BEILSTEIN JOURNAL OF ORGANIC CHEMISTRY

Supporting Information

for

Rh(III)-catalyzed chelation-assisted C–H activation/annulation of 2-arylimidazolines with cyclic diazo-1,3-dicarbonyl compounds: a novel approach to tetracyclic annulated derivatives of 2,3-dihydroimidazo[2,1-*a*]isoquinoline

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Detailed experimental procedures for the preparation of compounds 2–4, analytical data for compounds 4a–q, copies of their NMR spectra, and X-ray crystallography data for compounds 4a and 4f

Table of contents

1. General information

Solvents: Unless otherwise indicated, solvents were obtained from commercial suppliers. Dichloromethane (DCM) was dried by distillation from P_2O_5 and stored over molecular sieves (4 Å).

Reagents: Unless otherwise indicated, reagents were used as purchased from commercial suppliers. $[RhCp^*Cl_2]_2$ was obtained from $RhCl_3$ and 1,2,3,4,5-pentamethylcyclopentadiene according to the previously published protocol[1].

Nuclear magnetic resonance spectroscopy: NMR spectroscopic data were recorded with a Bruker Avance III 400 MHz spectrometer (400.13 MHz for ^1H and NOESY 100.61 MHz for $^{13}C\{^1H\}$ and 376.50 MHz for $^{19}F\{^1H\}$), and with a Bruker Avance III 500 MHz spectrometer (125.73 MHz for $^{13}C\{^1H\}$) in $CDCl_3$ and DMSO-d_6 and were referenced to residual solvent proton signals (δ_H = 7.26 and 2.50 ppm, respectively) and solvent carbon signals (δ_C = 77.16 and 39.52 ppm, respectively).

Melting points: Melting points were determined with a melting point apparatus REACH Devices RD-MP in the open capillary tubes.

Mass spectrometry: HRMS were recorded using a microOTOF-Q spectrometer (Brucker); ionization by electrospray, positive detection.

X-ray crystallography: Single crystal X-ray data were obtained using an Agilent Technologies SuperNova Atlas and an Agilent Technologies Xcalibur Eos diffractometers at a temperature of 100 K.

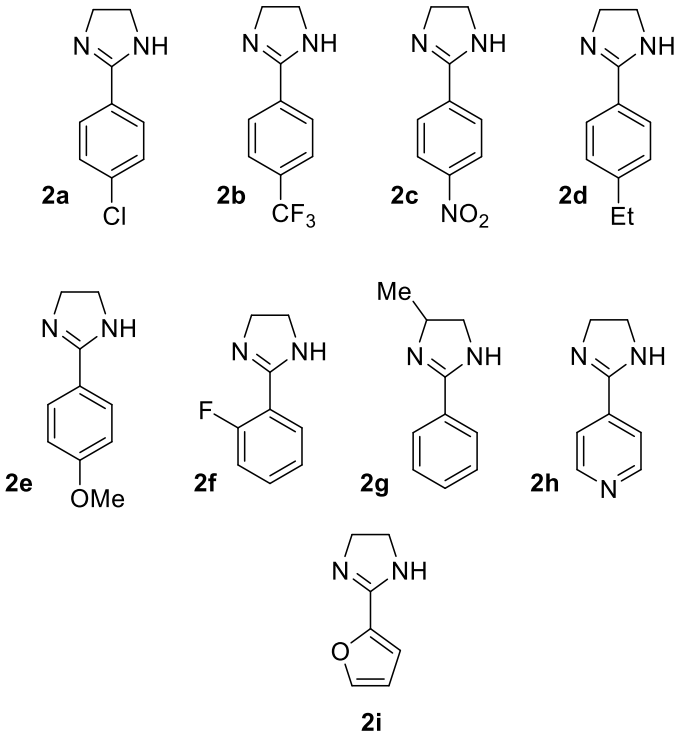
Thin layer chromatography: Thin layer chromatography (TLC) was performed on aluminum-backed pre-coated plates with silica gel 60 F_{254} with a suitable solvent system and was visualized using UV fluorescence.

Column chromatography: Column chromatography was carried out with silica gel grade 60 (0.040−0.063 mm) 230−400 mesh using Biotage Isolera Prime instrument.

Heating: An aluminum heating block was used to maintain the temperature of the reaction mixtures.

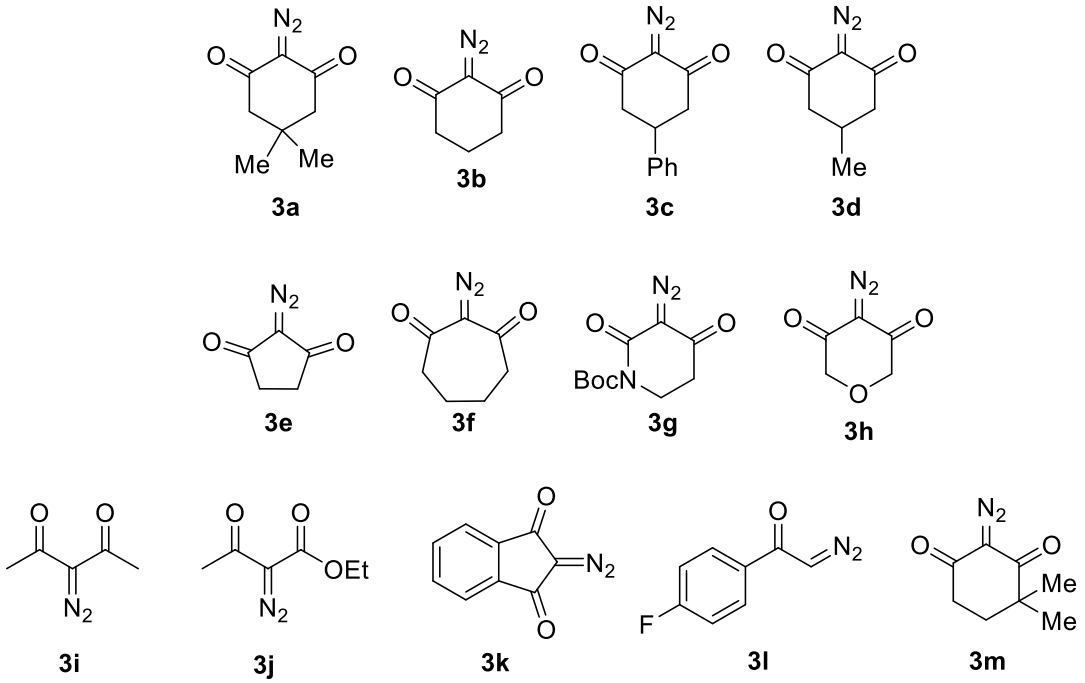
2. Experimental procedures

2.1 Preparation of the imidazolines 2a–i



Imidazolines **2a–i** were prepared according to the common protocol for condensation of equimolar amounts of diamine and arylaldehyde in dry DCM overnight at rt in the presence of NBS.[2]

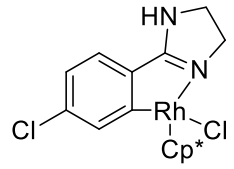
2.2 Preparation of diazo compounds 3a–m



The diazo compounds **3a**–**m** were obtained as described previously.[3]

2.3 Mechanism studies

Preparation of rhodocycle 5



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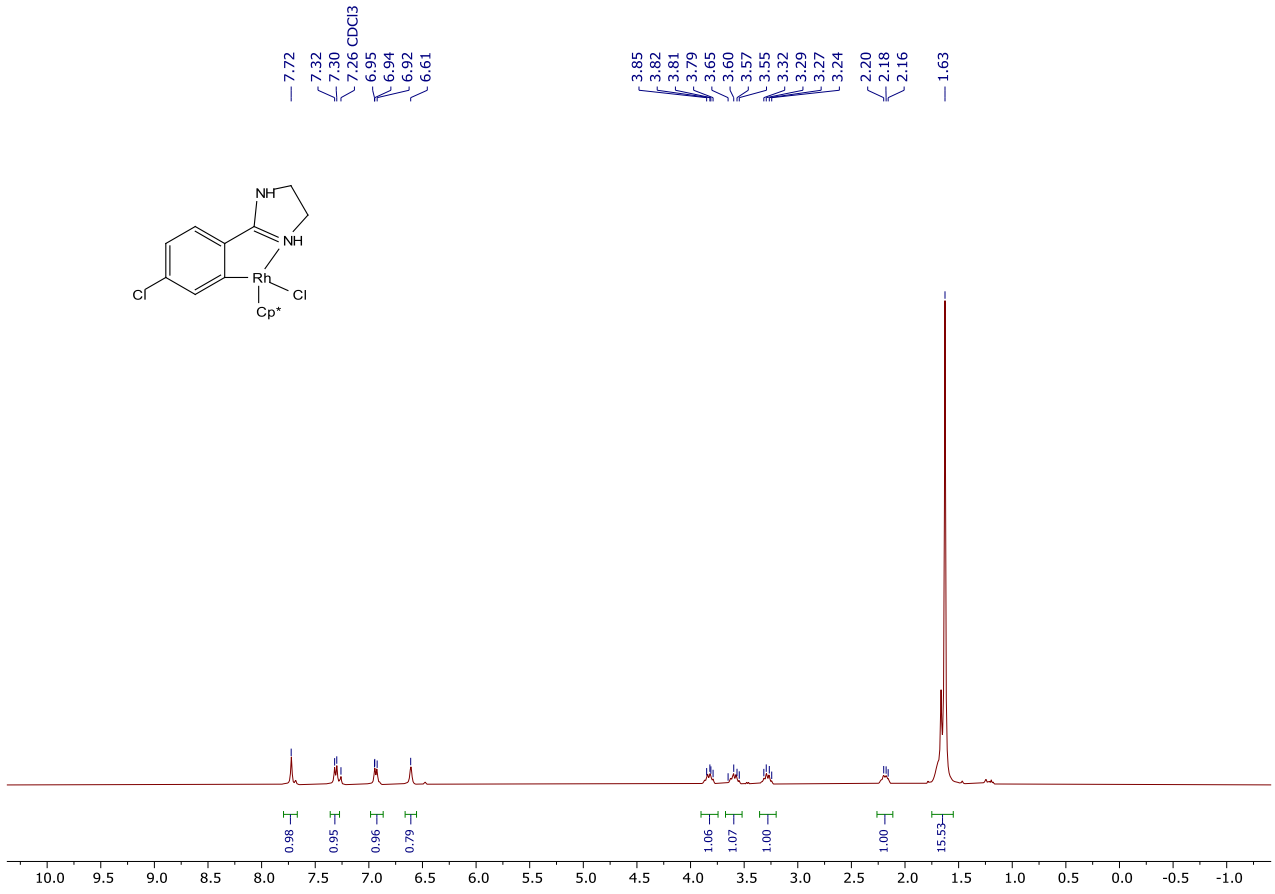
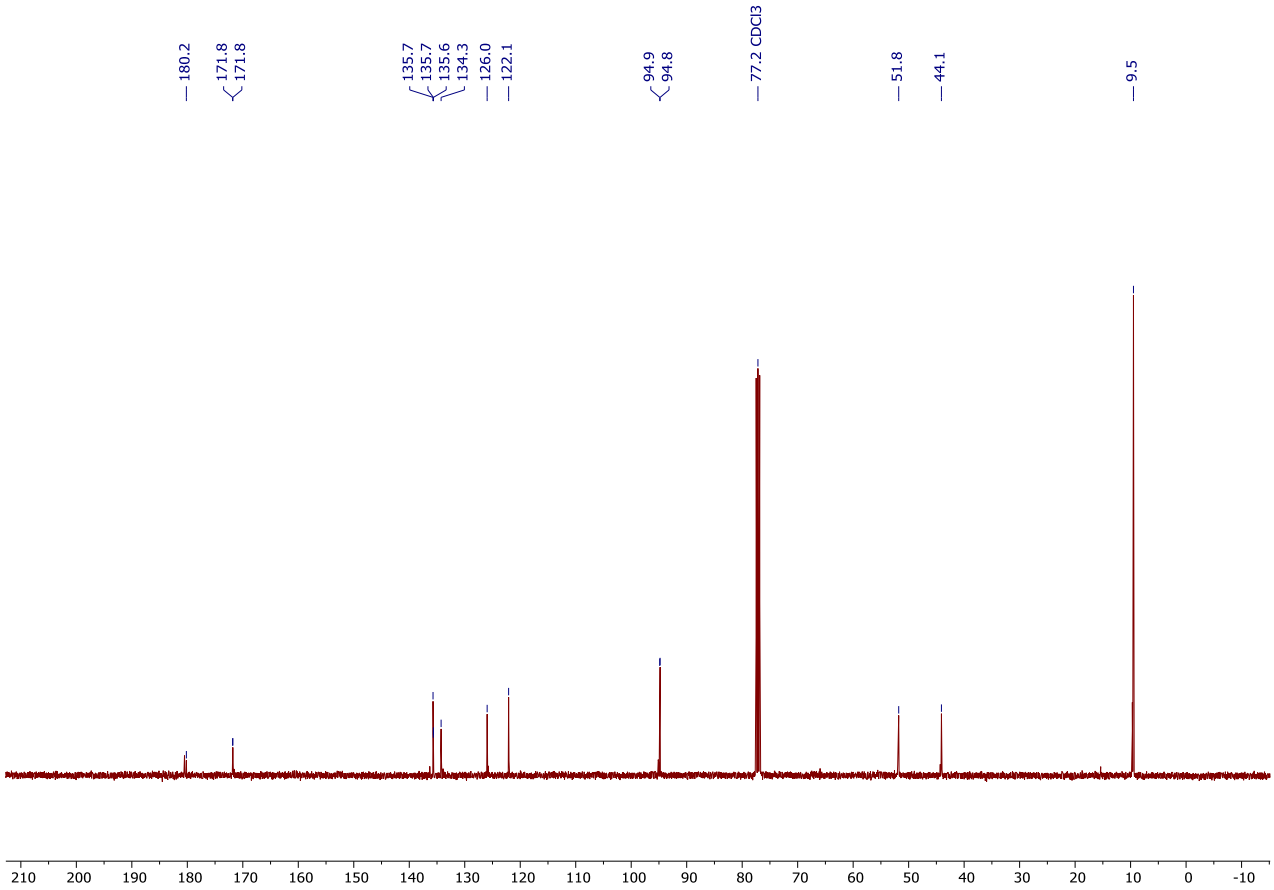
2-Arylimidazoline **2a** (0.14 mmol), $[RhCp^*Cl_2]_2$ (0.07 mmol), NaOAc (6.0 equiv), and DCM (2 mL) were charged into a pressure tube. The reaction mixture was stirred at room temperature for 12 h. After filtration, the solvent was removed under reduced pressure and the residue was washed with Et_2O for several times to afford the complex **5**. Yield: 22 mg, 35%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 1H), 7.34 – 7.25 (m, 1H), 6.97 – 6.90 (m, 1H), 6.61 (s, 1H), 3.89 – 3.77 (m, 1H), 3.67 – 3.52 (m, 1H), 3.34 – 3.22 (m, 1H), 2.25 – 2.12 (m, 1H), 1.63 (s, 15H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.2, 171.8 (d, J = 3.3 Hz), 135.7, 135.7 (d, J = 1.7 Hz), 134.3, 126.0, 122.1, 94.8 (d, J = 6.5 Hz), 51.8, 44.1, 9.5.

^1H and ^{13}C NMR of complex



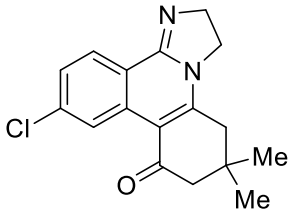


2.4 Preparation of Imidazoisoquinolines 4a–q

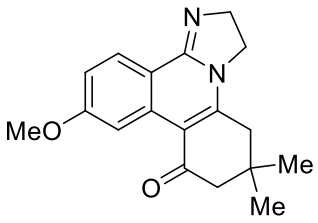
<u>General procedure A (GP1)</u>: **Preparation of imidazoisoquinoline 4a–q**

A solution of the corresponding imidazoline **2** (0.2 mmol, 1 equiv) and corresponding diazo compound **3** (0.24 mmol, 1.2 equiv) with $[RhCp^*Cl_2]_2$ (2.5 mol %, 0.005 mmol, 1.5 mg) and $AgNTf_2$ (10 mol %, 0.02 mmol, 7.8 mg) in TFE (2 mL) was placed in sealed vial (10 mL) equipped with a stirring bar. The reaction was stirred at 80 °C for 12 h. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography (absorption at λ = 254 nm).

*10-Chloro-6,6-dimethyl-2,5,6,7-tetrahydroimidazo[1,2-f]phenanthridin-8(3H)-one (**4a**).* Obtained according to GP1 from diazo compound **3a** (40 mg, 0.24 mmol, 1.2 equiv) and imidazoline **2a** (36 mg, 0.2 mmol, 1 equiv). Column chromatography was carried out on silica gel, eluent: DCM (with 1% Et_3N)/methanol, from 0 to 5% of methanol. Yield: 53 mg (88%). Pale orange solid; mp 203.8–204.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 – 9.24 (m, 1H), 8.02 – 7.96 (m, 1H), 7.28 – 7.22 (m, 1H), 4.17 – 3.98 (m, 4H), 2.53 (s, 2H), 2.38 (s, 2H), 1.12 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 155.1, 153.2, 138.8, 134.8, 127.2, 127.0, 126.0, 119.3, 106.5, 53.1, 52.2, 48.0, 42.3, 31.8, 28.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calc. for $C_{17}H_{18}ClN_2O$ 301.1102; Found 301.1105.

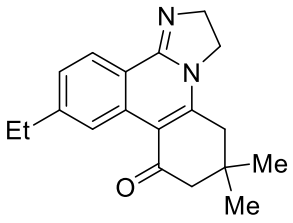


10-Methoxy-6,6-dimethyl-2,5,6,7-tetrahydroimidazo[1,2-f]phenanthridin-8(3H)-one ***(4b)***.

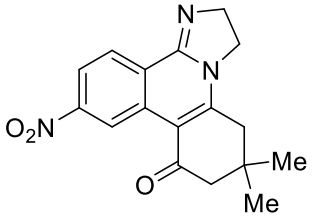


Obtained according to GP1 from diazo compound **3a** (40 mg, 0.24 mmol, 1.2 equiv) and imidazoline **2e** (35 mg, 0.2 mmol, 1 equiv). Column chromatography was carried out on silica gel, eluent: DCM (with 1% Et_3N)/methanol, from 0 to 7% of methanol. Yield: 27 mg (46 %). Yellow solid; mp 235.2–235.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 – 8.84 (m, 1H), 8.08 – 8.01 (m, 1H), 6.95 – 6.88 (m, 1H), 4.16 – 3.99 (m, 4H), 3.90 (s, 3H), 2.53 (s, 2H), 2.41 (s, 2H), 1.13 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.0, 163.0, 155.4, 152.5, 135.4, 127.4, 115.8, 113.6, 108.1, 107.4, 55.4, 52.3, 52.0, 47.9, 42.1, 31.7, 28.3. HRMS (ESI) *m/z*: $[M+H]^+$ Calc. for $C_{18}H_{21}N_2O_2$ 297.1598; Found 297.1602.

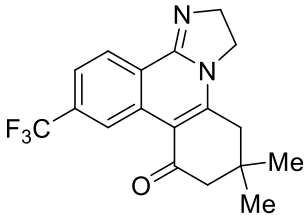
10-Ethyl-6,6-dimethyl-2,5,6,7-tetrahydroimidazo[1,2-f]phenanthridin-8(3H)-one ***(4c)***. Obtained according to GP1 from diazo compound **3a** (40 mg, 0.24 mmol, 1.2 equiv) and imidazoline **2d** (35 mg, 0.2 mmol, 1 equiv). Column chromatography was carried out on silica gel, eluent: DCM (with 1% Et_3N)/methanol, from 0 to 5% of methanol. Yield: 42 mg (71%). Beige solid; mp 215.3–215.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 – 9.05 (m, 1H), 8.04 – 7.98 (m, 1H), 7.20 – 7.13 (m, 1H), 4.12 – 3.90 (m, 4H), 2.71 (q, *J* = 7.6 Hz, 2H), 2.42 (s, 2H), 2.36 (s, 2H), 1.26 (t, *J* = 7.6 Hz, 3H), 1.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 155.6, 152.2, 149.0, 133.5, 126.7, 125.8, 125.2, 118.5, 107.2, 52.8, 52.3, 47.8, 42.1, 31.7, 29.5, 28.3, 15.4. HRMS (ESI) *m/z*: $[M+H]^+$ Calc. for $C_{19}H_{23}N_2O$ 295.1805; Found 295.1811.



6,6-Dimethyl-10-nitro-2,5,6,7-tetrahydroimidazo[1,2-f]phenanthridin-8(3H)-one ***(4d)***. Obtained according to GP1 from diazo compound **3a** (40 mg, 0.25 mmol, 1 equiv) and imidazoline **2c** (38 mg, 0.2 mmol, 1 equiv). Column chromatography was carried out on silica gel, eluent: DCM (with 1% Et_3N)/methanol, from 0 to 7% of methanol. Yield: 53 mg (86%). Orange solid; 216.4–216.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 – 9.28 (m, 1H), 8.25 – 8.19 (m, 1H), 7.71 – 7.64 (m, 1H), 4.50 (t, *J* = 9.8 Hz, 2H), 4.12 (t, *J* = 9.8 Hz, 2H), 2.90 (s, 2H), 2.46 (s, 2H), 1.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3, 155.2, 153.5, 139.7, 135.1, 127.9, 127.7, 124.9, 115.2, 108.3, 51.7, 48.3, 47.1, 40.1, 31.6, 27.6. HRMS (ESI) *m/z*: $[M+H]^+$ Calc. for $C_{17}H_{18}N_3O_3$ 312.1343; Found 312.1348.

