Electronic supplementary materials *Mendeleev Commun.*, 2026, **36**, 171–173

Catalyst-free cyclization of DBU with α,β-ynones: substituent-controlled divergence

Olga V. Petrova, Igor A. Ushakov and Boris A. Trofimov

Contents

General Experiment

The NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.1 MHz for ^{1}H, 100.6 MHz for ^{13}C) in $CDCl_3$. The residual solvent signals were used as references: 7.26 ppm for ^{1}H and 77.1 ppm for ^{13}C. Chemical shifts (δ) are quoted in parts per million (ppm). Coupling constants (J) were measured in hertz (Hz) from one-dimensional spectra, and multiplicities were abbreviated as follows: s (singlet), br. m (broad multiplet), d (doublet), dd (doublet of doublets), ddd (doublet of doublets of doublets), dt (doublet of triplet), q (quartet), t (triplet) and m (multiplet). IR spectra were recorded on a two-beam Bruker Vertex 70 spectrometer in a KBr pellets or film, CaF_2 glass. High-resolution mass spectra were recorded on an Agilent 6210 HRMS-TOF-ESI Mass spectrometer. Electrostatic sputtering, registration of positive ions. Sample solvent - MeCN with the addition of 0.1% heptafluorobutanoic acid and with the addition of calibration mixture for mass spectrometer. Melting points (uncorrected) were measured using a Stuart scientific melting point SMP3 apparatus. UV/Vis absorption spectra were measured on a Lambda-35 (Perkin-Elmer) or an Shimadzu UV 3101PC and an Ocean Optics HR 2000 spectrophotometers. Excitation and fluorescence spectra were measured on a FLSP-920 combined steady state and time resolved fluorescence spectrometers (Edinburgh Instrument) or on Shimadzu RF-6000. Fluorescence spectra were obtained with a Xenon lamp and 1.0 cm quartz cuvettes. All measurements have been carried out at room temperature (20–25 °C).

The starting alkynones **1a-f** were prepared according to the methods [S1, S2].

Reaction DBU with ynones 1a-f at 80 °C.

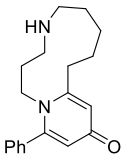
A mixture of ynone **1a-f** (1.0 mmol) and DBU (228 mg, 1.5 mmol) in acetonitrile (12 mL) were stirred at 80 °C for 3 h. After cooling to room temperature, the reaction mixture was diluted with brine (35-40 mL), extracted with diethyl ether (3 x 5 mL), the ether extracts were washed with water (6 x 15 mL) and dried over $MgSO_4$. After removing the solvent from the residue, compounds **2, 4a,b, 5a,d-e** were isolated by column chromatography (SiO_2, eluent diethyl ether/CH_2Cl_2, gradient from 1:0 to 0:1, than CH_2Cl_2/MeOH, gradient from 1:0 to 0:1).

The combined aqueous layers were extracted with chloroform (5 x 20 mL), dried over $MgSO_4$. Salts **3a-f** were obtained after purification of the crude product by column chromatography (SiO_2, eluent CH_2Cl_2/MeOH, gradient from 1:0 to 0:1).

Reaction DBU with ynones 1a-f at room temperature (20-25 °C).

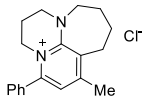
A mixture of ynone **1a-f** (1.0 mmol) and DBU (228 mg, 1.5 mmol) in acetonitrile (12 mL) were stirred at room temperature for 24 h. The reaction mixture was then diluted with brine (35-40 mL), extracted with diethyl ether (3 x 5 mL), the ether extracts were washed with water (6 x 15 mL) and dried over $MgSO_4$. Compounds **4a,b** were isolated after removing the solvent and purified by column chromatography (SiO_2, eluent CH_2Cl_2/MeOH, gradient from 1:0 to 0:1). The combined aqueous layers were extracted with chloroform (5 x 20 mL), dried over $MgSO_4$. Salts **3a,b,d-f** were obtained after purification of the crude product by column chromatography (SiO_2, eluent CH_2Cl_2/MeOH, gradient from 1:0 to 0:1).

13-Phenyl-2,3,4,5,6,7,8,9-octahydropyrido[1,2-*e*][1,5]diazacycloundecin-11(1*H*)-one (2)



Yield 47 mg (16%, at 80 °C), light yellow crystals, mp 181–183 °C. ^{1}H NMR δ: 7.42–7.41 (m, 3H, Ph), 7.32–7.31 (m, 2H, Ph), 6.30 (d, 1H, HC=, *J* 2.6 Hz), 6.18 (d, 1H, HC=, *J* 2.6 Hz), 4.35–4.12 (br. m, 1H, CH_2), 3.95–3.70 (br. m, 1H, CH_2), 3.42–3.08 (br. m, 1H, CH_2), 2.79–2.54 (br. m, 2H, CH_2), 2.53–2.26 (br. m, 3H, CH_2), 1.76–1.71 (m, 2H, CH_2), 1.67–1.59 (m, 2H, CH_2), 1.51–1.26 (br. m, 4H, CH_2). ^{13}C NMR, δ: 178.6, 154.4, 152.7, 136.0, 129.1, 128.6 (4C), 119.9, 117.3, 46.5, 45.9, 44.9, 31.2, 30.1, 27.1, 26.0, 25.2. IR (film), ν, cm^{-1}: 3056, 2927, 2852, 2812, 1625, 1602, 1551, 1484, 1450, 1350, 1241, 1176, 863, 752, 705; (CaF_2, film), ν, cm^{-1}: 3298. HRMS (ESI) *m/z*: calcd for $[C_{19}H_{25}N_2O]^+$: 297.1967 [*M* + H]$^+$; found 297.1965.

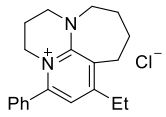
1-Methyl-3-phenyl-5,6,7,8,9,10-hexahydro-4*H*-6a-aza-3a-azoniacyclohepta-[1,2,3-*de*]naphthalene chloride (3a)



Yield 41 mg (13%, at 80 °C), 25 mg (8%, at rt), yellow solid, mp 131–134 °C. ^{1}H NMR, δ: 7.51–7.48 (m, 5H, Ph), 6.54 (s, 1H, HC=), 4.38–4.29 (m, 2H, CH_2), 3.86–3.82 (m, 2H, CH_2), 3.77-3.73 (m, 2H, CH_2), 2.91–2.87 (m, 2H, CH_2), 2.32 (s, 3H, Me), 2.19–

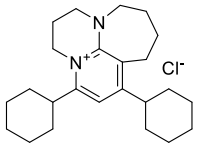
2.14 (m, 2H, CH_2), 2.11–2.05 (m, 2H, CH_2), 1.95–1.88 (m, 2H, CH_2). ^{13}C NMR δ: 153.6, 152.1, 147.7, 132.4, 130.5, 129.2 (2C), 129.1 (2C), 126.0, 118.5, 53.3, 49.7 (2C), 27.0, 23.6, 22.6, 22.2, 20.4. IR (film), ν, см$^{-1}$: 3057, 2922, 2861, 1624, 1600, 1567, 1446, 1318, 1251, 1181, 1142, 1124, 1076, 1002, 846, 704. HRMS (ESI) *m/z*: calcd for $[C_{19}H_{23}N_2]^+$: 279.1861 [*M* – Cl]$^+$; found 279.1865.

1-Ethyl-3-phenyl-5,6,7,8,9,10-hexahydro-4*H*-6a-aza-3a-azoniacyclohepta-[1,2,3-*de*]naphthalene chloride (3b)



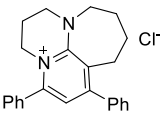
Yield 49 mg (15%, at 80 ºC), 26 mg (8%, at rt), yellow oil. ^{1}H NMR, δ: 7.52–7.49 (m, 5H, Ph), 6.57 (s, 1H, CH=), 4.36–4.33 (m, 2H, CH_2), 3.86–3.84 (m, 2H, CH_2), 3.80–3.77 (m, 2H, CH_2), 2.93–2.90 (m, 2H, CH_2), 2.64 (q, 2H, $\underline{CH_2}CH_3$, *J* 7.6 Hz), 2.20–2.14 (m, 2H, CH_2), 2.12–2.07 (m, 2H, CH_2), 1.94–1.88 (m, 2H, CH_2), 1.23 (t, 3H, $CH_2\underline{CH_3}$, *J* 7.6 Hz). ^{13}C NMR, δ: 157.2, 153.5, 147.9, 132.4, 130.3, 129.1 (2C), 128.9 (2C), 125.3, 116.6, 53.3, 49.8, 49.5, 26.4, 26.1, 23.5, 22.6, 22.5, 13.5. IR (film), ν, cm^{-1}: 3055, 2931, 2869, 1622, 1599, 1567, 1446, 1318, 1264, 1181, 1111, 775, 748, 705. HRMS (ESI) *m/z*: calcd for $[C_{20}H_{25}N_2]^+$: 293.2018 [*M* – Cl]$^+$; found 293.2019.

1,3-Dicyclohexyl-5,6,7,8,9,10-hexahydro-4*H*-6a-aza-3a-azoniacyclohepta-[1,2,3-*de*]naphthalene chloride (3c)



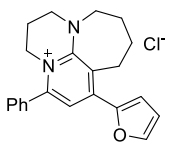
Yield 113 mg (29%, at 80 ºC), beige solid, mp 144–146 ºC. ^{1}H NMR, δ: 6.60 (s, 1H, HC=), 4.54–4.48 (m, 2H, CH_2), 3.76–3.71 (m, 4H, CH_2), 2.95–2.89 (m, 1H, CH_2), 2.84–2.81 (m, 2H, CH_2), 2.73–2.66 (m, 1H, CH_2), 2.36–2.30 (m, 2H, CH_2), 2.10–2.00 (m, 4H, CH_2), 1.97–1.78 (m, 8H, CH_2), 1.72–1.66 (m, 2H, CH_2), 1.53–1.43 (m, 2H, CH_2), 1.40–1.32 (m, 6H, CH_2), 1.30–1.23 (m, 2H, CH_2). ^{13}C NMR, δ: 160.9, 153.7, 153.5, 122.9, 109.9, 53.2, 49.4, 46.1, 40.5, 39.7, 32.7 (2C), 32.5 (2C), 26.2 (2C), 26.0 (2C), 25.9, 25.6, 25.6, 23.3, 23.1, 22.9. IR (film), ν, cm^{-1}: 2930, 2855, 1622, 1565, 1459, 1395, 1311, 1255, 1254, 1184, 998, 927, 846, 729, 639. HRMS (ESI) *m/z*: calcd for $[C_{24}H_{37}N_2]^+$: 353.2957 [*M* – Cl]$^+$; found 353.2958.

1,3-Diphenyl-5,6,7,8,9,10-hexahydro-4*H*-6a-aza-3a-azoniacyclohepta[1,2,3-*de*]-naphthalene chloride (3d)



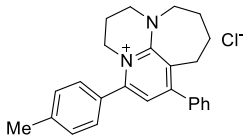
Yield 47 mg (12%, at 80 ºC), 158 mg (41%, at rt), yellow solid, mp 98–103 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$) δ: 7.50–7.45 (m 5H, Ph), 7.42–7.38 (m, 3H, Ph), 7.30–7.27 (m, 2H, Ph), 6.59 (s, 1H, HC=), 4.38–4.32 (m, 2H, CH_2), 3.93–3.89 (m, 2H, CH_2), 3.80–3.77 (m, 2H, CH_2), 2.77–2.74 (m, 2H, CH_2), 2.25–2.18 (m, 2H, CH_2), 2.14–2.05 (m, 2H, CH_2), 1.86–1.79 (m, 2H, CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 155.0, 154.4, 147.9, 137.1, 132.3, 130.4, 129.3 (2C), 129.1 (2C), 128.9 (2C), 128.7 (2C), 128.1, 125.6, 117.3, 53.5, 49.9, 49.7, 28.9, 23.7 (2C), 22.5. IR (KBr), ν, cm^{-1}: 3062, 2928, 2859, 1622, 1600, 1563, 1493, 1444, 1389, 1369, 1318, 1252, 1176, 1076, 1025, 1000, 849, 770, 704. HRMS (ESI) *m/z*: calcd for $[C_{24}H_{25}N_2]^+$: 341.2018 [*M* – Cl]$^+$; found 341.2023.

1-(2-Furyl)-3-phenyl-5,6,7,8,9,10-hexahydro-4*H*-6a-aza-3a-azoniacyclohepta-[1,2,3-*de*]naphthalene chloride (3e)



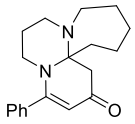
Yield 51 mg (14%, at 80 ºC), 154 mg (42%, at rt), yellow solid, mp 113–116 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$) δ: 7.64–7.63 (m, 1H, H-5, furan), 7.56–7.53 (m, 5H, Ph), 6.99 (s, 1H, HC=), 6.92-6.91 (m, 1H, H-3, furan), 6.61–6.60 (m, 1H, H-4, furan), 4.40–4.38 (m, 2H, CH_2), 3.95–3.93 (m, 2H, CH_2), 3.87–3.84 (m, 2H, CH_2), 3.13–3.10 (m, 2H, CH_2), 2.25–2.20 (m, 2H, CH_2), 2.16–2.12 (m, 2H, CH_2), 2.05–2.00 (m, 2H, CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 154.6, 148.6, 148.1, 145.6, 141.2, 132.5, 130.5, 129.2 (2C), 129.0 (2C), 122.4, 116.2, 113.3, 112.8, 53.6, 49.8, 49.6, 29.3, 23.7, 22.9, 22.5. IR (KBr), ν, cm^{-1}: 3055, 2955, 2866, 1622, 1599, 1562, 1481, 1456, 1446, 1367, 1318, 1265, 1178, 1079, 1030, 1001, 937, 884, 862, 775, 705. HRMS (ESI) *m/z*: calcd for $[C_{26}H_{30}N_3O]^+$: 331.1810 [*M* – Cl]$^+$; found 331.1812.

