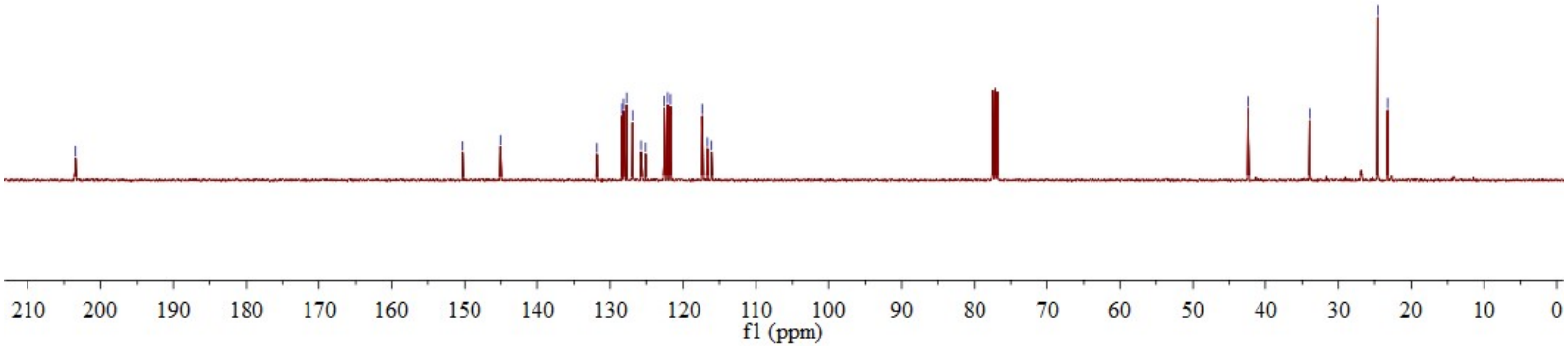
3ae ^{13}C NMR (100 MHz, $CDCl_3$)

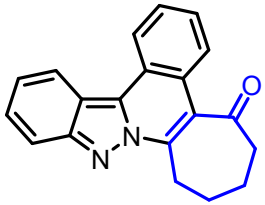


3ag ^{1}H NMR (400 MHz, $CDCl_3$)