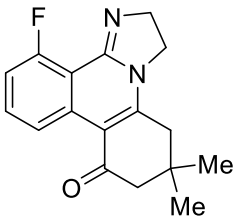


*6,6-Dimethyl-10-(trifluoromethyl)-2,5,6,7-tetrahydroimidazo[1,2-f]phenanthridin-8(3H)-one (**4e**).*



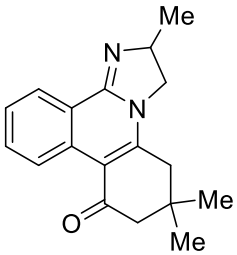
Obtained according to GP1 from diazo compound **3a** (40 mg, 0.24 mmol, 1.2 equiv) and imidazoline **2b** (43 mg, 0.2 mmol, 1 equiv). Column chromatography was carried out on silica gel, eluent: DCM (with 1% Et_3N)/methanol, from 0 to 5% of methanol. Yield: 53 mg (80%). White solid; mp 245.8–246.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 – 9.59 (m, 1H), 8.26 – 8.19 (m, 1H), 7.58 – 7.51 (m, 1H), 4.26 – 4.09 (m, 4H), 2.64 (s, 2H), 2.46 (s, 2H), 1.17 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 155.1, 153.2, 133.9 (q, *J* = 32.1 Hz), 133.9, 126.5, 124.1 (q, *J* = 273.0 Hz), 123.8 (q, *J* = 4.2 Hz), 123.3 – 123.3 (m), 122.9 (q, *J* = 3.5 Hz), 106.9, 53.1, 52.3, 48.1, 42.4, 31.9, 28.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.02. HRMS (ESI) *m/z*: $[M+H]^+$ Calc. for $C_{17}H_{18}ClN_2O$ 301.1102; Found 301.1107.

*12-Fluoro-6,6-dimethyl-2,5,6,7-tetrahydroimidazo[1,2-f]phenanthridin-8(3H)-one (**4f**).* Obtained



according to GP1 from diazo compound **3a** (40 mg, 0.24 mmol, 1.2 equiv) and imidazoline **2f** (33 mg, 0.2 mmol, 1 equiv). Column chromatography was carried out on silica gel, eluent: DCM (with 1% Et_3N)/methanol, from 0 to 5% of methanol. Yield: 57 mg (99%). White solid; 215.3–217.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 – 9.01 (m, 1H), 7.51 – 7.41 (m, 1H), 7.07 – 6.97 (m, 1H), 4.26 – 4.15 (m, 2H), 4.01 – 3.92 (m, 2H), 2.55 (s, 2H), 2.40 (s, 2H), 1.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 160.9 (d, *J* = 259.4 Hz), 153.1, 152.2 (d, *J* = 8.4 Hz), 135. 9 (d, *J* = 1.0 Hz), 133.0 (d, *J* = 9.6 Hz), 121.8 (d, *J* = 4.3 Hz), 113.6 (d, *J* = 21.0 Hz), 110.3 (d, *J* = 9.0 Hz), 106.8 (d, *J* = 1.8 Hz), 53.8, 52.3, 46.7, 42.5, 31.6, 28.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.38. HRMS (ESI) *m/z*: $[M+H]^+$ Calc. for $C_{17}H_{18}FN_2O$ 285.1398; Found 285.1403.

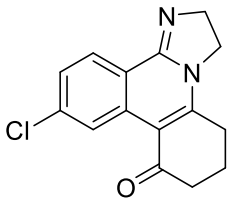
*2,6,6-Trimethyl-2,5,6,7-tetrahydroimidazo[1,2-f]phenanthridin-8(3H)-one (**4g**).* Obtained



according to GP1 from diazo compound **3a** (40 mg, 0.24 mmol, 1.2 equiv) and imidazoline **2g** (32 mg, 0.2 mmol, 1 equiv). Column chromatography was carried out on silica gel, eluent: DCM (with 1% Et_3N)/methanol, from 0 to 10% of methanol. Yield: 43 mg (77%). Beige solid. Mixture of regioisomers in ratio 87:13. *Major regioisomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 – 9.16 (m, 1H), 8.15 – 8.08 (m, 1H), 7.58 – 7.49 (m, 1H), 7.36 – 7.24 (m, 1H), 4.52 – 4.35 (m, 1H), 4.15 (t, *J* = 10.3 Hz, 1H), 3.58 (dd, *J* = 10.5, 7.5 Hz, 1H), 2.52 (s, 2H), 2.39 (s, 2H), 1.40 (d, *J* = 6.6 Hz, 3H), 1.11 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 154.5, 152.1, 133.5, 132.3, 126.6, 126.3, 125.9, 120.7, 107.5, 59.9, 54.8, 52.4, 42.2, 31.8, 28.5, 22.9. *Minor regioisomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 – 9.16 (m, 1H), 8.15 – 8.08 (m, 1H), 7.58 – 7.49 (m, 1H), 7.36 – 7.24 (m, 1H), 4.52 – 4.35 (m, 1H), 4.23 – 4.18 (m, 1H), 3.72 (dd, *J* = 14.8, 2.8 Hz, 1H), 2.43 (s, 2H), 2.41 (s, 2H), 1.36 (d, *J* = 6.3

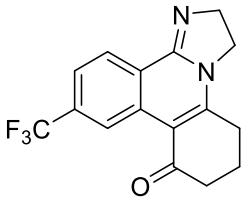
Hz, 3H), 1.14 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 154.8, 151.9, 133.3, 132.3, 126.7, 126.4, 125.7, 121.4, 108.0, 60.9, 55.7, 52.7, 41.3, 32.2, 28.1, 21.8. HRMS (ESI) *m/z*: $[M+H]^+$ Calc. for $C_{18}H_{21}N_2O$ 281.1648; Found 281.1651.

10-Chloro-2,5,6,7-tetrahydroimidazo[1,2-f]phenanthridin-8(3H)-one ***(4h)****.* Obtained according to



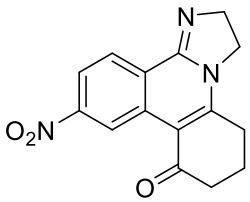
GP1 from diazo compound **3b** (33 mg, 0.24 mmol, 1.2 equiv) and imidazoline **2a** (36 mg, 0.2 mmol, 1 equiv). Column chromatography was carried out on silica gel, eluent: DCM (with 1% Et_3N)/methanol, from 0 to 5% of methanol. Yield: 48 mg (89%). Pale orange solid; mp 176.0–176.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 – 9.18 (m, 1H), 7.96 – 7.90 (m, 2H), 7.30 – 7.19 (m, 2H), 4.13 – 3.94 (m, 6H), 2.65 (t, *J* = 6.3 Hz, 4H), 2.49 (t, *J* = 6.6 Hz, 3H), 2.05 (p, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.6, 154.7, 154.7, 138.5, 134.9, 127.2, 126.8, 126.1, 119.3, 107.4, 53.0, 47.8, 38.5, 28.6, 20.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calc. for $C_{15}H_{14}ClN_2O$ 273.0789; Found 273.0793.

10-(Trifluoromethyl)-2,5,6,7-tetrahydroimidazo[1,2-f]phenanthridin-8(3H)-one ***(4i)****.* Obtained



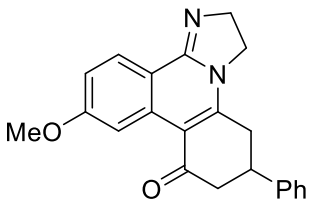
according to GP1 from diazo compound **3b** (33 mg, 0.24 mmol, 1.2 equiv) and imidazoline **2b** (43 mg, 0.2 mmol, 1 equiv). Column chromatography was carried out on silica gel, eluent: DCM (with 1% Et_3N)/methanol, from 0 to 10% of methanol. Yield: 45 mg (74%). White solid; mp 232.4–233.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 – 9.56 (m, 1H), 8.24 – 8.18 (m, 1H), 7.59 – 7.52 (m, 1H), 4.25 – 4.07 (m, 4H), 2.78 (t, *J* = 6.3 Hz, 2H), 2.58 (t, *J* = 6.4 Hz, 2H), 2.13 (p, *J* = 6.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 154.9, 154.7, 134.0, 133.8 (q, *J* = 32.1 Hz), 126.5, 124.1 (q, *J* = 273.1 Hz), 124.1 (q, *J* = 4.1 Hz), 123.6 – 123.5 (m), 122.9 (q, *J* = 3.6 Hz), 107.9, 53.2, 48.0, 38.6, 28.7, 20.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.00. HRMS (ESI) *m/z*: $[M+H]^+$ Calc. for $C_{16}H_{14}F_3N_2O$ 307.1053; Found 307.1058.

10-Nitro-2,5,6,7-tetrahydroimidazo[1,2-f]phenanthridin-8(3H)-one ***(4j)****.* Obtained according to



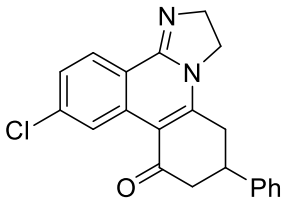
GP1 from diazo compound **3b** (33 mg, 0.24 mmol, 1.2 equiv) and imidazoline **2c** (38 mg, 0.2 mmol, 1 equiv). Column chromatography was carried out on silica gel, eluent: DCM (with 1% Et_3N)/methanol, from 0 to 7% of methanol. Yield: 43 mg (77%). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 – 10.04 (m, 1H), 8.21 – 8.14 (m, 1H), 8.09 – 8.02 (m, 1H), 4.25 – 4.08 (m, 4H), 2.80 (t, *J* = 6.1 Hz, 2H), 2.59 (t, *J* = 6.5 Hz, 2H), 2.15 (p, *J* = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 155.4, 154.3, 150.2, 134.6, 127.0, 125.4, 123.8, 122.1, 120.6, 107.5, 53.5, 48.0, 38.5, 28.7, 20.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calc. for $C_{15}H_{14}N_3O_3$ 284.1030; Found 284.1034.

10-Methoxy-6-phenyl-2,5,6,7-tetrahydroimidazo[1,2-f]phenanthridin-8(3H)-one ***(4k)***. Obtained



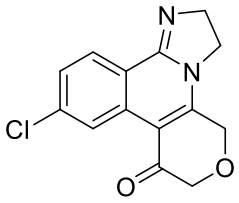
according to GP1 from diazo compound **3c** (52 mg, 0.24 mmol, 1.2 equiv) and imidazoline **2e** (38 mg, 0.2 mmol, 1 equiv). Column chromatography was carried out on silica gel, eluent: DCM (with 1% Et_3N)/methanol, from 0 to 3% of methanol. Yield: 64 mg (93%). Beige solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.91 – 8.85 (m, 1H), 8.09 – 8.03 (m, 1H), 7.44 – 7.36 (m, 2H), 7.34 – 7.28 (m, 3H), 6.98 – 6.91 (m, 1H), 4.18 – 4.06 (m, 3H), 4.04 – 3.98 (m, 1H), 3.92 (s, 3H), 3.54 – 3.41 (m, 1H), 3.01 – 2.91 (m, 2H), 2.86 – 2.79 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 162.8, 154.9, 153.8, 142.4, 135.4, 129.0, 127.5, 127.4, 115.5, 114.1, 108.5, 107.5, 55.4, 52.7, 47.8, 45.4, 38.5, 36.1. HRMS (ESI) *m/z*: $[M+H]^+$ Calc. for $C_{22}H_{21}N_2O_2$ 345.1598; Found 345.1602.

10-Chloro-6-phenyl-2,5,6,7-tetrahydroimidazo[1,2-f]phenanthridin-8(3H)-one ***(4l)***. Obtained



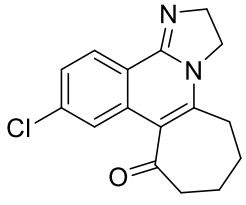
according to GP1 from diazo compound **3c** (52 mg, 0.24 mmol, 1.2 equiv) and imidazoline **2a** (36 mg, 0.2 mmol, 1 equiv). Column chromatography was carried out on silica gel, eluent: DCM (with 1% Et_3N)/methanol, from 0 to 3% of methanol. Yield: 63 mg (91%). White solid; mp 234.4–234.7 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.33 – 9.28 (m, 1H), 8.07 – 8.00 (m, 1H), 7.44 – 7.36 (m, 1H), 7.31 – 7.24 (m, 1H), 4.30 – 3.93 (m, 2H), 3.52 – 3.39 (m, 1H), 3.01 – 2.84 (m, 1H), 2.83 – 2.73 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 154.8, 153.9, 142.2, 138.9, 134.8, 129.2, 127.6, 127.3, 127.2, 126.2, 119.4, 107.2, 53.1, 48.0, 45.4, 38.6, 36.4. HRMS (ESI) *m/z*: $[M+H]^+$ Calc. for $C_{21}H_{18}ClN_2O$ 349.1102; Found 349.1107.

10-Chloro-2,5-dihydro-3H-imidazo[2,1-a]pyrano[3,4-c]isoquinolin-8(7H)-one ***(4m)***. Obtained



according to GP1 from diazo compound **3h** (34 mg, 0.24 mmol, 1.2 equiv) and imidazoline **2a** (36 mg, 0.2 mmol, 1 equiv). Column chromatography was carried out on silica gel, eluent: DCM (with 1% Et_3N)/methanol, from 0 to 13% of methanol. Yield: 32 mg (64%). Yellow solid; mp 180.4–181.7 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.05 – 9.00 (m, 1H), 7.98 – 7.92 (m, 1H), 7.32 – 7.25 (m, 1H), 4.58 (s, 1H), 4.21 – 4.12 (m, 2H), 3.93 (t, *J* = 9.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.3, 154.1, 151.8, 138.9, 133.3, 127.5, 127.3, 125.8, 119.3, 72.2, 64.4, 53.7, 46.4. HRMS (ESI) *m/z*: $[M+H]^+$ Calc. for $C_{14}H_{12}ClN_2O_2$ 275.0582; Found 275.0585.

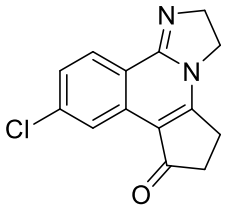
11-Chloro-2,3,5,6,7,8-hexahydro-9H-cyclohepta[c]imidazo[2,1-a]isoquinolin-9-one ***(4n)***.



Obtained according to GP1 from diazo compound **3f** (37 mg, 0.24 mmol, 1.2 equiv) and imidazoline **2a** (36 mg, 0.2 mmol, 1 equiv). Column chromatography was carried out on silica gel, eluent: DCM (with 1% Et_3N)/methanol, from 0 to 10% of methanol. Yield: 34 mg (60%). Pale yellow

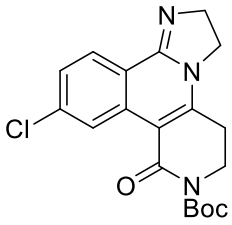
solid; mp 168.3–168.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.15 (m, 1H), 7.99 – 7.92 (m, 1H), 7.25 – 7.16 (m, 1H), 4.14 – 3.99 (m, 3H), 2.73 (t, *J* = 6.5 Hz, 1H), 2.59 (t, *J* = 6.1 Hz, 1H), 1.88 – 1.76 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.4, 155.6, 148.2, 138.9, 135.1, 127.6, 126.9, 124.2, 118.5, 112.6, 51.4, 48.3, 42.0, 29.2, 22.2, 20.6. HRMS (ESI) *m/z*: $[M+H]^+$ Calc. for $C_{16}H_{16}ClN_2O$ 273.0789; Found 273.0792.

9-Chloro-2,3,5,6-tetrahydro-7H-cyclopenta[c]imidazo[2,1-a]isoquinolin-7-one ***(4o)***. Obtained

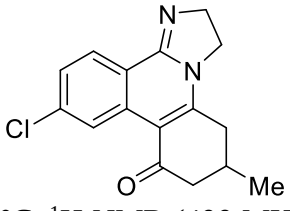


according to GP1 from diazo compound **3e** (30 mg, 0.24 mmol, 1.2 equiv) and imidazoline **2a** (36 mg, 0.2 mmol, 1 equiv). Column chromatography was carried out on silica gel, eluent: DCM (with 1% Et_3N)/methanol, from 0 to 15% of methanol. Yield: 45 mg (87%). White solid; mp 243.9–244.6 °C. ^{1}H NMR (400 MHz, DMSO-d_6+$CDCl_3$ in ratio 1:6) δ 8.46 – 8.41 (m, 1H), 7.51 – 7.47 (m, 1H), 7.24 – 7.17 (m, 1H), 4.19 – 4.09 (m, 2H), 4.06 – 3.96 (m, 2H), 2.81 – 2.74 (m, 2H), 2.58 – 2.51 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6+$CDCl_3$ in ratio 1:6) δ 197.8, 165.5, 154.8, 137.8, 132.1, 127.1, 126.5, 122.0, 118.5, 109.8, 53.6, 45.1, 34.1, 23.7. HRMS (ESI) *m/z*: $[M+H]^+$ Calc. for $C_{14}H_{12}ClN_2O$ 259.0633; Found 259.0638.

tert-Butyl 10-hloro-8-oxo-2,3,5,8-tetrahydrobenzo[c]imidazo[1,2-a][1,6]naphthyridine-7(6H)-carboxylate ***(4p)***. Obtained according to GP1 from diazo compound **3g** (57 mg, 0.24 mmol, 1.2 equiv) and imidazoline **2a** (36 mg, 0.2 mmol, 1 equiv). Column chromatography was carried out on silica gel, eluent: DCM (with 1% Et_3N)/methanol, from 0 to 15% of methanol. Yield: 54 mg (72%). Beige solid; mp 137.6–138.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 – 8.91 (m, 1H), 7.94 – 7.88 (m, 1H), 7.28 – 7.20 (m, 1H), 4.14 – 3.97 (m, 4H), 3.91 (t, *J* = 6.3 Hz, 2H), 2.77 (t, *J* = 6.3 Hz, 2H), 1.56 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.94, 154.7, 152.7, 149.6, 138.7, 134.9, 127.3, 127.0, 126.2, 119.7, 101.6, 83.1, 53.1, 47.5, 41.2, 28.3, 27.4. HRMS (ESI) *m/z*: $[M+H]^+$ Calc. for $C_{14}H_{13}ClN_3O$ 374.1266; Found 374.1271.



10-Chloro-6-methyl-2,5,6,7-tetrahydroimidazo[1,2-f]phenanthridin-8(3H)-one ***(4q)***. Obtained

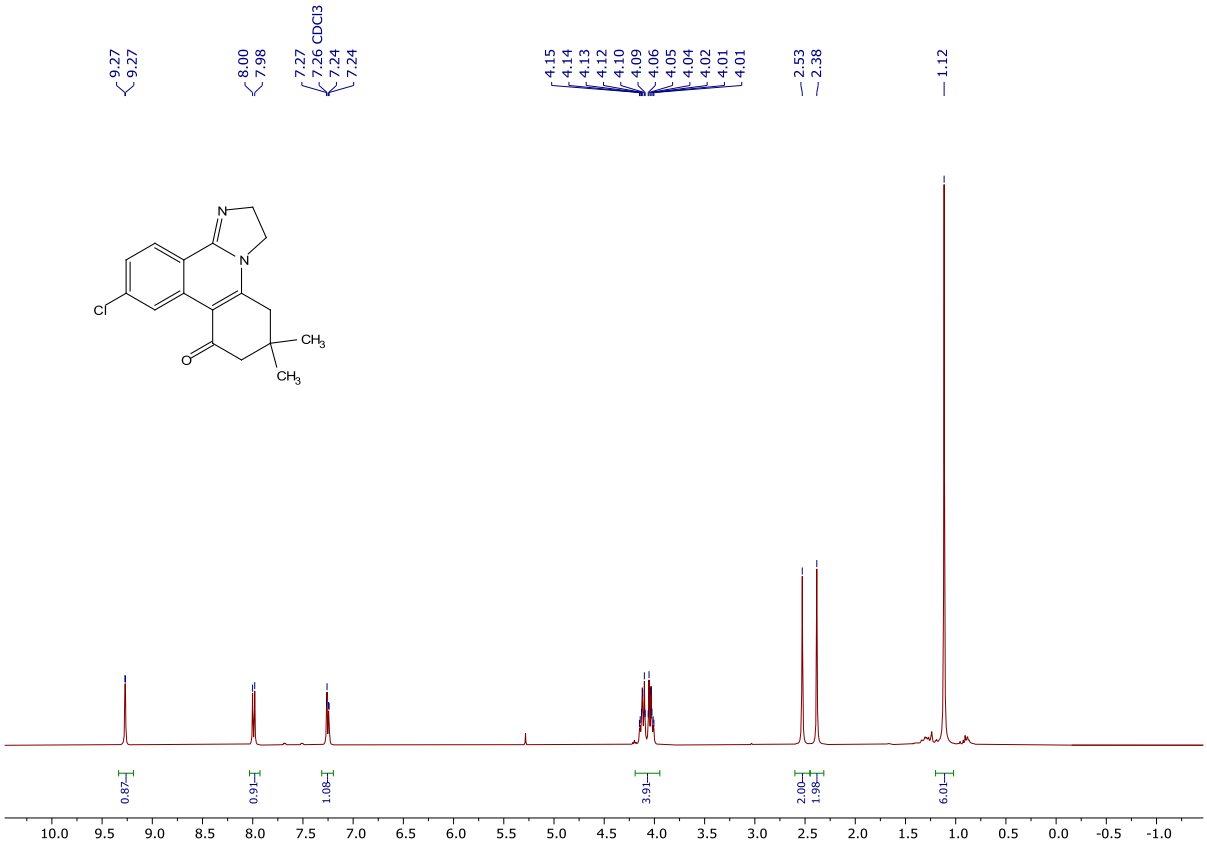


according to GP1 from diazo compound **3d** (37 mg, 0.24 mmol, 1.2 equiv) and imidazoline **2a** (36 mg, 0.2 mmol, 1 equiv). Column chromatography was carried out on silica gel, eluent: DCM (with 1% Et_3N)/methanol, from 0 to 7% of methanol. Yield: 35 mg (61%). White solid; mp 168.0–168.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 – 9.21 (m, 1H), 8.02 – 7.92 (m, 1H), 7.28 – 7.20 (m, 1H),

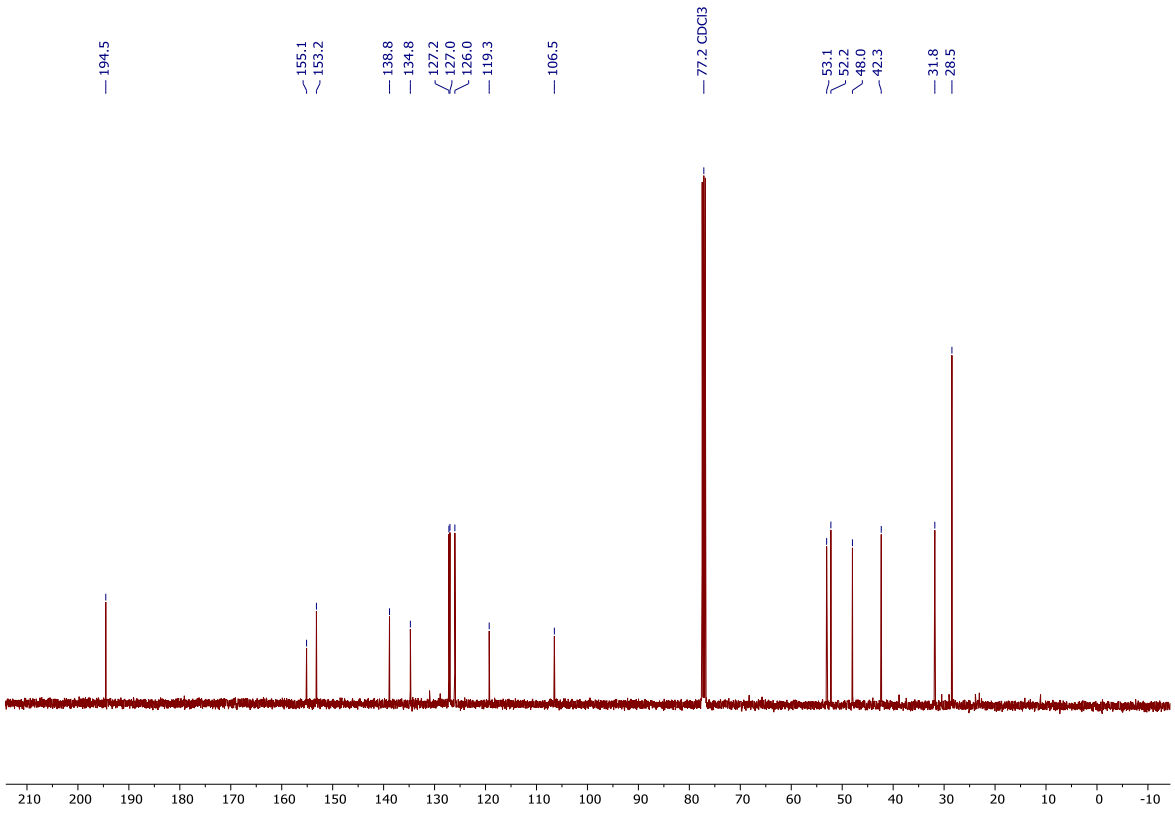
4.16 – 3.91 (m, 3H), 2.73 – 2.60 (m, 1H), 2.59 – 2.51 (m, 1H), 2.38 – 2.14 (m, 1H), 1.12 (d, *J* = 6.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.6, 154.9, 154.2, 138.75, 134.9, 127.2, 126.9, 126.1, 119.3, 107.1, 53.0, 47.9, 46.75, 36.6, 27.9, 21.1. HRMS (ESI) *m/z*: $[M+H]^+$ Calc. for $C_{16}H_{16}ClN_2O$ 273.0789; Found 273.0793.