3-(4-Methylphenyl)-1-phenyl-5,6,7,8,9,10-hexahydro-4*H*-6a-aza-3a-azoniacyclohepta-[1,2,3-*de*]naphthalene chloride (3f)



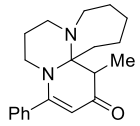
Yield 59 mg (15%, at 80 ºC), 153 mg (39%, at rt), light yellow solid, mp 102–106 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$) δ: 7.48–7.45 (m, 3H, Ph), 7.43–7.41 (m, 2H, 4-Me-C_6H_4), 7.33–7.31 (m, 4H, Ph, 4-Me-C_6H_4), 6.63 (s, 1H, HC=), 4.48–4.44 (m, 2H, CH_2), 3.99–3.95 (m, 2H, CH_2), 3.88–3.85 (m, 2H, CH_2), 2.81–2.78 (m, 2H, CH_2), 2.41 (s, 3H, Me), 2.29–2.21 (m, 2H, CH_2), 2.17–2.14 (m, 2H, CH_2), 1.90–1.83 (m, 2H, CH_2).^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 155.1, 154.5, 148.3, 140.9, 137.3, 129.9 (2C), 129.5, 129.4, 128.9 (2C), 128.8 (2C), 128.2 (2C), 125.5, 117.4, 53.6, 50.1, 49.8, 29.0, 23.9, 23.8, 22.7, 21.3. IR (KBr), ν, cm^{-1}: 3435, 3055, 2944, 2855, 1625, 1563, 1513, 1446, 1444, 1374, 1318, 1252, 1176, 1170, 998, 825, 775, 706. HRMS (ESI) *m/z*: calcd for $[C_{25}H_{27}N_2]^+$: 355.2174 [*M* – Cl]$^+$; found 355.2178.

4-Phenyl-7,8,11,12,13,14-hexahydro-6*H*,10*H*-pyrido[2',1':2,3]pyrimido-[1,2-*a*]azepin-2(1*H*)-one (4a)



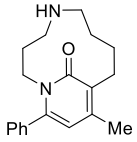
Yield 36 mp (12%, at 80 ºC), 65 mg (22%, at rt), light yellow crystals, mp 153–154 ºC. ^{1}H NMR, δ: 7.40–7.38 (m, 3H, Ph), 7.30–7.28 (m, 2H, Ph), 5.04 (s, 1H, HC=), 3.49 (dt, 1H, CH_2, *J* 12.5, 4.8 Hz), 3.33 (dd, 1H, CH_2, *J* 6.4, 1.6 Hz,), 3.18 (ddd, 1H, CH_2, *J* 10.4, 8.4, 2.4 Hz,), 3.10 (d, 1H, CH_2, *J* 16.3 Hz), 2.88 (ddd, 1H, CH_2, *J* 9.6, 5.2, 2.0 Hz), 2.83–2.81 (m, 2H, CH_2), 2.42 (dd, 1H, CH_2, *J* 9.6, 5.2 Hz,) , 2.36 (d, 1H, CH_2, *J* 16.3 Hz), 1.94 (dd, 1H, CH_2, *J* 9.1, 5.8 Hz), 1.88–1.76 (m, 2H, CH_2), 1.75–1.50 (m, 6H, CH_2). ^{13}C NMR, δ: 193.1, 163.0, 137.2, 129.6, 128.6 (2C), 127.8 (2C), 101.4, 79.3, 50.7, 45.2, 43.1, 41.4, 32.4, 30.8, 29.3, 23.8, 22.4. IR (film), ν, cm^{-1}: 3057, 2926, 2852, 1631, 1580, 1536, 1496, 1452, 1438, 1360, 1259, 1234, 1144, 1022, 769, 702. HRMS (ESI) *m/z*: calcd for $[C_{19}H_{25}N_2O]^+$: 297.1967 [*M* + H]$^+$; found 297.1966.

1-Methyl-4-phenyl-7,8,11,12,13,14-hexahydro-6*H*,10*H*-pyrido[2',1':2,3]pyrimido-[1,2-*a*]azepin-2(1*H*)-one (4b)



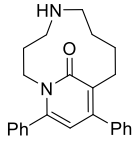
Yield 134 mg (43%, at 80 °C), 124 mg (40%, at rt), light yellow oil. The spectral characteristics of compound **4b** correspond with those given in the article [S3].

11-Methyl-13-phenyl-1,5-diazabicyclo[8.3.1]tetradeca-10,12-dien-14-one (5a)



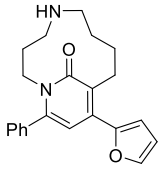
Yield 21 mg (7%, at 80 °C), yellow solid, mp 120-124 °C. The spectral characteristics of compound **5a** correspond with those given in the article [S4].

11,13-Diphenyl-1,5-diazabicyclo[8.3.1]tetradeca-10,12-dien-14-one (5d)



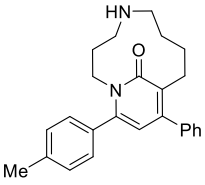
Yield 118 mg (33%, at 80 °C), yellow solid, mp 88–92 °C. The spectral characteristics of compound **5d** correspond with those given in the article [S4].

11-(2-Furyl)-13-phenyl-1,5-diazabicyclo[8.3.1]tetradeca-10,12-dien-14-one (5e)



Yield 122 mg (35%, at 80 °C), dark yellow solid, mp 99–103 °C. The spectral characteristics of compound **5e** correspond with those given in the article [S4].

13-(4-Methylphenyl)-11-phenyl-1,5-diazabicyclo[8.3.1]tetradeca-10,12-dien-14-one (5f)



Yield 130 mg (35%, at 80 °C), viscous oil. The spectral characteristics of compound **5f** correspond with those given in the article [S4].

Table S1 Photophysical properties of compounds **5d-f** (absorption and emission band maxima, Stokes shifts, molar extinction coefficients, and fluorescence quantum yields), solvent – MeCN.

compound	λ_{abs}, nm	λ_{em}, nm	Δ cm^{-1}	ε, M^{-1} cm^{-1}	Φ
5d	331	440	7500	7900	0.02
5e	344	460	7350	8100	0.04
5f	333	450	7800	8500	0.05

For more details see [S4].

References

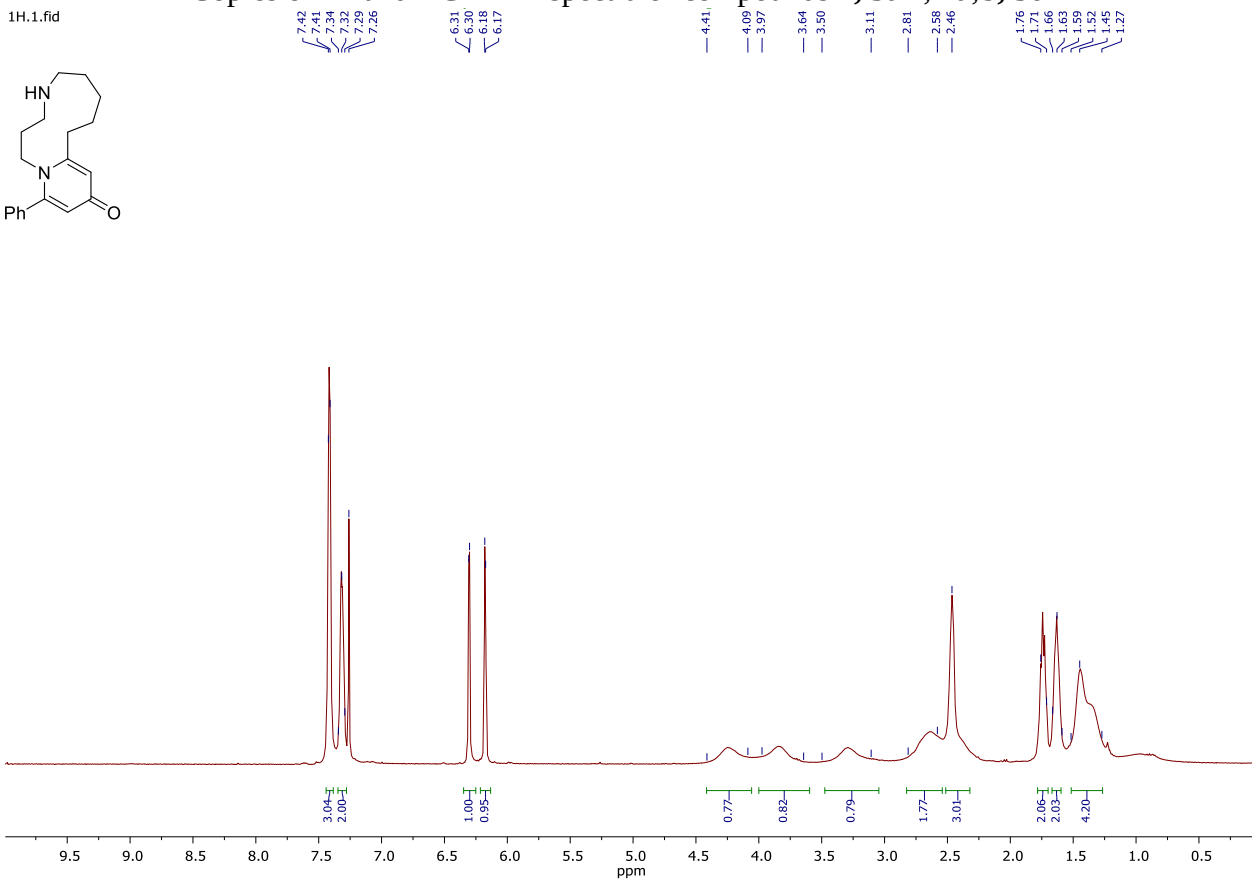
S1 A. S. Zanina, S. I. Shergina, I. E. Sokolov and I. L. Kotlyarevskii, *Bull. Acad. Sci. USSR. Div. Chem. Sci*., 1981, **39**, 918; doi.org/10.1007/BF00955319

S2 R. J. Cox, D. J. Ritson, T. A. Dane, J. Berge, J. P. H. Charmant and A. Kantacha, *Chem. Commun*., 2005, 1037; https://doi.org/10.1039/b414826f.

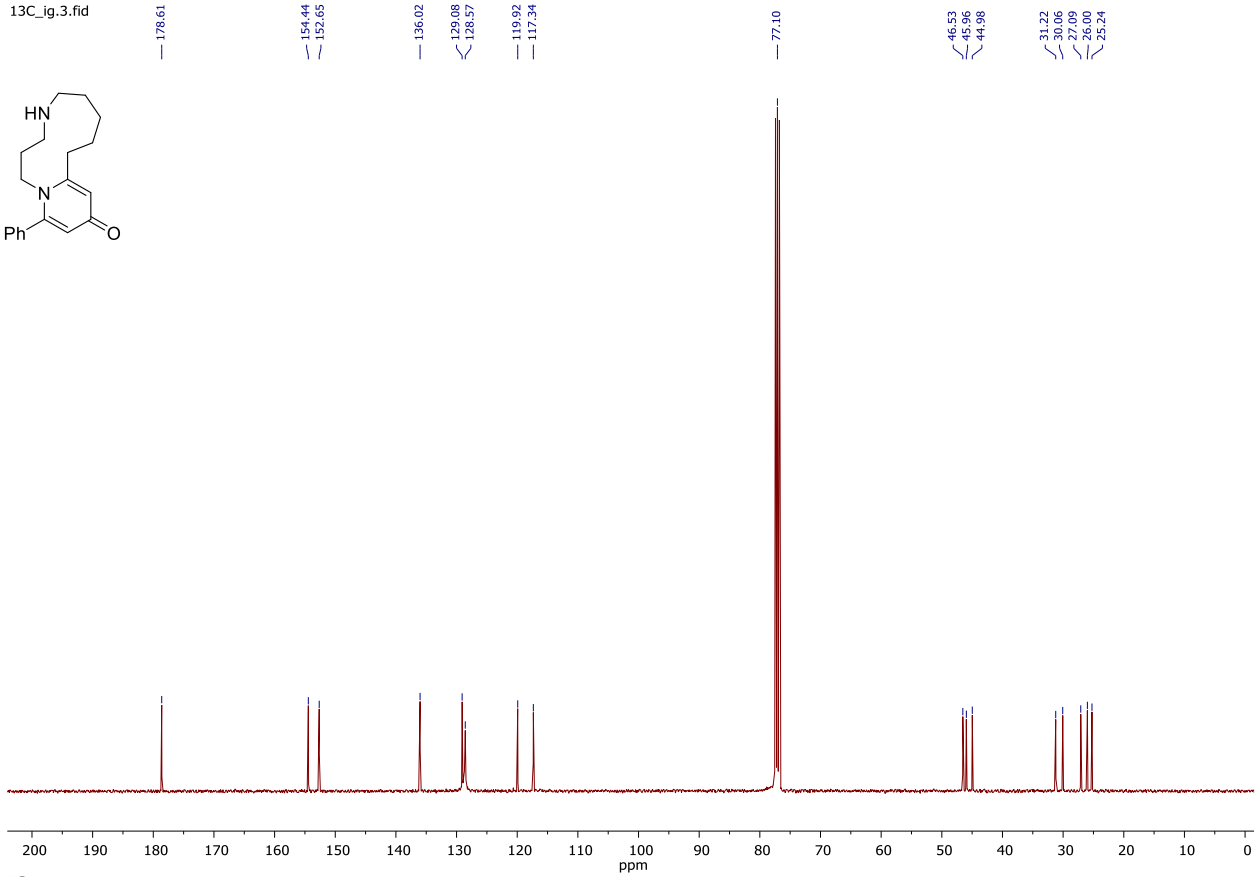
S3 T. P. Reddy, J. Gujral, P. Roy and D. B. Ramachary, *Org. Lett*., 2020, **22**, 9653; https://doi.org/10.1021/acs.orglett.0c03711

S4 B. A. Trofimov, L. N. Sobenina, O. V. Petrova, E. F. Sagitova, K. B. Petrushenko, D. N. Tomilin, E. G. Martyanova, V. F. Razumov, L. A. Oparina, I. A. Ushakov, D. V. Korchagin, A. M. Belogolova and A. B. Trofimov, *J. Org. Chem*., 2024, **89**, 18142; https://doi.org/10.1021/acs.joc.4c02002