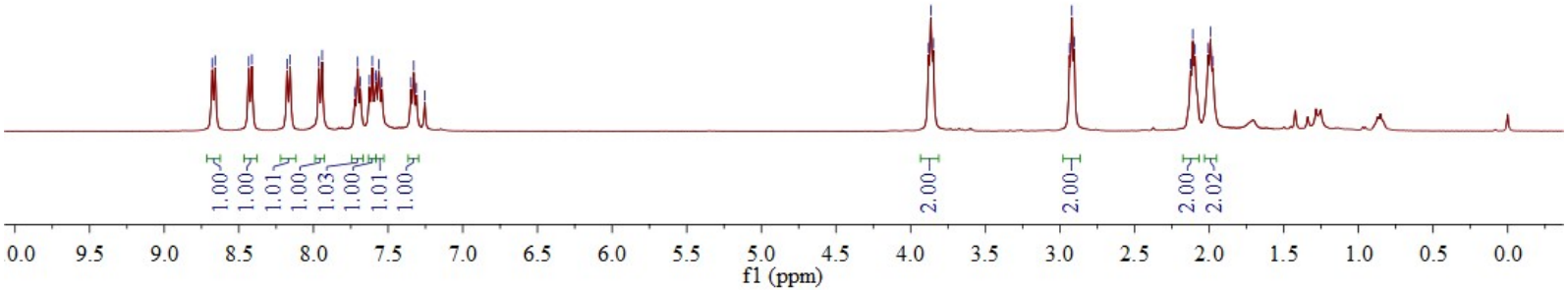


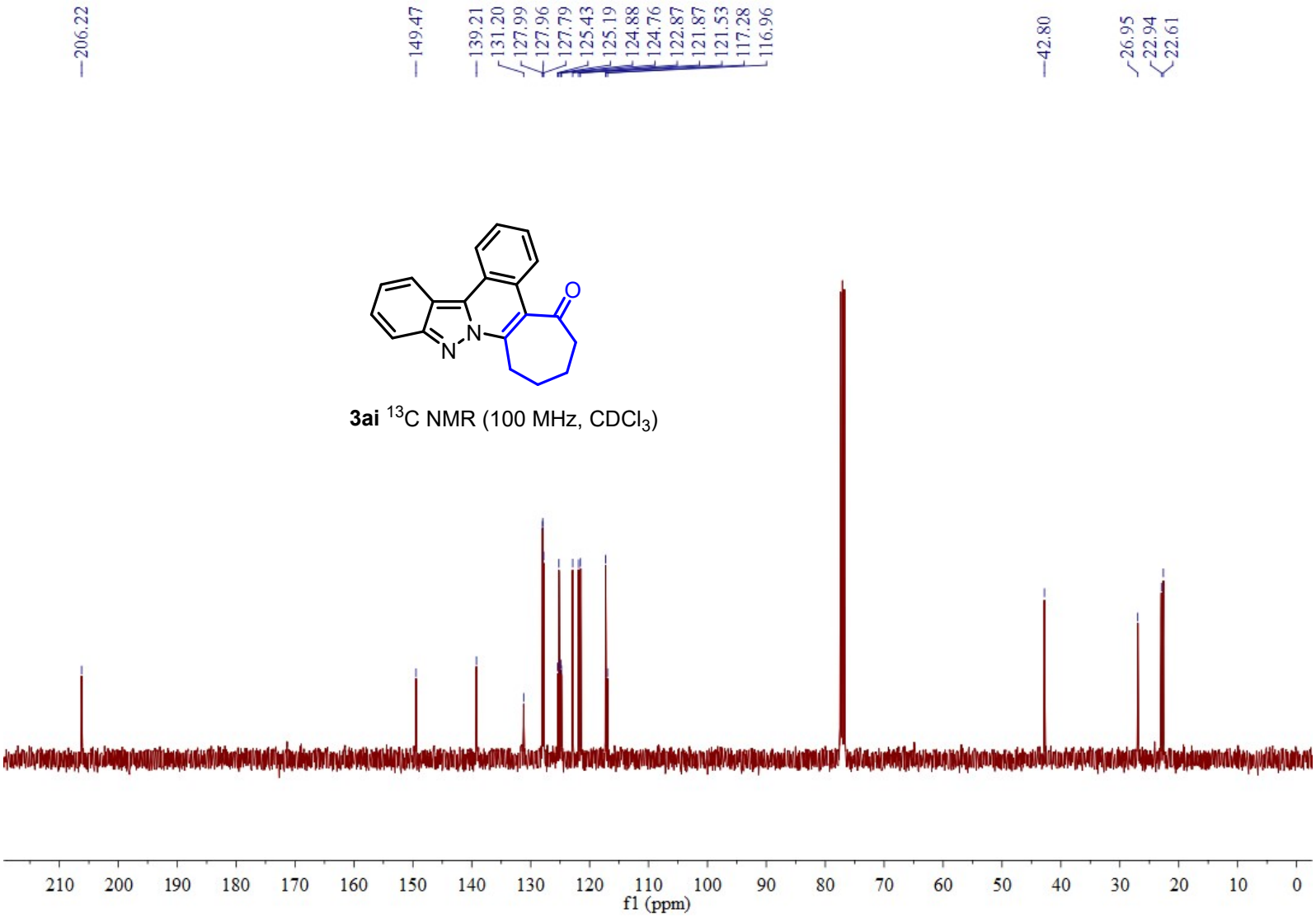
3ag ^{13}C NMR (100 MHz, $CDCl_3$)