2. Copies of NMR spectra

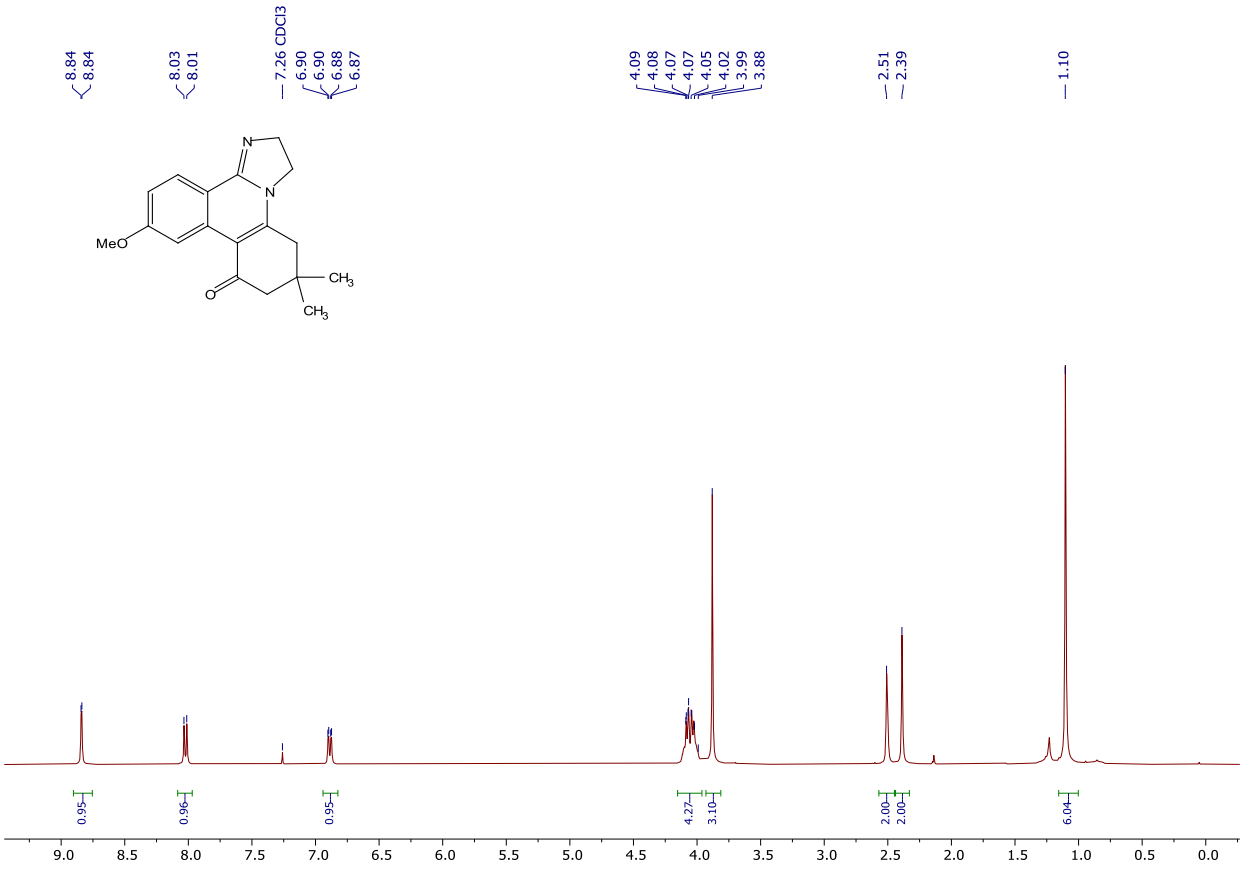
Copy of ^{1}H (400.13 MHz, $CDCl_3$) NMR spectrum of **4a**



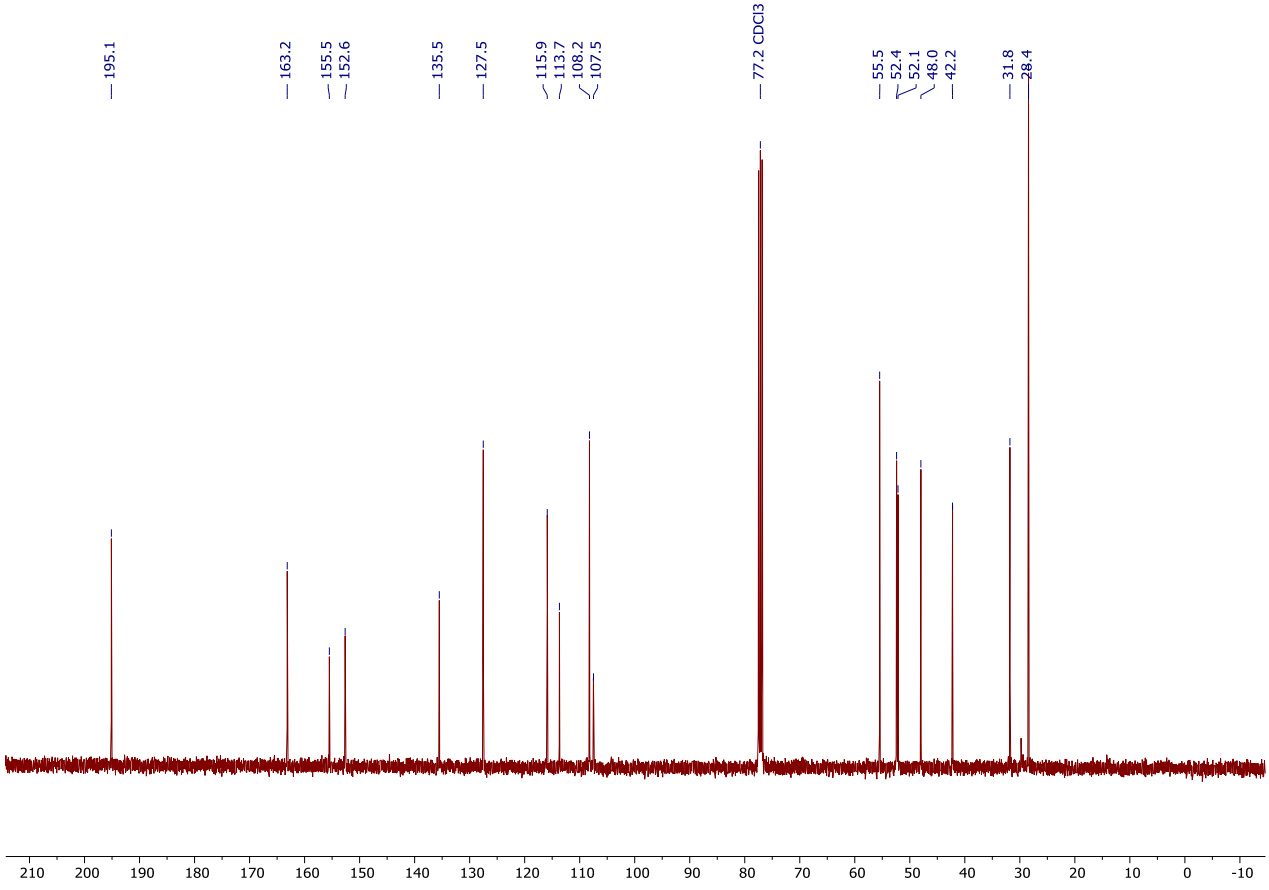
Copy of $^{13}C\{^{1}H\}$ (100.61 MHz, $CDCl_3$) NMR spectrum of **4a**



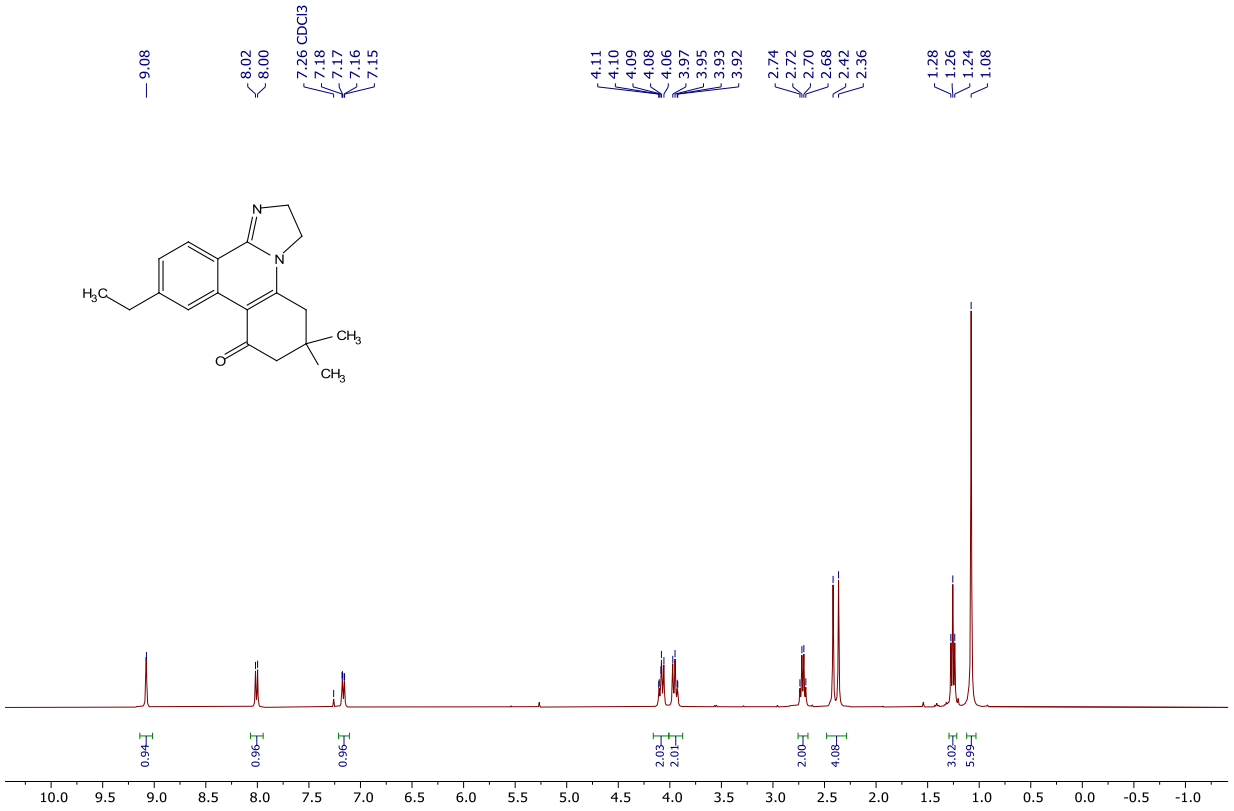
Copy of ^{1}H (400.13 MHz, $CDCl_3$) NMR spectrum of **4b**



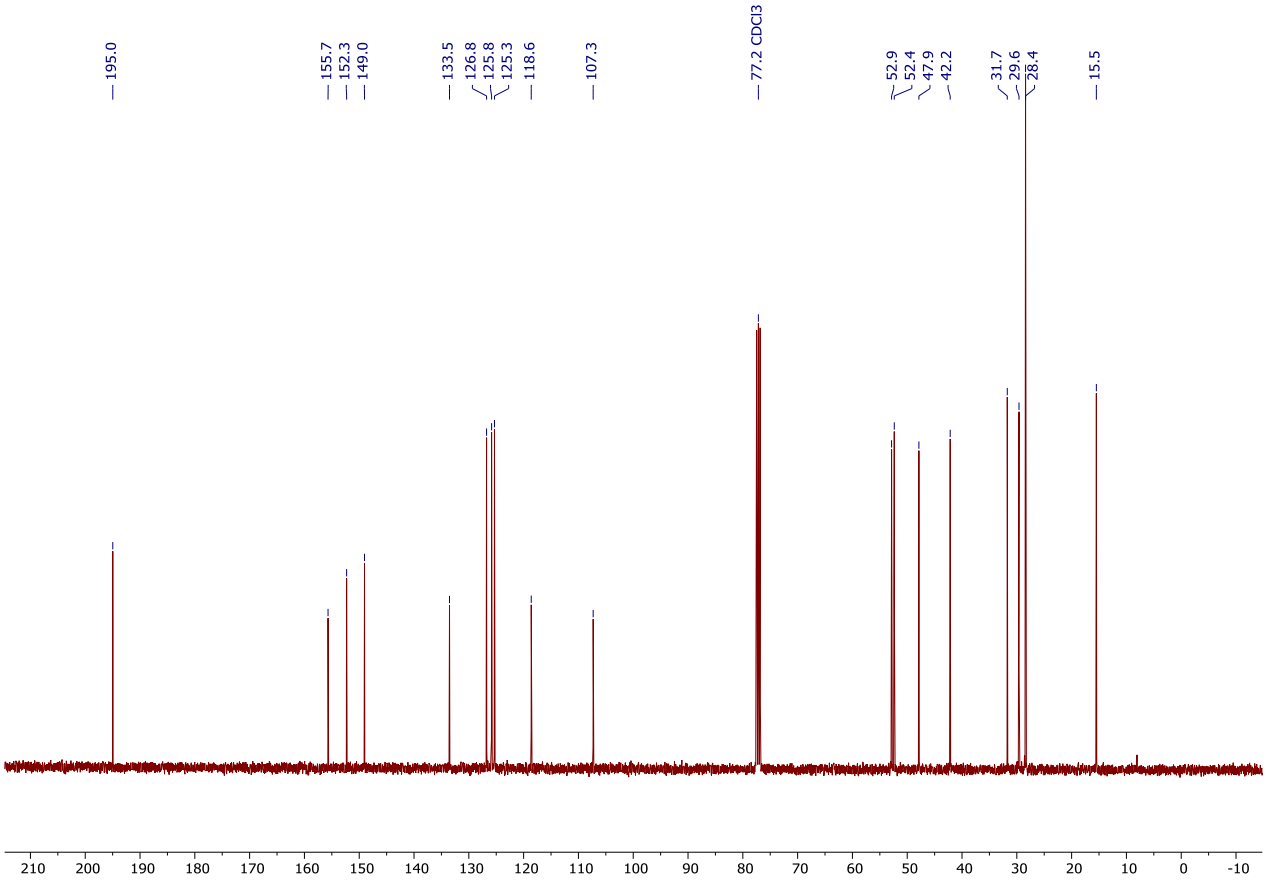
Copy of $^{13}C\{^{1}H\}$ (100.61 MHz, $CDCl_3$) NMR spectrum of **4b**



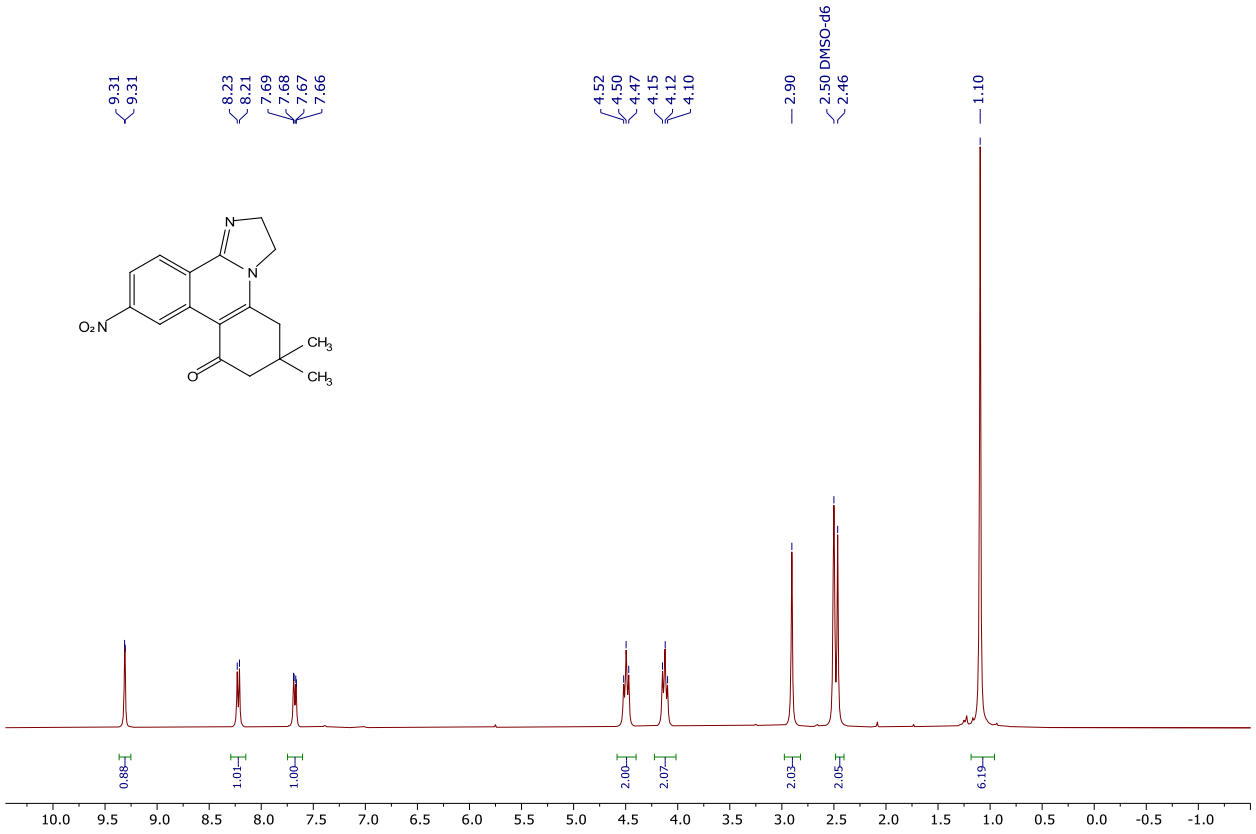
Copy of ^{1}H (400.13 MHz, $CDCl_3$) NMR spectrum of **4c**