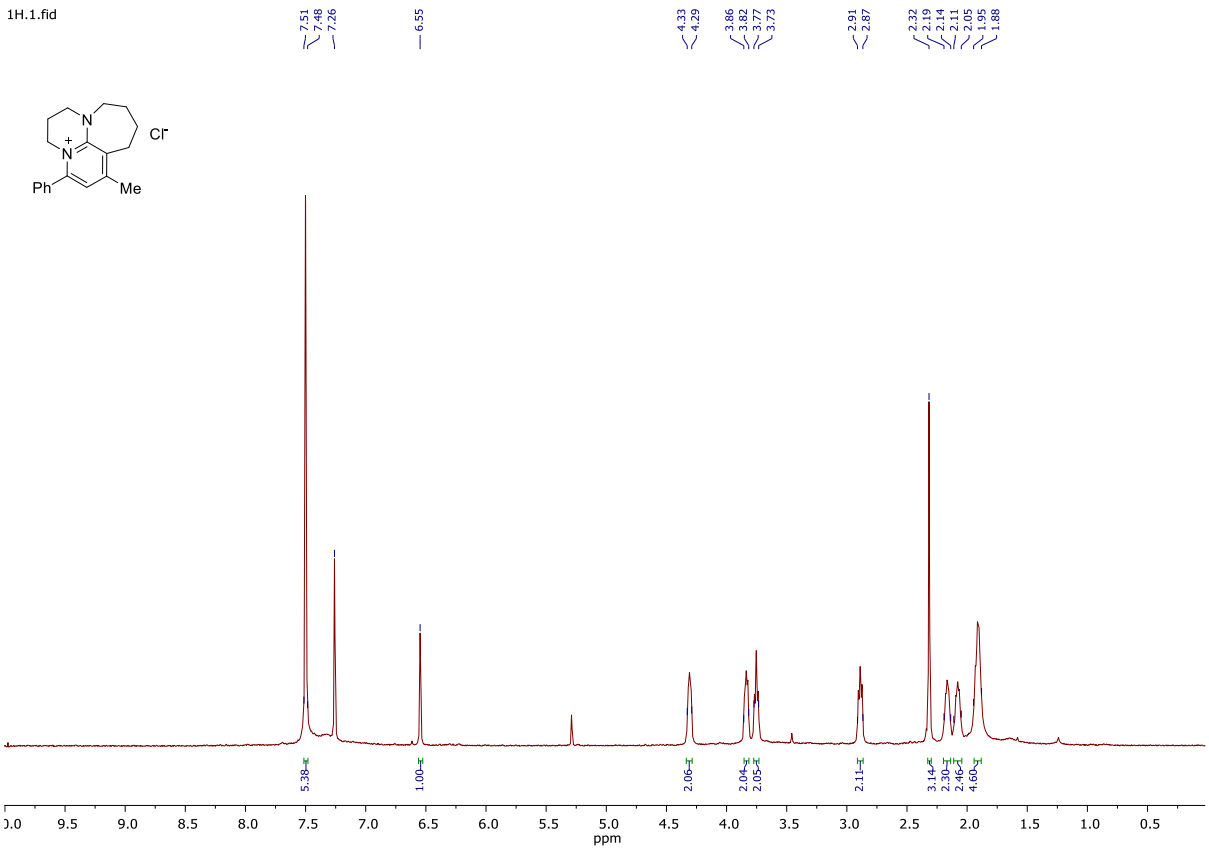
Copies of ^{1}H and ^{13}C NMR spectra of compounds **2, 3a-f**, **4a**,**b, 5d-f**



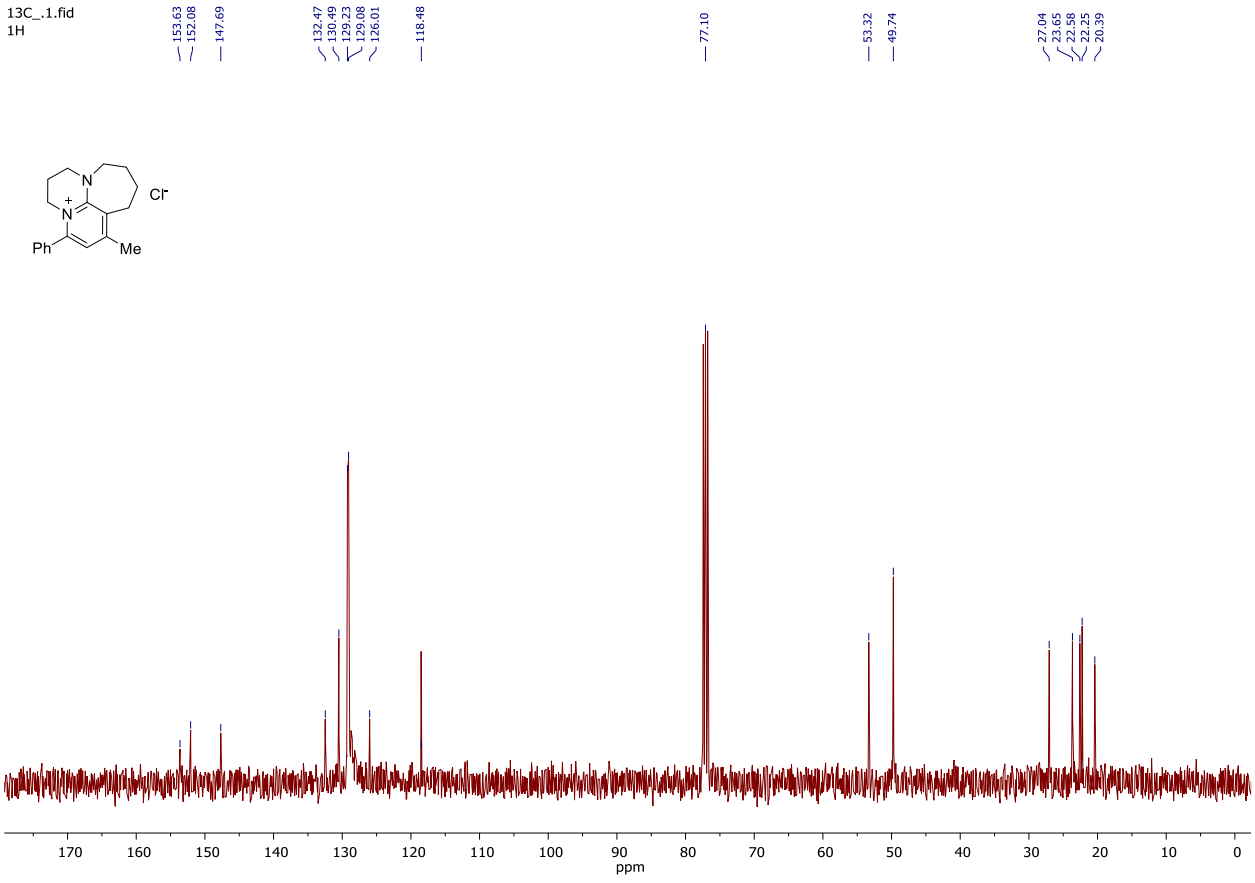
^{1}H NMR spectrum of compound **2** (400.13 MHz, $CDCl_3$)



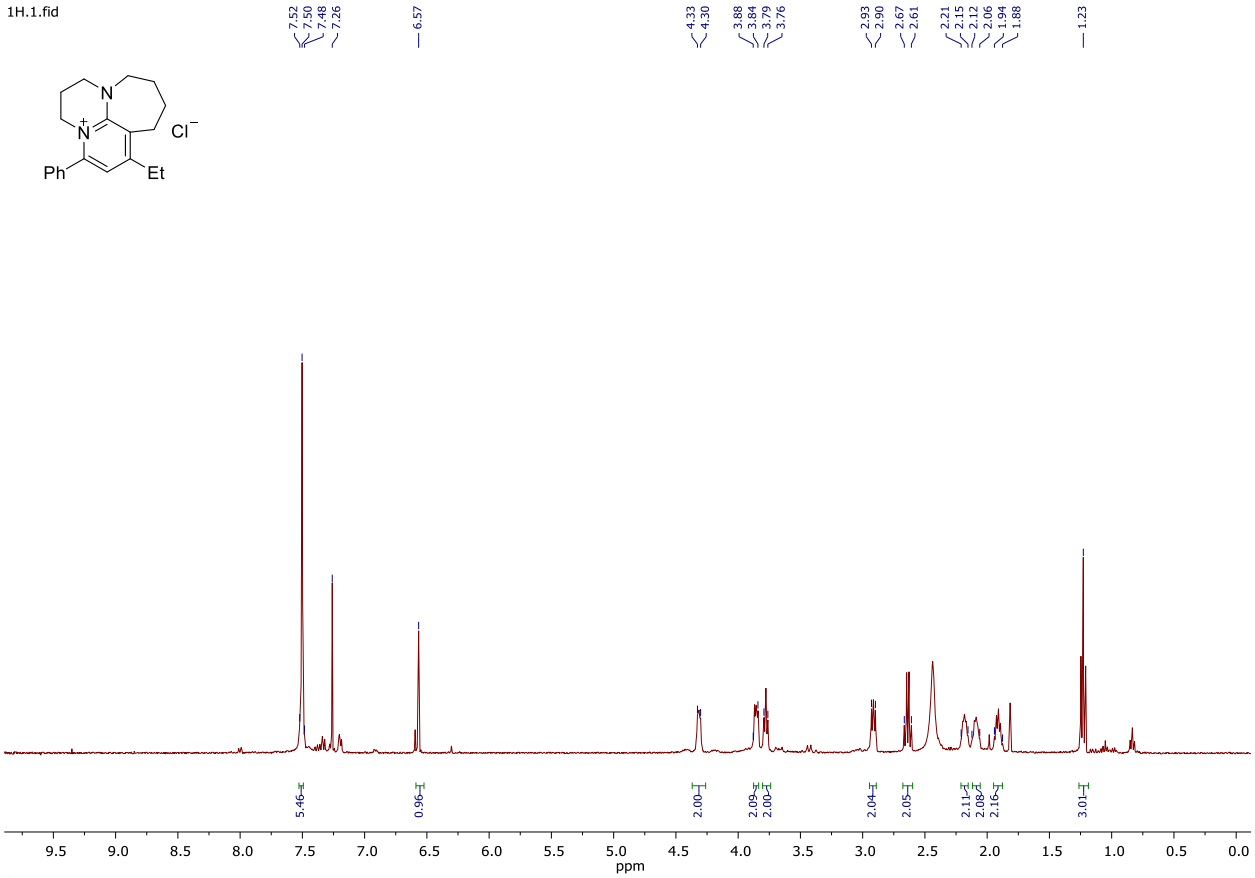
^{13}C NMR spectrum of compound **2** (100.6 MHz, $CDCl_3$)



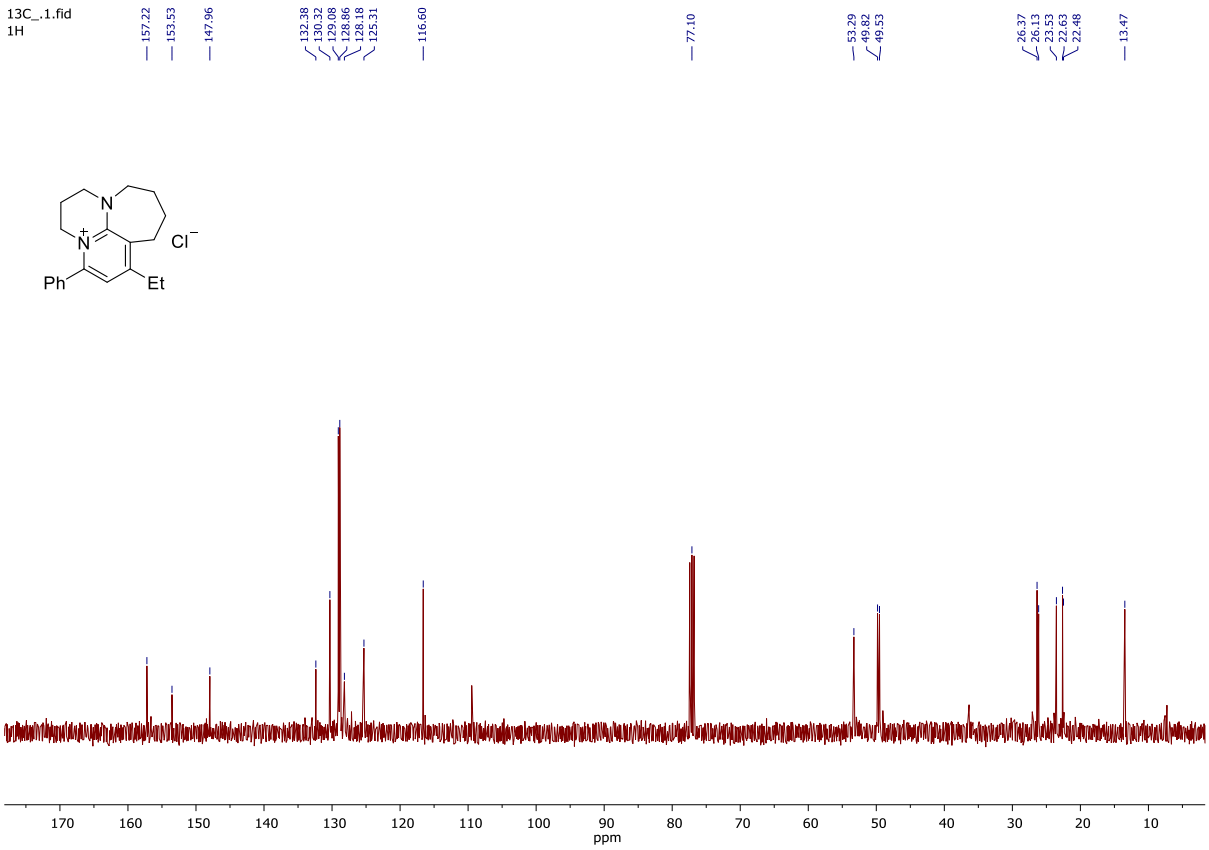
^{1}H NMR spectrum of compound **3a** (400.13 MHz, $CDCl_3$)