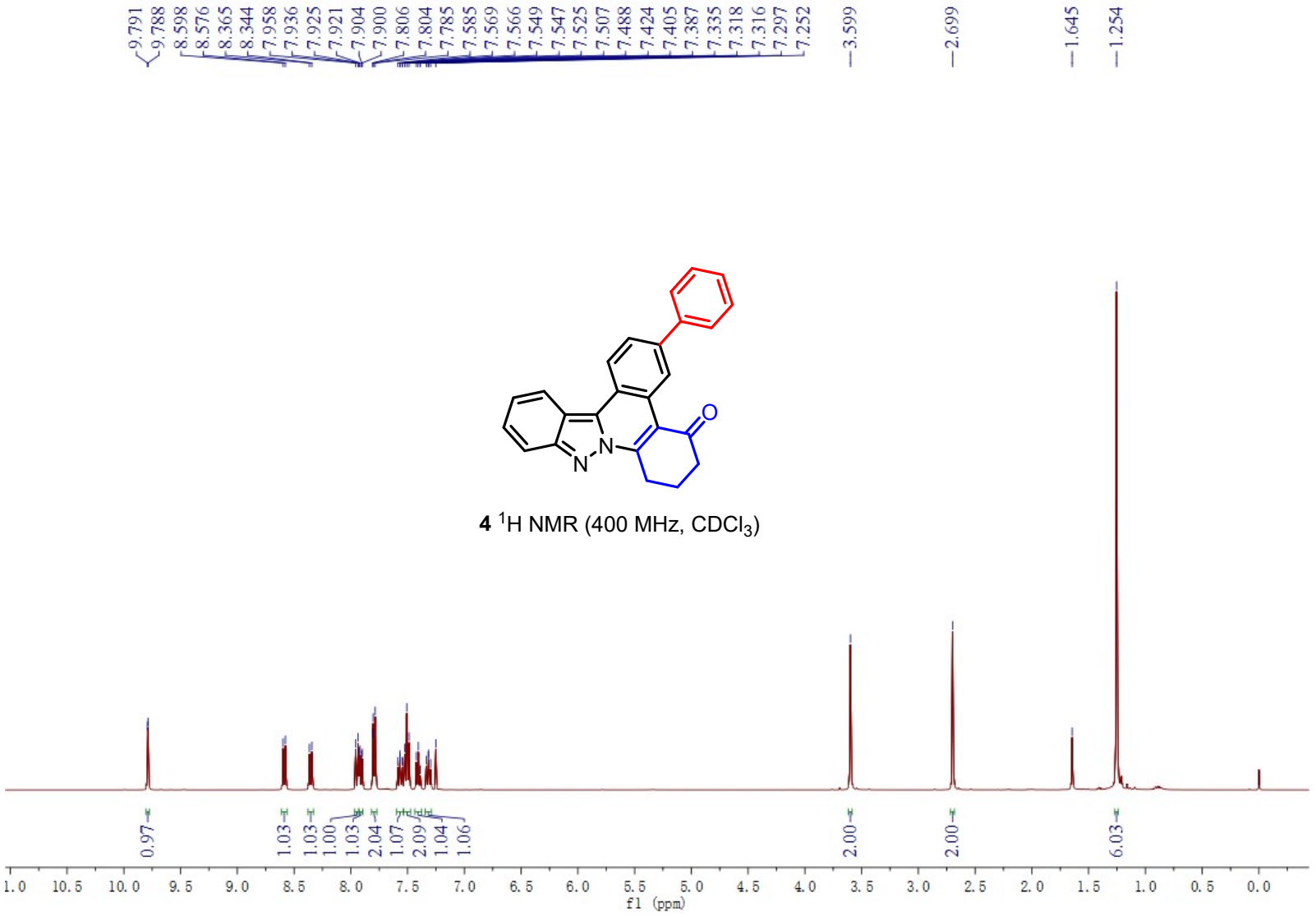


3ai ^{1}H NMR (400 MHz, $CDCl_3$)



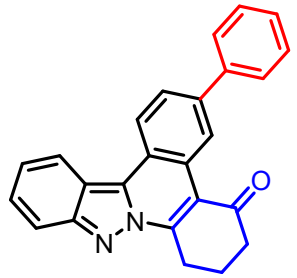


3ai ^{13}C NMR (100 MHz, $CDCl_3$)