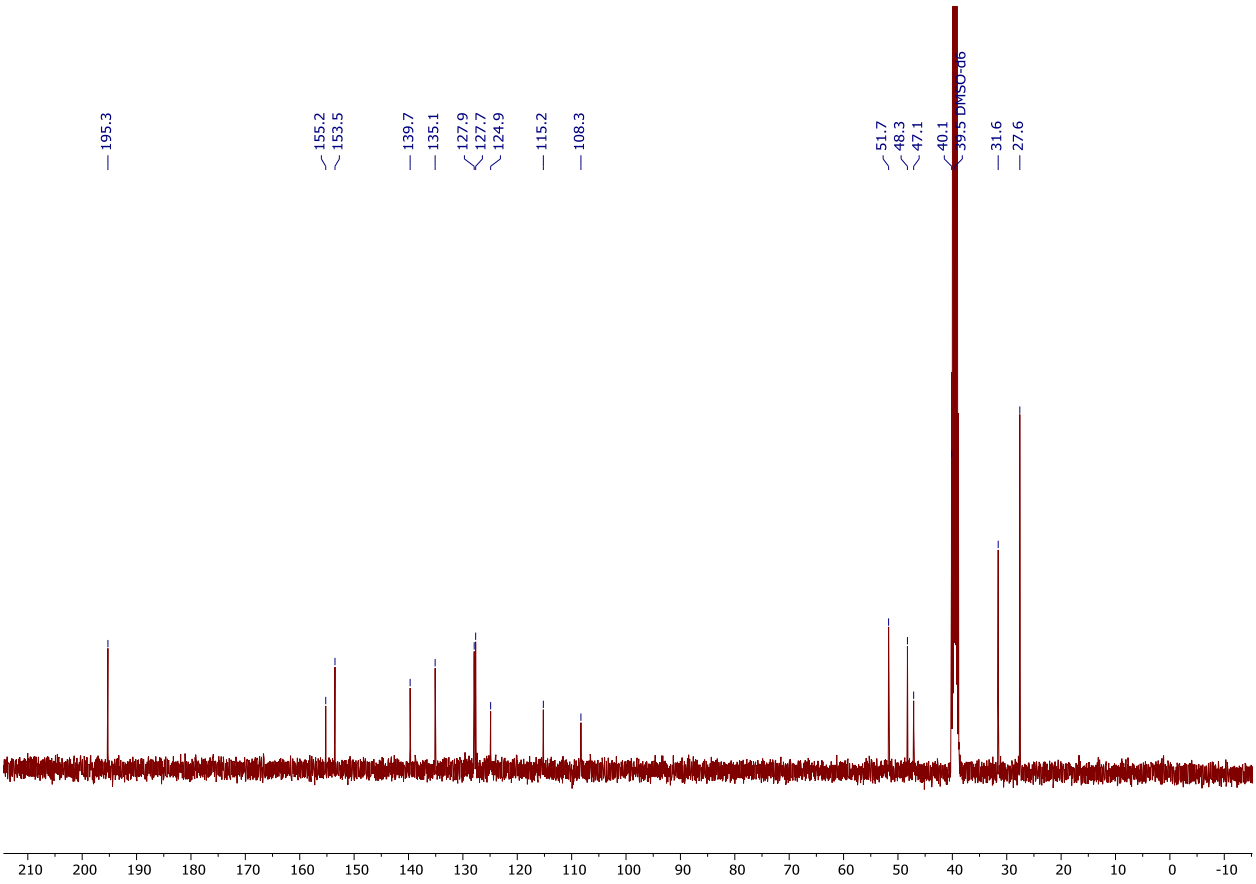
Copy of $^{13}C\{^{1}H\}$ (100.61 MHz, $CDCl_3$) NMR spectrum of **4c**



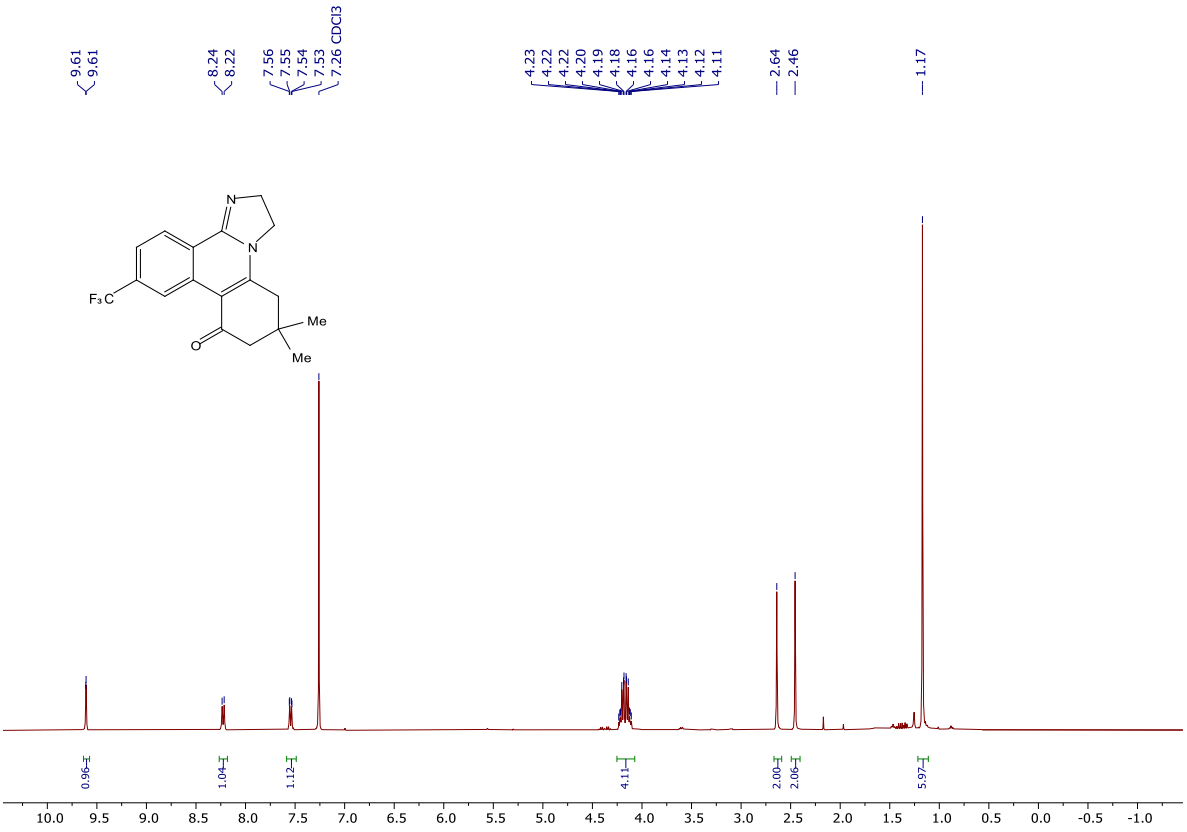
Copy of ^{1}H (400.13 MHz, DMSO-d_6) NMR spectrum of **4d**



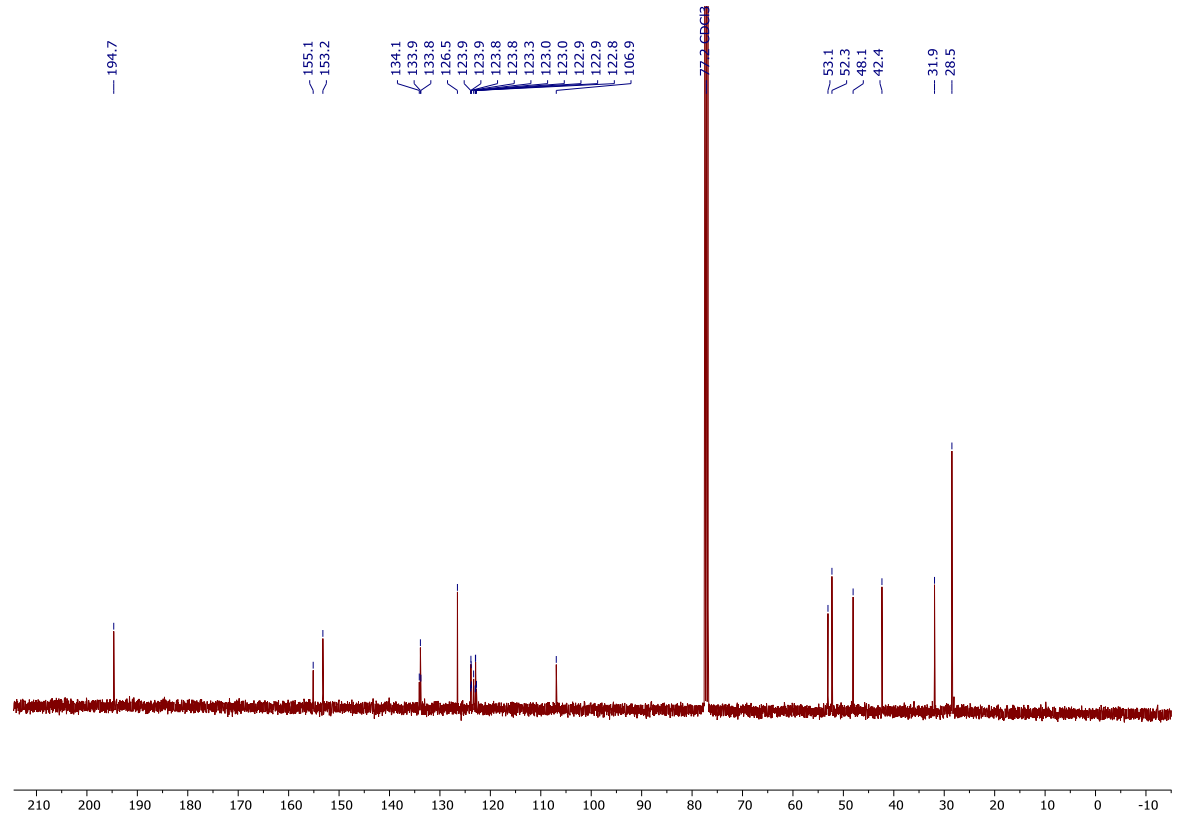
Copy of ^{13}C{^{1}H} (100.61 MHz, DMSO-d_6) NMR spectrum of **4d**



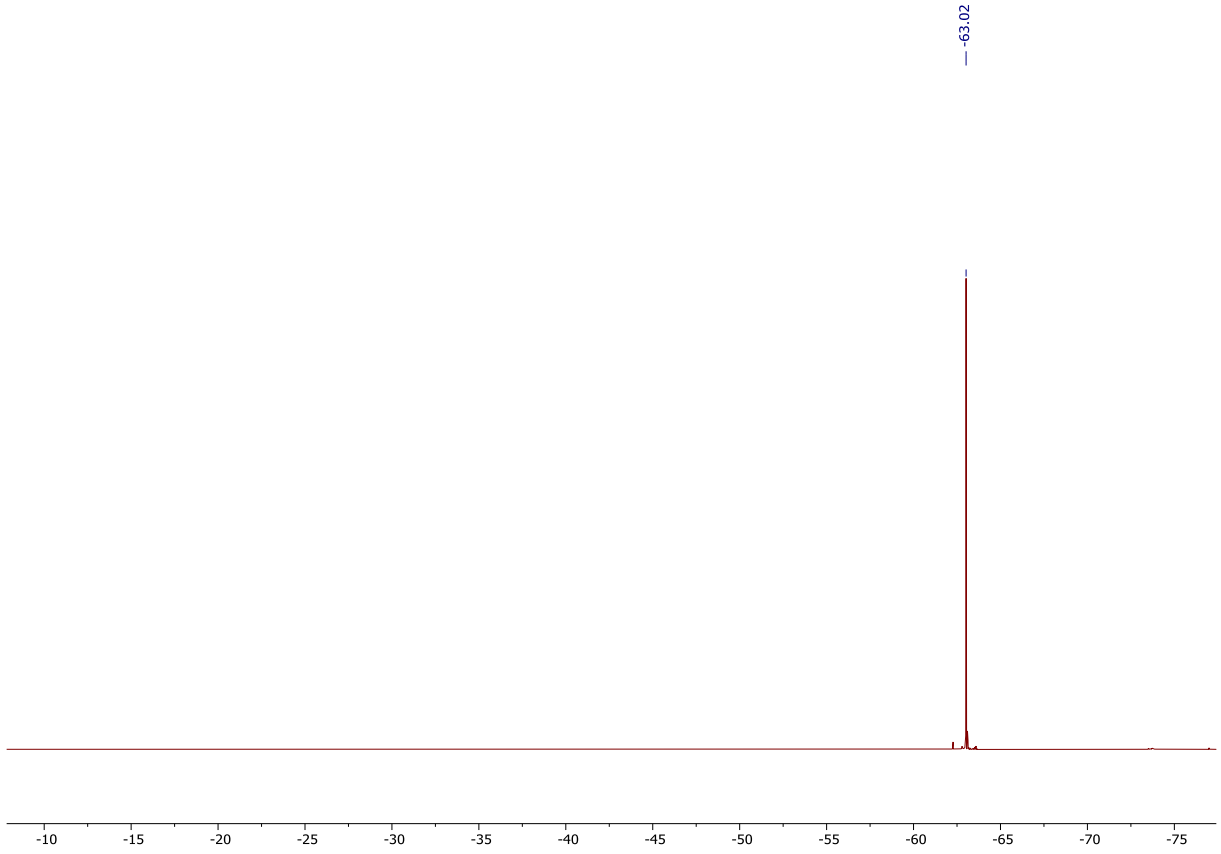
Copy of ^{1}H (400.13 MHz, $CDCl_3$) NMR spectrum of **4e**



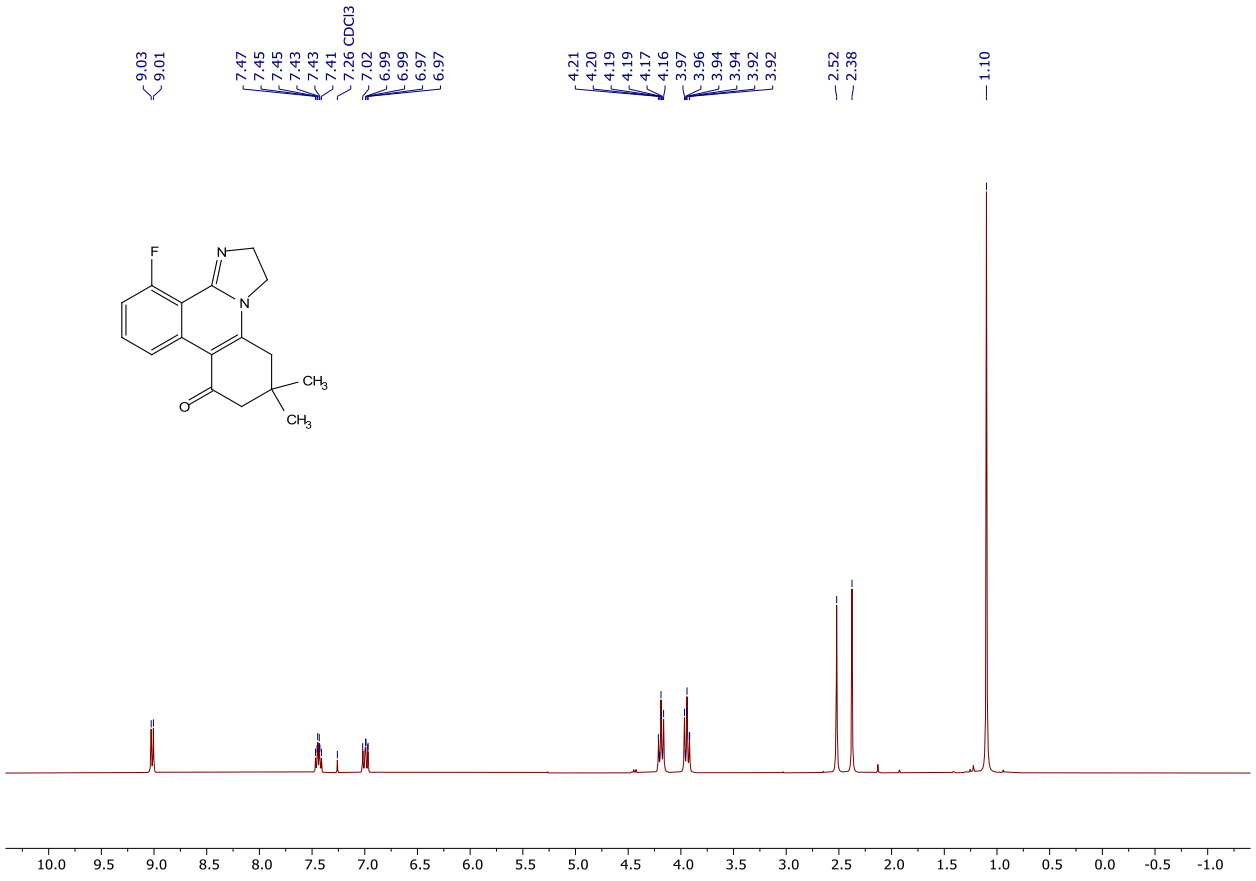
Copy of $^{13}C\{^{1}H\}$ (100.61 MHz, $CDCl_3$) NMR spectrum of **4e**



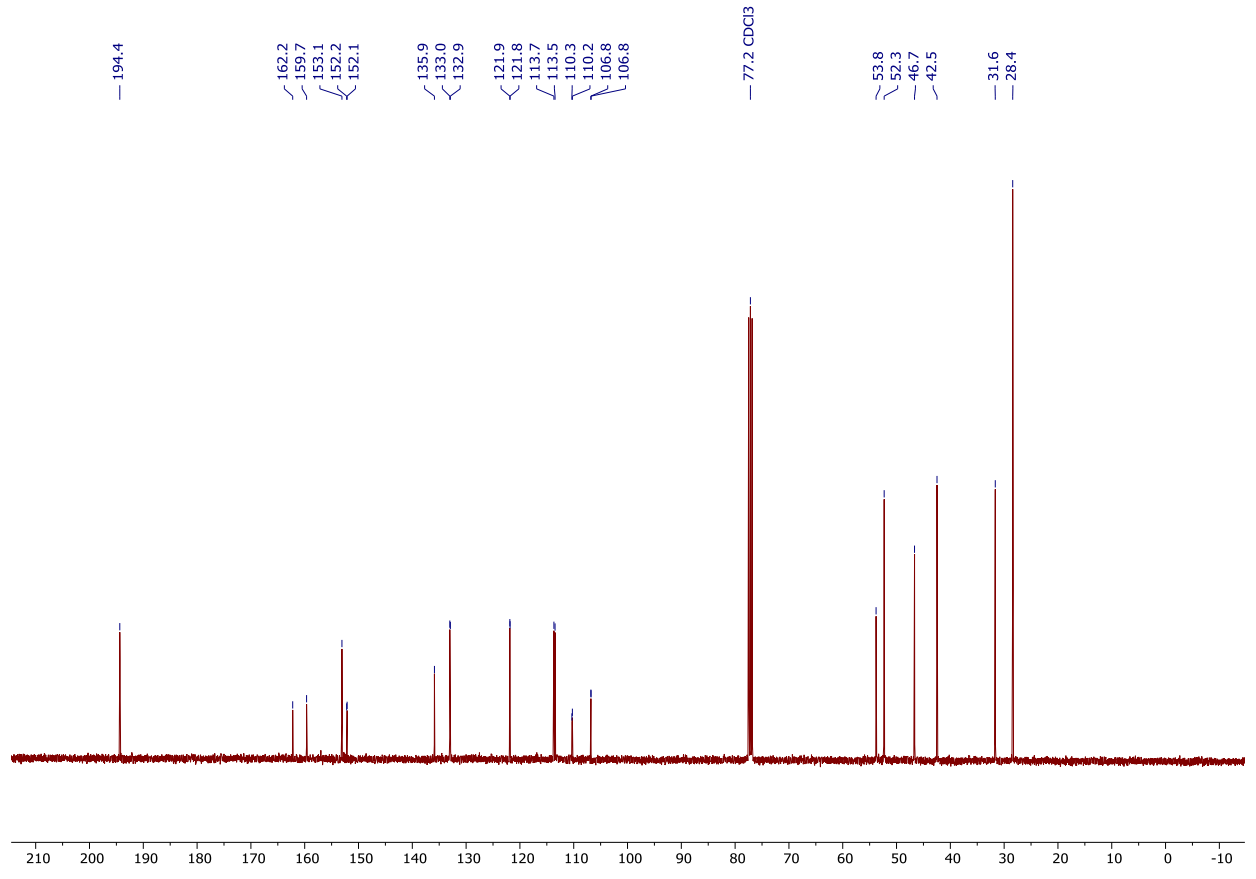
Copy of $^{19}F\{^{1}H\}$ (376.50 MHz, $CDCl_3$) NMR spectrum of **4e**



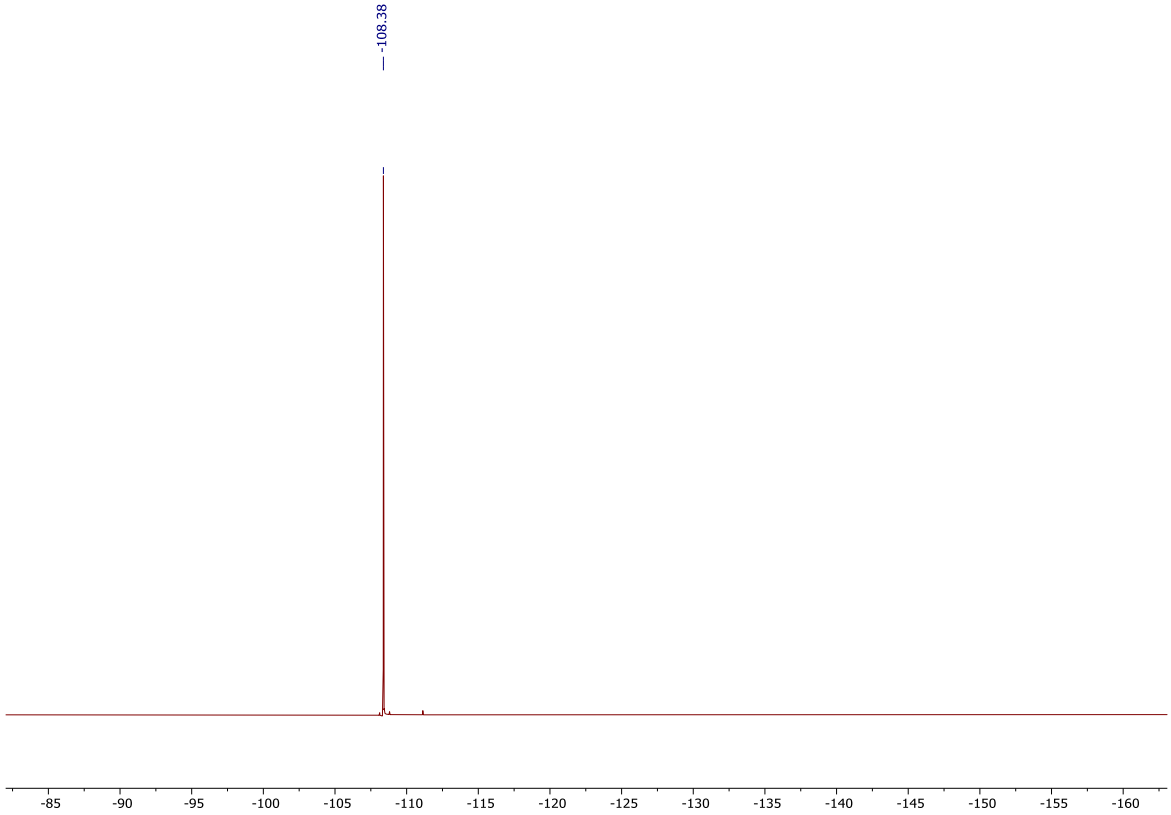
Copy of ^{1}H (400.13 MHz, $CDCl_3$) $^{19}F\{^{1}H\}$ (376.50 MHz, $CDCl_3$) NMR spectrum of **4f**