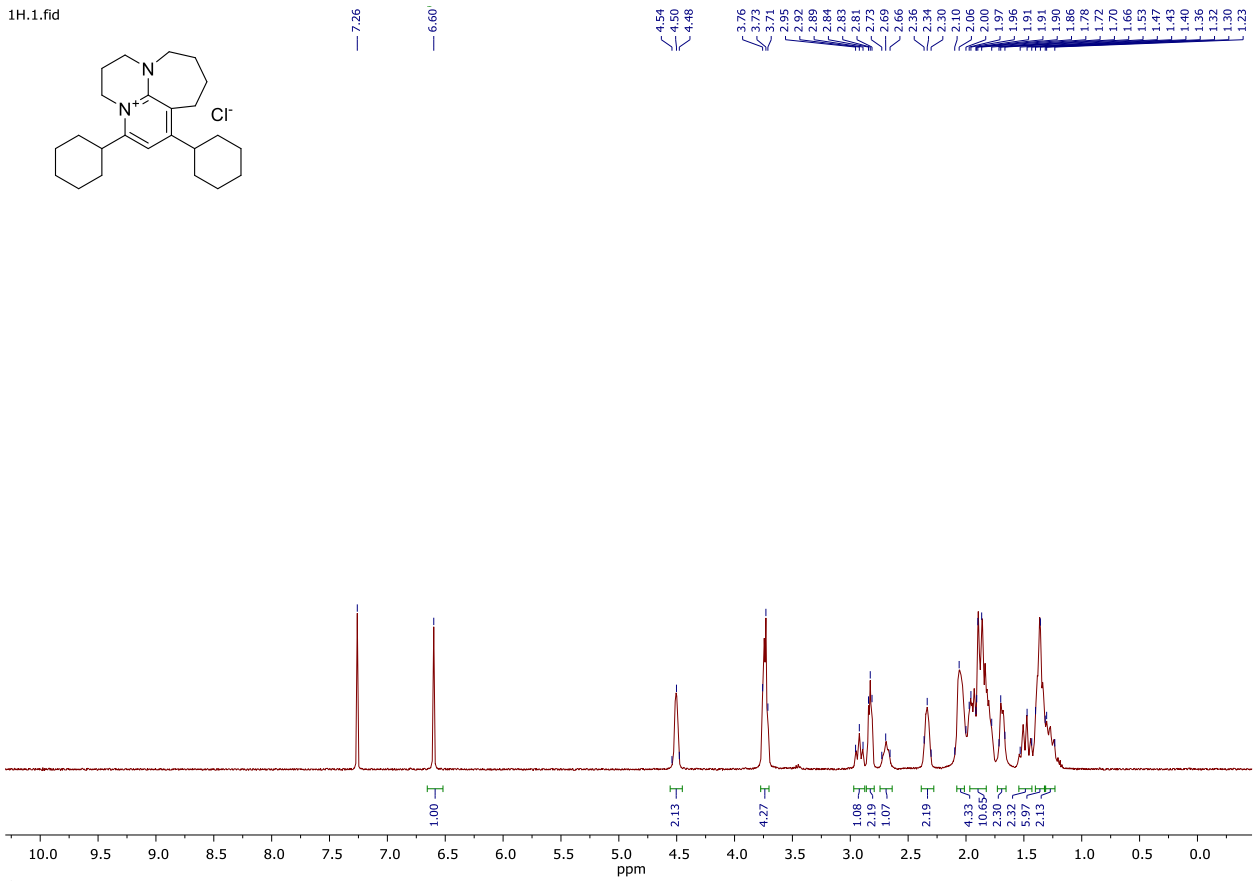
^{13}C NMR spectrum of compound **3a** (100.6 MHz, $CDCl_3$)



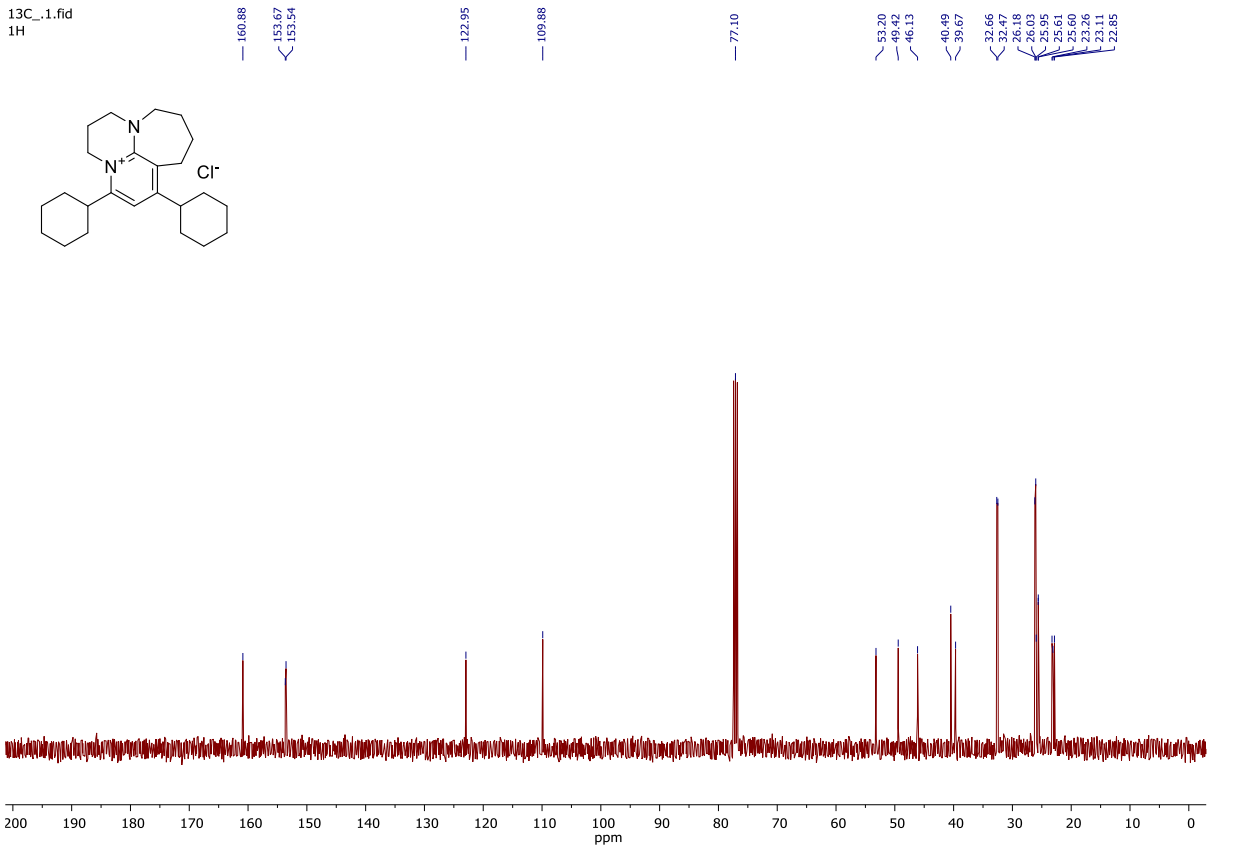
^{1}H NMR spectrum of compound **3b** (400.13 MHz, $CDCl_3$)



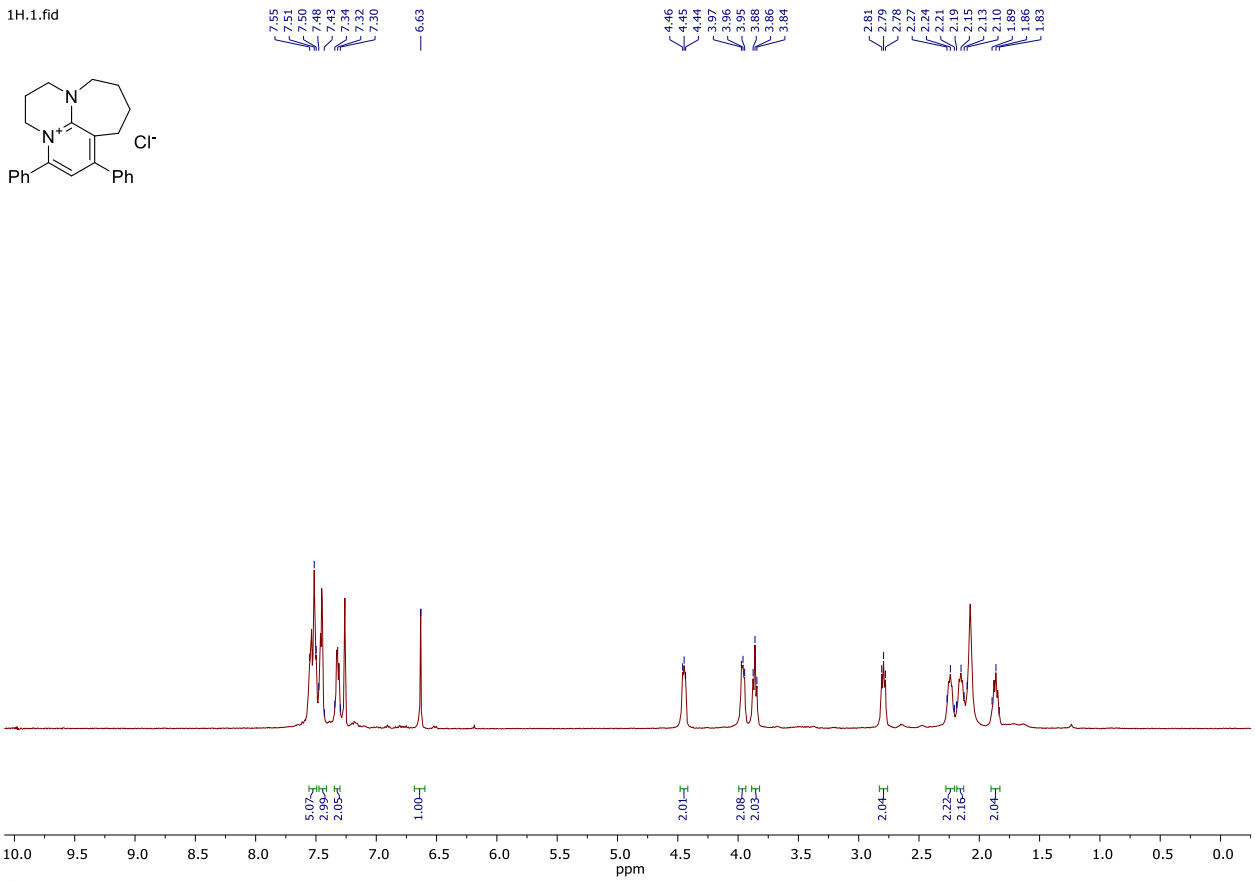
^{13}C NMR spectrum of compound **3b** (100.6 MHz, $CDCl_3$)



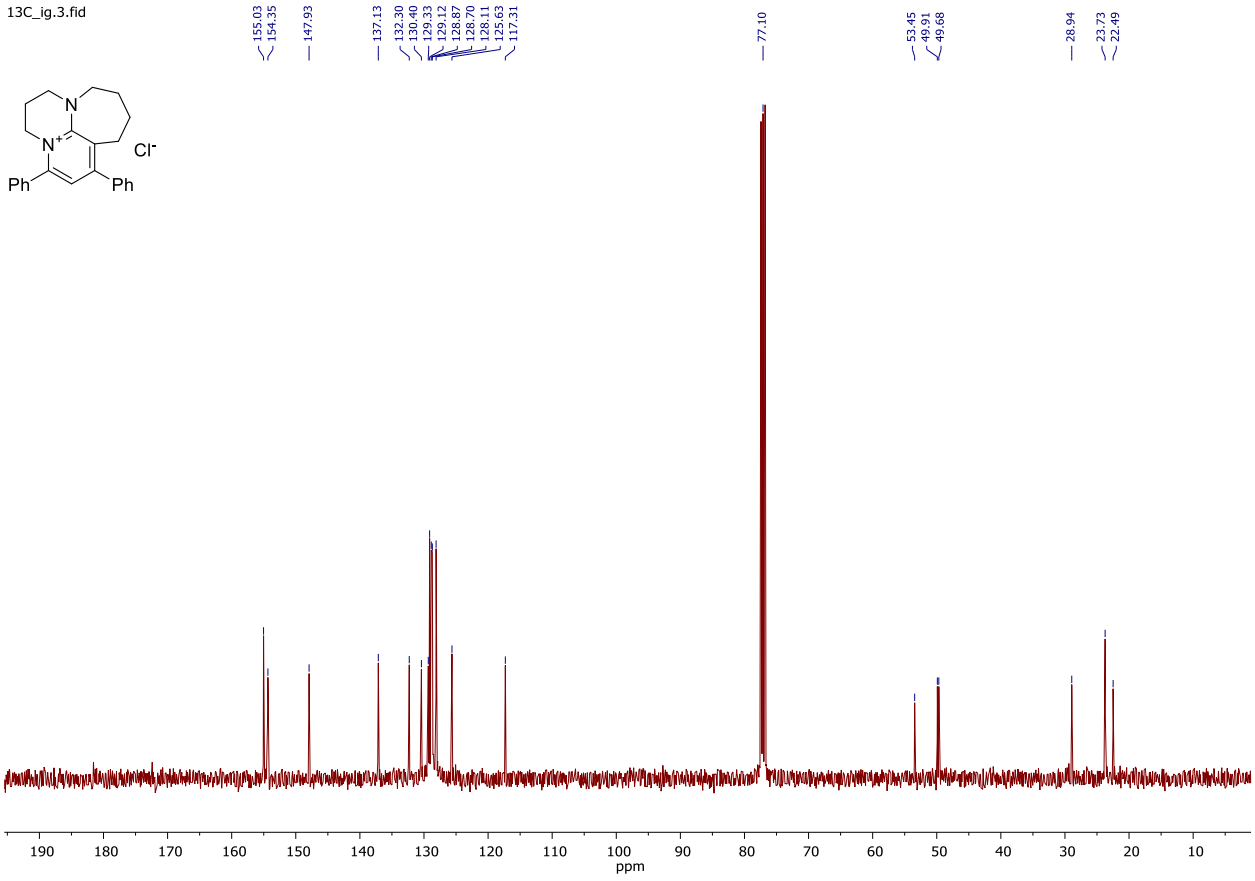
^{1}H NMR spectrum of compound **3c** (400.13 MHz, $CDCl_3$)