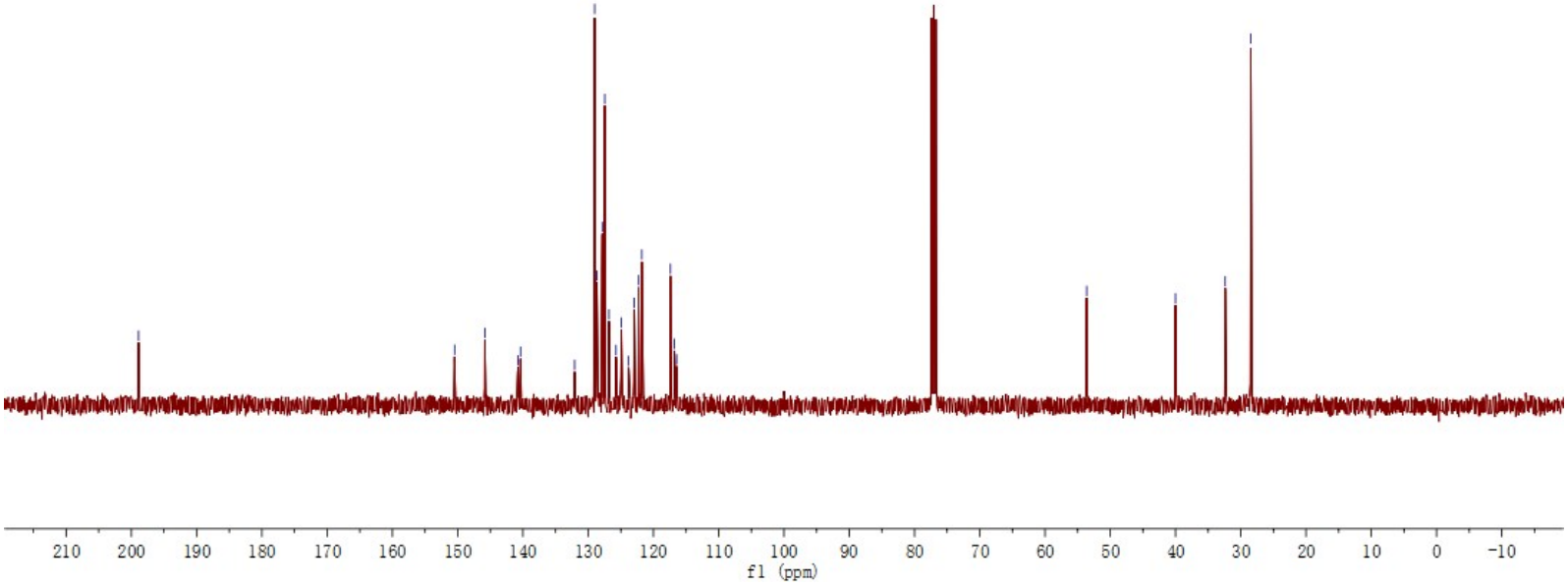


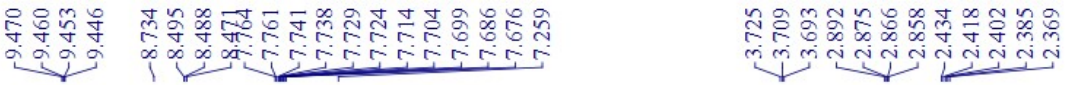
4 ^{1}H NMR (400 MHz, $CDCl_3$)

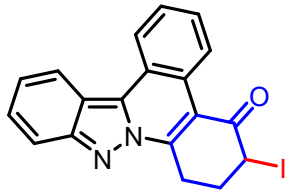
198.89
150.47
145.83
140.74
140.37
132.08
128.99
128.66
127.84
127.45
126.81
125.74
124.92
123.81
122.93
122.29
121.78
117.39
116.78
116.45
53.61
40.01
32.38
28.47



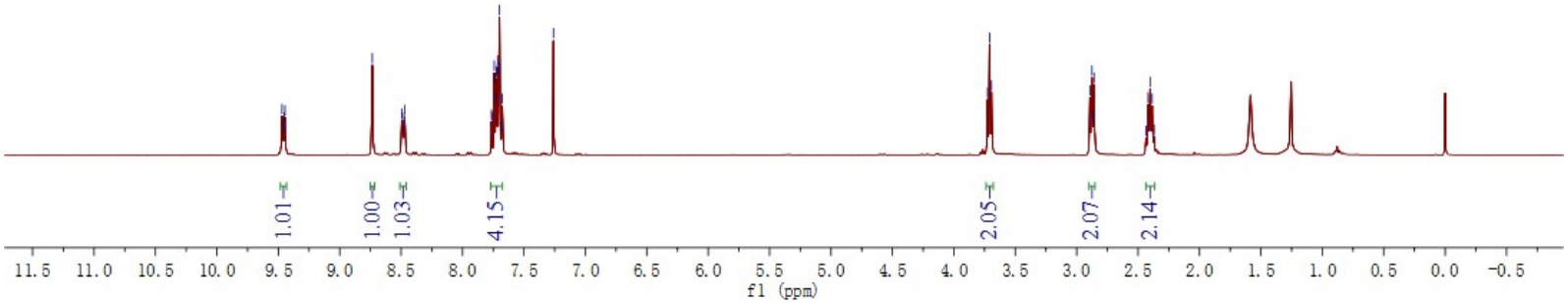
4 ^{13}C NMR (100 MHz, $CDCl_3$)