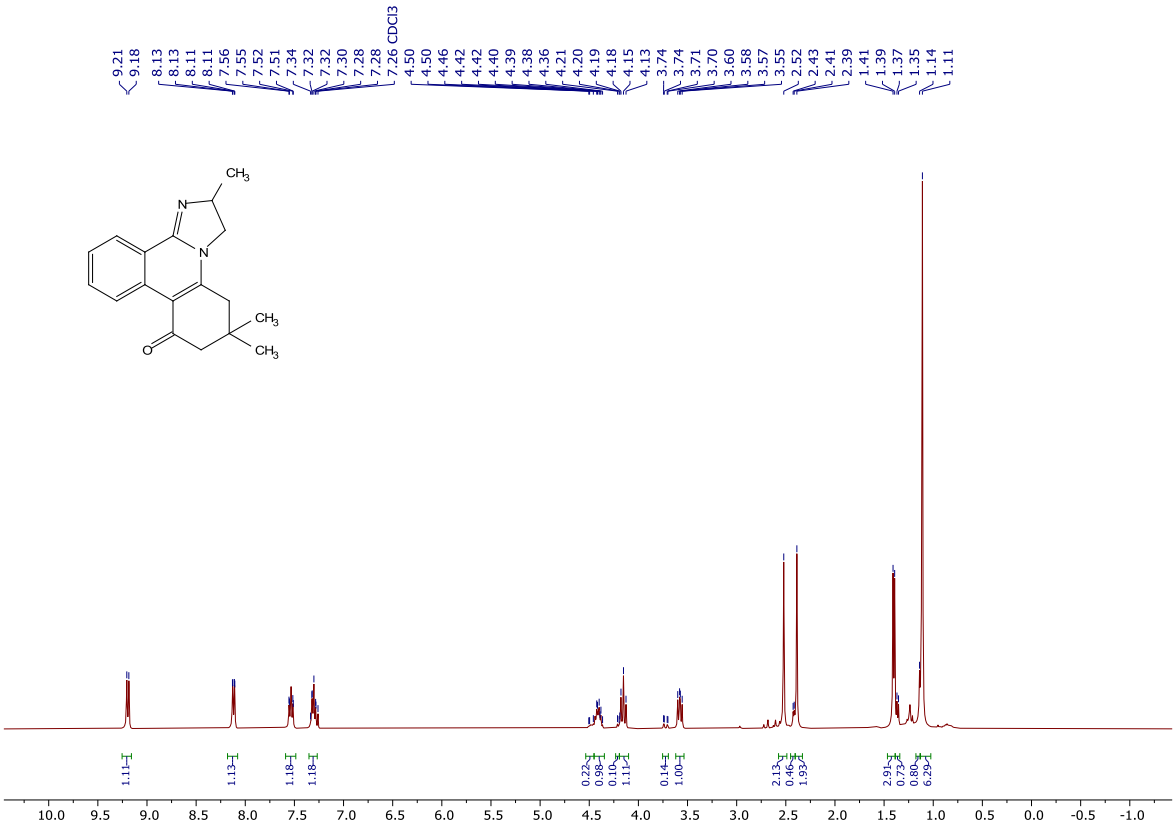
Copy of $^{13}C\{^{1}H\}$ (100.61 MHz, $CDCl_3$) NMR spectrum of **4f**



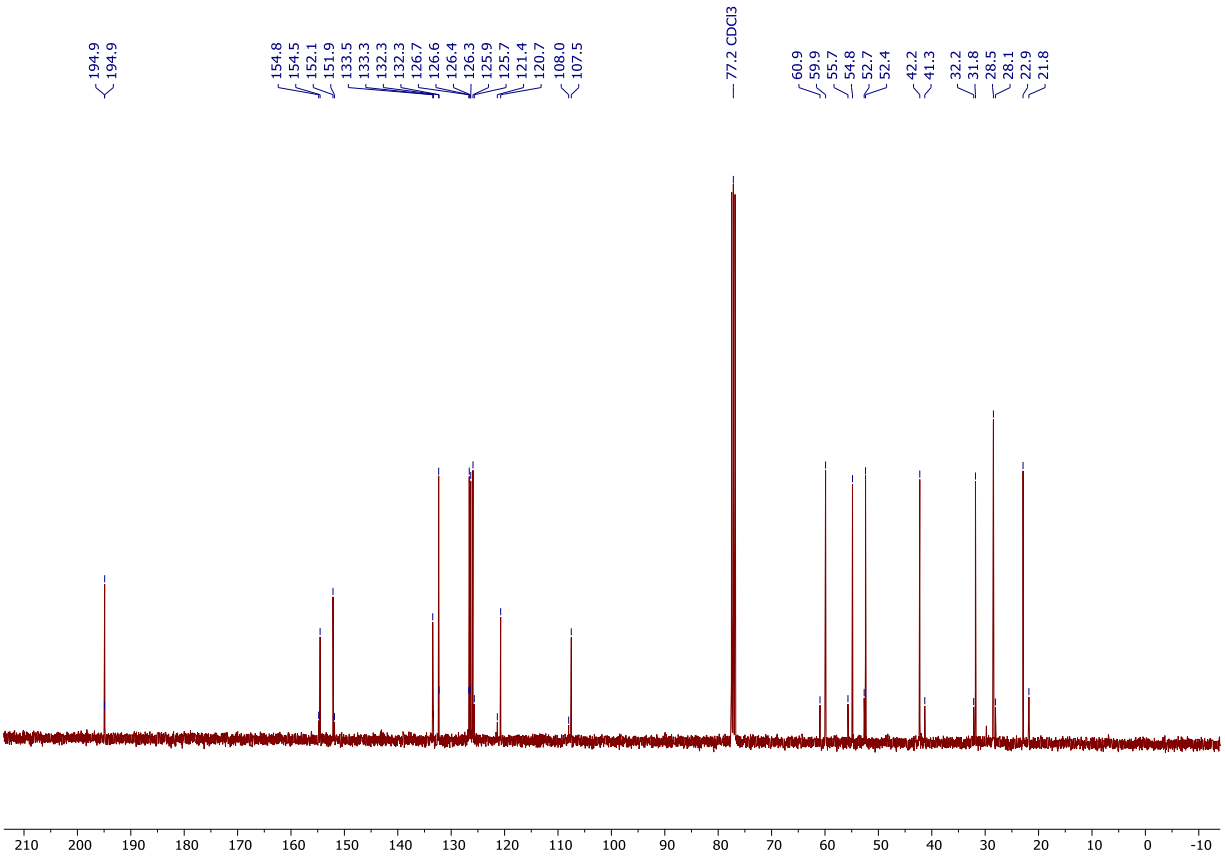
Copy of $^{19}F\{^{1}H\}$ (376.50 MHz, $CDCl_3$) NMR spectrum of **4f**



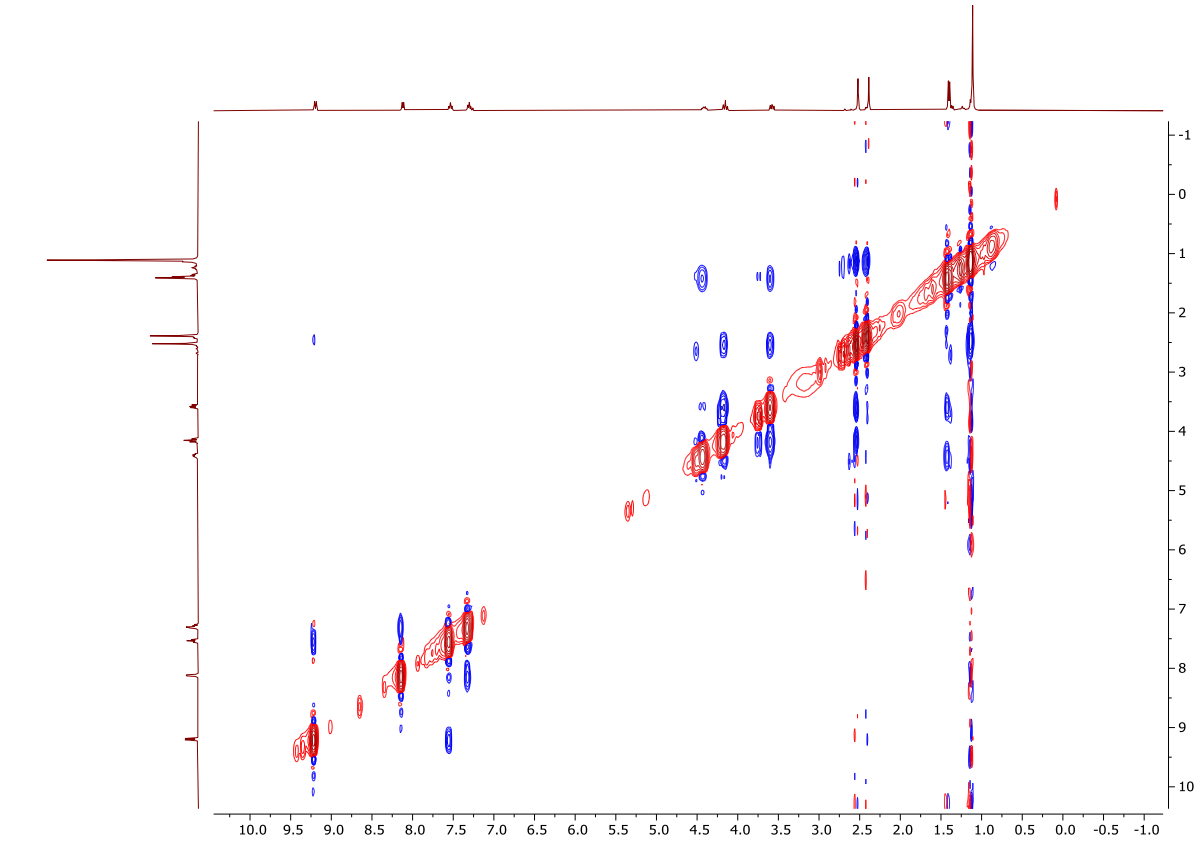
Copy of ^{1}H (400.13 MHz, $CDCl_3$) NMR spectrum of **4g + g'**

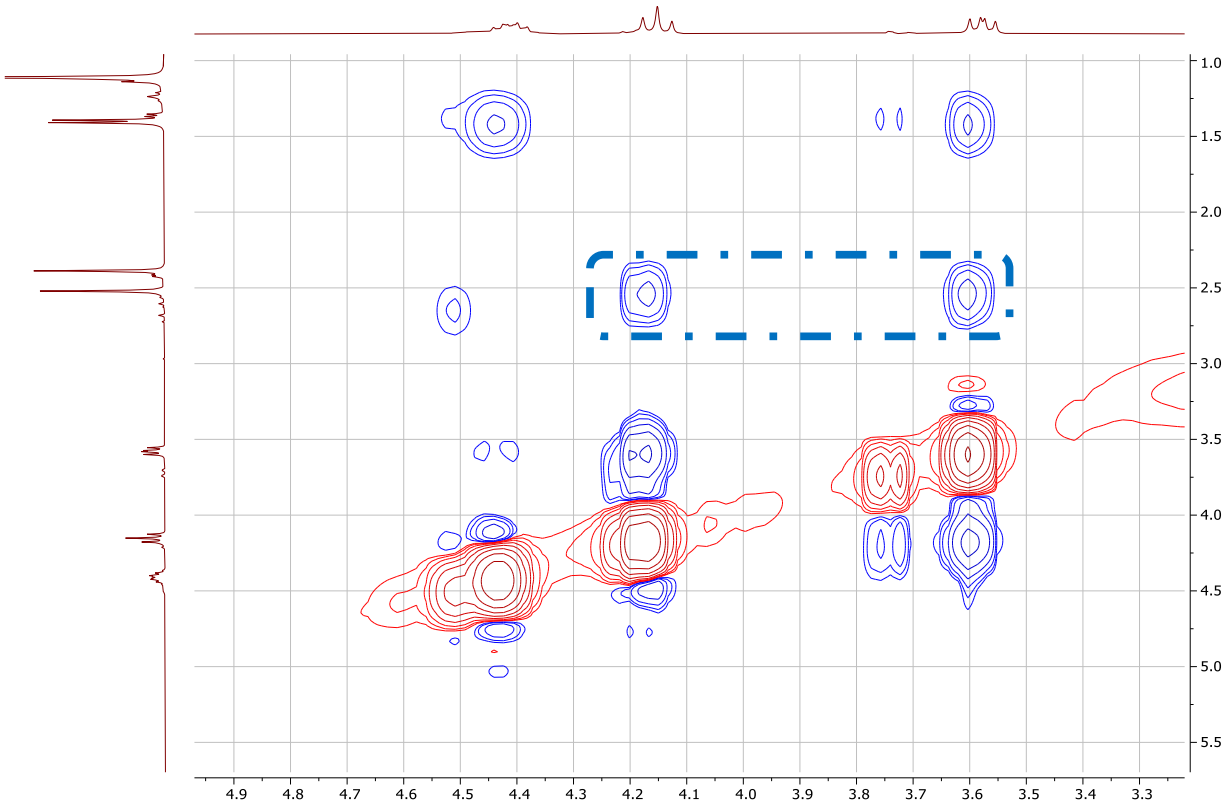


Copy of $^{13}C\{^{1}H\}$ (100.61 MHz, $CDCl_3$) NMR spectrum of **4g + g'**

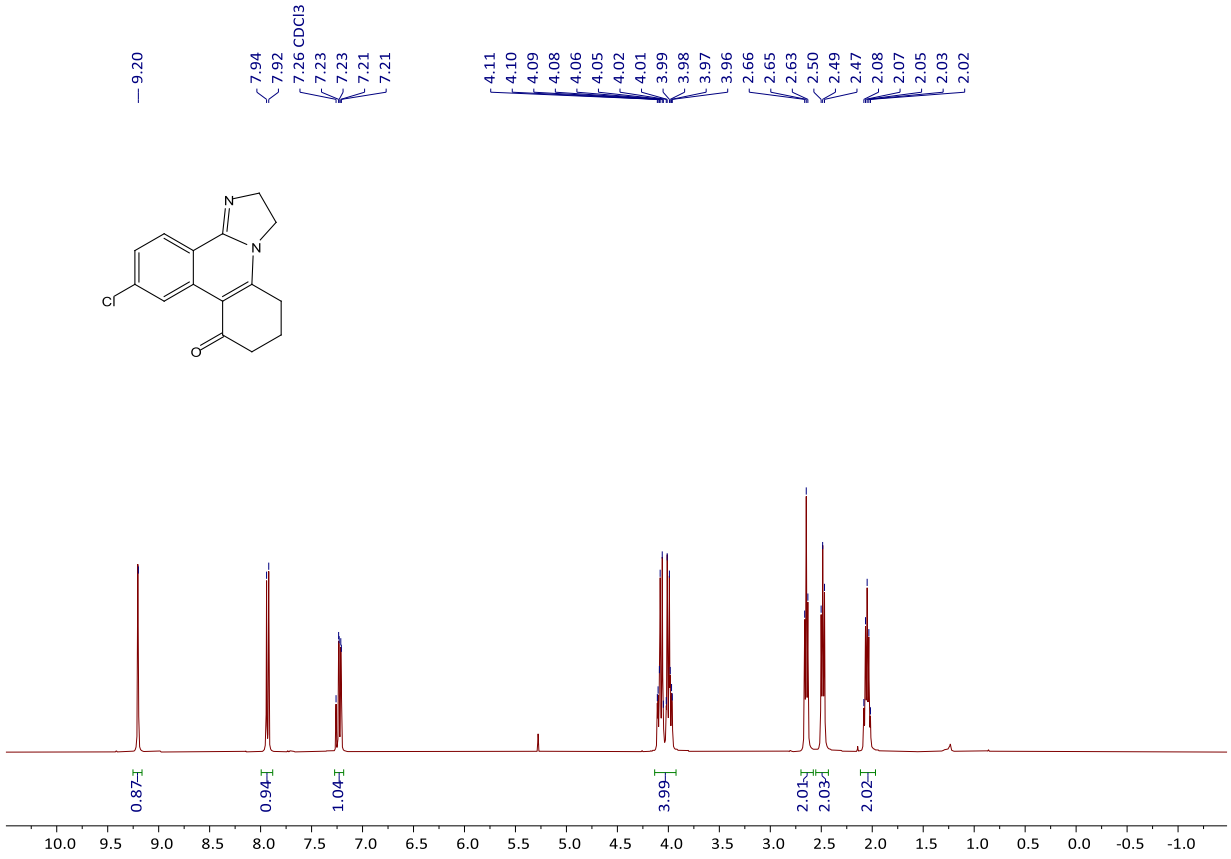


Copy of NOESY (400.13 MHz, $CDCl_3$) NMR spectrum of **4g + g'**

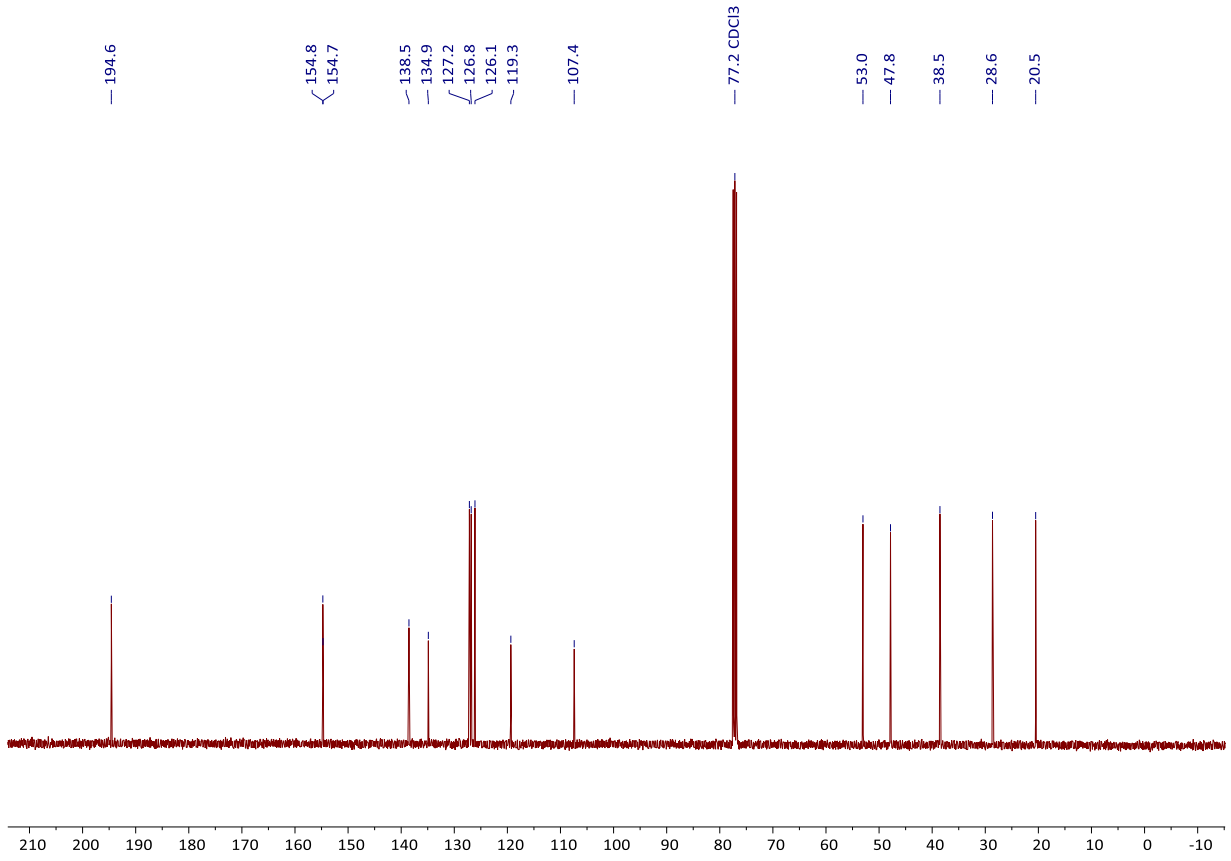




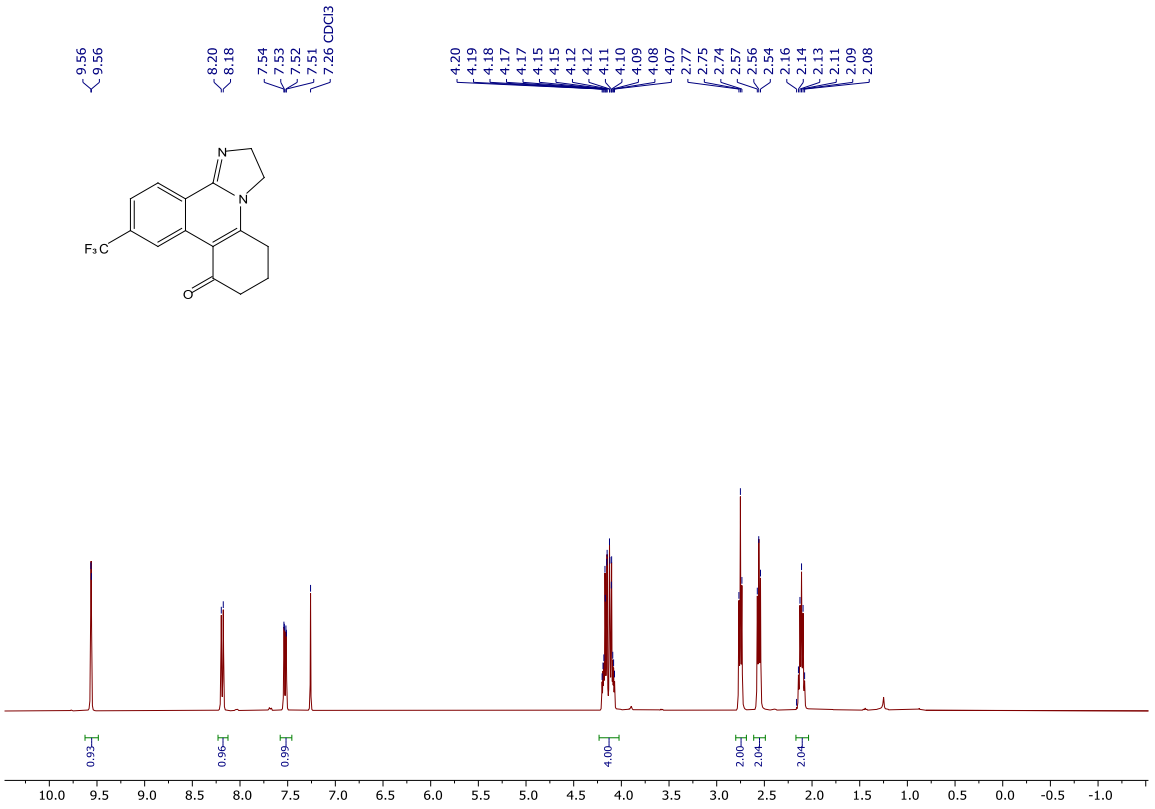
Copy of ^{1}H (400.13 MHz, $CDCl_3$) NMR spectrum of **4h**