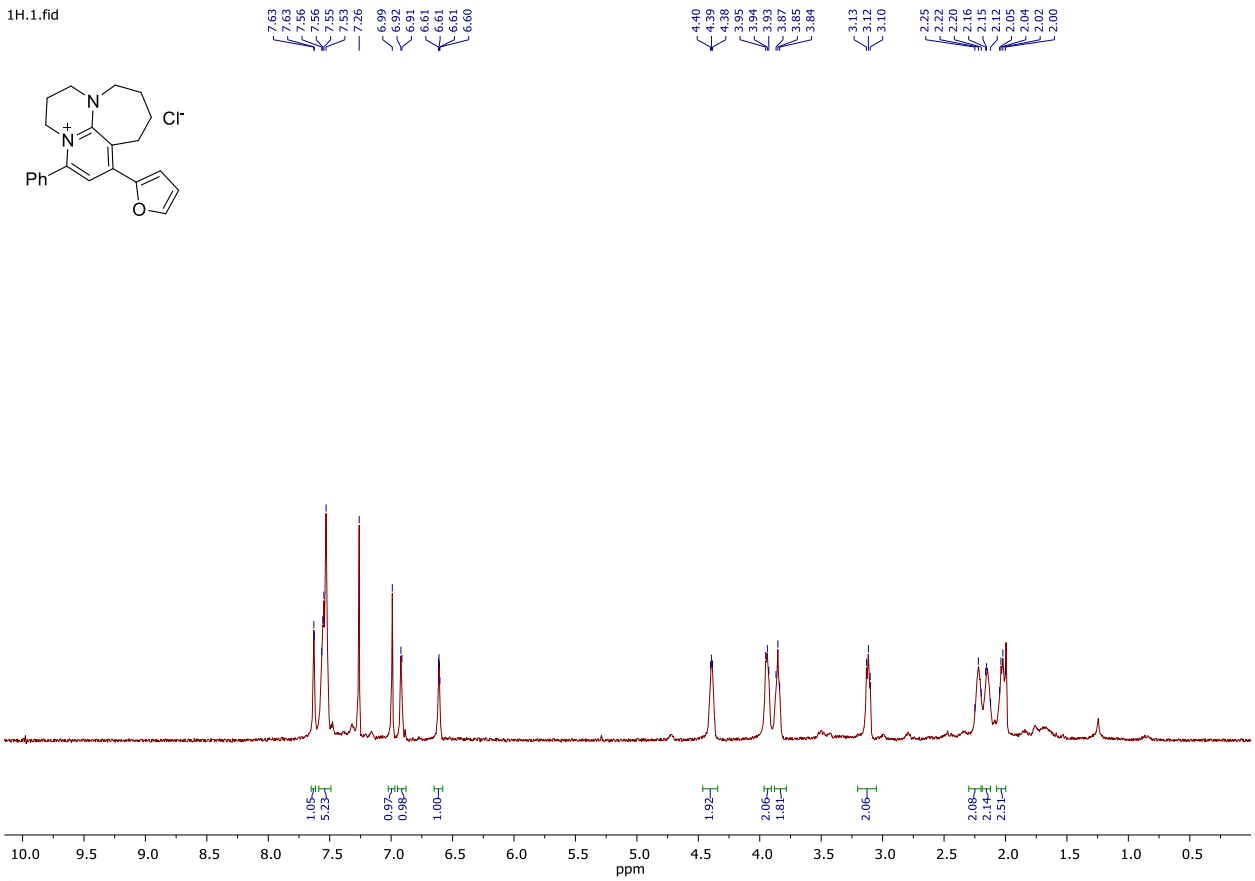
^{13}C NMR spectrum of compound **3c** (100.6 MHz, $CDCl_3$)



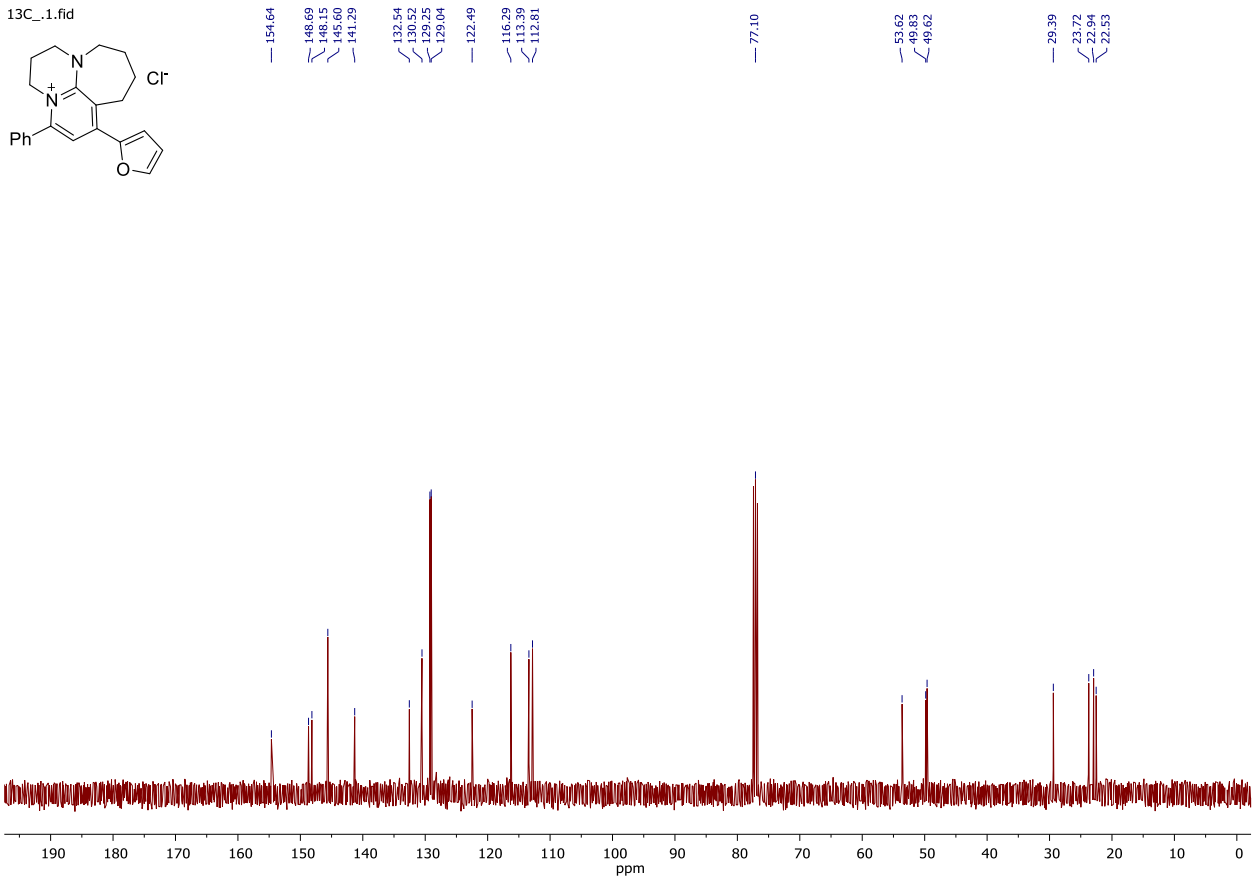
^{1}H NMR spectrum of compound **3d** (400.13 MHz, $CDCl_3$)



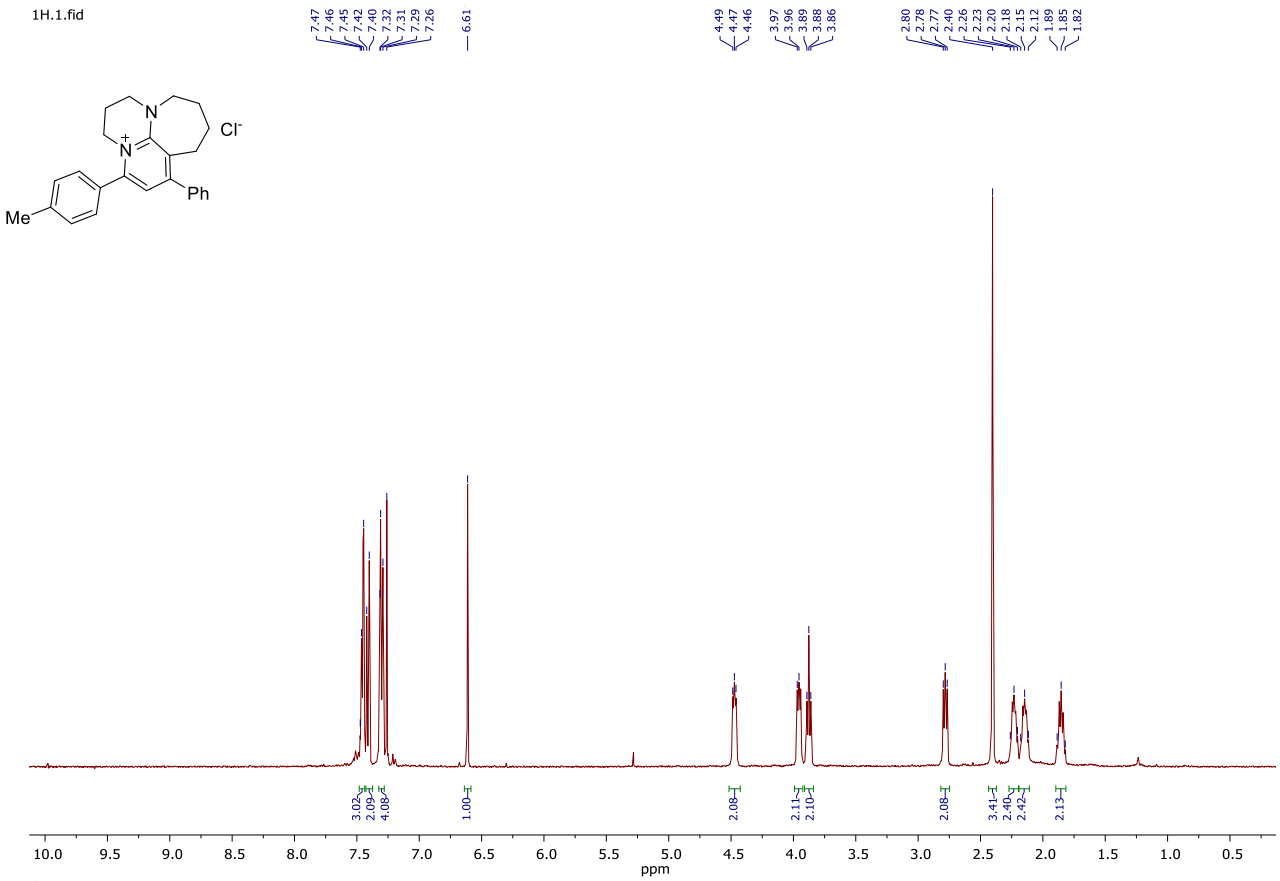
^{13}C NMR spectrum of compound **3d** (100.6 MHz, $CDCl_3$)



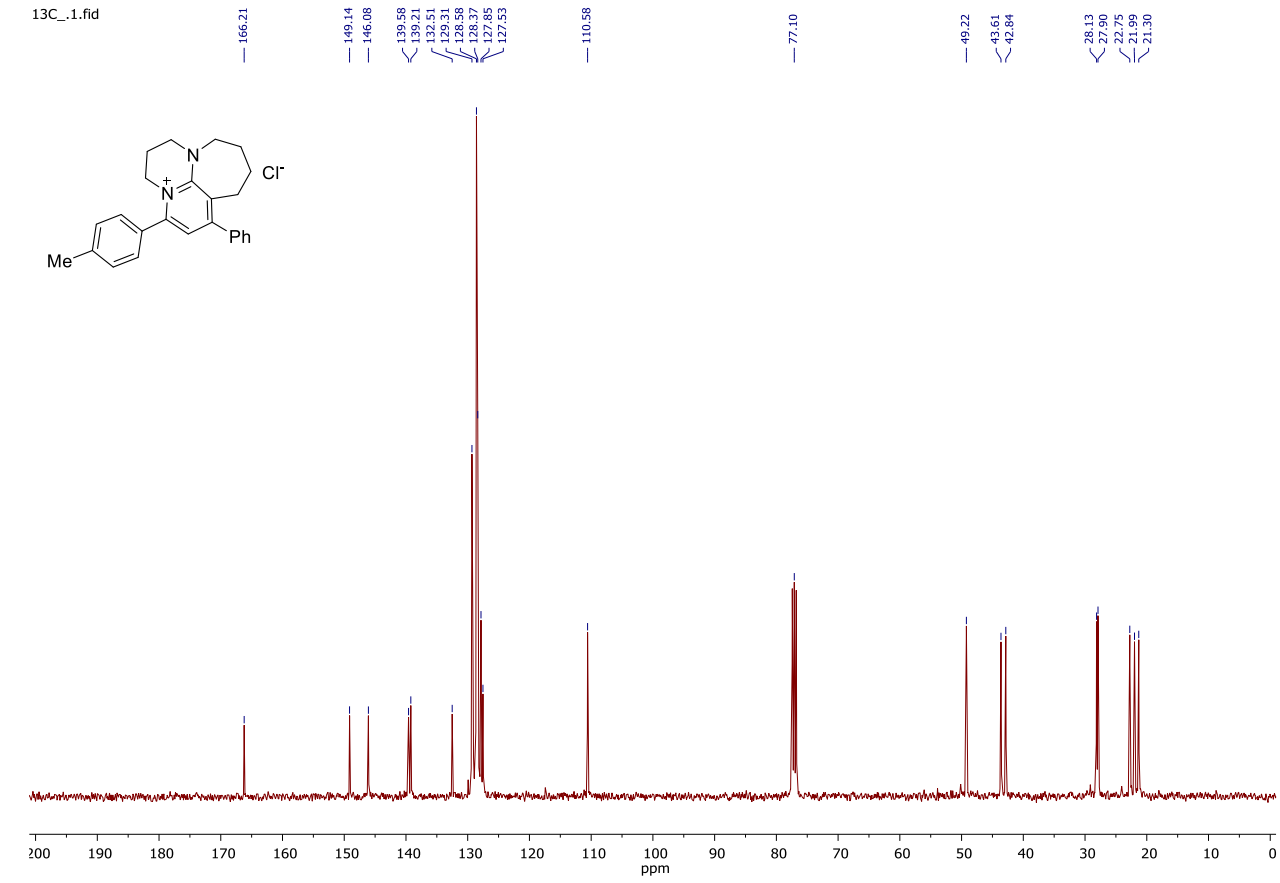
^{1}H NMR spectrum of compound **3e** (400.13 MHz, $CDCl_3$)