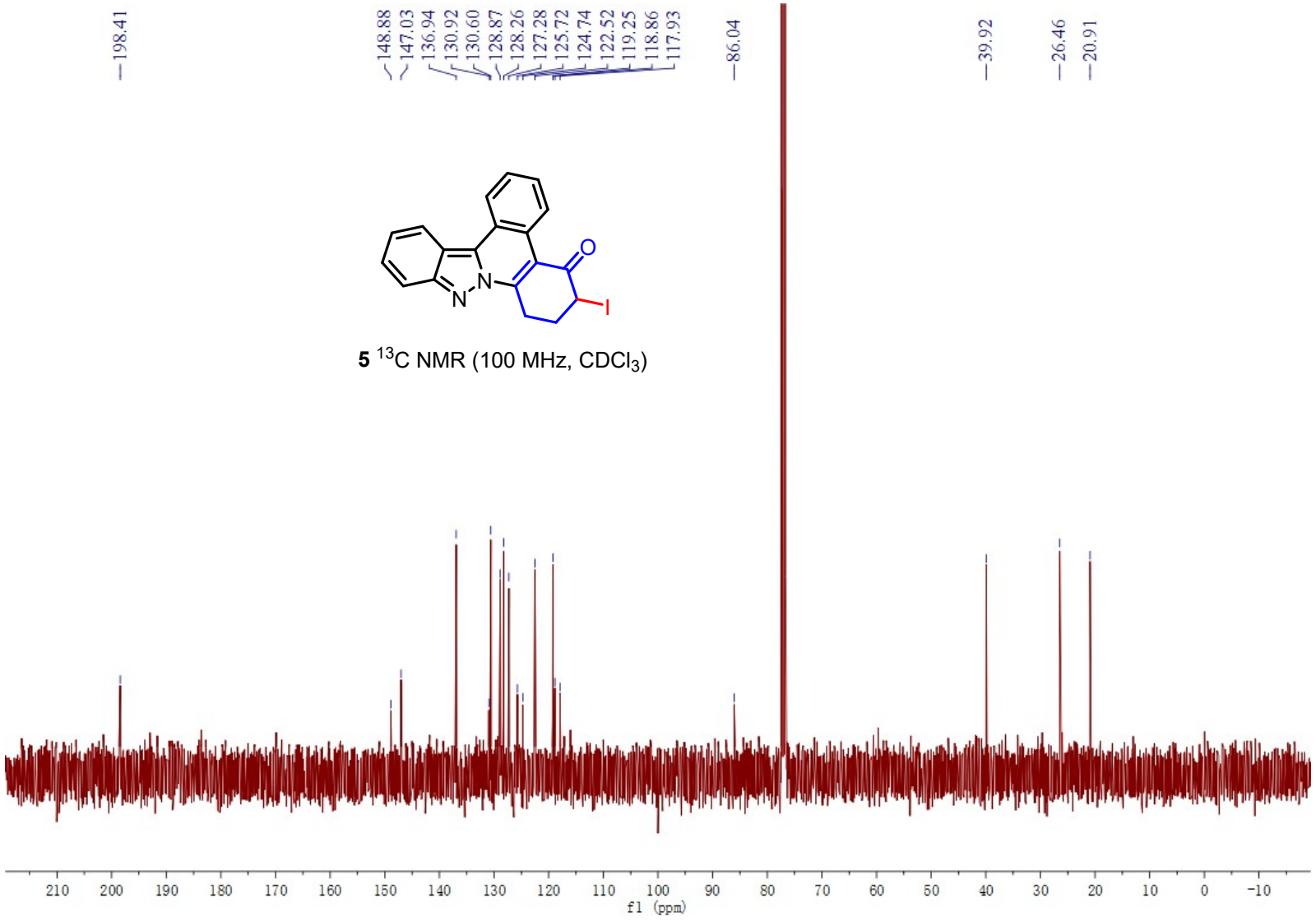






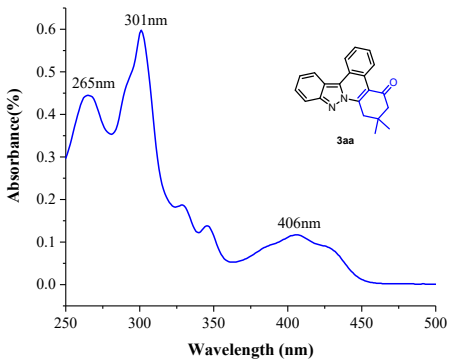
5 ^{1}H NMR (400 MHz, $CDCl_3$)

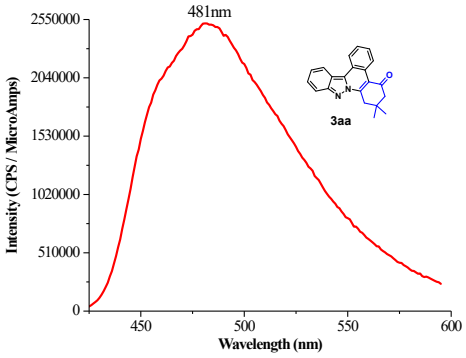


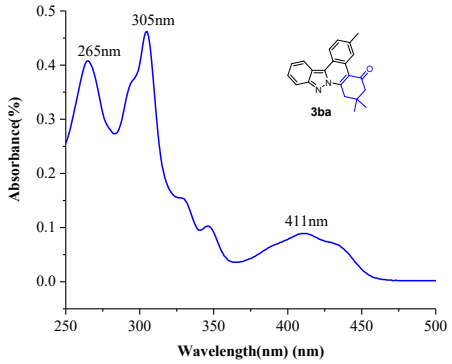


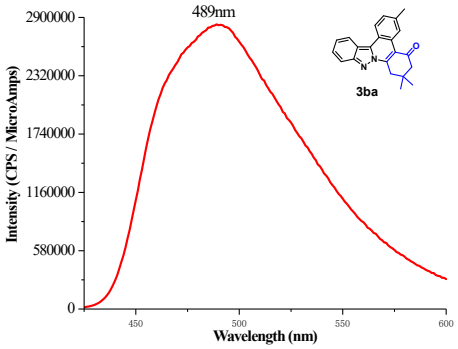
5 ^{13}C NMR (100 MHz, $CDCl_3$)