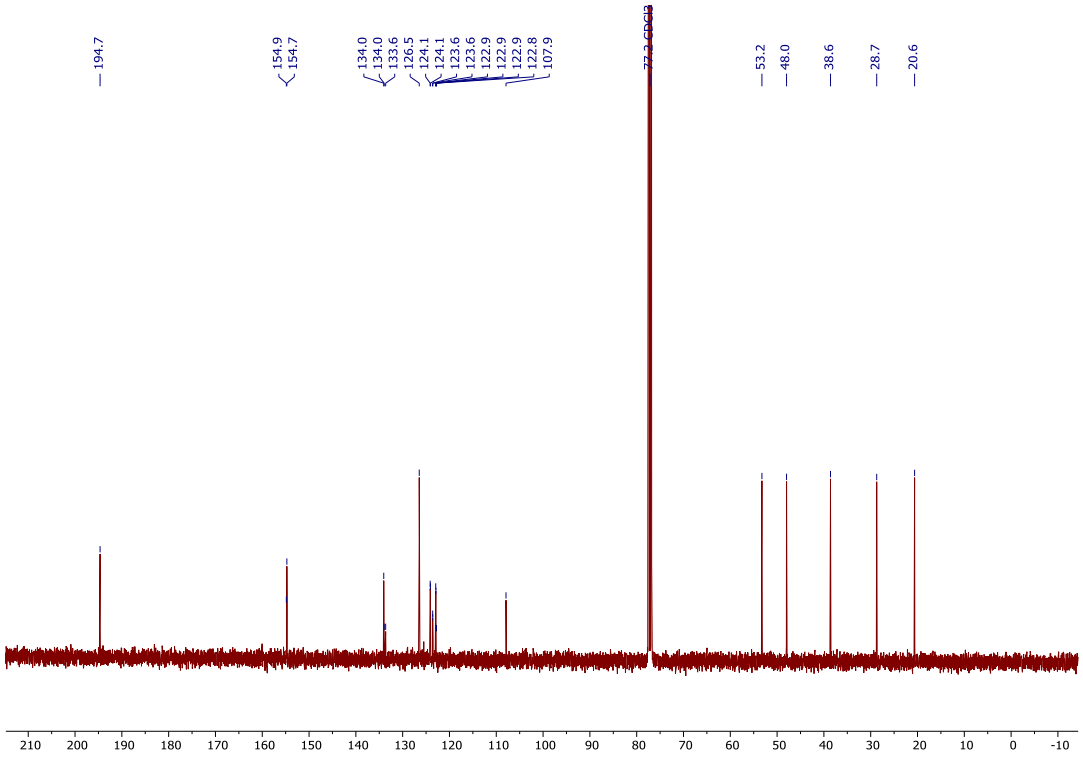
Copy of $^{13}C\{^{1}H\}$ (100.61 MHz, $CDCl_3$) NMR spectrum of **4h**



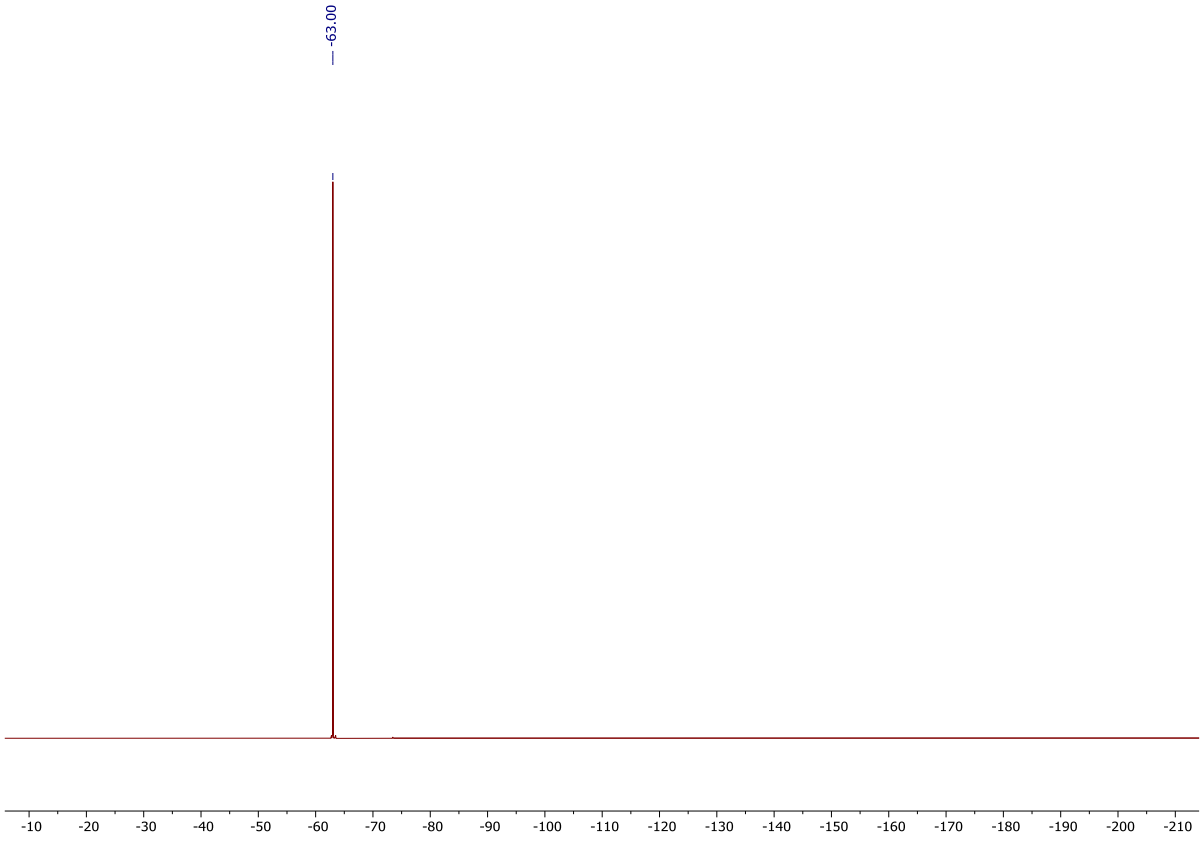
Copy of ^{1}H (400.13 MHz, $CDCl_3$) NMR spectrum of **4i**



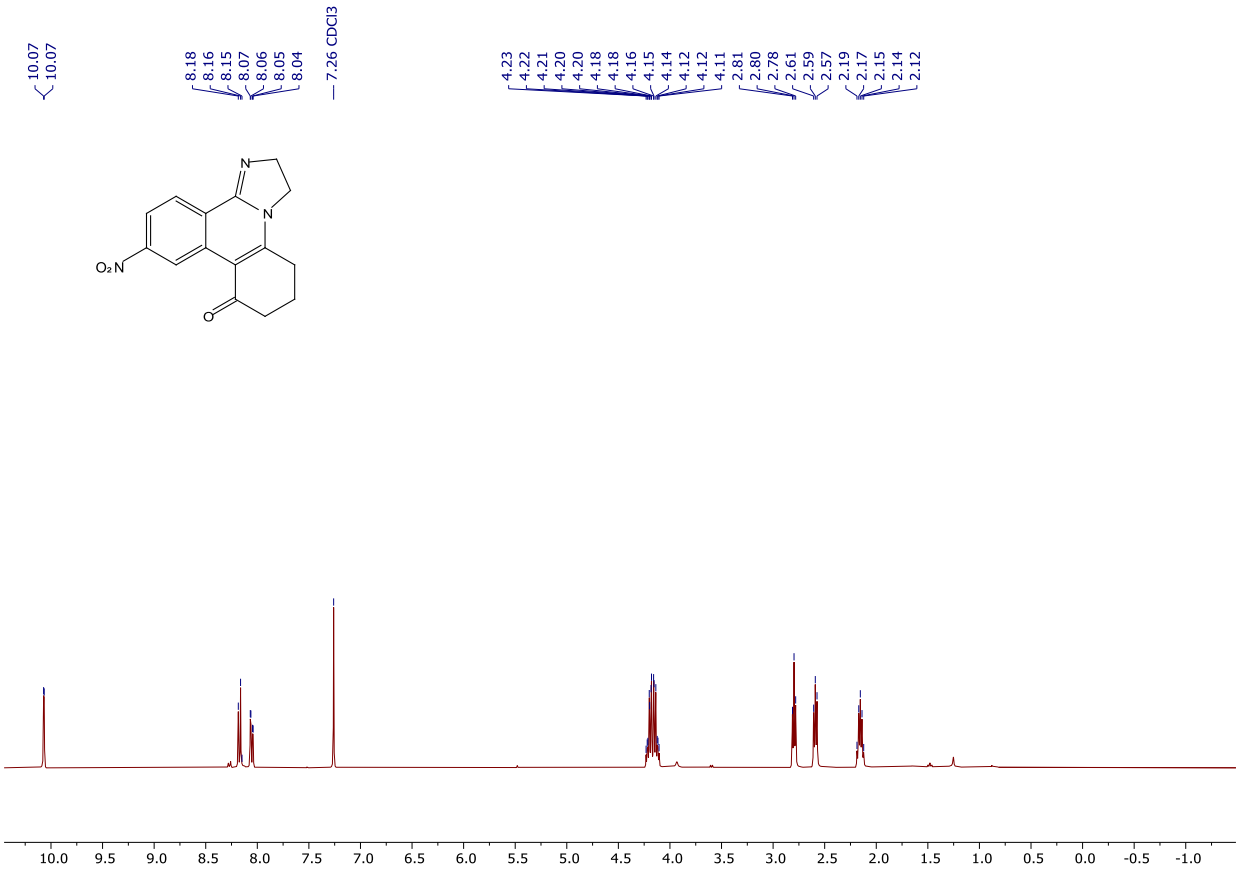
Copy of $^{13}C\{^{1}H\}$ (100.61 MHz, $CDCl_3$) vspectrum of **4i**



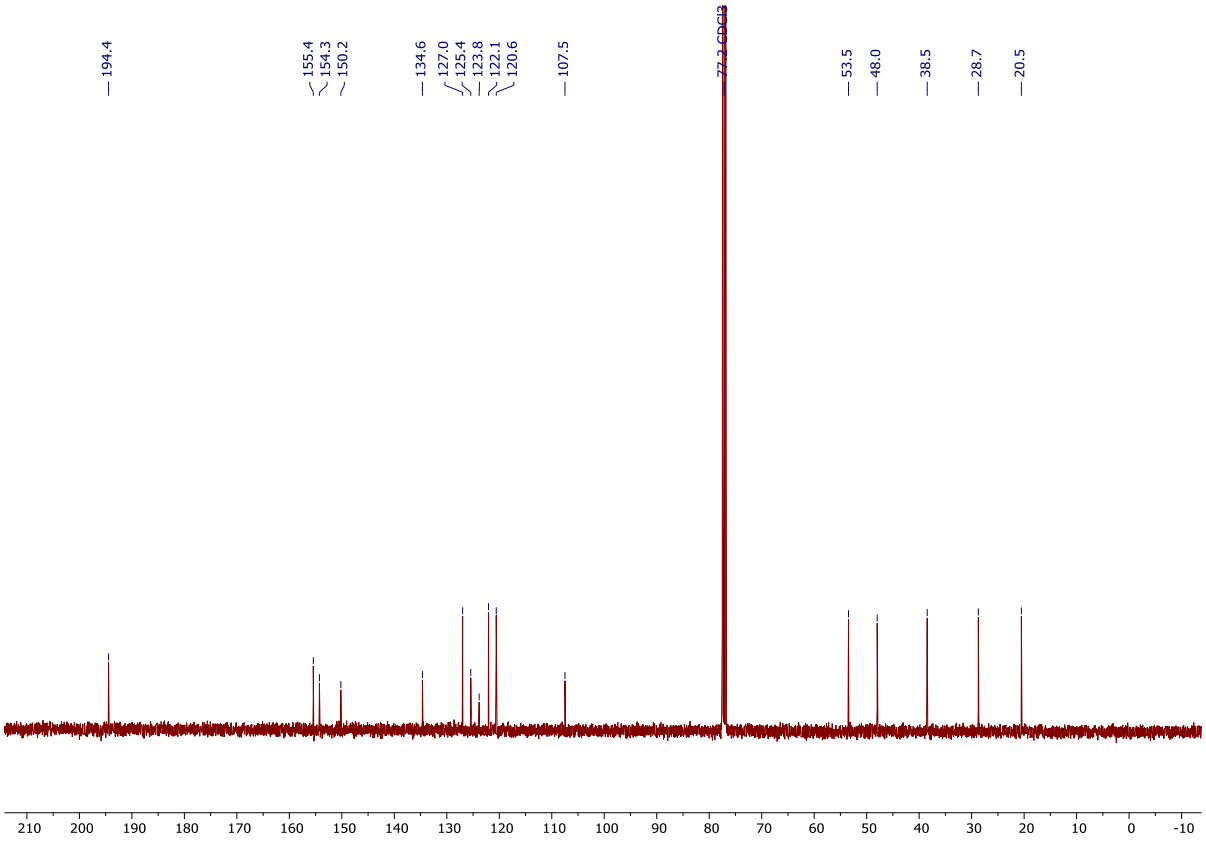
Copy of $^{19}F\{^{1}H\}$ (376.50 MHz, $CDCl_3$) NMR spectrum of **4i**



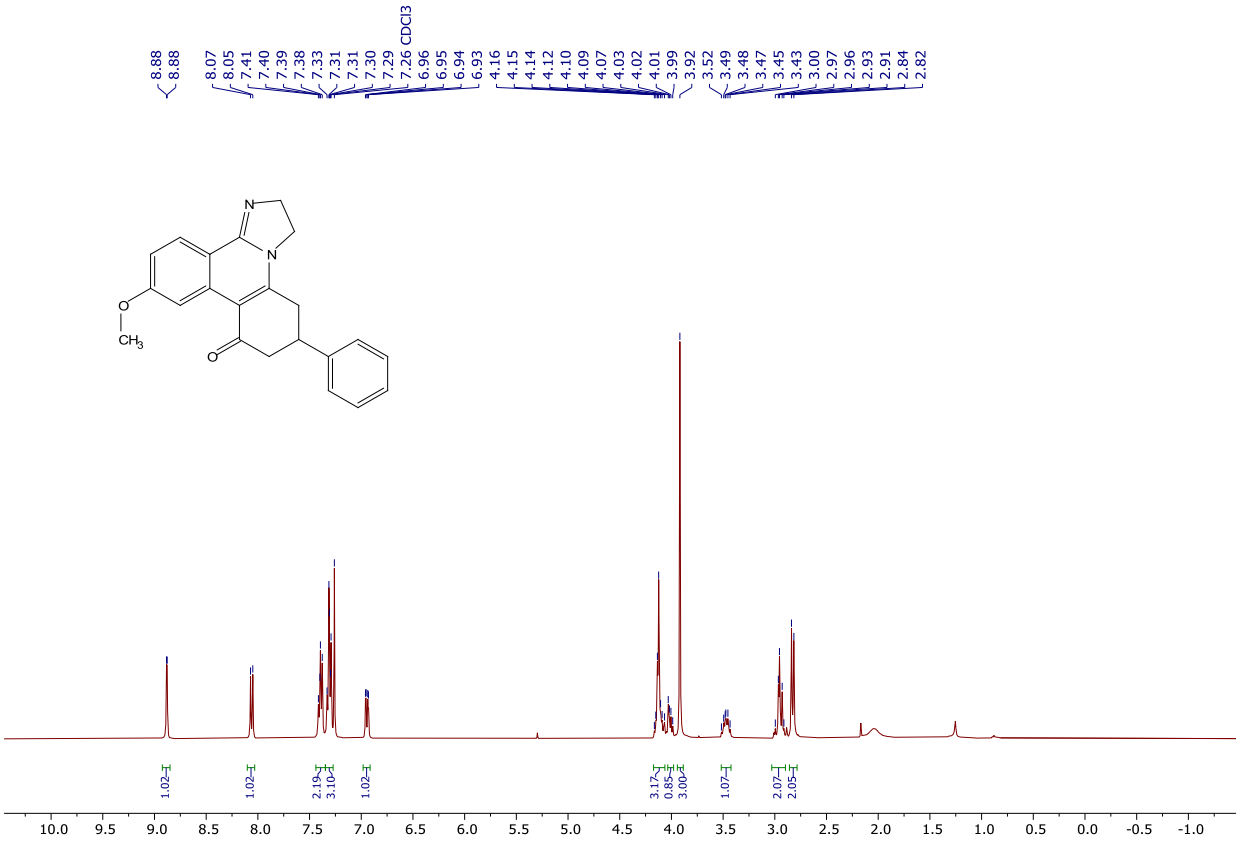
Copy of ^{1}H (400.13 MHz, $CDCl_3$) NMR spectrum of **4j**



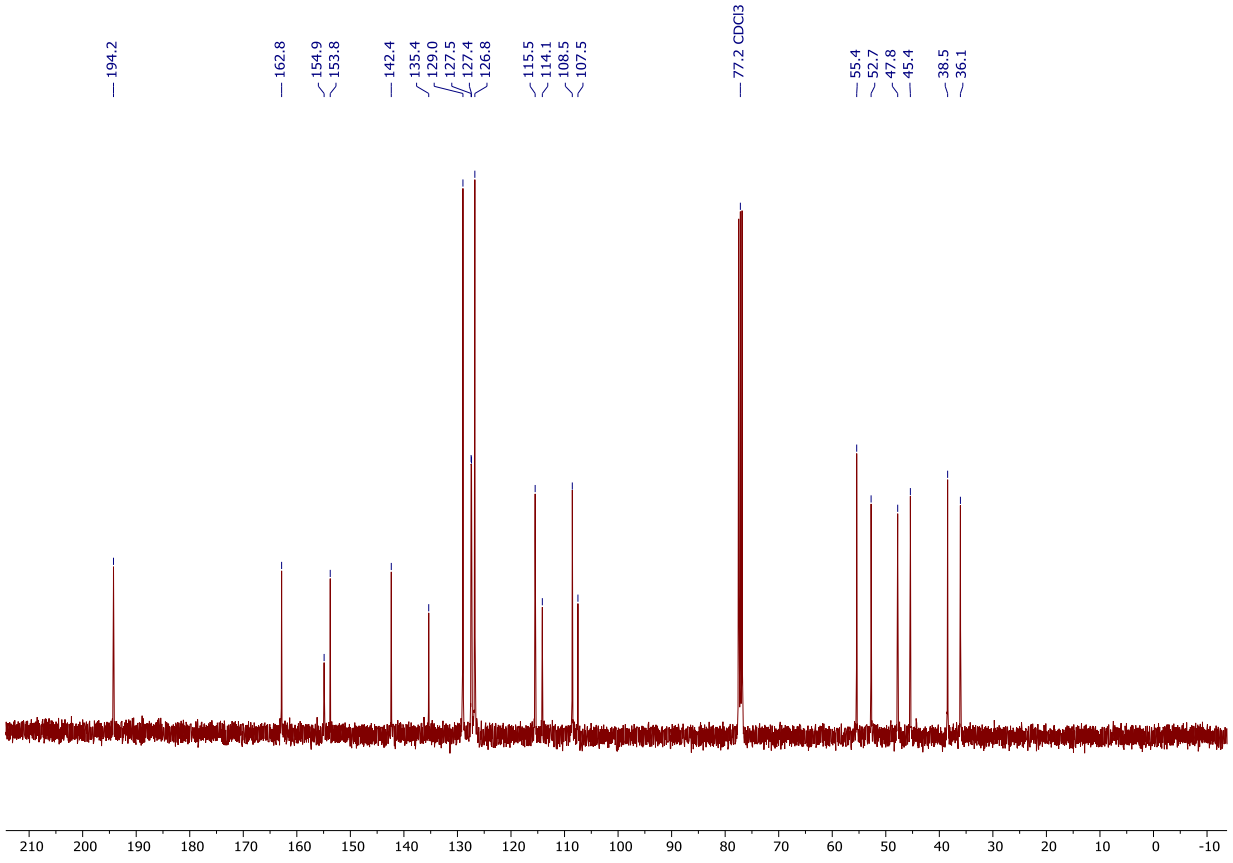
Copy of $^{13}C\{^{1}H\}$ (100.61 MHz, $CDCl_3$) NMR spectrum of **4j**