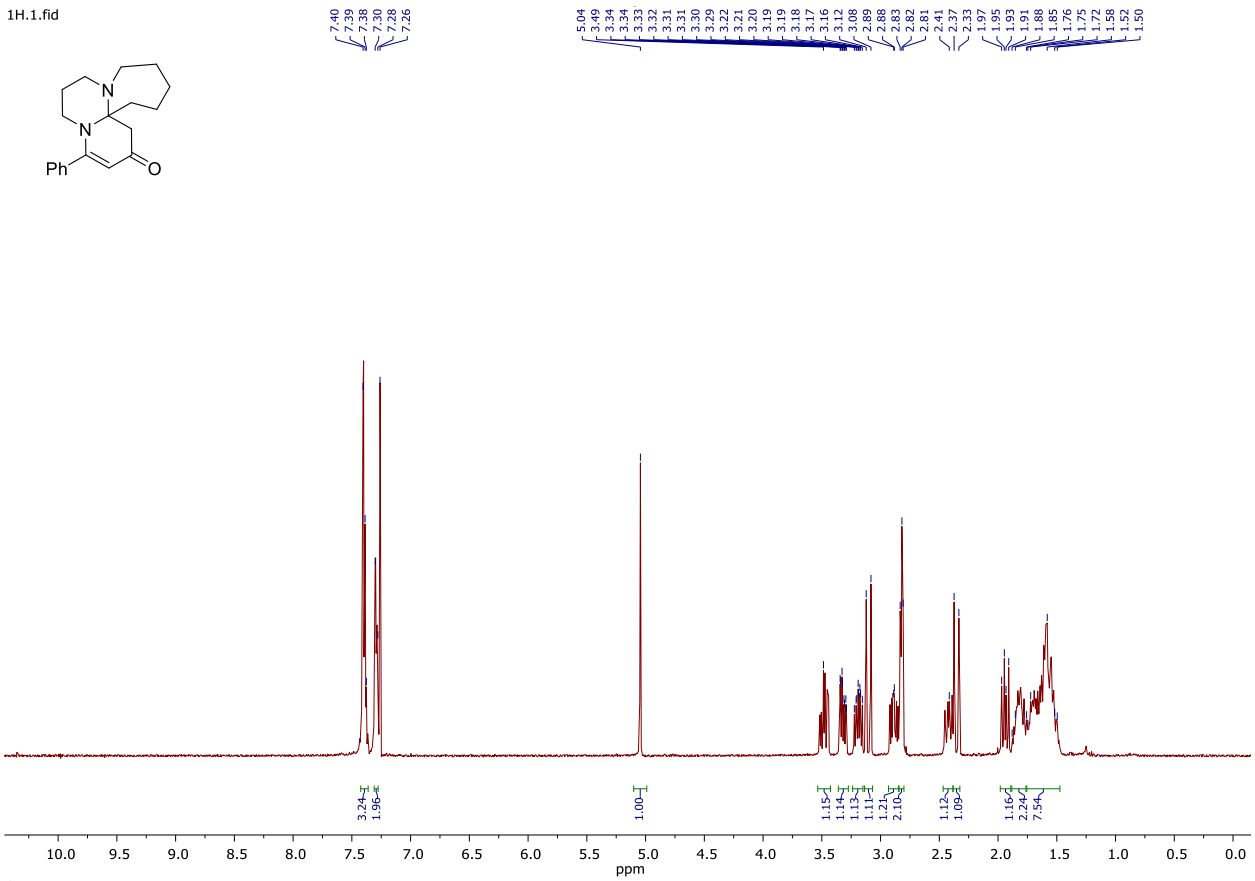
^{13}C NMR spectrum of compound **3e** (100.6 MHz, $CDCl_3$)



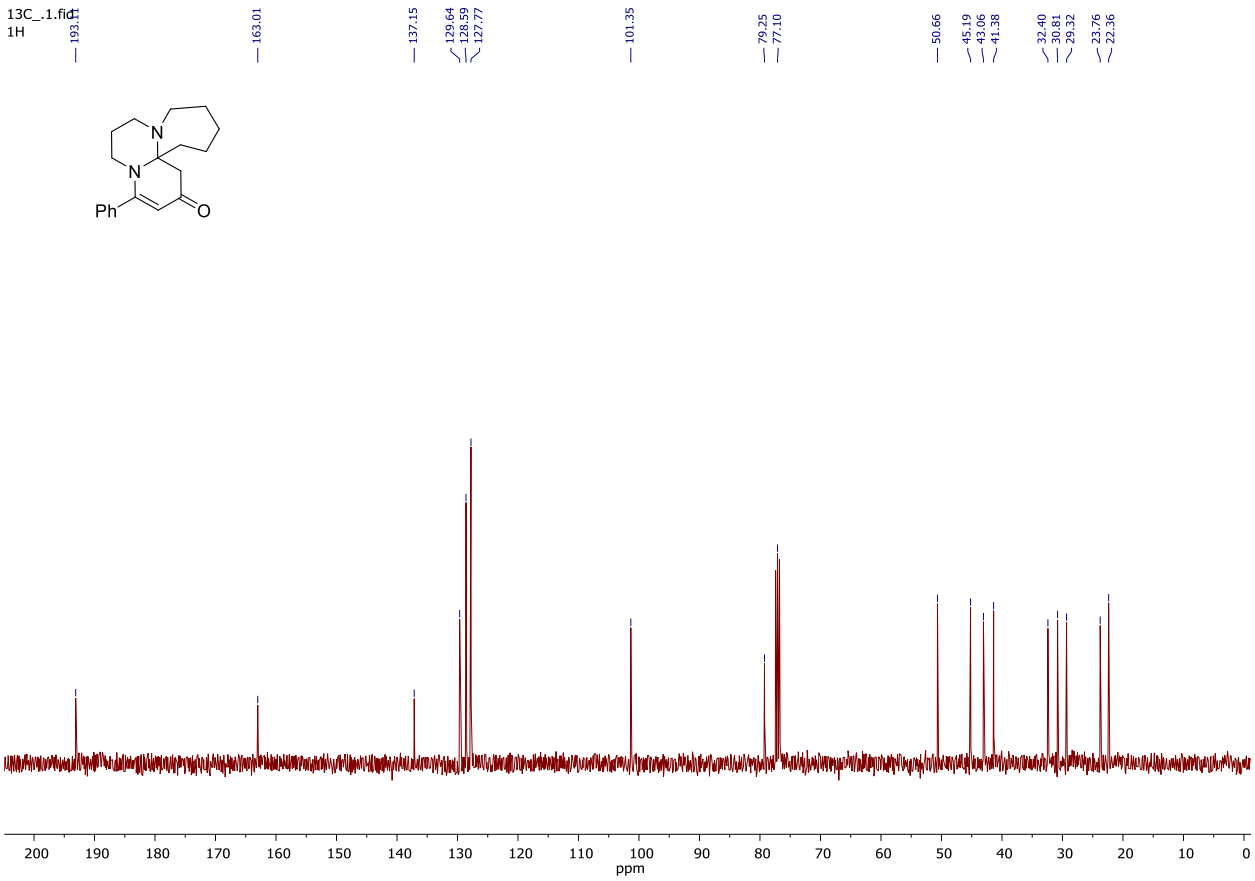
^{1}H NMR spectrum of compound **3f** (400.13 MHz, $CDCl_3$)



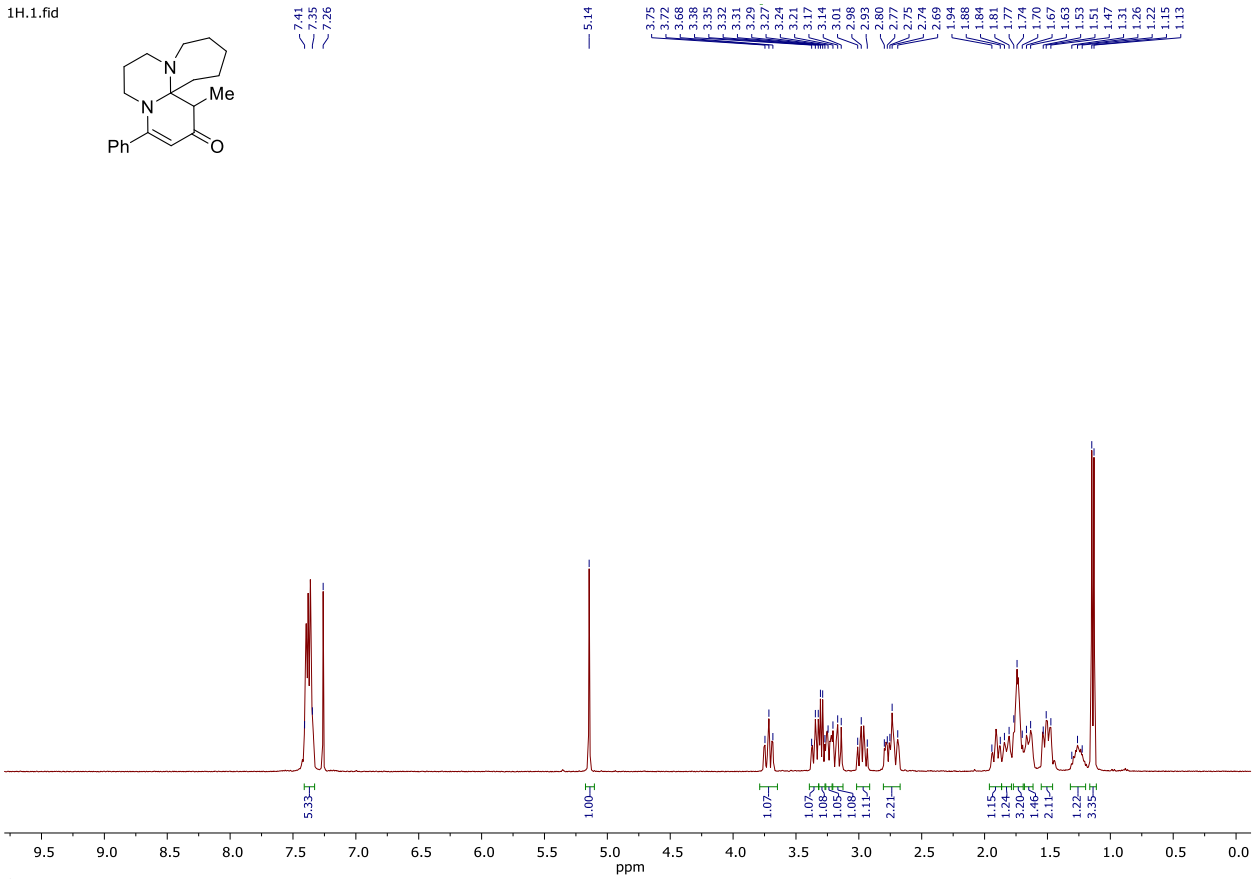
^{13}C NMR spectrum of compound **3f** (100.6 MHz, $CDCl_3$)



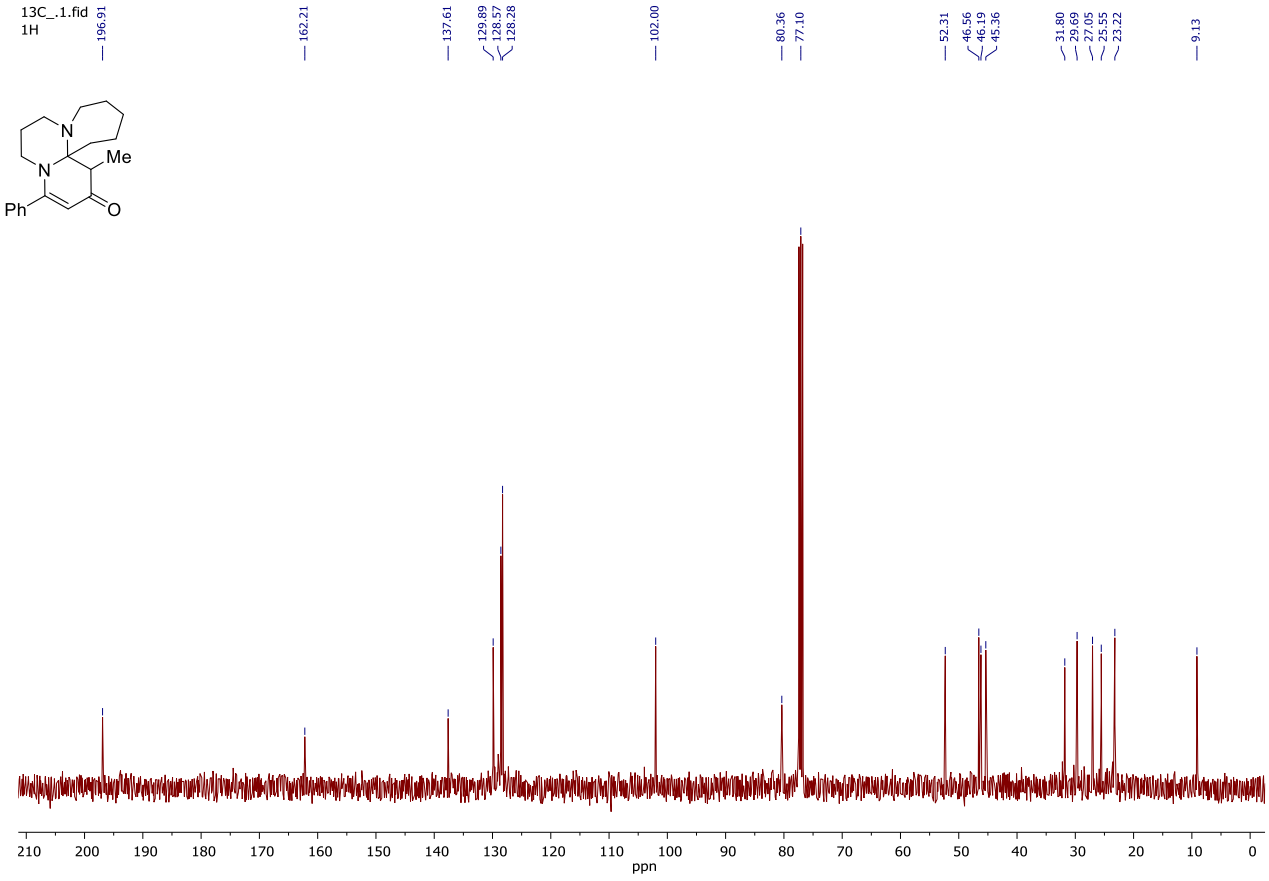
^{1}H NMR spectrum of compound **4a** (400.13 MHz, $CDCl_3$)