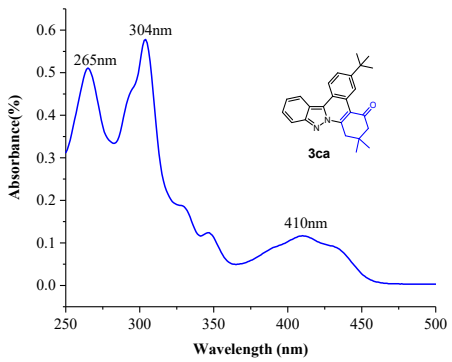
12. UV-Vis and emission spectrum

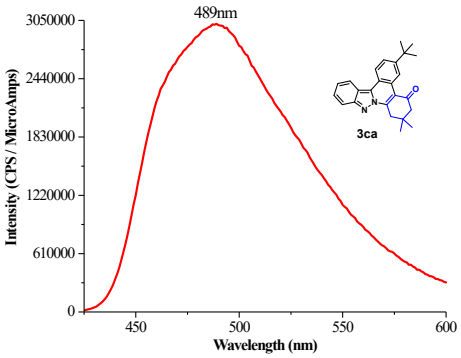


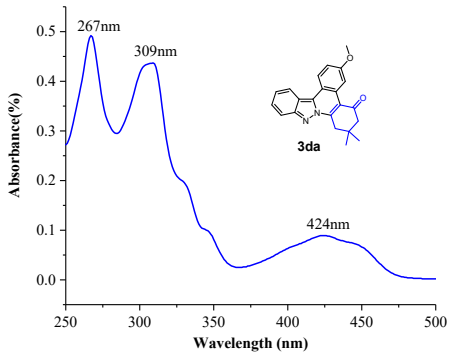


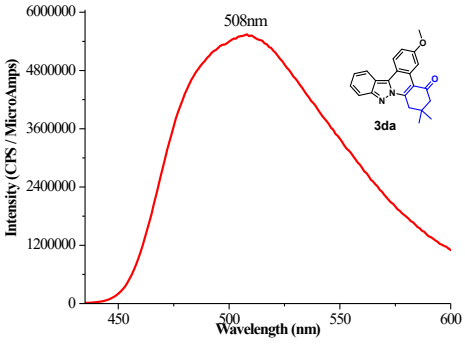


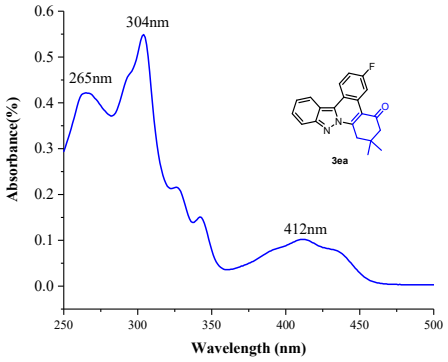


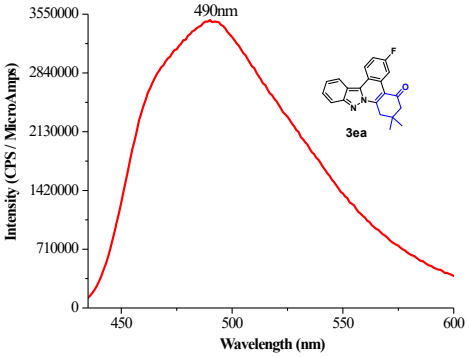


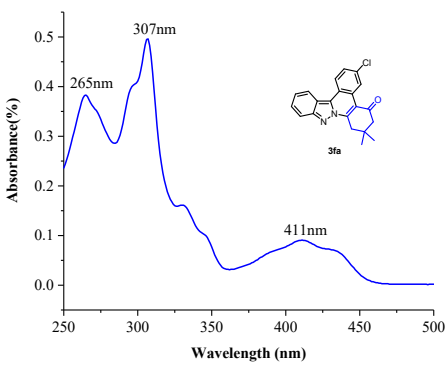


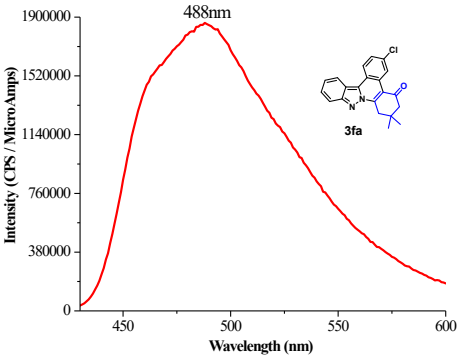


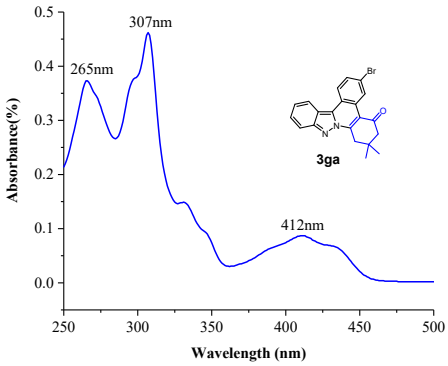


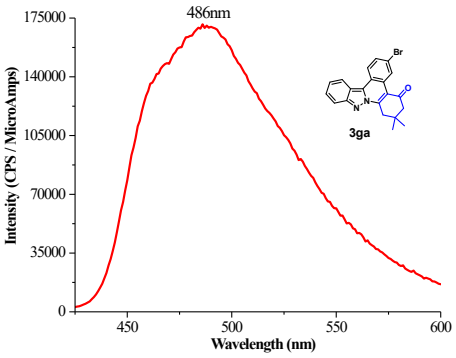

304nm
265nm
412nm
Absorbance(%)
Wavelength (nm)
3ea

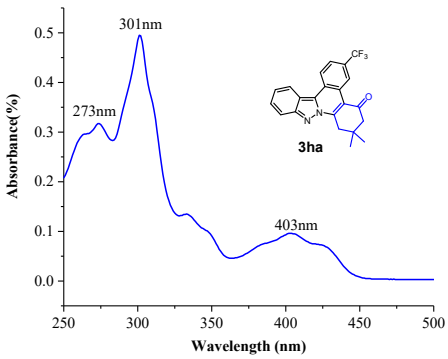

490nm
Intensity (CPS / MicroAmps)
Wavelength (nm)
3ea

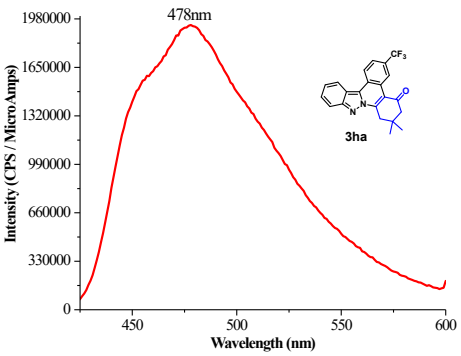