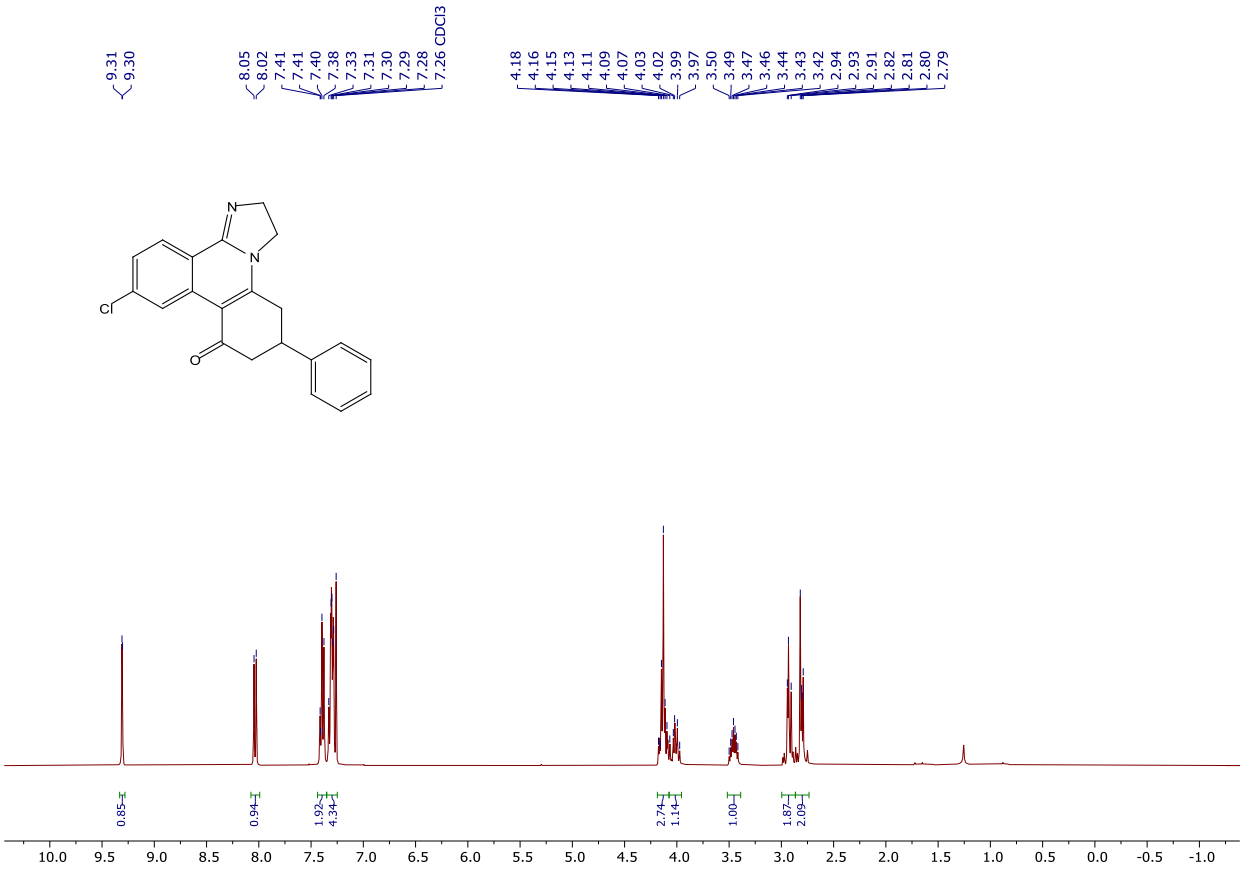
Copy of ^{1}H (400.13 MHz, $CDCl_3$) NMR spectrum of **4k**



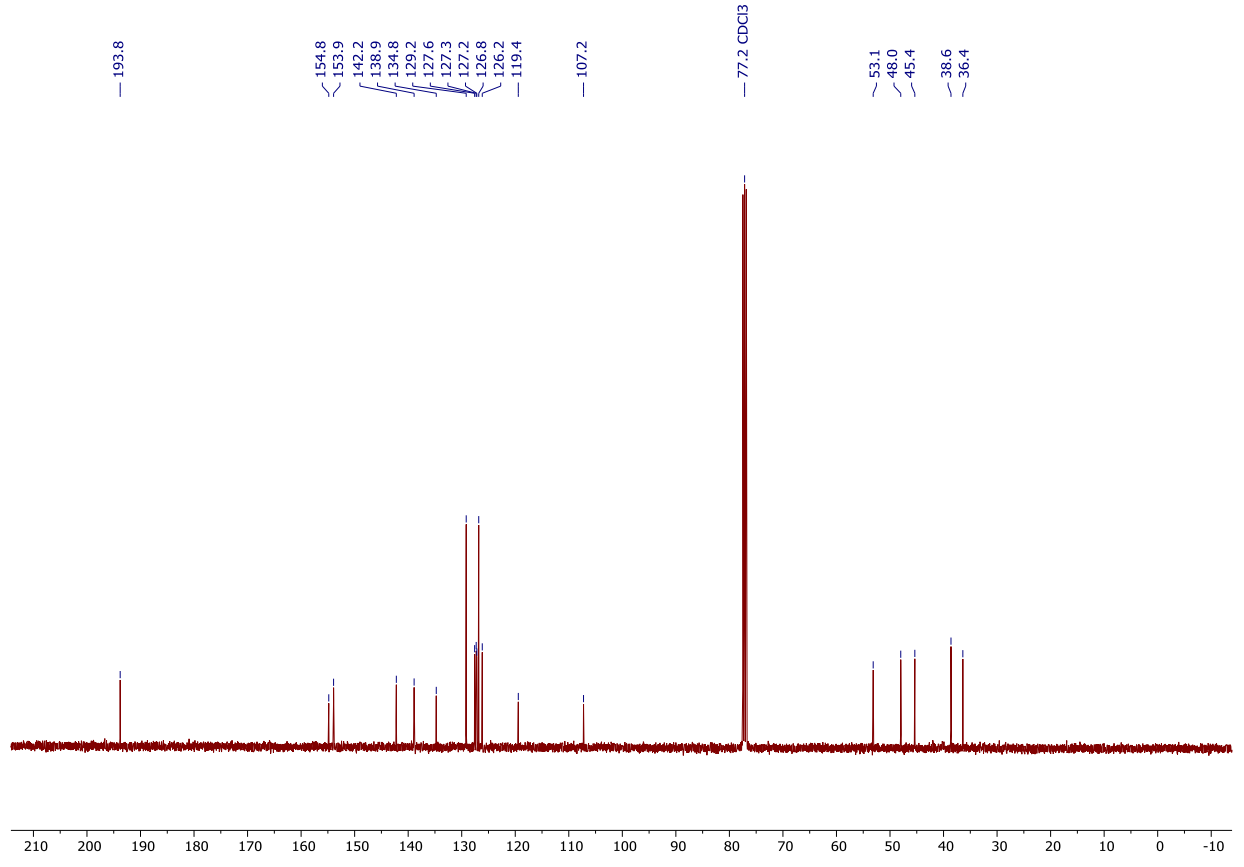
Copy of $^{13}C\{^{1}H\}$ (100.61 MHz, $CDCl_3$) NMR spectrum of **4k**



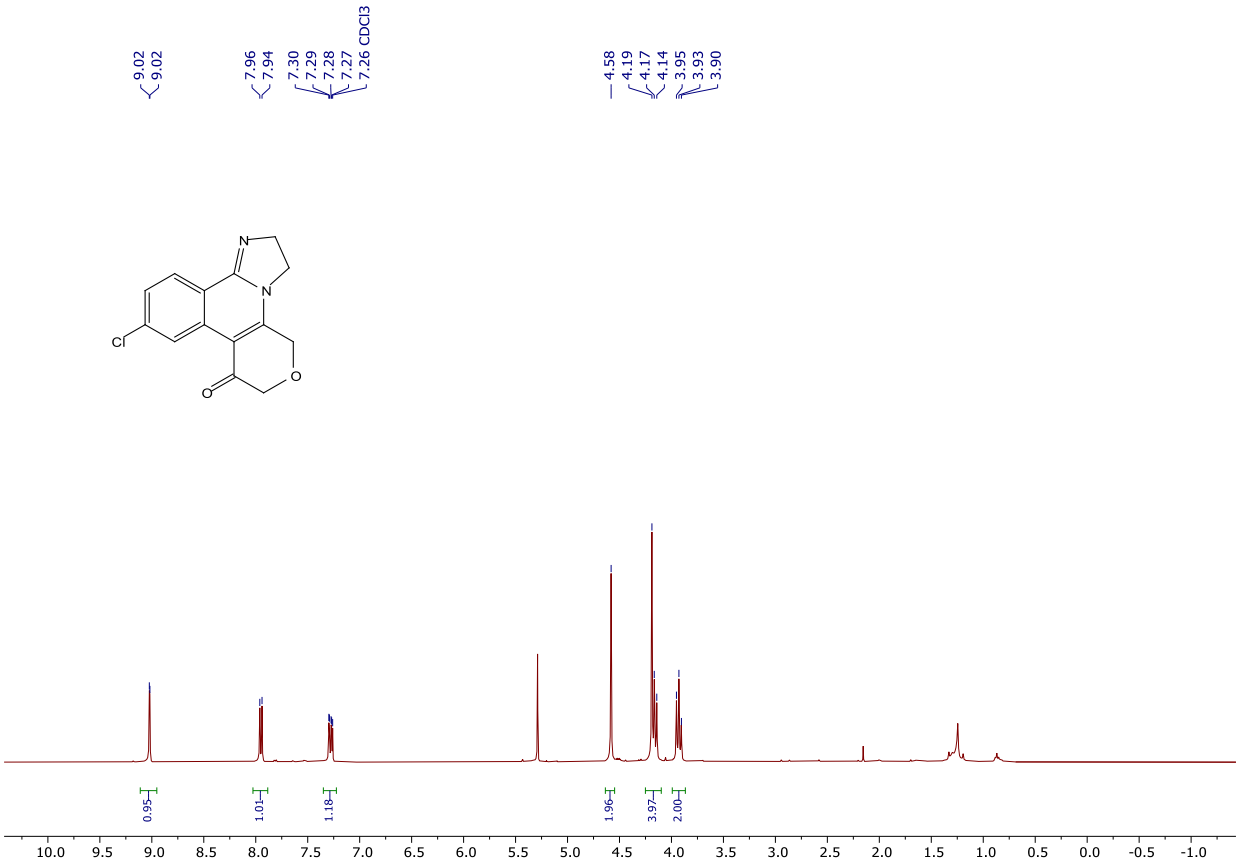
Copy of ^{1}H (400.13 MHz, $CDCl_3$) NMR spectrum of **4l**



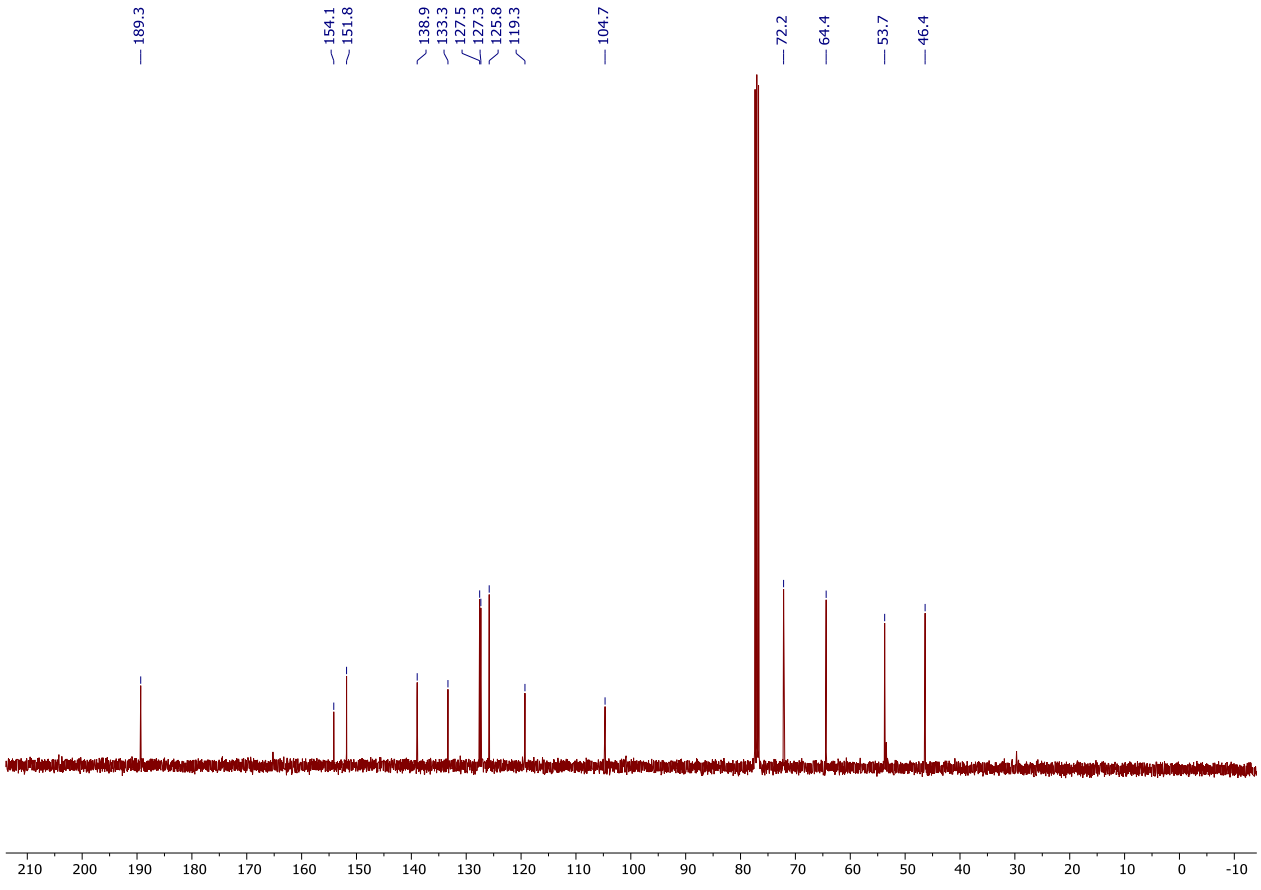
Copy of $^{13}C\{^{1}H\}$ (100.61 MHz, $CDCl_3$) NMR spectrum of **4l**



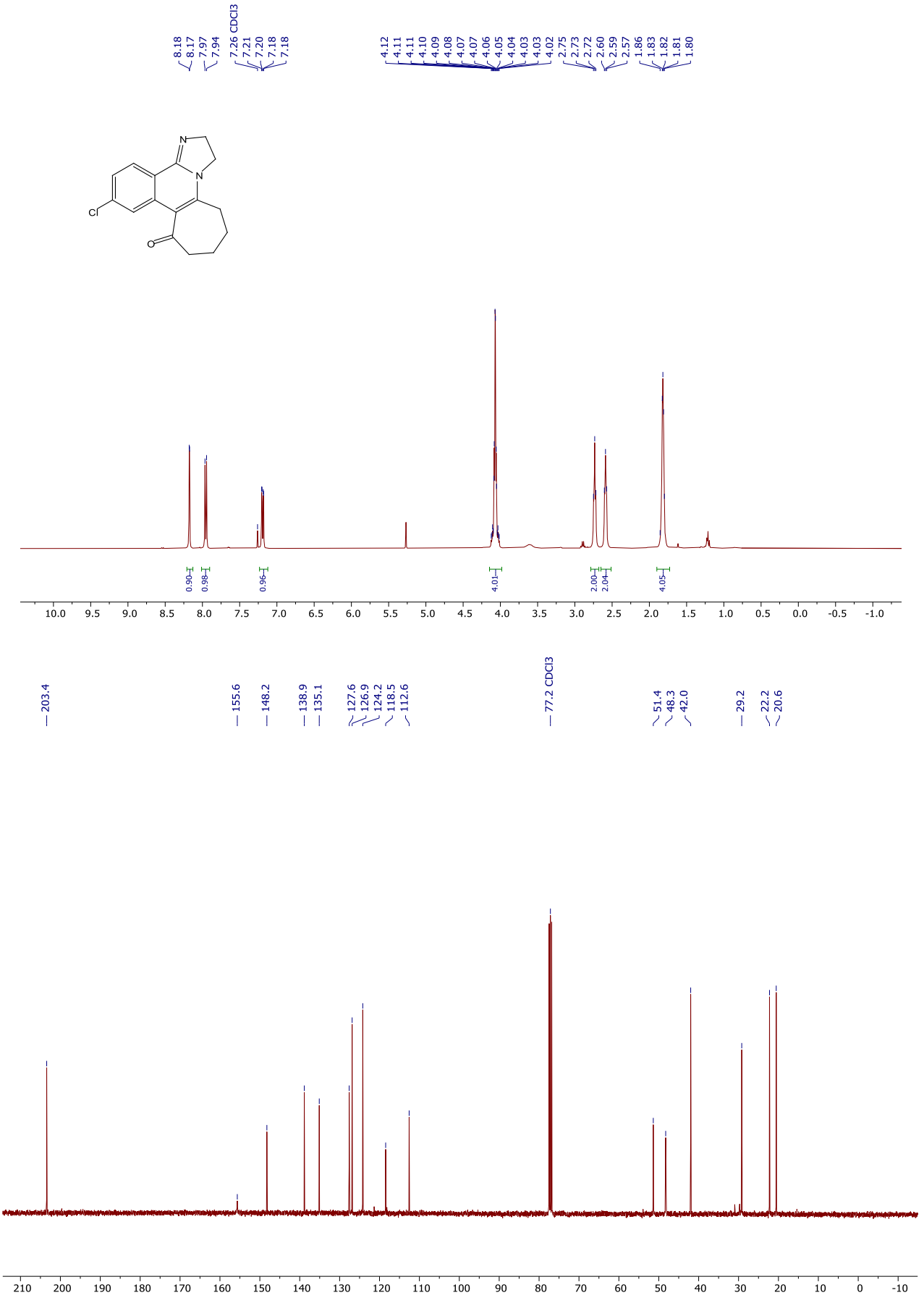
Copy of ^{1}H (400.13 MHz, $CDCl_3$) NMR spectrum of **4m**



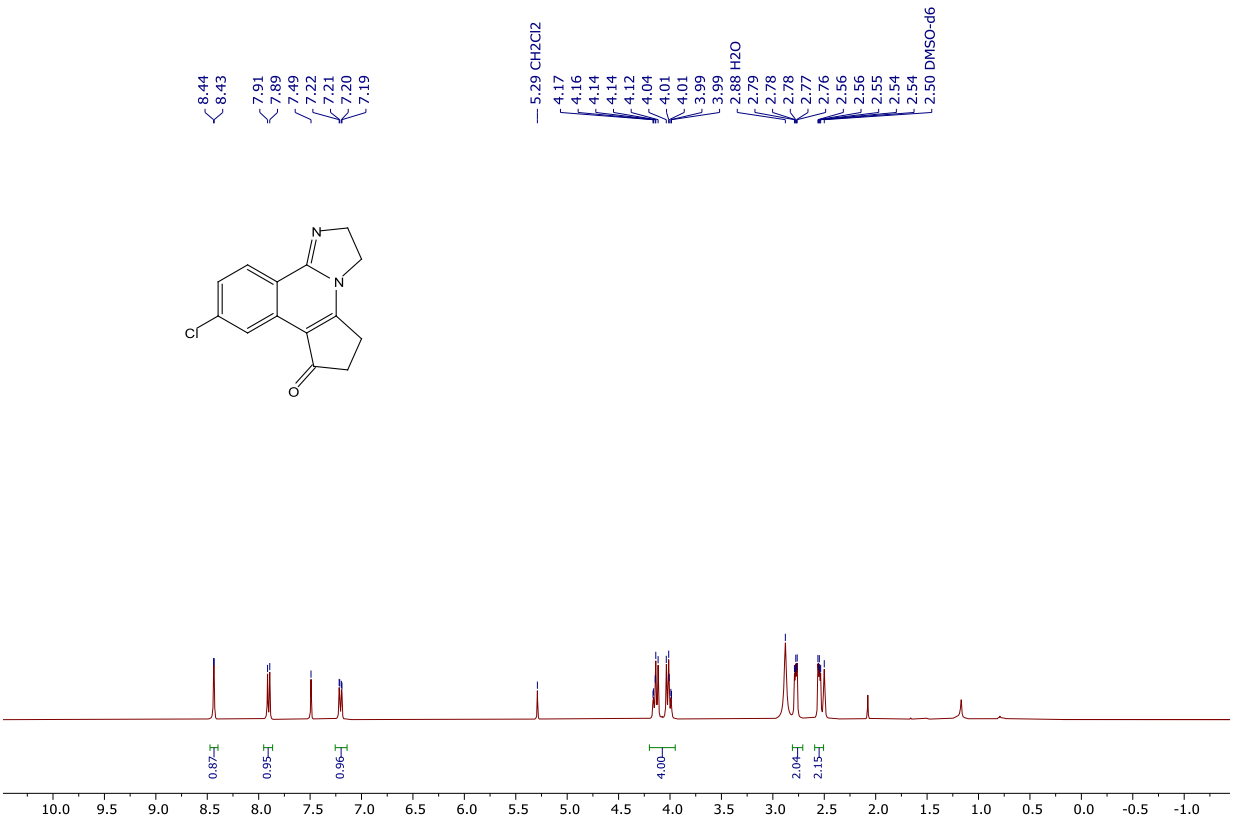
Copy of $^{13}C\{^{1}H\}$ (100.61 MHz, $CDCl_3$) NMR spectrum of **4m**