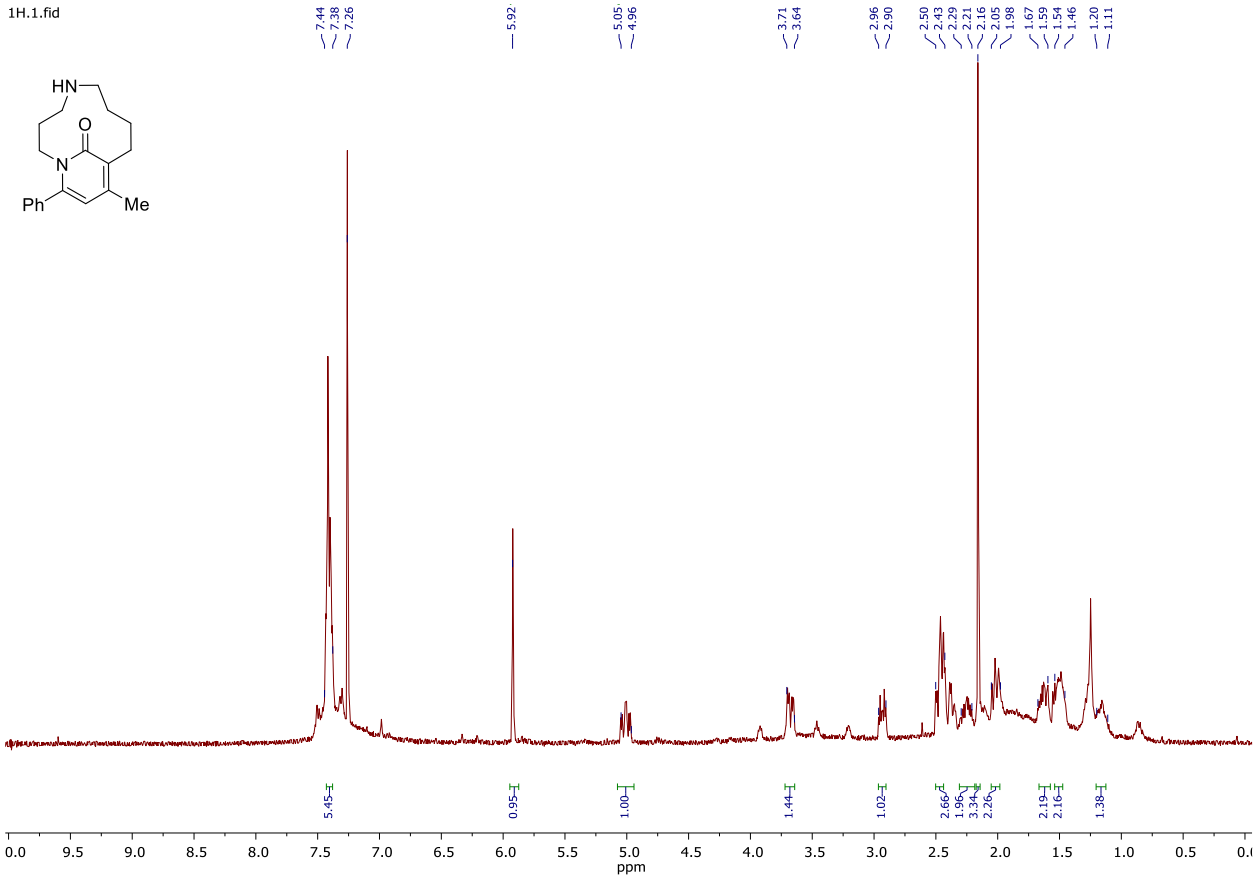
^{13}C NMR spectrum of compound **4a** (100.6 MHz, $CDCl_3$)



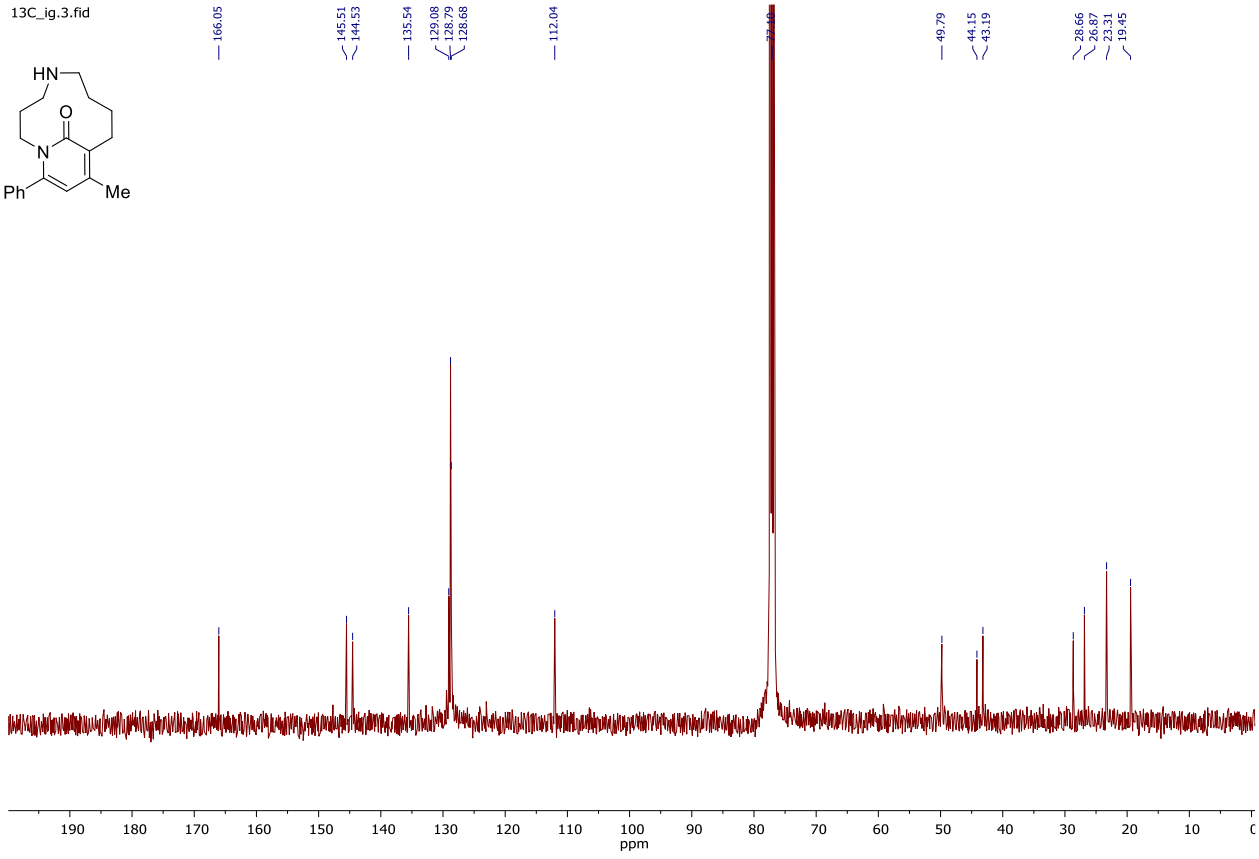
^{1}H NMR spectrum of compound **4b** (400.13 MHz, $CDCl_3$)



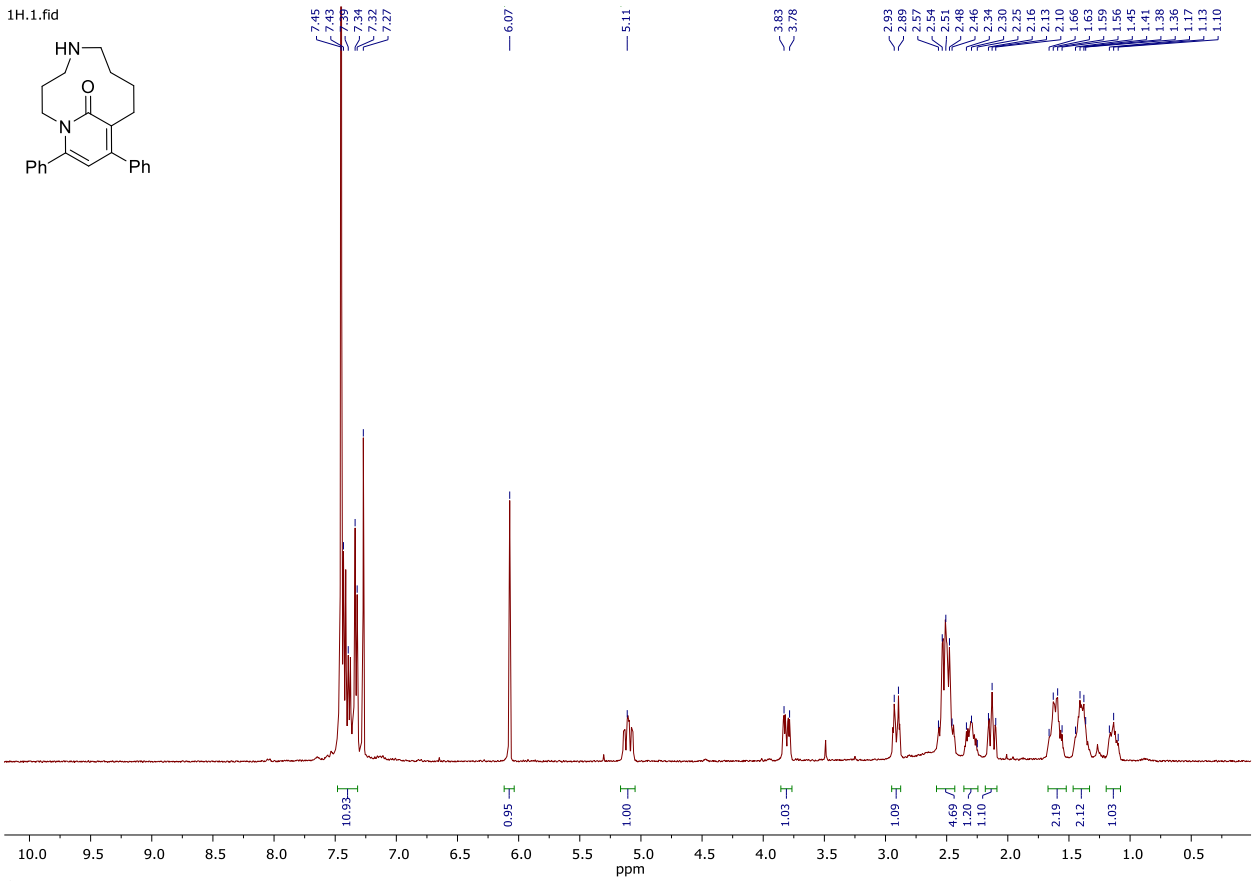
^{13}C NMR spectrum of compound **4b** (100.6 MHz, $CDCl_3$)



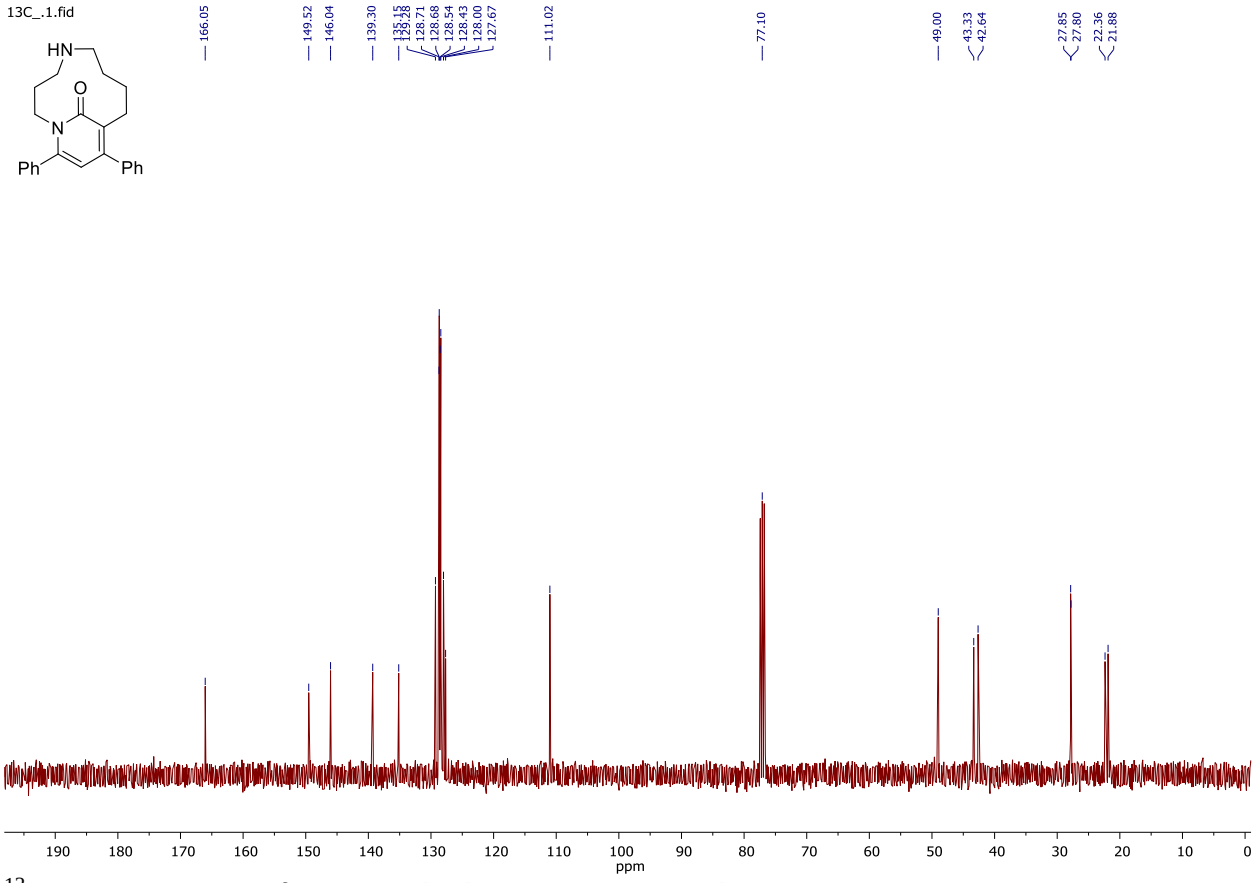
^{1}H NMR spectrum of compound **5a** (400.13 MHz, $CDCl_3$)