307nm
265nm
411nm
Absorbance(%)
Wavelength (nm)
3fa

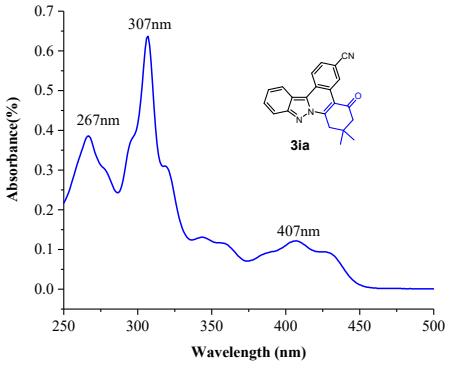

488nm
Intensity (CPS / MicroAmps)
Wavelength (nm)
3fa

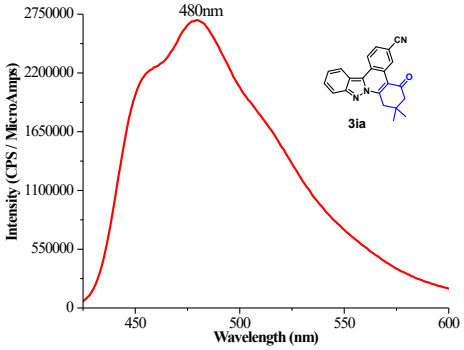

307nm
265nm
412nm
Absorbance(%)
Wavelength (nm)
3ga

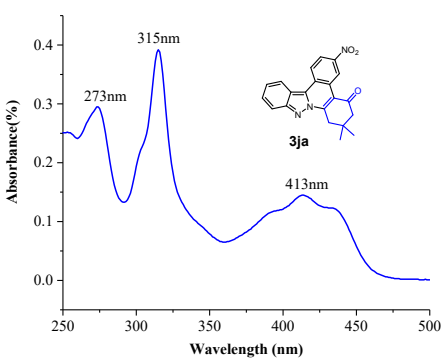

486nm
Intensity (CPS / MicroAmps)
Wavelength (nm)
3ga

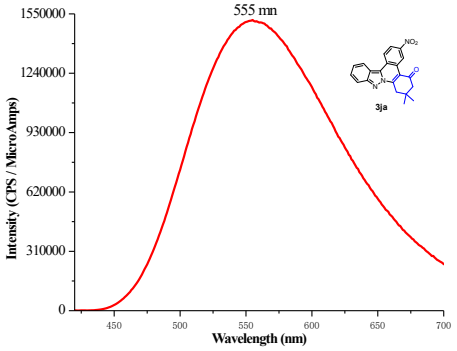

301nm
273nm
403nm
Absorbance(%)
Wavelength (nm)
3ha

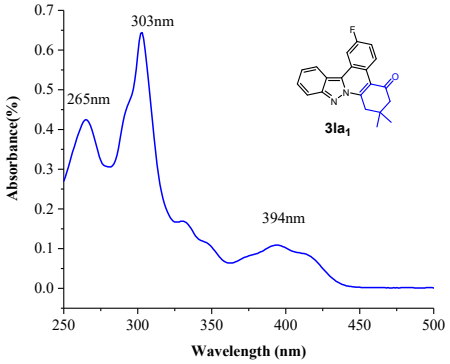

478nm
Intensity (CPS / MicroAmps)
Wavelength (nm)
3ha

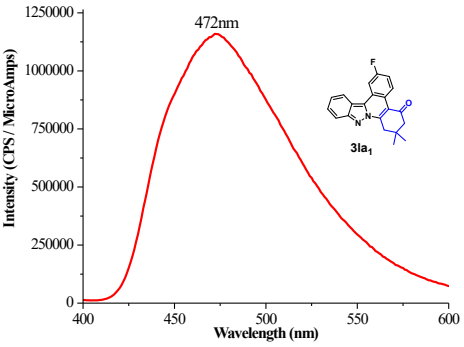

307nm
267nm
407nm
Absorbance(%)
Wavelength (nm)
3ia