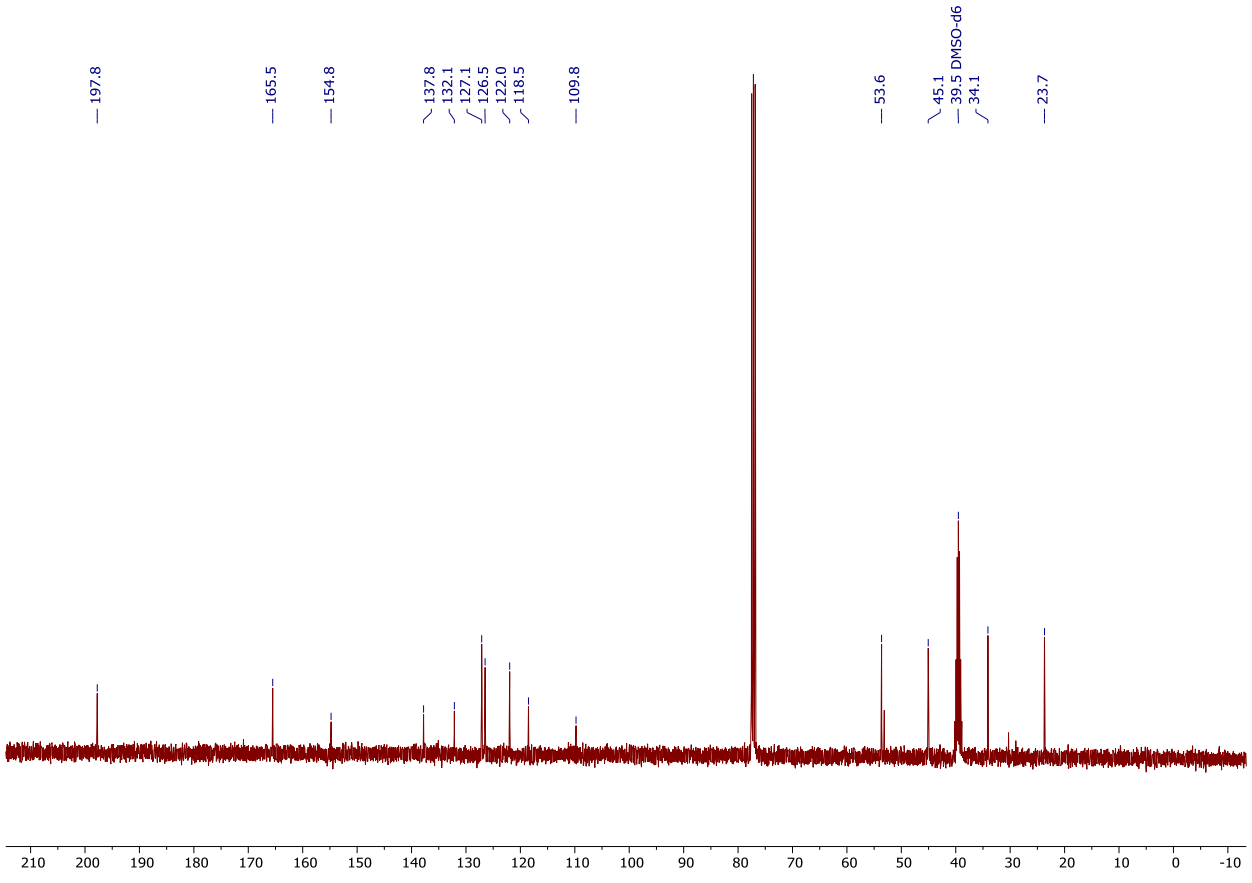
Copy of ^{1}H (400.13 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (100.61 MHz, $CDCl_3$) NMR spectrum of **4n**



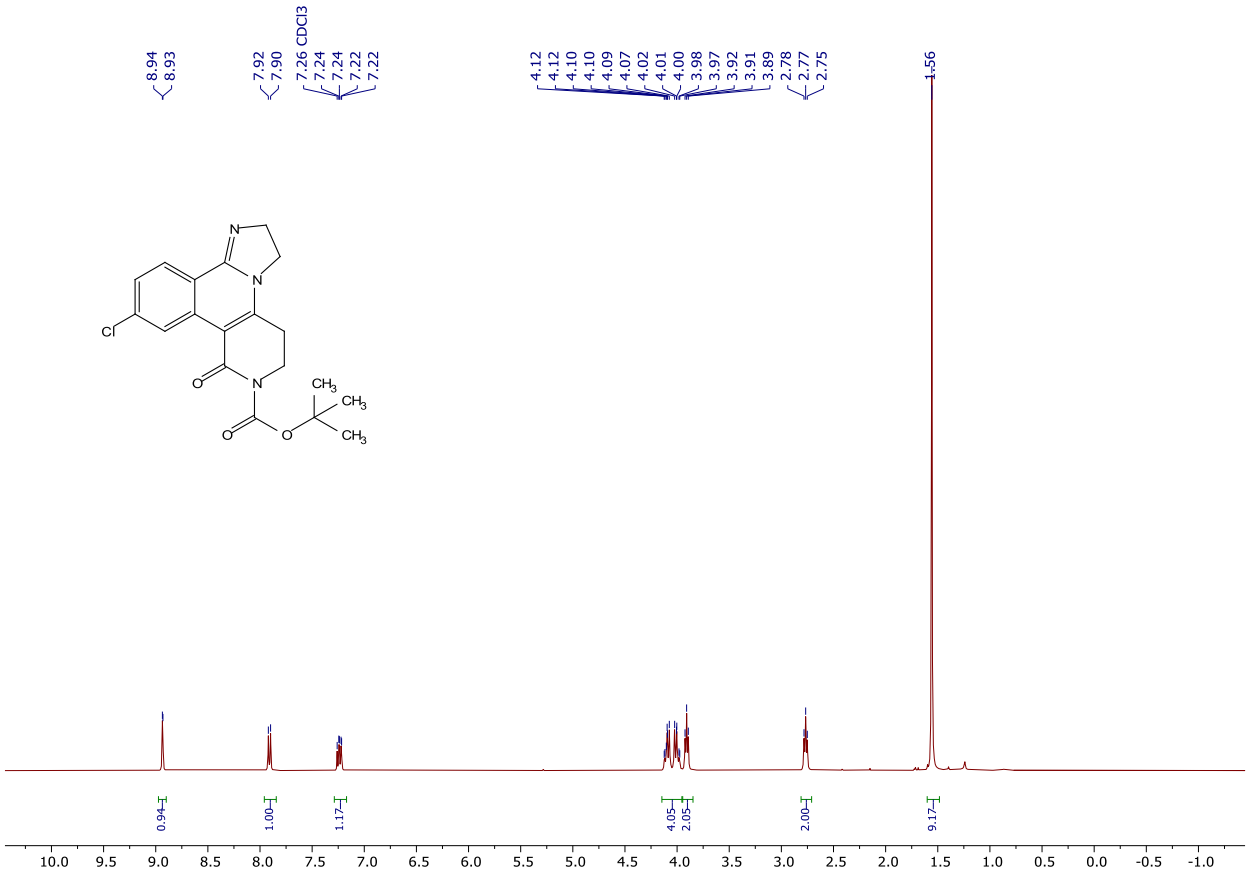
Copy of ^{1}H (400.13 MHz, DMSO-d_6+$CDCl_3$ in a ratio 1:6) NMR spectrum of **4o**



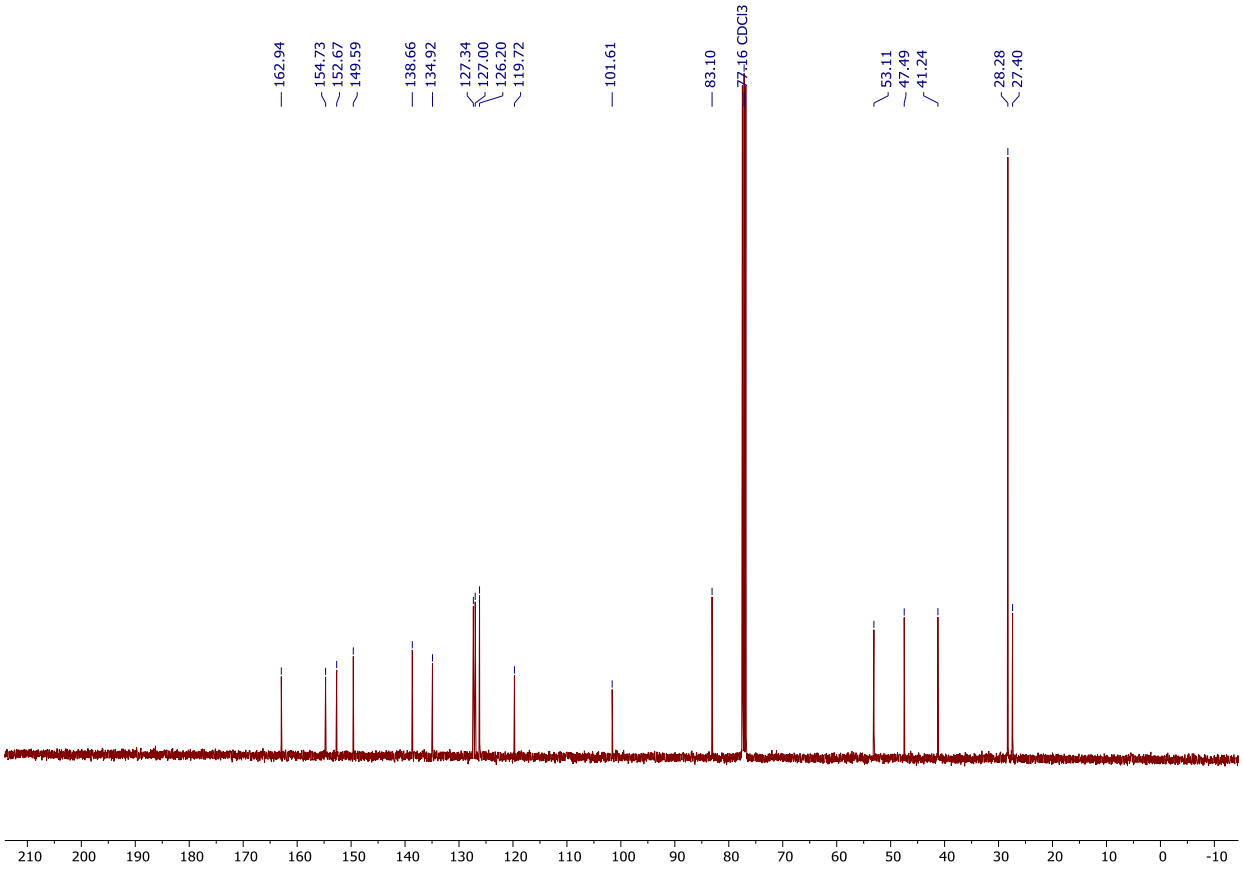
Copy of $^{13}C\{^{1}H\}$ (100.61 MHz, DMSO-d_6+$CDCl_3$ in a ratio 1:6) NMR spectrum of **4o**



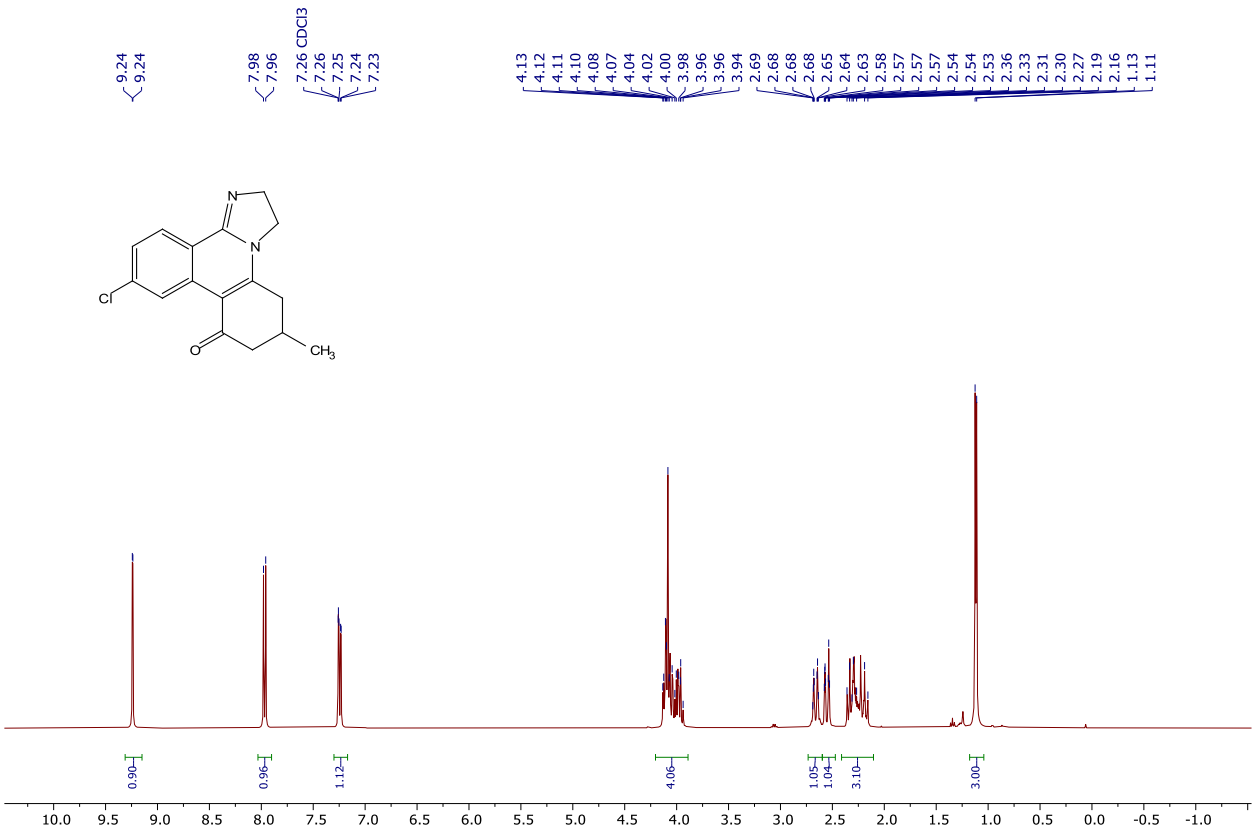
Copy of ^{1}H (400.13 MHz, $CDCl_3$) NMR spectrum of **4p**



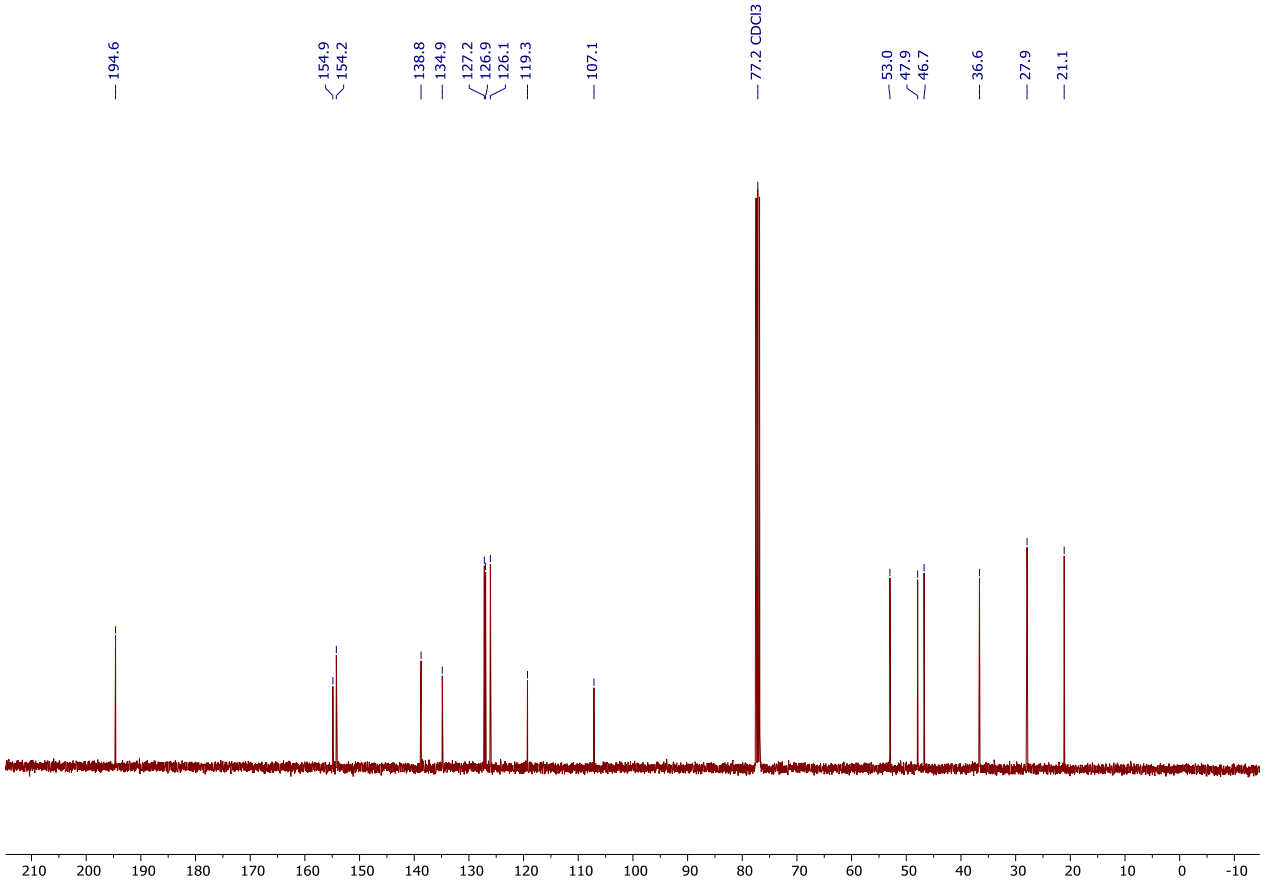
Copy of $^{13}C\{^{1}H\}$ (100.61 MHz, $CDCl_3$) NMR spectrum of **4p**



Copy of ^{1}H (400.13 MHz, $CDCl_3$) NMR spectrum of **4q**



Copy of $^{13}C\{^{1}H\}$ (100.61 MHz, $CDCl_3$) NMR spectrum of **4q**



3. Crystallographic data for compounds 4a and 4f

X-ray single crystal analysis was performed on a SuperNova diffractometer. Crystals were kept at 100(2) K during data collection. Using Olex2[4], the structures were solved with the SHELXT[5] structure solution program using intrinsic phasing and refined with the SHELXL[6] refinement package using least squares minimisation.

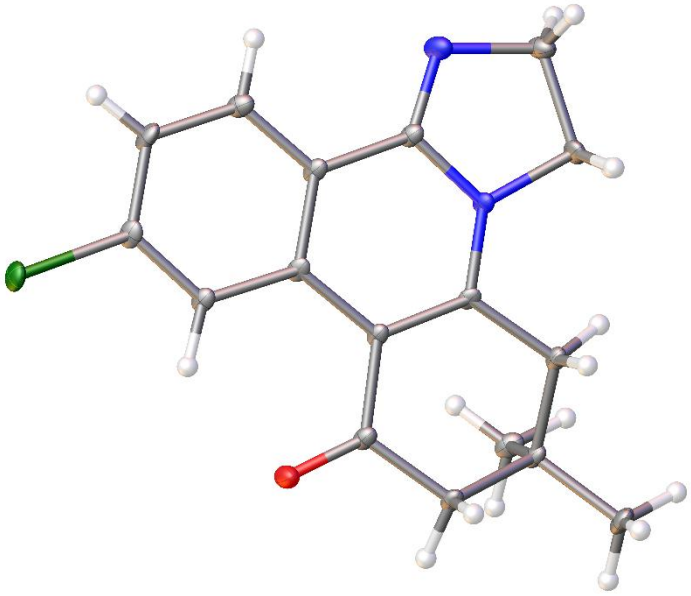


Figure S2. ORTEP representation of compound **4a** (thermal ellipsoids are shown at 50% probability).

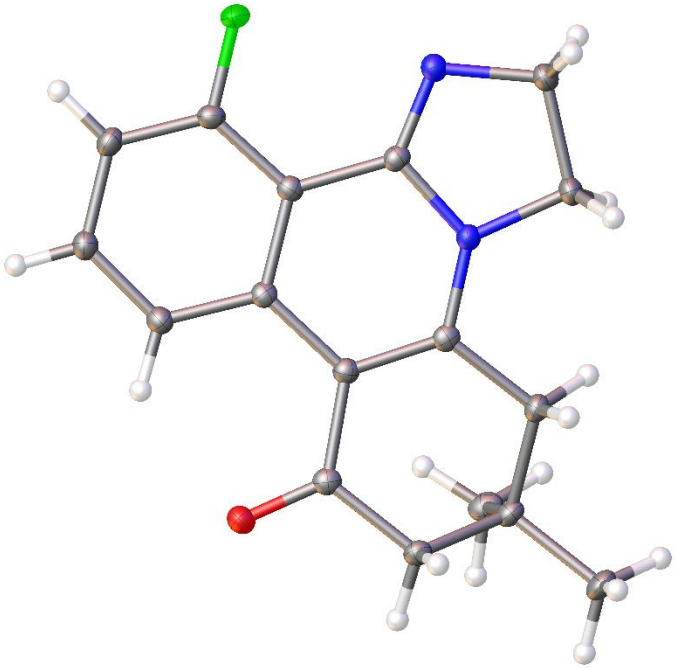


Figure S3. ORTEP representation of compound **4f** (thermal ellipsoids are shown at 50% probability).

Table S1. Crystal data and structure refinement for **4a** and **4f.**		
Compound number	**4a**	**4f**
CCDC	**2450071**	**2502221**
Empirical formula	$C_{17}H_{17}ClN_2O$	$C_{17}H_{17}FN_2O$
Formula weight	300.77	284.32
Temperature/K	99.9(2)	100.15
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	6.2845(2)	8.24950(10)
b/Å	13.6733(3)	13.9108(2)
c/Å	16.7189(4)	12.9245(2)
α/°	90	90
β/°	91.028(2)	106.252(2)
γ/°	90	90
Volume/Å^3	1436.42(7)	1423.91(4)
Z	4	4
ρ_{calc} g/cm^3	1.391	1.326
μ/mm^{-1}	2.347	0.755
F(000)	632.0	600.0
Crystal size/mm^3	0.22 × 0.16 × 0.12	0.18 × 0.14 × 0.12
Radiation	Cu Kα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.354 to 147.342	9.552 to 158.838
Index ranges	$-6 \le h \le 7$, $-16 \le k \le 9$, $-20 \le l \le 18$	$-10 \le h \le 9$, $-14 \le k \le 17$, $-13 \le l \le 16$
Reflections collected	5289	10502

Independent reflections	2804 [R_{int} = 0.0461, R_{sigma} = 0.0453]	2974 [R_{int} = 0.0237, R_{sigma} = 0.0243]
Data/restraints/parameters	2804/0/258	2974/0/192
Goodness-of-fit on F^2	1.057	1.096
Final R indexes [I>=2σ (I)]	R_1 = 0.0549, wR_2 = 0.1460	R_1 = 0.0442, wR_2 = 0.1233
Final R indexes [all data]	R_1 = 0.0583, wR_2 = 0.1521	R_1 = 0.0473, wR_2 = 0.1257
Largest diff. peak/hole / e $Å^{-3}$	0.73/−0.79	0.33/−0.29

4. References

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