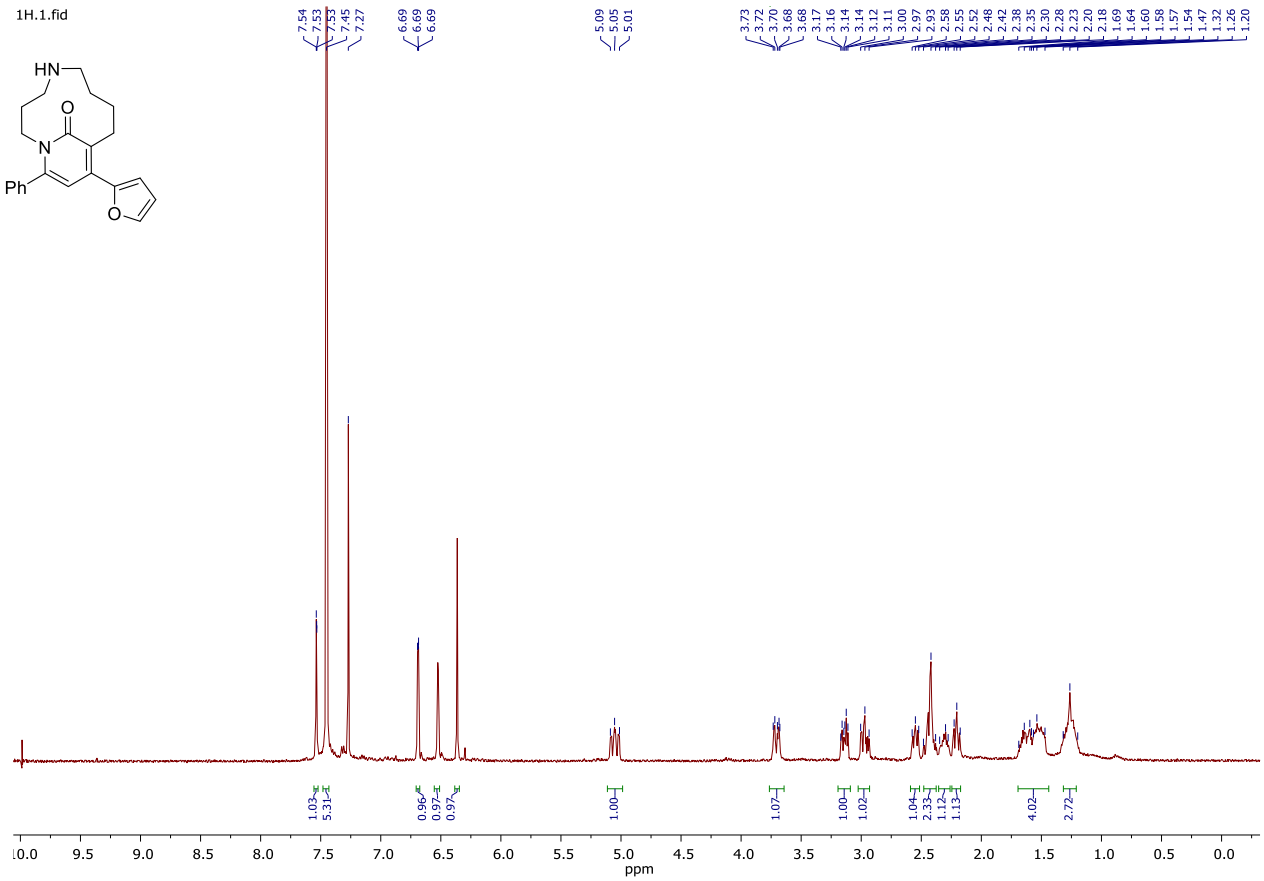
^{13}C NMR spectrum of compound **5d** (100.6 MHz, $CDCl_3$)



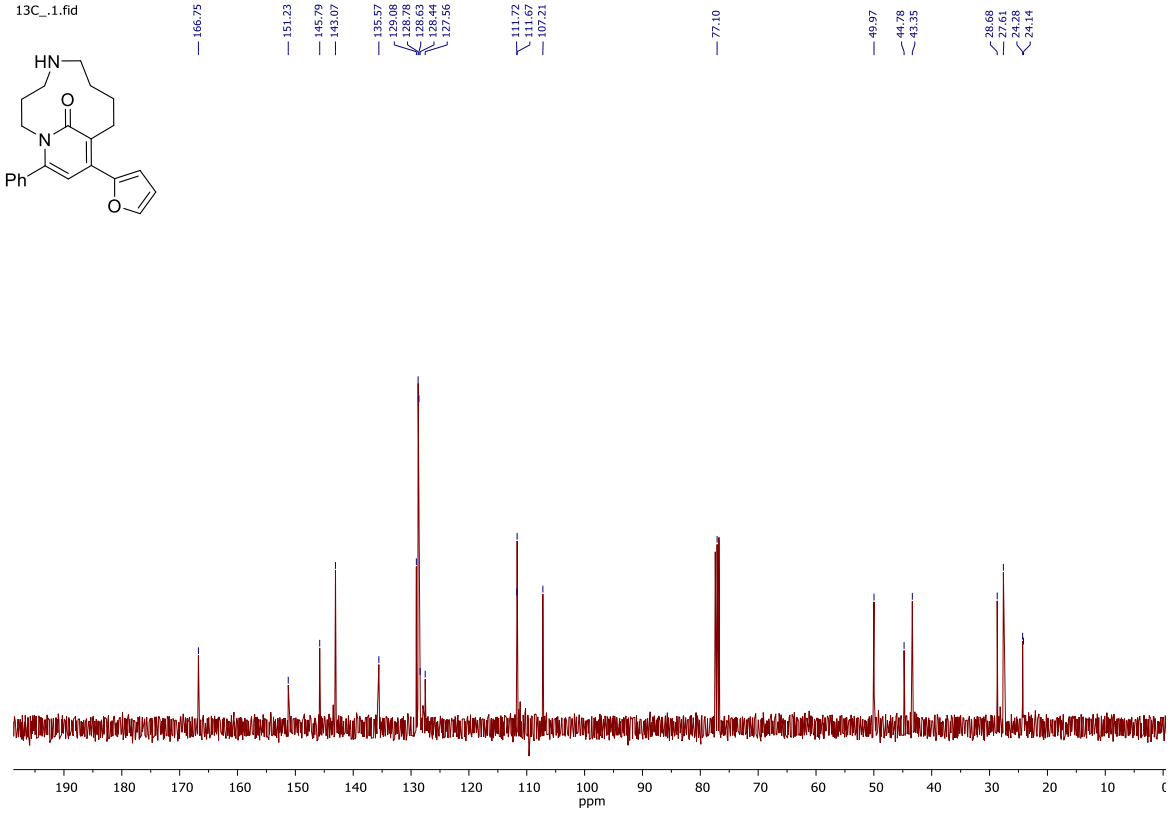
^{1}H NMR spectrum of compound **5d** (400.13 MHz, $CDCl_3$)



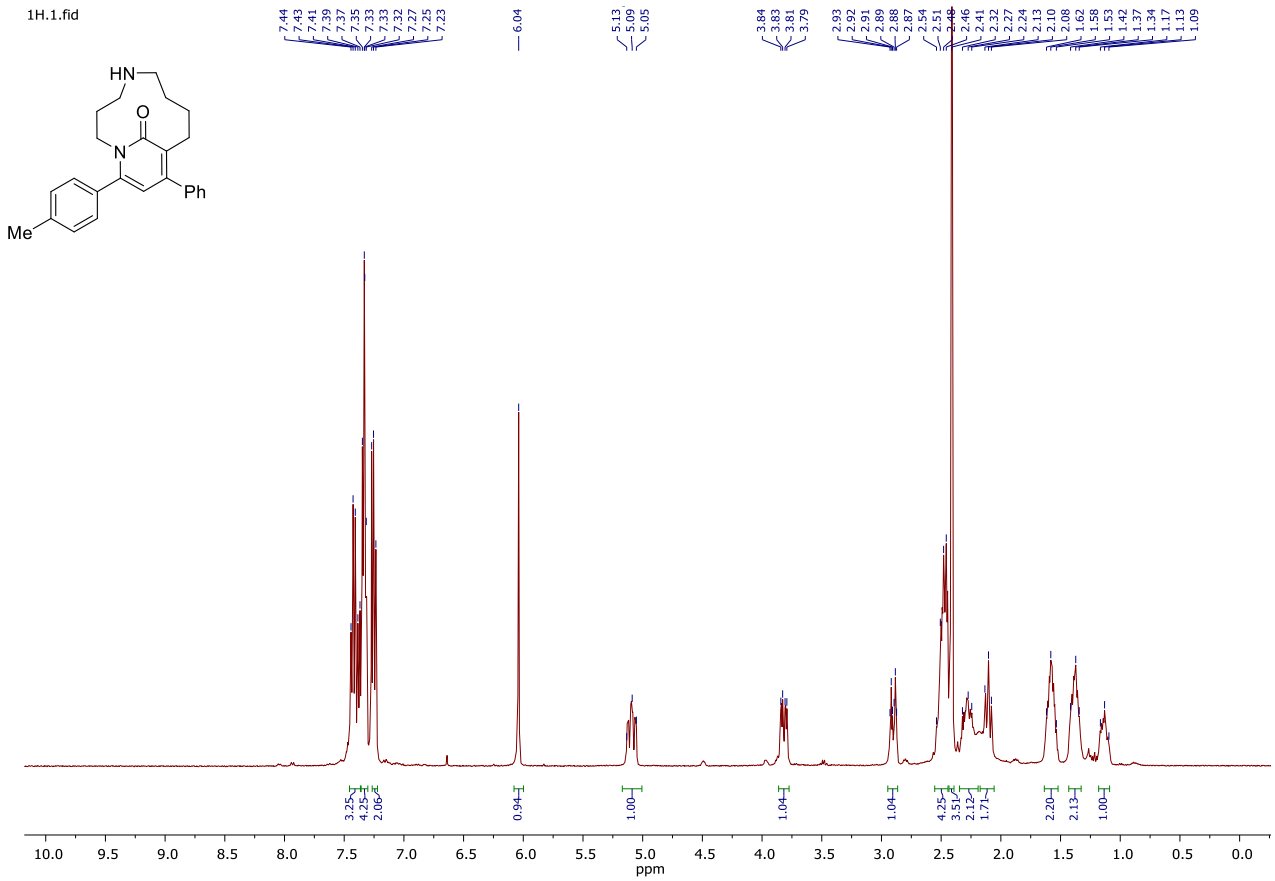
^{13}C NMR spectrum of compound **5d** (100.6 MHz, $CDCl_3$)



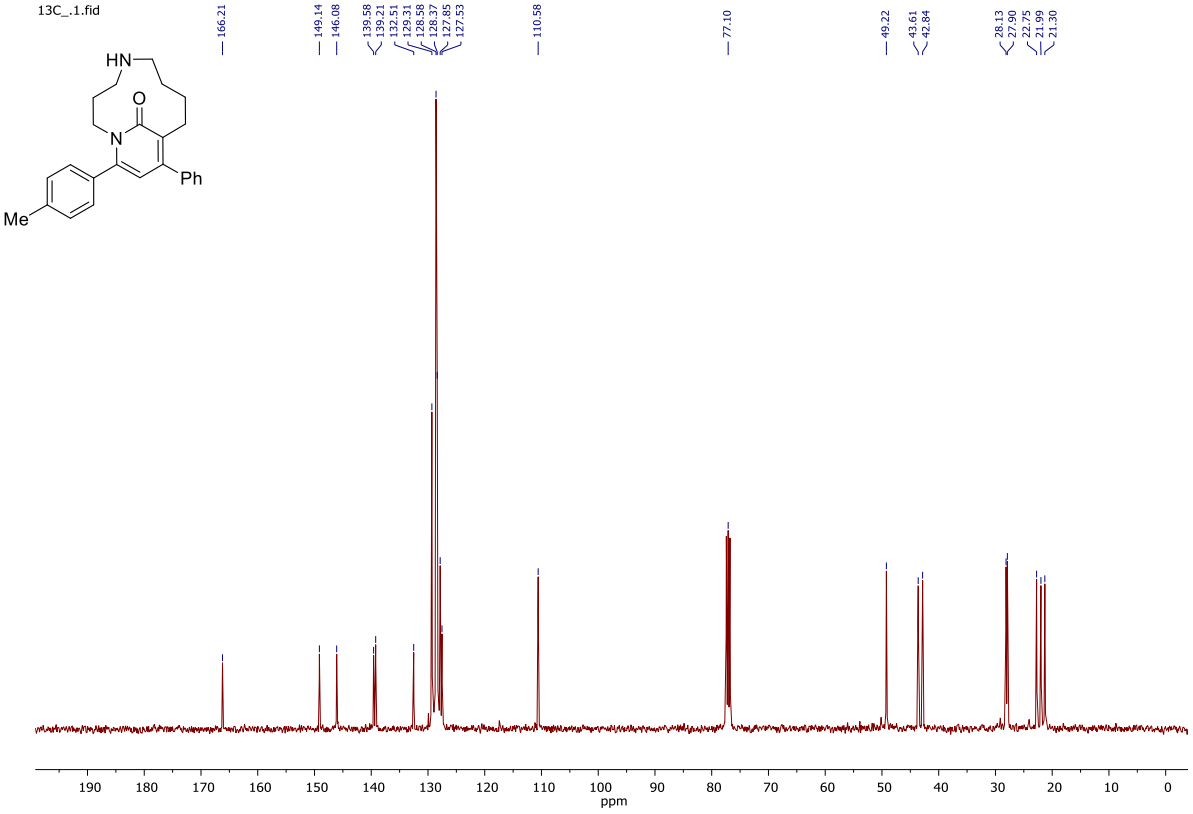
^{1}H NMR spectrum of compound **5e** (400.13 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **5e** (100.6 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound **5f** (400.13 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **5f** (100.6 MHz, $CDCl_3$)