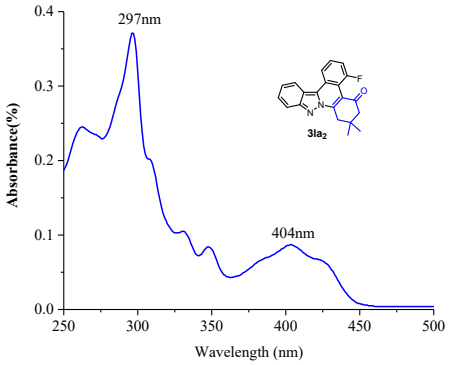

480nm
Intensity (CPS / MicroAmps)
Wavelength (nm)
3ia

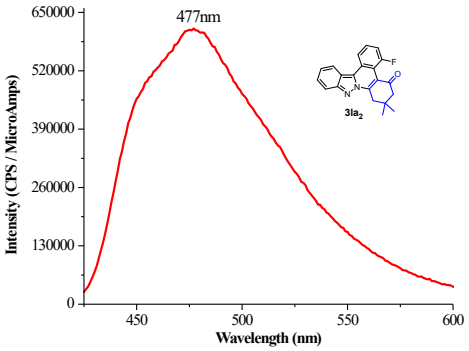

315nm
273nm
413nm
Absorbance(%)
Wavelength (nm)
3ja

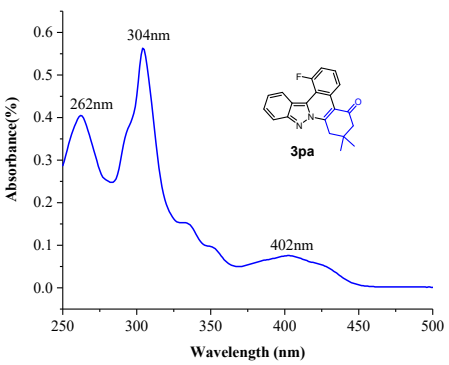

555 nm
Intensity (CPS / MicroAmps)
Wavelength (nm)
3ja

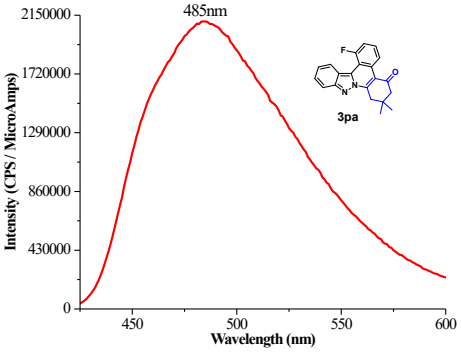

303nm
265nm
394nm
Absorbance(%)
Wavelength (nm)
3la1


472nm
Intensity (CPS / MicroAmps)
Wavelength (nm)
3la1


297nm
404nm
Absorbance(%)
Wavelength (nm)
3la2


477nm
Intensity (CPS / MicroAmps)
Wavelength (nm)
3la2


Absorbance(%)
Wavelength (nm)
262nm
304nm
402nm
3pa


Intensity (CPS / MicroAmps)
Wavelength (nm)
485nm
3pa